

# Supporting Information

## Catalytic Enantioselective Bromoamination of Allylic Alcohols

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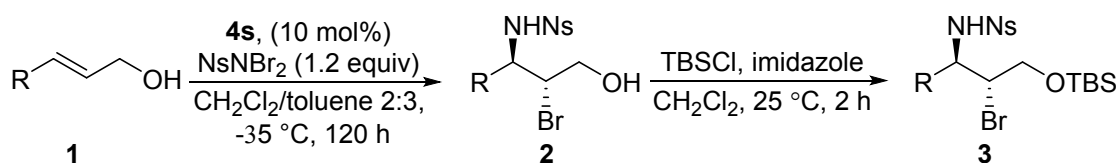
<sup>†</sup> These authors contributed equally to this work.

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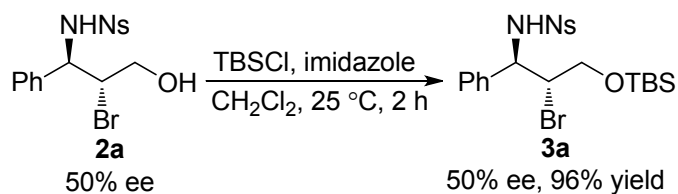
**General.** All reactions that required anhydrous conditions were carried by standard procedures under nitrogen atmosphere. Commercially available reagents were used as received. The solvents were dried by distillation over the appropriate drying reagents. Infrared spectra were recorded on a TENSOR 27 FT-IR spectrophotometer and reported in wave numbers ( $\text{cm}^{-1}$ ).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Varian (400 MHz) spectrometer. Chemical shifts ( $\delta$ ) are reported in ppm relative to TMS ( $\delta$  0.00) for the  $^1\text{H}$  NMR and to chloroform ( $\delta$  77.0) for the  $^{13}\text{C}$  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.

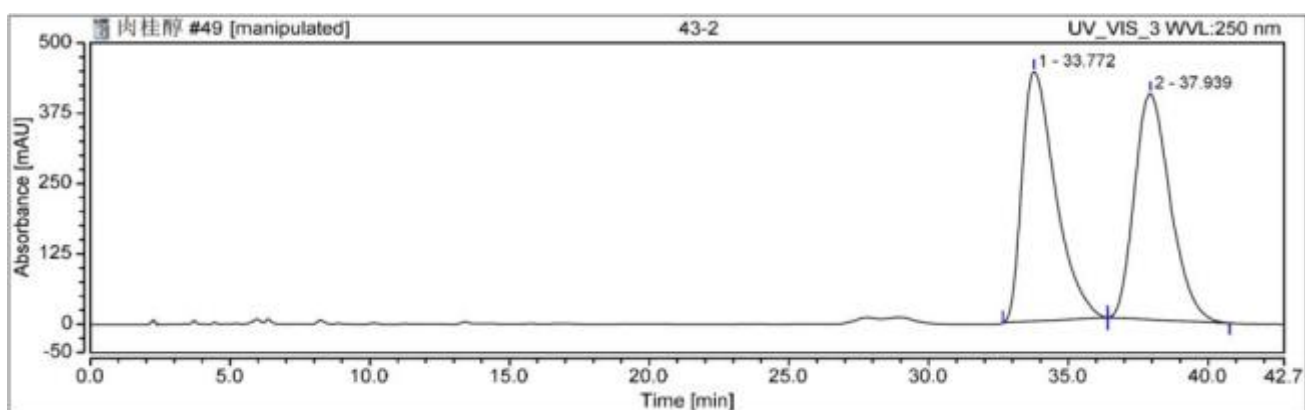


To a solution of allylic alcohol **1** (0.20 mmol, 1.00 equiv), catalyst **4s** (14.0 mg, 0.02 mmol, 0.10 equiv) in  $\text{CH}_2\text{Cl}_2/\text{toluene}$  (2:3, 5.0 mL) at  $-35\text{ }^\circ\text{C}$  in dark under  $\text{N}_2$  was added *NN*-dibromo-4-nitrobenzenesulfonamide (86.4 mg, 0.24 mmol, 1.20 equiv). The resulting mixture was stirred at  $-35\text{ }^\circ\text{C}$  for 120 h. The reaction was quenched with saturated  $\text{Na}_2\text{SO}_3$  (3.0 mL) at  $-35\text{ }^\circ\text{C}$  and then was warmed to  $25\text{ }^\circ\text{C}$ . The solution was diluted with water (3.0 mL) and extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 6$  mL). The combined extracts were washed with brine (10.0 mL), dried ( $\text{Na}_2\text{SO}_4$ ), filtered and concentrated *in vacuo*. The residue was purified by a short silica column to give a mixture of **2** and  $\text{NsNH}_2$ . To a solution of the mixture in  $\text{CH}_2\text{Cl}_2$  (2.0 mL) was added TBSCl (33.2 mg, 0.22 mmol) and imidazole (15.0 mg, 0.20 mmol) at  $25\text{ }^\circ\text{C}$ . The resulting mixture was stirred at  $25\text{ }^\circ\text{C}$  for 2 h, to the mixture was added brine (3 mL) and extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 5$  mL). The combined extracts were dried ( $\text{Na}_2\text{SO}_4$ ), filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography to yield the corresponding vicinal bromoamine **3**.

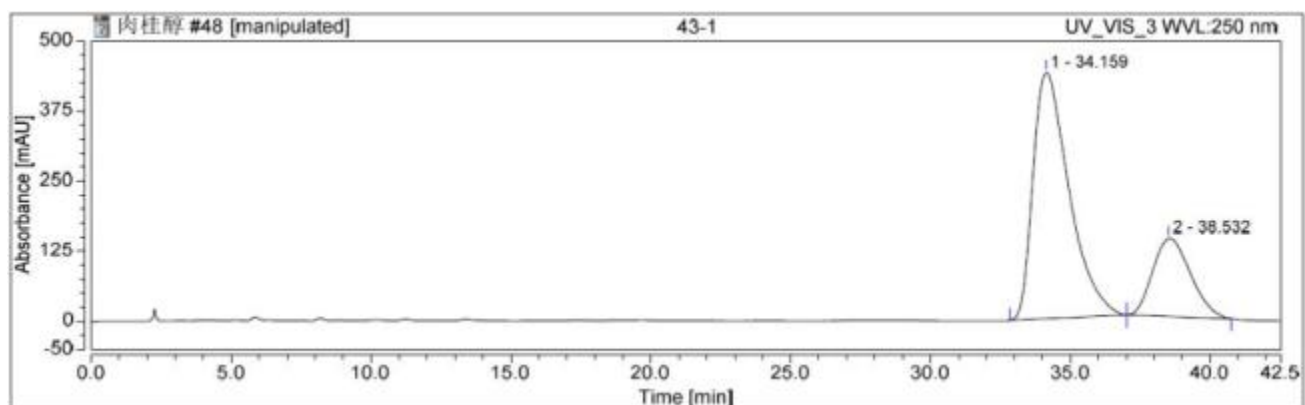
### Scheme S1. Silylation of **2a**.



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):

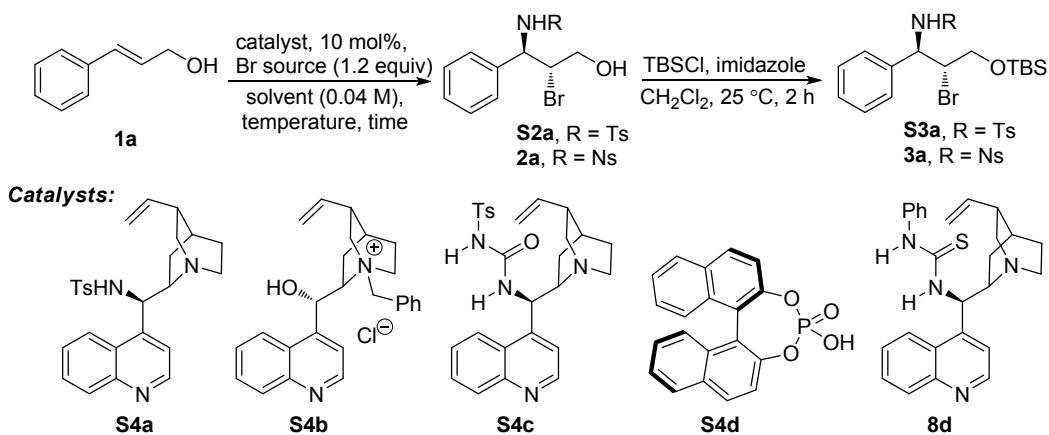


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		33.772	617.665	443.614	50.83	52.47	n.a.
2		37.939	597.550	401.822	49.17	47.53	n.a.
<b>Total:</b>			<b>1215.215</b>	<b>845.437</b>	<b>100.00</b>	<b>100.00</b>	



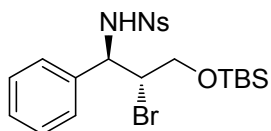
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		34.159	655.910	438.913	75.07	75.86	n.a.
2		38.532	217.808	139.696	24.93	24.14	n.a.
<b>Total:</b>			<b>873.719</b>	<b>578.609</b>	<b>100.00</b>	<b>100.00</b>	

**Table S1. Optimization of the Bromoamination of 1a.**



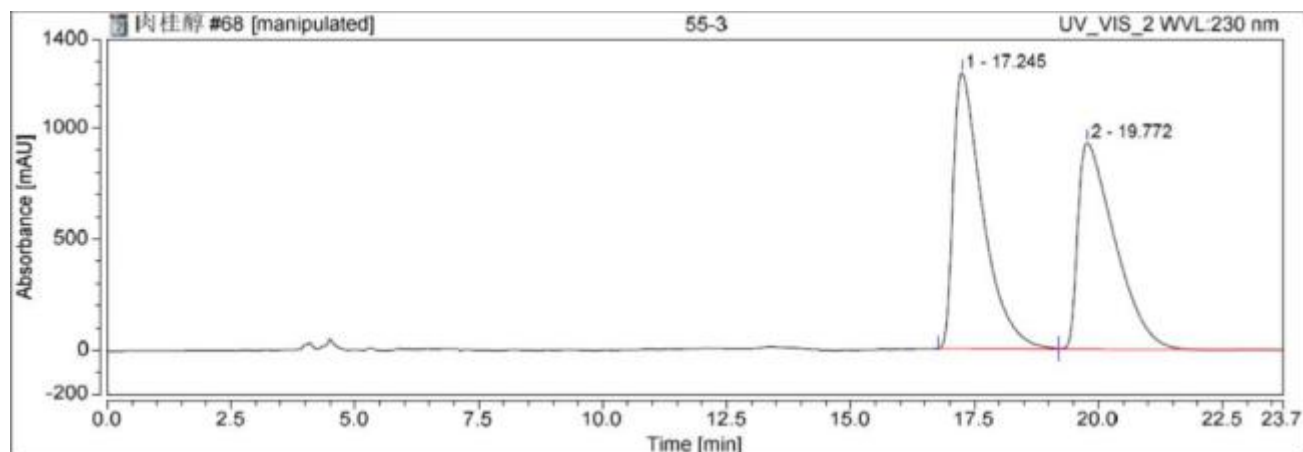
entr	catalyst	Br/amine source (equiv)	solvent	temp (°C)	time (h)	yield (%) <sup>b</sup>	ee
1	Cinchonine	NBS (1.2)/TsNH <sub>2</sub> (1.2)	CH <sub>2</sub> Cl <sub>2</sub>	rt	12	trace	-
2		TsNBr <sub>2</sub> (1.2)	CH <sub>2</sub> Cl <sub>2</sub>	rt	12	46	-
3	(DHQD) <sub>2</sub> PHA	TsNBr <sub>2</sub> (1.2)	CH <sub>2</sub> Cl <sub>2</sub>	-78	64	7	5
4	(DHQD) <sub>2</sub> Pyr	TsNBr <sub>2</sub> (1.2)	CH <sub>2</sub> Cl <sub>2</sub>	-78	64	6	4
5	(DHQD) <sub>2</sub> Pyr	NBS (1.2)/NsNH <sub>2</sub> (1.2)	CH <sub>2</sub> Cl <sub>2</sub>	-78	80	8	5
6	cinchonidine	NsNBr <sub>2</sub> (1.2)	CH <sub>2</sub> Cl <sub>2</sub>	-78	65	29	4
7	(DHQD) <sub>2</sub> Pyr	NsNBr <sub>2</sub> (1.2)	CH <sub>2</sub> Cl <sub>2</sub>	-78	65	25	11
8	(DHQ) <sub>2</sub> PHAL	NsNBr <sub>2</sub> (1.2)	CH <sub>2</sub> Cl <sub>2</sub>	-78	65	40	0
9	<b>S4a</b>	NsNBr <sub>2</sub> (1.2)	CH <sub>2</sub> Cl <sub>2</sub>	-78	65	63	0
10	<b>S4b</b>	NsNBr <sub>2</sub> (1.2)	CH <sub>2</sub> Cl <sub>2</sub>	-78	76	5	2
11	<b>S4c</b>	NsNBr <sub>2</sub> (1.2)	CH <sub>2</sub> Cl <sub>2</sub>	-78	76	20	0
12	<b>S4d</b>	NsNBr <sub>2</sub> (1.2)	CH <sub>2</sub> Cl <sub>2</sub>	-78	76	17	2
13	<b>8d</b>	NsNBr <sub>2</sub> (1.2)	CH <sub>2</sub> Cl <sub>2</sub>	-78	76	50	49
14	<b>8d</b>	NBS (1.2)/NsNH <sub>2</sub> (1.2)	CH <sub>2</sub> Cl <sub>2</sub>	-78	80	11	37
15	<b>8d</b>	NsNBr <sub>2</sub> (1.2)	CH <sub>2</sub> Cl <sub>2</sub>	-50	76	59	47
16	<b>4a</b>	NsNBr <sub>2</sub> (1.2)	CH <sub>2</sub> Cl <sub>2</sub>	-50	42	44	51
17	<b>4a</b>	TsNBr <sub>2</sub> (1.2)	CH <sub>2</sub> Cl <sub>2</sub>	-50	96	30	15
18	<b>4a</b>	NsNBr <sub>2</sub> (0.6)/NsNH <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	-50	60	23	44
19	<b>4a</b>	NBP (1.2)/NsNH <sub>2</sub> (1.2)	CH <sub>2</sub> Cl <sub>2</sub>	-50	138	27	49
20	<b>4a</b>	DBDMH (1.2)/NsNH <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	-50	138	Trace	-
21	<b>4a</b>	NsNBr <sub>2</sub> (1.2)	Toluene	-40	96	Trace	-
22	<b>4a</b>	NsNBr <sub>2</sub> (1.2)	Et <sub>2</sub> O	-50	96	70	0
23	<b>4a</b>	NsNBr <sub>2</sub> (1.2)	CH <sub>2</sub> Cl <sub>2</sub> /toluene, 1:1	-50	138	49	57
24	<b>4a</b>	NsNBr <sub>2</sub> (1.2)	CH <sub>2</sub> Cl <sub>2</sub> /hexane, 1:1	-50	96	71	26
25	<b>4a</b>	NsNBr <sub>2</sub> (1.2)	CHCl <sub>3</sub> /ClCH <sub>2</sub> CH <sub>2</sub> Cl,	-50	98	61	46
26	<b>4a</b>	NsNBr <sub>2</sub> (1.2)	CH <sub>2</sub> Cl <sub>2</sub> /toluene, 1:2	-50	138	36	41
27	<b>4a</b>	NsNBr <sub>2</sub> (1.2)	CH <sub>2</sub> Cl <sub>2</sub> /toluene, 2:1	-50	138	37	54
28	<b>4a</b>	NsNBr <sub>2</sub> (1.2)	CH <sub>2</sub> Cl <sub>2</sub> /toluene, 2:3	-50	75	24	59
29	<b>4a</b>	NsNBr <sub>2</sub> (1.2)	CH <sub>2</sub> Cl <sub>2</sub> /toluene, 2:3	-40	96	59	63
30	<b>4a</b>	NsNBr <sub>2</sub> (1.2)	CH <sub>2</sub> Cl <sub>2</sub> /toluene, 2:3	-30	72	53	47
31	<b>4s</b>	NsNBr <sub>2</sub> (1.2)	CH <sub>2</sub> Cl <sub>2</sub> /toluene, 2:3	-40	96	67	90
32	<b>4s</b>	NsNBr <sub>2</sub> (1.2)	CH <sub>2</sub> Cl <sub>2</sub> /toluene, 2:3	-35	120	64	86 <sup>c</sup>

<sup>a</sup> 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. <sup>b</sup> Isolated yield by two steps. <sup>c</sup> The concentration is 0.1 M.

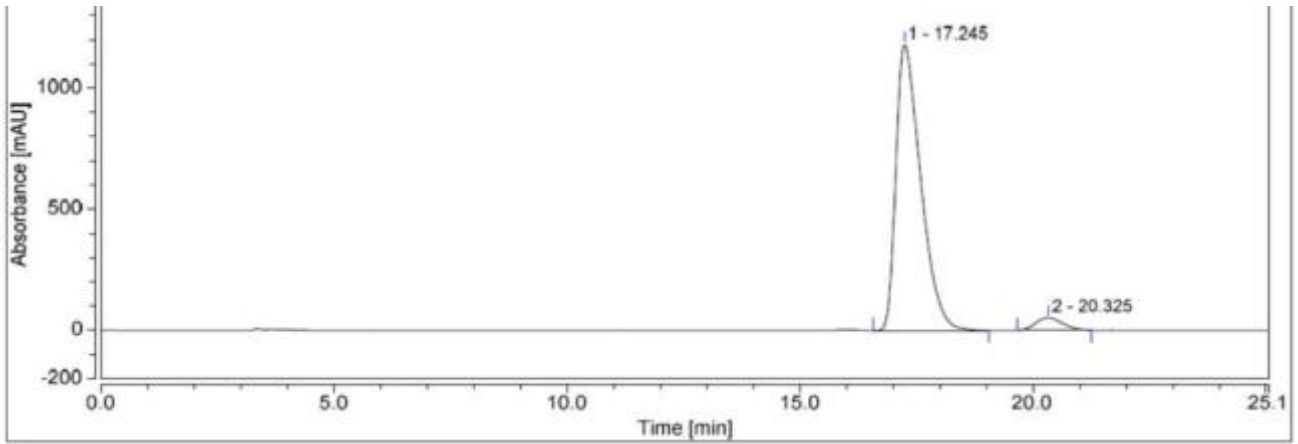


**(1*R*,2*R*)-*N*-(2-Bromo-3-((*tert*-butyldimethylsilyloxy)-1-phenylpropyl)-4-nitrobenzenesulfonamide (3a)**

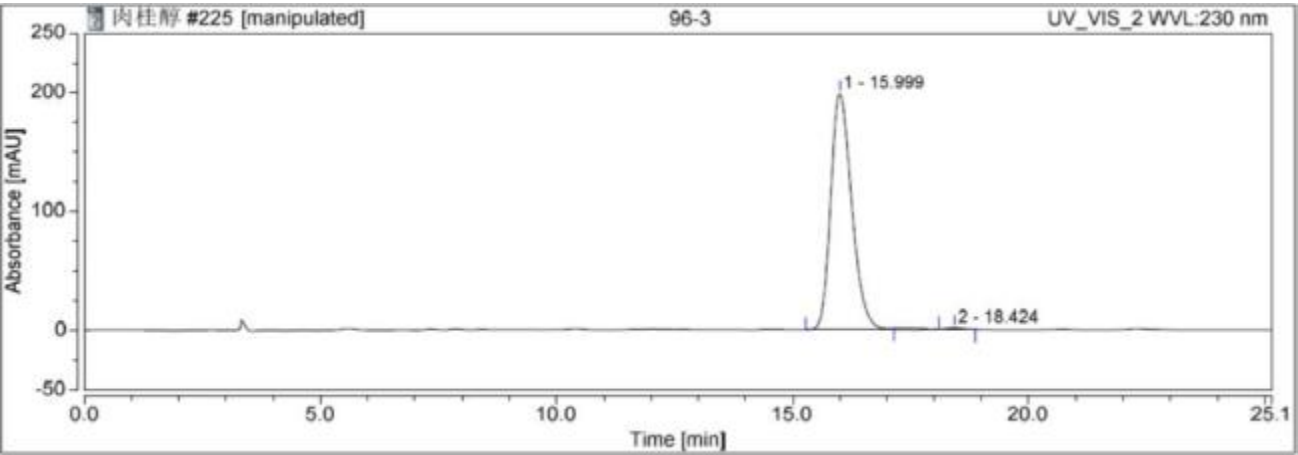
White solide,  $[\alpha]_{20}^D -51.9$  ( $c$  1.0,  $\text{CHCl}_3$ , 91% ee); IR (KBr): 3297, 2928, 1606, 1348, 1310, 1012, 836  $\text{cm}^{-1}$ ;  $^1\text{H}$ NMR (400 MHz, )  $\delta$  8.15 (d,  $J = 8.5$  Hz, 2H), 7.80 (d,  $J = 8.5$  Hz, 2H), 7.18-7.21 (m, 5H), 6.68 (d,  $J = 7.2$  Hz, 1H), 4.97 (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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{21}\text{H}_{29}\text{BrN}_2\text{O}_5\text{SSiNa}$   $m/z$   $[\text{M} + \text{Na}]^+$ : 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).



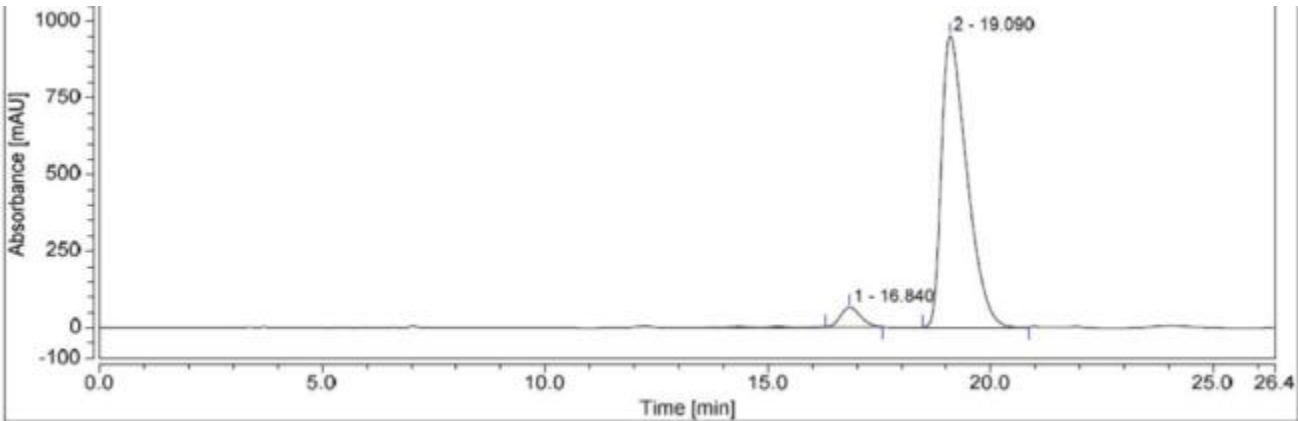
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.245	861.976	1243.837	50.75	57.20	n.a.
2		19.772	803.527	930.809	49.25	42.80	n.a.
Total:			1665.503	2174.646	100.00	100.00	



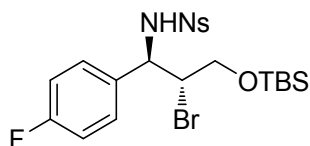
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.245	728.990	1181.208	95.48	95.79	n.a.
2		20.325	34.547	51.869	4.52	4.21	n.a.
<b>Total:</b>			<b>763.537</b>	<b>1233.077</b>	<b>100.00</b>	<b>100.00</b>	



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.
<b>Total:</b>			<b>103.230</b>	<b>200.257</b>	<b>100.00</b>	<b>100.00</b>	

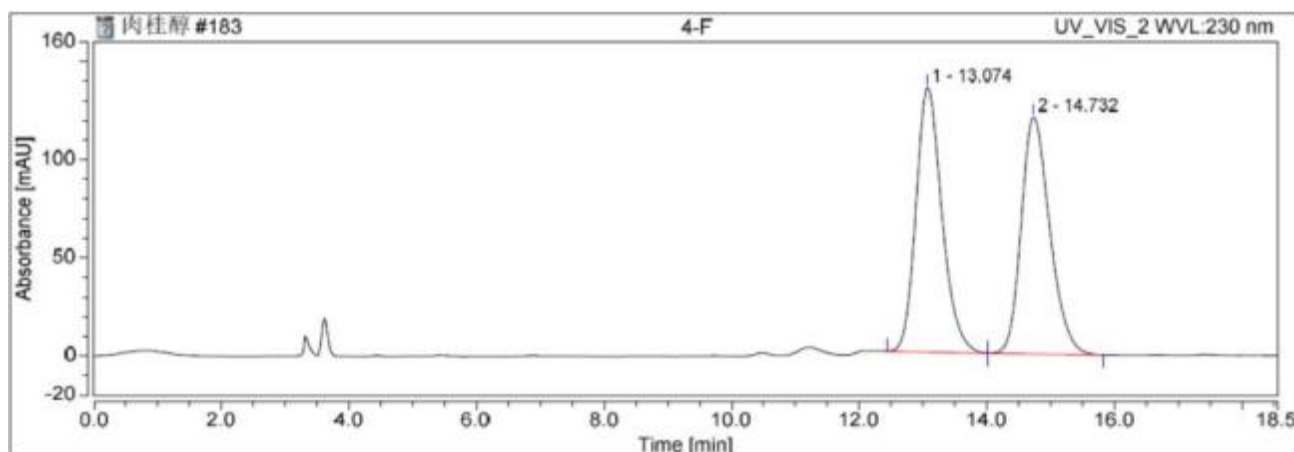


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.840	34.311	65.172	5.17	6.40	n.a.
2		19.090	629.310	952.434	94.83	93.60	n.a.
Total:			663.622	1017.606	100.00	100.00	

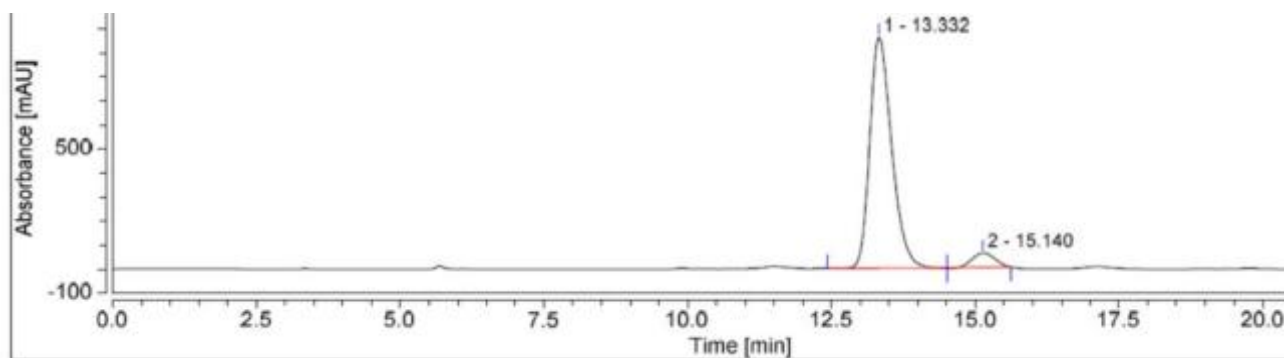


***N*-(2-Bromo-3-((*tert*-butyldimethylsilyl)oxy)-1-(4-fluorophenyl)propyl)-4-nitrobenzenesulfonamide (3b)**

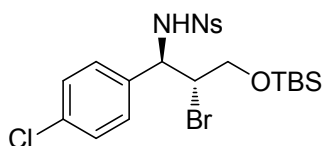
White solide,  $[\alpha]_{20}^D -21.8$  ( $c$  0.45,  $\text{CHCl}_3$ , 88% ee); IR (KBr): 3130, 1607, 1401, 1167, 1092, 838,  $\text{cm}^{-1}$ ;  $^1\text{H}$ NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.19 (d,  $J = 8.6$  Hz, 1H), 7.85 (d,  $J = 8.6$  Hz, 2H), 7.22-7.19 (m, 2H), 6.93-6.89 (m, 2H), 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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{21}\text{H}_{28}\text{BrFN}_2\text{O}_5\text{SSiNa}$   $m/z$   $[\text{M} + \text{Na}]^+$ : 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	



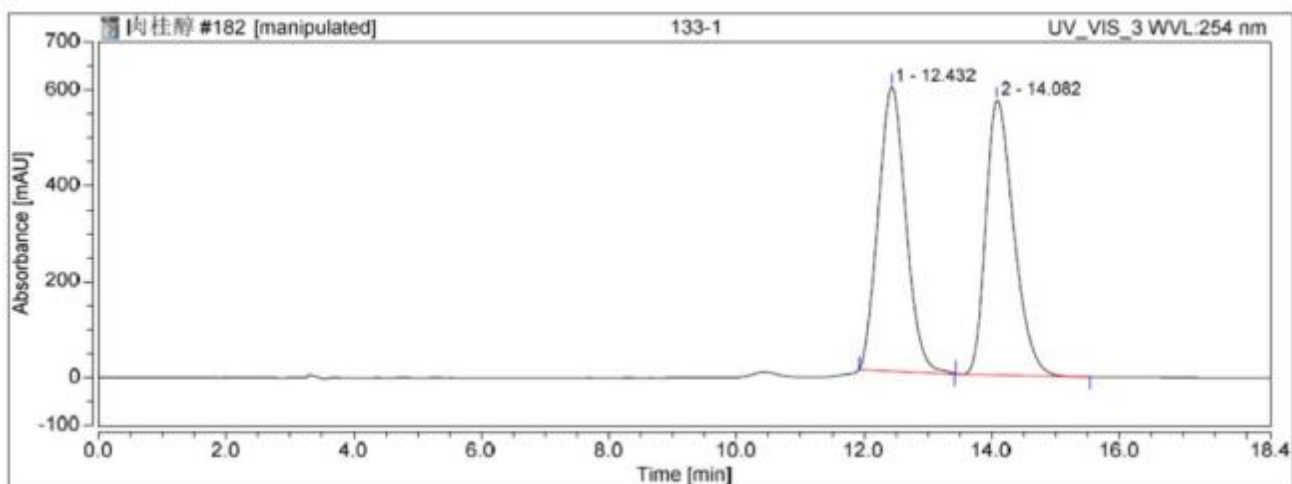
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.332	424.038	961.309	93.98	94.07	n.a.
2		15.140	27.172	60.562	6.02	5.93	n.a.
Total:			451.210	1021.871	100.00	100.00	



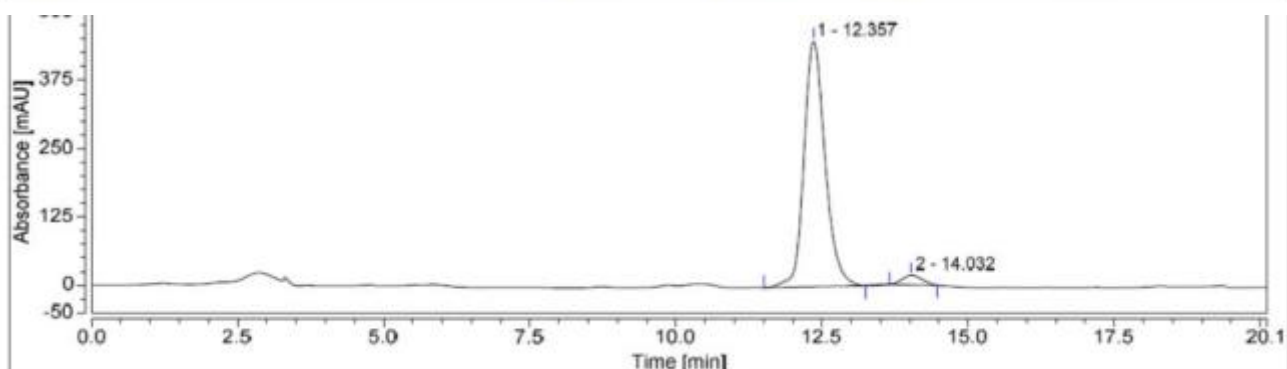
***N*-(2-Bromo-3-((*tert*-butyldimethylsilyl)oxy)propyl)-1-(4-chlorophenyl)propan-1-amine sulfonamide (**3c**)**

White solide,  $[\alpha]_{20}^D -35.0$  (*c* 2.5,  $\text{CHCl}_3$ , 93% ee), IR (KBr): 3296, 2927, 1607, 1532, 1349, 1311, 1014, 837  $\text{cm}^{-1}$ ;  $^1\text{H}$ NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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).  $^{13}\text{C}$ NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{21}\text{H}_{28}\text{BrClN}_2\text{O}_5\text{SSiNa}$   $m/z$   $[\text{M} + \text{Na}]^+$ : 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).

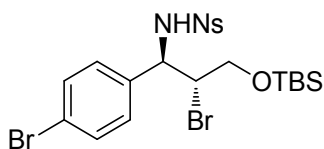




Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.432	297.214	593.730	50.46	50.83	n.a.
2		14.082	291.759	574.245	49.54	49.17	n.a.
Total:			588.973	1167.975	100.00	100.00	



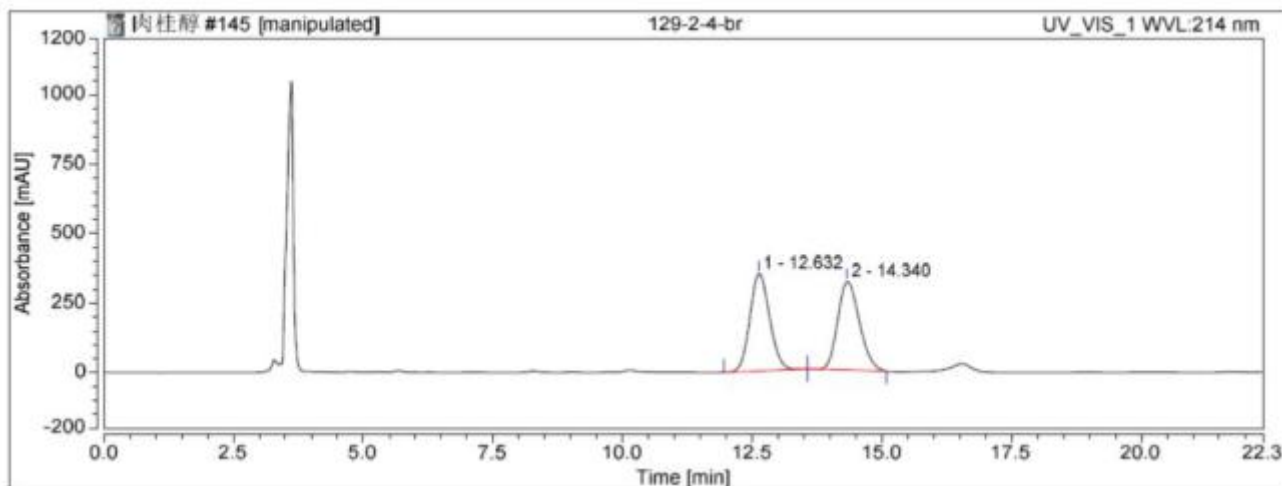
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.357	188.127	448.705	96.46	96.28	n.a.
2		14.032	6.902	17.320	3.54	3.72	n.a.
Total:			195.029	466.024	100.00	100.00	



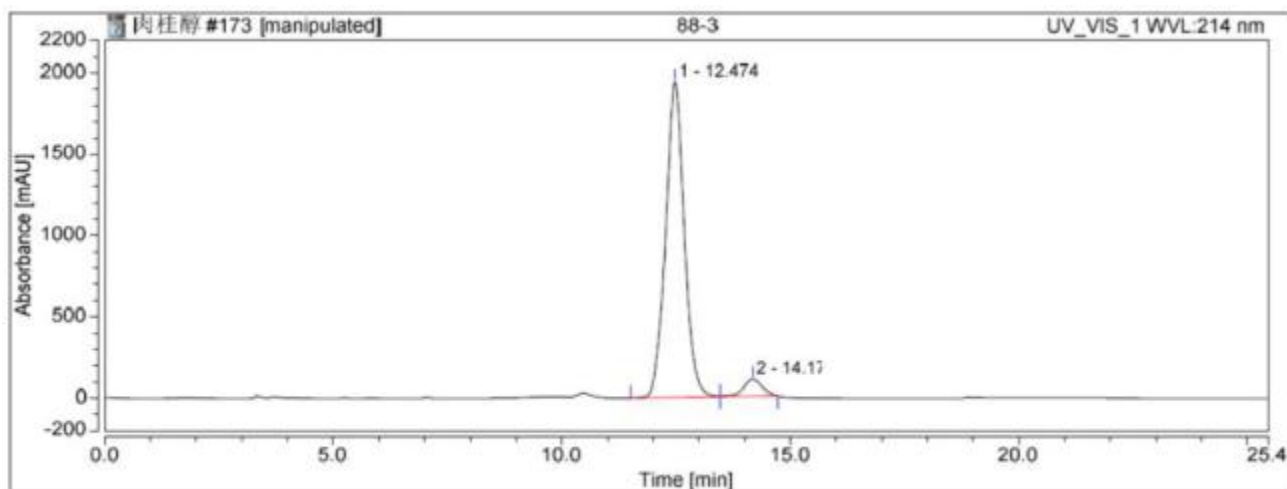
***N*-(2-Bromo-1-(4-bromophenyl)-3-((*tert*-butyldimethylsilyloxy)propyl)-4-nitrobenzenesulfonamide (3d)**

White solide ,  $[\alpha]_{20}^D -32.7$  (*c* 2.5, CHCl<sub>3</sub>, 90% ee); IR (KBr): 3440, 2925, 1736, 1624, 1532, 1463, 1166 cm<sup>-1</sup>; <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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),

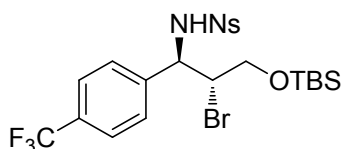
0.09 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.7, 146.0, 135.7, 131.6, 128.9, 128.3, 124.0, 122.5, 64.1, 60.9, 54.2, 25.7, 18.1, -5.5, -5.6; HRMS (ESI) calcd for  $\text{C}_{21}\text{H}_{28}\text{Br}_2\text{N}_2\text{O}_5\text{SSiNa}$   $m/z$   $[\text{M} + \text{Na}]^+$ : 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	

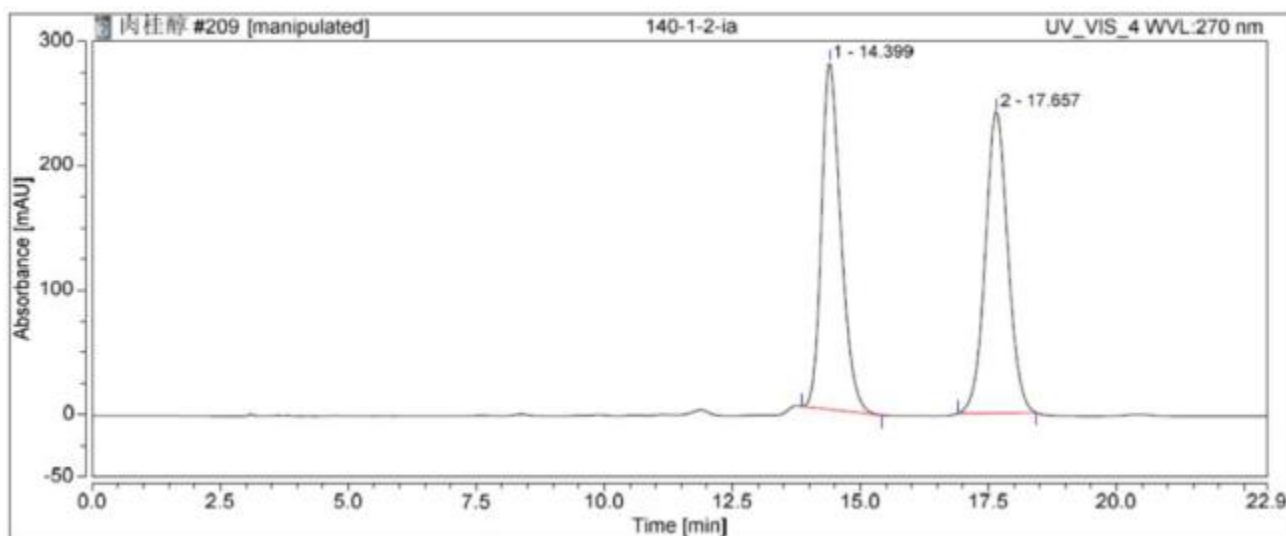


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.474	919.600	1942.626	94.77	94.82	n.a.
2		14.174	50.724	106.195	5.23	5.18	n.a.
Total:			970.324	2048.820	100.00	100.00	

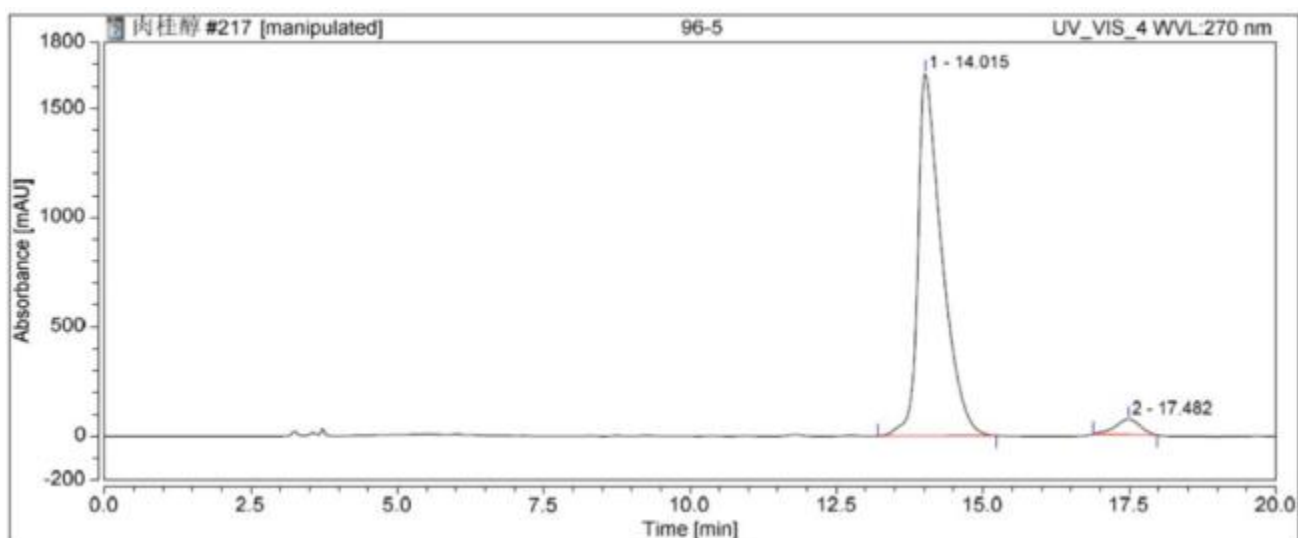


***N*-(2-Bromo-3-((*tert*-butyldimethylsilyl)oxy)-1-(4-(trifluoromethyl)phenyl)propyl)-4-nitrobenzenesulfonamide (3e)**

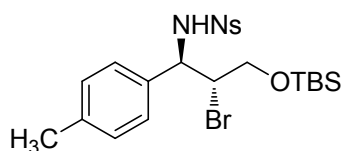
White solide,  $[\alpha]_{20}^D -30.3$  ( $c$  0.5,  $\text{CHCl}_3$ , 92% ee); IR (KBr): 3343, 2928, 1613, 1533, 1466, 1417, 1167, 1129  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.20 (d,  $J = 8.7$  Hz, 2H), 7.86 (d,  $J = 8.7$  Hz, 2H), 7.51 (d,  $J = 8.0$  Hz, 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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{22}\text{H}_{28}\text{BrF}_3\text{N}_2\text{O}_5\text{SSiNa}$   $m/z$   $[\text{M} + \text{Na}]^+$ : 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	

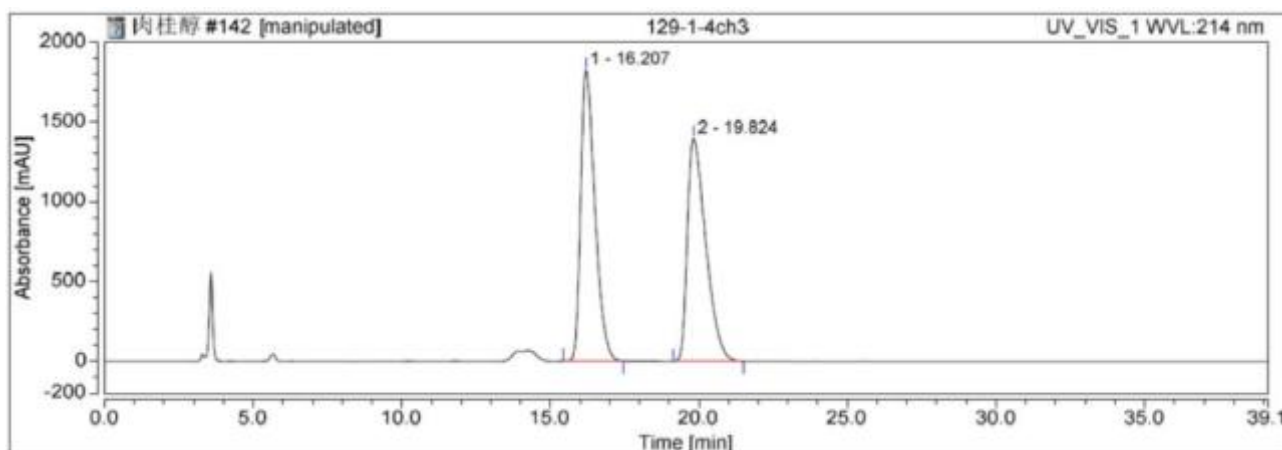


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.015	786.866	1657.364	95.77	95.88	n.a.
2		17.482	34.779	71.154	4.23	4.12	n.a.
Total:			821.645	1728.517	100.00	100.00	

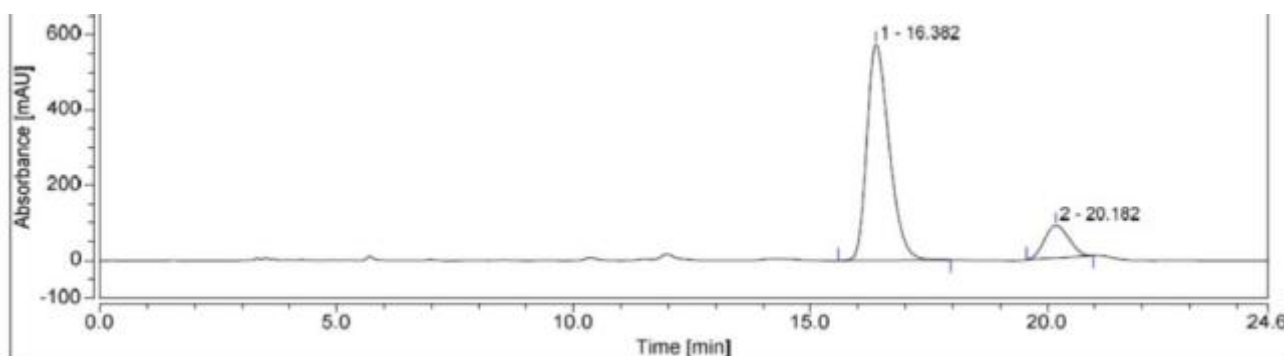


***N*-(2-Bromo-3-((*tert*-butyldimethylsilyl)oxy)-1-(*p*-tolyl)propyl)-4-nitrobenzenesulfonamide (3f)**

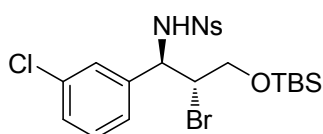
White solide,  $[\alpha]_{20}^D -15.0$  ( $c$  1.2,  $\text{CHCl}_3$ , 72% ee) IR (KBr): 3130, 1633, 1531, 1350, 1257, 1166, 1092.  $836\text{ cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 (d,  $J = 8.4$  Hz, 2H), 7.79 (d,  $J = 8.4$  Hz, 2H), 6.96-6.89 (m, 4H), 6.61 (d,  $J = 7.5$  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);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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) calcd for  $\text{C}_{22}\text{H}_{31}\text{BrN}_2\text{O}_5\text{SSiNa}$   $m/z$   $[\text{M} + \text{Na}]^+$ : 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
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	



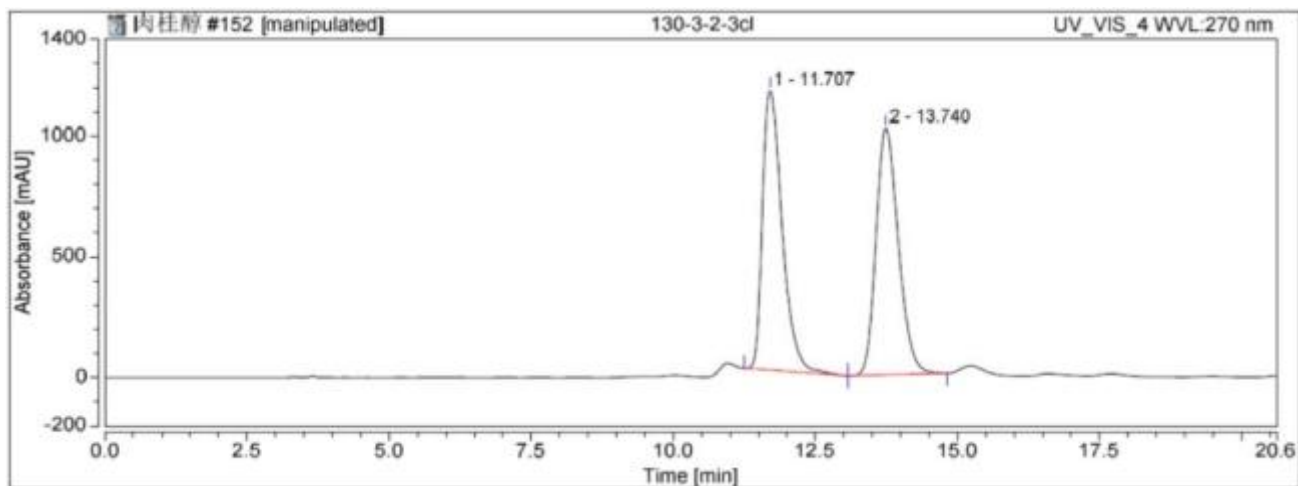
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		16.382	313.227	575.318	85.79	86.90	n.a.
2		20.182	51.872	86.694	14.21	13.10	n.a.
Total:			365.099	662.011	100.00	100.00	



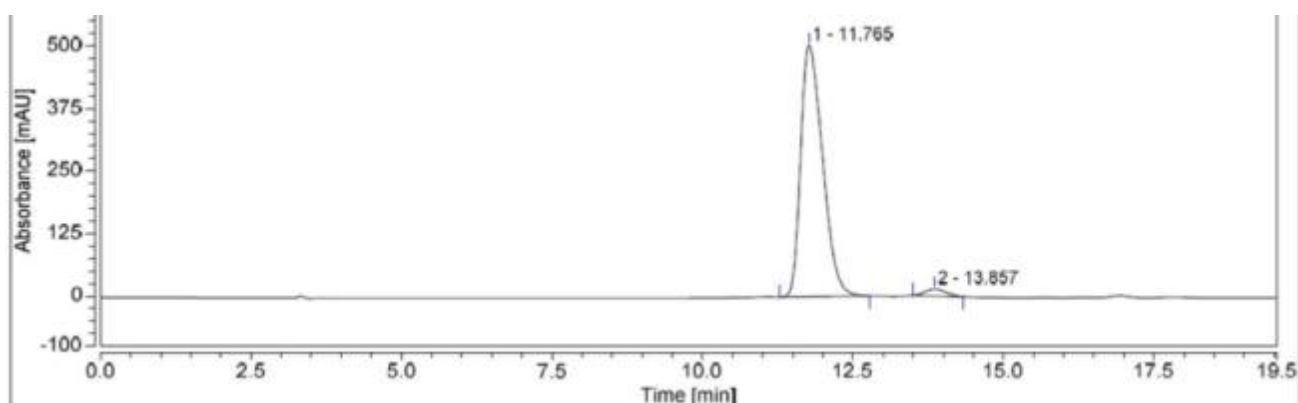
***N*-(2-Bromo-3-((*tert*-butyldimethylsilyloxy)propyl)-1-(3-chlorophenyl)propyl)-4-nitrobenzenesulfonamide (3g)**

Light yellow oil,  $[\alpha]_{20}^D -22.4$  ( $c$  2.6,  $\text{CHCl}_3$ , 95% ee); IR (KBr): 3295, 2929, 1730, 1532, 1350, 1168, 1091  $\text{cm}^{-1}$ ;  $^1\text{H}$ NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ )  $\delta$  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,

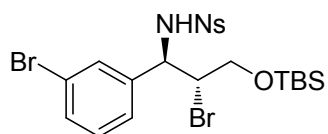
-5.7. HRMS (ESI) calcd for C<sub>21</sub>H<sub>28</sub>BrClN<sub>2</sub>O<sub>5</sub>SSiNa *m/z* [M + Na]<sup>+</sup>: 585.0252, found: 585.0261; HPLC (Daicel Chiralpak IC, *i*-PrOH/hexane = 8/92, 1.0 mL/min, 270 nm) *t*<sub>1</sub> = 11.8 min (major), *t*<sub>2</sub> = 13.9 min (minor).



