Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Visible-light enabled synthesis of cyclopropane-fused indolines via dearomatization of indoles

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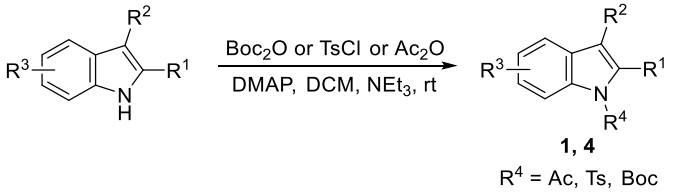
1. General Information

Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use.

^{1}H and ^{13}C NMR spectra were recorded on an Agilent instrument (400 MHz and 100 MHz, respectively) or an Agilent instrument (600 MHz and 150 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. ^{19}F NMR spectra were recorded on an Agilent instrument (376 MHz) and referenced relative to $CFCl_3$. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). The high resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS instrument or a High-Resolution LC-MS spectrometer Thermo Fisher Exactive. Melting points (m.p.) were determined in open capillaries without further correction.

2. General Procedure for the Synthesis of Substrates

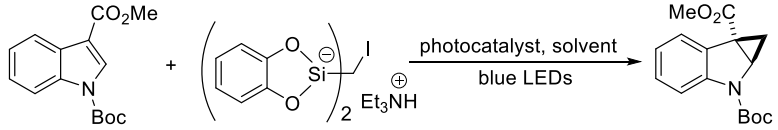


To a solution of *N*-unsubstituted indole derivatives (10 mmol, 1.0 equiv) in DCM (40 mL) was added DMAP (240 mg, 2 mmol, 0.2 equiv) at room temperature under argon. After stirring for 25 minutes, the corresponding acetic anhydride or sulfonyl chloride or di-tert-butyl dicarbonate (15 mmol, 1.5 equiv) and triethylamine (3.5 mL, 25 mmol, 2.5 equiv) were added slowly. The reaction was stirred at room temperature overnight. The resulted mixture was quenched with H_2O, extracted with DCM (25 mL×3), and dried over Na_2SO_4. After removal of Na_2SO_4 by filtration, the organic phase was concentrated *in vacuo* to give a dark residue, which was purified by column chromatography on silica gel (PE/EtOAc = 4/1) to afford the desired indole substrates.

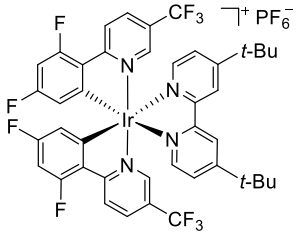
Alkylbis(catecholato)silicate **2** was prepared according to the procedures reported in the literature.[1]

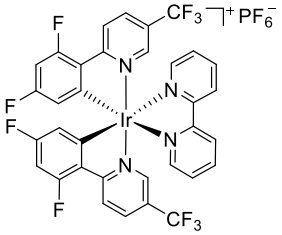
3. Detailed Screening of Reaction Conditions

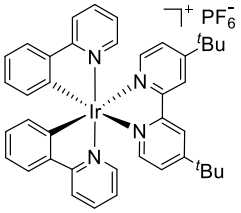
Table S1. Optimization of the Reaction Conditions for 3-Substituted Indoles[a]

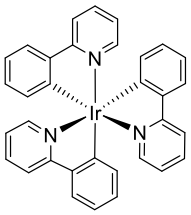


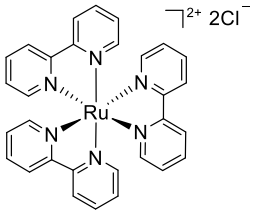
1a 2 3a

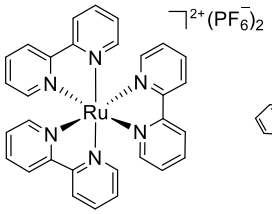

Ir(dFCF$_3$ppy)$_2$(dtbbpy)PF$_6$ (**I**)

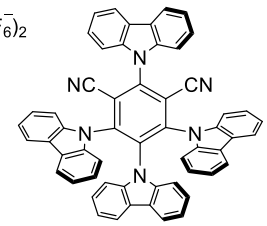

Ir(dFCF$_3$ppy)$_2$(bpy)PF$_6$ (**II**)

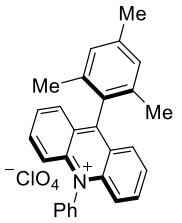

Ir(ppy)$_2$(dtbbpy)PF$_6$ (**III**)


Ir(ppy)$_3$ (**IV**)


Ru(bpy)$_3$Cl$_2$ (**V**)


Ru(bpy)$_3$(PF$_6$)$_2$ (**VI**)


4-CzIPN (**VII**)

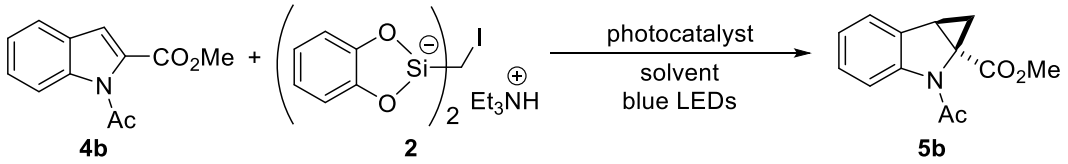

[Acr-Mes]ClO$_4$ (**VIII**)

entry	photocatalyst	solvent	yield (%) (**3a**)[b]
1	**I**	DMSO	92 (86)[c]
2	**II**	DMSO	10
3	**III**	DMSO	0
4	**IV**	DMSO	10
5	**VII**	DMSO	90
6	**VIII**	DMSO	0
7	**I**	DMF	60
8	**I**	DMA	42
9	**I**	CH_3CN	41
10	**I**	DMSO/CH_3CN (9/1)	75

11	**I**	THF	14
12	**I**	1,4-dioxane	trace
13	**I**	DCM	trace
14	**I**	$PhCF_3$	31
15[d]	--	DMSO	0
16[e]	**I**	DMSO	0
17[f]	**I**	DMSO	>95 (90)[c]

[a]Reaction conditions: A solution of **1a** (0.2 mmol), **2** (0.4 mmol) and photocatalyst (3.0 mol%) in the indicated solvent (c = 0.1 M) was irradiated by two 3 W blue LEDs at room temperature under argon for 12 h. [b]Yield determined by ^{1}H NMR using dibromomethane as an internal standard. [c]Isolated yield is reported in the parenthesis. [d]In the absence of photocatalyst. [e]Under dark. [f]Irradiated for 24 h.

Table S2. Optimization of the Reaction Conditions for 2-Substituted Indoles[a]

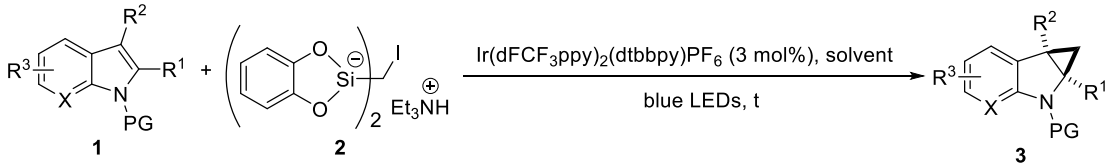


entry	photocatalyst	solvent	yield (%) (**5b**)[b]
1	**I**	DMSO	58
2	**III**	DMSO	38
3	**IV**	DMSO	9
4	**V**	DMSO	20
5	**VII**	DMSO	56
6	**VII**	DMF	53
7	**VII**	DMSO/CH_3CN (9/1)	62
8	**VII**	DMSO/CH_3CN (6/1)	62
9	**VII**	DMSO/CH_3CN (3/1)	60
10	**VII**	DMSO/CH_3CN (1/1)	59

11	**VII**	DMSO/CH_3CN (1/6)	36
12	**I**	DMSO/CH_3CN (9/1)	67(60)[c]
13[d]	**I**	DMSO/CH_3CN (9/1)	66
14[e]	—	DMSO/CH_3CN (9/1)	0
15[f]	**I**	DMSO/CH_3CN (9/1)	0

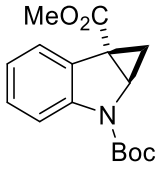
[a]Reaction conditions: A solution of **4b** (0.2 mmol), **2** (0.4 mmol) and photocatalyst (3.0 mol%) in the indicated solvent (c = 0.1 M) was irradiated by two 3 W blue LEDs at room temperature under argon for 12 h. [b]Determined by ^1H NMR using dibromomethane as an internal standard. [c]Isolated yield is reported in the parenthesis. [d] Irradiated for 24 h. [e]Without a photocatalyst. [f]Under dark.

4. General Procedure for Visible-Light Induced Dearomatization of Indole Derivatives

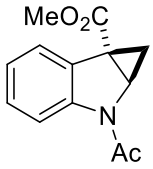


To a flame-dried sealed tube were added indole derivative **1** or **4** (0.2 mmol, 1.0 equiv), **2** (0.4 mmol, 2.0 equiv), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (6.7 mg, 0.006 mmol, 3 mol%) and solvent (DMSO or DMSO/CH_3CN = 9/1, 2 mL). The reaction mixture was degassed via freeze-pump-thaw for 3 cycles. After thoroughly degassed, the tube was sealed and positioned approximately 3 cm from two 3 W blue LEDs. After the reaction was complete (monitored by TLC), the reaction mixture was transferred to a separatory funnel and diluted with EtOAc (~10 mL) and 2 M aq NaOH (~5 mL). The layers were separated, and the organic layer was washed with additional 2 M aq NaOH (5 mL×2). The organic layer was then washed with deionized H_2O (~5 mL) and followed by brine (~5 mL). The organic layer was dried over Na_2SO_4. After removal of Na_2SO_4 by filtration, the organic phase was concentrated *in vacuo* by rotary evaporation. Further

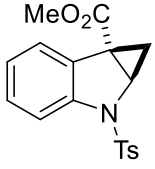
purification was accomplished by column chromatography on silica gel (PE/DCM = 1/1 to pure DCM). The analytical data of the products are summarized below.



3a, 24 h, white solid, 52.1 mg, 90% yield, m.p. = 91.1-92.4 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (brs, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.23-7.19 (m, 1H), 7.05-7.01 (m, 1H), 4.54 (brs, 1H), 3.79 (s, 3H), 1.98-1.95 (m, 1H), 1.59 (s, 9H), 0.74-0.72 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.8, 151.7, 141.5, 128.9, 127.7, 126.0, 122.4, 115.8, 87.2, 52.5, 46.6, 31.0, 28.5, 19.5. **IR** (thin film): ν_{max}/cm^{-1} = 1709, 1485, 1383, 1293, 1253, 1152, 1092, 1010, 964, 885, 853, 752, 652, 580, 483. **HRMS (EI)** calcd for $C_{16}H_{19}NO_4$ $[M]^+$: 289.1309, found: 289.1305.

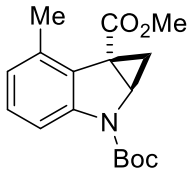


3b, 24 h, yellow foam, 29.2 mg, 63% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.26-7.24 (m, 1H), 7.12-7.08 (m, 1H), 4.36 (dd, *J* = 6.4, 4.0 Hz, 1H), 3.82 (s, 3H), 2.40 (s, 3H), 2.03-2.00 (m, 1H), 0.92-0.89 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 168.6, 141.9, 128.9, 128.2, 125.9, 123.7, 117.6, 52.7, 47.1, 32.3, 24.5, 20.7. **IR** (thin film): ν_{max}/cm^{-1} = 2922, 1729, 1673, 1438, 1390, 1304, 1243, 1197, 1114, 1076, 988, 776, 619, 549, 478. **HRMS (EI)** calcd for $C_{13}H_{13}NO_3$ $[M]^+$: 231.0890, found: 231.0888.

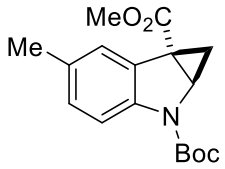


3c, 24 h, yellow oil, 42.6 mg, 62% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.4 Hz, 1H), 7.62-7.58 (m, 3H), 7.25-7.21 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.08-7.04 (m, 1H), 4.50 (dd, *J* = 6.8, 4.0 Hz, 1H), 3.70 (s, 3H), 2.35 (s, 3H), 1.81 (dd, *J* = 6.8, 5.6 Hz, 1H), 0.32 (dd, *J* = 5.6, 4.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.0, 144.6,

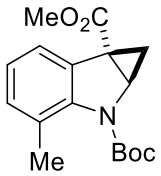
140.6, 133.7, 130.6, 129.7, 128.0, 127.5, 126.1, 124.1, 116.3, 52.5, 47.8, 31.2, 21.7, 18.5. **IR** (thin film): ν_{max}/cm^{-1} = 1725, 1438, 1358, 1292, 1164, 1088, 957, 813, 754, 718, 661, 573, 543. **HRMS (ESI)** calcd for $C_{18}H_{17}NO_4NaS$ $[M+Na]^+$: 366.0771, found: 366.0769.



3d, 24 h, yellow oil, 38.3 mg, 63% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (brs, 1H), 7.15-7.11 (m, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 4.35(brs, 1H), 3.77 (s, 3H), 2.35 (s, 3H), 2.07-2.05 (m, 1H), 1.59 (s, 9H), 0.74-0.71 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.2, 151.7, 142.0, 135.1, 128.4, 128.2, 124.6, 113.5, 81.5, 52.5, 46.9, 30.4, 28.5, 19.8, 16.7. **IR** (thin film): ν_{max}/cm^{-1} = 1706, 1459, 1371, 1249. 1155, 1108, 891, 777, 732, 672. **HRMS (EI)** calcd for $C_{17}H_{21}NO_4$ $[M]^+$: 303.1465, found: 303.1471.

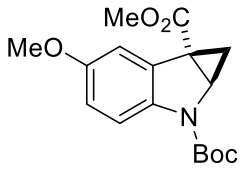


3e, 24 h, yellow oil, 51.2 mg, 84% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (brs, 1H), 7.51 (s, 1H), 7.03-7.00 (m, 1H), 4.51 (brs, 1H), 3.79 (s, 3H), 2.35 (s, 3H), 1.96-1.93 (m, 1H), 1.58 (s, 9H), 0.73-0.71 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.8, 151.8, 139.3, 132.0, 128.8, 128.3, 126.4, 115.5, 81.6, 52.4, 46.7, 30.9, 28.5, 21.1, 19.8. **IR** (thin film): ν_{max}/cm^{-1} = 1706, 1484, 1365, 1304, 1255, 1149, 1085, 896, 816, 758, 733, 641, 474. **HRMS (EI)** calcd for $C_{17}H_{21}NO_4$ $[M]^+$: 303.1465, found: 303.1463.

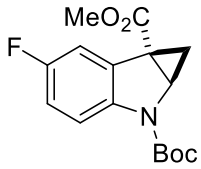


3f, 24 h, white solid, 52.6 mg, 87% yield, m.p. = 112.4-112.7 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58-7.56 (m, 1H), 7.08-7.03 (m, 2H), 4.66 (dd, *J* = 7.2, 4.0 Hz, 1H), 3.81 (s,

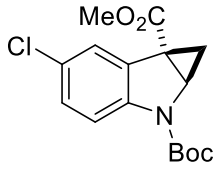
3H), 2.28 (s, 3H), 2.01 (dd, *J* = 7.2, 5.6 Hz, 1H), 1.56 (s, 9H), 0.47-0.45 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 153.0, 138.8, 131.6, 130.3, 128.9, 124.1, 122.9, 82.2, 52.4, 47.0, 30.7, 28.4, 20.6, 20.5. **IR** (thin film): ν_{max} (cm^{-1}) = 2976, 1718, 1457, 1362, 1293, 1247, 1152, 1118, 1071, 924, 844, 767, 553, 463. **HRMS (EI)** calcd for $C_{17}H_{21}NO_4$. $[M]^+$: 303.1465, found: 303.1460.



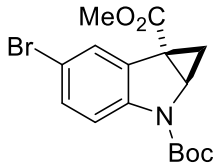
3g, 24 h, white foam, 57.9 mg, 91% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (brs, 1H), 7.29-7.28 (m, 1H), 6.76-6.73 (m, 1H), 4.67-4.51 (m, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 1.95-1.93 (m, 1H), 1.57 (s, 9H), 0.76-0.73 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 155.4, 151.8, 135.2, 130.1, 116.3, 112.9, 112.1, 81.5, 55.8, 52.4, 46.8, 30.3, 28.5, 20.0. **IR** (thin film): ν_{max}/cm^{-1} = 1702, 1481, 1429, 1380, 1331, 1299, 1255, 1154, 1077, 1048, 888, 805, 756, 733, 647, 462. **HRMS (ESI)** calcd for $C_{17}H_{21}NO_5Na$ $[M+Na]^+$: 342.1312, found: 342.1311.



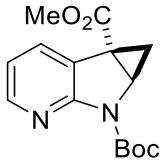
3h, 24 h, yellow oil, 45.7 mg, 74% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.43-7.41 (m, 1H), 6.93-6.87 (m, 1H), 4.67-4.55 (m, 1H), 3.80 (s, 3H), 1.98-1.95 (m, 1H), 1.58 (s, 9H), 0.76-0.74 (m, 1H). **^{13}C NMR** (100 MHz, d_6-DMSO, 110 °C) δ 168.4, 156.6, 150.5, 147.3 (d, *J* = 202.0 Hz), 130.4 (d, *J* = 6.0 Hz), 115.5 (d, *J* = 6.0 Hz), 113.2 (d, *J* = 16.0 Hz), 112.2 (d, *J* = 16.0 Hz), 81.3, 51.51, 51.48, 29.8 (d, *J* = 2.0 Hz), 27.4, 18.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -120.99 (s), **IR** (thin film): ν_{max}/cm^{-1} = 1707, 1480, 1381, 1302, 1230, 1149, 1080, 943, 814, 733, 639, 472. **HRMS (EI)** calcd for $C_{16}H_{18}FNO_4$ $[M]^+$: 307.1214, found: 307.1211.



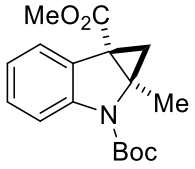
3i, 24 h, white foam, 46.4 mg, 72% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (brs, 1H), 7.673-7.668 (m, 1H), 7.17 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.55 (brs, 1H), 3.80 (s, 3H), 1.99-1.96 (m, 1H), 1.58 (s, 9H), 0.75-0.72 (m, 1H). **^{13}C NMR** (100 MHz, d_6-DMSO, 110 °C) δ 168.3, 150.4, 139.2, 130.6, 126.6, 125.6, 124.9, 115.8, 81.5, 51.5, 45.6, 29.7, 27.4, 17.9. **IR** (thin film): ν_{max}/cm^{-1} = 1706, 1474, 1380, 1298, 1253, 1155, 1072, 827, 749, 701, 618, 476. **HRMS (EI)** calcd for $C_{16}H_{18}ClNO_4$ $[M]^+$: 323.0919, found: 323.0910



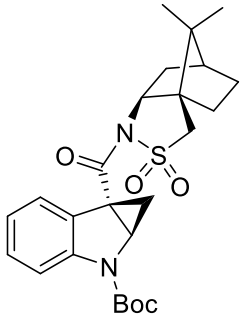
3j, 24 h, yellow oil, 68.7 mg, 93% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82-7.81 (m, 1H), 7.71 (brs, 1H), 7.31 (dd, *J* = 3.2, 2.4 Hz, 1H), 4.55 (brs, 1H), 3.80 (s, 3H), 1.98-1.95 (m, 1H), 1.58 (s, 9H), 0.74-0.71 (m, 1H). **^{13}C NMR** (100 MHz, d_6-DMSO, 110 °C) δ 168.3, 150.4, 139.7, 131.0, 129.6, 127.8, 116.3, 113.2, 81.6, 51.5, 45.6, 29.6, 27.4, 17.9. **IR** (thin film): ν_{max}/cm^{-1} = 1710, 1486, 1437, 1382, 1331, 1294, 1253, 1152, 1118, 1094, 1056, 1010, 963, 886, 856, 748, 653, 583, 532, 484. **HRMS (DART)** calcd for $C_{16}H_{19}{}^{79}BrNO_4$ $[M+H]^+$: 368.0492, found: 368.0492.



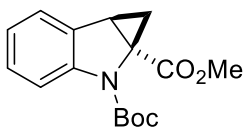
3k, 24 h, yellow oil, 33.4 mg, 58% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (dd, *J* = 5.2, 2.0 Hz, 1H), 7.98 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.95 (dd, *J* = 7.6, 5.2 Hz, 1H), 4.54 (dd, *J* = 6.4, 4.0 Hz, 1H), 3.81 (s, 3H), 2.00 (dd, *J* = 6.8, 5.6 Hz, 1H), 1.60 (s, 9H), 0.77 (dd, *J* = 5.6, 4.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.3, 154.6, 150.2, 147.4, 134.3, 123.0, 117.8, 82.6, 52.7, 44.9, 28.4, 28.4, 19.1. **IR** (thin film): ν_{max}/cm^{-1} = 1727, 1419, 1368, 1340, 1305, 1274, 1152, 1086, 844, 774. **HRMS (ESI)** calcd for $C_{15}H_{18}N_2O_4Na$ $[M+Na]^+$: 313.1159, found: 313.1156.



3l, 24 h, colorless oil, 30.4 mg, 50% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.20-7.17 (m, 1H), 7.02-6,98 (m, 1H), 3.81 (s, 3H), 2.02 (d, *J* = 5.2 Hz, 1H), 1.78 (s, 3H), 1.59 (s, 9H), 0.99 (d, *J* = 5.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.8, 152.5, 143.3, 129.4, 127.6, 125.8, 122.3, 115.8, 82.1, 54.3, 52.5, 38.1, 28.5, 24.6, 16.6. **IR** (thin film): ν_{max}/cm^{-1} = 1709, 1476, 1379, 1315, 1106, 843, 749, 461. **HRMS (EI)** calcd for $C_{17}H_{21}NO_4$ $[M]^+$: 303.1465, found: 303.1463.

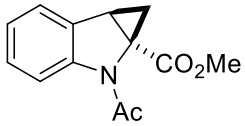


3m, 24 h, white solid, 65.0 mg, 69% yield, m.p. = 140.7-141.8 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (brs, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.21-7.17 (m, 1H), 6.97-6.93 (m, 1H), 4.70 (brs, 1H), 3.90 (t, *J* = 6.4 Hz, 1H), 3.52-3.41 (m, 2H), 2.11-2.06 (m, 2H), 1.91-1.88 (m, 3H), 1.82-1.79 (m, 1H), 1.58 (s, 9H), 1.49-1.45 (m, 1H), 1.38-1.34 (m, 1H), 1.29 (s, 3H), 0.98 (s, 3H), 0.83 (dd, *J* = 6.4, 4.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.8, 152.2, 141.0, 130.3, 127.9, 124.6, 122.1, 115.9, 84.2, 65.6, 52.9, 48.5, 48.1, 44.3, 43.4, 38.1, 35.0, 32.9, 28.5, 26.6, 20.9, 20.0, 18.0. **IR** (thin film): ν_{max}/cm^{-1} = 2955, 2644, 2317, 1739, 1665, 1469, 1374, 1330, 1240, 1193, 1109, 1009, 890, 813. **HRMS (ESI)** calcd for $C_{25}H_{32}N_2O_5NaS$ $[M+Na]^+$: 495.1924, found: 495.1922.

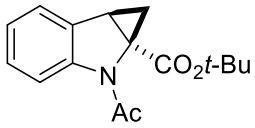


5a, 12 h, yellow oil, 17.3 mg, 30% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (brs, 1H), 7.23-7.21 (m, 1H), 7.19-7.15 (m, 1H), 6.96-6.91 (m, 1H), 3.76 (s, 3H), 2.93 (dd, *J* =

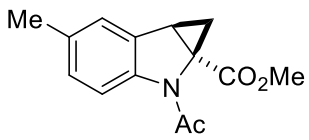
7.2, 5.6 Hz, 1H), 2.11 (dd, *J* = 7.2, 5.6 Hz, 1H), 1.54 (s, 9H), 0.84-0.81 (m, 1H), **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.3, 152.1, 143.0, 130.4, 127.6, 124.0, 122.5, 115.7, 81.8, 52.3, 48.6, 31.6, 28.1, 17.7. **IR** (thin film): ν_{max}/cm^{-1} = 2978, 1710, 1477, 1440, 1349, 1255, 1236, 1197, 1158, 1112, 1079, 998, 966, 915, 841, 748, 730.7, 625, 459. **HRMS (DART)** calcd for $C_{16}H_{20}O_4N$ $[M+H]^+$: 290.1387, found: 290.1387.



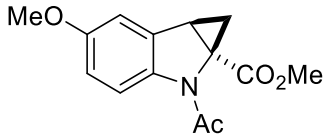
5b, 12 h, colorless oil, 27.8 mg, 60% yield, **^{1}H NMR** (600 MHz, DMSO-d_6) δ 7.86 (brs, 1H), 7.38-7.37 (m, 1H), 7.22-7.20 (m, 1H), 7.05-7.02 (m, 1H), 3.76 (s, 3H), 3.27 (dd, *J* = 9.6, 6.0 Hz, 1H), 2.22 (s, 3H), 2.17 (dd, *J* = 9.6, 5.4 Hz, 1H), 1.26-1.24 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.6, 168.7, 143.5, 130.0, 127.2, 124.0, 122.9, 116.1, 52.3, 49.1, 33.0, 23.5, 19.3. **IR** (thin film): ν_{max}/cm^{-1} = 3099, 3010, 2958, 2921, 2849, 1730, 1677, 1600, 1464, 1434, 1380, 1324, 1305, 1249, 1195, 1160, 1078, 1041, 1026, 1012, 996, 967, 932, 907, 874,5 860, 845, 781, 754, 740, 666, 621, 604, 573, 484. **HRMS (EI)** calcd for $C_{13}H_{13}NO_3$ $[M]^+$: 231.0890, found: 231.0885.



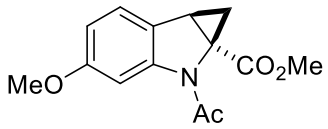
5c, 12 h, white solid, 33.1 mg, 61% yield, m.p. = 131.7-132.6 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (brs, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.23-7.19 (m, 1H), 7.04-7.00 (m, 1H), 3.06-3.02 (m, 1H), 2.32 (s, 3H), 2.21 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.49 (s, 9H), 1.04 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.8, 168.2, 144.4, 130.2, 127.9, 123.9, 123.6, 117.9, 82.9, 50.4, 34.4, 28.1, 24.3, 20.3. **IR** (thin film): ν_{max}/cm^{-1} = 2973, 2931, 1721, 1682, 1603, 1477, 1463, 1430, 1368, 1341, 1319, 1306, 1247, 1197, 1148, 1075, 1036, 1011, 971, 951, 884, 861, 840, 784, 755, 743, 663, 621, 607, 575, 529, 501, 464. **HRMS (EI)** calcd for $C_{16}H_{19}NO_3$ $[M]^+$: 273.1359, found: 273.1351.



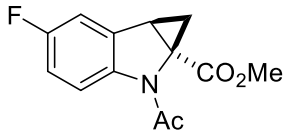
5d, 12 h, yellow oil, 24.8 mg, 51% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (brs, 1H), 7.09 (s, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 3.80 (s, 3H), 3.06 (s, 1H), 2.30-2.26 (m, 7H), 1.12 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 169.8, 142.0, 133.5, 129.8, 128.5, 124.6, 117.7, 52.9, 49.9, 35.0, 24.1, 21.0. **IR** (thin film): ν_{max}/cm^{-1} = 3004, 2953, 2921, 2855, 1723, 1676, 1586, 1479, 1444, 1372, 1329, 1300, 1251, 1227, 1198, 1165, 1071, 1034, 1017, 986, 973, 923, 886, 868, 823, 748, 730, 655, 629, 580, 548, 486, 449. 412. **HRMS (ESI)** calcd for $C_{14}H_{15}NO_3Na$ $[M+Na]^+$: 268.0944, found: 268.0950



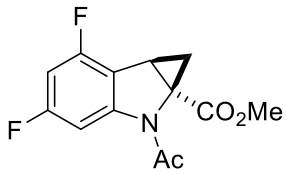
5e, 12 h, yellow oil, 27.4 mg, 52% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01-7.98 (m, 1H), 6.85-6.84 (m, 1H), 6.73 (dd, *J* = 8.8, 2.8 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.07-3.04 (m, 1H), 2.30-2.25 (m, 4H), 1.16 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.4, 169.7, 156.4, 138.0, 131.2, 118.6, 112.4, 110.5, 55.8, 52.9, 50.2, 34.9, 24.0, 21.1. **IR** (thin film): ν_{max}/cm^{-1} = 3003, 295, 2836, 1729, 1668, 1614, 1593, 1480, 1437, 1371, 1332, 1299, 1250, 1231, 1197, 1163 1147, 1068, 1032, 986, 957, 925, 870, 851, 819, 728, 653, 624, 592, 568, 547, 507. 480, 441. **HRMS (ESI)** calcd for $C_{14}H_{15}NO_4Na$ $[M+Na]^+$: 284.0893, found: 284.0887.



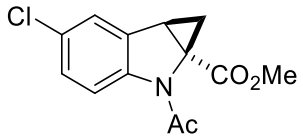
5f, 12 h, yellow solid, 30.8 mg, 59% yield, m.p. = 103.2-104.1 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (brs, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 6.57 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.06-3.03 (m, 1H), 2.28-2.22 (m, 4H), 1.11 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.9, 169.8, 159.9, 145.7, 124.1, 121.9, 109.8, 104.0, 55.7, 52.9, 50.4, 34.5, 24.2, 21.1. **IR** (thin film): ν_{max}/cm^{-1} = 3098, 3008, 2952, 2843, 1733, 1675, 1611, 1592, 1490, 1439, 1371, 1341, 1321, 1293, 1253, 1234, 1194, 1168, 1149, 1122, 1086, 1067, 1051, 1023, 983, 948, 888, 865, 844, 807, 772, 739, 723, 667, 643, 595, 520, 474. **HRMS (ESI)** calcd for $C_{14}H_{15}NO_4Na$ $[M+Na]^+$: 289.0893, found: 284.0895.



5g, 12 h, white solid, 25.9 mg, 52% yield, m.p. = 125.0-127.6 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (brs, 1H), 6.99-6.97 (m, 1H), 6.92-6.87 (m, 1H), 3.81 (s, 3H), 3.07 (dd, *J* = 9.2, 5.6 Hz, 1H), 2.32-2.27 (m, 4H), 1.15 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 169.4, 159.4 (d, *J* = 241.1 Hz), 140.4, 131.6, 114.3 (d, *J* = 22.7 Hz), 111.5 (d, *J* = 25.0 Hz), 53.0, 50.3, 34.3, 24.0, 20.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -119.27 (s). **IR** (thin film): ν_{max}/cm^{-1} = 3099, 3015, 2953, 1727, 1680, 1609, 1470, 1441, 1374, 1320, 1295, 1244, 1226, 1199, 1166, 1135, 1107, 1079, 1040, 1019, 961, 933, 882, 856, 826, 740, 655, 629, 590, 546, 515, 487, 444, 427. **HRMS (EI)** calcd for $C_{13}H_{12}FNO_3$ $[M]^+$: 249.0796, found: 249.0789.

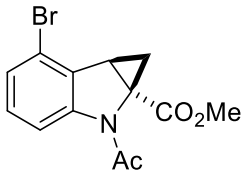


5h, 12 h, yellow solid, 32.5 mg, 61% yield, m.p. = 101.2-102.4 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (brs, 1H), 6.53-6.48 (m, 1H), 3.82 (s, 3H), 2.32 (dd, *J* = 9.2, 5.2 Hz, 1H), 2.28 (s, 3H), 1.16-1.13 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 169.0, 163.1 (dd, *J* = 244.1, 12.0 Hz), 158.2 (dd, *J* = 245.9, 14.7 Hz), 146.8, 112.5, 102.3 (d, *J* = 30.0 Hz), 99.0 (dd, *J* = 27.1, 23.9 Hz), 53.1, 50.4, 30.5, 24.2, 19.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -108.7--108.9 (m), -117.7 (s). **IR** (thin film): ν_{max}/cm^{-1} = 3106, 3013, 2956, 2922, 2852, 1738, 1689, 1631, 1603, 1488, 1439, 1366, 1306, 1256, 1204, 1183, 1164, 1112, 1086, 1043, 993, 975 919, 893, 874, 857, 817, 802, 770, 742, 701, 622, 601, 573, 536, 501, 481, 412. **HRMS (EI)** calcd for $C_{13}H_{11}F_2NO_3$ $[M]^+$: 267.0702, found: 267.0702.

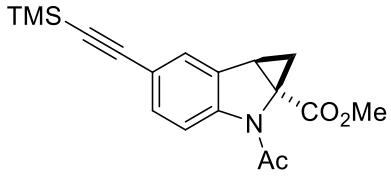


5i, 12 h, yellow solid, 27.2 mg, 51% yield, m.p. = 101.6-102.8 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (brs, 1H), 7.24 (d, *J* = 2.4 Hz, 1H), 7.17 (dd, *J* = 8.4, 2.0 Hz, 1H), 3.81 (s, 3H), 3.07 (dd, *J* = 9.2, 5.2 Hz, 1H), 2.32-2.28 (m, 4H), 1.13 (s, 1H). **^{13}C NMR** (100

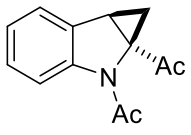
MHz, $CDCl_3$) δ 170.6, 169.3, 142.9, 131.6, 128.8, 128.0, 124.3, 118.8, 53.1, 50.1, 34.3, 24.1, 20.4. **IR** (thin film): ν_{max}/cm^{-1} = 2955, 2644, 2317, 1739, 1665, 1469, 1374, 1330, 1240, 1193, 1109, 1009, 890, 813. **HRMS (EI)** calcd for $C_{13}H_{12}ClNO_3$ $[M]^+$: 265.0500, found: 265.0492.



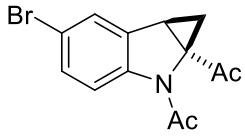
5j, 12 h, yellow solid, 38.6 mg, 60% yield, m.p. = 71.9-72.8 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (brs, 1H), 7.18-7.16 (m, 1H), 7.10-7.05 (m, 1H), 3.81 (s, 3H), 3.19 (dd, *J* = 9.6, 5.6 Hz, 1H), 2.34 (dd, *J* = 9.2, 5.2 Hz, 1H), 2.28 (s, 3H), 1.15 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.8, 169.1, 144.9, 130.6, 129.7, 126.7, 118.2, 116.6, 53.1, 49.3, 35.5, 24.2, 19.8. **IR** (thin film): ν_{max}/cm^{-1} = 3004, 2956, 1721, 1677, 1593, 1575, 1467, 1438, 1368, 1320, 1294, 1252, 1201, 1166, 1141, 1075, 1056, 1039, 1020, 985, 967, 944, 904, 875, 853, 777, 746, 696, 640, 607, 573, 537, 513, 485, 446, 412. **HRMS (EI)** calcd for $C_{13}H_{12}{}^{79}BrNO_3$ $[M]^+$: 308.9995, found: 308.9991.



5k, 12 h, yellow solid, 33.9 mg, 52% yield, m.p. = 127.9-129.0 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (brs, 1H), 7.38-7.37 (m, 1H), 7.33 (dd, *J* = 8.4, 2.0 Hz, 1H), 3.81 (s, 3H), 3.08-3.04 (m, 1H), 2.30-2.27 (m, 4H), 1.09 (s, 1H), 0.23 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 169.4, 144.2, 132.4, 130.0, 127.6, 118.5, 117.5, 104.9, 93.8, 53.0, 49.9, 34.4, 24.3, 20.4, 0.1. **IR** (thin film): ν_{max}/cm^{-1} = 2959, 2153, 1737, 1679, 1604, 1477, 1439, 1370, 1327, 1303 1249, 1228 1196, 1166, 1083, 1063, 1048, 1017, 990, 961, 930, 907, 884, 841, 826, 760, 743, 699, 667, 648, 624, 592, 577, 528, 506, 457. **HRMS (ESI)** calcd for $C_{18}H_{21}NO_3NaSi$ $[M+Na]^+$: 350.1183, found: 350.1178.

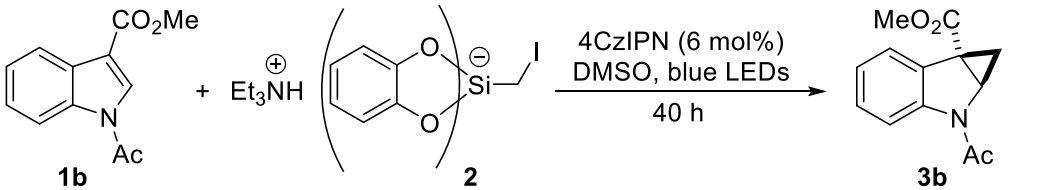


5l, 12 h, yellow oil, 34.3 mg, 80% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (brs, 1H), 7.29-7.21 (m, 2H), 7.06-7.02 (m, 1H), 2.98 (s, 1H), 2.41 (dd, *J* = 9.2, 5.2 Hz, 1H), 2.27-2.24 (m, 6H), 1.14 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.7, 170.4, 144.2, 130.1, 128.1, 123.9, 118.1, 58.2, 36.5, 26.1, 24.5, 20.4. **IR** (thin film): ν_{max}/cm^{-1} = 3104, 3015, 2920, 2851, 1687, 1669, 1599, 1476, 1463, 1436, 1373, 1339, 1321, 1310, 125, 1215, 1184, 1143, 1110, 1073, 1027, 990, 962, 931, 919, 821, 761, 681, 646, 608, 583, 556, 515, 487, 448. **HRMS (EI)** calcd for $C_{13}H_{13}NO_2$ $[M]^+$: 215.0941, found: 215.0935.



