Supporting Information

for

The Highly Enantioselective Addition of Indoles and Pyrroles to Isatins-derived *N*-Boc Imines Catalysed by Chiral Phosphoric Acid

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General information.

All commercially available reagents were used without further purification unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC), column chromatography purifications were carried out using silica gel. Proton nuclear magnetic resonance (^{1}HNMR) spectra were recorded on 300 MHz spectrometer in $CDCl_3$ and carbon nuclear magnetic resonance (^{13}CNMR) spectra were recorded on 75 MHz spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as internal standard. Data are presented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, dd = doublet

of doublets, t = triplet, m = multiplet, br = broad) and coupling constant in Hertz (Hz). Methylene chloride was freshly distilled from CaH_2 before use; other solvents (THF, Et_2O, 1,4-dioxane, tBuOMe and toluene) were freshly distilled from sodium. Racemates were obtained by reactions using catalytic amounts of Binaphthylphosphoric acid. BINOL-derived phosphoric acid 1**a-d,**[1] **1e** [2] were prepared according to literature procedures.

Proposed transition-state models for our catalytic system

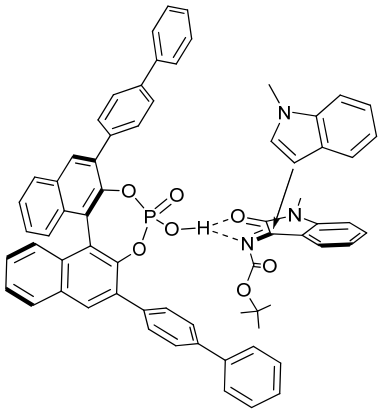


Figure 1. Transition-state model for addition of *N*-Me indoles

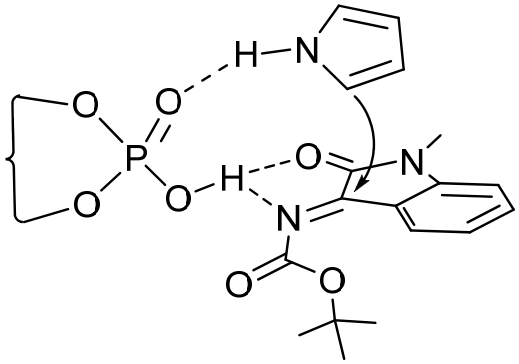
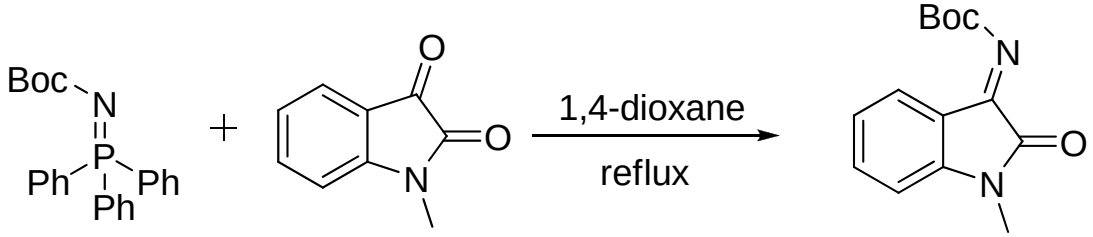


Figure 2. Transition-state model for addition of pyrrole

General procedure for preparation of isatins-derived 3-N-Boc ketimines.

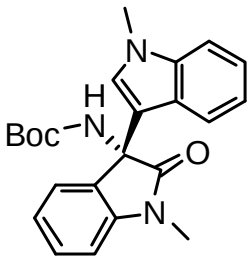
This compound was prepared following the reported procedure.[3] A solution of *N*-Boc-triphenyliminophosphorane (12mmol) and N-Methylisatin (10 mol) in 1,4-dioxane (20 mL) was refluxed for 6 h. The 1,4-dioxane was evaporated and the residue was purified by flash chromatography to afford the ketimine as a yellow solid.



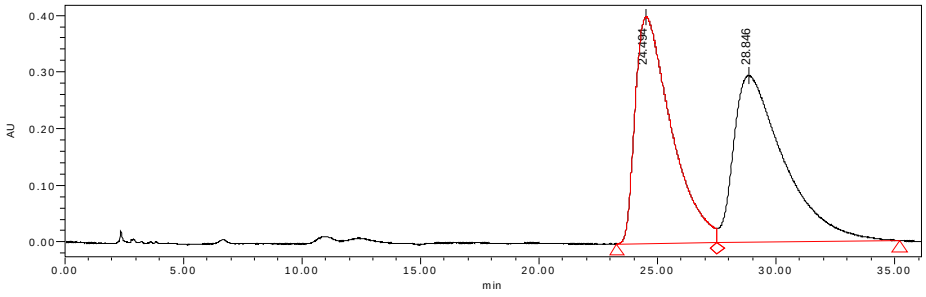
General procedure for the enantioselective F-C reaction Catalysed by Chiral Phosphoric Acids.

To a solution of isatins-derived ketimine **3a-j** (0.15 mmol) and chiral phosphoric acid (0.0075 mmol, 5 mol%) in Et_2O or other solvents (1.5 mL) were added 4 Å MS (4 beads, 0.12 – 0.14 g) and indole **2a-i** or pyrrole (0.3 mmol, 2.00 equiv) at 0 ^oC. After the reaction was complete (monitored by TLC), the solvent was removed and the residue was purified by flash column chromatography to afford the product **4a-s** or **6a-h.**

(*S*)-*tert*-Butyl 1,1'-dimethyl-2-oxo-3,3'-biindolin-3-ylcarbamate (4a)



The ee value determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel OD-H column (hexane : 2-propanol = 92 : 8, 1.0 mL/min, 94% ee). White solid, 96% yield; mp =153-154 ^{o}C ; [α]$_{D}^{20}$ = +116 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.24-7.28 (m, 2H), 7.21 (t, *J* = 1.8 Hz, 1H), 7.11-7.19 (m, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.52 (s, 1H), 5.72 (br.s, 1H), 3.63 (s, 3H), 3.18 (s, 3H), 1.28 (br.s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 175.7, 153.9, 143.7, 137.9, 130.7, 129.0, 128.3, 125.1, 123.4, 122.5, 122.4, 121.9, 120.0, 111.5, 109.7, 108.1, 80.3, 62.0, 32.8, 28.1, 26.5 ppm; IR (KBr): 3446, 3007, 2927, 1718, 1613, 1470, 1368, 1160, 1016, 901, 743, 693 cm^{-1}; HRMS calcd for $C_{23}H_{26}N_3O_3$ $(M+H)^+$ 392.1969, found 392.1978.



	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
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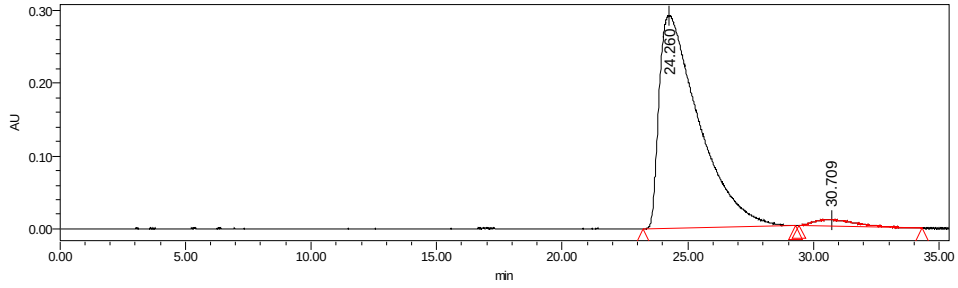
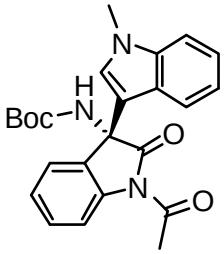
2		28.846	43530885	50.54	294790	VB	Unknown	

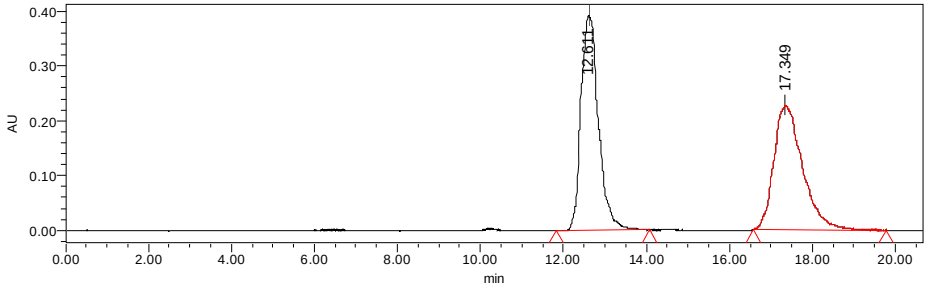


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		24.260	32348346	96.95	292922	bb	Unknown	
2		30.709	1017527	3.05	8712	bb	Unknown	

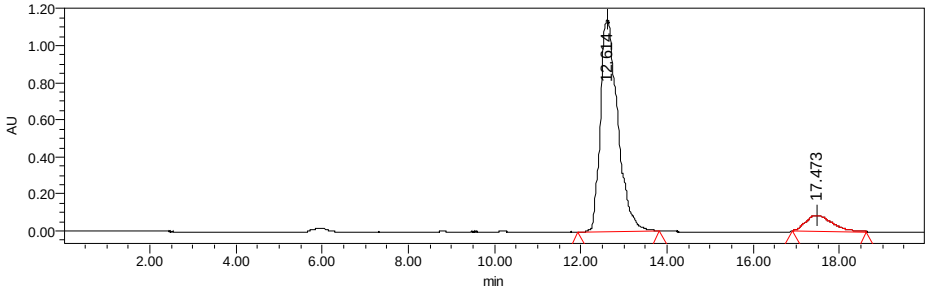
(*S*)-*tert*-Butyl 1-acetyl-1'-methyl-2-oxo-3,3'-biindolin-3-ylcarbamate (4b)



The ee value determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel OD-H column (hexane : 2-propanol = 80 : 20, 1.0 mL/min, 80% ee). White solid, 95% yield; mp = 144-146 ^{o}C; $[\alpha]_D^{20}$ = +257 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.32 (d, *J* = 8.1 Hz, 1H), 8.19 (d, *J* = 7.8 Hz, 1H), 7.40-7.47 (m, 2H), 7.21-7.31 (m, 4H), 6.36 (s, 1H), 5.89 (br.s, 0.52H) 5.63 (br.s, 0.46H), 3.64 (s, 3H), 2.59 (s, 3H), 1.37 (br.s, 5H), 1.13 (br.s, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 175.4, 171.2, 153.7, 140.0, 138.0, 129.4, 125.2, 124.8, 123.1, 122.8, 121.8, 120.4, 116.7, 110.8, 109.9, 80.8, 62.3, 32.9, 28.2, 26.6 ppm; IR (KBr): 3331, 2921, 1774, 1705, 1465, 1370, 1334, 1274, 1162, 746 cm^{-1}; HRMS calcd for $C_{23}H_{26}N_3O_4$ $(M+H)^+$ 420.1918, found 420.1921.

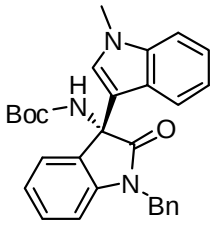


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		12.611	11502726	51.30	392510	bb	Unknown	
2		17.349	10918695	48.70	227344	bb	Unknown	

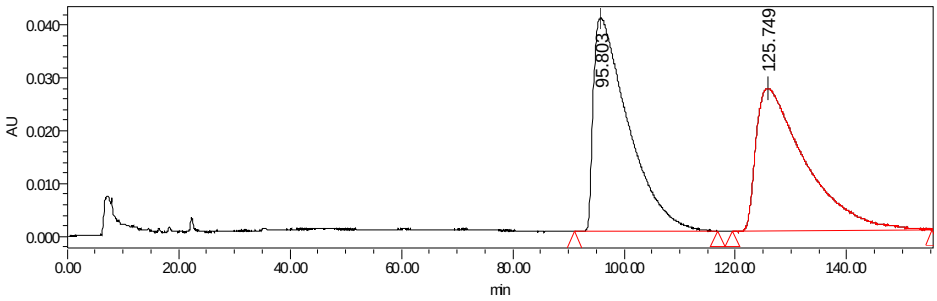


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		12.614	31903781	89.88	1144127	bb	Unknown	
2		17.473	3593315	10.12	83764	bb	Unknown	

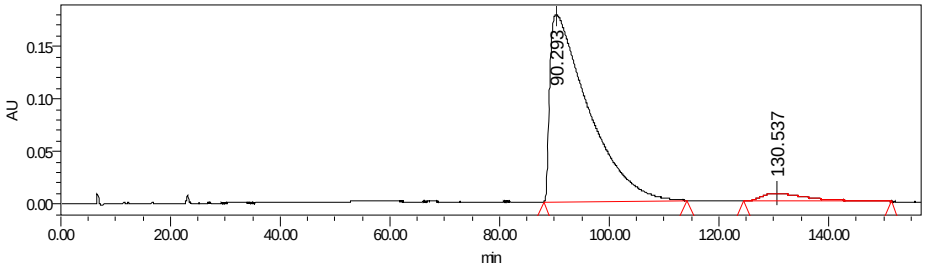
(*S*)-*tert*-Butyl 1-benzyl-1'-methyl-2-oxo-3,3'-biindolin-3-ylcarbamate (4c)



The ee value determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel OD-H column (hexane : 2-propanol = 97 : 3, 0.50 mL/min, 90% ee). White solid, 87% yield; mp = 122-124 ^{o}C; $[\alpha]_D^{20}$ = +128 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 6.6 Hz, 1H), 7.16-7.30 (m, 9H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.58 (s, 1H), 5.77 (br.s, 1H), 4.98 (br.s, 2H), 3.64 (s, 3H), 1.34 (br.s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 175.9, 153.9, 142.8, 137.9, 136.0, , 128.8, 128.6, 128.2, 127.3, 125.2, 123.5, 122.49, 122.45, 121.8, 120.0, 111.7, 109.7, 109.2, 80.3, , 44.1, 32.9, 28.2, 25.4 ppm; IR (KBr): 3018, 2920, 1715, 1486, 1469, 1215, 1160, 1060, 1021, 756 cm^{-1}; HRMS calcd for $C_{29}H_{29}N_3NaO_3$ $(M+Na)^+$ 490.2101, found 490.2118.

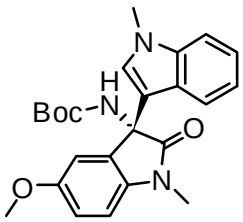


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		95.803	17545819	51.35	40438	bb	Unknown	
2		125.749	16621083	48.65	26937	bb	Unknown	

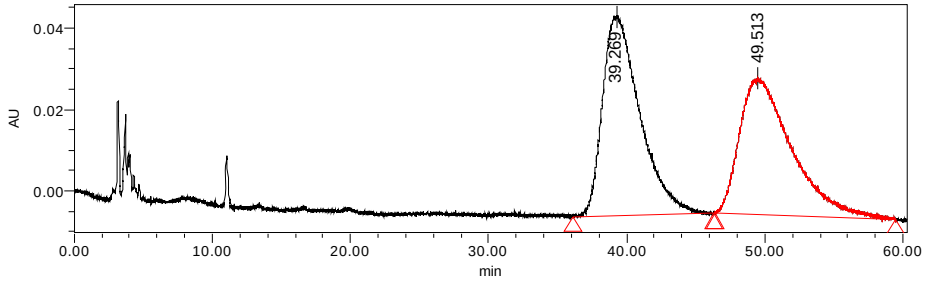


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		90.293	86591472	95.01	178012	Bb	Unknown	
2		130.537	4544683	4.99	7512	bb	Unknown	

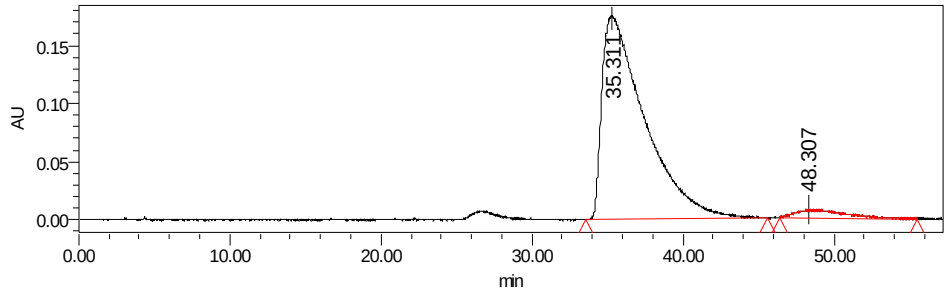
(*S*)-*tert*-Butyl 5-methoxy-1,1'-dimethyl-2-oxo-3,3'-biindolin-3-ylcarbamate (4d)



The ee value determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel OD-H column (hexane : 2-propanol = 92 : 8, 1.0 mL/min, 92% ee). White solid, 94% yield; mp = 123-124 ^{o}C; $[\alpha]_D^{20}$ = +299 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 7.5 Hz, 1H), 7.08-7.20 (m, 3H), 6.99 (d, *J* = 2.4 Hz, 1H), 6.80 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.47 (s, 1H), 5.64 (br.s, 1H), 3.74 (s, 3H), 3.55 (s, 3H), 3.08 (s, 3H), 1.22 (br.s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 175.4, 155.80, 153.75, 137.8, 137.2, 128.1, 125.0, 122.4, 121.8, 119.9, 112.8, 111.4, 111.0, 109.6, 108.3, 80.2, 62.1, 55.8, 32.7, 28.0, 26.5 ppm; IR (KBr): 3010, 2978, 1717, 1498, 1471, 1367, 1288, 1164, 1037, 753 cm^{-1}; HRMS calcd for $C_{24}H_{28}N_3O_4$ $(M+H)^+$ 422.2074, found 422.2070.

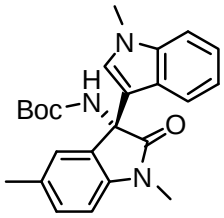


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		39.269	9267364	51.25	49002	bb	Unknown	
2		49.513	8813612	48.75	33417	bb	Unknown	

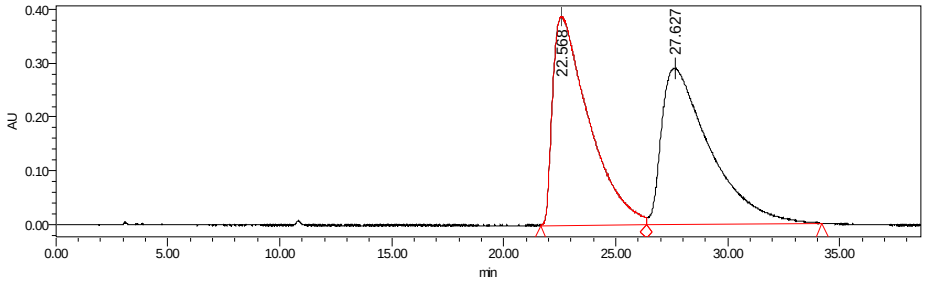


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		35.311	34401092	95.77	174526	bb	Unknown	
2		48.307	1519602	4.23	6818	bb	Unknown	

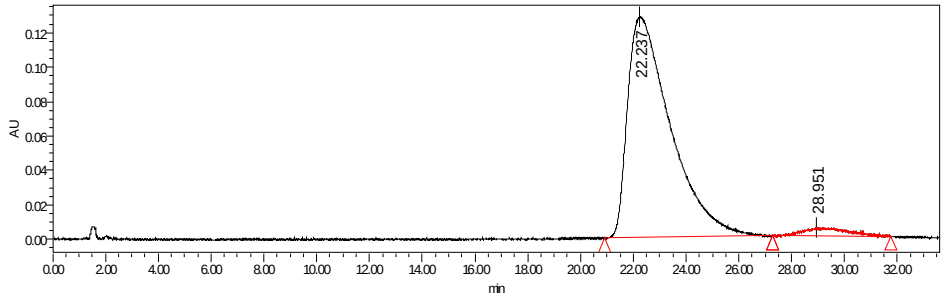
(*S*)-*tert*-Butyl 1,1',5-trimethyl-2-oxo-3,3'-biindolin-3-ylcarbamate (4e)



The ee value determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel OD-H column (hexane : 2-propanol = 92 : 8, 1.0 mL/min, 93% ee). White solid, 97% yield; mp = 108-110 ^{o}C; $[\alpha]_D^{20}$ = +104 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 7.8 Hz, 1H), 7.14-7.28 (m, 5H), 6.75 (d, *J* = 7.8 Hz, 1H), 6.54 (s, 1H), 5.65 (br.s, 1H), 3.64 (s, 3H), 3.16 (s, 3H), 2.38 (s, 3H), 1.26 (br.s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 175.7, 153.9, 141.3, 137.9, 131.9, 129.1, 128.2, 125.1, 124.2, 122.4, 121.9, 120.0, 111.7, 109.6, 107.8, 80.2, 62.0, 32.8, 28.1, 26.5, 21.3 ppm; IR (KBr): 3314, 2920, 1718, 1500, 1471, 1366, 1335, 1163, 746, 554 cm^{-1}; HRMS calcd for $C_{24}H_{28}N_3O_3$ $(M+H)^+$ 406.2125, found 406.2135.

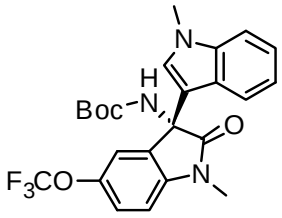


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		22.568	43493313	50.04	386584	BV	Unknown	
2		27.627	43431731	49.96	289251	VB	Unknown	

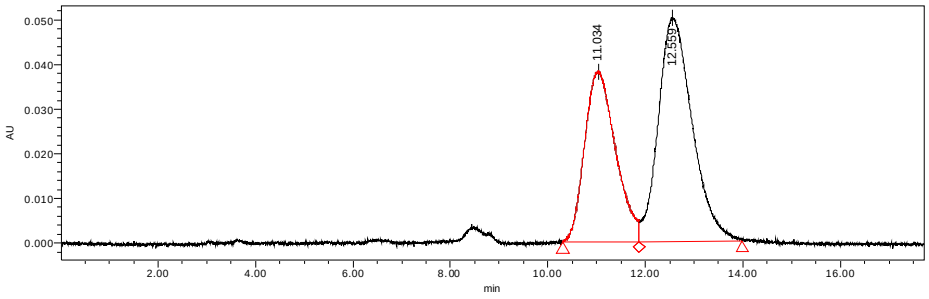


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		22.237	14566531	96.39	128419	bb	Unknown	
2		28.951	544814	3.61	4534	bb	Unknown	

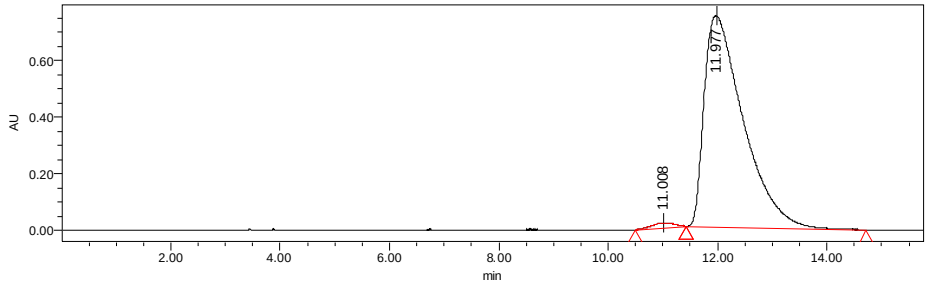
(*S*)-*tert*-Butyl 1,1'-dimethyl-2-oxo-5-(trifluoromethoxy)-3,3'-biindolin-3-ylcarbamate (4f)



The ee value determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel OD-H column (hexane : 2-propanol = 60 : 40, 1.0 mL/min, 97% ee). White solid, 98% yield; mp = 96-97 ^{o}C; $[\alpha]_D^{20}$ = +243 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 1.5 Hz, 1H), 7.17-7.28 (m, 4H), 6.84 (d, *J* = 2.7 Hz, 1H), 6.51 (s, 1H), 5.79 (br.s, 0.64H), 5.56 (br.s, 0.34H), 3.63 (s, 3H), 3.18 (s, 3H), 1.34 (br.s, 6H), 1.17 (br.s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 175.6, 153.7, 144.57, 144.55, 142.5, 137.9, 128.1, 125.0, 122.7, 122.3,122.1, 121.7, 120.2, 118.9, 117.5, 110.6, 109.8, 108.6, 80.7, 62.0, 32.9, 28.1, 26.7 ppm; IR (KBr): 3313, 2976, 2921, 1716, 1496, 1254, 1217, 1162, 1119, 1092 cm^{-1}; HRMS calcd for $C_{24}H_{24}F_3N_3NaO_4$ $(M+Na)^+$ 498.1611, found 498.1623.



	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		11.034	1691214	41.02	38162	BV	Unknown	
2		12.559	2431305	58.98	50109	VB	Unknown	



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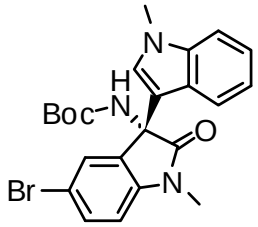
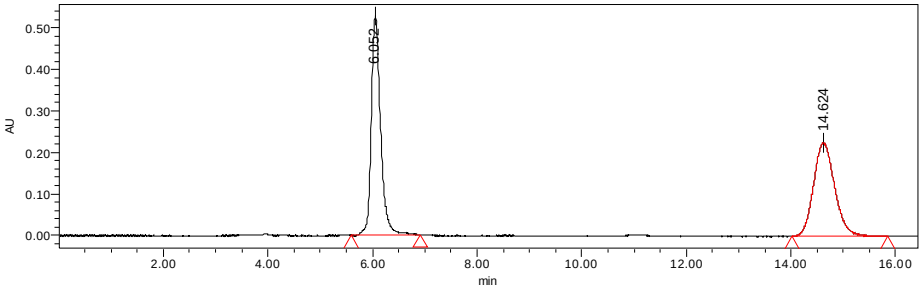
1		11.008	501931	1.33	17226	bb	Unknown	
2		11.977	37135930	98.67	747498	bB	Unknown	

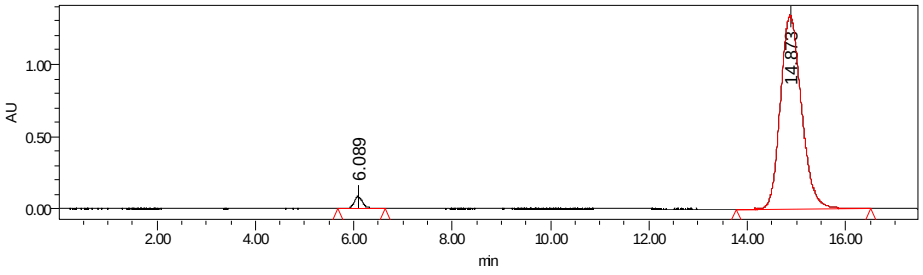
(*S*)-*tert*-Butyl 5-bromo-1,1'-dimethyl-2-oxo-3,3'-biindolin-3-ylcarbamate (4g)



The ee value determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel IA-H column (hexane : 2-propanol = 60 : 40, 1.0 mL/min, 95% ee). White solid, 93% yield; mp = 123-124 ^{o}C; $[\alpha]_D^{20}$ = +274 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 1.8 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.17-7.29 (m, 3H), 6.74 (d, *J* = 8.1 Hz, 1H), 6.53 (s, 1H), 5.76 (br.s, 1H), 3.64 (s, 3H), 3.16 (s, 3H), 1.34 (br.s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 175.2, 153.7, 142.8, 137.9, 131.8, 128.1, 126.5, 124.9, 122.6, 121.7, 120.2, 115.0, 110.7, 109.8, 80.6, 61.9, 32.9, 28.2, 26.6 ppm; IR (KBr): 3354, 2972, 1467, 1380, 1309, 1162, 1130, 1110, 953, 817 cm^{-1}; HRMS calcd for $C_{23}H_{24}BrN_3NaO_3$ $(M+Na)^+$ 492.0893, found 492.0913.

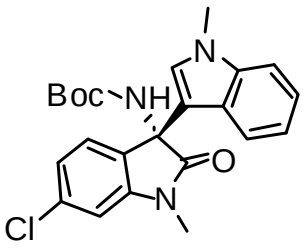


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		6.052	6558084	51.01	529035	bb	Unknown	
2		14.624	6297579	48.99	225534	bb	Unknown	

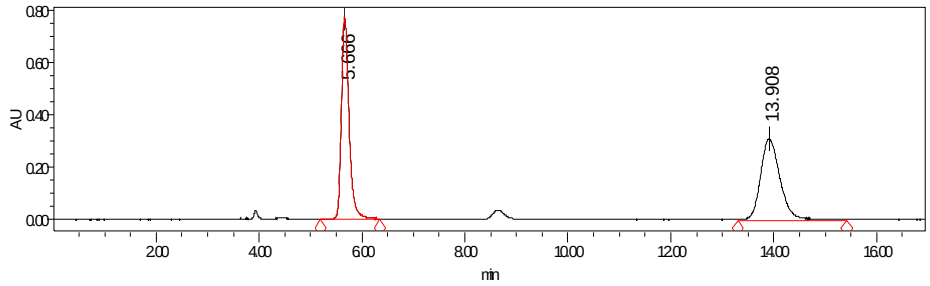


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		6.089	1091964	2.68	84748	bb	Unknown	
2		14.873	39727255	97.32	1337814	bb	Unknown	

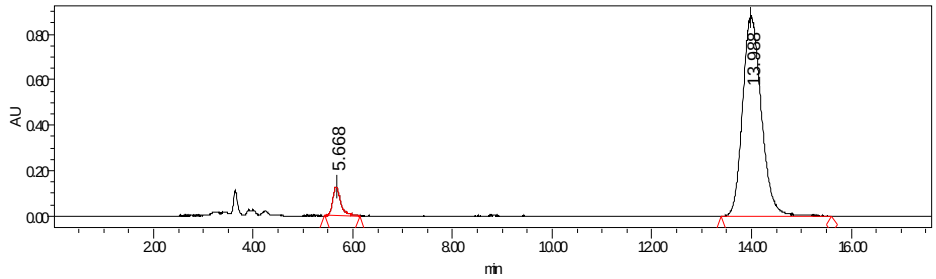
(*S*)-*tert*-Butyl 6-chloro-1,1'-dimethyl-2-oxo-3,3'-biindolin-3-ylcarbamate (4h)



The ee value determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel IA-H column (hexane : 2-propanol = 60 : 40, 1.0 mL/min, 89% ee). White solid, 98% yield; mp = 94-96 ^{o}C; $[\alpha]_D^{20}$ = +282 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.16-7.24 (m, 2H), 7.16-7.22 (m, 1H), 7.10 (d, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 1.5 Hz, 1H), 6.51 (s, 1H), 5.77 (br.s, 1H), 3.62 (s, 3H), 3.15 (s, 3H), 1.33 (br.s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 175.6, 153.8, 144.9, 137.9, 134.6, 128.2, 125.0, 124.3, 122.6, 122.2, 121.7, 120.1, 110.9, 109.8, 109.0, 80.5, 61.5, 32.9, 28.2, 26.7 ppm; IR (KBr): 3343, 2971, 1718, 1610, 1494, 1469, 1370, 1162, 952, 743 cm^{-1}; HRMS calcd for $C_{23}H_{25}ClN_3O_3$ $(M+H)^+$ 426.1579, found 426.1583.

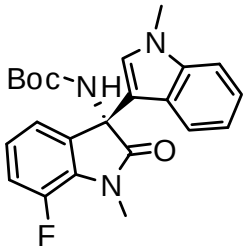


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		5.666	8107155	49.70	770491	VV	Unknown	
2		13.908	8204036	50.30	310346	VV	Unknown	

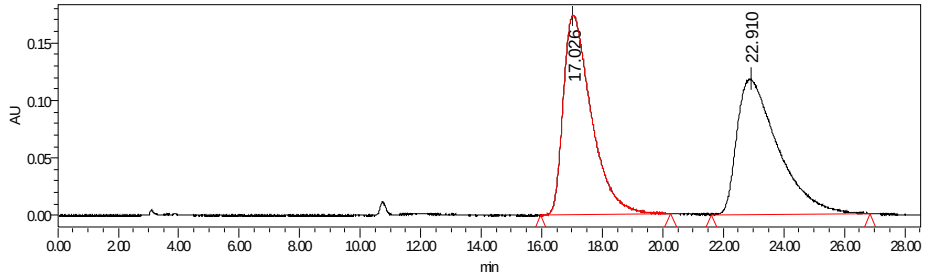


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		5.668	1404023	5.69	127175	bb	Unknown	
2		13.988	23274501	94.31	884014	BV	Unknown	

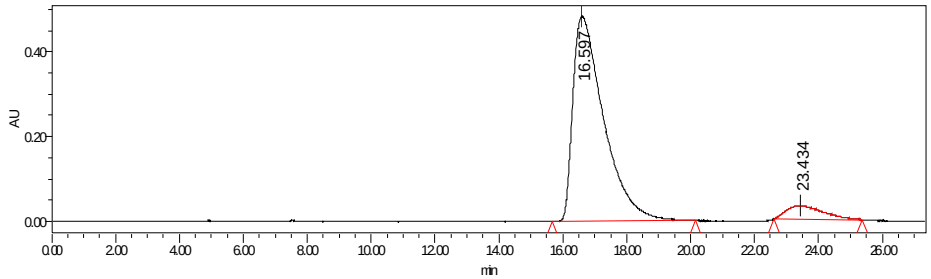
(*S*)-*tert*-Butyl 7-fluoro-1,1'-dimethyl-2-oxo-3,3'-biindolin-3-ylcarbamate (4i)



The ee value determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel OD-H column (hexane : 2-propanol = 80 : 20, 1.0 mL/min, 86% ee). White solid, 94% yield; mp = 128-130 ^{o}C; $[\alpha]_D^{20}$ = +229 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 7.8 Hz, 1H), 7.24-7.29 (m, 2H), 7.17-7.23 (m, 2H), 7.01-7.12 (m, 2H), 6.49 (s, 1H), 5.78 (br.s, 1H), 3.64 (s, 3H), 3.40 (s, 3H), 1.34 (br.s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 175.5, 153.8, 137.9, 130.4, 130.3, 128.3, 125.0, 122.9, 122.8, 122.6, 121.8, 120.1, 119.3, 119.2, 117.1, 116.8, 111.0, 109.8, 80.6, 62.0, 32.9, 29.0, 28.1 ppm; IR (KBr): 3019, 2400, 1716, 1486, 1369, 1238, 1216, 1161, 758, 669 cm^{-1}; HRMS calcd for $C_{23}H_{24}FN_3NaO_3$ $(M+Na)^+$ 432.1694, found 432.1707.

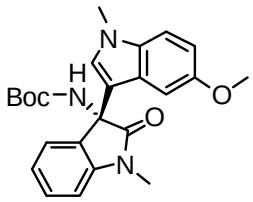


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		17.026	11201574	50.33	173483	bb	Unknown	
2		22.910	11056027	49.67	117248	bb	Unknown	

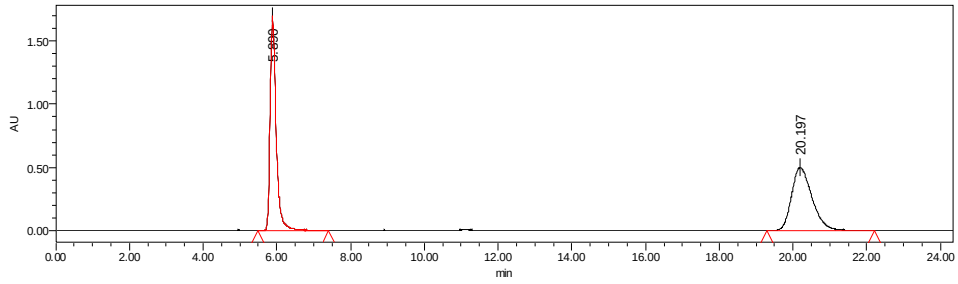


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		16.597	32491881	92.79	484293	bb	Unknown	
2		23.434	2523960	7.21	31479	bb	Unknown	

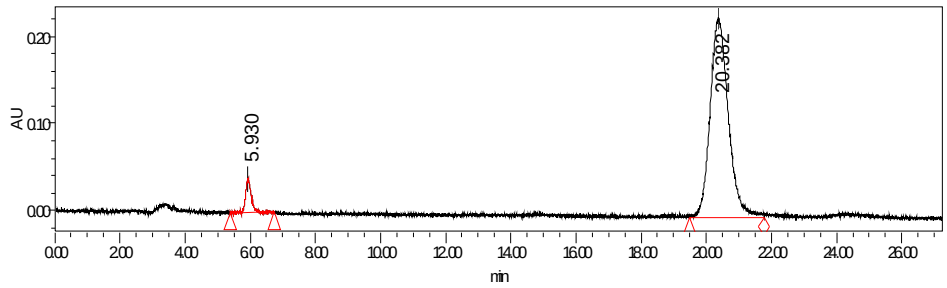
(*S*)-*tert*-Butyl 5'-methoxy-1,1'-dimethyl-2-oxo-3,3'-biindolin-3-ylcarbamate (4j)



The ee value determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel IA-H column (hexane : 2-propanol = 60 : 40, 1.0 mL/min, 90% ee). White solid, 98% yield; mp = 118-120 ^{o}C; $[\alpha]_D^{20}$ = +274 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59 (s, 1H), 7.39 (dd, *J* = 18.0, 7.5 Hz, 2H)), 7.11-7.15 (m, 2H), 6.85-6.91 (m, 2H), 6.51 (s, 1H), 5.69 (br.s, 0.44H), 5.51 (br.s, 0.53H), 3.89 (s, 3H), 3.59 (s, 3H), 3.18 (s, 3H), 1.30 (br.s, 4H), 1.16 (br.s, 5H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 175.8, 154.2, 153.9, 143.8, 133.1, 129.0, 128.7, 125.5, 123.5, 122.4, 113.0, 110.7, 110.4, 108.1, 103.2, 80.3, 61.9, 55.9, 33.0, 28.1, 26.5 ppm; IR (KBr): 3017, 2979, 1715, 1494, 1472, 1367, 1217, 1165, 754, 667 cm^{-1}; HRMS calcd for $C_{24}H_{28}N_3O_4$ $(M+H)^+$ 422.2074, found 422.2091.

