Supporting Information

Catalytic Enantioselective Bromoamination of Allylic Alcohols

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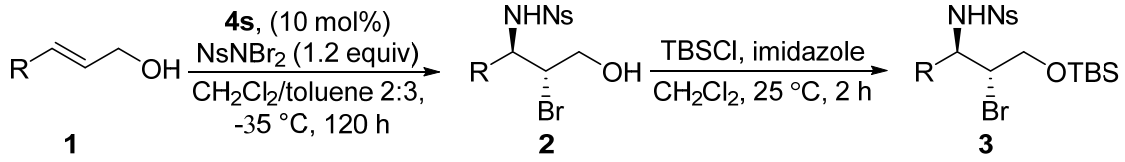
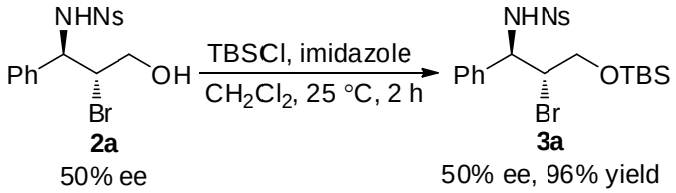
General. All reactions that required anhydrous conditions were carried by standard procedures under nitrogen atmosphere. Commercially available reagents were used as received. The solvents were dried by distillation over the appropriate drying reagents. Infrared spectra were recorded on a TENSOR 27 FT-IR spectrophotometer and reported in wave numbers (cm^{-1}). ^{1}H and ^{13}C NMR spectra were recorded on Varian (400 MHz) spectrometer. Chemical shifts (δ) are reported in ppm relative to TMS (δ 0.00) for the ^{1}H NMR and to chloroform (δ 77.0) for the ^{13}C NMR measurements. High resolution mass spectra were obtained on a UltiMate 3000 spectrometer. Enantiomeric excesses were determined by HPLC analysis on Dionex UltiMate 3000 HPLC units, including the following instruments: pump, LPG-3400SD; detector, VWD-3100; column, Daicel Chiralpak IA, IB or IC. Optical rotations were recorded on a Jasco DIP-1000 polarimeter. Reactions were followed with TLC (0.254mm silica gel 60-F plates). Visualization was accomplished with UV light. Flash chromatography separations were performed on 200-300 mesh silica gel.

General Procedure for the Bromoamination and Silylation of Allylic Alcohols.

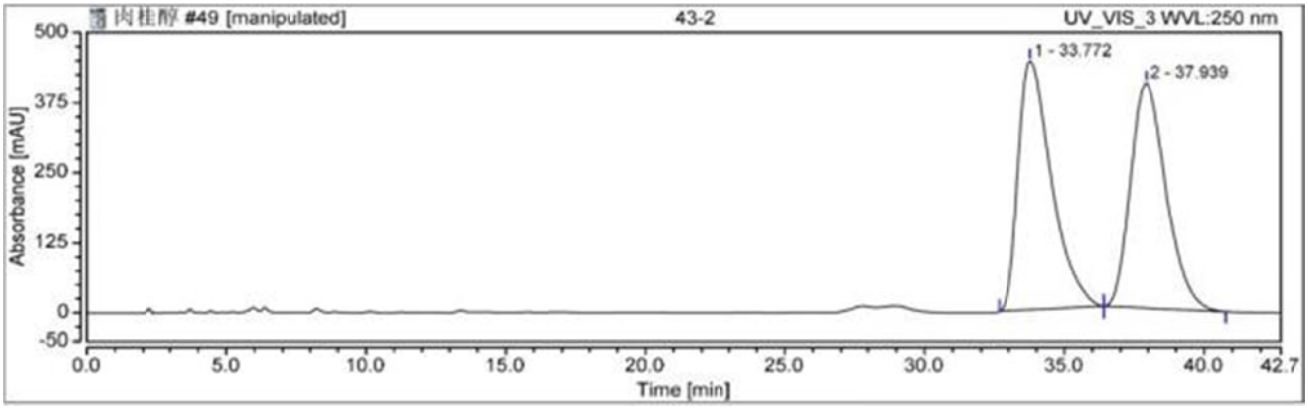


To a solution of allylic alcohol **1** (0.20 mmol, 1.00 equiv), catalyst **4s** (14.0 mg, 0.02 mmol, 0.10 equiv) in CH_2Cl_2/toluene (2:3, 5.0 mL) at –35 °C in dark under N_2 was added *NN*-dibromo-4-nitrobenzenesulfonamide (86.4 mg, 0.24 mmol, 1.20 equiv). The resulting mixture was stirred at –35 °C for 120 h. The reaction was quenched with saturated Na_2SO_3 (3.0 mL) at –35 °C and then was warmed to 25 °C. The solution was diluted with water (3.0 mL) and extracted with CH_2Cl_2 (3 × 6 mL). The combined extracts were washed with brine (10.0 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo*. The residue was purified by a short silica column to give a mixture of **2** and $NsNH_2$. To a solution of the mixture in CH_2Cl_2 (2.0 mL) was added TBSCl (33.2 mg, 0.22 mmol) and imidazole (15.0 mg, 0.20 mmol) at 25 °C. The resulting mixture was stirred at 25 °C for 2 h, to the mixture was added brine (3 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography to yield the corresponding vicinal bromoamine **3**.

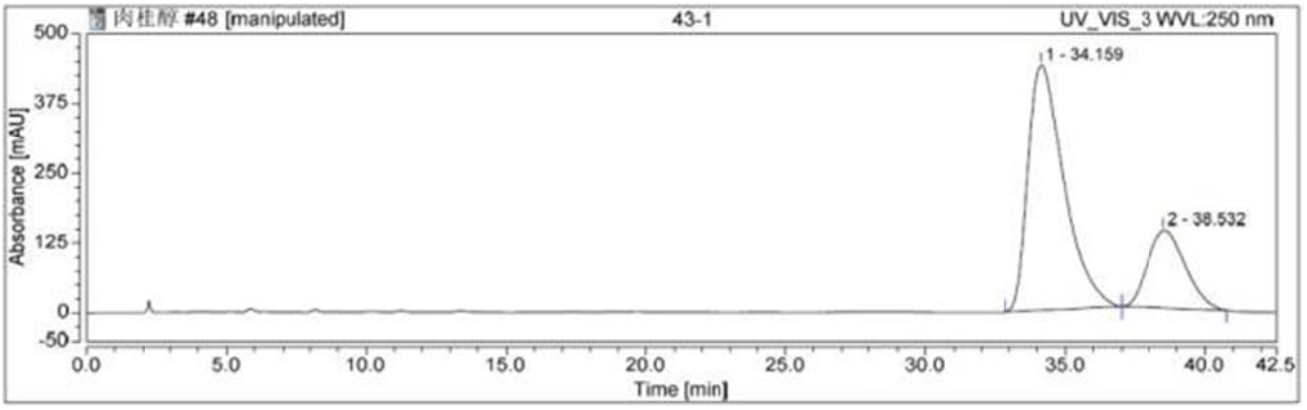
Scheme S1. Silylation of 2a.



Treatment of **2a** according to the general procedure (step 2) resulted in **3a** in 96% yield without change of enantiopurity. HPLC of **2a** (Daicel Chiralpak IC, *i*-PrOH/hexane = 10/90, 1.5 mL/min, 250 nm) t_1 = 34.2 min (major), t_2 = 38.5 min (minor):

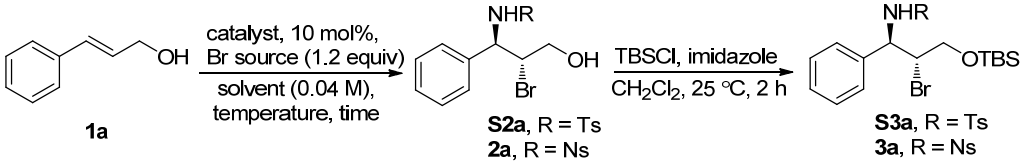


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		33.772	617.665	443.614	50.83	52.47	n.a.
2		37.939	597.550	401.822	49.17	47.53	n.a.
Total:			**1215.215**	**845.437**	**100.00**	**100.00**	

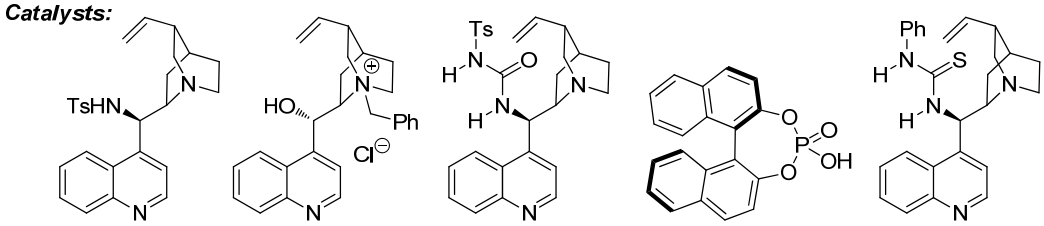


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		34.159	655.910	438.913	75.07	75.86	n.a.
2		38.532	217.808	139.696	24.93	24.14	n.a.
Total:			**873.719**	**578.609**	**100.00**	**100.00**	

Table S1. Optimization of the Bromoamination of 1a.



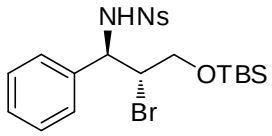
Catalysts:



S4a **S4b** **S4c** **S4d** **8d**

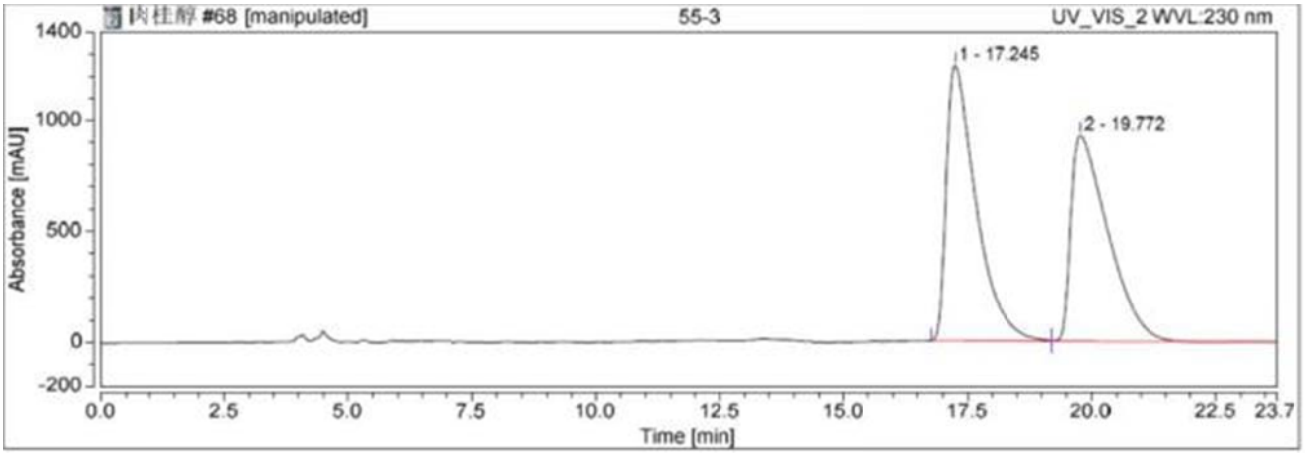
entr	catalyst	Br/amine source (equiv)	solvent	temp (^{o}C)	time (h)	yield (%)[b]	ee
1	Cinchonine	NBS (1.2)/$TsNH_2$ (1.2)	CH_2Cl_2	rt	12	trace	-
2		$TsNBr_2$ (1.2)	CH_2Cl_2	rt	12	46	-
3	$(DHQD)_2PHA$	$TsNBr_2$ (1.2)	CH_2Cl_2	–78	64	7	5
4	$(DHQD)_2Pyr$	$TsNBr_2$ (1.2)	CH_2Cl_2	–78	64	6	4
5	$(DHQD)_2Pyr$	NBS (1.2)/$NsNH_2$ (1.2)	CH_2Cl_2	–78	80	8	5
6	cinchonidine	$NsNBr_2$ (1.2)	CH_2Cl_2	–78	65	29	4
7	$(DHQD)_2Pyr$	$NsNBr_2$ (1.2)	CH_2Cl_2	–78	65	25	11
8	$(DHQ)_2PHAL$	$NsNBr_2$ (1.2)	CH_2Cl_2	–78	65	40	0
9	**S4a**	$NsNBr_2$ (1.2)	CH_2Cl_2	–78	65	63	0
10	**S4b**	$NsNBr_2$ (1.2)	CH_2Cl_2	–78	76	5	2
11	**S4c**	$NsNBr_2$ (1.2)	CH_2Cl_2	–78	76	20	0
12	**S4d**	$NsNBr_2$ (1.2)	CH_2Cl_2	–78	76	17	2
13	**8d**	$NsNBr_2$ (1.2)	CH_2Cl_2	–78	76	50	49
14	**8d**	NBS (1.2)/$NsNH_2$ (1.2)	CH_2Cl_2	–78	80	11	37
15	**8d**	$NsNBr_2$ (1.2)	CH_2Cl_2	–50	76	59	47
16	**4a**	$NsNBr_2$ (1.2)	CH_2Cl_2	–50	42	44	51
17	**4a**	$TsNBr_2$ (1.2)	CH_2Cl_2	–50	96	30	15
18	**4a**	$NsNBr_2$ (0.6)/$NsNH_2$	CH_2Cl_2	–50	60	23	44
19	**4a**	NBP (1.2)/$NsNH_2$ (1.2)	CH_2Cl_2	–50	138	27	49
20	**4a**	DBDMH (1.2)/$NsNH_2$	CH_2Cl_2	–50	138	Trace	-
21	**4a**	$NsNBr_2$ (1.2)	Toluene	–40	96	Trace	-
22	**4a**	$NsNBr_2$ (1.2)	Et_2O	–50	96	70	0
23	**4a**	$NsNBr_2$ (1.2)	CH_2Cl_2/toluene, 1:1	–50	138	49	57
24	**4a**	$NsNBr_2$ (1.2)	CH_2Cl_2/hexane, 1:1	–50	96	71	26
25	**4a**	$NsNBr_2$ (1.2)	$CHCl_3$/$ClCH_2CH_2Cl$,	–50	98	61	46
26	**4a**	$NsNBr_2$ (1.2)	CH_2Cl_2/toluene, 1:2	–50	138	36	41
27	**4a**	$NsNBr_2$ (1.2)	CH_2Cl_2/toluene, 2:1	–50	138	37	54
28	**4a**	$NsNBr_2$ (1.2)	CH_2Cl_2/toluene, 2:3	–50	75	24	59
29	**4a**	$NsNBr_2$ (1.2)	CH_2Cl_2/toluene, 2:3	–40	96	59	63
30	**4a**	$NsNBr_2$ (1.2)	CH_2Cl_2/toluene, 2:3	–30	72	53	47
31	**4s**	$NsNBr_2$ (1.2)	CH_2Cl_2/toluene, 2:3	–40	96	67	90
32	**4s**	$NsNBr_2$ (1.2)	CH_2Cl_2/toluene, 2:3	–35	120	64	86[c]

[a] Reactions were carried out with **1a** (0.20 mmol), catalyst (0.02 mmol) and bromine source (equiv), amine source (equiv) in solvent (0.04 M) in the absence of light. [b] Isolated yield by two steps. [c] The concentration is 0.1 M.

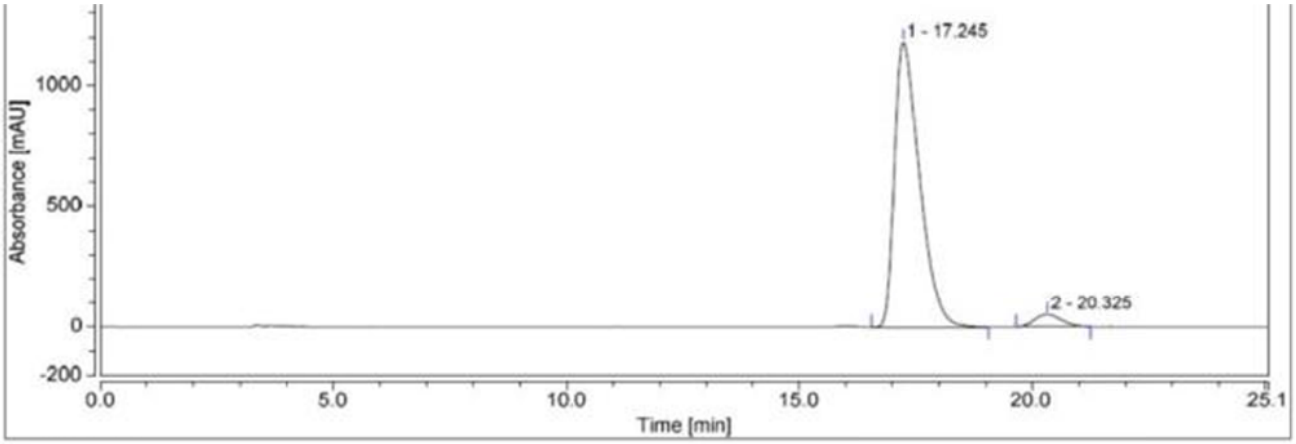


(*1R,2R*)-*N*-(-2-Bromo-3-((*tert*-butyldimethylsilyl)oxy)-1-phenylpropyl)-4-nitrobenzenesulfonamide (3a)

White solide, $[\alpha]_D^{20}$ –51.9 (*c* 1.0, $CHCl_3$, 91% ee); IR (KBr): 3297, 2928, 1606, 1348, 1310, 1012, 836 cm^{-1}; ^{1}HNMR (400 MHz,) δ 8.15 (d, *J* = 8.5 Hz, 2H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.18-7.21 (m, 5H), 6.68 (d, *J* = 7.2 Hz, 1H), 4.97 (dd, *J* = 6.8, 4.0 Hz, 1H), 4.20 (s, 1H), 3.81 (d, *J* = 11.2 Hz, 1H), 3.52 (dd, *J* = 11.2, 5.6 Hz, 1H), 0.98 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 146.3, 136.3, 128.4, 128.4, 128.2, 127.3, 123.8, 64.2, 61.3, 54.8, 25.7, 18.1, –5.56, –5.61; HRMS (ESI) calcd for $C_{21}H_{29}BrN_2O_5SSiNa$ *m/z* $[M + Na]^+$: 551.0642, found: 551.0655; HPLC (Daicel Chiralpak IC, *i*-PrOH/hexane = 8/92, 1.0 mL/min, 250 nm) t_1 = 17.2 min (major), t_2 = 20.3 min (minor).

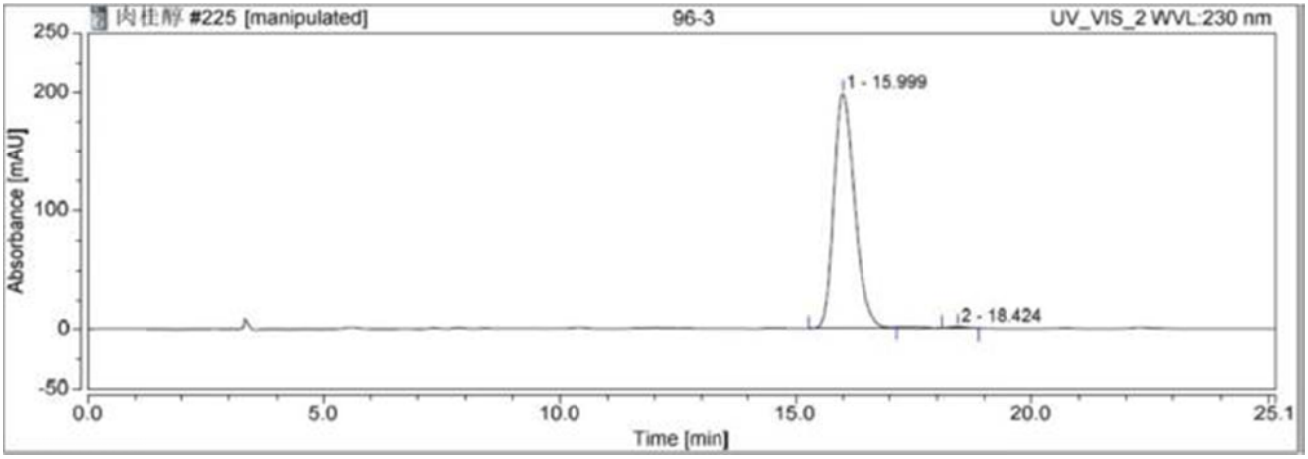


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.245	861.976	1243.837	50.75	57.20	n.a.
2		19.772	803.527	930.809	49.25	42.80	n.a.
Total:			**1665.503**	**2174.646**	**100.00**	**100.00**	



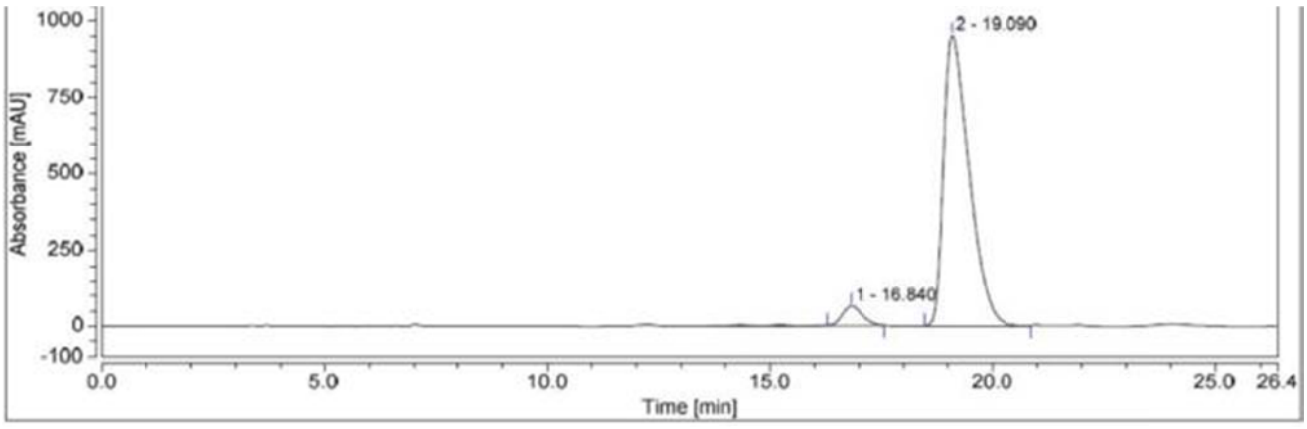
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.245	728.990	1181.208	95.48	95.79	n.a.
2		20.325	34.547	51.869	4.52	4.21	n.a.
Total:			**763.537**	**1233.077**	**100.00**	**100.00**	

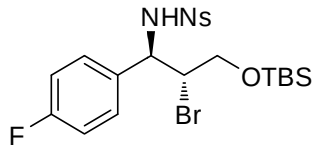


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.999	102.631	198.939	99.42	99.34	n.a.
2		18.424	0.598	1.317	0.58	0.66	n.a.
Total:			**103.230**	**200.257**	**100.00**	**100.00**	

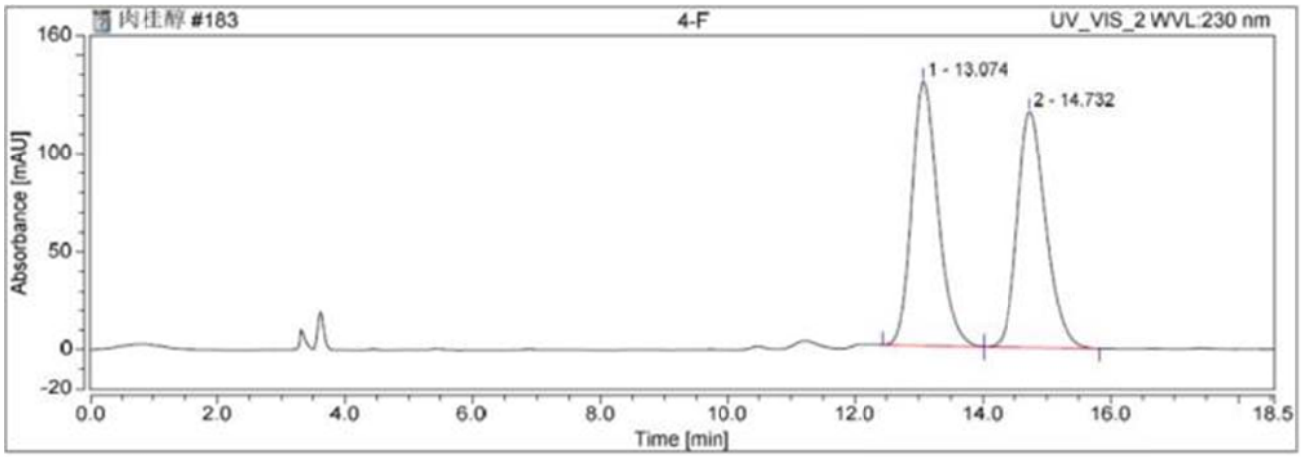


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.840	34.311	65.172	5.17	6.40	n.a.
2		19.090	629.310	952.434	94.83	93.60	n.a.
Total:			**663.622**	**1017.606**	**100.00**	**100.00**	

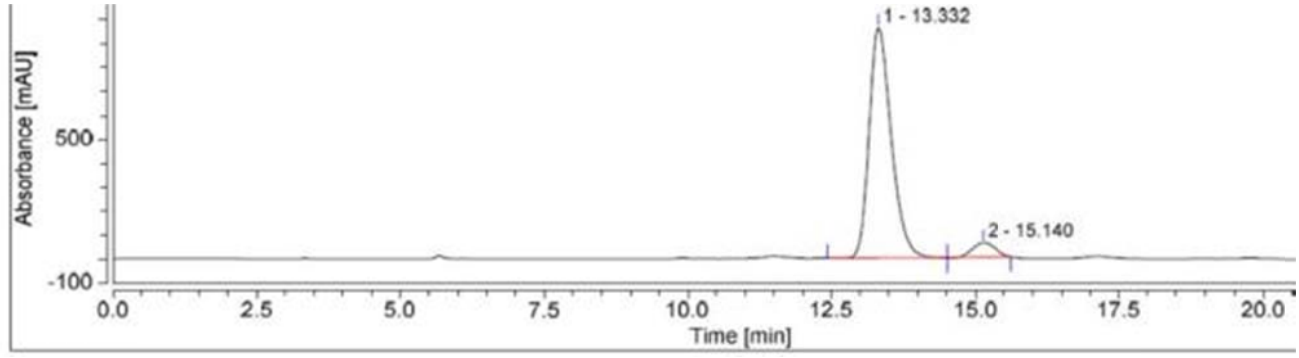


***N*-(2-Bromo-3-((*tert*-butyldimethylsilyl)oxy)-1-(4-fluorophenyl)propyl)-4-nitrobenzenesulfonamide (3b)**

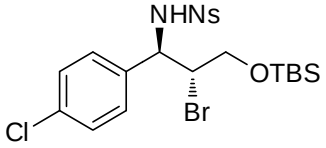
White solide, $[\alpha]_D^{20}$ –21.8 (*c* 0.45, $CHCl_3$, 88% ee); IR (KBr): 3130, 1607, **1**401, 1167, 1092, 838, cm^{-1}; ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.6 Hz, 1H), 7.85 (d, *J* = 8.6 Hz, 2H), 7.22-7.19 (m, 2H), 6.93-6.89 (m, 2H), 6.68 (d, *J* = 6.9 Hz, 1H), 4.95-4.93 (m, 1H), 4.16 (s, 1H), 3.79-3.76 (m, 1H), 3.49-3.45 (m, 1H), 0.98 (s, 9H), 0.09 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, *J* = 247.0 Hz), 149.7, 146.1, 132.2, 129.0, 128.7 (d, *J* = 88.0 Hz), 123.9, 115.3 (d, *J* = 21.0 Hz), 64.0, 60.2, 54.9, 25.7, 18.0, –5.6; HRMS (ESI) calcd for $C_{21}H_{28}BrFN_2O_5SSiNa$ *m/z* $[M + Na]^+$: 569.0548, found: 569.0557, HPLC (Daicel Chiralpak IC, *i*-PrOH/hexane = 8/92, 1.0 mL/min, 230 nm) t_1 = 13.3 min, (major), t_2 = 15.1 min (minor).



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.074	63.596	134.780	50.42	52.77	n.a.
2		14.732	62.547	120.647	49.58	47.23	n.a.
Total:			**126.142**	**255.427**	**100.00**	**100.00**	

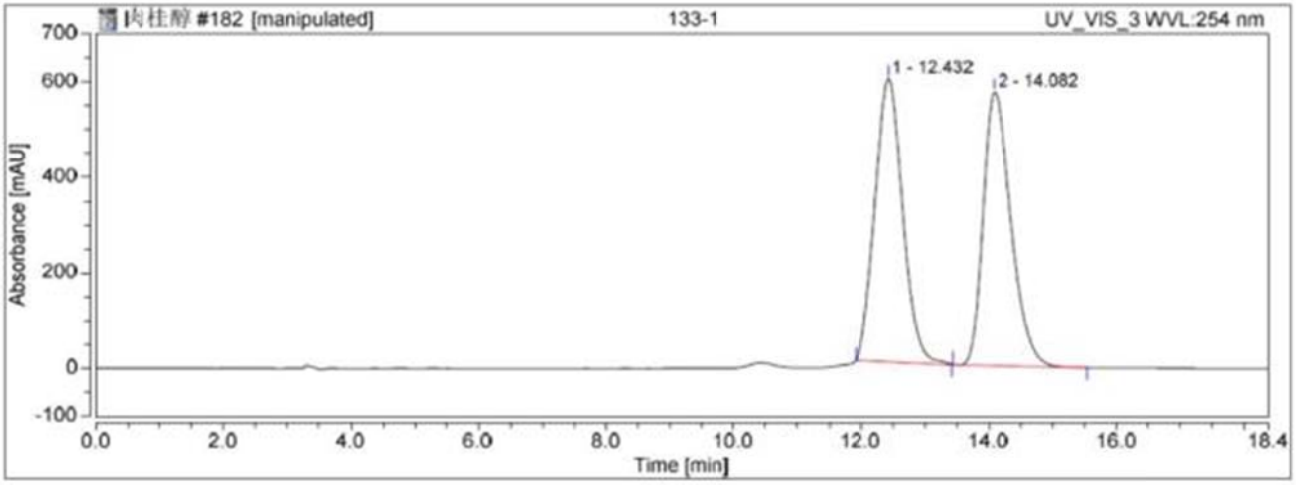


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.332	424.038	961.309	93.98	94.07	n.a.
2		15.140	27.172	60.562	6.02	5.93	n.a.
Total:			**451.210**	**1021.871**	**100.00**	**100.00**	

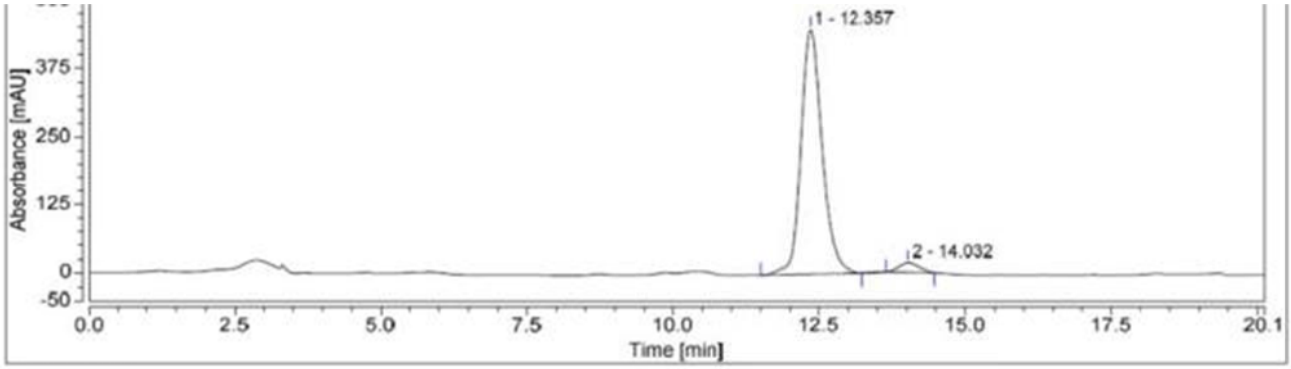


***N*-(2-Bromo-3-((*tert*-butyldimethylsilyl)oxy)-1-(4-chlorophenyl)propyl)-4-nitrobenzenesulfonamide (3c)**

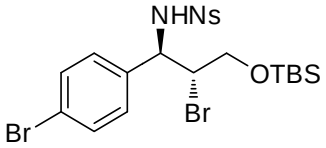
White solide, $[\alpha]_D^{20}$ –35.0 (*c* 2.5, $CHCl_3$, 93% ee), IR (KBr): 3296, 2927, 1607, 1532, 1349, 1311, 1014, 837 cm^{-1}; ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.2 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.2-7.18 (m, 4H), 6.63 (d, *J* = 7.2 Hz, 1H), 4.91 (dd, *J* = 6.8, 4.0 Hz, 1H), 4.14 (s, 1H), 3.79 (d, *J* = 11.3 Hz, 1H), 3.50 (dd, *J* = 11.2, 6.0 Hz, 1H), 0.97 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H). ^{13}CNMR (100 MHz, $CDCl_3$) δ 149.8, 146.18, 135.2, 134.5, 128.7, 128.3, 124.0, 64.2, 60.7, 54.4, 25.7, 18.1, –5.5, –5.6; HRMS (ESI) calcd for $C_{21}H_{28}BrClN_2O_5SSiNa$ *m/z* $[M + Na]^+$: 585.0252, found: 585.0257, HPLC (Daicel Chiralpak IC,*i*-PrOH/hexane = 8/92, 1.0 mL/min, 254 nm) t_1 = 12.3 min (major), t_2 = 14.0 min (minor).



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.432	297.214	593.730	50.46	50.83	n.a.
2		14.082	291.759	574.245	49.54	49.17	n.a.
Total:			**588.973**	**1167.975**	**100.00**	**100.00**	



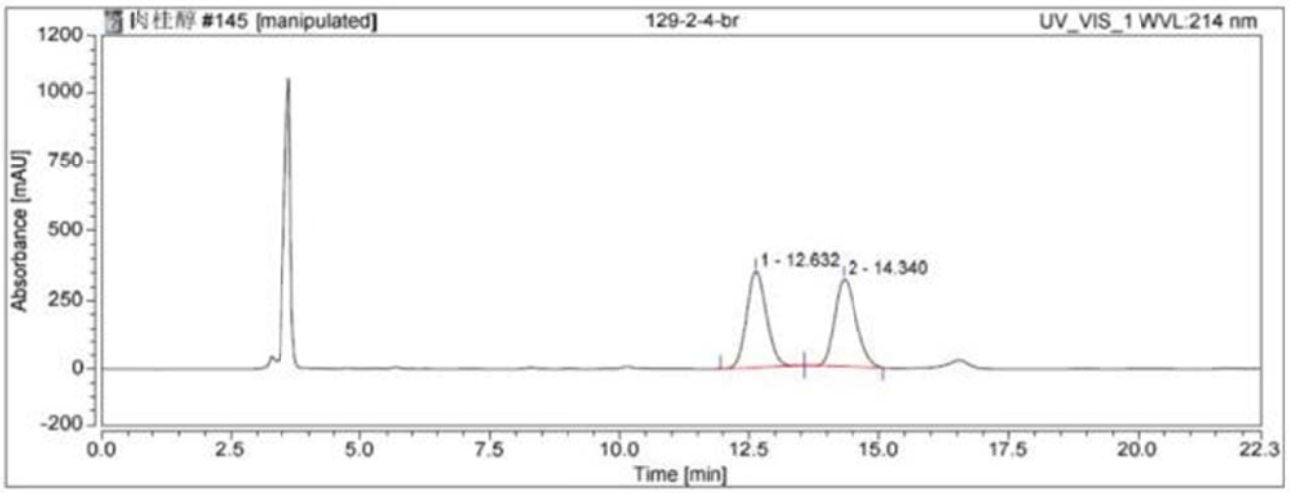
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.357	188.127	448.705	96.46	96.28	n.a.
2		14.032	6.902	17.320	3.54	3.72	n.a.
Total:			**195.029**	**466.024**	**100.00**	**100.00**	



***N*-(2-Bromo-1-(4-bromophenyl)-3-((*tert*-butyldimethylsilyl)oxy)propyl)-4-nitrobenzenesulfonamide (3d)**

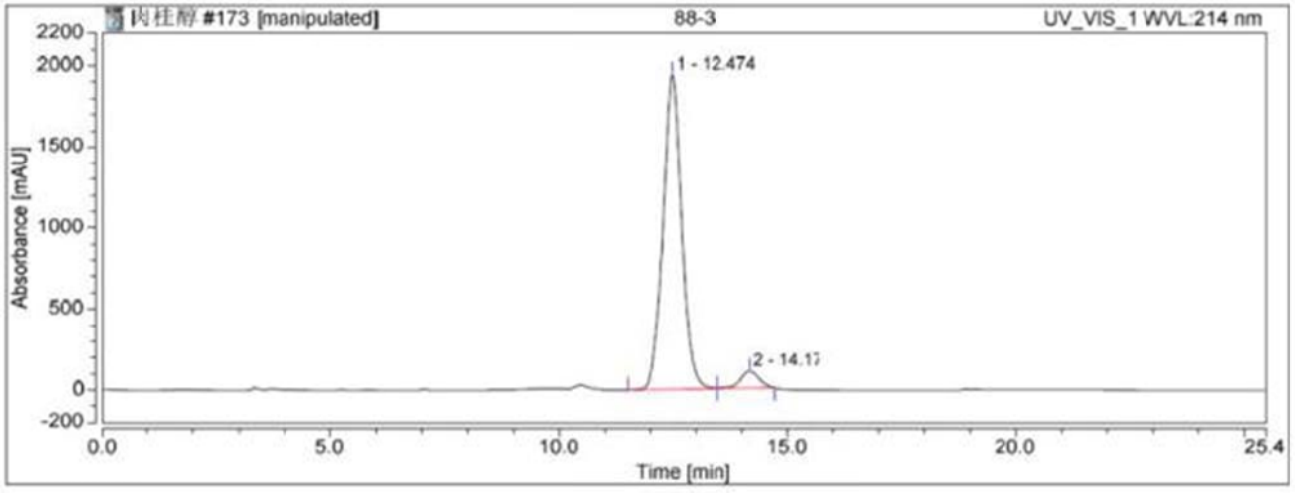
White solide , $[\alpha]_D^{20}$ –32.7 (*c* 2.5, $CHCl_3$, 90% ee); IR (KBr): 3440, 2925, 1736, 1624, 1532, 1463, 1166 cm^{-1}; ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.6 Hz, 2H), 7.85 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 6.63 (d, *J* = 7.0 Hz, 1H), 4.90 (dd, *J* = 6.4, 4.4 Hz, 1H), 4.14 (s, 1H), 3.81 (d, *J* = 11.3 Hz, 1H), 3.51 (dd, *J* = 11.2, 6.0 Hz, 1H), 0.97 (s, 9H), 0.10 (s, 3H),

0.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 146.0, 135.7, 131.6, 128.9, 128.3, 124.0, 122.5, 64.1, 60.9, 54.2, 25.7, 18.1, –5.5, –5.6; HRMS (ESI) calcd for $C_{21}H_{28}Br_2N_2O_5SSiNa$ *m/z* $[M + Na]^+$: 628.9747, found: 628.9753; HPLC (Daicel Chiralpak IC, *i*-PrOH/hexane = 8/92, 1.0 mL/min, 214 nm) t_1 = 12.4 min (major), t_2 = 14.1 min (minor).



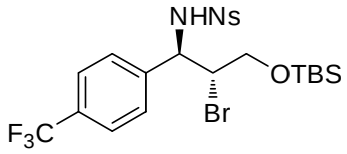
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.632	155.105	350.803	49.93	52.40	n.a.
2		14.340	155.526	318.694	50.07	47.60	n.a.
Total:			**310.631**	**669.496**	**100.00**	**100.00**	



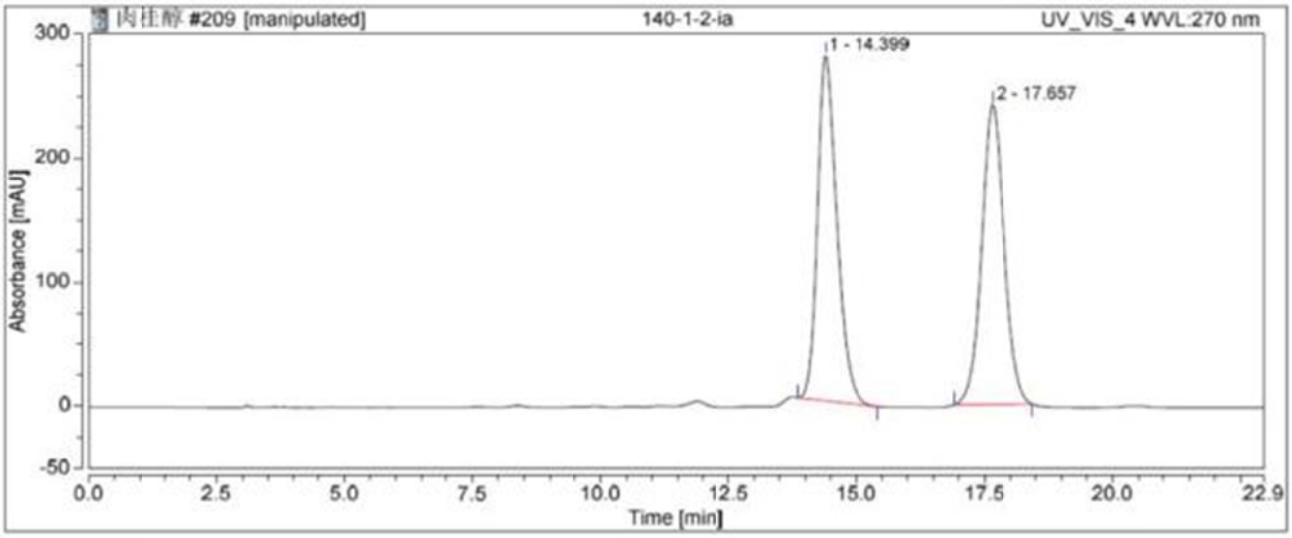
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.474	919.600	1942.626	94.77	94.82	n.a.
2		14.174	50.724	106.195	5.23	5.18	n.a.
Total:			**970.324**	**2048.820**	**100.00**	**100.00**	



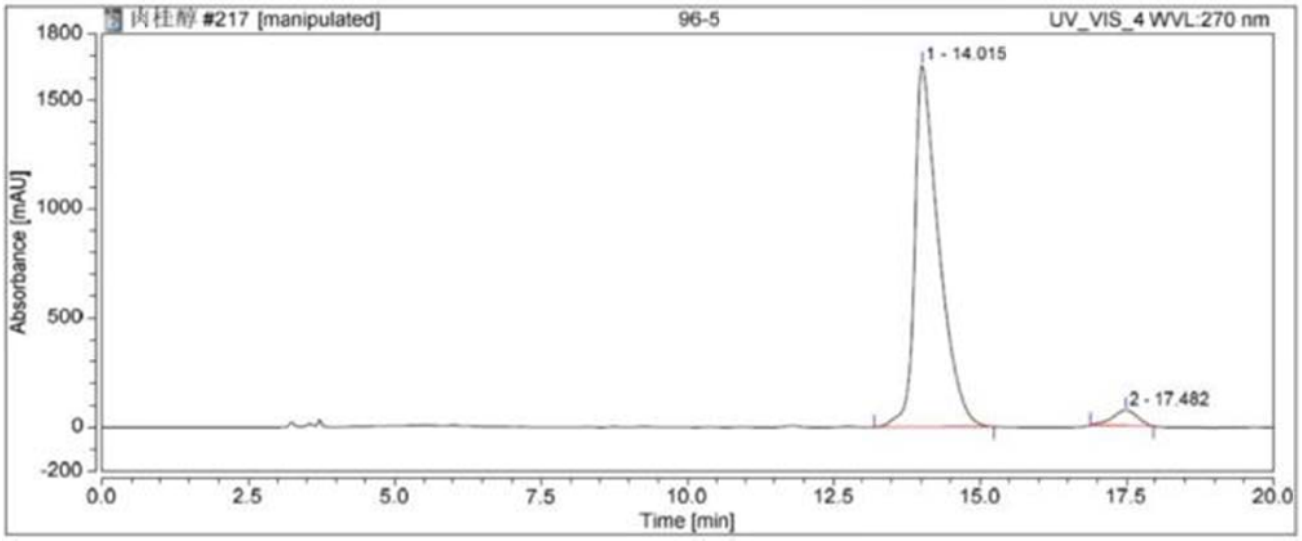
***N*-(2-Bromo-3-((*tert*-butyldimethylsilyl)oxy)-1-(4-(trifluoromethyl)phenyl)propyl)-4-nitrobenzenesulfonamide (3e)**

White solide, $[\alpha]_D^{20}$ –30.3 (*c* 0.5, $CHCl_3$, 92% ee); IR (KBr): 3343, 2928, 1613, 1533, 1466, 1417, 1167, 1129 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.7 Hz, 2H), 7.86 (d, *J* = 8.7 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 6.77 (d, *J* = 7.4 Hz, 1H), 5.00 (dd, *J* = 7.2, 4.4 Hz, 1H), 4.18 (dd, *J* = 3.6, 2.4 Hz, 1H), 3.79 (dd, *J* = 11.2, 2.4 Hz, 1H), 3.50 (dd, *J* = 11.2, 6.0 Hz, 1H), 0.98 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 145.9, 140.7, 130.7 (q, *J* = 32 Hz), 128.3, 127.8, 125.5, 125.4 (q, *J* = 3.5 Hz), 124.0, 64.1, 60.9, 53.9, 25.7, 18.0, –5.5, –5.6. HRMS (ESI) calcd for $C_{22}H_{28}BrF_3N_2O_5SSiNa$ *m/z* $[M + Na]^+$: 619.0516, found: 619.0528; HPLC (Daicel Chiralpak IA, *i*-PrOH/hexane = 8/92, 1.0 mL/min, 270 nm) t_1 = 14.0 min, (major), t_2 = 17.4 min (minor).

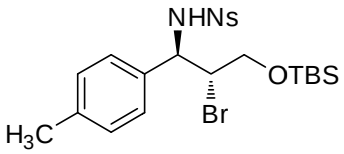


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.399	122.441	278.864	49.64	53.51	n.a.
2		17.657	124.193	242.303	50.36	46.49	n.a.
Total:			**246.634**	**521.167**	**100.00**	**100.00**	

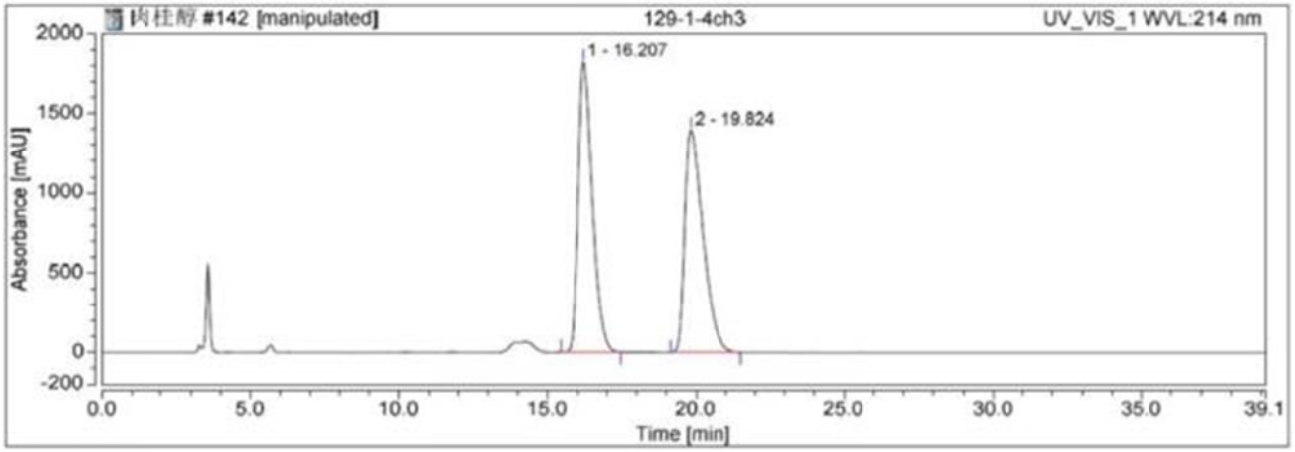


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.015	786.866	1657.364	95.77	95.88	n.a.
2		17.482	34.779	71.154	4.23	4.12	n.a.
Total:			**821.645**	**1728.517**	**100.00**	**100.00**	

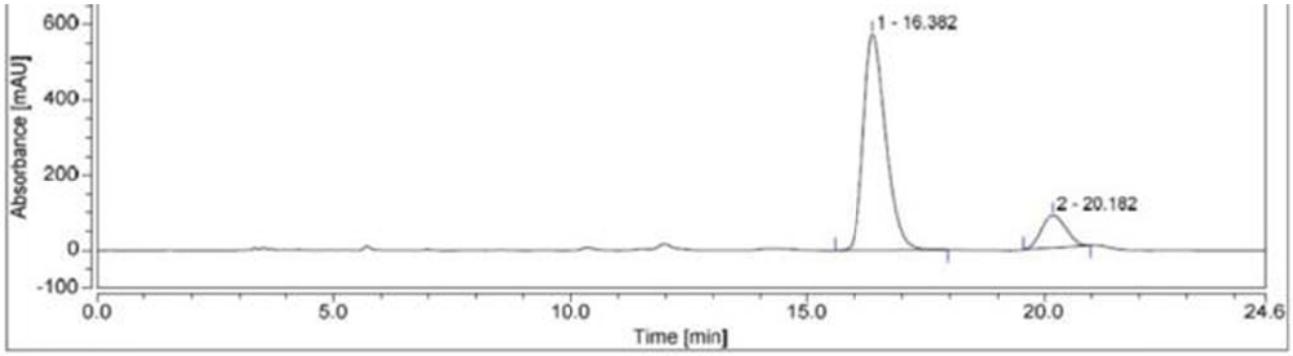


***N*-(2-Bromo-3-((*tert*-butyldimethylsilyl)oxy)-1-(p-tolyl)propyl)-4-nitrobenzenesulfonamide (3f)**

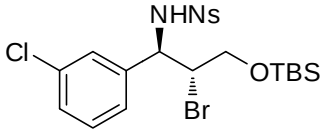
White solide, $[\alpha]_D^{20}$ –15.0 (*c* 1.2, $CHCl_3$, 72% ee) IR (KBr): 3130, 1633, 1531, 1350, 1257, 1166, 1092. 836 cm^{-1}; ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 6.96-6.89 (m, 4H), 6.61 (d, *J* = 7.5 Hz, 1H), 4.92 (dd, *J* = 4.0, 2.8 Hz, 1H), 4.19 (s, 1H), 3.82 (d, *J* = 11.0 Hz, 1H), 3.51 (dd, *J* = 11.2, 6.0 Hz, 1H), 2.27 (s, 3H), 0.97 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 149.5, 146.3, 138.3, 133.2, 129.0, 128.2, 127.3, 123.7, 64.2, 61.0, 55.1, 25.7, 21.0, 18.1, –5.5, –5.6. HRMS (ESI) calcdfor $C_{22}H_{31}BrN_2O_5SSiNa$ *m/z* $[M + Na]^+$: 565.0799, found: 565.0808; HPLC (Daicel Chiralpak IC, *i*-PrOH/hexane = 8/92, 1.0 mL/min, 214 nm) t_1 = 16.3 min (major), t_2 = 20.1 min (minor).



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.207	1009.970	1822.077	50.19	56.64	n.a.
2		19.824	1002.335	1394.988	49.81	43.36	n.a.
Total:			**2012.305**	**3217.065**	**100.00**	**100.00**	



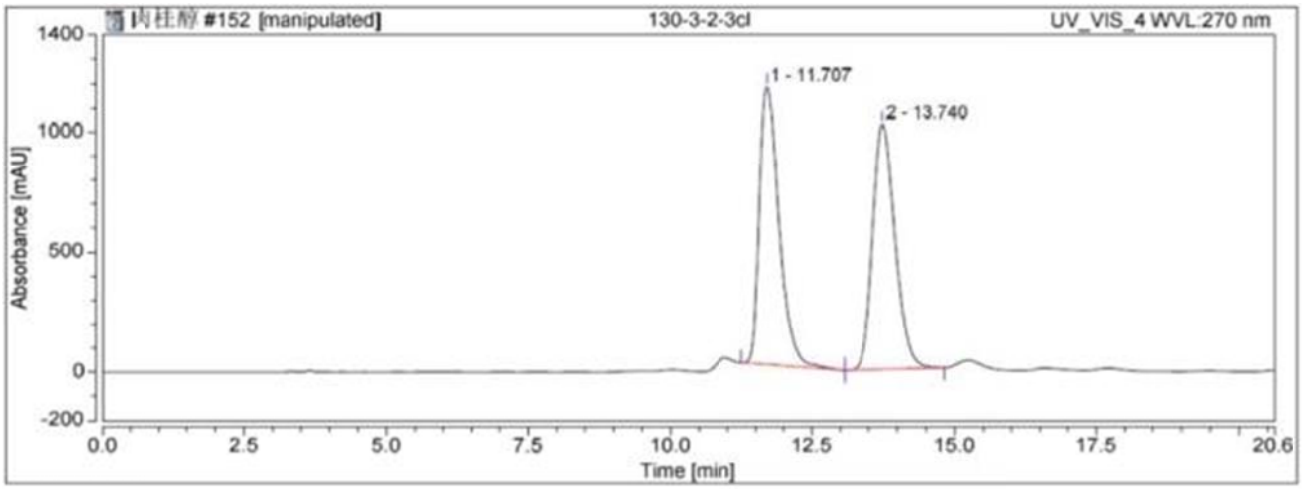
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.382	313.227	575.318	85.79	86.90	n.a.
2		20.182	51.872	86.694	14.21	13.10	n.a.
Total:			**365.099**	**662.011**	**100.00**	**100.00**	



***N*-(2-Bromo-3-((*tert*-butyldimethylsilyl)oxy)-1-(3-chlorophenyl)propyl)-4-nitrobenzenesulfonamide (3g)**

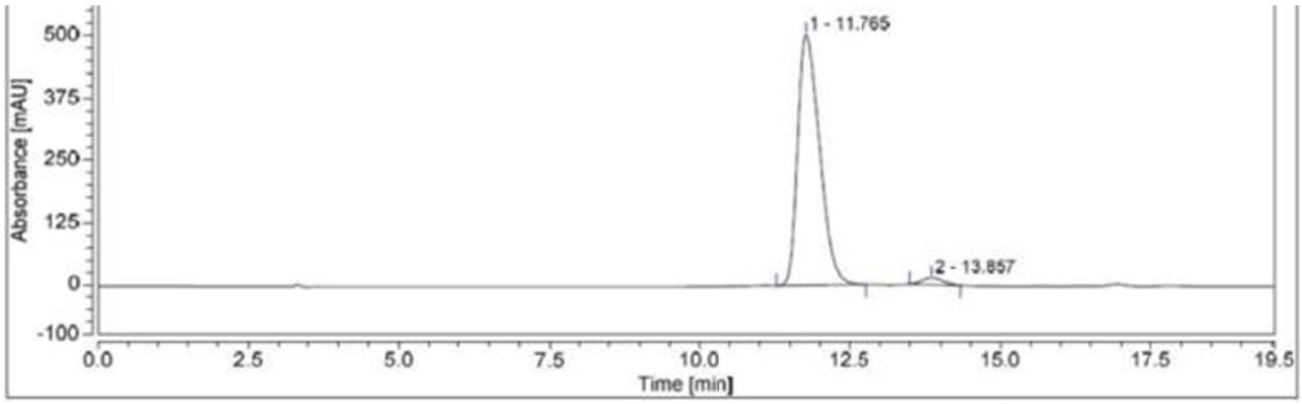
Light yellow oil, $[\alpha]_D^{20}$ –22.4 (*c* 2.6, $CHCl_3$, 95% ee); IR (KBr): 3295, 2929, 1730, 1532, 1350, 1168, 1091 cm^{-1}; ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.1 Hz, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.19-7.1 (m, 4H), 6.63 (d, *J* = 7.0 Hz, 1H), 4.94 (s, 1H), 4.17 (s, 1H), 3.80 (d, *J* = 11.0 Hz, 1H), 3.51 (dd, *J* = 11.2, 6.0 Hz, 1H), 0.90 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 149.7, 146.0, 138.2, 134.4, 129.7, 128.5, 128.1, 127.5, 125.7, 123.9, 64.1, 60.5, 54.2, 25.7, 18.0, –5.6, –5.7.

HRMS (ESI) calcd for $C_{21}H_{28}BrClN_2O_5SSiNa$ *m/z* $[M + Na]^+$: 585.0252, found: 585.0261; HPLC (Daicel Chiralpak IC, *i*-PrOH/hexane = 8/92, 1.0 mL/min, 270 nm) t_1 = 11.8 min (major), t_2 = 13.9 min (minor).



