Highly Selective Synthesis of Dihydrobenzo[*d*]isoxazoles and Dihydrobenzo[*d*]oxazoles from Oximes and Arynes via in situ Generation of Nitrones

Tuanli Yao,* Beige Ren, Bo Wang and Yanna Zhao

College of Chemistry & Chemical Engineering, Shaanxi University of Science & Technology, 6 Xuefu Road, Weiyang District, Xi'an, Shaanxi, China 710021

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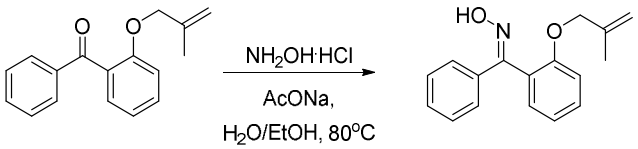
General Information:

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 400 spectrometer (operating at 400 and 101 MHz respectively) in $CDCl_3$ (residual internal standard $CHCl_3$= δ 7.26) or DMSO-d6 (residual internal standard CD_3SOCD_2H = δ 2.50). An Agilent 6224 TOF mass spectrometer was used to produce high resolution mass spectra. Melting points were determined on a Stanford Research Systems OptiMelt apparatus. The infrared (IR) spectra were acquired as thin films using a universal ATR sampling accessory on a PerkinElmer Spectrum 100 FT-IR spectrometer and the absorption frequencies are reported in cm^{-1}. Flash chromatography separations were carried out using partially deactivated Silica Gel (Silica Gel was immersed in 100:1 hexane/triethylamine overnight before using). All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, HRMS and IR. The structure of known compounds was further confirmed by comparing their ^{1}H NMR and ^{13}C NMR data with those of literature. All reagents and solvents were used as received from commercial sources without further purification. Compounds **1a**[1], **1b**[2], **1c**[3], **1d**[1], **1e**[4], **1f**[5], **1g**[4], **1h**[6], **1i-l**[1], **1p**[2], **1q**[1], **1r**[4], **1s**[7] and **1t**[1] were prepared by following literature procedure. CCDC 1545446 (**3a**), CCDC 1545450 (**3j**), CCDC 1545449 (**3a'**) and CCDC 1545448 (**3i**') contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

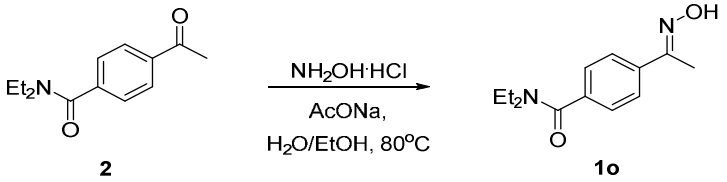
Experimental Procedures



1 **1m**

(*E*)-(2-((2-Methylallyl)oxy)phenyl)(phenyl)methanone oxime (1m). A mixture of the ketone **1**[8] (0.505 g, 2.0 mmol), $NH_2OH·HCl$ (0.208 g, 3.0 mmol) and AcONa (0.246 g, 3.0 mmol) in ethanol (1 mL) and water (1 mL) was

stirred at 80 °C overnight. The reaction mixture was cooled. The precipitate was filtered with suction, thoroughly washed with water and dried in the air. The crude product was recrystallized using ethyl acetate to produce **1m** as a white solid (0.3582 g, 67%): mp 101–103 °C; ^{1}H NMR (400 MHz, DMSO) δ 11.17 (s, 1H), 7.41 –7.35 (m, 3H), 7.34 – 7.29 (m, 3H), 7.10 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.07 (d, *J* = 8.2 Hz, 1H), 7.02 (td, *J* = 7.4, 0.8 Hz, 1H), 4.84 (s, 1H), 4.77 (s, 1H), 4.36 (s, 2H), 1.50 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 155.0, 153.1, 140.7, 136.4, 129.7, 129.6, 128.5, 128.2, 126.0, 123.0, 120.3, 112.5, 111.9, 70.8, 18.8; IR (neat) 2985, 1655, 1592, 1492, 1369 cm^{-1}; HRMS calcd for $C_{17}H_{17}NO_2Na^+$ (M^++Na): 290.1151, found 290.1168.

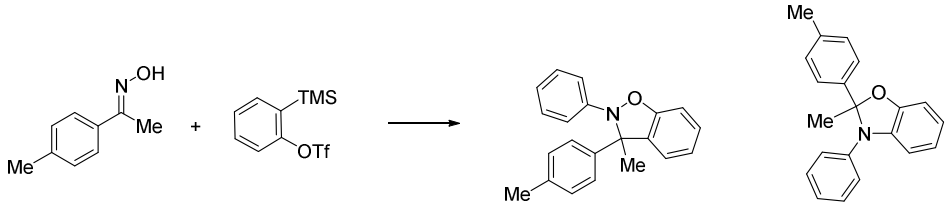


2 **1o**

(*E*)-*N*,*N*-Diethyl-4-(1-(hydroxyimino)ethyl)benzamide (1o).

This compound was prepared from ketone **2**[9] by following the same procedure as compound **1m** and was obtained as a yellow solid (0.4592 g, 98%): mp 124–126 °C; ^{1}H NMR (400 MHz, CDCl3) δ 8.82 (s, 1H), 7.65 – 7.60 (m, 2H), 7.39 – 7.34 (m, 2H), 3.53 (s, 2H), 3.24 (s, 2H), 2.26 (s, 3H), 1.23 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 171.1, 155.5, 138.0, 137.6, 126.7, 126.3, 43.5, 39.5, 14.4, 13.1, 12.2; IR (neat) 1605, 1514, 1368, 846 cm^{-1}; HRMS calcd for $C_{13}H_{18}N_2O_2Na^+$ (M^++Na): 257.1260, found 257.1276.

Table 1. Optimization for the preparation of dihydrobenzo[*d*]isoxazole (**3a**) and dihydrobenzo[*d*]oxazole (**3a'**) from Oxime (**1a**) and *o*-(Trimethylsilyl)phenyl Trifluoromethanesulfonate (**2a**)[a]

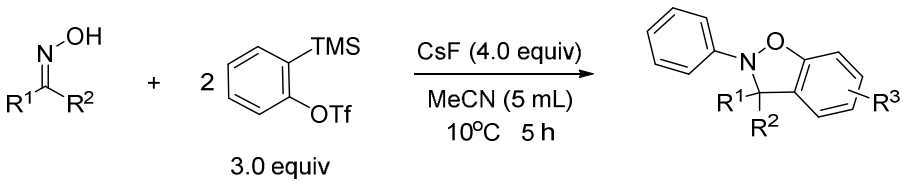


1a **2a** **3a** **3a'**

Entry	**2a** (equiv)	CsF (equiv)	Solvent	Temp. (°C)	Ratio (**3a**:**3a'**)	Yield (%)[b]
1	3.0	4.0	MeCN	10	38:1	85
2	2.2	3.0	MeCN	10	35:1	73
3	3.0	4.0	toluene	10		0[c]
4	3.0	4.0	DMF	10		trace[c]
5	3.0	4.0	THF	10		trace[c]
6	3.0	4.0	MeCN	40	1:6	94
7	2.2	3.0	MeCN	40	1:6	90
8	2.2	3.0	MeCN	60	1:16	98
9	2.2	3.0	MeCN	80	< 1:99	97

[a]Representative procedure: **1a** (0.25 mmol), **2a**, CsF and solvent (5 mL） were placed in a 4-dram vial and the reaction was stirred at indicated temperature. [b]Isolated overall yield. [c]**1a** was recovered.

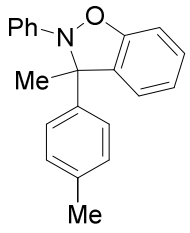
General procedure for the one-pot synthesis of dihydrobenzo[*d*] isoxazoles:



1 **2** **3**

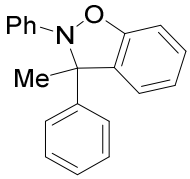
To a solution of the appropriate ketoxime **1** (0.25 mmol) and silylaryl triflate **2** (0.75 mmol, 3.0 eq) in acetonitrile (5 mL) at 10 °C was added CsF (1.0 mmol, 4.0 eq). The resulting mixture was stirred at 10 °C for 5h. The reaction mixture

was diluted with dichloromethane (20 mL), washed with water (1 x 20 mL) and brine (1 x 20 mL), dried ($MgSO_4$) and filtered. Solvent was removed under reduced pressure and the residue was purified by column chromatography (partially deactivated Silica Gel) using 100:1 hexane / triethylamine as the eluent.



3a

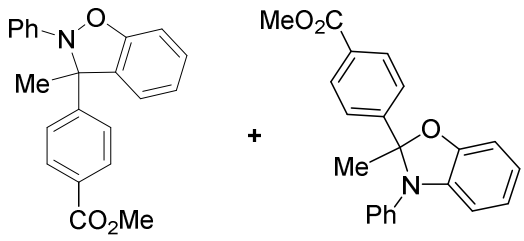
3-Methyl-2-phenyl-3-(*p*-tolyl)-2,3-dihydrobenzo[*d*]isoxazole (3a). This product was obtained as a 38:1 mixture with **3a'** after flash chromatography (0.0640 g, 85%). Pure **3a** was obtained as a white solid after recrystallization (EtOAc / petroleum ether): mp 89–90 °C; ^{1}H NMR (400 MHz, DMSO) δ 7.44 (d, *J* = 8.2 Hz, 2H), 7.28 – 7.17 (m, 5H), 7.04 (d, *J* = 8.0 Hz, 1H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.96 – 6.91 (m, 2H), 6.86 (dd, *J* = 8.5, 0.9 Hz, 2H), 2.30 (s, 3H), 1.57 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 153.9, 146.6, 140.8, 136.8, 134.8, 129.0, 128.7, 128.6, 127.0, 123.5, 123.2, 122.0, 117.6, 107.2, 73.3, 22.8, 20.6; IR (neat) 2925, 1594, 1483, 1373, 1237 cm^{-1}; HRMS calcd for $C_{21}H_{19}NONa^+$ (M^++Na): 324.1359, found 324.1367.



3b

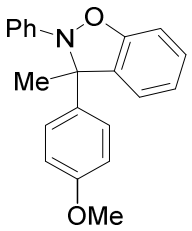
3-Methyl-2,3-diphenyl-2,3-dihydrobenzo[*d*]isoxazole (3b). This product was obtained as a 13:1 mixture with **3b'** after flash chromatography (0.0388 g, 54%). Pure **3b** was obtained as a white solid after recrystallization (EtOAc /

petroleum ether): mp 71–73 °C; ^{1}H NMR (400 MHz, DMSO) δ 7.56 (d, *J* = 7.7 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.34 – 7.19 (m, 4H), 7.11 – 6.92 (m, 4H), 6.88 (d, *J* = 7.8 Hz, 2H), 1.60 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 154.0, 146.6, 143.8, 134.4, 128.8, 128.6, 128.4, 127.5, 127.0, 123.6, 123.3, 122.1, 117.8, 107.2, 73.4, 22.9; IR (neat) 2927, 1592, 1486, 1376, 1237 cm^{-1}; HRMS calcd for $C_{20}H_{18}NO^{+}$ (M^{+}+H): 288.1383, found 288.1387.



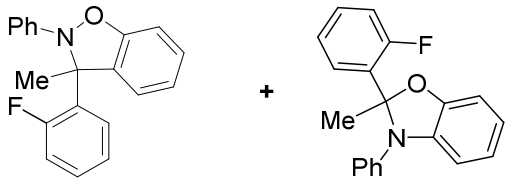
3c : **3c'** = 11 : 1

Methyl 4-(3-methyl-2-phenyl-2,3-dihydrobenzo[*d*]isoxazol-3-yl)benzoa te (3c). This product was obtained as an 11:1 mixture with **3c'** after flash chromatography (0.0586 g, 68%): mp 99–100 °C; ^{1}H NMR (400 MHz, DMSO) δ 8.01 – 7.94 (m, 2.16H), 7.73 (d, *J* = 7.0 Hz, 2H), 7.68 (d, *J* = 6.8 Hz, 0.16H), 7.53 – 7.43 (m, 0.16H), 7.33 – 7.20 (m, 3.08H), 7.17 – 7.11 (m, 0.16H), 7.11 – 6.94 (m, 4H), 6.88 (d, *J* = 7.8 Hz, 2H), 6.81 (d, *J* = 7.5 Hz, 0.16H), 6.73 (d, *J* = 7.6 Hz, 0.16H), 3.85 (s, 3.24H), 1.94 (s, 0.25H), 1.62 (s, 3H); ^{13}C NMR of 3c (101 MHz, DMSO) δ 166.0, 154.1, 149.1, 146.3, 133.6, 129.4, 129.1, 128.76, 128.73, 127.4, 124.0, 123.4, 122.3, 118.1, 107.4, 73.4, 52.2, 22.9; IR (neat) 2926, 1723, 1589, 1482, 1279 cm^{-1}; HRMS calcd for $C_{22}H_{19}NO_3Na^{+}$ (M^{+}+Na): 368.1257, found 368.1265.



3d

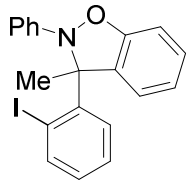
3-(4-Methoxyphenyl)-3-methyl-2-phenyl-2,3-dihydrobenzo[*d*]isoxazole (3d). This product was obtained as an 11:1 mixture with **3d'** after flash chromatography (0.0590 g, 74%). Pure **3d** was obtained as a white solid after recrystallization (EtOAc / petroleum ether): mp 67–69 °C; ^{1}H NMR (400 MHz, DMSO) δ 7.44 (d, *J* = 8.8 Hz, 2H), 7.30 – 7.19 (m, 3H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.99 (dd, *J* = 13.8, 6.5 Hz, 1H), 6.96 – 6.91 (m, 4H), 6.86 (d, *J* = 7.9 Hz, 2H), 3.75 (s, 3H), 1.57 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 158.5, 153.9, 146.6, 135.4, 135.0, 128.6, 128.6, 128.5, 123.5, 123.1, 122.0, 117.6, 113.7, 107.3, 73.1, 55.1, 22.8; IR (neat) 2926, 1594, 1483, 1242, 749 cm^{-1}; HRMS calcd for $C_{21}H_{19}NO_2Na^+$: (M^++Na): 340.1308, found 340.1302.



3e **3e'**

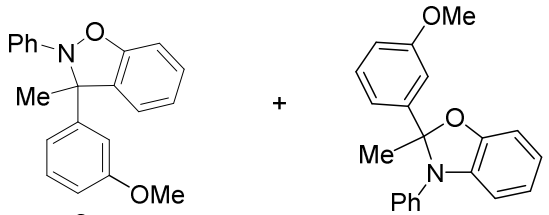
3e : **3e'** = 11 : 1

3-(2-fluorophenyl)-3-methyl-2-phenyl-2,3-dihydrobenzo[*d*]isoxazole (3e). This product was obtained as a colorless oil which is an unseparatable 11:1 mixture with **3e'** (0.0324 g, 42%): ^{1}H NMR (400 MHz, DMSO) δ 7.60 (t, *J* = 7.6 Hz, 0.09H), 7.46 (t, *J* = 7.9 Hz, 1.09H), 7.42 – 7.34 (m, 1H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.28 – 7.11 (m, 5.36H), 7.10 – 6.98 (m, 3.27H), 6.93 (d, *J* = 7.9 Hz, 2H), 6.82 – 6.77 (m, 0.27H), 6.75 – 6.69 (m, 0.09H), 2.01 (s, 0.27H), 1.67 (s, 3H); ^{13}C NMR of **3e** (101 MHz, DMSO) δ 160.3 (d, *J* =250.5), 155.2, 146.6, 132.1, 130.5 (d, *J* =10.1), 130.4 (d, *J* =9.1), 129.3, 129.1, 128.9 (d, *J* =4.0), 128.6, 124.2, 123.4 (d, *J* =2.0), 122.1, 118.8, 116.7 (d, *J* =22.2), 107.1, 72.1 (d, *J* =3.0), 23.5 (d, *J* =3.0); IR (neat) 1592, 1485, 1232, 753, 695 cm^{-1}; HRMS calcd for $C_{20}H_{16}FNONa^+$: (M^++Na): 328.1108, found 328.1115.



3f

3-(2-Iodophenyl)-3-methyl-2-phenyl-2,3-dihydrobenzo[*d*]isoxazole (3f). This product was obtained as a yellow oil after flash chromatography (0.0656 g, 63%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.57 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.44 (td, *J* = 7.7, 1.3 Hz, 1H), 7.25 (td, *J* = 8.1, 1.3 Hz, 1H), 7.21 – 7.14 (m, 2H), 7.03 (td, *J* = 7.6, 1.6 Hz, 1H), 6.99 – 6.92 (m, 2H), 6.89 (td, *J* = 7.5, 0.7 Hz, 1H), 6.81(d, *J* = 7.6 Hz, 2H), 6.67 (dd, *J* = 7.5, 0.8 Hz, 1H), 1.62 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 146.4, 144.1, 141.9, 134.2, 129.9, 129.1, 129.0, 128.7, 128.2, 123.1, 122.2, 121.6, 117.3, 107.1, 98.3, 74.3, 23.6; IR (neat) 3059, 1592, 1485, 1236, 1012 cm^{-1}; HRMS calcd for $C_{20}H_{16}NOINa^{+}$: (M^{+}+Na): 436.0169, found 436.0173.

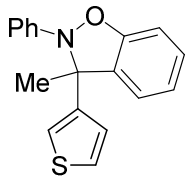


3g **3g'**

3g : **3g'** = 13 : 1

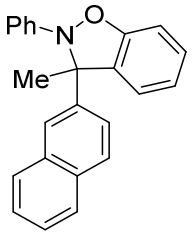
3-(3-Methoxyphenyl)-3-methyl-2-phenyl-2,3-dihydrobenzo[*d*]isoxazole (3g) This product was obtained as a colorless oil which is a 13:1 unseparatable mixture with **3g'** (0.0332 g, 42%): ^{1}H NMR (400 MHz, DMSO) δ 7.34 – 7.21 (m, 4.24H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.11 – 7.08 (m, 1.16H), 7.07 – 7.01 (m, 3.24H), 6.97 (dd, *J* = 15.0, 7.8 Hz, 1.08H), 6.92 – 6.86 (m, 3H), 6.80 – 6.74 (m, 0.24H), 6.73 – 6.67 (m, 0.08H), 3.72 (s, 3H), 3.71 (s, 0.24H), 1.92 (s, 0.24H), 1.58 (s, 3H); ^{13}C NMR of **3g** (101 MHz, DMSO) δ 159.3, 153.9, 146.6, 145.5, 134.3, 129.6, 128.8, 128.6, 123.6, 123.3, 122.1, 119.2, 117.8, 113.1, 112.5, 107.2, 73.3, 55.1, 23.0; IR (neat) 2928, 1594, 1484, 1242, 1042 cm^{-1}; HRMS calcd for

$C_{21}H_{19}NO_2Na^+$: (M^++H): 340.1308, found 340.1315.



3h

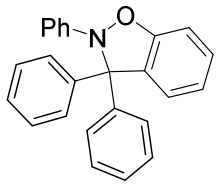
3-Methyl-2-phenyl-3-(thiophen-3-yl)-2,3-dihydrobenzo[*d*]isoxazole (3h). This product was obtained as a 27:1 mixture with **3h'** after flash chromatography (0.0214 g, 29%). Pure **3h** was obtained as a white solid after recrystallization (EtOAc / petroleum ether): mp 88 °C; ^{1}H NMR (400 MHz, DMSO) δ 7.52 – 7.47 (m, 2H), 7.31 – 7.20 (m, 3H), 7.07 – 6.99 (m, 4H), 6.97 (td, *J* = 7.4, 0.8 Hz, 1H), 6.90 (dd, *J* = 8.6, 1.0 Hz, 2H), 1.63 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 154.0, 146.6, 144.9, 134.0, 128.8, 128.5, 127.2, 126.7, 123. 8, 123.0, 122.9, 122.0, 118.1, 107.3, 71.7, 23.7; IR (neat) 2924, 1593, 1487, 1235 cm^{-1}; HRMS calcd for $C_{18}H_{15}NOSNa^+$ (M^++Na): 316.0767, found 316.0774.



3i

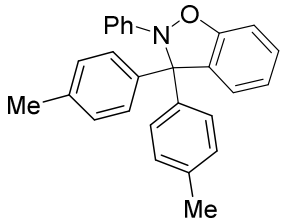
3-Methyl-3-(naphthalen-2-yl)-2-phenyl-2,3-dihydrobenzo[*d*]isoxazole (3i). This product was obtained as a 25:1 mixture with **3i'** after flash chromatography (0.0563 g, 67%). Pure **3i** was obtained as a white solid after recrystallization (EtOAc / petroleum ether): mp 87–90 °C; ^{1}H NMR (400 MHz, DMSO) δ 8.13 (s, 1H), 8.02 – 7.94 (m, 1H), 7.91 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.59 – 7.50 (m, 2H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.03 – 6.91 (m, 3H), 6.89 (d, *J* = 8.0 Hz, 2H), 1.70

(s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 153.8, 146.5, 141.1, 134.5, 132.6, 132.2, 128.8, 128.6, 128.3, 128.1, 127.4, 126.5, 126.4, 125.7, 125.3, 123.5, 123.2, 122.1, 117.5, 107.3, 73.6, 22.6; IR (neat) 3059, 1593, 1589, 1485, 1375, 1237 cm^{-1}; HRMS calcd for $C_{24}H_{19}NONa^+$ (M^++Na): 360.1359, found 360.1367.



3j

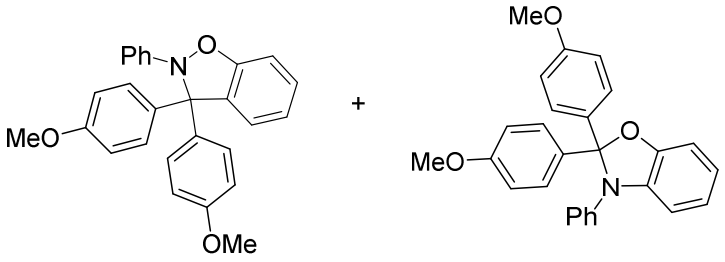
2,3,3-Triphenyl-2,3-dihydrobenzo[*d*]isoxazole (3j). This product was obtained as a white solid (0.0754g, 86%) after flash chromatography, which was further purified by recrystallization (EtOAc / petroleum ether): mp 124 °C; ^{1}H NMR (400 MHz, DMSO) δ 7.36 (t, *J* = 7.7 Hz, 1H), 7.30 – 7.19 (m, 11H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 7.8 Hz, 2H), 6.85 (t, *J* = 7.3 Hz, 1H), 6.68 (d, *J* = 7.7 Hz, 2H); ^{13}C NMR (101 MHz, DMSO) δ 156.5, 147.2, 140.9, 131.5, 129.4, 128.9, 127.9, 127.8, 127.6, 125.3, 124.5, 122.5, 120.5, 107.4, 82.2; IR (neat) 3061, 1591, 1480, 1237, 747, 698 cm^{-1}; HRMS calcd for $C_{25}H_{19}NONa^+$ (M^++Na): 372.1359, found 372.1365.



3k

2-Phenyl-3,3-di-*p*-tolyl-2,3-dihydrobenzo[*d*]isoxazole (3k) This product was obtained as a light yellow oil (0.0246 g, 26%): ^{1}H NMR (400 MHz, DMSO) δ 7.37 – 7.30 (m, 1H), 7.19 (d, *J* = 6.8 Hz, 1H), 7.13 – 7.07 (m, 5H), 7.07 – 7.01 (m, 5H), 7.00 – 6.94 (m, 2H), 6.86 (t, *J* = 7.3 Hz, 2H), 6.71 – 6.64 (m, 2H), 2.22 (s, 6H); ^{13}C NMR (101 MHz, DMSO) δ 156.3, 147.3, 138.1, 136.7, 132.0,

129.2, 128.8, 128.4, 127.8, 125.1, 124.3, 122.4, 120.3, 107.3, 81.8, 20.6; IR (neat) 3031, 1593, 1478, 1322, 1225 cm^{-1}; HRMS calcd for $C_{27}H_{23}NONa^{+}$: (M^{+}+Na): 400.1672, found 400.1672.

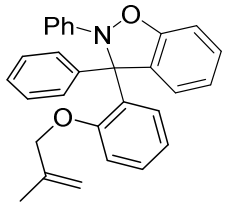


3l **3l'**

3l : **3l'** = 10 : 1

3,3-Bis(4-methoxyphenyl)-2-phenyl-2,3-dihydrobenzo[*d*]isoxazole (3l)

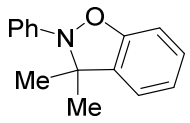
This product was obtained as a light yellow oil, which is a 10:1 unseparatable mixture with **3l'** after reverse-phase chromatography (C18, MeCN / H_2O) (0.0633 g, 62%) (the initial ratio before chromatography was 18:1): ^{1}H NMR (400 MHz, DMSO) δ 7.37 – 7.27 (m, 1.4H), 7.18 (d, *J* = 7.1 Hz, 1H), 7.16 – 7.08 (m, 5.2H), 7.08 – 6.95 (m, 3.2H), 6.91-6.85 (m, 1.6H), 6.81-6.77 (**3l'**: m, 0.3 H), 6.80 (**3l**: d, *J* = 8.9 Hz, 4H), 6.67 (d, *J* = 7.6 Hz, 2H), 3.73 (s, 0.6H), 3.69 (s, 6H); ^{13}C NMR of **3l** (101 MHz, DMSO) δ 158.4, 156.3, 147.3, 133.0, 132.2, 130.0, 129.1, 127.8, 125.0, 124.2, 122.4, 120.2, 113.1, 107.3, 81.5, 55.0; IR (neat) 3005, 2838, 1601, 1589, 1253, 1034 cm^{-1}; HRMS calcd for $C_{27}H_{24}NO_3^{+}$: (M^{+}+H): 410.1751, found 410.1757.



3m

3-(2-((2-Methylallyl)oxy)phenyl)-2,3-diphenyl-2,3-dihydrobenzo[*d*]isoxazole (3m). This product was obtained as a colorless oil (0.0608 g, 58%): ^{1}H NMR (400 MHz, DMSO) δ 8.07 (d, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 1H),

7.33 – 7.24 (m, 2H), 7.15 – 6.87 (m, 11H), 6.83 (t, *J* = 7.2 Hz, 1H), 6.60 (d, *J* = 7.7 Hz, 2H), 4.71 (s, 1H), 4.53 (s, 1H), 4.09 (s, 2H), 1.25 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 157.7, 155.0, 147.3, 140.5, 130.2, 130.0, 129.4, 129.1, 128.7, 128.1, 127.6, 127.5, 127.3, 126.4, 124.6, 121.9, 121.4, 120.2, 112.6, 112.4, 107.1, 81.0, 71.1, 18.7 (one carbon missing due to overlap); IR (neat) 3065, 1591, 1486, 1232, 1014 cm^{-1}; HRMS calcd for $C_{29}H_{26}NO_2^+$: (M^++H): 420.1958, found 420.1962.



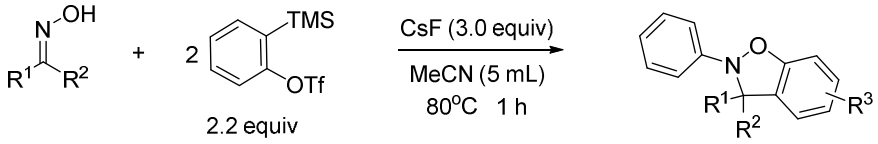
3n

3,3-Dimethyl-2-phenyl-2,3-dihydrobenzo[*d*]isoxazole (3n). This product was obtained as a colorless oil, which is a 67:1 unseparatable mixture with **3n'** (0.0282g, 50%): ^{1}H NMR (400 MHz, DMSO) δ 7.39 – 7.31 (m, 2H), 7.30 – 7.20 (m, 2H), 7.20 – 7.10 (m, 3H), 7.02 – 6.92 (m,2H), 1.36 (s, 6H); ^{13}C NMR (101 MHz, DMSO) δ 154.4, 146.9, 134.2, 128.7, 128.4, 124.6, 122.4, 121.6, 119.5, 106.9, 68.9, 26.6; IR (neat) 2973, 1593, 1480, 1370, 1237 cm^{-1}; HRMS calcd for $C_{15}H_{16}NO^+$ (M^++H): 226.1226, found 226.1230.

Scaling up experiment of 3a:

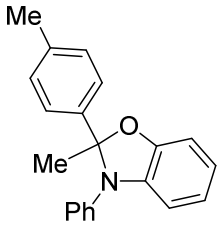
To a solution of ketoxime **1a** (0.149 g, 1 mmol, 1.0 equiv) and silylaryl triflate **2a** (0.895 g, 3.0 mmol, 3.0 equiv) in acetonitrile (25 mL) at 10 °C was added CsF (0.608 g, 4.0 mmol, 4.0 equiv). The resulting mixture was stirred at 10 °C for 7 h. The completed reaction was diluted with dichloromethane (40 mL), washed with water (1 x 20 mL) and brine (1 x 20 mL), dried ($MgSO_4$) and filtered. Solvent was removed under reduced pressure and the residue was purified by chromatography (basic Al_2O_3) using 100:1 hexane/triethylamine as the eluent. This product was obtained as a 25:1 mixture with **3a'** (0.227 g, 75%).

General procedure for the one-pot synthesis of dihydrobenzo[*d*]oxazole:



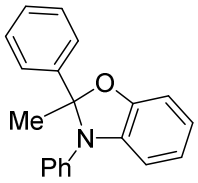
1 **2** **3**

To a solution of the appropriate ketoxime **1** (0.25 mmol) and silylaryl triflate **2** (2.2 eq, 0.55 mmol) in acetonitrile (5 mL) was added CsF (3.0 eq, 0.75 mmol). The resulting mixture was stirred at 80 °C for 1 h. The reaction mixture was diluted with dichloromethane (20 mL), washed with water (1 x 20mL) and brine (1 x 20 mL), dried ($MgSO_4$) and filtered. Solvent was removed under reduced pressure and the residue was purified by chromatography (partially deactivated Silica Gel) using 100:1 hexane/triethylamine as the eluent.



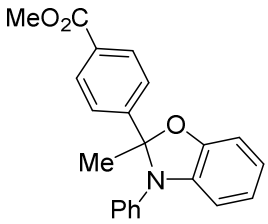
3a'

2-Methyl-3-phenyl-2-(p-tolyl)-2,3-dihydrobenzo[*d*]oxazole (3a'). This product was obtained as a white solid (0.0728 g, 97%): mp 112–115 °C; ^{1}H NMR (400 MHz, DMSO) δ 7.41 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.24 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.10 – 7.00 (m, 3H), 6.81 – 6.72 (m, 3H), 6.72 – 6.66 (m, 1H), 2.30 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 148.9, 140.1, 138.8, 138.3, 135.6, 129.4, 129.0, 126.1, 124.1, 122.3, 121.0, 119.8, 108.3, 108.0, 103.3, 23.4, 20.7 (two carbon missing due to overlap); IR (neat) 2992, 1588, 1489, 1375, 1233 cm^{-1}; HRMS calcd for $C_{21}H_{19}NONa^+$: (M^++Na): 324.1359, found 324.1366.



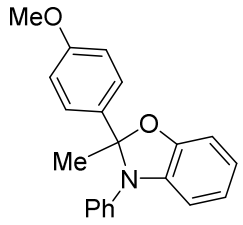
3b'

2-Methyl-2,3-diphenyl-2,3-dihydrobenzo[d]oxazole (3b'). This product was obtained as a white solid (0.0563 g, 78%): mp 80–81 °C; ^{1}H NMR (400 MHz, DMSO) δ 7.57 – 7.49 (m, 2H), 7.44 – 7.35 (m, 3H), 7.28 (dd, *J* = 8.3, 7.5 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 2H), 6.82 – 6.74 (m, 3H), 6.71 (dd, *J* = 7.0, 1.5 Hz, 1H), 1.94 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 148.9, 141.6, 140.1, 135.6, 129.3, 128.9, 128.4, 126.0, 124.2, 122.5, 121.0, 119.8, 108.4, 108.0, 103.3, 79.1, 23.4 (one carbon missing due to overlap); IR (neat) 2927, 1586, 1489, 1379, 1225 cm^{-1}; HRMS calcd for $C_{20}H_{17}NONa^{+}$: (M^{+}+Na): 310.1202, found 310.1209.



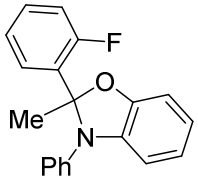
3c'

Methyl 4-(2-methyl-3-phenyl-2,3-dihydrobenzo[d]oxazol-2-yl)benzoate (3c'). This product was obtained as a white solid (0.0620 g, 72%): mp 133 °C; ^{1}H NMR (400 MHz, DMSO) δ 7.98 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 8.6 Hz, 2H), 7.29 (dd, *J* = 8.3, 7.5 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.02 (dd, *J* = 8.5, 1.0 Hz, 2H), 6.83 – 6.77 (m, 2H), 6.76 – 6.70 (m, 2H), 3.85 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 165.8, 148.8, 146.3, 139.9, 135.6, 130.0, 129.5, 129.4, 126.5, 124.6, 122.9, 121.3, 120.1, 108.8, 108.1, 102.8, 52.2, 23.5 (two carbon missing due to overlap); IR (neat) 3056, 1722, 1583, 1492, 1280 cm^{-1}; HRMS calcd for $C_{22}H_{19}NO_3Na^{+}$: (M^{+}+Na): 368.1257, found 368.1262.



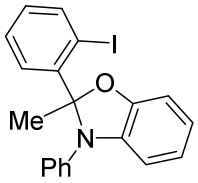
3d'

2-(4-Methoxyphenyl)-2-methyl-3-phenyl-2,3-dihydrobenzo[d]oxazole (3d'). This product was obtained as a white solid (0.0754 g, 95%): mp 92–93 °C; ^{1}H NMR (400 MHz, DMSO) δ 7.45 (d, *J* = 8.9 Hz, 2H), 7.31 – 7.24 (m, 2H), 7.10 – 7.00 (m, 3H), 6.94 (d, *J* = 8.9 Hz, 2H), 6.80 – 6.72 (m, 3H), 6.69 (ddd, *J* = 7.9, 6.3, 2.2 Hz, 1H), 3.75 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 159.52, 148.8, 140.1, 135.6, 133.7, 129.3, 127.6, 124.1, 122.3, 120.9, 119.7, 113.7, 108.2, 108.0, 103.3, 55.1, 23.4 (two carbon missing due to overlap); IR (neat) 2837, 1586, 1493, 1380, 1232 cm^{-1}; HRMS calcd for $C_{21}H_{20}NO_2^+$: (M^++H): 318.1489, found 318.1496.



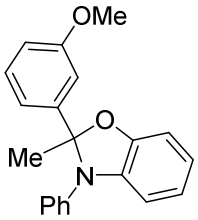
3e'

2-(2-Fluorophenyl)-2-methyl-3-phenyl-2,3-dihydrobenzo[d]oxazole (3e'). This product was obtained as colorless oil (0.0628 g, 82%): ^{1}H NMR (400 MHz, DMSO) δ 7.60 (td, *J* = 7.9, 1.6 Hz, 1H), 7.47 – 7.40 (m, 1H), 7.29 – 7.13 (m, 4H), 7.10 – 7.02 (m, 3H), 6.82 – 6.69 (m, 4H), 2.00 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 160.2(d, *J* = 251.5), 149.1, 140.2, 135.0, 131.6 (d, *J* = 9.1), 129.3, 128.8 (d, *J* = 3.0), 128.0 (d, *J* = 10.1), 124.1, 122.1, 121.0, 120.1, 116.7 (d, *J* = 22.2), 109.12, 108.1, 102.1, 24.7(d, *J* = 3.0) (three carbon missing due to overlap); IR (neat) 1589, 1490, 1378, 1232, 746, 692 cm^{-1}; HRMS calcd for $C_{20}H_{16}FNONa^+$: (M^++Na): 328.1108, found 328.1118.



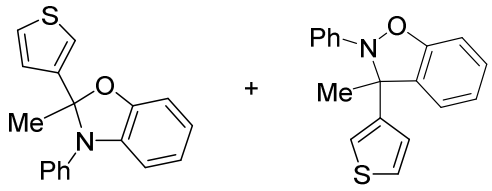
3f'

2-(2-Iodophenyl)-2-methyl-3-phenyl-2,3-dihydrobenzo[d]oxazole (3f'). This product was obtained as a light yellow oil (0.0734g, 71%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 2H), 7.08 – 6.96 (m, 4H), 6.88 – 6.74 (m, 4H), 1.95 (s, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 150.3, 143.5, 141.6, 140.3, 136.7, 130.8, 130.0, 129.3, 127.8, 124.7, 123.5, 121.4, 120.3, 109.4, 109.2, 104.1, 95.0, 23.3 (two carbon missing due to overlap); IR (neat) 3058, 1588, 1490, 1229, 1012 cm^{-1}; HRMS calcd for $C_{20}H_{16}INONa^{+}$: (M^{+}+Na): 436.0169, found 436.0176.



3g'

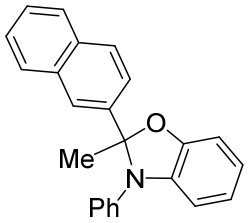
2-(3-Methoxyphenyl)-2-methyl-3-phenyl-2,3-dihydrobenzo[d]oxazole (3g'). This product was obtained as a colorless oil (0.0512 g, 65%): ^{1}H NMR (400 MHz, DMSO) δ 7.36 – 7.26 (m, 3H), 7.14 – 7.08 (m, 2H), 7.08 – 7.03 (m, 2H), 7.03 – 7.00 (m, 1H), 6.98 – 6.93 (m, 1H), 6.81 – 6.74 (m, 3H), 6.73 – 6.67 (m, 1H), 3.71 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 159.3, 148.9, 143.2, 140.1, 135.6, 129.7, 129.4, 124.2, 122.4, 121.1, 119.9, 118.3, 113.9, 112.2, 108.5, 108.1, 103.2, 55.1, 23.6 (two carbon missing due to overlap); IR (neat) 2852, 1591, 1492, 1379, 1227, 1030 cm^{-1}; HRMS calcd for $C_{21}H_{19}NO_2Na^{+}$: (M^{+}+Na): 340.1308, found 340.1319.



3h' + **3h**

3h' : **3h** = 0.8 : 1

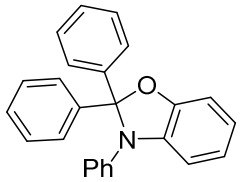
2-Methyl-3-phenyl-2-(thiophen-3-yl)-2,3-dihydrobenzo[d]oxazole (3h'). This product was obtained as a colorless oil which is a 0.8 : 1 unseparatable mixture with **3h** (0.0345 g, 47%): ^{1}H NMR (400 MHz, DMSO) δ 7.64 (dd, *J* = 2.9, 1.3 Hz, 0.8H), 7.53 (dd, *J* = 5.1, 2.9 Hz, 0.8H), 7.50 – 7.47 (m, 2H), 7.32 – 7.20 (m, 4.6H), 7.13 – 7.07 (m, 1.6H), 7.07 – 7.00 (m, 5.6H), 6.97 (t, *J* = 7.3 Hz, 1H), 6.91 (dd, *J* = 8.6, 1.0 Hz, 2H), 6.80 – 6.74 (m, 1.6H), 6.72 – 6.67 (m, 1.6H), 1.92 (s, 2.4H), 1.64 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 153.9, 148.8, 146.5, 144.9, 143.7, 139.9, 135.6, 134.0, 129.3, 128.8, 128.5, 127.2, 126.7, 126.1, 124.4, 124.2, 123.7, 122.9, 122.9, 122.7, 121.9, 121.0, 119.6, 118.0, 108.1, 107.9, 107.3, 100.9, 71.6, 24.2, 23.7 (five carbon missing due to overlap); IR (neat) 2926, 1593, 1488, 1377, 1235 cm^{-1}; HRMS calcd for $C_{18}H_{15}NOSNa^{+}$: (M^{+}+Na): 316.0767, found 316.0775.



3i'

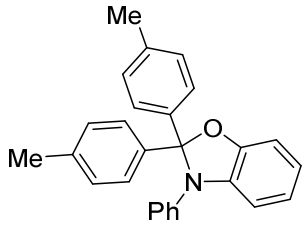
2-Methyl-2-(naphthalen-2-yl)-3-phenyl-2,3-dihydrobenzo[d]oxazole (3i'). This product was obtained as a white solid (0.0813 g, 96%): mp 131 °C; ^{1}H NMR (400 MHz, DMSO) δ 8.09 (s, 1H), 8.00 – 7.88 (m, 3H), 7.66 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.59 – 7.50 (m, 2H), 7.25 (t, *J* = 7.8 Hz, 2H), 7.10 – 7.00 (m, 3H), 6.84 – 6.77 (m, 3H), 6.77 – 6.69 (m, 1H), 2.04 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 149.0, 140.1, 138.9, 135.7, 132.9, 132.3, 129.4, 128.6, 128.4, 127.5,

126.9, 126.6, 125.1, 124.4, 124.2, 122.6, 121.1, 119.9, 108.6, 108.1, 103.5, 23.3 (one carbon missing due to overlap); IR (neat) 3055, 1587, 1488, 1376, 1232 cm^{-1}; HRMS calcd for $C_{24}H_{19}NONa^{+}$: (M^{+}+Na): 360.1359, found 360.1372.



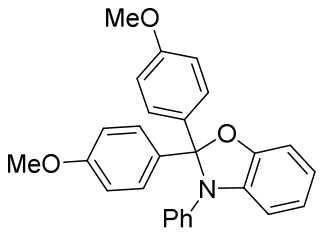
3j'

2,2,3-Triphenyl-2,3-dihydrobenzo[d]oxazole (3j'). This product was obtained as a white solid (0.0720 g, 83%): mp 146–147 °C; ^{1}H NMR (400 MHz, DMSO) δ 7.47 – 7.28 (m, 10H), 7.11 (t, *J* = 7.8 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.87 (dt, *J* = 23.6, 8.4 Hz, 4H), 6.77 (t, *J* = 7.5 Hz, 1H); ^{13}C NMR (101 MHz, DMSO) δ 149.0, 141.11, 141.09, 139.18, 139.16, 135.31, 135.25, 129.0, 128.8, 128.4, 128.0, 123.59, 123.56, 122.5, 122.4, 121.4, 120.7, 110.1, 108.3, 106.3; IR (neat) 3059, 1585, 1488, 1227 cm^{-1}; HRMS calcd for $C_{25}H_{19}NONa^{+}$: (M^{+}+Na): 372.1359, found 327.1361.



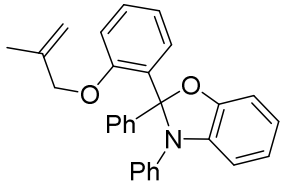
3k'

3-Phenyl-2,2-di-p-tolyl-2,3-dihydrobenzo[d]oxazole (3k'). This product was obtained as a light yellow oil (0.0710 g, 75%): ^{1}H NMR (400 MHz, DMSO) δ 7.26 (d, *J* = 8.1 Hz, 4H), 7.18 – 7.07 (m, 6H), 6.95 (d, *J* = 8.1 Hz, 2H), 6.92 – 6.86 (m, 2H), 6.85 – 6.78 (m, 2H), 6.74 (t, *J* = 7.5 Hz, 1H), 2.27 (s, 6H); ^{13}C NMR (101 MHz, DMSO) δ 149.0, 141.0, 138.3, 136.4, 135.2, 128.8, 128.5, 128.5, 123.3, 122.0, 121.2, 120.5, 109.7, 108.3, 106.2, 99.5, 20.7 (one carbon missing due to overlap); IR (neat) 3035, 1591, 1493, 1380, 1237 cm^{-1}; HRMS calcd for $C_{27}H_{23}NONa^{+}$: (M^{+}+Na): 400.1672, found 400.1686.



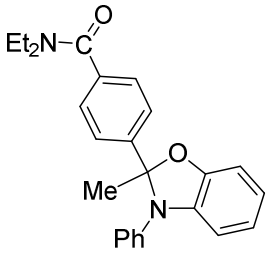
3l'

2,2-Bis(4-methoxyphenyl)-3-phenyl-2,3-dihydrobenzo[*d*]oxazole (3l'). This product was obtained as a light yellow oil (0.0877 g, 86%): ^{1}H NMR (400 MHz, DMSO) δ 7.29 (d, *J* = 8.8 Hz, 4H), 7.12 (t, *J* = 7.9 Hz, 2H), 6.95 (d, *J* = 7.7 Hz, 2H), 6.92 – 6.87 (m, 6H), 6.85 – 6.77 (m, 2H), 6.77 – 6.70 (m, 1H), 3.72 (s, 6H); ^{13}C NMR (101 MHz, DMSO) δ 159.5, 149.0, 141.0, 135.1, 131.3, 130.0, 128.9, 123.2, 121.8, 121.2, 120.5, 113.3, 109.8, 108.3, 106.2, 55.2 (two carbon missing due to overlap); IR (neat) 3061, 2961, 1603, 1499, 1243, 1173 cm^{-1}; HRMS calcd for $C_{27}H_{24}NO_3^+$: (M^++H): 410.1751, found 410.1759.



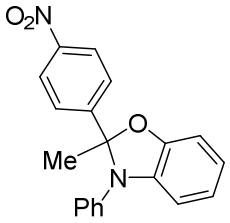
3m'

2-(2-((2-Methylallyl)oxy)phenyl)-2,3-diphenyl-2,3-dihydrobenzo[*d*]oxazole (3m'). This product was obtained as a colorless oil (0.0902 g, 86%): ^{1}H NMR (400 MHz, DMSO) δ 7.46 – 7.39 (m, 2H), 7.36 – 7.24 (m, 5H), 7.07 – 7.01 (m, 2H), 6.99 – 6.87 (m, 5H), 6.86 – 6.69 (m, 4H), 4.65 (s, 1H), 4.58 (s, 1H), 4.16 (d, *J* = 12.6 Hz, 1H), 4.04 (d, *J* = 12.6 Hz, 1H), 1.37 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 156.9, 149.7, 141.3, 140.4, 140.2, 135.2, 131.1, 130.7, 128.4, 128.2, 127.8, 127.7, 125.9, 122.8, 121.5, 120.8, 120.5, 119.5, 113.0, 111.8, 110.5, 108.3, 106.1, 71.3, 18.8 (two carbon missing due to overlap); IR (neat) 3062, 1592, 1491, 1314, 1234 cm^{-1}; HRMS calcd for $C_{29}H_{26}NO_2^+$: (M^++H): 420.1958, found 420.1970.



