Supporting Information

An efficient iodine pentoxide-triggered iodocarbocyclizations for the synthesis of iodooxindoles in water

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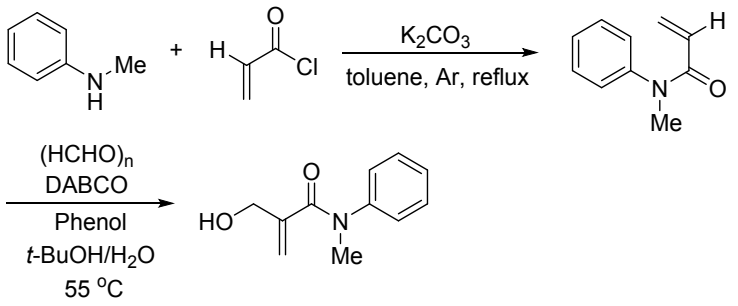
1. General remarks

All reagents used were obtained commercially and used without further purification unless indicated otherwise. Column chromatography was carried out on silica gel (300-400 grading). ^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ at room temperature on the Bruker spectrometer (400 MHz ^{1}H). The chemical-shifts scale is based on internal TMS. Multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quintet), m (multiplet) and coupling constants (*J*) are reported in hertz. HRMS was measured on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. Melting points were determined using XT-4 apparatus and are uncorrected.

2. Typical experimental procedure

2.1 Typical procedure for the preparation of substrates

All *N*-arylacrylamides **1** were synthesized from the corresponding aminobenzenes and acid chlorides, and the NMR spectroscopies are consistent with literature values.[1,2] hydroxymethyl group substituted *N*-arylacrylamide was synthesized according to literature procedures:[3]



2.2 Typical procedure for iodine pentoxide-triggered iodocarbocyclization of alkenes

To a 35 mL Sealed tube were added *N*-arylacrylamide **1** (35 mg, 0.2 mmol), iodine pentoxide (I_2O_5: 152 mg, 2.2 equiv), KI (41 mg, 1.2 equiv) and H_2O (1 mL). Then the tube was stirred at 80 °C for the indicated time until complete consumption of the starting material as monitored by TLC (usually 12 h). After the reaction was finished, ethyl acetate (EtOAc, 30 mL) was added, the reaction mixture was washed with sat. $Na_2S_2O_3$ and brine, the organic layers dried over Na_2SO_4, filtered, and concentrated in vacuum. The desired product was obtained after purification by flash column chromatography (dichloromethane or dichloromethane/ methanol).

2.3 Typical procedure for the 0.2 mmol scale iodocarbocyclization of *N*-arylacrylamide 1a for the synthesis of iodooxindoles

To a 100 mL Sealed tube were added *N*-arylacrylamide **1** (0.35 g, 2 mmol), iodine pentoxide (I_2O_5: 1.53 g, 2.2 equiv), KI (0. 41 g, 1.2 equiv) and H_2O (10.0 mL). Then the tube was stirred at 80 °C for 16 h. After the reaction was finished, ethyl acetate (EtOAc, 100 mL) was added, the reaction mixture was washed with sat. $Na_2S_2O_3$ and brine, and the organic layers dried over Na_2SO_4, filtered, and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (using dichloromethane as an eluent) to obtain the desired product **2a** in 83% (0.71 g) yield.

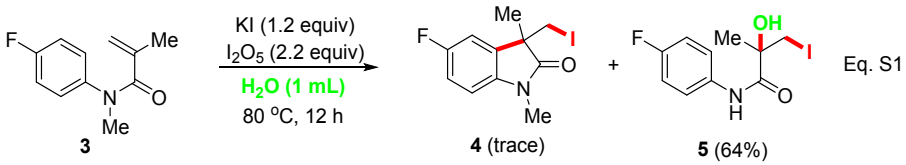
2.4 Typical procedure for the gram scale iodocarbocyclization of *N*-arylacrylamide 1a for the synthesis of iodooxindoles

To a 100 mL Sealed tube were added *N*-arylacrylamide **1** (1.0 g, 5.7 mmol), iodine pentoxide (I_2O_5: 4.315 g, 2.2 equiv), KI (1.16 g, 1.2 equiv) and H_2O (15.0 mL). Then the tube was stirred at 80 °C for 24 h. After the reaction was finished, ethyl acetate (EtOAc, 150 mL) was added, the reaction mixture was washed with sat. $Na_2S_2O_3$ and brine, and the organic layers dried over Na_2SO_4, filtered, and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (using dichloromethane as an eluent) to obtain the desired product **2a** in 86% (2.1 g) yield.

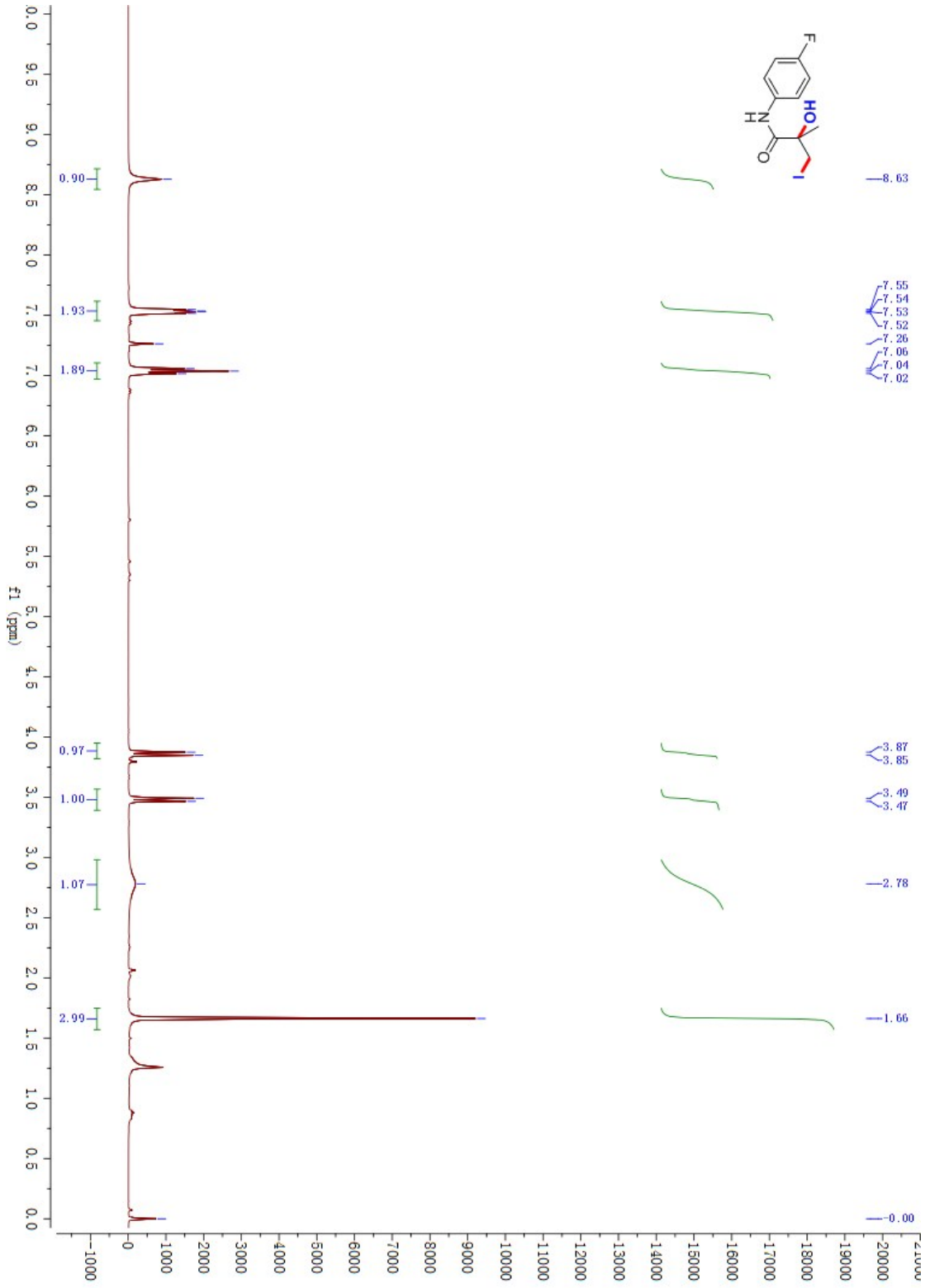
3. Preliminary mechanistic studies

3.1 Electrophilic process verification experiments

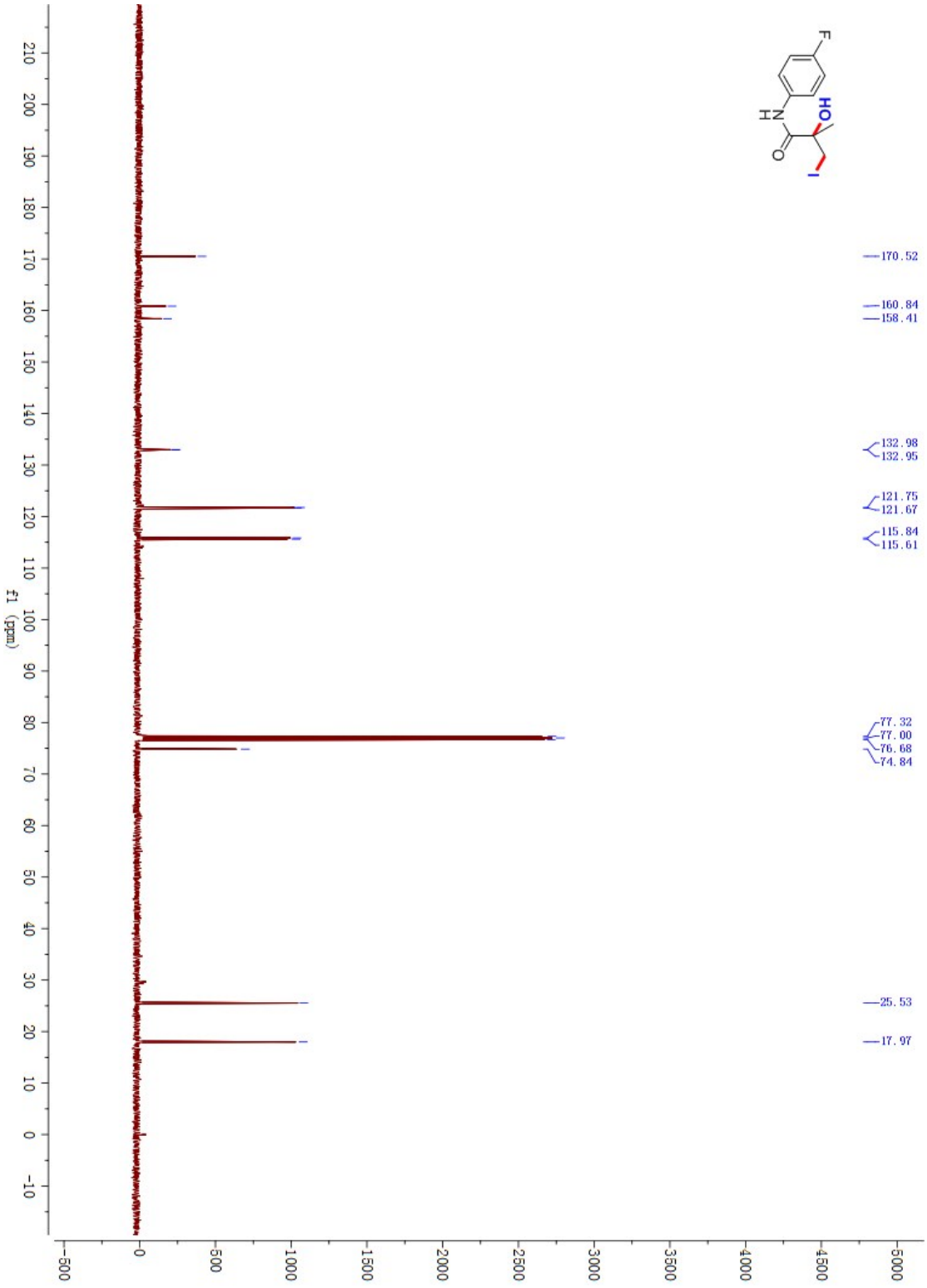
When *para*-fluorine-substituted *N*-arylacrylamide **3** was used as a substrate, the desired iodooxindole **4** was not obtained, whereas the iodohydroxylated product **5** was produced in 60% yield (Eq. S1).



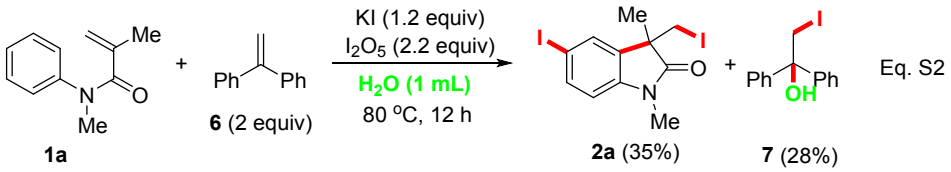
^{1}H NMR Spectra of iodohydroxylated product (**5**)


F
HO
N
H
O
f1 (ppm)
0.90
1.93
1.89
0.97
1.00
1.07
2.99
8.63
7.55
7.54
7.53
7.52
7.26
7.06
7.04
7.02
3.87
3.85
3.49
3.47
2.78
1.66
0.00

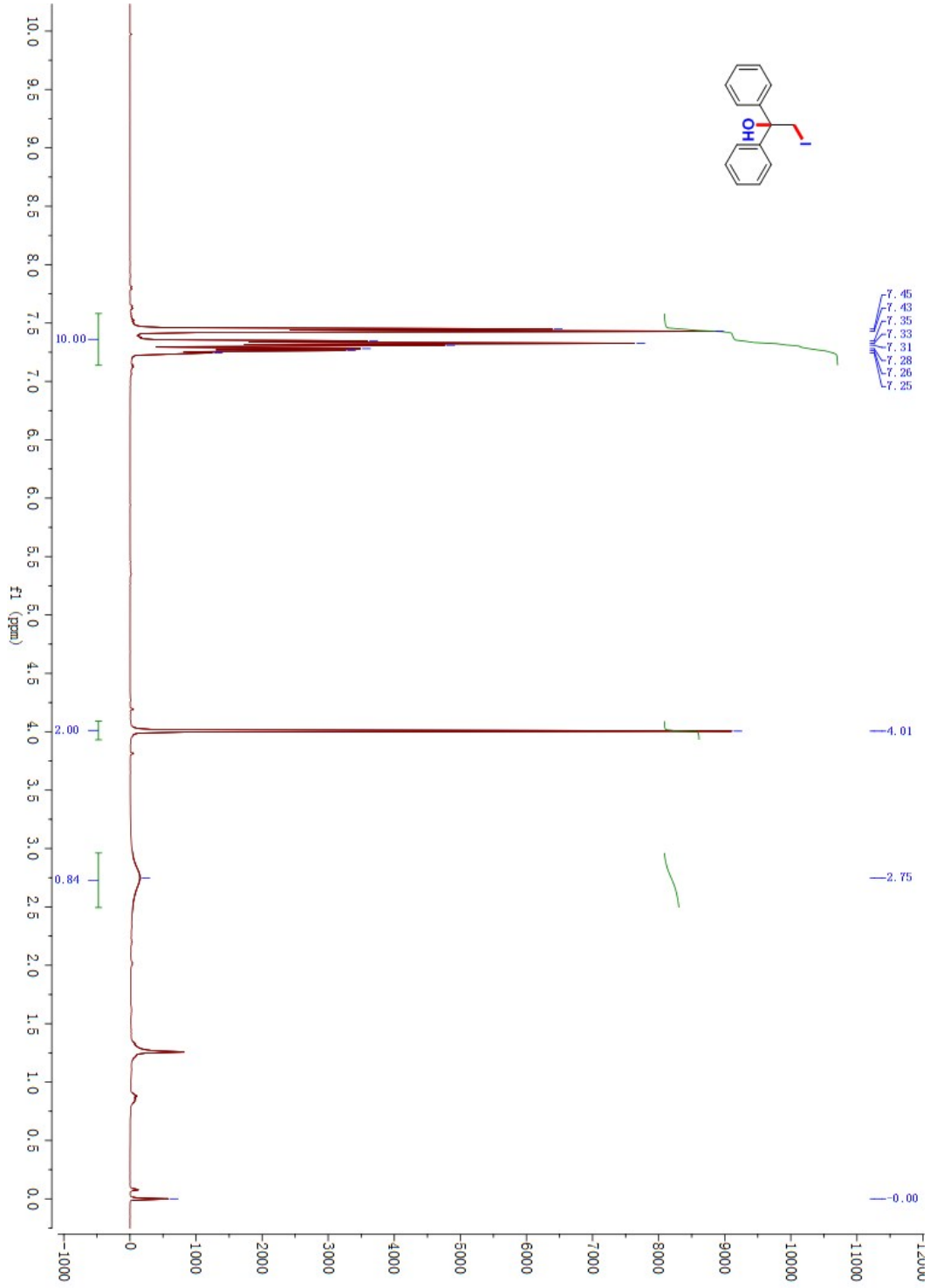
^{13}C NMR Spectra of iodohydroxylated product (**5**)



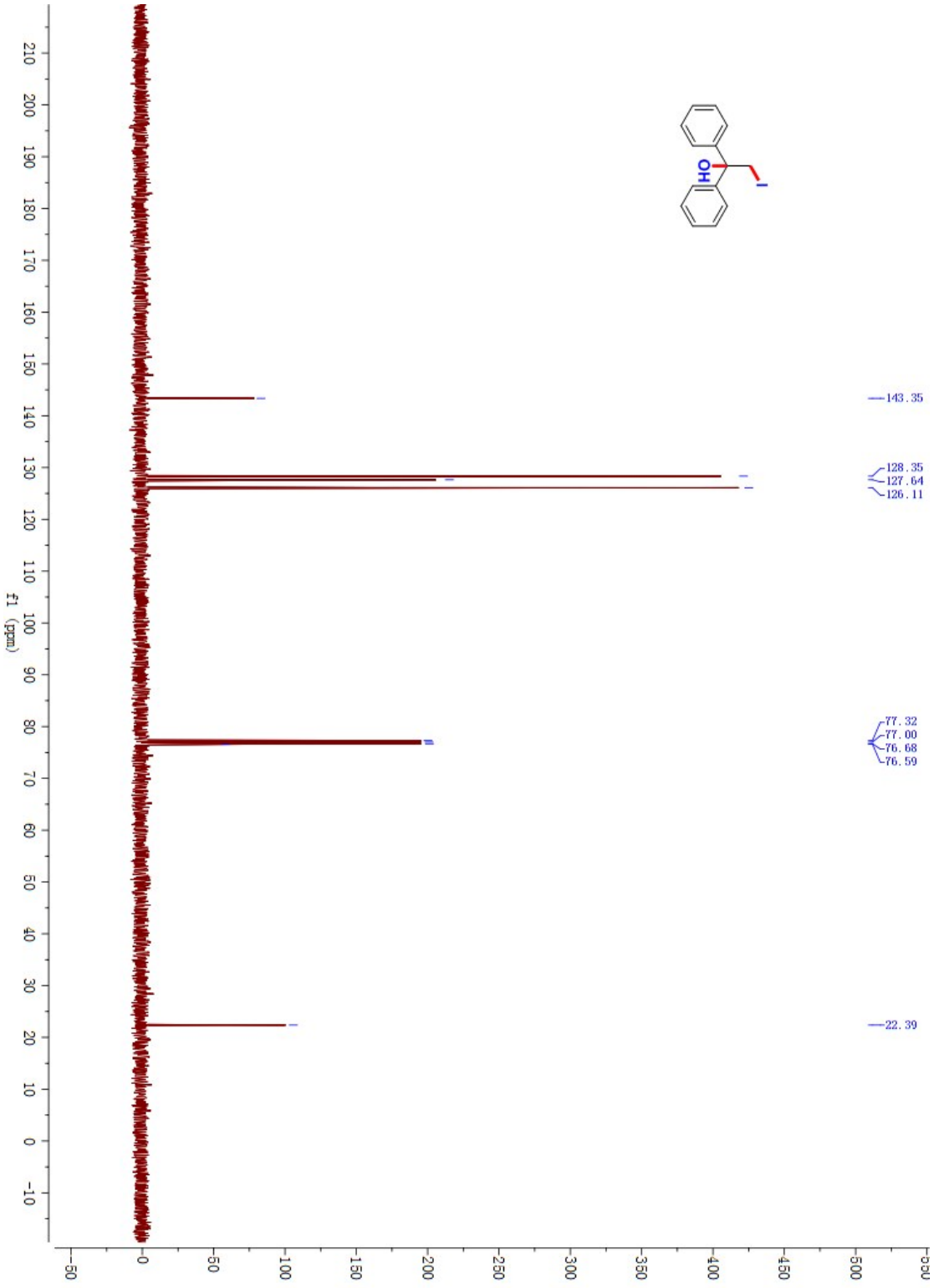
By addition of 2.0 equiv. ethene-1,1-diyldibenzene **6**, the reaction provided the iodohydroxylated product **7** in 29% isolated yield (Eq. S2).



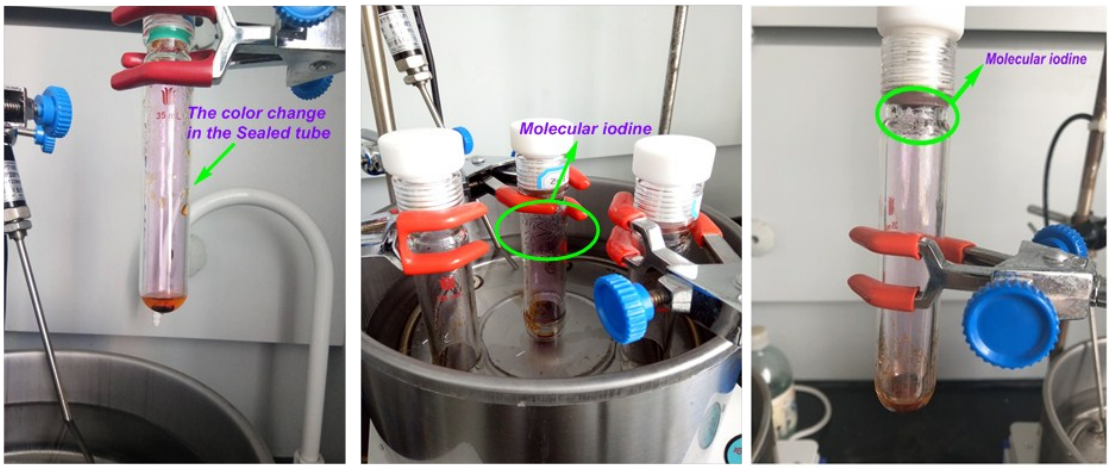
^{1}H NMR Spectra of iodohydroxylated product (**7**)



^{13}C NMR Spectra of iodohydroxylated product (**7**)



3.2 Figure S1. The formation of molecular iodine

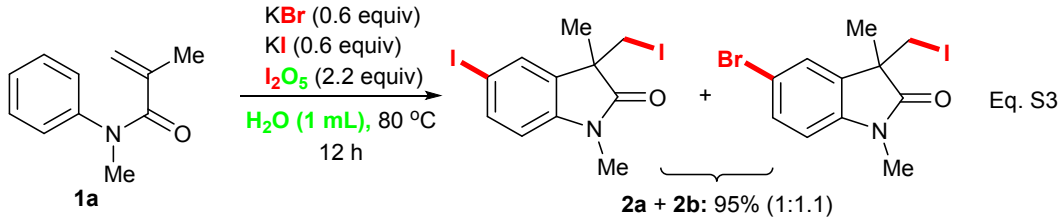


(a) (b) (c)

Figure S1. Molecular iodine formation: (a) The color change of the reaction mixture; (b) Confirmation of the formation of molecular iodine in I_2O_5/KI/H_2O system; (c) Confirmation of the formation of molecular iodine in I_2O_5 /H_2O system.

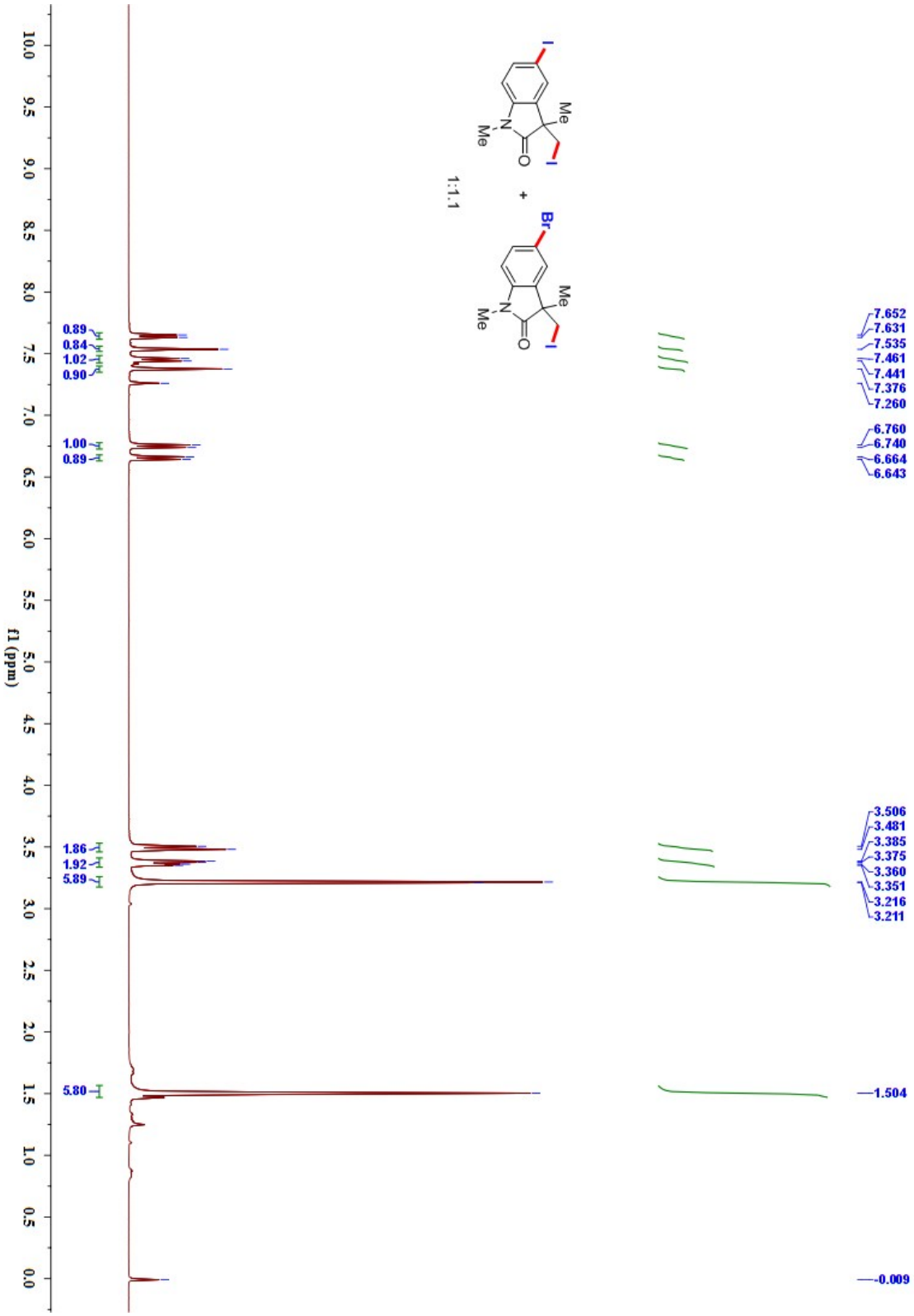
3.3 Competition experiment using KBr and KI

When 0.6 equiv of both KBr and KI were used as the halide source in the presence of 2.2 equiv of I_2O_5, the reaction gave a 95% yield of an inseparable mixture of diiodooxindole **2a** and iodobromooxindole **2b**, and the ratio of **2a/2b** was ca. 1:1.1 as determined by ^{1}H NMR analyse (Eq. S3).