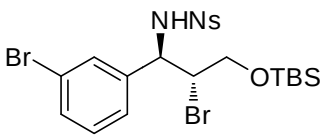
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.707	465.618	1156.906	49.99	53.10	n.a.
2		13.740	465.877	1021.763	50.01	46.90	n.a.
Total:			**931.495**	**2178.669**	**100.00**	**100.00**	



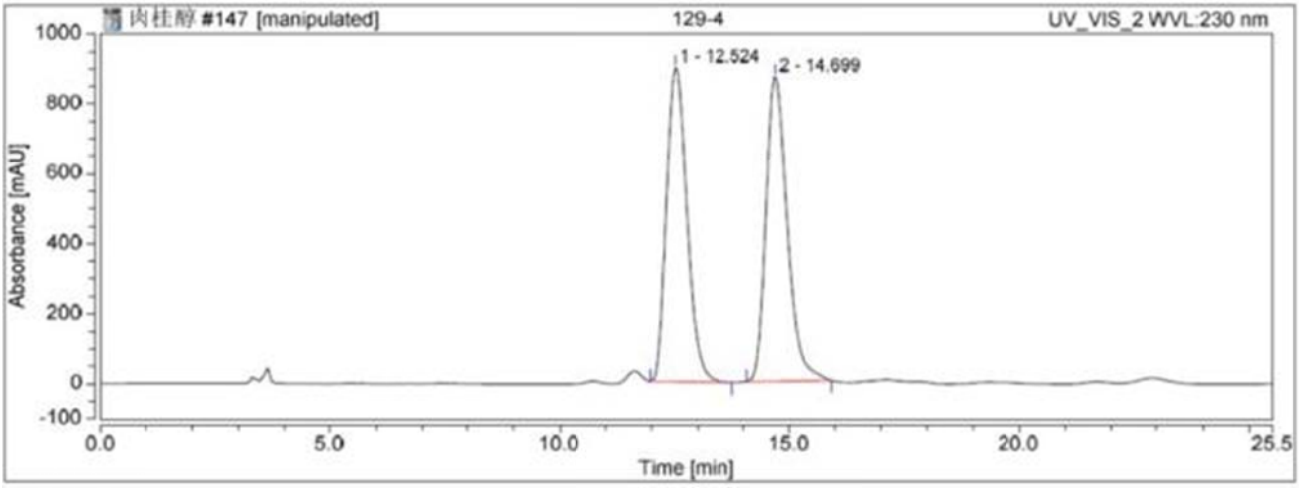
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.765	211.888	502.759	97.42	97.35	n.a.
2		13.857	5.617	13.661	2.58	2.65	n.a.
Total:			**217.505**	**516.420**	**100.00**	**100.00**	

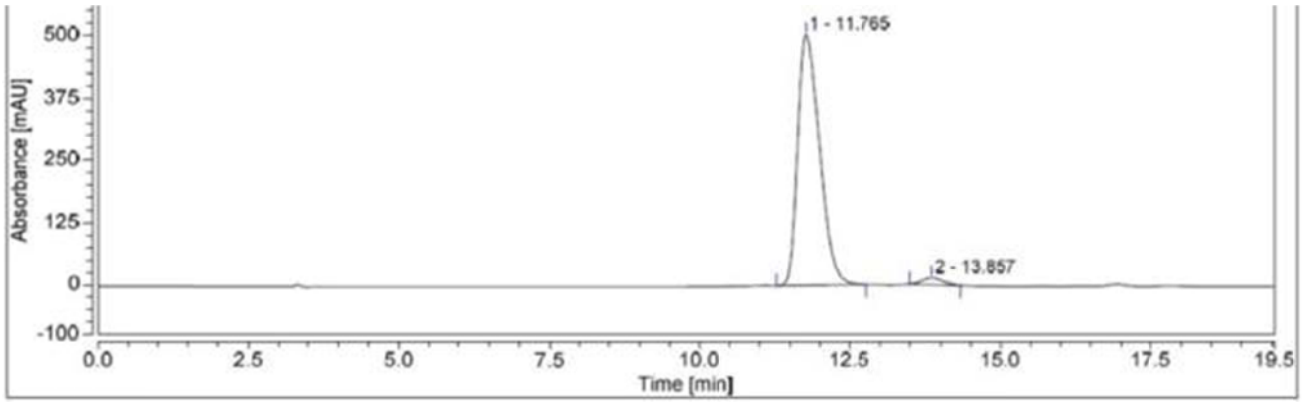


_N_-(2-Bromo-1-(3-bromophenyl)-3-((*tert*-butyldimethylsilyl)oxy)propyl)-4-nitrobenzenesulfonamide (3h)

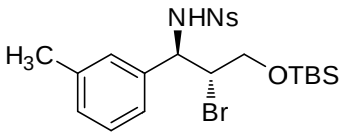
White solide, $[\alpha]_D^{20}$ –28.5 (*c* 2.7, $CHCl_3$, 91% ee); IR (KBr): 3129, 1605, 1257, 1167, 838, 782, 739, 687 cm^{-1}; ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.4 Hz, 2H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.20 (m, 4H), 6.60 (d, *J* = 6.6 Hz, 1H), 4.92 (d, *J* = 4.3 Hz, 1H), 4.16 (s, 1H), 3.80 (d, *J* = 11.2 Hz, 1H), 3.50 (dd, *J* = 11.2, 6.0 Hz, 1H), 0.98 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 149.8, 146.1, 138.4, 131.5, 130.5, 130.0, 128.1, 126.3, 123.9, 122.6, 64.2, 60.5, 54.1, 25.7, 18.1, –5.5, –5.6. HRMS (ESI) calcd for $C_{21}H_{28}Br_2N_2O_5SSiNa$ *m/z* $[M + Na]^+$: 628.9747, found: 628.9766; HPLC (Daicel Chiralpak IC, *i*-PrOH/hexane = 8/92, 1.0 mL/min, 230 nm) t_1 = 12.2 min (major), t_2 = 14.2 min (minor).



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.524	463.579	897.881	49.86	50.77	n.a.
2		14.699	466.157	870.618	50.14	49.23	n.a.
Total:			**929.736**	**1768.499**	**100.00**	**100.00**	

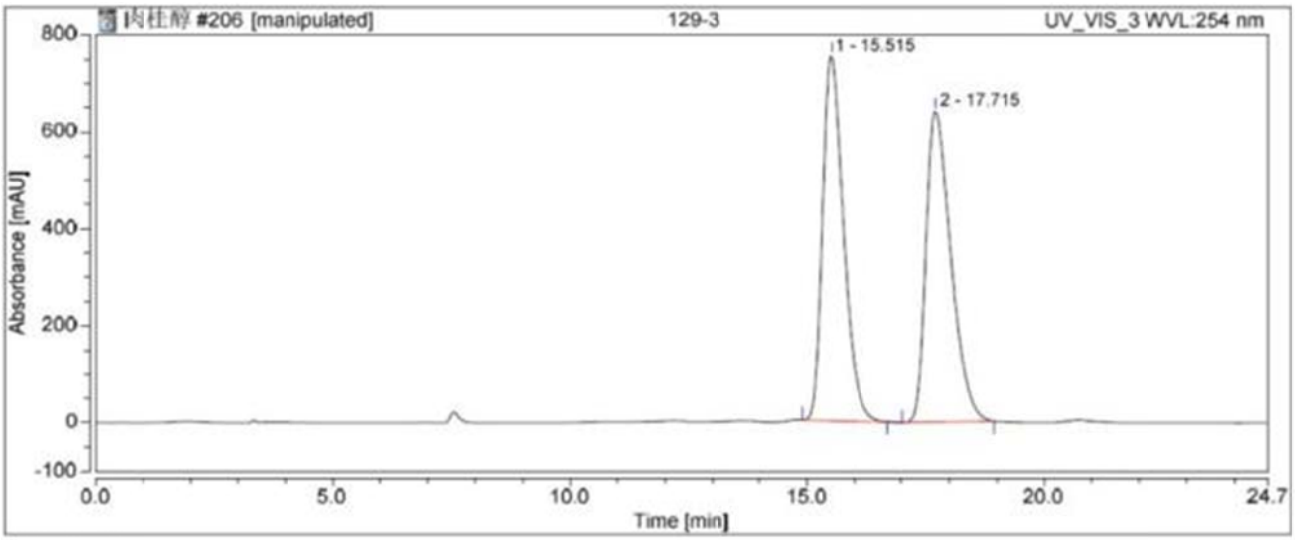


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.232	413.062	865.217	95.49	94.95	n.a.
2		14.232	19.496	46.032	4.51	5.05	n.a.
Total:			**432.558**	**911.249**	**100.00**	**100.00**	

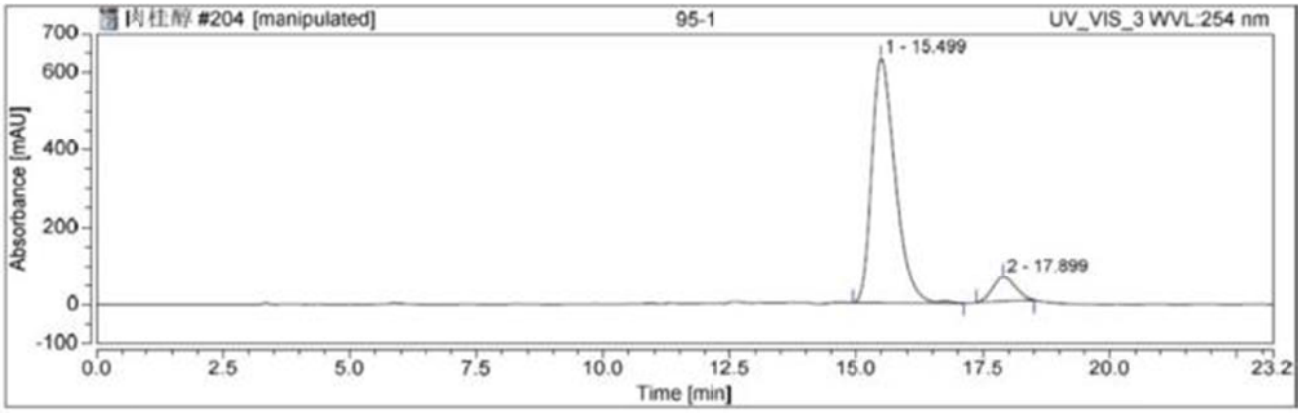


***N*-(2-Bromo-3-((*tert*-butyldimethylsilyl)oxy)-1-(m-tolyl)propyl)-4-nitrobenzenesulfonamide (3i)**

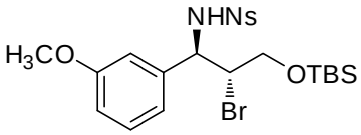
White solide, $[\alpha]_D^{20}$ –21.6 (*c* 1.0, $CHCl_3$, 82% ee); IR (KBr): 3129, 1610, 1531, 1351, 1167, 1095, 839 cm^{-1}; ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.2 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.05-6.91 (m, 4H), 6.69 (d, *J* = 7.6 Hz, 1H), 4.93 (s, 1H), 4.19 (s, 1H), 3.79 (d, *J* = 9.3 Hz, 1H), 3.50 (dd, *J* = 11.2, 6.0 Hz,1H), 2.16 (s, 3H), 0.89 (s, 9H), 0.09 (s, 3H), 0.07 (s, 3H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 149.4, 148.9, 146.2, 137.8, 135.9, 128.9, 128.1, 128.0, 124.5, 123.5, 64.1, 60.9, 55.0, 25.6, 21.1, 18.0, –5.6, –5.7; HRMS (ESI) calcd for $C_{22}H_{31}BrN_2O_5SSiNa$ *m/z* $[M + Na]^+$: 565.0799, found: 565.0801; HPLC (Daicel Chiralpak IC, *i*-PrOH/hexane = 8/92, 1.0 mL/min, 254 nm) t_1 = 15.4 min (major), t_2 = 17.8 min (minor).



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.515	386.549	754.005	49.94	54.02	n.a.
2		17.715	387.440	641.704	50.06	45.98	n.a.
Total:			**773.990**	**1395.710**	**100.00**	**100.00**	

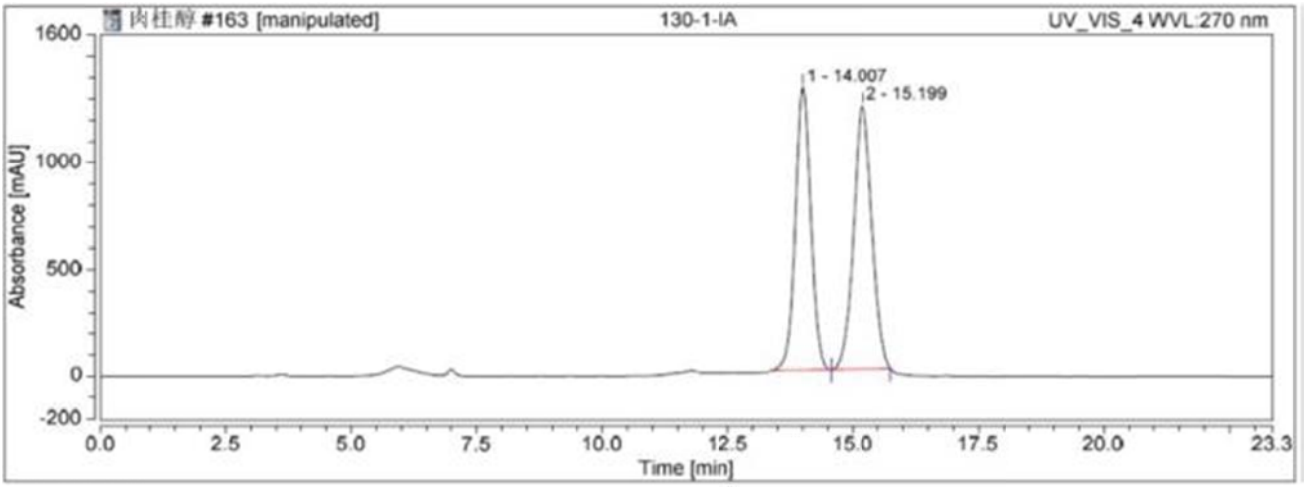


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.499	336.881	632.804	90.76	90.78	n.a.
2		17.899	34.295	64.297	9.24	9.22	n.a.
Total:			**371.176**	**697.100**	**100.00**	**100.00**	

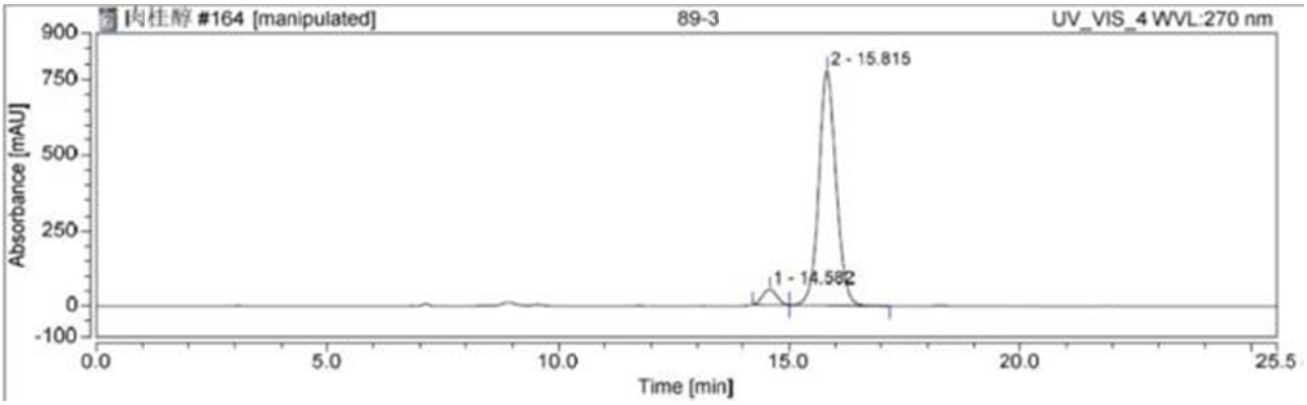


***N*-(2-Bromo-3-((*tert*-butyldimethylsilyl)oxy)-1-(3-methoxyphenyl)propyl)-4-nitrobenzenesulfonamide (3j)**

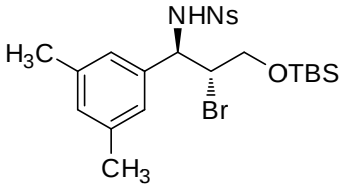
Colourless oil, $[\alpha]_D^{20}$ –22.2 (*c* 2.4, $CHCl_3$, 90% ee); IR (KBr): 3453, 2928, 1604, 1349, 1258, 1165, 1092 cm^{-1}; ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.1 Hz, 2H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.77-6.64 (m, 4H), 4.94 (d, *J* = 4.0 Hz, 1H), 4.20 (s, 1H), 3.83 (d, *J* = 11.2 Hz, 1H), 3.67 (s, 3H), 3.52 (dd, *J* = 11.2, 6.0 Hz, 1H), 0.96 (s, 9H), 0.10 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 149.5, 146.2, 137.6, 129.4, 128.1, 123.7, 119.7, 113.3, 113.2, 64.2, 61.0, 55.0, 54.8, 25.7, 18.0, –5.6, –5.7. HRMS (ESI) calcd for $C_{22}H_{31}BrN_2O_6SSiNa$ *m/z* $[M + Na]^+$: 581.0748, found: 581.0731; HPLC (Daicel Chiralpak IC, i-PrOH/hexane = 10/90, 1.5mL/min, 270 nm) t_1 = 18.2 min (major), t_2 = 22.2 min (minor).



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.007	473.857	1327.324	48.96	51.72	n.a.
2		15.199	535.235	1239.033	51.04	48.28	n.a.
Total:			**1009.093**	**2566.357**	**100.00**	**100.00**	



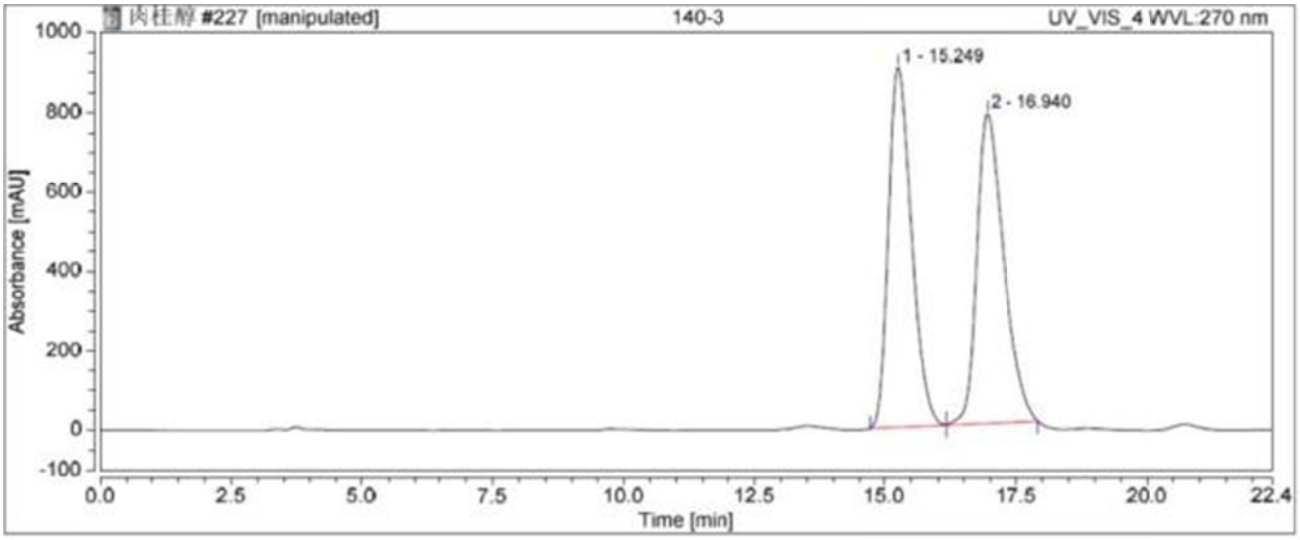
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.582	18.266	51.410	5.16	6.21	n.a.
2		15.815	335.427	776.946	94.84	93.79	n.a.
Total:			**353.693**	**828.356**	**100.00**	**100.00**	



***N*-(2-Bromo-3-((*tert*-butyldimethylsilyl)oxy)-1-(3,5-dimethylphenyl)propyl)-4-nitrobenzenesulfonamide (3k)**

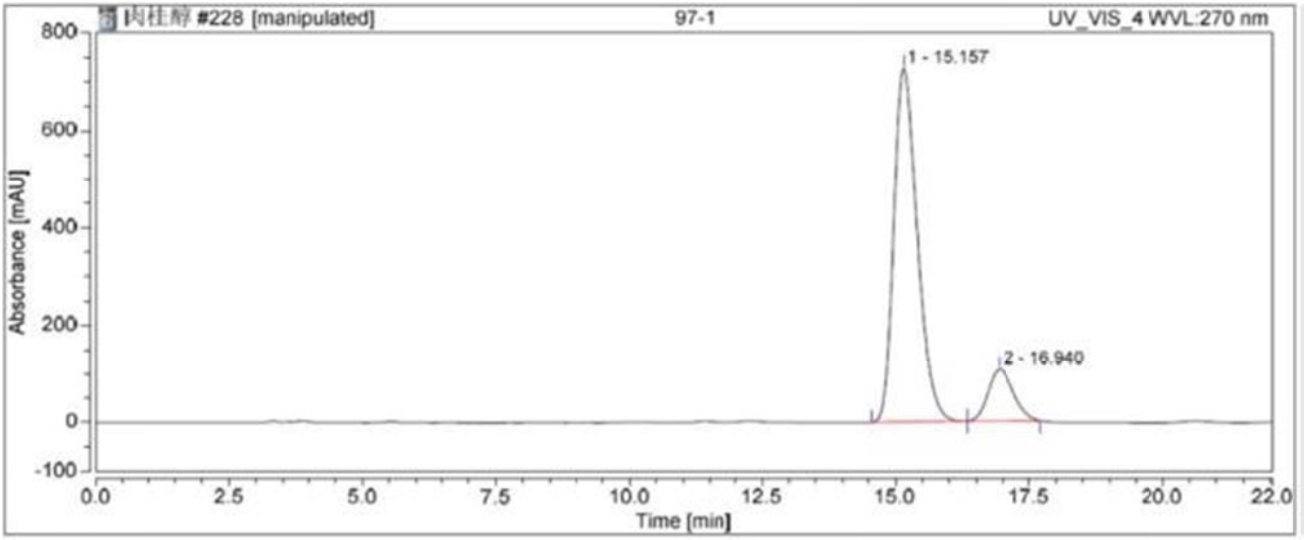
Yellow solide, $[\alpha]_D^{20}$ –17.7 (*c* 0.7, $CHCl_3$, 72% ee) IR (KBr): 3361, 2972, 1068, 1532, 1348, 1165, 952 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.6 Hz, 2H), 7.80 (d, *J* = 8.6 Hz, 2H), 6.82 (s, 1H), 6.72 (d, *J* = 12.5 Hz, 2H), 6.62 (d, *J* = 7.7 Hz, 1H), 4.88 (dd, *J* = 7.4, 4.1 Hz, 1H), 4.17 (s, 1H),

3.82 (m, 1H), 3.53 (dd, J = 11.2, 5.4 Hz, 1H), 2.17 (s, 3H), 2.13 (s, 3H), 0.98 (s, 9H), 0.11 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 146.4, 137.9, 136.1, 129.8, 128.2, 125.2, 123.5, 64.3, 61.4, 54.7, 25.7, 21.1, 18.1, –5.7; HRMS (ESI) calcd for $C_{23}H_{33}BrN_2O_5SSiNa$ *m/z* $[M + Na]^+$: 579.0955, found: 579.0954; HPLC (Daicel Chiralpak IC, *i*-PrOH/hexane = 8/92, 1.0 mL/min, 270 nm) t_1 = 15.1 min (major), t_2 = 16.9 min (minor).



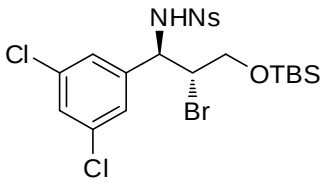
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.249	457.844	905.090	49.55	53.66	n.a.
2		16.940	466.228	781.701	50.45	46.34	n.a.
Total:			**924.072**	**1686.791**	**100.00**	**100.00**	



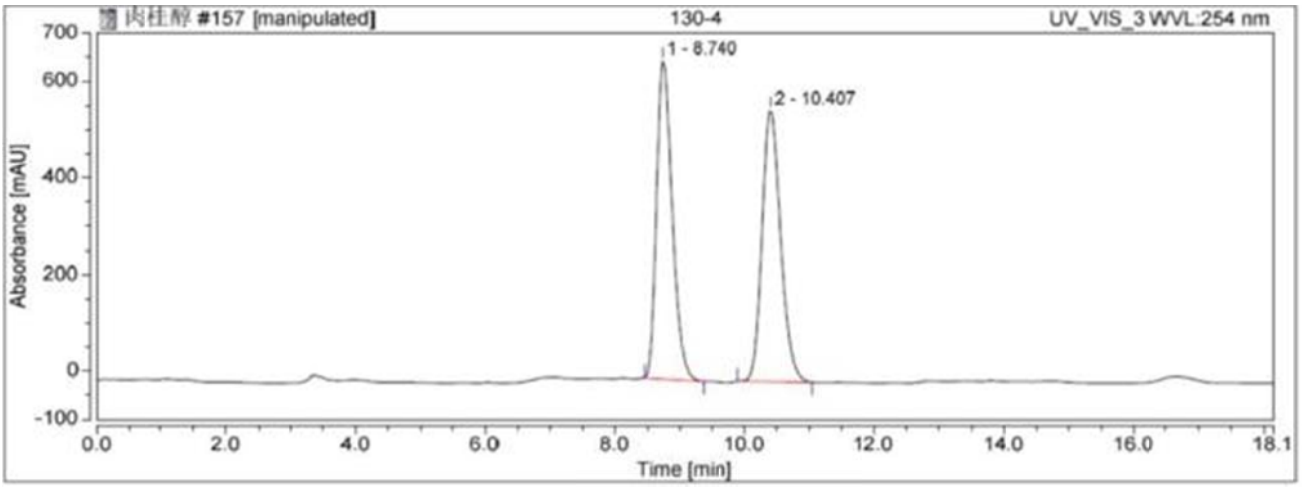
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.157	366.950	726.796	86.08	87.13	n.a.
2		16.940	59.342	107.360	13.92	12.87	n.a.
Total:			**426.292**	**834.156**	**100.00**	**100.00**	

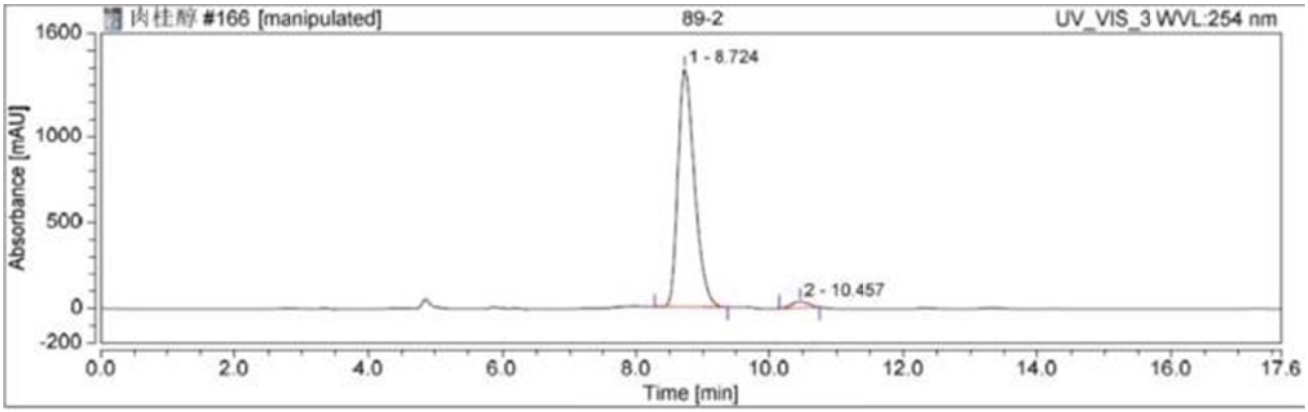


_N_-(2-Bromo-3-((*tert*-butyldimethylsilyl)oxy)-1-(3,5-dichlorophenyl)propyl)-4-nitrobenzenesulfonamide (3l)

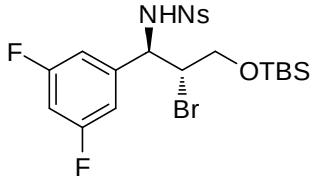
White solide, $[\alpha]_D^{20}$ –9.2 (*c* 2.8, $CHCl_3$, 95% ee), IR (KBr): 3442, 2927, 1609, 1532, 1468, 1350, 1168, 1092 cm^{-1}; ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.24 (s, 1H), 7.07 (s, 2H), 6.59 (d, *J* = 7.0 Hz, 1H), 4.89 (dd, *J* = 6.4, 4.0 Hz, 1H), 4.14-4.09 (m, 1H), 3.80 (d, *J* = 10.5 Hz, 1H), 3.50 (dd, *J* = 11.2, 6.0 Hz, 1H), 0.98 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 149.9, 145.9, 139.6, 135.2, 128.5, 128.2, 126.1, 124.0, 64.2, 60.1, 53.6, 25.7, 18.1, –5.6, –5.7; HRMS (ESI) calcd for $C_{21}H_{27}BrCl_2N_2O_5SSiNa$ *m/z* $[M + Na]^+$: 618.9863, found: 618.9850; HPLC (Daicel Chiralpak IC, *i*-PrOH/hexane = 8/92, 1.0 mL/min, 254 nm) t_1 = 8.7 min (major), t_2 = 10.4 min (minor).



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.740	183.737	661.004	49.62	53.96	n.a.
2		10.407	186.524	564.088	50.38	46.04	n.a.
Total:			**370.261**	**1225.092**	**100.00**	**100.00**	

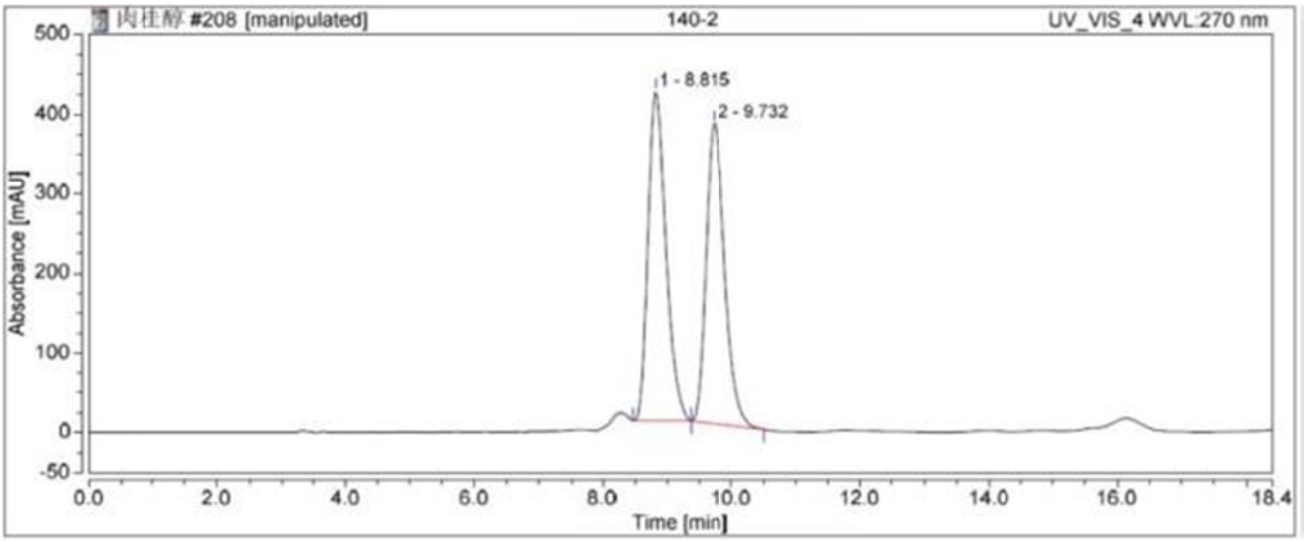


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.724	396.027	1387.302	97.39	97.46	n.a.
2		10.457	10.597	36.180	2.61	2.54	n.a.
Total:			**406.624**	**1423.482**	**100.00**	**100.00**	

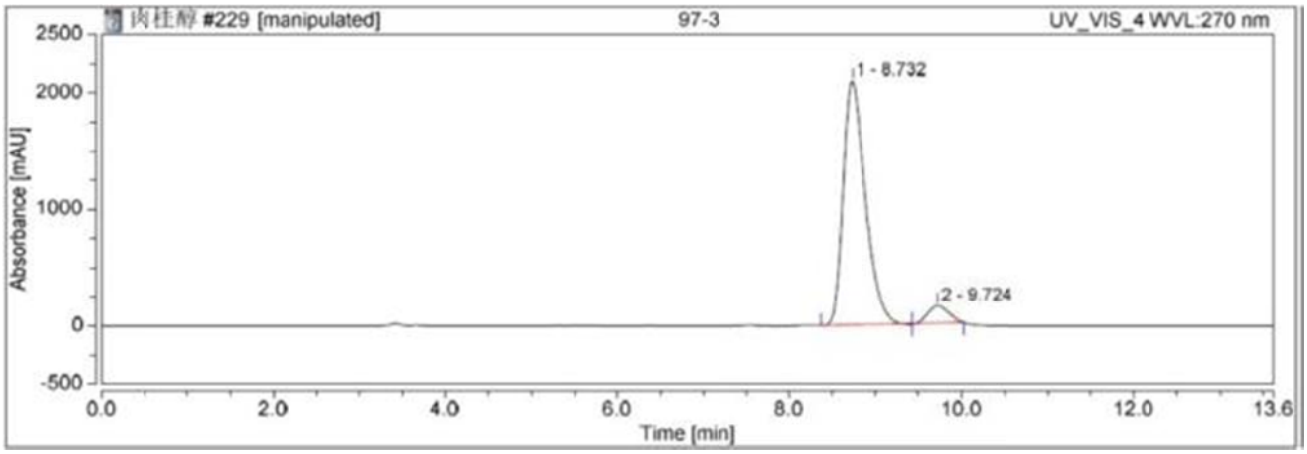


***N*-(2-Bromo-3-((*tert*-butyldimethylsilyl)oxy)-1-(3,5-difluorophenyl)propyl)-4-nitrobenzenesulfonamide (3m)**

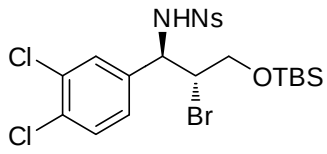
Light yellow oil, $[\alpha]_D^{20}$ –18.0 (*c* 2.3, $CHCl_3$, 88% ee), IR (KBr): 3298, 2925, 1601, 1532, 1352, 1169, 994 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.5 Hz, 2H), 7.90 (d, *J* = 8.6 Hz, 2H), 6.69-6.80 (m, 4H), 4.92 (d, *J* = 3.7 Hz, 1H), 4.15 (s, 1H), 3.80 (d, *J* = 11.3 Hz, 1H), 3.52 (dd, *J* = 11.3, 6.0 Hz, 1H), 0.97 (s, 9H), 0.11 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (dd, *J* = 250.0, 10.0 Hz), 149.9, 145.9, 140.7 (t, *J* = 8.6 Hz), 128.3, 124.0, 110.5 (dd, *J* = 24.2, 4.5 Hz), 103.9 (t, *J* = 24.7 Hz), 64.1, 60.4, 53.7, 25.7, 18.0, –5.6, –5.7. HRMS (ESI) calcd for $C_{21}H_{27}BrF_2N_2O_5SSiNa$ *m/z* $[M + Na]^+$: 587.0454, found: 587.0452; HPLC (Daicel Chiralpak IC, *i*-PrOH/hexane = 8/92, 1.0 mL/min, 270 nm) t_1 = 8.7 min (major), t_2 = 9.7 min (minor).



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.815	132.937	414.419	50.96	52.27	n.a.
2		9.732	127.926	378.495	49.04	47.73	n.a.
Total:			**260.863**	**792.914**	**100.00**	**100.00**	



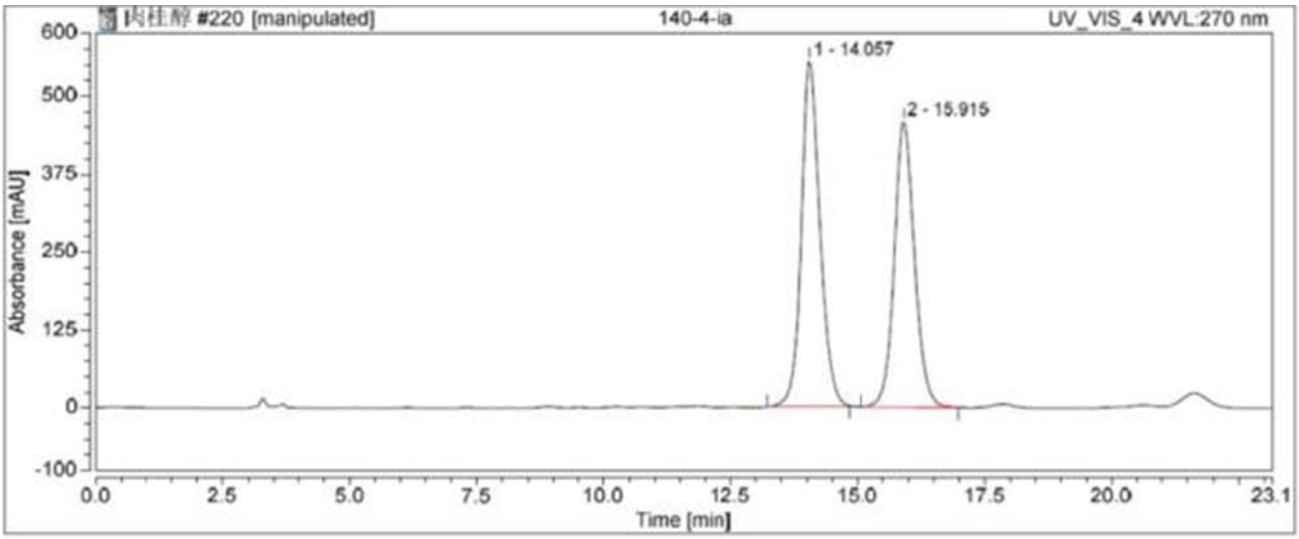
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.732	628.688	2095.380	93.76	93.34	n.a.
2		9.724	41.856	149.628	6.24	6.66	n.a.
Total:			**670.544**	**2245.009**	**100.00**	**100.00**	



_N_-(2-Bromo-3-((*tert*-butyldimethylsilyl)oxy)-1-(3,4-dichlorophenyl)propyl)-4-nitrobenzenesulfonamide (3n)

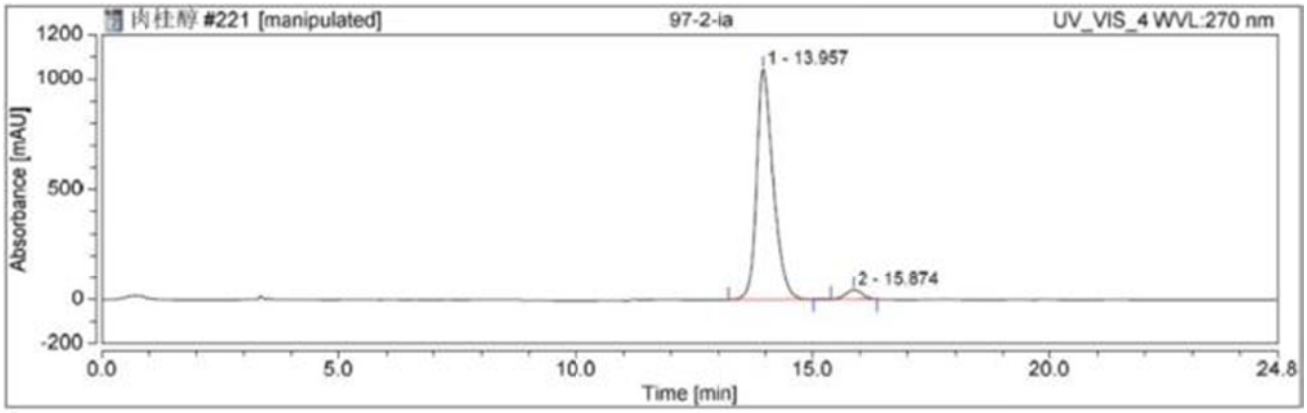
White solide, $[\alpha]_D^{20}$ –35.0 (*c* 0.4, $CHCl_3$, 92% ee); IR (KBr): 3301, 2927, 1607, 1532, 1350, 1168, 1092, 837 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.5 Hz, 2H), 7.85 (d, *J* = 8.5 Hz, 2H),

7.36-7.34 (m, 2H), 7.11 (d, *J* = 8.1 Hz, 1H), 6.61 (d, *J* = 7.0 Hz, 1H), 4.89 (dd, *J* = 4.4, 2.8 Hz, 1H), 4.13 (d, *J* = 2.4 Hz, 1H), 3.82-3.79 (m, 1H), 3.50 (dd, *J* = 11.2, 6.0 Hz, 1H), 0.97 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 145.9, 136.7, 132.8, 130.4, 129.4, 128.2, 126.8, 124.0, 64.2, 60.2, 53.9, 25.7, 17.9, –5.5, –5.6. HRMS (ESI) calcd for $C_{21}H_{27}BrCl_2N_2O_5SSiNa$ *m/z* [M + Na]$^+$: 618.9863, found: 618.9875; HPLC (Daicel Chiralpak IA, *i*-PrOH/hexane = 8/92, 1.0 mL/min, 270 nm) t_1 = 13.9 min (major), t_2 = 15.8 min (minor).



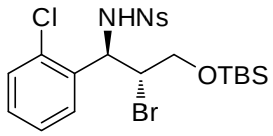
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.057	236.168	555.614	51.01	54.74	n.a.
2		15.915	209.371	459.332	48.99	45.26	n.a.
Total:			**445.539**	**1014.946**	**100.00**	**100.00**	



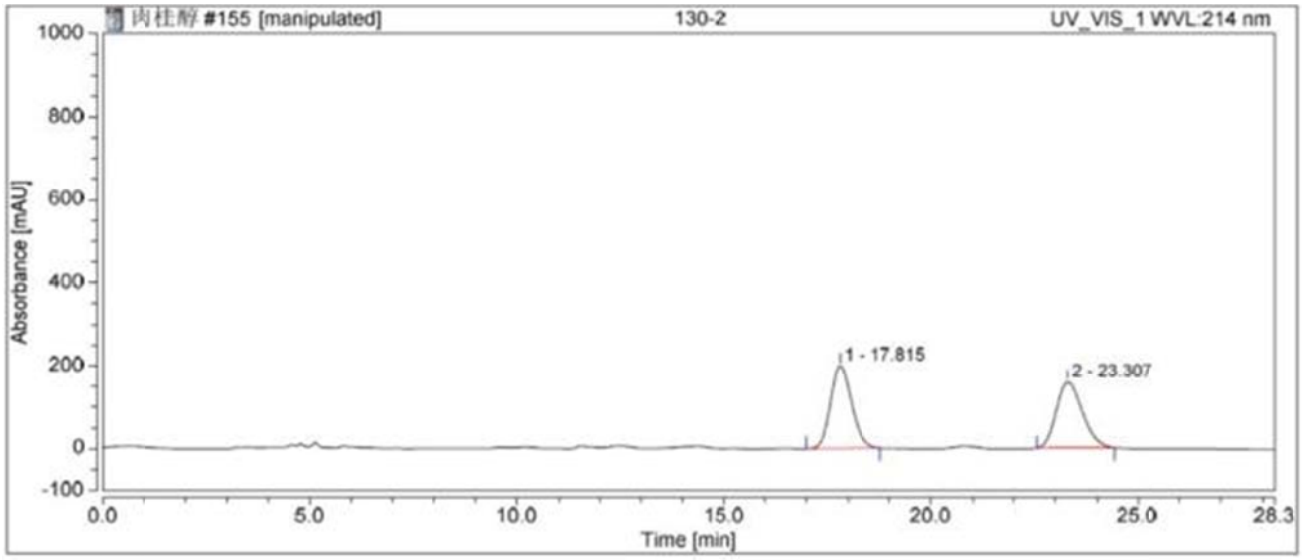
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.957	423.792	1045.179	95.90	96.03	n.a.
2		15.874	18.137	43.170	4.10	3.97	n.a.
Total:			**441.929**	**1088.349**	**100.00**	**100.00**	

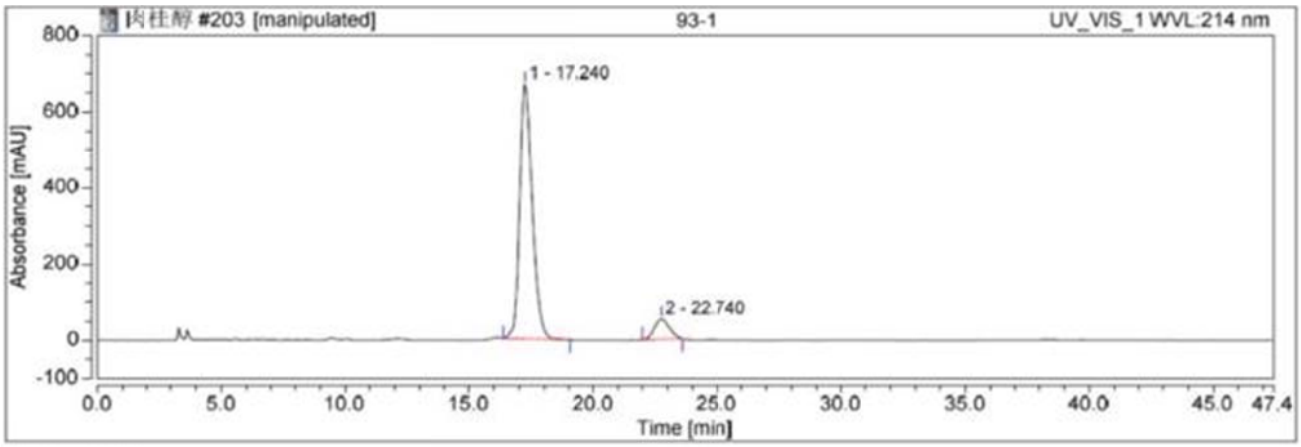


***N*-(2-Bromo-3-((*tert*-butyldimethylsilyl)oxy)-1-(2-chlorophenyl)propyl)-4-nitrobenzenesulfonamide (3o)**

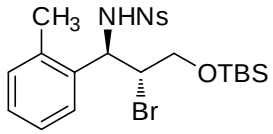
White solide; $[\alpha]_D^{20}$ –34.5 (*c* 0.6, $CHCl_3$, 83% ee); IR (KBr): 3320, 2927, 1607, 1532, 1351, 1168, 1098 cm^{-1}; ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.2 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.49 (s, 1H), 7.32-7.18 (m, 4H), 5.19 (s, 1H), 4.29 (s, 1H), 3.83 (d, *J* = 11.6 Hz, 1H), 3.68 (d, *J* = 11.4 Hz, 1H), 1.00 (s, 9H), 0.13 (s, 3H), 0.10 (s, 3H); ^{13}CNMR (100MHz, $CDCl_3$) δ 149.8, 146.1, 145.8, 135.5, 132.3, 129.9, 129.7, 128.4, 127.2, 123.9, 64.6, 60.6, 50.6, 25.7, 18.1, –5.6, –5.7; HRMS (ESI) calcd for $C_{21}H_{28}BrClN_2O_5SSiNa$ *m/z* $[M + Na]^+$: 585.0252, found: 585.0257; HPLC (Daicel Chiralpak IC, *i*-PrOH/hexane = 8/92, 1.0 mL/min, 214 nm) t_1 = 17.2 min (major), t_2 = 22.7 min (minor).



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.815	118.983	200.337	50.57	55.68	n.a.
2		23.307	116.278	159.496	49.43	44.32	n.a.
Total:			**235.261**	**359.833**	**100.00**	**100.00**	

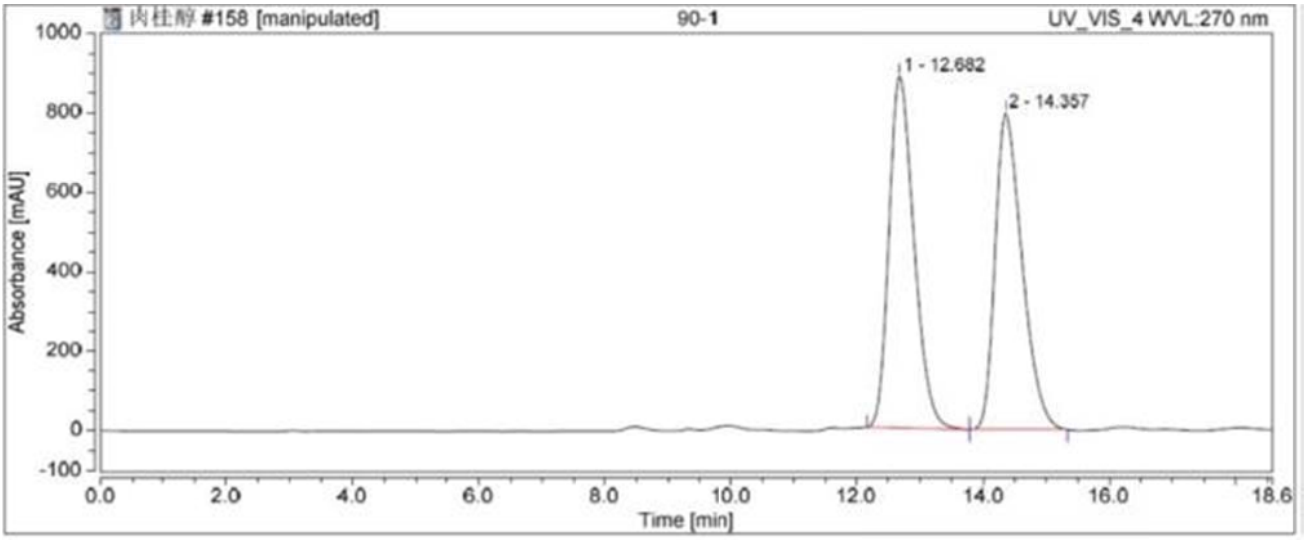


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.240	389.872	668.539	91.42	92.76	n.a.
2		22.740	36.600	52.199	8.58	7.24	n.a.
Total:			**426.471**	**720.738**	**100.00**	**100.00**	

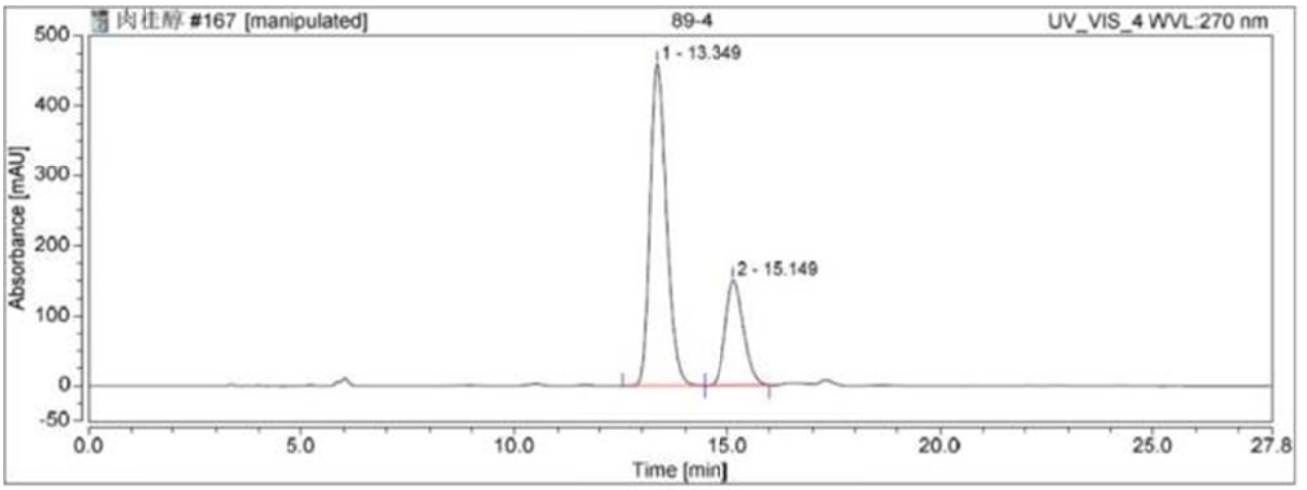


***N*-(2-Bromo-3-((*tert*-butyldimethylsilyl)oxy)-1-(o-tolyl)propyl)-4-nitrobenzenesulfonamide (3p)**

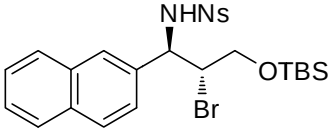
White solide, $[\alpha]_D^{20}$ –15.9 (*c* 1.6, $CHCl_3$, 46% ee) IR (KBr): 3447, 2926, 1609, 1532, 1463, 1351, 1311 cm^{-1}; ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.6 Hz, 2H), 7.74 (d, *J* = 8.6 Hz, 2H), 7.14 (m, 4H), 6.97 (d, *J* = 5.5 Hz, 1H), 5.13 (t, *J* = 4.2 Hz, 1H), 4.03-3.96 (m, 2H), 3.72 (dd, *J* = 11.6, 3.5 Hz, 1H), 2.36 (s, 3H), 1.00 (s, 9H), 0.15 (s, 3H), 0.12 (s, 3H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 149.5, 146.5, 135.65, 135.2, 130.8, 128.2, 128.1, 126.7, 126.2, 123.7, 64.9, 59.9, 51.8, 25.7, 19.1, 18.1, –5.6; HRMS (ESI) calcd for $C_{22}H_{31}BrN_2O_5SSiNa$ *m/z* $[M + Na]^+$: 565.0799, found: 565.0797; HPLC (Daicel Chiralpak IC, *i*-PrOH/hexane = 8/92, 1.0 mL/min, 270 nm) t_1 = 13.3 min (major), t_2 = 15.1 min (minor).



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.682	403.515	885.952	49.86	52.61	n.a.
2		14.357	405.761	798.062	50.14	47.39	n.a.
Total:			**809.277**	**1684.014**	**100.00**	**100.00**	



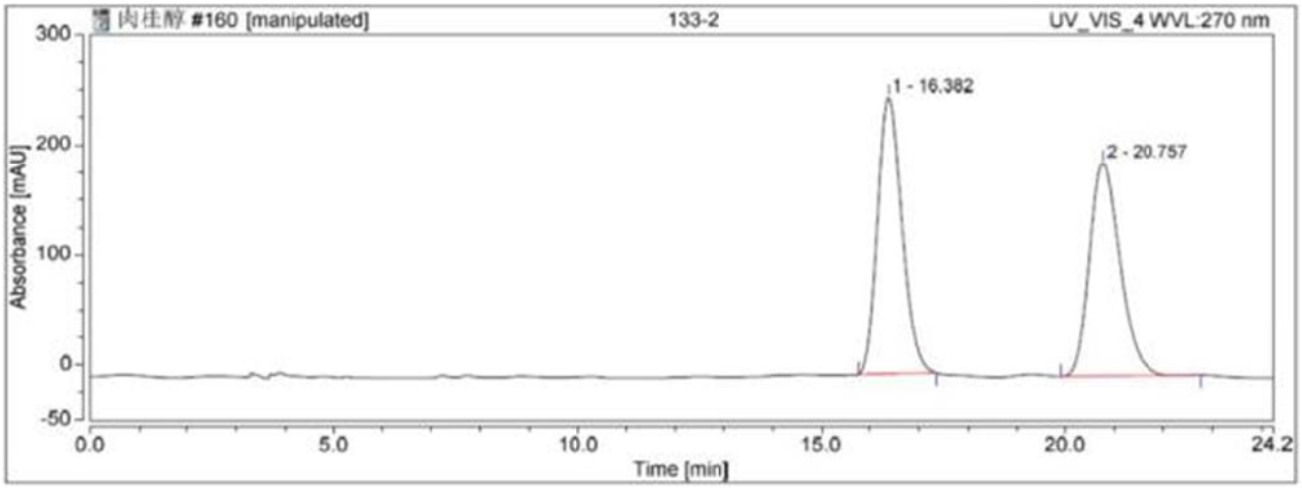
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.349	204.316	459.529	73.14	75.32	n.a.
2		15.149	75.016	150.608	26.86	24.68	n.a.
Total:			**279.332**	**610.136**	**100.00**	**100.00**	



_N_-(2-Bromo-3-((*tert*-butyldimethylsilyl)oxy)-1-(naphthalen-2-yl)propyl)-4-nitrobenzenesulfonamide (3q)

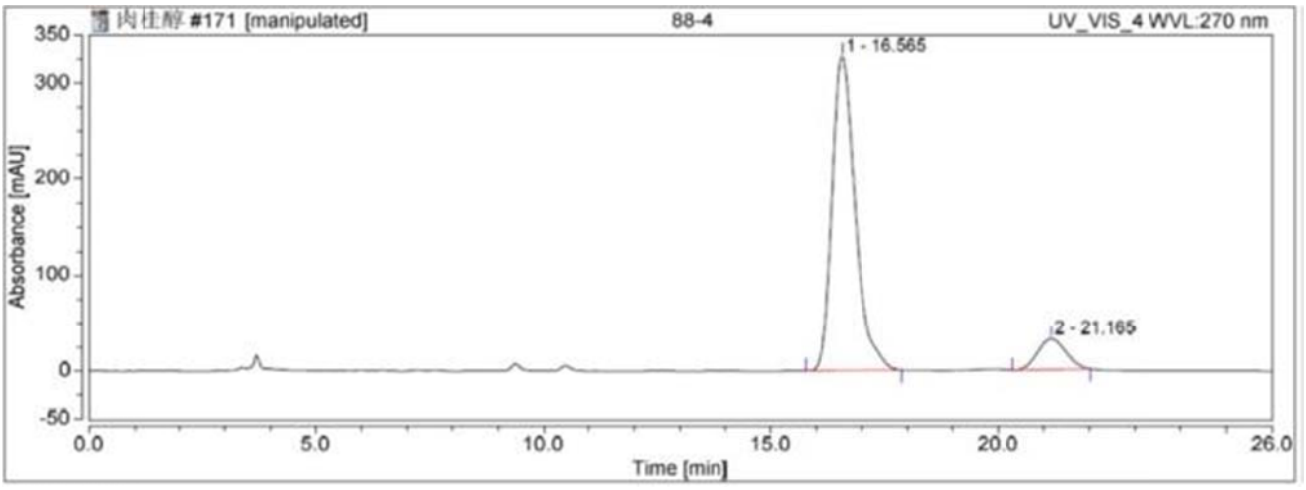
White solide, $[\alpha]_D^{20}$ –36.0 (*c* 1.0, $CHCl_3$, 79% ee), IR (KBr): 3290, 2928, 1728, 1606, 1531, 1348, 1167, 1091 cm^{-1}; ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 2H),

7.68-7.59 (m, 4H), 7.47-7.45 (m, 2H), 7.29 (d, *J* = 8.2 Hz, 1H), 6.78 (d, *J* = 7.4 Hz, 1H), 5.14-5.12 (m, 1H), 4.30 (s, 1H), 3.85 (dd, *J* = 11.2, 2.2 Hz, 1H), 3.56 (dd, *J* = 11.2, 6.0 Hz, 1H), 1.01 (s, 9H), 0.12 (s, 3H), 0.11 (s, 3H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 149.3, 146.1, 133.4, 132.8, 132.6, 128.2, 128.1, 127.6, 127.5, 127.1, 126.7, 126.6, 124.7, 123.6, 64.3, 61.4, 54.7, 25.7, 18.1, –5.5, –5.6; HRMS (ESI) calcdfor$C_{25}H_{31}BrN_2O_5SSiNa$ *m/z* $[M + Na]^+$: 601.0799, found: 601.0792, HPLC (Daicel Chiralpak IC, *i*-PrOH/hexane = 8/92, 1.0 mL/min, 270 nm) t_1 = 16.5 min (major), t_2 = 21.1 min (minor).