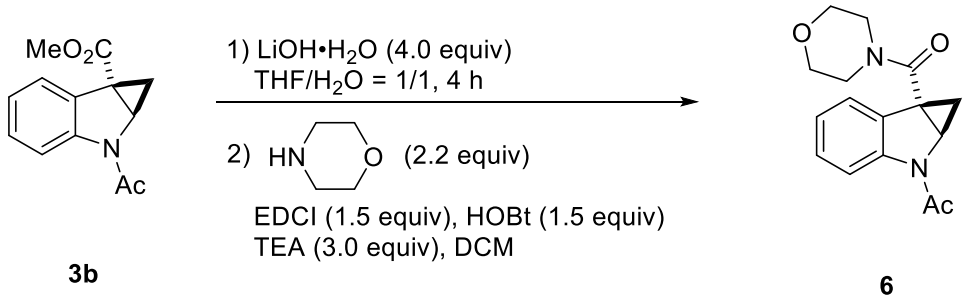
5m, 12 h, yellow oil, 42.9 mg, 73% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (brs, 1H), 7.389-7.386 (m, 1H), 7.33 (dd, *J* = 6.0, 1.2 Hz, 1H), 2.91 (dd, *J* = 6.4, 3.6 Hz, 1H), 2.40 (dd, *J* = 6.4, 3.6 Hz, 1H), 2.27-2.25 (m, 6H), 1.08-1.06 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6, 170.1, 143.2, 132.9, 131.0, 127.4, 118.9, 116.6, 58.4, 34.8, 25.8, 24.3, 19.7. **IR** (thin film): ν_{max}/cm^{-1} = 1690, 1663, 1595, 1467, 1418, 1371, 1334, 1296, 1244, 1196, 1179, 1141, 1058, 1030, 983, 964, 932, 878, 828, 738, 698, 659, 614, 568, 514, 492, 456. **HRMS (EI)** calcd for $C_{13}H_{12}{}^{79}BrNO_3$ $[M]^+$: 293.0046, found: 293.0042.

5. Scale-up Experiment and Transformations of 3b, 4b and 3m



To a flame-dried sealed tube were added indole derivative **1b** (1.09 g, 5 mmol, 1.0 equiv), **2** (4.87 g, 10 mmol, 2.0 equiv), 4CzIPN (236.7 mg, 0.3 mmol, 6 mol%) and DMSO (50 mL). The reaction mixture was degassed via freeze-pump-thaw for 3 cycles. After thoroughly degassed, the tube was sealed and positioned approximately 3 cm from two 3 W blue LEDs. After the reaction was complete (monitored by TLC), the reaction mixture was transferred to a separatory funnel and diluted with EtOAc (~300 mL) and 2 M aq NaOH (~100 mL). The layers were separated, and the organic layer

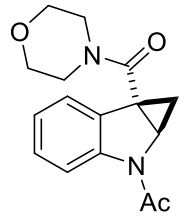
was washed with additional 2 M aq NaOH (100 mL×2). The organic layer was then washed with deionized H_2O (~100 mL), and followed by brine (~100 mL). The organic layer was dried over Na_2SO_4. After removal of Na_2SO_4 by filtration, the organic phase was concentrated *in vacuo* by rotary evaporation. Further purification was accomplished by column chromatography on silica gel (PE/DCM = 1/1 to pure DCM) to afford **3b** in 65% yield (0.75g).



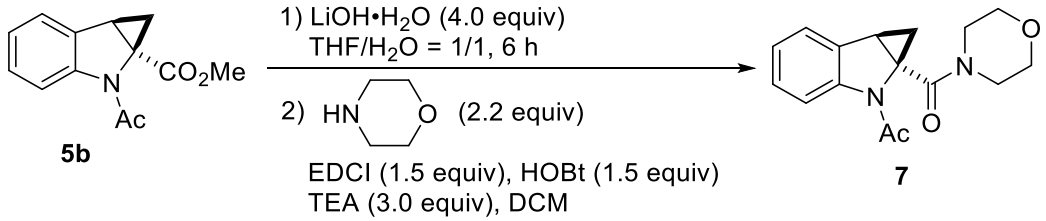
3b **6**

A solution of compound **3b** (85.6 mg, 0.37 mmol, 1.0 equiv) in THF (2 mL) was slowly added to a solution of $LiOH·H_2O$ (62.2 mg, 1.48 mmol, 4.0 equiv) in water (2 mL). The resulting mixture was vigorously stirred at room temperature for 4 h. THF was then evaporated under reduced pressure. The resulting aqueous solution was acidified with 2M HCl to pH = 2, and then extracted with DCM (25 mL×3). The combined organic layers were dried over anhydrous Na_2SO_4. After removal of Na_2SO_4 by fitration, the solvent was concentrated *in vacuo* by rotary evaporation. The product was used directly without further purification.

To a solution of the above obtained carboxylic acid (0.37 mmol) in DCM (4 mL) were added HOBt (75.0 mg, 0.56 mmol, 1.5 equiv), EDCI (106.4 mg, 0.56 mmol, 1.5 equiv) at room temperature under argon. After stirring for 5 minutes, morpholine (71 μL, 0.82 mmol, 2.2 equiv) and triethylamine (128 μL, 0.93 mmol, 2.5 equiv) were added slowly. The reaction mixture was stirred at room temperature overnight. The mixture was quenched with H_2O (10 mL) and extracted with DCM (25 mL×3). The combined organic layers were dried over anhydrous Na_2SO_4. After removal of Na_2SO_4 by filtration, the solvent was concentrated *in vacuo* to give a dark residue, which was purified by column chromatography on silica gel (DCM/MeOH = 40/1) to afford the desired product.



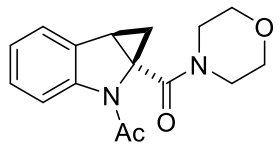
6, yellow solid, 88.4 mg, 83% yield over two steps, m.p. = 131.7-132.4 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 3.2 Hz, 1H), 7.29-7.23 (m, 2H), 7.08-7.05 (m, 1H), 4.22-4.19 (m, 1H), 3.86-3.26 (m, 8H), 2.41 (s, 3H), 1.76-1.73 (m, 1H), 0.77 (dd, *J* = 6.0, 3.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) 168.9, 166.5, 141.0, 131.7, 128.5, 123.9, 123.1, 118.3, 66.7, 44.3, 34.1, 24.5, 16.3. **IR** (thin film): ν_{max}/cm^{-1} = 3089, 2969, 2916, 2860, 1708, 1668, 1639, 1597, 1473, 1428, 1402, 1338, 1298, 1273, 1249, 1198, 1149, 1113, 1088, 1068, 1045, 1019, 987, 955, 934, 914, 877, 854, 809, 766, 742, 707, 619, 601, 554, 525, 462, 441. **HRMS (ESI)** calcd for $C_{16}H_{18}N_2O_3Na$ $[M+Na]^+$: 309.1210, found: 309.1209.



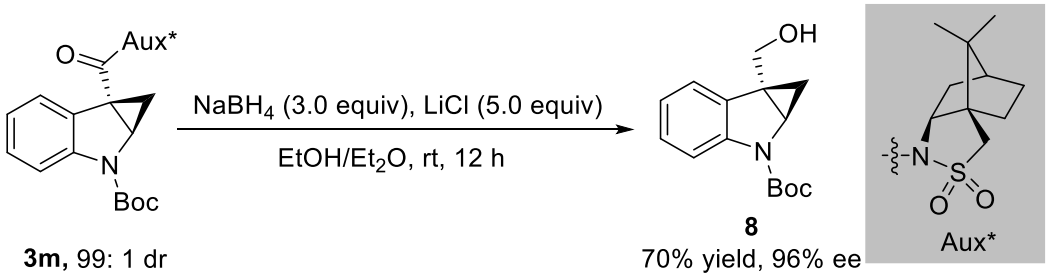
A solution of compound **5b** (128.3 mg, 0.55 mmol, 1.0 equiv) in THF (3 mL) was slowly added to a solution of $LiOH·H_2O$ (92.4 mg, 1.48 mmol, 4.0 equiv) in water (3 mL). The resulting mixture was vigorously stirred at room temperature for 6 h. THF was then evaporated under reduced pressure. The resulting aqueous solution was acidified with 2M HCl to pH = 2, and then extracted with DCM (25 mL×3). The combined organic layers were dried over anhydrous Na_2SO_4. After removal of Na_2SO_4 by fitration, the solvent was concentrated *in vacuo* by rotary evaporation. The product was used directly without further purification.

To a solution of the above obtained carboxylic acid (0.55 mmol) in DCM (5 mL) were added HOBt (111.5 mg, 0.83 mmol, 1.5 equiv), EDCI (158.2 mg, 0.56 mmol, 1.5 equiv) at room temperature under argon. After stirring for 5 minutes, morpholine (105.4 μL, 1.21 mmol, 2.2 equiv) and triethylamine (191 μL, 1.38 mmol, 2.5 equiv) were added slowly. The reaction mixture was stirred at room temperature overnight. The mixture was quenched with H_2O (10 mL) and extracted with DCM (25 mL×3). The

combined organic layers were dried over anhydrous Na_2SO_4. After removal of Na_2SO_4 by filtration, the solvent was concentrated *in vacuo* to give a dark residue, which was purified by column chromatography on silica gel (DCM/MeOH = 40/1) to afford the desired product.



7, yellow solid, 96.6 mg, 61% yield over two steps, m.p. = 131.3-133.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (brs, 1H), 7.32-7.30 (m, 1H), 7.23-7.19 (m, 1H), 7.07-7.03 (m, 1H), 3.65-3.10 (m, 8H), 2.88 (dd, *J* = 9.2, 4.8 Hz, 1H), 2.29 (s, 3H), 2.07 (dd, *J* = 9.2, 5.6 Hz, 1H), 0.80-0.78 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) 170.3, 166.7, 142.6, 130.8, 128.1, 124.4, 118.5, 66.7, 50.5, 46.5, 43.6, 30.2, 24.3, 16.6. **IR** (thin film): ν_{max}/cm^{-1} = 3005, 2970, 2920, 2860, 2110, 1931, 1678, 1640, 1459, 1424, 1376, 1319, 1271, 1249, 1196, 1113, 1064, 1026, 970, 946, 869, 838, 786, 765, 720, 683, 663, 644, 613, 576, 483, 441. **HRMS (ESI)** calcd for $C_{16}H_{18}N_2O_3Na$ $[M+Na]^+$: 309.1210, found: 309.1212.

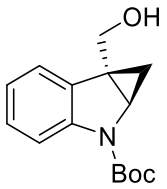


3m, 99: 1 dr

8
70% yield, 96% ee

To a solution of compound **3m** (94.5 mg, 0.2 mmol, 1.0 equiv) in EtOH/Et_2O (1 mL, 3/1) were added LiCl (42 mg, 1.0 mmol, 5.0 equiv) and $NaBH_4$ (22.7 mg, 0.6 mmol, 3.0 equiv). The resulting mixture was vigorously stirred at room temperature for 24 h. The mixture was quenched with saturated NH_4Cl aqueous solution and extracted with DCM (25 mL×3). The combined organic layers were dried over anhydrous Na_2SO_4. After removal of Na_2SO_4 by filtration, the solvent was concentrated in vacuo to give a dark residue, which was purified by column chromatography on silica gel (PE/EtOAc = 4/1) to afford the chiral alcohol in 70% yield with 96% ee.

The racemic product was prepared by using **3a** instead of **3m.**



8, colorless oil, 36.5 mg, 70% yield, 96% ee. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (brs, 1H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.20-7.16 (m, 1H), 7.01-6.98 (m, 1H), 4.16, (d, *J* = 12.0 Hz, 1H), 4.14 (brs, 1H), 3.87 (d, *J* = 11.6 Hz, 1H), 1.69-1.59 (m, 10H), 1.19-1.16 (m, 1H), 0.44 (dd, *J* = 5.6, 2.8 Hz, 1H). **^{13}C NMR** (100 MHz, d_6-DMSO, 110 ^{o}C) δ 151.2, 140.7, 134.1, 125.8, 122.6, 121.1, 114.3, 80.3, 60.6, 41.3, 30.5, 27.6, 13.4. **IR** (thin film): ν_{max}/cm^{-1} = 3409, 3051, 2976, 2928, 2872, 1700, 1677, 1605, 1480, 1433, 1388, 1344, 1327, 1251, 1152, 1099, 1059, 1022, 932, 886, 846, 815, 749, 719, 685, 636, 586, 559, 465. **HRMS (EI)** calcd for $C_{15}H_{19}NO_3$ $[M]^+$: 261.1359, found: 261.1356. $[\alpha]_D^{27}$ = -45.5 (c = 1, $CHCl_3$). HPLC (AD–H, n-hexane/2-propanol = 98/02, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 28.21 min (minor), 30.99 min (major).

6. Stern-Volmer Luminescence Quenching Studies

Stern-Volmer quenching experiments were conducted on a Hitachi F4600 Fluorescence Spectrophotometer. Stern-Volmer luminescence quenching experiments were run with freshly prepared solutions of 1.0×10^{-3} M $[Ir(dFCF_3bpy)(dtbbpy)]PF_6$ and the appropriate amount of quencher in DMSO at room temperature. After degassing with argon for 5 min, the emission spectra of the samples were collected. The solutions were irradiated at 340 nm and luminescence was measured at 550 nm. The data summarized in the tables are the phosphorescence intensity measured three times for each sample. The data illustrated in the graphs are the average of three experiments.

Table S3: Luminescence quenching data for $[Ir(dFCF_3bpy)(dtbbpy)]PF_6$ and **1a** in DMSO.

Vial	1	2	3	Average	I_0/I	[1a]
0	1421	1322	1349	1364	0	0
1	1336	1312	1301	1316	1.036	0.00005
2	1344	1280	1290	1305	0.957	0.0001

3	1305	1267	1206	1259	1.037	0.0002
4	1423	1448	1377	1416	1.085	0.0004
5	1503	1496	1423	1474	0.961	0.0006
6	1265	1221	1096	1194	0.843	0.0008
7	1574	1547	1521	1547	0.772	0.001

Table S4: Luminescence quenching data for [Ir(dFCF$_3$bpy)(dtbbpy)]PF$_6$ and **4b** in DMSO.

Vial	**1**	**2**	**3**	**Average**	**I_0/I**	**[4b]**
0	2368	2119	2068	2185	1	0
1	1998	1990	1970	1986	1.10	0.00005
2	2177	2177	2174	2176	1.00	0.0001
3	1779	1888	1902	1856	1.18	0.0002
4	1790	1786	1778	1784	1.22	0.0004
5	1597	1575	1571	1581	1.38	0.0006
6	1375	1378	1386	1379	1.58	0.0008
7	1148	1125	1099	1124	1.68	0.001

Table S5: Luminescence quenching data for [Ir(dFCF$_3$bpy)(dtbbpy)]PF$_6$ and **2** in DMSO.

Vial	**1**	**2**	**3**	**Average**	**I_0/I**	**[2]**
0	1448	1433	1422	1434	1	0
1	1284	1267	1258	1269	1.13	0.00005
3	919	910	899	909.	1.29	0.0002
4	637	632	629	633	1.58	0.0004
5	448	442	438	443	2.26	0.0006
6	146	145	144	145	3.24	0.0008
7	364	359	358	360	3.97	0.001

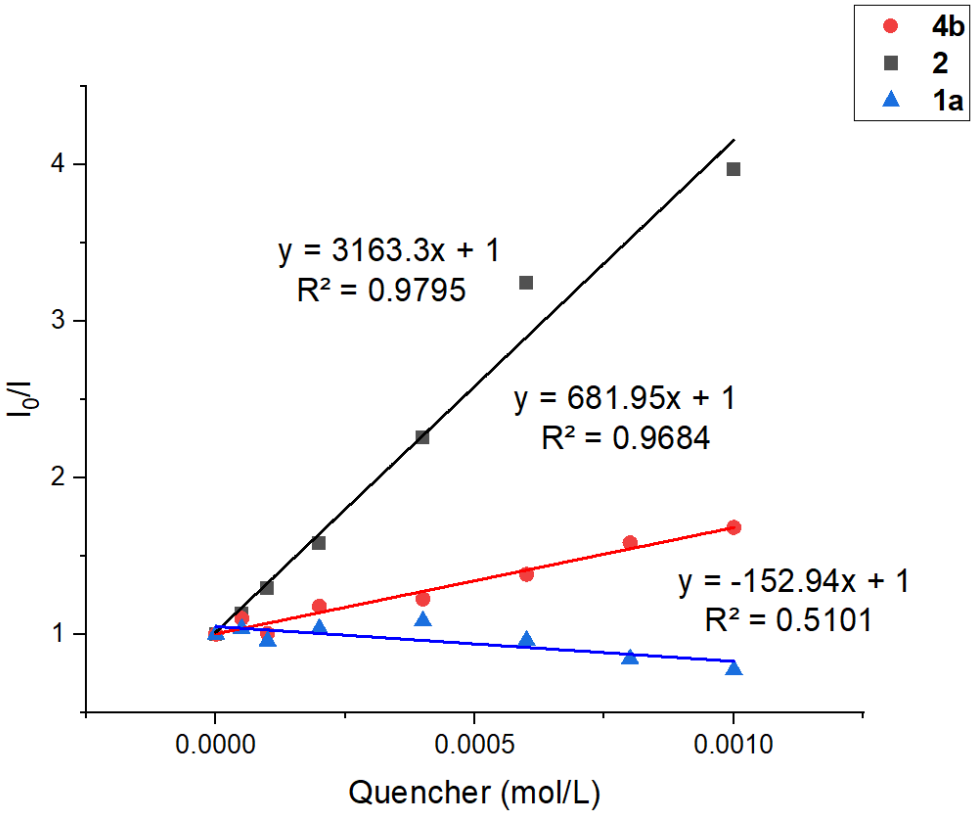


Figure S1: Luminescence quenching of $[Ir(dFCF_3bpy)(dtbbpy)]PF_6$ with varying concentrations of **1a** (blue), **4b** (red) and **2** (black) in DMSO.

7. X-Ray Crystal Data of 5m

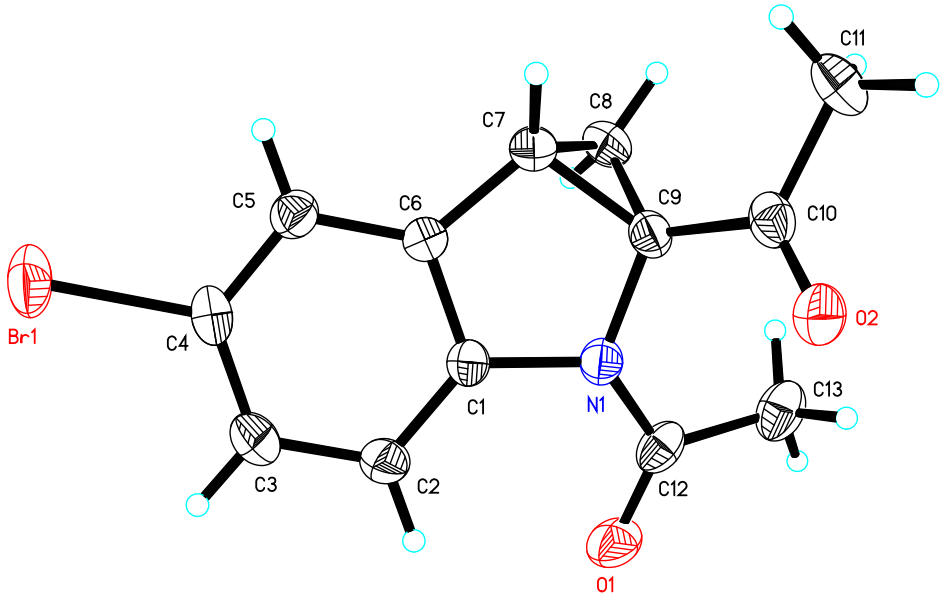


Figure S2. X-ray structure of **5m.** (The crystal was obtained by slow evaporation of the solution of DCM at 0 ^{o}C) (CCDC 2184389):

Table S6. Crystal data and structure refinement for mo_d8v191167_0m.

Identification code	mo_d8v191167_0m	
Empirical formula	C13 H12 Br N O2	
Formula weight	294.15	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 9.3599(9) Å	α= 90°.
	b = 11.1041(9) Å	β= 90°.
	c = 11.8507(11) Å	γ = 90°.
Volume	1231.68(19) $Å^3$	
Z	4	
Density (calculated)	1.586 Mg/m^3	
Absorption coefficient	3.326 mm^{-1}	
F(000)	592	
Crystal size	0.180 x 0.150 x 0.110 mm^3	
Theta range for data collection	2.514 to 25.470°.	
Index ranges	-9<=h<=11, -13<=k<=13, -14<=l<=12	
Reflections collected	5815	
Independent reflections	2290 [R(int) = 0.0410]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.4528	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2290 / 0 / 156	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R1 = 0.0451, wR2 = 0.1023	
R indices (all data)	R1 = 0.0727, wR2 = 0.1135	
Absolute structure parameter	0.467(9)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.357 and -0.266 $e.Å^{-3}$	

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for mo_d8v191167_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	4621(1)	8833(1)	4346(1)	75(1)
O(1)	3928(7)	3200(5)	6911(4)	63(2)
O(2)	4631(7)	1597(4)	3760(4)	60(1)
N(1)	3620(6)	3504(5)	5047(4)	41(1)
C(1)	3979(8)	4753(6)	5030(6)	40(2)
C(2)	4651(9)	5441(6)	5829(6)	50(2)
C(3)	4864(8)	6661(6)	5625(7)	54(2)
C(4)	4373(8)	7158(6)	4624(6)	50(2)
C(5)	3688(8)	6489(6)	3823(6)	45(2)
C(6)	3490(8)	5268(6)	4030(5)	39(2)
C(7)	2811(8)	4353(6)	3302(6)	43(2)
C(8)	1530(8)	3714(7)	3748(6)	49(2)
C(9)	2977(8)	3177(6)	3969(6)	42(2)
C(10)	3572(9)	2084(6)	3405(6)	47(2)
C(11)	2796(10)	1623(8)	2374(6)	64(2)
C(12)	3454(9)	2851(6)	6021(6)	48(2)
C(13)	2624(9)	1697(7)	5922(7)	62(2)

Table S8. Bond lengths [Å] and angles [°] for mo_d8v191167_0m.

Br(1)-C(4)	1.902(6)
O(1)-C(12)	1.208(9)
O(2)-C(10)	1.204(9)
N(1)-C(12)	1.372(8)
N(1)-C(1)	1.426(9)
N(1)-C(9)	1.458(8)
C(1)-C(2)	1.370(10)
C(1)-C(6)	1.394(10)
C(2)-C(3)	1.390(10)
C(2)-H(2)	0.9300
C(3)-C(4)	1.388(10)
C(3)-H(3)	0.9300
C(4)-C(5)	1.365(9)
C(5)-C(6)	1.390(9)
C(5)-H(5)	0.9300
C(6)-C(7)	1.476(9)
C(7)-C(8)	1.490(10)
C(7)-C(9)	1.535(9)
C(7)-H(7)	0.9800
C(8)-C(9)	1.503(10)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-C(10)	1.494(10)
C(10)-C(11)	1.511(10)
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(12)-C(13)	1.503(11)
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(12)-N(1)-C(1)	123.5(6)
C(12)-N(1)-C(9)	123.9(6)
C(1)-N(1)-C(9)	109.1(5)

C(2)-C(1)-C(6)	120.6(6)
C(2)-C(1)-N(1)	129.9(7)
C(6)-C(1)-N(1)	109.5(6)
C(1)-C(2)-C(3)	119.3(7)
C(1)-C(2)-H(2)	120.3
C(3)-C(2)-H(2)	120.3
C(4)-C(3)-C(2)	119.3(7)
C(4)-C(3)-H(3)	120.4
C(2)-C(3)-H(3)	120.4
C(5)-C(4)-C(3)	122.2(6)
C(5)-C(4)-Br(1)	118.0(6)
C(3)-C(4)-Br(1)	119.8(5)
C(4)-C(5)-C(6)	118.1(7)
C(4)-C(5)-H(5)	120.9
C(6)-C(5)-H(5)	120.9
C(5)-C(6)-C(1)	120.4(6)
C(5)-C(6)-C(7)	128.7(6)
C(1)-C(6)-C(7)	110.8(6)
C(6)-C(7)-C(8)	117.8(6)
C(6)-C(7)-C(9)	104.0(6)
C(8)-C(7)-C(9)	59.6(5)
C(6)-C(7)-H(7)	119.6
C(8)-C(7)-H(7)	119.6
C(9)-C(7)-H(7)	119.6
C(7)-C(8)-C(9)	61.7(4)
C(7)-C(8)-H(8A)	117.6
C(9)-C(8)-H(8A)	117.6
C(7)-C(8)-H(8B)	117.6
C(9)-C(8)-H(8B)	117.6
H(8A)-C(8)-H(8B)	114.7
N(1)-C(9)-C(10)	116.2(7)
N(1)-C(9)-C(8)	115.2(6)
C(10)-C(9)-C(8)	125.5(7)
N(1)-C(9)-C(7)	106.3(5)
C(10)-C(9)-C(7)	119.9(6)
C(8)-C(9)-C(7)	58.7(5)
O(2)-C(10)-C(9)	121.0(7)

O(2)-C(10)-C(11)	121.8(7)
C(9)-C(10)-C(11)	117.2(7)
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
O(1)-C(12)-N(1)	121.5(7)
O(1)-C(12)-C(13)	122.1(7)
N(1)-C(12)-C(13)	116.3(7)
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S9. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for mo_d8v191167_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	100(1)	37(1)	87(1)	-6(1)	8(1)	-12(1)
O(1)	87(4)	63(3)	38(3)	6(3)	-3(3)	12(3)
O(2)	67(4)	48(3)	63(3)	-6(2)	-1(3)	9(3)
N(1)	49(4)	36(3)	39(3)	0(2)	1(3)	0(3)
C(1)	42(4)	35(3)	42(4)	-2(3)	0(3)	2(3)
C(2)	61(5)	49(4)	41(4)	-4(3)	-8(5)	3(4)
C(3)	59(5)	51(4)	53(4)	-13(4)	-4(4)	-5(4)
C(4)	54(5)	35(3)	61(5)	-6(3)	7(4)	-8(3)
C(5)	50(5)	44(4)	42(4)	4(3)	1(3)	0(4)
C(6)	40(4)	39(3)	38(4)	1(3)	-2(3)	0(3)
C(7)	49(5)	43(4)	37(4)	1(3)	-2(4)	-1(3)
C(8)	45(4)	52(4)	50(4)	-6(4)	-7(4)	-8(4)
C(9)	45(5)	37(4)	44(4)	-4(3)	-2(3)	-5(3)
C(10)	56(5)	39(4)	46(4)	-1(3)	7(4)	-11(4)
C(11)	72(6)	64(5)	57(5)	-26(4)	1(4)	-6(5)
C(12)	51(5)	46(4)	48(5)	8(3)	12(4)	15(4)
C(13)	71(6)	51(4)	64(5)	14(4)	17(5)	4(4)

Table S10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for mo_d8v191167_0m.

	x	y	z	U(eq)
H(2)	4961	5096	6501	60
H(3)	5331	7138	6154	65
H(5)	3364	6839	3158	55
H(7)	2996	4359	2488	52
H(8A)	918	3308	3208	59
H(8B)	1032	4076	4380	59
H(11A)	2821	2224	1792	97
H(11B)	1821	1450	2566	97
H(11C)	3251	902	2108	97
H(13A)	3215	1090	5581	93
H(13B)	1794	1828	5462	93
H(13C)	2334	1435	6659	93

Table S11. Torsion angles [°] for mo_d8v191167_0m.

C(12)-N(1)-C(1)-C(2)	23.2(12)
C(9)-N(1)-C(1)-C(2)	-177.0(8)
C(12)-N(1)-C(1)-C(6)	-154.8(7)
C(9)-N(1)-C(1)-C(6)	5.0(8)
C(6)-C(1)-C(2)-C(3)	-1.1(12)
N(1)-C(1)-C(2)-C(3)	-178.9(7)
C(1)-C(2)-C(3)-C(4)	0.9(12)
C(2)-C(3)-C(4)-C(5)	-0.3(12)
C(2)-C(3)-C(4)-Br(1)	178.7(6)
C(3)-C(4)-C(5)-C(6)	-0.2(12)
Br(1)-C(4)-C(5)-C(6)	-179.2(6)
C(4)-C(5)-C(6)-C(1)	0.1(11)
C(4)-C(5)-C(6)-C(7)	-179.0(7)
C(2)-C(1)-C(6)-C(5)	0.6(12)
N(1)-C(1)-C(6)-C(5)	178.8(7)
C(2)-C(1)-C(6)-C(7)	179.8(7)
N(1)-C(1)-C(6)-C(7)	-2.0(8)
C(5)-C(6)-C(7)-C(8)	-119.8(8)
C(1)-C(6)-C(7)-C(8)	61.1(9)
C(5)-C(6)-C(7)-C(9)	177.6(8)
C(1)-C(6)-C(7)-C(9)	-1.6(8)
C(6)-C(7)-C(8)-C(9)	-90.3(7)
C(12)-N(1)-C(9)-C(10)	-69.8(9)
C(1)-N(1)-C(9)-C(10)	130.5(7)
C(12)-N(1)-C(9)-C(8)	91.3(8)
C(1)-N(1)-C(9)-C(8)	-68.4(7)
C(12)-N(1)-C(9)-C(7)	153.9(6)
C(1)-N(1)-C(9)-C(7)	-5.8(8)
C(7)-C(8)-C(9)-N(1)	94.4(6)
C(7)-C(8)-C(9)-C(10)	-106.5(7)
C(6)-C(7)-C(9)-N(1)	4.4(8)
C(8)-C(7)-C(9)-N(1)	-109.9(7)
C(6)-C(7)-C(9)-C(10)	-129.9(7)
C(8)-C(7)-C(9)-C(10)	115.7(8)
C(6)-C(7)-C(9)-C(8)	114.3(7)

N(1)-C(9)-C(10)-O(2)	-8.6(10)
C(8)-C(9)-C(10)-O(2)	-167.5(7)
C(7)-C(9)-C(10)-O(2)	121.5(8)
N(1)-C(9)-C(10)-C(11)	171.7(6)
C(8)-C(9)-C(10)-C(11)	12.8(10)
C(7)-C(9)-C(10)-C(11)	-58.3(10)
C(1)-N(1)-C(12)-O(1)	-18.2(11)
C(9)-N(1)-C(12)-O(1)	-175.0(7)
C(1)-N(1)-C(12)-C(13)	160.5(7)
C(9)-N(1)-C(12)-C(13)	3.7(10)

Symmetry transformations used to generate equivalent atoms:

Table S12. Hydrogen bonds for mo_d8v191167_0m [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(2)-H(2)...O(1)	0.93	2.37	2.880(9)	114.5
C(5)-H(5)...O(1)#1	0.93	2.61	3.355(9)	138.0
C(8)-H(8A)...O(1)#2	0.97	2.51	3.325(9)	141.8
C(8)-H(8B)...Br(1)#3	0.97	3.07	3.964(8)	154.3
C(13)-H(13A)...O(2)	0.96	2.59	3.178(10)	119.5

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,-y+1,z-1/2 #2 x-1/2,-y+1/2,-z+1 #3 x-1/2,-y+3/2,-z+1

8. Reference

1. J. P. Phelan, S. B. Lang, J. S. Compton, C. B. Kelly, R. Dykstra, O. Gutierrez and G. A. Molander, Redox-Neutral Photocatalytic Cyclopropanation via Radical/Polar Crossover, *J. Am. Chem. Soc.* 2018, **140**, 8037-8047.

9. Copies of NMR Spectra

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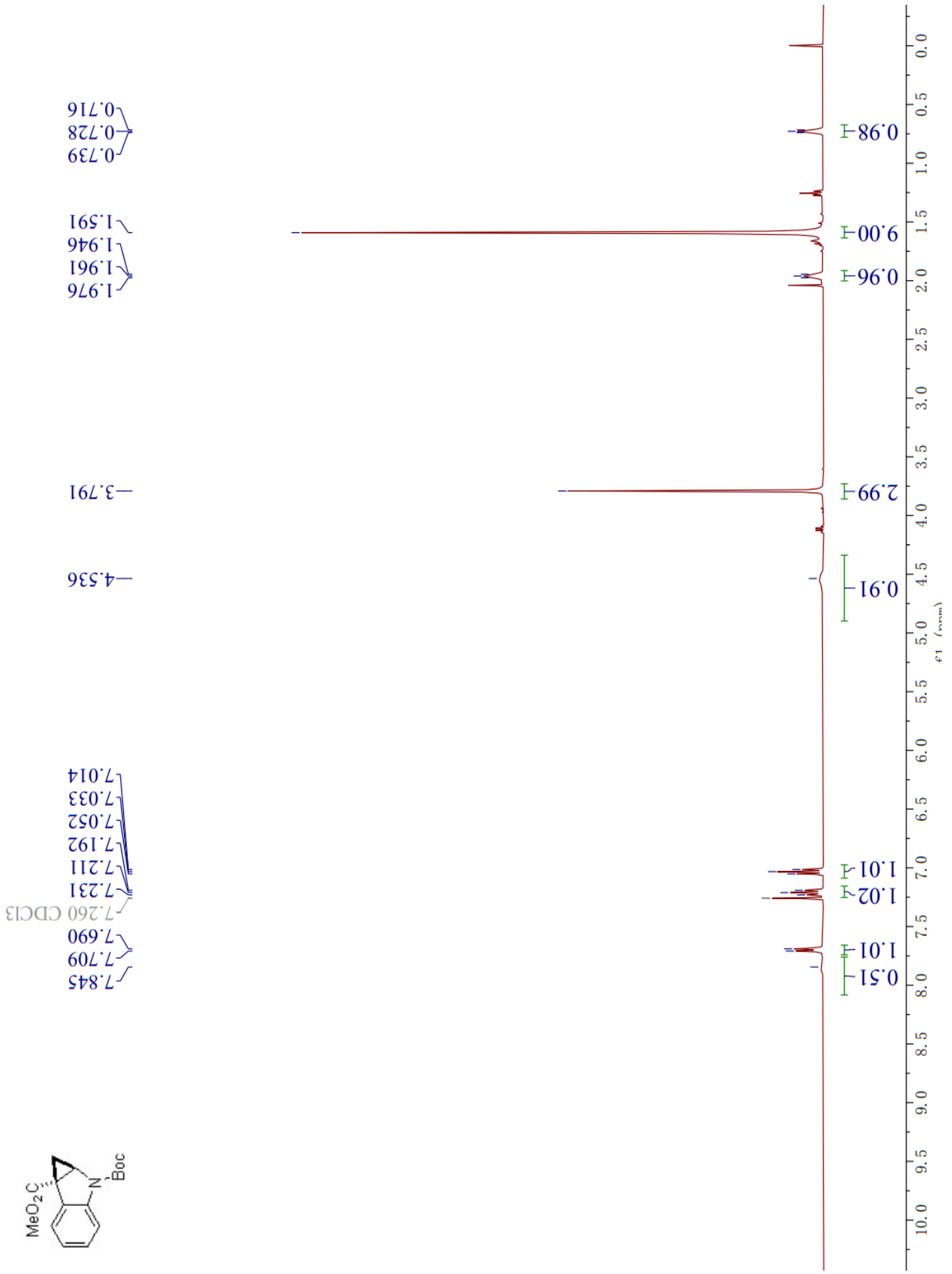