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	

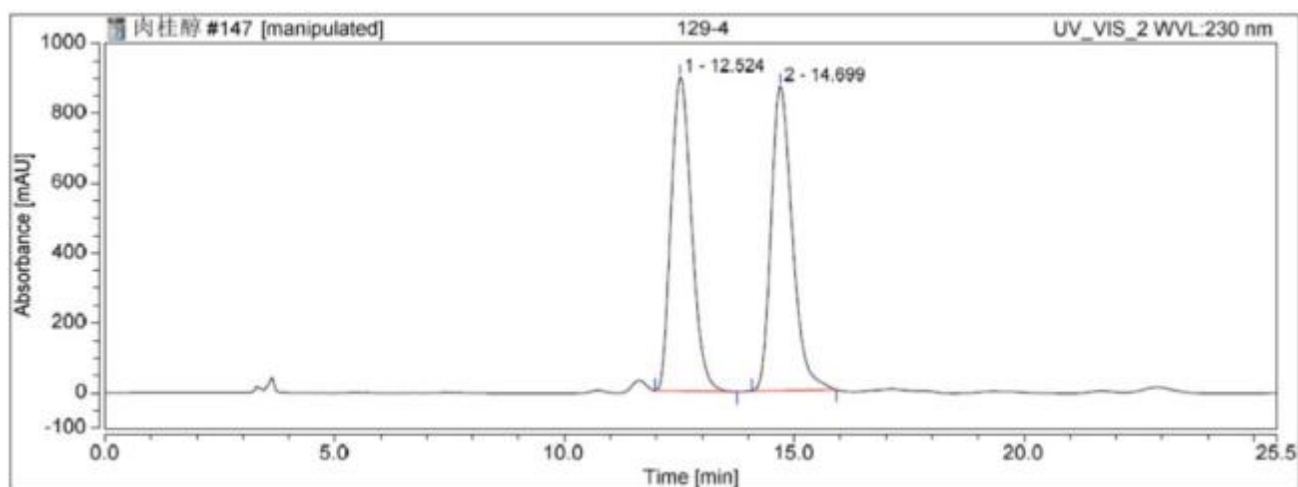


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.765	211.888	502.759	97.42	97.35	n.a.
2		13.857	5.617	13.661	2.58	2.65	n.a.
Total:			217.505	516.420	100.00	100.00	

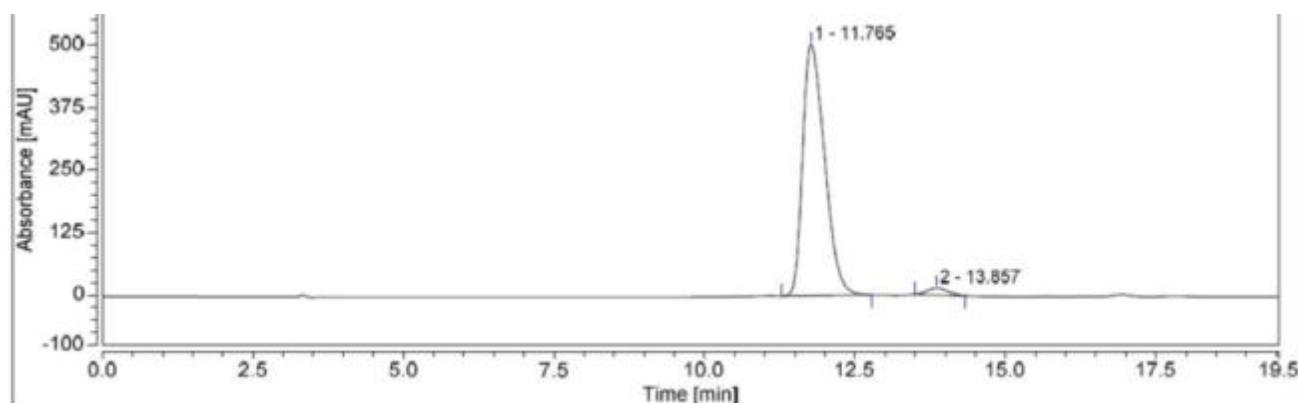


***N*-(2-Bromo-1-(3-bromophenyl)-3-((*tert*-butyldimethylsilyl)oxy)propyl)-4-nitrobenzenesulfonamide (3h)**

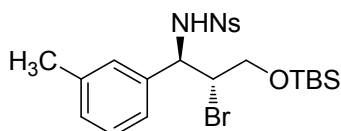
White solide,  $[\alpha]_{20}^D -28.5$  ( $c$  2.7,  $\text{CHCl}_3$ , 91% ee); IR (KBr): 3129, 1605, 1257, 1167, 838, 782, 739, 687  $\text{cm}^{-1}$ ;  $^1\text{H}$ NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.17 (d,  $J = 7.4$  Hz, 2H), 7.80 (d,  $J = 8.1$  Hz, 2H), 7.20 (m, 4H), 6.60 (d,  $J = 6.6$  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);  $^{13}\text{C}$ NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{21}\text{H}_{28}\text{Br}_2\text{N}_2\text{O}_5\text{SSiNa}$   $m/z$   $[\text{M} + \text{Na}]^+$ : 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	897.891	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	

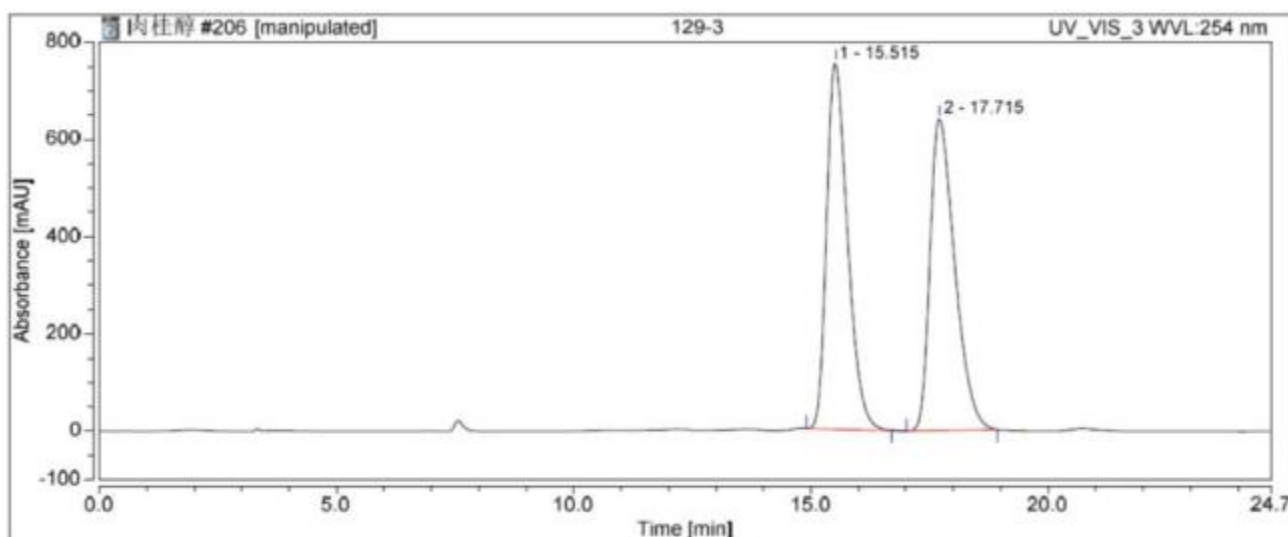


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.232	413.062	865.217	95.49	94.95	n.a.
2		14.232	19.496	46.032	4.51	5.05	n.a.
Total:			432.558	911.249	100.00	100.00	



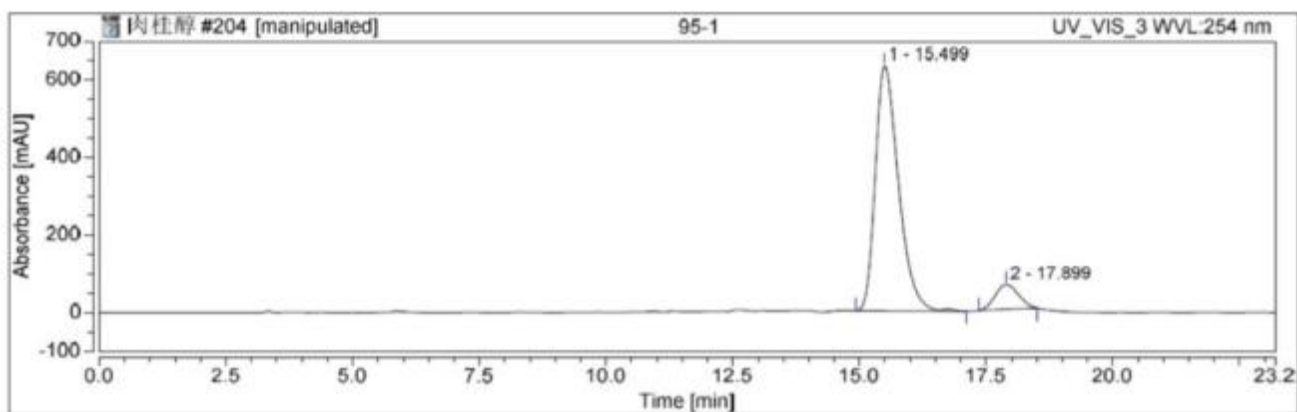
***N*-(2-Bromo-3-((*tert*-butyldimethylsilyloxy)-1-(*m*-tolyl)propyl)-4-nitrobenzenesulfonamide (3i)**

White solide,  $[\alpha]_{20}^D -21.6$  ( $c$  1.0,  $\text{CHCl}_3$ , 82% ee); IR (KBr): 3129, 1610, 1531, 1351, 1167, 1095, 839  $\text{cm}^{-1}$ ;  $^1\text{H}$ NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$ NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{22}\text{H}_{31}\text{BrN}_2\text{O}_5\text{SSiNa}$   $m/z$   $[\text{M} + \text{Na}]^+$ : 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).

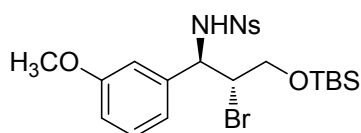


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.515	388.549	754.005	49.94	54.02	n.a.
2		17.715	387.440	641.704	50.06	45.98	n.a.
<b>Total:</b>			<b>773.990</b>	<b>1395.710</b>	<b>100.00</b>	<b>100.00</b>	



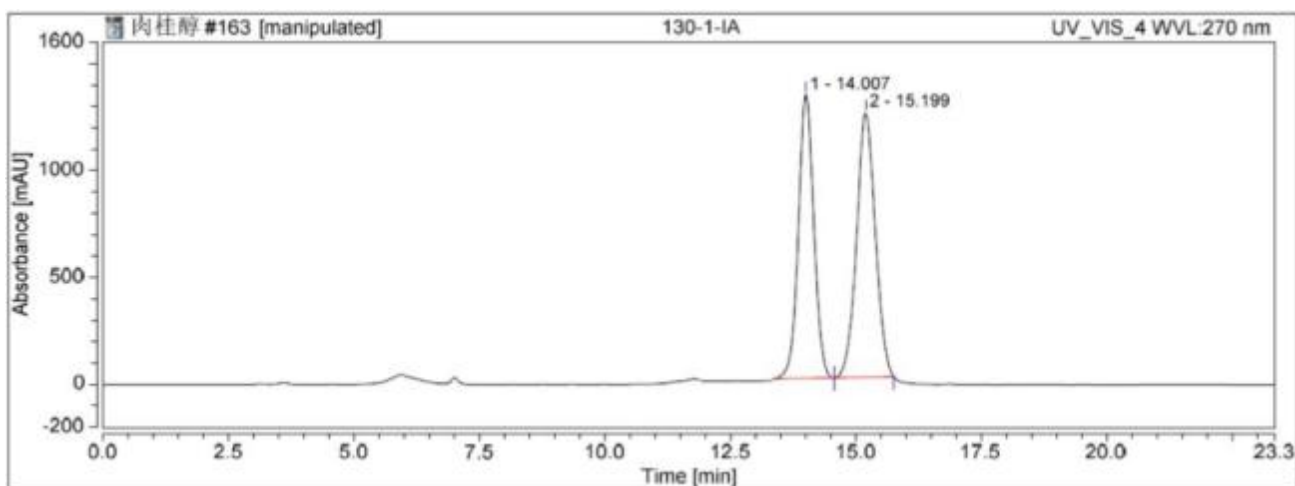


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.499	336.881	632.804	90.76	90.78	n.a.
2		17.899	34.295	64.297	9.24	9.22	n.a.
Total:			371.176	697.100	100.00	100.00	

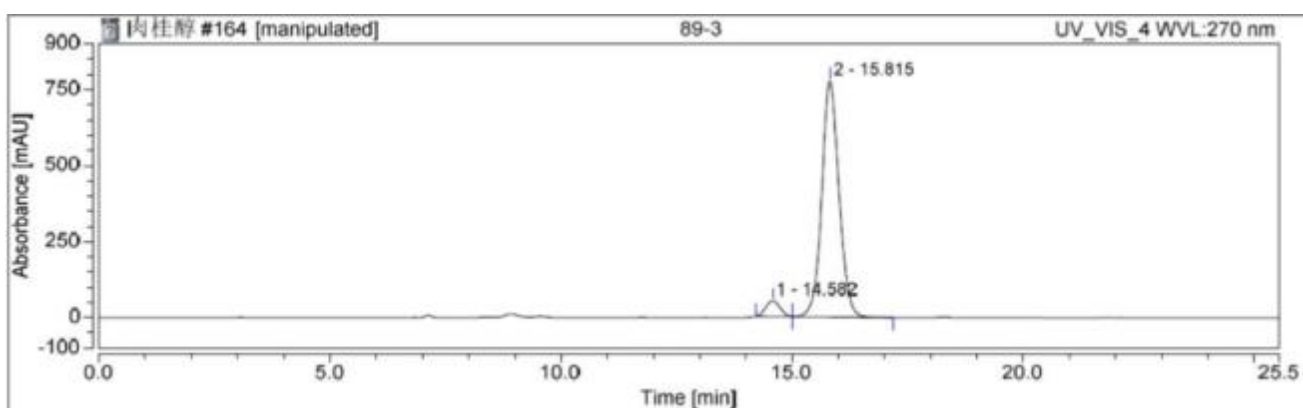


***N*-(2-Bromo-3-((*tert*-butyldimethylsilyl)oxy)-1-(3-methoxyphenyl)propyl)-4-nitrobenzenesulfonamide (3j)**

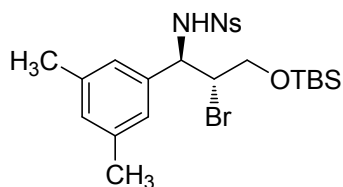
Colourless oil,  $[\alpha]_{20}^D -22.2$  ( $c$  2.4,  $\text{CHCl}_3$ , 90% ee); IR (KBr): 3453, 2928, 1604, 1349, 1258, 1165, 1092  $\text{cm}^{-1}$ ;  $^1\text{H}$ NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 (d,  $J = 8.1$  Hz, 2H), 7.80 (d,  $J = 8.2$  Hz, 2H), 7.10 (t,  $J = 8.0$  Hz, 1H), 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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{22}\text{H}_{31}\text{BrN}_2\text{O}_6\text{SSiNa}$   $m/z$   $[\text{M} + \text{Na}]^+$ : 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	



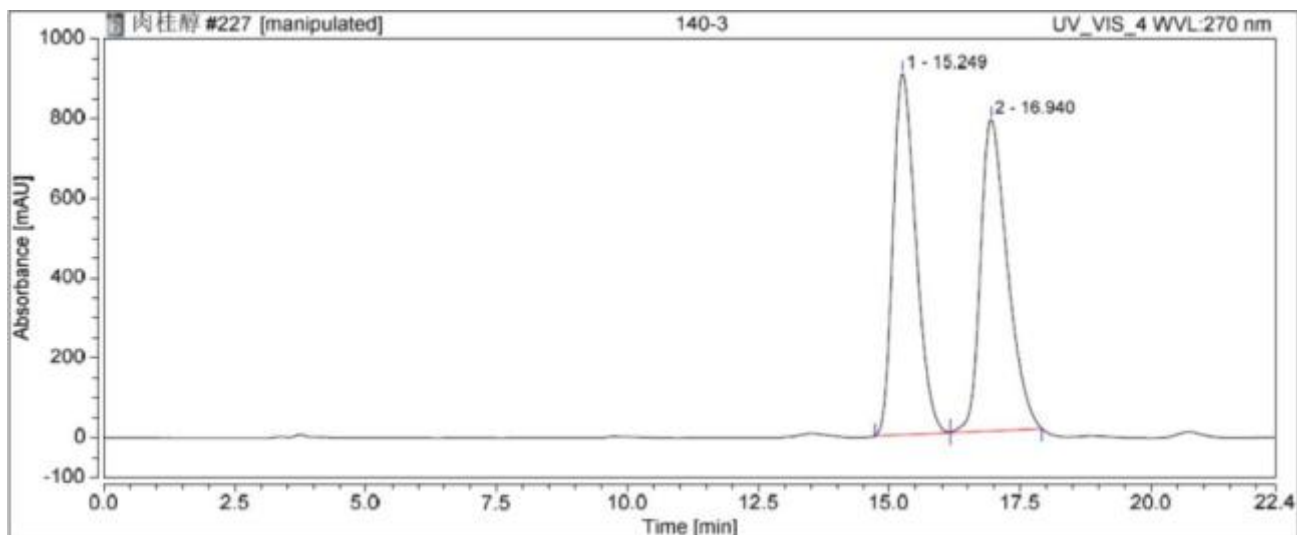
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.582	18.266	51.410	5.16	6.21	n.a.
2		15.815	335.427	776.946	94.84	93.79	n.a.
Total:			353.693	828.356	100.00	100.00	



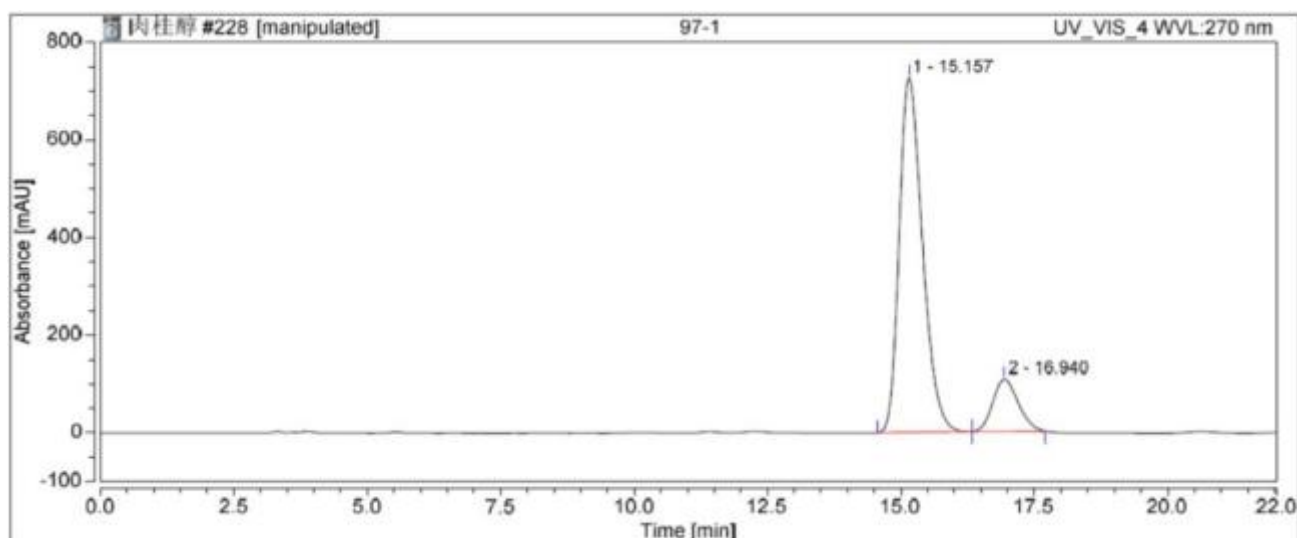
***N*-(2-Bromo-3-((*tert*-butyldimethylsilyl)oxy)-1-(3,5-dimethylphenyl)propyl)-4-nitrobenzenesulfonamide (3k)**

Yellow solid,  $[\alpha]_{20}^D -17.7$  ( $c$  0.7,  $\text{CHCl}_3$ , 72% ee) IR (KBr): 3361, 2972, 1068, 1532, 1348, 1165, 952  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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),

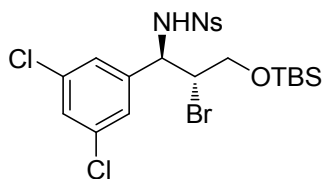
3.82 (m, 1H), 3.53 (dd,  $J = 11.2, 5.4$  Hz, 1H), 2.17 (s, 3H), 2.13 (s, 3H), 0.98 (s, 9H), 0.11 (s, 3H), 0.09 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.5, 146.4, 137.9, 136.1, 129.8, 128.2, 125.2, 123.5, 64.3, 61.4, 54.7, 25.7, 21.1, 18.1,  $-5.7$ ; HRMS (ESI) calcd for  $\text{C}_{23}\text{H}_{33}\text{BrN}_2\text{O}_5\text{SSiNa}$   $m/z$   $[\text{M} + \text{Na}]^+$ : 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	

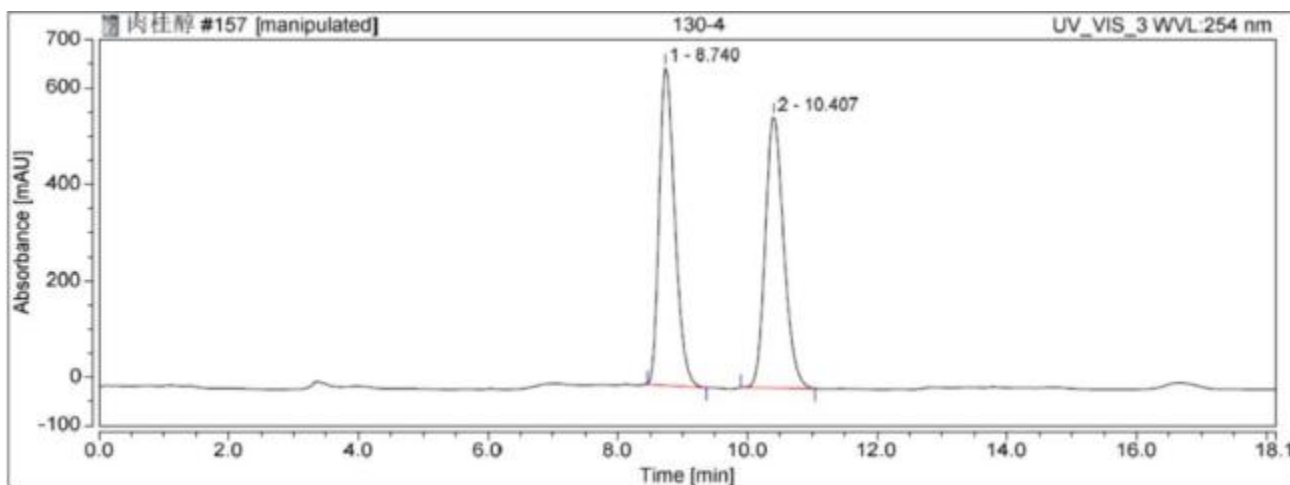


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.157	366.950	726.796	86.08	87.13	n.a.
2		16.940	59.342	107.360	13.92	12.87	n.a.
Total:			426.292	834.156	100.00	100.00	

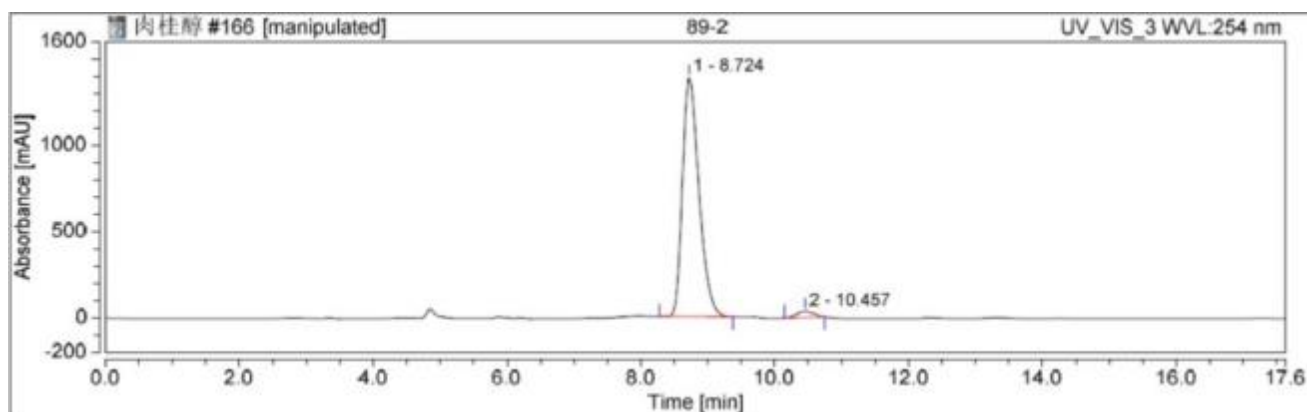


***N*-(2-Bromo-3-((*tert*-butyldimethylsilyl)oxy)-1-(3,5-dichlorophenyl)propyl)-4-nitrobenzenesulfonamide (3I)**

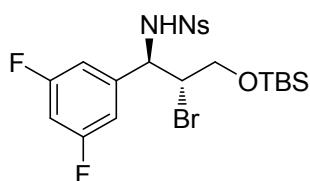
White solide,  $[\alpha]_{20}^D -9.2$  ( $c$  2.8,  $\text{CHCl}_3$ , 95% ee), IR (KBr): 3442, 2927, 1609, 1532, 1468, 1350, 1168, 1092  $\text{cm}^{-1}$ ;  $^1\text{H}$ NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.23 (d,  $J = 8.4$  Hz, 2H), 7.85 (d,  $J = 8.5$  Hz, 2H), 7.24 (s, 1H), 7.07 (s, 2H), 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);  $^{13}\text{C}$ NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{21}\text{H}_{27}\text{BrCl}_2\text{N}_2\text{O}_5\text{SSiNa}$   $m/z$   $[\text{M} + \text{Na}]^+$ : 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	

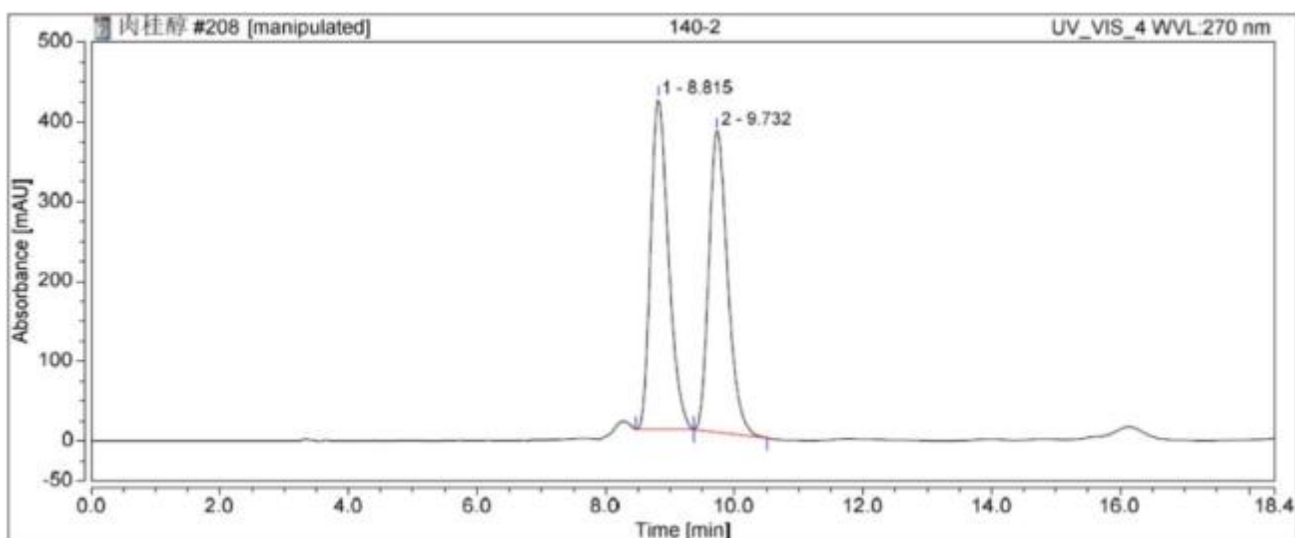


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.724	396.027	1387.302	97.39	97.46	n.a.
2		10.457	10.597	36.180	2.61	2.54	n.a.
Total:			406.624	1423.482	100.00	100.00	

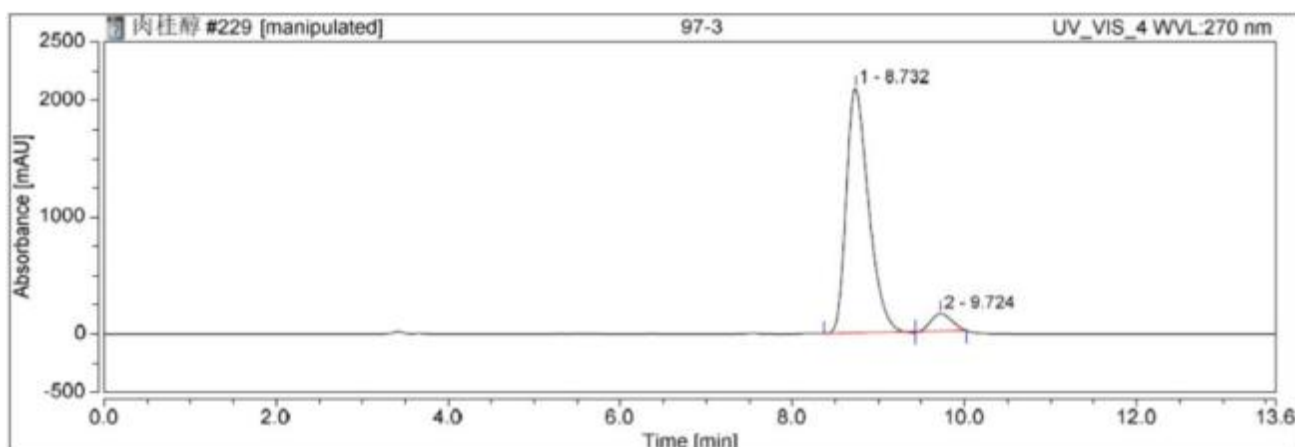


***N*-(2-Bromo-3-((*tert*-butyldimethylsilyloxy)-1-(3,5-difluorophenyl)propyl)-4-nitrobenzenesulfonamide (3m)**

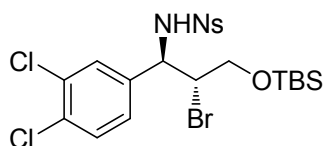
Light yellow oil,  $[\alpha]_{20}^D -18.0$  ( $c$  2.3,  $\text{CHCl}_3$ , 88% ee), IR (KBr): 3298, 2925, 1601, 1532, 1352, 1169, 994  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.25 (d,  $J = 8.5$  Hz, 2H), 7.90 (d,  $J = 8.6$  Hz, 2H), 6.69-6.80 (m, 4H), 4.92 (d,  $J = 3.7$  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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{21}\text{H}_{27}\text{BrF}_2\text{N}_2\text{O}_5\text{SSiNa}$   $m/z$   $[\text{M} + \text{Na}]^+$ : 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	



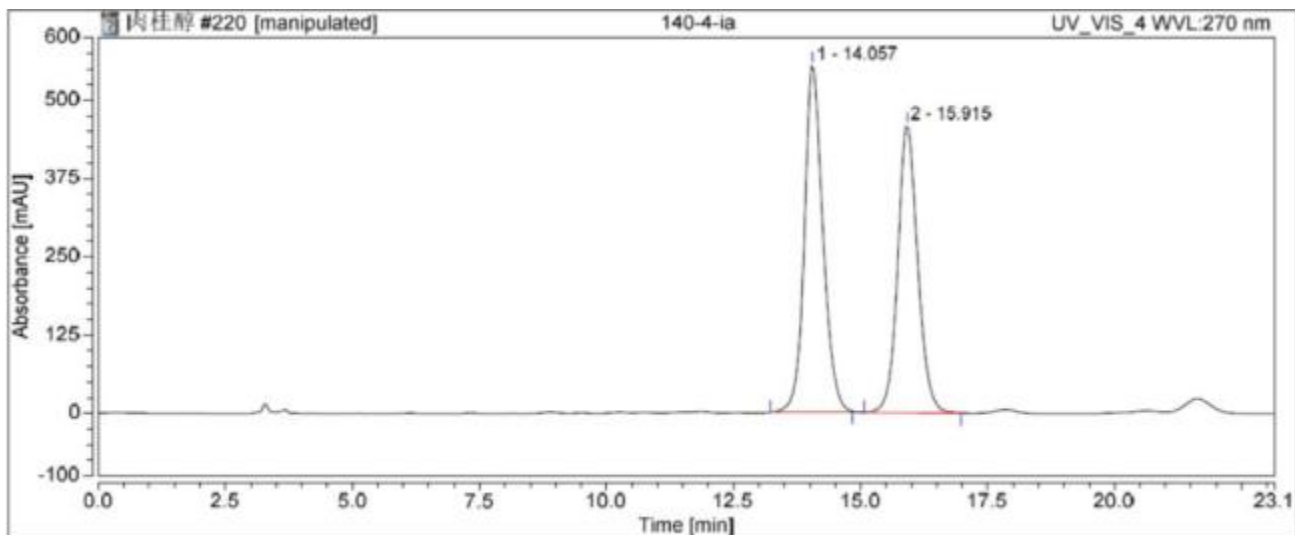
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.732	628.688	2095.380	93.76	93.34	n.a.
2		9.724	41.856	149.628	6.24	6.66	n.a.
Total:			670.544	2245.009	100.00	100.00	



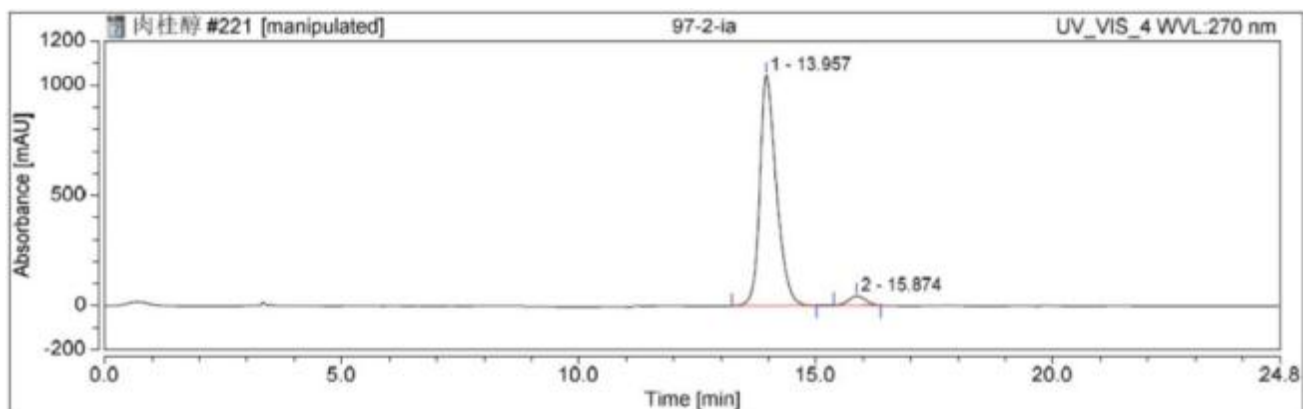
***N*-(2-Bromo-3-((*tert*-butyldimethylsilyloxy)propyl)-1-(3,4-dichlorophenyl)propyl)-4-nitrobenzenesulfonamide (3n)**

White solide,  $[\alpha]_{20}^D -35.0$  ( $c$  0.4,  $\text{CHCl}_3$ , 92% ee); IR (KBr): 3301, 2927, 1607, 1532, 1350, 1168, 1092, 837  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.23 (d,  $J = 8.5$  Hz, 2H), 7.85 (d,  $J = 8.5$  Hz, 2H),

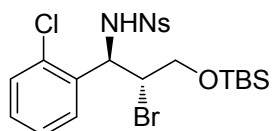
7.36-7.34 (m, 2H), 7.11 (d,  $J = 8.1$  Hz, 1H), 6.61 (d,  $J = 7.0$  Hz, 1H), 4.89 (dd,  $J = 4.4, 2.8$  Hz, 1H), 4.13 (d,  $J = 2.4$  Hz, 1H), 3.82-3.79 (m, 1H), 3.50 (dd,  $J = 11.2, 6.0$  Hz, 1H), 0.97 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{21}\text{H}_{27}\text{BrCl}_2\text{N}_2\text{O}_5\text{SSiNa}$   $m/z$   $[\text{M} + \text{Na}]^+$ : 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	

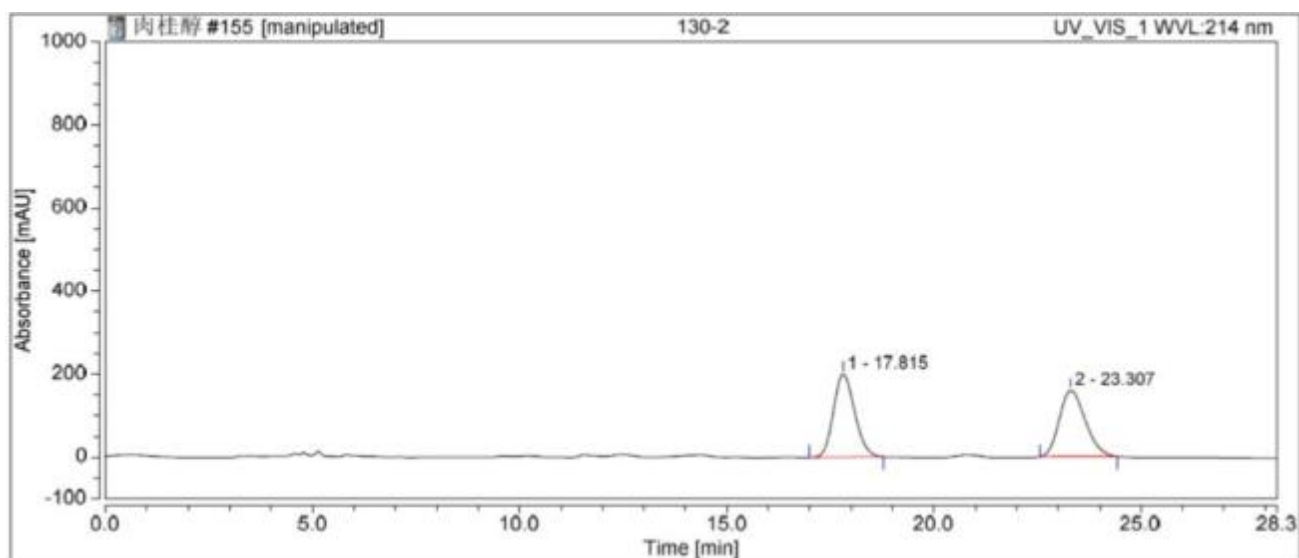


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.957	423.792	1045.179	95.90	96.03	n.a.
2		15.874	18.137	43.170	4.10	3.97	n.a.
Total:			441.929	1088.349	100.00	100.00	



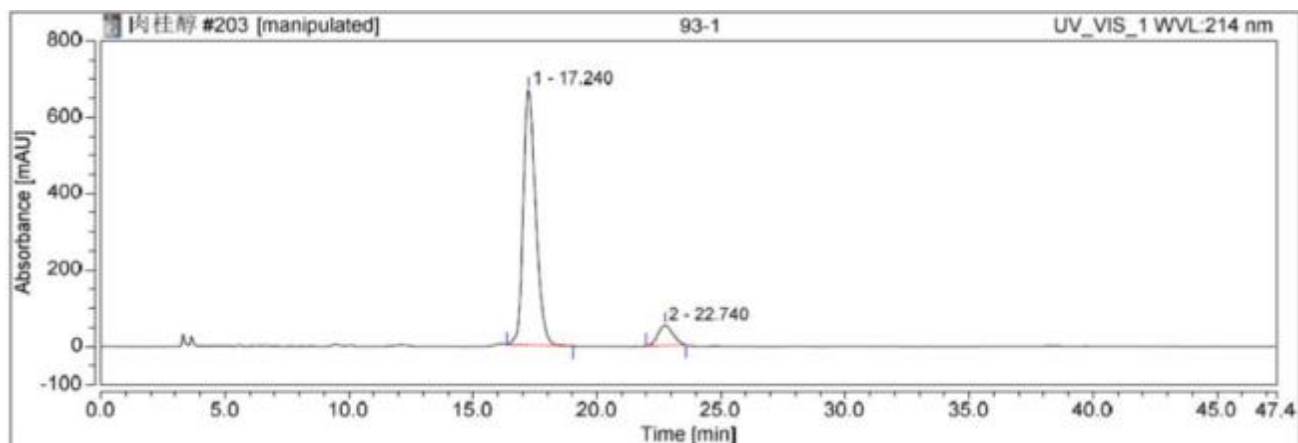
***N*-(2-Bromo-3-((*tert*-butyldimethylsilyl)oxy)-1-(2-chlorophenyl)propyl)-4-nitrobenzenesulfonamide (3o)**

White solide;  $[\alpha]_{20}^D -34.5$  ( $c$  0.6,  $\text{CHCl}_3$ , 83% ee); IR (KBr): 3320, 2927, 1607, 1532, 1351, 1168, 1098  $\text{cm}^{-1}$ ;  $^1\text{H}$ NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$ NMR (100MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{21}\text{H}_{28}\text{BrClN}_2\text{O}_5\text{SSiNa}$   $m/z$   $[\text{M} + \text{Na}]^+$ : 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).

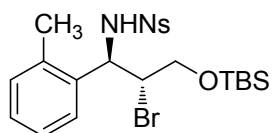


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.815	118.983	200.337	50.57	55.68	n.a.
2		23.307	116.278	159.496	49.43	44.32	n.a.
Total:			235.261	359.833	100.00	100.00	



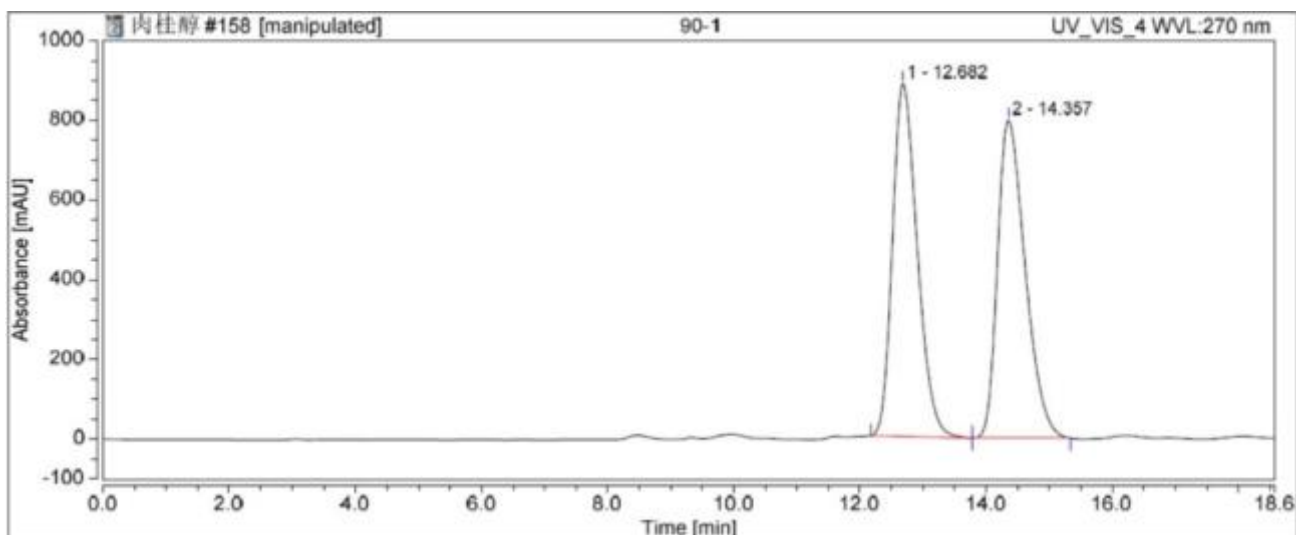


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.240	389.872	668.539	91.42	92.76	n.a.
2		22.740	36.600	52.199	8.58	7.24	n.a.
Total:			426.471	720.738	100.00	100.00	

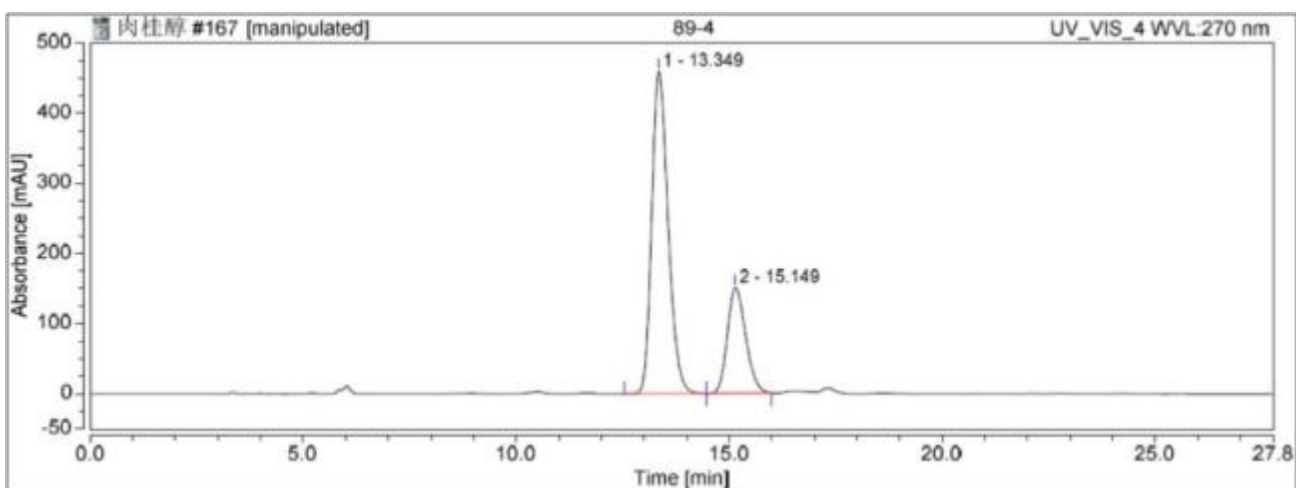


***N*-(2-Bromo-3-((*tert*-butyldimethylsilyl)oxy)-1-(*o*-tolyl)propyl)-4-nitrobenzenesulfonamide (3p)**

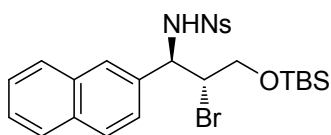
White solide,  $[\alpha]_{20}^D -15.9$  ( $c$  1.6,  $\text{CHCl}_3$ , 46% ee) IR (KBr): 3447, 2926, 1609, 1532, 1463, 1351, 1311  $\text{cm}^{-1}$ ;  $^1\text{H}$ NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 (d,  $J = 8.6$  Hz, 2H), 7.74 (d,  $J = 8.6$  Hz, 2H), 7.14 (m, 4H), 6.97 (d,  $J = 5.5$  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);  $^{13}\text{C}$ NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{22}\text{H}_{31}\text{BrN}_2\text{O}_5\text{SSiNa}$   $m/z$   $[\text{M} + \text{Na}]^+$ : 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	



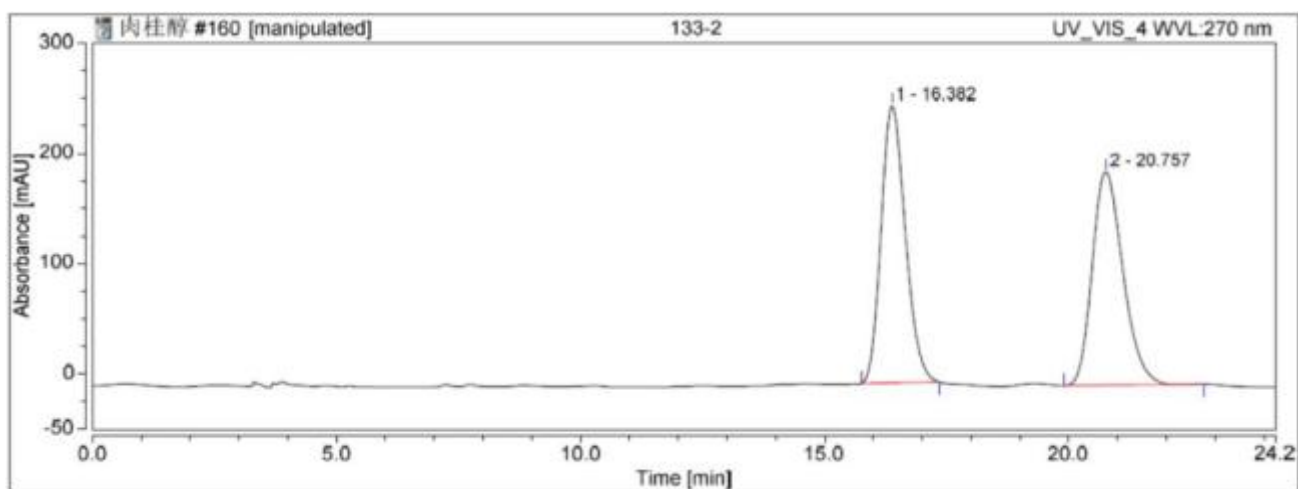
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.349	204.316	459.529	73.14	75.32	n.a.
2		15.149	75.016	150.608	26.86	24.68	n.a.
Total:			279.332	610.136	100.00	100.00	



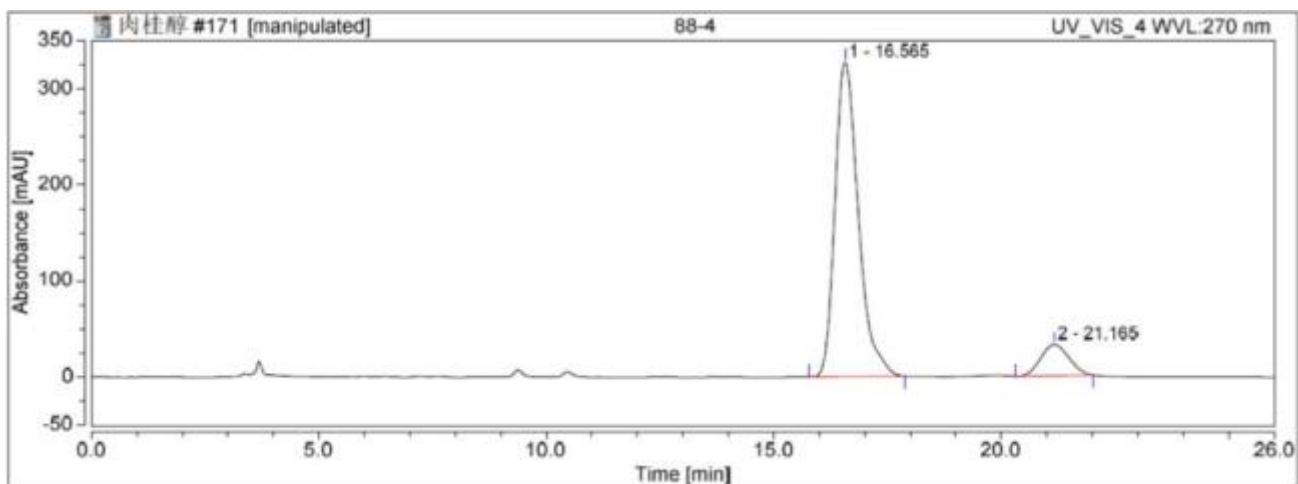
***N*-(2-Bromo-3-((*tert*-butyldimethylsilyloxy)propyl)-1-(naphthalen-2-yl)propyl)-4-nitrobenzenesulfonamide (3q)**

White solide,  $[\alpha]_{20}^D -36.0$  ( $c$  1.0,  $\text{CHCl}_3$ , 79% ee), IR (KBr): 3290, 2928, 1728, 1606, 1531, 1348, 1167, 1091  $\text{cm}^{-1}$ ;  $^1\text{H}$ NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J = 8.5$  Hz, 2H), 7.75 (d,  $J = 8.5$  Hz, 2H),

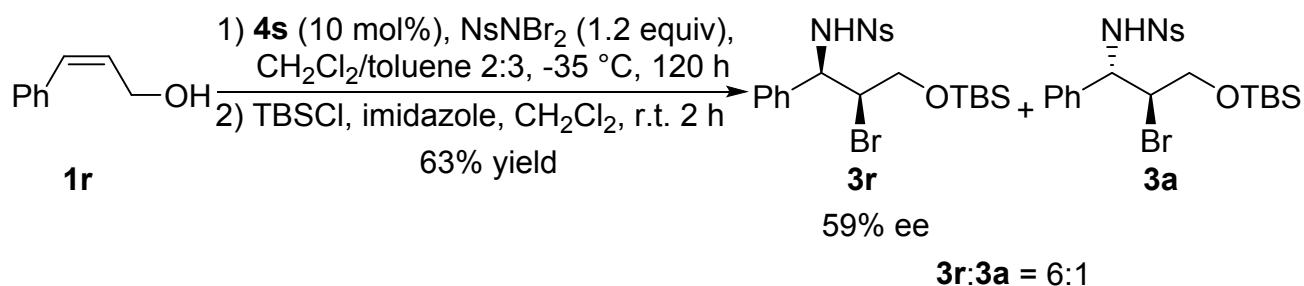
7.68-7.59 (m, 4H), 7.47-7.45 (m, 2H), 7.29 (d,  $J = 8.2$  Hz, 1H), 6.78 (d,  $J = 7.4$  Hz, 1H), 5.14-5.12 (m, 1H), 4.30 (s, 1H), 3.85 (dd,  $J = 11.2, 2.2$  Hz, 1H), 3.56 (dd,  $J = 11.2, 6.0$  Hz, 1H), 1.01 (s, 9H), 0.12 (s, 3H), 0.11 (s, 3H);  $^{13}\text{C}$ NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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) calcd for  $\text{C}_{25}\text{H}_{31}\text{BrN}_2\text{O}_5\text{SSiNa}$   $m/z$   $[\text{M} + \text{Na}]^+$ : 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
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
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	

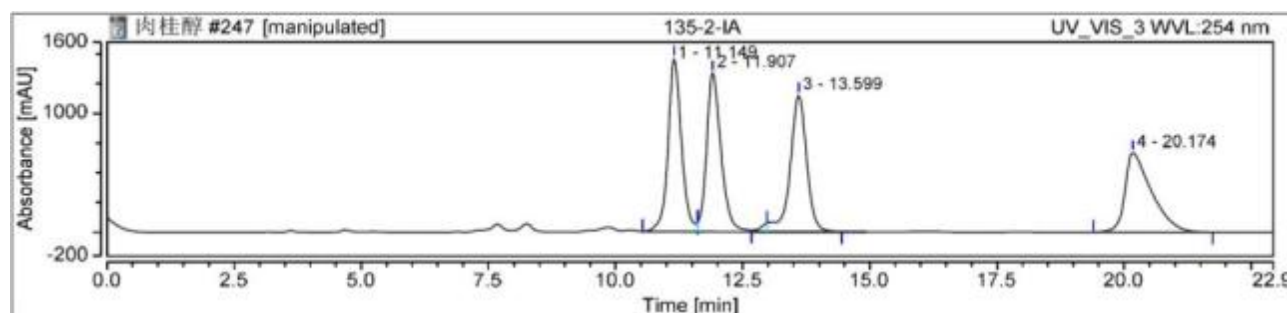
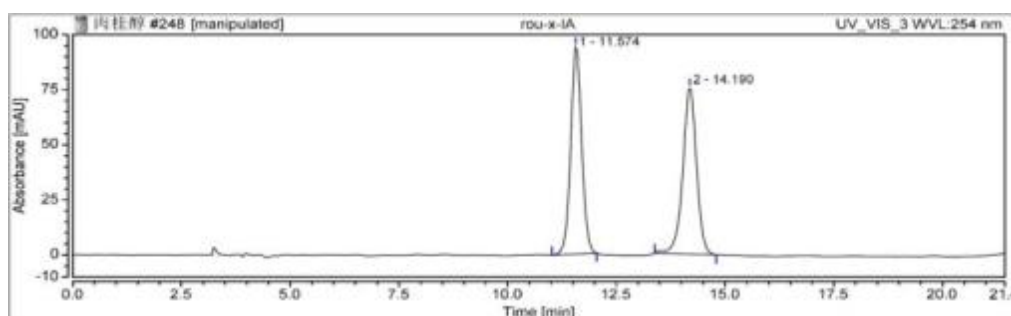


The absolute configuration of **3r** was not determined. Compounds **3r** and **3a** have similar polarity, which could not be separated by column chromatography.