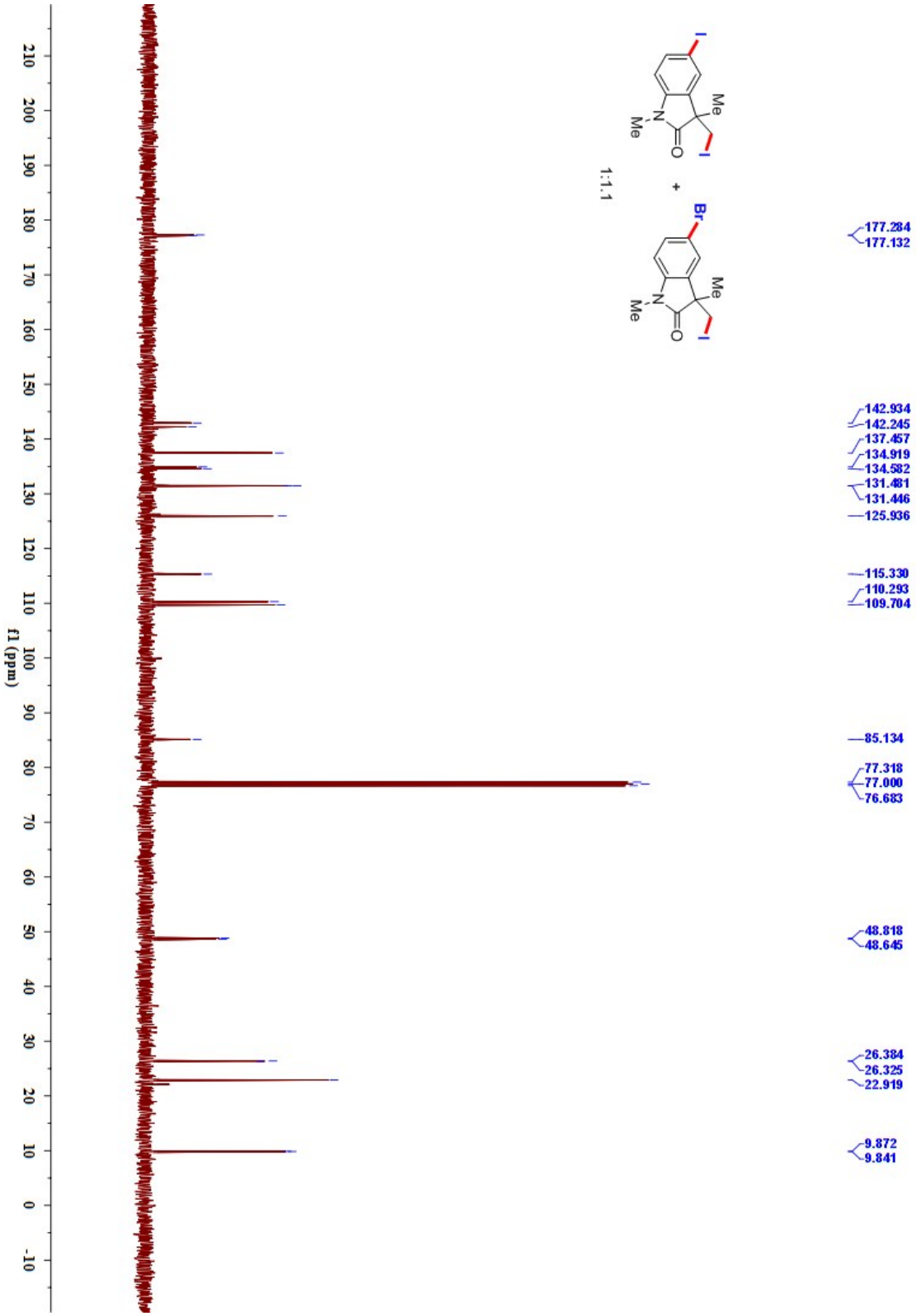


Eq. S3

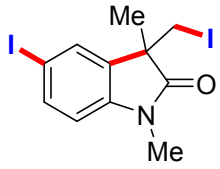
^{1}H NMR Spectra of dihalooxindoles **2a** and **2b**



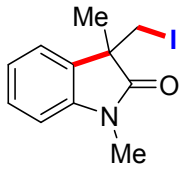
^{13}C NMR Spectra of dihalooxindoles **2a** and **2b**



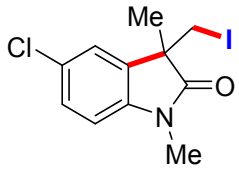
4. Characterization data of products



*5-Iodo-3-(iodomethyl)-1,3-dimethylindolin-2-one (**2a**):* The product was isolated via the general procedure as a white solid in 92% yield (78.6 mg); flash chromatography (dichloromethane); mp 129-131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.1 Hz, 1H), 7.54 (s, 1H), 6.66 (d, J = 8.1 Hz, 1H), 3.49 (d, J = 9.9 Hz, 1H), 3.36 (d, J = 9.9 Hz, 1H), 3.21 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 143.0 137.5, 135.0, 131.5, 110.4, 85.2, 48.7, 26.4, 23.0, 9.9; HRMS *m/z* (ESI) calcd for $C_{11}H_{11}I_2NO^+[M^+]$: 426.8930; found 426.8931.

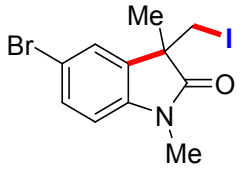


*3-(Iodomethyl)-1,3-dimethylindolin-2-one (**2a'**):* The product was isolated in a small amount from various reactions during initial survey of reaction conditions; flash chromatography (dichloromethane/methanol, 500:1); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, J = 7.7 Hz, 1H), 7.27 (d, J = 7.1 Hz, 1H), 7.11 (t, J = 7.5 Hz, 1H), 6.88 (d, J = 7.7 Hz, 1H), 3.52 (d, J = 9.8 Hz, 1H), 3.43 (d, J = 9.7 Hz, 1H), 3.24 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 143.0, 132.5, 128.5, 122.6, 122.5, 108.2, 48.5, 26.2, 22.8, 10.7; HRMS *m/z* (ESI) calcd for $C_{11}H_{12}INO^+[M^+]$: 300.9964; found 300.9965.

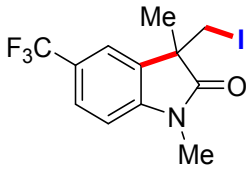


*5-Chloro-3-(iodomethyl)-1,3-dimethylindolin-2-one (**2b**):* The product was isolated via the general procedure as a white solid in 76% yield (75 mg); flash chromatography (dichloromethane); mp 79−81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.3 Hz, 1H), 7.25 (s, 1H), 6.80 (d, J = 8.2 Hz, 1H), 3.51 (d, J = 9.9 Hz, 1H), 3.39 (d, J = 9.9 Hz, 1H), 3.23 (s, 3H), 1.52 (s, 3H); ^{13}C NMR

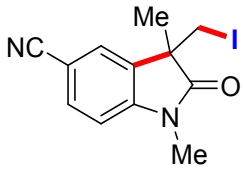
(100 MHz, $CDCl_3$) δ 177.4, 141.8, 134.2, 128.6, 128.1, 123.2, 109.1, 48.9, 26.4, 22.9, 9.8; HRMS *m/z* (ESI) calcd for $C_{11}H_{11}ClINO^+[M^+]$: 334.9574; found 334.9572.



*5-Bromo-3-(iodomethyl)-1,3-dimethylindolin-2-one (**2c**):* The product was isolated via the general procedure as a white solid in 82% yield (85.4 mg); flash chromatography (dichloromethane); mp 98−101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.2 Hz, 1H), 7.38 (s, 1H), 6.75 (d, J = 8.2 Hz, 1H), 3.50 (d, J = 9.9 Hz, 1H), 3.38 (d, J = 9.9 Hz, 1H), 3.22 (s, 3H), 1.51 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.3, 142.3, 134.6, 131.5, 126.0, 115.4, 109.7, 48.9, 26.4, 22.9, 9.8; HRMS *m/z* (ESI) calcd for $C_{11}H_{11}BrINO^+[M^+]$: 378.9069; found 378.9070.

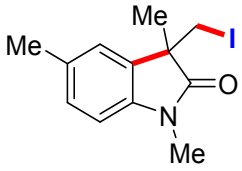


*3-(Iodomethyl)-1,3-dimethyl-5-(trifluoromethyl)indolin-2-one (**2e**):* The product was isolated via the general procedure as a white solid in 68% yield (83.7 mg); flash chromatography (dichloromethane); mp 132−135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.2 Hz, 1H), 7.50 (s, 1H), 6.95 (d, J = 8.2 Hz, 1H), 3.53 (d, J = 9.9 Hz, 1H), 3.42 (d, J = 9.9 Hz, 1H), 3.28 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.9, 146.2, 133.2, 126.6, 126.6, 126.5, 126.5, 125.7, 125.2, 124.9, 123.0, 119.8, 119.8, 119.8, 119.7, 108.1, 48.7, 29.7, 26.5, 22.9, 9.5; HRMS *m/z* (ESI) calcd for $C_{12}H_{11}F_3INO^+[M^+]$: 368.9837; found 368.9840.

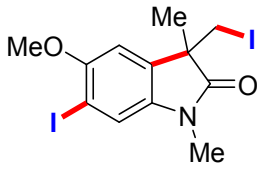


*3-(Iodomethyl)-1,3-dimethyl-2-oxoindoline-5-carbonitrile (**2f**):* The product was isolated via the general procedure as a white solid in 72% yield (72.2 mg); flash chromatography (dichloromethane); mp 139−141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.1 Hz, 1H), 7.52 (s, 1H), 6.95 (d, J = 8.1 Hz, 1H), 3.51 (d, J = 10.0 Hz, 1H), 3.40 (d, J = 10.0 Hz, 1H), 3.27 (s, 3H),

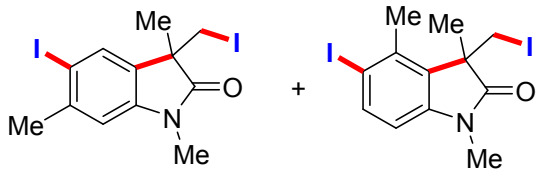
1.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 147.0, 134.0, 133.6, 126.1, 119.0, 108.8, 105. 9, 48.5, 26.5, 22.8, 9.1; HRMS *m/z* (ESI) calcd for $C_{12}H_{11}IN_2O^+[M^+]$: 325.9916; found 325.9919.



3-(Iodomethyl)-1,3,5-trimethylindolin-2-one ***(2g)****:* The product was isolated via the general procedure as a white solid in 97% yield (61.1 mg); flash chromatography (dichloromethane); mp 67−69 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 7.8 Hz, 1H), 7.08 (s, 1H), 6.76 (d, J = 7.8 Hz, 1H), 3.51 (d, J = 9.7 Hz, 1H), 3.40 (d, J = 9.8 Hz, 1H), 3.21 (s, 3H), 2.36 (s, 3H), 1.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 140.7, 132.5, 132.2, 128.8, 123.4, 108.0, 48.6, 26.3, 22.9, 21.1, 10.9; HRMS *m/z* (ESI) calcd for $C_{12}H_{14}INO^+[M^+]$: 315.0120; found 315.0122.

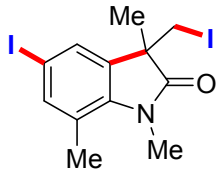


6-Iodo-3-(iodomethyl)-5-methoxy-1,3-dimethylindolin-2-one ***(2h)****:* The product was isolated via the general procedure as a white solid in 98% yield (89.5 mg); flash chromatography (dichloromethane); mp 103−105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 1H), 6.86 (s, 1H), 3.90 (s, 3H), 3.49 (d, J = 9.9 Hz, 1H), 3.41 (d, J = 9.9 Hz, 1H), 3.20 (s, 3H), 1.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 154.7, 137.8, 134.2, 118.9, 107.1, 84.9, 57.3, 49.1, 29.7, 26.5, 23.1, 10.4; HRMS *m/z* (ESI) calcd for $C_{12}H_{13}I_2NO_2^+[M^+]$: 456.9036; found 456.9035.

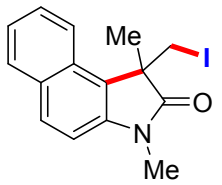


5-Iodo-3-(iodomethyl)-1,3,6-trimethylindolin-2-one ***(2i)*** *and 5-Iodo-3-(iodomethyl)-1,3,4-trimethylindolin-2-one* ***(2i')****:* The product was isolated via the general procedure as a colorless oil in 93% yield (82 mg); flash chromatography (dichloromethane); ^{1}H NMR (**2i**, 400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 6.78 (s, 1H), 3.47 (d, J = 9.6 Hz, 1H), 3.35 (d, J = 9.6 Hz, 1H), 3.20 (s, 3H), 2.46 (s, 3H), 1.47 (s, 3H); ^{1}H NMR (**2i'**, 400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.1 Hz, 1H), 6.48 (d, J = 8.1 Hz,

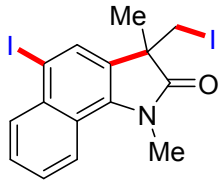
1H), 3.63 (d, J = 9.6 Hz, 1H), 3.57 (d, J = 10.0 Hz, 1H), 3.20 (s, 3H), 2.40 (s, 3H), 1.57 (s, 3H); ^{13}C NMR (**2i**, 100 MHz, $CDCl_3$) δ 177.4, 143.6, 139.0, 132.5, 132.0, 109.8, 91.8, 48.3, 28.7, 26.3, 22.9, 10.3; ^{13}C NMR (**2i'**, 100 MHz, $CDCl_3$) δ 177.5, 143.7, 141.7, 137.0, 130.7, 108.0, 94.8, 50.7, 26.3, 23.4, 21.1, 8.0; HRMS *m/z* (ESI) calcd for $C_{12}H_{13}I_2NO^+[M^+]$: 440.9087; found 440.9088.



*5-Iodo-3-(iodomethyl)-1,3,7-trimethylindolin-2-one (**2j**):* The product was isolated via the general procedure as a white solid in 61% yield (53.8 mg); flash chromatography (dichloromethane); mp 158−159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.34 (s, 1H), 3.50 (d, J = 7.6 Hz, 1H), 3.49 (s, 3H), 3.32 (d, J = 9.8 Hz, 1H), 2.54 (s, 3H), 1.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.1, 141.0, 140.8, 135.5, 129.3, 122.4, 85.3, 48.1, 29.7, 23.2, 18.7, 10.2; HRMS *m/z* (ESI) calcd for $C_{12}H_{13}I_2NO^+[M^+]$: 440.9087; found 440.9089.

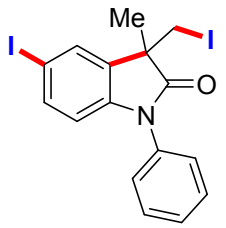


*1-(Iodomethyl)-1,3-dimethyl-1,3-dihydro-2H-benzo[e]indol-2-one (**2k**):* The product was isolated via the general procedure as a white solid in 97% yield (68.1 mg); flash chromatography (dichloromethane); mp 125−128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (t, J = 7.2 Hz, 2H), 7.76 (t, J = 11.4 Hz, 1H), 7.52 (dd, J = 14.3, 6.8 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.23 (d, J = 8.6 Hz, 1H), 3.88 (d, J = 9.7 Hz, 1H), 3.81 (d, J = 10.1 Hz, 1H), 3.36 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.3, 141.0, 130.5, 130.0, 130.0, 129.3, 127.5, 123.9, 123.7, 120.9, 109.6, 50.7, 26.5, 22.3, 9.5; HRMS *m/z* (ESI) calcd for $C_{15}H_{14}INO^+[M^+]$: 351.0120; found 351.0119.

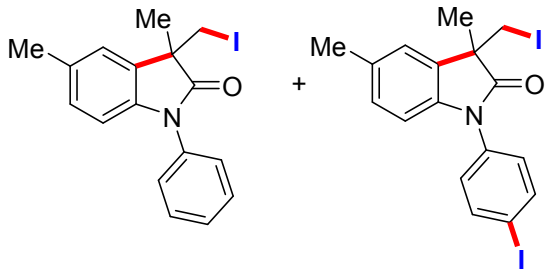


*5-Iodo-3-(iodomethyl)-1,3-dimethyl-1,3-dihydro-2H-benzo[g]indol-2-one（**2l**）：* The product was isolated via the general procedure as a white solid in 90% yield (86.3 mg); flash

chromatography (dichloromethane); mp 140−142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 8.0 Hz, 1H), 8.20 (d, J = 8.0 Hz, 1H), 7.94 (s, 1H), 7.60-7.53 (m, 2H), 3.84 (s, 3H), 3.59 (d, J = 9.9 Hz, 1H), 3.43 (d, J = 9.8 Hz, 1H), 1.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.2, 139.7, 134.7, 134.0, 131.2, 129.7, 127.6, 126.8, 122.3, 122.2, 91.8, 48.5, 31.1, 23.0, 9.7; HRMS *m/z* (ESI) calcd for $C_{15}H_{13}I_2NO^+[M^+]$: 476.9087; found 476.9088.

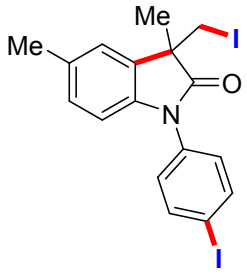


*5-Iodo-3-(iodomethyl)-3-methyl-1-phenylindolin-2-one (**2n**):* The product was isolated via the general procedure as a white solid in 98% yield (95.8 mg); flash chromatography (dichloromethane); mp 155−156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.51 (m, 4H), 7.42 (t, J = 8.9 Hz, 3H), 6.62 (d, J = 8.2 Hz, 1H), 3.64 (d, J = 9.8 Hz, 1H), 3.43 (d, J = 9.8 Hz, 1H), 1.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 143.1, 137.4, 134.7, 133.9, 131.6, 129.7, 128.5, 126.5, 111.6, 85.7, 48.7, 23.0, 10.2; HRMS *m/z* (ESI) calcd for $C_{16}H_{13}I_2NO^+[M^+]$: 488.9087; found 488.9085.

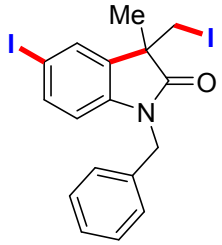


*3-(Iodomethyl)-3,5-dimethyl-1-phenylindolin-2-one (**2o**) and 3-(Iodomethyl)-1-(4-iodophenyl)-3,5-dimethylindolin-2-one (**2o'**):* The product was isolated via the general procedure as a colorless oil in 97% yield (determined by TLC analyse); flash chromatography (dichloromethane); ^{1}H NMR (**2o** + **2o'**, 400 MHz, $CDCl_3$) δ 7.51 (t, J = 7.5 Hz, 2H), 7.46-7.38 (m, 3H), 7.32-7.23 (m, 2 + 0.37H), 7.15-7.11 (m, 1 + 0.38H), 7.05 (d, J = 8.0 Hz, 1H), 6.81 (d, J = 8.0 Hz, 0.36H), 6.74 (d, J = 8.0 Hz, 1H), 3.66 (d, J = 9.6 Hz, 1 + 0.37H), 3.47 (t, J = 8.0 Hz, 1 + 0.39H), 2.42 (s, 1H), 2.38 (s, 3H), 1.63 (s, 3 + 1H); ^{13}C NMR (**2o**, 100 MHz, $CDCl_3$) δ 177.4, 140.9, 134.5, 132.7, 130.2, 129.5, 128.0, 126.5, 123.5, 122.7, 109.3, 48.7, 23.0, 21.2, 11.2; ^{13}C NMR (**2o'**, 100 MHz, $CDCl_3$) δ 177.5, 143.9, 138.2, 132.3, 131.6, 128.8, 128.5, 126.5, 123.0, 122.7, 109.5, 48.6, 23.0, 21.2, 11.2;

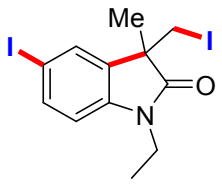
HRMS *m/z* (ESI) calcd for $C_{17}H_{16}INO^+[M^+]$: 377.0277; found 377.0276; HRMS *m/z* (ESI) calcd for $C_{17}H_{15}I_2NO^+[M^+]$: 502.9243; found 502.9242.



*3-(Iodomethyl)-1-(4-iodophenyl)-3,5-dimethylindolin-2-one (**2o'**):* The product was isolated in a small amount from a mixture of products **2o** and **2o'**; flash chromatography (dichloromethane/methanol, 500:1); white solid; mp 159−161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.5 Hz, 2H), 7.36-7.27 (m, 4H), 6.59 (d, J = 8.3 Hz, 1H), 3.63 (d, J = 9.7 Hz, 1H), 3.42 (d, J = 9.7 Hz, 1H), 2.42 (s, 3H), 1.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 143.4, 138.6, 137.4, 134.7, 131.6, 131.2, 130.4, 126.4, 111.6, 85.5, 48.7, 23.0, 21.3, 10.3; HRMS *m/z* (ESI) calcd for $C_{17}H_{15}I_2NO^+[M^+]$: 502.9243; found 502.9242.

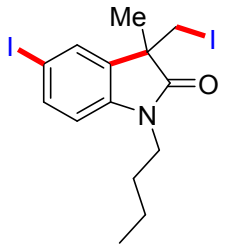


*1-Benzyl-5-iodo-3-(iodomethyl)-3-methylindolin-2-one (**2p**):* The product was isolated via the general procedure as a white solid in 92% yield (92.6 mg); flash chromatography (dichloromethane); mp 170−171 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.50 (m, 2H), 7.32-7.25 (m, 5H), 6.51 (d, J = 8.2 Hz, 1H), 4.98 (d, J = 15.7 Hz, 1H), 4.84 (d, J = 15.7 Hz, 1H), 3.58 (d, J = 9.9 Hz, 1H), 3.42 (d, J = 9.9 Hz, 1H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 142.0, 137.4, 135.1, 135.0, 131.5, 128.8, 127.8, 127.4, 111.5, 85.3, 48.8, 44.0, 23.6, 9.4; HRMS *m/z* (ESI) calcd for $C_{17}H_{15}I_2NO^+[M^+]$: 502.9243; found 502.9244.

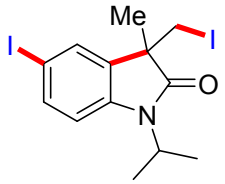


*1-Ethyl-5-iodo-3-(iodomethyl)-3-methylindolin-2-one (**2q**):* The product was isolated via the

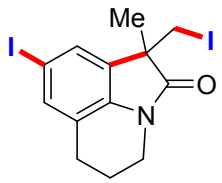
general procedure as a white solid in 94% yield (82.9 mg); flash chromatography (dichloromethane); mp 90−92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.1 Hz, 1H), 7.53 (s, 1H), 6.68 (d, J = 8.2 Hz, 1H), 3.86 (dq, J = 14.3, 7.2 Hz, 1H), 3.66 (dq, J = 14.2, 7.1 Hz, 1H), 3.52 (d, J = 9.8 Hz, 1H), 3.36 (d, J = 9.8 Hz, 1H), 1.50 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 142.1, 137.4, 135.2, 131.6, 110.5, 84.9, 48.5, 35.0, 22.9, 12.6, 9.8; HRMS *m/z* (ESI) calcd for $C_{12}H_{13}I_2NO^+[M^+]$: 440.9087; found 440.9090.



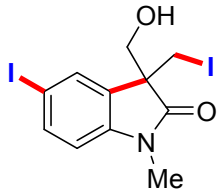
1-Butyl-5-iodo-3-(iodomethyl)-3-methylindolin-2-one ***(2r)****:* The product was isolated via the general procedure as a white solid in 96% yield (90 mg); flash chromatography (dichloromethane); mp 108−111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.1 Hz, 1H), 7.53 (s, 1H), 6.67 (d, J = 8.1 Hz, 1H), 3.77 (dt, J = 14.2, 7.2 Hz, 1H), 3.62 (dt, J = 13.8, 7.0 Hz, 1H), 3.51 (d, J = 9.8 Hz, 1H), 3.37 (d, J = 9.8 Hz, 1H), 1.67 (dd, J = 14.1, 6.8 Hz, 2H), 1.50 (s, 3H), 1.43-1.38 (m, 2H), 0.95 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 142.5, 137.4, 135.2, 131.6, 110.7, 84.9, 48.6, 40.1, 29.5, 23.2, 20.3, 13.8, 9.8; HRMS *m/z* (ESI) calcd for $C_{14}H_{17}I_2NO^+[M^+]$: 468.9400; found 468.9405.



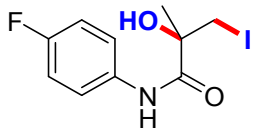
5-Iodo-3-(iodomethyl)-1-isopropyl-3-methylindolin-2-one ***(2s)****:* The product was isolated via the general procedure as a white solid in 90% yield (82 mg); flash chromatography (dichloromethane); mp 99−102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.1 Hz, 1H), 7.50 (s, 1H), 6.82 (d, J = 8.2 Hz, 1H), 3.52 (d, J = 9.7 Hz, 1H), 3.33 (d, J = 9.7 Hz, 1H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 141.8, 137.2, 135.6, 131.7, 112.1, 84.8, 77.3, 48.3, 44.3, 22.9, 19.4, 19.38, 10.1; HRMS *m/z* (ESI) calcd for $C_{13}H_{15}I_2NO^+[M^+]$: 454.9243; found 454.9240.



8-Iodo-1-(iodomethyl)-1-methyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1H)-one ***(2t)****:* The product was isolated via the general procedure as a white solid in 85% yield (77 mg); flash chromatography (dichloromethane); mp 110−112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.41 (s, 1H), 3.79-3.65 (m, 2H), 3.48 (d, J = 9.8 Hz, 1H), 3.38 (d, J = 9.9 Hz, 1H), 2.83-2.71 (m, 2H), 2.02-1.97 (m, 2H), 1.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 138.7, 136.2, 133.4, 129.4, 122.8, 84.7, 49.9, 38.8, 24.3, 22.7, 20. 9, 10.3; HRMS *m/z* (ESI) calcd for $C_{13}H_{13}I_2NO^+[M^+]$: 452.9087; found 452.9085.