3o'

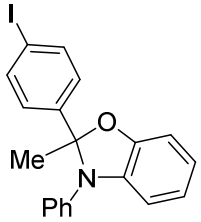
***N,N*-Diethyl-4-(2-methyl-3-phenyl-2,3-dihydrobenzo[*d*]oxazol-2-yl) benzamide (3o')**. This product was obtained as a white solid (0.0680 g, 70%): mp 81 °C; ^{1}H NMR (400 MHz, DMSO) δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.25 (m, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 2H), 6.83 – 6.77 (m, 2H), 6.77 – 6.69 (m, 2H), 3.41 (s, 2H), 3.13 (s, 2H), 1.96 (s, 3H), 1.13 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 169.4, 148.9, 142.0, 140.1, 137.7, 135.6, 129.4, 126.2, 126.1, 124.5, 122.8, 121.1, 120.0, 108.6, 108.0, 103.1, 42.8, 38.7, 23.6, 14.0, 12.8 (two carbon missing due to overlap); IR (neat) 2974, 1625, 1494, 1380, 1226 cm^{-1}; HRMS calcd for $C_{25}H_{26}N_2O_2Na^+$: (M^++Na): 409.1886, found 409.1899.



3p'

2-Methyl-2-(4-nitrophenyl)-3-phenyl-2,3-dihydrobenzo[*d*]oxazole(3p'). This product was obtained as a yellow solid (0.0490 g, 59%): mp 147–150 °C; ^{1}H NMR (400 MHz, DMSO) δ 8.26 (d, *J* = 8.9 Hz, 2H), 7.81 (d, *J* = 9.0 Hz, 2H), 7.36 – 7.29 (m, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 2H), 6.85 – 6.79 (m, 2H), 6.78 – 6.72 (m, 2H), 1.97 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 148.7, 148.3, 147.7, 139.9, 135.6, 129.6, 127.5, 124.9, 123.8, 123.2, 121.5, 120.4, 109.2, 108.3, 102.5, 23.6 (two carbon missing due to overlap); IR (neat)

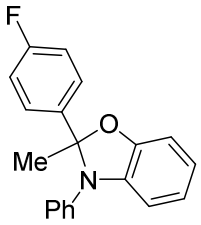
1585, 1489, 1354, 1224 cm^{-1}; HRMS calcd for $C_{20}H_{16}N_2O_3Na^+$: (M^++Na): 355.1053, found 355.1066.



3q'

2-(4-Iodophenyl)-2-methyl-3-phenyl-2,3-dihydrobenzo[*d*]oxazole(3q').

This product was obtained as a white solid (0.0945 g, 91%): mp 116 °C; ^{1}H NMR (400 MHz, DMSO) δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.37 – 7.27 (m, 4H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 2H), 6.82 – 6.68 (m, 4H), 1.90 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 148.8, 141.4, 140.0, 137.3, 135.5, 129.4, 128.3, 124.5, 122.7, 121.2, 120.0, 108.7, 108.1, 103.0, 95.7, 23.4 (two carbon missing due to overlap); IR (neat) 3054, 1582, 1490, 1383, 1262 cm^{-1}; HRMS calcd for $C_{20}H_{17}INO^+$: (M^++H): 414.0349, found 414.0370.

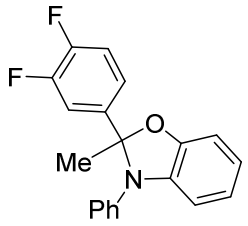


3r'

2-(4-Fluorophenyl)-2-methyl-3-phenyl-2,3-dihydrobenzo[*d*]oxazole (3r').

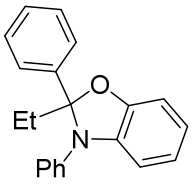
This product was obtained as a white solid (0.0614 g, 80%): mp 83–85 °C; ^{1}H NMR (400 MHz, DMSO) δ 7.61 – 7.54 (m, 2H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.22 (t, *J* = 8.8 Hz, 2H), 7.10 (t, *J* = 7.3 Hz,1H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.82 – 6.68 (m, 4H), 1.93 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 162.2 (d, *J* = 246.4), 148.8, 140.0, 138.0, 135.5, 129.4, 128.5(d, *J* = 8.1), 124.4, 122.7, 121.1, 119.9, 115.2 (d, *J* = 22.2), 108.3(d, *J* = 49.5), 102.9, 23.6 (three carbon missing due to overlap); IR (neat) 3054, 1589, 1492, 1380, 1228 cm^{-1}; HRMS calcd for

$C_{20}H_{17}FNO^+$: (M^++H): 306.1289, found 306.1310.



3s'

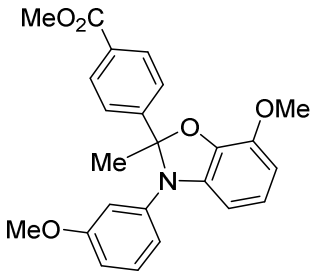
2-(3,4-Difluorophenyl)-2-methyl-3-phenyl-2,3-dihydrobenzo[*d*]oxazole (3s'). This product was obtained as a white solid (0.0559 g, 69%): mp 88 °C; ^{1}H NMR (400 MHz, DMSO) δ 7.60 – 7.51 (m, 1H), 7.50 – 7.41 (m, 1H), 7.40 – 7.35 (m, 1H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 2H), 6.83 – 6.77 (m, 2H), 6.76 – 6.69 (m, 2H), 1.92 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 148.7, 140.0, 139.4, 135.5, 129.5, 124.7, 123.3 (dd, *J* = 7.1, 3.0), 123.0, 121.3, 120.2, 116.6 (dd, *J* = 204.0, 17,2), 109.0, 108.2, 102.4, 23.6 (three carbon missing due to overlap); IR (neat) 3057, 1586, 1491, 1317, 1226, 1109 cm^{-1}; HRMS calcd for $C_{20}H_{16}F_2NO^+$: (M^++H): 324.1194, found 324.1203.



3t'

2-Ethyl-2,3-diphenyl-2,3-dihydrobenzo[*d*]oxazole (3t'). This product was obtained as a white solid (0.0534 g, 71%): mp 127 °C; ^{1}H NMR (400 MHz, DMSO) δ 7.46 –7.40 (m, 2H), 7.40 – 7.33 (m, 3H), 7.28 (dd, *J* = 8.3, 7.6 Hz, 2H), 7.10 – 7.01 (m, 3H), 6.80 – 6.74 (m, 3H), 6.70 – 6.65 (m, 1H), 2.47 (q, *J* = 8.0 Hz, 2H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, DMSO) δ 149.6, 141.0, 139.7, 136.0, 129.3, 128.8, 128.5, 125.7, 123.9, 121.8, 120.8, 119.4, 107.5, 107.4, 105.0, 28.3, 6.9 (two carbon missing due to overlap); IR (neat) 2974, 1589, 1492, 1228, 736, 693 cm^{-1}; HRMS calcd for $C_{21}H_{19}NONa^+$:

(M^++Na): 324.1359, found 324.1370.



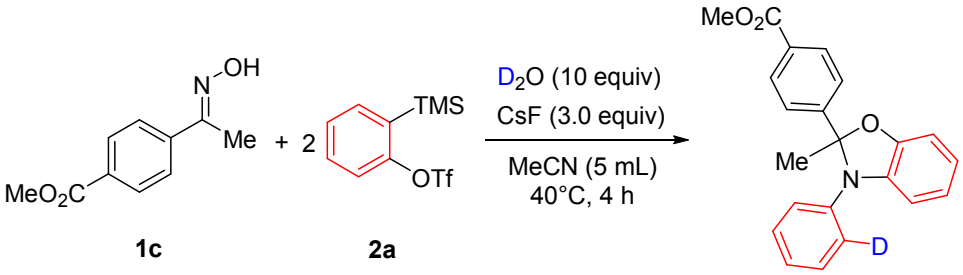
3u'

Methyl 4-(7-methoxy-3-(3-methoxyphenyl)-2-methyl-2,3-dihydrobenzo [*d*]oxazol-2-yl)benzoate (3u'). This product was obtained as a colorless oil (0.0839 g, 83%): ^{1}H NMR (400 MHz, DMSO) δ 7.93 (d, *J* = 8.6 Hz, 2H), 7.64 (d, *J* = 8.6 Hz, 2H), 7.28 (t, *J* = 8.2 Hz, 1H), 7.12 (t, *J* = 8.4 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 6.64 – 6.58 (m, 2H), 6.38 (m, 2H), 3.84 (s, 3H), 3.63 (s, 3H), 3.59 (s, 3H), 1.69 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 166.0, 159.4, 155.5, 155.1, 148.8, 147.4, 130.7, 129.5, 129.0, 128.5, 127.6, 119.2, 110.6, 109.3, 105.5, 104.4, 100.3, 73.4, 55.6, 54.9, 52.1, 21.0; IR (neat) 1716, 1597, 1492, 1371, 1284 cm^{-1}; HRMS calcd for $C_{24}H_{24}NO_5^+$: (M^++H): 406.1649, found 406.1655.

Scaling up experiment of 3a'

To a solution of ketoxime **1a** (0.149 g, 1 mmol, 1.0 equiv) and silylaryl triflate **2a** (0.656 g, 2.2 mmol, 2.2 equiv) in acetonitrile (25 mL) was added CsF (0.456 g, 3.0 mmol, 3.0 equiv). The resulting mixture was stirred at 80 °C for 1 h. The reaction mixture was diluted with dichloromethane (40 mL), washed with water (1 x 20mL) and brine (1 x 20 mL), dried ($MgSO_4$) and filtered. Solvent was removed under reduced pressure and the residue was recrystallized (EtOAc/petroleum ether) to afford **3a'** as a white solid (0.187 g, 62%).

Deuterated reaction



1c **2a**

70% D incorporation

To a solution of ketoxime **1c** (0.0386 g, 0.2 mmol, 1.0 equiv), silylaryl triflate **2a** (0.131 g, 0.44 mmol, 2.2 equiv) and deuterium oxide (0.040 g, 2mmol, 10 equiv) in acetonitrile (5 mL) was added CsF (0.091 g, 0.6 mmol, 3.0 equiv). The resulting mixture was stirred at 40 °C for 5 h. The reaction mixture was diluted with dichloromethane (20 mL), washed with water (1 x 10 mL) and brine (1 x 10 mL), dried ($MgSO_4$) and filtered. Solvent was removed under reduced pressure and the residue was purified by chromatography (partially deactivated Silica Gel) using 100:1 hexane/triethylamine as the eluent. This product was obtained as a white solid (0.0348 g, 50%). ^{1}H NMR (400 MHz, DMSO) δ 7.98 (d, J = 8.5 Hz, 2H), 7.68 (d, J = 8.5 Hz, 2H), 7.34 – 7.25 (m, 2H), 7.11 (t, J = 6.9 Hz, 1H), 7.02 (d, J = 8.0 Hz, 1.3H), 6.80 (t, J = 6.7 Hz, 2H), 6.77 – 6.69 (m, 2H), 3.85 (s, 3H), 1.95 (s, 3H).

Reference

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78, 5314-5327.

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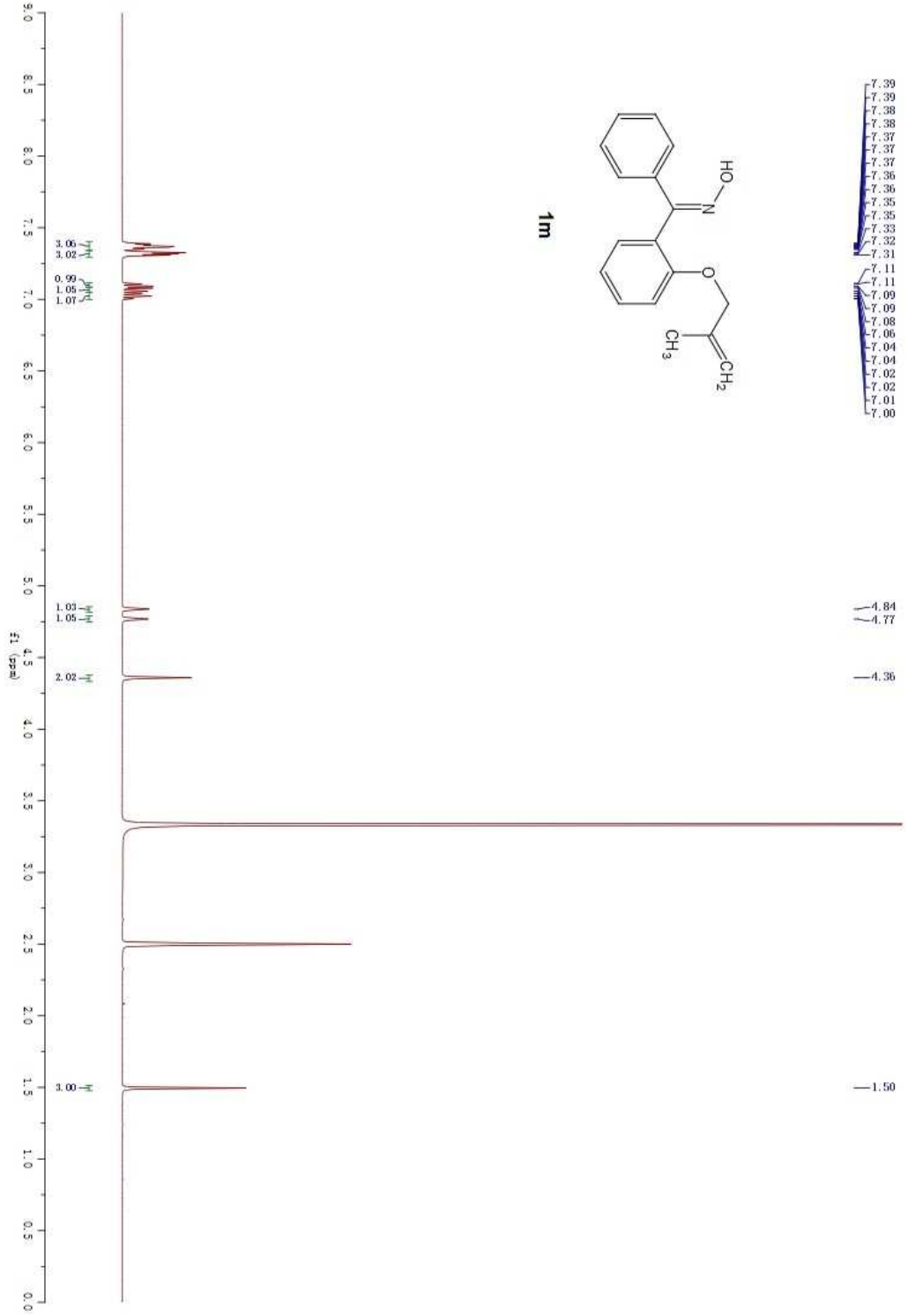
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7.04
7.04
7.02
7.02
7.01
7.00
4.84
4.77
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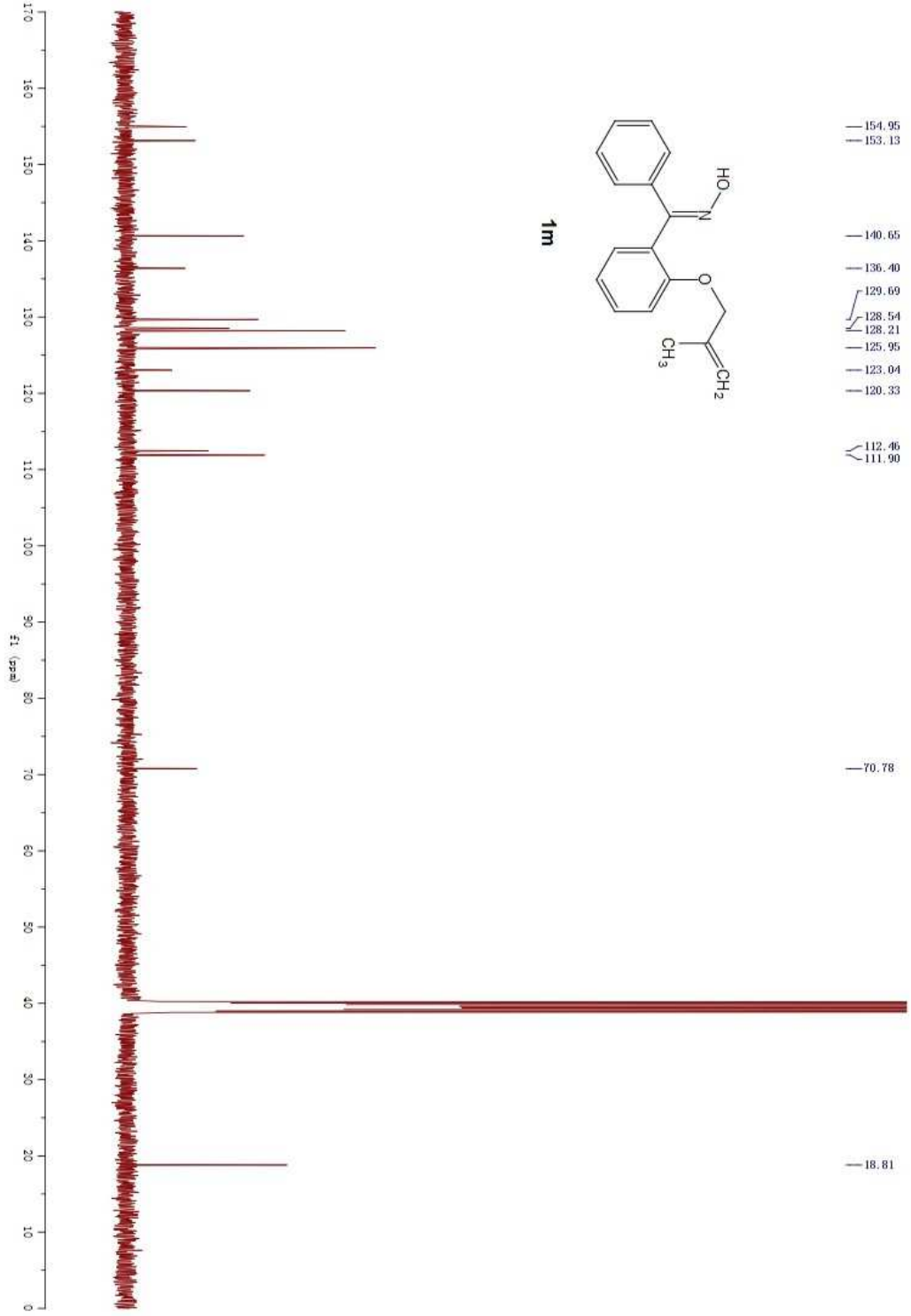
1.05
1.07
1.03
1.05
2.02
3.00
f1 (ppm)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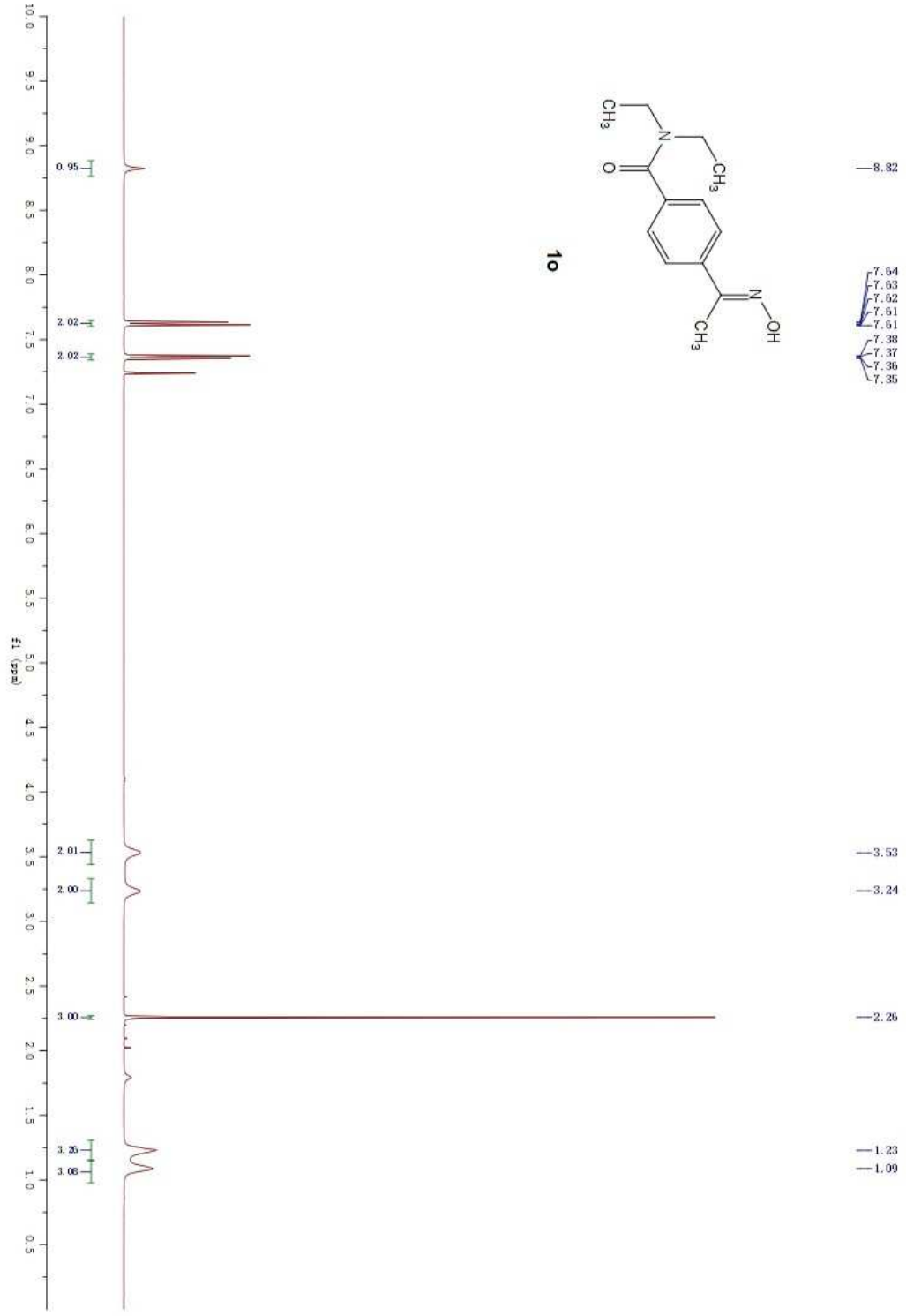
f1 (ppm)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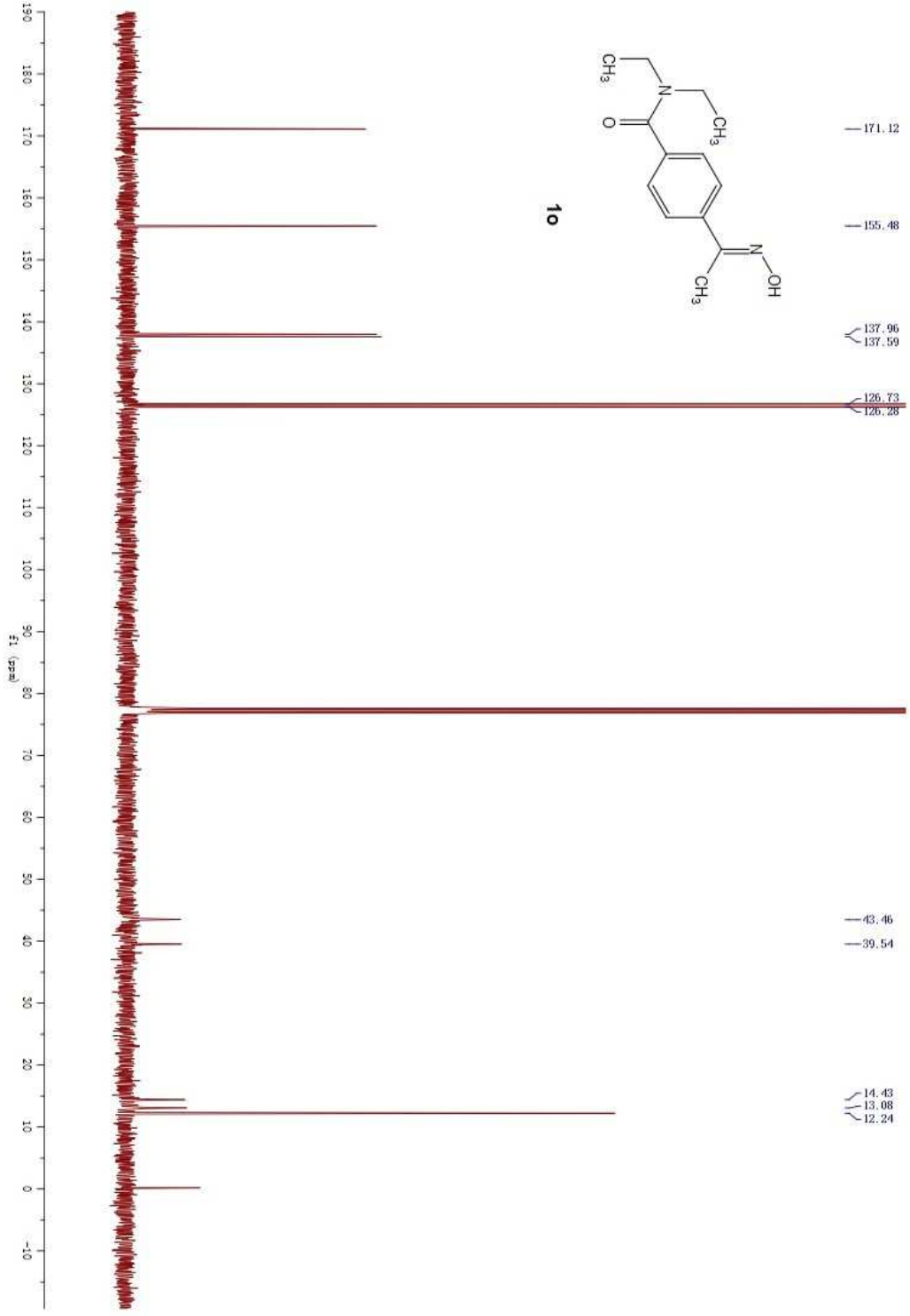
f1 (ppm)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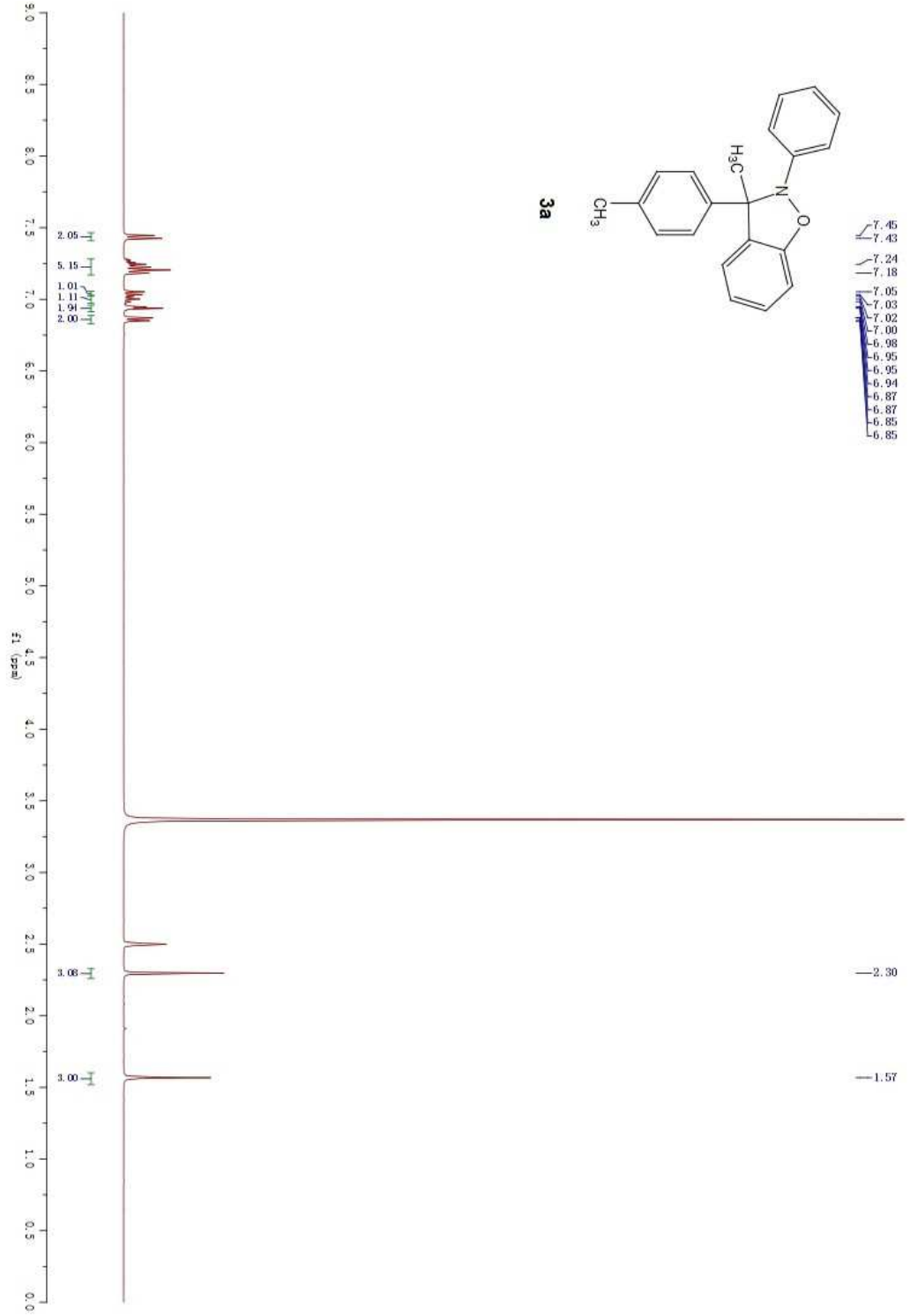
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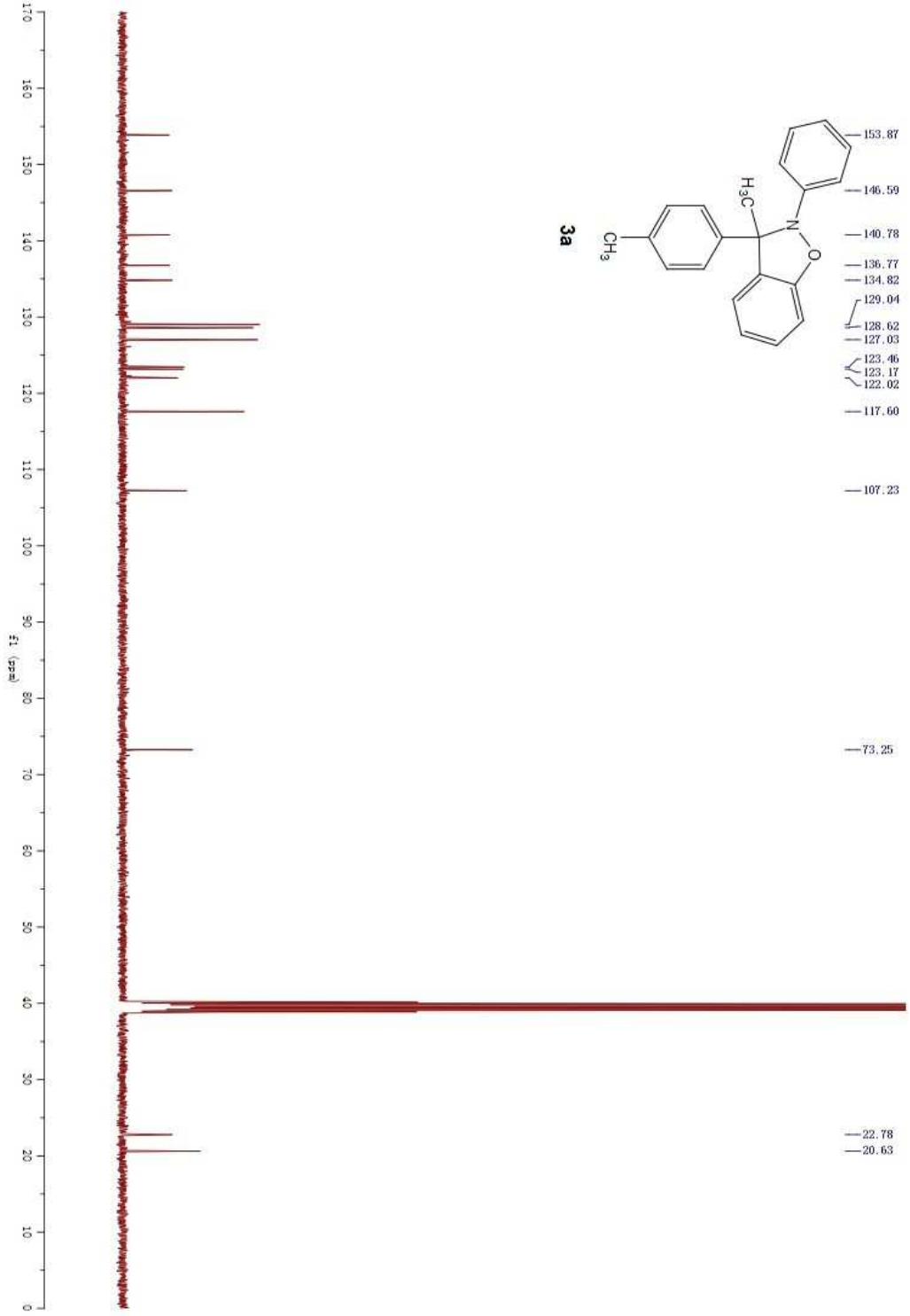
f1 (ppm)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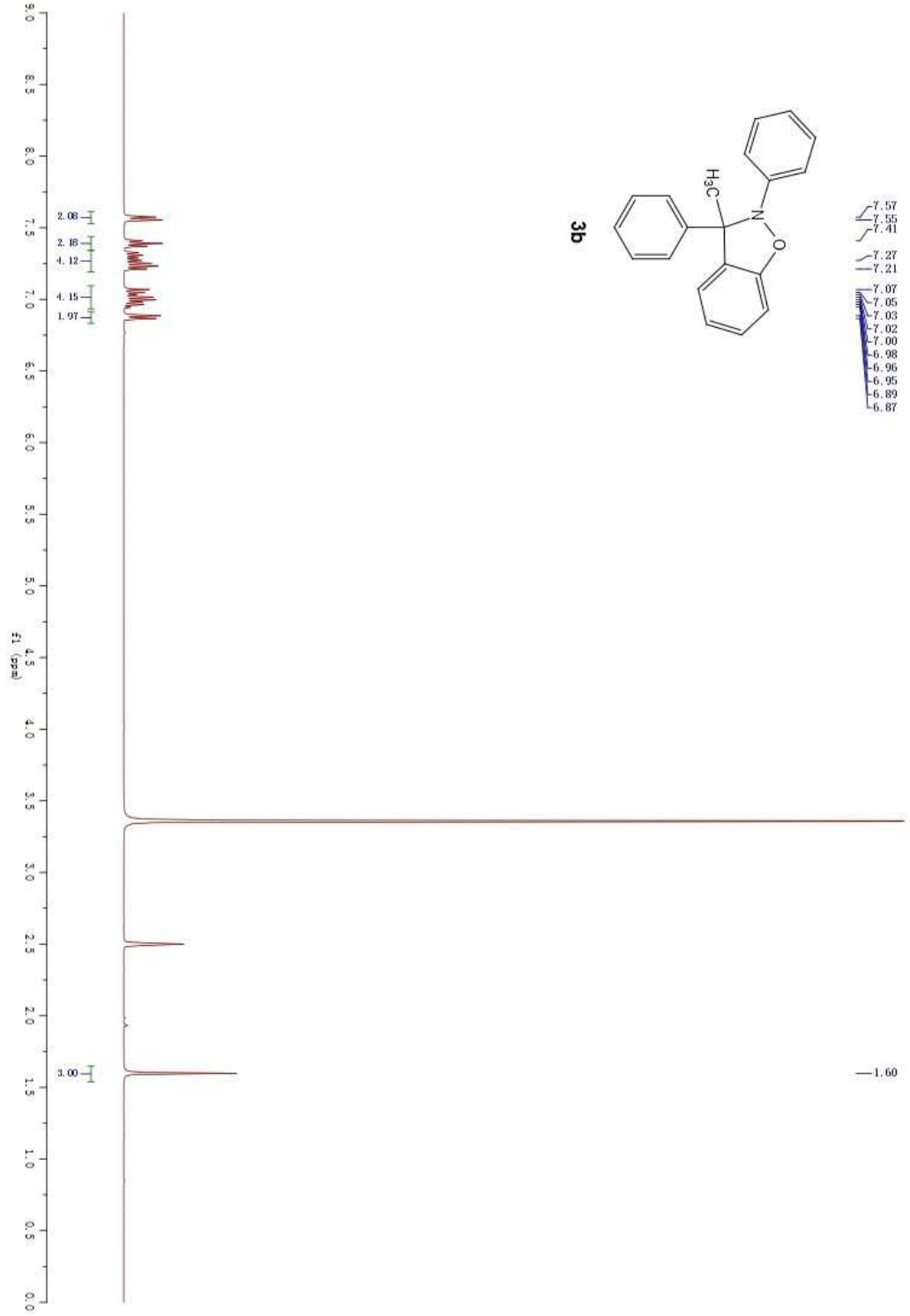
f1 (ppm)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O
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7.03
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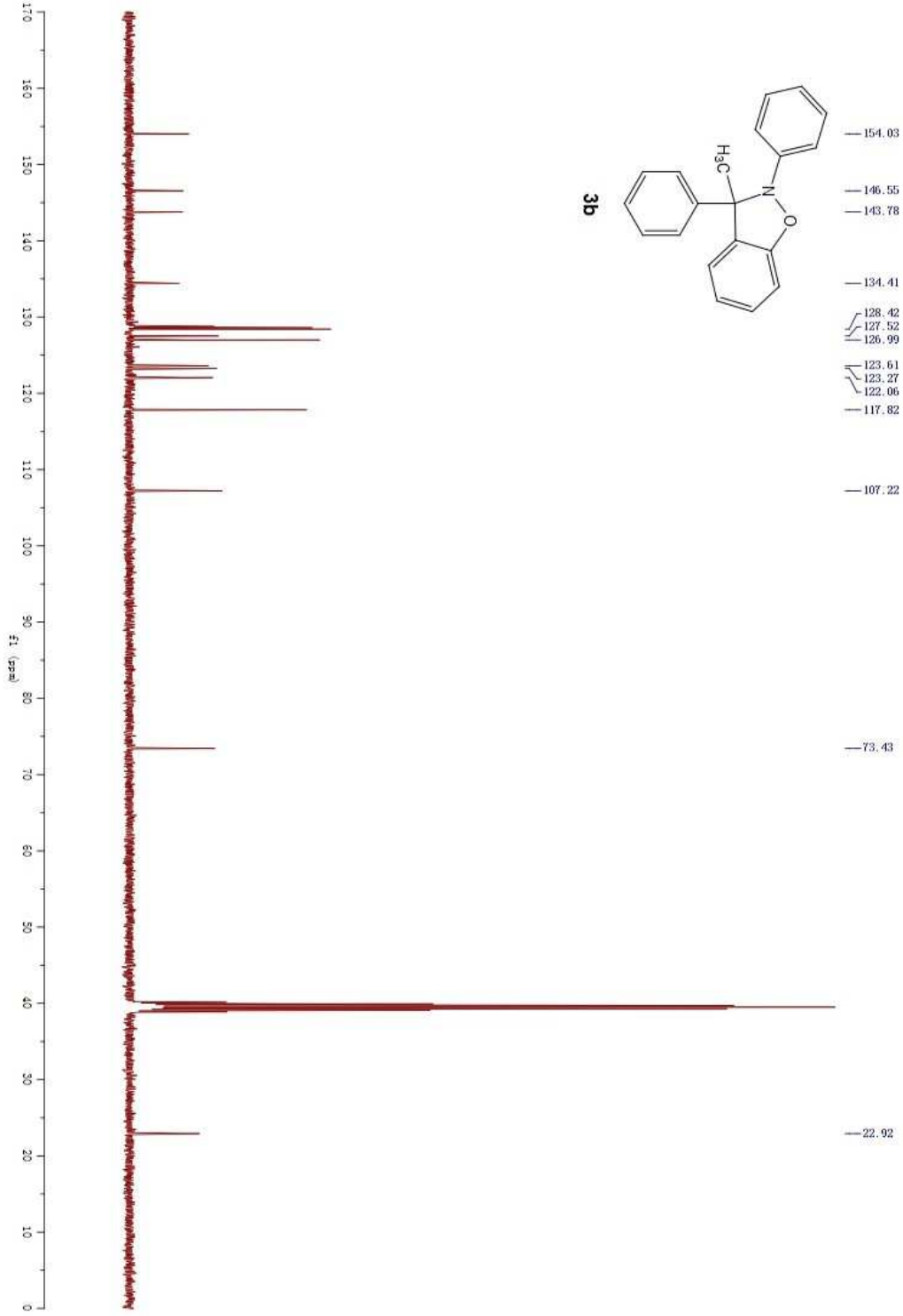
f1 (ppm)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O
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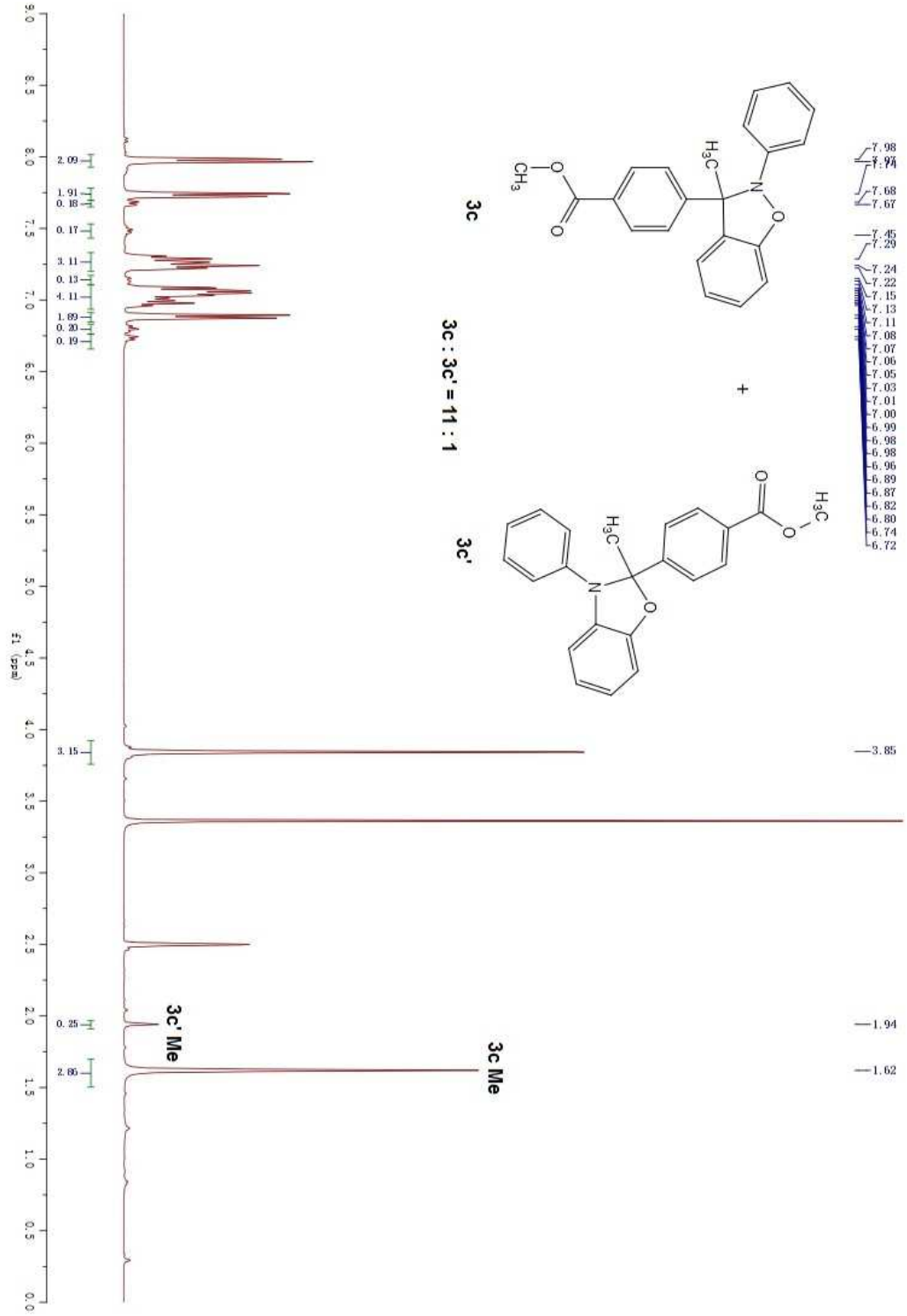
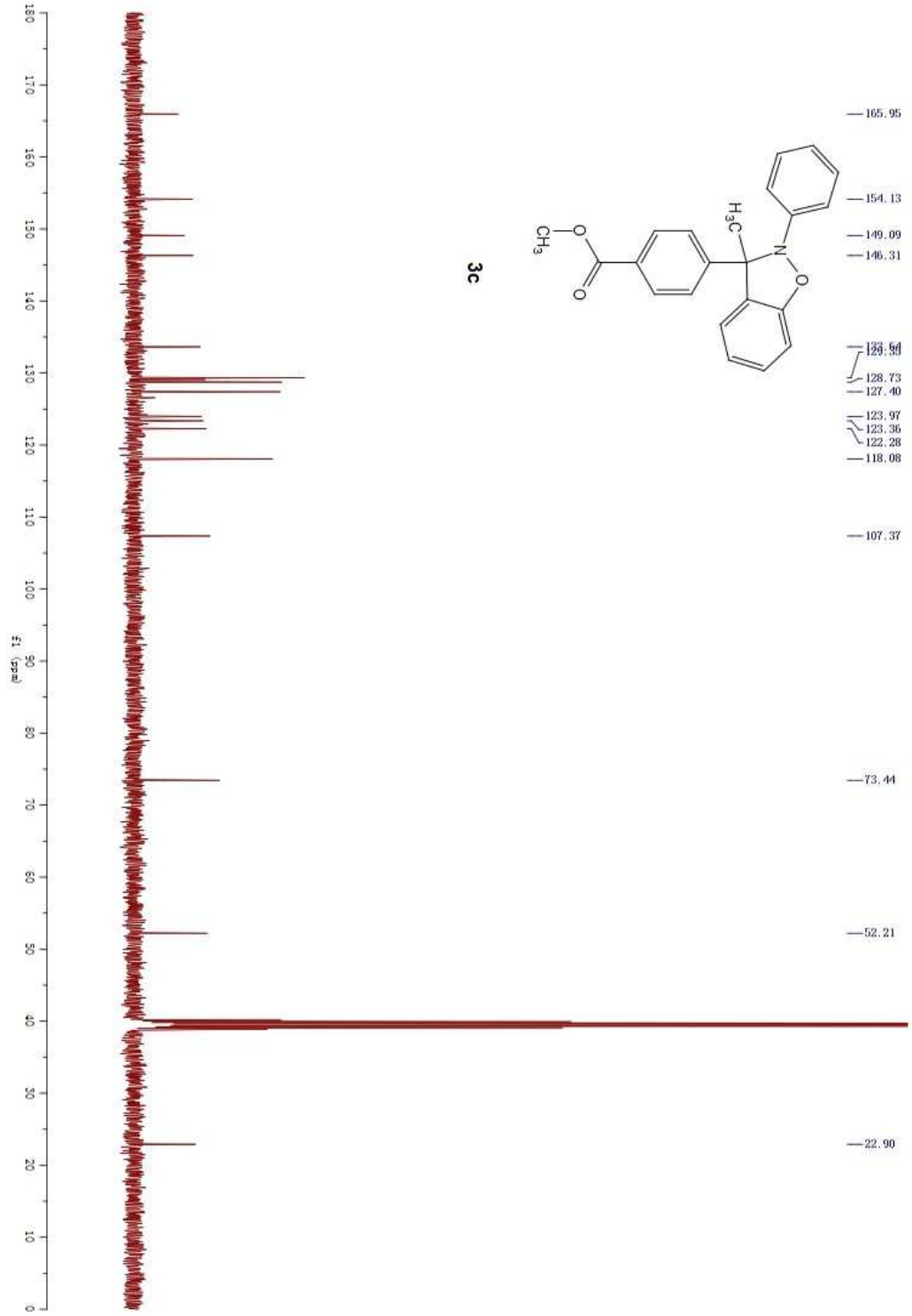