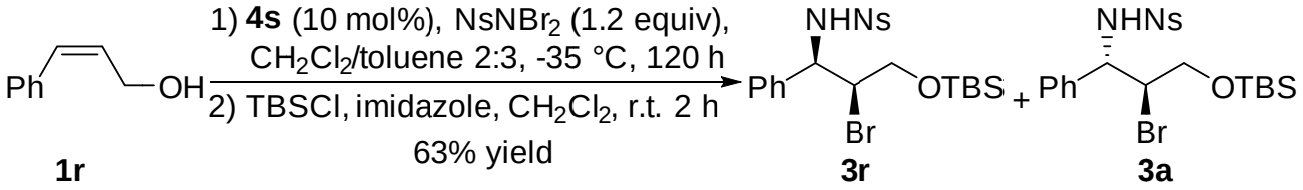
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.382	144.745	251.455	50.62	56.47	n.a.
2		20.757	141.215	193.798	49.38	43.53	n.a.
Total:			**285.960**	**445.253**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.565	195.594	328.122	89.31	91.02	n.a.
2		21.165	23.405	32.382	10.69	8.98	n.a.
Total:			**218.999**	**360.504**	**100.00**	**100.00**	

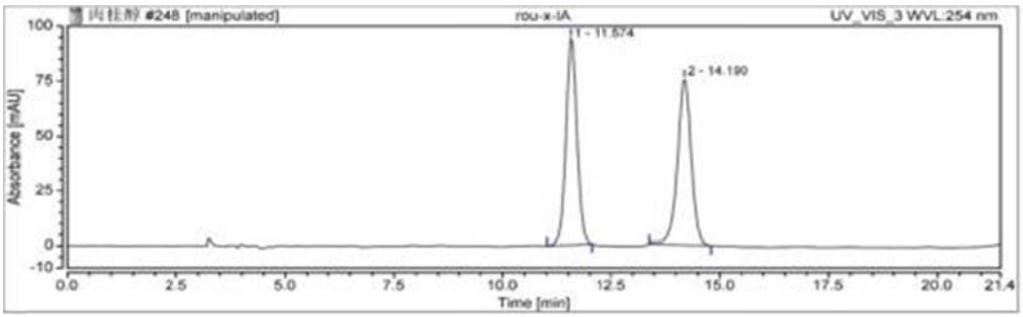


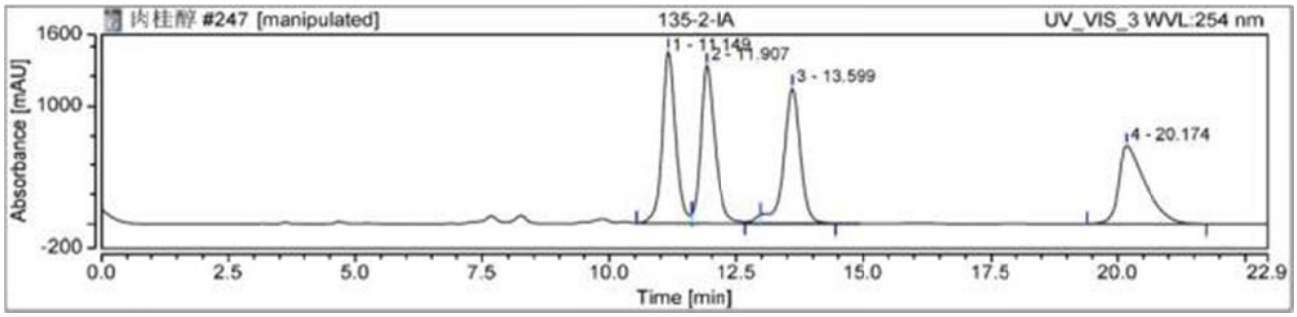
The absolute configuration of **3r** was not determined. Compounds **3r** and **3a** have similar polarity, which could not be separated by column chromatography.

***N*-(2-Bromo-3-((*tert*-butyldimethylsilyl)oxy)-1-phenylpropyl)-4-nitrobenzenesulfonamide (3r)**

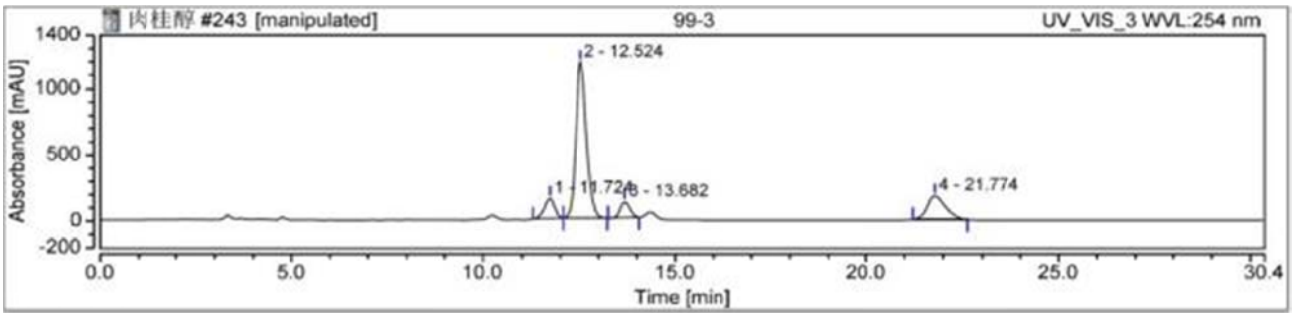
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.18-7.03 (m, 5H), 5.93 (d, *J* = 7.6 Hz, 1H), 5.03 (d, *J* = 4.8 Hz, 1H), 4.14-4.01 (m, 2H), 3.83-3.75 (m, 2H), 0.95 (s, 9H), 0.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 146.2, 136.2, 128.2, 128.1, 127.4, 123.7, 58.3, 57.2, 25.8, 18.1, -5.46, -5.49; HPLC (Daicel Chiralpak IA, *i*-PrOH/hexane = 8/92, 1.0 mL/min, 254 nm) t_1 = 12.5 min (major), t_2 = 21.8 min (minor).

3a (IA):

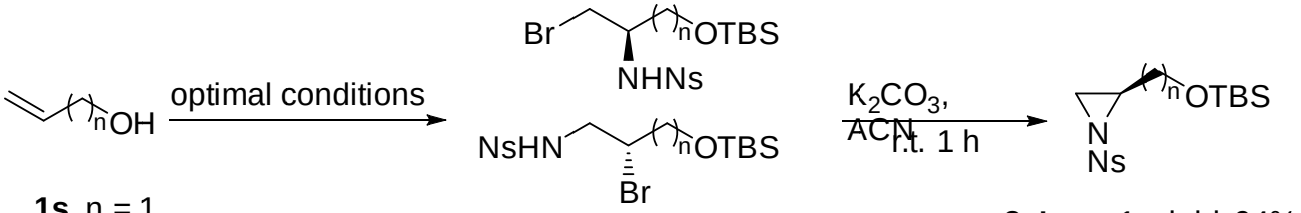




Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.149	446.707	1460.305	25.87	31.62	n.a.
2		11.907	439.439	1338.019	25.45	28.97	n.a.
3		13.599	437.034	1152.070	25.31	24.94	n.a.
4		20.174	403.444	668.613	23.37	14.48	n.a.
Total:			**1726.624**	**4619.007**	**100.00**	**100.00**	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.724	46.290	151.816	8.28	9.34	n.a.
2		12.524	378.763	1173.081	67.79	72.20	n.a.
3		13.682	35.046	120.384	6.27	7.41	n.a.
4		21.774	98.671	179.558	17.66	11.05	n.a.
Total:			**558.771**	**1624.840**	**100.00**	**100.00**	



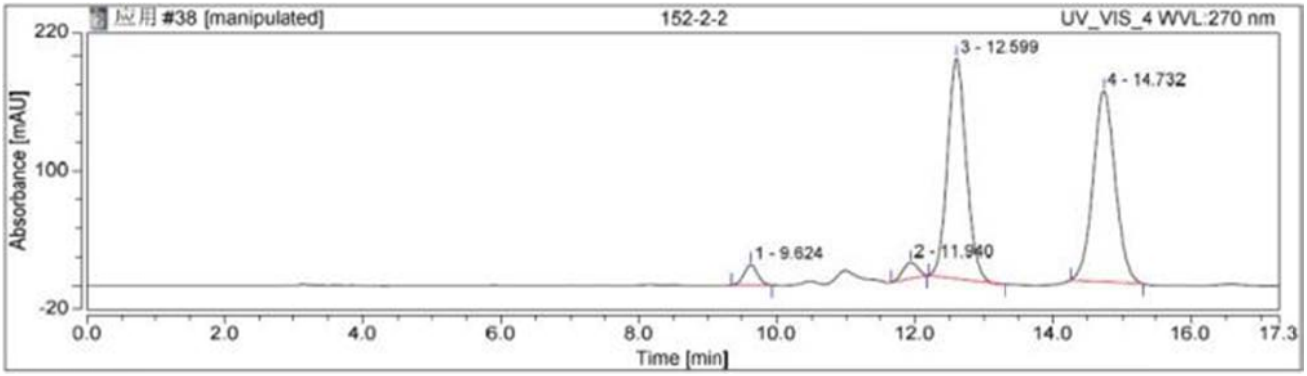
1s, n = 1
1t, n = 2

3s, n = 1, yield: 59%; regioisomer: 2:1
44% ee, major isomer.
3t, n = 2, yield: 61%; regioisomer: 5:1
52% ee, major isomer.

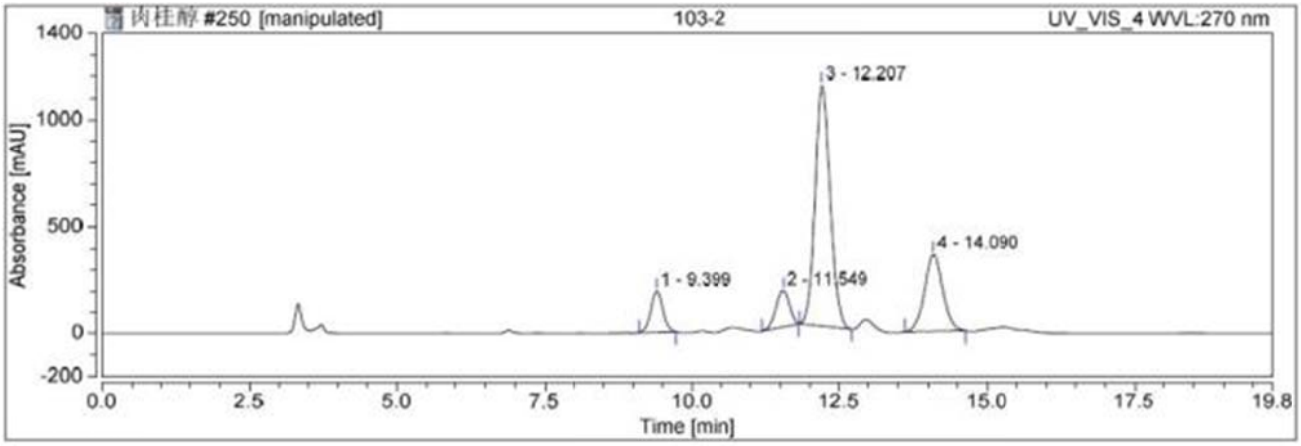
3s', n = 1, yield: 94%
3t', n = 2, yield: 95%

The absolute configuration of **3s**, **3t** were not determined, the ratio of the regioisomers of **3s** and **3t** is 2:1 and 5:1, respectively.6 Which have similar polarity and are difficult to be separated by column chromatography. To gain pure NMR, further cyclization were performed smoothly.

HPLC of **3s**: Daicel Chiralpak IA, *i*-PrOH/hexane = 8/92, 1.0 mL/min, 270 nm) t_1 = 12.2 min (major), t_2 = 14.1 min (minor).

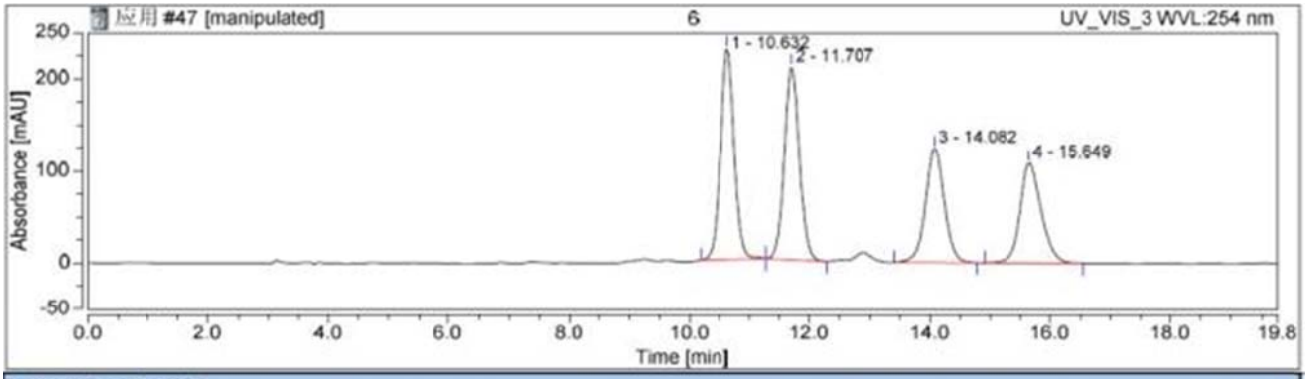


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.624	4.021	17.697	3.13	4.54	n.a.
2		11.940	3.524	14.128	2.74	3.62	n.a.
3		12.599	59.559	191.783	46.31	49.19	n.a.
4		14.732	61.515	166.245	47.83	42.64	n.a.
Total:			**128.619**	**389.853**	**100.00**	**100.00**	

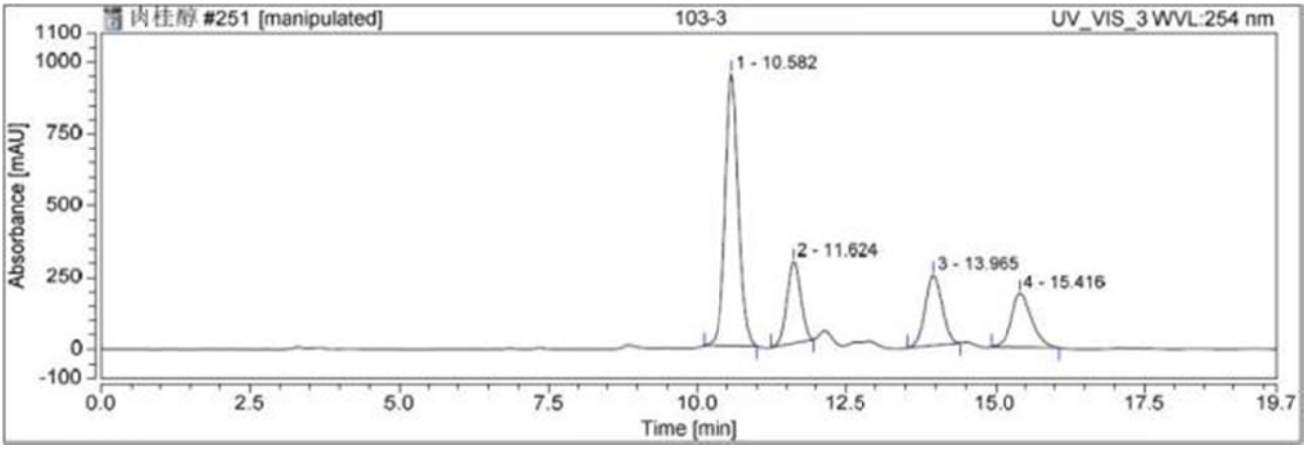


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.399	45.249	196.126	8.18	10.52	n.a.
2		11.549	45.849	176.651	8.29	9.47	n.a.
3		12.207	333.401	1127.873	60.25	60.48	n.a.
4		14.090	128.847	364.184	23.29	19.53	n.a.
Total:			**553.347**	**1864.834**	**100.00**	**100.00**	

HPLC of **3t**: Daicel Chiralpak IA, *i*-PrOH/hexane = 8/92, 1.0 mL/min, 270 nm) t_1 = 12.2 min (major), t_2 = 14.1 min (minor).



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.632	60.480	228.904	28.80	34.06	n.a.
2		11.707	60.624	209.756	28.87	31.21	n.a.
3		14.082	44.748	124.304	21.31	18.50	n.a.
4		15.649	44.152	109.008	21.02	16.22	n.a.
Total:			**210.003**	**671.972**	**100.00**	**100.00**	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.582	244.610	947.737	51.36	56.76	n.a.
2		11.624	76.830	286.032	16.13	17.13	n.a.
3		13.965	79.871	246.237	16.77	14.75	n.a.
4		15.416	74.935	189.791	15.73	11.37	n.a.
Total:			**476.247**	**1669.797**	**100.00**	**100.00**	

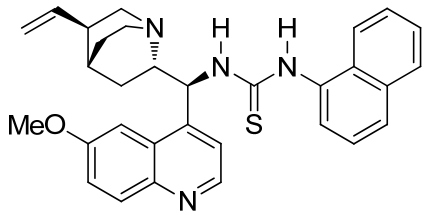
2-(((*tert*-Butyldimethylsilyl)oxy)methyl)-1-((4-nitrophenyl)sulfonyl)aziridine (3s′)

Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.6 Hz, 2H), 8.16 (d, *J* = 8.6 Hz, 2H), 3.79 (dd, *J* = 11.6, 3.0 Hz, 1H), 3.56 (dd, *J* = 7.6, 5.6 Hz, 1H), 3.09-3.03 (m, 1H), 2.76 (d, *J* = 7.2 Hz, 1H), 2.32 (d, *J* = 4.5 Hz, 1H), 0.78 (s, 9H), -0.04 (s, 3H), -0.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 144.0, 129.2, 124.2, 61.9, 41.8, 30.9, 25.6, 18.2, -5.5,-5.6; HRMS (ESI) calcd for $C_{15}H_{24}N_2O_5SSiNa$ *m/z* $[M + Na]^+$: 395.1067, found: 395.1064.

2-(2-((*tert*-Butyldimethylsilyl)oxy)ethyl)-1-((4-nitrophenyl)sulfonyl)aziridine (3t')

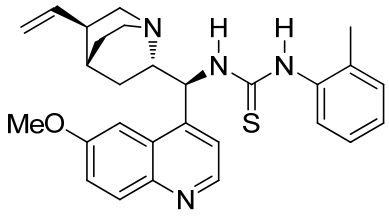
White solide; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.4 Hz, 2H), 8.16 (d, *J* = 8.2 Hz, 2H), 3.63-3.58 (m, 1H), 3.54-3.50 (m, 1H), 3.03-3.05 (m, 1H), 2.77 (d, *J* = 7.0 Hz, 1H), 2.23 (d, *J* = 4.4 Hz, 1H), 1.80-1.75 (m, 1H), 1.63-1.56 (m, 1H), 0.86 (s, 9H), 0.01 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 144.0, 129.2, 124.2, 60.1, 39.0, 34.4, 34.3, 25.8, 18.1, -5.4, -5.5; HRMS (ESI) calcd for $C_{16}H_{26}N_2O_5SSiNa$ *m/z* $[M + Na]^+$: 409.1224, found: 409.1235.

Catalysts 4a,[1] 4l,[1] 4n,[1] 4o,[2] 4p,[1] 8a,[3] 8b,[3] 8c,[4] 8d,[2] S4a,[5] S4b,[6] are known compounds, all catalysts were synthesized according to the report procedure.[1,2,6]



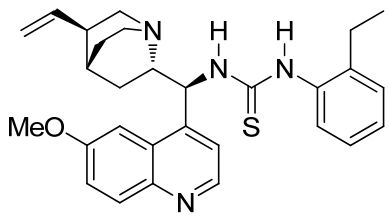
4b

White solide, $[\alpha]_D^{20}$ –65.3 (*c* 1.0, $CHCl_3$); IR (KBr): 3441, 2926, 1623. 1510, 1261, 1165, 1030 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.27(s, 2H), 7.89-7.87 (m, 3H), 7.50-7.28 (m, 4H), 7.10 (s, 1H), 5.91(s, 1H), 5.57-5.51 (m, 1H), 4.87-4.83 (m, 2H), 4.12-3.88 (m, 3H), 3.25-2.86 (m, 3H), 2.52-2.40 (m, 2H), 2.15 (s, 1H),2.03 (s, 1H), 1.58-1.50 (m, 3H), 1.26-1.25 (m, 2H), 0.92 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.8, 157.4, 147.1, 144.4, 140.4, 134.4, 133.2, 131.3, 129.9, 128.1, 126.9, 126.5, 125.3, 125.2, 122.8, 121.6, 114.6, 102.1, 60.2, 55.4, 54.8, 41.1, 38.8, 27.3, 27.0, 20.9, 14.0. HRMS (ESI) calcd for $C_{31}H_{32}N_4OS$ *m/z* $[M + H]^+$: 473.2370, found: 473.2379.



4c

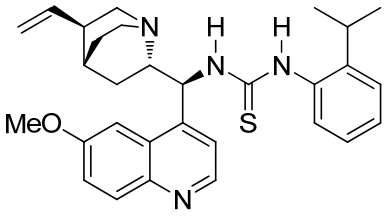
White solide, $[\alpha]_D^{20}$ –99.2 (*c*, 1.0 $CHCl_3$); IR (KBr): 3436, 2926, 1734, 1622, 1348, 1166, 1086, 1032 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.08 (s, 1H), 8.34 (s, 2H), 7.88 (d, *J* = 9.2 Hz, 1H), 7.21 (m, 6H), 5.92 (s, 1H), 5.54-5.46 (m, 1H), 4.85-4.79 (m, 2H), 3.85 (s, 3H), 3.28-3.14 (m, 2H), 3.00-2.94 (m, 2H), 2.59-2.52 (m, 2H), 2.15 (s, 1H), 1.96 (s, 3H), 1.59-1.50 (m, 3H), 1.24-1.19 (m, 1H), 0.88-0.85 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.8, 157.3, 147.1, 144.1, 140.0, 135.7, 134.9, 131.9, 131.0, 130.9, 127.6, 127.3, 126.3, 121.5, 114.6, 102.0, 55.4, 54.5, 53.3, 41.0, 38.5, 26.8, 24.9, 17.4. HRMS (ESI) calcd for $C_{28}H_{33}N_4OS$ *m/z* $[M + H]^+$: 473.2370, found: 473.2381.



4d

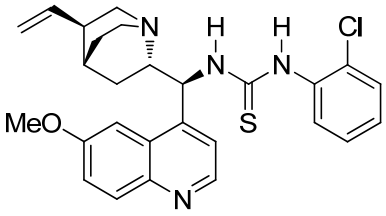
White solide, $[\alpha]_D^{20}$ –111.9 (*c*, 1.0 $CHCl_3$); IR (KBr): 3442, 2926, 1622. 1511, 1262, 1166, 1031 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.62-8.48 (m, 3H), 7.96 (d, *J* = 9.1 Hz, 1H), 7.35-7.25 (m, 5H), 5.95

(s, 1H), 5.64-5.55 (m, 1H), 4.94-4.90 (m, 2H), 4.33(s, 1H), 3.94 (s, 3H), 3.34-3.06 (m, 3H), 2.64 (s, 2H), 2.43 (s, 2H), 2.27 (s, 1H), 1.66-1.62 (m, 3H), 1.31-1.23 (m, 2H), 1.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.3, 157.5, 147.2, 144.3, 140.9, 140.1, 134.0, 131.9, 131.2, 129.1, 128.0, 126.5, 121.7, 114.9, 102.1, 61.1, 60.3, 55.5, 54.7, 40.9, 38.7, 27.0, 26.9, 25.2, 24.0, 14.0. HRMS (ESI) calcd for $C_{29}H_{35}N_4OS$ *m/z* $[M + H]^+$: 487.2526, found: 487.2532.



4e

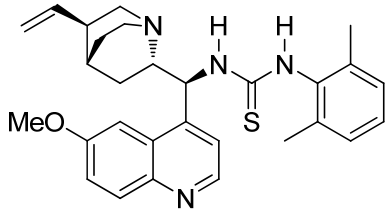
White solide, $[\alpha]_D^{20}$ –128.7 (*c*, 1.0 $CHCl_3$); IR (KBr): 3422, 2926, 1735, 1622, 1512, 1262, 1084, 1031 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.16 (s, 1H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.9-7.16 (m, 6H), 5.73 (s, 1H), 5.53-5.50 (m, 1H), 4.85-4.80 (m, 2H), 4.02-4.04(m, 1H), 3.85 (m, 3H), 3.16-2.98 (m, 4H), 2.56-2.50 (m, 2H), 2.17 (s, 1H), 1.95 (s, 2H), 1.57 (s, 3H), 1.22-0.94 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.6, 157.4, 147.2, 145.9, 144.4, 140.5, 133.9, 132.0, 131.9, 131.3, 128.5, 128.3, 126.5, 121.6, 114.6, 102.2, 60.2, 56.3, 55.5, 55.0, 40.9, 39.0, 27.9, 27.4, 27.0, 26.8, 23.3, 22.8, 14.0. HRMS (ESI) calcd for $C_{30}H_{36}N_4OSNa$ *m/z* $[M + Na]^+$: 523.2513, found: 523.2502.



4f

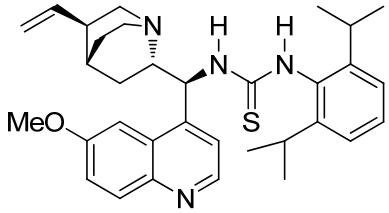
White solide, $[\alpha]_D^{20}$ –81.0 (*c*, 1.0 $CHCl_3$); IR (KBr): 3447, 2925, 1624, 1511, 1470, 1262, 1031 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.53 (s, 1H), 7.98 (d, *J* = 9.1 Hz, 1H), 7.79 (s, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.40-7.16 (m, 5H), 5.95 (s, 1H), 5.66-5.57 (m, 1H), 4.97-4.92 (m, 2H), 3.95 (s, 3H), 3.45-3.11 (m, 3H), 2.68 (d, *J* = 7.6 Hz, 2H), 2.30 (s, 1H), 1.99 (s, 1H), 1.69-1.64 (m, 3H), 1.37-1.25 (m, 1H), 1.01-0.98 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.2, 157.7, 147.4, 144.6, 139.9, 135.0, 131.4, 129.9, 129.7, 128.0, 127.5, 127.1, 126.5, 121.8, 115.1, 102.1, 60.2, 55.6, 54.7,

41.1, 38.6, 27.5, 27.0, 26.9; HRMS (ESI) calcd for $C_{27}H_{30}ClN_4OSNa$ *m/z* $[M + H]^+$: 493.1823, found: 493.1821.



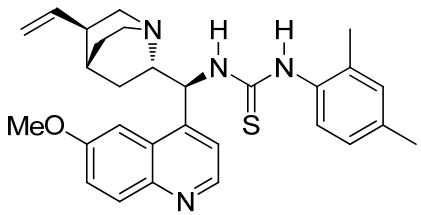
4g

White solide, $[\alpha]_D^{20}$ –86.9 (*c*, 1.0 $CHCl_3$); IR (KBr): 3440, 2924, 1737, 1623, 1510, 1466, 1381, 1228, 1166 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.66-8.53 (m, 2H), 7.91 (d, *J* = 8.9 Hz, 1H), 7.44-6.8 (m, 5H), 5.78-5.57 (m, 2H), 4.88-4.84 (m, 2H), 4.13-3.97 (m, 4H), 3.14-3.03 (m, 2H), 2.72-2.63 (m, 2H), 2.33-2.03 (m, 9H), 1.65-1.61 (m, 3H), 1.26-1.22 (m, 2H), 0.97 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.6, 170.9, 157.4, 147.1, 144.3, 140.9, 137.3, 136.9, 133.3, 131.9, 131.8, 128.7, 128.5, 128.4, 128.2, 114.3, 102.2, 60.1, 55.5, 40.9, 39.2, 27.7, 27.0, 20.8, 18.1, 17.6, 14.0; HRMS (ESI) calcd for $C_{29}H_{35}N_4OS$ *m/z* $[M + H]^+$: 487.2526, found: 487.2524.



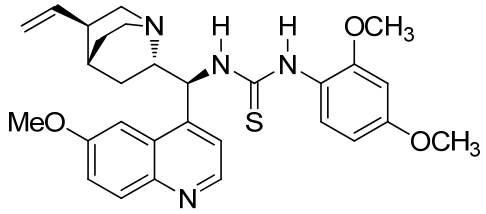
4h

White solide, $[\alpha]_D^{20}$ –58.1 (*c*, 1.0 $CHCl_3$); IR (KBr): 3439, 2961, 1622, 1511, 1263, 1083, 1032 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.76-8.66 (m, 1H), 7.98-7.93 (m, 2H), 7.38-7.22 (m, 5H), 7.03 (d, *J* = 7.5 Hz, 2H), 6.80 (d, *J* = 7.5 Hz, 1H), 6.48 (s, 1H), 5.94 (s, 1H), 5.66-5.56 (m, 1H), 4.90-4.85 (m, 1H), 3.99 (s, 6H), 3.22-3.18 (m, 2H), 2.96-2.61 (m, 3H), 1.60-1.16 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.2, 157.7, 147.8, 147.5, 147.1, 144.4, 141.0, 140.1, 132.3, 131.2, 129.7, 128.7, 124.1, 123.9, 123.5, 122.6, 121.9, 118.7, 118.4, 114.3, 102.4, 61.2, 55.7, 40.9, 39.3, 28.6, 28.2, 27.8, 25.0, 24.8, 24.5, 24.3, 22.3; HRMS (ESI) calcd for $C_{33}H_{43}N_4OS$ *m/z* $[M + H]^+$: 543.3152, found: 543.3154.



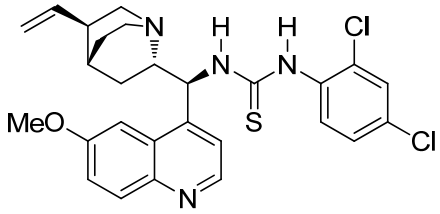
4i

White solide, $[\alpha]_D^{20}$ –100.4 (*c*, 2.6 $CHCl_3$); IR (KBr): 3258, 2925, 1736, 1621, 1510, 1228, 1084, 1031 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.33 (s, 1H), 7.88 (d, J = 9.0 Hz, 1H), 7.26-6.98 (m, 5H), 5.57-5.49 (m, 1H), 4.86-4.80 (m, 2H), 4.00-3.86 (m, 3H), 3.23-2.94 (m, 3H), 2.53 (s, 2H), 2.26-2.15 (m, 4H), 2.07-1.94 (m, 4H), 1.55 (m, 3H), 1.19-1.16 (m, 2H), 0.88-078 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.1, 157.5, 147.3, 144.4, 140.6, 137.6, 135.1, 132.9, 132.0, 131.7, 131.3, 127.6, 127.3, 114.6, 102.2, 60.3, 55.5, 55.0, 41.1, 39.0, 27.4, 27.1, 21.0, 17.5, 14.1; HRMS (ESI) calcd for $C_{29}H_{35}N_4OS$ *m/z* $[M + H]^+$: 487.2526, found: 487.2536.



4j

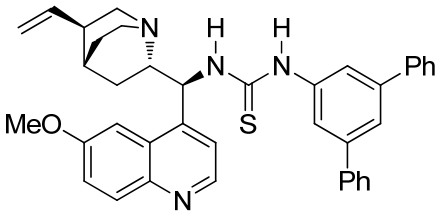
White solide, $[\alpha]_D^{20}$ –104.2 (*c*, 2.3 $CHCl_3$); IR (KBr): 3278, 2936, 1619, 1510, 1209, 1166, 1033 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.57-8.39 (m, 2H), 7.97-7.93 (m, 2H), 7.38 (s, 3H), 6.43 (s, 2H), 6.2 (s, 1H), 5.63-5.32 (m, 2), 4.95 (s, 2H), 4.10 (s, 3H), 3.96 (s, 3H), 3.78 (s, 3H), 3.47 (s, 1H), 3.24 (s, 1H), 2.78 (s, 2H), 2.36 (s, 1H), 2.03-1.72 (m, 2H), 1.80 (m, 2H), 1.39-1.26 (m, 2H), 1.02 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.0, 158.9, 157.6, 153.9, 147.2, 144.3, 139.3, 131.0, 128.0, 127.5, 121.8, 119.3, 115.2, 103.7, 102.3, 98.8, 60.1, 55.5, 55.2, 55.1, 54.3, 41.1, 38.1, 26.9, 26.3, 24.8, 23.4; HRMS (ESI) calcd for $C_{29}H_{35}N_4O_3S$ *m/z* $[M + H]^+$: 519.2424, found: 519.2538.



4k

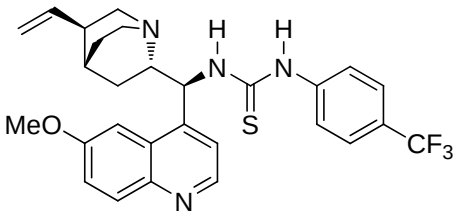
White solide, $[\alpha]_D^{20}$ –83.4 (*c*, 4.6 $CHCl_3$); IR (KBr): 3238, 2927, 1733, 1621, 1528, 1228, 1167, 1098 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.98 (d, *J* = 9.1 Hz, 1H), 7.82 (s, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.44-7.34 (m, 3H), 7.19 (d, *J* = 8.2 Hz, 1H), 6.09 (s, 1H), 5.64-5.58 (m, 1H), 4.99-4.93 (m, 2H), 4.12-4.08 (m,1H), 4.06 (s, 2H),3.96 (s, 2H), 3.40 (s, 2H), 3.19-3.13 (m, 1H), 2.72 (s, 2H), 2.31 (s, 1H), 2.02 (d, *J* = 10.2 Hz, 1H), 1.70 (s, 2H), 1.37-1.23 (m, 2H), 0.97 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.2, 157.7, 147.2, 144.34 (s), 139.5, 134.0, 131.8, 131.2, 130.0, 129.3, 128.5,

127.9, 127.1, 121.8, 115.2, 102.1, 60.2, 55.5, 54.5, 41.1, 38.3, 26.8, 26.6, 24.9, 24.0, 14.0; HRMS (ESI) calcd for $C_{27}H_{29}Cl_2N_4OS$ *m/z* $[M + H]^+$: 527.1434, found: 527.1423.



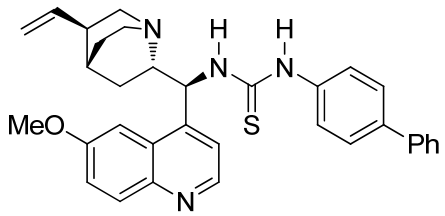
4m

White solide, $[\alpha]_D^{20}$ –173.7 (*c*, 1.0 $CHCl_3$); IR (KBr): 3235, 2926, 1732, 1620, 1527, 1166, 1099 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 8.40 (s, 2H), 7.96 (d, *J* = 9.2 Hz, 1H), 7.85-7.25 (m, 12H), 7.08 (s, 1H), 6.09 (s, 1H), 5.64-5.55 (m, 1H), 4.93-4.89 (m, 2H), 4.12-4.10 (q, 1H), 3.94 (s, 3H), 3.49 (s, 1H), 3.21 (s, 1H), 2.90 (s, 1H), 2.66 (d, *J* = 9.1 Hz, 2H), 2.23-2.15 (m, 2H), 1.63-1.58 (m, 2H), 1.29-1.23 (m, 2H), 0.92-0.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.2, 157.7, 147.4, 144.6, 142.9, 140.5, 134.0, 138.4, 131.5, 128.8, 127.7, 127.1, 123.7, 122.8, 121.8, 114.8, 102.3, 60.3, 55.7, 54.9, 41.6, 38.9, 27.6, 27.4, 27.2, 25.4, 21.0, 15.4, 14.1; HRMS (ESI) calcd for $C_{39}H_{39}N_4OS$ *m/z* $[M + H]^+$: 611.2839, found: 611.2852.



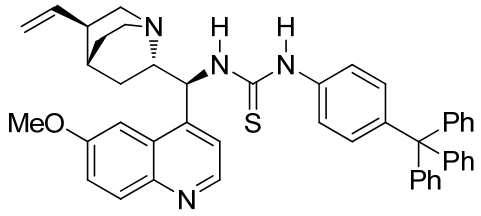
4q

White solide, $[\alpha]_D^{20}$ –122.4 (*c*, 1.5 $CHCl_3$); IR (KBr): 3425, 2926, 1736, 1621, 1513, 1324, 1262, 1119, 1067 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.98 (d, *J* = 8.9 Hz, 1H), 7.78 (s, 1H), 7.55-7.26 (m, 6H), 6.08 (s, 1H), 5.67-5.61 (m, 1H), 4.98-4.96 (m, 2H), 3.95 (s, 3H), 3.47-3.38 (m, 2H), 3.20-3.14 (m, 1H), 2.34 (s, 2H), 2.34 (s, 1H), 1.72 (s, 4H), 1.39-1.37 (m, 1H), 0.96 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 158.0, 147.5, 144.7, 141.3, 139.8, 131.6, 128.0, 126.3, 125.2, 123.6, 122.5, 122.1, 115.4, 102.2, 55.7, 54.78, 41.5, 38.6, 37.9, 37.9, 27.0, 26.9, 25.2, 24.2; HRMS (ESI) calcd for $C_{28}H_{30}F_3N_4OS$ *m/z* $[M + H]^+$: 527.2087, found: 527.2101.



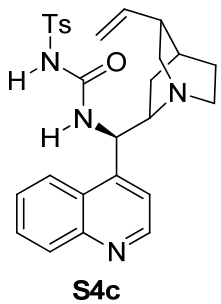
4r

White solide, $[\alpha]_D^{20}$ –158.1 (*c*, 1.0 $CHCl_3$); IR (KBr): 3441, 2924, 1736, 1621, 1512, 1379, 1229, 1164, 1083 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.69 (s, 1H), 8.79 (s, 1H), 8.40 (d, *J* = 90.0 Hz, 1H), 7.97 (s, 2H), 7.54-7.33 (m, 10H), 6.23 (s, 1H), 5.59-5.57 (m, 1H), 4.94-4.89 (m, 2H), 3.95 (s, 3H), 3.57-3.40 (m, 2H), 3.16 (s, 1H), 2.75 (s, 2H), 2.26 (s, 1H), 1.95 (s, 1H), 1.71-1.63 (m, 3H), 1.32 (s, 2H), 0.94-0.85 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.0, 157.6, 147.2, 144.3, 139.7, 138.3, 137.0, 131.0, 128.5, 128.0, 127.4, 127.0, 126.5, 126.3, 124.6, 121.8, 114.9, 102.2, 55.4, 54.4, 41.3, 38.3, 26.8, 26.7, 24.9, 23.9; HRMS (ESI) calcd for $C_{33}H_{35}N_4OS$ *m/z* $[M + H]^+$: 535.2526, found: 535.2531.



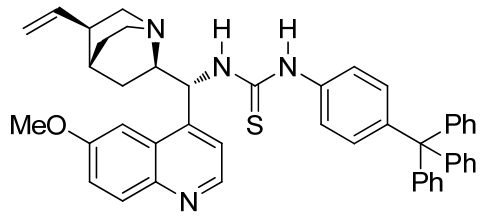
4s

White solide, $[\alpha]_D^{20}$ –141.2 (*c*, 1.0 $CHCl_3$); IR (KBr): 3266, 2926, 1734, 1620, 1510 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 8.45 (s, 1H), 7.94 (d, *J* = 9.1 Hz, 1H), 7.76 (s, 1H), 7.43-7.20 (m, 19H), 7.11(d, *J* = 8.3 Hz, 2H) 5.85 (s, 1H), 5.68-5.60 (m, 1H), 4.97-4.91 (m, 2H), 3.88 (s, 3H), 3.26-2.98 (m, 3H), 2.65-2.57 (m, 2H), 2.24 (s, 1H), 1.63-1.55 (m, 3H), 1.31-1.16 (m, 3H), 0.94-0.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.2, 157.5, 147.3, 146.3, 144.8, 144.4, 140.7, 135.3, 131.8, 131.3, 130.8, 127.4, 125.9, 123.7, 121.7, 114.6, 102.1, 64.5, 60.2, 55.5, 55.0, 41.1, 39.1, 27.0, 20.9, 18.3, 14.0; HRMS (ESI) calcd for $C_{46}H_{46}N_4OS$ *m/z* $[M + H]^+$: 701.3309 found: 701.3322.



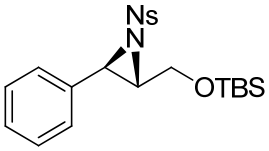
S4c

White solide, $[\alpha]_D^{20}$ +89.3 (c, 1.0 $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.17-8.12 (m, 2H), 7.75-7.41 (m, 5H), 7.16-7.02 (m, 2H), 6.06-5.71 (m, 5H), 5.18-5.10 (m, 2H), 4.11-3.94 (m, 1H), 3.52-3.16 (m, 2H), 2.71-2.68 (m, 1H), 2.30 (s, 3H), 1.66 (s, 2H), 1.57-1.26 (m, 2H), 0.94-0.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 149.9, 147.8, 145.3, 141.5, 140.5, 137.4, 129.0, 128.4, 126.6, 126.5, 125.8, 124.0, 123.4, 119.1, 116.1, 59.5, 48.3, 46.1, 45.5, 45.0, 37.0, 26.5, 24.3, 21.1, 8.3; HRMS (ESI) calcd for $C_{27}H_{31}N_4O_3S$ *m/z* $[M + H]^+$: 491.2111, found: 491.2104.



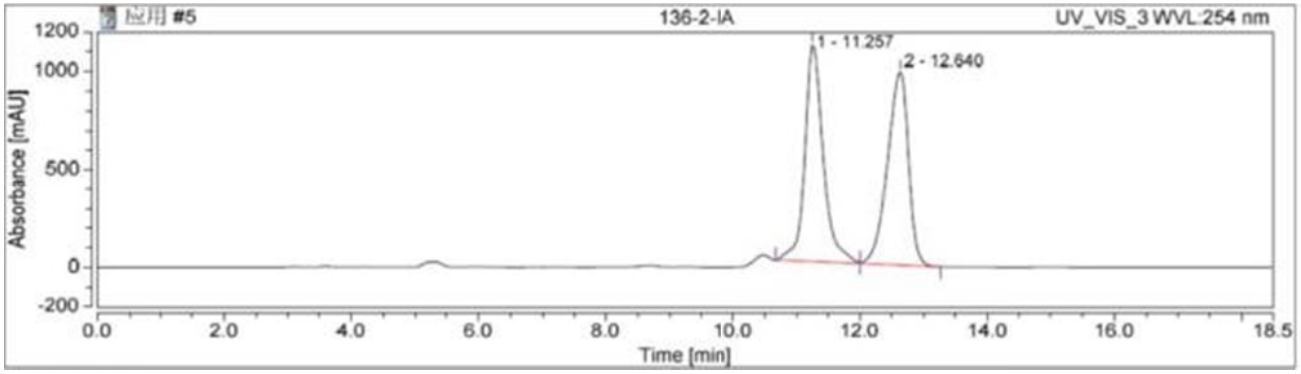
5

White solide, $[\alpha]_D^{20}$ +188.8 (*c*, 1.0 $CHCl_3$); IR (KBr): 3271, 2926, 1735, 1621, 1508, 1320, 1227, 1082, 1031 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.98 (d, *J* = 9.0 Hz, 1H), 7.60 (s, 1H), 7.35-7.13 (m, 18H), 5.94-5.85 (m, 1H), 5.62 (s, 1H), 5.16-5.12 (m, 2H), 3.90 (s, 3H), 3.48 (s, 2H), 2.95-2.76 (m, 4H), 2.28-2.17 (m, 2H), 1.65-1.13 (m, 8H), 0.87-0.85 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 157.5, 147.3, 146.3, 144.9, 144.4, 139.9, 135.2, 131.9, 130.9, 127.5, 125.9, 122.9, 123.7, 122.1, 114.9, 101.7, 64.6, 55.4, 50.3, 48.5, 47.0, 38.8, 27.0, 26.2. 22.5, 11.3; HRMS (ESI) calcd for $C_{46}H_{46}N_4OS$ *m/z* $[M + H]^+$: 701.3309, found: 701.3327.



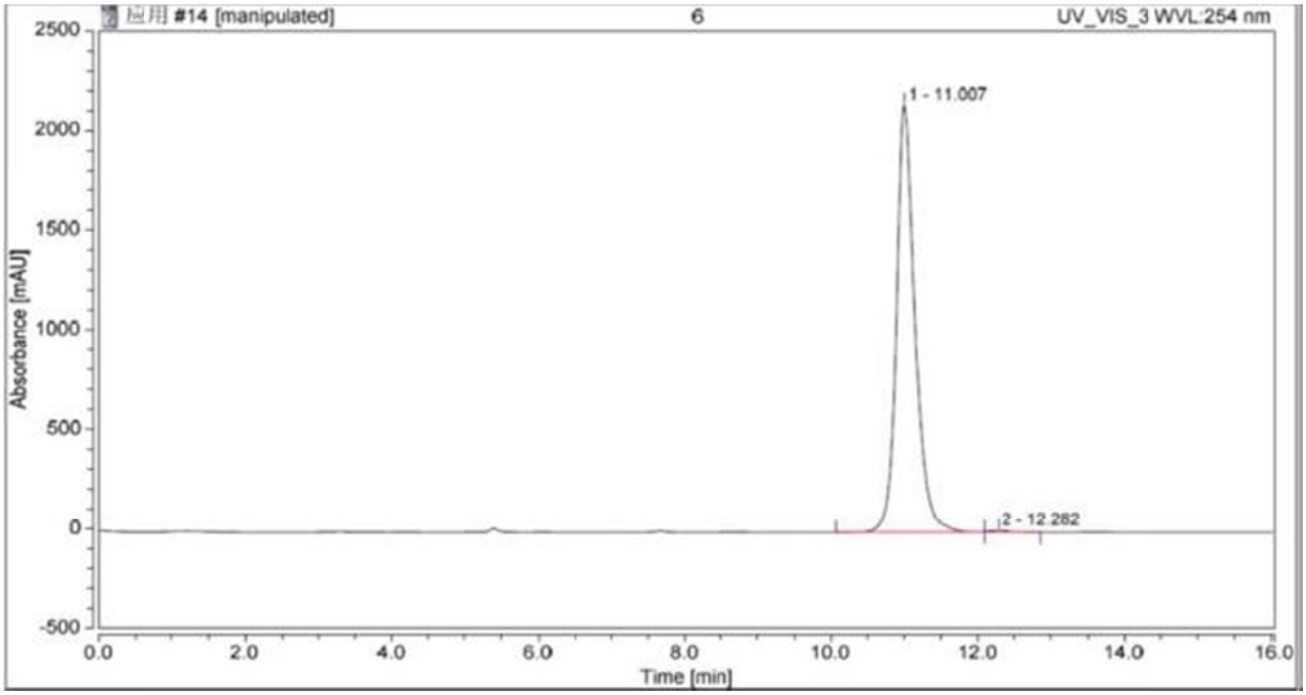
(*2S, 3R*)-2-(((*tert*-Butyldimethylsilyl)oxy)methyl)-1-((4-nitrophenyl)sulfonyl)-3-phenylaziridine (9)

Colourless oil, $[\alpha]_D^{20}$ –11.3 (*c* 1.7, $CHCl_3$, 99% ee) IR (KBr): 2926, 1737, 1622, 1532, 1463, 1379, 1165 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.6 Hz, 2H), 8.12 (d, *J* = 8.6 Hz, 2H), 7.19-7.29 (m, 5H), 4.31 (dd, *J* = 11.3, 5.4 Hz, 1H), 4.16 (dd, *J* = 11.2, 5.6 Hz, 1H), 3.99 (d, *J* = 4.2 Hz, 1H), 3.25 (dd, *J* = 5.6, 4.2 1H), 0.90 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 145.9, 133.7, 128.7, 128.6, 128.5,126.8, 124.1, 60.6, 53.2, 47.8, 25.8, 18.3, –5.3, –5.4. HRMS (ESI) calcd for $C_{21}H_{28}N_2O_5SSiNa$ *m/z* $[M + Na]^+$: 471.1380, found: 417.1385; HPLC (Daicel Chiralpak IA, *i*-PrOH/hexane = 8/92, 1.0 mL/min, 254 nm) t_1 = 11.0 min (major), t_2 = 12.4 min (minor).



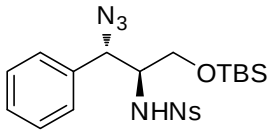
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.257	370.323	1108.454	49.86	52.90	n.a.
2		12.640	372.358	986.794	50.14	47.10	n.a.
Total:			**742.681**	**2095.249**	**100.00**	**100.00**	



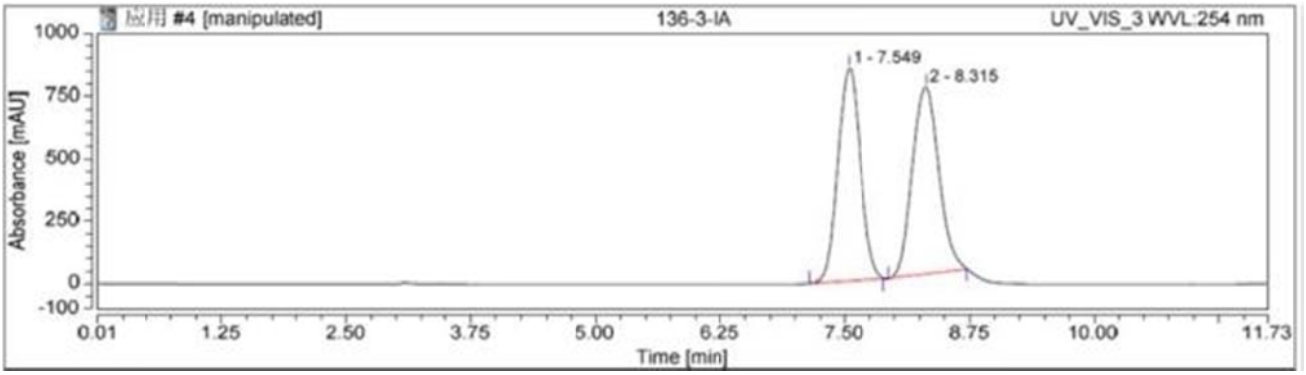
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.007	623.841	2145.463	99.44	99.47	n.a.
2		12.282	3.492	11.470	0.56	0.53	n.a.
Total:			**627.333**	**2156.933**	**100.00**	**100.00**	

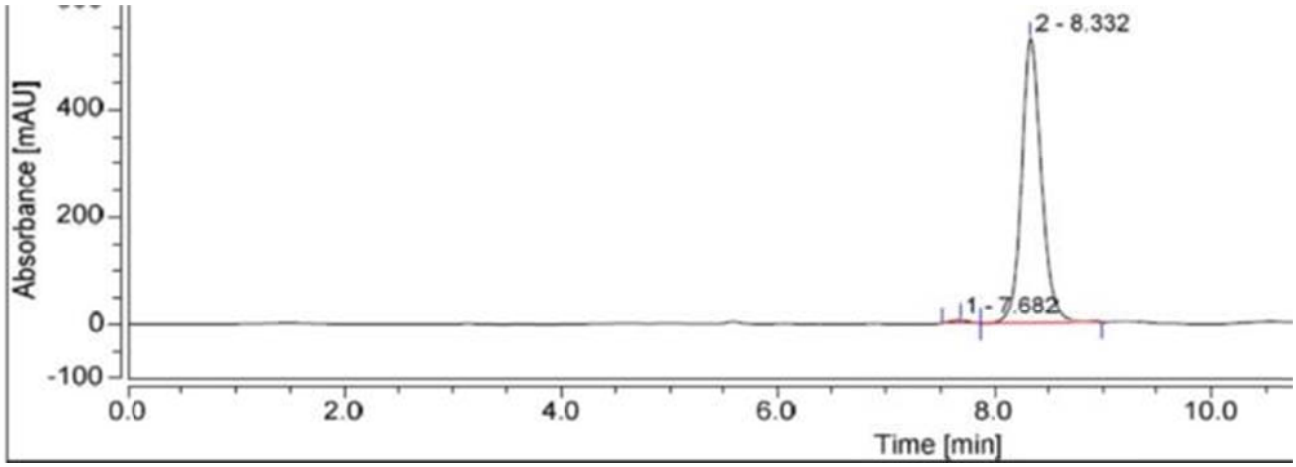


((1*S*,2*S*)-*N*-1-Azido-3-((*tert*-butyldimethylsilyl)oxy)-1-phenylpropan-2-yl)-4-nitrobenzenesulfonamide (10)

White solide, $[\alpha]_D^{20}$ +52.8 (*c* 1.5, $CHCl_3$, 98% ee) IR (KBr): 3443, 2927, 2105, 1531, 1463, 1348, 1255, 1165 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.10-7.21 (m, 5H), 5.00 (d, *J* = 9.2 Hz, 1H), 4.60 (d, *J* = 8.3 Hz, 1H), 3.96-3.98 (m, 1H), 3.65-3.53 (m, 2H), 0.91 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 145.9, 136.0, 128.8, 128.7, 127.9, 127.6, 124.0, 65.0, 62.0, 59.1, 25.8, 18.3, –5.5, –5.6. HRMS (ESI) calcd for $C_{21}H_{29}N_5O_5SSiNa$ *m/z* $[M + Na]^+$: 514.1551, found: 514.1568; HPLC (Daicel Chiralpak IA, *i*-PrOH/hexane = 8/92, 1.0 mL/min, 254 nm) t_1 = 7.6 min (major), t_2 = 8.3 min (minor).