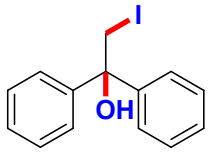


3-(Hydroxymethyl)-5-iodo-3-(iodomethyl)-1-methylindolin-2-one ***(2u)****:* The product was isolated via the general procedure as a white solid in 72% yield (63.8 mg); flash chromatography (dichloromethane/methanol, 300:1); mp 110−112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.2 Hz, 1H), 7.61 (s, 1H), 6.69 (d, J = 8.1 Hz, 1H), 3.87 (q, J = 11.1 Hz, 2H), 3.63 (d, J = 12.0 Hz, 1H), 3.49 (d, J = 12.0 Hz, 1H), 3.23 (s, 3H), 2.46 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 143.7, 138.1, 132.1, 131.4, 110. 6, 85.5, 66.1, 54.4, 29.7, 26.4; HRMS *m/z* (ESI) calcd for $C_{11}H_{11}I_2NO_2^+[M^+]$: 442.8879; found 442.8880.

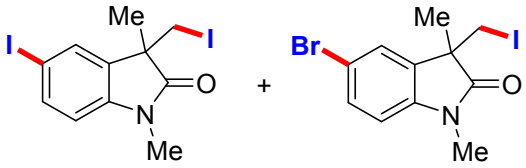


N-(4-Fluorophenyl)-3-hydroxy-2-iodo-2-methylpropanamide ***(5)****:* The product was isolated via the general procedure as a colorless oil in 64% yield (41.4 mg); flash chromatography (dichloromethane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.53 (dd, J = 7.4, 5.0 Hz, 2H), 7.04 (t, J = 8.1 Hz, 2H), 3.86 (d, J = 10.3 Hz, 1H), 3.48 (d, J = 10.3 Hz, 1H), 2.78 (s, 1H), 1.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 159.6 (d, J = 243.0 Hz), 133.0 (d, J = 3.0 Hz), 121.7 (d, J = 8.0 Hz), 115.7 (d, J = 23.0 Hz), 74.8, 25.5, 18.0; HRMS *m/z* (ESI) calcd for

$C_{10}H_{11}FINO_2^+[M^+]$: 322.9818; found 322.9815.



2-Iodo-1,1-diphenylethan-1-ol (7): The product was isolated as a yellow oil in 28% yield (36.3 mg); flash chromatography (dichloromethane/methanol, 500:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.25 (m, 10H), 4.01 (s, 2H), 2.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 128.4, 127.6, 126.1, 76.6, 22.4; HRMS *m/z* (ESI) calcd for $C_{14}H_{13}IO^+[M^+]$: 324.0011; found 324.0009.



5-Iodo-3-(iodomethyl)-1,3-dimethylindolin-2-one ***(2a)*** *and 5-Bromo-3-(iodomethyl)-1,3-dimethylindolin-2-one* ***(2b)***: The product was isolated as a white solid in 95% yield (determined by TLC analyse); flash chromatography (dichloromethane); mp 106-108 ^{o}C; ^{1}H NMR (**2a**, 400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.2 Hz, 1H), 7.54 (s, 1H), 6.65 (d, J = 8.0 Hz, 1H), 3.49 (d, J = 9.8 Hz, 1H), 3.37 (d, J = 13.6 Hz, 1H), 3.21 (s, 3H), 1.50 (s, 3H); ^{1}H NMR (**2b**, 400 MHz, $CDCl_3$) δ ^{1}H NMR (**2b**, 400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.0 Hz, 1H), 7.38 (s, 1H), 6.75 (d, J = 8.0 Hz, 1H), 3.49 (d, J = 9.8 Hz, 1H), 3.37 (d, J = 10.0 Hz, 1H), 3.22 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (**2a**, 100 MHz, $CDCl_3$) δ 177.1, 142.2, 137.5, 134.9, 131.4, 110.3, 85.1, 48.6, 26.3, 22.9, 9.9; ^{13}C NMR (**2b**, 100 MHz, $CDCl_3$) δ 177.3, 142.9, 134.6, 131.5, 125.9, 115.3, 109.7, 48.8, 26.4, 22.9, 9.8; HRMS *m/z* (ESI) calcd for $C_{11}H_{11}I_2NO^+[M^+]$: 426.8930; found 426.8933; HRMS *m/z* (ESI) calcd for $C_{11}H_{11}BrINO^+[M^+]$: 378.9069; found 378.9066.

5. References

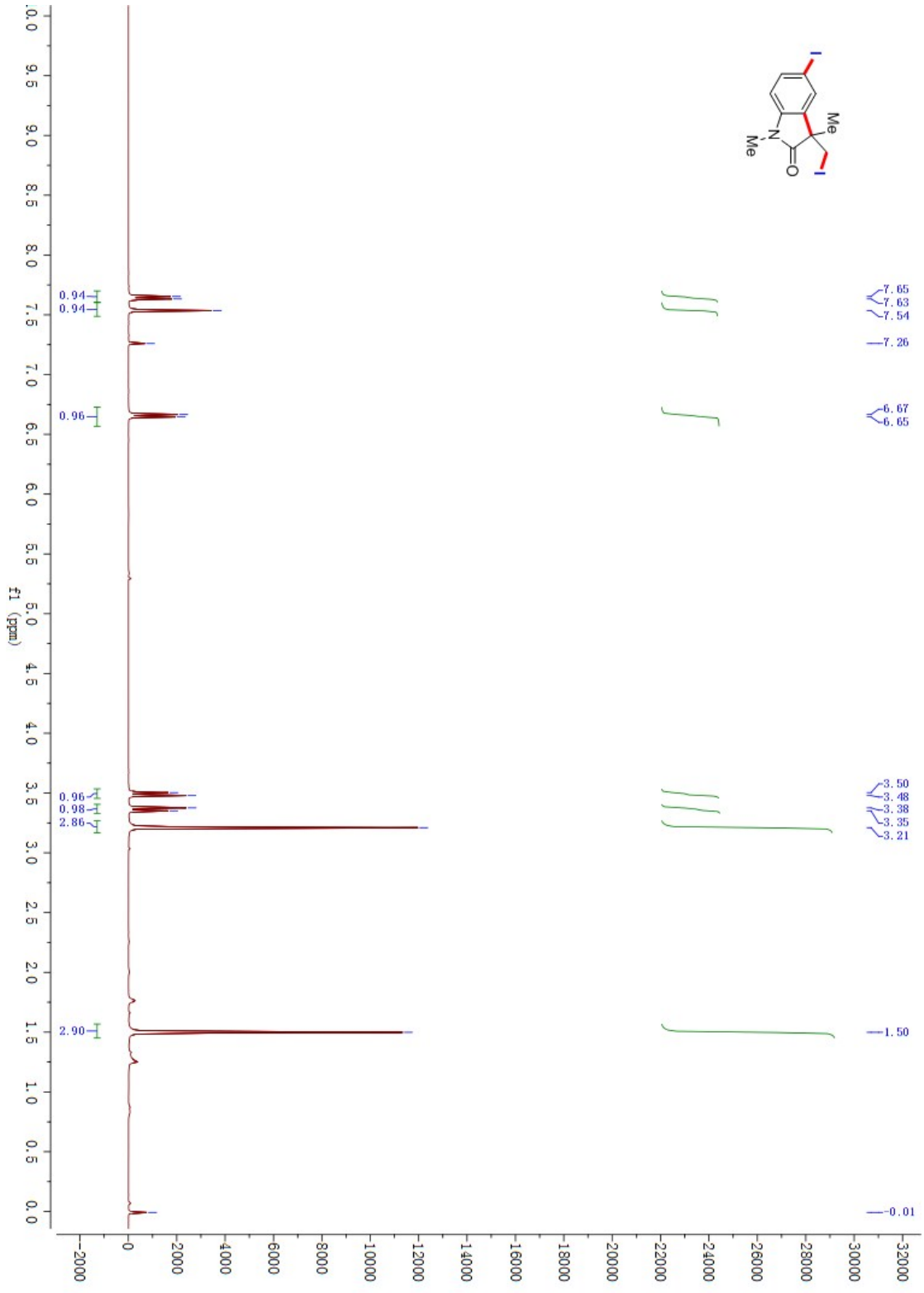
(1) Wei, H.-L.; Piou, T.; Dufour, J.; Neuville, L.; Zhu, J. P. *Org. Lett.* **2011**, *13*, 2244.

(2) Fabry, D. C.; Stodulski, M.; Hoerner, S.; Gulder, T. *Chem. Eur. J.* **2012**, *18*, 10834.

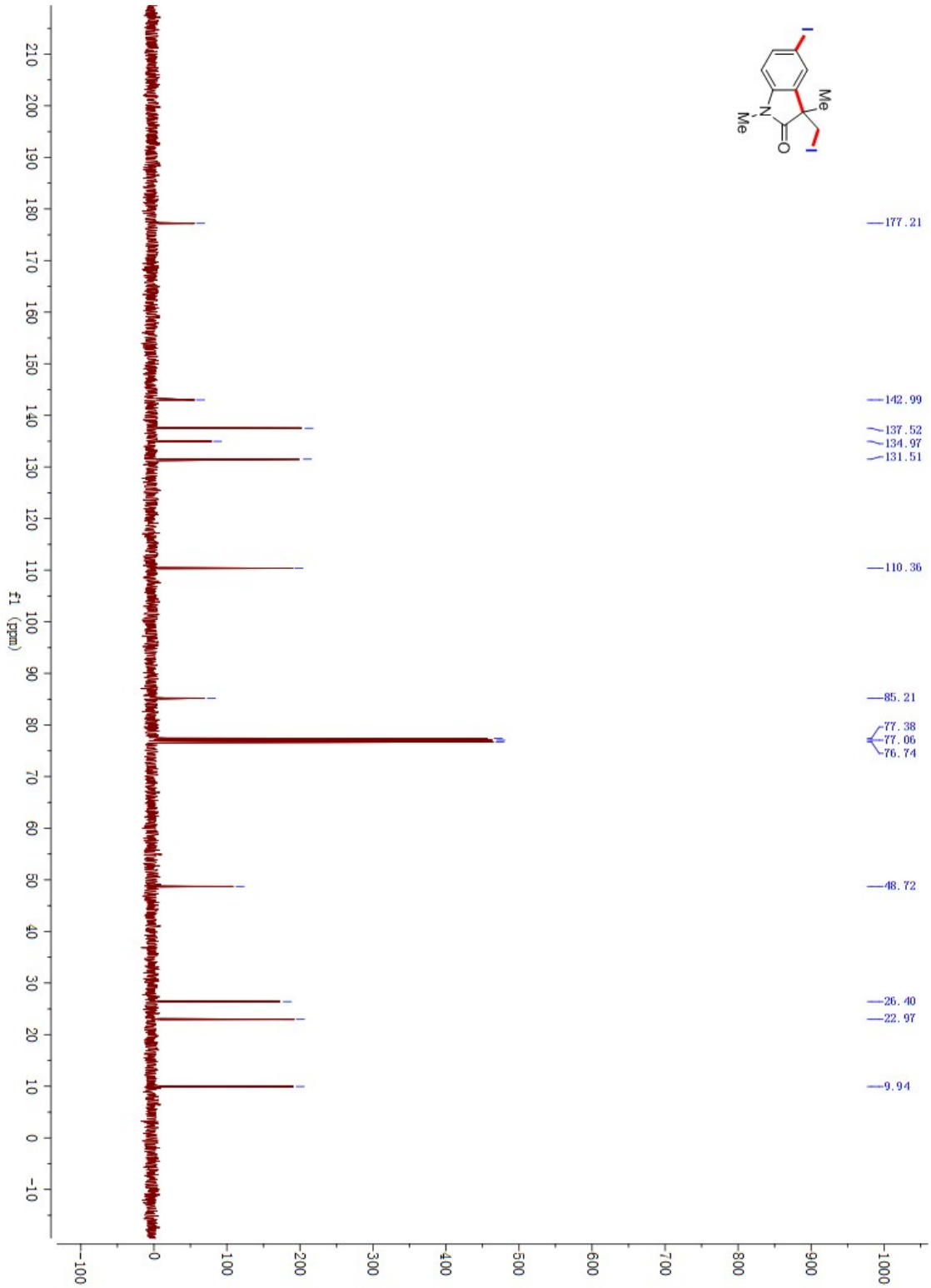
(3) Wu, T.; Mu, X.; Liu, G. *Angew. Chem., Int. Ed.* **2011**, *50*, 12578.