3c
3c : 3c' = 11 : 1
3c'
+
3c' Me
3c Me
f1 (ppm)


3c
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123.97
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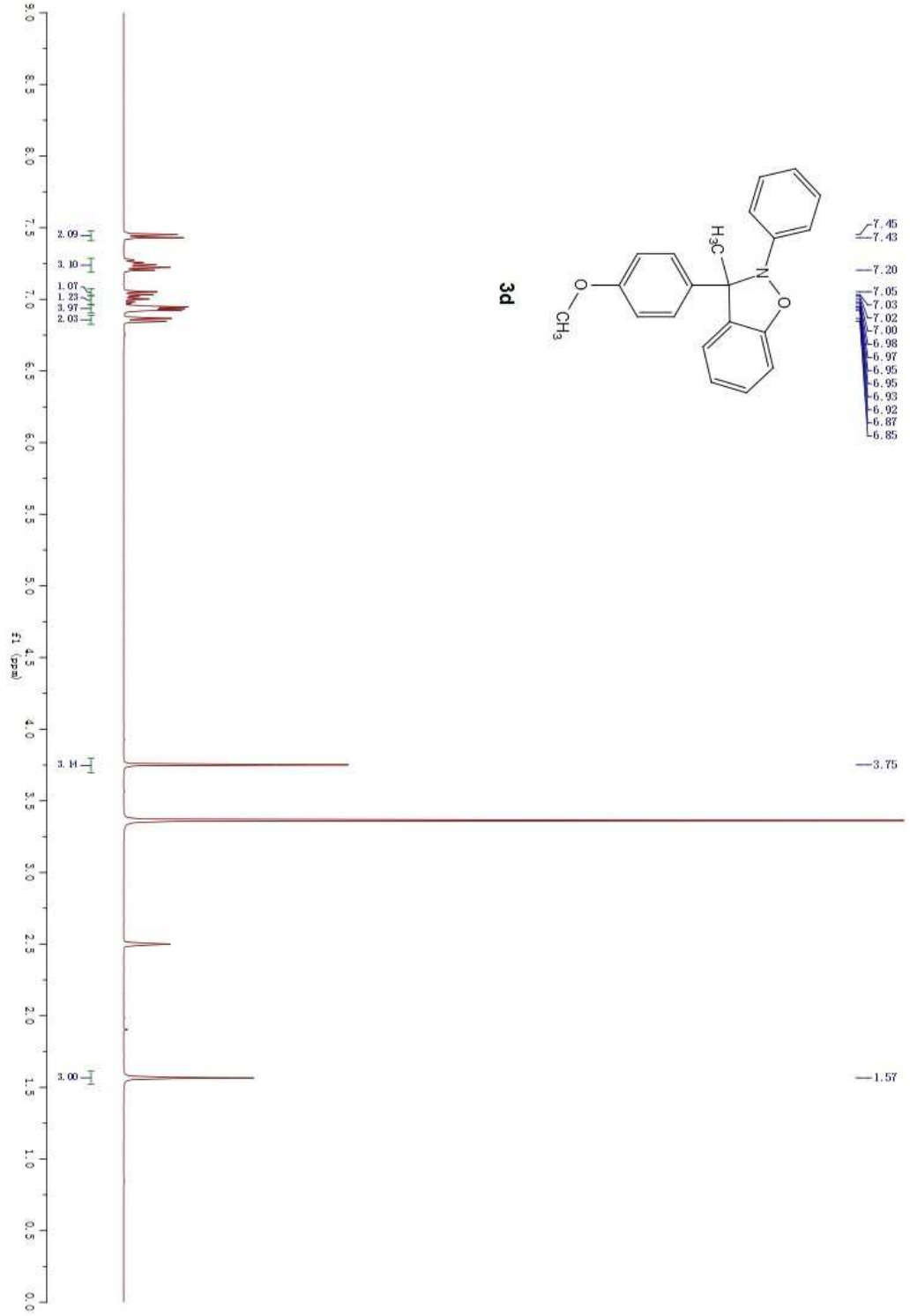
73.44
52.21
22.90
f1 (ppm)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O
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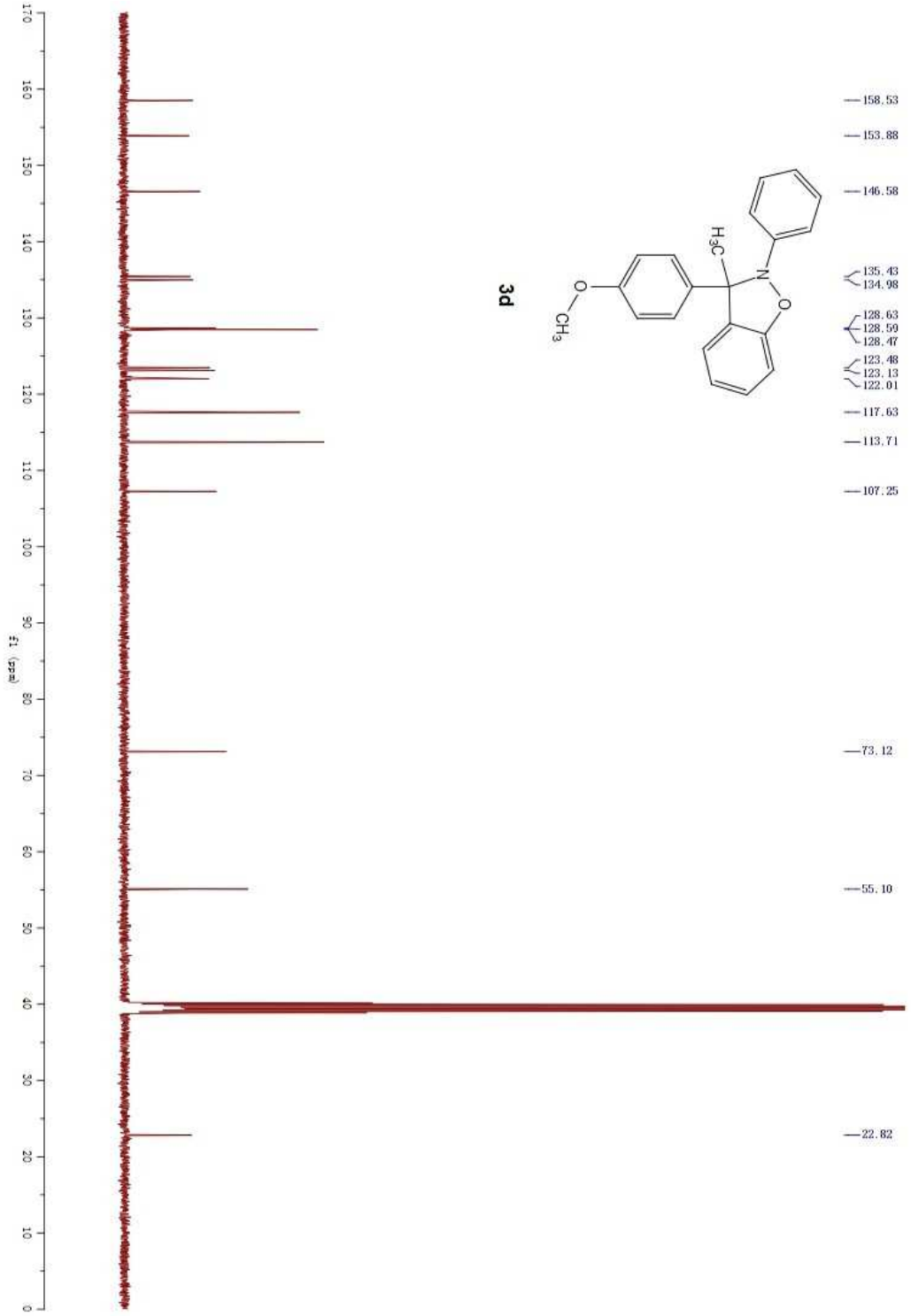
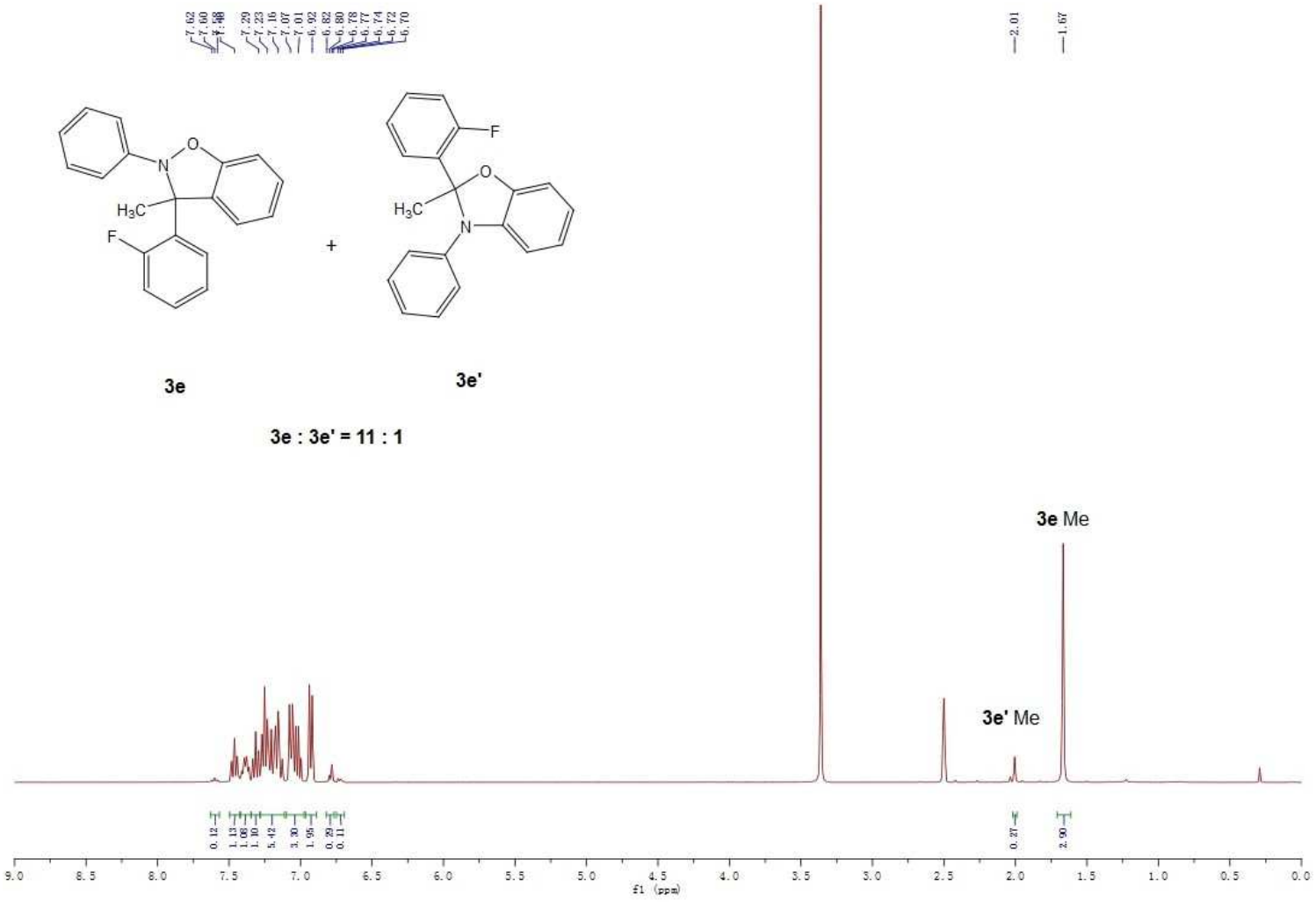
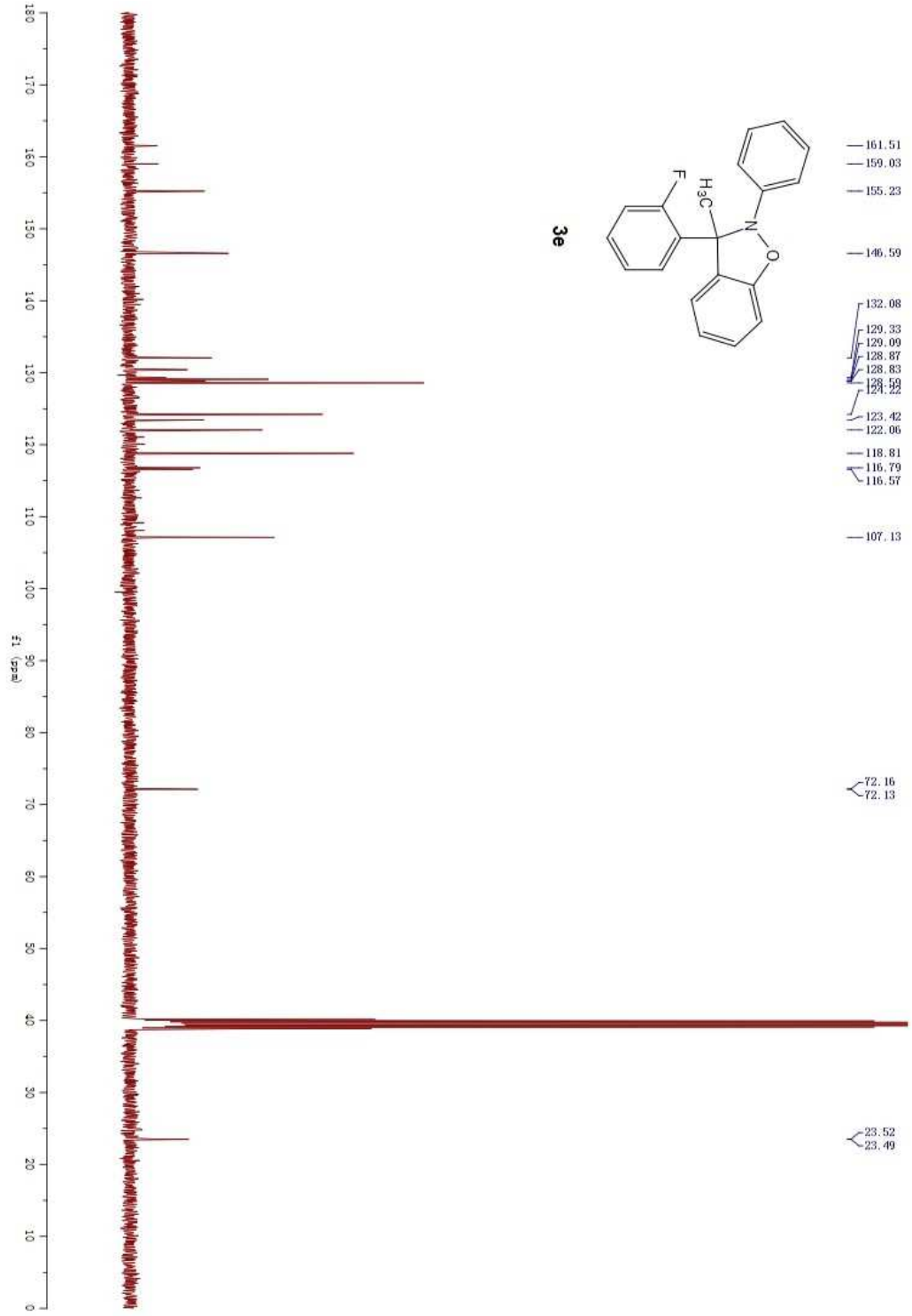
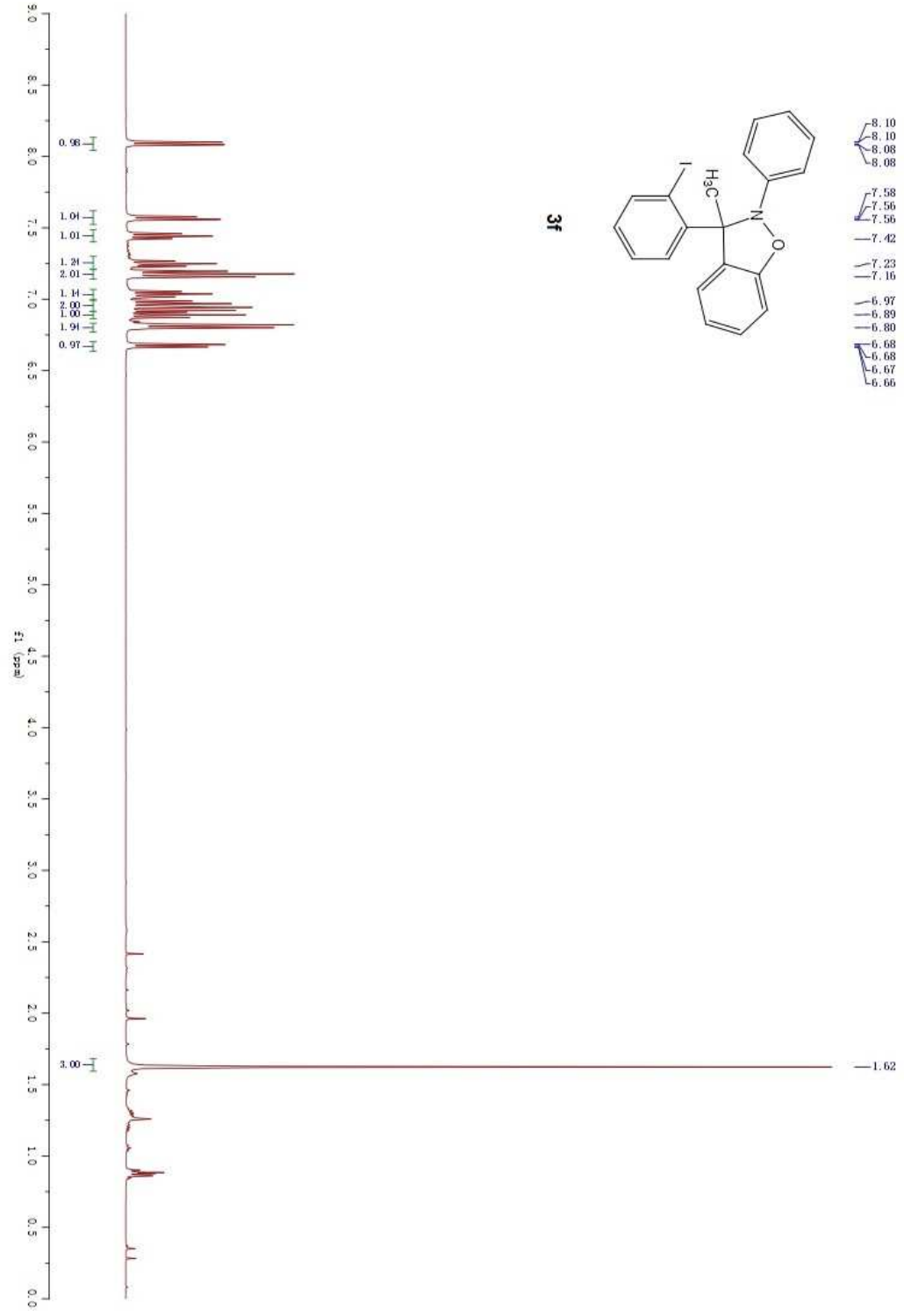
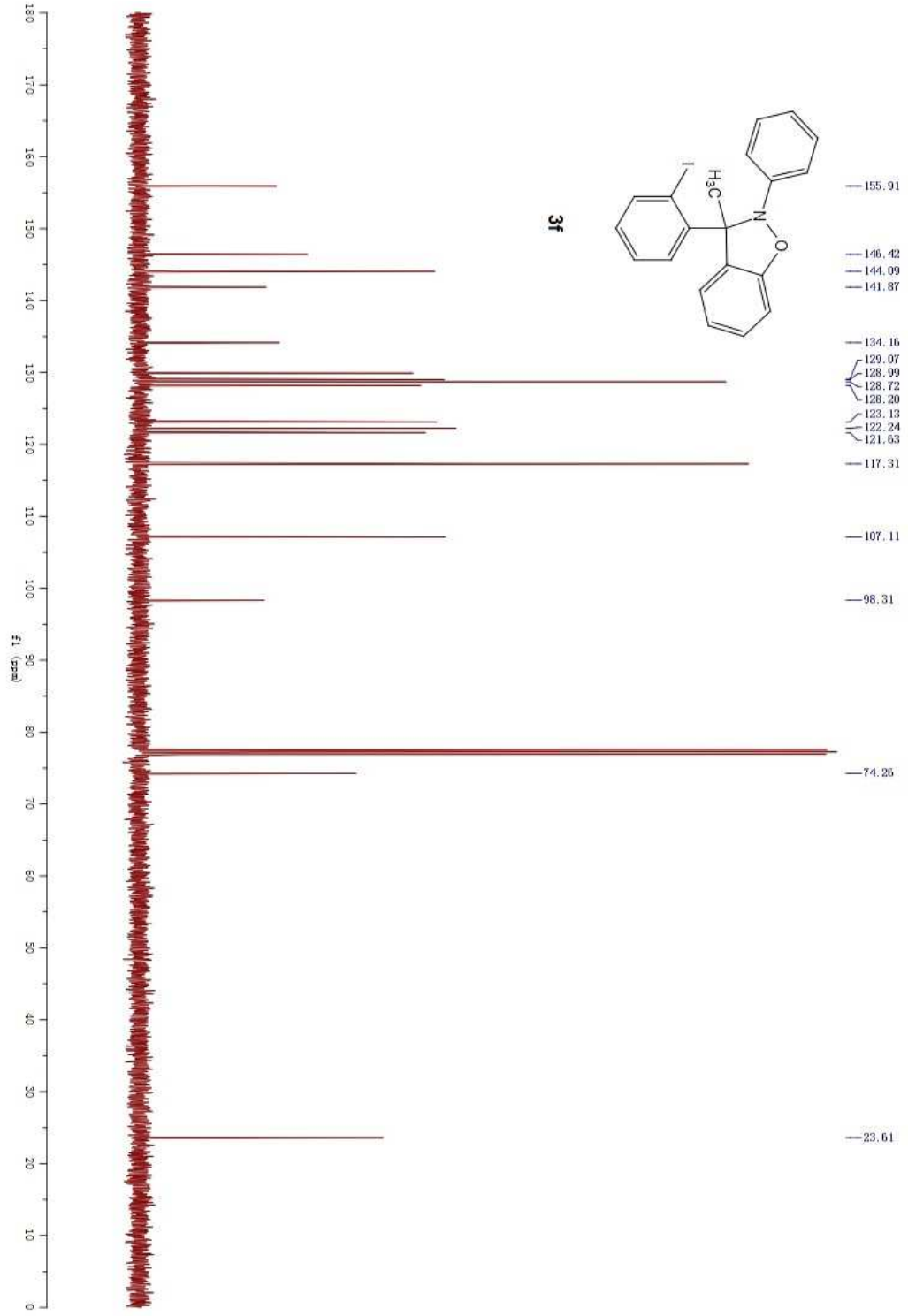
6.93
6.92
6.87
6.85
3.75
1.57
2.09
3.10
1.07
1.23
3.97
2.03
3.14
3.00
f1 (ppm)

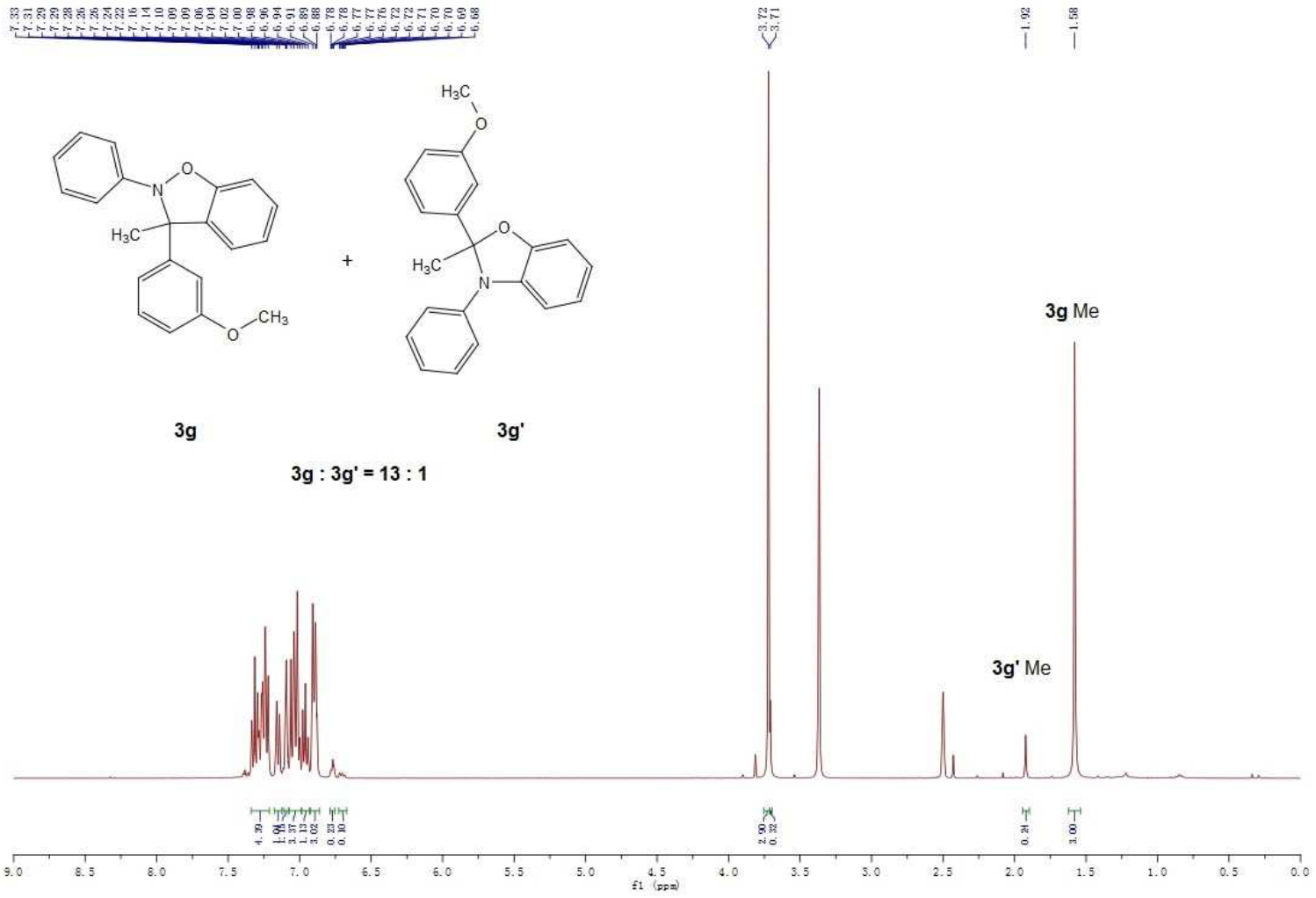

158.53
153.88
146.58
135.43
134.98
128.63
128.59
128.47
123.48
123.13
122.01
117.63
113.71
107.25
73.12
55.10
22.82
3d
f1 (ppm)

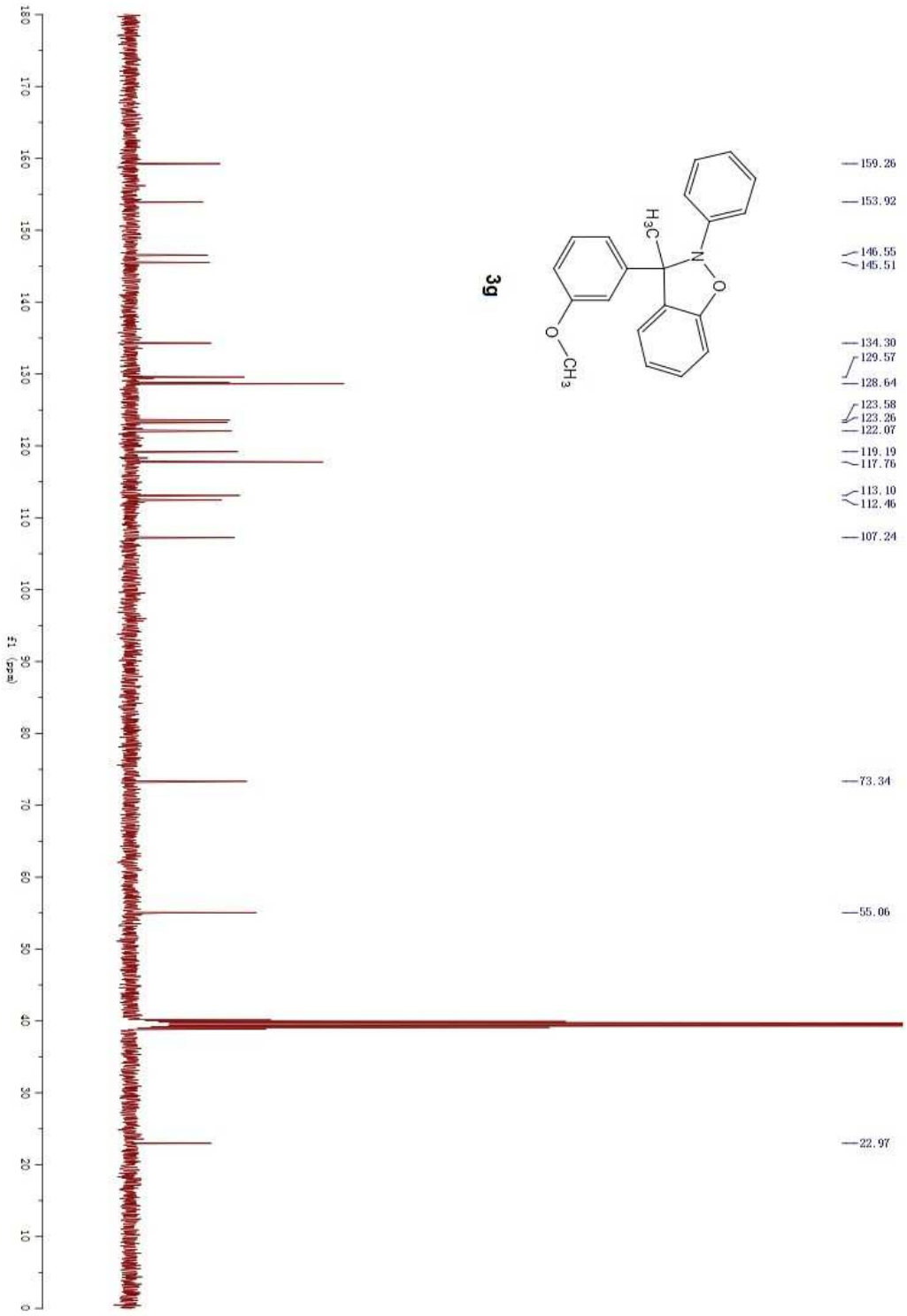

7.62
7.60
7.29
7.23
7.16
7.07
7.01
6.92
6.82
6.80
6.78
6.77
6.74
6.72
6.70
2.01
1.67
O
N
H3C
F
+
F
O
H3C
N
3e
3e'
3e : 3e' = 11 : 1
3e Me
3e' Me
0.12
1.13
1.06
1.10
5.42
3.30
1.95
0.29
0.11
0.27
2.90
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

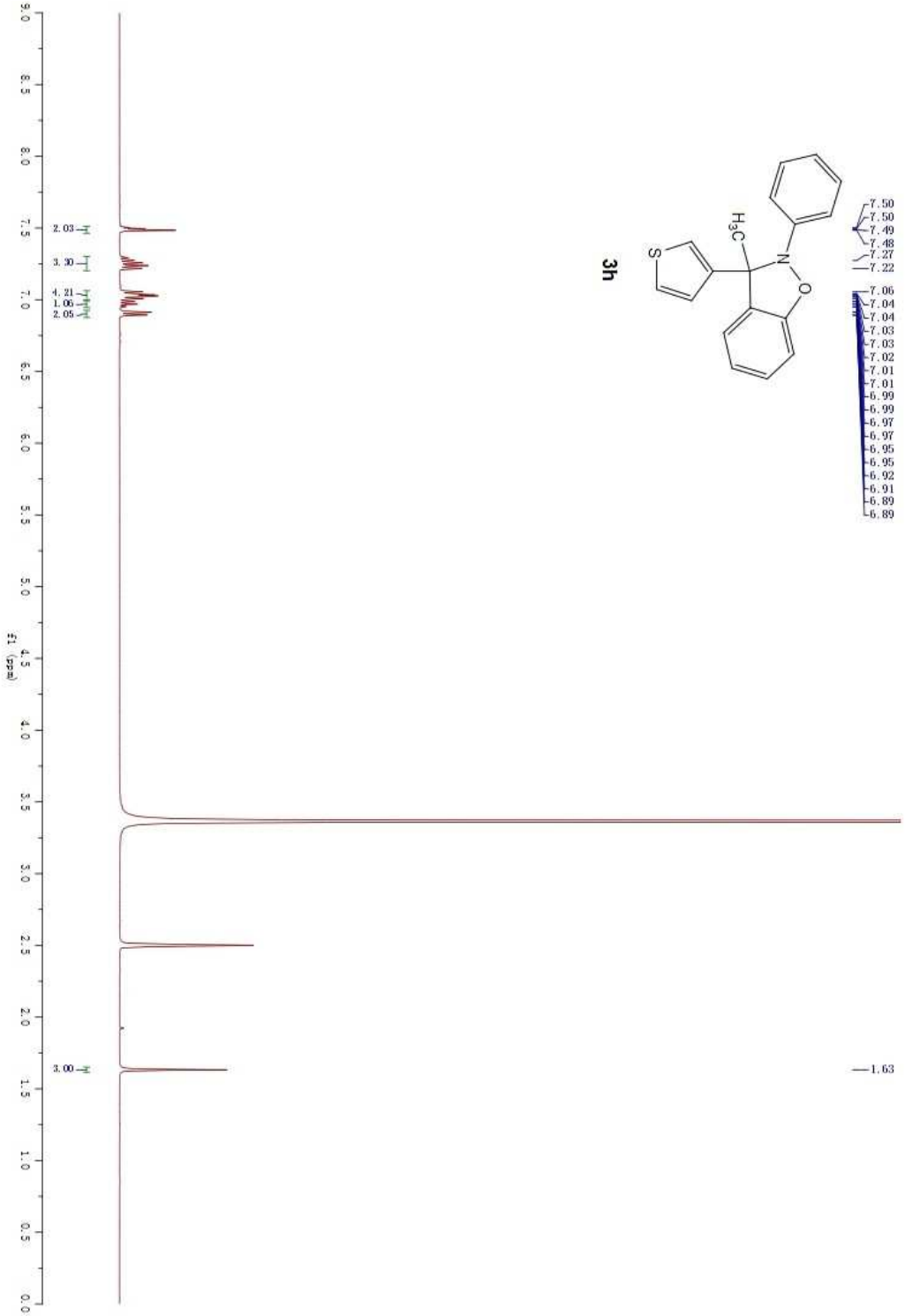

3e
F
H3C
N
O
161.51
159.03
155.23
146.59
132.08
129.33
129.09
128.87
128.83
128.59
124.22
123.42
122.06
118.81
116.79
116.57
107.13
72.16
72.13
23.52
23.49
f1 (ppm)

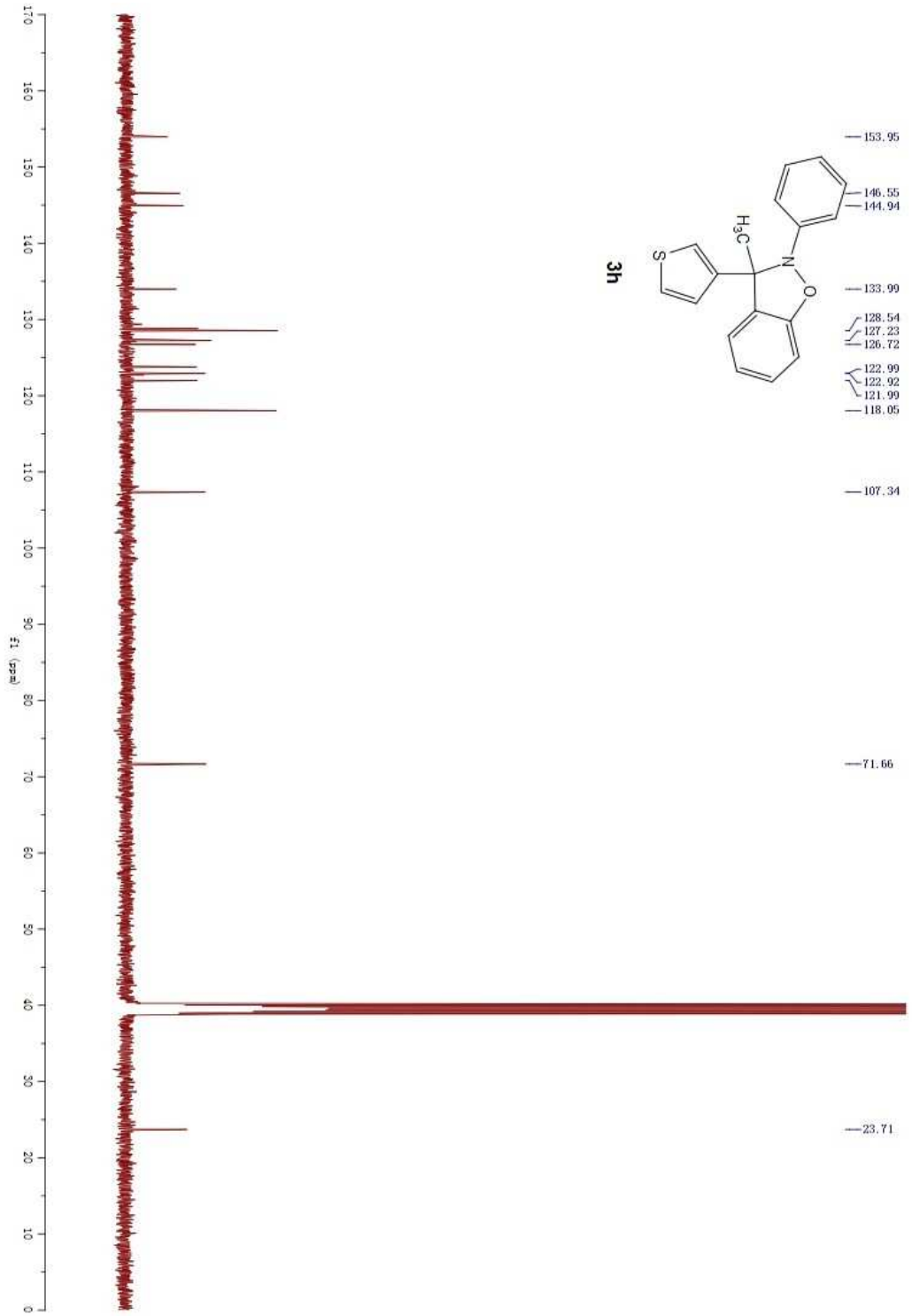

3f
I
H3C
N
O
8.10
8.10
8.08
8.08
7.58
7.56
7.56
7.42
7.23
7.16
6.97
6.89
6.80
6.68
6.68
6.67
6.66
1.62
0.98
1.04
1.01
1.24
2.01
1.14
2.00
1.00
1.94
0.97
3.00
f1 (ppm)

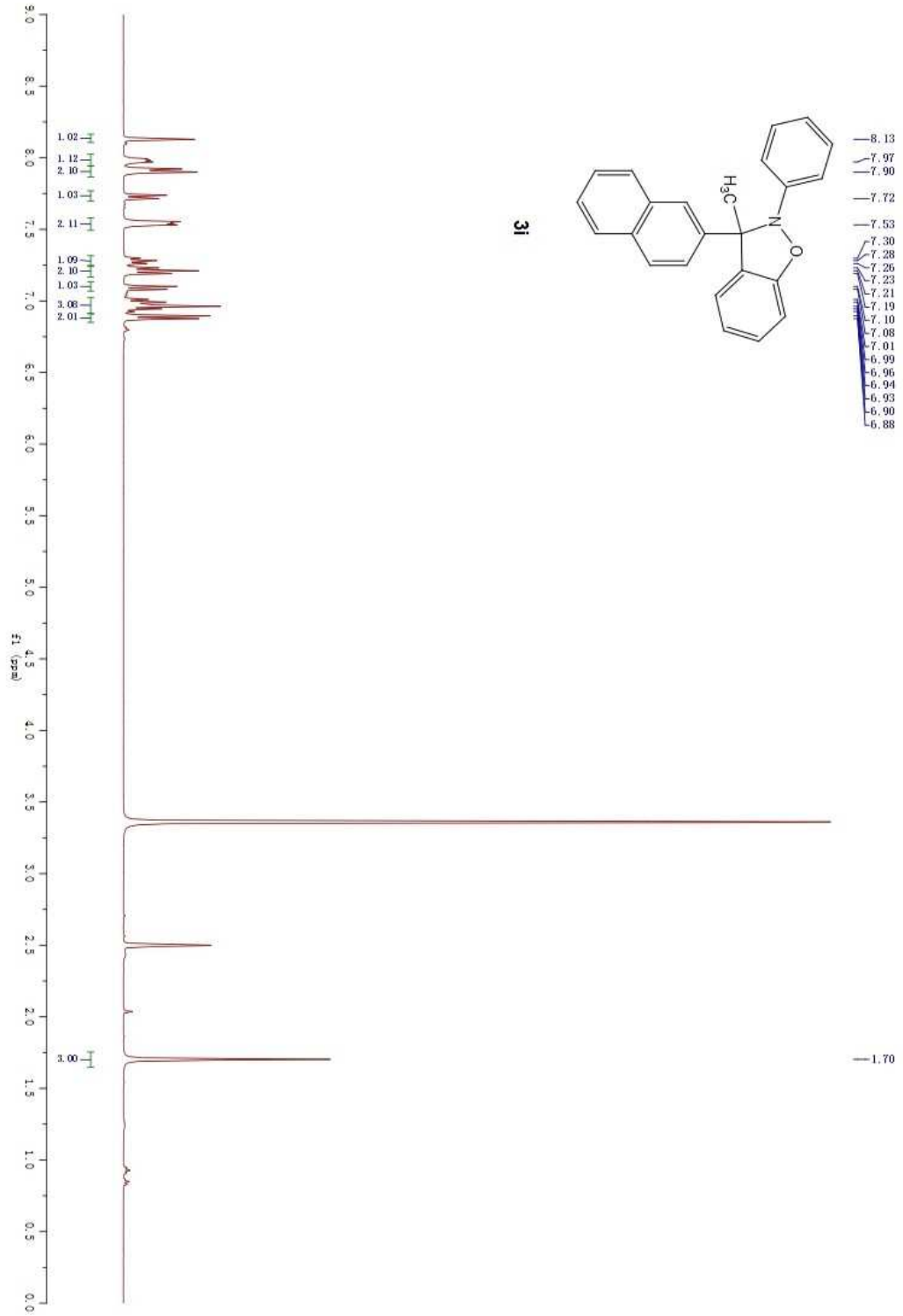

3f
I
H3C
N
O
155.91
146.42
144.09
141.87
134.16
129.07
128.99
128.72
128.20
123.13
122.24
121.63
117.31
107.11
98.31
74.26
23.61
f1 (ppm)

