Supporting Information

Zinc-Catalyzed Hydroxyl-Directed Regioselective Ring Opening of Aziridines in S_N2 Reaction Pathway

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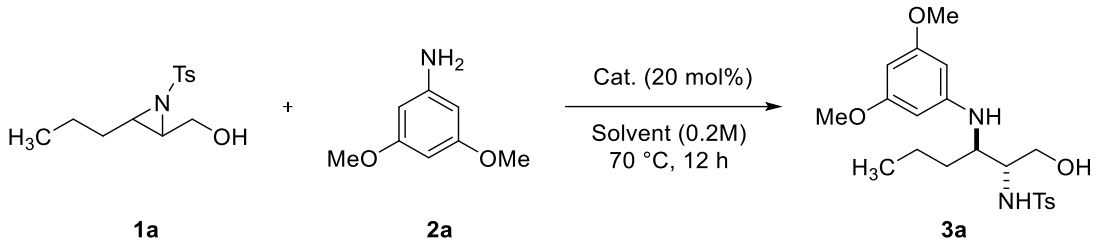
General Methods and Materials

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance 400M NMR spectrometers at ambient temperature in $CDCl_3$, DMSO-d_6 at 400 and 101 MHz. The chemical shifts are given in ppm relative to tetramethylsilane [^{1}H: δ= ($SiMe_4$)= 0.00 ppm] as an internal standard or relative to the resonance of the solvent [^{1}H: δ=($CDCl_3$)= 7.26, ^{13}C: δ= ($CDCl_3$)= 77.16 ppm, ^{1}H: δ= (DMSO-d_6)= 2.05, ^{13}C: δ= (DMSO-d_6)= 29.84, 206.26 ppm]. Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets), etc. Coupling constants are reported as *J* values in Hz. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF. HPLC was performed on Thermo UltiMate 3000. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system.

Optimization of the Reaction Conditions[a]

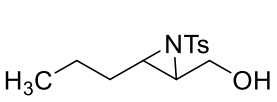


1a **2a** **3a**

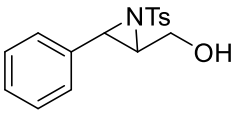
Entry	Catalyst	Solvent	T (°C)	Yield (%)[b]	C3:C2[c]
1	$Fe(BF_4)_2$	THF	60	65	88:12
2	$AgBF_4$	THF	60	41	81:19
3	$AgClO_4$	THF	60	38	85:15
4	$VO(acac)_2$	THF	60	0	-
5	$Sc(OTf)_3$	THF	60	65	83:17
6	$Bi(OTf)_3$	THF	60	36	90:10
7	$In(OTf)_3$	THF	60	60	91:9
8	$Hf(OTf)_4$	THF	60	45	87:13
9	$Zn(OTf)_2$	THF	60	53	95:5
10	$Y(OTf)_3$	THF	60	31	82:18
11	$Yb(OTf)_3$	THF	60	38	86:14
12	$Pr(OTf)_3$	THF	60	41	91:9
13	$Er(OTf)_3$	THF	60	45	88:12
14	$Tb(OTf)_3$	THF	60	53	89:11
15	$Ho(OTf)_3$	THF	60	21	92:8
16	$Eu(OTf)_3$	THF	60	55	89:11
17	$Zn(OTf)_2$	THF	60	53	95:5
18	$Zn(OTf)_2$	MeCN	60	66	>98:2
19	$Zn(OTf)_2$	toluene	60	89	97:3
20	$Zn(OTf)_2$	DCE	60	66	97:3
21	$Zn(OTf)_2$	HFIP	60	45	94:6
22	$Zn(OTf)_2$	EtOAc	60	85	>98:2
23	$Zn(OTf)_2$	monoglyme	60	38	95:5
24	$Zn(OTf)_2$	chloroform	60	65	96:4
25	$Zn(OTf)_2$	1,4-dioxane	60	66	97:3
26	$Zn(OTf)_2$	t-BuOH	60	0	-
27	**$Zn(OTf)_2$**	**EtOAc**	**70**	**98**	**>98:2**
28	$Zn(OTf)_2$	EtOAc	50	75	>98:2
29	$Zn(OTf)_2$	EtOAc	rt	trace	n.d.

[a] Reactions were performed on a 0.2 mmol scale of the aziridinyl alcohol **1a** using 1.5 equiv 3,5-dimethoxy aniline (**2a**), 20 mol% catalyst in 1.0 mL solvent for 12 h. [b] Yields of the isolated product after flash chromatography. [c] Determined by ^{1}H-spectrocopy.

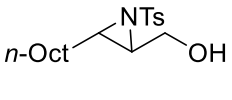
Procedures for Synthesis of 2,3-Aziridinyl Alcohols



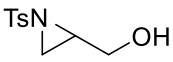
1a



1b



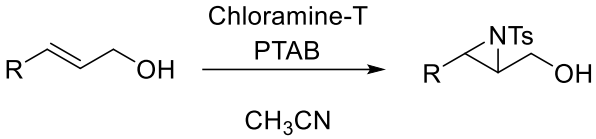
1g



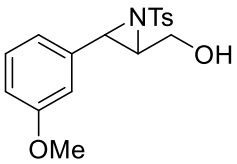
1i

The aziridines **1a**, **1b**, **1g** and **1i** are known compounds, and their NMR-data are consistent with these reported in the literature.[1],[2]

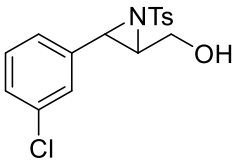
Procedure for Synthesis of the Aziridines 1c-f, 1h, 1j and 1k



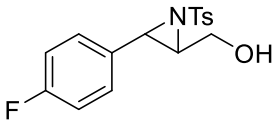
To a stirred suspension of chloroamine-T (3.4 g, 15 mmol, 1.5 equiv) and phenyltrimethylammonium tribromide (PTAB) (367 mg, 1 mmol, 0.1 equiv) in MeCN (40 mL) were added the allylic alcohols (10 mmol, 1 equiv) at room temperature. The mixture was stirred for 12 h, filtered and concentrated under reduced pressure. Purification of the residue through column chromatography (petroleum ether/ethyl acetate) gave the corresponding aziridines.



trans-(3-(3-Methoxyphenyl)-1-tosylaziridin-2-yl)methanol (**1c**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 2:1) as a colorless syrup (1.72 g, 86%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.84 (d, *J*= 8.0 Hz, 2H), 7.31 (d, *J*= 8.0 Hz, 2H), 7.18 (t, *J*= 7.9 Hz, 1H), 6.86-6.71 (m, 2H), 6.65 (dd, *J*= 2.5, 1.7 Hz, 1H), 4.39-4.28 (m, 1H), 4.21-4.13 (m, 1H), 4.00 (d, *J*= 4.3 Hz, 1H), 3.72 (s, 3H), 3.20-3.15 (m, 1H), 3.14-3.10 (m, 1H), 2.41 (s, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 159.8, 144.4, 137.0, 136.2, 129.7 (3C), 127.2 (2C), 118.7, 114.1, 111.7, 60.7, 55.2, 54.8, 46.4, 21.6 ppm. HRMS (ESI): calcd. for $C_{17}H_{20}NO_4S$ $[M+H]^+$:356.0932, found: 356.0920.

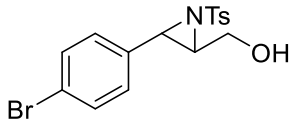


trans-(3-(3-Chlorophenyl)-1-tosylaziridin-2-yl)methanol (**1d**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 2:1) as a colorless syrup (1.45 g, 83%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.84 (d, *J*= 8.0 Hz, 2H), 7.31 (d, J= 8.0 Hz, 2H), 7.26-7.16 (m, 2H), 7.12-7.09 (m, 1H), 7.08-7.02 (m, 1H), 4.36-4.30 (m, 1H), 4.22-4.15 (m, 1H), 3.99 (d, *J*= 4.3 Hz, 1H), 3.19-3.11 (m, 1H), 3.10 (dd, *J*= 9.7, 5.0 Hz, 1H). 2.42 (s, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 144.7, 136.8, 136.7, 134.6, 129.9, 129.8 (2C), 128.6, 127.2 (2C), 126.5, 124.7, 60.4, 54.8, 45.4, 21.6 ppm. HRMS (ESI): calcd. for $C_{16}H_{17}ClNO_3S$ $[M+Na]^+$:360.0437, found: 360.0437.

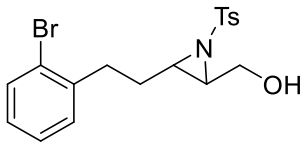


trans-(3-(4-Fluorophenyl)-1-tosylaziridin-2-yl)methanol (**1e**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 2:1) as a brown syrup (1.25 g, 78%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.82 (d, *J*= 8.0 Hz, 2H), 7.30 (d, *J*= 8.0 Hz, 2H), 7.16-7.10 (m, 2H), 7.00-6.92 (m, 2H), 4.35-4.26 (m, 1H), 4.10-4.13 (m, 1H), 4.00 (d, *J*= 4.4 Hz, 1H), 3.20-3.15 (m, 1H), 3.14-3.09 (m, 1H), 2.41 (s, 3H) ppm. ^{13}C

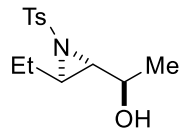
NMR (101 MHz, Chloroform-*d*) δ= 162.7 (d, *J*= 247.5 Hz), 144.5, 137.0, 130.3 (d, *J*= 3.2 Hz), 129.7 (2C), 128.2 (d, *J*= 8.3 Hz) (2C), 127.1 (2C), 115.6 (d, *J* = 21.8 Hz) (2C), 60.5, 54.6, 45.7, 21.6 ppm. HRMS (ESI): calcd. for $C_{16}H_{17}FNO_3S$ $[M+H]^+$:322.0913, found: 322.0913.



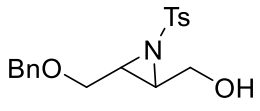
trans-(3-(4-Bromophenyl)-1-tosylaziridin-2-yl)methanol (**1f**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 2:1) as a white solid (1.35 g, 71%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.81 (d, *J*= 8.0 Hz, 2H), 7.39 (d, *J*= 8.0 Hz), 7.33-7.27 (m, 2H), 7.09-6.95 (m, 2H), 4.36-4.27 (m, 1H), 4.21-4.13 (m, 1H), 3.97 (d, *J*= 4.3 Hz, 1H), 3.20-3.13 (m, 1H), 3.13-3.05 (m, 1H), 2.42 (s, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 144.6, 136.9, 133.7, 131.8 (2C), 129.8 (2C), 128.1 (2C), 127.1 (2C), 122.4, 60.4, 54.7, 45.6, 21.7 ppm. HRMS (ESI): calcd. for $C_{16}H_{17}BrNO_3S$ $[M+Na]^+$:403.9932, found: 403.9936.



trans-(3-Phenethyl-1-tosylaziridin-2-yl)methanol (**1h**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 2:1) as a colorless syrup (1.32 g, 80%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.86 (d, *J*= 8.0 Hz, 2H), 7.49 (dd, *J*= 8.0, 1.3 Hz, 1H), 7.33 (d, *J*= 8.0 Hz, 2H), 7.19-7.24 (m, 1H), 7.13 (dd, *J*= 7.7, 1.8 Hz, 1H), 7.09-7.02 (m, 1H), 4.05-3.07 (m, 1H), 3.97-3.79 (m, 1H), 3.05-2.95 (m, 1H), 2.91-2.85 (m, 1H), 2.77-2.69 (m, 1H), 2.69-2.62 (m, 1H), 2.43 (s, 3H), 2.06-1.94 (m, 1H), 1.93-1.82 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 144.4, 139.7, 137.1, 132.9, 130.3, 129.7 (2C) , 128.1, 127.6, 127.4 (2C), 124.3, 60.9, 51.5, 45.7, 33.6, 30.4, 21.6 ppm. HRMS (ESI): calcd. for $C_{18}H_{21}BrNO_3S$ $[M+H]^+$:410.0426, found: 410.0426.

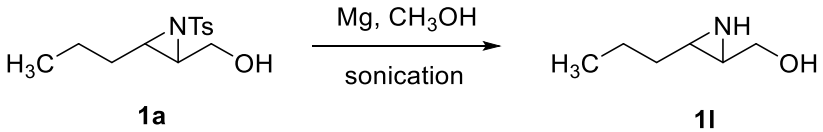


1,2-anti-2,3-trans-3-Ethyl-1-tosylaziridin-2-yl)ethan-1-ol (**1j**) was isolated through preparative TLC on silica gel (petroleum ether/ethyl acetate= 2:1) as a colorless syrup (215 mg, 40%, 2 mmol the corresponding allylic alcohol used as precursor). ^{1}H NMR (500 MHz, Chloroform-*d*) δ= 7.76 (d, *J*= 8.1 Hz, 2H), 7.26 (d, *J*= 7.9 Hz, 2H), 3.92-3.80 (m, 1H) 2.81-2.72 (m, 2H), 2.37 (s, 3H), 1.97-1.87 (m, 1H), 1.87-1.75 (m, 1H), 1.11 (d, *J*= 6.4 Hz, 3H), 0.96 (t, *J*= 7.4 Hz, 3H) ppm. ^{13}C NMR (126 MHz, Chloroform-*d*) δ= 144.3, 137.4, 129.7 (2C), 127.4 (2C), 64.2, 52.5, 48.0, 21.9, 21.6, 20.2, 12.1. ppm. HRMS (ESI): calcd. for $C_{13}H_{20}NO_3S$ $[M+Na]^+$:292.0983, found: 292.0987.



trans-(3-((Benzyloxy)methyl)-1-tosylaziridin-2-yl)methanol (**1k**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 2:1) as a colorless syrup (1.16 g, 67%). ^{1}H NMR (400 MHz, Chloroform-d) δ= 7.85 (d, *J*= 8.0 Hz, 2H), 7.34-7.25 (m, 5H), 7.20-7.14 (m, 2H), 4.50-4.37 (m, 2H), 4.19-4.05 (m, 1H), 4.01-3.90 (m, 1H), 3.69 (dd, *J*= 11.0, 4.4 Hz, 1H), 3.50 (dd, *J*= 11.0, 6.6 Hz, 1H), 3.30-2.95(m, 1H), 3.09-3.01 (m, 1H), 2.82 (dd, *J*= 9.2, 5.1 Hz, 1H), 2.42 (s, 3H) ppm.^{13}C NMR (101 MHz, Chloroform-*d*) δ= 144.4 , 137.6, 136.9, 129.6 (2C) , 128.4 (2C), 127.8, 127.5 (2C) , 127.4 (2C), 73.1, 68.4, 60.6, 48.9, 44.6, 21.6 ppm. HRMS (ESI): calcd. for $C_{18}H_{22}NO_4S$ $[M+Na]^+$: 370.1089, found: 370.1086.

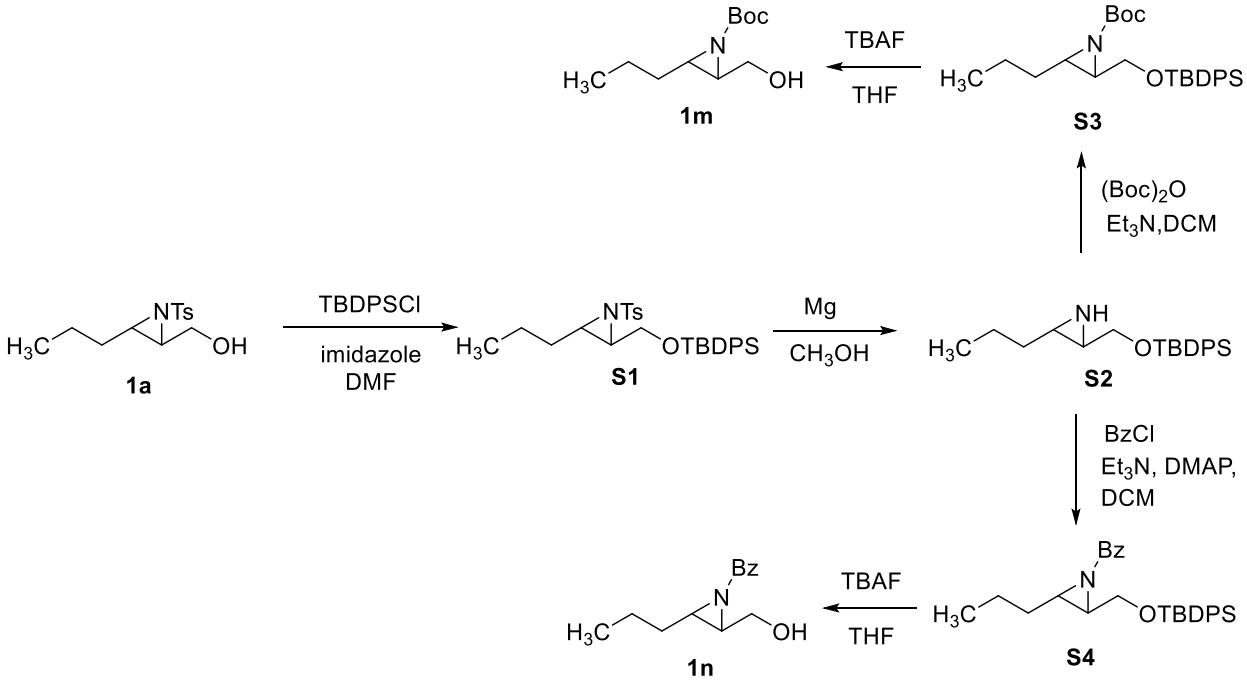
Procedure for Synthesis of the Aziridines 1l



1a **1l**

To a solution of **1a** (2.69 g, 10 mmol, 1.0 equiv) in anhydrous CH_3OH (40 mL) was added Mg powder (1.2 g, 50 mmol, 5.0 equiv), and the mixture was sonicated under N_2 at room temperature for 1.5 h. After the reaction was quenched with saturated aq. NH_4Cl solution (40 mL), the organic layer was separated, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified through column chromatography on silica gel (petroleum ether: EtOAc= 1:1-EtOAc), to afford *trans-(3-propylaziridin-2-yl)methanol* (**1l**) as a colorless syrup (115 mg, 10%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 3.82 (dd, *J*= 11.9, 3.3 Hz, 1H), 3.37 (dd, *J*= 11.9, 6.1 Hz, 1H), 2.03-1.93 (m, 1H), 1.89-1.77 (m, 1H), 1.52-1.36 (m, 4H), 0.95 (t, *J*= 8.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 63.0, 38.6, 35.8, 34.9, 20.8, 13.9 ppm. HRMS (ESI): calcd. for $C_6H_{14}NO$ $[M+H]^+$:116.1075, found: 116.1074.

Procedure for Synthesis of the Aziridines 1m and 1n



To a stirred solution of **1a** (2.7 g, 10 mmol, 1 equiv) in DMF was added imidazole (748 mg, 11 mmol, 1.1 equiv), and the resulting mixture was stirred for 2 h. Then the reaction was diluted with ethyl acetate and washed with saturated aq. NaCl solution for 3 times. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford the crude *trans-2-(((tert-butyldiphenylsilyl)oxy)methyl)-3-propyl-1-tosylaziridine* (**S1**) without further purification. To a solution of the crude **S1** in anhydrous CH_3OH (40 ml) was added magnesium powder (1.2 g, 50 mmol, 5 equiv) and the resulting mixture was sonicated under N_2 for 1.5 hour. The reaction was quenched with saturated aq. NH_4Cl solution (100 mL), and the aqueous layer was extracted with ethyl acetate for 3 times. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified through column chromatography (petroleum ether/ethyl acetate= 5:1) to afford *trans-2-(((tert-butyldiphenylsilyl)oxy)methyl)-3-propylaziridin*e (**S2**) as a colorless syrup (1.06 g, 30%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.68-7.63 (m, 4H), 7.45-7.33 (m, 6H), 3.79-3.67 (m, 2H), 1.88-1.79 (m, 2H), 1.49-.39 (m, 2H), 1.32-1.23 (m, 2H), 1.05 (s, 9H), 0.93 (t, *J*= 8.0 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 135.5 (4C), 133.4 (2C), 129.8 (2C), 127.7 (4C), 38.1, 35.5, 34.0, 29.3, 26.8 (3C), 20.7, 19.3, 13.9 ppm. HRMS (ESI): calcd. for $C_{22}H_{32}NOSi$ $[M+H]^+$: 354.2253, found: 354.2255.

To a stirred solution of **S2** (3 mmol, 1.06 g, 1 equiv) in DCM were added Et_3N (6 mmol, 612 mg, 2 equiv) and $(Boc)_2O$ (6 mmol, 1.3 g, 2 eq) at 0 °C. The resulting mixture was stirred for 2 h and diluted with

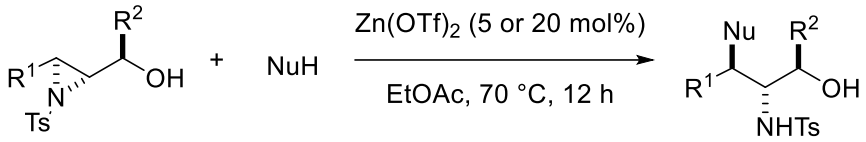
saturated aq. $NaHCO_3$ solution. The organic layer was separated, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified through column chromatography (petroleum ether/ethyl acetate= 10:1) to afford *trans-tert-butyl 2-(((tert-butyldiphenylsilyl)oxy)methyl)-3-propylaziridine- 1-carboxylate* (**S3**) as a colorless syrup (1.8 g, 80%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.69-7.63 (m, 4H), 7.43-7.37 (m, 5H), 3.96 (dd, *J*= 11.2, 4.2 Hz, 1H), 3.55 (dd, *J*= 11.2, 5.7 Hz, 1H), 2.43-2.37 (m, 1H), 2.36-2.27 (m, 1H), 1.73-1.62 (m, 1H), 1.54-1.43 (m, 1H), 1.42 (s, 9H), 1.30-.25 (m, 1H), 1.22-1.12 (m, 1H), 1.05 (s, 9H), 0.96 (t, *J*= 7.4 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 160.6, 135.4 (2C), 135.6 (2C), 133.4, 133.2, 129.8 (4C), 127.7 (2C), 80.8, 63.3, 43.7, 41.7, 32.8, 28.0 (3C), 26.8 (3C), 20.4, 19.2, 13.8 ppm. HRMS (ESI): calcd. for $C_{27}H_{40}NO_3Si$ $[M+H]^+$: 454.2777, found: 454.2778.

To a stirred solution of **S3** (2 mmol, 900 mg, 1 equiv) in anhydrous THF was added TBAF (1M in THF) (4 mmol, 4 mL, 2 equiv), and the resulting mixture was stirred for 2 h. The reaction was quenched with saturated aq. $NaHCO_3$ solution, and the organic layer was separated, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified through column chromatography (petroleum ether/ethyl acetate= 4:1) to afford *trans-tert-butyl 2-(hydroxymethyl)-3-propylaziridine-1-carboxylate* (**1m**) as a colorless syrup (301 mg, 70%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 4.06-3.96 (m, 1H), 3.50-3.40 (m, 1H), 2.74 (dd, *J*= 9.1, 4.3 Hz, 1H), 2.54-2.42 (m, 1H), 2.34 (brs, 1H), 1.58-1.50 (m, 3H), 1.48 (s, 9H), 1.43-1.35 (m, 1H), 0.97 (t, *J*= 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 161.7, 81.6, 62.8, 44.4, 40.8, 33.1, 28.0 (3C), 20.2, 13.7 ppm. HRMS (ESI): calcd. for $C_{11}H_{12}NO_3$ $[M+Na]^+$: 238.1419, found: 238.1411.

To a stirred solution of **S2** (3 mmol, 1.06 g, 1 equiv) in DCM were added Et_3N (6 mmol, 612 mg, 2 equiv), DMAP (0.3 mmol, 40.5 mg, 0.1 equiv) and benzoyl chloride (6 mmol, 1.3 g, 2 equiv) at 0 °C. The resulting mixture was stirred for 2 hours at rt and diluted with saturated aq. $NaHCO_3$ solution. The organic layer was separated, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified through column chromatography (petroleum ether/ethyl acetate= 10:1) to afford *trans-(2-(((tert-butyl-diphenylsilyl)oxy)methyl)-3-propylaziridin-1-yl)(phenyl)methanone* (**S4**) as a colorless syrup (1.2 g, 90%).^{1}H NMR (400 MHz, Chloroform-*d*) δ= 8.02 (dd, *J*= 8.2, 1.4 Hz, 2H), 7.59-7.52 (m, 3H), 7.47-7.39 (m, 4H), 7.39-7.32 (m, 4H), 7.31-7.25 (m, 2H), 3.86 (dd, *J*= 11.6, 3.4 Hz, 1H), 3.72 (dd, *J*= 11.6, 3.7 Hz, 1H), 2.83-2.76 (m, 1H), 2.74-2.69 (m, 1H), 1.82-1.66 (m, 1H), 1.56-1.41 (m, 2H), 1.25-1.11 (m, 1H), 0.97 (s, 9H), 0.94 (t, *J*= 7.4 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 176.9, 135.5 (2C), 135.4 (2C), 134.3, 132.9, 132.2 (2C), 129.7, 129.6, 128.9 (2C), 128.3 (2C), 127.7 (2C), 127.6 (2C), 61.5, 45.1, 39.8, 33.2, 26.6 (3C), 20.4, 19.1, 13.8 ppm. HRMS (ESI): calcd. for $C_{29}H_{36}NO_2Si$ $[M+H]^+$: 458.2515, found: 458.2513.

To a stirred solution of **S4** (2 mmol, 914 mg, 1 equiv) in anhydrous THF was added TBAF (1M in THF) (2 4mmol, 4 mL, 2eq), and the resulting mixture was stirred for 2 h. The reaction was quenched with saturated aq. $NaHCO_3$ solution, and the organic layer was separated, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified through column chromatography (petroleum ether/ethyl acetate= 2:1) to afford *trans-(2-(hydroxymethyl)-3-propylaziridin-1-yl)(phenyl)methanon*e (**1n**) as a colorless syrup (337 mg, 77%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 8.08-8.03 (m, 2H), 7.60-7.52 (m, 1H), 7.44 (dd, *J*= 8.3, 7.0 Hz, 2H), 4.50-4.33 (m, 1H), 4.17 (dd, *J*= 11.7, 6.9 Hz, 2H), 2.18-2.07 (m, 2H), 1.98-1.82 (m, 2H), 1.50-1.46 (m, 3H), 1.46-1.40 (m, 1H), 0.96 (t, *J*= 7.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 166.5, 133.0, 130.0, 129.6 (2C), 128.3 (2C), 67.6, 35.7 (2C), 35.1, 20.8, 13.8 ppm.HRMS (ESI): calcd. for $C_{13}H_{18}NO_2$ $[M+H]^+$: 220.1338, found: 220.1331.

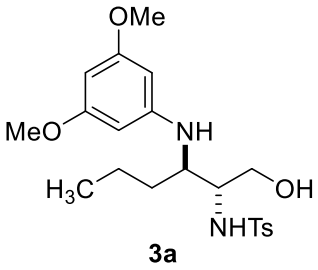
General Procedure for the Hydroxyl-Directed Zinc Catalyzed Regioselective Nucleophilic Ring Opening of Aziridines



(±)-**1** **2** or **4** (±)-**3** or (±)-**5**

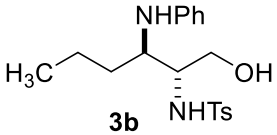
To a suspension of $Zn(OTf)_2$ (5 or 20 mol%, see below)[a] in ethyl acetate (1 mL) were added the aziridines **1** (0.2 mmol, 1 equiv) and amines **2** or thiophenols **4** (0.3 mmol, 1.5 equiv) at room temperature. The resulting mixture was heated to 70 °C and stirred at this temperature for 12 h. Then the reaction was cooled to room temperature, and the solvent was removed in vacuum. The residue was purified through column chromatography on silica gel (petroleum ether/ethyl acetate) affording the corresponding products **3** or **5**.

[a] Catalyst loading: 20 mol% for **3a-3o**, **3r-3t**, **3x-3ac**, **5a-5l**; 5 mol% for **3o-3q**, **3u**, **3w**.



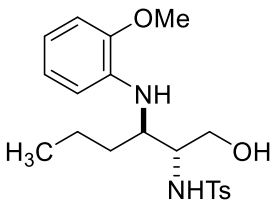
3a

(±)-*erythro-N-3-((3,5-Dimethoxyphenyl)amino)-1-hydroxyhexan-2-yl)-4-methylbenzenesulfonamide* (**3a**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a brown syrup (83 mg, 98%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.72 (d, *J*= 8.0 Hz, 2H), 7.27 (d, *J*= 8.0 Hz, 2H), 5.85 (d, *J*= 2.1 Hz, 1H), 5.60 (d, *J*= 2.2 Hz, 2H), 5.44 (d, *J*= 8.3 Hz, 1H),4.00-3.85 (brs, 1H), 3.78 (dd, *J*= 11.5, 3.8 Hz, 1H), 3.72 (s, 6H), 3.66 (dd, *J*= 11.5, 3.5 Hz, 1H), 3.38-3.32 (m, 1H), 3.30-3.20 (m, 1H), 2.43 (s, 3H), 2.40-2.28 (brs, 1H), 1.50-1.37 (m, 2H), 1.32-1.16 (m, 2H), 0.80 (t, *J*= 7.3 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 161.7 (2C), 149.5, 143.7, 137.3, 129.9 (2C), 127.0 (2C), 92.2 (2C), 90.0, 62.5, 56.2, 55.2 (2C), 55.1, 34.4, 21.5, 19.4, 13.9 ppm. HRMS (ESI): calcd. for $C_{21}H_{31}N_2O_5S$ $[M+H]^+$: 423.1948, found: 423.1948.



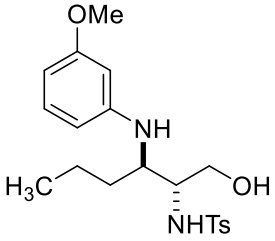
3b

(±)-*erythro-N-(1-Hydroxy-3-(phenylamino)hexan-2-yl)-4-methylbenzenesulfonamide* (**3b**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a yellow syrup (70 mg, 96%).^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.71 (d, *J*= 8.3 Hz, 2H), 7.25 (d, *J*= 8.1 Hz, 2H), 7.18-7.02 (m, 2H), 6.69-6.64 (m, 1H), 6.46-6.29 (m, 2H), 5.57 (d, *J*= 7.4 Hz, 1H), 3.78 (dd, *J*= 11.5, 4.1 Hz, 1H), 3.66 (dd, *J*= 11.5, 3.7 Hz, 1H), 3.41-3.35 (m, 1H), 3.35-3.26 (m, 1H), 2.42 (s, 3H), 1.49-1.35 (m, 2H), 1.29-1.16 (m, 2H), 0.79 (t, *J*= 7.3 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 147.5, 143.6, 137.4, 129.8 (2C), 129.3 (2C), 127.1 (2C), 117.8, 113.4 (2C), 62.6, 56.2, 55.1, 34.2, 21.6, 19.4, 13.9 ppm. HRMS (ESI): calcd. for $C_{19}H_{27}N_2O_3S$ $[M+H]^+$: 363.1737, found: 363.1737.



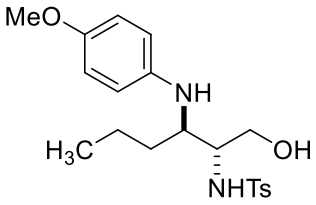
3c

(±)-*erythro-N-(1-Hydroxy-3-((2-methoxyphenyl)amino)hexan-2-yl)-4-methylbenzene sulfonamide* (**3c**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a yellow syrup (67 mg, 86%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.72 (d, *J*= 8.3 Hz, 2H), 7.25 (d, *J*= 8.0 Hz, 2H), 6.78-6.70 (m, 2H), 6.64 (m, 1H), 6.32 (dd, *J*= 8.0, 1.7 Hz, 1H), 5.44 (d, *J*= 8.2 Hz, 1H), 3.80 (s, 3H), 3.80-3.72 (m, 1H), 3.63 (dd, *J*= 11.4, 3.5 Hz, 1H), 3.42-3.35 (m, 1H), 3.36-3.30 (m, 1H), 2.41 (s, 3H), 1.58-1.31 (m, 2H), 1.27-1.17 (m, 2H), 0.79 (t, *J*= 7.3 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 147.0, 143.5, 137.4, 137.3, 129.7 (2C), 127.1 (2C), 121.1, 117.1, 110.3, 109.8, 62.2, 56.7, 55.5, 55.0, 34.5, 21.6, 19.3, 13.9. HRMS (ESI): calcd. for $C_{20}H_{29}N_2O_4S$ $[M+H]^+$:393.1843, found: 363.1848.



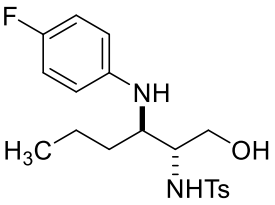
3d

(±)-*erythro-N-(1-Hydroxy-3-((3-methoxyphenyl)amino)hexan-2-yl)-4-methylbenzene sulfonamide* (**3d**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a yellow syrup (71 mg, 90%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.75-7.67 (m, 2H), 7.28-7.22 (m, 2H), 6.98 (t, *J*= 8.1 Hz, 1H), 6.24 (m, 1H), 6.00 (m, 1H), 5.95 (t, *J*= 2.3 Hz, 1H), 5.54 (d, *J*= 8.2 Hz, 1H), 3.77 (dd, *J*= 11.7, 4.1 Hz, 1H), 3.73 (s, 3H), 3.66 (dd, *J*= 11.5, 3.7 Hz, 1H), 3.36 (dd, *J*= 8.2, 4.2 Hz, 1H), 3.28 (d, *J*= 6.1 Hz, 1H), 2.42 (s, 3H), 1.49-1.37 (m, 2H), 1.27-1.14 (m, 2H), 0.79 (t, *J*= 7.3 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 160.8, 148.9, 143.7, 137.3, 130.0, 129.8, 127.0 (2C), 106.4 (2C), 102.8, 99.4, 62.5, 56.2 (2C), 55.1, 34.3, 21.6, 19.4, 13.8 ppm. HRMS (ESI): calcd. for $C_{20}H_{29}N_2O_4S$ $[M+H]^+$:393.1843, found: 363.1848.



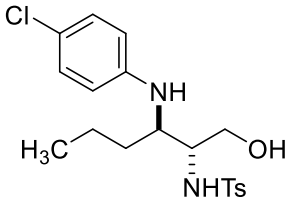
3e

(±)-*erythro-N-(1-Hydroxy-3-((4-methoxyphenyl)amino)hexan-2-yl)-4-methylbenz enesulfonamide* (**3e**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a yellow syrup (77 mg, 98%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.73 (d, *J*= 8.3 Hz, 2H), 7.27 (d, *J*= 7.9 Hz, 2H), 6.68 (d, *J*= 8.9 Hz, 1H), 6.36 (d, *J*= 8.9 Hz, 1H), 5.65 (d, *J*= 8.1 Hz, 1H), 3.76 (dd, *J*= 11.5, 4.2 Hz, 1H), 3.73 (s, 3H), 3.65 (dd, *J*= 11.5, 3.7 Hz, 1H), 3.40-3.32 (m, 1H), 3.25-3.15 (m, 1H), 2.42 (s, 3H), 1.48-1.38 (m, 2H), 1.28-1.19 (m, 2H), 0.78 (t, *J*= 7.3 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 152.4, 143.6, 141.5, 137.6, 129.8 (2C), 127.1 (2C), 115.1 (2C), 114.8 (2C), 62.5, 56.7, 56.1, 55.7, 34.2, 21.6, 19.4, 13.8 ppm. HRMS (ESI): calcd. for $C_{20}H_{29}N_2O_4S$ $[M+H]^+$:393.1843, found: 363.1848.



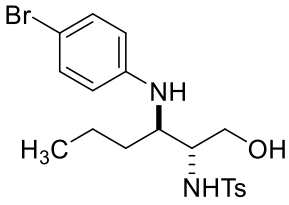
3f

(±)-*erythro-N-(3-((4-Fluorophenyl)amino)-1-hydroxyhexan-2-yl)-4-methylbenzenesu lfonamide* (**3f**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a yellow syrup (67 mg, 88%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.75-7.66 (m, 2H), 7.25 (d, *J*= 8.6 Hz, 2H), 6.85-6.69 (m, 2H), 6.37-6.21 (m, 2H), 5.62 (d, *J*= 8.3 Hz, 1H), 3.78 (dd, *J*= 11.5, 4.1 Hz, 1H), 3.66 (dd, *J*= 11.5, 3.8 Hz, 1H), 3.42-3.34 (m, 1H), 3.30-3.22 (m,1H), 2.42 (s, 3H), 1.47-1.35 (m, 2H), 1.27-1.16 (m, 2H), 0.79 (t, *J*= 7.3 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 155.9 (d, *J*= 235.5 Hz), 143.8 (d, *J*= 2.1 Hz), 143.7 , 137.3, 129.8 (2C), 127.0 (2C), 115.6 (d, *J*= 22.2 Hz, 2C), 114.3 (d, *J*= 7.4 Hz, 2C), 62.6, 56.0 (2C), 34.0, 21.5, 19.4, 13.8 ppm. ^{19}F NMR (376 MHz, Chloroform-*d*) δ= –127.68 (s, 1F) ppm; HRMS (ESI): calcd. for $C_{19}H_{26}FN_2O_3S$ $[M+H]^+$:381.1643, found: 381.1647.



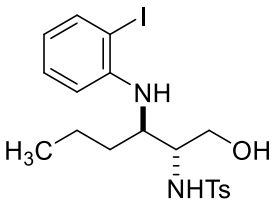
3g

(±)-erythro-N-(3-((4-Chlorophenyl)amino)-1-hydroxyhexan-2-yl)-4-methylbenzenesulfonamide (**3g**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a yellow syrup (63 mg, 79%) ^{1}H NMR (400 MHz, Chloroform-*d*) 7.68 (d, *J*= 8.3 Hz, 2H), 7.23 (d, *J*= 8.0 Hz, 2H), 6.99 (d, *J*= 8.8 Hz, 2H), 6.27 (d, *J*= 8.9 Hz, 2H). 5.64 (d, *J*= 8.3 Hz, 1H),4.01-3.88 (brs, 1H), 3.78 (dd, *J*= 11.5, 4.1 Hz, 1H), 3.66 (dd, *J*= 11.5, 3.8 Hz, 1H), 3.42-3.34 (m, 1H), 3.26 (m, 1H), 2.73-2.58)brs, 1H), 2.42 (s, 3H), 1.46-1.34 (m, 2H), 1.28-1.18 (m, 2H), 0.79 (t, *J*= 7.3 Hz, 3H) ppm. 13C NMR (101 MHz, Chloroform-*d*) δ= 146.1, 143.8, 137.2, 129.8 (2C), 129.0 (2C), 127.0 (2C), 122.0, 114.3 (2C), 62.6, 56.1, 55.2, 33.8, 21.6, 19.4, 13.8 ppm. HRMS (ESI): calcd. for $C_{19}H_{26}ClN_2O_3S$ $[M+H]^+$:397.1347, found: 397.1355.



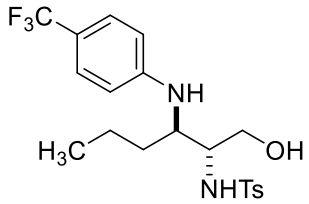
3h

(±)-*erythro-N-(3-((4-Bromophenyl)amino)-1-hydroxyhexan-2-yl)-4-methylbenzenesulfonamide* (**3h**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a yellow syrup (74 mg, 84%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.68 (d, *J*= 8.4 Hz, 2H), 7.23 (d, *J*= 8.1 Hz, 2H), 7.11 (d, *J*= 8.8 Hz, 2H), 6.22 (d, *J*= 8.9 Hz, 2H). 5.65 (d, *J*= 8.3 Hz, 1H), 4.02-3.94 (brs, 1H), 3.78 (dd, *J*= 11.5, 4.0 Hz, 1H), 3.66 (dd, *J*= 11.5, 3.8 Hz, 1H), 3.41-3.33 (m, 1H), 3.30-3.26 (m, 1H), 2.74-2.60 (brs, 1H), 2.42 (s, 3H), 1.47-1.32 (m, 2H), 1.31-1.15 (m, 2H), 0.79 (t, *J*= 7.3 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 146.5, 143.8, 137.1, 131.8 (2C), 129.8 (2C), 127.0 (2C), 114.7 (2C), 108.8, 62.6, 56.1, 54.9, 33.8, 21.6, 19.4, 13.8 ppm. HRMS (ESI): calcd. for $C_{19}H_{26}BrN_2O_3S$ $[M+H]^+$:441.0842, found: 441.0842.



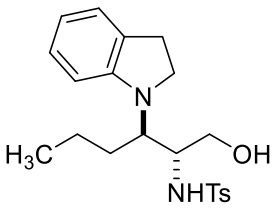
3i

(±)-*erythro-N-(1-Hydroxy-3-((2-iodophenyl)amino)hexan-2-yl)-4-methylbenzenesulfonamide* (**3i**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a yellow syrup (79 mg, 81%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.63 (d, *J*= 8.3 Hz, 2H), 7.60 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.21 (d, *J*= 8.0 Hz, 2H), 7.07 (m, 1H), 6.40 (m, 1H), 6.27 (dd, *J*= 8.3, 1.4 Hz, 1H), 5.46 (d, *J*= 8.0 Hz, 1H), 3.90-3.82 (m, 1H), 3.75-3.63 (m, 1H), 3.48-3.36 (m, 2H), 2.39 (s, 3H), 1.57-1.37 (m, 2H), 1.29-1.21 (m, 2H), 0.81 (t, *J*= 7.3 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 146.6, 143.6, 139.2, 137.1, 129.8 (2C), 129.30, 127.0 (2C), 118.9, 110.8, 86.3, 62.4, 56.0, 55.3, 34.0, 21.6, 19.4, 13.9 ppm. HRMS (ESI): calcd. for $C_{19}H_{26}IN_2O_3S$ $[M+H]^+$:489.0703, found: 441.0712.



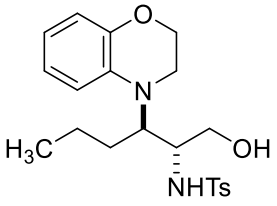
3j

(±)-*erythro-N-(1-Hydroxy-3-((4-(trifluoromethyl)phenyl)amino)hexan-2-yl)-4-methylbenzenesulfonamide* (**3j**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a yellow syrup (73 mg, 85%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.66 (m, 2H), 7.29-7.25 (m, 2H), 7.21 (d, *J*= 8.0 Hz, 2H), 6.35 (d, *J*= 8.5 Hz, 2H), 5.63 (d, *J*= 7.9 Hz, 1H), 3.88-3.76 (m, 1H), 3.75-3.65 (m, 1H), 3.44-3.32 (m, 2H), 2.41 (s, 3H), 1.52-1.37 (m, 2H), 1.25-1.18 (m, 2H), 0.81 (t, *J*= 7.3 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 150.1, 143.9, 137.0, 129.8 (2C), 127.0 (2C), 126.5 (q, *J*= 3.8 Hz, 2C), 124.9 (q, *J*= 270.3 Hz), 118.7 (q, *J*= 32.5 Hz), 112.0 (2C), 62.6, 55.9, 54.4, 33.8, 21.5, 19.4, 13.8 ppm. ^{19}F NMR (376 MHz, Chloroform-*d*) δ= –61.03 (s, 3F) ppm; HRMS (ESI): calcd. for $C_{20}H_{26}F_3N_2O_3S$ $[M+H]^+$:431.1611, found: 431.1612.



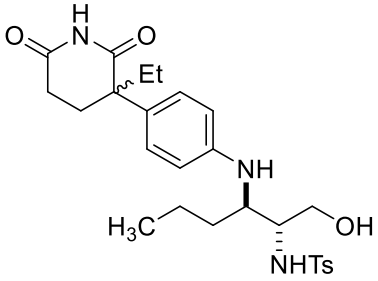
3k

(±)-*erythro-N-(1-Hydroxy-3-(indolin-1-yl)hexan-2-yl)-4-methylbenzenesulfonamide* (**3k**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a yellow syrup (65 mg, 84%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.81-7.75 (m, 2H), 7.31 (d, *J*= 8.0 Hz, 2H), 7.01-6.92 (m, 2H), 6.54 (m, 1H), 6.18 (d, *J*= 7.8 Hz, 1H), 5.35 (d, *J* = 9.1 Hz, 1H) 3.56 (dd, *J*= 11.0, 3.8 Hz, 1H), 3.53-3.38 (m, 2H), 3.34 (dd, *J*= 10.9, 8.0 Hz, 2H), 3.29-3.20 (m, 1H), 3.01-2.83 (m, 2H), 2.43 (s, 3H), 1.65 (m, 1H), 1.43 (m, 1H), 1.15 (m, 2H), 0.78 (t, *J*= 7.3 Hz, 3H). ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 151.5, 143.7, 137.9, 129.8 (2C), 128.4, 127.4, 127.1 (2C), 124.8, 116.7, 105.1, 61.6, 57.2, 54.8, 46.1, 30.2, 28.1, 21.6, 20.1, 13.9 ppm. HRMS (ESI): calcd. for $C_{21}H_{29}N_2O_3S$ $[M+H]^+$:389.1893, found: 389.1893.



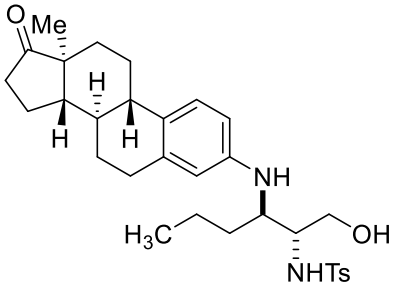
3l

(±)-*erythro-N-(3-(2,3-Dihydro-4H-benzo[b][1,4]oxazin-4-yl)-1-hydroxyhexan-2-yl)-4-methylbenzenesulfonamide* (**3l**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a yellow syrup (55 mg, 68%).^{1}H NMR (400 MHz, DMSO-d_6) δ= 7.67 (d, *J*= 8.0 Hz, 2H), 7.51 (d, *J*= 9.4 Hz, 1H), 7.34 (d, *J*= 8.0 Hz, 2H), 6.75 (d, *J*= 8.2 Hz, 1H), 6.73-6.67 (m, 1H), 6.64 (dd, *J*= 7.8, 1.4 Hz, 1H), 6.43 (t, *J*= 8.0 Hz 1H), 4.12-3.98 (m, 2H), 3.96-3.90 (1H), 3.45-3.40 (m, 1H), 3.35-3.28 (m, 1H), 3.25-3.20 (m, 1H), 3.13 (dd, *J*= 10.7, 7.2 Hz, 1H), 2.98 (dd, *J*= 10.7, 4.4 Hz, 1H), 2.37 (s, 3H), 1.59-1.49 (m, 2H), 1.24-1.17 (m, 1H), 1.12- 1.00 (m, 1H), 0.80 (t, *J*= 7.3 Hz, 3H).^{13}C NMR (101 MHz, DMSO-d_6) δ= 143.5, 142.8, 139.9, 134.0, 129.9 (2C), 126.8 (2C), 121.7, 116.4, 115.9, 111.3, 64.5, 61.0, 56.9, 53.9 (2C), 28.3, 21.4 , 19.8, 14.4 ppm. HRMS (ESI): calcd. for $C_{21}H_{29}N_2O_4S$ $[M+H]^+$:405.1843, found: 405.1844.



3m

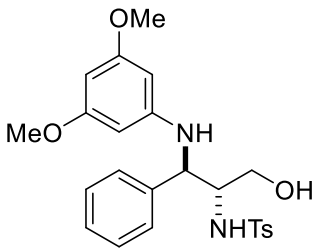
(±)-*erythro-N-(3-((4-(3-Ethyl-2,6-dioxopiperidin-3-yl)phenyl)amino)-1-hydroxyhexan-2-yl)-4-methylbenzenesulfonamide* (**3m**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:2) as a white solid (78 mg, 76%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.71 (dd, *J*= 8.2, 1.5 Hz, 2H), 7.28-7.23 (m, 2H), 7.00-6.92 (m, 2H), 6.43-6.30 (m, 2H), 3.77 (dd, *J*= 11.0, 3.1 Hz, 1H), 3.69-3.56 (m, 1H), 3.42-3.3.29 (m, 2H), 2.62-2.46 (m, 2H), 2.42 (s, 3H), 2.32-2.24 (m, 1H), 2.22-2.10 (m, 1H), 2.06-1.92 (m, 1H), 1.90-1.80 (m, 1H), 1.52-1.38 (m, 2H), 1.32-1.18 (m, 2H), 0.85 (t, *J*= 8.0, 3H), 0.80 (t, *J*= 8.0 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-d) δ= 175.7, 172.8, 146.8, 143.7, 137.5, 129.8 (2C), 127.1 (2C), 127.0 (3C), 113.5 (2C), 62.4, 56.1, 55.2, 50.2, 34.2, 32.9, 29.4, 26.9 , 21.6, 19.4, 13.8, 9.0 ppm. HRMS (ESI): calcd. for $C_{26}H_{36}N_3O_5S$ $[M+H]^+$:502.2370, found: 502.2372..



3n

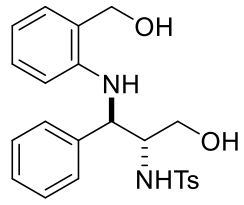
(±)-*erythro-N-(1-Hydroxy-3-(((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)amino)hexan-2-yl)-4-methylbenzenesulfonamide* (**3n**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:2) as a white solid (78 mg, 92%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.79-7.70 (m, 2H), 7.30 (d, *J*= 8.0 Hz, 2H), 7.03 (d, *J*= 8.4 Hz, 1H), 6.24 (dt, *J*= 8.4, 2.8 Hz, 1H), 6.18 (dd, *J*= 10.9, 2.5 Hz, 1H), 5.45 (d, *J*= 8.3 Hz, 1H), 3.78 (dd, *J*= 11.5, 3.9 Hz, 1H), 3.67 (dd, *J*= 11.5, 1.0 Hz, 1H), 3.41-3.34 (m, 1H), 3.29-3.20 (m, 1H), 2.89-2.69 (m, 2H), 2.50 (dd, *J*= 18.8, 8.5 Hz, 1H), 2.45 (s, 3H), 2.39-2.30 (m, 1H), 2.20 (d, *J*= 14.6 Hz, 1H), 2.17-2.07 (m, 1H), 2.07-1.90 (m, 2H), 1.68-1.54 (m, 2H), 1.54-1.34 (m, 8H), 1.30-1.14

(m, 2H), 0.91 (s, 3H), 0.80 (t, *J*= 8.0 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-d) δ= 221, 145.4, 143.6, 137.6, 137.4, 129.8 (2C), 129.6, 127.1 (2C), 126.2, 113.7, 111.4, 62.5, 56.2, 55.6, 55.5, 50.4, 48.1, 44.0, 38.5, 35.9, 34.5, 31.6, 29.7, 26.7, 25.9, 21.6, 19.4, 13.9 (2C) ppm. HRMS (ESI): calcd. for $C_{31}H_{43}N_2O_4S$ $[M+H]^+$:539.2938, found: 529.2947.



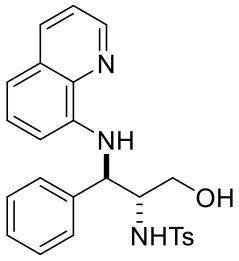
3o

(±)-*erythro-N-(1-((3,5-Dimethoxyphenyl)amino)-3-hydroxy-1-phenylpropan-2-yl) -4-methylbenzenesulfonamide* (**3o**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a white solid (82 mg, 89%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.82-7.75 (m, 2H), 7.29-7.22 (m, 5H), 7.22-7.14 (m, 2H), 5.77 (t, *J*= 2.1 Hz, 1H), 5.59 (d, *J*= 8.8 Hz, 1H), 5.49 (d, *J*= 2.1 Hz, 1H), 4.34 (dd, *J*= 7.8, 4.1 Hz, 1H), 3.62 (s, 6H), 3.61-3.57 (m, 1H), 3.52-3.48 (m, 2H), 2.41 (s, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 161.4 (2C), 148.4, 144.0, 138.9, 137.2 (2C), 130.0 (2C), 128.9, 127.7 (2C), 127.0 (2C), 126.8 (2C), 92.3, 89.9, 62.1, 59.2, 57.7, 55.0 (2C), 21.6 ppm. HRMS (ESI): calcd. for $C_{24}H_{29}N_2O_5S$ $[M+H]^+$:457.1792, found: 457.1789.



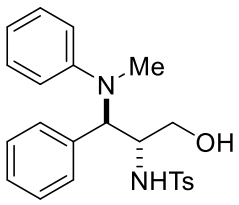
3p

(±)-*erythro-N-(3-Hydroxy-1-((2-(hydroxymethyl)phenyl)(methyl)amino)-1-phenylpropa n-2-yl)-4-methylbenzenesulfonamide* (**3p**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:2) as a white solid (70 mg, 88%).^{1}H NMR (400 MHz, DMSO-*d*6) δ= 7.65-7.58 (m, 2H), 7.51 (d, *J*= 8.6 Hz, 1H), 7.32-7.22 (m, 6H), 7.22-7.13 (m, 1H), 6.88 (t, *J*= 7.9 Hz, 1H), 6.43 (dd, *J*= 5.0, 1.9 Hz, 2H), 6.20-6.08 (m, 1H), 5.80 (d, *J*= 7.6 Hz, 1H), 4.50 (dd, *J*= 7.6, 4.9 Hz, 1H), 4.30 (d, *J*= 5.4 Hz, 2H), 3.53-3.42 (m, 1H), 3.29-3.17 (m, 1H), 3.19-3.11 (m, 1H), 2.34 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ= 147.6, 143.5, 142.9, 140.6, 138.9, 129.9 (2C), 128.9, 128.4 (2C), 128.2 (2C), 127.3, 126.9 (2C), 114.9, 111.6, 111.2, 63.6, 60.0, 59.5, 57.3, 21.4 ppm. HRMS (ESI): calcd. for $C_{23}H_{27}N_2O_4S$ $[M+H]^+$:427.1686, found: 427.1689.



3q

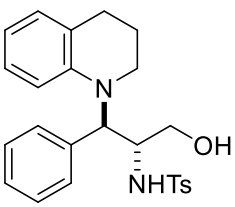
(±)-*erythro-N-(3-Hydroxy-1-phenyl-1-(quinolin-8-ylamino)propan-2-yl)-4-methylbenze nesulfonamide* (**3q**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:2) as a white solid (77 mg, 86%). ^{1}H NMR (400 MHz, DMSO-d_6) δ= 8.81 (dd, *J*= 4.2, 1.7 Hz, 1H), 8.18 (dd, *J*= 8.3, 1.8 Hz, 1H), 7.77-7.69 (m, 2H), 7.67 (d, *J*= 7.8 Hz, 1H), 7.57 (d, *J*= 8.4 Hz, 1H), 7.51 (dd, *J*= 8.3, 4.2 Hz, 1H), 7.38-7.32 (m, 2H), 7.31-7.25 (m, 4H), 7.23-7.17 (m, 1H), 7.15 (t, *J*= 7.9 Hz, 1H), 7.00 (dd, *J*= 8.2, 1.2 Hz, 1H), 6.21 (dd, *J*= 7.9, 1.2 Hz, 1H), 5.06 (brs, 1H), 4.83 (dd, *J*= 7.7, 3.9 Hz, 1H), 3.72-3.62 (m, 1H), 3.25-3.10 (m, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ= 147.6, 143.8, 142.9, 139.7, 139.0, 138.2, 136.3, 129.9 (2C), 128.7, 128.6 (2C), 128.1 (2C), 127.9, 127.6 , 127.1 (2C), 122.2, 113.9, 105.8, 60.1, 58.9, 57.5, 21.4 ppm. HRMS (ESI): calcd. for $C_{25}H_{26}N_3O_3S$ $[M+H]^+$: 448.1695, found: 448.1703.



3r

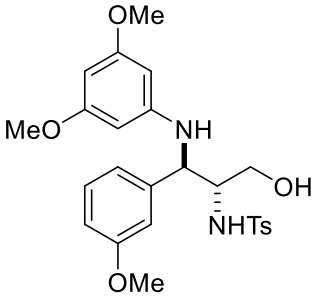
(±)-*erythro-N-(3-Hydroxy-1-(methyl(phenyl)amino)-1-phenylpropan-2-yl)-4-methylbenz enesulfonamide* (**3r**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a yellow syrup (66 mg, 80%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.62-7.56 (m, 2H), 7.27-7.21 (m, 4H), 7.21-7.16 (m, 1H), 7.13-7.07 (m, 2H), 6.93-6.84 (m, 4H), 6.83-6.80 (m, 1H), 4.98 (d, *J*= 10.8 Hz, 1H), 4.79-4.61 (m, 1H), 4.06 (m, 1H), 3.86 (m, 2H), 2.44 (s, 3H), 2.43 (s, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 150.1, 143.6, 137.1, 134.7, 129.7 (2C), 129.3 (2C), 128.3 (2C), 128.3 (2C), 127.7, 127.2 (2C), 118.90 , 115.5 (2C), 64.5, 61.8, 54.4, 32.3, 21.6. HRMS (ESI):

calcd. for $C_{23}H_{27}N_2O_3S$ $[M+H]^+$: 411.1737, found: 411.1739.



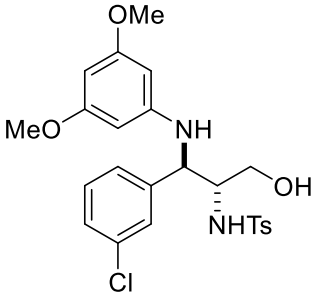
3s

(±)-*erythro-N-(1-(3,4-Dihydroquinolin-1(2H)-yl)-3-hydroxy-1-phenylpropan-2-yl)-4-methylbenzenesulfonamide* was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 2:1) as a yellow syrup (67 mg, 77%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.62-7.56 (m, 2H), 7.25-7.21 (m, 2H), 7.19-7.16 (m, 1H), 7.14-7.10 (m, 2H), 7.08-7.03 (m, 4H), 6.91-6.87 (m, 1H), 6.66-6.52 (m, 1H), 5.13 (d, *J*= 10.7 Hz, 1H), 4.85 (d, *J*= 7.4 Hz, 1H), 4.10 (td, *J*= 7.5, 3.7 Hz, 1H), 3.85-3.74 (m, 2H), 3.05-2.95 (m, 1H), 2.85-2.74 (m, 1H), 2.64-2.55 (m, 2H), 2.43 (s, 3H), 1.75-1.62 (m, 1H), 1.55-1.45 (m, 1H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 145.0, 143.6, 137.3, 135.9, 129.9, 129.7 (2C), 128.5 (2C), 128.4 (2C), 127.7, 127.3, 127.2 (2C), 123.5, 117.0, 112.3, 61.6, 60.6, 54.4, 43.0, 28.1, 21.6, 21.5 ppm. HRMS (ESI): calcd. for $C_{25}H_{29}N_2O_3S$ $[M+H]^+$:437.1893, found: 437.1893.



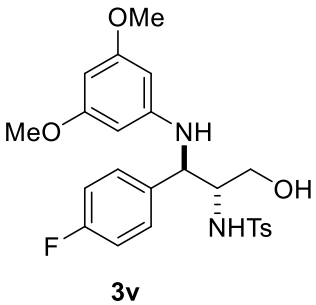
3t

(±)-*erythro-N-(1-((3,5-Dimethoxyphenyl)amino)-3-hydroxy-1-(3-methoxyphenyl) propan-2-yl)-4-methylbenzenesulfonamide* (**3t**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a yellow syrup (82 mg, 84%). ^{1}H NMR (400 MHz, DMSO-d_6) δ= 7.61-7.55 (m, 2H), 7.54 (d, *J*= 8.7 Hz, 1H), 7.27-7.22 (m, 2H), 7.17 (t, *J*= 7.9 Hz, 1H), 6.86 (dt, *J*= 7.7, 1.2 Hz, 1H), 6.80 (dd, *J*= 2.6, 1.5 Hz, 1H), 6.75 (ddd, *J*= 8.2, 2.6, 0.9 Hz, 1H), 5.68 (t, *J*= 2.1 Hz, 1H), 5.54 (d, *J*= 2.2 Hz, 2H), 4.38 (m, 1H), 3.68 (s, 3H), 3.57 (s, 6H), 3.45-3.36 (m, 1H), 3.27 (dd, *J*= 10.9, 4.7 Hz, 1H), 3.23-3.14 (m, 1H), 2.33 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ= 161.3 (2C), 159.5, 149.6, 142.8, 142.4, 138.9, 129.8 (2C), 129.4, 126.9 (2C), 120.5, 113.9, 112.3, 92.1 (2C), 89.1, 60.2, 59.4, 57.5, 55.2, 55.1 (2C), 21.4. HRMS (ESI): calcd. for $C_{25}H_{31}N_2O_6S$ $[M+H]^+$:487.1897, found: 487.1902.



3u

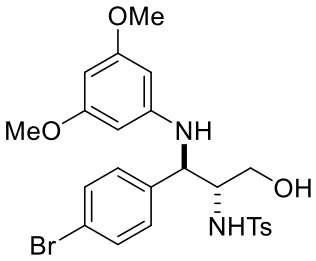
(±)-*erythro-N-(1-(3-Chlorophenyl)-1-((3,5-dimethoxyphenyl)amino)-3-hydroxypropan-2-yl)-4-methylbenzenesulfonamide* (**3u**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:2) as a yellow syrup (78 mg, 80%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.77-7.72 (m, 2H), 7.29-7.24 (m, 2H), 7.20-7.15 (m, 2H), 7.14-7.11 (m, 1H), 7.09-7.03 (m, 1H), 5.80 (t, *J*= 2.1 Hz, 1H), 5.64 (d, *J*= 8.6 Hz, 1H), 5.48 (d, *J*= 2.2 Hz, 2H), 4.35-4.28 (m, 1H), 3.64 (s, 6H), 3.61-3.55 (m, 1H), 3.55-3.49 (m, 2H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 161.5 (2C), 148.1, 144.0, 141.5, 137.1, 134.8, 130.1, 130.0 (2C), 127.9, 127.0 (2C), 126.9, 125.1, 92.3 (2C), 90.1, 62.0, 59.1, 57.6, 55.1 (2C), 21.5 ppm. HRMS (ESI): calcd. for $C_{24}H_{28}ClN_2O_5S$ $[M+H]^+$:491.1402, found: 491.1404.



3v

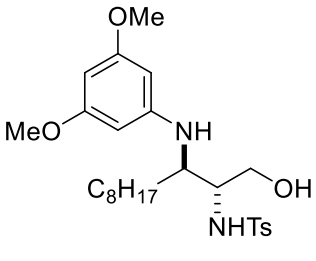
(±)-*erythro-N-(1-((3,5-Dimethoxyphenyl)amino)-1-(4-fluorophenyl)-3-hydroxypropan-2-yl)-4-methylbenzenesulfonamide* (**3v**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:2) as a yellow syrup (84 mg, 89%). ^{1}H NMR (400 MHz, DMSO-d6) δ= 7.57-7.48 (m, 2H), 7.35-7.21 (m, 4H), 7.09-6.93 (m, 2H), 5.91 (d, *J*= 7.7 Hz, 1H), 5.67 (t, *J*= 2.1 Hz, 1H), 5.52 (d, *J*= 2.2 Hz, 2H), 4.86 (t, *J*= 5.0 Hz, 1H), 4.42 (dd, *J*= 7.7, 5.7 Hz, 1H), 3.57 (s, 6H), 3.48-3.37 (m, 1H), 3.32-3.22 (m, 1H), 3.22-3.09 (m, 1H), 2.35 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ= 161.7 (d, *J*= 242.4 Hz), 161.4 (2C), 149.3, 142.8 138.9, 136.7 (d, *J*= 2.9 Hz), 129.9 (d, *J*= 6.8 Hz, 2C), 129.9 (2C), 126.8 (2C), 115.1 (d, *J*= 21.2 Hz, 2C), 92.1 (2C), 89.2, 60.3, 59.3, 56.5, 55.1 (2C), 21.4. ^{19}F NMR (376 MHz, DMSO-d6) δ= –113.09 (s, 1F)

ppm; HRMS (ESI): calcd. for $C_{24}H_{28}FN_2O_5S$ $[M+H]^+$:475.1697, found: 475.1699.



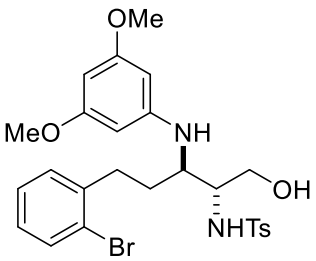
3w

(±)-*erythro-N-(1-(4-Bromophenyl)-1-((3,5-dimethoxyphenyl)amino)-3-hydroxypropan-2-yl)-4-methylbenzenesulfonamide* (**3w**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:2) as a yellow syrup (89 mg, 84%).^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.74 (d, *J*= 8.2 Hz, 2H), 7.37 (d, *J*= 8.4 Hz, 2H) 7.28 (d, *J*= 8.2 Hz, 2H), 7.05 (d, *J*= 8.4 Hz, 2H), 5.80 (t, *J*= 2.1 Hz, 1H), 5.48 (d, *J*= 2.1 Hz, 2H), 5.31 (d, *J*= 8.0 Hz, 1H), 4.31 (dd, *J*= 7.7, 4.2 Hz, 1H), 3.65 (s, 6H), 3.57 (dd, *J*= 8.6, 4.1 Hz, 2H), 3.55-3.45 (m, 1H), 2.43 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ=161.5 (2C), 148.1, 144.0, 138.0, 137.2, 132.0 (2C), 130.0 (2C), 128.6 (2C), 127.0 (2C), 121.6, 92.4 (2C), 90.1, 62.1, 58.8, 57.5, 55.1 (2C), 21.6 ppm. HRMS (ESI): calcd. for $C_{24}H_{28}BrN_2O_5S$ $[M+H]^+$:535.0897, found: 535.0895.



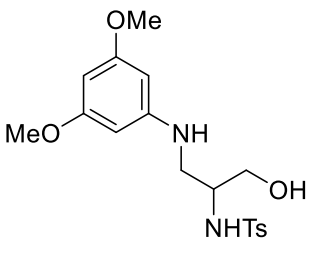
3x

(±)-*erythro-N-(3-((3,5-Dimethoxyphenyl)amino)-1-hydroxyundecan-2-yl)-4-methylbenzenesulfonamide* (**3x**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:2) as a yellow syrup (97 mg, 98%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.75-7.70 (m, 2H), 7.30-7.26 (m, 2H), 5.85 (t, *J*= 2.1 Hz, 1H), 5.59 (d, *J*= 2.1 Hz, 2H), 5.45 (d, *J*= 8.3 Hz, 1H), 3.83-3.76 (m, 1H), 3.72 (s, 6H), 3.71-3.63 (m, 1H), 3.40-3.30 (m, 1H), 3.25-3.15 (m, 1H), 2.43 (s, 3H), 1.43 (dd, *J*= 8.7, 5.1 Hz, 2H), 1.32-1.04 (m, 12H), 0.87 (t, *J*= 7.0 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 161.7 (2C), 149.4, 143.7, 137.3, 129.9 (2C), 127.1 (2C), 92.2 (2C), 90.0, 62.5, 56.0, 55.3, 55.1 (2C), 32.0, 31.8, 29.4, 29.3, 29.2, 26.1, 22.7, 21.6, 14.1 ppm. HRMS (ESI): calcd. for $C_{26}H_{41}N_2O_5S$ $[M+H]^+$:493.2731, found: 493.2725.



