Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

NaI- mediated Divergent Synthesis of Isatins and Isoindigoes: A New Protocol Enabled by Oxidation Relay Strategy

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Content

General Information:

All reactions were carried out in a dry solvent under dry oxygen or dry air atmosphere unless otherwise noted. NMR spectra were recorded on Bruker 400 MHz (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) spectrometers. Proton chemical shifts are reported relative to a residual solvent peak ($CDCl_3$ at 7.26 ppm, DMSO at 2.50 ppm).

Carbon chemical shifts are reported relative to a residual solvent peak ($CDCl_3$ at 77ppm, DMSO at 39.96 ppm). The following abbreviations were used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad. High-resolution mass spectra (HRMS) were measured on a Brucker Daltonics Apex Ⅱ 47e Specification (for HRMS). Substrates were purchased from commercial sources and used as received. Substrates **1a-1b, 1k-1s**, are commercially available. Substrates **1c-1j**[1], **1t-1v**[2],**1w**[1],**I**[3] are known compounds.

General Procedure A

Synthesis of 1-methylindoline-2,3-dione(2a):

A mixture of 1-methylindolin-2-one (14.7 mg, 0.1 mmol) with NaI (15.0 mg, 0.1mmol) and THF (1.0 mL) was stirred at 60 °C in the schlenk tube for 12 h under dry air condition. The mixture was cooled to room temperature, and the solvent was distillation under reduced pressure, then diluted with water, extracted with ethyl acetate, dried over sodium sulfate and concentrated. The crude products were purified by column chromatography on silica gel to give the corresponding products.

General Procedure B

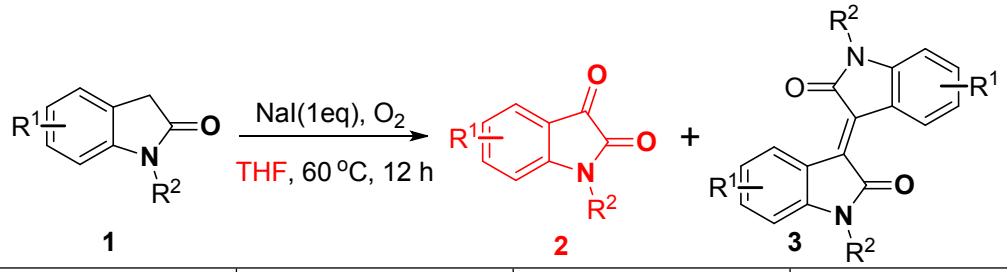
Synthesis of (E)-1,1'-dimethyl-[3,3'-biindolinylidene]-2,2'-diones(3a):

A mixture of 1-methylindolin-2-one (14.7 mg, 0.1 mmol) with NaI (15.0 mg, 0.1 mmol) and DMSO (1.0 mL) was stirred at 100 °C in the schlenk tube for 12 h under dry air condition. The mixture was then cooled to room temperature, diluted with water, extracted with ethyl acetate, organic phase was washed with brine, dried over sodium sulfate and concentrated. The crude products were purified by column chromatography on silica gel to give the corresponding products.

Reference

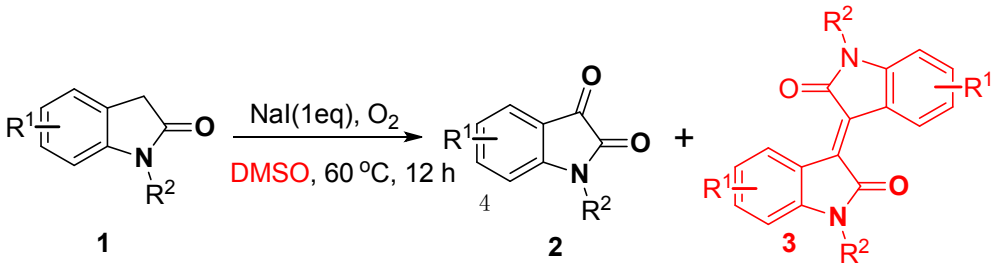
1. X.-H. Xu, X. Wang, G.-k. Liu, E. Tokunaga and N. Shibata, *Org. Lett.,* 2012, **14**, 2544.
2. X. Wang, K. Dong, B. Yan, C. Zhang, L. Qiu and X. Xu, *RSC Adv.,* 2016, **6**, 70221.
3. S. Ghosh, S. Chaudhuri and A. Bisai, *Org. Lett.,* 2015, **17**, 1373.

Table 1: Chemoselectivity of the reaction in THF



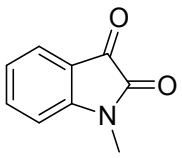
R^1	R^2	2 Yield (%)	3 Yield (%)
H	Me	82	15
H	H	80	16
H	Et	83	13
H	Allyl	78	< 5
H	Bn	86	9
H	Ph	90	< 5
H	4-Me-Ph	92	< 5
H	4-OMe-Ph	92	< 5
H	4-Cl-Ph	89	< 5
H	Boc	0	0
5-Me	H	92	< 5
5-OMe	H	92	< 5
5-F	H	80	8
5-Cl	H	82	< 5
5-Br	H	83	< 5
5-NO_2	H	81	9
7-Cl	H	81	9
7-Me	H	91	< 5
6-Br	H	85	9
5-F	Me	82	10
5-Cl	Me	83	11
5-Br	Me	80	9
6-Br	Bu	85	12

Table 2: Chemoselectivity of the reaction in DMSO

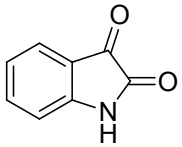


R^1	R^2	2 Yield (%)	3 Yield (%)
H	Me	29	65
H	H	30	60
H	Et	25	65
H	Ph	25	64
H	Bn	26	64
H	4-Me-Ph	29	62
H	4-OMe-Ph	28	61
H	4-Cl-Ph	30	53
H	Boc	0	0
5-F	H	29	52
6-Br	Bu	24	63

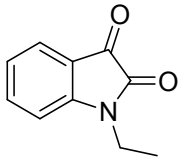
Copies of ^1H, ^{13}C NMR Spectra



1-methylindoline-2,3-dione (2a): orange solid (13.2 mg, 82%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.9 Hz, 1H), 3.24 (d, *J* = 0.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.30, 158.18, 151.41, 138.38, 125.22, 123.79, 117.39, 109.90, 26.18. IR (KBr ν/cm^{-1}) 2922, 1722, 1605, 1469, 1327, 1113, 1090, 757, 474. HRMS (ESI^+) Calcd for $C_9H_7NO_2$ $[M + H]^+$ 162.0555, found 162.0556.



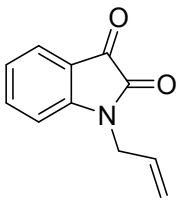
Indoline-2,3-dione(2b): orange solid (11.8 mg, 80%); ^1H NMR (400 MHz, DMSO) δ 11.03 (s, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 7.9 Hz, 1H) . ^{13}C NMR (100 MHz, DMSO) δ 184.79, 159.76, 151.13, 138.78, 125.09, 123.17, 118.23, 112.60. IR (KBr ν/cm^{-1}) 3189, 1733, 1618, 1459, 1333, 1269, 1203, 1095, 770, 662. HRMS (ESI^+) Calcd for $C_8H_5NO_2$ $[M + H]^+$ 148.0399, found 148.0397.



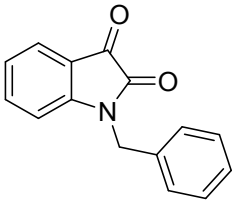
1-ethylindoline-2,3-dione(2c): orange solid (14.5 mg, 83%); ^1H NMR (400 MHz, DMSO) δ 7.67 (t, *J* = 7. 8 Hz, 1H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.20 (d, *J* = 7.9 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 3.71 (q, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 4H). ^{13}C NMR (100 MHz, DMSO) δ 184.08, 158.19, 150.82, 138.62, 124.93, 123.52, 117.94, 111.04, 34.72, 12.72. IR (KBr ν/cm^{-1}) 2989, 1731, 1649, 1470, 1359, 1289, 1049, 826, 764, 474. HRMS (ESI^+) Calcd for

$C_{10}H_9NO_2$ [M+H]$^+$ 176.0712, found = 176.0718.

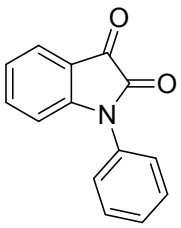
1-allylindoline-2,3-dione(2d): yellow solid (14.6 mg, 78%); ^{1}H NMR (400 MHz, DMSO) δ 7.66 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 7.4 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 5.87 (ddd, *J* = 22.2, 10.2, 5.0 Hz, 1H), 5.34 (d, *J* = 17.2 Hz, 1H), 5.20 (d, *J* = 10.3 Hz, 1H), 4.32 (d, *J* = 3.3 Hz, 2H). ^{13}C NMR (100 MHz, DMSO) δ 183.64, 158.36, 150.93, 138.43, 131.75, 124.84, 123.64, 118.02, 117.87, 111.53, 42.12. IR (KBr ν/cm^{-1}) 2958, 1729, 1658, 1467, 1352, 1125, 1082, 929,760, 486. HRMS (ESI$^+$) Calcd for $C_{11}H_9NO_2$ [M + H]$^+$ 188.0712, found 188.0713.



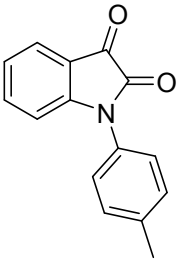
1-benzylindoline-2,3-dione(2e)： yellow solid (20.4 mg, 86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.4 Hz, 1H), 7.48 (td, *J* = 7.9, 1.2 Hz, 1H), 7.37 – 7.31 (m, 5H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 4.94 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.20, 158.25, 150.71, 138.27, 134.49, 129.04, 128.15, 127.41, 125.40, 123.84, 117.68, 110.97, 44.05. IR (KBr ν/cm^{-1}) 3028, 1739, 1614, 1470, 1351, 1178, 1079, 755, 695, 487. HRMS (ESI$^+$) Calcd for $C_{15}H_{11}NO_2$ [M + H]$^+$ 238.0868, found 238.0866.



1-phenylindoline-2,3-dione(2f)： yellow solid (20.1 mg, 90%); ^{1}H NMR (400 MHz, DMSO) δ 7.63 (dd, *J* = 25.2, 7.3 Hz, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.3 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO) δ 183.22, 157.90, 151.69, 138.46, 133.78, 130.16, 128.89, 126.94, 125.14, 124.09, 118.10, 111.18. IR (KBr ν/cm^{-1}) 3076, 1740, 1608, 1469, 1368, 1195, 1150, 756, 699, 461. HRMS (ESI$^+$) Calcd for $C_{14}H_9NO_2$ [M + H]$^+$ 224.0712, found 224.0716.

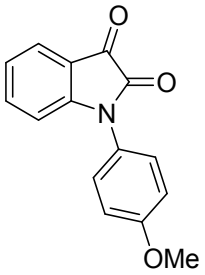


1-(p-tolyl) indoline-2,3-dione(2g)： yellow solid (21.8 mg, 92%); ^{1}H NMR (400 MHz, DMSO) δ 7.74 – 7.51 (m, 1H), 7.37 (dd, *J* = 18.7, 8.3 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 2.39 (s, 2H). ^{13}C NMR (100 MHz, DMSO) δ 183.34, 157.96, 151.87, 138.46, 131.14, 130.62, 126.78, 125.09, 124.00, 118.06, 111.17,

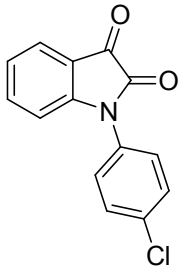


21.24. IR (KBr ν/cm^{-1}) 3089, 2965, 1739, 1612, 1515, 1467, 1366, 1301, 1182, 1094, 814, 755, 551, 476. HRMS (ESI$^+$) Calcd for $C_{15}H_{11}NO_2$ [M + H]$^+$ 238.0868, found 238.0866.

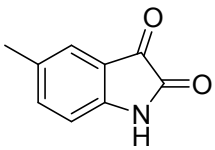
1-(4-methoxyphenyl)indoline-2,3-dione(2h)： yellow solid (23.3 mg, 92%); ^{1}H NMR (400 MHz, DMSO) δ 7.67 – 7.55 (m, 1H), 7.39 (d, *J* = 8.9 Hz, 1H), 7.16 (dd, *J* = 18.1, 8.2 Hz, 2H), 6.74 (d, *J* = 8.0 Hz, 1H), 3.83 (s, 2H). ^{13}C NMR (100 MHz, DMSO) δ 183.47, 159.48, 158.14, 152.18, 138.49, 128.47, 126.25, 125.01, 123.93, 118.01, 115.38, 111.12, 55.89. IR (KBr ν/cm^{-1}) 2998, 1739, 1612, 1515, 1467, 1369, 1299, 1250, 1183, 1094, 1030, 827, 751, 484. HRMS (ESI$^+$) Calcd for $C_{15}H_{11}NO_3$ [M + H]$^+$ 254.0817, found 254.0813.



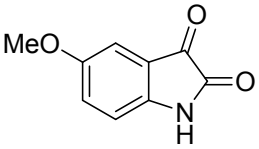
1-(4-chlorophenyl)indoline-2,3-dione(2i): yellow solid (22.9 mg, 89%); ^{1}H NMR (400 MHz, DMSO) δ 7.71 – 7.58 (m, 1H), 7.52 (d, *J* = 8.7 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO) δ 182.92, 157.87, 151.32, 138.43, 133.16, 132.71, 130.22, 128.83, 125.17, 124.21, 118.17, 111.17. IR (KBr ν/cm^{-1}) 3092, 1739, 1614, 1497, 1467, 1364, 1295, 1253, 1180, 1096, 1016, 833, 756, 727, 469. HRMS (ESI$^+$) Calcd for $C_{14}H_8ClNO_2$ [M + H]$^+$ 258.0322, found 258.0326.



5-methylindoline-2,3-dione(2k): orange solid (14.5 mg, 90%); ^{1}H NMR (400 MHz, DMSO) δ 10.92 (s, 1H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.32 (s, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 185.01, 159.89, 148.97, 139.21, 132.43, 125.22, 118.21, 112.44, 20.52. IR (KBr ν/cm^{-1}) 3264, 1739, 1659, 1493, 1300, 1197, 1124, 826, 764. HRMS (ESI$^+$) Calcd for C9H7NO2 [M + H]$^+$ 162.0555, found 162.0556.

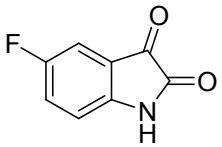


5-methoxyindoline-2,3-dione(2l)： yellow solid (16.3 mg, 92%); ^{1}H NMR (400 MHz, DMSO) δ 10.85 (s, 1H), 7.18 (dd, *J* = 8.5, 2.6 Hz, 1H), 7.07 (d, *J* = 2.5 Hz, 1H), 6.85 (d, *J* = 8.5 Hz,

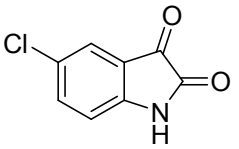


1H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 185.11, 159.98, 155.73, 145.12, 125.30, 118.53, 113.66, 109.21, 56.22. IR (KBr ν/cm^{-1}) 2922, 2853, 1742, 1605, 1493, 1303, 1027, 976, 826, 740. HRMS (ESI$^+$) Calcd for $C_9H_7NO_3$ [M + H]$^+$ 178.0504, found 178.0507.

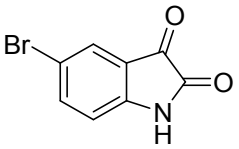
5-fluoroindoline-2,3-dione（2m）： red solid (13.2 mg, 80%); ^{1}H NMR (400 MHz, DMSO) δ 11.04 (s, 1H), 7.76 – 5.88 (m, 3H). ^{13}C NMR (100 MHz, DMSO) δ 184.28, 159.87, 159.68, 157.30, 147.38, 125.02, 124.78, 118.94, 118.87, 113.91, 113.83, 111.90, 111.66. IR (KBr ν/cm^{-1}) 3073, 1709, 1623, 1469, 1261, 1200, 844, 690. HRMS (ESI$^+$) Calcd for $C_8H_4NO_2$ [M + H]$^+$ 166.0304, found 166.0301.



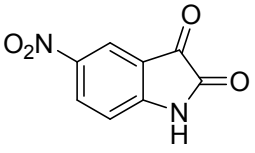
5-chloroindoline-2,3-dione(2n): orange solid (14.8 mg, 82%); ^{1}H NMR (400 MHz, DMSO) δ 11.13 (s, 1H), 7.87 – 7.39 (m, 2H), 6.92 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (100 MHz, DMSO) δ 183.74, 159.55, 149.63, 137.66, 127.21, 124.53, 119.55, 114.24. IR (KBr ν/cm^{-1}) 3170, 2257, 2130, 1655, 1450, 1307, 1211, 1122, 828, 766. HRMS (ESI$^+$) Calcd for $C_8H_4ClNO_2$ [M + H]$^+$ 182.0009, found = 182.0006.

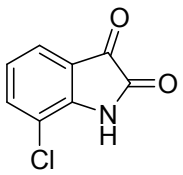


5-bromoindoline-2,3-dione（2o）： pale yellow solid (18.7 mg, 83%); ^{1}H NMR (400 MHz, DMSO) δ 11.14 (s, 1H), 7.81 – 7.59 (m, 2H), 6.87 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (100 MHz, DMSO) δ 183.22, 159.00, 149.62, 140.08, 126.93, 119.61, 114.32. IR (KBr ν/cm^{-1}) 3212, 1746, 1713, 1657, 1442, 1271, 1211, 1027, 826, 764. HRMS (ESI$^+$) Calcd for $C_8H_4BrNO_2$ [M + H]$^+$ 225.9504, found 225.9501.



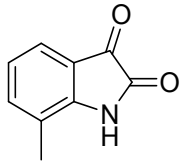
5-nitroindoline-2,3-dione(2p): yellow solid (15.6 mg, 81%); ^{1}H NMR (400 MHz, DMSO) δ 11.66 (s, 1H), 8.43 (dd, *J* = 8.7, 2.4 Hz, 1H), 8.19 (d, *J* = 2.4 Hz, 1H), 7.08 (d, *J* = 8.7 Hz, 1H). ^{13}C NMR (100 MHz, DMSO) δ 182.94, 160.43, 155.90, 142.98, 133.50, 119.99, 118.57, 112.98. IR (KBr ν/cm^{-1}) 3067, 1754, 1657, 1441, 1342, 1027, 827, 764. HRMS (ESI$^+$) Calcd for $C_8H_4N_2O_4$ [M + H]$^+$ 193.0249, found 193.0247.



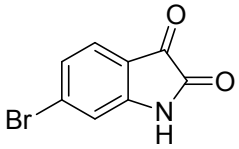


7-chloroindoline-2,3-dione(2q): yellow solid (14.7 mg, 81%); ^{1}H NMR (400 MHz, DMSO) δ 11.45 (s, 1H), 7.67 (d, *J* = 9.1 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.08 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO) δ 183.83, 160.01, 148.16, 137.81, 124.15, 123.54, 120.34, 116.62. IR (KBr ν/cm^{-1}) 3214, 1747, 1615, 1450, 1320, 1172, 1115, 821, 689. HRMS (ESI$^+$) Calcd for $C_8H_4ClNO_2$ [M + H]$^+$ 182.0009, found = 182.0006.

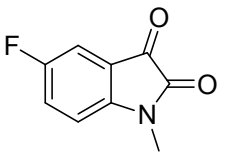
7-methylindoline-2,3-dione(2r): yellow solid (14.6 mg, 91%); ^{1}H NMR (400 MHz, DMSO) δ 11.09 (s, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 184.83, 160.06, 149.34, 139.53, 122.68, 122.12, 121.64, 117.65, 15.52. IR (KBr ν/cm^{-1}) 3201, 1739, 1659, 1495, 1323, 1199, 1028, 825, 762. HRMS (ESI$^+$) Calcd for $C_9H_7NO_2$ [M + H]$^+$ 162.0555, found 162.0554.



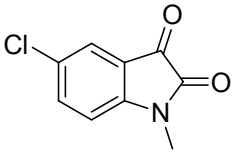
6-bromoindoline-2,3-dione（2s）： yellow solid (19.1 mg, 85%); ^{1}H NMR (400 MHz, DMSO) δ 11.14 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.26 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.07 (d, *J* = 1.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO) δ 183.61, 159.72, 152.08, 132.02, 126.59, 126.04, 117.48, 115.40. IR (KBr ν/cm^{-1}) 3204, 1742, 1709, 1605, 1446, 1325, 1208, 1101, 843, 680. HRMS (ESI$^+$) Calcd for $C_8H_4BrNO_2$ [M + H]$^+$ 225.9504, found 225.9507.



5-fluoro-1-methylindoline-2,3-dione(2t): yellow solid (14.7mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 8.6, 2.7 Hz, 1H), 7.30 (dd, *J* = 6.5, 2.5 Hz, 1H), 6.87 (dd, *J* = 8.5, 3.6 Hz, 1H), 3.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.73, 160.57, 158.12, 157.94, 147.48, 124.75, 124.51, 118.00, 117.93, 112.47, 112.23, 111.06, 110.99, 26.31. IR (KBr ν/cm^{-1}) 3091, 1751, 1733, 1623, 1485, 1358, 1321, 1262, 1215, 1148, 1112, 908, 826, 785, 712, 478. HRMS (ESI$^+$) Calcd for $C_9H_6FNO_2$ [M + H]$^+$ 180.0461, found 180.0463.

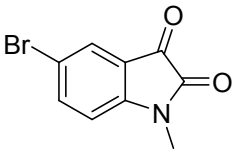


5-chloro-1-methylindoline-2,3-dione(2u): yellow solid (16.2 mg, 83%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 2H), 6.86 (dd, *J* = 8.0, 0.6 Hz, 1H), 3.25 (s, 3H). ^{13}C NMR (100 MHz,

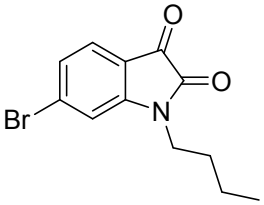


$CDCl_3$) δ 182.29, 157.64, 149.66, 137.71, 129.65, 125.20, 118.20, 111.17, 26.35. IR (KBr ν/cm^{-1}) 3092, 1739, 1734, 1610, 1463, 1351, 1325, 1177, 1109, 833, 728, 682, 471. HRMS (ESI^+) Calcd for $C_9H_6ClNO_2$ $[M + H]^+$ 196.0165, found 196.0168.

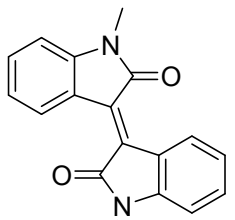
5-bromo-1-methylindoline-2,3-dione(2v): yellow solid (18.7 mg, 80%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.68 (m, 2H), 6.81 (d, *J* = 8.1 Hz, 1H), 3.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.12, 157.47, 150.11, 140.57, 128.08, 118.58, 116.66, 111.57, 26.35. IR (KBr ν/cm^{-1}) 3090, 1750, 1732, 1607, 1472, 1440, 1354, 1323, 1175, 1108, 826, 714, 525, 472. HRMS (ESI^+) Calcd for $C_9H_6BrNO_2$ $[M + H]^+$ 239.9660, found 239.9664.



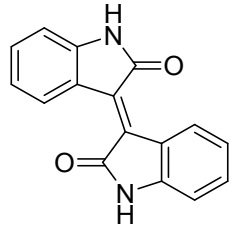
6-bromo-1-butylindoline-2,3-dione(2w): yellow solid (23.9 mg, 85%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.9 Hz, 1H), 7.26 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.06 (d, *J* = 1.4 Hz, 1H), 3.70 (t, *J* = 7.3 Hz, 2H), 1.71 – 1.63 (m, 2H), 1.40 (dd, *J* = 15.2, 7.5 Hz, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.32, 157.94, 151.81, 133.50, 126.78, 126.35, 116.22, 113.73, 40.21, 29.17, 20.08, 13.61. IR (KBr ν/cm^{-1}) 3485, 3198, 1733, 1606, 1469, 1433, 1362, 1280, 1103, 1064, 834, 792, 533, 480. HRMS (ESI^+) Calcd for $C_{12}H_{12}BrNO_2$ $[M + H]^+$ 282.0130, found 282.0134.



(E)-1,1'-dimethyl-[3,3'-biindolinylidene]-2,2'-dione(3a): red solid (9.4 mg, 65%); ^1H NMR (400 MHz, $CDCl_3$) δ 9.20 (dd, *J* = 8.0, 0.5 Hz, 2H), 7.37 (td, *J* = 7.7, 1.1 Hz, 2H), 7.07 (td, *J* = 8.0, 1.0 Hz, 2H), 6.78 (d, *J* = 7.6 Hz, 2H), 3.28 (s, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 167.92, 145.12, 133.39, 132.35, 129.75, 122.38, 121.48, 107.65, 26.11. IR (KBr ν/cm^{-1}) 2910, 1683, 1606, 1470, 1375, 1344, 1118, 1092, 773, 738, 669. HRMS (ESI^+) Calcd for $C_{18}H_{14}N_2O_2$ $[M + H]^+$ 291.1134, found 291.1132.

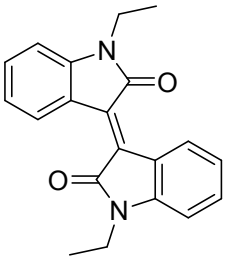


(E)-[3,3'-biindolinylidene]-2,2'-dione(3b): red solid (7.9 mg, 60%); ^1H NMR (400 MHz, DMSO) δ 10.89 (s, 2H), 9.07 (s, 1H), 9.05 (s, 1H), 7.34 (td, *J* = 7.6, 1.1 Hz, 2H), 6.99 – 6.94 (m, 2H), 6.84 (d, *J* = 7.7 Hz, 2H). ^{13}C NMR (100 MHz, DMSO) δ 183.61,

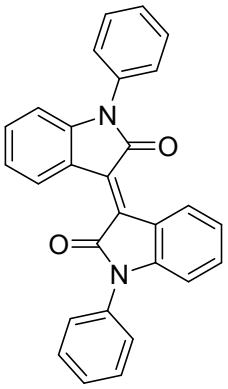


159.72, 152.08, 132.02, 126.59, 126.04, 117.48, 115.40. IR (KBr ν/cm^{-1}) 3080, 1660, 1624, 1458, 1334, 1273, 1209, 1027, 826, 764. HRMS (ESI$^+$) Calcd for $C_{16}H_{10}N_2O_2$ $[M + H]^+$ 263.0821, found 263.0824.

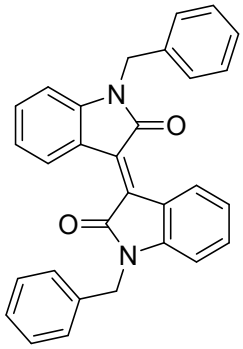
(E)-1,1'-diethyl-[3,3'-biindolinylidene]-2,2'-dione(3c): red solid (10.3 mg, 65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (dd, *J* = 8.0, 0.7 Hz, 2H), 7.36 (td, *J* = 7.7, 1.1 Hz, 2H), 7.05 (td, *J* = 8.0, 1.1 Hz, 2H), 6.81 (d, *J* = 7.6 Hz, 2H), 3.84 (q, *J* = 7.2 Hz, 4H), 1.30 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.50, 144.23, 133.54, 132.32, 129.94, 122.15, 121.65, 107.70, 34.65, 12.61. IR (KBr ν/cm^{-1}) 3020, 2920, 1738, 1645, 1472, 1370, 1288, 1120, 1089, 776, 738, 668. HRMS (ESI$^+$) Calcd for $C_{20}H_{18}N_2O_2$ $[M + H]^+$ 319.1447, found 319.1442.



(E)-1,1'-diphenyl-[3,3'-biindolinylidene]-2,2'-dione(3d): red solid (13.2 mg, 64%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (d, *J* = 8.1 Hz, 2H), 7.58 (dd, *J* = 8.2, 7.2 Hz, 4H), 7.50 – 7.44 (m, 6H), 7.29 (td, *J* = 7.8, 1.2 Hz, 2H), 7.09 – 7.03 (m, 2H), 6.75 (d, *J* = 7.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.49, 145.37, 134.15, 133.72, 132.52, 130.26, 129.76, 128.41, 127.11, 122.83, 121.52, 109.05. IR (KBr ν/cm^{-1}) 3078, 2919, 1700, 1605, 1500, 1465, 1372, 1299, 1180, 1107, 934, 772, 745, 699, 482. HRMS (ESI$^+$) Calcd for $C_{28}H_{18}N_2O_2$ $[M + H]^+$ 415.1447, found 415.1442.

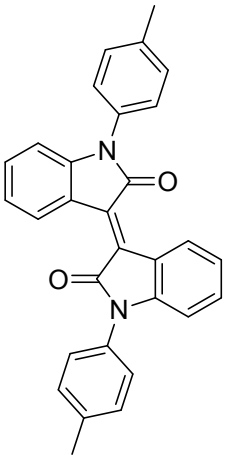


(E)-1,1'-dibenzyl-[3,3'-biindolinylidene]-2,2'-dione(3e): red solid (14.1 mg, 64%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 9.22 (s, 1H), 7.36 – 7.27 (m, 12H), 7.05 (t, *J* = 7.8 Hz, 2H), 6.73 (s, 1H), 6.71 (s, 1H), 5.02 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.05, 144.50, 135.71, 133.54, 132.48, 129.98, 128.82, 127.65, 127.21, 122.49, 121.69, 108.64, 43.69. IR (KBr ν/cm^{-1}) 3022,

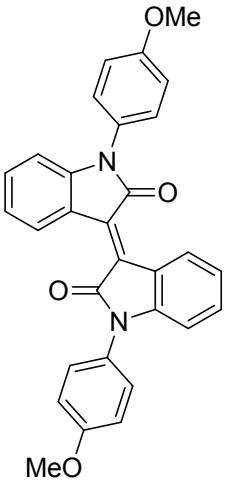


1690, 1610, 1466, 1365, 1182, 1105, 1021, 747, 687, 479. HRMS (ESI^+) Calcd for $C_{30}H_{22}N_2O_2$ $[M + H]^+$ 443.1760, found 443.1764.

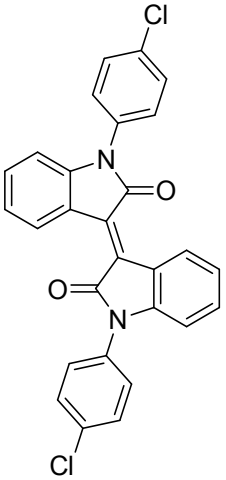
(E)-1,1'-di-p-tolyl-[3,3'-biindolinylidene]-2,2'-dione(3f): red solid (13.7 mg, 62%); ^1H NMR (400 MHz, $CDCl_3$) δ 9.23 (d, *J* = 0.6 Hz, 1H), 9.21 (d, *J* = 0.6 Hz, 1H), 7.38 – 7.32 (m, 8H), 7.28 (dd, *J* = 7.7, 1.1 Hz, 2H), 7.04 (td, *J* = 8.2, 1.1 Hz, 2H), 6.73 (d, *J* = 0.5 Hz, 1H), 6.71 (s, 1H), 2.45 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.63, 145.56, 138.43, 133.71, 132.43, 131.44, 130.37, 130.22, 126.91, 122.68, 121.50, 109.00, 21.26. IR (KBr ν/cm^{-1}) 3135, 2922, 1702, 1605, 1517, 1465, 1374, 1299, 1168, 1105, 934, 772, 744, 663. HRMS (ESI^+) Calcd for $C_{30}H_{22}N_2O_2$ $[M + H]^+$ 443.1760, found 443.1758.



(E)-1,1'-bis(4-methoxyphenyl)-[3,3'-biindolinylidene]-2,2'-dione(3g): red solid (14.5 mg, 61%); ^1H NMR (400 MHz, $CDCl_3$) δ 9.22 (d, *J* = 7.9 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 4H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.06 (dd, *J* = 15.1, 8.2 Hz, 6H), 6.69 (d, *J* = 7.8 Hz, 2H), 3.88 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.82, 159.42, 145.76, 133.69, 132.48, 130.21, 128.44, 126.68, 122.69, 121.44, 115.06, 108.96, 55.58. IR (KBr ν/cm^{-1}) 3002, 1739, 1644, 1515, 1469, 1374, 1299, 1251, 1182, 1105, 1029, 834, 750. HRMS (ESI^+) Calcd for $C_{30}H_{22}N_2O_4$ $[M + H]^+$ 475.1658, found 475.1656.

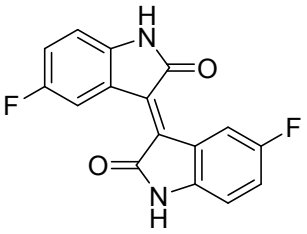


(E)-1,1'-bis(4-chlorophenyl)-[3,3'-biindolinylidene]-2,2'-dione(3h): red solid (12.7 mg, 53%); ^1H NMR (400 MHz, $CDCl_3$) δ 9.18 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 4H), 7.42 (d, *J* = 8.5 Hz, 4H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.08 (t, *J* = 7.7 Hz, 2H), 6.74 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.33, 144.91, 134.16, 133.55, 132.73, 132.60, 130.30, 130.02,



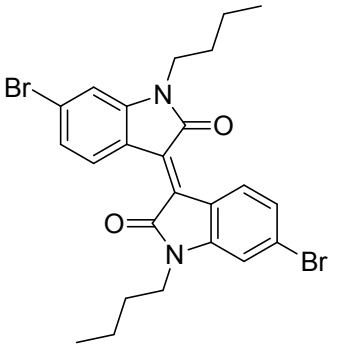
128.39, 123.12, 121.50, 108.95. IR (KBr ν/cm^{-1}) 3089, 1703, 1606, 1498, 1461, 1374, 1293, 1245, 1180, 1090, 1015, 933, 773, 749, 680, 478. HRMS (ESI$^+$) Calcd for $C_{28}H_{16}Cl_2N_2O_2$ [M + H]$^+$ 482.0589, found 482.0587.

(E)-5,5'-difluoro-[3,3'-biindolinylidene]-2,2'-dione(3j):



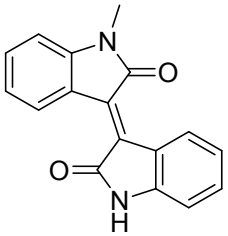
red solid (7.7 mg, 52%); ^{1}H NMR (400 MHz, DMSO) δ 11.00 (s, 2H), 8.99 (dd, *J* = 11.4, 2.4 Hz, 2H), 7.24 (dt, *J* = 8.7, 4.3 Hz, 2H), 6.84 (dd, *J* = 8.5, 4.9 Hz, 2H). ^{13}C NMR (100 MHz, DMSO) δ 169.43, 156.32, 141.27, 141.25, 134.41, 122.62, 119.80, 116.83, 116.54, 110.72, 110.64. IR (KBr ν/cm^{-1}) 3072, 1659, 1620, 1478, 1298, 1027, 826, 764. HRMS (ESI$^+$) Calcd for $C_{16}H_8F_2N_2O_2$ [M + H]$^+$ 299.0632, found 299.0637.

(E)-6,6'-dibromo-1,1'-dibutyl-[3,3'-biindolinylidene]-2,2'-dione（3k）：



red solid (16.7 mg, 63%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (d, *J* = 8.6 Hz, 2H), 7.16 (dd, *J* = 8.6, 1.8 Hz, 2H), 6.92 (d, *J* = 1.8 Hz, 2H), 3.73 (t, *J* = 7.4 Hz, 4H), 1.72 – 1.62 (m, 4H), 1.46 – 1.36 (m, 4H), 0.97 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.72, 145.75, 132.61, 131.19, 126.72, 125.12, 120.40, 111.29, 40.02, 29.44, 20.25, 13.75. IR (KBr ν/cm^{-1}) 3482, 2952, 2926, 2862, 1703, 1687, 1595, 1474, 1432, 1358, 1105, 1072, 826, 789, 535, 478. HRMS (ESI$^+$) Calcd for $C_{24}H_{24}Br_2N_2O_2$ [M + H]$^+$ 531.0283, found 531.0286.

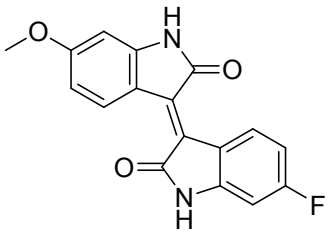
(E)-1-methyl-[3,3'-biindolinylidene]-2,2'-dione（3l）：



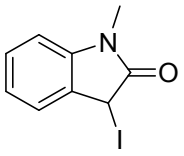
red solid (12.4 mg, 45%); ^{1}H NMR (400 MHz, DMSO) δ 10.92 (s, 1H), 9.10 (dd, *J* = 7.7, 4.0 Hz, 2H), 7.44 (td, *J* = 7.7, 1.1 Hz, 1H), 7.35 (td, *J* = 7.6, 1.1 Hz, 1H), 7.07 – 7.01 (m, 2H), 6.99 – 6.95 (m, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 3.23 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 169.30, 167.64, 145.42, 144.66, 134.20, 133.28, 132.99, 132.68, 129.84, 129.38, 122.21, 122.07, 121.63, 121.24, 110.04, 108.89, 26.50. IR (KBr ν/cm^{-1}) 3082, 2910, 1668, 1608, 1465, 1375, 1334, 1269, 1118, 1080, 826, 738, 669. HRMS (ESI$^+$)

Calcd for $C_{17}H_{12}N_2O_2$ $[M + H]^+$ 277.0977, found 277.0975.

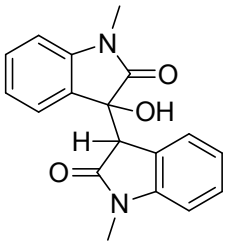
(E)-5-fluoro-5'-methoxy-[3,3'-biindolinylidene]-2,2'-dione（3m）： red solid (14.3 mg, 46%); ^{1}H NMR (400 MHz, DMSO) δ 10.90 (s, 1H), 10.76 (s, 1H), 8.98 (dd, *J* = 11.5, 2.7 Hz, 1H), 8.86 (d, *J* = 2.6 Hz, 1H), 7.21 (td, *J* = 8.7, 2.8 Hz, 1H), 6.98 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.83 (dd, *J* = 8.6, 4.9 Hz, 1H), 6.75 (d, *J* = 8.5 Hz, 1H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 169.53, 169.47, 158.64, 156.33, 154.52, 140.96, 138.81, 135.65, 133.40, 122.86, 122.59, 119.56, 119.44, 119.31, 116.63, 116.34, 116.05, 110.49, 110.35, 55.96. IR (KBr ν/cm^{-1}) 3022, 1739, 1665, 1640, 1489, 1460, 1376, 1299, 1180, 1106, 1027, 830, 758. HRMS (ESI$^+$) Calcd for $C_{17}H_{12}FN_2O_3$ $[M + H]^+$ 311.0832, found 311.0835.