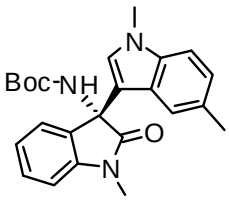


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		5.890	19357448	49.88	1680162	BB	Unknown	
2		20.197	19446709	50.12	498620	BB	Unknown	

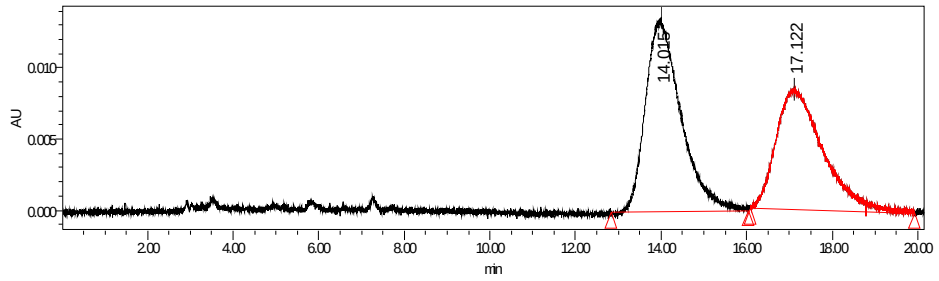


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		5.930	470233	4.98	38865	bb		
2		20.382	8967377	95.02	229692	BV		

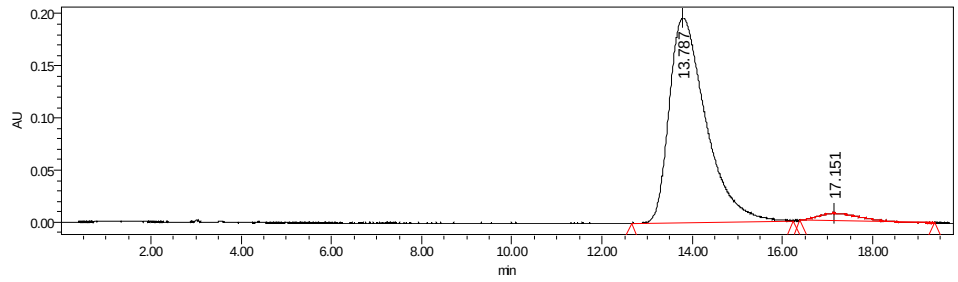
(*S*)-*tert*-Butyl 1,1',5'-trimethyl-2-oxo-3,3'-biindolin-3-ylcarbamate (4k)



The ee value determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel OD-H column (hexane : 2-propanol = 90 : 10, 1.0 mL/min, 92% ee). White solid, 96% yield; mp = 139-140 ^{o}C; $[\alpha]_D^{20}$ = +279 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01 (br.s, 1H), 7.33-7.43 (m, 2H), 7.04-7.15 (m, 3H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.43 (s, 1H), 5.54 (br.s, 1H), 3.57 (s, 3H), 3.17 (s, 3H), 2.50 (s, 3H), 1.16 (br.s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 175.8, 153.9, 143.7, 136.4, 129.3, 128.9, 128.3 125.3, 124.2, 123.4, 122.4, 121.5, 110.8, 109.4, 108.0, 80.3, 62.0, 32.8, 28.1, 26.5, 21.7 ppm; IR (KBr): 3018, 2921, 1715, 1614, 1492, 1472, 1371, 1216, 754, 667 cm^{-1}; HRMS calcd for $C_{24}H_{28}N_3O_3$ $(M+H)^+$ 406.2125, found 406.2144.

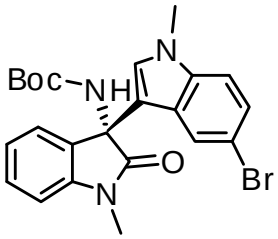


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		14.015	779996	54.58	13422	bb	Unknown	
2		17.122	648982	45.42	8439	bb	Unknown	

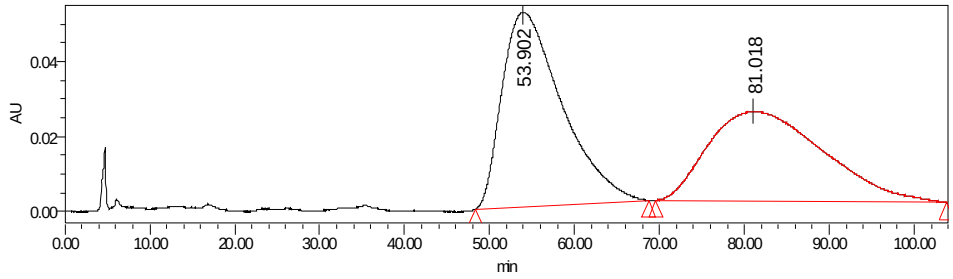


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		13.787	11065094	95.76	196775	bb	Unknown	I08
2		17.151	489911	4.24	7575	bb	Unknown	

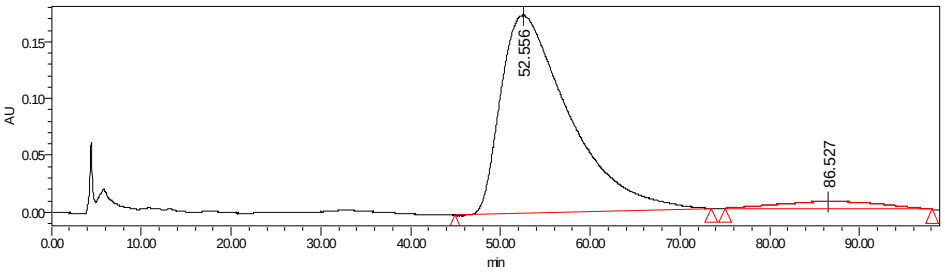
(*S*)-*tert*-Butyl 5'-bromo-1,1'-dimethyl-2-oxo-3,3'-biindolin-3-ylcarbamate (4l)



The ee value determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel OJ-H column (hexane : 2-propanol = 97 : 3, 0.8 mL/min, 90% ee). White solid, 96% yield; mp = 117-119 ^{o}C; $[\alpha]_D^{20}$ = +268 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.31 (s, 1H), 7.41 (dd, *J* = 15.0, 7.5 Hz, 2H), 7.27 (d, *J* = 9.6 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H) 7.08 (d, *J* = 9.0 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.52 (s, 1H), 5.57 (br.s, 1H), 3.59 (s, 3H), 3.17 (s, 3H), 1.25 (br.s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 175.5, 153.8, 143.7, 136.6, 129.4, 129.1, 126.7, 125.5, 124.3, 123.4, 122.5, 113.6, 111.2, 111.1, 108.2, 80.5, 61.7, 33.0, 28.1, 26.5 ppm; IR (KBr): 2920, 2848, 1720, 1471, 1422, 1369, 1288, 1250, 1164, 752 cm^{-1}; HRMS calcd for $C_{23}H_{24}BrN_3NaO_3$ $(M+Na)^+$ 492.0893, found 492.0915.

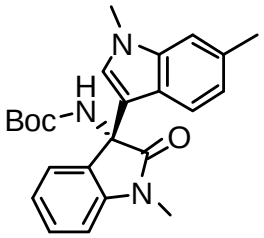


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		53.901	27160079	52.69	54998	bb	Unknown	
2		81.169	24389411	47.31	25326	bb	Unknown	

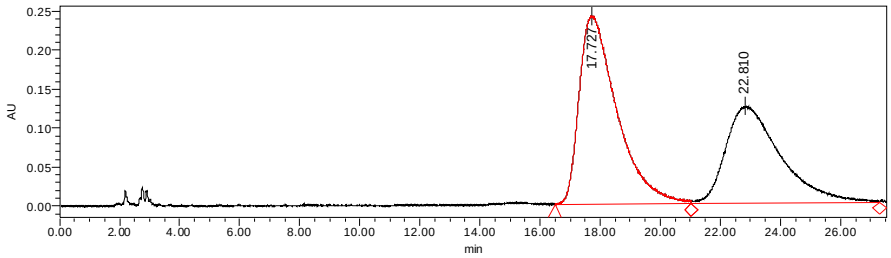


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		52.556	92490248	94.75	174466	bb	Unknown	
2		86.527	5129374	5.25	6407	bb	Unknown	

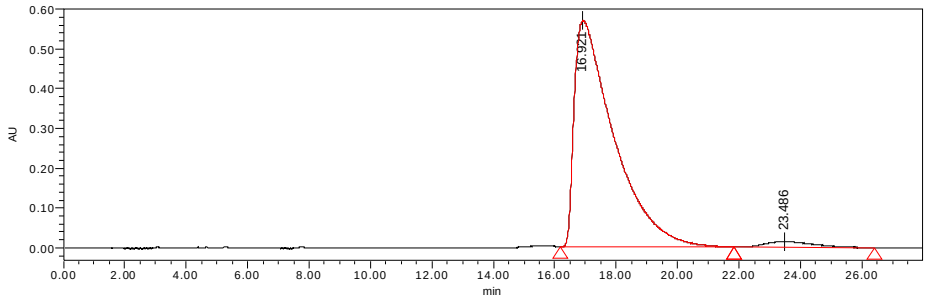
(*S*)-*tert*-Butyl 1,1',6'-trimethyl-2-oxo-3,3'-biindolin-3-ylcarbamate (4m)



The ee value determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel OD-H column (hexane : 2-propanol = 90 : 10, 1.0 mL/min, 94% ee). White solid, 98% yield; mp = 149-150 ^{o}C; $[\alpha]_D^{20}$ = +275 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 7.8 Hz, 1H), 7.41 (d, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.04 (s, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.45 (s, 1H), 5.65 (br.s, 1H), 3.58 (s, 3H), 3.18 (s, 3H), 2.47 (s, 3H), 1.26 (br.s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 175.8, 153.9, 143.7, 138.3, 132.4, 128.9, 127.7, 123.4, 122.9, 122.4, 121.8, 121.5, 111.4, 109.6, 108.0, 80.2, 61.9, 32.7, 28.1, 26.5, 21.8 ppm; IR (KBr): 3015, 2921, 1716, 1614, 1473, 1371, 1351, 1216, 753, 666 cm^{-1}; HRMS calcd for $C_{24}H_{28}N_3O_3$ $(M+H)^+$ 406.2125, found 406.2144.

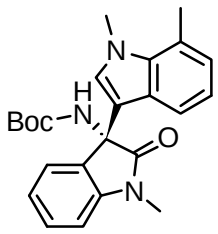


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		17.727	21286228	57.40	242293	BV	Unknown	
2		22.810	15797245	42.60	123955	VV	Unknown	

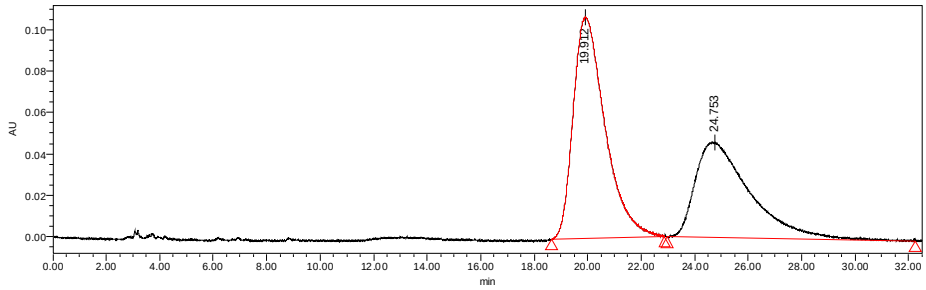


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		16.921	51129984	96.96	569216	bb	Unknown	
2		23.486	1605365	3.04	14454	bb	Unknown	

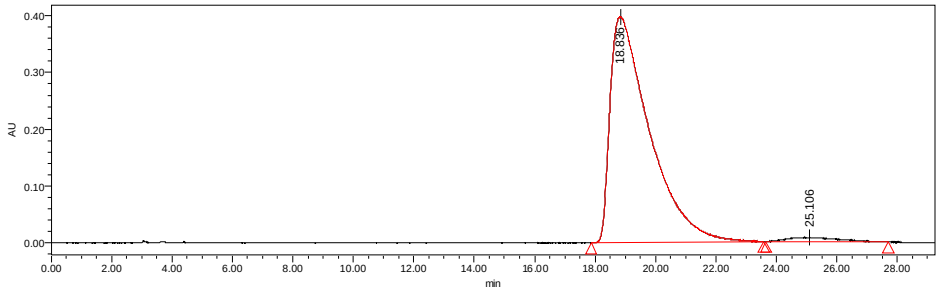
(*S*)-*tert*-Butyl 1,1',7'-trimethyl-2-oxo-3,3'-biindolin-3-ylcarbamate (4n)



The ee value determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel OD-H column (hexane : 2-propanol = 90 : 10, 1.0 mL/min, 96% ee). White solid, 98% yield; mp = 126-128 ^{o}C; $[\alpha]_D^{20}$ = +276 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 7.8 Hz, 1H), 7.41 (d, *J* = 7.2 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 7.2 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.38 (br.s, 1H), 5.65 (br.s, 1H), 3.87 (s, 3H), 3.17 (s, 3H), 2.69 (s, 3H), 1.26 (br.s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 175.7, 153.9, 143.7, 136.7, 129.9, 128.9, 126.2, 125.1, 123.4, 122.4, 121.6, 120.2, 120.0, 111.1, 108.1, 80.3, 61.9, 37.0, 28.1, 26.5, 19.8 ppm; IR (KBr): 2976, 2931, 1720, 1614, 1493, 1471, 1368, 1347, 1164, 753 cm^{-1}; HRMS calcd for $C_{24}H_{28}N_3O_3$ $(M+H)^+$ 406.2125, found 406.2139.

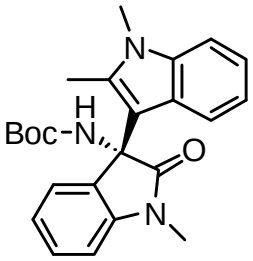


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		19.912	8815195	57.55	106909	Bb	Unknown	
2		24.753	6501299	42.45	45976	Bb	Unknown	

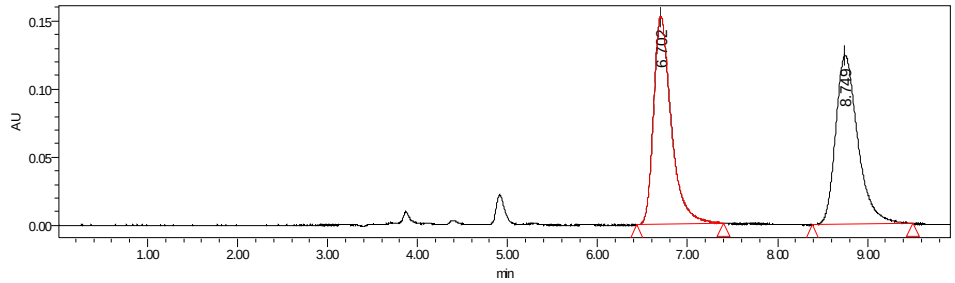


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		18.836	35956220	97.76	397654	Bb	Unknown	
2		25.106	823015	2.24	7192	Bb	Unknown	

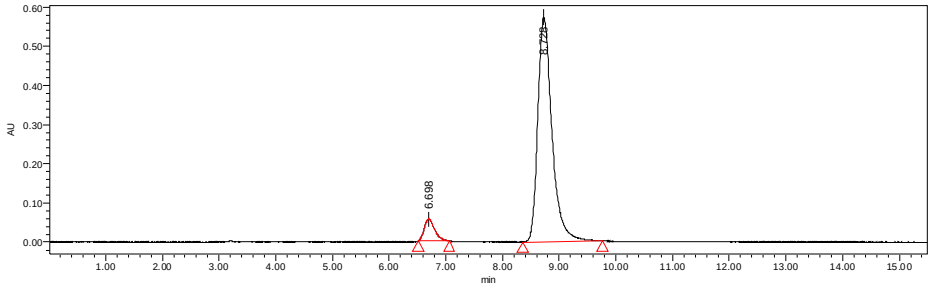
(*S*)-*tert*-Butyl 1,1',2'-trimethyl-2-oxo-3,3'-biindolin-3-ylcarbamate (4o)



The ee value determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel IA-H column (hexane : 2-propanol = 70 : 30, 1.0 mL/min, 87% ee). White solid, 98% yield; mp = 210-211 ^{o}C; $[\alpha]_D^{20}$ = +126 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35-7.42 (m, 2H), 7.18 (d, *J* = 8.1 Hz, 1H), 7.06-7.11 (m, 2H), 6.86-6.92 (m, 3H), 5.70 (br.s, 1H), 3.56 (s, 3H), 3.18 (s, 3H), 2.37 (s, 3H), 1.25 (br.s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 176.5, 154.0, 144.0, 136.6, 131.7, 129.1, 125.4, 124.3, 122.5, 121.0, 120.1, 119.6, 108.9, 108.1, 107.0, 80.4, 62.6, 29.5, 28.1, 26.5, 12.2 ppm; IR (KBr): 3005, 2920, 1719, 1612, 1491, 1470, 1368, 1242, 1165, 748 cm^{-1}; HRMS calcd for $C_{24}H_{28}N_3O_3$ $(M+H)^+$ 406.2125, found 406.2140.

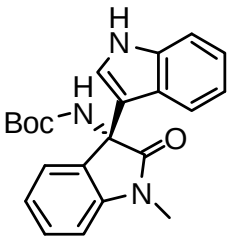


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		6.702	2088680	49.61	152583	bb	Unknown	
2		8.749	2121730	50.39	124026	bb	Unknown	

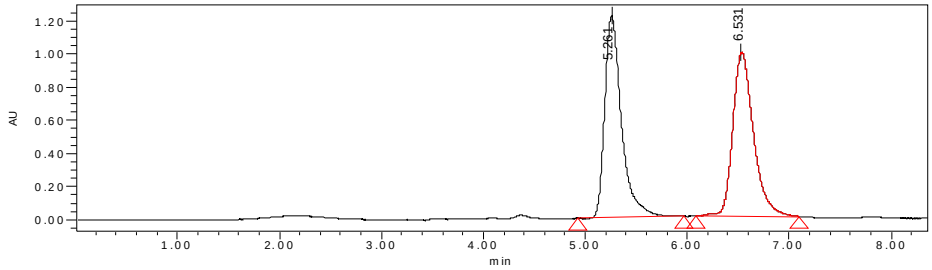


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		6.698	719207	6.73	56109	bb	Unknown	
2		8.728	9961817	93.27	573829	bb	Unknown	

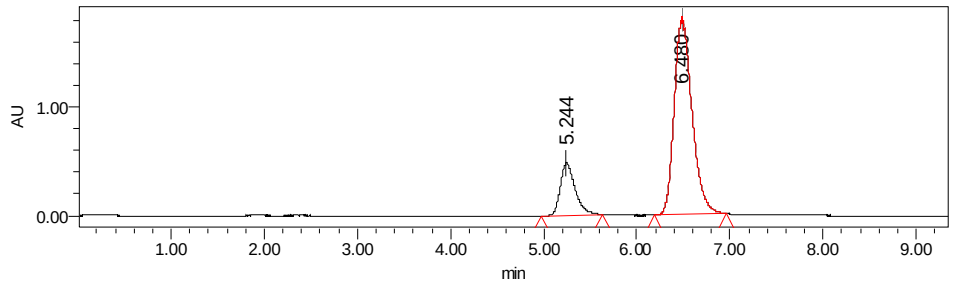
(*S*)-*tert*-Butyl 1-methyl-2-oxo-3,3'-biindolin-3-ylcarbamate (4p)



The ee value determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel IA-H column (hexane : 2-propanol = 60 : 40, 1.0 mL/min, 64% ee). White solid, 97% yield; mp = 142-143 ^{o}C; $[\alpha]_D^{20}$ = +184 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.78 (s, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.31 (s, 1H), 7.24 (dd, *J* = 7.2, 1.5 Hz, 1H), 7.08-77.16 (m, 3H), 6.79 (d, *J* = 6.6 Hz, 1H), 6.50 (d, *J* = 2.1 Hz, 1H), 5.81 (br.s, 1H), 3.09 (s, 3H), 1.29 (br.s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 175.9, 154.0, 143.6, 137.2, 129.0, 124.5, 124.2, 123.4, 122.61, 122.55, 121.4, 120.1, 112.5, 111.9, 108.2, 80.5, 62.0, 28.1, 26.5 ppm; IR (KBr): 3328, 3019, 1714, 1615, 1472, 1370, 1216, 1165, 758, 669 cm^{-1}; HRMS calcd for $C_{22}H_{23}N_3NaO_3$ $(M+Na)^+$ 400.1637, found 400.1647.

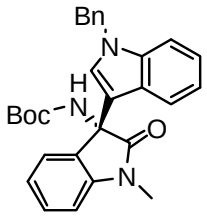


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		5.261	13957363	49.94	1222237	bb	Unknown	
2		6.531	13992568	50.06	989766	bb	Unknown	

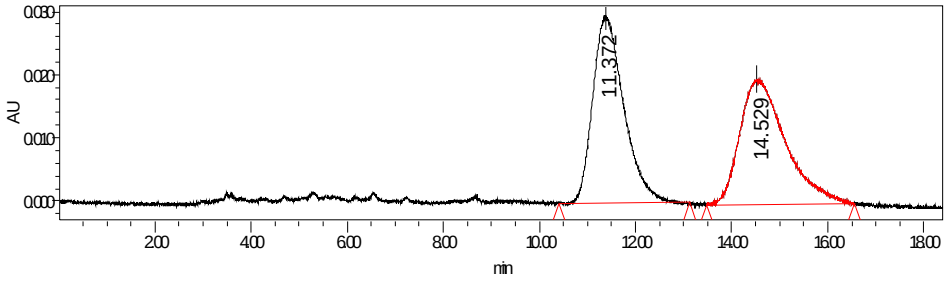


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		5.244	5289329	18.09	479636	bb	Unknown	I08
2		6.480	23953365	81.91	1798727	bb	Unknown	

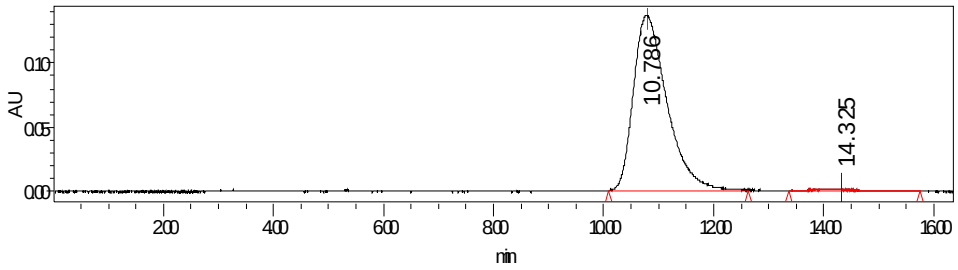
(*S*)-*tert*- Butyl 1'-benzyl-1-methyl-2-oxo-3,3'-biindolin-3-ylcarbamate (4q)



The ee value determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel IA-H column (hexane : 2-propanol = 80 : 20, 1.0 mL/min, 98% ee). White solid, 96% yield; mp = 102-104 ^{o}C; $[\alpha]_D^{20}$ = +244 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 6.0 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.23-7.24 (m, 8H), 7.08-7.19 (m, 8H), 7.00 (d, *J* = 5.7 Hz, 1H), 6.98 (s, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.64 (s, 1H), 5.72 (br.s, 1H), 5.14 (s, 2H), 3.19 (s, 3H), 1.27 (br.s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 175.7, 153.8, 143.8, 137.5, 136.9, 129.0, 128.8, 127.9, 127.7, 126.5, 125.4, 123.4, 122.7, 122.5, 122.1, 120.3, 112.3, 110.3, 108.2, 80.3, 61.9, 50.2, 28.1, 26.6 ppm; IR (KBr): 3005, 2922, 1719, 1613, 1492, 1469, 1369, 1164, 746, 695 cm^{-1}; HRMS calcd for $C_{29}H_{29}N_3NaO_3$ $(M+Na)^+$ 490.2107, found 490.2112.

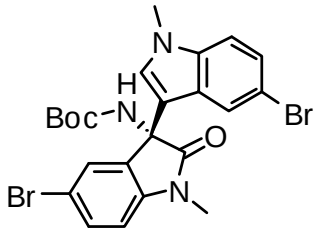


	name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		11.372	1331611	50.71	29464	bb	Unknown	
2		14.529	1294480	49.29	19684	bb	Unknown	

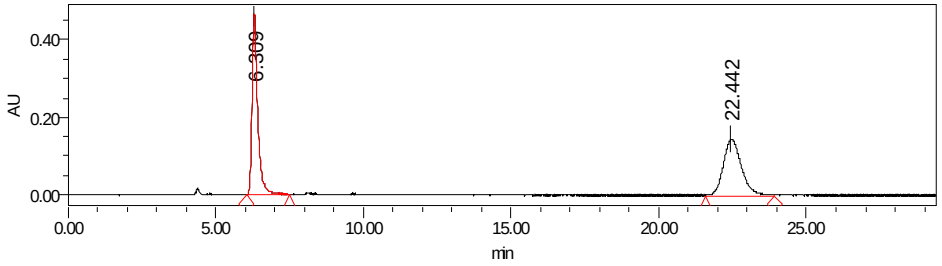


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		10.786	5798655	98.96	136394	BB	Unknown	
2		14.325	61186	1.04	1386	bb	Unknown	

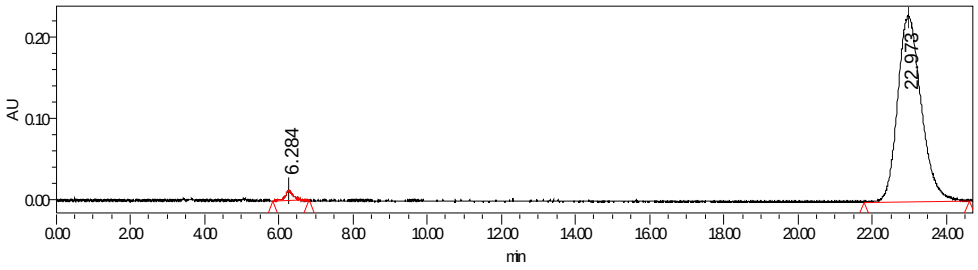
(*S*)-*tert*-Butyl 5,5'-dibromo-1,1'-dimethyl-2-oxo-3,3'-biindolin-3-ylcarbamate (4s)



The ee value determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel IA-H column (hexane : 2-propanol = 70 : 30, 1.0 mL/min, 96% ee). White solid, 96% yield; mp = 243-244 ^{o}C; $[\alpha]_D^{20}$ = +237 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.34 (s, 1H), 7.44-7.57 (m, 2H), 7.26-7.33 (m, 1H), 7.12 (d, *J* = 8.7 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.52 (s, 1H), 5.62 (br.s, 1H), 3.63 (s, 3H), 3.16 (s, 3H), 1.37 (br.s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 174.9, 153.7, 142.8, 136.6, 133.1, 132.0, 129.3, 128.6, 126.5, 125.7, 124.3, 115.0, 113.8, 111.2, 110.4, 109.7, 80.9, 61.6, 33.1, 28.1, 26.6 ppm; IR (KBr): 3425, 2258, 1709, 1659, 1051, 1027, 1005, 825, 763, 624 cm^{-1}; HRMS calcd for $C_{23}H_{23}Br_2N_3NaO_3$ $(M+Na)^+$ 569.9998, found 570.0007.

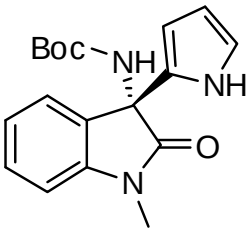


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		6.309	6276531	50.37	467641	VB	Unknown	
2		22.442	6184168	49.63	145790	BV	Unknown	

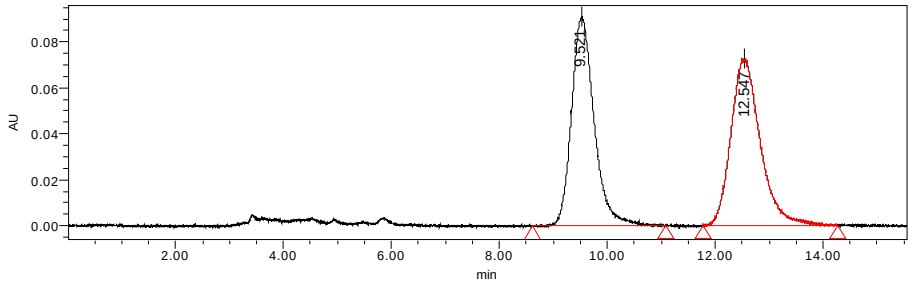


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		6.284	211196	2.06	12596	bb	Unknown	
2		22.973	10055122	97.94	228711	bb	Unknown	

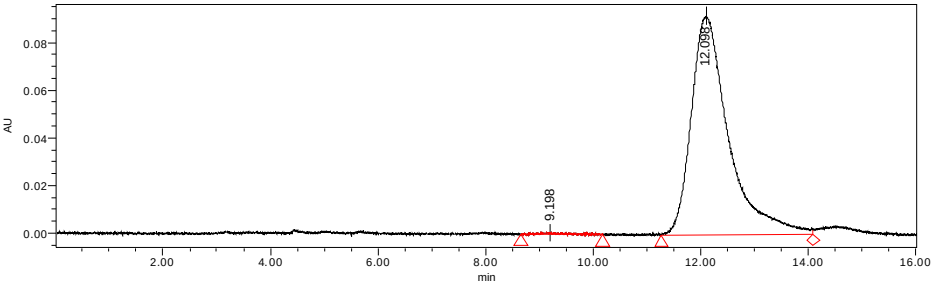
(*R*)-*tert*- Butyl 1-methyl-2-oxo-3-(1H-pyrrol-2-yl)indolin-3-ylcarbamate (6a)



The ee value determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel AD-H column (hexane : 2-propanol = 60 : 40, 1.0 mL/min, 99% ee). White solid, 97% yield; mp = 93-94 ^{o}C; $[\alpha]_D^{20}$ = +143 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.11 (br.s, 1H), 7.40 (d, *J* = 6.9 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.80 (s, 1H), 6.77 (s, 1H), 6.14 (br.s, 1H), 5.91 (d, *J* = 1.8 Hz, 1H), 5.74 (s, 1H), 3.15 (s, 3H), 1.14 (br.s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 174.8, 152.1, 142.4, 128.1, 124.0, 122.5, 121.8, 120.3, 108.6, 107.6, 107.0, 106.5, 79.6, 59.3, 26.9, 25.6 ppm; IR (KBr): 3318, 3007, 2975, 2932, 1709, 1616, 1495, 1472, 1371, 1255, 1161, 988, 895, 753, 541 cm^{-1}; HRMS calcd for $C_{18}H_{22}N_3O_3$ $(M+H)^+$ 328.1656, found 328.1657.

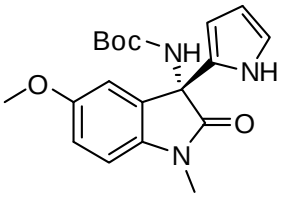


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		9.521	2650216	49.11	90835	bb	Unknown	
2		12.547	2745923	50.89	72257	bb	Unknown	

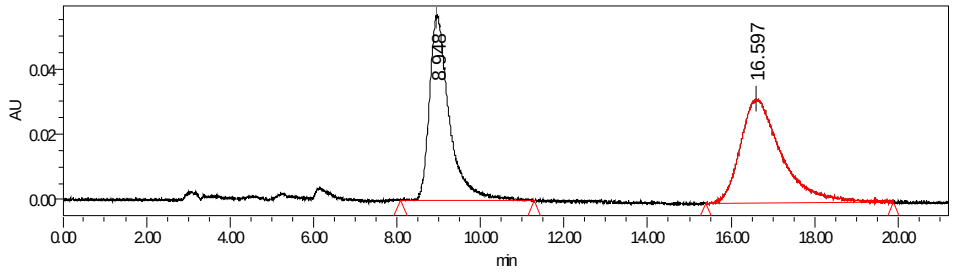


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		9.198	17467	0.39	543	bb	Unknown	
2		12.098	4406629	99.61	91726	BV	Unknown	

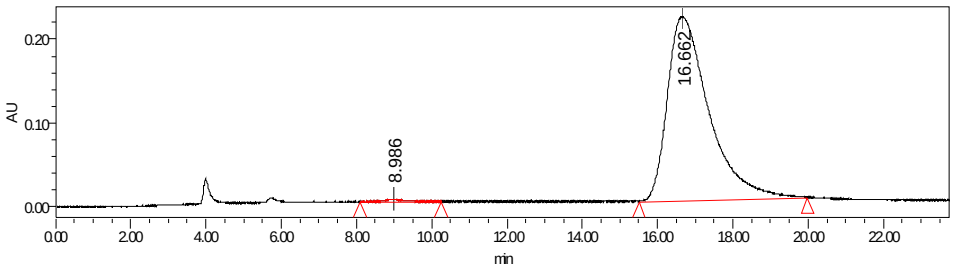
(*R*)-*tert*- Butyl 5-methoxy-1-methyl-2-oxo-3-(1H-pyrrol-2-yl)indolin-3-ylcarbamate (6b)



The ee value determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel AD-H column (hexane : 2-propanol = 60 : 40, 1.0 mL/min, 99% ee). White solid, 96% yield; mp = 91-93 ^{o}C; [α]$_D^{20}$ = +167 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.24 (br.s, 1H), 7.10 (d, *J* = 2.1 Hz, 1H), 6.84-6.89 (m, 2H), 6.76 (t, *J* = 8.1 Hz, 1H), 6.22 (br.s, 1H), 5.99 (d, *J* = 3.0 Hz, 1H), 5.85 (s, 1H), 3.84 (s, 3H), 3.21 (br.s, 3H), 1.21 (br.s, 6H), 1.09 (br.s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 175.5, 156.1, 153.1, 136.9, 130.6, 125.0, 121.4, 112.9, 111.3, 109.6, 108.9, 107. 5, 80.7, 60.5, 55.9, 27.9, 26.7 ppm; IR (KBr): 3315, 2922, 1705, 1498, 1473, 1368, 1289, 1162, 1935, 754 cm^{-1}; HRMS calcd for $C_{19}H_{24}N_3O_4$ $(M+H)^+$ 358.1761 found 358.1761.

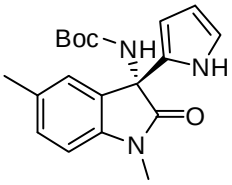


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		8.948	1886636	46.74	56363	bb	Unknown	
2		16.597	2149629	53.26	31670	bb	Unknown	I08

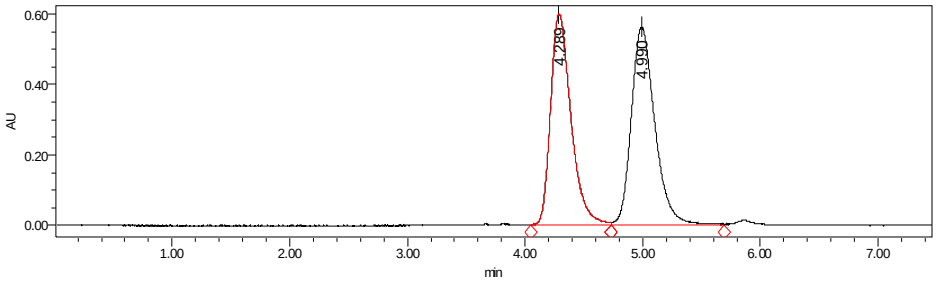


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		8.986	108670	0.64	2882	bb	Unknown	
2		16.662	16832993	99.36	219258	BB	Unknown	

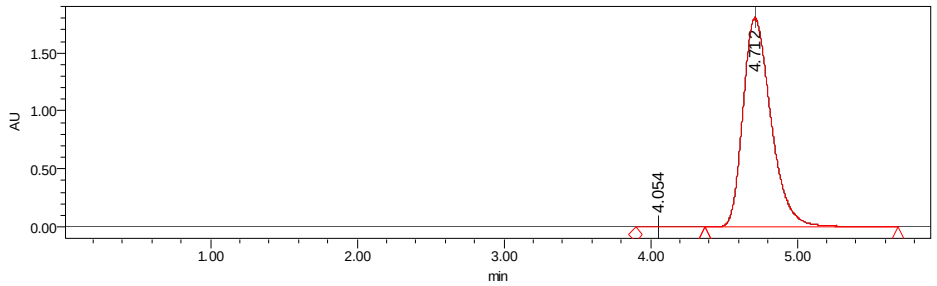
(*R*)-*tert*-Butyl 1,5-dimethyl-2-oxo-3-(1H-pyrrol-2-yl)indolin-3-ylcarbamate (6c)



The ee value determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel OD-H column (hexane : 2-propanol = 60 : 40, 1.0 mL/min, 99% ee). White solid, 97% yield; mp = 111-113 ^{o}C; $[\alpha]_D^{20}$ = +168 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.26 (br.s, 0.62H), 10.04 (br.s, 0.36H), 7.27 (d, *J* = 6.3 Hz, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 6.84 (dd, *J* = 4.2, 1.8 Hz, 1H), 6.75 (d, *J* = 7.5 Hz, 1H), 6.22 (br.s, 0.66H), 5.98 (d, *J* = 3.0 Hz, 1H), 5.90 (br.s, 0.33H), 5.82 (s, 1H), 3.21 (s, 3H), 2.40 (s, 3H), 1.22 (br.s, 6H), 1.08 (br.s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 175.7, 153.1, 141.1, 132.3, 129.4, 125.3, 124.3, 121.3, 109.6, 108.4, 107.4, 80.7, 60.4, 28.0, 26.7, 21.3 ppm; IR (KBr): 3314, 2921, 1707, 1501, 1366, 1161, 1094, 811, 754, 698 cm^{-1}; HRMS calcd for $C_{19}H_{24}N_3O_3$ $(M+H)^+$ 342.1812 found 342.1810.