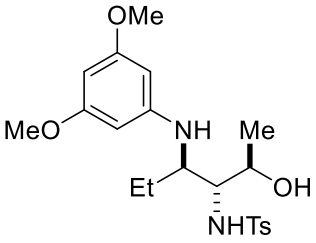
3y

(±)-erythro-N-(3-((3,5-Dimethoxyphenyl)amino)-1-hydroxy-5-phenylpentan-2-yl)-4-methylbenzenesulfonamide was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a yellow syrup (73 mg, 75%) ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.71 (d, *J*= 8.0 Hz, 2H), 7.48 (d, *J*= 7.9 Hz, 1H), 7.24 (d, *J*= 8.0 Hz, 2H), 7.16 (t, *J*= 7.4 Hz, 1H), 7.11-7.00 (m, 2H), 5.86 (t, *J*= 2.1 Hz, 1H), 5.64 (d, *J*= 2.0 Hz, 2H), 5.47 (d, *J*= 8.3 Hz, 1H), 3.81 (dd, *J*= 11.5, 3.7 Hz, 1H), 3.71 (s, 6H), 3.65 (dd, *J*= 11.5, 3.7 Hz, 1H), 3.41 (dd, *J*= 8.4, 4.3 Hz, 1H), 3.40-3.30 (m, 1H), 2.68 (dd, *J*= 10.2, 5.0 Hz, 1H), 2.66-2.58 (m, 1H), 2.40 (s, 3H), 1.89-1.80 (m, 1H), 1.67 (dd, *J*= 9.3, 4.6 Hz, 1H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 161.7 (2C), 149.3, 143.7, 140.4, 137.2, 132.8, 130.4, 129.9 (2C), 127.8, 127.6, 127.1 (2C), 124.2, 92.3 (2C), 90.3, 62.5, 56.4 (2C), 55.2, 33.1, 32.4, 21.6 ppm. HRMS (ESI): calcd. for $C_{26}H_{32}BrN_2O_5S$ $[M+H]^+$:563.1215, found: 563.1215.



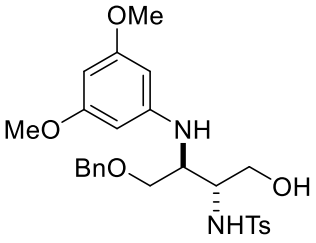
3z

(±)-*N-(1-((3,5-Dimethoxyphenyl)amino)-3-hydroxypropan-2-yl)-4-methylbenzenesulfonamide* (**3z**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a yellow syrup (66 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.73 (d, *J*= 8.3 Hz, 2H), 7.24 (d, *J*= 8.0 Hz, 2H), 5.86 (t, *J*= 2.1 Hz, 1H), 5.64 (d, *J*= 2.1 Hz, 2H), 5.50 (d, *J*= 7.1 Hz, 1H), 3.71 (s, 6H), 3.63 (d, *J*= 3.8 Hz, 2H), 3.52-3.37 (m, 1H), 3.23-3.10 (m, 2H), 2.40 (s, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 161.7 (2C), 149.3, 143.8, 136.8, 129.8 (2C), 127.1 (2C) , 91.8 (2C), 90.4, 63.1, 55.2 (2C), 53.7, 44.9, 21.5 ppm. HRMS (ESI): calcd. for $C_{18}H_{25}N_2O_5S$ $[M+H]^+$:381.1479, found: 381.1488..



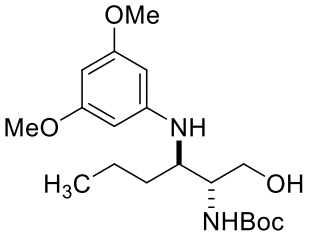
3aa

(±)-*1,2-anti-2,3-anti-N-(1-((3,5-Dimethoxyphenyl)amino)-3-hydroxypropan-2-yl)-4-methylbenzenesulfonamide* (**3aa**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a yellow syrup (71 mg, 85%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.80-7.62 (m, 2H), 7.37-7.21 (m, 2H), 5.84 (t, *J*= 2.1 Hz, 1H), 5.51 (d, *J*= 2.2 Hz, 2H), 5.42 (d, *J*= 8.9 Hz, 1H), 4.15-4.09 (m, 1H), 3.72 (s, 6H), 3.24-3.16 (m, 1H), 3.00-2.92 (m, 1H), 2.45 (s, 3H), 1.52 (td, *J*= 13.8, 13.3, 6.5 Hz, 1H), 1.43 (dd, *J*= 14.3, 7.2 Hz, 1H), 1.19 (d, *J*= 6.3 Hz, 3H), 0.78 (t, *J*= 7.4 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 161.6 (2C), 149.5, 143.6, 137.8, 129.9 (2C), 127.0 (2C), 92.4 (2C), 89.9, 66.4, 58.0, 57.9, 55.1 (2C), 25.2, 21.6, 21.5, 10.9 ppm. HRMS (ESI): calcd. for $C_{21}H_{31}N_2O_5S$ $[M+H]^+$:423.1948, found: 423.1958.



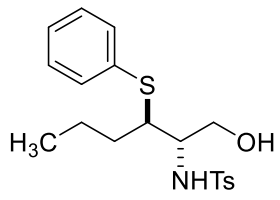
3ab

(±)-*erythro-N-(4-(Benzyloxy)-3-((3,5-dimethoxyphenyl)amino)-1-hydroxybutan-2-yl)-4-methylbenzenesulfonamide* (**3ab**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a yellow syrup (98 mg, 98%).^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.73-7.67 (m, 2H), 7.39-7.32 (m, 3H), 7.30-7.21 (m, 4H), 5.85 (t, *J*= 2.1 Hz, 1H), 5.62 (d, *J*= 2.1 Hz, 2H), 4.57-4.38 (m, 2H), 3.71 (s, 6H), 3.72-3.62 (m, 2H), 3.59-3.50 (m, 3H), 3.40-3.30 (m, 1H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 161.8 (2C), 148.1, 143.7, 137.1, 136.9, 129.8 (2C), 128.7 (2C), 128.3, 128.0 (2C), 127.1 (2C), 92.1 (2C), 90.2, 73.8, 68.4, 62.9, 56.1, 55.2 (2C), 54.0, 21.5 ppm. HRMS (ESI): calcd. for $C_{26}H_{33}N_2O_6S$ $[M+H]^+$:501.2054, found: 501.2051.



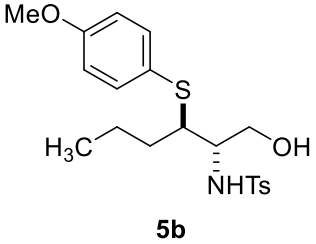
3ad

(±)-tert-butyl((2R,3R)-3-((3,5-dimethoxyphenyl)amino)-1-hydroxyhexan-2-yl)carbamate (**3ad**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 2:1) as a yellow syrup (33mg, 45%).^{1}H NMR (400 MHz, Chloroform-*d*) δ= 5.86 (t, *J*= 2.1 Hz, 1H), 5.82 (d, *J*= 2.1 Hz, 2H), 5.24 (d, *J*= 8.7 Hz, 1H), 3.88-3.77 (m, 2H), 3.74 (s, 6H), 3.72-3.66 (m, 1H), 3.62-3.51 (m, 1H), 1.64-1.49 (m, 2H), 1.44 (s, 9H), 1.39-1.25 (m, 2H), 0.90 (t, *J*= 7.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 161.8 (2C), 156.0, 150.2, 92.0 (2C), 89.7, 79.7, 62.5, 55.4, 55.1, 54.0, 35.2, 28.3 (3C), 19.5, 14.1 ppm. HRMS (ESI): calcd. for $C_{19}H_{33}N_2O_5$ $[M+H]^+$:369.2389, found: 369.2383.



5a

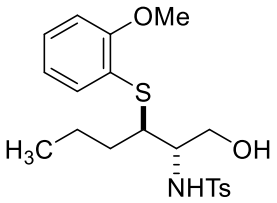
(±)-erythro-N-(1-Hydroxy-3-(phenylthio)hexan-2-yl)-4-methylbenzenesulfonamide (**5a**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a yellow syrup (51 mg, 68%).^{1}H NMR (400 MHz, $CDCl_3$) δ= 7 .71 (dd, *J*= 8.5, 1.9 Hz, 2H), 7.32-7.16 (m, 5H), 7.03-6.82 (m, 2H), 3.81-3.69 (m, 1H), 3.62-3.54 (m, 1H), 3.50-3.40 (m, 1H), 3.02-2.94 (m, 1H), 2.42 (s, 3H), 1.66-1.57 (m, 1H), 1.53-1.21 (m, 3H), 0.81 (t, *J*= 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 147.5, 143.6, 137.4, 129.8 (2C), 129.3 (2C), 127.1 (2C), 117.8, 113.4 (2C), 62.6, 56.2, 55.1, 34.2, 21.6, 19.4, 13.9 ppm. HRMS (ESI): calcd. for $C_{19}H_{25}NNaO_3S_2$ $[M+H]^+$:402.1168, found: 402.1169.



5b

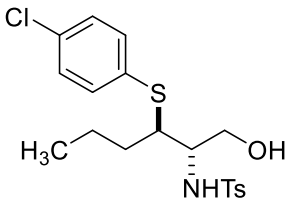
(±)-N-(1-Hydroxy-3-((4-methoxyphenyl)thio)hexan-2-yl)-4-methylbenzenesulfonamide (**5b**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a yellow syrup (45 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$)

δ= 7.69 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 5.39 (d, *J*= 8.4 Hz, 1H), 3.80 (s, 3H), 3.78-3.73 (m, 1H), 3.60-3.50 (m, 1H), 3.48-3.39 (m, 1H), 2.85-2.79 (m, 1H), 2.41 (s, 3H), 1.62-1.51 (m, 1H), 1.47-1.26 (m, 3H), 0.79 (t, *J*= 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ= 159.6, 143.6, 137.4, 134.8 (2C), 129.7 (2C), 127.2 (2C), 124.8 (2C), 114.8, 62.1, 58.2, 55.4, 54.1, 34.4, 21.6, 20.5, 13.6 ppm. HRMS (ESI): calcd. for $C_{20}H_{27}NNaO_4S_2$ $[M+H]^+$:432.1274, found: 432.1280.



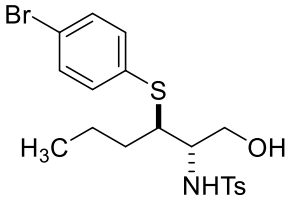
5c

(±)-N-(1-Hydroxy-3-((2-methoxyphenyl)thio)hexan-2-yl)-4-methylbenzenesulfonamide (**5c**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a yellow syrup (54 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.50 (d, *J*= 8.3 Hz, 2H), 7.39-7.25 (m, 2H), 7.16-7.10 (m, 2H), 6.96 (d, *J*= 8.2 Hz, 1H), 6.91 (td, *J*= 7.5, 0.8 Hz, 1H), 3.99 (s, 3H), 3.90-3.72 (m, 1H), 3.62-3.52 (m, 1H), 3.36 (m, 1H), 2.65-2.55 (m, 1H), 2.36 (s, 3H), 1.56-1.45 (m, 2H), 1.44-1.18 (m, 2H), 0.73 (t, *J*= 7.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ= 158.9, 143.4, 137.2, 136.5, 130.4, 129.7 (2C), 127.0 (2C), 122.5, 121.5, 111.4, 61.8, 58.1, 56.2, 54.0, 35.8, 21.5, 20.3, 13.4 ppm. HRMS (ESI): calcd. for $C_{20}H_{27}NNaO_4S_2$ $[M+H]^+$:432.1274, found: 432.1280.



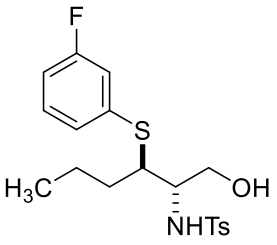
5d

(±)-*N-(3-((4-Chlorophenyl)thio)-1-hydroxyhexan-2-yl)-4-methylbenzenesulfonamide* (**5d**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 2:1) as a yellow syrup (37 mg, 45%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.65-7.60 (m, 2H), 7.18 (d, *J*= 7.8 Hz, 2H), 7.14-7.08 (m, 2H), 7.08-7.03 (m, 2H), 3.69 (dd, *J*= 11.6, 5.8 Hz, 1H), 3.51 (dd, *J*= 11.6, 4.0 Hz, 1H), 3.40 (m, 1H), 3.03-2.91 (m, 1H), 2.36 (s, 3H), 1.62-1.50 (m, 1H), 1.45-1.31 (m, 2H), 1.31-1.16 (m, 1H), 0.75 (t, *J*= 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 143.8, 137.3, 133.5, 133.3, 132.6 (2C), 129.8 (2C), 129.2 (2C), 127.1 (2C), 62.0, 57.8, 53.1, 34.5, 21.6, 20.5, 13.6 ppm. HRMS (ESI): calcd. for $C_{19}H_{24}ClNNaO_3S_2$ $[M+Na]^+$:436.0778, found: 436.0780.



5e

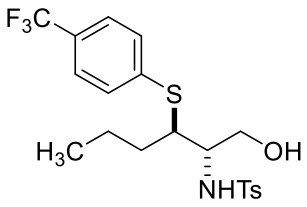
(±)-*N-(3-((4-Bromophenyl)thio)-1-hydroxyhexan-2-yl)-4-methylbenzenesulfonamide* (**5e**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 2:1) as a yellow syrup (72 mg, 84%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.74-7.64 (m, 2H), 7.37-7.30 (m, 2H), 7.30-7.18 (m, 2H), 7.12-6.98 (m, 2H), 5.48 (d, *J*= 8.3 Hz, 1H), 3.84-3.74 (m, 1H), 3.63-3.55 (m, 1H), 3.52-3.44 (m, 1H), 3.05 (dt, *J*= 8.4, 5.2 Hz, 1H), 2.42 (s, 3H), 1.69-1.58 (m, 1H), 1.50-1.40 (m, 2H), 1.38-1.25 (m, 1H), 0.81 (t, *J*= 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 143.7, 137.3, 134.4, 132.7 (2C), 132.1 (2C), 129.8 (2C), 127.1 (2C), 121.1, 62.0, 57.8, 52.8, 34.4, 21.6, 20.5, 13.7 ppm. HRMS (ESI): calcd. for $C_{19}H_{24}BrNNaO_3S_2$ $[M+Na]^+$:480.0273, found: 480.0287.



5f

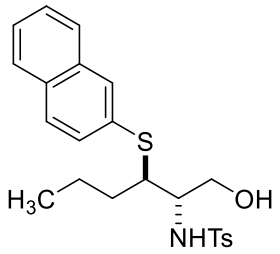
(±)-*N-(3-((4-Fluorophenyl)thio)-1-hydroxyhexan-2-yl)-4-methylbenzenesulfonamide* (**5f**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 2:1) as a yellow syrup (72 mg, 84%).^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.73-7.66 (m, 2H), 7.26 (dd, *J*= 8.5, 0.8 Hz, 2H), 7.25-7.15 (m, 1H), 7.0-6.97 (m, 1H), 6.94-6.86 (m, 1H), 6.92-6.76 (m, 1H), 5.37 (d, *J*= 8.4 Hz, 1H), 3.79-3.69 (m, 1H), 3.65-3.55 (m, 1H), 3.56-3.46 (m, 1H), 3.09 (dt, *J*= 8.5, 5.2 Hz, 1H), 2.42 (s, 3H), 1.70-1.60 (m, 1H), 1.49-1.40 (m, 2H), 1.38-1.30 (m, 1H), 0.82 (t, *J*= 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 162.7 (d, *J*= 249.0 Hz), 143.9, 137.5 (d, *J* = 7.3 Hz), 137.2, 130.4 (d, *J*= 8.6 Hz), 129.8 (2C), 127.1 (2C), 126.2 (d, *J*= 3.0 Hz), 117.3 (d, *J*= 22.7 Hz), 114.0 (d, *J*= 21.1 Hz), 62.1, 57.8, 52.2, 34.4, 21.5, 20.5, 13.6 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ= –111.59

(s, 1F) ppm; HRMS (ESI): calcd. for $C_{19}H_{24}FNNaO_3S_2$ $[M+Na]^+$:420.1074, found: 420.1078.



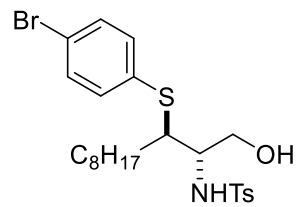
5g

(±)-N-(1-Hydroxy-3-((3-(trifluoromethyl)phenyl)thio)hexan-2-yl)-4-methylbenzene sulfonamide (**5f**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 2:1) as a yellow syrup (59 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.74-7.65 (m, 2H), 7.47-7.39 (m, 2H), 7.27-7.18 (m, 4H), 3.78 (dd, *J*= 11.4, 5.7 Hz, 1H), 3.67-3.56 (m, 1H), 3.54 (d, *J*= 4.6 Hz, 1H), 3.31-3.18 (m, 1H), 2.40 (s, 3H), 1.72-1.64 (m, 1H), 1.53-1.41 (m, 2H), 1.41-1.31 (m, 1H), 0.84 (t, *J*= 7.2 Hz, 3H) ppm. 13C NMR (101 MHz, Chloroform-*d*) δ= 143.8, 140.8, 137.2, 129.8 (2C), 129.5 (2C), 127.1 (2C), 125.9 (q, *J*= 111.1), 125.8 (q, *J*= 33.3 Hz), 122.6 (2C), 62.0, 57.6, 51.4, 34.4, 21.5, 20.5, 13.7 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ= –62.57 (s, 3F) ppm; HRMS (ESI): calcd. for $C_{20}H_{24}F_3NNaO_3S_2$ $[M+Na]^+$:470.1042, found: 470.1048.



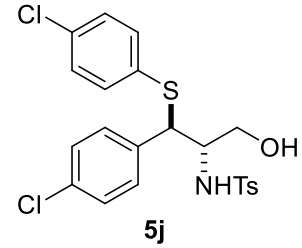
5h

(±)-*N-(1-Hydroxy-3-(naphthalen-2-ylthio)hexan-2-yl)-4-methylbenzenesulfonamide* (**5h**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 2:1) as a yellow syrup (72 mg, 84%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.82-7.77 (m, 1H), 7.72-7.66 (m, 3H), 7.65-7.60 (m, 2H), 7.5-7.44 (m, 2H), 7.29-7.24 (m, 1H), 7.17-7.05 (m, 2H), 5.38 (d, *J*= 8.4 Hz, 1H), 3.86-3.76 (m, 1H), 3.66-3.58 (m, 1H), 3.58-3.50 (m, 1H), 3.19-3.12 (m, 1H), 2.32 (s, 3H), 1.72-1.63 (m, 1H), 1.59-1.47 (m, 2H), 1.43-1.34 (m, 1H), 0.83 (t, *J*= 7.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 143.6, 137.2, 133.6, 132.3, 132.2, 129.9, 129.7 (2C), 128.8, 128.6, 127.7, 127.3, 127.0 (2C), 126.7, 126.4, 62.1, 58.0, 52.6, 34.6, 21.5, 20.6, 13.7 ppm. HRMS (ESI): calcd. for $C_{23}H_{28}NO_3S_2$ $[M+H]^+$:430.1505, found: 430.1508.



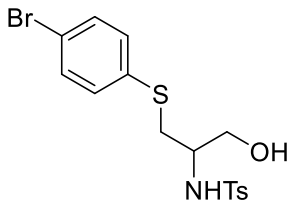
5i

(±)-N-(3-((4-Bromophenyl)thio)-1-hydroxyundecan-2-yl)-4-methylbenzenesulfonamide (**5i**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 2:1) as a yellow syrup (59mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.72-7.63 (m, 2H), 7.27-7.23 (m, 2H), 7.21-7.16 (m, 2H), 7.16-7.09 (m, 2H), 5.35 (d, *J*= 8.3 Hz, 1H), 3.86-3.66 (m, 1H), 3.65-3.55 (m, 1H), 3.52-3.39 (m, 1H), 3.13-2.89 (m, 1H), 2.43 (s, 3H), 1.70-1.59 (m, 1H), 1.48-1.36 (m, 1H), 1.36-1.05 (m, 12H), 0.88 (t, *J*= 7.0 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ= 143.8, 137.3, 133.6, 133.3, 132.7 (2C), 129.8 (2C), 129.2 (2C), 127.1 (2C), 62.1, 57.8, 53.3, 32.3, 31.8, 29.3, 29.2, 29.1, 27.2, 22.7, 21.6, 14.1 ppm. HRMS (ESI): calcd. for $C_{24}H_{34}BrNNaO_3S_2$ $[M+H]^+$:550.1056, found: 430.1508.



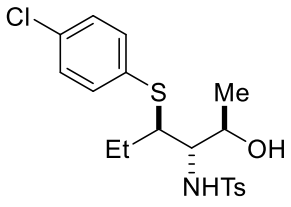
5j

(±)-*N-(1-(4-Chlorophenyl)-1-((4-chlorophenyl)thio)-3-hydroxypropan-2-yl)-4-methylbenzenesulfonamide* (**5j**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 2:1) as a white solid (46 mg, 48%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.60-7.55 (m, 2H), 7.21-7.16 (m, 2H), 7.14-7.11 (m, 2H), 7.10-7.07 (m, 3H), 7.03-6.97 (m, 3H), 4.19 (d, *J*= 7.0 Hz, 1H), 3.88 (d, *J*= 11.5 Hz, 1H), 3.77-3.60 (m, 2H), 2.40 (s, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 143.8, 140.4, 136.8, 134.5, 133.7, 133.0 (2C), 132.2, 129.8, 129.7 (2C), 129.1 (2C), 128.4, 128.0, 126.9 (2C), 126.8, 62.0, 59.0, 55.1, 21.6 ppm. HRMS (ESI): calcd. for $C_{22}H_{22}Cl_2NO_3S_2$ $[M+H]^+$:482.0413, found: 482.0413.



5k

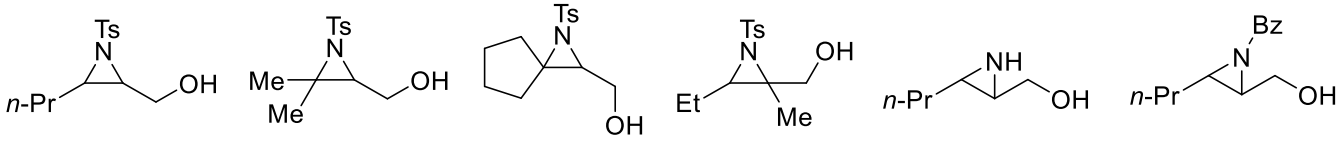
(±)-*N-(1-((4-Bromophenyl)amino)-3-hydroxypropan-2-yl)-4-methylbenzenesulfonamide* (**5k**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 2:1) as a white solid (44 mg, 56%). ^{1}H NMR (400 MHz, CDCl3) δ= 7.68-7.64 (m, 2H), 7.24 (d, *J*= 8.0 Hz, 2H), 7.20-7.15 (m, 2H), 7.13-7.04 (m, 2H), 3.87-3.56 (m, 2H), 3.34-3.21 (m, 1H), 3.04-2.91 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ= 143.9, 136.7, 133.2, 132.6, 130.7 (2C), 129.8 (2C), 129.2 (2C), 127.2 (2C), 62.8, 53.8, 35.1, 21.6. ppm. HRMS (ESI): calcd. for $C_{16}H_{19}BrNO_3S_2$ $[M+H]^+$:415.9984, found: 415.9984..



5l

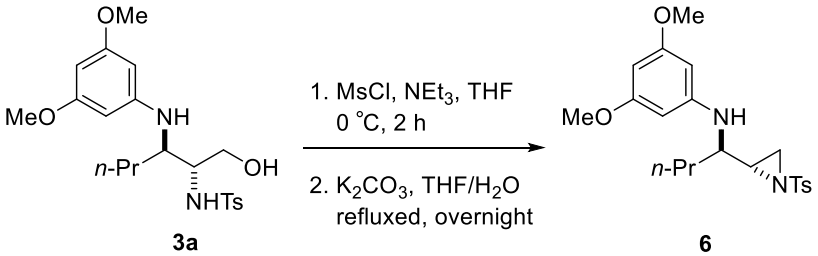
(±)-*1,2-anti-2,3-anti-N-(4-((4-Chlorophenyl)thio)-2-hydroxyhexan-3-yl)-4-methylbenzenesulfonamide* (**5l**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 2:1) as a yellow syrup (58mg, 71%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.70-7.61 (m, 2H), 7.27-7.22 (m, 3H), 7.19 (m, 4H), 5.37 (d, *J*= 8.7 Hz, 1H), 4.23-4.09 (m, 1H), 3.41-3.56 (m, 1H), 3.04-2.98 (m, 1H), 2.42 (s, 3H), 1.76-1.64 (m, 1H), 1.62-1.47 (m, 1H), 1.01 (d, *J*= 6.4 Hz, 3H), 0.98 (t, *J*= 7.3 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 143.5, 138.1, 134.1, 133.2, 132.6 (2C), 129.7 (2C), 129.2 (2C), 126.9 (2C), 65.9, 60.0, 56.8, 26.5, 21.6, 21.0, 12.2 ppm. HRMS (ESI): calcd. for $C_{19}H_{24}ClNNaO_3S_2$ $[M+Na]^+$:436.0778, found: 436.0779.

Unsuccessful Aziridines for the Zn-Catalyzed Ring Opening Reaction



Procedure for Derivatizations of the Ring Opening Product

Procedure for Synthesis of Compound 6

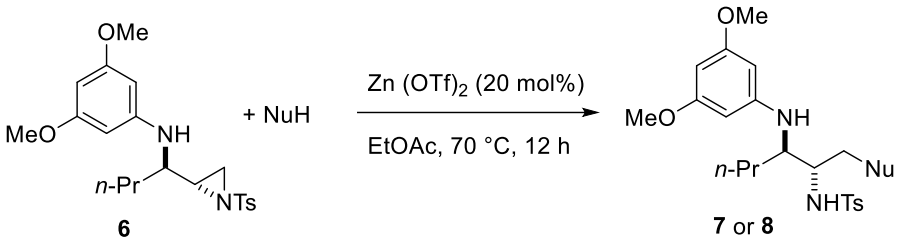


3a **6**

To the mixture of **3a** (840 mg, 2 mmol, 1 equiv) in THF (8 mL) at 0°C was added a solution of MsCl (252 mg, 2.2 mmol, 1.1 equiv) in THF (2 mL) dropwise, and the mixture was stirred at 0°C for 2h. The reaction was quenched by adding 20 mL saturated aq. NaCl solution, and the organic layer was separated, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was dissolved in THF/saturated aq. K_2CO_3=10:1 (10 mL), and then refluxed overnight, before the reaction was quenched with saturated aq. NH_4Cl solution. The organic layer was separated, dried over $MgSO_4$, filtered and concentrated under

reduced pressure. The residue was purified through column chromatography on silica gel (petroleum ether: EtOAc= 2:1) to afford (±)-*3,5-dimethoxy-N-(-1-1-tosylaziridin-2-yl)butyl)aniline* **6** as a yellow syrup (790 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.77 (d, *J*= 8.4 Hz, 2H), 7.42-7.28 (m, 2H), 5.86 (t, *J*= 2.1 Hz, 1H), 5.71 (d, *J*= 2.1 Hz, 2H), 3.75 (s, 6H), 3.78-3.69 (m, 1H), 2.81 (dd, *J* = 11.8, 5.2 Hz, 1H), 2.59 (d, *J*= 7.0 Hz, 1H), 2.45 (s, 3H), 2.31 (d, *J*= 4.6 Hz, 1H), 1.51-1.38 (m, 2H), 1.38-1.24 (m, 2H), 0.84 (t, *J*= 6.9 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ= 161.7 (2C), 149.2, 144.7, 134.7, 129.7 (2C), 128.2 (2C), 92.2 (2C), 90.0, 55.2 (2C), 53.0, 42.7, 35.0, 32.4, 21.6, 18.9, 13.9 ppm. HRMS (ESI): calcd. for $C_{21}H_{29}N_2O_4S$ $[M+H]^+$:405.1843, found: 405.1843.

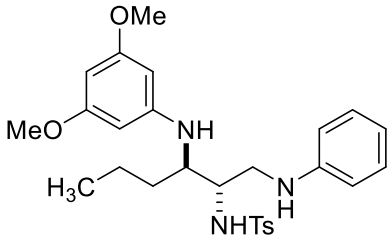
Procedure for Synthesis of Compounds 7 and 8



6 **7** or **8**

NuH: $PhNH_2$ or 3,4-$(MeO)_2C_6H_3SH$.

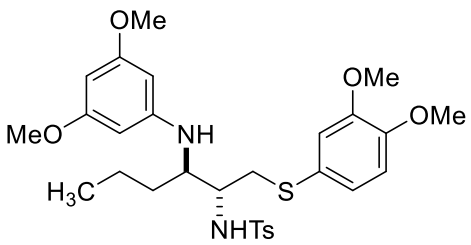
To a suspension of $Zn(OTf)_2$ (14.5 mg, 0.04 mmol, 20 mol%) in ethyl acetate (1 mL) were added **6** (80 mg, 0.2 mmol, 1 equiv) and aniline (27.9 mg, 0.3 mmol, 1.5 equiv) or 3,4-dimethoxy thiophenol (51 mg, 0.3 mmol, 1.5 equiv) at room temperature. The resulting mixture was heated to 70 °C and stirred at this temperature for 12 h. Then the reaction was cooled to room temperature, and the solvent was removed in vacuum. The residue was purified through column chromatography on silica gel (petroleum ether/ethyl acetate), affording the corresponding products **7** or **8**.



7

(±)-*N-(3-((3,5-Dimethoxyphenyl)amino)-1-(phenylamino)hexan-2-yl)-4-methylbenzenesulfonamide* was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a yellow syrup (80 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.59 (d, *J*= 8.1 Hz, 2H), 7.17 (d, *J*= 7.9 Hz, 2H), 7.01 (t, *J*= 7.7 Hz, 2H), 6.59 (t, *J*= 7.2 Hz, 1H), 6.43 (d, *J*= 8.0 Hz, 2H), 5.81 (s, 1H), 5.59 (t, *J*= 3.7 Hz, 2H), 3.59 (s, 6H), 3.50-3.40 (m, 2H), 3.21-3.11 (m, 1H), 2.94-2.82 (m, 1H), 2.34 (s, 3H), 1.47-1.27 (m, 3H), 1.27-1.12 (m, 1H), 0.76 (t, *J*= 7.1 Hz, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ= 161.8 (2C), 149.0, 148.3, 143.6, 136.6, 129.9 (2C), 129.5 (2C), 127.1 (2C), 117.9, 113.5 (2C), 92.7 (2C), 90.9, 55.9 (2C), 55.8, 55.2, 43.3, 35.1, 21.5, 19.7, 14.0 ppm. HRMS (ESI): calcd. for $C_{27}H_{36}N_3O_4S$ $[M+H]^+$:498.2421, found: 498.2422.

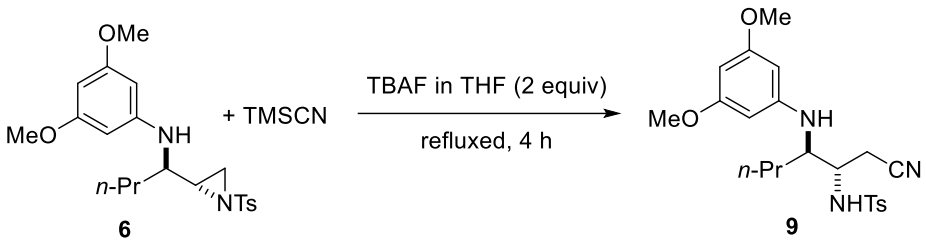
(±)-*N-(3-((3,5-Dimethoxyphenyl)amino)-1-((3,4-dimethoxyphenyl)thio)hexan-2-yl)-4-methylbenzenesulfonamide* (**8**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a yellow syrup (95 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.73 (d, *J*= 7.6 Hz, 2H), 7.30 (d, *J*= 5.8 Hz, 2H), 6.93-6.87 (m, 1H), 6.76-6.65 (m, 2H), 5.86 (t, *J*= 2.0 Hz, 1H) 5.56 (d, *J*= 1.9 Hz, 2H), 3.95-3.85 (m, 1H), 3.84 (s, 3H), 3.76-3.65 (s, 6H), 3.63 (s, 3H), 3.40-3.30 (m, 1H), 3.25-3.15 (m, 1H), 3.04-2.89 (m, 1H), 2.44 (s, 3H), 1.56-1.48 (m, 2H), 1.40-1.22 (m, 2H), 0.86 (t, *J*= 6.7 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ= 161.8 (2C), 149.3,



8

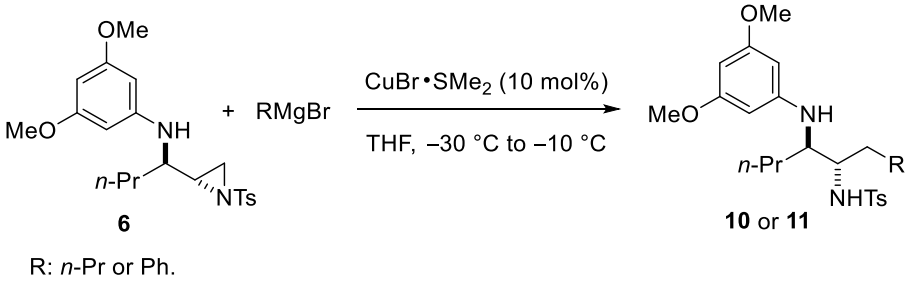
148.9, 148.5, 143.6, 136.9, 129.8 (2C), 127.1 (2C), 126.0, 125.6, 115.7, 111.4, 93.0 (2C), 90.9 56.5, 55.9, 55.7, 55.1 (2C), 53.8, 43.4, 35.4, 21.5, 20.8, 13.8 ppm. HRMS (ESI): calcd. for $C_{29}H_{39}N_2O_6S_2$ $[M+H]^+$:575.2244, found: 575.2246.

Procedure for Synthesis of Compound 9[3]



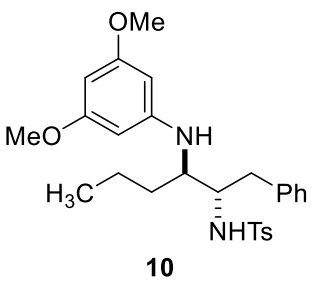
To a stirred solution of **6** (80 mg, 0.2 mmol, 1 equiv) in anhydrous THF (1 mL) was added TBAF (1 M in THF) (0.4 mmol, 0.4 mL, 2 equiv) dropwise. Subsequently, TMSCN (39.6 mg, 0.4 mmol, 2 equiv) was added to the mixture. The mixture was refluxed for 4 h and quenched with saturated aq. NH_4Cl solution. The organic layer was separated, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified through column chromatography on silica gel (petroleum ether: EtOAc= 4:1) to afford (±)-*N-(1-cyano-3-((3,5-dimethoxyphenyl)amino)hexan-2-yl)-4-methylbenzenesulfonamide* (**9**) as a yellow syrup (77 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.71 (d, *J*= 8.3 Hz, 2H), 7.24 (d, *J*= 8.1 Hz, 2H), 5.86 (t, *J*= 2.0 Hz, 1H), 5.66 (d, *J*= 2.0 Hz, 2H), 5.53 (d, *J*= 7.5 Hz, 1H), 3.72 (s, 6H), 3.55-3.46 (m, 2H). 2.74 (dd, *J* = 17.0, 5.0 Hz, 1H), 2.55 (dd, *J*= 17.0, 7.2 Hz, 1H), 2.40 (s, 3H), 1.57-1.40 (m, 1H), 1.40-1.31 (m, 1H), 1.31-1.14 (m, 2H), 0.81 (t, *J*= 7.0 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ= 161.8 (2C), 148.8, 144.1, 136.4, 129.9 (2C), 127.1 (2C), 117.4, 92.0 (2C), 90.6, 55.2, 52.6 (3C), 33.2, 21.5, 20.8, 19.3, 13.8 ppm. HRMS (ESI): calcd. for $C_{22}H_{30}N_3O_4S$ $[M+H]^+$:432.1952, found: 432.1957.

Procedure for Synthesis of Compound 10 and 11[4]



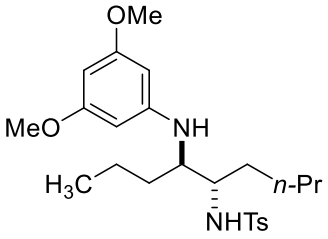
R: *n*-Pr or Ph.

$CuBr{\cdot}SMe_2$ (0.02 mmol, 6.1 mg, 0.1 equiv) was added to a solution of **6** (0.2 mmol, 80 mg, 1 equiv) in anhydrous THF (1 mL) under N_2. The mixture was then cooled to −30 °C, then the Grignard reagent (0.4 mmol, 2 equiv) was added. The reaction was stirred for 1.5 h and then allowed to warm to −10 °C for another 2 h. Next, the reaction mixture was quenched with saturated aq. NH_4Cl solution. The organic layer was separated, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue by column chromatography (petroleum ether: EtOAc) gave the corresponding products **10** and **11**.



(±)-*N-(3-((3,5-Dimethoxyphenyl)amino)-1-phenylhexan-2-yl)-4-methylbenzenes ulfonamide* (**10**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 2:1) as a yellow syrup (84 mg, 87%).^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.39 (d, *J*= 8.3 Hz, 2H), 7.13-7.06 (m, 3H), 7.00 (d, *J*= 8.0 Hz, 2H), 6.98-6.87 (m, 2H), 5.75 (t, *J*= 2.1 Hz, 1H), 5.47 (d, *J*= 2.1 Hz, 2H), 4.85 (d, *J*= 8.2 Hz, 1H), 3.59 (s, 6H), 3.53-3.42 (m, 2H), 2.70-2.57 (m, 2H), 2.28 (s, 3H),

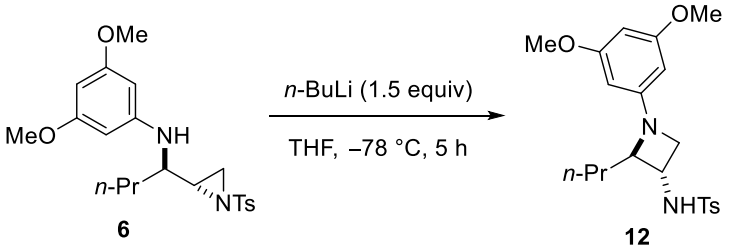
1.52-1.44 (m, 1H), 1.41-1.30 (m, 2H), 1.27-1.16 (m, 1H), 0.80 (t, *J*= 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ= 161.6 (2C), 149.6, 143.1, 137.3, 136.7, 129.5 (2C), 129.1 (2C), 128.6 (2C), 127.0 (2C), 126.6, 91.8 (2C), 90.4, 57.9, 55.2 (2C), 54.9, 37.7, 33.1, 21.5, 19.7, 14.0 ppm. HRMS (ESI): calcd. for $C_{27}H_{35}N_2O_4S$ $[M+H]^+$:483.2312, found: 483.2310.



11

(±)-*N-(4-((3,5-Dimethoxyphenyl)amino)nonan-5-yl)-4-methylbenzenesulfonamid e* (**11**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 2:1) as a yellow syrup (79 mg, 88%).^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.70 (d, *J*= 8.3 Hz, 2H), 7.26 (d, *J*= 8.0 Hz, 2H), 5.86 (t, *J*= 2.1 Hz, 1H), 5.65 (d, *J*= 2.1 Hz, 2H), 4.77 (d, *J*= 9.1 Hz, 1H), 3.75 (s, 6H), 3.35-3.25 (m, 2H), 2.42 (s, 3H), 1.43-1.29 (m, 4H), 1.32-1.26 (m, 4H), 1.20-1.10 (m, 2H), 0.84 (t, *J*= 6.6 Hz, 3H), 0.77 (t, *J*= 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ= 161.7 (2C), 149.9, 143.3, 137.9, 129.7 (2C), 127.2 (2C), 92.3 (2C), 90.0, 56.6, 56.2, 55.2 (2C), 34.0, 30.2, 28.0, 22.4, 21.5, 19.7, 14.0, 13.9. HRMS (ESI): calcd. for $C_{24}H_{37}N_2O_4S$ $[M+H]^+$:449.2469, found: 449.2471.

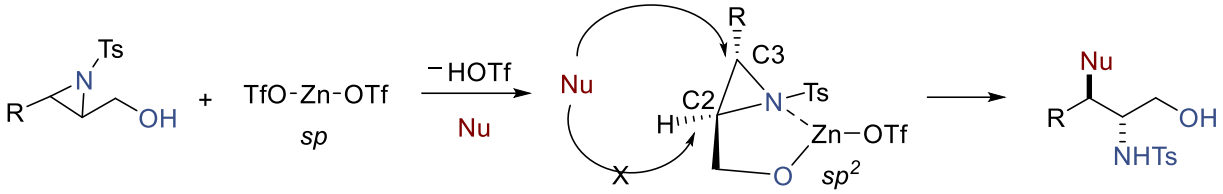
Procedure for Synthesis of Compound 12



6 **12**

To a stirred solution of **6** (80 mg, 0.2 mmol, 1 equiv) in anhydrous THF (1 mL) was added *n*-BuLi (2.5 M in hexane) (0.3 mmol, 0.12 mL, 1.5 equiv) dropwise under N_2 at −78°C. After stirring for 5 h, the reaction was quenched with saturated aq. NH_4Cl solution. The organic layer was separated, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified through column chromatography on silica gel (petroleum ether: EtOAc= 2:1) to afford (±)-*N-(1-(3,5-dimethoxyphenyl)-2-propylazetidin-3-yl)-4-methylbenzenesulfonamide* (**12**) as a yellow syrup (63 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.72 (d, *J*= 8.3 Hz, 2H), 7.30 (d, *J*= 8.0 Hz, 2H). 6.11 (t, *J*= 2.2 Hz, 1H), 6.04 (d, *J*= 2.2 Hz, 2H), 3.75 (s, 6H), 3.35-3.25 (m, 1H), 3.00-2.86 (m, 1H), 2.41 (s, 3H), 2.27-2.16 (m, 2H), 1.66-1.56 (m, 2H), 1.54-1.33 (m, 2H), 0.88 (t, *J*= 7.4 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ= 161.2 (2C), 151.1, 143.5, 136.8, 129.8 (2C), 127.1 (2C), 99.4 (2C), 94.8, 55.3 (2C), 44.6, 43.2, 42.9, 31.1, 21.5, 20.7, 13.9 ppm. HRMS (ESI): calcd. for $C_{21}H_{29}N_2O_4S$ $[M+H]^+$:405.1843, found: 405.1840.

Proposed Model for the C-3 Selectivity



In the proposed transition state relying on the Sharpless hypothesis for regioselective ring opening of 2,3-epoxy alcohols,[5] both the hydroxyl and amino group coordinate to the sp^2-hybridized Zn-center in rigid manner, to form a bicyclic complex, in which the bond between the C3 atom and the nitrogen of the aziridine is better oriented to overlap with the empty p-orbital of the Zn^{2+} than the bond between the C2 and the nitrogen atom, leading to the favored C3-N bond cleavage.

References

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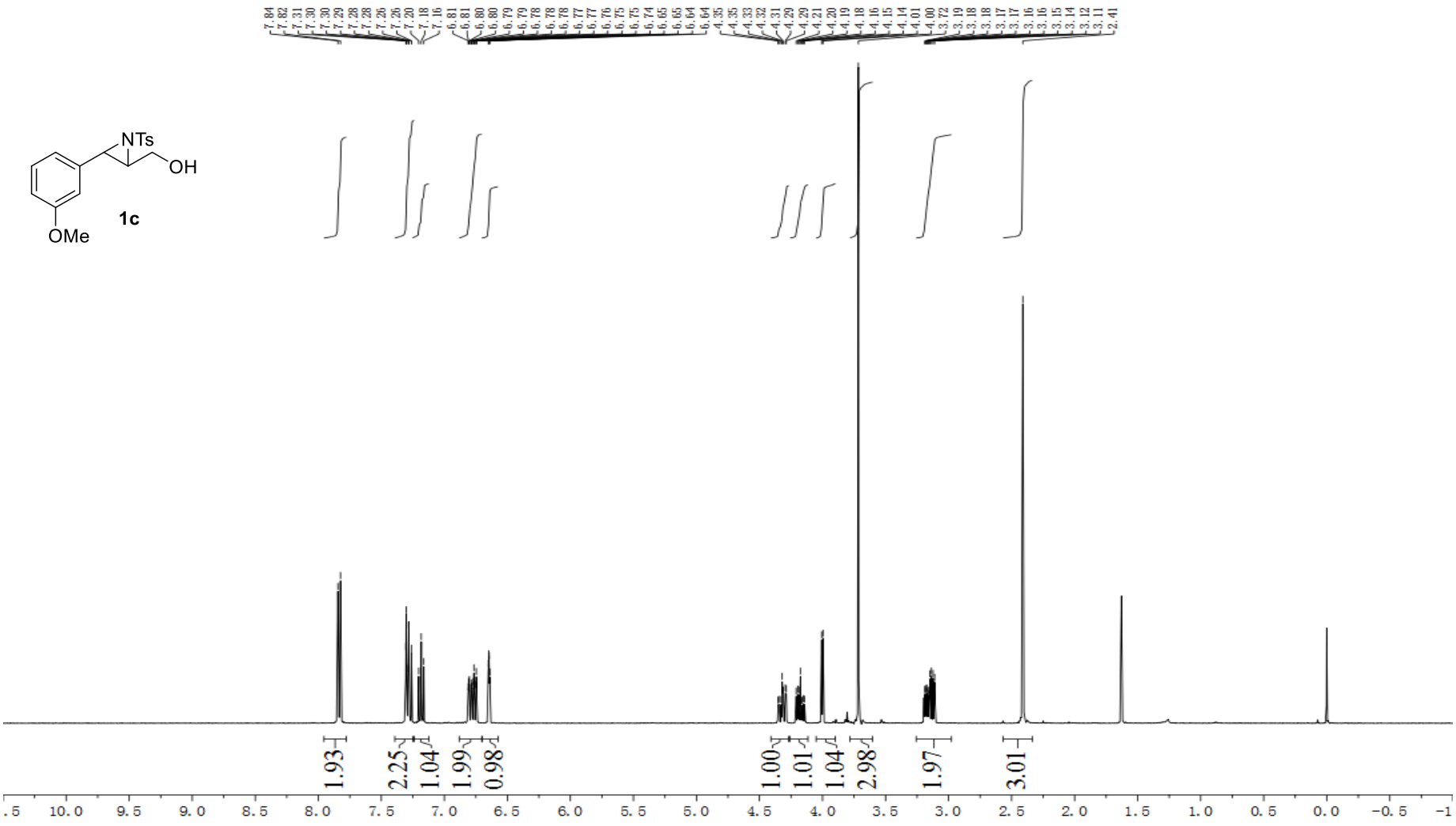
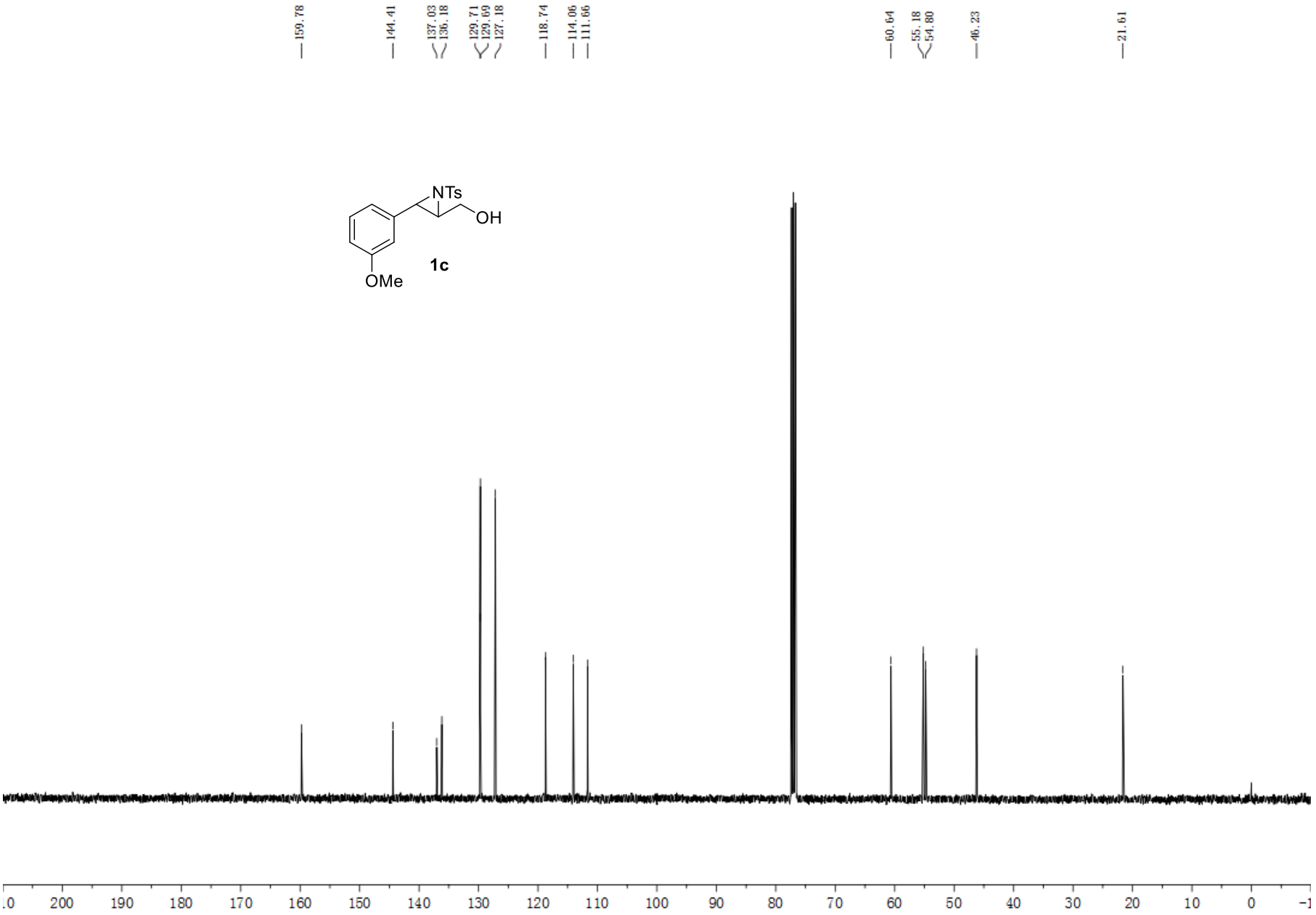
[5] Caron, M.; Sharpless, K. B. Titanium Isopropoxide-Mediated Nucleophilic Openings of 2,3-Epoxy Alcohols. A Mild Procedure for Regioselective Ring-Opening. *J. Org. Chem.* **1985**, *50*, 1557−1560.