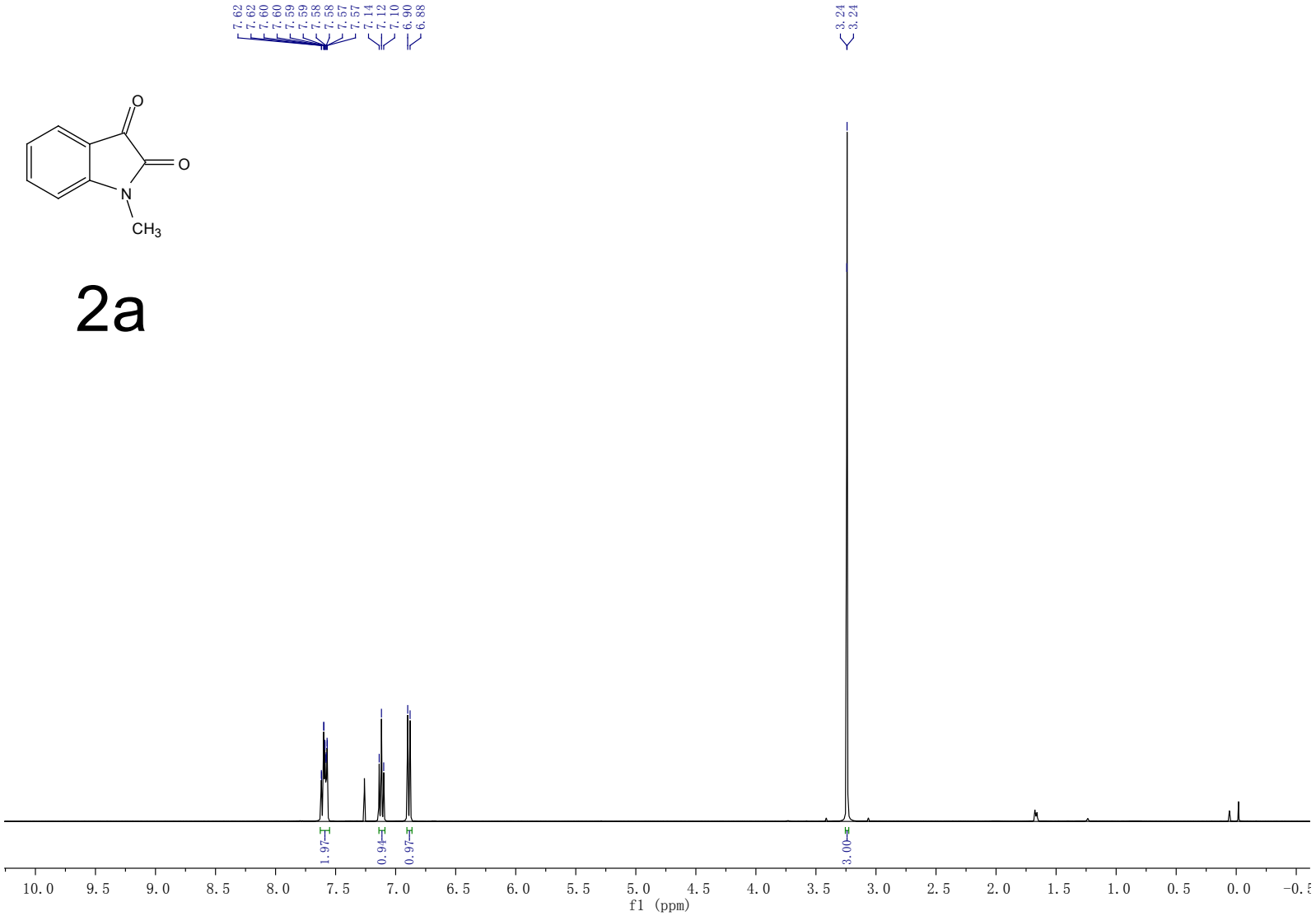


3-iodo-1-methylindolin-2-one（I）： yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.4 Hz, 1H), 7.30 (s, 1H), 7.08 (s, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 5.67 (s, 1H), 3.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.20, 143.13, 129.78, 127.82, 126.08, 123.29, 108.87, 26.93, 12.60. IR (KBr ν/m^{-1}) 2910, 1712, 1649, 1612, 1470, 1373, 1126, 1088, 751, 669, 558. HRMS (ESI$^+$) Calcd for C9H8INO $[M + H]^+$ 272.9651, found 272.9653.



3-hydroxy-1,1'-dimethyl-[3,3'-biindoline]-2,2'-dione（II）： white solid(4.5mg, 30%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.3 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.21 (td, *J* = 7.7, 1.2 Hz, 1H), 7.13 – 7.07 (m, 1H), 6.92 (dt, *J* = 5.7, 2.9 Hz, 2H), 6.70 – 6.65 (m, 2H), 6.09 (d, *J* = 7.1 Hz, 1H), 4.09 (s, 1H), 3.10 (s, 3H), 2.77 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 175.57, 172.09, 144.86, 144.01, 129.85, 128.73, 127.40, 126.34, 124.84, 123.00, 121.93, 121.66, 108.53, 108.20, 75.35, 51.36, 25.98, 25.68. IR (KBr ν/cm^{-1}) 3580, 2908, 1678, 1605, 1465, 1367, 1344, 1200,1114, 1034, 825, 762, 668. HRMS (ESI$^+$) Calcd for $C_{18}H_{16}N_2O_3$ $[M + H]^+$ 309.1239, found 309.1236.