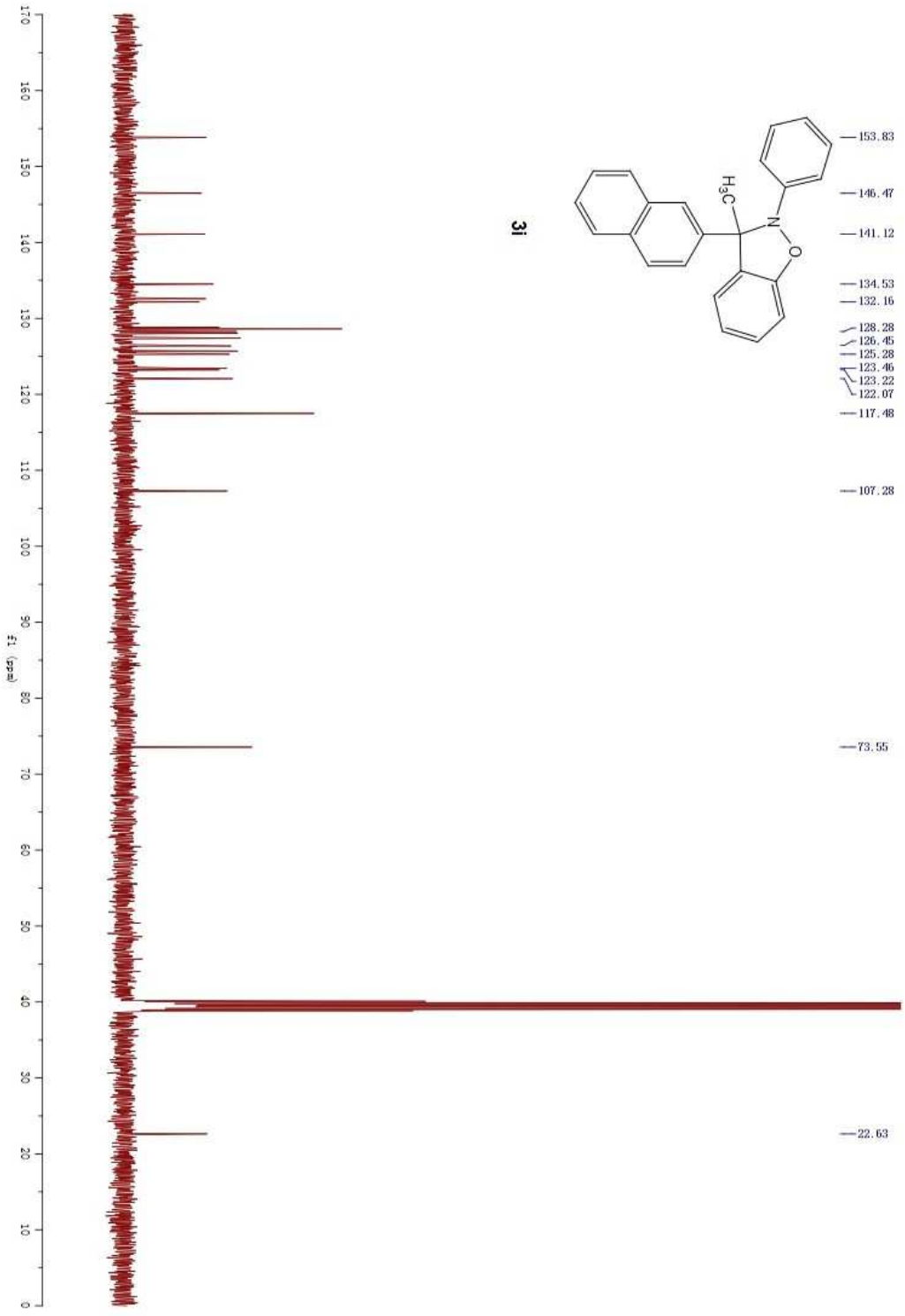

3g
3g'
3g : 3g' = 13 : 1
3g Me
3g' Me
f1 (ppm)

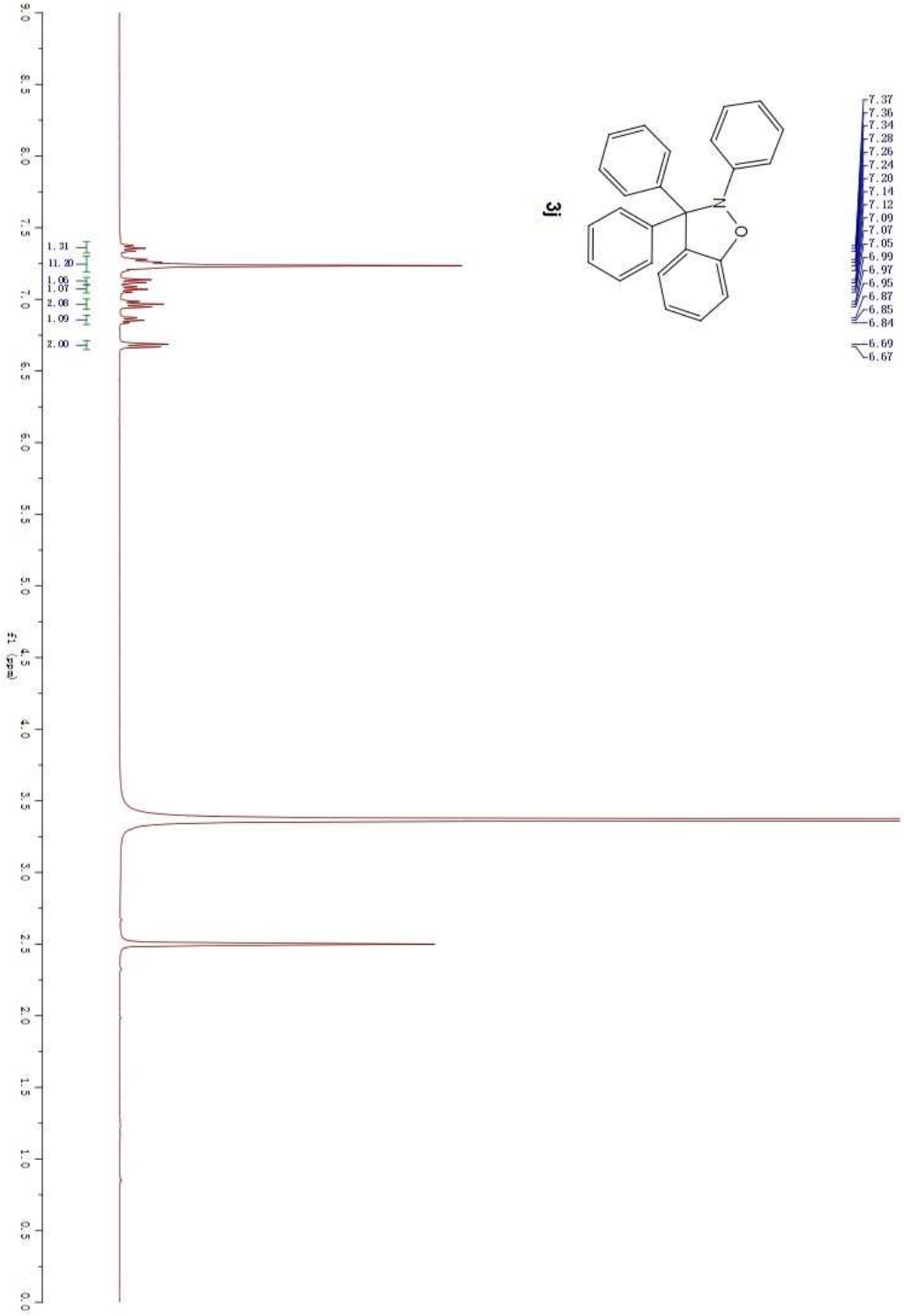

3g
H3C
O
CH3
N
O
159.26
153.92
146.55
145.51
134.30
129.57
128.64
123.58
123.26
122.07
119.19
117.76
113.10
112.46
107.24
73.34
55.06
22.97
f1 (ppm)

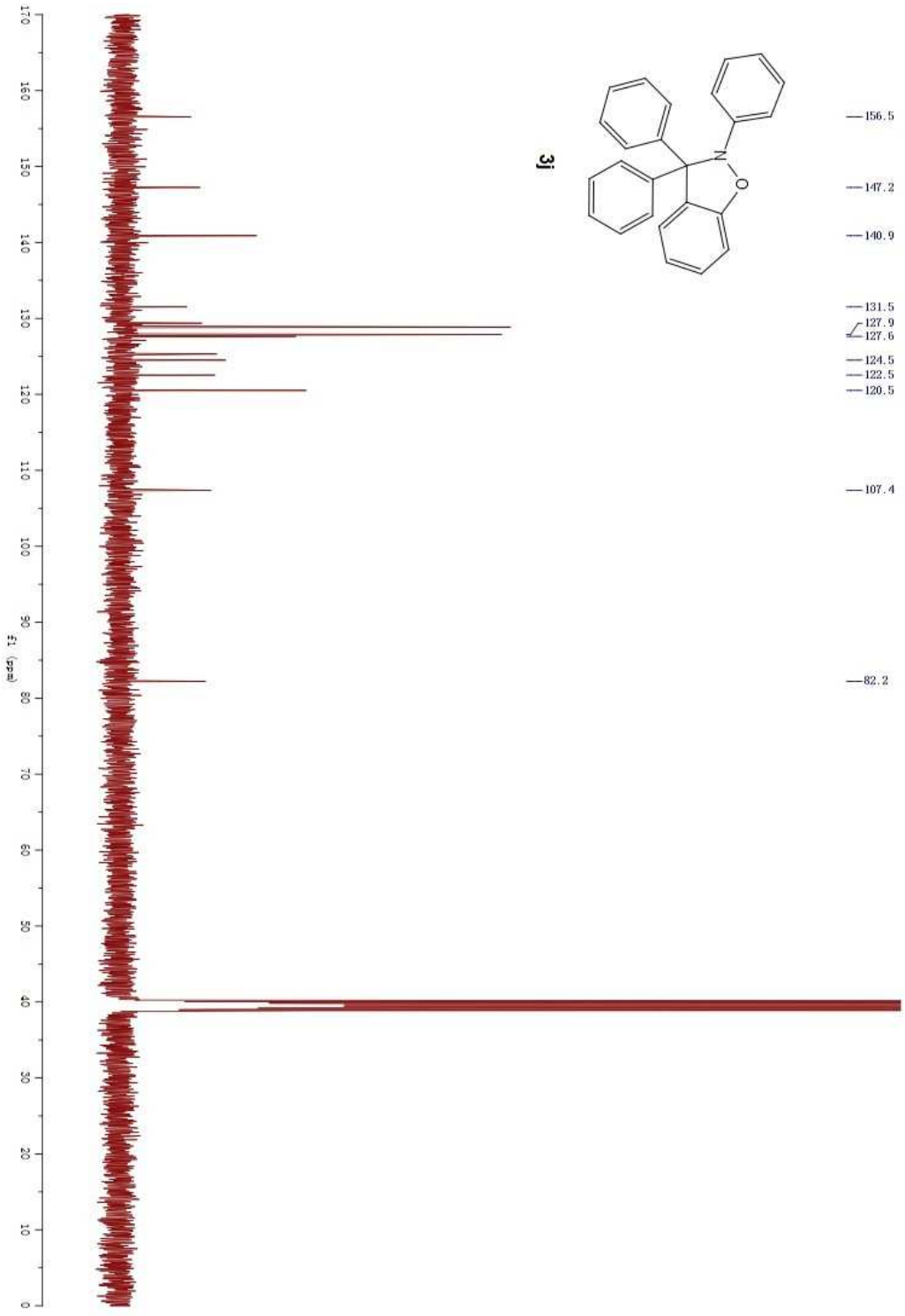

3h
H3C
S
N
O
7.50
7.50
7.49
7.48
7.27
7.22
7.06
7.04
7.04
7.03
7.03
7.02
7.01
7.01
6.99
6.99
6.97
6.97
6.95
6.95
6.92
6.91
6.89
6.89
2.03
3.30
4.21
1.06
2.05
3.00
1.63
f1 (ppm)

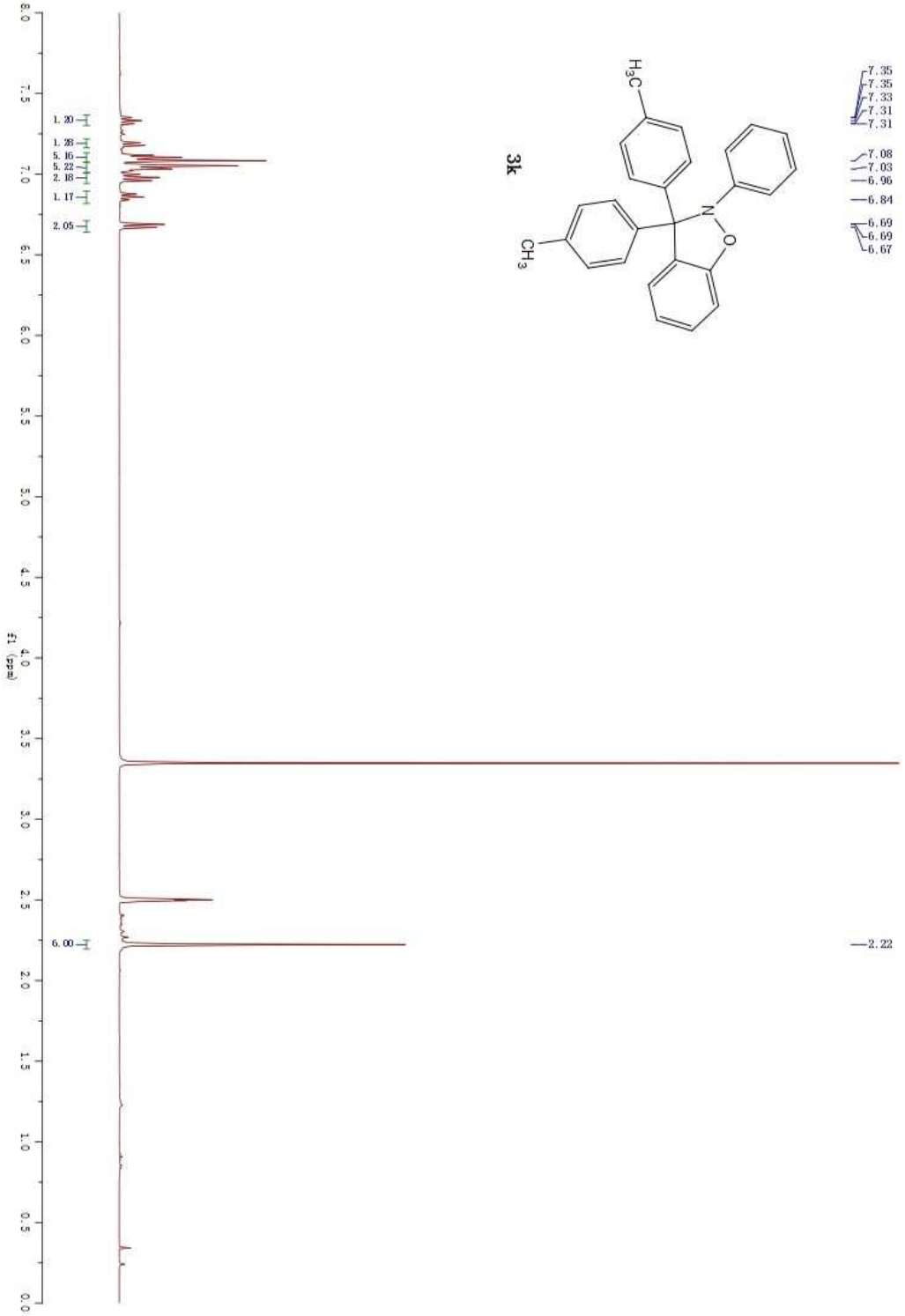

153.95
146.55
144.94
133.99
128.54
127.23
126.72
122.99
122.92
121.99
118.05
107.34
71.66
23.71
3h
H3C
S
N
O
f1 (ppm)

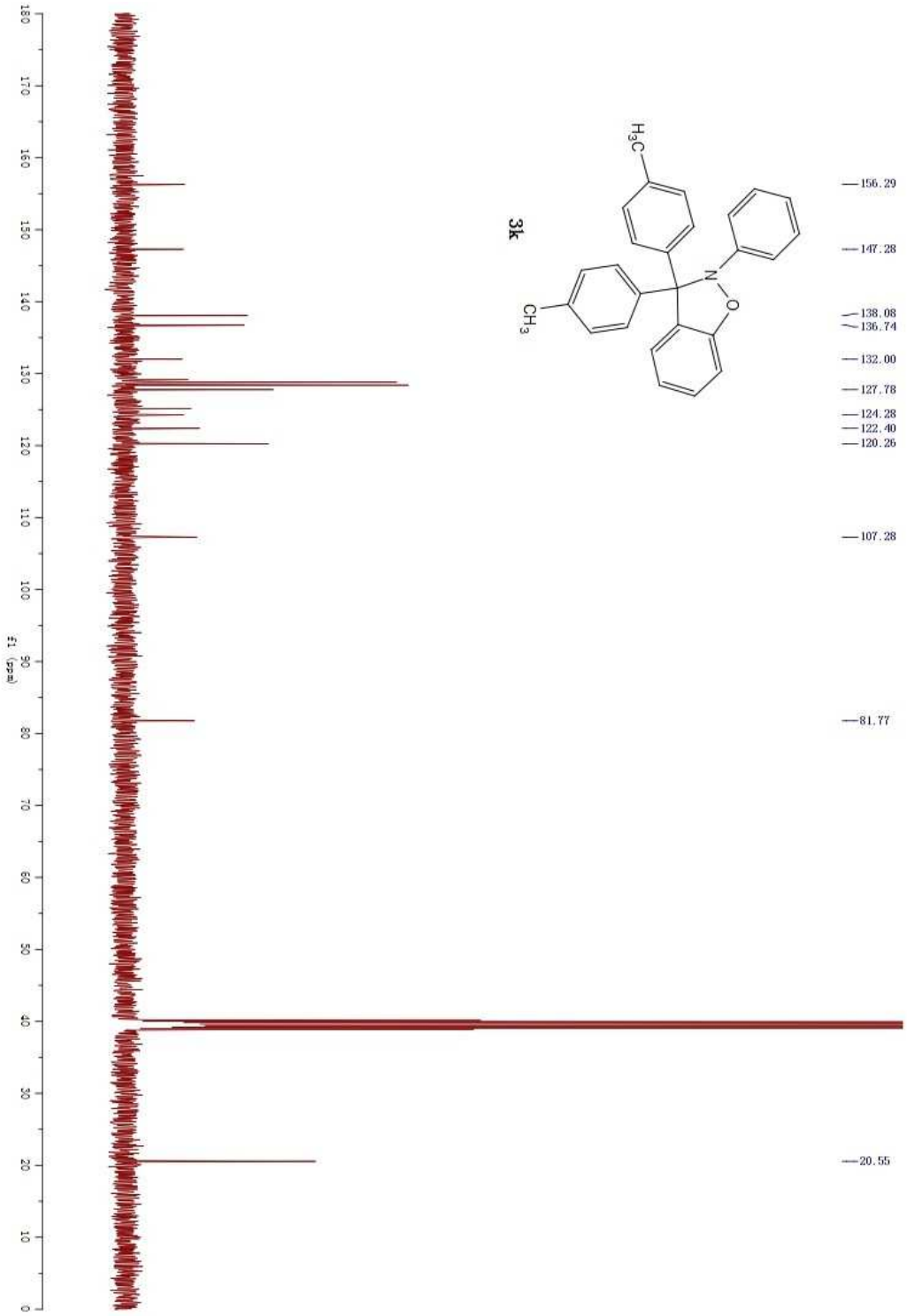

3i
H3C
N
O
8.13
7.97
7.90
7.72
7.53
7.30
7.28
7.26
7.23
7.21
7.19
7.10
7.08
7.01
6.99
6.96
6.94
6.93
6.90
6.88
1.70
1.02
1.12
2.10
1.03
2.11
1.09
2.10
1.03
3.08
2.01
3.00
f1 (ppm)

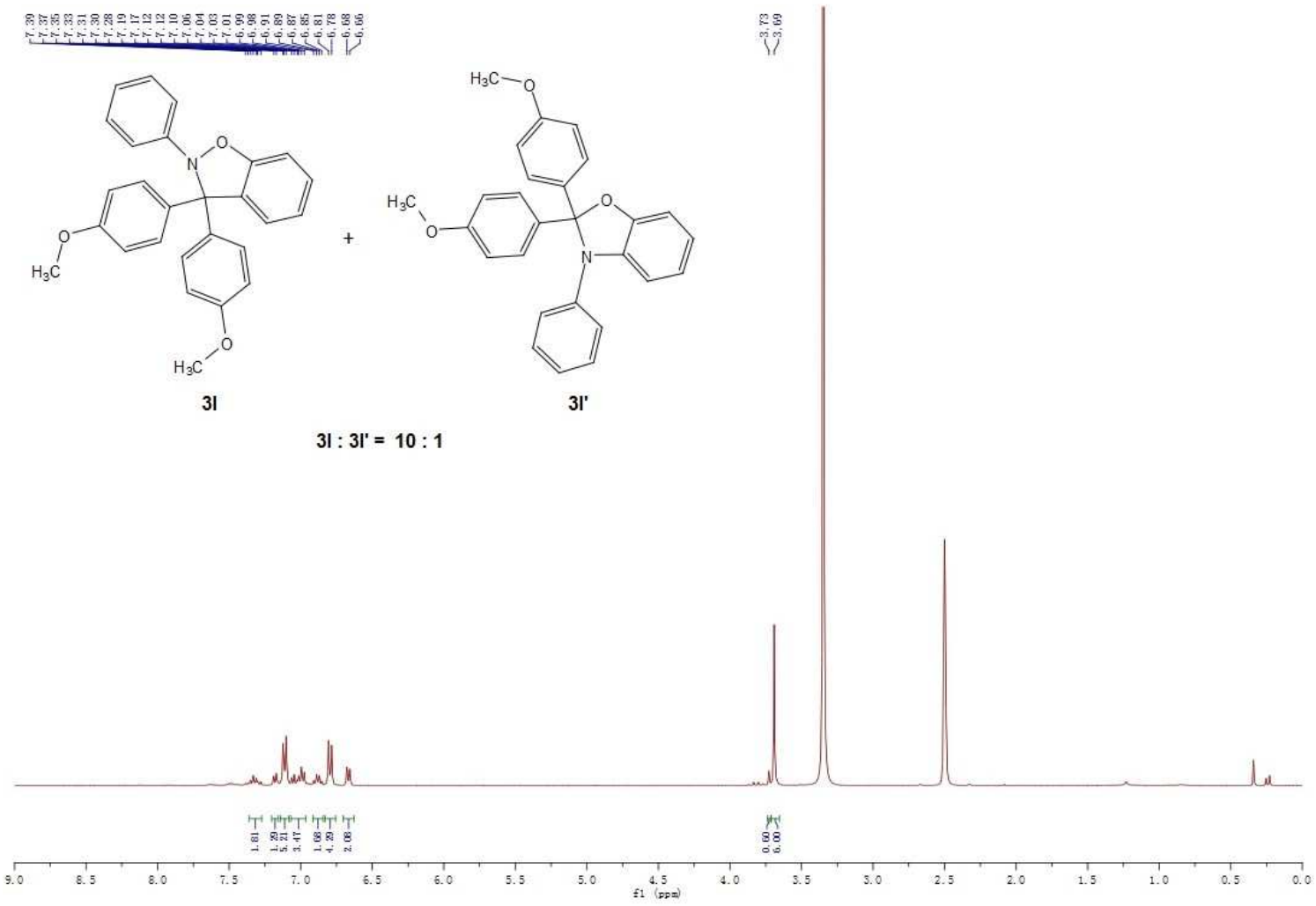

3i
H3C
N
O
153.83
146.47
141.12
134.53
132.16
128.28
126.45
125.28
123.46
123.22
122.07
117.48
107.28
73.55
22.63
f1 (ppm)


3j
7.37
7.36
7.34
7.28
7.26
7.24
7.20
7.14
7.12
7.09
7.07
7.05
6.99
6.97
6.95
6.87
6.85
6.84
6.69
6.67
1.31
11.20
1.06
1.07
2.08
1.09
2.00
f1 (ppm)


3j
156.5
147.2
140.9
131.5
127.9
127.6
124.5
122.5
120.5
107.4
82.2
f1 (ppm)

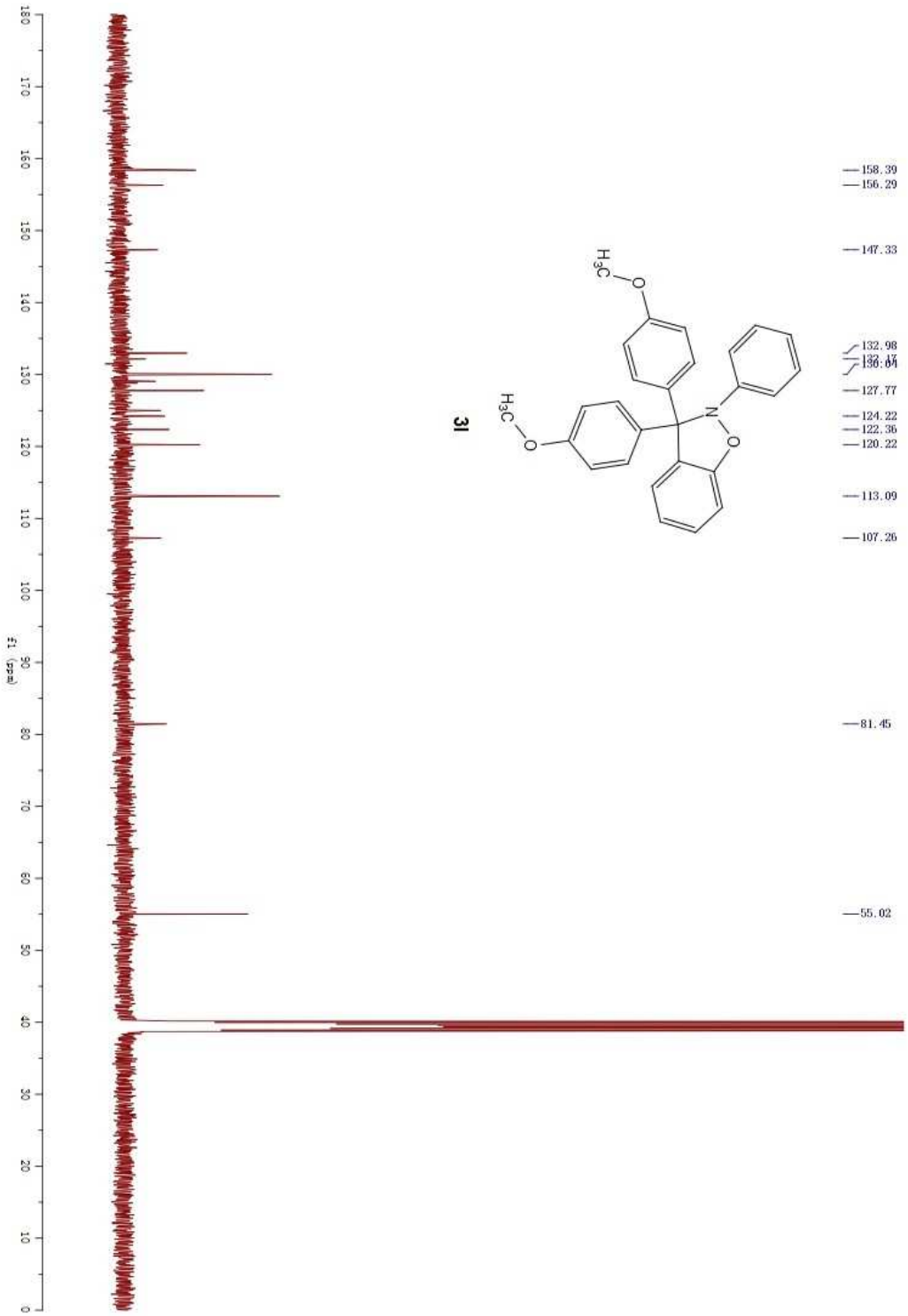

3k
H3C
CH3
N
O
7.35
7.35
7.33
7.31
7.31
7.08
7.03
6.96
6.84
6.69
6.69
6.67
1.20
1.28
5.16
5.22
2.18
1.17
2.05
6.00
2.22
f1 (ppm)

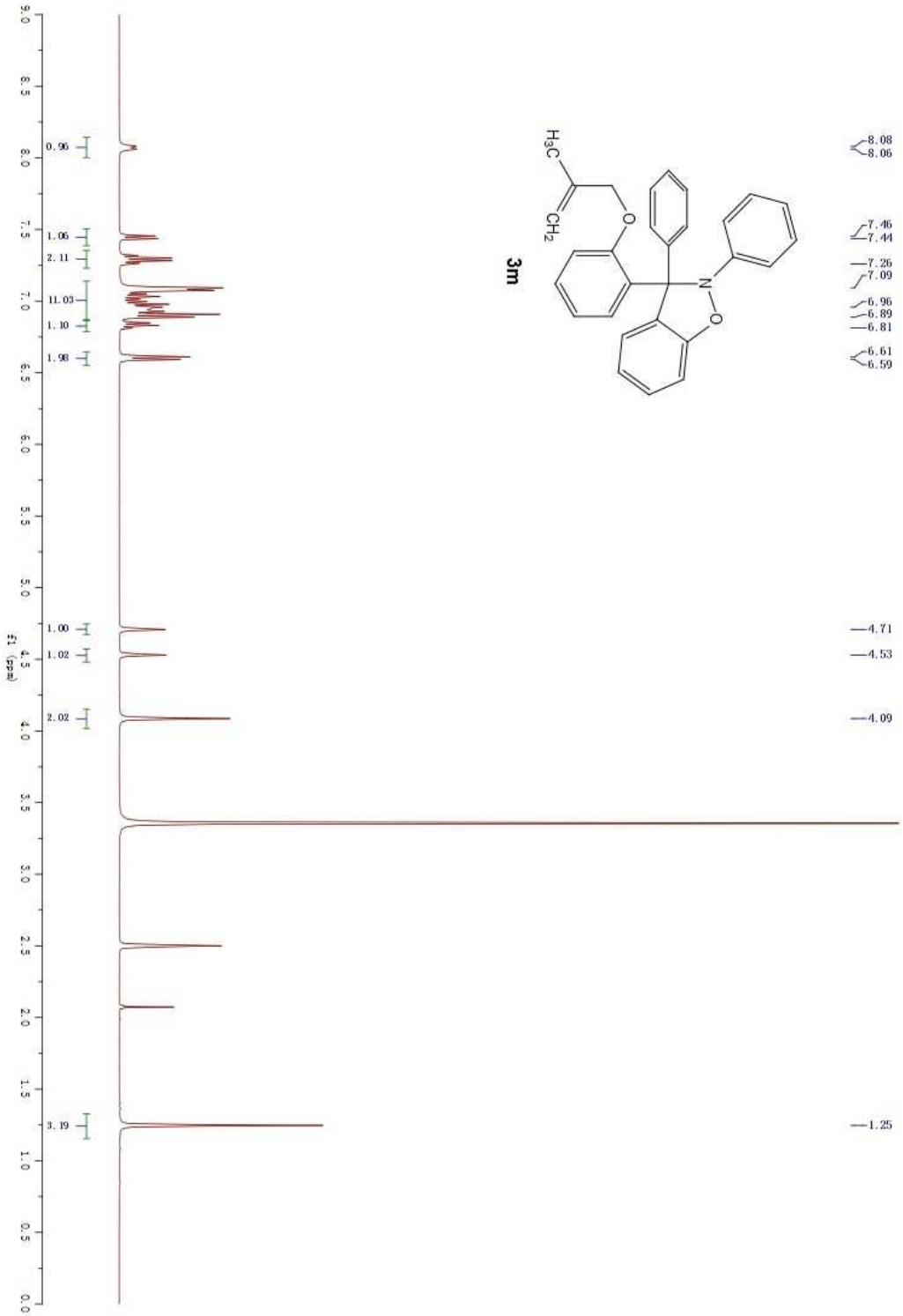

3k
H3C
CH3
N
O
156.29
147.28
138.08
136.74
132.00
127.78
124.28
122.40
120.26
107.28
81.77
20.55
f1 (ppm)

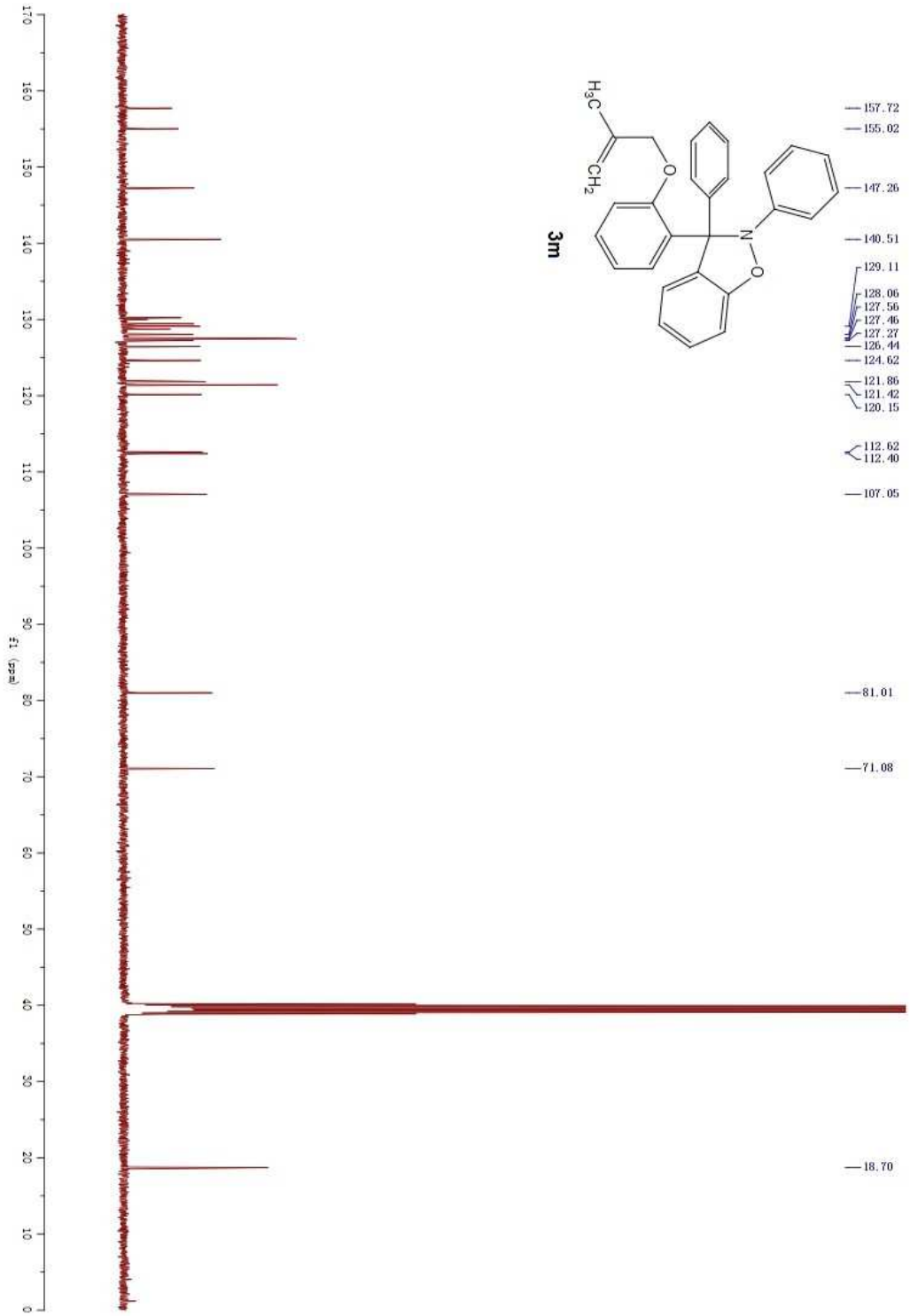


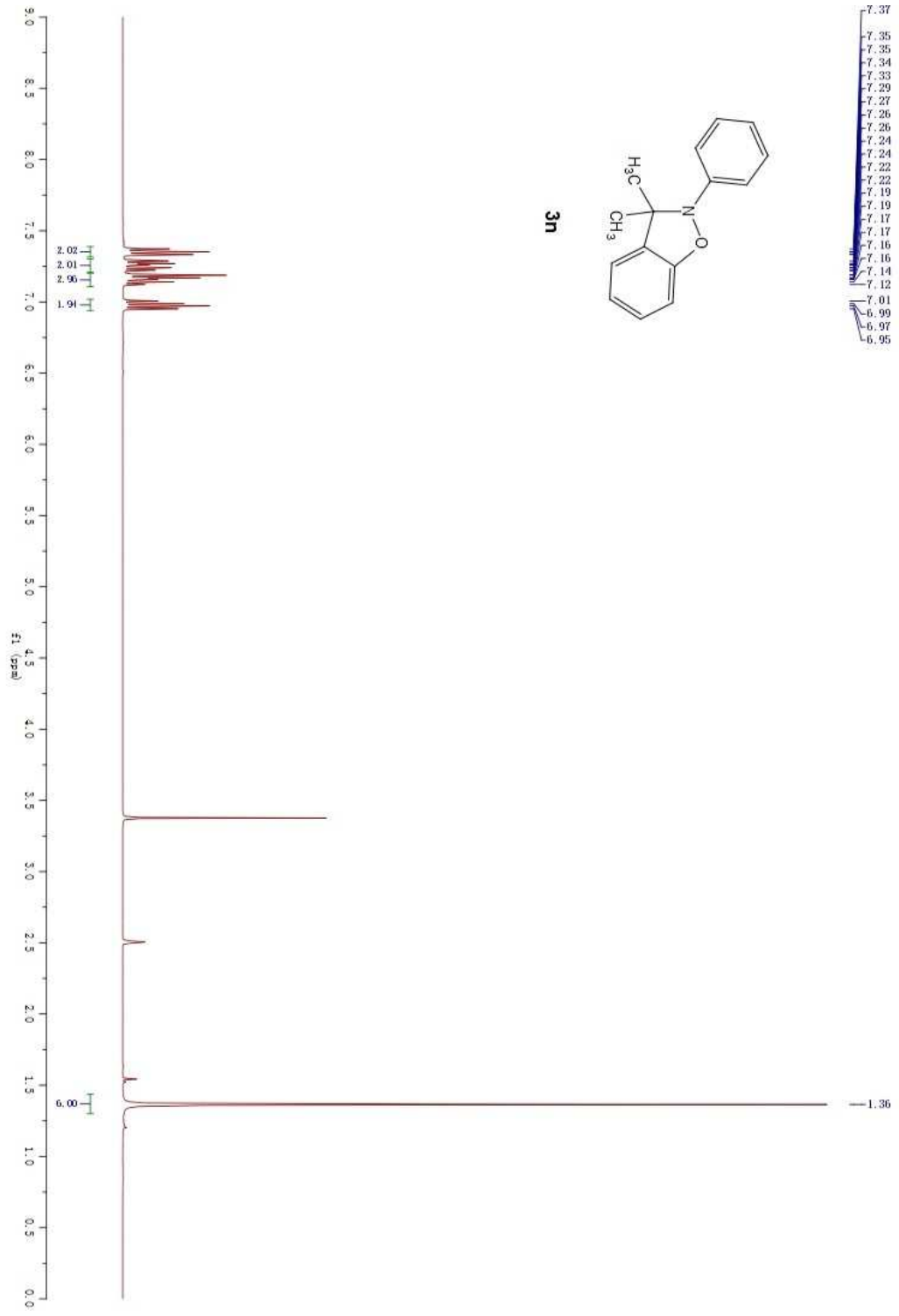
3l + **3l'**

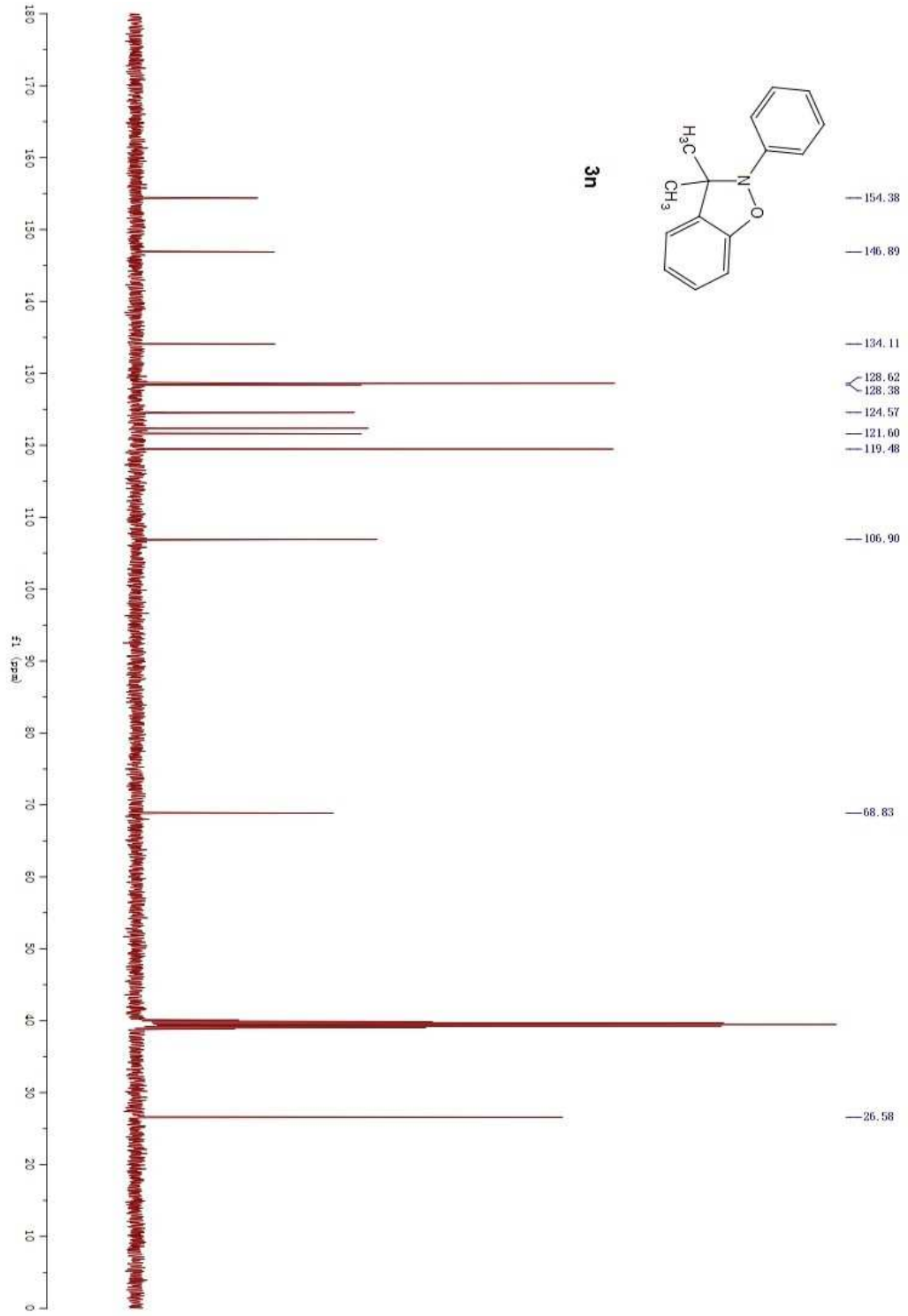
3l : 3l' = 10 : 1

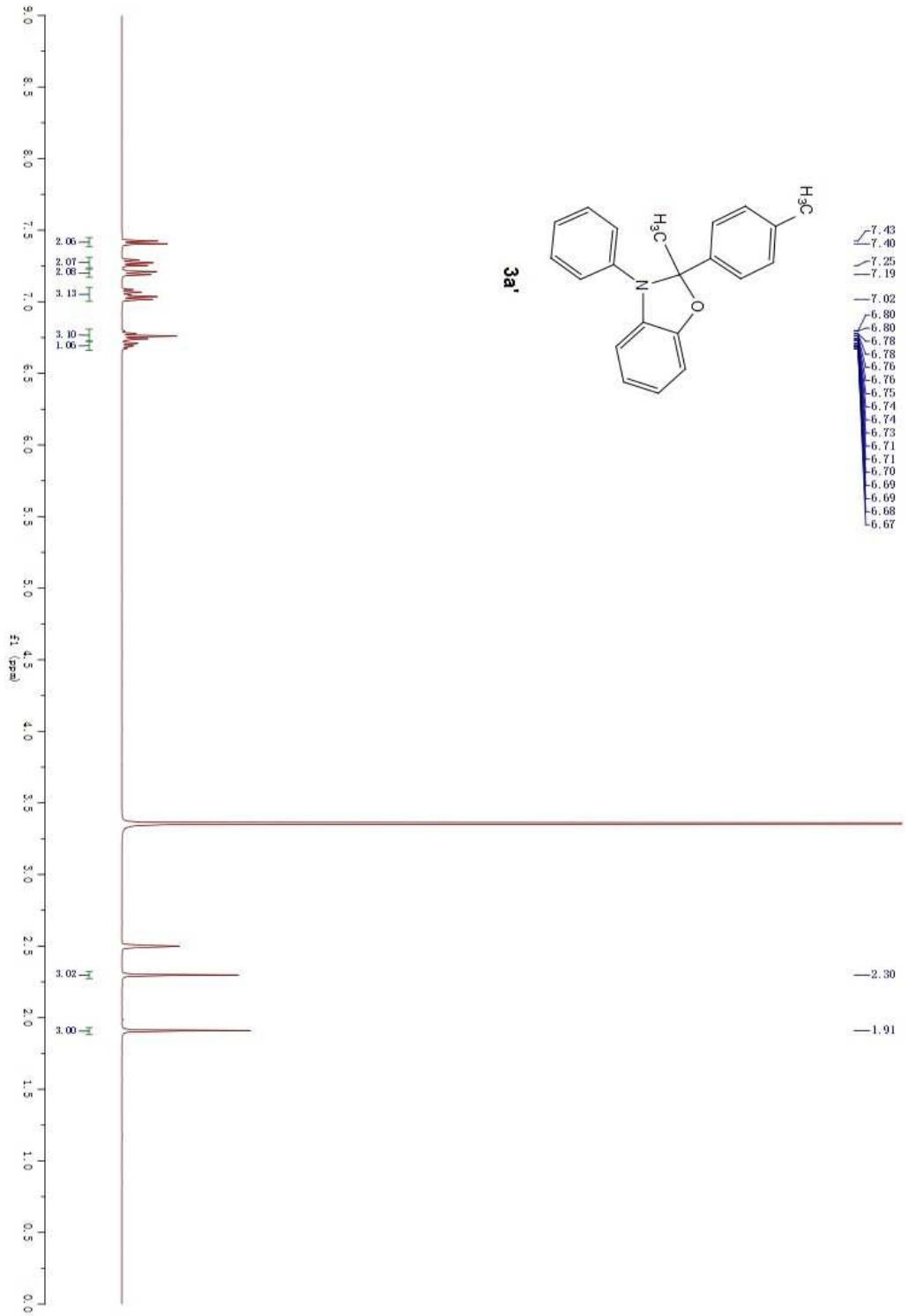

158.39
156.29
147.33
132.98
132.17
130.64
127.77
124.22
122.36
120.22
113.09
107.26
81.45
55.02
H3C
O
H3C
O
N
O
3l
f1 (ppm)