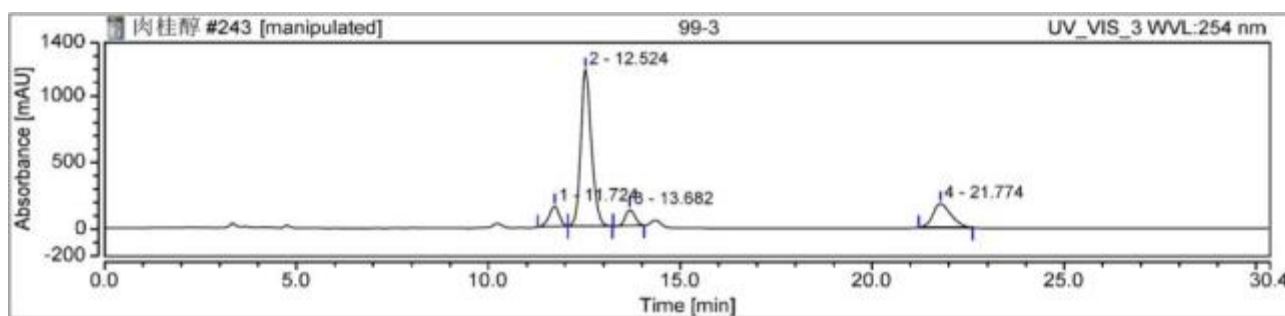
### *N*-(2-Bromo-3-((*tert*-butyldimethylsilyl)oxy)-1-phenylpropyl)-4-nitrobenzenesulfonamide (**3r**)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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*<sub>1</sub> = 12.5 min (major), *t*<sub>2</sub> = 21.8 min (minor).

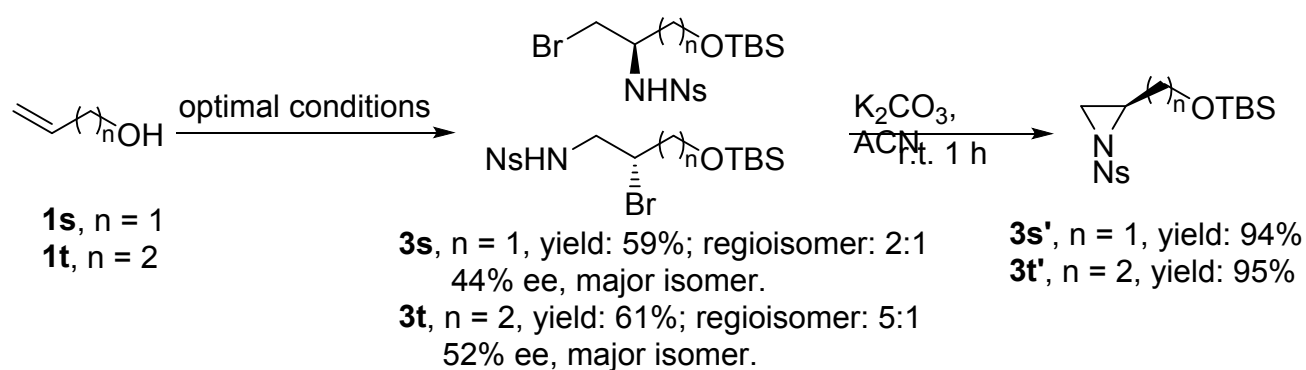
**3a** (IA):



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	

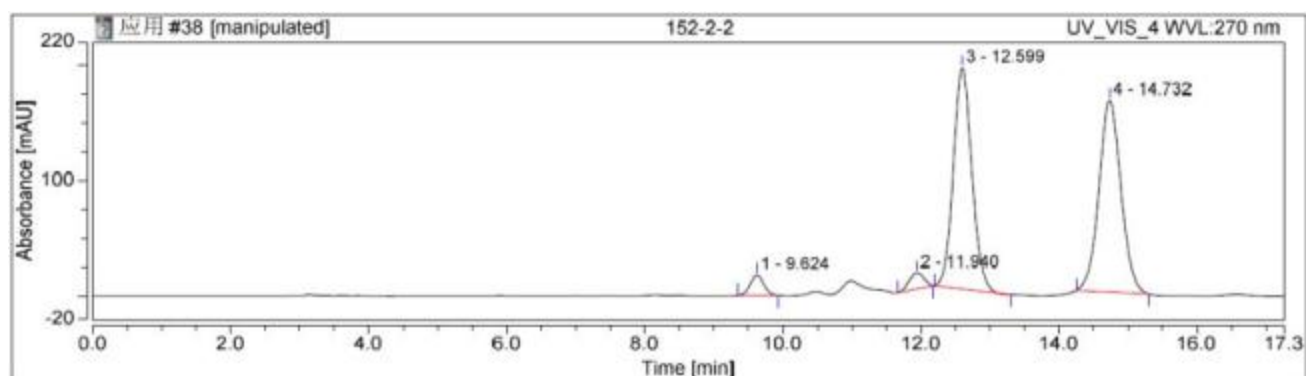


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		11.724	46.290	151.816	8.28	9.34	n.a.
2		12.524	378.763	1173.081	67.79	72.20	n.a.
3		13.682	35.046	120.384	6.27	7.41	n.a.
4		21.774	98.671	179.558	17.66	11.05	n.a.
Total:			558.771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

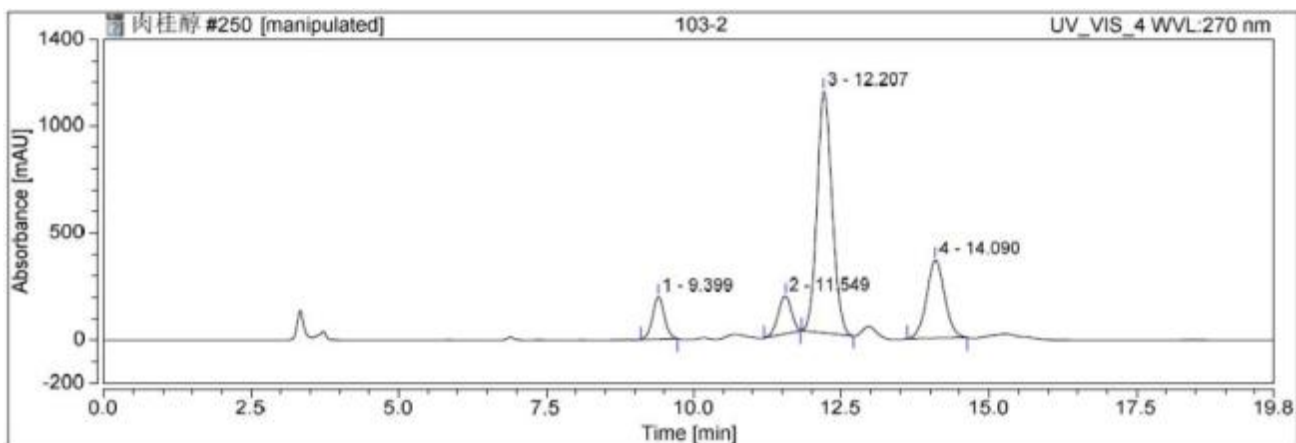


The absolute configuration of **3s**, **3t** were not determined, the ratio of the regioisomers of **3s** and **3t** is 2:1 and 5:1, respectively.<sup>6</sup> Which have similar polarity and are difficult to be separated by column chromatography. To gain pure NMR, further cyclization were performed smoothly.

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).

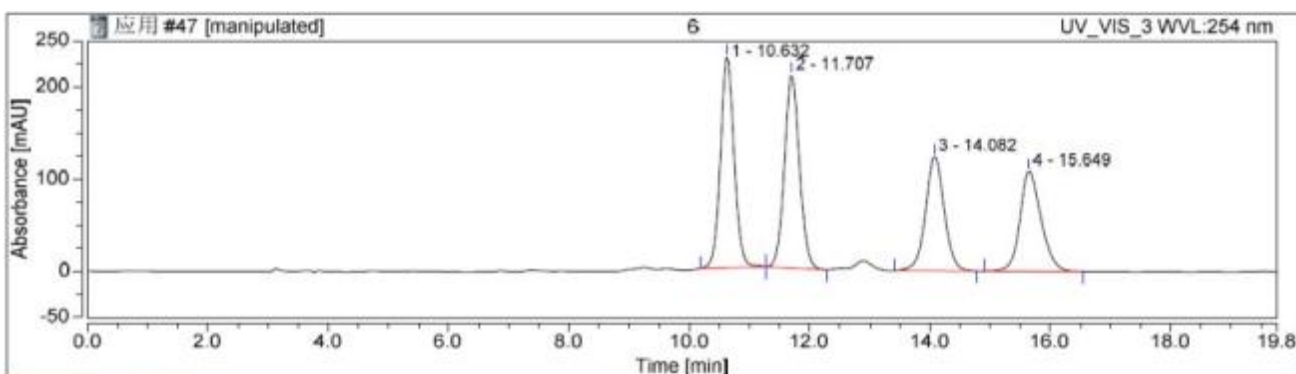


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.624	4.021	17.697	3.13	4.54	n.a.
2		11.940	3.524	14.128	2.74	3.62	n.a.
3		12.599	59.559	191.783	46.31	49.19	n.a.
4		14.732	61.515	166.245	47.83	42.64	n.a.
Total:			128.619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

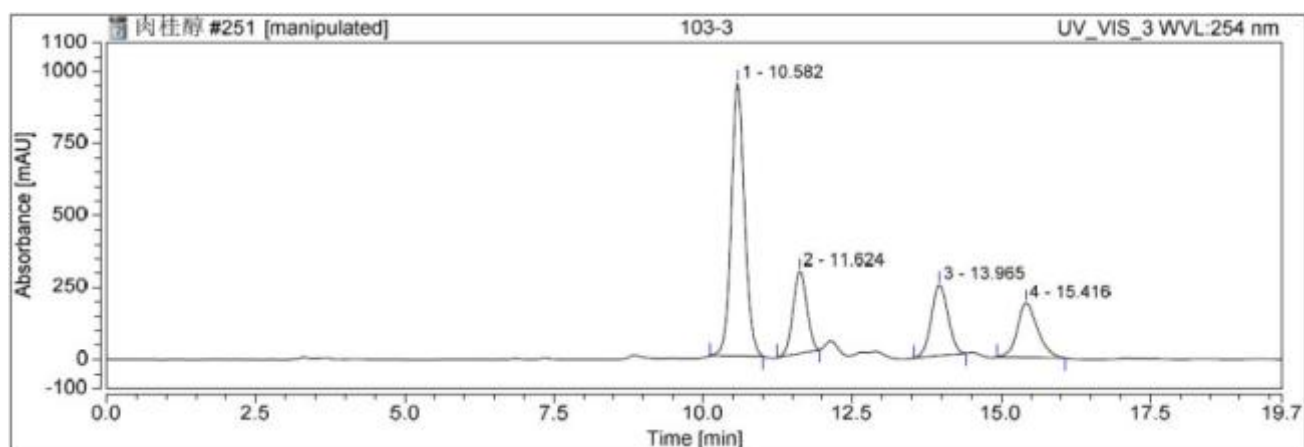


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.399	45.249	196.126	8.18	10.52	n.a.
2		11.549	45.849	176.651	8.29	9.47	n.a.
3		12.207	333.401	1127.873	60.25	60.48	n.a.
4		14.090	128.847	364.184	23.29	19.53	n.a.
Total: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

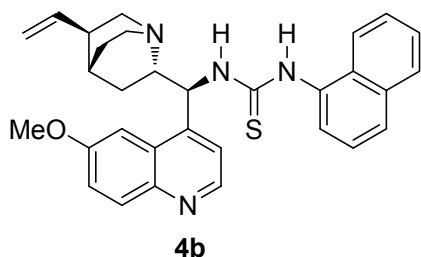
### 2-(((*tert*-Butyldimethylsilyl)oxy)methyl)-1-((4-nitrophenyl)sulfonyl)aziridine (**3s'**)

Light yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{15}\text{H}_{24}\text{N}_2\text{O}_5\text{SSiNa}$   $m/z$   $[\text{M} + \text{Na}]^+$ : 395.1067, found: 395.1064.

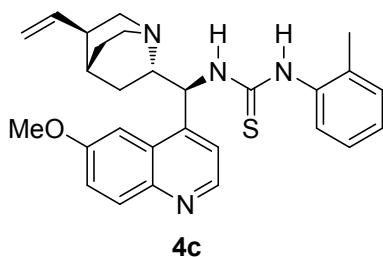
### 2-(2-(((*tert*-Butyldimethylsilyl)oxy)ethyl)-1-((4-nitrophenyl)sulfonyl)aziridine (**3t'**)

White solide;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{16}\text{H}_{26}\text{N}_2\text{O}_5\text{SSiNa}$   $m/z$   $[\text{M} + \text{Na}]^+$ : 409.1224, found: 409.1235.

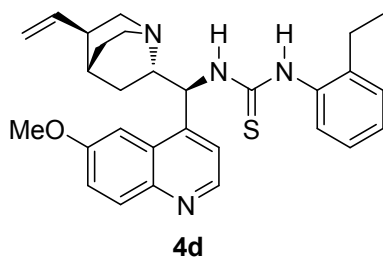
**Catalysts 4a,<sup>1</sup> 4l,<sup>1</sup> 4n,<sup>1</sup> 4o,<sup>2</sup> 4p,<sup>1</sup> 8a,<sup>3</sup> 8b,<sup>3</sup> 8c,<sup>4</sup> 8d,<sup>2</sup> S4a,<sup>5</sup> S4b,<sup>6</sup> are known compounds, all catalysts were synthesized according to the report procedure.<sup>1,2,6</sup>**



White solide,  $[\alpha]_{20}^D -65.3$  ( $c$  1.0,  $\text{CHCl}_3$ ); IR (KBr): 3441, 2926, 1623, 1510, 1261, 1165, 1030  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{31}\text{H}_{32}\text{N}_4\text{OS}$   $m/z$   $[\text{M} + \text{H}]^+$ : 473.2370, found: 473.2379.



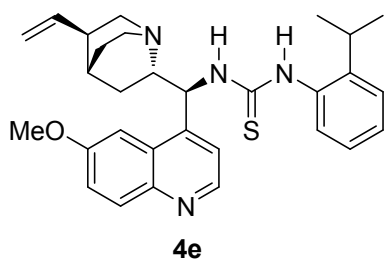
White solide,  $[\alpha]_{20}^D -99.2$  ( $c$ , 1.0  $\text{CHCl}_3$ ); IR (KBr): 3436, 2926, 1734, 1622, 1348, 1166, 1086, 1032  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.08 (s, 1H), 8.34 (s, 2H), 7.88 (d,  $J = 9.2$  Hz, 1H), 7.21 (m, 6H), 5.92 (s, 1H), 5.54-5.46 (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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{28}\text{H}_{33}\text{N}_4\text{OS}$   $m/z$   $[\text{M} + \text{H}]^+$ : 473.2370, found: 473.2381.



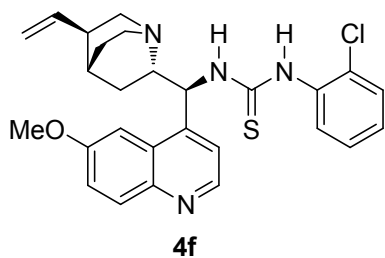
White solide,  $[\alpha]_{20}^D -111.9$  ( $c$ , 1.0  $\text{CHCl}_3$ ); IR (KBr): 3442, 2926, 1622, 1511, 1262, 1166, 1031  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.62-8.48 (m, 3H), 7.96 (d,  $J = 9.1$  Hz, 1H), 7.35-7.25 (m, 5H),



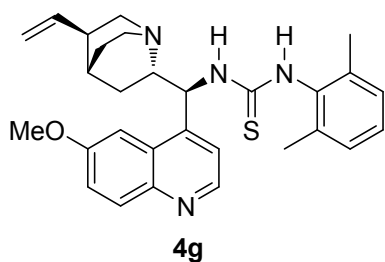
5.95 (s, 1H), 5.64-5.55 (m, 1H), 4.94-4.90 (m, 2H), 4.33(s, 1H), 3.94 (s, 3H), 3.34-3.06 (m, 3H), 2.64 (s, 2H), 2.43 (s, 2H), 2.27 (s, 1H), 1.66-1.62 (m, 3H), 1.31-1.23 (m, 2H), 1.04 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 181.3, 157.5, 147.2, 144.3, 140.9, 140.1, 134.0, 131.9, 131.2, 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<sub>29</sub>H<sub>35</sub>N<sub>4</sub>OS *m/z* [M + H]<sup>+</sup>: 487.2526, found: 487.2532.



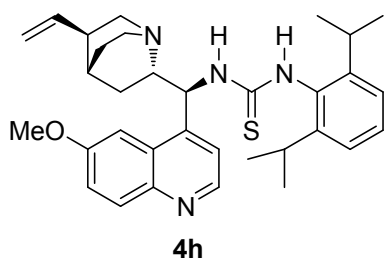
White solide, [α]<sub>20</sub> D -128.7 (*c*, 1.0 CHCl<sub>3</sub>); IR (KBr): 3422, 2926, 1735, 1622, 1512, 1262, 1084, 1031 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.51 (s, 1H), 8.16 (s, 1H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.9-7.16 (m, 6H), 5.73 (s, 1H), 5.53-5.50 (m, 1H), 4.85-4.80 (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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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<sub>30</sub>H<sub>36</sub>N<sub>4</sub>OSNa *m/z* [M + Na]<sup>+</sup>: 523.2513, found: 523.2502.



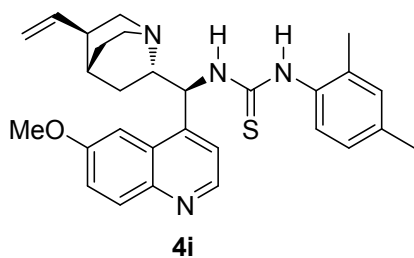
White solide, [α]<sub>20</sub> D -81.0 (*c*, 1.0 CHCl<sub>3</sub>); IR (KBr): 3447, 2925, 1624, 1511, 1470, 1262, 1031 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.99 (s, 1H), 8.53 (s, 1H), 7.98 (d, *J* = 9.1 Hz, 1H), 7.79 (s, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.40-7.16 (m, 5H), 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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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<sub>27</sub>H<sub>30</sub>ClN<sub>4</sub>OSNa *m/z* [M + H]<sup>+</sup>: 493.1823, found: 493.1821.



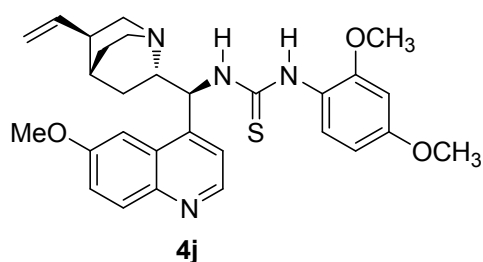
White solide,  $[\alpha]_{20}^D -86.9$  (*c*, 1.0 CHCl<sub>3</sub>); IR (KBr): 3440, 2924, 1737, 1623, 1510, 1466, 1381, 1228, 1166 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.66-8.53 (m, 2H), 7.91 (d, *J* = 8.9 Hz, 1H), 7.44-6.8 (m, 5H), 5.78-5.57 (m, 2H), 4.88-4.84 (m, 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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>29</sub>H<sub>35</sub>N<sub>4</sub>OS *m/z* [M + H]<sup>+</sup>: 487.2526, found: 487.2524.



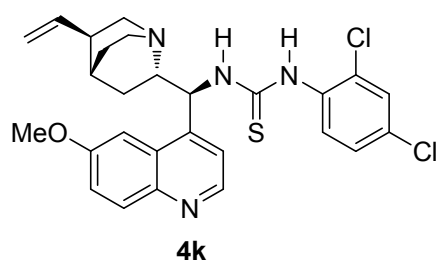
White solide,  $[\alpha]_{20}^D -58.1$  (*c*, 1.0 CHCl<sub>3</sub>); IR (KBr): 3439, 2961, 1622, 1511, 1263, 1083, 1032 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.76-8.66 (m, 1H), 7.98-7.93 (m, 2H), 7.38-7.22 (m, 5H), 7.03 (d, *J* = 7.5 Hz, 2H), 6.80 (d, *J* = 7.5 Hz, 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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>33</sub>H<sub>43</sub>N<sub>4</sub>OS *m/z* [M + H]<sup>+</sup>: 543.3152, found: 543.3154.



White solide,  $[\alpha]_{20}^D -100.4$  (*c*, 2.6 CHCl<sub>3</sub>); IR (KBr): 3258, 2925, 1736, 1621, 1510, 1228, 1084, 1031 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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), 0.88-0.78 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>29</sub>H<sub>35</sub>N<sub>4</sub>OS *m/z* [M + H]<sup>+</sup>: 487.2526, found: 487.2536.

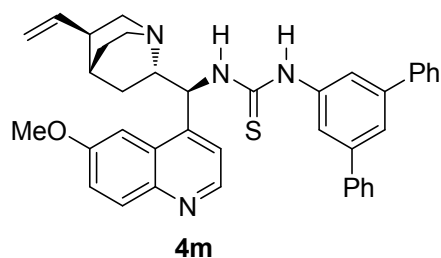


White solide,  $[\alpha]_{20}^D -104.2$  (*c*, 2.3 CHCl<sub>3</sub>); IR (KBr): 3278, 2936, 1619, 1510, 1209, 1166, 1033 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.57-8.39 (m, 2H), 7.97-7.93 (m, 2H), 7.38 (s, 3H), 6.43 (s, 2H), 6.2 (s, 1H), 5.63-5.32 (m, 2), 4.95 (s, 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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>29</sub>H<sub>35</sub>N<sub>4</sub>O<sub>3</sub>S *m/z* [M + H]<sup>+</sup>: 519.2424, found: 519.2538.

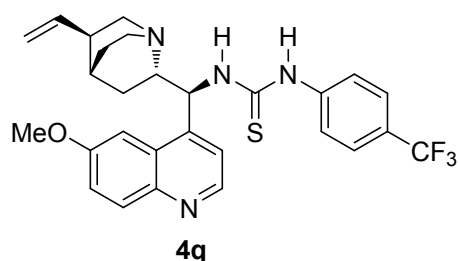


White solide,  $[\alpha]_{20}^D -83.4$  (*c*, 4.6 CHCl<sub>3</sub>); IR (KBr): 3238, 2927, 1733, 1621, 1528, 1228, 1167, 1098 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.57 (s, 1H), 7.98 (d, *J* = 9.1 Hz, 1H), 7.82 (s, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.44-7.34 (m, 3H), 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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  181.2, 157.7, 147.2, 144.34 (s), 139.5, 134.0, 131.8, 131.2, 130.0, 129.3, 128.5,

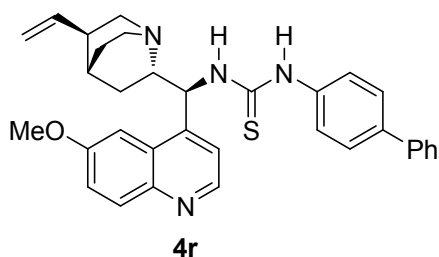
127.9, 127.1, 121.8, 115.2, 102.1, 60.2, 55.5, 54.5, 41.1, 38.3, 26.8, 26.6, 24.9, 24.0, 14.0; HRMS (ESI) calcd for  $C_{27}H_{29}Cl_2N_4OS$   $m/z$   $[M + H]^+$ : 527.1434, found: 527.1423.



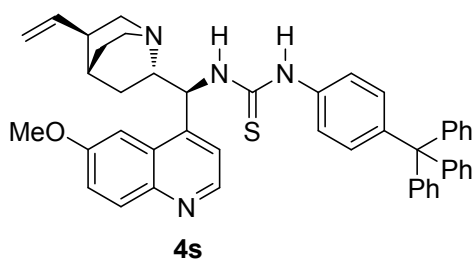
White solide,  $[\alpha]_{20}^D -173.7$  ( $c$ , 1.0  $CHCl_3$ ); IR (KBr): 3235, 2926, 1732, 1620, 1527, 1166, 1099  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  9.44 (s, 1H), 8.40 (s, 2H), 7.96 (d,  $J = 9.2$  Hz, 1H), 7.85-7.25 (m, 12H), 7.08 (s, 1H), 6.09 (s, 1H), 5.64-5.55 (m, 1H), 4.93-4.89 (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,  $CDCl_3$ )  $\delta$  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.



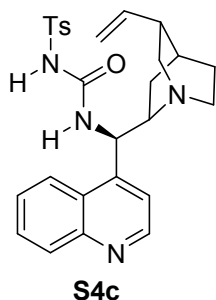
White solide,  $[\alpha]_{20}^D -122.4$  ( $c$ , 1.5  $CHCl_3$ ); IR (KBr): 3425, 2926, 1736, 1621, 1513, 1324, 1262, 1119, 1067  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.59 (s, 1H), 7.98 (d,  $J = 8.9$  Hz, 1H), 7.78 (s, 1H), 7.55-7.26 (m, 6H), 6.08 (s, 1H), 5.67-5.61 (m, 1H), 4.98-4.96 (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,  $CDCl_3$ )  $\delta$  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.



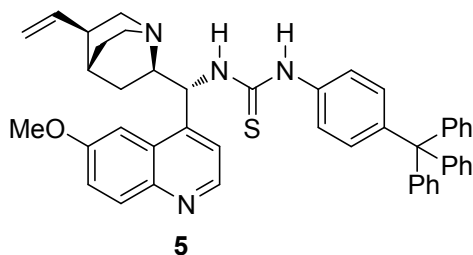
White solide,  $[\alpha]_{20}^D -158.1$  (*c*, 1.0 CHCl<sub>3</sub>); IR (KBr): 3441, 2924, 1736, 1621, 1512, 1379, 1229, 1164, 1083 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.69 (s, 1H), 8.79 (s, 1H), 8.40 (d, *J* = 90.0 Hz, 1H), 7.97 (s, 2H), 7.54-7.33 (m, 10H), 6.23 (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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>33</sub>H<sub>35</sub>N<sub>4</sub>OS *m/z* [M + H]<sup>+</sup>: 535.2526, found: 535.2531.



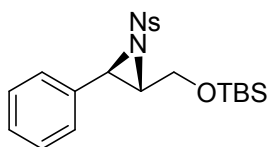
White solide,  $[\alpha]_{20}^D -141.2$  (*c*, 1.0 CHCl<sub>3</sub>); IR (KBr): 3266, 2926, 1734, 1620, 1510 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.23 (s, 1H), 8.45 (s, 1H), 7.94 (d, *J* = 9.1 Hz, 1H), 7.76 (s, 1H), 7.43-7.20 (m, 19H), 7.11 (d, *J* = 8.3 Hz, 2H), 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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>46</sub>H<sub>46</sub>N<sub>4</sub>OS *m/z* [M + H]<sup>+</sup>: 701.3309 found: 701.3322.



White solide,  $[\alpha]_{20}^D +89.3$  (*c*, 1.0 CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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<sub>27</sub>H<sub>31</sub>N<sub>4</sub>O<sub>3</sub>S *m/z* [M + H]<sup>+</sup>: 491.2111, found: 491.2104.

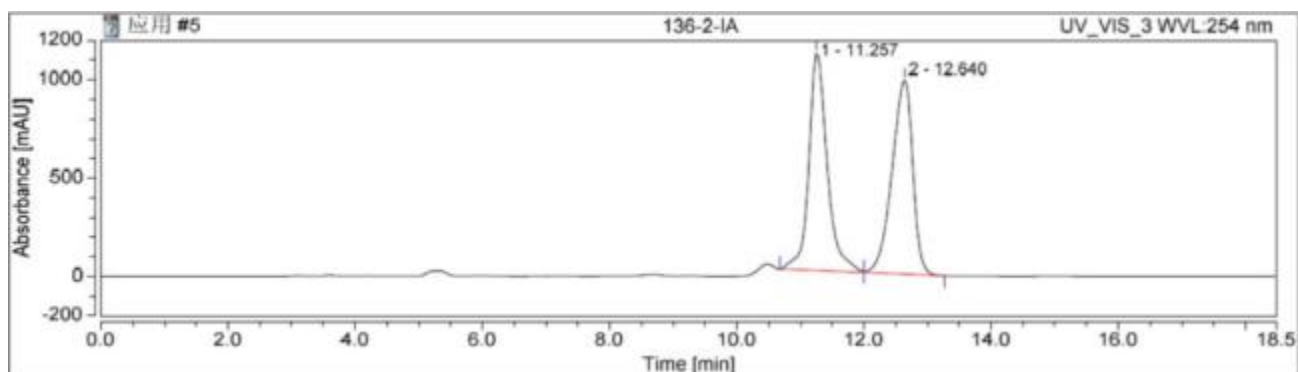


White solide,  $[\alpha]_{20}^D +188.8$  (*c*, 1.0 CHCl<sub>3</sub>); IR (KBr): 3271, 2926, 1735, 1621, 1508, 1320, 1227, 1082, 1031 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.61 (s, 1H), 7.98 (d, *J* = 9.0 Hz, 1H), 7.60 (s, 1H), 7.35-7.13 (m, 18H), 5.94-5.85 (m, 1H), 5.62 (s, 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). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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<sub>46</sub>H<sub>46</sub>N<sub>4</sub>OS *m/z* [M + H]<sup>+</sup>: 701.3309, found: 701.3327.

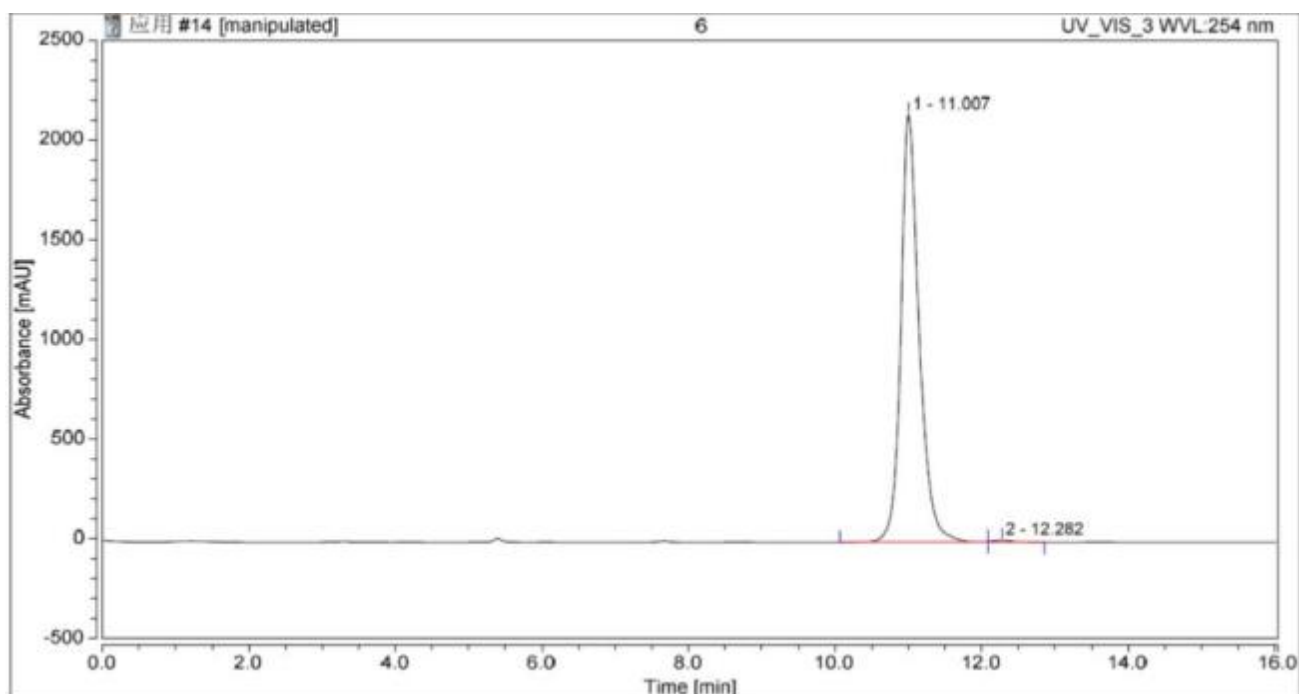


**(2*S*, 3*R*)-2-(((*tert*-Butyldimethylsilyloxy)methyl)-1-((4-nitrophenyl)sulfonyl)-3-phenylaziridine (9)**

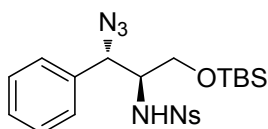
Colourless oil,  $[\alpha]_{20}^D -11.3$  (*c* 1.7, CHCl<sub>3</sub>, 99% ee) IR (KBr): 2926, 1737, 1622, 1532, 1463, 1379, 1165 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.30 (d, *J* = 8.6 Hz, 2H), 8.12 (d, *J* = 8.6 Hz, 2H), 7.19-7.29 (m, 5H), 4.31 (dd, *J* = 11.3, 5.4 Hz, 1H), 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 Hz, 1H), 0.90 (s, 9H), 0.10 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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<sub>21</sub>H<sub>28</sub>N<sub>2</sub>O<sub>5</sub>SSiNa *m/z* [M + Na]<sup>+</sup>: 471.1380, found: 471.1385; HPLC (Daicel Chiralpak IA, *i*-PrOH/hexane = 8/92, 1.0 mL/min, 254 nm) *t*<sub>1</sub> = 11.0 min (major), *t*<sub>2</sub> = 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	

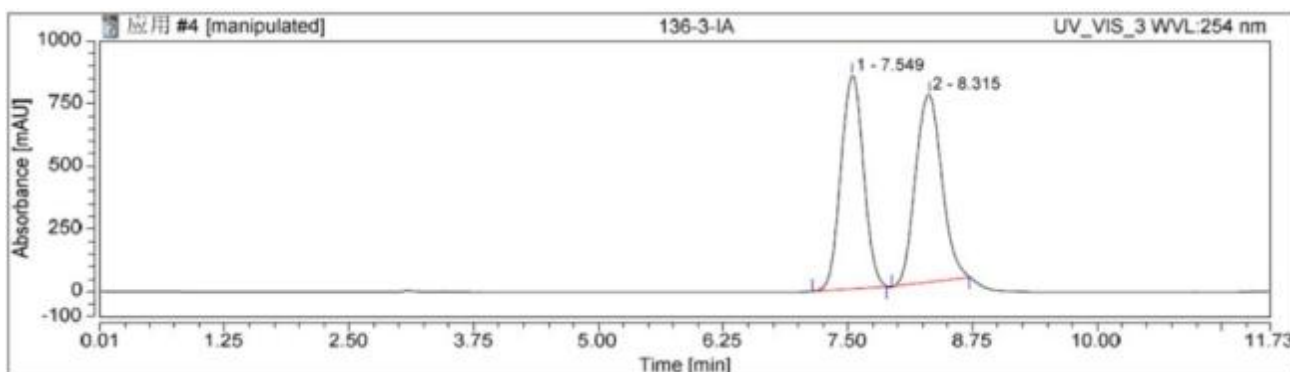


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.007	623.841	2145.463	99.44	99.47	n.a.
2		12.282	3.492	11.470	0.56	0.53	n.a.
Total:			627.333	2156.933	100.00	100.00	



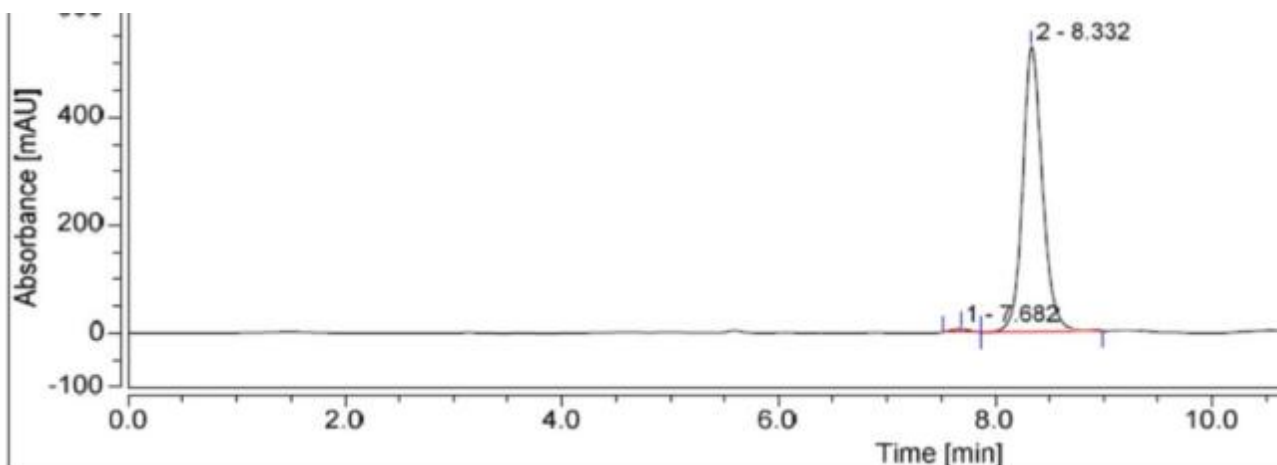
***(1S,2S)*-N-1-Azido-3-((*tert*-butyldimethylsilyl)oxy)-1-phenylpropan-2-yl)-4-nitrobenzenesulfonamide (10)**

White solide,  $[\alpha]_{20}^D +52.8$  ( $c$  1.5,  $\text{CHCl}_3$ , 98% ee) IR (KBr): 3443, 2927, 2105, 1531, 1463, 1348, 1255, 1165  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{21}\text{H}_{29}\text{N}_5\text{O}_5\text{SSiNa}$   $m/z$   $[\text{M} + \text{Na}]^+$ : 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	



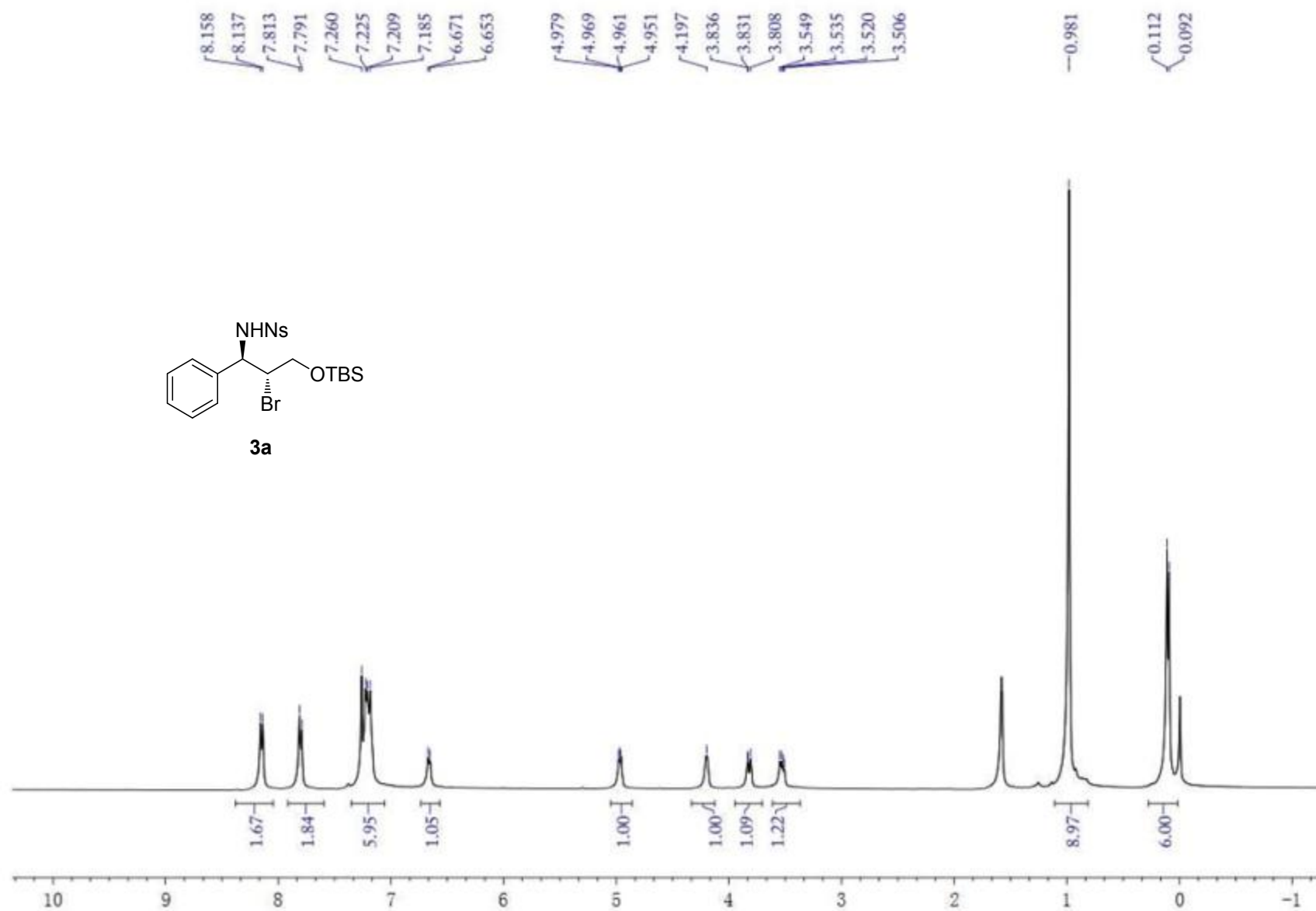
#### Integration Results

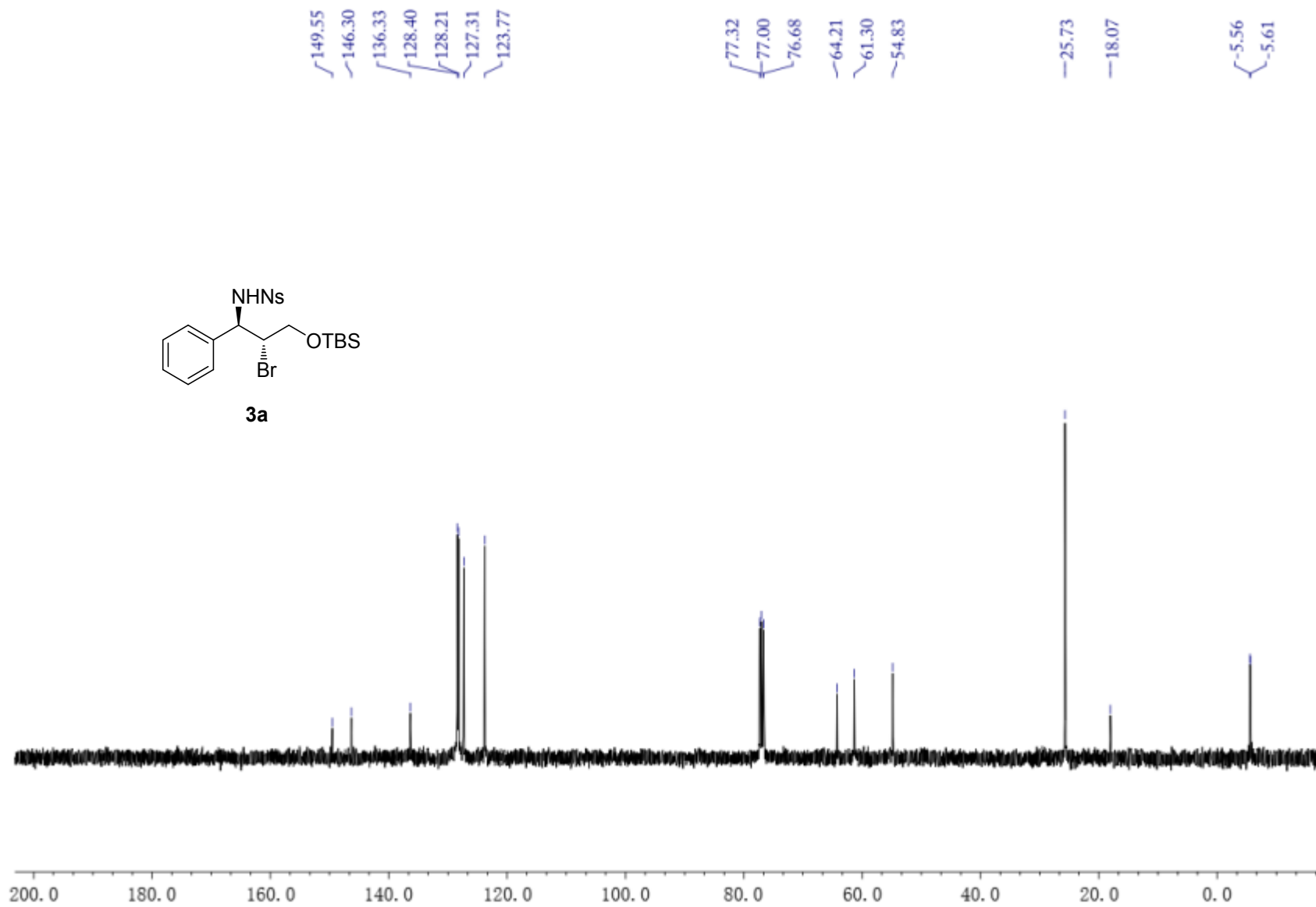
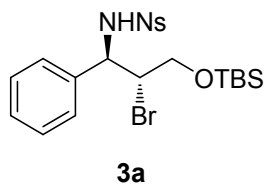
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.682	1.156	5.852	1.01	1.10	n.a.
2		8.332	113.275	528.330	98.99	98.90	n.a.
Total:			114.431	534.182	100.00	100.00	

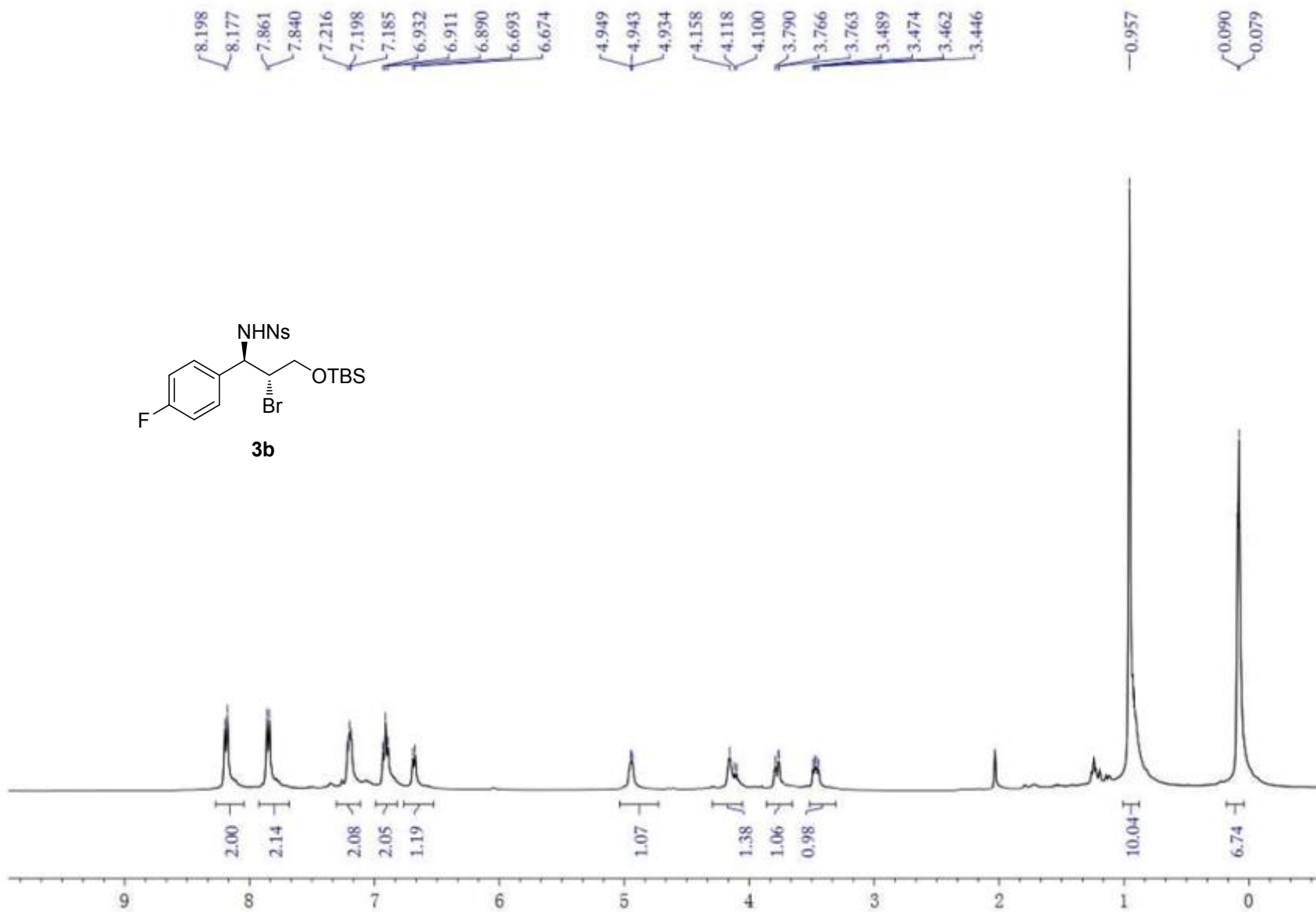
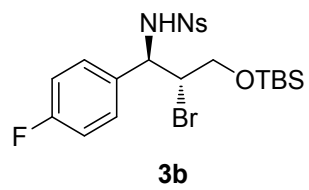


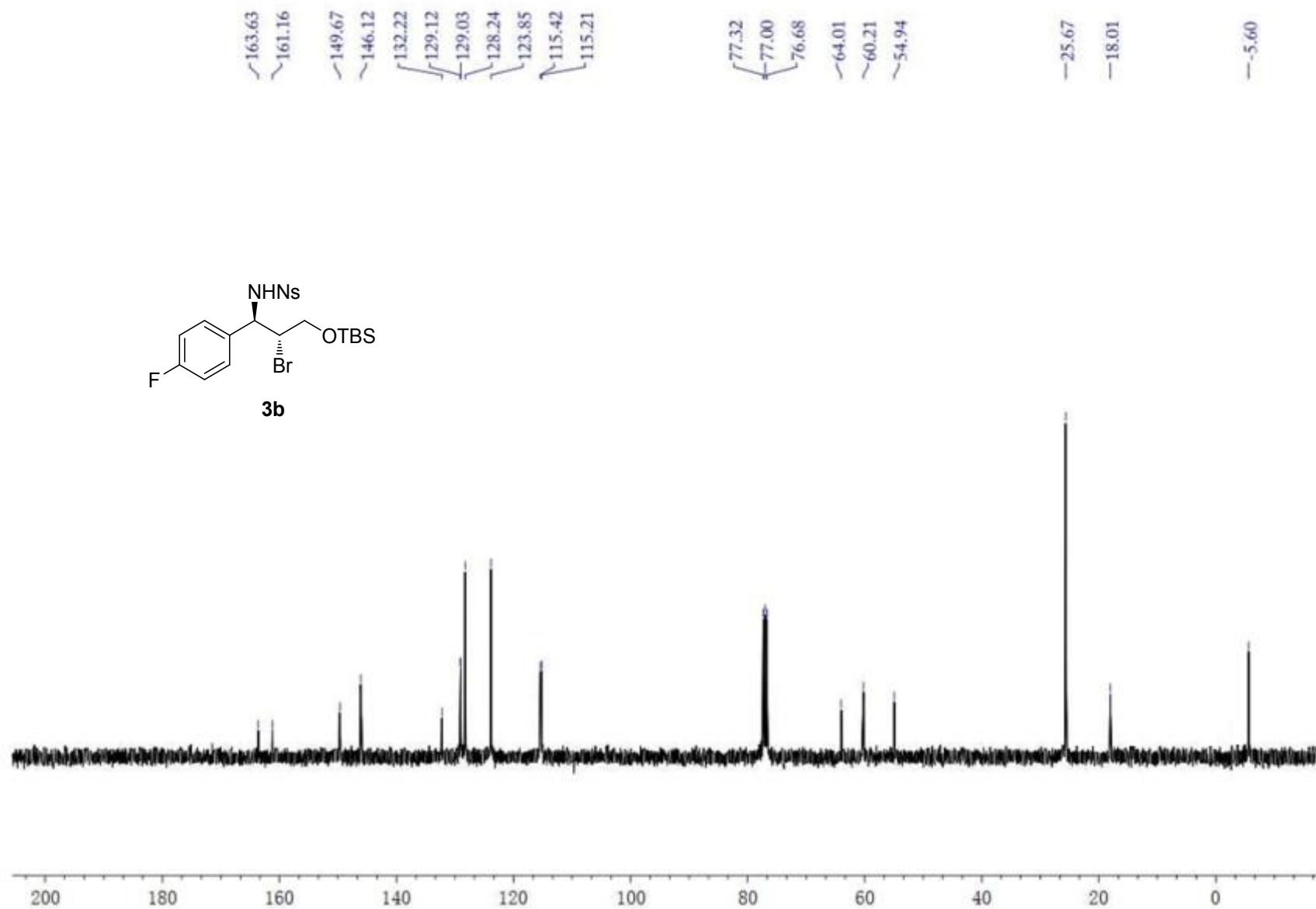
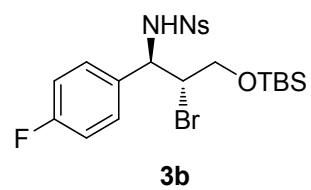
## Reference