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.549	224.920	850.999	49.51	53.22	n.a.
2		8.315	229.402	748.039	50.49	46.78	n.a.
Total:			454.322	1599.037	100.00	100.00	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.682	1.156	5.852	1.01	1.10	n.a.
2		8.332	113.275	528.330	98.99	98.90	n.a.
Total:			114.431	534.182	100.00	100.00	

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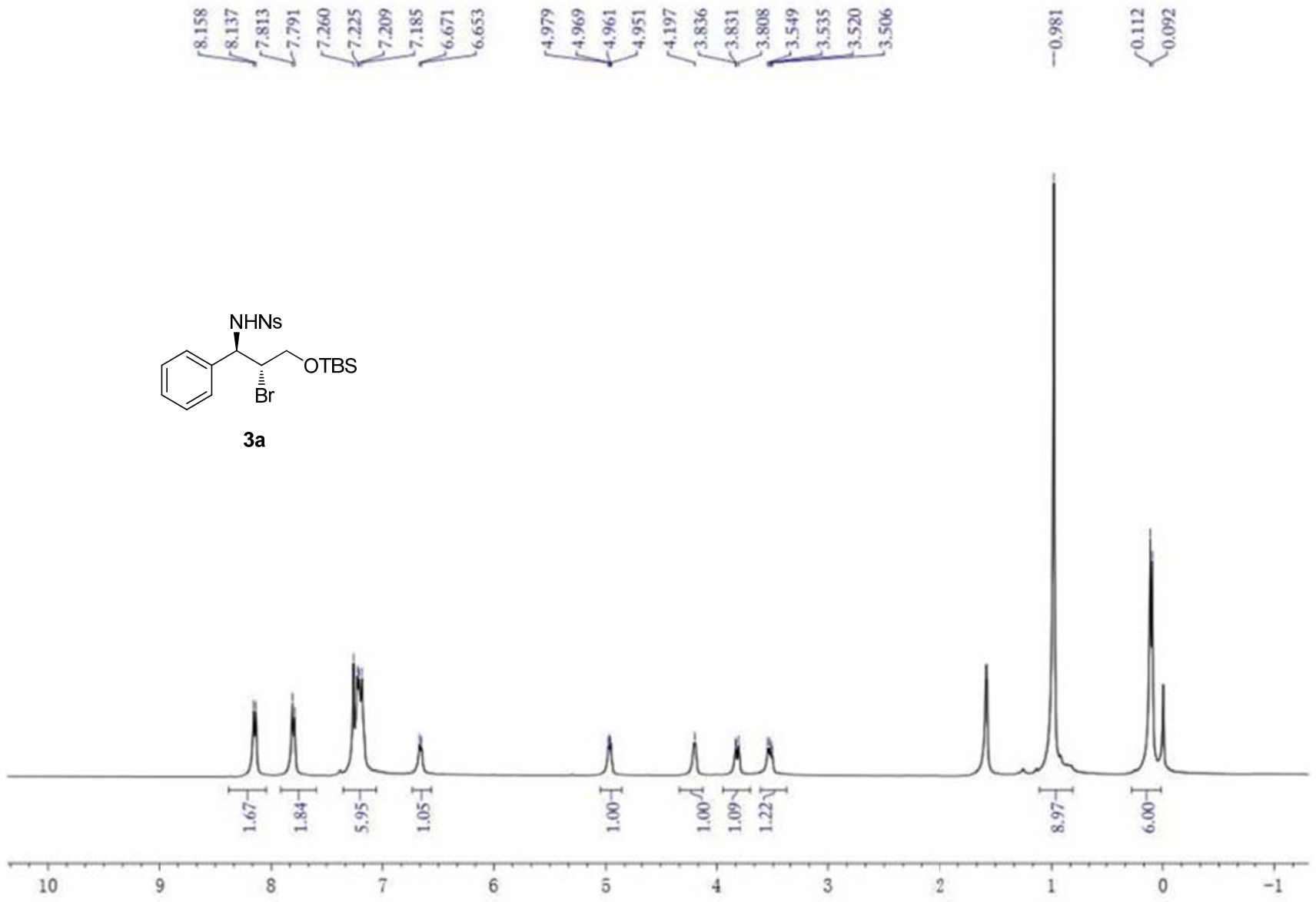
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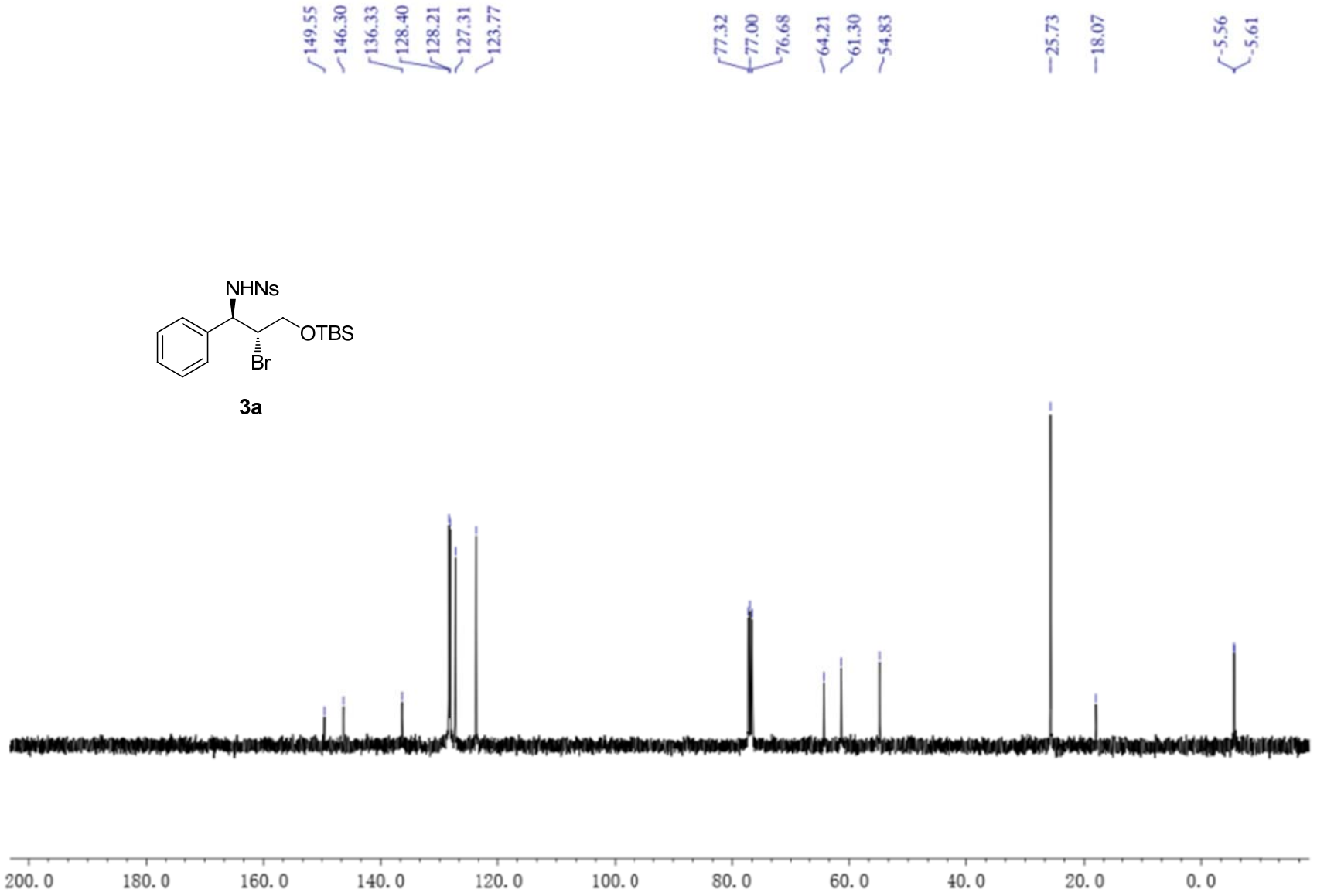
3a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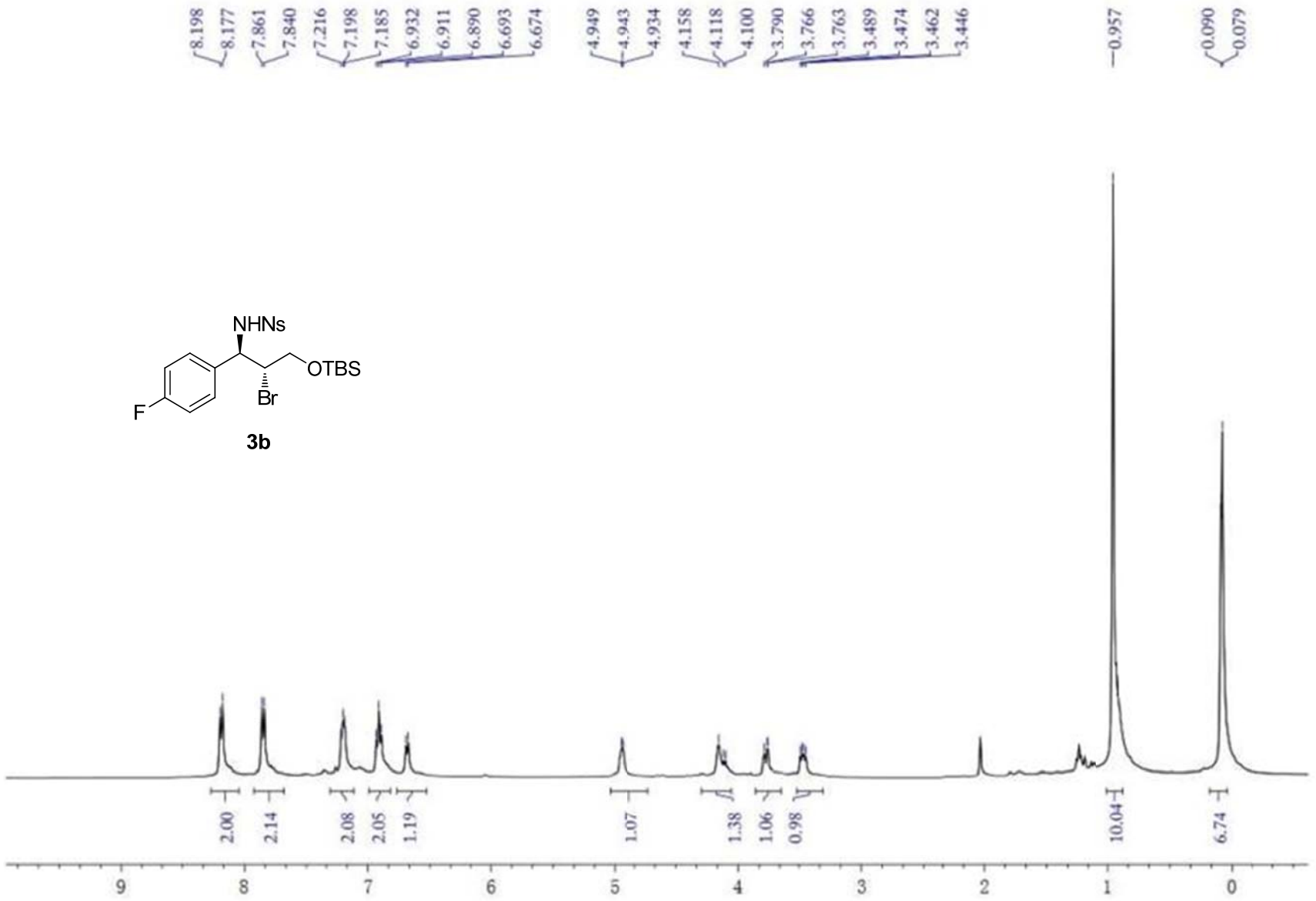
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4.118
4.100
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3.474
3.462
3.446
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0.090
0.079
NHNs
OTBS
Br
F
3b
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2.14
2.08
2.05
1.19
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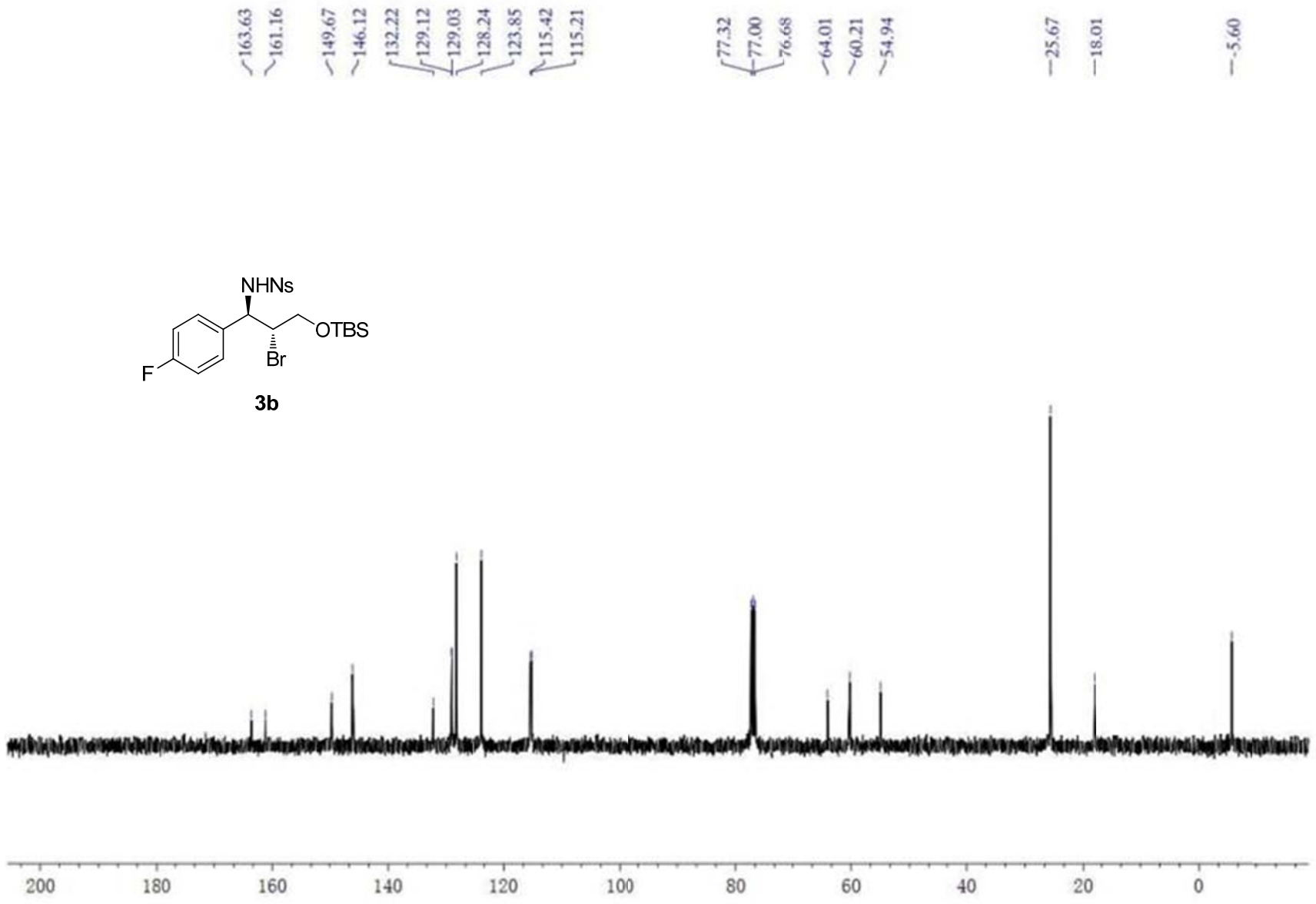
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64.01
60.21
54.94
25.67
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OTBS
Br
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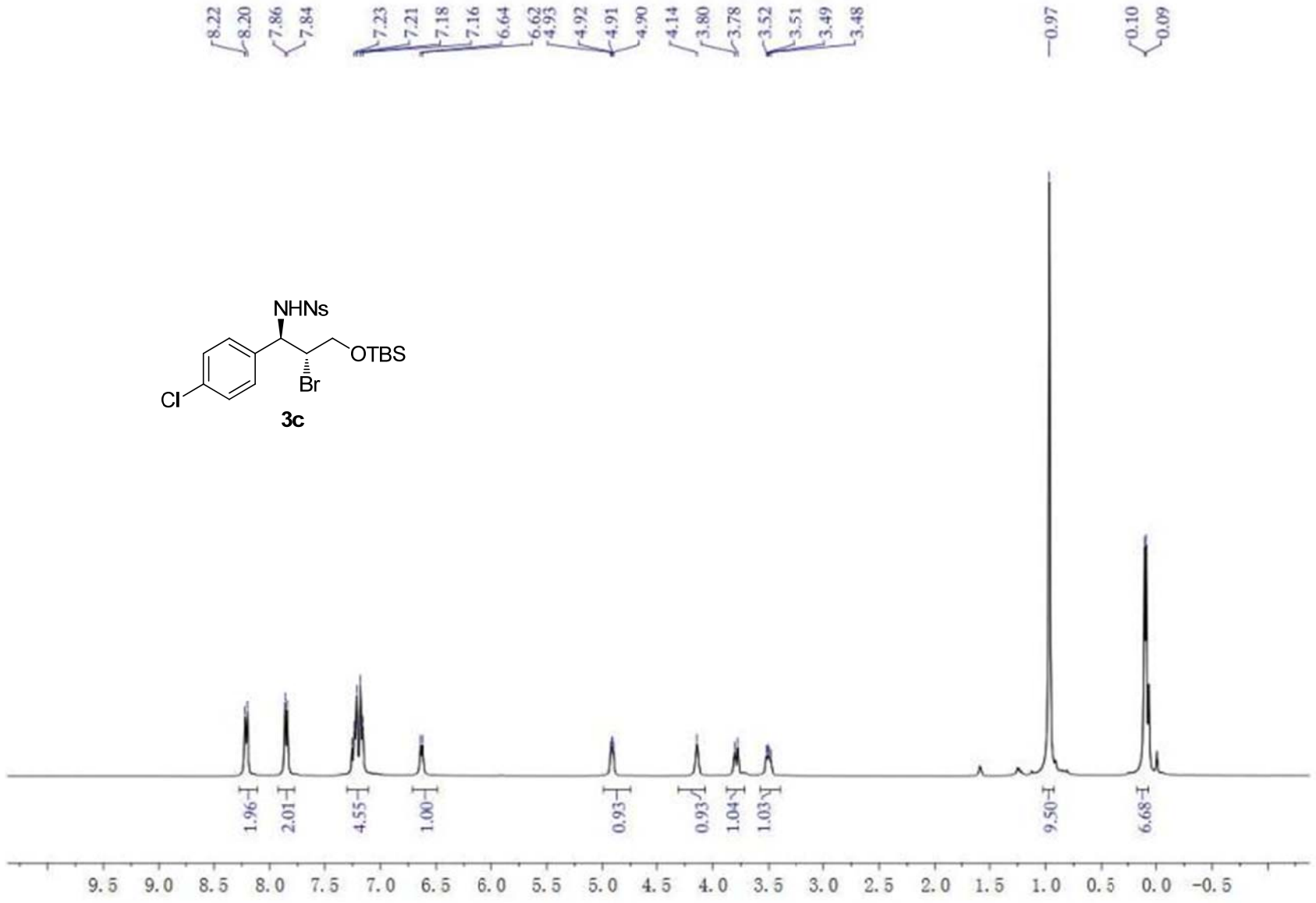
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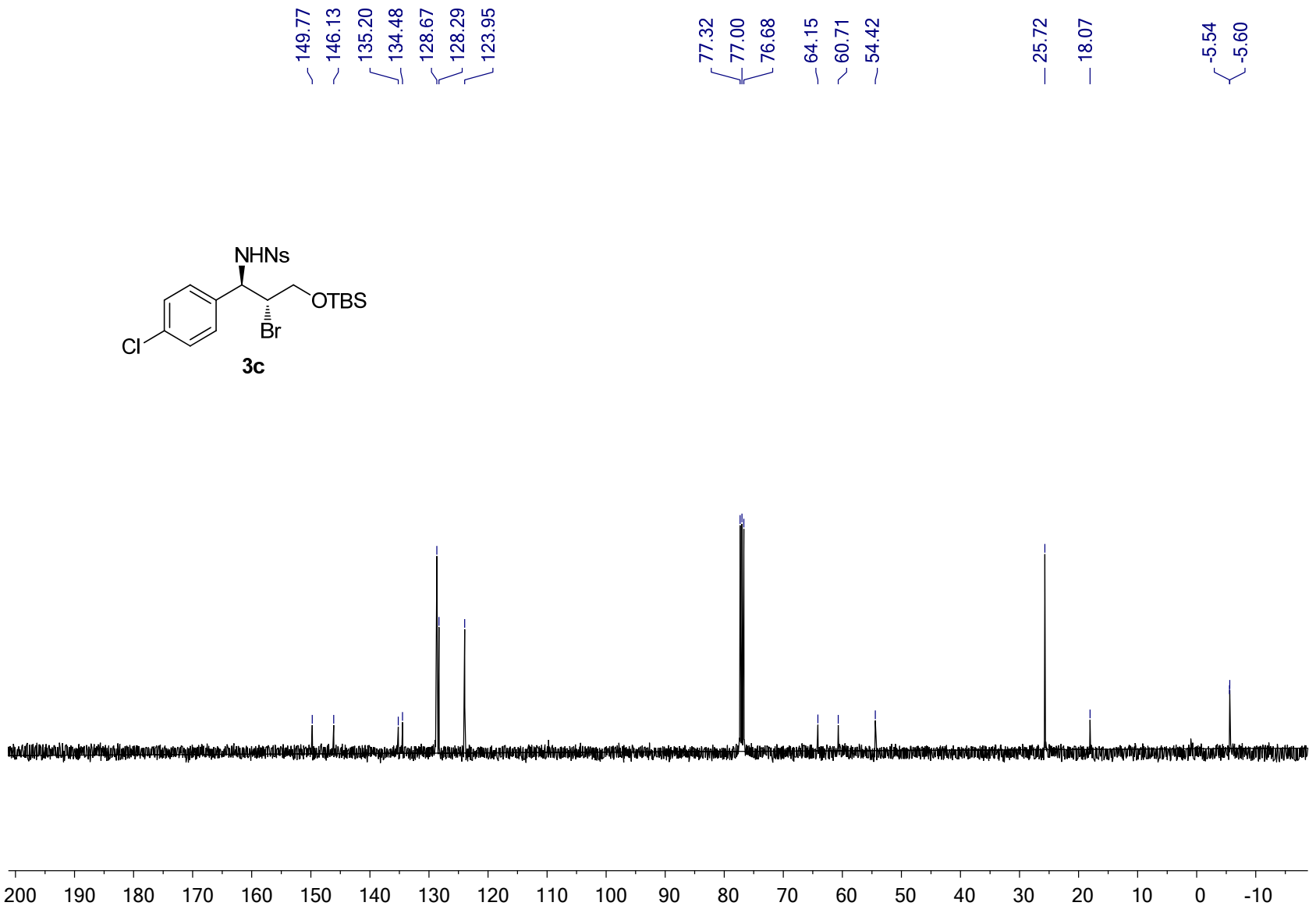
4.91
4.90
4.14
3.80
3.78
3.52
3.51
3.49
3.48
0.97
0.10
0.09
NHNs
OTBS
Br
Cl
3c
1.96
2.01
4.55
1.00
0.93
0.93
1.04
1.03
9.50
6.68
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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18.07
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-5.60
NHNs
OTBS
Br
Cl
3c
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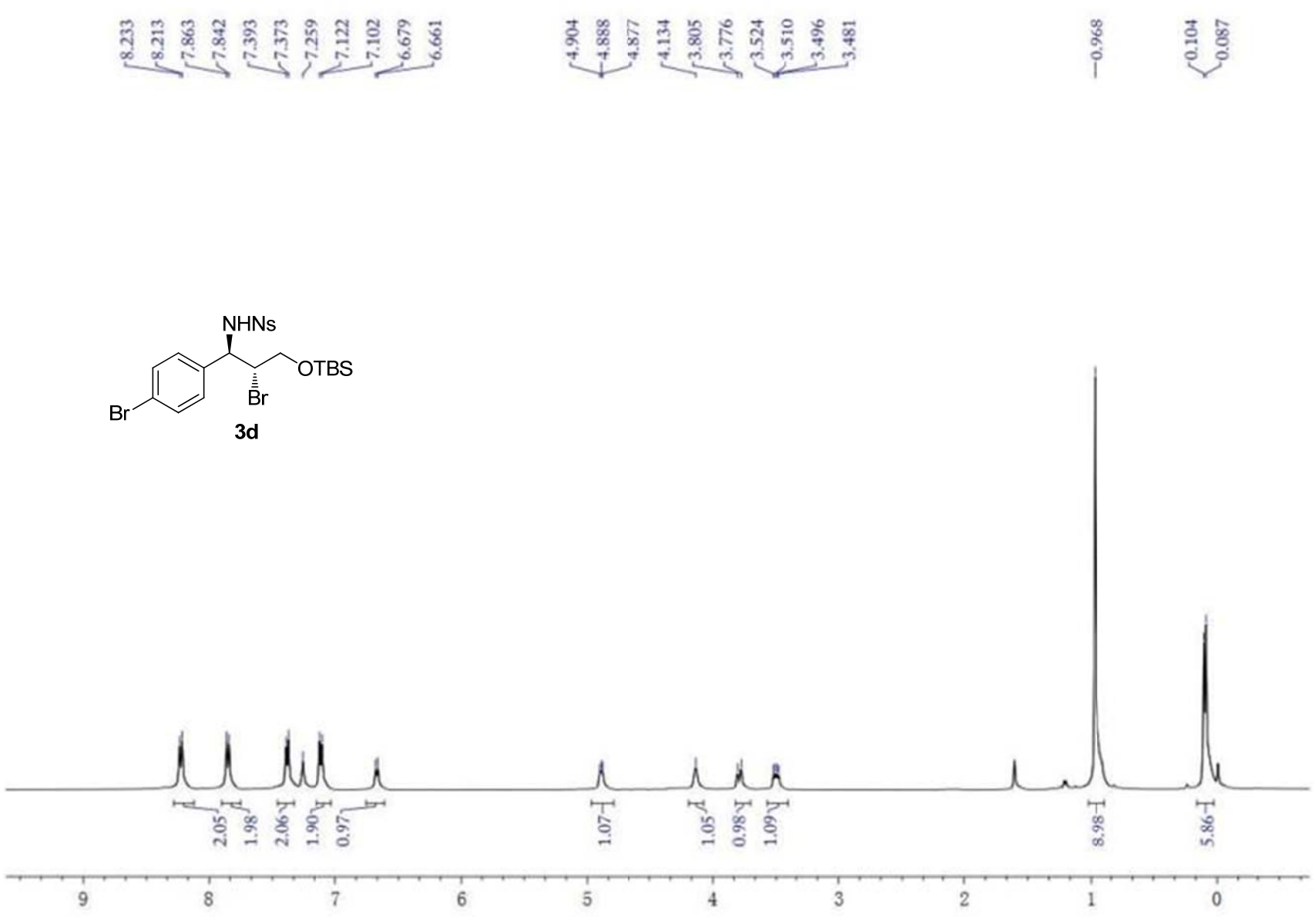
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4.877
4.134
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3.776
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3.510
3.496
3.481
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0.087
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OTBS
Br
Br
3d
2.05
1.98
2.06
1.90
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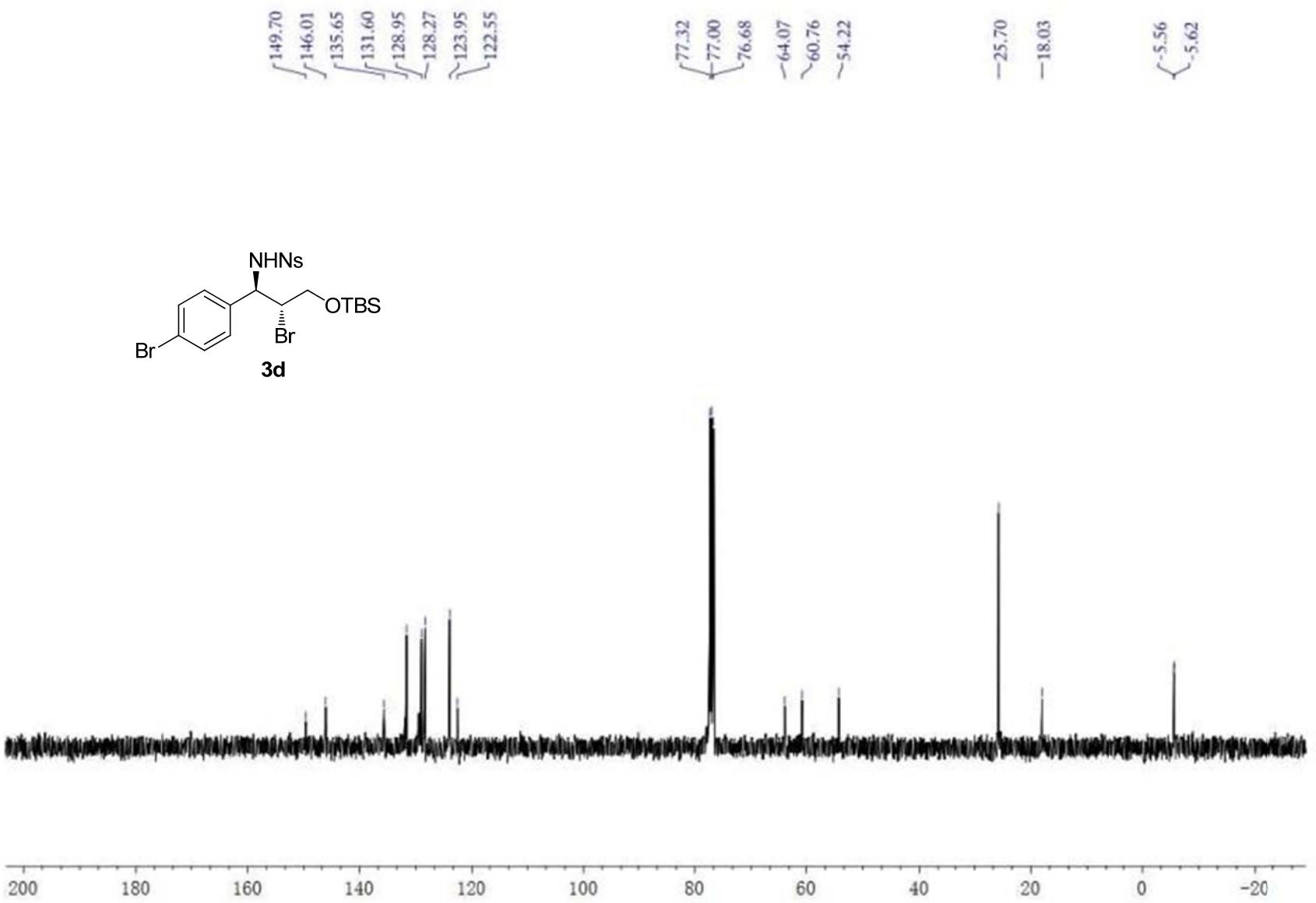
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Br
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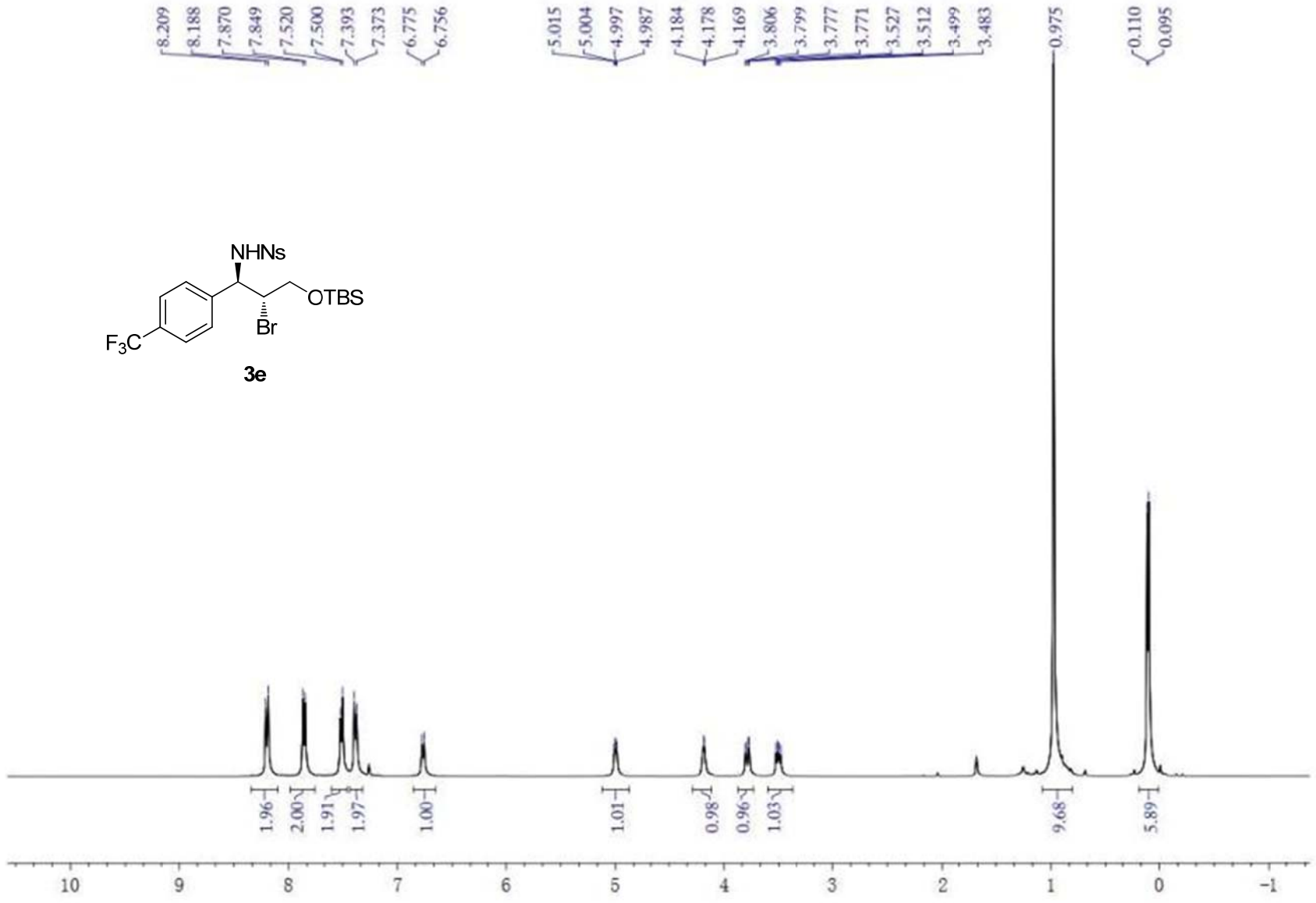
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7.373
6.775
6.756
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4.997
4.987
4.184
4.178
4.169
3.806
3.799
3.777
3.771
3.527
3.512
3.499
3.483
0.975
0.110
0.095
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OTBS
Br
F3C
3e
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2.00
1.91
1.97
1.00
1.01
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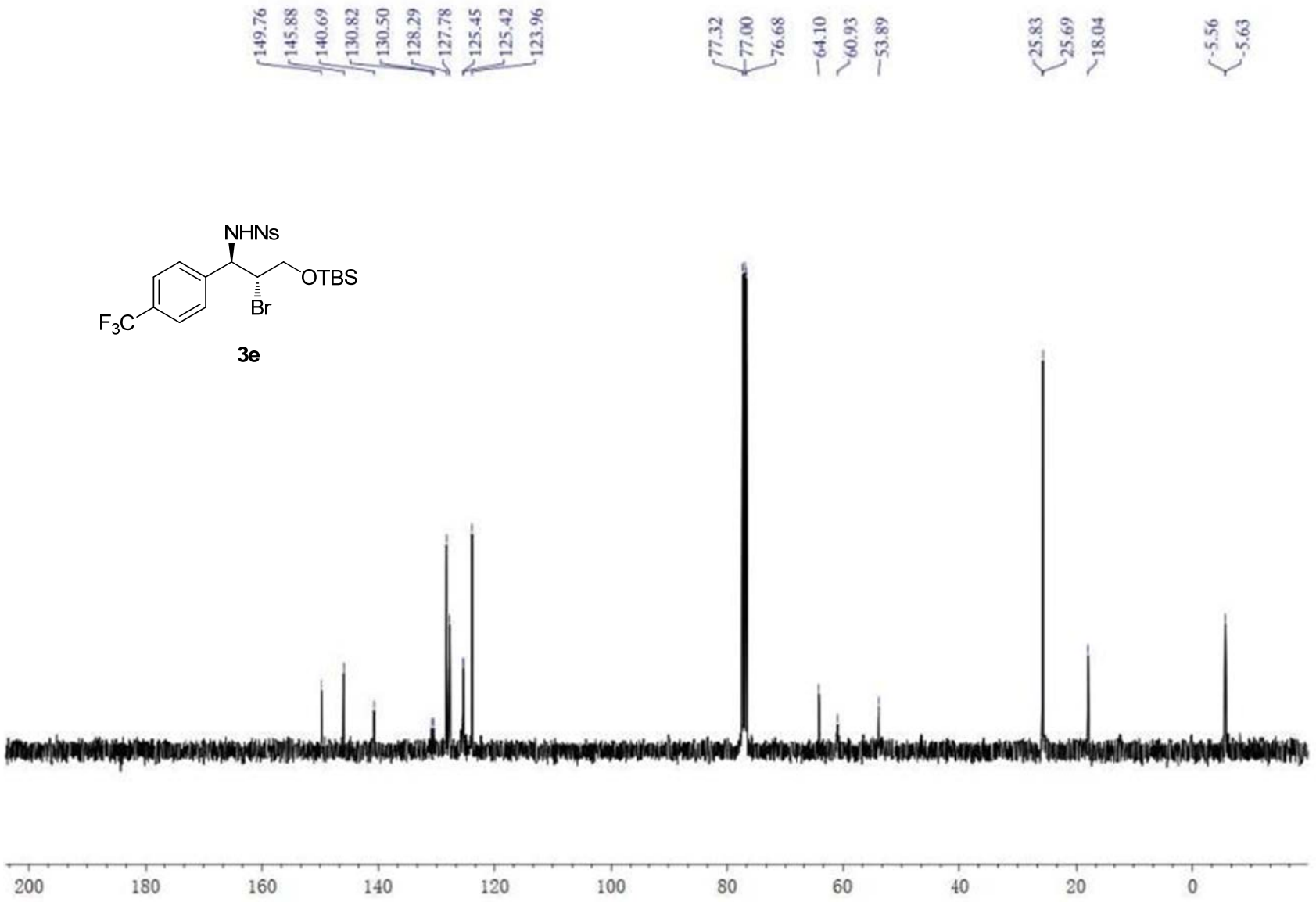
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77.00
76.68
64.10
60.93
53.89
25.83
25.69
18.04
-5.56
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OTBS
Br
F3C
3e
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140
120
100
80
60
40
20
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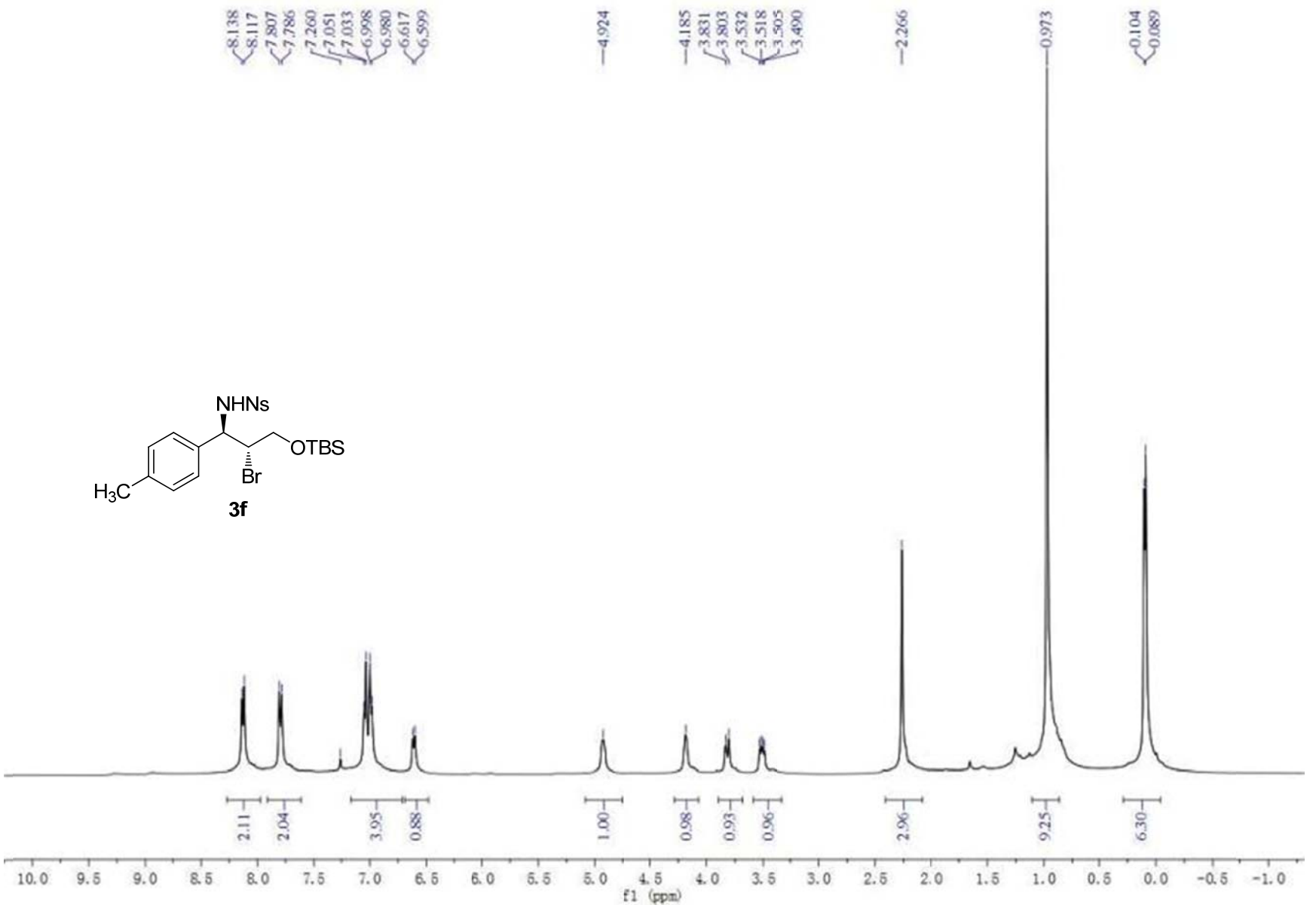
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4.185
3.831
3.803
3.532
3.518
3.505
3.400
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0.089
NHNs
OTBS
Br
H3C
3f
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2.96
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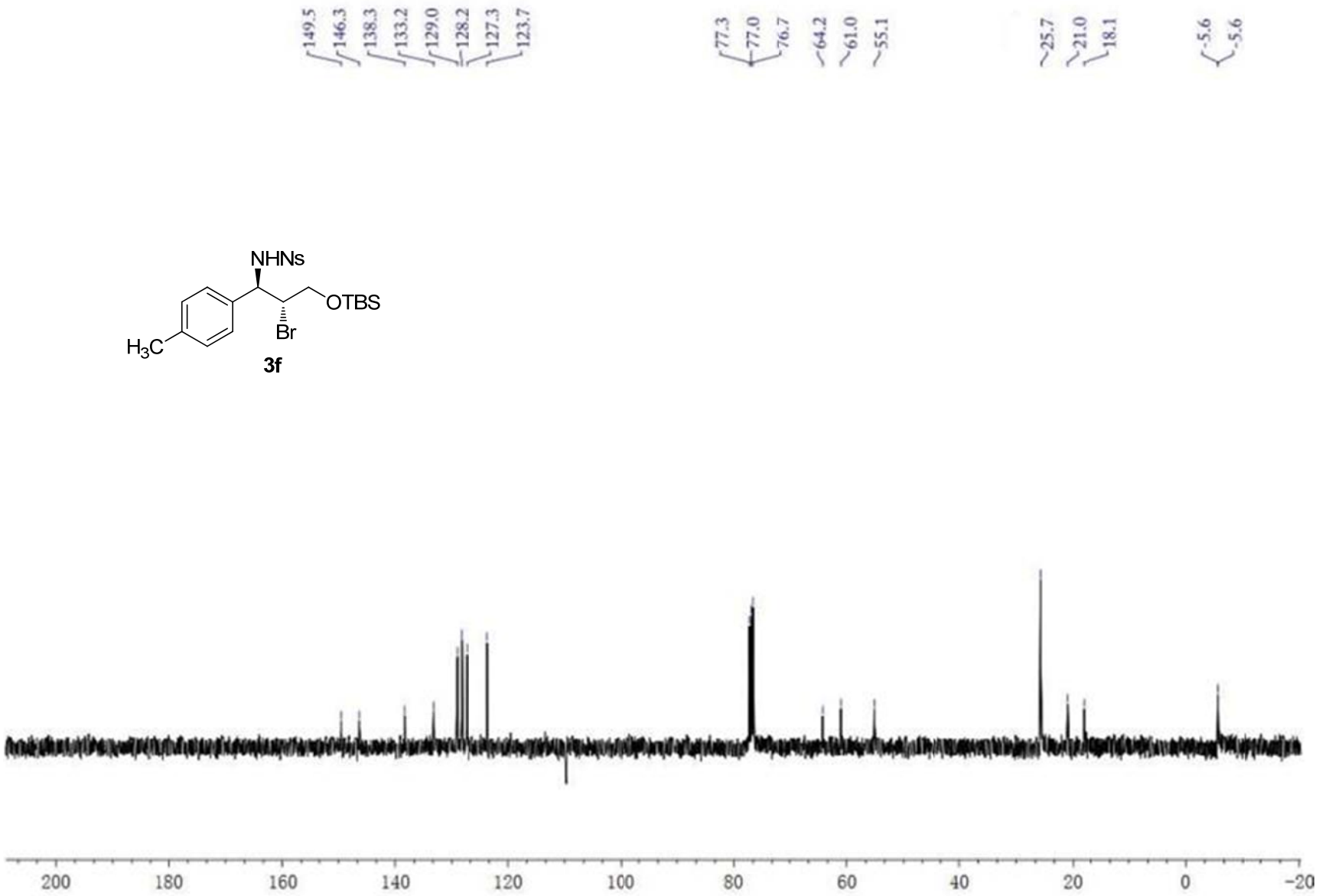
6.30
f1 (ppm)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76.7
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55.1
25.7
21.0
18.1
-5.6
-5.6
NHNs
OTBS
Br
H3C
3f
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120
100
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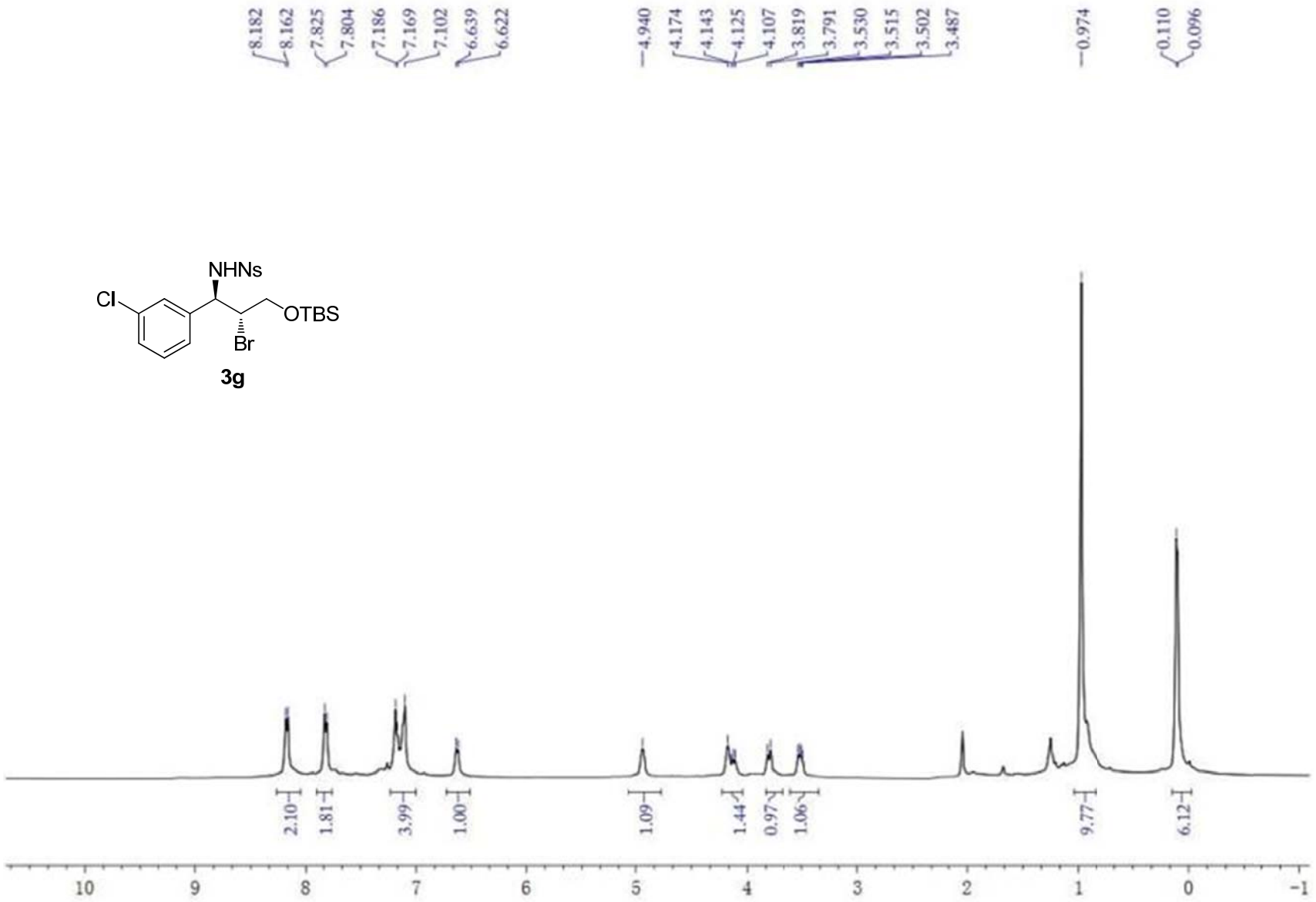
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4.125
4.107
3.819
3.791
3.530
3.515
3.502
3.487
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0.110
0.096
NHNs
Cl
OTBS
Br
3g
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3.99
1.00
1.09
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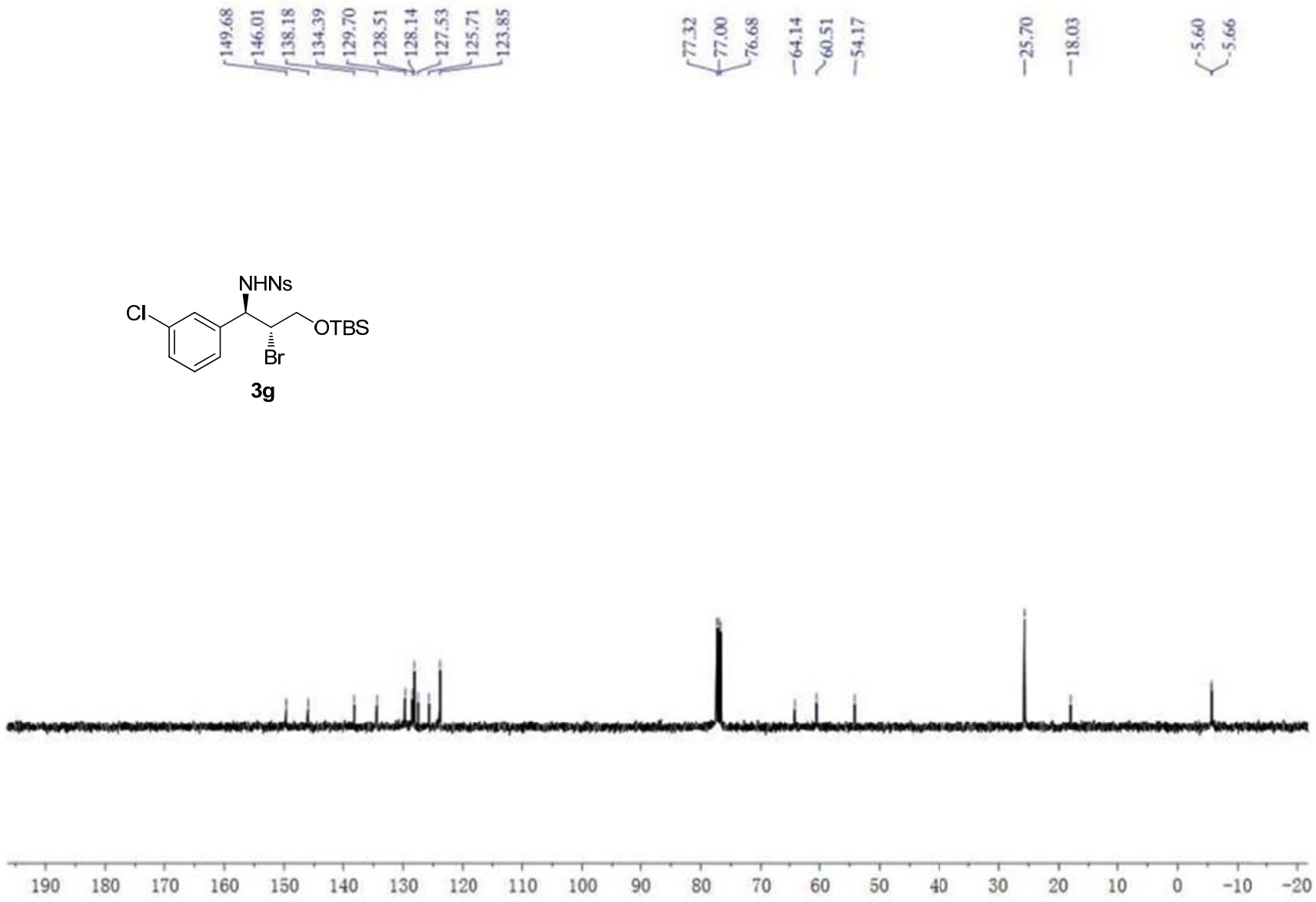
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77.00
76.68
64.14
60.51
54.17
25.70
18.03
-5.60
-5.66
NHNs
Cl
OTBS
Br
3g
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180
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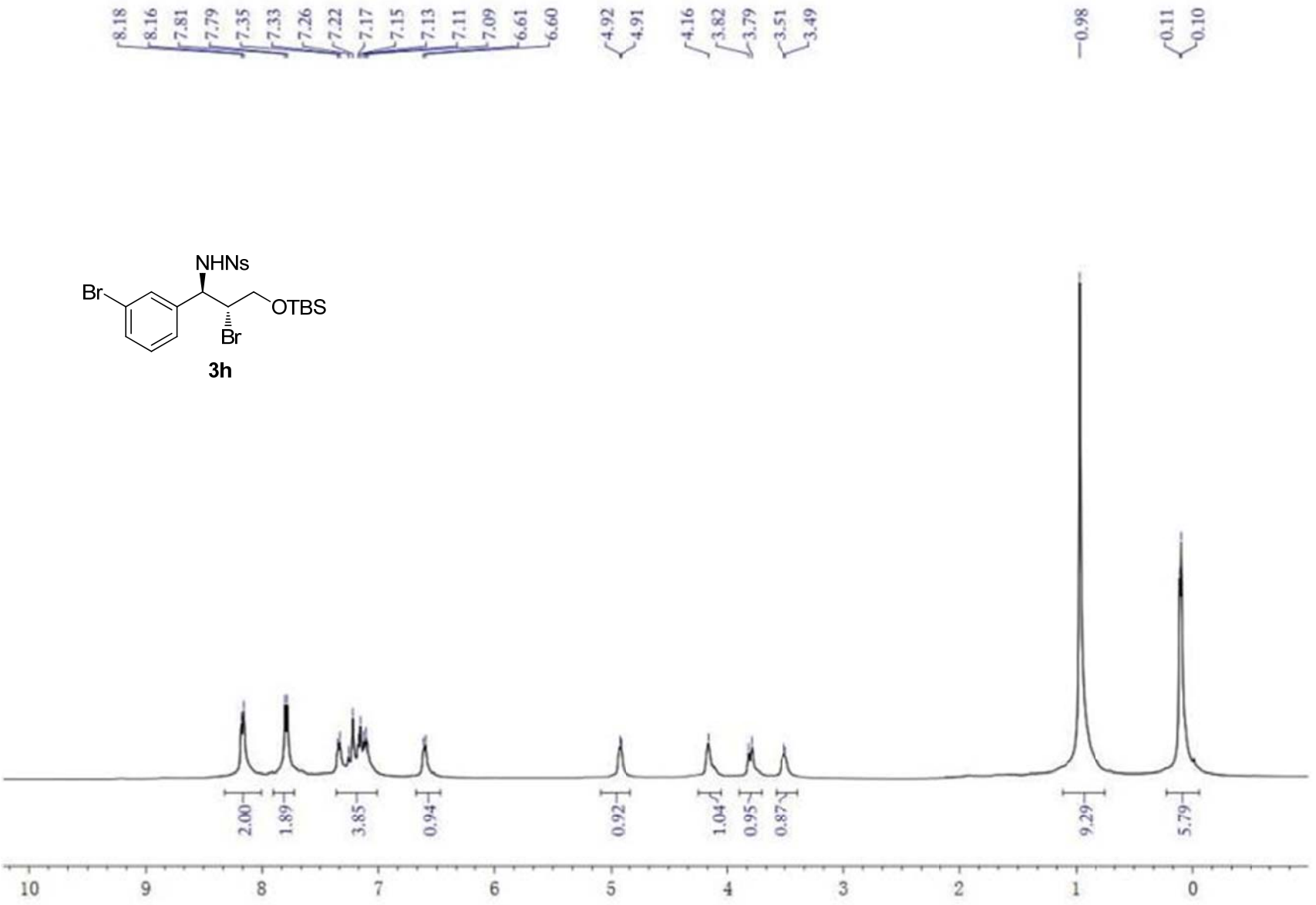
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7.09
6.61
6.60
4.92
4.91
4.16
3.82
3.79
3.51
3.49
0.98
0.11
0.10
NHNs
Br
OTBS
Br
3h
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0.94
0.92
1.04
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0.87
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5.79
10
9
8
7
6
5
4
3
2
1
0