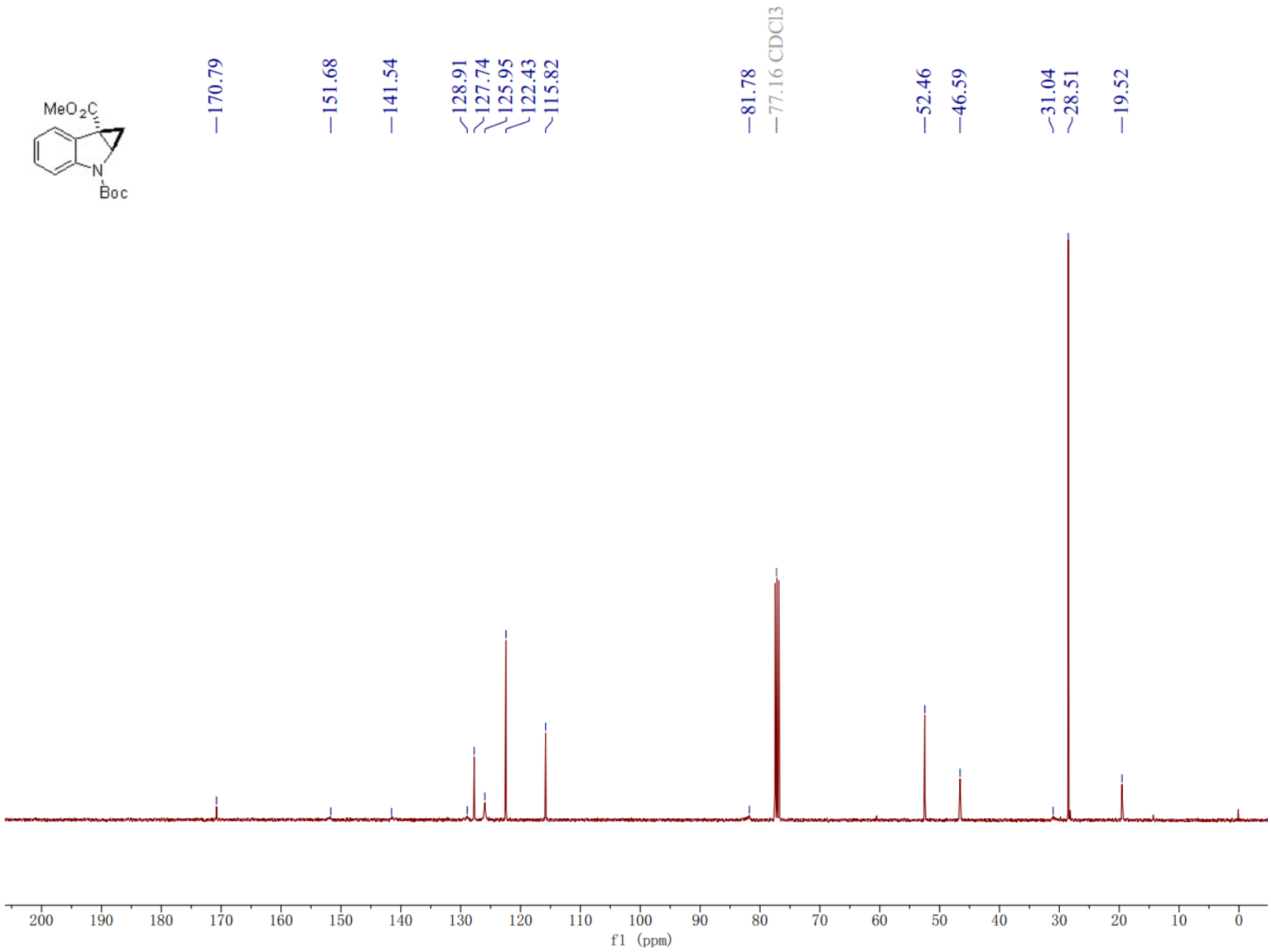
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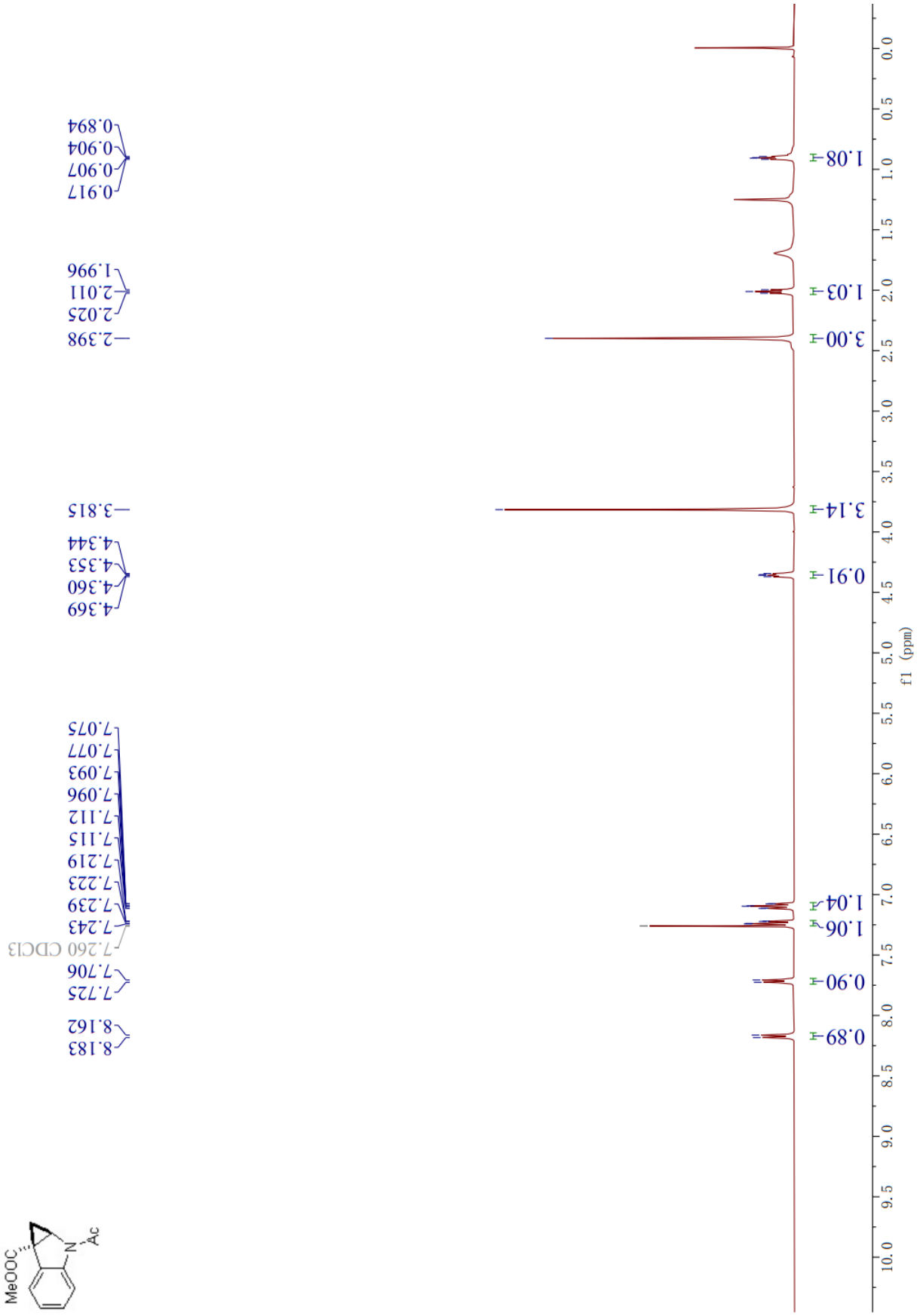
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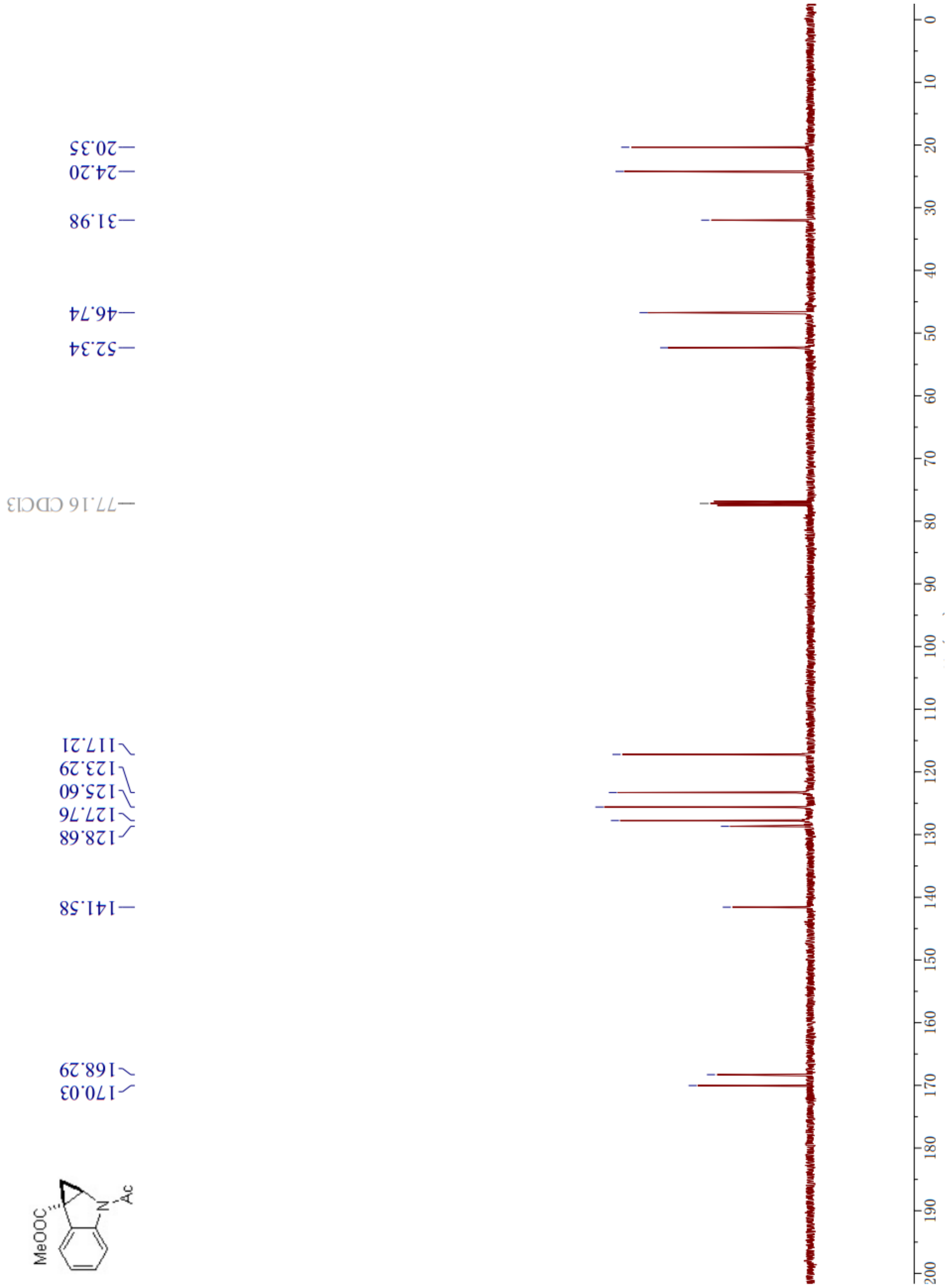

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200

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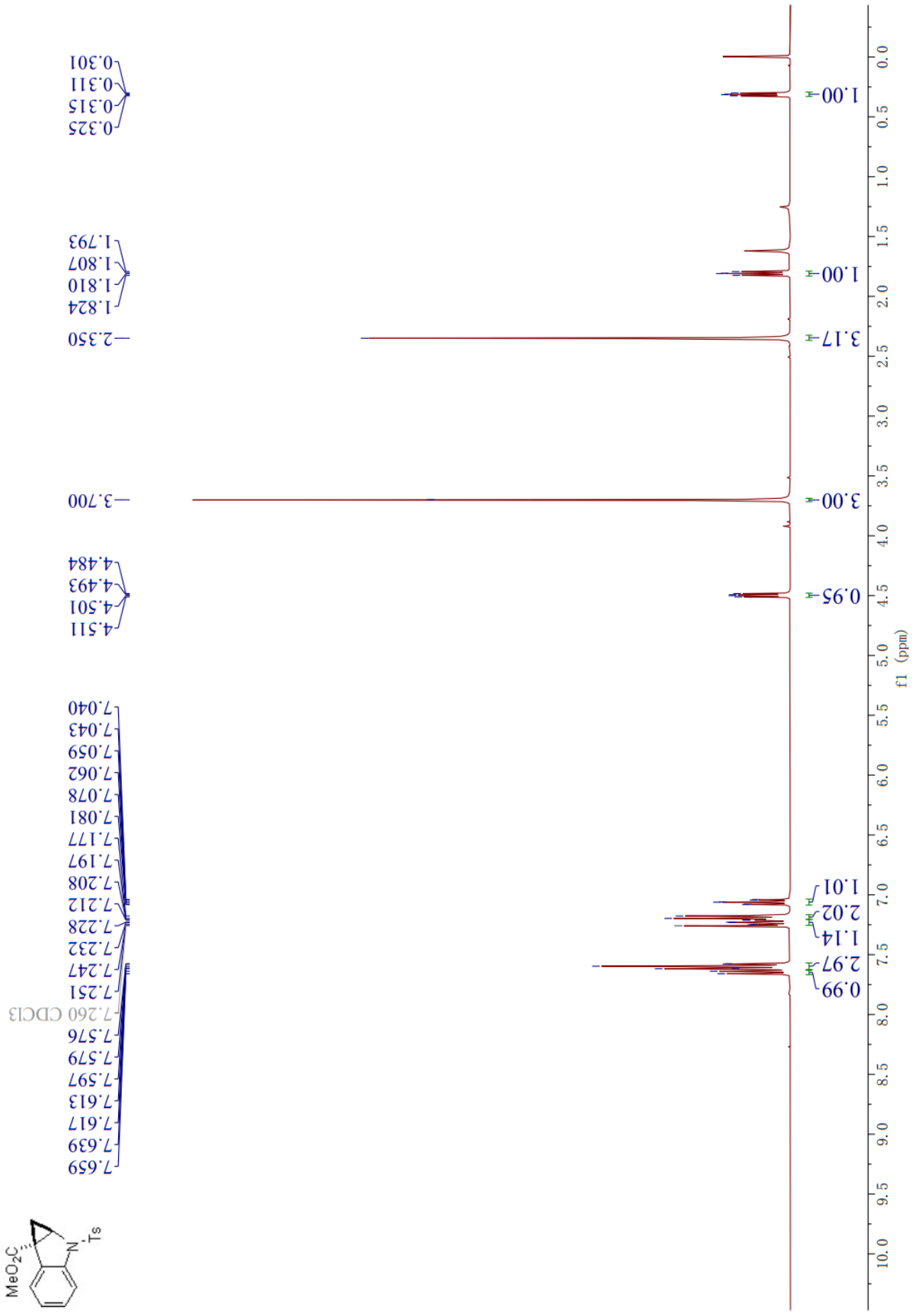
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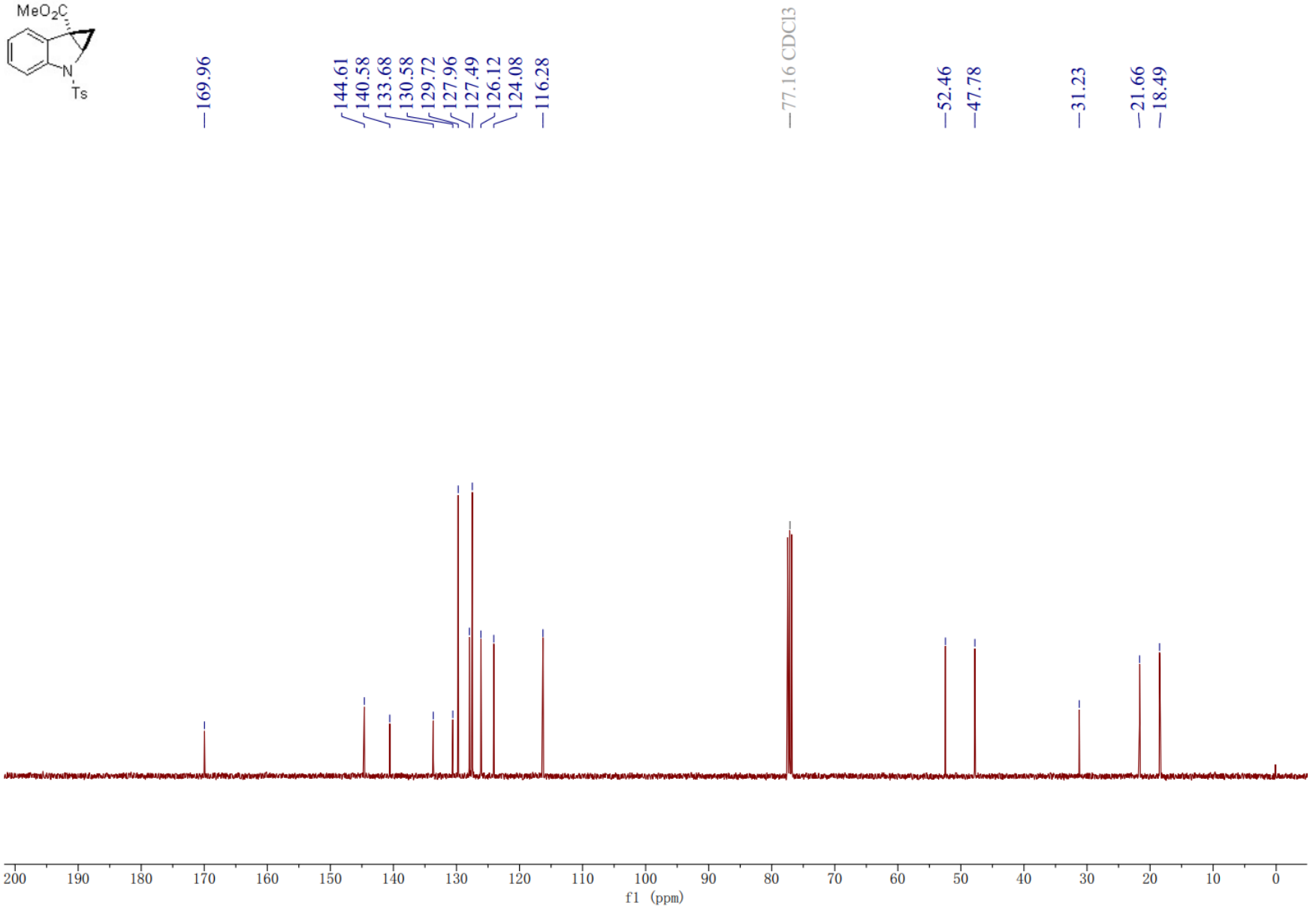
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21.66
18.49
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f1 (ppm)

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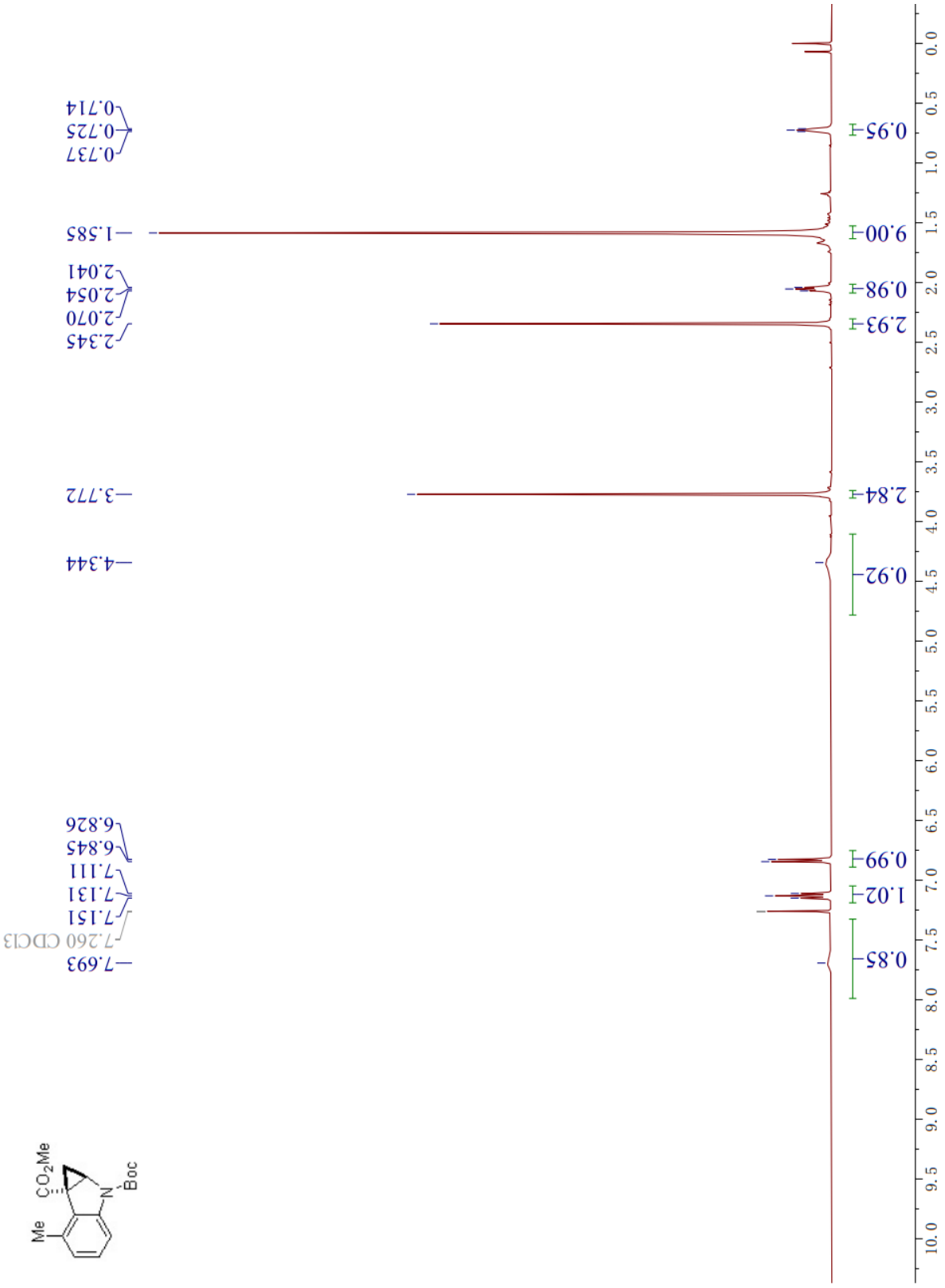
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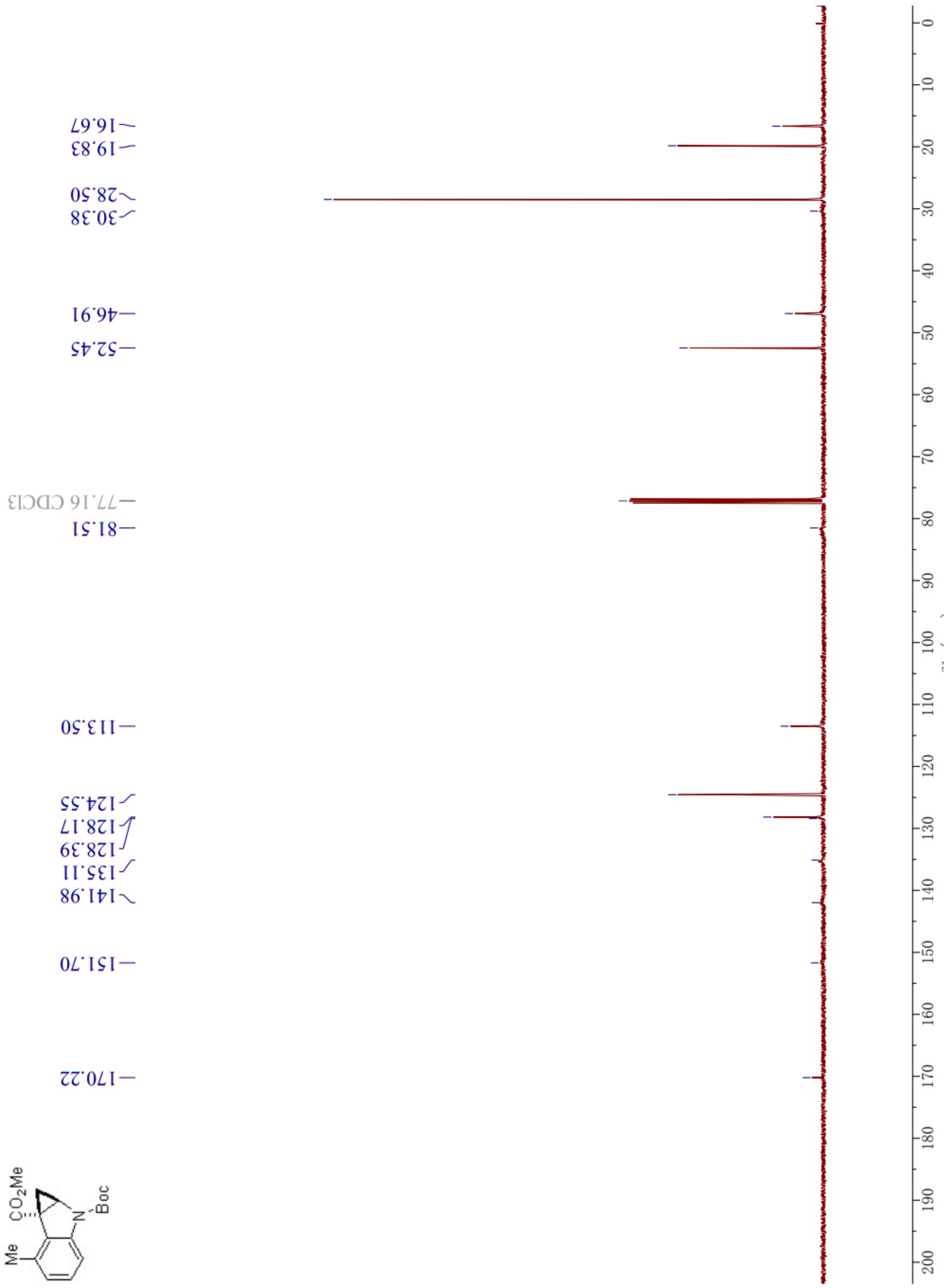
Boc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N
Boc
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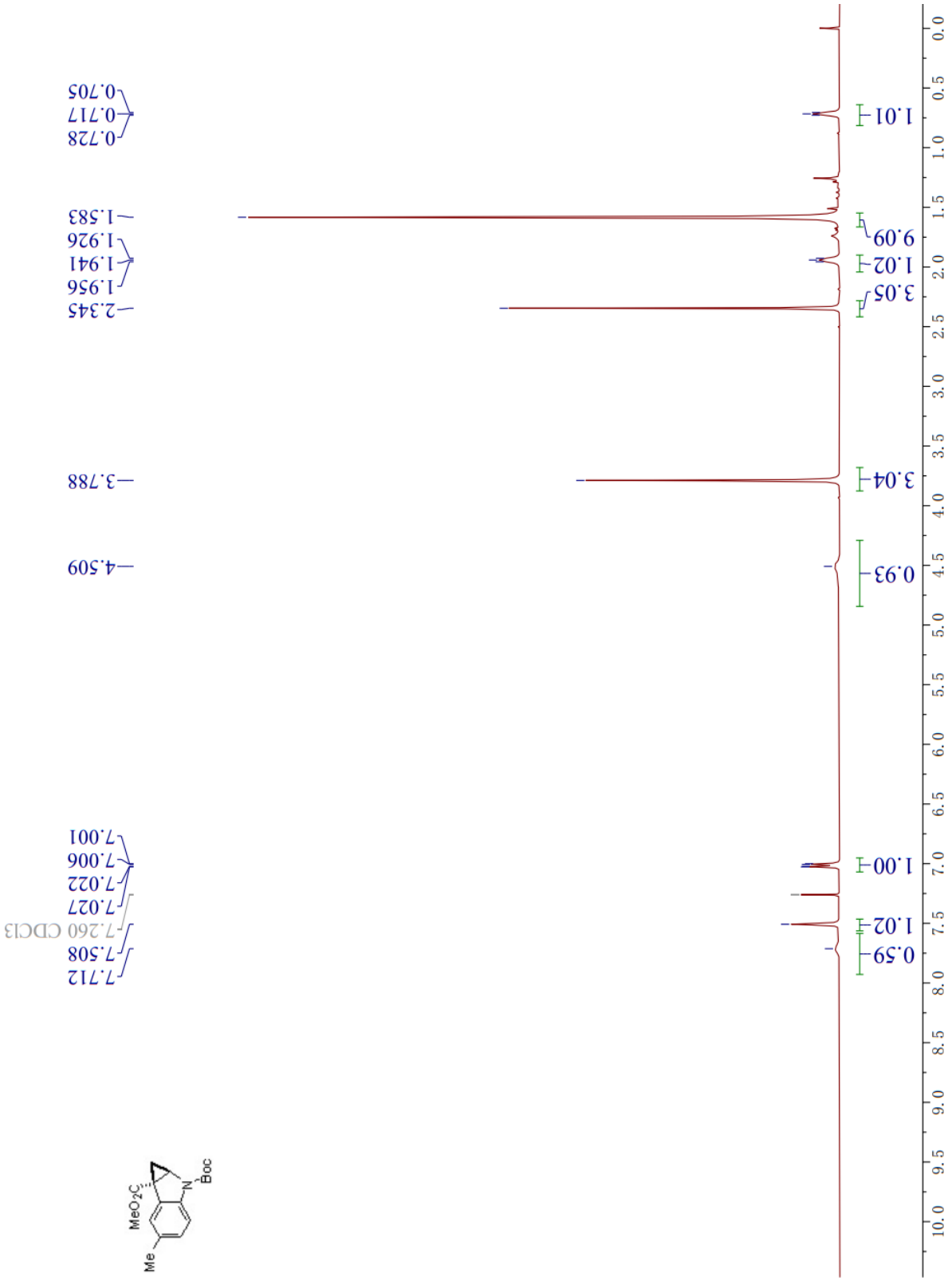
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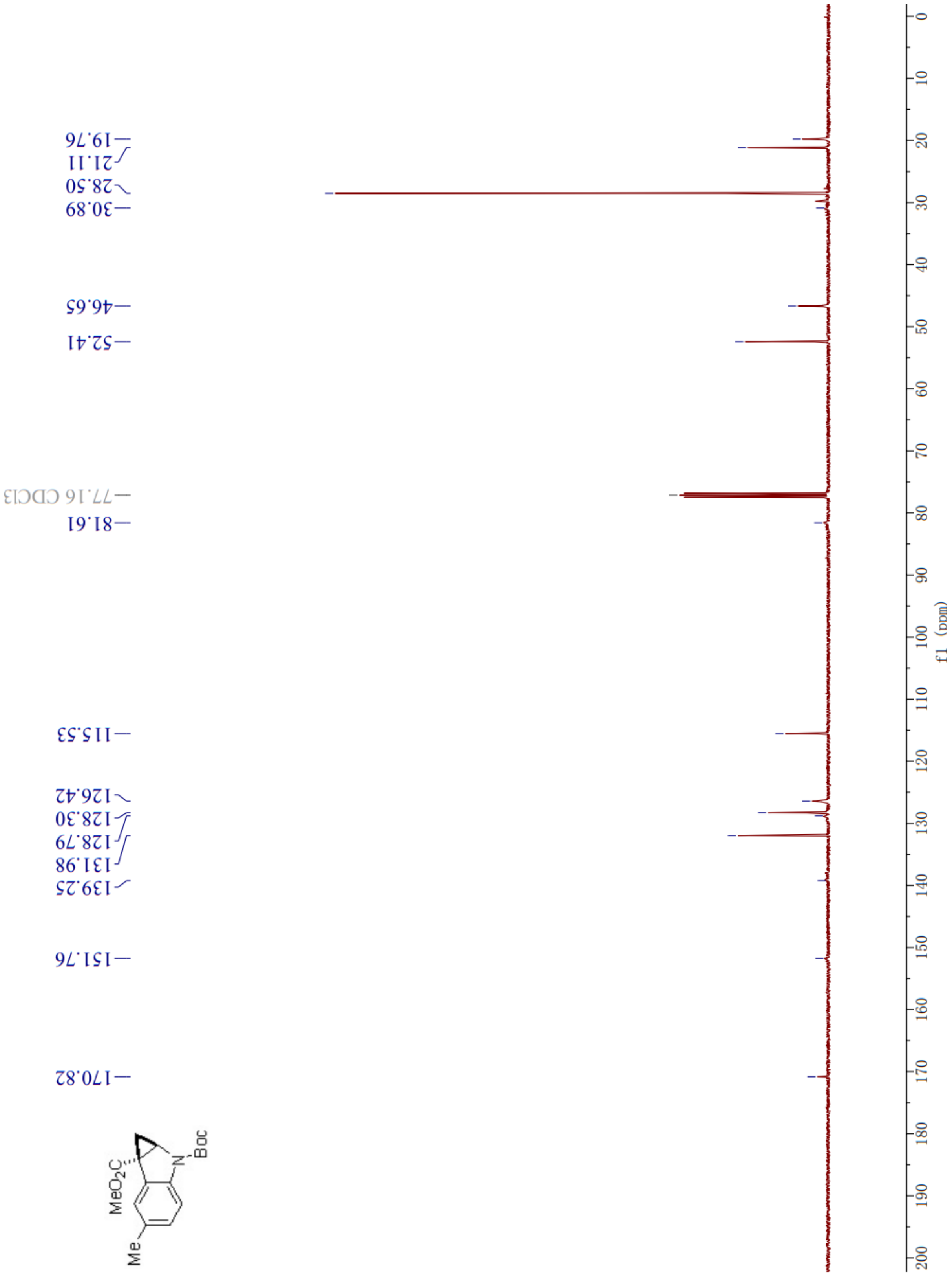

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170.82
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Me
N
Boc
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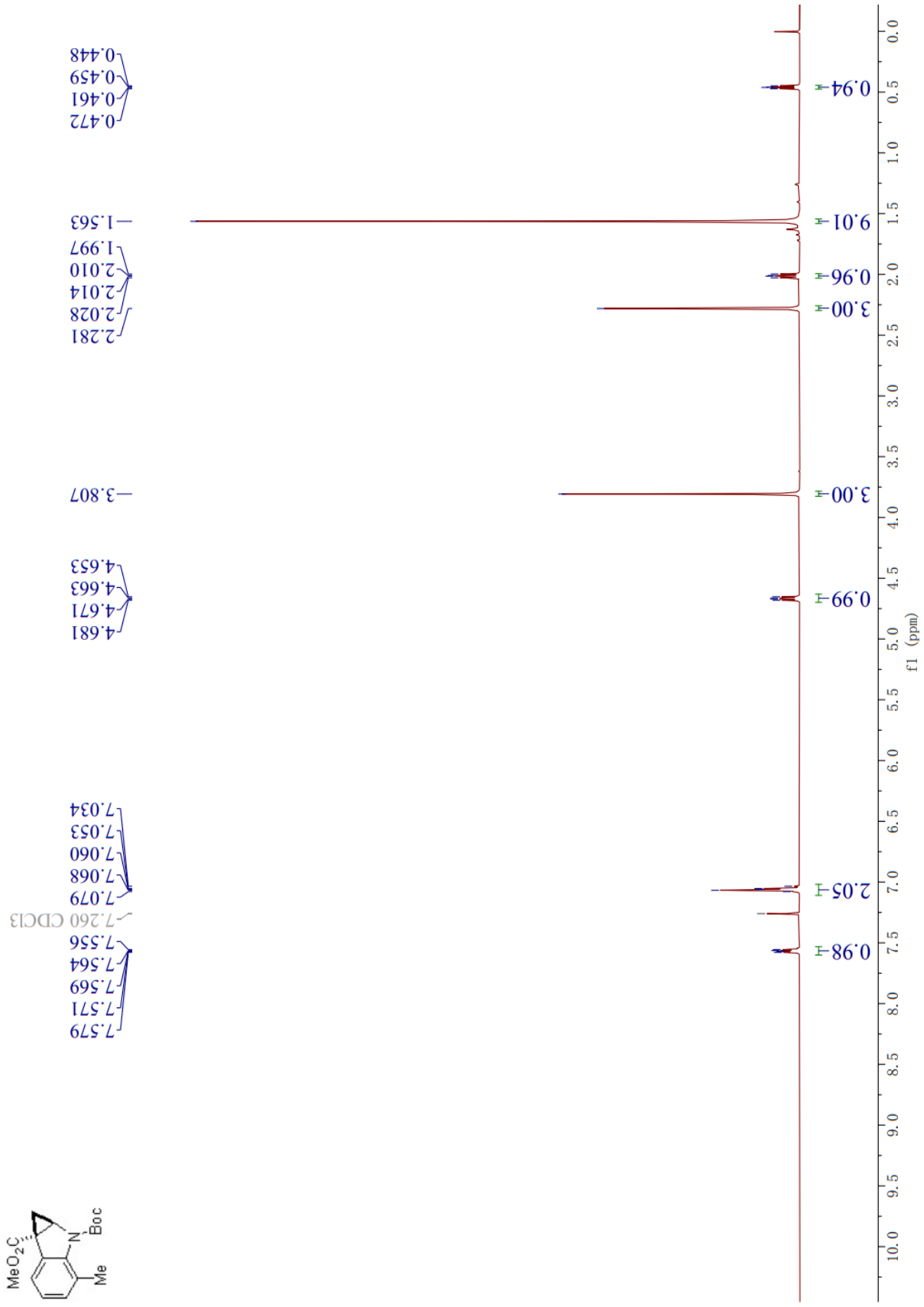
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Boc
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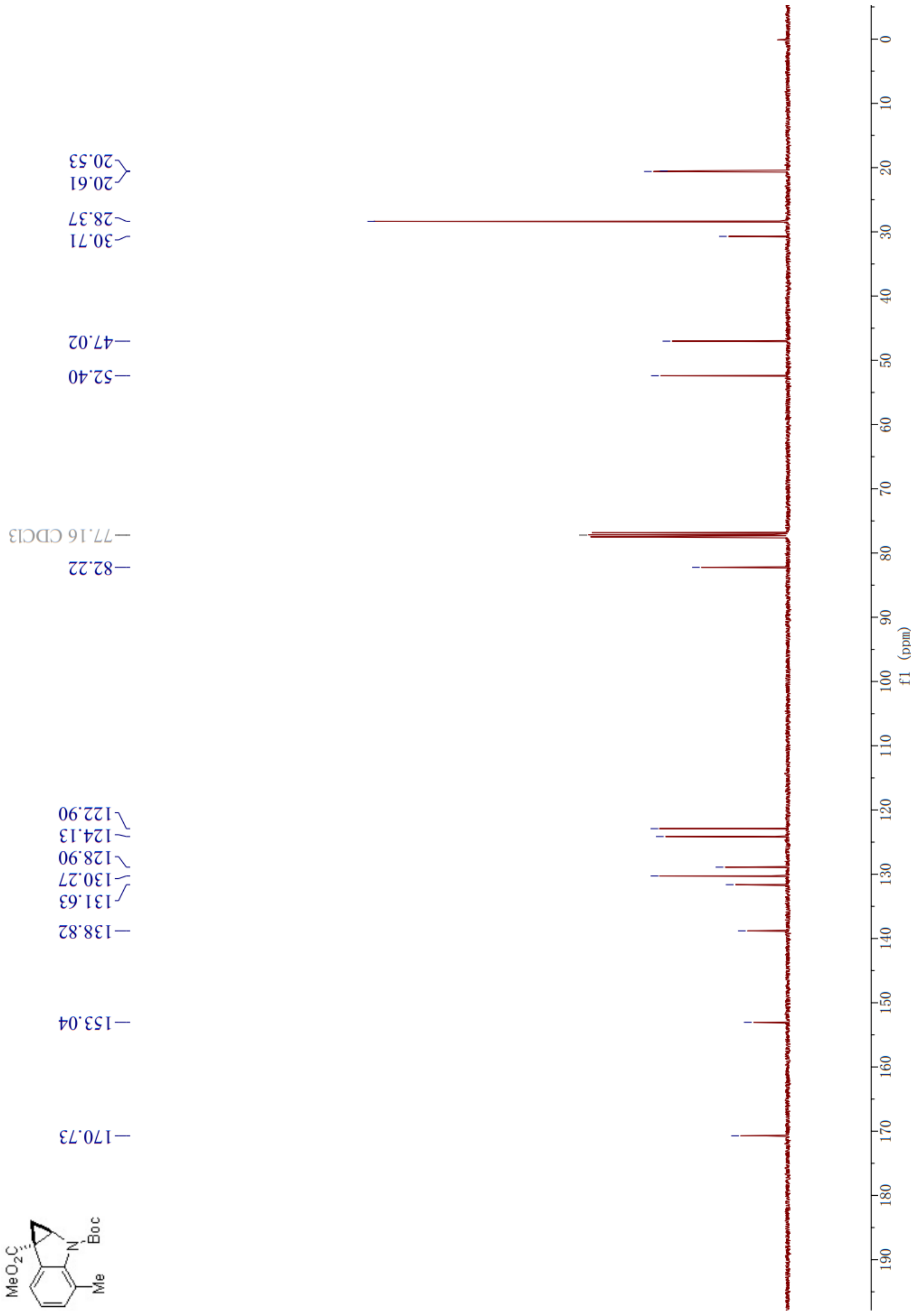
f1 (ppm)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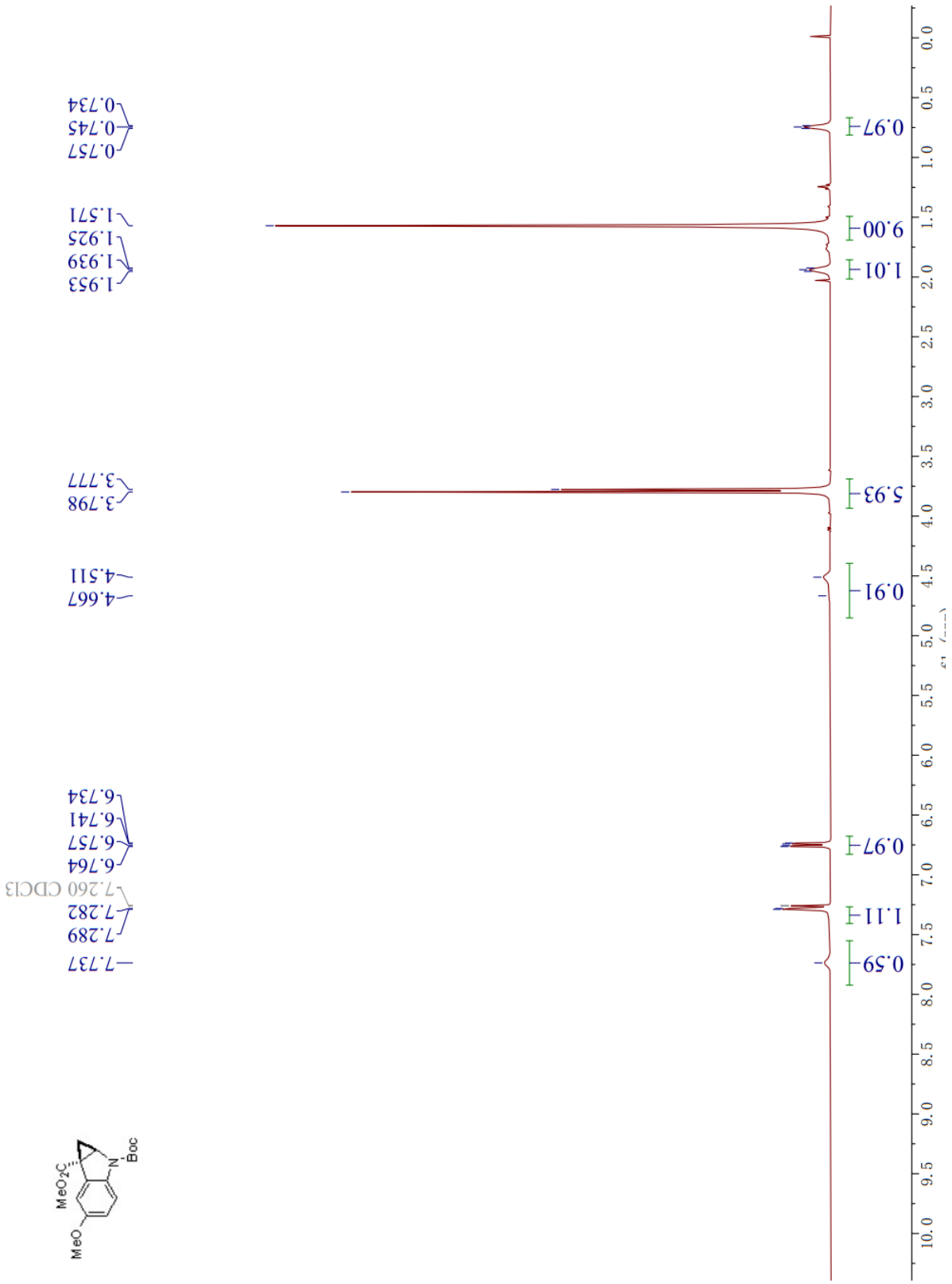
N
Boc
Me
f1 (ppm)