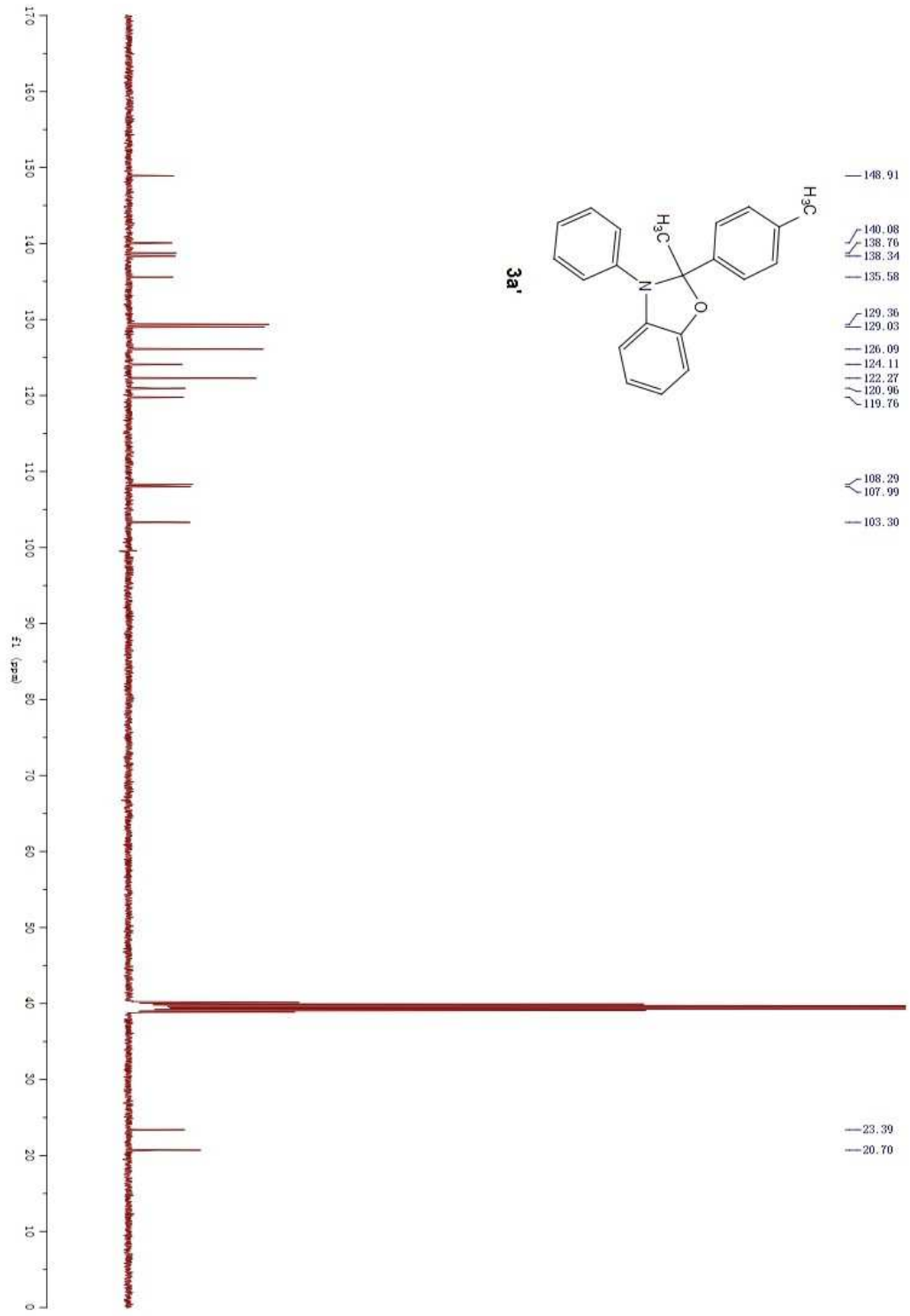

3m
8.08
8.06
7.46
7.44
7.26
7.09
6.96
6.89
6.81
6.61
6.59
4.71
4.53
4.09
1.25
0.96
1.06
2.11
11.03
1.10
1.98
1.00
1.02
2.02
3.19
f1 (ppm)

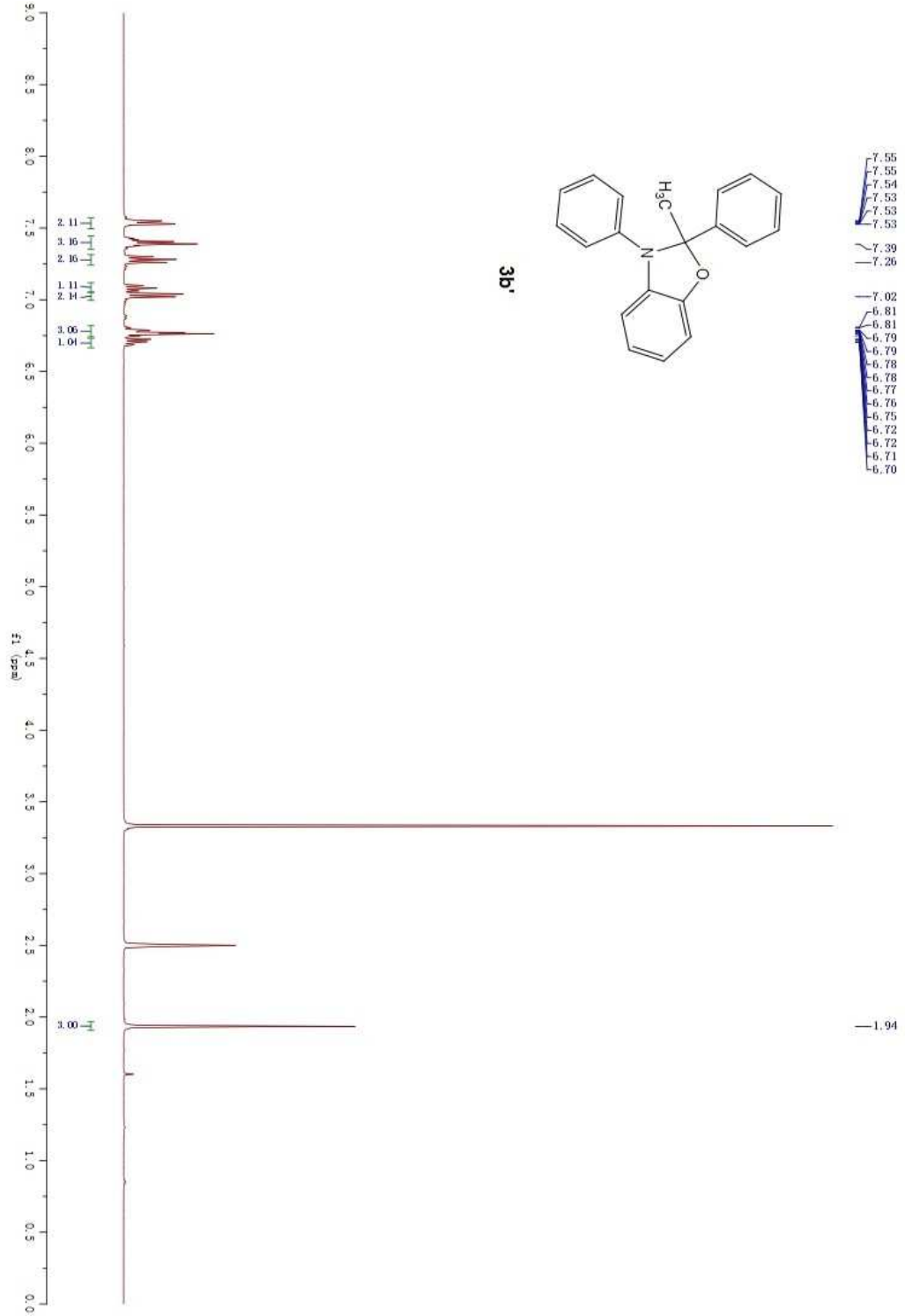

3m
157.72
155.02
147.26
140.51
129.11
128.06
127.56
127.46
127.27
126.44
124.62
121.86
121.42
120.15
112.62
112.40
107.05
81.01
71.08
18.70
f1 (ppm)

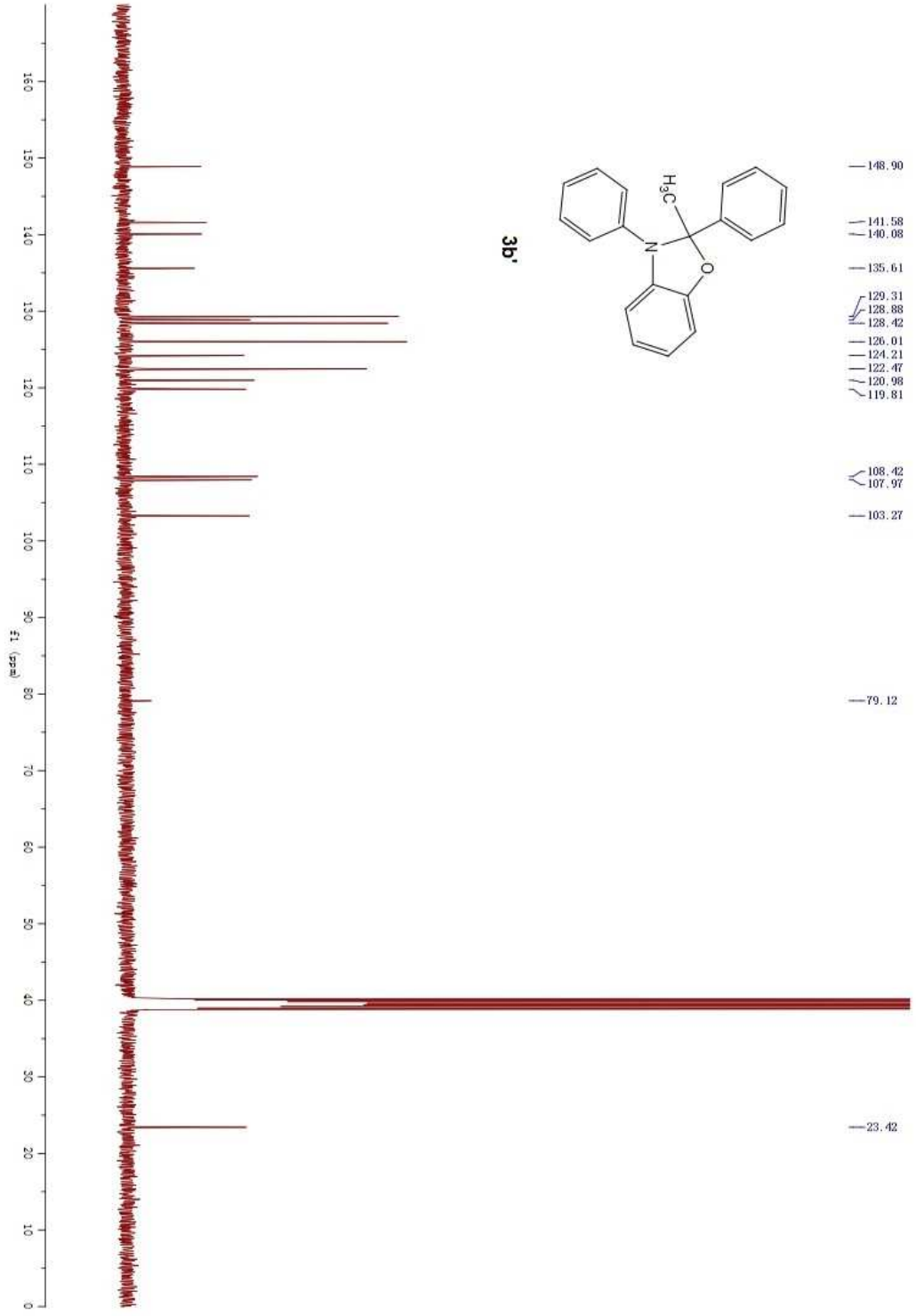

3n
H3C
CH3
N
O
7.37
7.35
7.35
7.34
7.33
7.29
7.27
7.26
7.26
7.24
7.24
7.22
7.22
7.19
7.19
7.17
7.17
7.16
7.16
7.14
7.12
7.01
6.99
6.97
6.95
2.02
2.01
2.96
1.94
6.00
1.36
f1 (ppm)

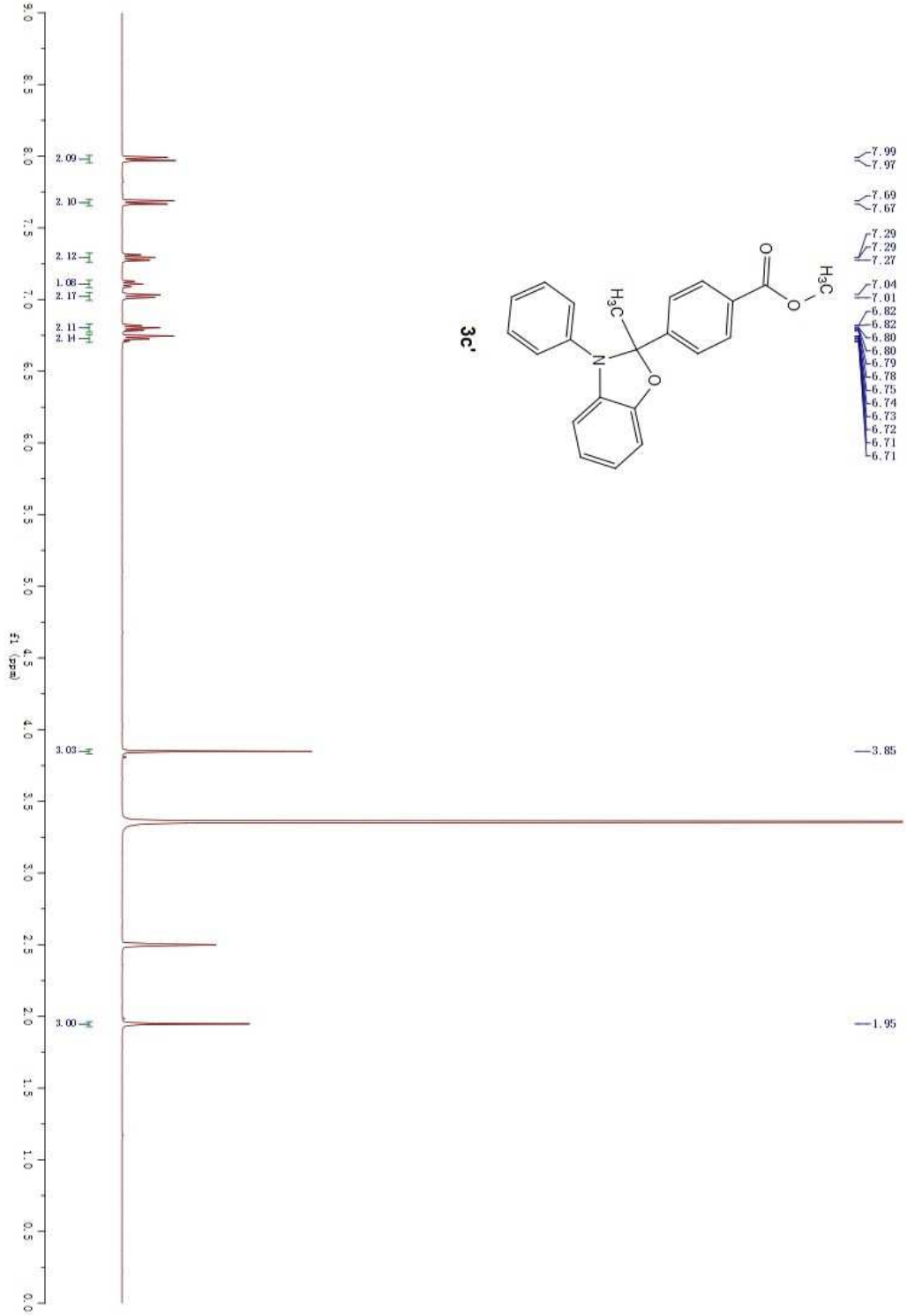

3n
H3C
CH3
N
O
154.38
146.89
134.11
128.62
128.38
124.57
121.60
119.48
106.90
68.83
26.58
f1 (ppm)

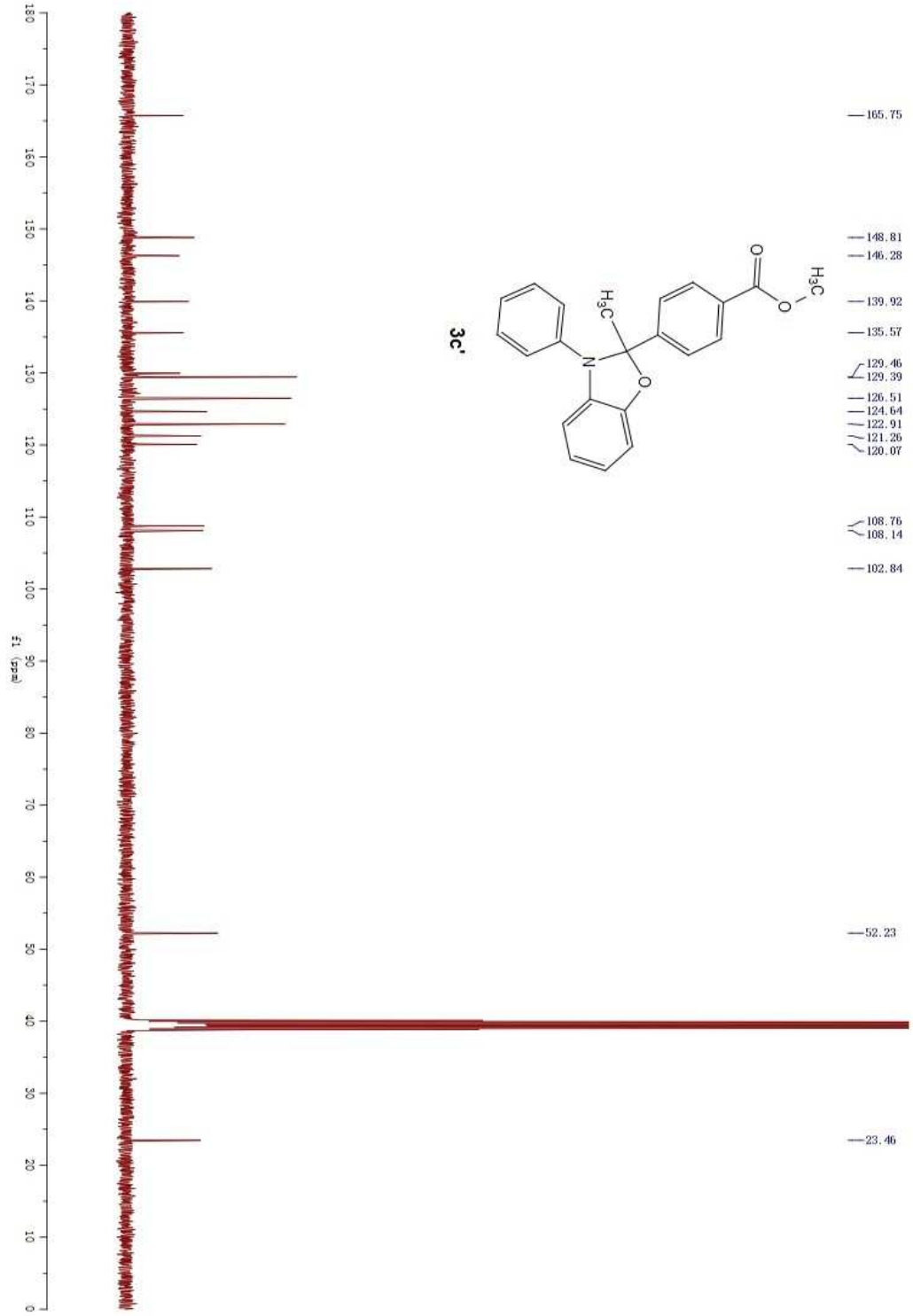

3a'
H3C
H3C
N
O
f1 (ppm)
2.06
2.07
2.08
3.13
3.10
1.06
3.02
3.00
7.43
7.40
7.25
7.19
7.02
6.80
6.80
6.78
6.78
6.76
6.76
6.75
6.74
6.74
6.73
6.71
6.71
6.70
6.69
6.69
6.68
6.67
2.30
1.91

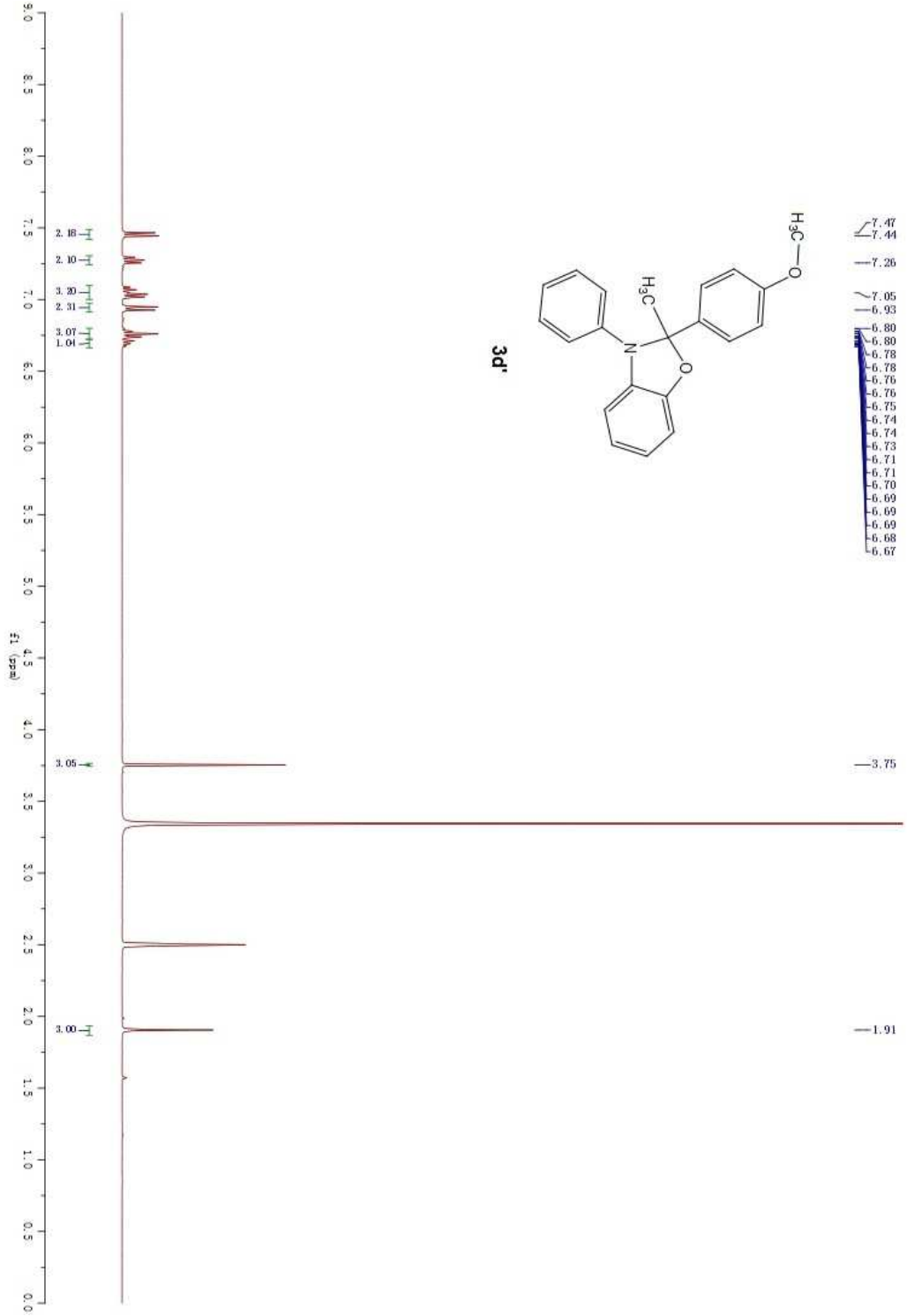

3a'
H3C
H3C
N
O
148.91
140.08
138.76
138.34
135.58
129.36
129.03
126.09
124.11
122.27
120.96
119.76
108.29
107.99
103.30
23.39
20.70
f1 (ppm)

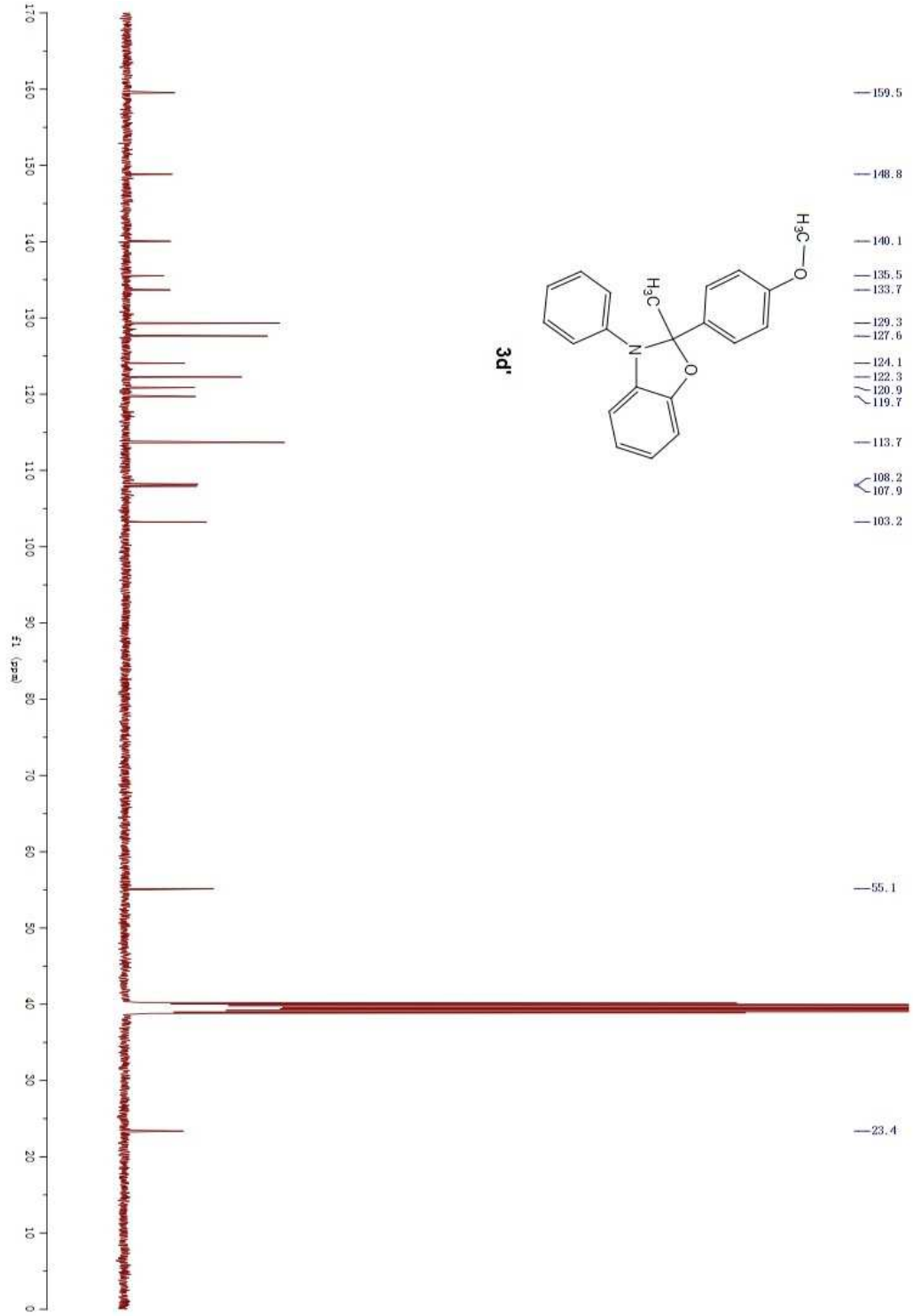

3b'
H3C
N
O
7.55
7.55
7.54
7.53
7.53
7.53
7.39
7.26
7.02
6.81
6.81
6.79
6.79
6.79
6.78
6.78
6.77
6.76
6.75
6.72
6.72
6.71
6.70
1.94
2.11
3.16
2.16
1.11
2.14
3.06
1.04
3.00
f1 (ppm)

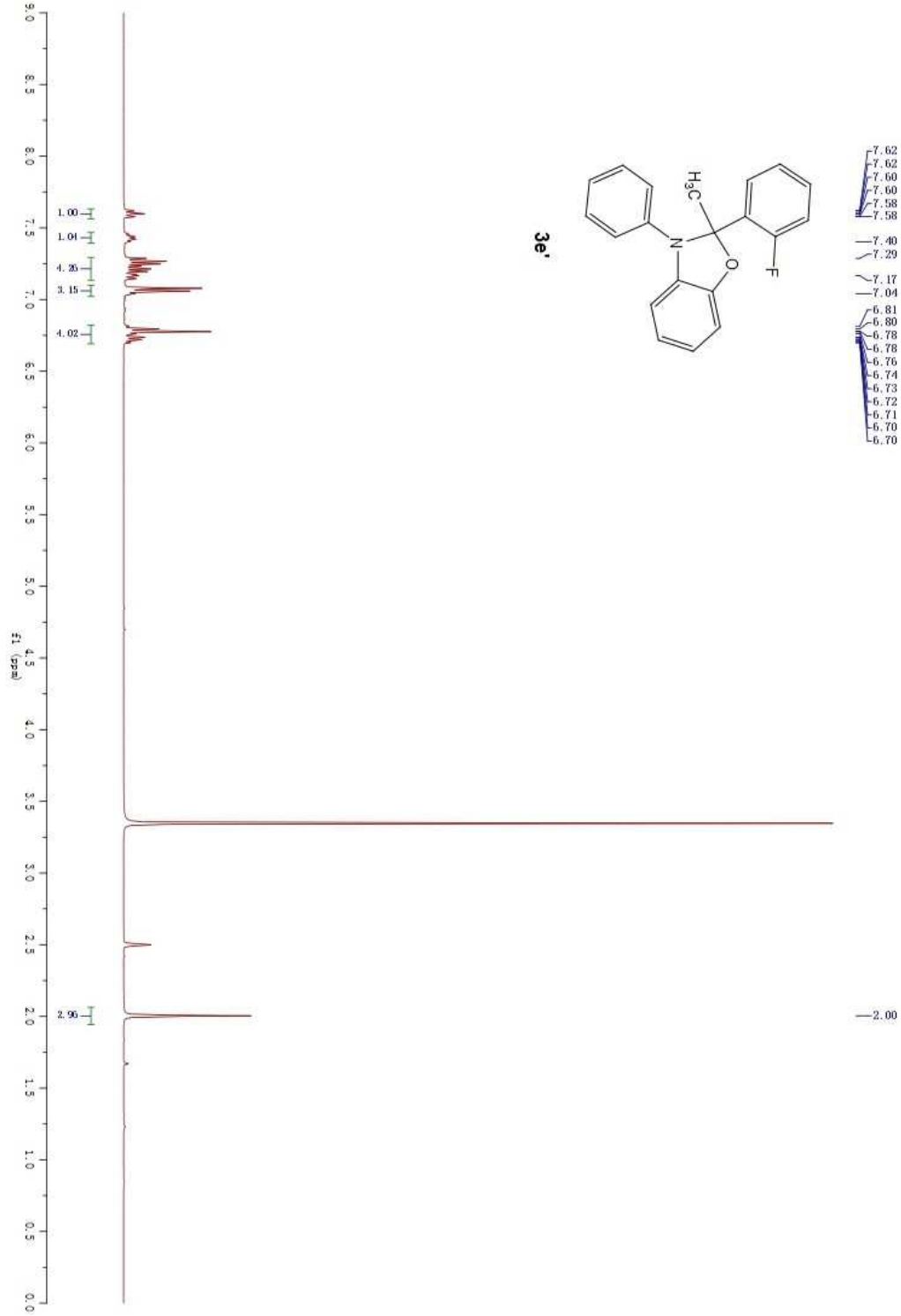

3b'
148.90
141.58
140.08
135.61
129.31
128.88
128.42
126.01
124.21
122.47
120.98
119.81
108.42
107.97
103.27
79.12
23.42
f1 (ppm)

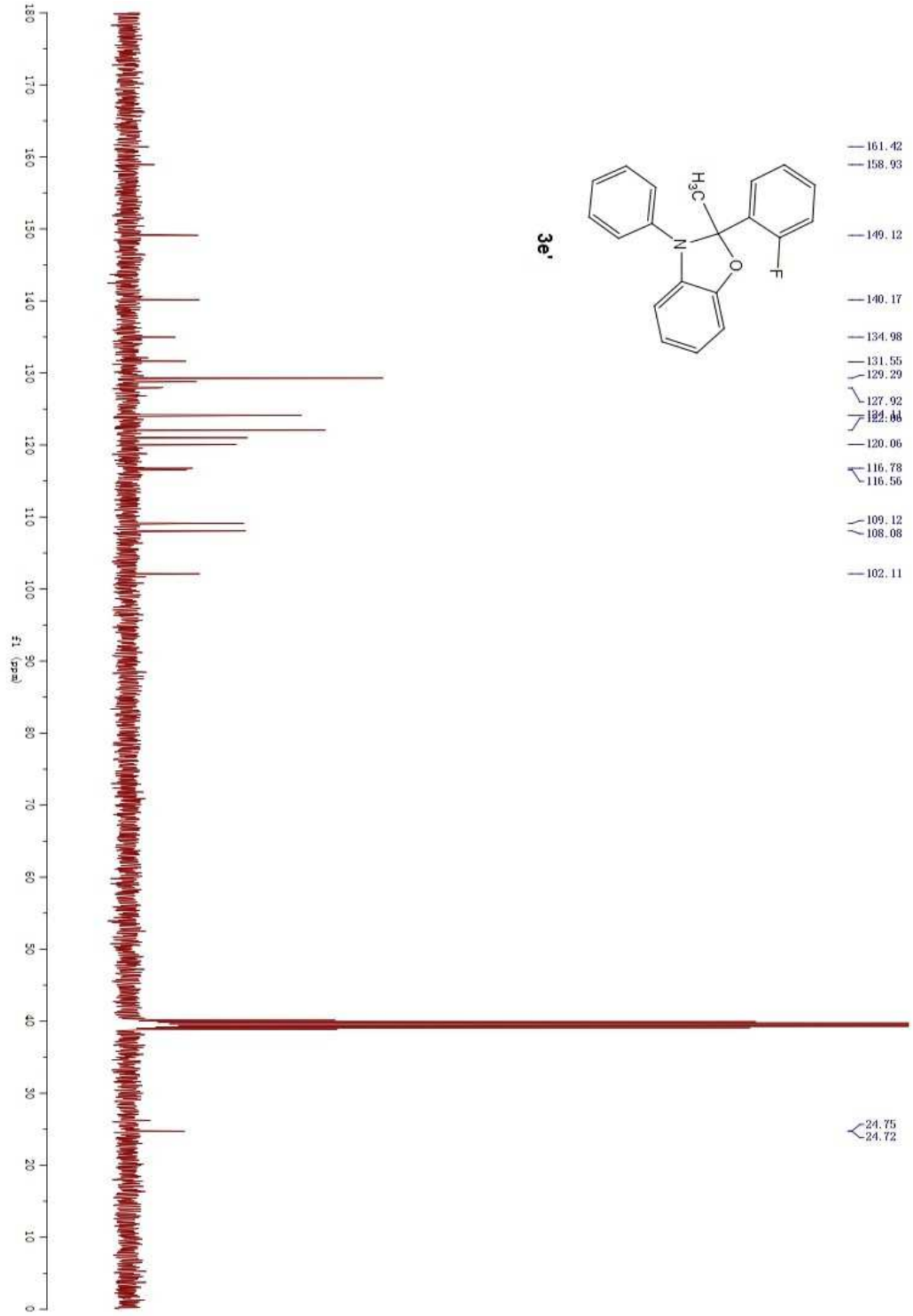

3c'
H3C
O
O
H3C
N
O
7.99
7.97
7.69
7.67
7.29
7.29
7.27
7.04
7.01
6.82
6.82
6.80
6.80
6.79
6.78
6.75
6.74
6.73
6.72
6.71
6.71
2.09
2.10
2.12
1.08
2.17
2.11
2.14
3.03
3.00
3.85
1.95
f1 (ppm)

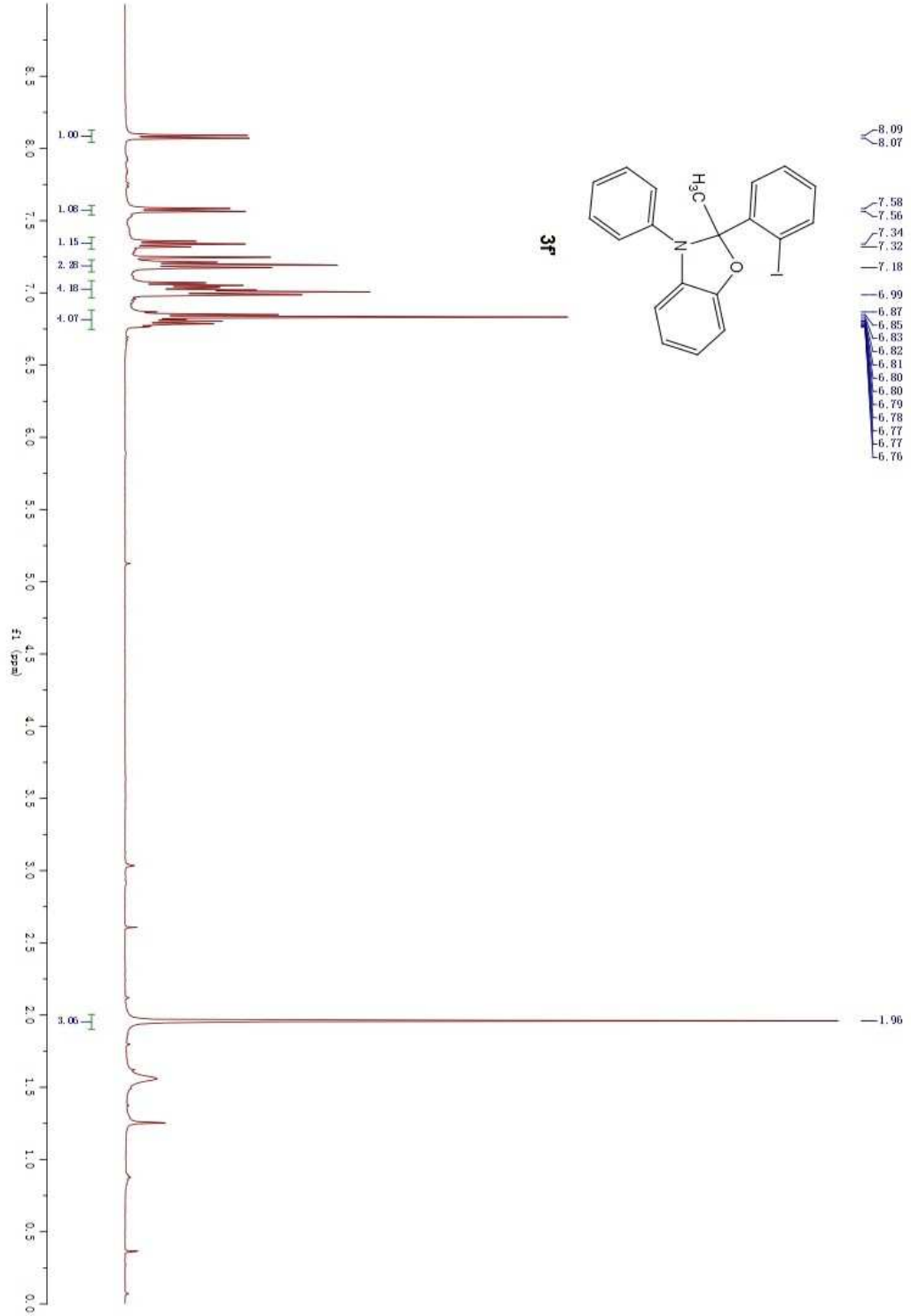

3c'
H3C
O
O
H3C
N
O
165.75
148.81
146.28
139.92
135.57
129.46
129.39
126.51
124.64
122.91
121.26
120.07
108.76
108.14
102.84
52.23
23.46
f1 (ppm)


3d'
H3C
O
N
O
H3C
O
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)
2.18
2.10
3.20
2.31
3.07
1.04
3.05
3.00
7.47
7.44
7.26
7.05
6.93
6.80
6.80
6.78
6.78
6.76
6.76
6.75
6.74
6.74
6.73
6.71
6.71
6.70
6.69
6.69
6.69
6.68
6.67
3.75
1.91


3d'
159.5
148.8
140.1
135.5
133.7
129.3
127.6
124.1
122.3
120.9
119.7
113.7
108.2
107.9
103.2
55.1
23.4
f1 (ppm)


3e'
H3C
N
O
F
7.62
7.62
7.60
7.60
7.58
7.58
7.40
7.29
7.17
7.04
6.81
6.80
6.78
6.78
6.76
6.74
6.73
6.72
6.71
6.70
6.70
1.00
1.04
4.26
3.15
4.02
2.96
2.00
f1 (ppm)


3e'
H3C
N
O
F
161.42
158.93
149.12
140.17
134.98
131.55
129.29
127.92
120.06
116.78
116.56
109.12
108.08
102.11
24.75
24.72
f1 (ppm)