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7.60
7.60
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7.58
7.58
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7.57
7.14
7.12
7.10
6.90
6.88
3.24
3.24
O
O
N
CH3
2a
1.97
0.94
0.97
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
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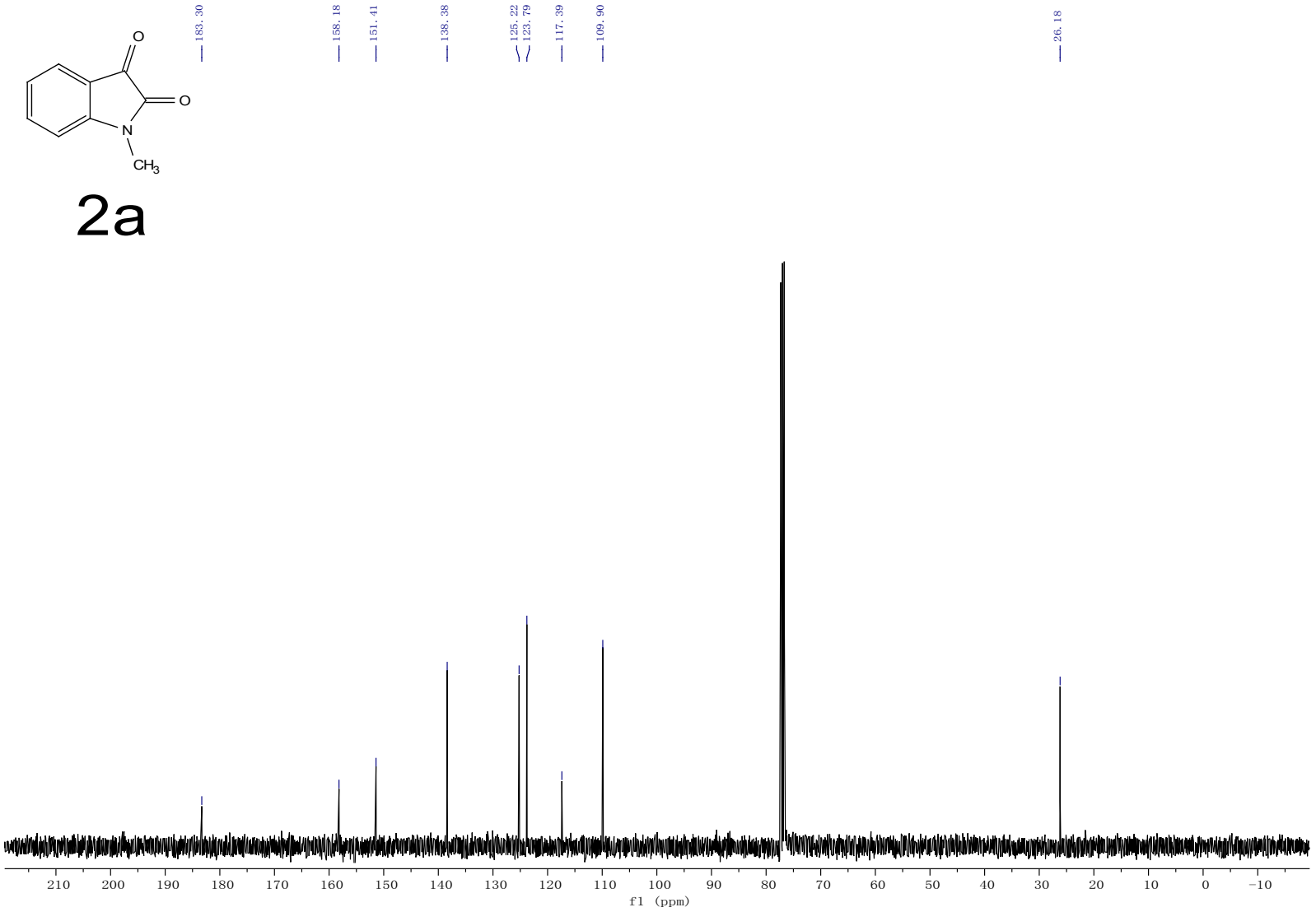
f1 (ppm)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O
N
CH3
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200
190
180
170
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80
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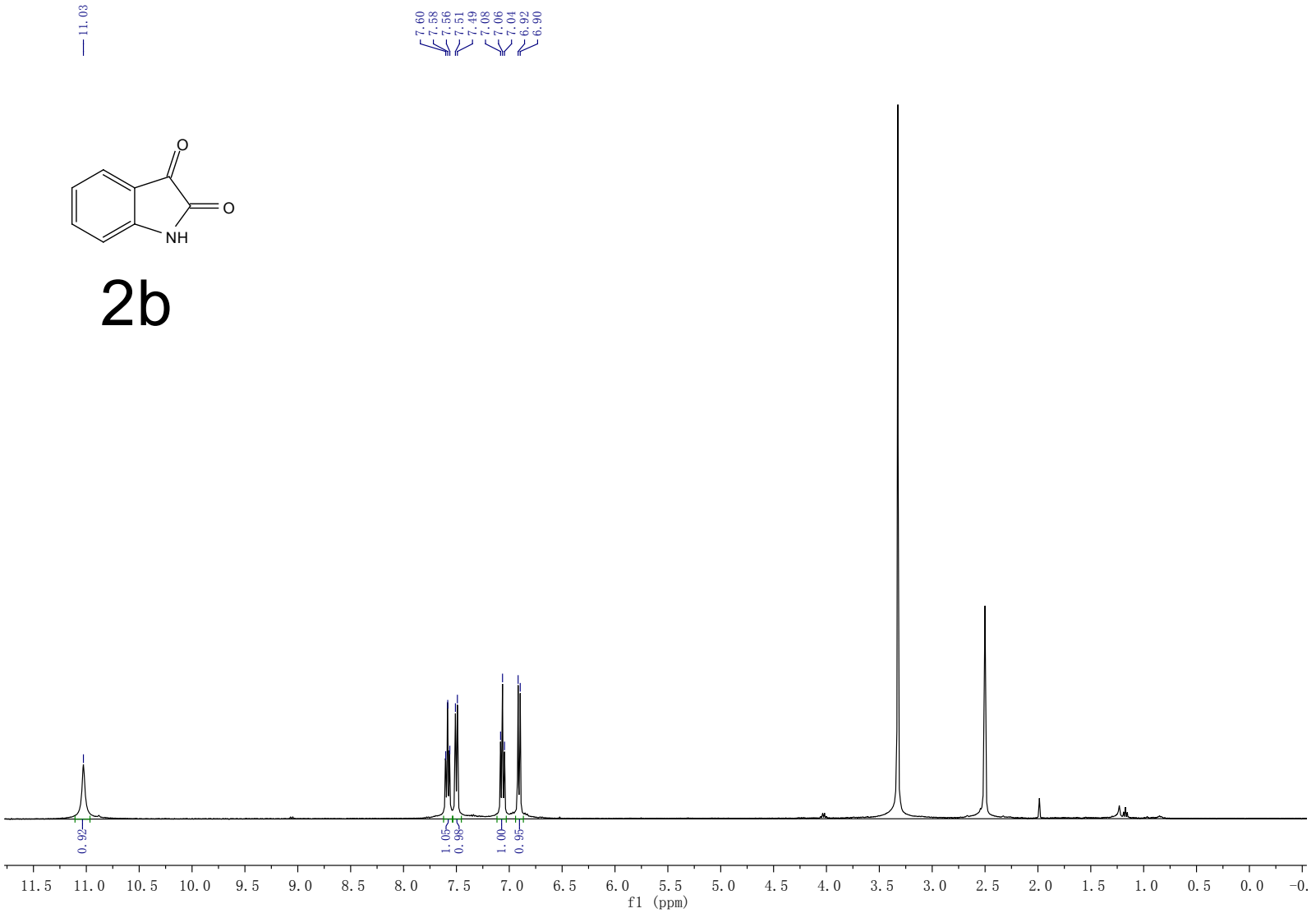
40
30
20
10
0
−10
f1 (ppm)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7.56
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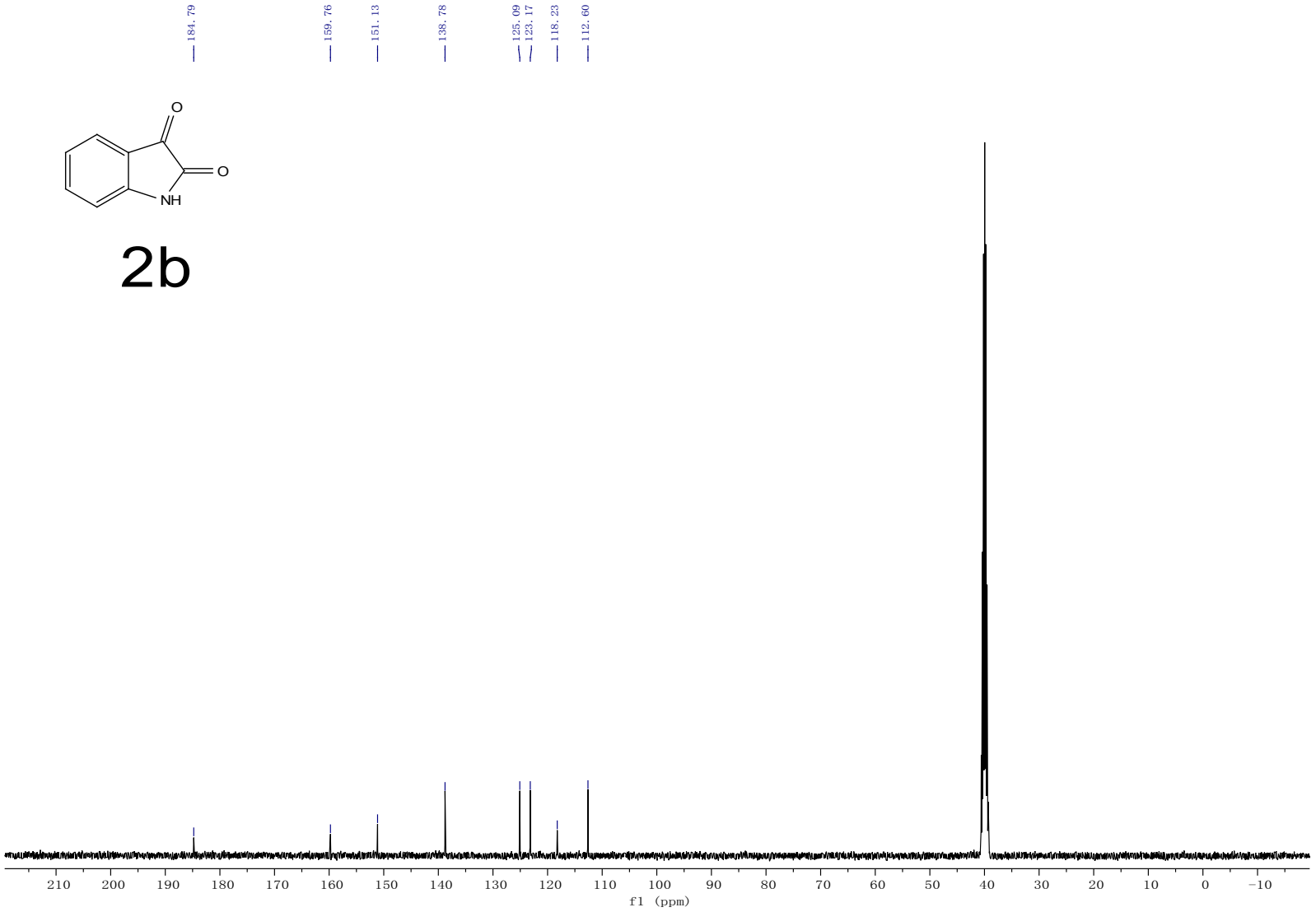
7.08
7.06
7.04
6.92
6.90
O
O
NH
2b
0.92
1.05
0.98
1.00
0.95
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)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2b
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80
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40
30
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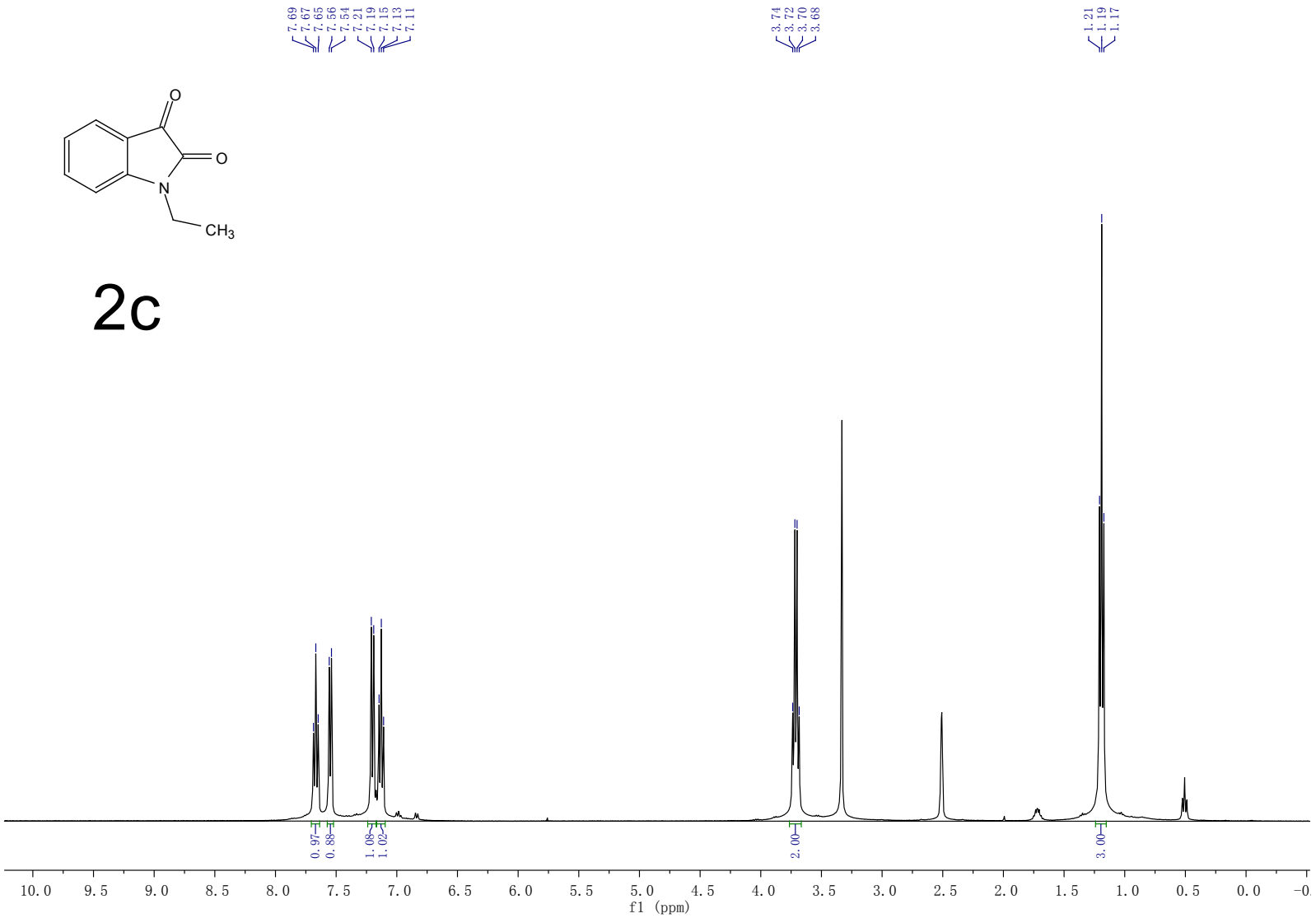
−10
f1 (ppm)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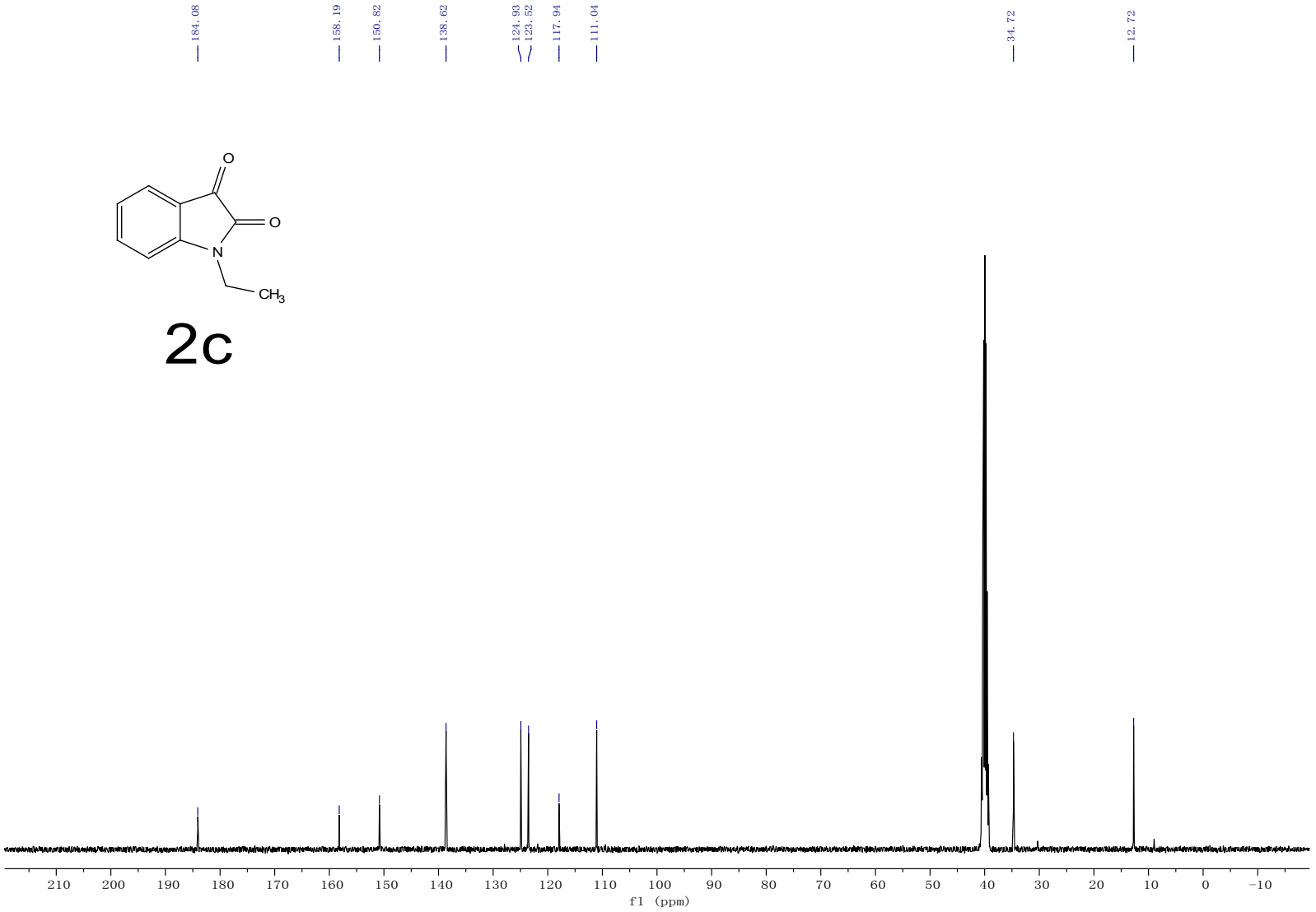
3.70
3.68
1.21
1.19
1.17
O
O
N
CH3
2c
0.97
0.88
1.08
1.02
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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111.04
34.72
12.72
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O
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200
190
180
170
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120
110
100
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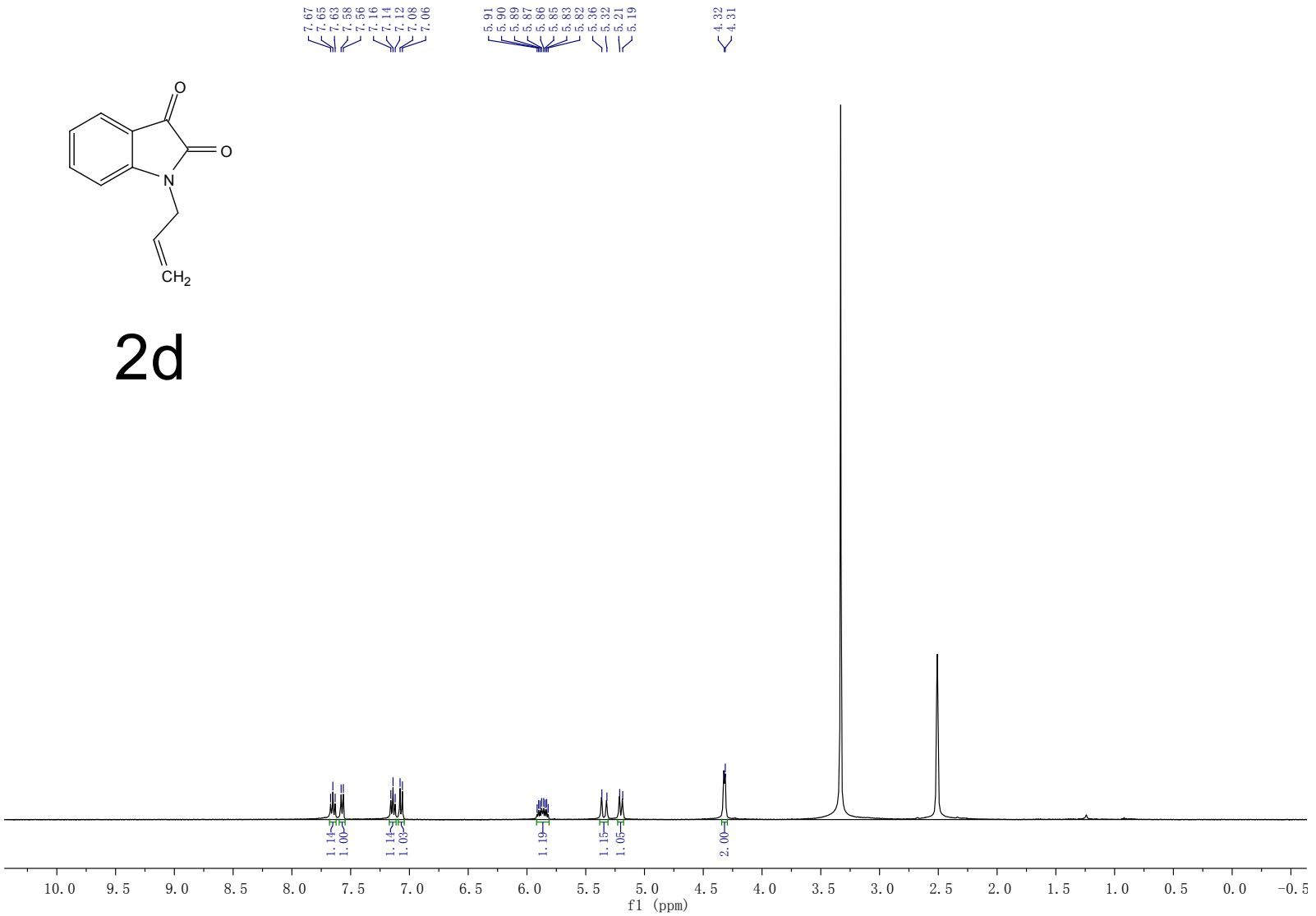
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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CH2
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1.14
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1.15
1.05
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5.0
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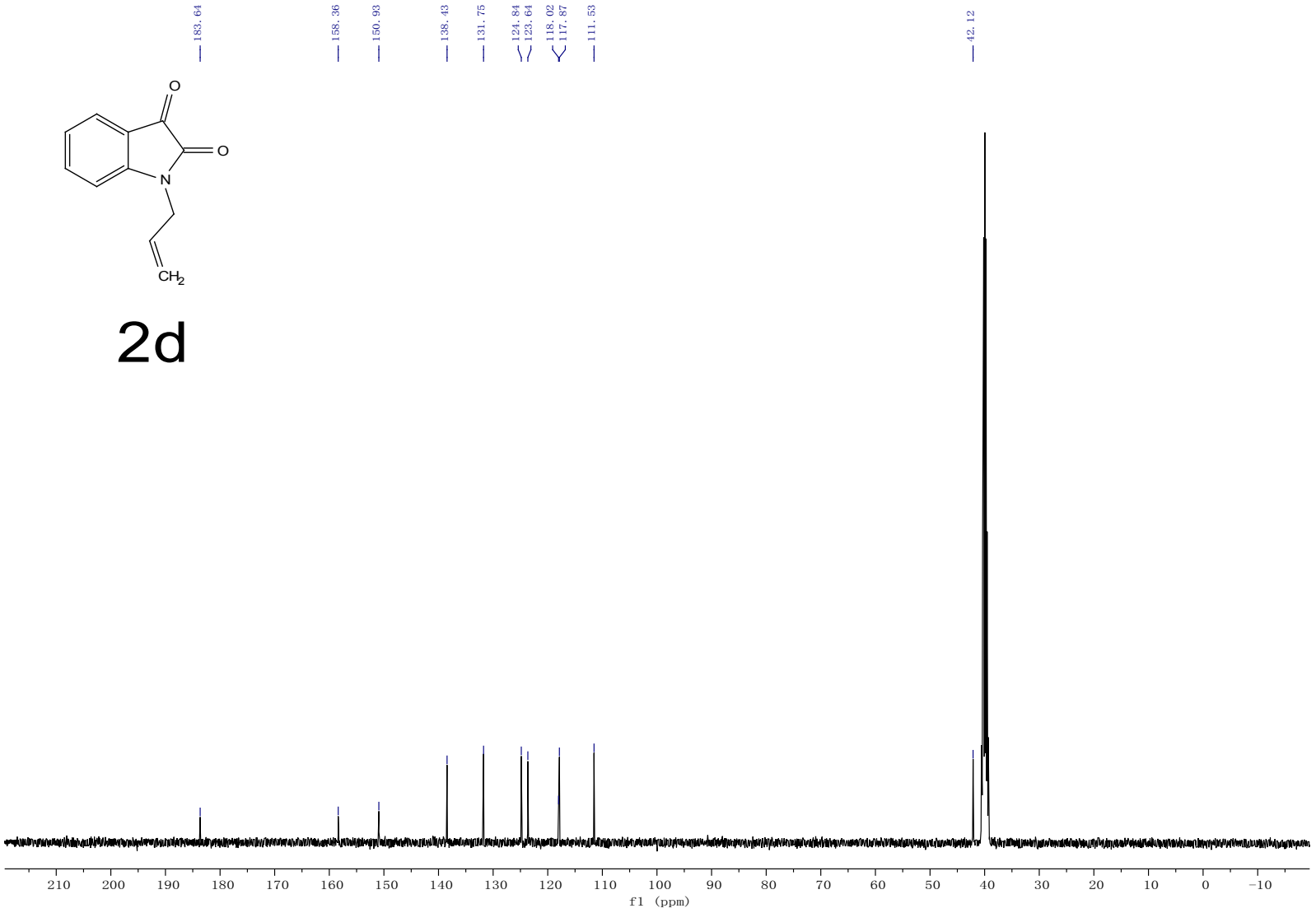
f1 (ppm)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111.53
42.12
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O
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CH2
2d
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200
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180
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120
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40
30
20
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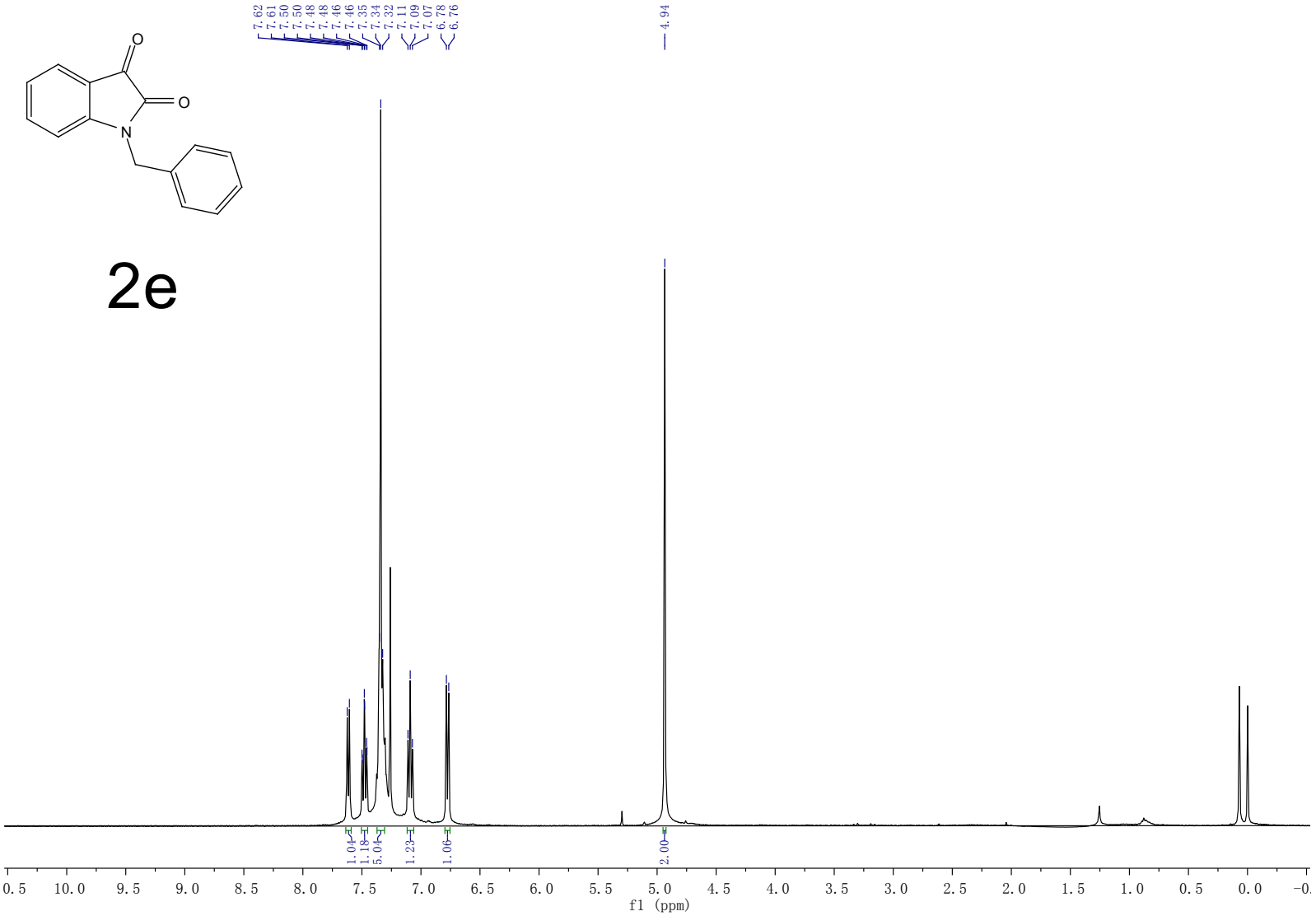
0
−10
f1 (ppm)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7.32
7.11
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6.78
6.76
4.94
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O
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2e
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1.18
5.04
1.23
1.06
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10.0
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
2.0
1.5
1.0
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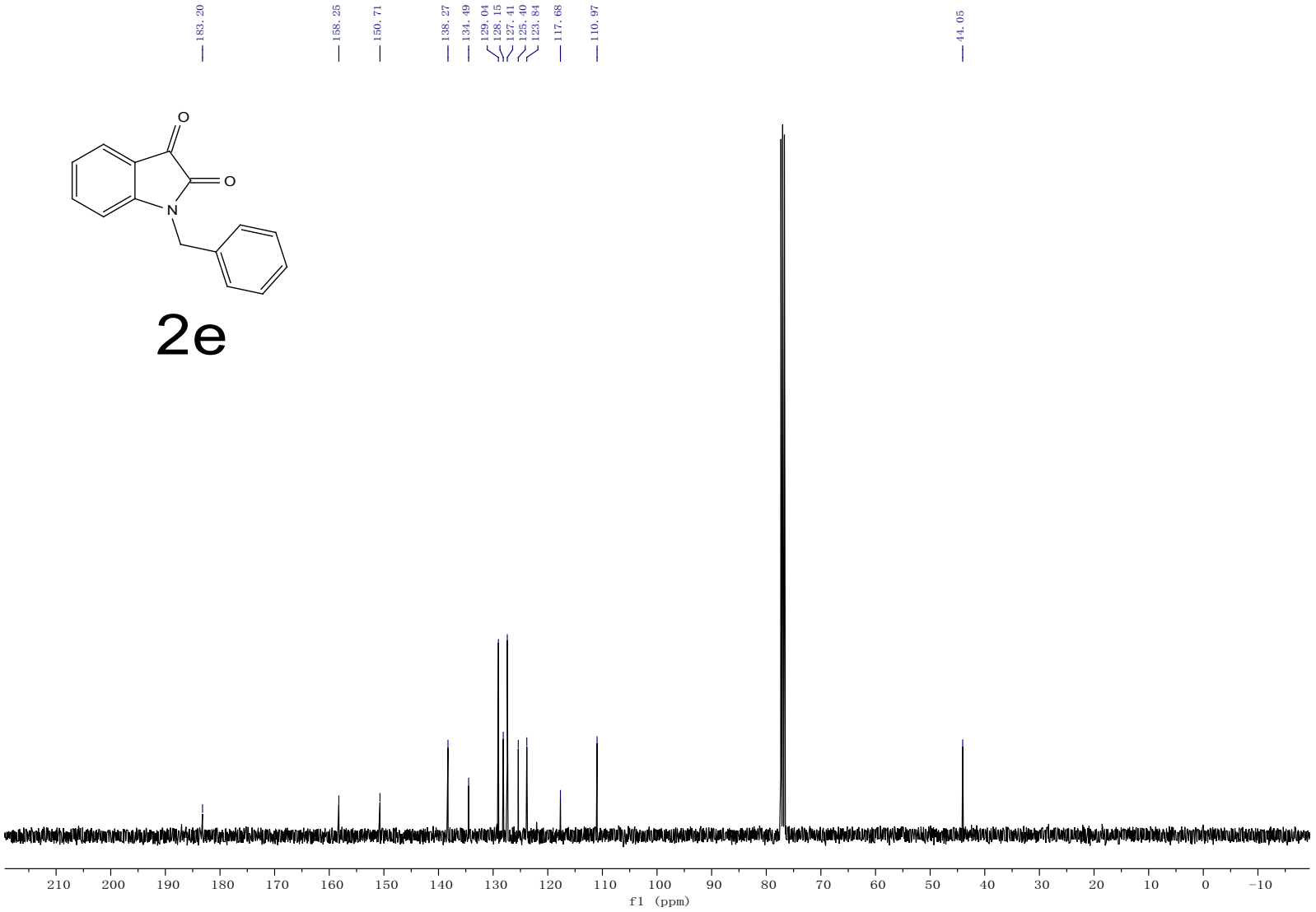
0.0
f1 (ppm)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200
190
180
170
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60
50
40
30
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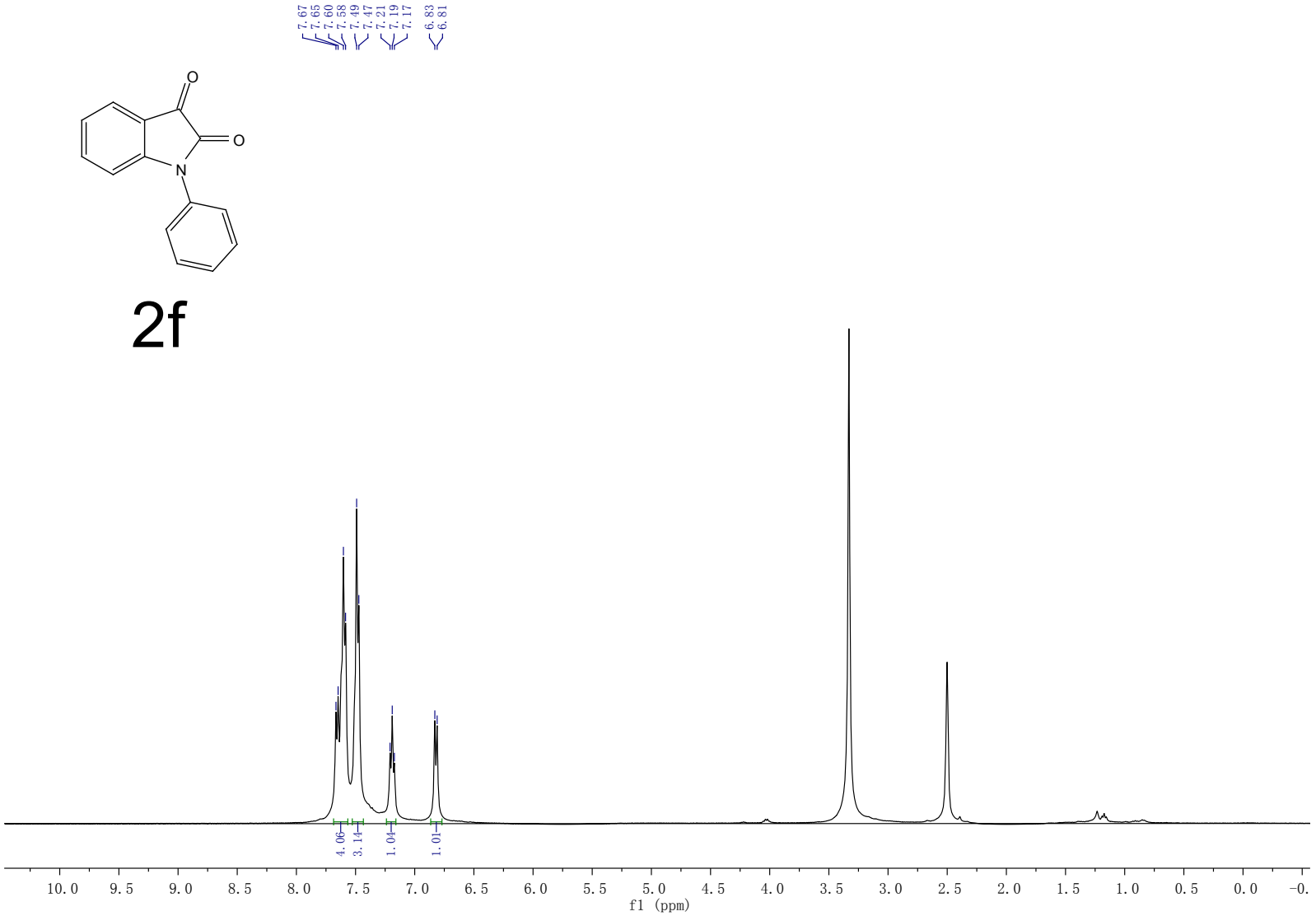
f1 (ppm)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O
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1.01
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7.0
6.5
6.0
5.5
5.0
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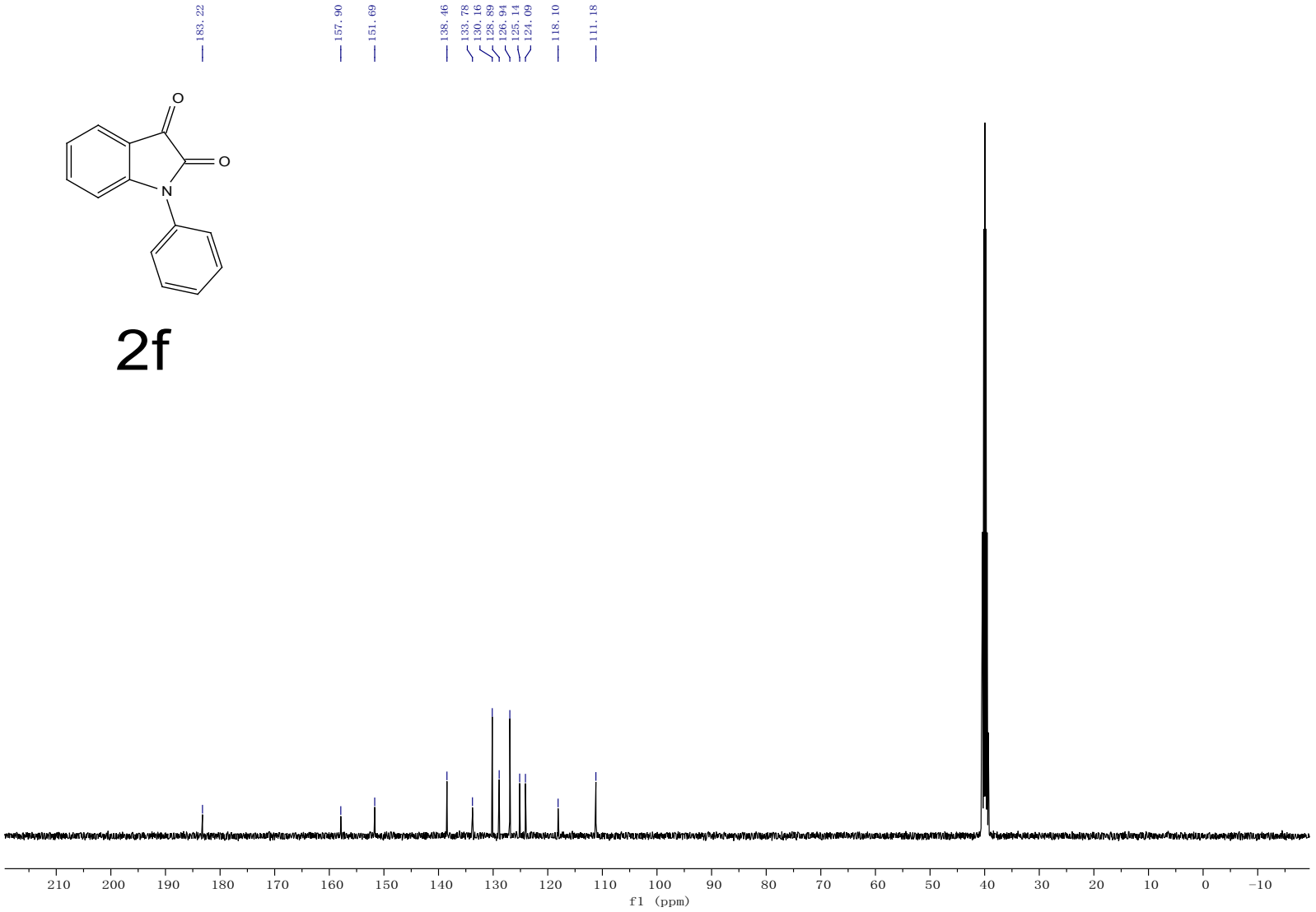
f1 (ppm)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124.09
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200
190
180
170
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40
30
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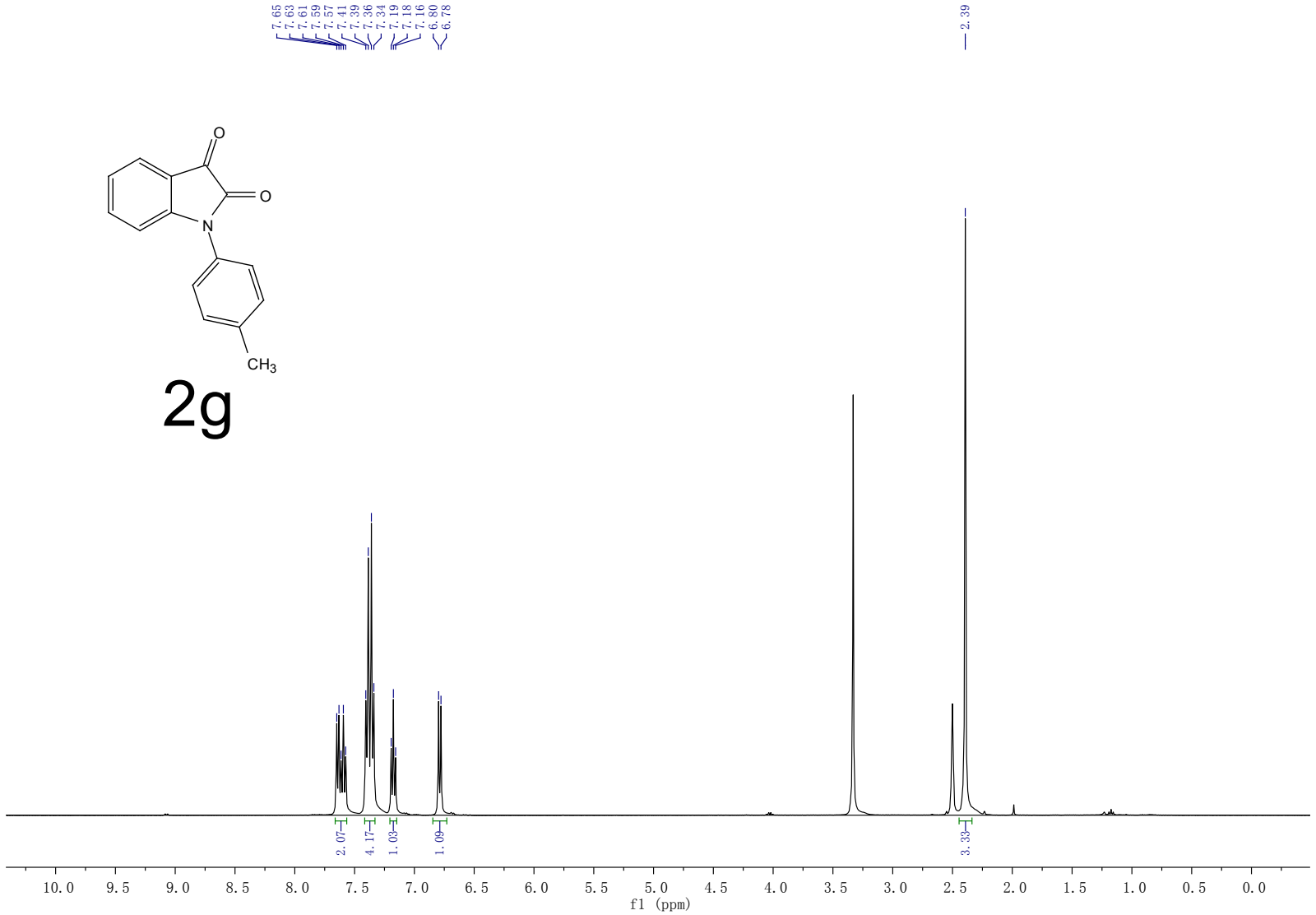
f1 (ppm)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7.18
7.16
6.80
6.78
2.39
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O
N
CH3
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2.07
4.17
1.03
1.09
3.33
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.0
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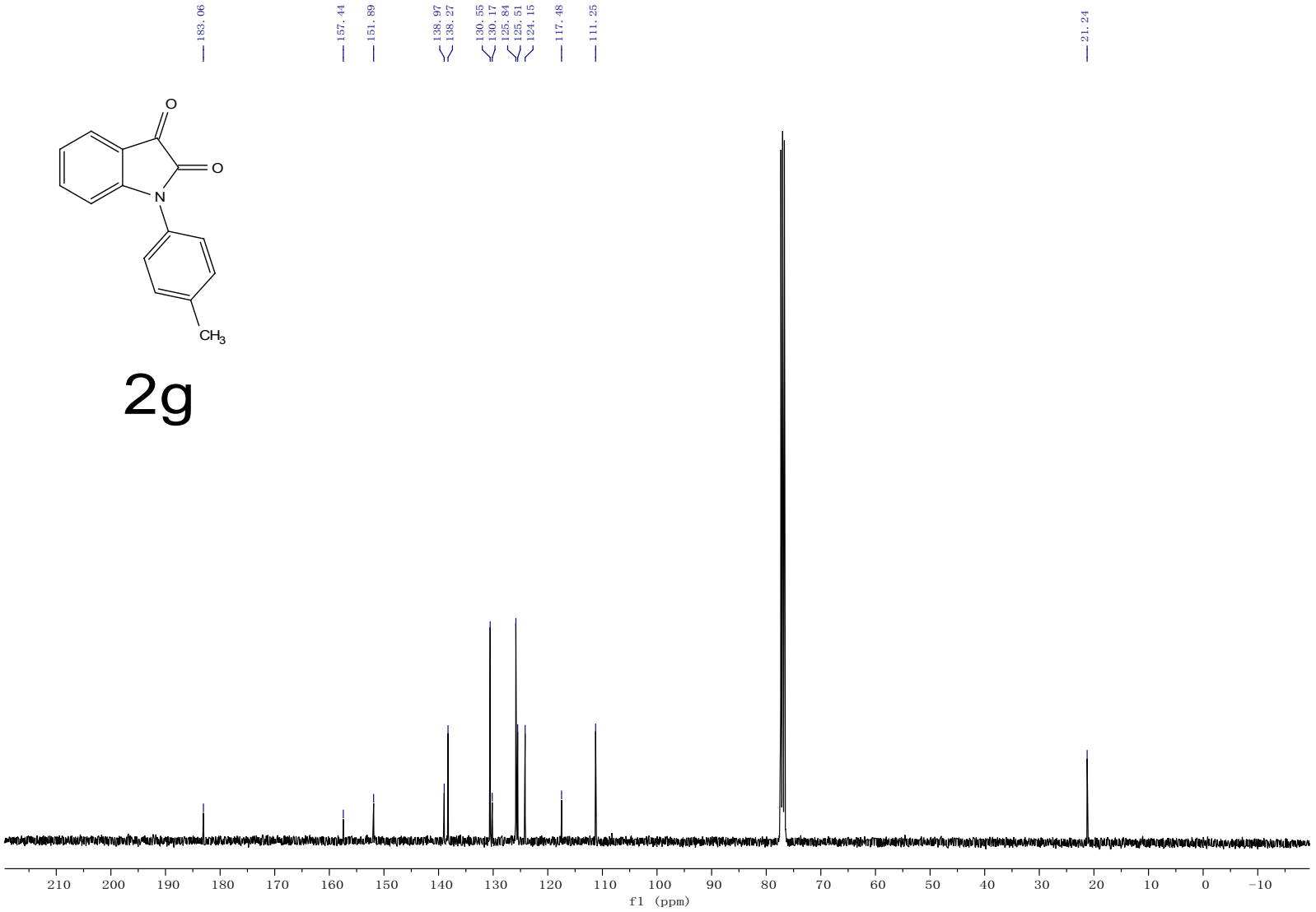
1.0
0.5
0.0
f1 (ppm)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117.48
111.25
21.24
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O
N
CH3
2g
210
200
190
180
170
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40
30
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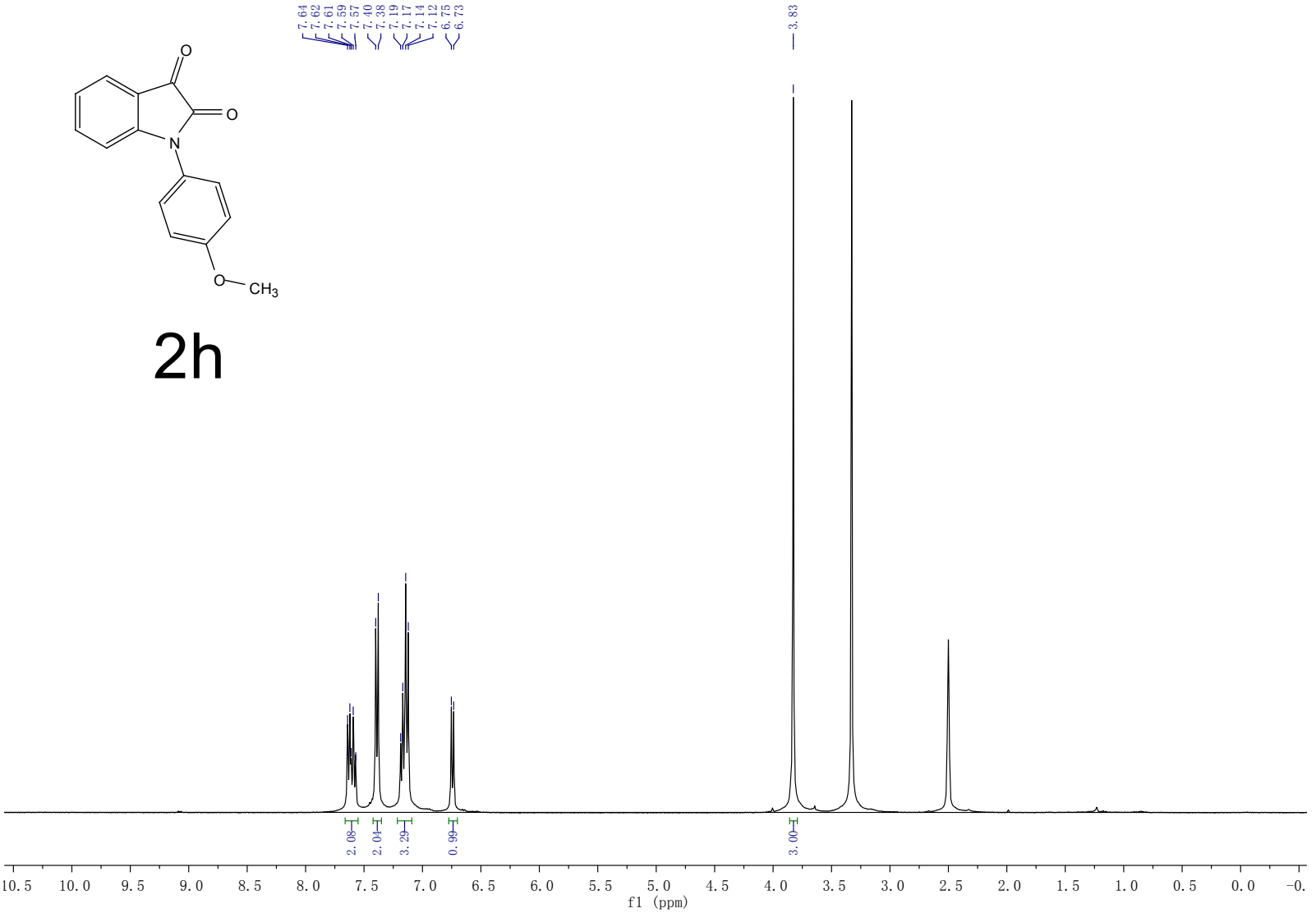
f1 (ppm)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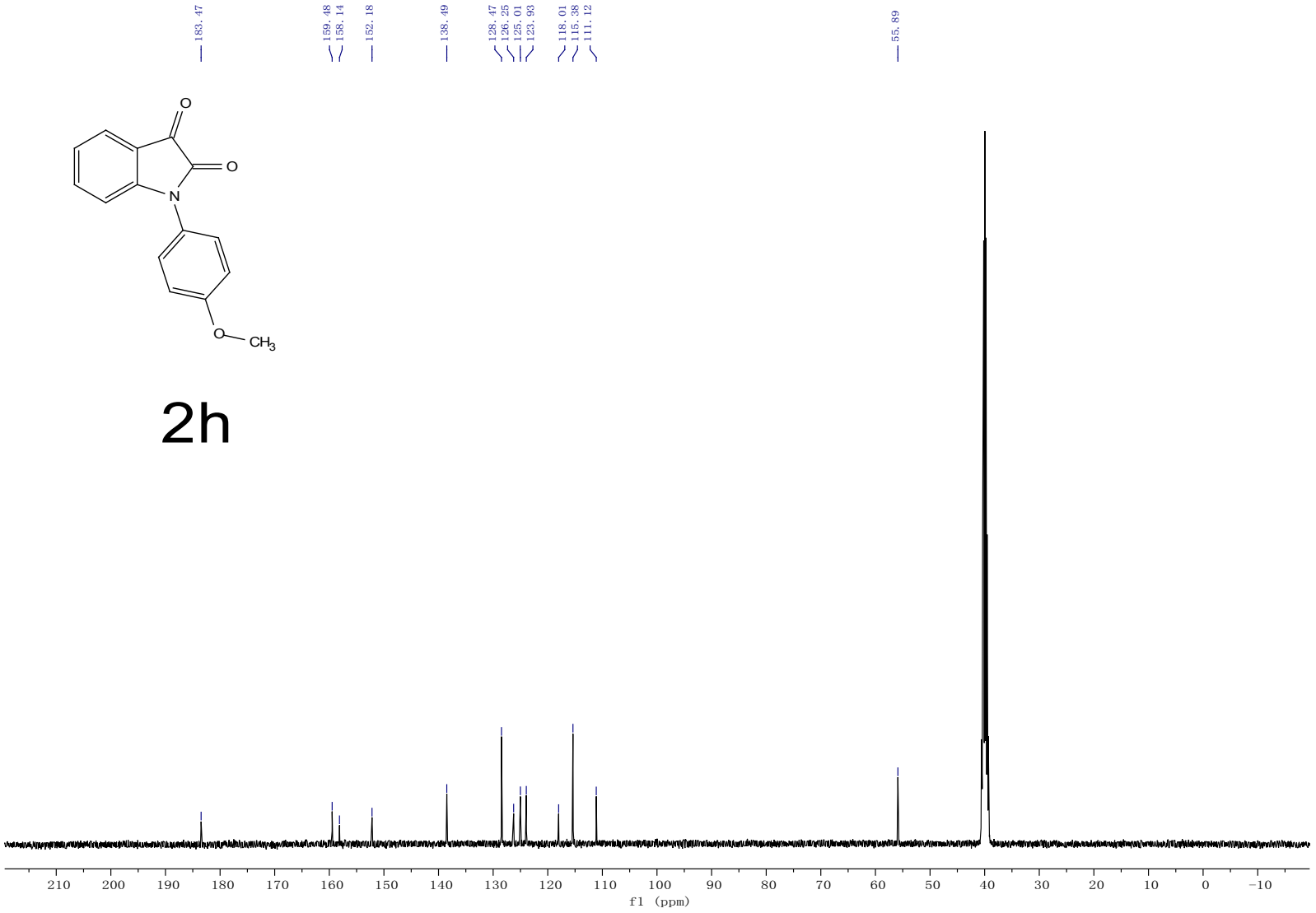
6.73
3.83
O
O
N
O
CH3
2h
2.08
2.04
3.29
0.99
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)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111.12
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O
O
N
O
CH3
2h
210
200
190
180
170
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120
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100
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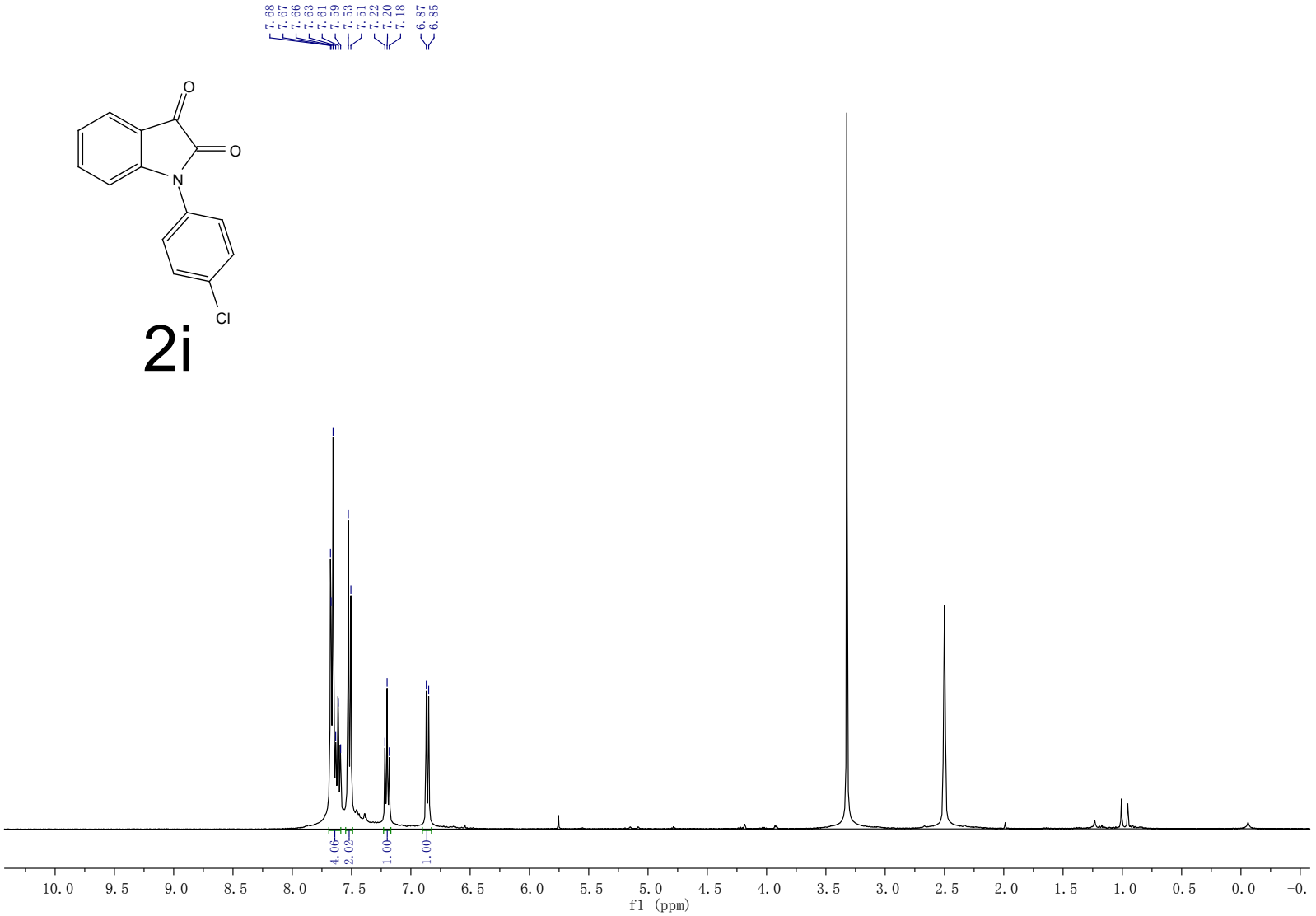
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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Cl
2i
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2.02
1.00
1.00
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.0
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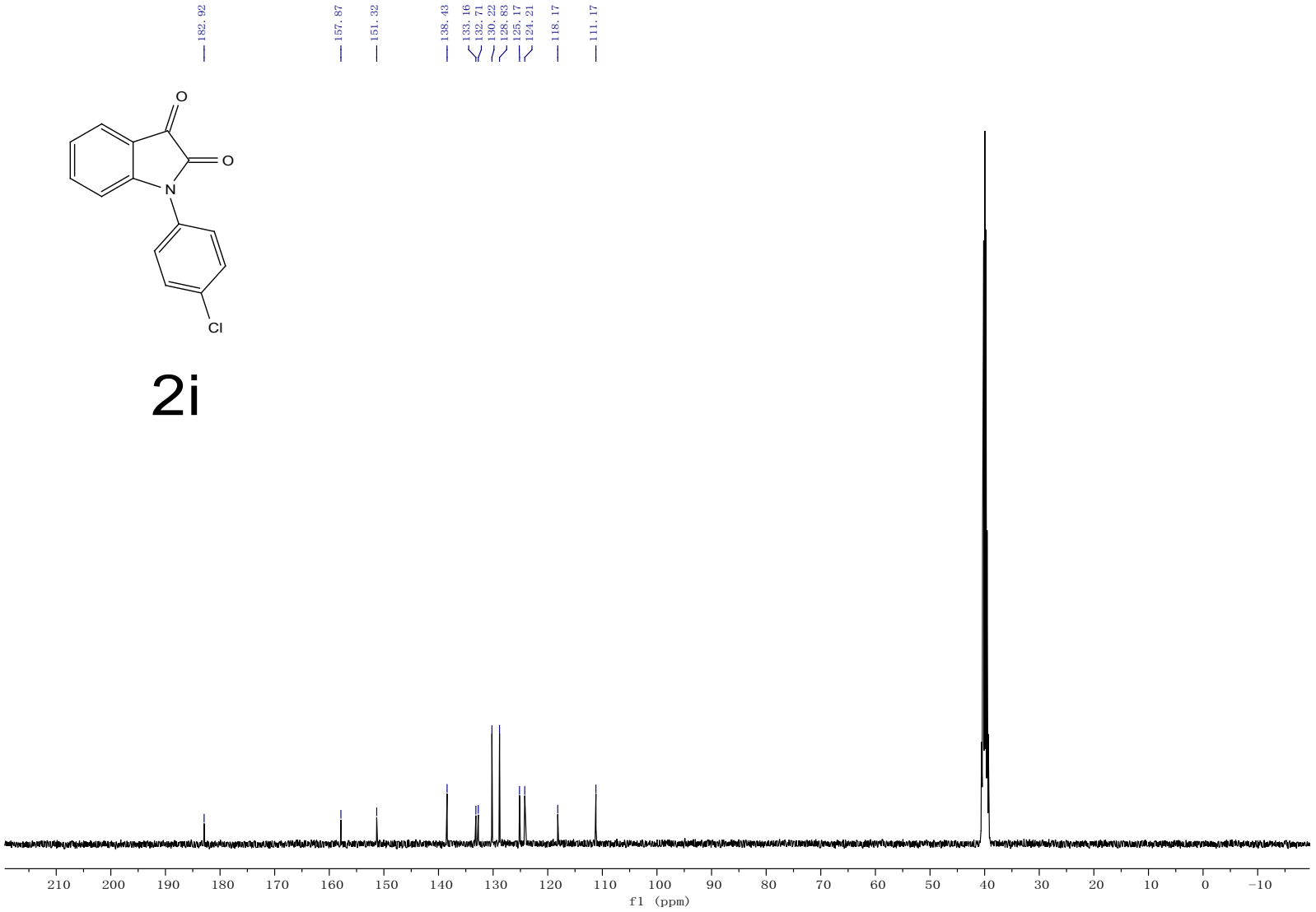
f1 (ppm)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118.17
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O
N
Cl
2i
210
200
190
180
170
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100
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80
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60
50
40
30
20
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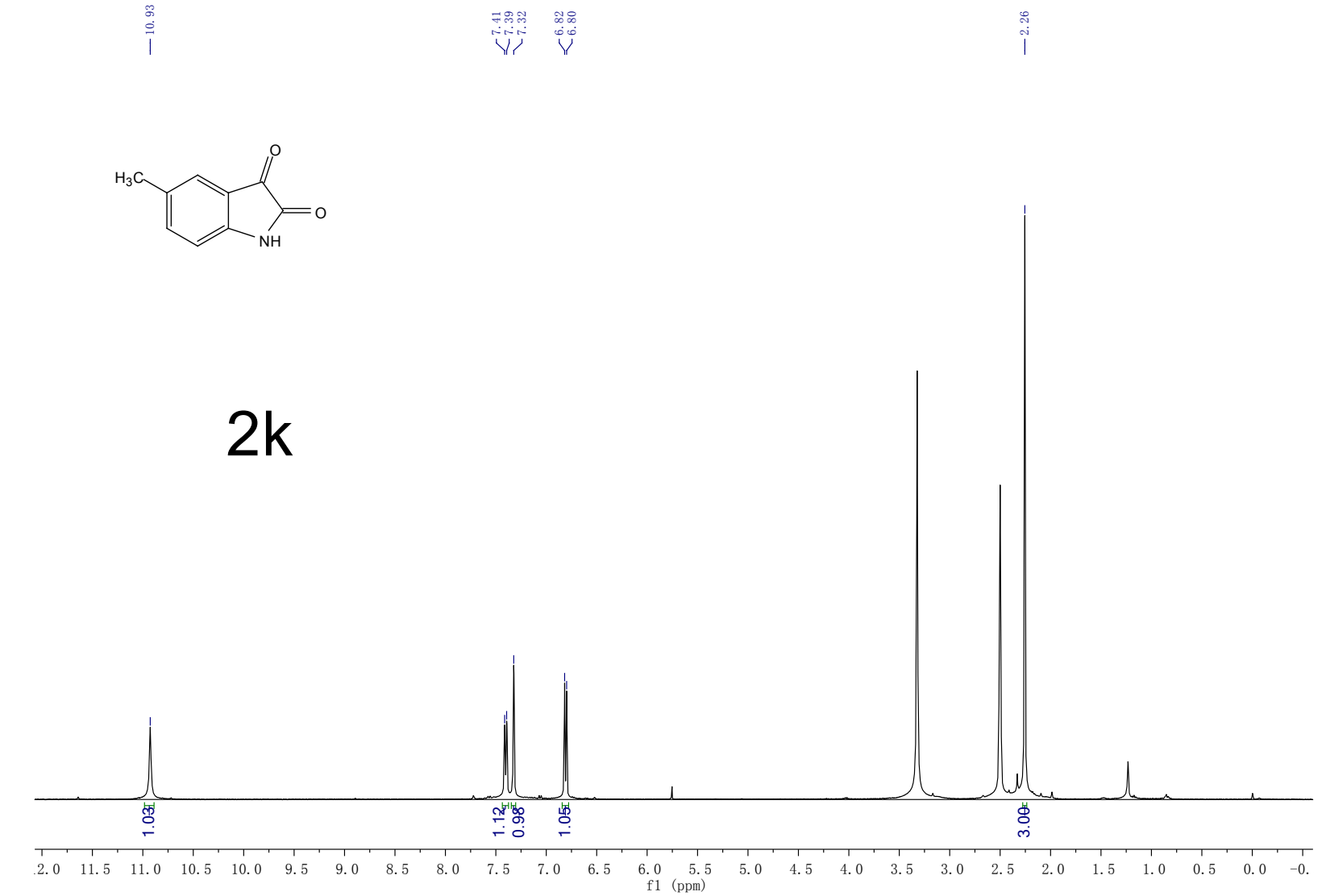
0
−10
f1 (ppm)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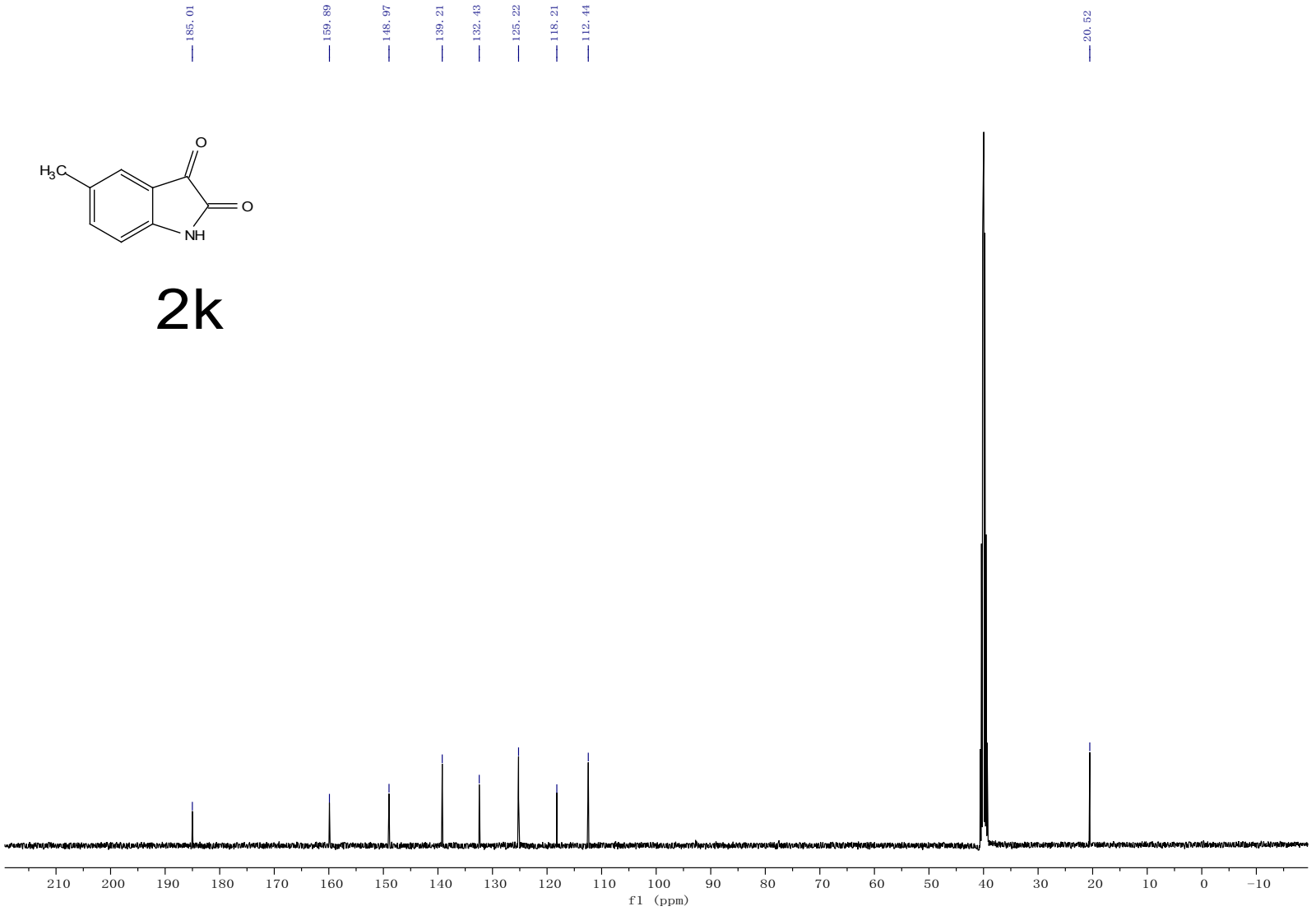
3.00
f1 (ppm)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200
190
180
170
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100
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80
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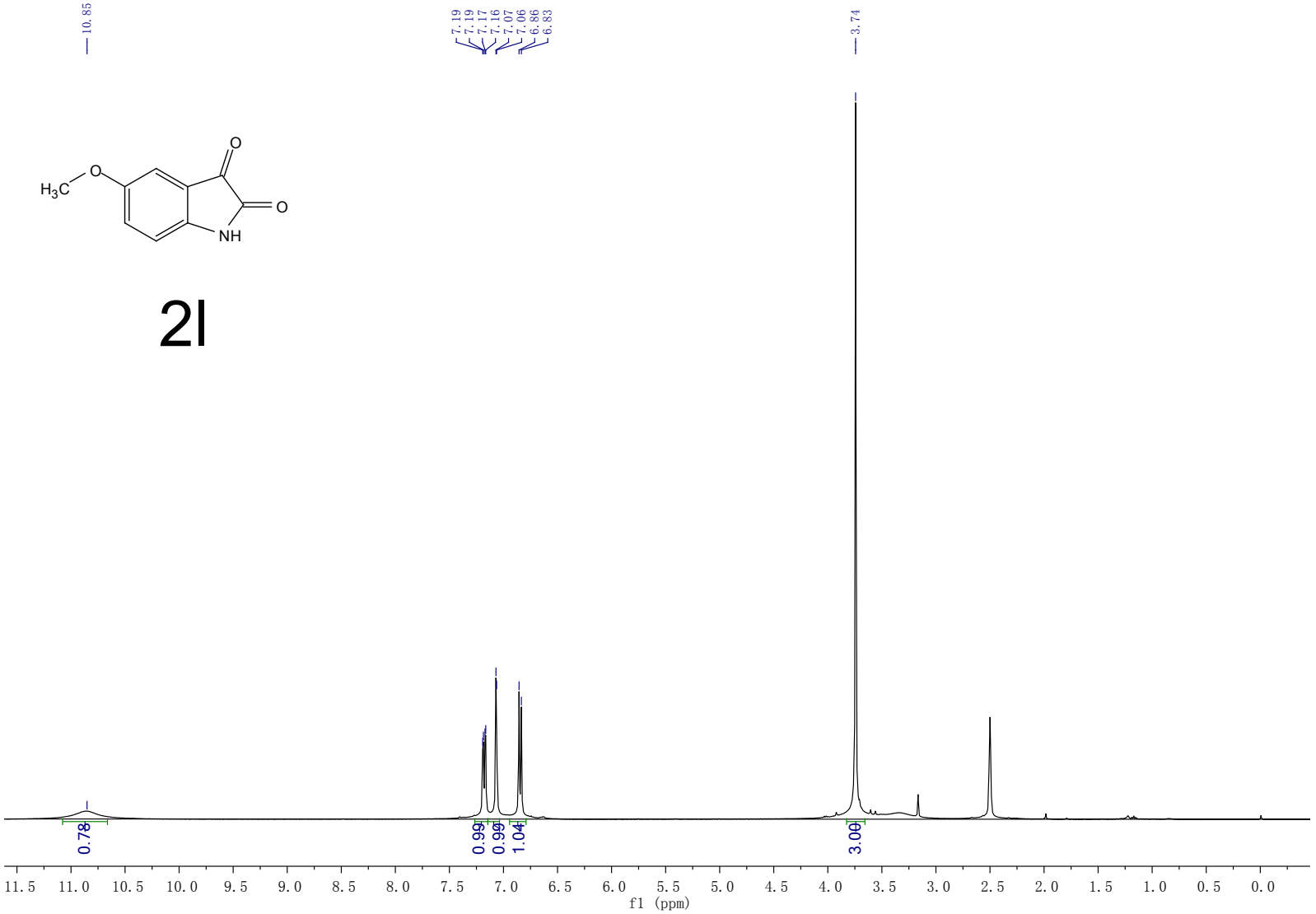
60
50
40
30
20
10
0
−10
f1 (ppm)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H_3C
NH
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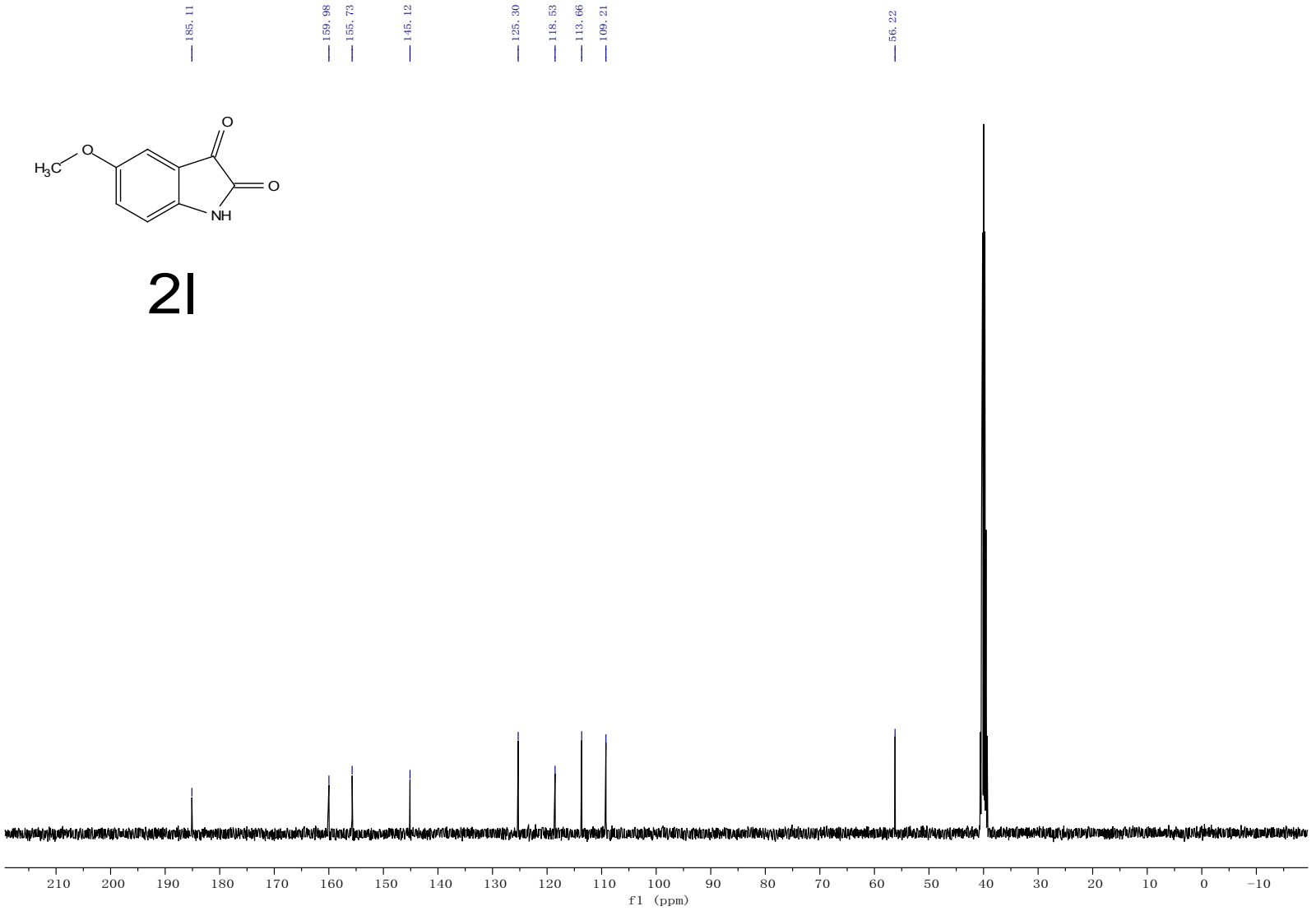
0.99
0.99
1.04
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