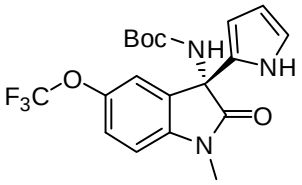


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		4.289	7281242	48.02	600877	VV	Unknown	
2		4.990	7881982	51.98	562256	VV	Unknown	

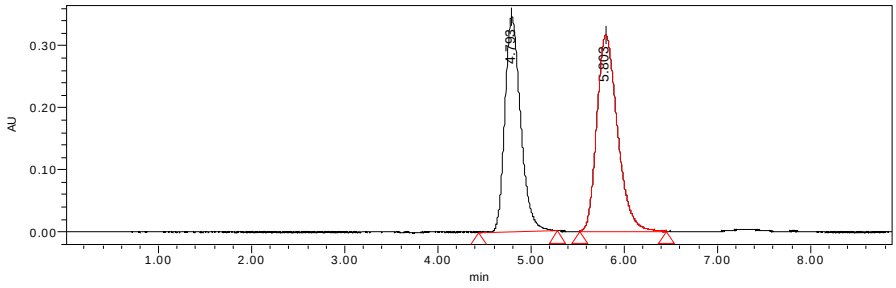


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		4.054	57322	0.24	4245	VB	Unknown	
2		4.712	24015884	99.76	1808176	Bb	Unknown	

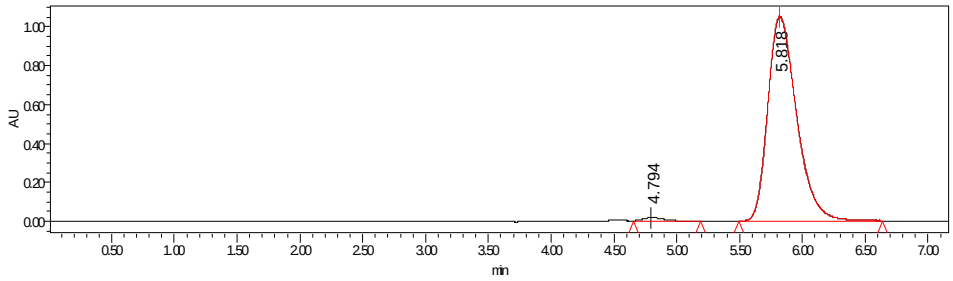
(*R*)-*tert*-Butyl 1-methyl-2-oxo-3-(1H-pyrrol-2-yl)-5-(trifluoromethoxy)indolin-3-ylcarbamate (6d)



The ee value determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel OD-H column (hexane : 2-propanol = 60 : 40, 1.0 mL/min, 98% ee). White solid, 98% yield; mp = 119-120 ^{o}C; [α]$_D^{20}$ = +186 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.12 (br.s, 1H), 7.37 (s, 1H), 7.25 (d, *J* = 7.2 Hz, 1H), 6.86 (dd, *J* = 7.5, 3.0 Hz, 2H), 6.18 (br.s, 0.63H), 6.05 (br.s, 0.31H), 6.11 (dd, *J* = 6.0, 1.8 Hz, 1H), 5.81 (s, 1H), 3.25 (s, 3H), 1.23 (br.s, 6H), 1.07 (br.s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 176.0, 153.9, 153.0, 144.9, 142.1, 130.9, 125.7, 123.8, 122.3, 122.0, 118.9, 117.6, 115.5, 109.8, 109.3, 108.9, 107.6, 81.3, 61.0, 60.4, 27.8, 26.8 ppm; IR (KBr): 3325, 2976, 1713, 1498, 1369, 1257, 1218, 1162, 1120, 736 cm^{-1}; HRMS calcd for $C_{19}H_{20}F_3N_3NaO_4$ $(M+Na)^+$ 434.1298, found 434.1298.

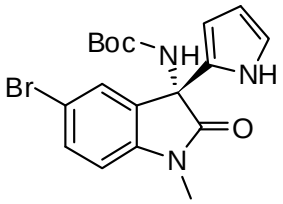


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		4.794	181507	1.07	17077	bb	Unknown	
2		5.818	16801303	98.93	1051520	BB	Unknown	

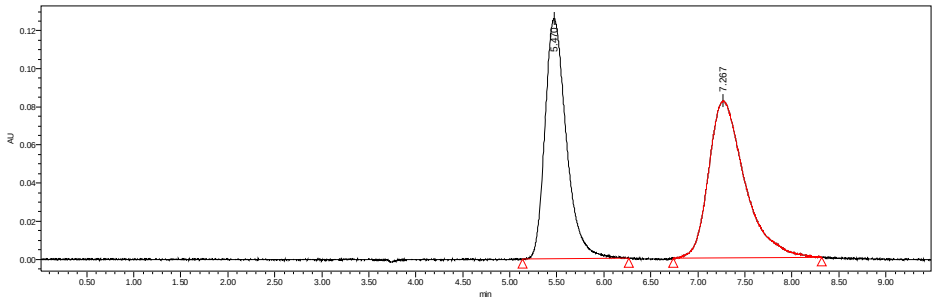


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		4.794	178022	1.05	16930	bb	Unknown	
2		5.818	16720730	98.95	1050996	Bb	Unknown	

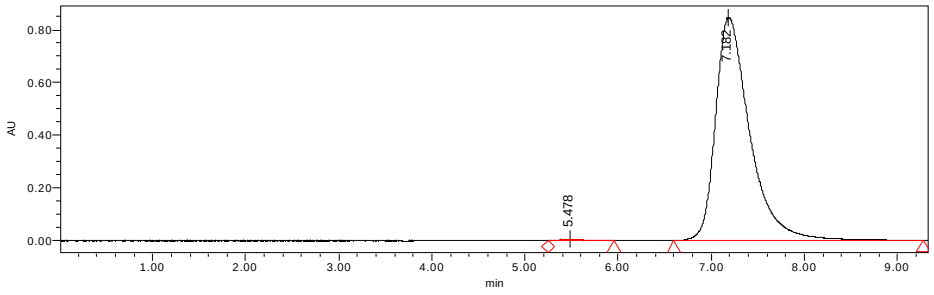
(*R*)-*tert*-Butyl 5-bromo-1-methyl-2-oxo-3-(1H-pyrrol-2-yl)indolin-3-ylcarbamate (6e)



The ee value determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel OD-H column (hexane : 2-propanol = 80 : 20, 1.0 mL/min, 99% ee). White solid, 95% yield; mp = 203-205 ^{o}C; $[\alpha]_D^{20}$ = +151 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.15 (br.s, 1H), 7.56 (s, 1H), 7.49 (d, *J* = 8.1 Hz, 1H), 6.84 (d, *J* = 1.2 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.15 (br.s, 1H), 6.00 (d, *J* = 1.8 Hz, 1H), 5.83 (s, 1H), 3.20 (s, 3H), 1.23 (br.s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 175.3, 153.2, 142.5, 135.0, 132.0, 126.6, 124.1, 121.7, 115.5, 110.2, 109.9, 107.7, 81.1, 60.2, 28.3, 28.0, 26.8 ppm; IR (KBr): 3328, 2919, 1711, 1610, 1489, 1420, 1366, 1162, 1097, 754 cm^{-1}; HRMS calcd for $C_{18}H_{20}BrN_3NaO_3$ $(M+Na)^+$ 428.0580, found 428.0587.

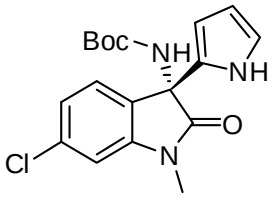


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		5.470	1991068	47.49	126387	bb	Unknown	
2		7.267	2201238	52.51	82411	bb	Unknown	

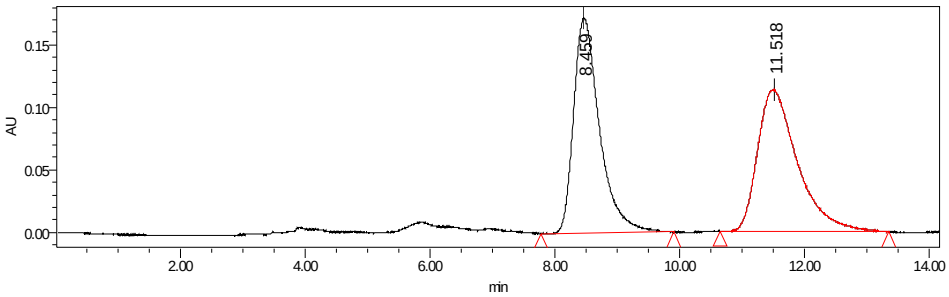


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		5.478	100743	0.46	5800	VB	Unknown	
2		7.182	21780650	99.54	845747	BB	Unknown	

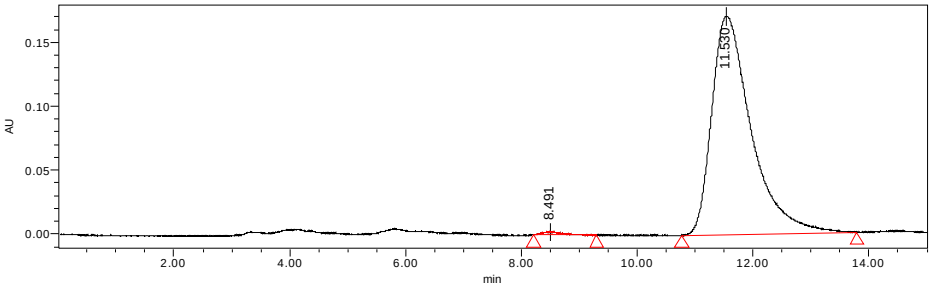
(*R*)-*tert*-Butyl 6-chloro-1-methyl-2-oxo-3-(1H-pyrrol-2-yl)indolin-3-ylcarbamate (6f)



The ee value determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel AD-H column (hexane : 2-propanol = 60 : 40, 1.0 mL/min, 99% ee). White solid, 98% yield; mp = 142-143 ^{o}C; $[\alpha]_D^{20}$ = +187 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.19 (br.s, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 6.84-6.88 (m, 2H), 6.26 (br.s, 1H), 5.99 (d, *J* = 3.0 Hz, 1H) 5.79 (s, 1H), 3.21 (br.s, 3H), 1.20 (br.s, 7H), 1.10 (br.s, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 175.9, 153.0, 144.7, 134.9, 127.7, 124.3, 122.7, 121.7, 109.8, 109.5, 107.6, 81.0, 60.0, 27.9, 26.8 ppm; IR (KBr): 3328, 2974, 1712, 1612, 1496, 1370, 1244, 1161, 1074, 734 cm^{-1}; HRMS calcd for $C_{18}H_{20}ClN_3NaO_3$ $(M+Na)^+$ 384.1085, found 384.1090.

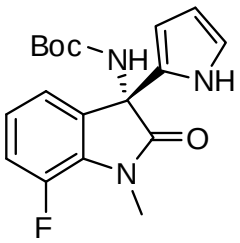


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		8.459	4977619	49.72	172406	bb	Unknown	
2		11.518	5033007	50.28	112944	bb	Unknown	

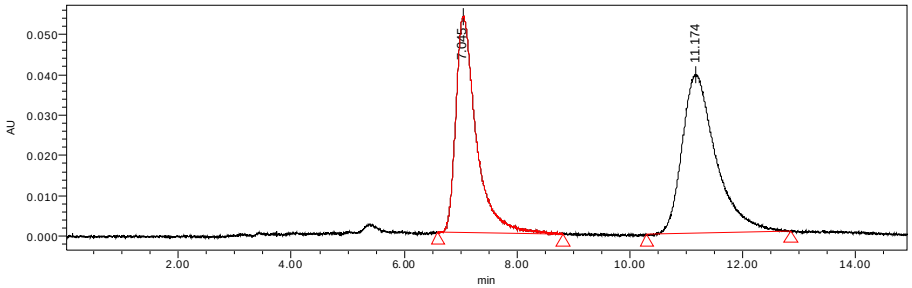


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		8.491	55877	0.68	2443	bb	Unknown	I08
2		11.530	8124417	99.32	170951	BB	Unknown	

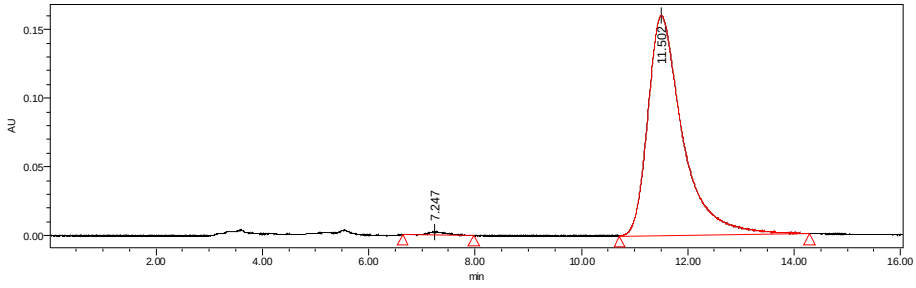
(*R*)-*tert*-Butyl 7-fluoro-1-methyl-2-oxo-3-(1H-pyrrol-2-yl)indolin-3-ylcarbamate (6g)



The ee value determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel AD-H column (hexane : 2-propanol = 60 : 40, 1.0 mL/min, 99% ee). White solid, 95% yield; mp = 92-94 ^{o}C; $[\alpha]_D^{20}$ = +150 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.24 (br.s, 0.68H), 10.13 (br.s, 0.30H), 7.26 (s, 1H), 7.10 (d, *J* = 4.5 Hz, 1H), 7.07 (s, 1H), 6.86 (dd, *J* = 7.2, 1.8 Hz, 1H), 6.29 (br.s, 0.67H), 6.04 (br.s, 0.31H), 5.99 (dd, *J* = 5.7, 1.8 Hz, 1H), 5.77-5.80 (m, 1H), 3.45 (s, 3H), 1.21 (br.s, 6H), 1.12 (br.s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 175.6, 153.8, 153.1, 149.6, 146.4, 132.2, 130.1, 124.3, 123.4, 123.3, 121.7, 119.4, 117.4, 117.1, 109.9, 107.6, 81.0, 60.4, 29.3, 27.9 ppm; IR (KBr): 3327, 2976, 1713, 1632, 1484, 1369, 1236, 1161, 753, 733 cm^{-1}; HRMS calcd for $C_{18}H_{21}FN_3O_3$ $(M+H)^+$ 346.1561, found 346.1559.

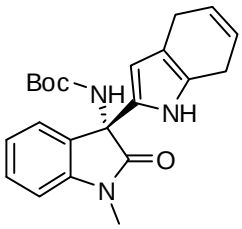


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		7.045	1360136	45.48	53572	bb	Unknown	
2		11.174	1630381	54.52	39294	bb	Unknown	

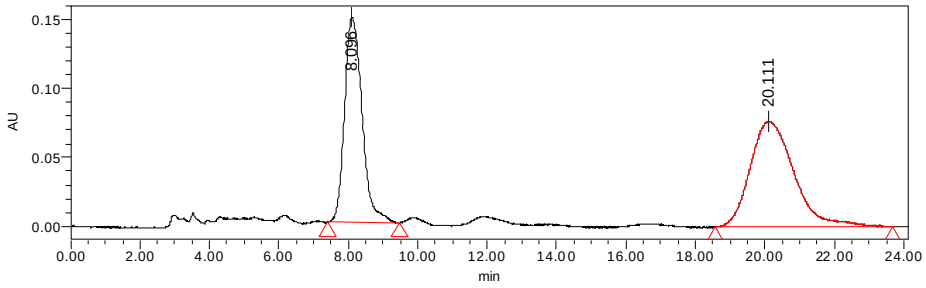


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		7.247	53183	0.73	2201	bb	Unknown	
2		11.502	7251616	99.27	159899	Bb	Unknown	

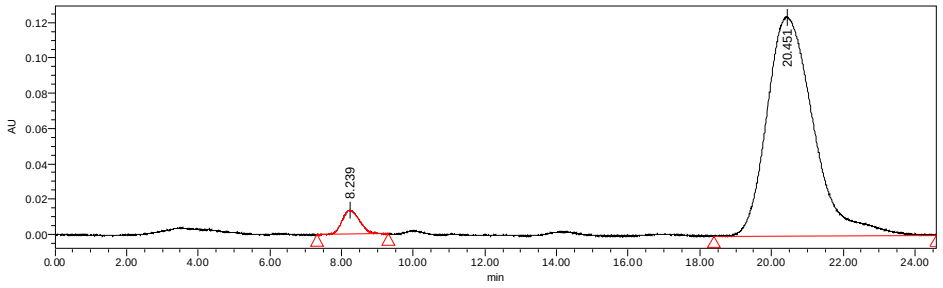
(*R*)-*tert*-Butyl 1'-methyl-2'-oxo-2,3'-biindolin-3'-ylcarbamate (6h)



The ee value determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel AD-H column (hexane : 2-propanol = 80 : 20, 1.0 mL/min, 92% ee). White solid, 96% yield; mp = 126-128 ^{o}C; [α]$_D^{20}$ = +144 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.34 (br.s, 0.68H), 9.54 (br.s, 0.24H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.34-7.39 (m, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.45 (br.s, 1H), 5.77 (s, 2H), 5.58 (s, 1H), 3.16-3.29 (m, 5H), 3.01-3.06 (m, 2H), 1.15 (br.s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 176.1, 152.8, 143.4, 129.4, 129.0, 128.3, 125.2, 123.4, 123.2, 122.7, 113.1, 108.7, 108.2, 80.7, 60.4, 27.7, 26.6, 24.6, 23.9 ppm; IR (KBr): 3381, 3309, 3025, 2971, 2928, 1708, 1616, 1493, 1369, 1246, 1157, 1122, 752 cm^{-1}; HRMS calcd for $C_{22}H_{25}N_3NaO_3$ $(M+Na)^+$ 402.1794, found 402.1804.

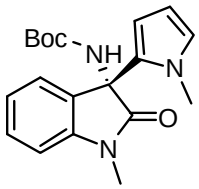


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		8.096	5254251	43.72	149796	bb	Unknown	I08
2		20.111	6765022	56.28	76682	bb	Unknown	



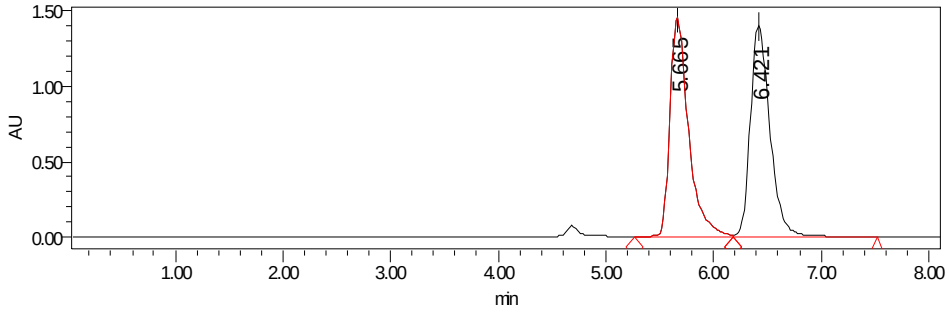
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		8.239	469955	4.04	13489	bb	Unknown	
2		20.451	11151960	95.96	123719	bb	Unknown	

(*R*)-*tert*- Butyl 1-methyl-2-oxo-3-(1H-pyrrol-2-yl)indolin-3-ylcarbamate (6i)

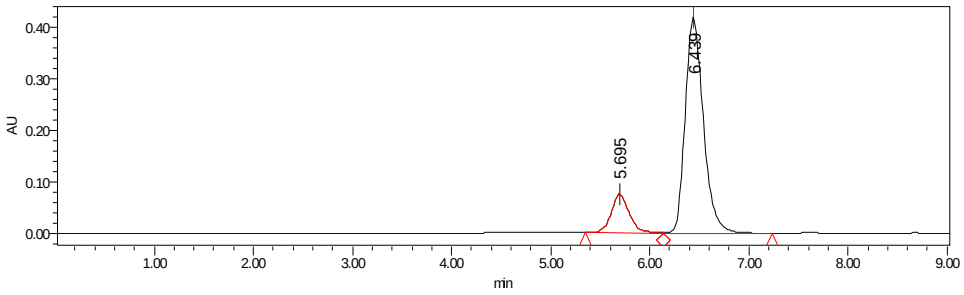


6i

The ee value determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel OD-H column (hexane : 2-propanol = 80 : 20, 0.8 mL/min, 70% ee). White solid, 49% yield; mp = 90-91 ^{o}C; $[\alpha]_D^{20}$ = +160 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 7.2 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 6.64 (t, *J* = 2.1 Hz, 1H), 5.84 (t, *J* = 3.0 Hz, 1H), 5.84 (br.s, 1H), 5.47 (t, *J* = 1.8 Hz, 1H), 4.09 (s, 3H), 3.14 (s, 3H), 1.20 (br.s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 174.6, 153.8, 143.6, 130.5, 129.2, 127.0, 126.6, 124.0, 122.6, 111.7, 107.9, 106.4, 80.7, 62.1, 36.9, 28.0, 26.5 ppm; IR (KBr): 3336, 2976, 2929, 1723, 1613, 1493, 1472, 1370, 1164, 754 cm^{-1}; HRMS calcd for $C_{18}H_{22}N_3O_3$ $(M+H)^+$ 342.1812, found 342.1809.



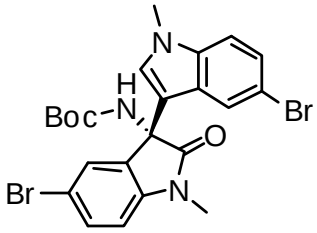
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		52.556	92490248	94.75	174466	bb	Unknown	
2		86.527	5129374	5.25	6407	bb	Unknown	

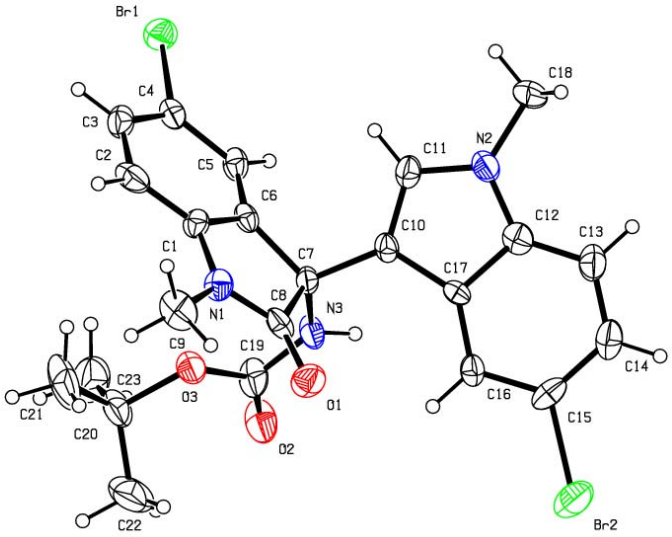


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type	Peak Codes
1		5.695	934925	14.89	75216	BV	Unknown	
2		6.439	5345020	85.11	418858	VB	Unknown	

X-Ray Structure of 4s

(*S*)-*tert*-Butyl 5,5'-dibromo-1,1'-dimethyl-2-oxo-3,3'-biindolin-3-ylcarbamate (CCDC: 879849)



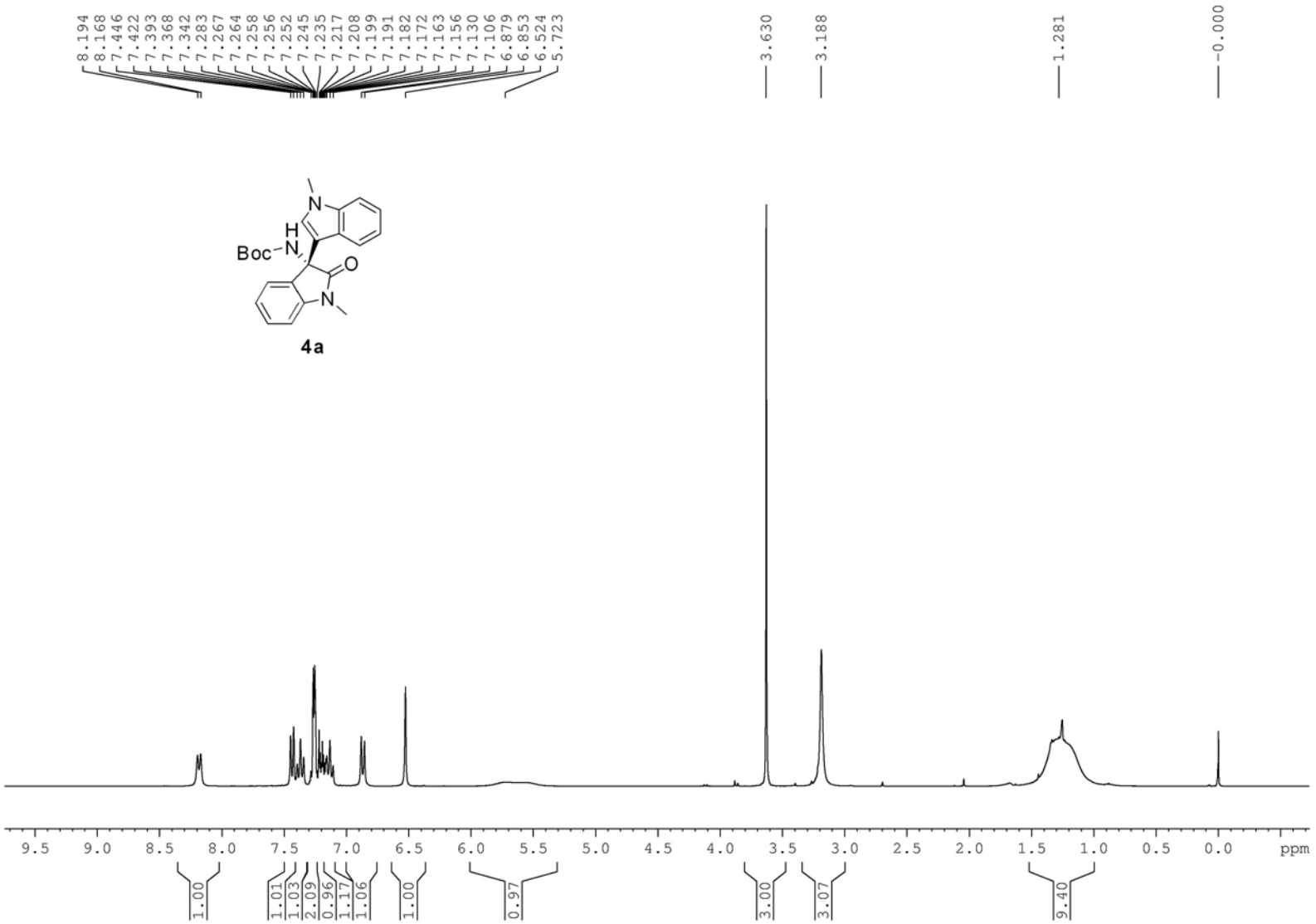


Reference

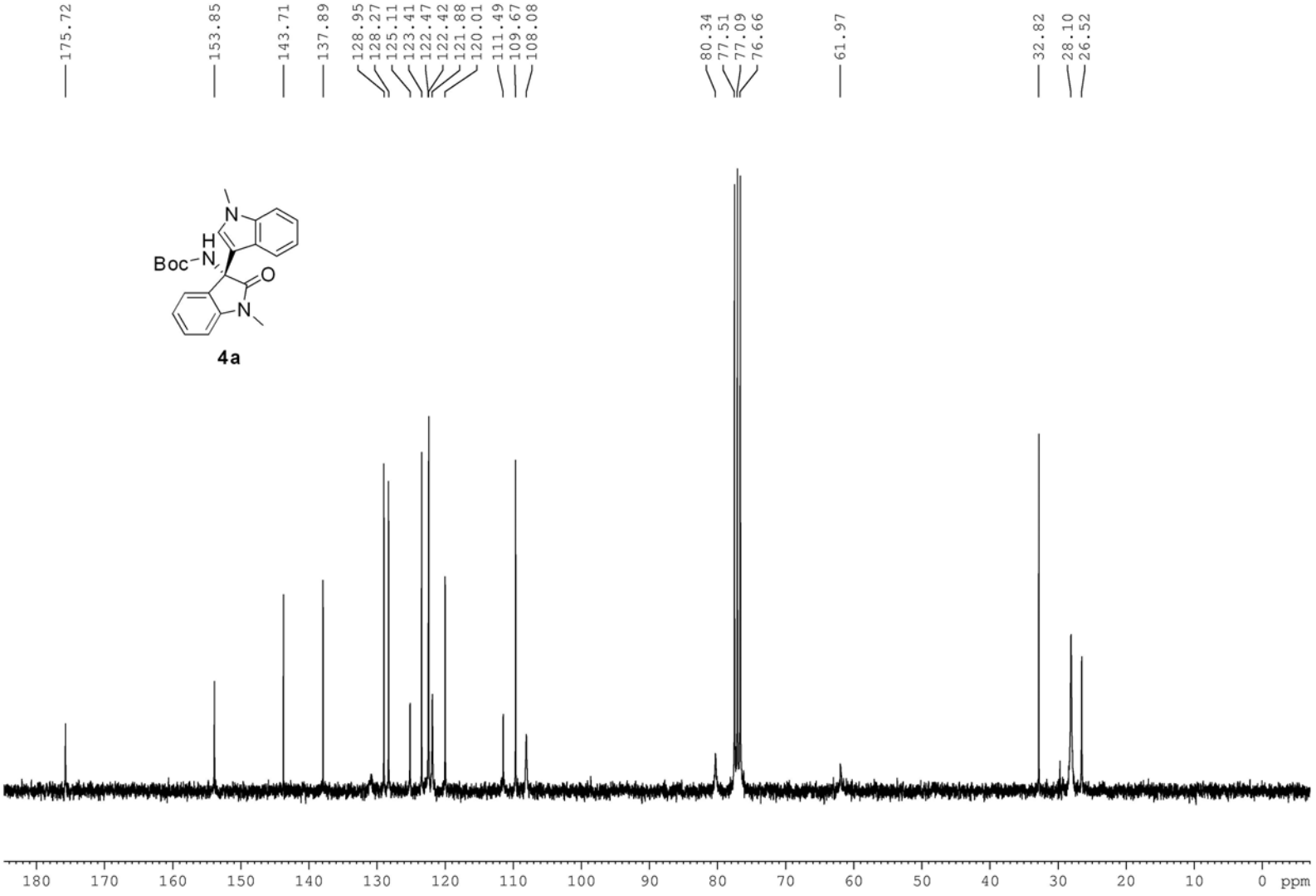
1 (a) X-H. Chen, Q. Wei, S.-W. Luo, H. Xiao, L.-Z. Gong, *J. Am. Chem. Soc.* **2009**, *131*, 13819. (b) T. W. Wu, L. Shen, J. M. Chong, *Org. Lett.* **2004**, *6*, 2701. (c) M. Hatano, T. Ikeno,; T. Matsumura, S. Torii, K. Ishihara, *Adv. Synth. Catal.* **2008**, *350*, 1776

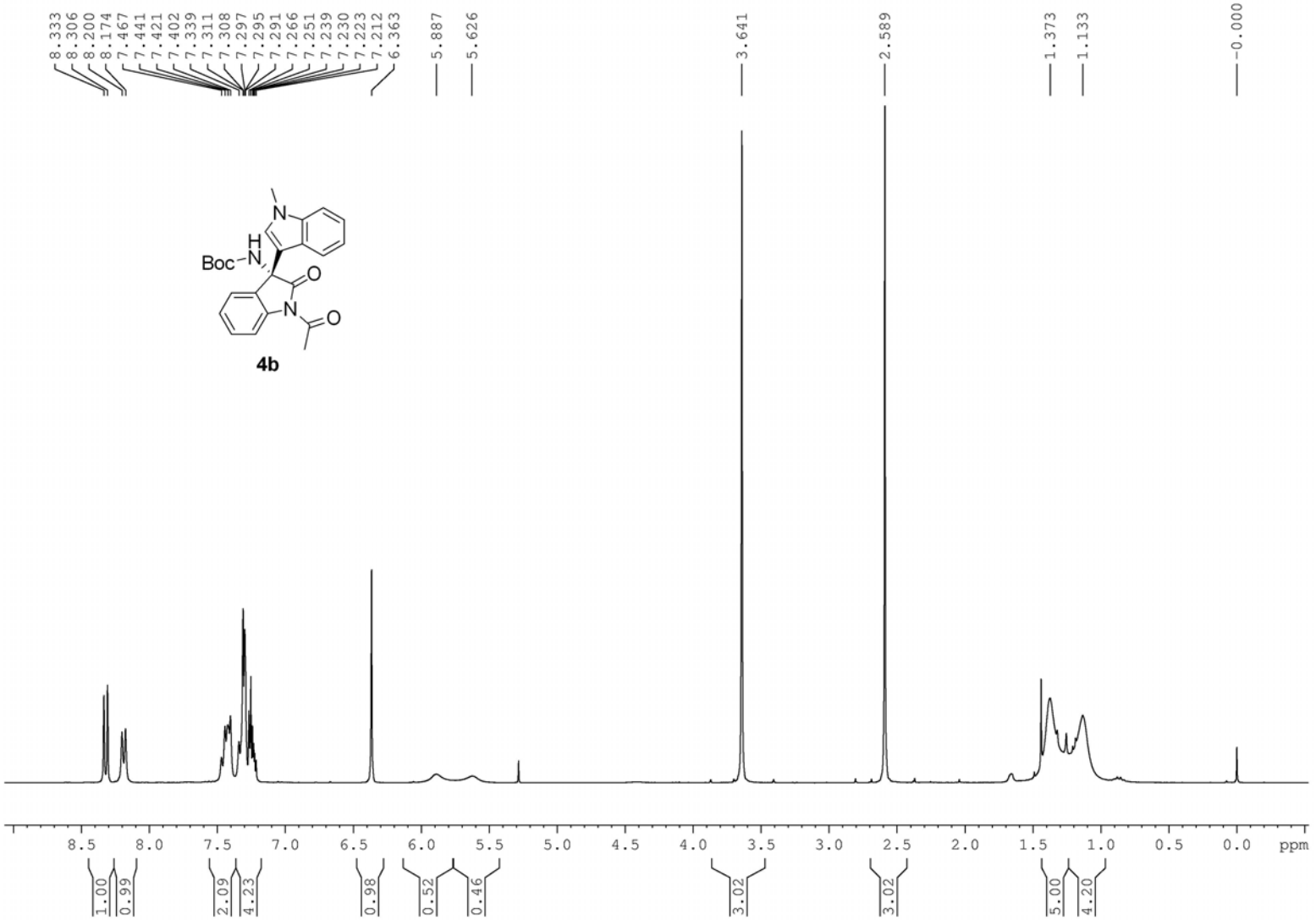
2 M. Klussmann, L. Ratjen, S. Hoffmann, V. Wakchaure, R. Goddard, B. List, *Synlett.* **2010**, *14*, 2189.