6. Copies of NMR spectra

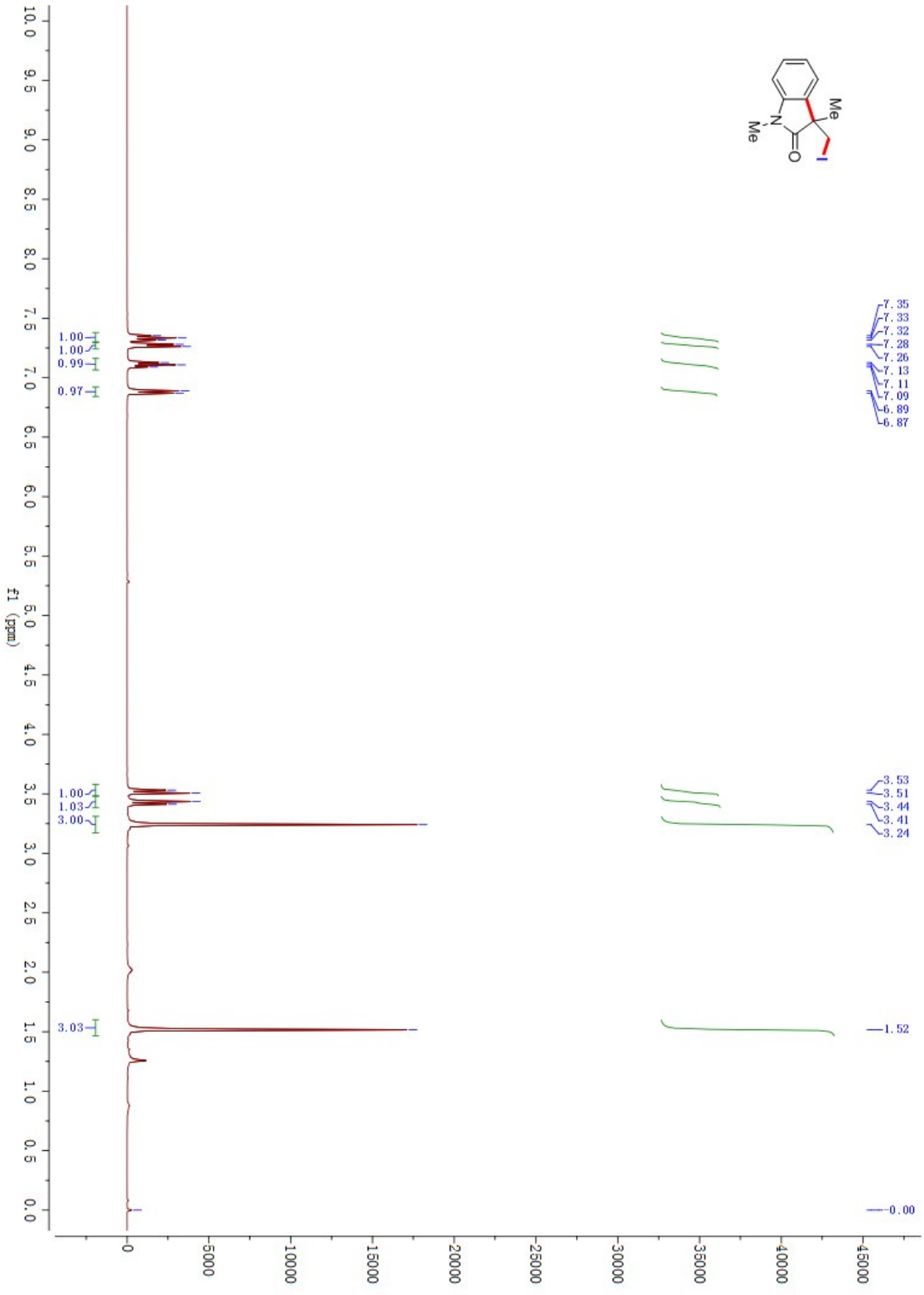
^{1}H NMR Spectra for **2a**



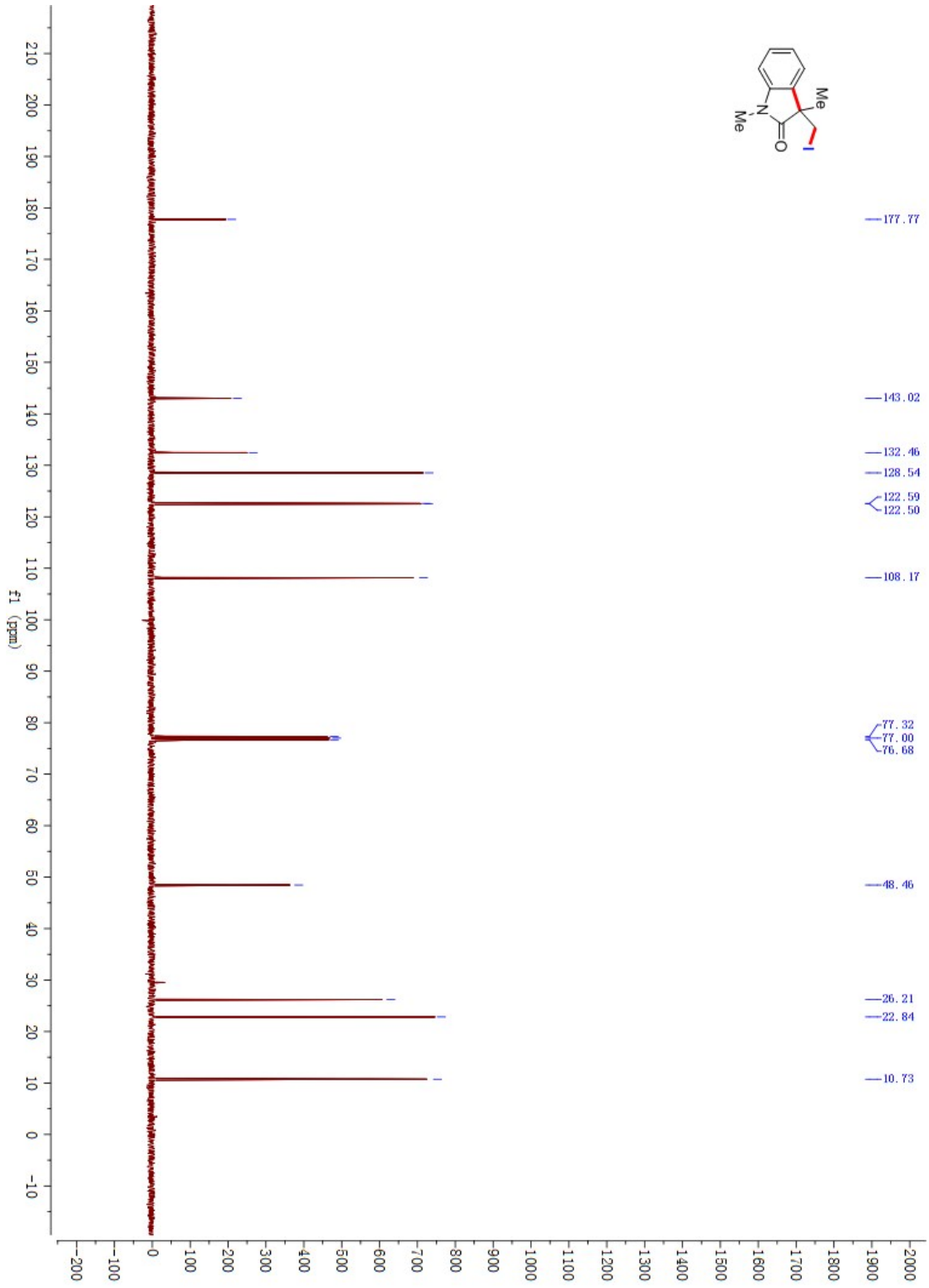
^{13}C NMR Spectra for **2a**



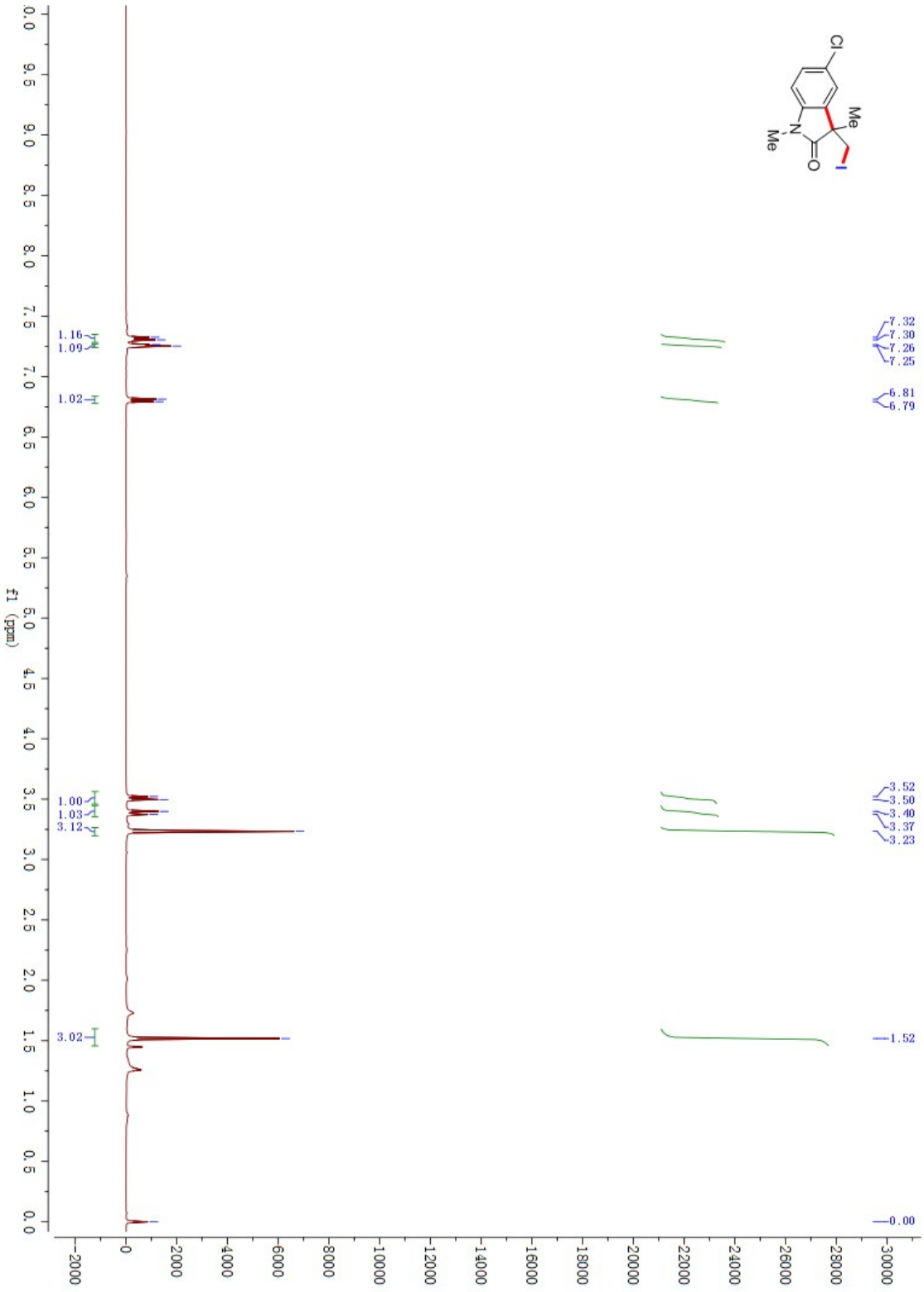
^{1}H NMR Spectra for **2a'**



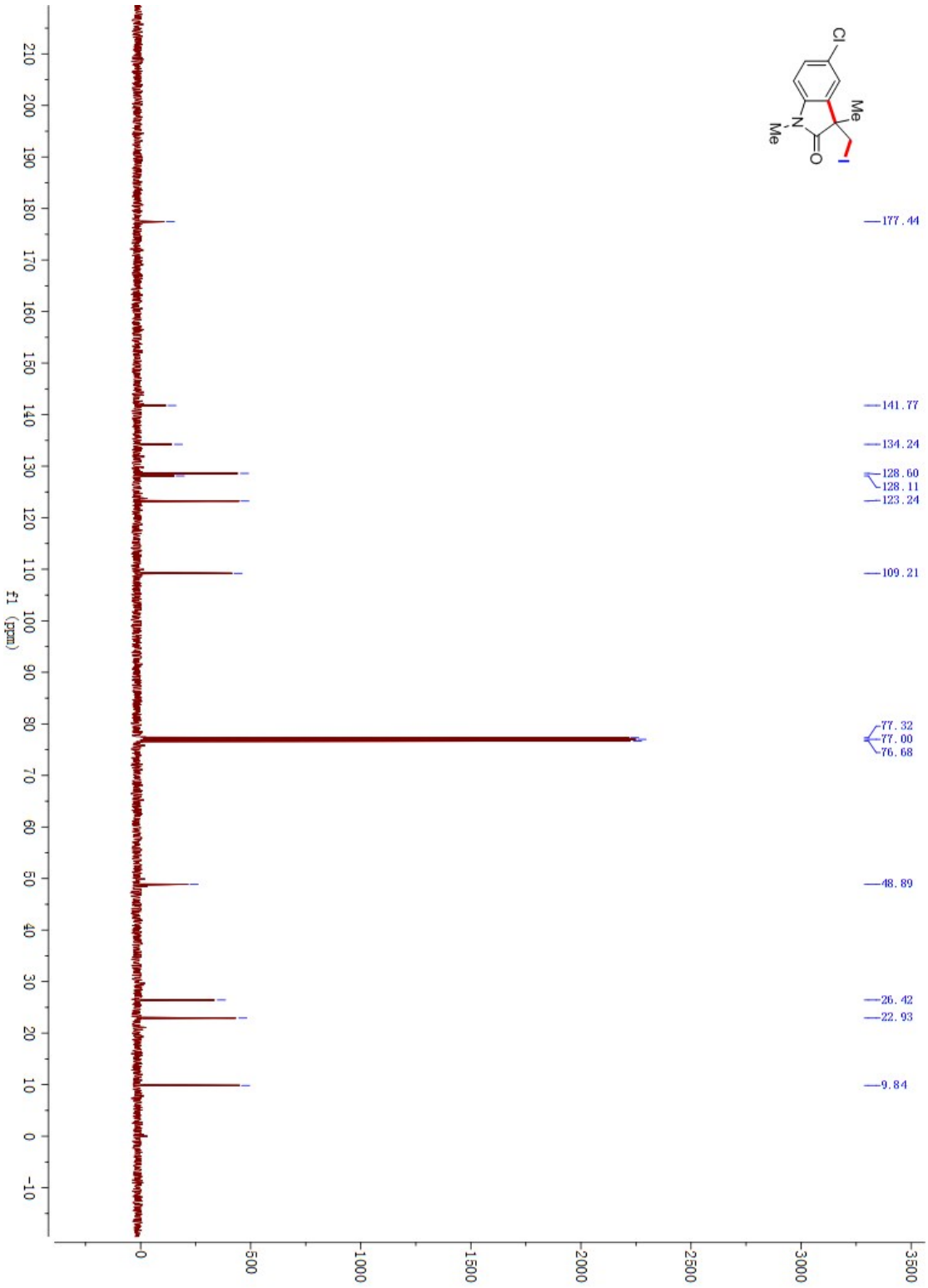
^{13}C NMR Spectra for **2a'**



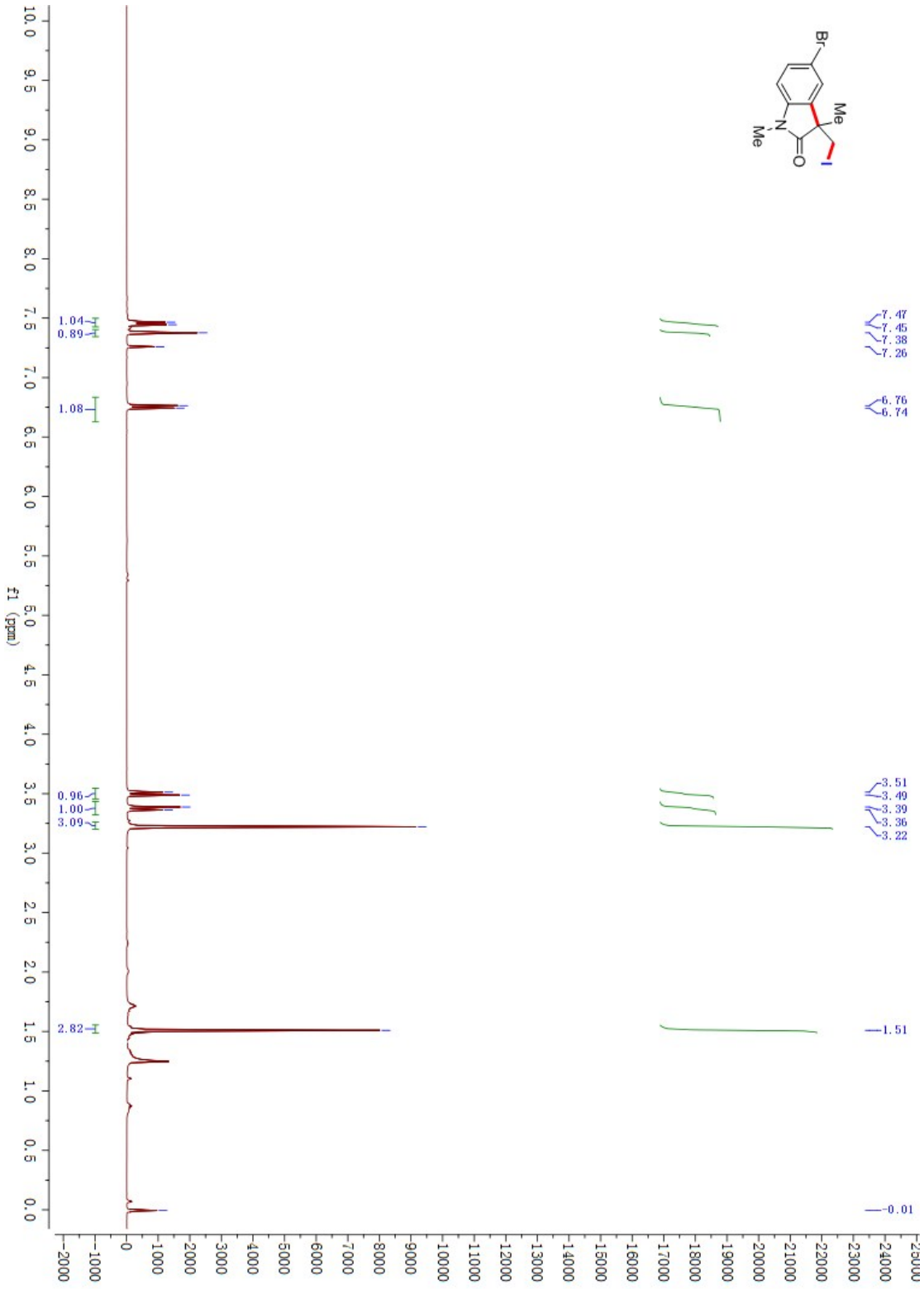
^{1}H NMR Spectra for **2b**



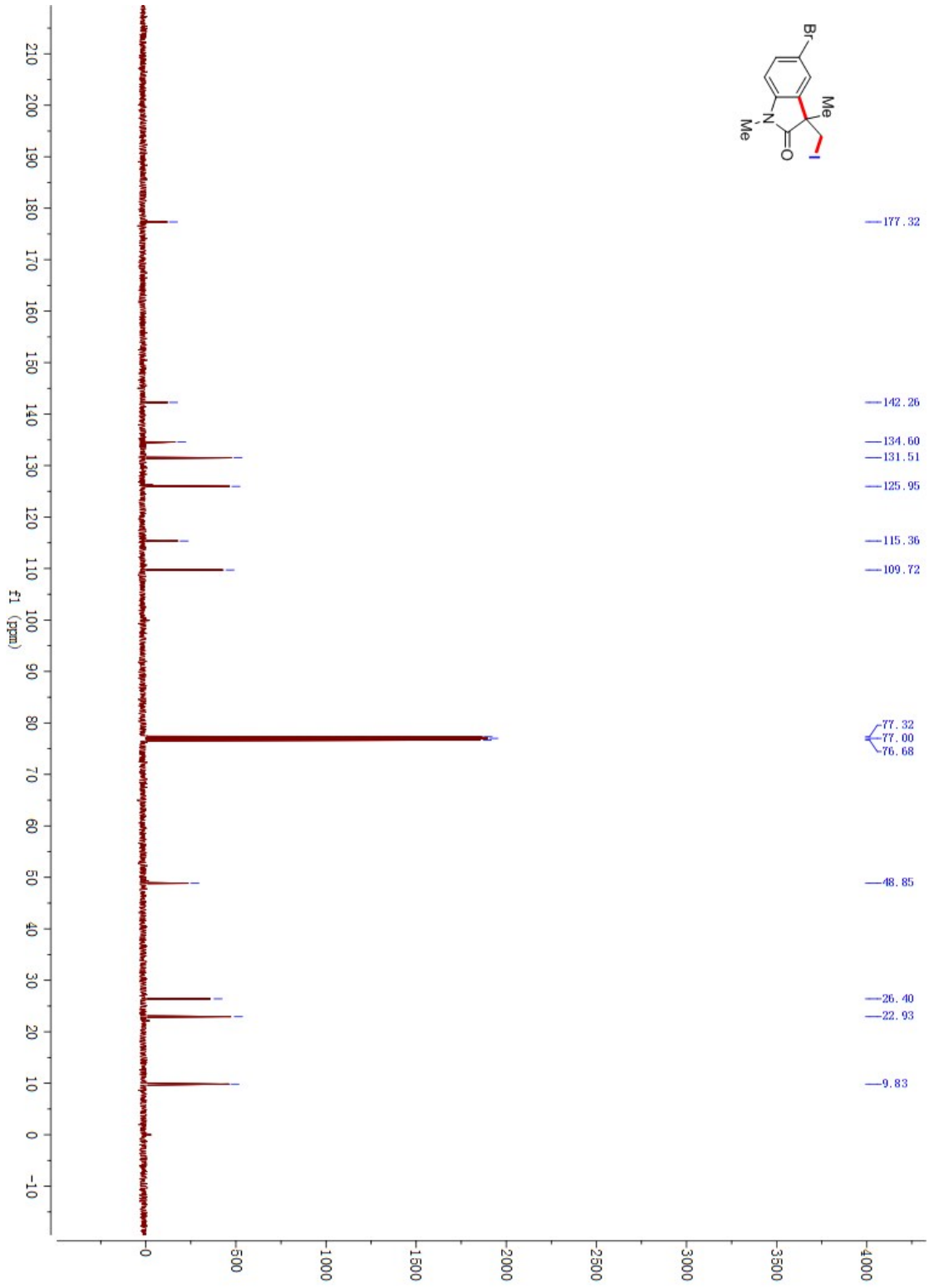
^{13}C NMR Spectra for **2b**



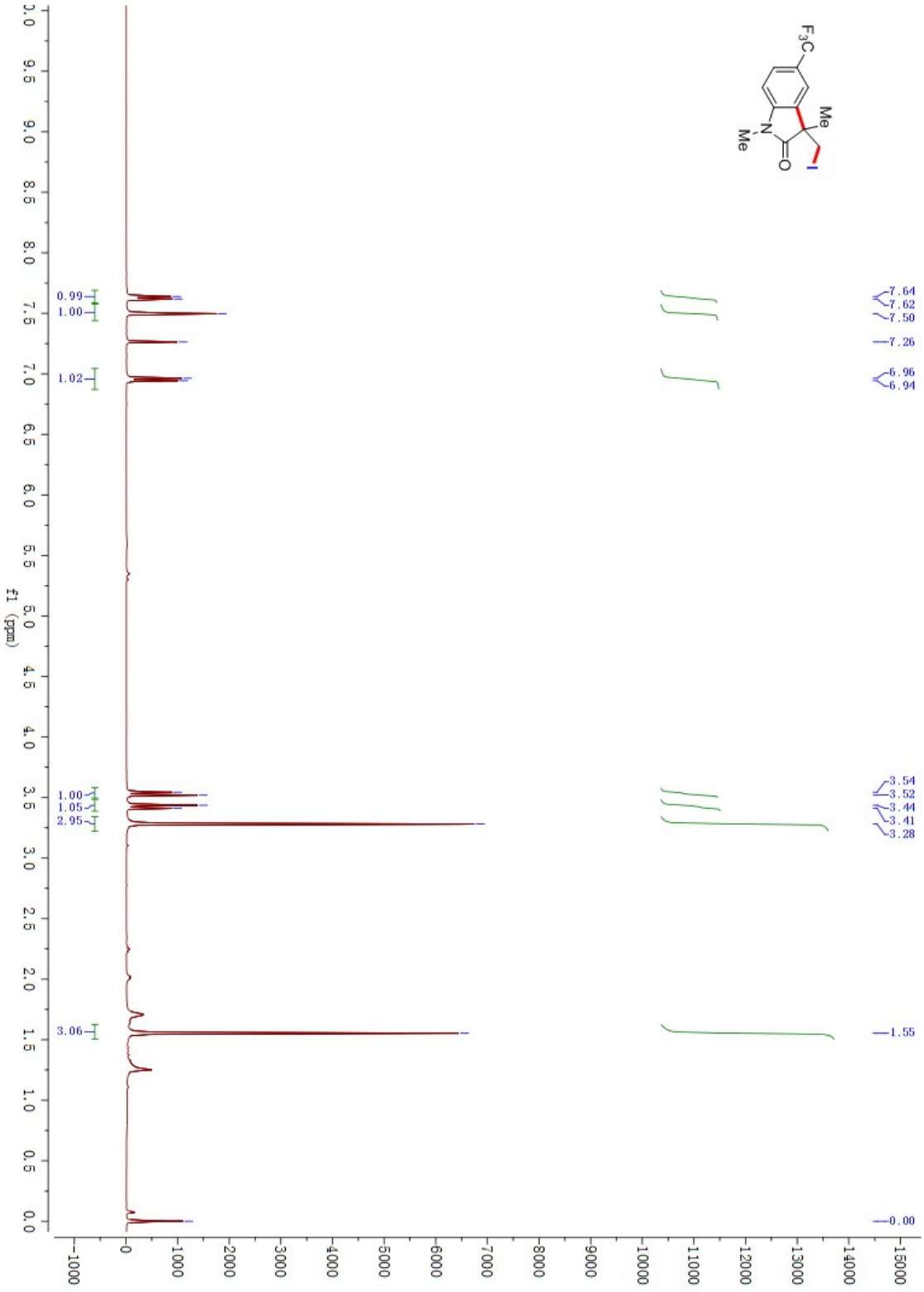
^{1}H NMR Spectra for **2c**



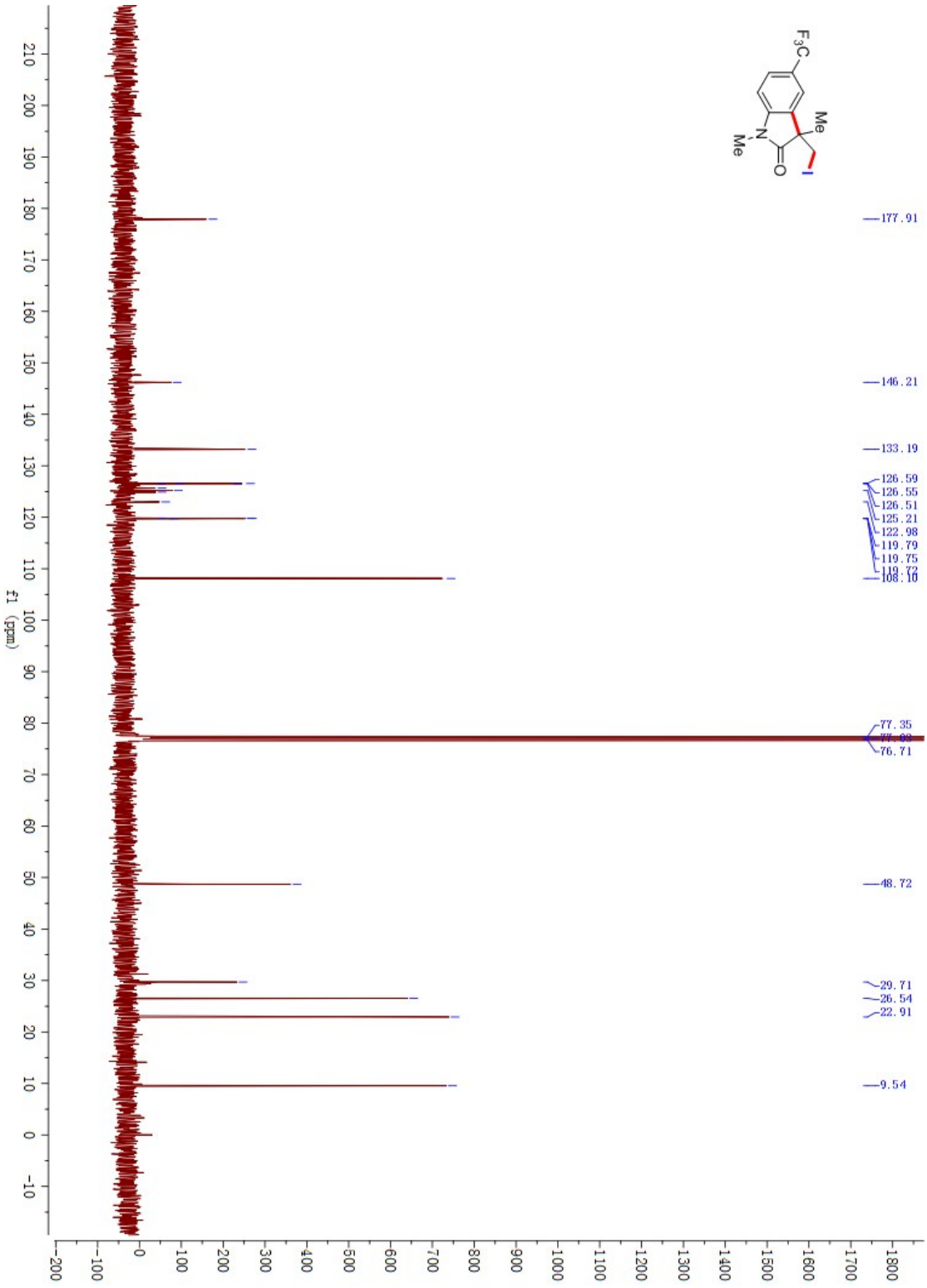
^{13}C NMR Spectra for **2c**



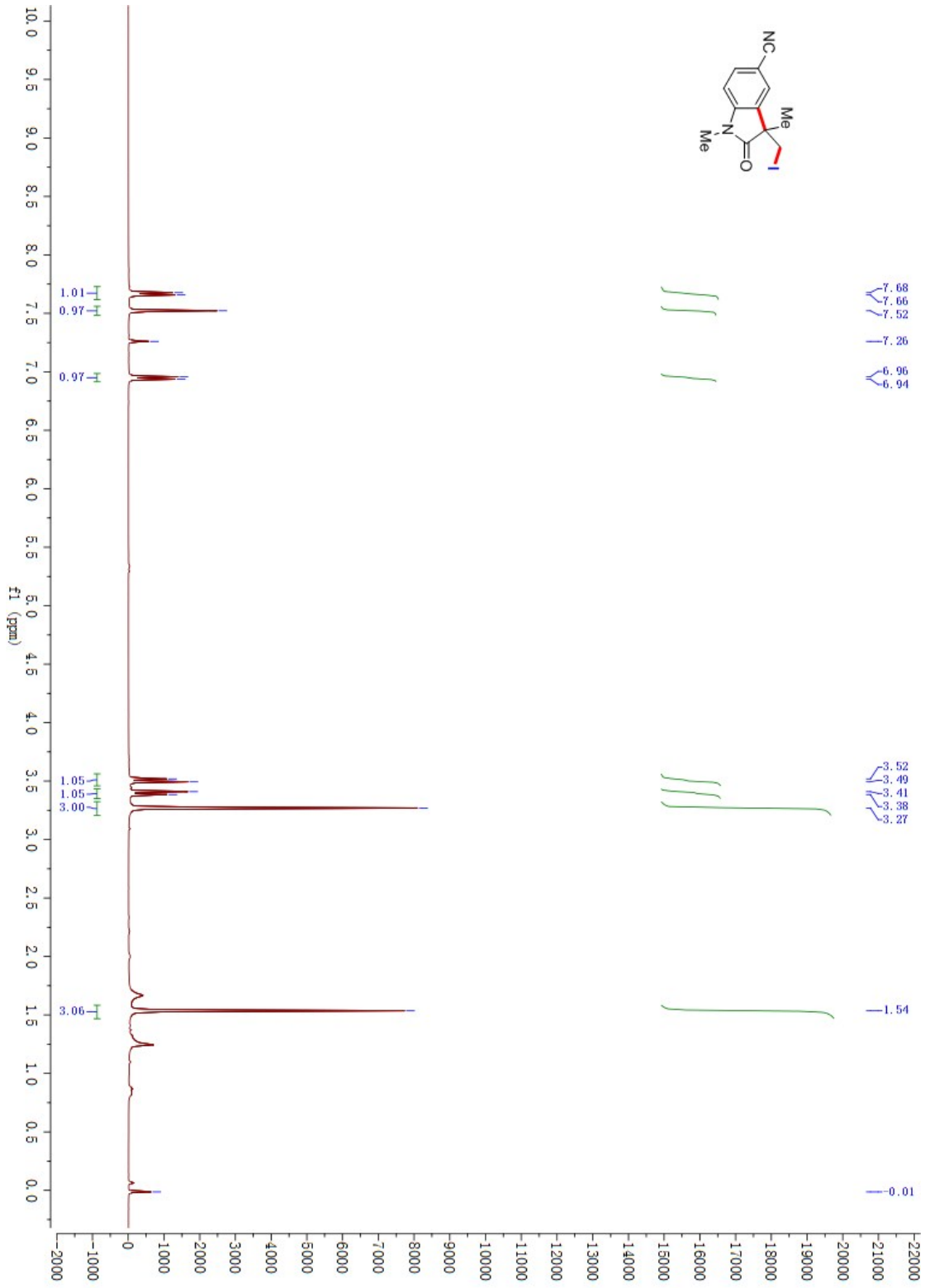
^{1}H NMR Spectra for **2e**



