Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Manganese-mediated/-catalyzed oxidative carboazidation of acrylamides

Danwei Zhao[a], Kai Kang[a], Wen Wan[a,b], Haizhen Jiang[a], Hongmei Deng[c], Yunrong Chen[a,*], Jian Hao[a,b,*]

[a] Department of Chemistry, Innovative Drug Research Center, ShanghaiUniversity, Shangda Road 99, Shanghai, 200444, P. R. China
[b] Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Ling Ling Road 345, Shanghai, 200032 P. R. China
[c] Laboratory of Microstructures, Shanghai University, Shangda Road 99, Shanghai 200444, P. R. China

email: cir.chen@hotmail.com, jhao@shu.edu.cn

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General methods

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen. ^{1}H and ^{13}C NMR spectra were recorded on a on a Bruker AV-500 spectrometer (500 MHz and 126 MHz MHz, respectively). ^{1}H, ^{13}C NMR chemical shifts are reported vs tetramethylsilane signal or residual protio solvent signals. High resolution mass spectra (HRMS) was recorded on Agilent G6500 iFunnel Q-TOF LC/MS.

Toluene, dioxane and THF were distilled over sodium benzophenone ketyl under nitrogen. Acetonitrile (ACN) and 1,2-Dichloroethane (DCE) were distilled over CaH_2 under nitrogen. Dimethyl sulfoxide, N,N-dimethylformamide and N,N-dimethylacetamide were used before vacuum distillation over CaH_2 under nitrogen.

Acrylamides substrates were synthesized following the literature procedures[1]. All other chemicals and solvents were purchased from commercial company and used as received.

Experimental Details and Characterization Data

Expermential Procedures for Table 2 & 3.

Procedure for Mn-catalytic reactions:

An oven-dried 10 mL seal tube was charged with $Mn(OAc)_3•2H_2O$ 8.0 mg (0.03 mmol, 10 mol%) and acrylamide **1**(0.30 mmol, 1.0 equiv.), 2 mL DCE, TBPB 84 μL (0.45 mmol, 1.5 equiv.) and $TMSN_3$ 78 μL (0.60 mmol, 2.0 equiv.) under nitrogen atmosphere. The reaction mixture was stirred at 100 °C for 12 h monitored by TLC and then was concentrated under vacuum. The residue was purified by flash chromatography on silica gel with petroleum ether and ethyl acetate (typically, petroleum ether/ethyl acetate = 10/1) to obtain the desired product.

Sometimes benzoic acid, the decomposition product of TBPB, is easy to come out along with the desired product through the silica gel. There are two methods listed below to deal with this problem.

1) Neutralized with $NaHCO_3$: After the reactions cool to room temperature, 2 mL water, 2 mL ethyl acetate and 150 mg $NaHCO_3$ is added to the tube. The mixture is stirred vigorously for 30 min, then it is extracted with 30 mL ethyl acetate. The organic phase was dried over $MgSO_4$, filtered and concentrated under vacuum. Then the residue was purified by flash chromatography.

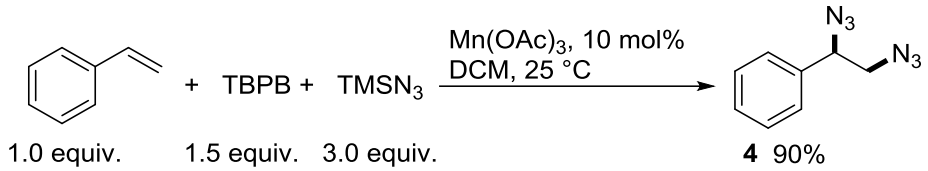
2) Flash chromatography under alkaline condition: An easier way is to add 1~2% Et_3N to the eluent.

Procedure for Mn-mediated reactions:

An oven-dried 10 mL seal tube was charged with $Mn(OAc)_3•2H_2O$ 241 mg (0.90

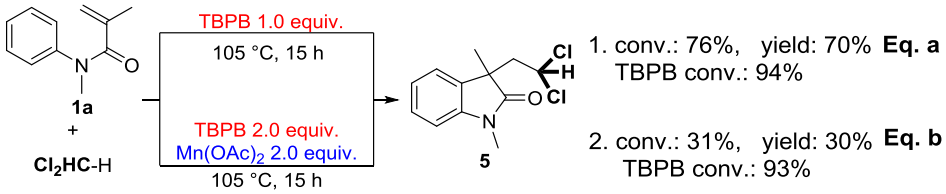
mmol, 3.0 equiv.) and acrylamide **1**(0.30 mmol, 1.0 equiv.) 2 mL DCE and $TMSN_3$ 78 μL (0.60 mmol, 2.0 equiv.) under nitrogen atmosphere. The reaction mixture was stirred at 100 °C for 12 h monitored by TLC and then was concentrated under vacuum. The residue was purified by flash chromatography on silica gel with petroleum ether and ethyl acetate (typically, petroleum ether/ethyl acetate = 10/1) to obtain the desired product.

Diazidation of styrene

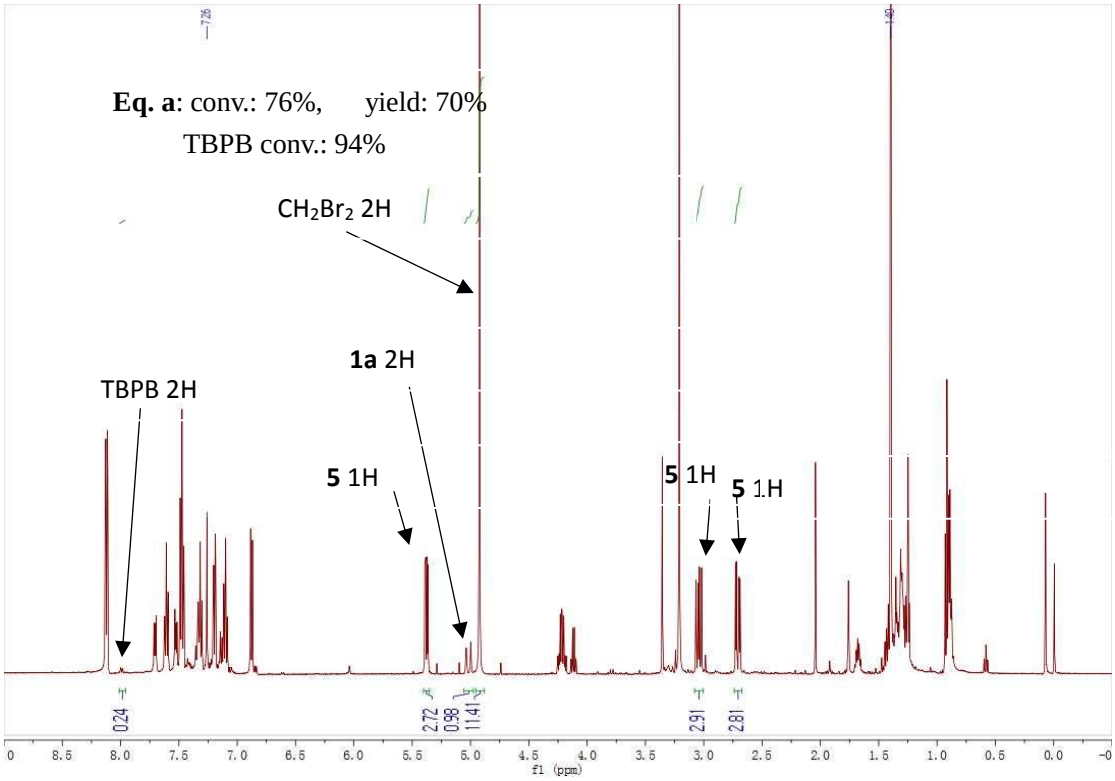


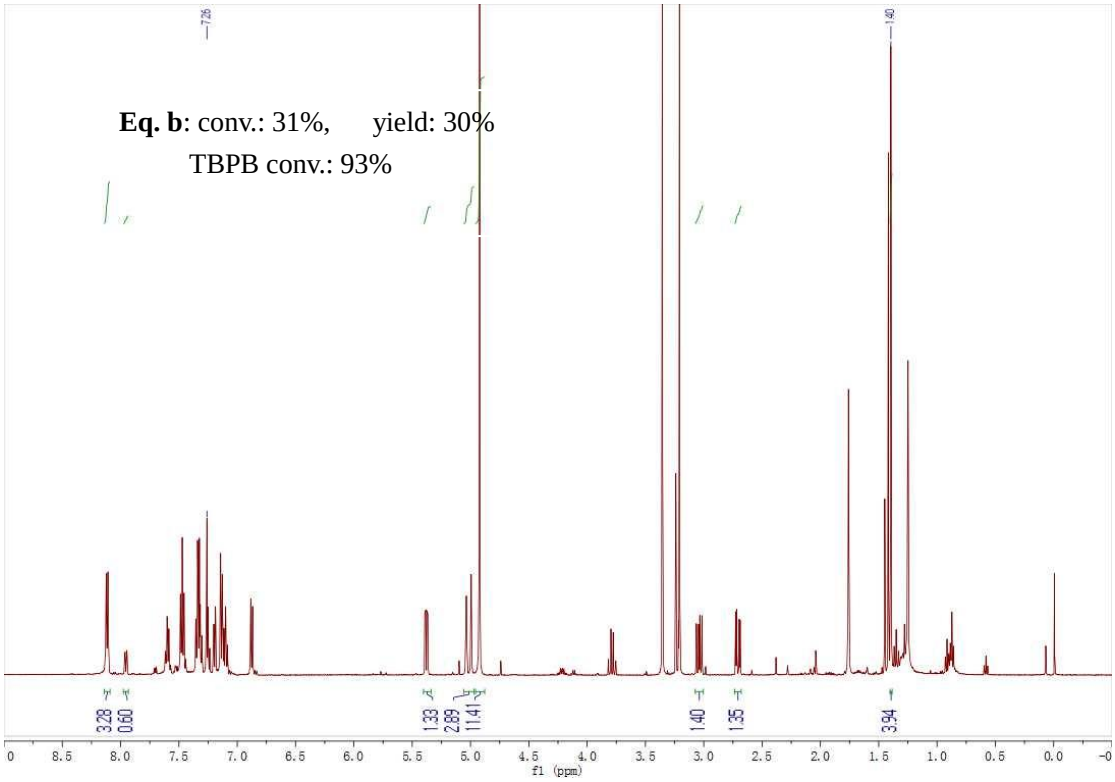
An oven-dried 10 mL Schlenk tube was charged with 2 mL DCE, styrene 34 μL (0.30 mmol, 1.0 equiv.), TBPB 84 μL (0.45 mmol, 1.5 equiv.) and $TMSN_3$ 118 μL (0.9 mmol, 3.0 equiv.) under nitrogen atmosphere. The reaction mixture was stirred at 25 °C for 12 h and then was concentrated under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether and ether (petroleum ether/ether = 40/1) to afford the diazidation product 51 mg (90%).

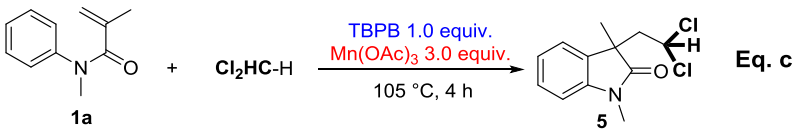
Procedure for Reactions for detecting oxy-radical



An oven-dried 10 mL seal tube was charged with acrylamide **1a** 35 mg (0.20 mmol, 1.0 equiv.), 2 mL DCM, TBPB 38 μL (0.20 mmol, 1.0 equiv.) (for Eq. a, or TBPB 75 μL (0.4mmol, 2.0 equiv.) and $Mn(OAc)_2$ 69 mg (0.4 mmol, 2.0 equiv) for Eq. b) under nitrogen atmosphere. The reaction mixture was stirred at 105 °C for 15 h and then was filtered through short silica gel column, concentrated under vacuum and NMR yields were obtained using 40 μL CBr_2H_2 as internal standard.

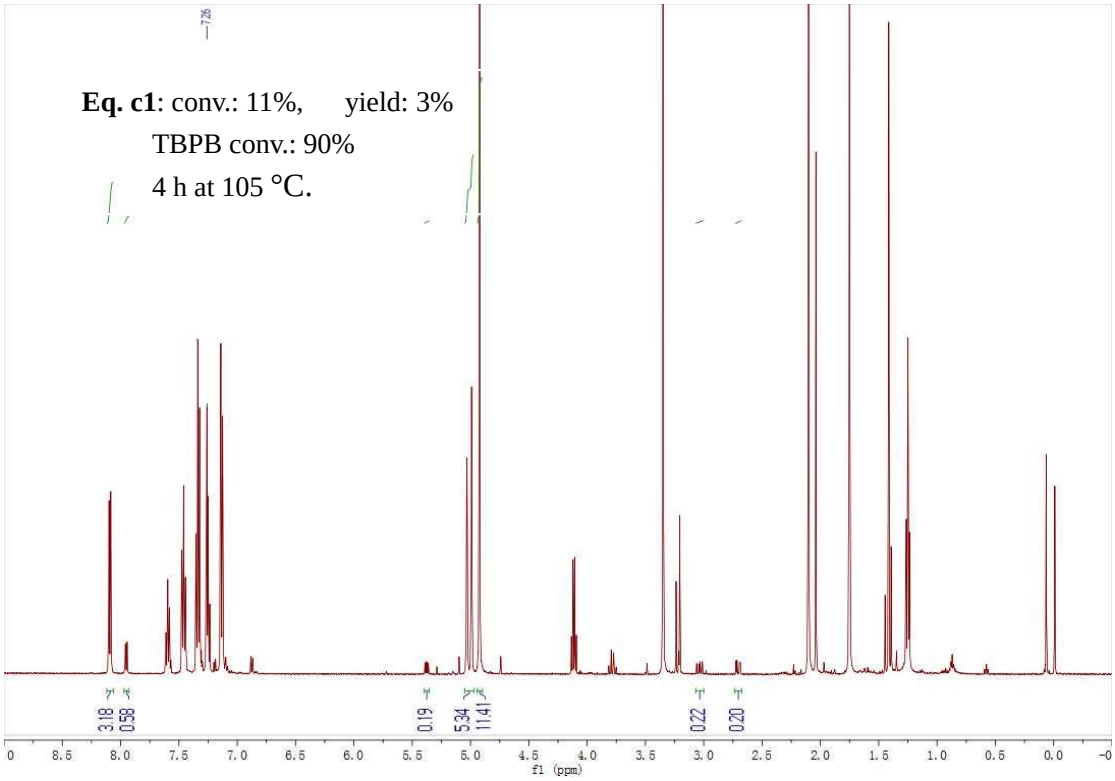






3. conv.: 11%, yield: 3%
TBPB conv.: 90%

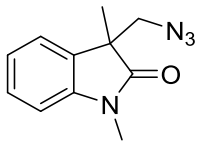
An oven-dried 10 mL seal tube was charged with acrylamide **1a** 53 mg (0.30 mmol, 1.0 equiv.), 3 mL DCM, TBPB 57 μL (0.30 mmol, 1.0 equiv.) and $Mn(OAc)_3$ 241 mg (0.9 mmol, 3.0 equiv.) under nitrogen atmosphere. The reaction mixture was stirred at 105 °C then was filtered through short silica gel column, concentrated under vacuum and NMR yields were obtained using 40 μL CBr_2H_2 as internal standard.



Reference：

1. Y. Li, M. Sun, H. Wang, Q. Tian, S. Yang. *Angew. Chem. Int. Ed.* **2013**, *52*, 3972.

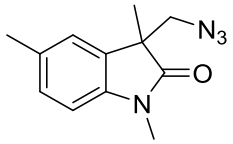
Characterization of products



3-(azidomethyl)-1,3-dimethylindolin-2-one

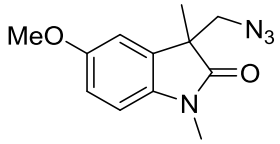
Table 2, **2a**. (CAS: 1449116-88-4). Colorless oil. 86% yield for manganese-catalyzed reaction; 97% yield for manganese-mediated reaction. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 (td, *J* = 7.7, 1.3 Hz, 1H), 7.28 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.10 (td, *J* = 7.5, 1.0 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 3.66 – 3.59 (m, 2H), 3.23 (s, 3H), 1.37 (s, 3H). **^{13}C NMR**

(126 MHz, $CDCl_3$) δ 177.5, 142.4, 133.4, 131.4, 126.3, 115.4, 109.7, 56.9, 48.8, 26.4, 20.3.



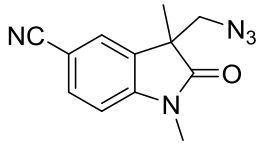
3-(azidomethyl)-1,3,5-trimethylindolin-2-one

Table 2, **2b**. (CAS: 1449116-92-0). Colorless oil. 66% yield for manganese-catalyzed reaction; 70% yield for manganese-mediated reaction. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.17 – 7.10 (m, 2H), 6.79 (d, *J* = 7.8 Hz, 1H), 3.65 (s, 2H), 3.24 (s, 3H), 2.38 (s, 3H), 1.39 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.1, 141.0, 132.3, 131.3, 128.8, 123.8, 108.0, 57.2, 48.7, 26.3, 21.1, 20.5.



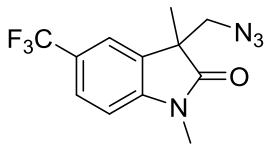
3-(azidomethyl)-5-methoxy-1,3-dimethylindolin-2-one

Table 2, **2c**. (CAS: 1449116-93-1). White solid. 77% yield for manganese-catalyzed reaction; 83% yield for manganese-mediated reaction. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.89 (d, *J* = 2.5 Hz, 1H), 6.83 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.77 (d, *J* = 8.5 Hz, 1H), 3.79 (s, 3H), 3.61 (s, 2H), 3.19 (s, 3H), 1.35 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 177.7, 156.1, 136.8, 132.7, 112.6, 110.7, 108.6, 57.1, 55.7, 49.0, 26.3, 20.4.



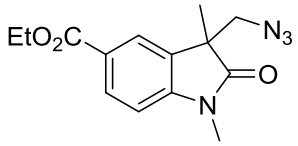
3-(azidomethyl)-1,3-dimethyl-2-oxoindoline-5-carbonitrile

Table 2, **2d**. (CAS: 1449116-98-6). Yellow oil. 88% yield for manganese-catalyzed reaction; 92% yield for manganese-mediated reaction. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.53 (d, *J* = 1.6 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 3.71 – 3.59 (m, 2H), 3.25 (s, 3H), 1.38 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 177.8, 147.3, 133.9, 132.4, 126.4, 118.9, 108.7, 105.9, 56.8, 48.5, 26.6, 20.2.



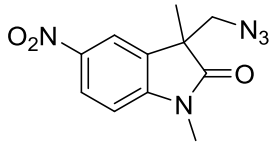
3-(azidomethyl)-1,3-dimethyl-5-(trifluoromethyl)indolin-2-one

Table 2, **2e**. (CAS: 1449116-91-9). Yellow oil. 75% yield for manganese-catalyzed reaction; 80% yield for manganese-mediated reaction. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.51 (d, *J* = 1.8 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 3.71 – 3.62 (m, 2H), 3.26 (s, 3H), 1.39 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.1, 146.4 (q, J_{F-C} = 1.1 Hz), 132.0, 126.4 (q, J_{F-C} = 4.0 Hz), 125.0 (q, J_{F-C} = 32.5 Hz), 124.3 (q, J_{F-C} = 269.9 Hz), 120.1 (q, J_{F-C} = 3.6 Hz), 108.1, 56.9, 48.6, 26.5, 20.2.



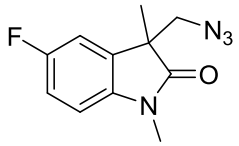
ethyl 3-(azidomethyl)-1,3-dimethyl-2-oxoindoline-5-carboxylate

Table 2, **2f**. Yellow oil. 86% yield for manganese-catalyzed reaction; 88% yield for manganese-mediated reaction. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.92 (d, *J* = 1.7 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.67 (s, 2H), 3.25 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.37 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.5, 166.2, 147.5, 131.32, 131.28, 125.0, 124.2, 107.9, 61.0, 57.0, 48.6, 26.6, 20.4, 14.4. **HRMS** m/z (ESI) calcd. for $C_{14}H_{17}N_4O_3$ $(M+H)^+$: 289.1295, found 289.1298.



3-(azidomethyl)-1,3-dimethyl-5-nitroindolin-2-one

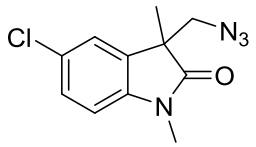
Table 2, **2g**. (CAS: 1543011-86-4). Yellow oil. 75% yield for manganese-catalyzed reaction; 82% yield for manganese-mediated reaction. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 8.6, 2.3 Hz, 1H), 8.17 (d, *J* = 2.3 Hz, 1H), 6.97 (d, *J* = 8.6 Hz, 1H), 3.73 (s, 2H), 3.31 (s, 3H), 1.43 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.3, 149.1, 143.5, 132.2, 126.0, 119.0, 107.9, 56.8, 48.7, 26.8, 20.2.



3-(azidomethyl)-5-fluoro-1,3-dimethylindolin-2-one

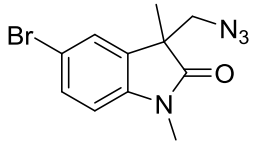
Table 2, **2h**. (CAS: 1449116-94-2). Colorless oil. 68% yield for manganese-catalyzed reaction; 92% yield for manganese-mediated reaction. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.06 – 6.99 (m, 2H), 6.80 (dd, *J* = 8.3, 4.1 Hz, 1H), 3.63 (s, 2H), 3.22 (s, 3H), 1.37 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 177.7 (d, J_{F-C} = 1.3 Hz), 159.4 (d, J_{F-C} = 239.4 Hz), 139.3 (d, J_{F-C} = 2.0 Hz), 133.0 (d, J_{F-C} = 7.8 Hz), 114.8 (d, J_{F-C} = 23.4 Hz), 111.3

(d, J_{F-C} = 24.8 Hz), 108.8 (d, J_{F-C} = 8.1 Hz), 57.0, 49.1 (d, J_{F-C} = 1.9 Hz), 26.46, 20.33.