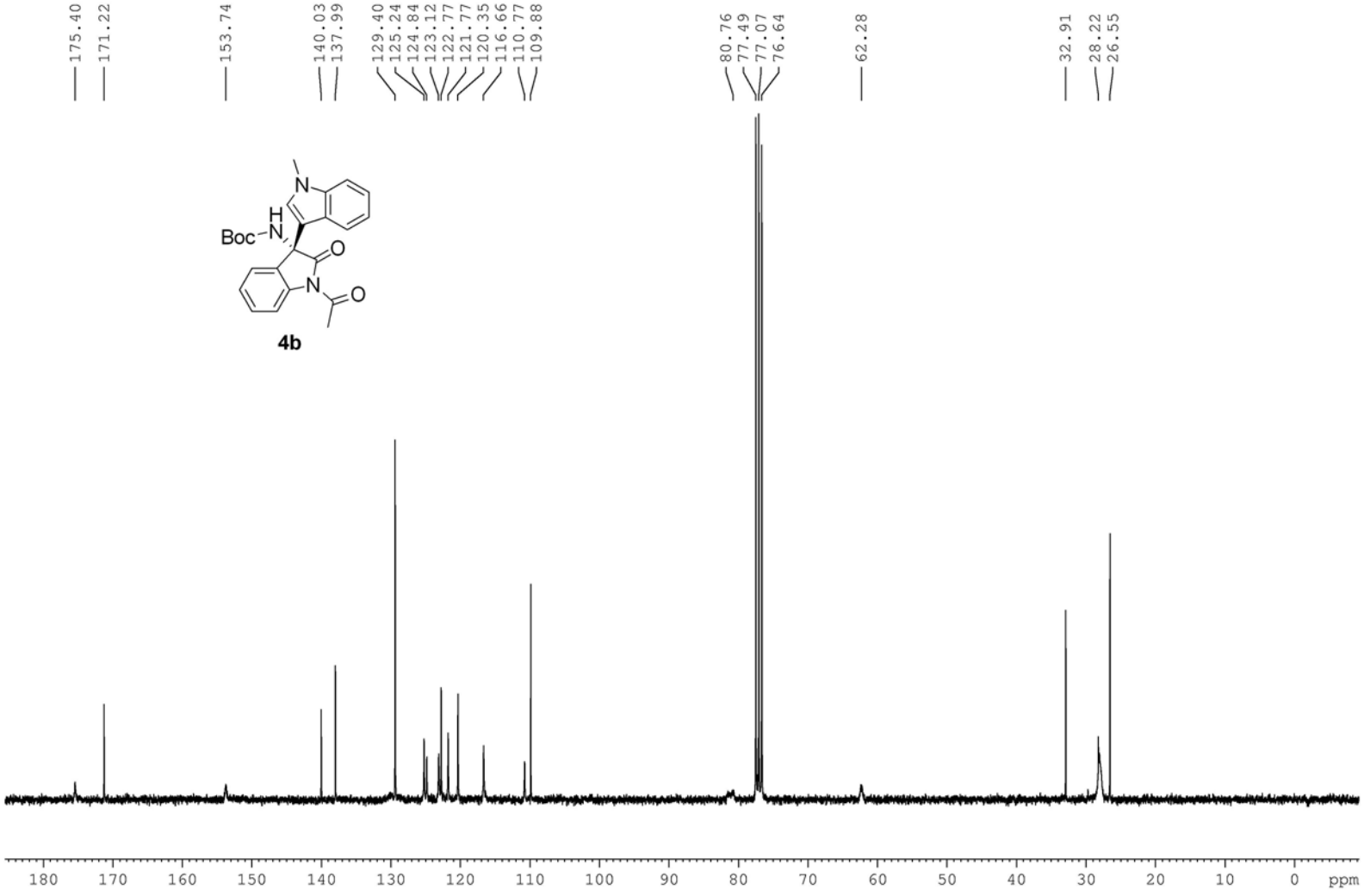
3 W. Yan, D. Wang, J. Feng, P. Li, D. Zhao, R. Wang, *Org. Lett.* **2012**, DOI: 10.1021/ol3007953.

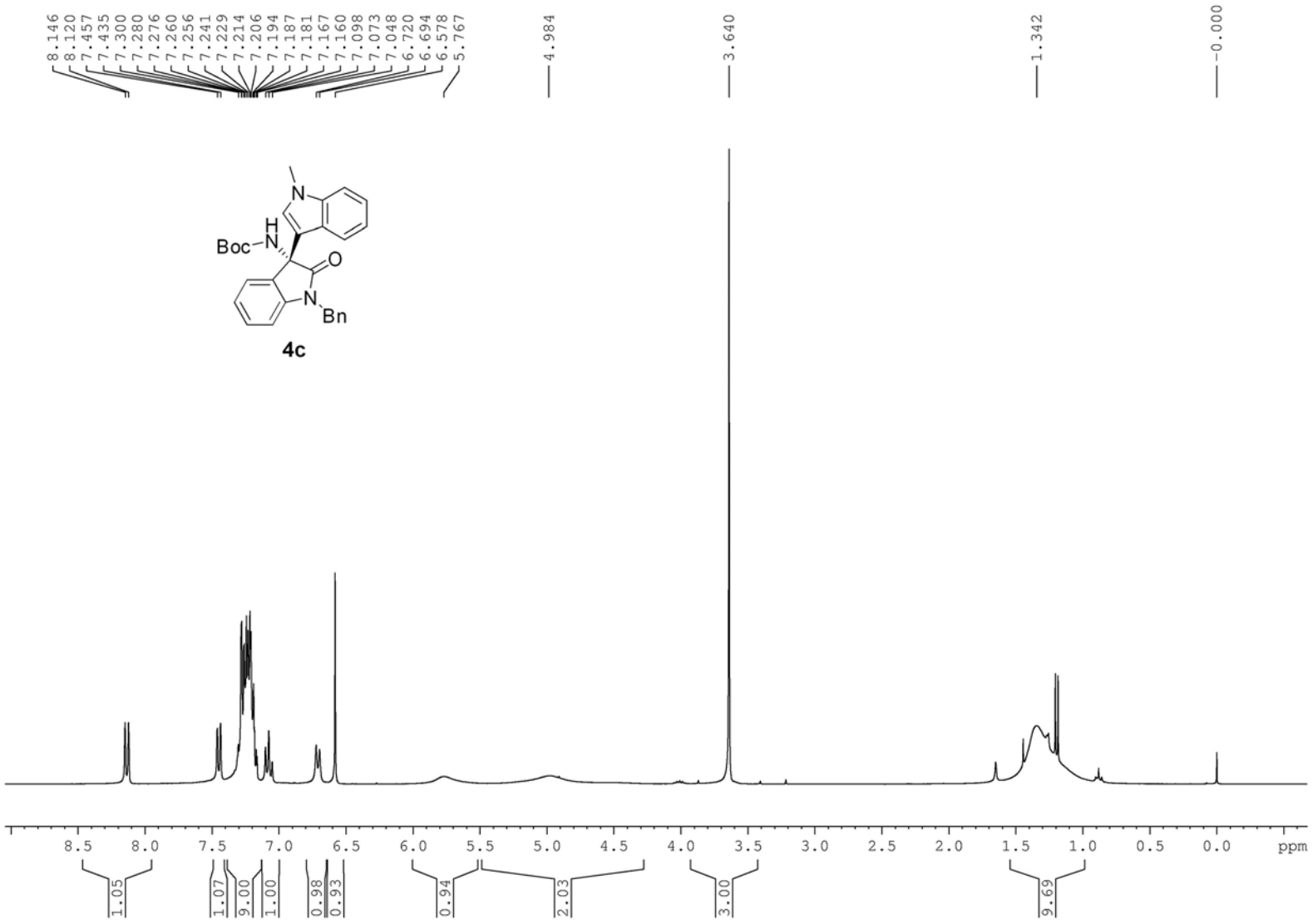


4a





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7.214
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7.194
7.187
7.181
7.167
7.160
7.098
7.073
7.048
6.720
6.694
6.578
5.767
4.984
3.640
1.342
0.000
Boc
H
N
O
N
Bn
4c
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7.5
7.0
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6.0
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3.0
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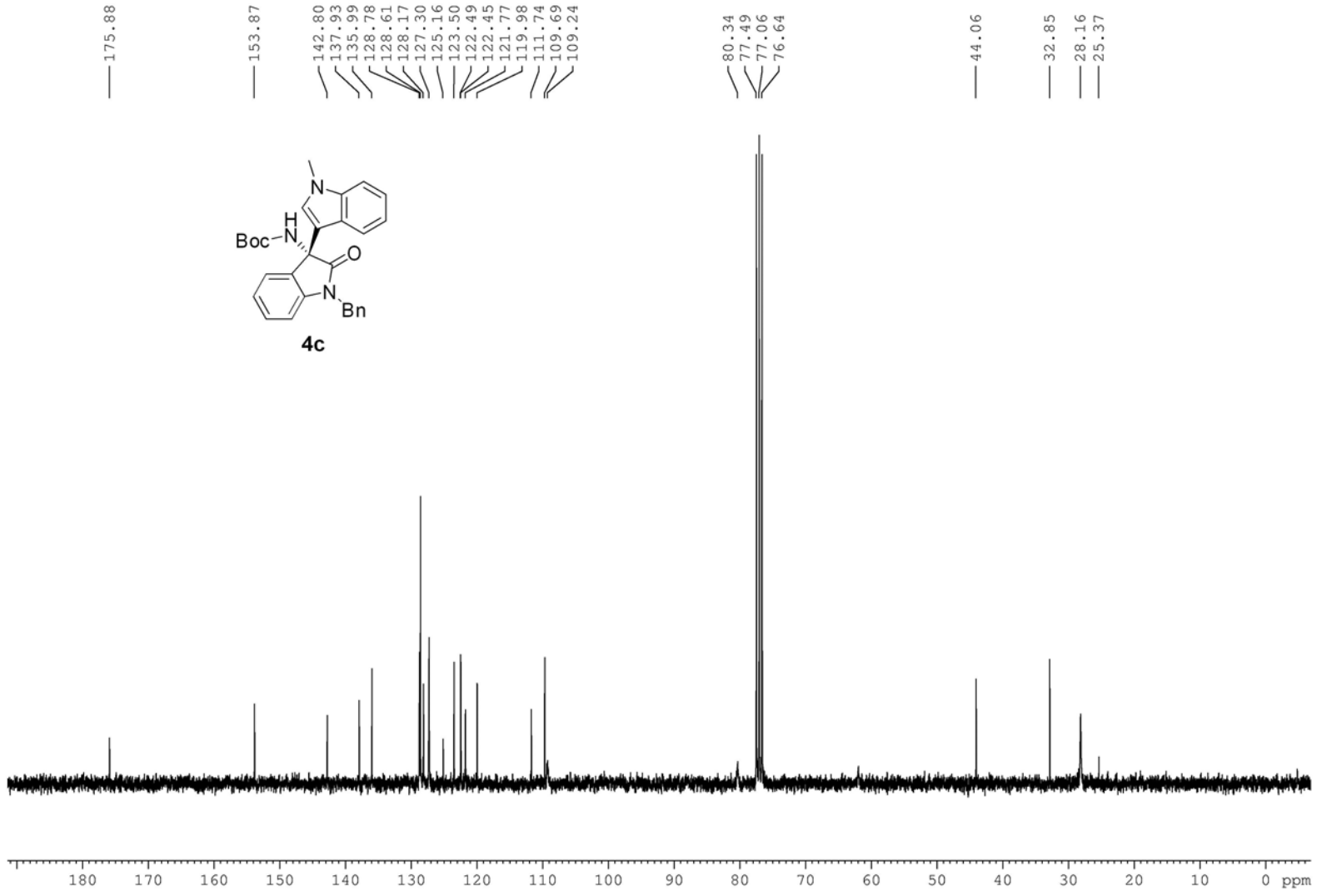
9.69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123.50
122.49
122.45
121.77
119.98
111.74
109.69
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80.34
77.49
77.06
76.64
44.06
32.85
28.16
25.37
Boc
H
N
N
O
N
Bn
4c
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130
120
110
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70
60
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30
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10
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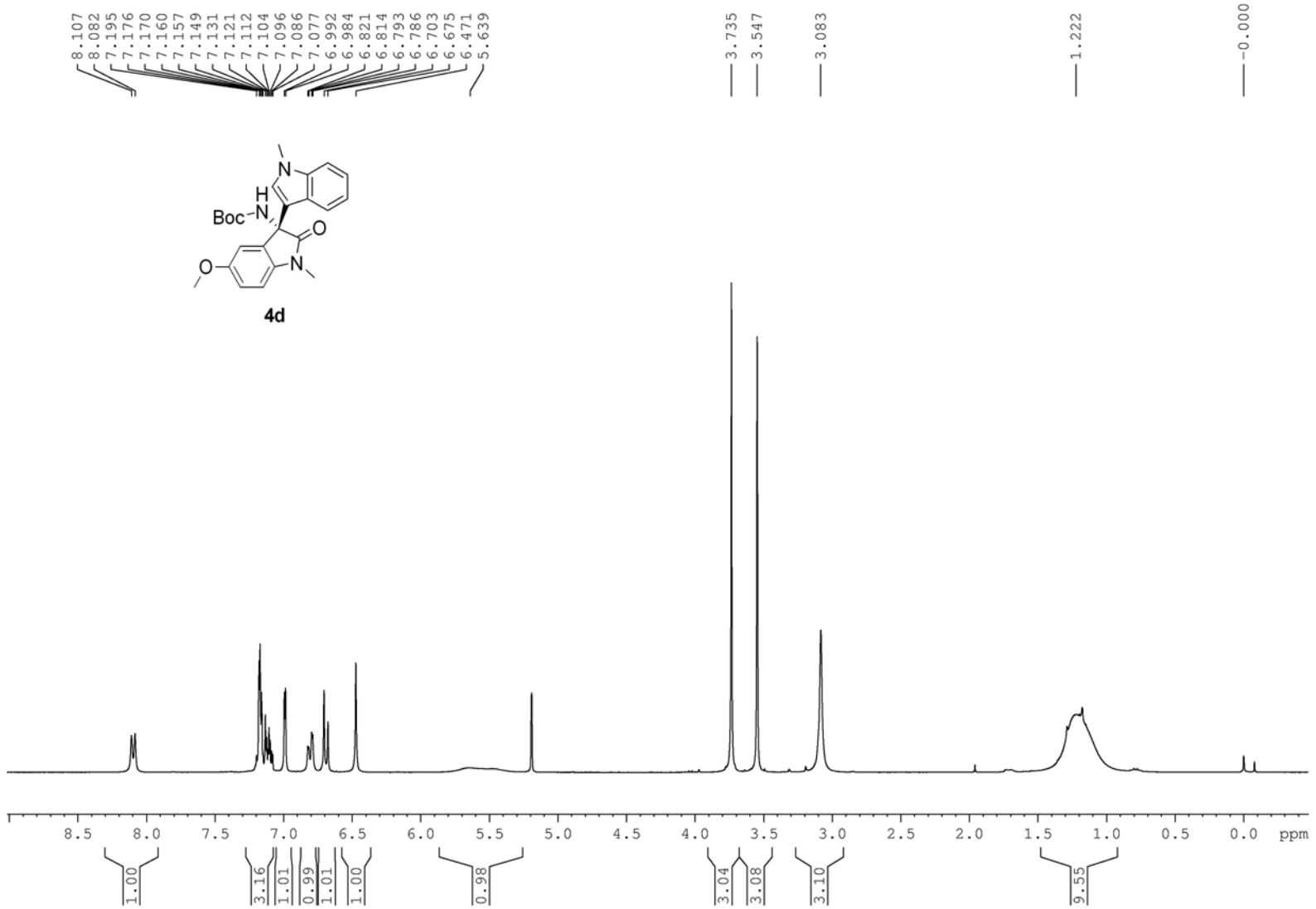
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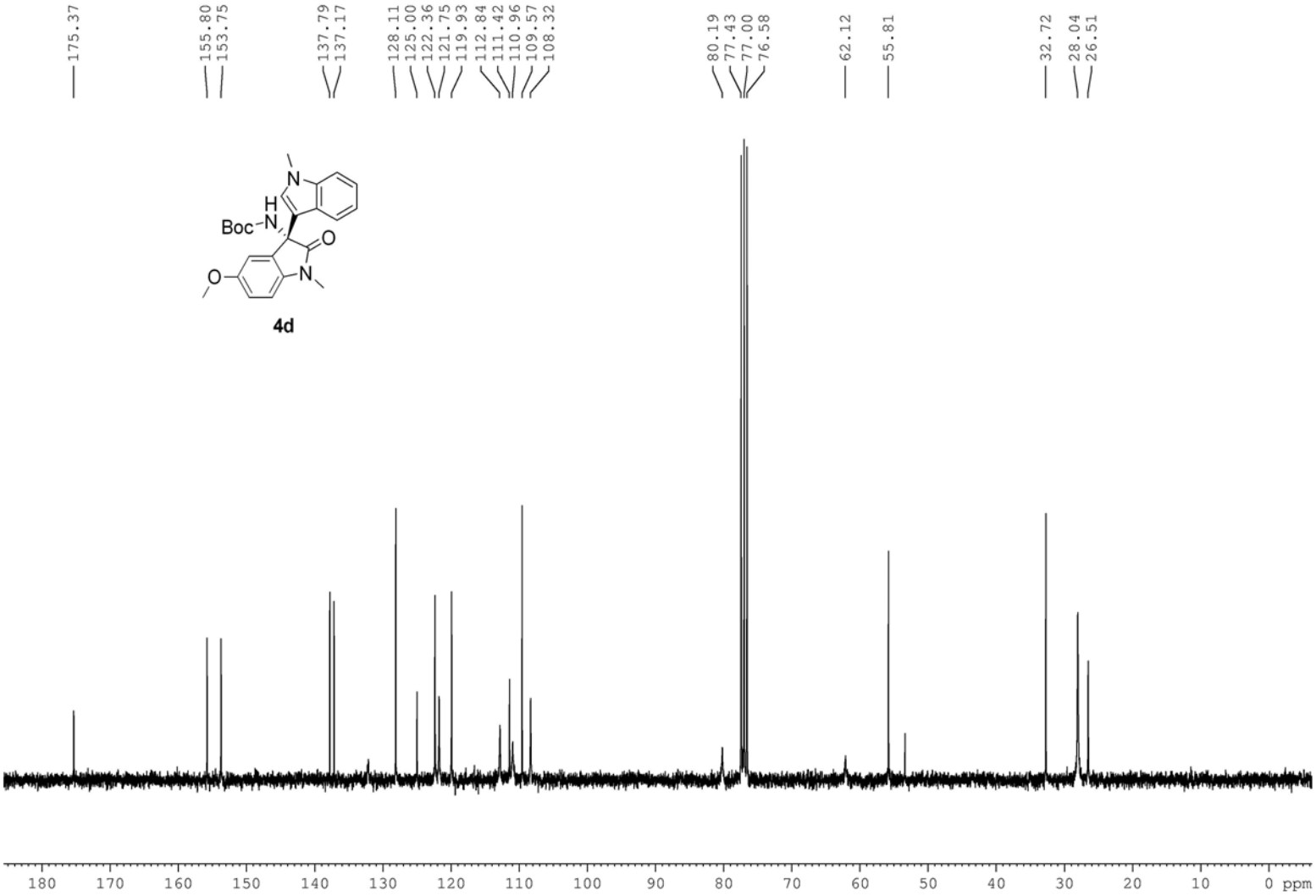
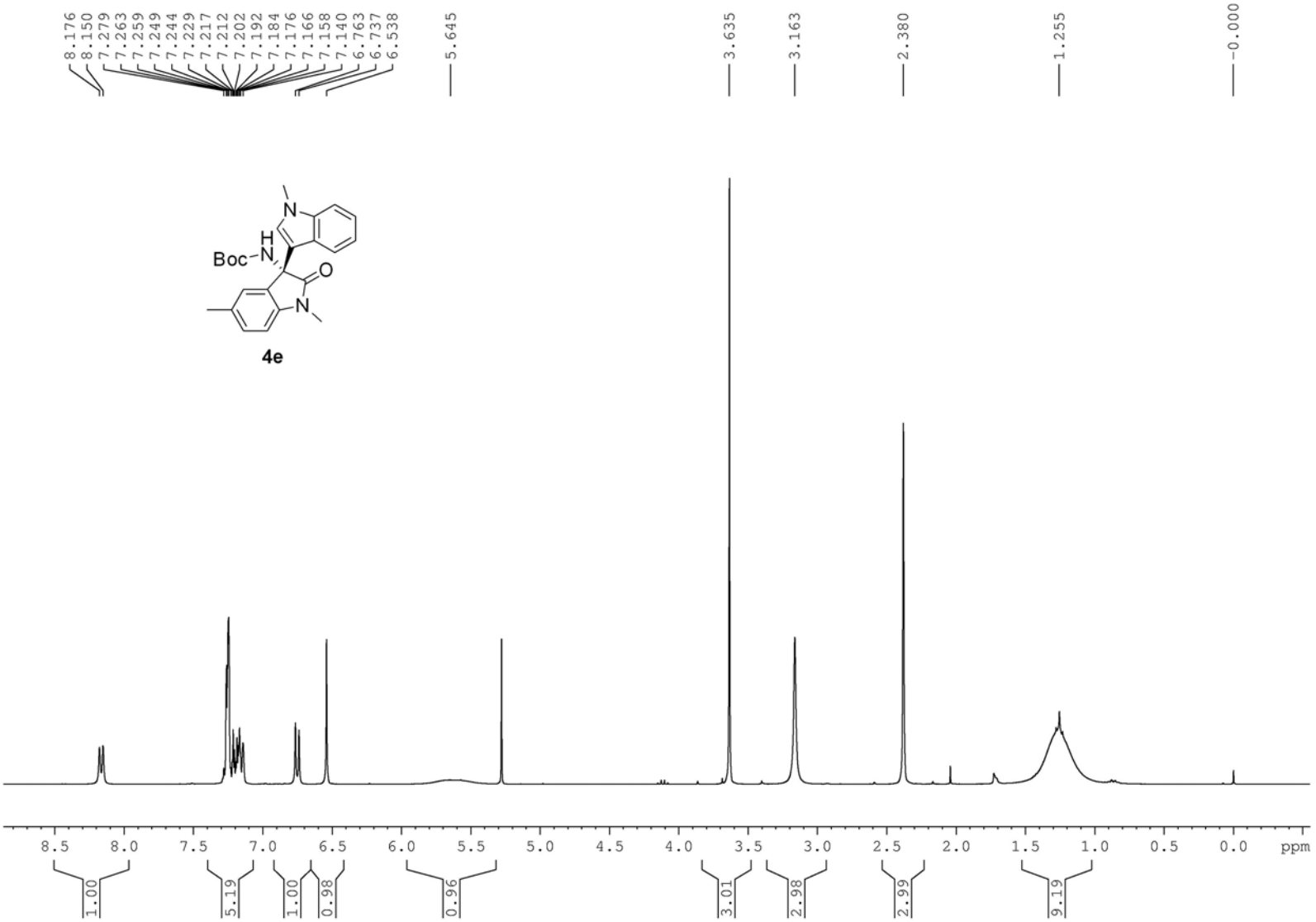


4d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H
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ppm
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1.00
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3.01
2.98
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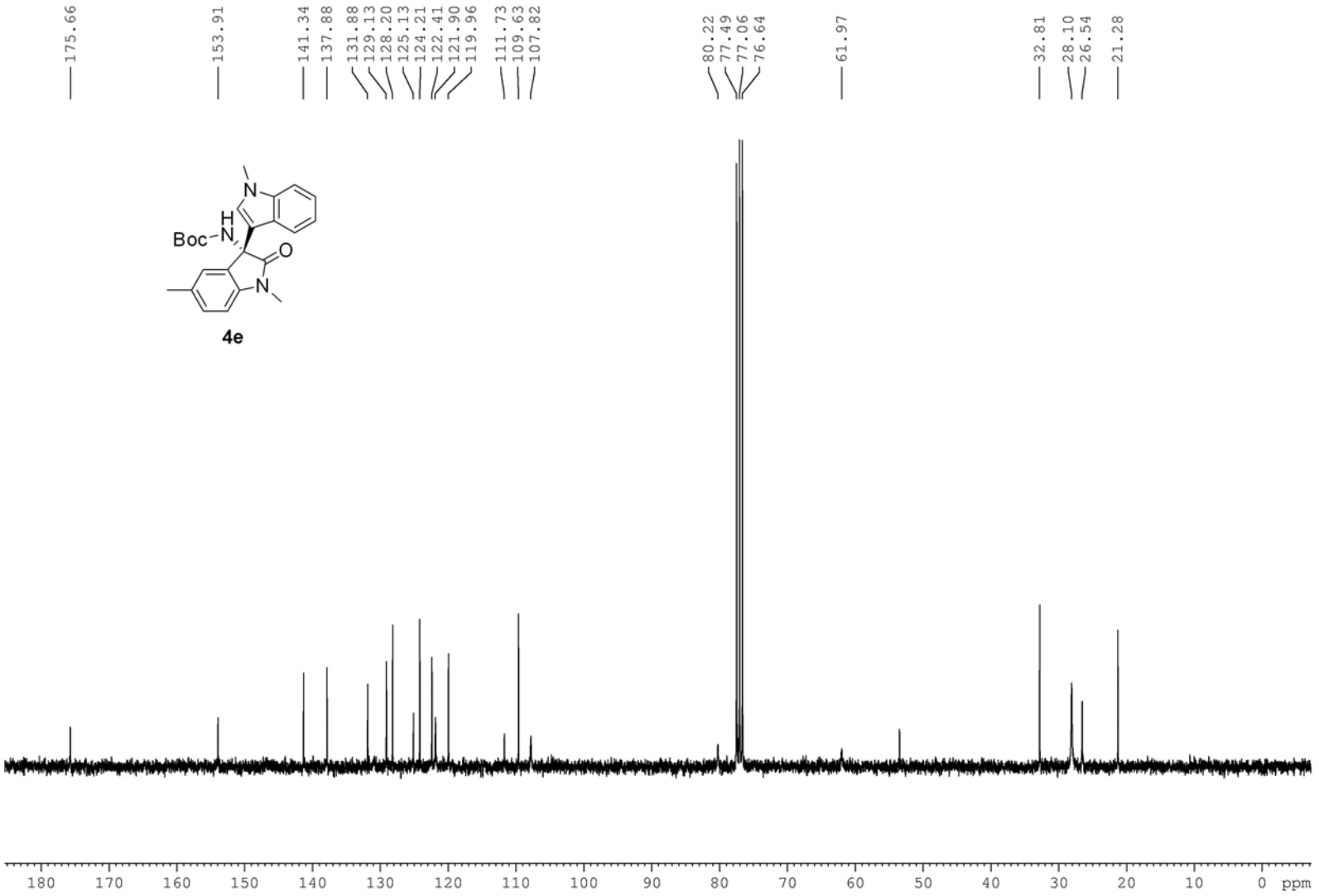

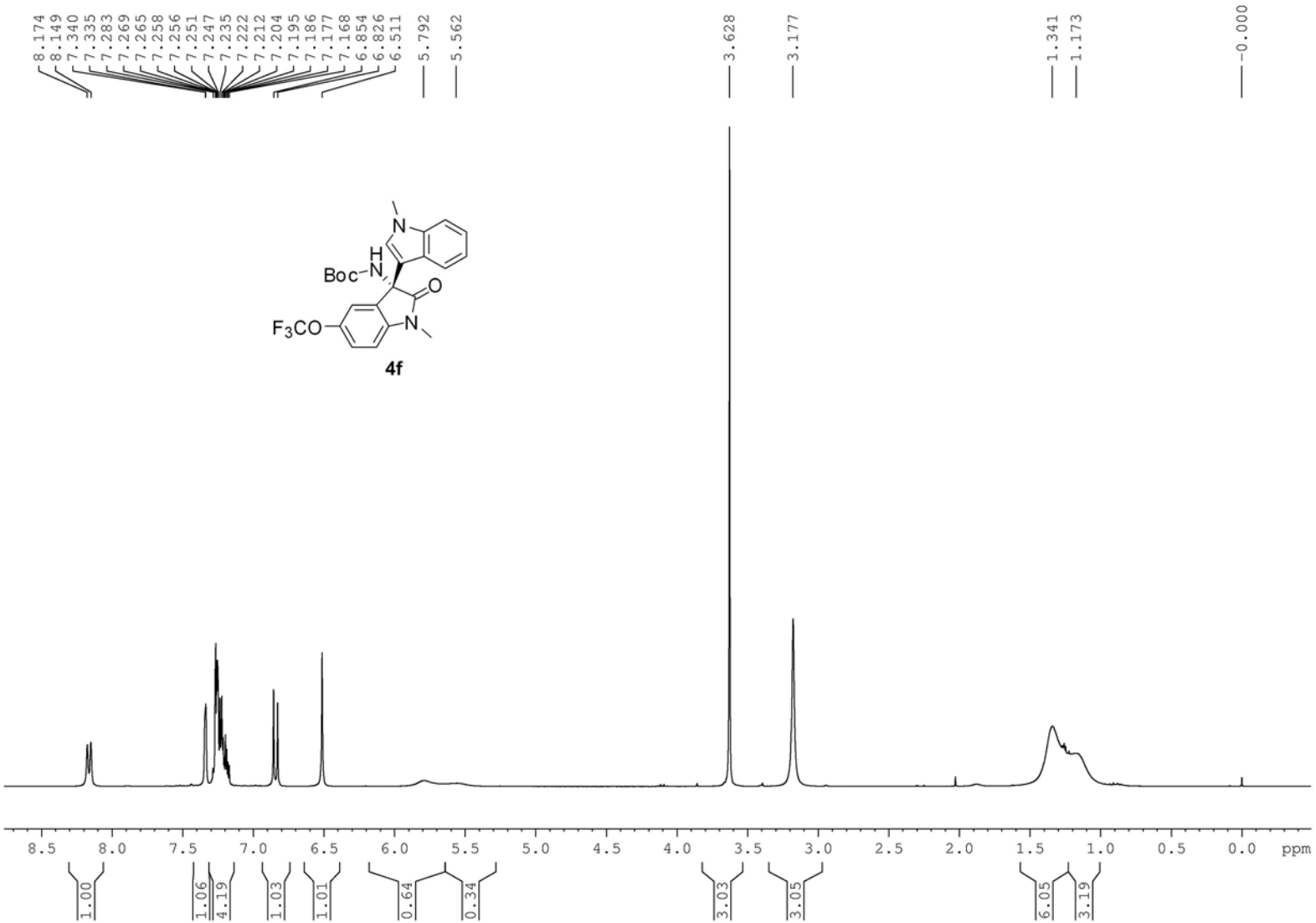
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O
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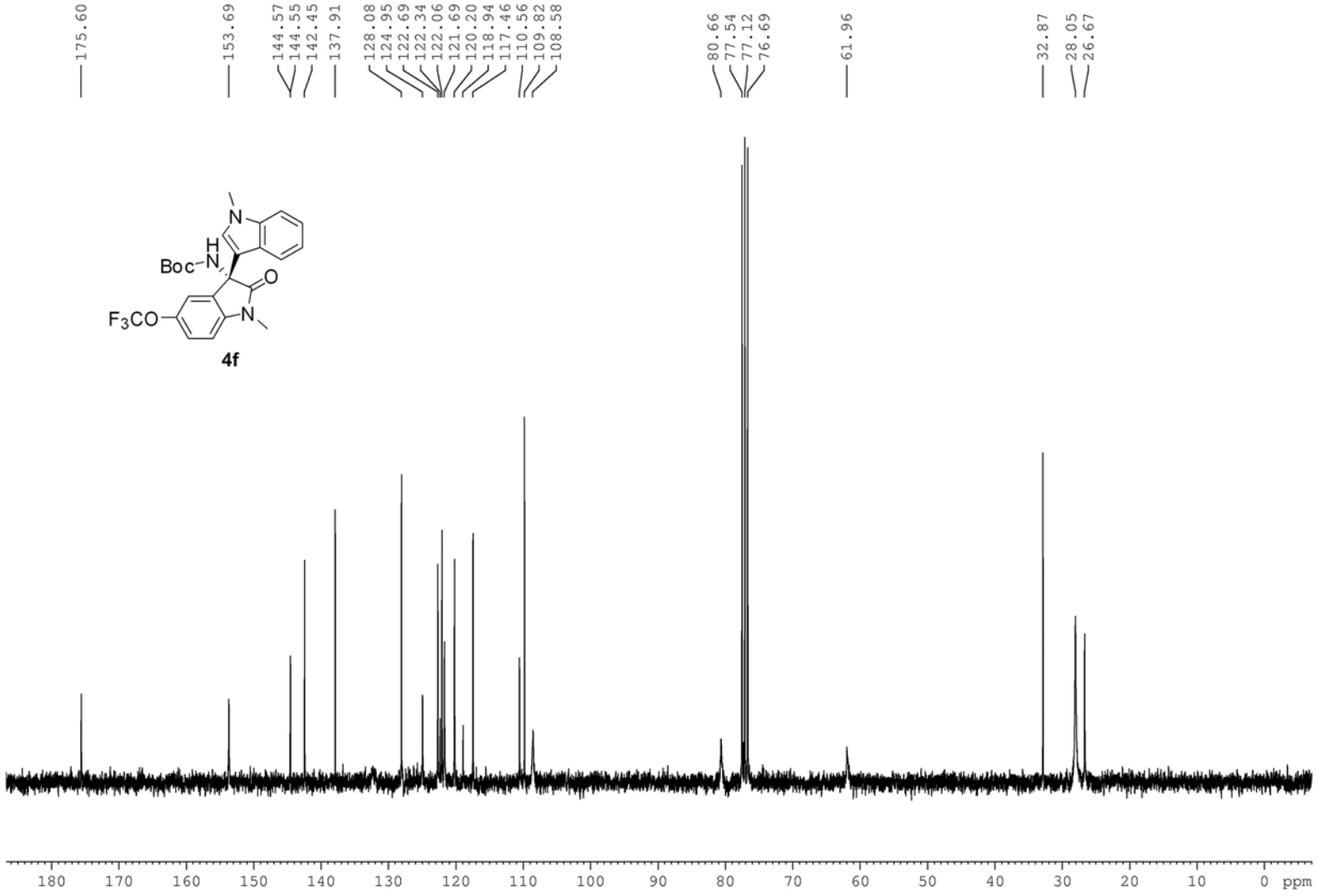

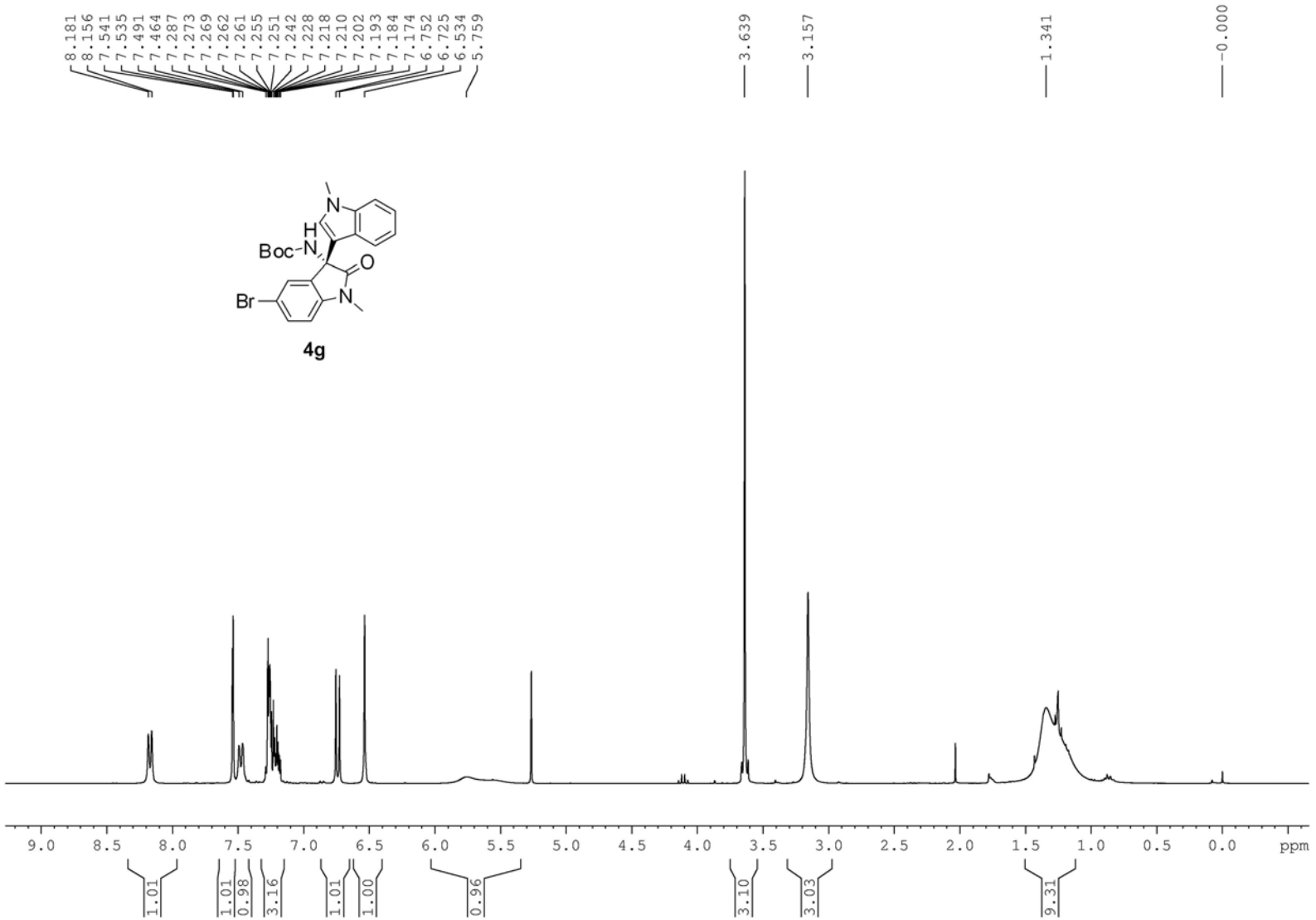
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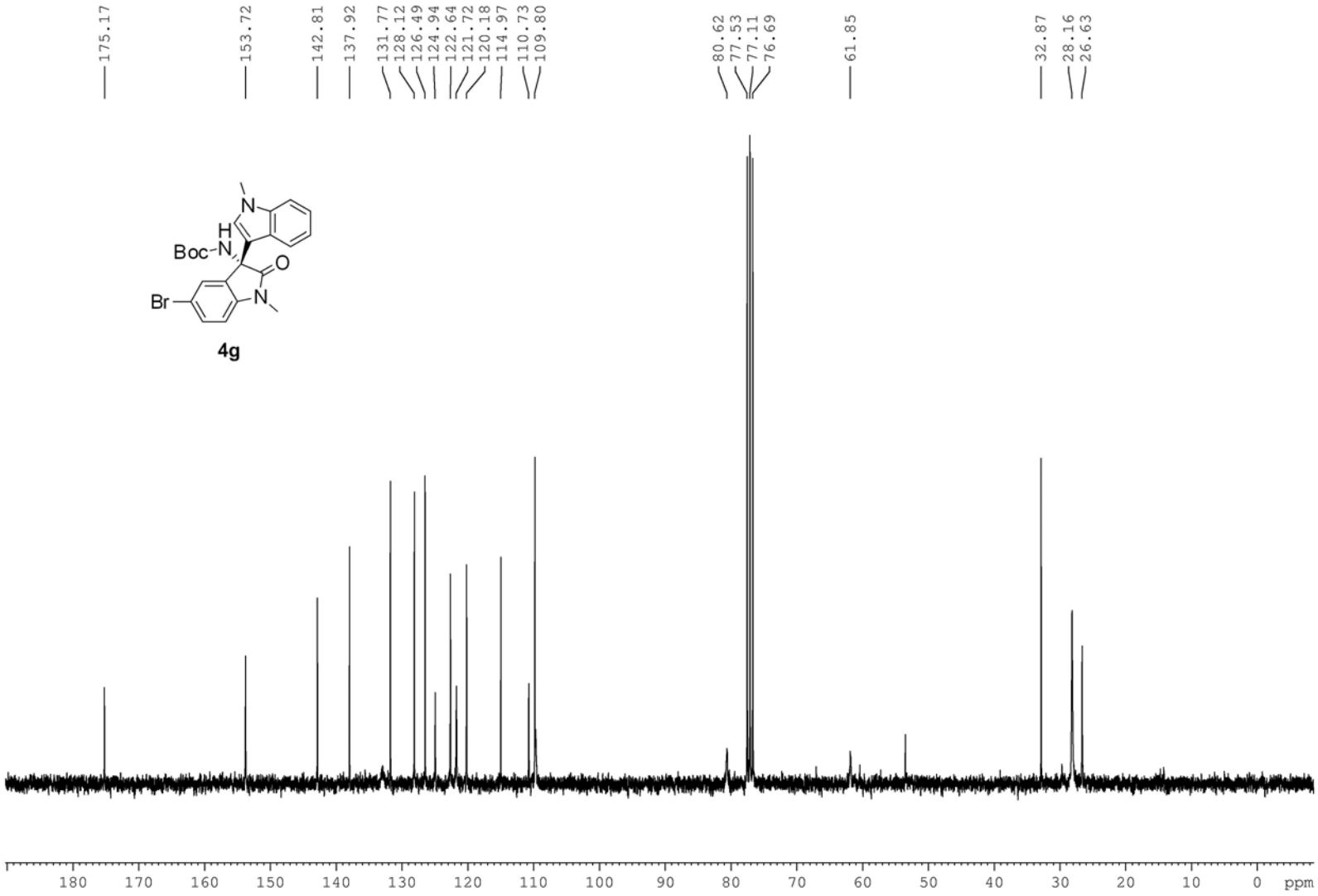