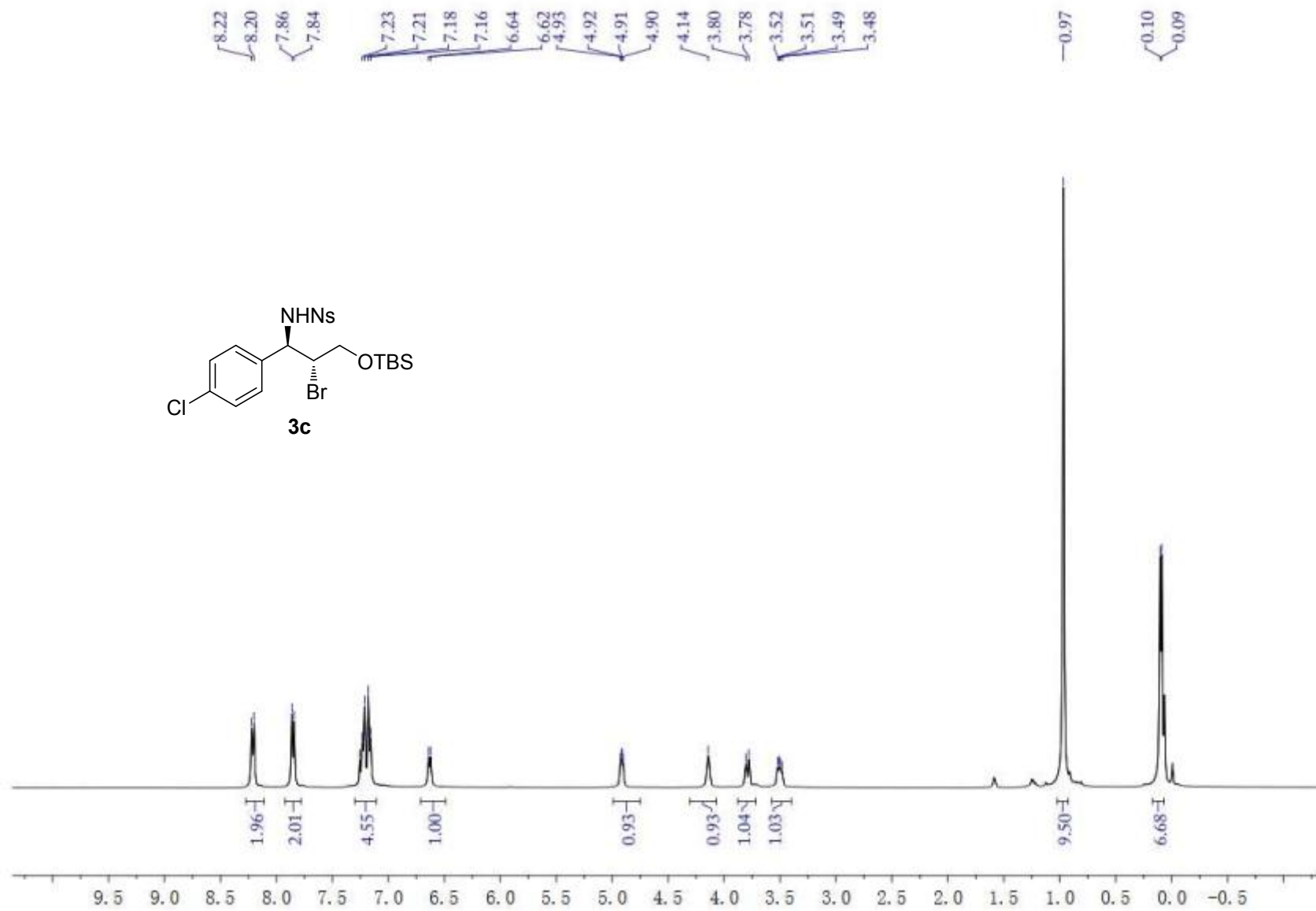
- (1) X. Li, H. Deng, B. Zhang, J. Li, L. Zhang, S. Luo and J.-P. Cheng, *Chem. Eur. J.*, 2010, **16**, 450.
- (2) J. Xu, Y. Hu, D. Huang, K.-H. Wang, C. Xu and T. Niu, *Adv. Synth. Catal.*, 2012, **354**, 515
- (3) L. Zhou, C. K. Tan, X. Jiang, F. Chen and Y.-Y. Yeung, *J. Am. Chem. Soc.*, 2010, **132**, 15474.
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- (5) Z.-q. Zhou,; L.-h. Wu and Y. Liu, *Huaxue Shiji*, 2008, **30**, 729.
- (6) E.-M. Tanzer, W. B. Schweizer, M.-O. Ebert and R. Gilmour, *Chem. Eur. J.*, 2012, **18**, 2006

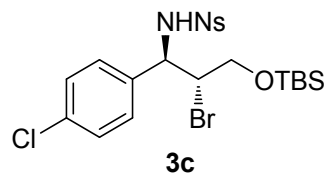










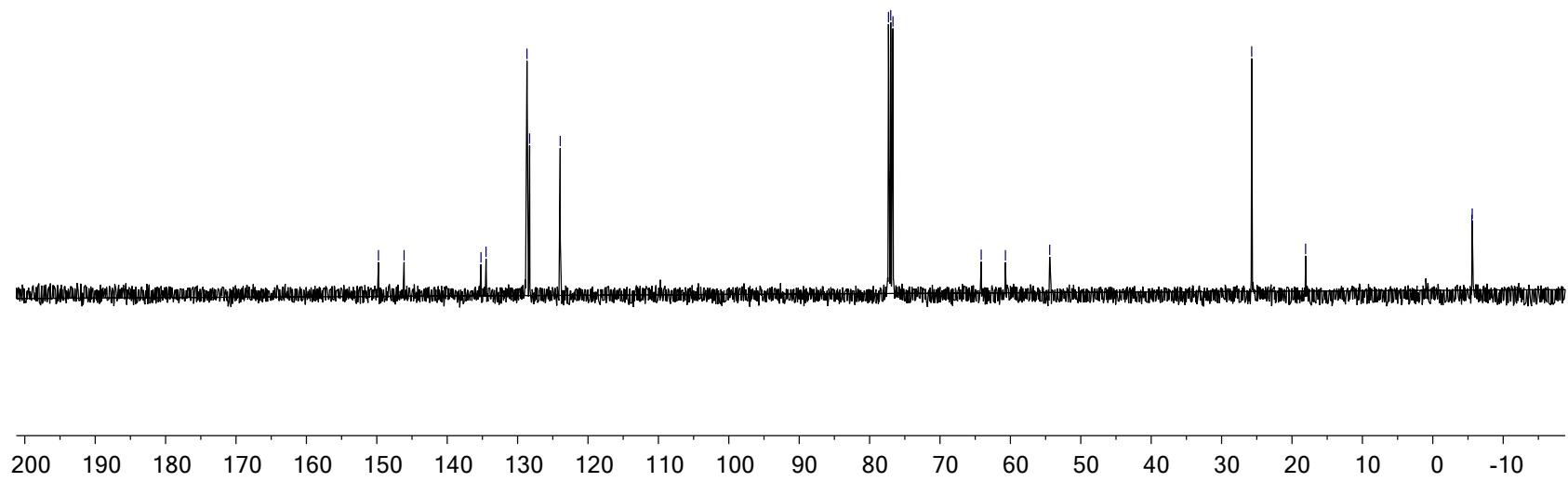


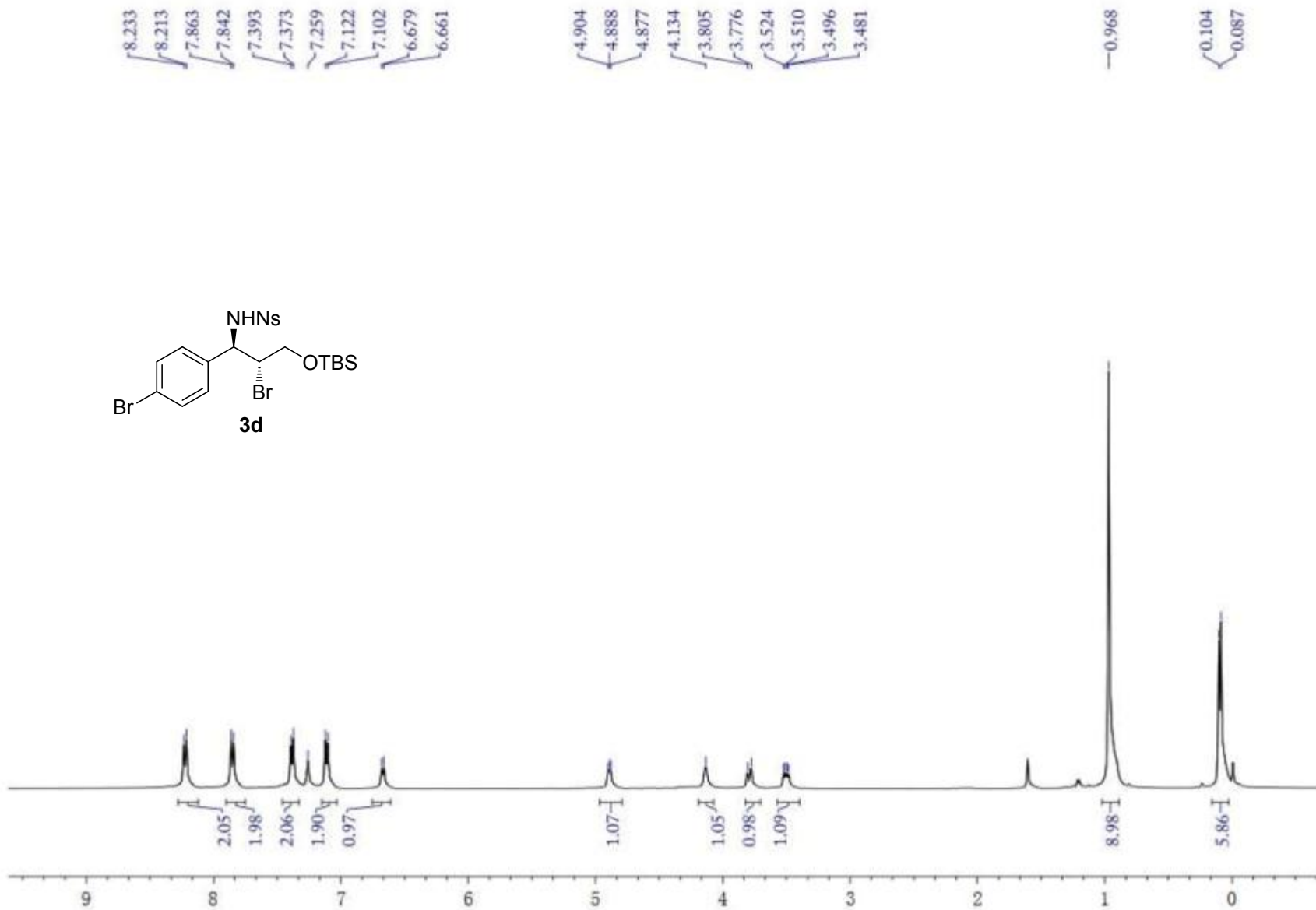
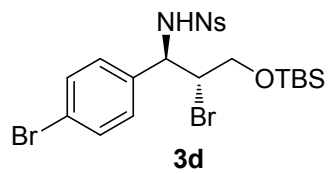
149.77  
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 123.95

77.32  
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 76.68  
 64.15  
 60.71  
 54.42

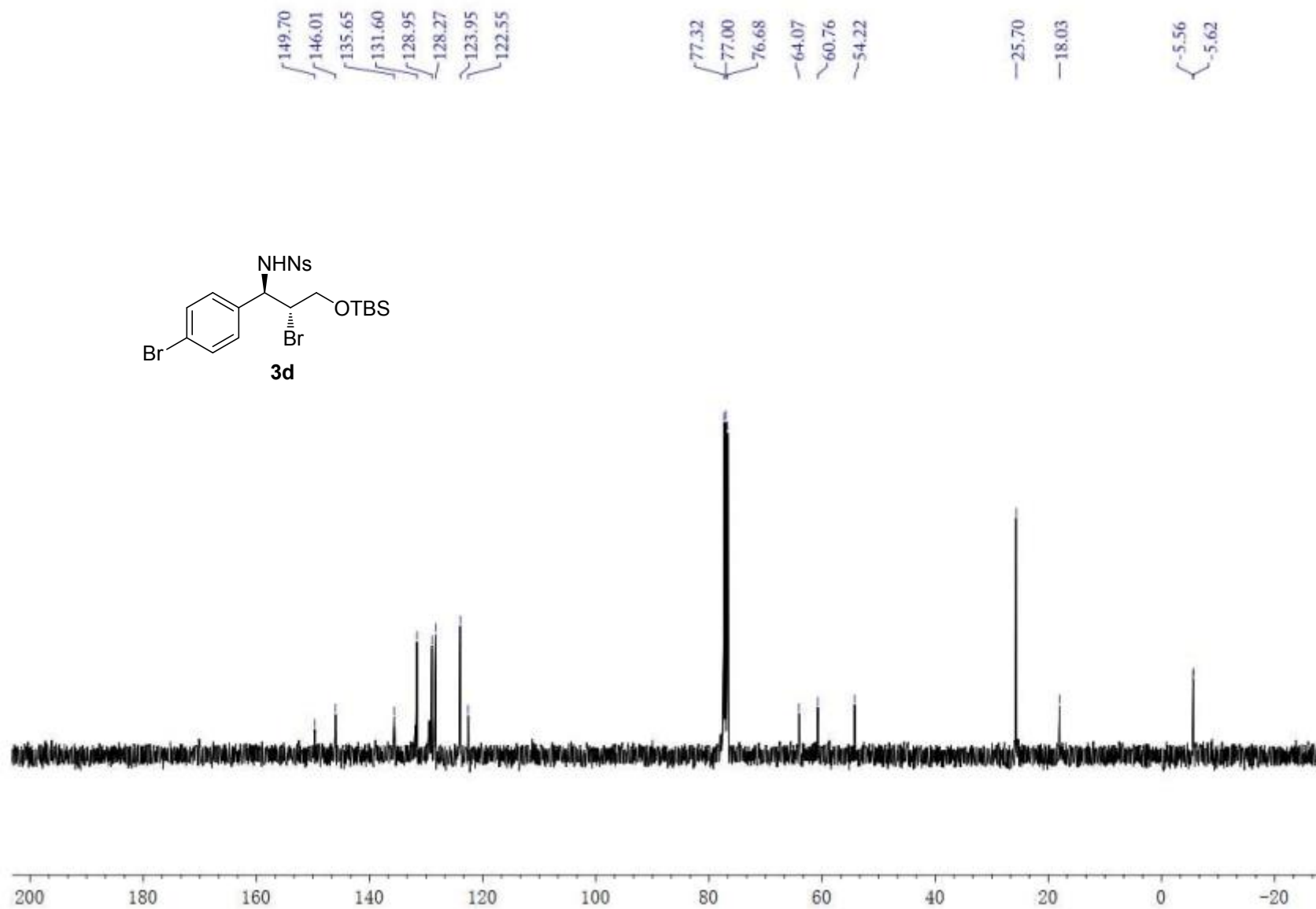
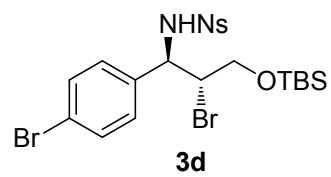
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 18.07

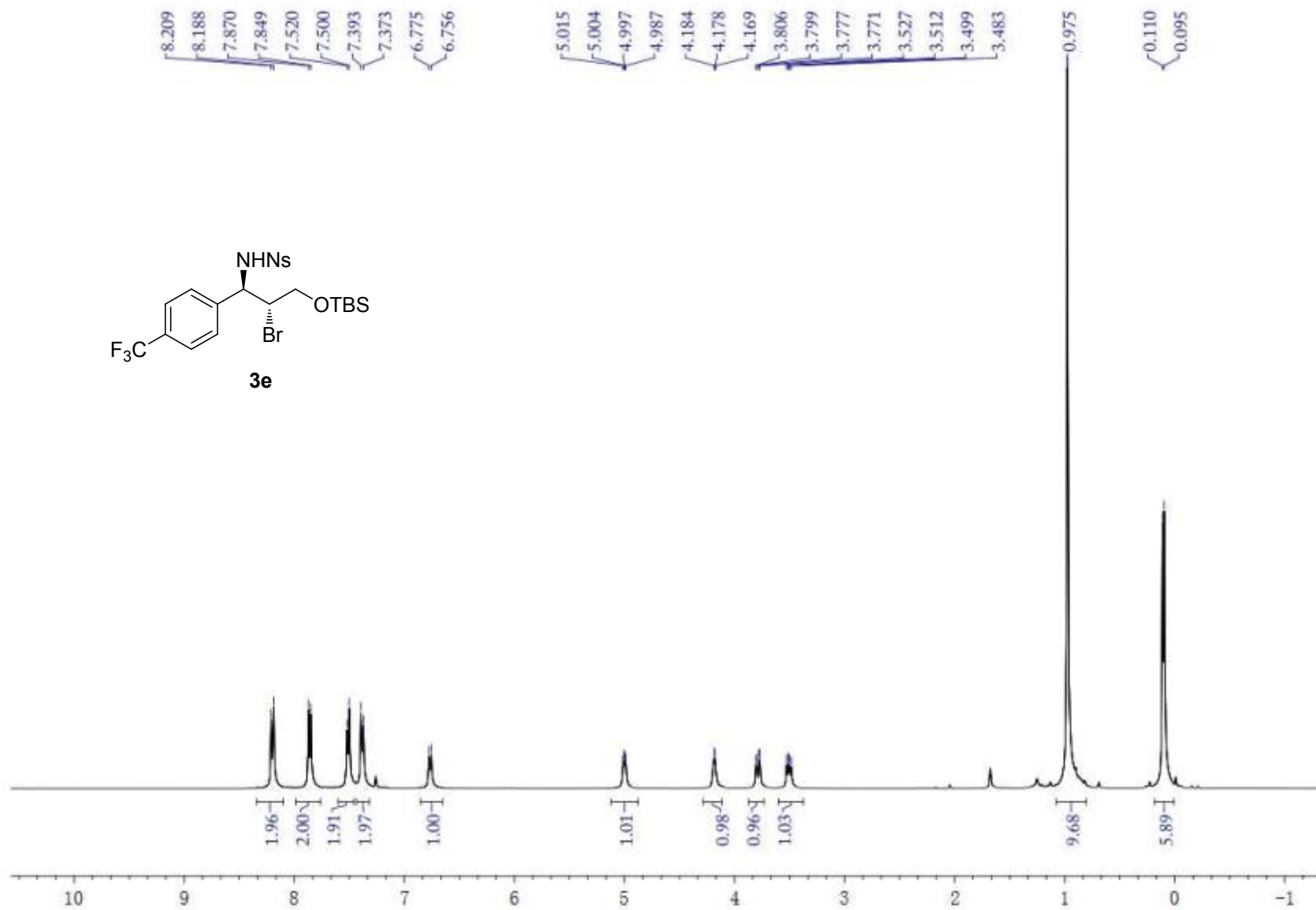
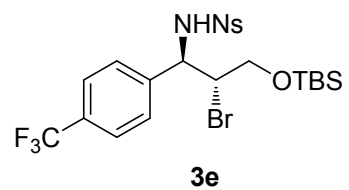
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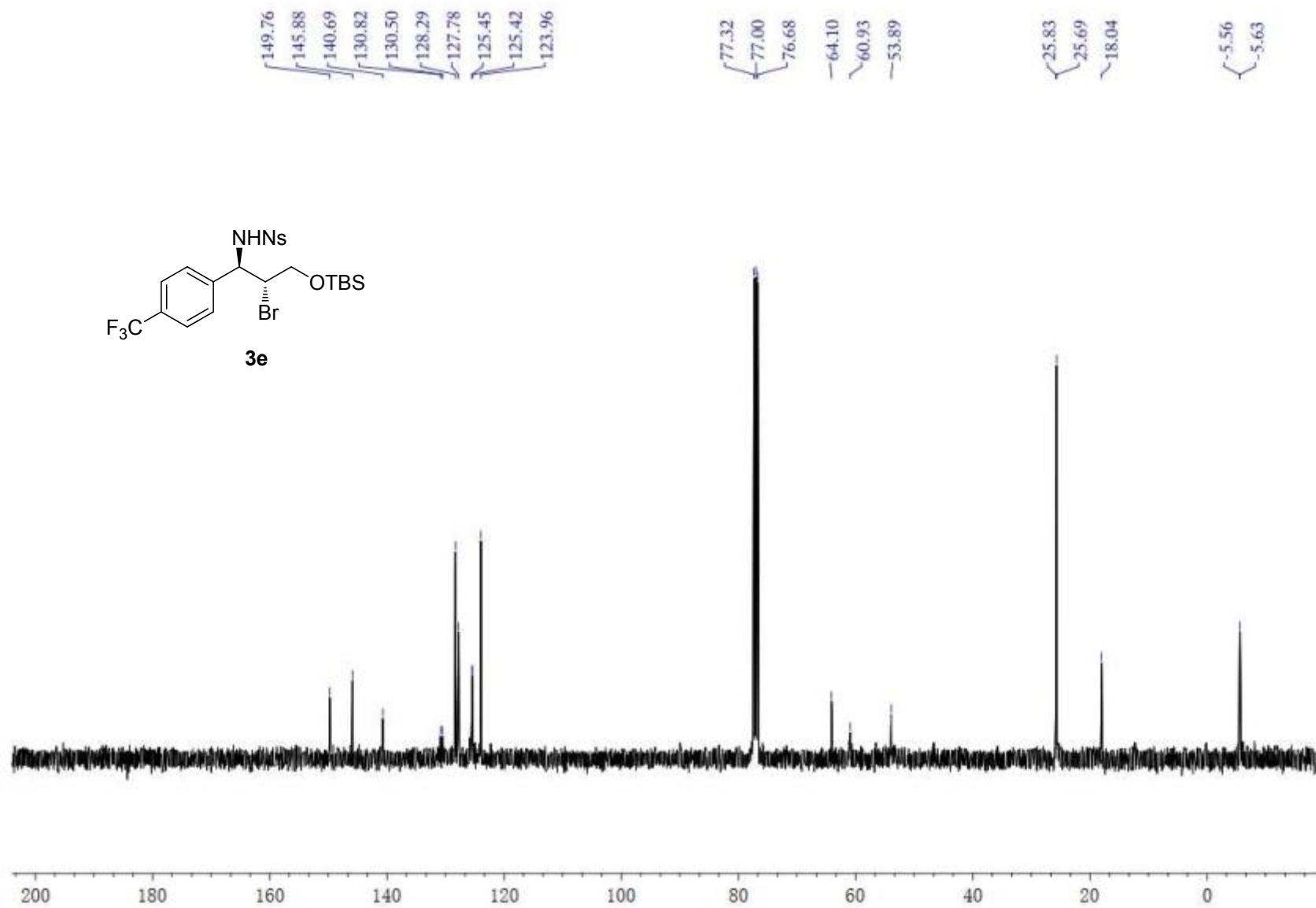


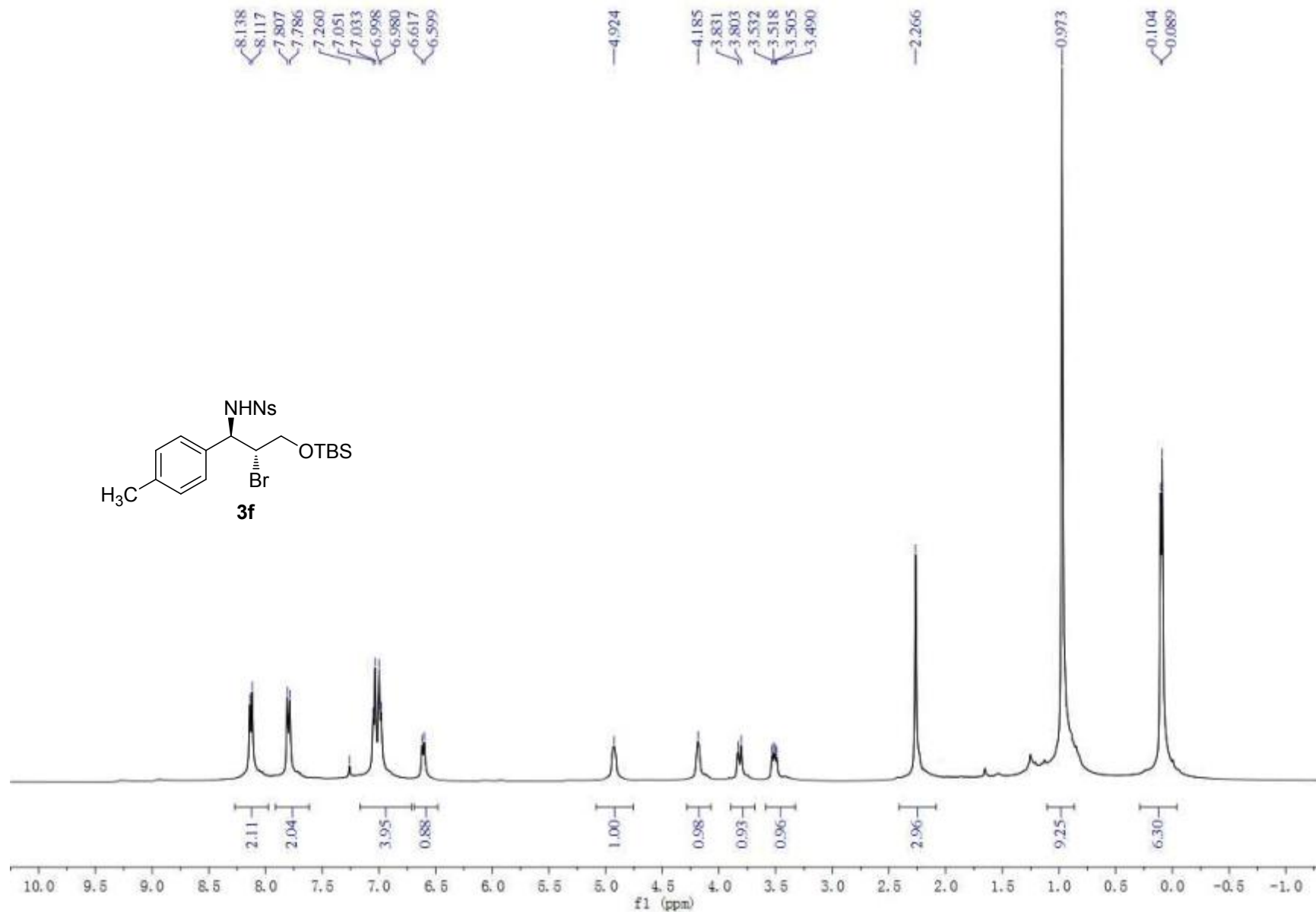


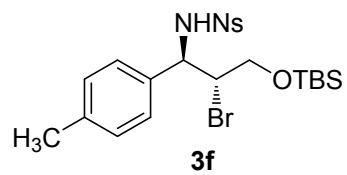










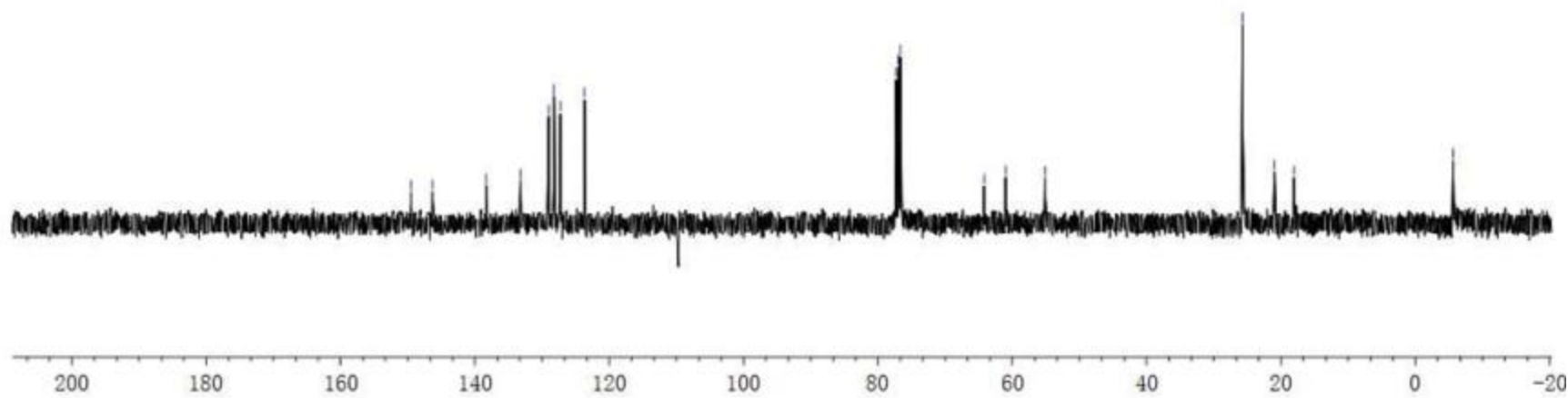


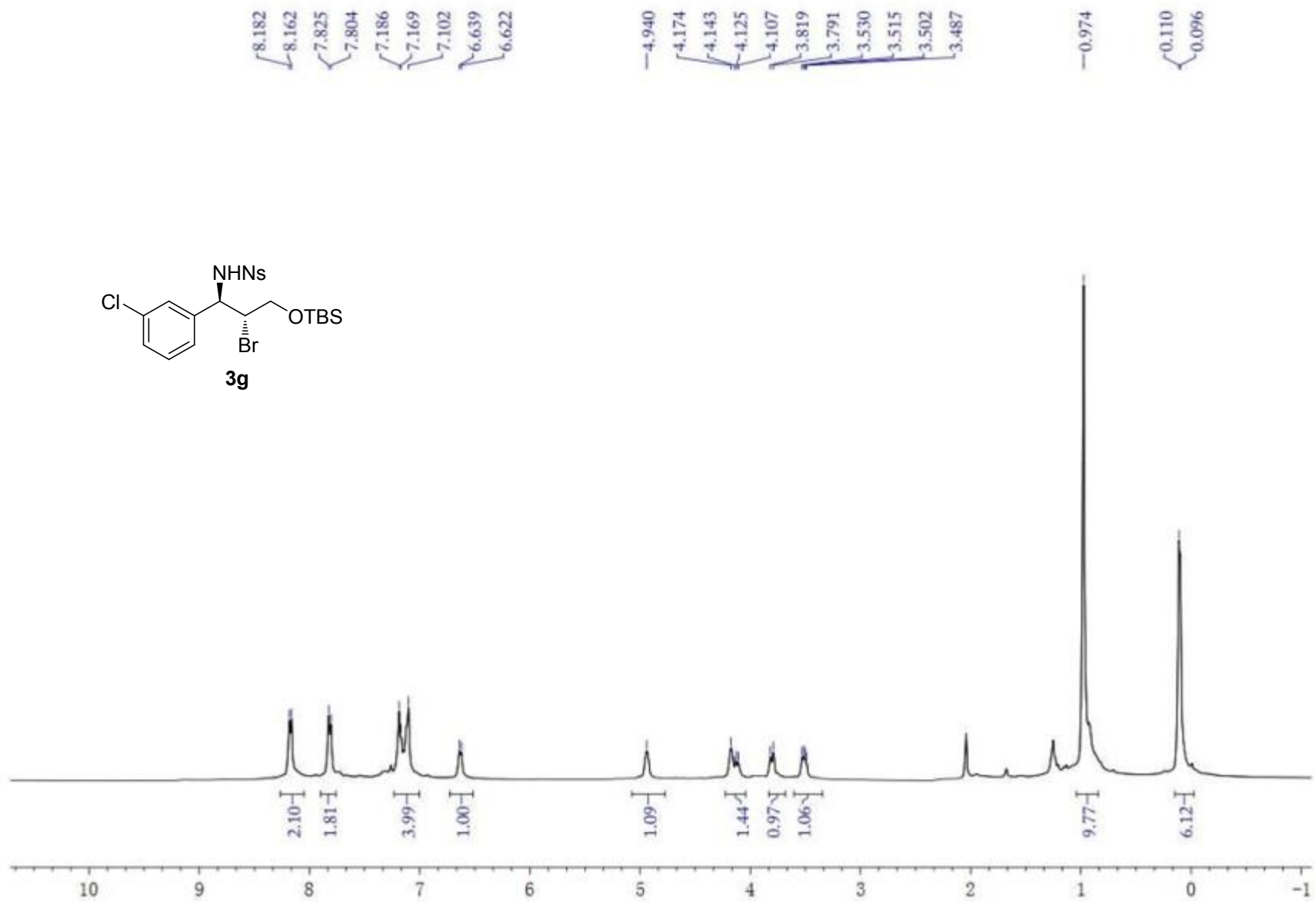
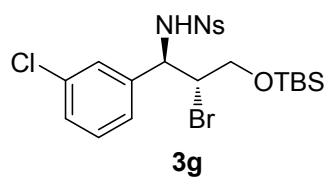
149.5  
 146.3  
 138.3  
 133.2  
 129.0  
 128.2  
 127.3  
 123.7

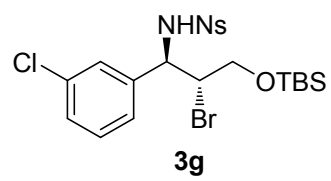
77.3  
 77.0  
 76.7  
 64.2  
 61.0  
 55.1

25.7  
 21.0  
 18.1

-5.6  
 -5.6





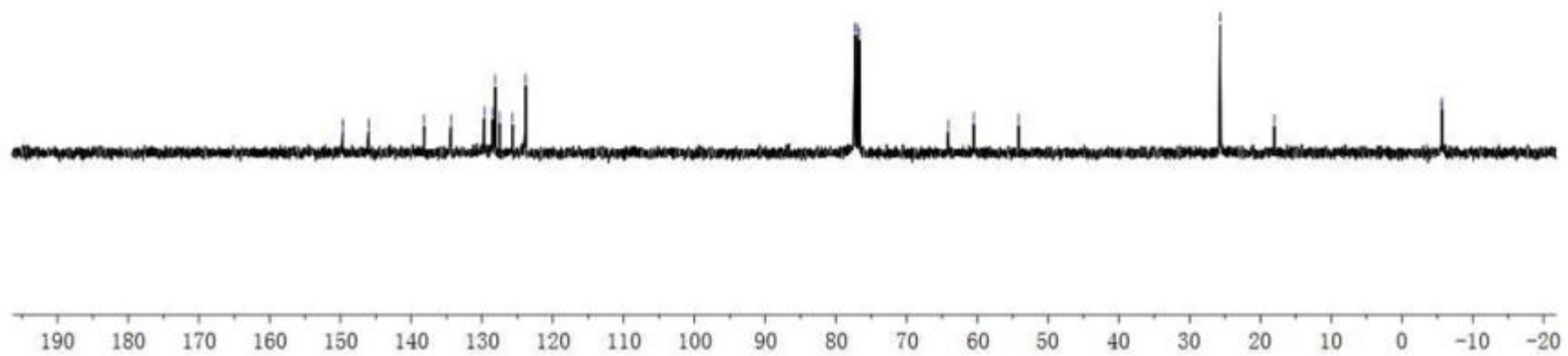


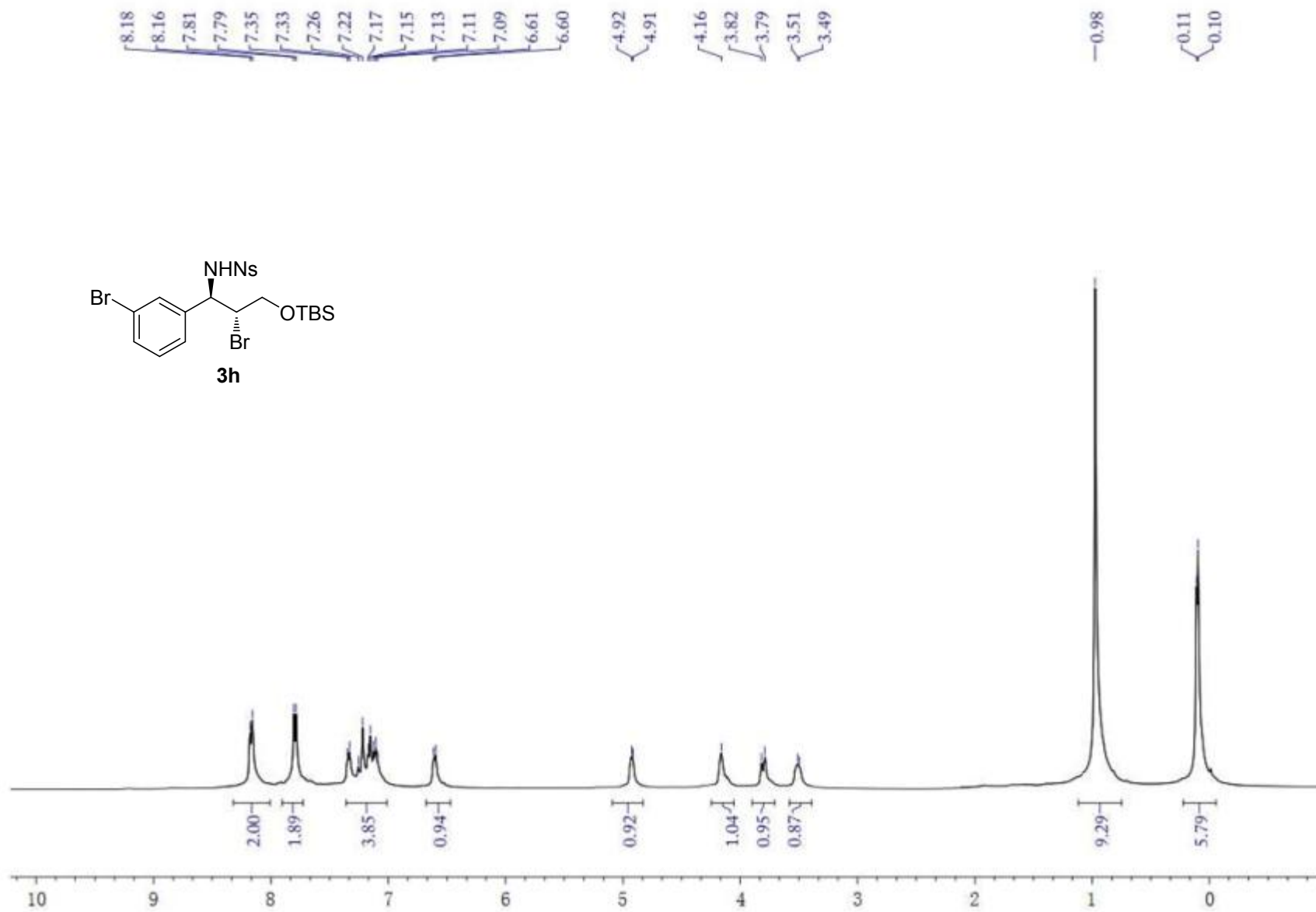
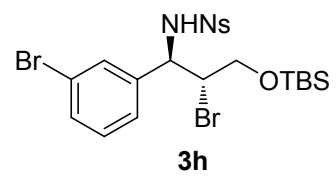
149.68  
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138.18  
134.39  
129.70  
128.51  
128.14  
127.53  
125.71  
123.85

77.32  
77.00  
76.68  
64.14  
60.51  
54.17

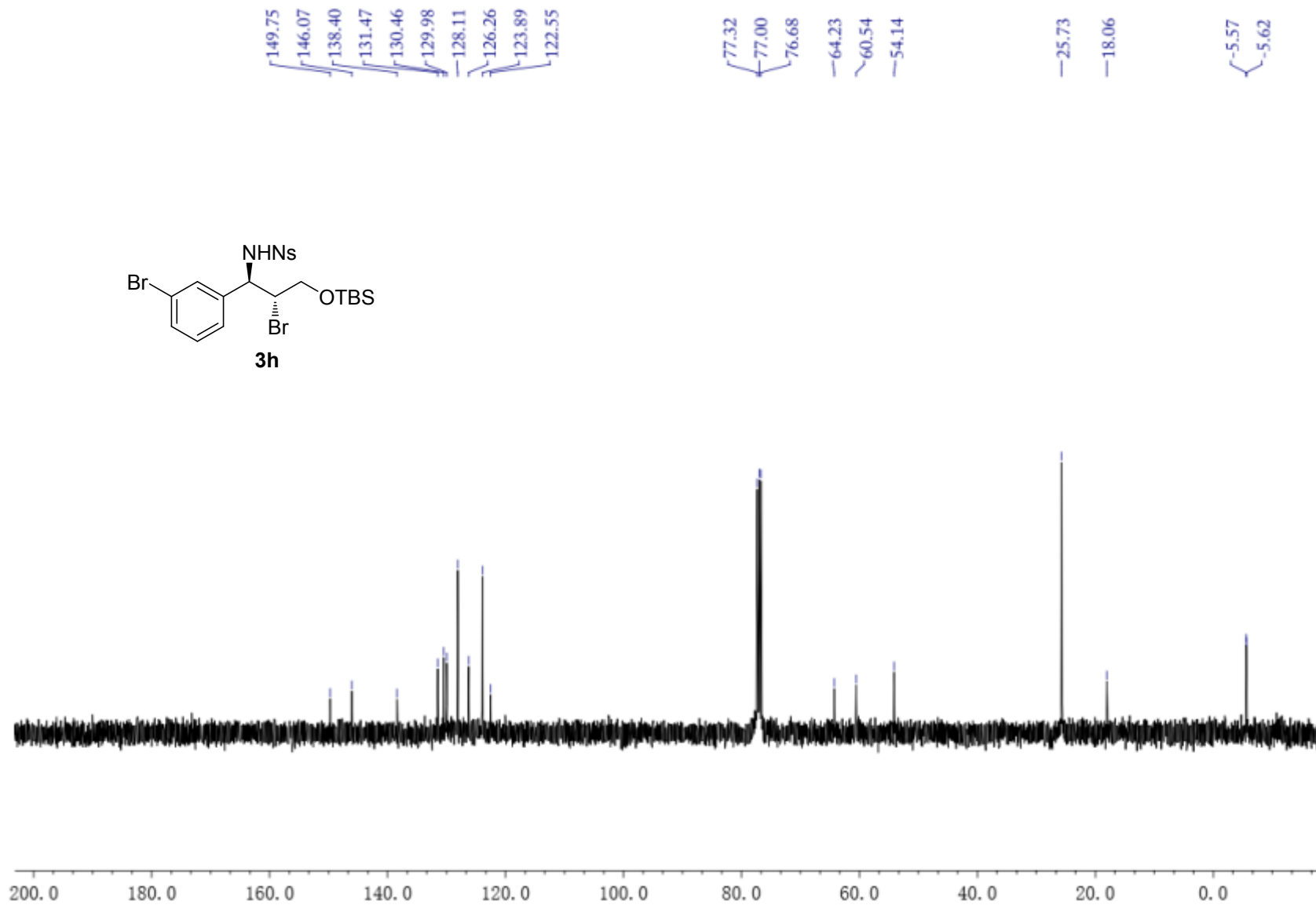
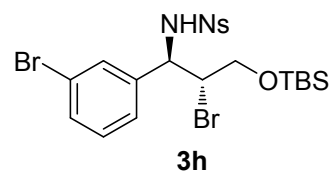
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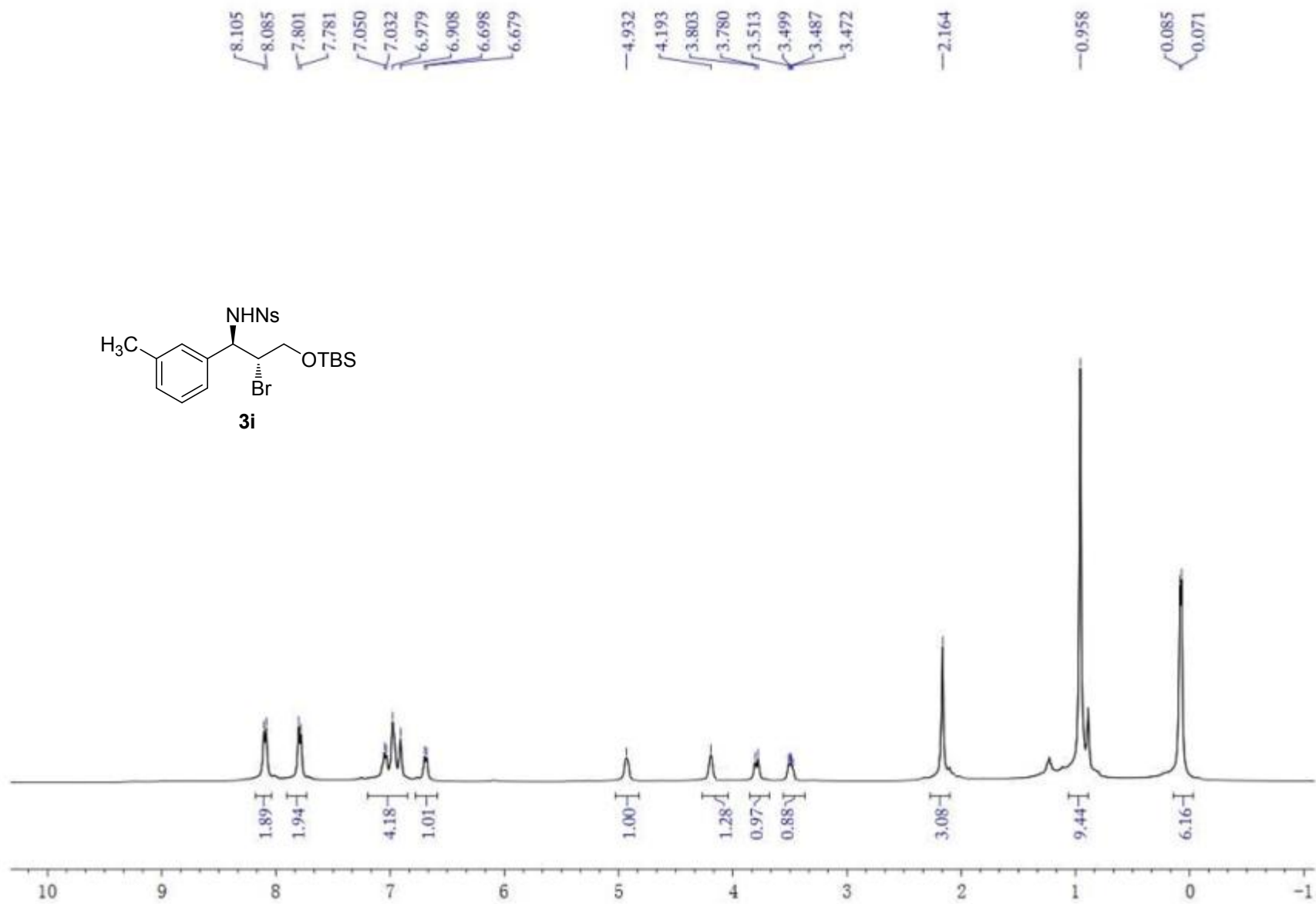
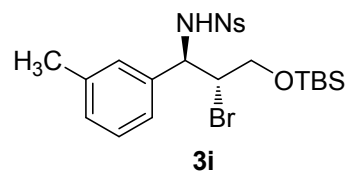
-5.60  
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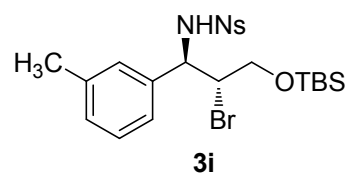










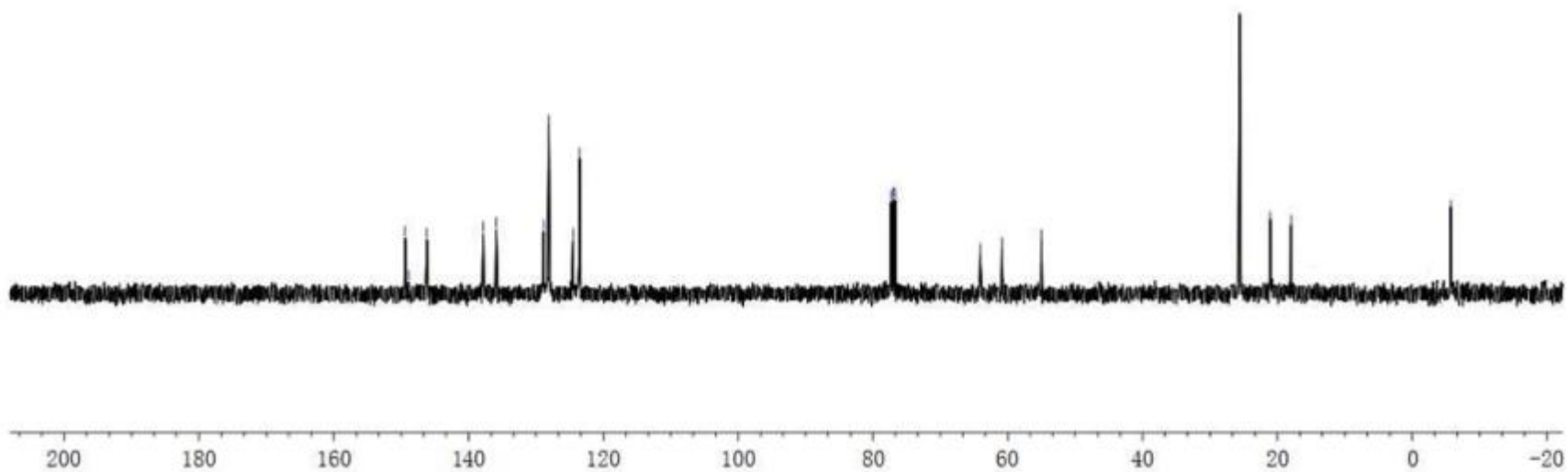


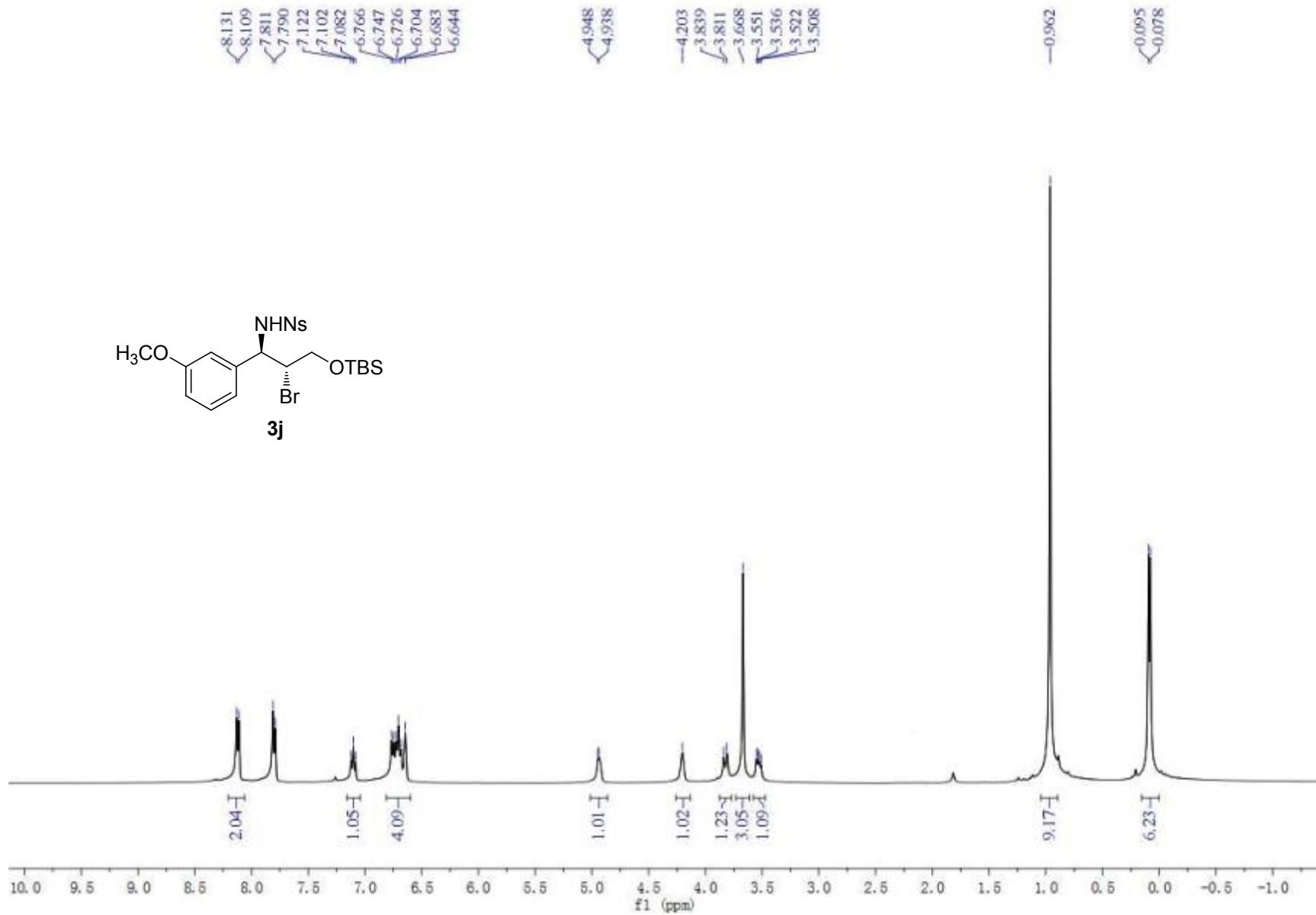
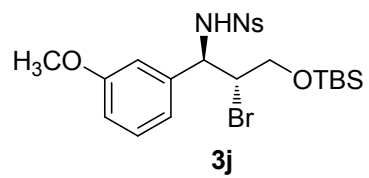
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 135.89  
 128.86  
 128.13  
 127.97  
 124.50  
 123.53