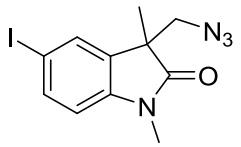
3-(azidomethyl)-5-chloro-1,3-dimethylindolin-2-one

Table 2, **2i**. (CAS: 1449116-95-3). Yellow oil. 77% yield for manganese-catalyzed reaction; 99% yield for manganese-mediated reaction. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.25 (d, *J* = 2.1 Hz, 1H), 6.79 (d, *J* = 8.3 Hz, 1H), 3.66 – 3.59 (m, 2H), 3.21 (s, 3H), 1.36 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 177.6, 141.9, 133.0, 128.5, 128.1, 123.6, 109.2, 56.9, 48.8, 26.4, 20.3.



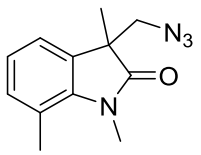
3-(azidomethyl)-5-bromo-1,3-dimethylindolin-2-one

Table 2, **2j**. (CAS: 1449116-96-4).Yellow oil. 84% yield for manganese-catalyzed reaction; 87% yield for manganese-mediated reaction. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 (dt, *J* = 8.3, 1.5 Hz, 1H), 7.38 (s, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 3.62 (s, 2H), 3.20 (s, 3H), 1.35 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 177.5, 142.4, 133.4, 131.4, 126.3, 115.3, 109.7, 56.9, 48.8, 26.4, 20.3.



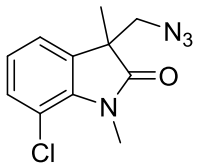
3-(azidomethyl)-5-iodo-1,3-dimethylindolin-2-one

Table 2, **2k**. (CAS: 1449116-97-5).Yellow oil. 68% yield for manganese-catalyzed reaction; 86% yield for manganese-mediated reaction. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.55 (d, *J* = 1.7 Hz, 1H), 6.66 (d, *J* = 8.2 Hz, 1H), 3.66 – 3.58 (m, 2H), 3.20 (s, 3H), 1.35 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 177.3, 143.1, 137.4, 133.8, 131.9, 110.3, 85.2, 56.9, 48.7, 26.4, 20.3.



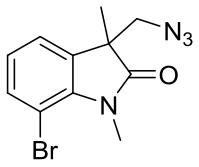
3-(azidomethyl)-1,3,7-trimethylindolin-2-one

Table 2, **2l**. (CAS: 1449117-01-4). Yellow oil. 68% yield for manganese-catalyzed reaction; 88% yield for manganese-mediated reaction. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.11 (ddd, *J* = 7.2, 1.4, 0.6 Hz, 1H), 7.05 (ddd, *J* = 7.7, 1.4, 0.7 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 3.65 – 3.58 (m, 2H), 3.52 (s, 3H), 2.60 (s, 3H), 1.34 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.9, 141.2, 132.4, 132.0, 122.7, 120.8, 120.0, 57.5, 48.0, 29.7, 20.9, 19.0.



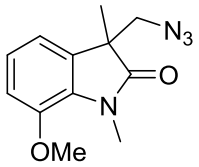
3-(azidomethyl)-7-chloro-1,3-dimethylindolin-2-one

Table 2, **2m**. (CAS: 1449117-04-7).Yellow oil. 70% yield for manganese-catalyzed reaction; 87% yield for manganese-mediated reaction. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.16 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.00 (dd, *J* = 8.2, 7.3 Hz, 1H), 3.65 – 3.58 (m, 2H), 3.60 (s, 3H), 1.36 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.4, 139.4, 134.2, 131.0, 123.5, 121.5, 115.8, 57.3, 48.5, 29.7, 20.7.



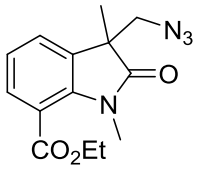
3-(azidomethyl)-7-bromo-1,3-dimethylindolin-2-one

Table 2, **2n**. (CAS: 1449117-05-8).Yellow oil. 56% yield for manganese-catalyzed reaction; 77% yield for manganese-mediated reaction. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.19 (dd, *J* = 7.3, 1.2 Hz, 1H), 6.94 (dd, *J* = 8.2, 7.3 Hz, 1H), 3.68 – 3.57 (m, 2H), 3.61 (s, 3H), 1.36 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.6, 140.8, 134.5, 134.3, 123.9, 122.0, 102.7, 57.3, 48.4, 30.0, 20.7.



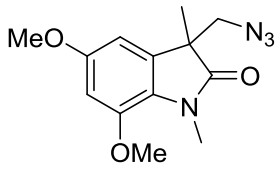
3-(azidomethyl)-7-methoxy-1,3-dimethylindolin-2-one

Table 2, **2o**. (CAS: 1449117-02-5). White solid. 72% yield for manganese-catalyzed reaction; 91% yield for manganese-mediated reaction. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.04 (td, *J* = 7.9, 1.1 Hz, 1H), 6.93 – 6.85 (m, 2H), 3.86 (s, 3H), 3.64 – 3.57 (m, 2H), 3.50 (s, 3H), 1.34 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.3, 145.4, 132.9, 131.2, 123.3, 115.5, 112.4, 57.3, 55.8, 48.7, 29.6, 20.6.



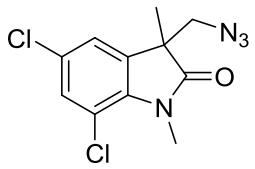
ethyl 3-(azidomethyl)-1,3-dimethyl-2-oxoindoline-7-carboxylate

Table 2, **2p**. Colorless oil. 32% yield for manganese-catalyzed reaction; 59% yield for manganese-mediated reaction. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.37 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.11 (t, *J* = 7.7 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 3.64 (s, 2H), 3.30 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.38 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 179.2, 166.8, 142.2, 133.3, 129.8, 125.6, 122.0, 116.4, 61.7, 57.3, 47.6, 30.2, 20.6, 14.3. **HRMS** m/z (ESI) calcd. for $C_{14}H_{17}N_4O_3$ $(M+H)^+$: 289.1295, found 289.1298.



3-(azidomethyl)-4,6-dimethoxy-1,3-dimethylindolin-2-one

Table 2, **2q**. White solid. 59% yield for manganese-catalyzed reaction; 72% yield for manganese-mediated reaction. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.46 (q, *J* = 2.3 Hz, 2H), 3.83 (s, 3H), 3.79 (s, 3H), 3.63 – 3.53 (m, 2H), 3.44 (s, 3H), 1.32 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.0, 156.8, 146.1, 133.6, 124.7, 100.7, 99.7, 57.3, 55.9, 55.9, 49.3, 29.6, 20.7. **HRMS** m/z (ESI) calcd. for $C_{13}H_{17}N_4O_3$ $(M+H)^+$: 277.1295, found 277.1299.



3-(azidomethyl)-4,6-dichloro-1,3-dimethylindolin-2-one

Table 2, **2r**. (CAS: 1613294-66-8). White solid. 80% yield for manganese-catalyzed reaction; 87% yield for manganese-mediated reaction. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.46 (q, *J* = 2.3 Hz, 2H), 3.83 (s, 3H), 3.79 (s, 3H), 3.63 – 3.53 (m, 2H), 3.44 (s, 3H), 1.32 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 177.9, 138.1, 135.4, 130.3, 128.2, 122.2, 116.1, 57.0, 48.7, 29.7, 20.6.

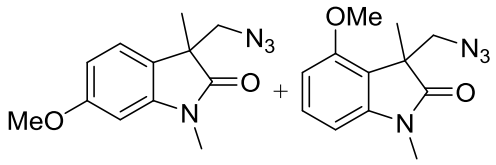
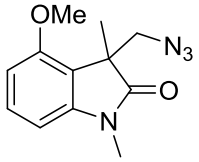
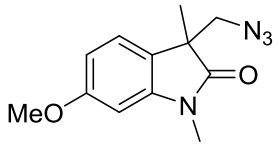


Table 2, **2s**. 82% yield (1.8/1) for manganese-catalyzed reaction; 93% yield (1.7/1) for manganese-mediated reaction.



3-(azidomethyl)-6-methoxy-1,3-dimethylindolin-2-one

CAS: 1502874-49-8. White solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 1H), 6.67 – 6.62 (m, 1H), 6.55 (dd, *J* = 7.8, 0.7 Hz, 1H), 3.97 (d, *J* = 11.8 Hz, 1H), 3.87 (d, *J* = 1.1 Hz, 3H), 3.63 (d, *J* = 11.7 Hz, 1H), 3.21 (s, 3H), 1.39 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.8, 156.1, 144.9, 123.0, 116.2, 105.8, 101.7, 55.3, 54.9, 49.3, 26.5, 18.8.



3-(azidomethyl)-6-methoxy-1,3-dimethylindolin-2-one

CAS: 1502874-50-1. White solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.2 Hz, 1H), 6.60 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.47 (d, *J* = 2.3 Hz, 1H), 3.84 (s, 3H), 3.60 (s, 2H), 3.22 (s, 3H), 1.35 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.8, 160.6, 144.7, 123.6, 123.2, 106.5, 96.5, 57.4, 55.5, 48.3, 26.4, 20.6.

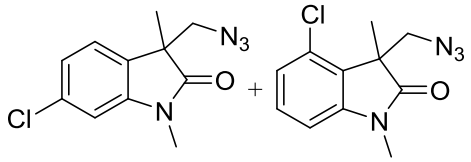
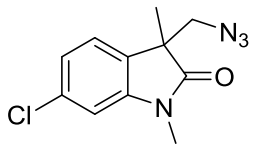
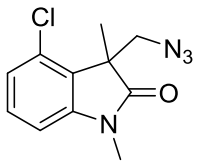


Table 2, **2t**. Yellow oil. 74% yield (2.2/1) for manganese-catalyzed reaction; 87% yield (2.1/1) for manganese-mediated reaction.



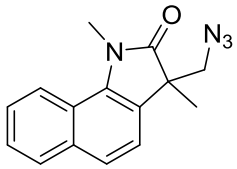
3-(azidomethyl)-6-chloro-1,3-dimethylindolin-2-one

CAS: 1613294-63-5. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 1H), 7.06 – 7.01 (m, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 4.17 (d, *J* = 12.0 Hz, 1H), 3.73 (d, *J* = 11.9 Hz, 1H), 3.24 (s, 3H), 1.47 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 177.8, 145.5, 130.7, 130.0, 127.1, 123.7, 106.9, 54.2, 50.5, 26.6, 18.2.



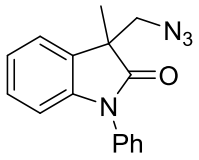
3-(azidomethyl)-4-chloro-1,3-dimethylindolin-2-one

CAS: 1613294-60-2. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 7.8 Hz, 1H), 7.08 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.88 (d, *J* = 1.9 Hz, 1H), 3.62 (s, 2H), 3.22 (s, 3H), 1.36 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.1, 144.6, 134.5, 129.7, 123.9, 122.6, 109.1, 57.1, 48.5, 26.4, 20.4.



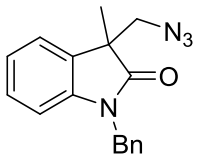
3-(azidomethyl)-1,3-dimethyl-1,3-dihydro-2H-benzo[g]indol-2-one

Table 2, **2u**. (CAS: 1449117-10-5). White solid. 48% yield for manganese-catalyzed reaction; 71% yield for manganese-mediated reaction. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 (dd, 1H), 7.61 – 7.53 (m, 2H), 7.50 – 7.42 (m, 2H), 7.00 (dd, 1H), 4.20 (d, *J* = 11.9 Hz, 1H), 3.69 (d, *J* = 11.8 Hz, 1H), 3.57 (s, 3H), 1.66 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.3, 136.4, 135.2, 133.4, 126.9, 126.9, 126.5, 122.9, 122.8, 119.7, 108.9, 62.0, 48.2, 29.9, 27.6.



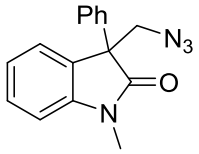
3-(azidomethyl)-3-methyl-1-phenylindolin-2-one

Table 2, **2v**. (CAS: 1502874-62-5). White solid. 96% yield for manganese-catalyzed reaction; 98% yield for manganese-mediated reaction. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 2H), 7.47 – 7.41 (m, 3H), 7.36 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.27 (td, *J* = 7.8, 1.3 Hz, 1H), 7.15 (td, *J* = 7.5, 1.0 Hz, 1H), 6.88 (dt, *J* = 7.9, 0.7 Hz, 1H), 3.82 – 3.69 (m, 2H), 1.51 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 177.6, 143.4, 134.2, 131.1, 129.5, 128.5, 128.1, 126.5, 123.18, 123.13, 109.6, 57.6, 48.9, 20.6.



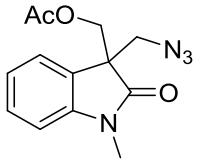
3-(azidomethyl)-1-benzyl-3-methylindolin-2-one

Table 2, **2w**. (CAS: 1449116-90-8). Yellow oil. 85% yield for manganese-catalyzed reaction; 85% yield for manganese-mediated reaction. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 – 7.15 (m, 6H), 7.11 (td, *J* = 7.5, 1.1 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 4.94 (d, *J* = 15.7 Hz, 1H), 4.78 (d, *J* = 15.7 Hz, 1H), 3.68 – 3.58 (m, 2H), 1.35 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.3, 142.5, 135.5, 131.2, 128.7, 128.5, 127.5, 127.0, 122.9, 122.7, 109.3, 57.3, 48.7, 43.7, 20.6.



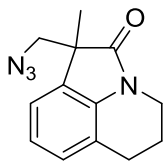
3-(azidomethyl)-1-methyl-3-phenylindolin-2-one

Table 2, **2x**. (CAS: 1449117-13-8). White solid. 68% yield for manganese-catalyzed reaction; 93% yield for manganese-mediated reaction. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 – 7.39 (m, 4H), 7.37 – 7.28 (m, 3H), 7.20 (td, *J* = 7.6, 1.1 Hz, 1H), 7.00 – 6.93 (m, 1H), 4.10 (s, 2H), 3.25 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 176.1, 144.1, 136.5, 129.3, 129.1, 128.7, 128.0, 126.9, 125.3, 122.7, 108.6, 57.1, 56.5, 26.5.



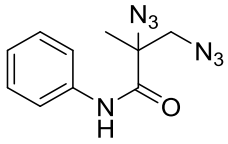
(3-(azidomethyl)-1-methyl-2-oxoindolin-3-yl)methyl acetate

Table 2, **2y**. (CAS: 1449117-17-2). White solid. 66% yield for manganese-catalyzed reaction; 93% yield for manganese-mediated reaction. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 2H), 7.09 (td, *J* = 7.6, 1.0 Hz, 1H), 6.89 (dt, *J* = 7.8, 0.8 Hz, 1H), 4.51 (d, *J* = 11.1 Hz, 1H), 4.17 (d, *J* = 11.0 Hz, 1H), 3.81 (d, *J* = 12.1 Hz, 1H), 3.68 (d, *J* = 12.1 Hz, 1H), 3.23 (s, 3H), 1.94 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.9, 170.1, 144.0, 129.3, 127.1, 124.9, 122.8, 108.4, 64.6, 53.6, 52.3, 26.4, 20.5.



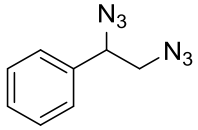
1-(azidomethyl)-1-methyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1H)-one

Table 2, **2z**. (CAS: 1449116-89-5). Colorless oil. 69% yield for manganese-catalyzed reaction; 90% yield for manganese-mediated reaction. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.13 – 7.09 (m, 1H), 7.09 – 7.05 (m, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 3.78 – 3.69 (m, 2H), 3.63 (s, 2H), 2.85 – 2.75 (m, 2H), 2.07 – 1.97 (m, 2H), 1.38 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 176.9, 139.1, 129.9, 127.4, 122.2, 120.8, 120.4, 57.1, 50.0, 38.9, 24.5, 21.1, 20.2.



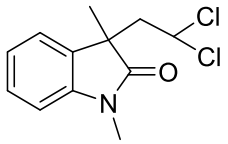
2,3-diazido-2-methyl-N-phenylpropanamide

3, White solid. 67% yield for manganese-catalyzed reaction; 61% yield for manganese-mediated reaction. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.29 (m, 2H), 7.22 – 7.11 (m, 1H), 3.81 (d, *J* = 12.7 Hz, 1H), 3.64 (d, *J* = 12.8 Hz, 1H), 1.66 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.5, 136.7, 129.0, 125.0, 120.0, 67.1, 57.6, 20.1. **HRMS** m/z (ESI) calcd. for $C_{14}H_{17}N_4O_3$ $(M+H)^+$: 246.1103, found 246.1099.



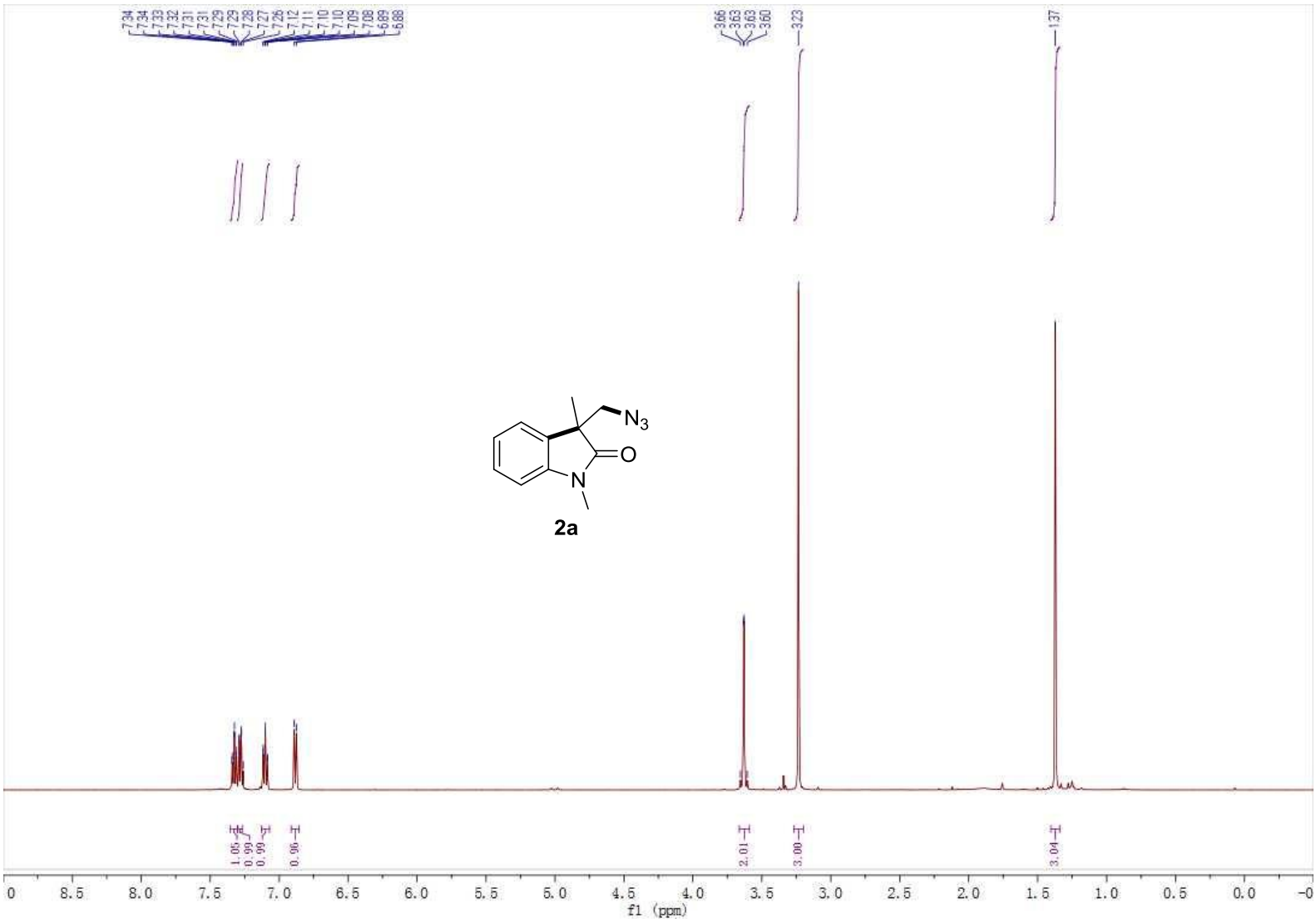
(1,2-diazidoethyl)benzene

4, CAS: 22710-73-2. Colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 (ddd, 5H), 4.68 (dd, *J* = 8.4, 4.8 Hz, 1H), 3.48 (dd, *J* = 21.6, 12.8 Hz, 1H), 3.51 (dd, *J* = 12.8, 8.4 Hz, 1H), 3.44 (dd, *J* = 12.8, 4.9 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.2, 129.0, 128.9, 126.9, 65.4, 55.8.