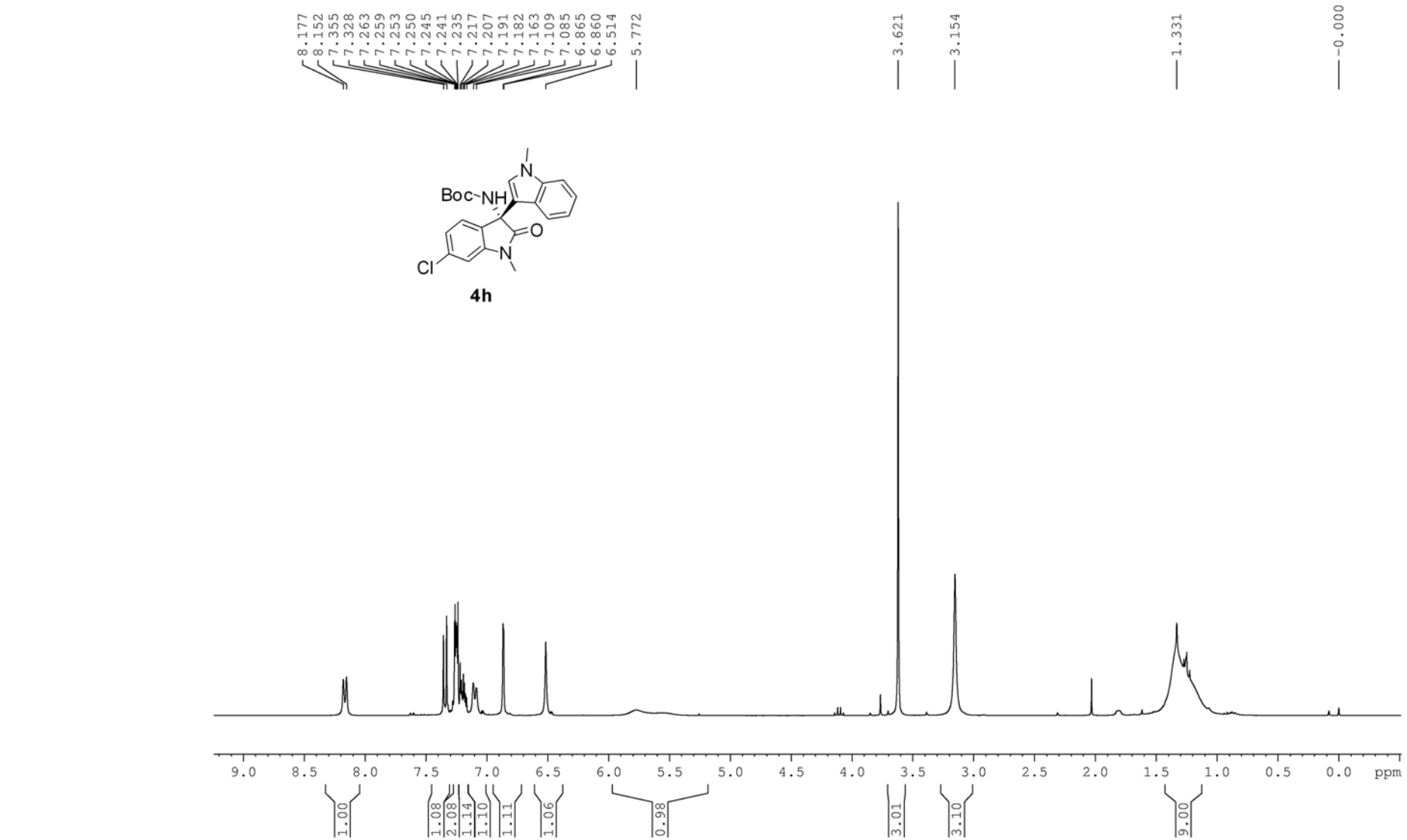

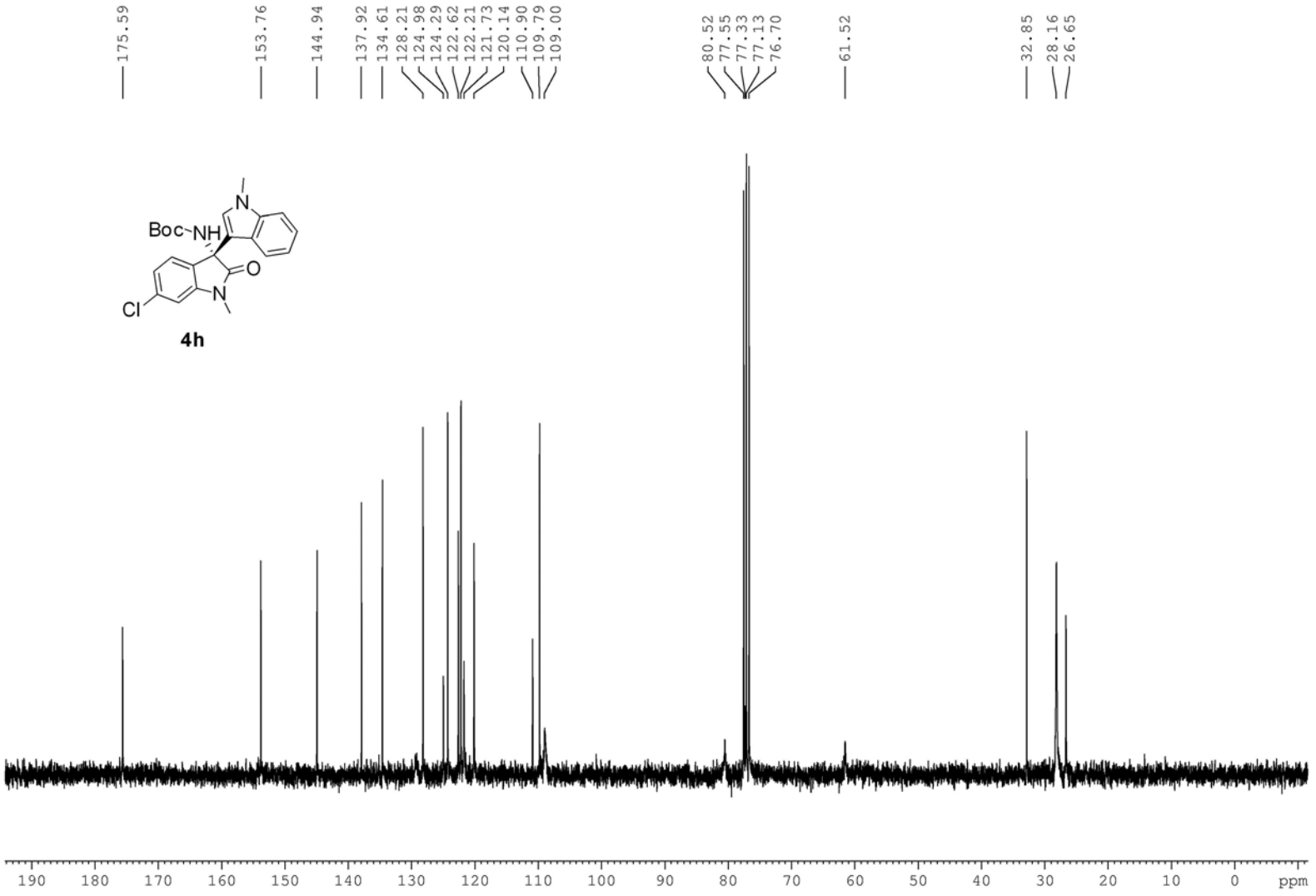

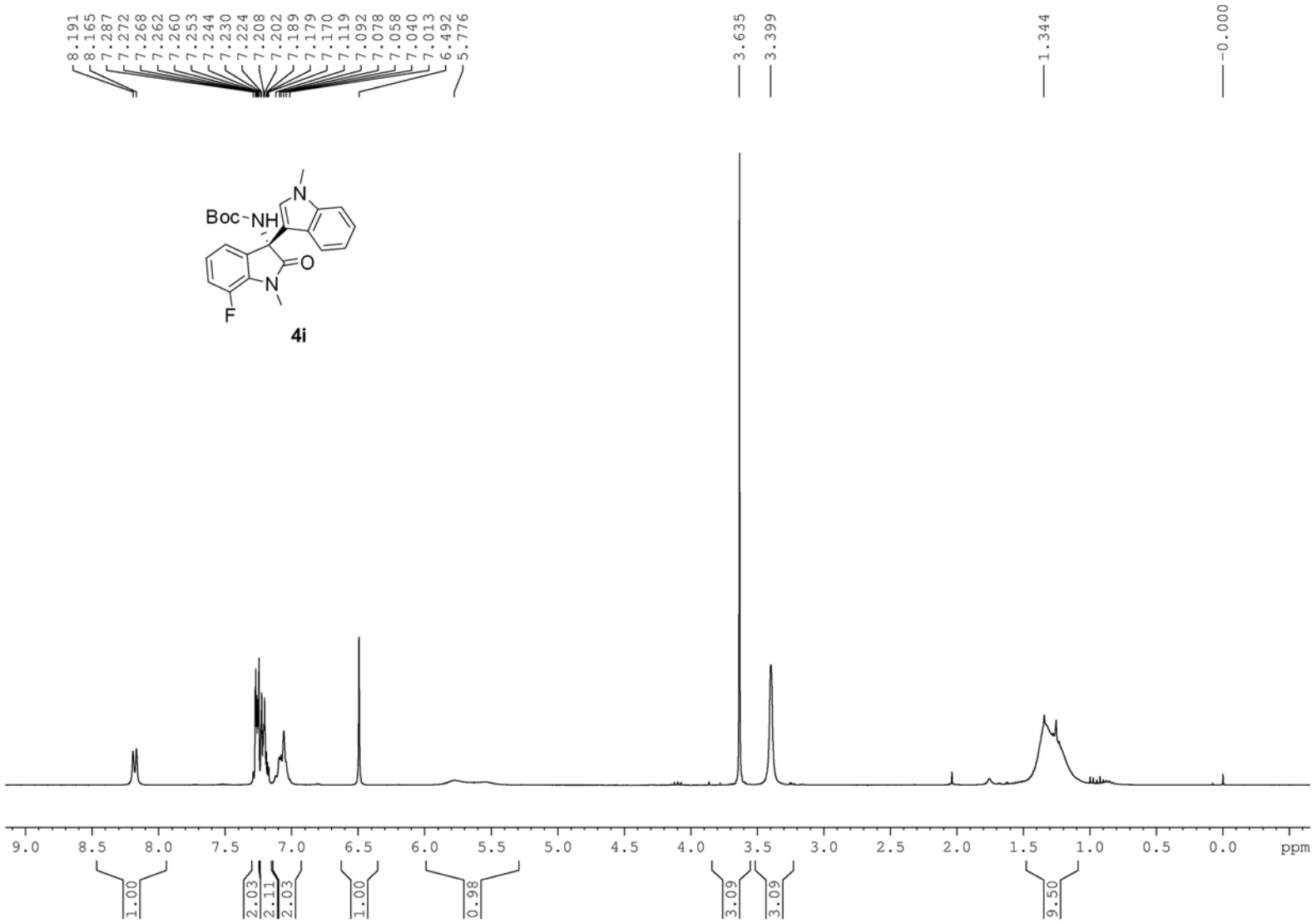

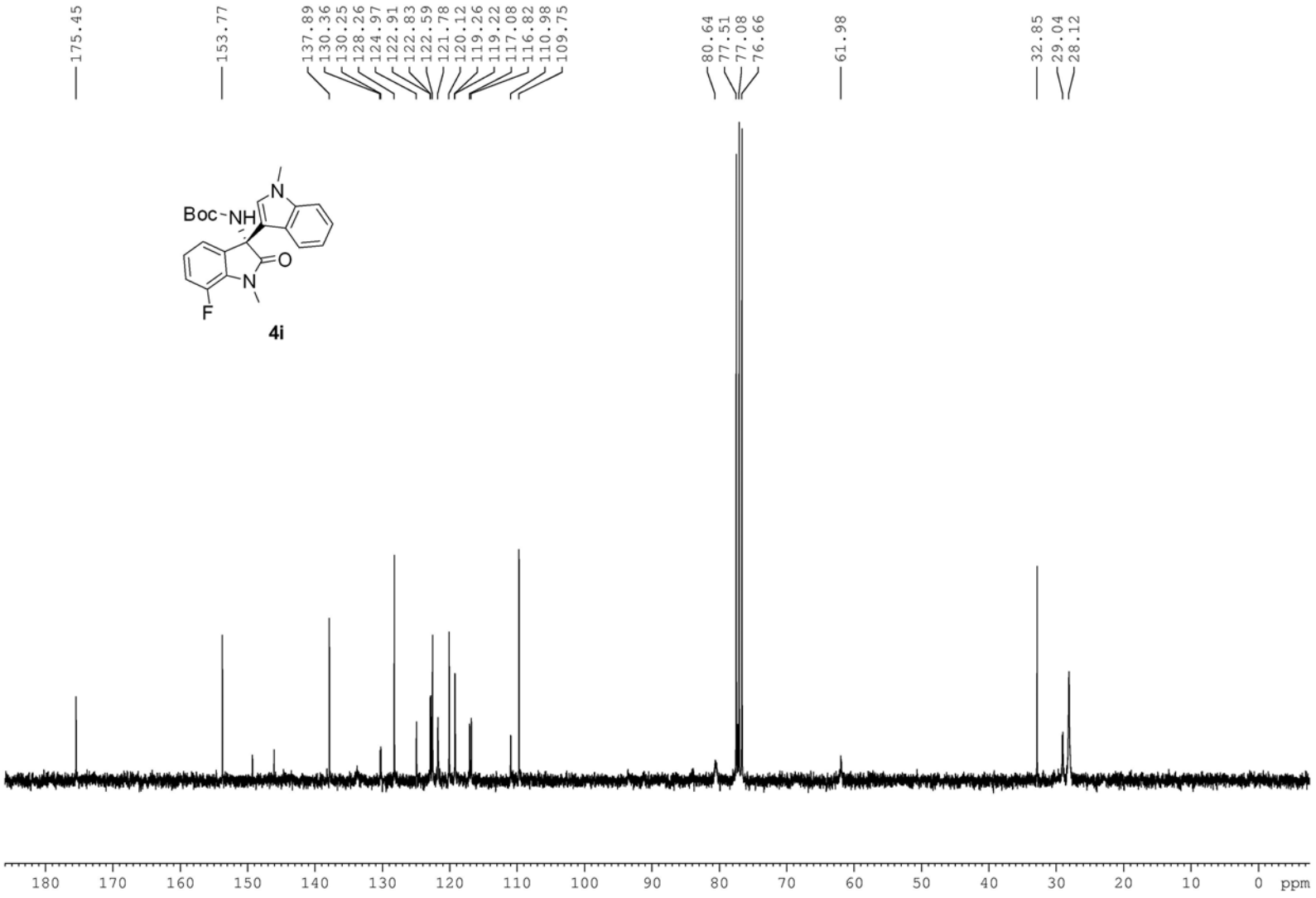

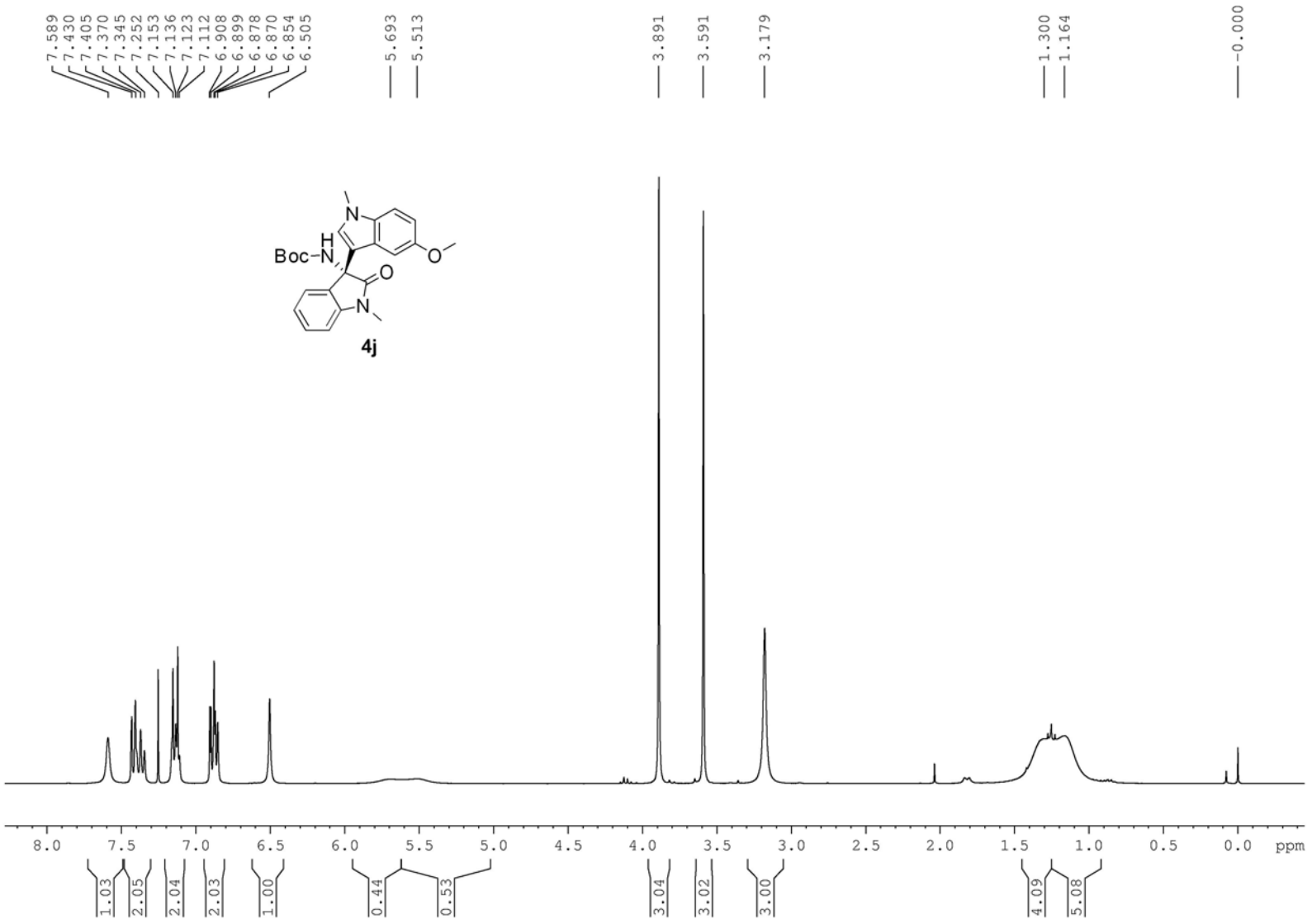

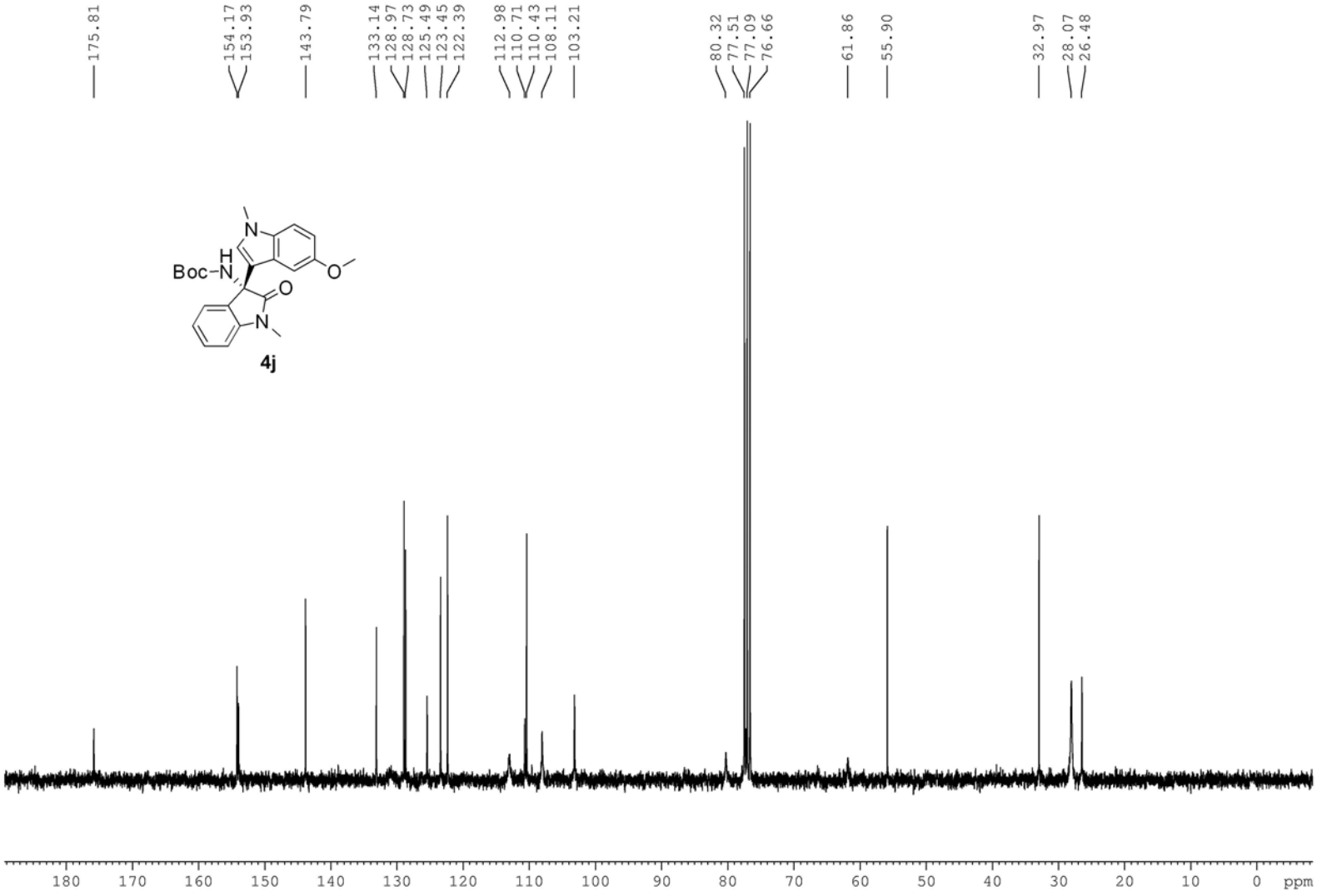

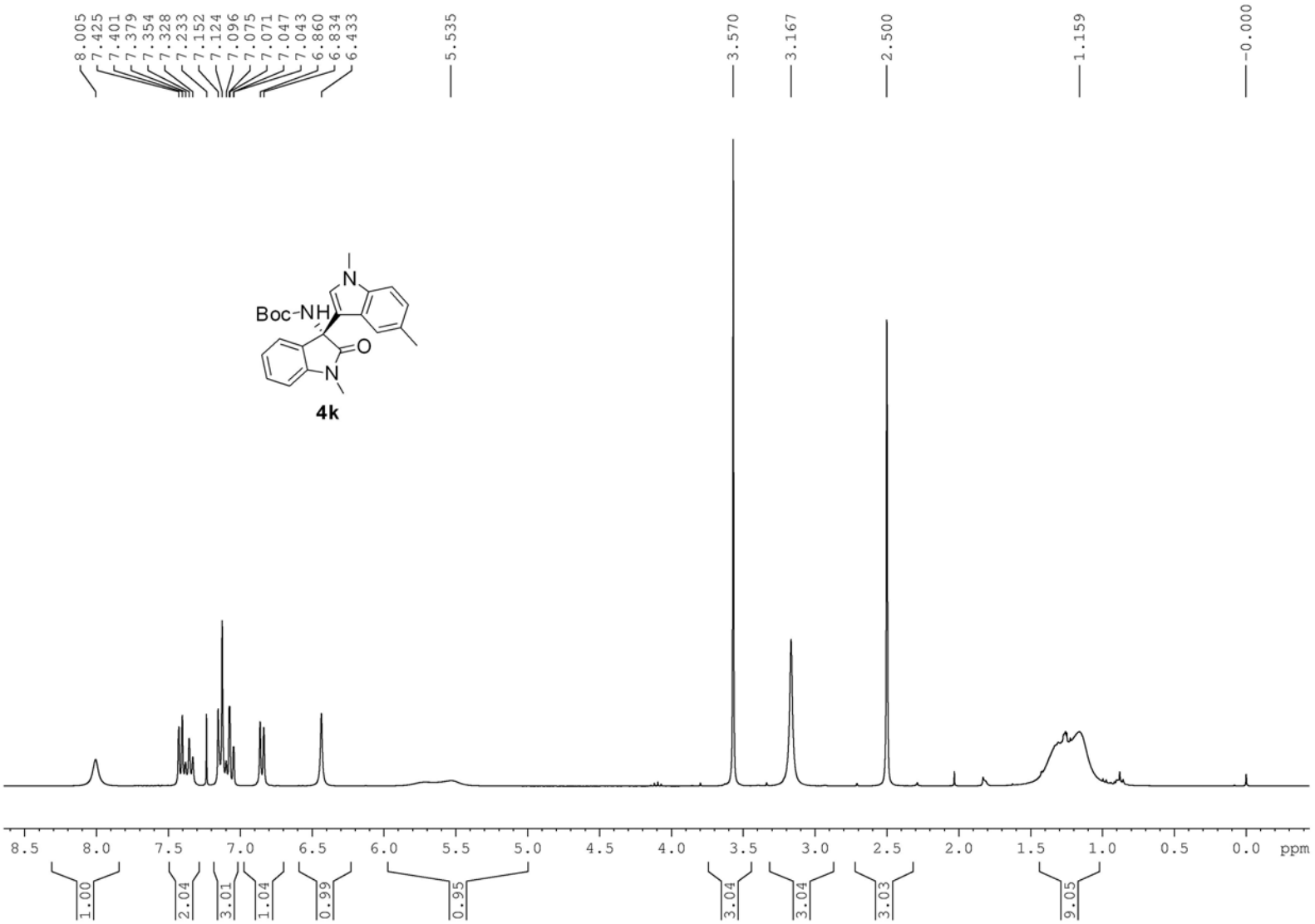

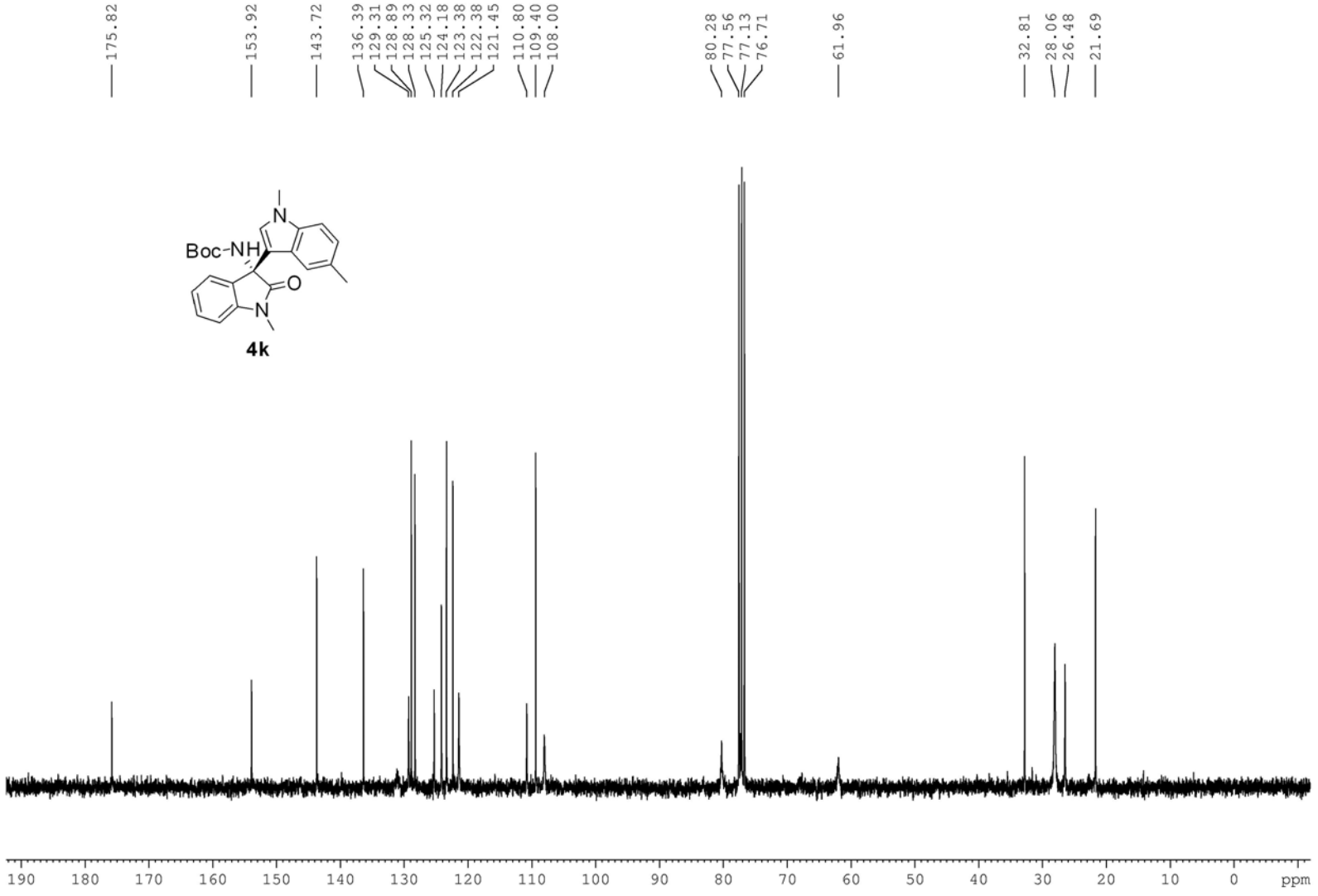

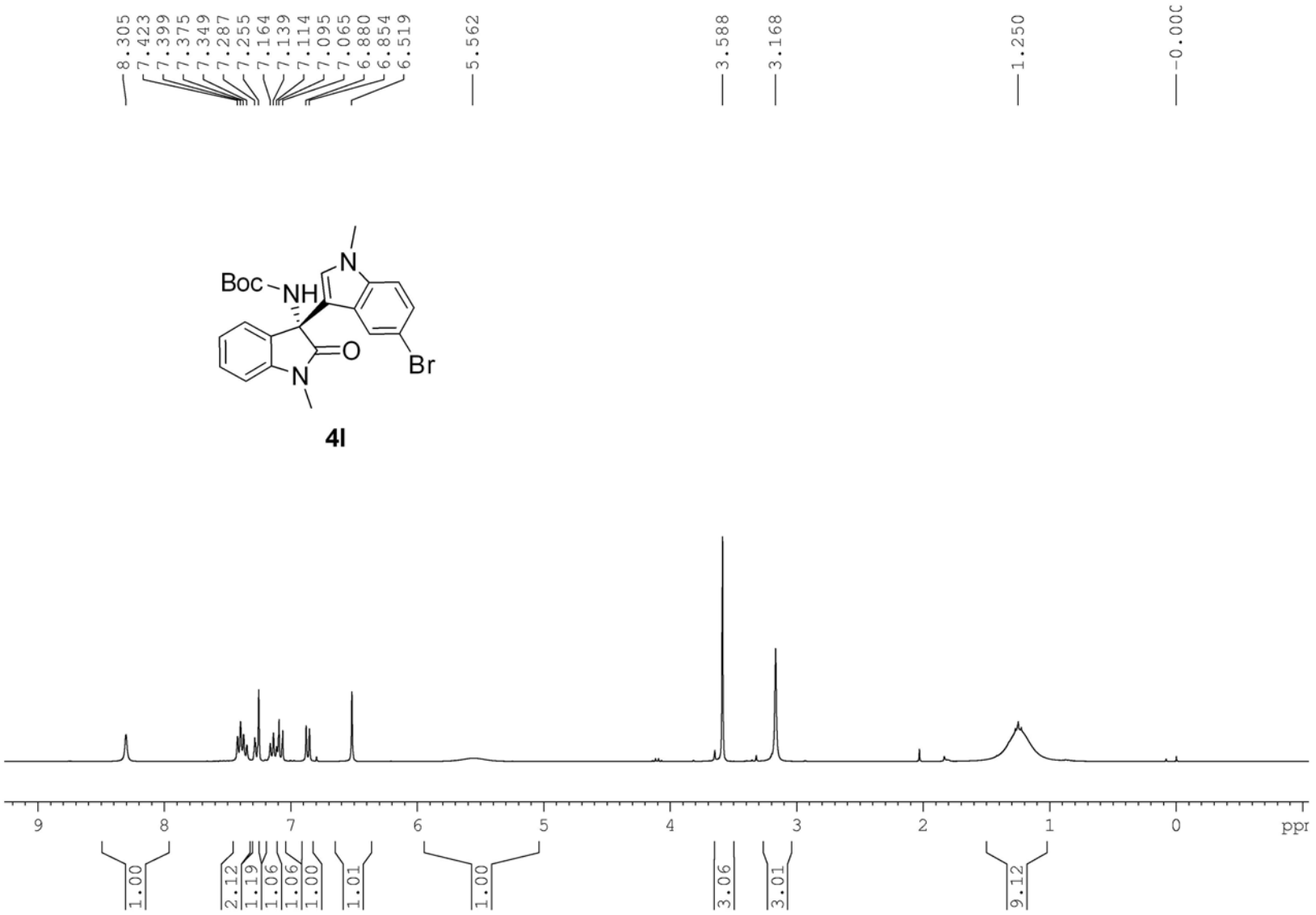
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O
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Br
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8
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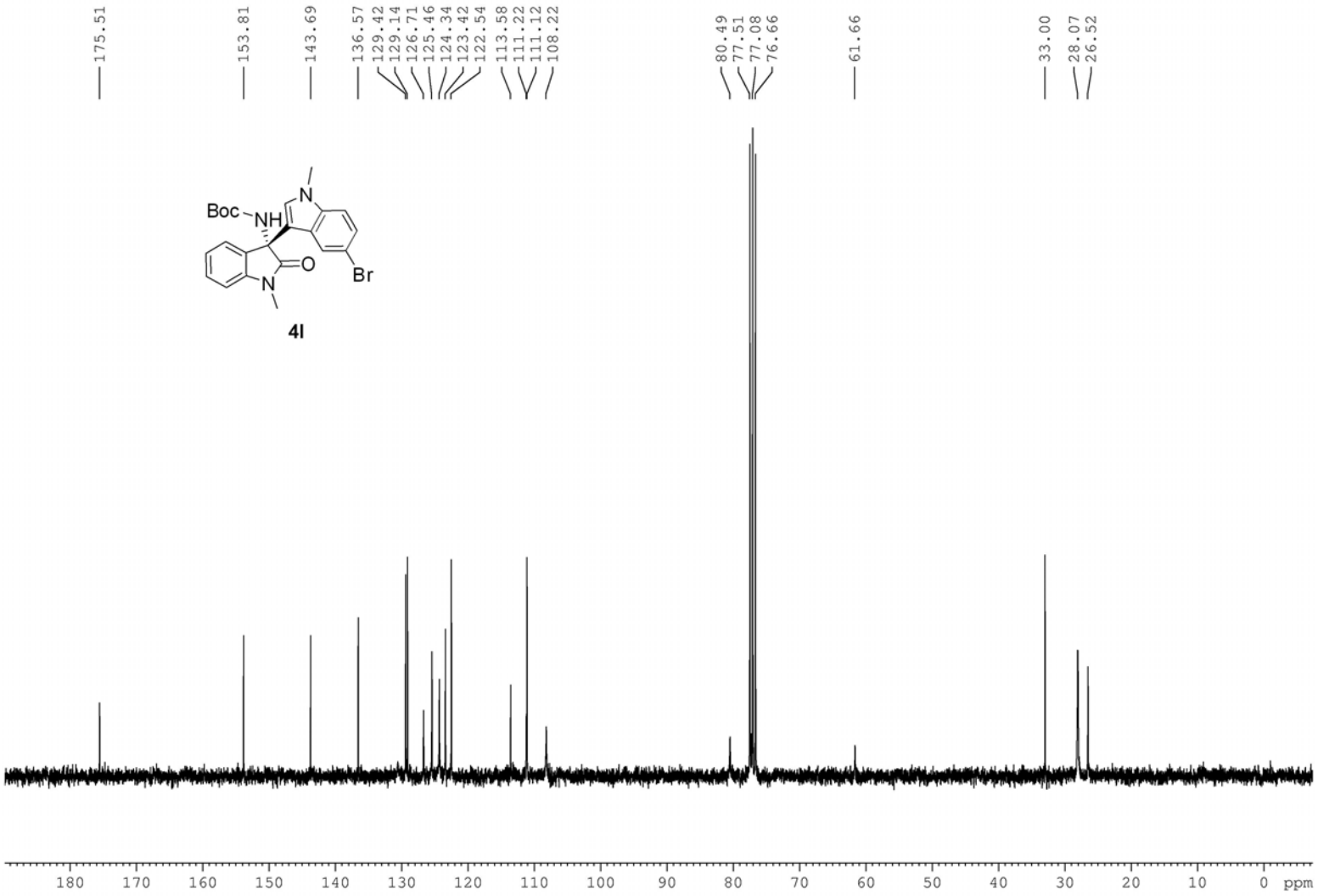