2l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109.21
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O
O
H3C
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200
190
180
170
160
150
140
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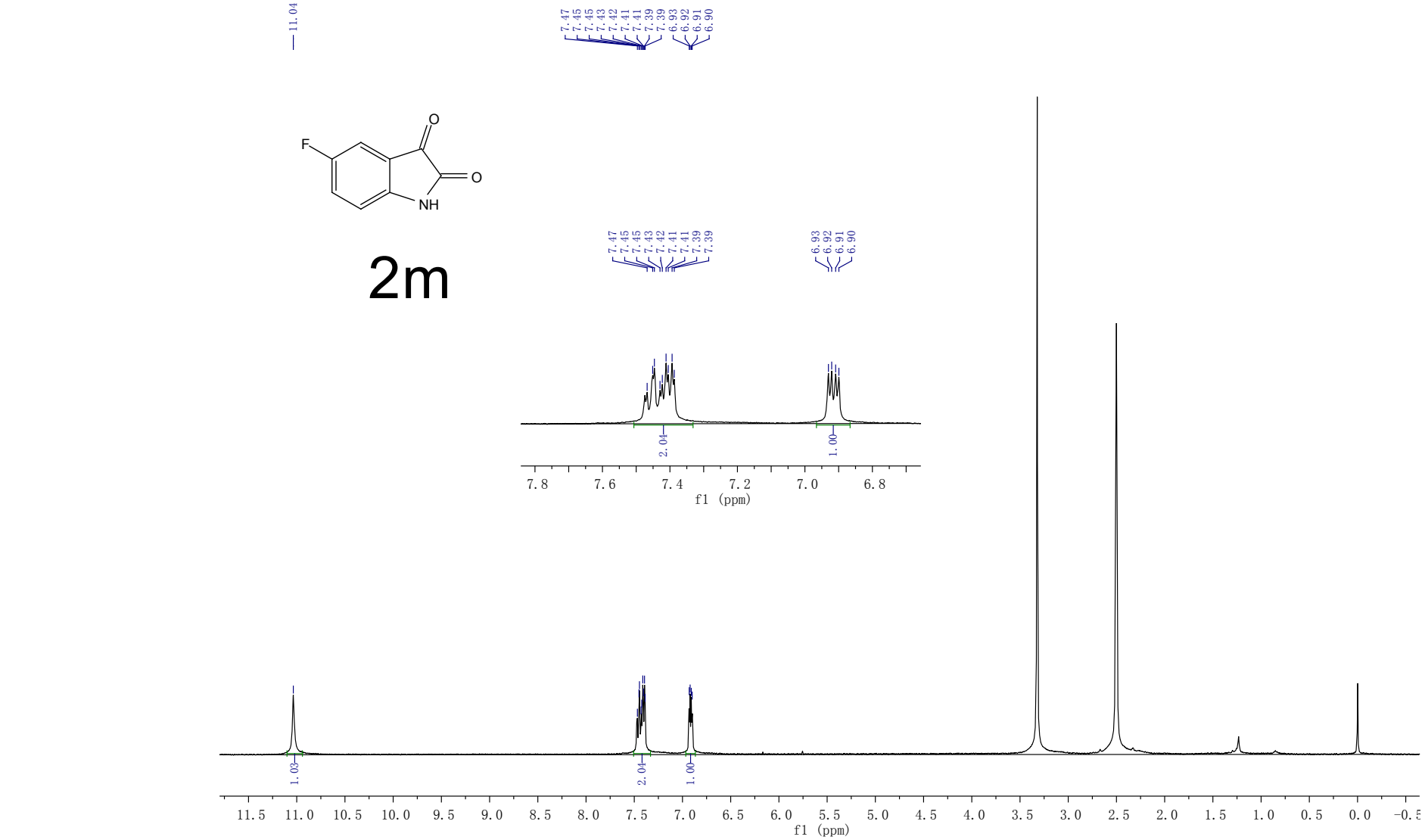
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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6.91
6.90
F
O
O
NH
2m
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7.45
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7.41
7.39
7.39
6.93
6.92
6.91
6.90
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7.8
7.6
7.4
7.2
7.0
6.8
f1 (ppm)
1.03
2.04
1.00
11.5
11.0
10.5
10.0
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8.0
7.5
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4.5
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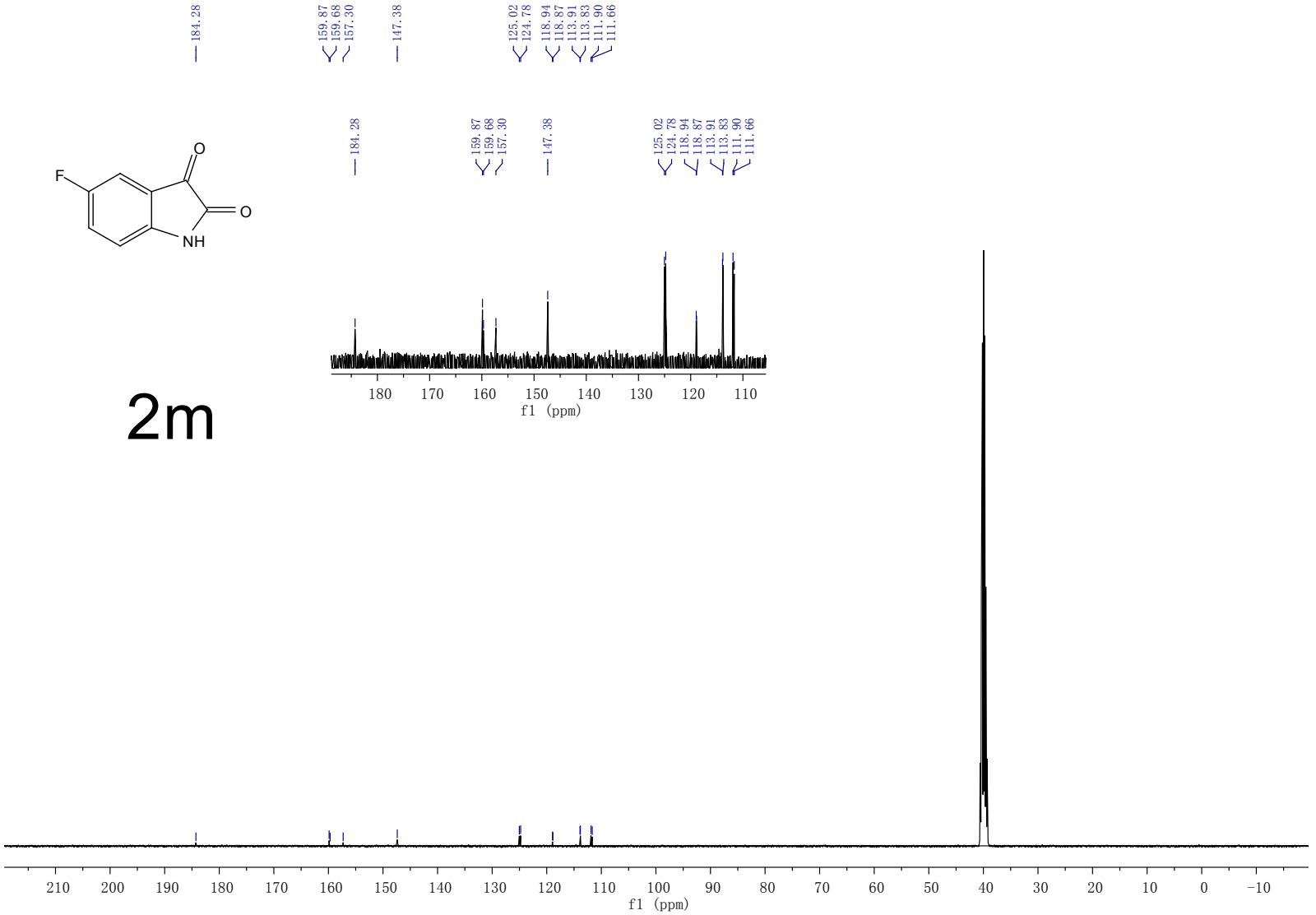
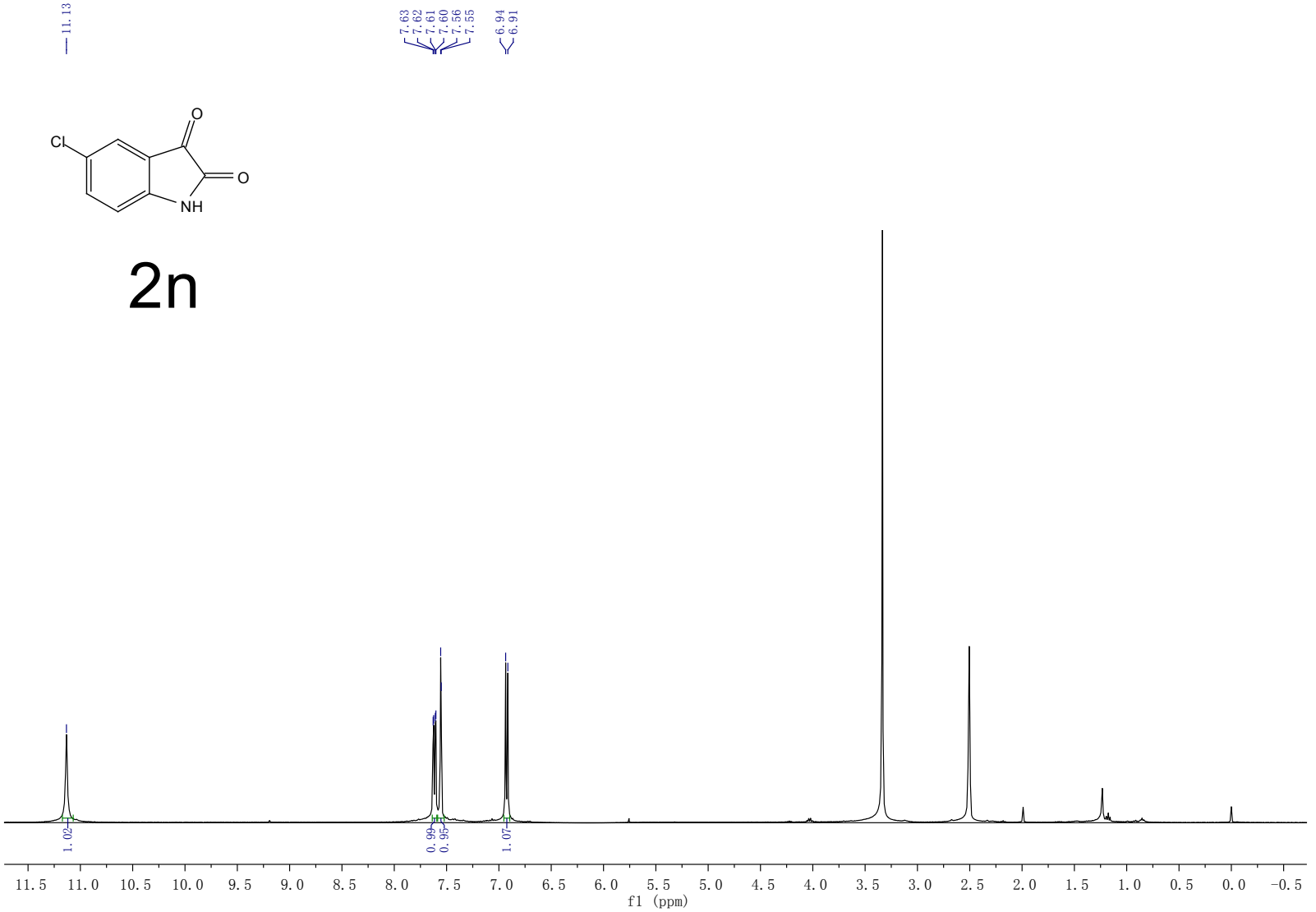
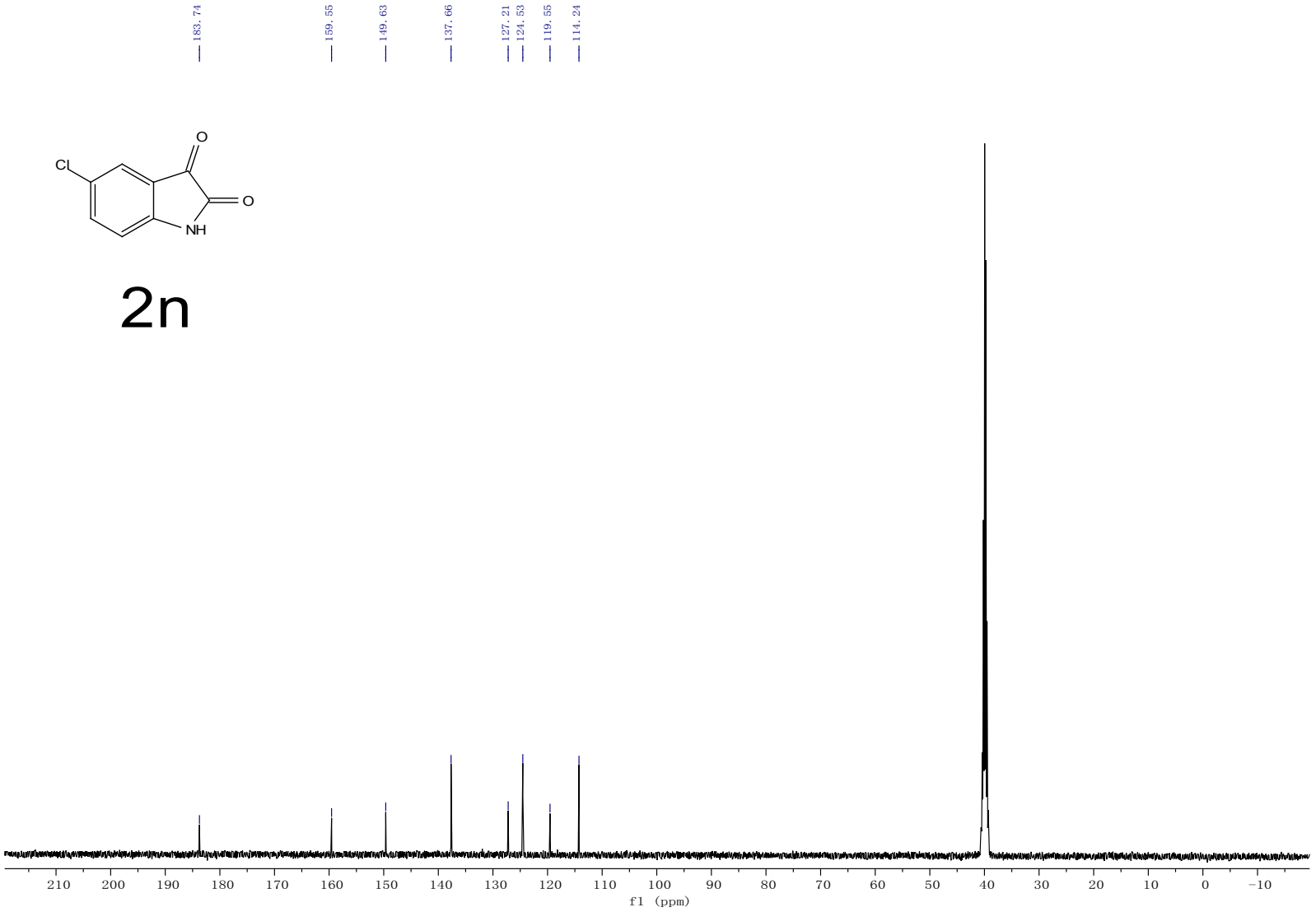
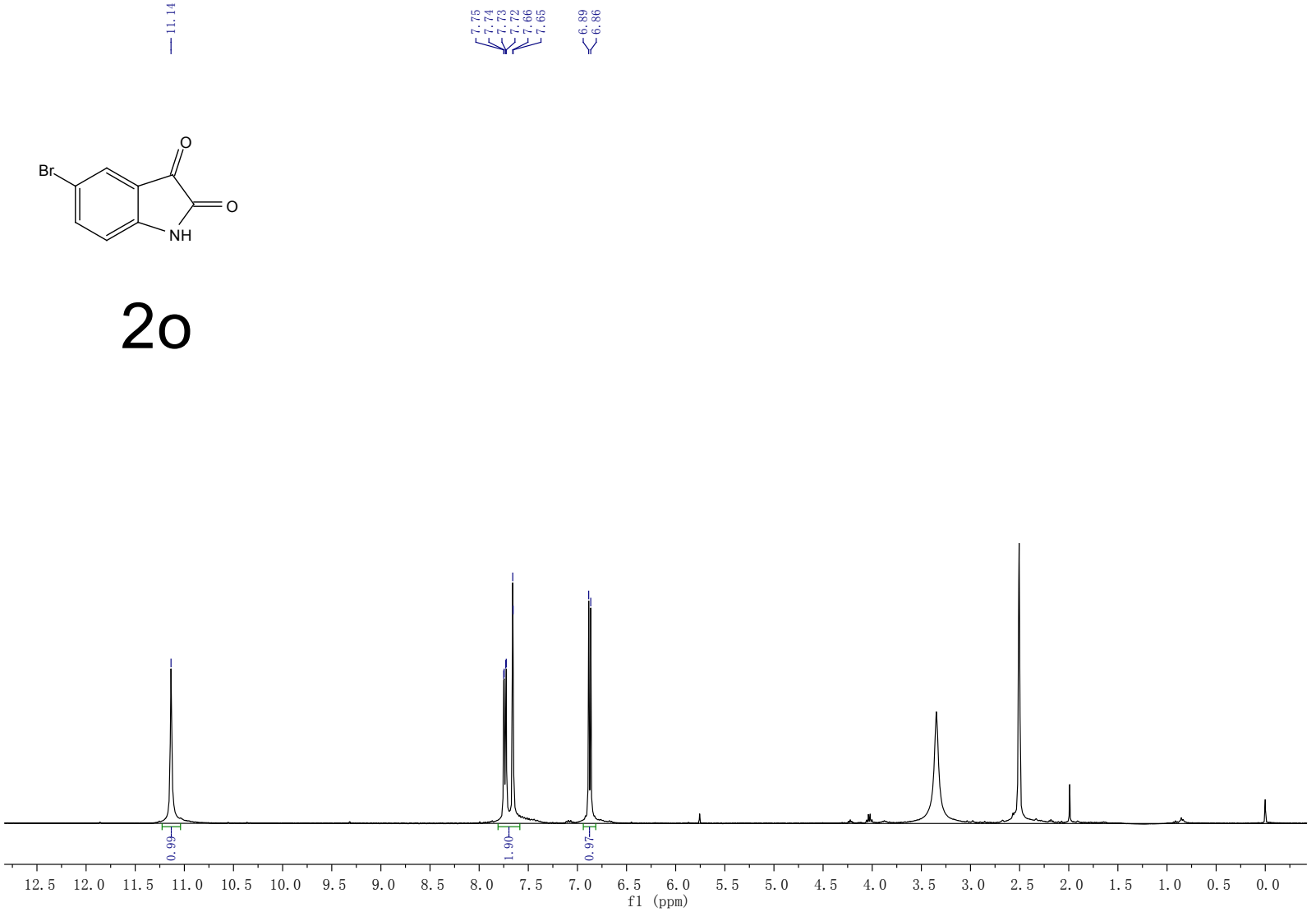
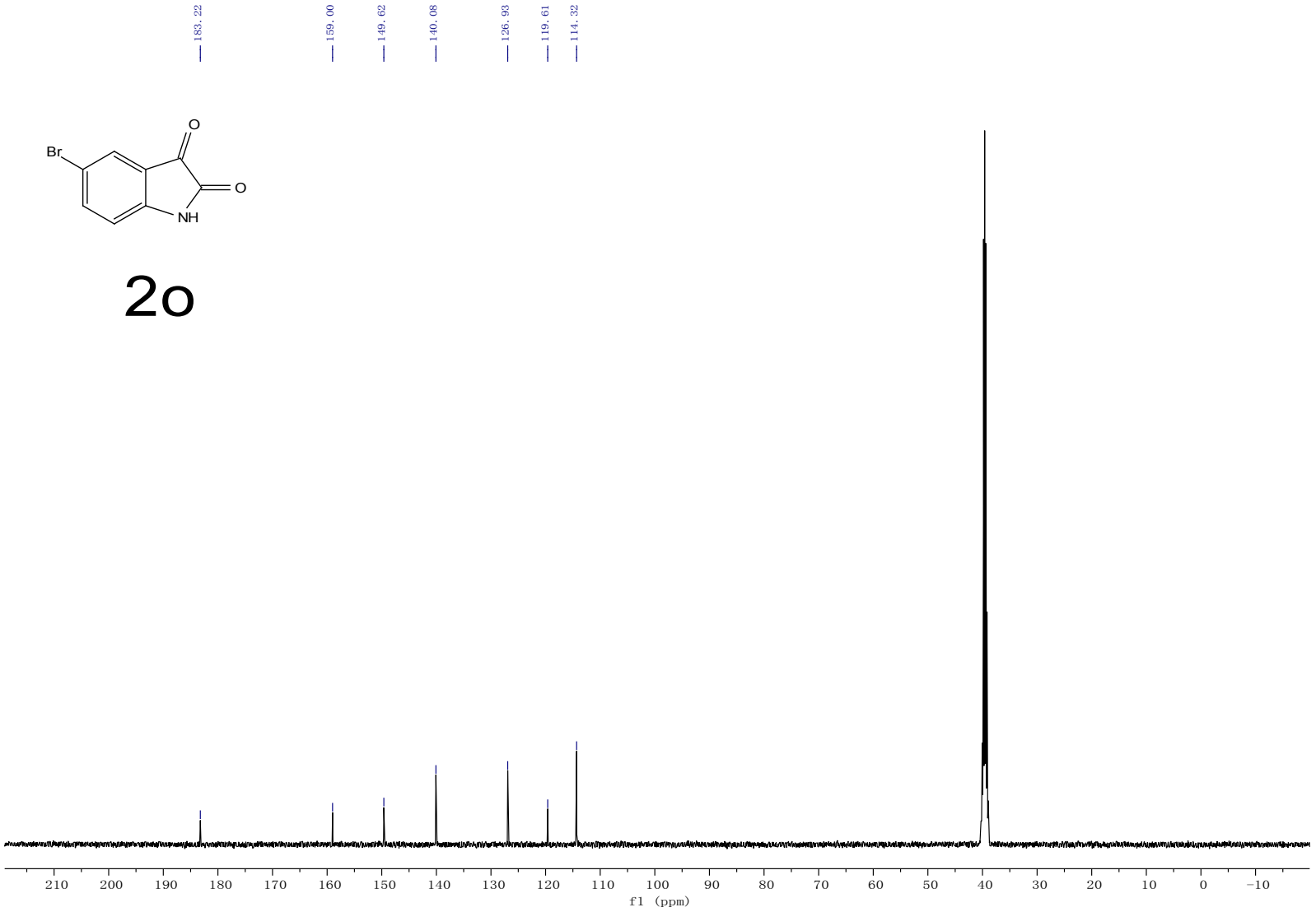
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

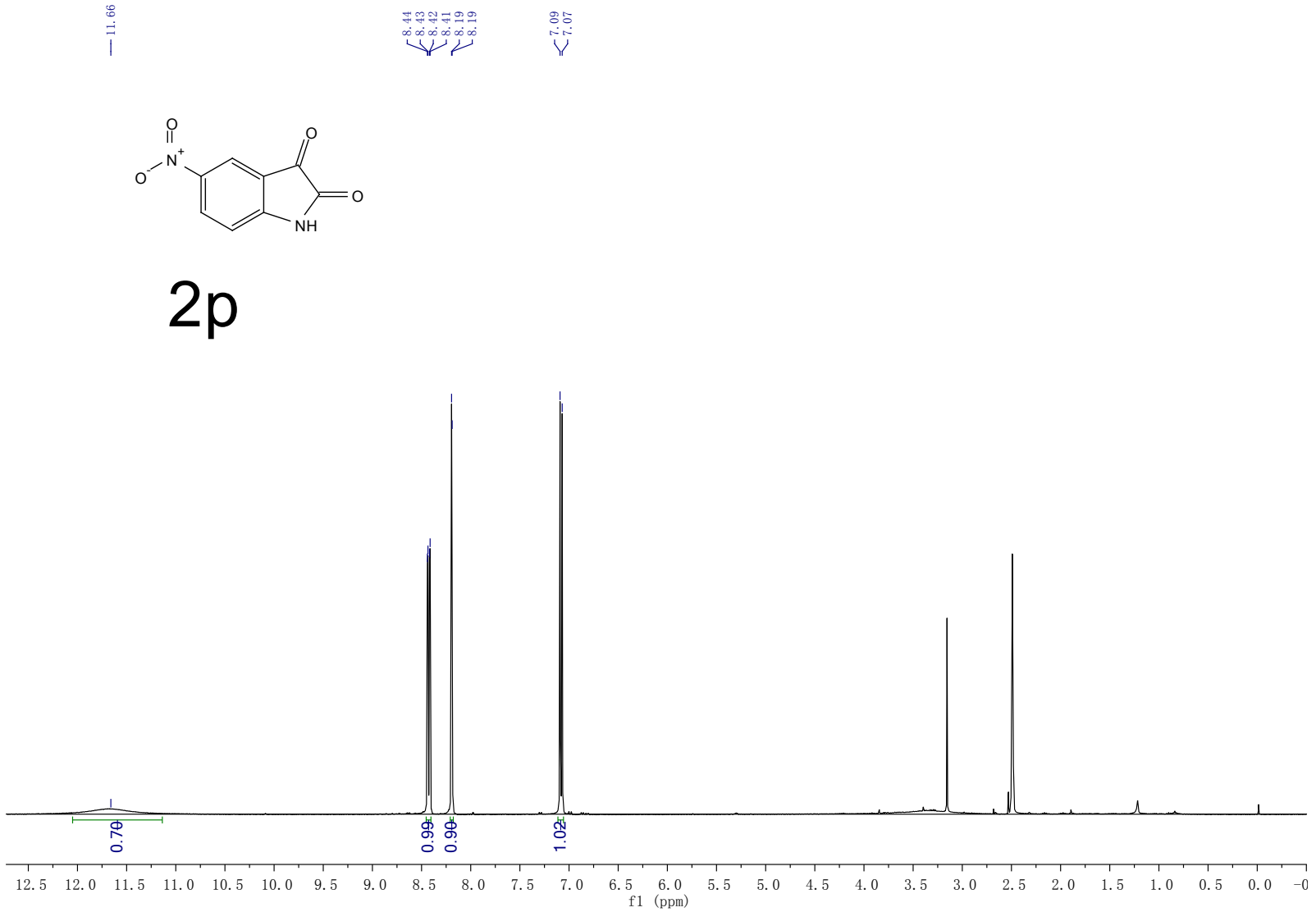

184.28
159.87
159.68
157.30
147.38
125.02
124.78
118.94
118.87
113.91
113.83
111.90
111.66
F
O
O
NH
2m
180
170
160
150
140
130
120
110
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

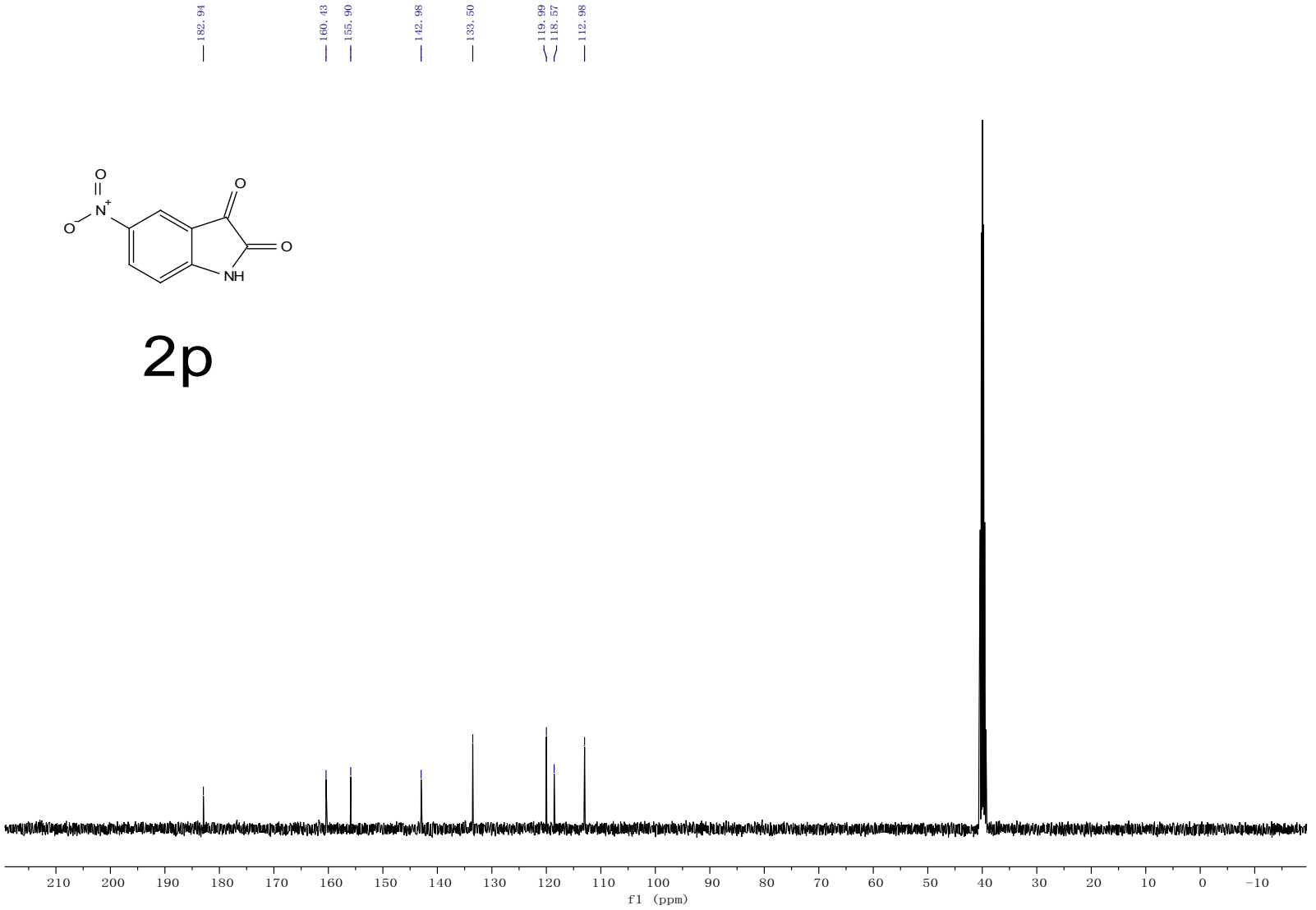

11.13
7.63
7.62
7.61
7.60
7.56
7.55
6.94
6.91
Cl
O
O
NH
2n
1.02
0.99
0.95
1.07
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

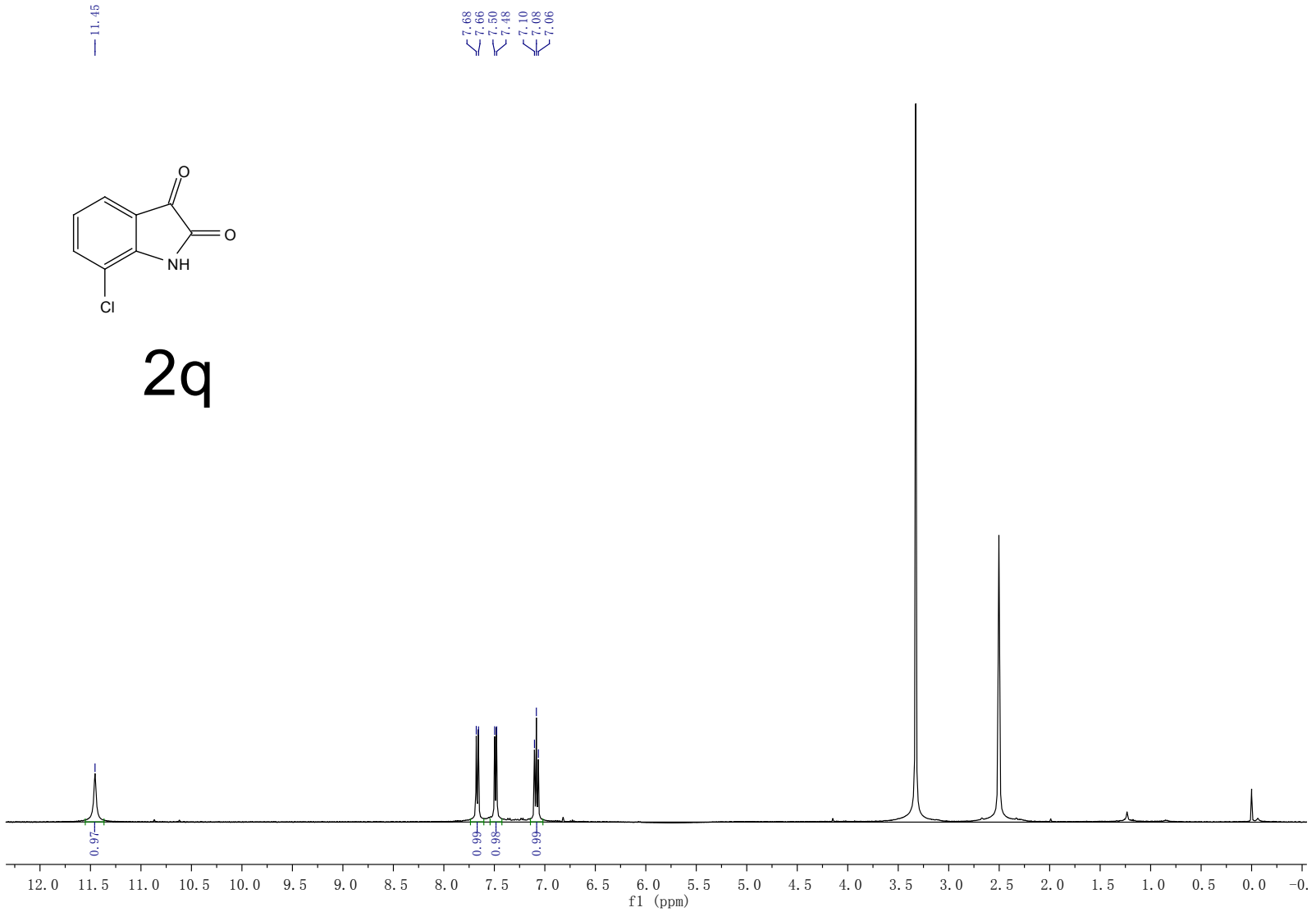

183.74
159.55
149.63
137.66
127.21
124.53
119.55
114.24
Cl
O
O
NH
2n
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