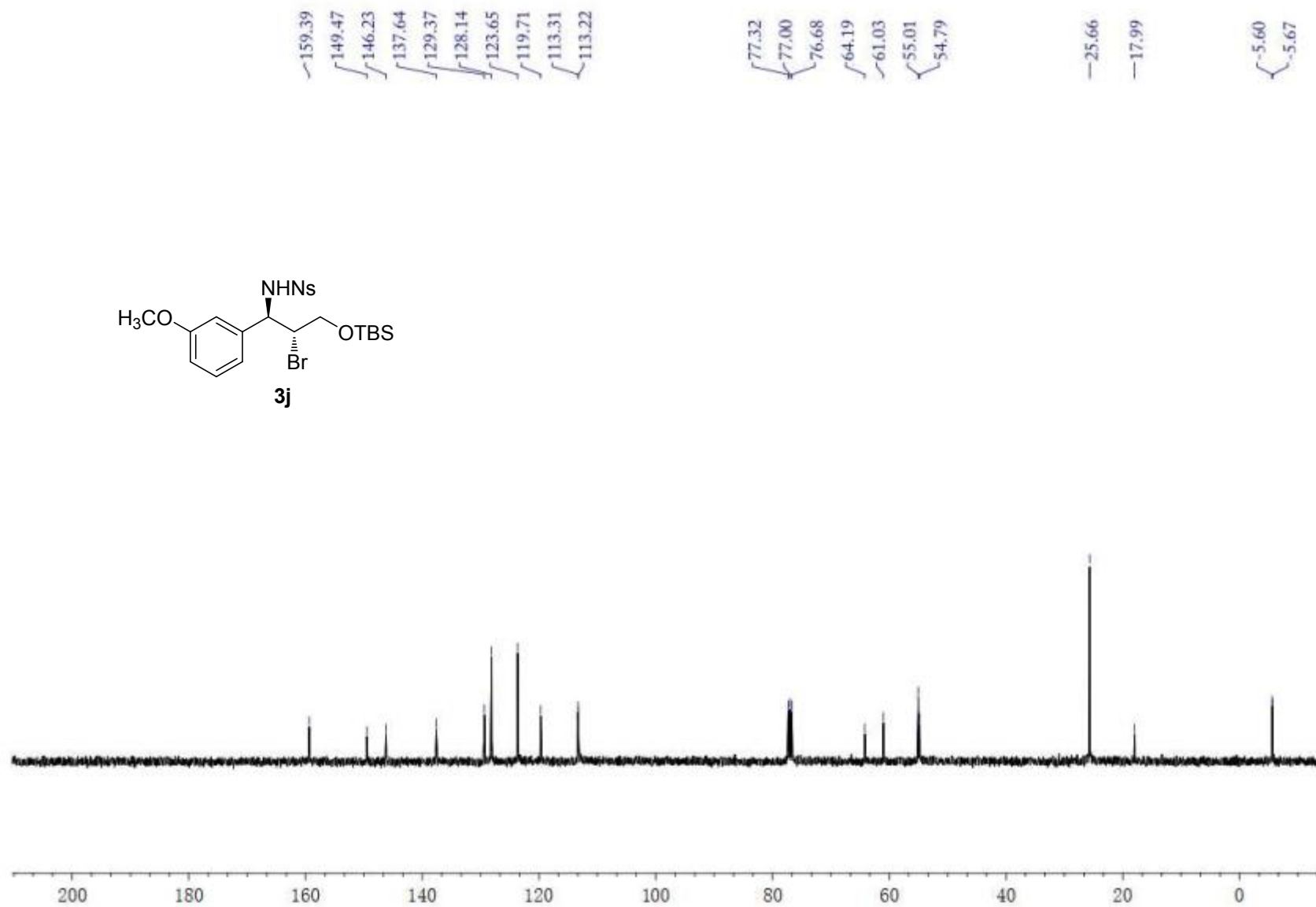
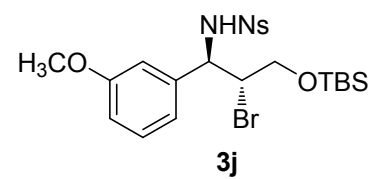
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 76.68  
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 60.85  
 55.03

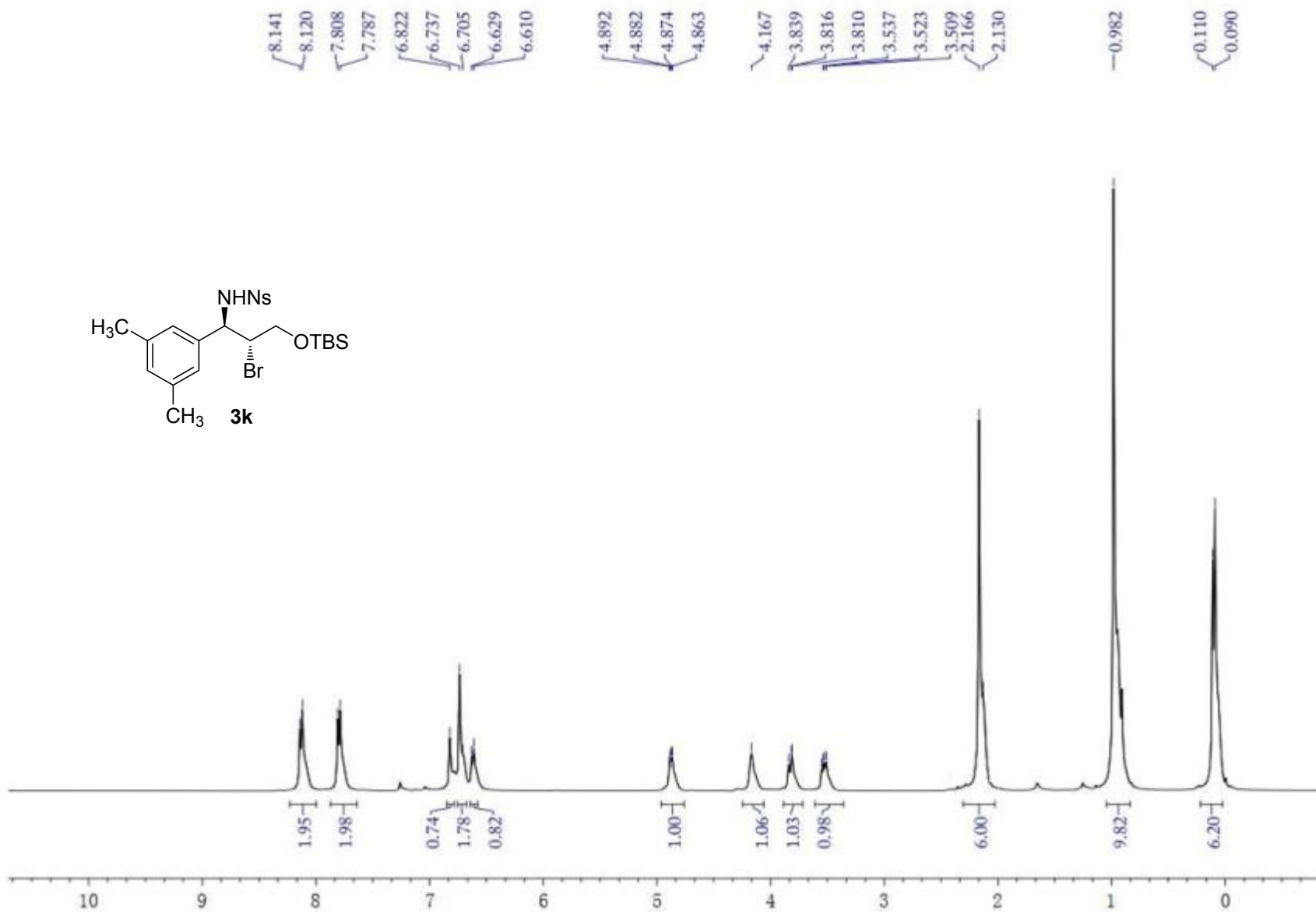
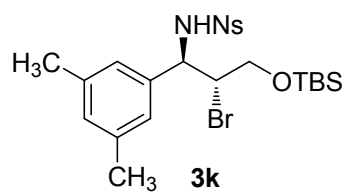
25.62  
 25.53  
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 17.96

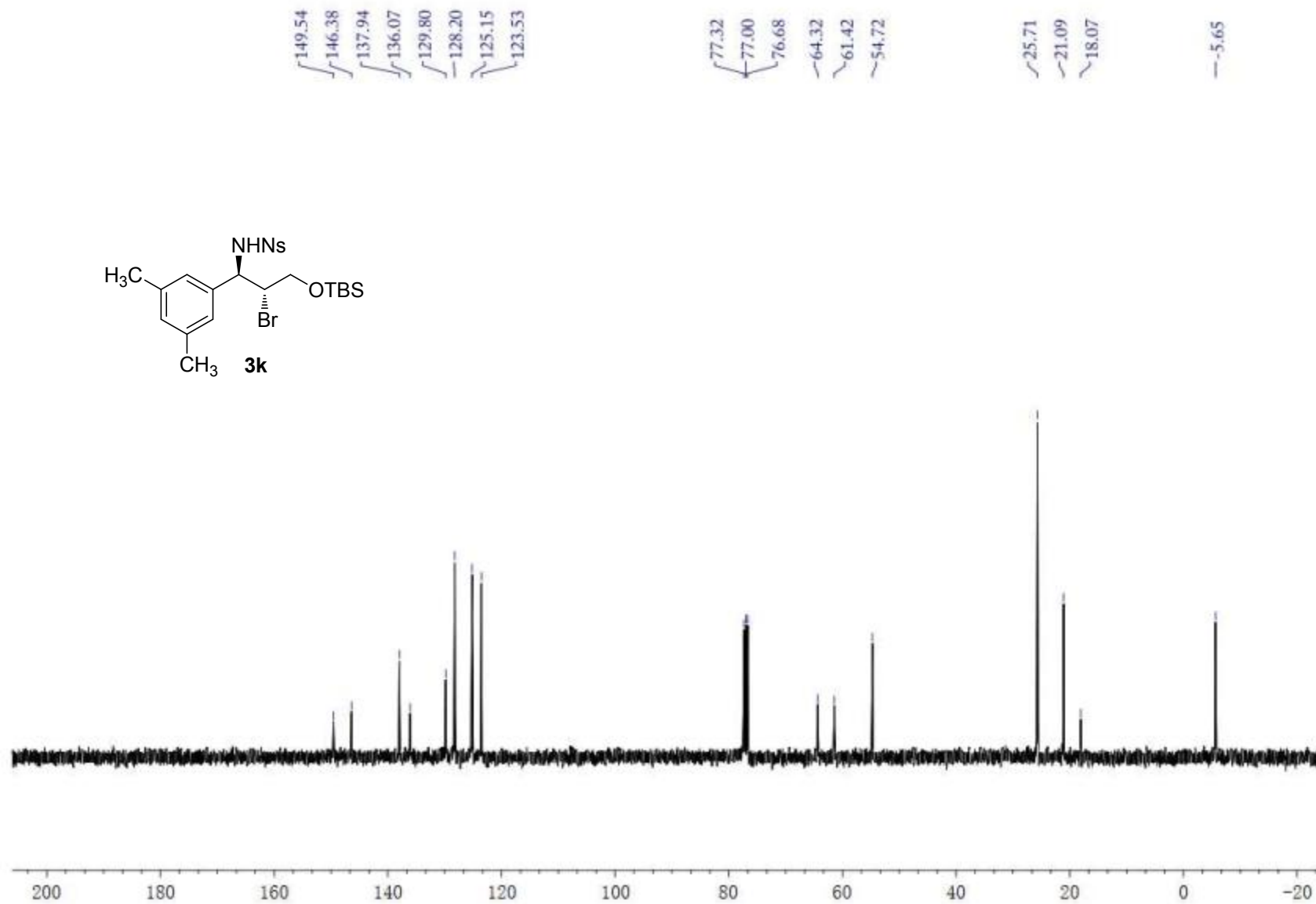
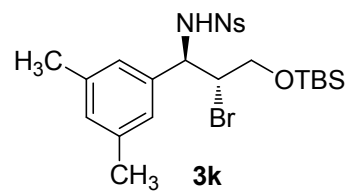
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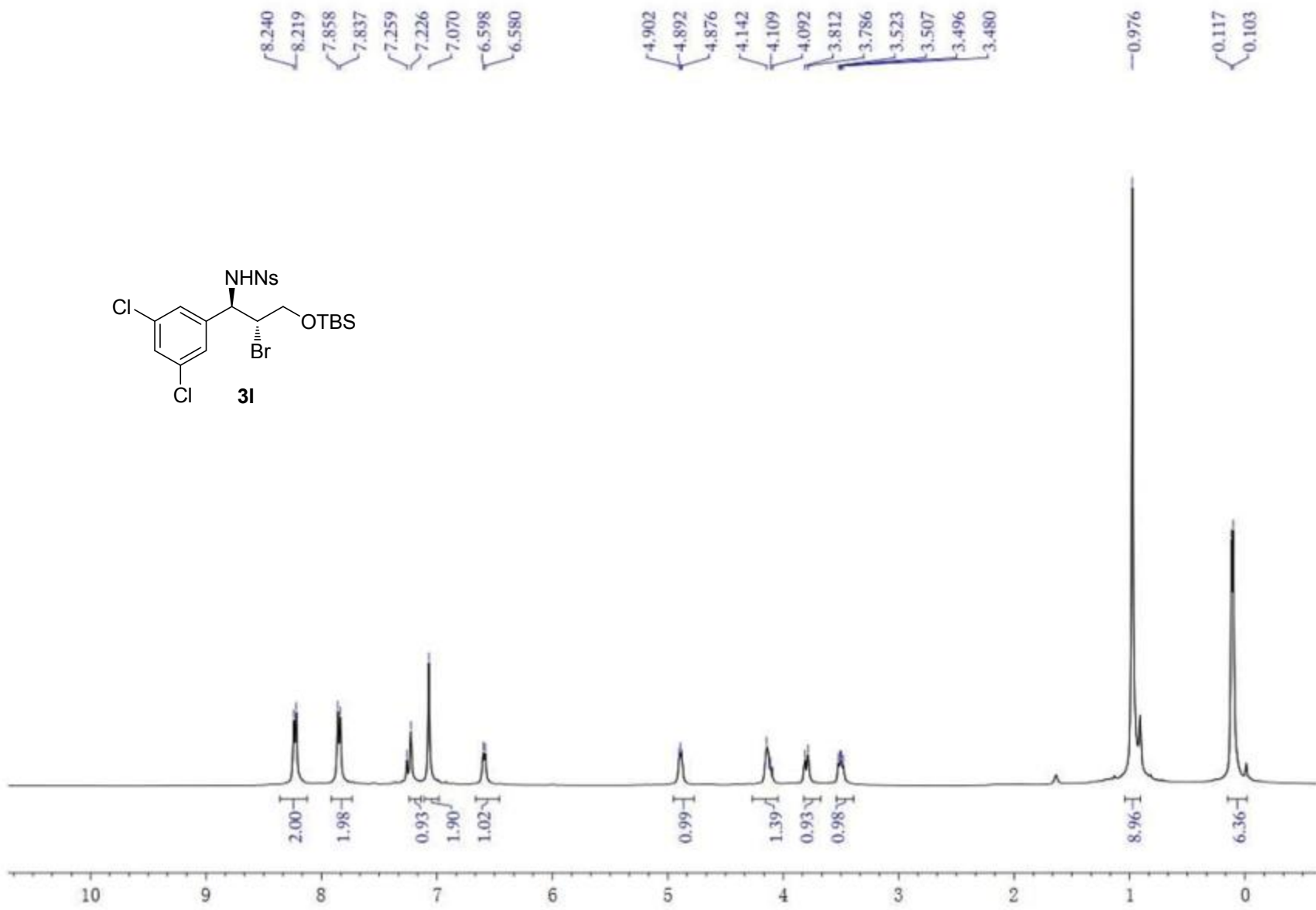
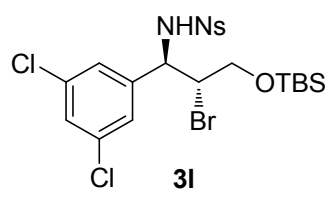




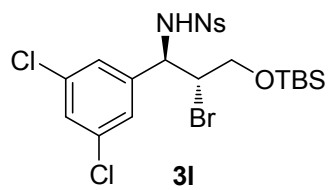










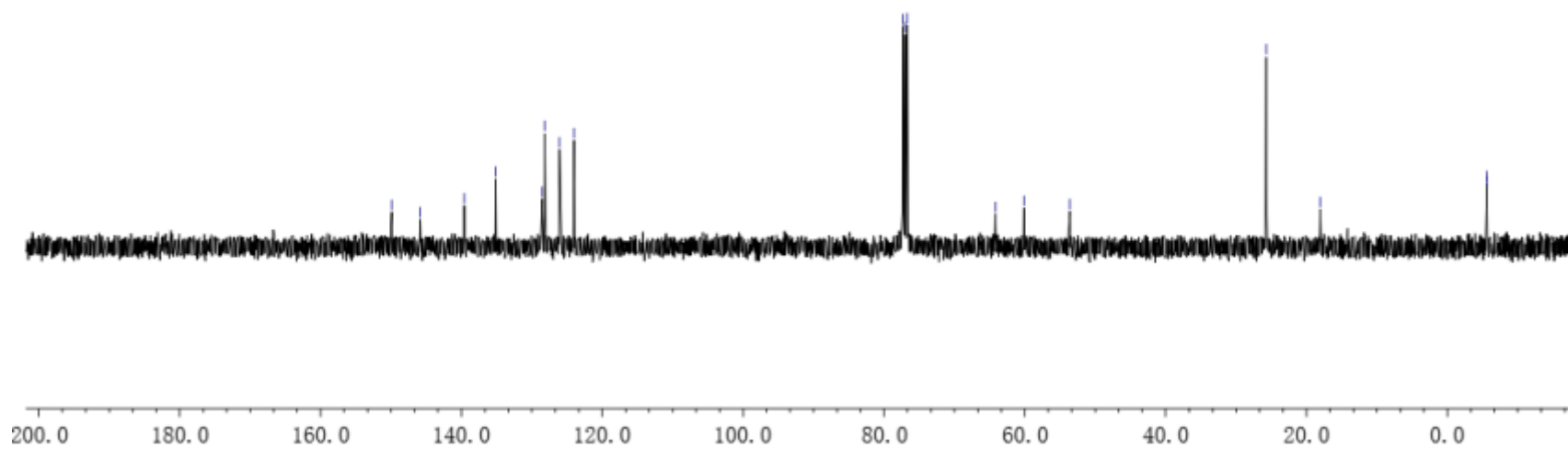


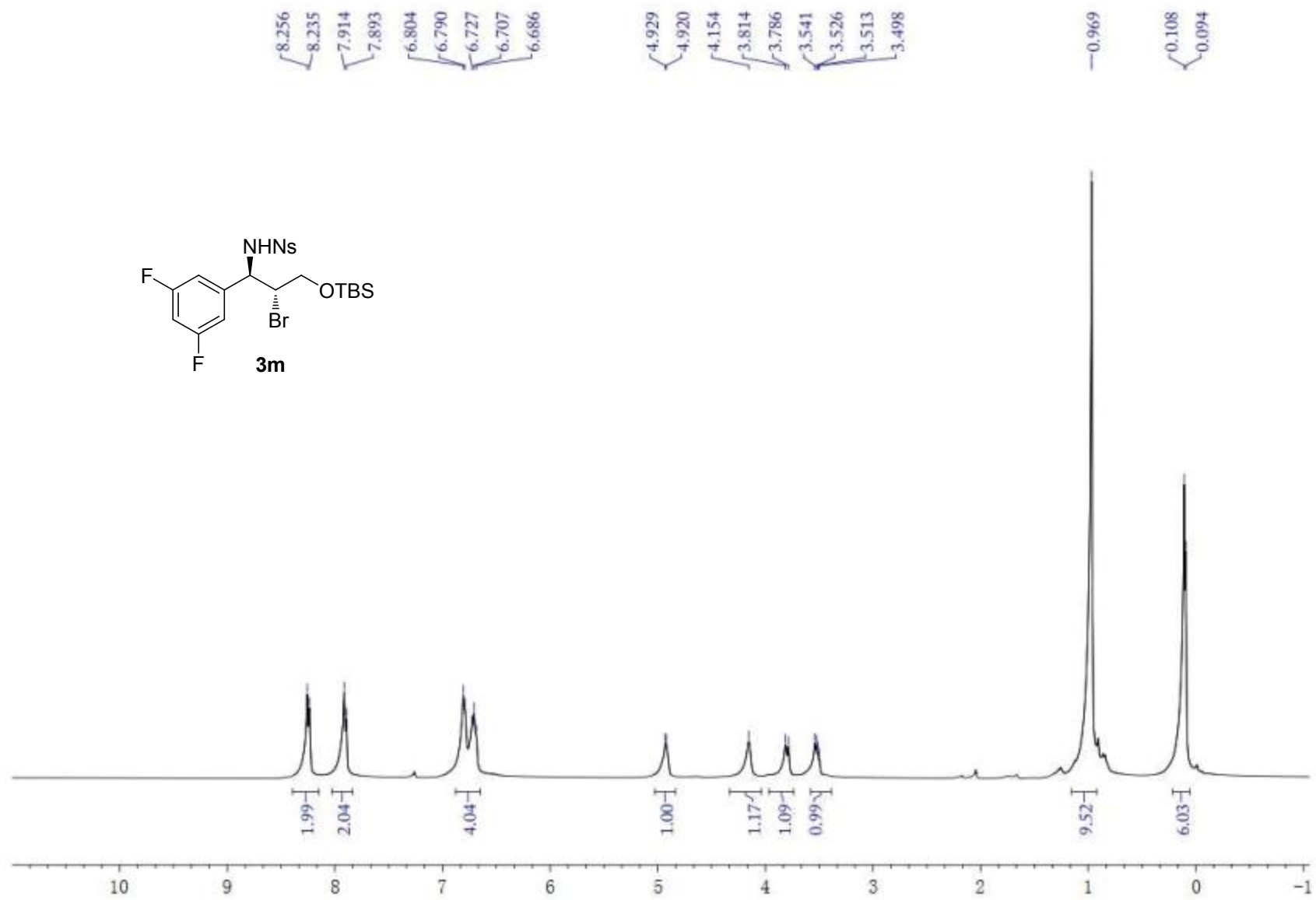
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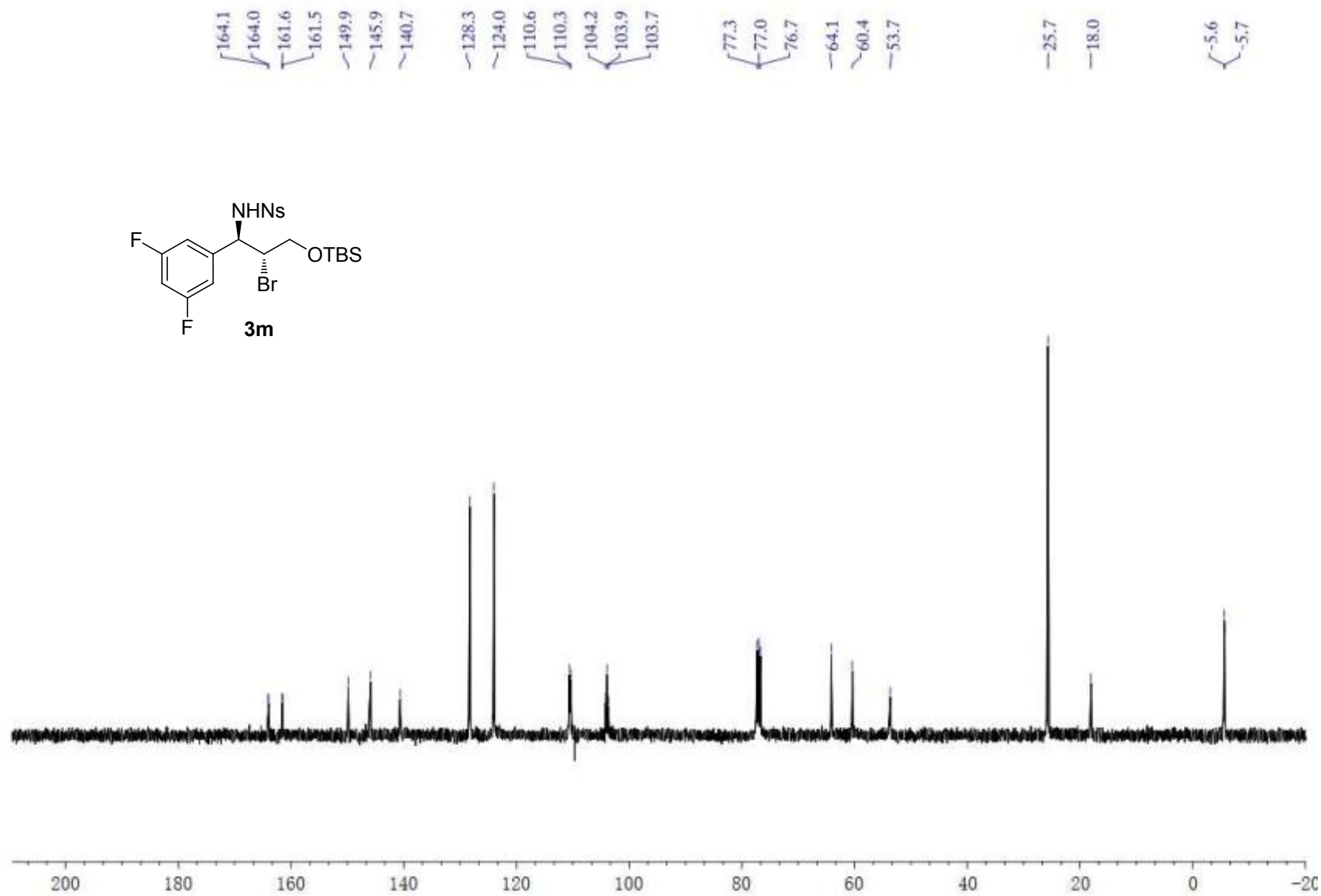
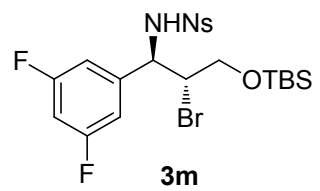
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 76.68  
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 60.09  
 53.59

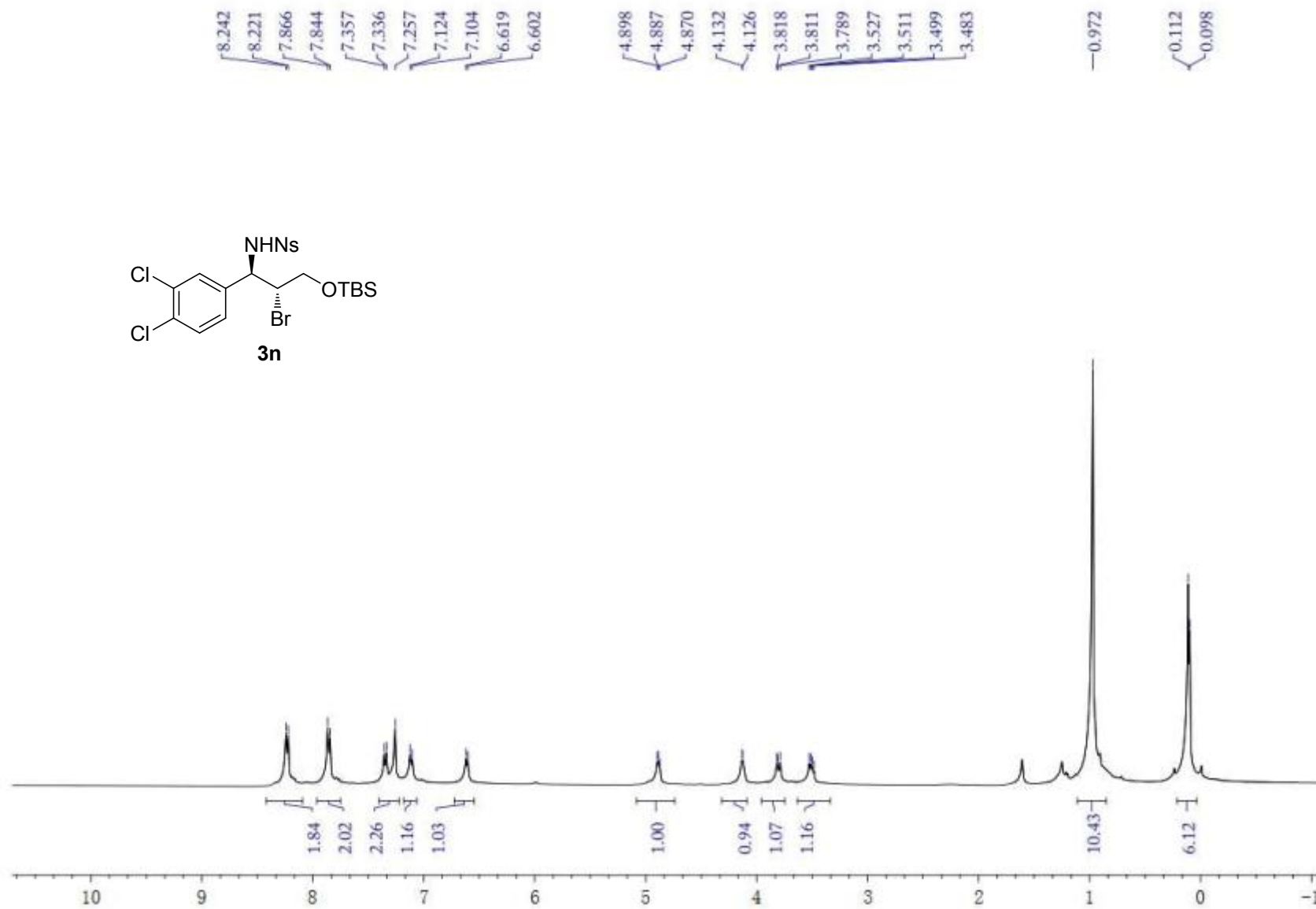
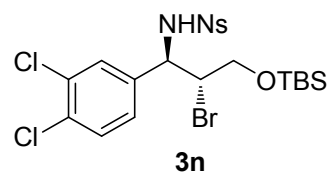
25.72  
 18.06

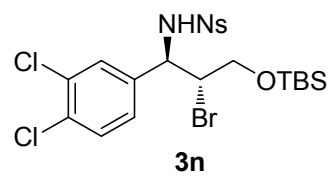
5.60  
 5.66









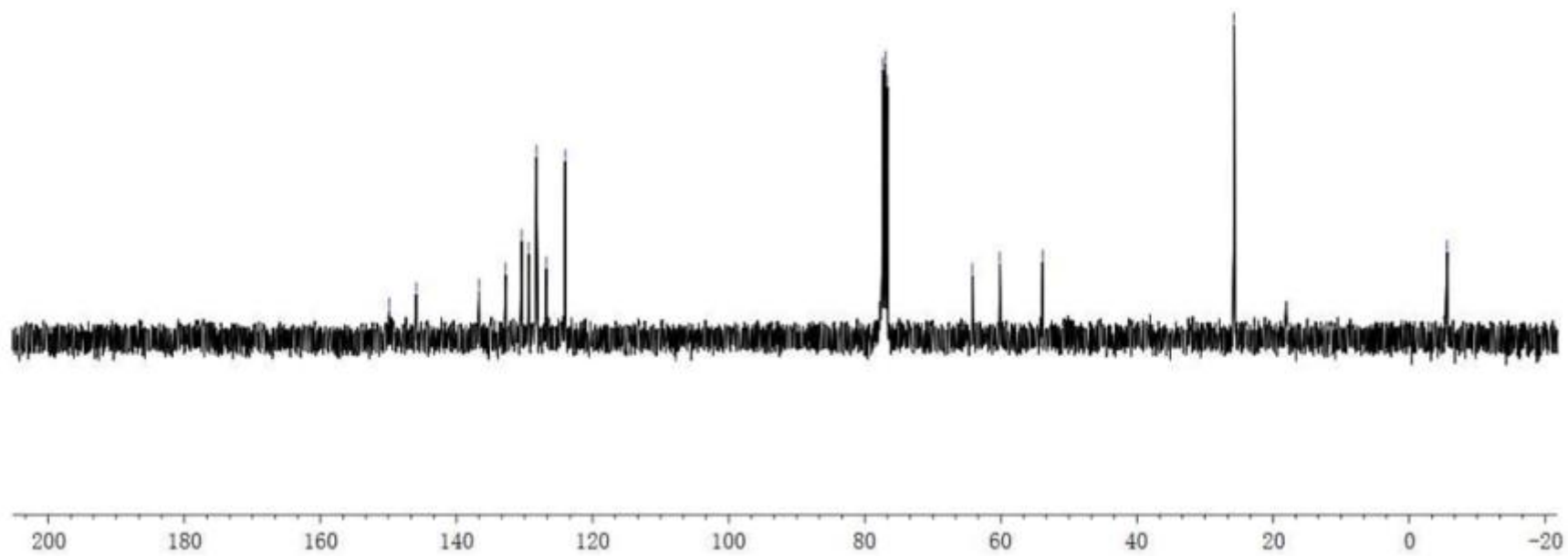


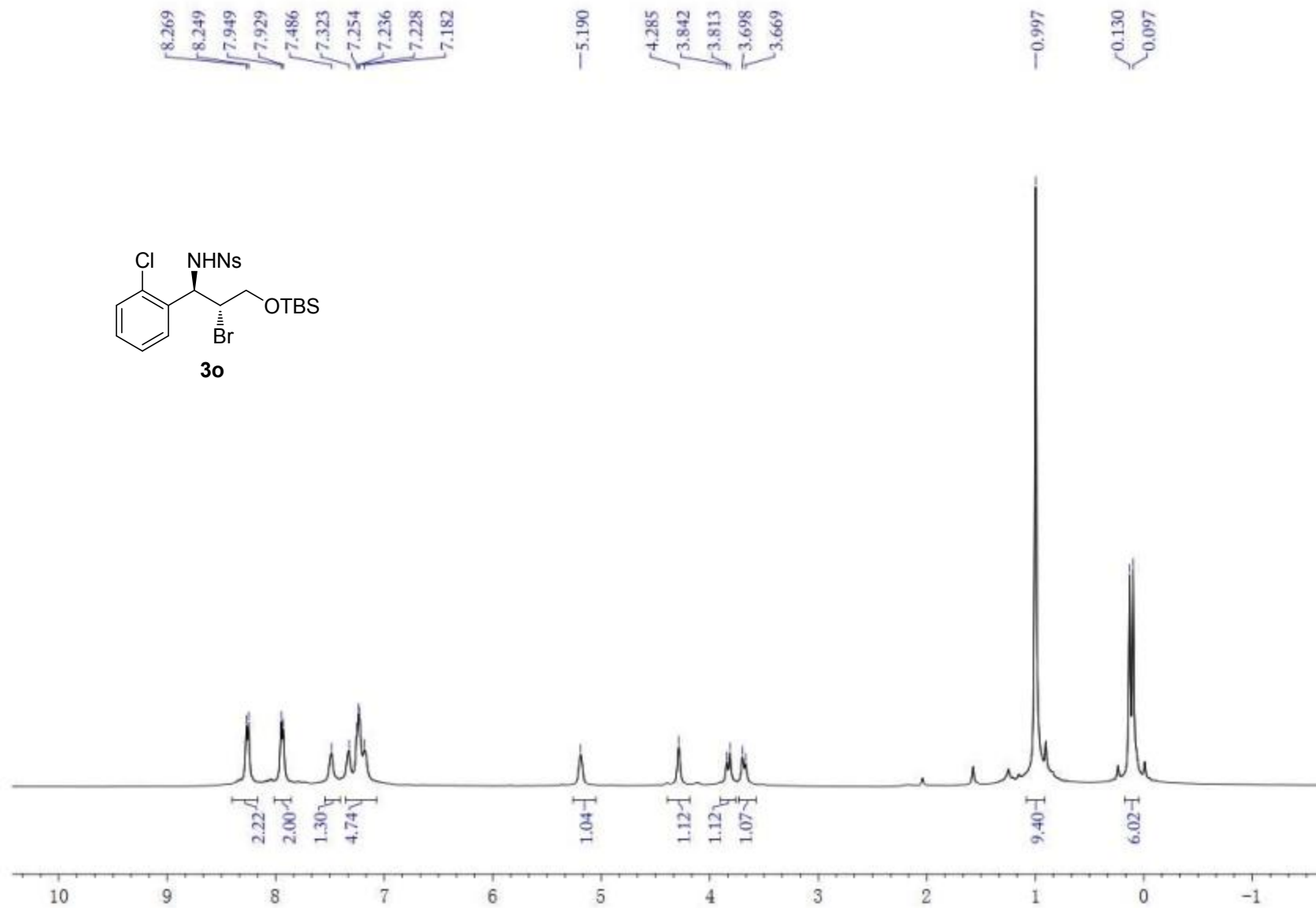
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124.00

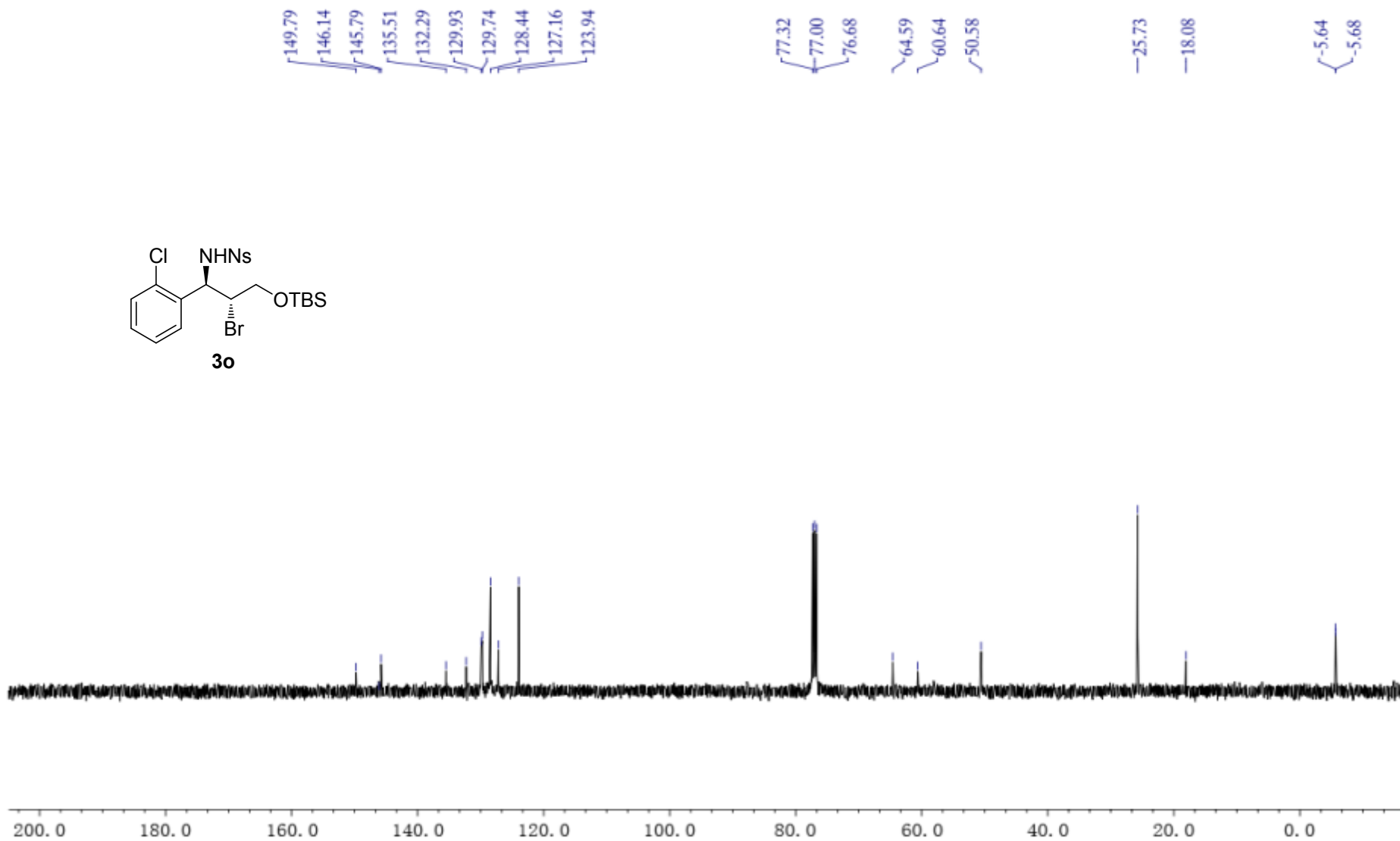
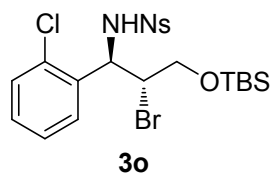
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76.68  
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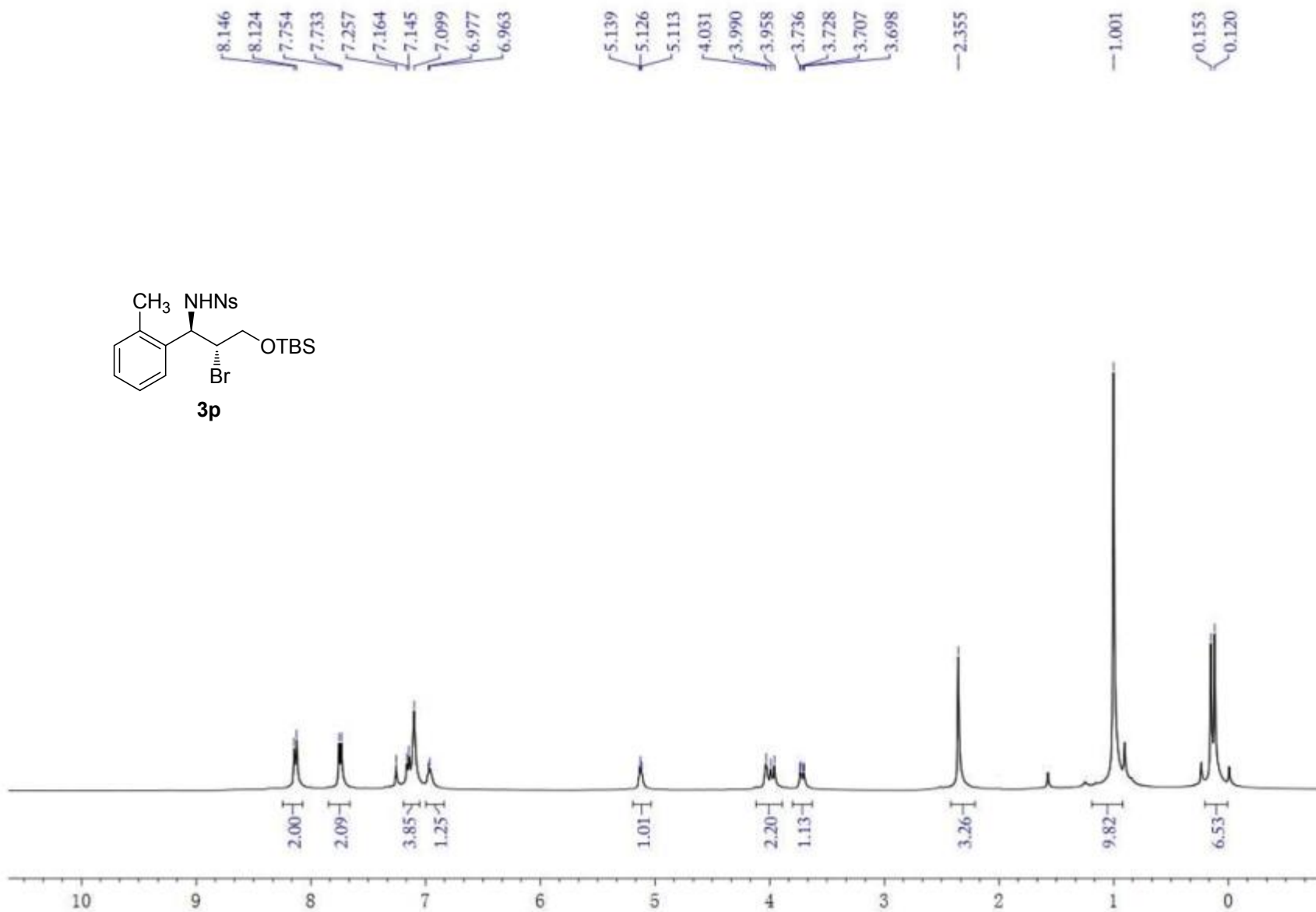
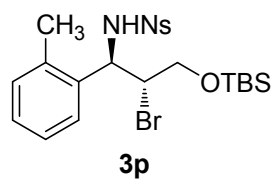
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-5.56  
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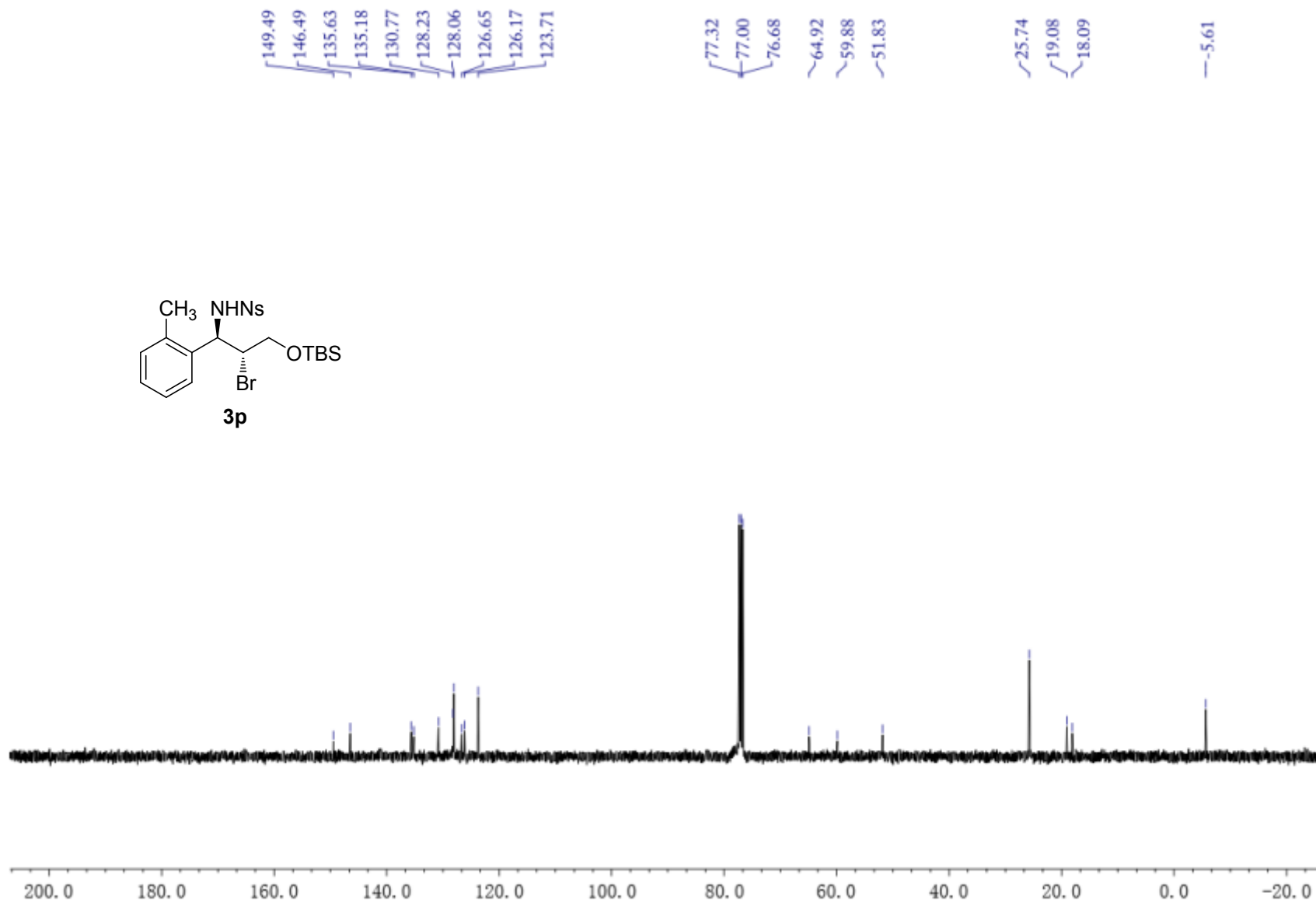
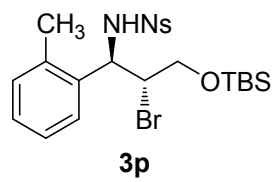


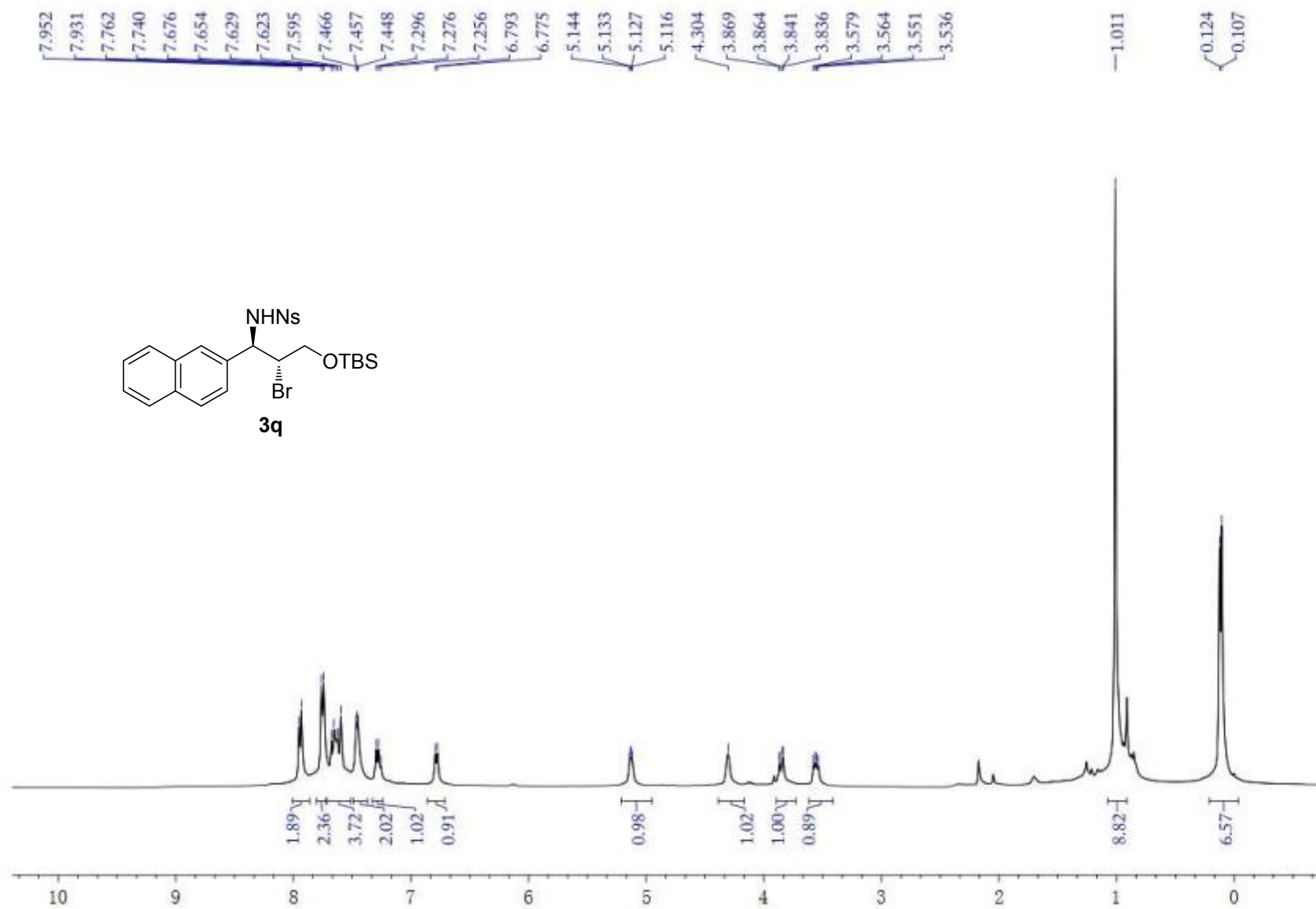


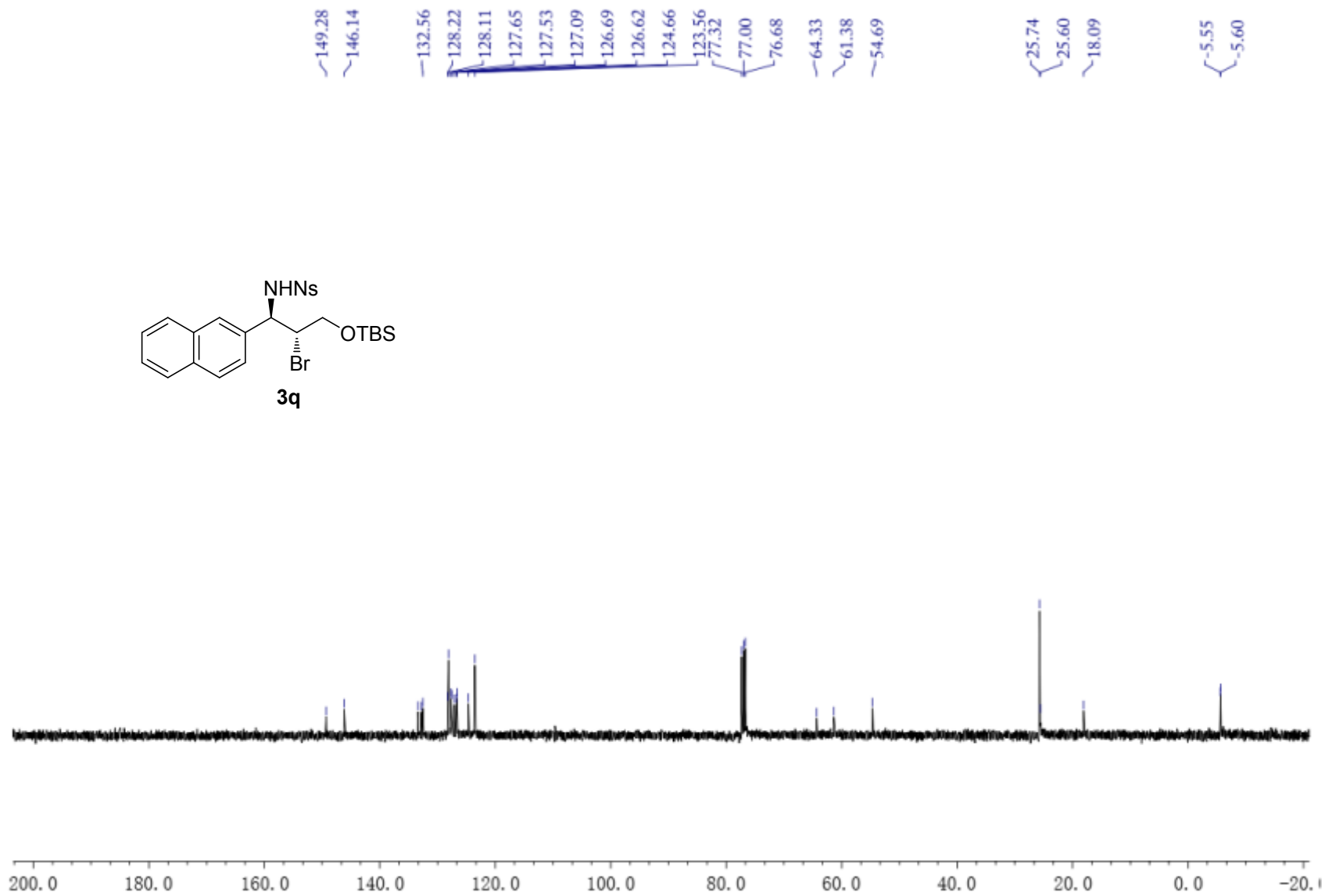
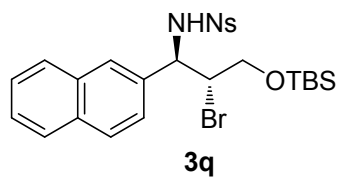