NMR Spectra

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54.80
46.23
21.61
NTs
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OMe
1c
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70
60
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30
20
10
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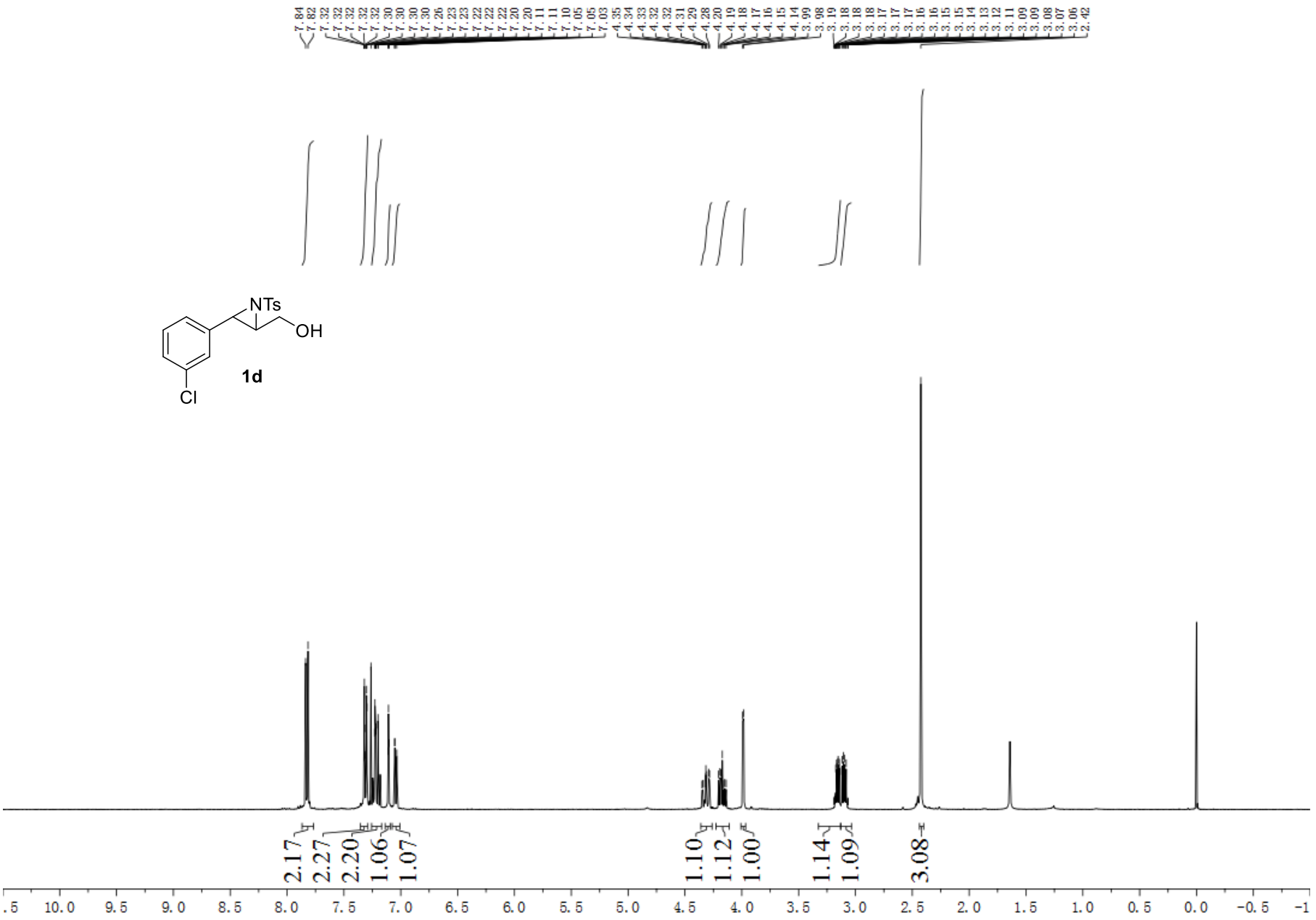
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7.23
7.22
7.22
7.22
7.20
7.20
7.11
7.11
7.10
7.05
7.05
7.03
4.35
4.34
4.33
4.32
4.32
4.31
4.29
4.28
4.20
4.19
4.18
4.17
4.16
4.15
4.14
3.99
3.98
3.19
3.18
3.18
3.18
3.17
3.17
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3.16
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3.15
3.15
3.14
3.13
3.12
3.11
3.09
3.09
3.08
3.07
3.06
2.42
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2.27
2.20
1.06
1.07
1.10
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1.14
1.09
3.08
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10.0
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9.0
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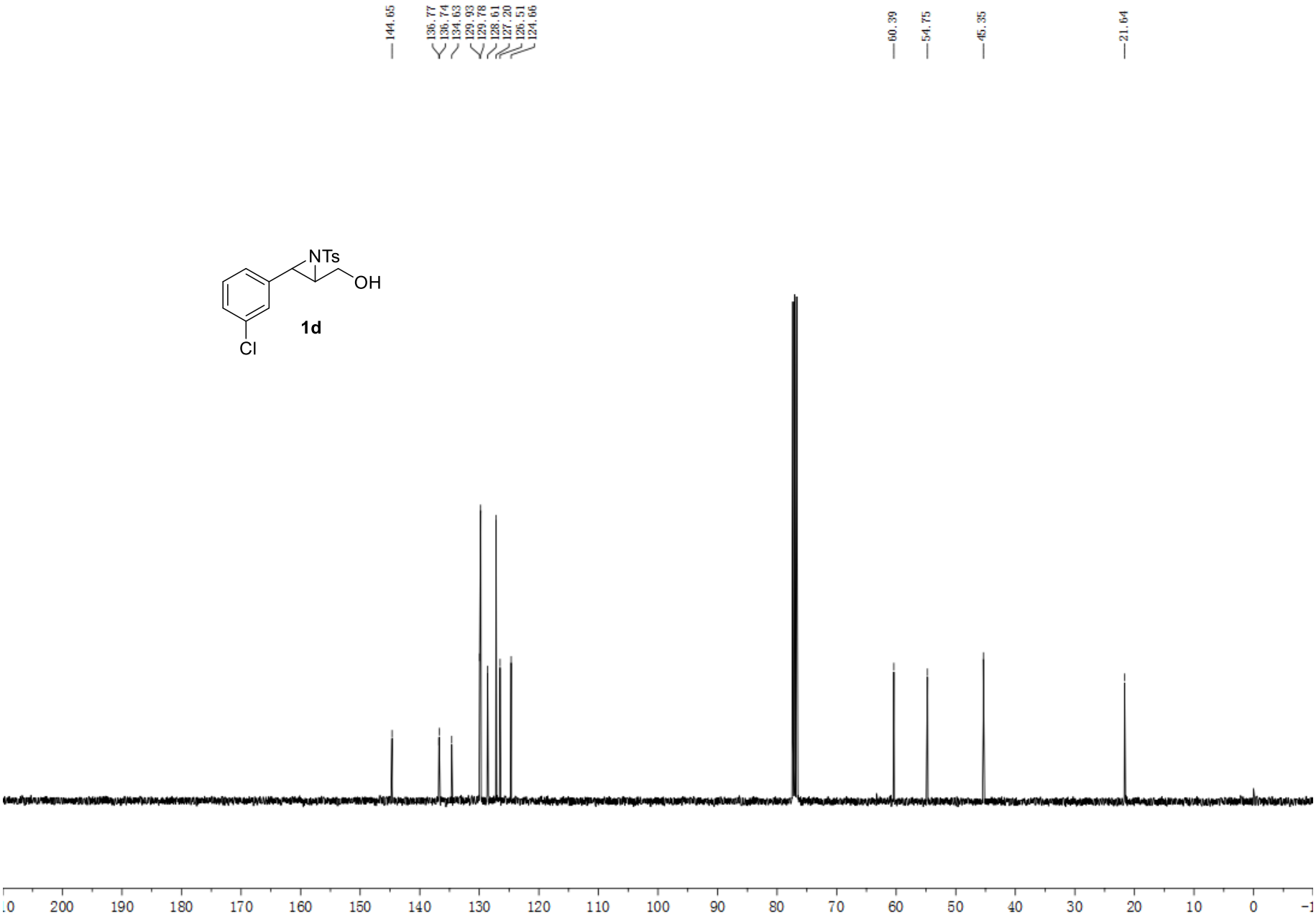
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OH
Cl
1d
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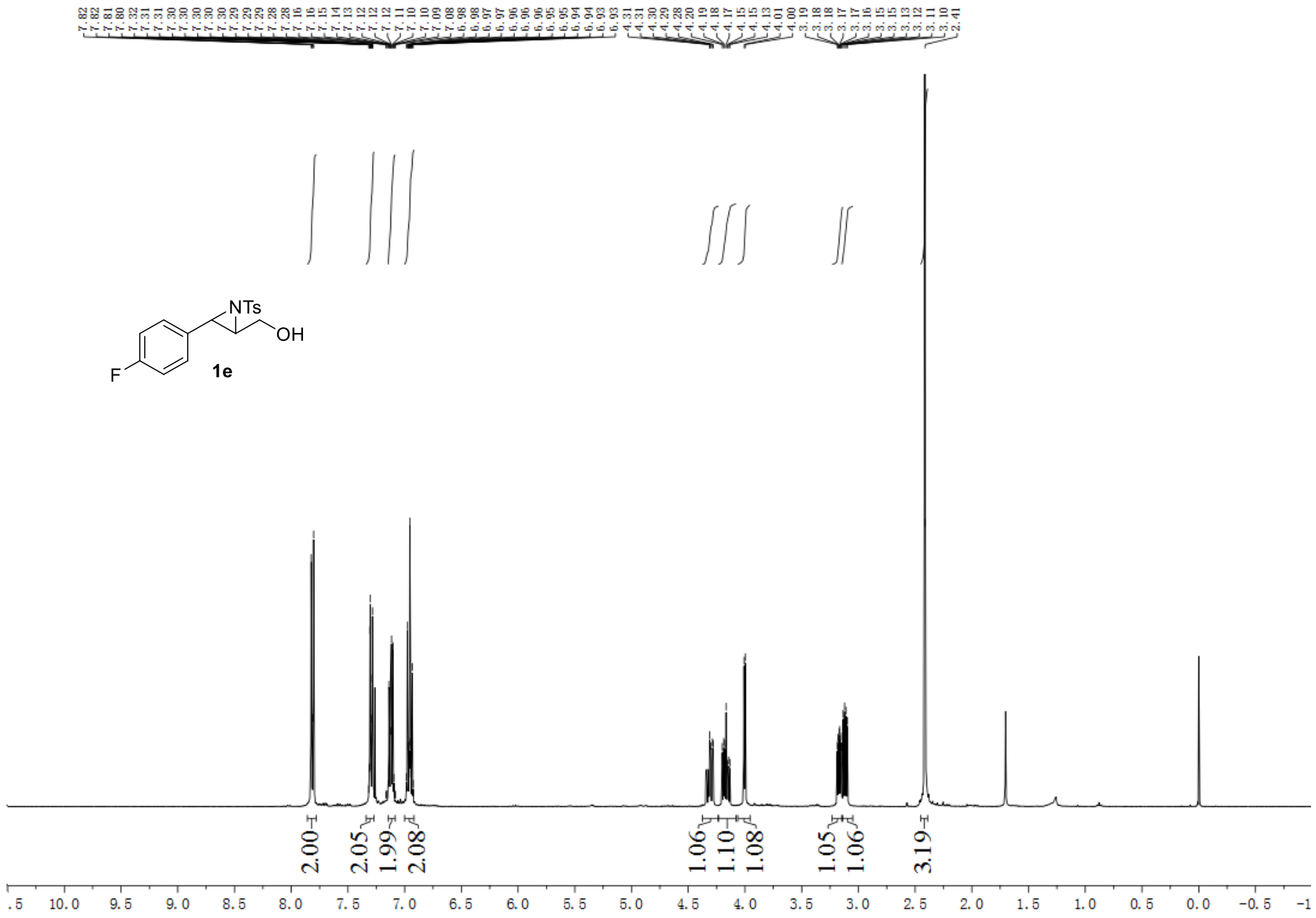
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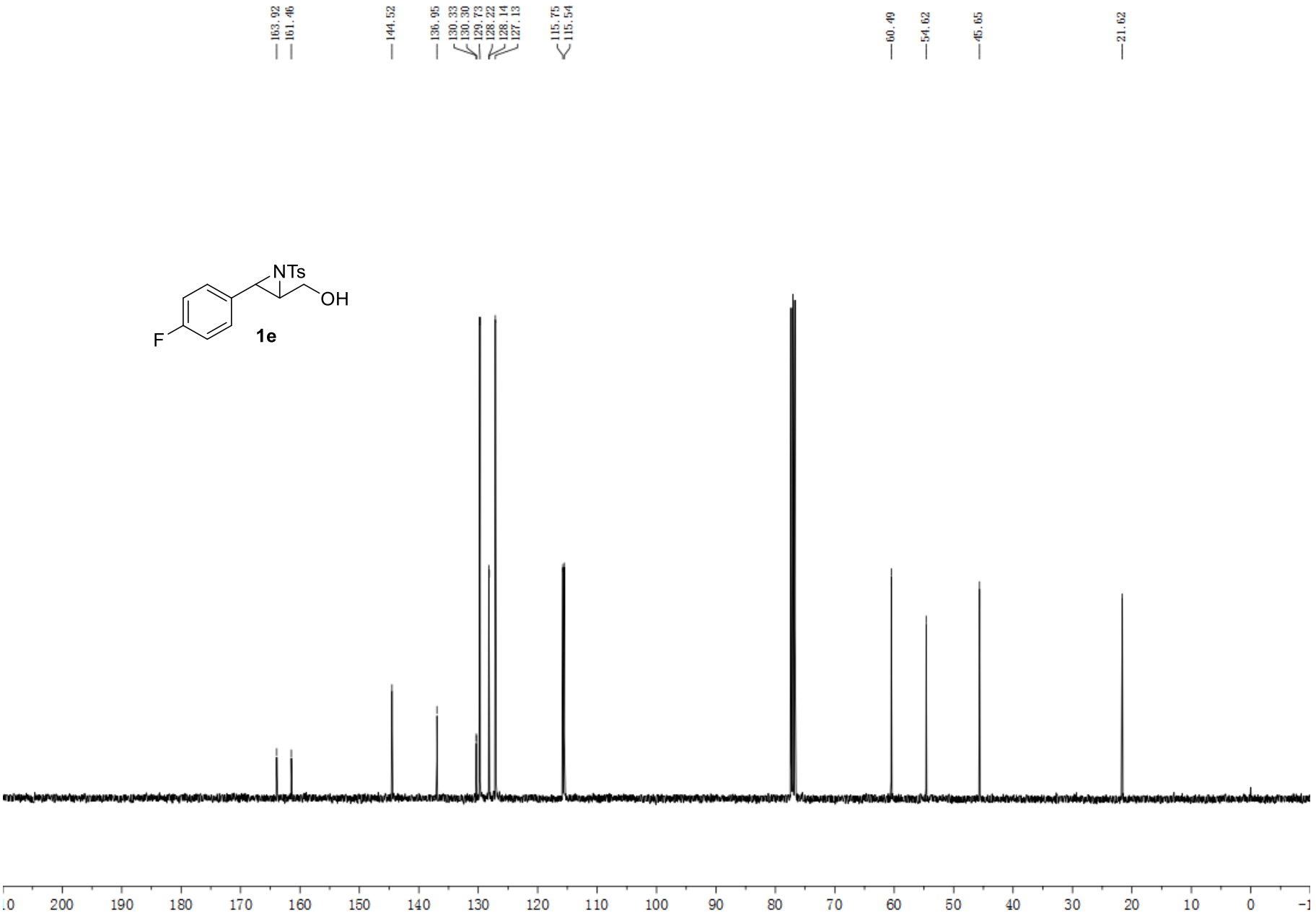
3.19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54.62
45.65
21.62
NTs
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F
1e
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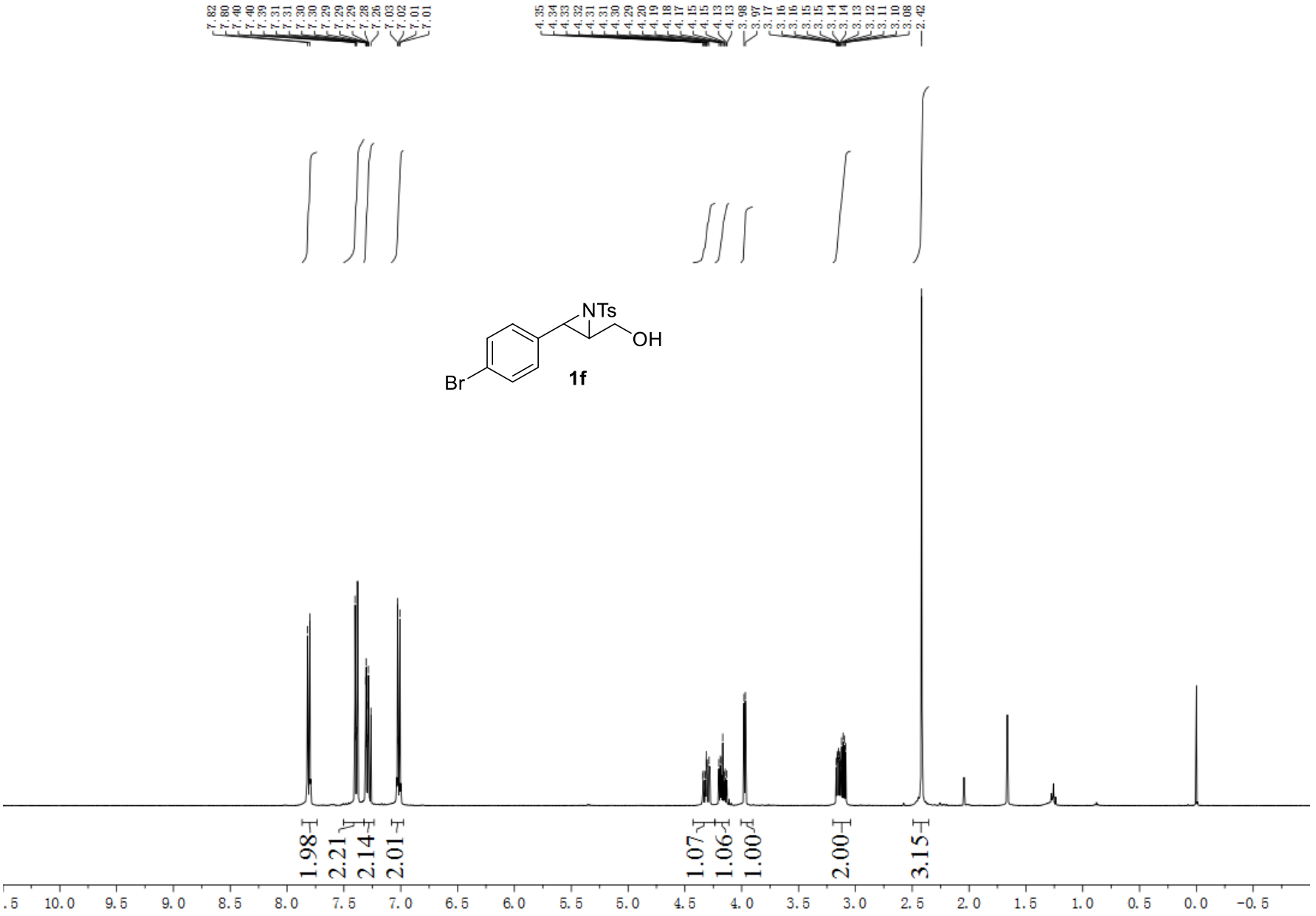
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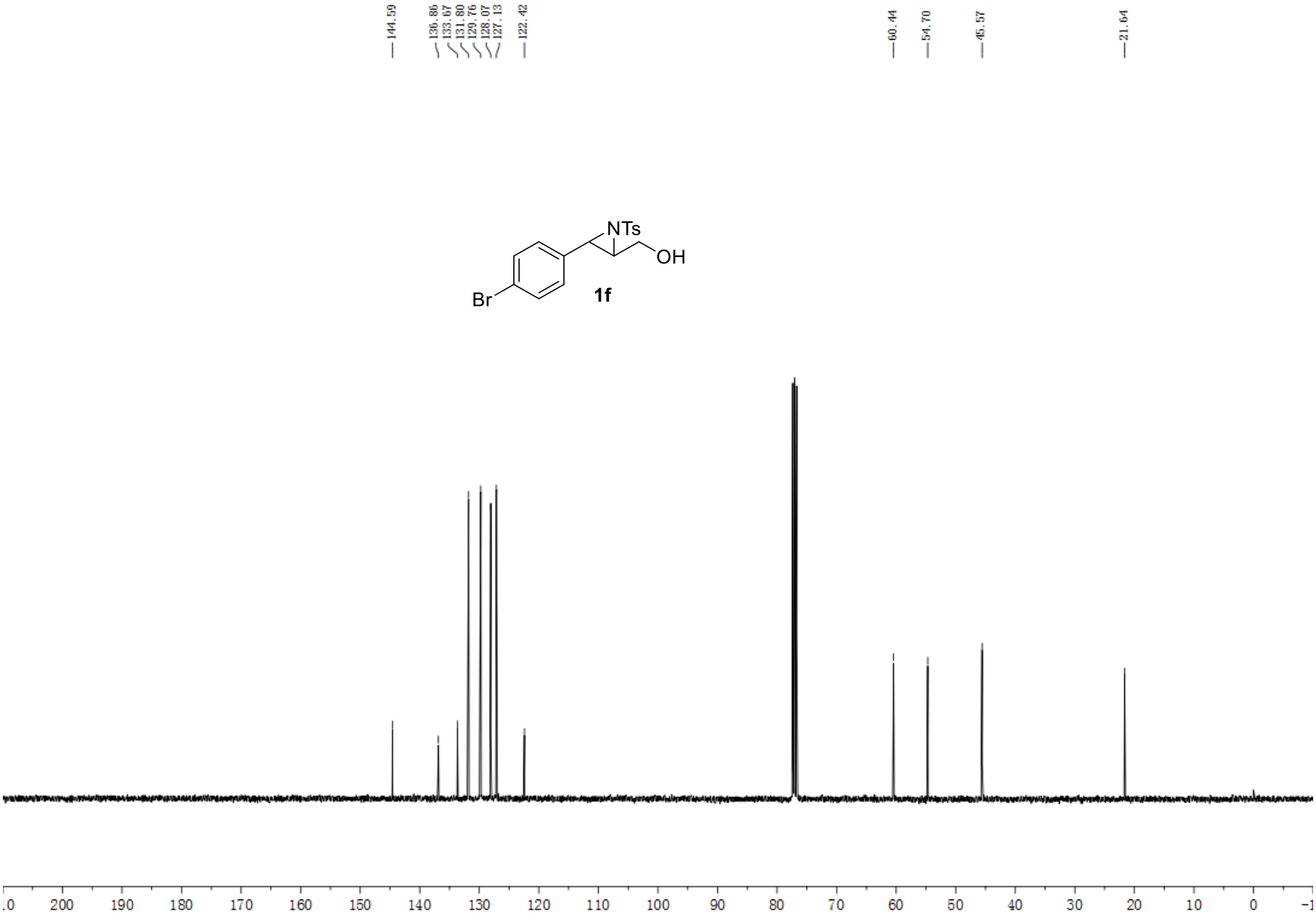
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1f
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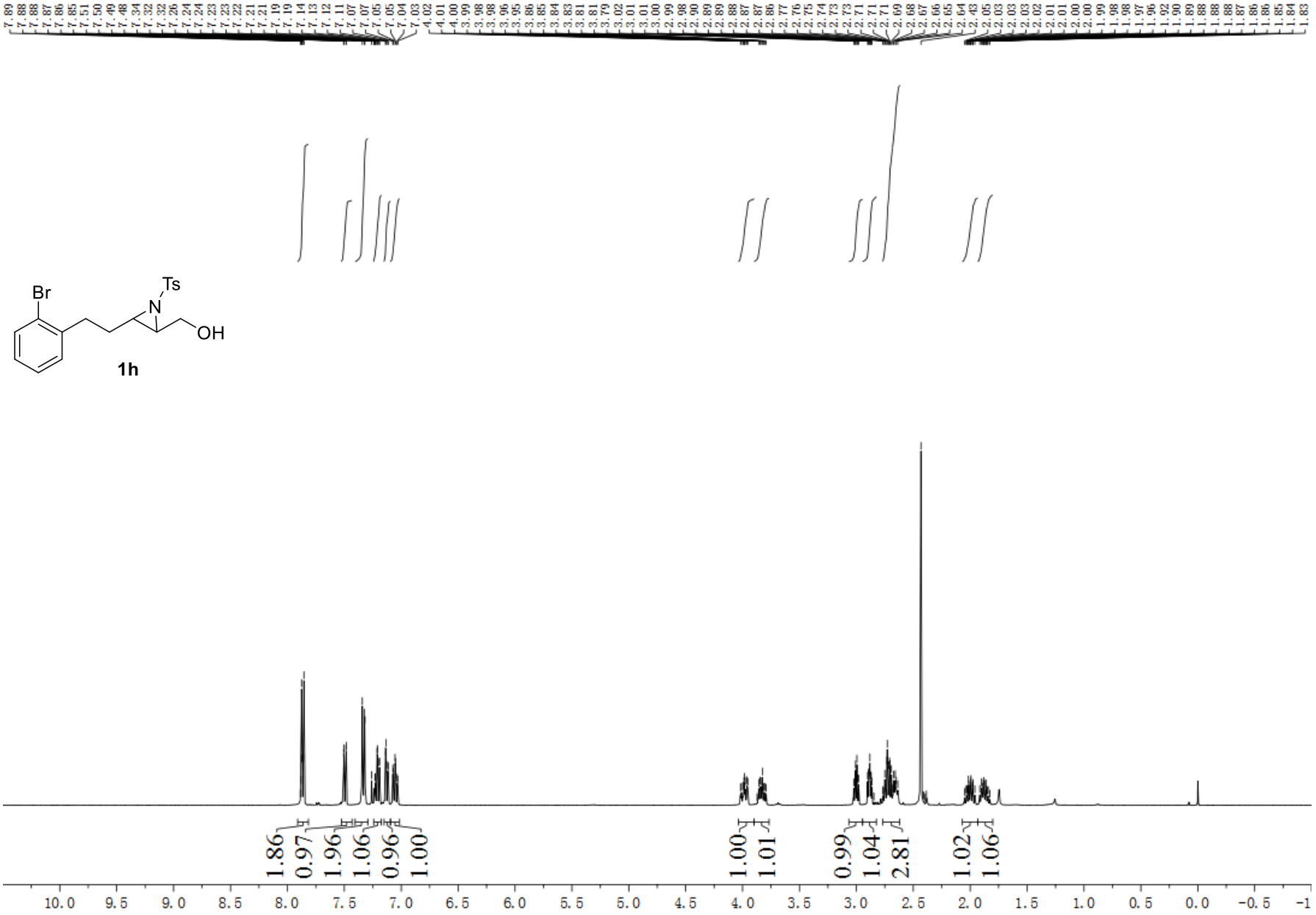
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1.02
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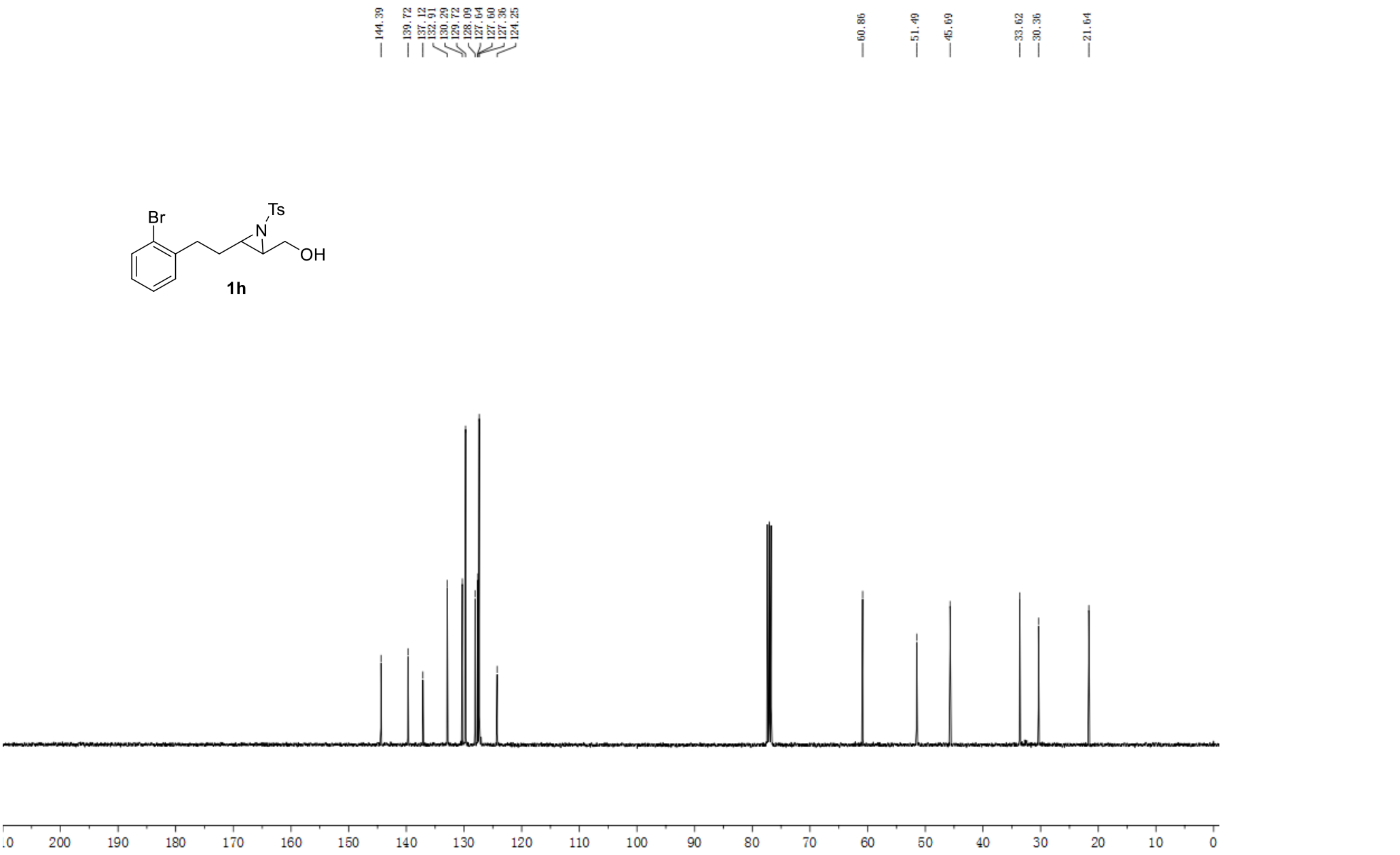
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Ts
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OH
1h
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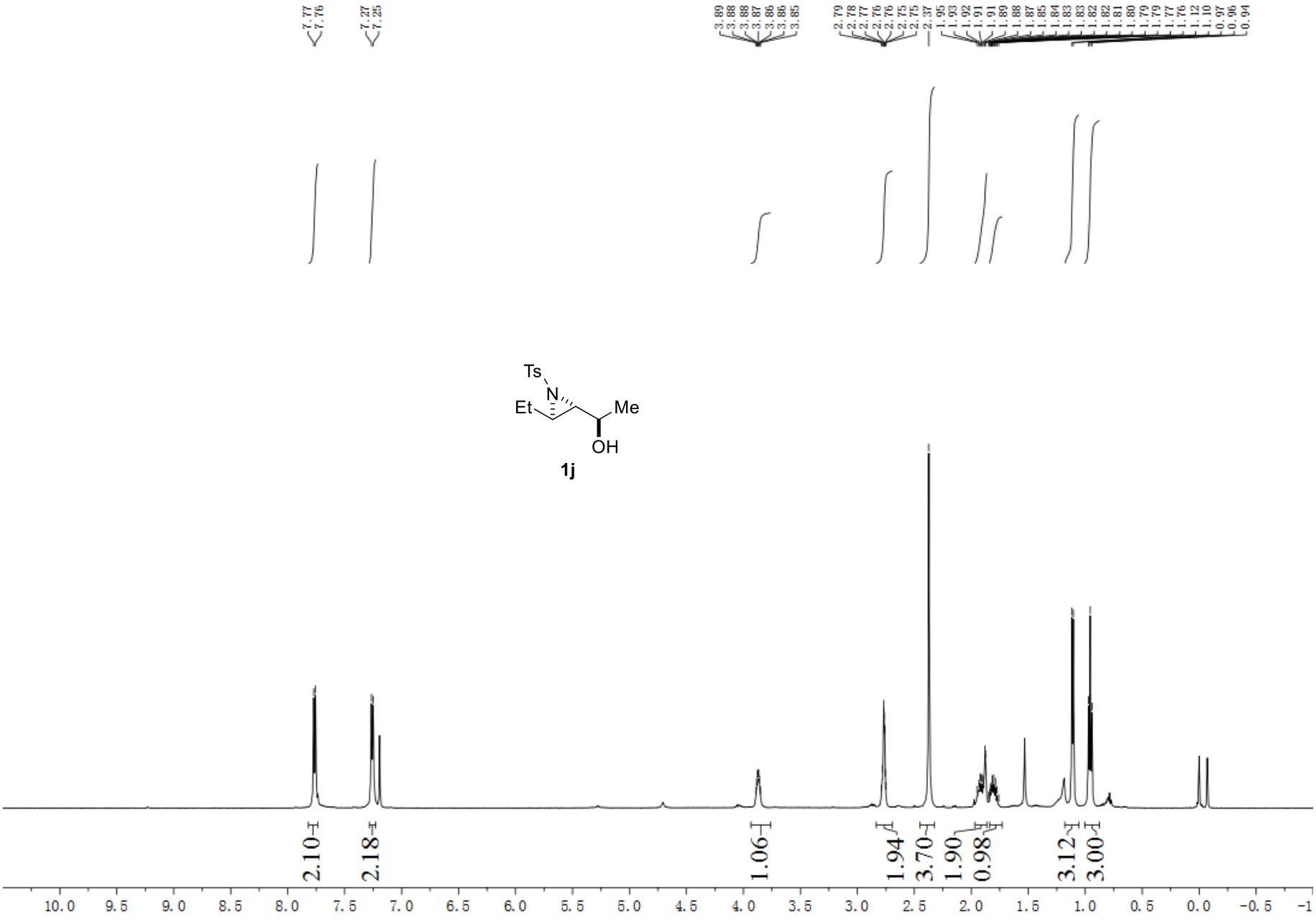
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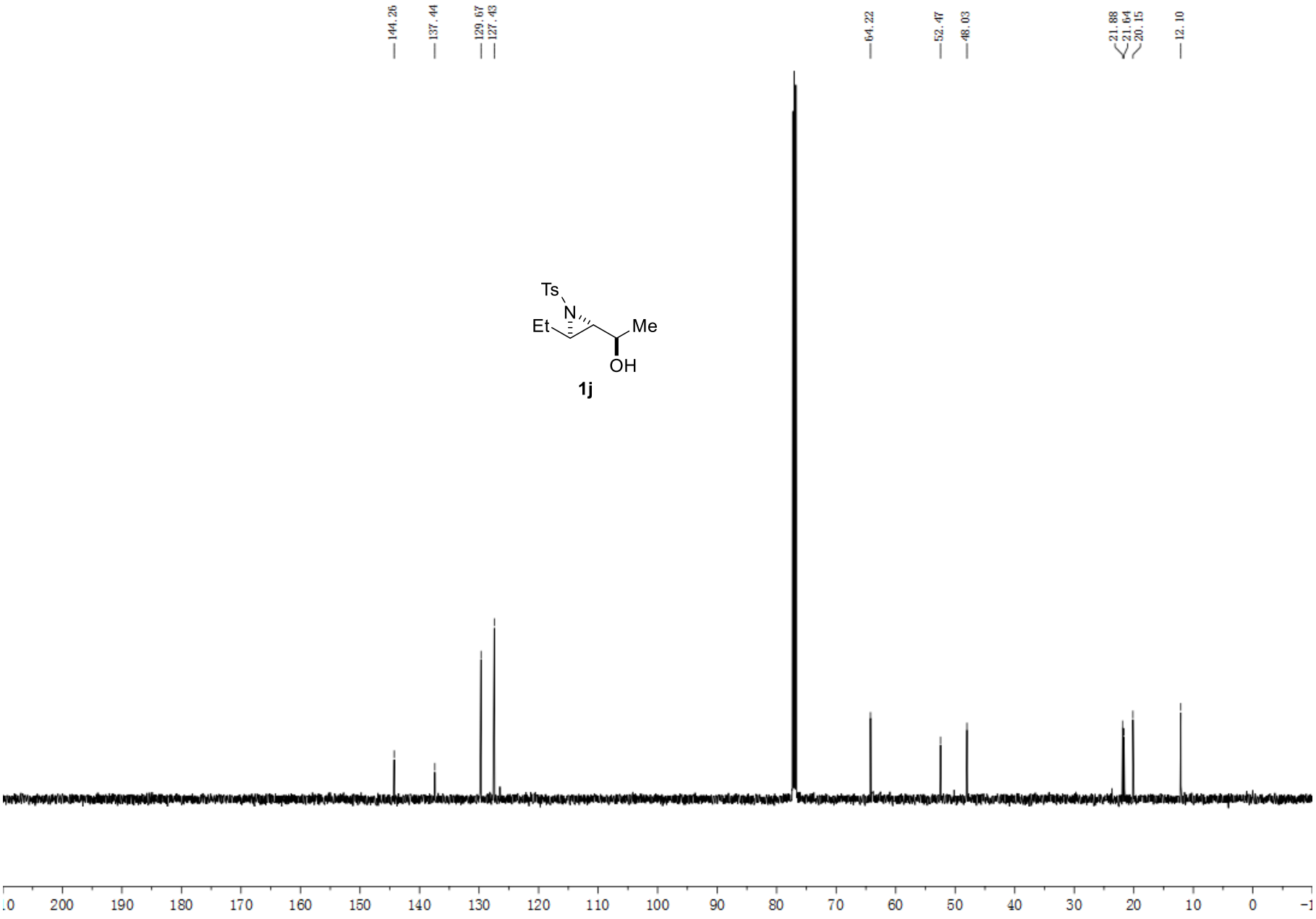
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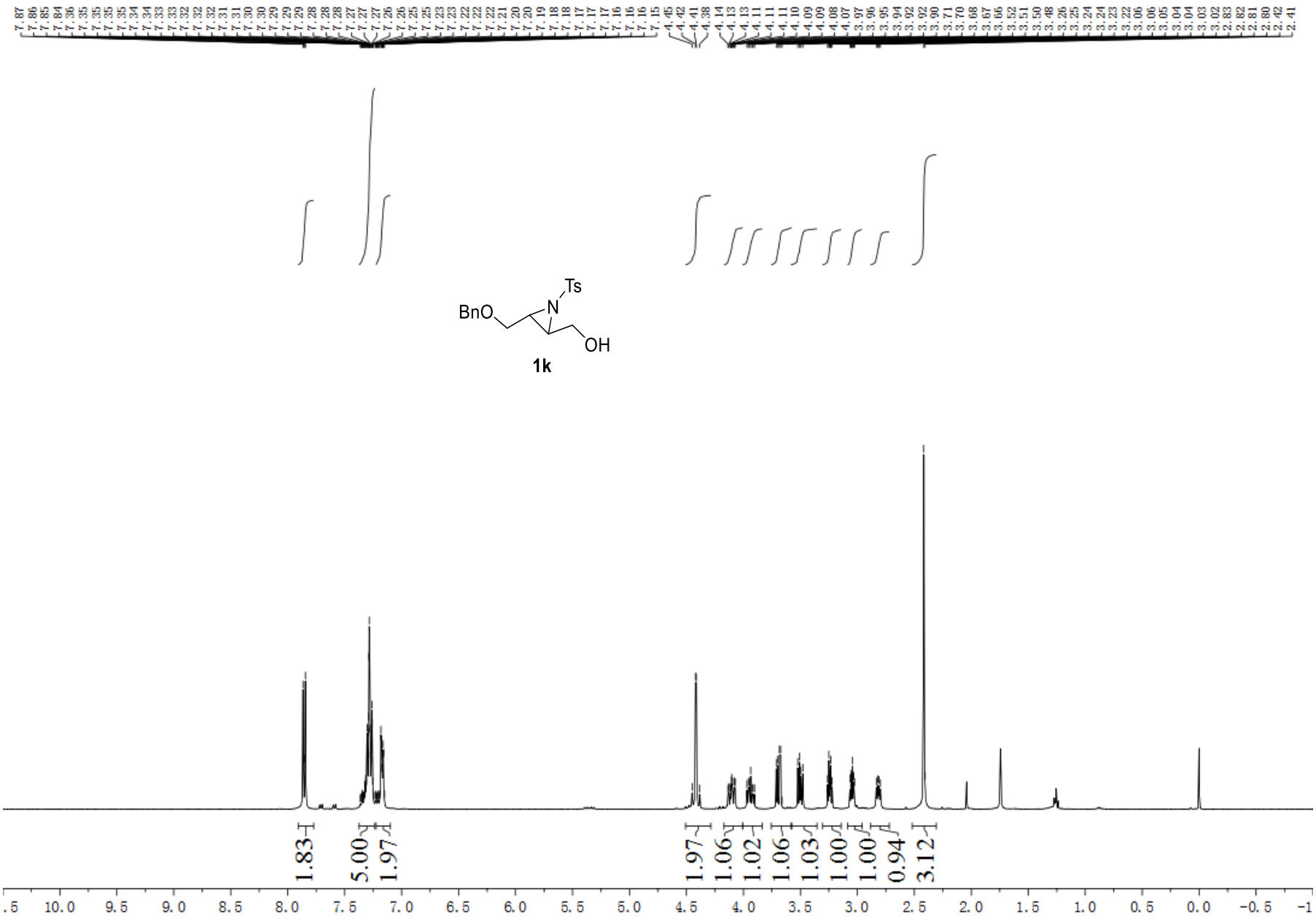
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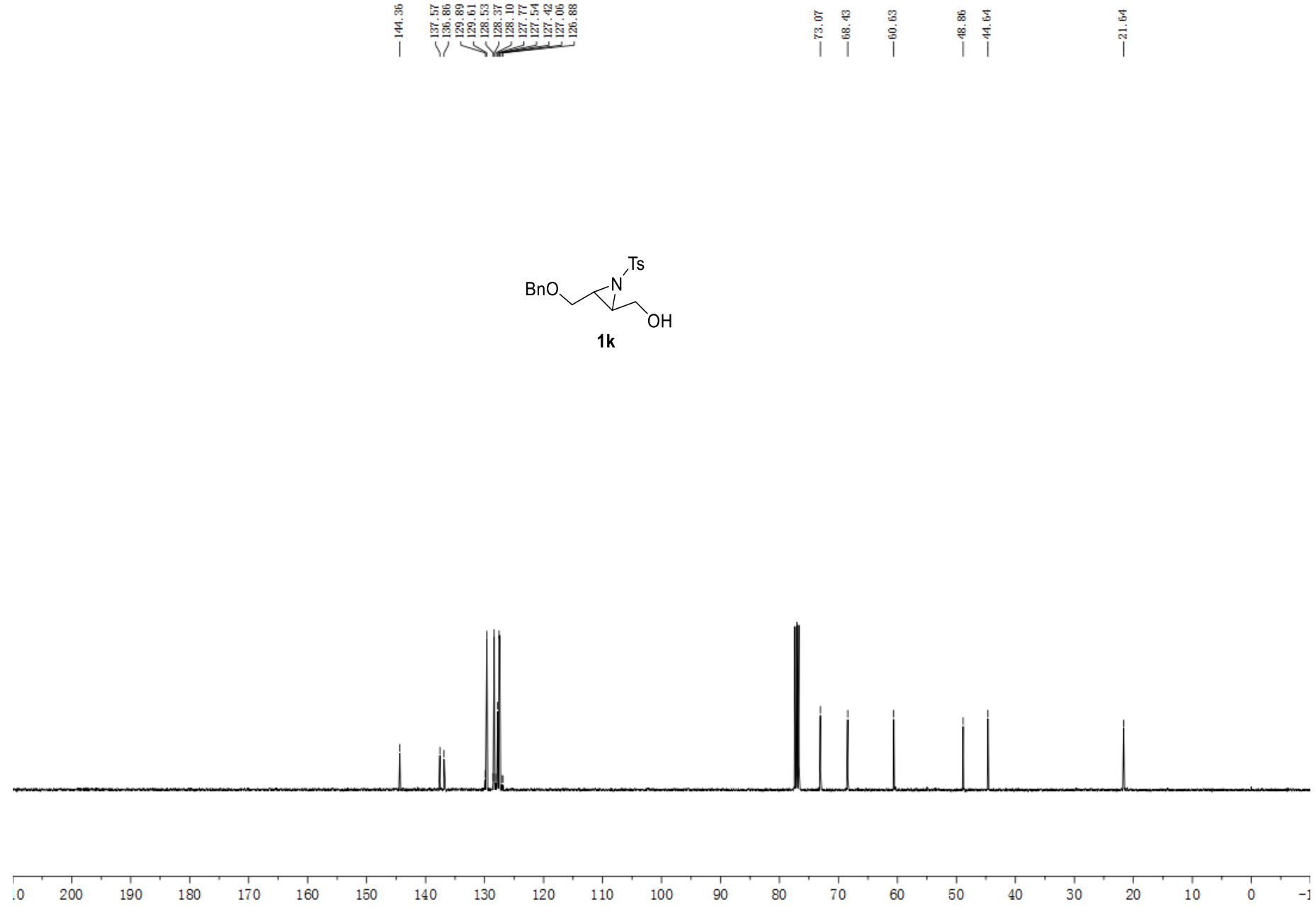
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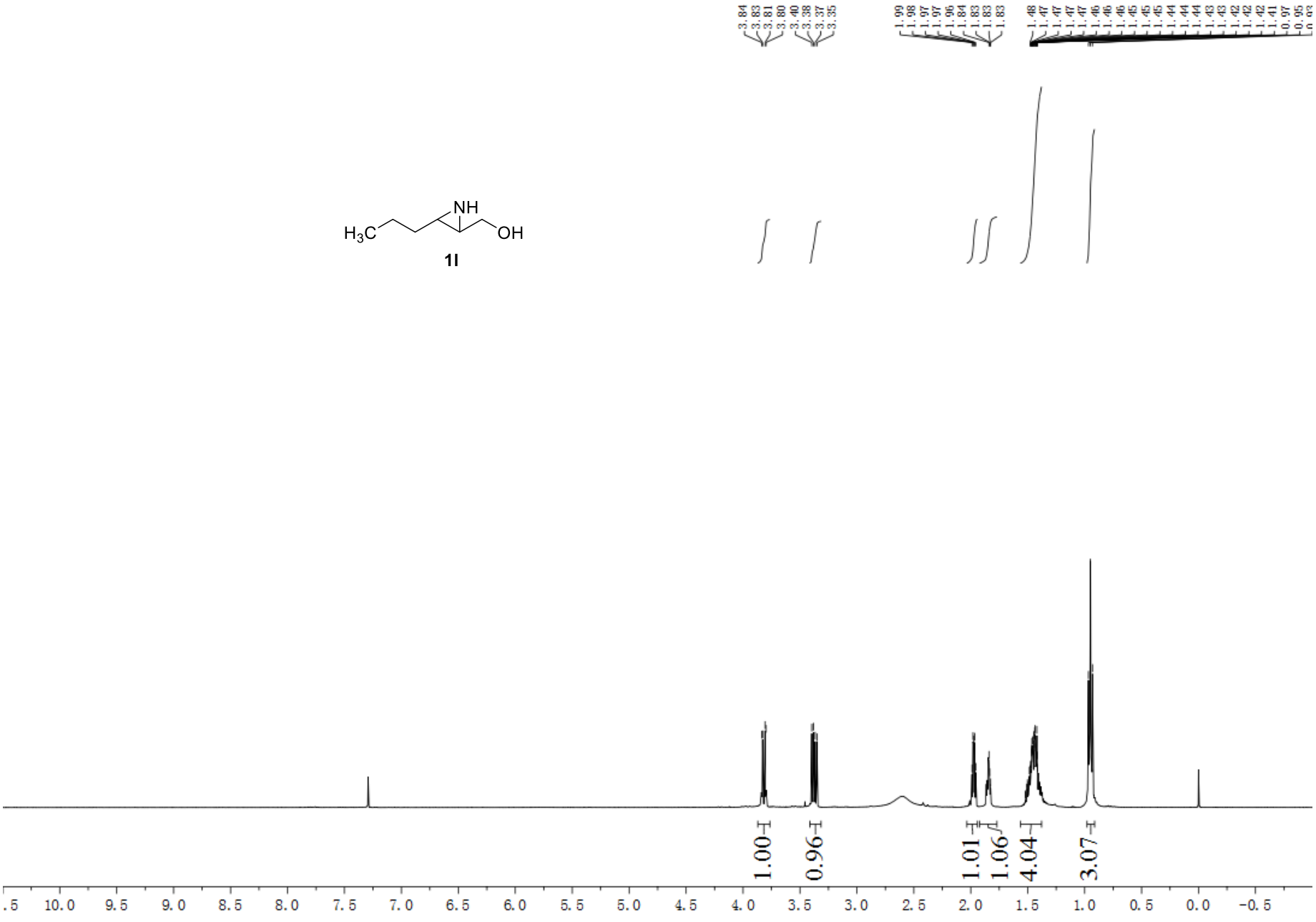

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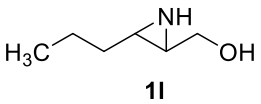
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1l

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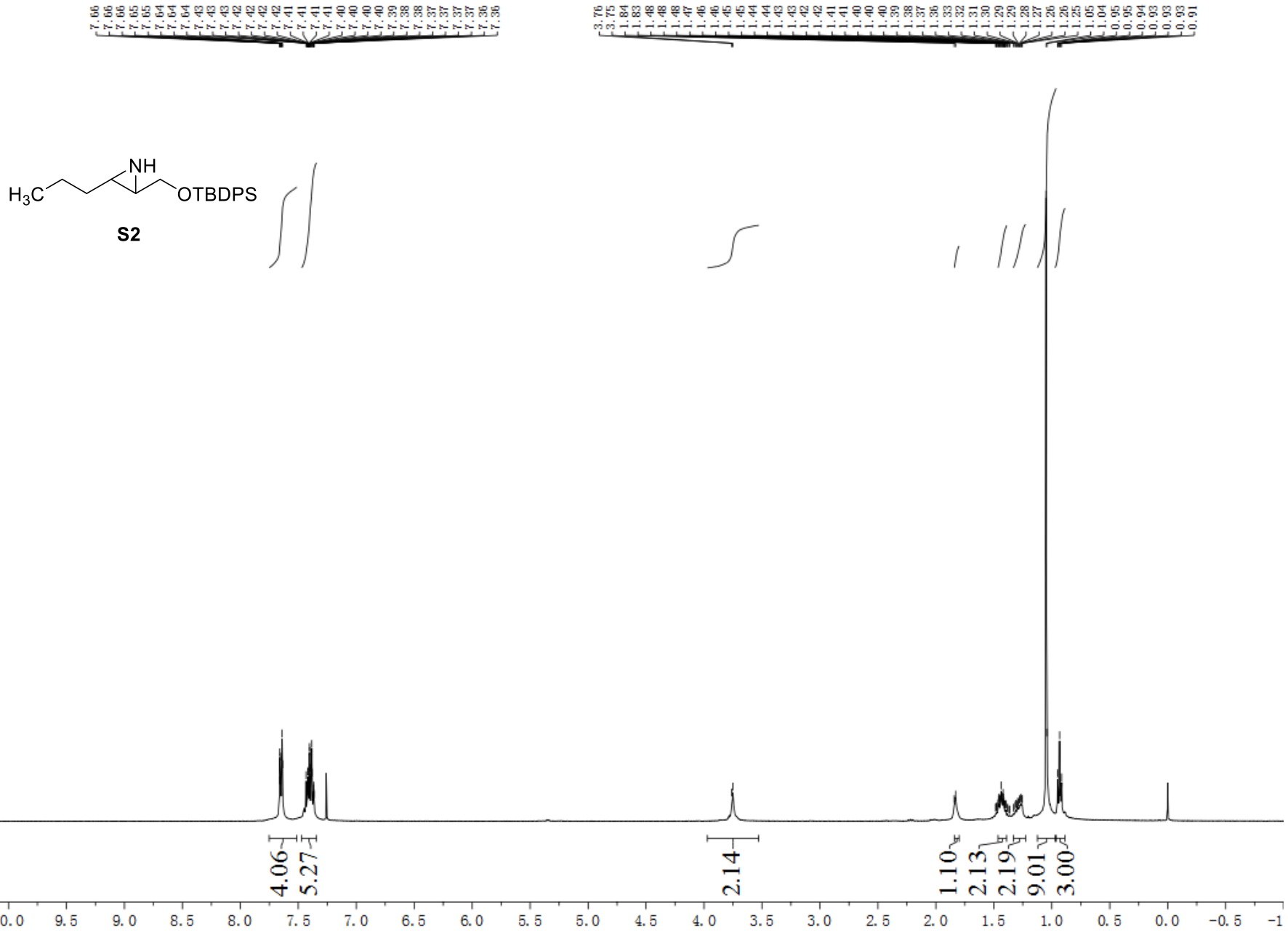
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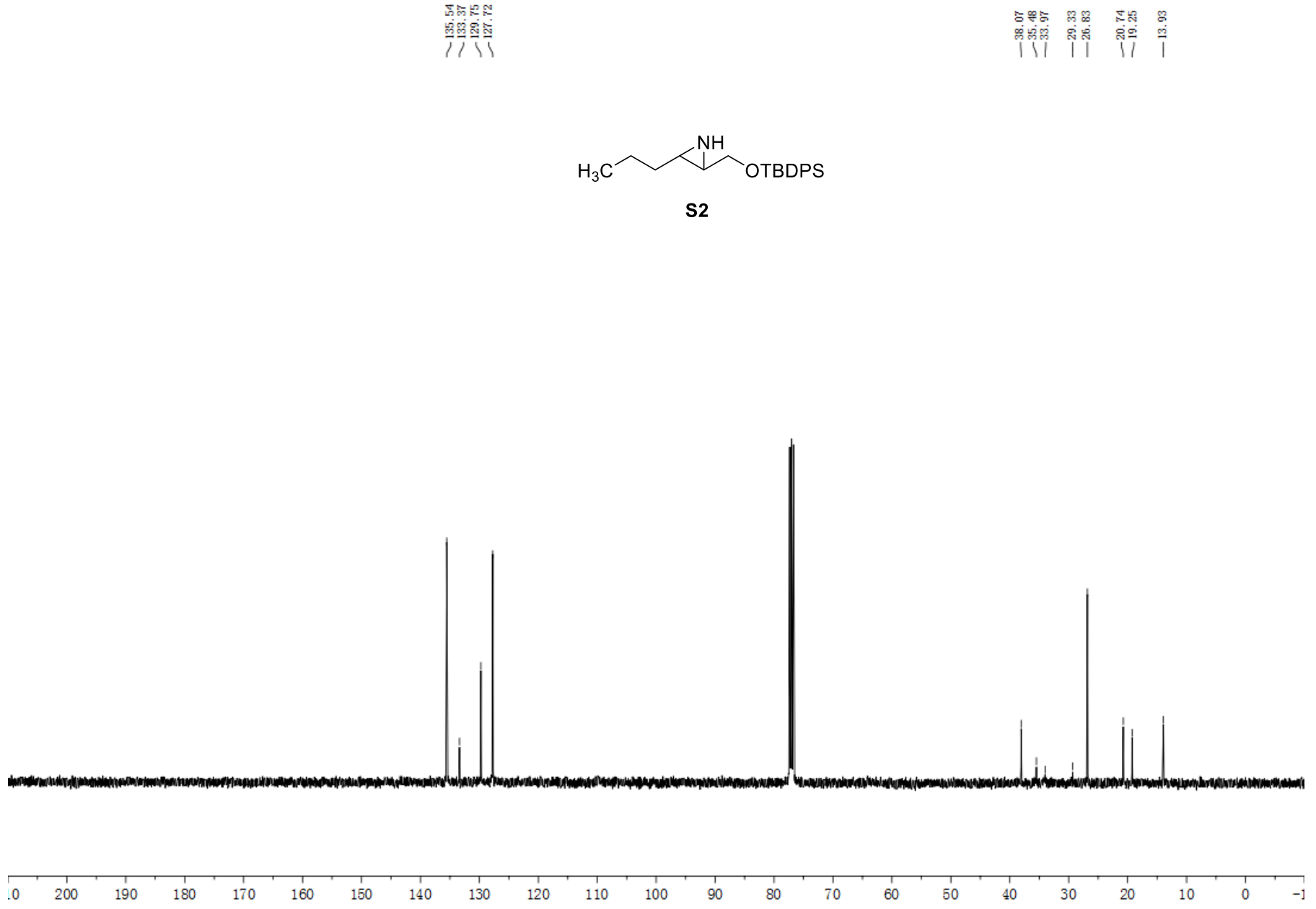
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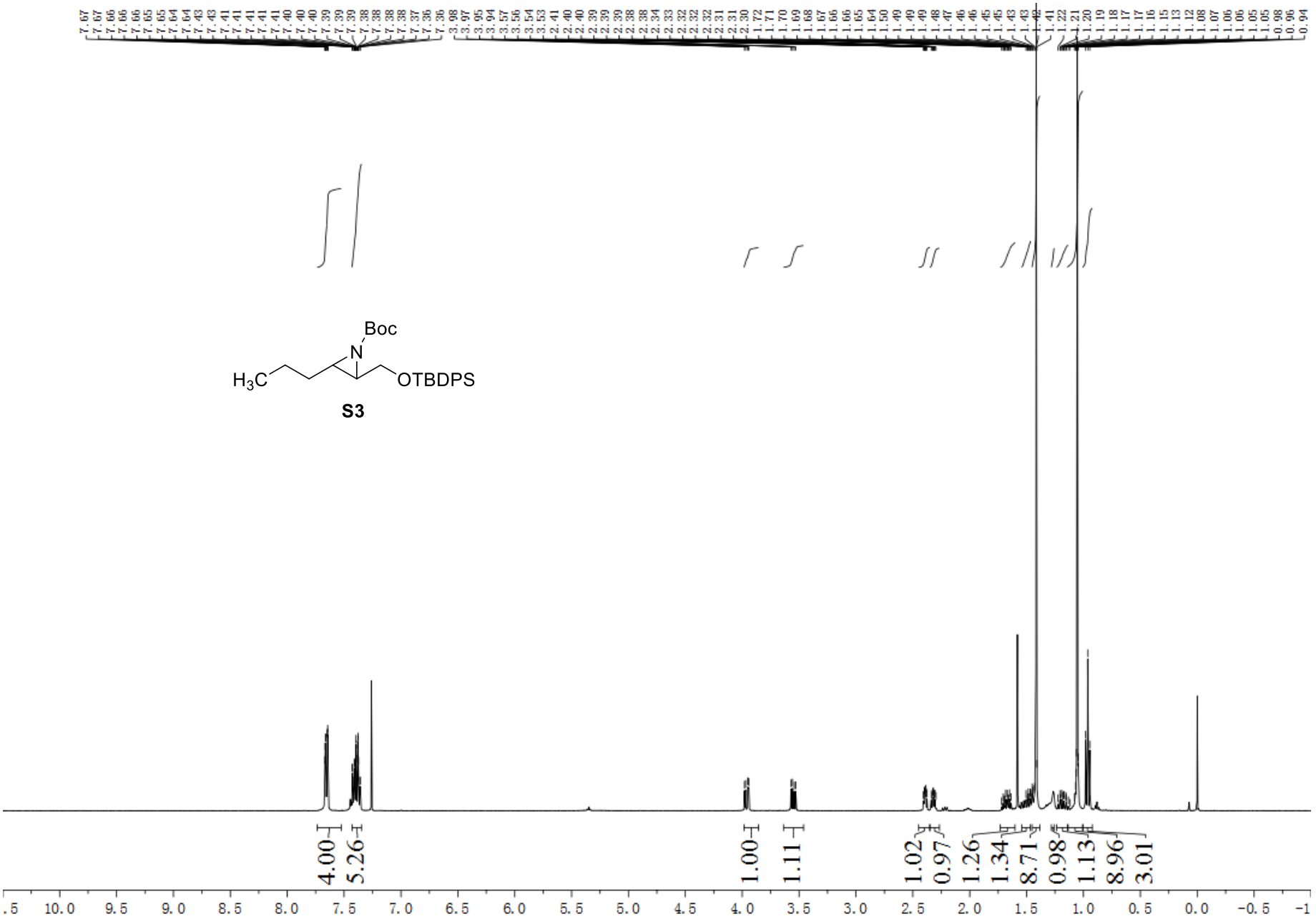
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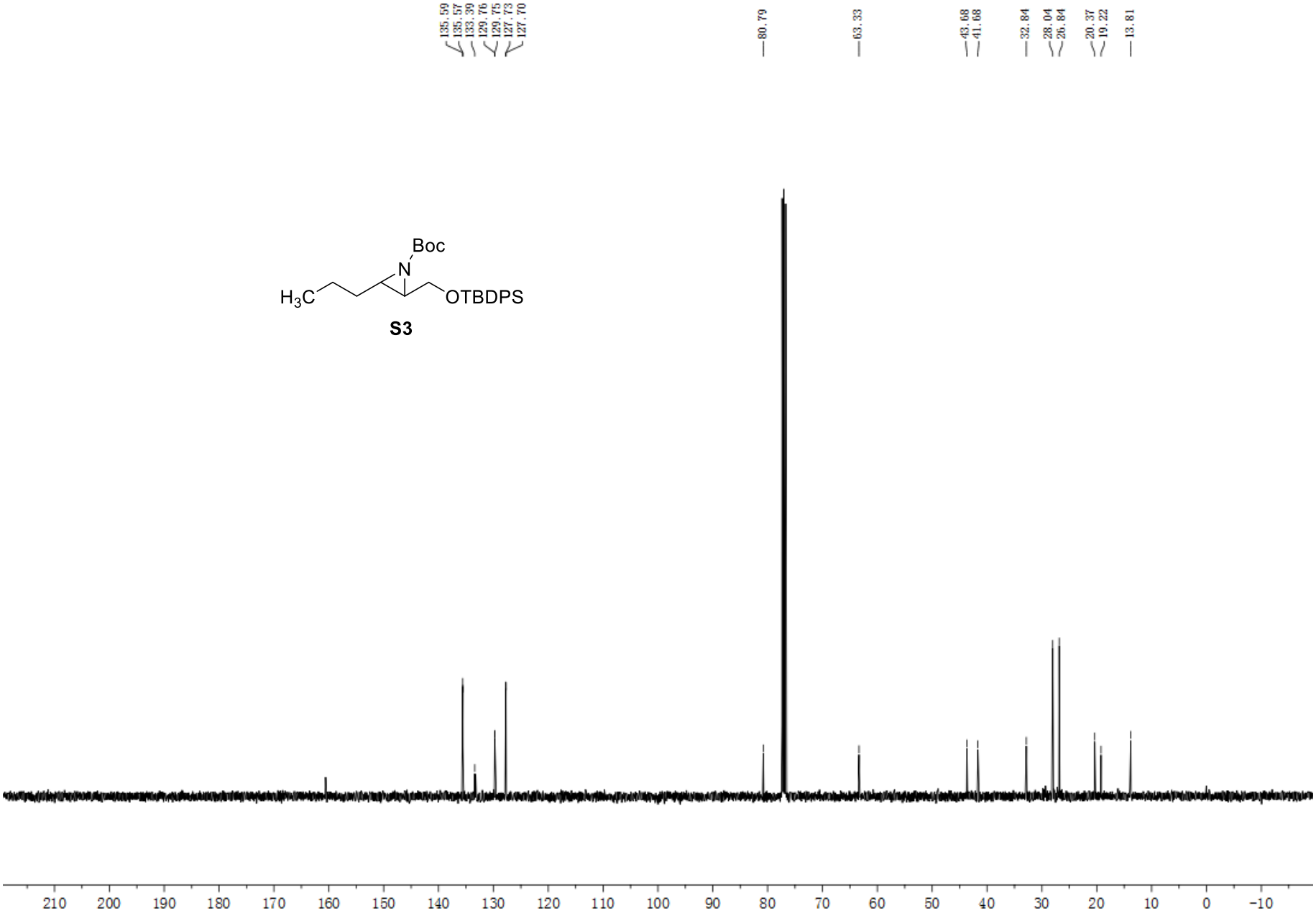
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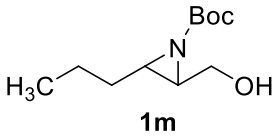

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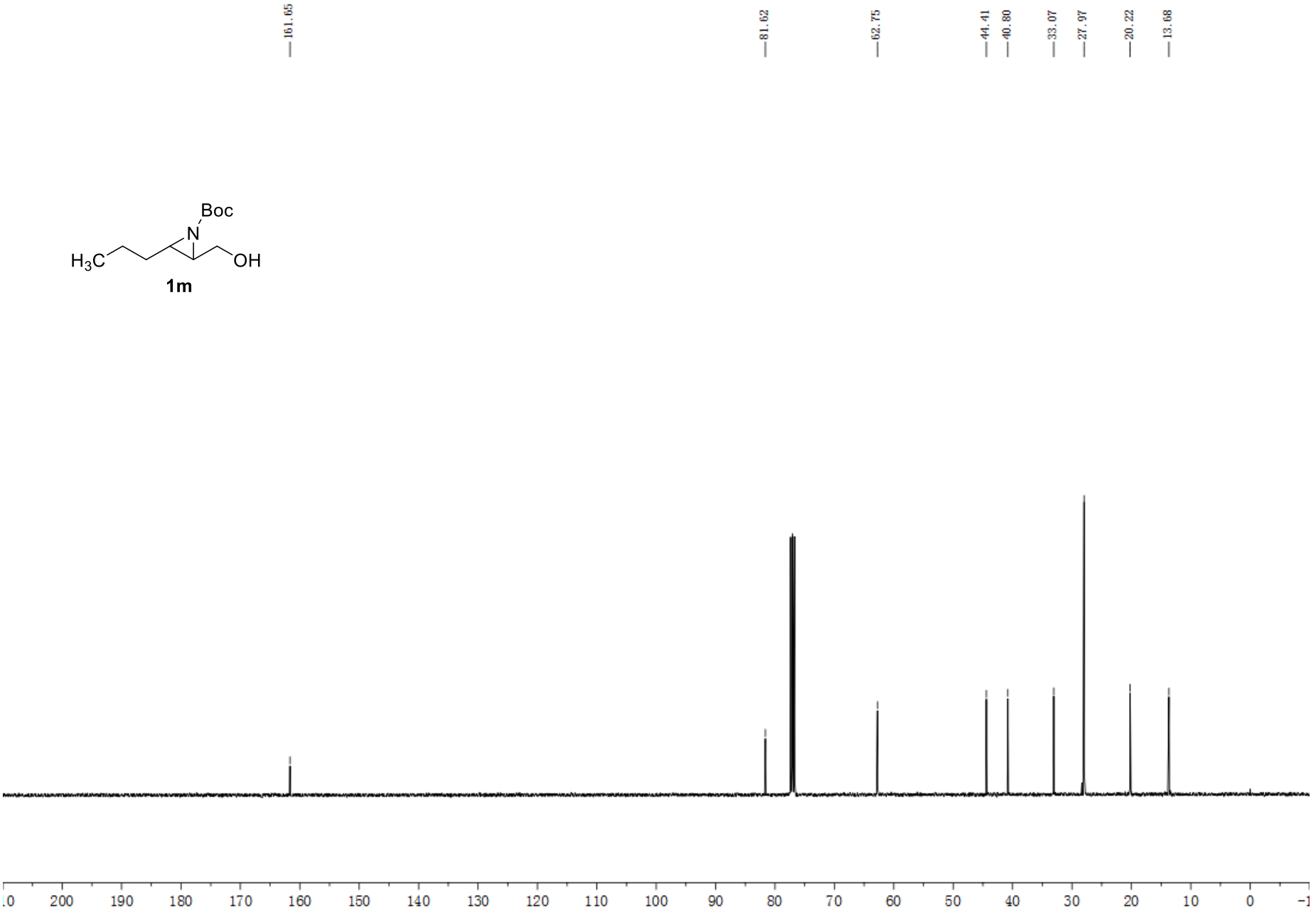
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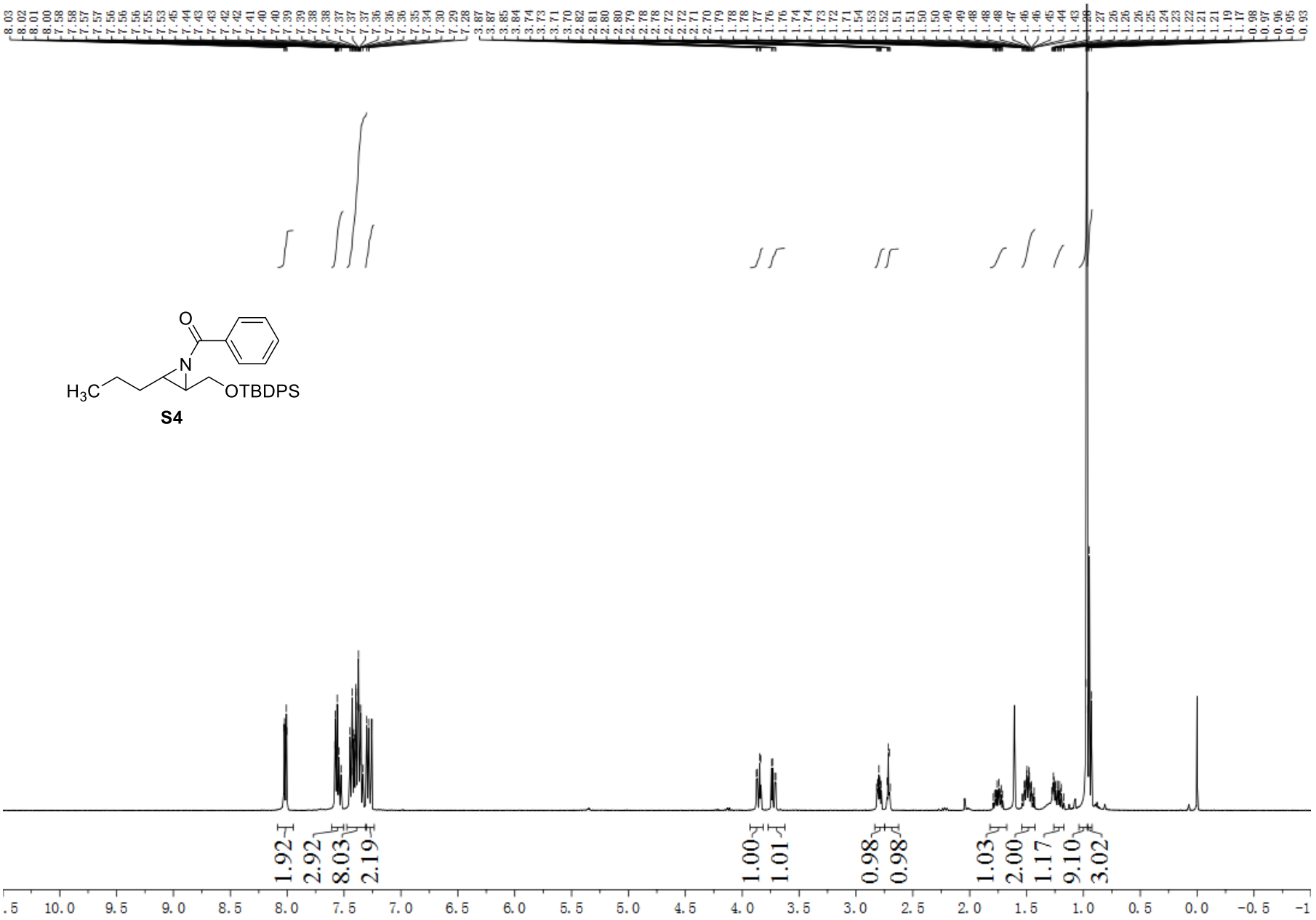
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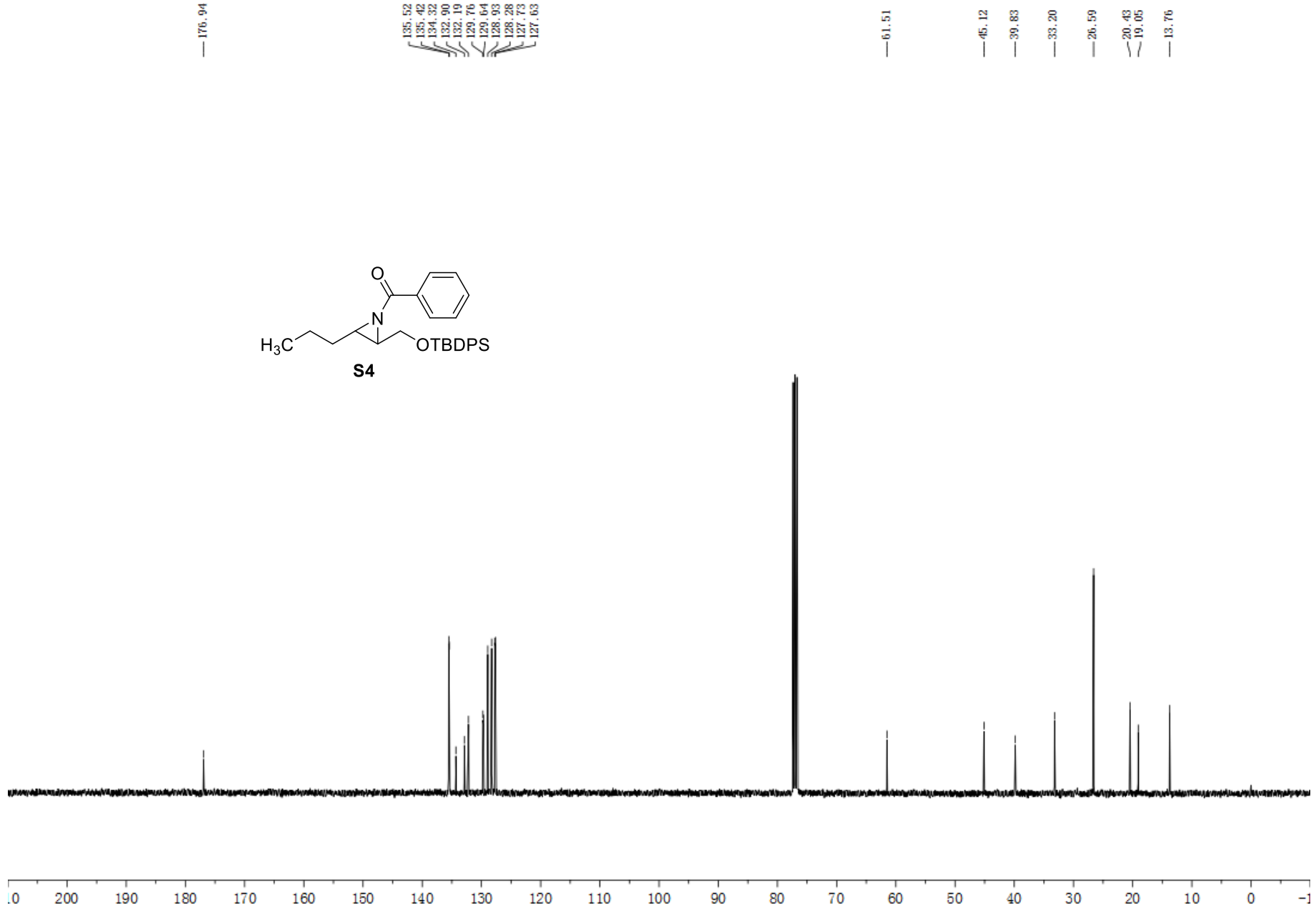
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H3C
OTBDPS
S4
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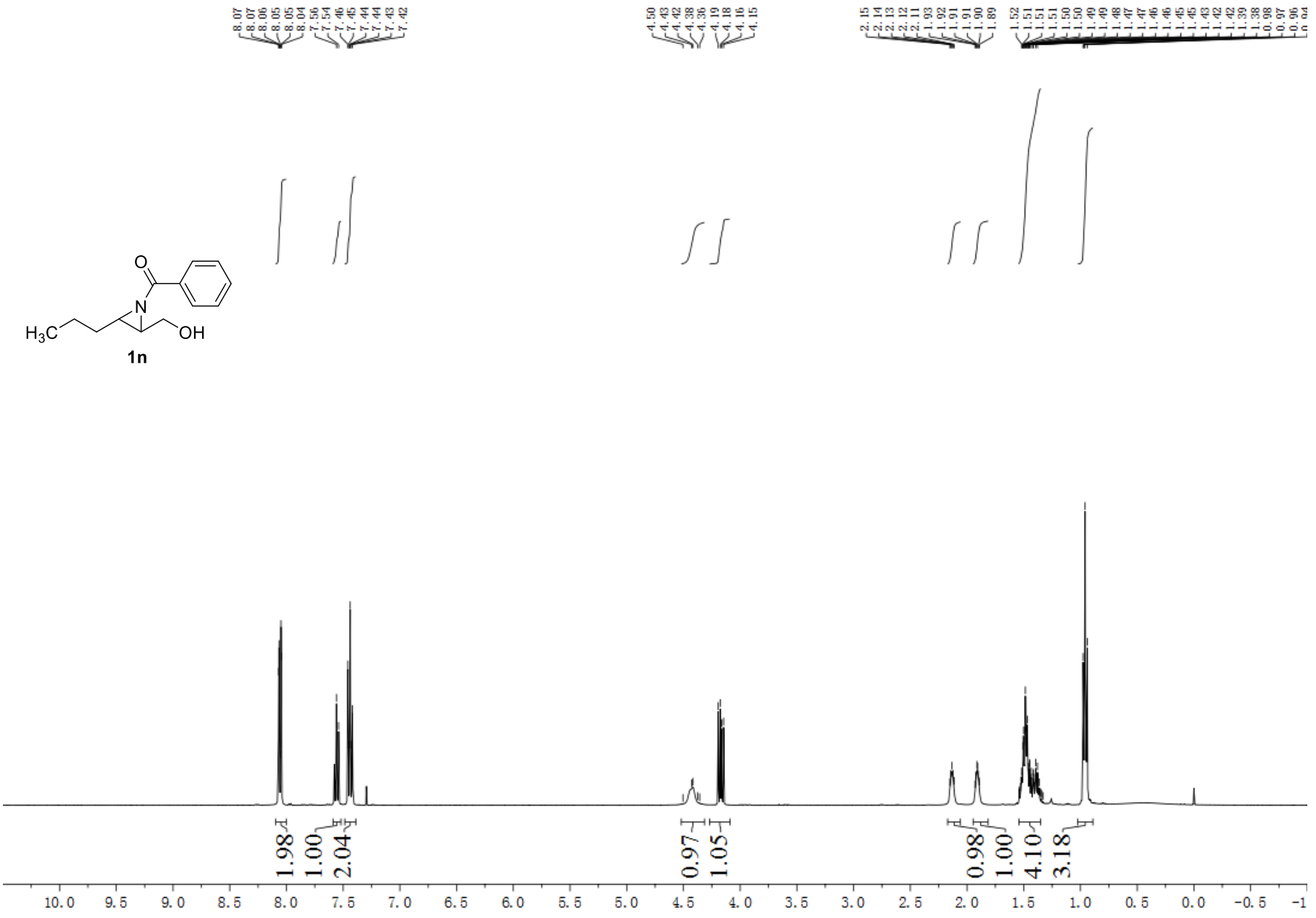
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4.43
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4.36
4.19
4.18
4.16
4.15
2.15
2.14
2.13
2.12
2.11
1.93
1.92
1.91
1.91
1.90
1.89
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1.51
1.51
1.51
1.50
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1.48
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1.47
1.46
1.46
1.45
1.45
1.43
1.42
1.42
1.39
1.38
0.98
0.97
0.96
O
N
H3C
OH
1n
1.98
1.00
2.04
0.97
1.05
0.98
1.00
4.10
3.18
10.0
9.5
9.0
8.5
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7.5
7.0
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6.0
5.5
5.0
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3.0
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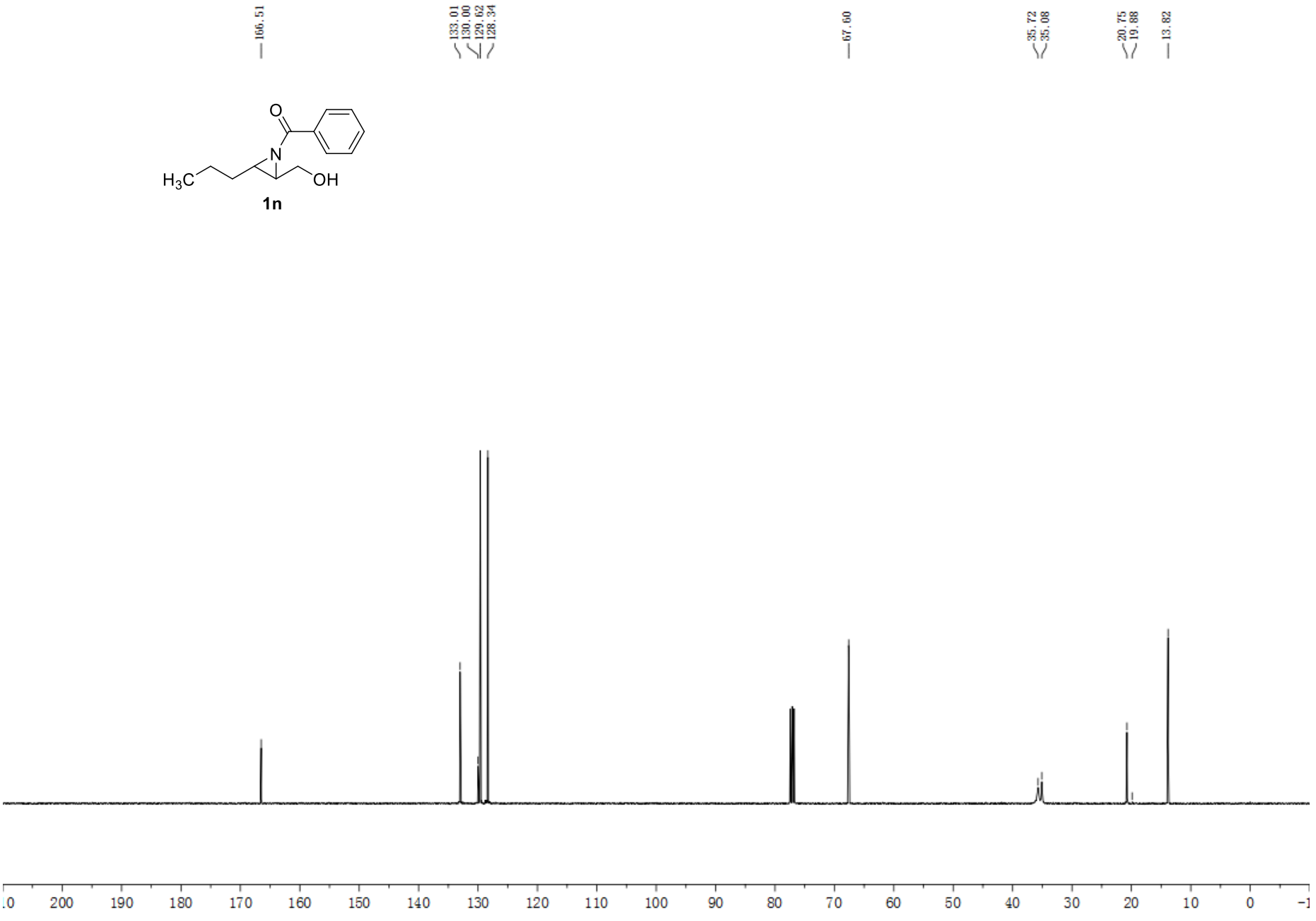
-1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35.72
35.08
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19.88
13.82
O
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H3C
OH
1n
200
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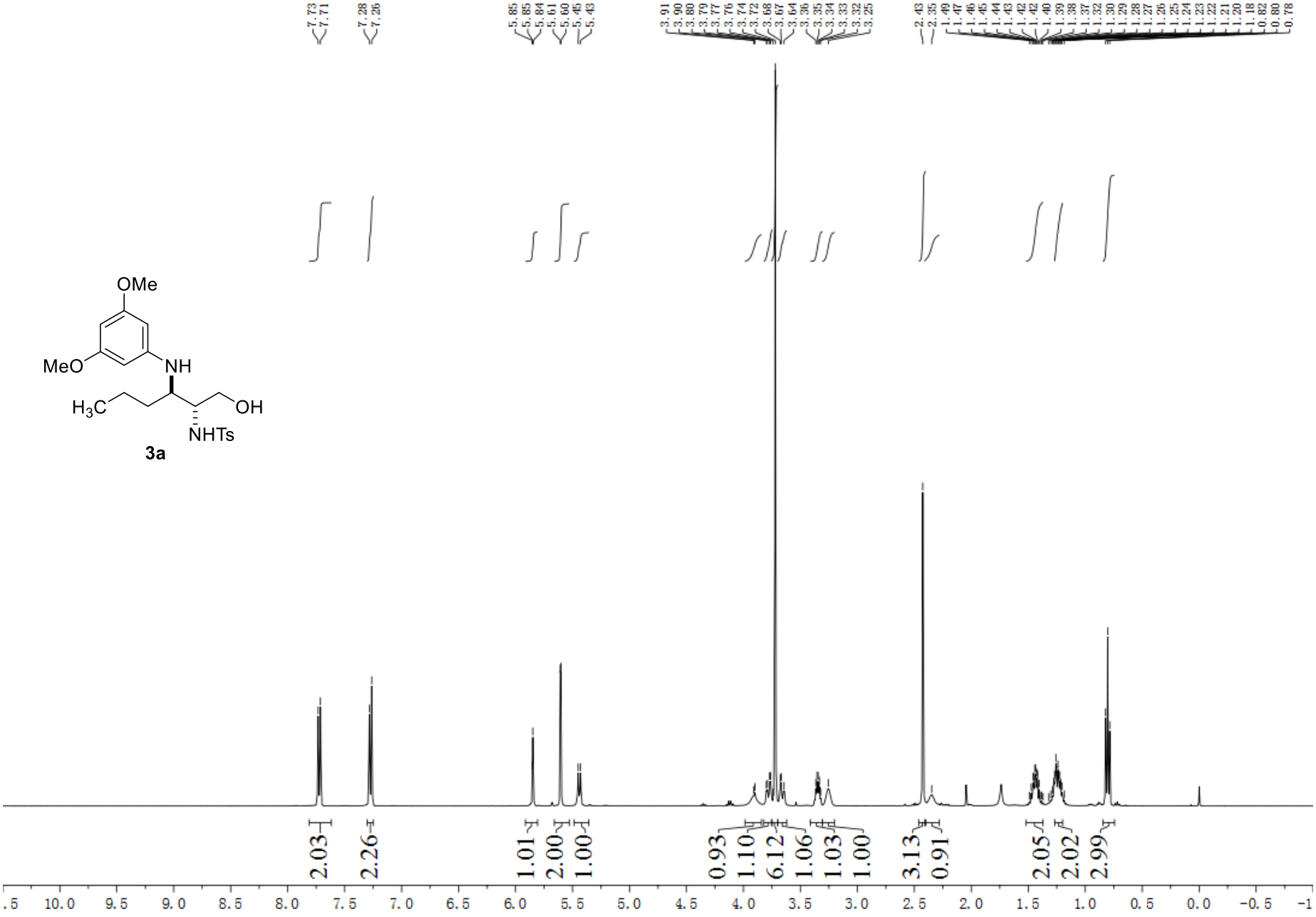
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7.26
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5.85
5.84
5.61
5.60
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5.43
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3.90
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3.79
3.77
3.76
3.74
3.72
3.68
3.67
3.64
3.36
3.35
3.34
3.33
3.32
3.25
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2.35
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1.47
1.46
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1.42
1.42
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1.29
1.28
1.27
1.26
1.25
1.24
1.23
1.22
1.21
1.20
1.18
0.82
0.80
0.78
OMe
MeO
NH
H3C
OH
NHTs
3a
2.03
2.26
1.01
2.00
1.00
0.93
1.10
6.12
1.06
1.03
1.00
3.13
0.91
2.05
2.02
2.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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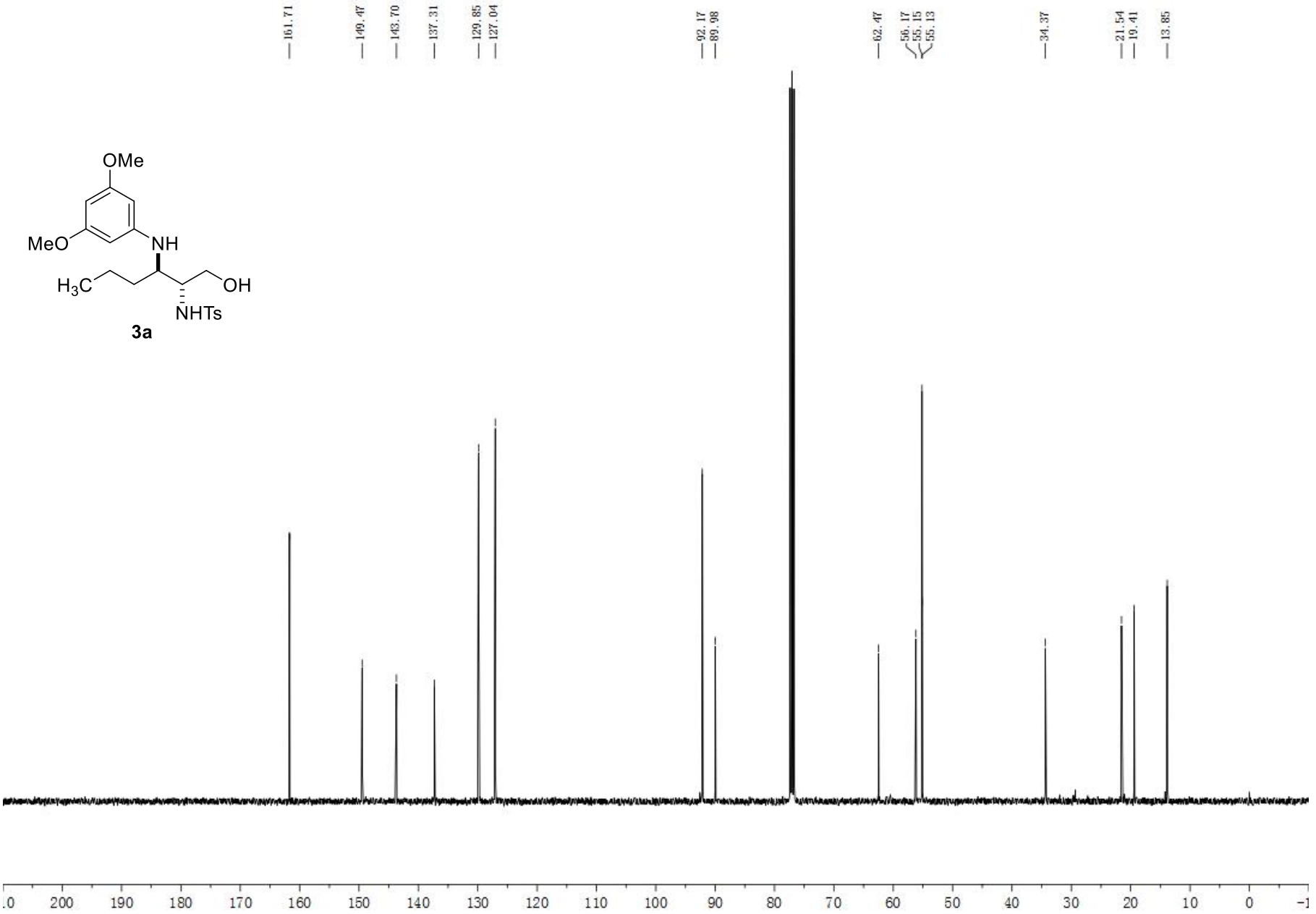
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89.98
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55.15
55.13
34.37
21.54
19.41
13.85
OMe
MeO
NH
H3C
OH
NHTs
3a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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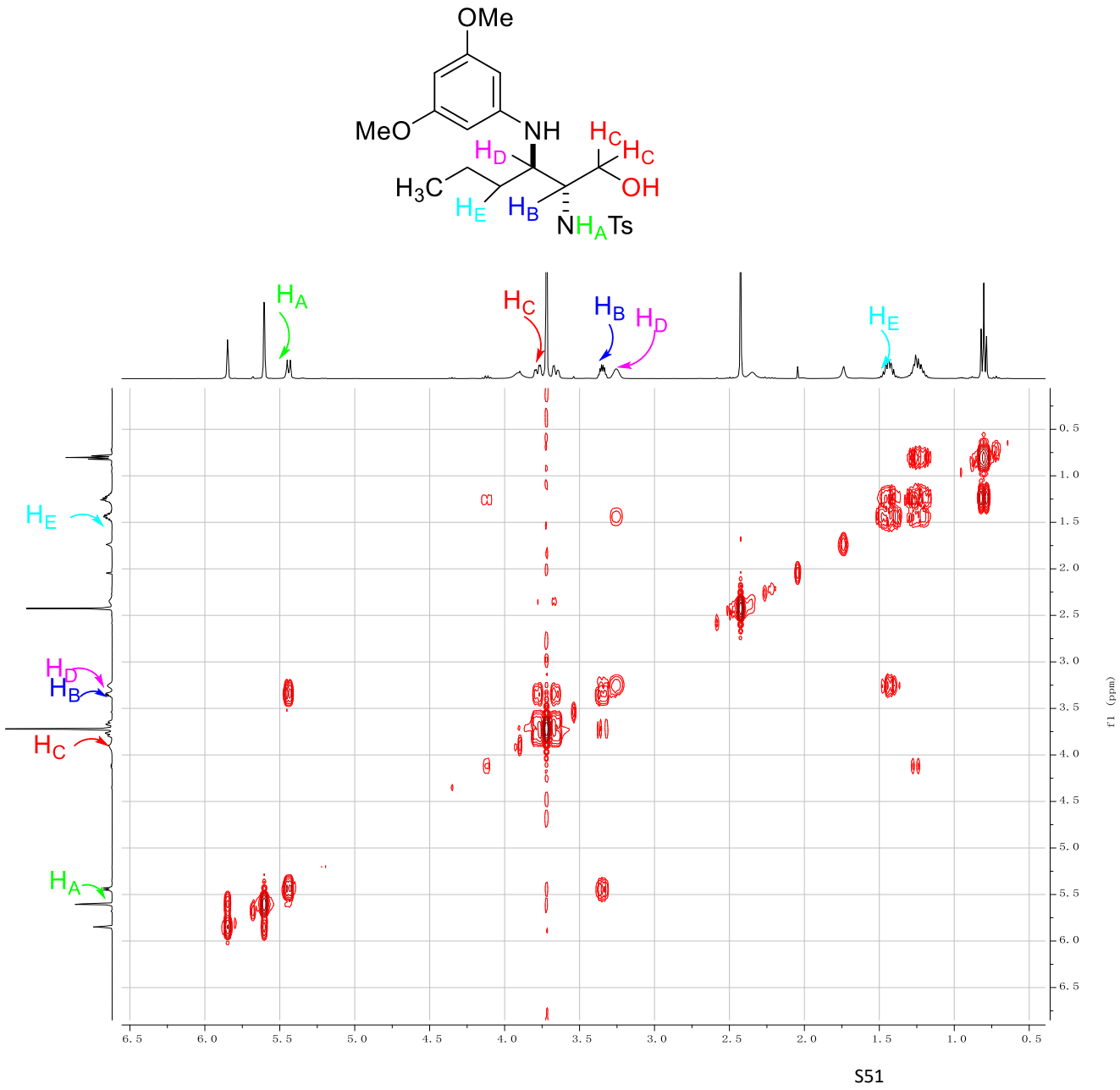
50
40
30
20
10
0