3f
H3C
N
O
I
8.09
8.07
7.58
7.56
7.34
7.32
7.18
6.99
6.87
6.85
6.83
6.82
6.81
6.80
6.80
6.79
6.78
6.77
6.77
6.76
1.96
1.00
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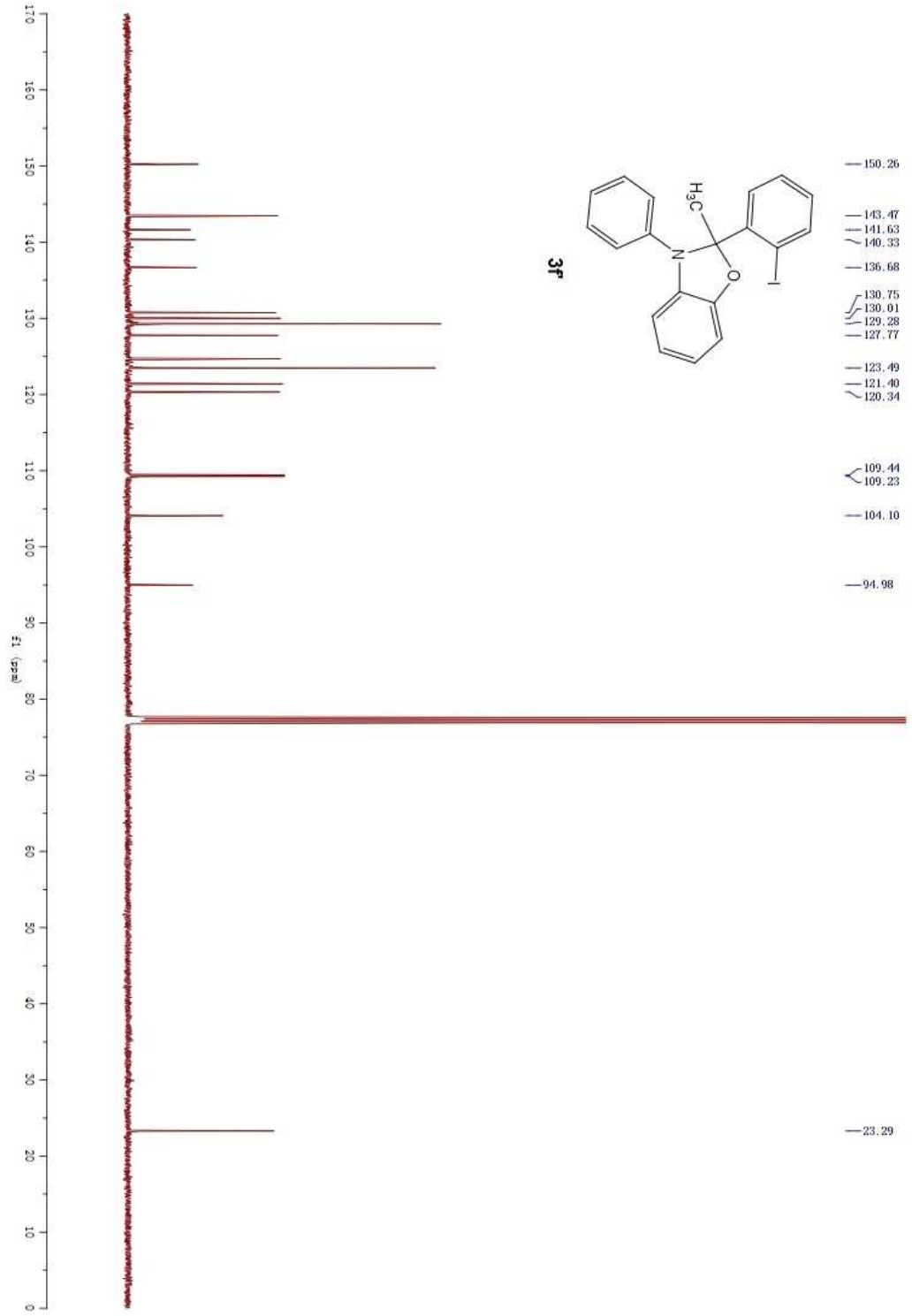
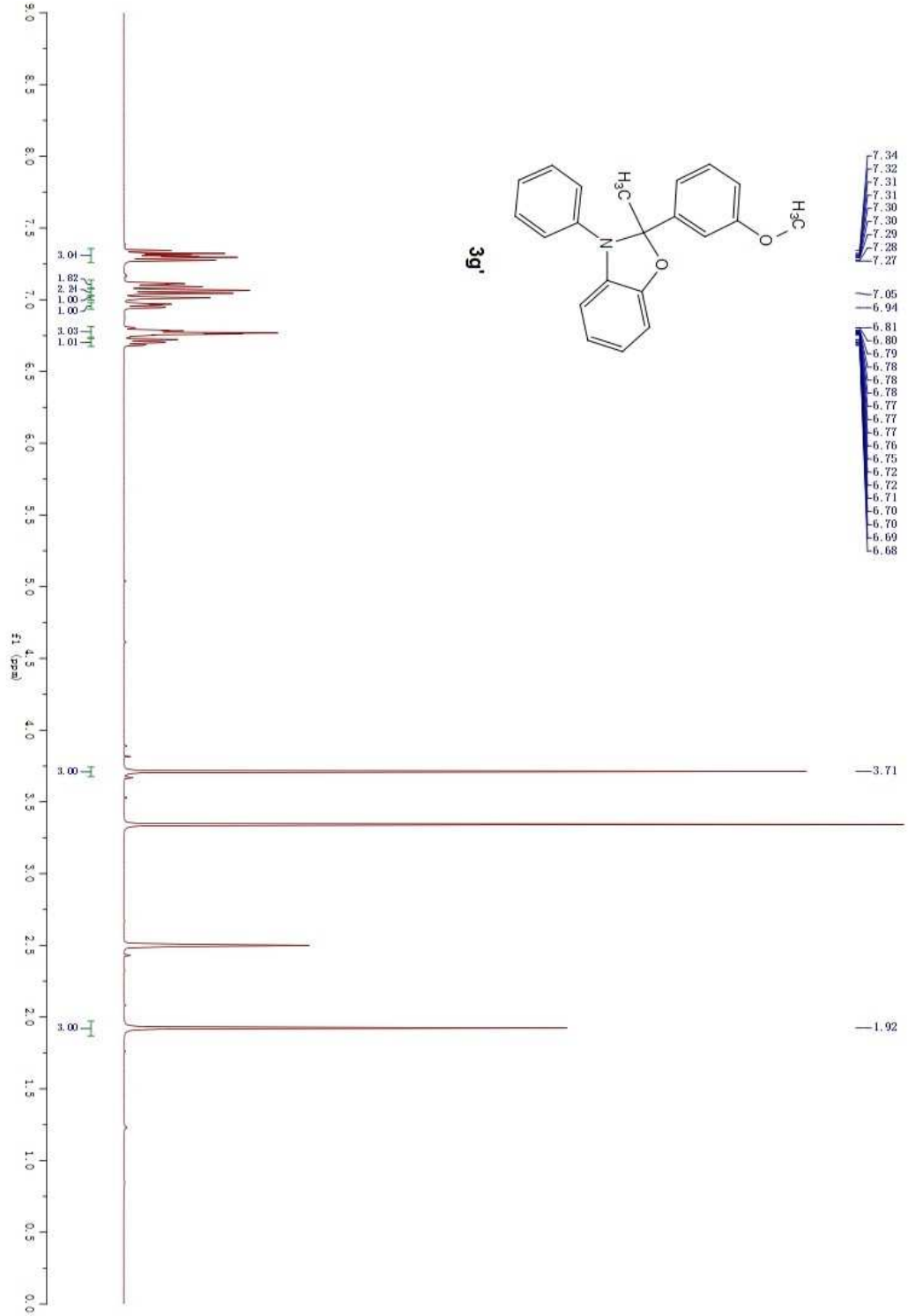
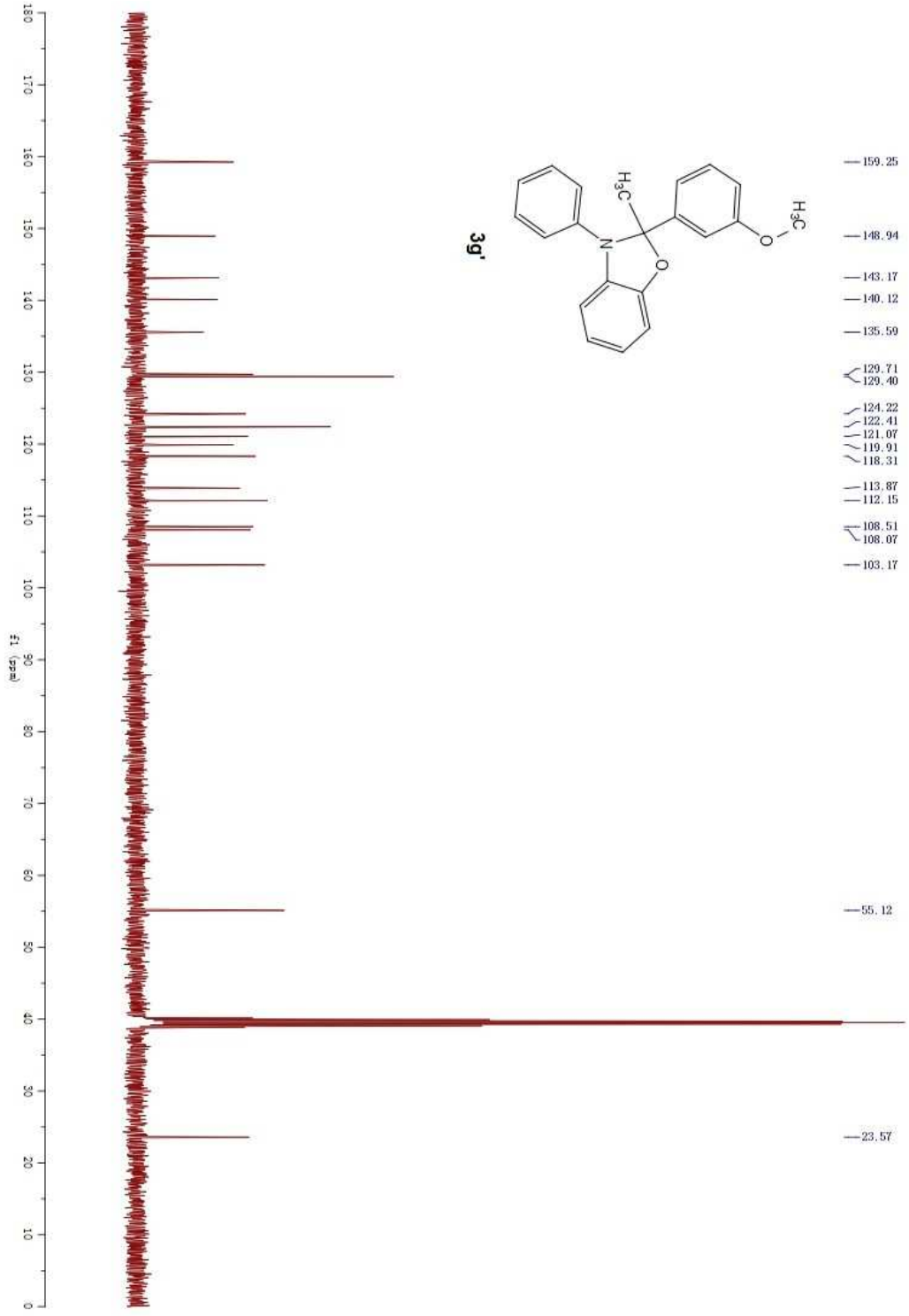
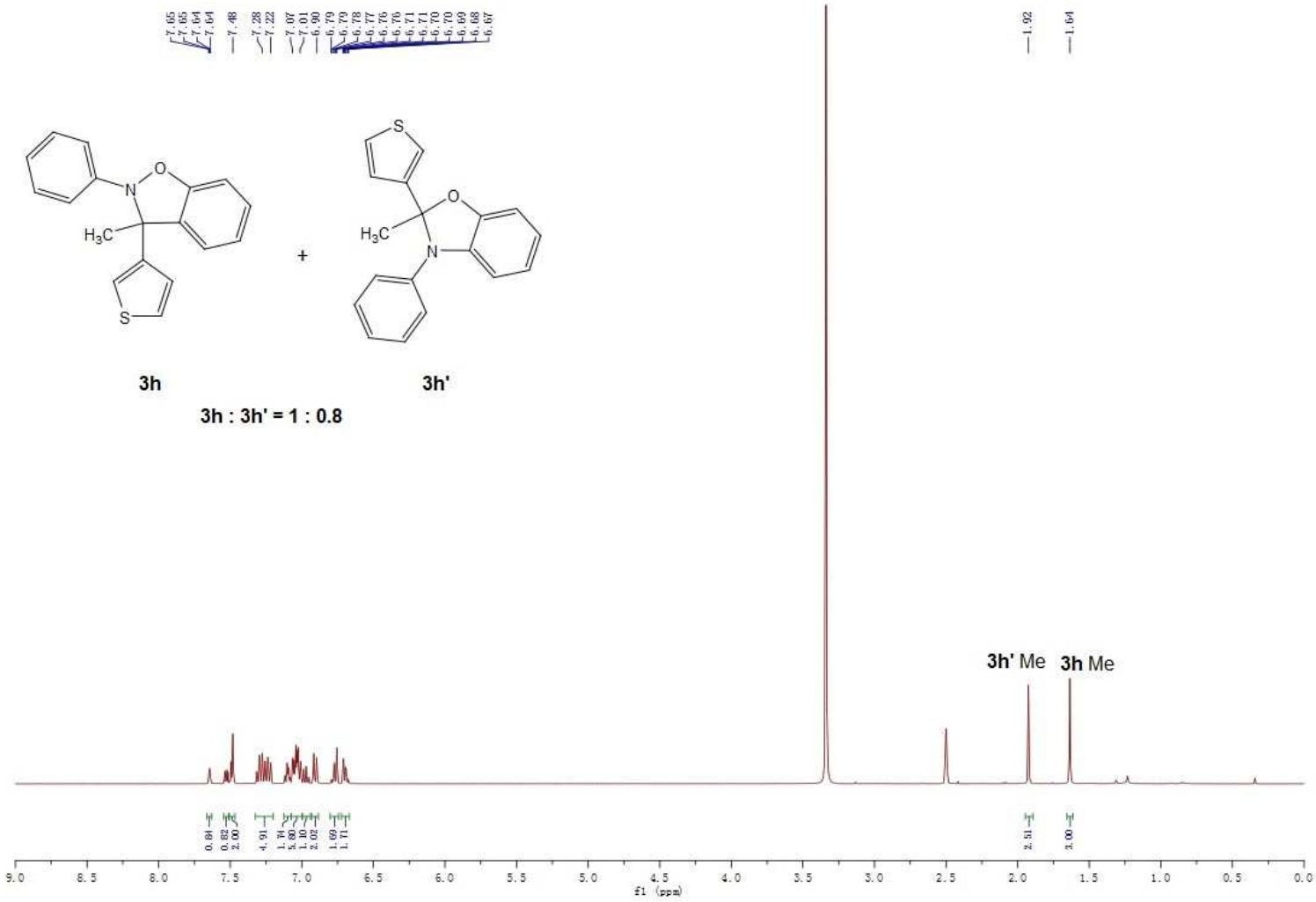
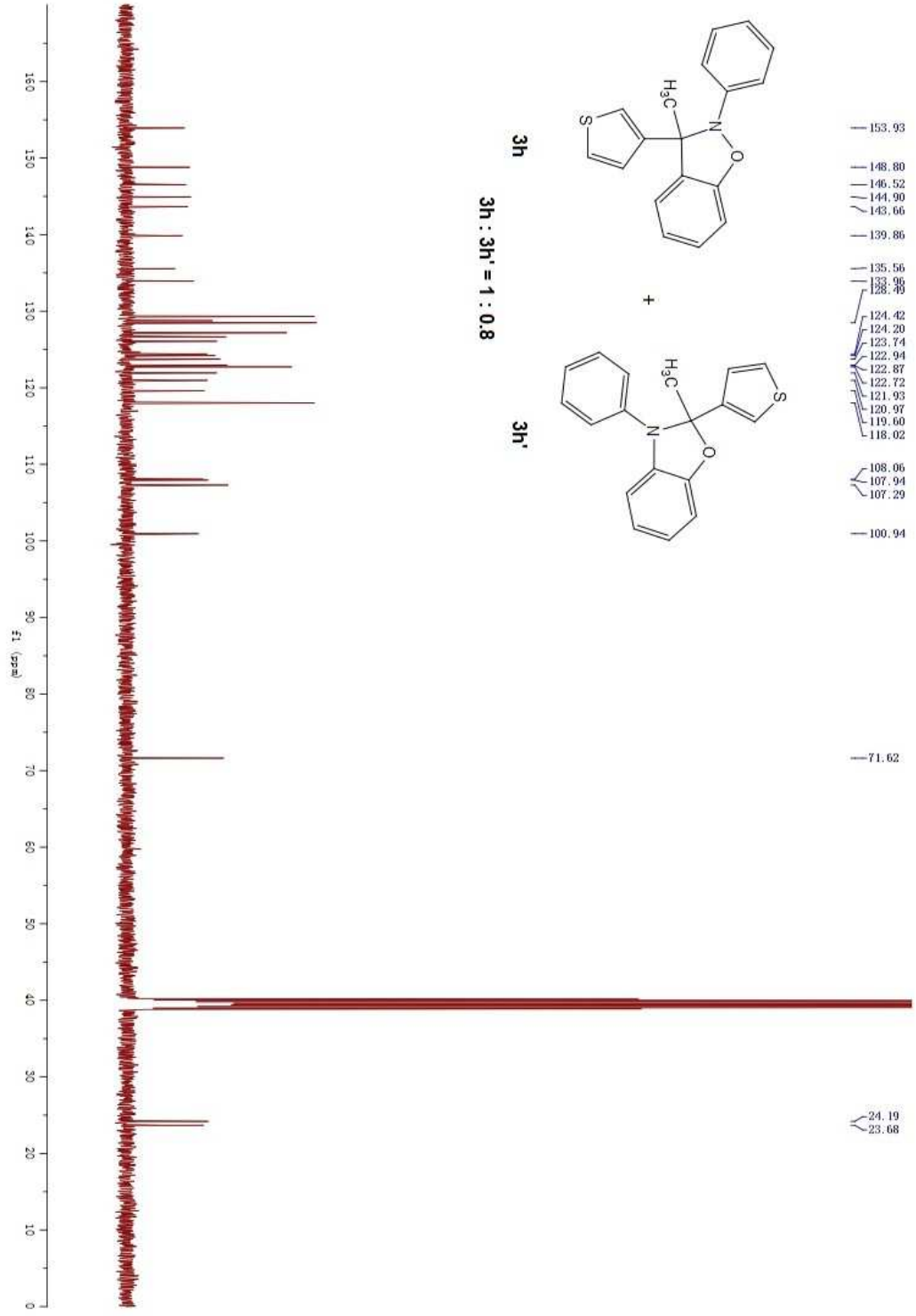
1.15
2.28
4.18
4.07
3.06
f1 (ppm)

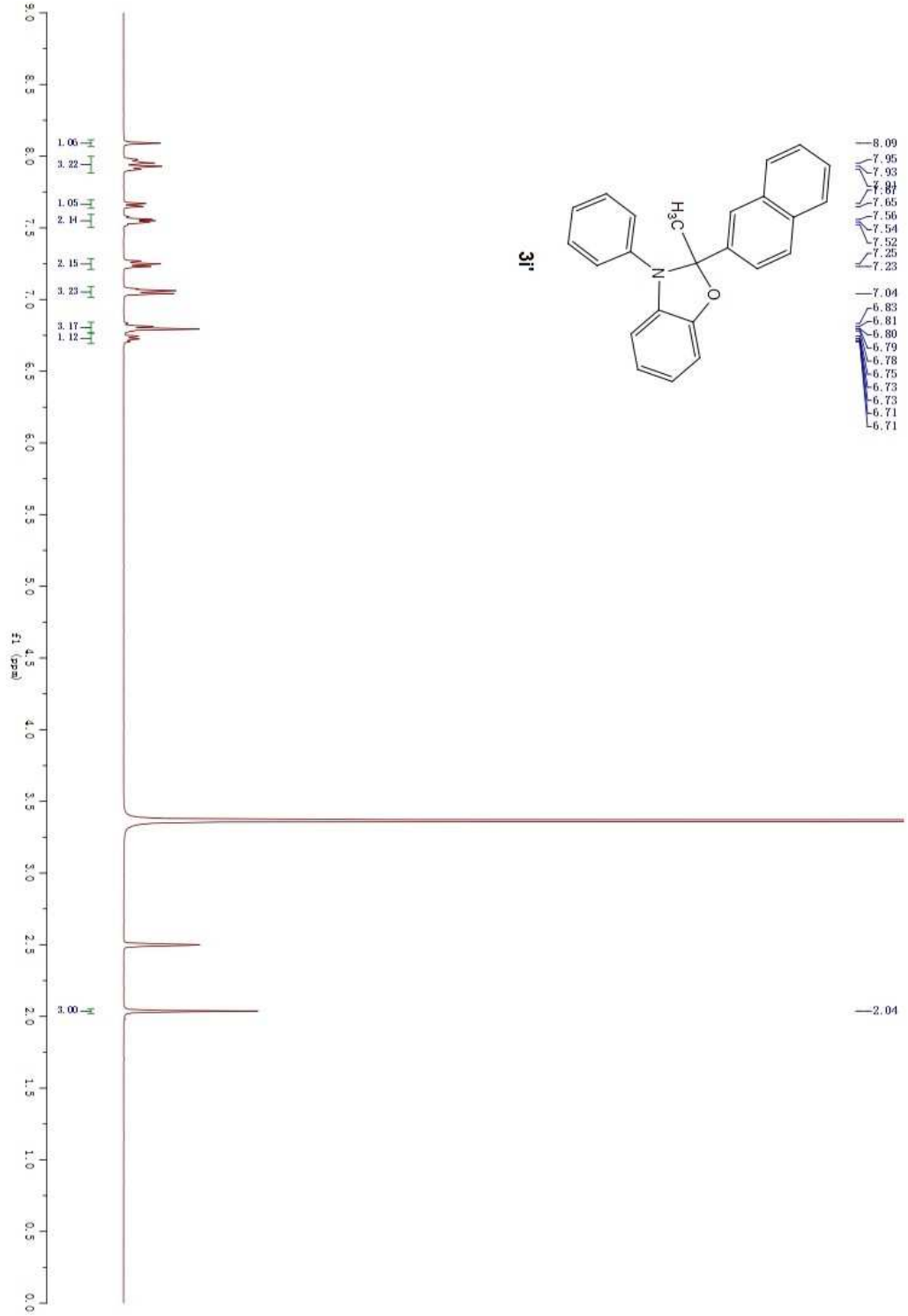

3f
150.26
143.47
141.63
140.33
136.68
130.75
130.01
129.28
127.77
123.49
121.40
120.34
109.44
109.23
104.10
94.98
23.29
f1 (ppm)

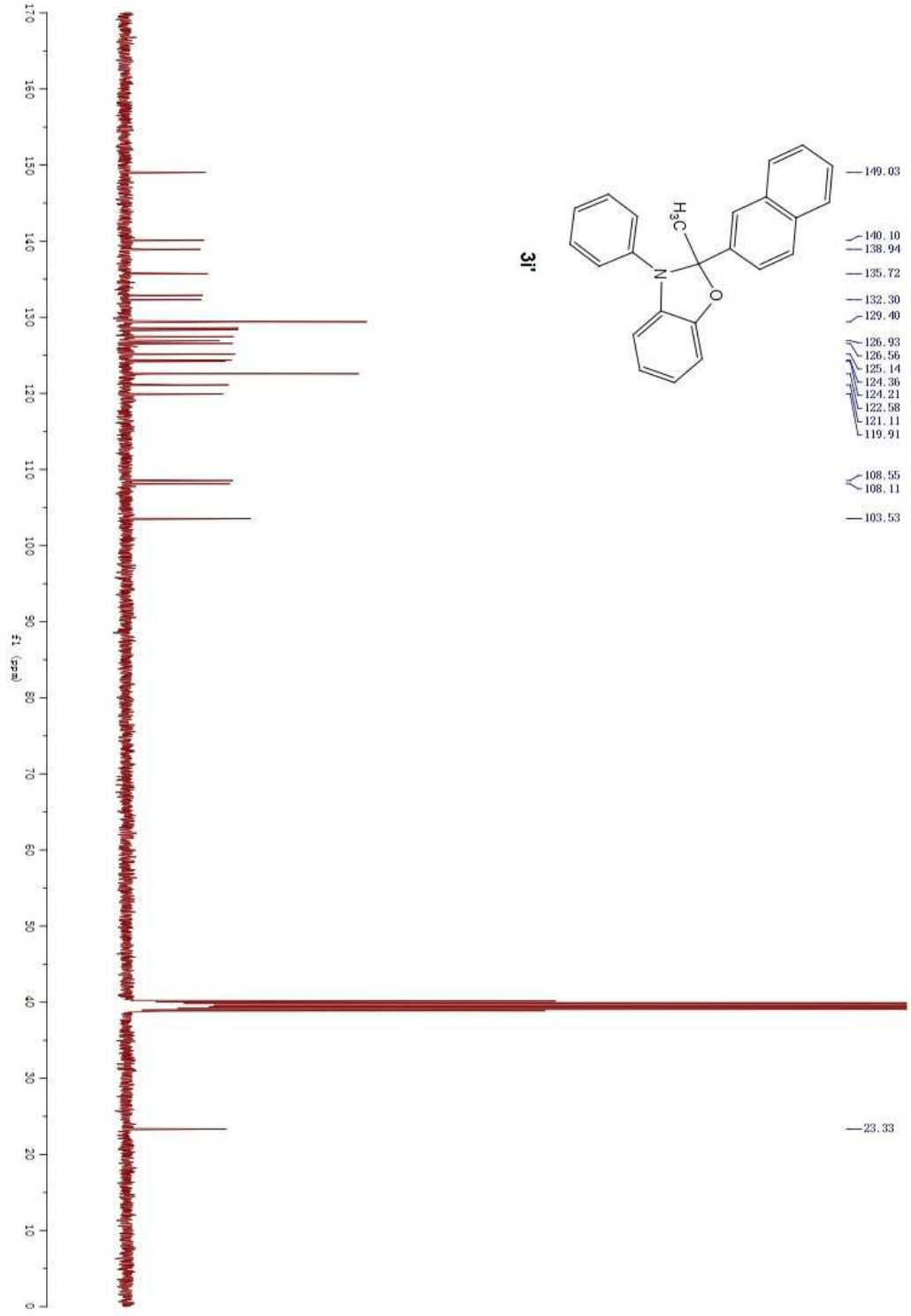

3g'
H3C
N
O
O
H3C
7.34
7.32
7.31
7.31
7.30
7.30
7.29
7.28
7.27
7.05
6.94
6.81
6.80
6.79
6.78
6.78
6.78
6.77
6.77
6.77
6.76
6.75
6.72
6.72
6.71
6.70
6.70
6.69
6.68
3.71
1.92
3.04
1.62
2.24
1.00
1.00
3.03
1.01
3.00
3.00
f1 (ppm)

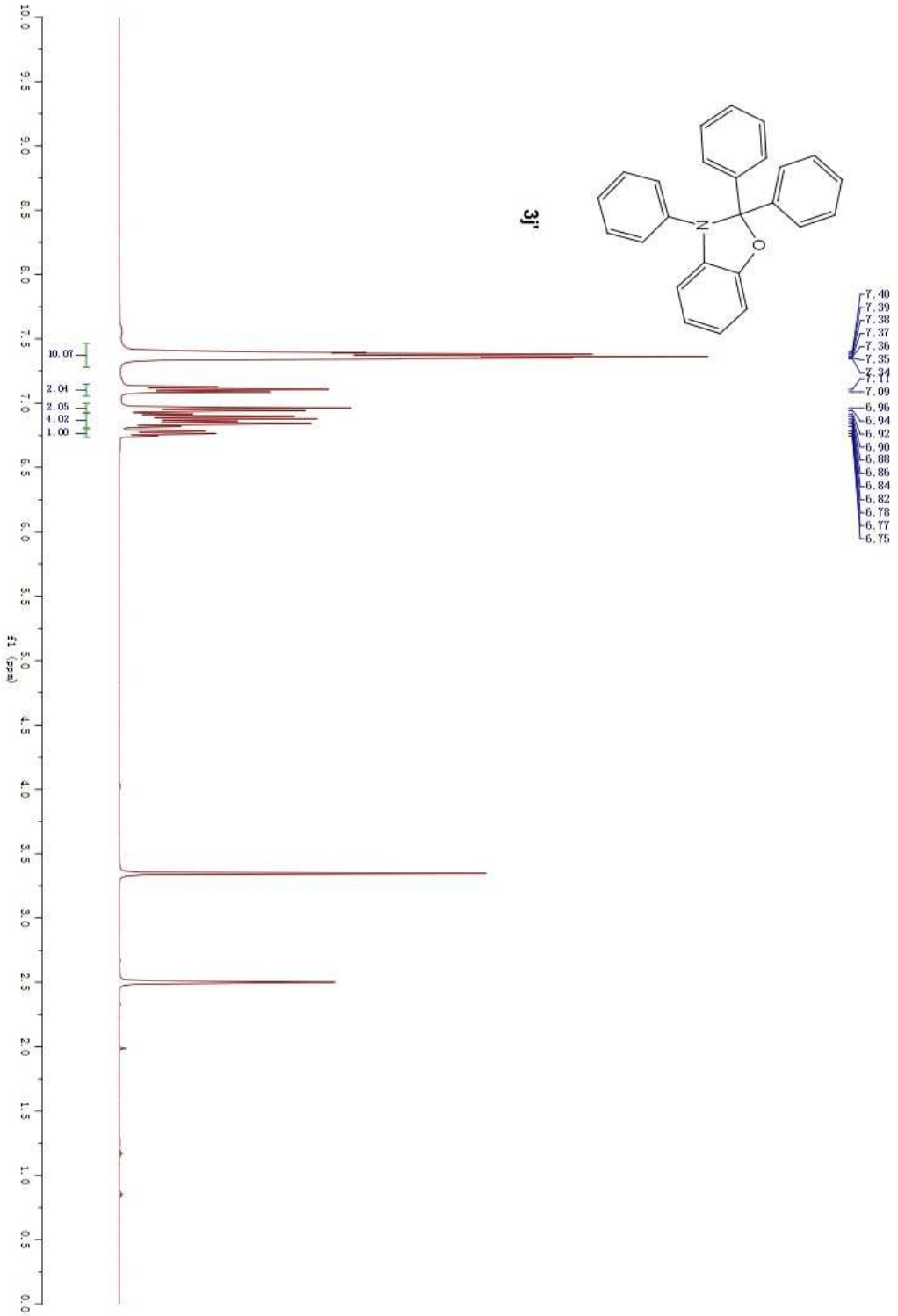

3g'
H3C
N
O
O
H3C
159.25
148.94
143.17
140.12
135.59
129.71
129.40
124.22
122.41
121.07
119.91
118.31
113.87
112.15
108.51
108.07
103.17
55.12
23.57
f1 (ppm)


7.65
7.65
7.64
7.64
7.48
7.28
7.22
7.07
7.01
6.90
6.79
6.79
6.78
6.77
6.76
6.76
6.71
6.70
6.70
6.69
6.68
6.67
1.92
1.64
O
N
H3C
S
+
S
O
H3C
N
3h
3h'
3h : 3h' = 1 : 0.8
3h' Me
3h Me
0.84
0.82
2.00
4.91
1.74
5.80
1.10
2.02
1.69
1.71
2.51
3.00
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)


3h
3h : 3h' = 1 : 0.8
3h'
153.93
148.80
146.52
144.90
143.66
139.86
135.56
133.96
128.49
124.42
124.20
123.74
122.94
122.87
122.72
121.93
120.97
119.60
118.02
108.06
107.94
107.29
100.94
71.62
24.19
23.68
f1 (ppm)


3i'
H3C
N
O
8.09
7.95
7.93
7.65
7.56
7.54
7.52
7.25
7.23
7.04
6.83
6.81
6.80
6.79
6.78
6.75
6.73
6.73
6.71
6.71
1.06
3.22
1.05
2.14
2.15
3.23
3.17
1.12
3.00
2.04
f1 (ppm)


3i'
H3C
N
O
149.03
140.10
138.94
135.72
132.30
129.40
126.93
126.56
125.14
124.36
124.21
122.58
121.11
119.91
108.55
108.11
103.53
23.33
f1 (ppm)


3j'
10.07
2.04
2.05
4.02
1.00
7.40
7.39
7.38
7.37
7.36
7.35
7.34
7.11
7.09
6.96
6.94
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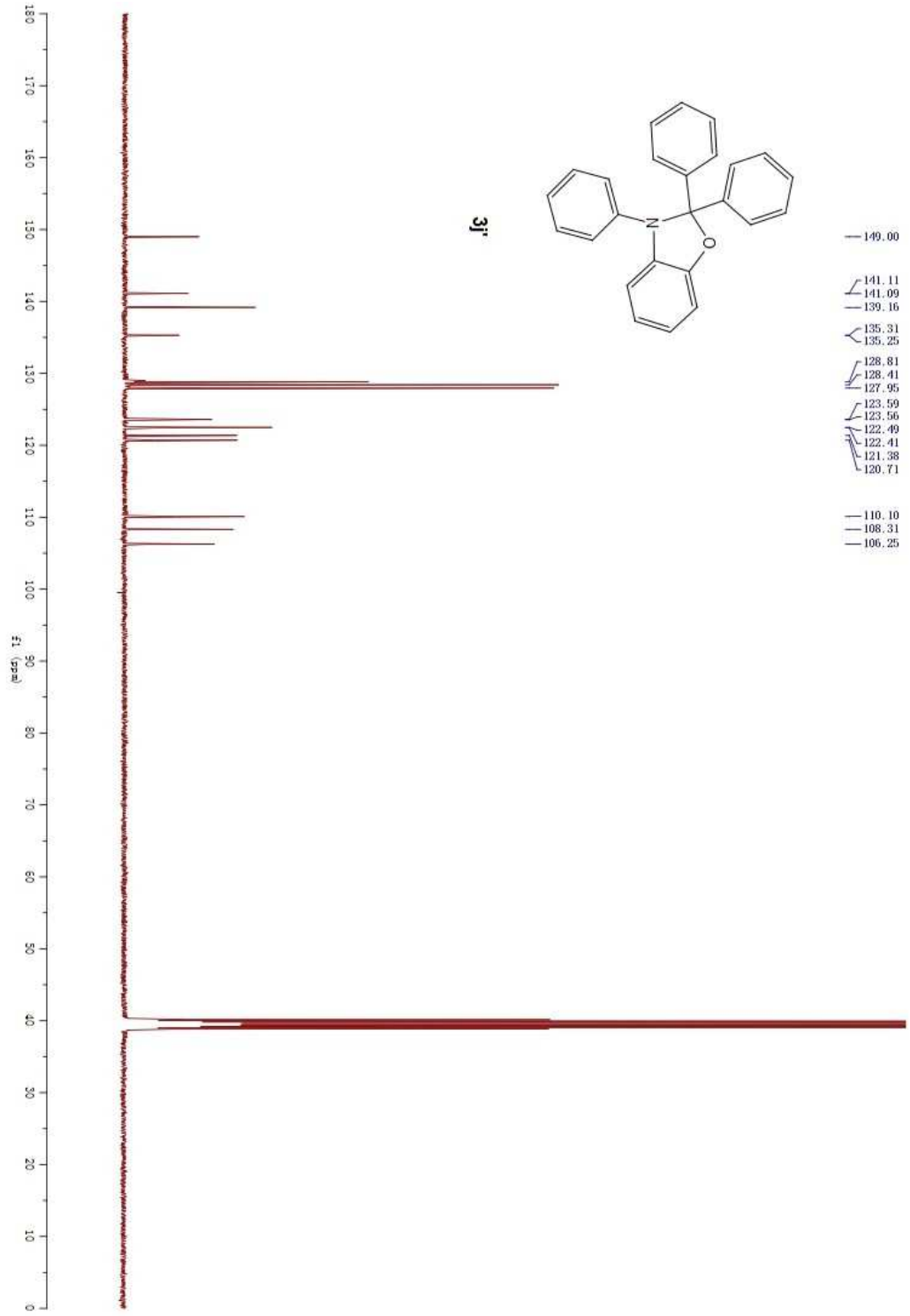
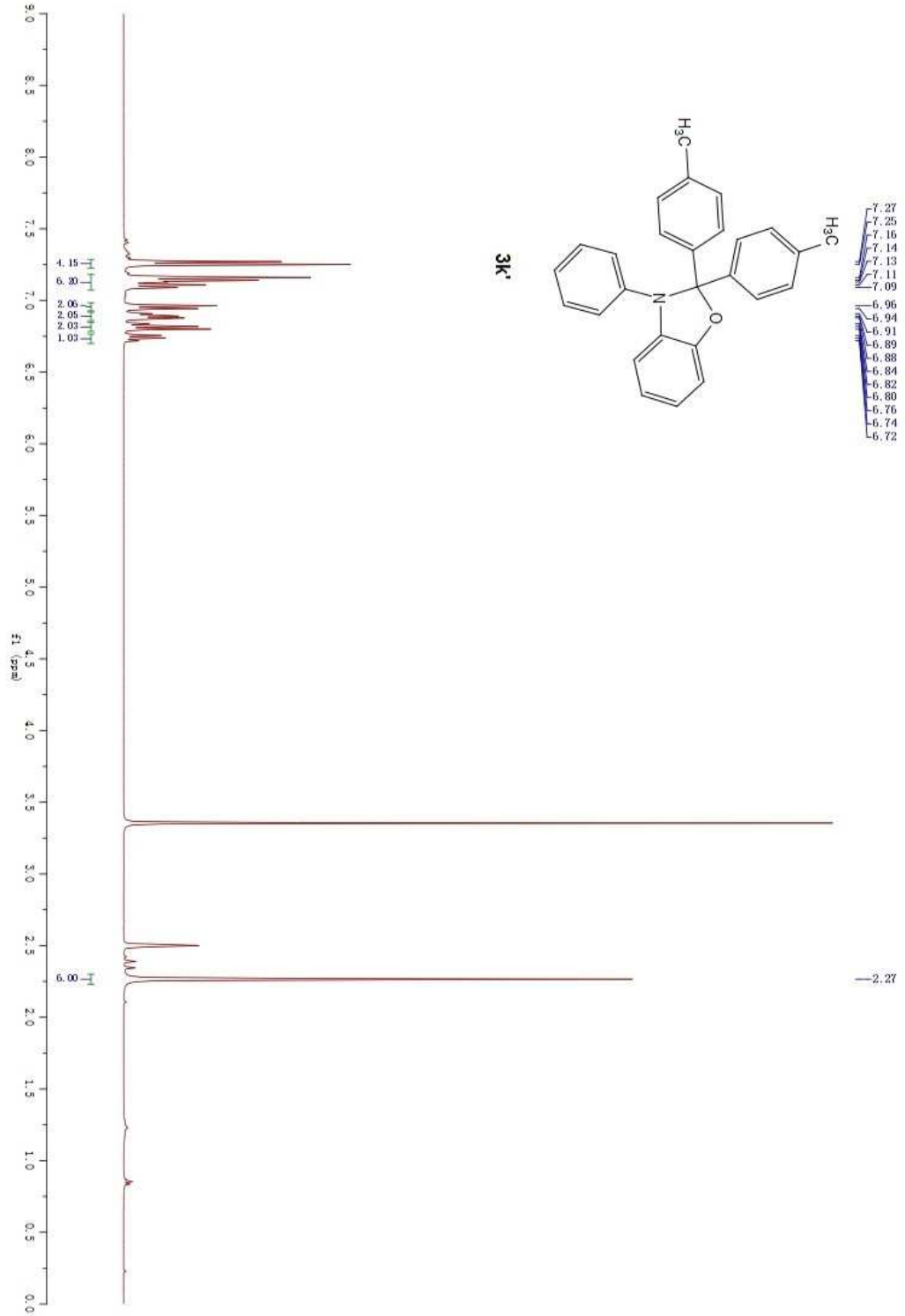
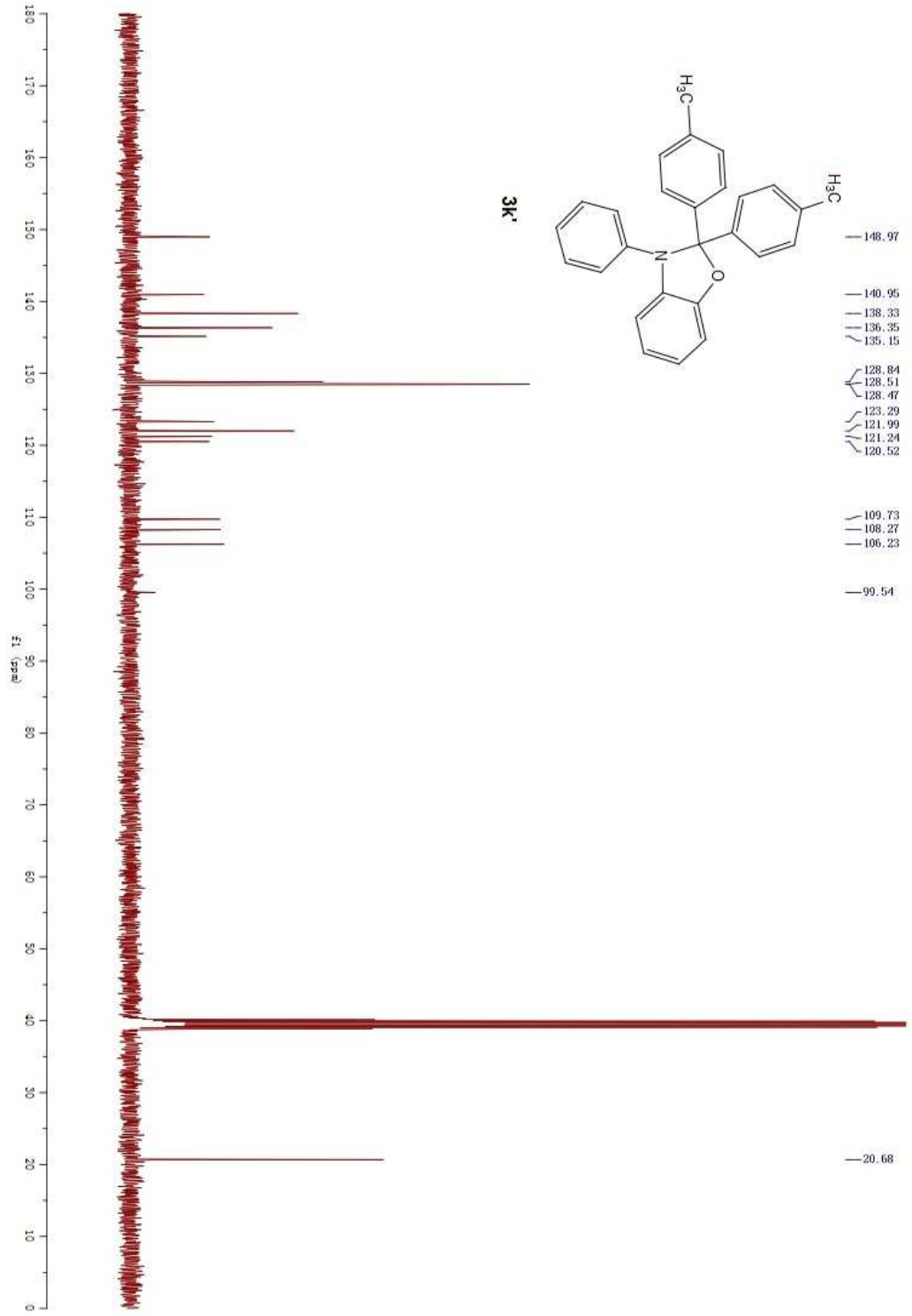
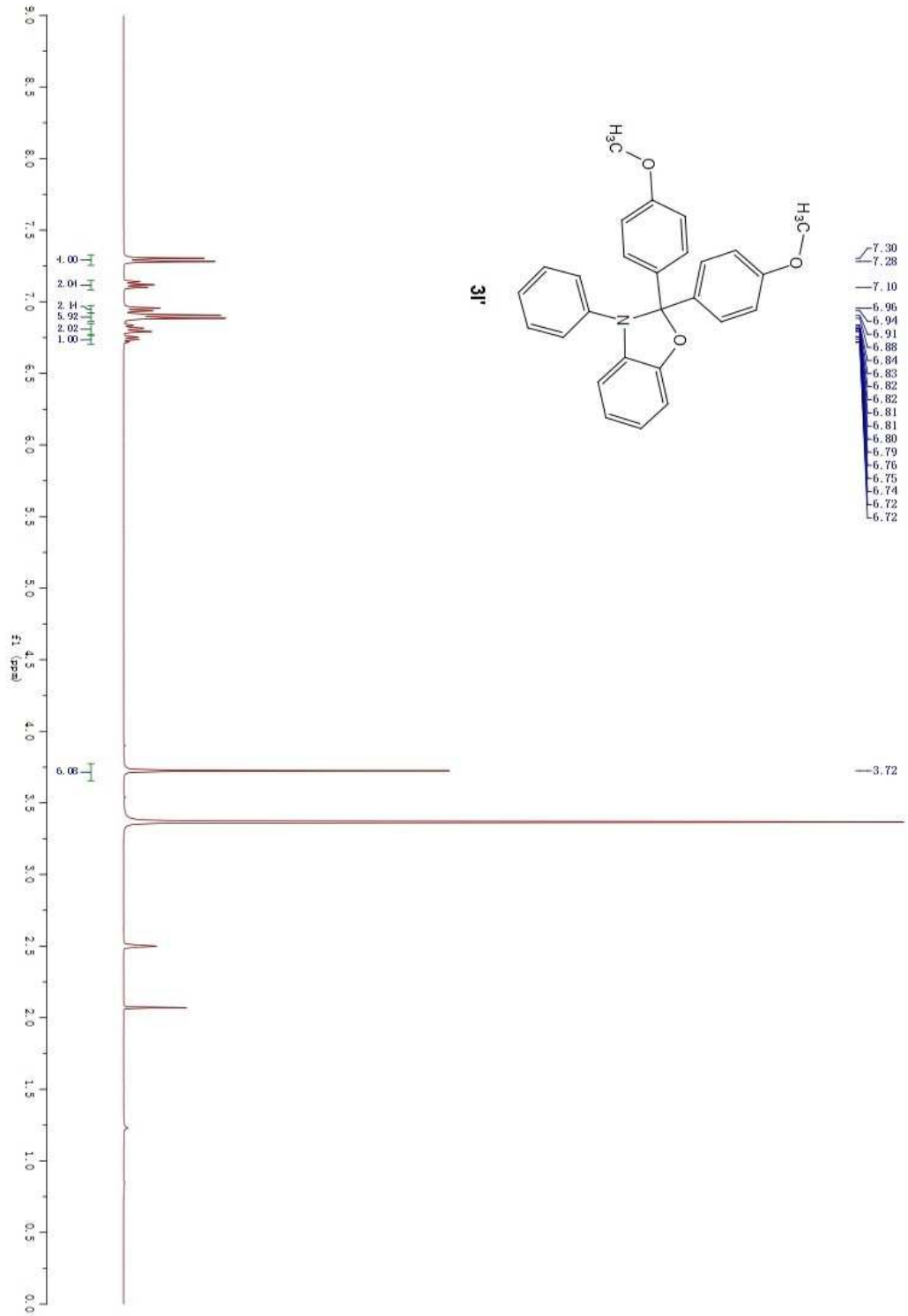
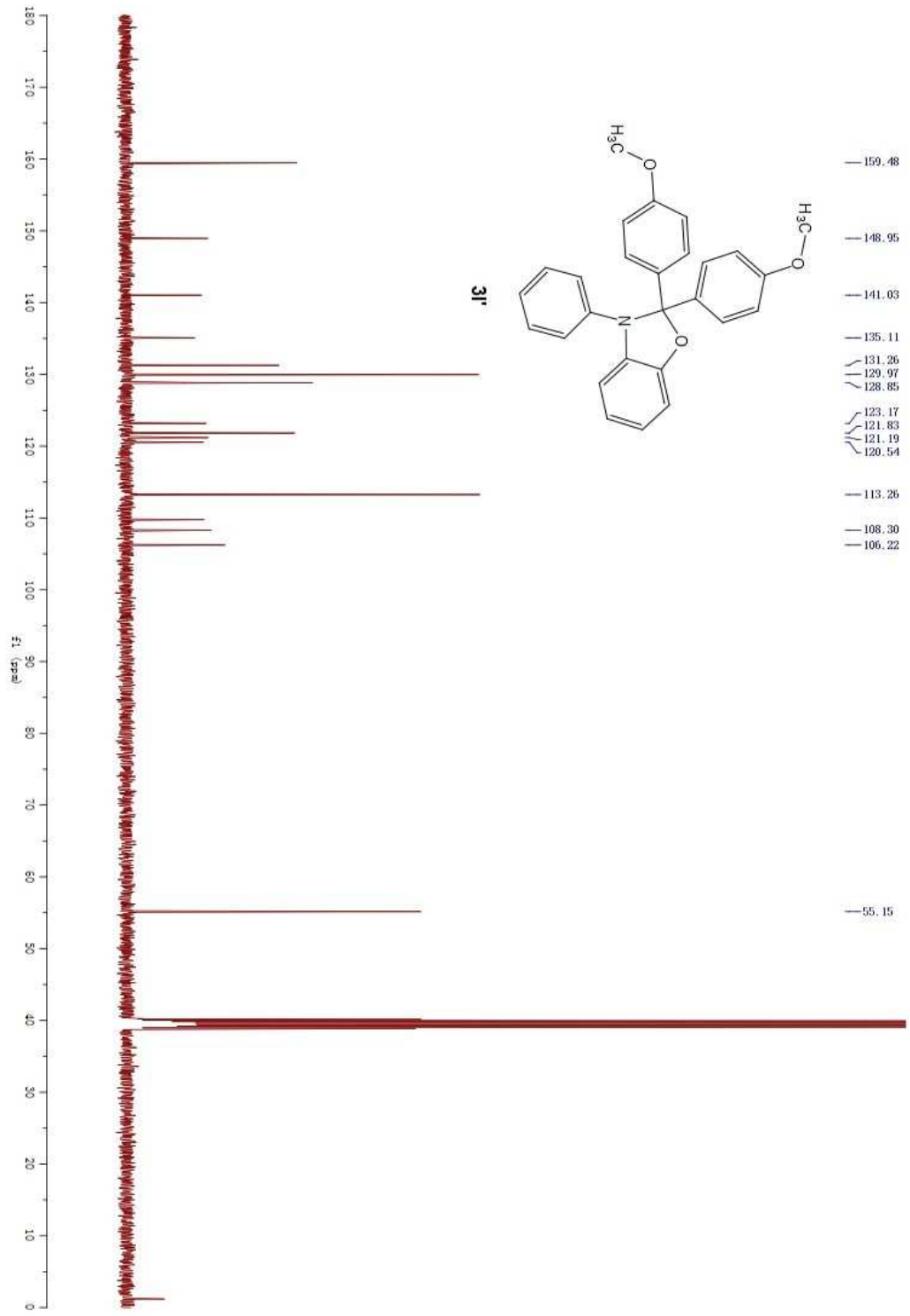
6.90
6.88
6.86
6.84
6.82
6.78
6.77
6.75
f1 (ppm)