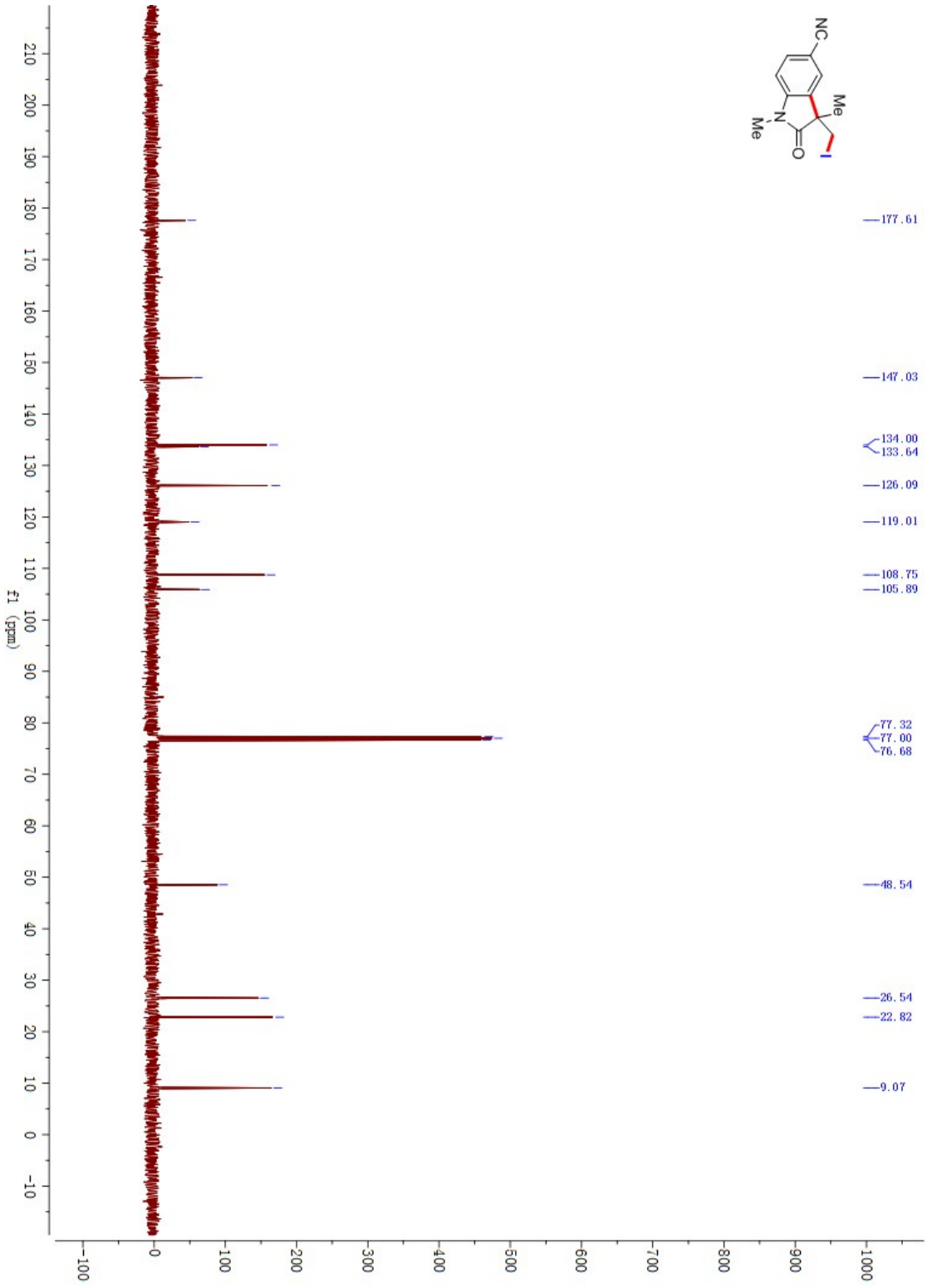
^{13}C NMR Spectra for **2e**



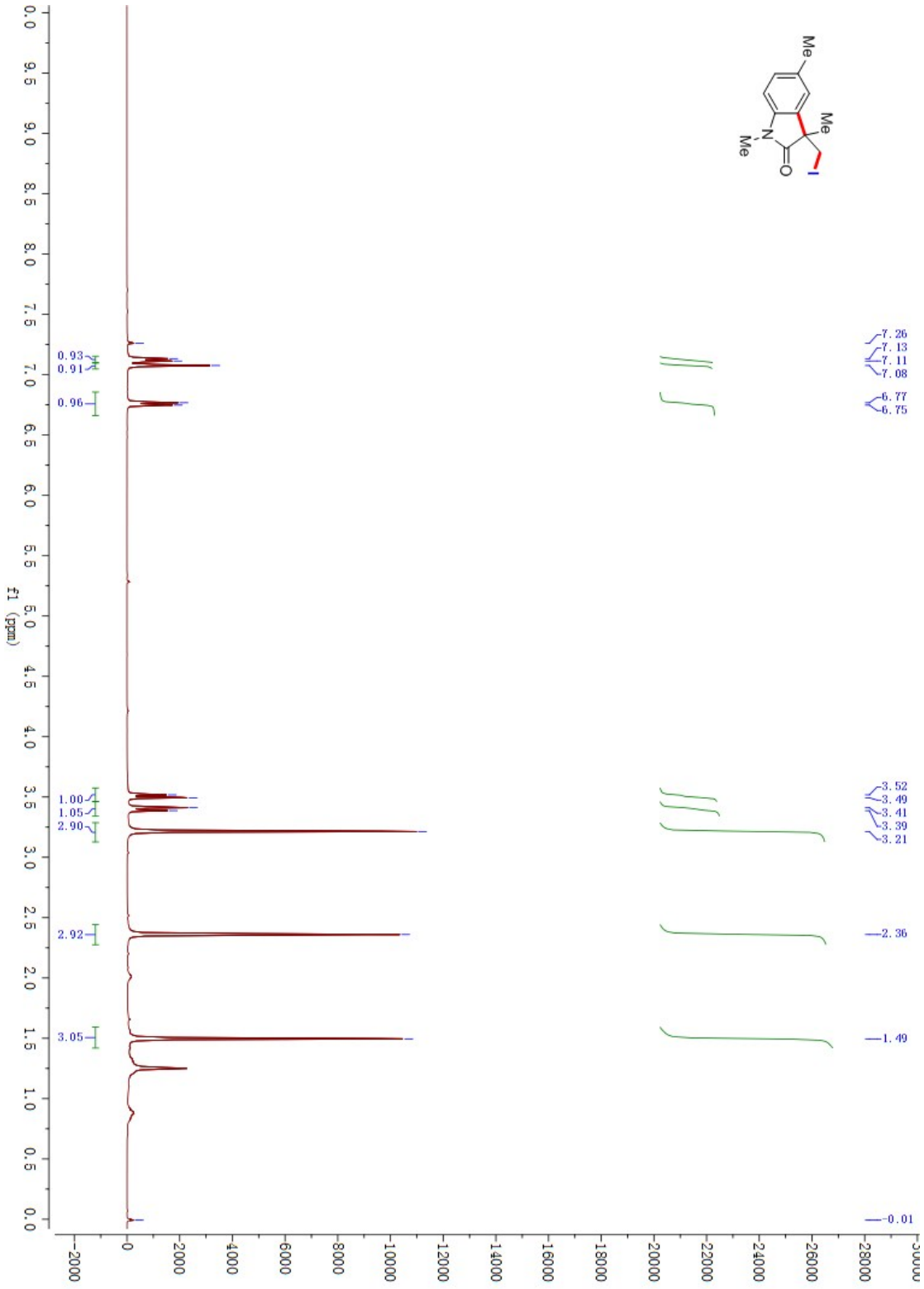
^{1}H NMR Spectra for **2f**



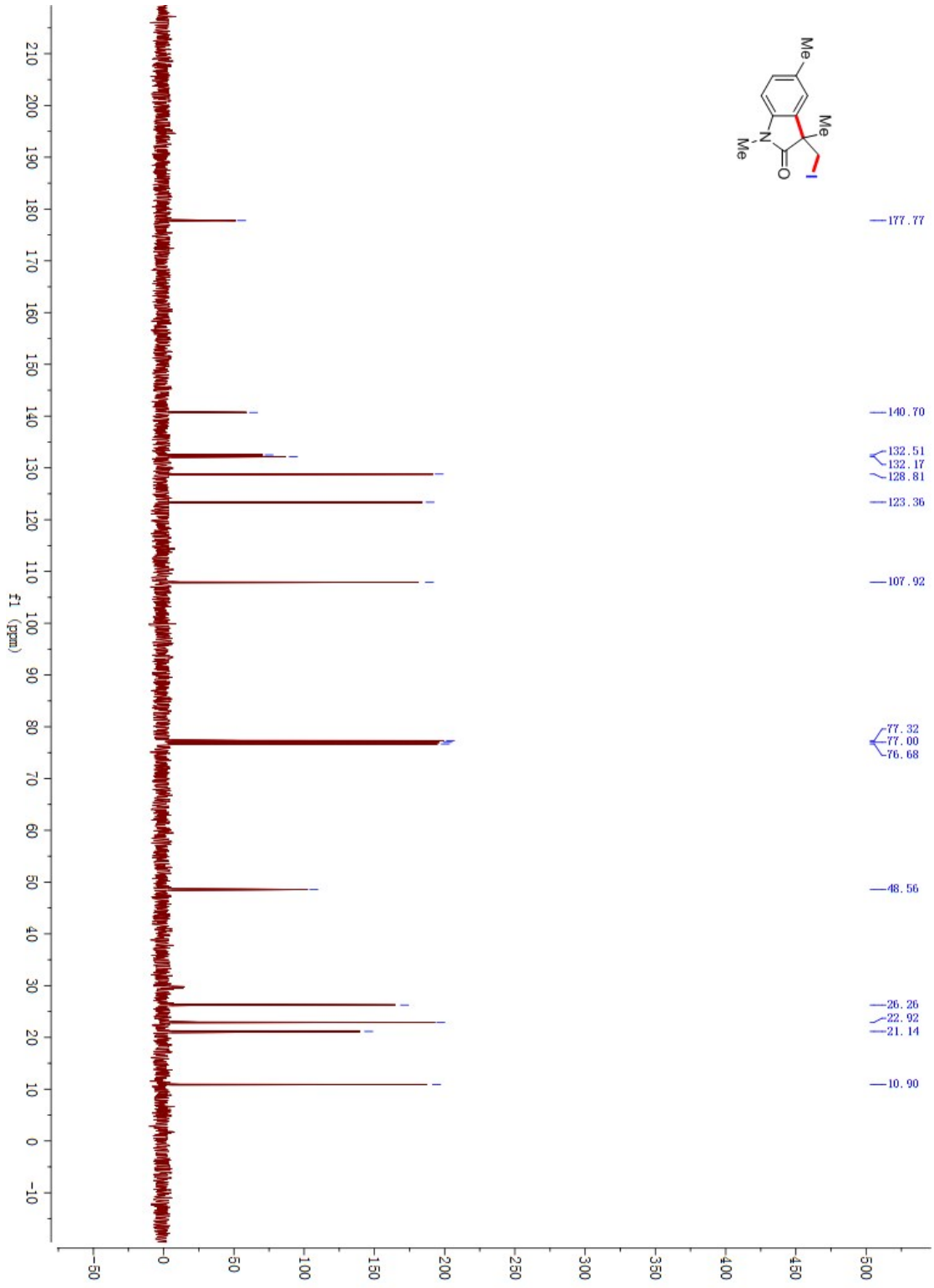
^{13}C NMR Spectra for **2f**



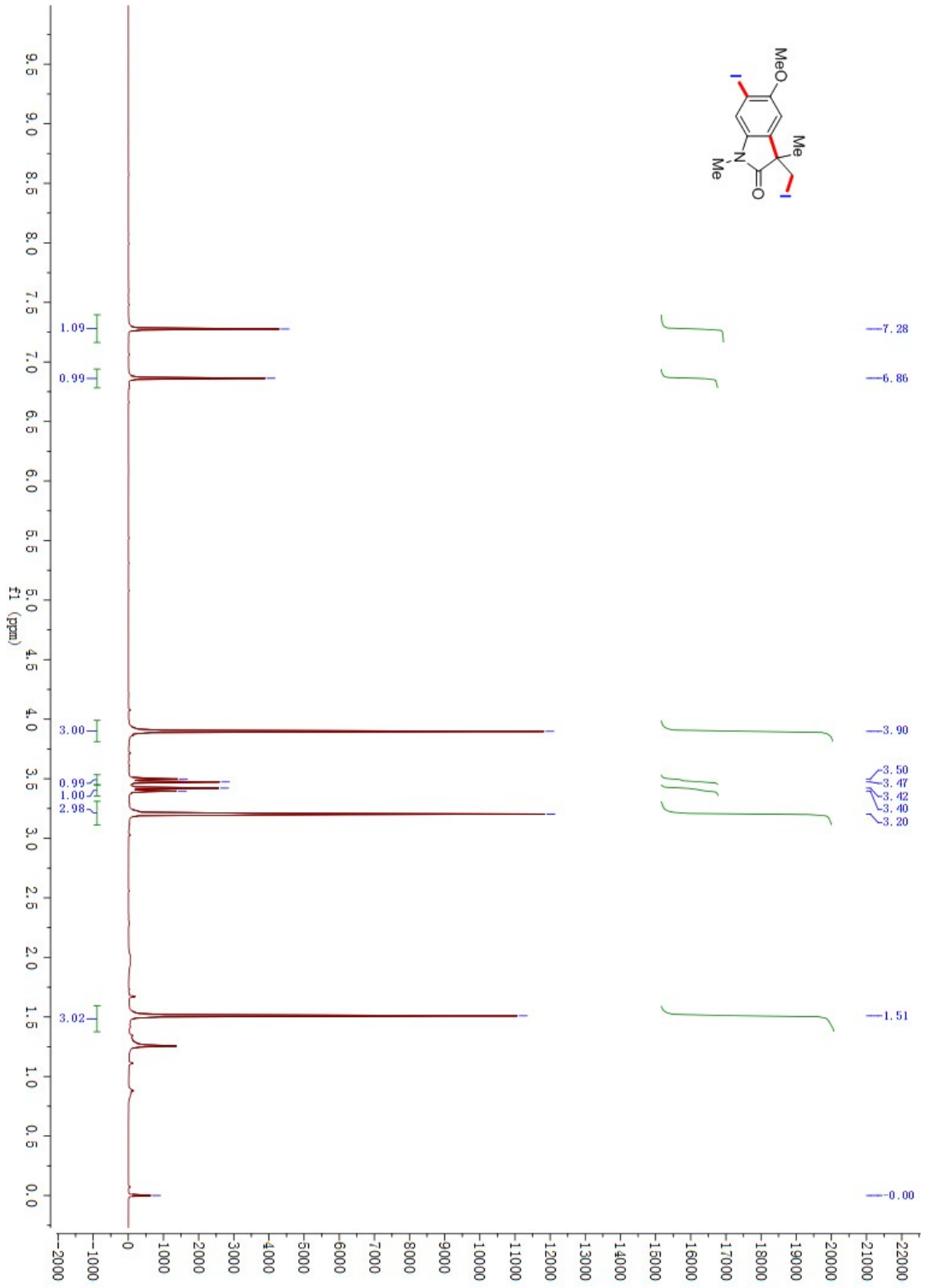
^{1}H NMR Spectra for **2g**



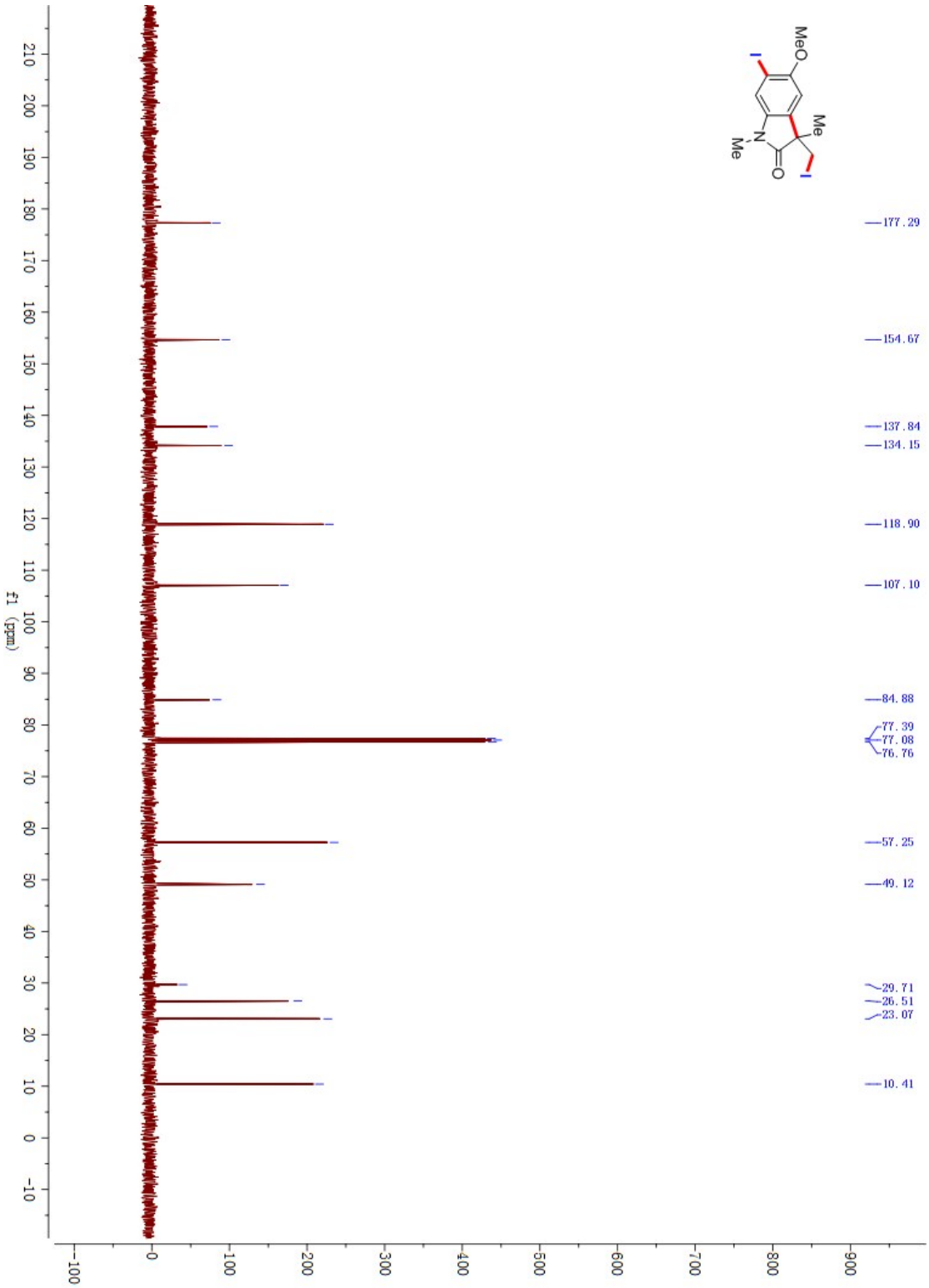
^{13}C NMR Spectra for **2g**



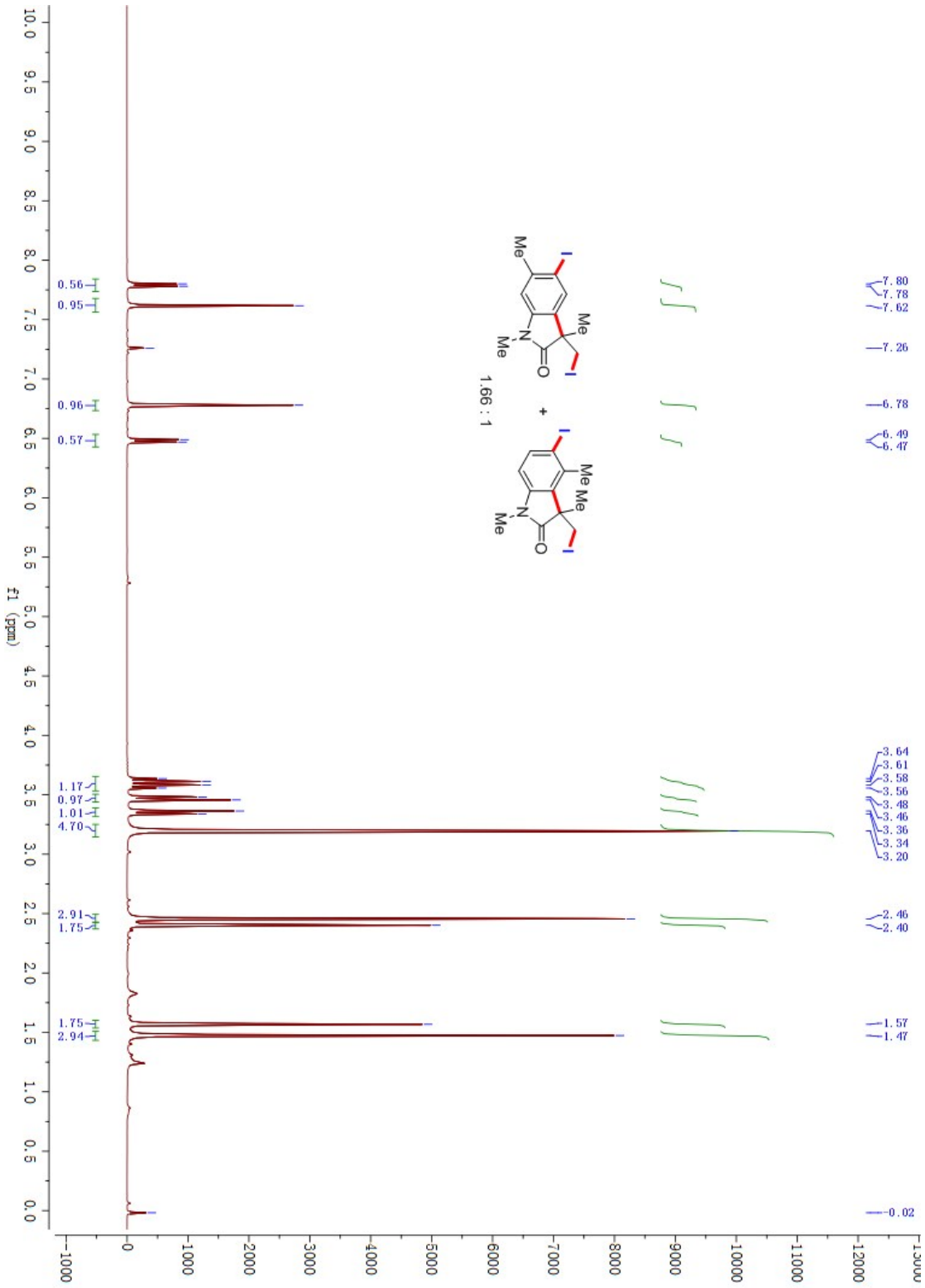
^{1}H NMR Spectra for **2h**



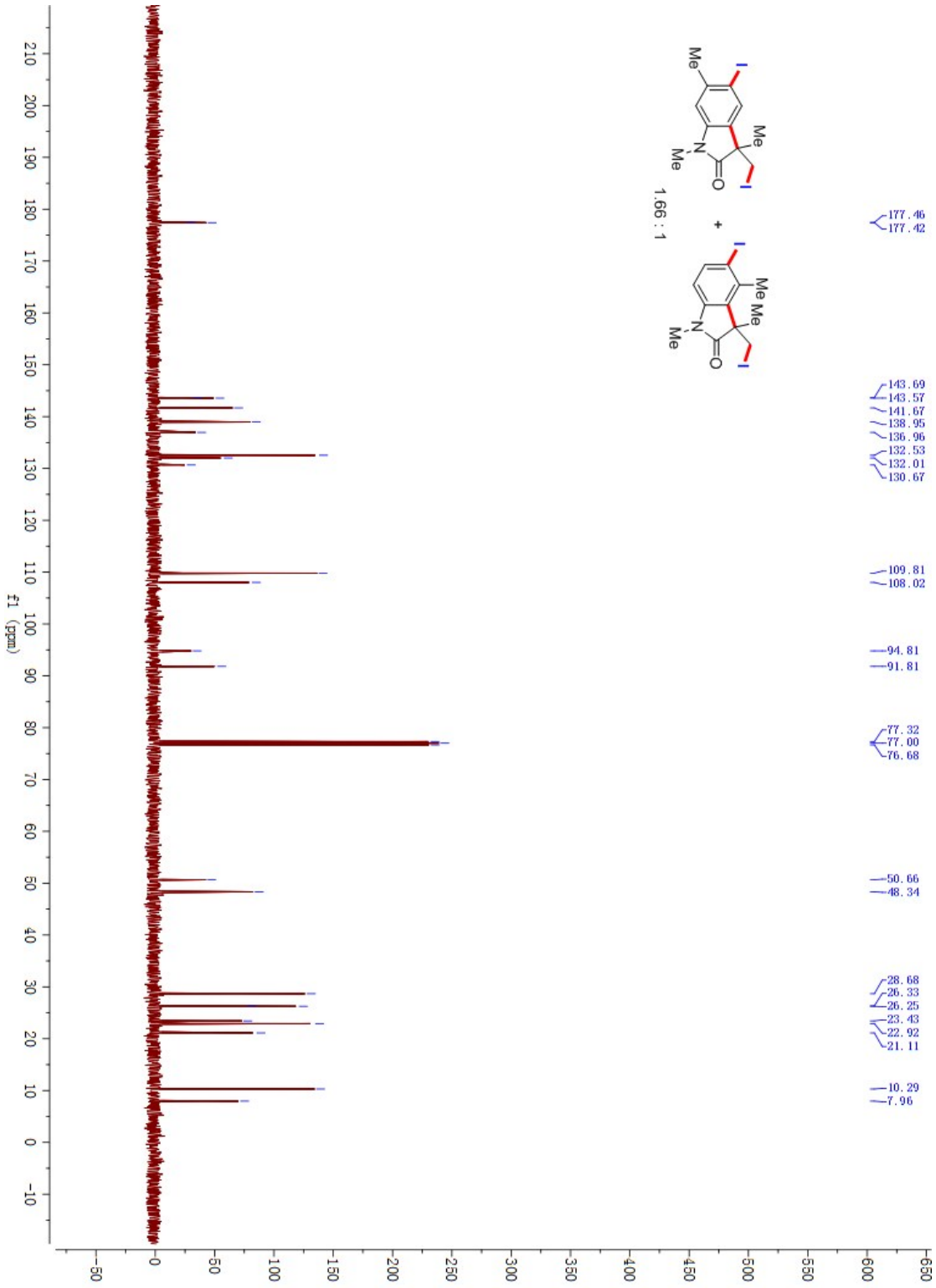
^{13}C NMR Spectra for **2h**



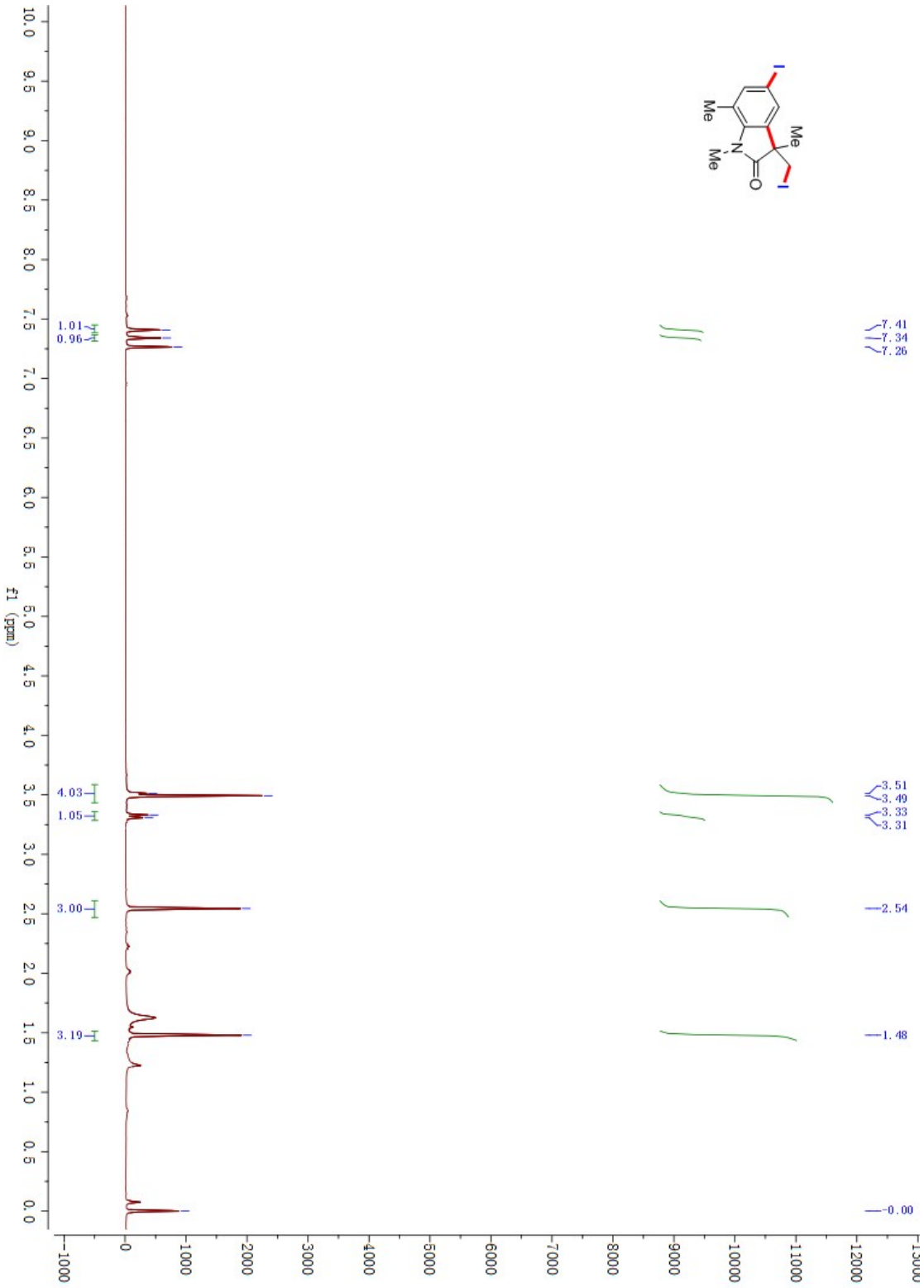
^{1}H NMR Spectra for **2i** and **2i'**



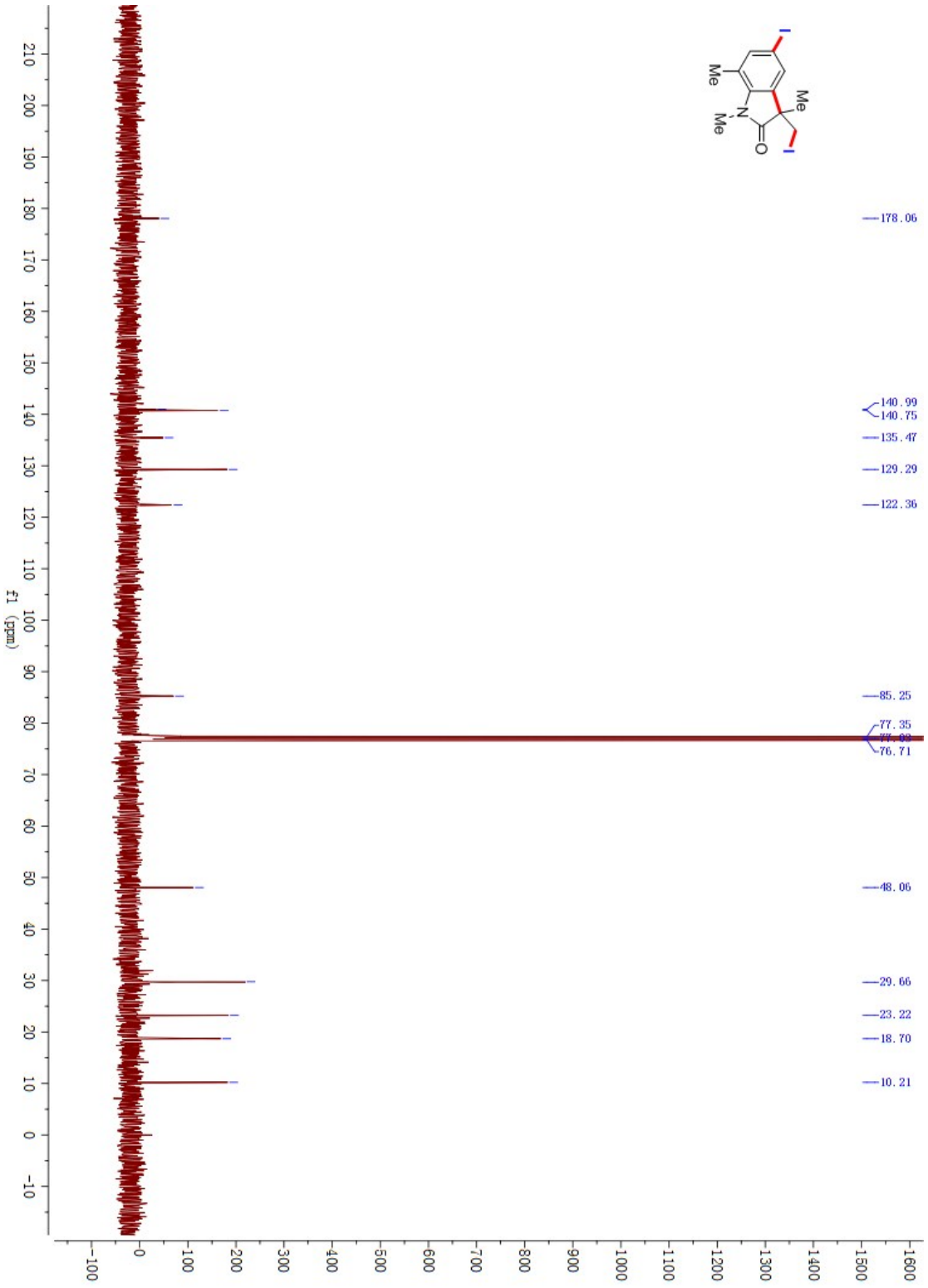
^{13}C NMR Spectra for **2i** and **2i'**