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128.11
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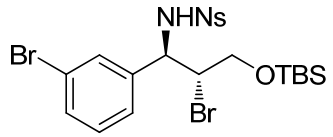
-5.62



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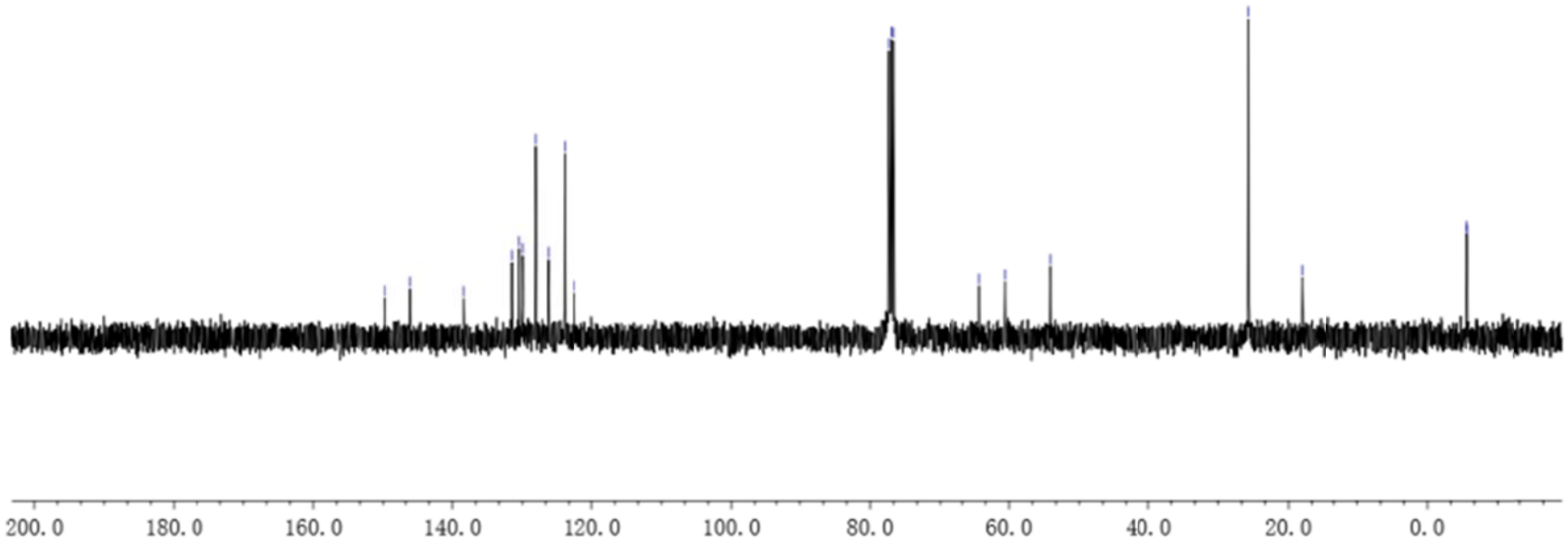

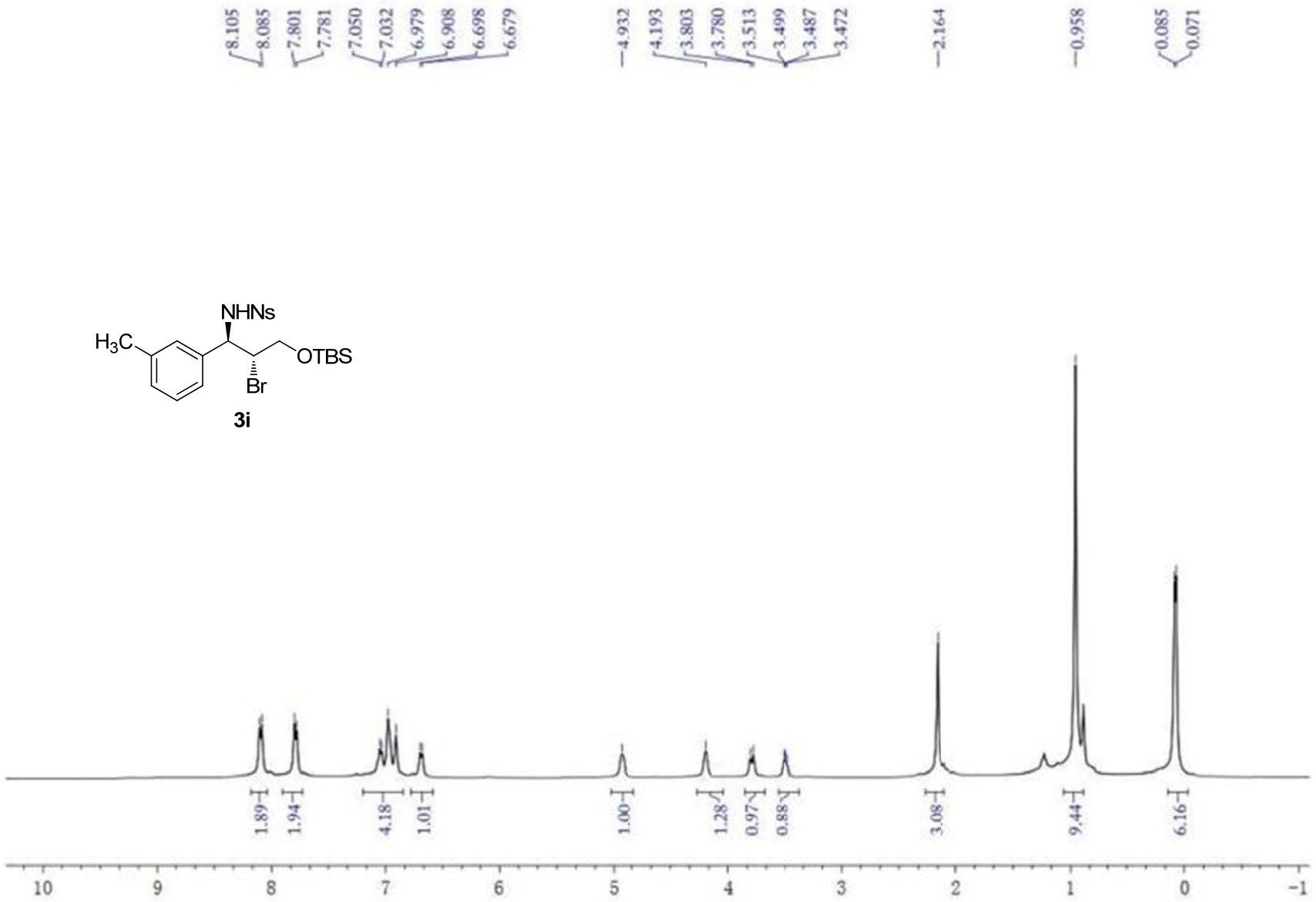
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3.780
3.513
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3.487
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0.071
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H3C
OTBS
Br
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1.00
1.28
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8
7
6
5
4
3
2
1
0
-1

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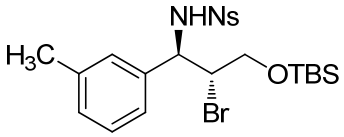
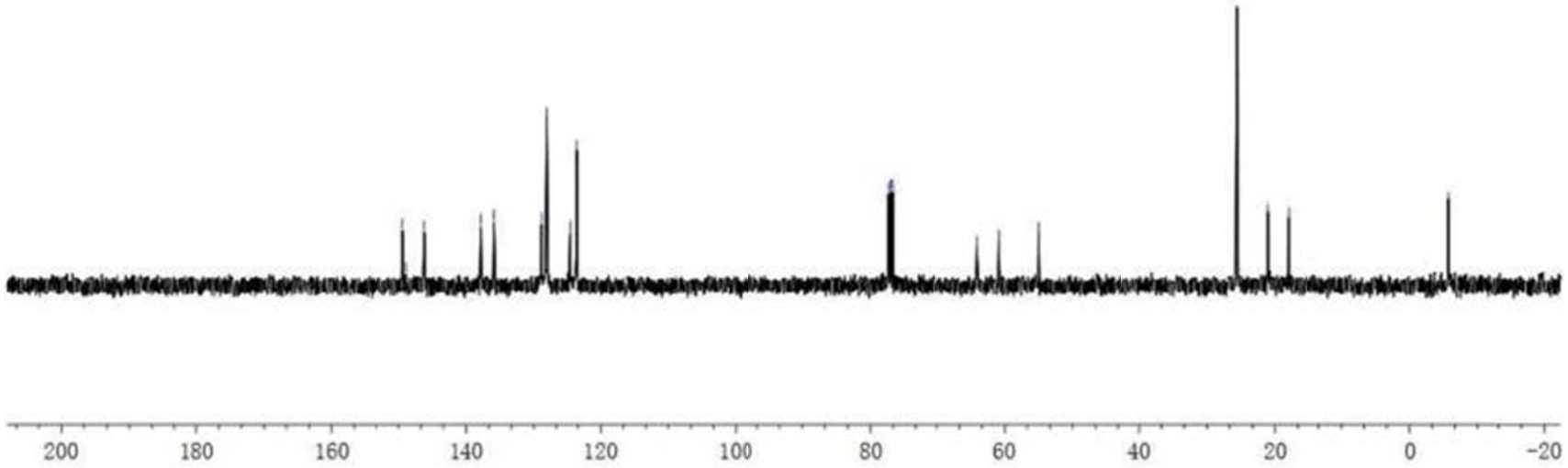
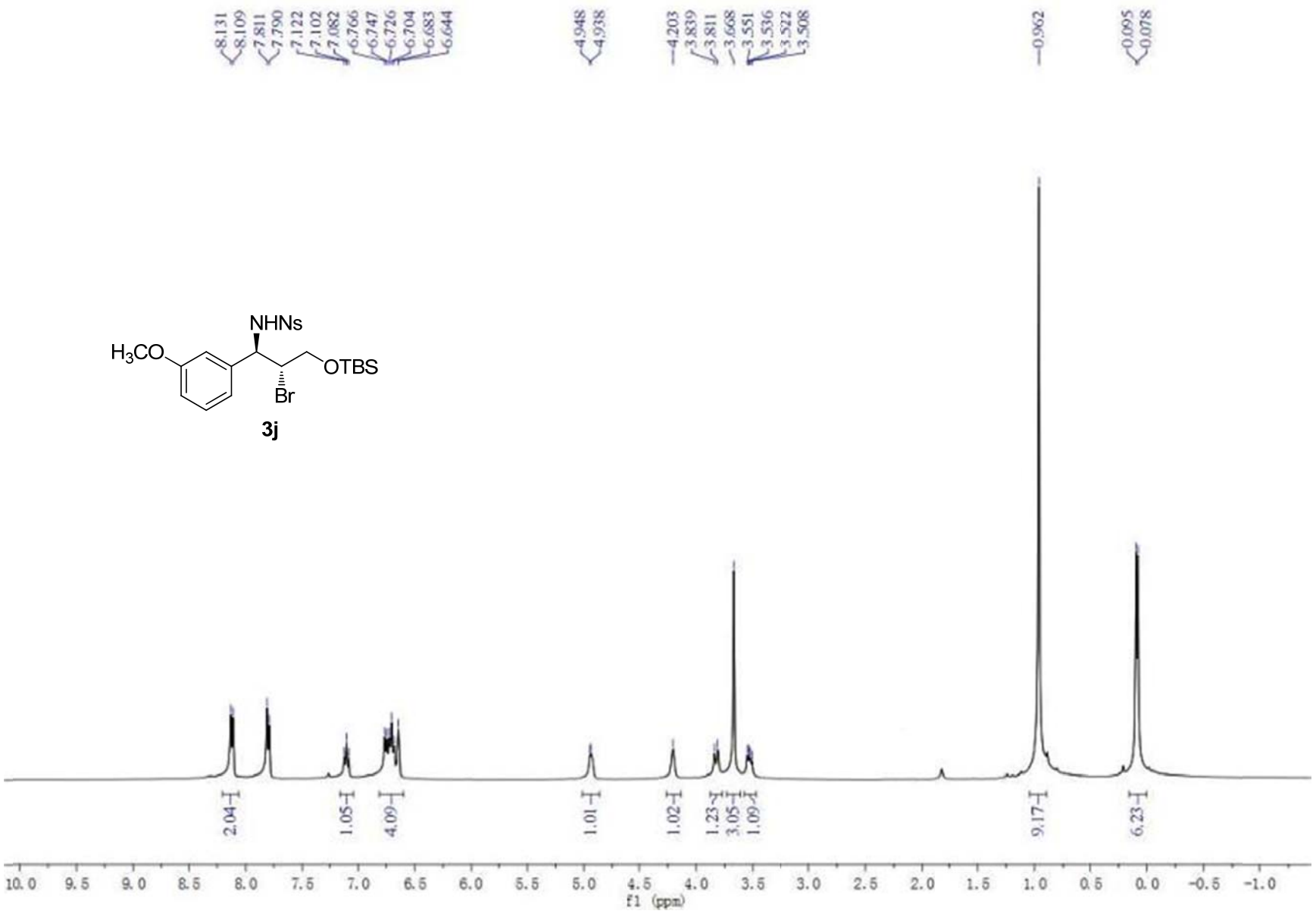
-5.73



3i

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4.938
4.203
3.839
3.811
3.668
3.551
3.536
3.522
3.508
0.962
0.095
0.078
NHNs
H3CO
OTBS
Br
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4.09
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1.02
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1.09
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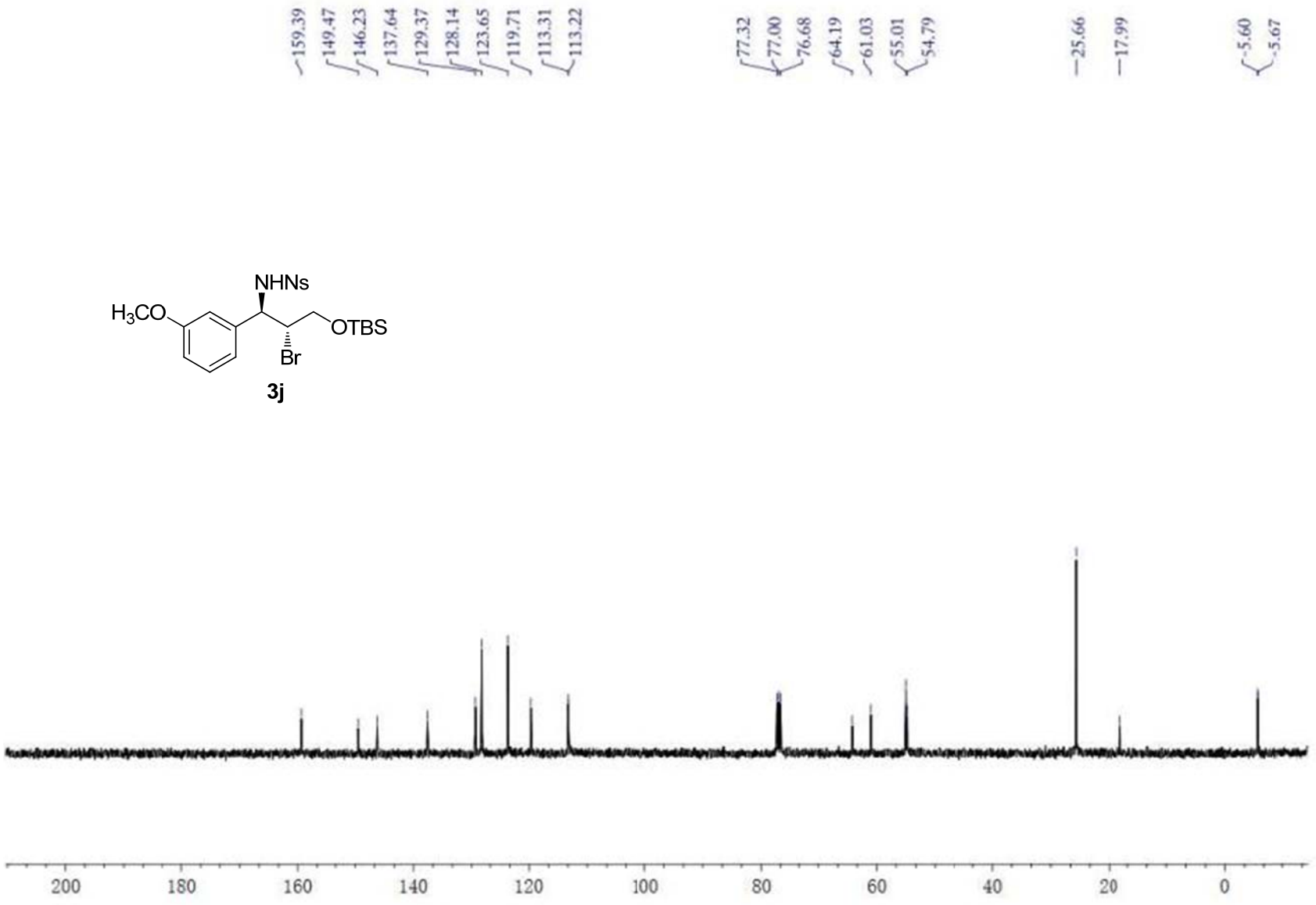
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77.00
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-5.60
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H3CO
OTBS
Br
3j
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140
120
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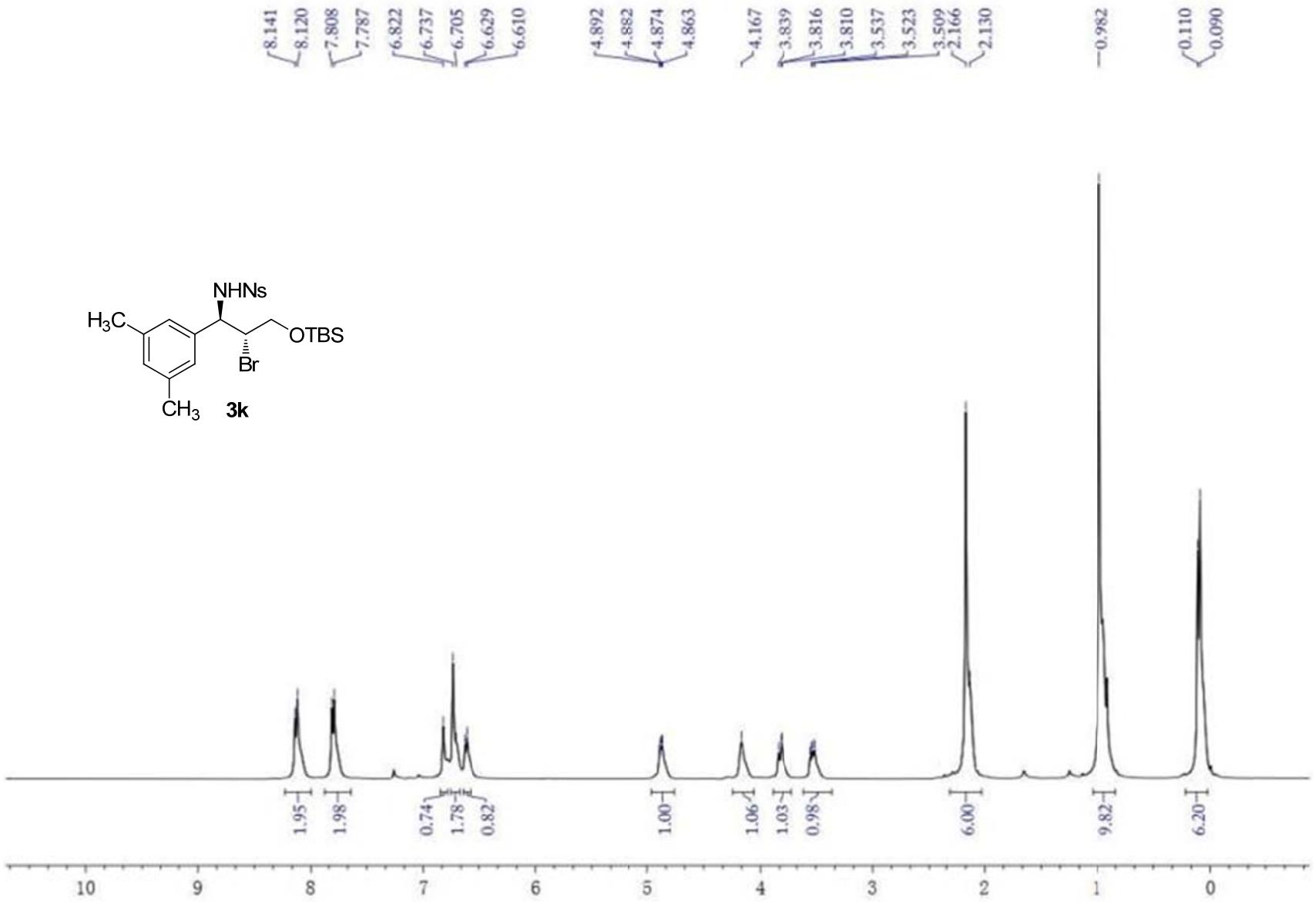
20
0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6.610
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4.874
4.863
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3.810
3.537
3.523
3.509
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0.110
0.090
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H3C
OTBS
Br
CH3
3k
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1.98
0.74
1.78
0.82
1.00
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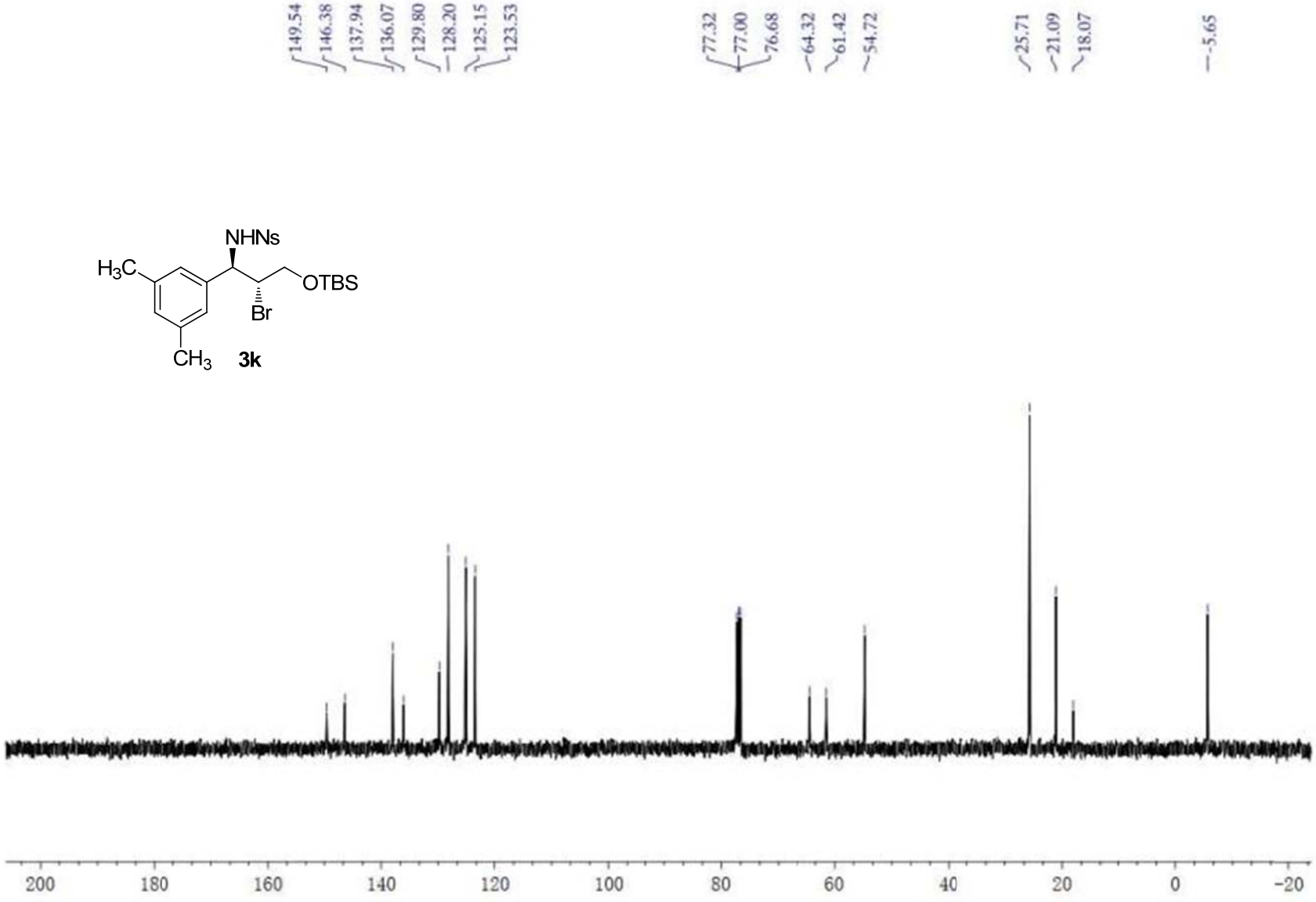
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64.32
61.42
54.72
25.71
21.09
18.07
-5.65
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Br
CH3
3k
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120
100
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40
20
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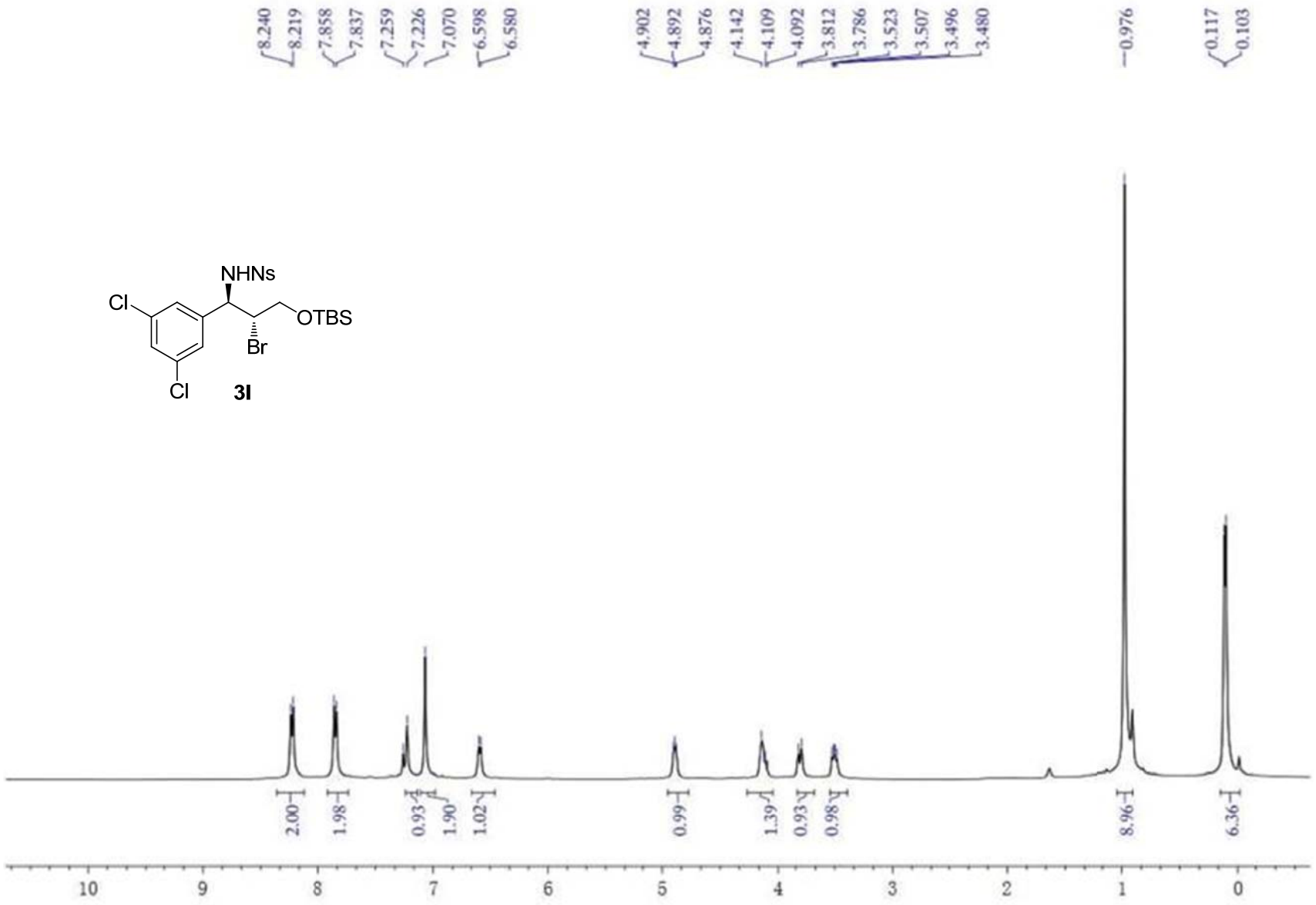
-20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4.109
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0.103
NHNs
Cl
OTBS
Br
Cl
3l
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1.02
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0.93
0.98
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7
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5
4
3
2
1
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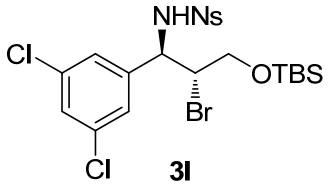

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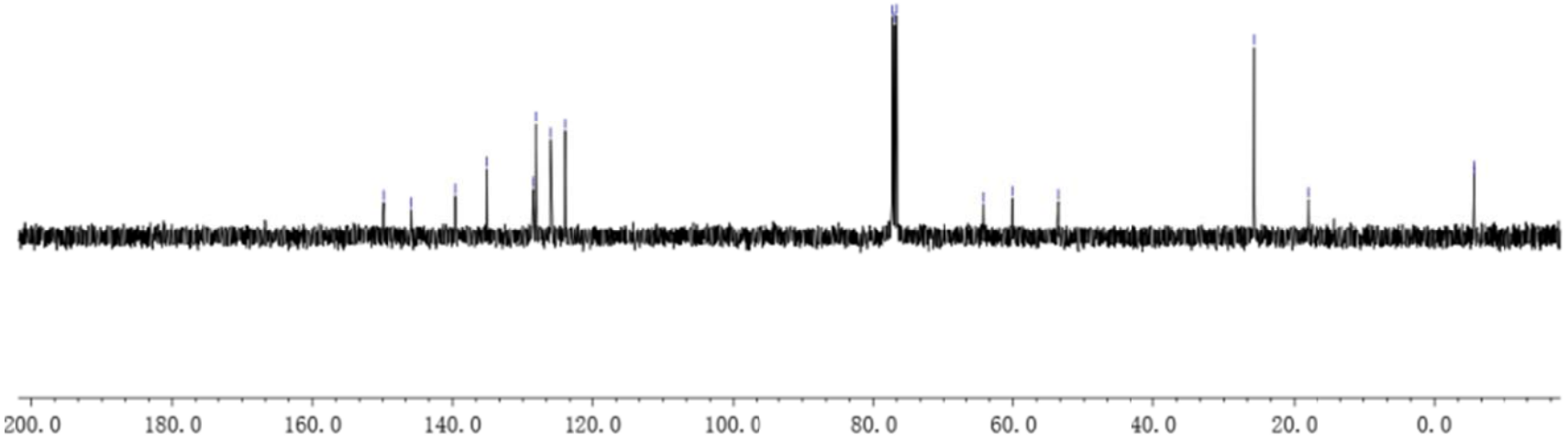

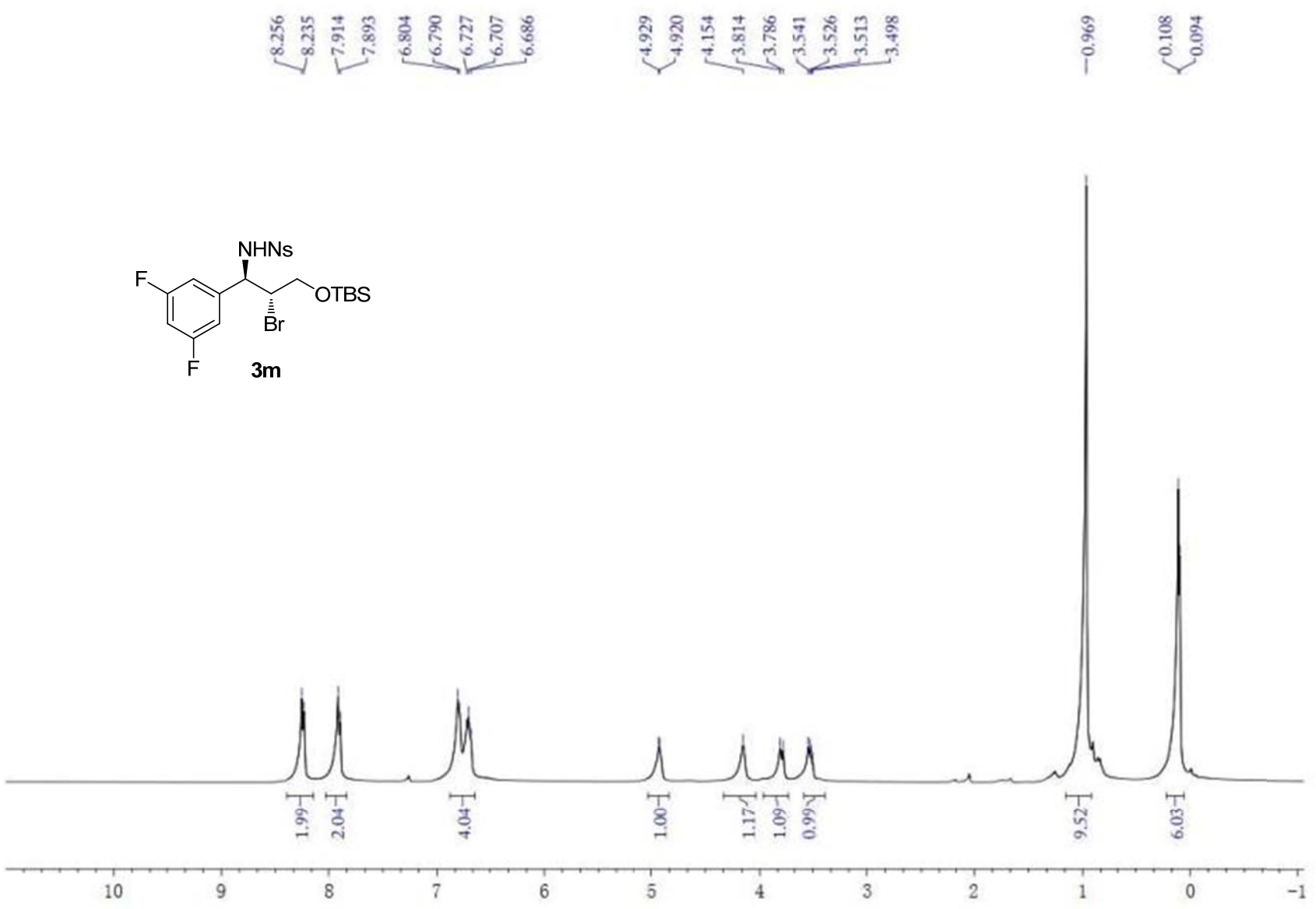
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3.513
3.498
0.969
0.108
0.094
NHNs
F
OTBS
Br
F
3m
1.99
2.04
4.04
1.00
1.17
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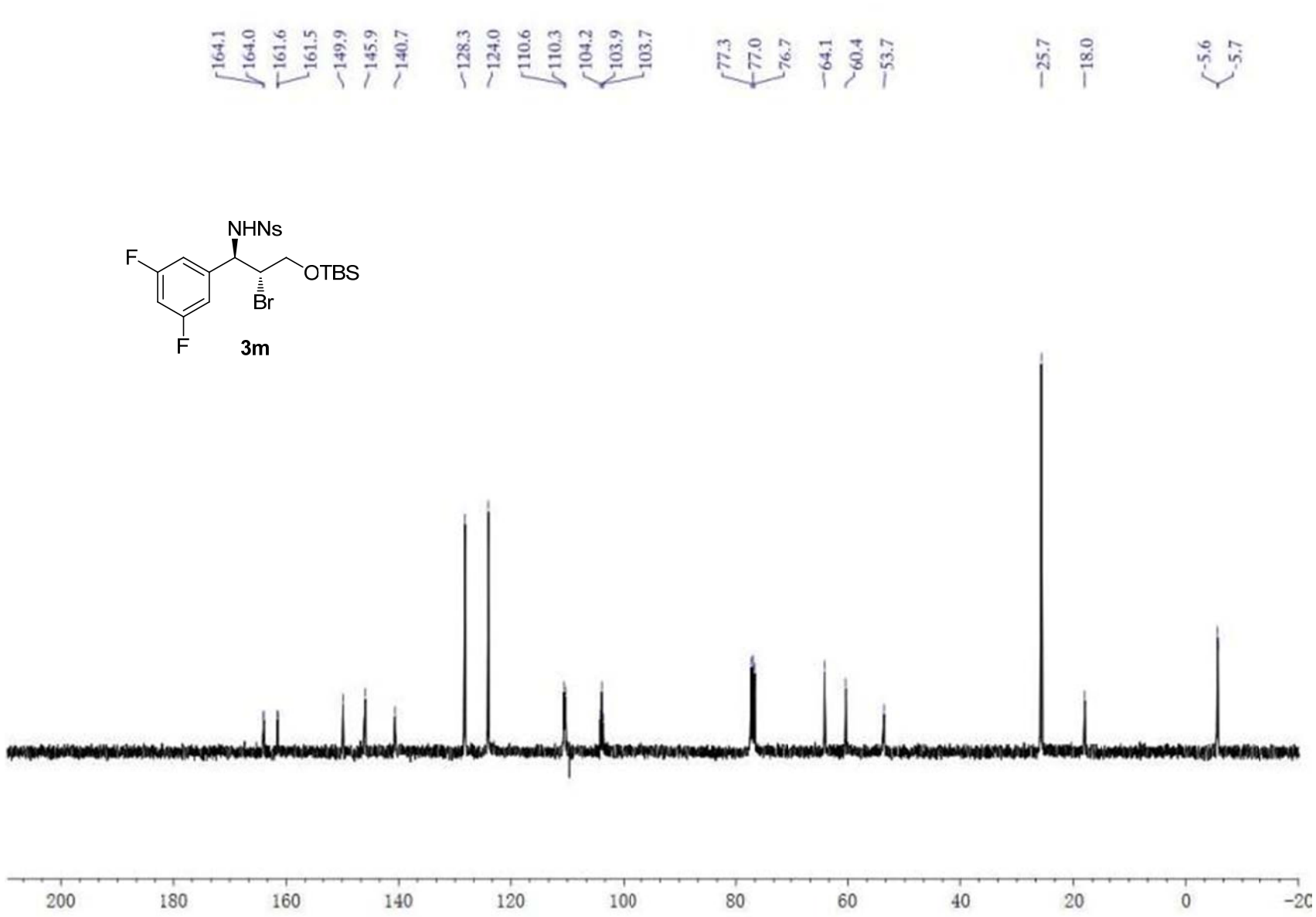
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110.3
104.2
103.9
103.7
77.3
77.0
76.7
64.1
60.4
53.7
25.7
18.0
-5.6
-5.7
NHNs
F
OTBS
Br
F
3m
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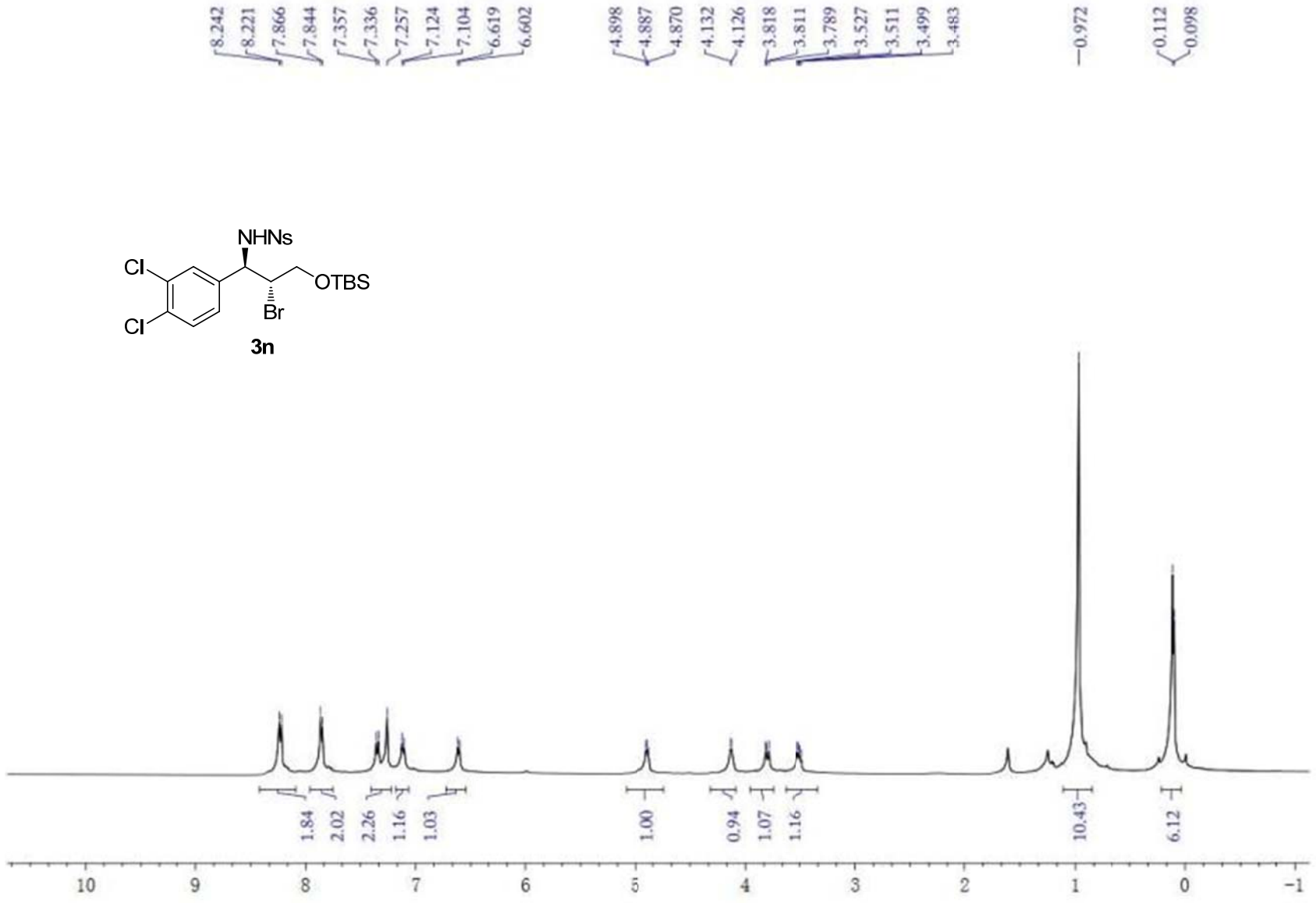
0
-20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7.336
7.257
7.124
7.104
6.619
6.602
4.898
4.887
4.870
4.132
4.126
3.818
3.811
3.789
3.527
3.511
3.499
3.483
0.972
0.112
0.098
NHNs
Cl
Cl
OTBS
Br
3n
1.84
2.02
2.26
1.16
1.03
1.00
0.94
1.07
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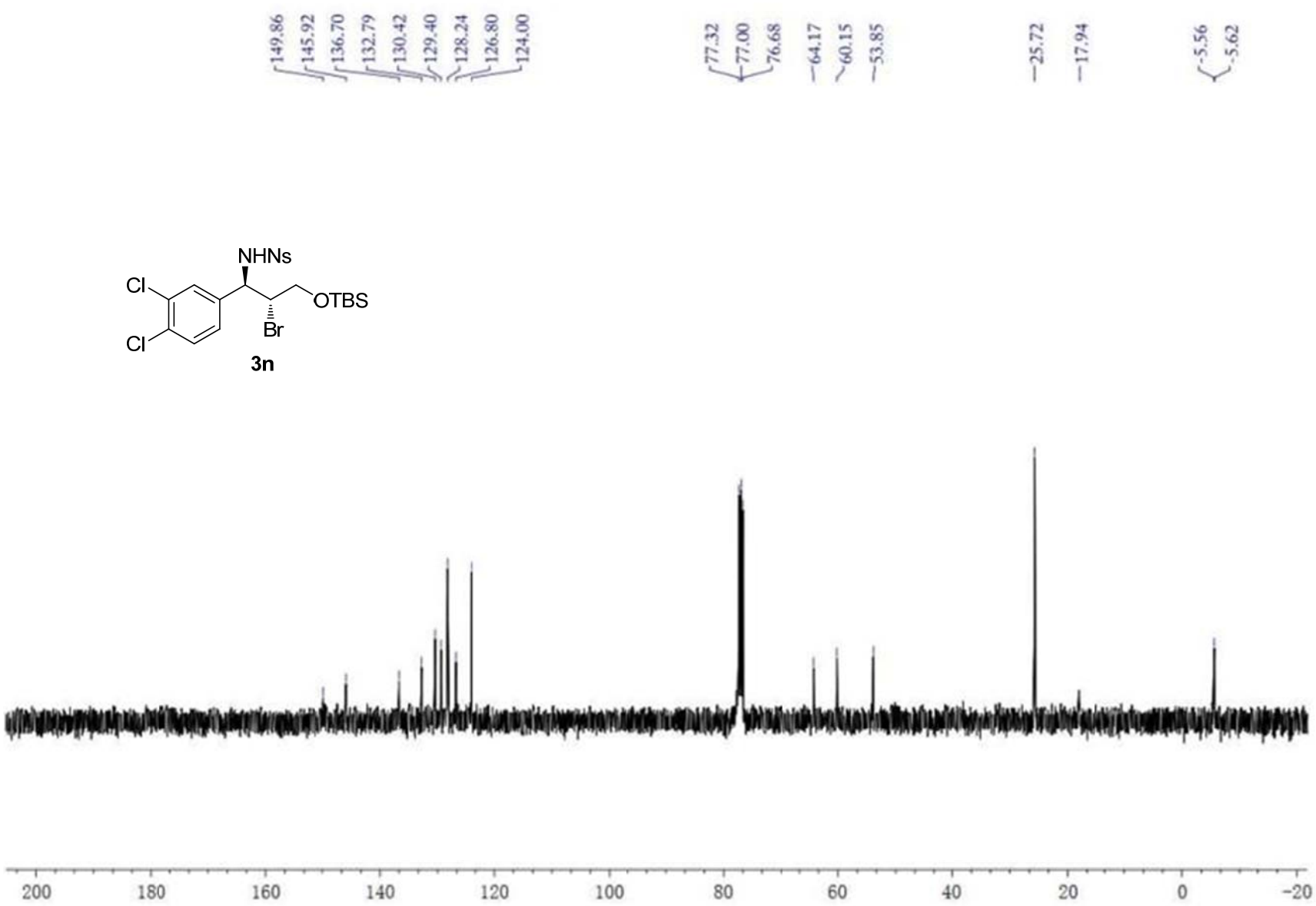
-1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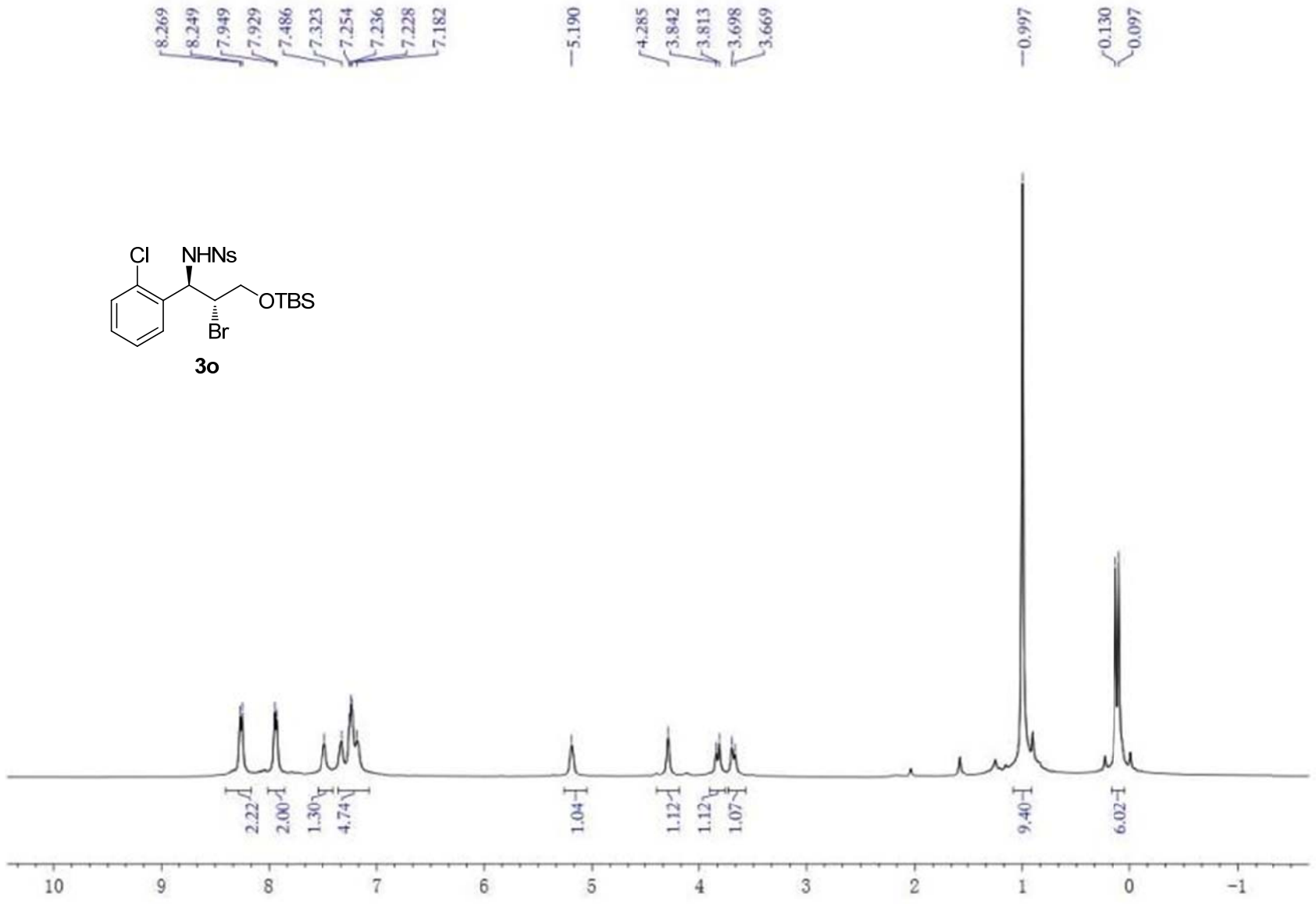
145.92
136.70
132.79
130.42
129.40
128.24
126.80
124.00
77.32
77.00
76.68
64.17
60.15
53.85
25.72
17.94
-5.56
-5.62
NHNs
Cl
Cl
OTBS
Br
3n
200
180
160
140
120
100
80
60
40
20
0
-20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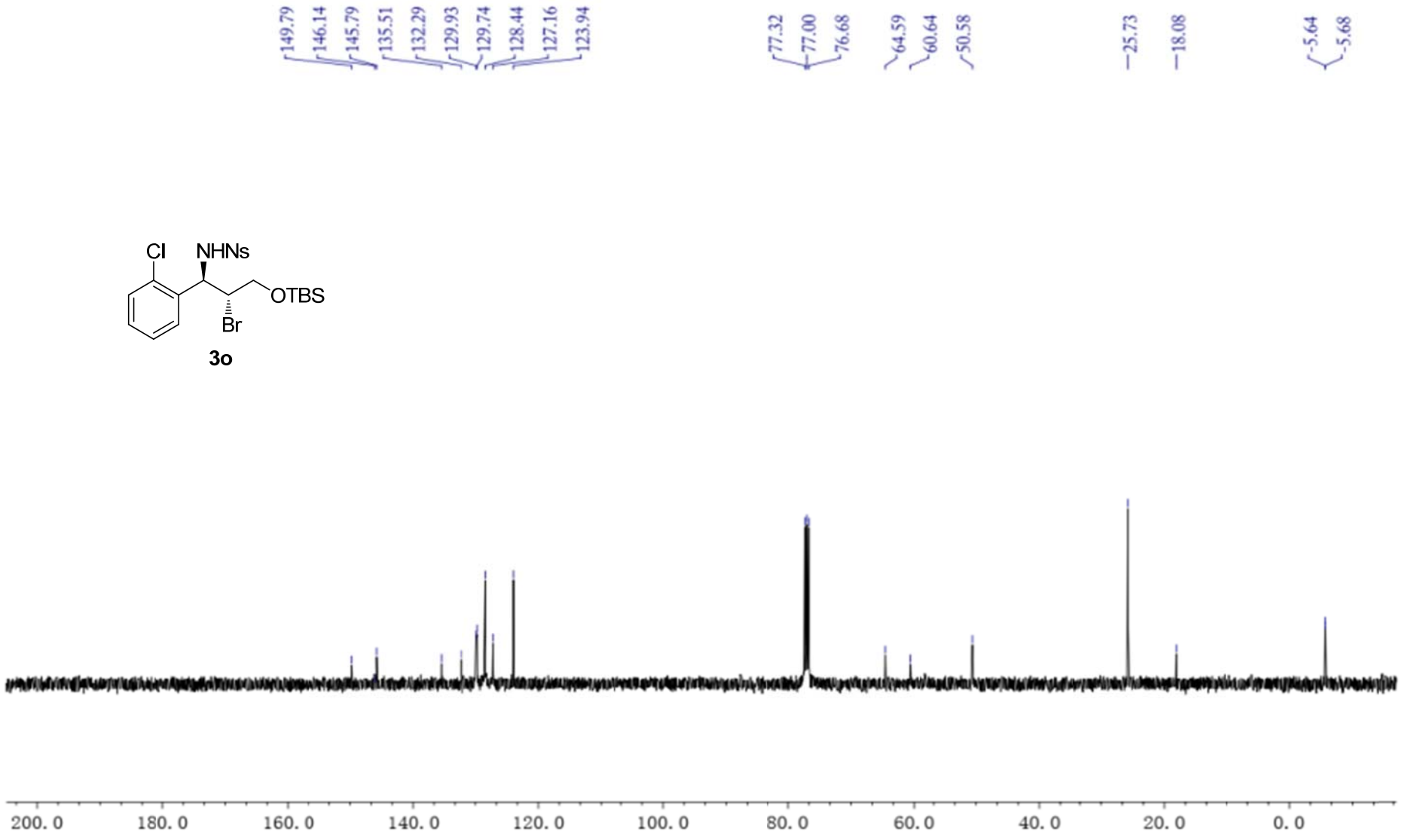
8.249
7.949
7.929
7.486
7.323
7.254
7.236
7.228
7.182
5.190
4.285
3.842
3.813
3.698
3.669
0.997
0.130
0.097
Cl
NHNs
OTBS
Br
3o
2.22
2.00
1.30
4.74
1.04
1.12
1.12
1.07
9.40
6.02
10
9
8
7
6
5
4
3
2
1
0
−1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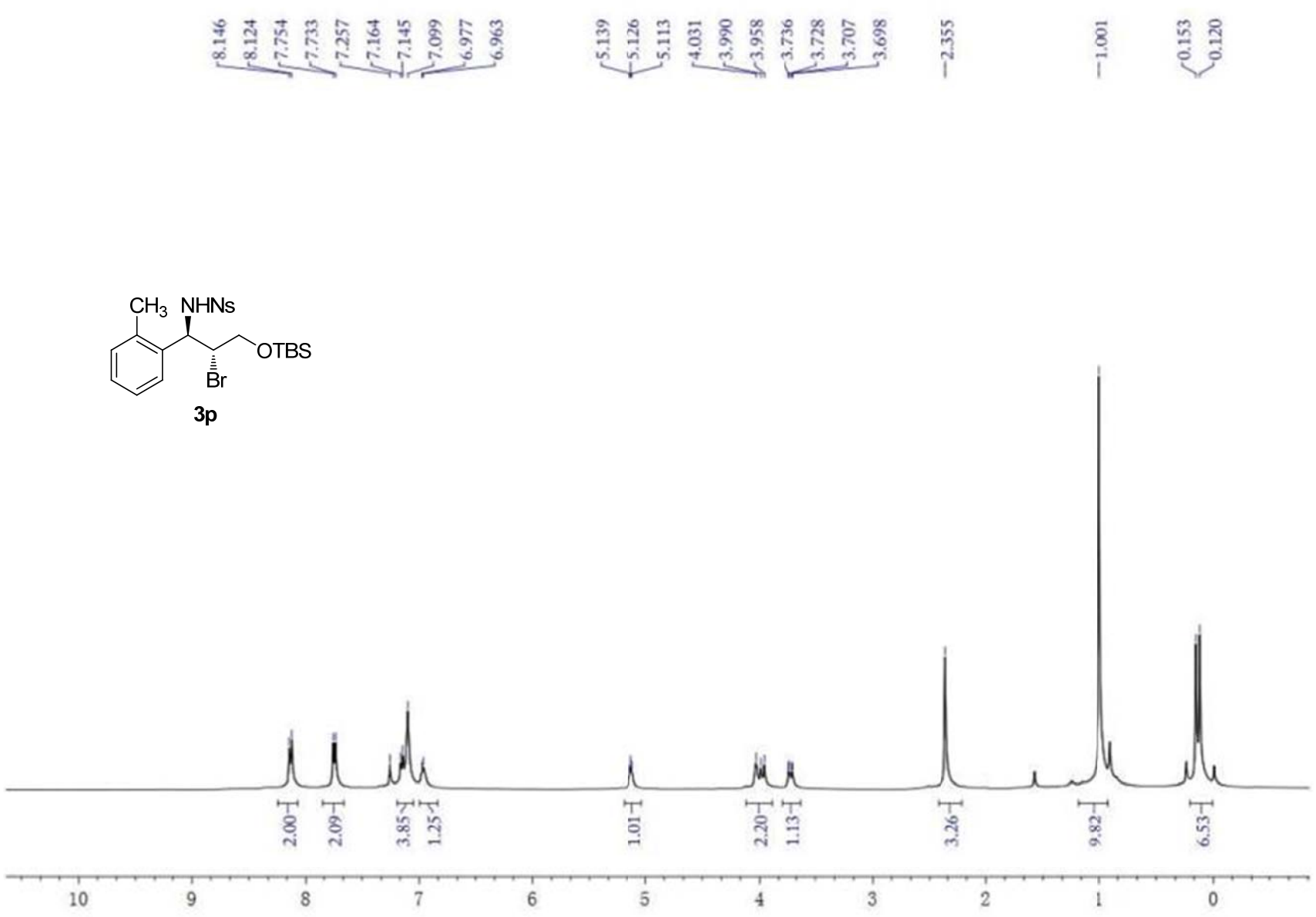
146.14
145.79
135.51
132.29
129.93
129.74
128.44
127.16
123.94
77.32
77.00
76.68
64.59
60.64
50.58
25.73
18.08
-5.64
-5.68
Cl
NHNs
OTBS
Br
3o
200. 0
180. 0
160. 0
140. 0
120. 0
100. 0
80. 0
60. 0
40. 0
20. 0
0. 0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7.754
7.733
7.257
7.164
7.145
7.099
6.977
6.963
5.139
5.126
5.113
4.031
3.990
3.958
3.736
3.728
3.707
3.698
2.355
1.001
0.153
0.120
CH3
NHNs
OTBS
Br
3p
2.00
2.09
3.85
1.25
1.01
2.20
1.13
3.26
9.82
6.53
10
9
8
7
6
5
4
3
2
1
0