3-(2,2-dichloroethyl)-1,3-dimethylindolin-2-one

5, CAS: 1627605-52-0. Colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 (td, *J* = 7.7, 1.3 Hz, 1H), 7.22 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.13 (td, *J* = 7.6, 1.0 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 5.41 (dd, *J* = 9.2, 4.1 Hz, 1H), 3.23 (s, 3H), 3.06 (dd, *J* = 14.8, 9.3 Hz, 1H), 2.73 (dd, *J* = 14.8, 4.1 Hz, 1H), 1.42 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.9, 143.3, 131.0, 128.6, 122.6, 122.6, 108.6, 69.6, 50.1, 47.1, 26.4, 25.4.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7.08
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3.63
3.63
3.60
3.23
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1.06
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0.99
0.96
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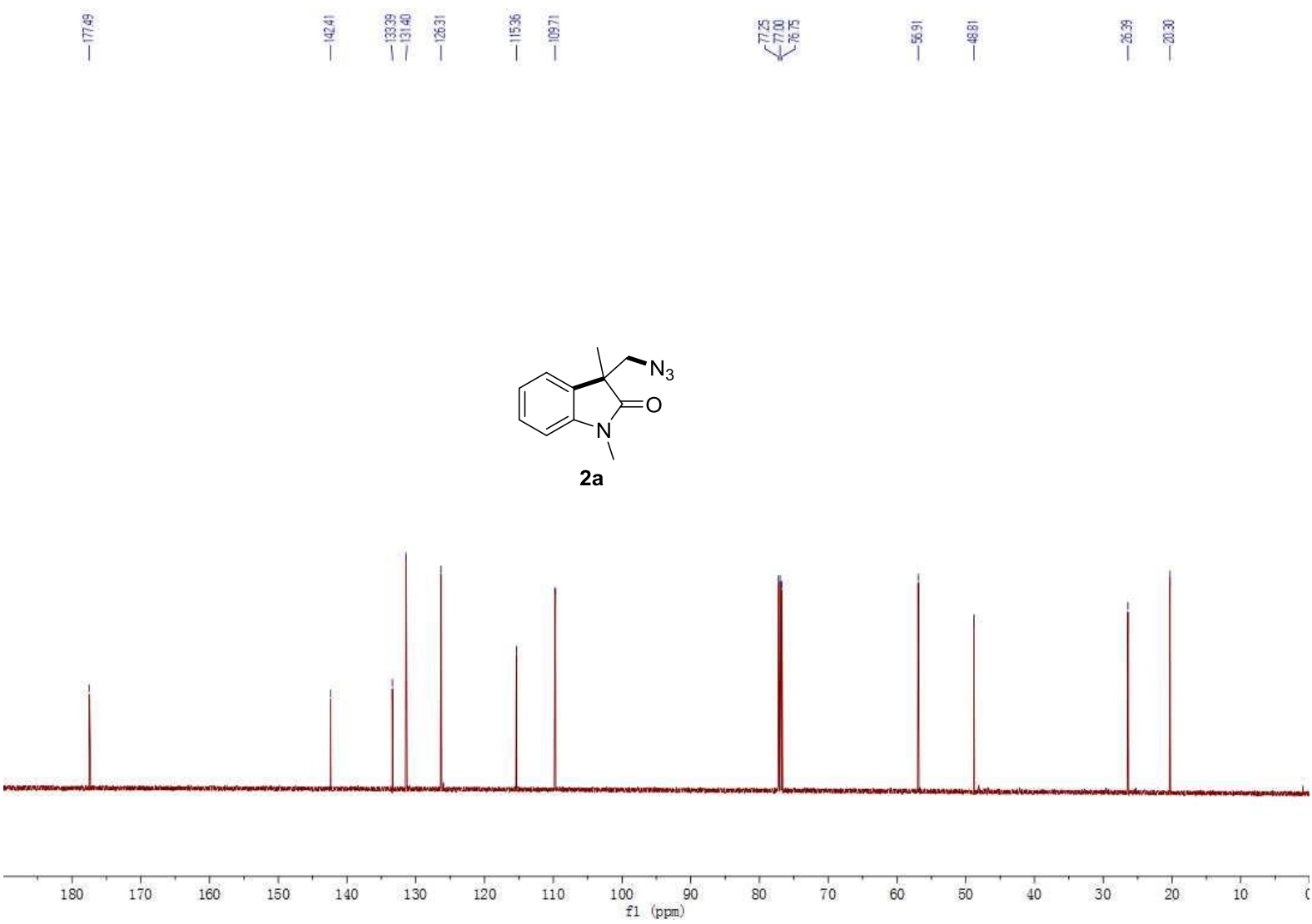
3.00
3.04
f1 (ppm)

N3
O
N

2a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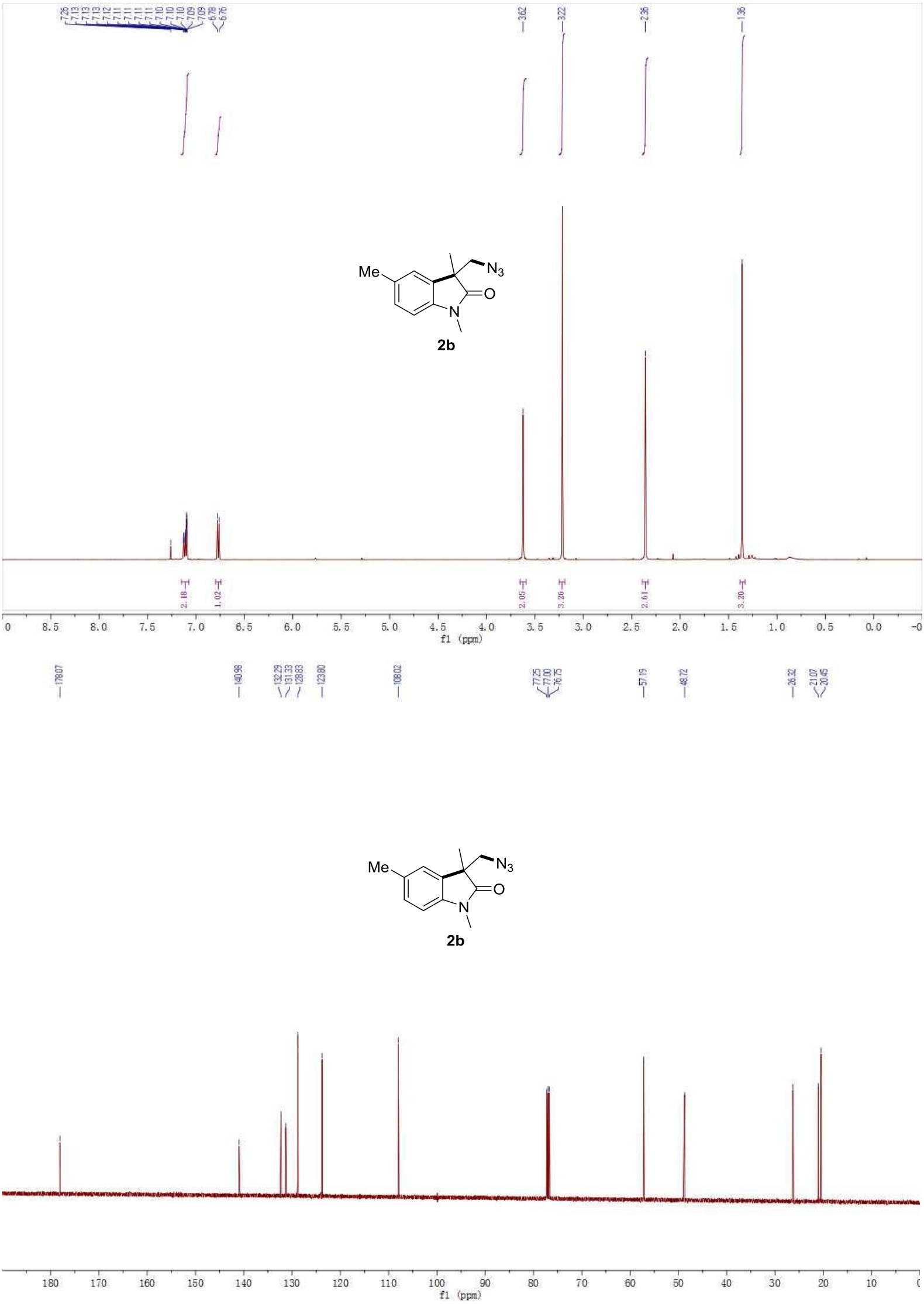
f1 (ppm)