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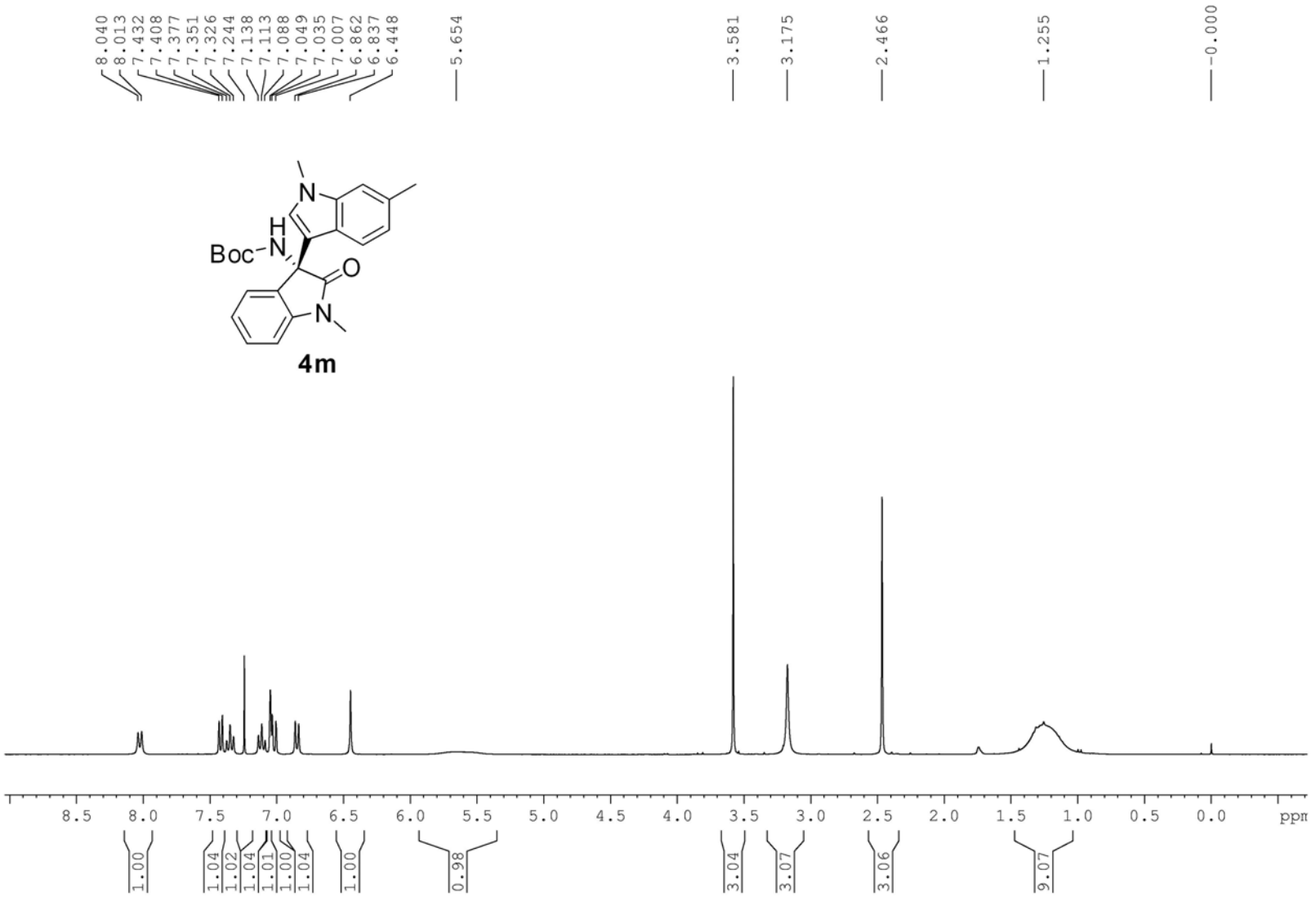