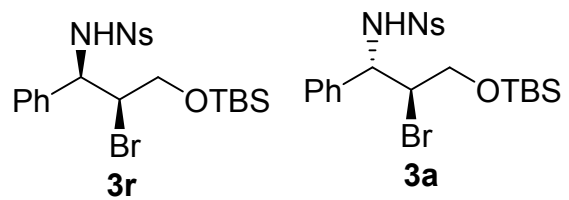




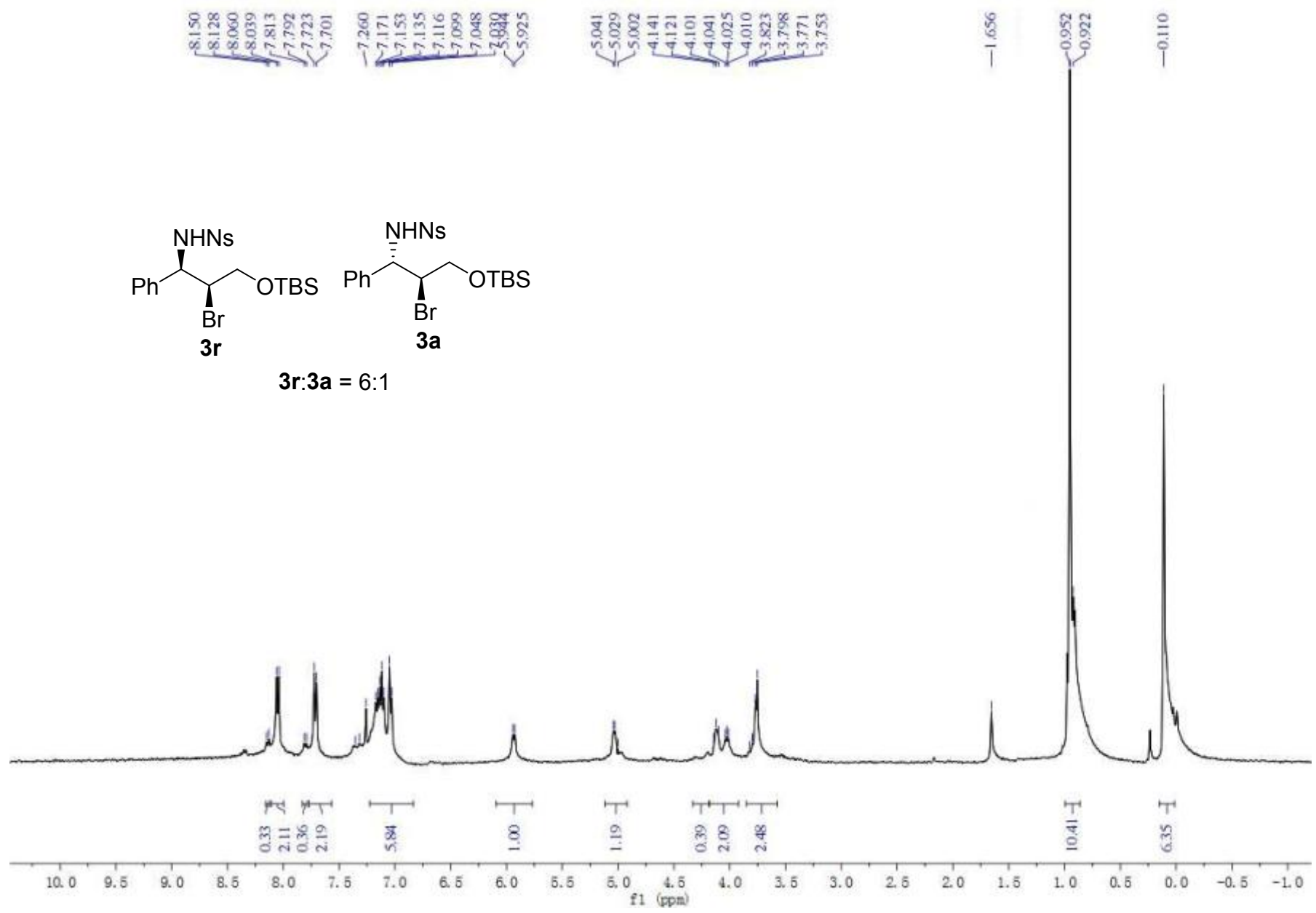








**3r:3a = 6:1**



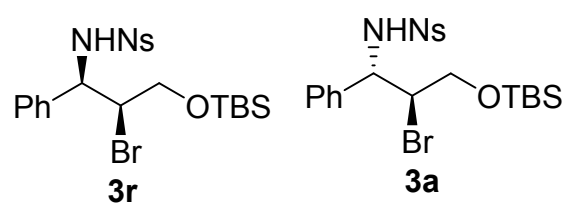
— 149.540  
— 146.196  
— 136.221  
128.242  
128.193  
128.136  
127.370  
123.684

77.318  
77.000  
76.682

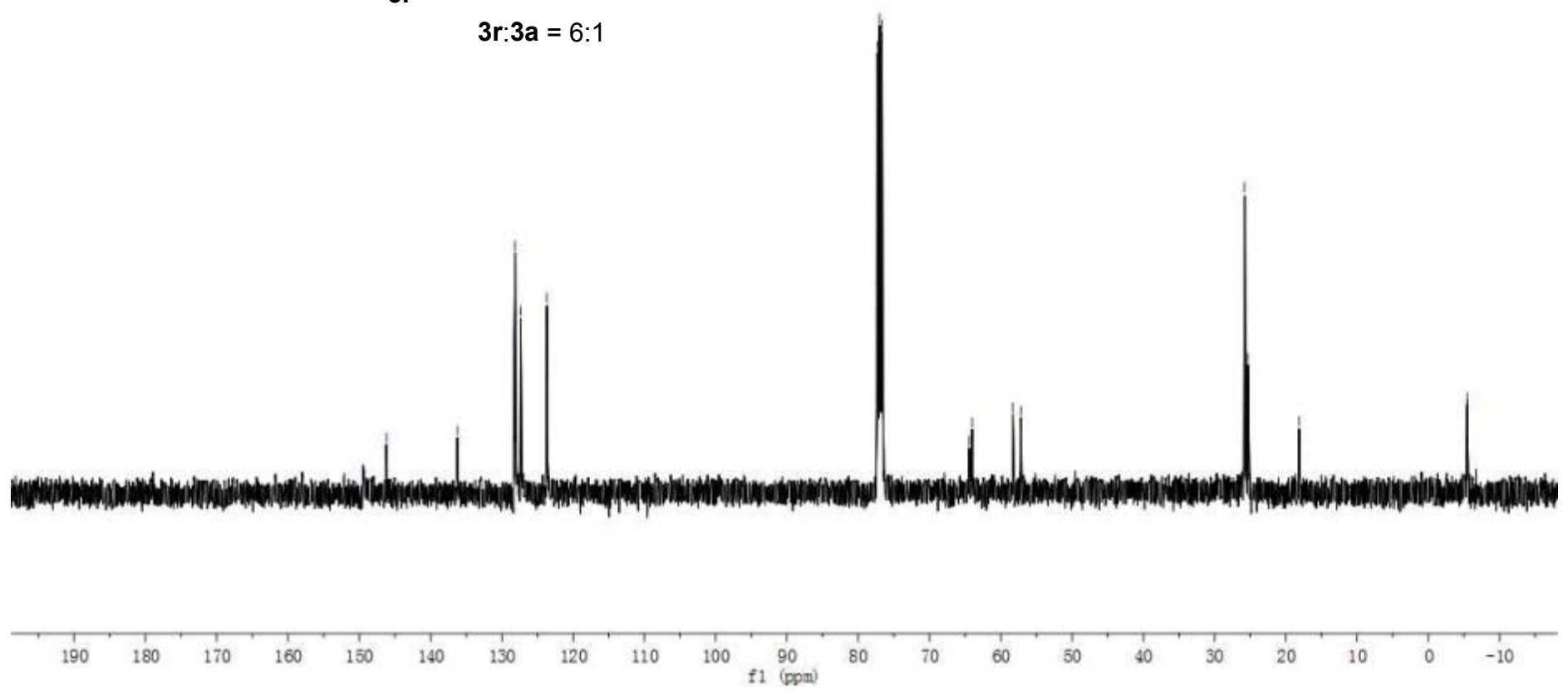
64.434  
64.023  
58.309  
57.178

25.771  
25.333  
— 18.137

— 5.457  
— 5.489



**3r:3a = 6:1**

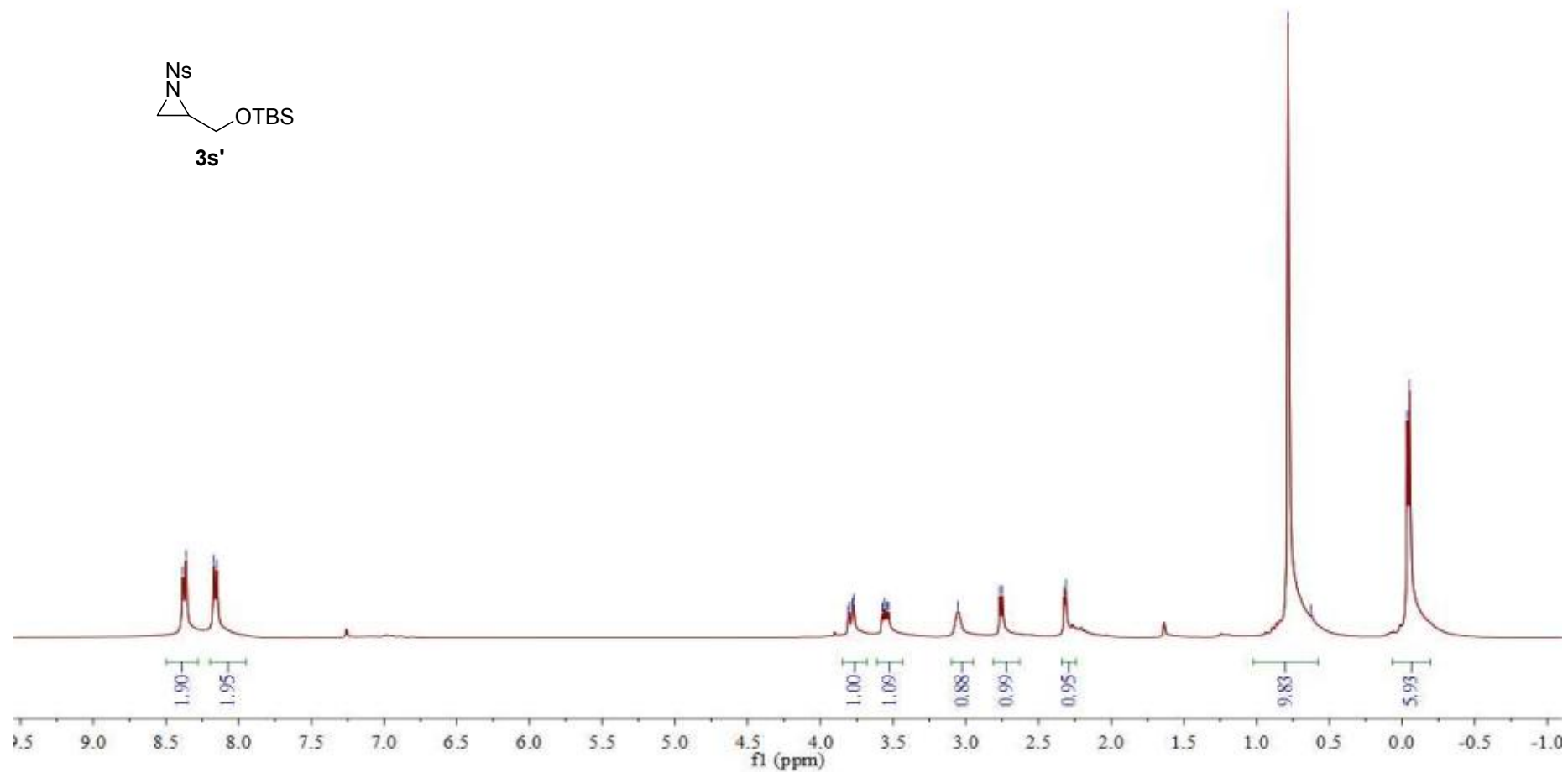
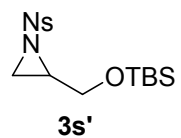


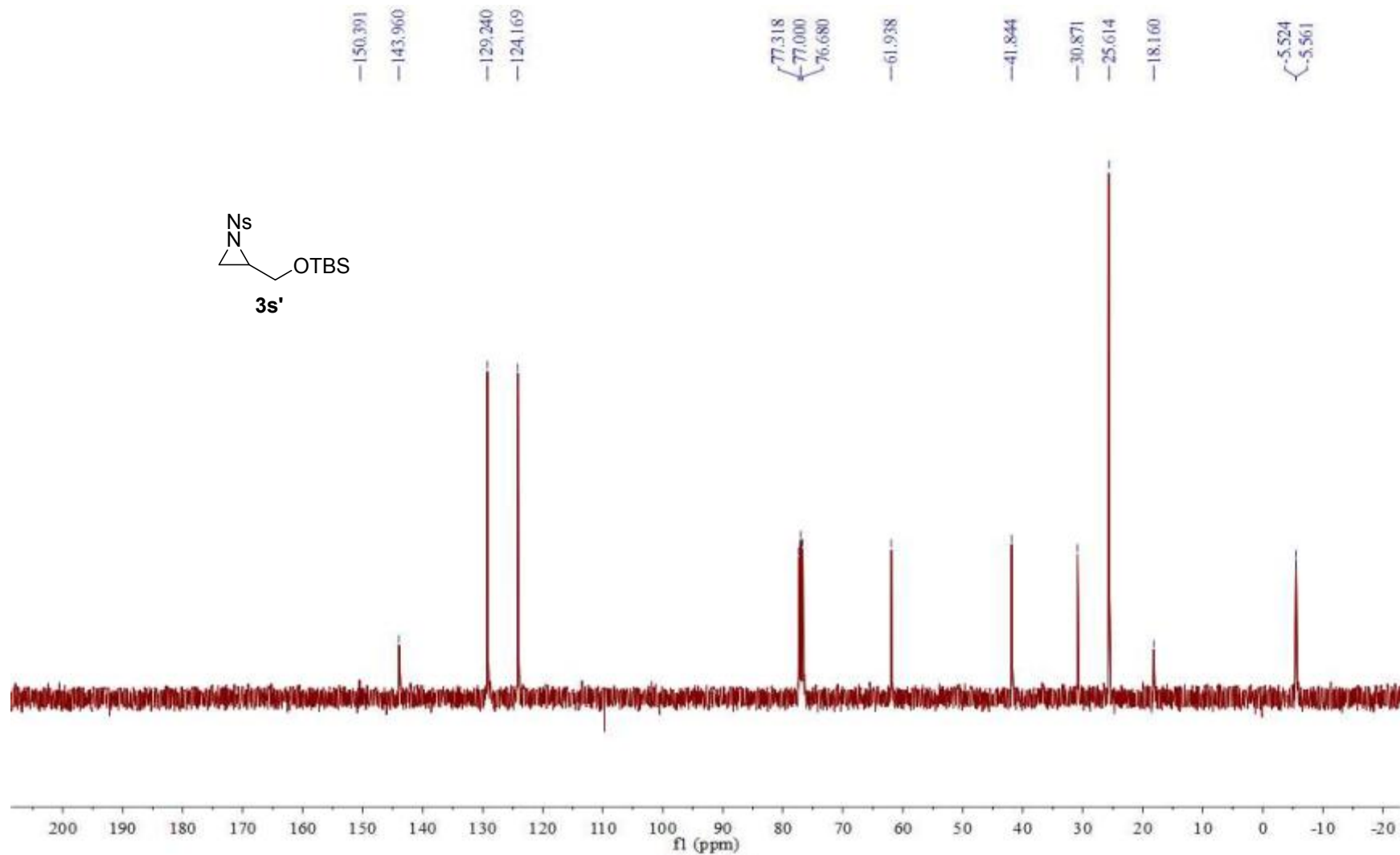
8.384  
8.363  
8.171  
8.150

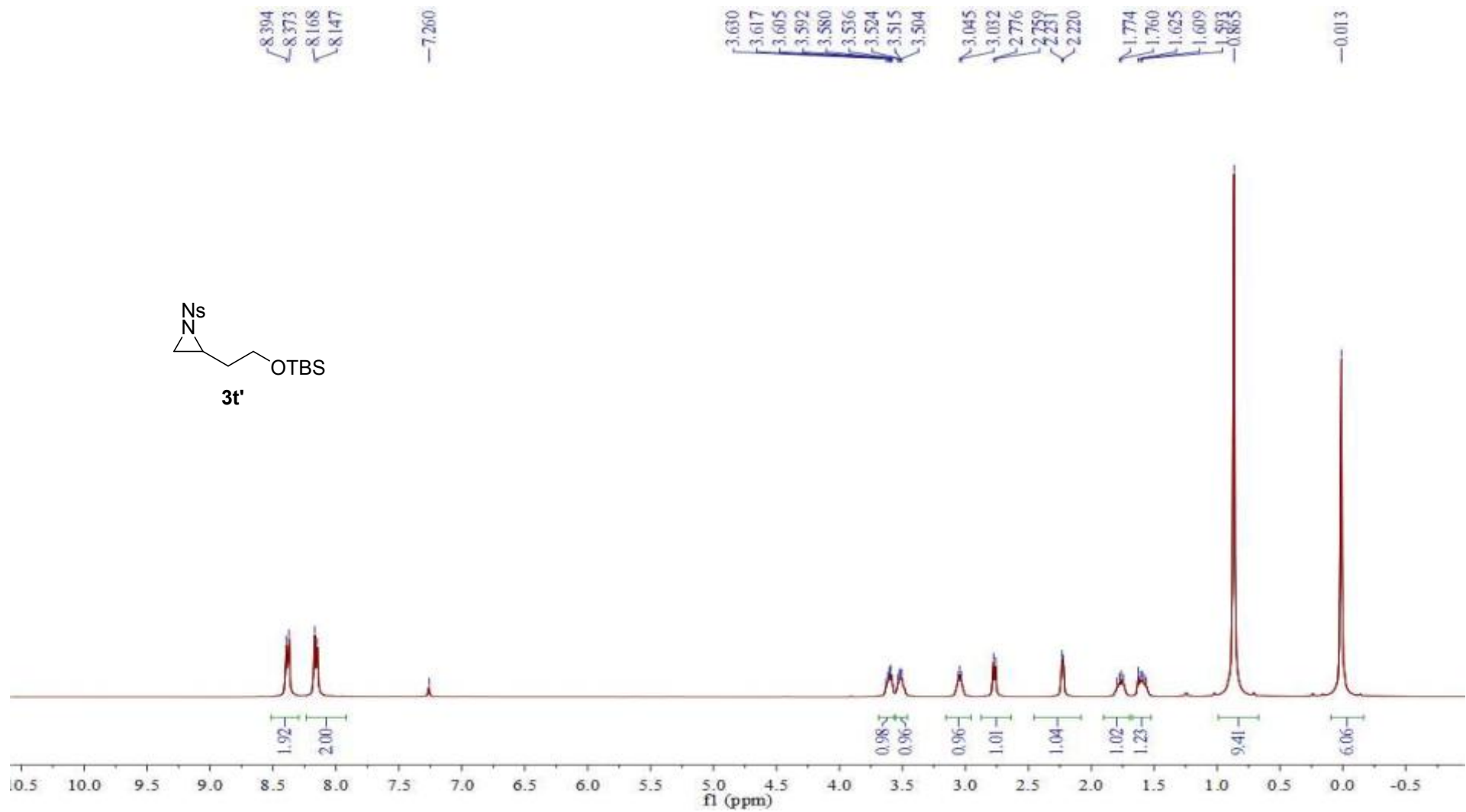
3.808  
3.801  
3.779  
3.771  
3.574  
3.560  
3.545  
3.531  
3.053  
2.766  
2.748  
2.324  
2.313

-0.784  
-0.626

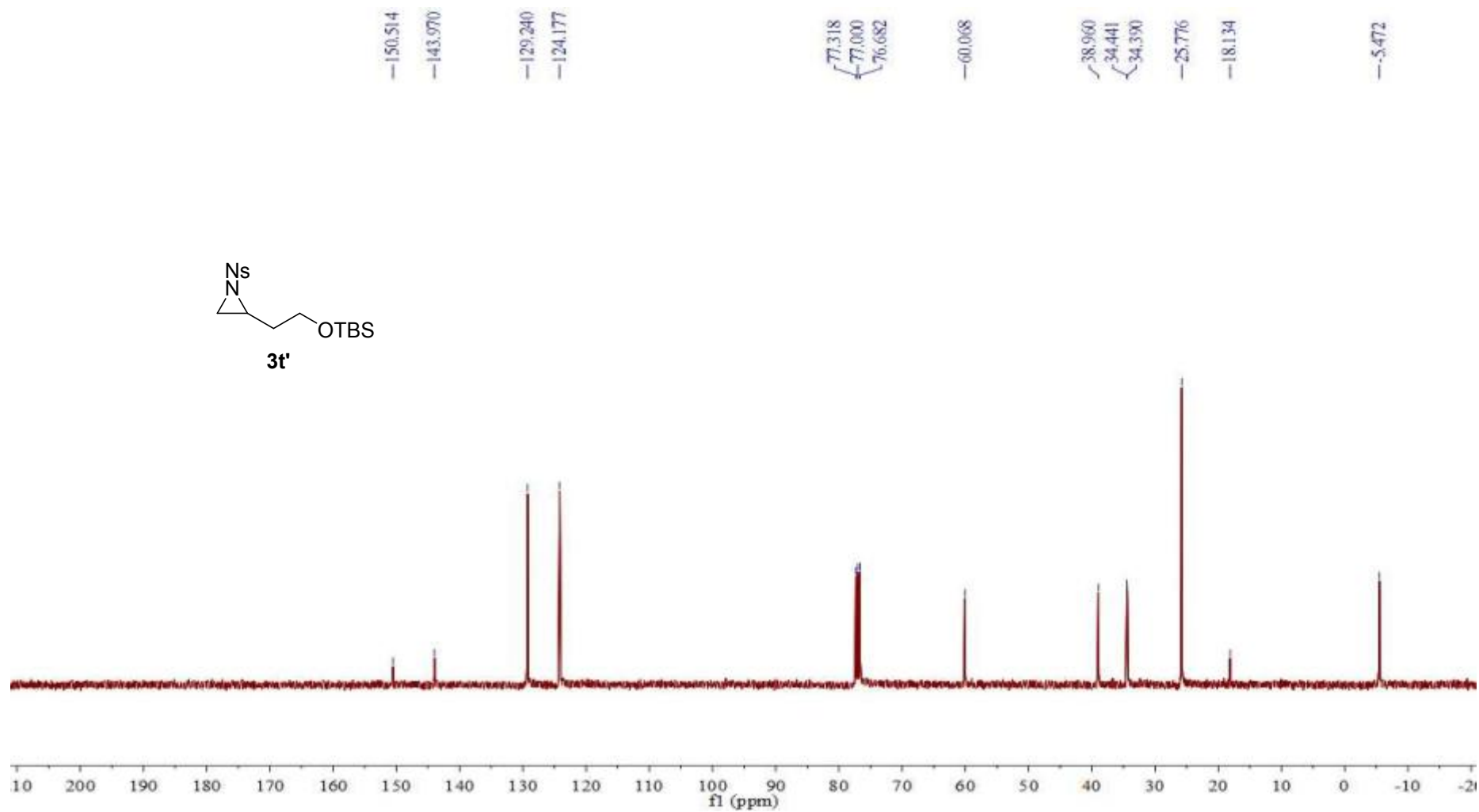
-0.035  
-0.051

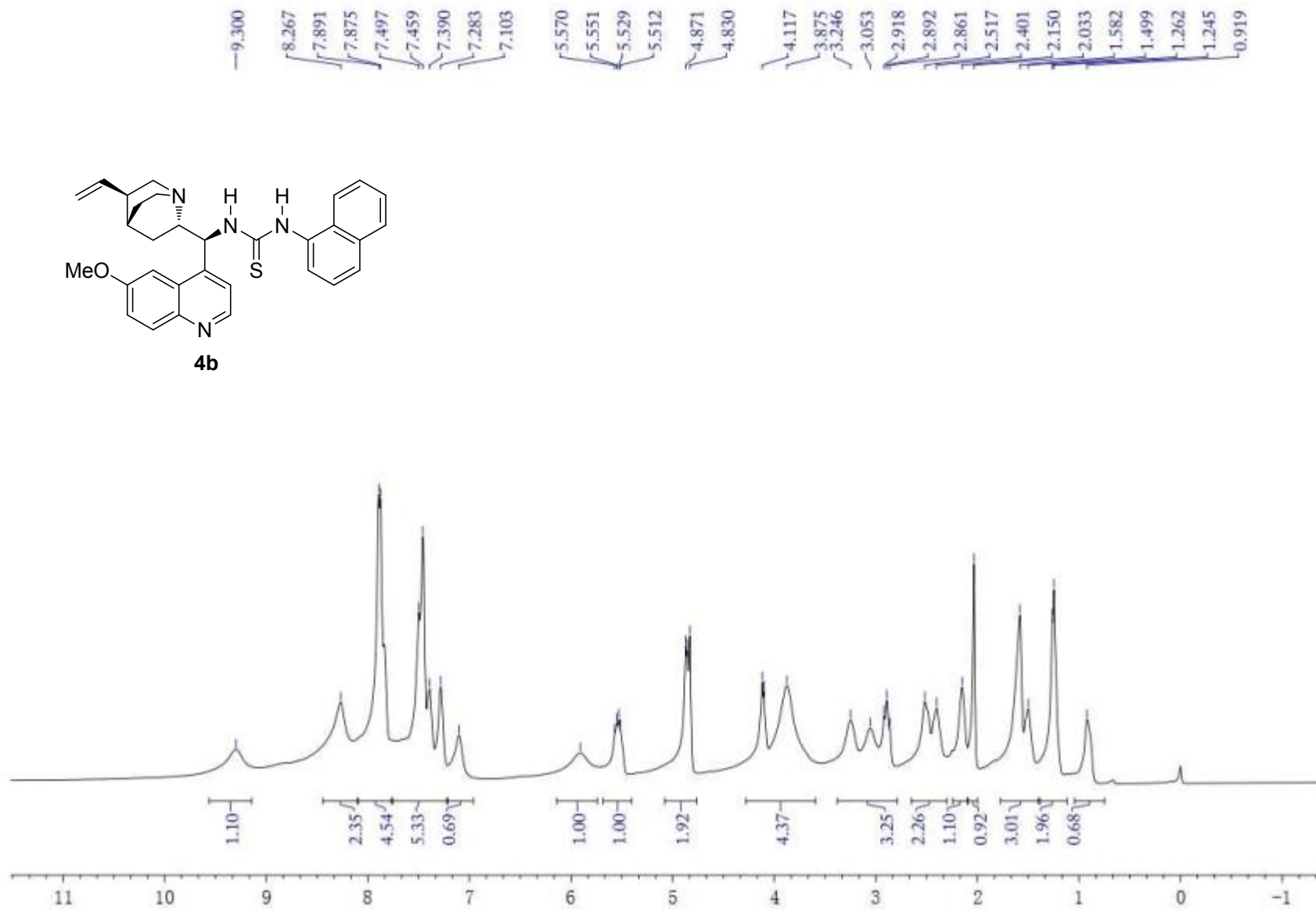
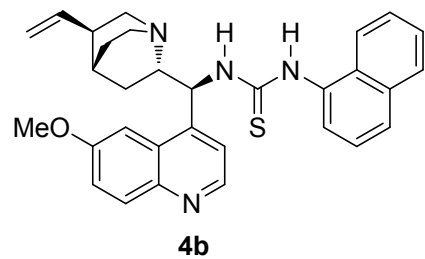


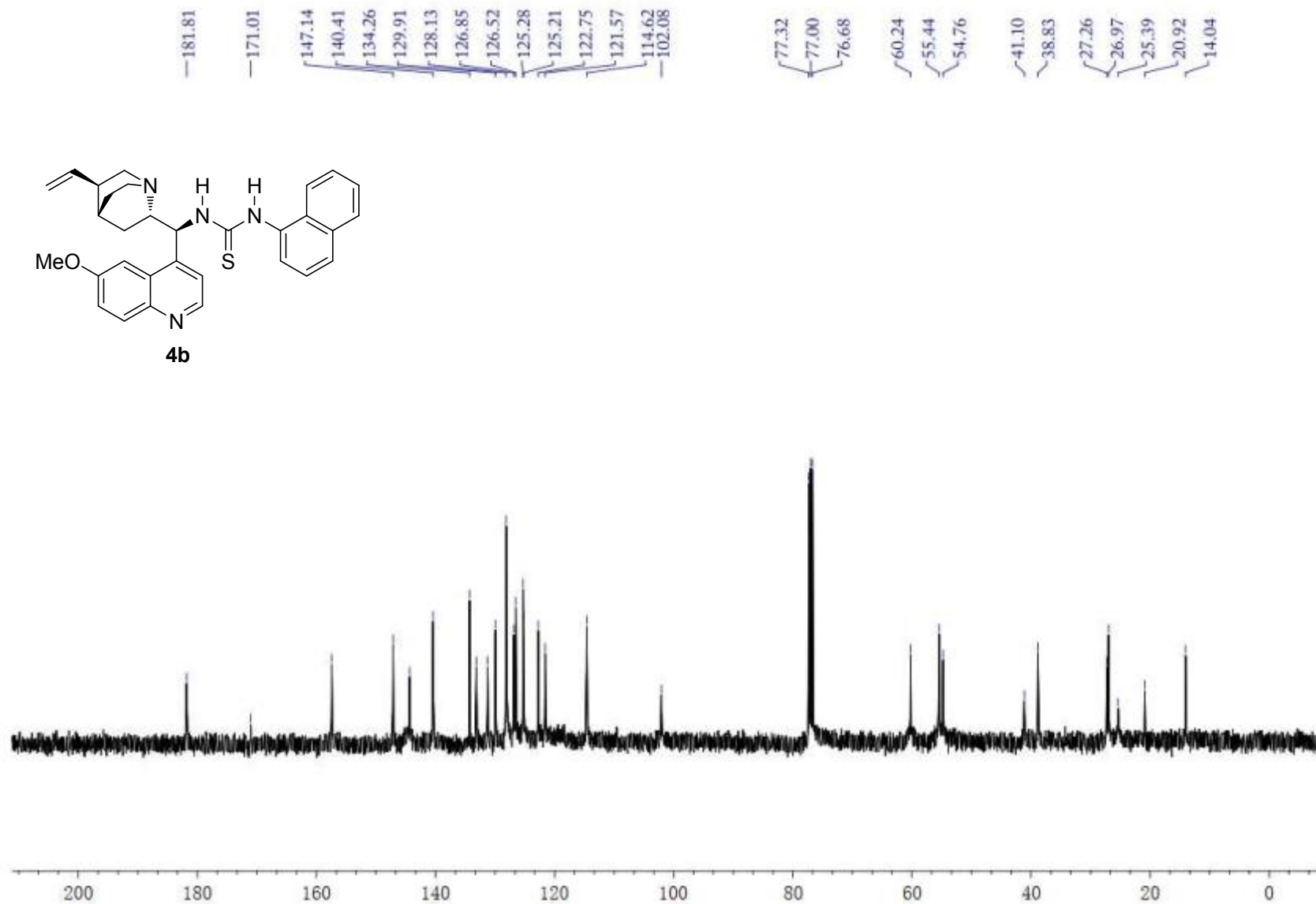
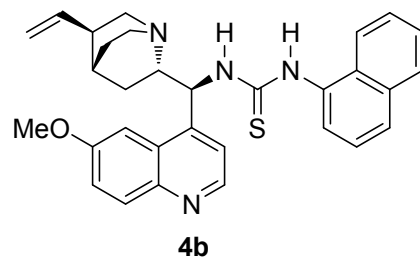


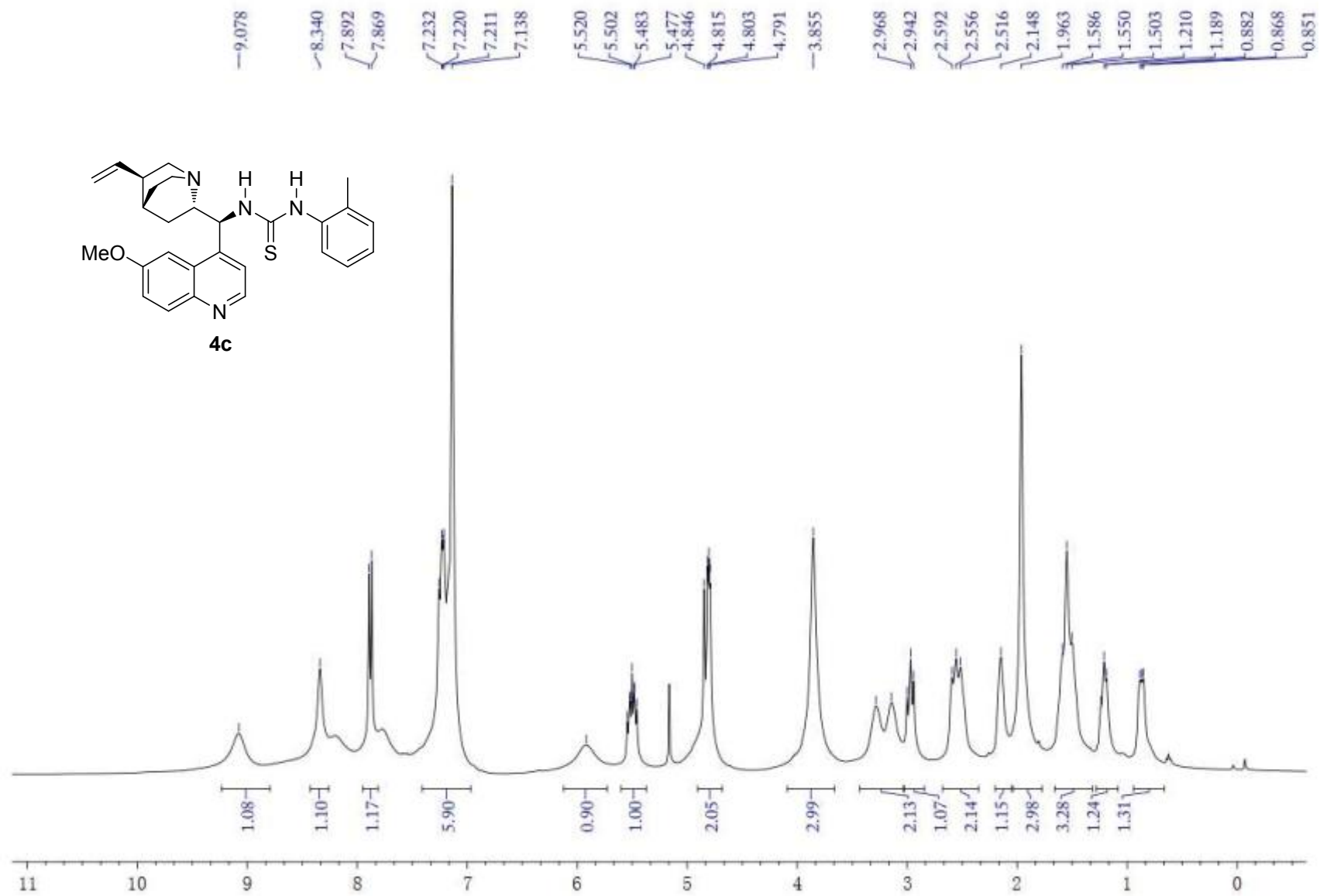


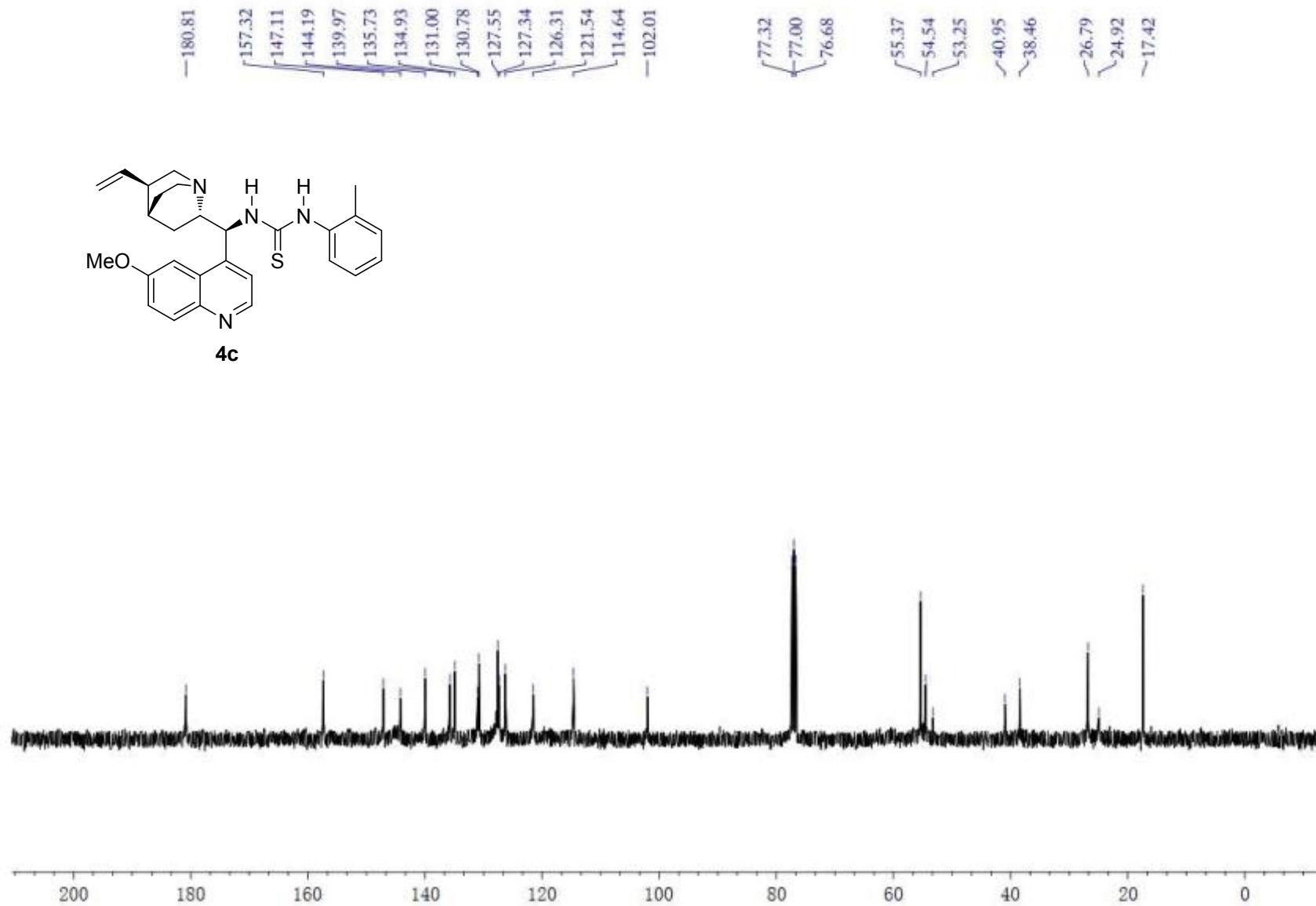
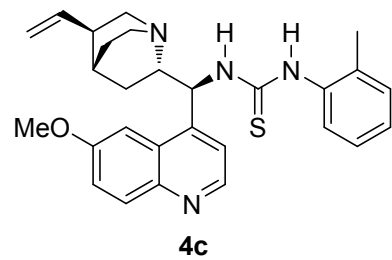


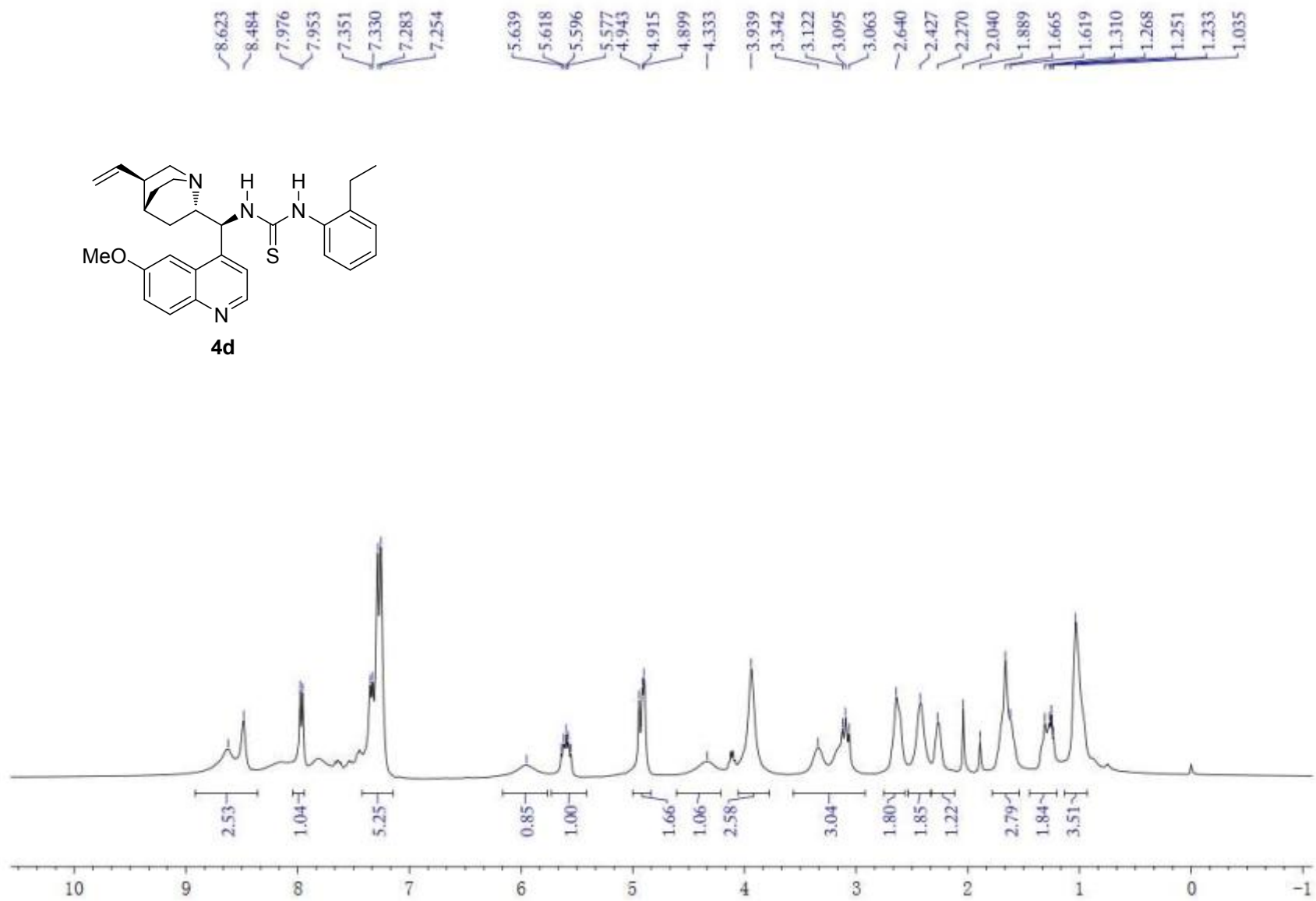
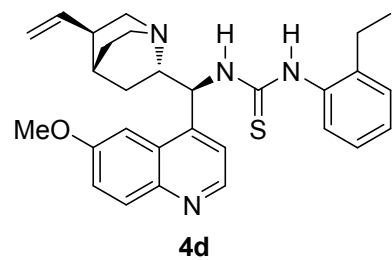


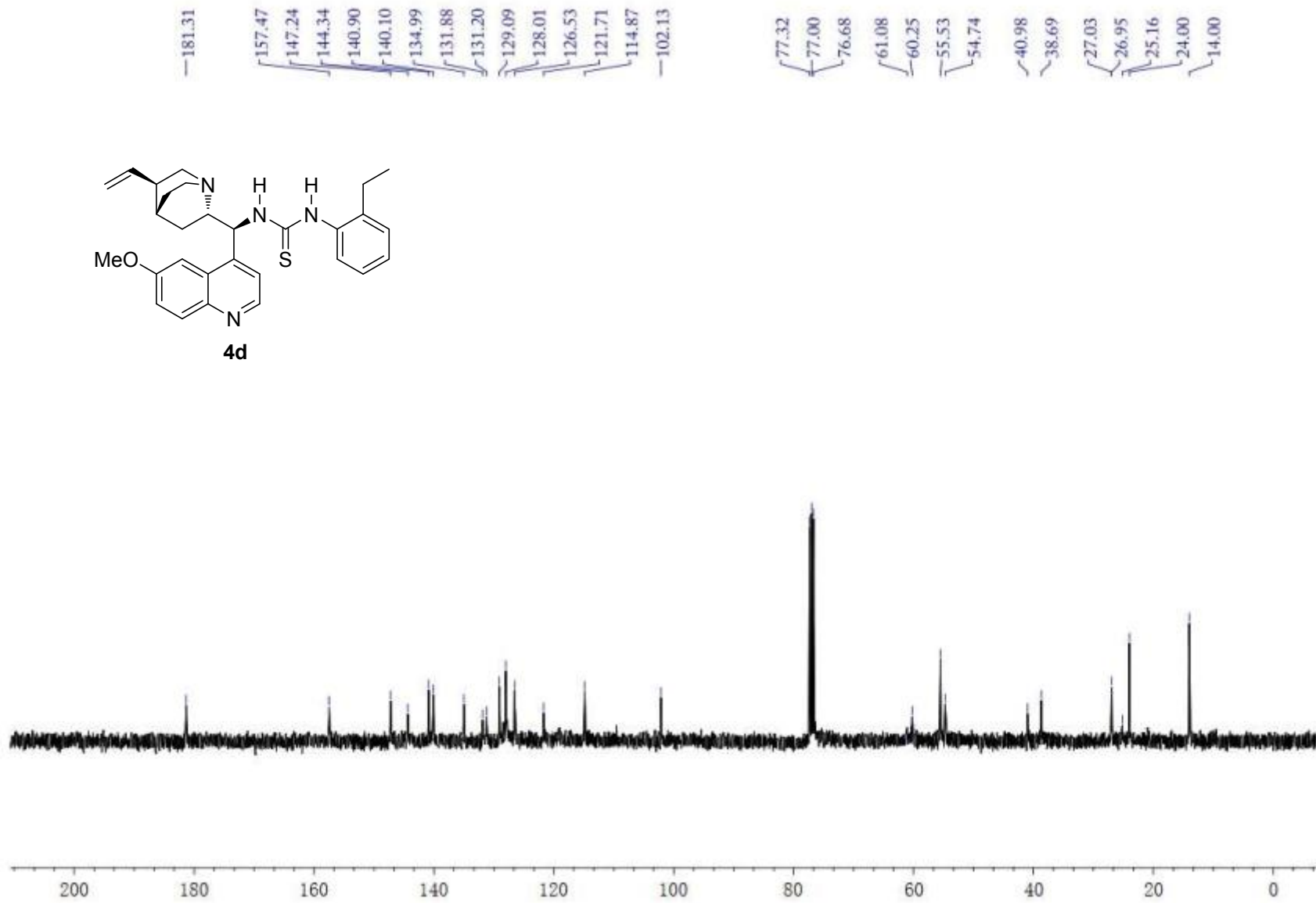


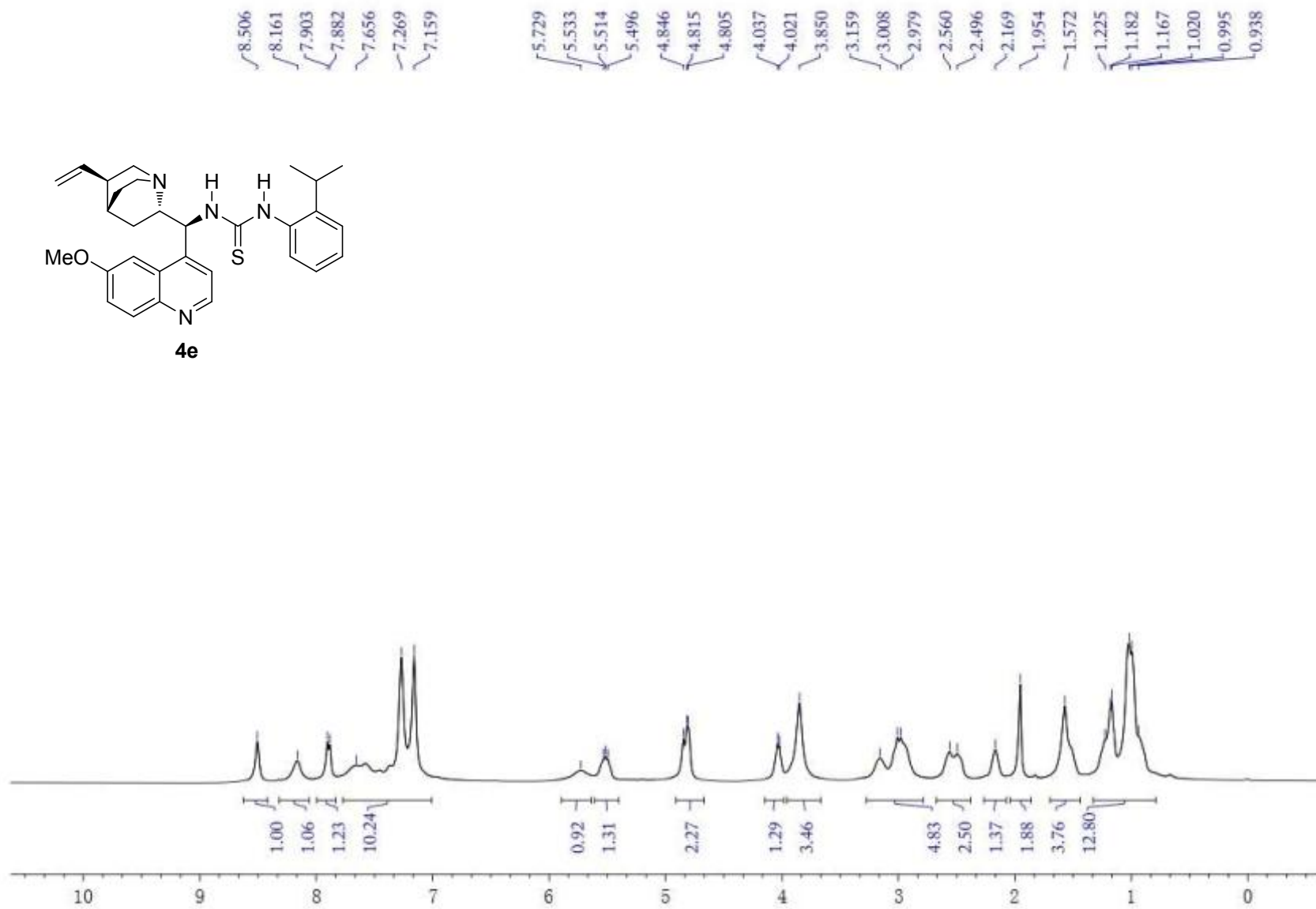
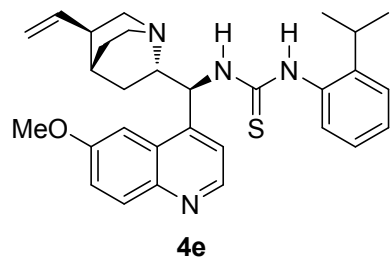