N3
O
N

2a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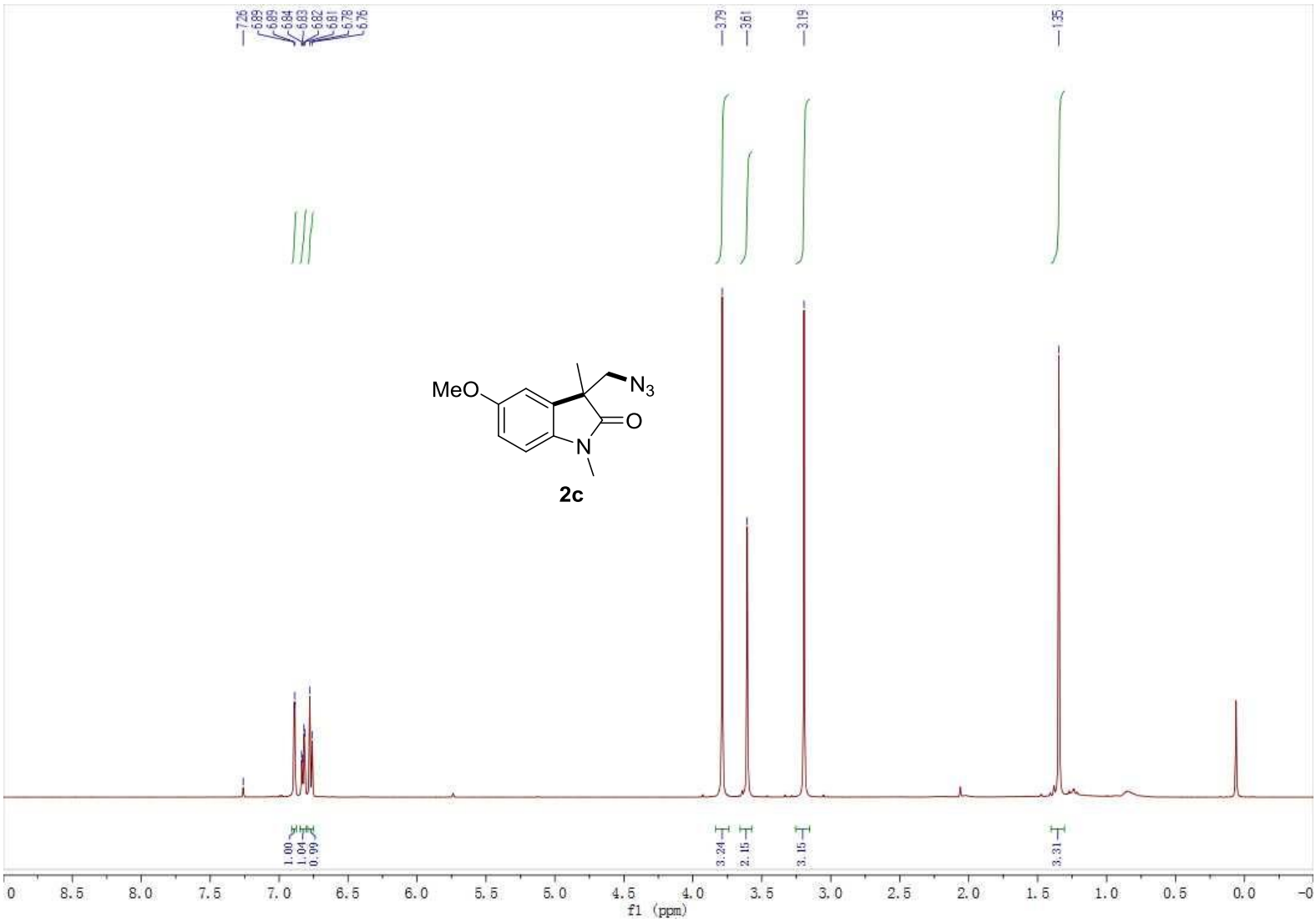
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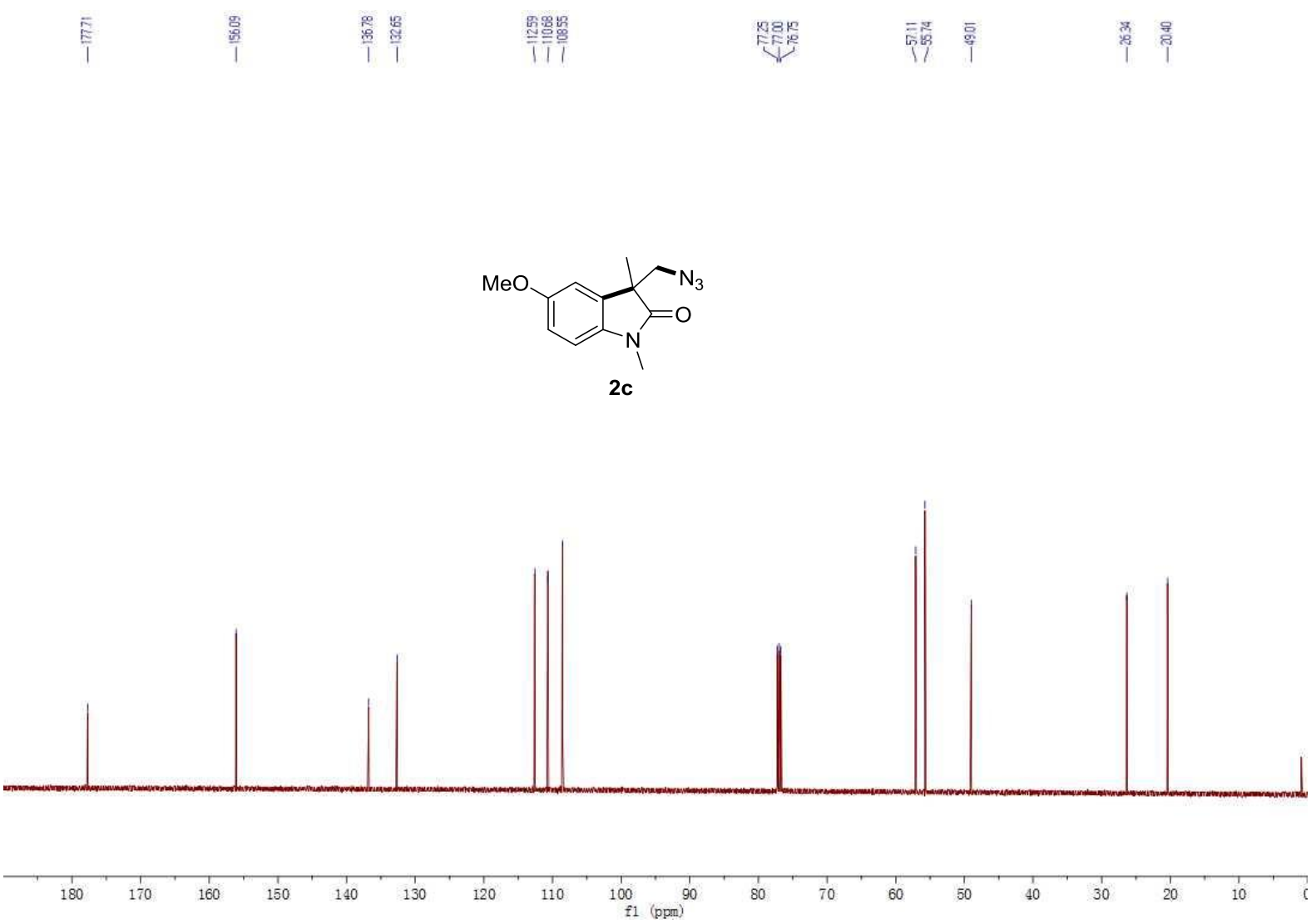
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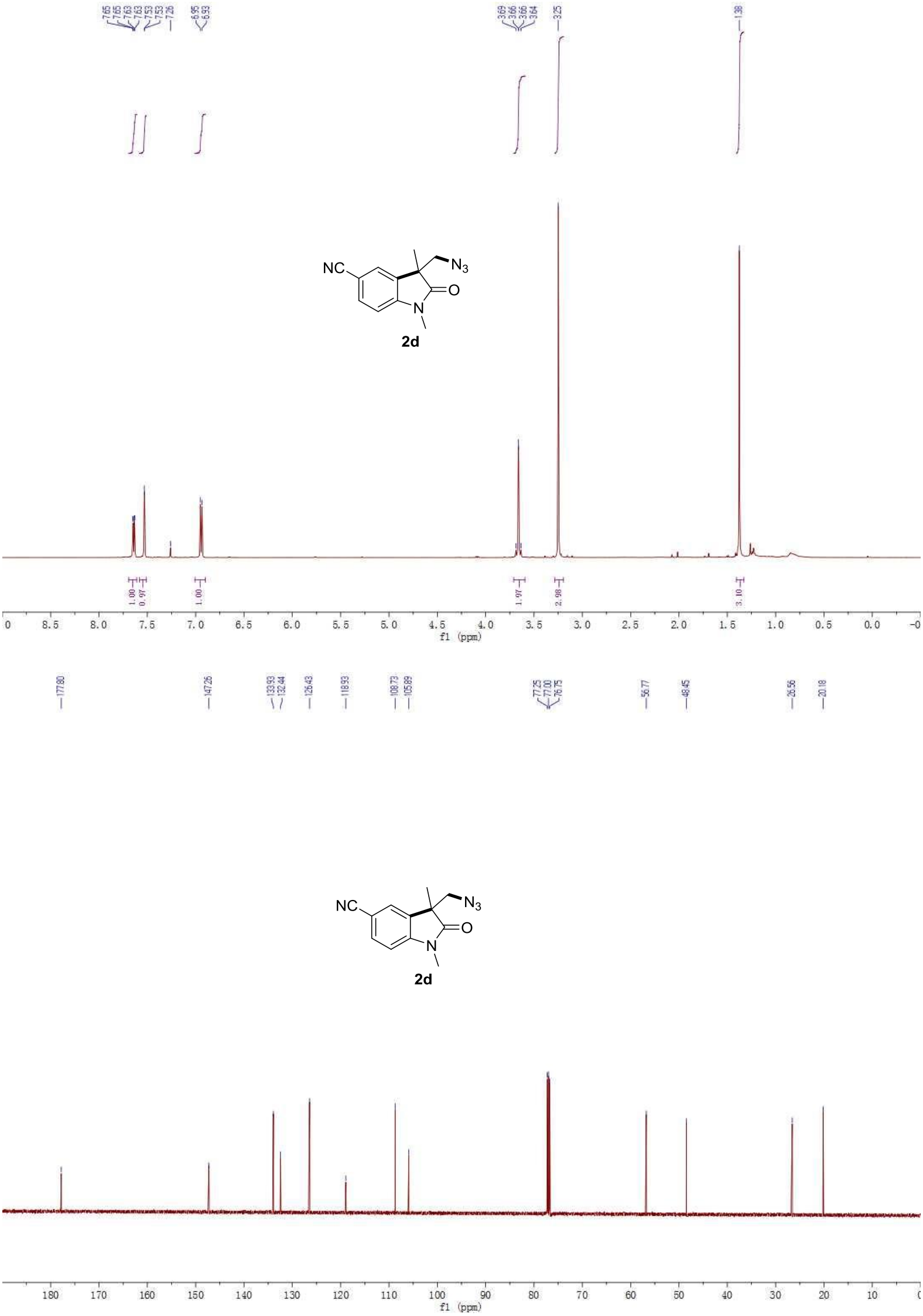
f1 (ppm)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N3
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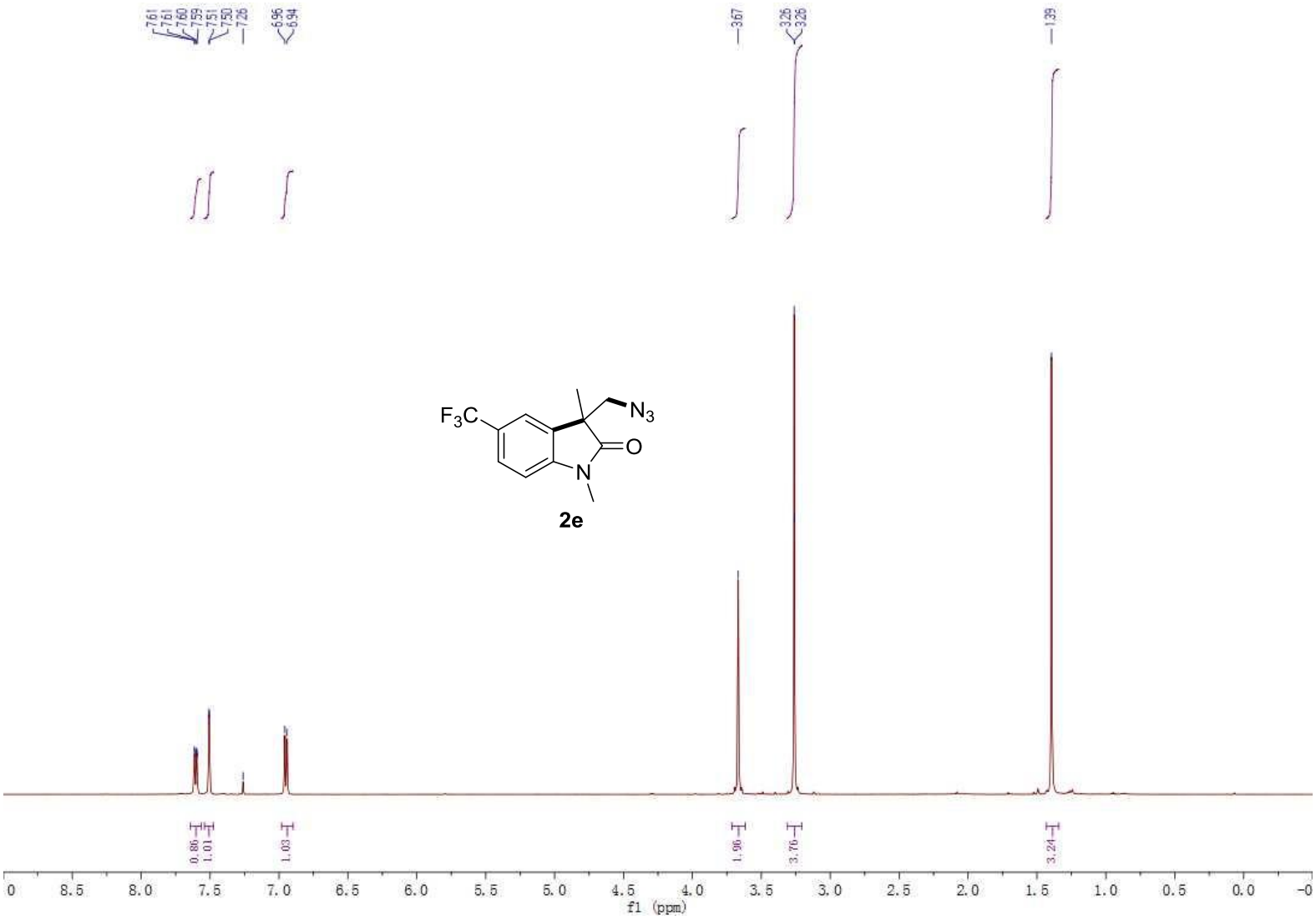
2d
f1 (ppm)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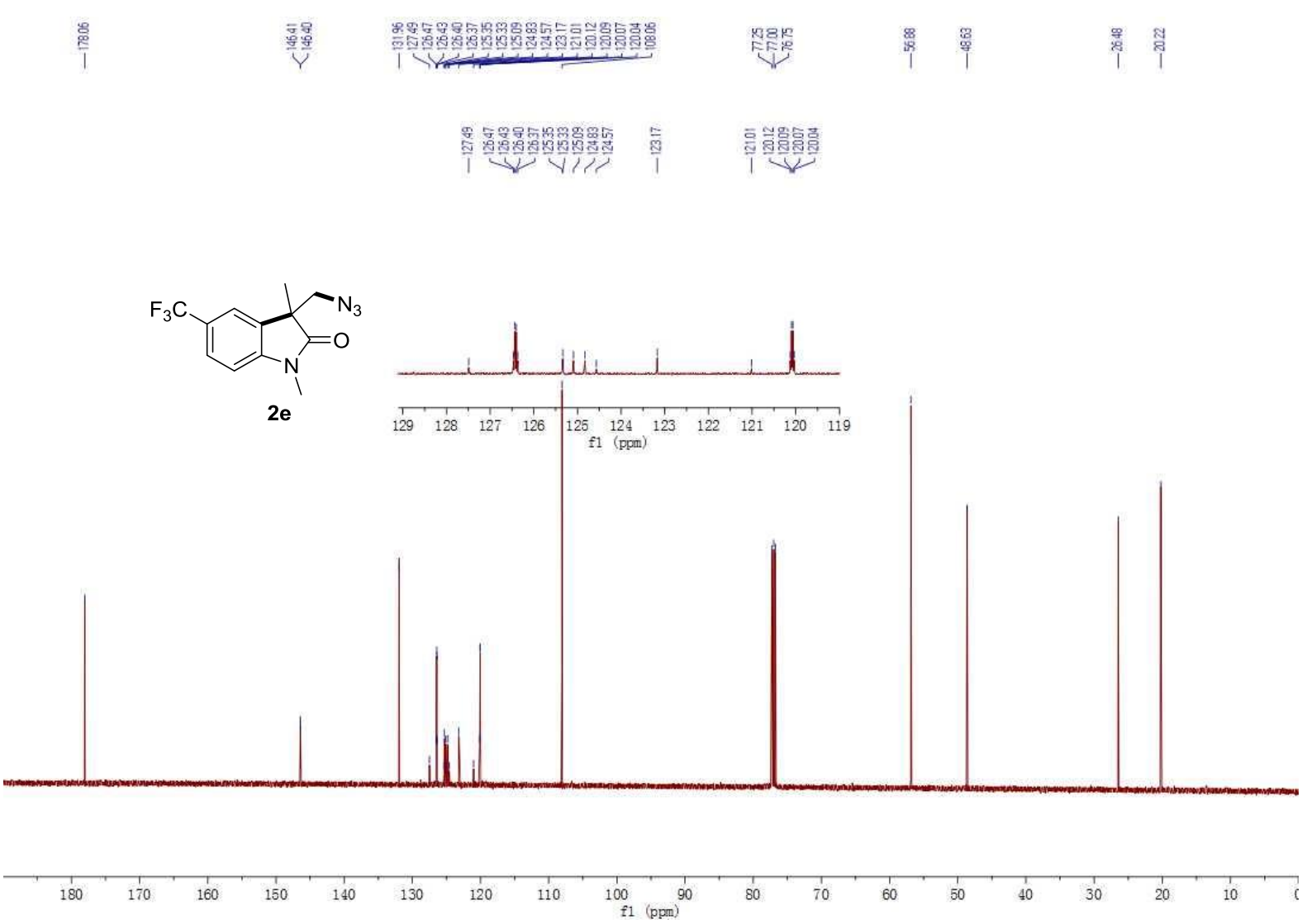
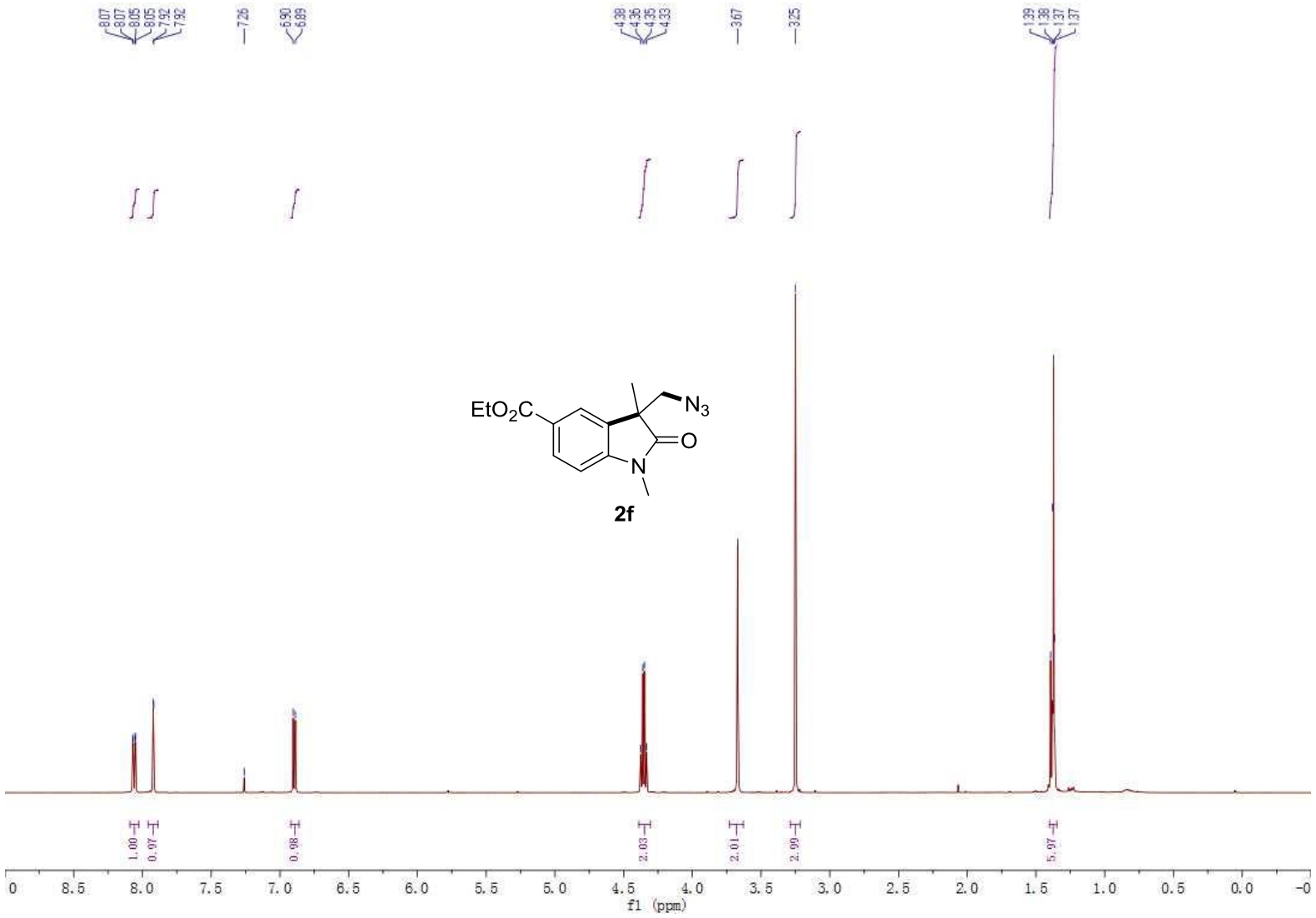
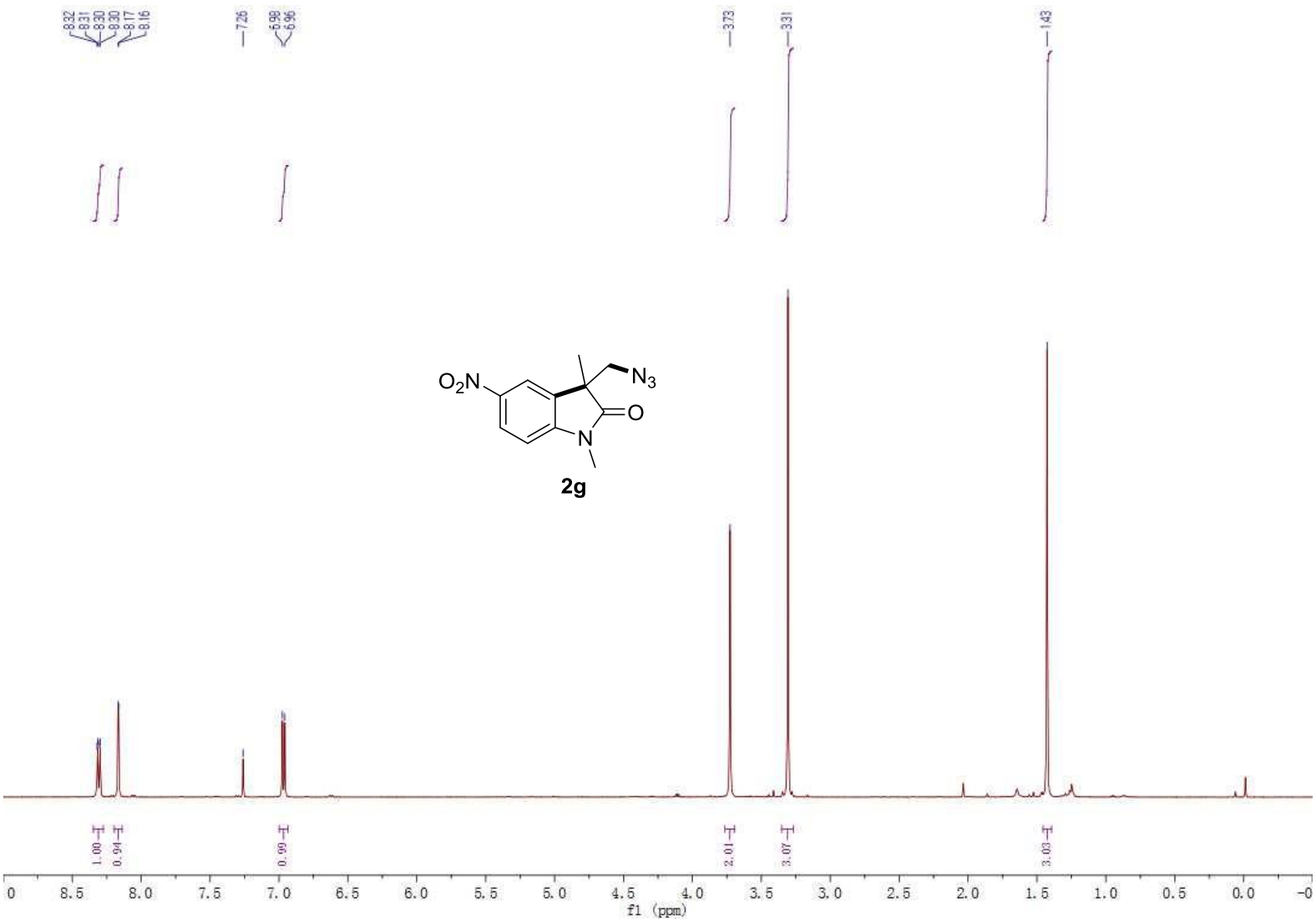
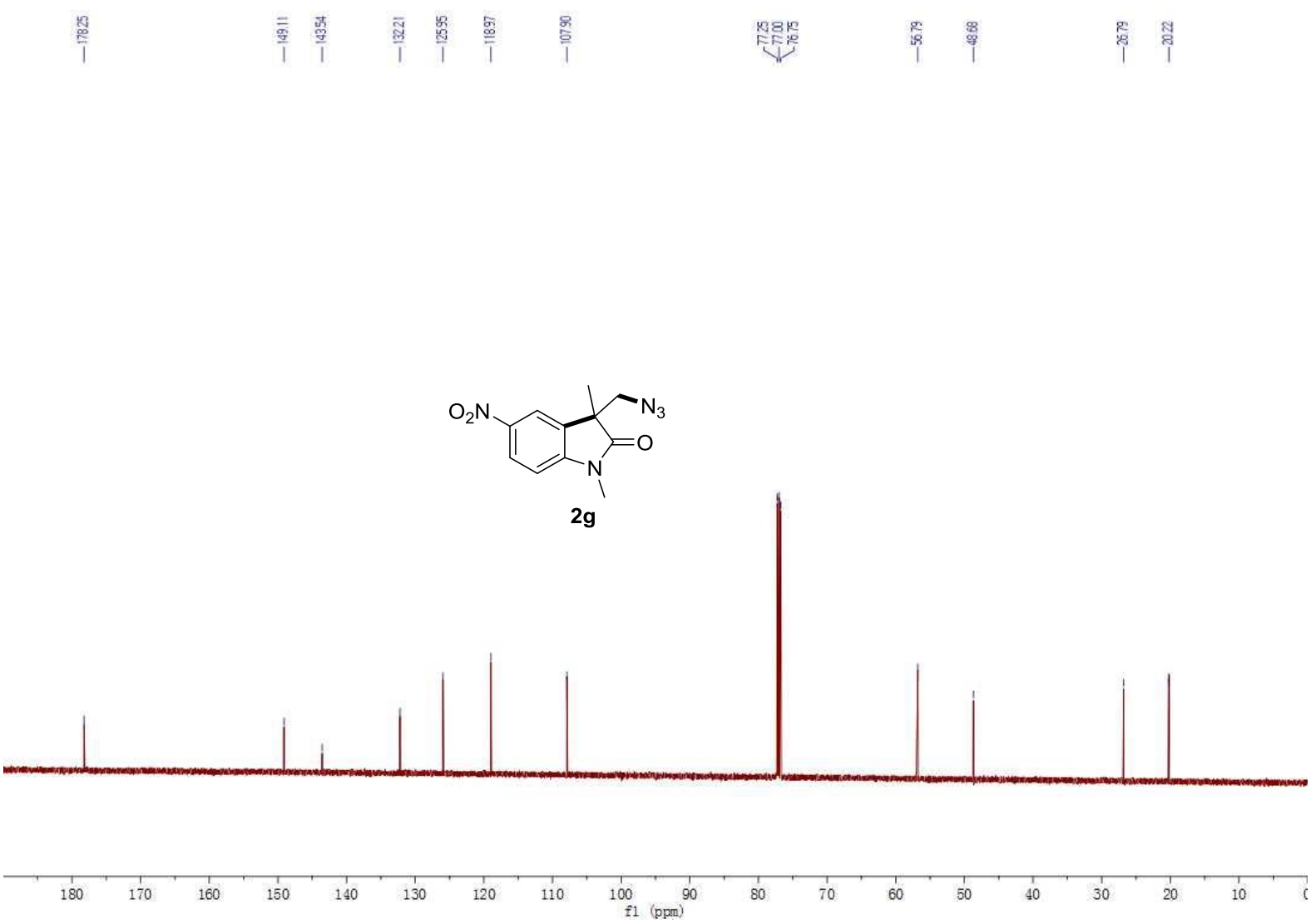
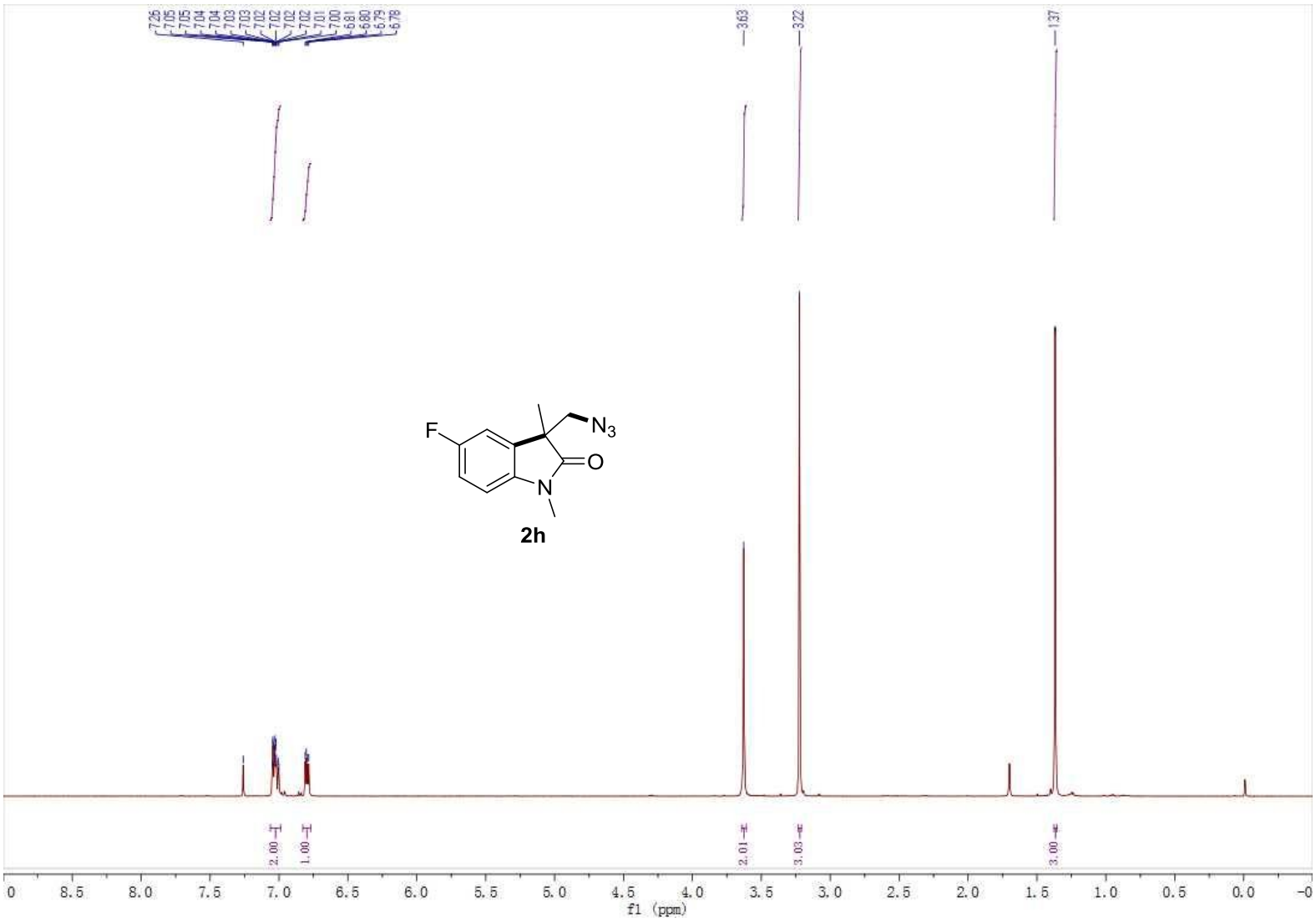
7.61
7.60
7.59
7.51
7.50
7.26
6.96
6.94
3.67
3.26
3.26
1.39
F3C
N3
O
N
2e
0.86
1.01
1.03
1.96
3.76
3.24
f1 (ppm)

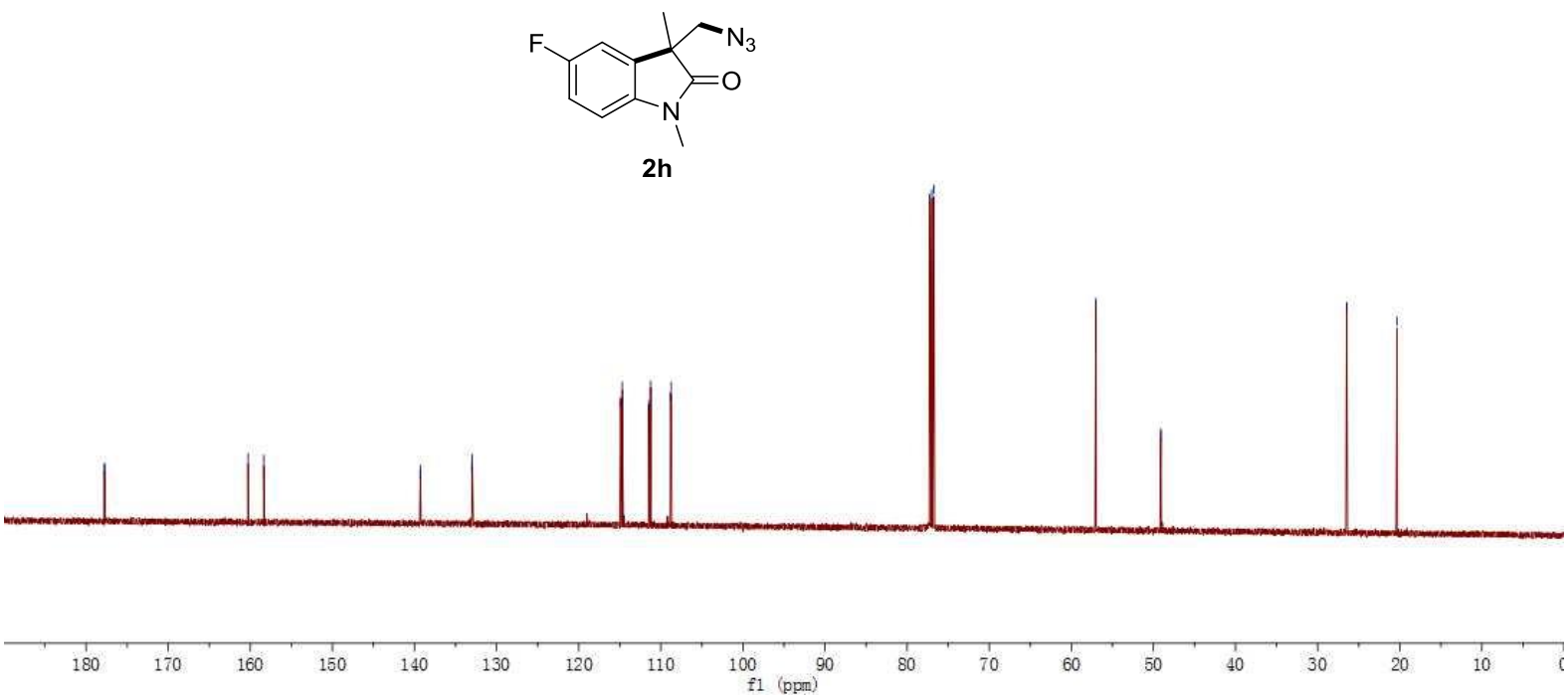

178.06
146.41
146.40
131.96
127.49
126.47
126.43
126.40
126.37
125.35
125.33
125.09
124.83
124.57
123.17
121.01
120.12
120.09
120.07
120.04
108.06
77.25
77.00
76.75
56.88
48.63
26.48
20.22
F3C
N3
O
N
2e
f1 (ppm)
f1 (ppm)