149.49
146.49
135.63
135.18
130.77
128.23
128.06
126.65
126.17
123.71
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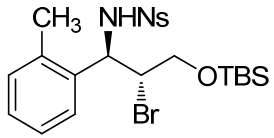
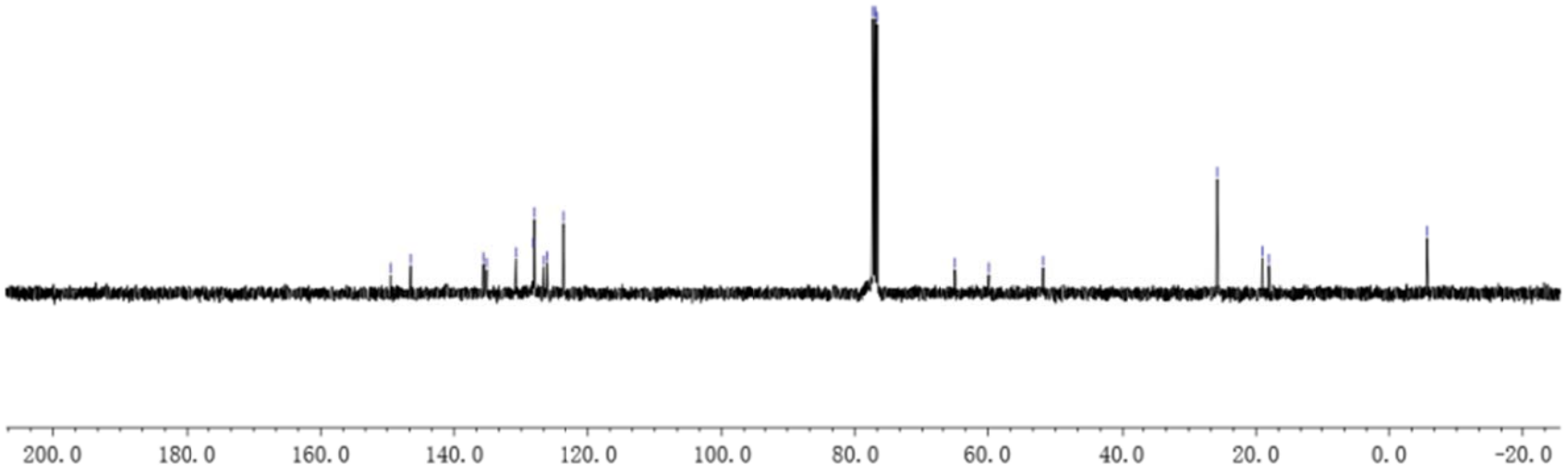
51.83
25.74
19.08
18.09
-5.61


CH3
NHNs
OTBS
Br

3p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140.0
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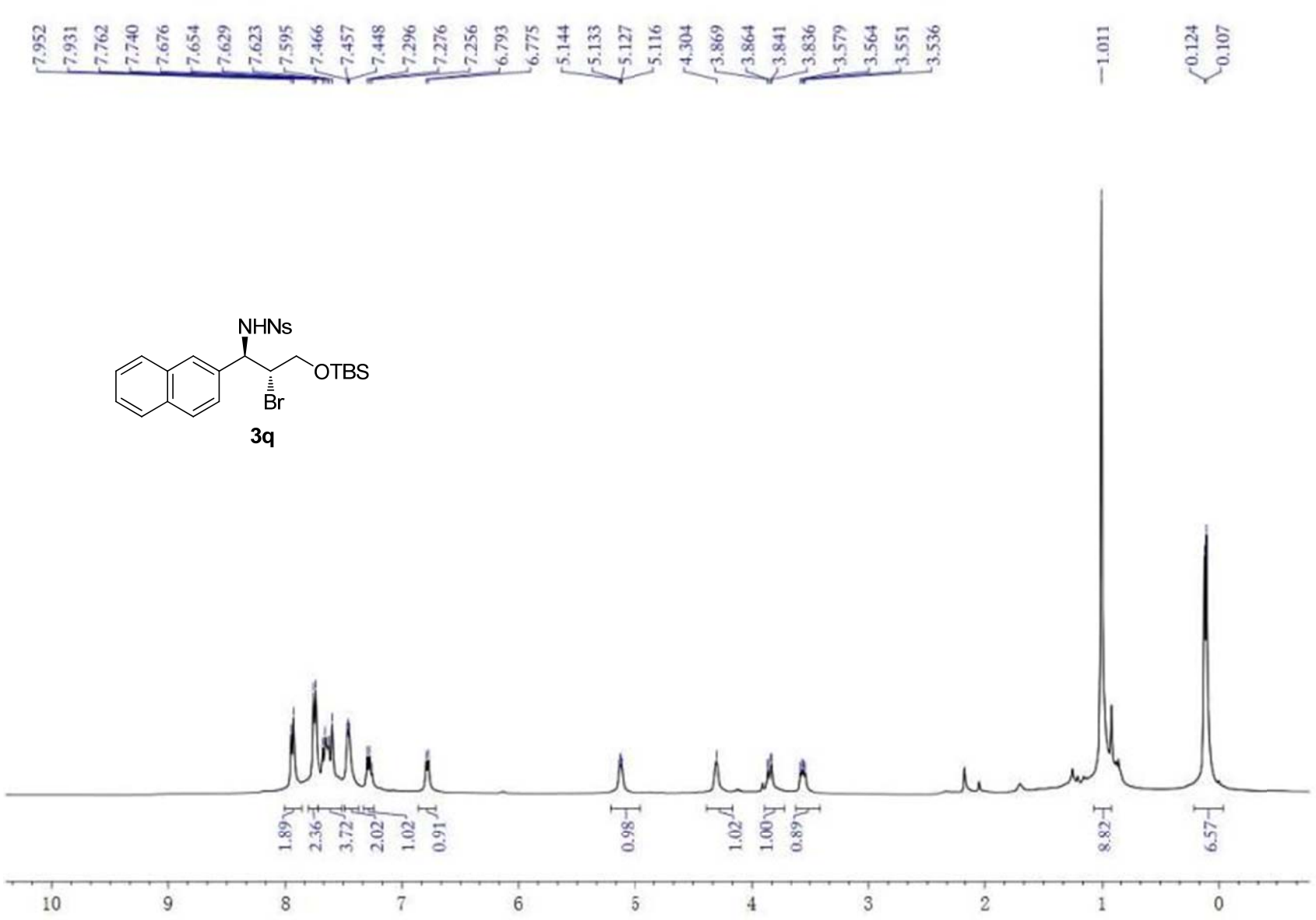
100.0
80.0
60.0
40.0
20.0
0.0
-20.0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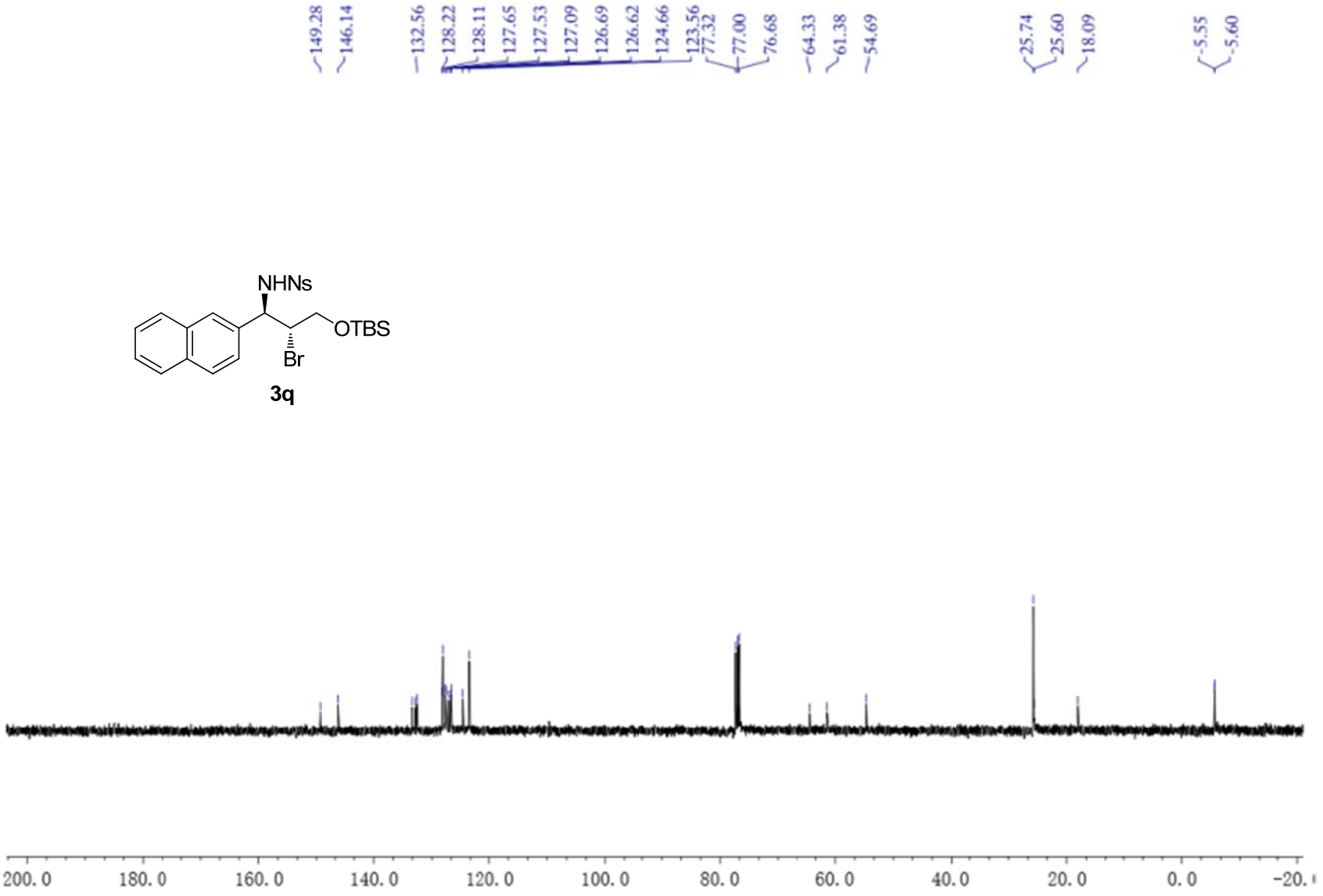
7.931
7.762
7.740
7.676
7.654
7.629
7.623
7.595
7.466
7.457
7.448
7.296
7.276
7.256
6.793
6.775
5.144
5.133
5.127
5.116
4.304
3.869
3.864
3.841
3.836
3.579
3.564
3.551
3.536
1.011
0.124
0.107
NHNs
OTBS
Br
3q
1.89
2.36
3.72
2.02
1.02
0.91
0.98
1.02
1.00
0.89
8.82
6.57
10
9
8
7
6
5
4
3
2
1
0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146.14
132.56
128.22
128.11
127.65
127.53
127.09
126.69
126.62
124.66
123.56
77.32
77.00
76.68
64.33
61.38
54.69
25.74
25.60
18.09
-5.55
-5.60
NHNs
OTBS
Br
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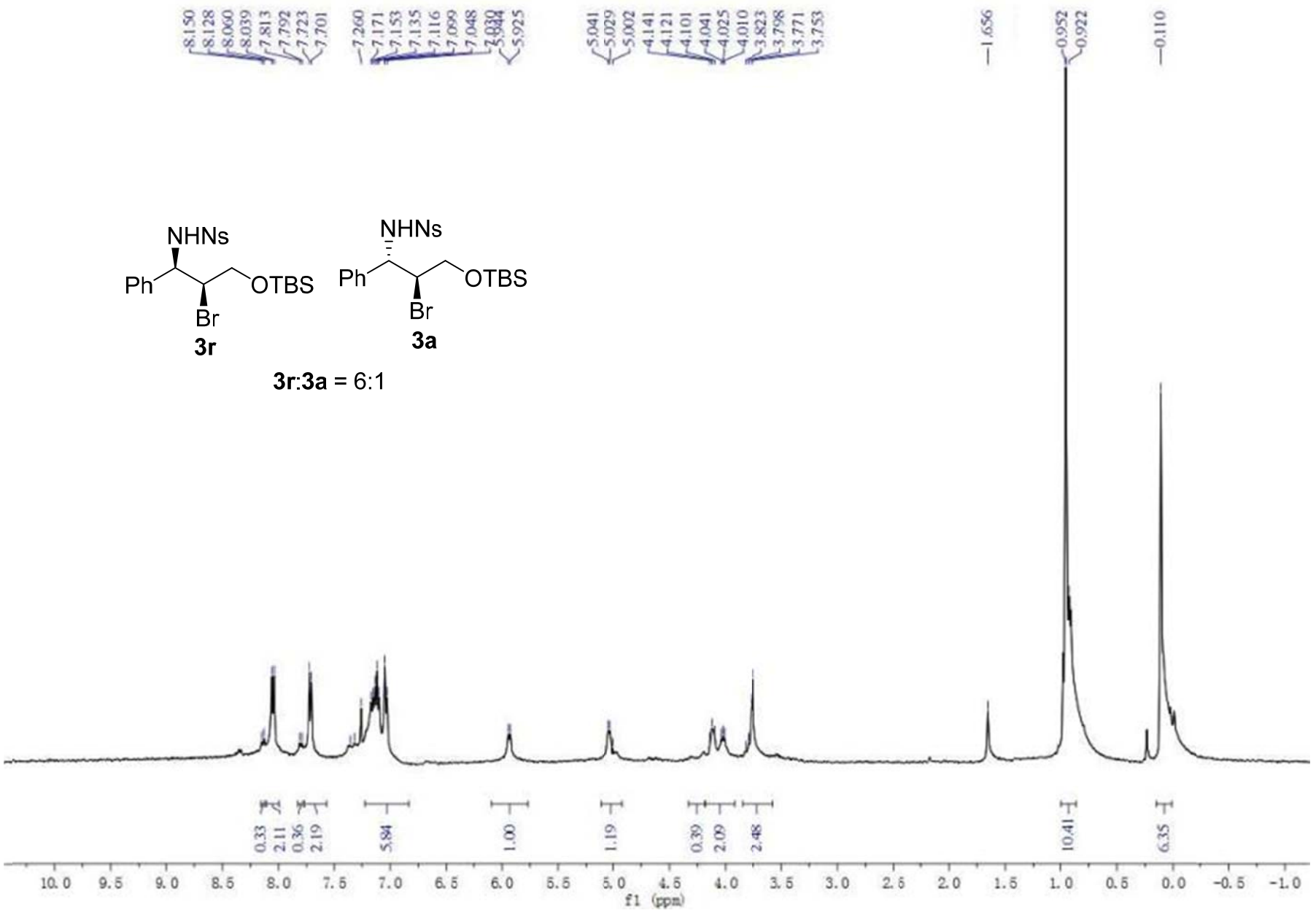
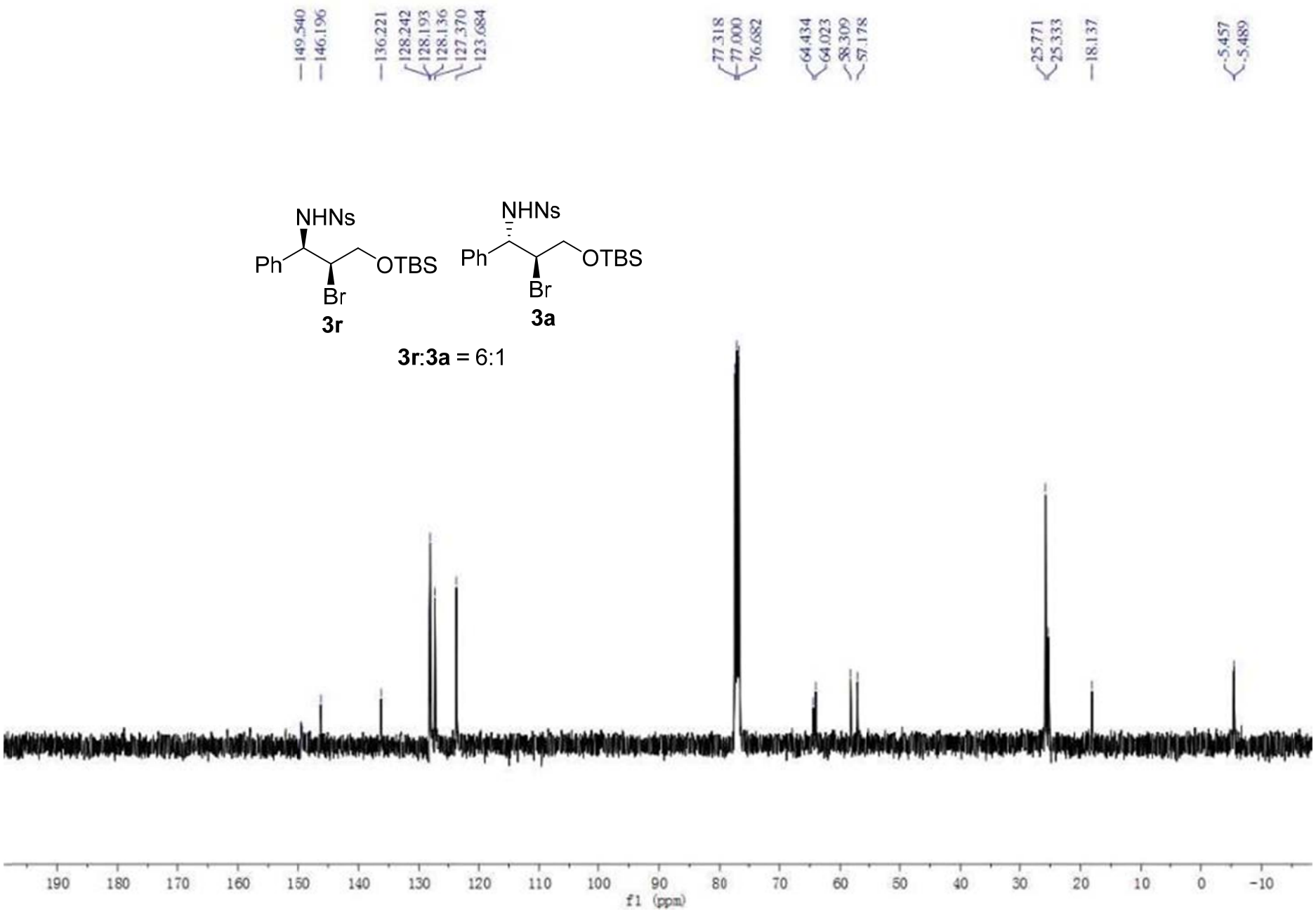
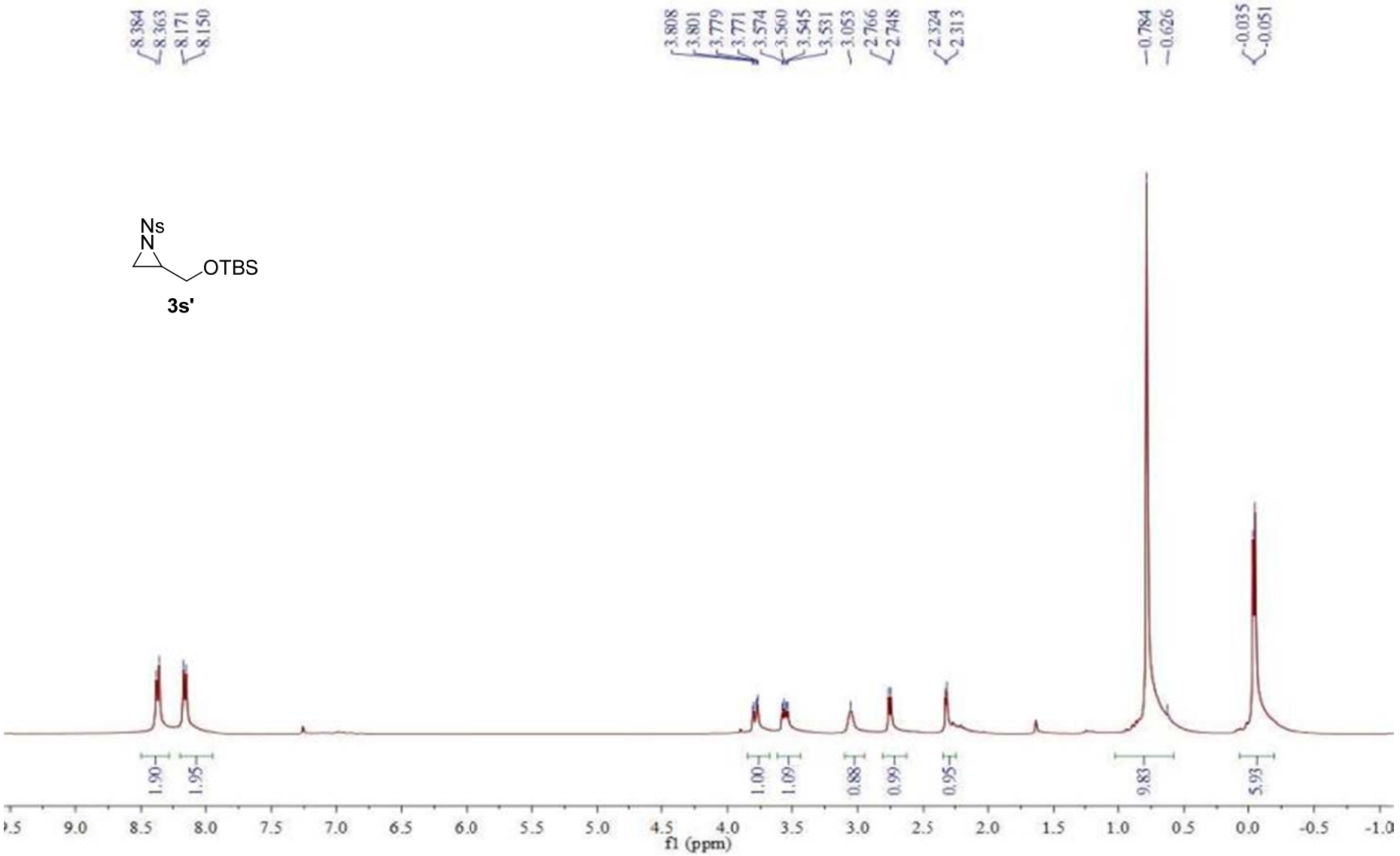
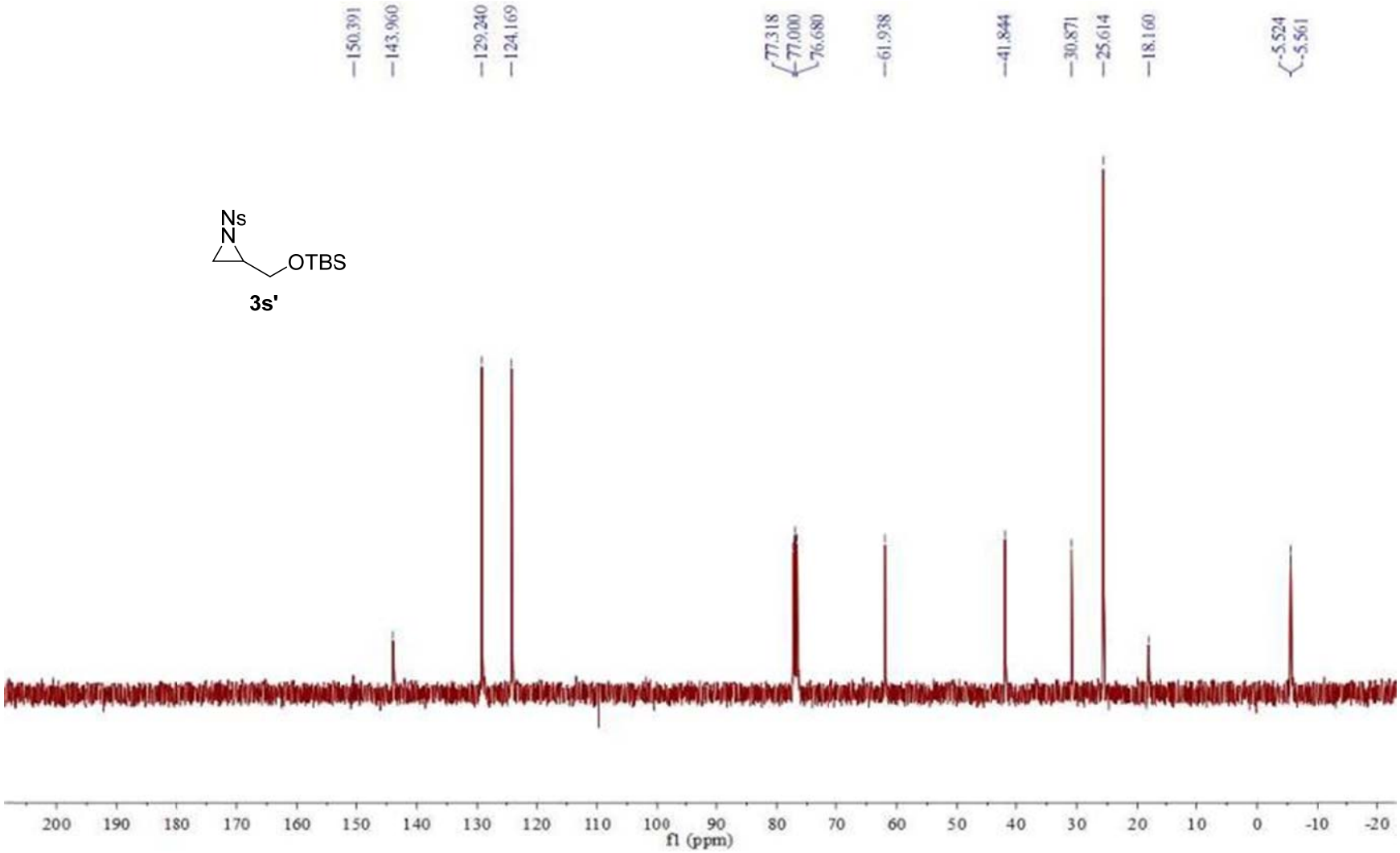
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0

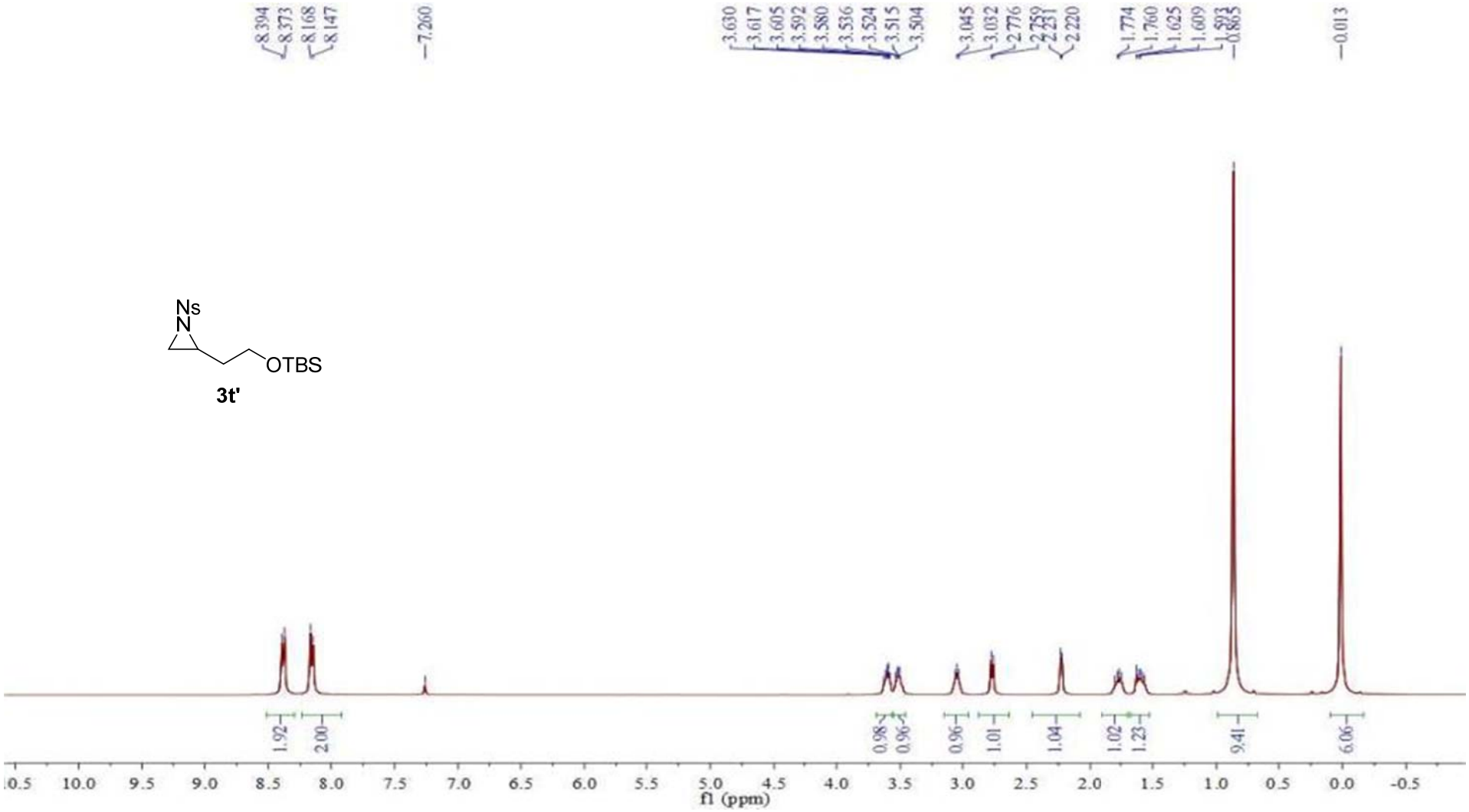
3q

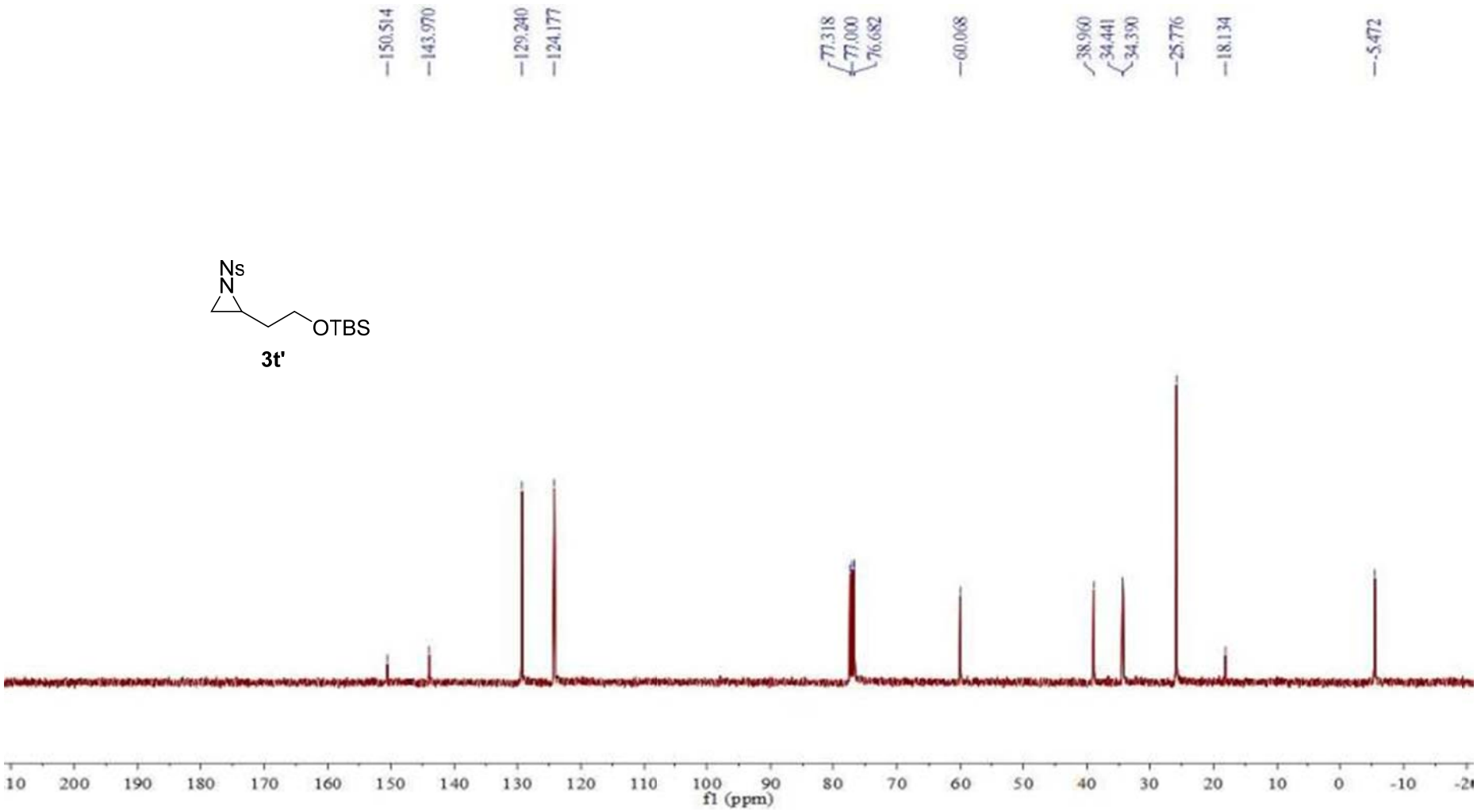

8.150
8.128
8.000
8.039
7.813
7.792
7.723
7.701
7.260
7.171
7.153
7.135
7.116
7.099
7.048
5.925
5.041
5.029
5.002
4.141
4.121
4.101
4.041
4.025
4.010
3.823
3.798
3.771
3.753
1.656
0.952
0.922
0.110
NHNs
Ph
OTBS
Br
3r
NHNs
Ph
OTBS
Br
3a
3r:3a = 6:1
0.33
2.11
0.36
2.19
5.84
1.00
1.19
0.39
2.09
2.48
10.41
6.35
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
-1.0
f1 (ppm)


149.540
146.196
136.221
128.242
128.193
128.136
127.370
123.684
77.318
77.000
76.682
64.434
64.023
58.309
57.178
25.771
25.333
18.137
-5.457
-5.489
NHNs
Ph
OTBS
Br
3r
NHNs
Ph
OTBS
Br
3a
3r:3a = 6:1
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

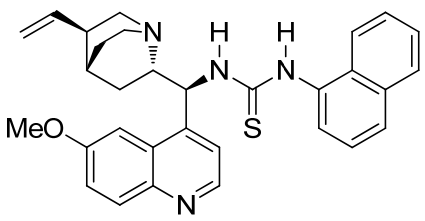

8.384
8.363
8.171
8.150
3.808
3.801
3.779
3.771
3.574
3.560
3.545
3.531
3.053
2.766
2.748
2.324
2.313
0.784
0.626
-0.035
-0.051
Ns
N
OTBS
3s'
1.90
1.95
1.00
1.09
0.88
0.99
0.95
9.83
5.93
f1 (ppm)


150.391
143.960
129.240
124.169
77.318
77.000
76.680
61.938
41.844
30.871
25.614
18.160
-5.524
-5.561
Ns
N
OTBS
3s'
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

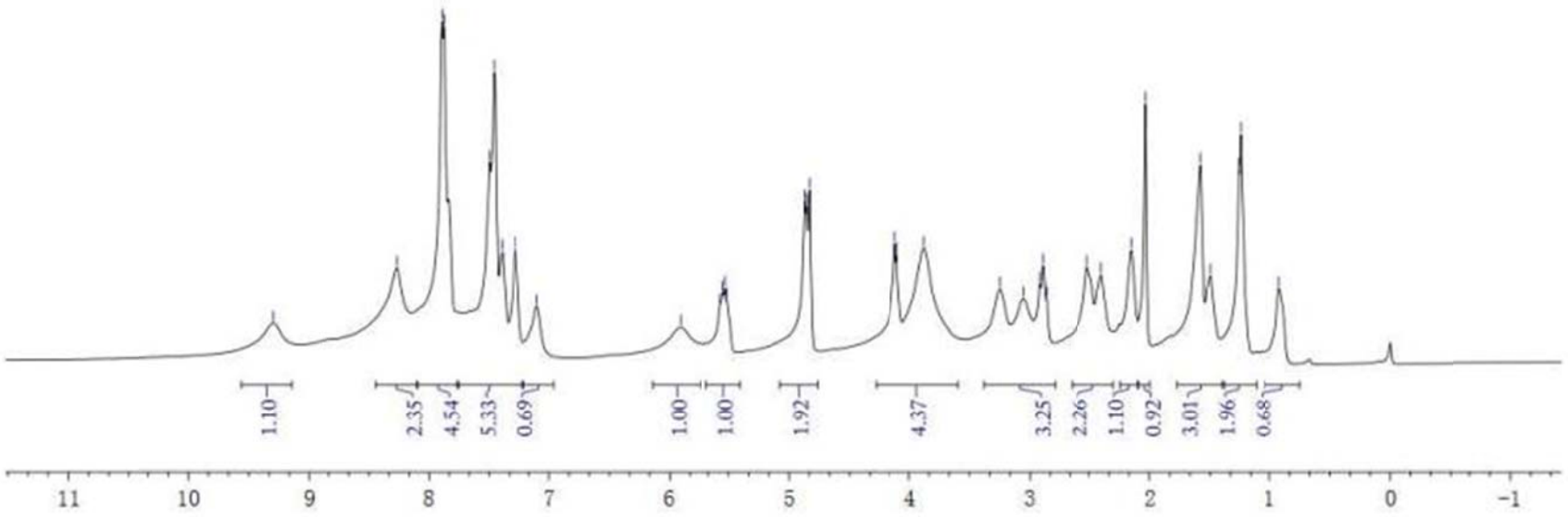

8.394
8.373
8.168
8.147
7.260
3.630
3.617
3.605
3.592
3.580
3.536
3.524
3.515
3.504
3.045
3.032
2.776
2.759
2.231
2.220
1.774
1.760
1.625
1.609
0.865
0.013
Ns
N
OTBS
3t'
1.92
2.00
0.98
0.96
0.96
1.01
1.04
1.02
1.23
9.41
6.06
f1 (ppm)

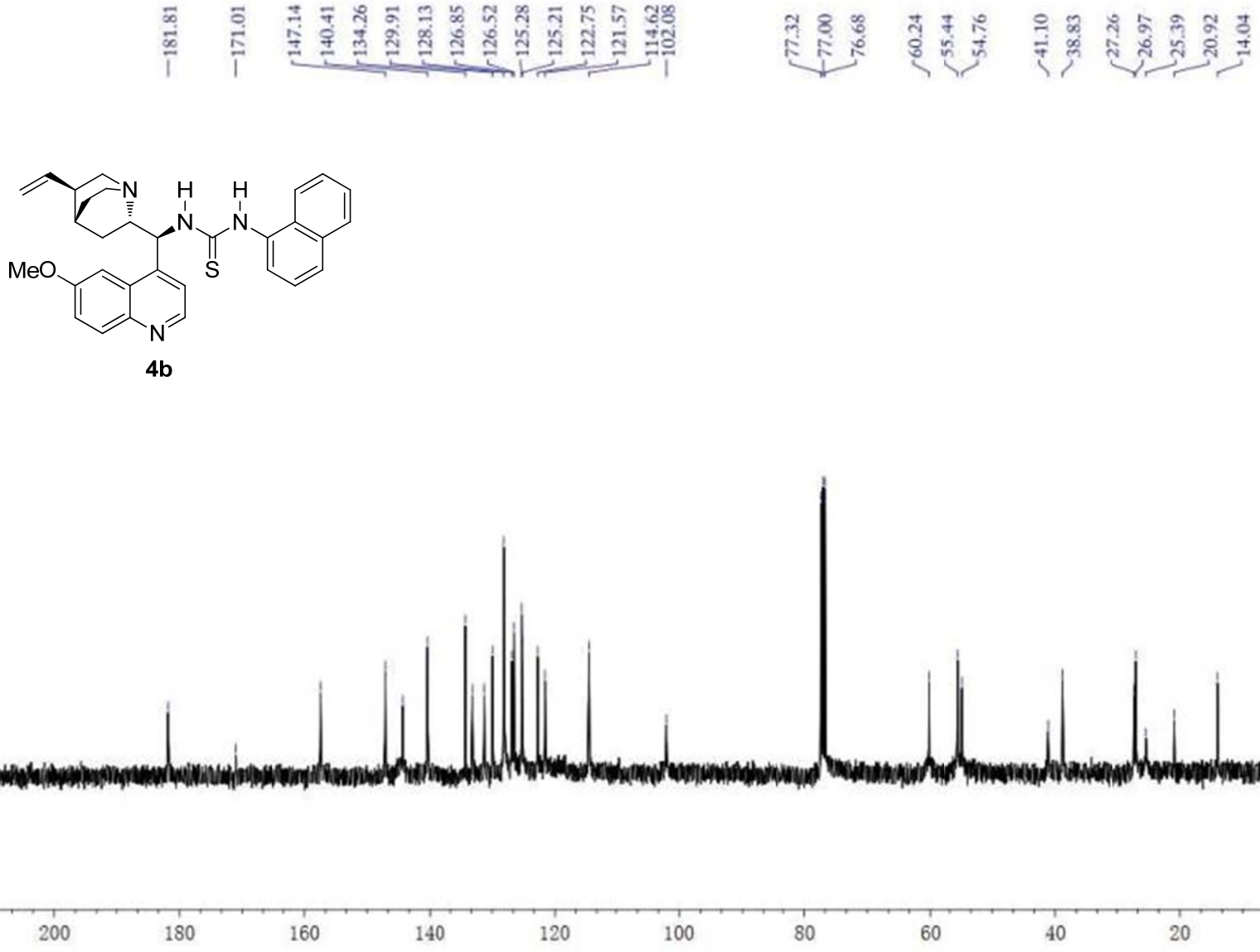

150.514
143.970
129.240
124.177
77.318
77.000
76.682
60.068
38.960
34.441
34.390
25.776
18.134
-5.472
Ns
N
OTBS
3t'
f1 (ppm)


9.300
8.267
7.891
7.875
7.497
7.459
7.390
7.283
7.103
5.570
5.551
5.529
5.512
4.871
4.830
4.117
3.875
3.246
3.053
2.918
2.892
2.861
2.517
2.401
2.150
2.033
1.582
1.499
1.262
1.245
0.919

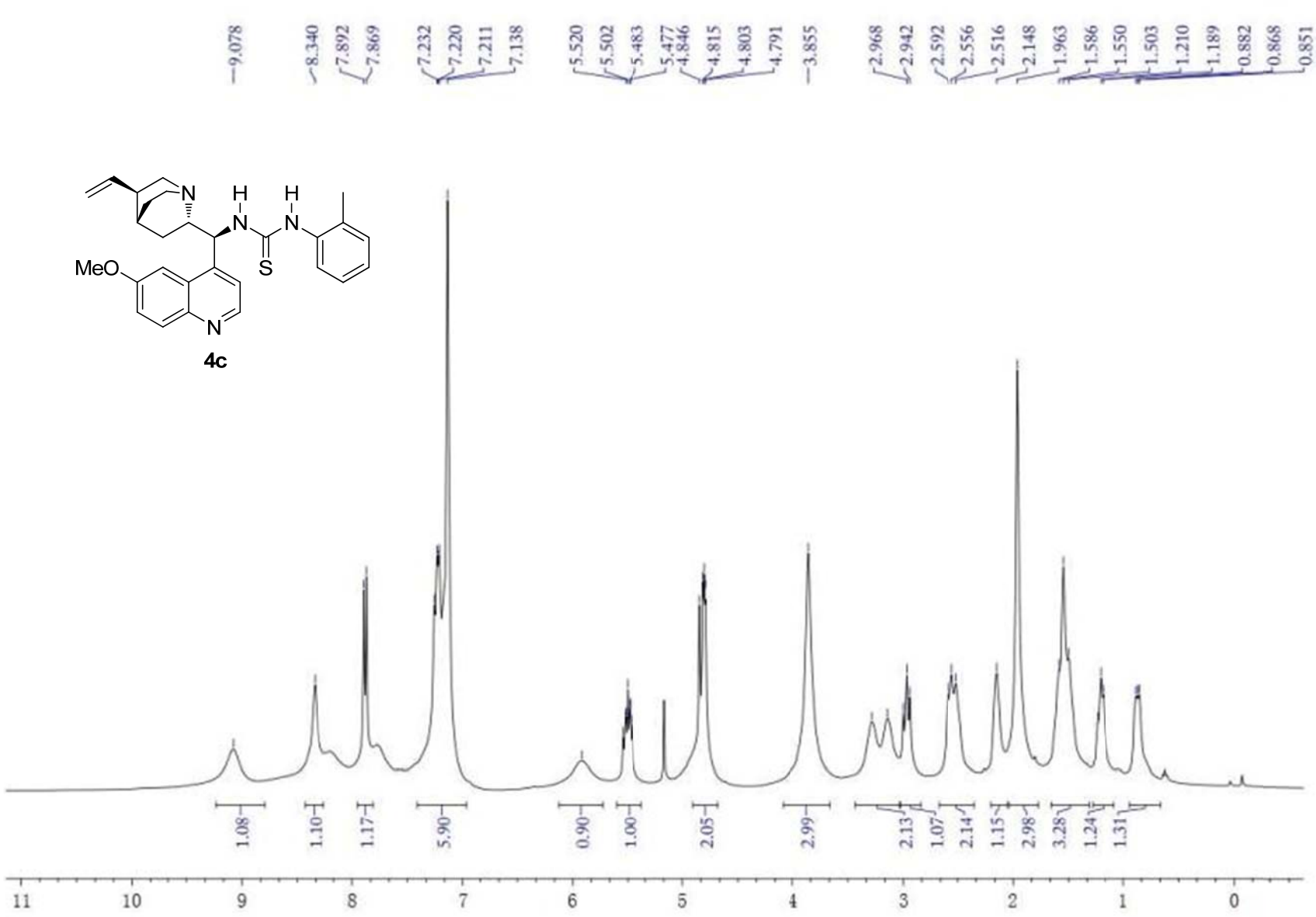

MeO
N
H
N
H
N
S
N

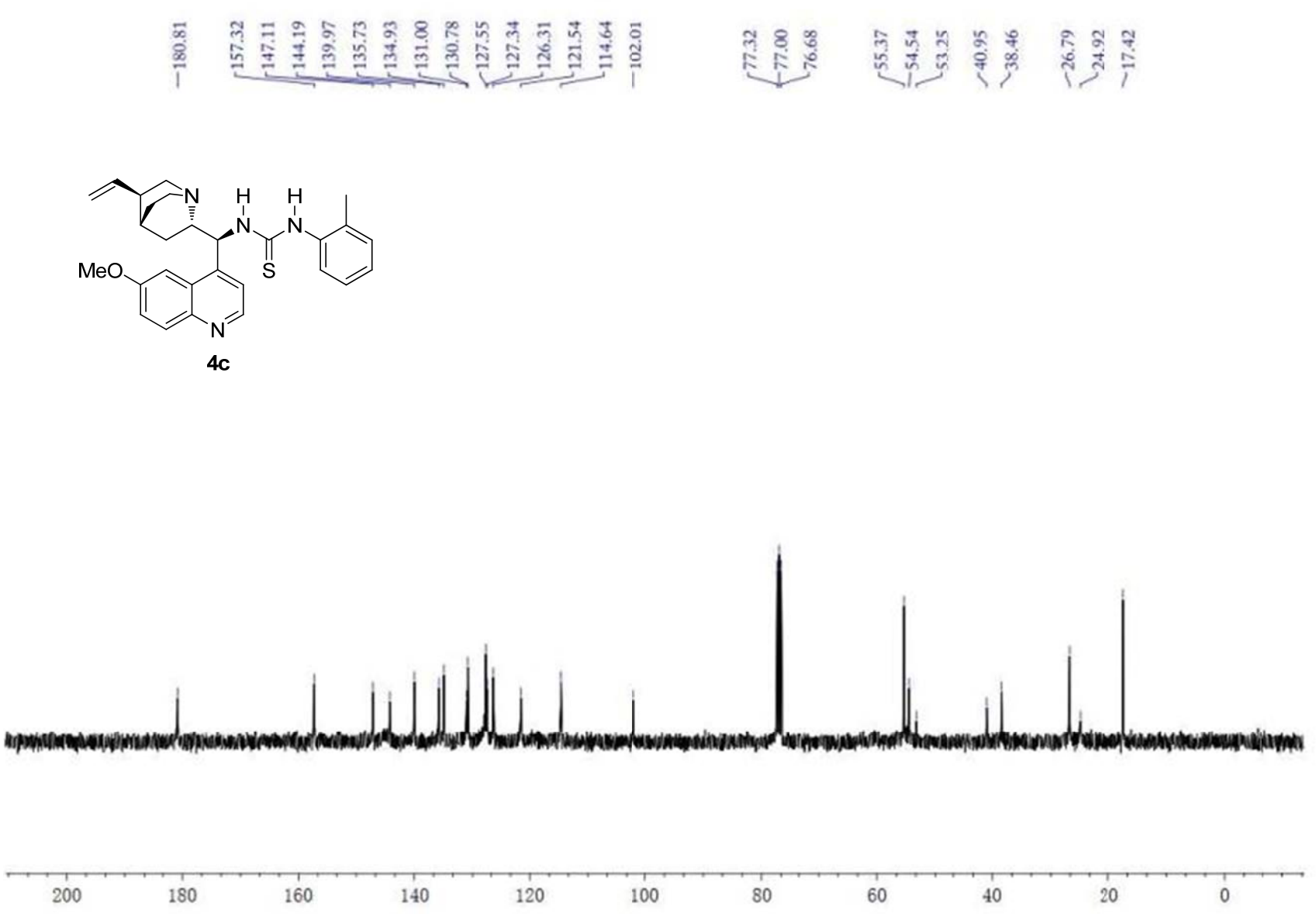
4b


1.10
2.35
4.54
5.33
0.69
1.00
1.00
1.92
4.37
3.25
2.26
1.10
0.92
3.01
1.96
0.68
11
10
9
8
7
6
5
4
3
2
1
0
-1


181.81
171.01
147.14
140.41
134.26
129.91
128.13
126.85
126.52
125.28
125.21
122.75
121.57
114.62
102.08
77.32
77.00
76.68
60.24
55.44
54.76
41.10
38.83
27.26
26.97
25.39
20.92
14.04
MeO
N
H
N
H
N
S
N
200
180
160
140
120
100
80
60
40
20
0

4b


9.078
8.340
7.892
7.869
7.232
7.220
7.211
7.138
5.520
5.502
5.483
5.477
4.846
4.815
4.803
4.791
3.855
2.968
2.942
2.592
2.556
2.516
2.148
1.963
1.586
1.550
1.503
1.210
1.189
0.882
0.868
0.851
MeO
N
H
N
H
N
S
N
4c
1.08
1.10
1.17
5.90
0.90
1.00
2.05
2.99
2.13
1.07
2.14
1.15
2.98
3.28
1.24
1.31
11
10
9
8
7
6
5
4
3
2
1
0


180.81
157.32
147.11
144.19
139.97
135.73
134.93
131.00
130.78
127.55
127.34
126.31
121.54
114.64
102.01
77.32
77.00
76.68
55.37
54.54
53.25
40.95
38.46
26.79
24.92
17.42
MeO
N
H
N
H
N
S
N
200
180
160
140
120
100
80
60
40
20
0

4c


8.623
8.484
7.976
7.953
7.351
7.330
7.283
7.254
5.639
5.618
5.596
5.577
4.943
4.915
4.899
4.333
3.939
3.342
3.122
3.095
3.063
2.640
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1.665
1.619
1.310
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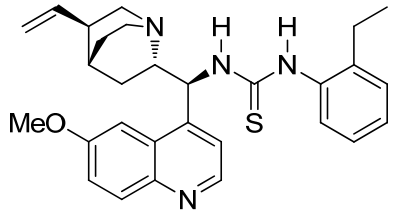
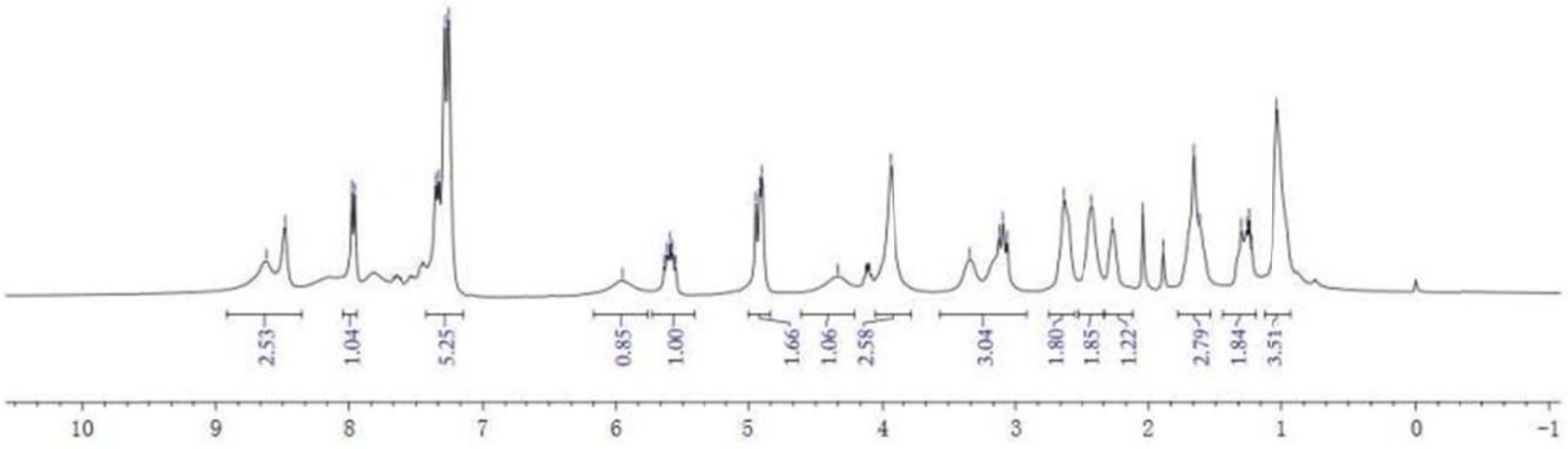
1.251
1.233
1.035


MeO
N
H
N
H
N
S
N

4d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1.04
5.25
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1.00
1.66
1.06
2.58
3.04
1.80
1.85
1.22
2.79
1.84
3.51
10
9
8
7
6
5
4
3
2
1
0
-1