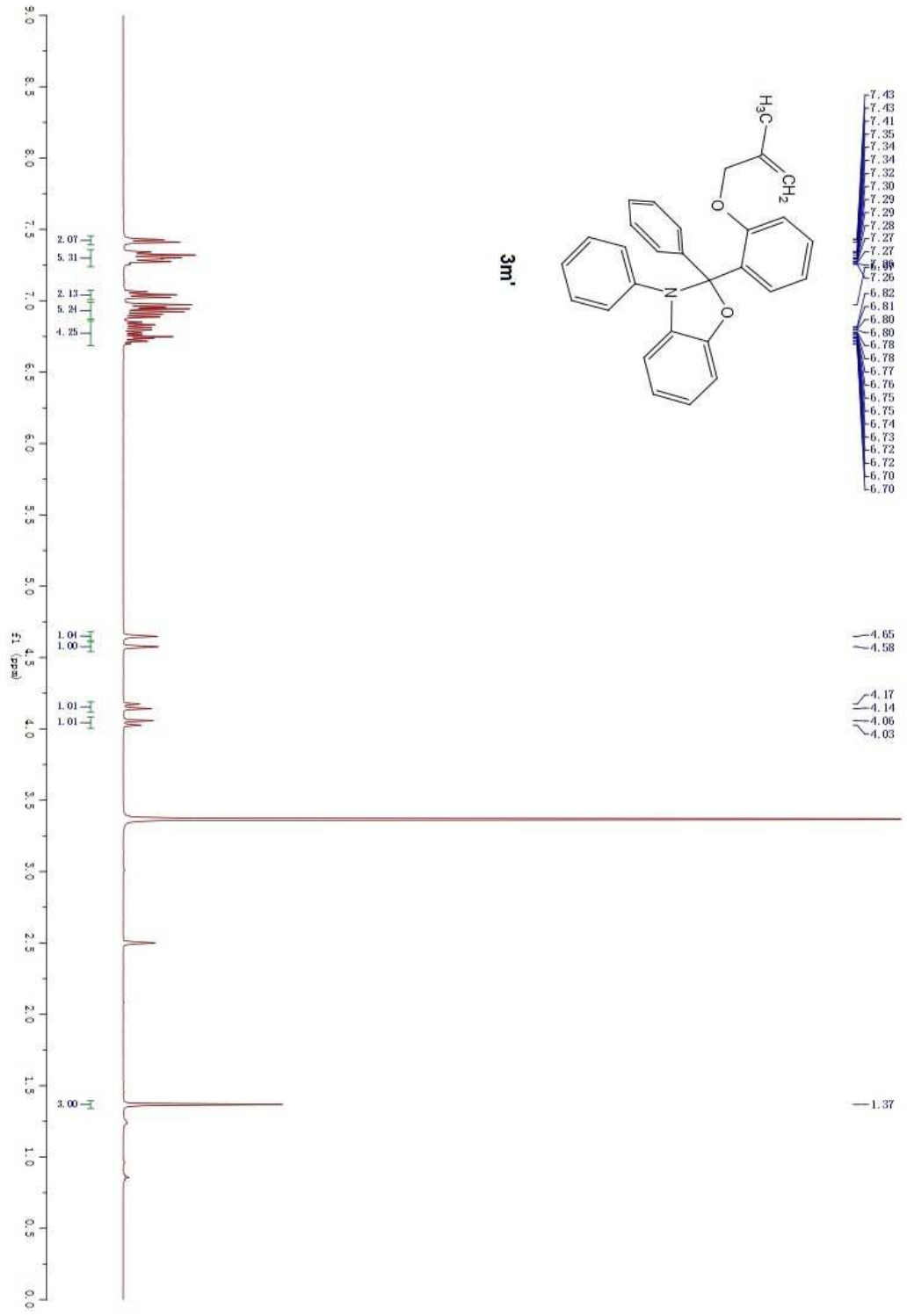

3j'
149.00
141.11
141.09
139.16
135.31
135.25
128.81
128.41
127.95
123.59
123.56
122.49
122.41
121.38
120.71
110.10
108.31
106.25
f1 (ppm)

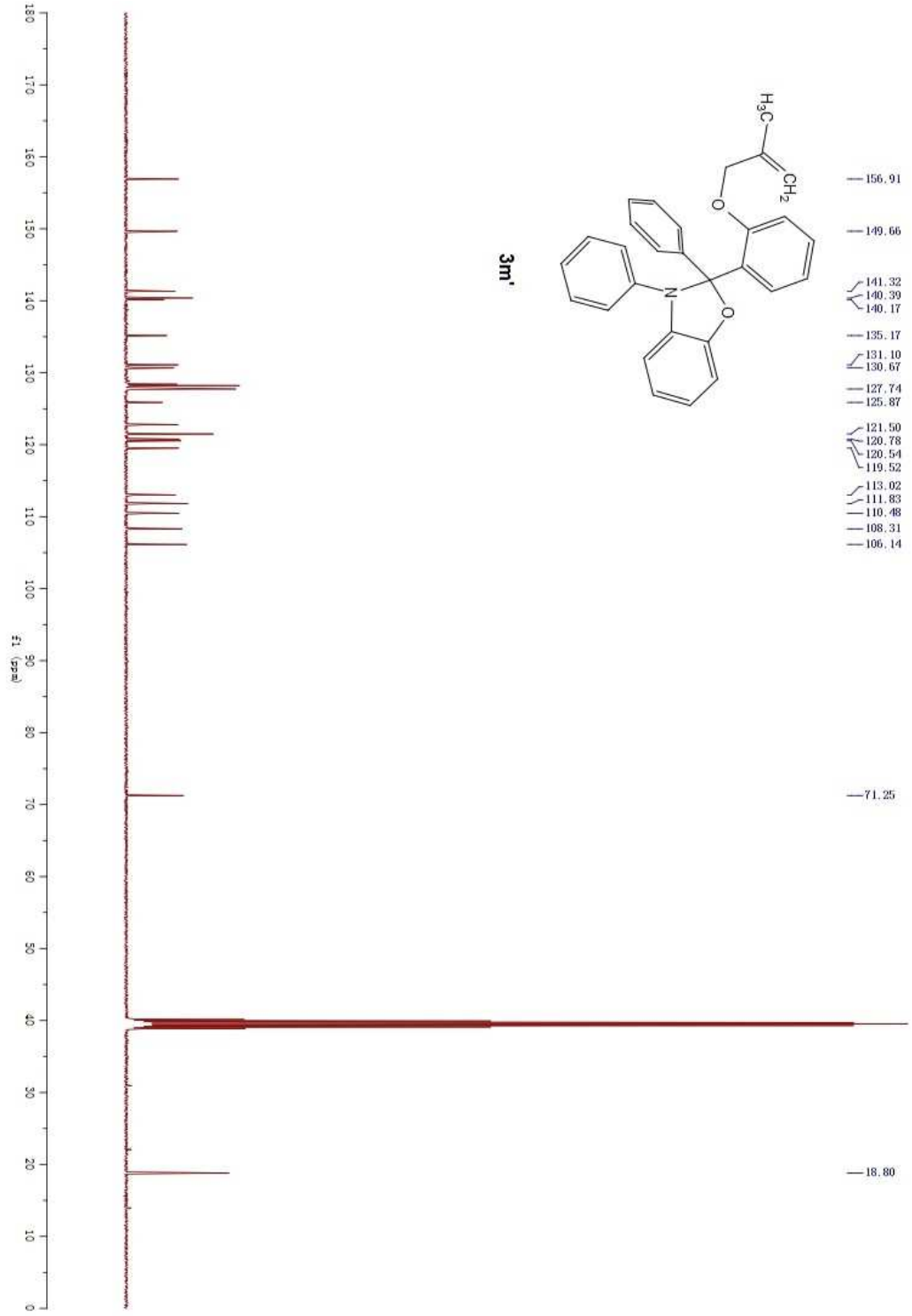

3k'
H3C
H3C
N
O
7.27
7.25
7.16
7.14
7.13
7.11
7.09
6.96
6.94
6.91
6.89
6.88
6.84
6.82
6.80
6.76
6.74
6.72
4.15
6.20
2.06
2.05
2.03
1.03
6.00
2.27
f1 (ppm)

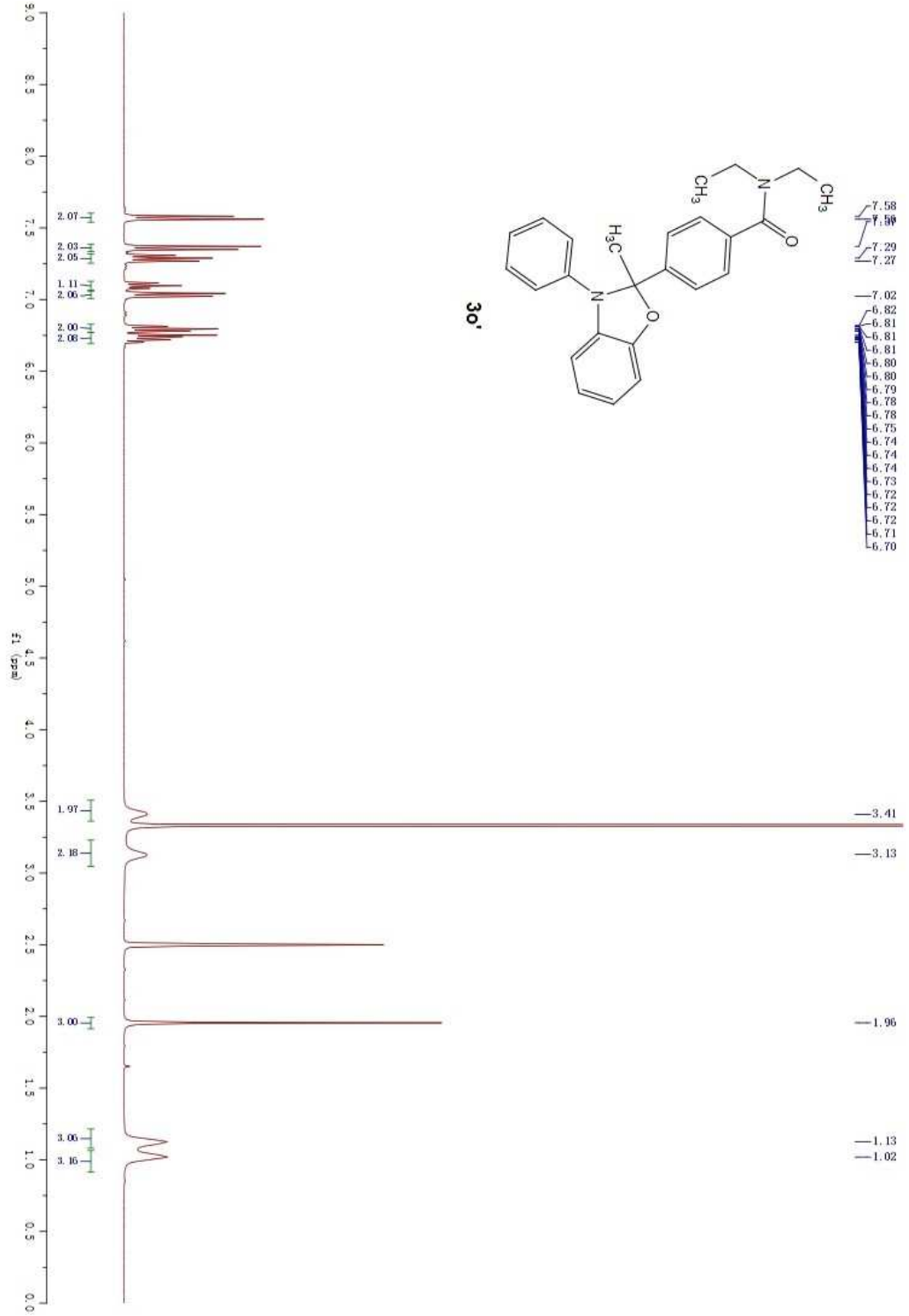

3k'
H3C
H3C
N
O
148.97
140.95
138.33
136.35
135.15
128.84
128.51
128.47
123.29
121.99
121.24
120.52
109.73
108.27
106.23
99.54
20.68
f1 (ppm)


3l'
H3C
O
H3C
O
N
O
4.00
2.04
2.14
5.92
2.02
1.00
6.08
7.30
7.28
7.10
6.96
6.94
6.91
6.88
6.84
6.83
6.82
6.82
6.81
6.81
6.80
6.79
6.76
6.75
6.74
6.72
6.72
3.72
f1 (ppm)


3l'
H3C
O
H3C
O
N
O
159.48
148.95
141.03
135.11
131.26
129.97
128.85
123.17
121.83
121.19
120.54
113.26
108.30
106.22
55.15
f1 (ppm)


3m'
H3C
CH2
O
N
O
7.43
7.43
7.41
7.35
7.34
7.34
7.32
7.30
7.29
7.29
7.28
7.27
7.27
7.26
6.82
6.81
6.80
6.80
6.78
6.78
6.77
6.76
6.75
6.75
6.74
6.73
6.72
6.72
6.70
6.70
4.65
4.58
4.17
4.14
4.06
4.03
1.37
2.07
5.31
2.13
5.24
4.25
1.04
1.00
1.01
1.01
3.00
f1 (ppm)


3m'
H3C
CH2
O
N
O
156.91
149.66
141.32
140.39
140.17
135.17
131.10
130.67
127.74
125.87
121.50
120.78
120.54
119.52
113.02
111.83
110.48
108.31
106.14
71.25
18.80
f1 (ppm)


3o'
f1 (ppm)
2.07
2.03
2.05
1.11
2.06
2.00
2.08
1.97
2.18
3.00
3.06
3.16
7.58
7.29
7.27
7.02
6.82
6.81
6.81
6.81
6.80
6.80
6.79
6.78
6.78
6.75
6.74
6.74
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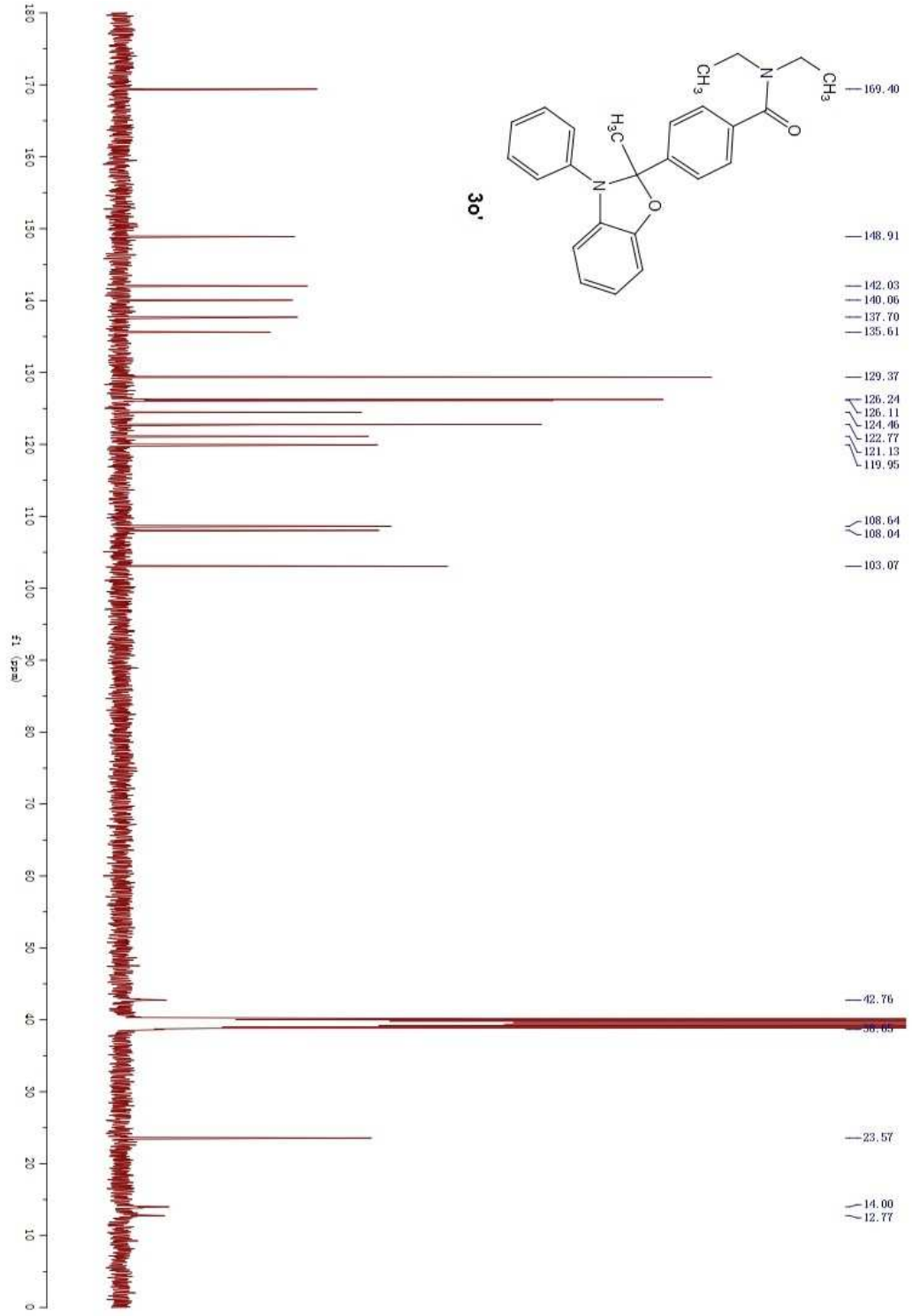
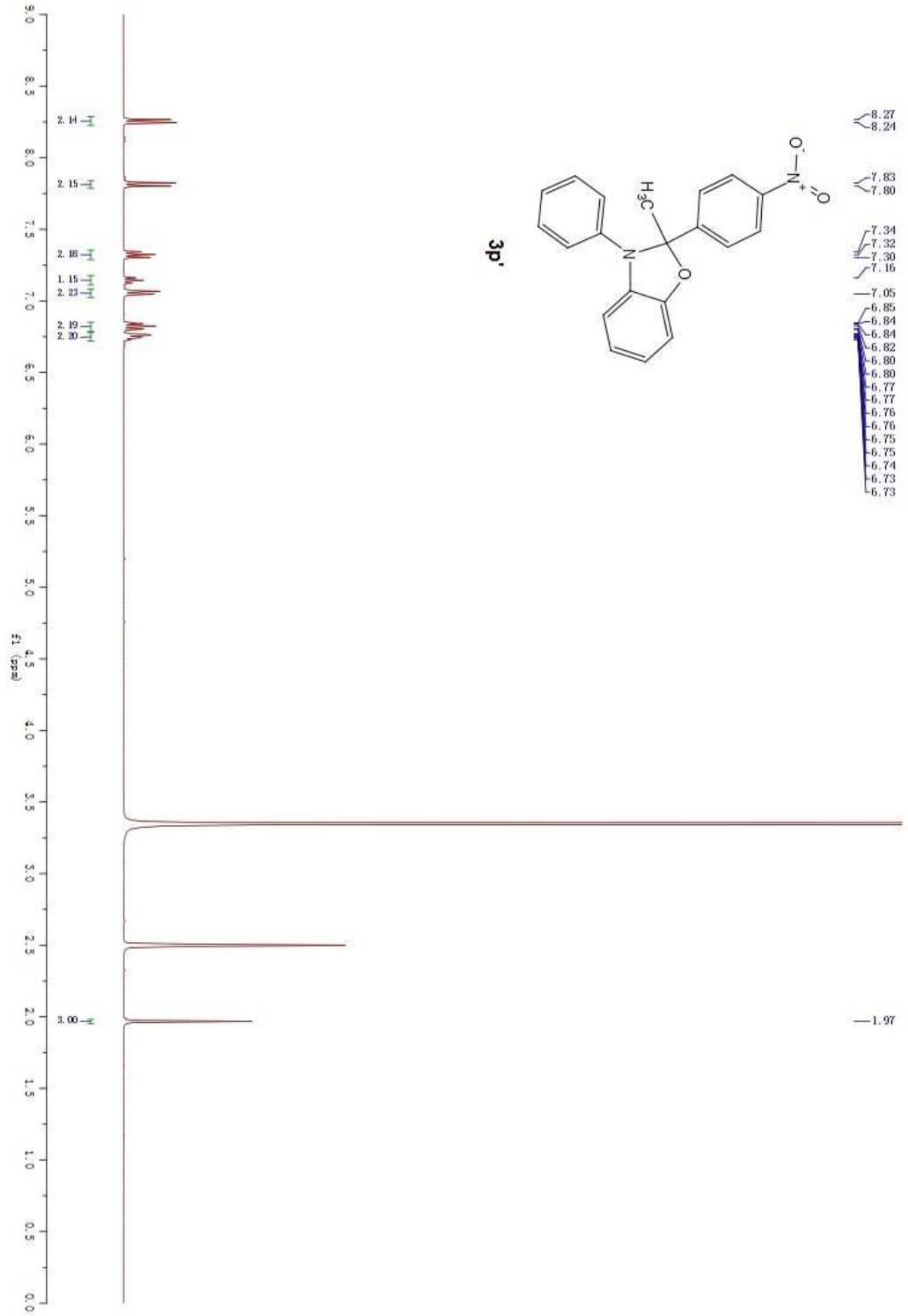
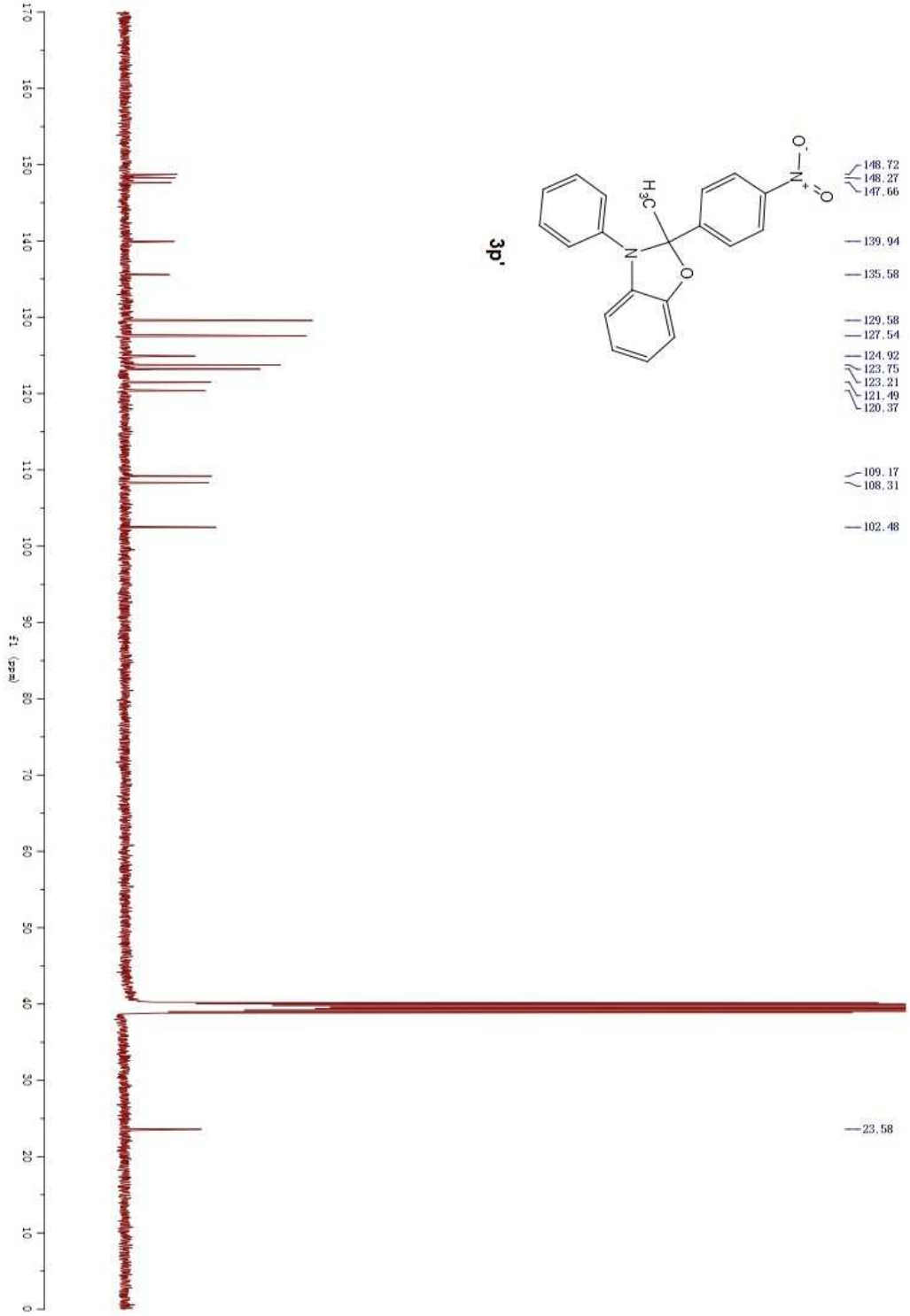
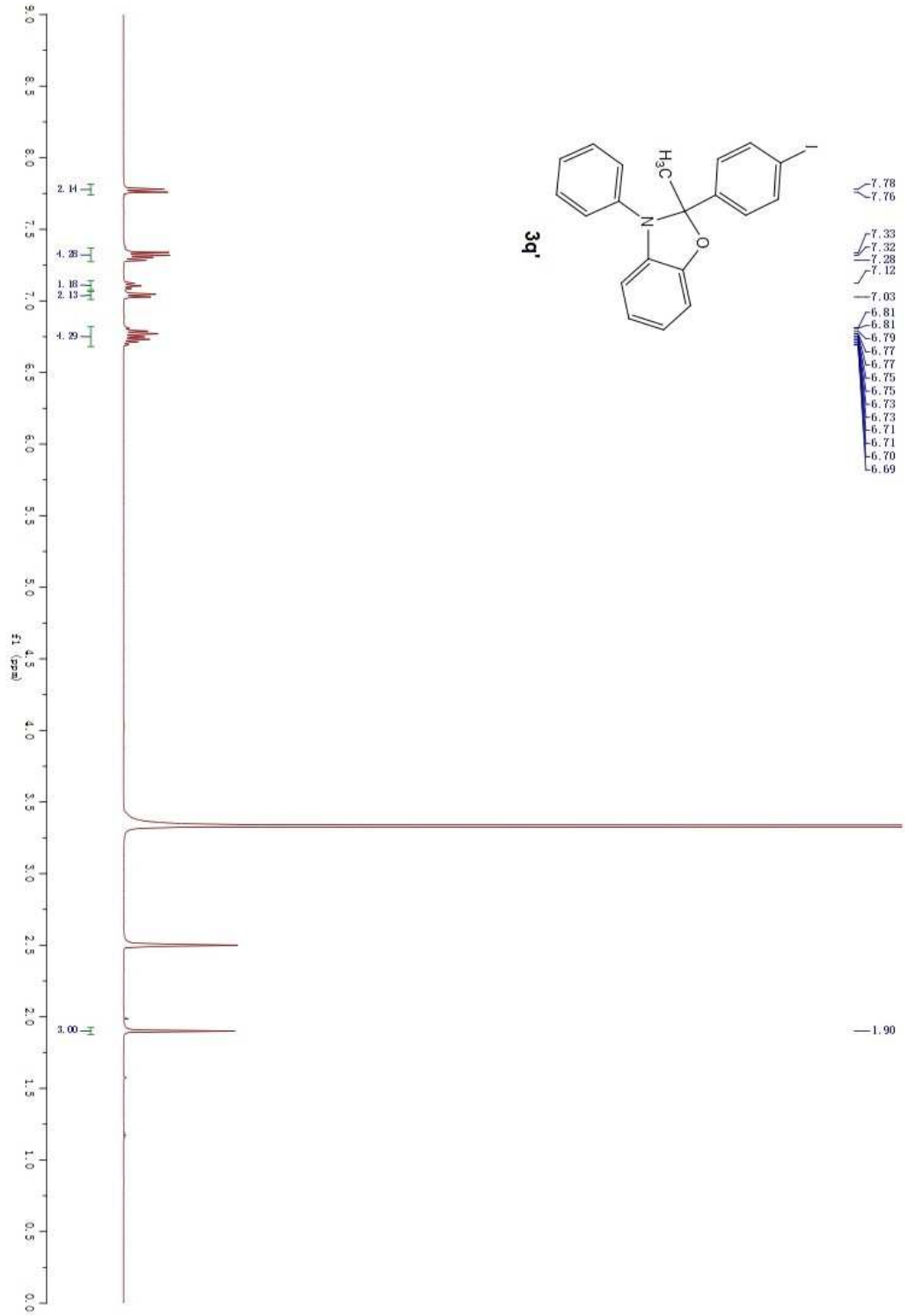
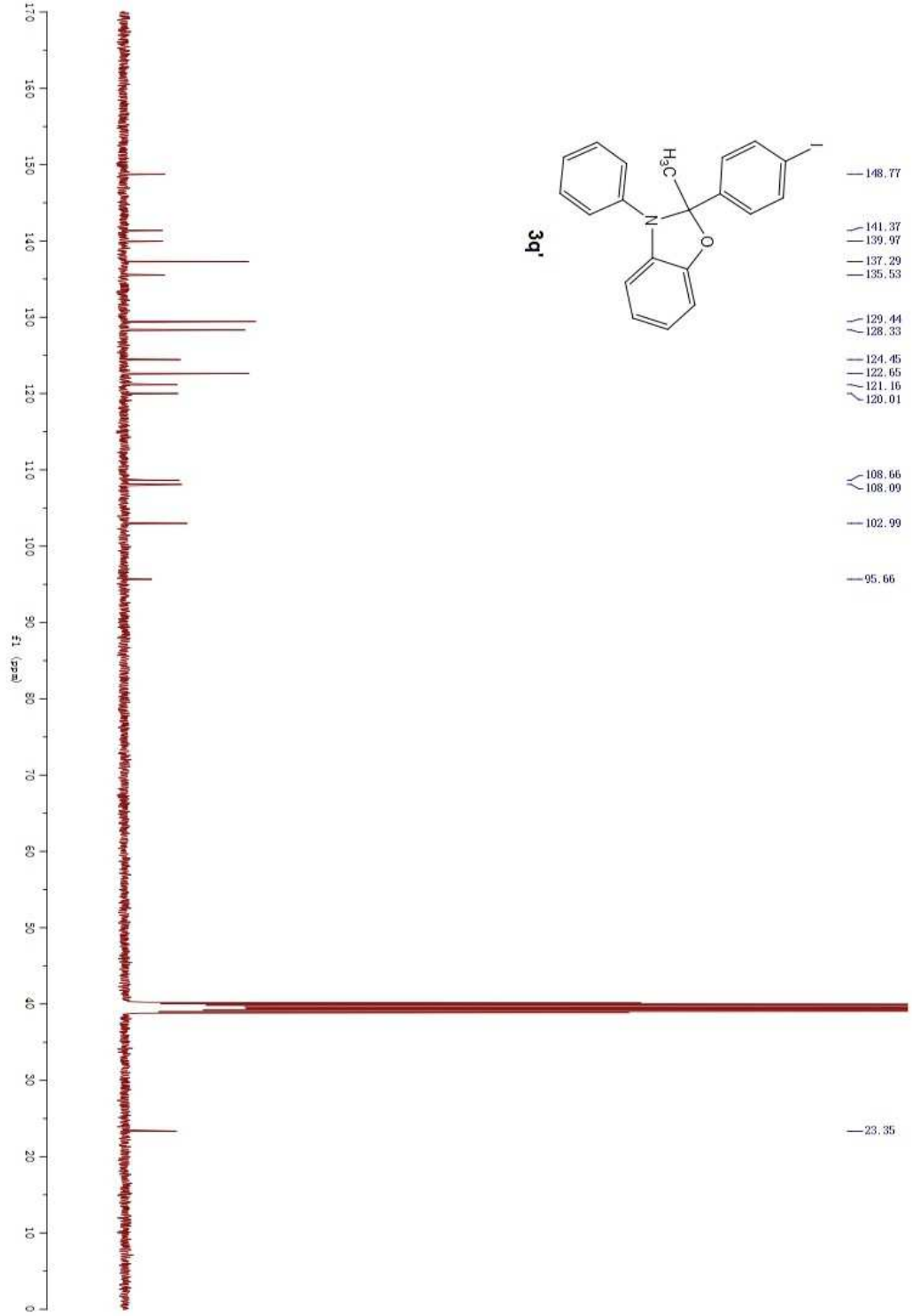
6.70
3.41
3.13
1.96
1.13
1.02

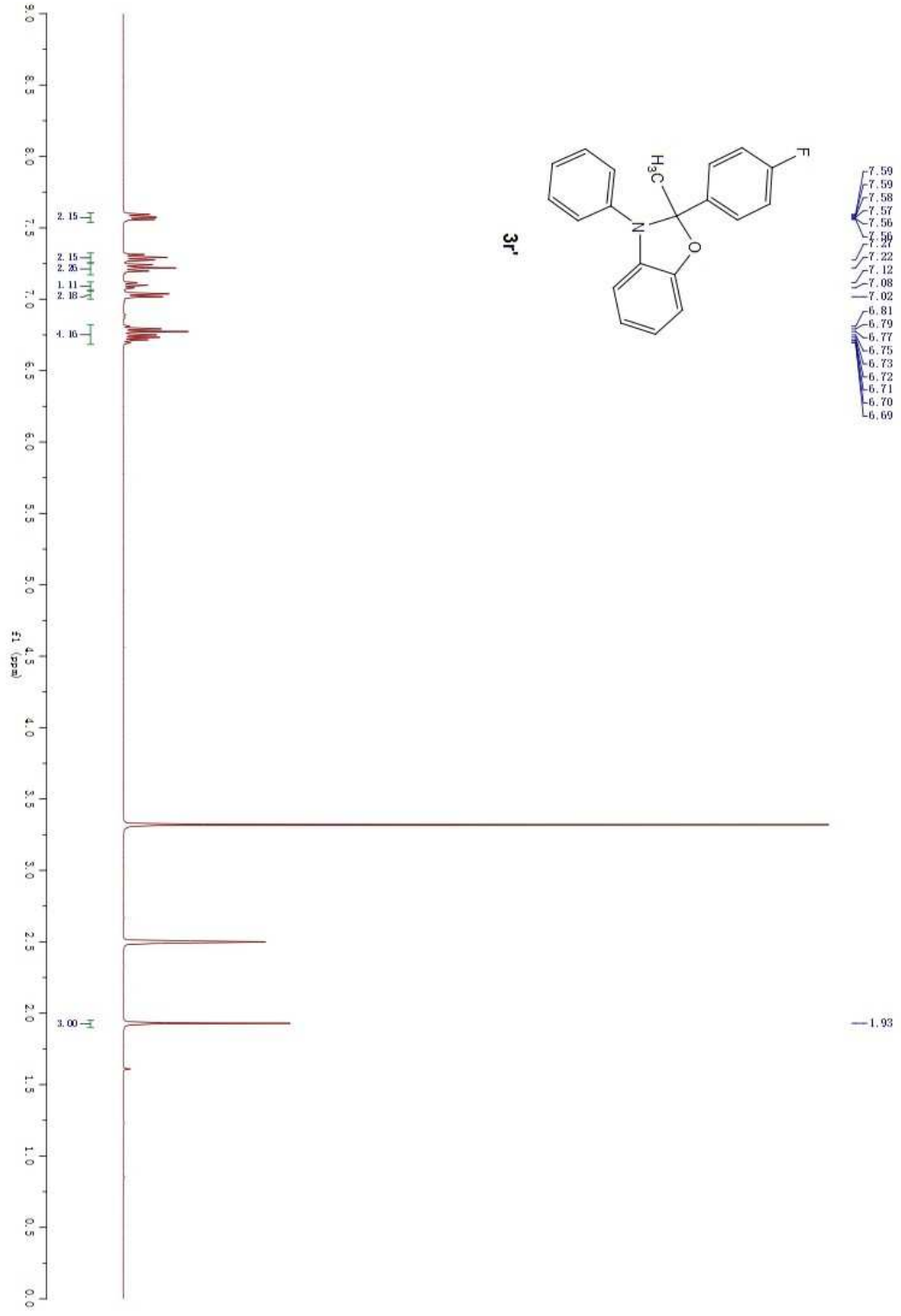

3o'
169.40
148.91
142.03
140.06
137.70
135.61
129.37
126.24
126.11
124.46
122.77
121.13
119.95
108.64
108.04
103.07
42.76
23.57
14.00
12.77
f1 (ppm)

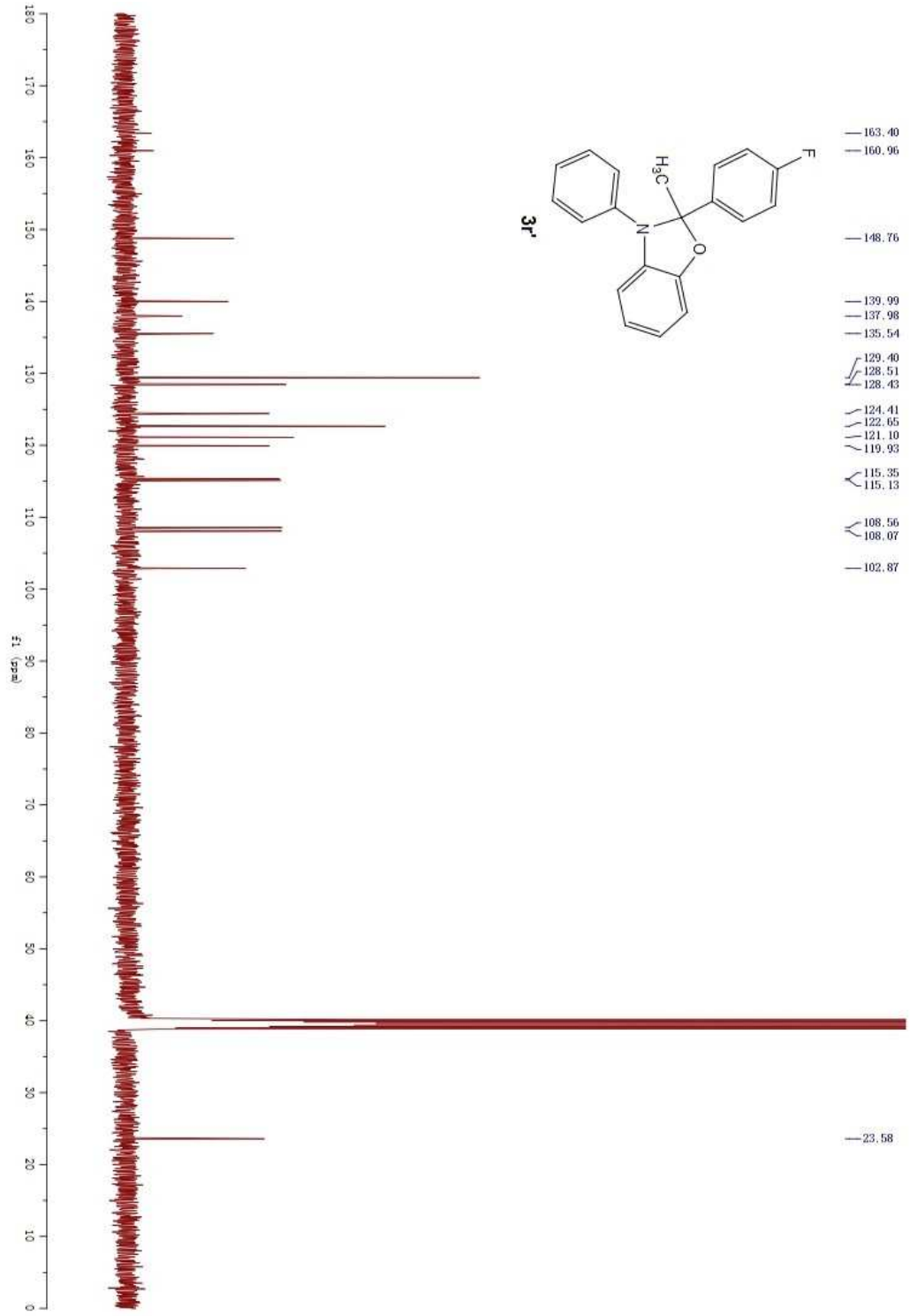

3p'
8.27
8.24
7.83
7.80
7.34
7.32
7.30
7.16
7.05
6.85
6.84
6.84
6.82
6.80
6.80
6.77
6.77
6.76
6.76
6.75
6.75
6.74
6.73
6.73
1.97
2.14
2.15
2.18
1.15
2.23
2.19
2.20
3.00
f1 (ppm)

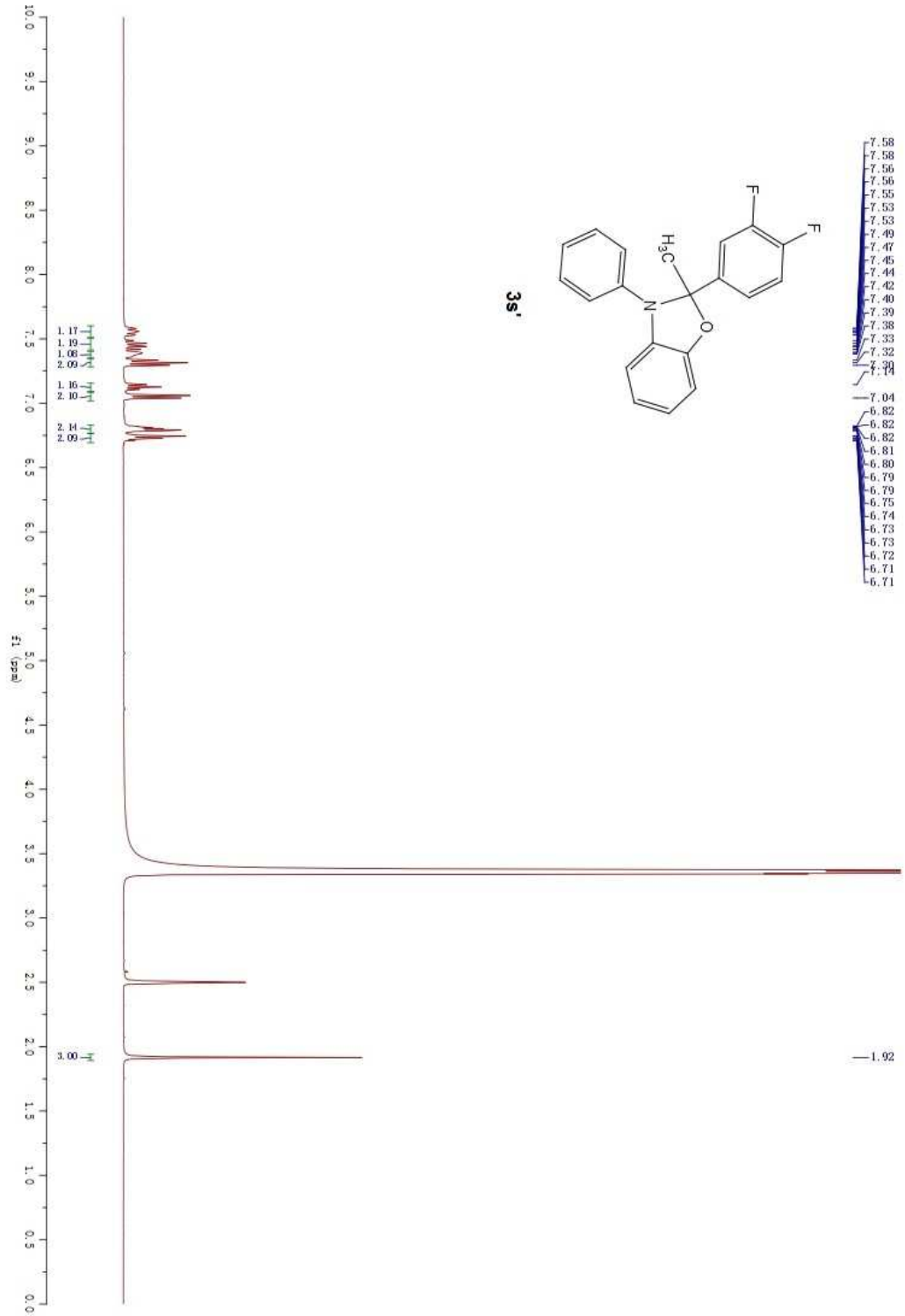

3p'
148.72
148.27
147.66
139.94
135.58
129.58
127.54
124.92
123.75
123.21
121.49
120.37
109.17
108.31
102.48
23.58
f1 (ppm)