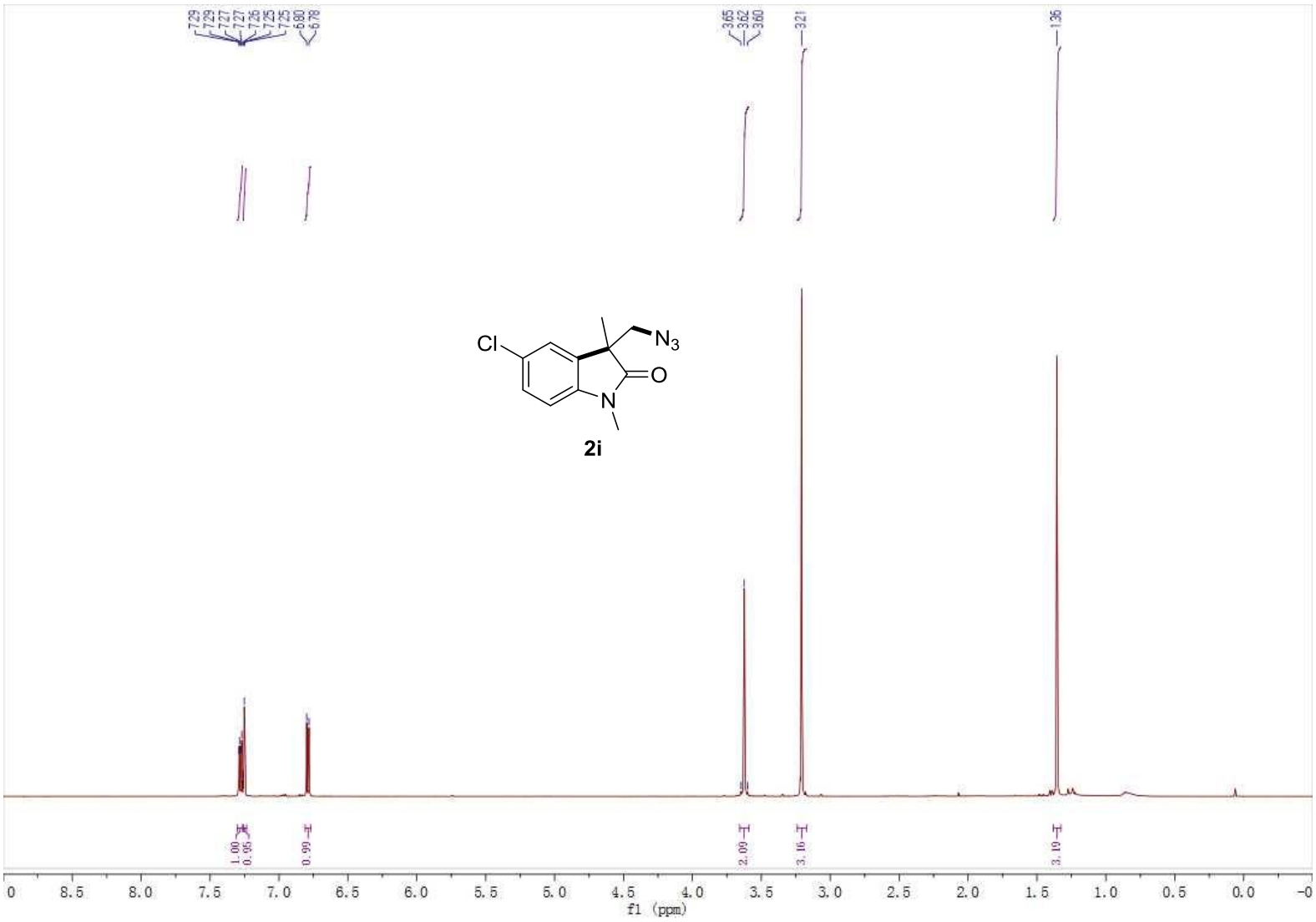

8.07
8.07
8.05
8.05
7.92
7.92
7.26
6.90
6.89
4.38
4.36
4.35
4.33
3.67
3.25
1.39
1.38
1.37
1.37
EtO2C
N3
O
N
2f
1.00
0.97
0.98
2.03
2.01
2.99
5.97
f1 (ppm)
178.32
166.03
147.36
131.14
131.10
124.86
123.97
107.70
77.25
77.00
76.74
60.78
56.79
48.40
26.38
20.17
14.20
EtO2C
N3
O
N
2f
f1 (ppm)

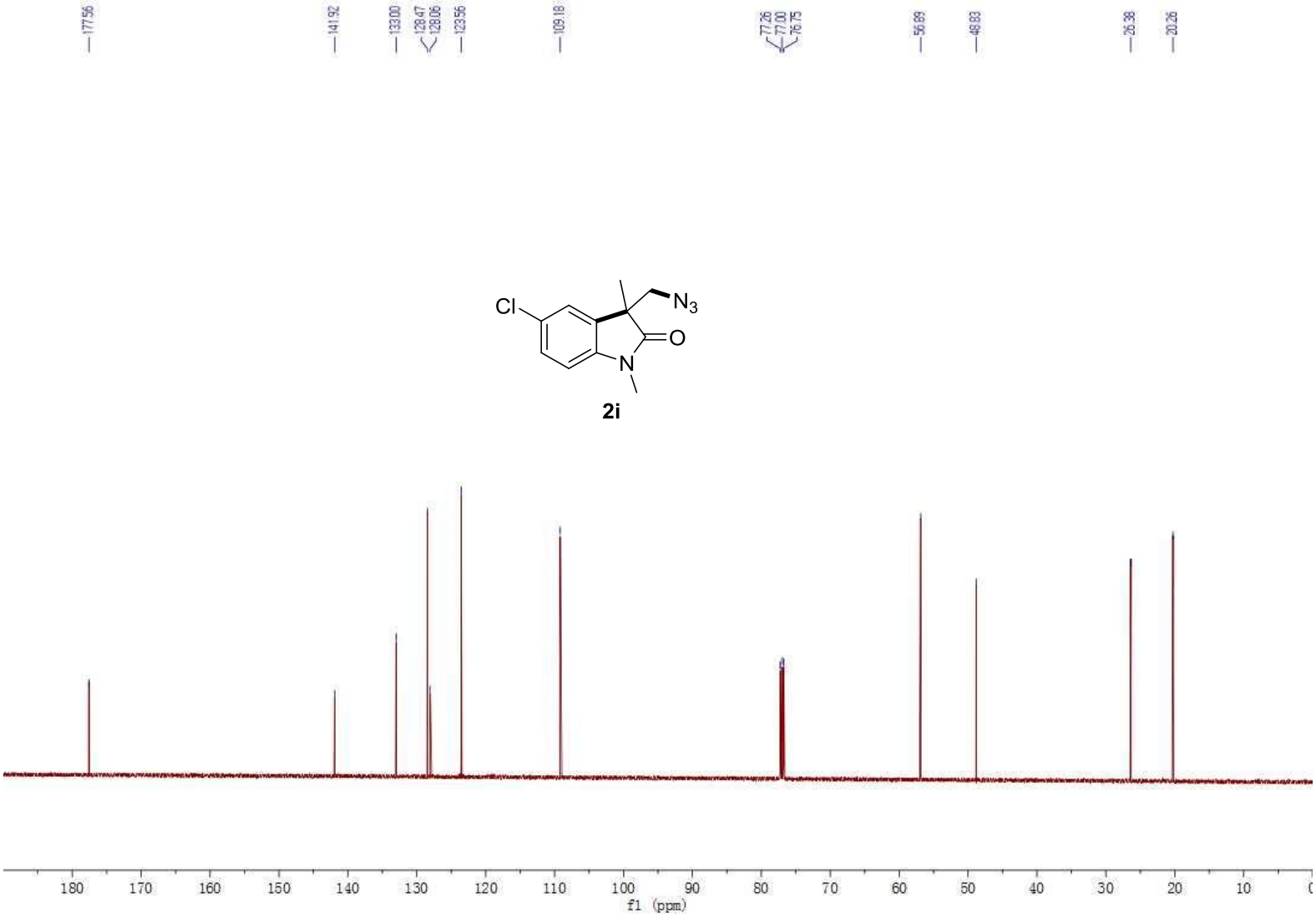

8.32
8.31
8.30
8.30
8.17
8.16
7.26
6.98
6.96
3.73
3.31
1.43
O_2N
N_3
O
N
2g
1.00
0.94
0.99
2.01
3.07
3.03
f1 (ppm)

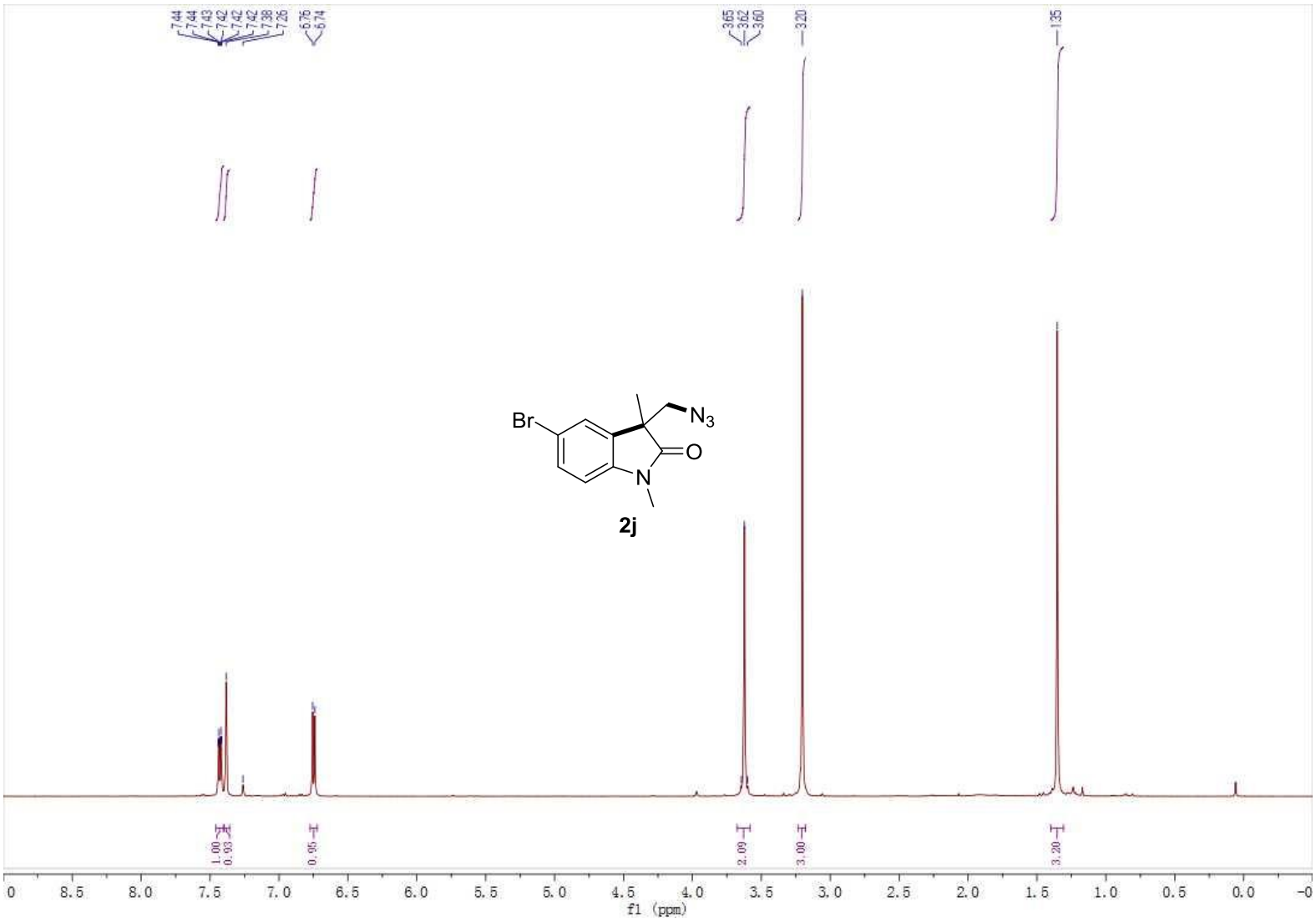

178.25
149.11
143.54
132.21
125.95
118.97
107.90
77.25
77.00
76.75
56.79
48.68
26.79
20.22
O_2N
N_3
O
N
2g
f1 (ppm)

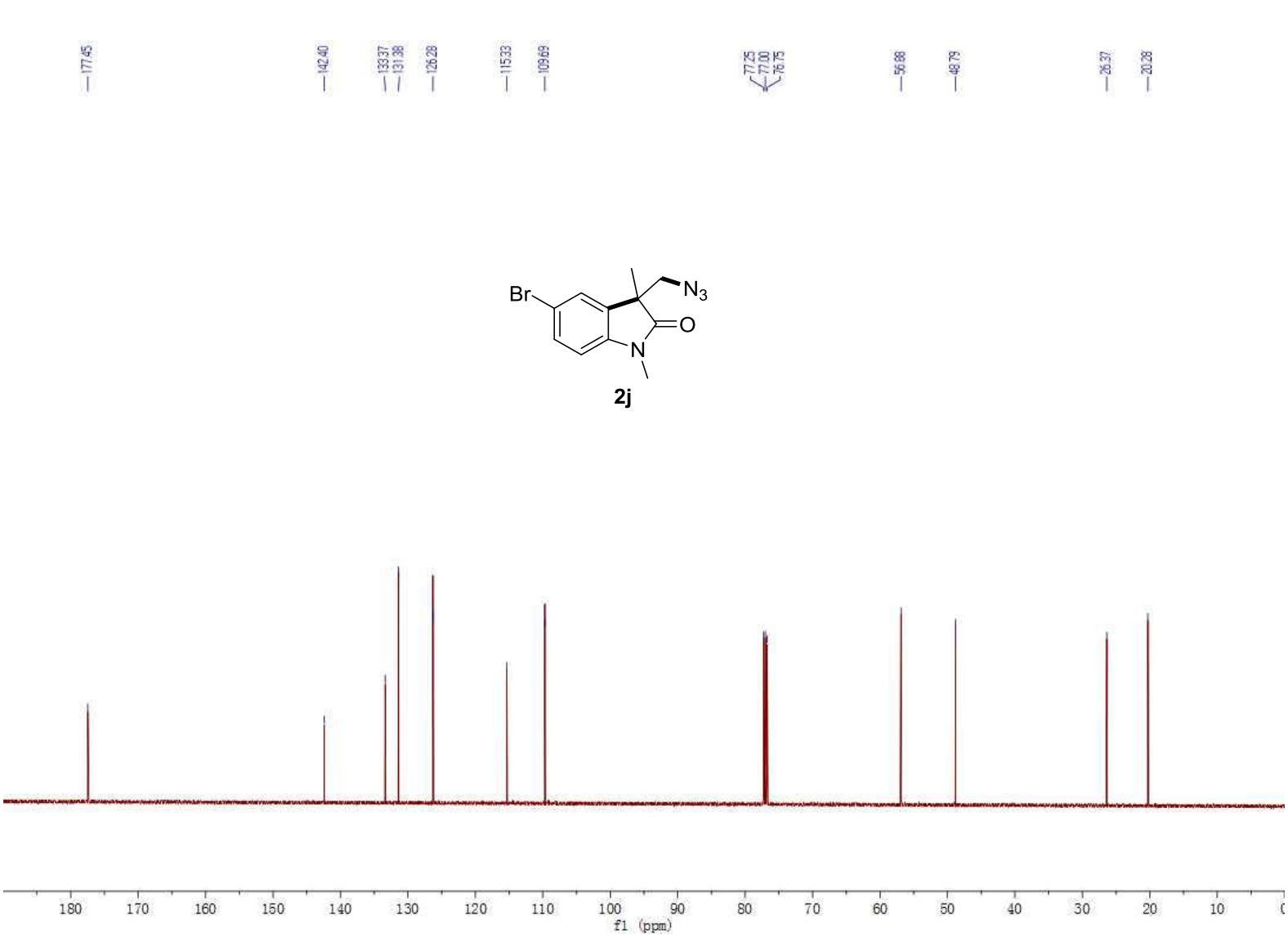

F
N3
O
N
2h
f1 (ppm)

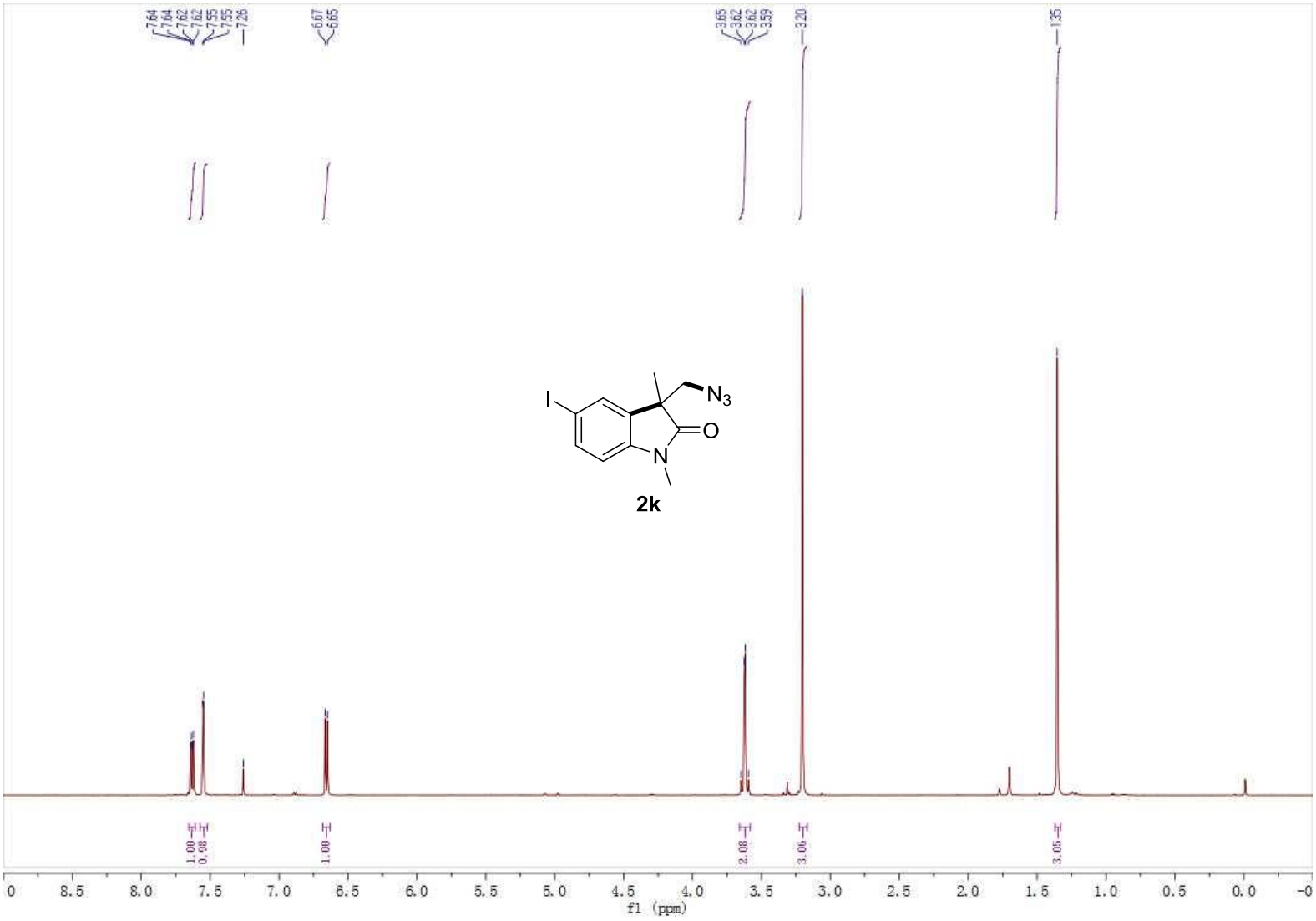

F
N3
O
N
2h
f1 (ppm)