3g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MeO2C
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Boc
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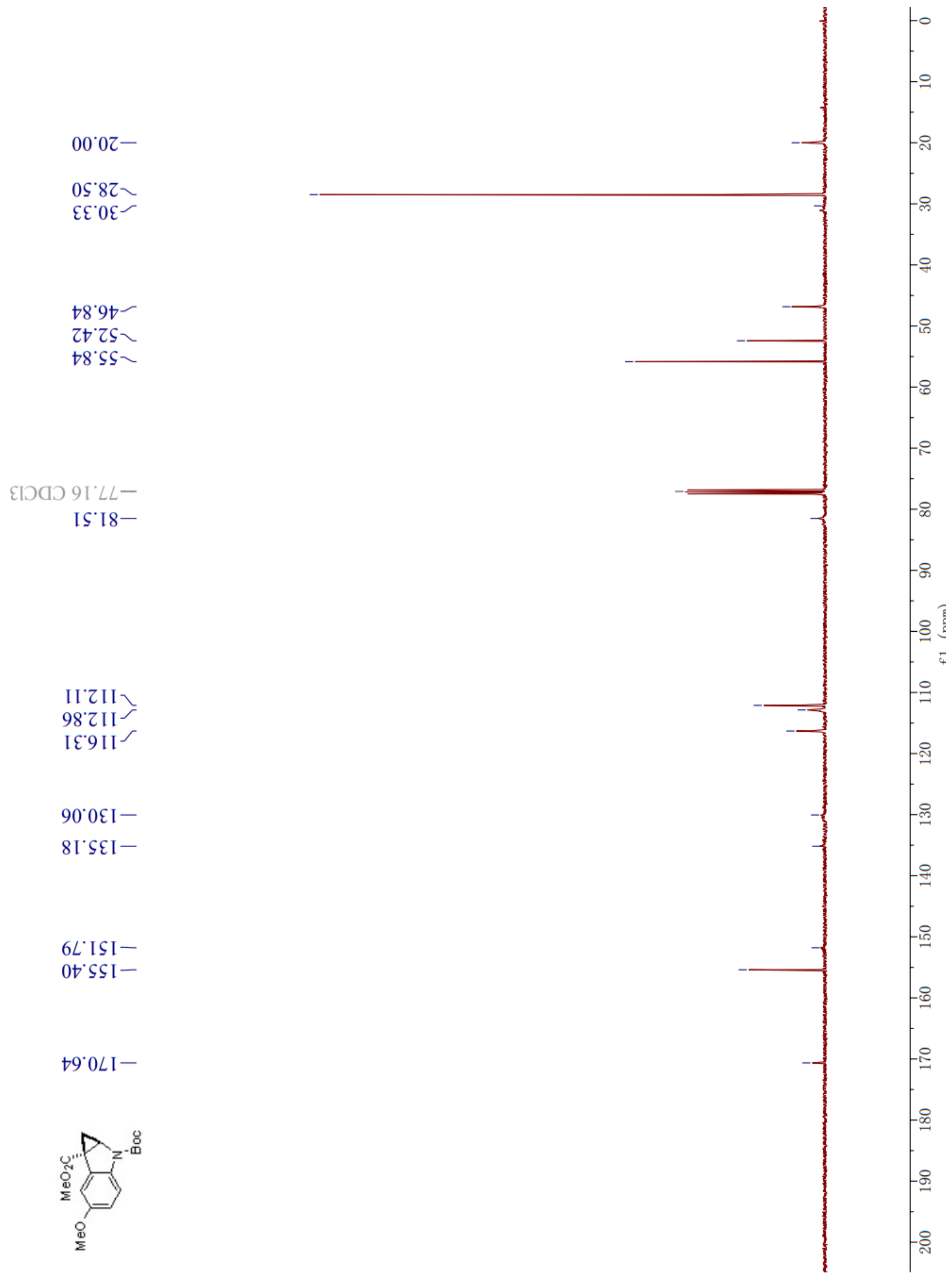
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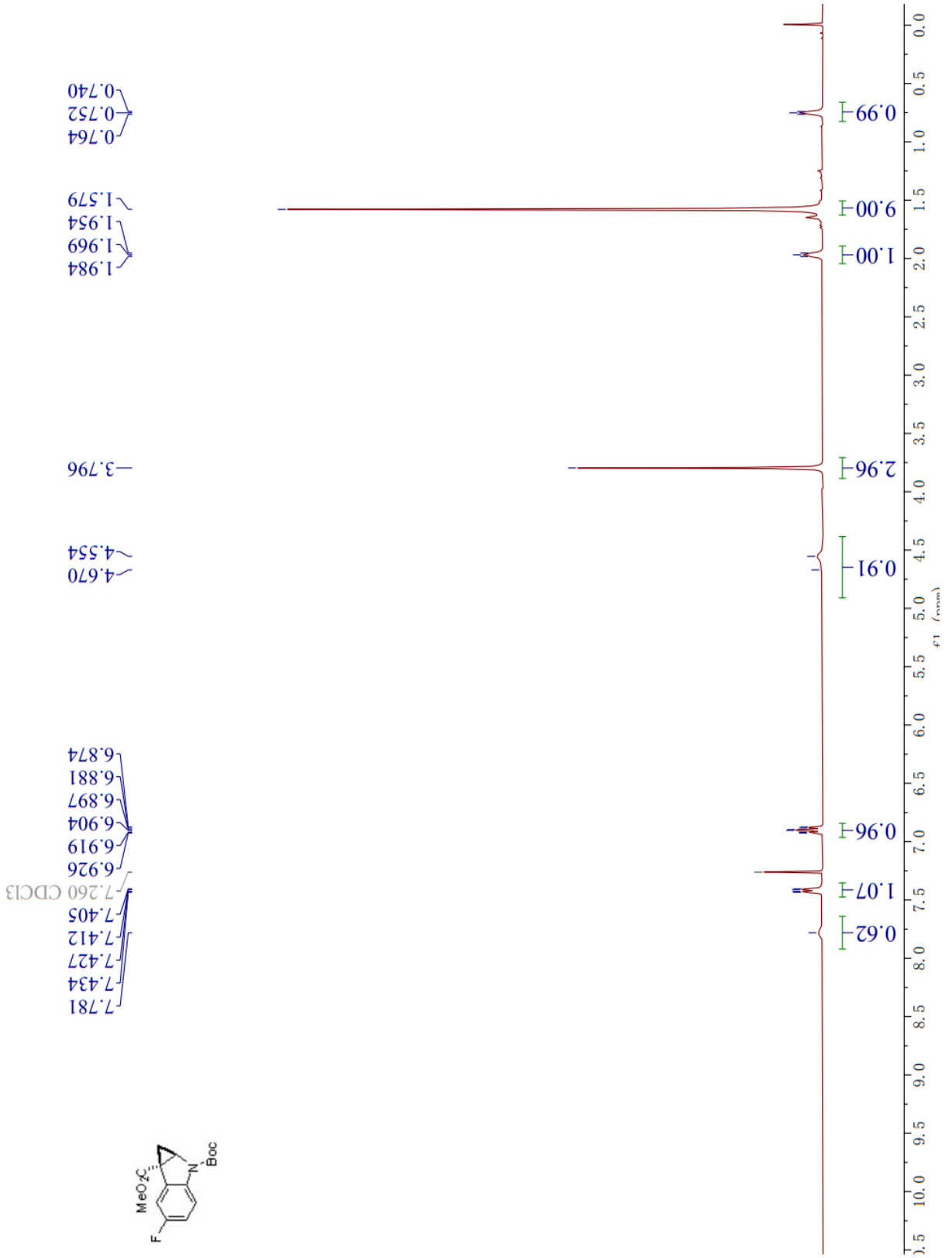
Boc
f1 (ppm)

3h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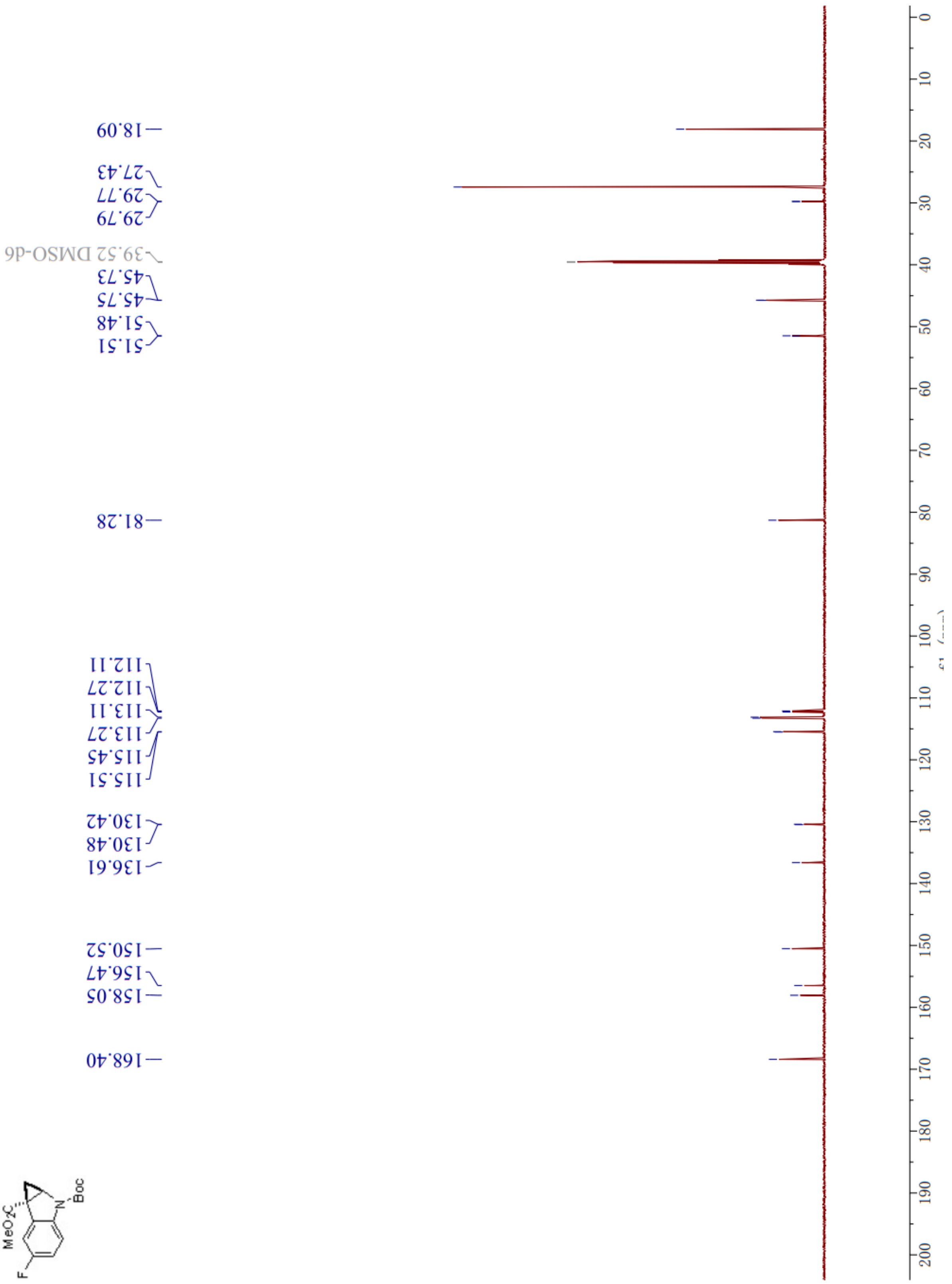
Boc
F
f1 (ppm)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113.11
113.27
115.45
115.51
130.42
130.48
136.61
150.52
156.47
158.05
168.40
MeO2C
N
Boc
F
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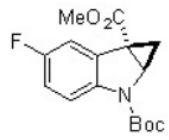
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N
Boc

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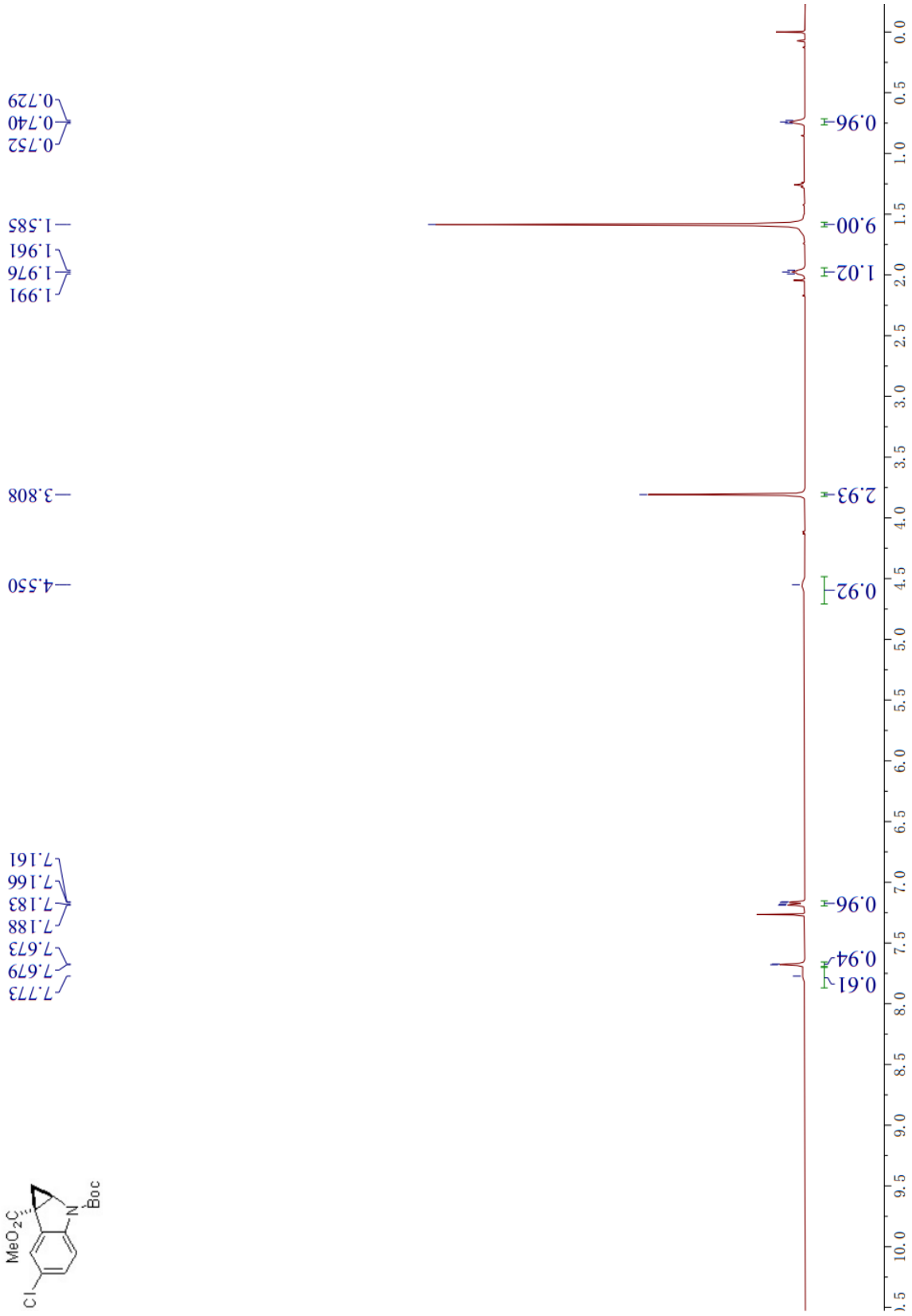
3i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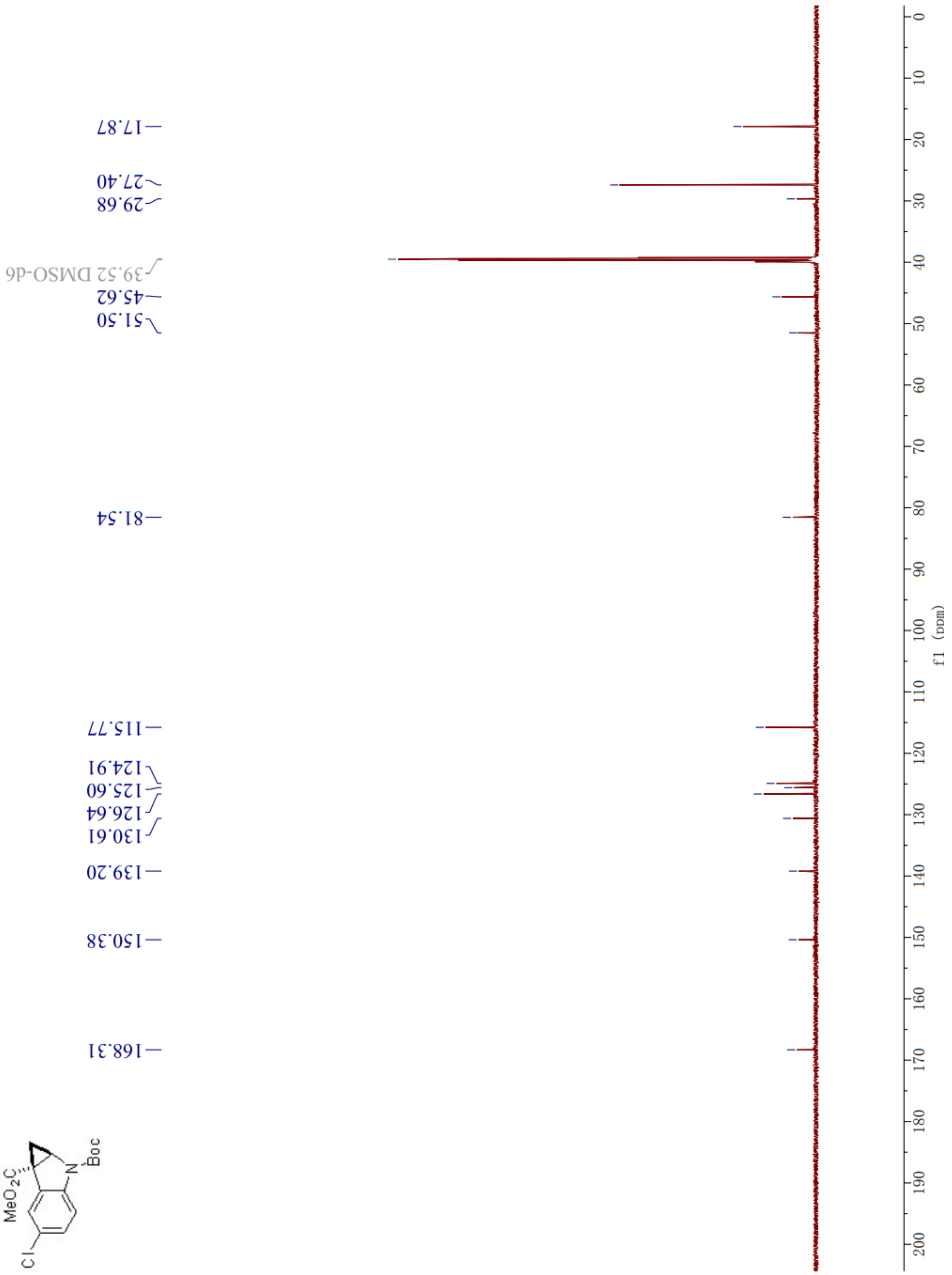
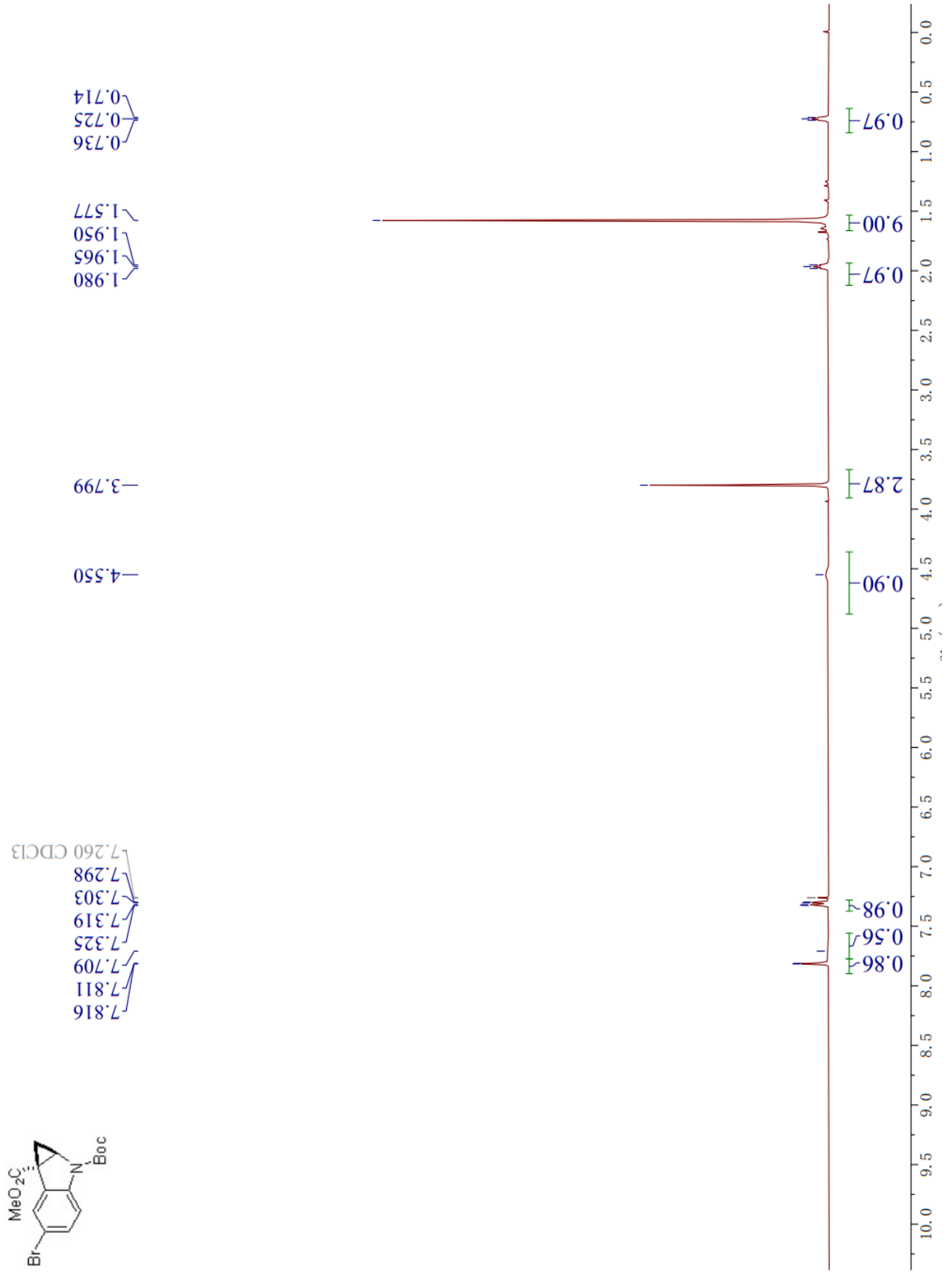
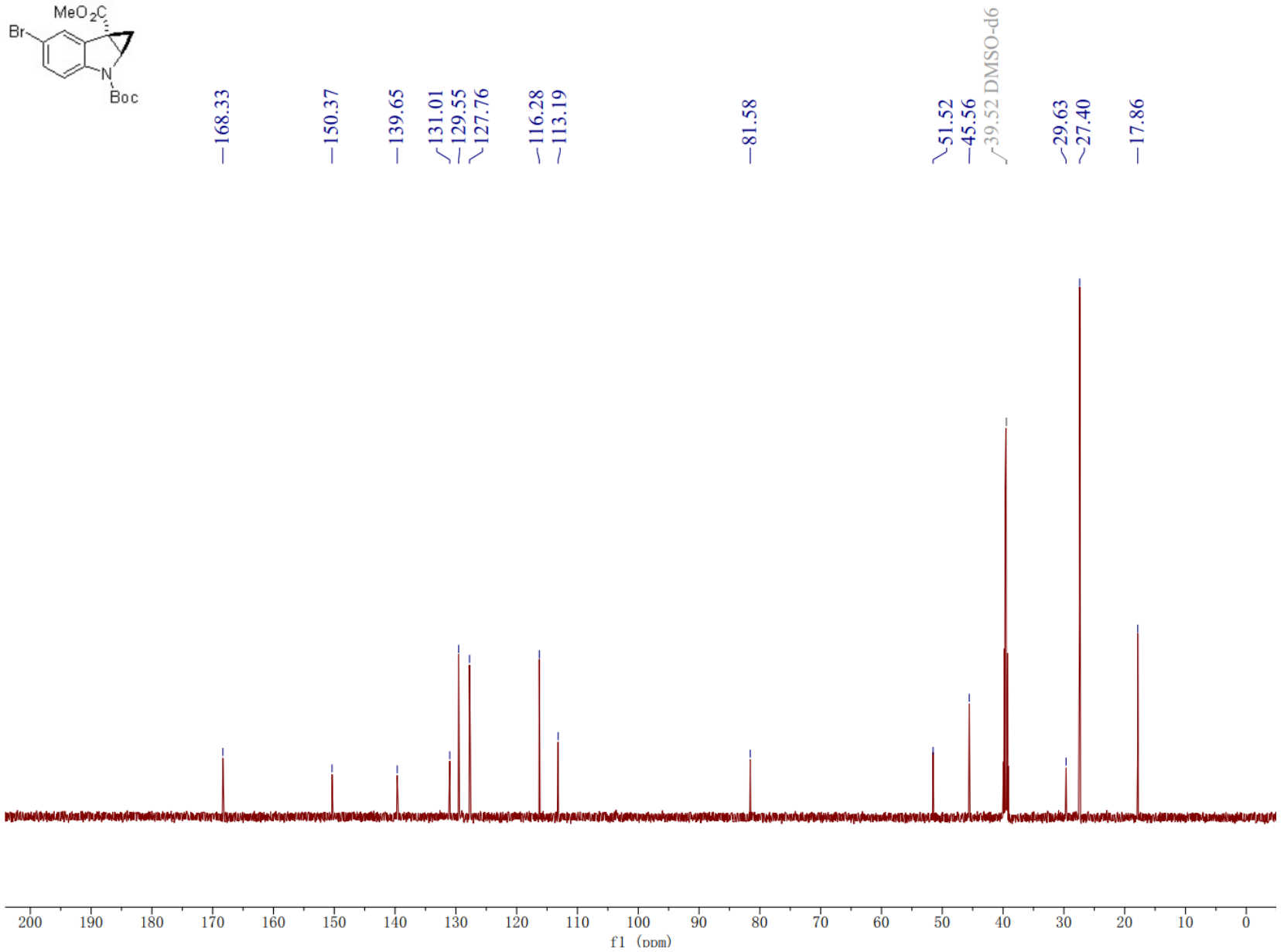
7.673
7.679
7.773
0.96
9.00
1.02
2.93
0.92
0.96
0.94
0.61
MeO2C
Cl
N
Boc

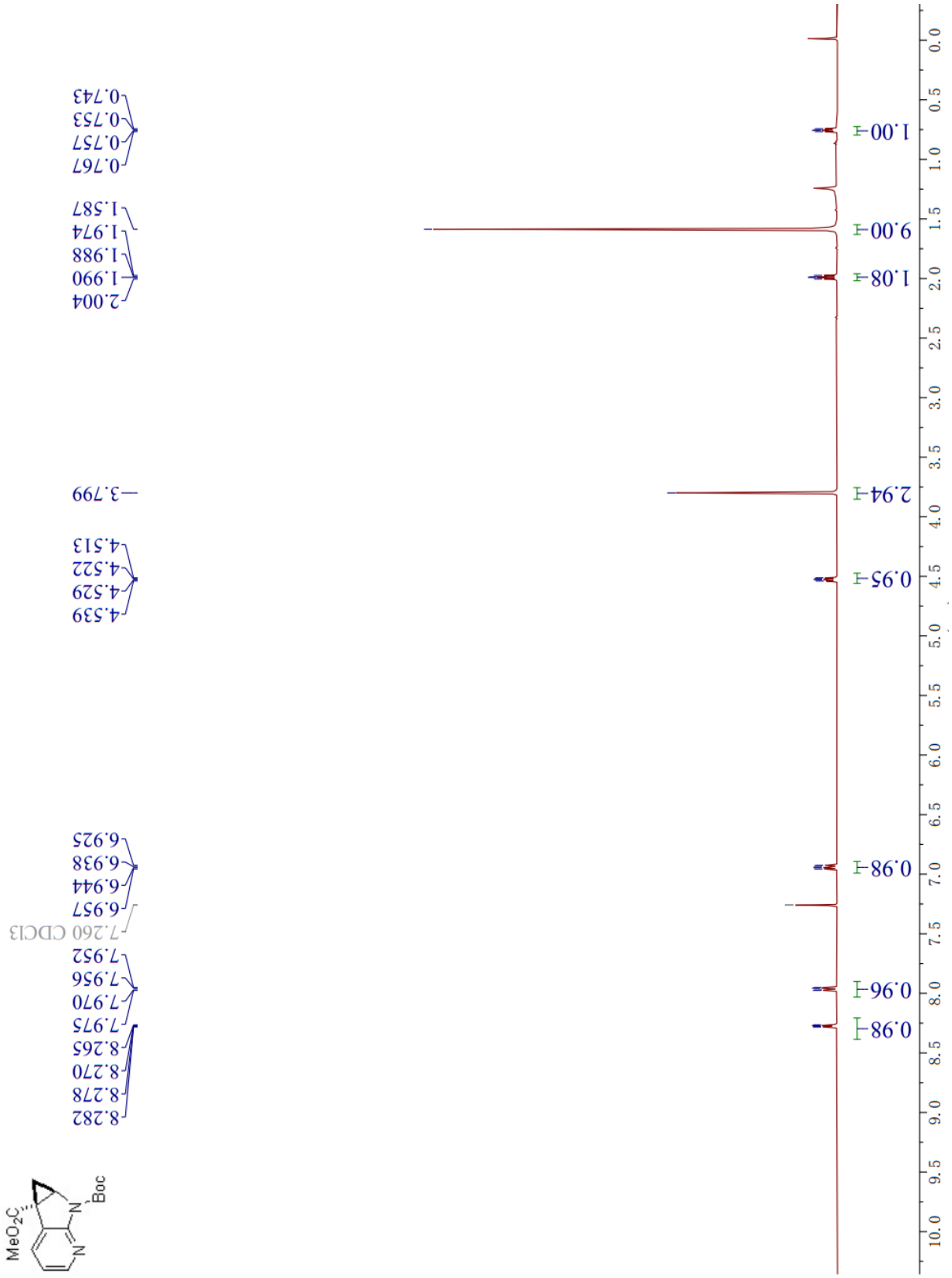

17.87
27.40
29.68
39.52 DMSO-d6
45.62
51.50
81.54
115.77
124.91
125.60
126.64
130.61
139.20
150.38
168.31
f1 (ppm)
MeO2C
N
Boc
Cl

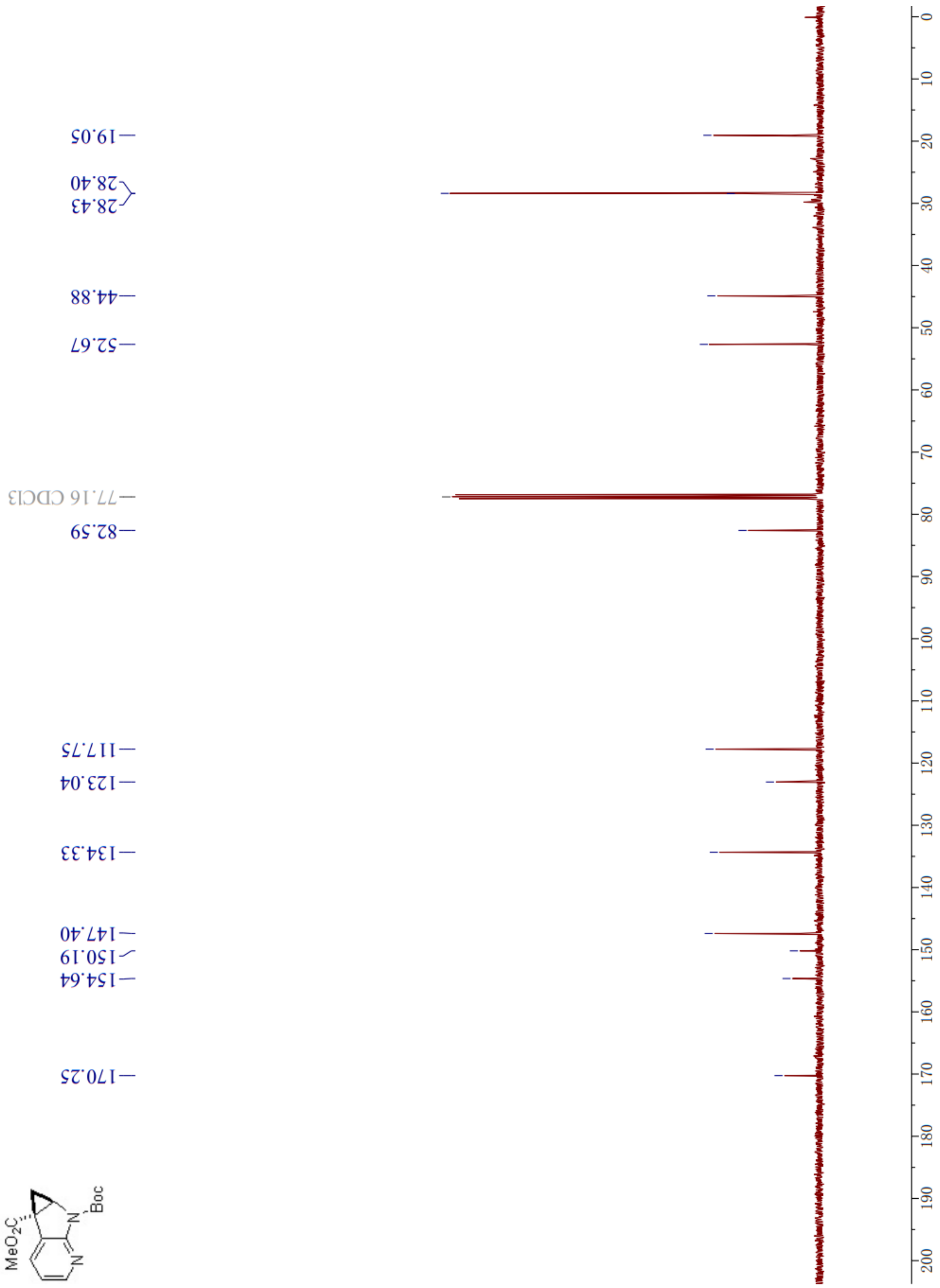
3j


0.714
0.725
0.736
1.577
1.950
1.965
1.980
3.799
4.550
7.260 CDCl3
7.298
7.303
7.319
7.325
7.709
7.811
7.816
0.97
9.00
0.97
2.87
0.90
0.98
0.56
0.86
MeO2C
Boc
N
Br