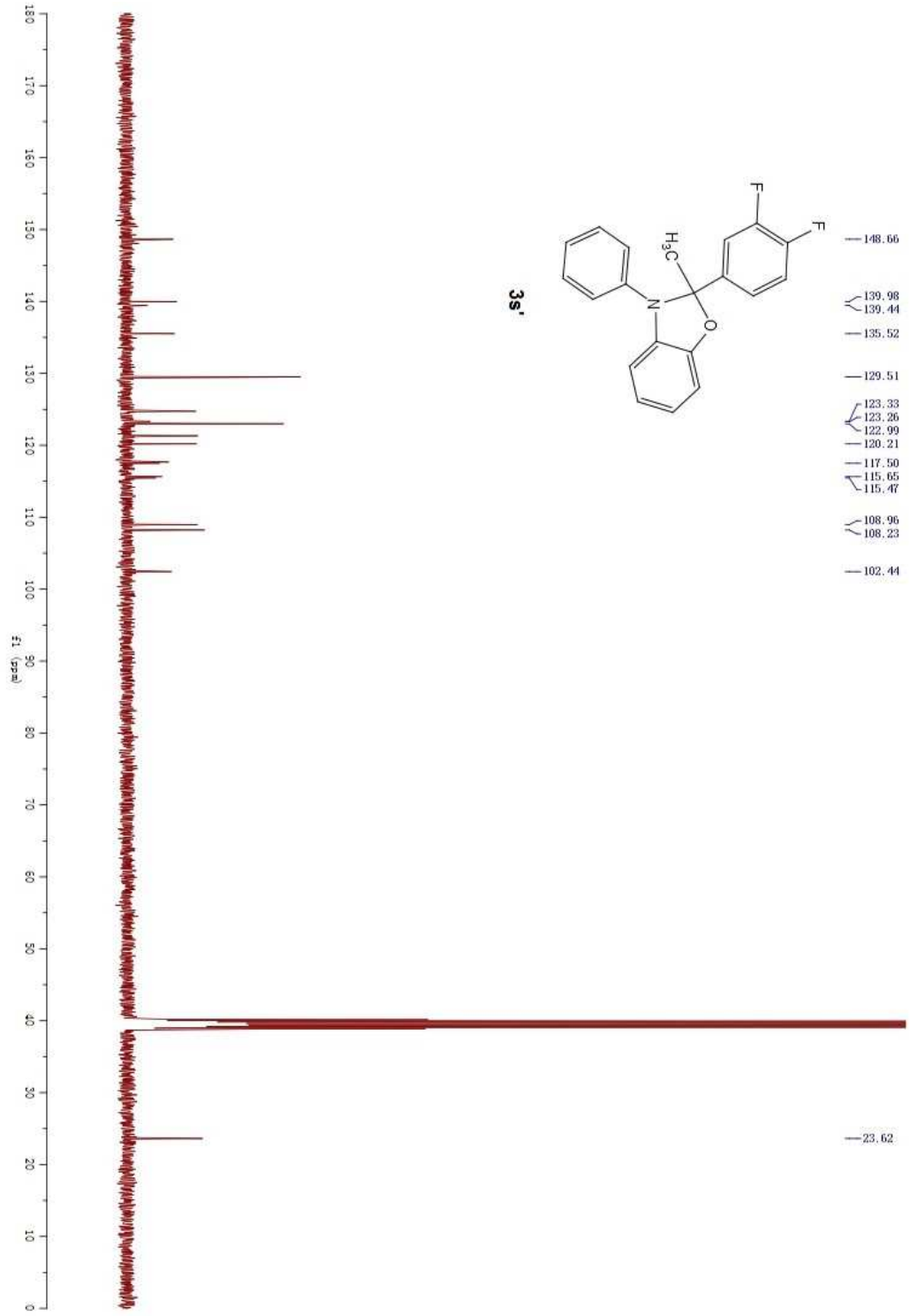

3q'
H3C
N
O
I
7.78
7.76
7.33
7.32
7.28
7.12
7.03
6.81
6.81
6.79
6.77
6.77
6.75
6.75
6.73
6.73
6.71
6.71
6.70
6.69
2.14
4.26
1.18
2.13
4.29
3.00
1.90
f1 (ppm)

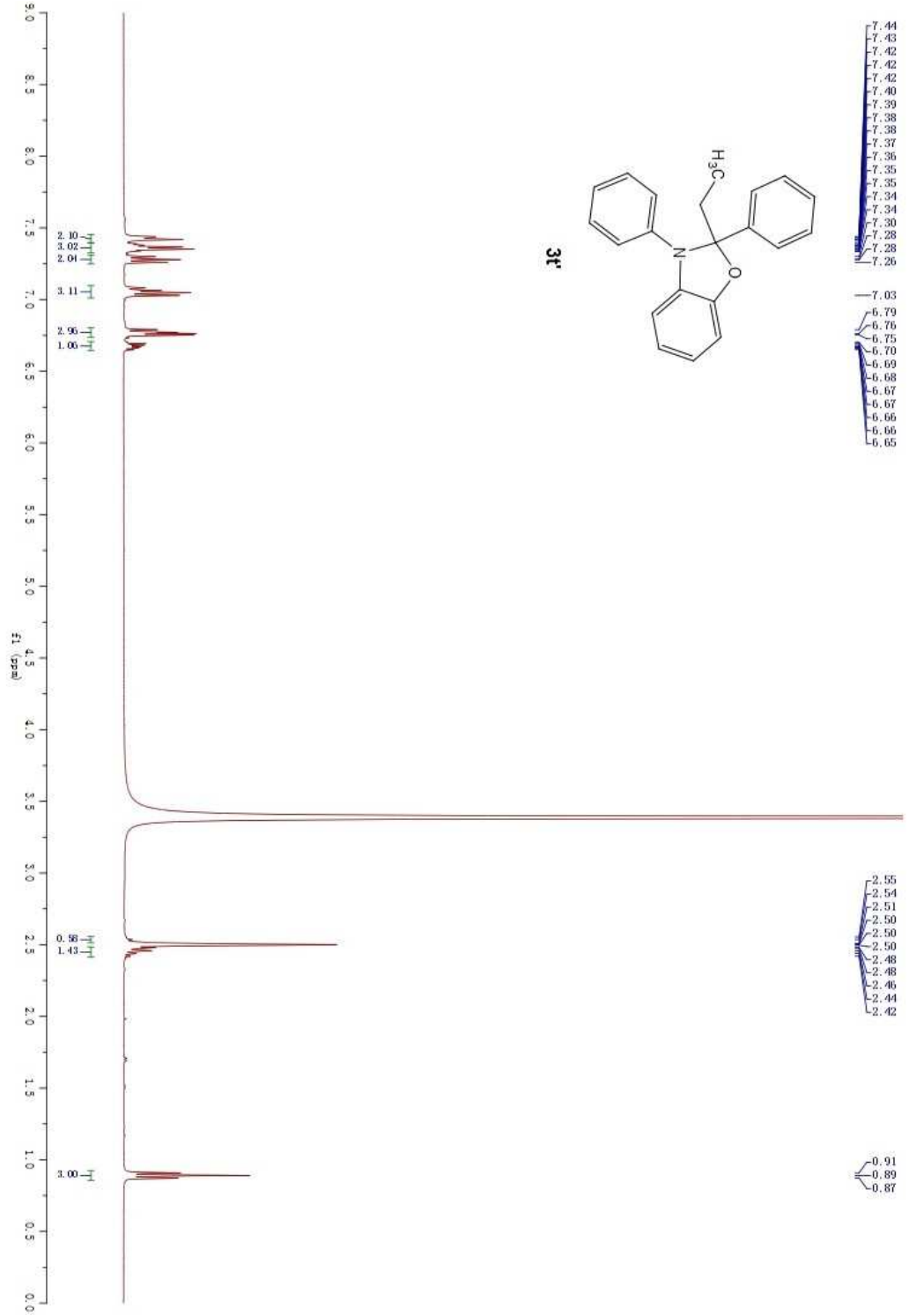

3q'
148.77
141.37
139.97
137.29
135.53
129.44
128.33
124.45
122.65
121.16
120.01
108.66
108.09
102.99
95.66
23.35
f1 (ppm)

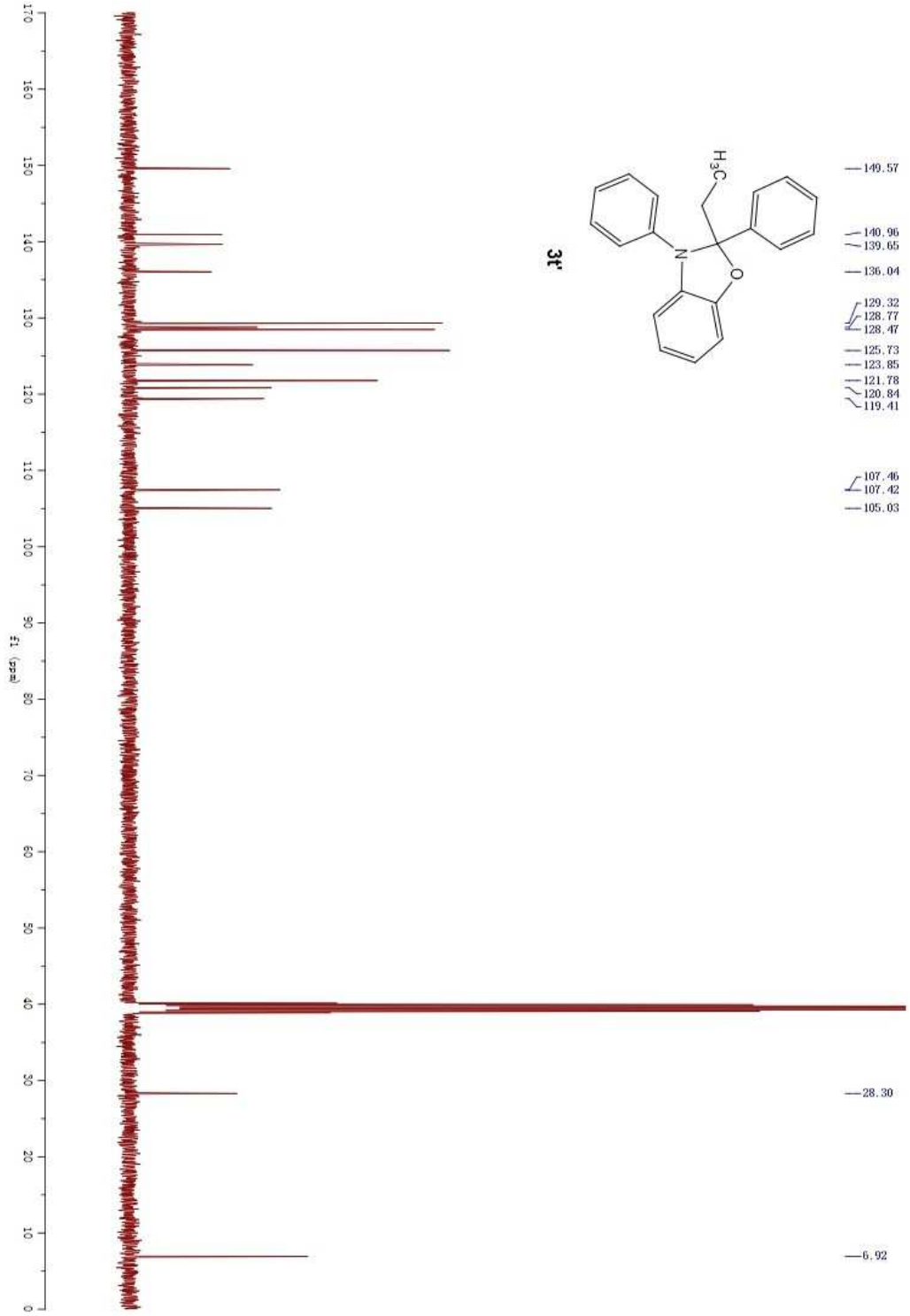

3r'
F
H3C
N
O
7.59
7.59
7.58
7.57
7.56
7.50
7.27
7.22
7.12
7.08
7.02
6.81
6.79
6.77
6.75
6.73
6.72
6.71
6.70
6.69
2.15
2.15
2.25
1.11
2.18
4.16
3.00
1.93
f1 (ppm)

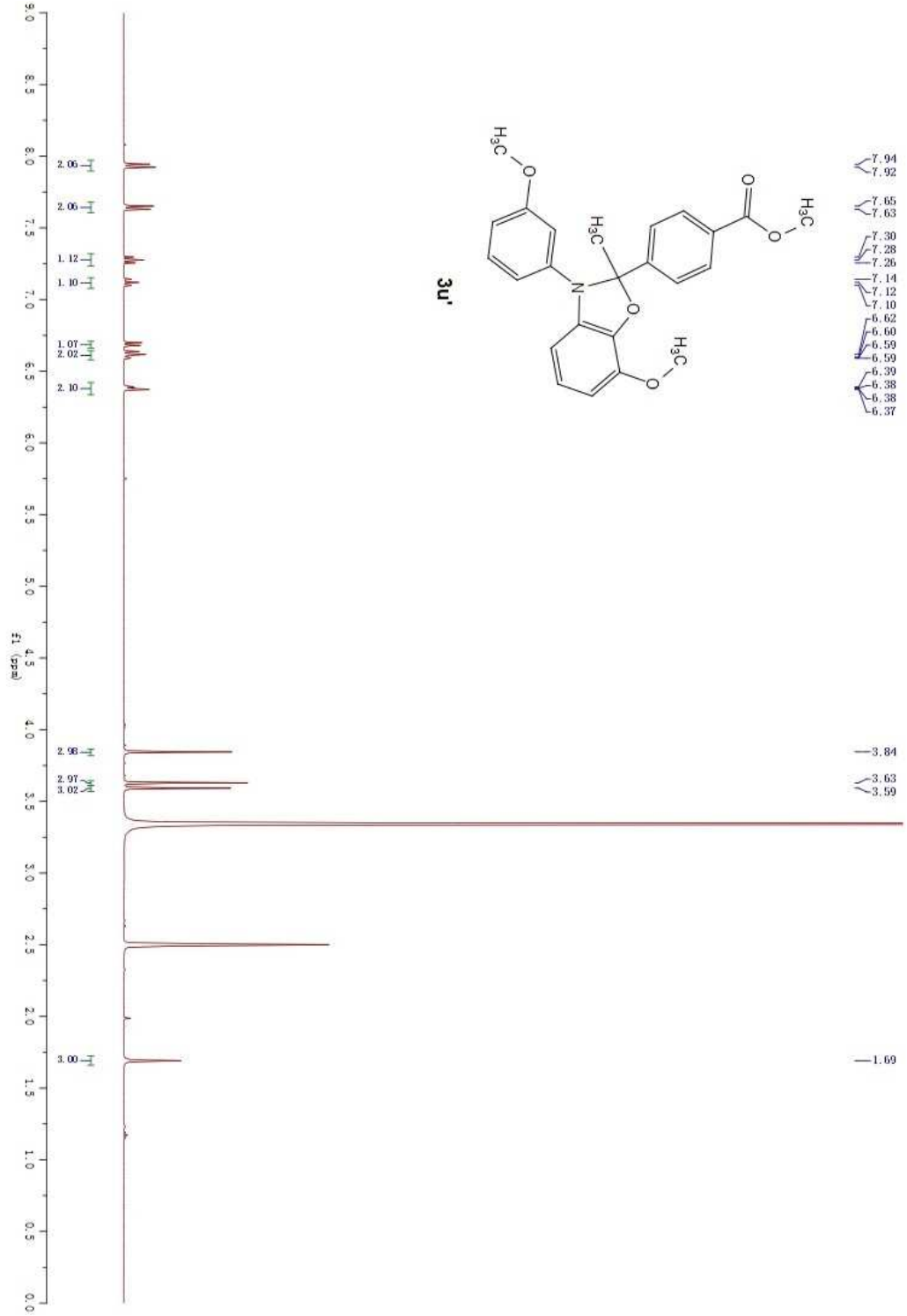

3r'
H3C
F
N
O
163.40
160.96
148.76
139.99
137.98
135.54
129.40
128.51
128.43
124.41
122.65
121.10
119.93
115.35
115.13
108.56
108.07
102.87
23.58
f1 (ppm)

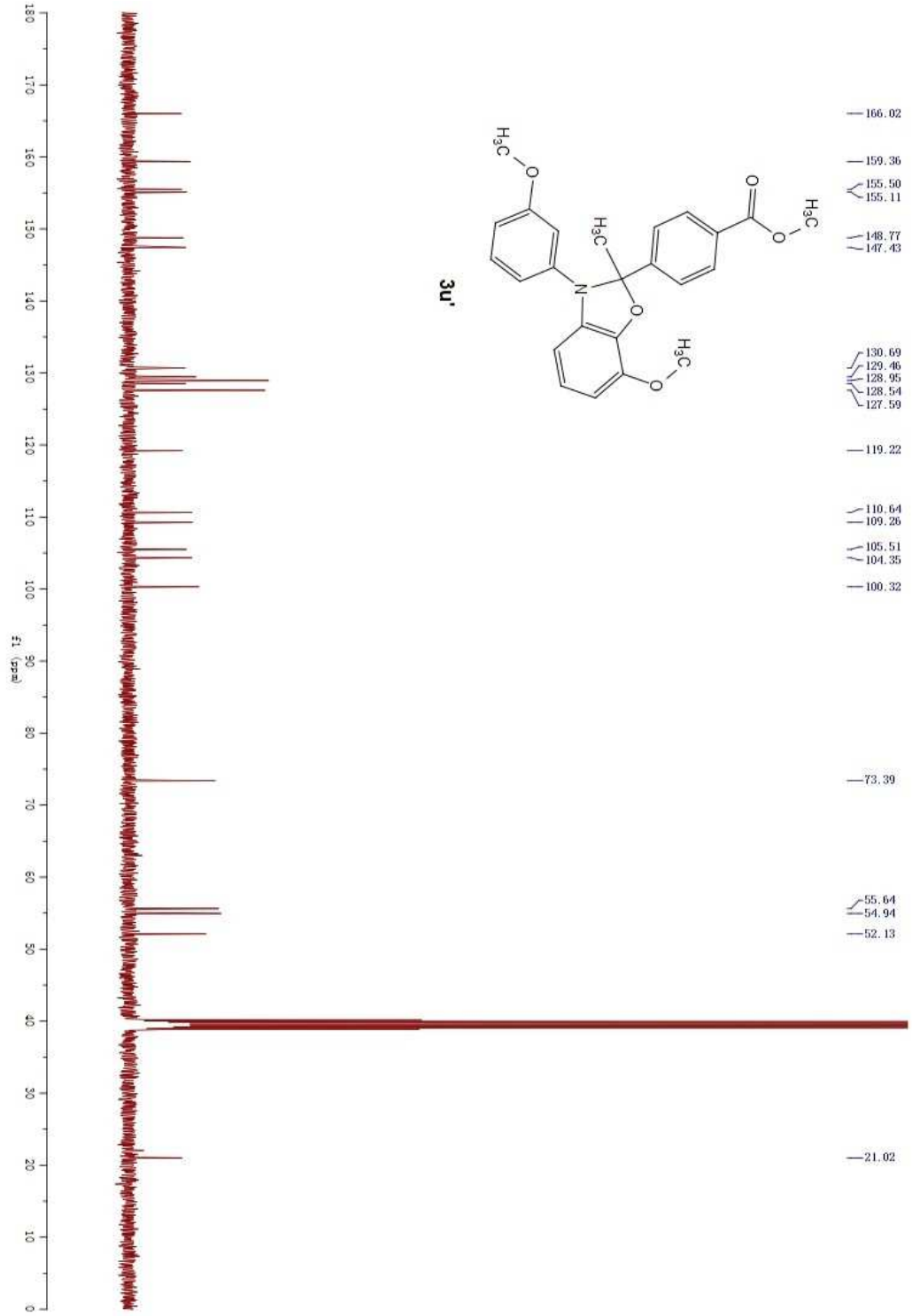

3s'
F
F
H3C
N
O
7.58
7.58
7.56
7.56
7.55
7.53
7.53
7.49
7.47
7.45
7.44
7.42
7.40
7.39
7.38
7.33
7.32
7.30
7.14
7.04
6.82
6.82
6.82
6.81
6.80
6.79
6.79
6.75
6.74
6.73
6.73
6.72
6.71
6.71
1.17
1.19
1.08
2.09
1.16
2.10
2.14
2.09
3.00
1.92
f1 (ppm)

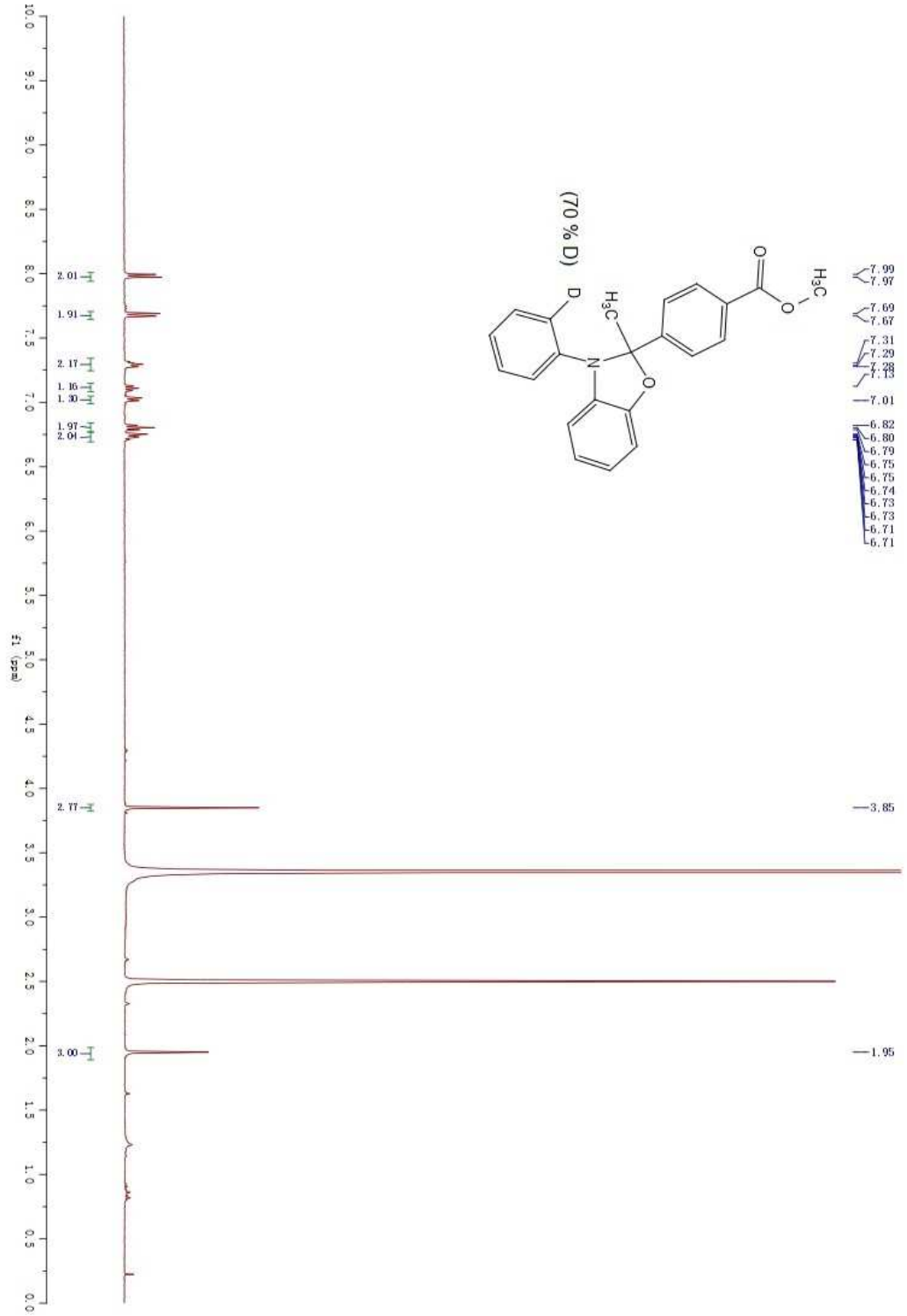

3s'
F
F
H3C
N
O
148.66
139.98
139.44
135.52
129.51
123.33
123.26
122.99
120.21
117.50
115.65
115.47
108.96
108.23
102.44
23.62
f1 (ppm)

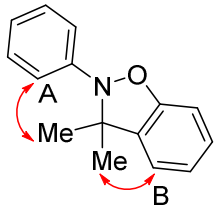

3t'
H3C
N
O
7.44
7.43
7.42
7.42
7.42
7.40
7.39
7.38
7.38
7.37
7.36
7.35
7.35
7.34
7.34
7.30
7.28
7.28
7.26
7.03
6.79
6.76
6.75
6.70
6.69
6.68
6.67
6.67
6.66
6.66
6.65
2.55
2.54
2.51
2.50
2.50
2.50
2.48
2.48
2.46
2.44
2.42
0.91
0.89
0.87
2.10
3.02
2.04
3.11
2.96
1.06
0.98
1.43
3.00
f1 (ppm)

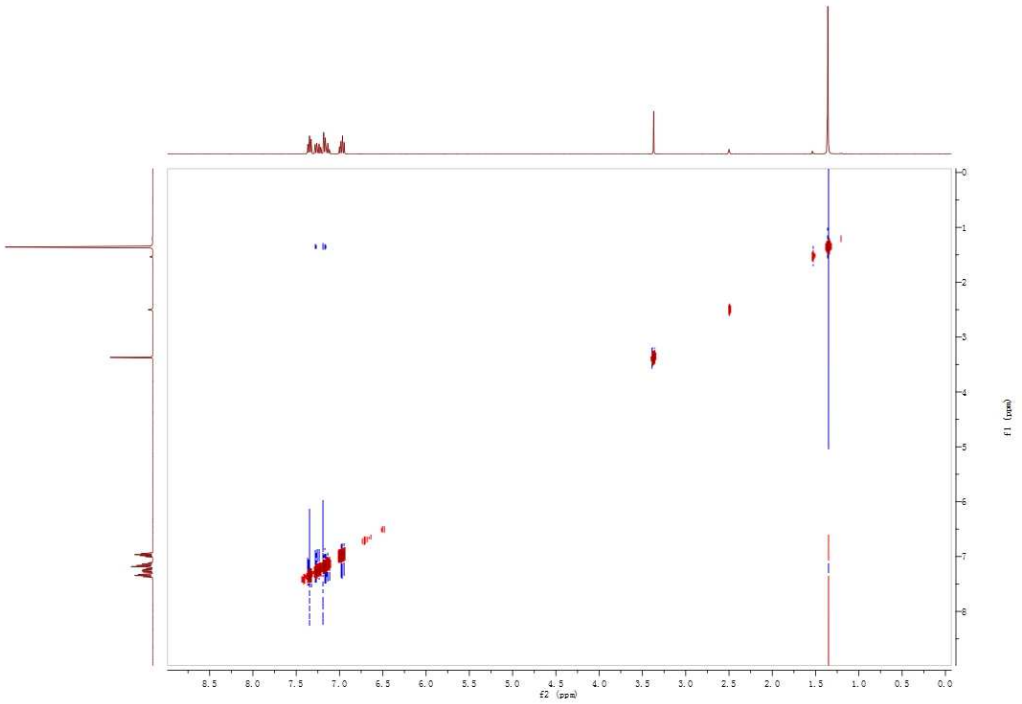

3t'
H3C
N
O
149.57
140.96
139.65
136.04
129.32
128.77
128.47
125.73
123.85
121.78
120.84
119.41
107.46
107.42
105.03
28.30
6.92
f1 (ppm)

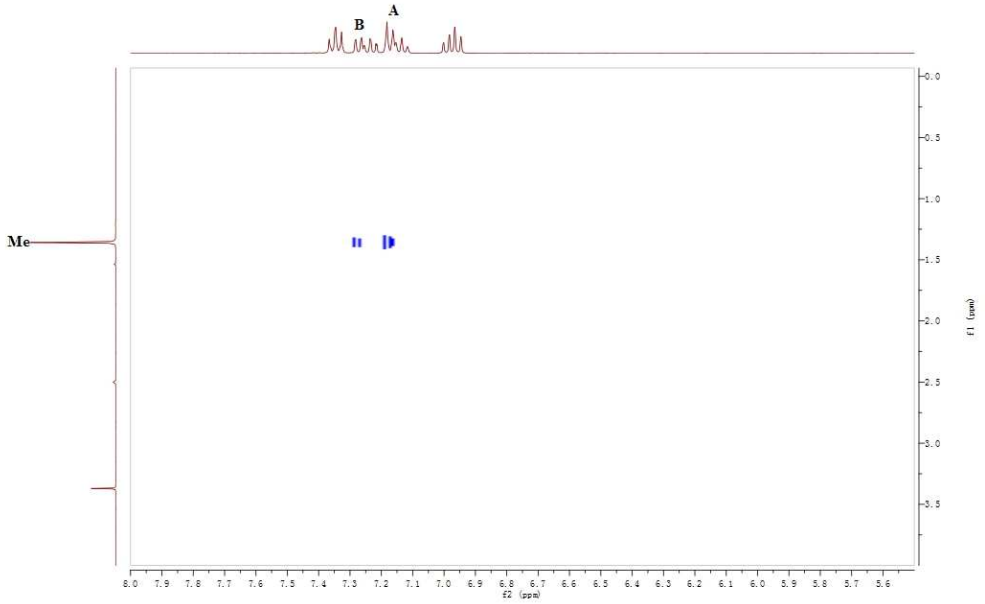

3u'
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
2.06
2.06
1.12
1.10
1.07
2.02
2.10
2.98
2.97
3.02
3.00
7.94
7.92
7.65
7.63
7.30
7.28
7.26
7.14
7.12
7.10
6.62
6.60
6.59
6.59
6.39
6.38
6.38
6.37
3.84
3.63
3.59
1.69
H3C
O
H3C
O
O
H3C
N
O
H3C
O

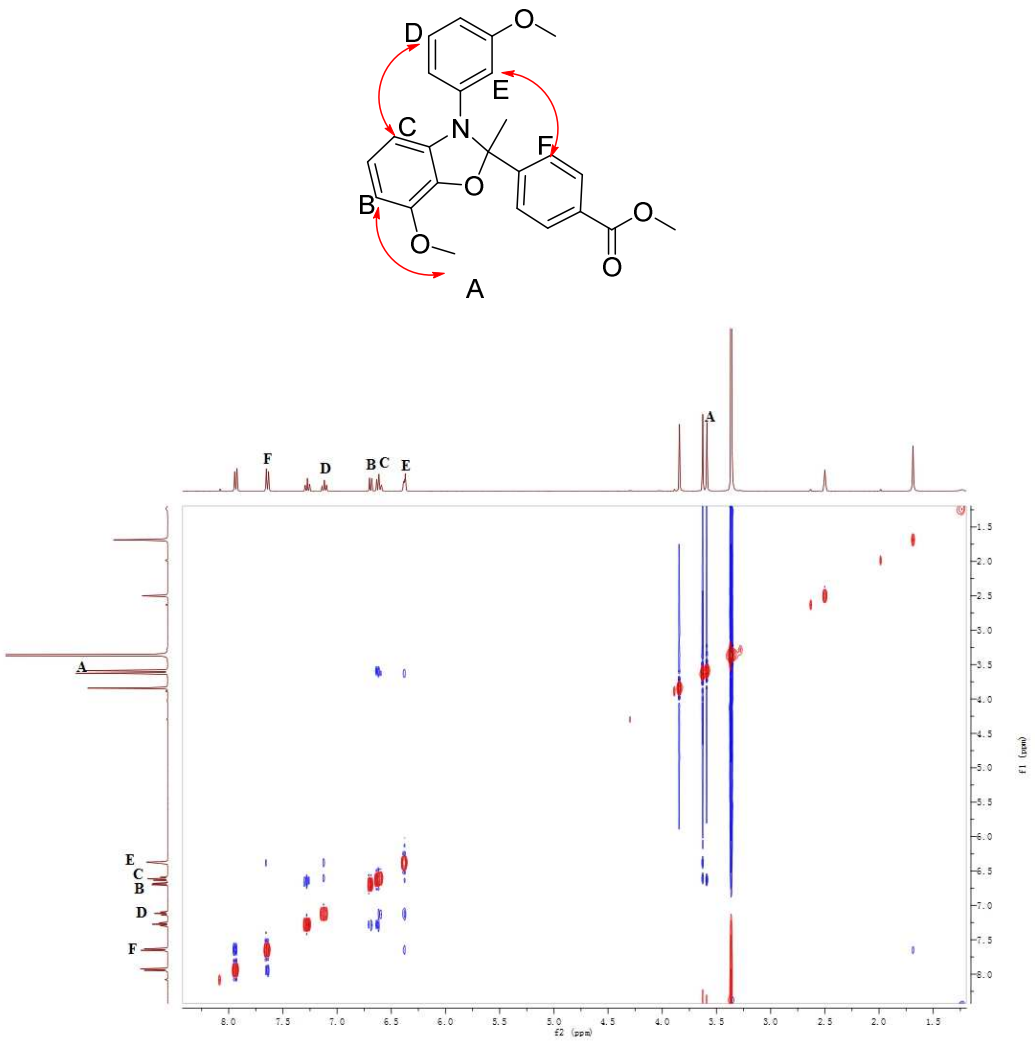

3u'
166.02
159.36
155.50
155.11
148.77
147.43
130.69
129.46
128.95
128.54
127.59
119.22
110.64
109.26
105.51
104.35
100.32
73.39
55.64
54.94
52.13
21.02
f1 (ppm)


(70 % D)
D
H3C
N
O
O
O
H3C
7.99
7.97
7.69
7.67
7.31
7.29
7.28
7.13
7.01
6.82
6.80
6.79
6.75
6.75
6.74
6.73
6.73
6.71
6.71
3.85
1.95
2.01
1.91
2.17
1.16
1.30
1.97
2.04
2.77
3.00
f1 (ppm)


A
N
O
Me
Me
B


f2 (ppm)
f1 (ppm)


A
B
Me
f2 (ppm)
f1 (ppm)


D
O
E
C
N
F
B
O
O
O
A
F
D
B C
E
A
E
C
B
D
F
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
f2 (ppm)
f1 (ppm)

3a

Bond precision: C-C = 0.0045 A Wavelength=0.71073

Cell:	a=9.4297(16)	b=9.7758(16)	c=18.503(3)
	alpha=90	beta=103.717(11)	gamma=90
Temperature:	276 K		

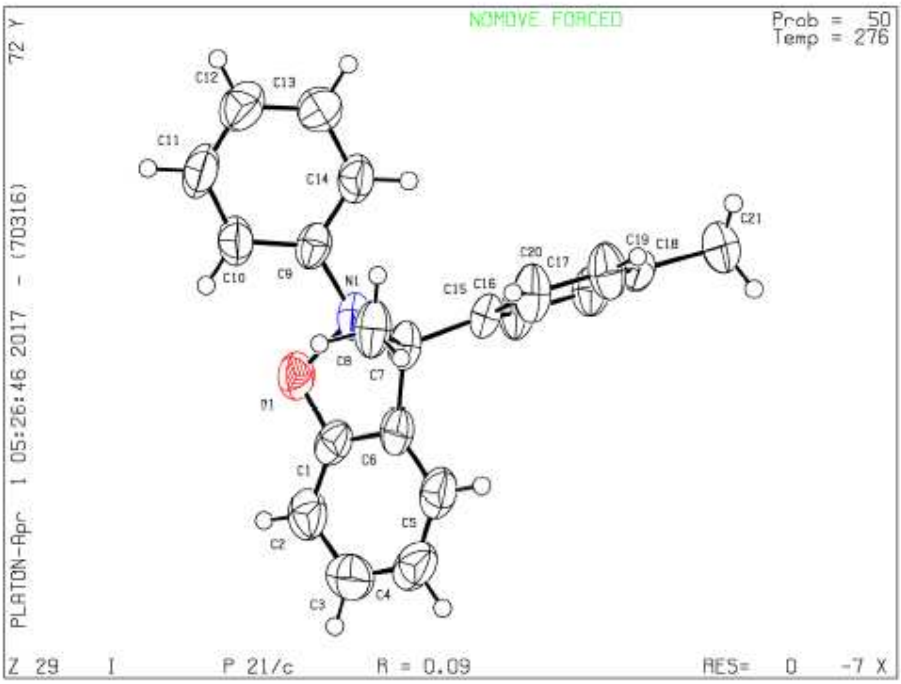
	Calculated	Reported
Volume	1657.0(5)	1657.1(5)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C21 H19 N O	?
Sum formula	C21 H19 N O	C21 H19 N O
Mr	301.37	301.37
Dx,g cm-3	1.208	1.208
Z	4	4
Mu (mm-1)	0.074	0.074
F000	640.0	640.0
F000'	640.25	
h,k,lmax	12,12,24	12,12,24
Nref	3828	3809
Tmin,Tmax	0.985,0.987	0.578,0.746
Tmin'	0.985	

Correction method= # Reported T Limits: Tmin=0.578 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.995 Theta(max)= 27.548

R(reflections)= 0.0850(2149) wR2(reflections)= 0.1976(3809)

S = 1.073 Npar= 210


NOMOVE FORCED
Prob = 50
Temp = 276
72 Y
PLATON-Apr 1 05:26:46 2017 - (70316)
C12
C13
C11
C14
C10
C9
N1
C8
C7
C15
C16
C20
C17
C19
C18
C21
O1
C1
C6
C2
C5
C3
C4
Z 29 I P 21/c R = 0.09 RES= 0 -7 X

3j

Bond precision: C-C = 0.0043 A Wavelength=0.71073

Cell:	a=10.4008(8)	b=19.8632(15)	c=8.9591(7)
	alpha=90	beta=91.710(2)	gamma=90
Temperature:	296 K		

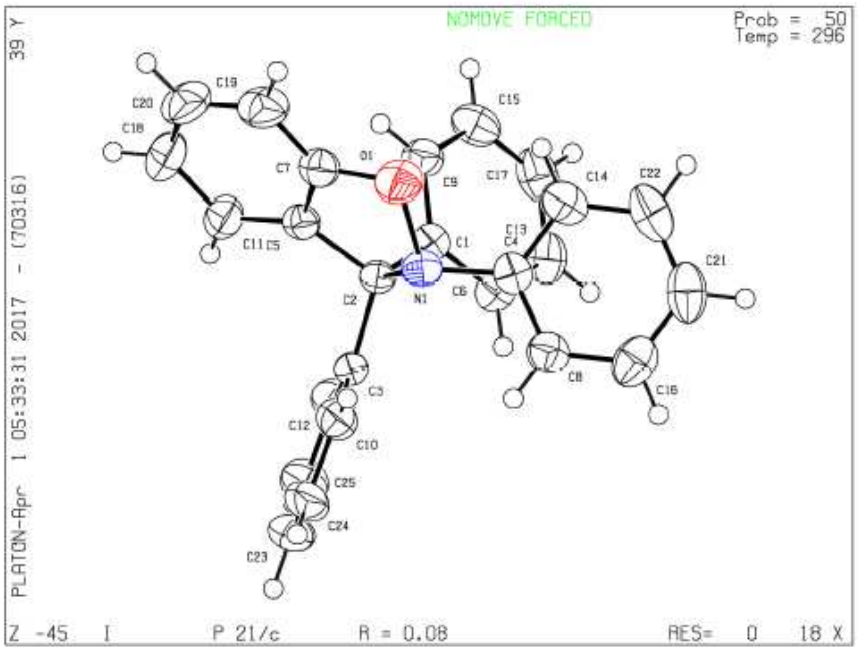
	Calculated	Reported
Volume	1850.1(2)	1850.1(2)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C25 H19 N O	?
Sum formula	C25 H19 N O	C25 H19 N O
Mr	349.41	349.41
Dx,g cm-3	1.255	1.254
Z	4	4
Mu (mm-1)	0.076	0.076
F000	736.0	736.0
F000'	736.29	
h,k,lmax	13,26,11	13,26,11
Nref	4605	4565
Tmin,Tmax	0.981,0.983	0.666,0.746
Tmin'	0.981	

Correction method= # Reported T Limits: Tmin=0.666 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.991 Theta(max)= 28.348

R(reflections)= 0.0845(2943) wR2(reflections)= 0.1859(4565)

S = 1.095 Npar= 244



3a'

Bond precision: C-C = 0.0028 A Wavelength=0.71073

Cell: a=9.468(3) b=19.074(7) c=9.275(3)
alpha=90 beta=103.80(2) gamma=90
Temperature: 276 K

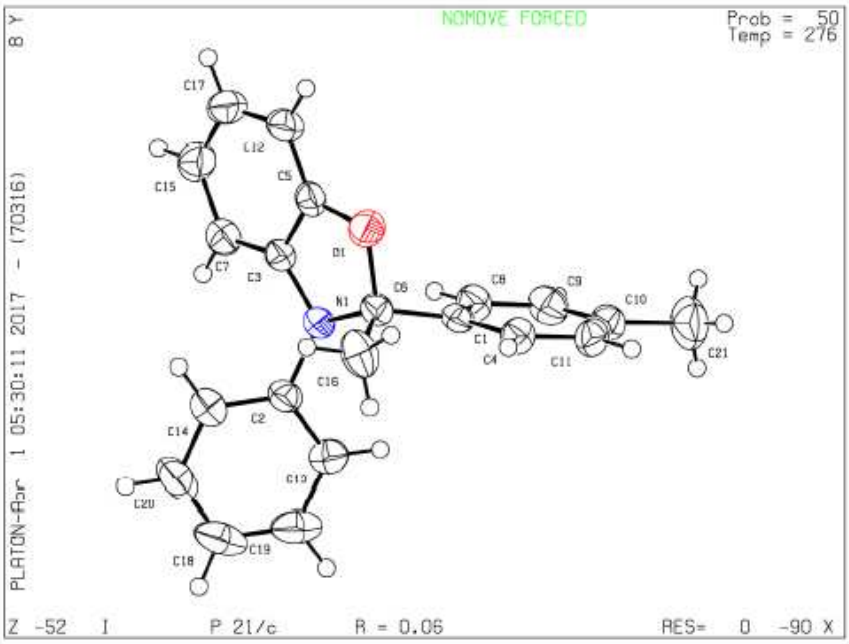
	Calculated	Reported
Volume	1626.7(10)	1626.6(10)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C21 H19 N O	?
Sum formula	C21 H19 N O	C21 H19 N O
Mr	301.37	301.37
Dx,g cm-3	1.231	1.231
Z	4	4
Mu (mm-1)	0.075	0.075
F000	640.0	640.0
F000'	640.25	
h,k,lmax	12,25,12	12,24,12
Nref	3894	3812
Tmin,Tmax	0.985,0.987	0.697,0.746
Tmin'	0.985	

Correction method= # Reported T Limits: Tmin=0.697 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.979 Theta(max)= 27.911

R(reflections)= 0.0557(2572) wR2(reflections)= 0.1453(3812)

S = 1.030 Npar= 211



3i'

Bond precision: C-C = 0.0039 A Wavelength=0.71073

Cell: a=9.1845(3) b=6.2326(3) c=15.9525(7)
alpha=90 beta=104.976(2) gamma=90
Temperature: 298 K

	Calculated	Reported
Volume	882.16(6)	882.16(6)
Space group	P 21	P 21
Hall group	P 2yb	P 2yb
Moiety formula	C24 H19 N O	?
Sum formula	C24 H19 N O	C24 H19 N O
Mr	337.40	337.40
Dx,g cm-3	1.270	1.270
Z	2	2
Mu (mm-1)	0.077	0.077
F000	356.0	356.0
F000'	356.14	
h,k,lmax	12,8,21	12,8,21
Nref	4389[2393]	4309
Tmin,Tmax	0.989,0.992	0.706,0.746
Tmin'	0.989	

Correction method= # Reported T Limits: Tmin=0.706 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 1.80/0.98 Theta(max)= 28.304

R(reflections)= 0.0463(3274) wR2(reflections)= 0.1194(4309)

S = 1.054 Npar= 236