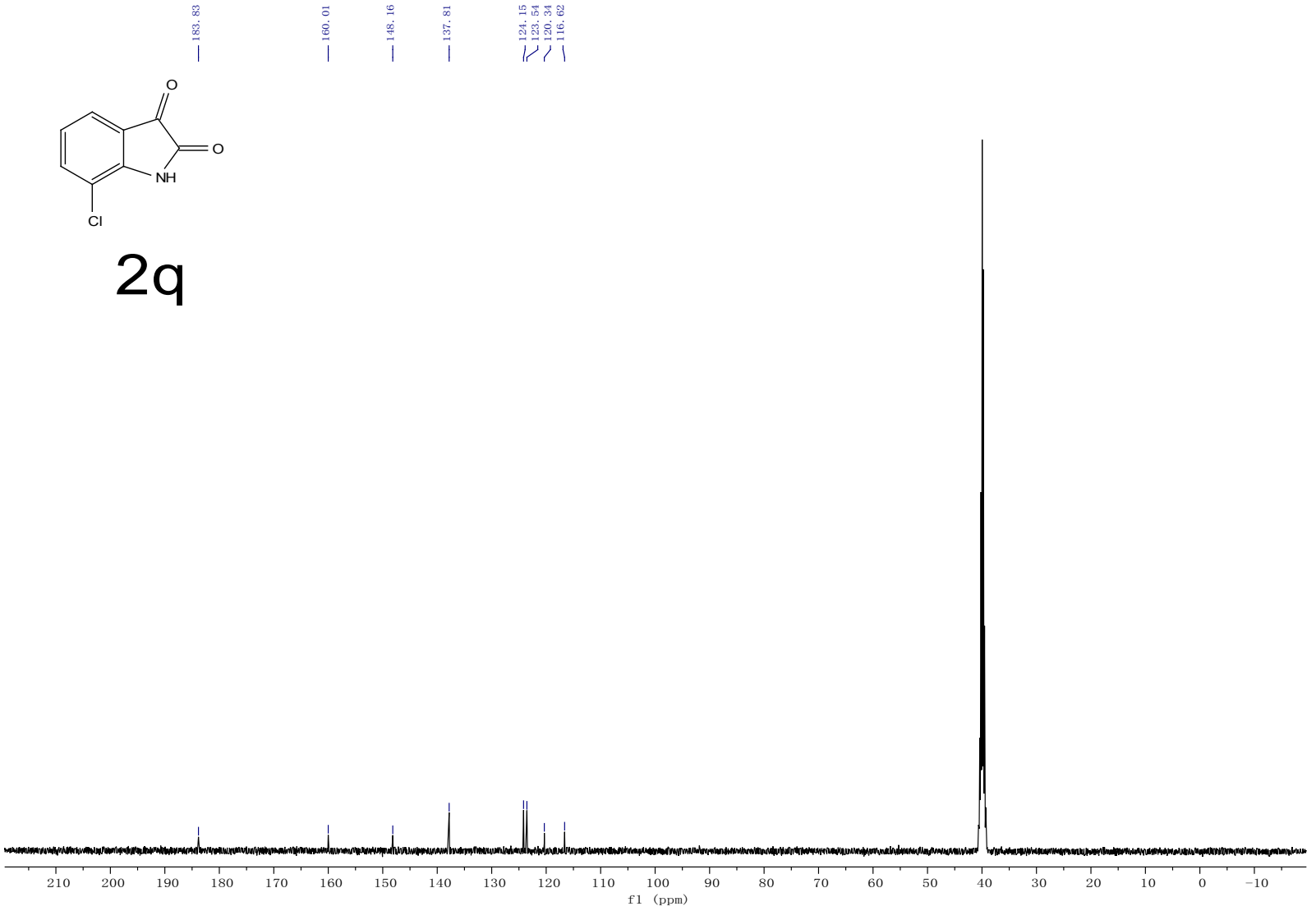

11.14
7.75
7.74
7.73
7.72
7.66
7.65
6.89
6.86
Br
O
O
NH
2o
0.99
1.90
0.97
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

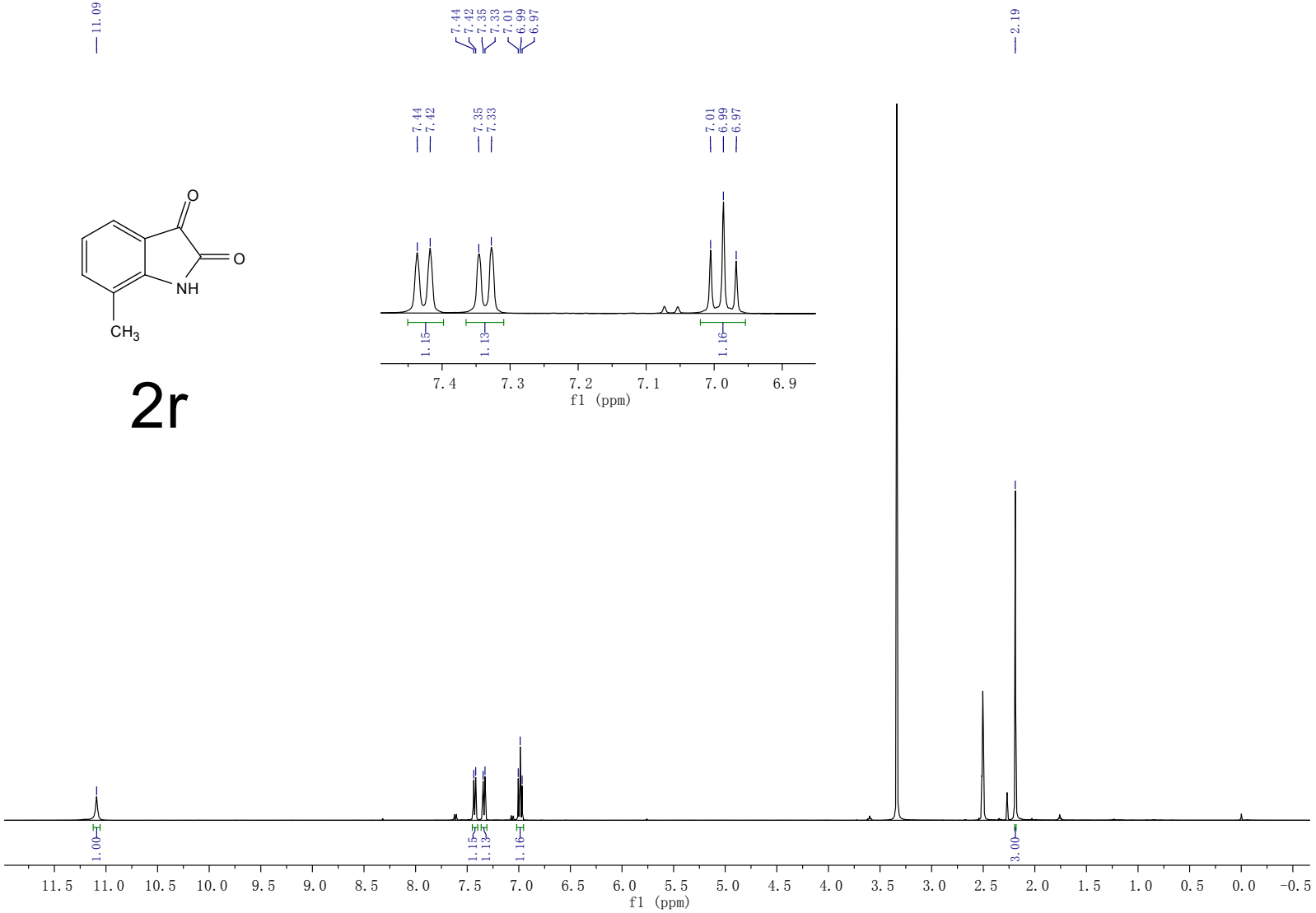

183.22
159.00
149.62
140.08
126.93
119.61
114.32
Br
O
O
NH
2o
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

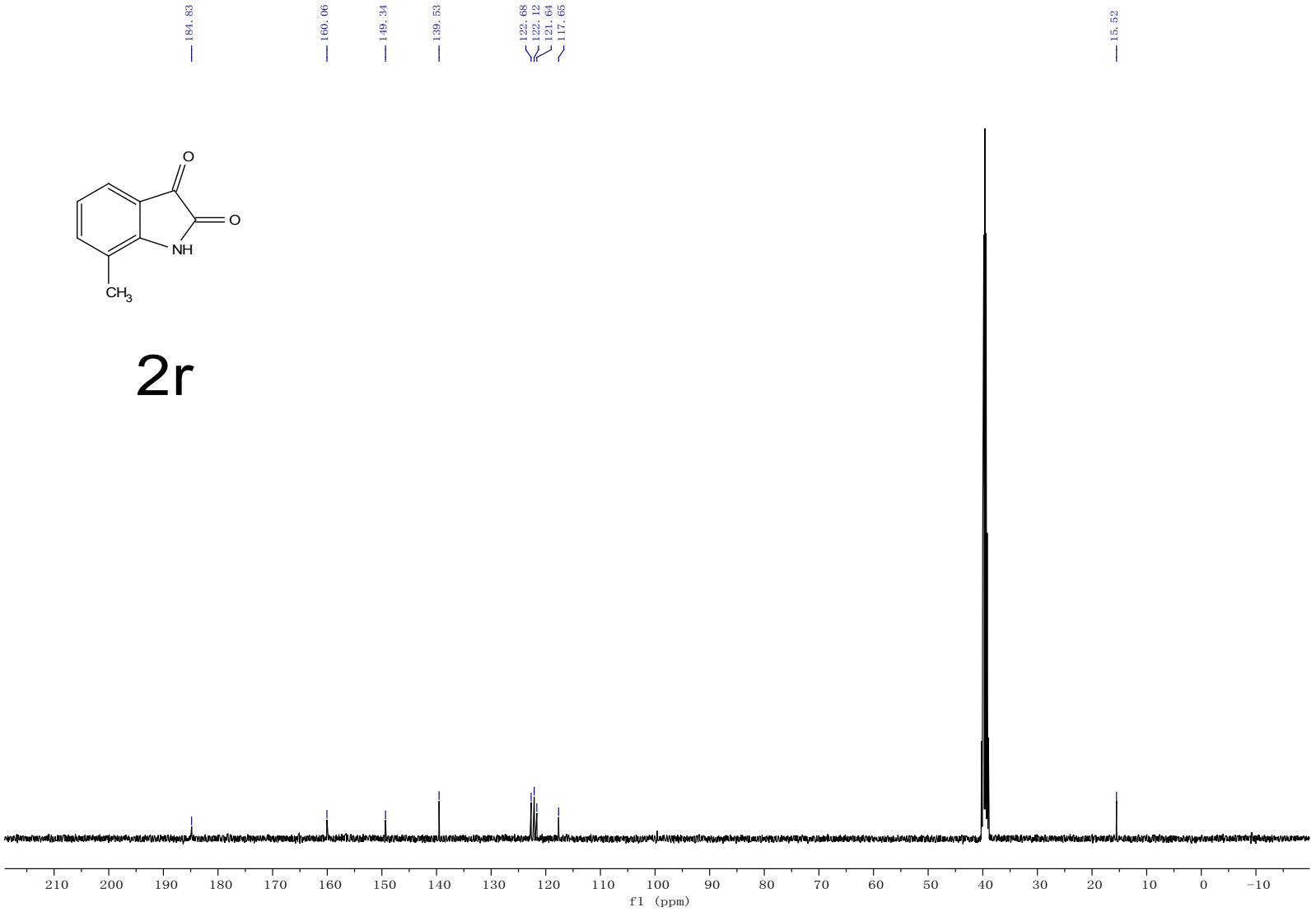

11.66
8.44
8.43
8.42
8.41
8.19
8.19
7.09
7.07
O
N+
O-
O
O
NH
2p
0.70
0.99
0.90
1.02
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

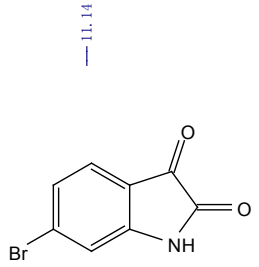

182.94
160.43
155.90
142.98
133.50
119.99
118.57
112.98
O
N+
O-
O
O
NH
2p
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


11.45
7.68
7.66
7.50
7.48
7.10
7.08
7.06
O
O
NH
Cl
2q
0.97
0.99
0.98
0.99
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


183.83
160.01
148.16
137.81
124.15
123.54
120.34
116.62
O
O
NH
Cl
2q
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

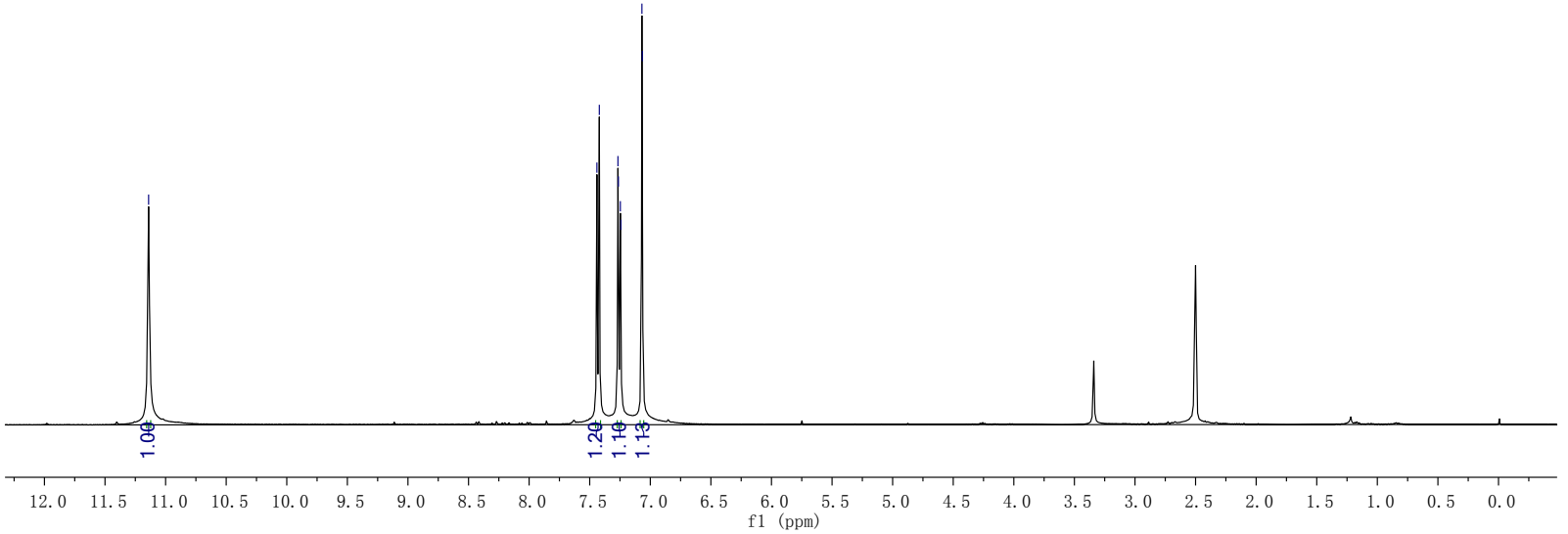

11.09
7.44
7.42
7.35
7.33
7.01
6.99
6.97
2.19
O
O
NH
CH3
2r
1.15
1.13
1.16
f1 (ppm)
1.00
3.00

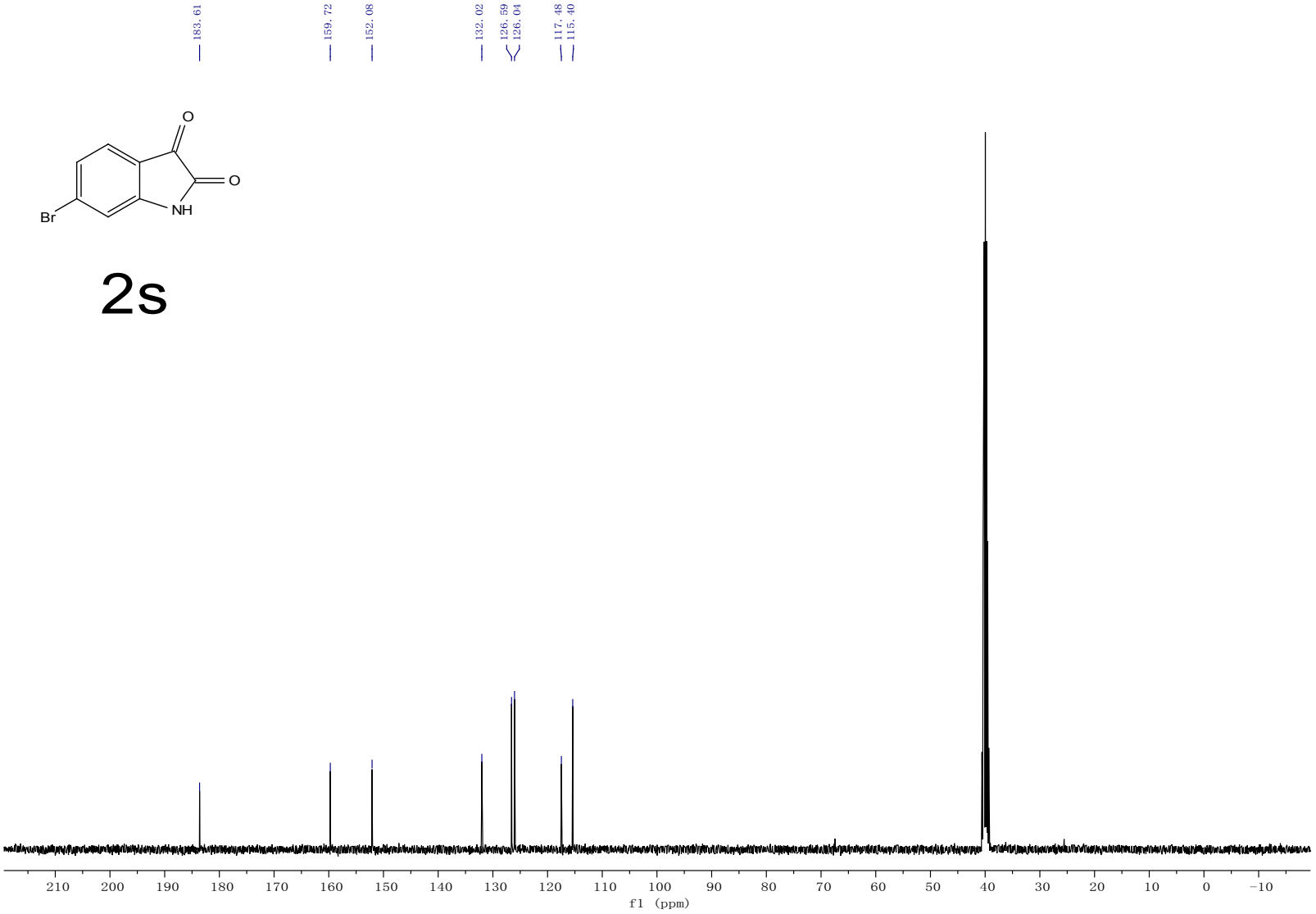

184.83
160.06
149.34
139.53
122.68
122.12
121.64
117.65
15.52
O
O
NH
CH3
2r
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

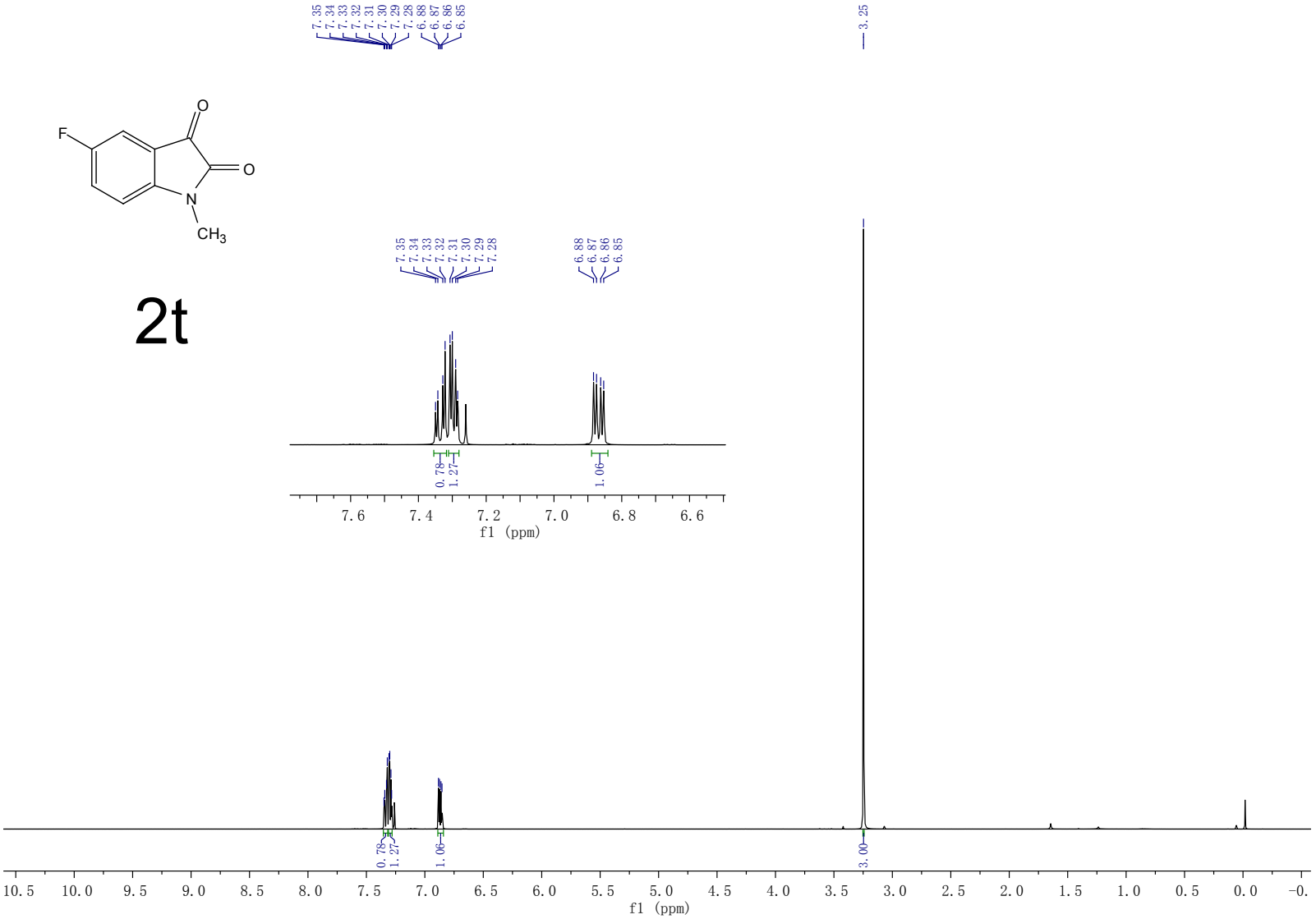

11.14
O
O
NH
Br

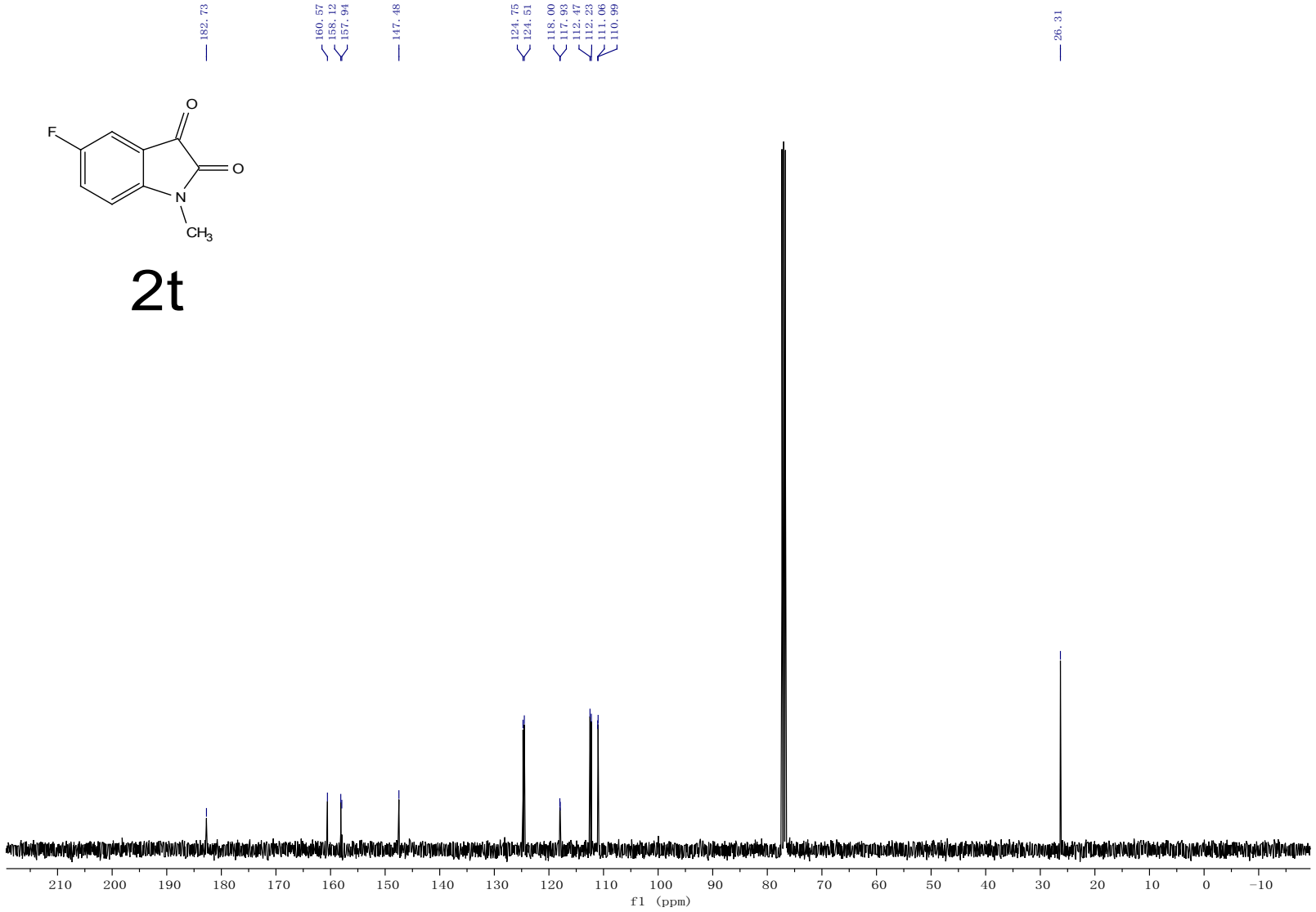

7.44
7.42
7.27
7.26
7.25
7.24
7.07
7.07

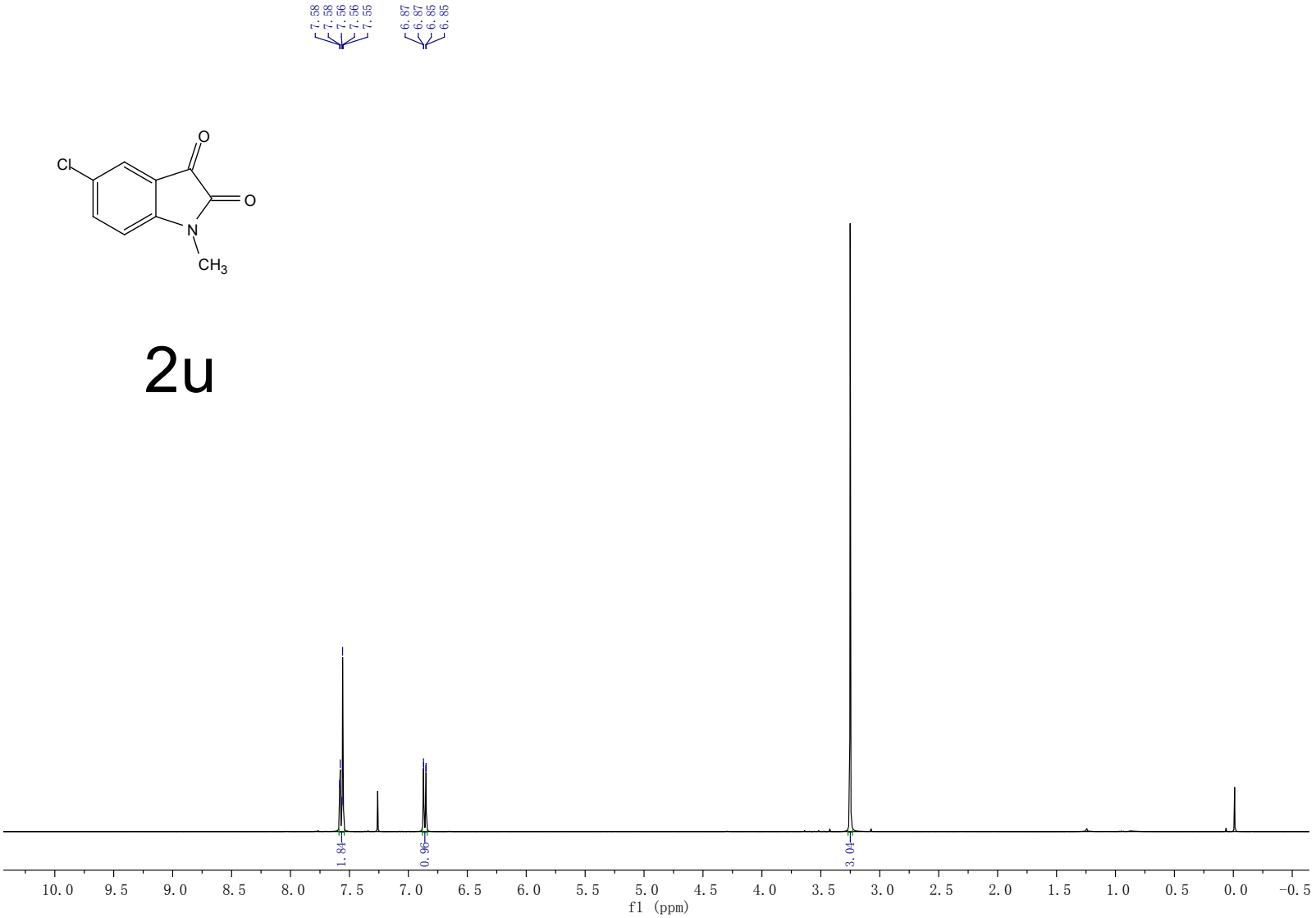
2s

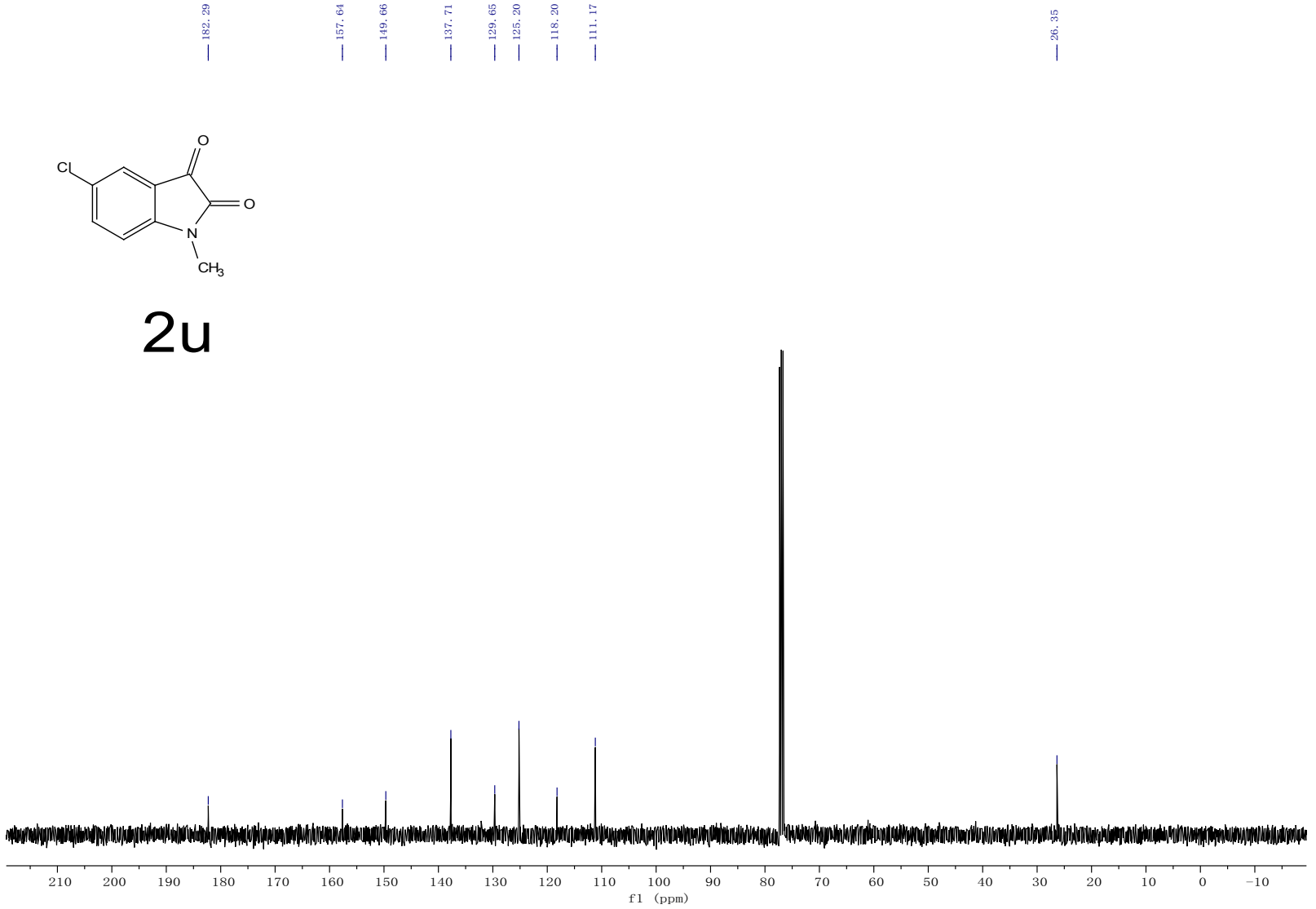

1.00
1.20
1.10
1.13
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

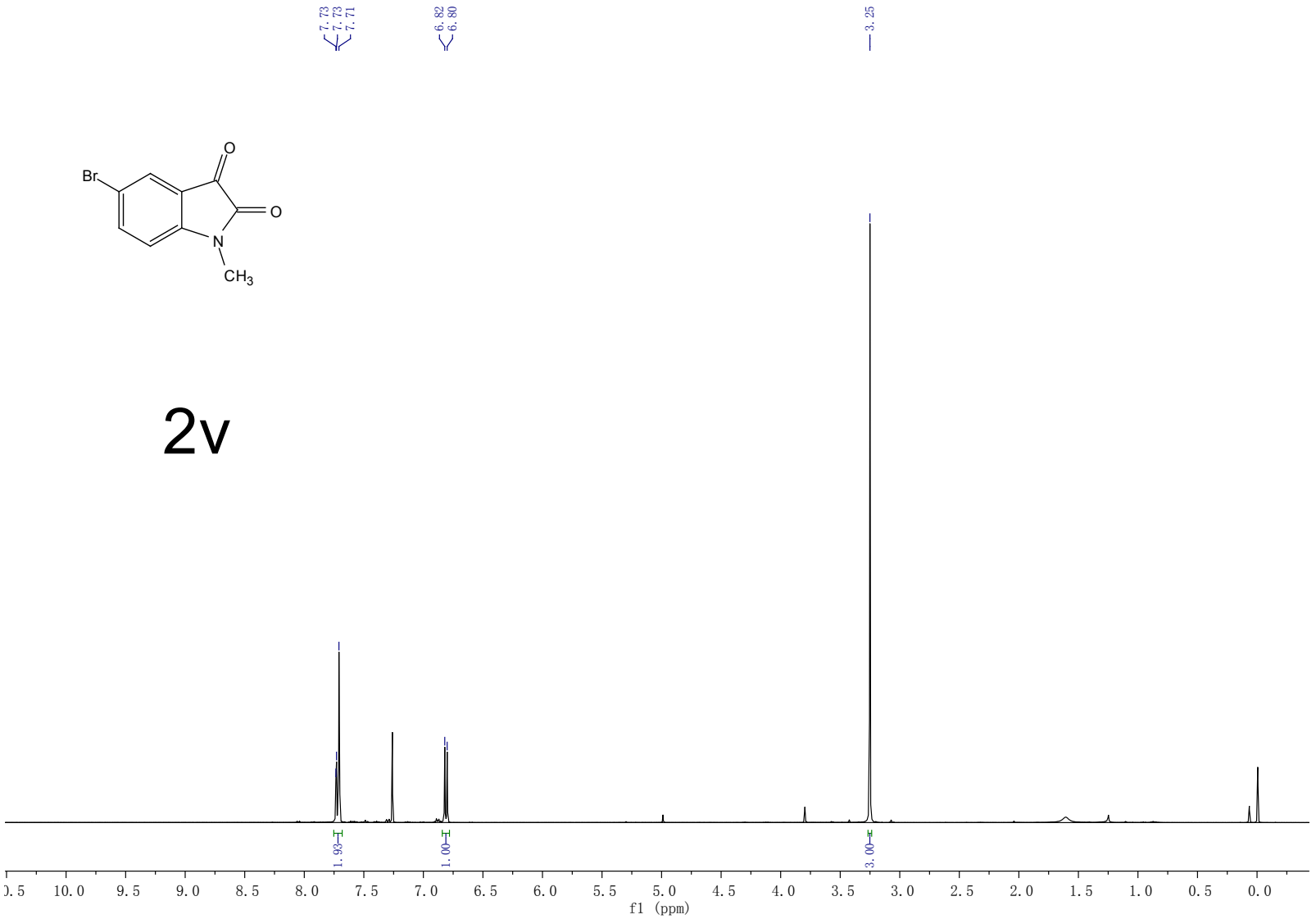

183.61
159.72
152.08
132.02
126.59
126.04
117.48
115.40
O
O
NH
Br
2s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

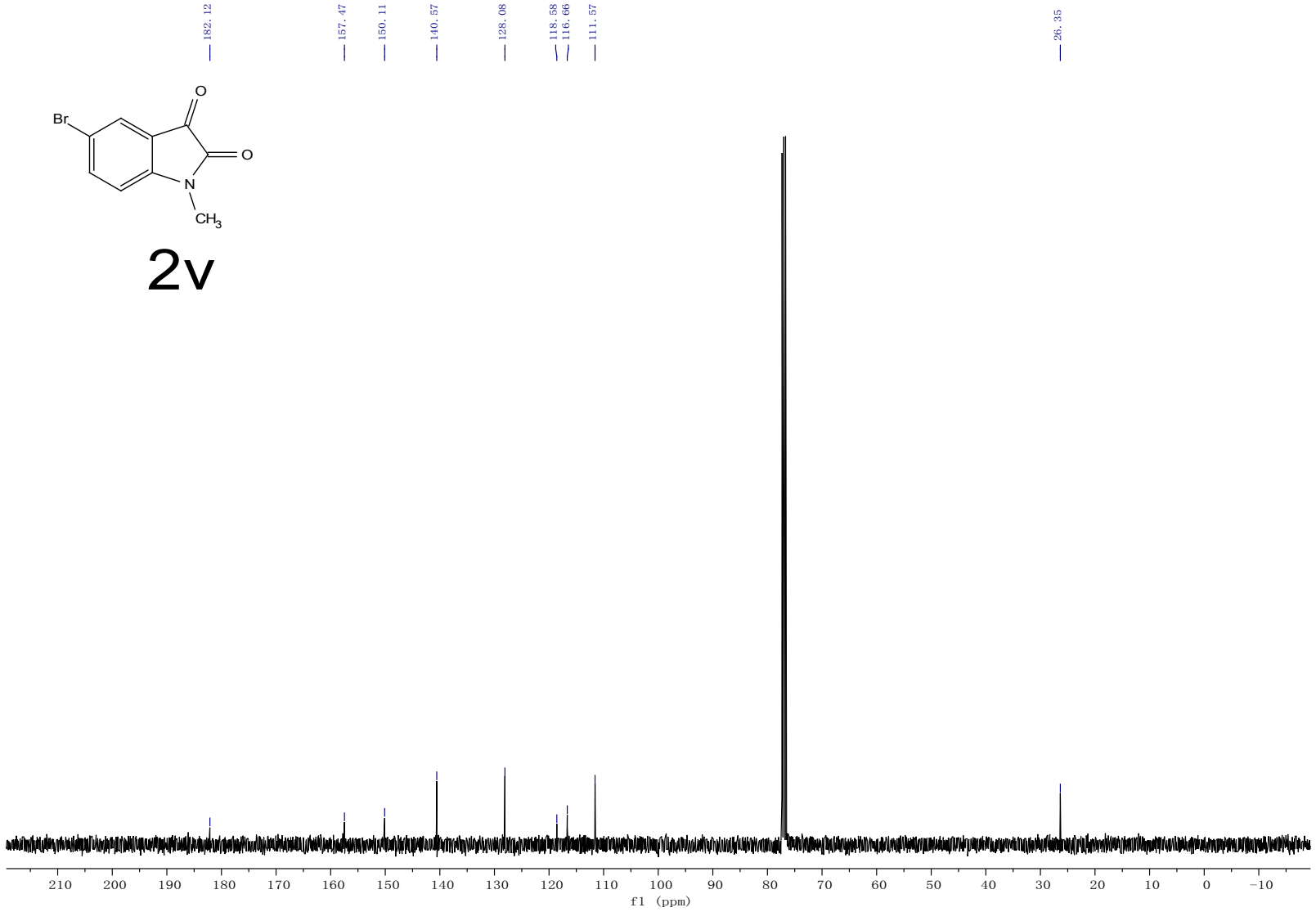

F
O
O
N
CH3
2t
7.35
7.34
7.33
7.32
7.31
7.30
7.29
7.28
6.88
6.87
6.86
6.85
3.25
0.78
1.27
1.06
3.00
f1 (ppm)