181.31
157.47
147.24
144.34
140.90
140.10
134.99
131.88
131.20
129.09
128.01
126.53
121.71
114.87
102.13
77.32
77.00
76.68
61.08
60.25
55.53
54.74
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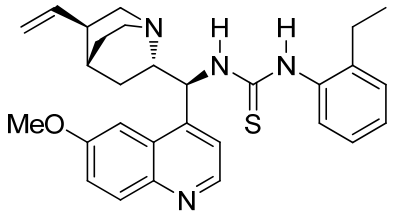
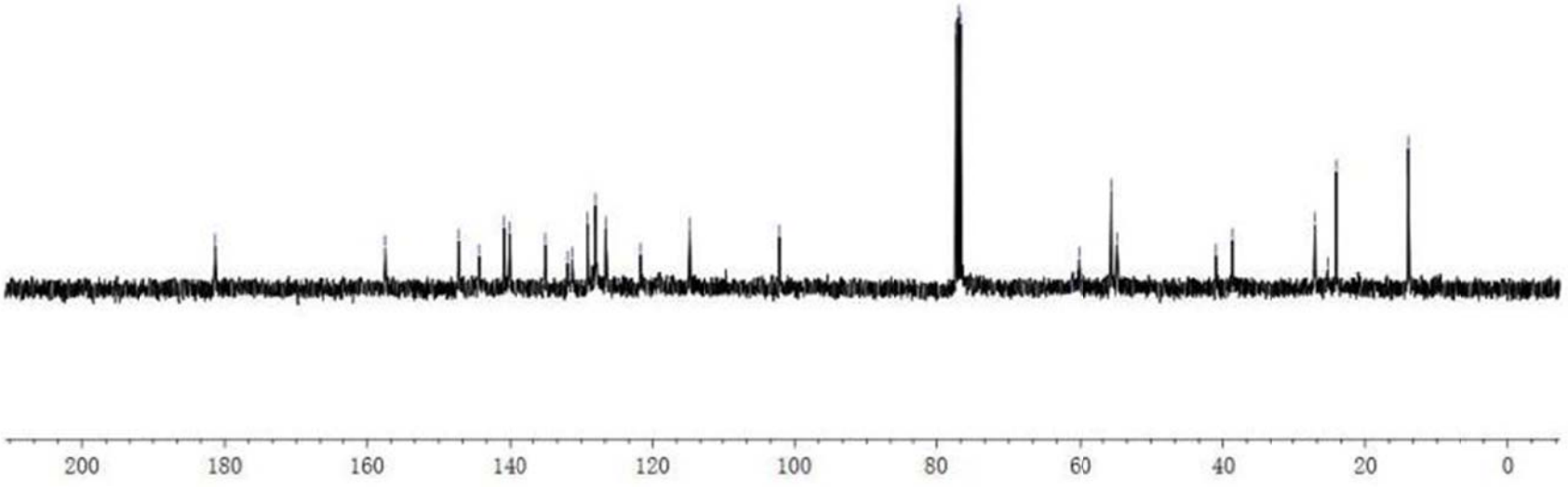
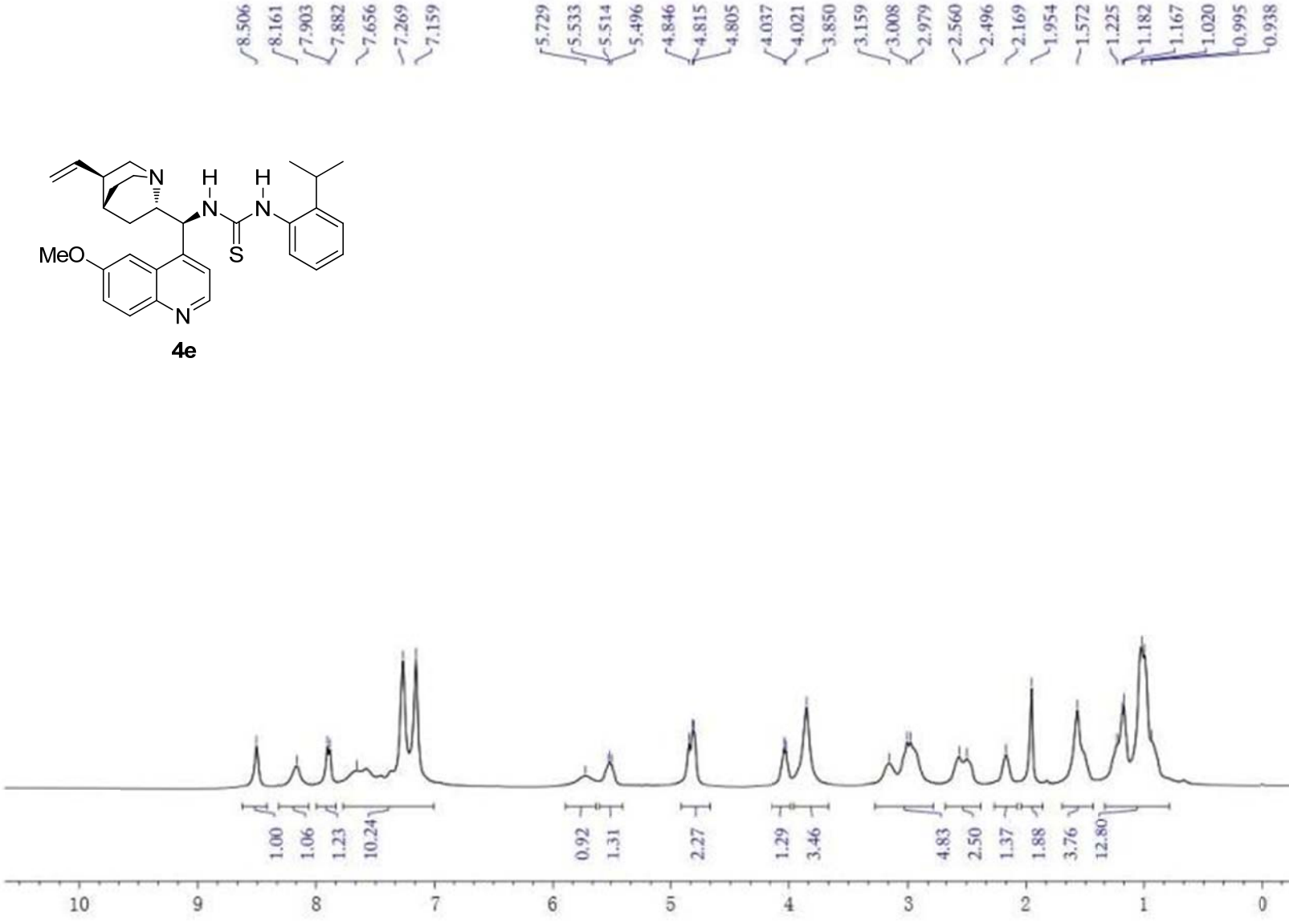
38.69
27.03
26.95
25.16
24.00
14.00


MeO
N
H
N
H
N
S
N

4d


200
180
160
140
120
100
80
60
40
20
0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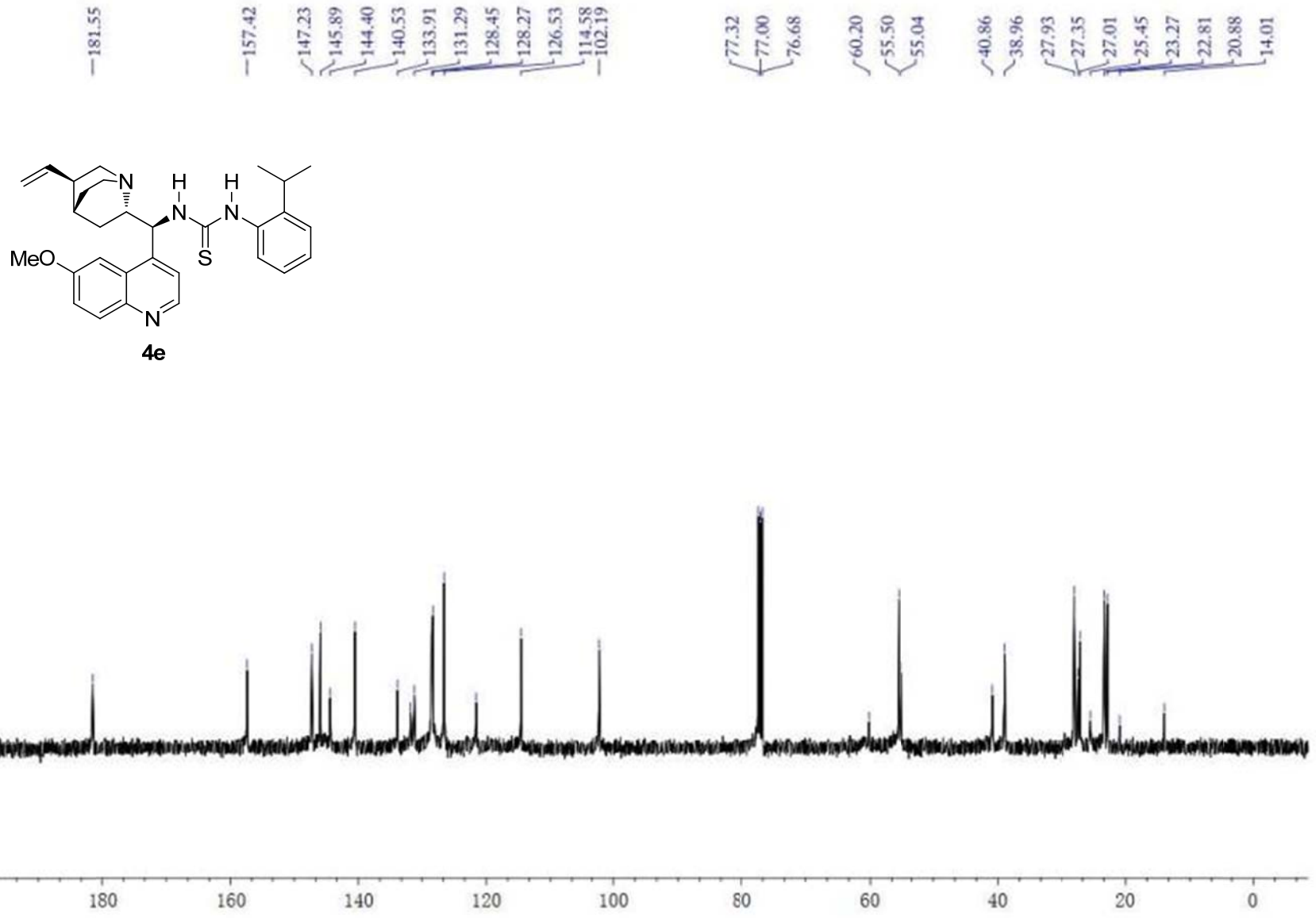
8.161
7.903
7.882
7.656
7.269
7.159
5.729
5.533
5.514
5.496
4.846
4.815
4.805
4.037
4.021
3.850
3.159
3.008
2.979
2.560
2.496
2.169
1.954
1.572
1.225
1.182
1.167
1.020
0.995
0.938
MeO
N
H
N
H
N
S
N
4e
1.00
1.06
1.23
10.24
0.92
1.31
2.27
1.29
3.46
4.83
2.50
1.37
1.88
3.76
12.80
10
9
8
7
6
5
4
3
2
1
0


181.55
157.42
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144.40
140.53
133.91
131.29
128.45
128.27
126.53
114.58
102.19
77.32
77.00
76.68
60.20
55.50
55.04
40.86
38.96
27.93
27.35
27.01
25.45
23.27
22.81
20.88
14.01
MeO
N
H
N
H
N
S
N
180
160
140
120
100
80
60
40
20
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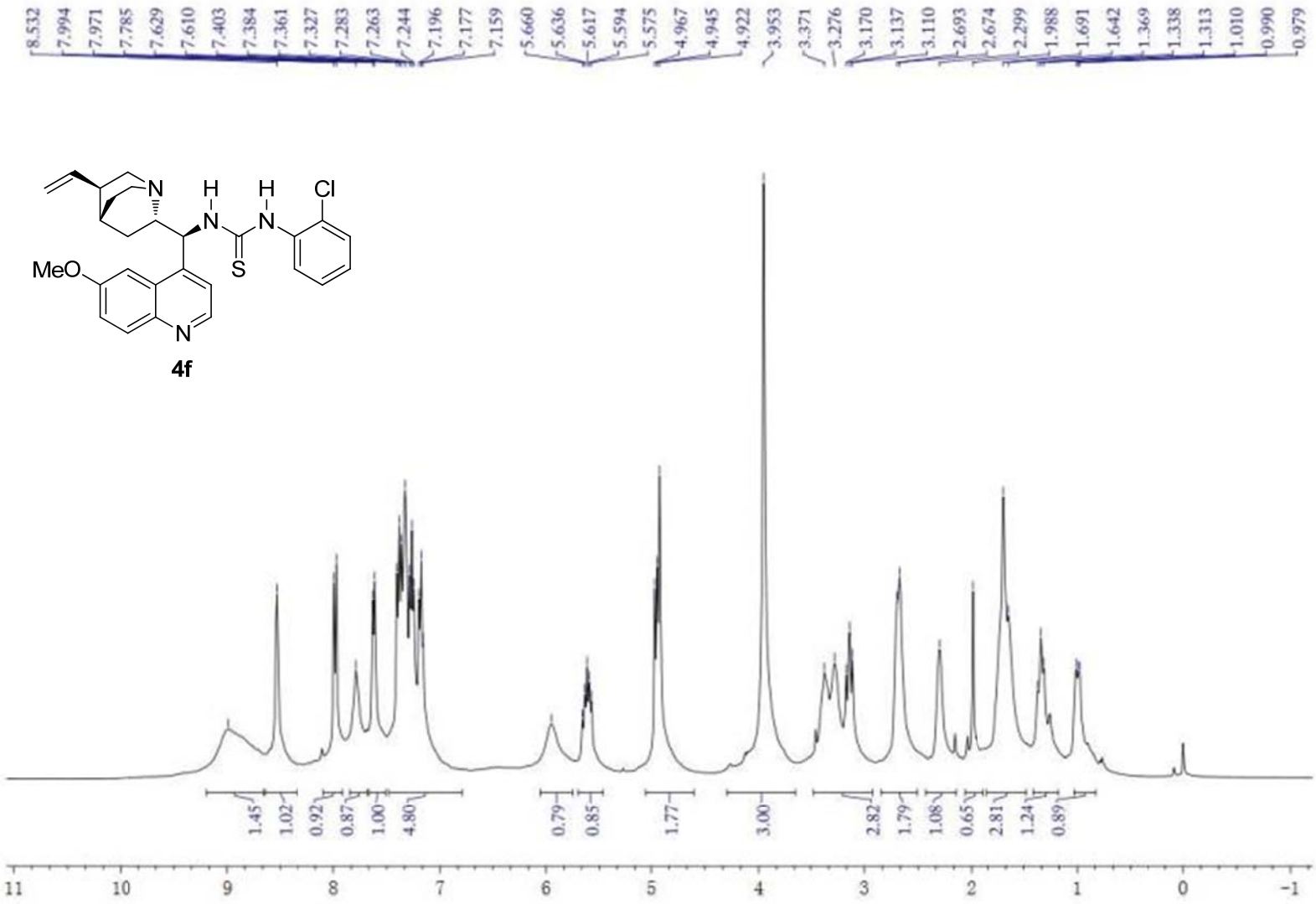
4e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H
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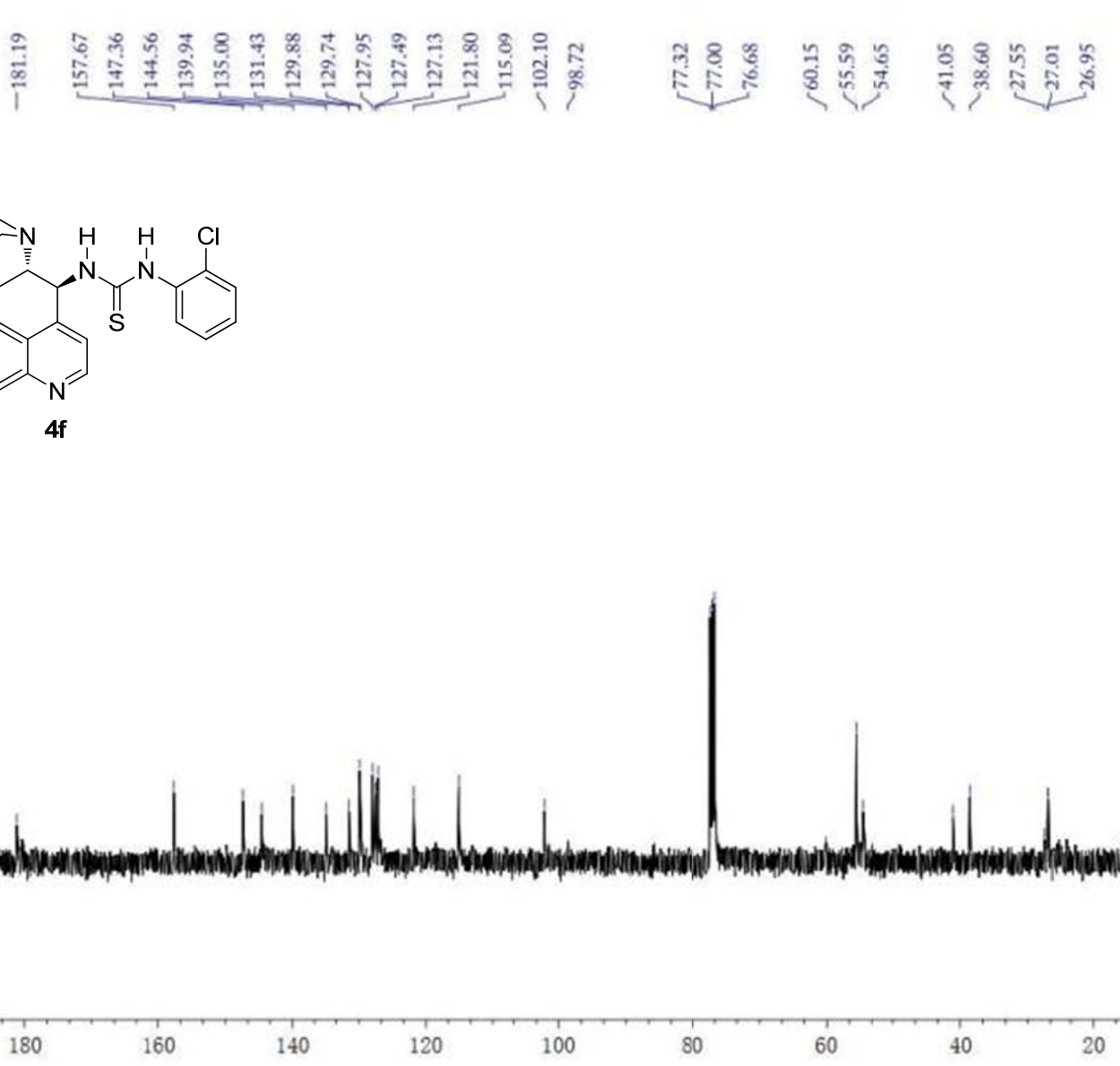
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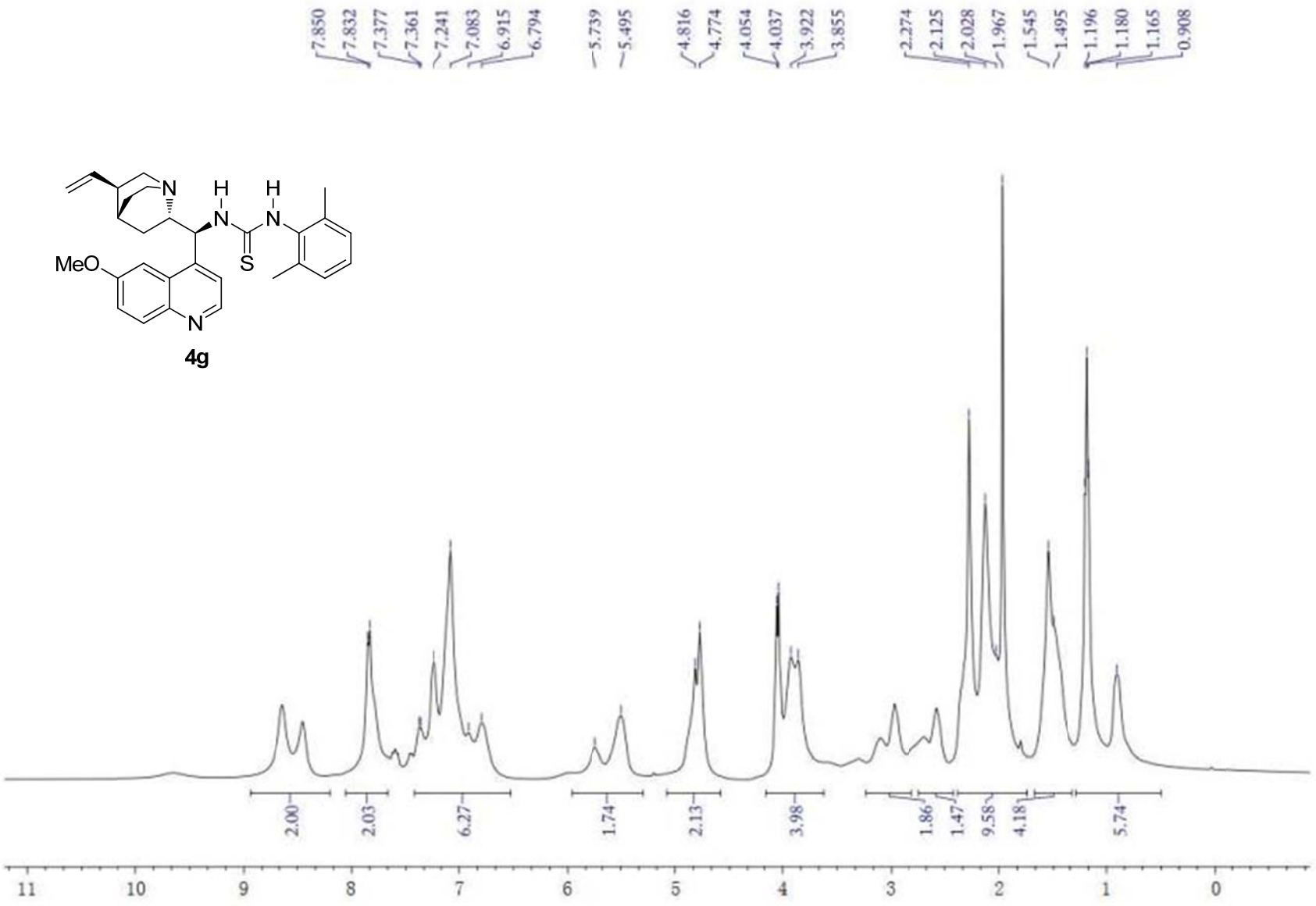
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H
N
H
N
S
N
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6
5
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3
2
1
0


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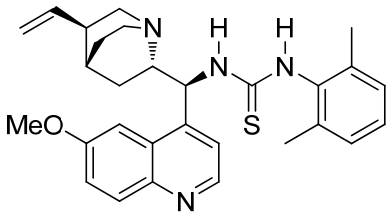
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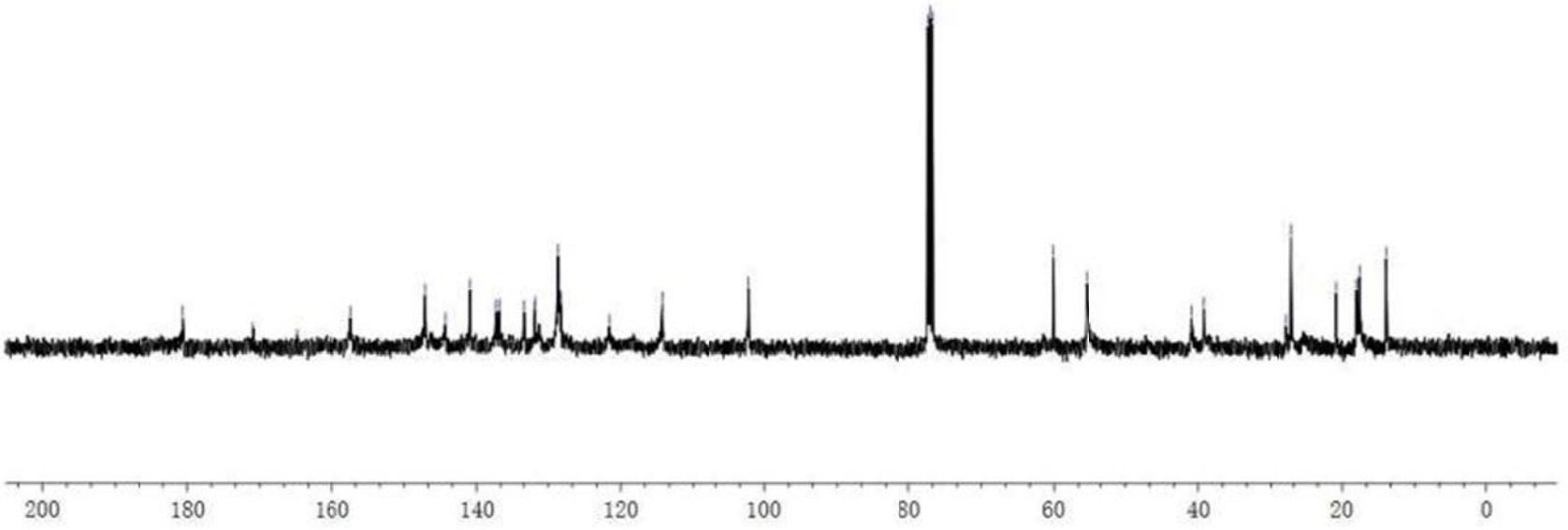
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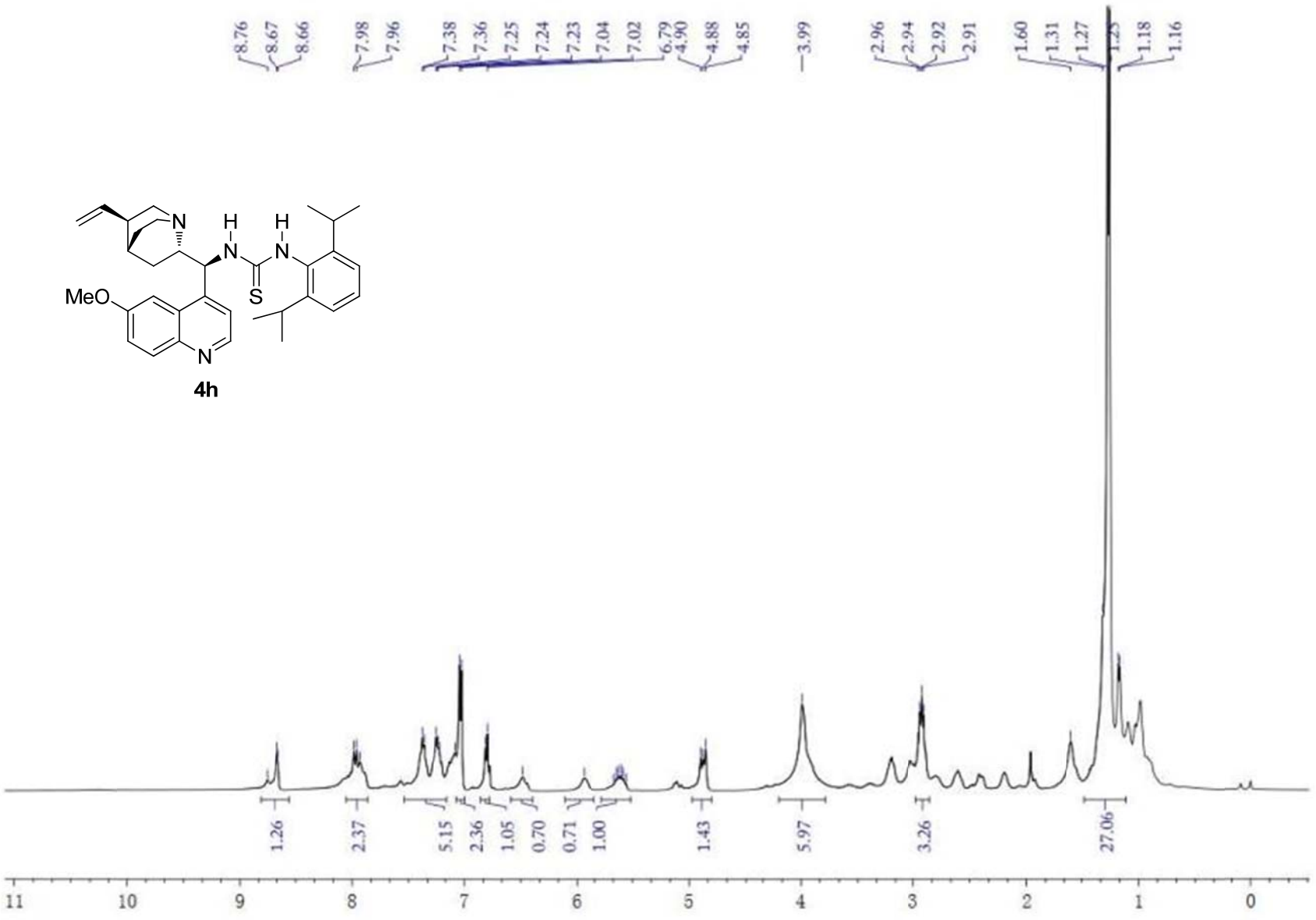
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3.99
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2.92
2.91
1.60
1.31
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1.16
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H
N
H
N
S
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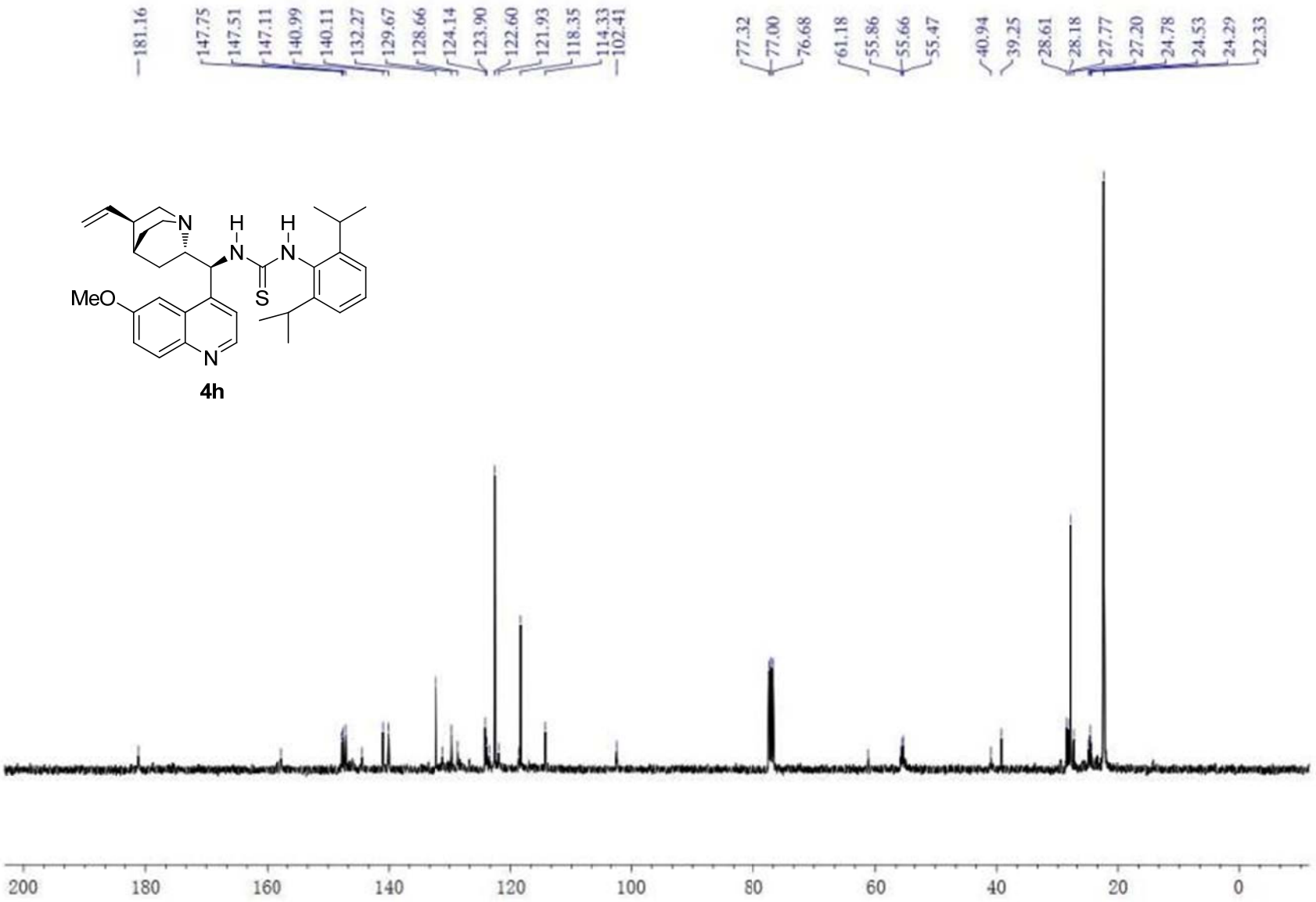
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77.00
76.68
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55.86
55.66
55.47
40.94
39.25
28.61
28.18
27.77
27.20
24.78
24.53
24.29
22.33
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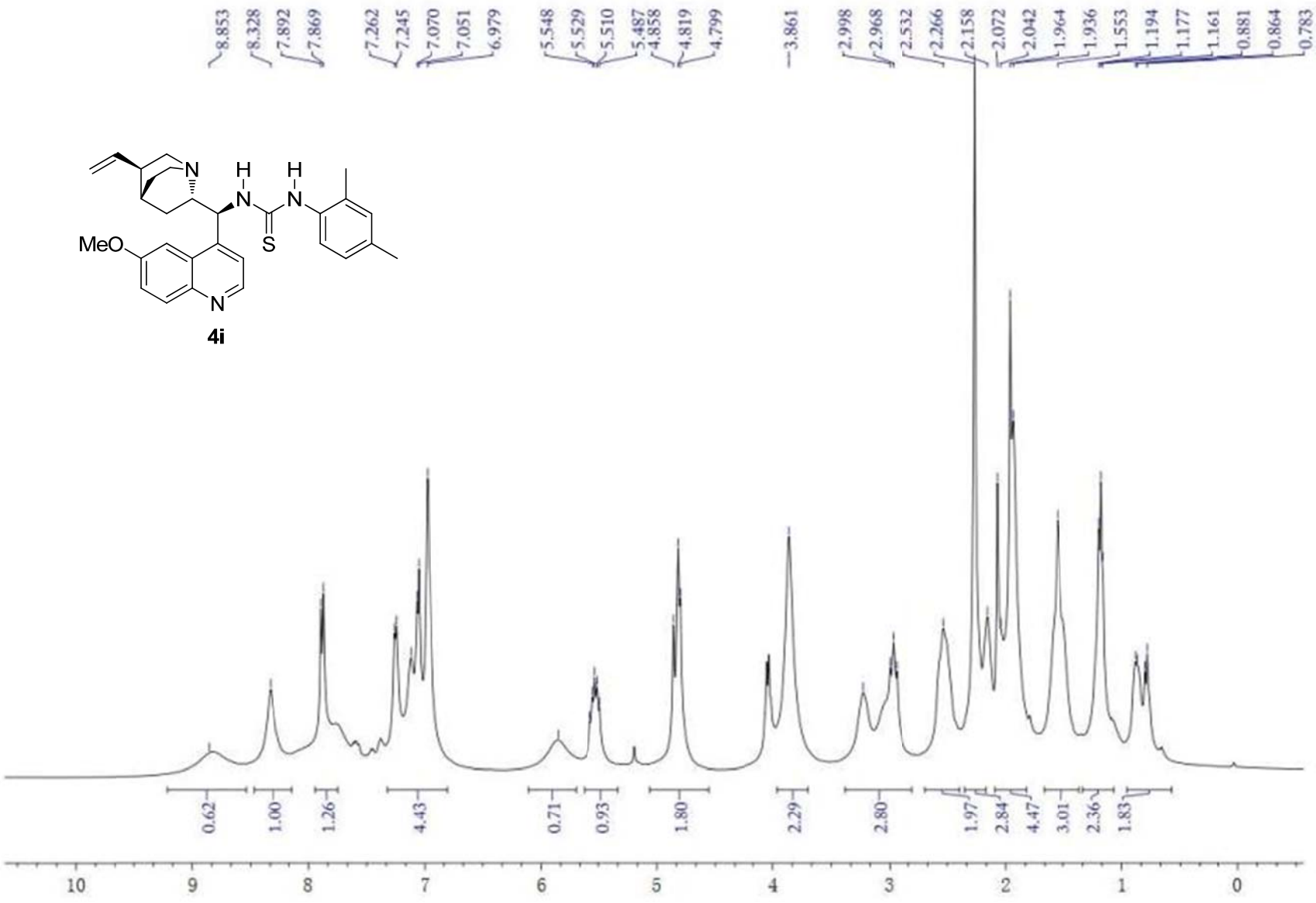
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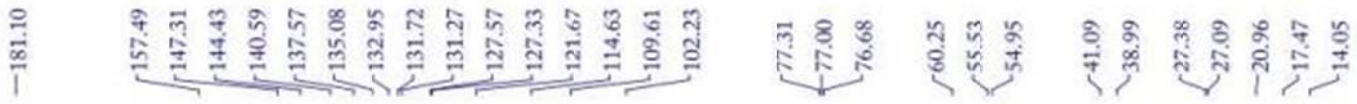
4i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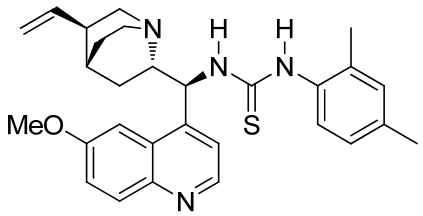
14.05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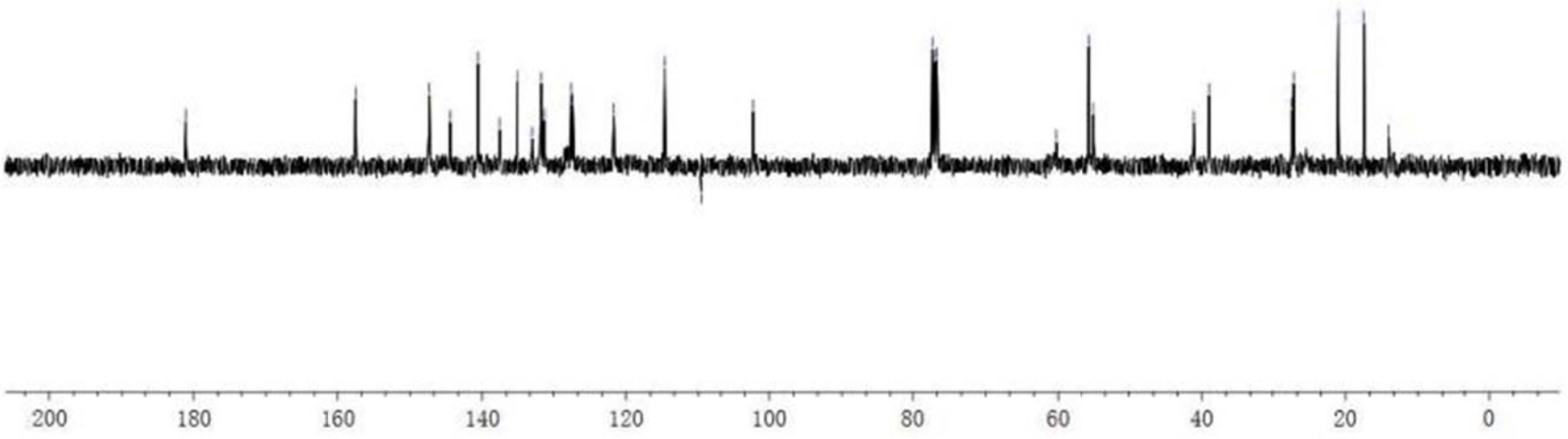
4i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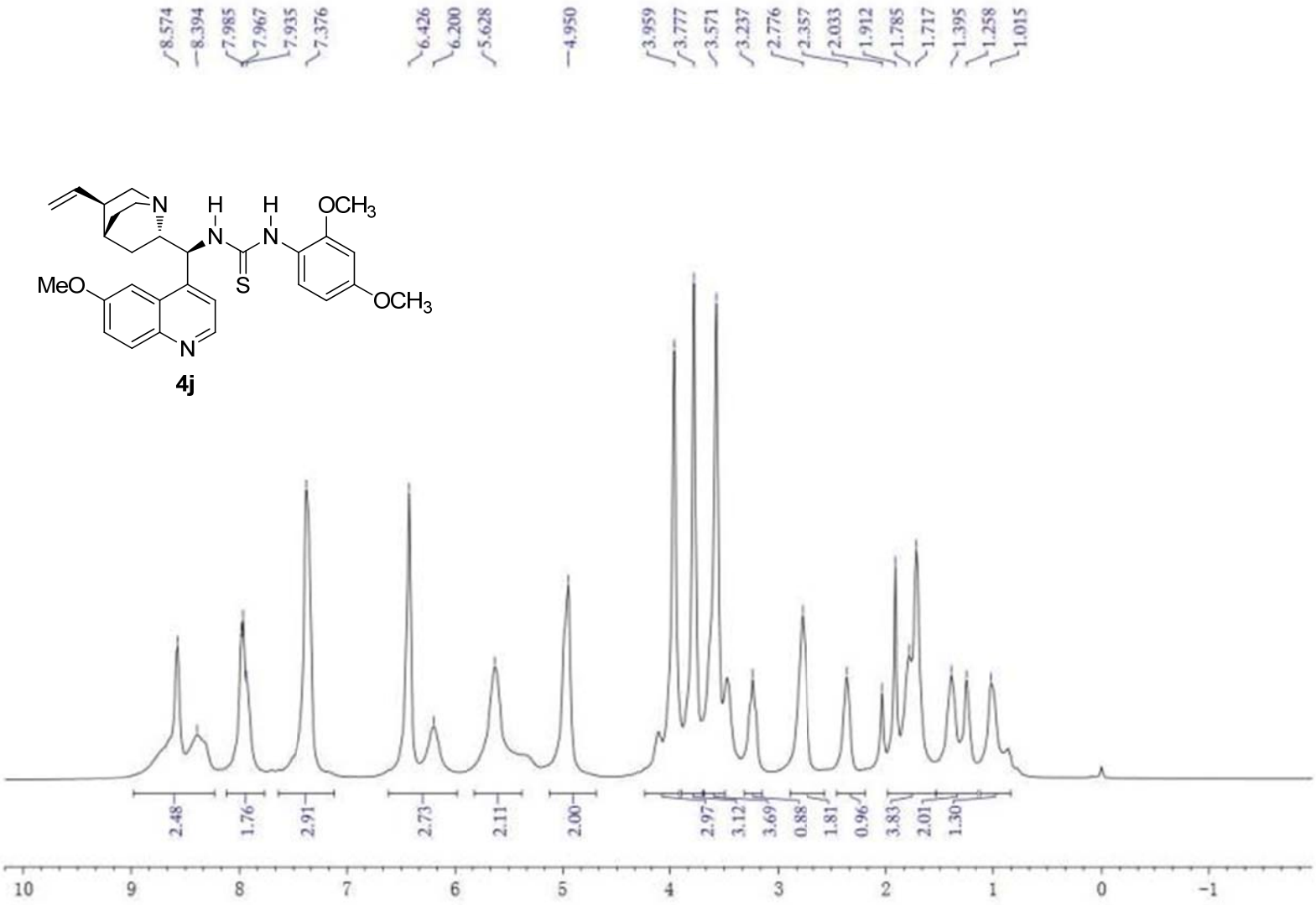
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OCH3
4j
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2.91
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3.12
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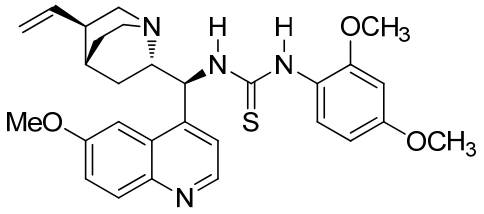
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4j