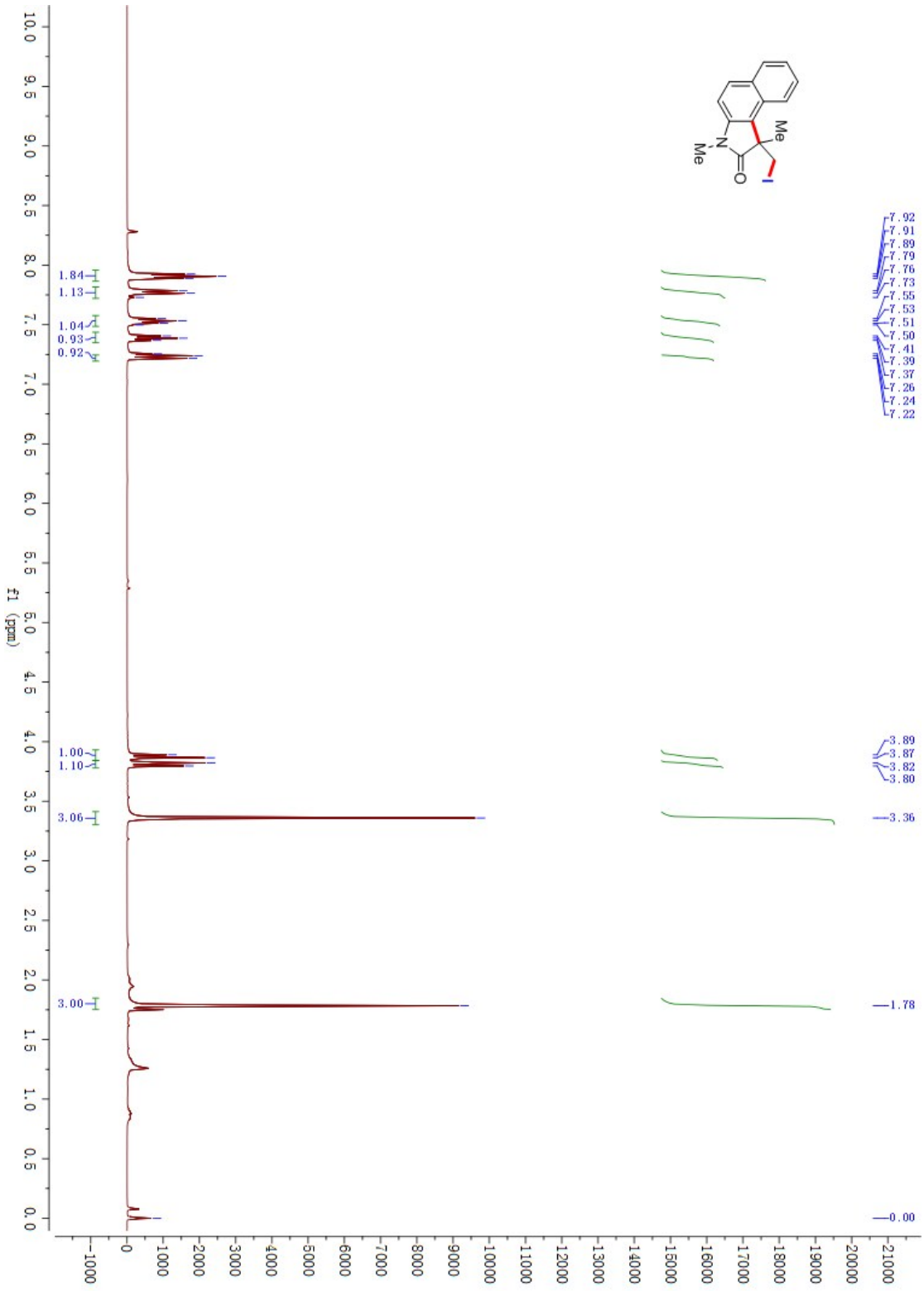
^{1}H NMR Spectra for **2j**



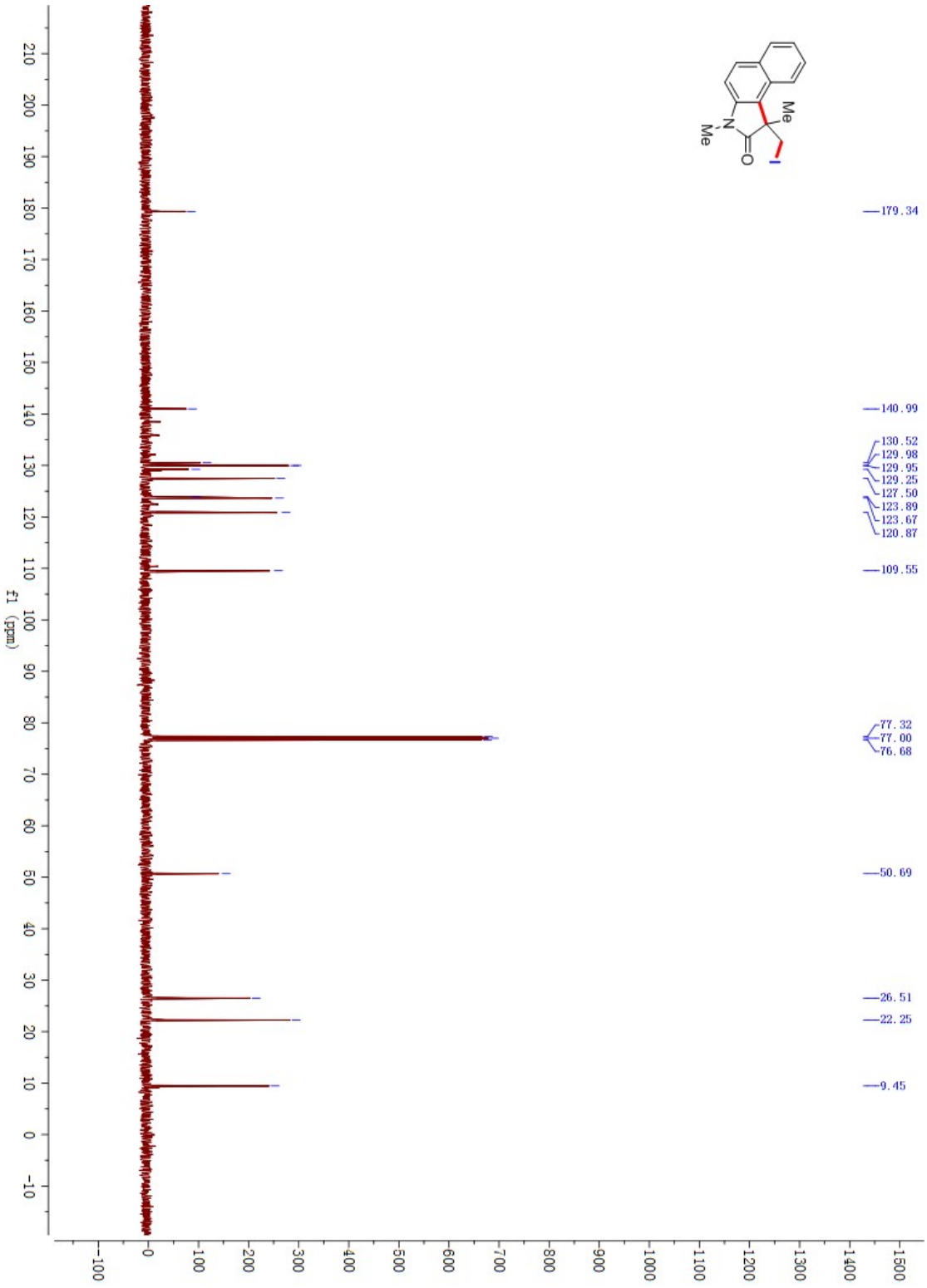
^{13}C NMR Spectra for **2j**



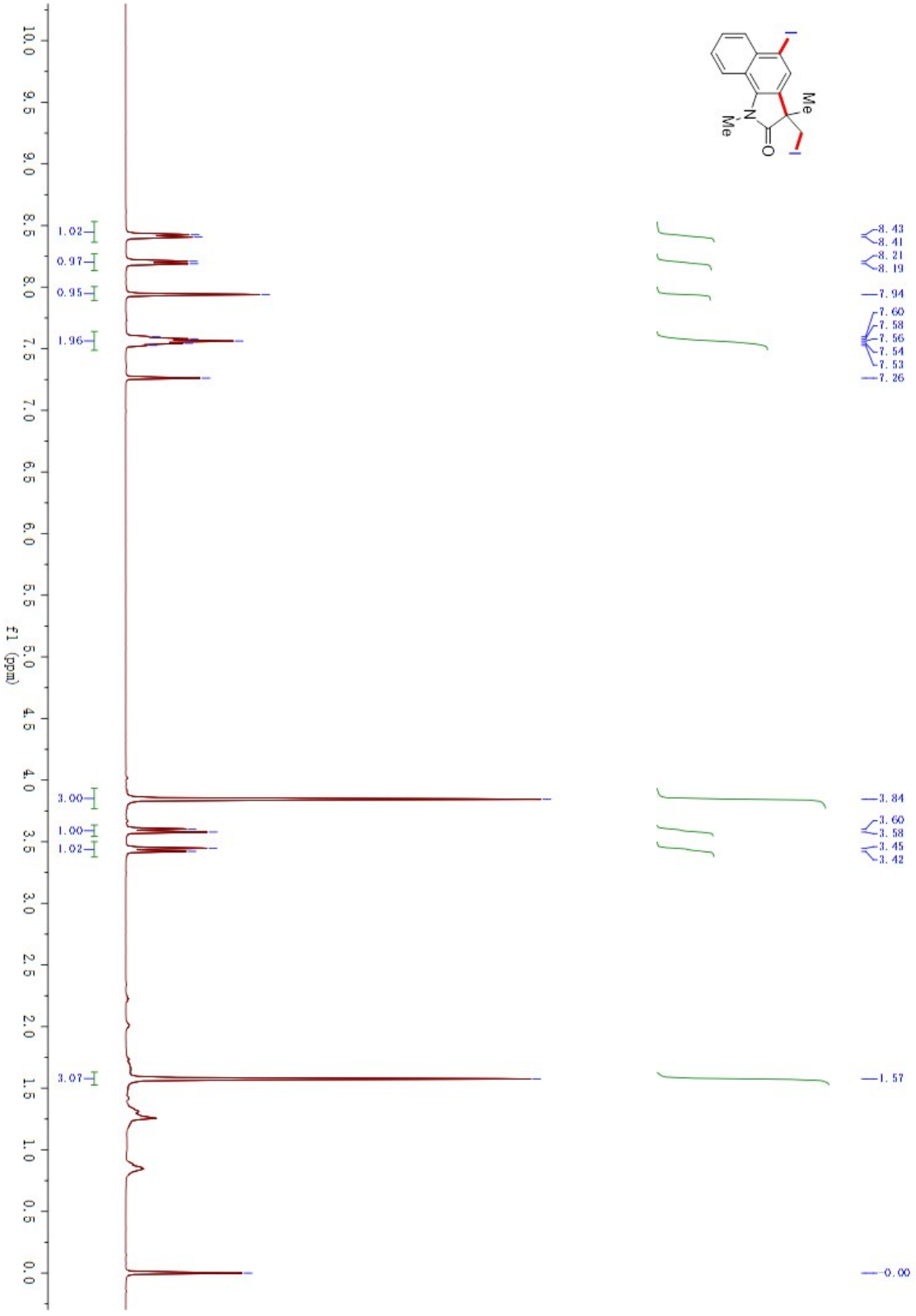
^{1}H NMR Spectra for **2k**



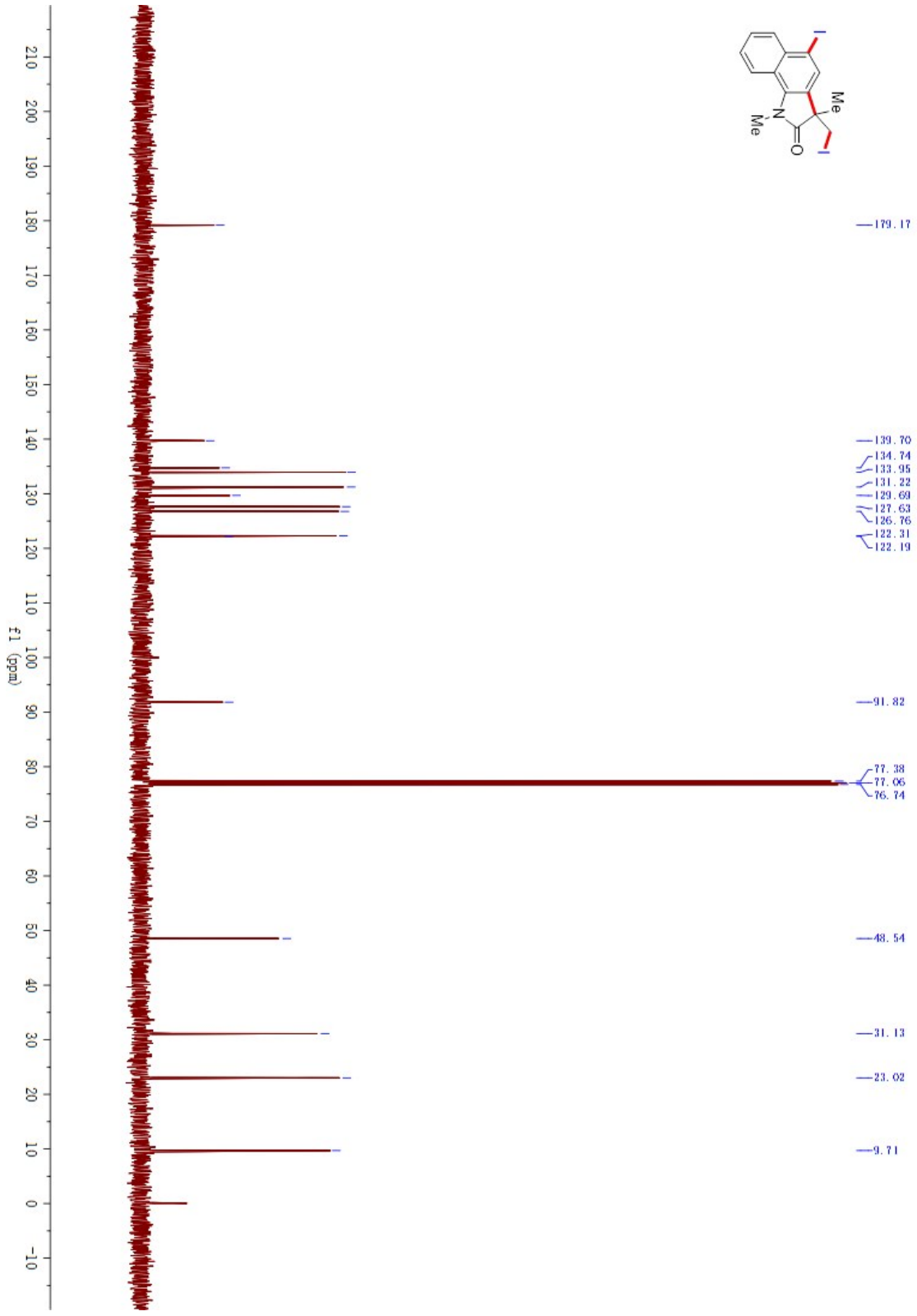
^{13}C NMR Spectra for **2k**



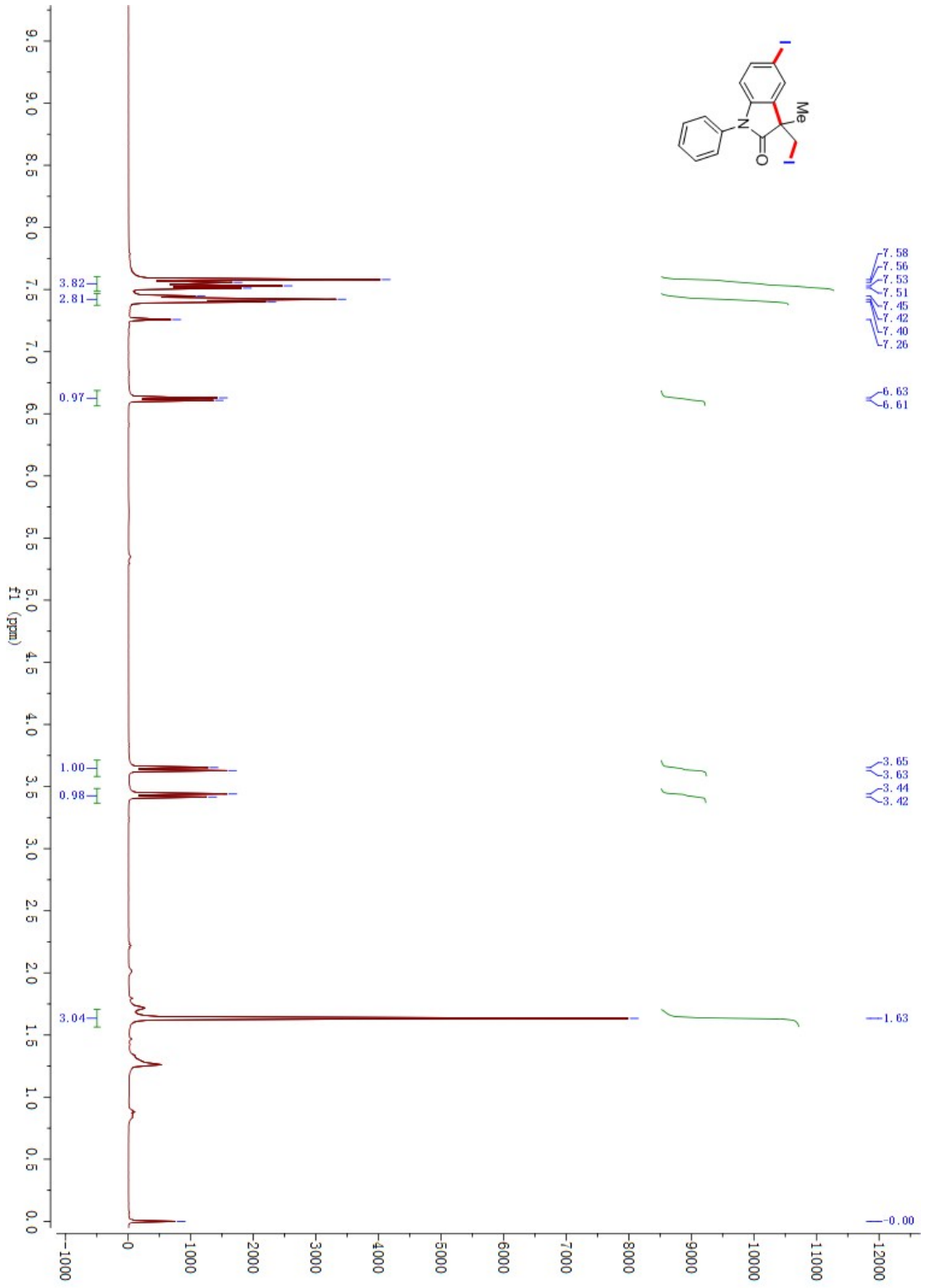
^{1}H NMR Spectra for **2l**



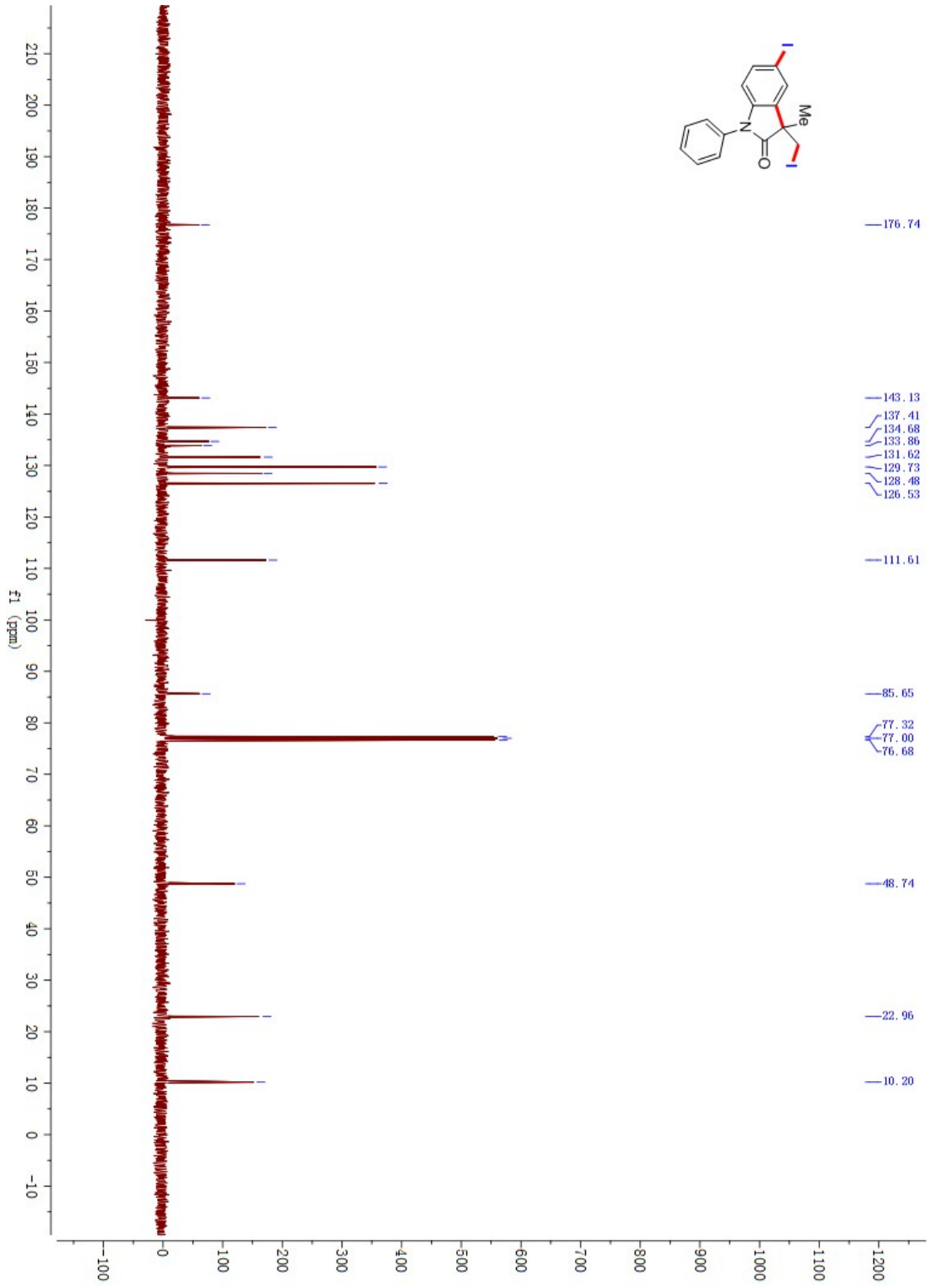
^{13}C NMR Spectra for **2l**



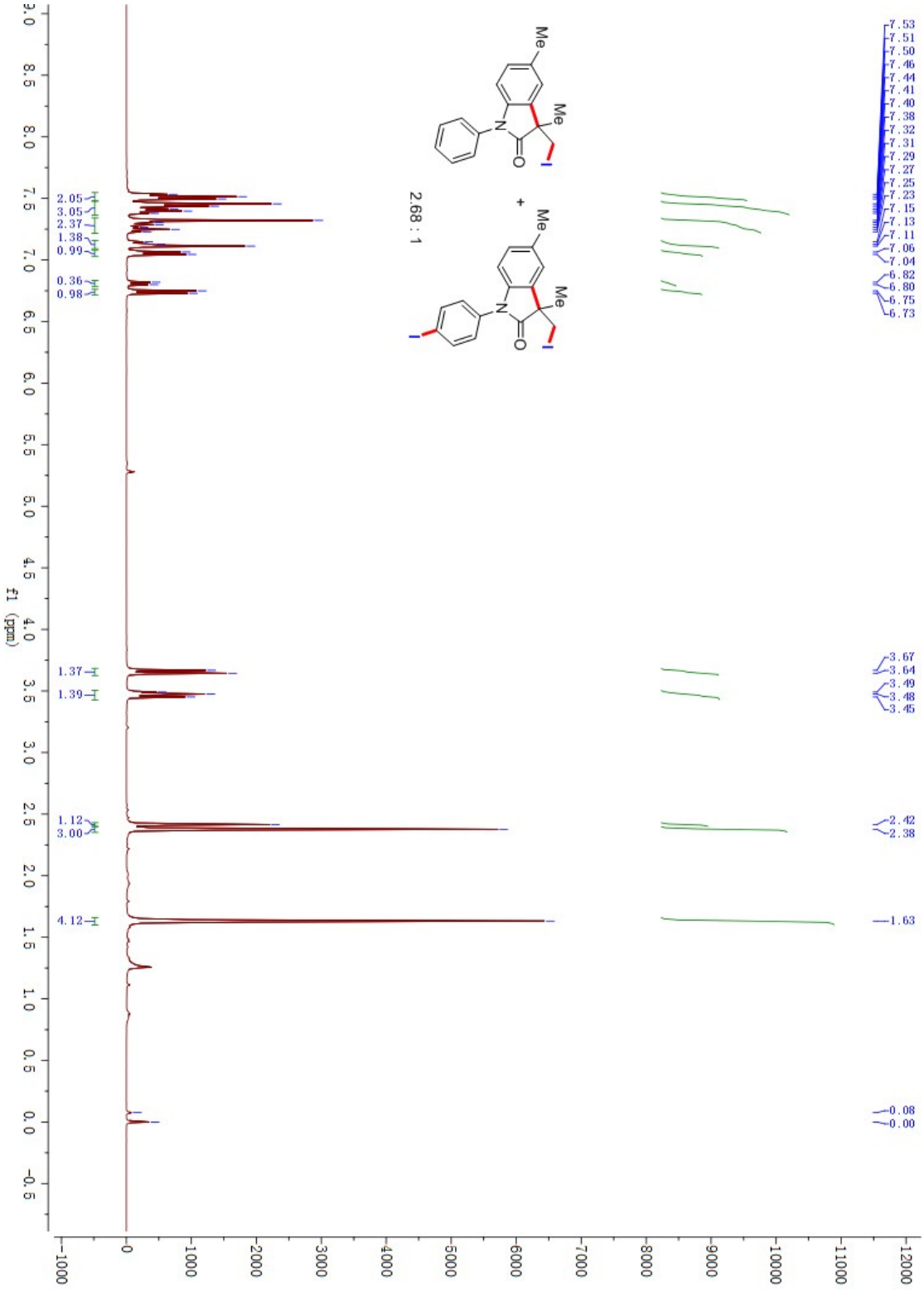
^{1}H NMR Spectra for **2n**



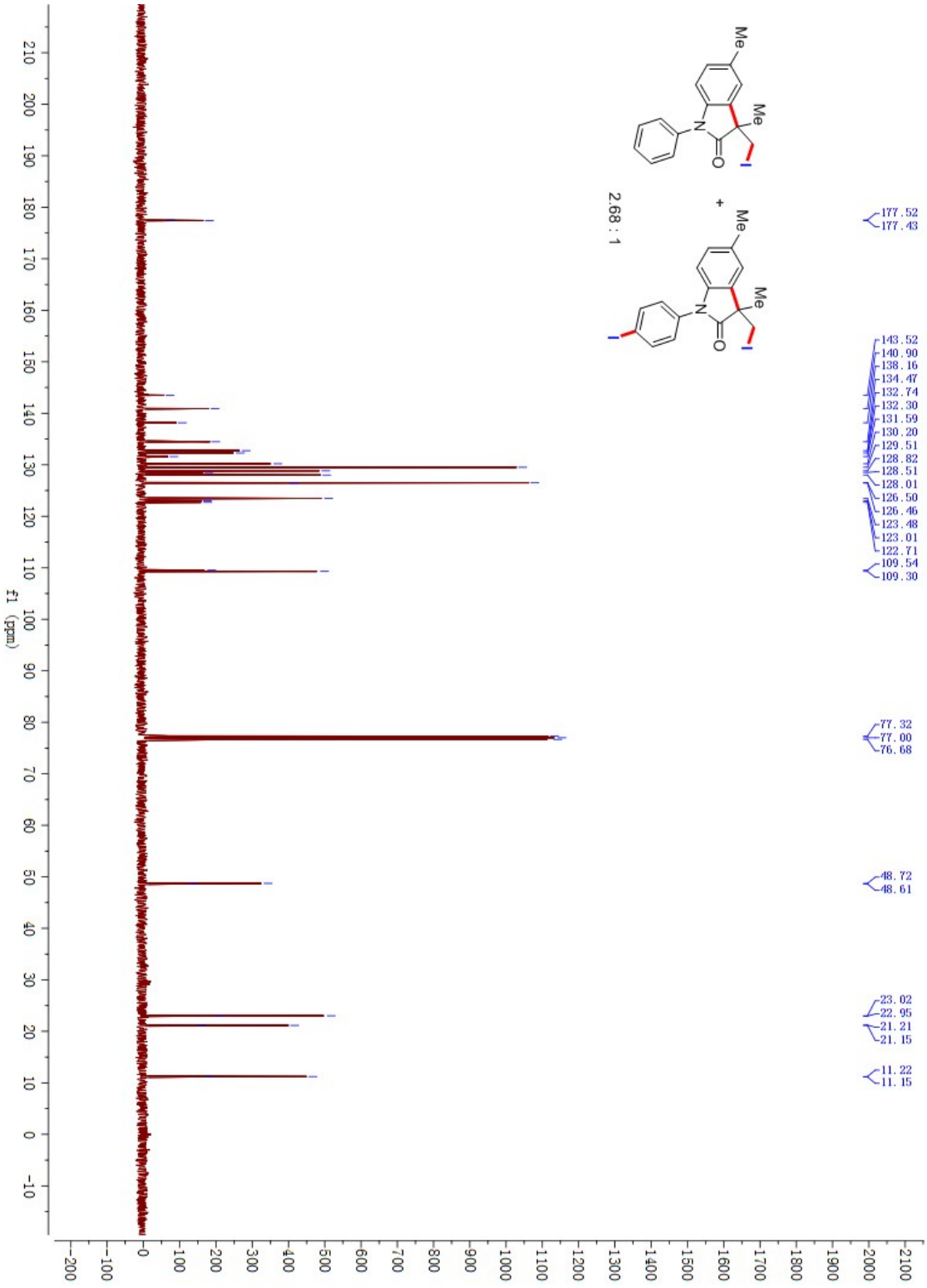
^{13}C NMR Spectra for **2n**


Me
N
O
176.74
143.13
137.41
134.68
133.86
131.62
129.73
128.48
126.53
111.61
85.65
77.32
77.00
76.68
48.74
22.96
10.20
f1 (ppm)

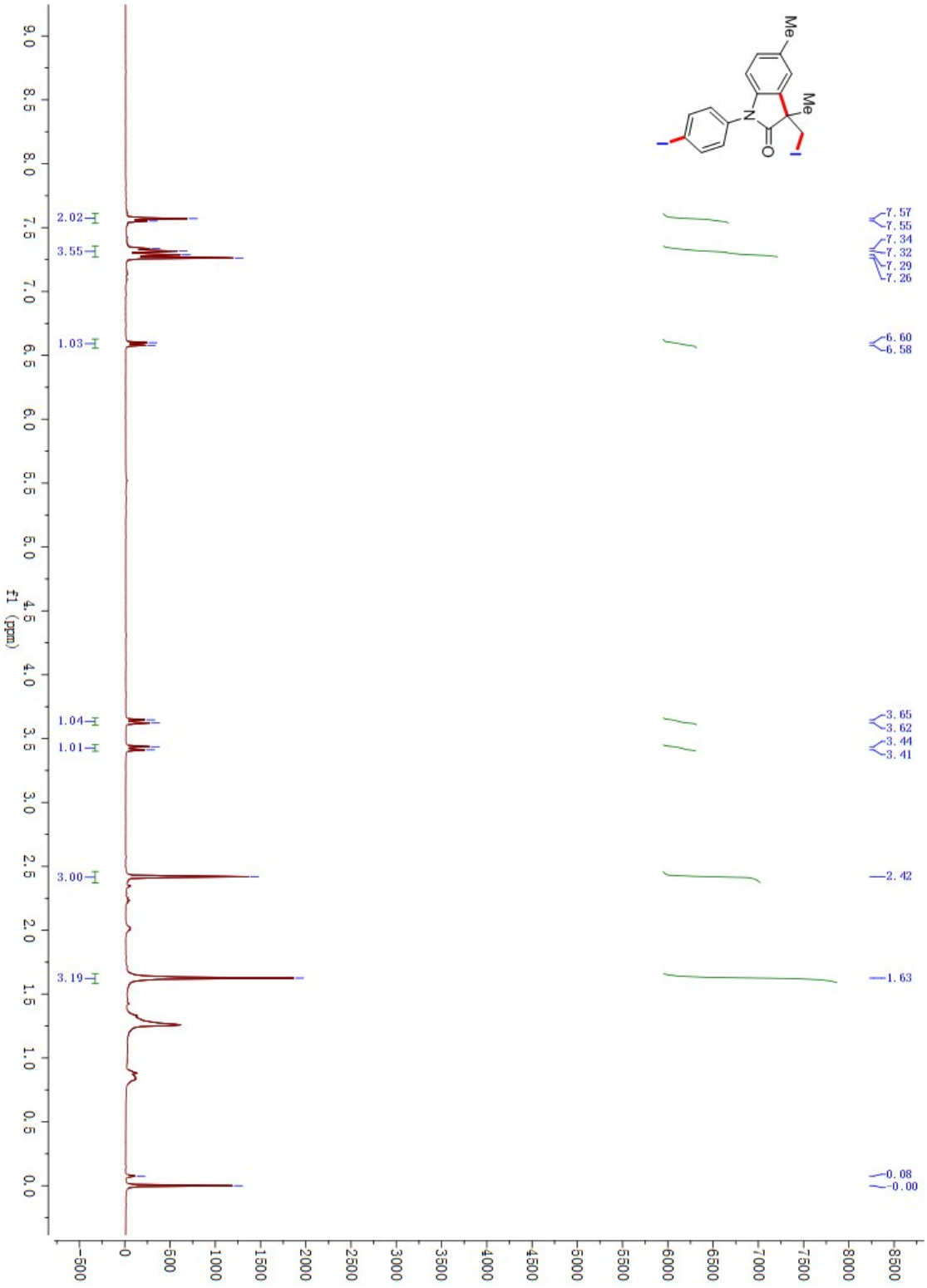
^{1}H NMR Spectra for **2o** and **2o'**



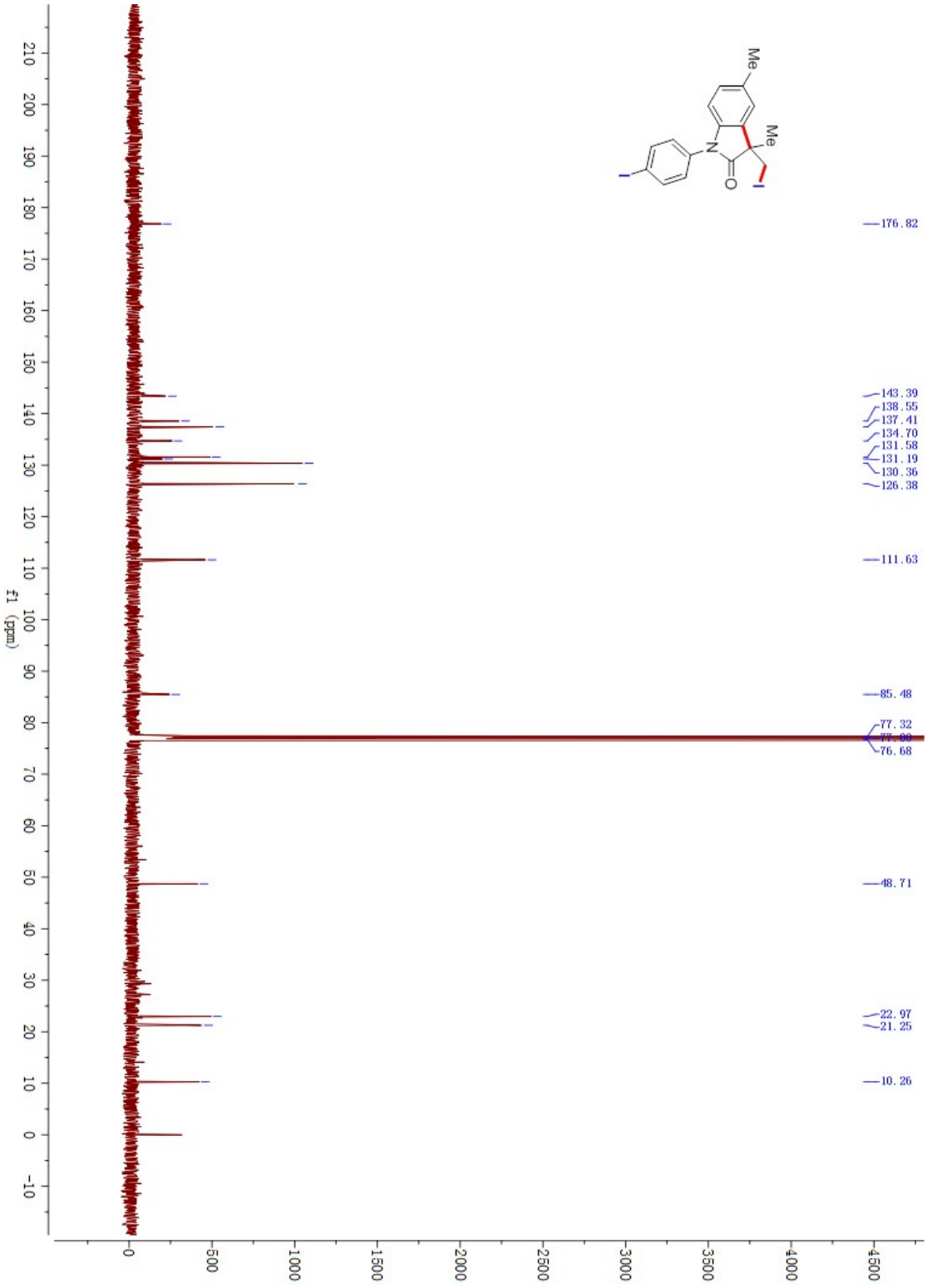
^{13}C NMR Spectra for **2o** and **2o'**