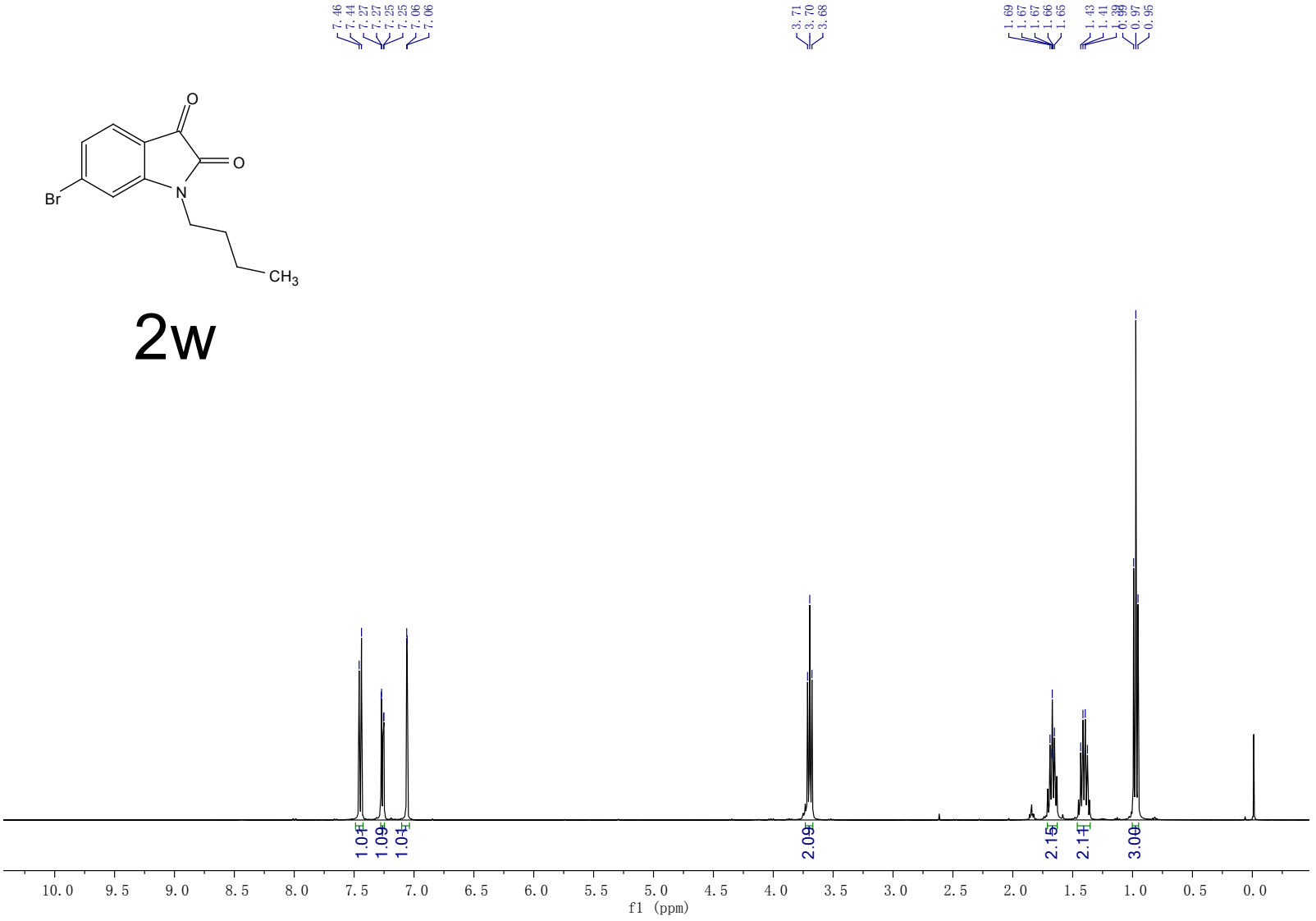

182.73
160.57
158.12
157.94
147.48
124.75
124.51
118.00
117.93
112.47
112.23
111.06
110.99
26.31
F
O
O
N
CH3
2t
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

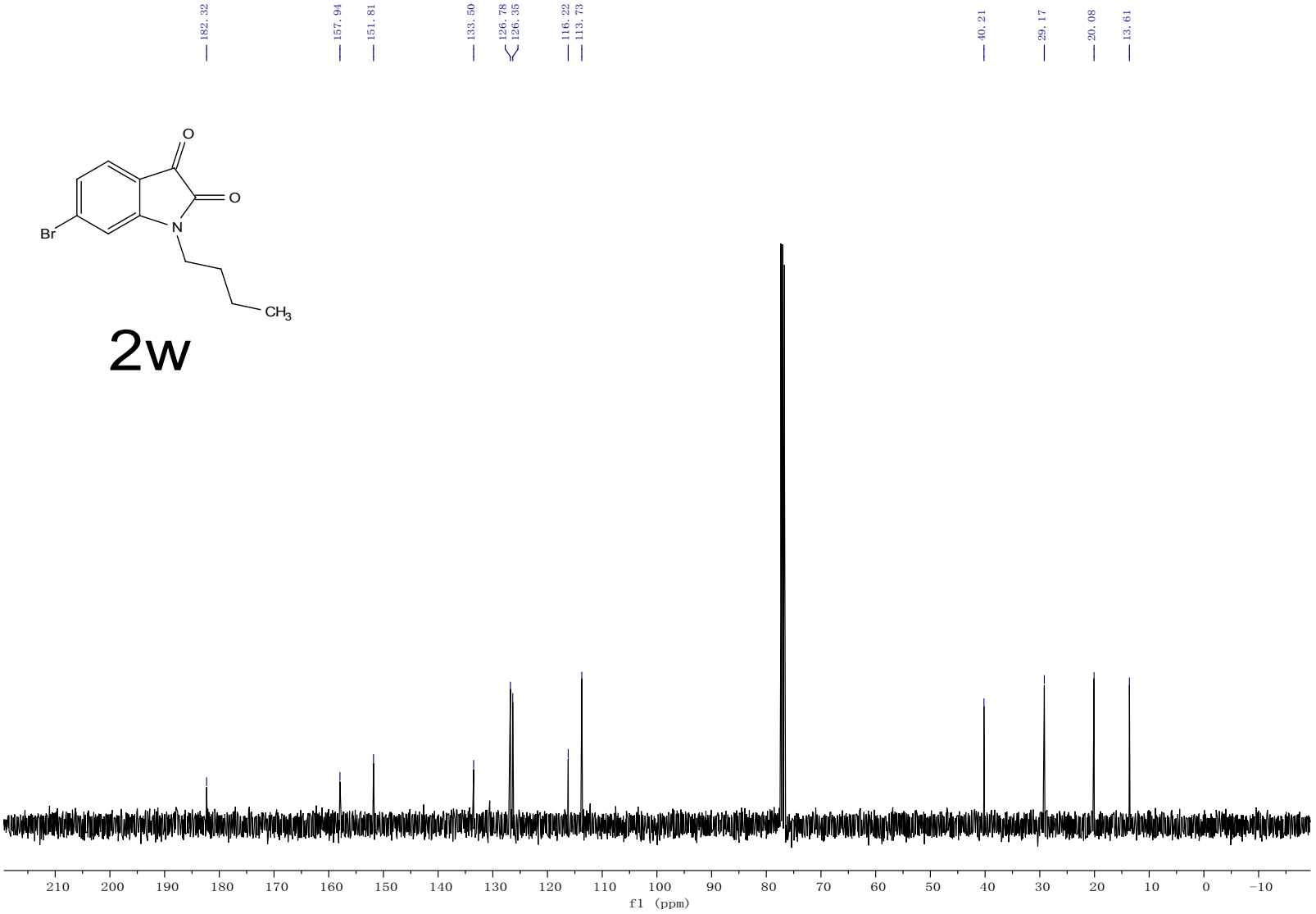

7.58
7.58
7.56
7.56
7.55
6.87
6.87
6.85
6.85
Cl
O
O
N
CH3
2u
1.84
0.96
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

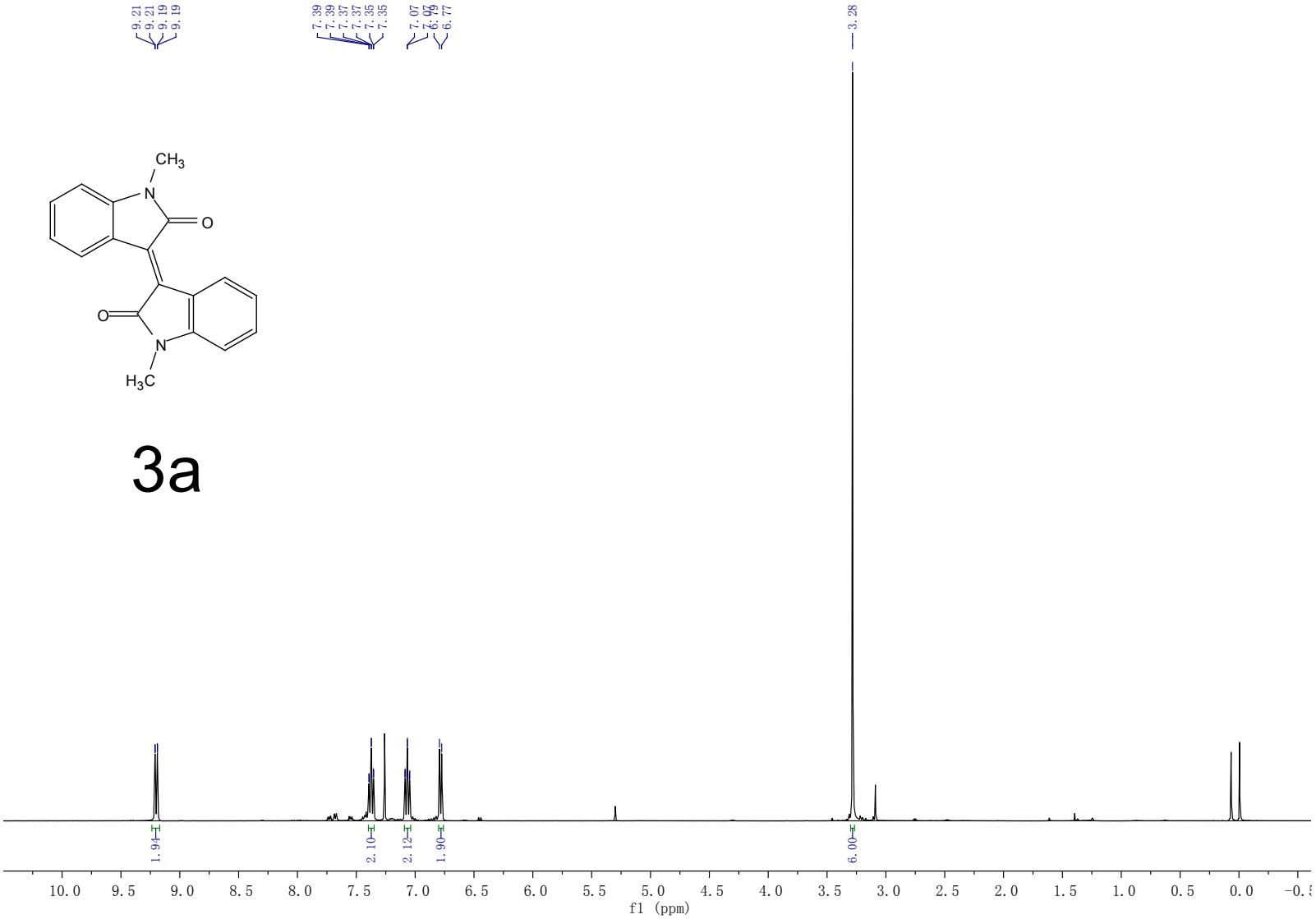

182.29
157.64
149.66
137.71
129.65
125.20
118.20
111.17
26.35
Cl
O
O
N
CH3
2u
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.73
7.73
7.71
6.82
6.80
3.25
Br
O
O
N
CH3
2v
1.93
1.00
3.00
f1 (ppm)

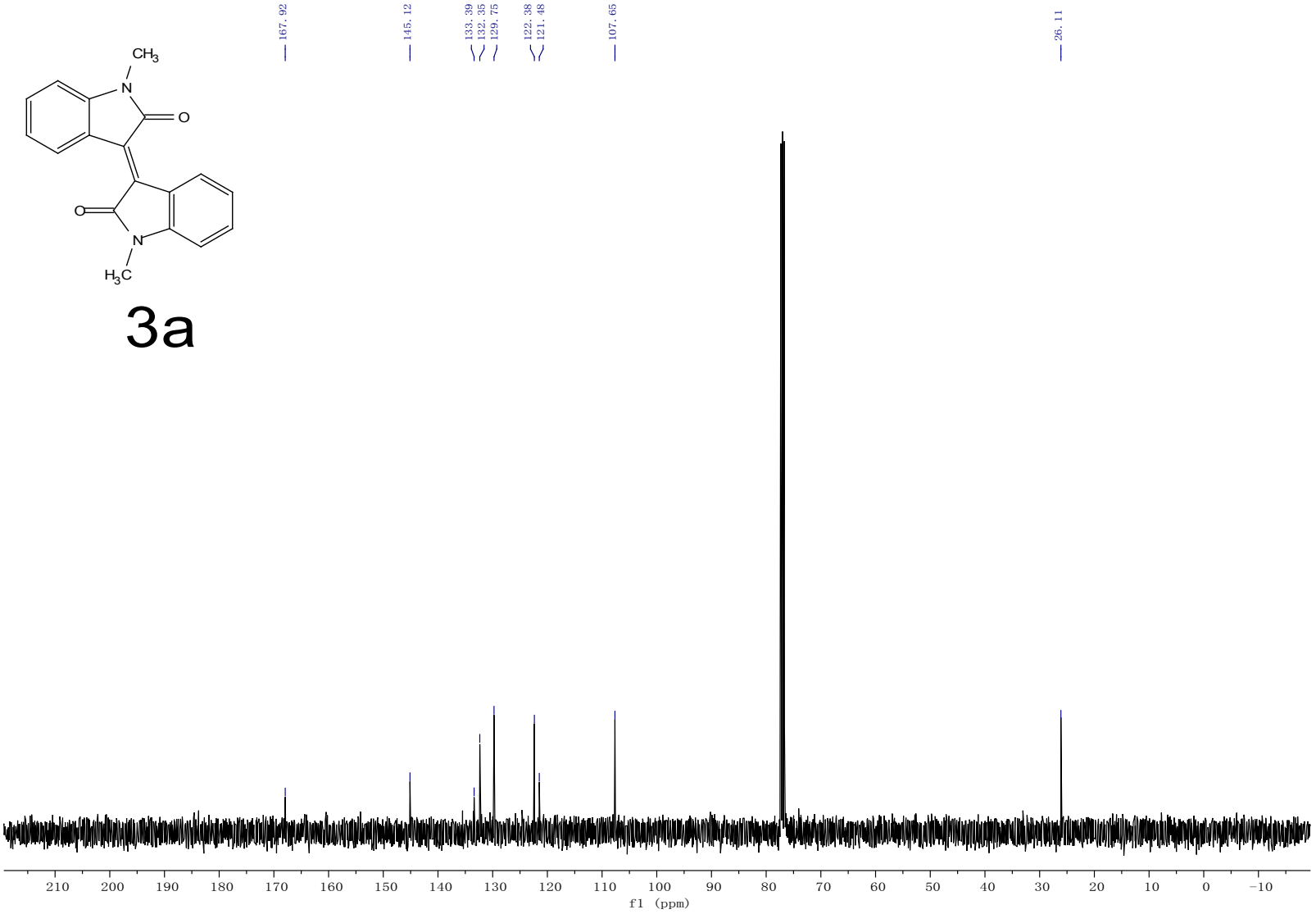

182.12
157.47
150.11
140.57
128.08
118.58
116.66
111.57
26.35
Br
O
O
N
CH3
2v
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.46
7.44
7.27
7.27
7.25
7.25
7.06
7.06
3.71
3.70
3.68
1.69
1.67
1.67
1.66
1.65
1.43
1.41
0.97
0.95
O
O
Br
N
CH3
2w
1.01
1.09
1.01
2.09
2.15
2.11
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

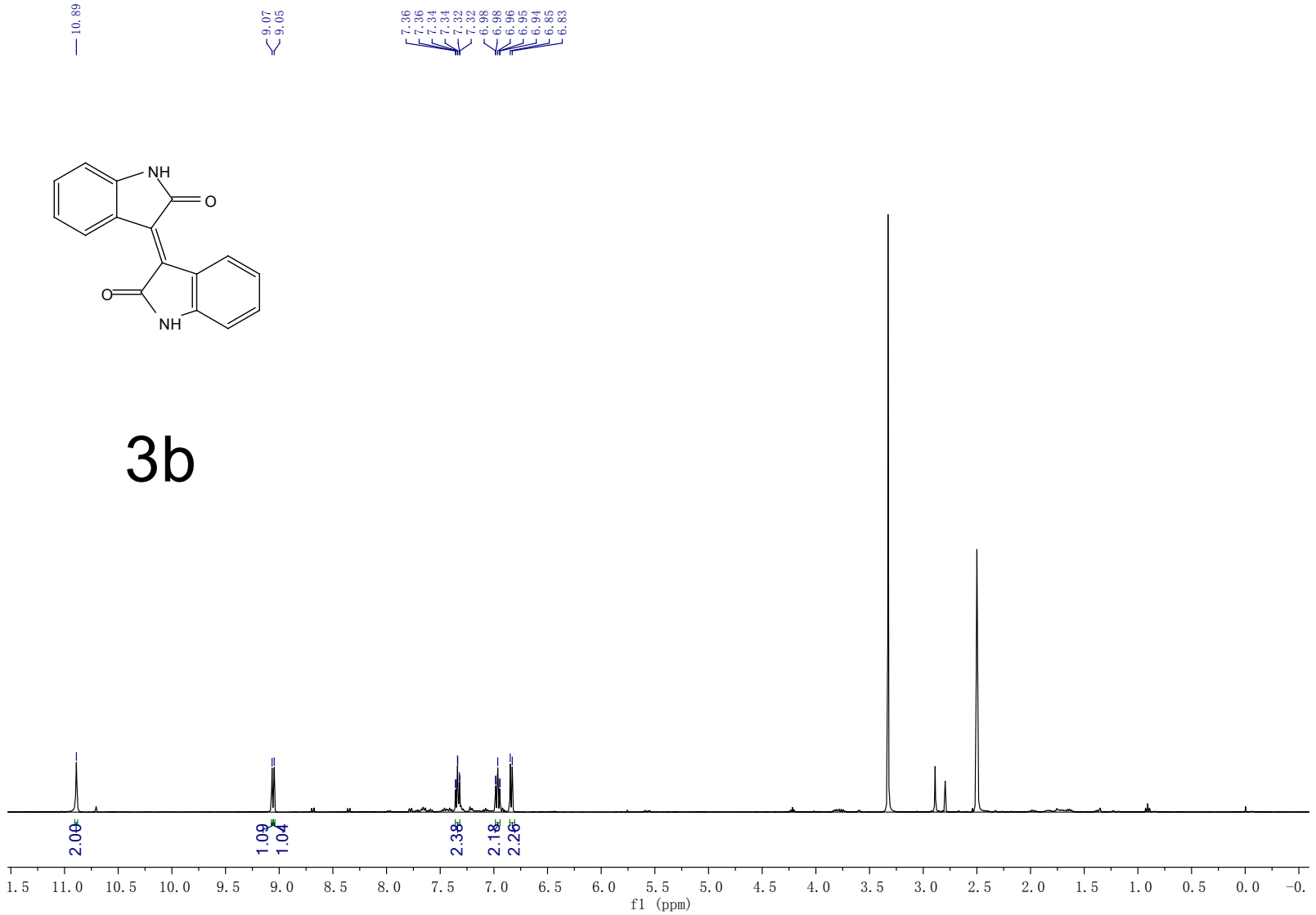

182.32
157.94
151.81
133.50
126.78
126.35
116.22
113.73
40.21
29.17
20.08
13.61
O
O
Br
N
CH3
2w
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

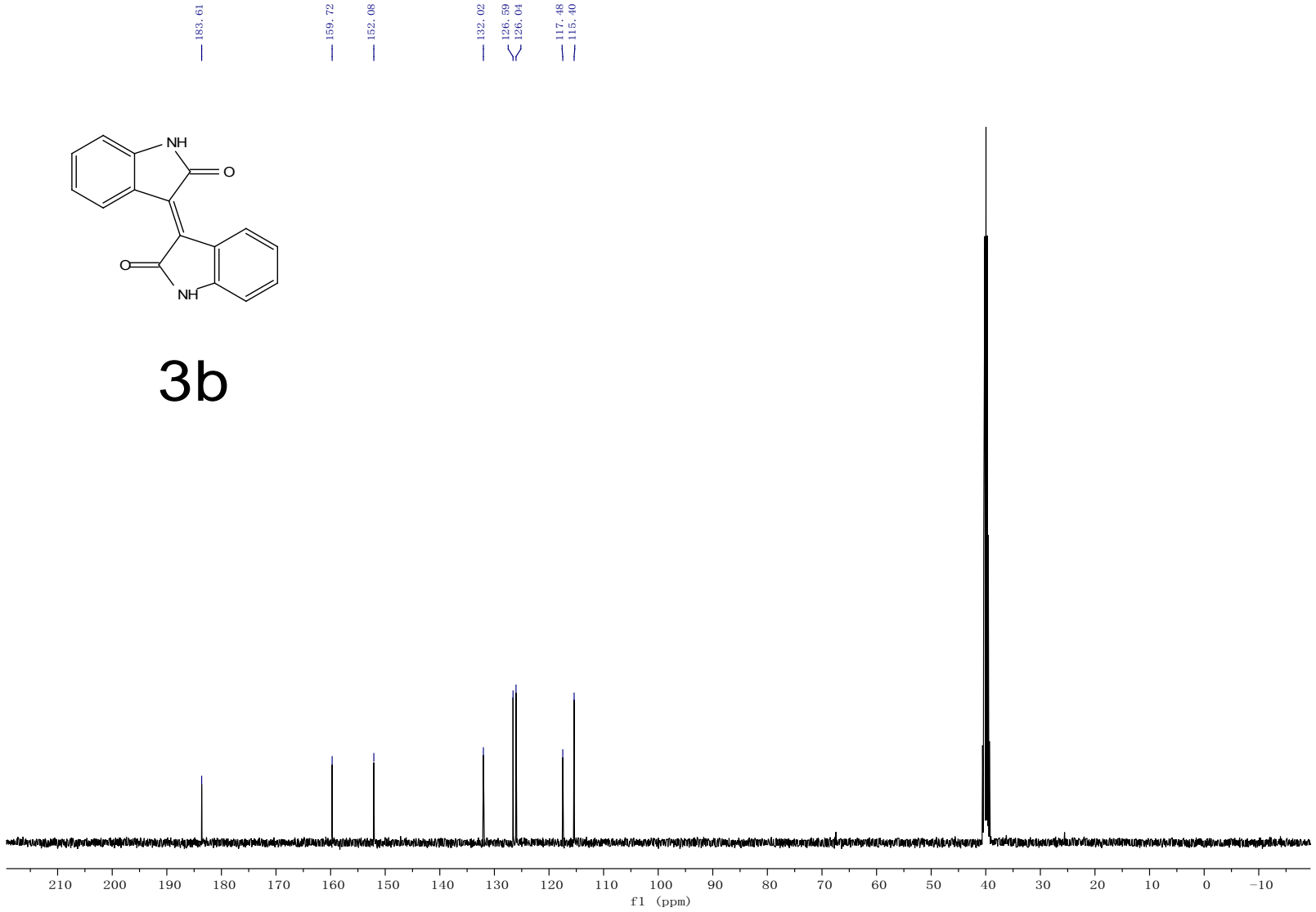

9.21
9.21
9.19
9.19
7.39
7.39
7.37
7.37
7.35
7.35
7.07
6.77
3.28
CH3
N
O
O
N
H3C
1.94
2.10
2.12
1.90
6.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

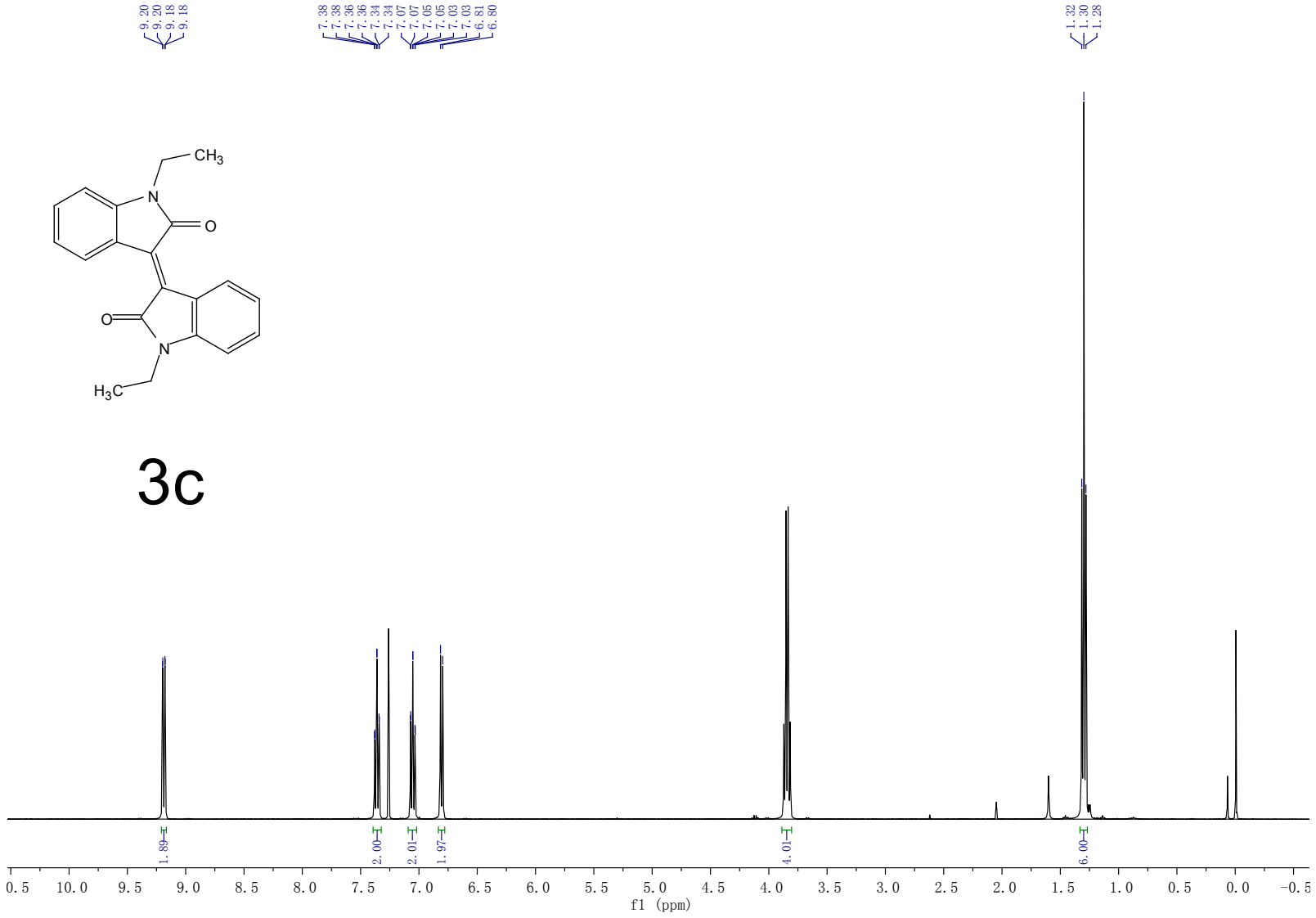
3a

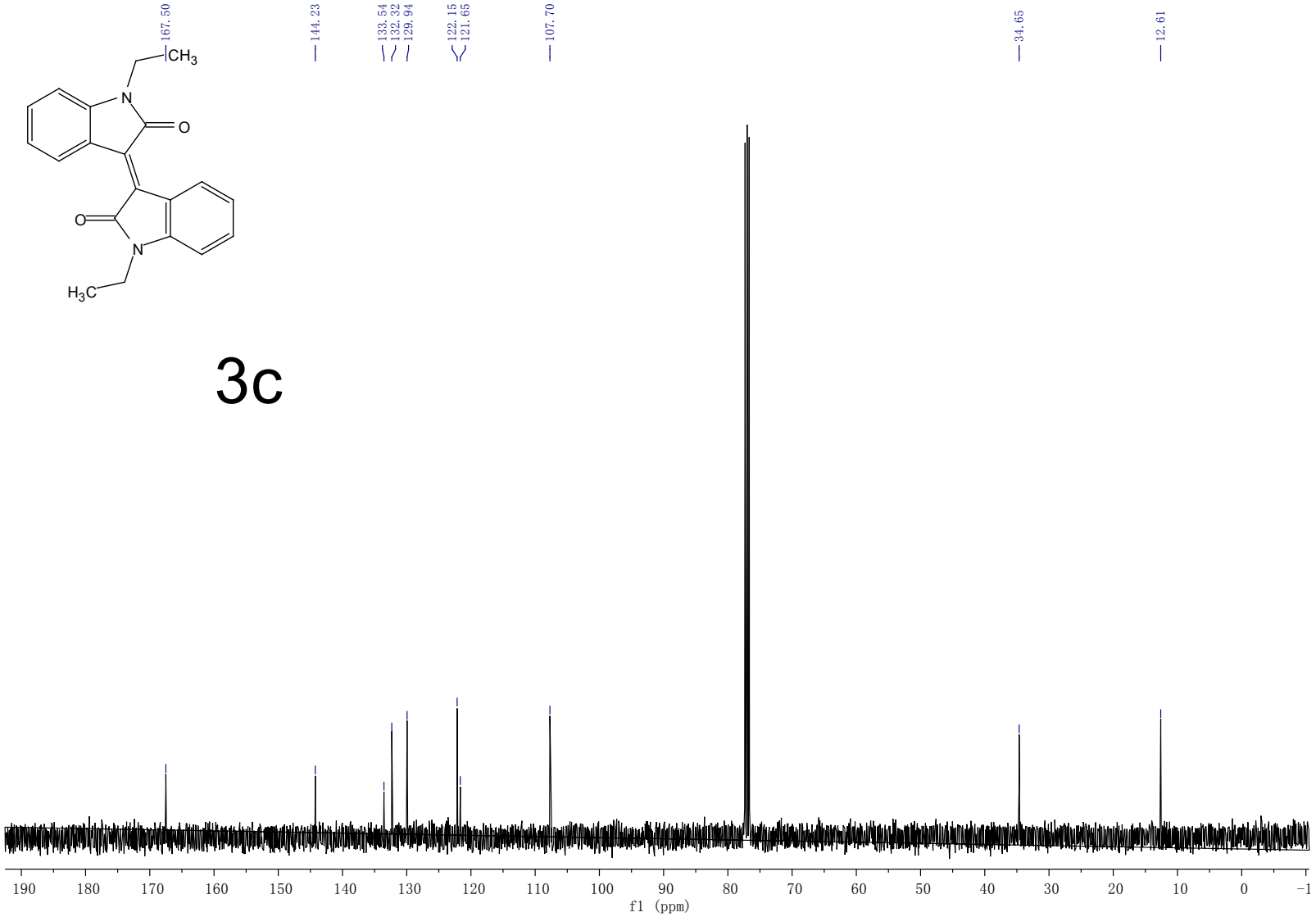

167.92
145.12
133.39
132.35
129.75
122.38
121.48
107.65
26.11
CH3
N
O
O
N
H3C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

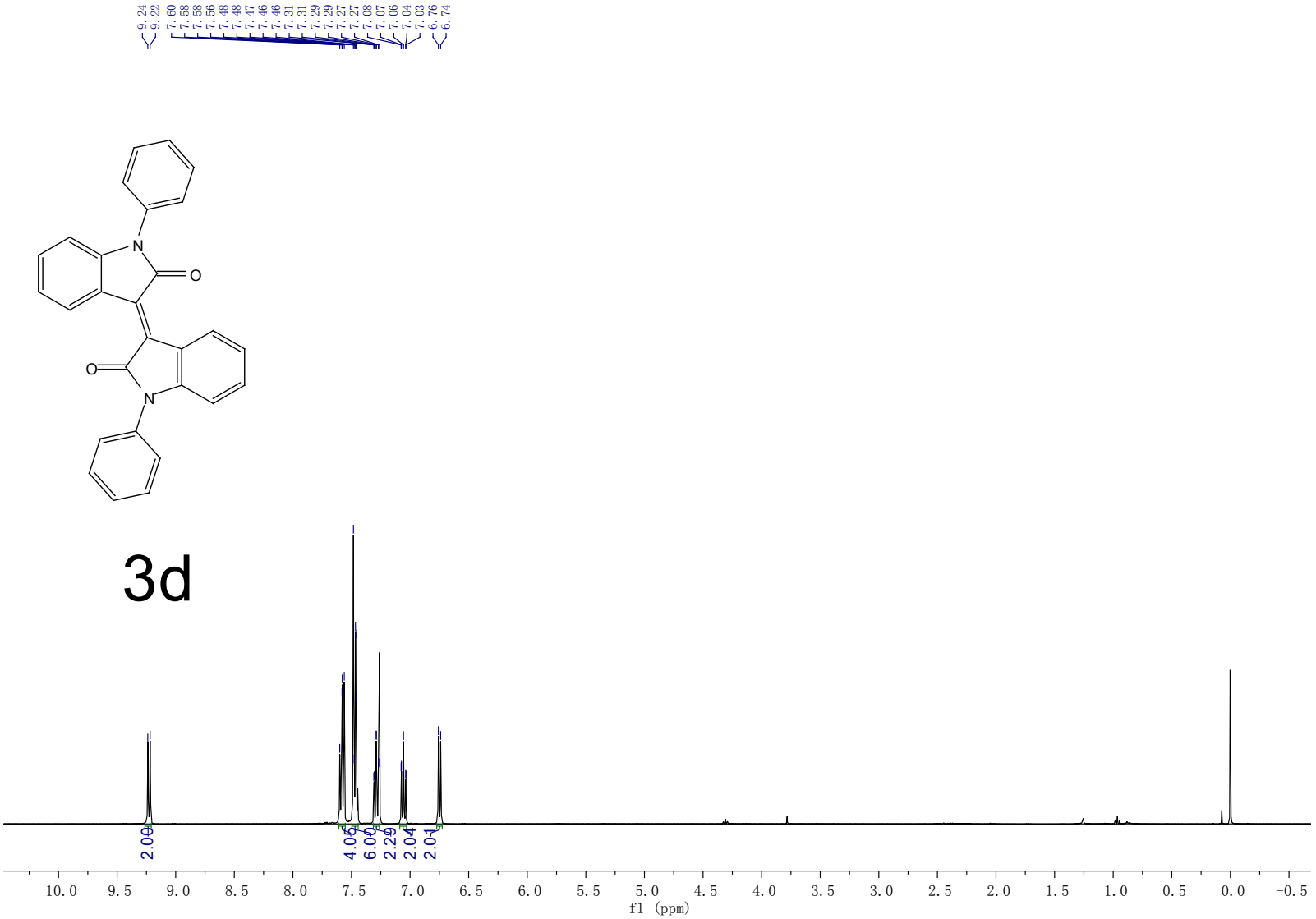
3a

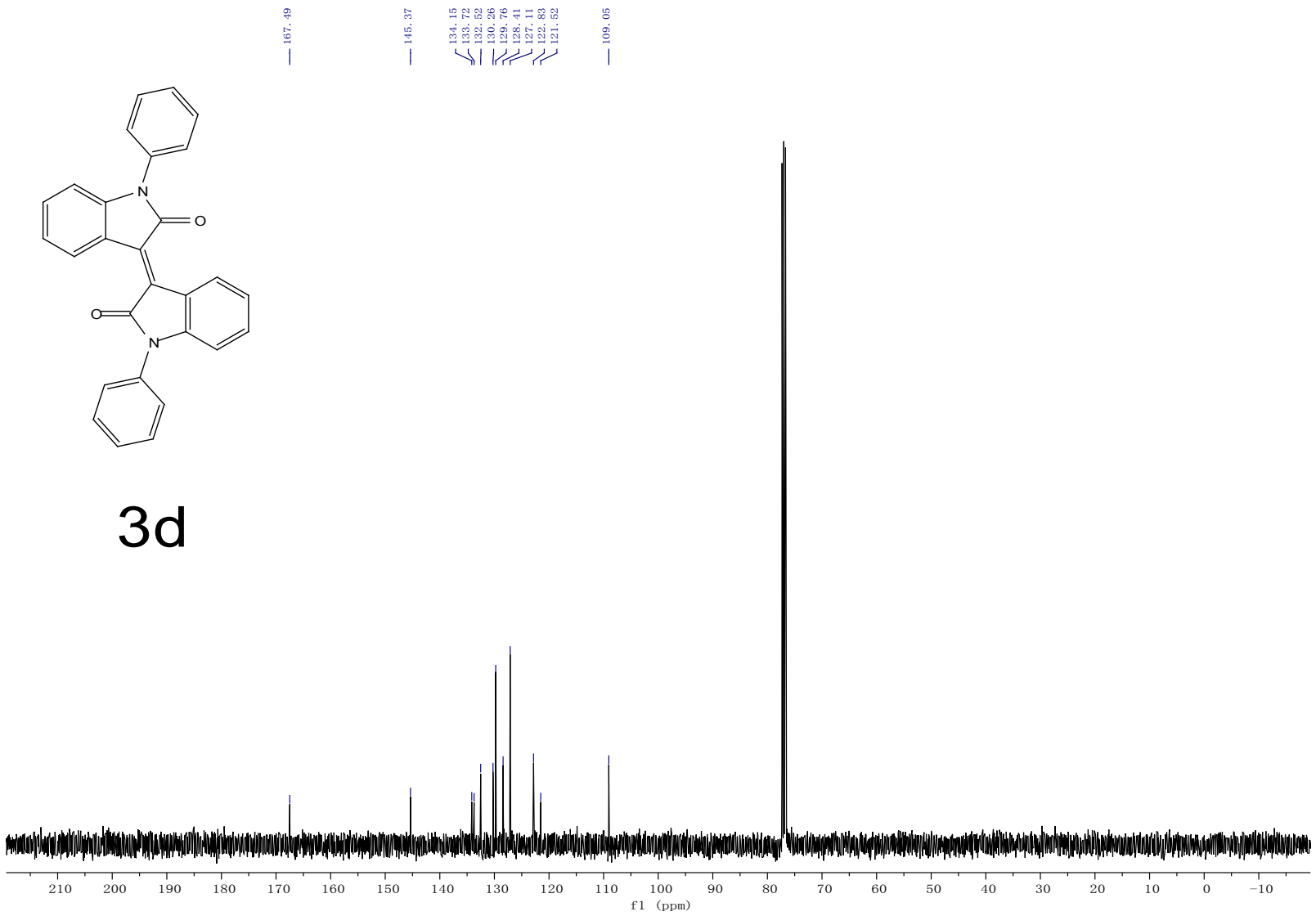

10.89
9.07
9.05
7.36
7.36
7.34
7.34
7.32
7.32
6.98
6.98
6.96
6.95
6.94
6.85
6.83
NH
O
O
NH
3b
2.00
1.09
1.04
2.38
2.18
2.26
1.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