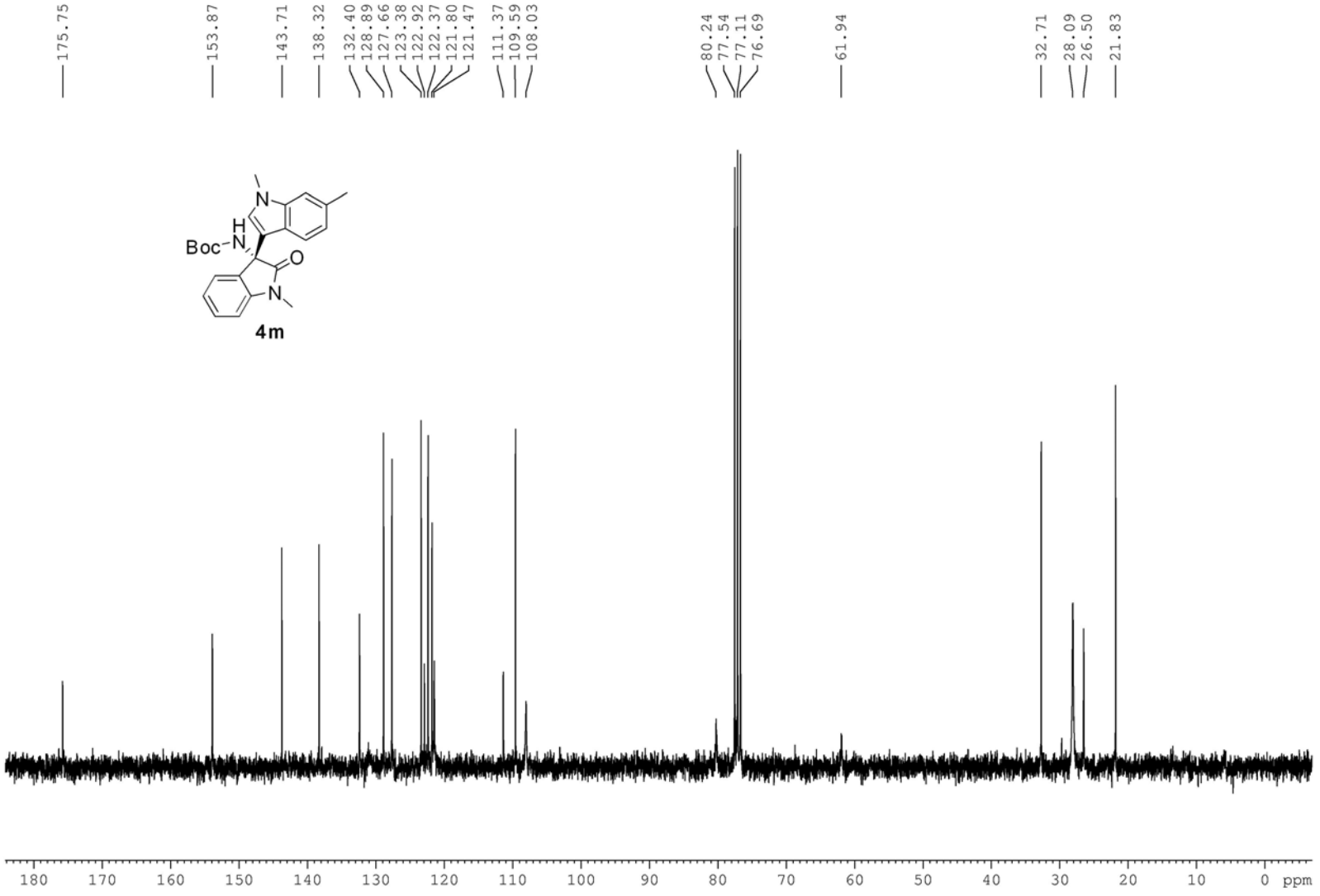

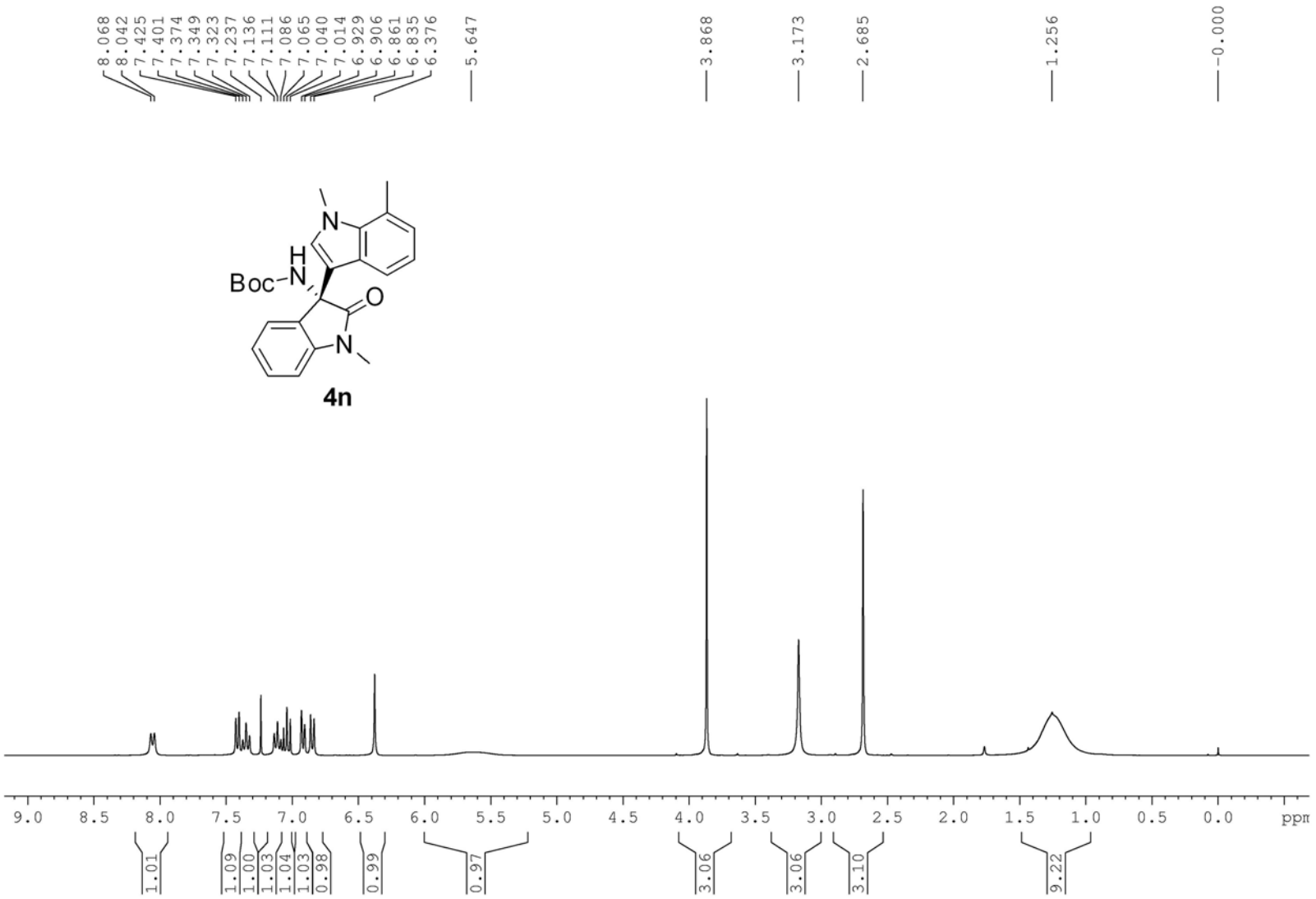

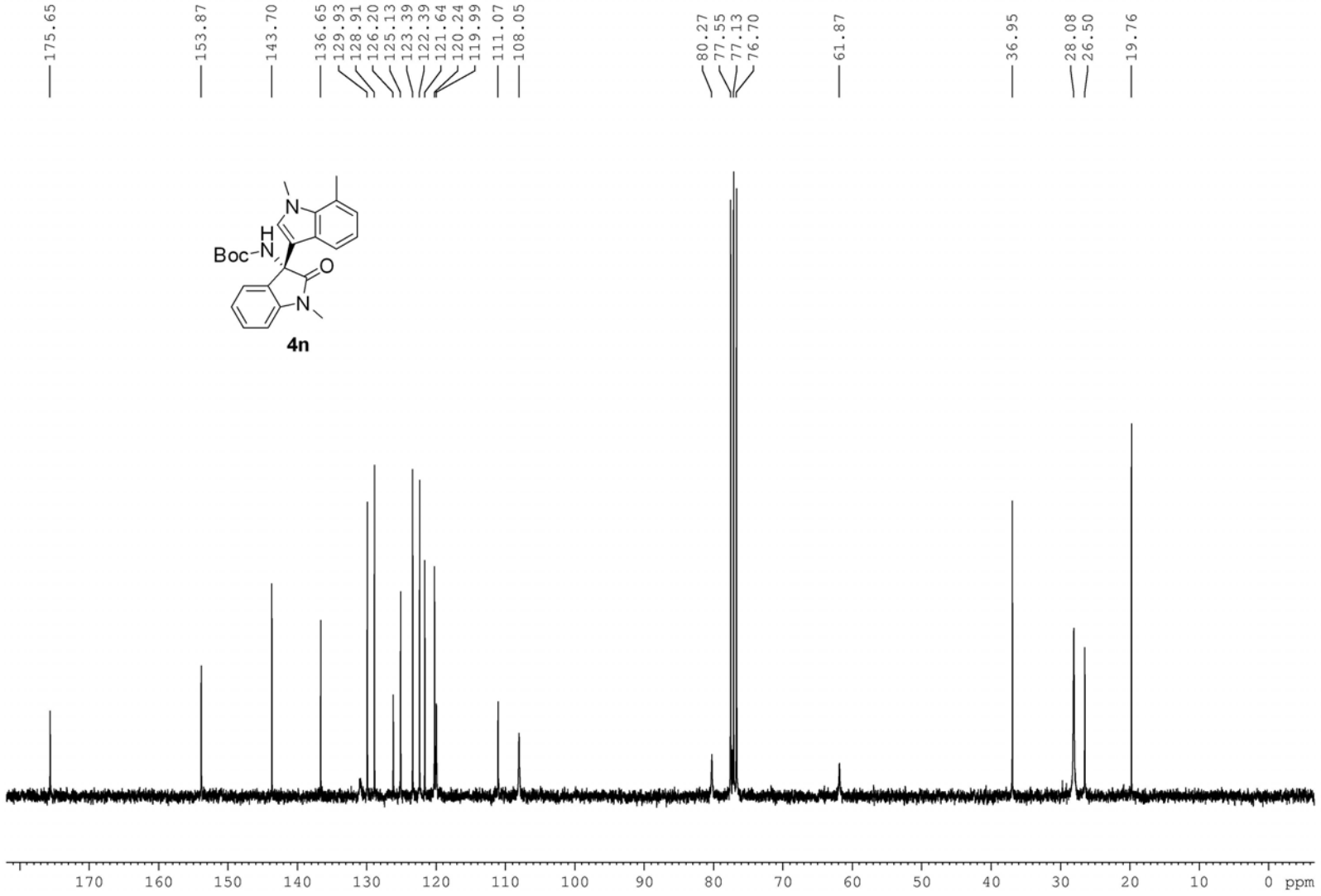

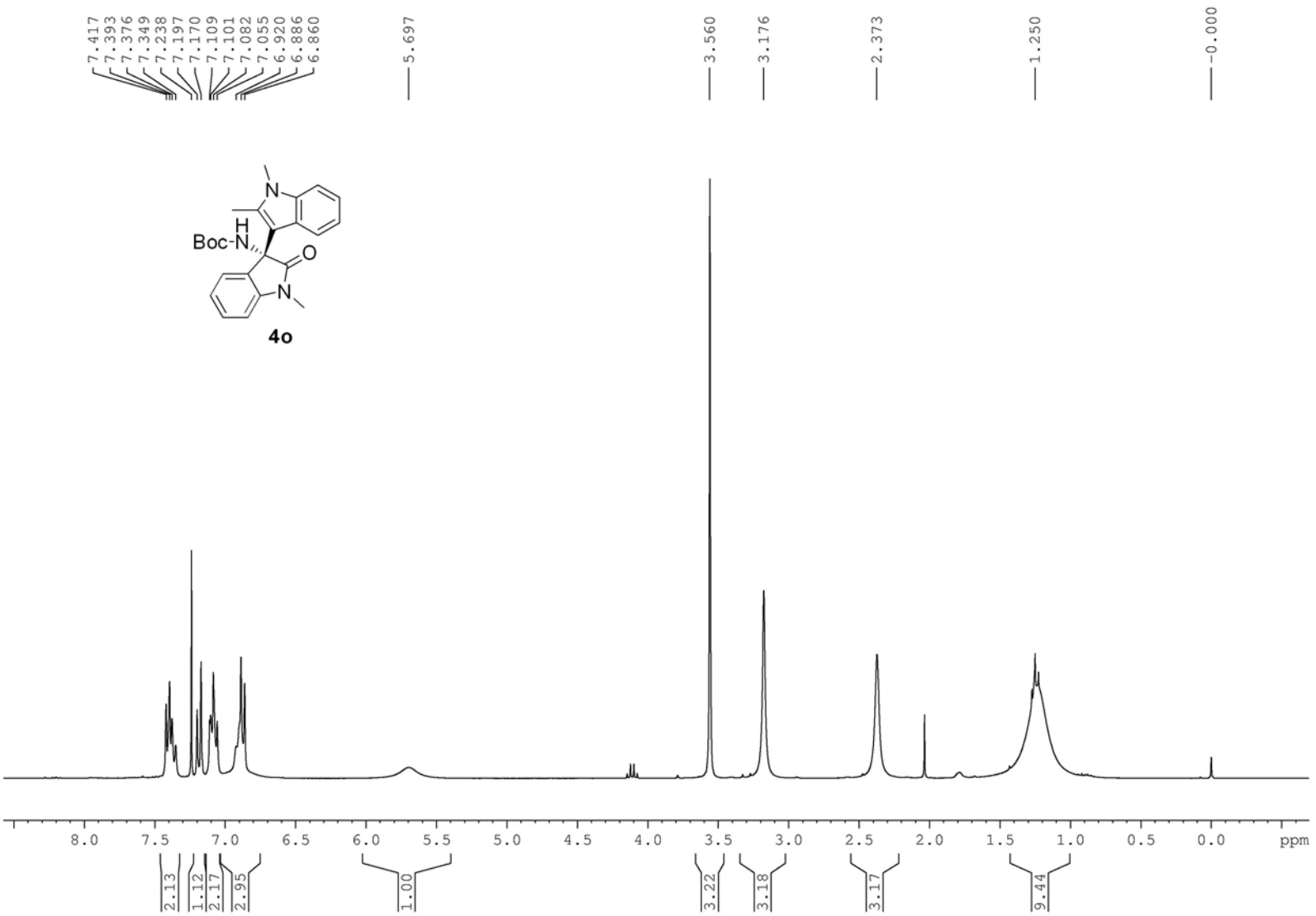

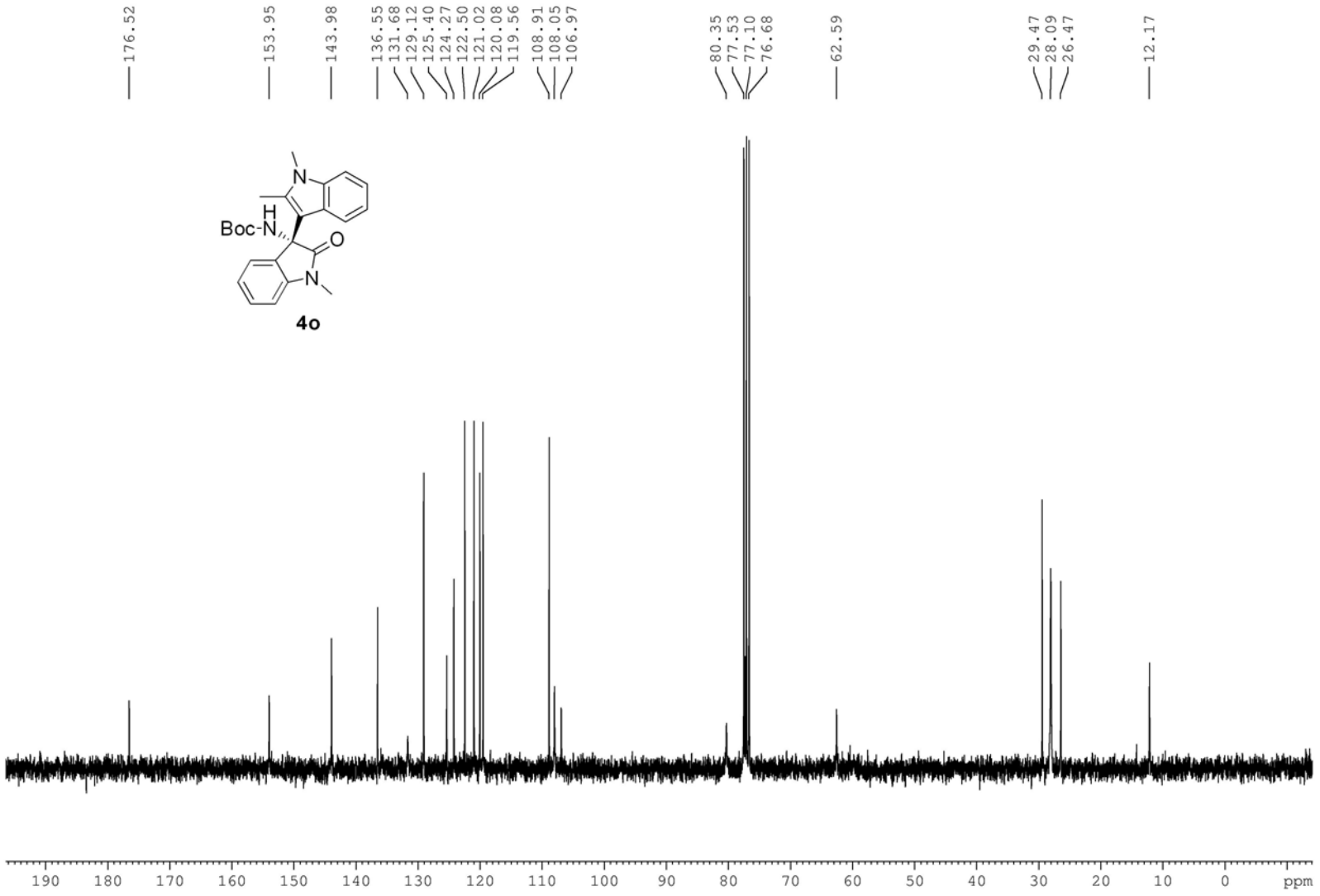

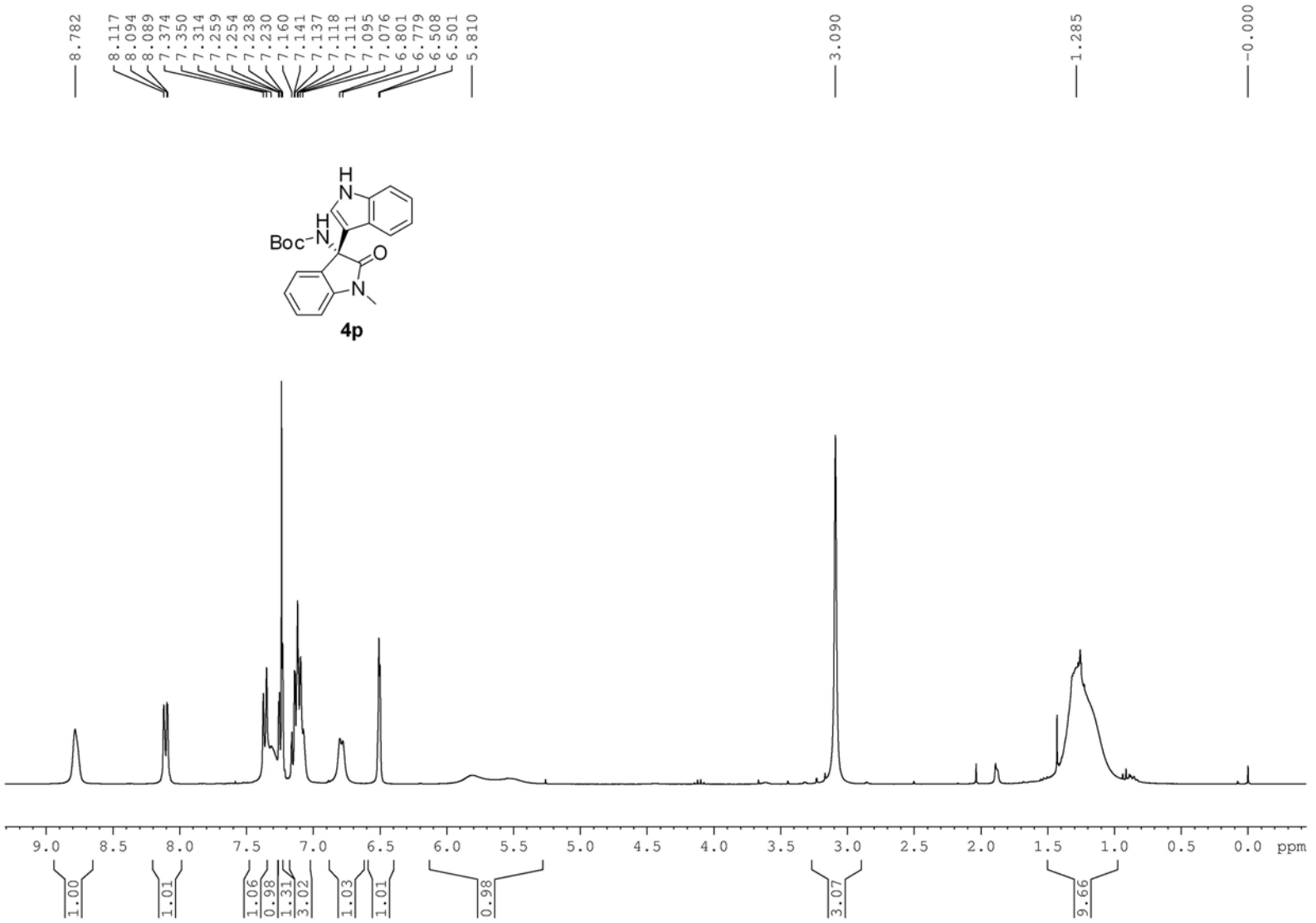

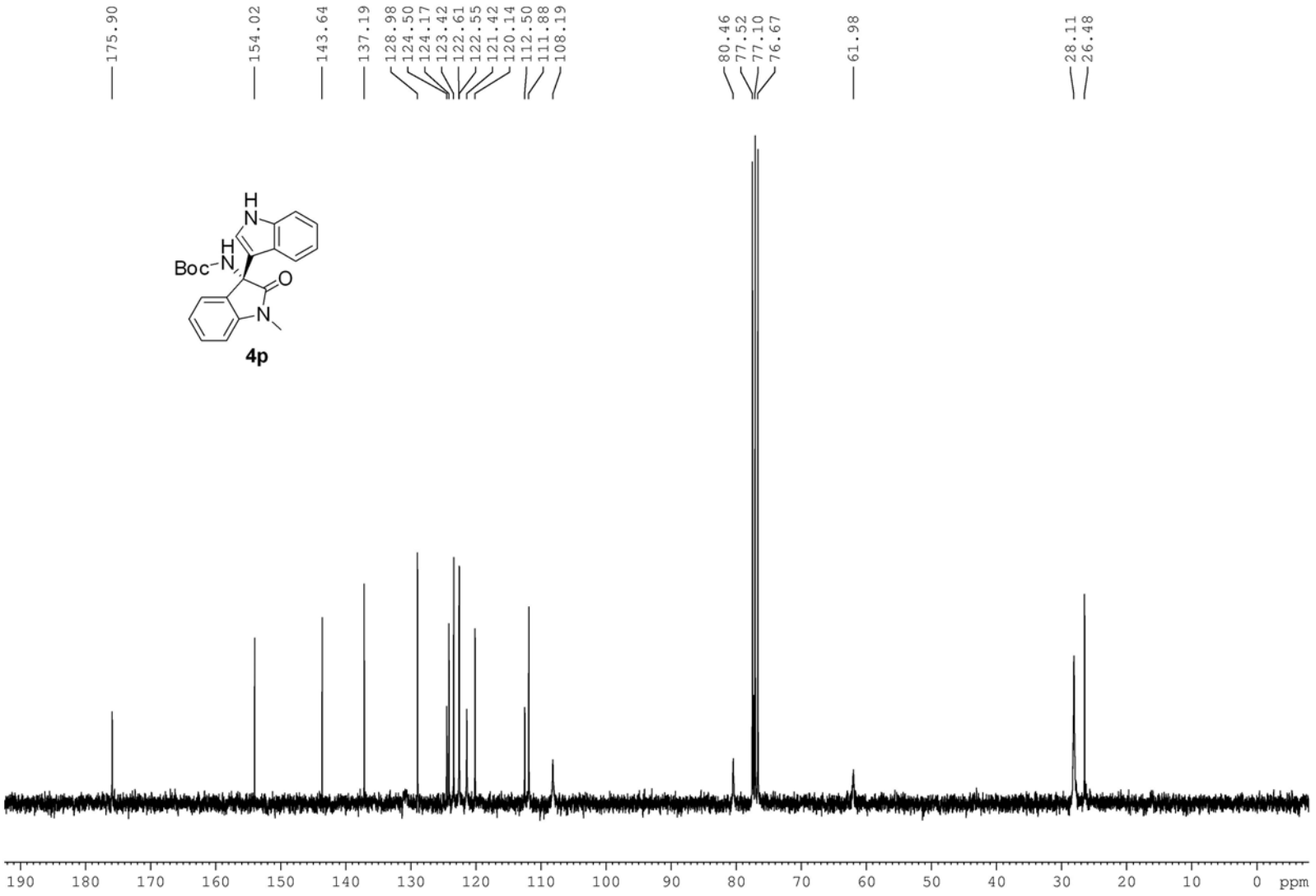

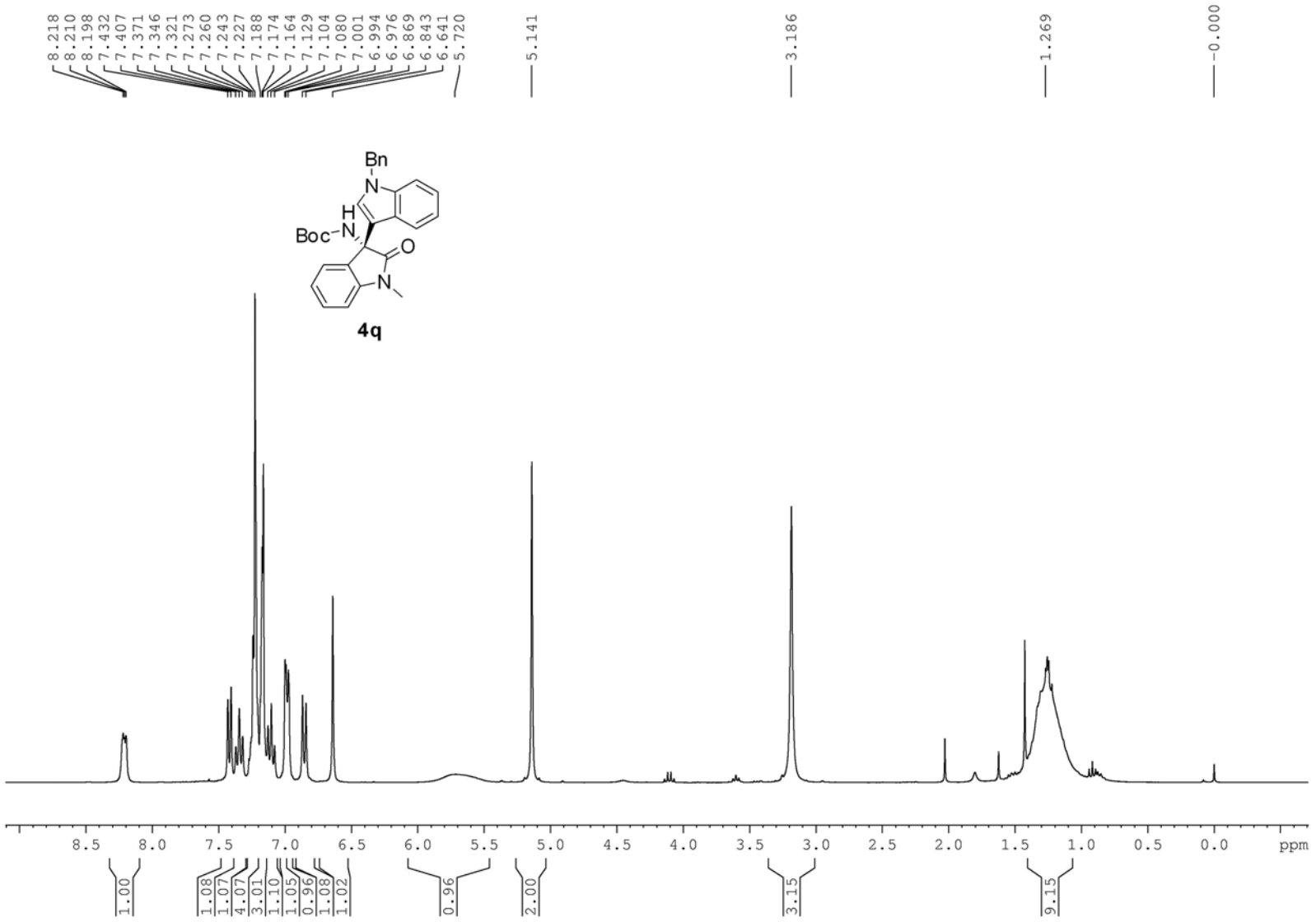

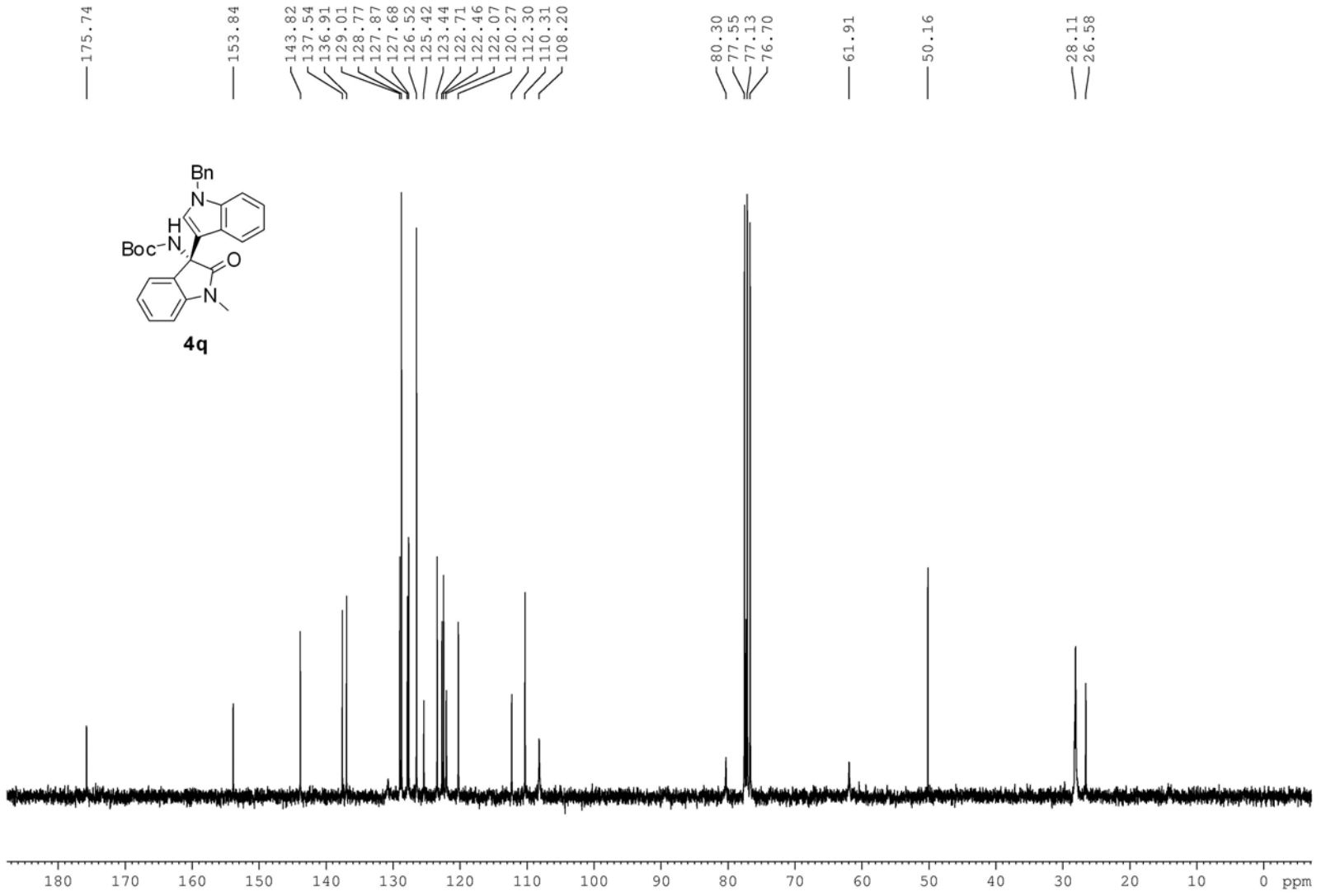

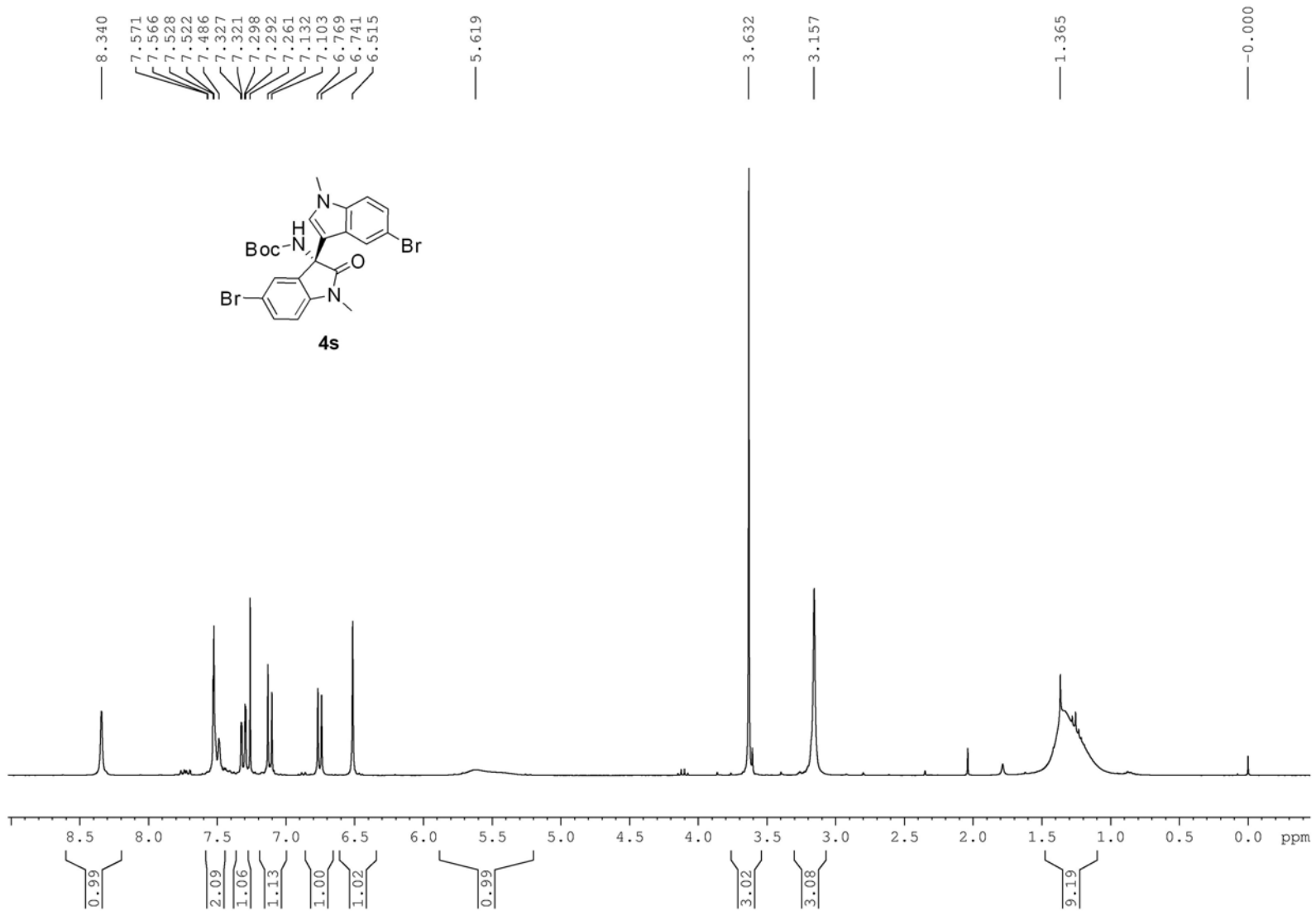

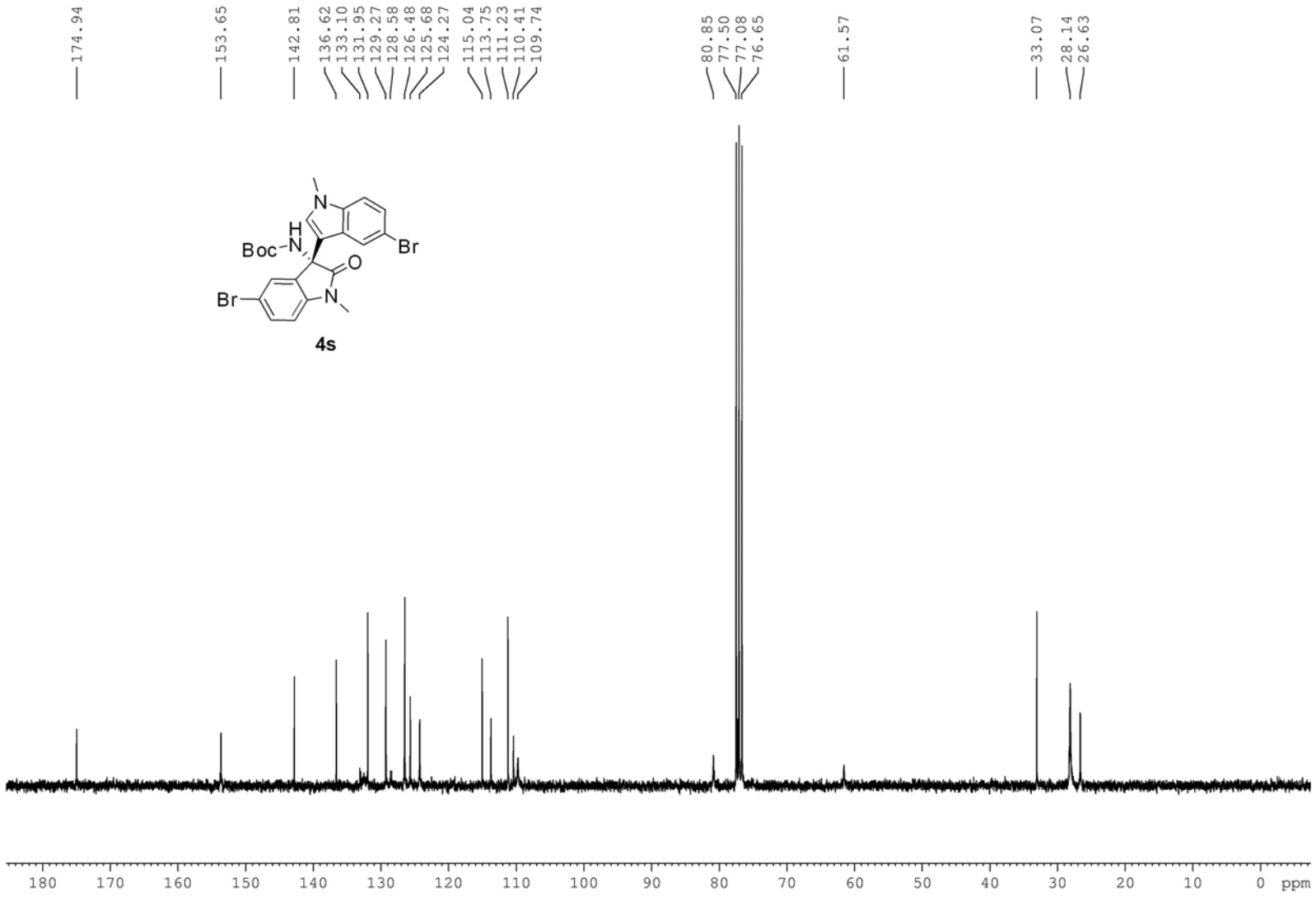

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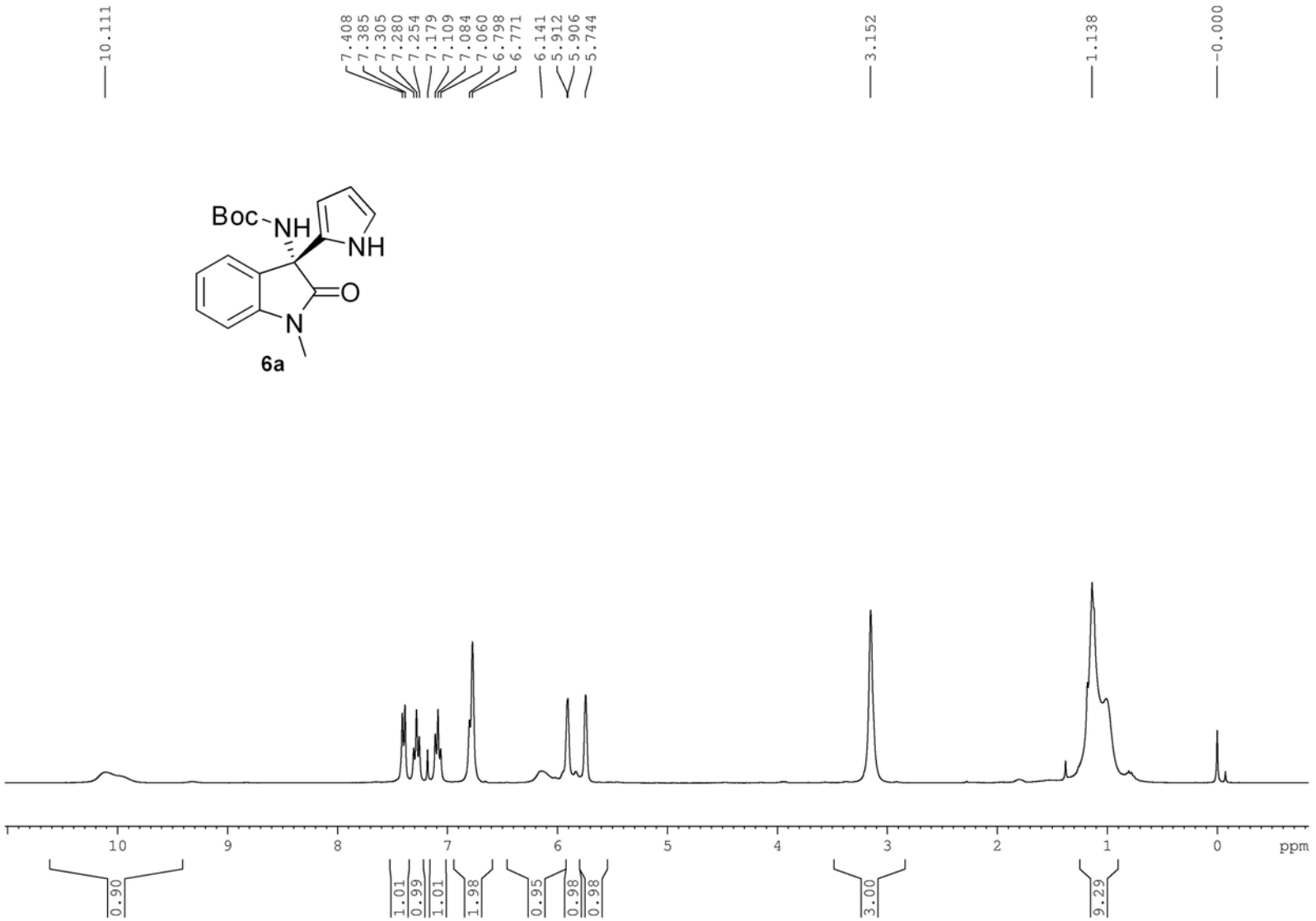

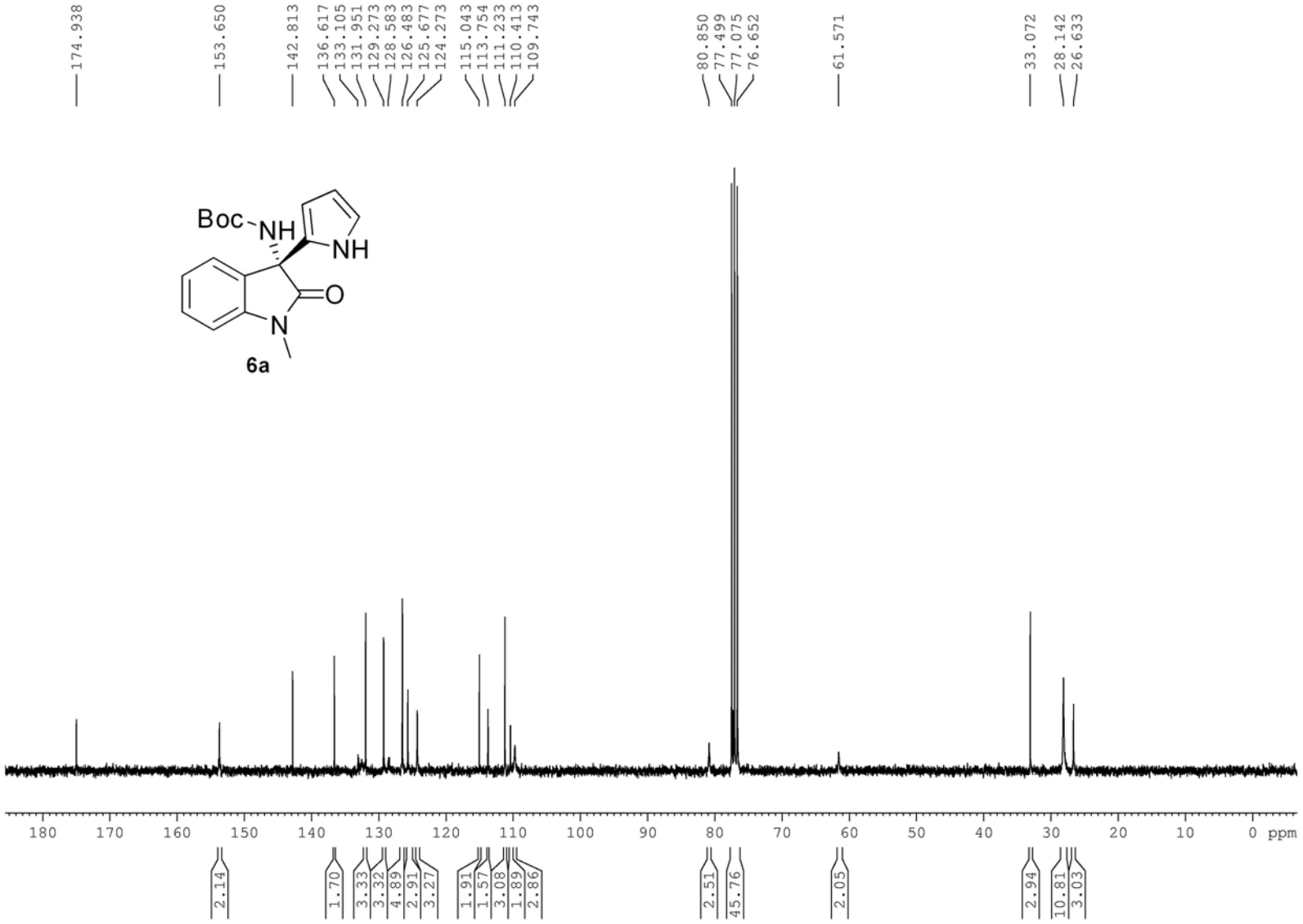

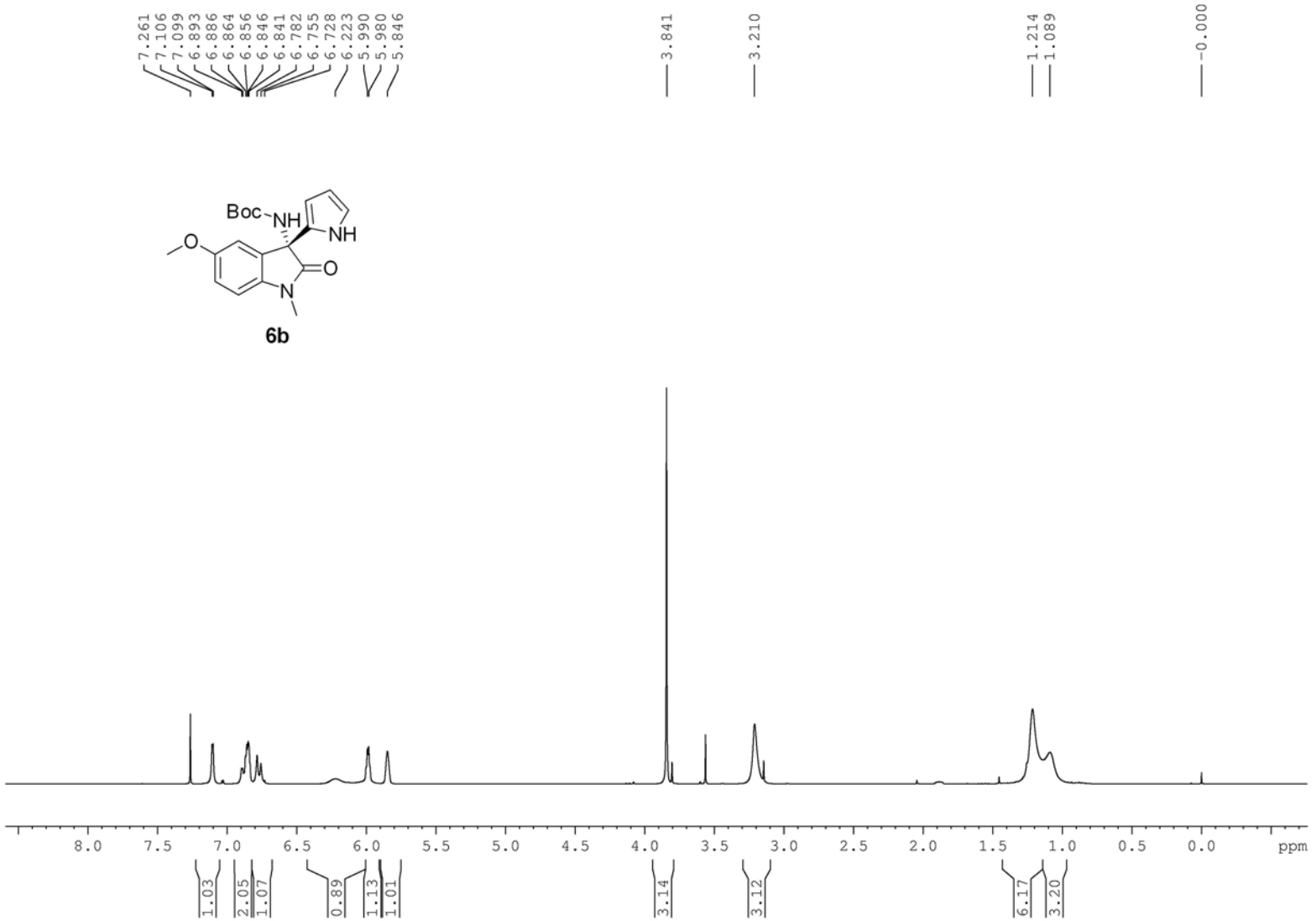

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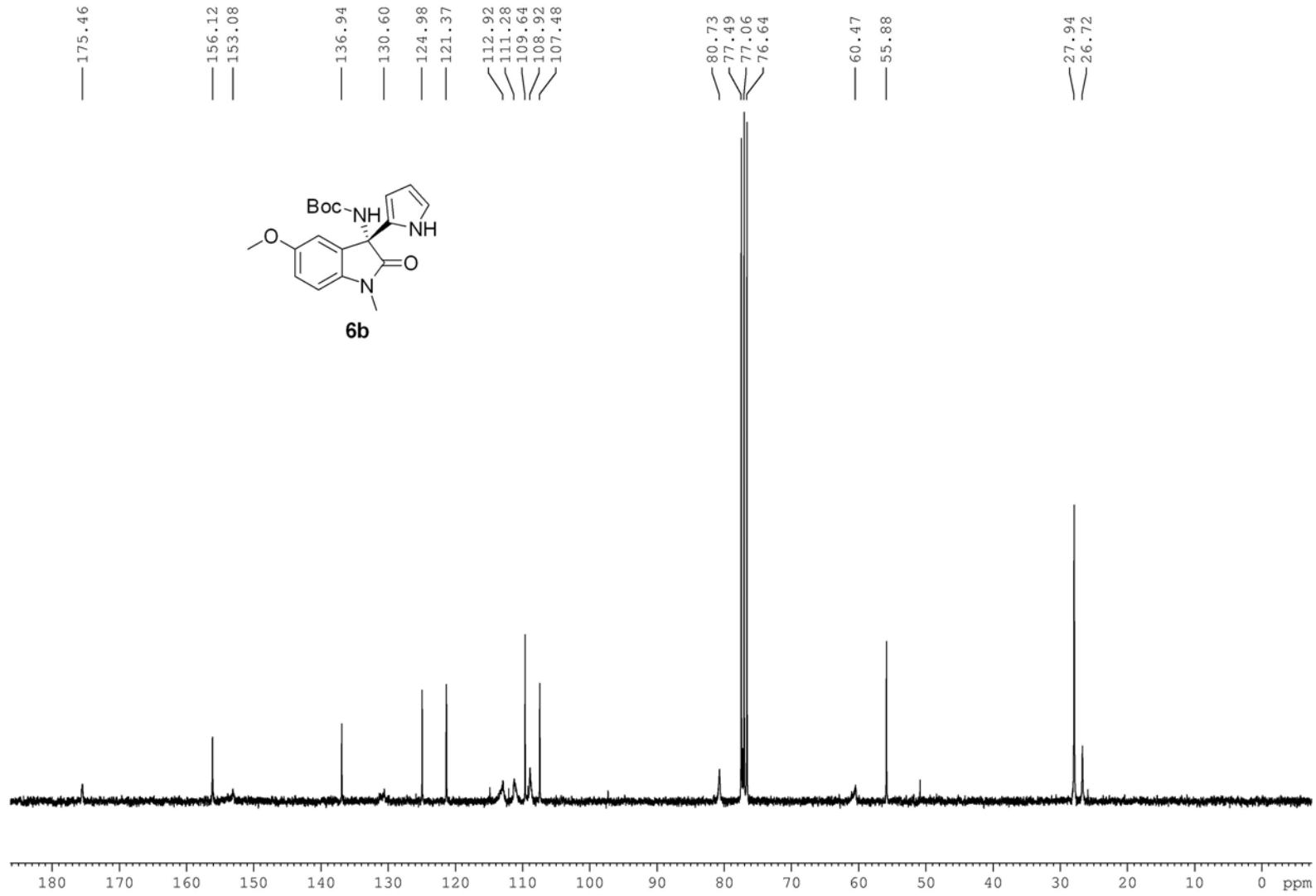

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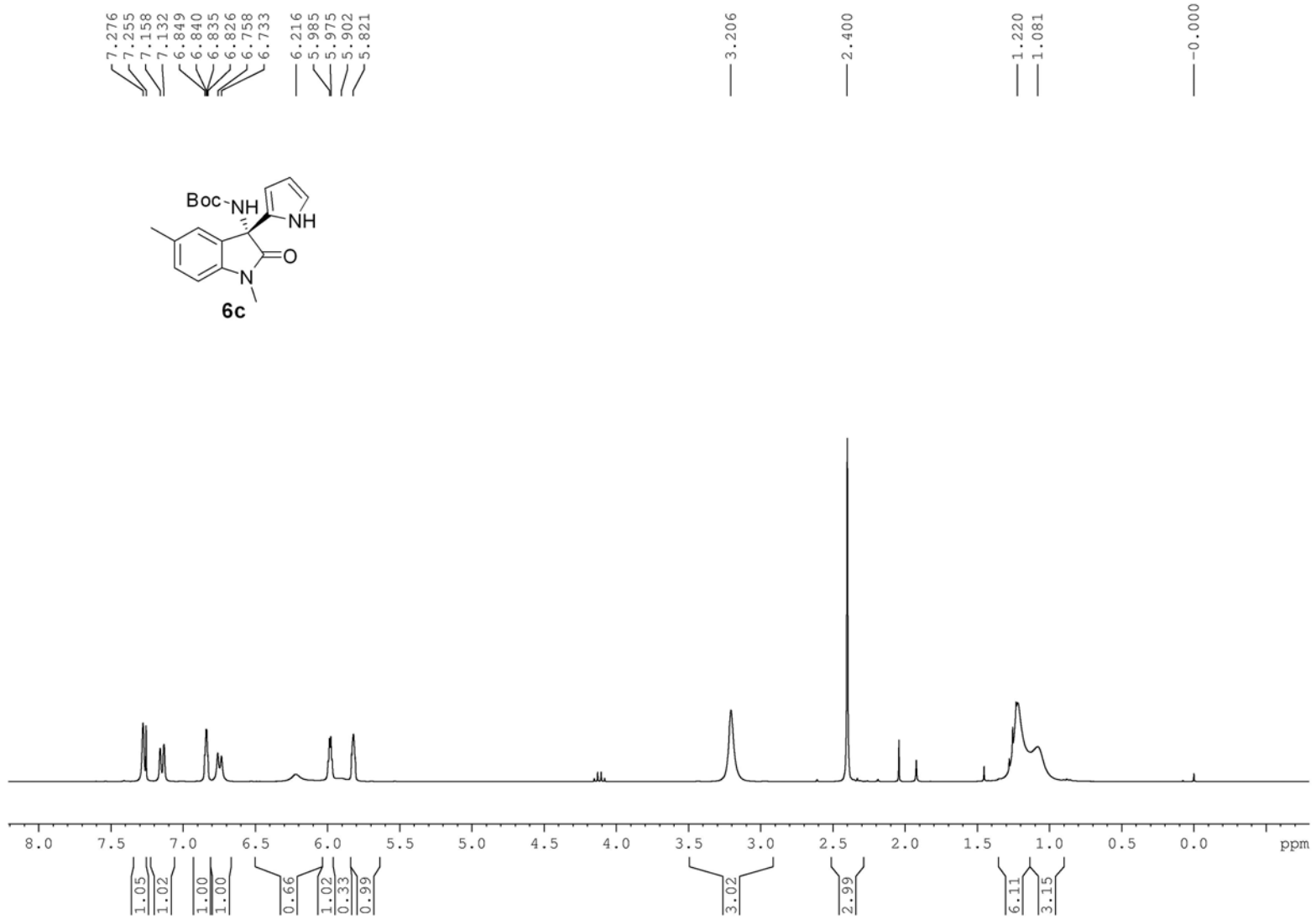