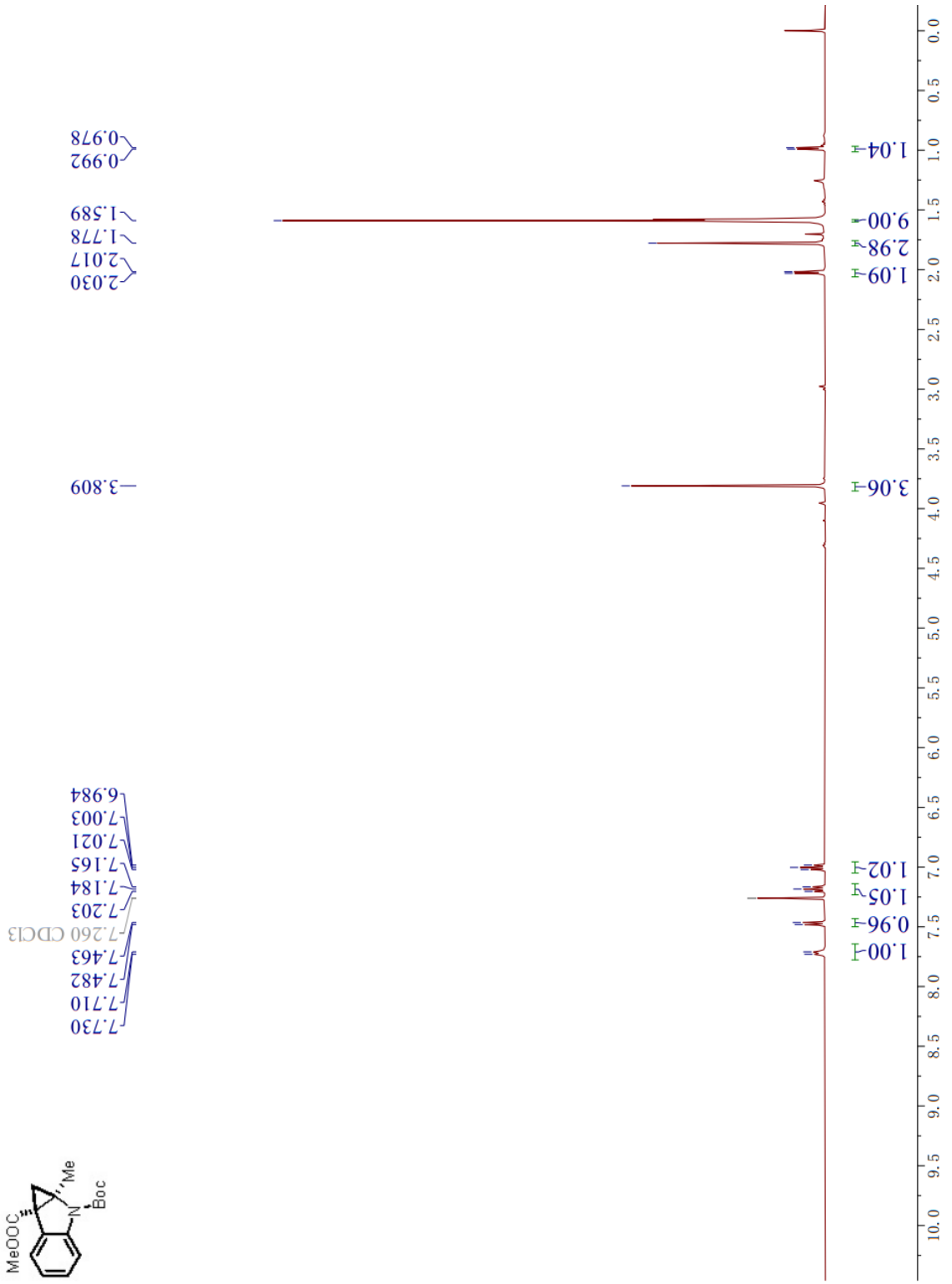

MeO2C
Br
N
Boc
168.33
150.37
139.65
131.01
129.55
127.76
116.28
113.19
81.58
51.52
45.56
39.52 DMSO-d6
29.63
27.40
17.86
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

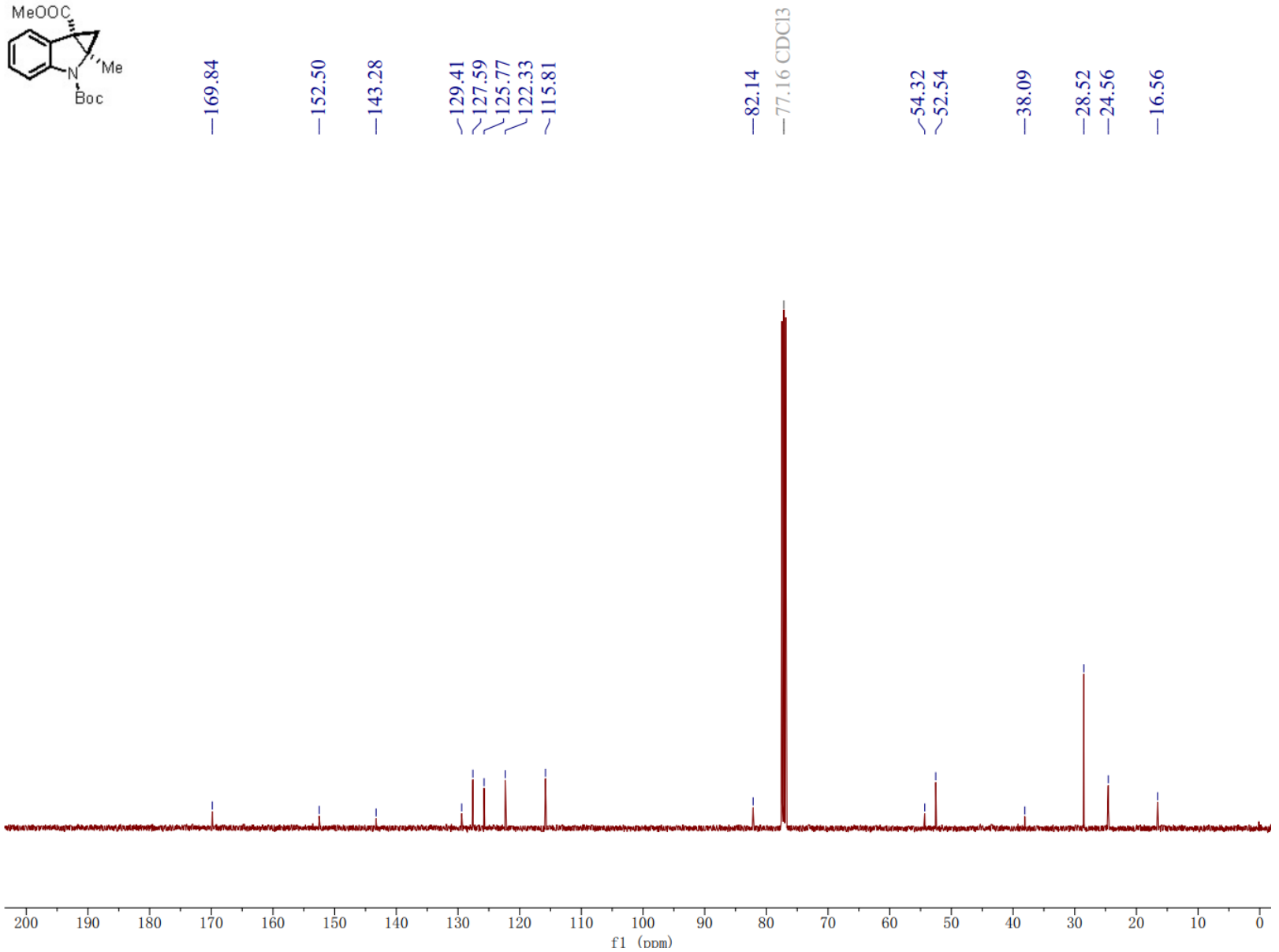
3k


8.282
8.278
8.270
8.265
7.975
7.970
7.956
7.952
7.260 CDCl3
6.957
6.944
6.938
6.925
4.539
4.529
4.522
4.513
3.799
2.004
1.990
1.988
1.974
1.587
0.767
0.757
0.753
0.743
1.00
9.00
1.08
2.94
0.95
0.98
0.96
0.98
MeO2C
Boc
N
N

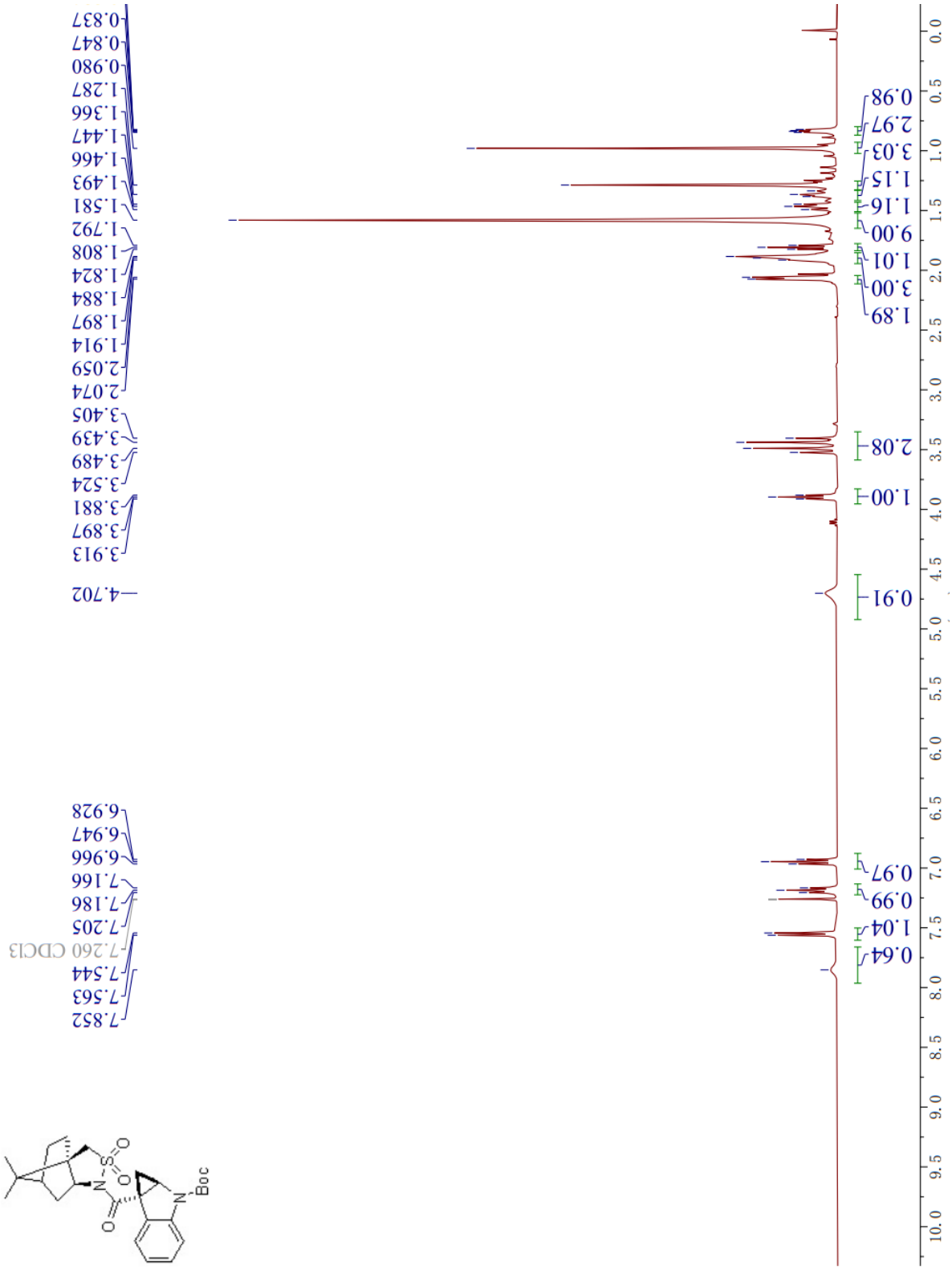

19.05
28.40
28.43
44.88
52.67
77.16 CDCl3
82.59
117.75
123.04
134.33
147.40
150.19
154.64
170.25
MeO2C
N
Boc

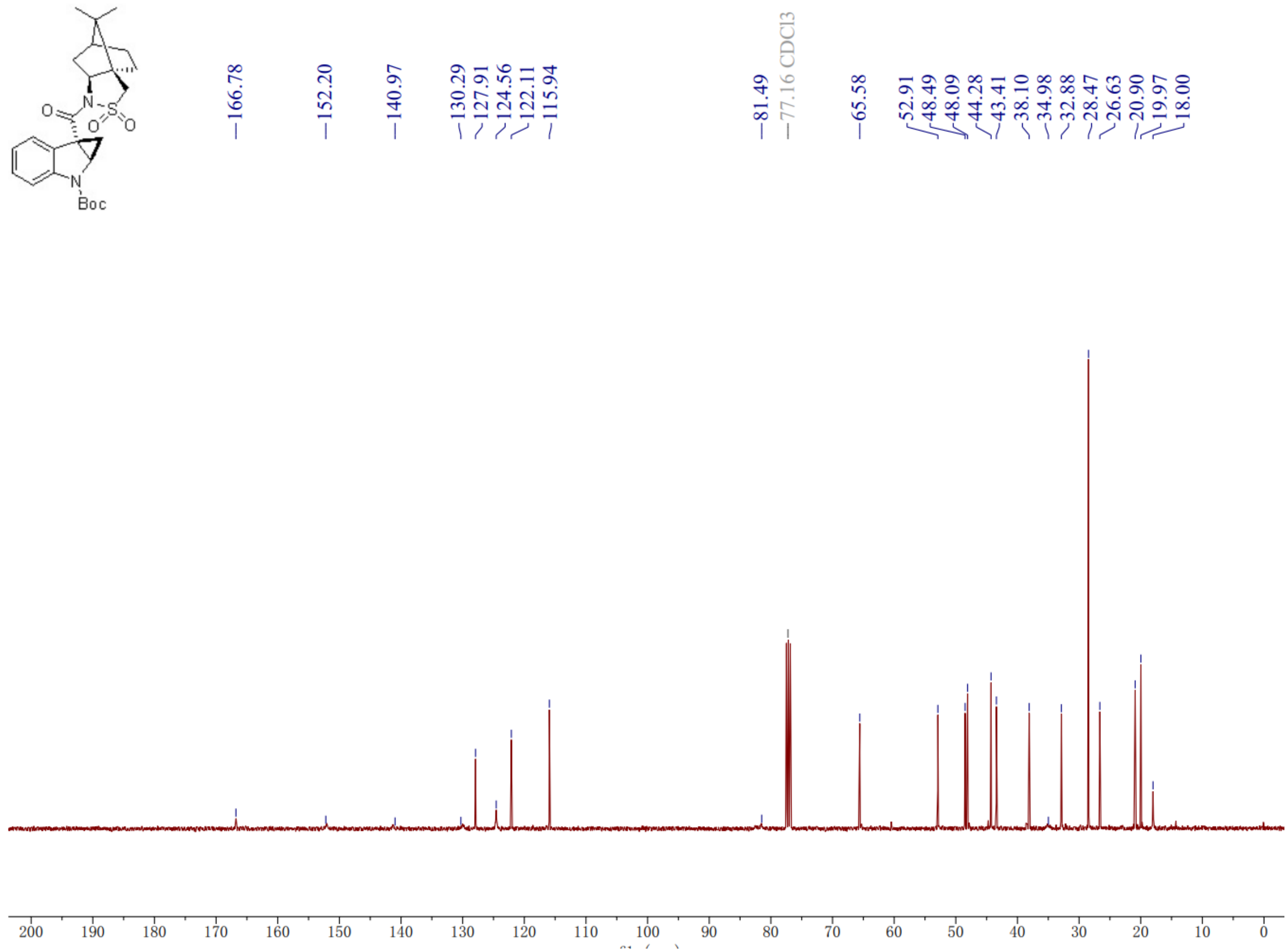
3l


0.978
0.992
1.589
1.778
2.017
2.030
3.809
6.984
7.003
7.021
7.165
7.184
7.203
7.260 CDCl3
7.463
7.482
7.710
7.730
1.04
9.00
2.98
1.09
3.06
1.02
1.05
0.96
1.00
MeOOC
Me
N
Boc

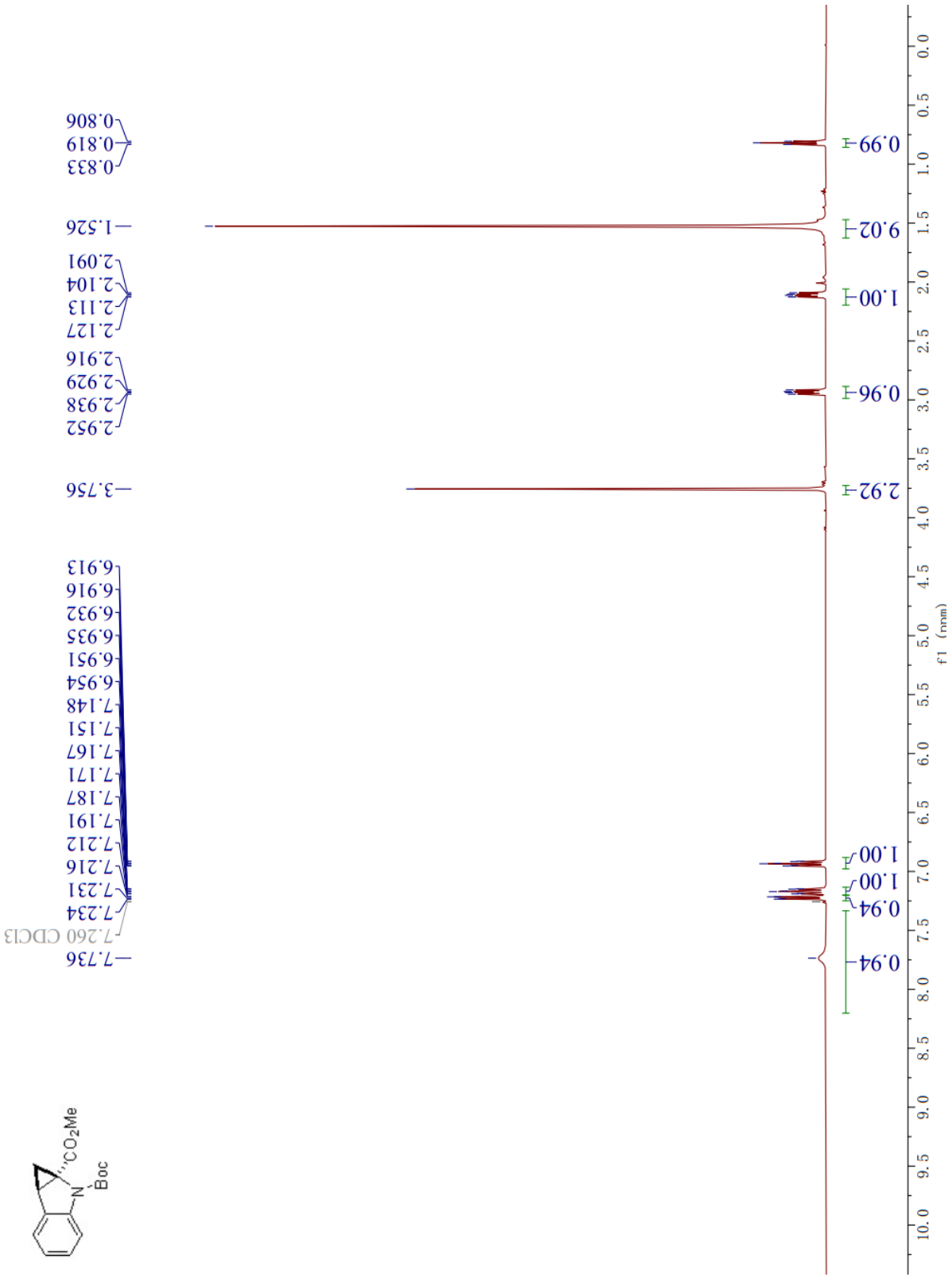

MeOOC
Me
N
Boc
169.84
152.50
143.28
129.41
127.59
125.77
122.33
115.81
82.14
77.16 CDCl3
54.32
52.54
38.09
28.52
24.56
16.56
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

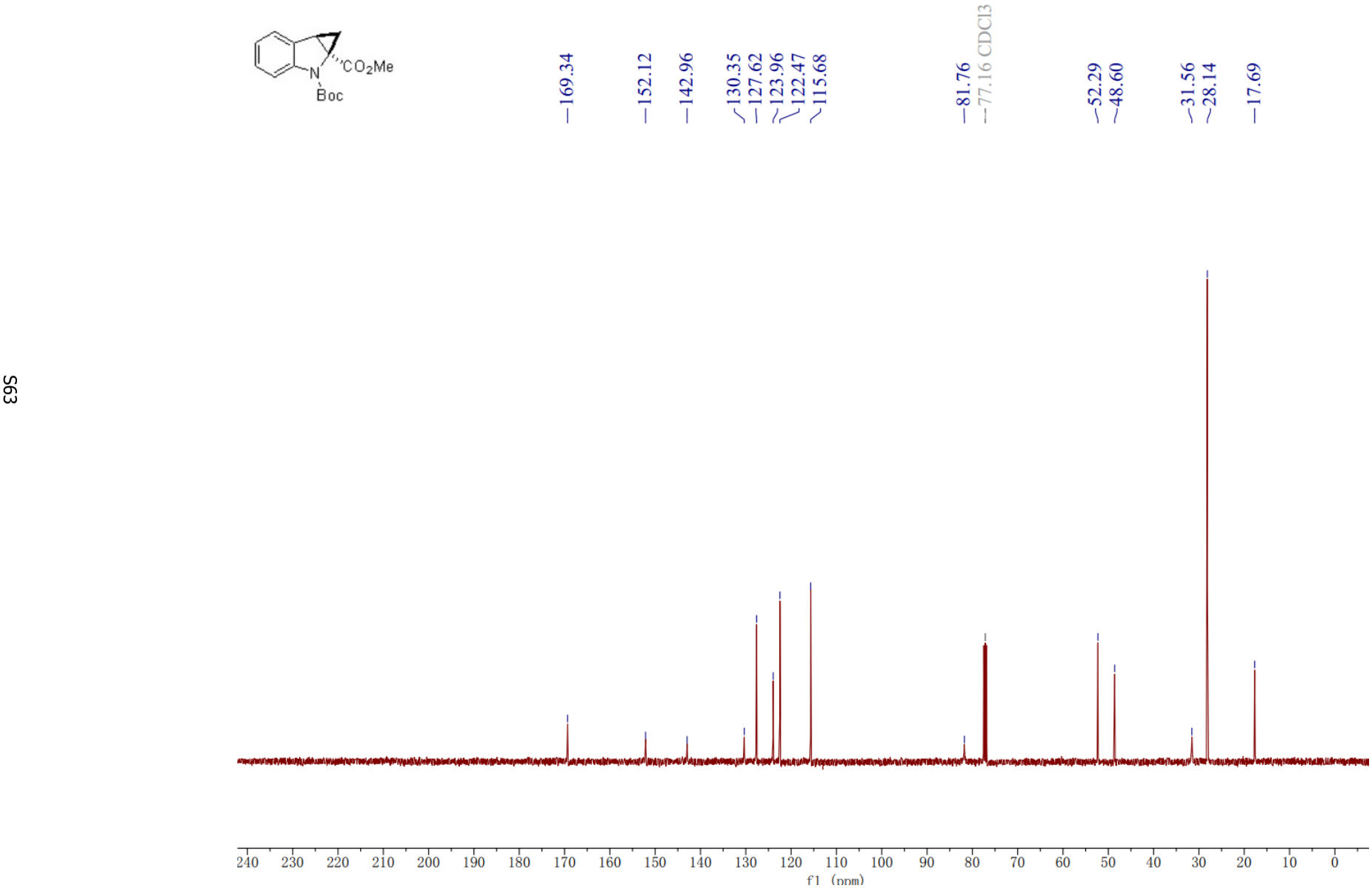
3m


0.837
0.847
0.980
1.287
1.366
1.447
1.466
1.493
1.581
1.792
1.808
1.824
1.884
1.897
1.914
2.059
2.074
3.405
3.439
3.489
3.524
3.881
3.897
3.913
4.702
6.928
6.947
6.966
7.166
7.186
7.205
7.260 CDCl3
7.544
7.563
7.852
0.98
2.97
3.03
1.15
1.16
9.00
1.01
3.00
1.89
2.08
1.00
0.91
0.97
0.99
1.04
0.64
Boc

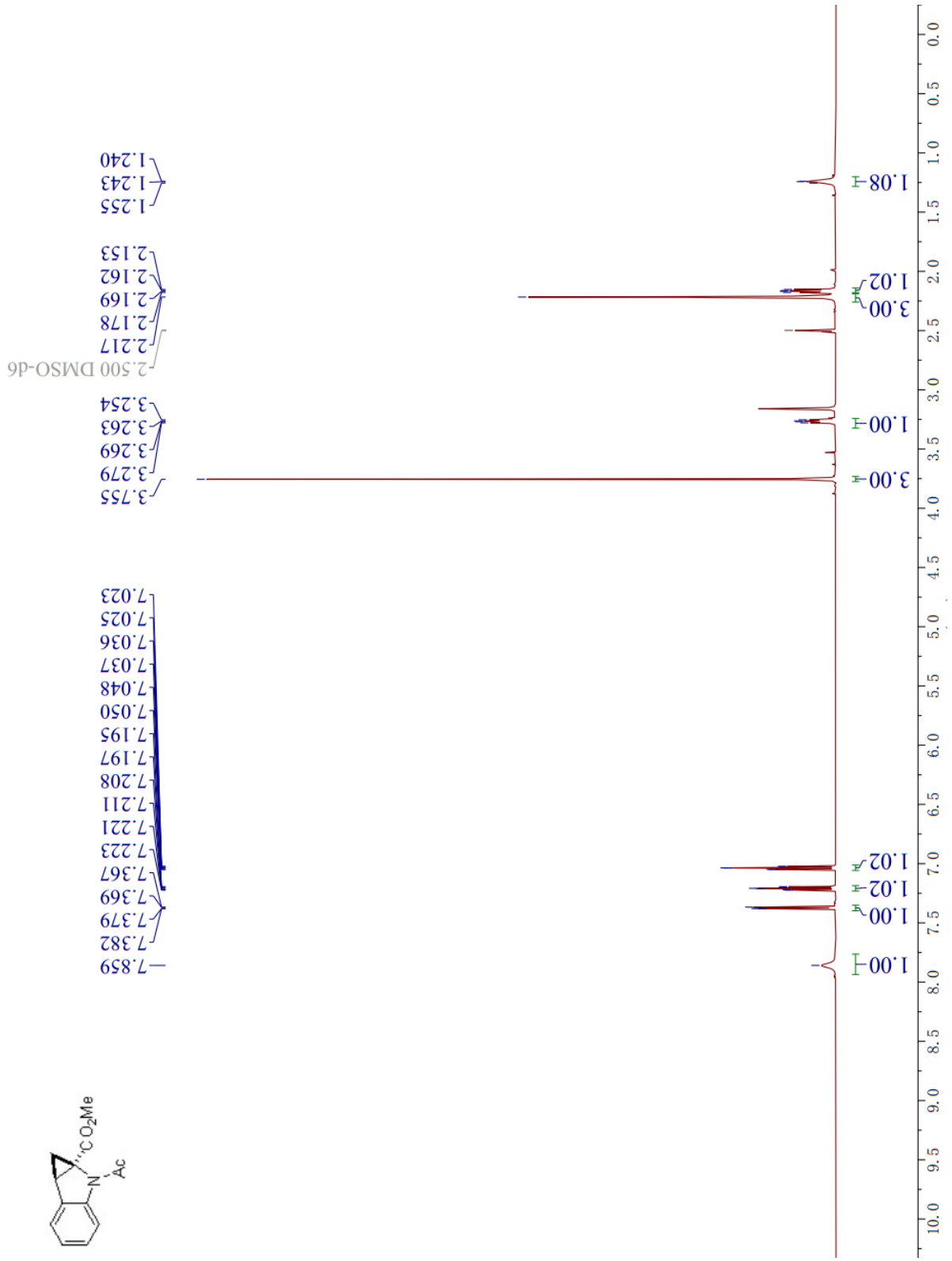

166.78
152.20
140.97
130.29
127.91
124.56
122.11
115.94
81.49
77.16 CDCl3
65.58
52.91
48.49
48.09
44.28
43.41
38.10
34.98
32.88
28.47
26.63
20.90
19.97
18.00
Boc
N
O
S
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

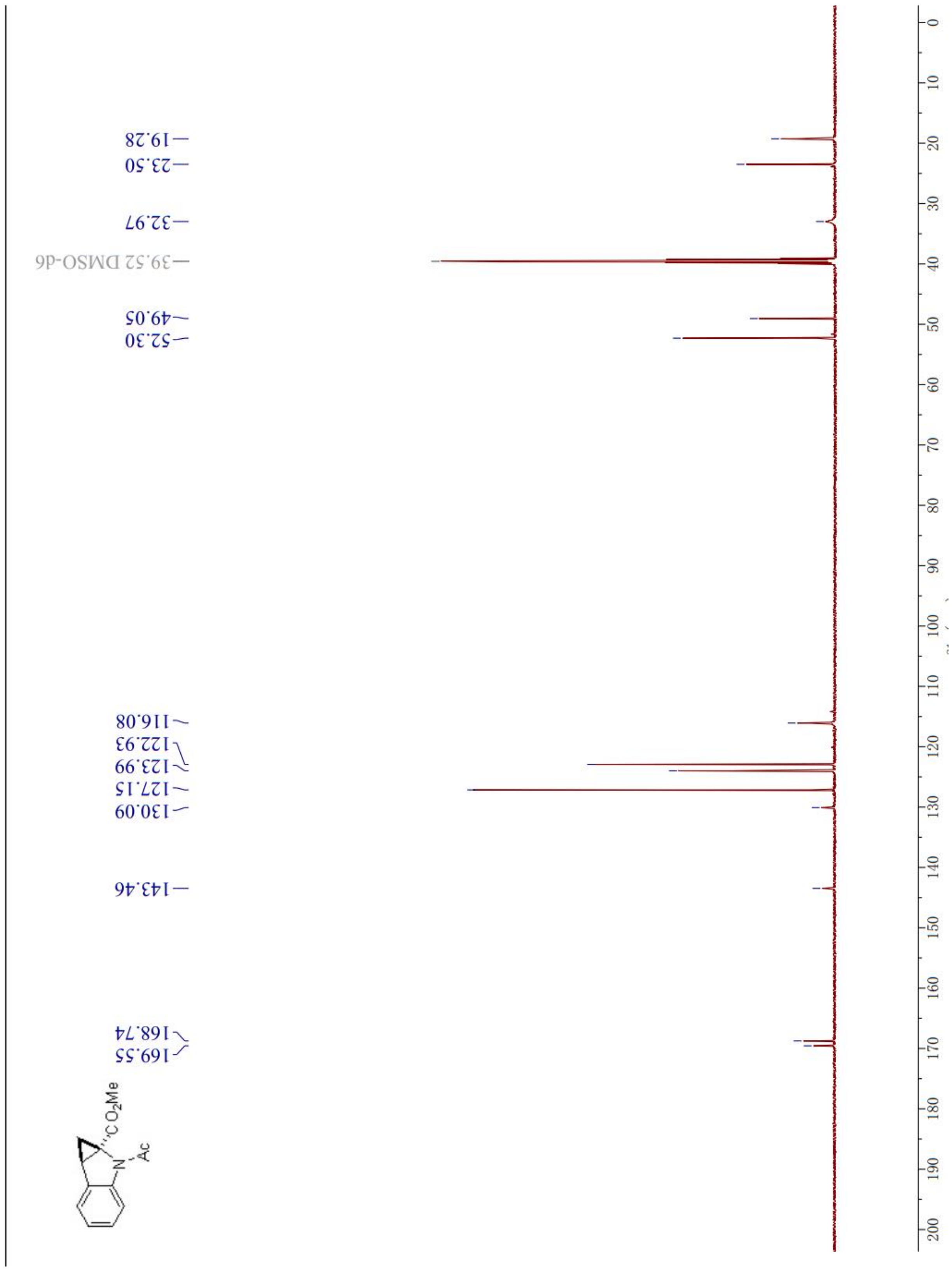
5a


0.806
0.819
0.833
1.526
2.091
2.104
2.113
2.127
2.916
2.929
2.938
2.952
3.756
6.913
6.916
6.932
6.935
6.951
6.954
7.148
7.151
7.167
7.171
7.187
7.191
7.212
7.216
7.231
7.234
7.260 CDCl3
7.736
0.99
9.02
1.00
0.96
2.92
1.00
1.00
0.94
0.94
CO2Me
Boc
N
f1 (ppm)

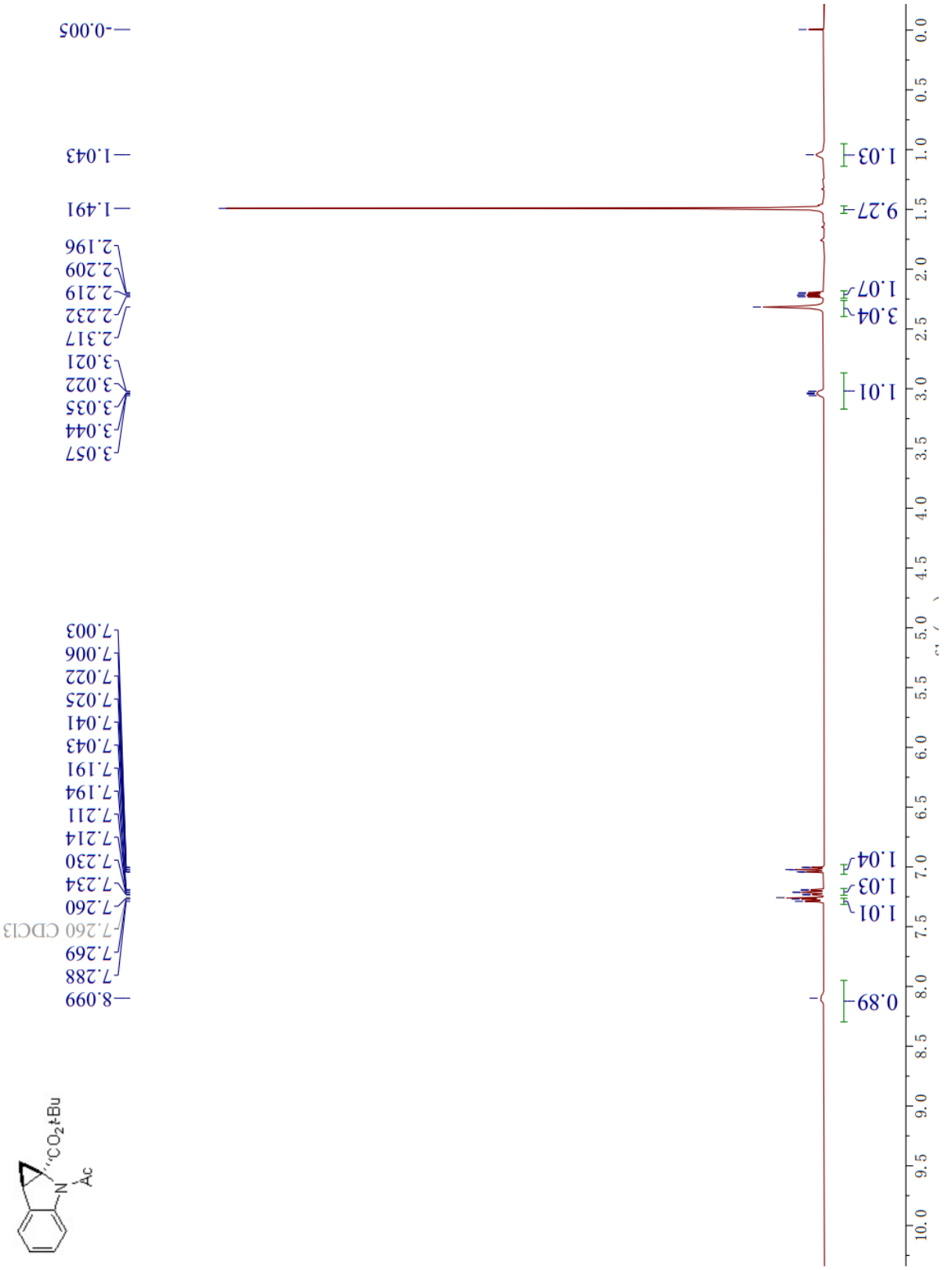

CO2Me
N
Boc
169.34
152.12
142.96
130.35
127.62
123.96
122.47
115.68
81.76
77.16 CDCl3
52.29
48.60
31.56
28.14
17.69
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

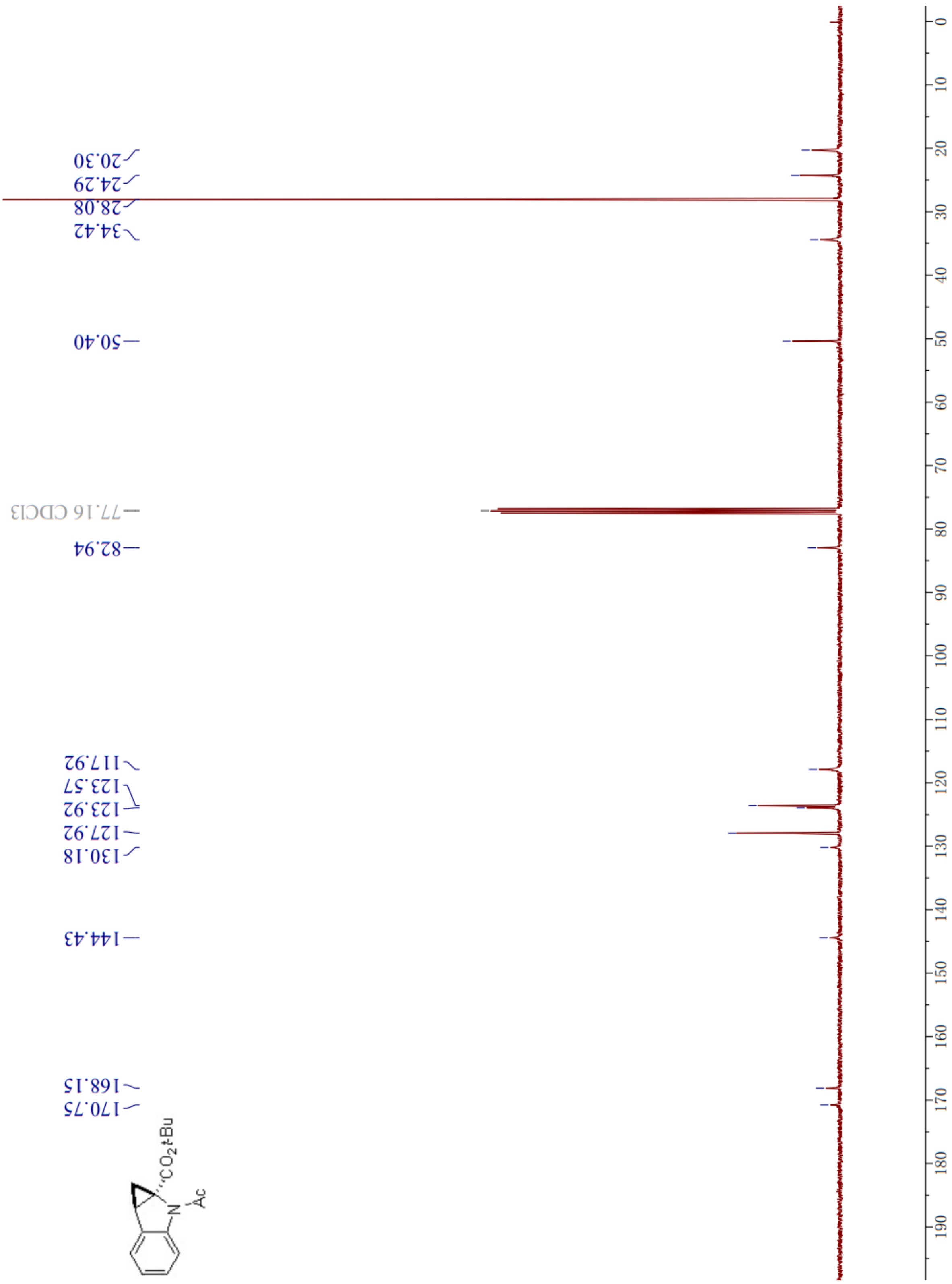
5b


1.240
1.243
1.255
2.153
2.162
2.169
2.178
2.217
2.500 DMSO-d6
3.254
3.263
3.269
3.279
3.755
7.023
7.025
7.036
7.037
7.048
7.050
7.195
7.197
7.208
7.211
7.221
7.223
7.367
7.369
7.379
7.382
7.859
1.08
1.02
3.00
1.00
3.00
1.02
1.02
1.00
1.00
CO2Me
Ac