COSY of 3a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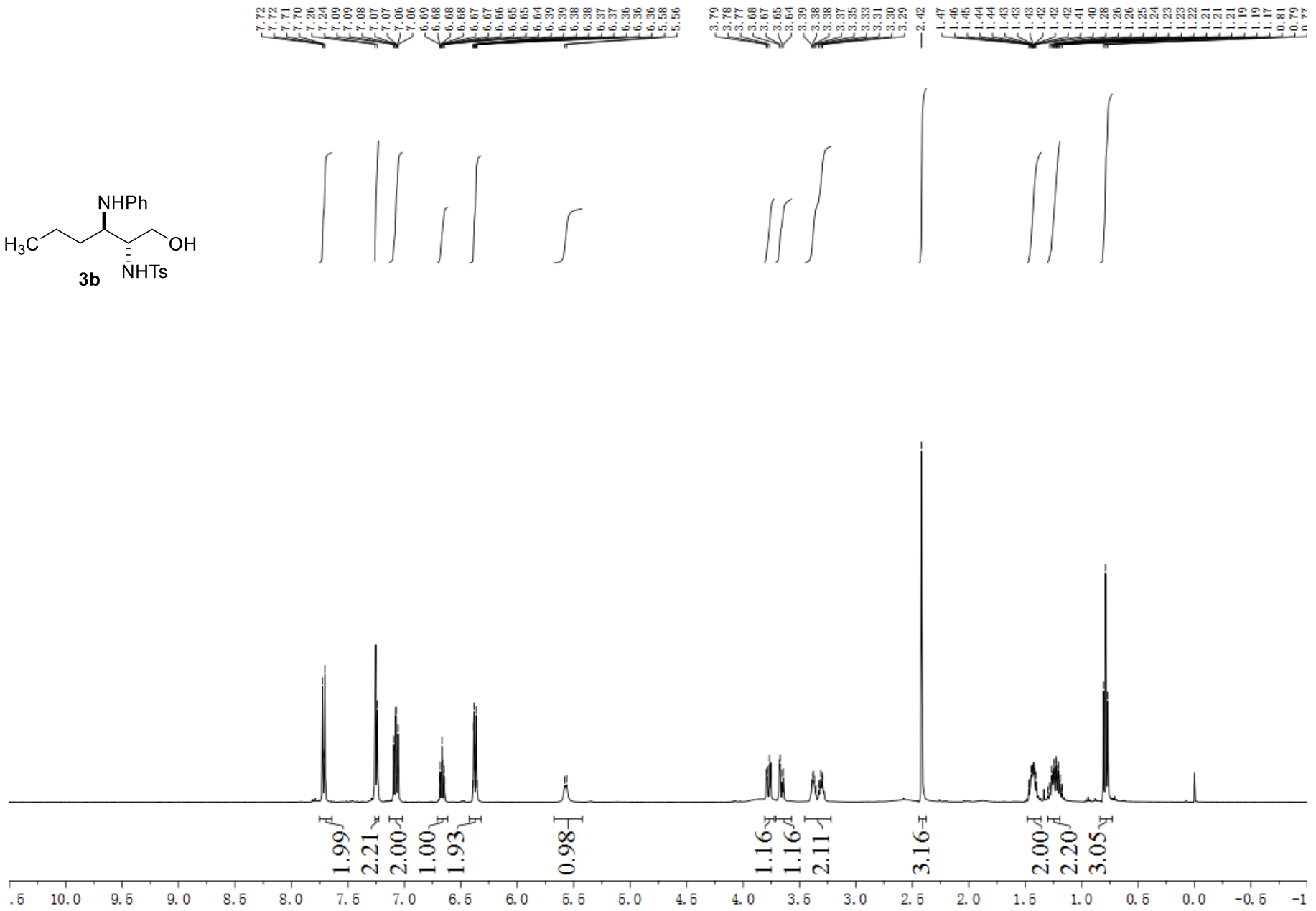
MeO
NH
HC HC
HD
H3C
OH
HE
HB
NHATs
HA
HC
HB HD
HE
HE
HD
HB
HC
HA
6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5
f1 (ppm)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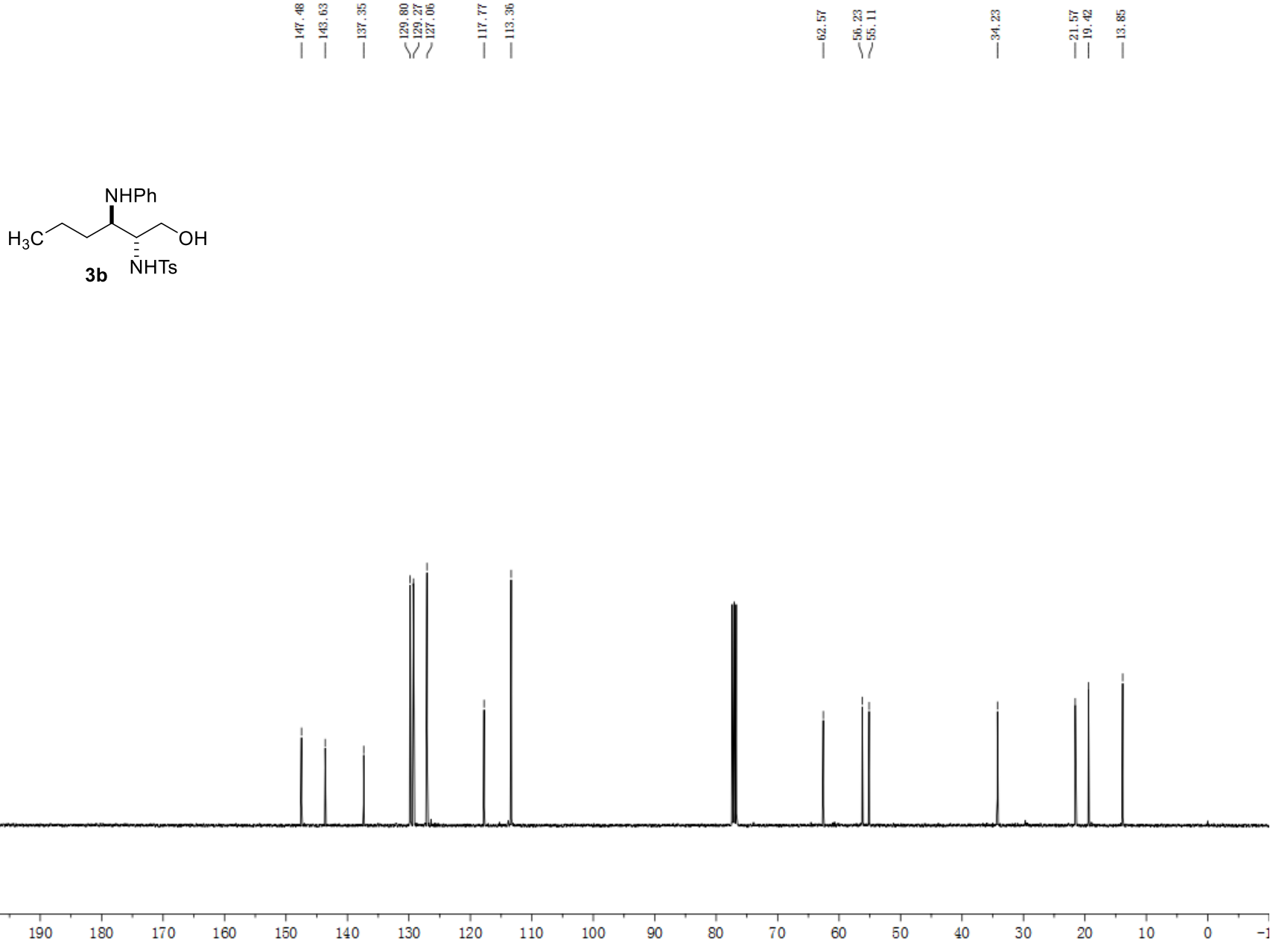
H3C
OH
NHTs
3b
1.99
2.21
2.00
1.00
1.93
0.98
1.16
1.16
2.11
3.16
2.00
2.20
3.05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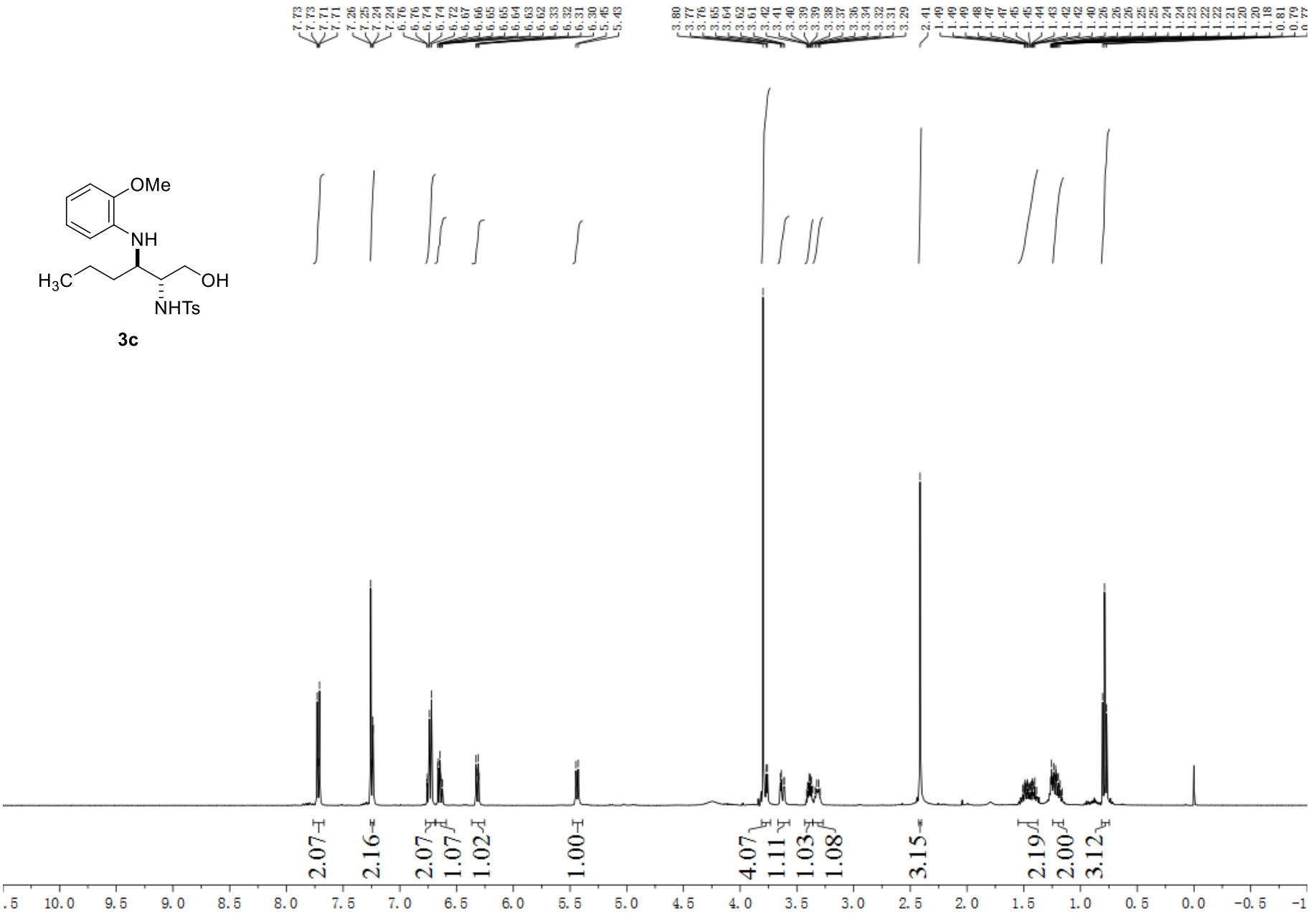
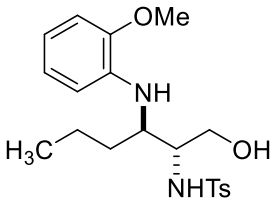
143.63
137.35
129.80
129.27
127.06
117.77
113.36
62.57
56.23
55.11
34.23
21.57
19.42
13.85
NHPh
H3C
OH
NHTs
3b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


OMe
NH
H3C
OH
NHTs
3c


OMe
NH
H3C
OH
NHTs

3c

146.97
143.52
137.42
137.25
129.72
127.05
121.14
117.05
110.28
109.75
62.24
56.67
55.47
54.99
34.49
21.57
19.32
13.84
200
190
180
170
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150
140
130
120
110
100
90
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70
60
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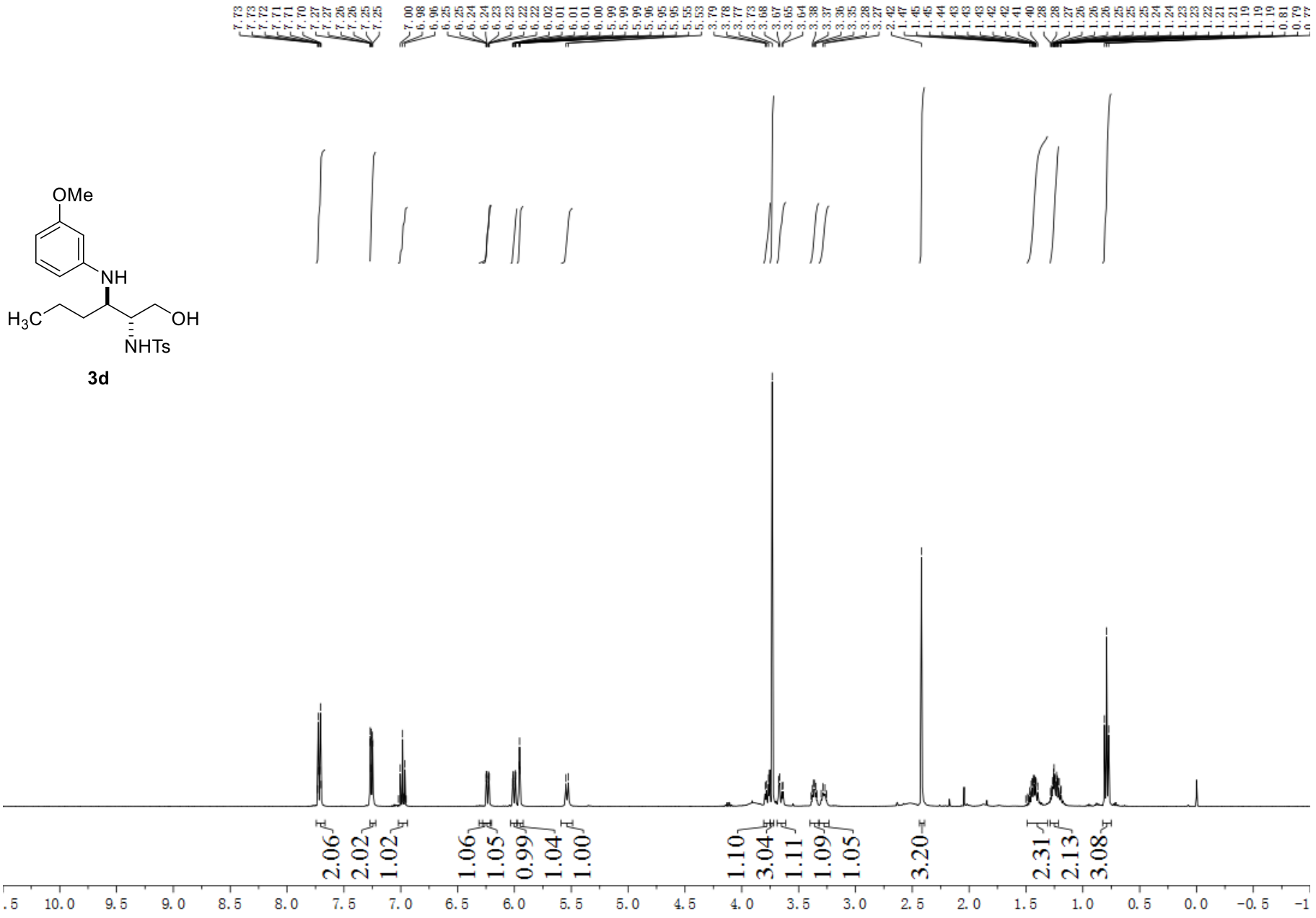
30
20
10
0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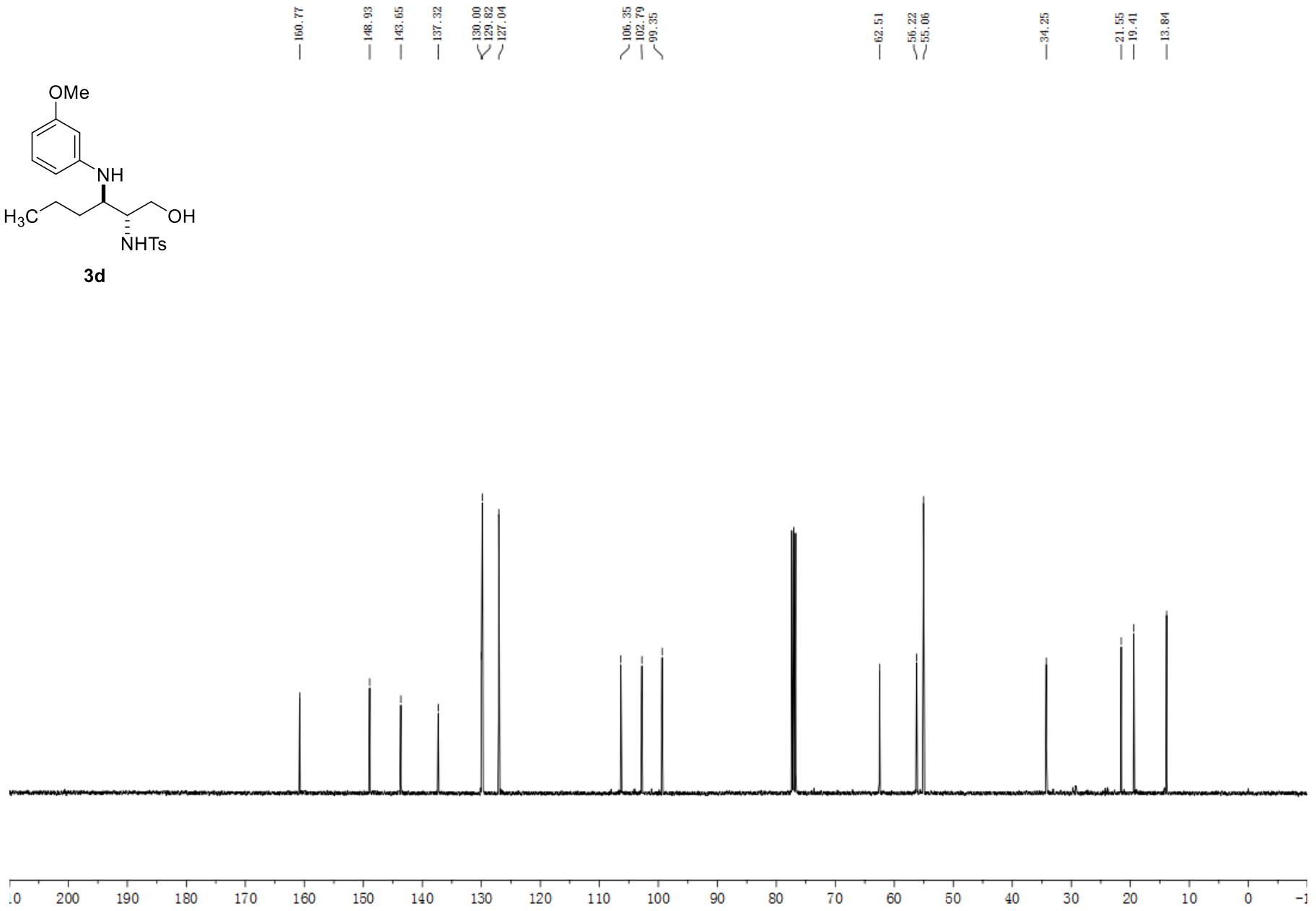
NH
H3C
OH
NHTs
3d
2.06
2.02
1.02
1.06
1.05
0.99
1.04
1.00
1.10
3.04
1.11
1.09
1.05
3.20
2.31
2.13
3.08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130.00
129.82
127.04
106.35
102.79
99.35
62.51
56.22
55.06
34.25
21.55
19.41
13.84
OMe
NH
H3C
OH
NHTs
3d
200
190
180
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160
150
140
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120
110
100
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30
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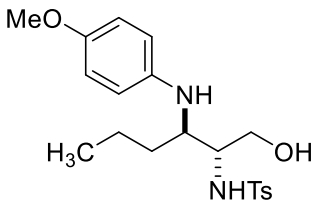
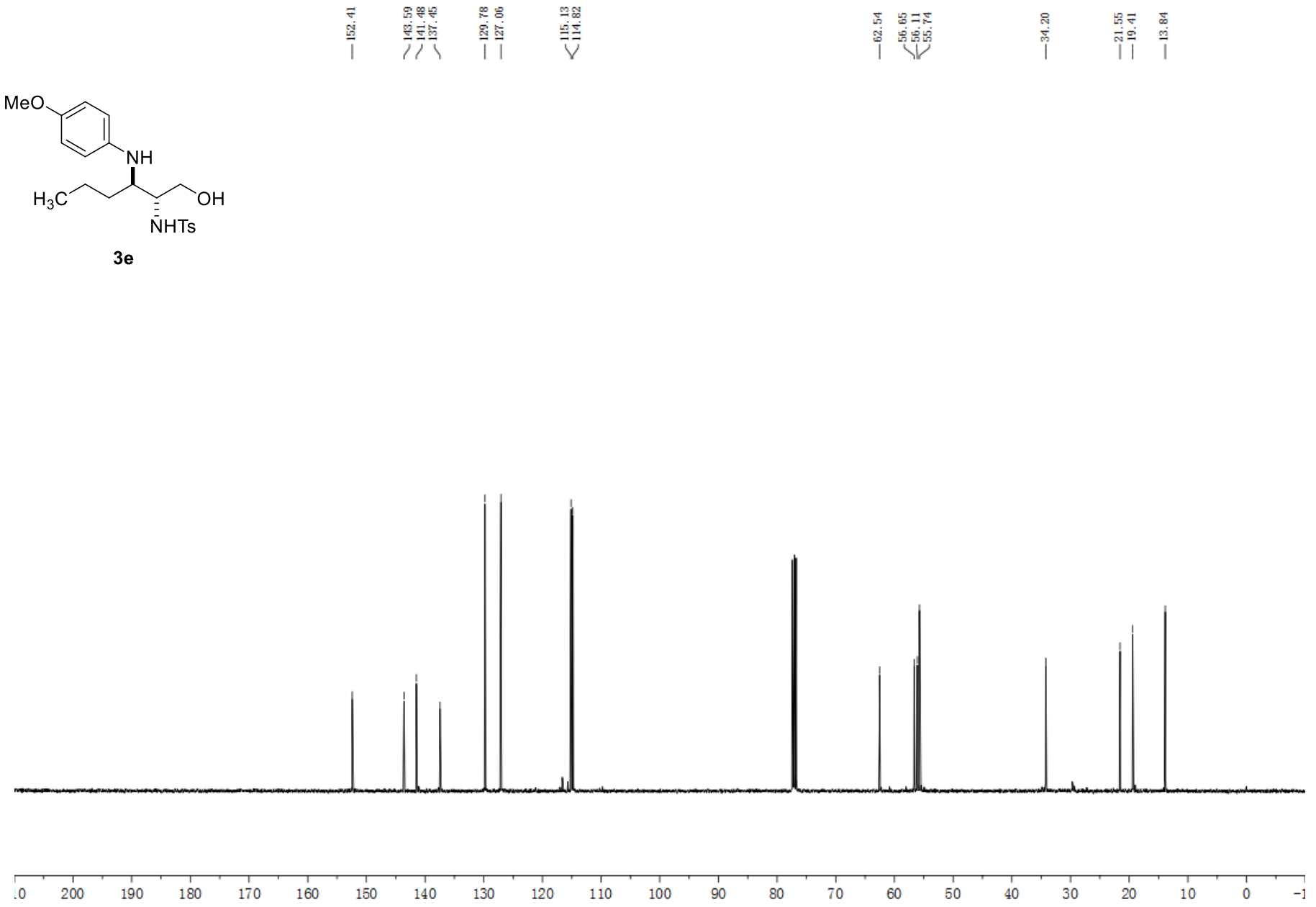
10
0



3e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127.06
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114.82
62.54
56.65
56.11
55.74
34.20
21.55
19.41
13.84
MeO
NH
H3C
OH
NHTs
3e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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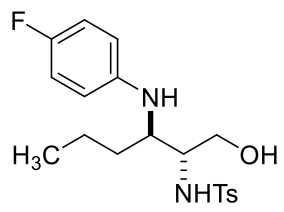
30
20
10
0


F
NH
H3C
OH
NHTs

3f

7.72
7.70
7.26
7.24
7.24
6.80
6.77
6.77
6.75
6.32
6.32
6.31
6.31
6.30
6.30
6.29
5.63
5.61
3.80
3.79
3.77
3.76
3.68
3.67
3.65
3.64
3.40
3.39
3.38
3.37
3.36
3.35
3.25
3.23
3.22
3.20
2.42
1.45
1.44
1.44
1.43
1.43
1.42
1.42
1.41
1.41
1.41
1.40
1.39
1.39
1.26
1.26
1.25
1.24
1.24
1.23
1.23
1.22
1.21
1.21
1.20
1.19
1.19
0.81
0.79
0.77
2.04
2.18
2.04
2.03
1.00
1.23
1.15
1.05
0.77
3.04
2.11
2.22
3.08
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9.0
8.5
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7.0
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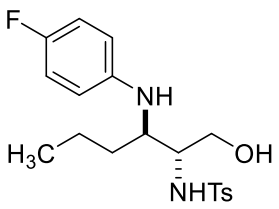

3f

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154.68
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143.74
143.71
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127.03
115.73
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114.38
114.30
62.58
56.01
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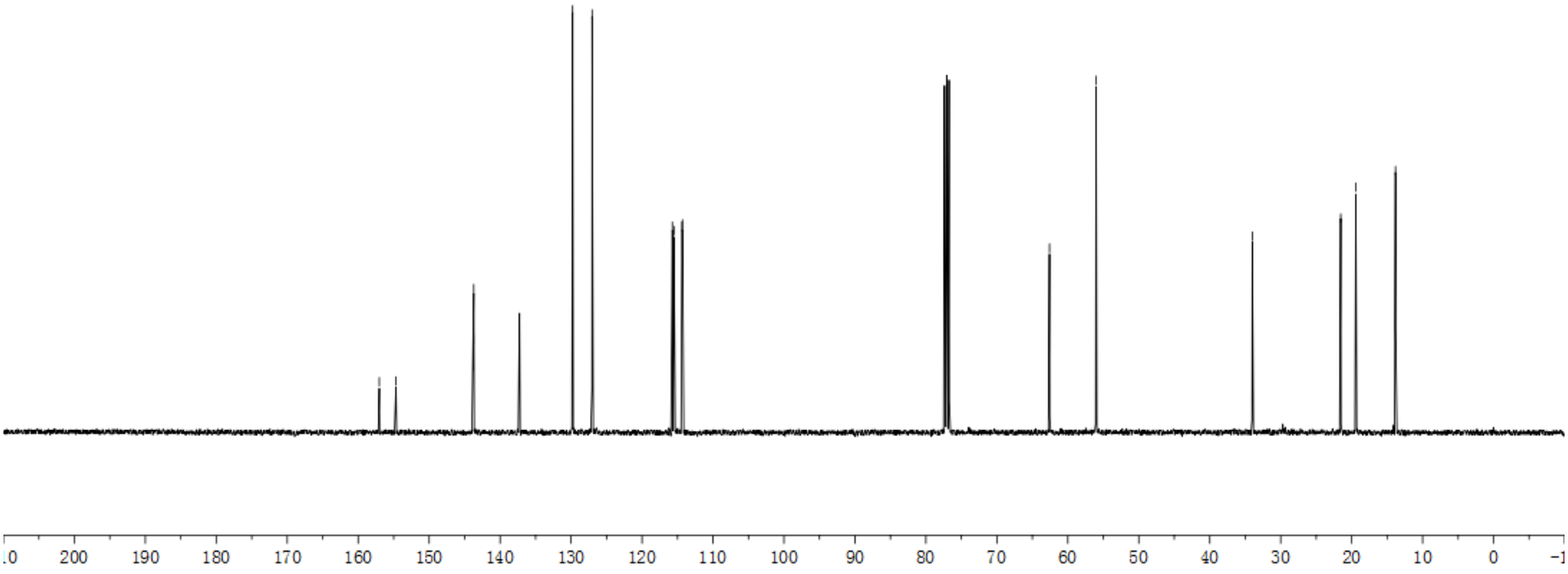
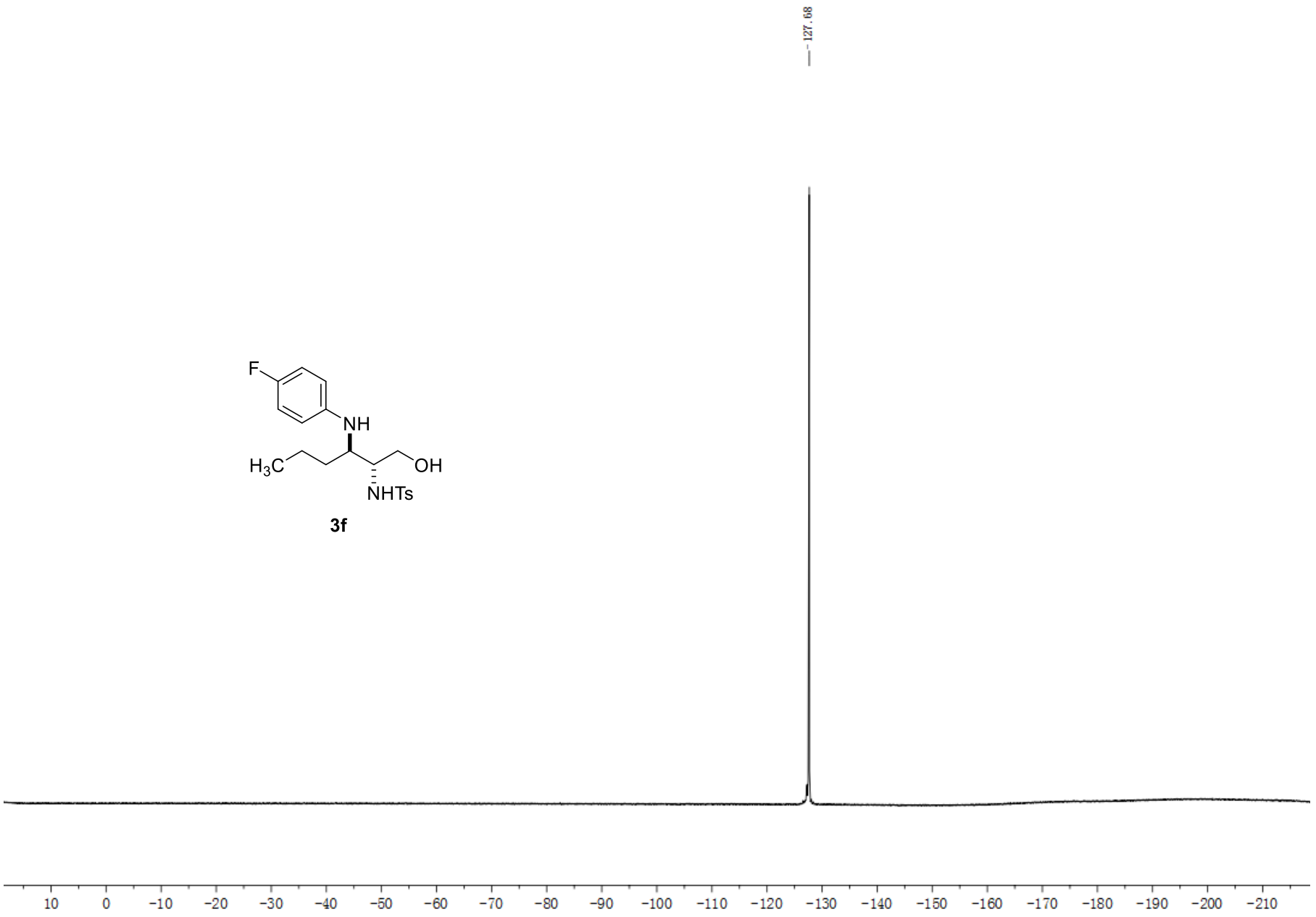
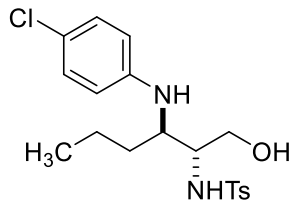
21.54
19.42
13.82




127.68
F
NH
H3C
OH
NHTs
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210

3f


Cl
NH
H3C
OH
NHTs

3g

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1.00
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1.06
1.04
0.99
0.95
3.14
1.97
2.16
3.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
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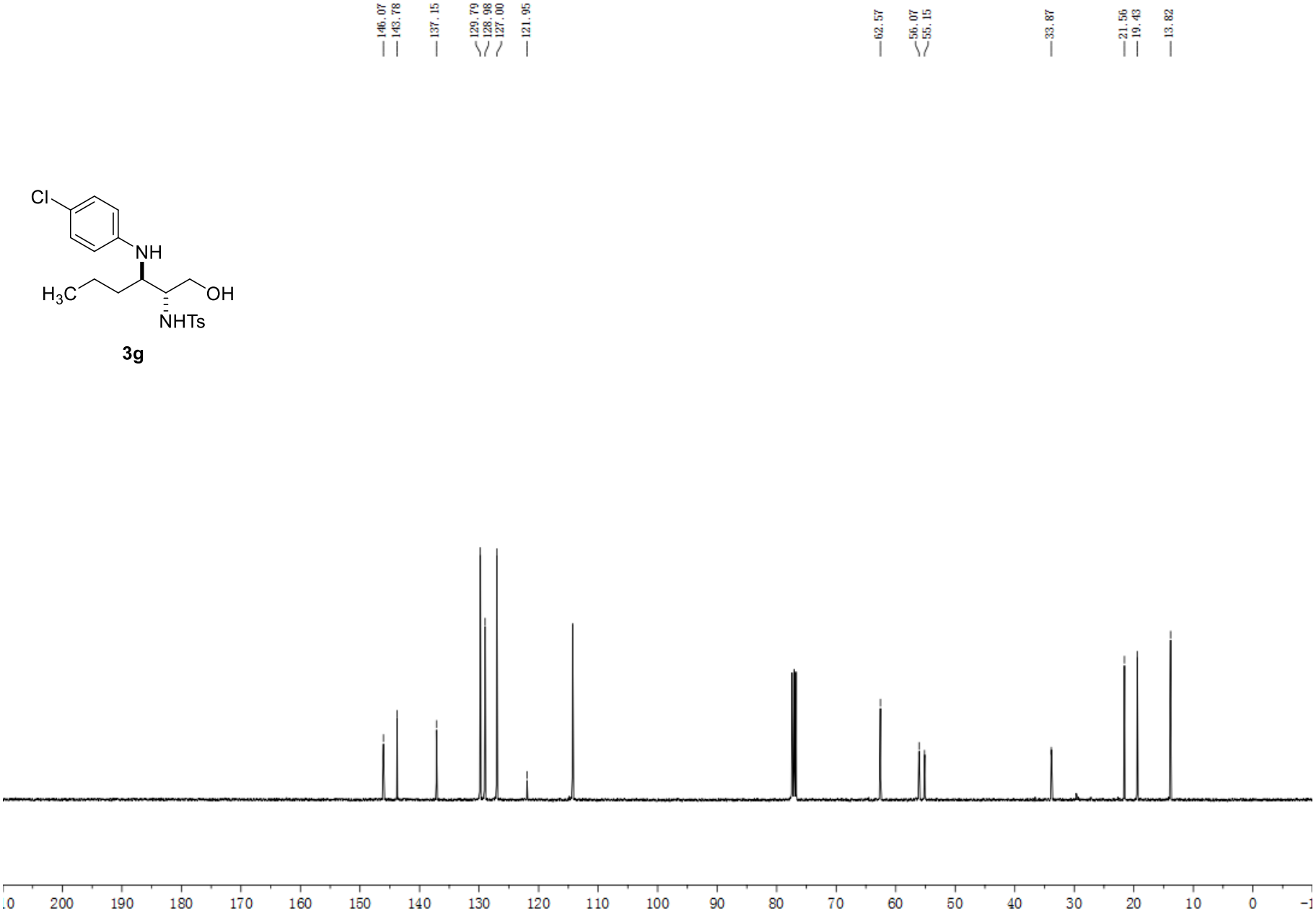
-1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33.87
21.56
19.43
13.82
Cl
NH
H3C
OH
NHTs
3g
200
190
180
170
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150
140
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120
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100
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70
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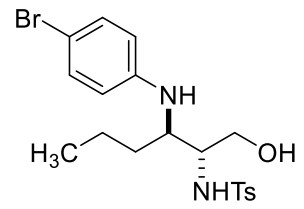
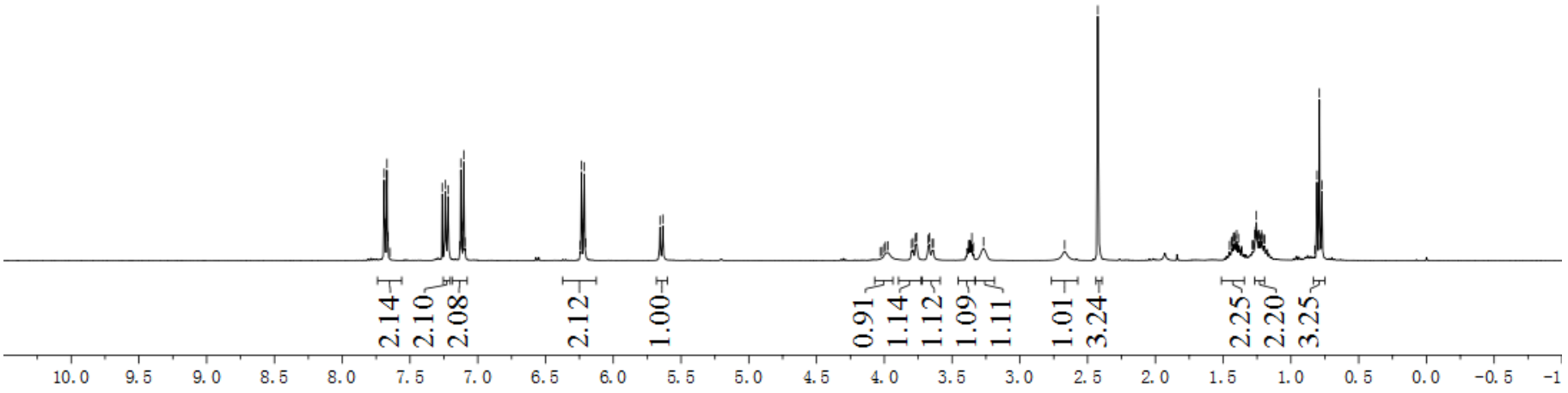

Br
NH
H3C
OH
NHTs

3h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2.20
3.25
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9.5
9.0
8.5
8.0
7.5
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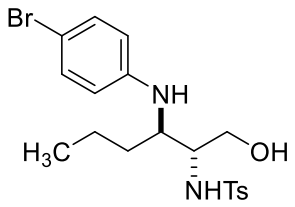
Br
NH
H3C
OH
NHTs

3h

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62.05
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13.64
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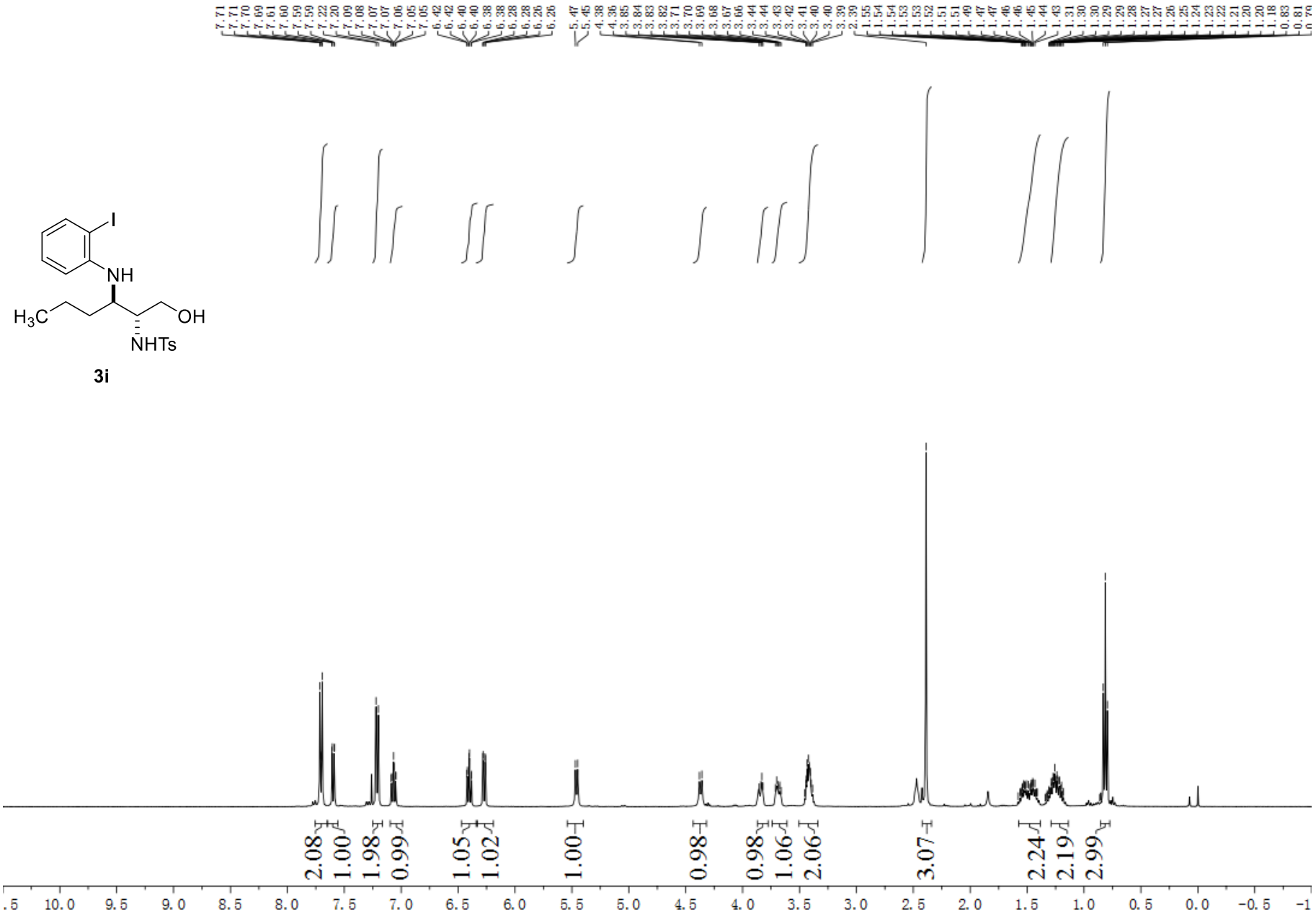
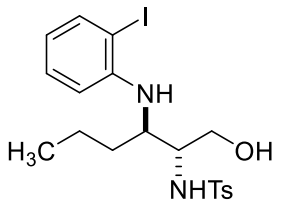


3i


I
NH
H3C
OH
NHTs

3i

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55.29
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19.38
13.88
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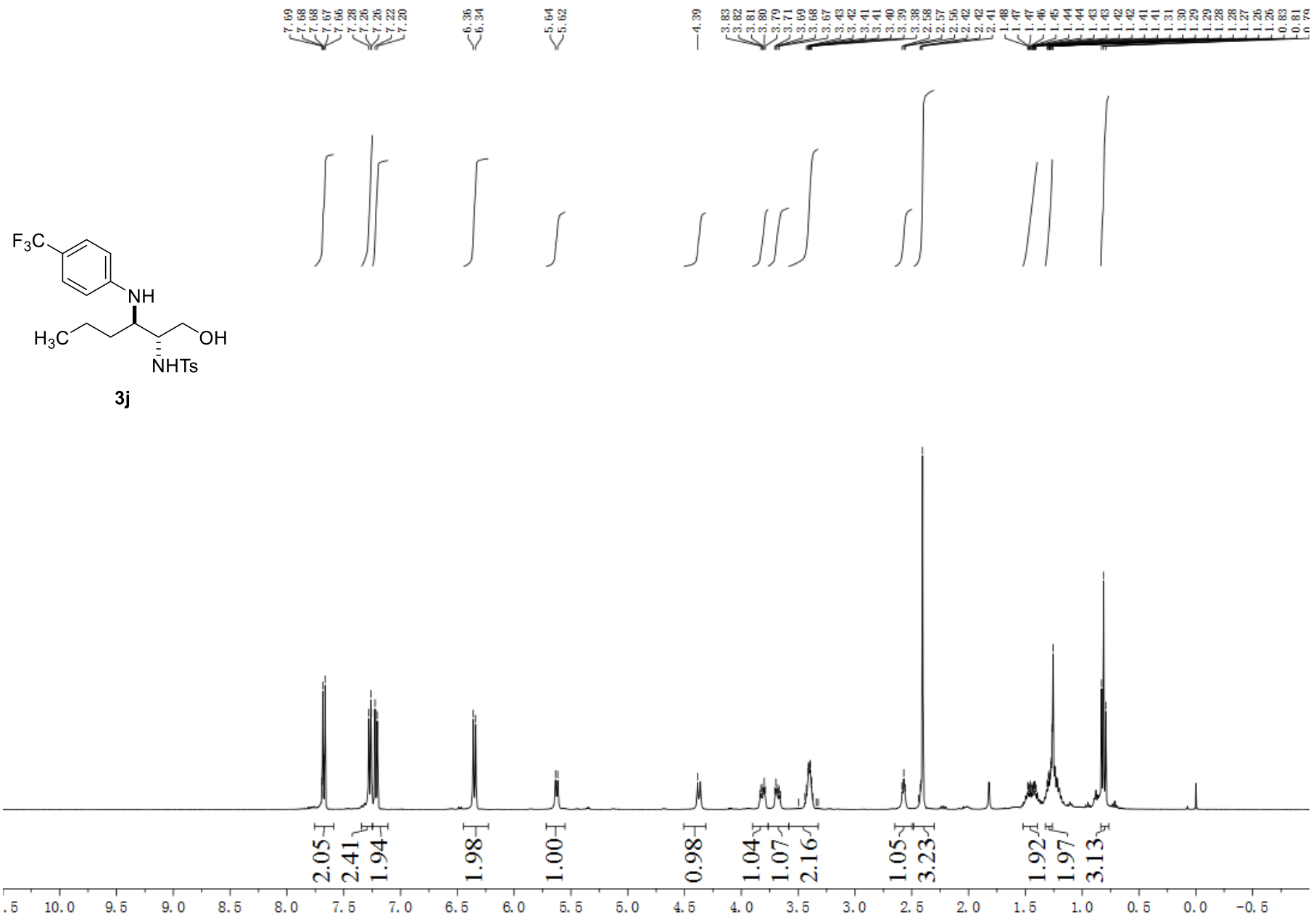
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3.68
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1.41
1.41
1.31
1.30
1.29
1.29
1.28
1.28
1.27
1.26
1.26
0.83
0.81
F3C
NH
H3C
OH
NHTs
2.05
2.41
1.94
1.98
1.00
0.98
1.04
1.07
2.16
1.05
3.23
1.92
1.97
3.13
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8.5
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6.0
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5.0
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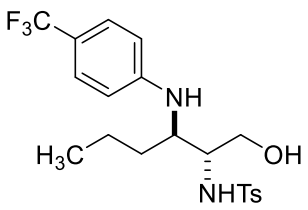
3j


F3C
NH
H3C
OH
NHTs

3j

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143.88
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126.53
126.50
119.14
118.82
118.50
118.18
112.02
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33.77
21.50
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13.81
10
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180
170
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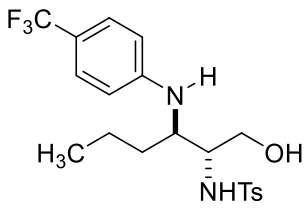
F3C
N
H
H3C
OH
NHTs

3j

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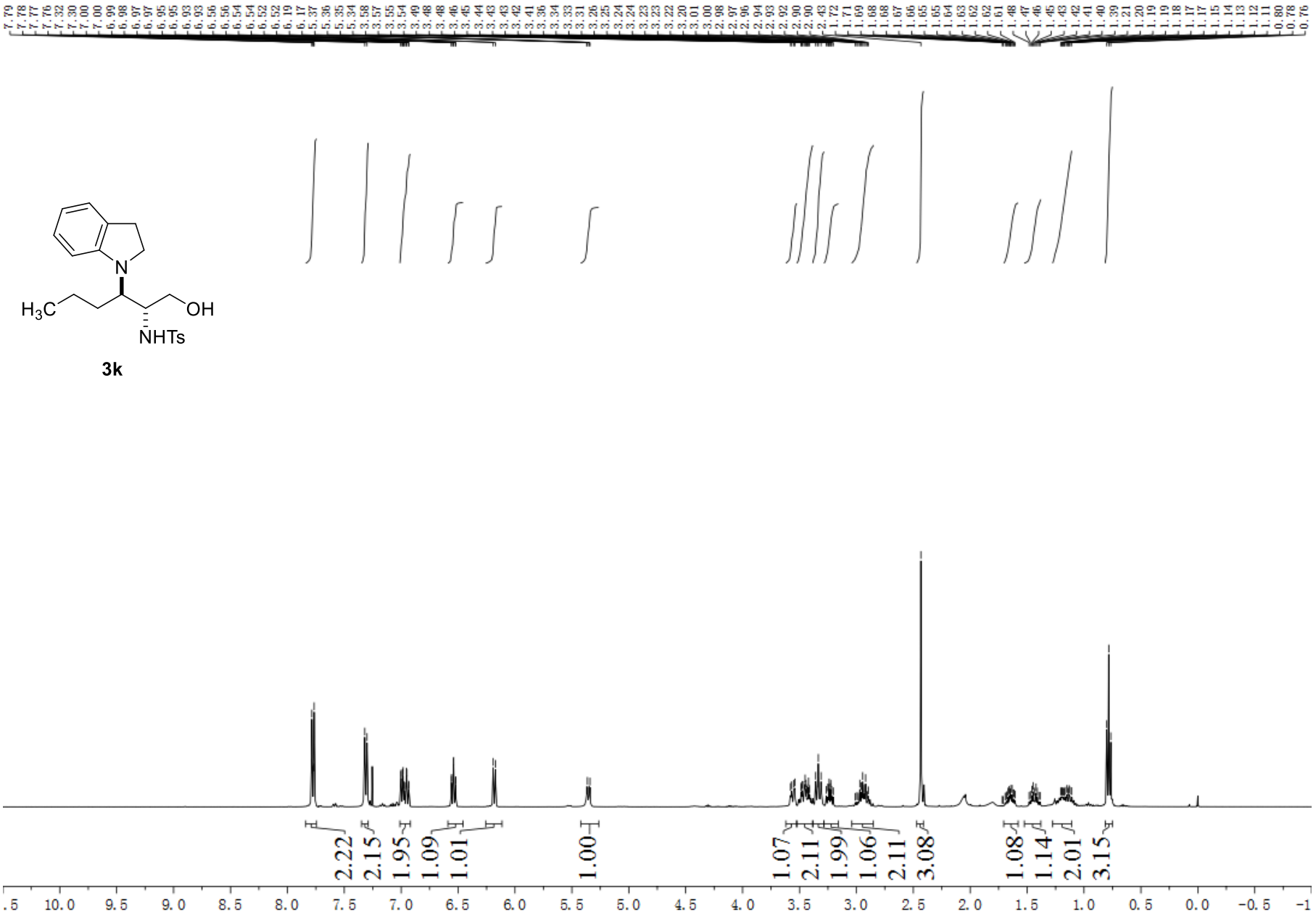
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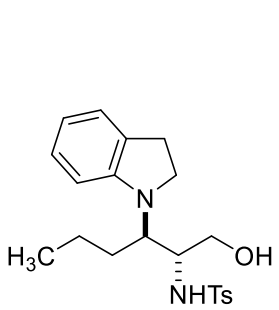
N
H3C
OH
NHTs
3k
2.22 2.15 1.95 1.09 1.01 1.00 1.07 2.11 1.99 1.06 2.11 3.08 1.08 1.14 2.01 3.15
.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1


N
H3C
OH
NHTs

3k

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46.10
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21.59
20.07
13.92
13.66
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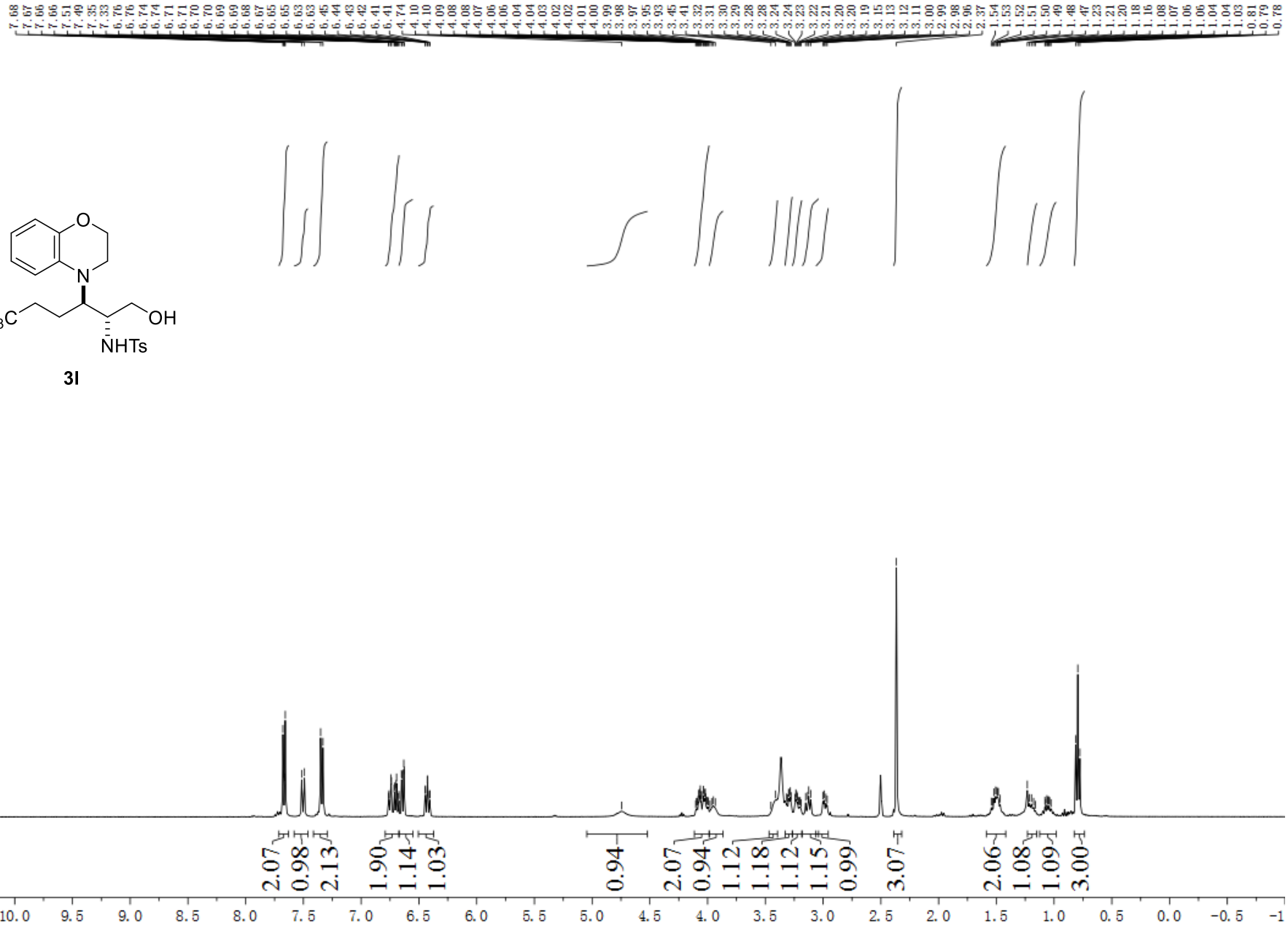
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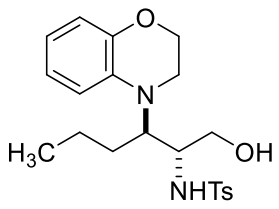
O
N
H3C
OH
NHTs
2.07 0.98 2.13 1.90 1.14 1.03 0.94 2.07 0.94 1.12 1.18 1.12 1.15 0.99 3.07 2.06 1.08 1.09 3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1