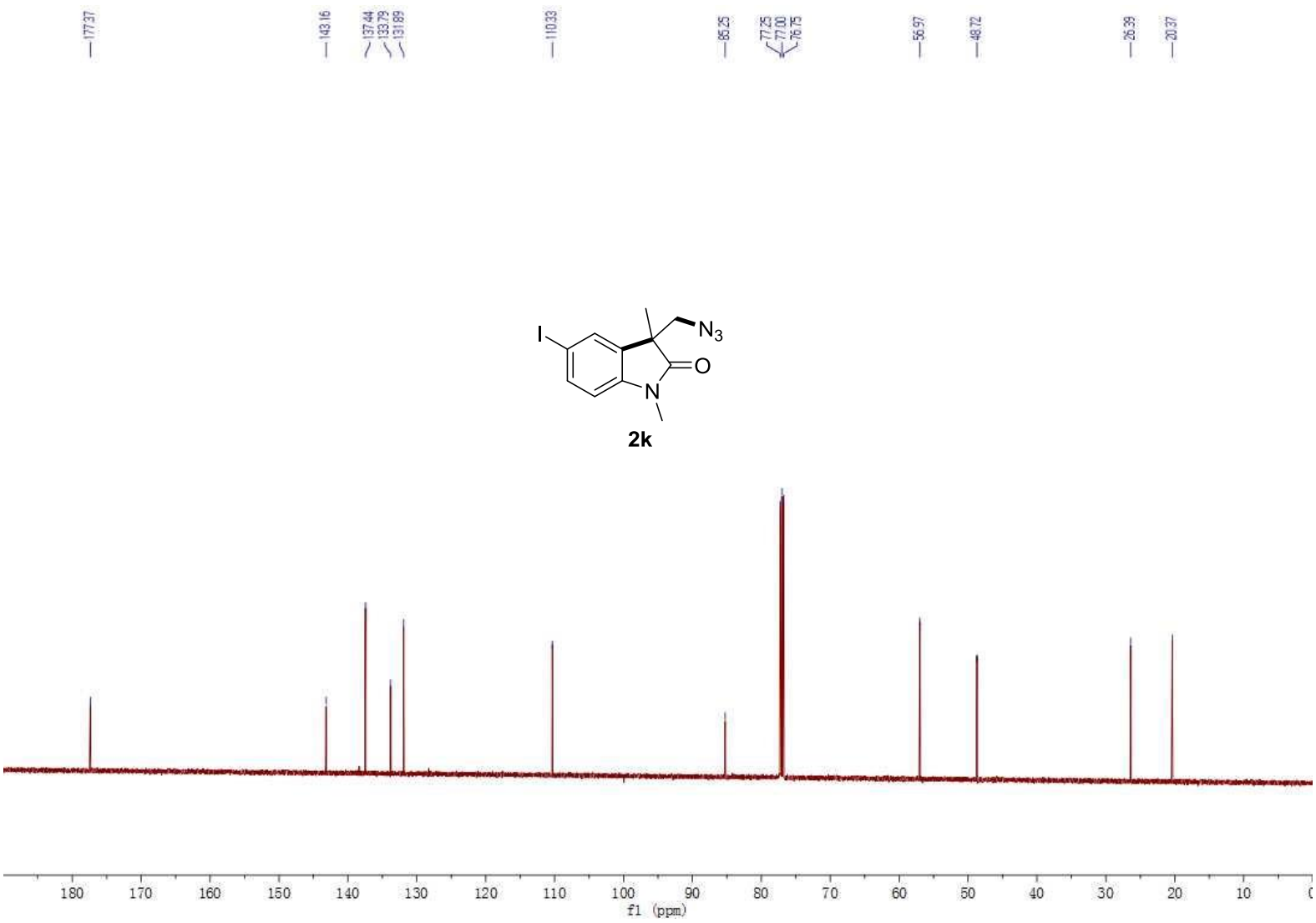

7.29
7.29
7.27
7.27
7.26
7.25
7.25
6.80
6.78
3.65
3.62
3.60
3.21
1.36
Cl
N3
O
N
2i
1.00
0.93
0.99
2.09
3.16
3.19
f1 (ppm)

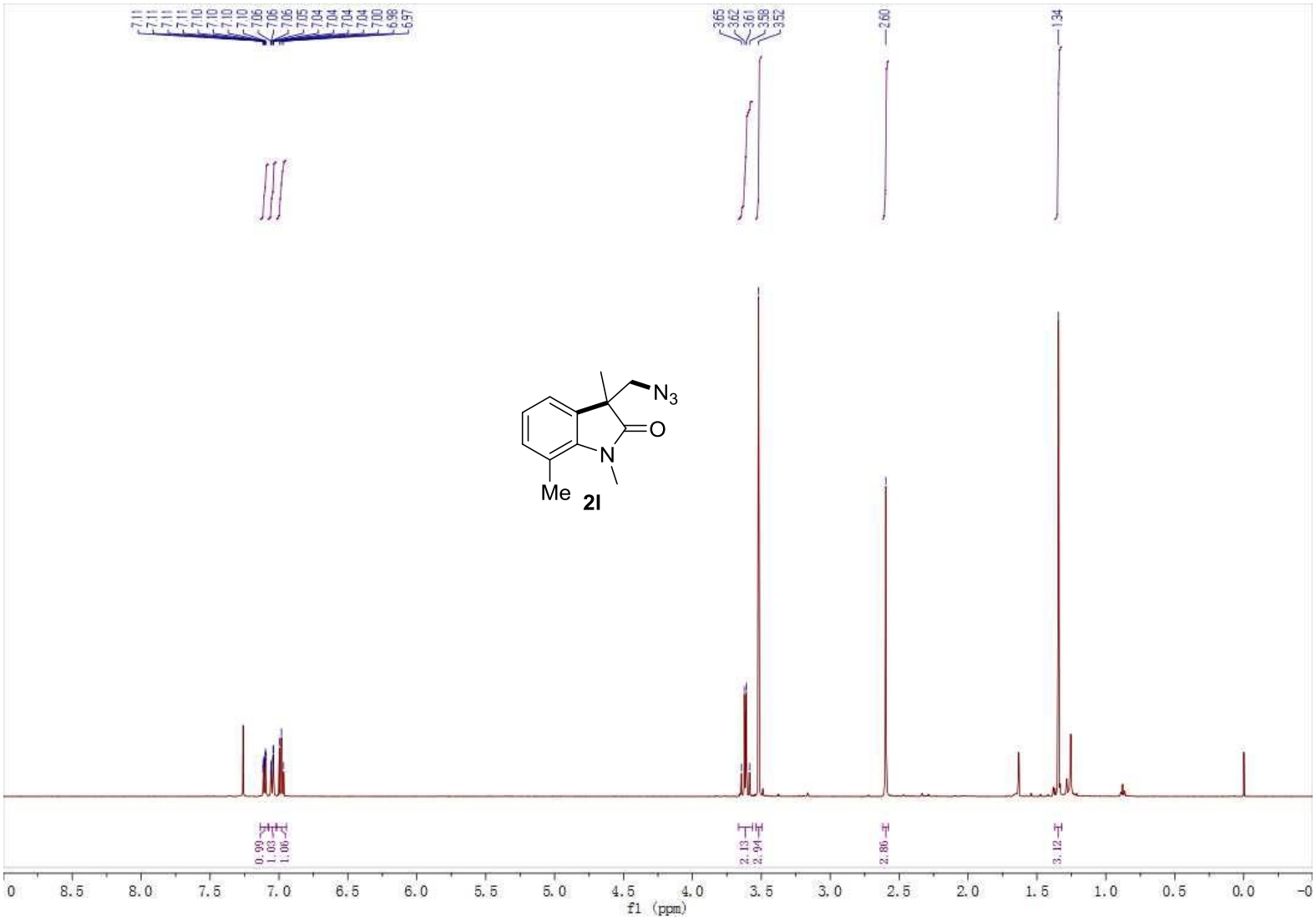

177.56
141.92
133.00
128.47
128.06
123.56
109.18
77.26
77.00
76.75
56.89
48.83
26.38
20.26
Cl
N3
O
N
2i
f1 (ppm)

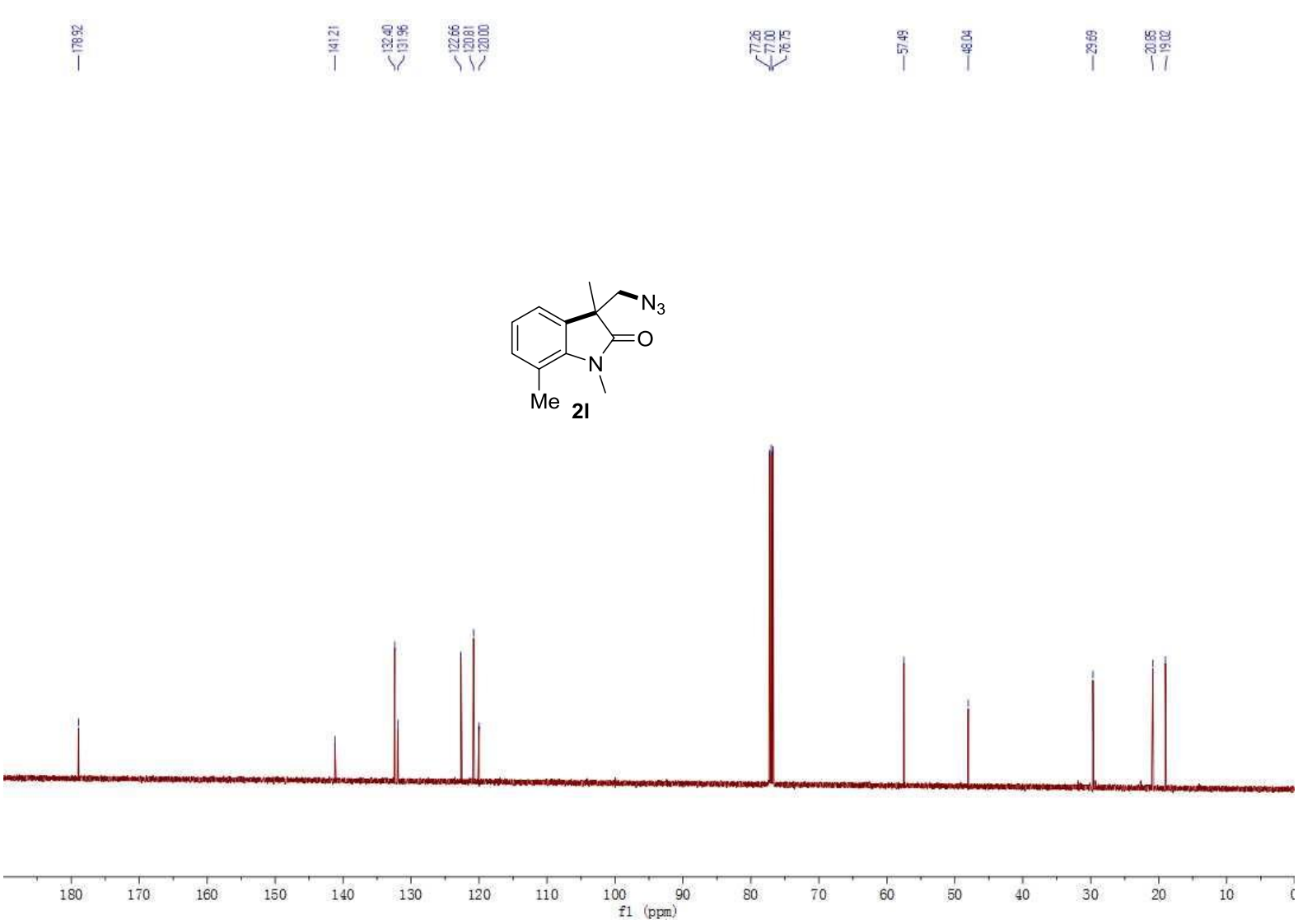

7.44
7.44
7.43
7.42
7.42
7.42
7.38
7.26
6.76
6.74
3.65
3.62
3.60
3.20
1.35
Br
N3
O
N
2j
1.00
0.93
0.95
2.09
3.00
3.20
f1 (ppm)

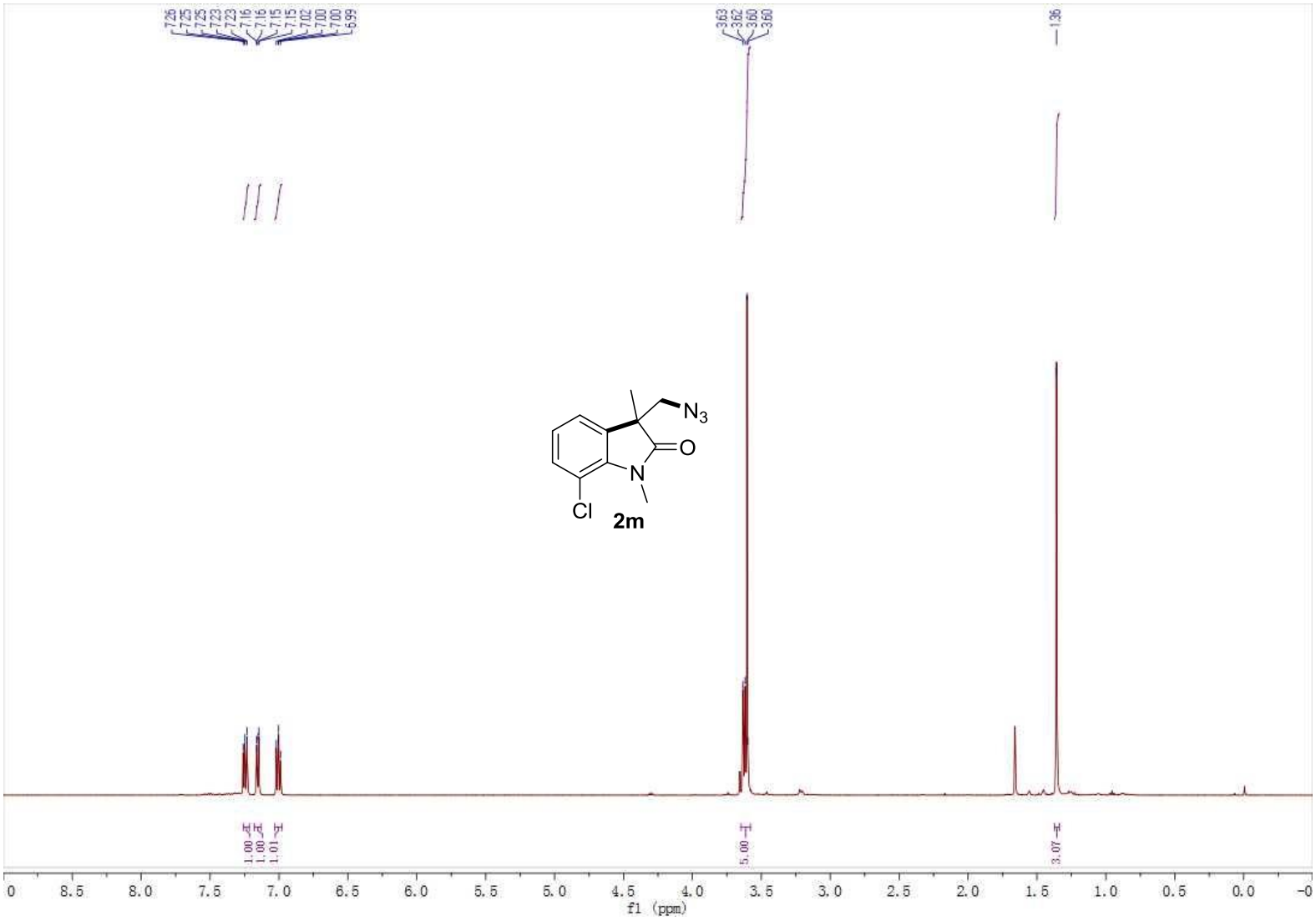

177.45
142.40
133.37
131.38
126.28
115.33
109.69
77.25
77.00
76.75
56.88
49.79
26.37
20.28
Br
N3
O
N
2j
f1 (ppm)

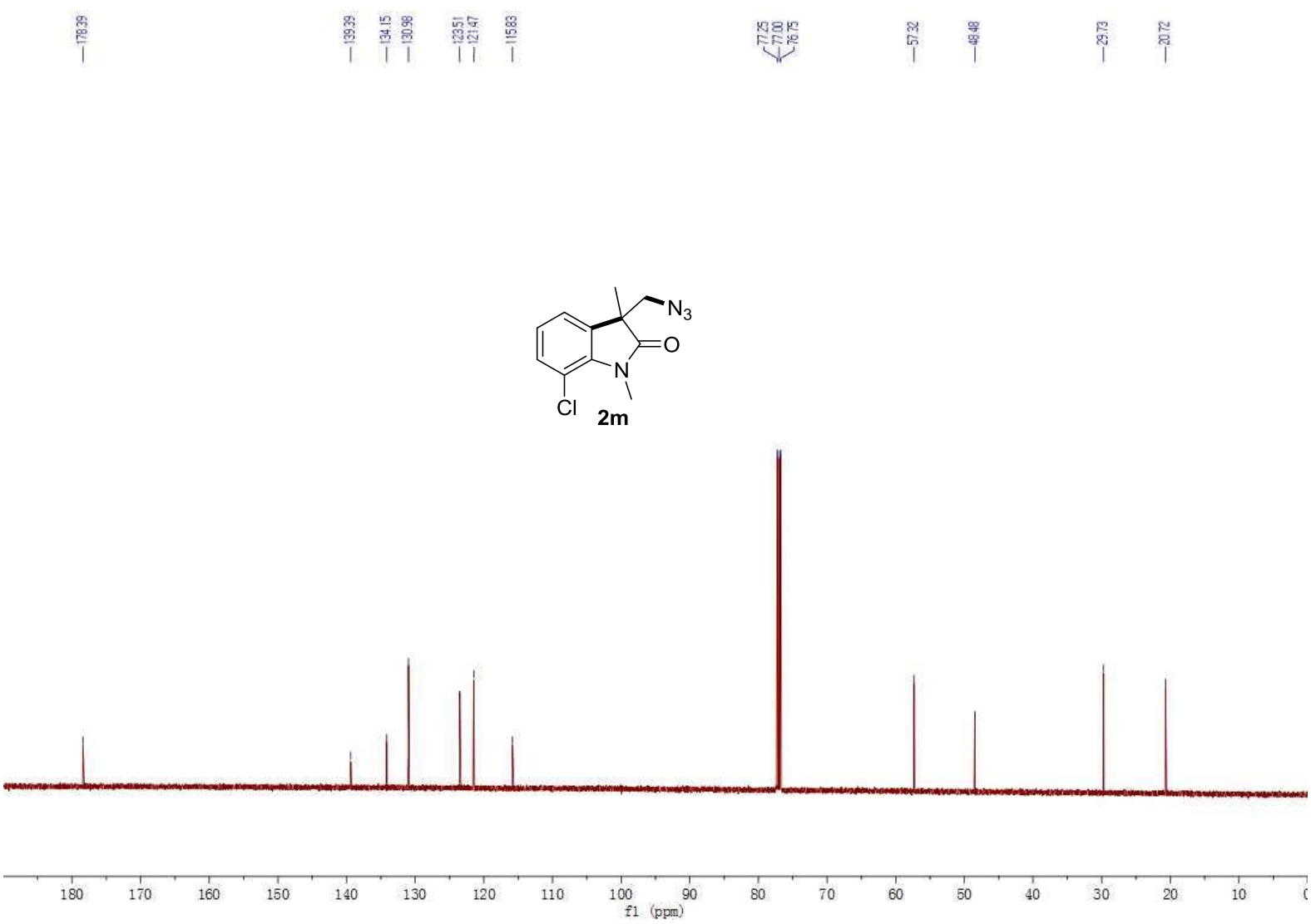

7.64
7.64
7.62
7.62
7.55
7.35
7.26
6.67
6.65
3.65
3.62
3.62
3.59
3.20
1.35
I
N3
O
N
2k
1.00
0.98
1.00
2.08
3.06
3.05
f1 (ppm)

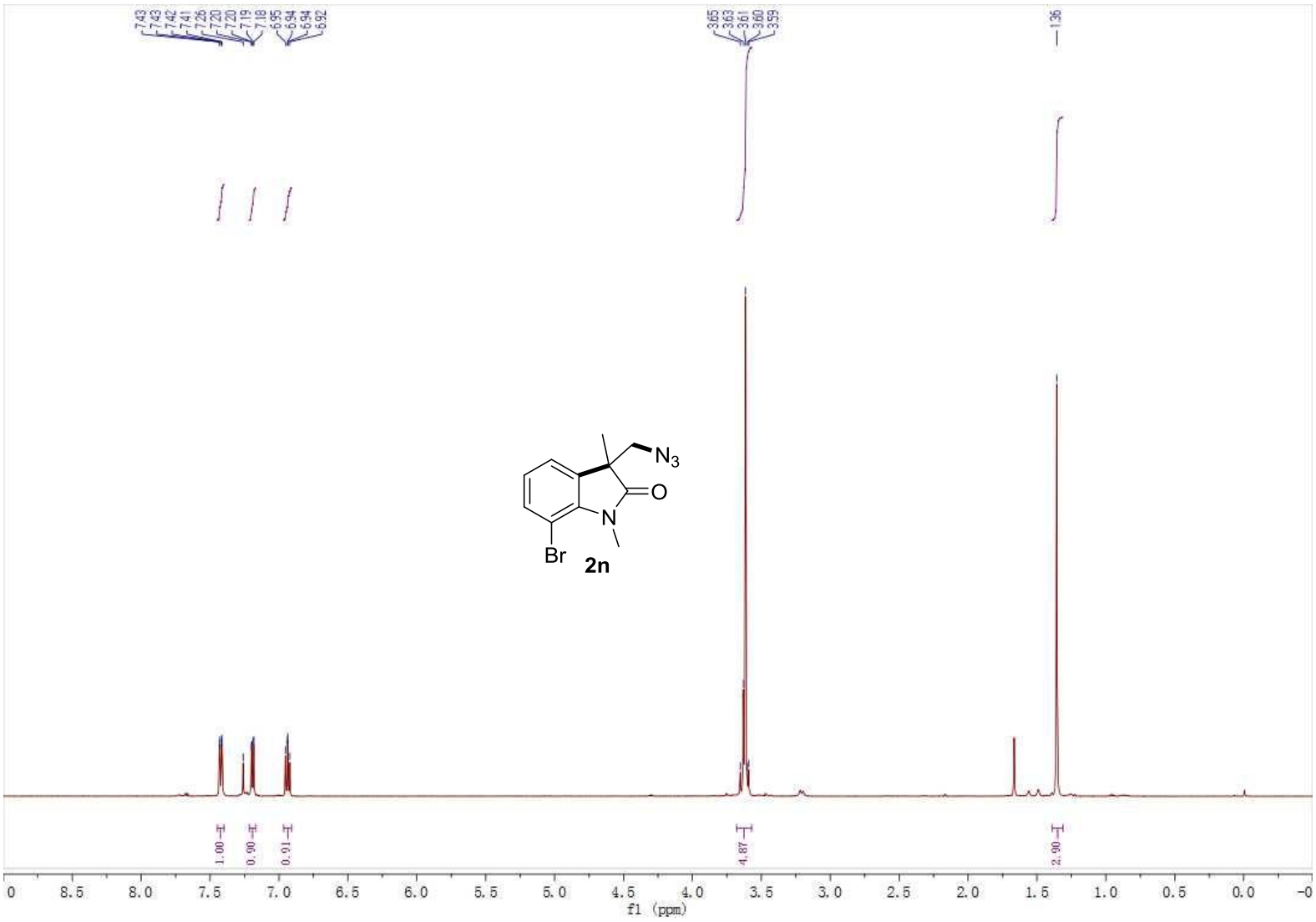

177.37
143.16
137.44
133.79
131.89
110.33
85.25
77.25
77.00
76.75
56.97
48.72
26.39
20.37
I
N3
O
N
2k
f1 (ppm)