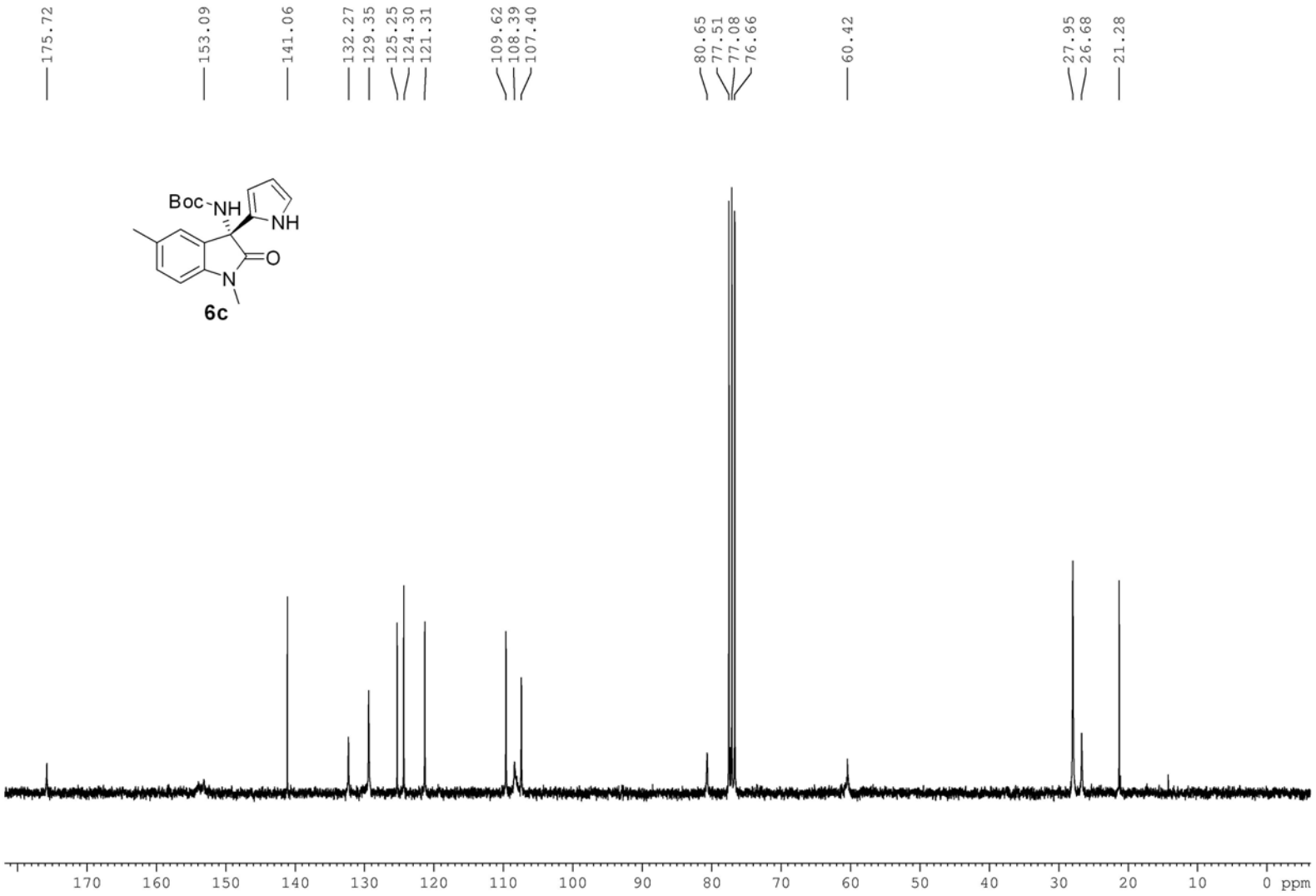

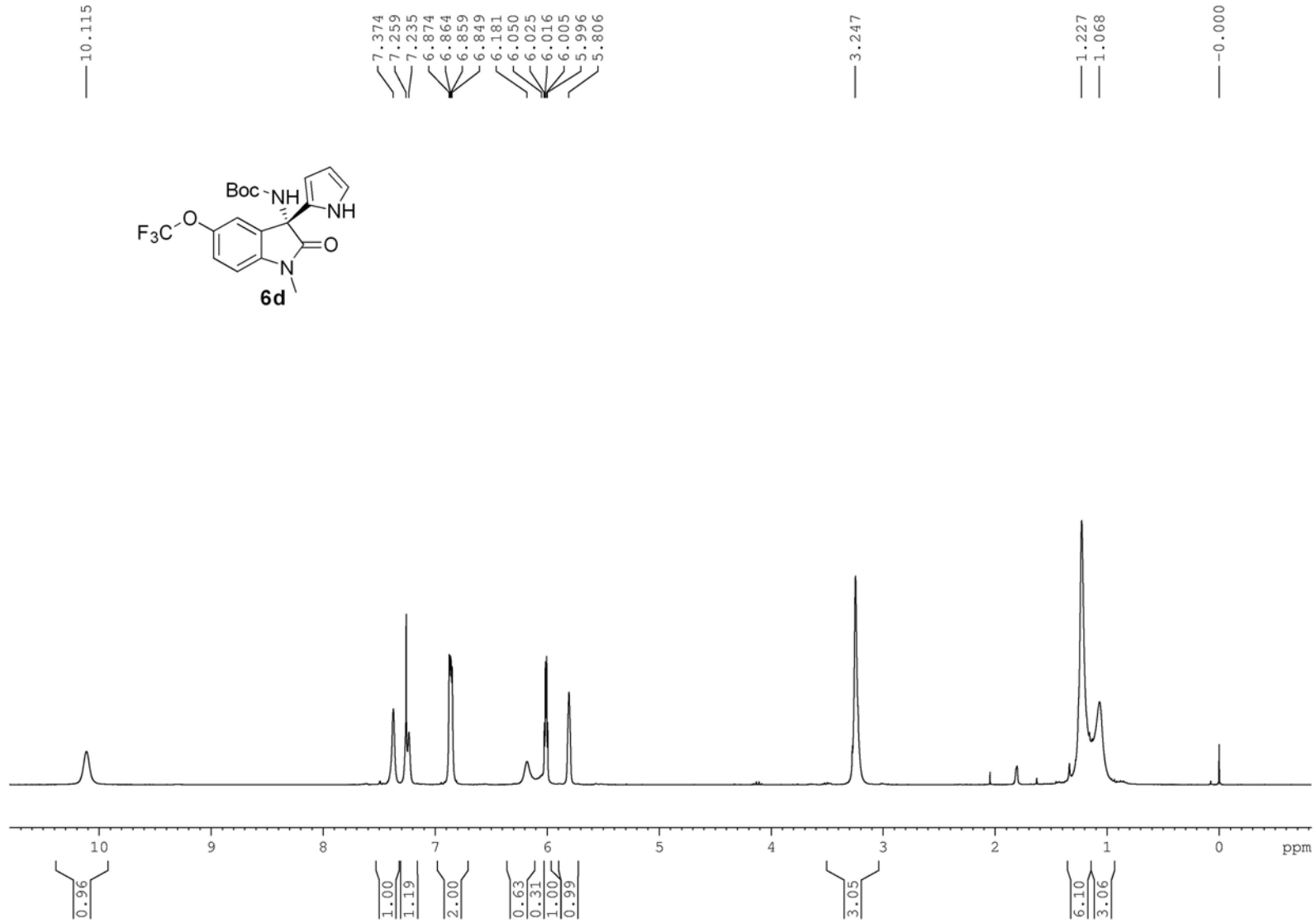

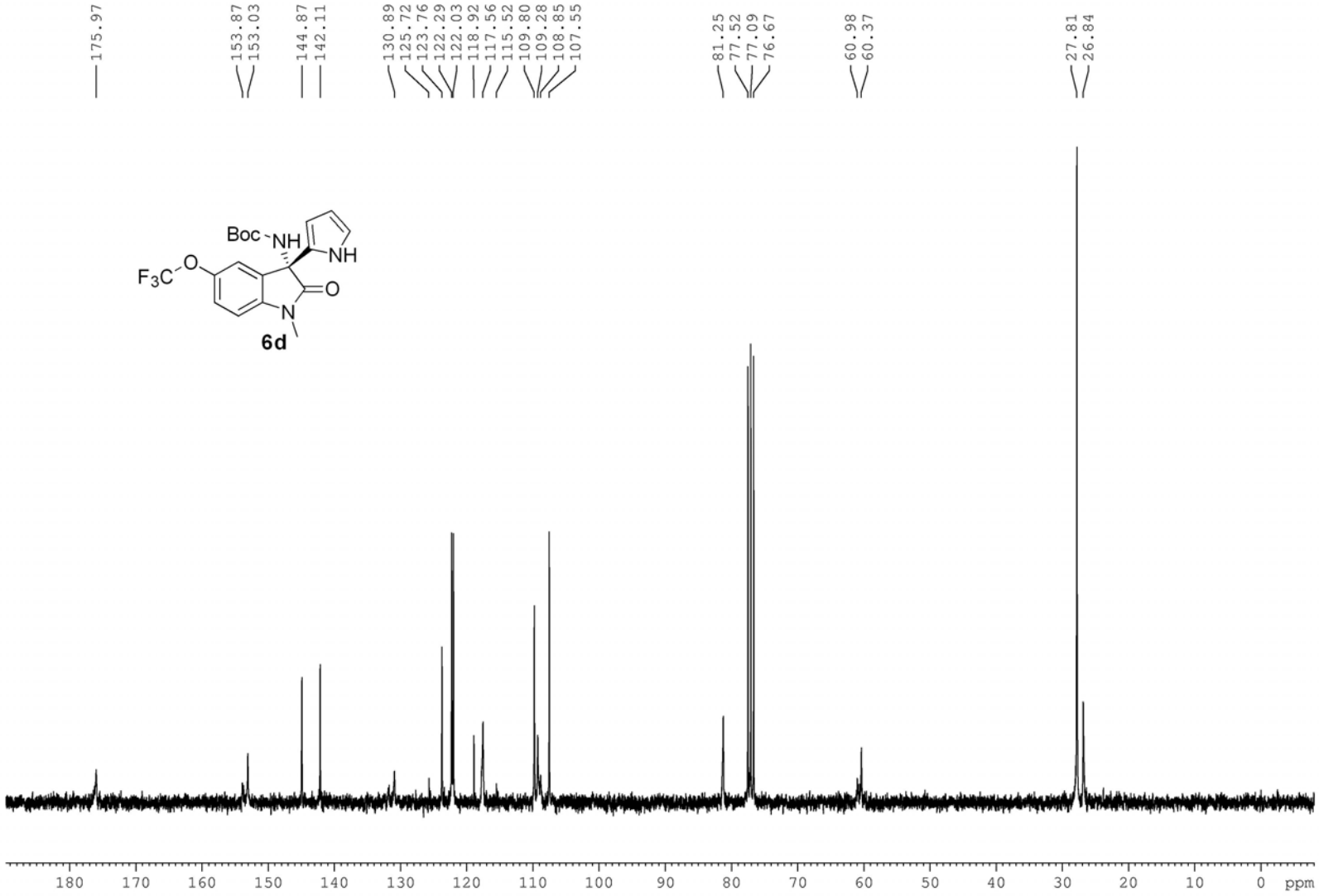

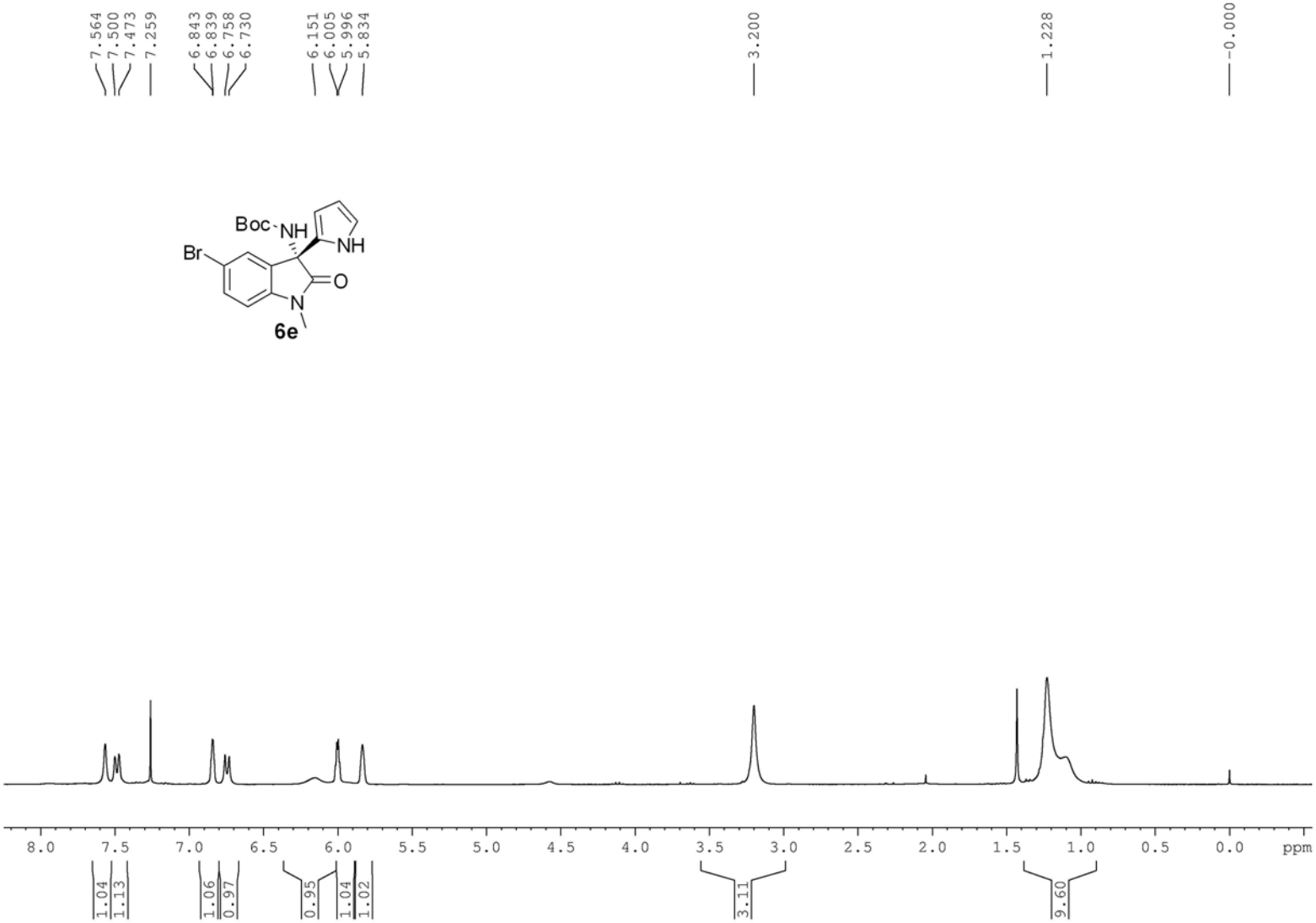

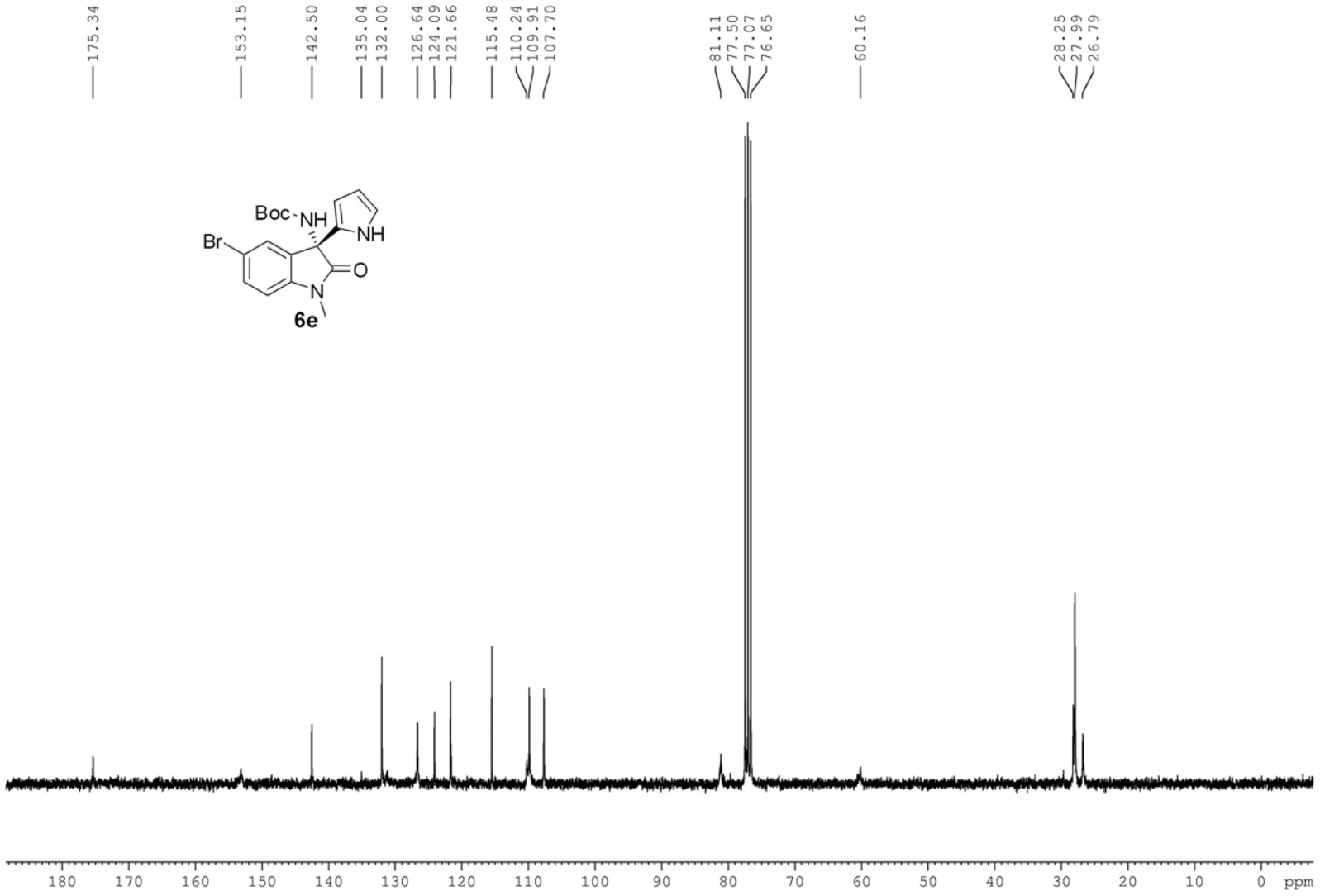

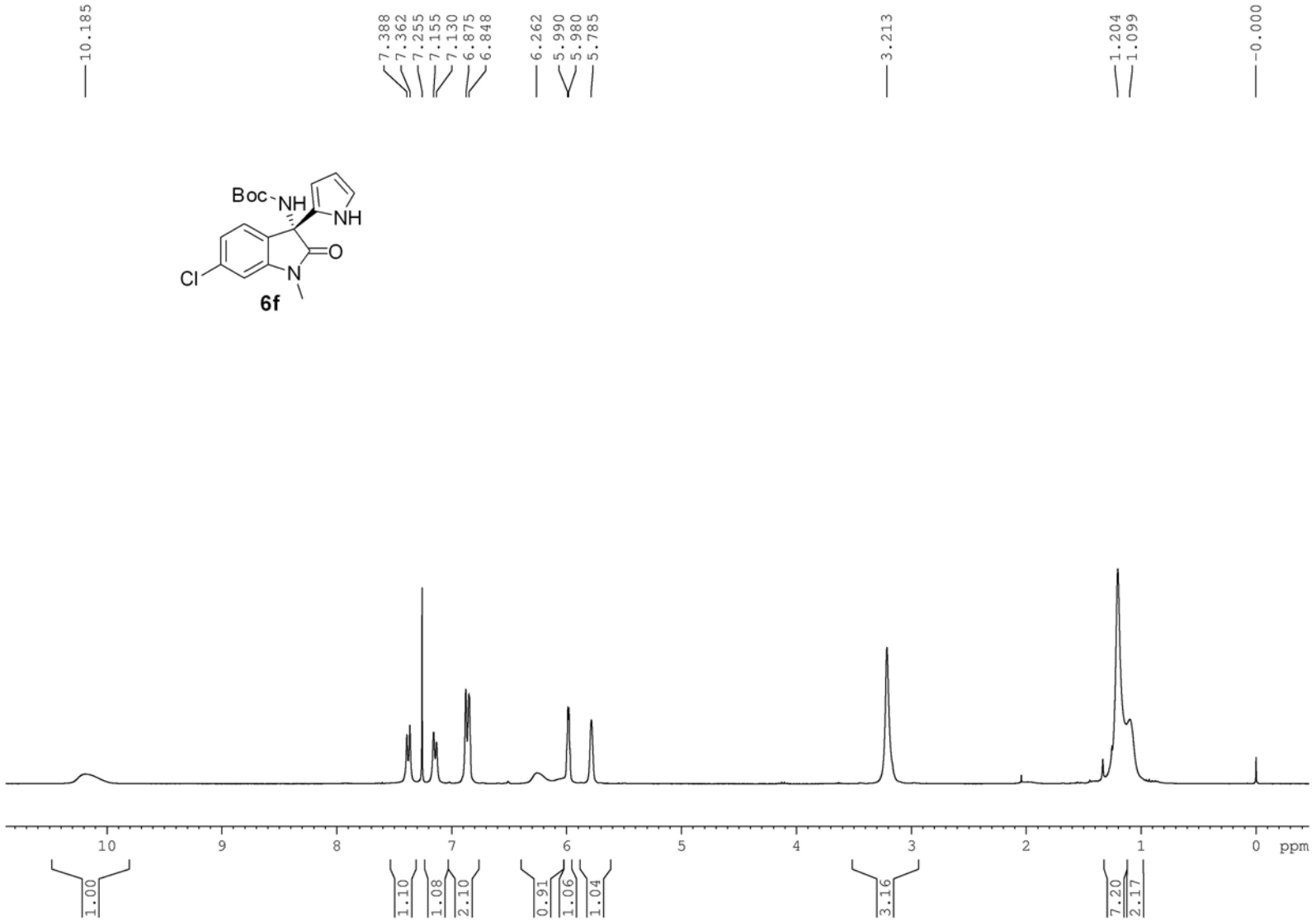

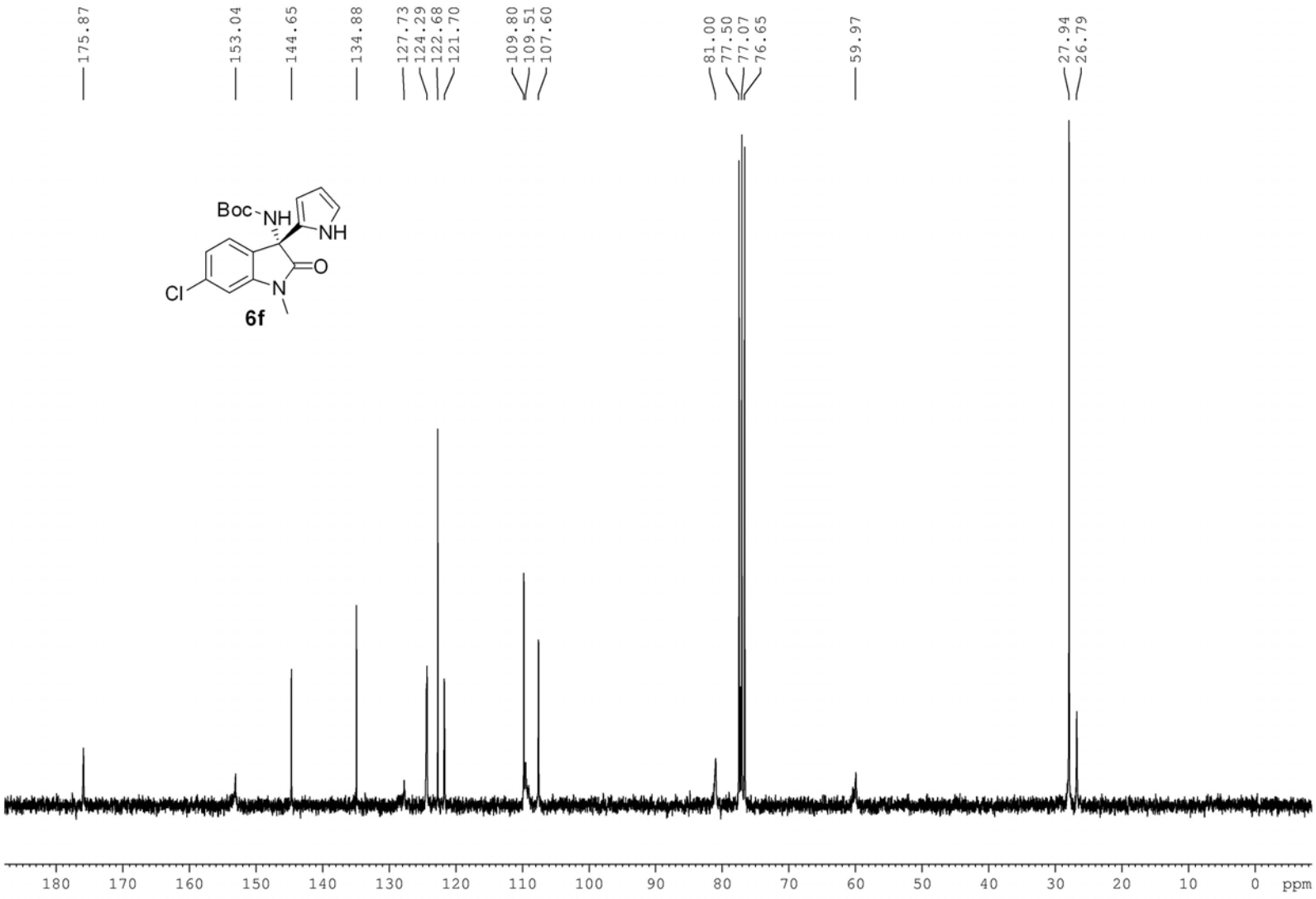

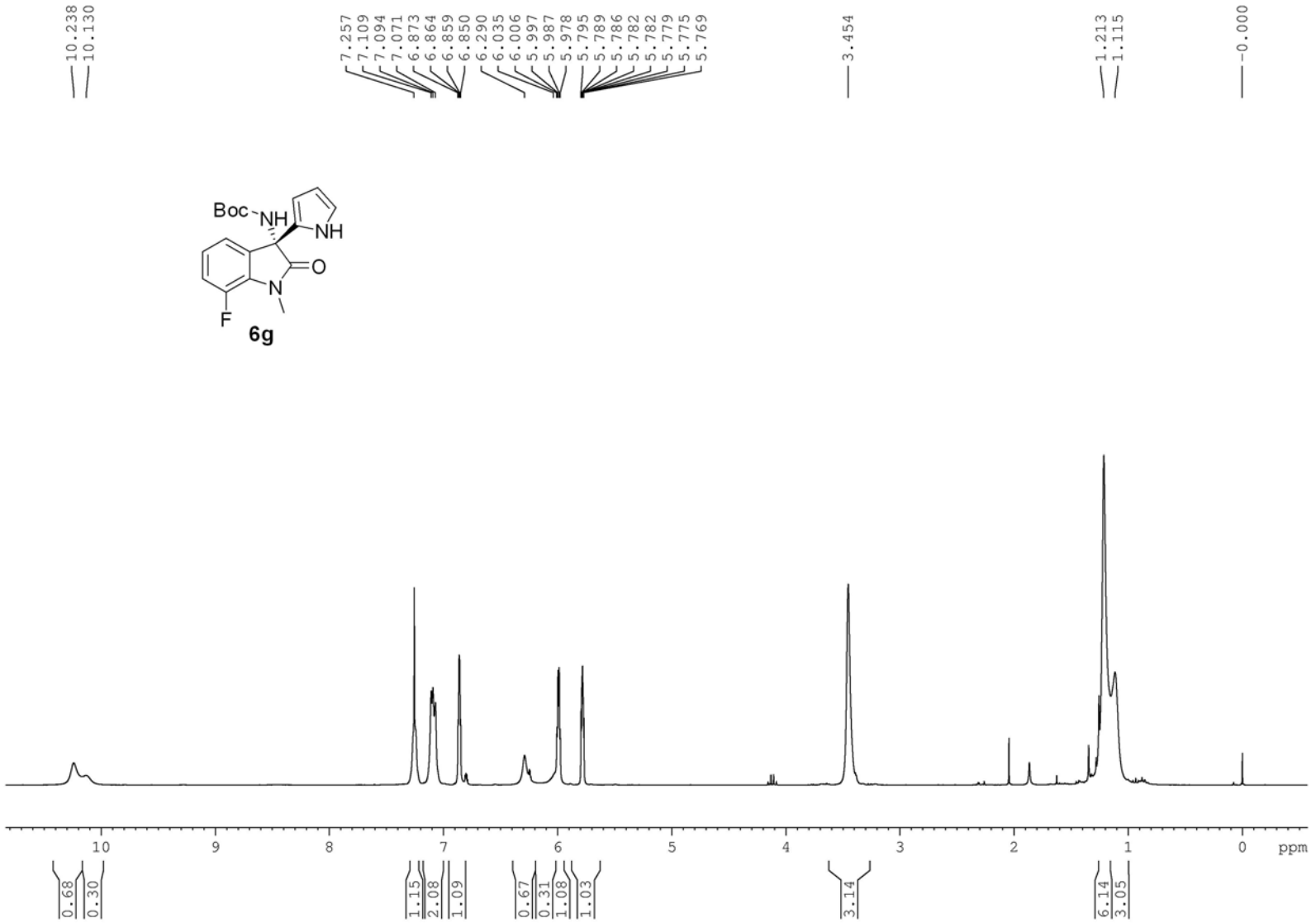

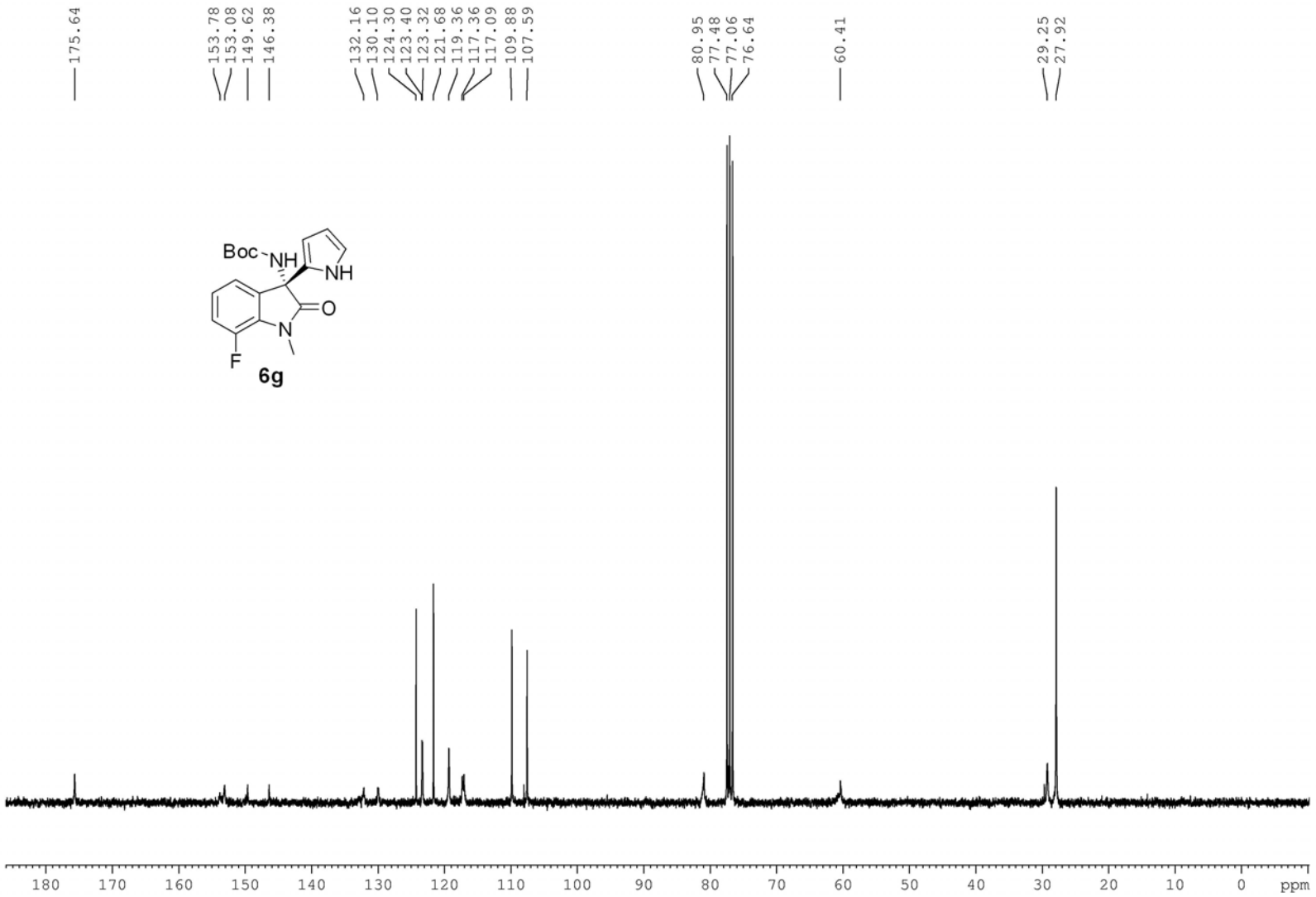

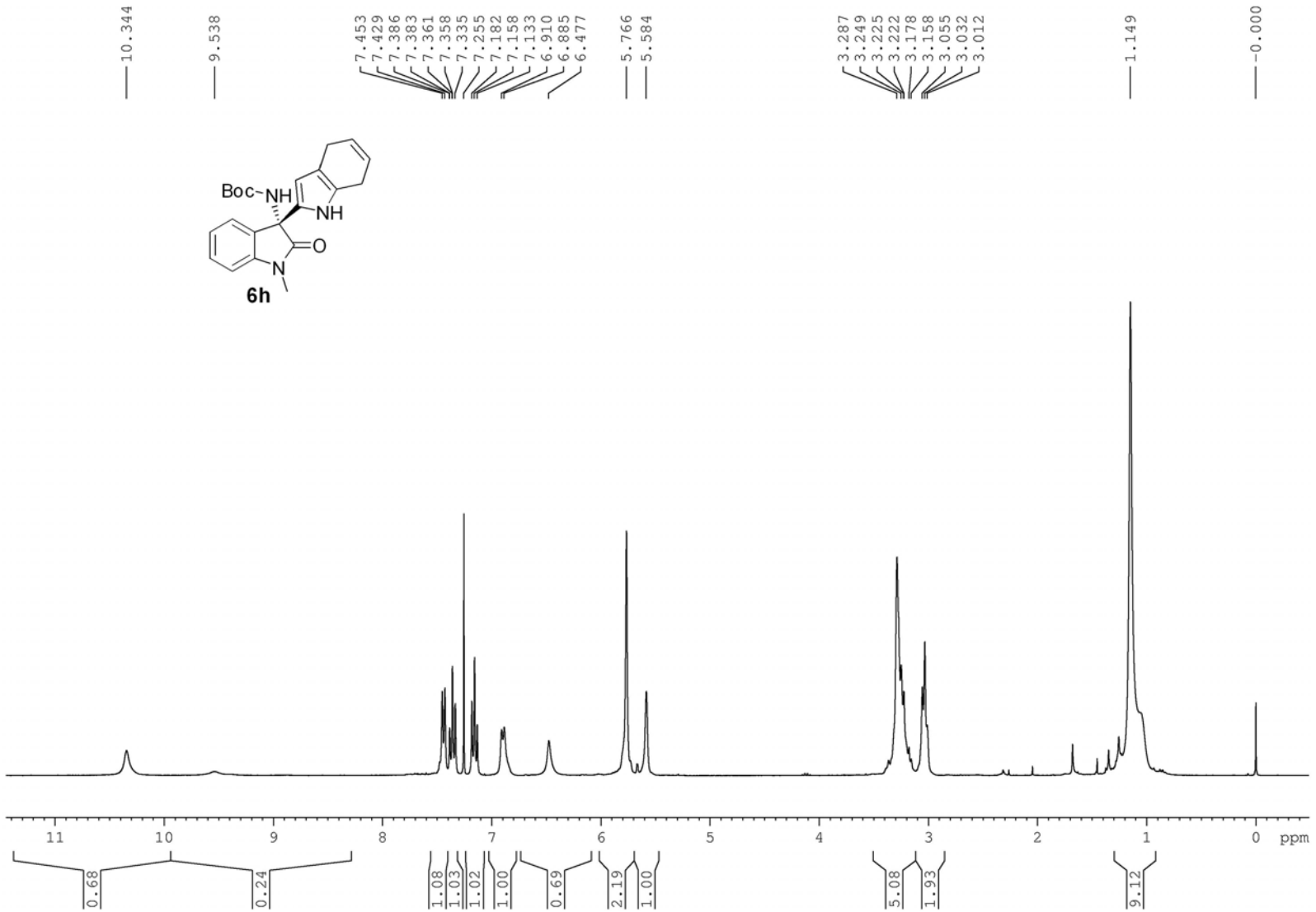

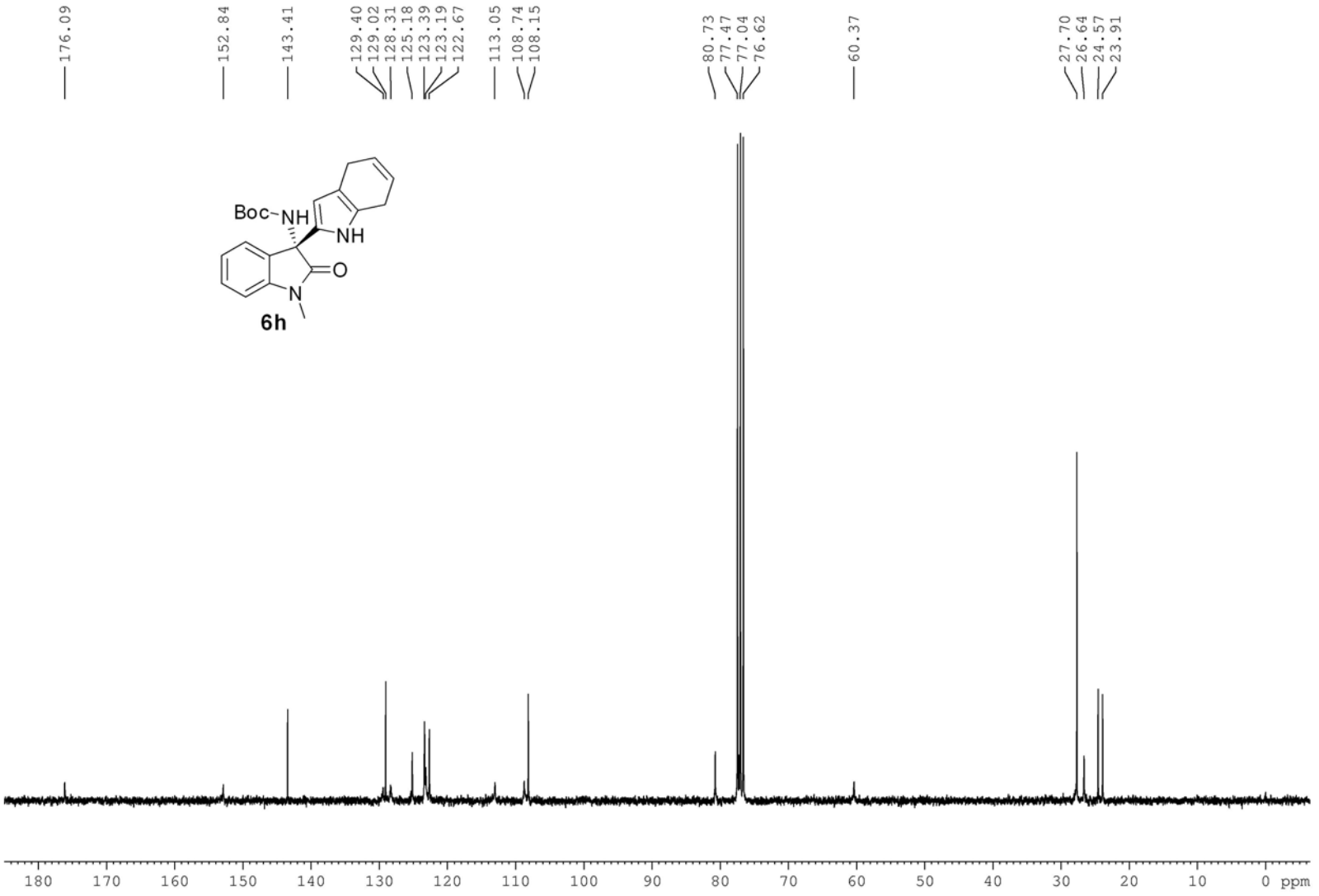

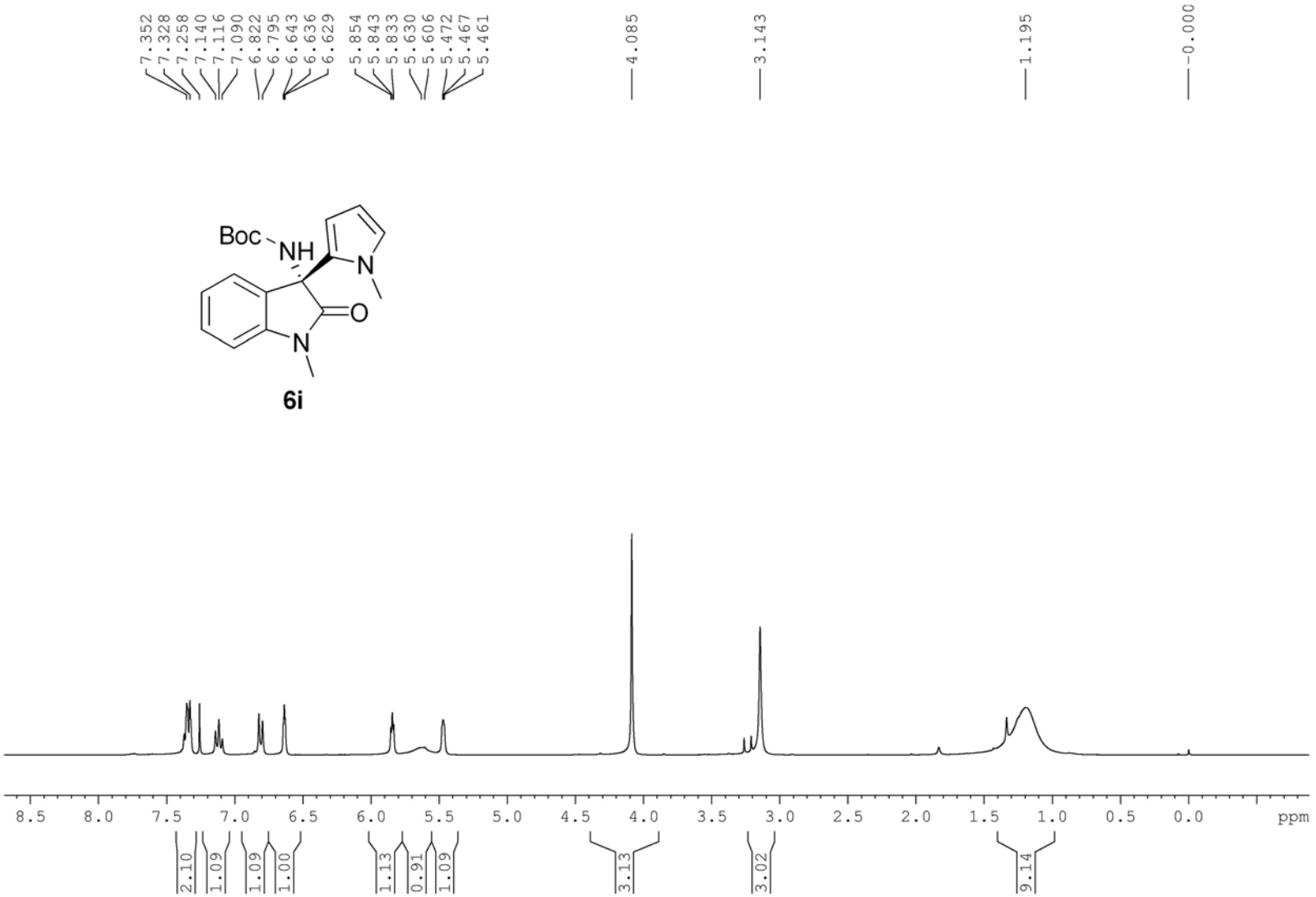

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