3l


O
N
H3C
OH
NHTs

3l

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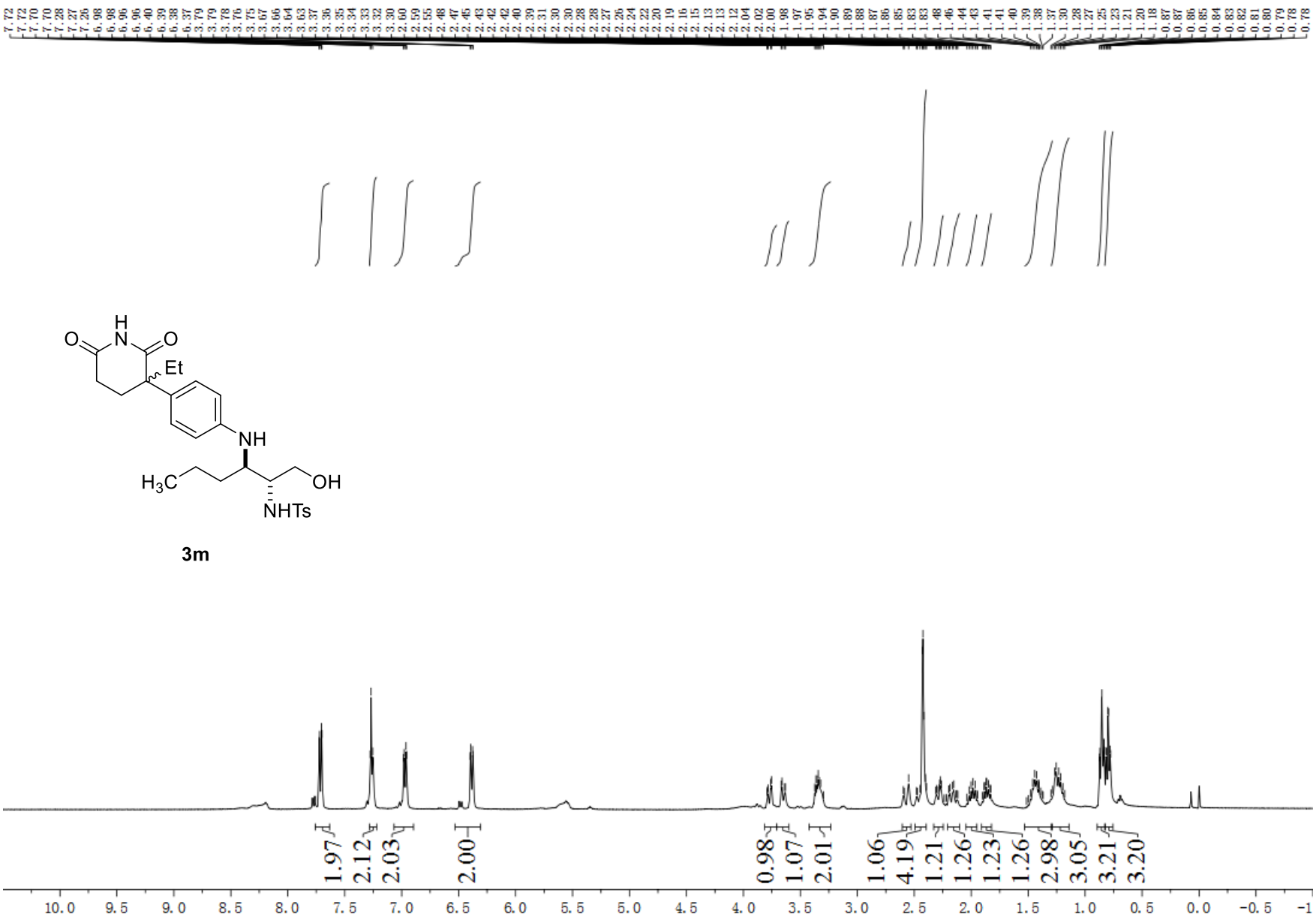
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O
H
N
O
Et
NH
H3C
OH
NHTs
1.97 2.12 2.03 2.00 0.98 1.07 2.01 1.06 4.19 1.21 1.26 1.23 1.26 2.98 3.05 3.21 3.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1

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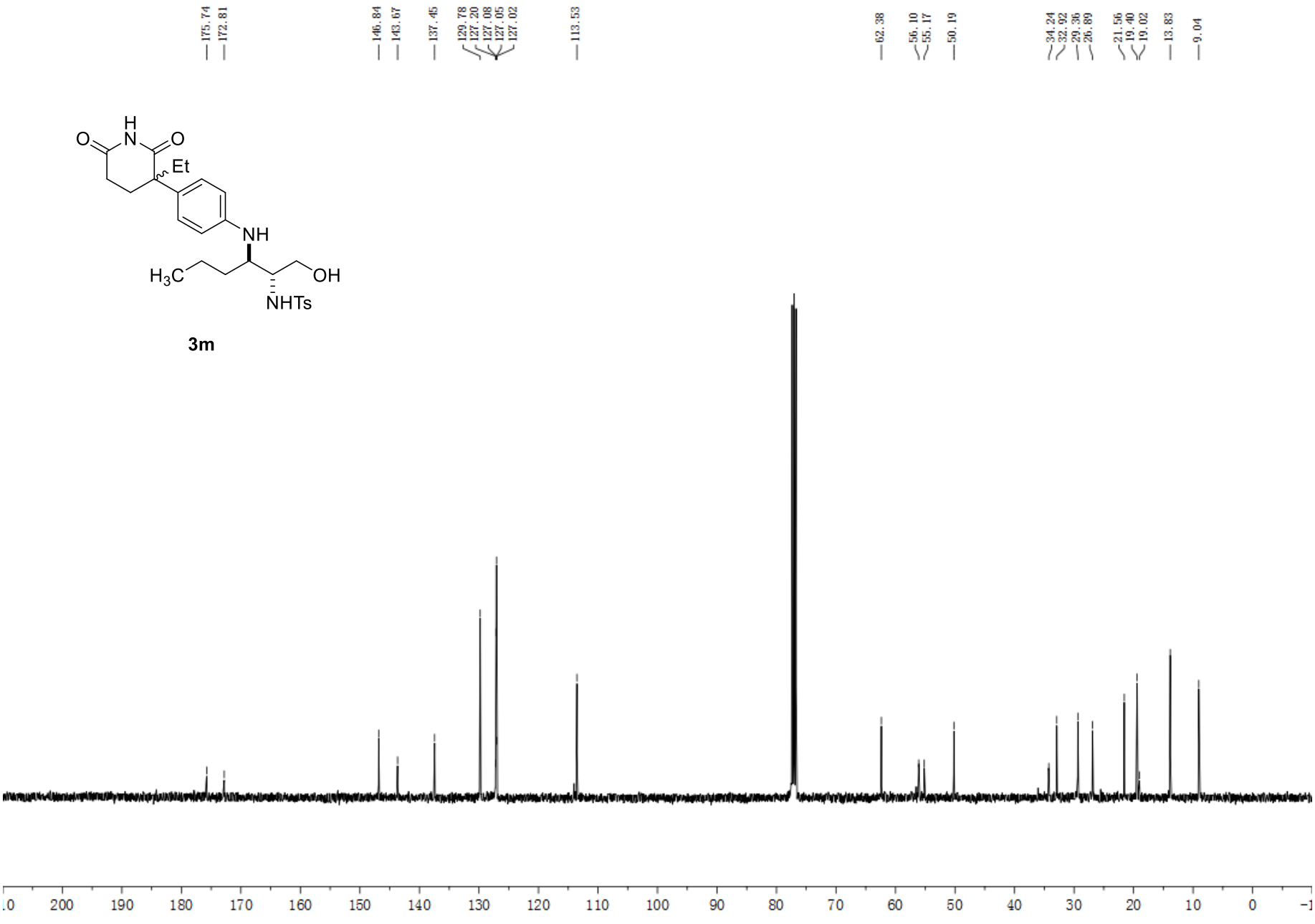
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56.10
55.17
50.19
34.24
32.92
29.36
26.89
21.56
19.40
19.02
13.83
9.04
H
N
O
O
Et
NH
H3C
OH
NHTs
3m
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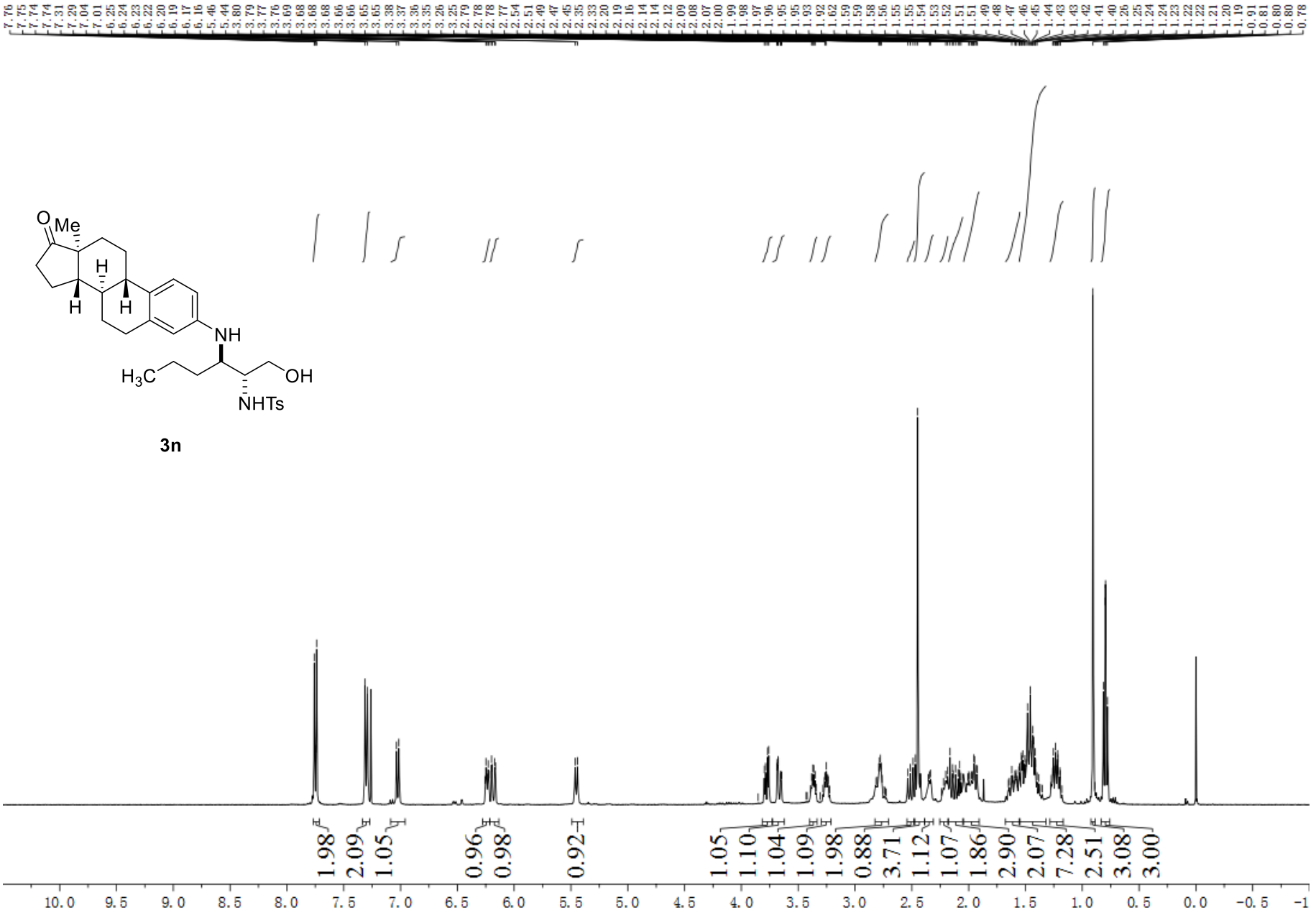

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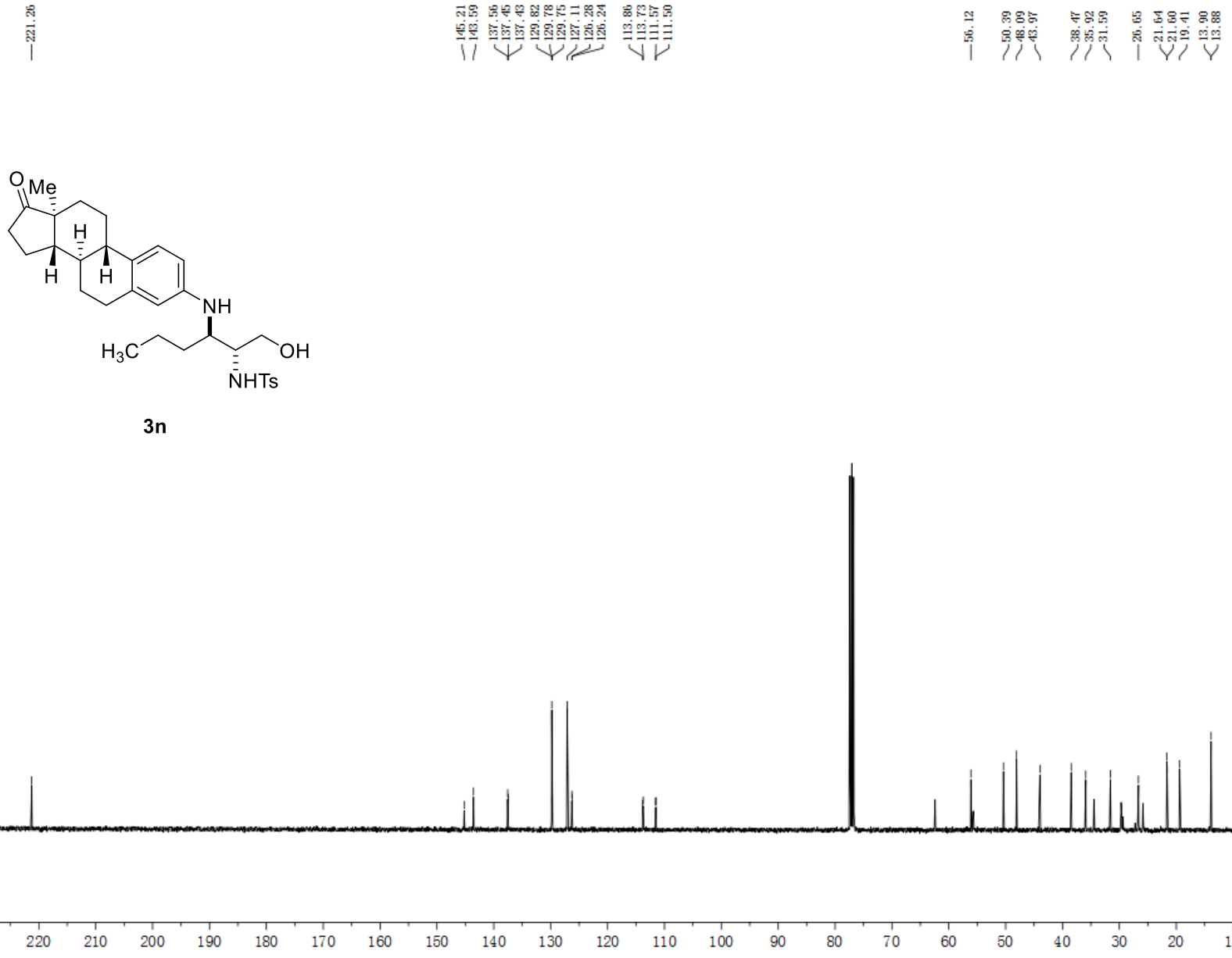
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111.57
111.50
56.12
50.39
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43.97
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35.92
31.59
26.65
21.64
21.60
19.41
13.90
13.88
O
Me
H
H
H
NH
H3C
OH
NHTs
220
210
200
190
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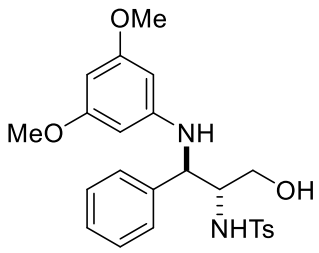
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MeO
NH
OH
NHTs

3o

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7.28
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7.27
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2.05
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3.03
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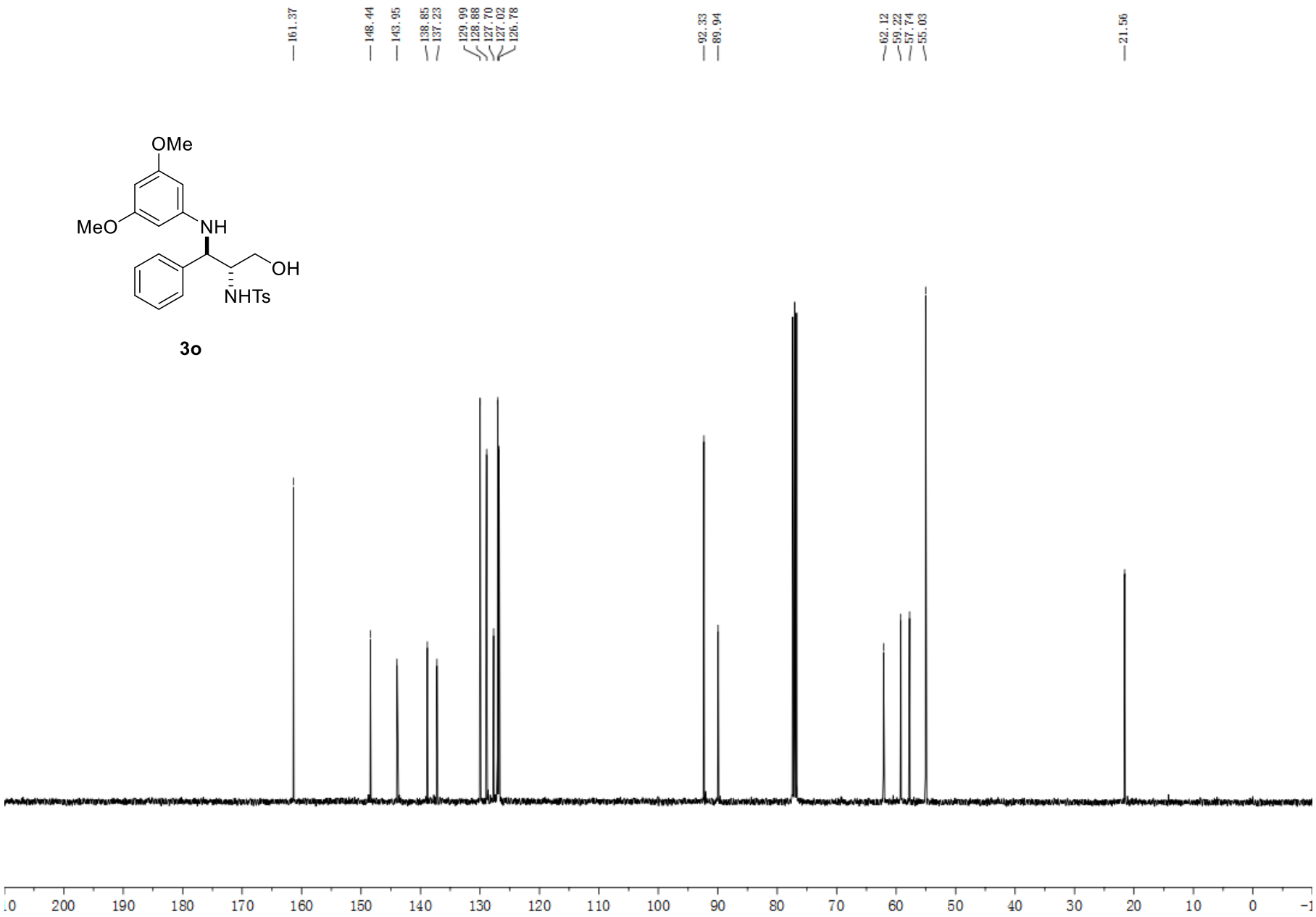
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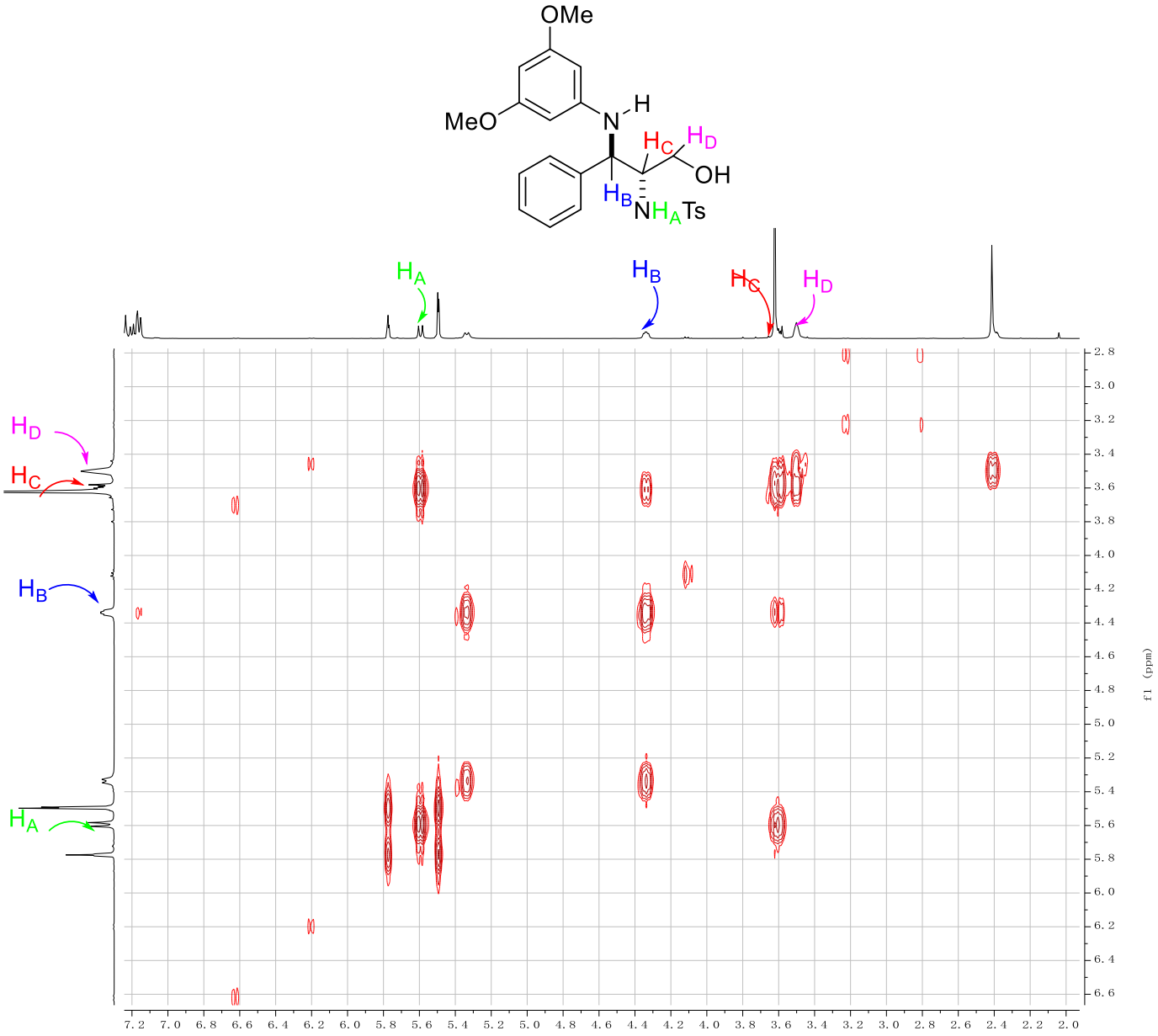
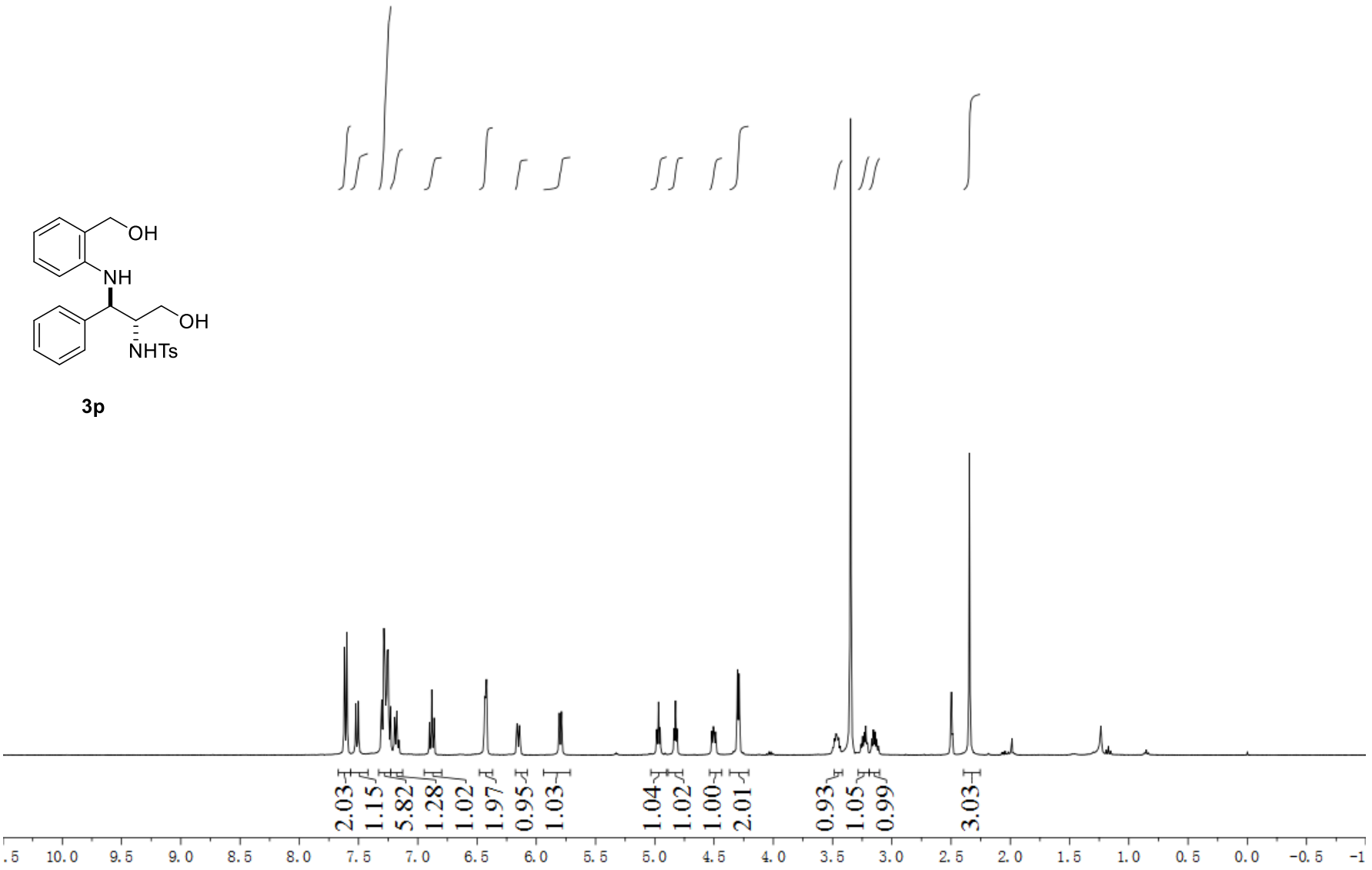
127.70
127.02
126.78
92.33
89.94
62.12
59.22
57.74
55.03
21.56
OMe
MeO
NH
OH
NHTs
3o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Cosy of 3o

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2.01
0.93
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0.99
3.03
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8.0
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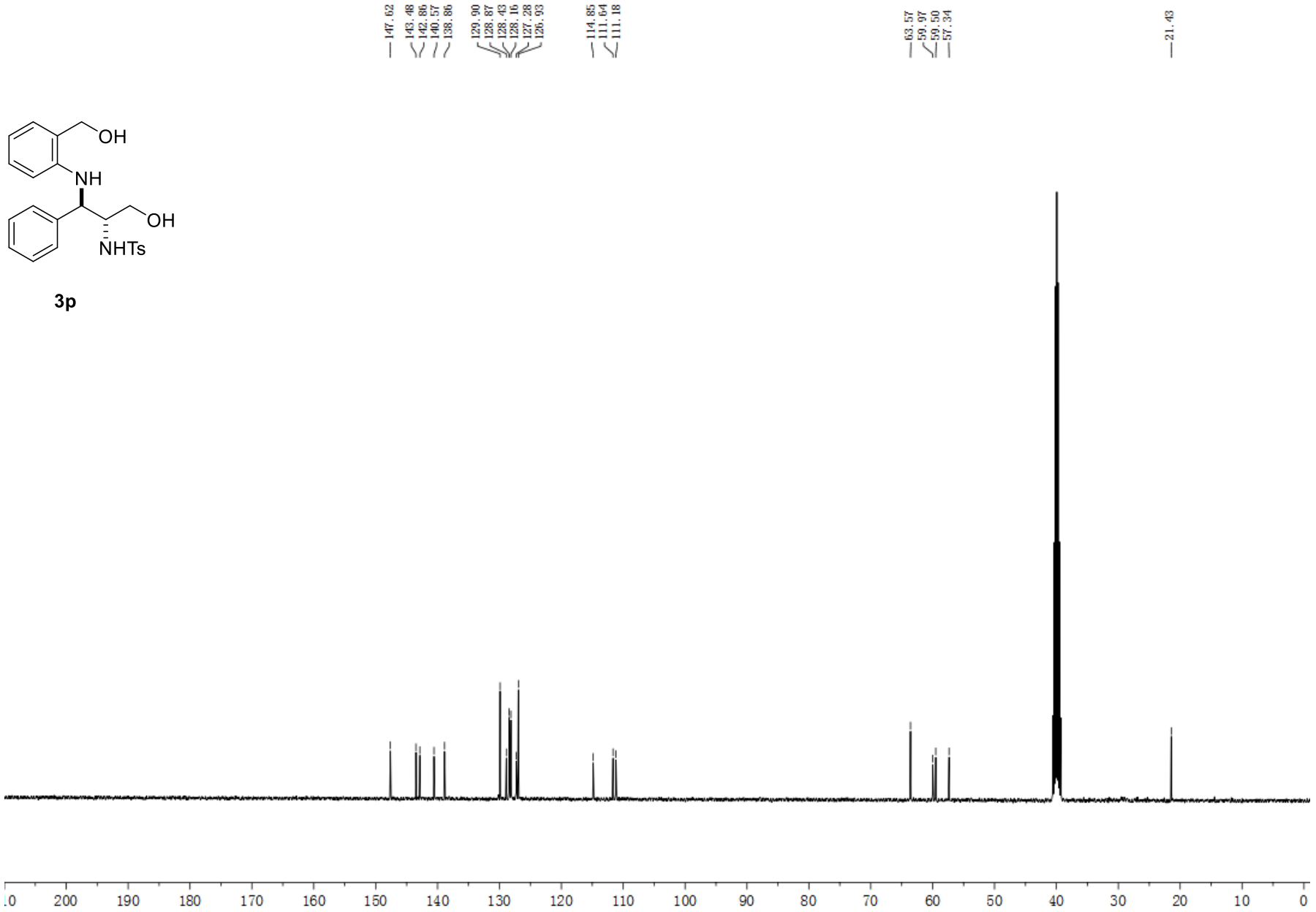
3p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111.18
63.57
59.97
59.50
57.34
21.43
OH
NH
OH
NHTs
3p
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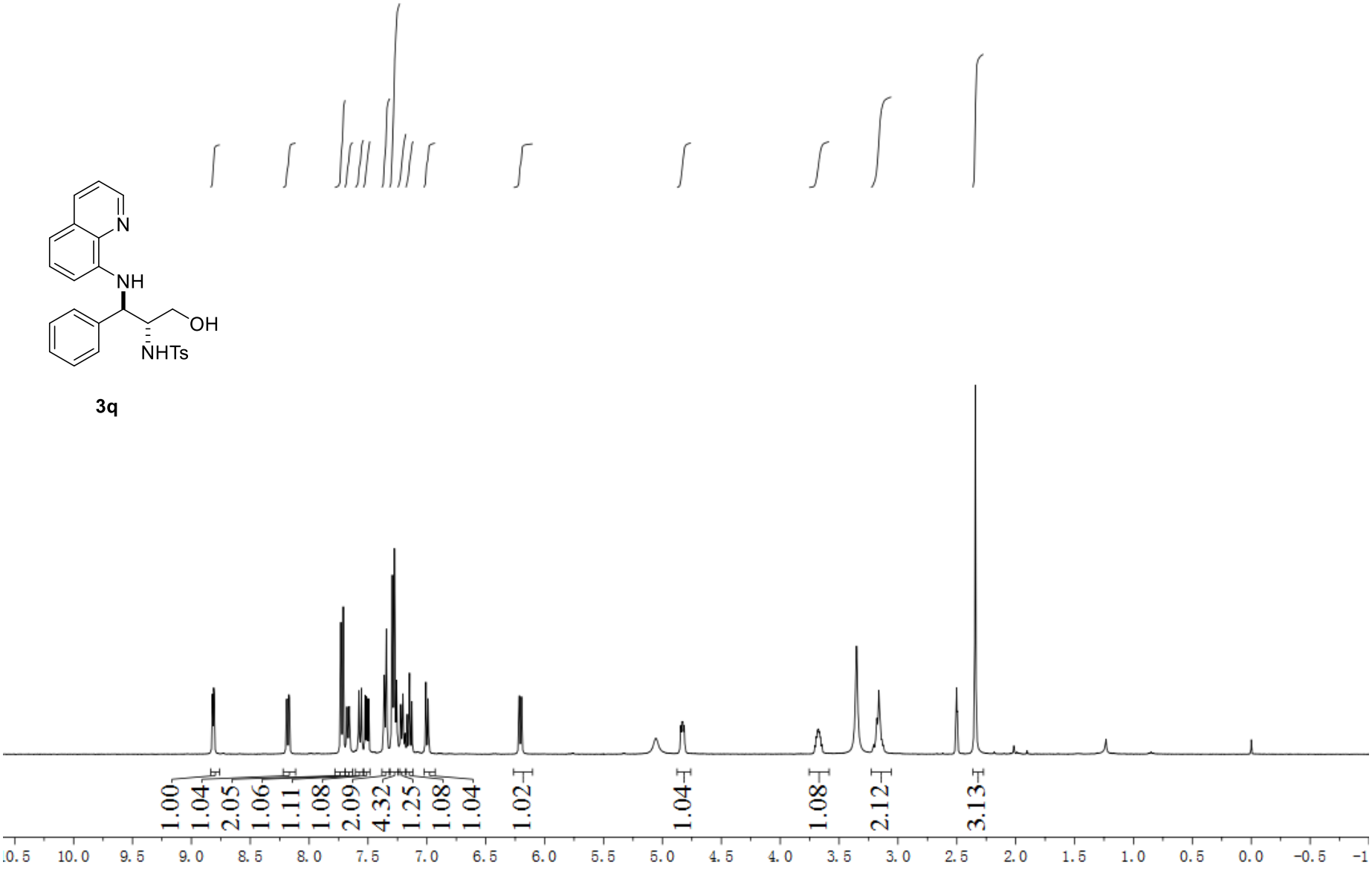
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OH
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1.08
1.04
1.02
1.04
1.08
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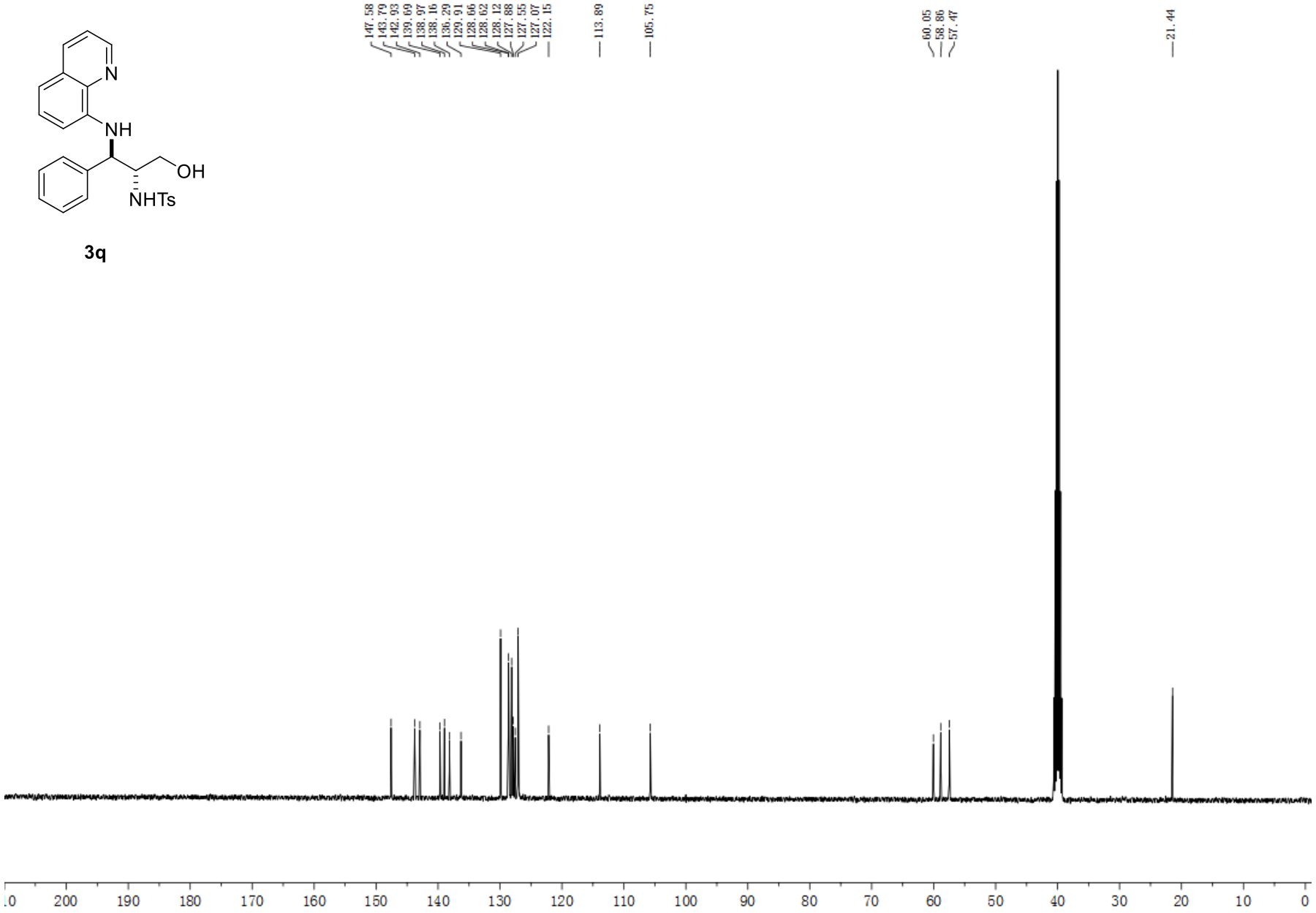
3q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127.07
122.15
113.89
105.75
60.05
58.86
57.47
21.44
N
NH
OH
NHTs
3q
200
190
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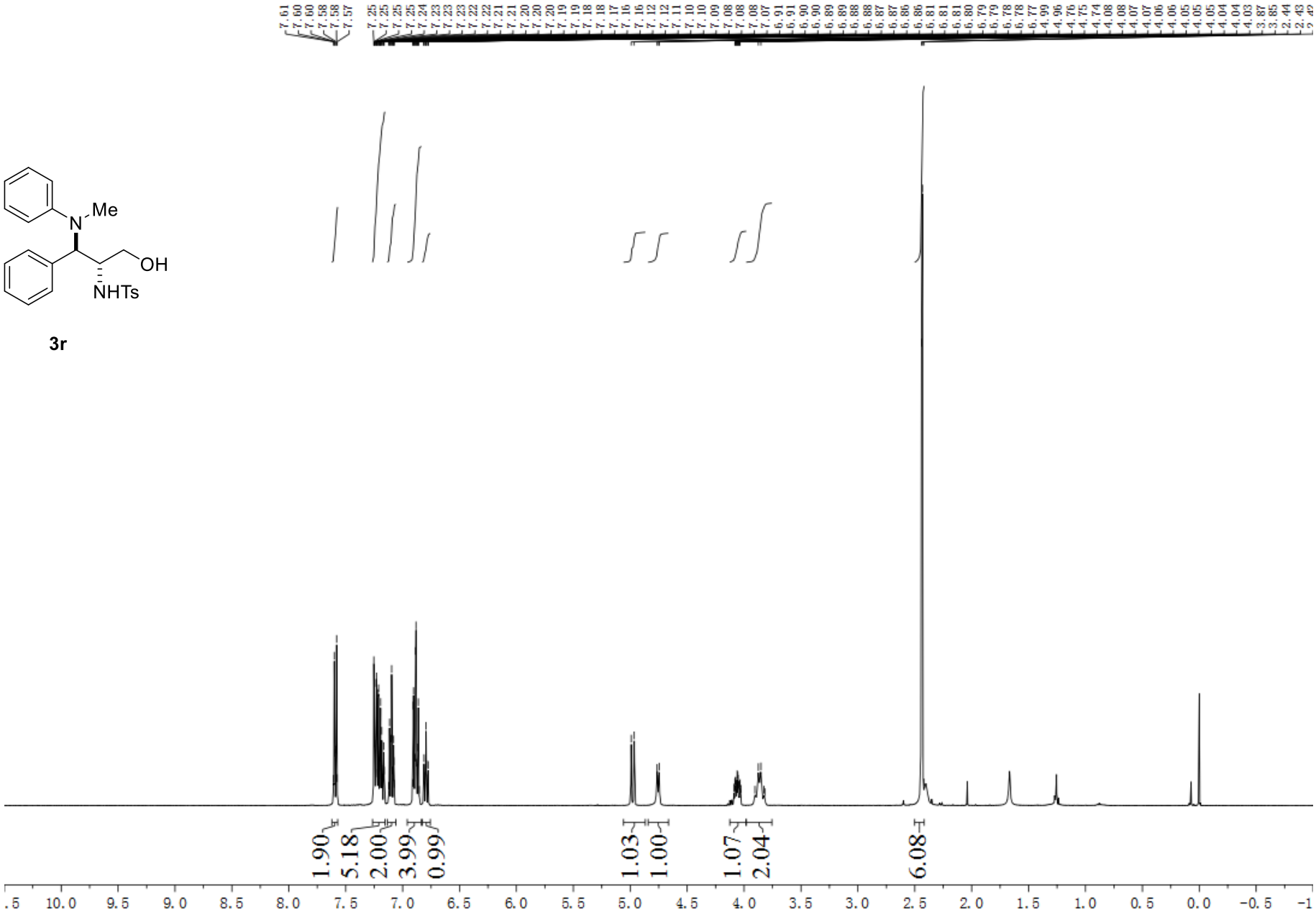

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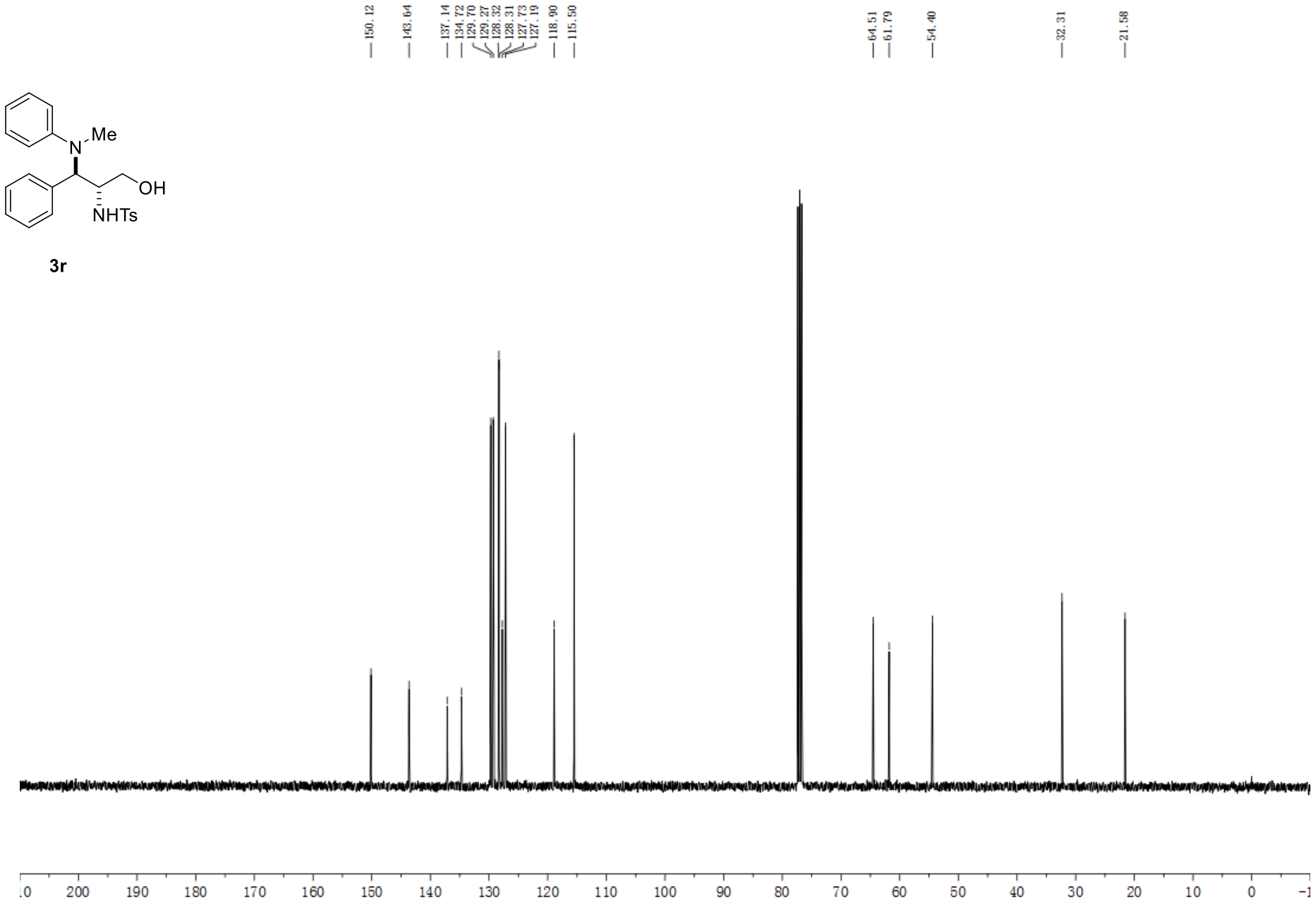
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32.31
21.58
N
Me
OH
NHTs
3r
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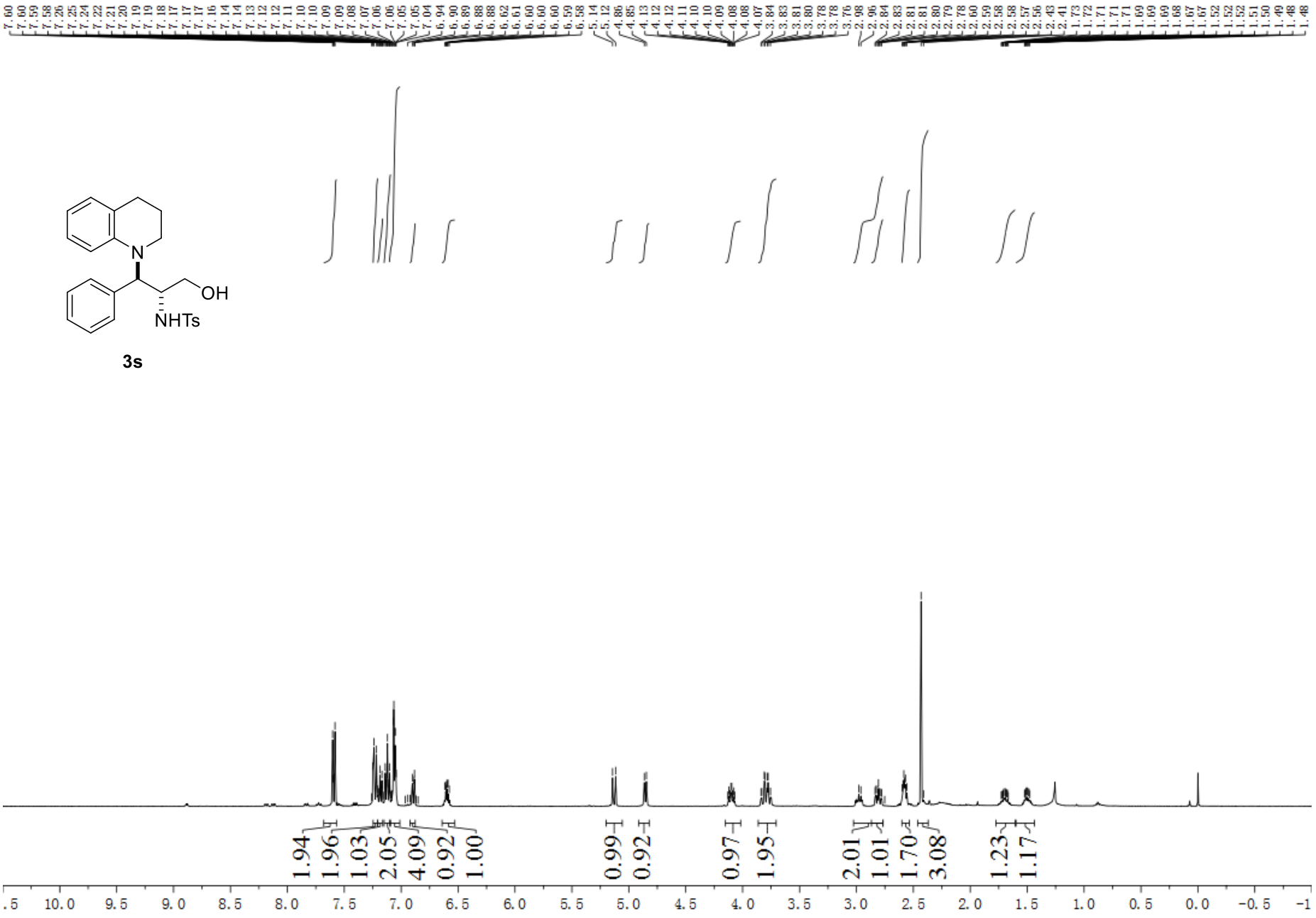
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N
OH
NHTs
1.94 1.96 1.03 2.05 4.09 0.92 1.00 0.99 0.92 0.97 1.95 2.01 1.01 1.70 3.08 1.23 1.17
.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1

3s


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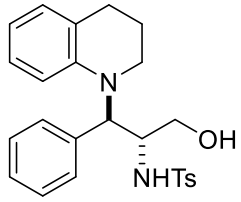
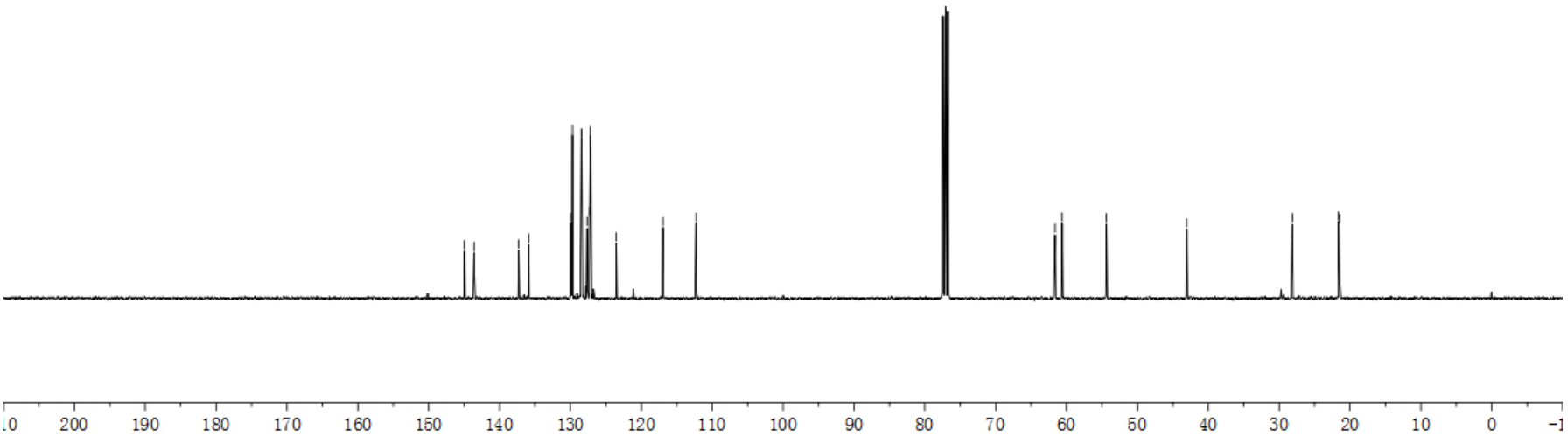

N
OH
NHTs

3s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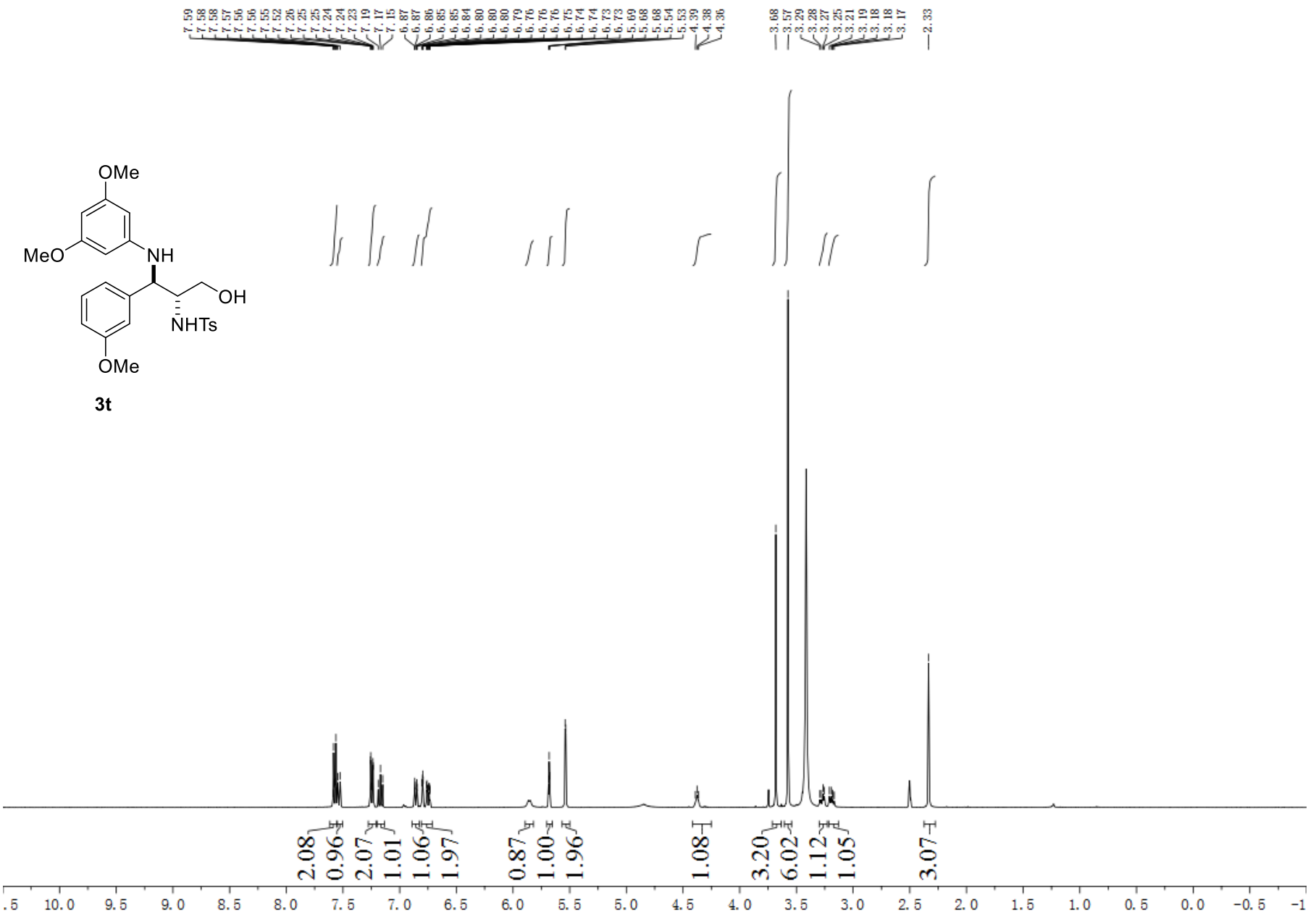
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MeO
NH
OH
NHTs
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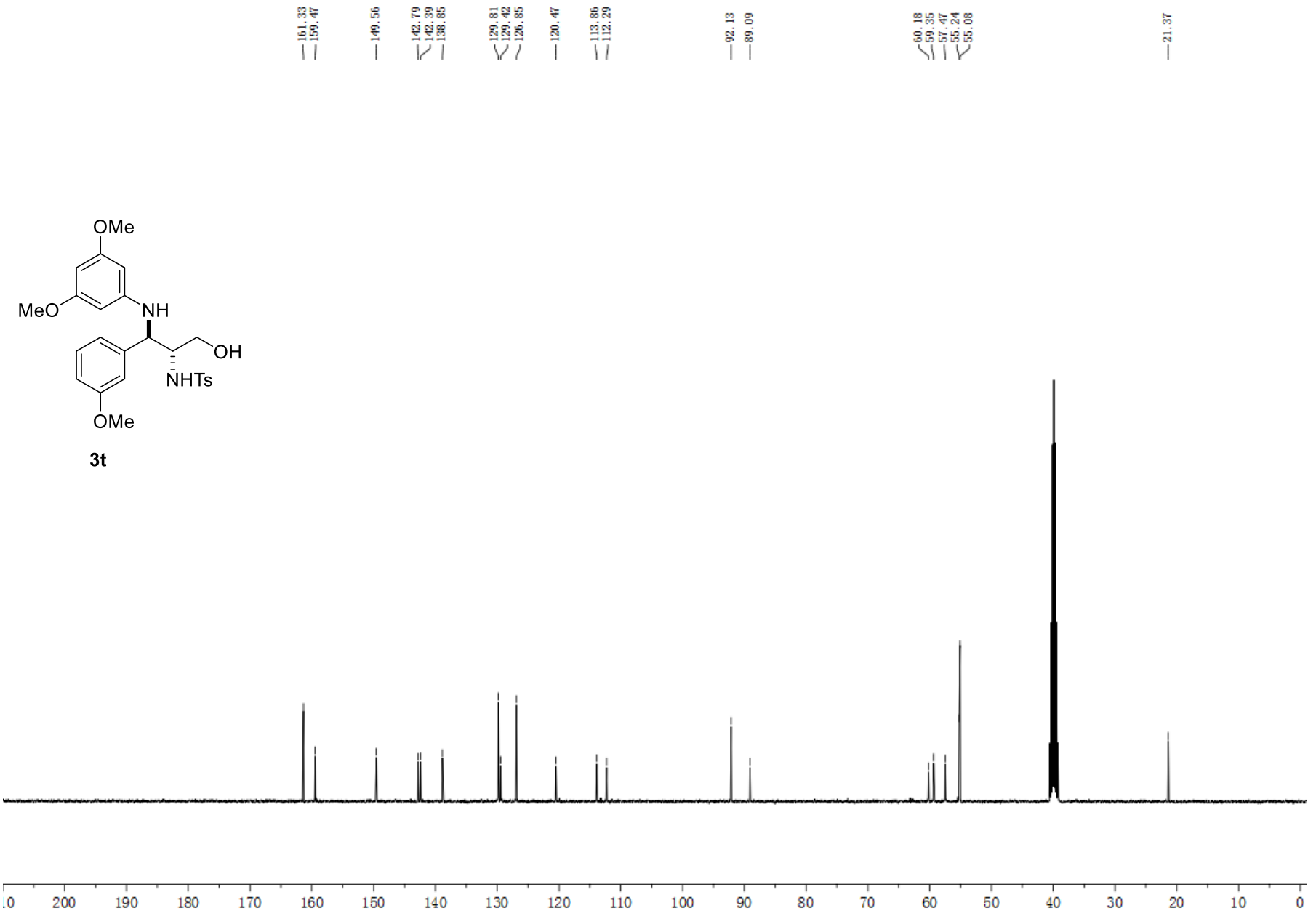
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113.86
112.29
92.13
89.09
60.18
59.35
57.47
55.24
55.08
21.37
OMe
MeO
NH
OH
NHTs
OMe
3t
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
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30
20
10
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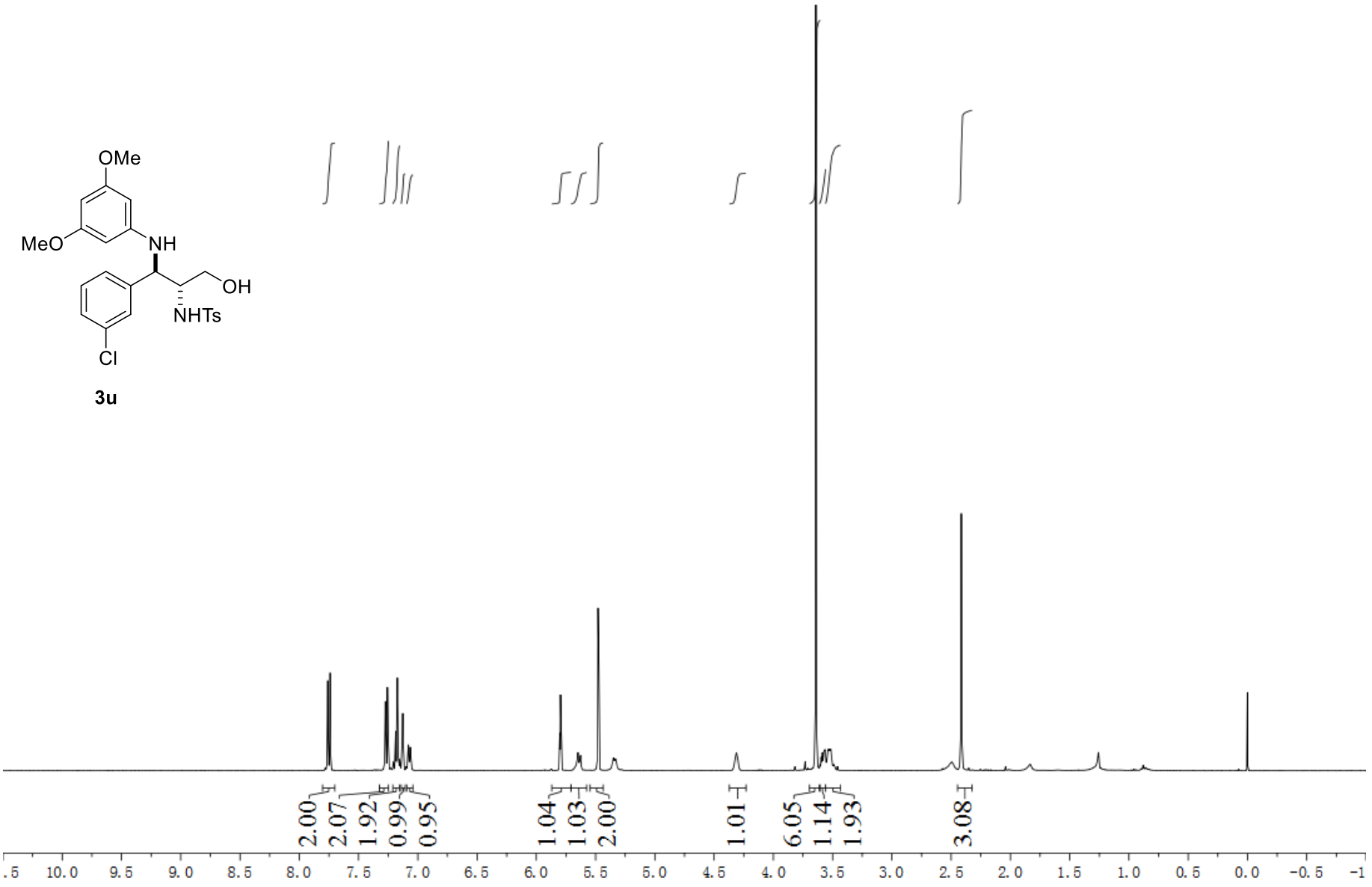
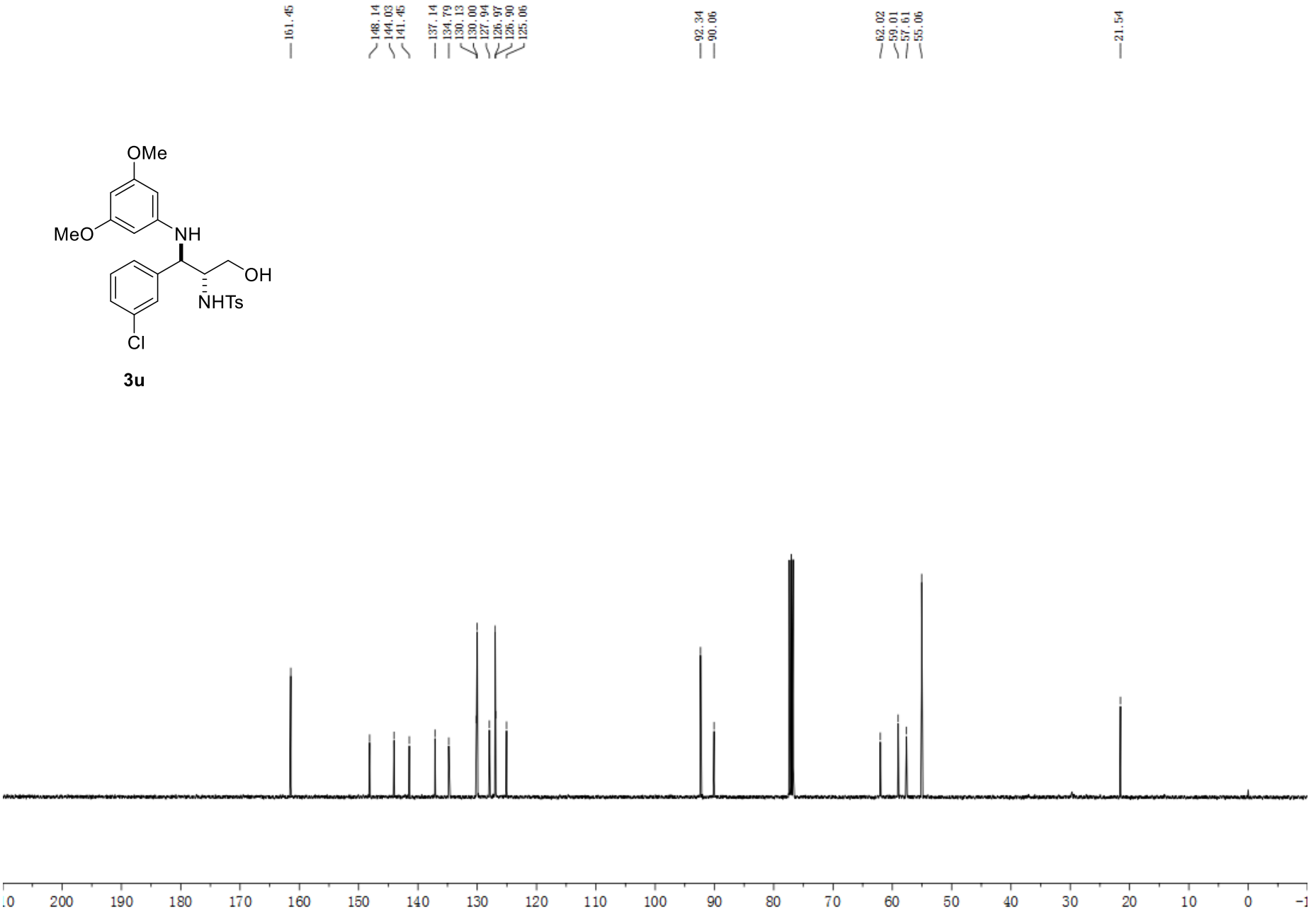

OMe
MeO
NH
OH
NHTs
Cl
2.00
2.07
1.92
0.99
0.95
1.04
1.03
2.00
1.01
6.05
1.14
1.93
3.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