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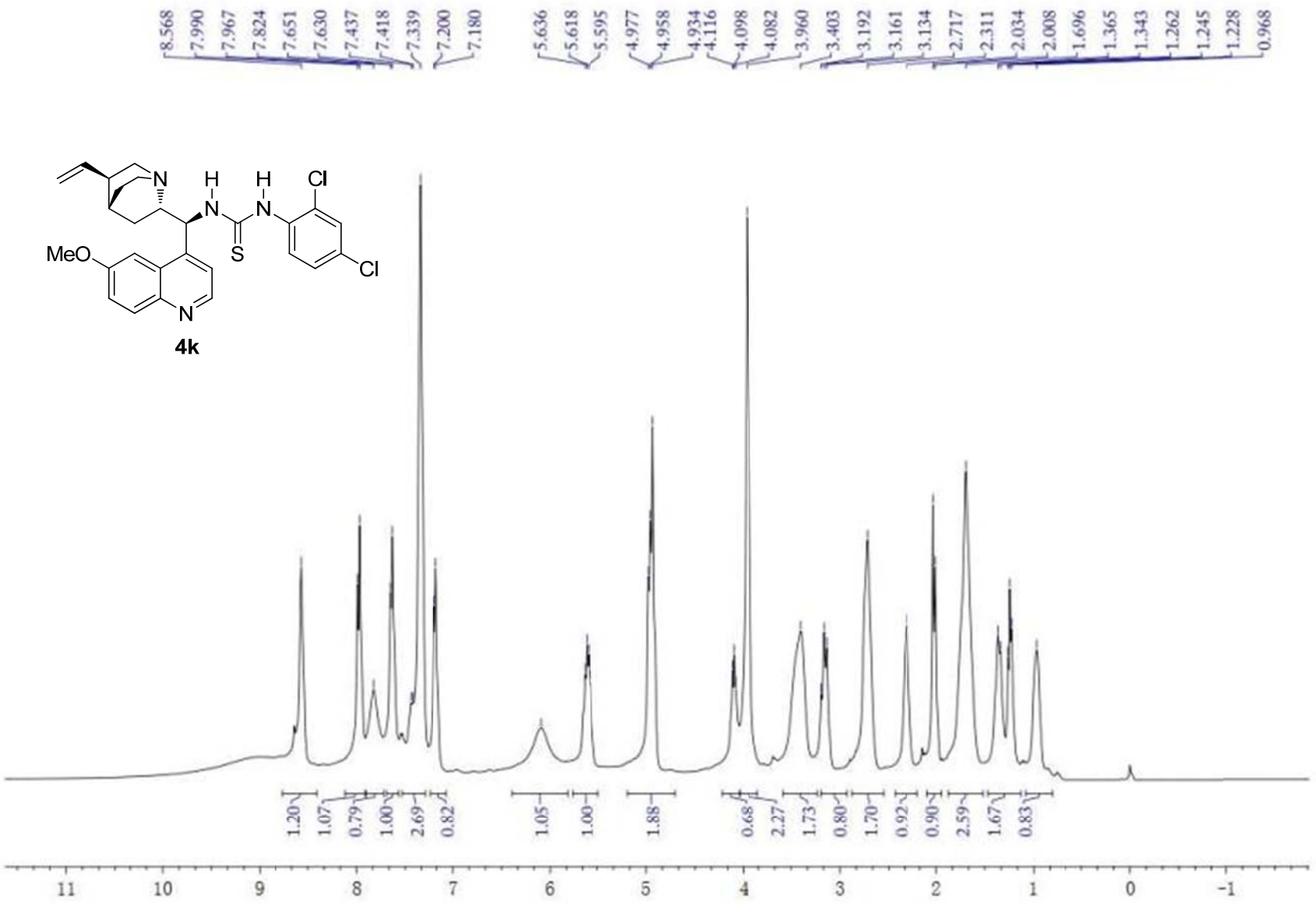
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S
Cl
Cl
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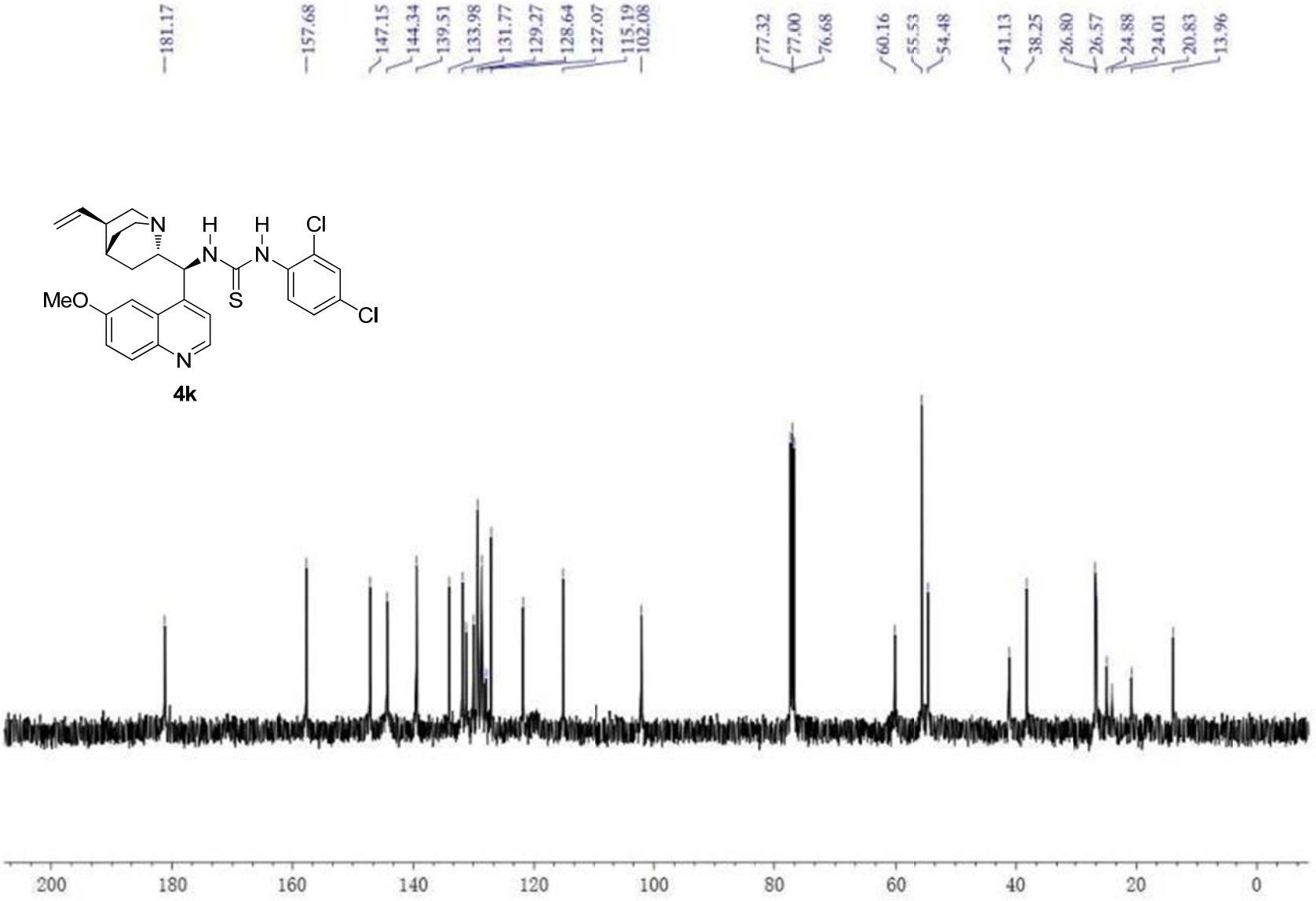
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26.57
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N
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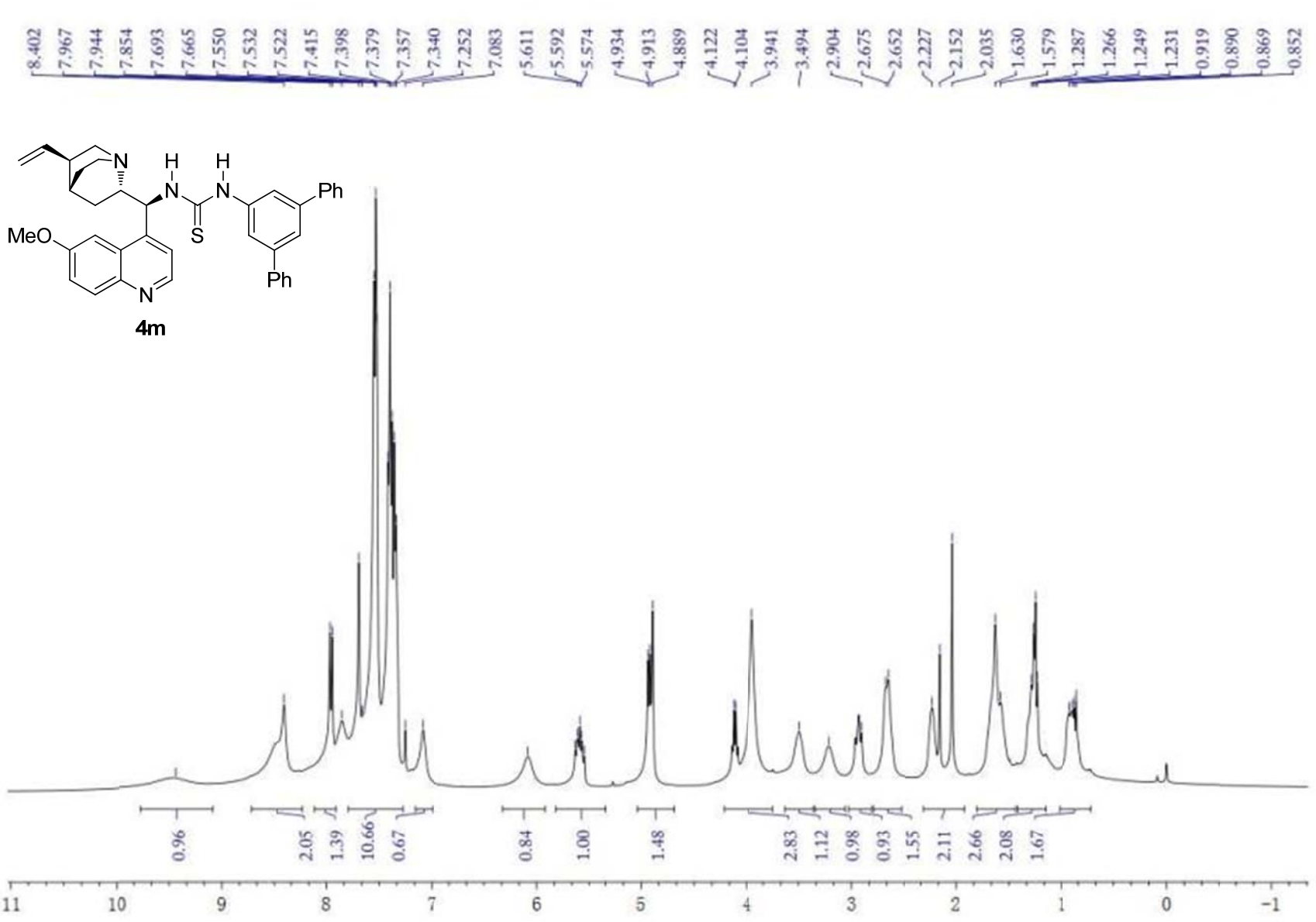
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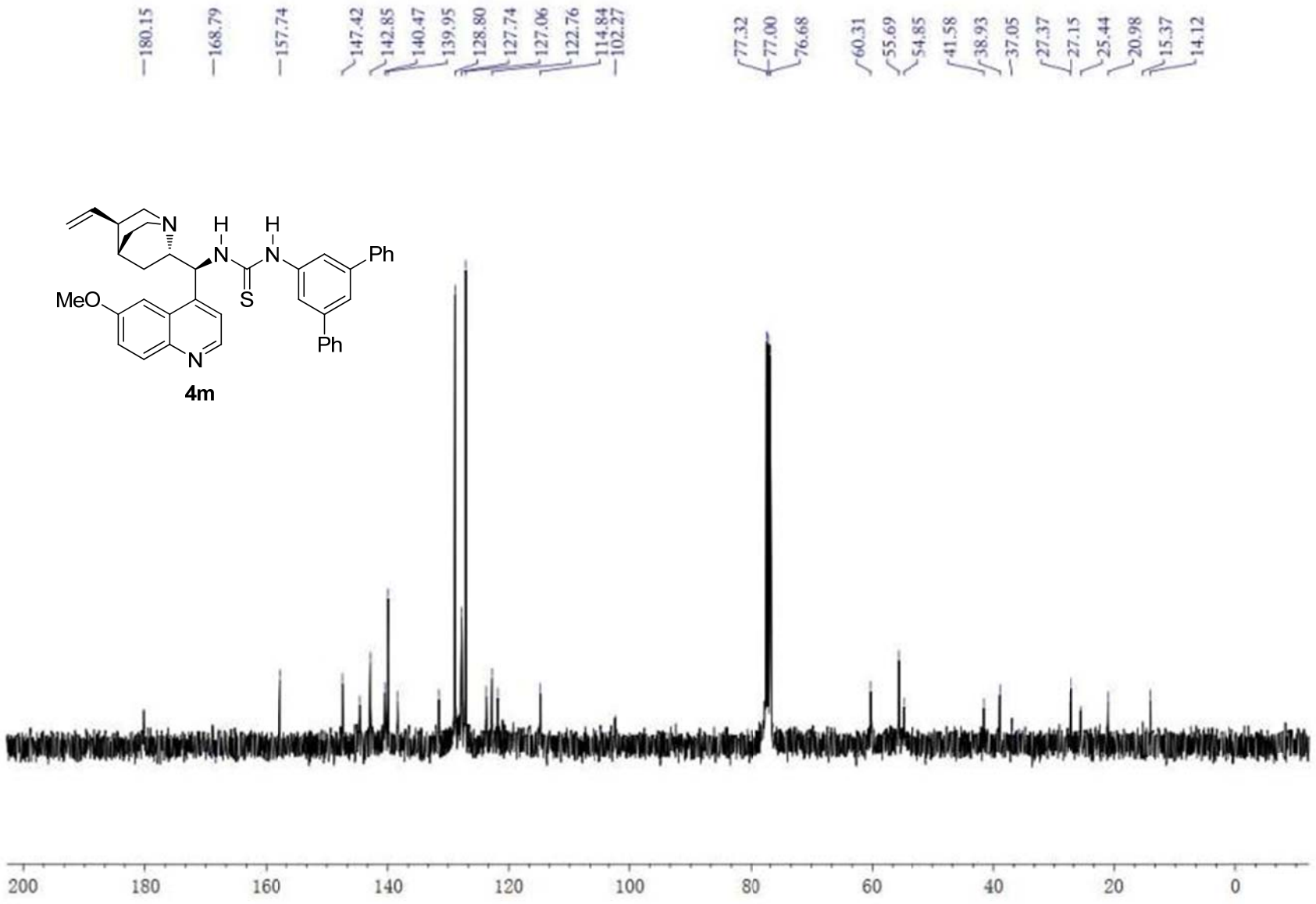
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MeO
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Ph
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4m
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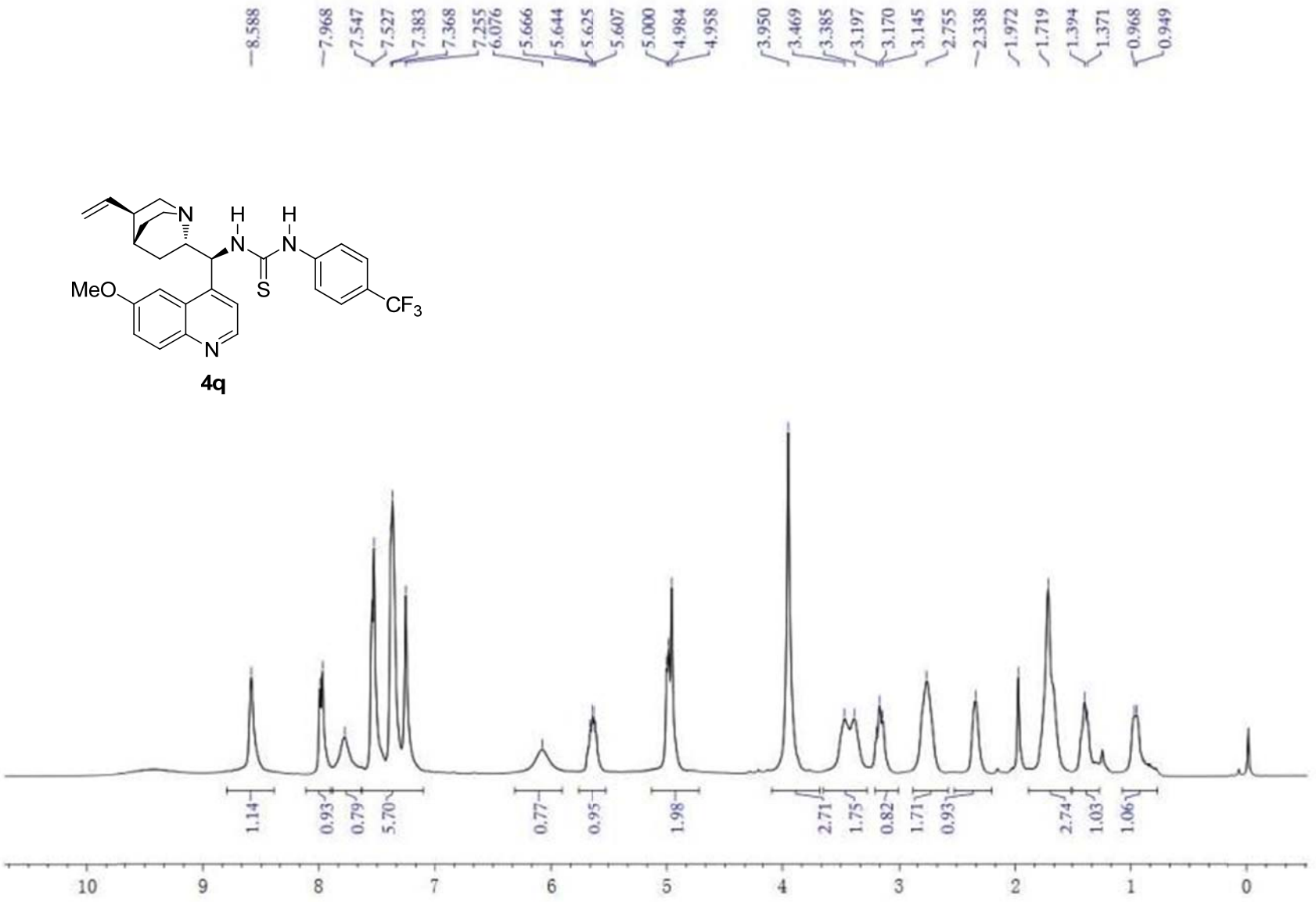
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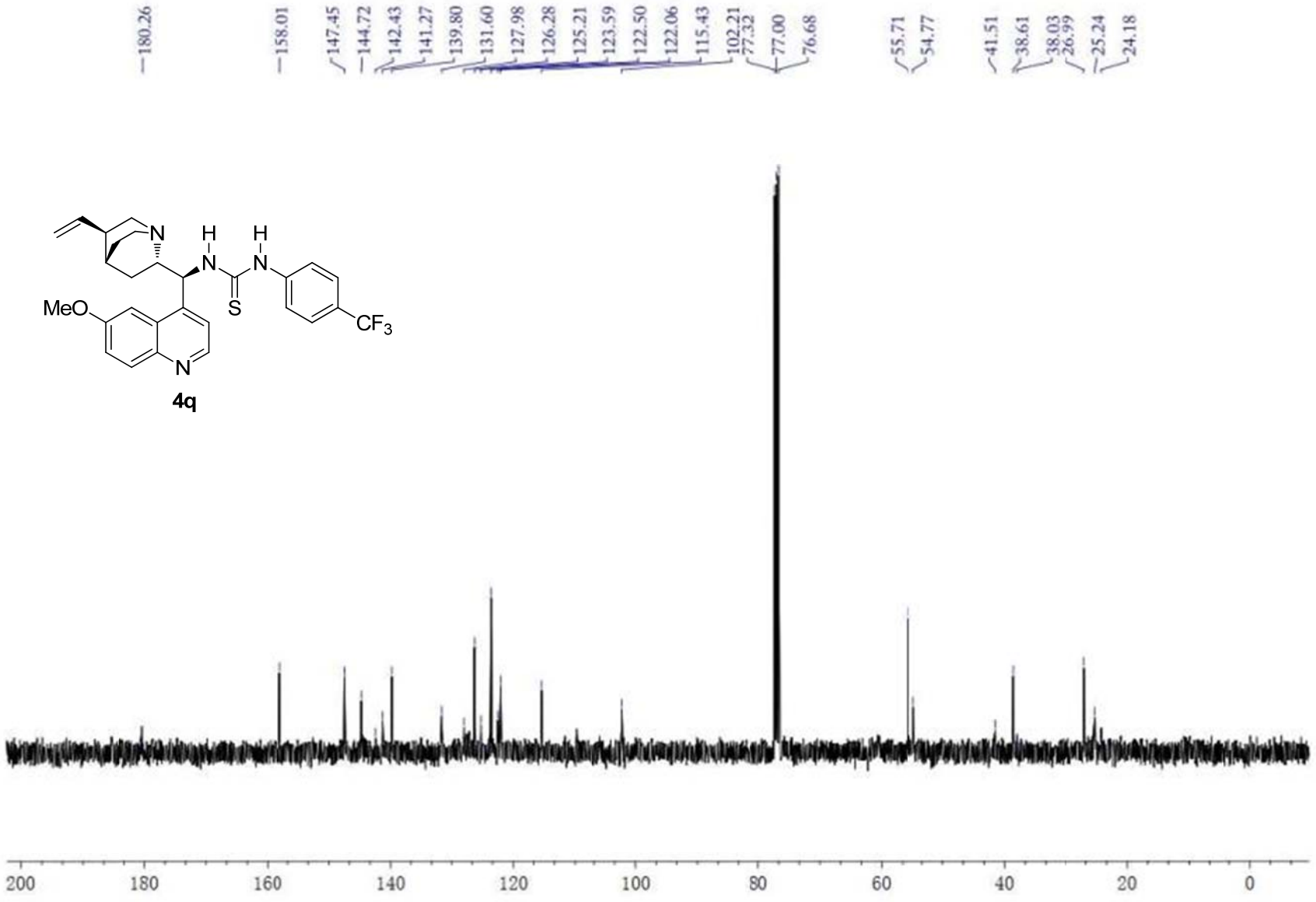
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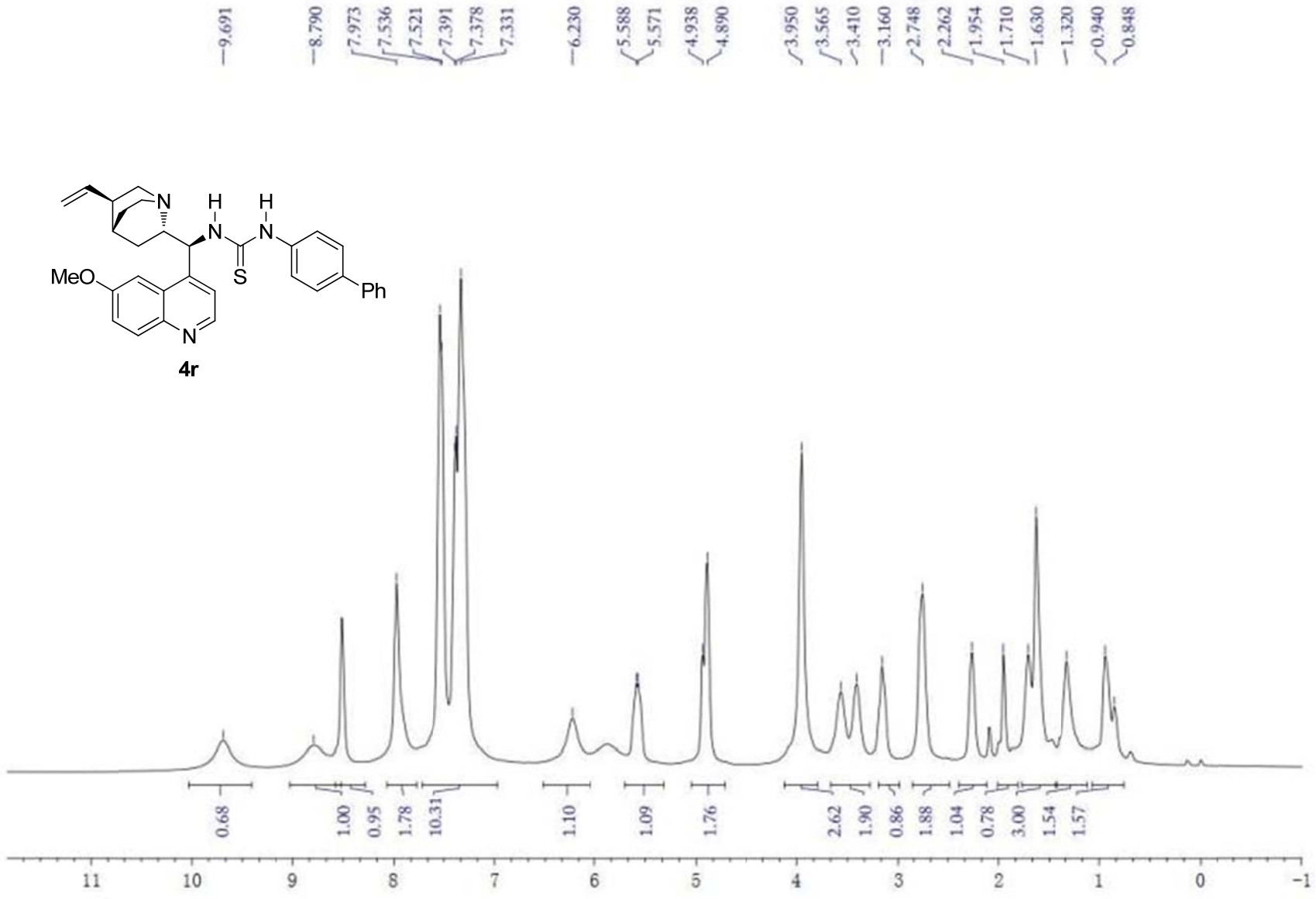
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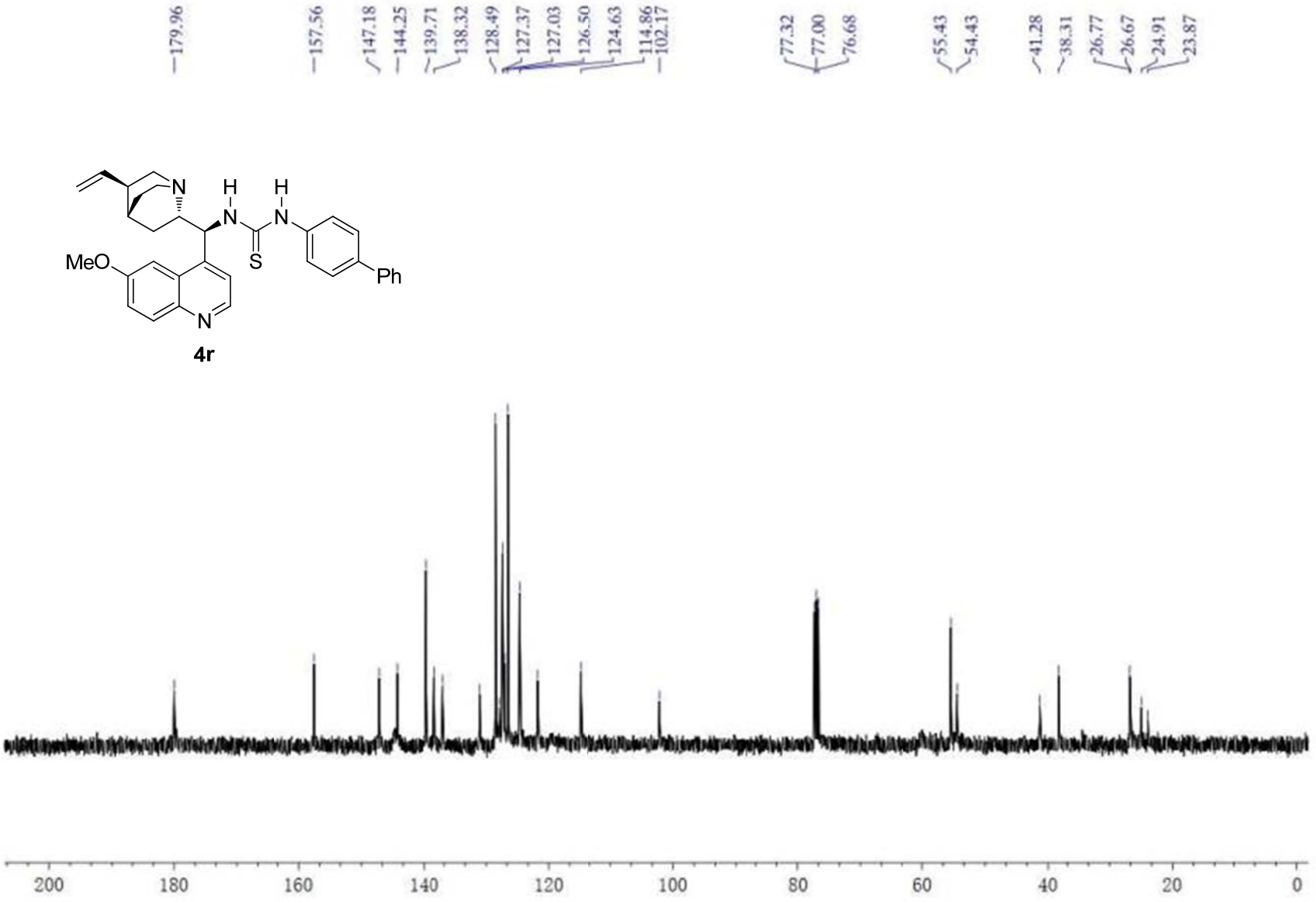
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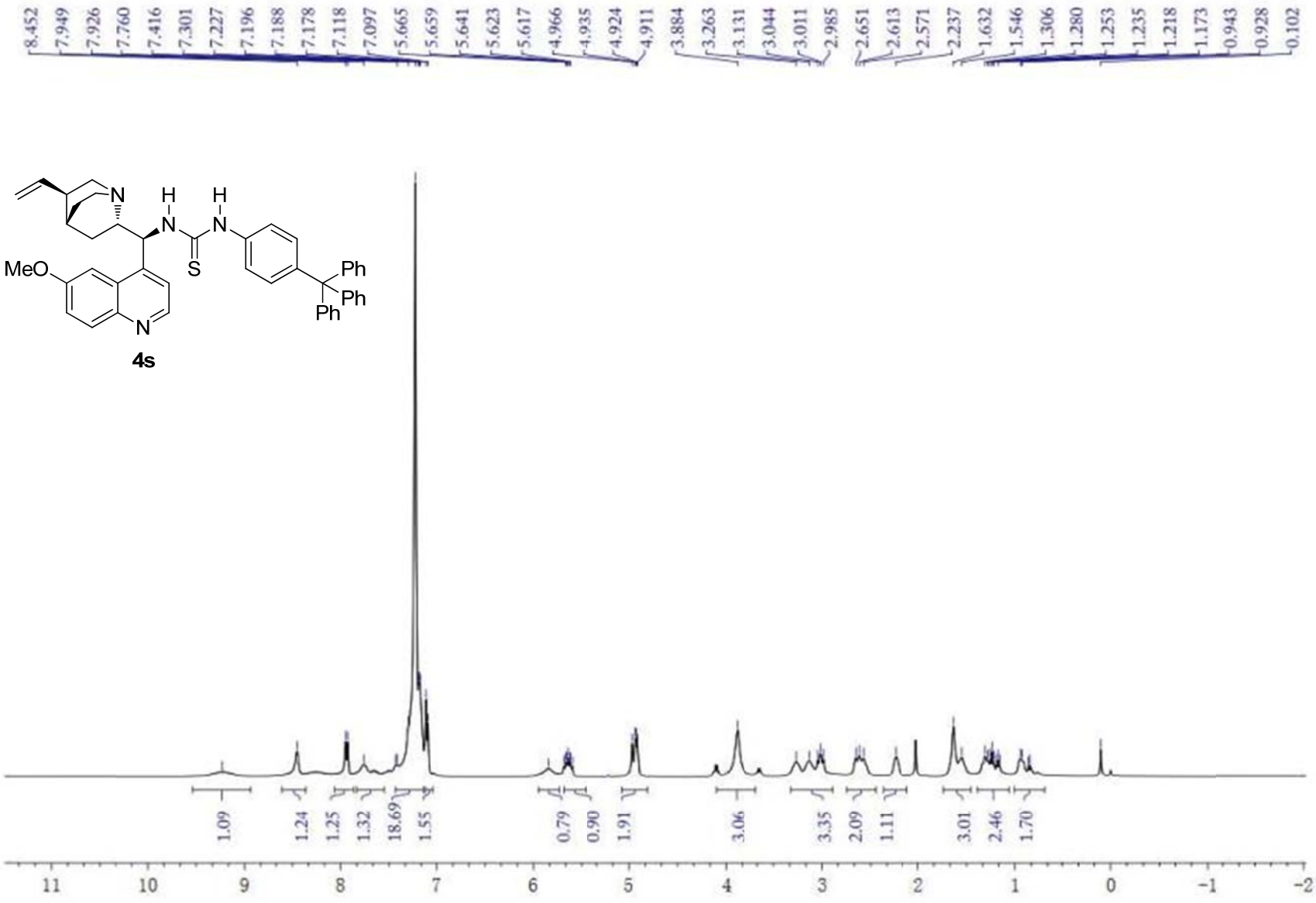
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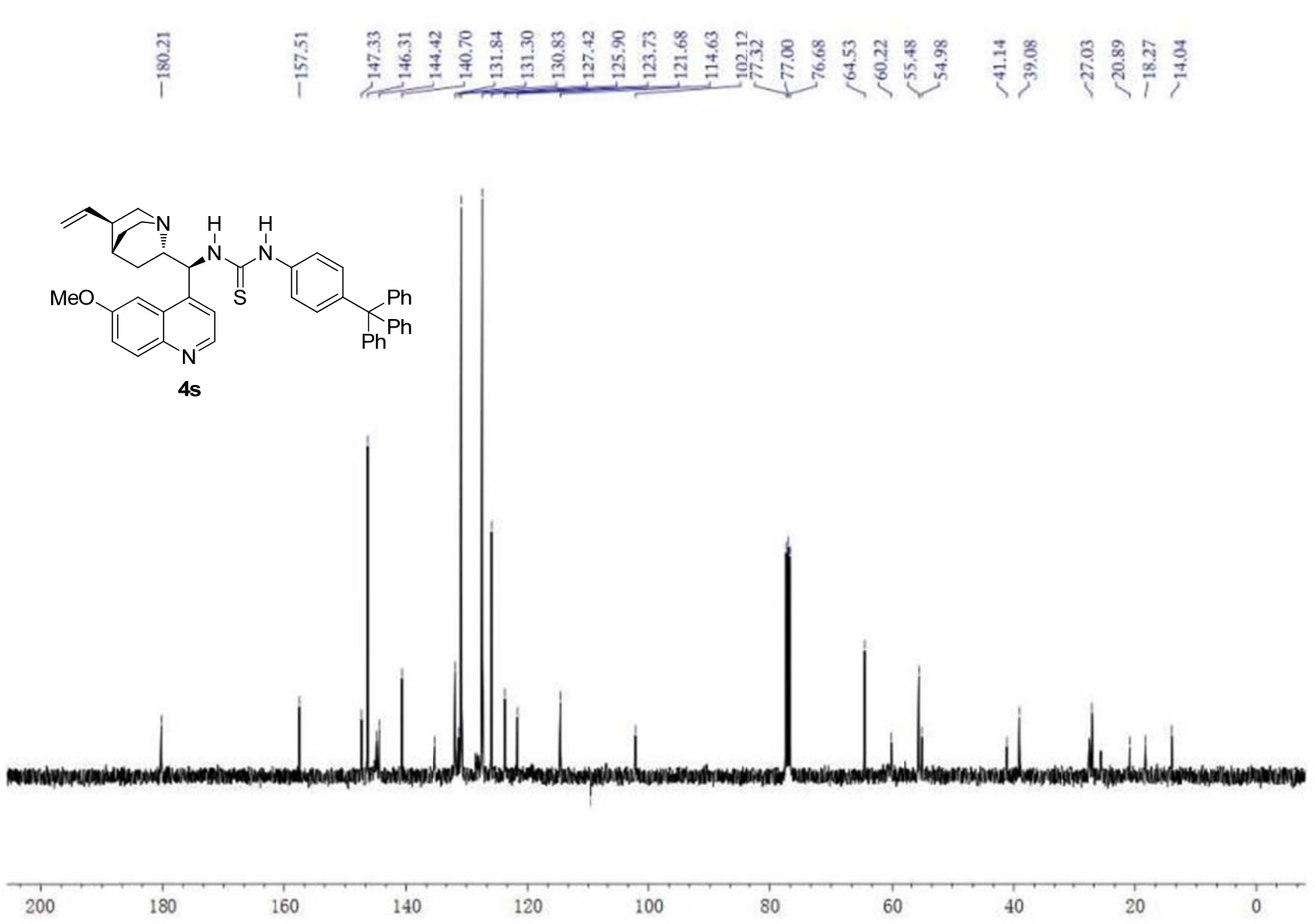
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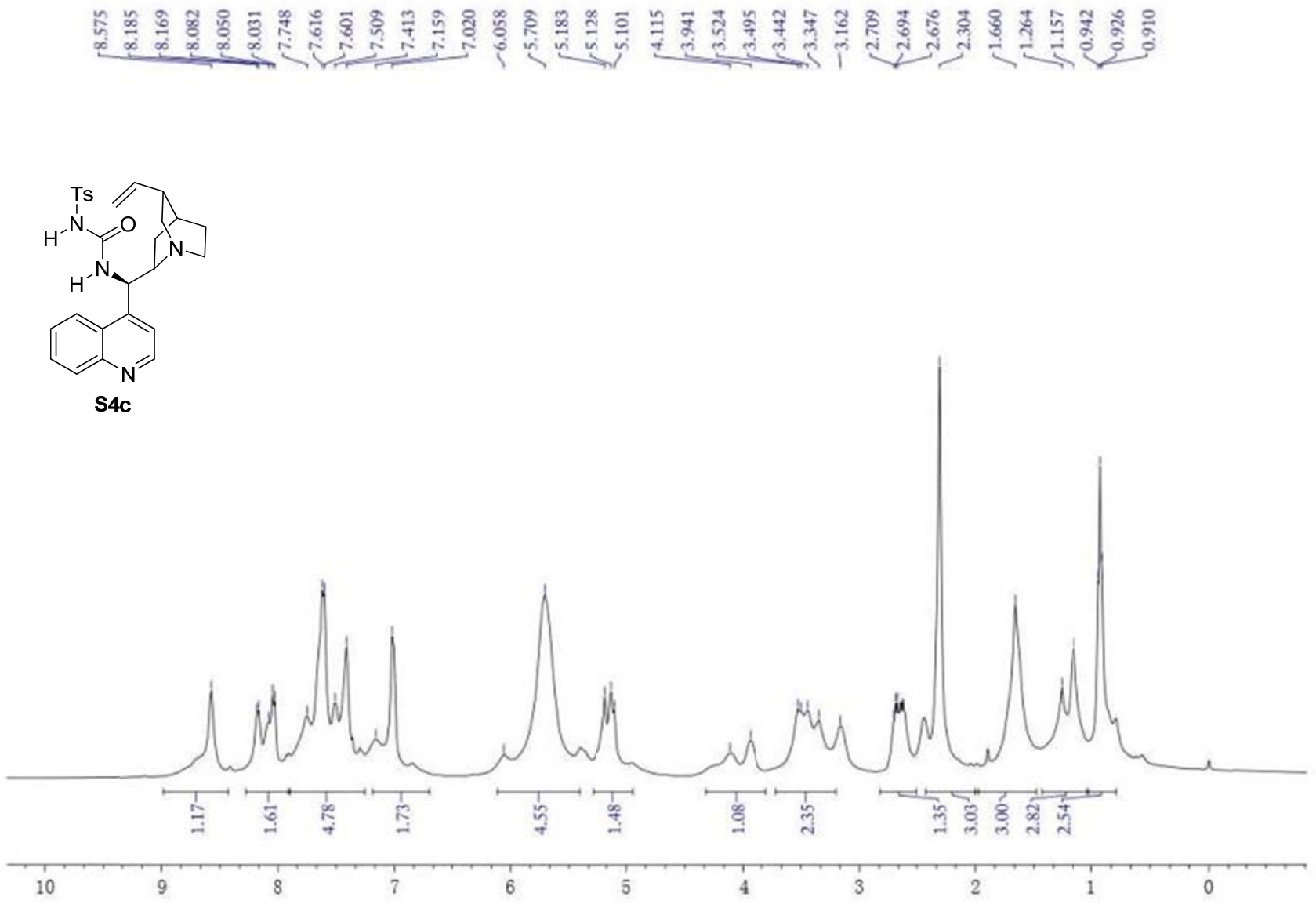
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H
N
N
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4.55
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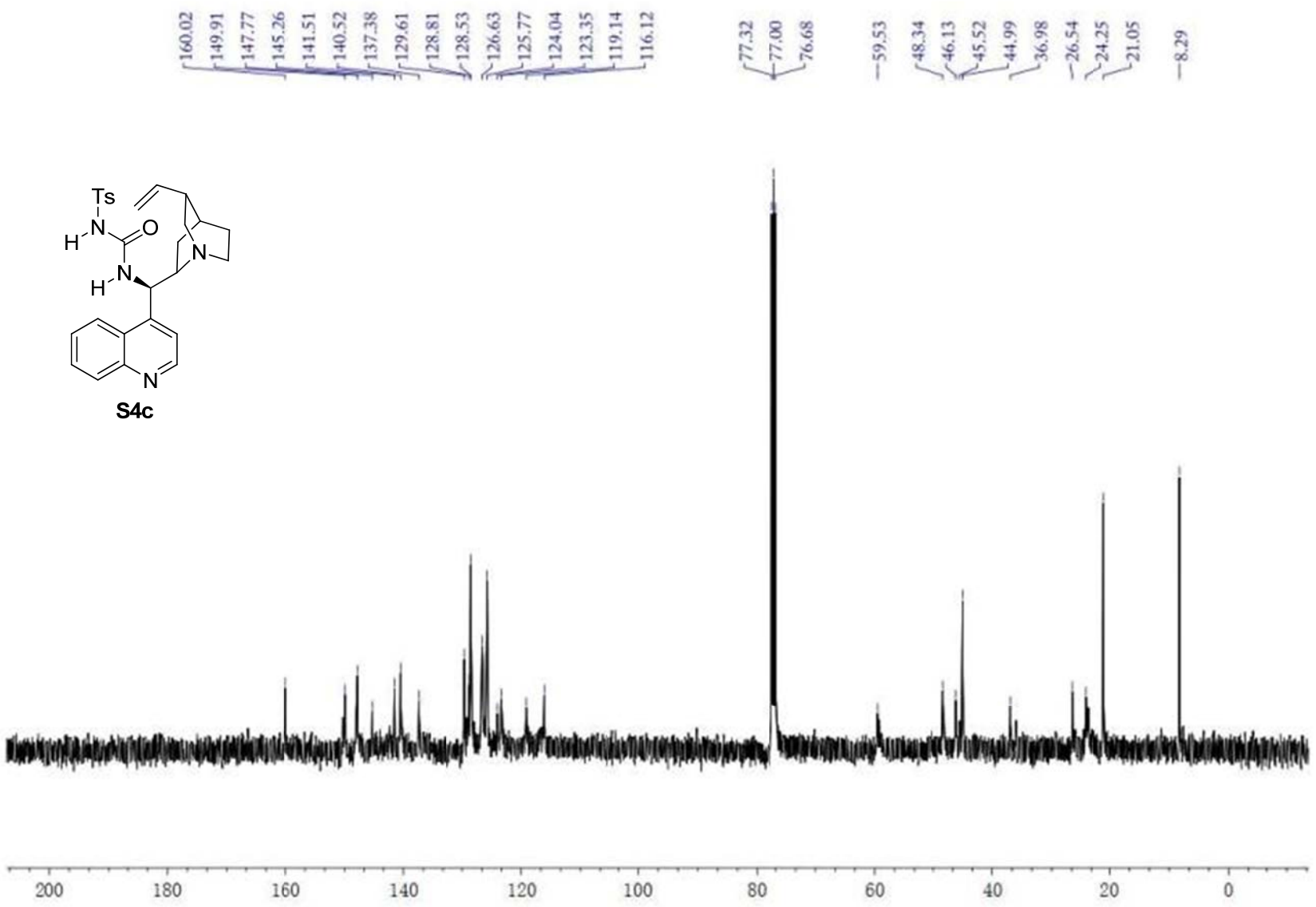
S4c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123.35
119.14
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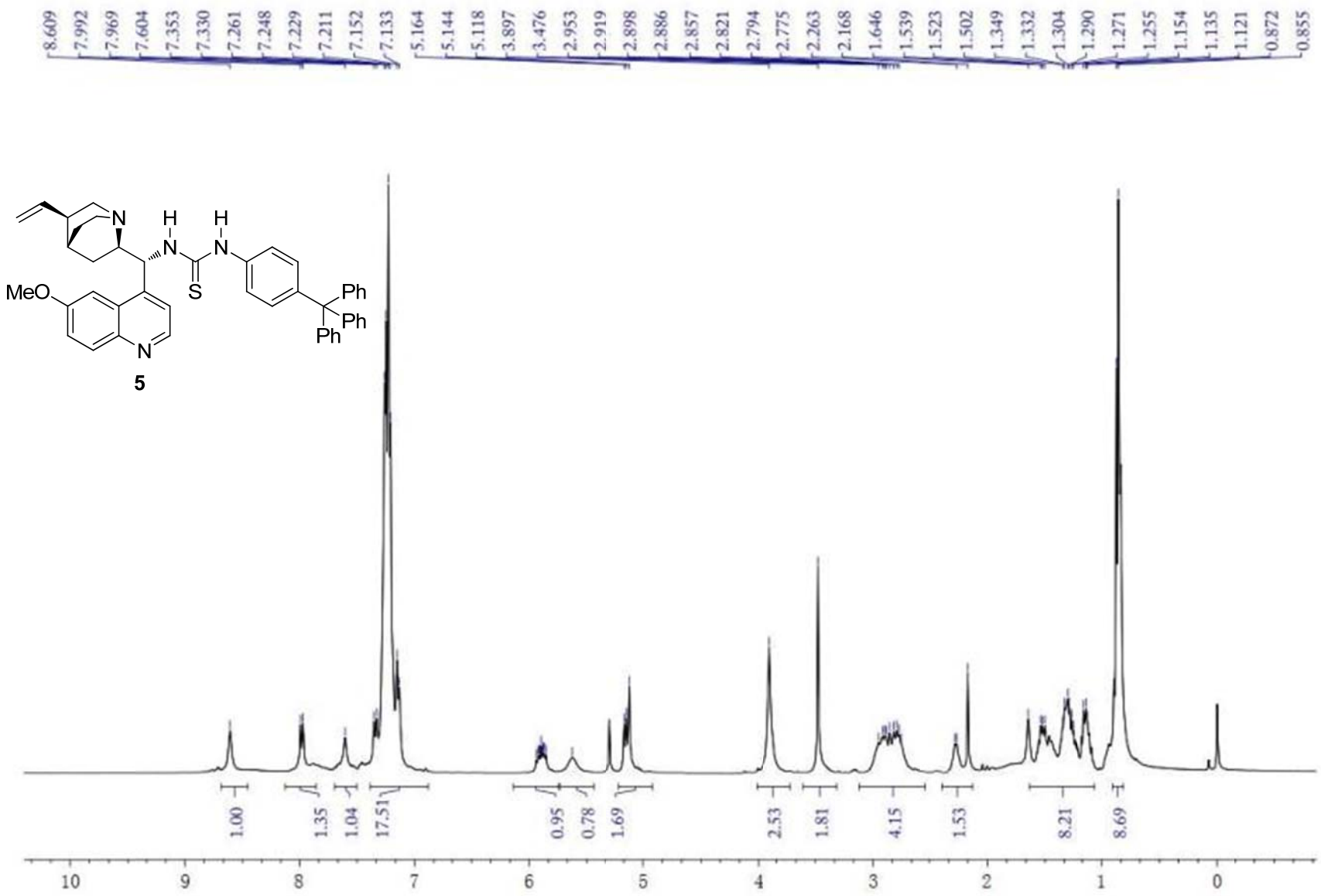
S4c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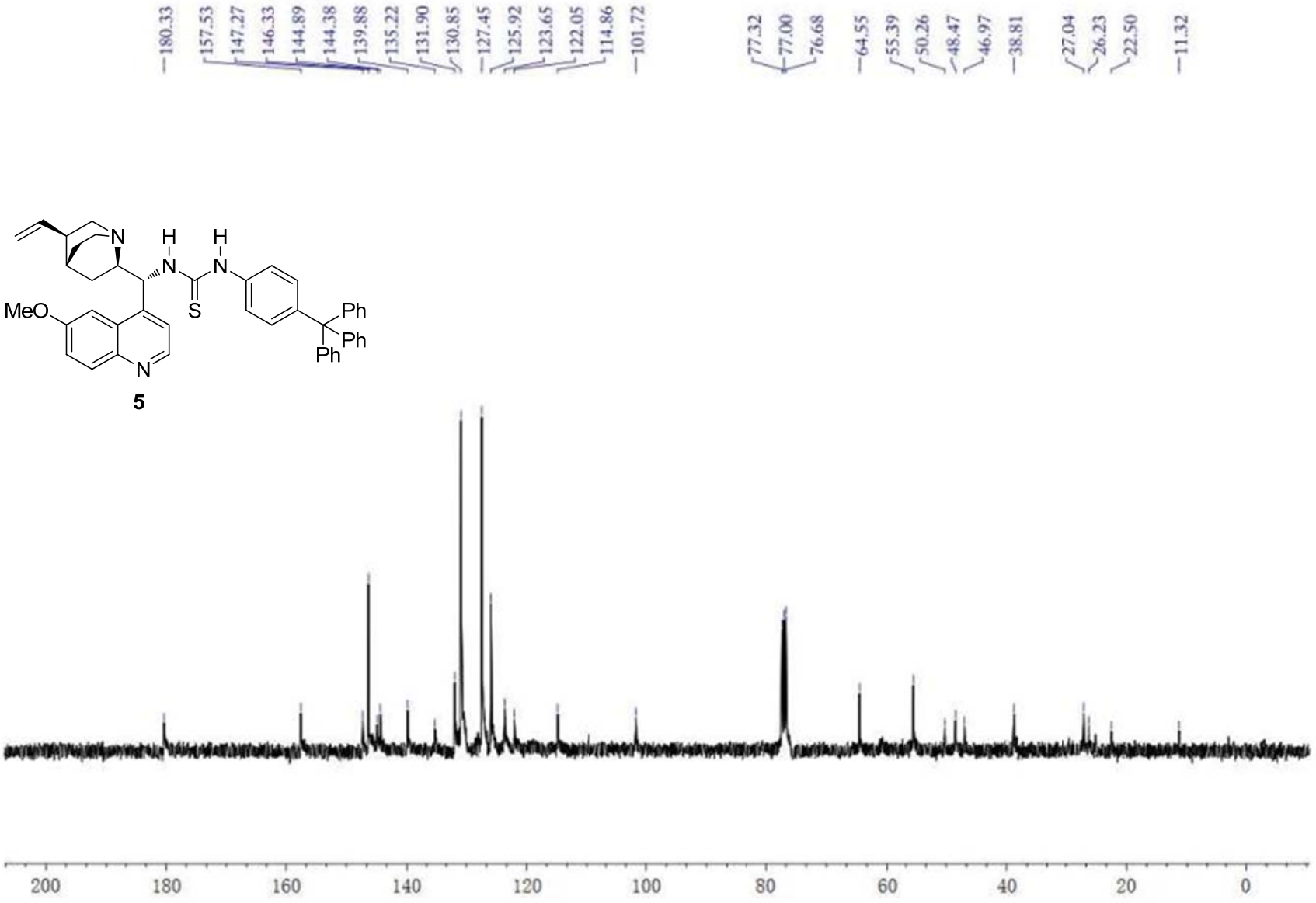
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27.04
26.23
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11.32
MeO
N
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Ph
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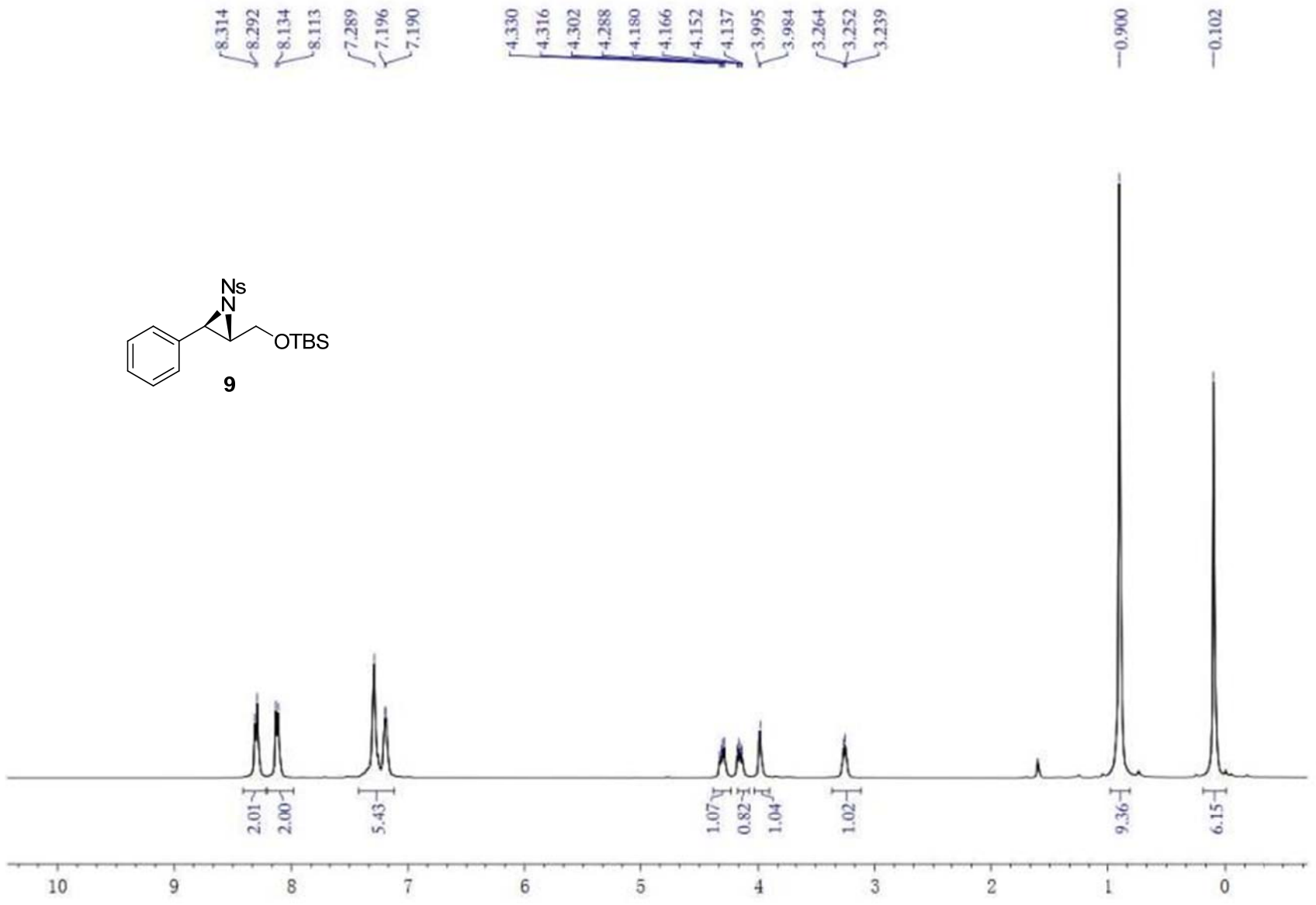
5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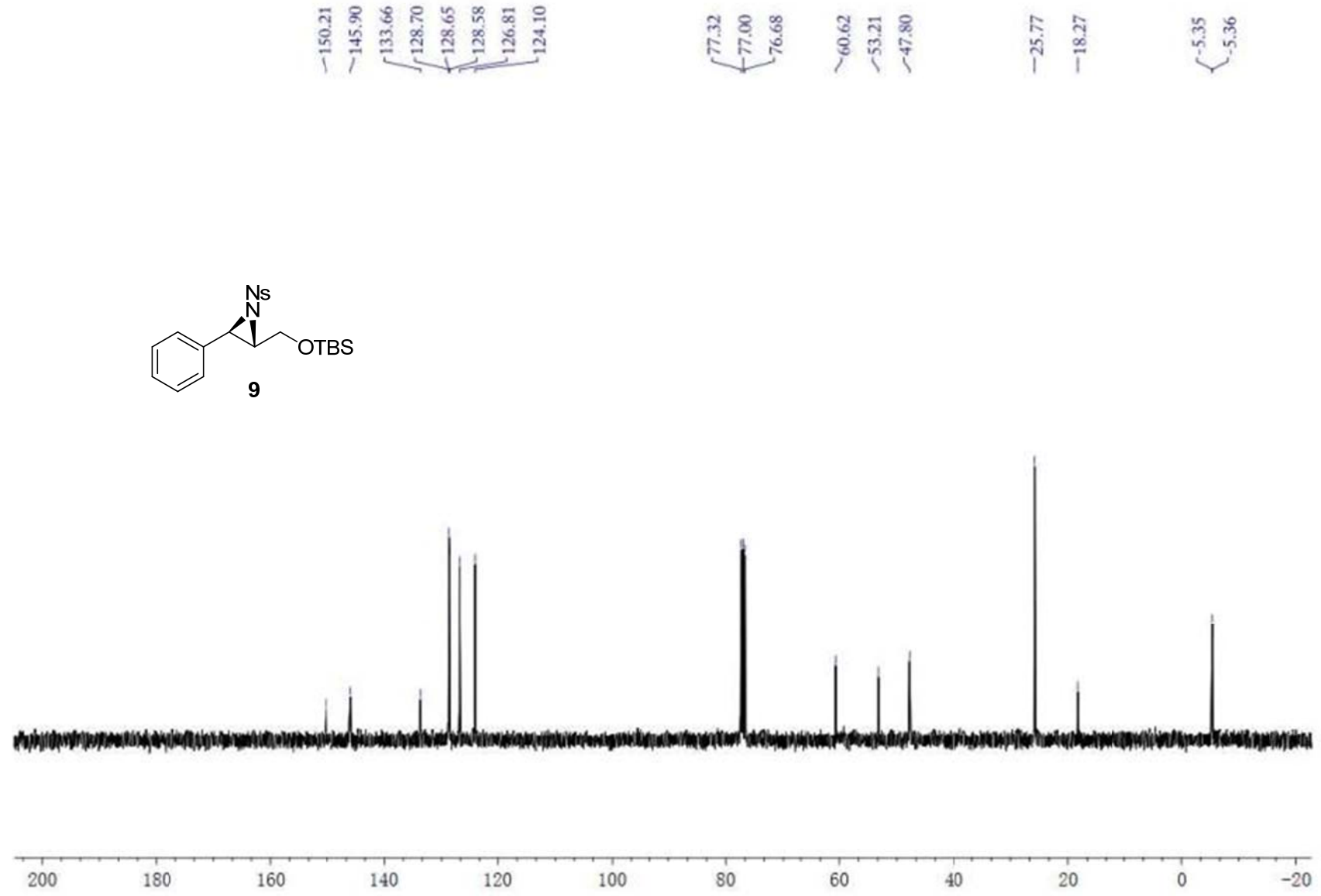
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18.27
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OTBS
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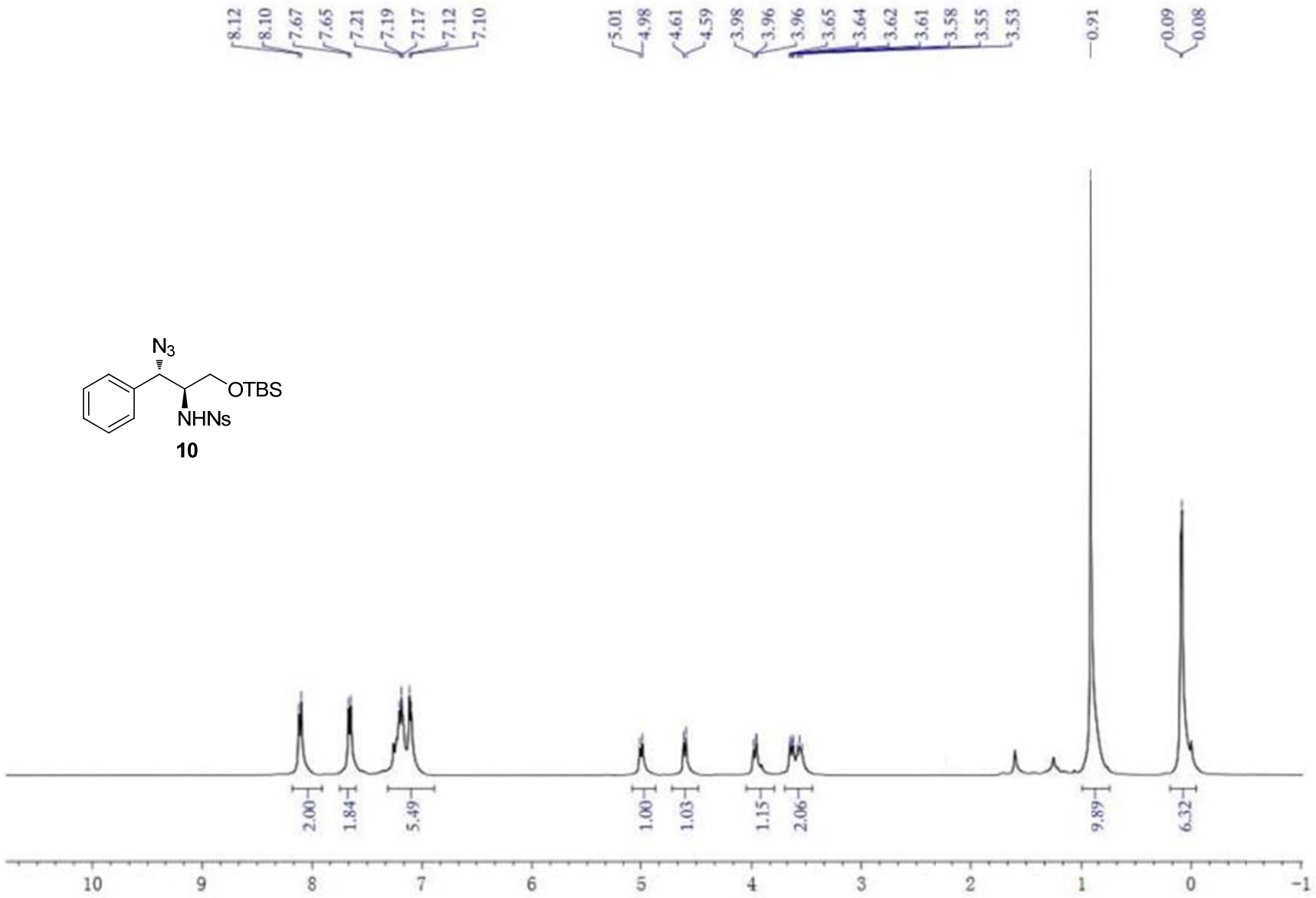
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OTBS
NHNs
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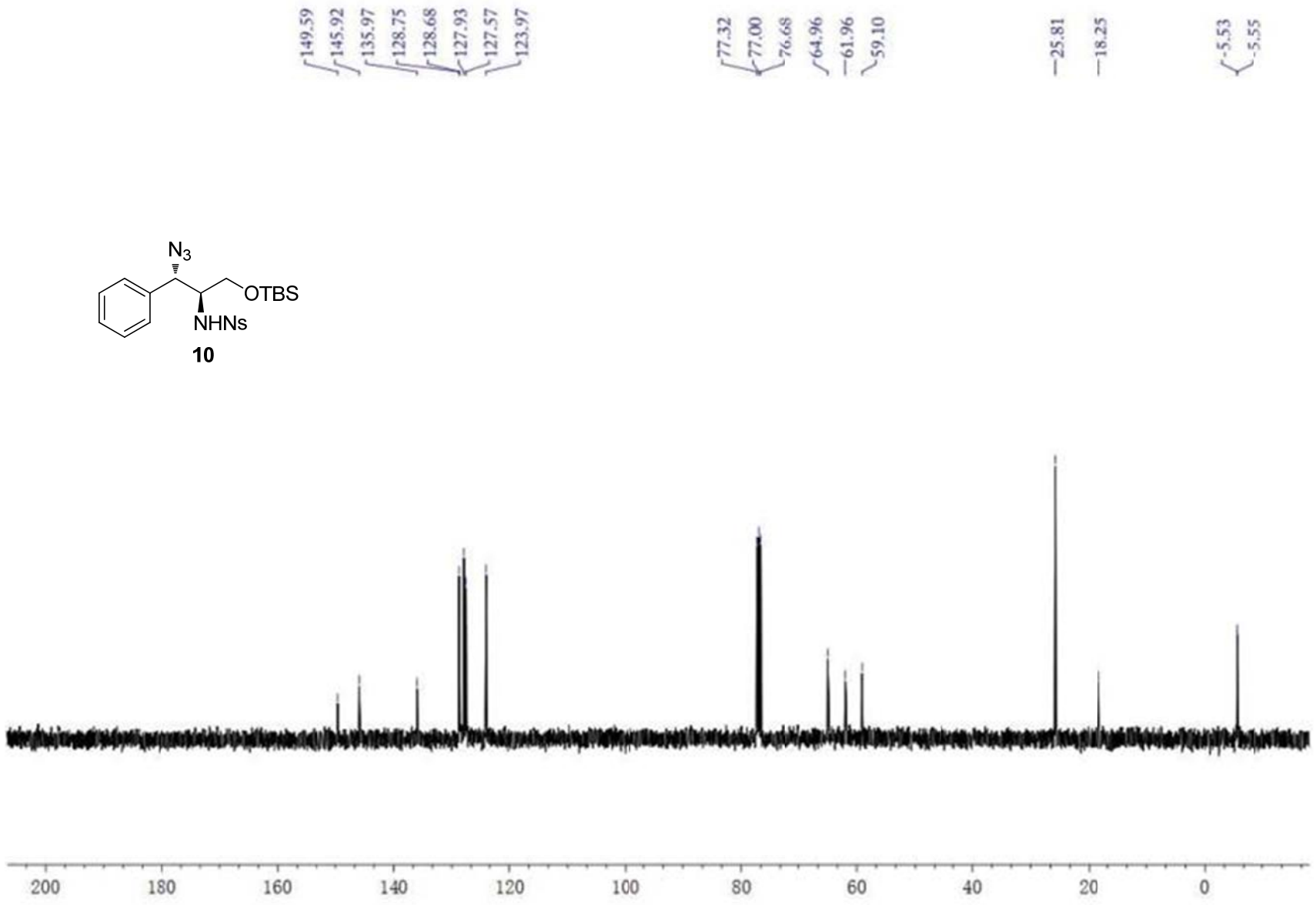
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18.25
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OTBS
NHNs
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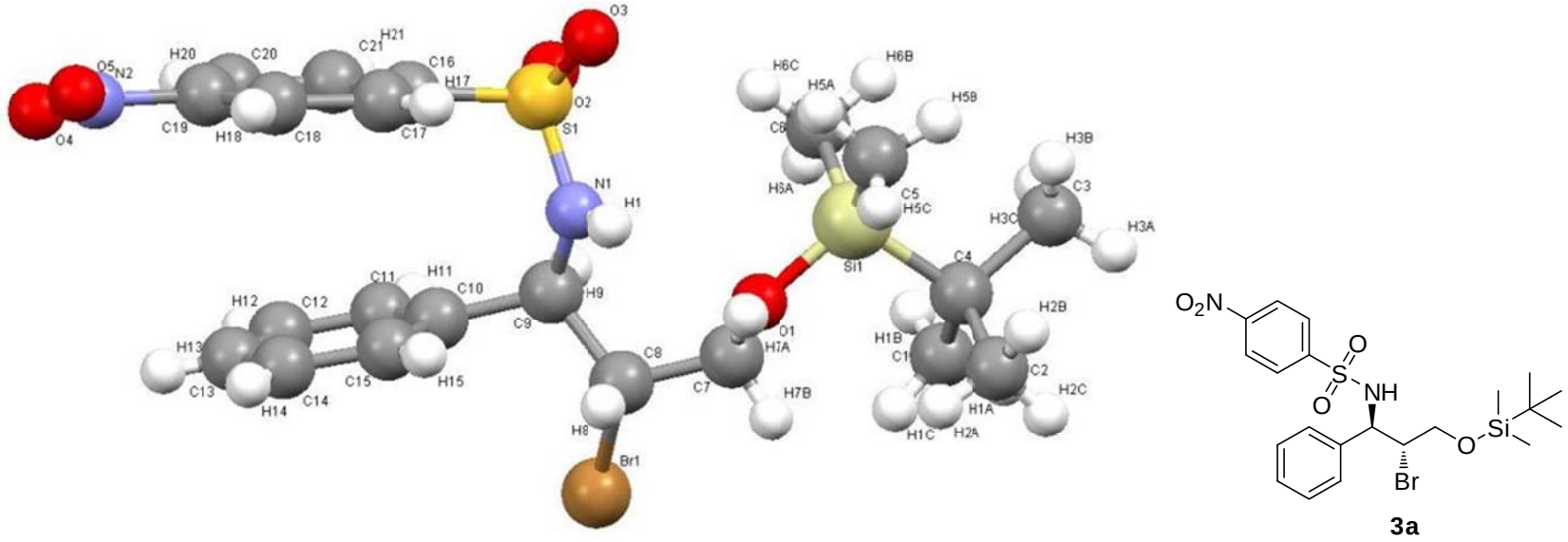

3a

Figure S1. X-ray structure of **3a.**