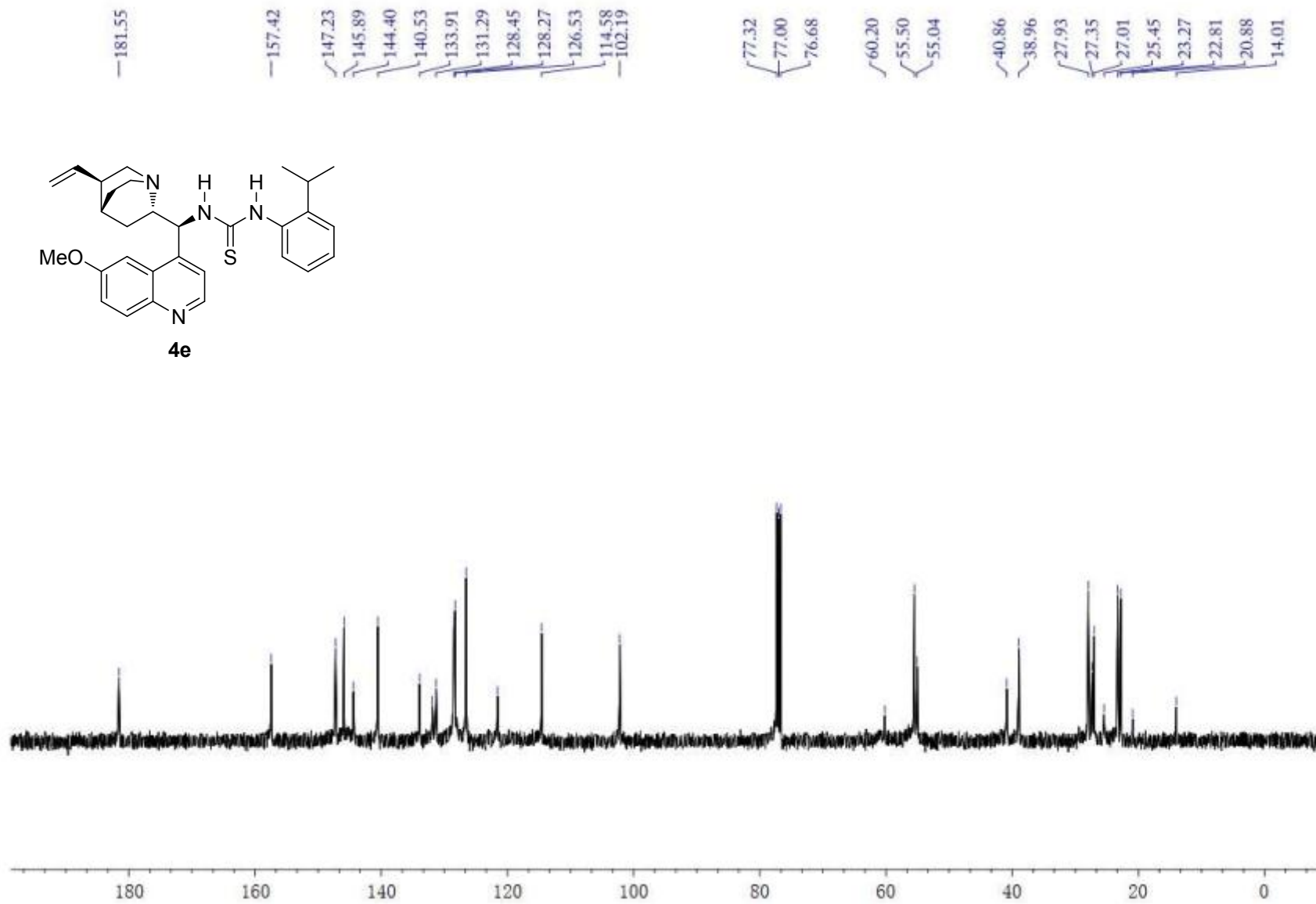


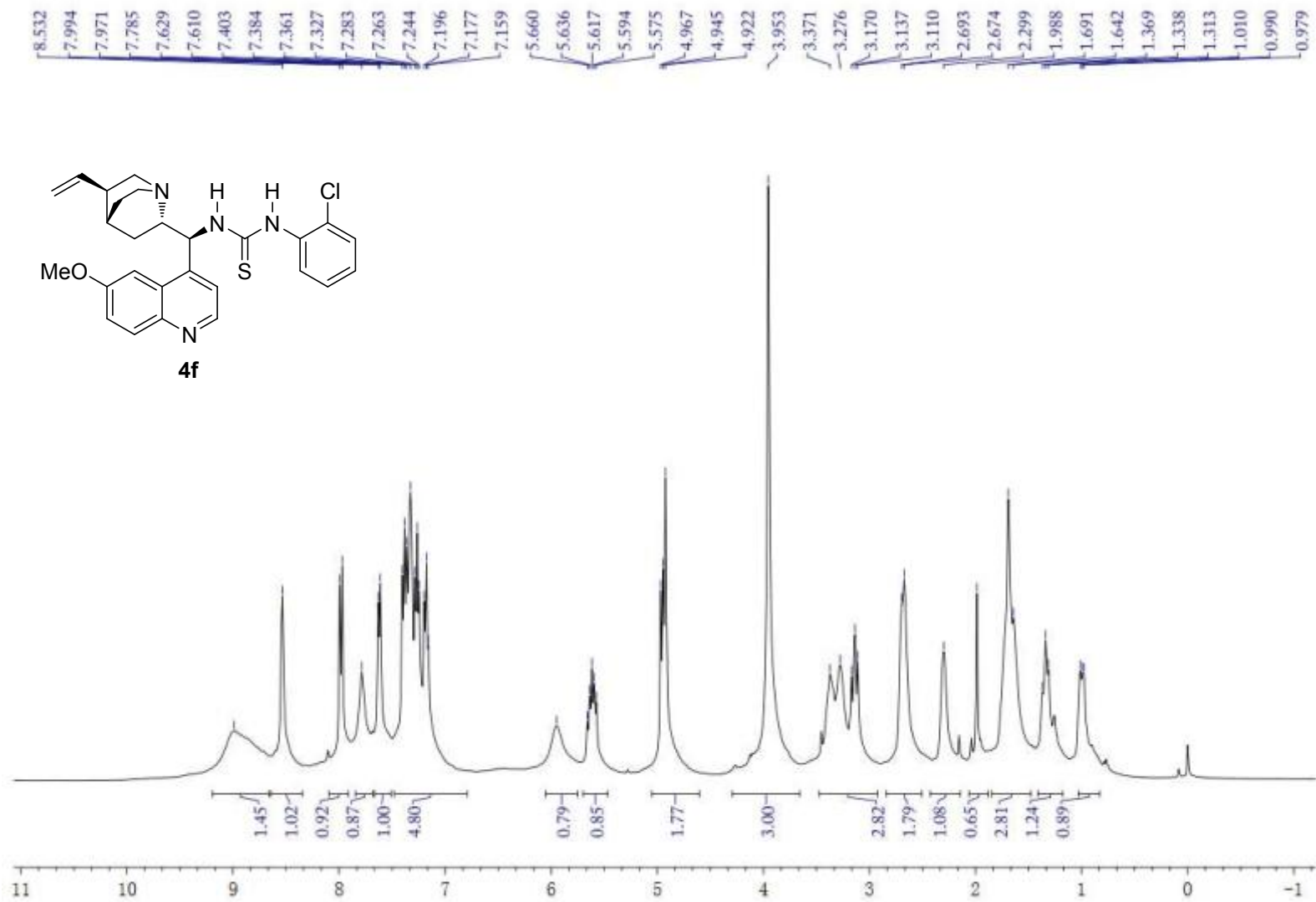


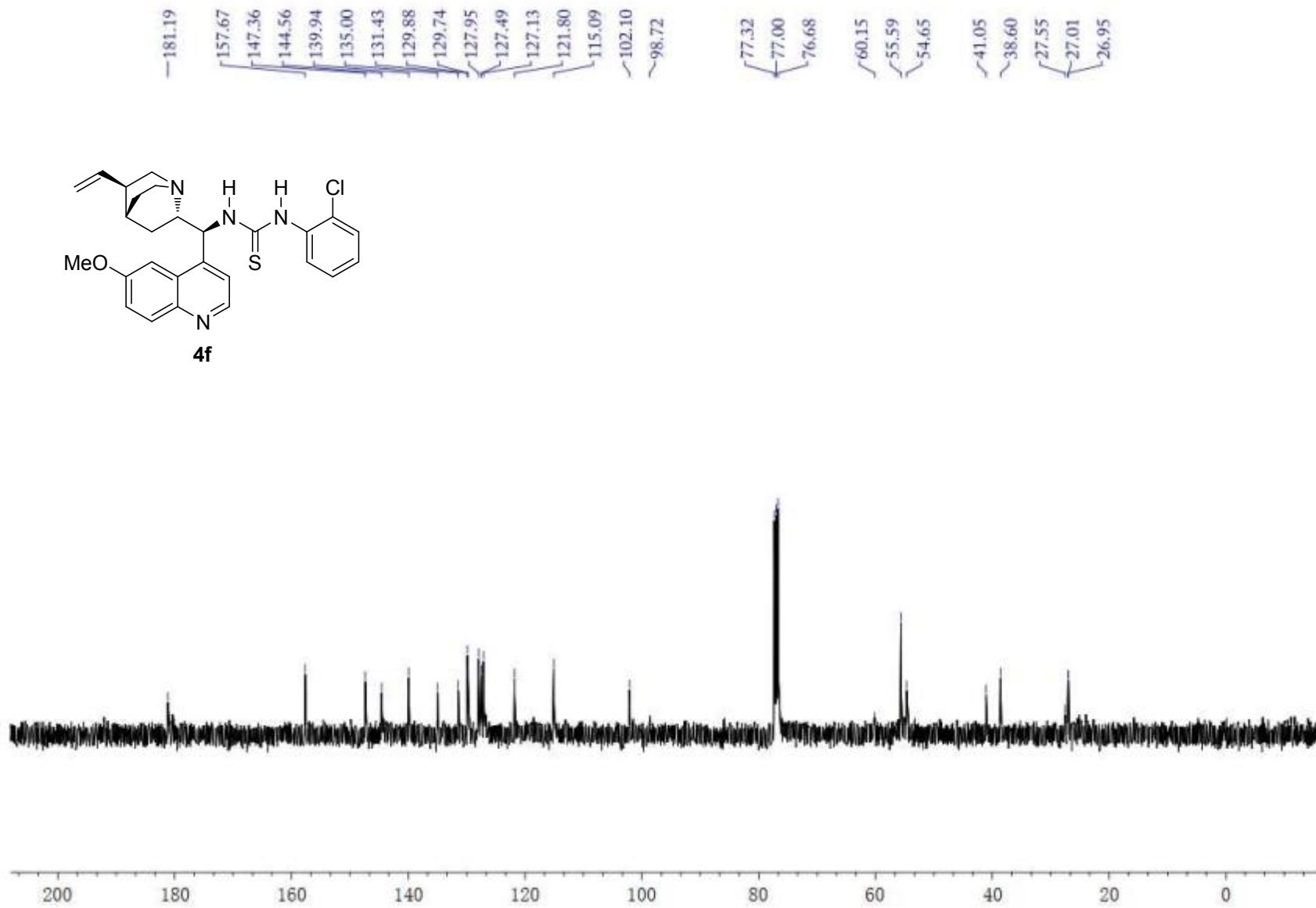
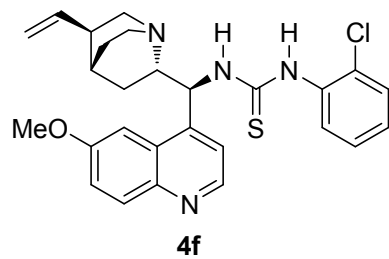


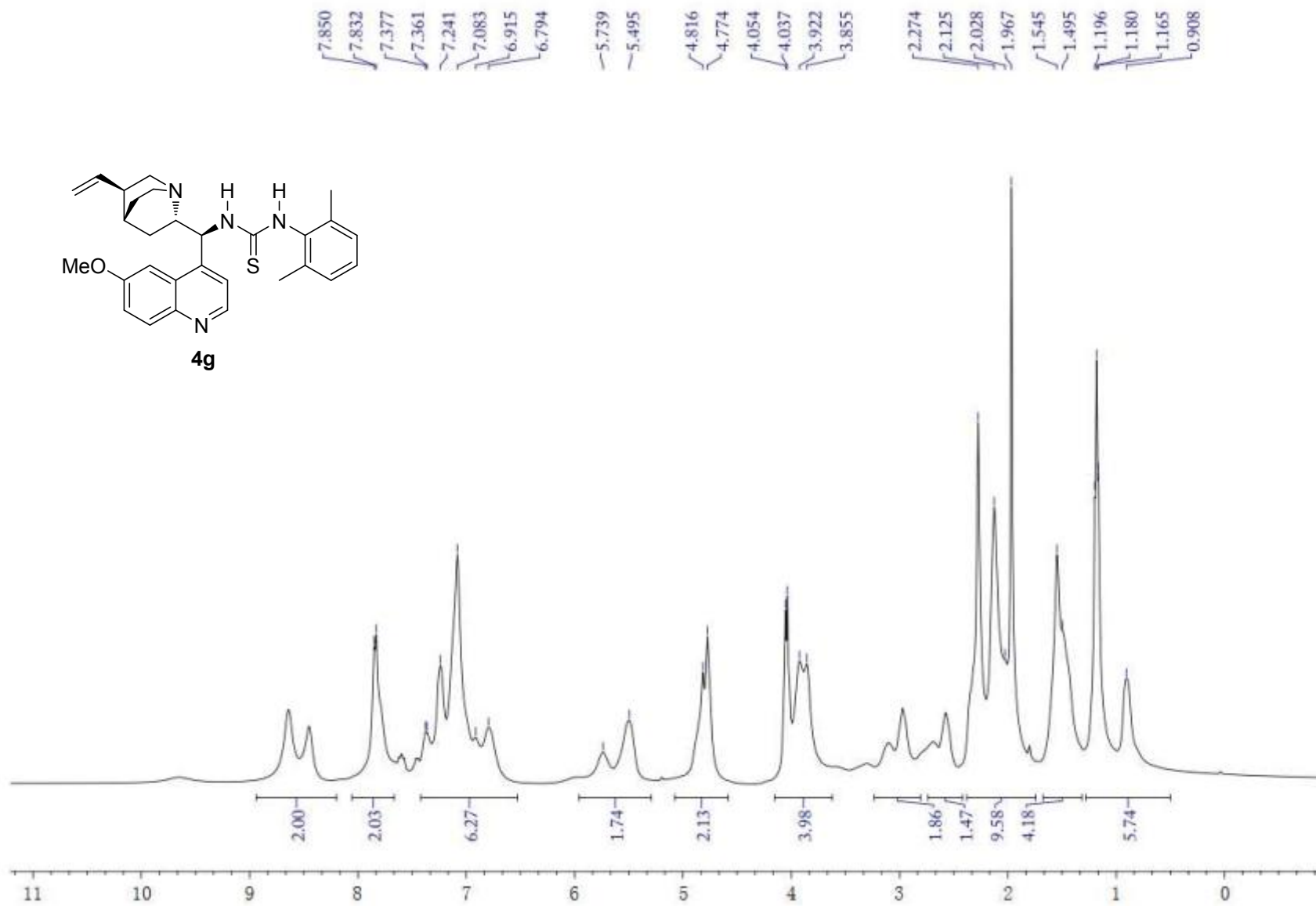
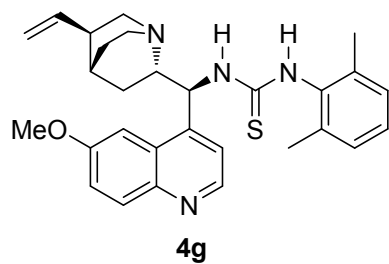


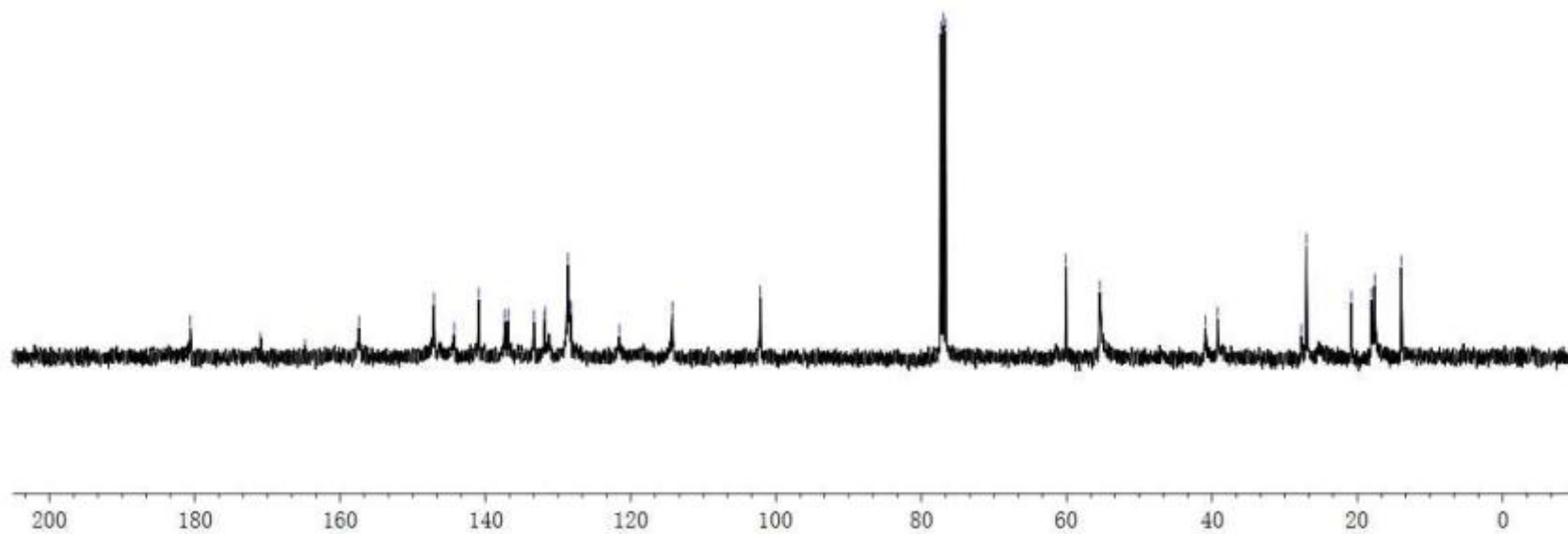
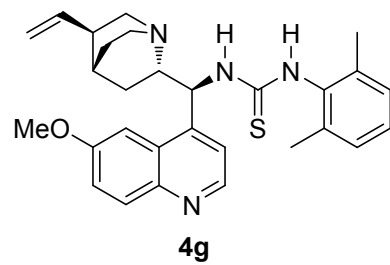


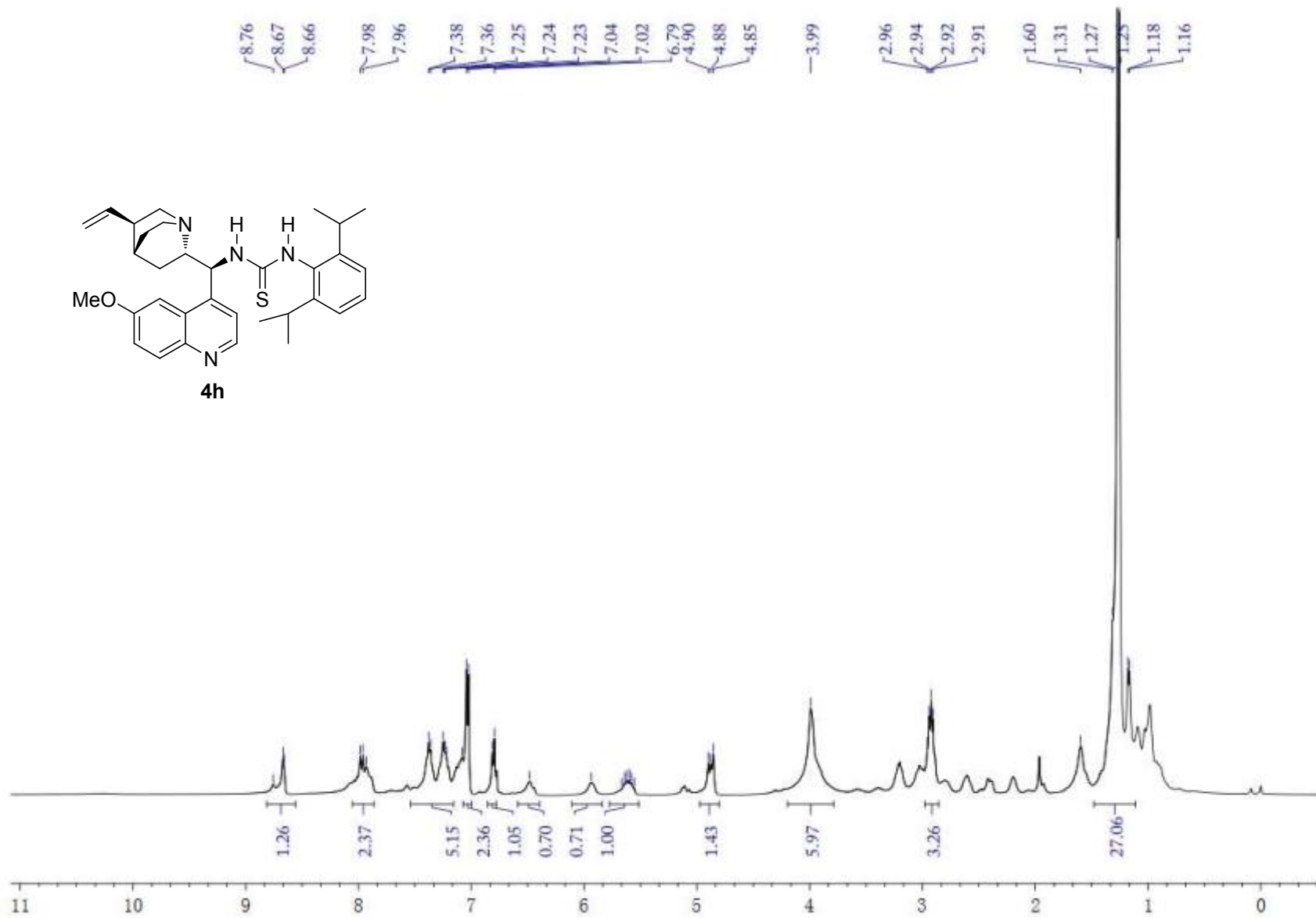


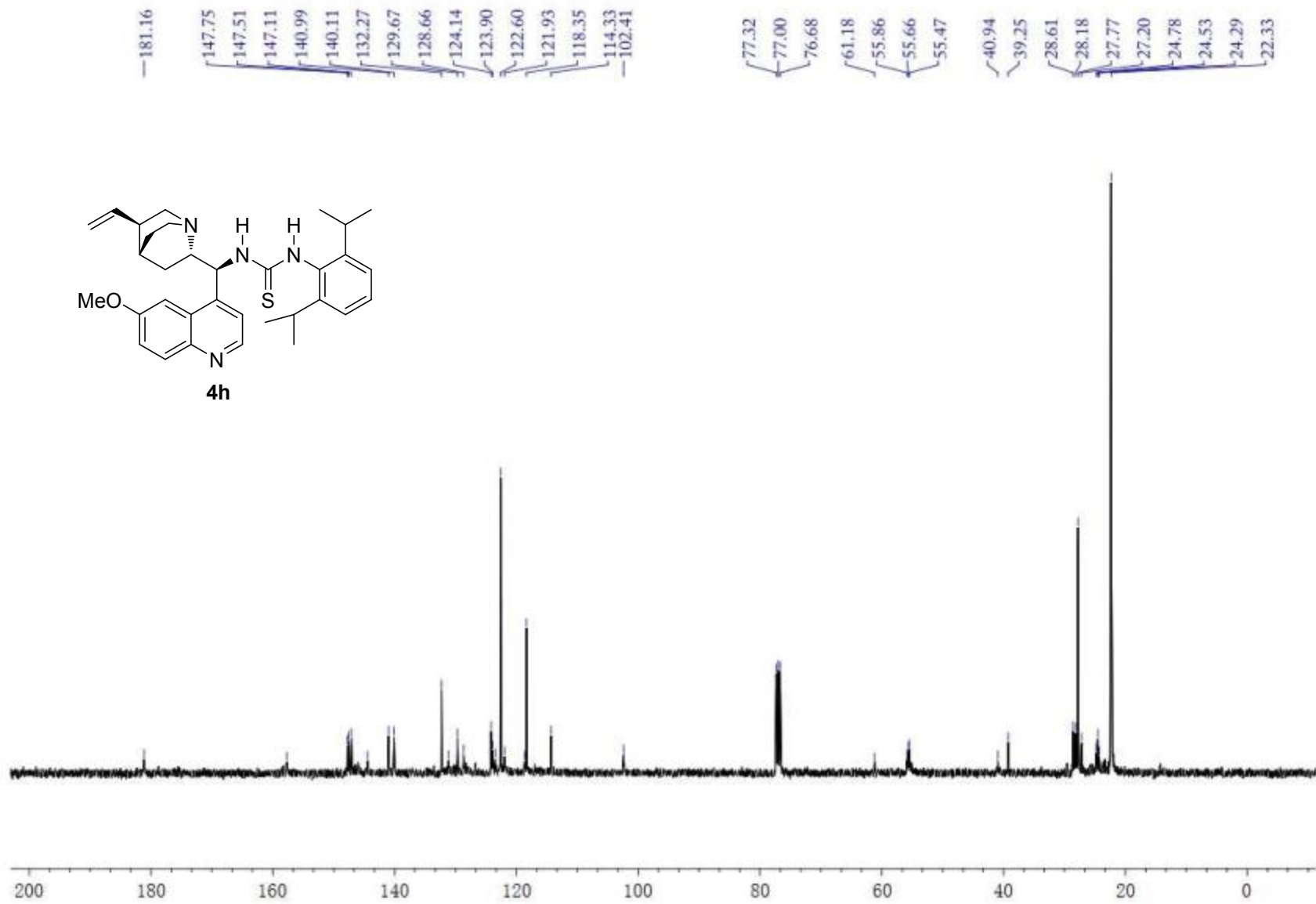


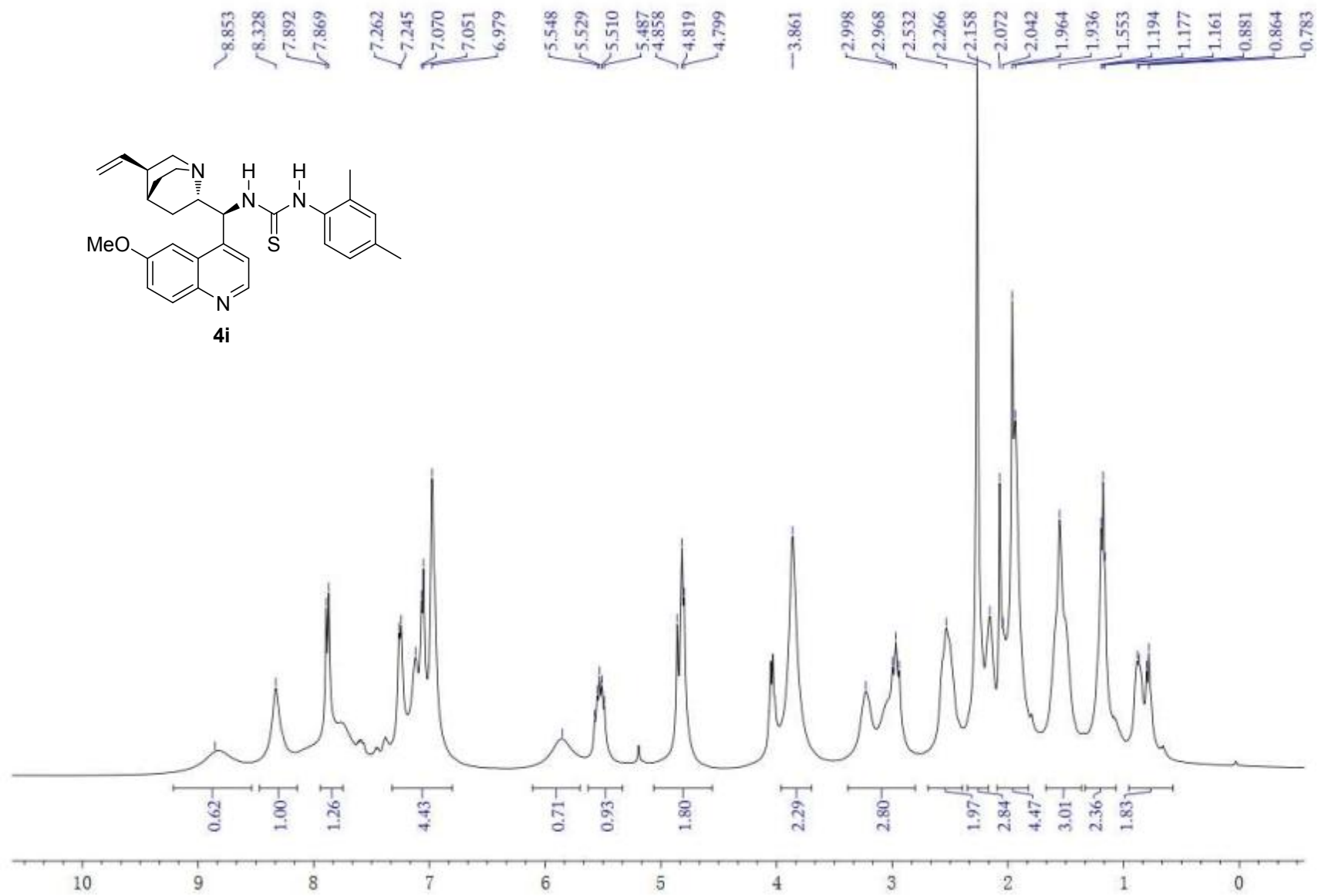




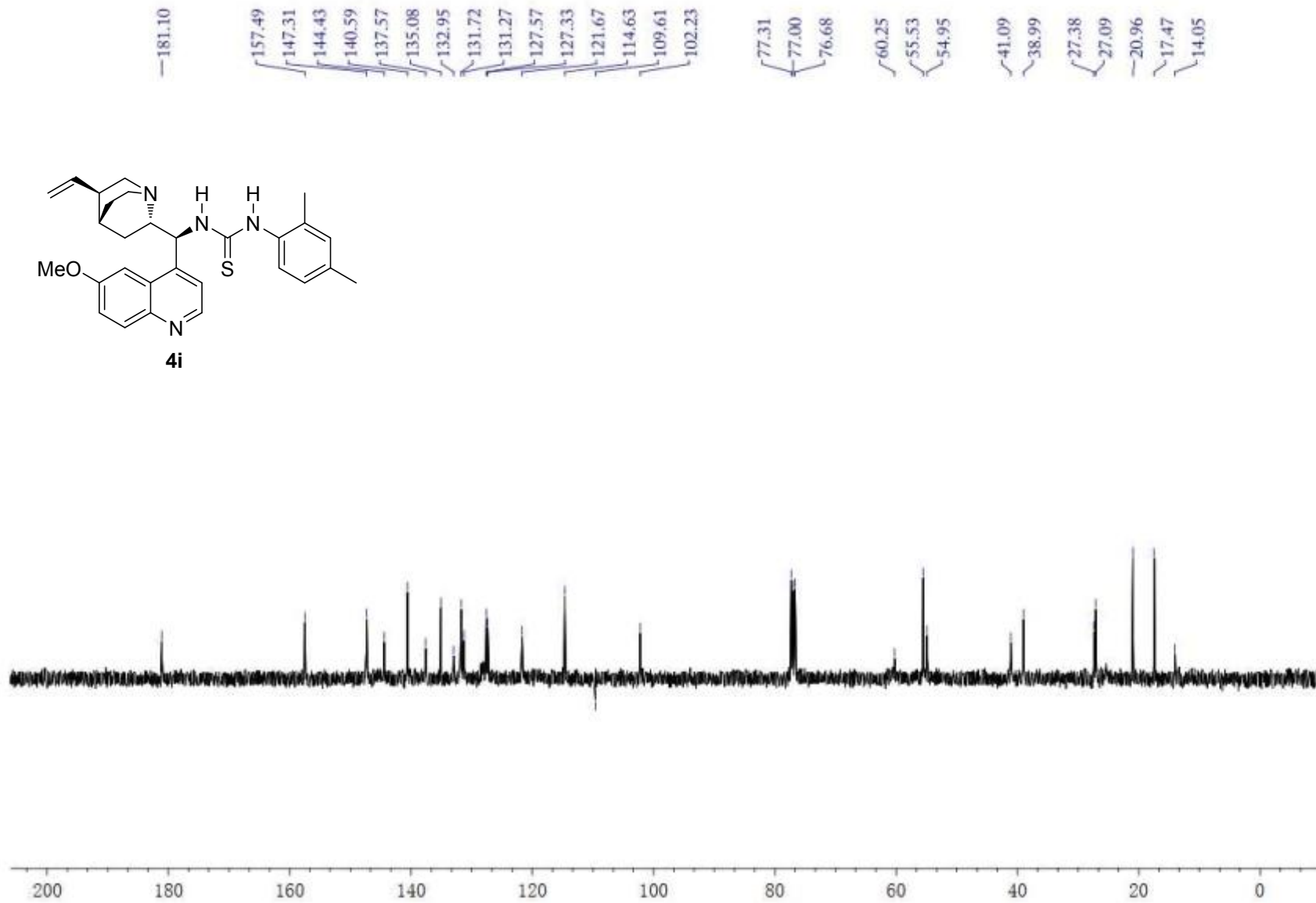


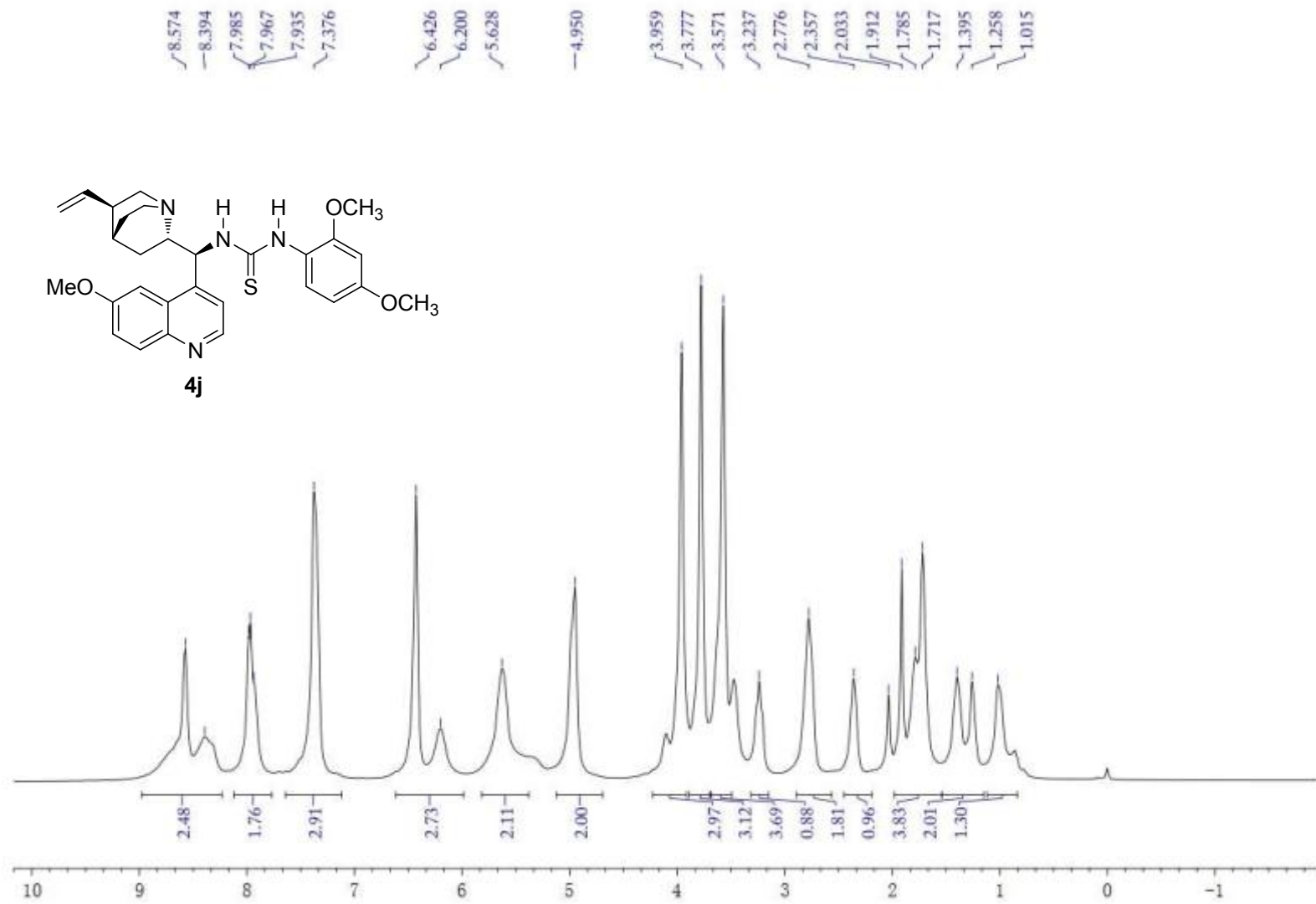


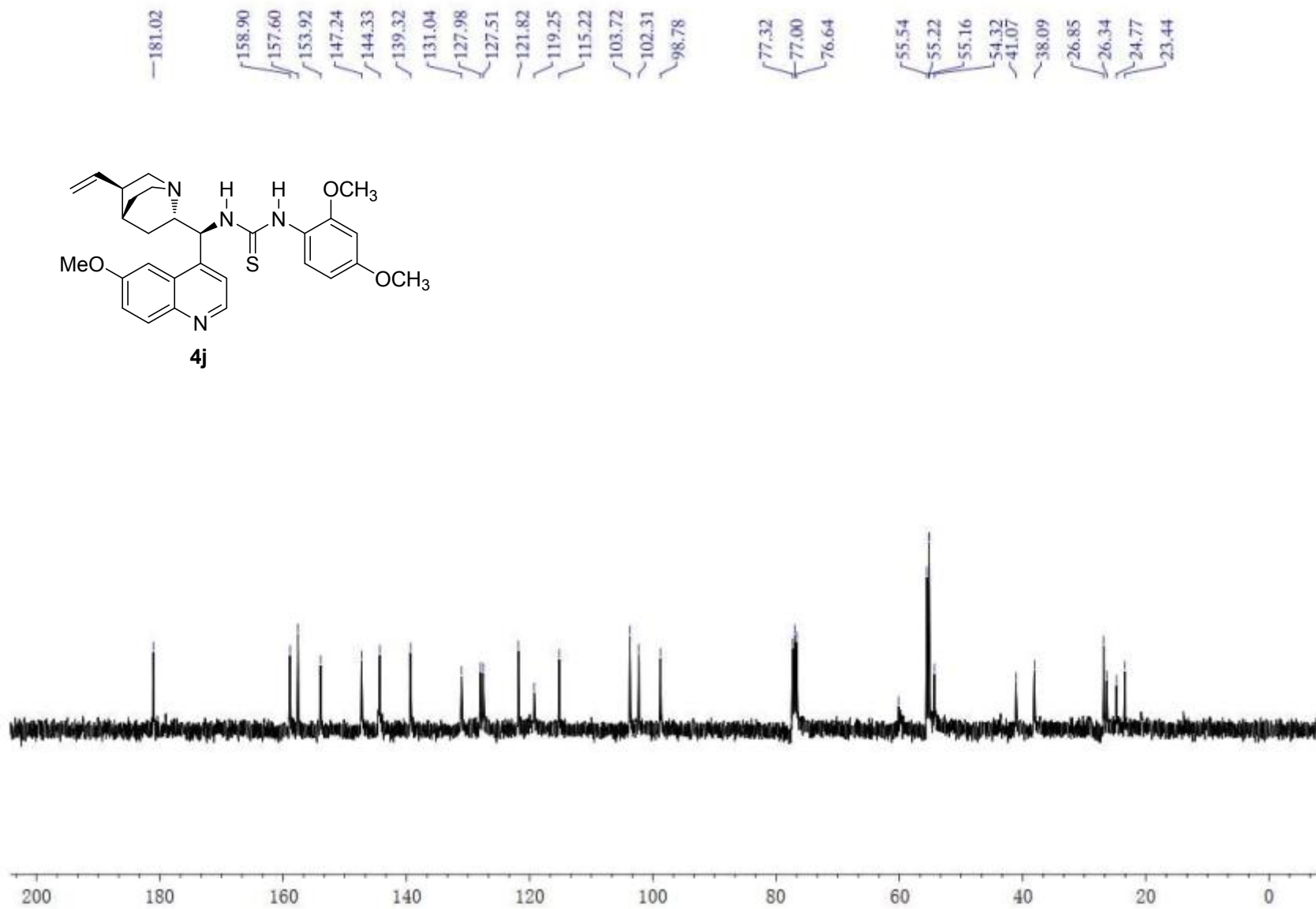


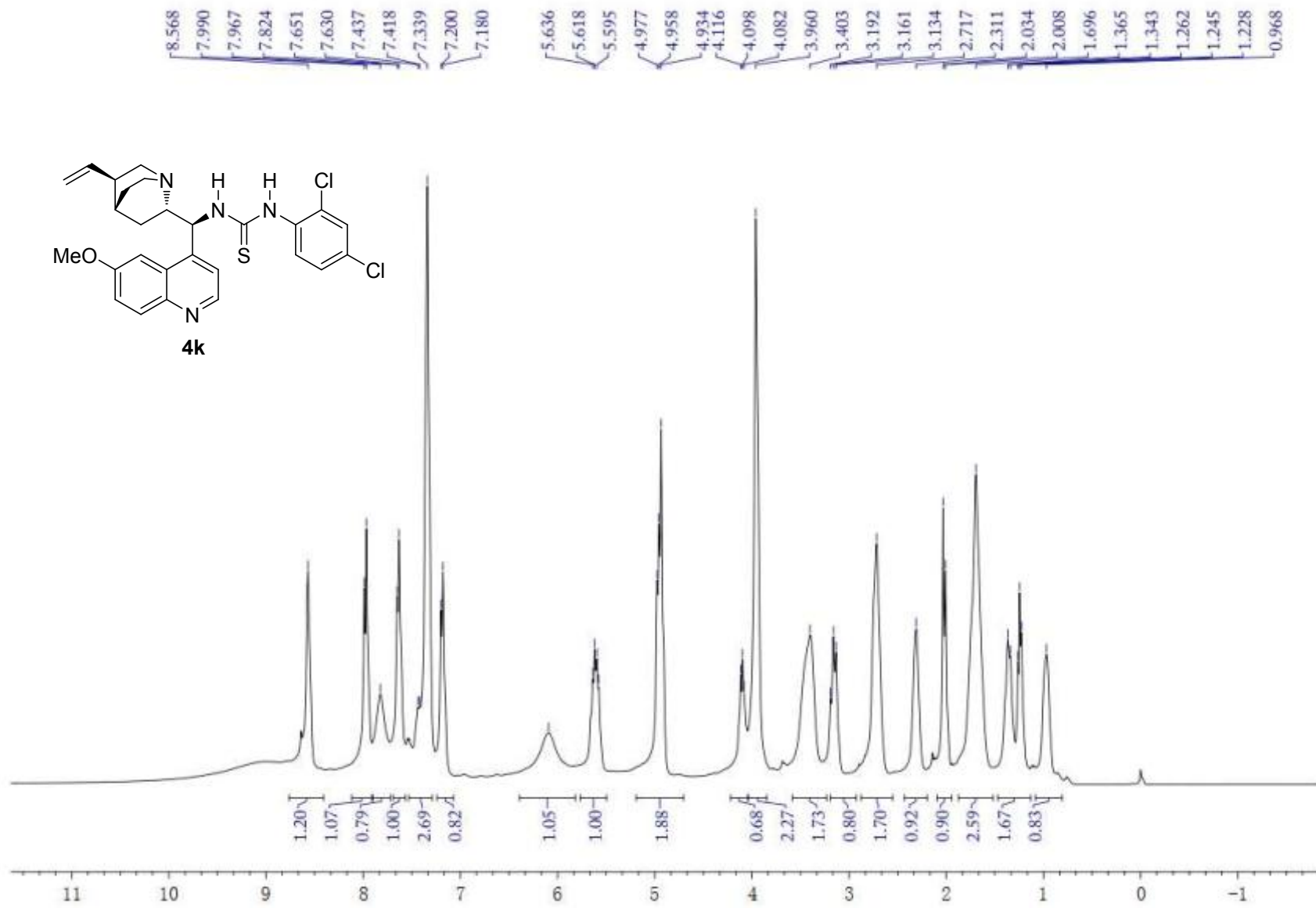


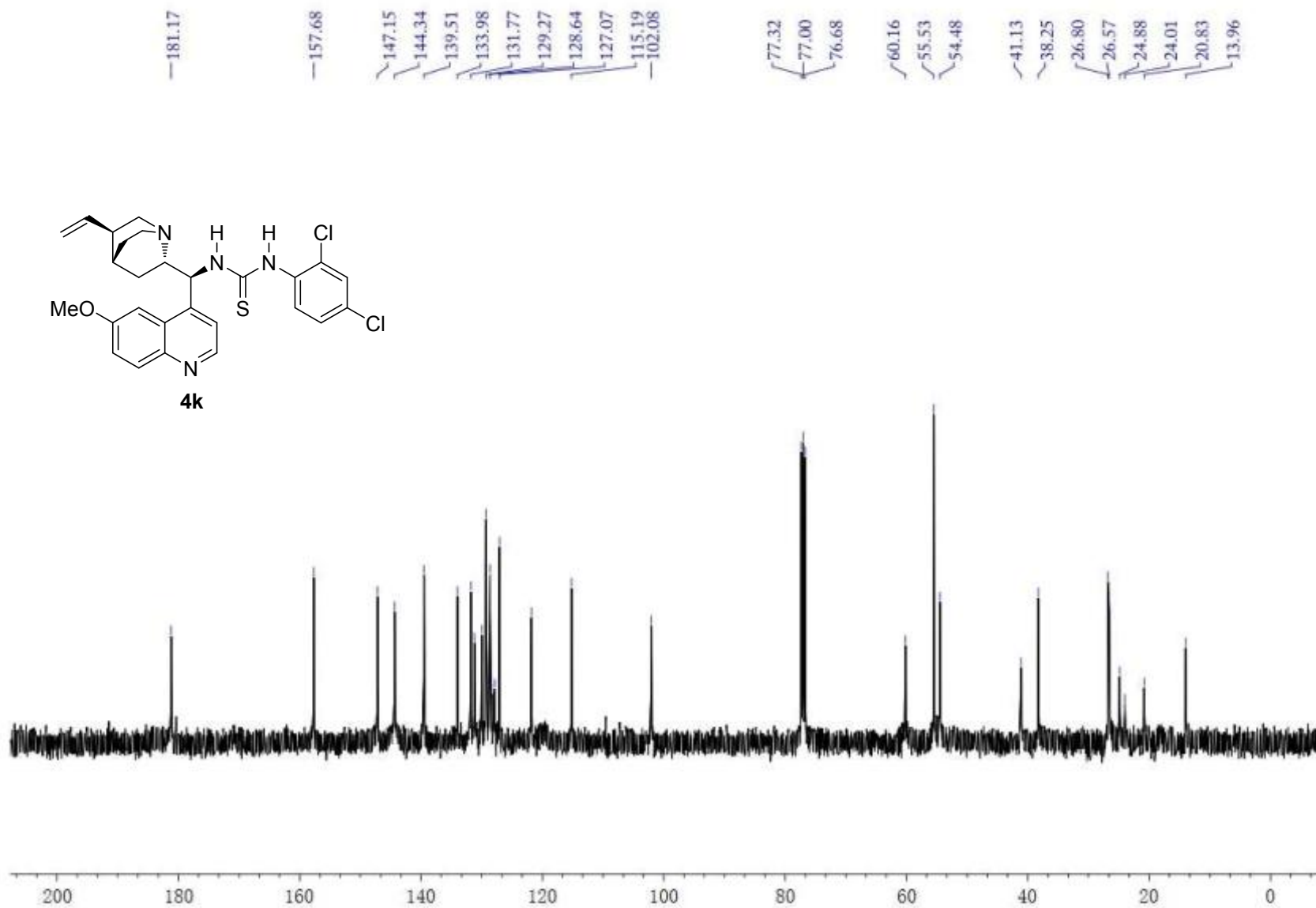


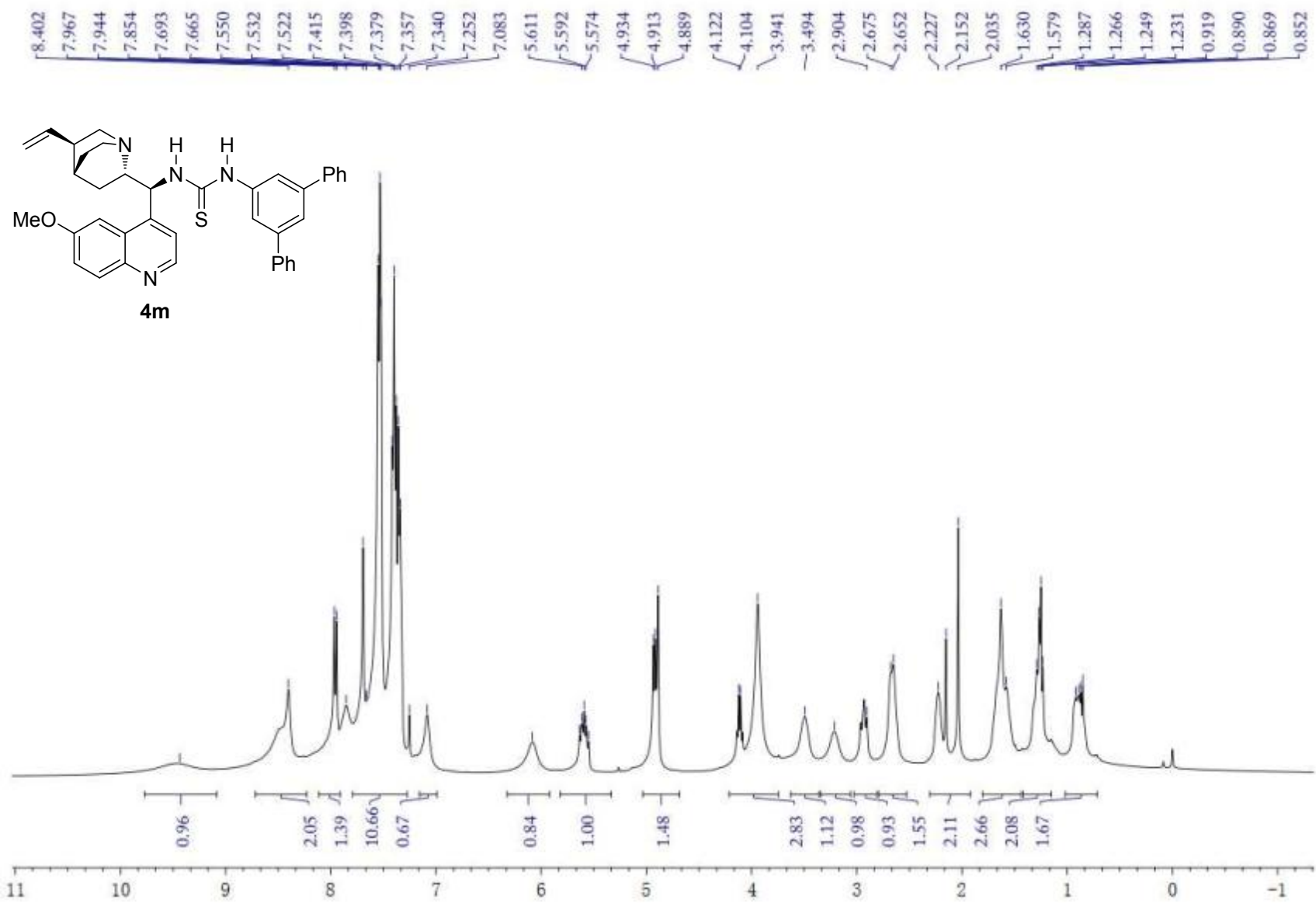


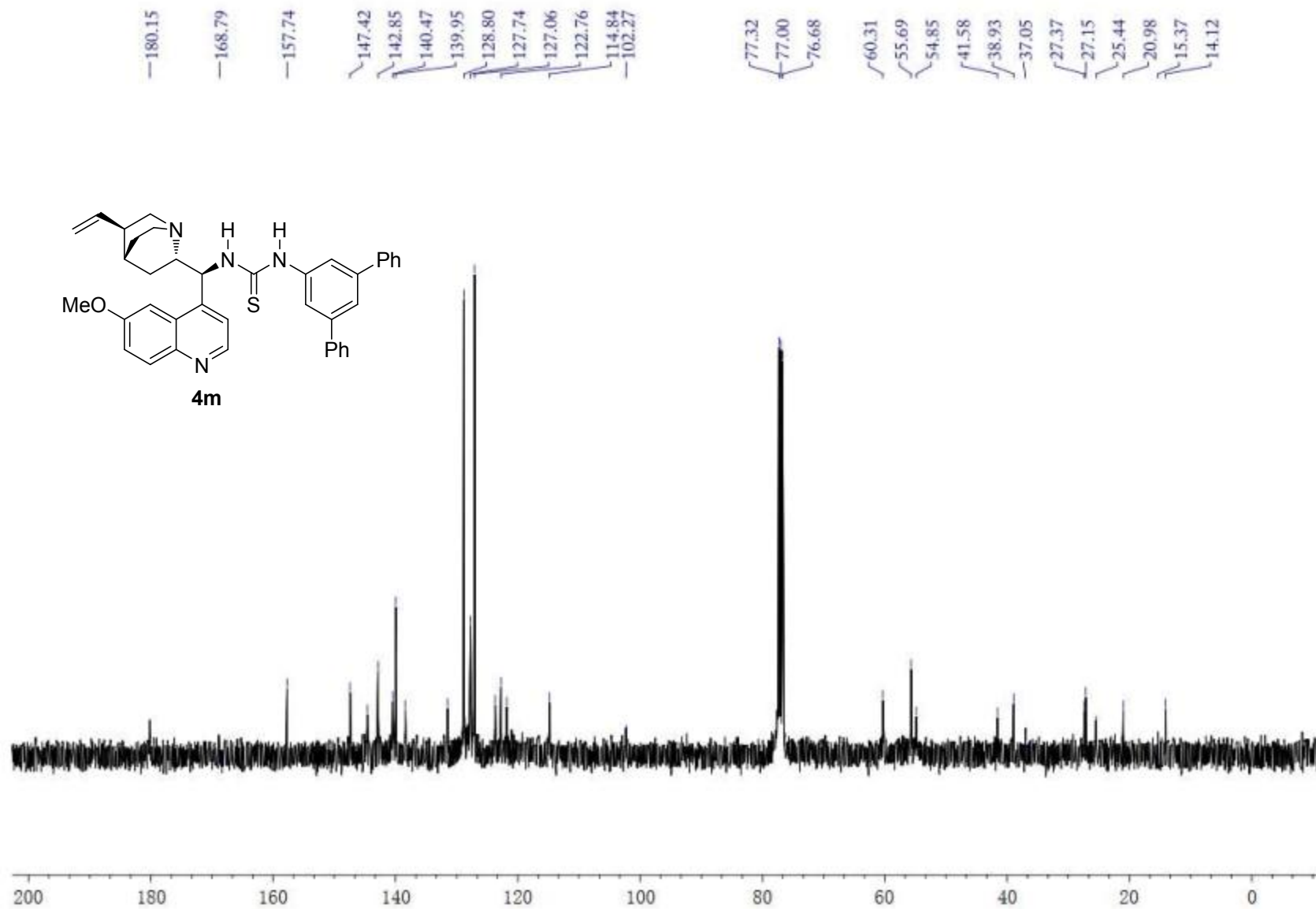


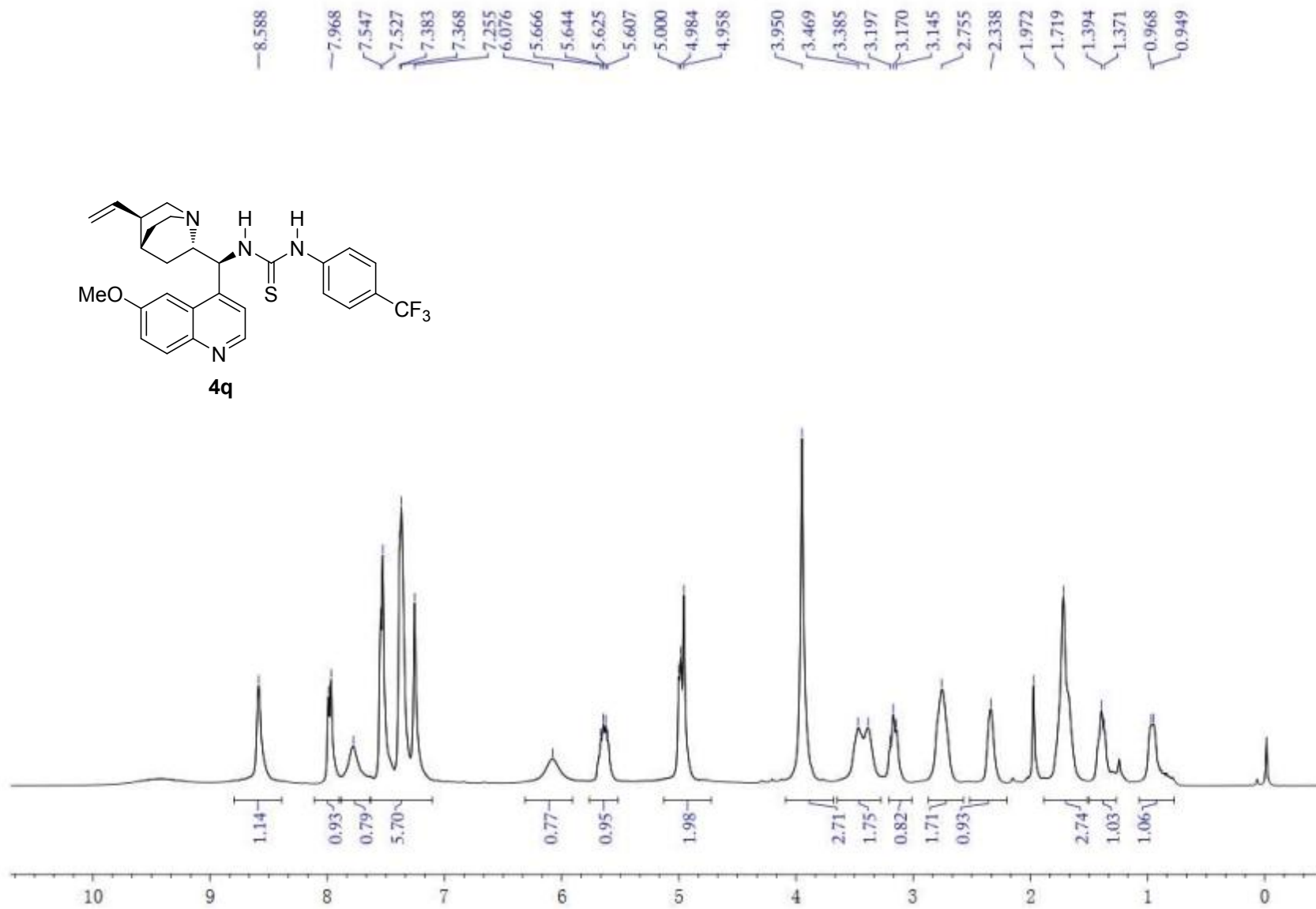
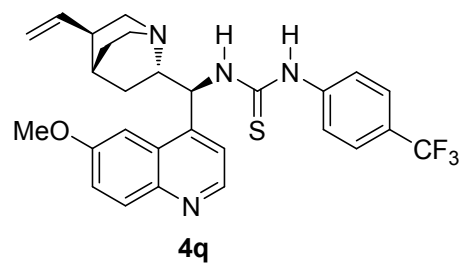