3u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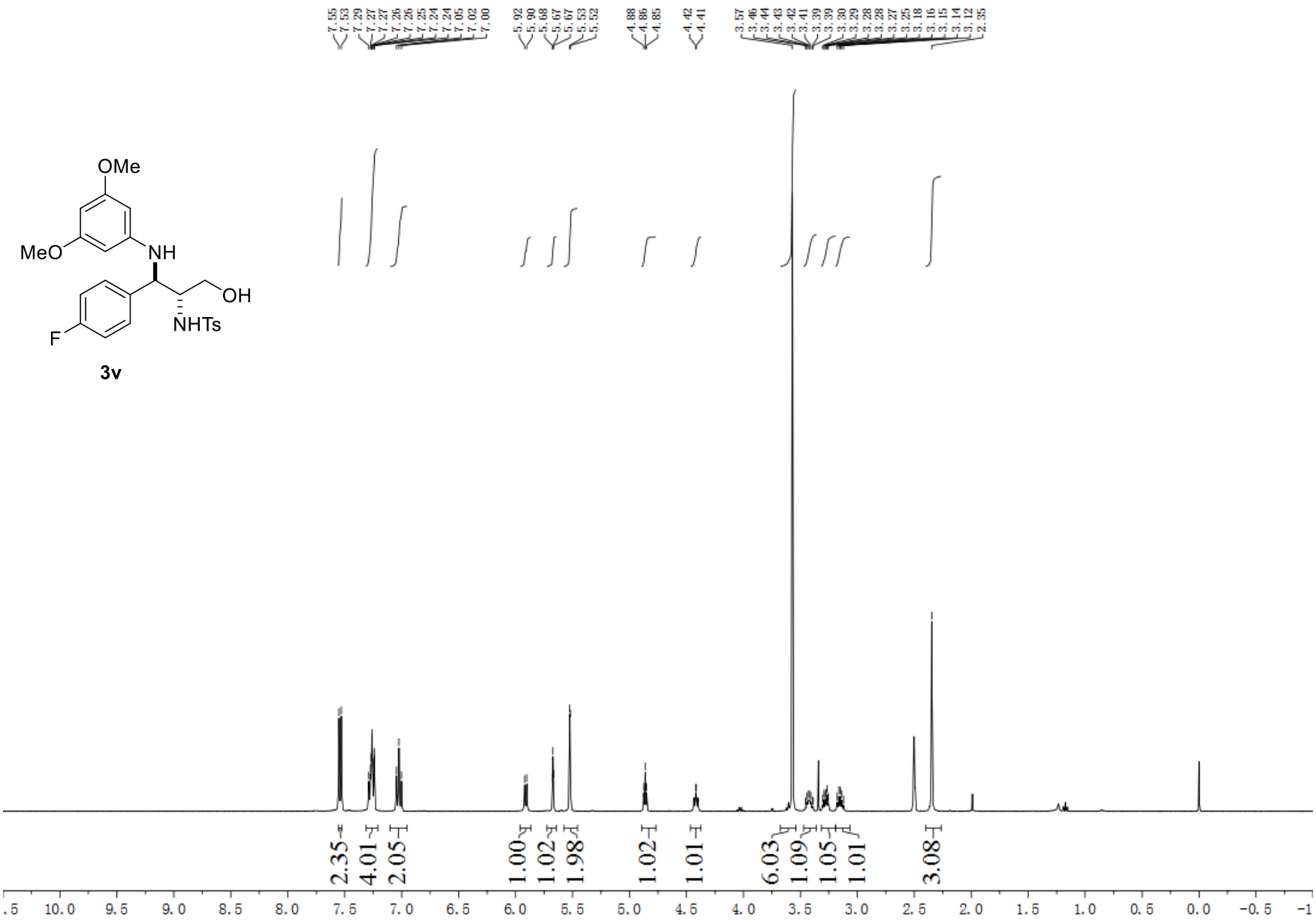
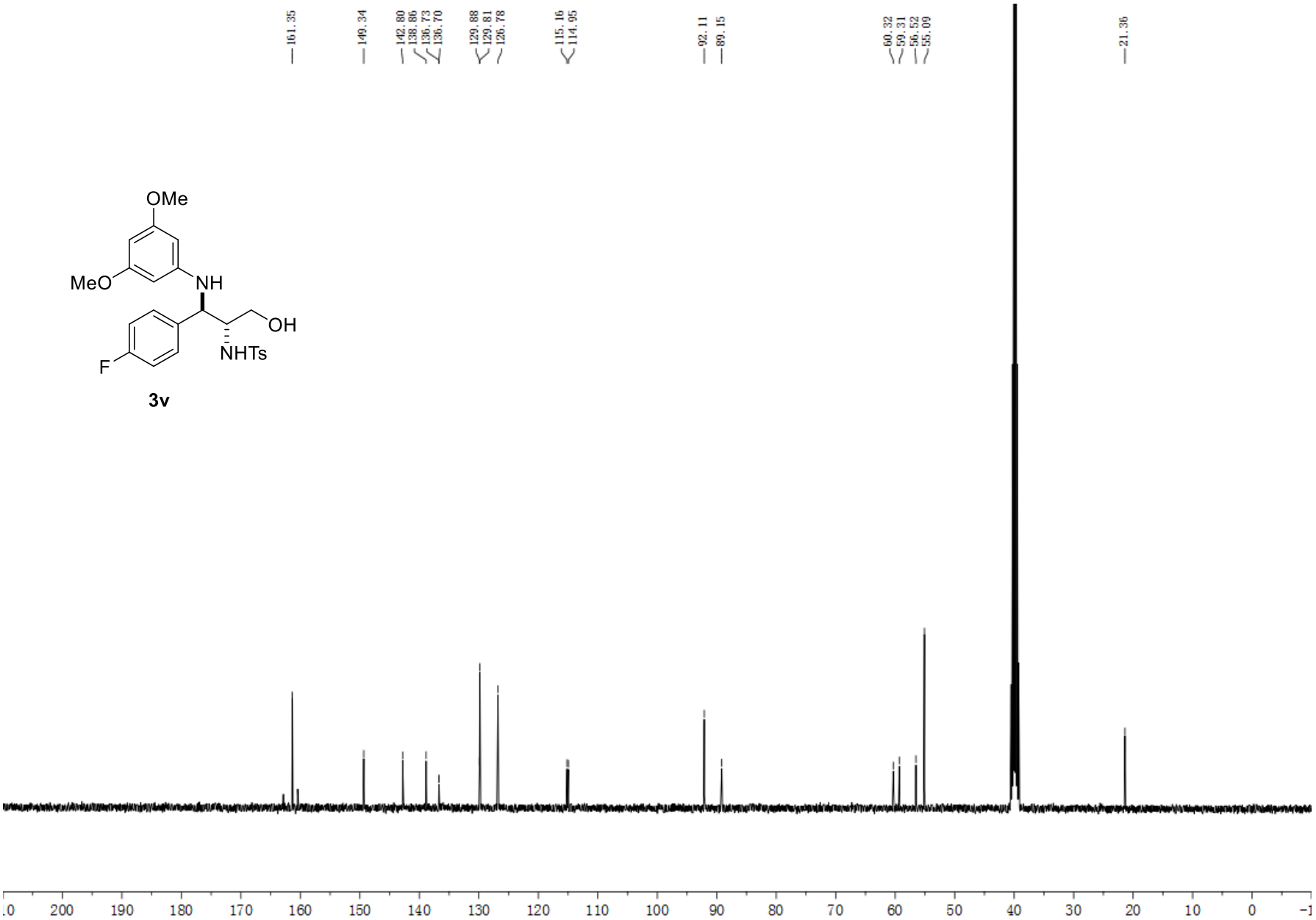
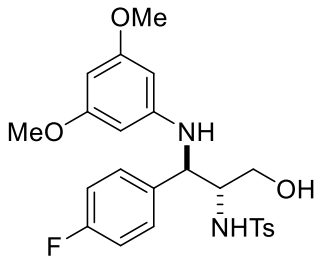
148.14
144.03
141.45
137.14
134.79
130.13
130.00
127.94
126.97
126.90
125.06
92.34
90.06
62.02
59.01
57.61
55.06
21.54
OMe
MeO
NH
OH
NHTs
Cl
3u
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

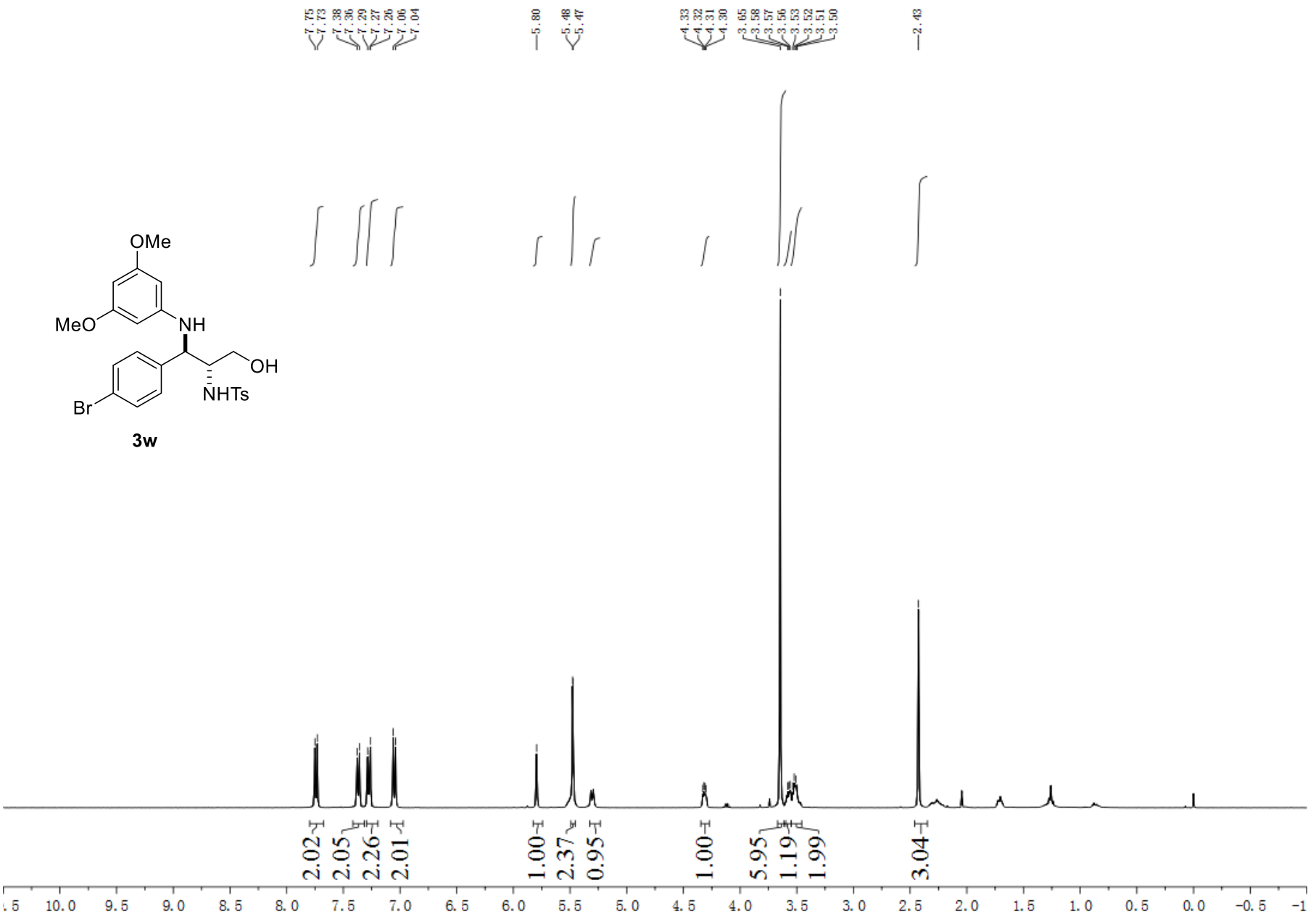

OMe
MeO
NH
OH
NHTs
F
3v
7.55 7.53 7.29 7.27 7.27 7.26 7.26 7.25 7.24 7.24 7.05 7.02 7.00
5.92 5.90 5.68 5.67 5.67 5.53 5.52
4.88 4.86 4.85
4.42 4.41
3.57 3.46 3.44 3.43 3.42 3.41 3.39 3.39 3.30 3.29 3.28 3.27 3.25 3.18 3.16 3.15 3.14 3.12 2.35
2.35 4.01 2.05 1.00 1.02 1.98 1.02 1.01 6.03 1.09 1.05 1.01 3.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1

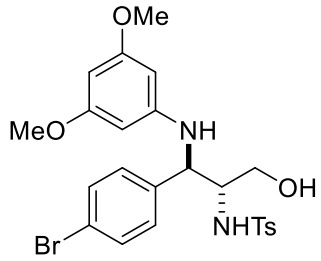

161.35
149.34
142.80
138.86
136.73
136.70
129.88
129.81
126.78
115.16
114.95
92.11
89.15
60.32
59.31
56.52
55.09
21.36
OMe
MeO
NH
OH
NHTs
F
3v
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


OMe
MeO
NH
OH
NHTs
F

3v

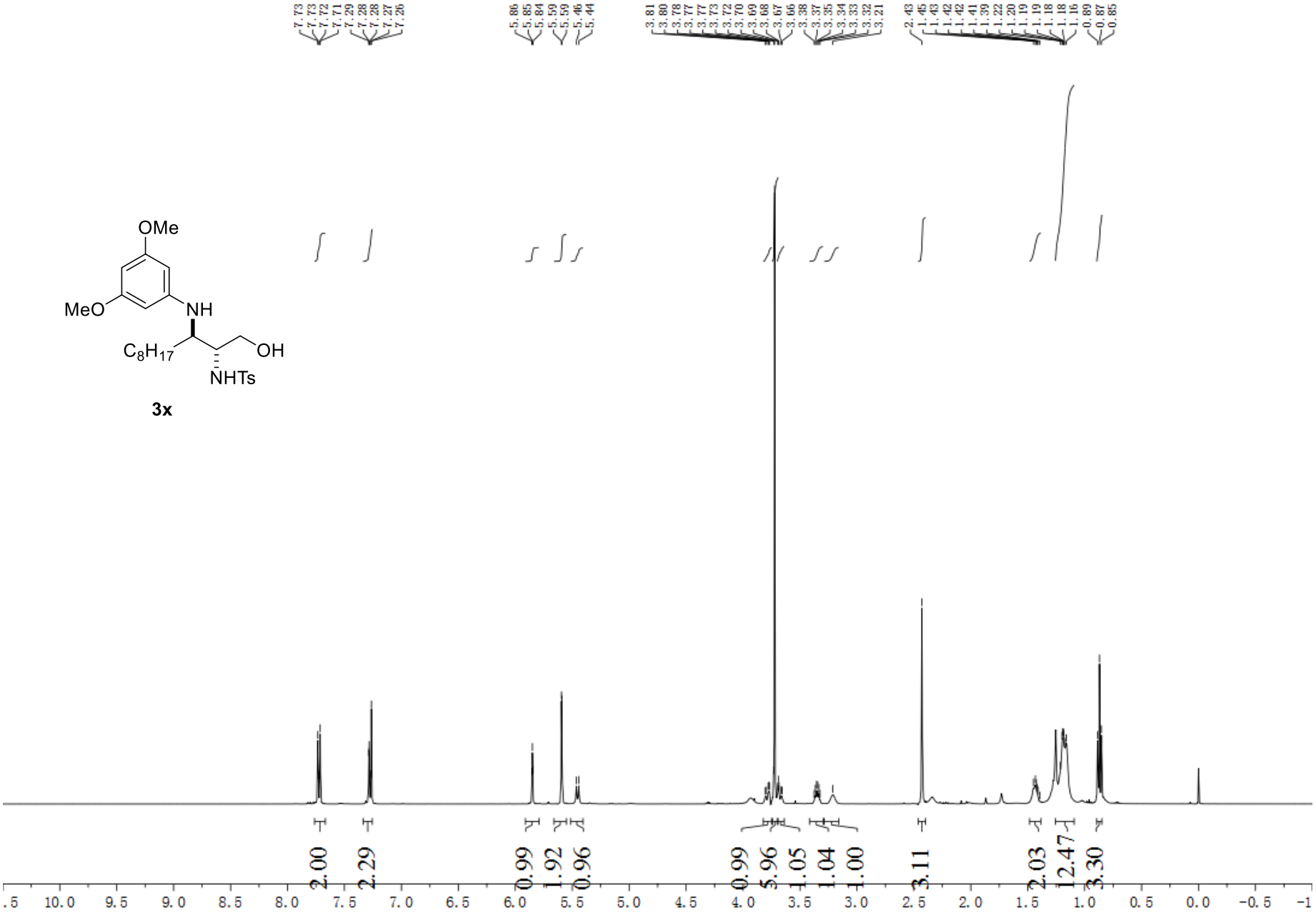
113.09
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210

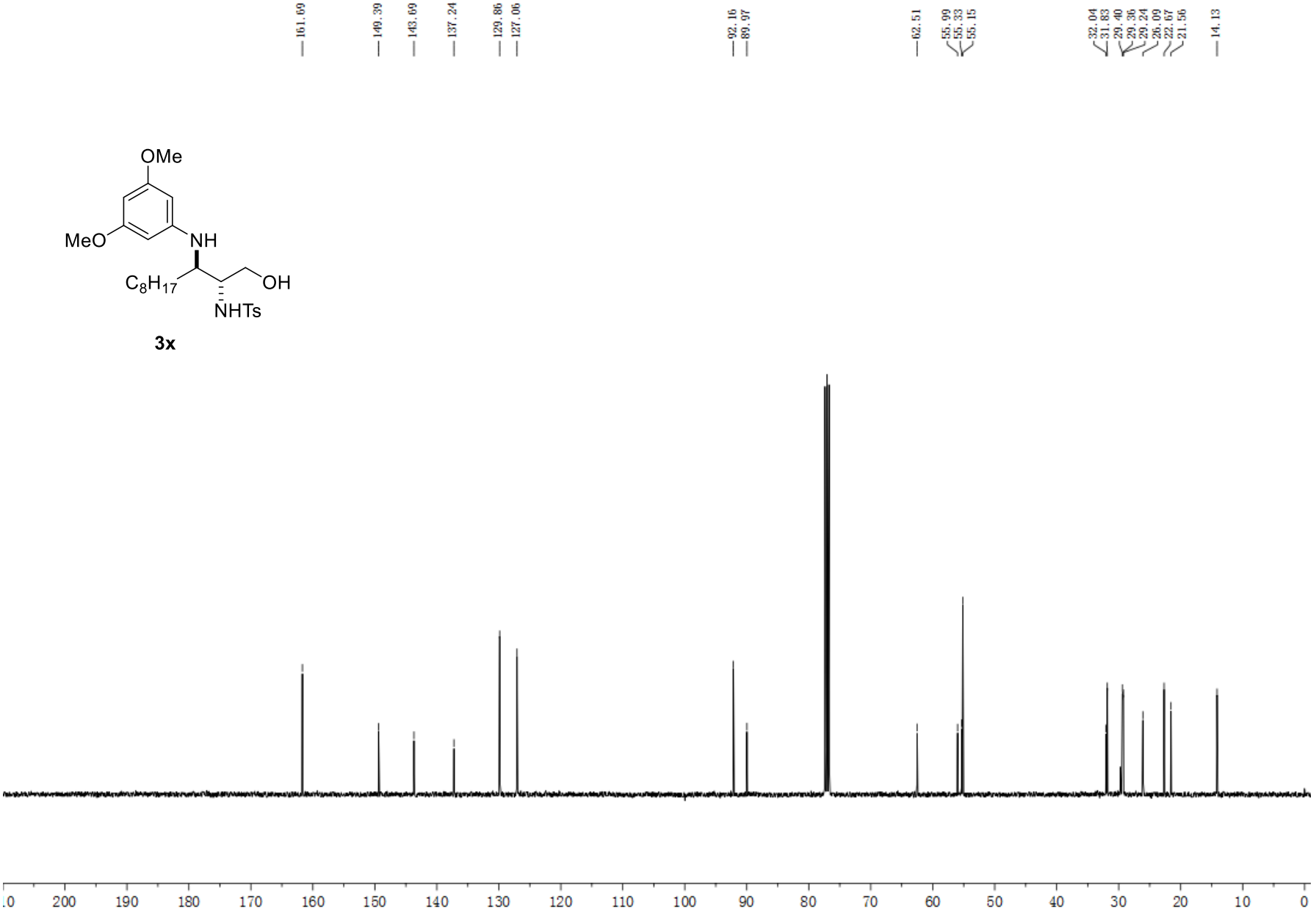

7.75
7.73
7.38
7.36
7.29
7.27
7.26
7.06
7.04
5.80
5.48
5.47
4.33
4.32
4.31
4.30
3.65
3.58
3.57
3.56
3.53
3.52
3.51
3.50
2.43
OMe
MeO
NH
OH
NHTs
Br
3w
2.02
2.05
2.26
2.01
1.00
2.37
0.95
1.00
5.95
1.19
1.99
3.04

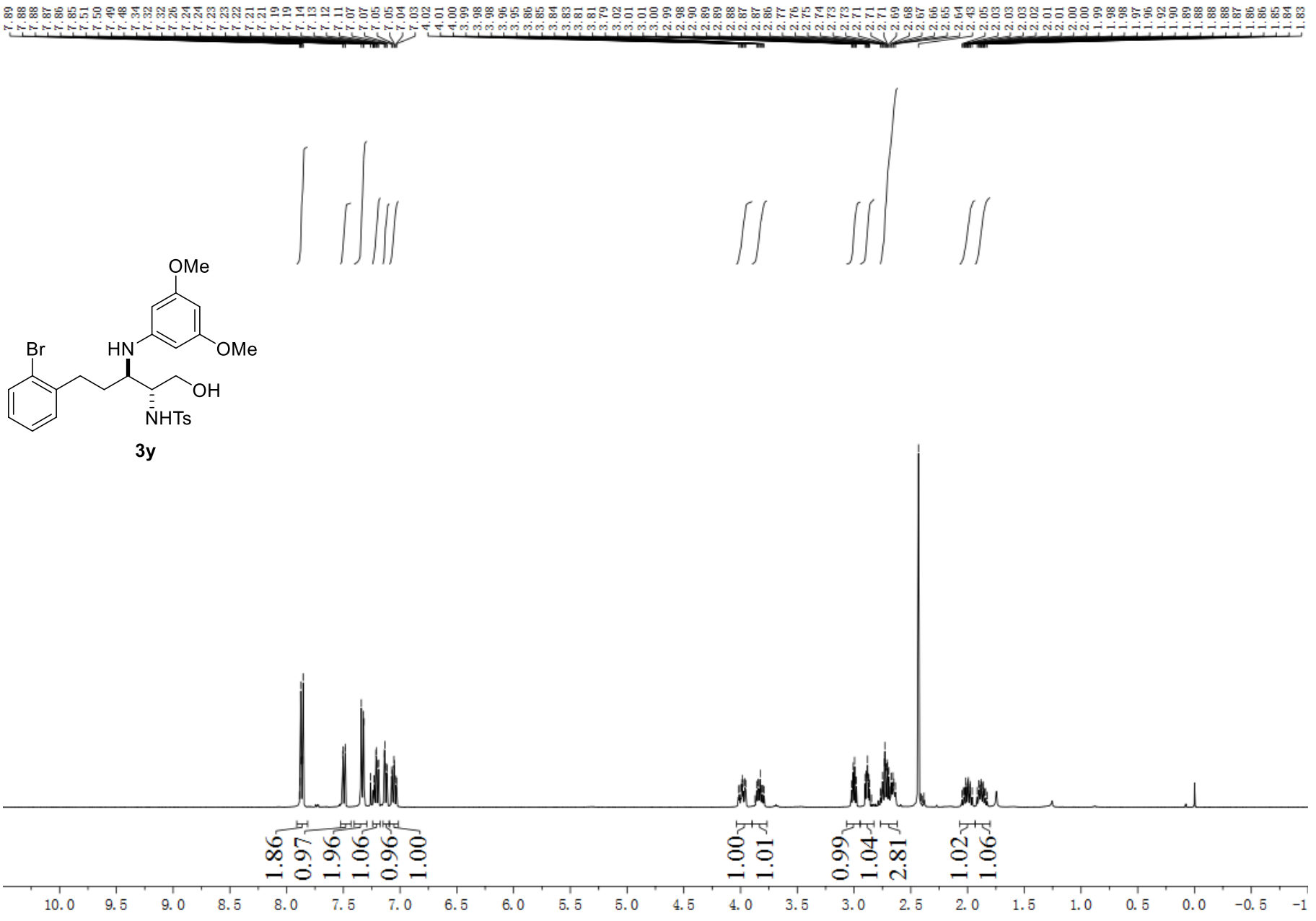

OMe
MeO
NH
OH
NHTs
Br

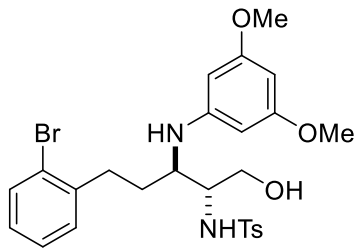
3w

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10


OMe
MeO
NH
C8H17
OH
NHTs
3x

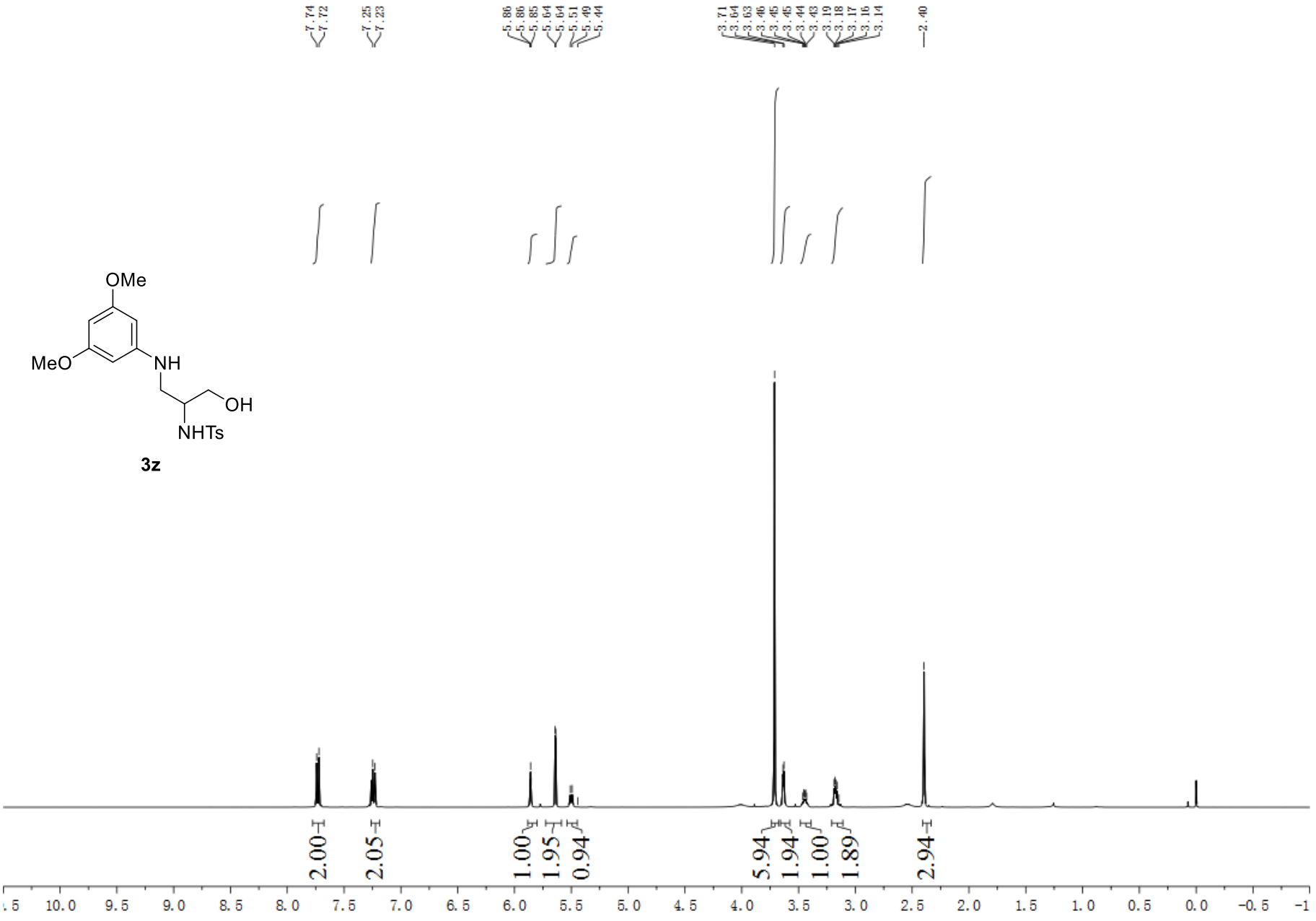

161.69
149.39
143.69
137.24
129.86
127.06
92.16
89.97
62.51
55.99
55.33
55.15
32.04
31.83
29.40
29.36
29.24
26.09
22.67
21.56
14.13
OMe
MeO
NH
C8H17
OH
NHTs
3x
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

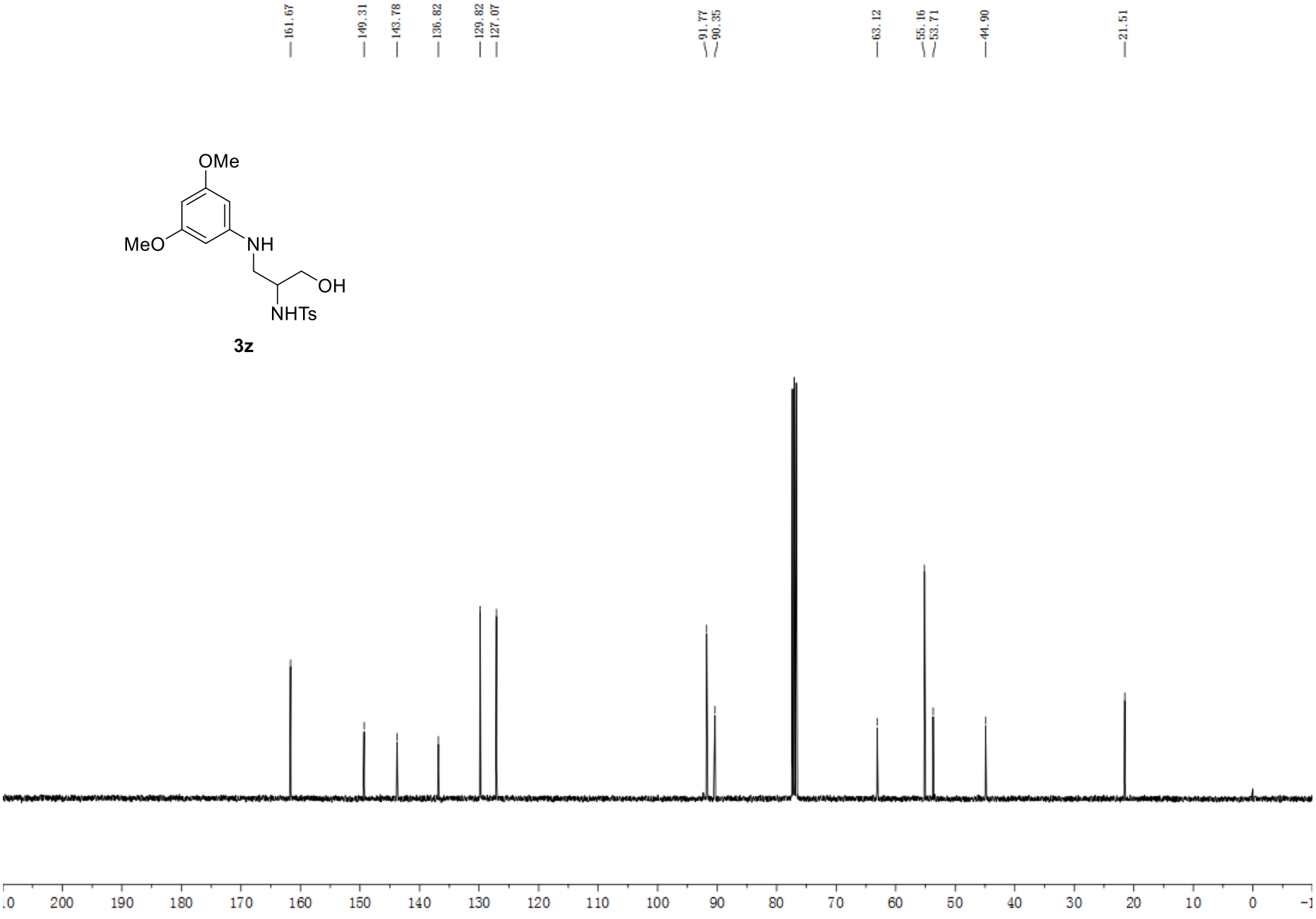

OMe
Br
HN
OMe
OH
NHTs
3y
1.86
0.97
1.96
1.06
0.96
1.00
1.00
1.01
0.99
1.04
2.81
1.02
1.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1


OMe
Br
HN
OMe
OH
NHTs

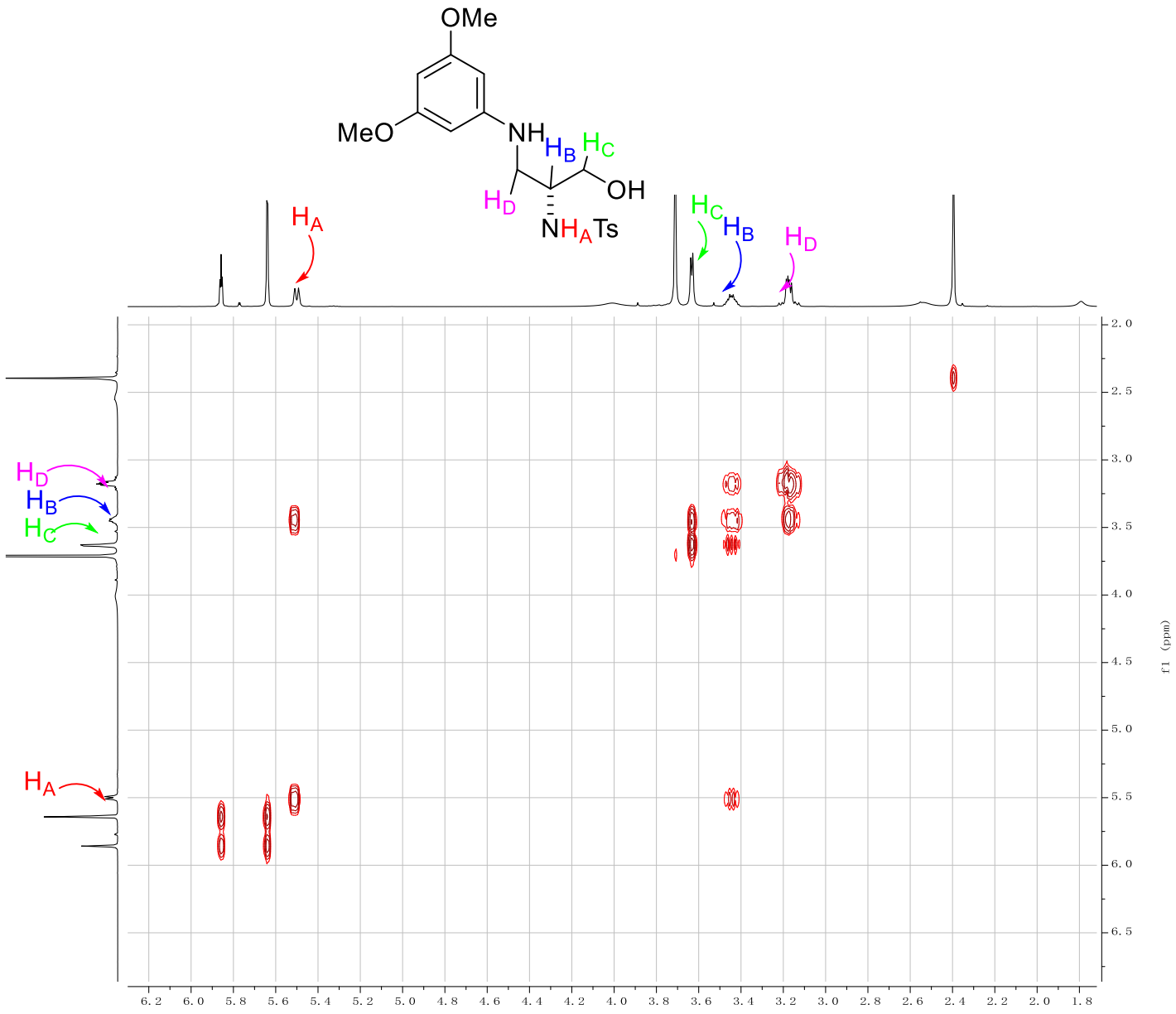
3y

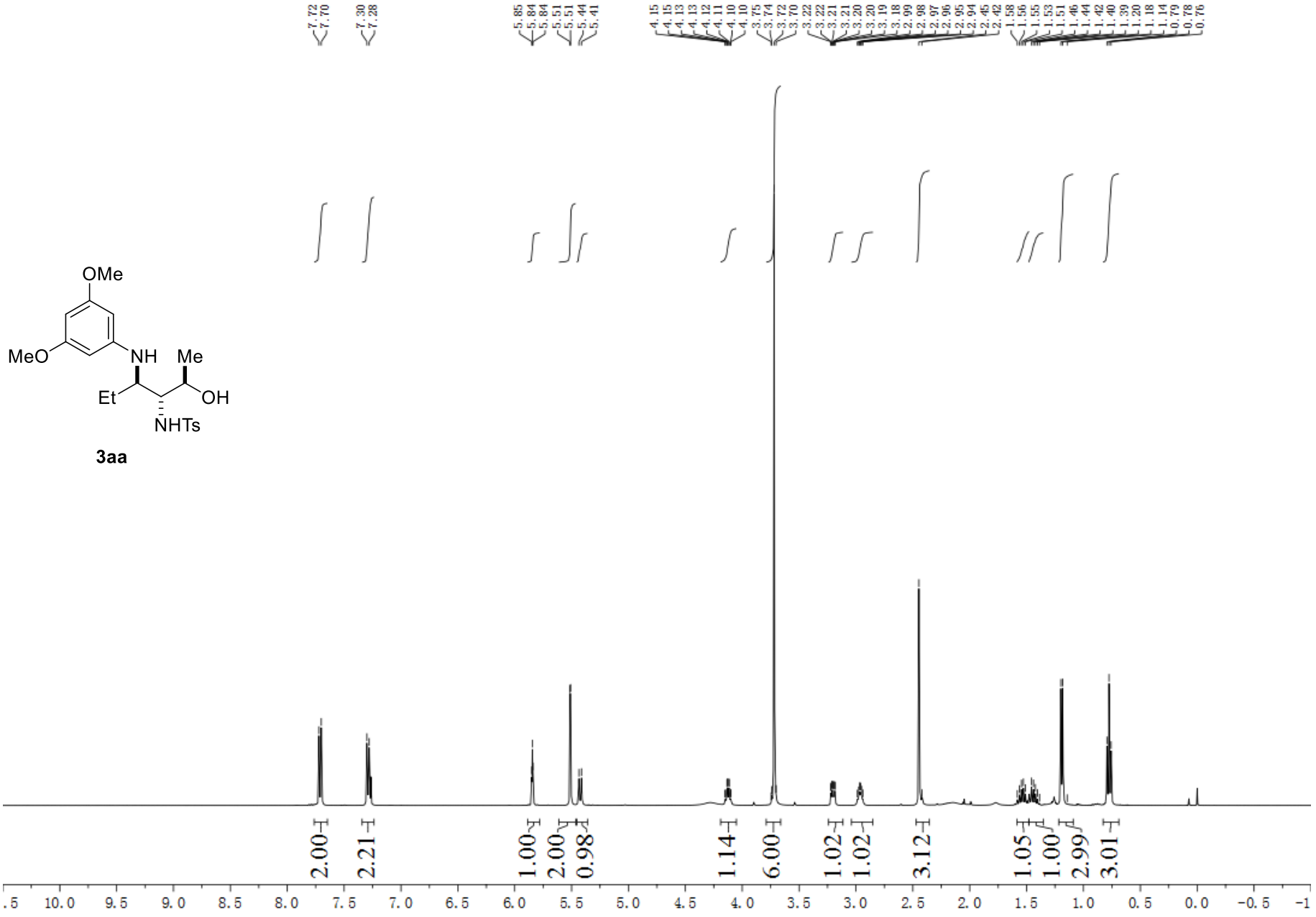
144.39
139.72
137.12
132.91
130.29
129.72
128.09
127.64
127.60
127.36
124.25
60.86
51.49
45.69
33.62
30.36
21.64
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.74
7.72
7.25
7.23
5.86
5.86
5.85
5.64
5.64
5.51
5.49
5.44
3.71
3.64
3.63
3.46
3.45
3.45
3.44
3.43
3.19
3.18
3.17
3.16
3.14
2.40
OMe
MeO
NH
OH
NHTs
3z
2.00
2.05
1.00
1.95
0.94
5.94
1.94
1.00
1.89
2.94
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1

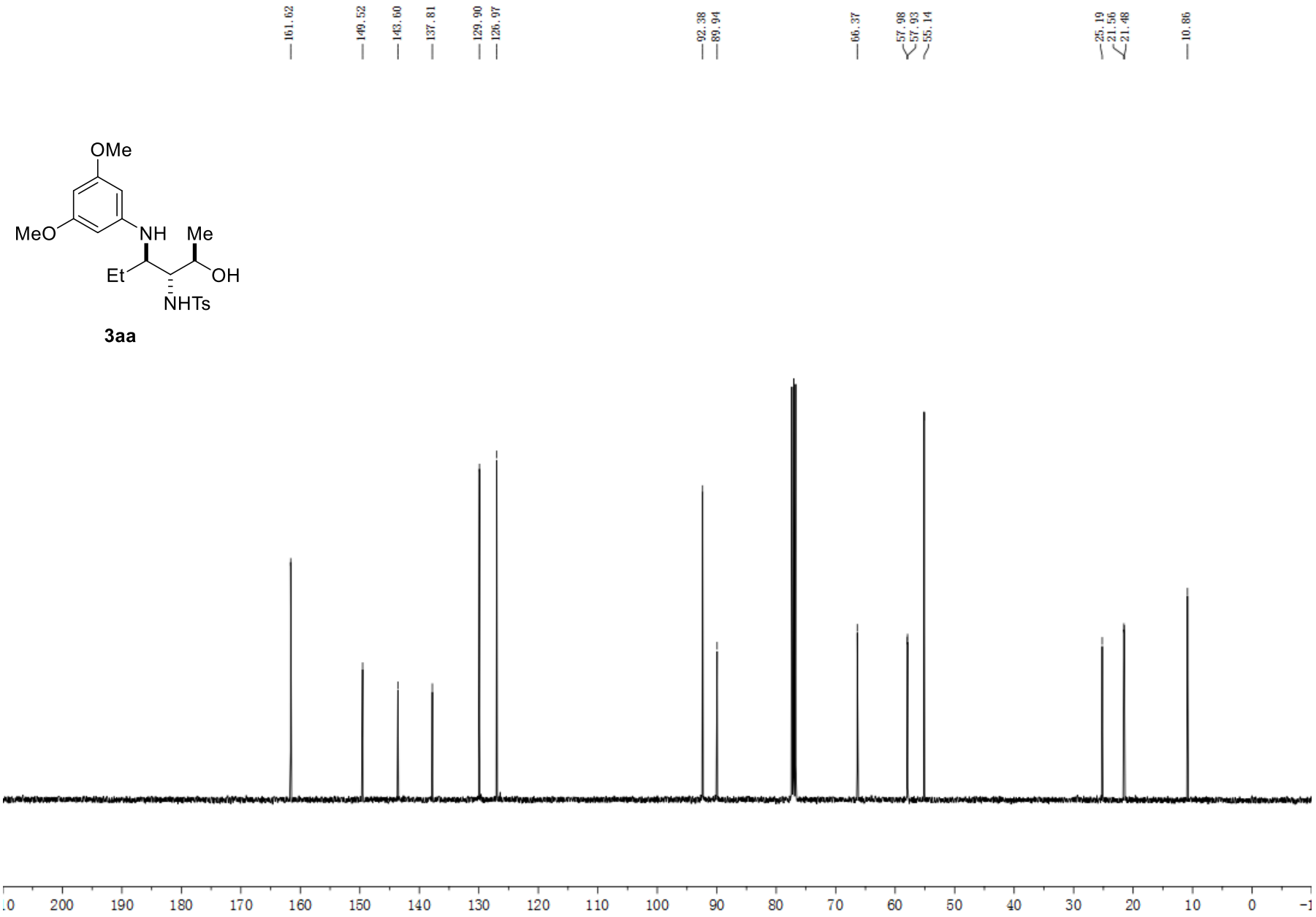

161.67
149.31
143.78
136.82
129.82
127.07
91.77
90.35
63.12
55.16
53.71
44.90
21.51
OMe
MeO
NH
OH
NHTs
3z
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

COSY of 3z

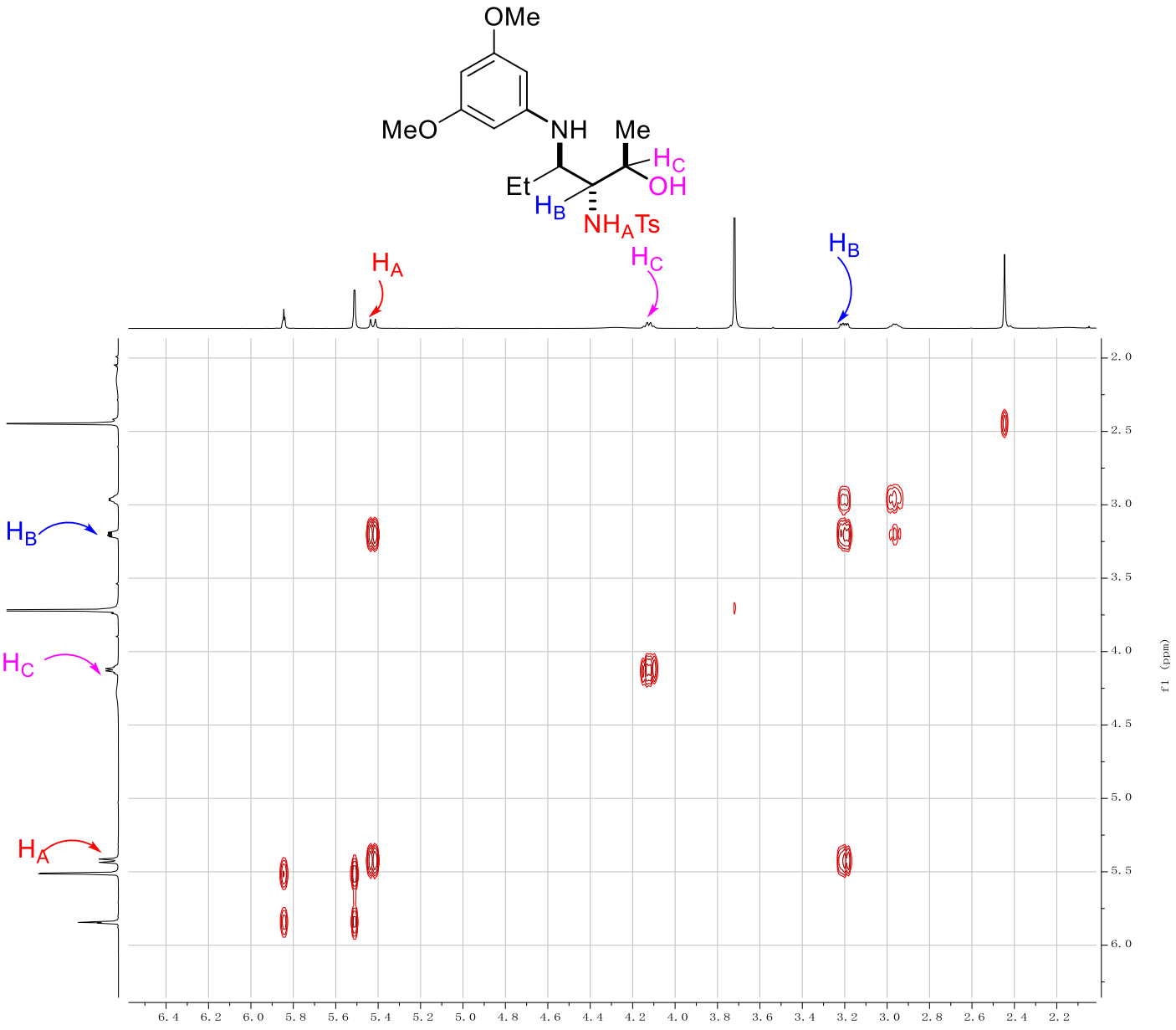


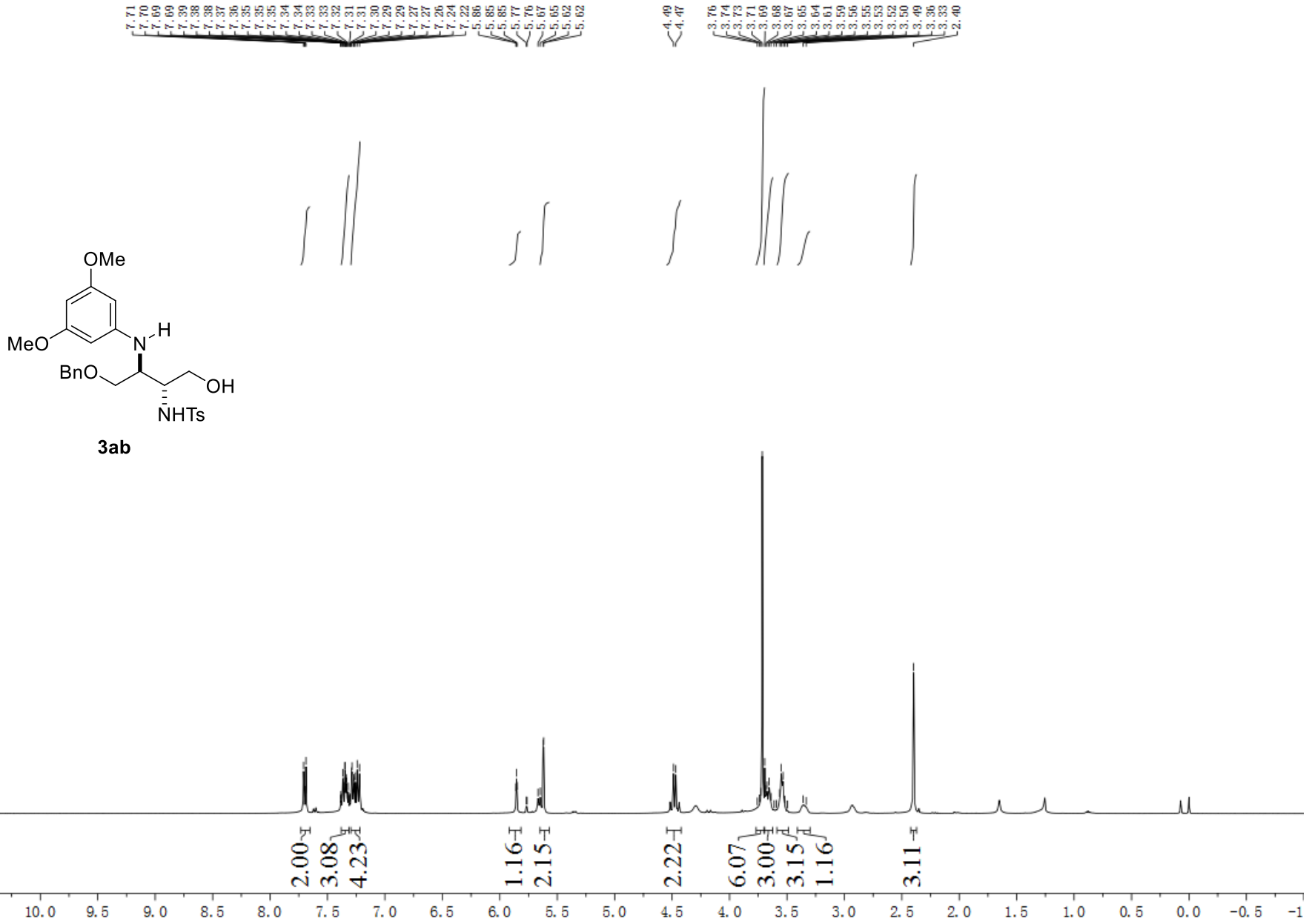

OMe
MeO
NH
Me
Et
OH
NHTs
7.72
7.70
7.30
7.28
5.85
5.84
5.84
5.51
5.51
5.44
5.41
4.15
4.15
4.13
4.13
4.12
4.11
4.10
4.10
3.75
3.74
3.72
3.70
3.22
3.22
3.21
3.21
3.20
3.20
3.19
3.18
2.99
2.98
2.97
2.96
2.95
2.94
2.45
2.42
1.58
1.56
1.55
1.53
1.51
1.46
1.44
1.42
1.40
1.39
1.20
1.18
1.14
0.79
0.78
0.76
2.00
2.21
1.00
2.00
0.98
1.14
6.00
1.02
1.02
3.12
1.05
1.00
2.99
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

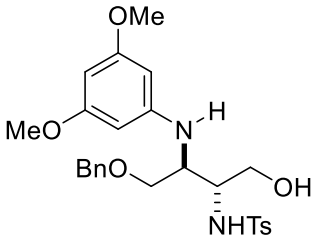
3aa


161.62
149.52
143.60
137.81
129.90
126.97
92.38
89.94
66.37
57.98
57.93
55.14
25.19
21.56
21.48
10.86
OMe
MeO
NH
Me
Et
OH
NHTs
3aa
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

COSY of 3aa

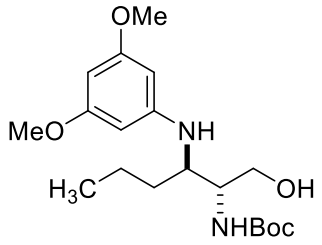

OMe
MeO
NH
Me
Et
H_C
OH
H_B
NH_ATs
H_A
H_C
H_B
H_B
H_C
H_A
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
f1 (ppm)
6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2


7.71 7.70 7.69 7.69 7.39 7.38 7.38 7.37 7.36 7.35 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.31 7.31 7.30 7.29 7.29 7.27 7.27 7.26 7.24 7.22 5.86 5.85 5.85 5.77 5.76 5.67 5.65 5.62 5.62 4.49 4.47 3.76 3.74 3.73 3.71 3.69 3.68 3.67 3.65 3.64 3.61 3.59 3.56 3.55 3.53 3.52 3.50 3.49 3.36 3.33 2.40
OMe
MeO
N
H
BnO
OH
NHTs
3ab
2.00 3.08 4.23 1.16 2.15 2.22 6.07 3.00 3.15 1.16 3.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1

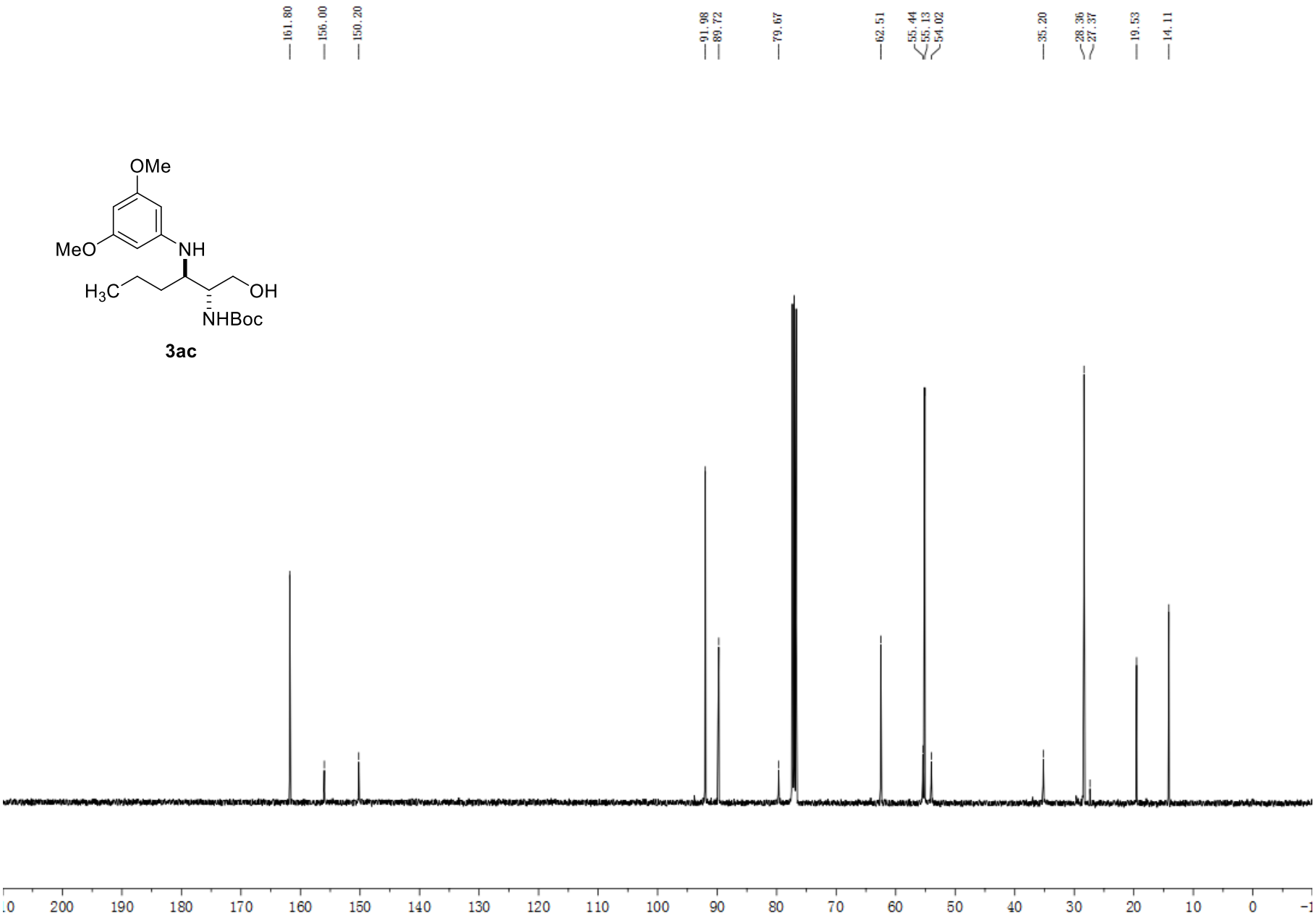

OMe
MeO
N
H
BnO
OH
NHTs

3ab

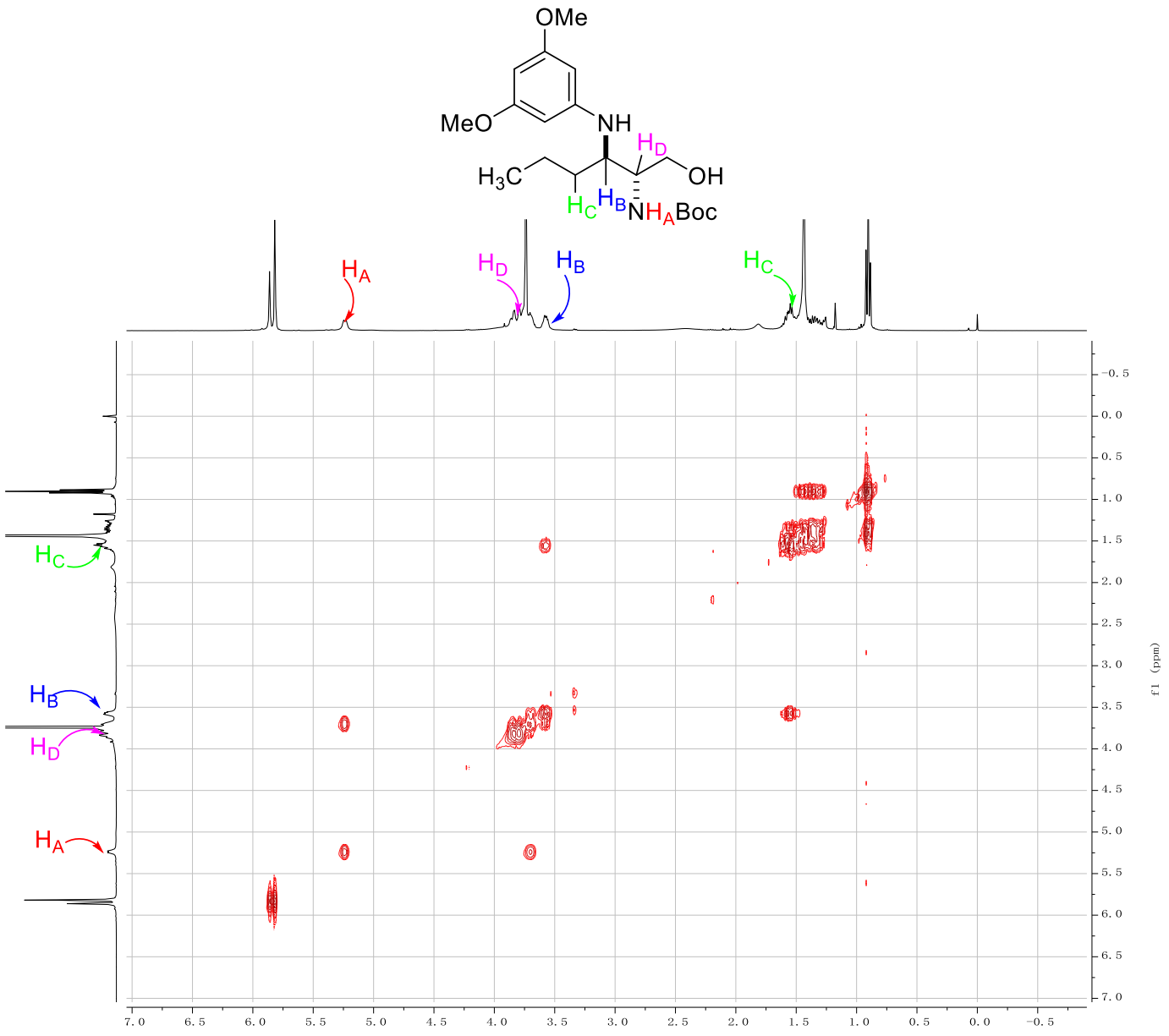
161.75
148.12
143.69
137.08
136.85
129.81
128.67
128.26
127.95
127.05
92.11
90.19
73.76
68.36
62.85
56.11
55.17
53.98
21.51
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

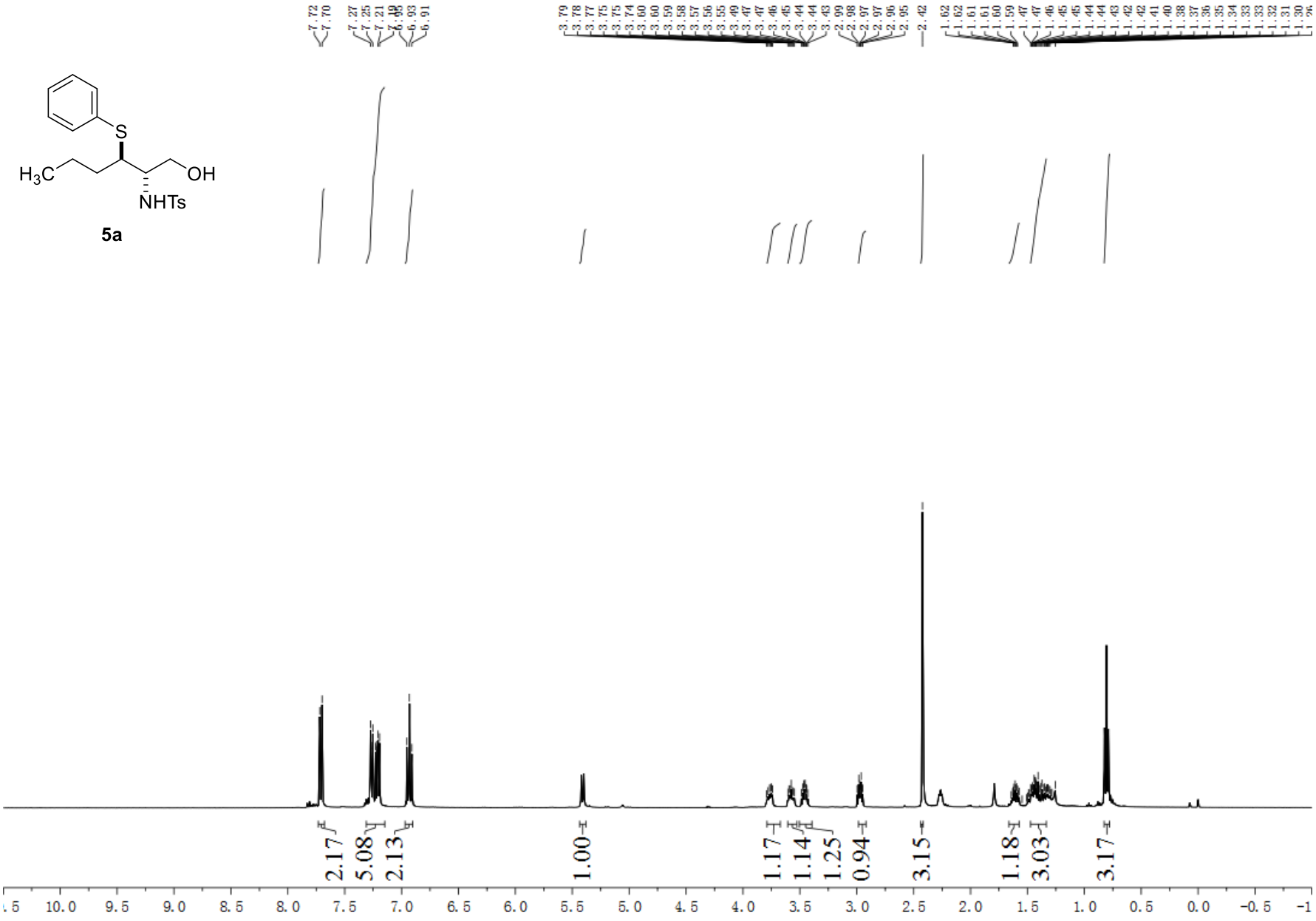


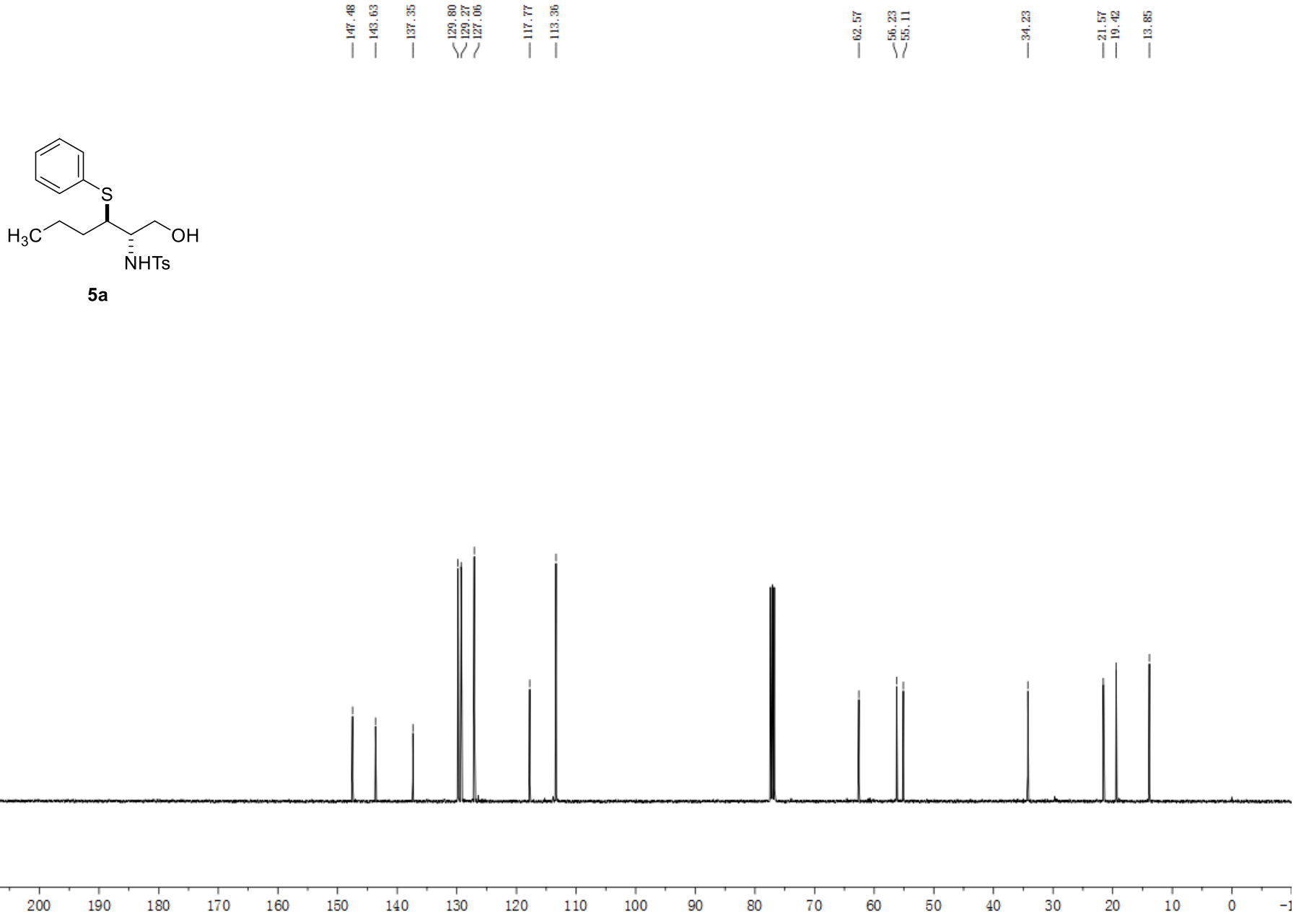
3ac

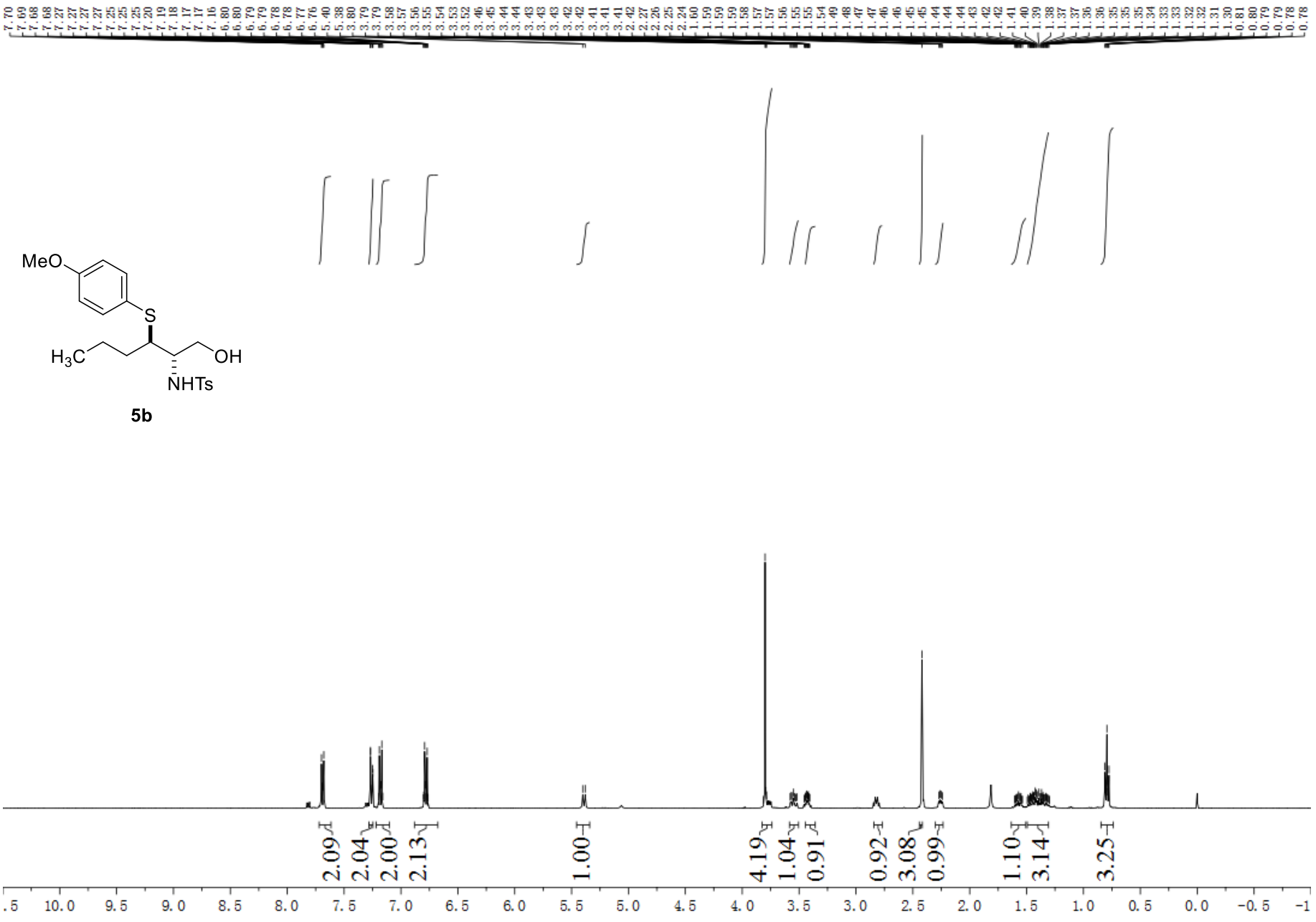

161.80
156.00
150.20
91.98
89.72
79.67
62.51
55.44
55.13
54.02
35.20
28.36
27.37
19.53
14.11
OMe
MeO
NH
H3C
OH
NHBoc
3ac
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