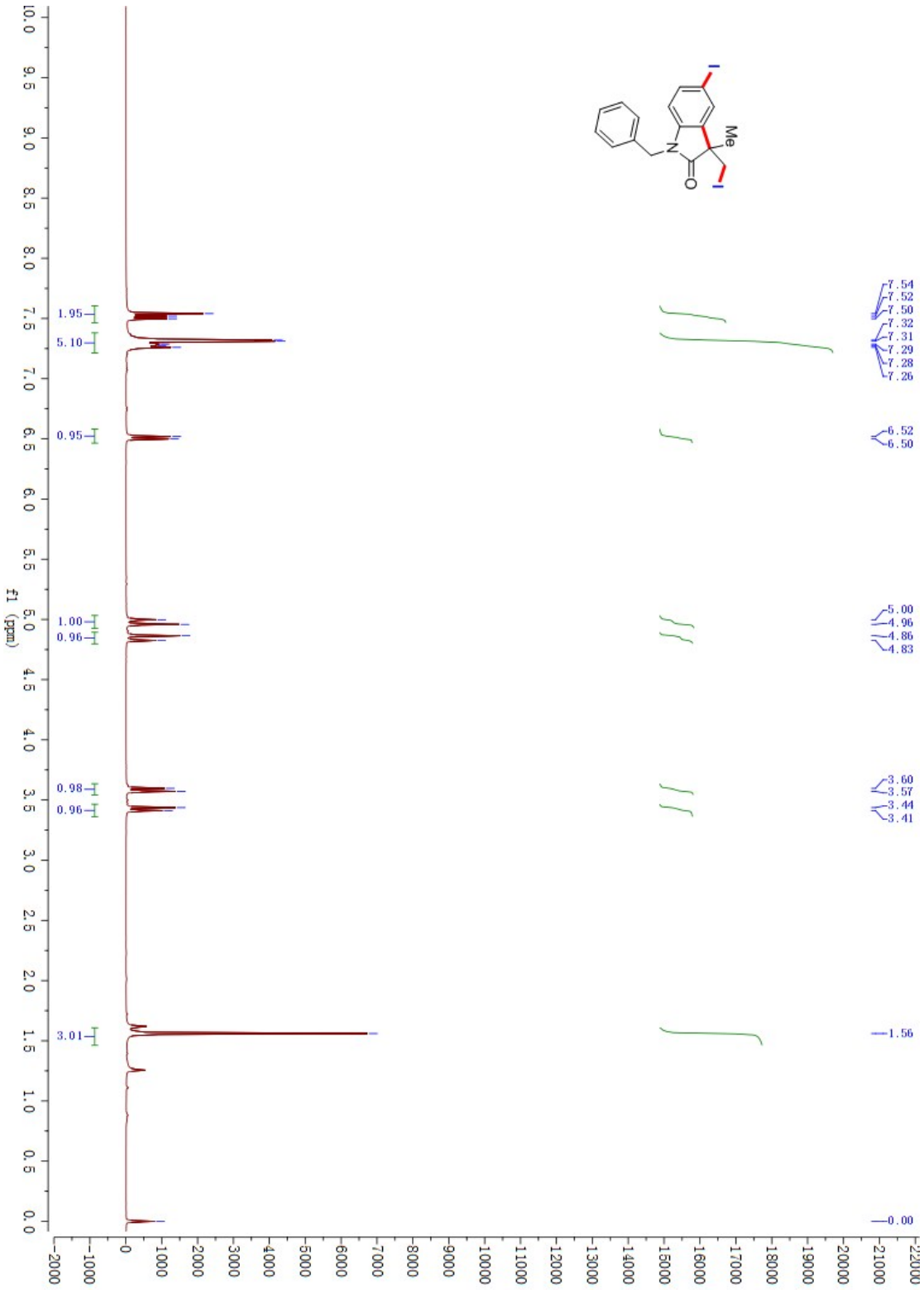
^{1}H NMR Spectra for **2o'**



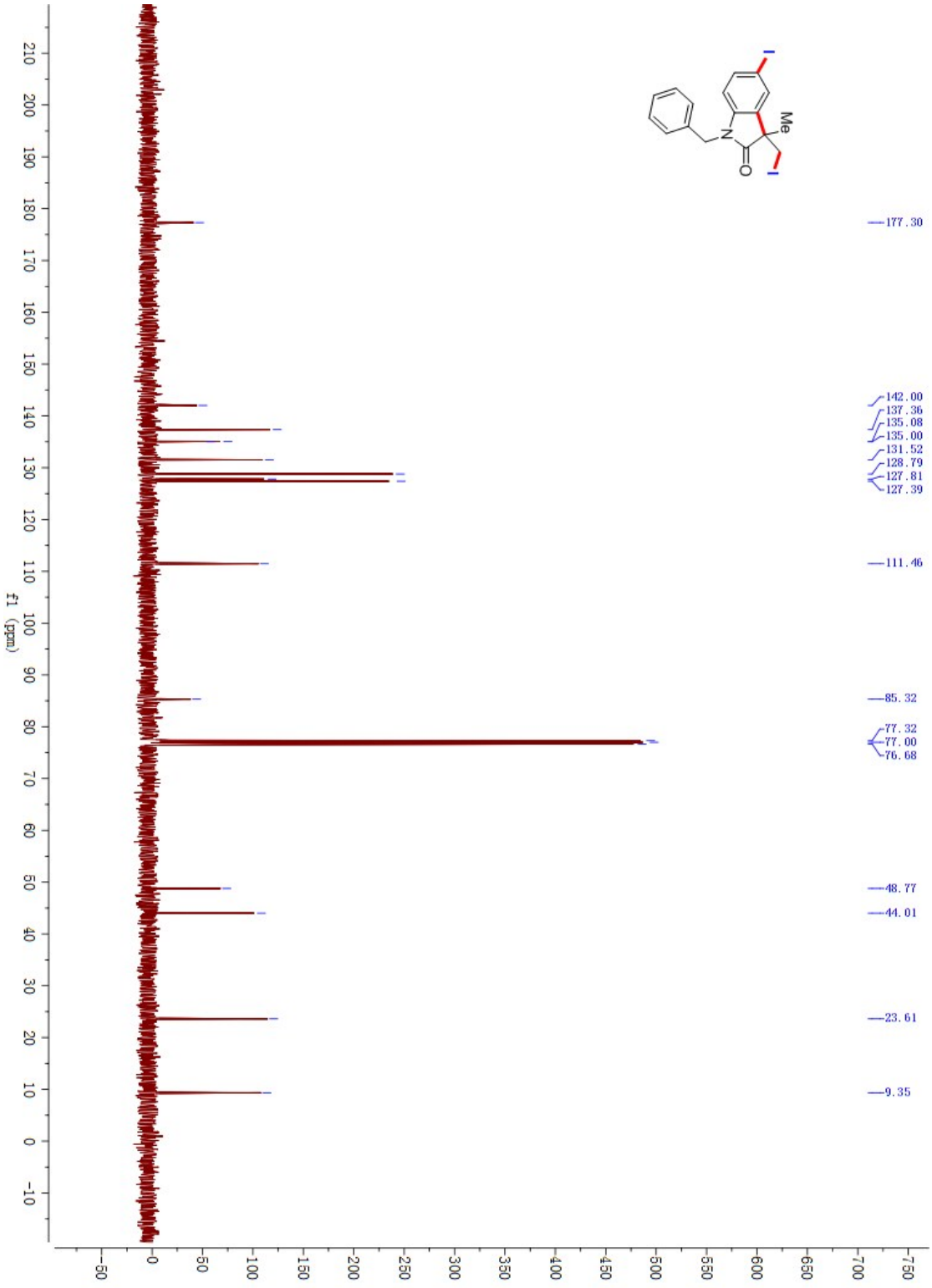
^{13}C NMR Spectra for **2o'**



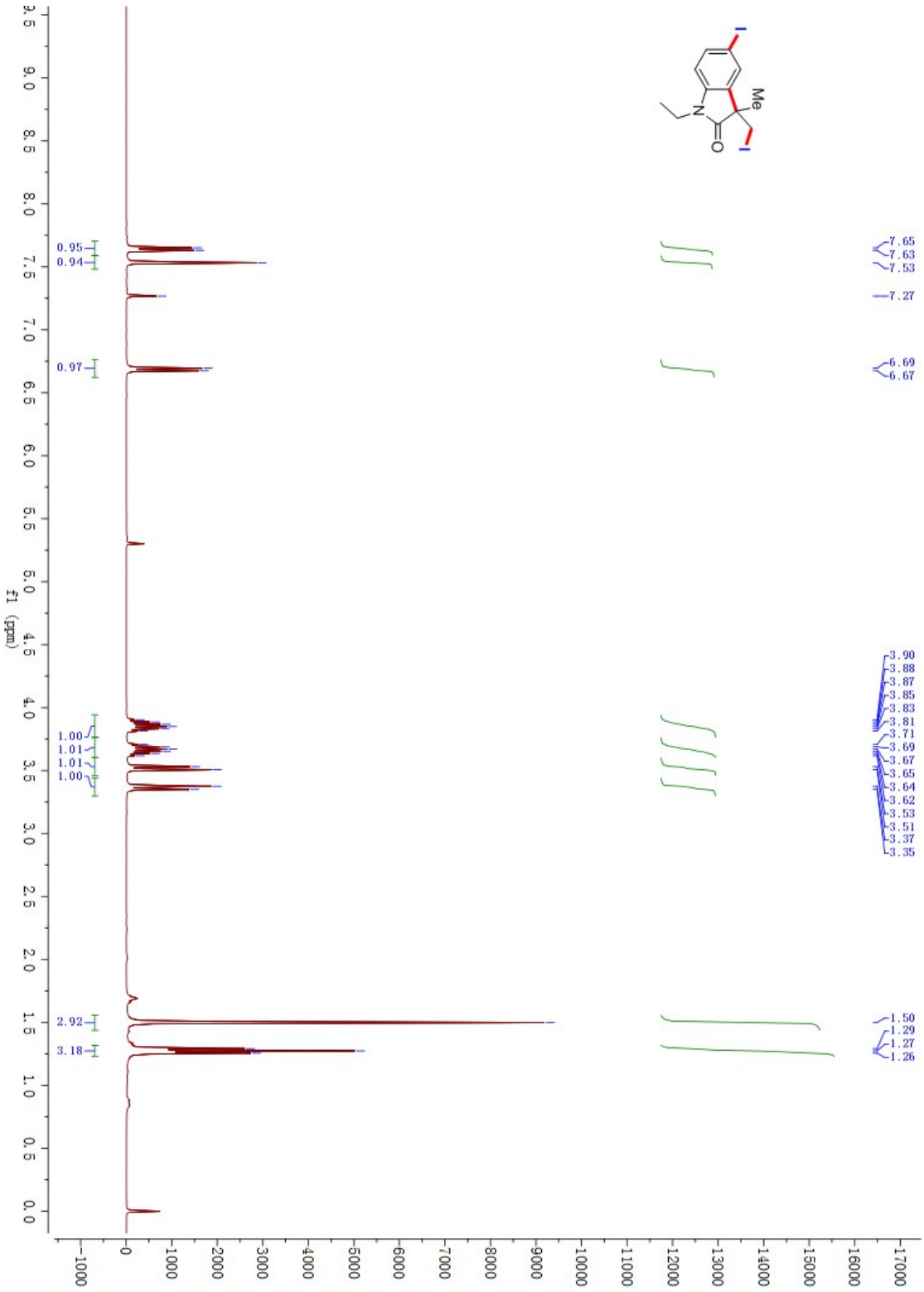
^{1}H NMR Spectra for **2p**



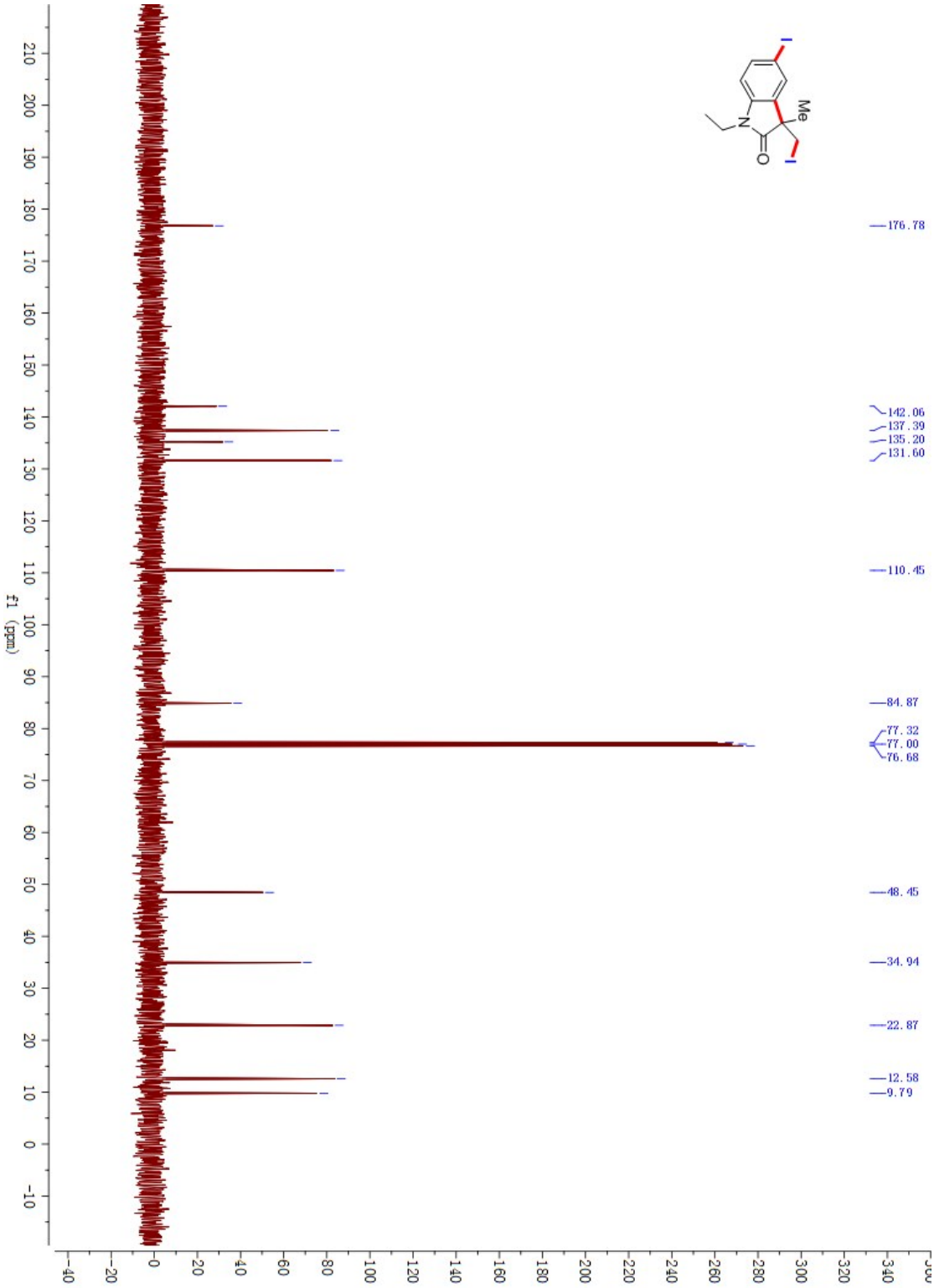
^{13}C NMR Spectra for **2p**



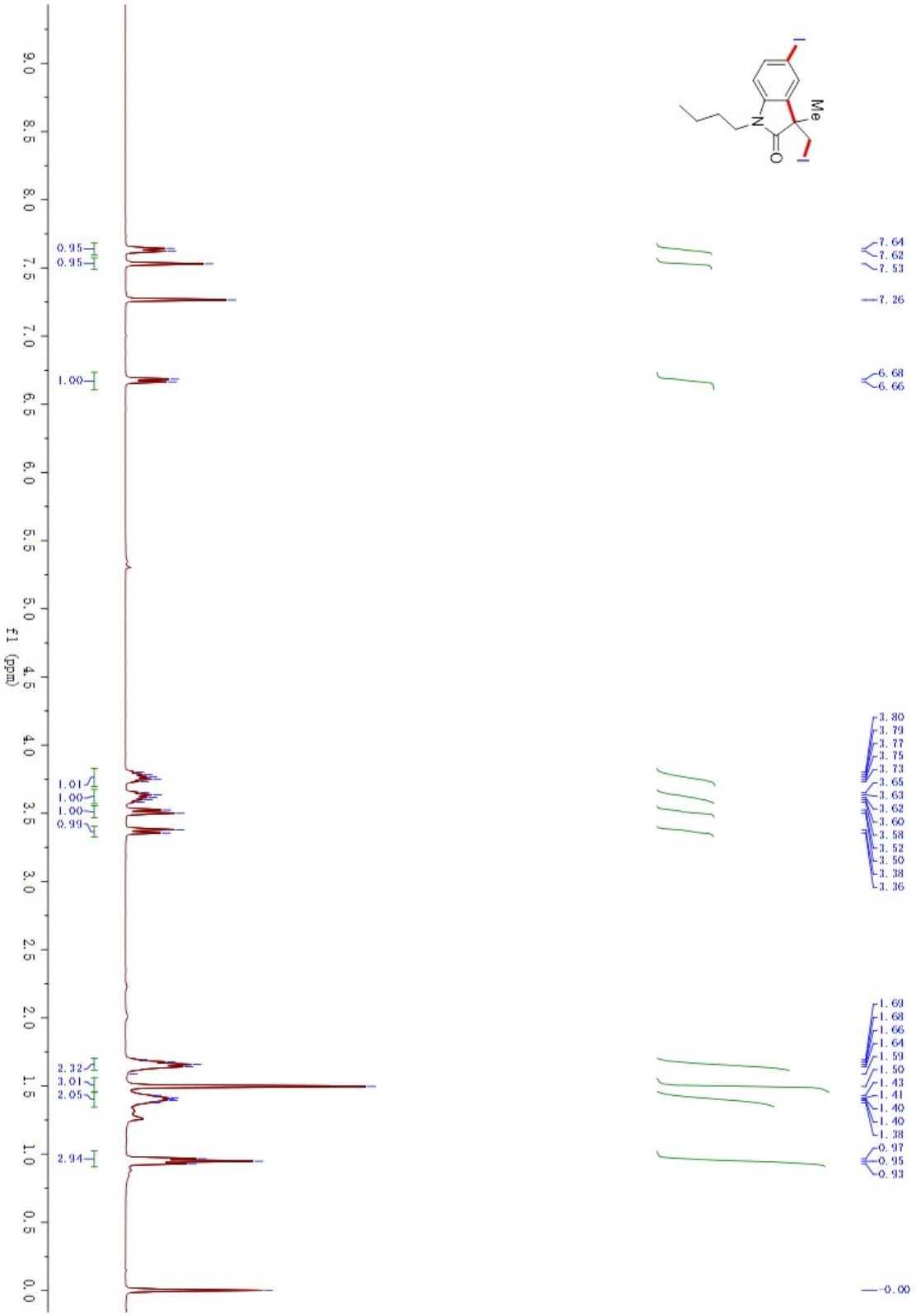
^{1}H NMR Spectra for **2q**



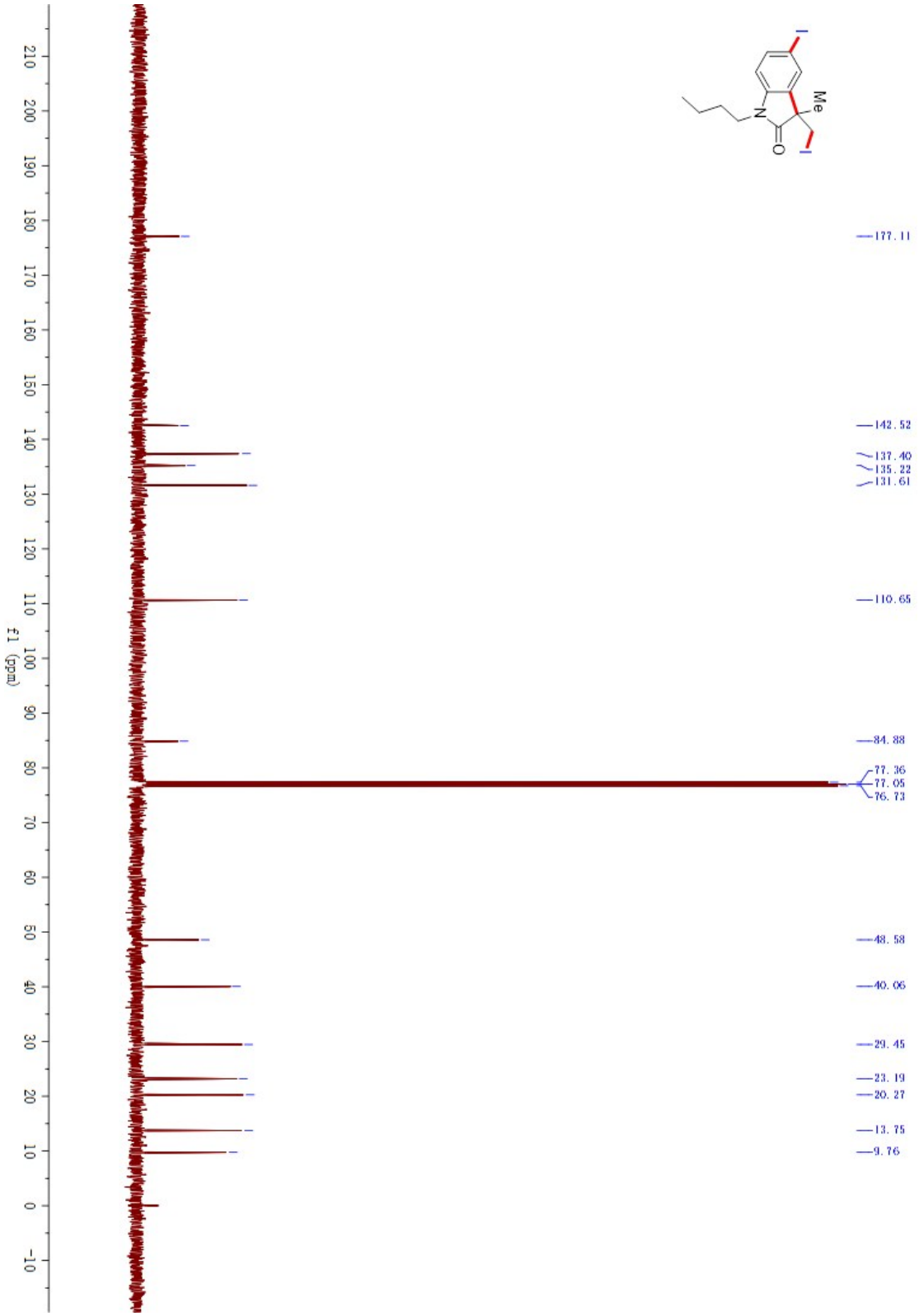
^{13}C NMR Spectra for **2q**