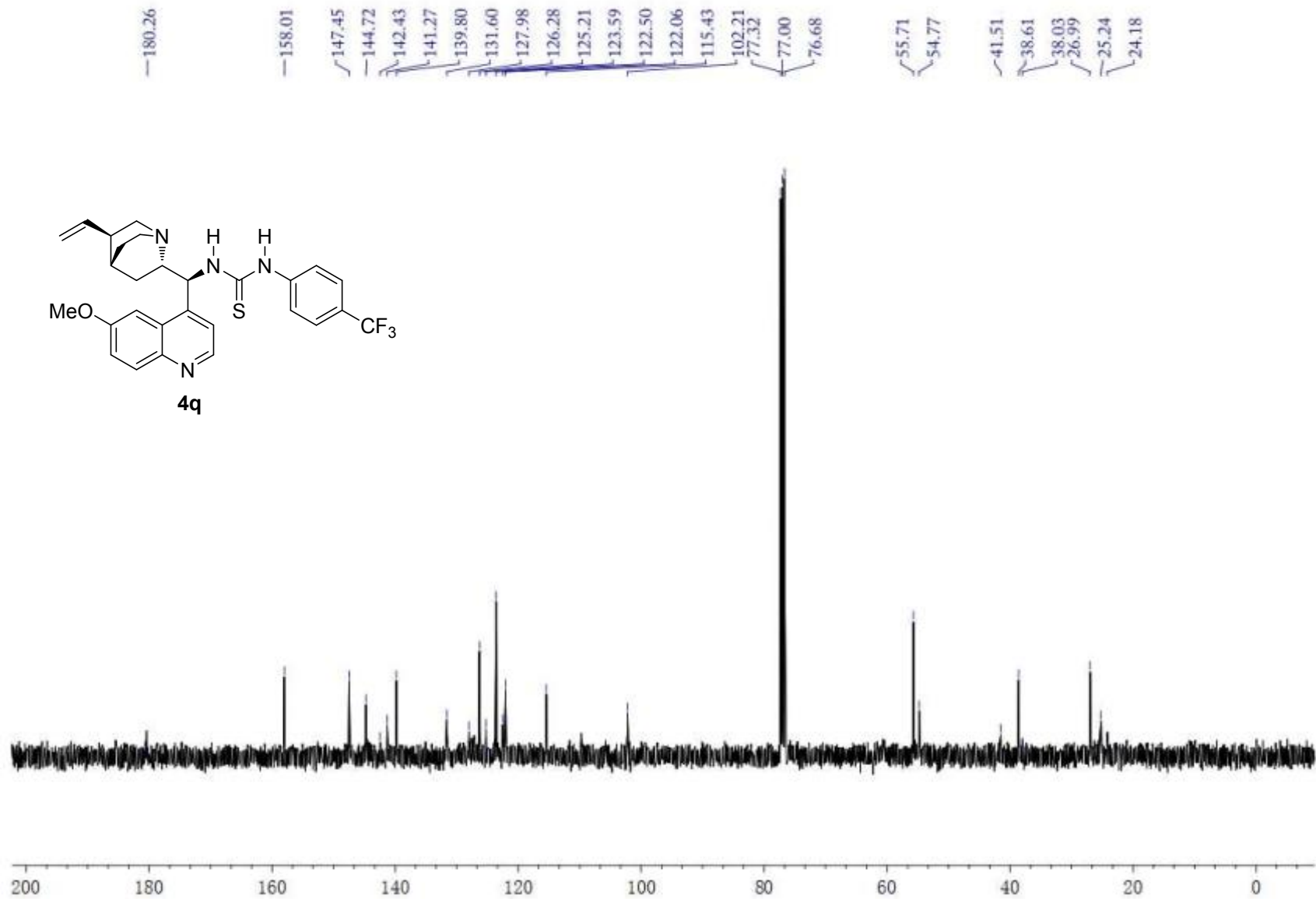


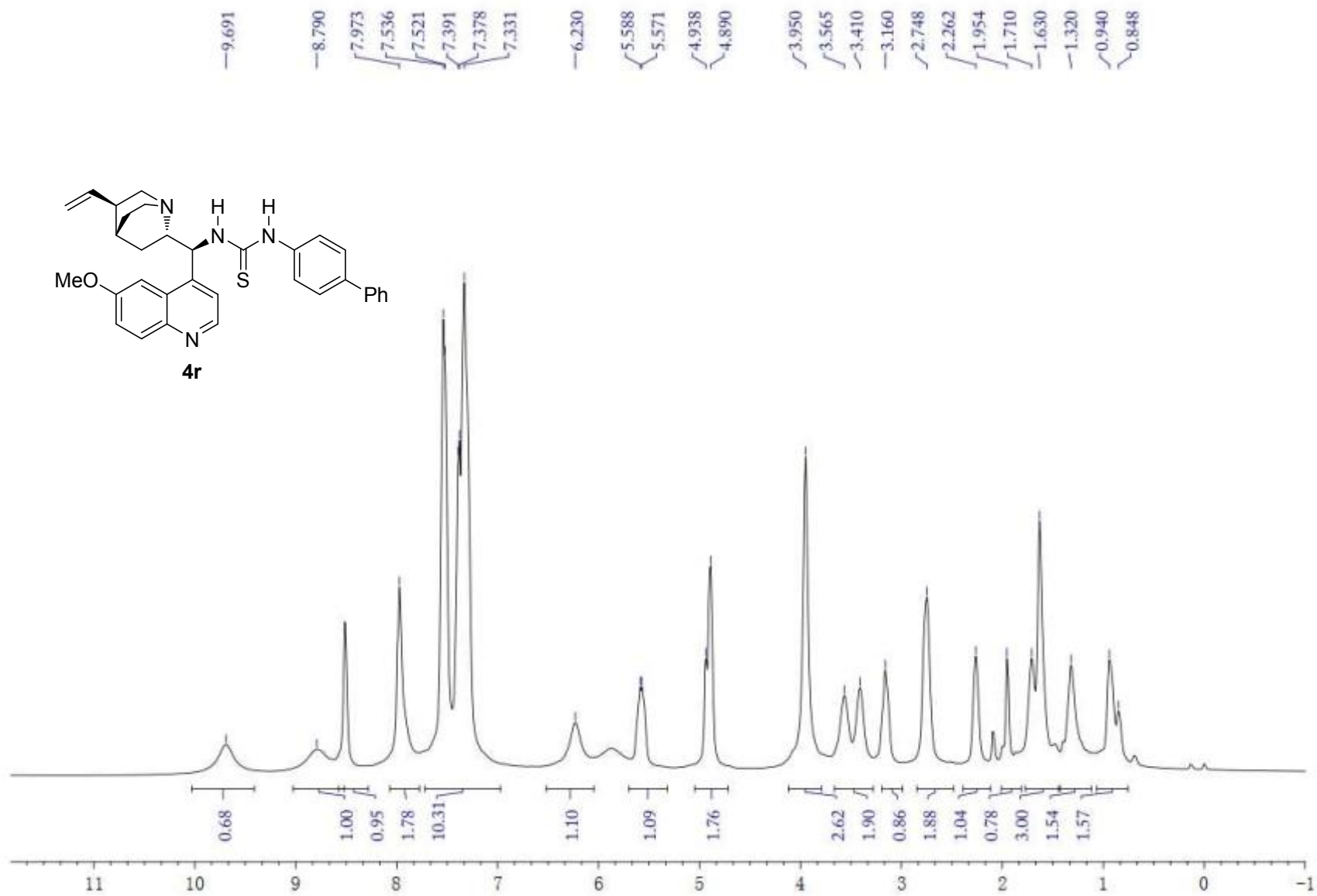


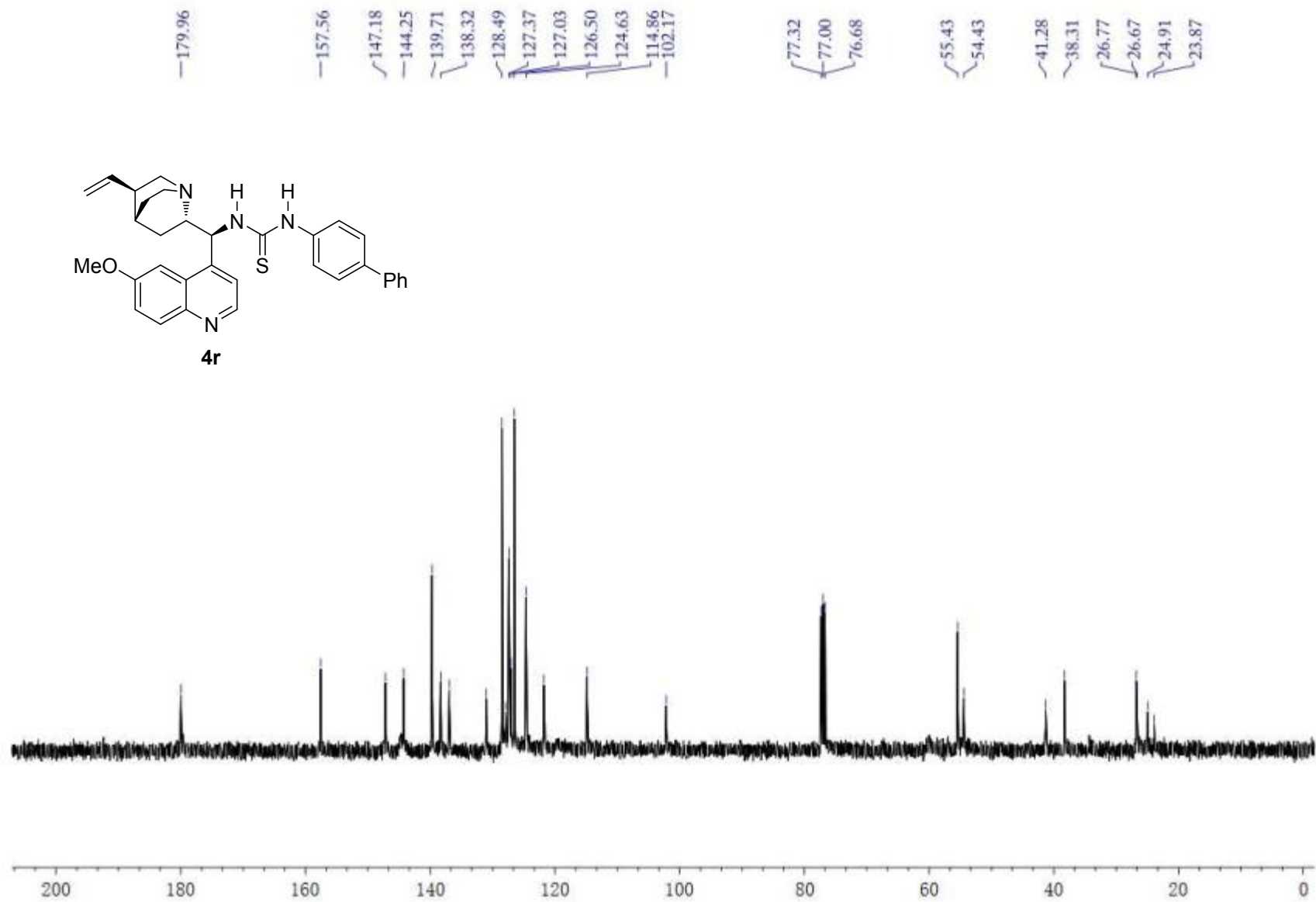
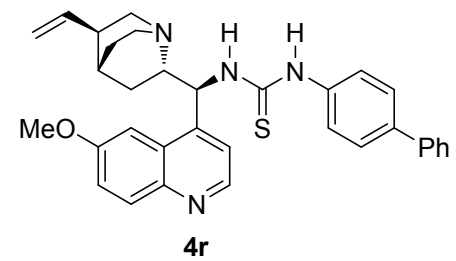


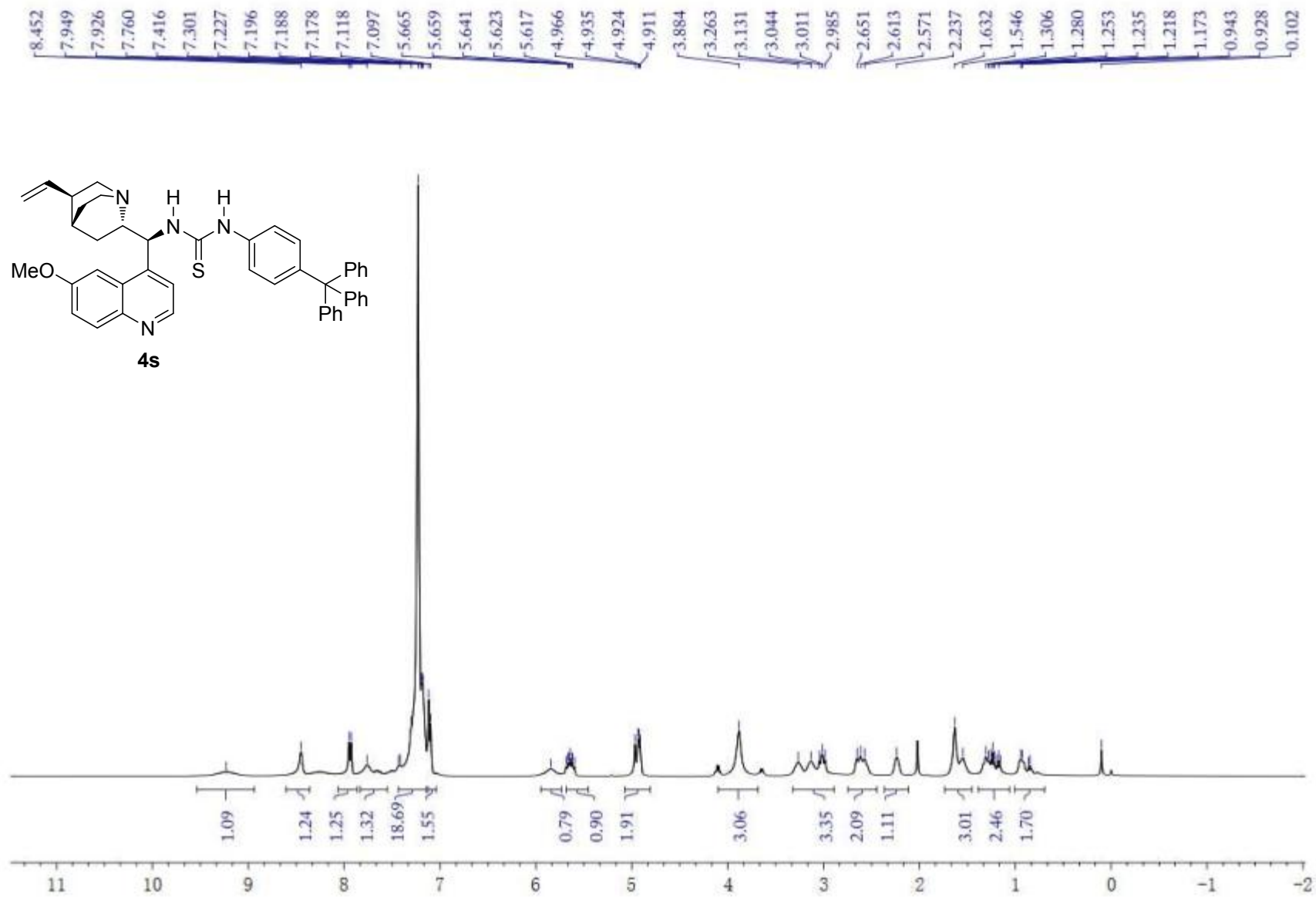


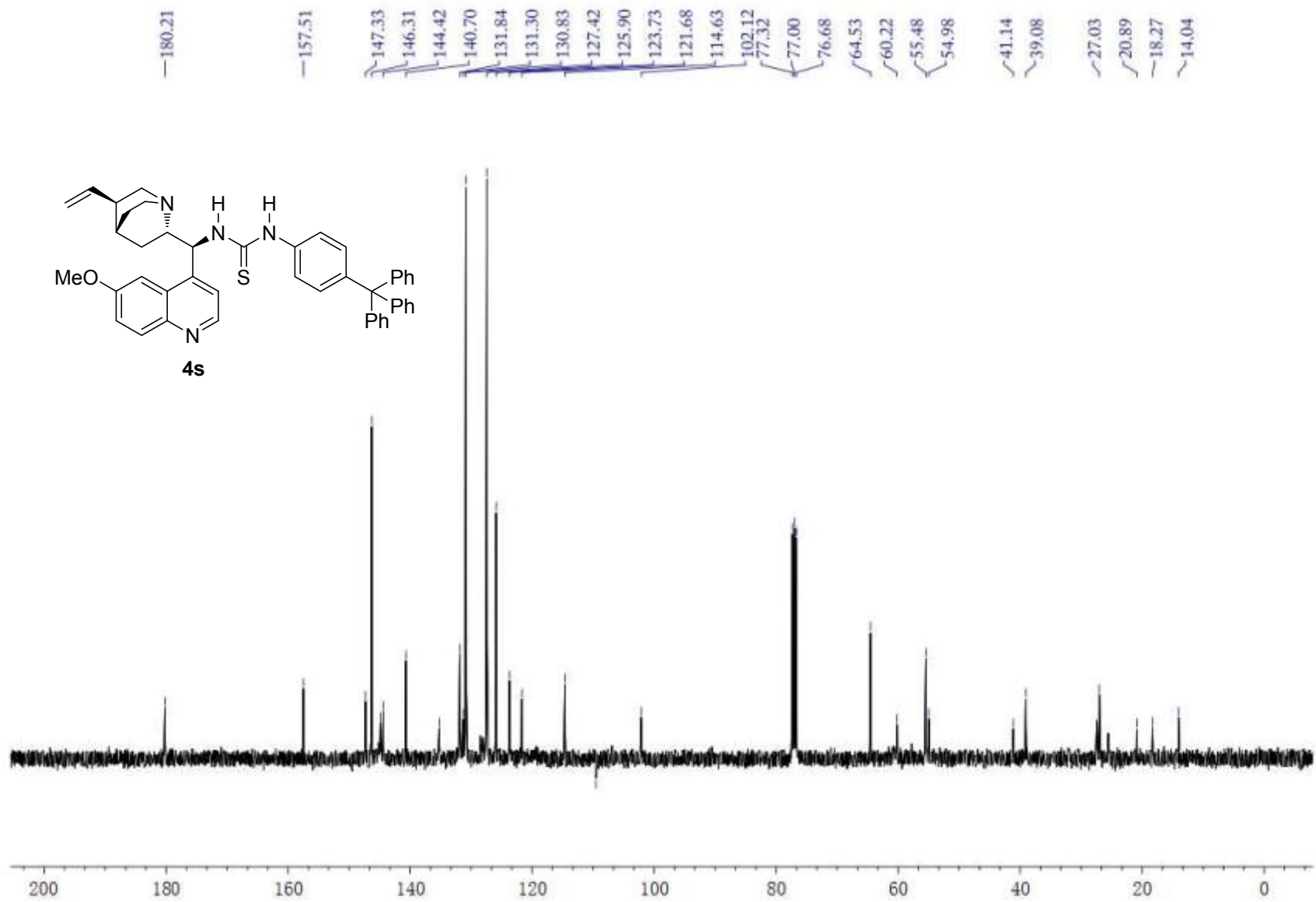


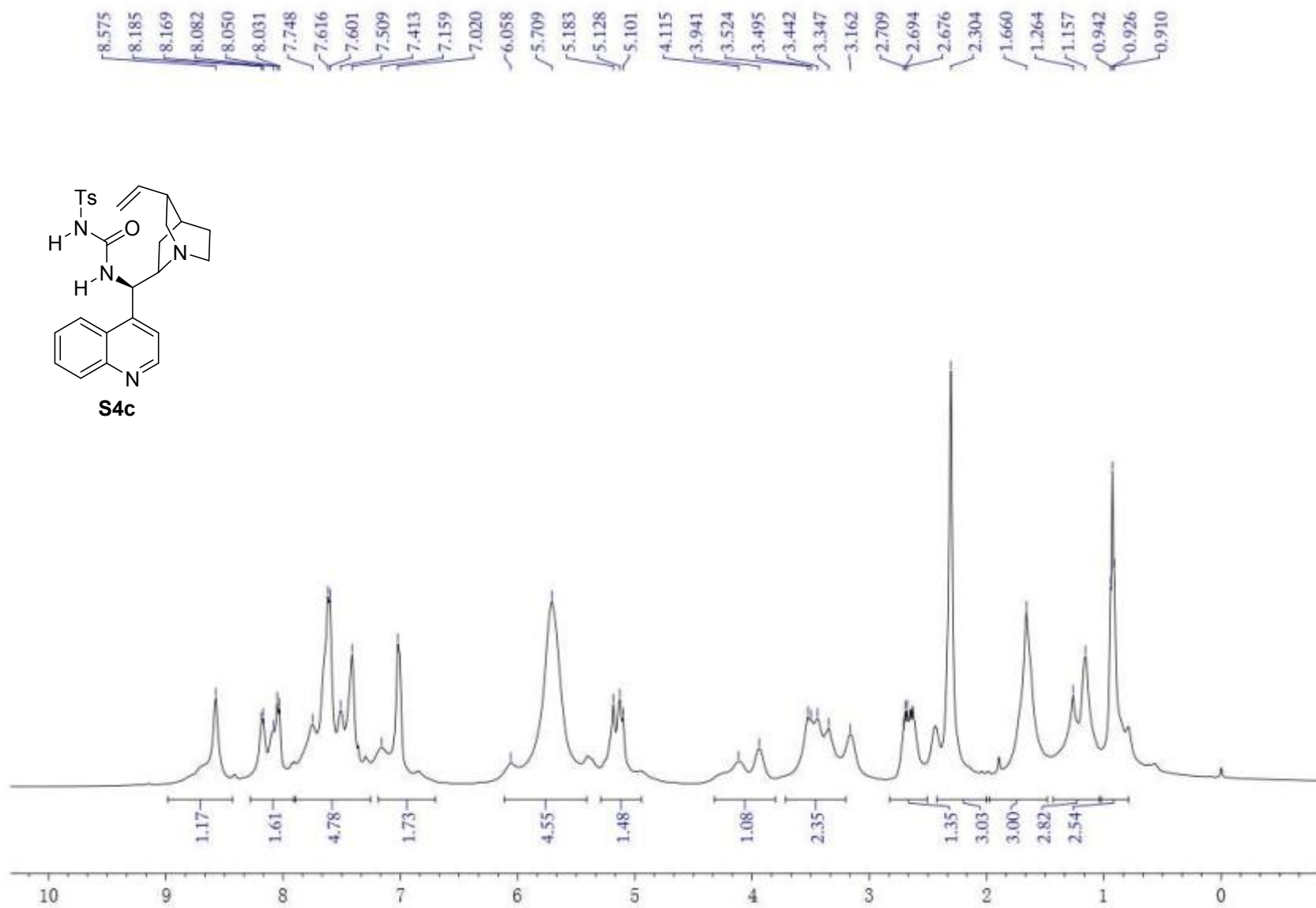
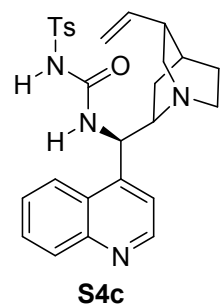


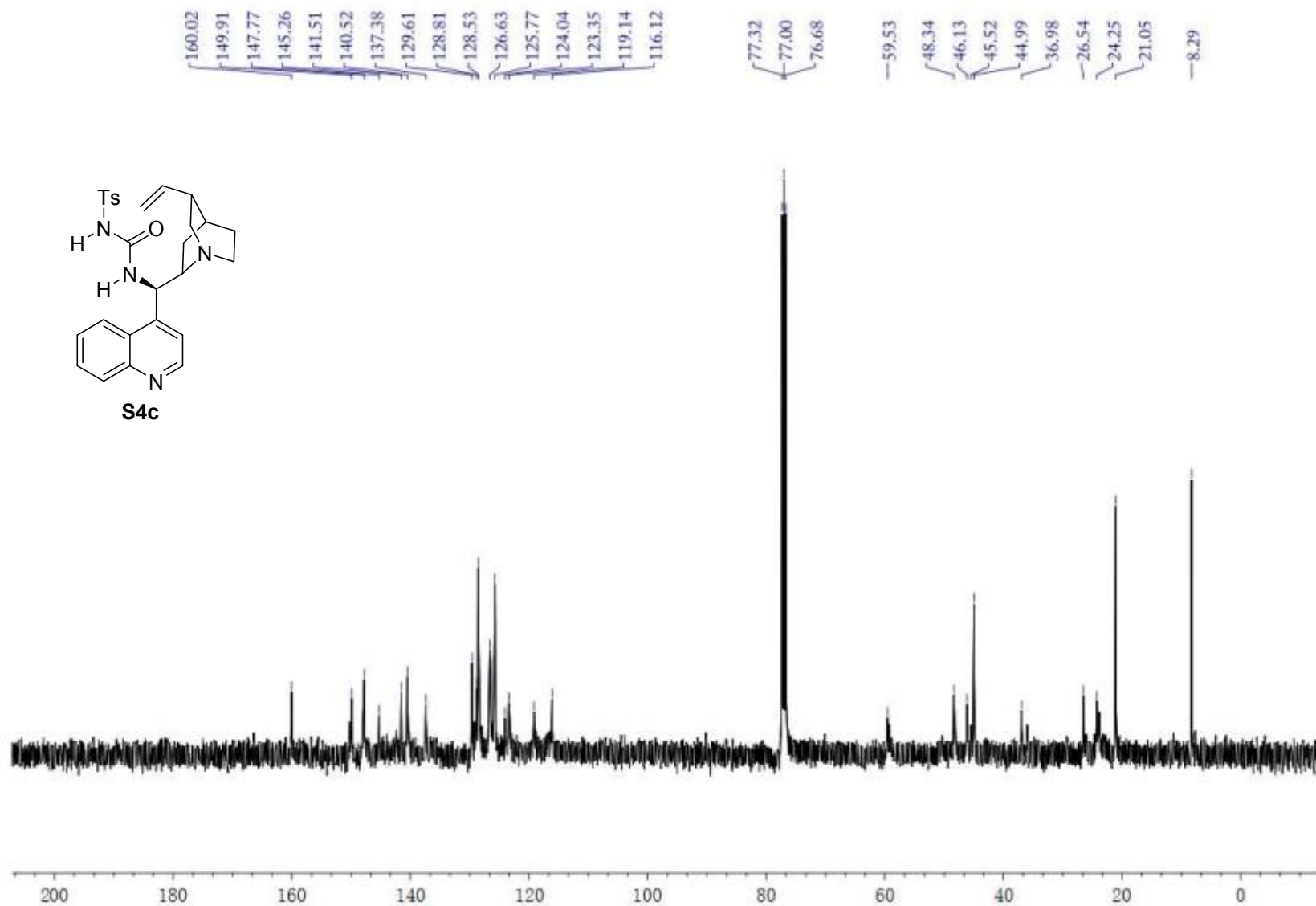


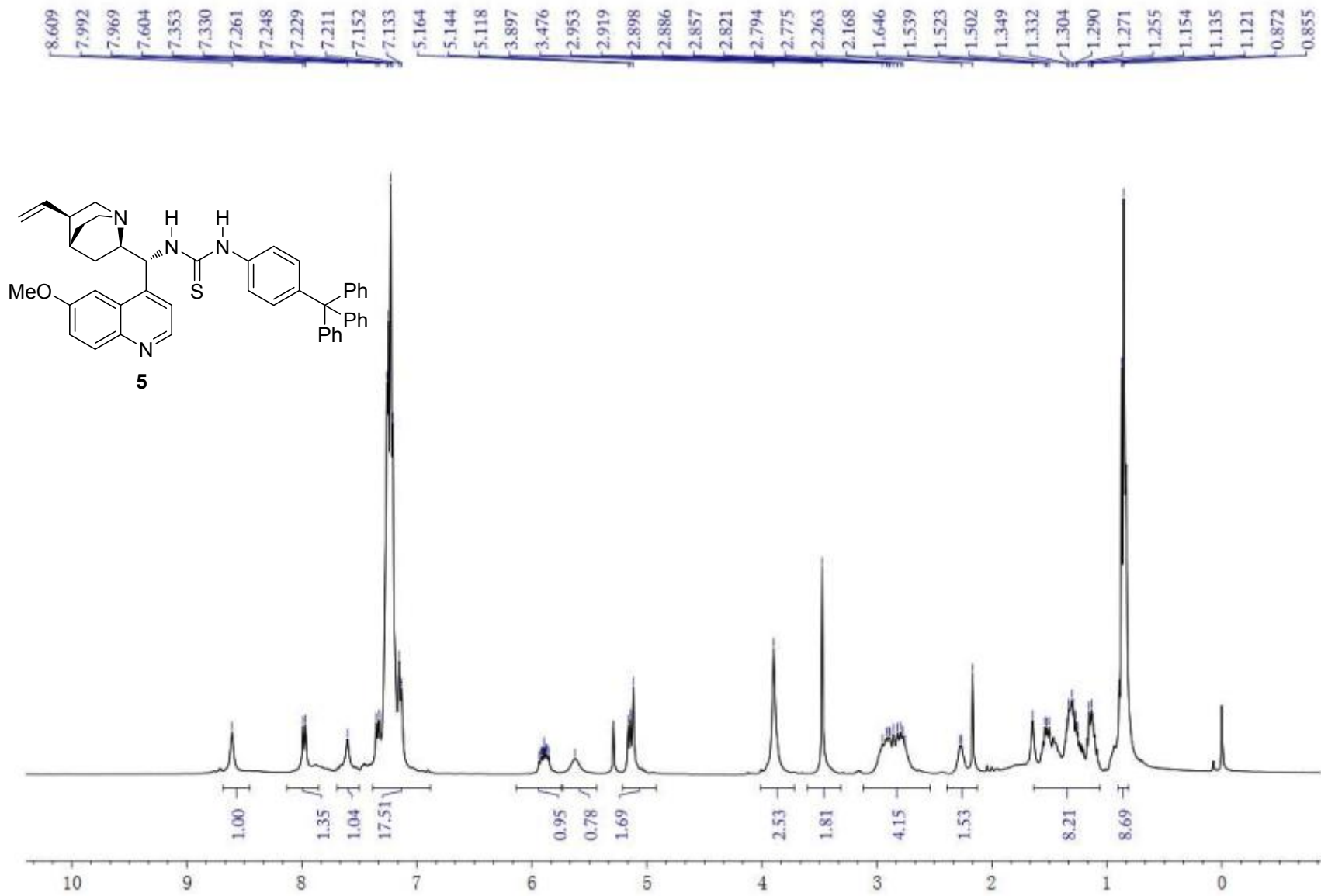




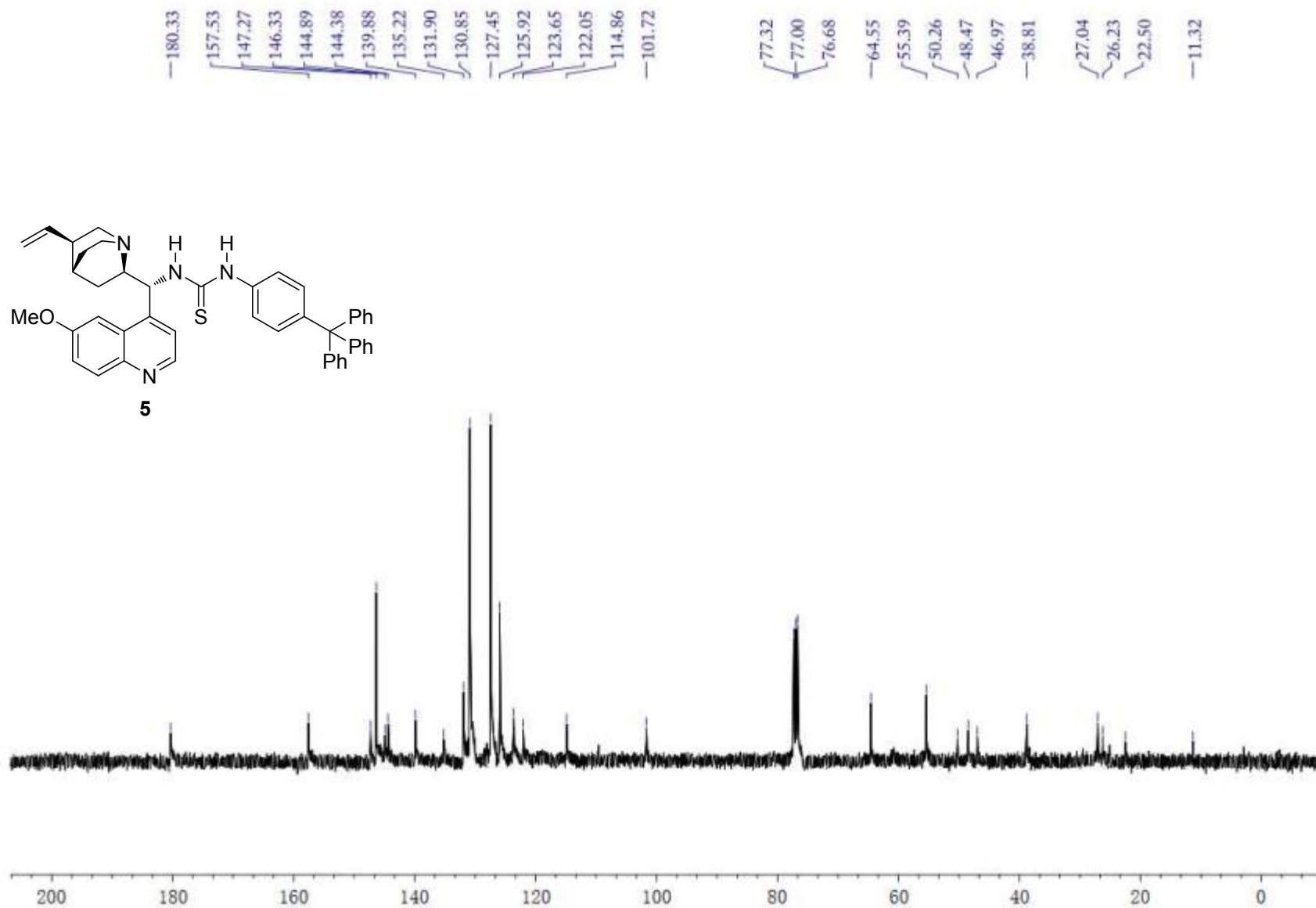


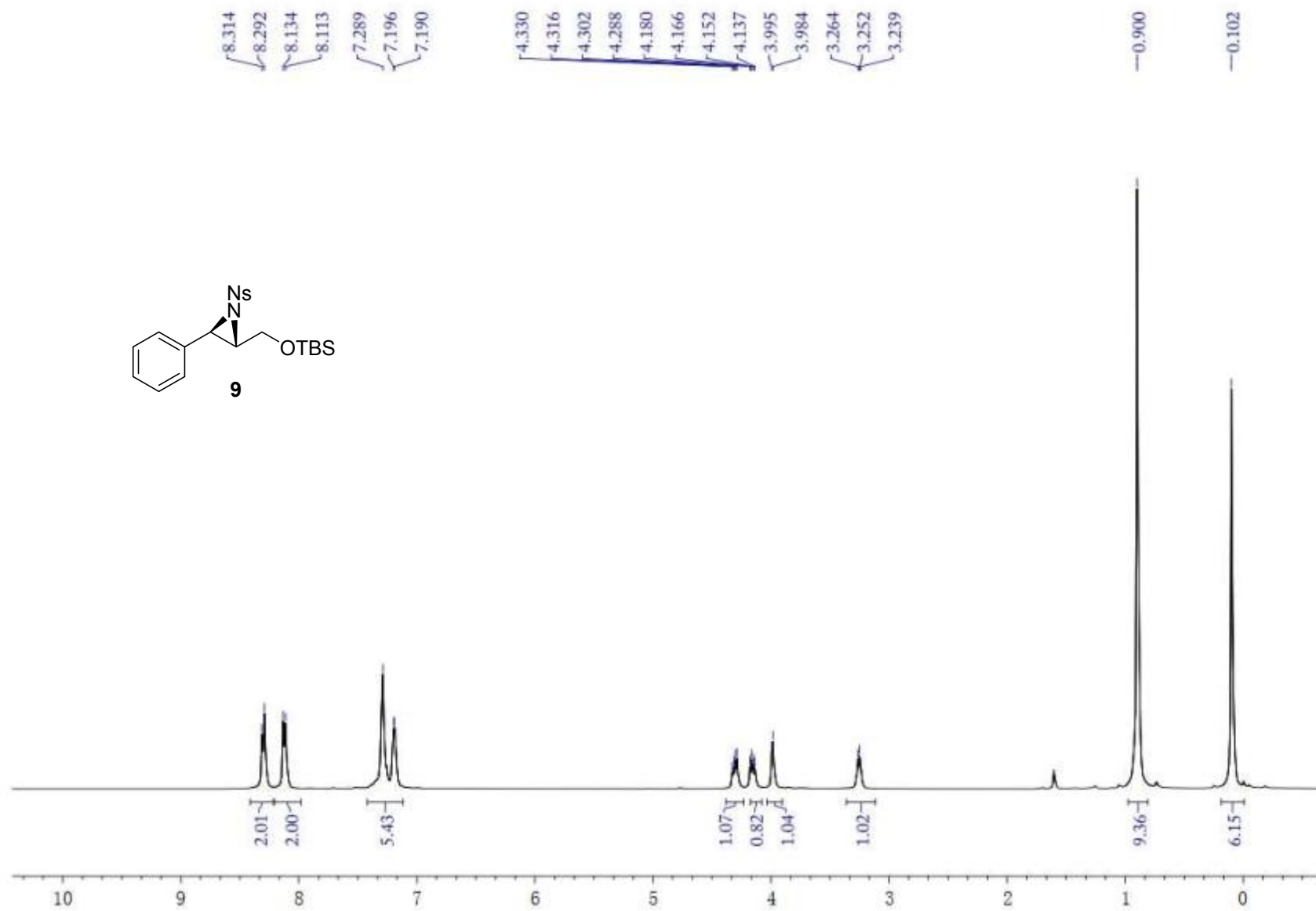


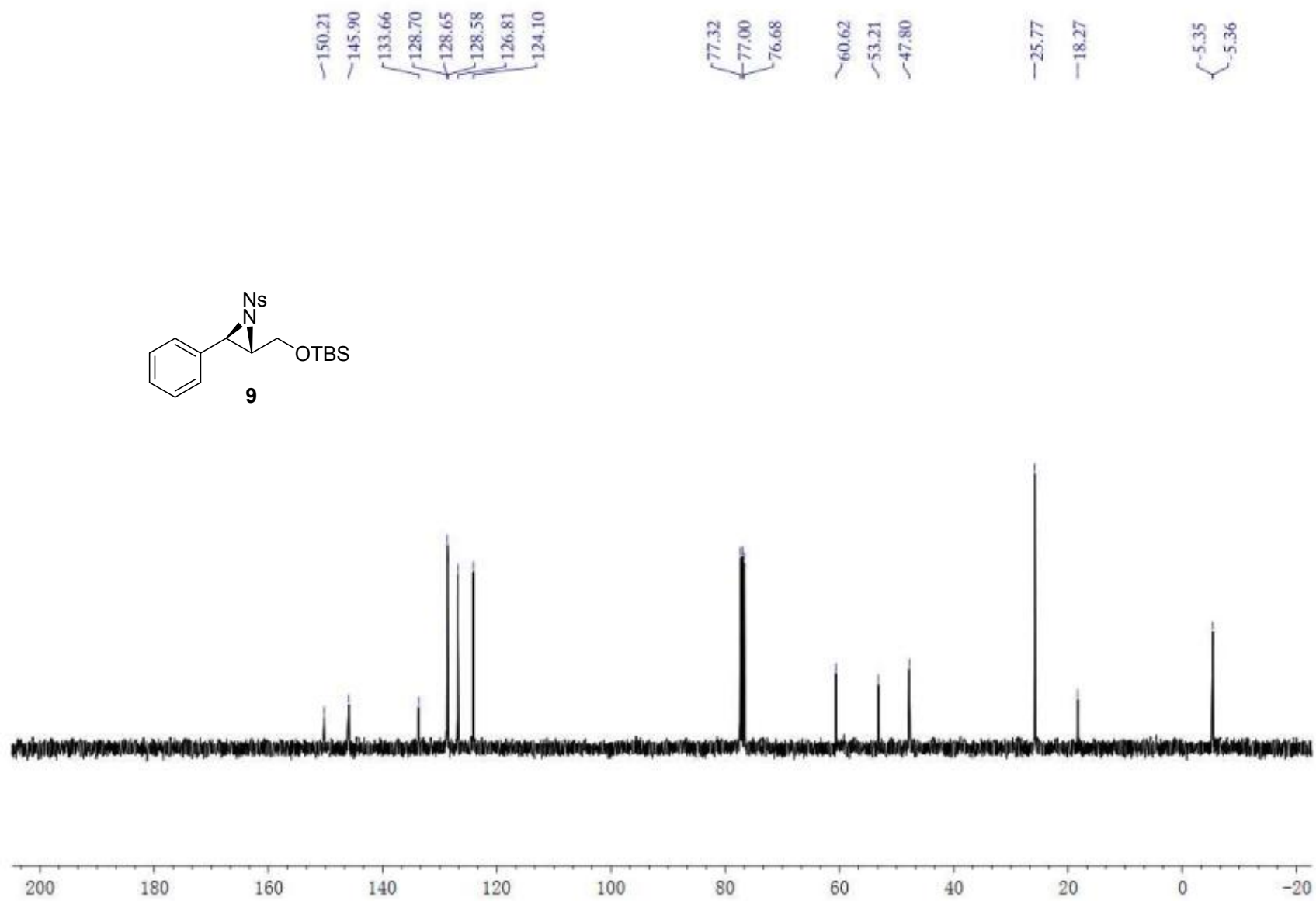
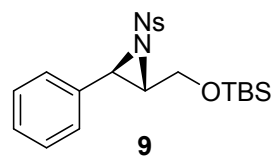


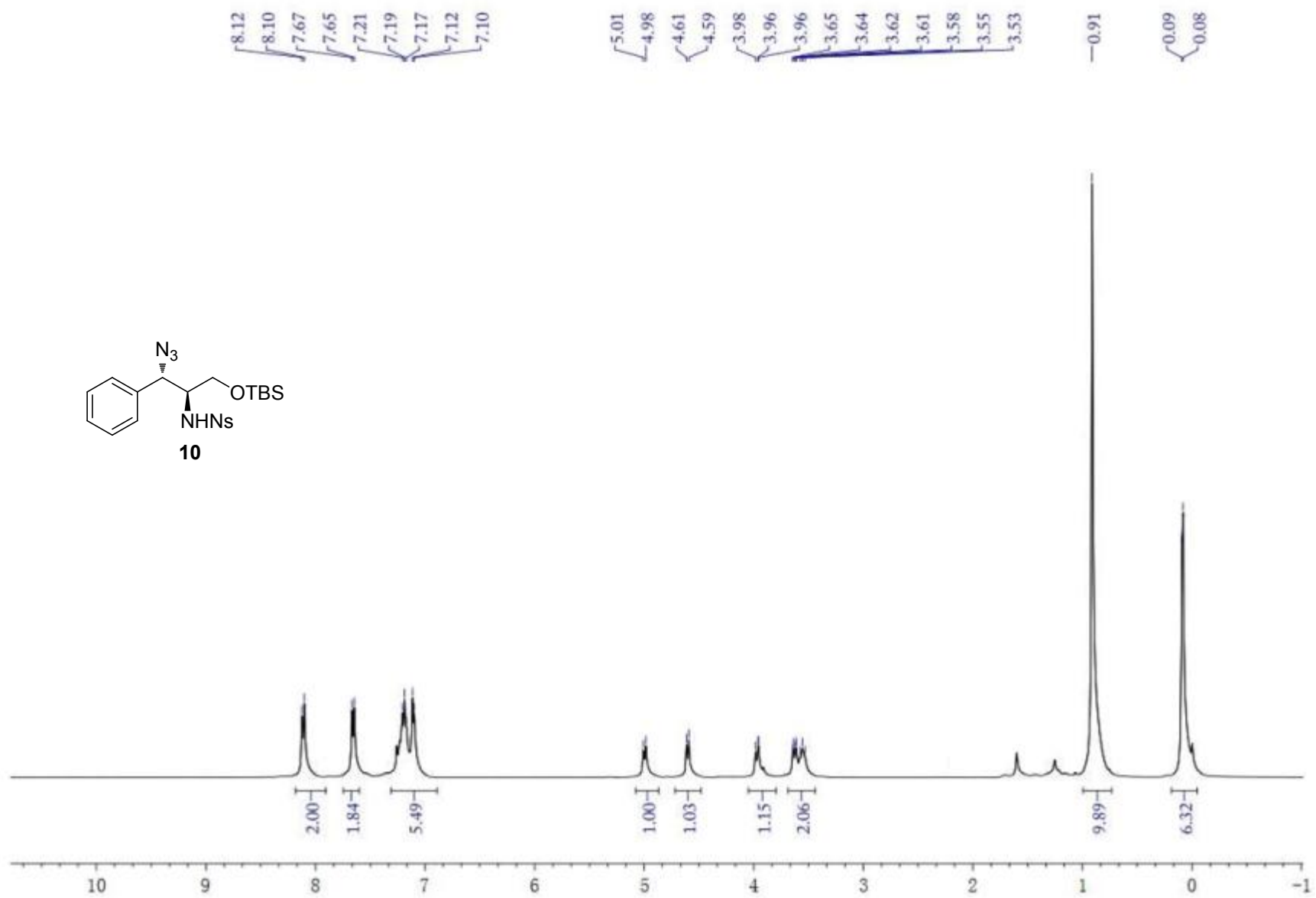
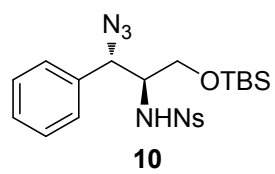


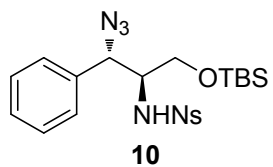










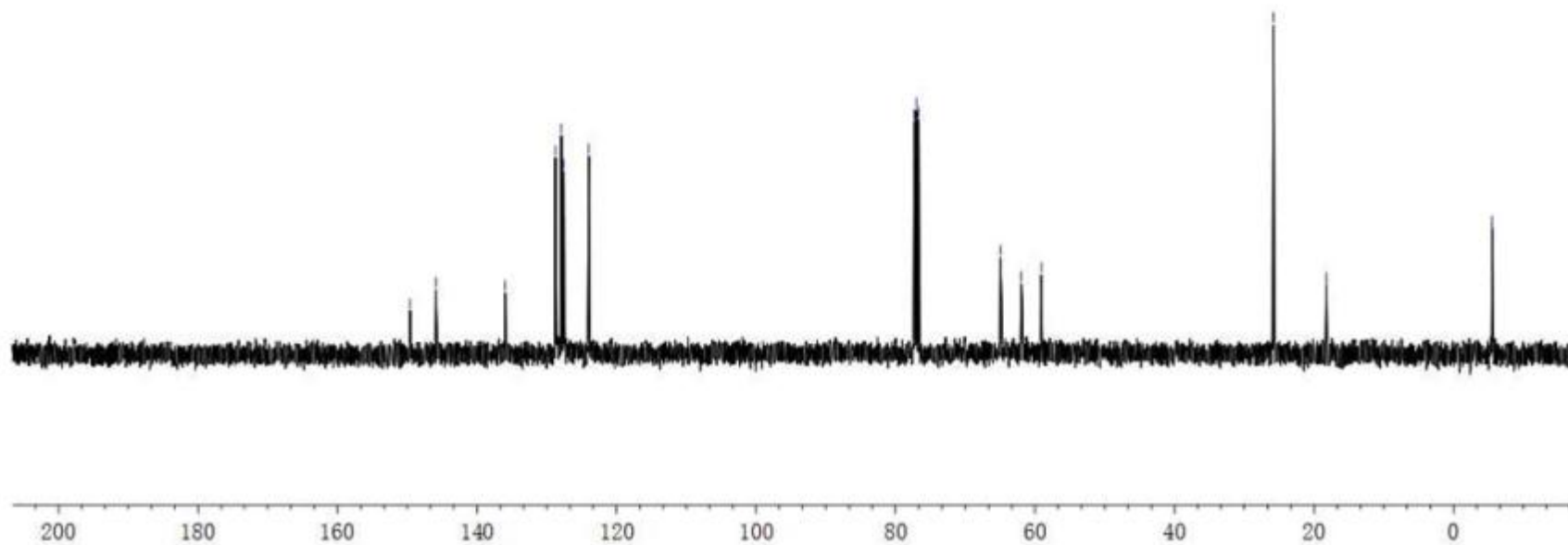


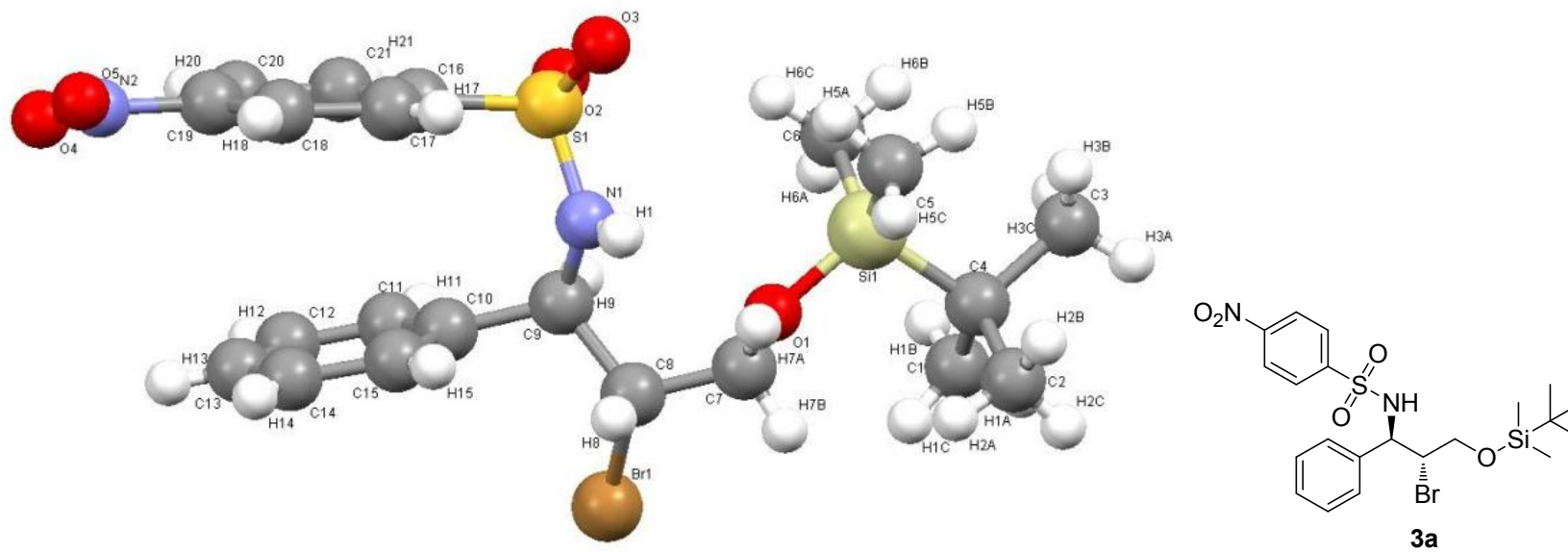
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123.97

77.32  
77.00  
76.68  
64.96  
61.96  
59.10

25.81  
18.25

-5.53  
-5.55





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