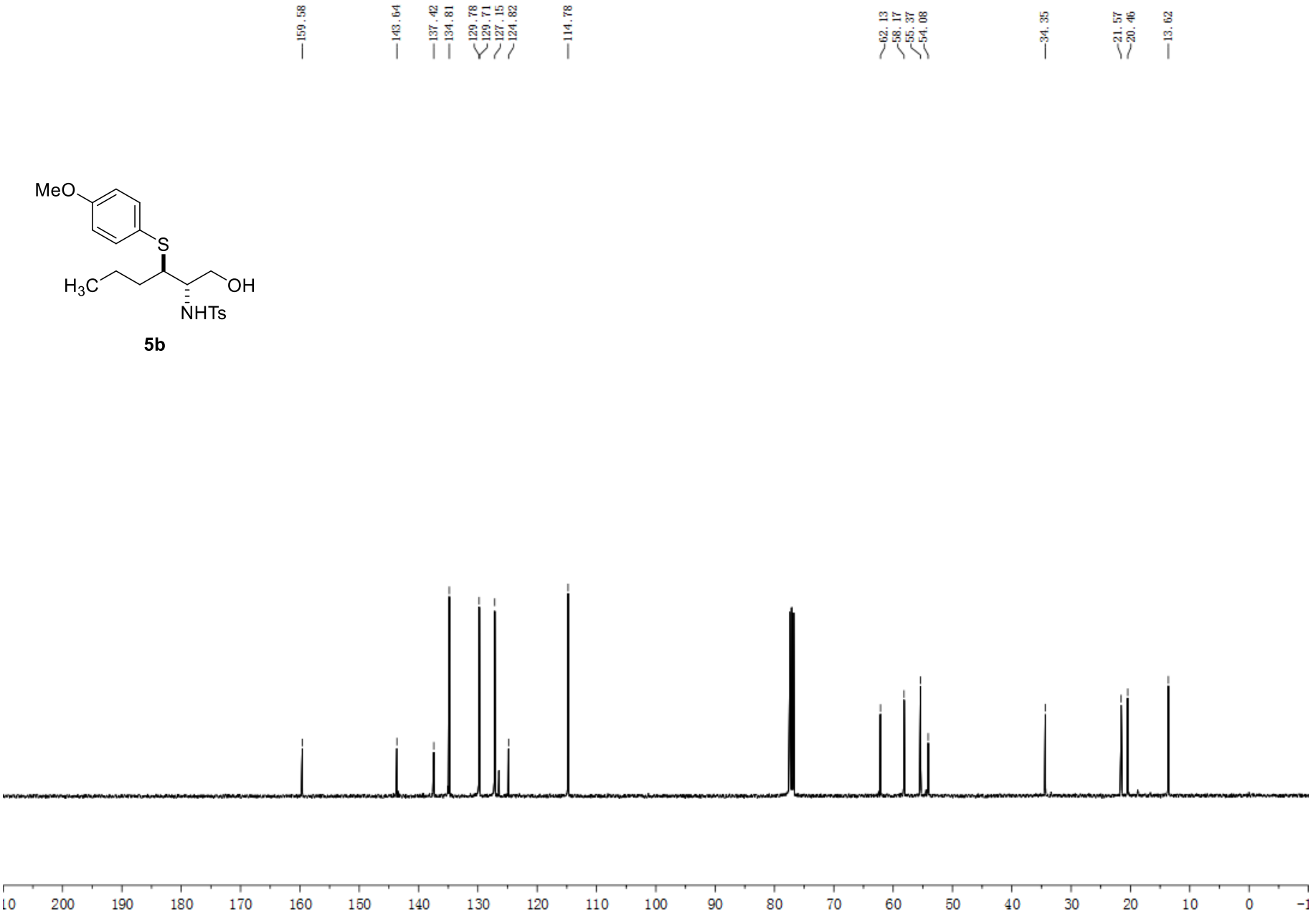
COSY of 3ac


OMe
MeO
NH
H_D
H_3C
OH
H_C H_B NH_ABoc
H_A
H_D
H_B
H_C
H_C
H_B
H_D
H_A
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
−0.5 0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0
f1 (ppm)

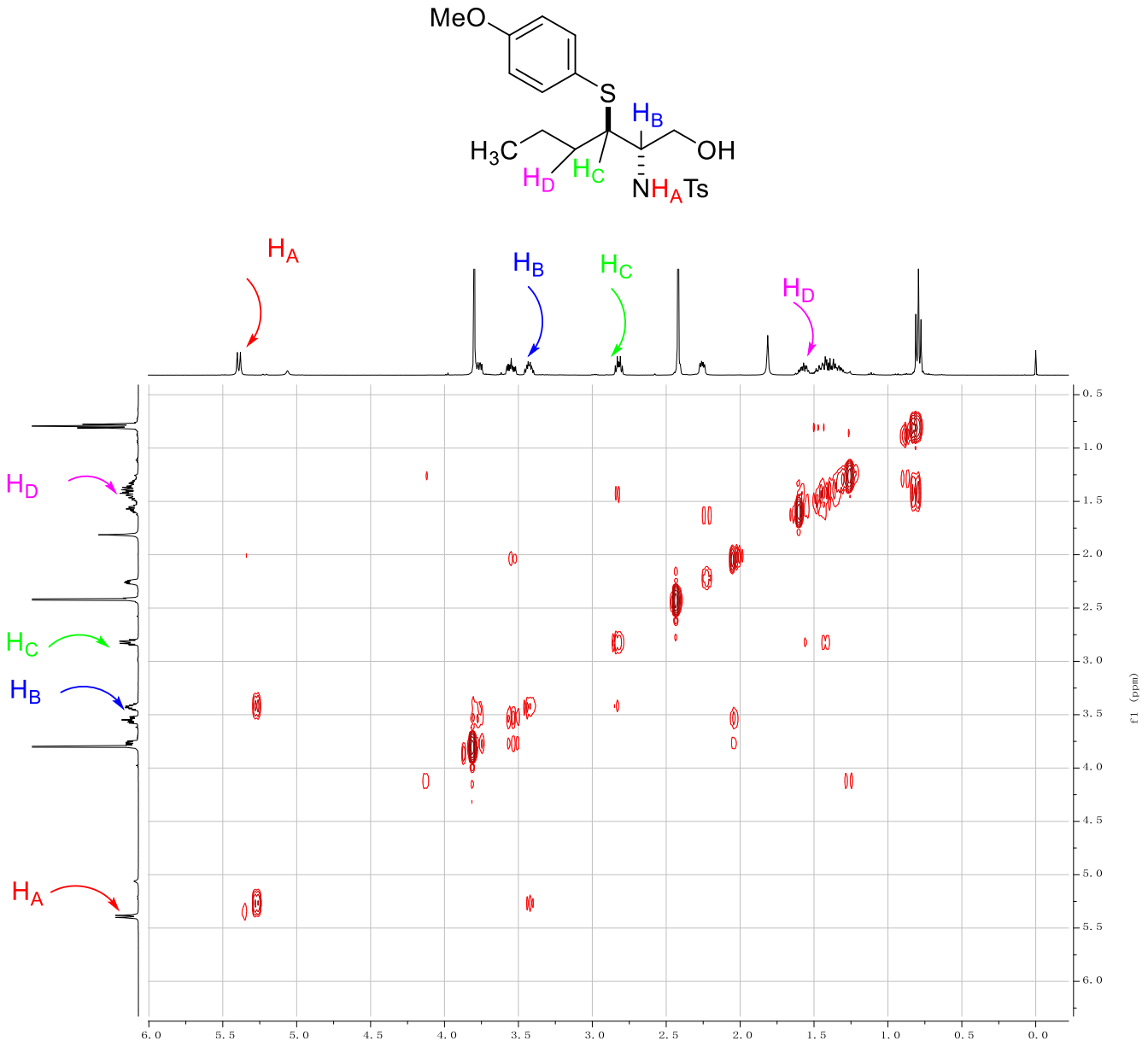

S
H3C
OH
NHTs
5a
7.72
7.70
7.27
7.25
7.21
6.93
6.91
3.79
3.78
3.77
3.75
3.75
3.74
3.60
3.59
3.58
3.57
3.56
3.55
3.49
3.47
3.47
3.46
3.45
3.44
3.44
3.43
2.99
2.98
2.97
2.97
2.96
2.95
2.42
1.62
1.62
1.61
1.61
1.60
1.59
1.47
1.47
1.46
1.45
1.45
1.44
1.44
1.43
1.42
1.42
1.41
1.40
1.38
1.37
1.36
1.35
1.34
1.33
1.33
1.32
1.31
1.30
2.17
5.08
2.13
1.00
1.17
1.14
1.25
0.94
3.15
1.18
3.03
3.17
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1

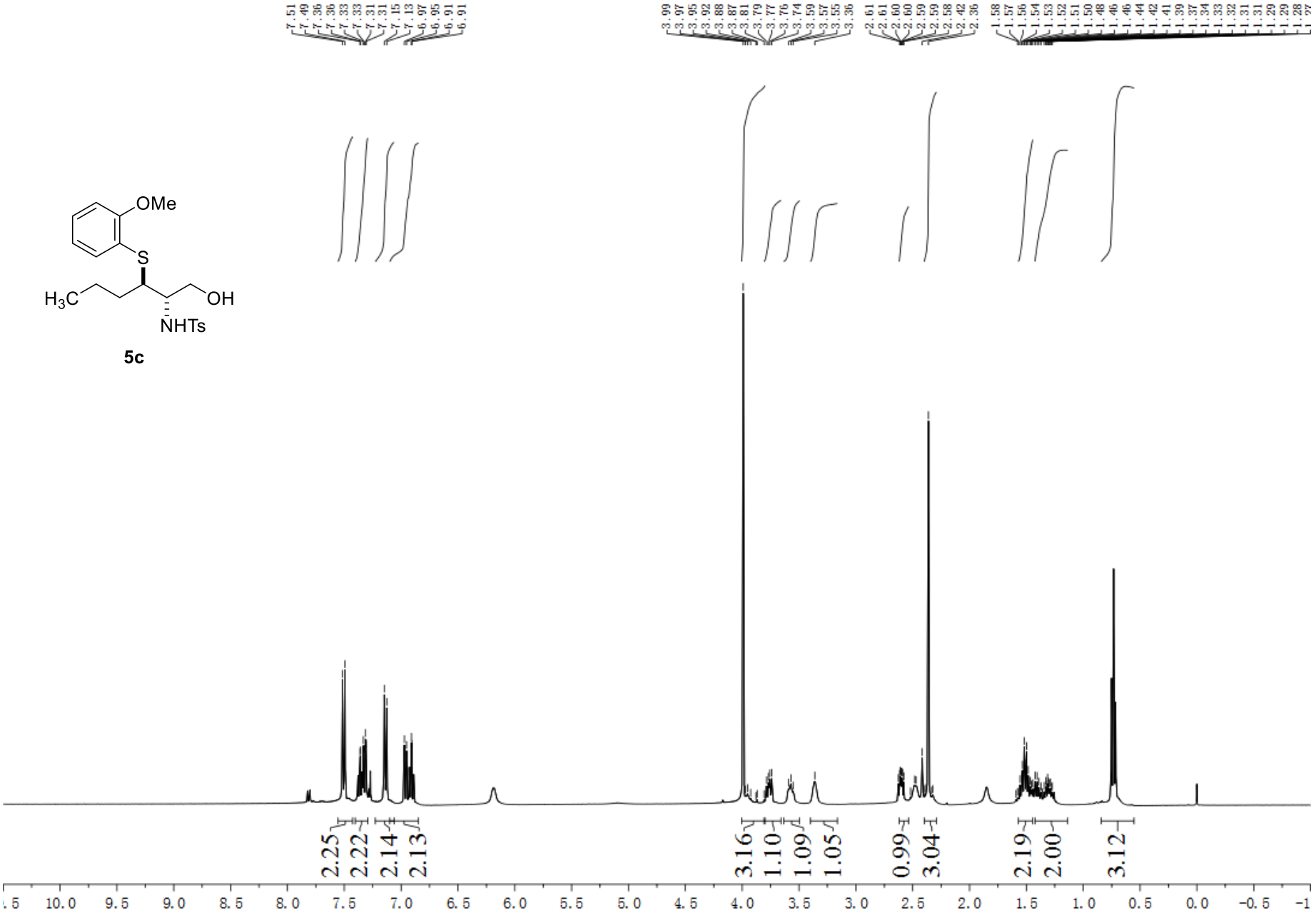

147.48
143.63
137.35
129.80
129.27
127.06
117.77
113.36
62.57
56.23
55.11
34.23
21.57
19.42
13.85
S
H3C
OH
NHTs
5a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

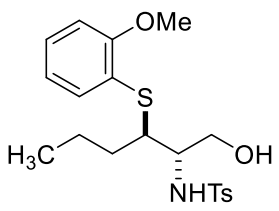

MeO
S
H3C
OH
NHTs
5b
2.09
2.04
2.00
2.13
1.00
4.19
1.04
0.91
0.92
3.08
0.99
1.10
3.14
3.25


159.58
143.64
137.42
134.81
129.78
129.71
127.15
124.82
114.78
62.13
58.17
55.37
54.08
34.35
21.57
20.46
13.62
MeO
S
H3C
OH
NHTs
5b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

COSY of 5b


MeO
S
H_B
H_3C
OH
H_D
H_C
NH_ATs
H_A
H_B
H_C
H_D
H_D
H_C
H_B
H_A
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


OMe
S
H3C
OH
NHTs
5c


OMe
S
H3C
OH
NHTs

5c

158.83
143.39
136.45
136.44
130.41
129.64
126.99
121.52
111.41
61.80
58.10
56.17
53.94
53.92
35.75
21.54
21.49
20.32
13.42
200
190
180
170
160
150
140
130
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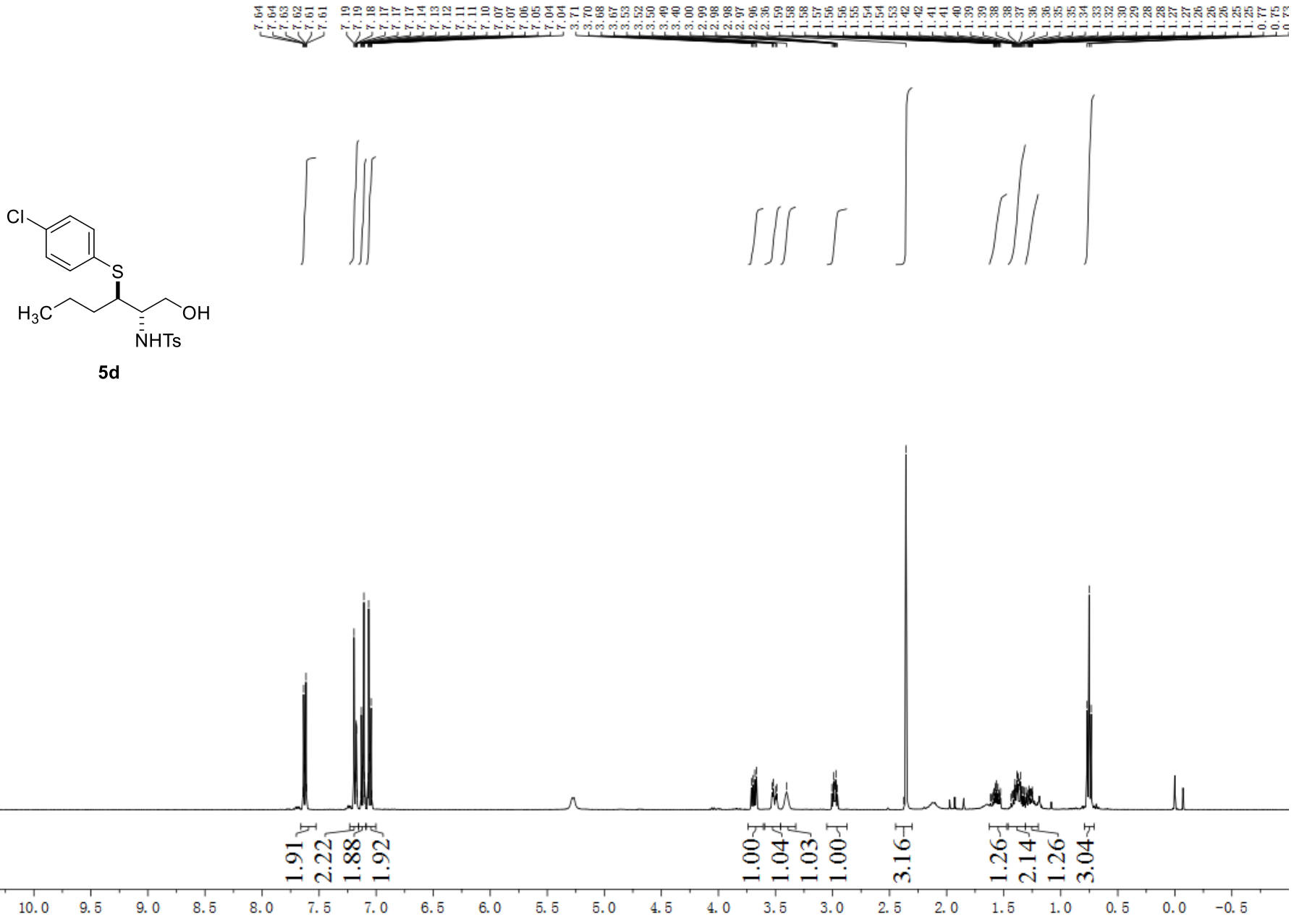
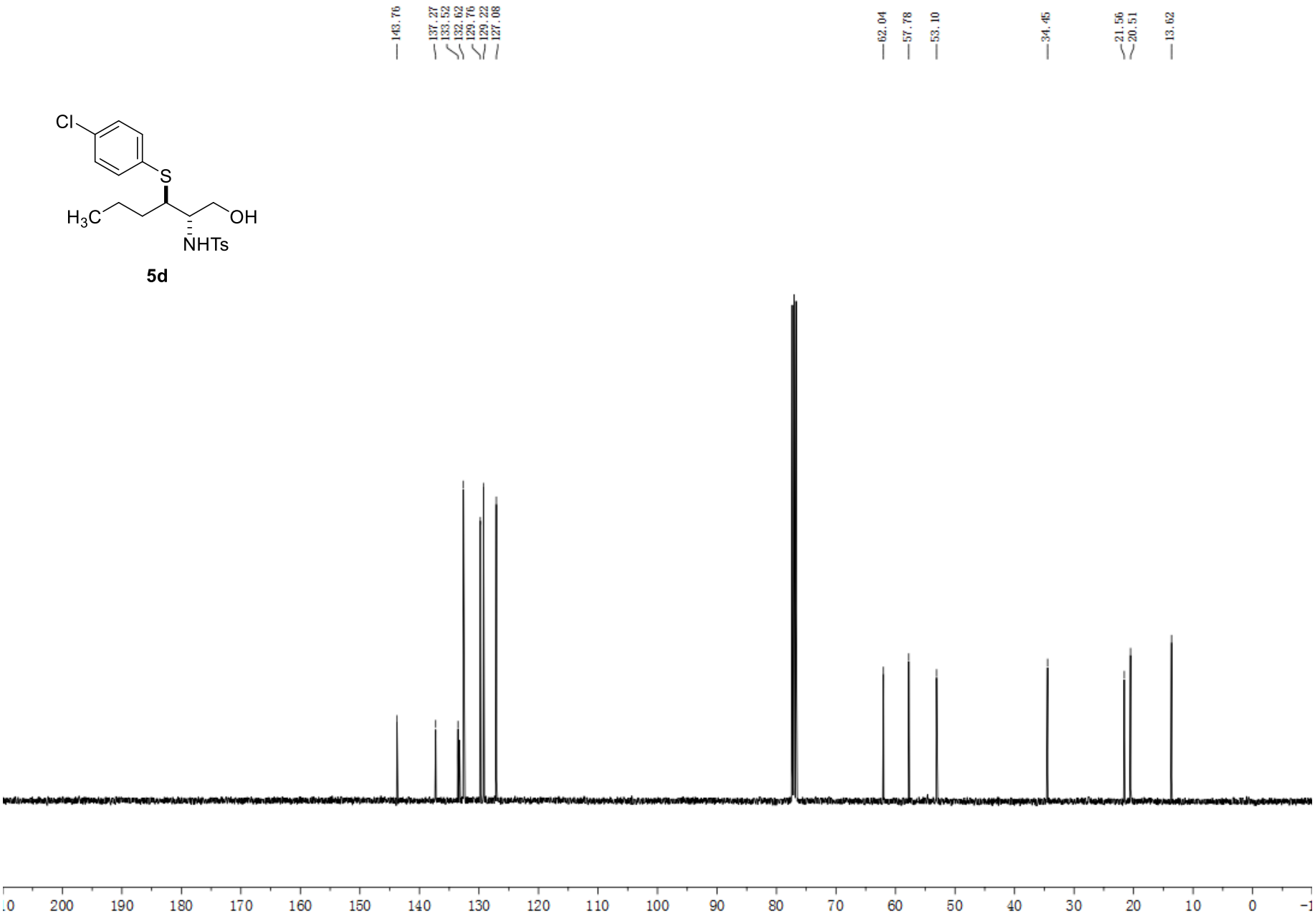
110
100
90
80
70
60
50
40
30
20
10
0


Cl
S
H3C
OH
NHTs
5d
1.91
2.22
1.88
1.92
1.00
1.04
1.03
1.00
3.16
1.26
2.14
1.26
3.04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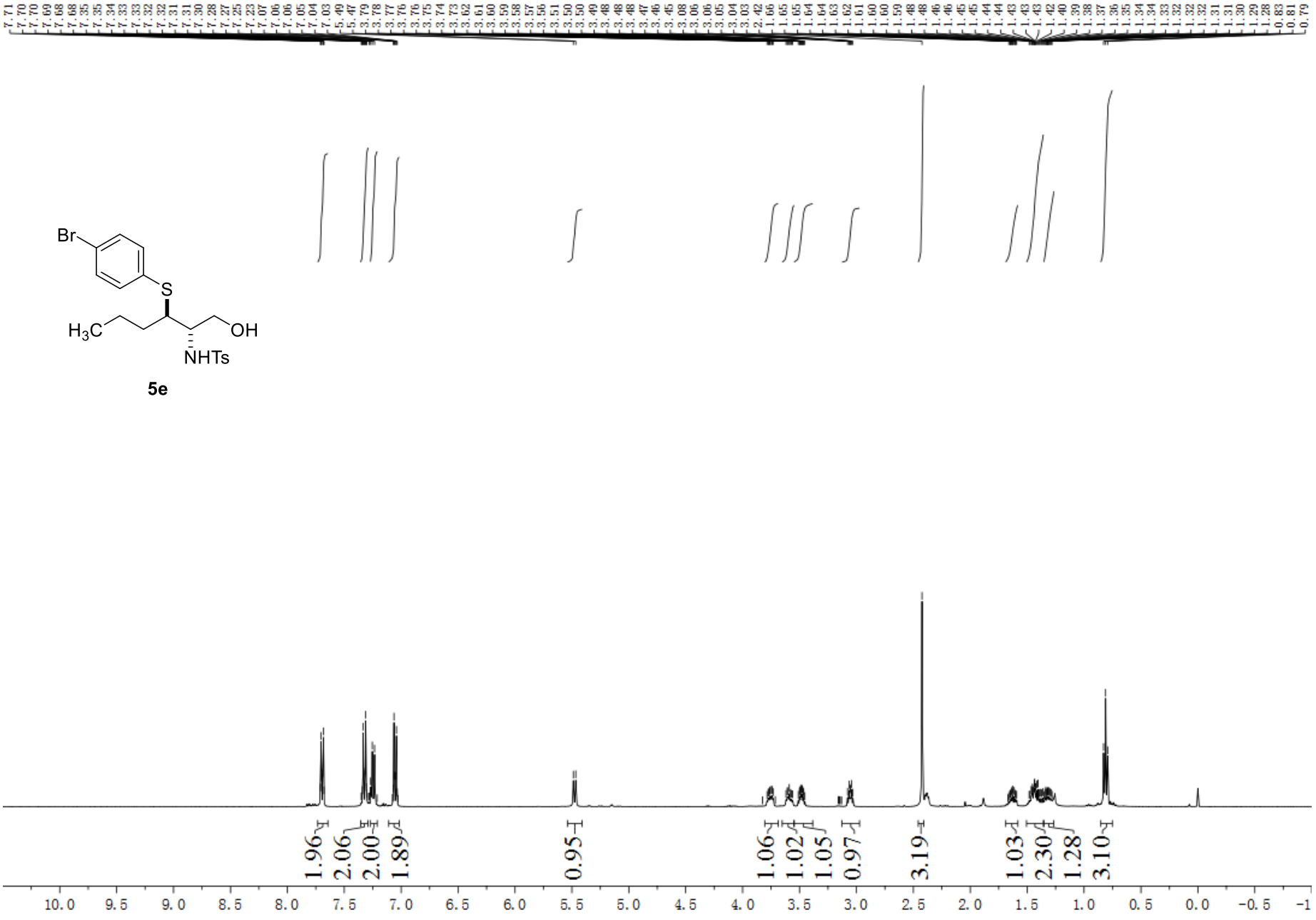
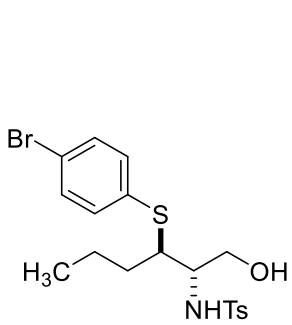
137.27
133.52
132.62
129.76
129.22
127.08
62.04
57.78
53.10
34.45
21.56
20.51
13.62
Cl
S
H3C
OH
NHTs
5d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.71 7.70 7.70 7.69 7.68 7.68 7.35 7.35 7.34 7.33 7.32 7.32 7.31 7.31 7.30 7.28 7.27 7.25 7.23 7.07 7.06 7.06 7.05 7.04 7.03 5.49 5.47 3.79 3.78 3.77 3.76 3.76 3.75 3.74 3.73 3.62 3.61 3.60 3.59 3.58 3.57 3.56 3.51 3.50 3.50 3.49 3.48 3.48 3.48 3.47 3.46 3.45 3.08 3.06 3.06 3.05 3.04 3.03 2.42 1.66 1.65 1.65 1.64 1.64 1.63 1.62 1.61 1.60 1.60 1.59 1.48 1.48 1.46 1.46 1.45 1.45 1.44 1.44 1.43 1.43 1.43 1.42 1.40 1.39 1.38 1.37 1.36 1.35 1.34 1.34 1.33 1.32 1.32 1.32 1.31 1.31 1.30 1.29 1.28 0.83 0.81 0.79
Br
S
H3C
OH
NHTs
5e
1.96
2.06
2.00
1.89
0.95
1.06
1.02
1.05
0.97
3.19
1.03
2.30
1.28
3.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1


Br
S
H3C
OH
NHTs

5e

143.74
137.32
134.39
132.73
132.11
129.76
127.08
121.10
62.01
57.82
52.77
34.44
21.59
20.51
13.65
200
190
180
170
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150
140
130
120
110
100
90
80
70
60
50
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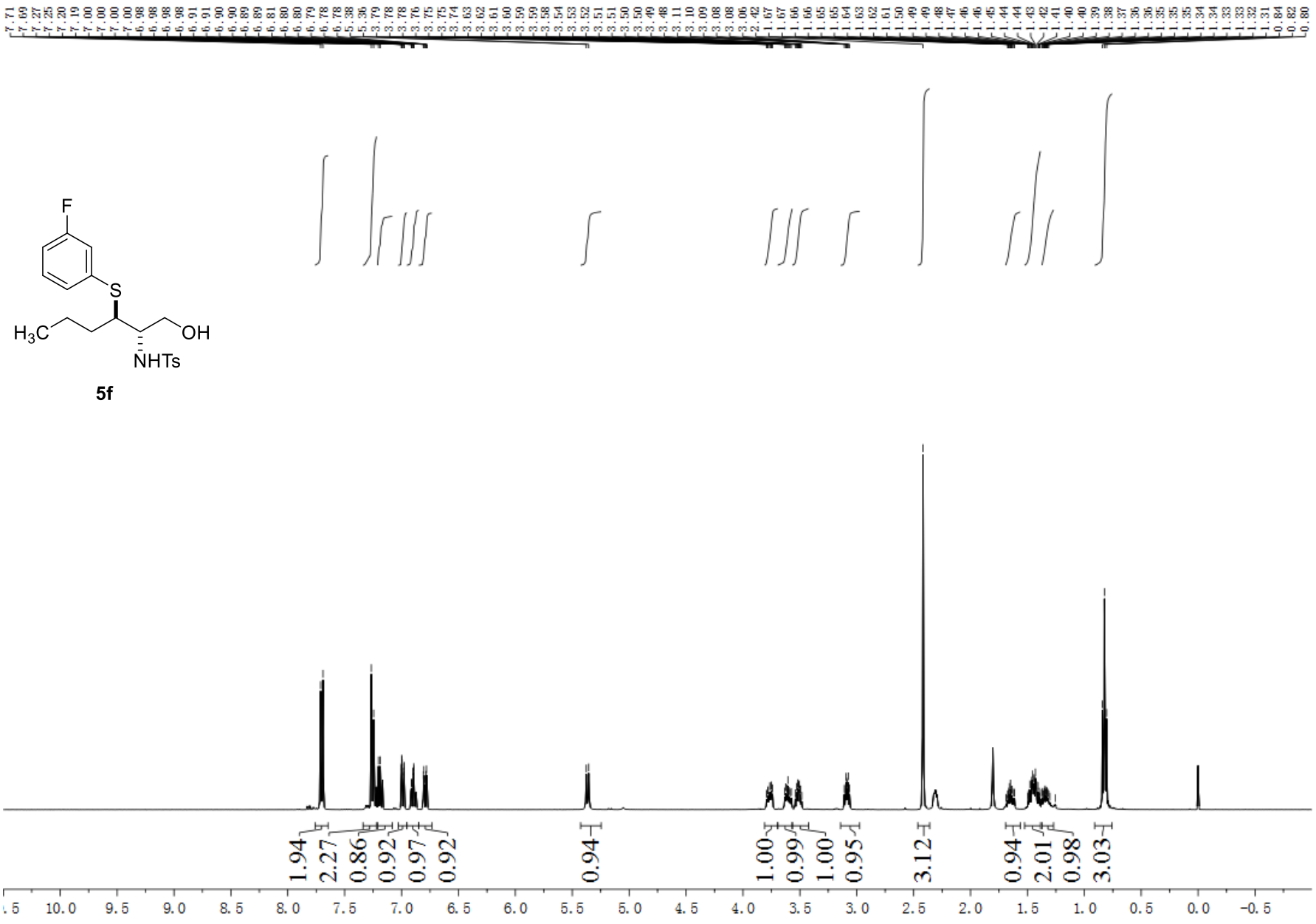
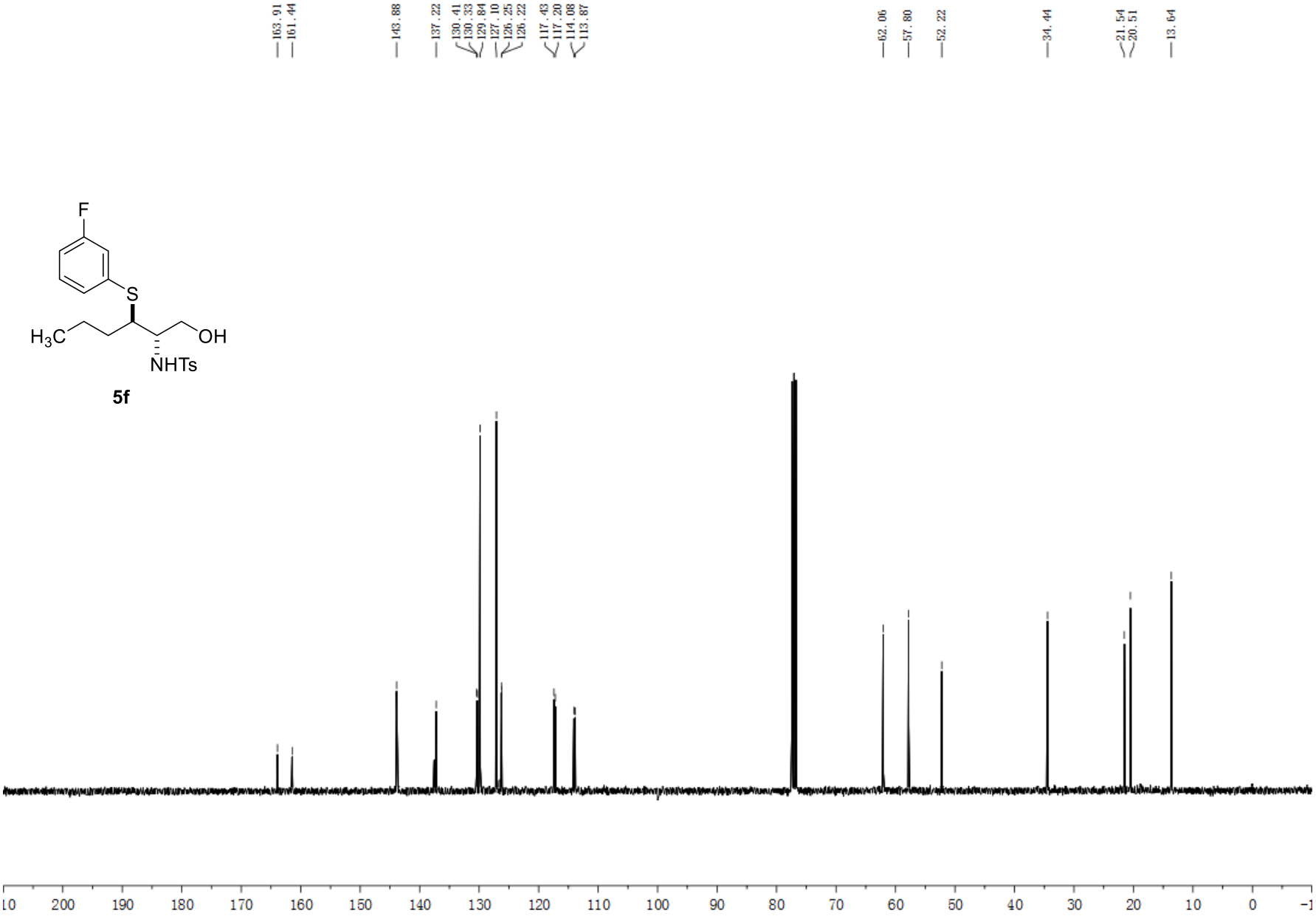
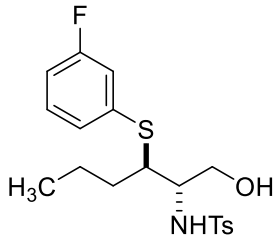
30
20
10
0

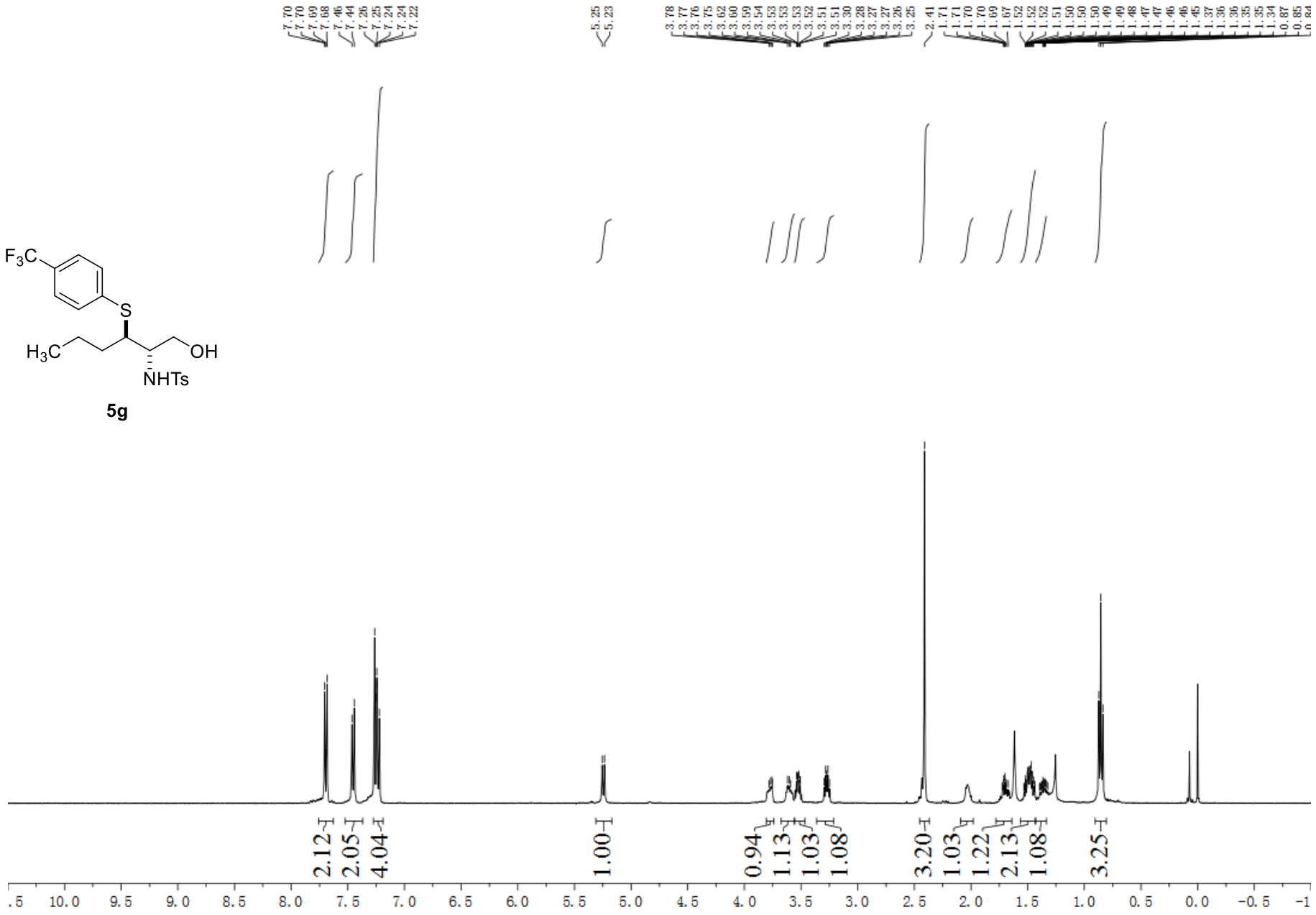

F
S
H3C
OH
NHTs
5f
1.94
2.27
0.86
0.92
0.97
0.92
0.94
1.00
0.99
1.00
0.95
3.12
0.94
2.01
0.98
3.03

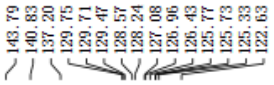

163.91
161.44
143.88
137.22
130.41
130.33
129.84
127.10
126.25
126.22
117.43
117.20
114.08
113.87
62.06
57.80
52.22
34.44
21.54
20.51
13.64
F
S
H3C
OH
NHTs
5f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


F
S
H3C
OH
NHTs

5f

-111.59
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210


F3C
S
H3C
OH
NHTs
5g
7.70
7.70
7.69
7.68
7.46
7.44
7.26
7.25
7.24
7.24
7.22
5.25
5.23
3.78
3.77
3.76
3.75
3.62
3.60
3.59
3.54
3.53
3.53
3.53
3.52
3.51
3.51
3.30
3.28
3.27
3.27
3.26
3.25
2.41
1.71
1.71
1.70
1.70
1.69
1.67
1.52
1.52
1.52
1.51
1.50
1.50
1.50
1.49
1.49
1.48
1.47
1.47
1.46
1.46
1.45
1.37
1.36
1.36
1.35
1.35
1.34
0.87
0.85
0.84
2.12
2.05
4.04
1.00
0.94
1.13
1.03
1.08
3.20
1.03
1.22
2.13
1.08
3.25
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5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140.83
137.20
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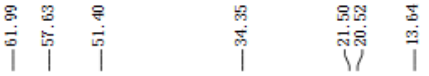
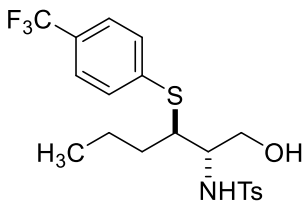
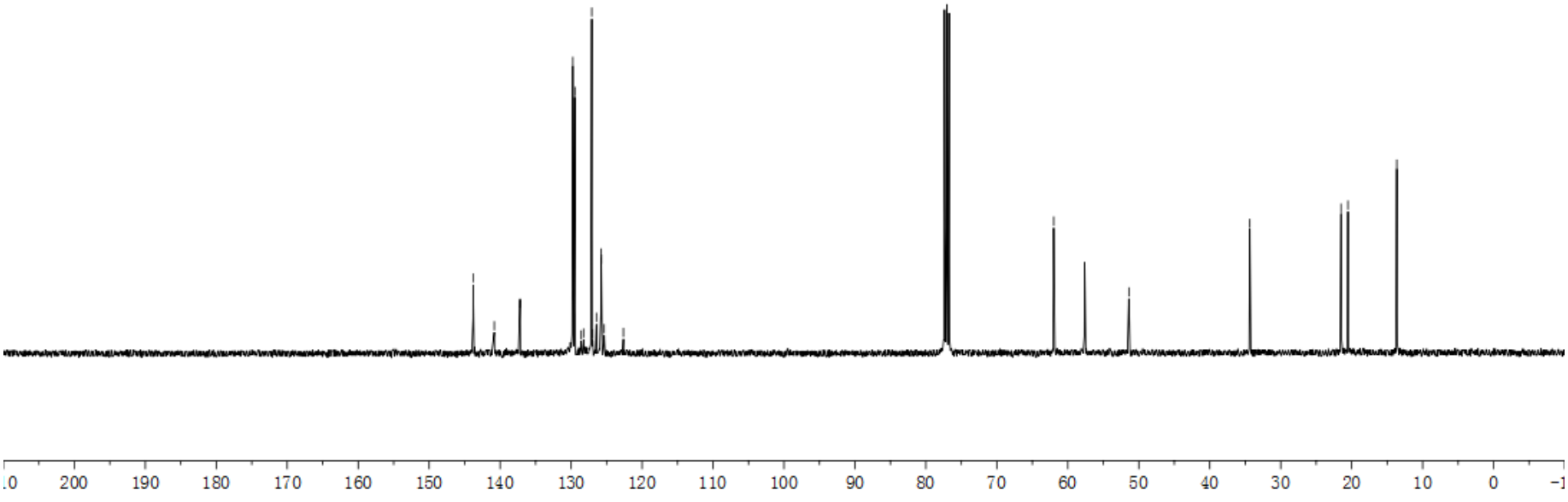
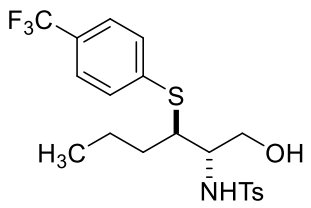
129.47
128.57
128.24
127.08
126.96
126.43
125.77
125.73
125.33
122.63


61.99
57.63
51.40
34.35
21.50
20.52
13.64


F3C
S
H3C
OH
NHTs

5g


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


F3C
S
H3C
OH
NHTs

5g

-62.57
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
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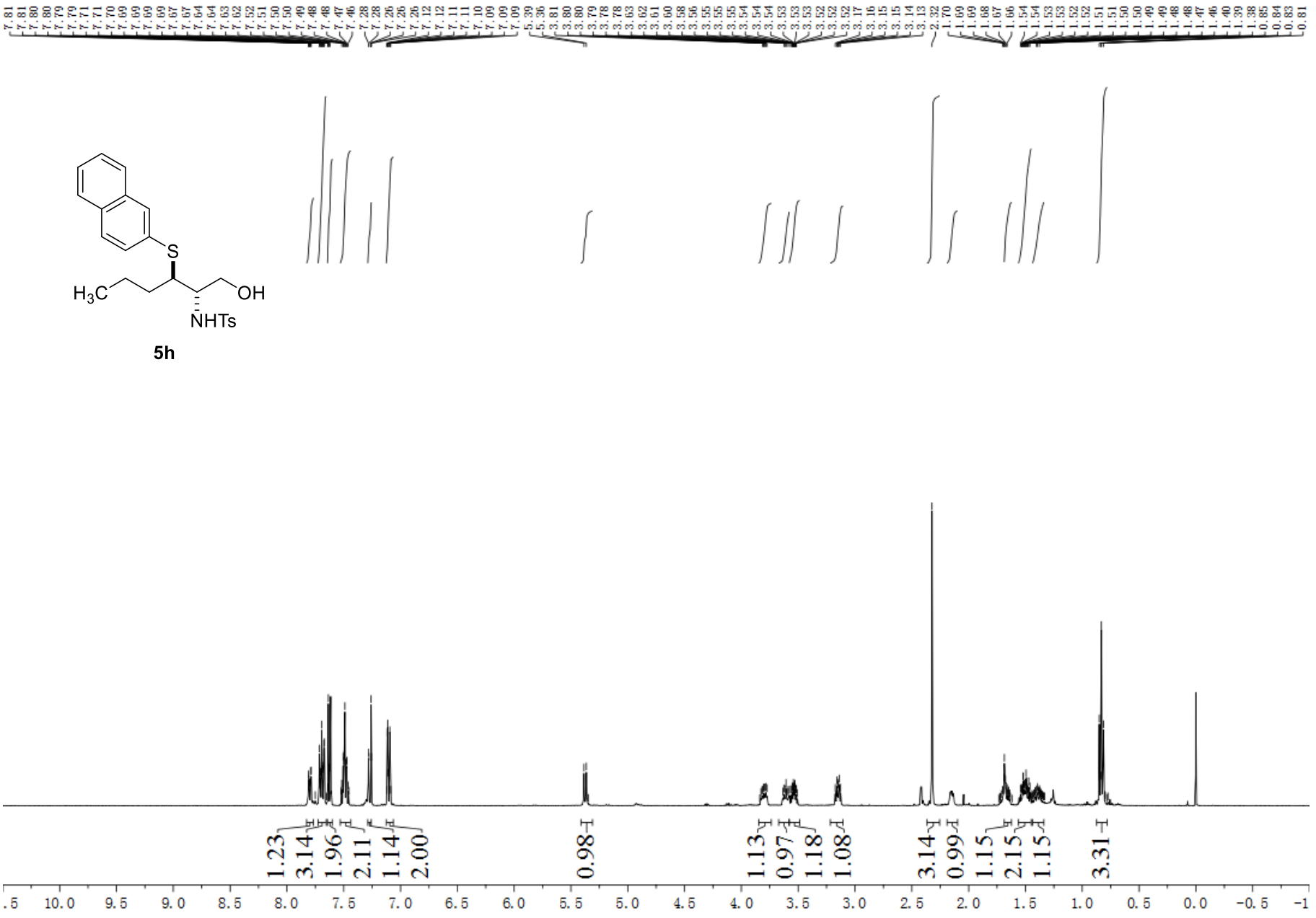
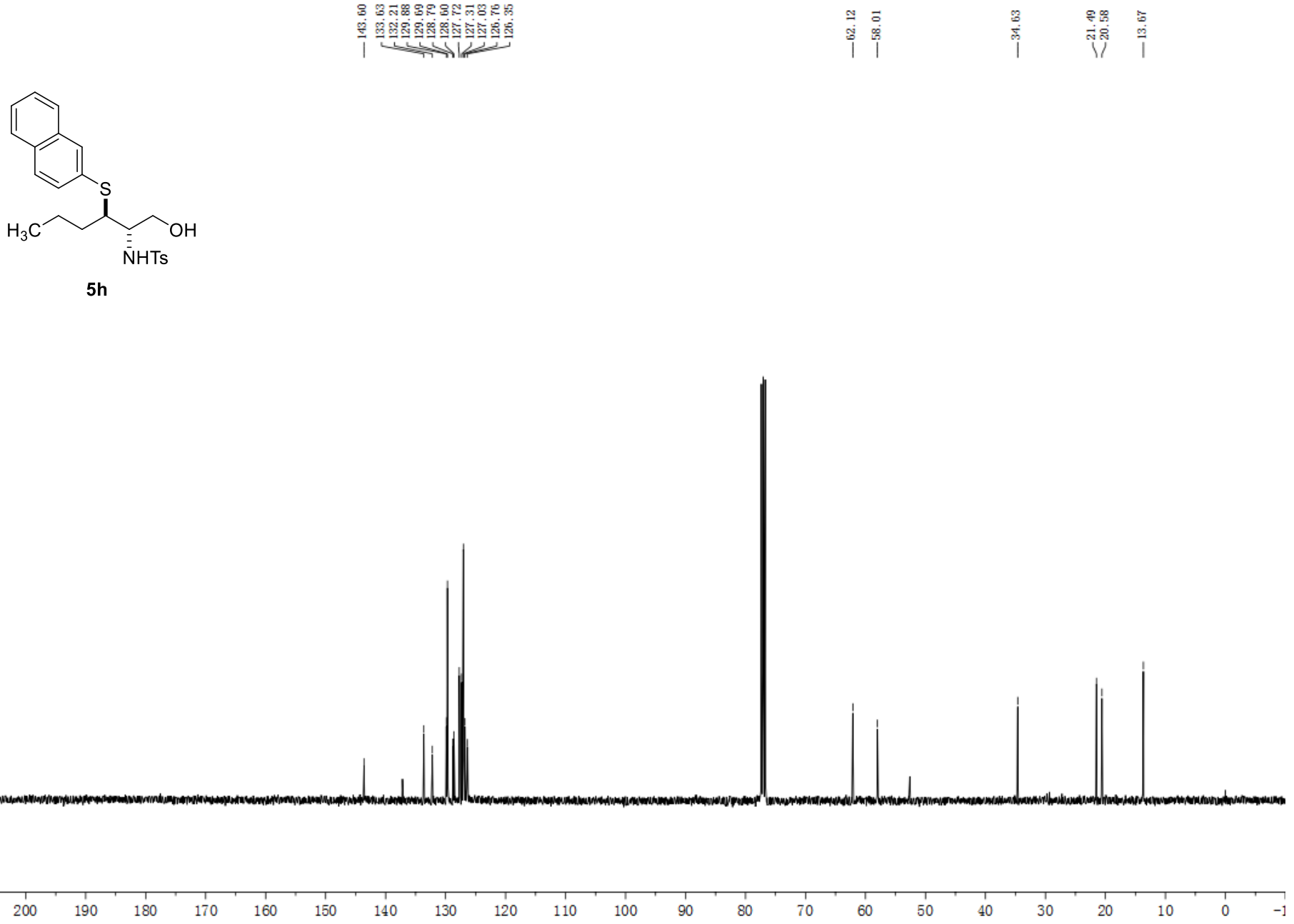
-190
-200
-210


7.81 7.81 7.80 7.80 7.79 7.79 7.71 7.71 7.70 7.69 7.69 7.69 7.69 7.67 7.67 7.64 7.64 7.63 7.62 7.52 7.51 7.50 7.50 7.49 7.48 7.48 7.47 7.46 7.28 7.28 7.26 7.26 7.26 7.12 7.11 7.11 7.10 7.09 7.09 5.39 5.36 3.81 3.80 3.80 3.79 3.78 3.63 3.62 3.61 3.60 3.58 3.56 3.55 3.55 3.55 3.54 3.54 3.54 3.53 3.53 3.52 3.52 3.52 3.17 3.16 3.15 3.15 3.14 3.13 2.32 1.70 1.69 1.69 1.68 1.67 1.66 1.54 1.54 1.53 1.53 1.52 1.52 1.51 1.51 1.50 1.50 1.49 1.49 1.48 1.48 1.47 1.46 1.40 1.39 1.38 0.85 0.84 0.83 0.81
S
H3C
OH
NHTs
1.23 3.14 1.96 2.11 1.14 2.00 0.98 1.13 0.97 1.18 1.08 3.14 0.99 1.15 2.15 1.15 3.31
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1

5h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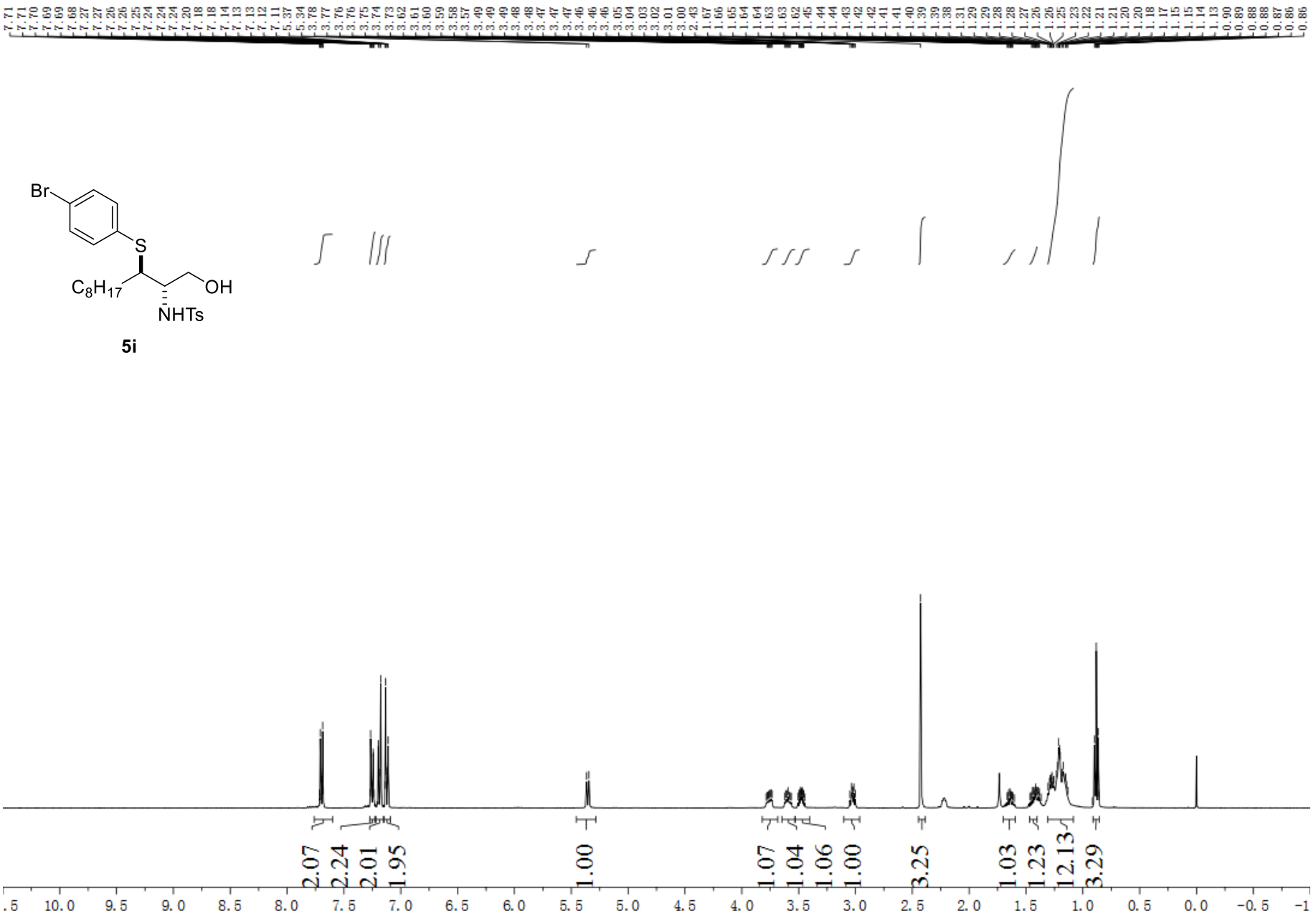
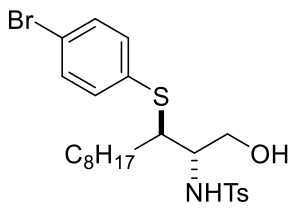
128.79
128.60
127.72
127.31
127.03
126.76
126.35
62.12
58.01
34.63
21.49
20.58
13.67
S
H3C
OH
NHTs
5h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Br
S
C_8H_{17}
OH
NHTs
2.07
2.24
2.01
1.95
1.00
1.07
1.04
1.06
1.00
3.25
1.03
1.23
12.13
3.29

5i


Br
S
C_8H_{17}
OH
NHTs

5i

143.75
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133.55
133.27
132.67
129.77
129.21
127.11
62.08
57.78
53.29
32.31
31.83
29.34
29.22
29.13
27.23
22.67
21.58
14.13
200
190
180
170
160
150
140
130
120
110
100
90
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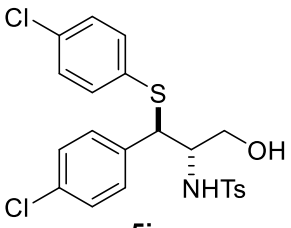
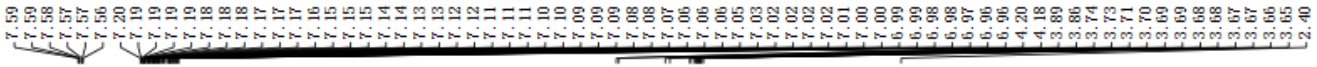
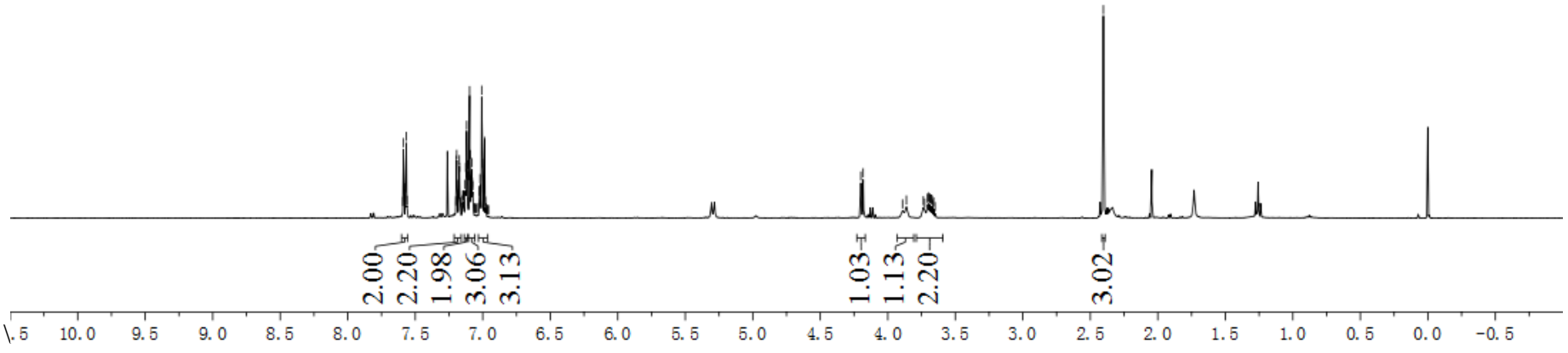
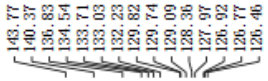
70
60
50
40
30
20
10
0


Cl
S
OH
NHTs
Cl

5j




2.00
2.20
1.98
3.06
3.13
1.03
1.13
2.20
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


143.77
140.37
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134.54
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133.03
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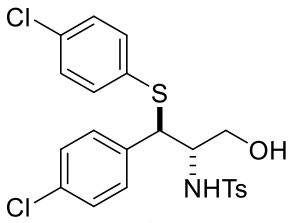
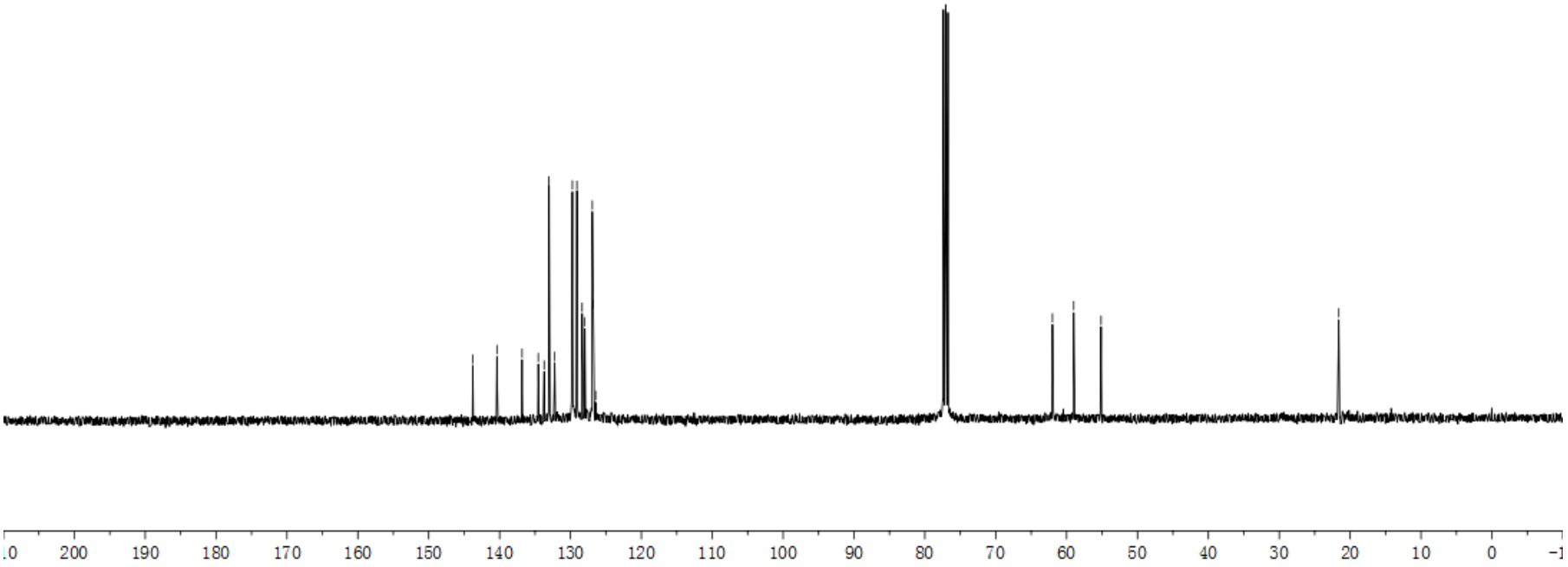
128.36
127.97
126.92
126.77
126.46