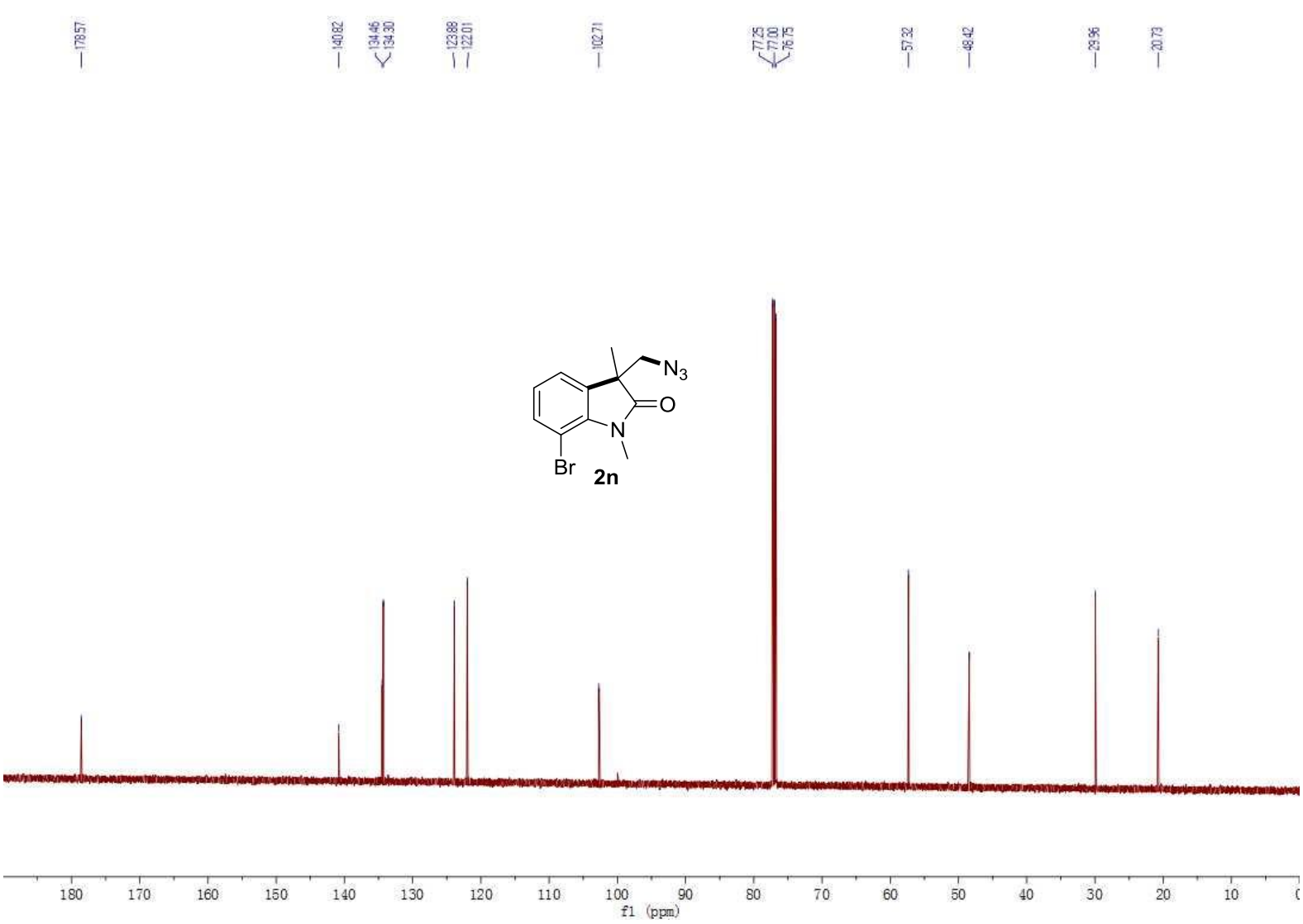

7.11
7.11
7.11
7.11
7.10
7.10
7.10
7.10
7.06
7.06
7.06
7.05
7.04
7.04
7.04
7.04
7.00
6.98
6.97
3.65
3.62
3.61
3.58
3.52
2.60
1.34
N3
O
N
Me
2l
0.99
1.03
1.06
2.13
2.94
2.86
3.12
f1 (ppm)

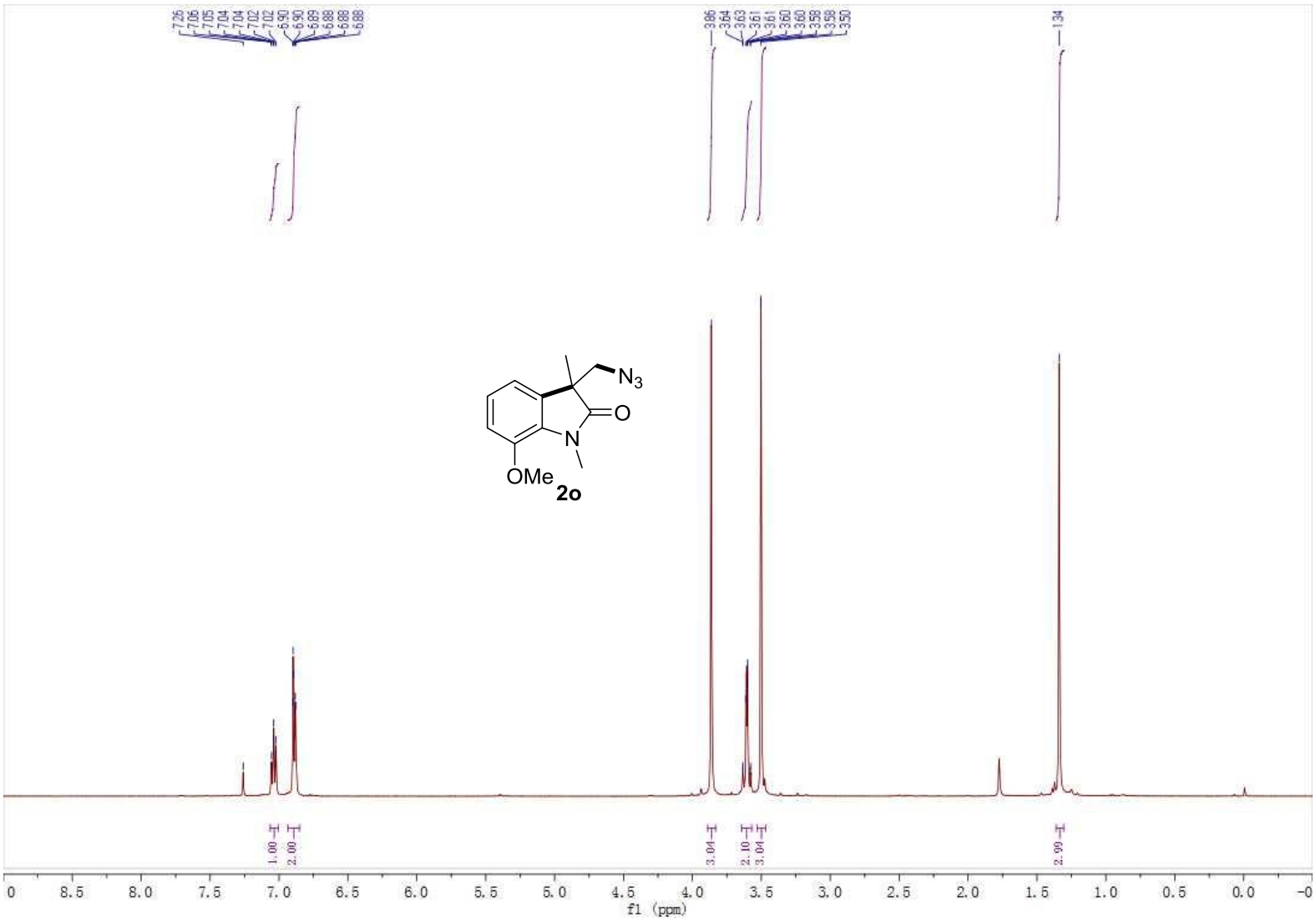

178.92
141.21
132.40
131.96
122.66
120.81
120.00
77.26
77.00
76.75
57.49
48.04
29.69
20.85
19.02
N3
O
N
Me
2l
f1 (ppm)

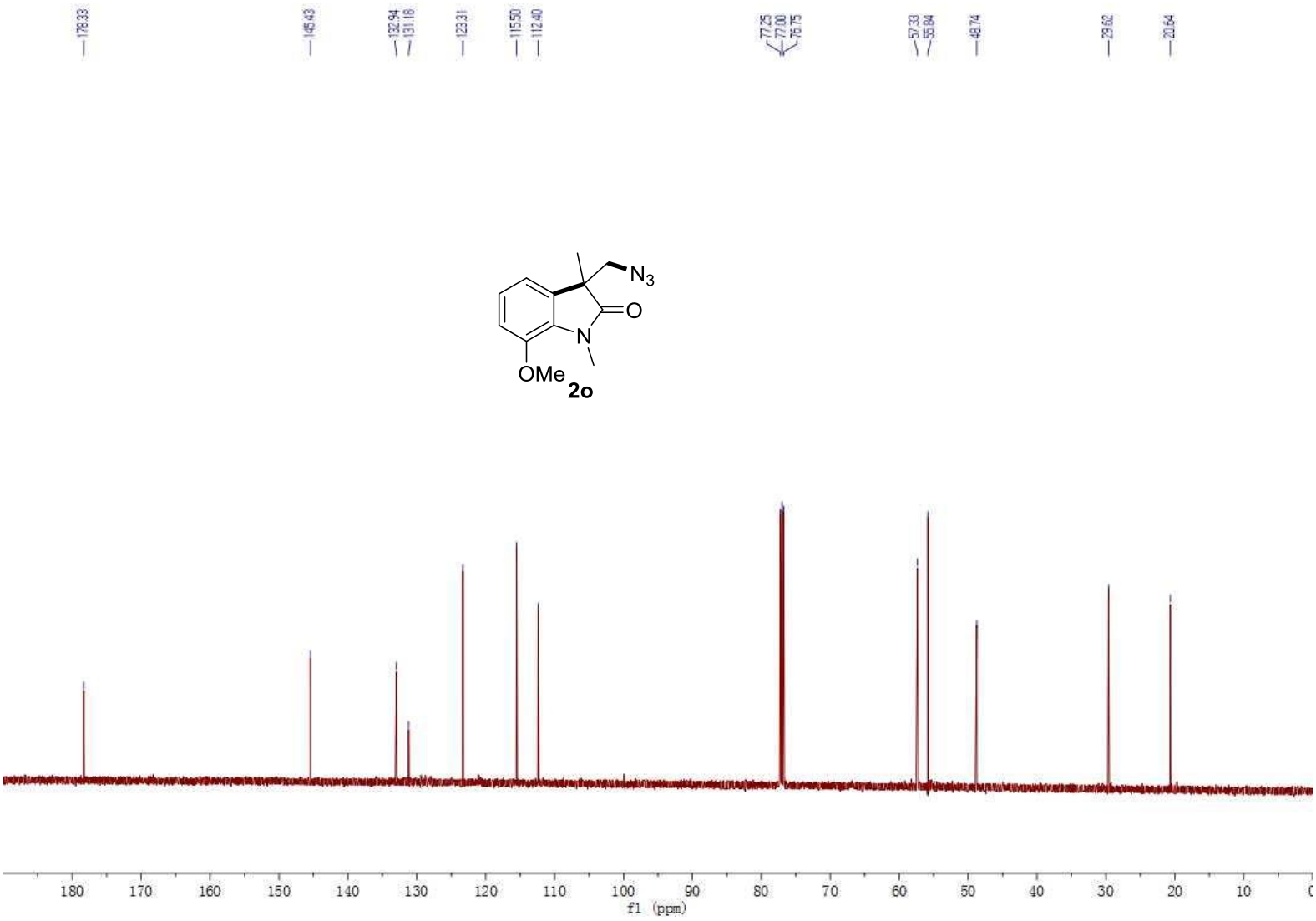

7.26
7.25
7.25
7.23
7.23
7.16
7.16
7.15
7.15
7.02
7.00
7.00
6.99
3.63
3.62
3.60
3.60
1.36
N3
O
N
Cl
2m
1.00
1.00
1.01
5.00
3.07
f1 (ppm)

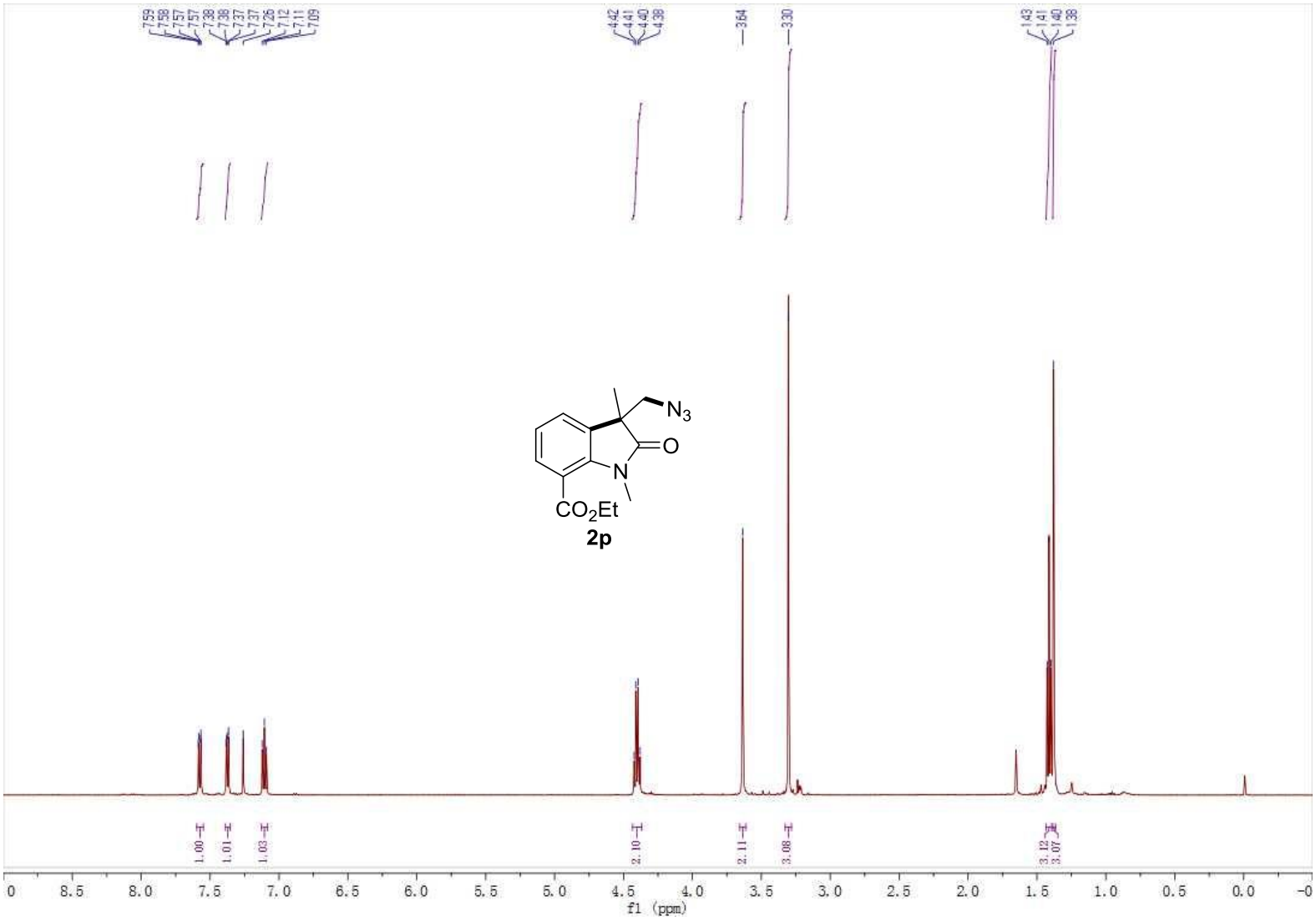

178.39
139.39
134.15
130.98
123.51
121.47
115.83
77.25
77.00
76.75
57.32
48.48
29.73
20.72
N3
O
N
Cl
2m
f1 (ppm)


7.43
7.43
7.42
7.41
7.26
7.20
7.20
7.19
7.18
6.95
6.94
6.94
6.92
3.65
3.63
3.61
3.60
3.59
1.36
N3
O
N
Br
2n
1.00
0.90
0.91
4.87
2.90
f1 (ppm)


17.857
140.82
134.46
134.30
123.88
122.01
102.71
77.25
77.00
76.75
57.32
48.42
29.96
20.73
N3
O
N
Br
2n
f1 (ppm)


7.26
7.06
7.05
7.04
7.04
7.02
7.02
6.90
6.90
6.89
6.88
6.88
6.88
3.86
3.64
3.63
3.61
3.61
3.60
3.60
3.58
3.58
3.50
1.34
N3
O
N
OMe
2o
1.00
2.00
3.04
2.10
3.04
2.99
f1 (ppm)