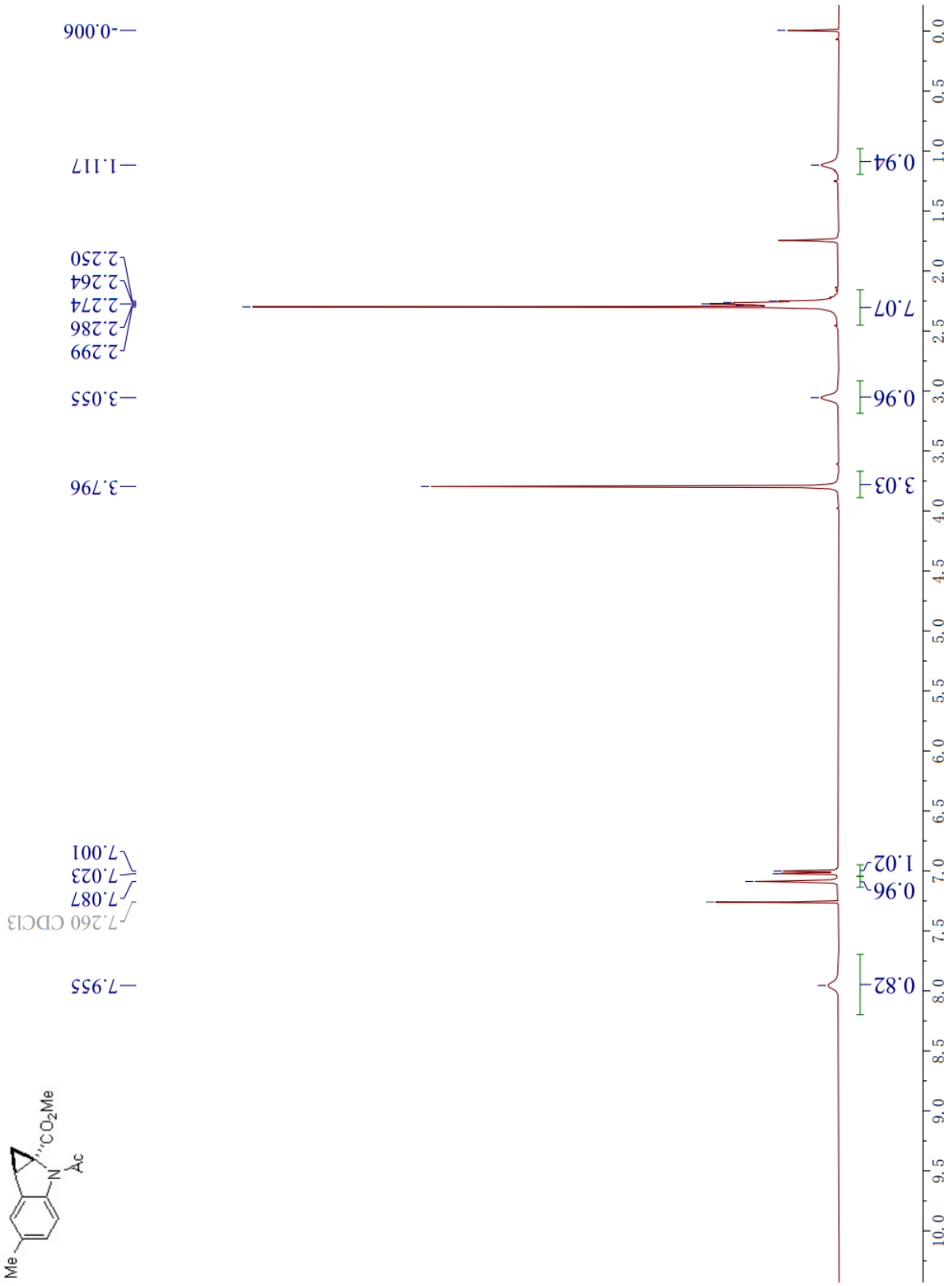

19.28
23.50
32.97
39.52 DMSO-d6
49.05
52.30
116.08
122.93
123.99
127.15
130.09
143.46
168.74
169.55
CO2Me
N
Ac

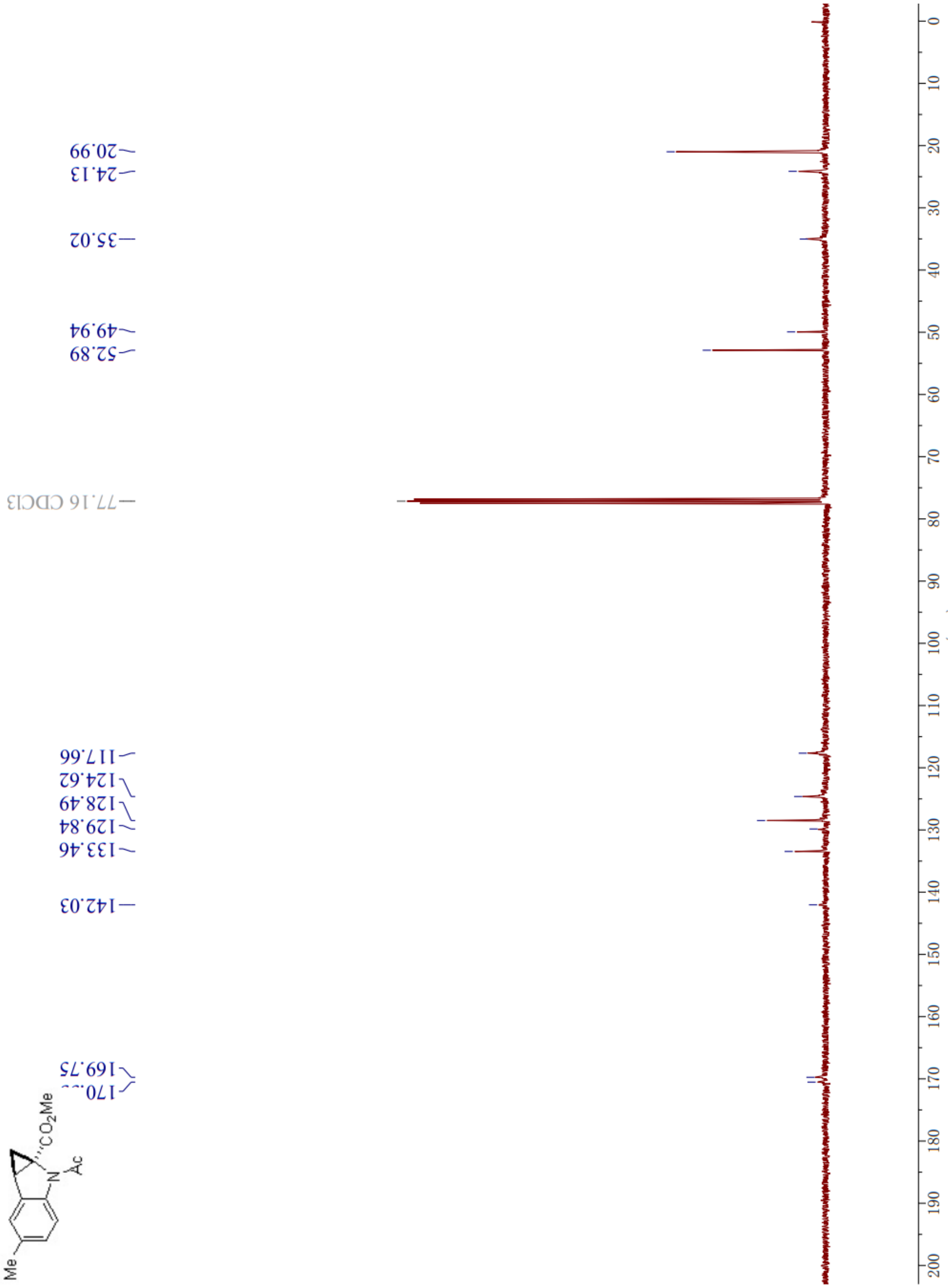
5c


-0.005
1.043
1.491
2.196
2.209
2.219
2.232
2.317
3.021
3.022
3.035
3.044
3.057
7.003
7.006
7.022
7.025
7.041
7.043
7.191
7.194
7.211
7.214
7.230
7.234
7.260
7.260 CDCl3
7.269
7.288
8.099
1.03
9.27
1.07
3.04
1.01
1.04
1.03
1.01
0.89
CO2tBu
Ac
N


20.30
24.29
28.08
34.42
50.40
77.16 CDCl3
82.94
117.92
123.57
123.92
127.92
130.18
144.43
168.15
170.75
CO2tBu
N
Ac
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190

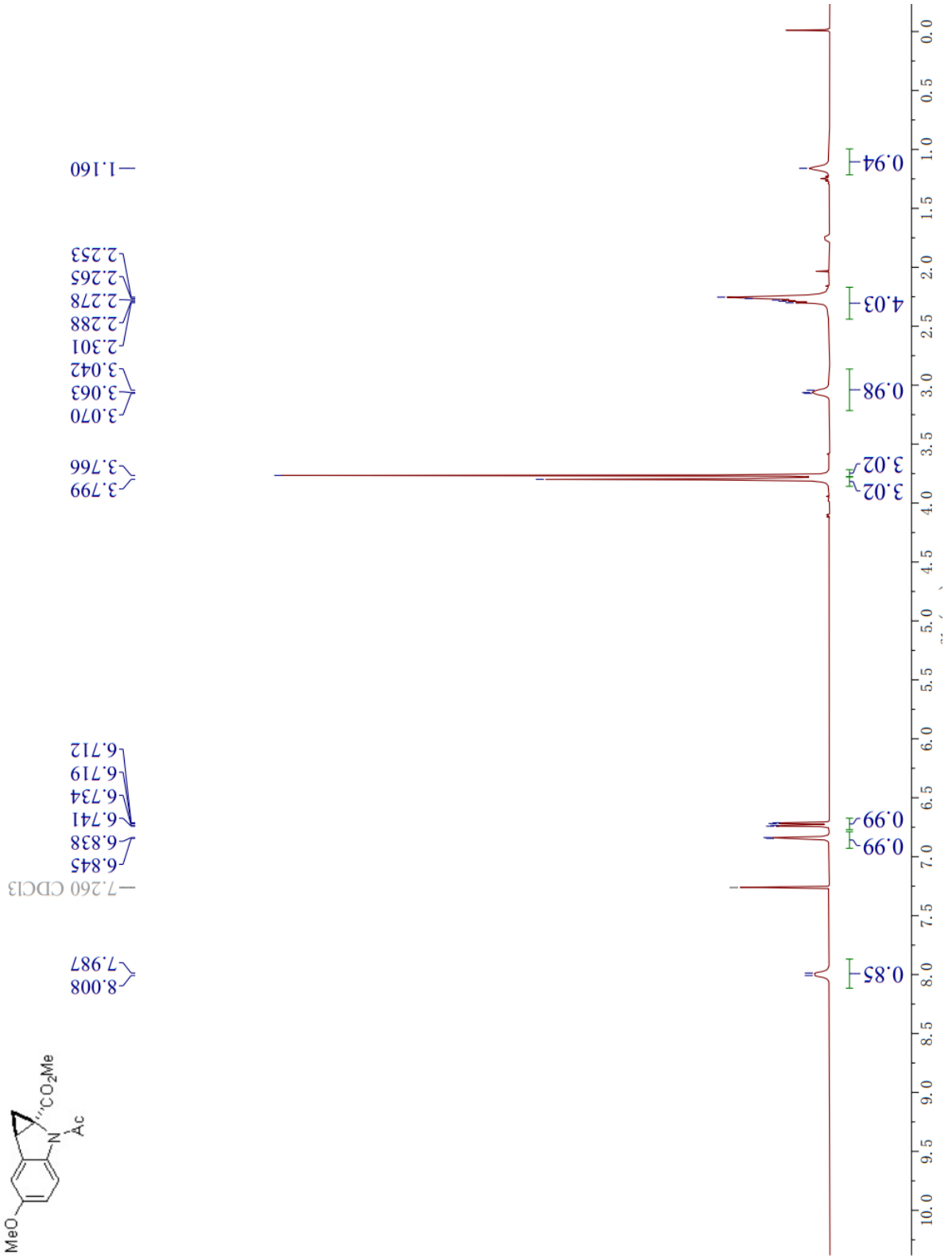
5d

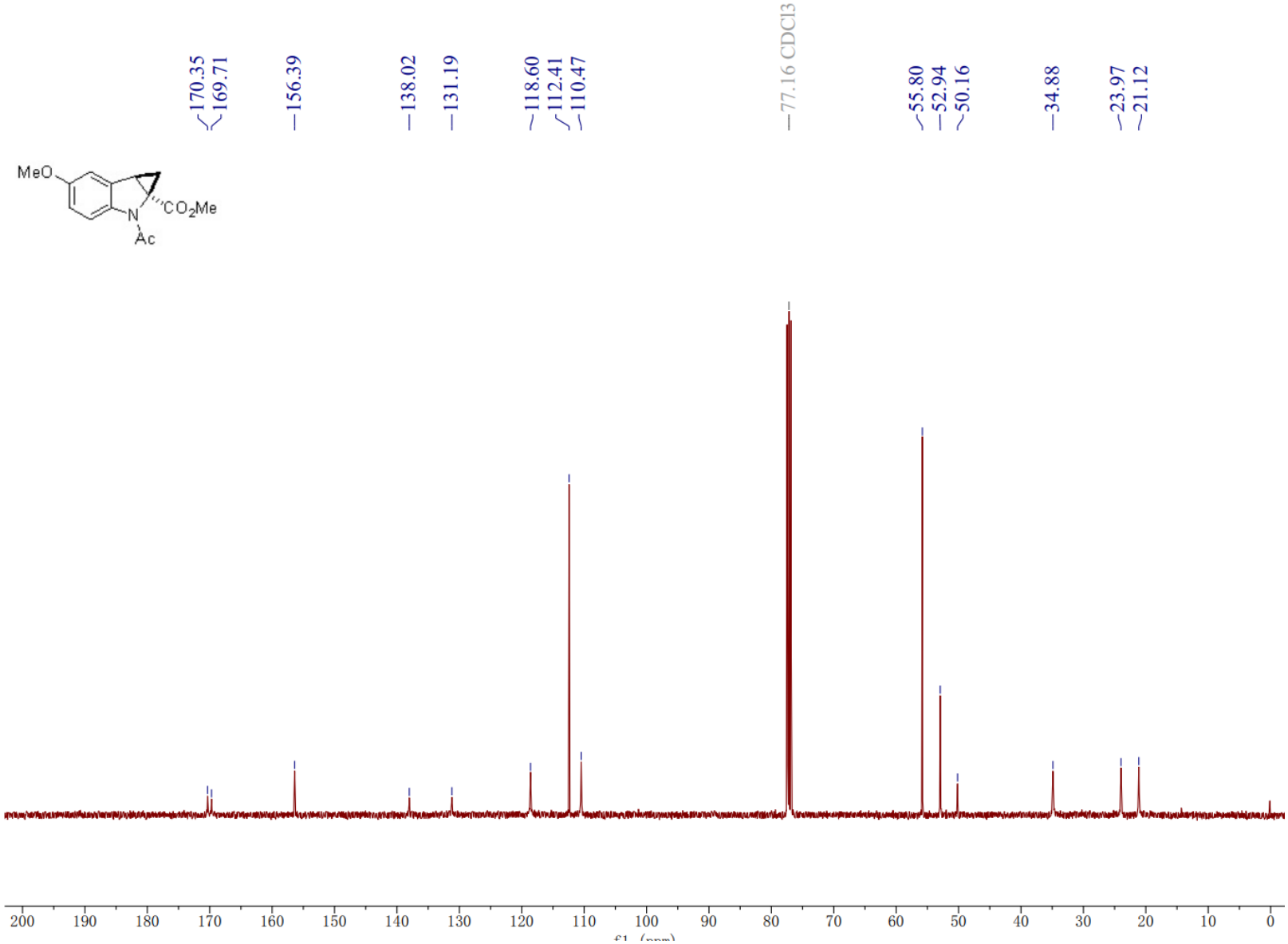

0.006
1.117
2.250
2.264
2.274
2.286
2.299
3.055
3.796
7.001
7.023
7.087
7.260 CDCl3
7.955
0.94
7.07
0.96
3.03
1.02
0.96
0.82
Me
N
Ac
CO2Me



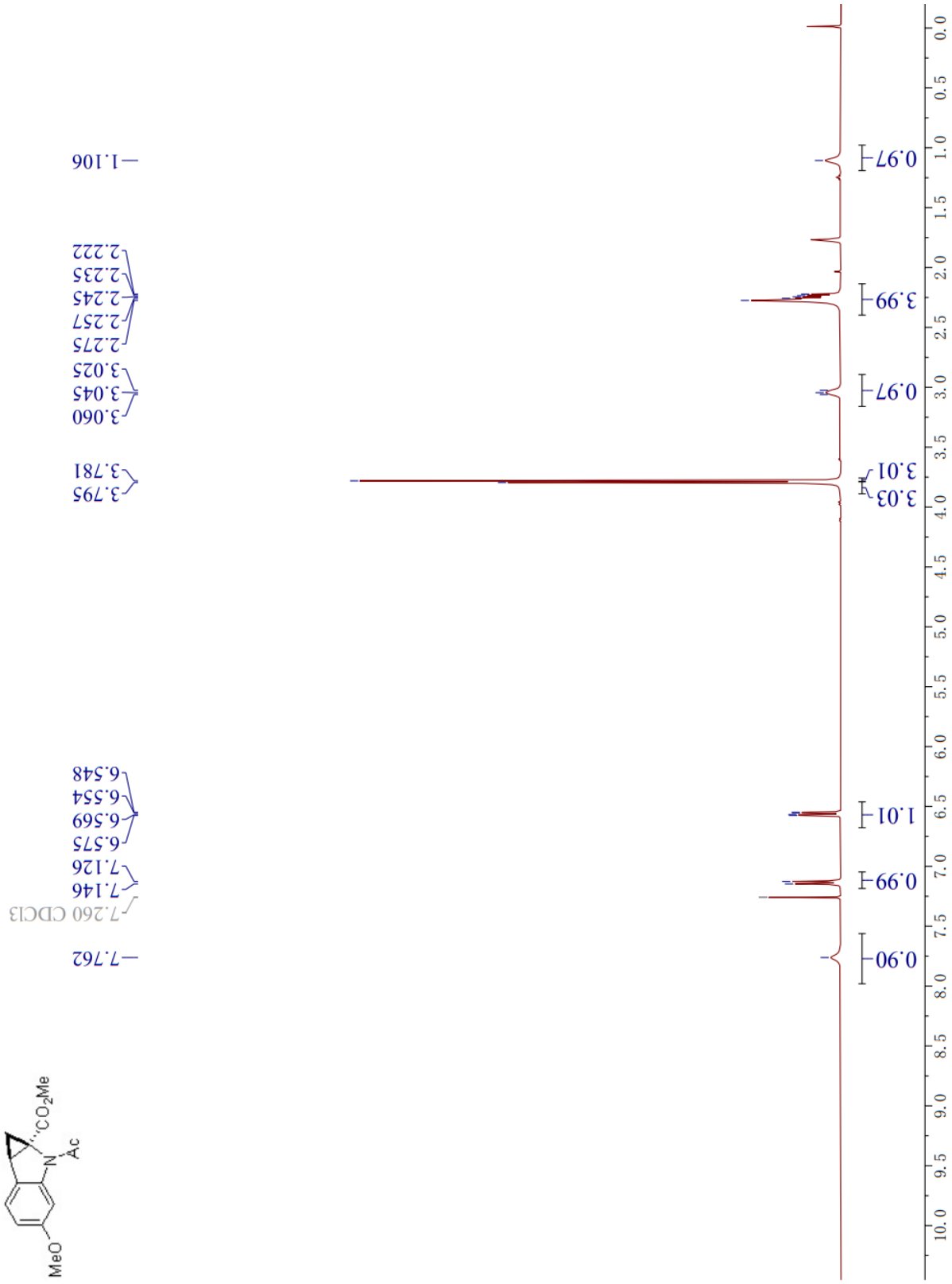
20.99
24.13
35.02
49.94
52.89
77.16 CDCl3
117.66
124.62
128.49
129.84
133.46
142.03
169.75
Me
N
Ac
CO2Me
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200

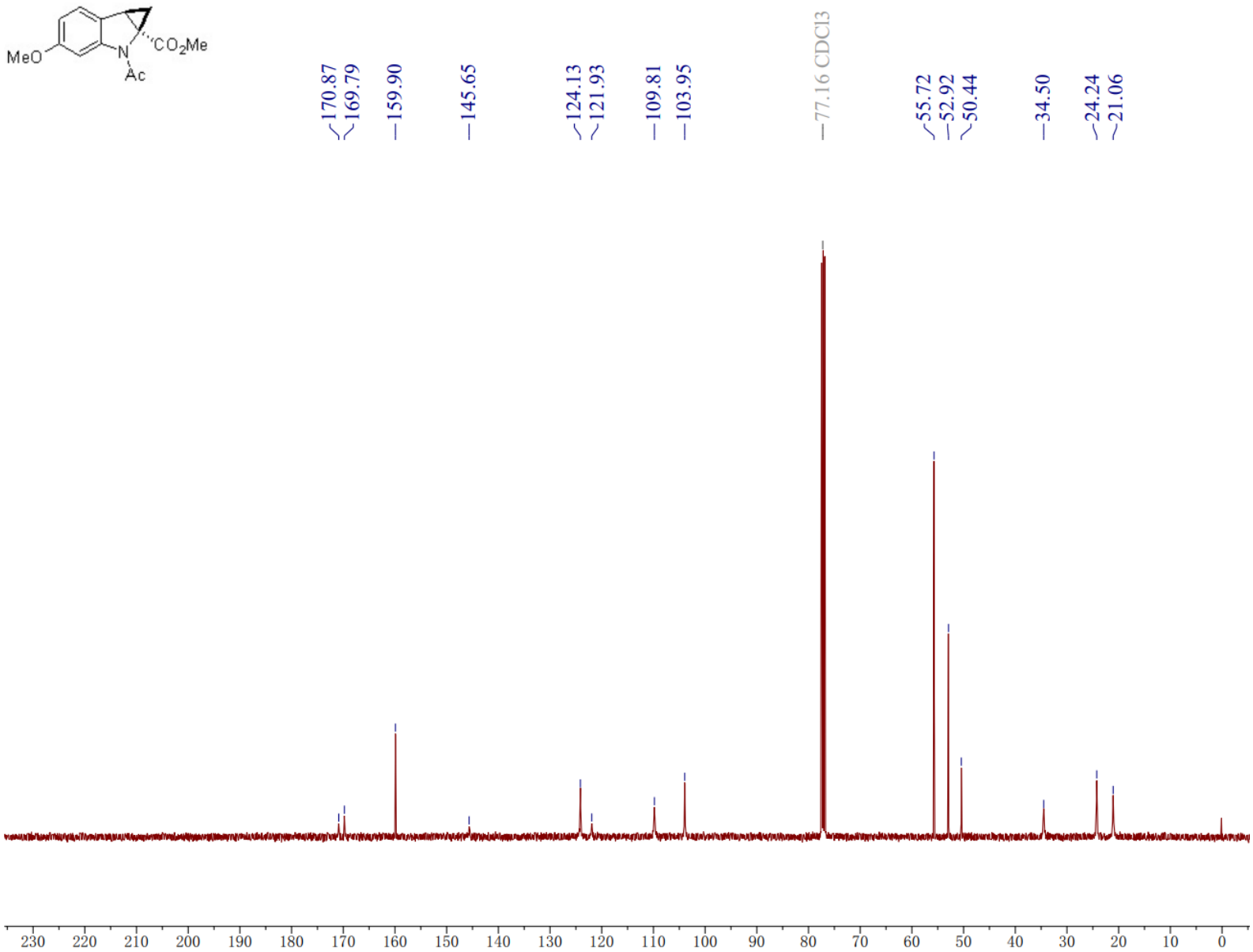
5e


1.160
2.253
2.265
2.278
2.288
2.301
3.042
3.063
3.070
3.766
3.799
6.712
6.719
6.734
6.741
6.838
6.845
7.260 CDCl3
7.987
8.008
0.94
4.03
0.98
3.02
3.02
0.99
0.99
0.85
MeO
N
Ac
CO2Me

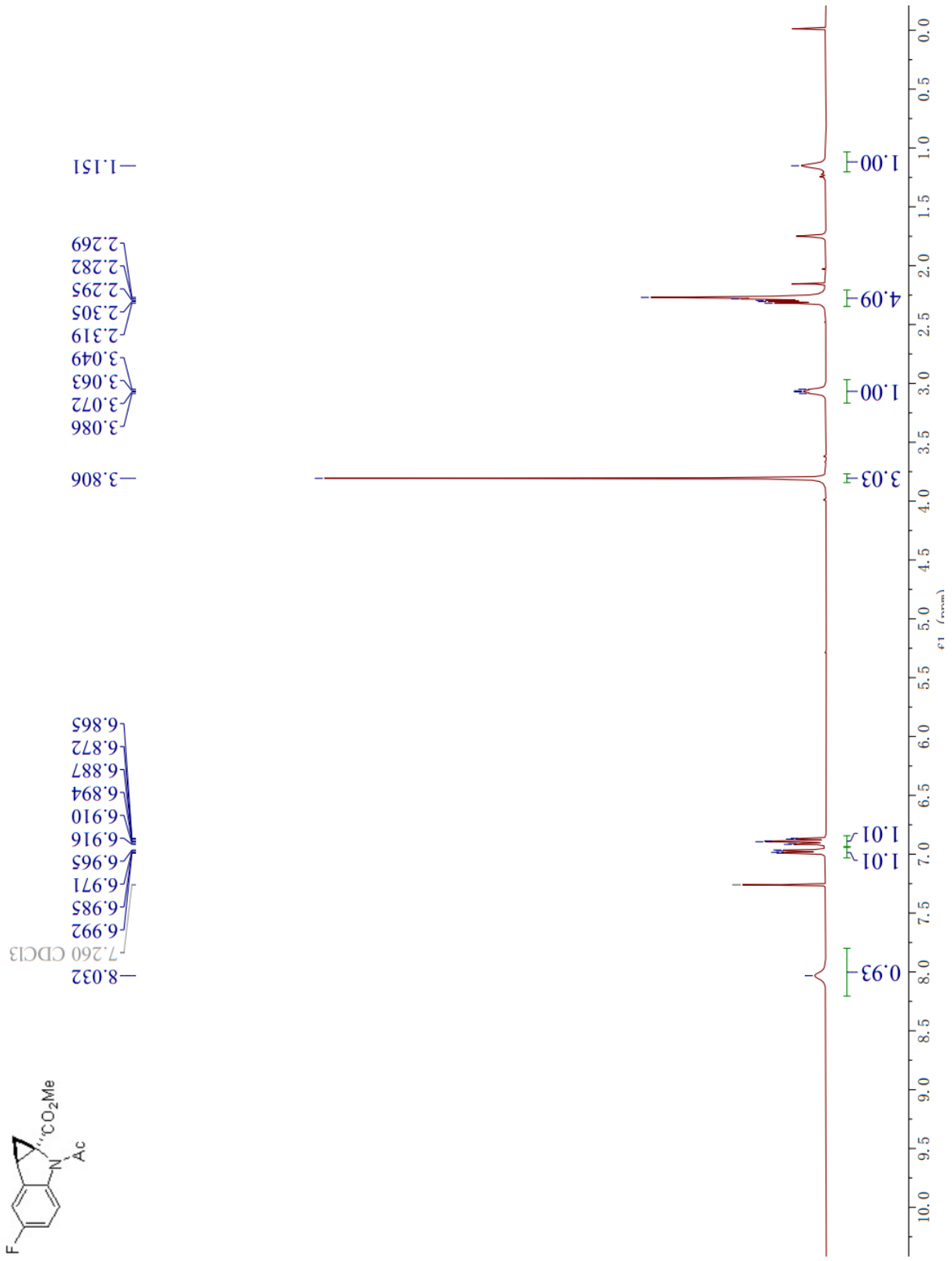

170.35
169.71
156.39
138.02
131.19
118.60
112.41
110.47
77.16 CDCl3
55.80
52.94
50.16
34.88
23.97
21.12
MeO
CO2Me
N
Ac
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

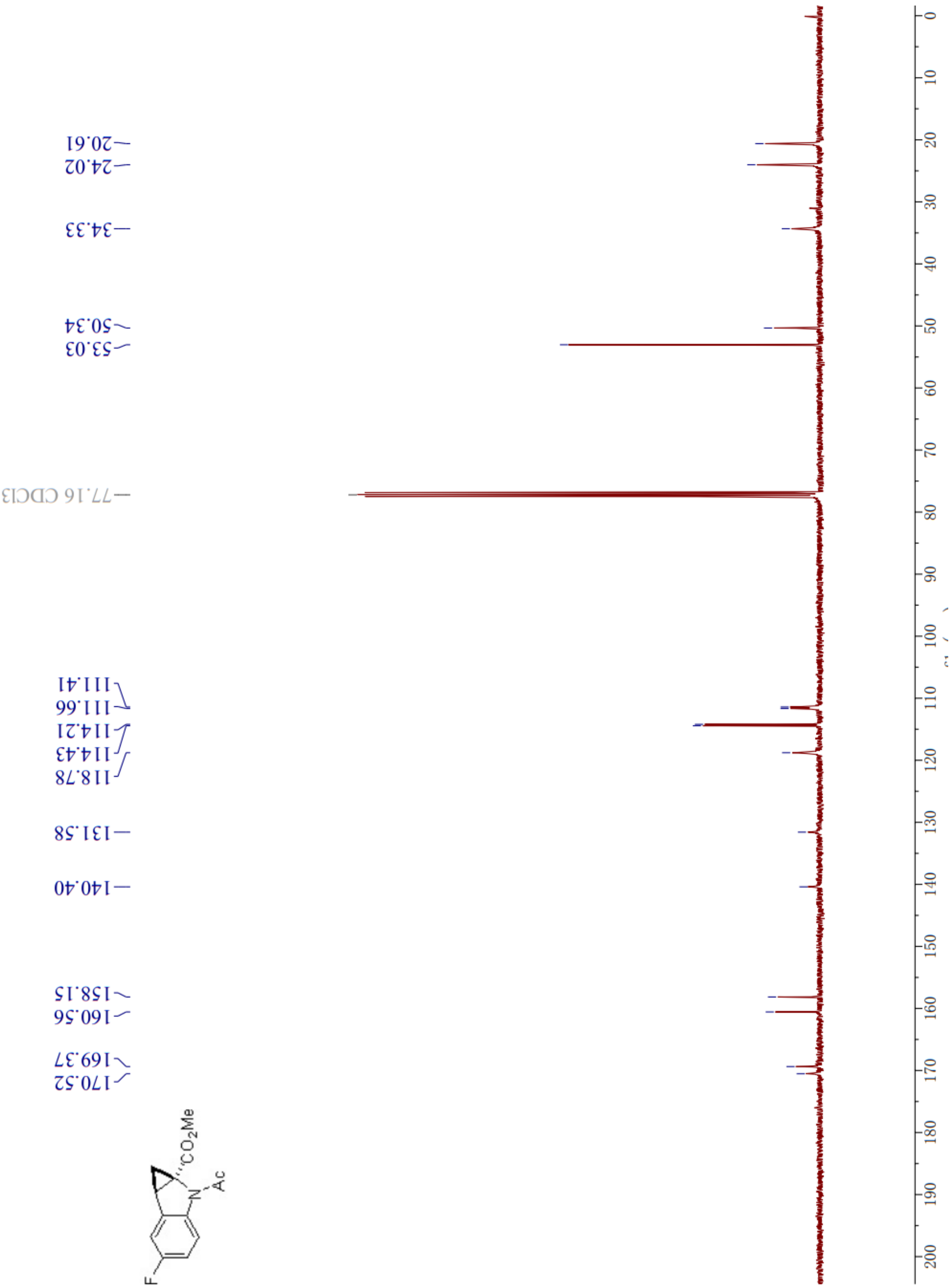
5f

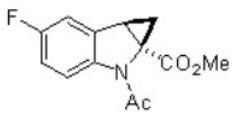

1.106
2.222
2.235
2.245
2.257
2.275
3.025
3.045
3.060
3.781
3.795
6.548
6.554
6.569
6.575
7.126
7.146
7.260 CDCl3
7.762
0.97
3.99
0.97
3.01
3.03
1.01
0.99
0.90
CO2Me
Ac
N
MeO


MeO
CO2Me
N
Ac
170.87
169.79
159.90
145.65
124.13
121.93
109.81
103.95
77.16 CDCl3
55.72
52.92
50.44
34.50
24.24
21.06
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

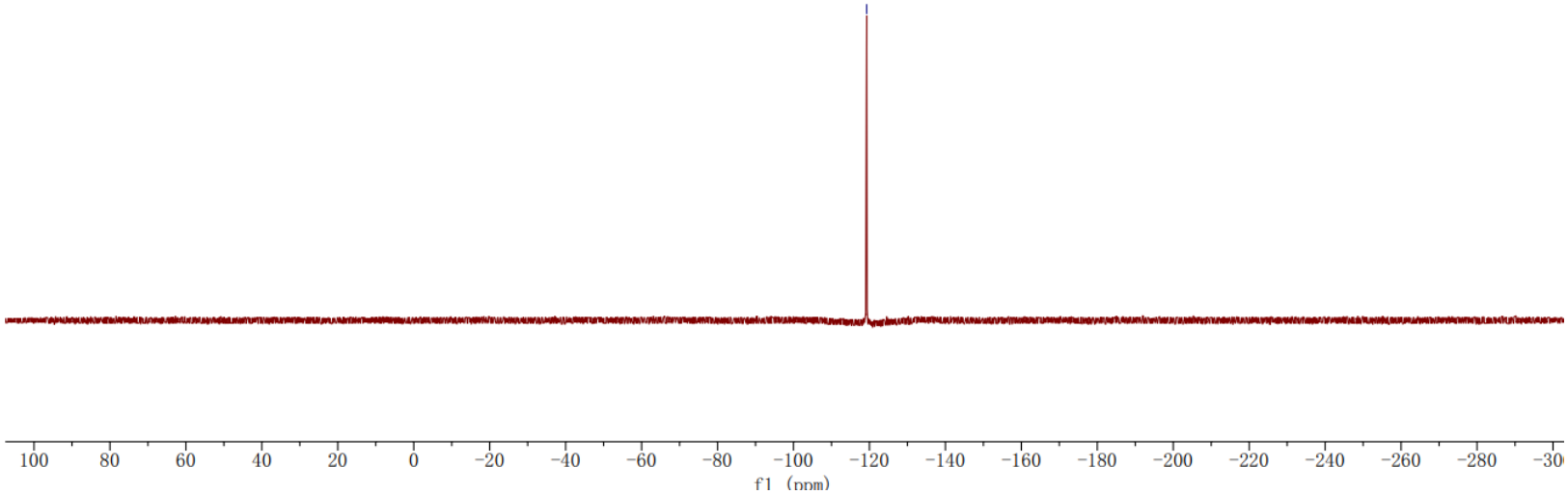
5g


8.032
7.260 CDCl3
6.992
6.985
6.971
6.965
6.916
6.910
6.894
6.887
6.872
6.865
3.806
3.086
3.072
3.063
3.049
2.319
2.305
2.295
2.282
2.269
1.151
1.00
4.09
1.00
3.03
1.01
1.01
0.93
F
N
Ac
CO2Me