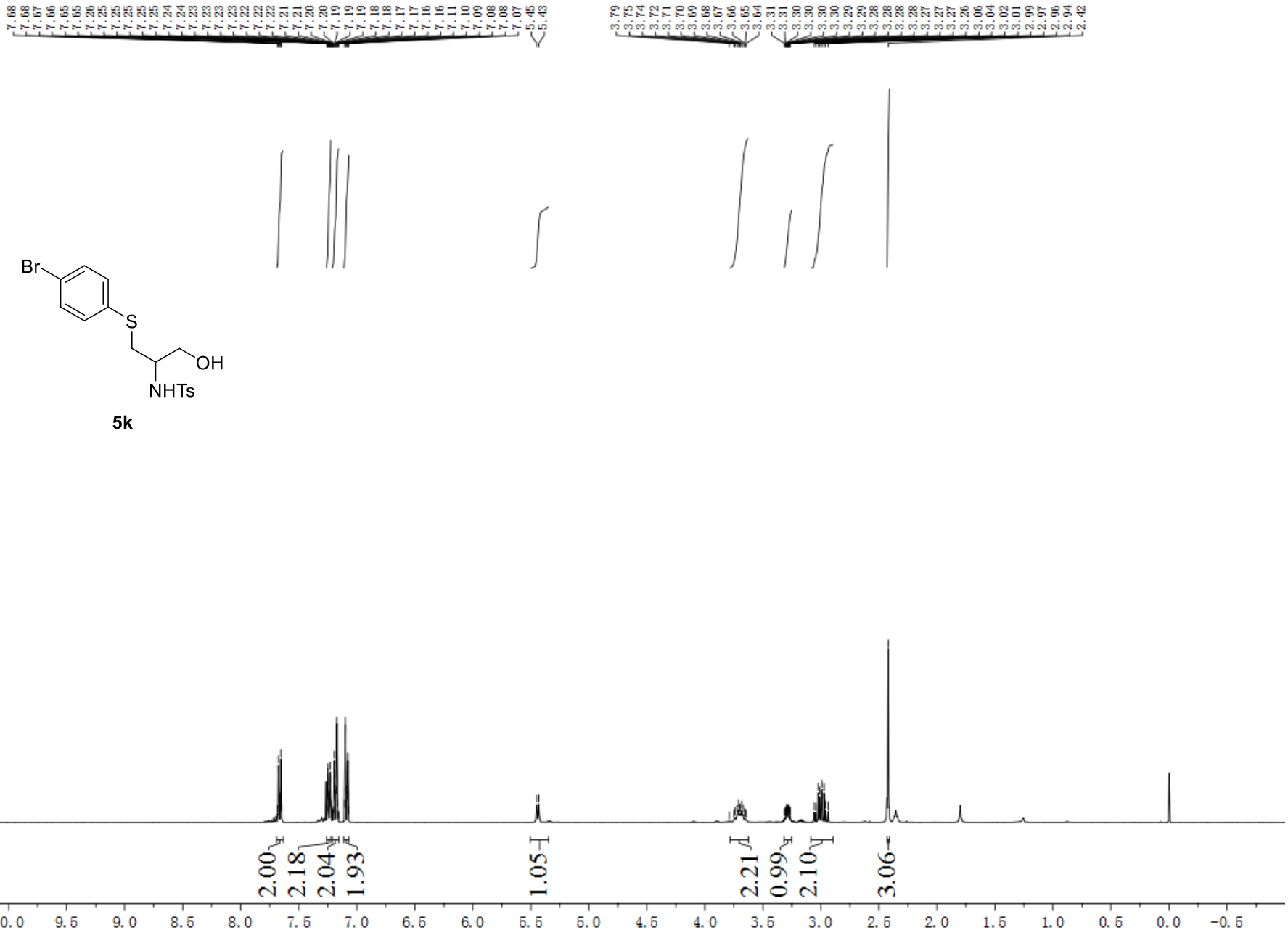

62.00
59.00
55.14

21.61


Cl
S
OH
NHTs
Cl

5j


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.68 7.68 7.67 7.66 7.65 7.65 7.26 7.25 7.25 7.25 7.25 7.24 7.24 7.23 7.23 7.23 7.22 7.22 7.22 7.21 7.21 7.20 7.19 7.19 7.19 7.18 7.18 7.17 7.17 7.16 7.16 7.11 7.10 7.09 7.08 7.08 7.07 5.45 5.43
3.79 3.75 3.74 3.72 3.71 3.70 3.69 3.68 3.67 3.66 3.65 3.64 3.31 3.31 3.30 3.30 3.30 3.30 3.29 3.29 3.28 3.28 3.28 3.28 3.27 3.27 3.27 3.26 3.06 3.04 3.02 3.01 2.99 2.97 2.96 2.94 2.42
Br
S
OH
NHTs
2.00
2.18
2.04
1.93
1.05
2.21
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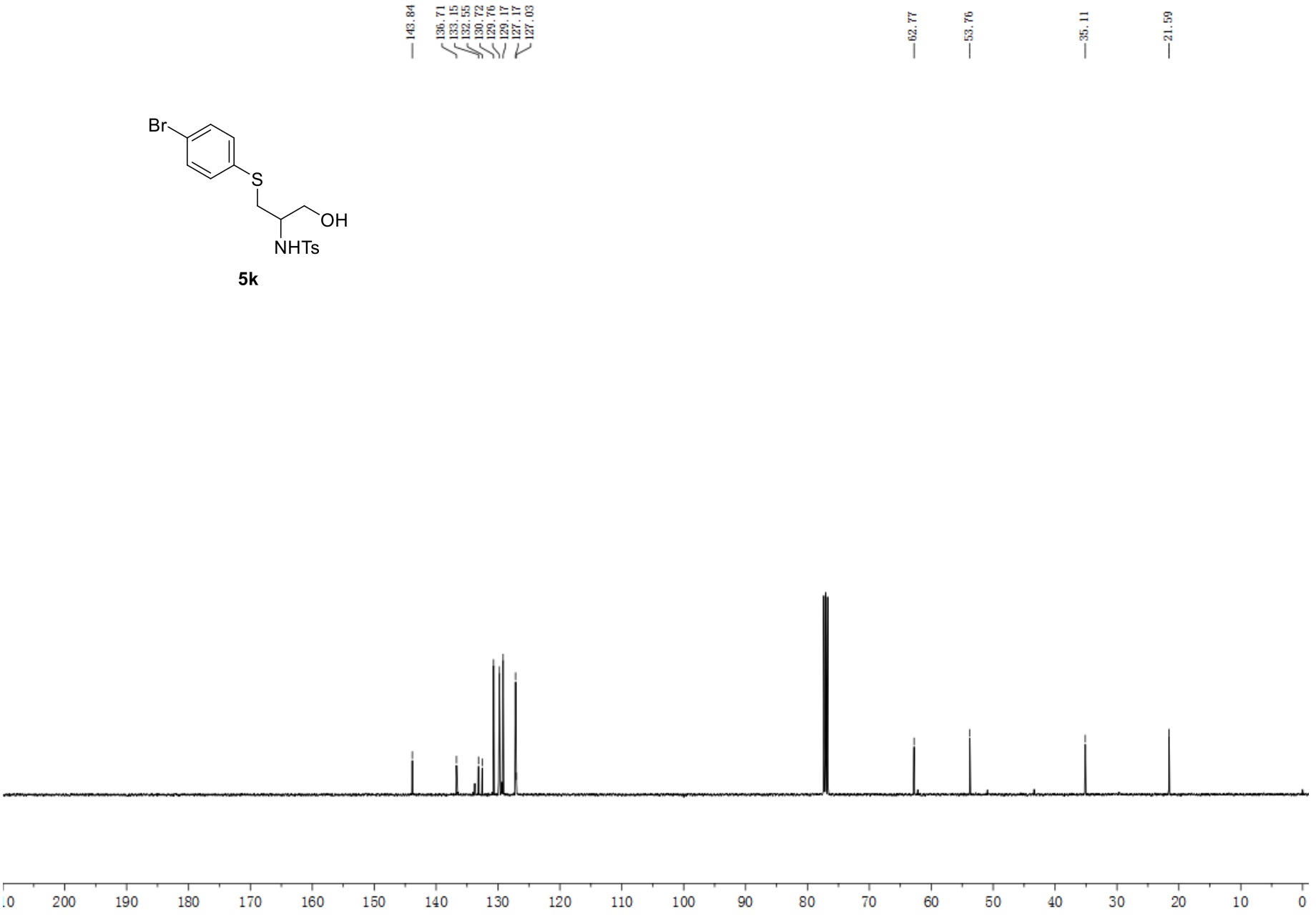
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OH
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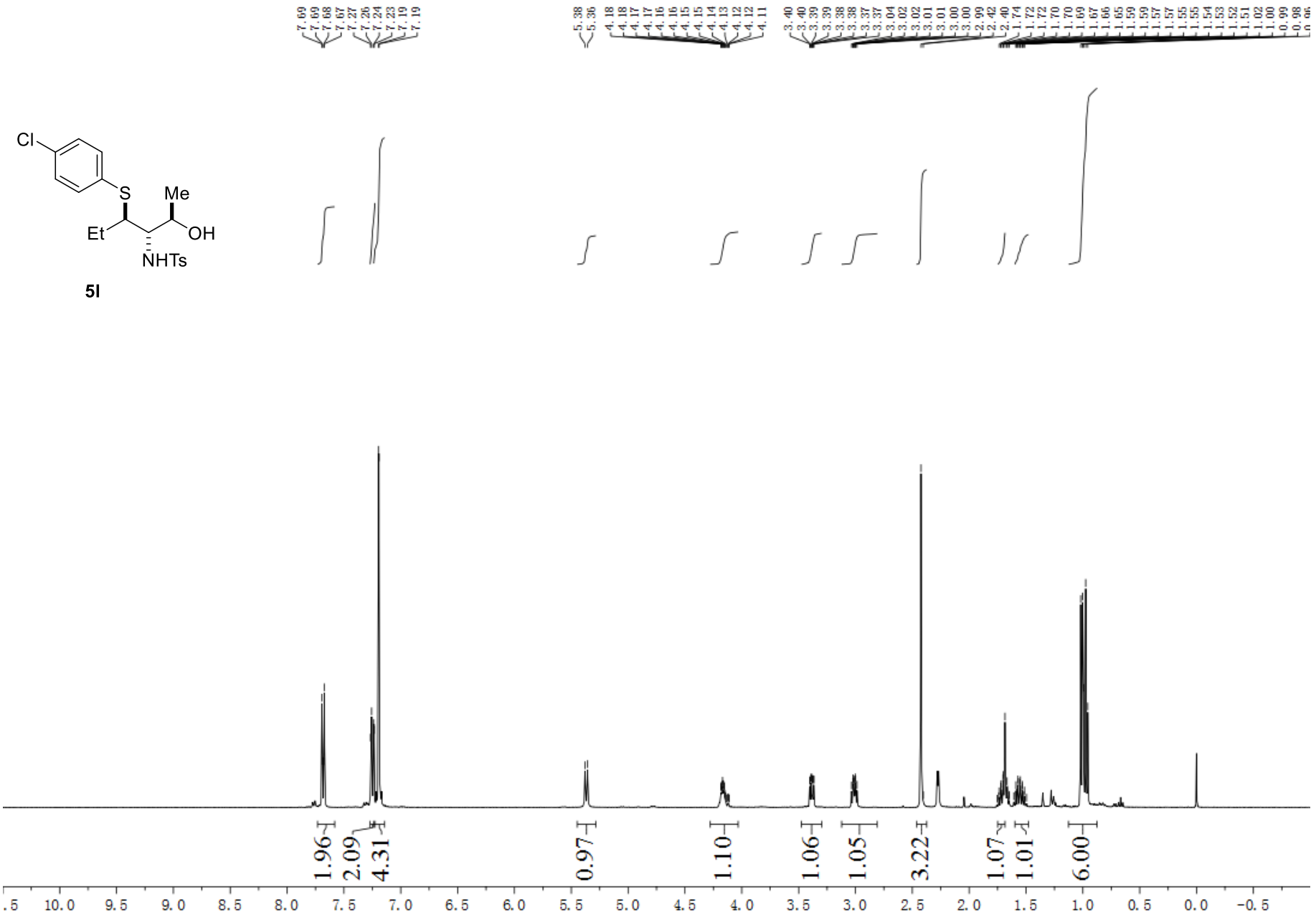
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4.17
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4.15
4.15
4.14
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4.12
4.12
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3.38
3.37
3.37
3.04
3.02
3.02
3.01
3.01
3.00
3.00
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2.40
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1.69
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1.07
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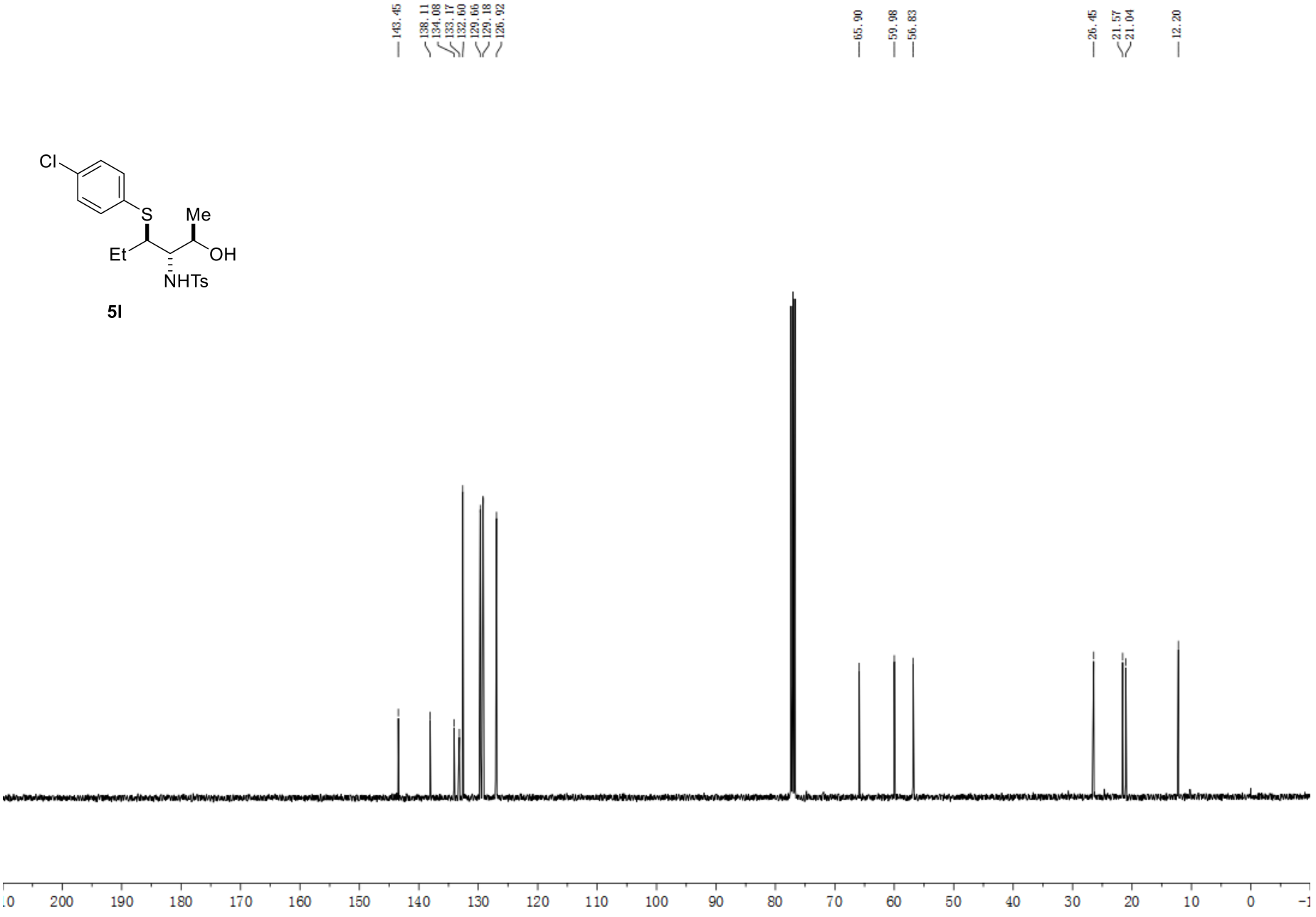
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Me
Et
OH
NHTs
5l
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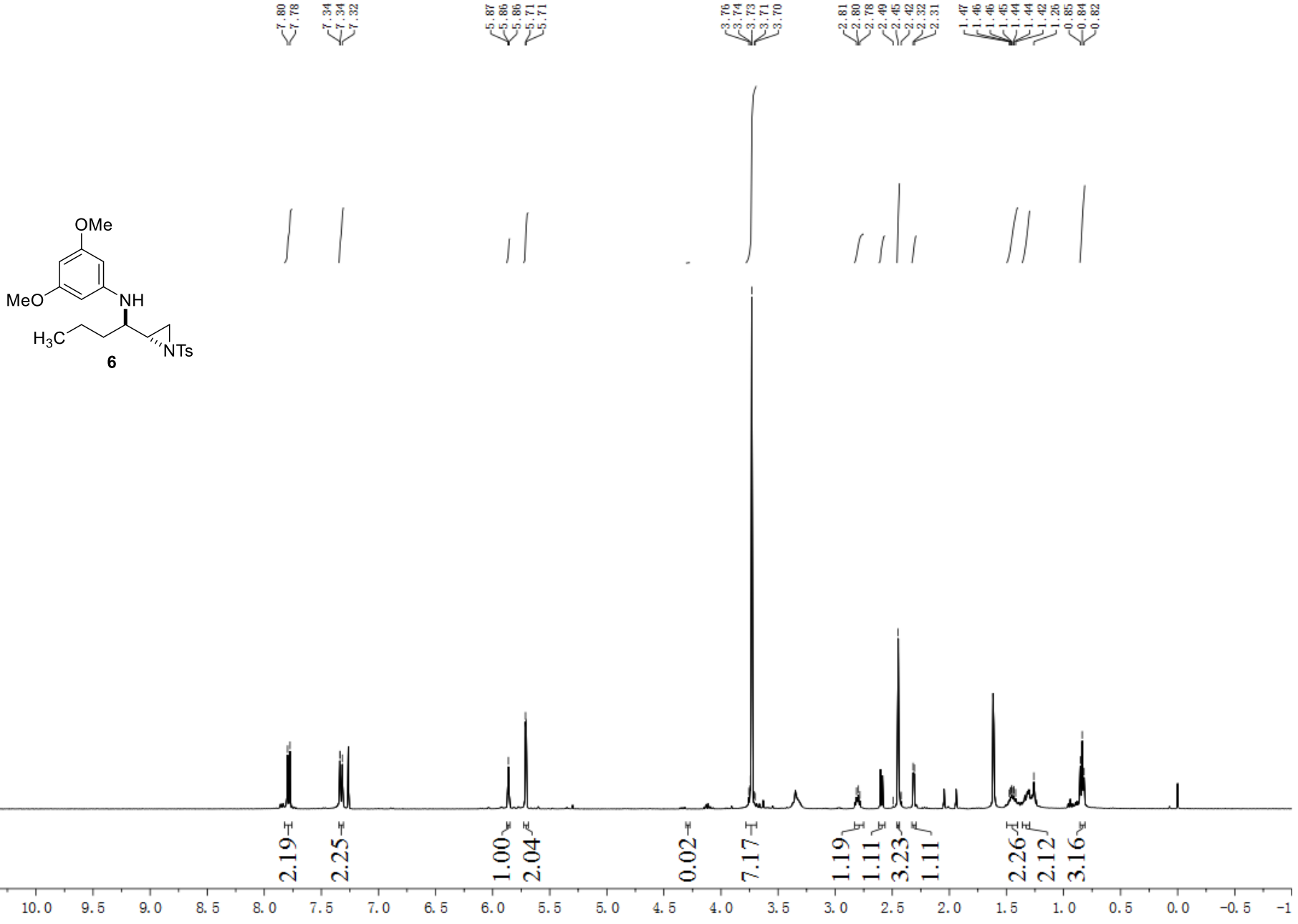
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1.44
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0.82
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MeO
NH
H3C
NTs
6
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2.04
0.02
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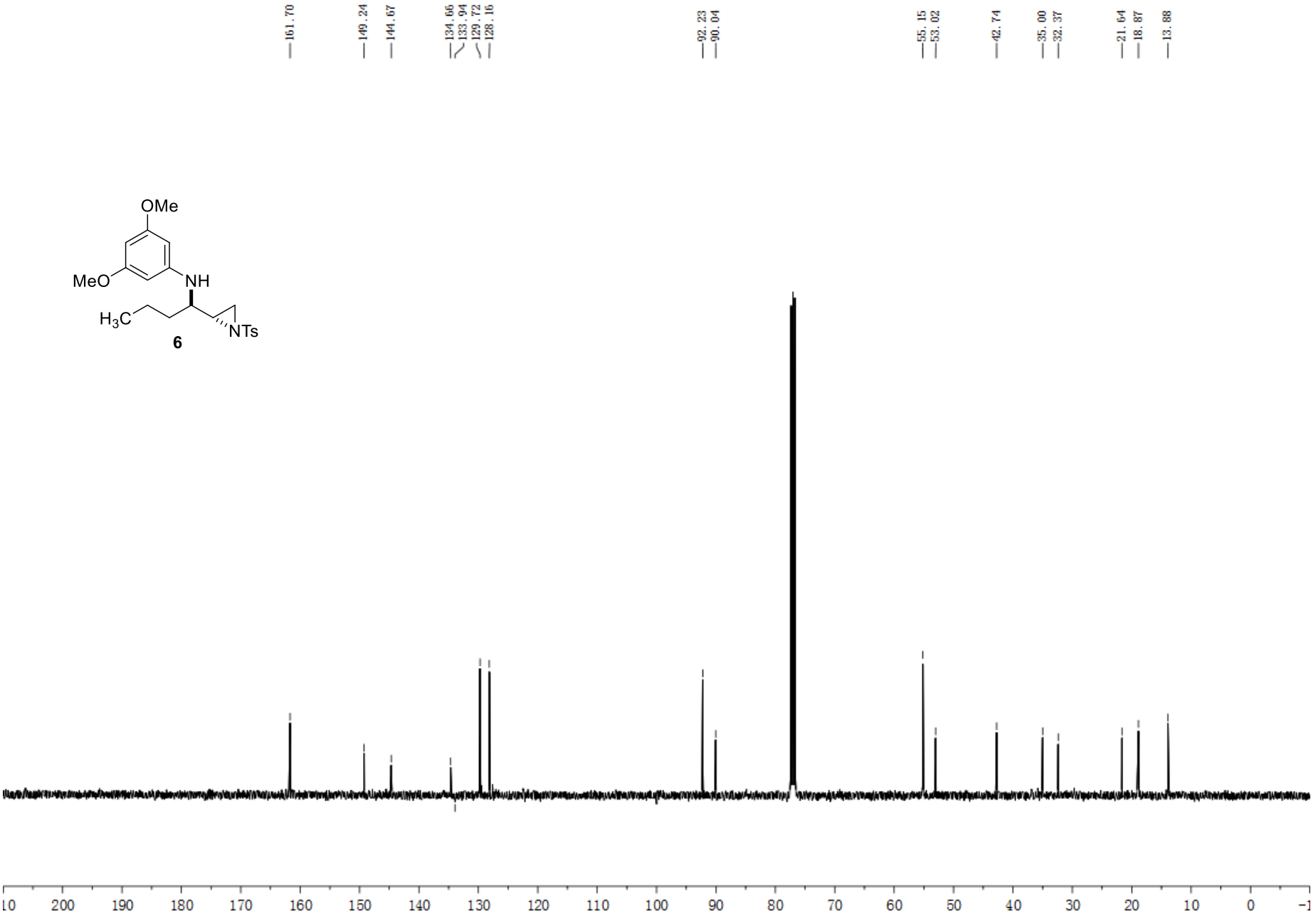
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NTs
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190
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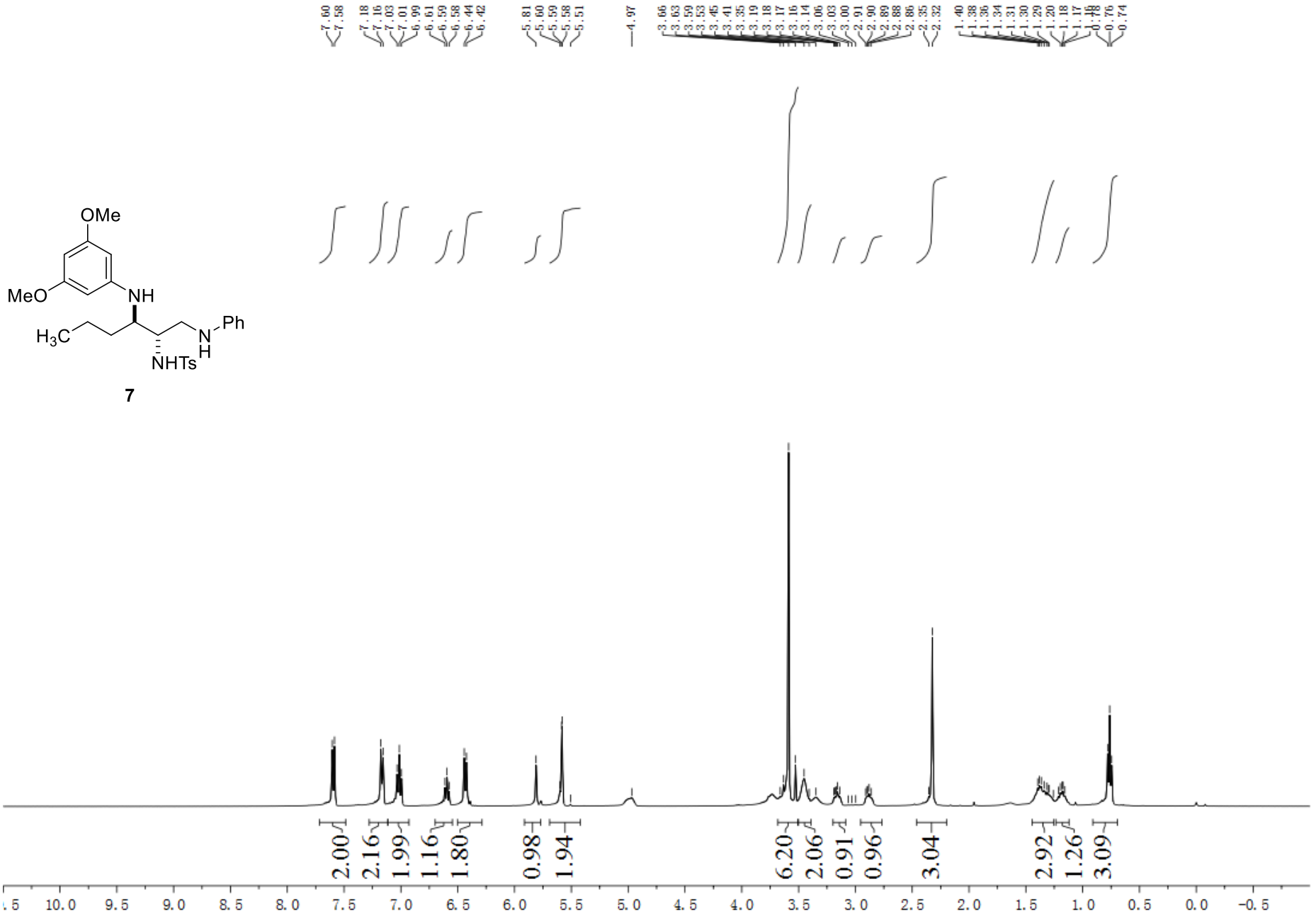
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3.63
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3.18
3.17
3.16
3.14
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H
H3C
NHTs
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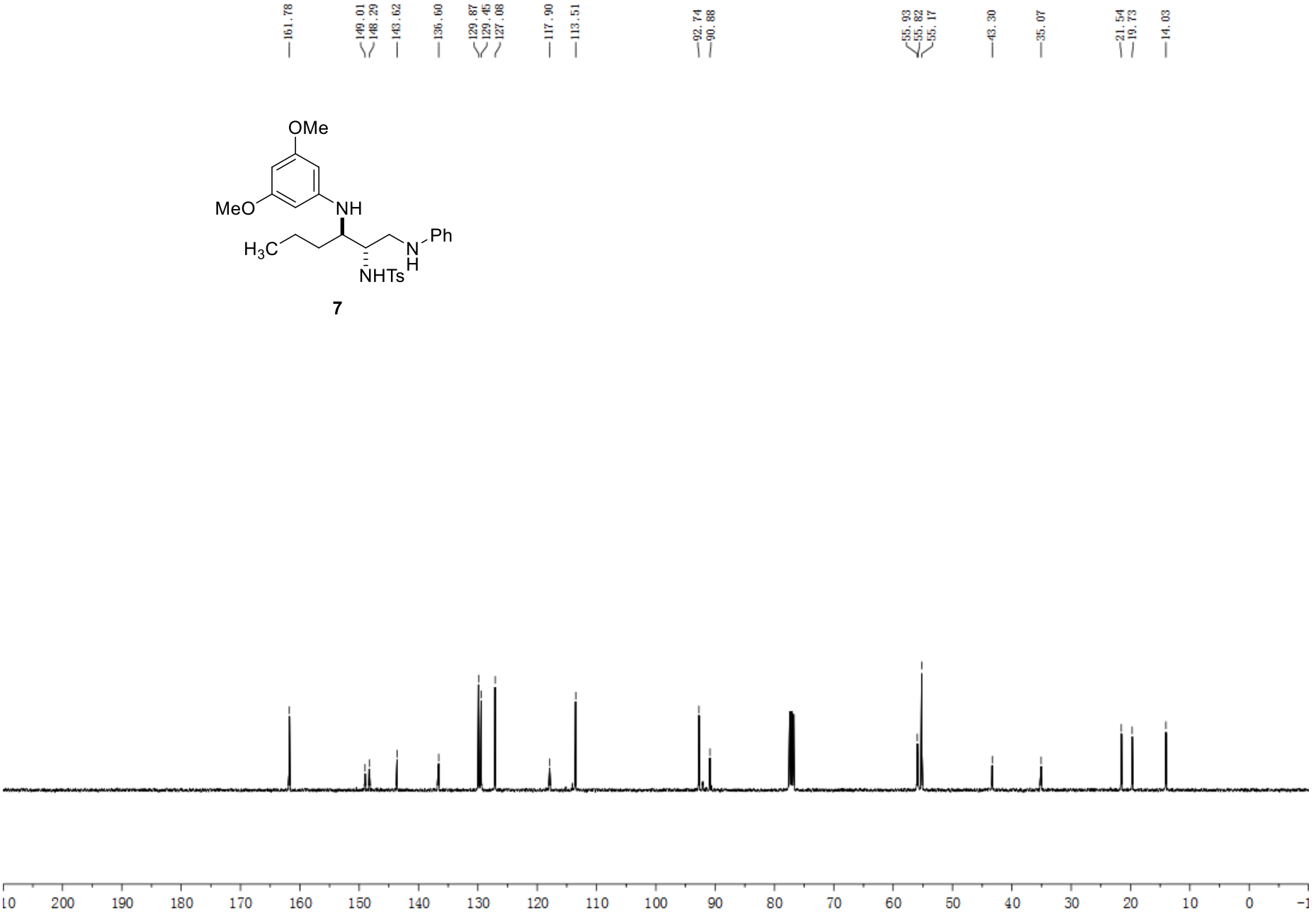
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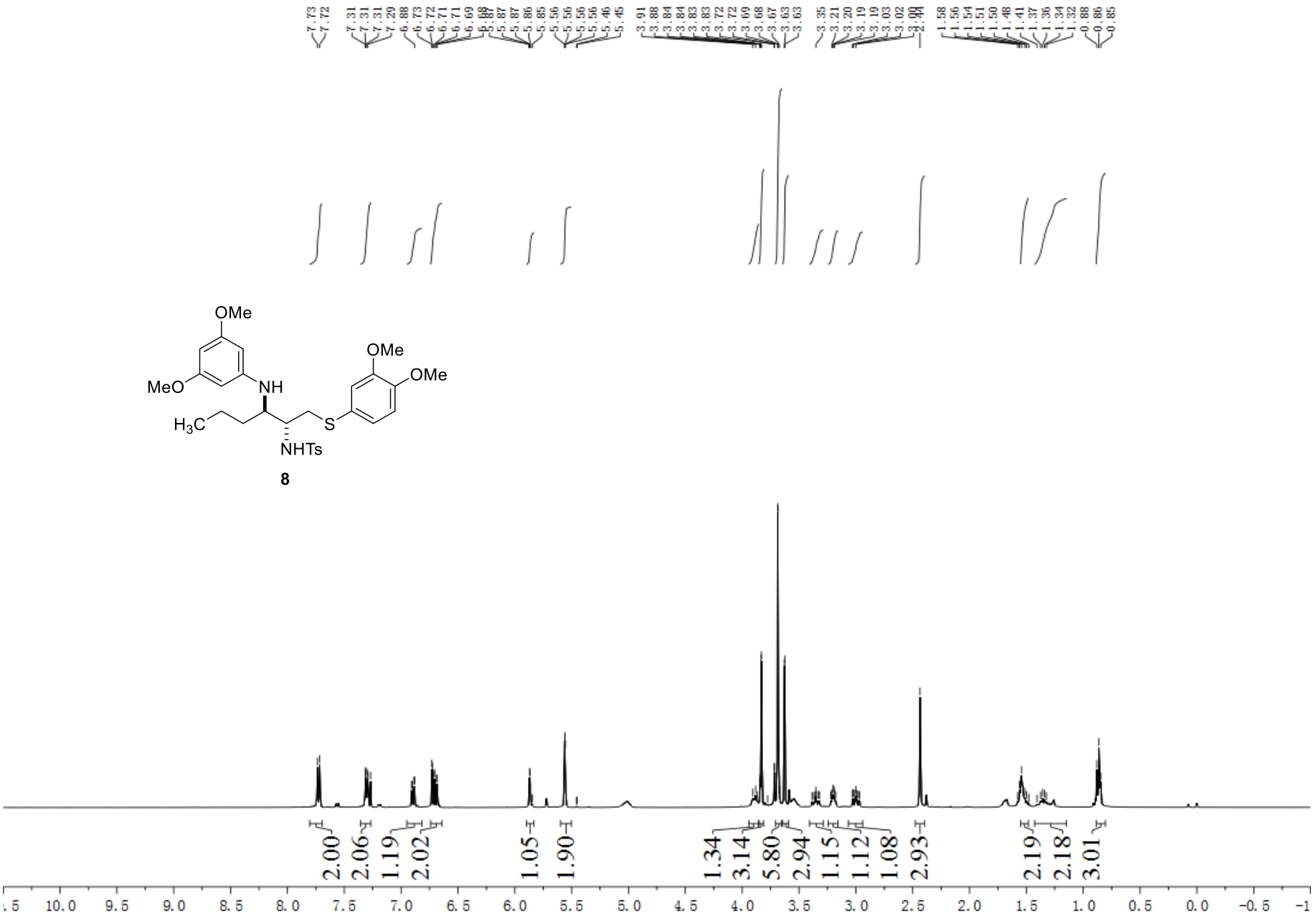
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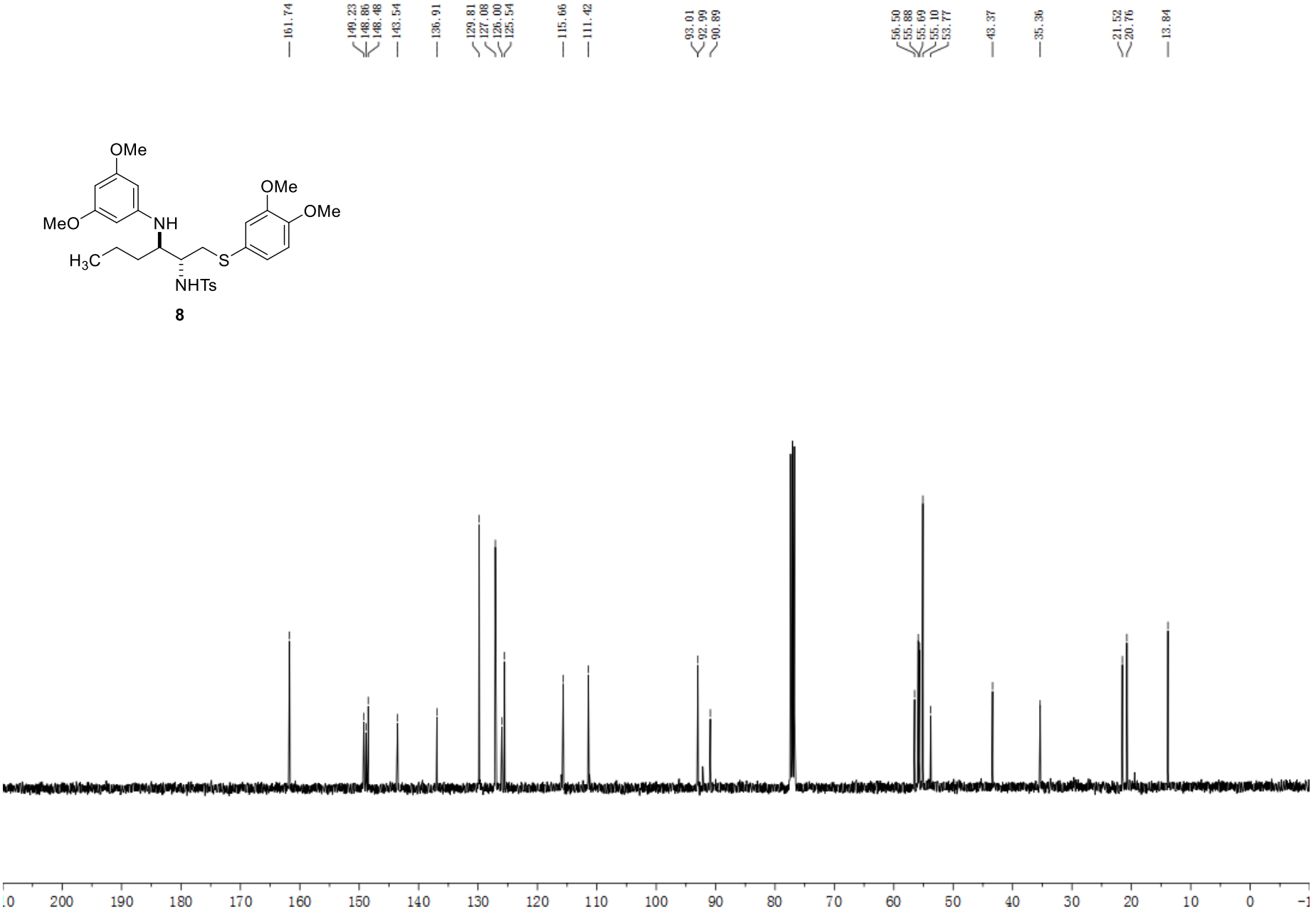
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MeO
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OMe
OMe
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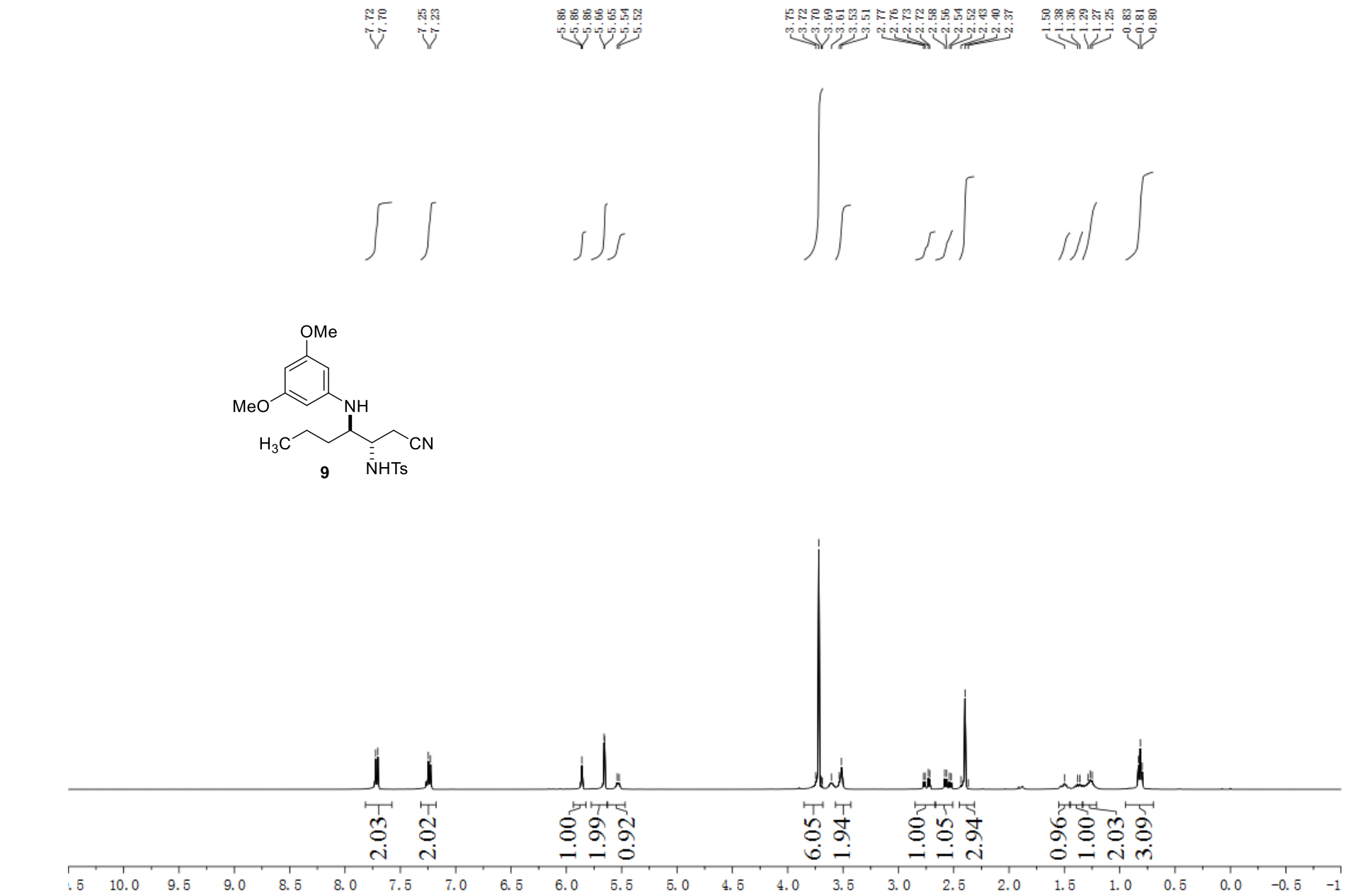
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H3C
CN
NHTs
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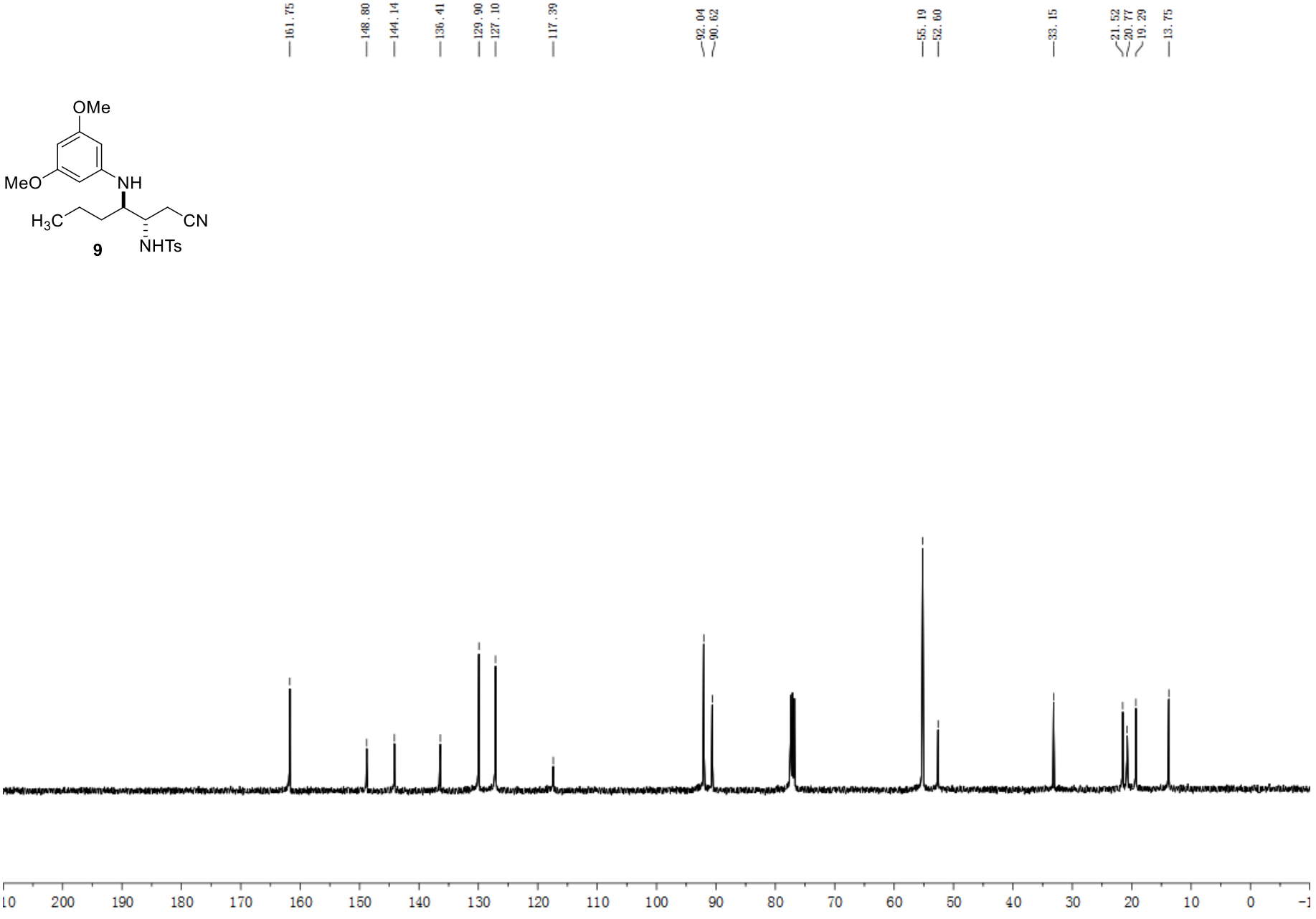
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H3C
CN
NHTs
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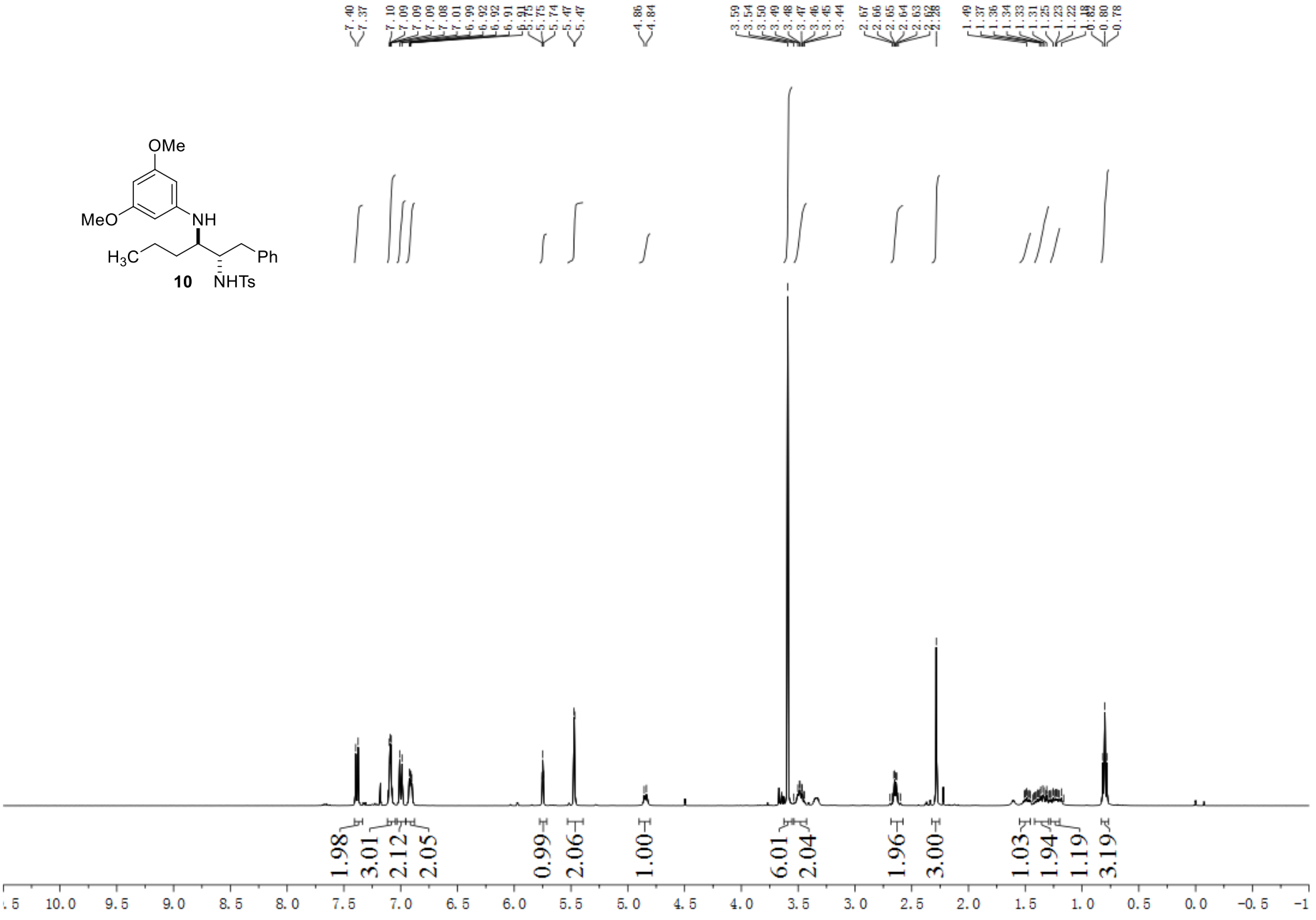
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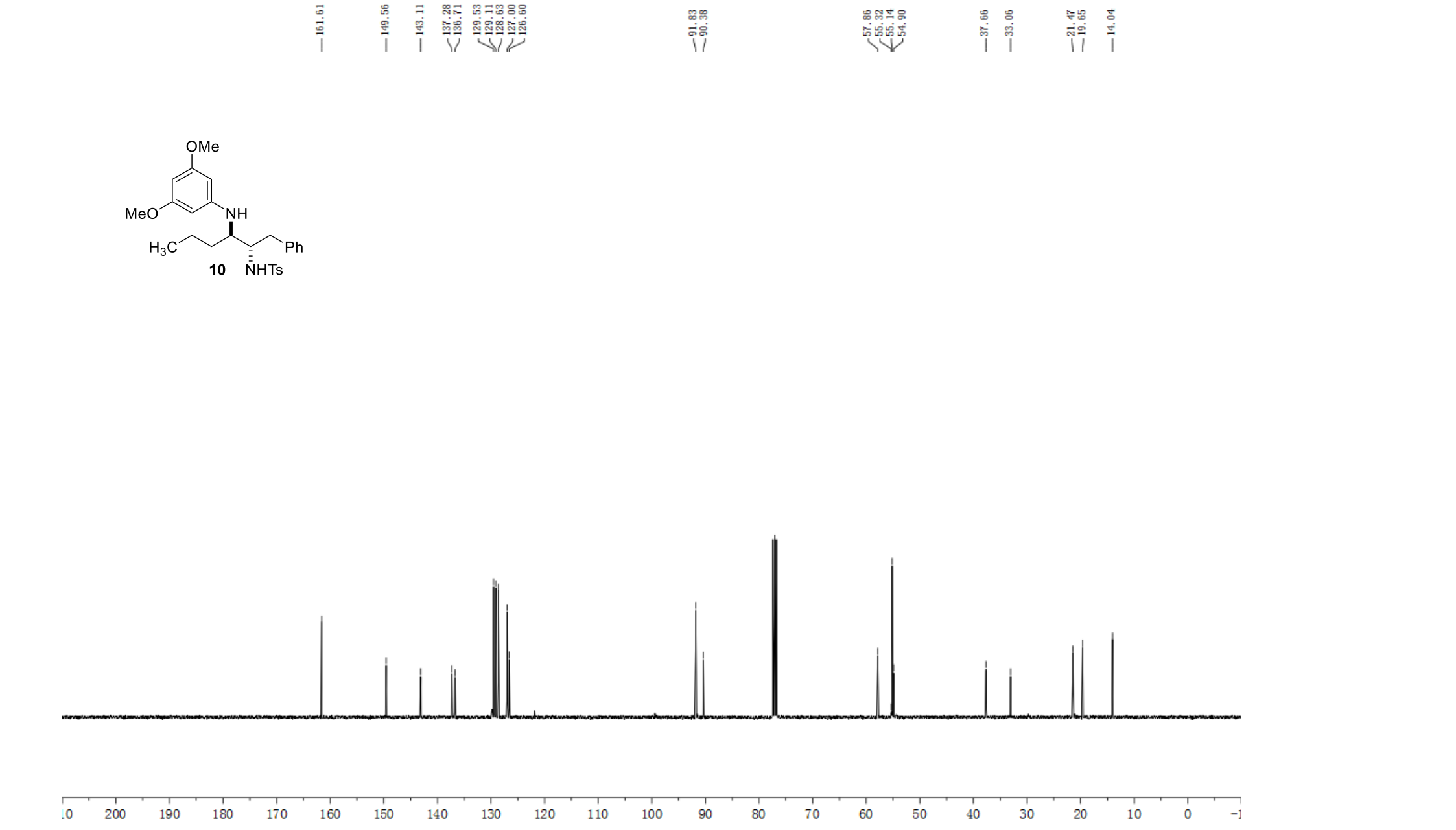
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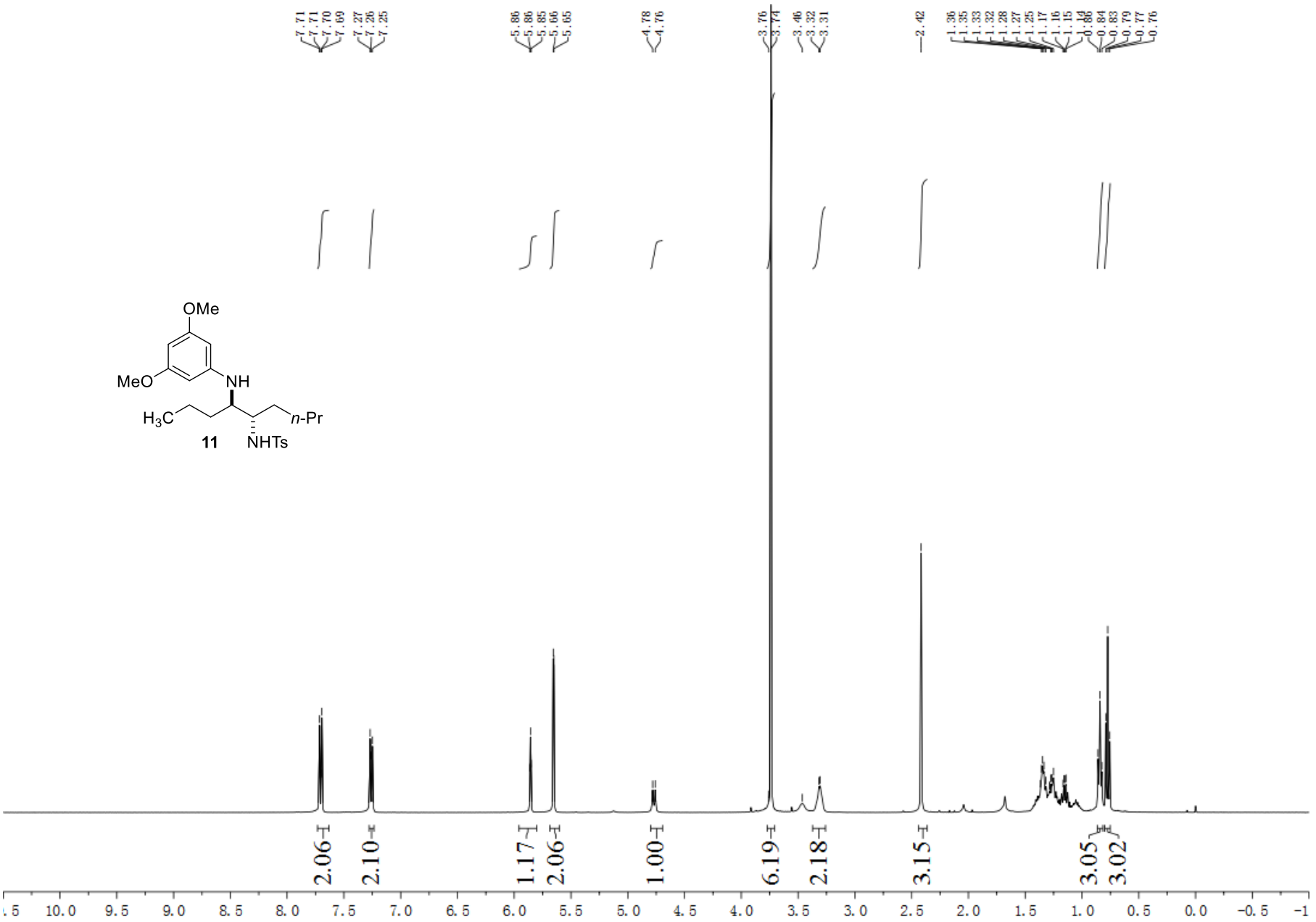
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OMe
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H3C
n-Pr
NHTs
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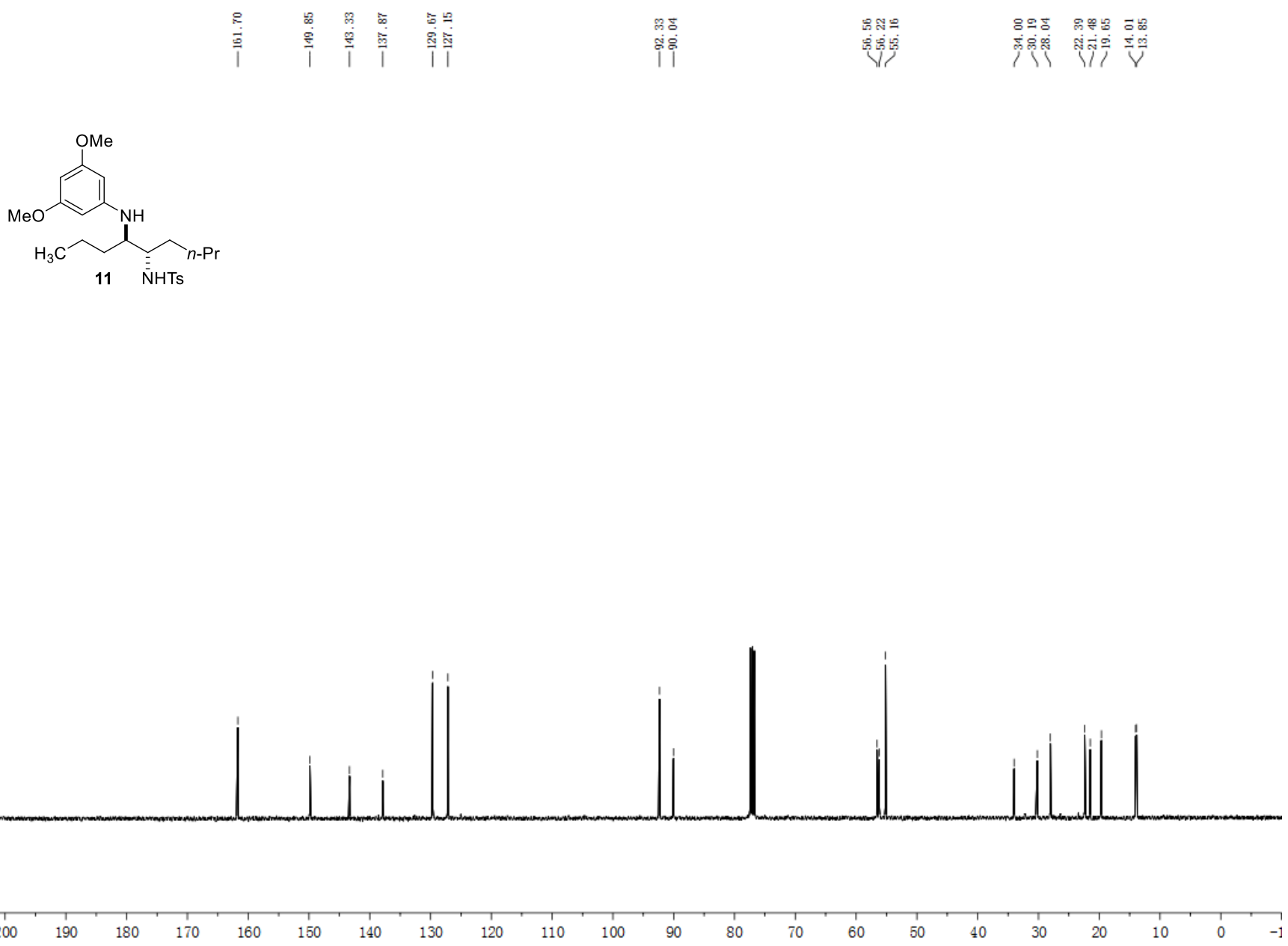
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MeO
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H3C
n-Pr
NHTs
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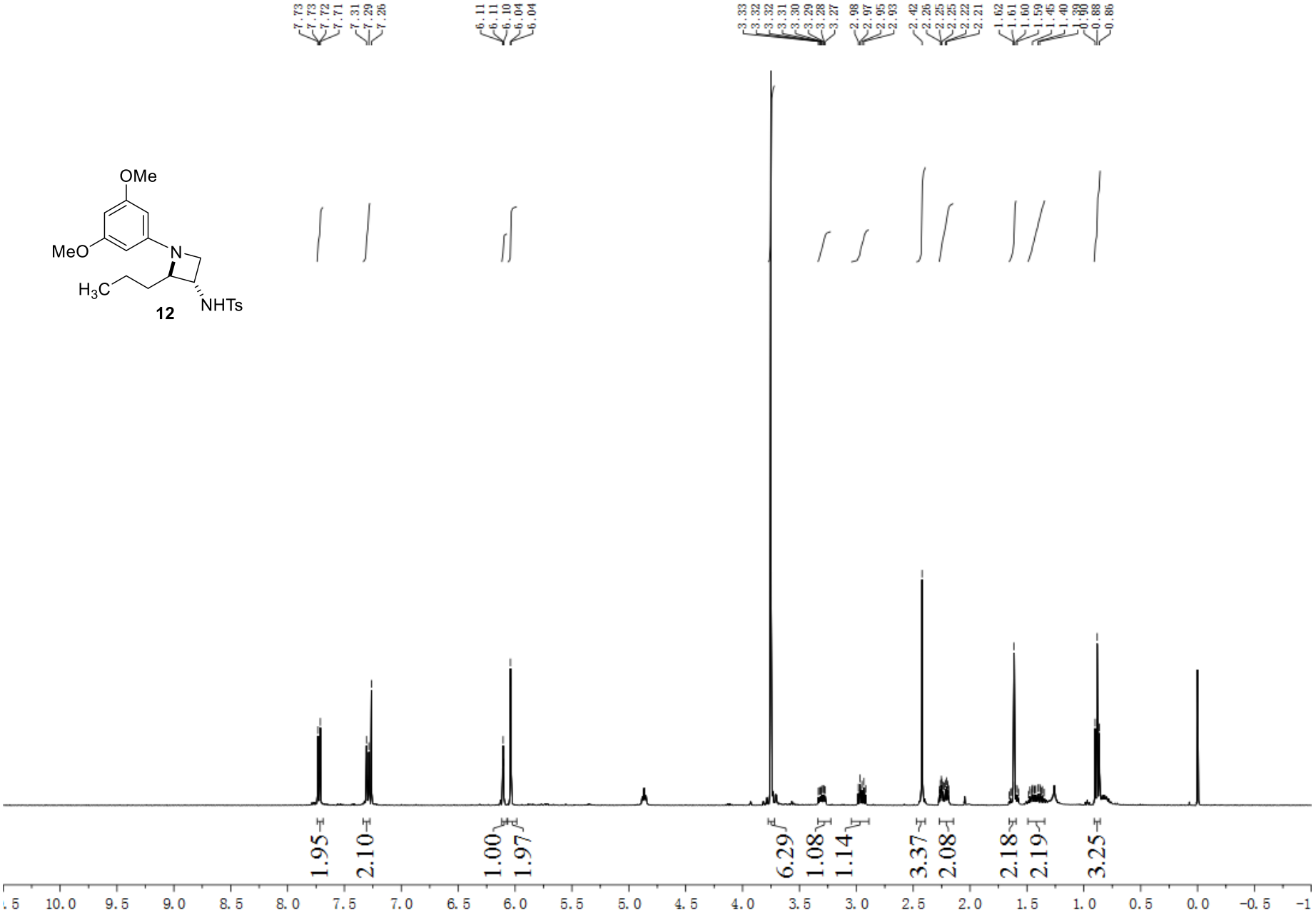
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NHTs
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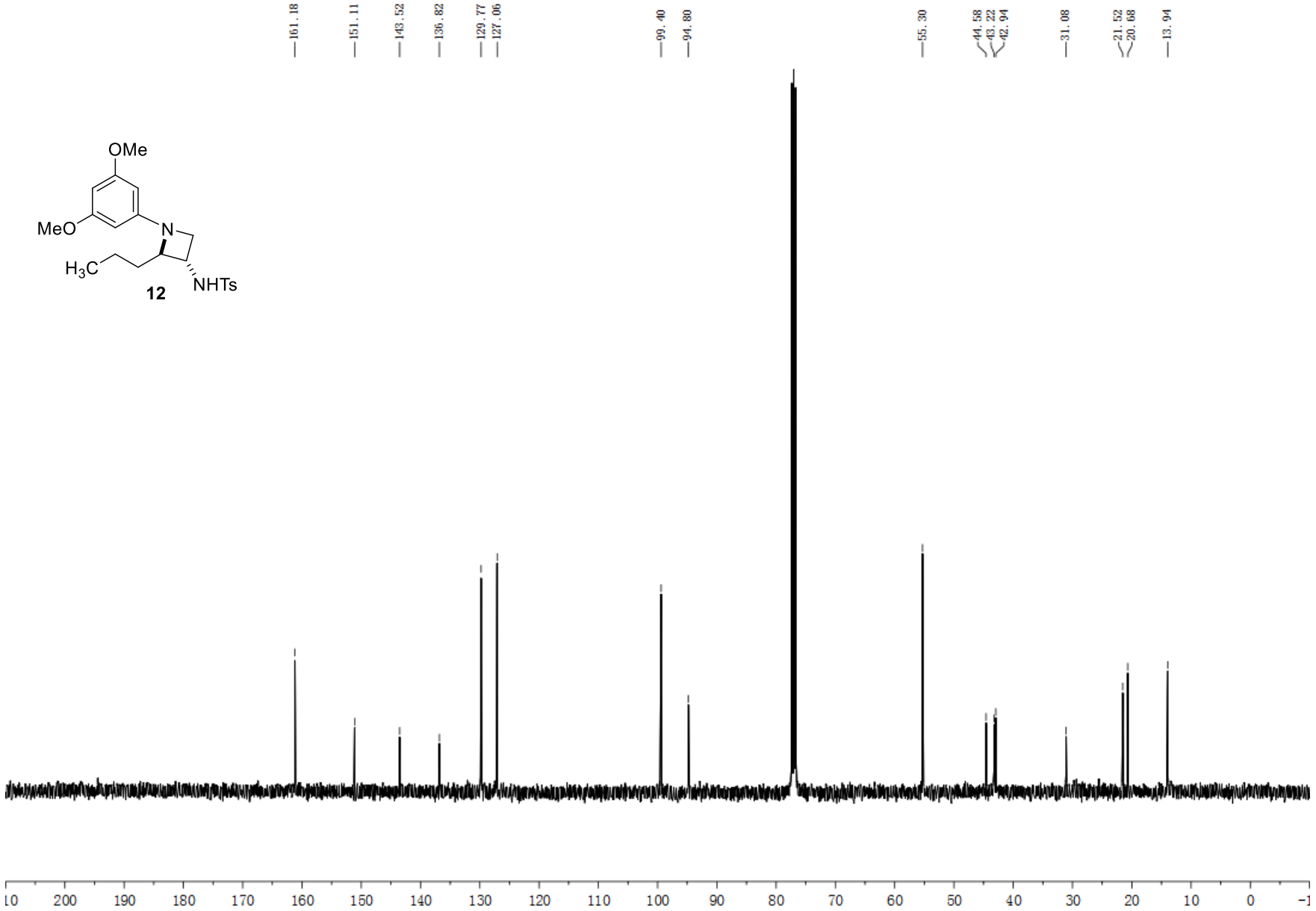
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