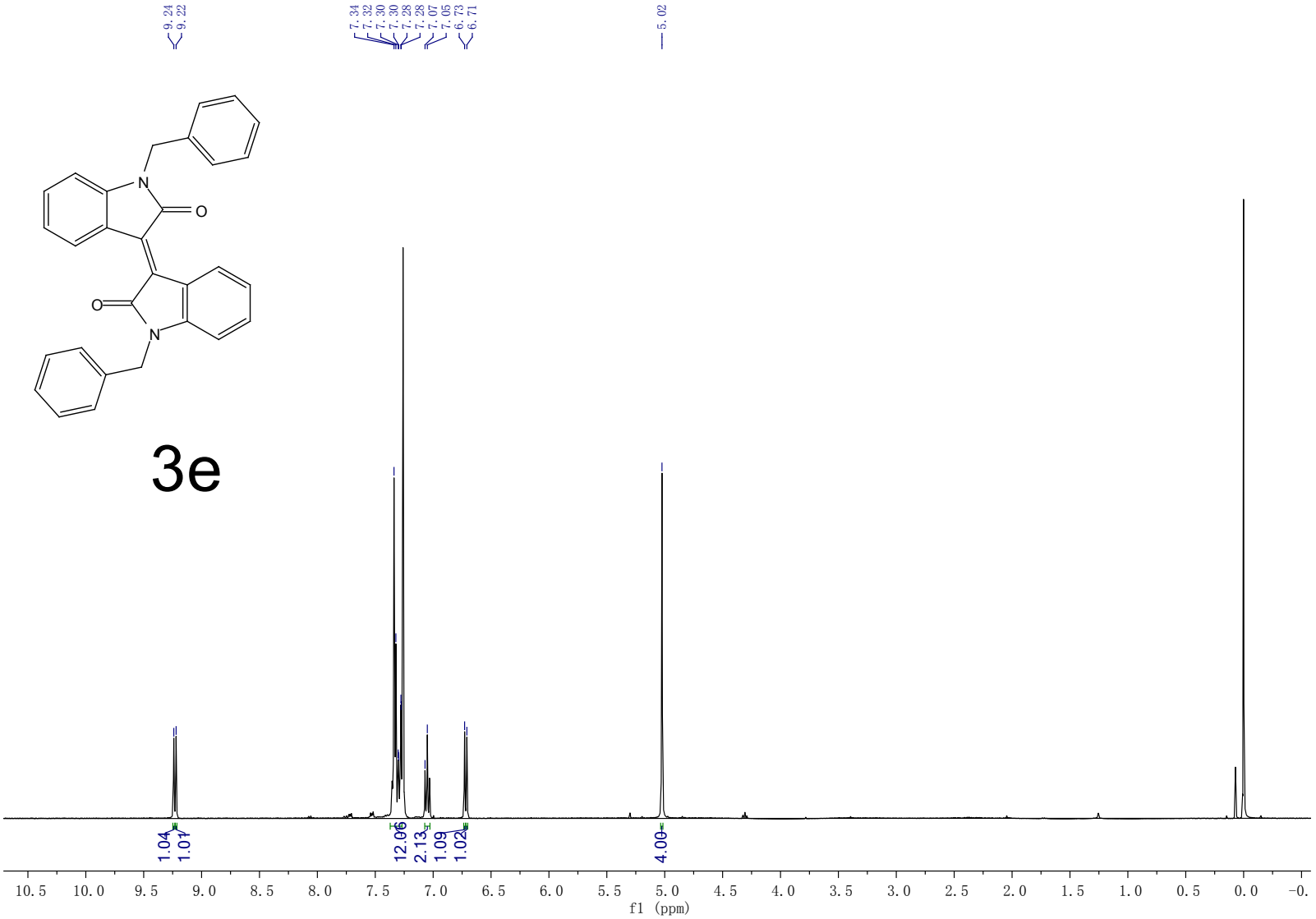

183.61
159.72
152.08
132.02
126.59
126.04
117.48
115.40
NH
O
O
NH
3b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

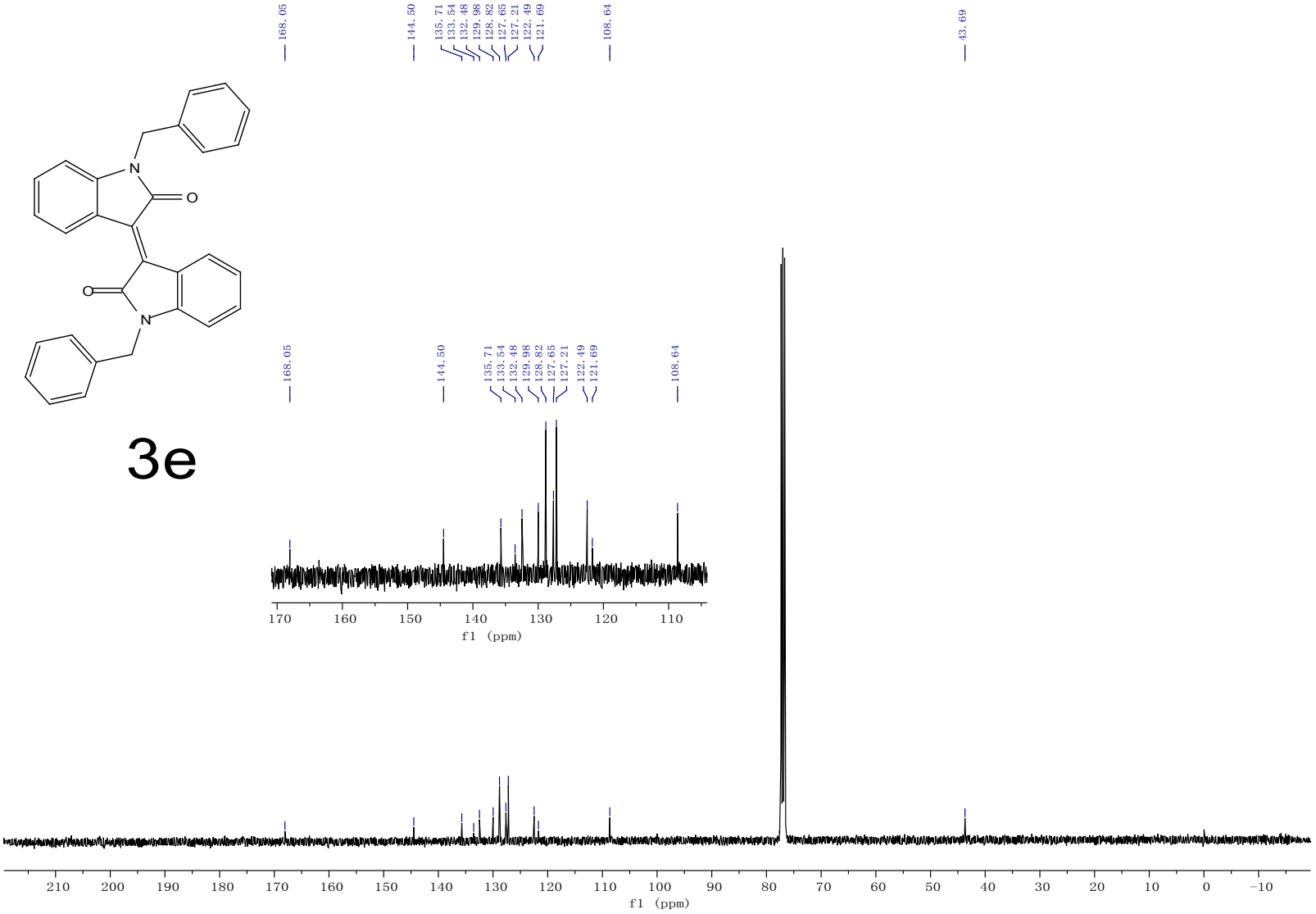

9.20
9.20
9.18
9.18
7.38
7.38
7.36
7.36
7.34
7.34
7.07
7.07
7.05
7.05
7.03
7.03
6.81
6.80
1.32
1.30
1.28
CH3
N
O
O
N
H3C
3c
1.89
2.00
2.01
1.97
4.01
6.00
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

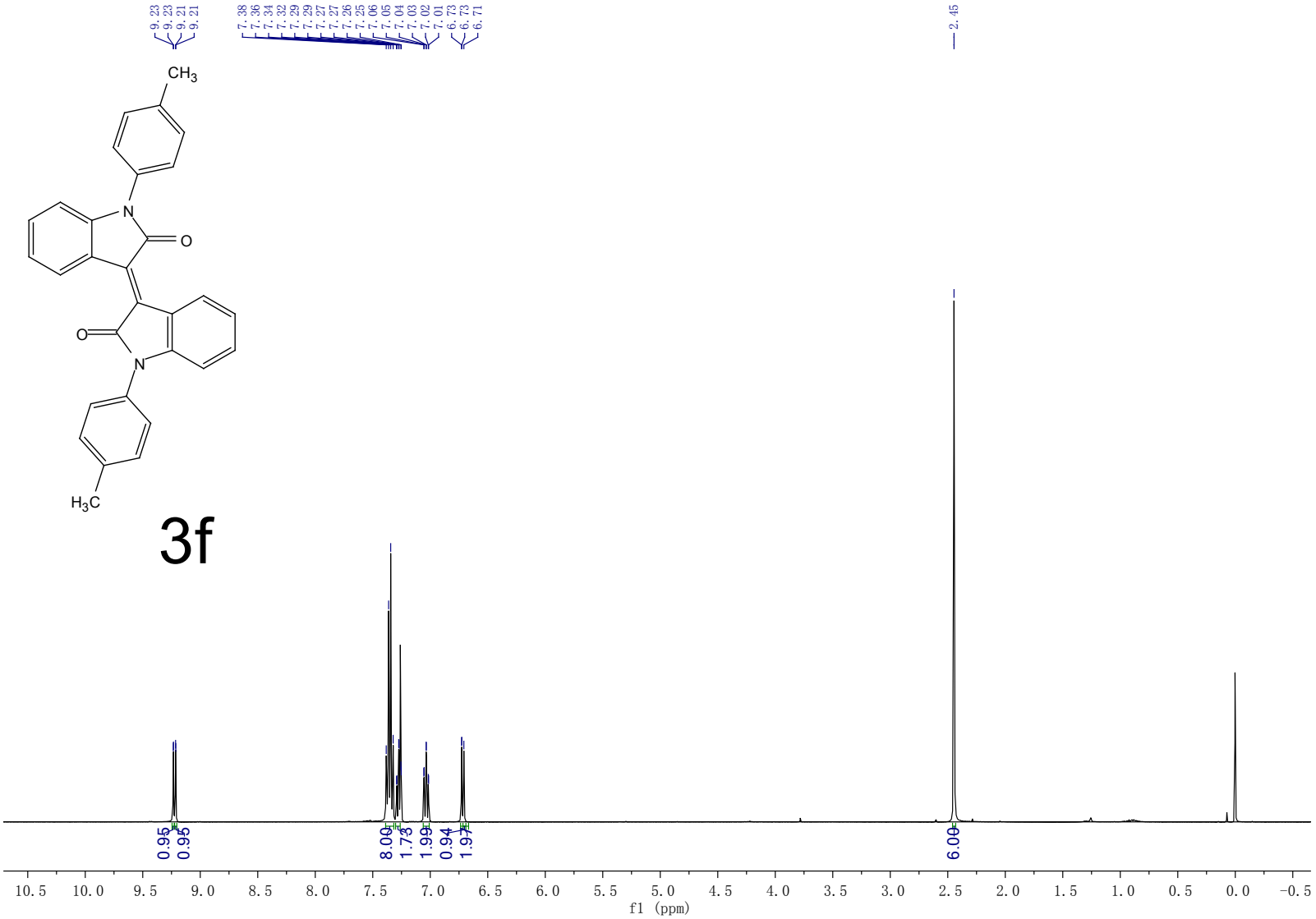

167.50
144.23
133.54
132.32
129.94
122.15
121.65
107.70
34.65
12.61
CH3
N
O
O
N
H3C
3c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

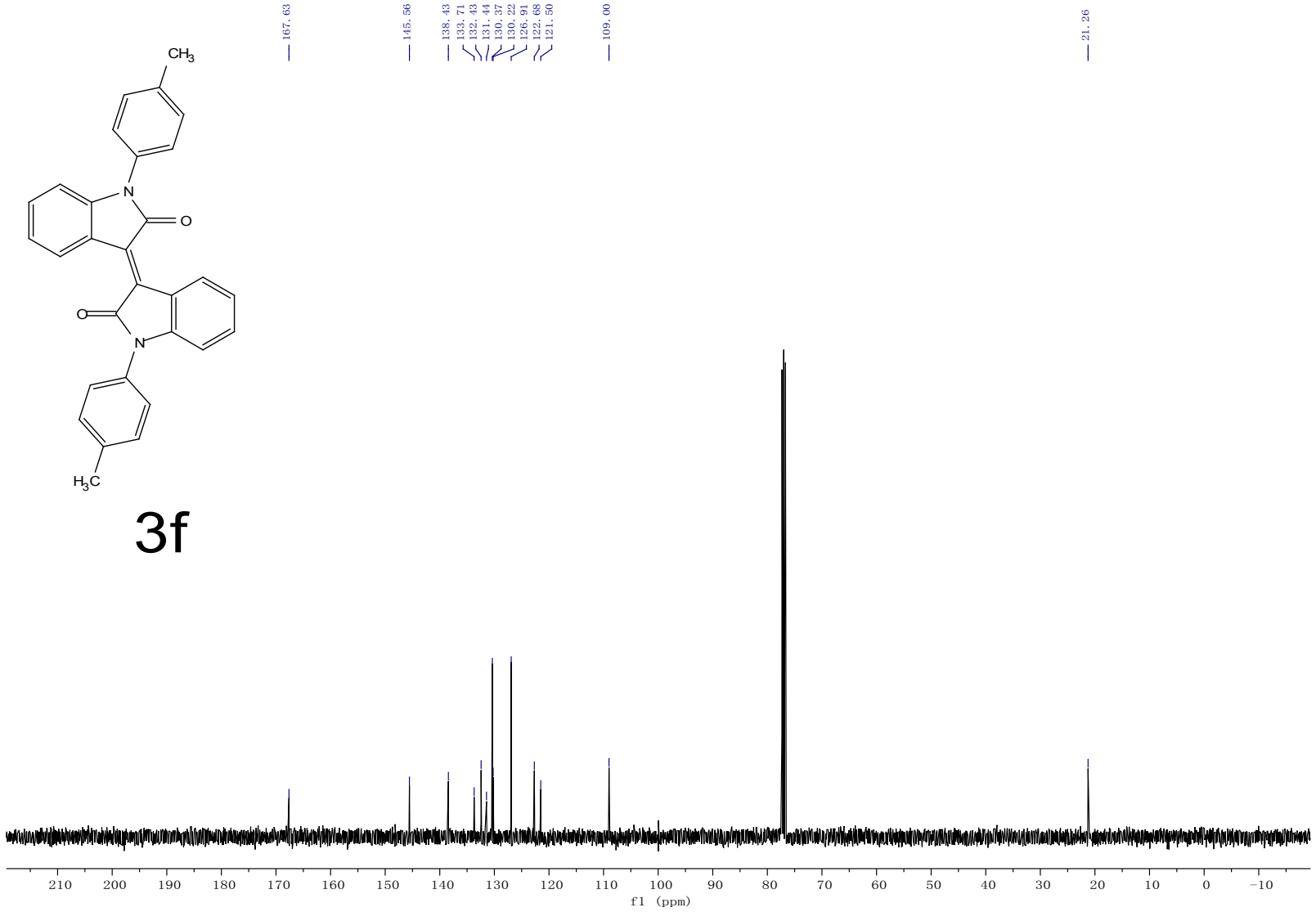

9.24
9.22
7.60
7.58
7.58
7.56
7.48
7.48
7.47
7.46
7.46
7.31
7.31
7.29
7.29
7.27
7.27
7.08
7.07
7.06
7.04
7.03
6.76
6.74
N
O
O
N
3d
2.00
4.05
6.00
2.29
2.04
2.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

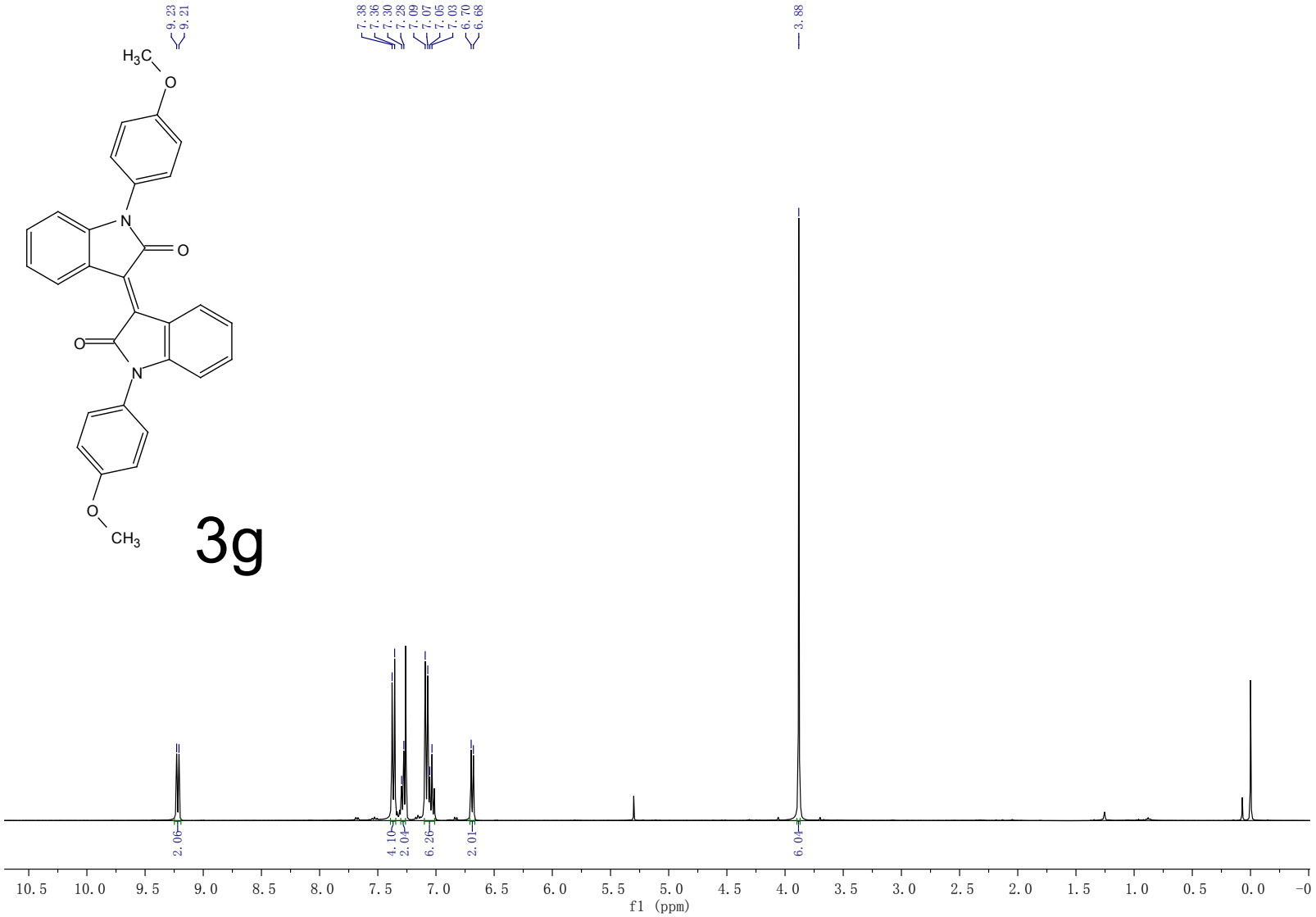

167.49
145.37
134.15
133.72
132.52
130.26
129.76
128.41
127.11
122.83
121.52
109.05
O
O
N
N
3d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

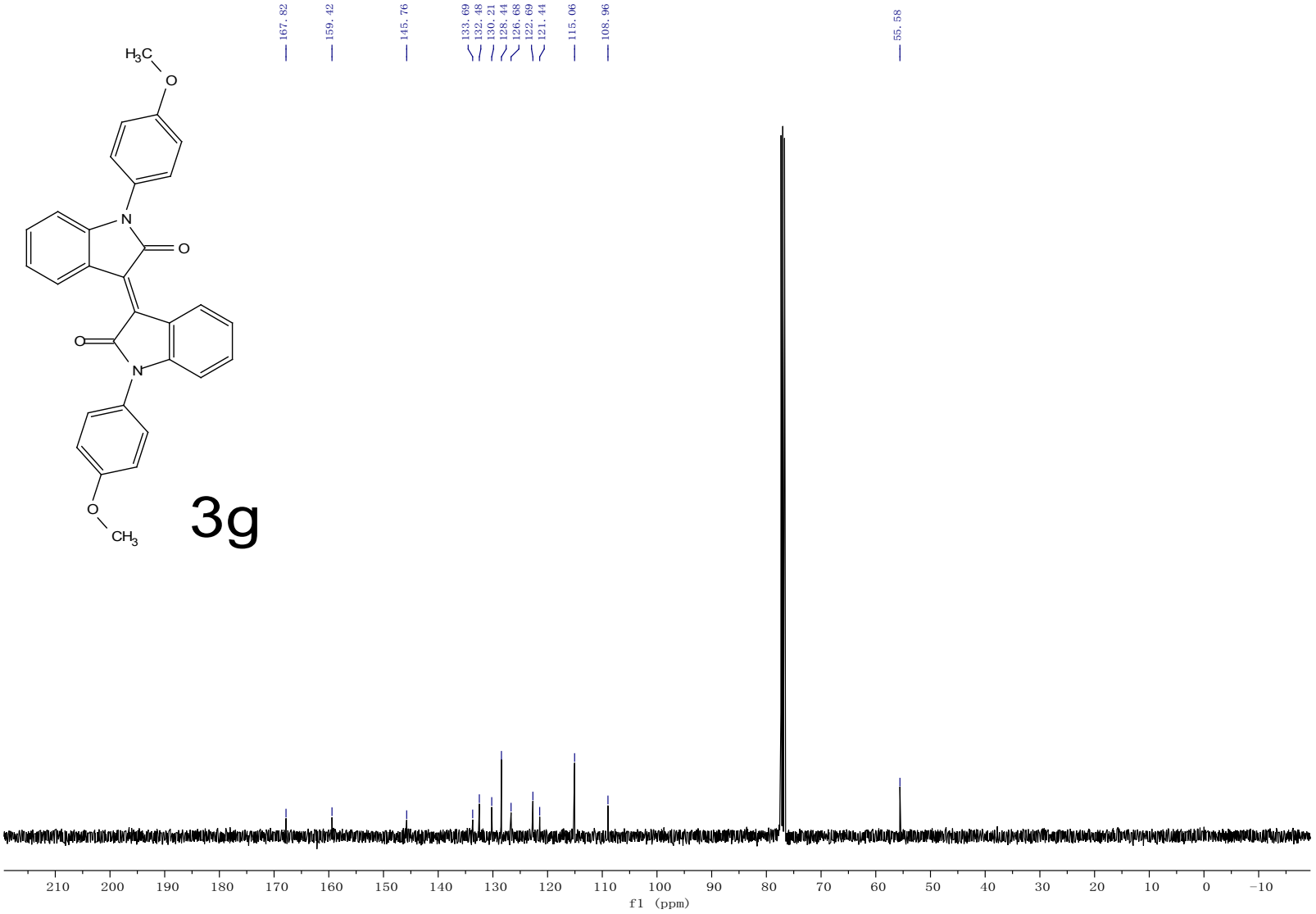

9.24
9.22
7.34
7.32
7.30
7.30
7.28
7.28
7.07
7.05
6.73
6.71
5.02
O
O
N
N
3e
1.04
1.01
12.06
2.13
1.09
1.02
4.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

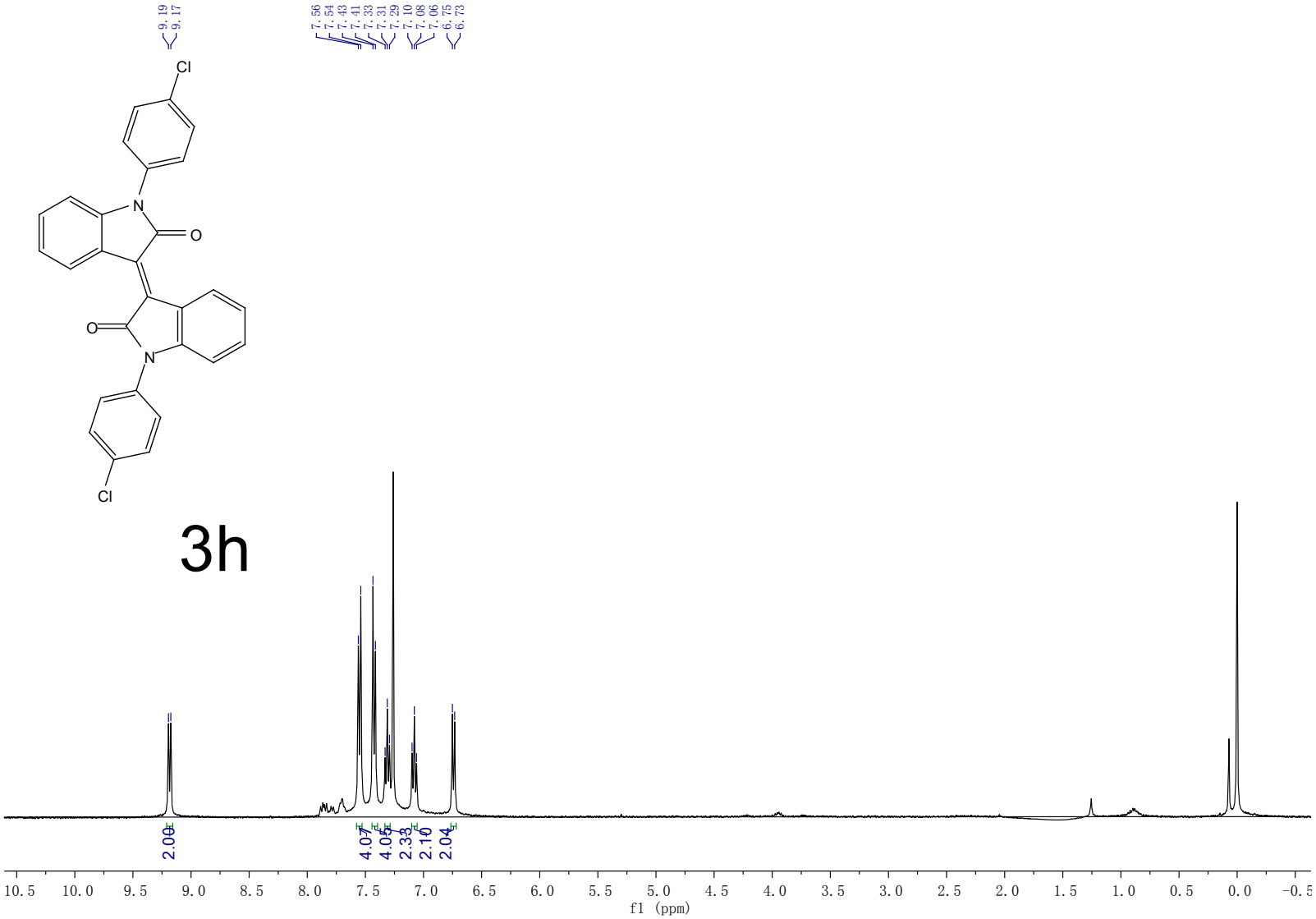

168.05
144.50
135.71
133.54
132.48
129.98
128.82
127.65
127.21
122.49
121.69
108.64
43.69
O
O
N
N
3e
f1 (ppm)

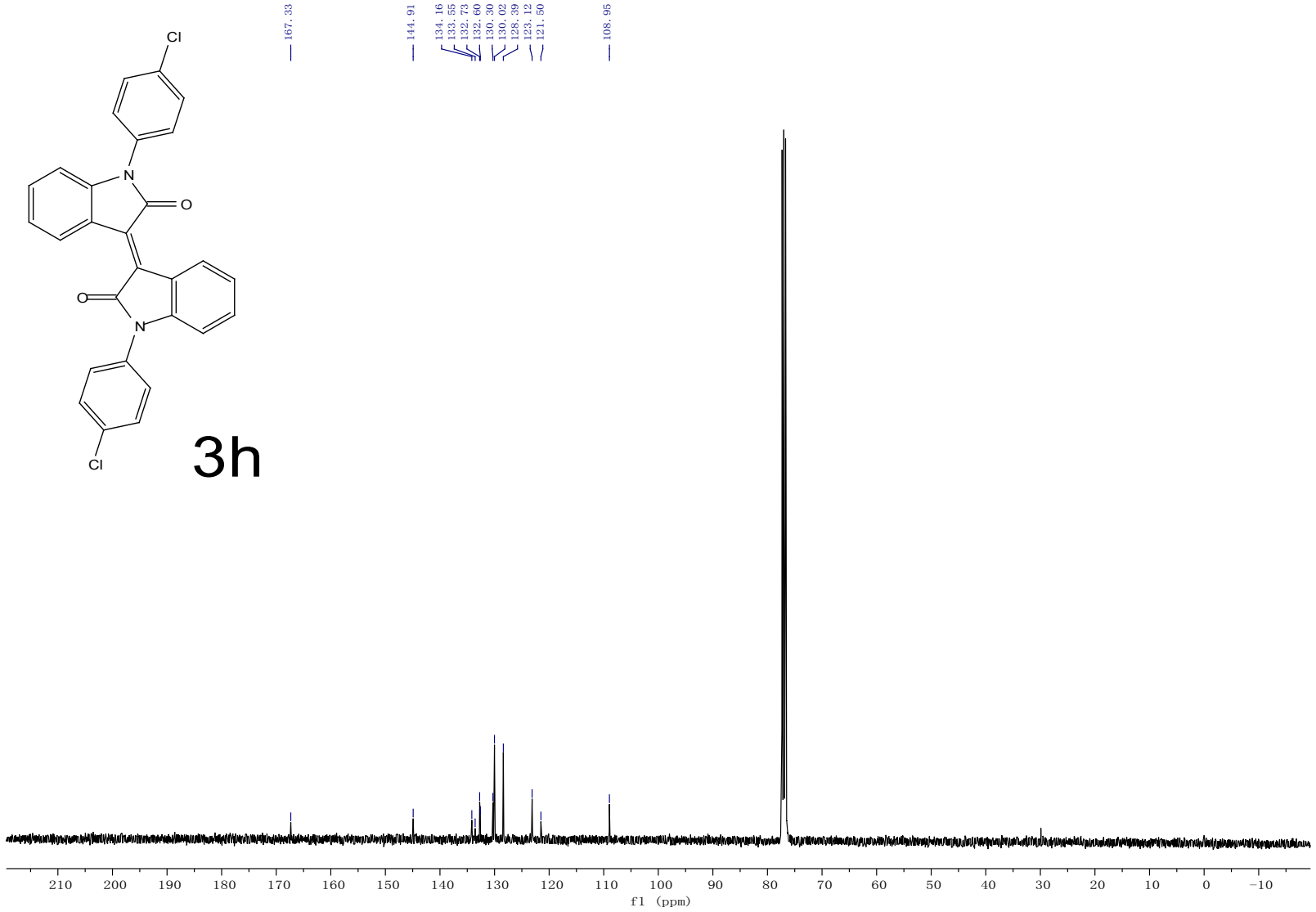

9.23
9.23
9.21
9.21
7.38
7.36
7.34
7.32
7.29
7.29
7.27
7.27
7.26
7.25
7.06
7.05
7.04
7.03
7.02
7.01
6.73
6.73
6.71
2.45
CH3
N
O
O
N
H3C
3f
0.95
0.95
8.00
1.73
1.99
0.94
1.97
6.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

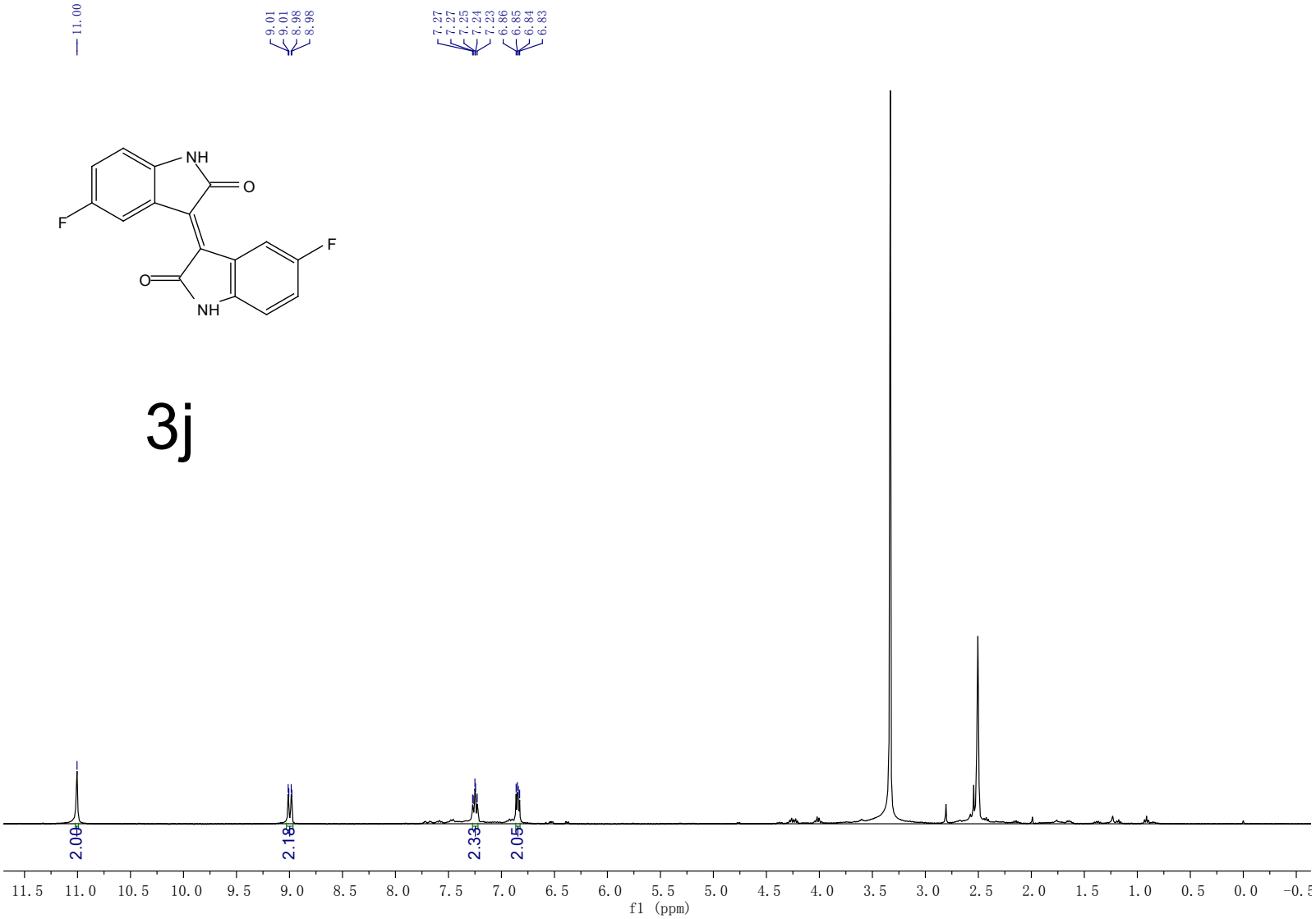

167.63
145.56
138.43
133.71
132.43
131.44
130.37
130.22
126.91
122.68
121.50
109.00
21.26
CH3
N
O
O
N
H3C
3f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

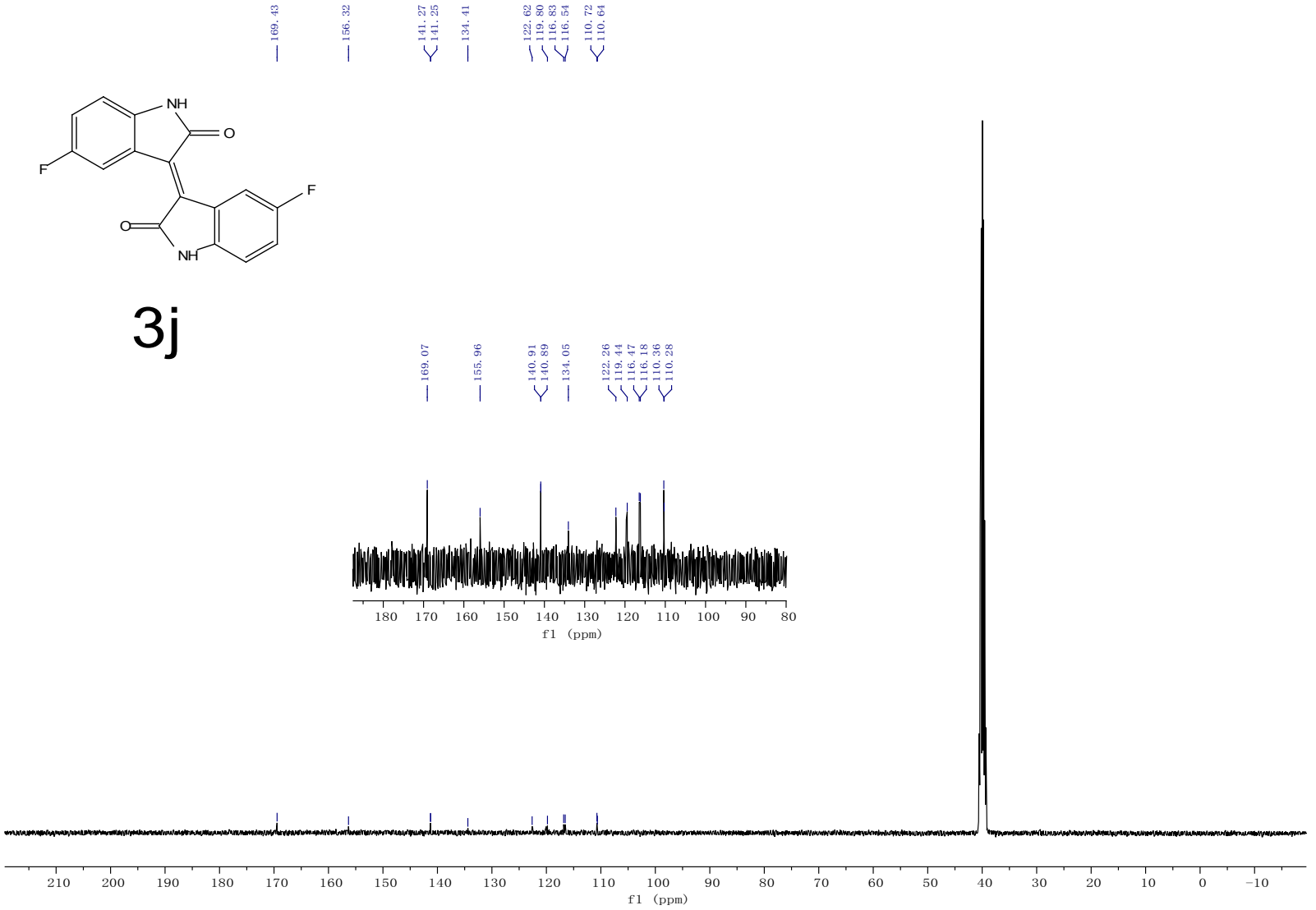

9.23
9.21
7.38
7.36
7.30
7.28
7.09
7.07
7.05
7.03
6.70
6.68
3.88
H3C
O
N
O
O
N
O
CH3
3g
2.06
4.10
2.04
6.26
2.01
6.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