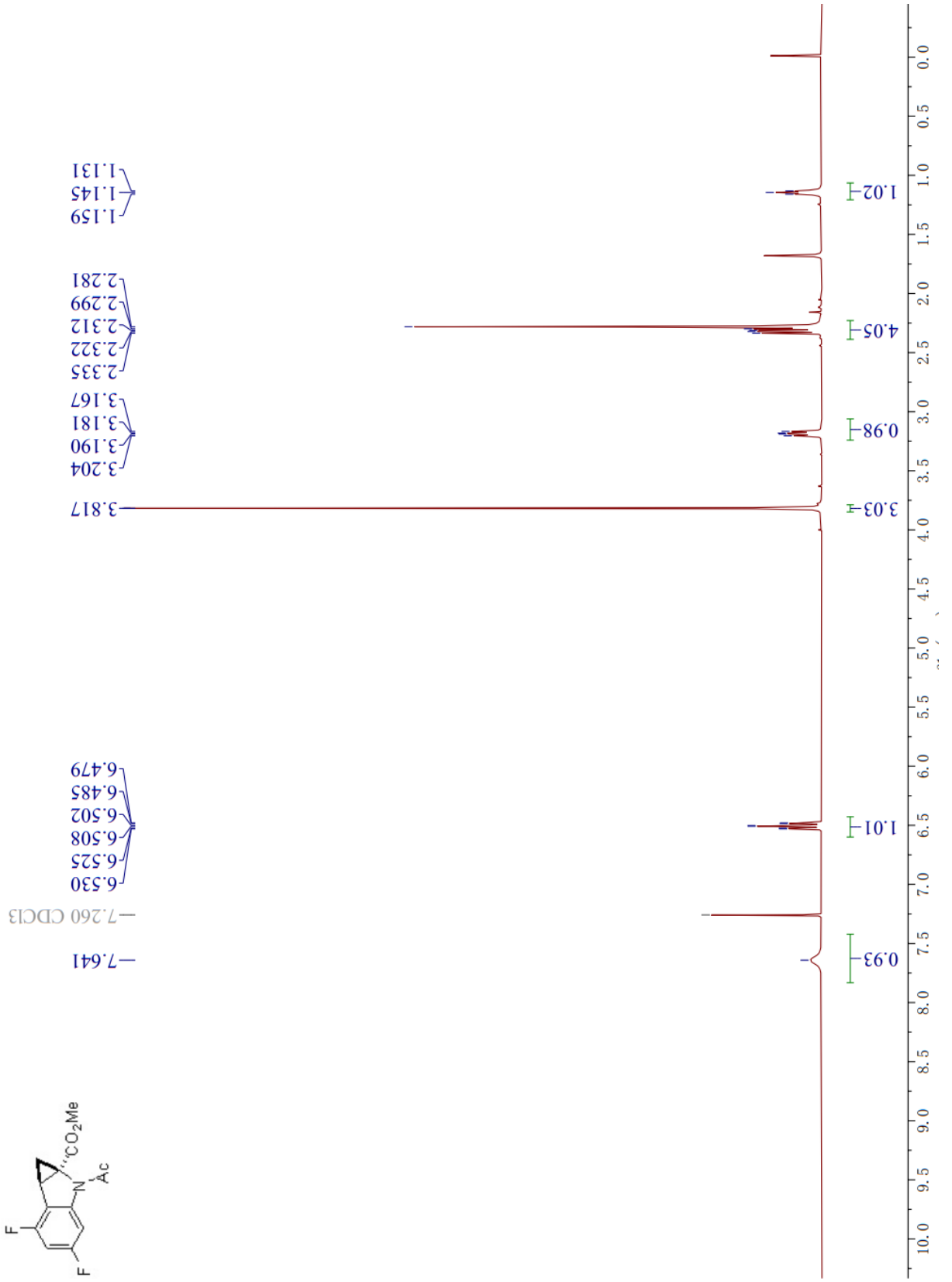

20.61
24.02
34.33
50.34
53.03
77.16 CDCl3
111.41
111.66
114.21
114.43
118.78
131.58
140.40
158.15
160.56
169.37
170.52
CO2Me
N
Ac
F

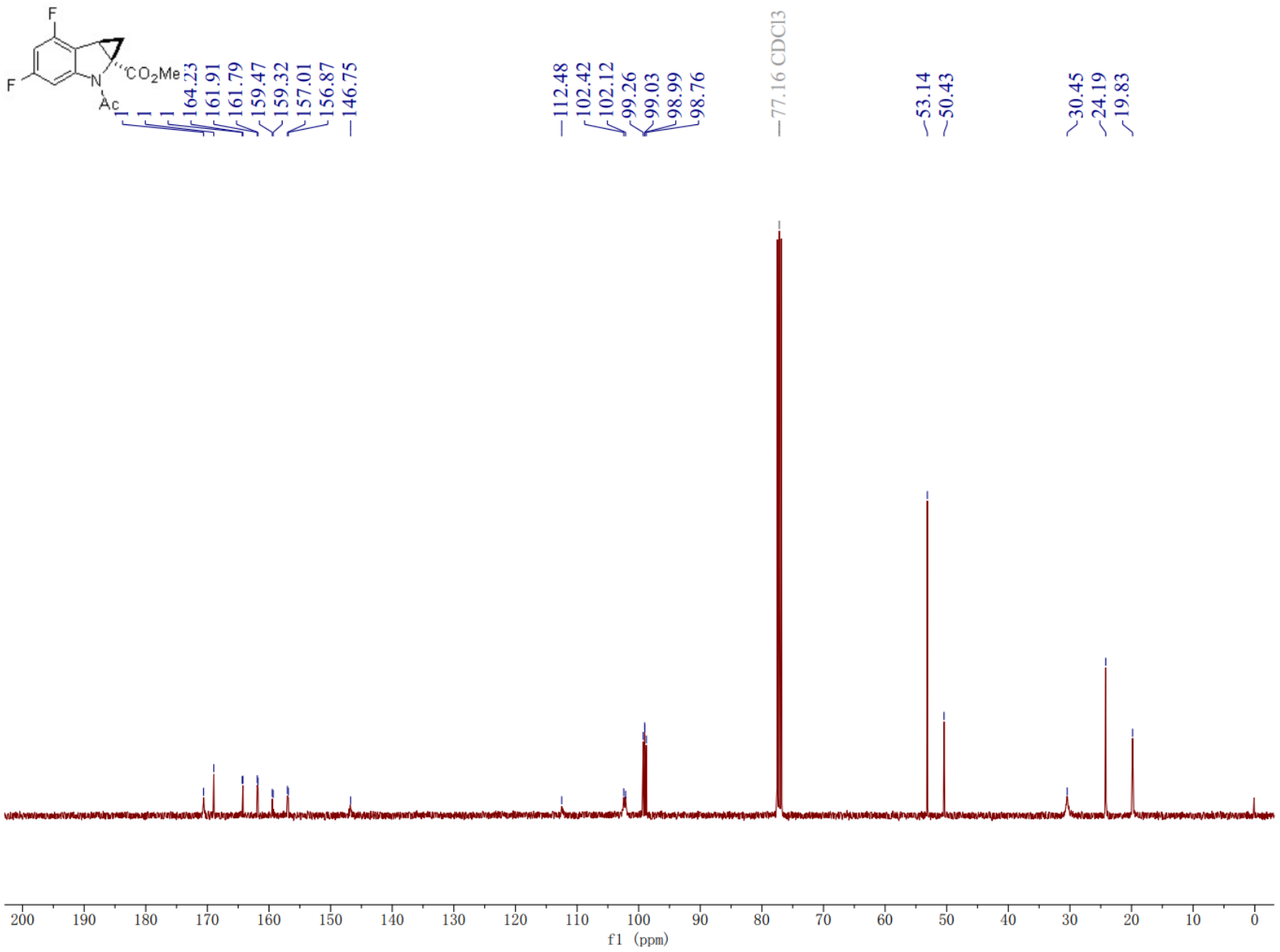

F
CO2Me
N
Ac

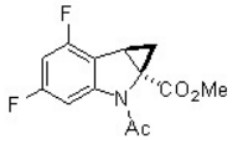
-119.27


100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
f1 (ppm)

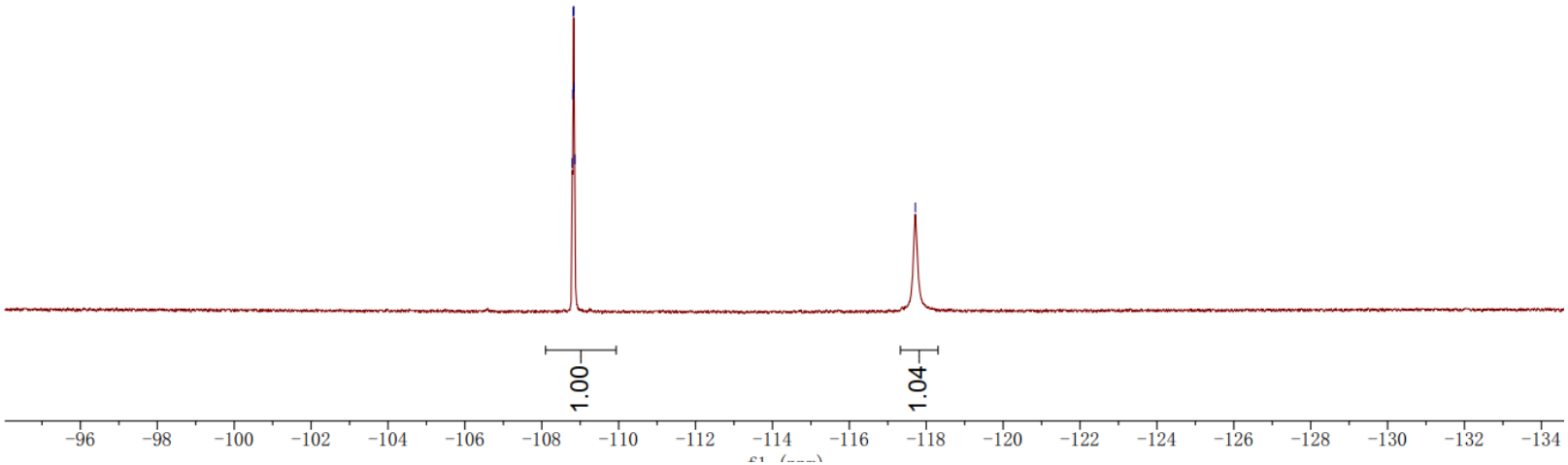
5h


1.131
1.145
1.159
2.281
2.299
2.312
2.322
2.335
3.167
3.181
3.190
3.204
3.817
6.479
6.485
6.502
6.508
6.525
6.530
7.260 CDCl3
7.641
1.02
4.05
0.98
3.03
1.01
0.93
F
F
N
Ac
CO2Me

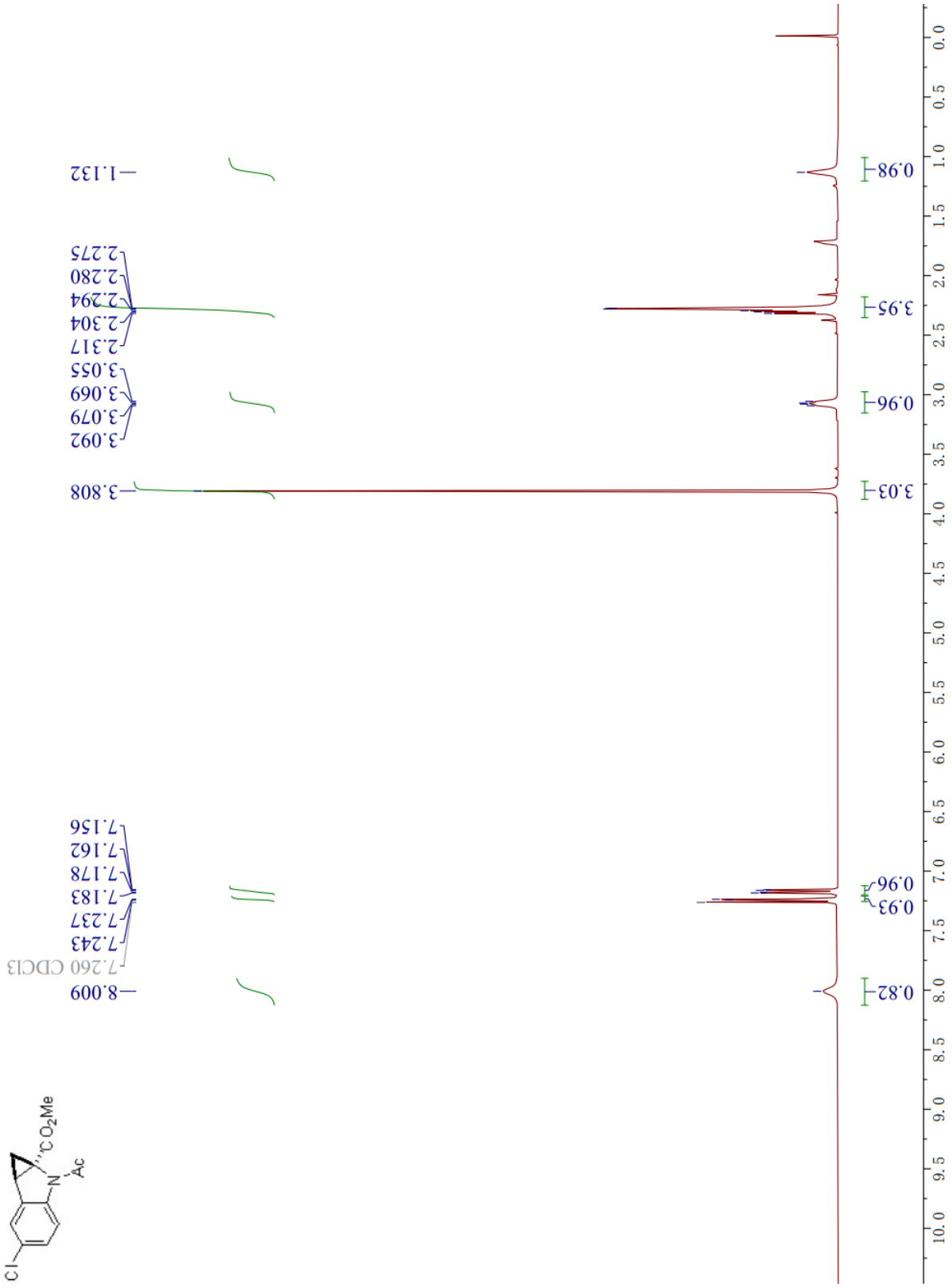

F
F
N
Ac
CO2Me
164.23
161.91
161.79
159.47
159.32
157.01
156.87
146.75
112.48
102.42
102.12
99.26
99.03
98.99
98.76
77.16 CDCl3
53.14
50.43
30.45
24.19
19.83
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

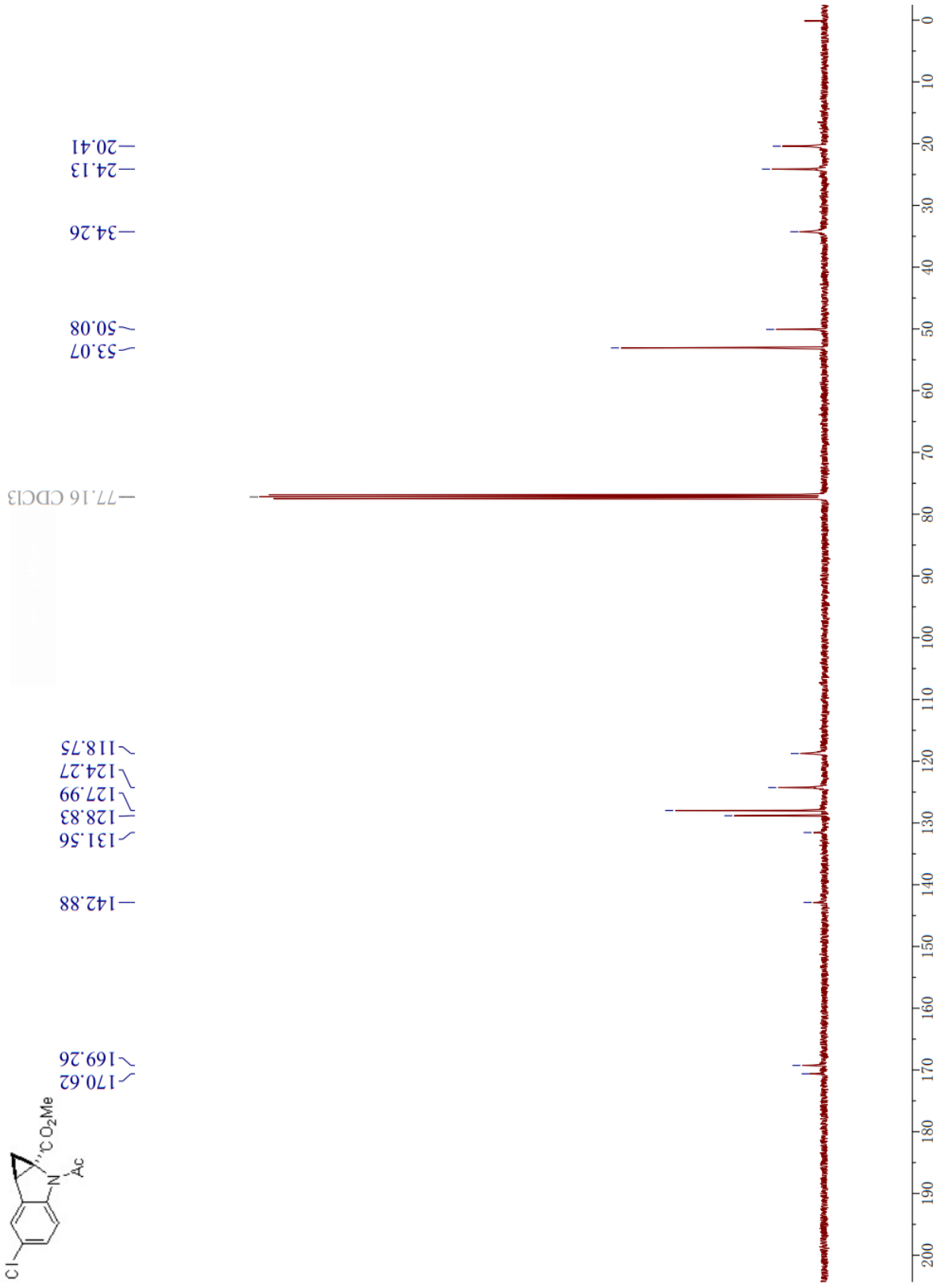

F
F
N
Ac
CO2Me


-108.79
-108.81
-108.82
-108.83
-108.84
-108.86
-117.72

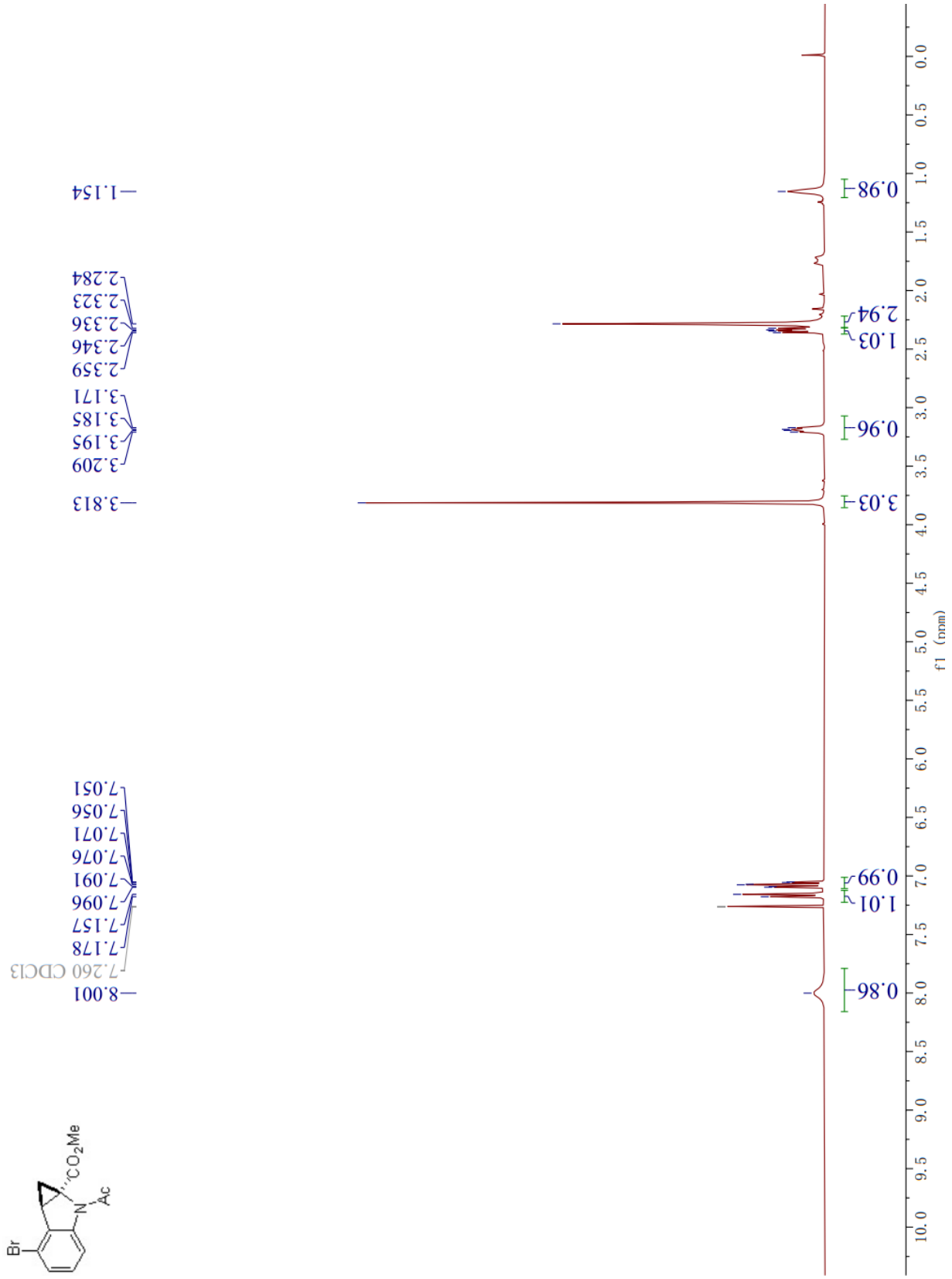

1.00
1.04
-96
-98
-100
-102
-104
-106
-108
-110
-112
-114
-116
-118
-120
-122
-124
-126
-128
-130
-132
-134

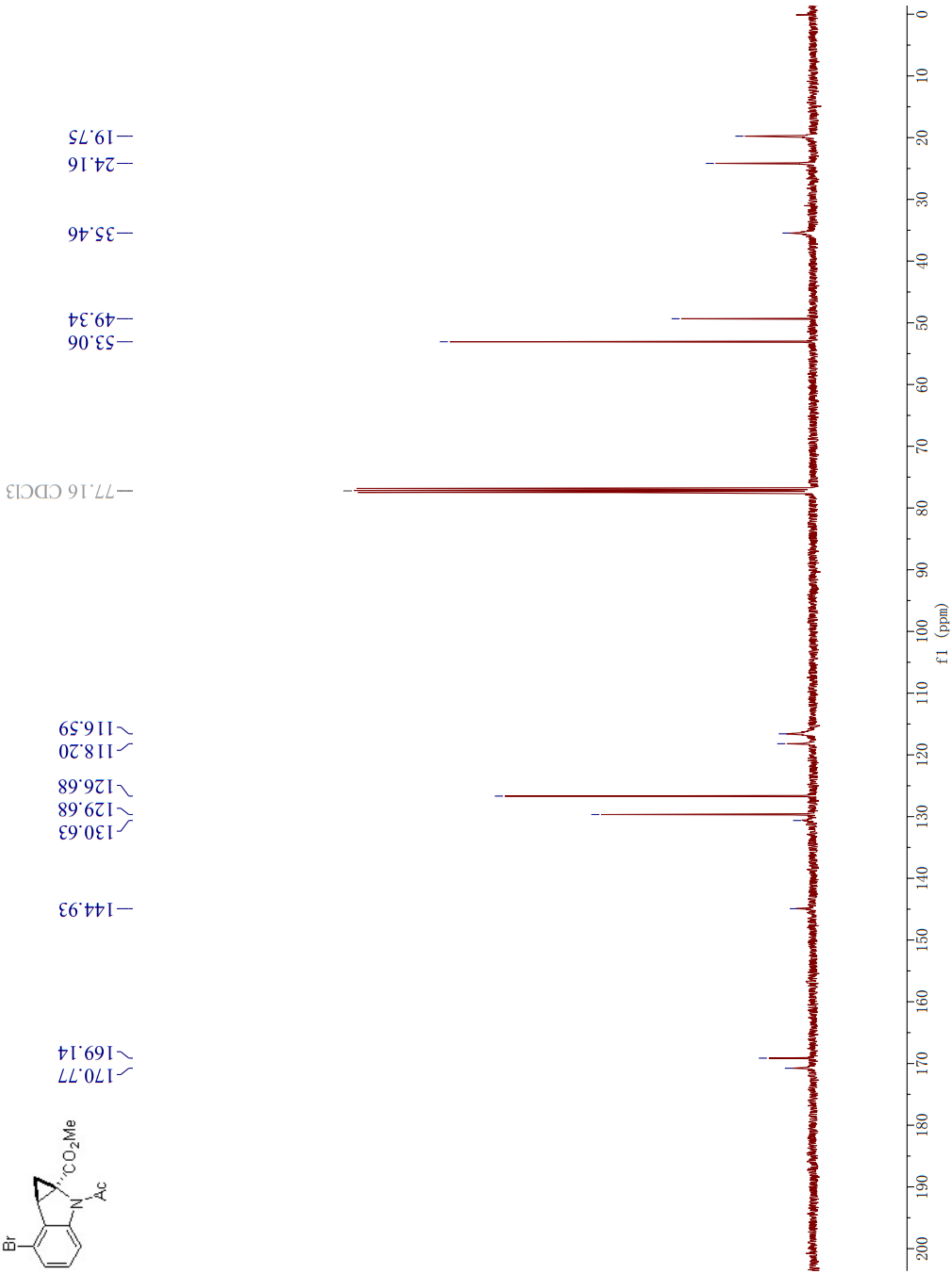
5i


8.009
7.260 CDCl3
7.243
7.237
7.183
7.178
7.162
7.156
3.808
3.092
3.079
3.069
3.055
2.317
2.304
2.294
2.280
2.275
1.132
0.82
0.96
0.93
3.03
0.96
3.95
0.98
Cl
N
Ac
CO2Me

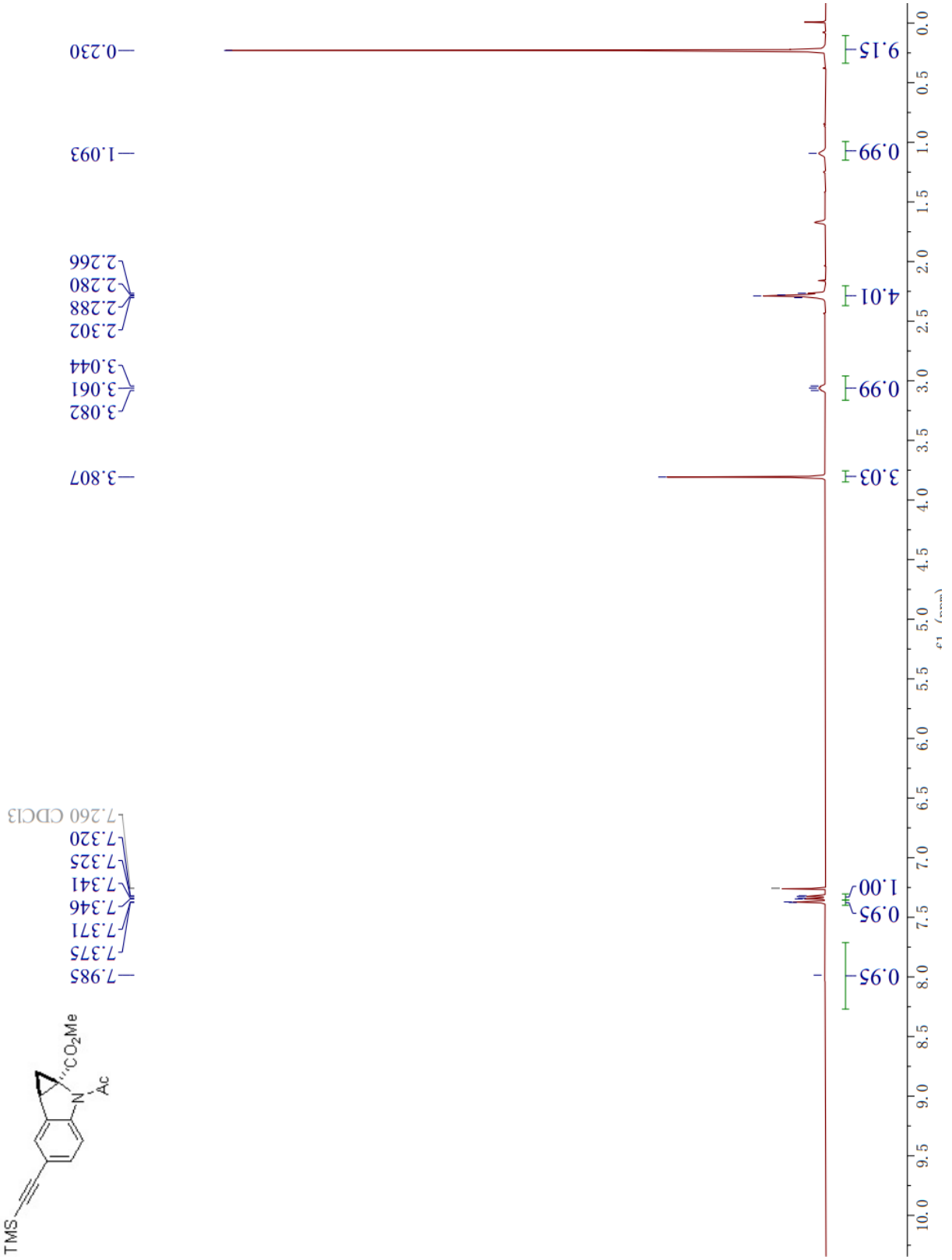

170.62
169.26
142.88
131.56
128.83
127.99
124.27
118.75
77.16 CDCl3
53.07
50.08
34.26
24.13
20.41
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
Cl
N
Ac
CO2Me

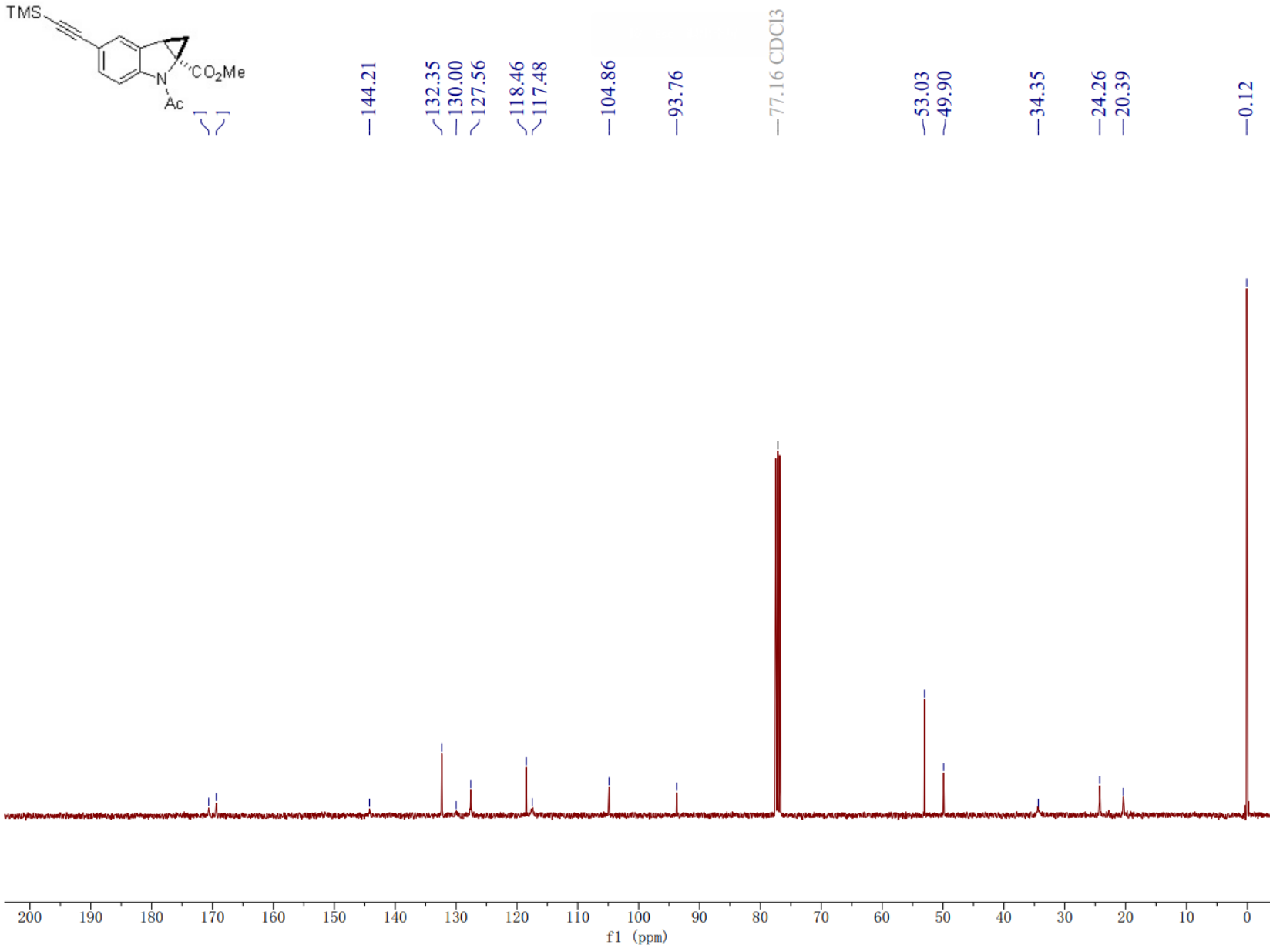
5j


1.154
2.284
2.323
2.336
2.346
2.359
3.171
3.185
3.195
3.209
3.813
7.051
7.056
7.071
7.076
7.091
7.096
7.157
7.178
7.260 CDCl3
8.001
0.98
2.94
1.03
0.96
3.03
0.99
1.01
0.86
f1 (ppm)
Br
N
Ac
CO2Me

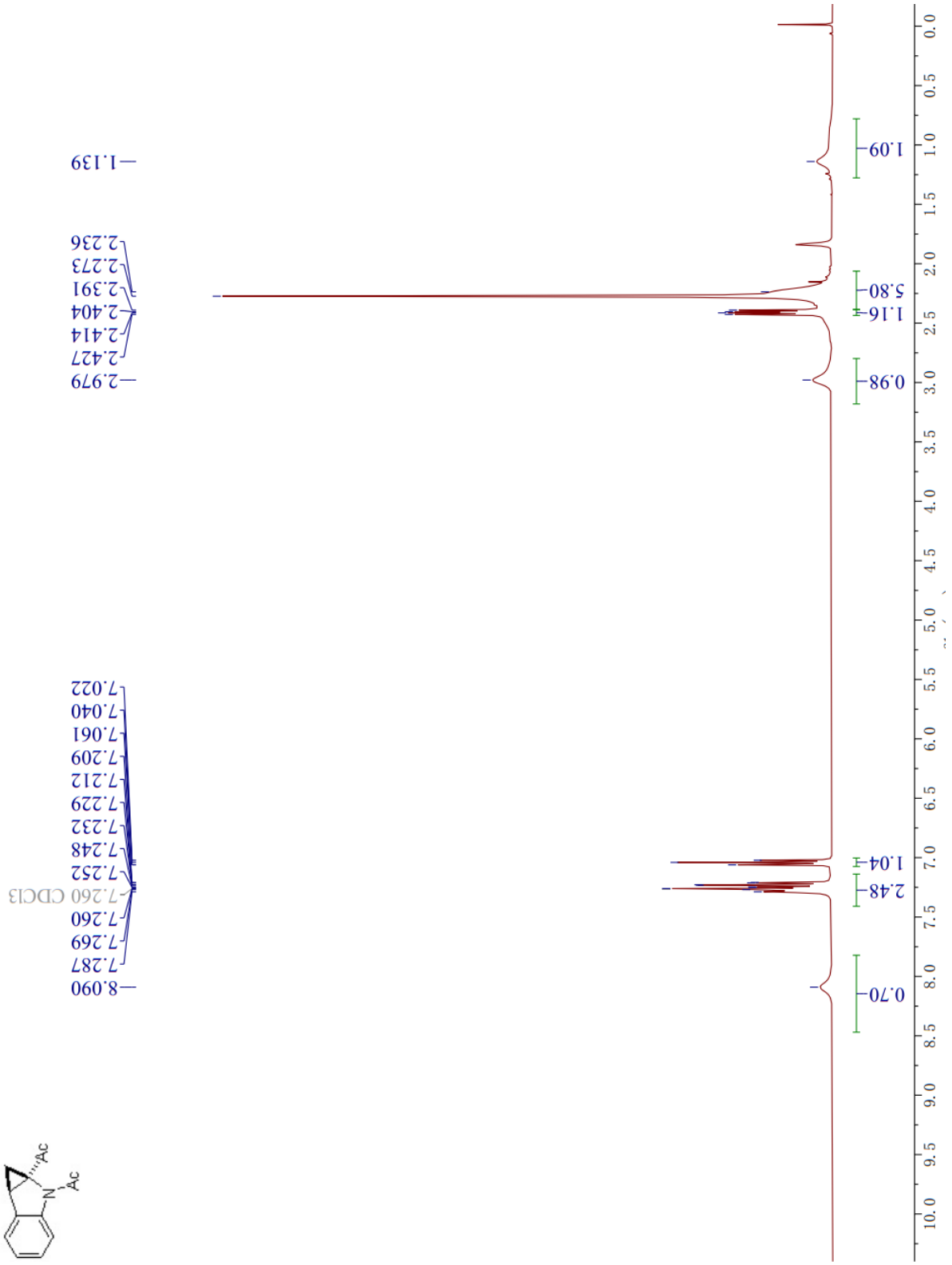

19.75
24.16
35.46
49.34
53.06
77.16 CDCl3
116.59
118.20
126.68
129.68
130.63
144.93
169.14
170.77
Br
N
Ac
CO2Me
f1 (ppm)