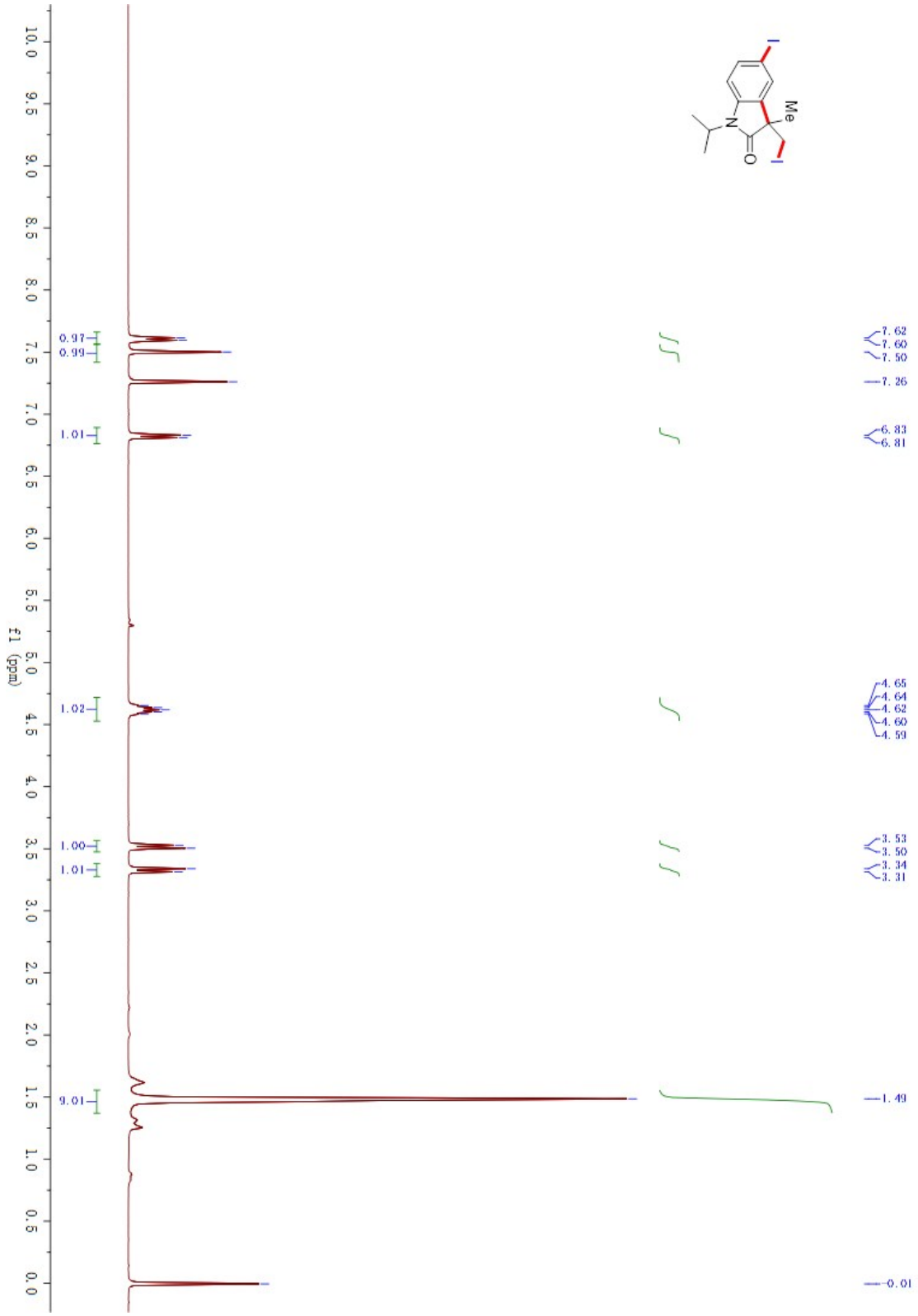
^{1}H NMR Spectra for **2r**



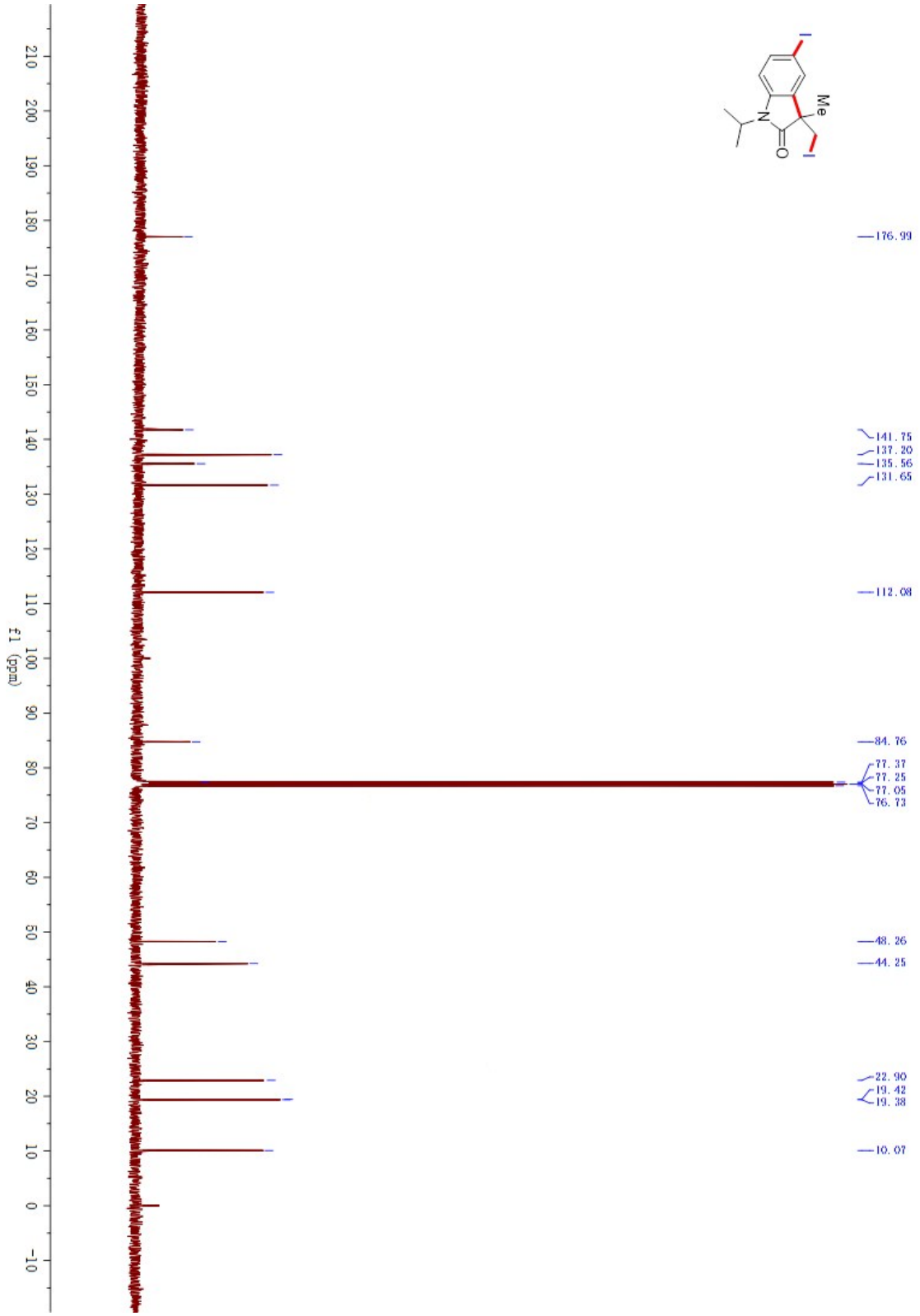
^{13}C NMR Spectra for **2r**



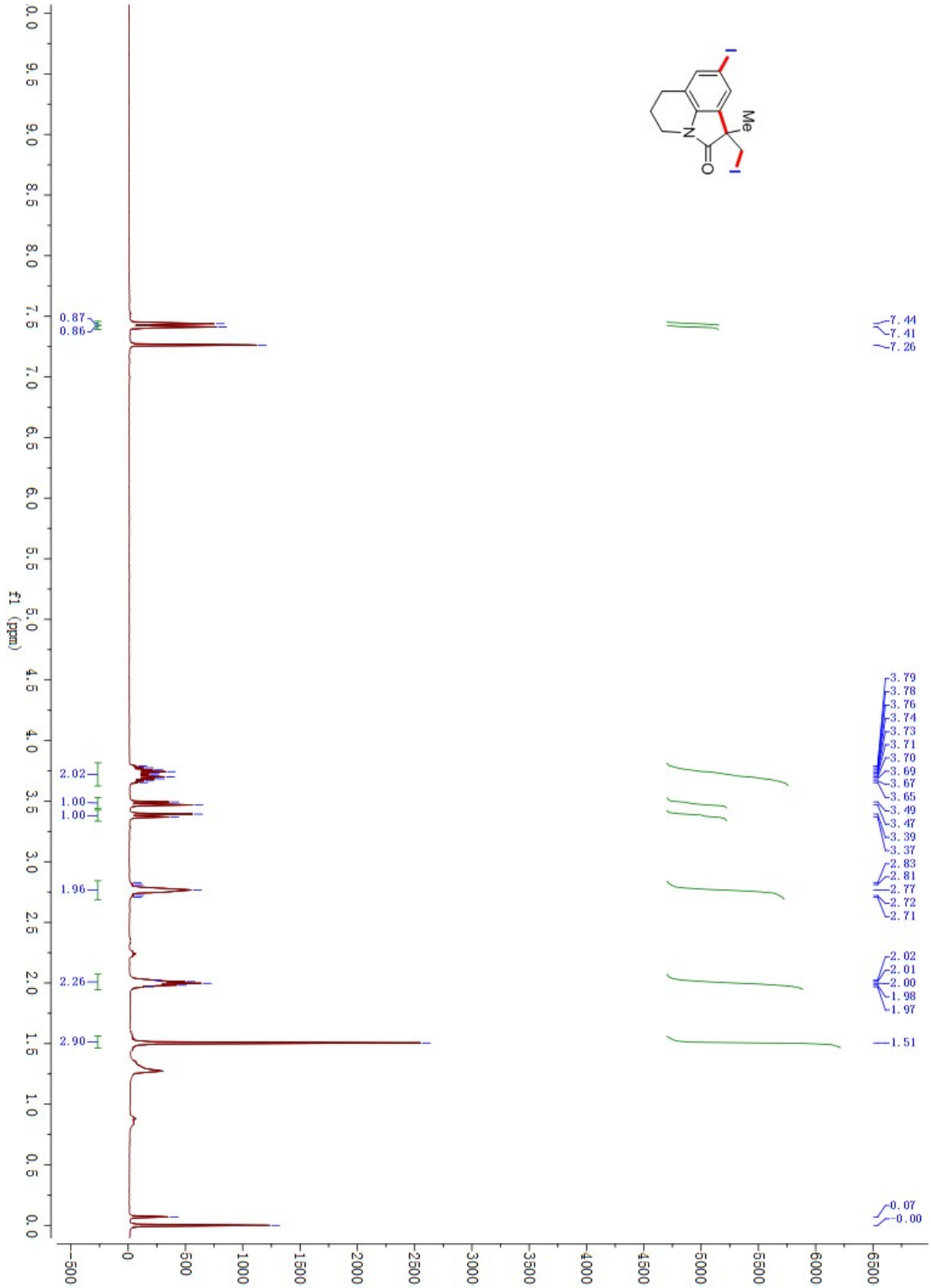
^{1}H NMR Spectra for **2s**



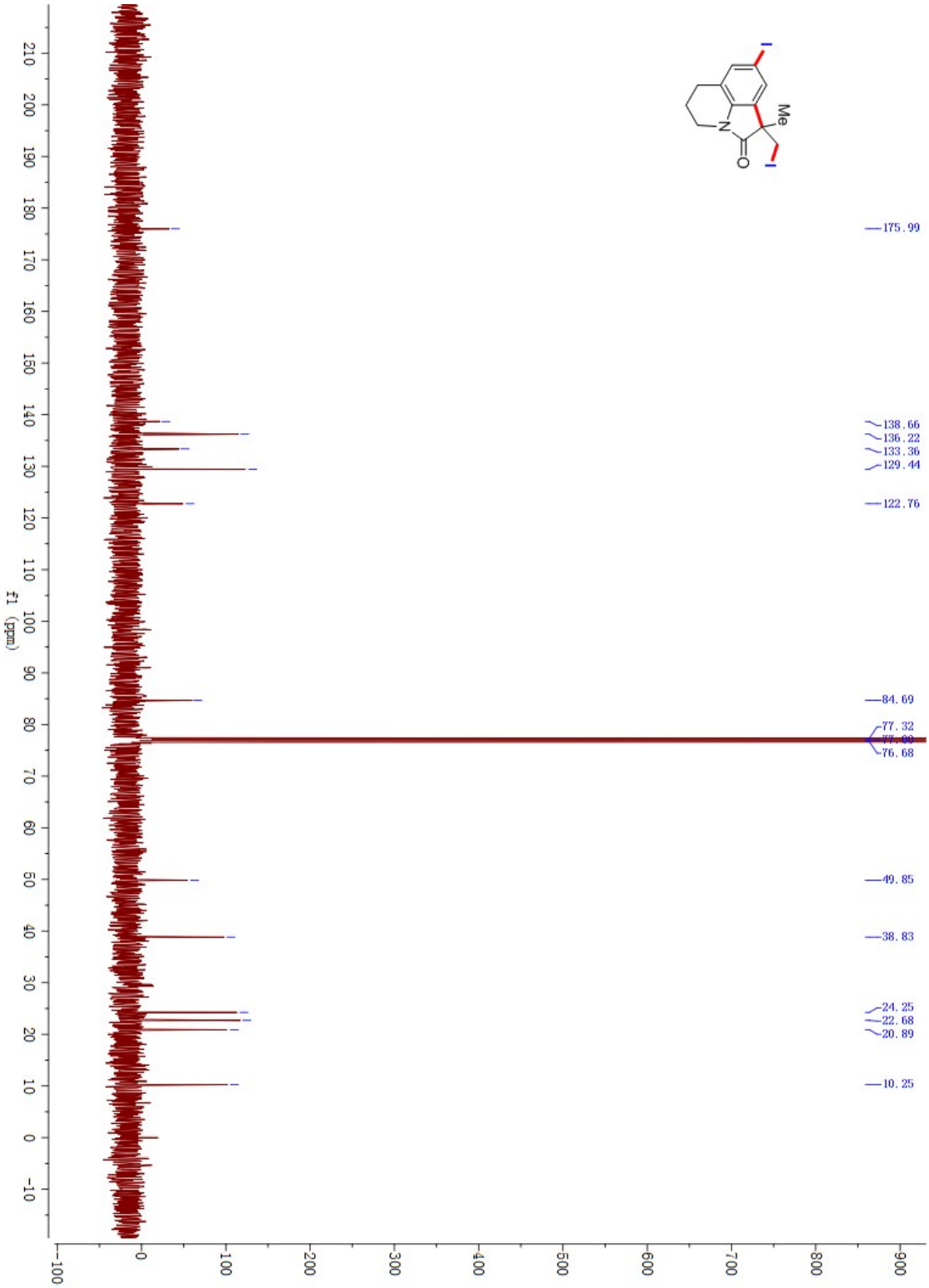
^{13}C NMR Spectra for **2s**



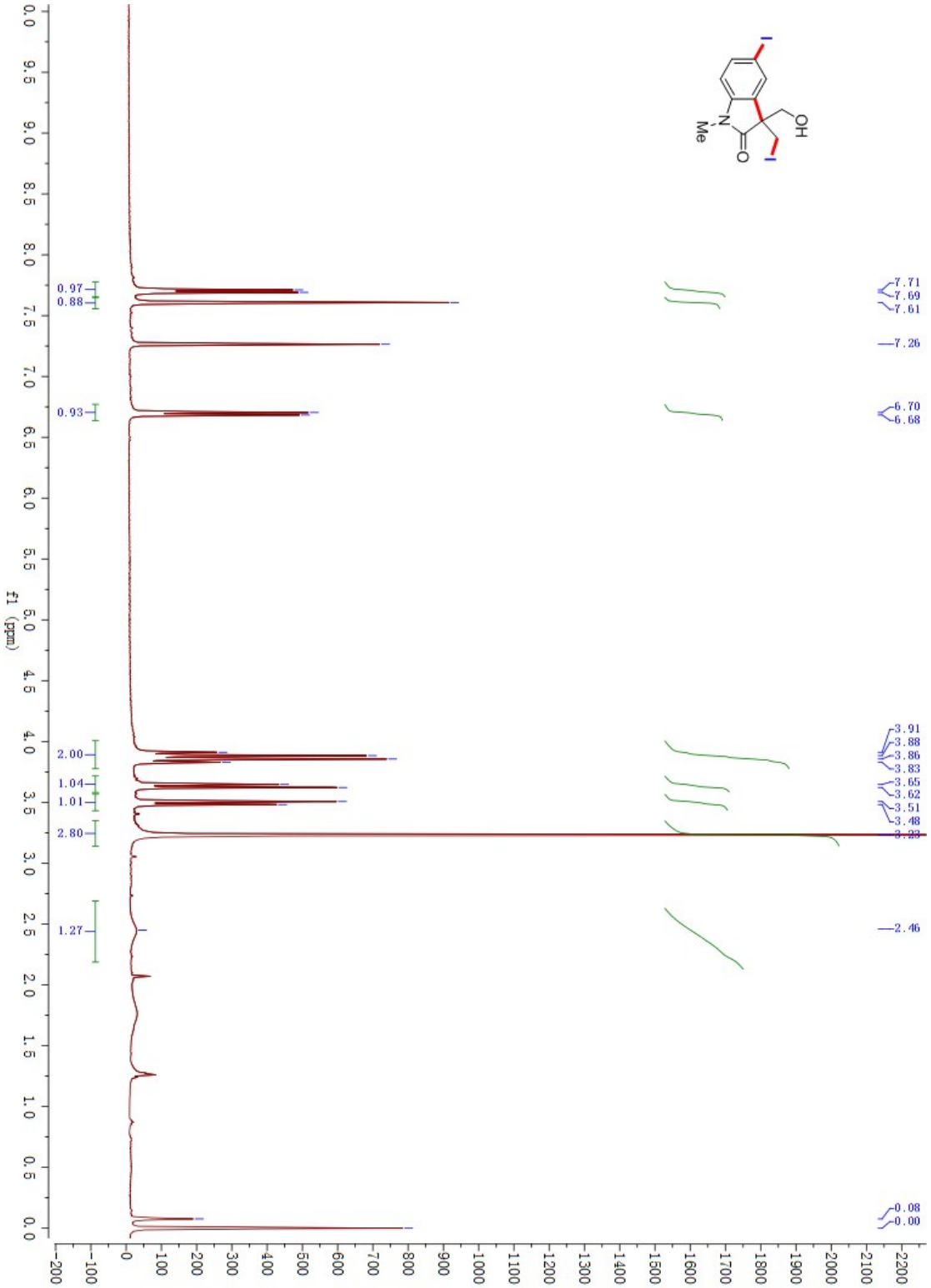
^{1}H NMR Spectra for **2t**



^{13}C NMR Spectra for **2t**



^{1}H NMR Spectra for **2u**



^{13}C NMR Spectra for **2u**