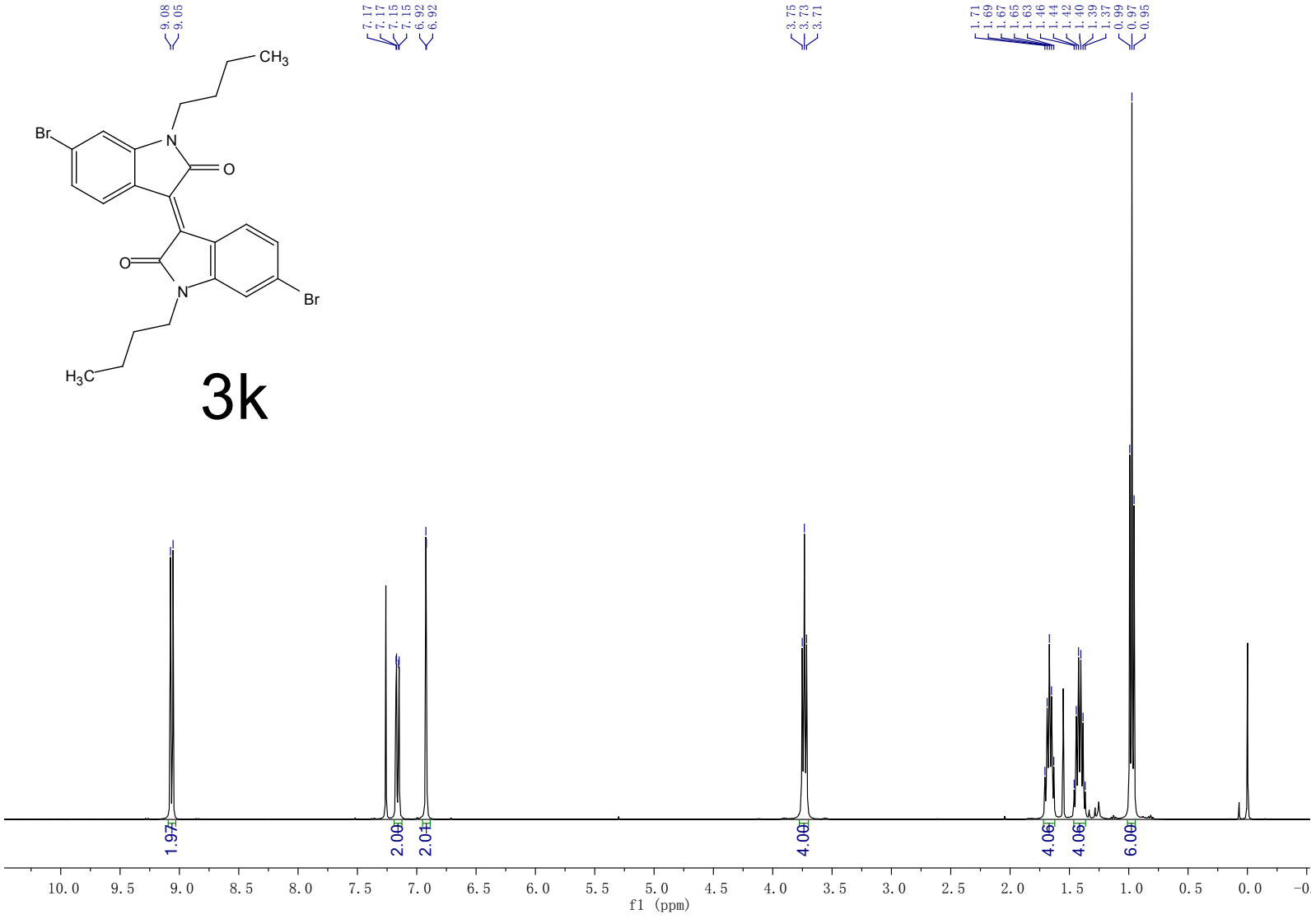

167.82
159.42
145.76
133.69
132.48
130.21
128.44
126.68
122.69
121.44
115.06
108.96
55.58
H3C
O
N
O
O
N
O
CH3
3g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

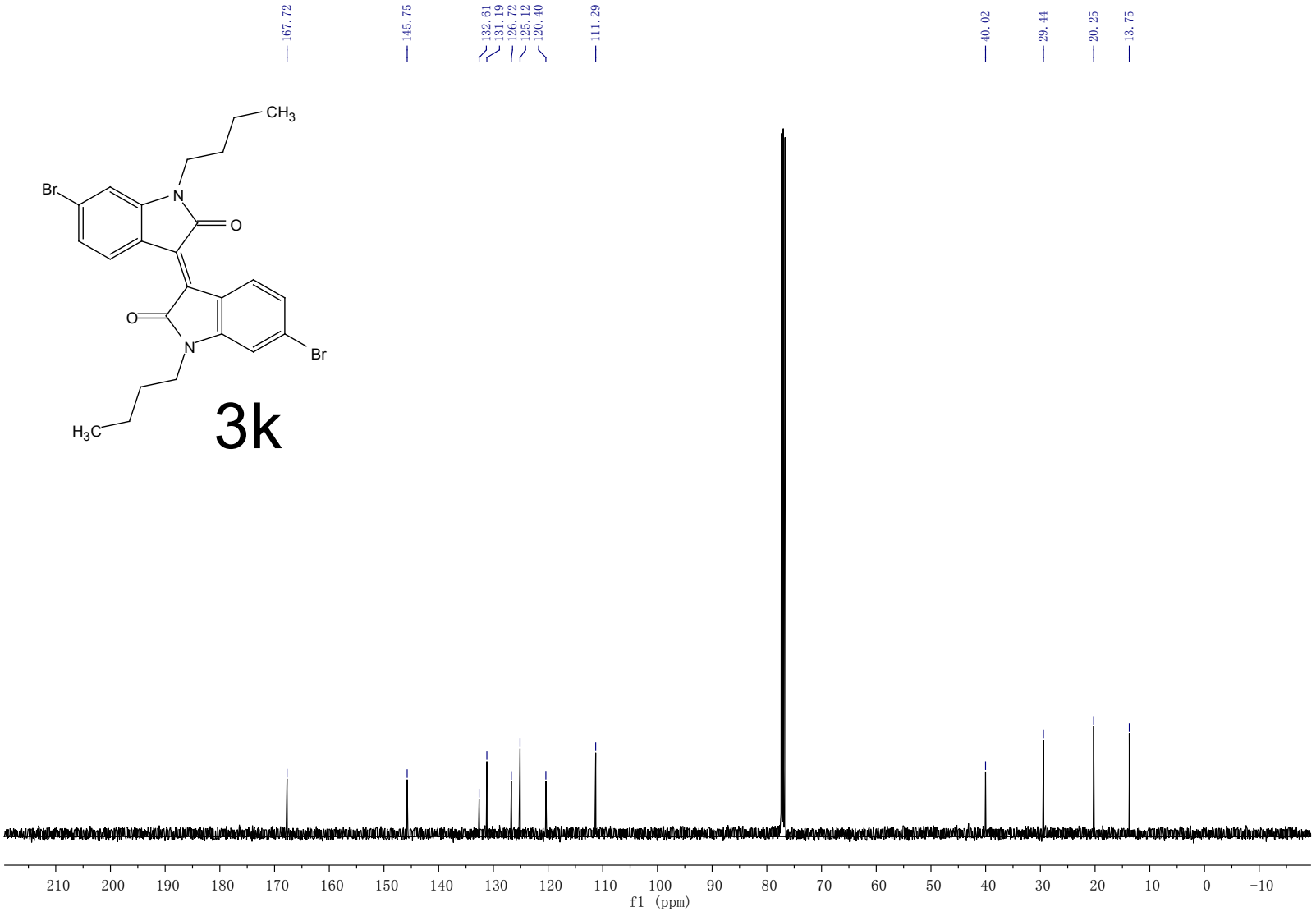

9.19
9.17
7.56
7.54
7.43
7.41
7.33
7.31
7.29
7.10
7.08
7.06
6.75
6.73
Cl
N
O
O
N
Cl
3h
2.00
4.07
4.05
2.33
2.10
2.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

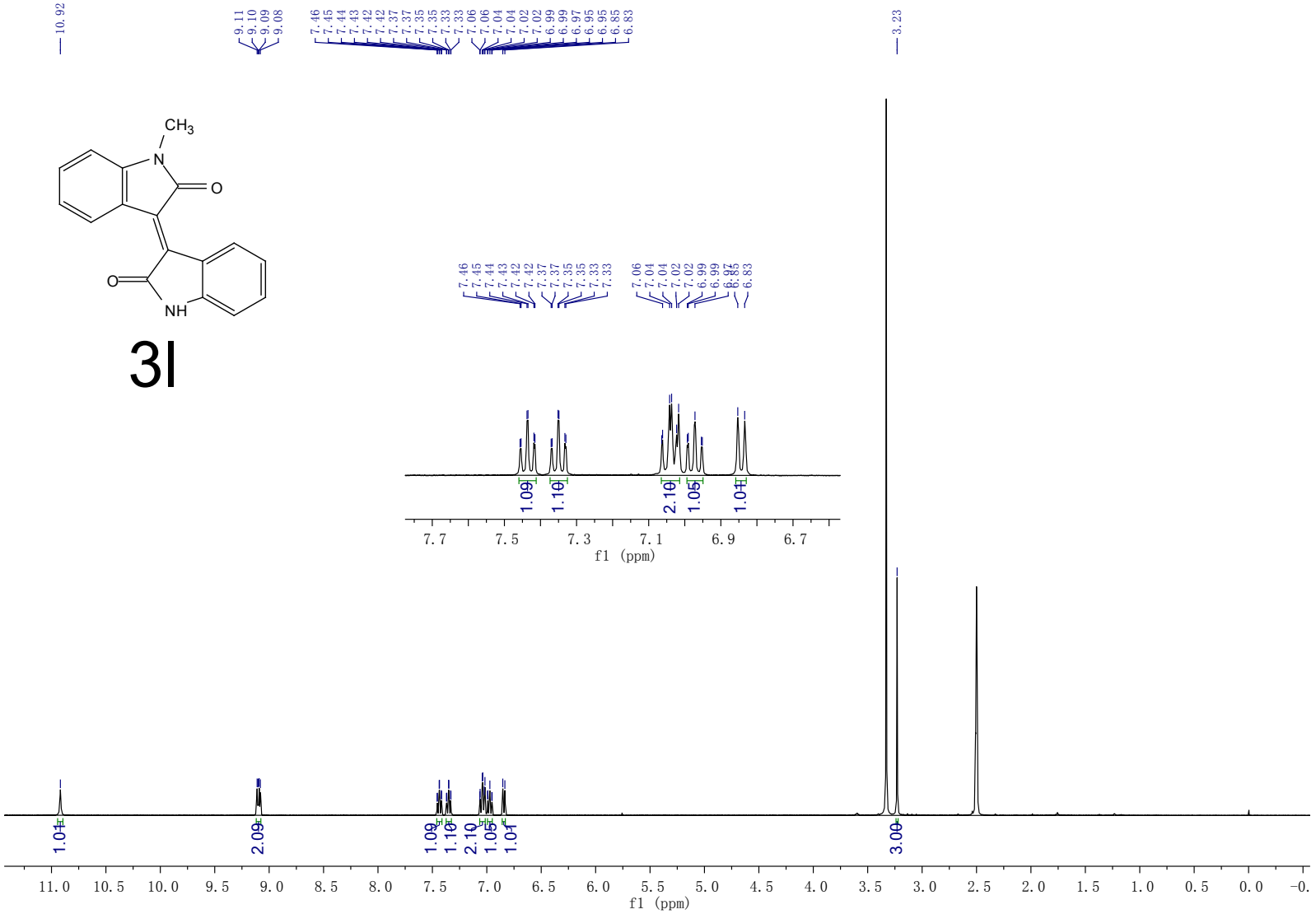

Cl
N
O
O
N
Cl
3h
167.33
144.91
134.16
133.55
132.73
132.60
130.30
130.02
128.39
123.12
121.50
108.95
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

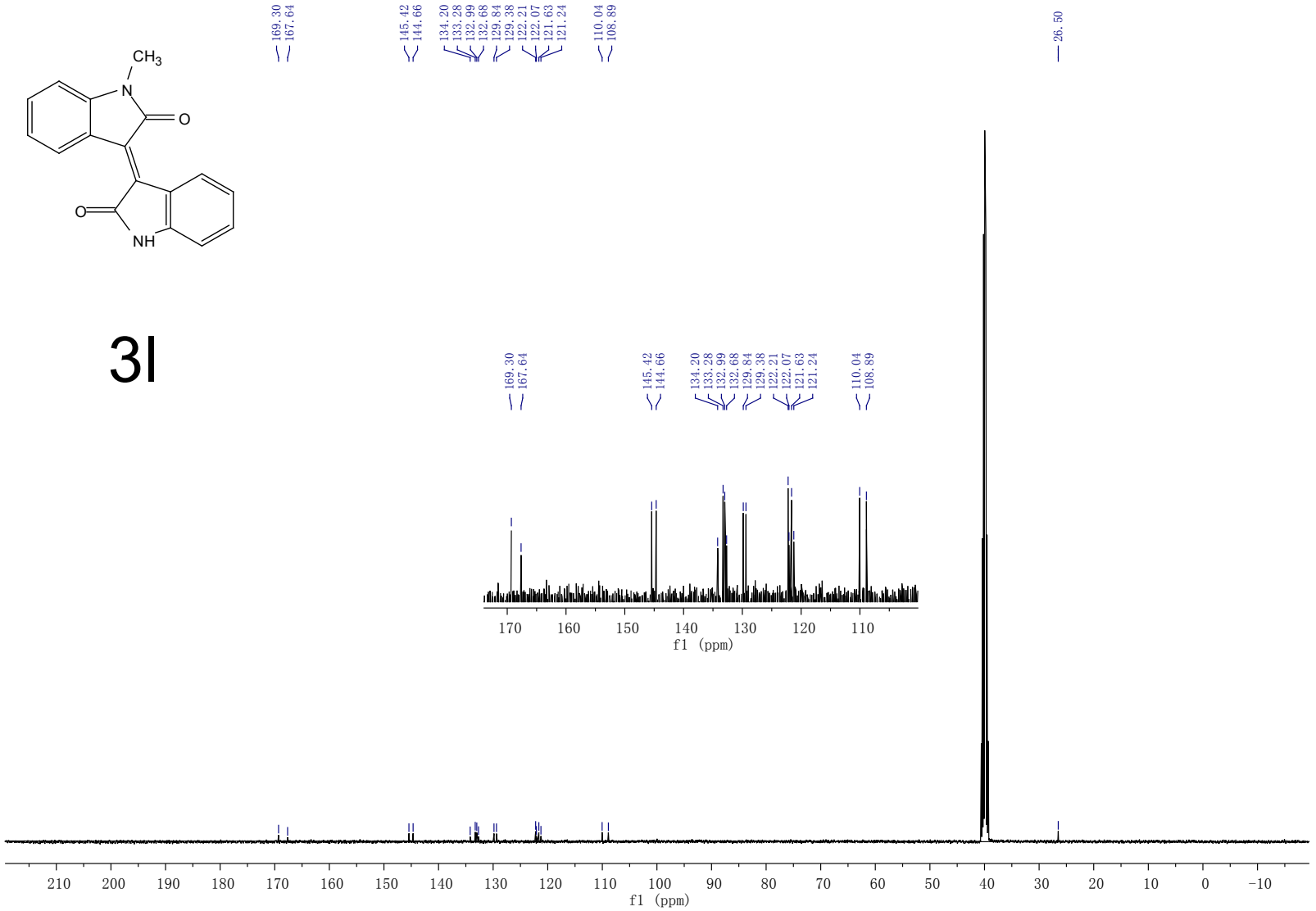

11.00
9.01
9.01
8.98
8.98
7.27
7.27
7.25
7.24
7.23
6.86
6.85
6.84
6.83
NH
O
F
F
O
NH
3j
2.00
2.19
2.33
2.05
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


169.43
156.32
141.27
141.25
134.41
122.62
119.80
116.83
116.54
110.72
110.64
NH
O
F
F
O
NH
3j
169.07
155.96
140.91
140.89
134.05
122.26
119.44
116.47
116.18
110.36
110.28
180 170 160 150 140 130 120 110 100 90 80
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

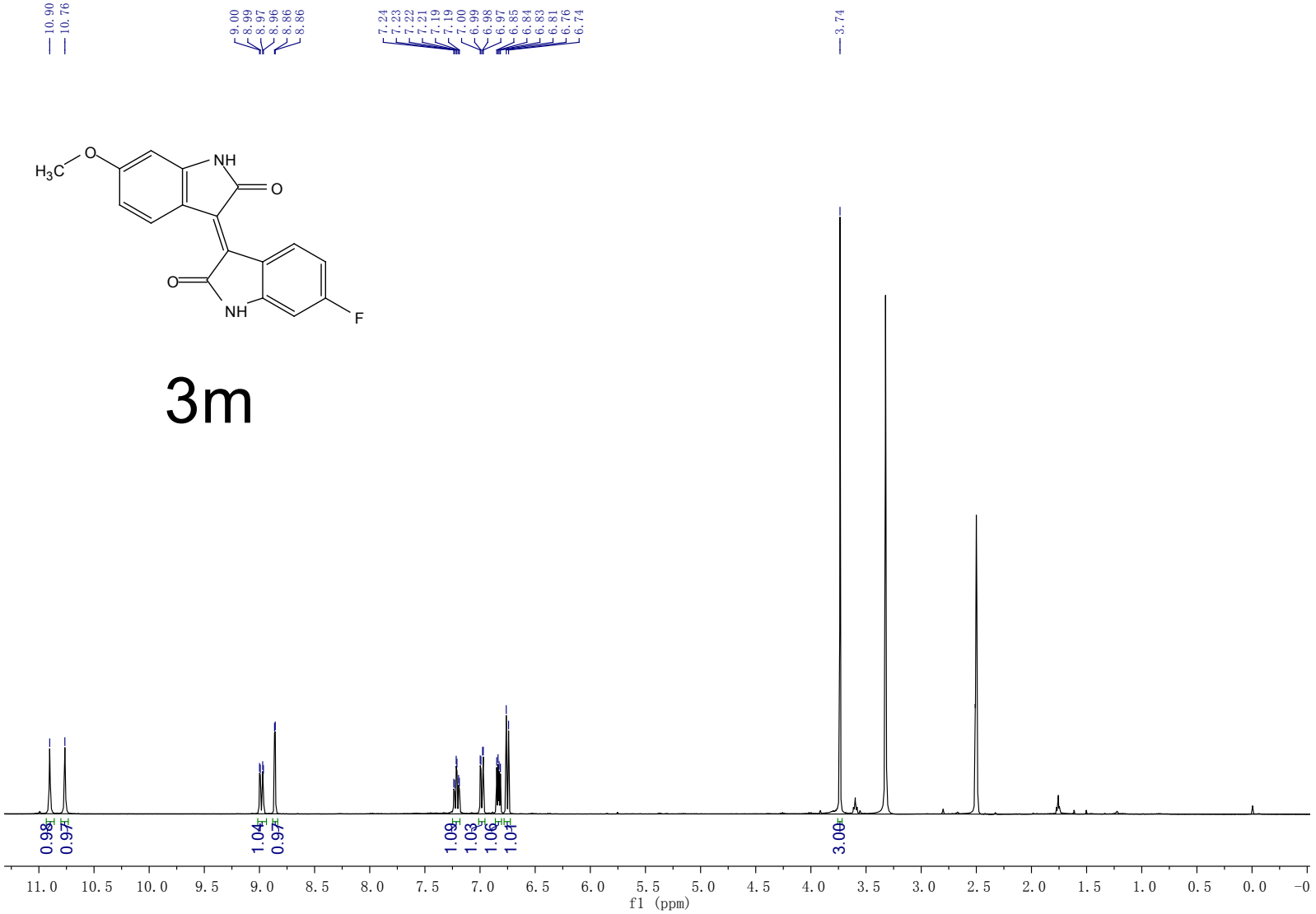

9.08
9.05
7.17
7.17
7.17
7.15
7.15
6.92
6.92
3.75
3.73
3.71
1.71
1.69
1.67
1.65
1.63
1.46
1.44
1.42
1.40
1.39
1.37
0.99
0.97
0.95
CH3
Br
N
O
O
N
Br
H3C
3k
1.97
2.00
2.01
4.00
4.06
4.06
6.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

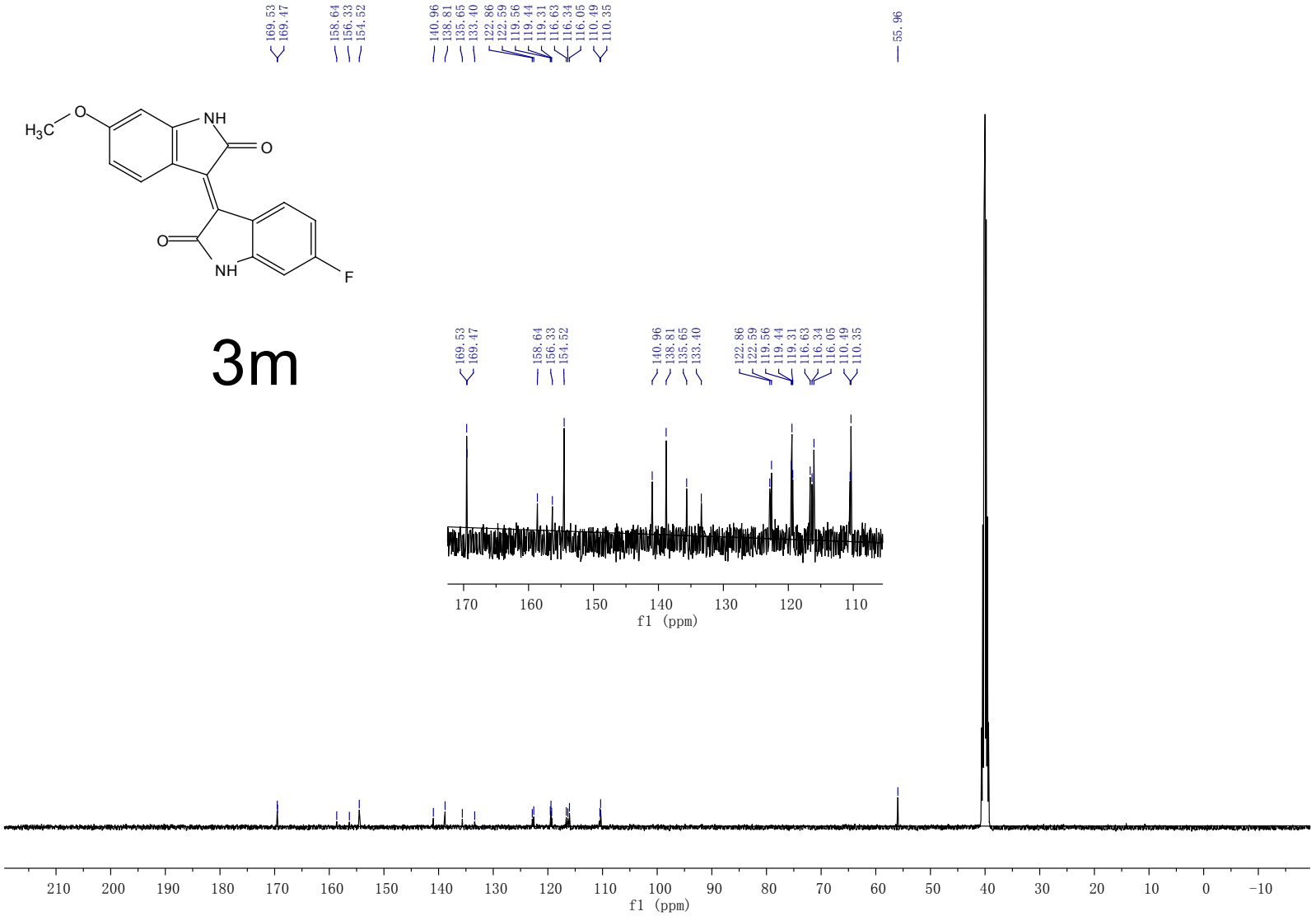

167.72
145.75
132.61
131.19
126.72
125.12
120.40
111.29
40.02
29.44
20.25
13.75
CH3
Br
N
O
O
N
Br
H3C
3k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

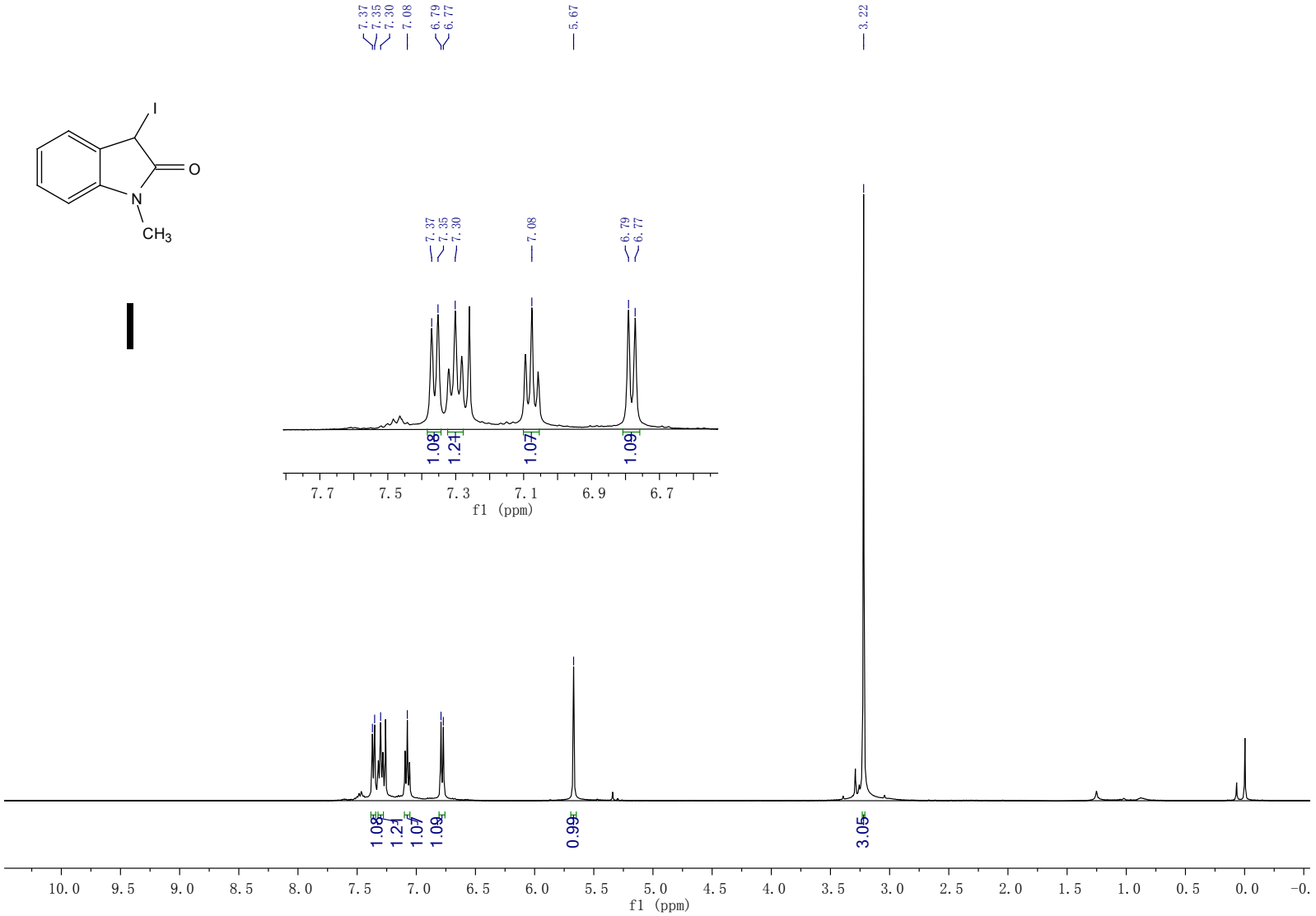

10.92
9.11
9.10
9.09
9.08
7.46
7.45
7.44
7.43
7.42
7.42
7.37
7.37
7.35
7.35
7.33
7.33
7.06
7.06
7.04
7.04
7.02
7.02
6.99
6.99
6.97
6.95
6.95
6.85
6.83
3.23
CH3
N
O
O
NH
3l
1.09
1.10
2.10
1.05
1.01
7.7
7.5
7.3
7.1
6.9
6.7
f1 (ppm)
1.01
2.09
1.09
1.10
2.10
1.05
1.01
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

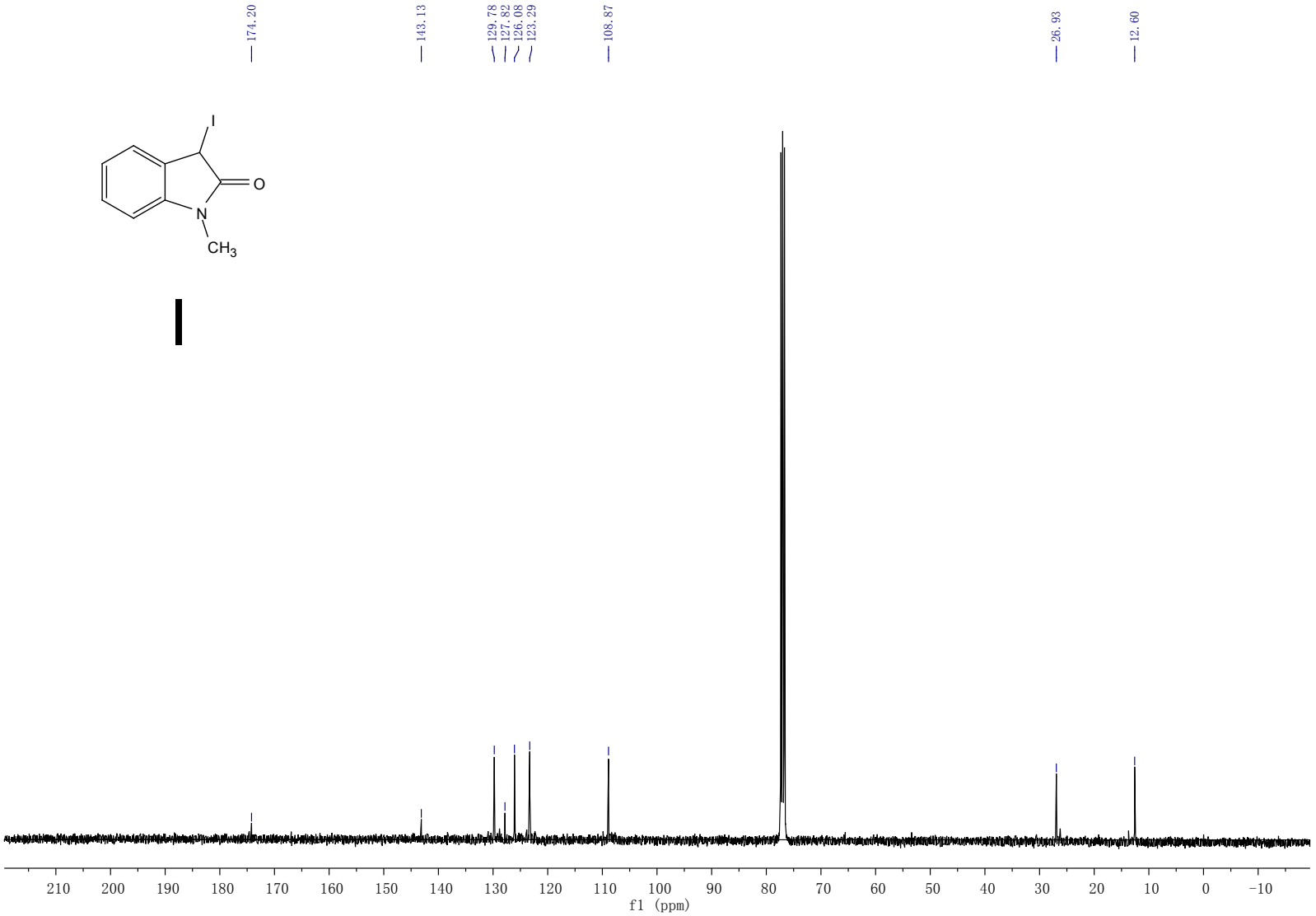

CH3
N
O
O
NH
169.30
167.64
145.42
144.66
134.20
133.28
132.99
132.68
129.84
129.38
122.21
122.07
121.63
121.24
110.04
108.89
26.50
f1 (ppm)

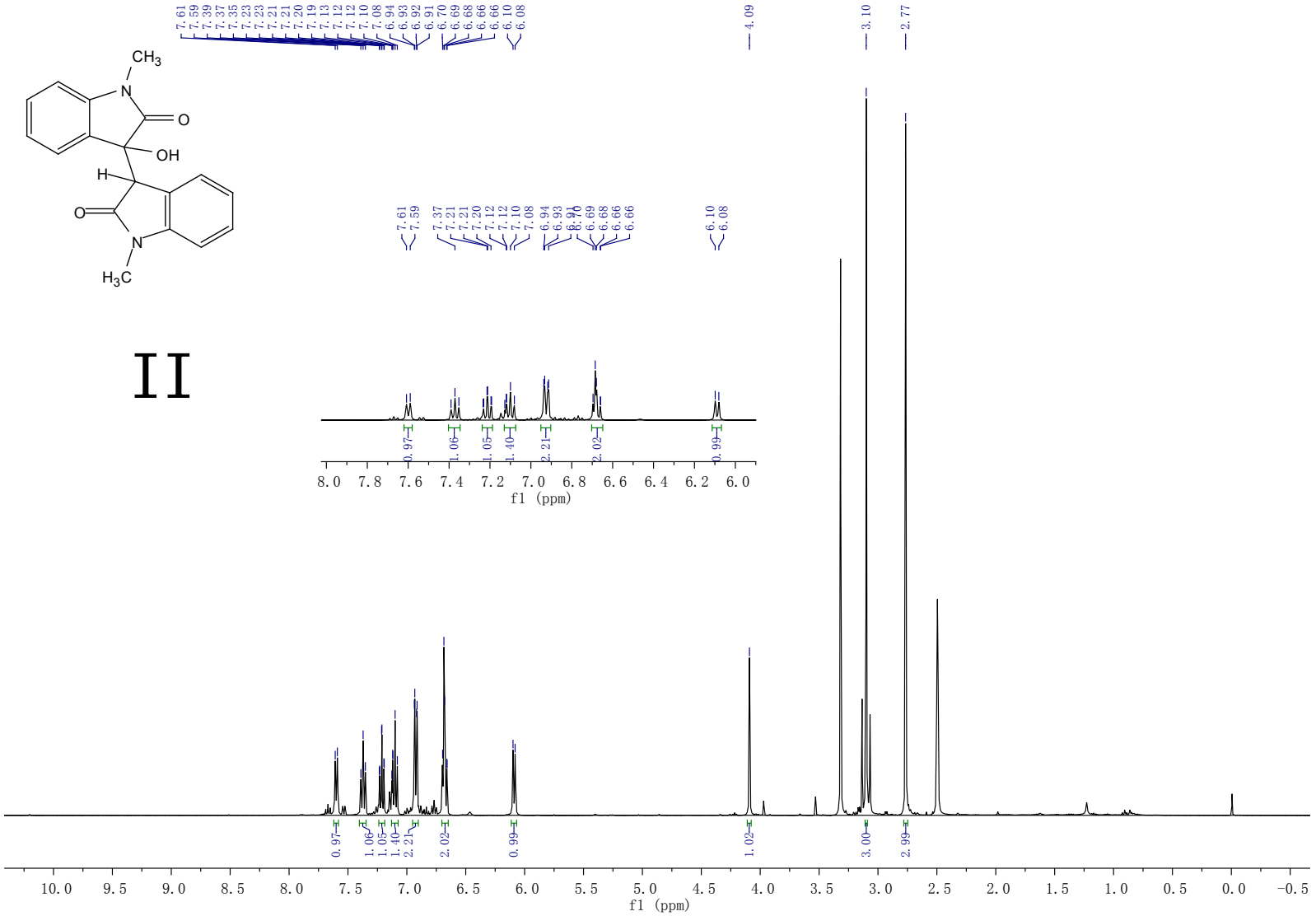
3l

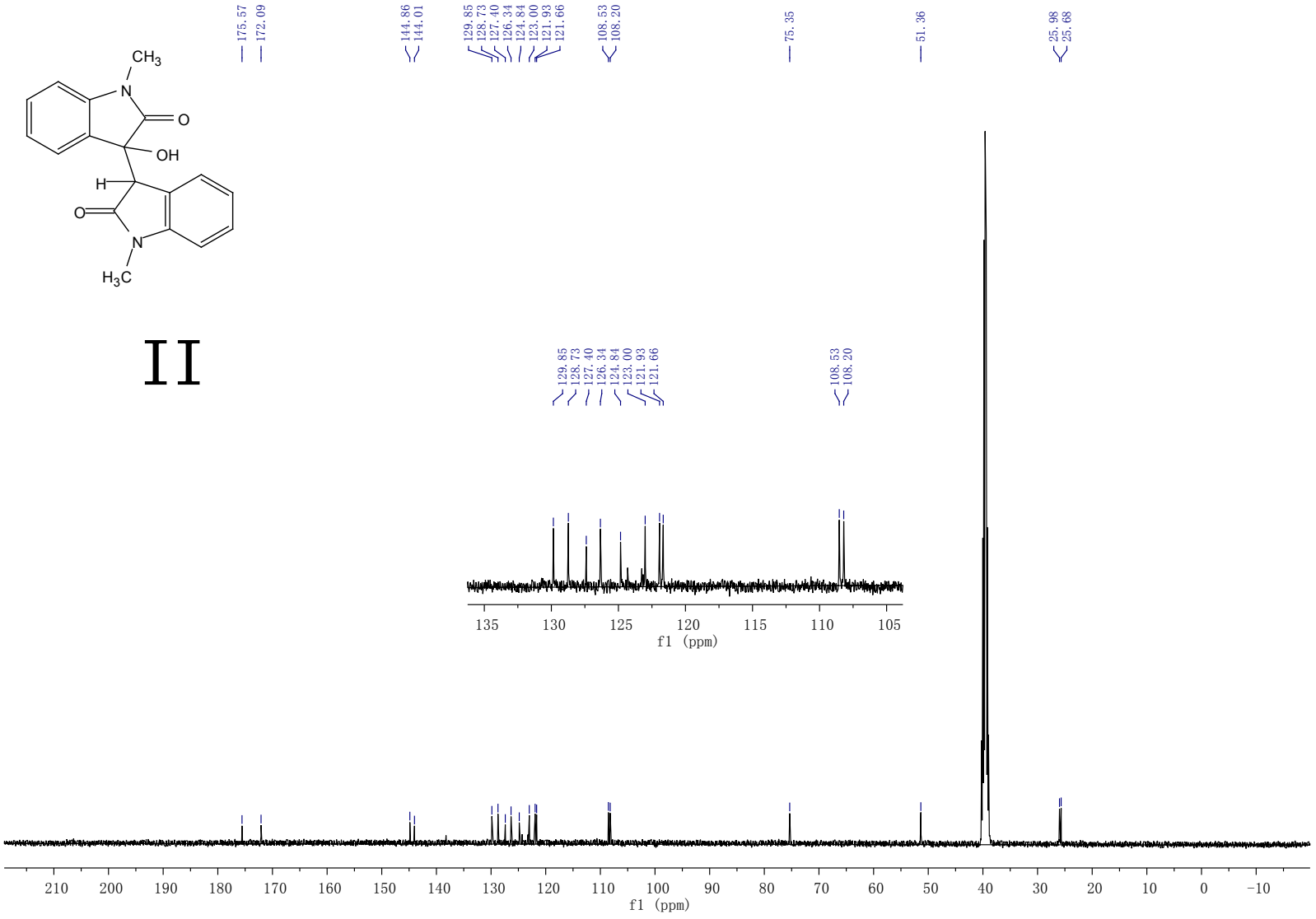

10.90
10.76
9.00
8.99
8.97
8.96
8.86
8.86
7.24
7.23
7.22
7.21
7.19
7.19
7.00
6.99
6.98
6.97
6.85
6.84
6.83
6.81
6.76
6.74
3.74
H3C
O
NH
O
O
NH
F
3m
0.98
0.97
1.04
0.97
1.03
1.03
1.06
1.07
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


169.53
169.47
158.64
156.33
154.52
140.96
138.81
135.65
133.40
122.86
122.59
119.56
119.44
119.31
116.63
116.34
116.05
110.49
110.35
55.96
H3C
O
NH
O
O
NH
F
3m
f1 (ppm)
f1 (ppm)


7.37
7.35
7.30
7.08
6.79
6.77
5.67
3.22
I
O
N
CH3
1.08
1.21
1.07
1.09
0.99
3.05
f1 (ppm)


174.20
143.13
129.78
127.82
126.08
123.29
108.87
26.93
12.60
I
O
N
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


II
CH3
N
O
OH
H
O
N
H3C
7.61 7.59 7.39 7.37 7.35 7.23 7.23 7.21 7.21 7.20 7.19 7.13 7.12 7.12 7.12 7.10 7.08 6.94 6.93 6.92 6.91 6.70 6.69 6.68 6.66 6.66 6.10 6.08
4.09
3.10
2.77
0.97 1.06 1.05 1.40 2.21 2.02 0.99 1.02 3.00 2.99
f1 (ppm)


175.57
172.09
144.86
144.01
129.85
128.73
127.40
126.34
124.84
123.00
121.93
121.66
108.53
108.20
75.35
51.36
25.98
25.68
CH3
N
O
OH
H
O
N
H3C
II
f1 (ppm)
f1 (ppm)