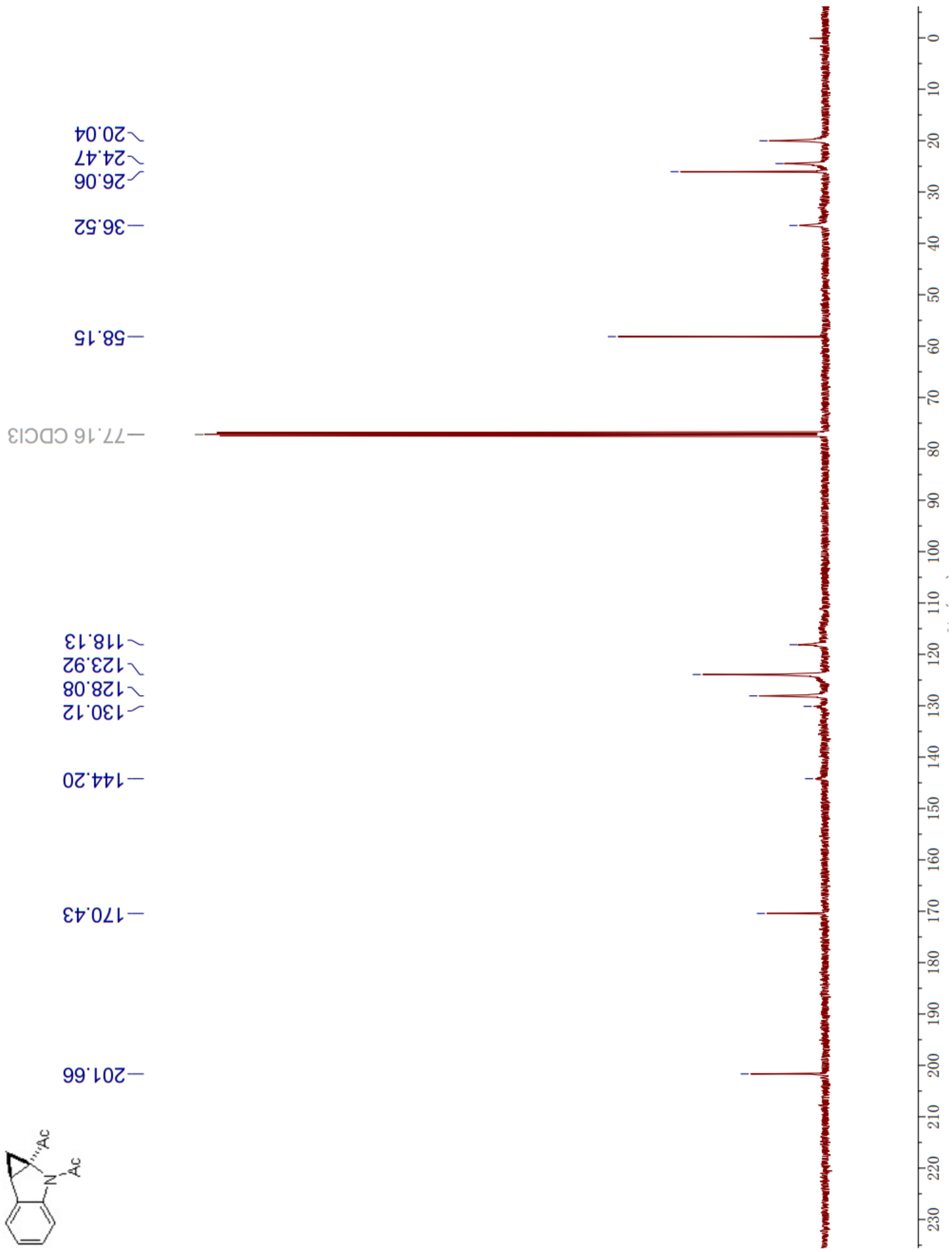
5k


0.230
1.093
2.266
2.280
2.288
2.302
3.044
3.061
3.082
3.807
7.260 CDCl3
7.320
7.325
7.341
7.346
7.371
7.375
7.985
9.15
0.99
4.01
0.99
3.03
1.00
0.95
0.95
TMS
CO2Me
Ac
N

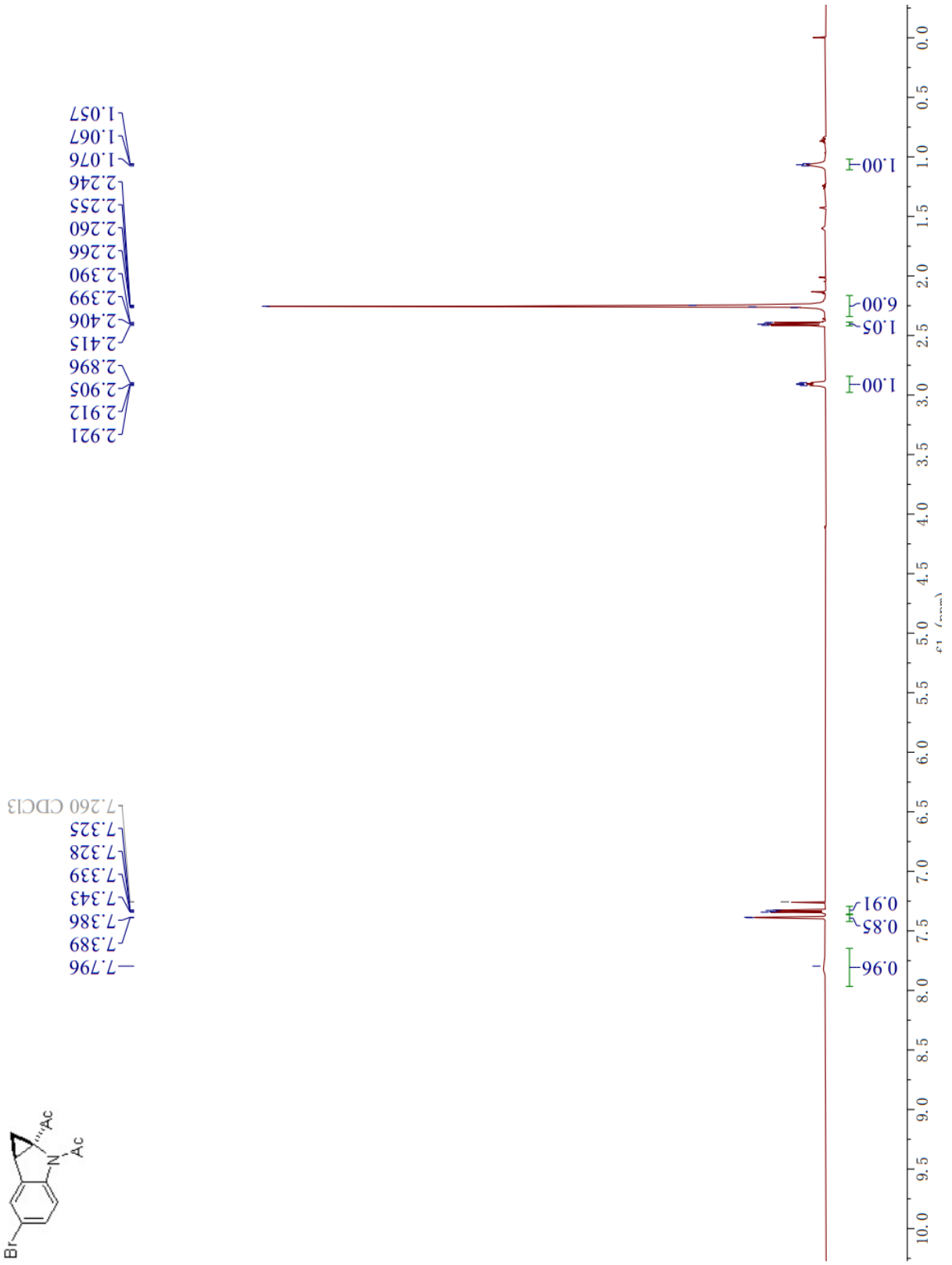

TMS
CO2Me
N
Ac
144.21
132.35
130.00
127.56
118.46
117.48
104.86
93.76
77.16 CDCl3
53.03
49.90
34.35
24.26
20.39
0.12
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

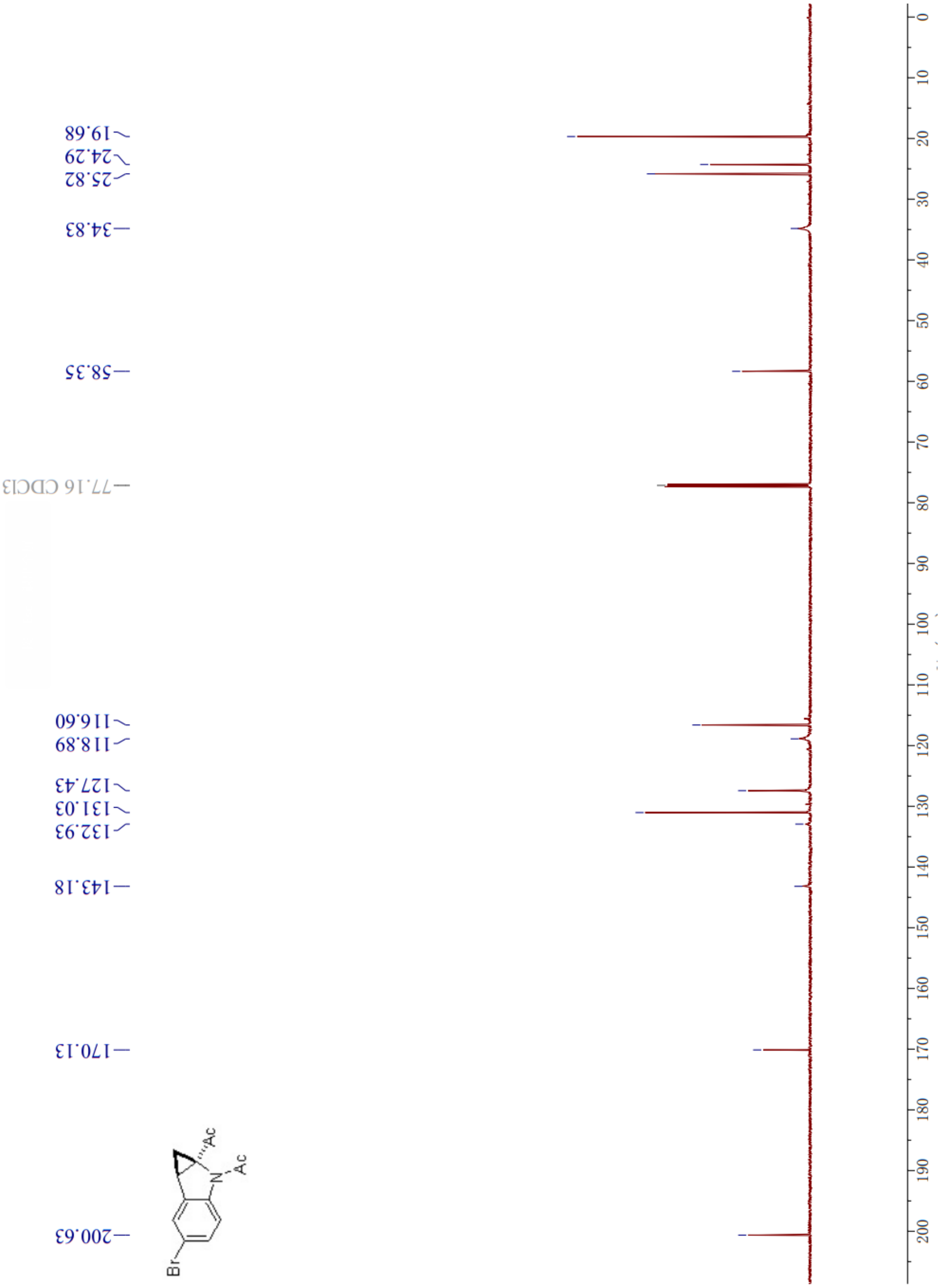
5l


8.090
7.287
7.269
7.260
7.260 CDCl3
7.252
7.248
7.232
7.229
7.212
7.209
7.061
7.040
7.022
2.979
2.427
2.414
2.404
2.391
2.273
2.236
1.139
0.70
2.48
1.04
0.98
1.16
5.80
1.09
Ac
Ac
N

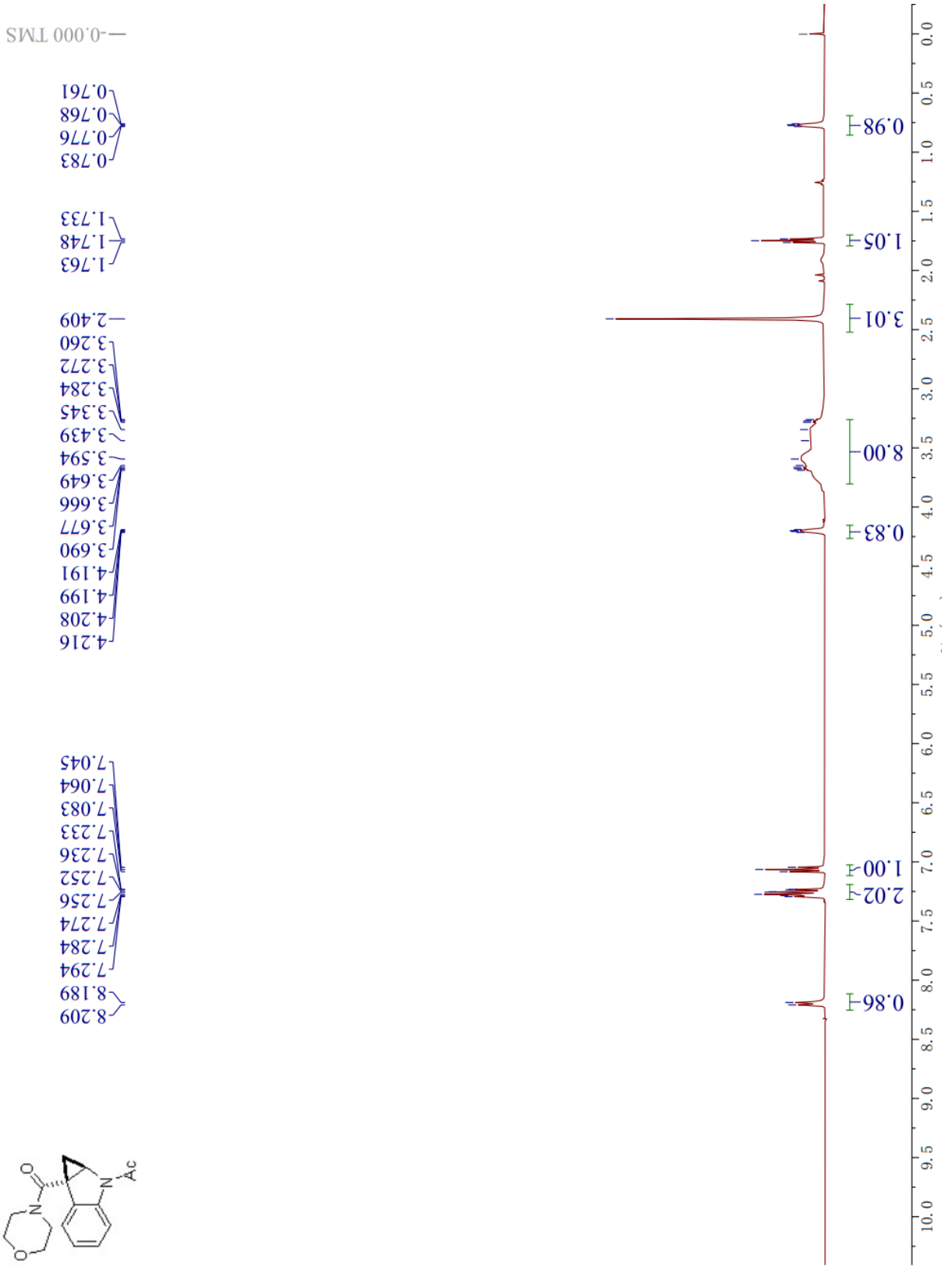

20.04
24.47
26.06
36.52
58.15
77.16 CDCl3
118.13
123.92
128.08
130.12
144.20
170.43
201.66
Ac
N
Ac

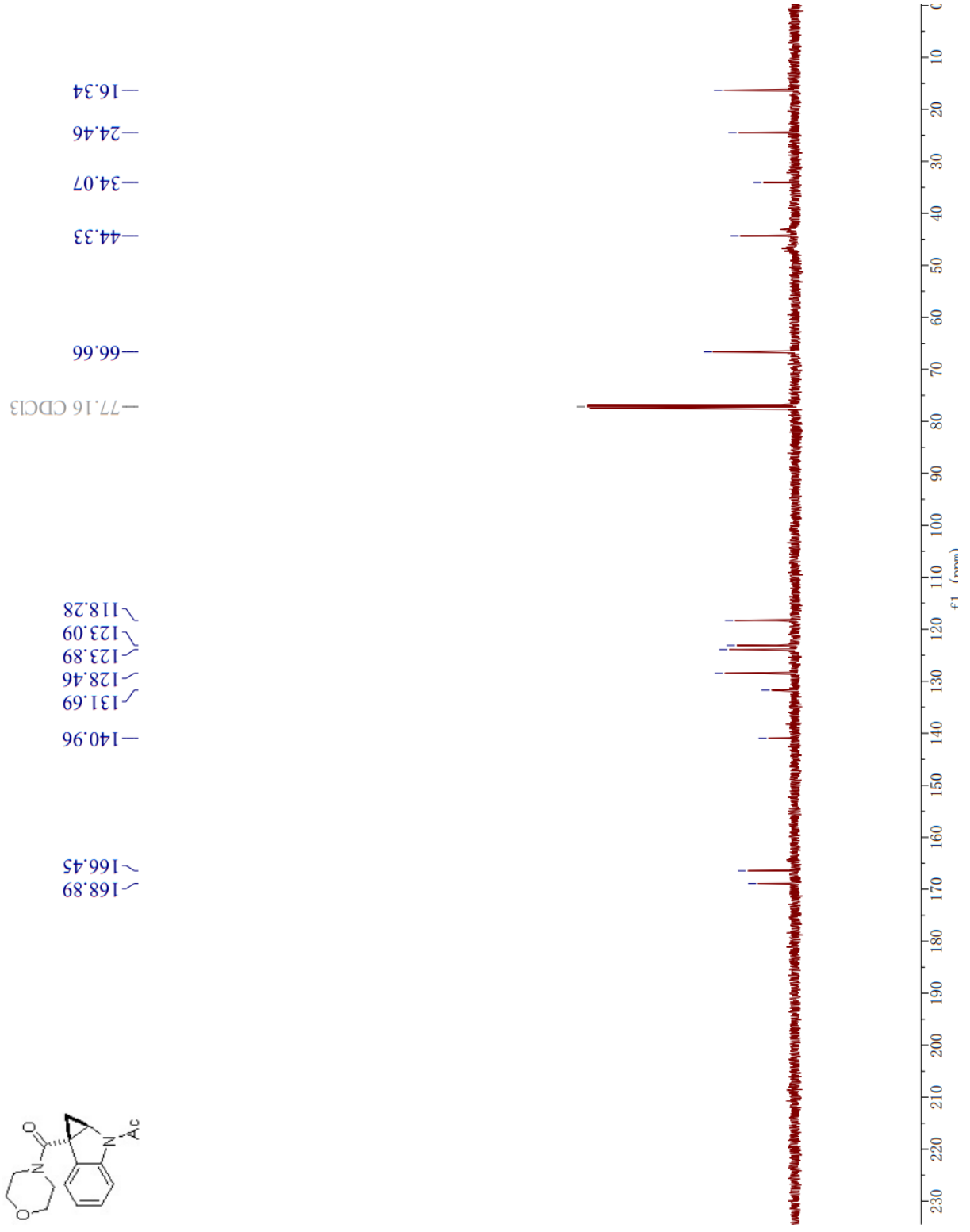
5m


1.057
1.067
1.076
2.246
2.255
2.260
2.266
2.390
2.399
2.406
2.415
2.896
2.905
2.912
2.921
7.260 CDCl3
7.325
7.328
7.339
7.343
7.386
7.389
7.796
1.00
6.00
1.05
1.00
0.91
0.85
0.96
Ac
Ac
N
Br

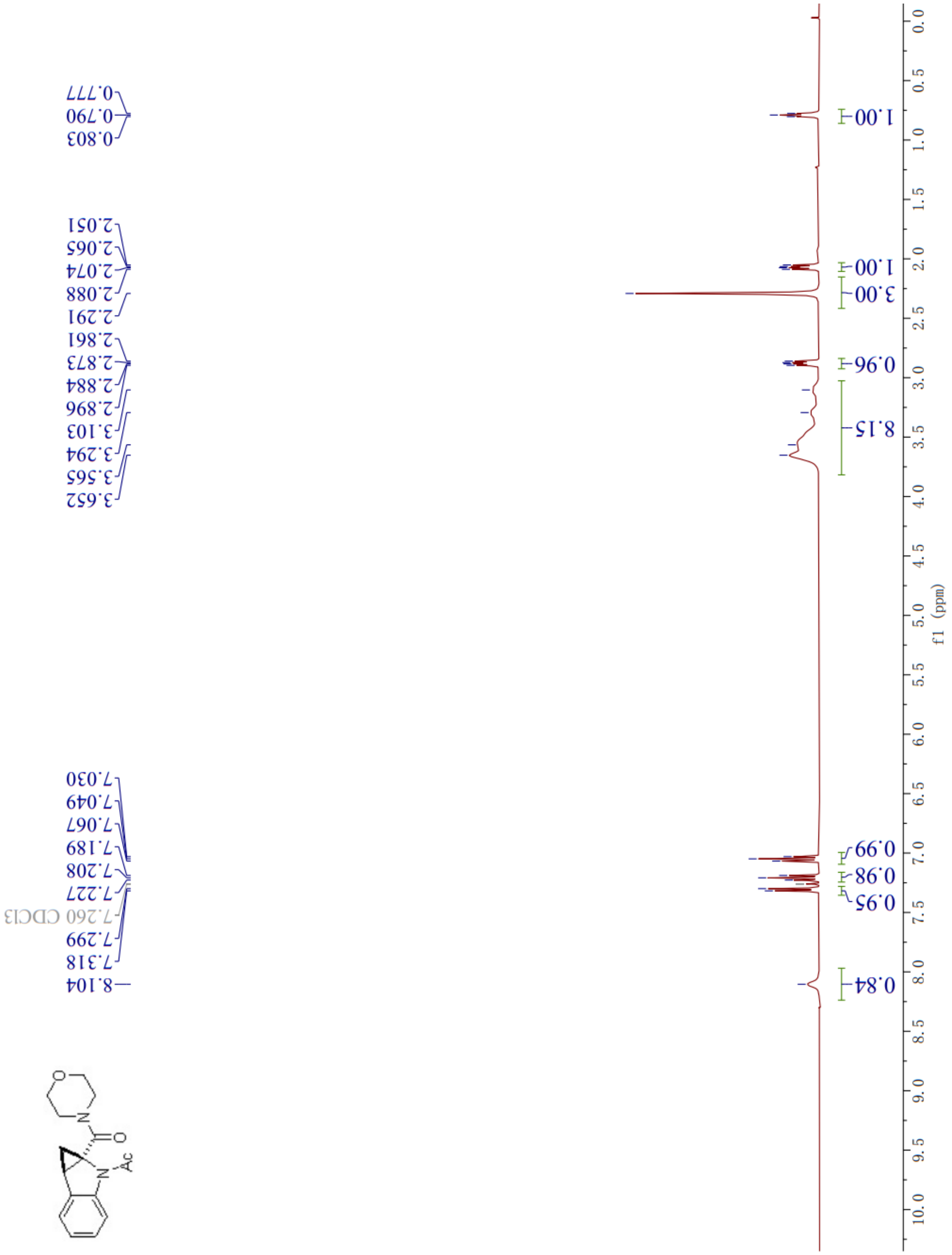

19.68
24.29
25.82
34.83
58.35
77.16 CDCl3
116.60
118.89
127.43
131.03
132.93
143.18
170.13
200.63
Br
N
Ac
Ac
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200

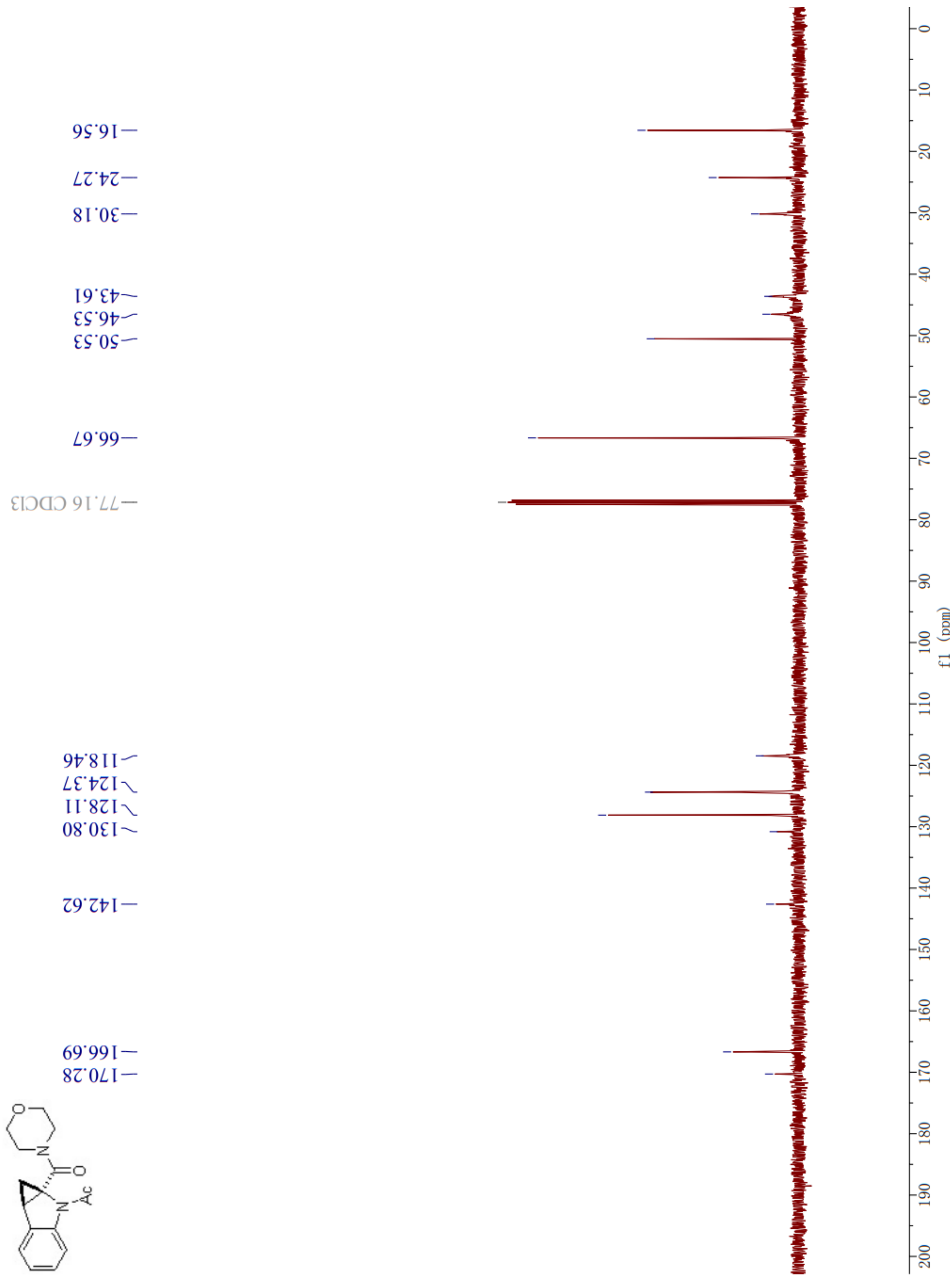
6


TMS 0.000
0.761
0.768
0.776
0.783
1.733
1.748
1.763
2.409
3.260
3.272
3.284
3.345
3.439
3.594
3.649
3.666
3.677
3.690
4.191
4.199
4.208
4.216
7.045
7.064
7.083
7.233
7.236
7.252
7.256
7.274
7.284
7.294
8.189
8.209
0.86
1.00
2.02
0.83
8.00
3.01
1.05
0.98
Ac
N
O
N
O

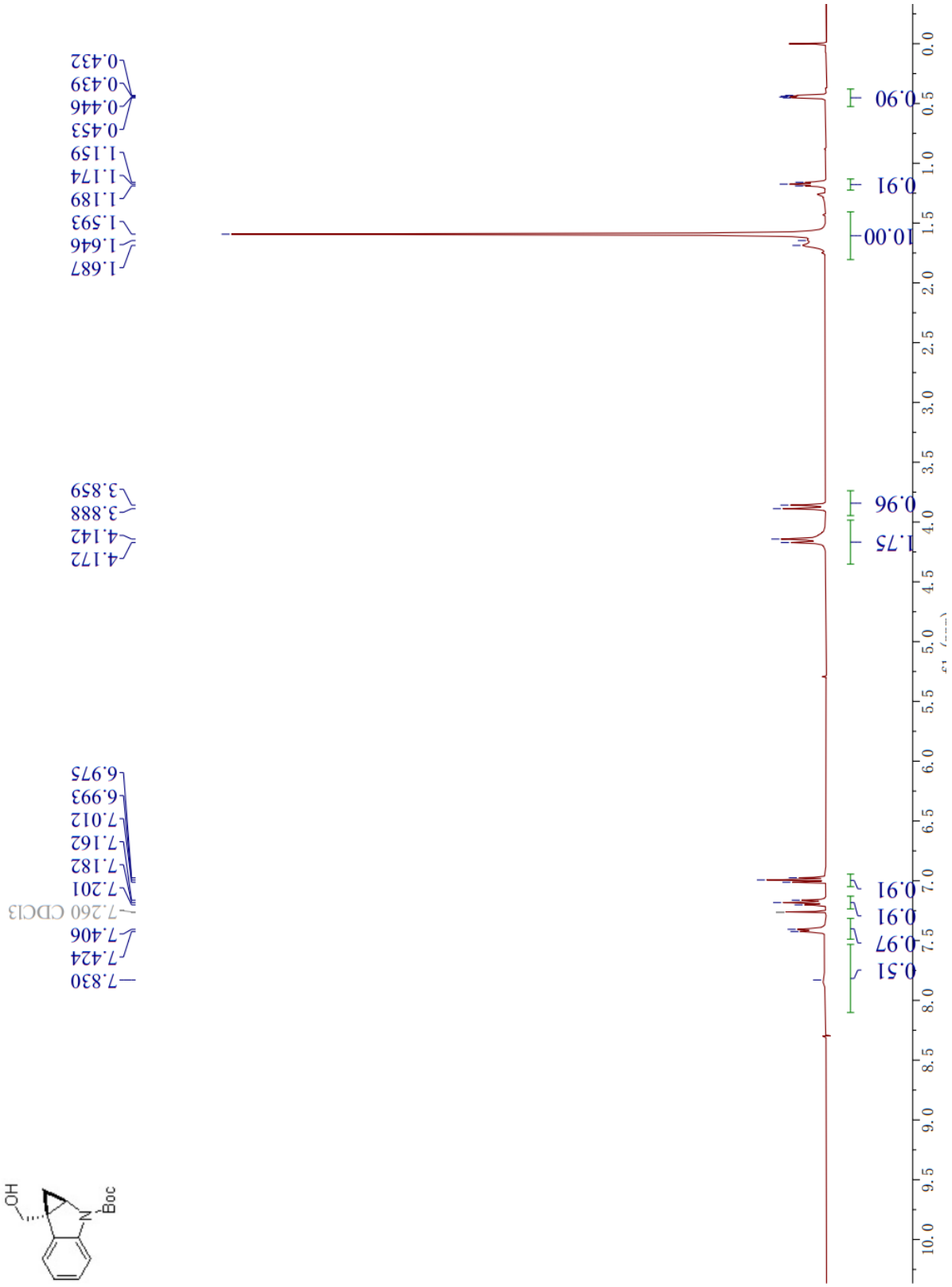

16.34
24.46
34.07
44.33
66.66
77.16 CDCl3
118.28
123.09
123.89
128.46
131.69
140.96
166.45
168.89
Ac
f1 (ppm)

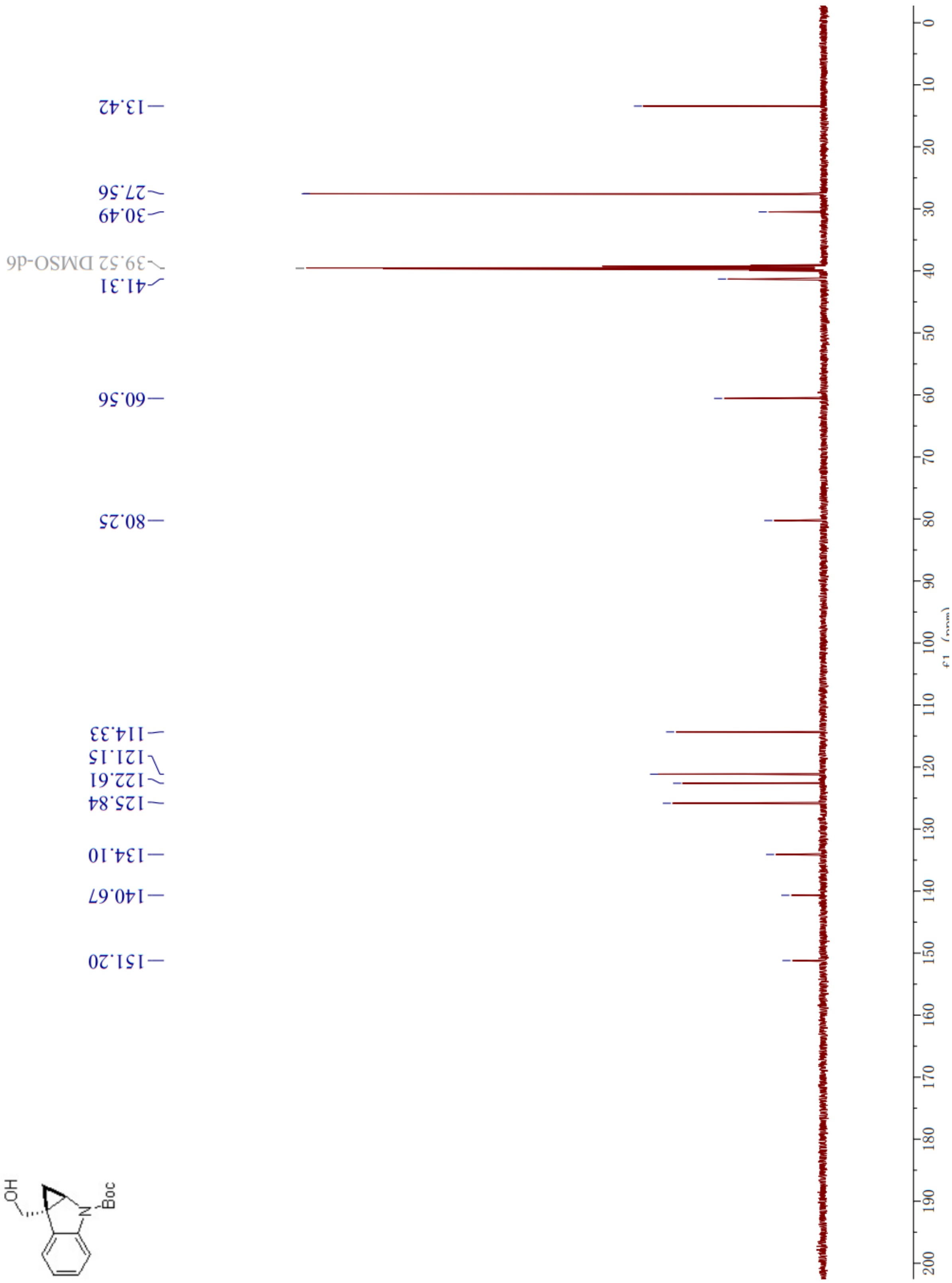
7


0.777
0.790
0.803
2.051
2.065
2.074
2.088
2.291
2.861
2.873
2.884
2.896
3.103
3.294
3.565
3.652
7.030
7.049
7.067
7.189
7.208
7.227
7.260 CDCl3
7.299
7.318
8.104
1.00
1.00
3.00
0.96
8.15
0.99
0.98
0.95
0.84
f1 (ppm)


16.56
24.27
30.18
43.61
46.53
50.53
66.67
77.16 CDCl3
118.46
124.37
128.11
130.80
142.62
166.69
170.28
f1 (ppm)
N
O
Ac

8

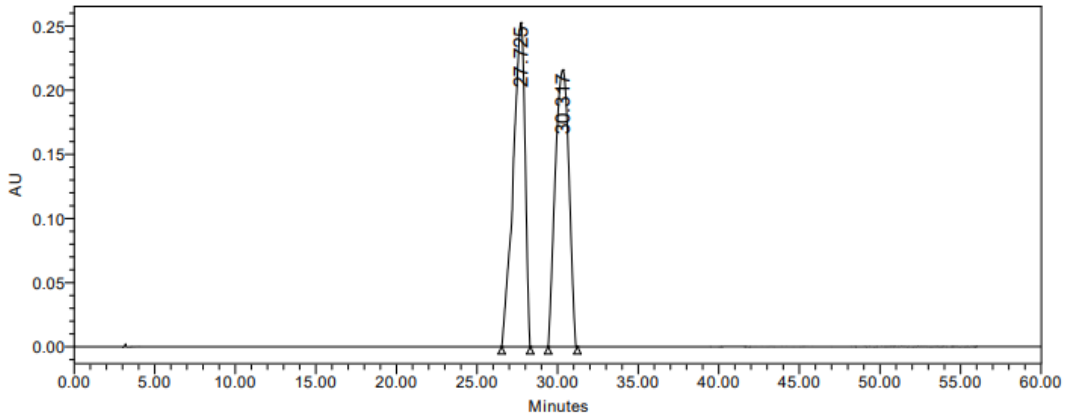

0.432
0.439
0.446
0.453
1.159
1.174
1.189
1.593
1.646
1.687
3.859
3.888
4.142
4.172
6.975
6.993
7.012
7.162
7.182
7.201
7.260 CDCl3
7.406
7.424
7.830
0.51
0.97
0.91
0.91
0.91
1.75
0.96
10.00
0.91
0.90
OH
N
Boc



13.42
27.56
30.49
39.52 DMSO-d6
41.31
60.56
80.25
114.33
121.15
122.61
125.84
134.10
140.67
151.20
OH
N
Boc
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200

10. Copies of HPLC Spectra

8



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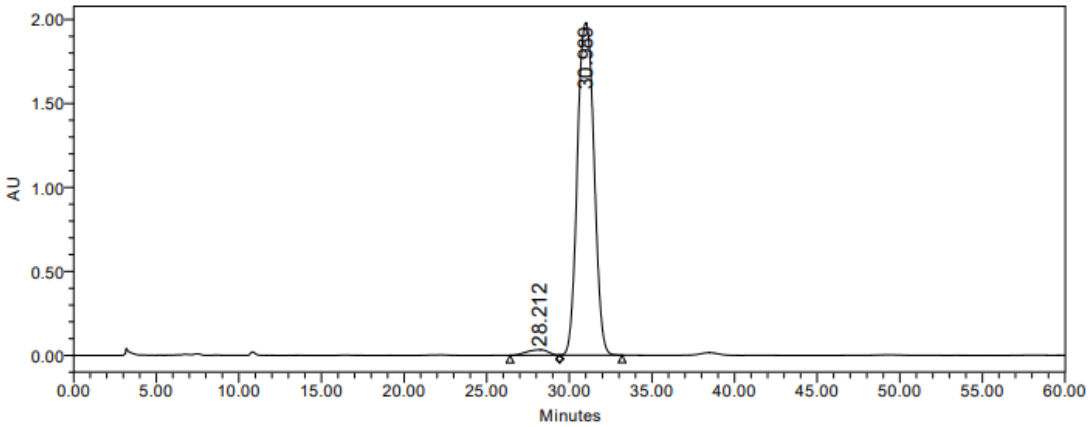
1	27.725	12899465	50.22	252575
2	30.317	12785877	49.78	215809



	RT	Area	% Area	Height
1	28.212	2942125	2.08	32784
2	30.989	138709700	97.92	1977697