178.33
145.43
132.94
131.18
123.31
115.50
112.40
77.25
77.00
76.75
57.33
55.84
48.74
29.62
20.64
N3
O
N
OMe
2o
f1 (ppm)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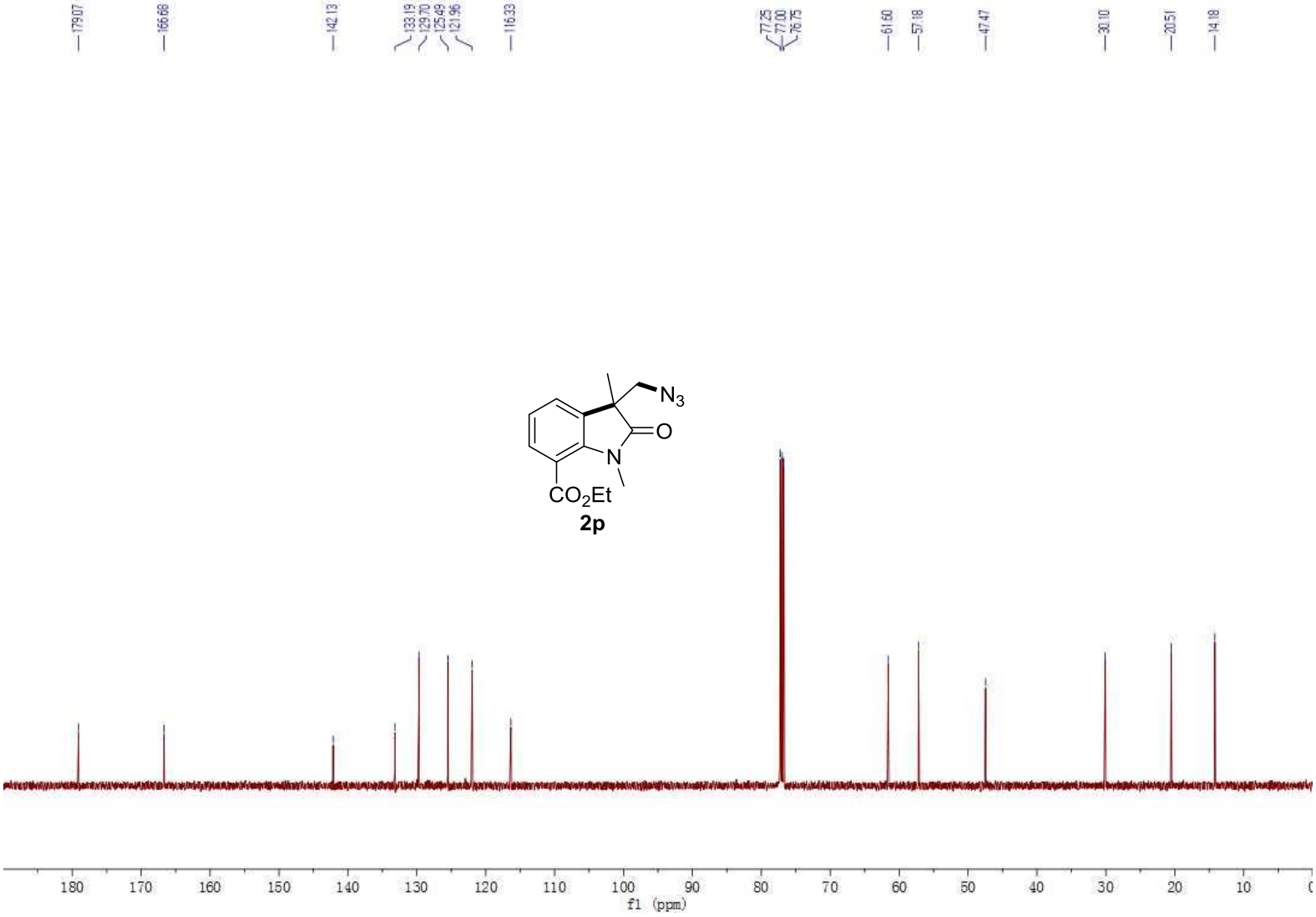
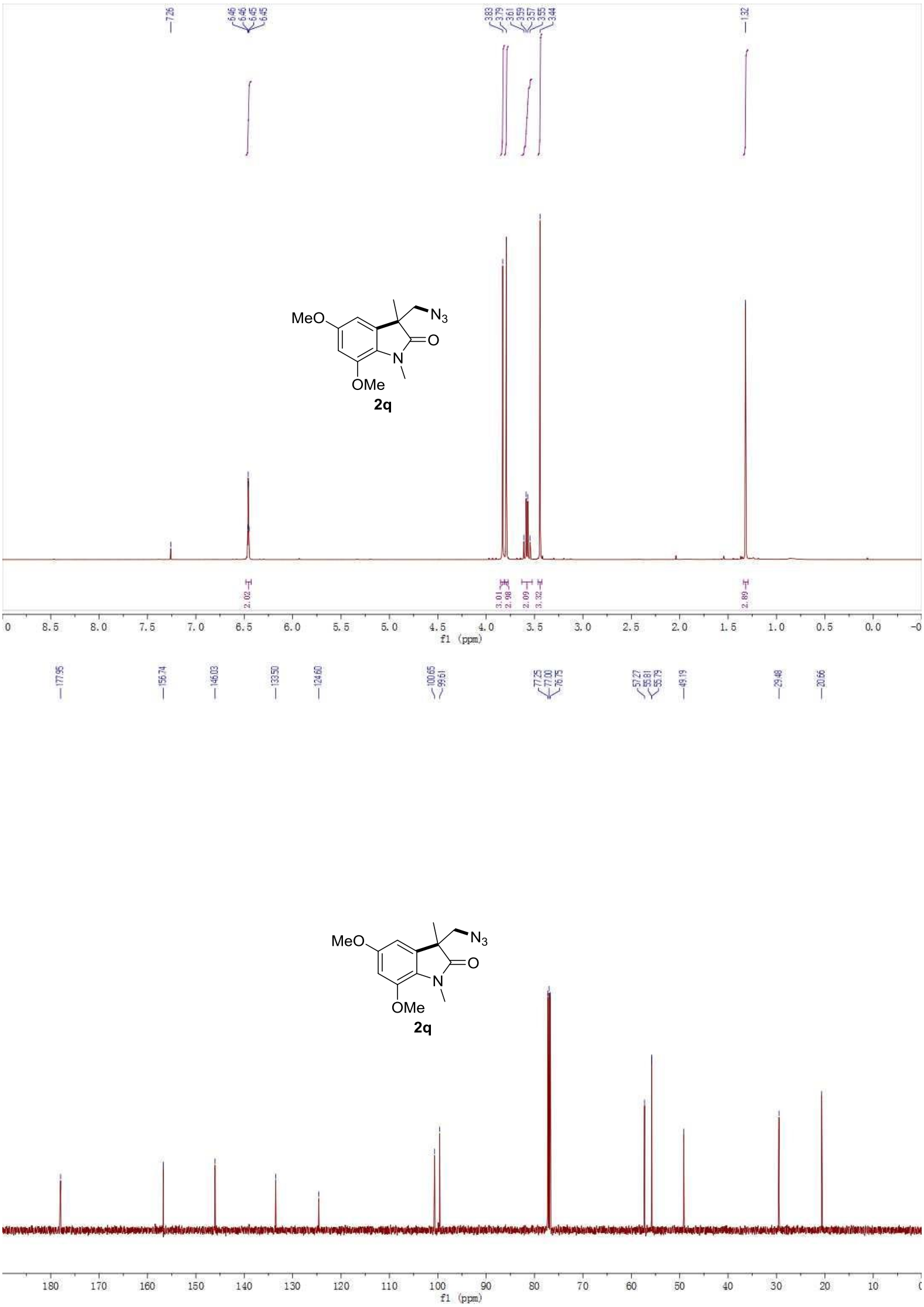
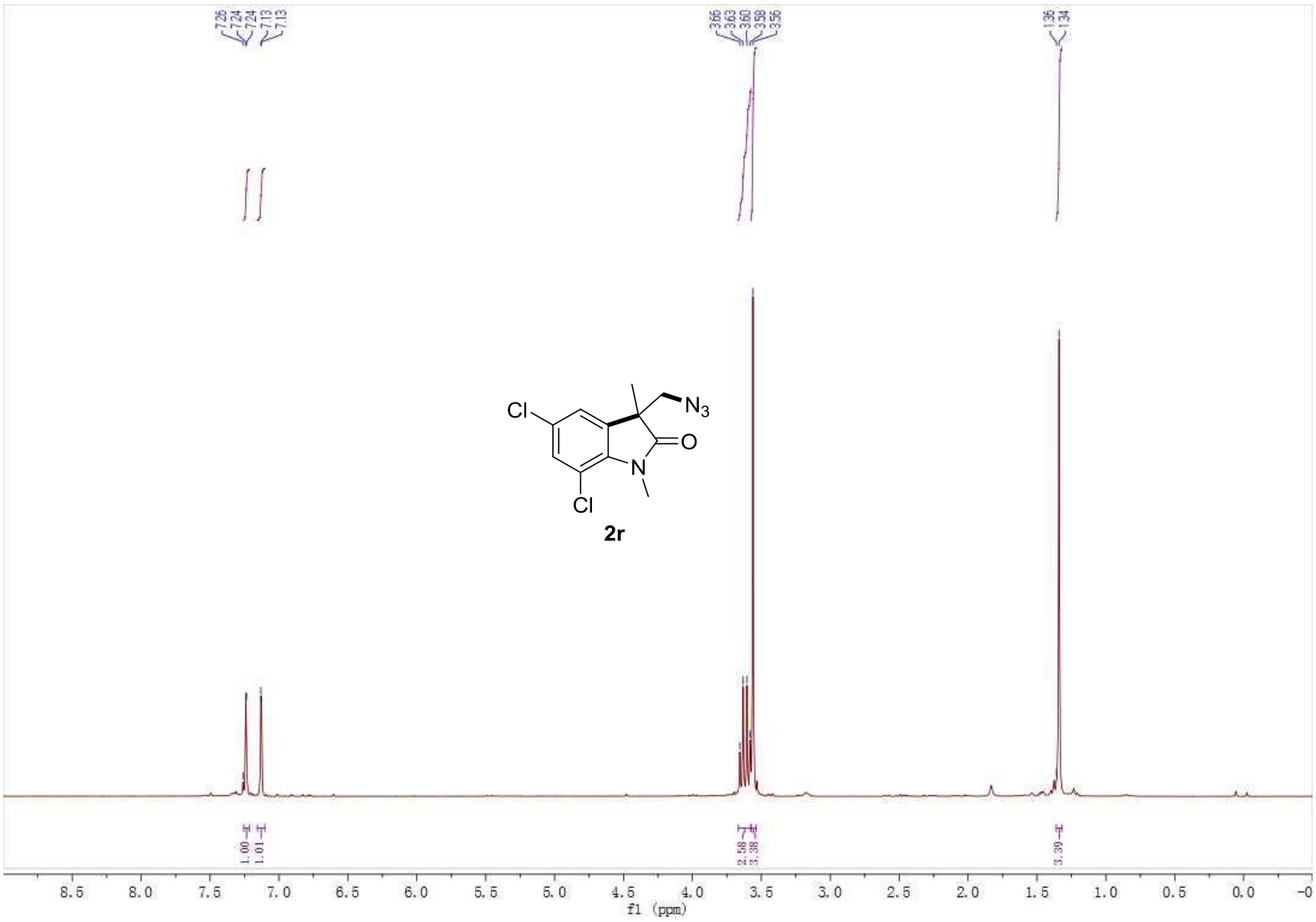
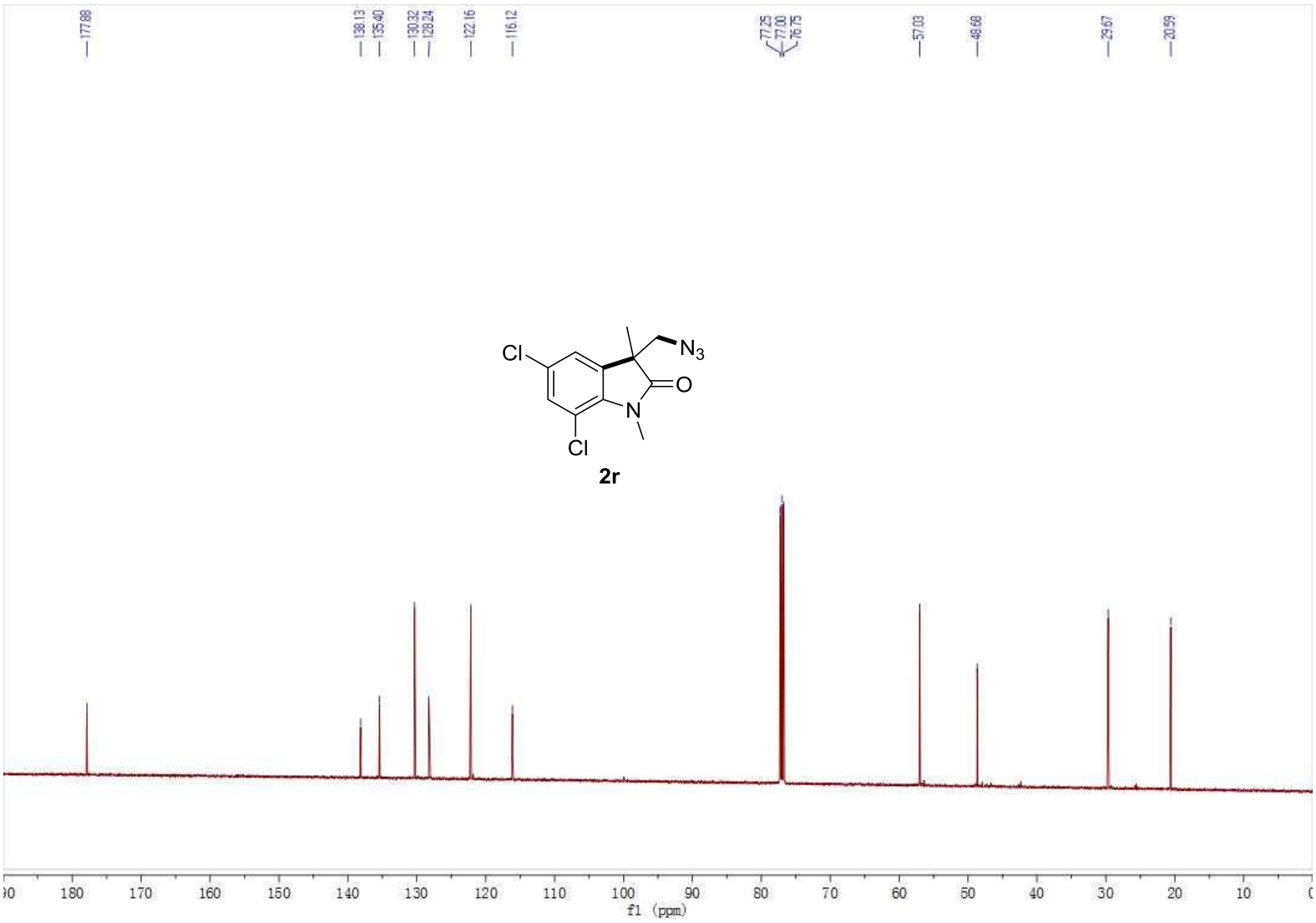
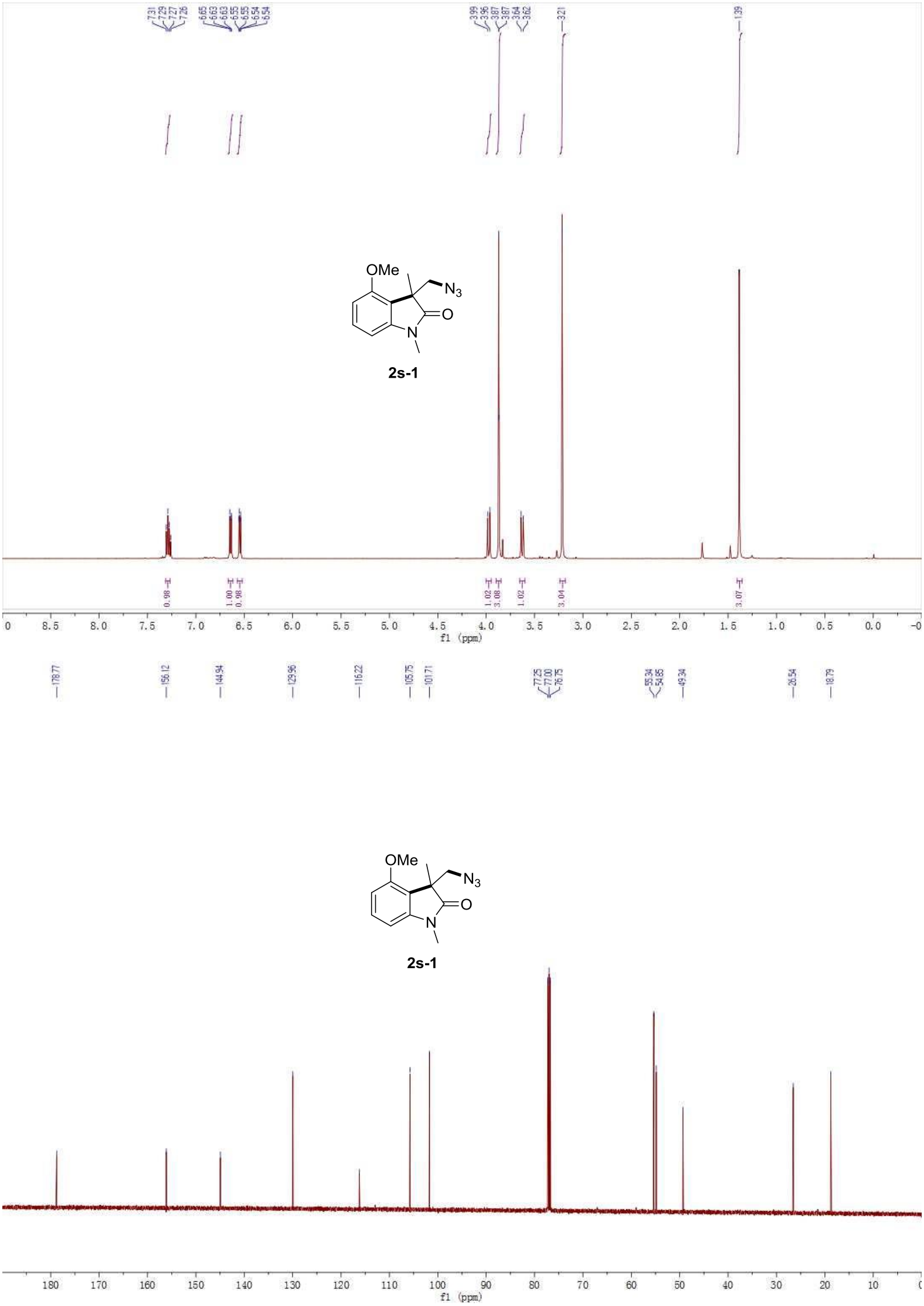
7.58
7.57
7.57
7.38
7.38
7.37
7.37
7.26
7.12
7.11
7.09
4.42
4.41
4.40
4.38
3.64
3.30
1.43
1.41
1.40
1.38
N3
O
N
CO2Et
2p
1.00
1.01
1.03
2.10
2.11
3.08
3.12
3.07
f1 (ppm)

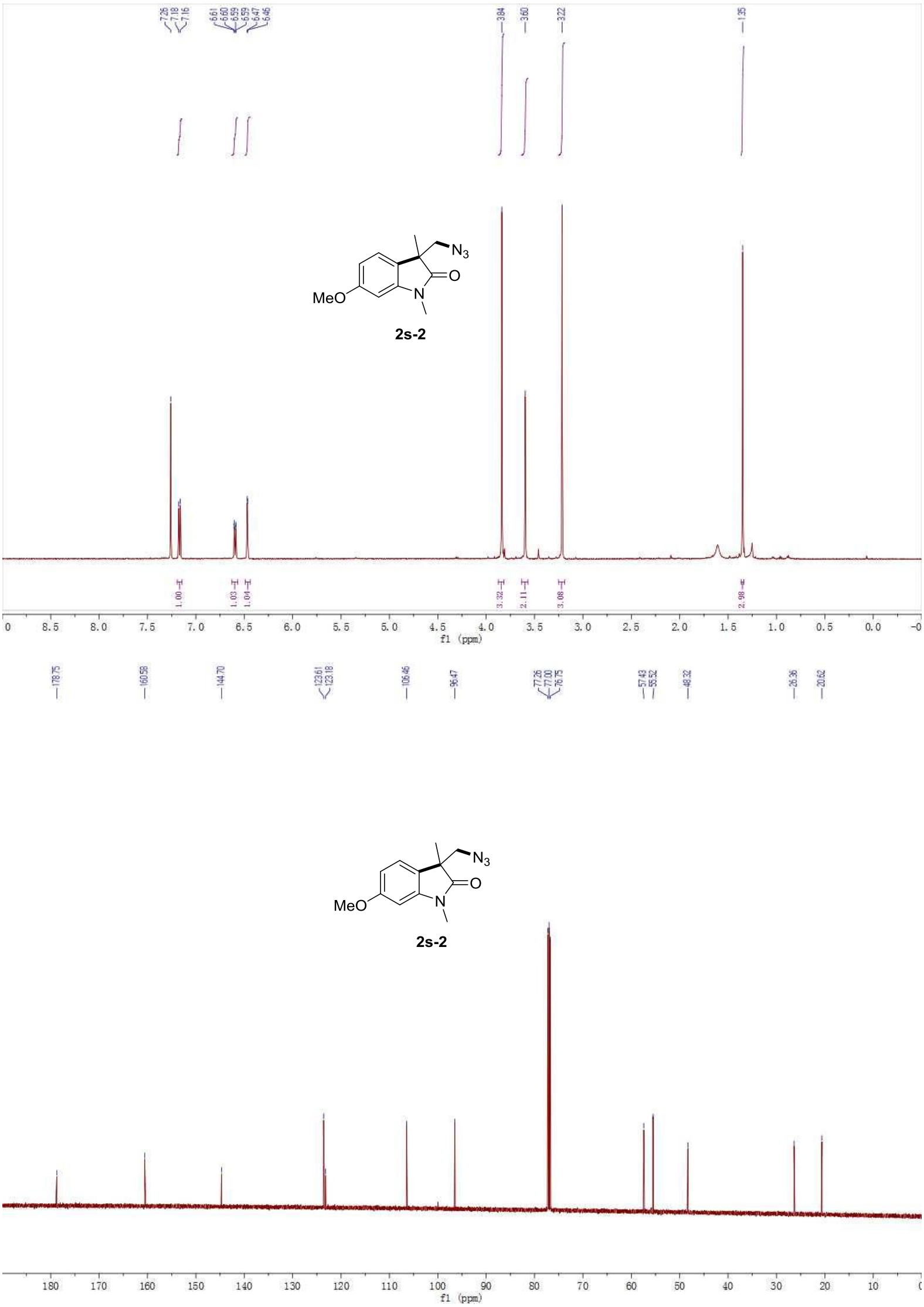

179.07
166.68
142.13
133.19
129.70
125.49
121.96
116.33
77.25
77.00
76.75
61.60
57.18
47.47
30.10
20.51
14.18
N3
O
N
CO2Et
2p
f1 (ppm)

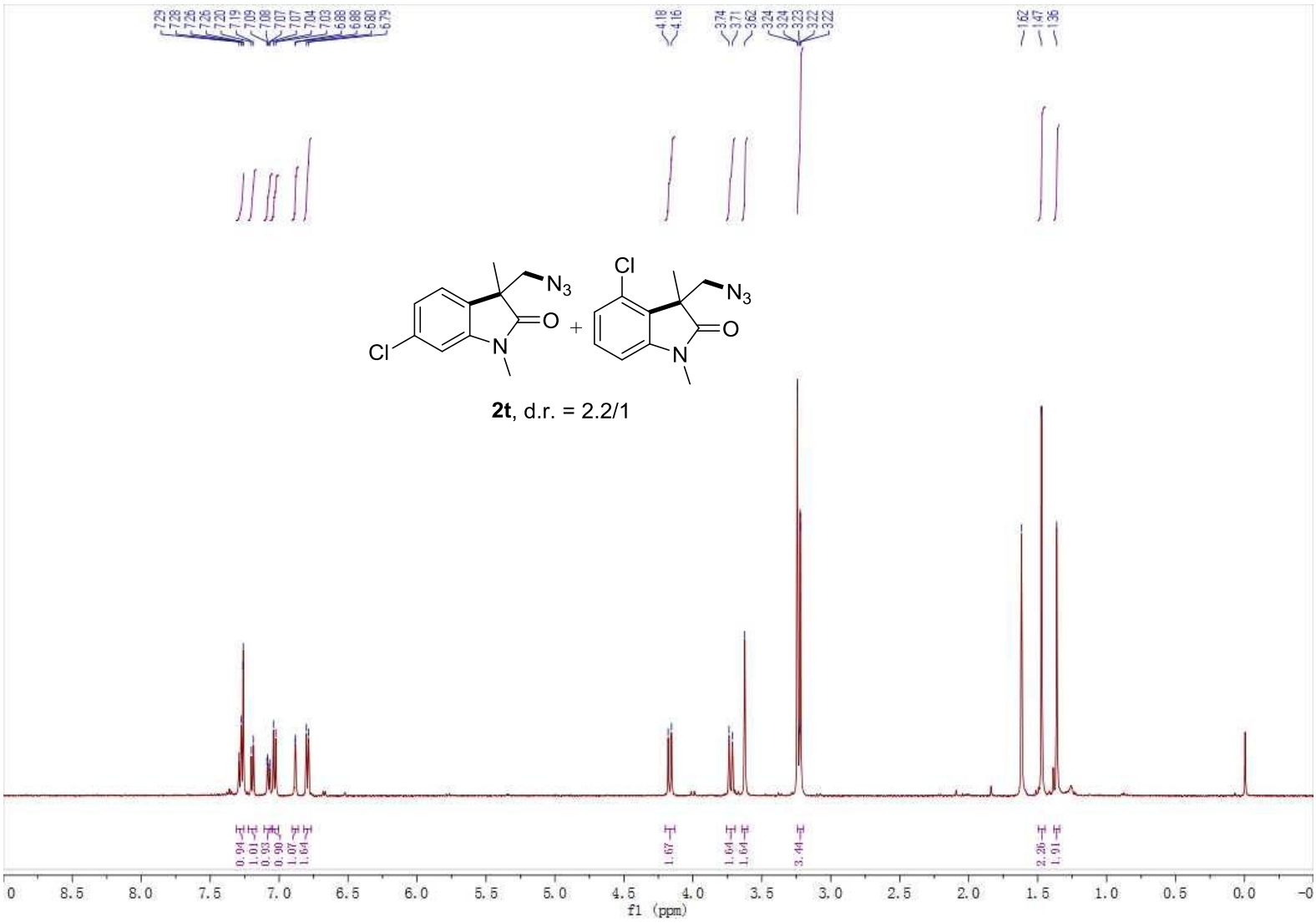

MeO
N3
O
N
OMe
2q
f1 (ppm)


7.26
7.24
7.24
7.13
7.13
3.66
3.63
3.60
3.58
3.56
1.36
1.34
Cl
N3
O
N
Cl
2r
1.00
1.01
2.58
3.38
3.39
f1 (ppm)

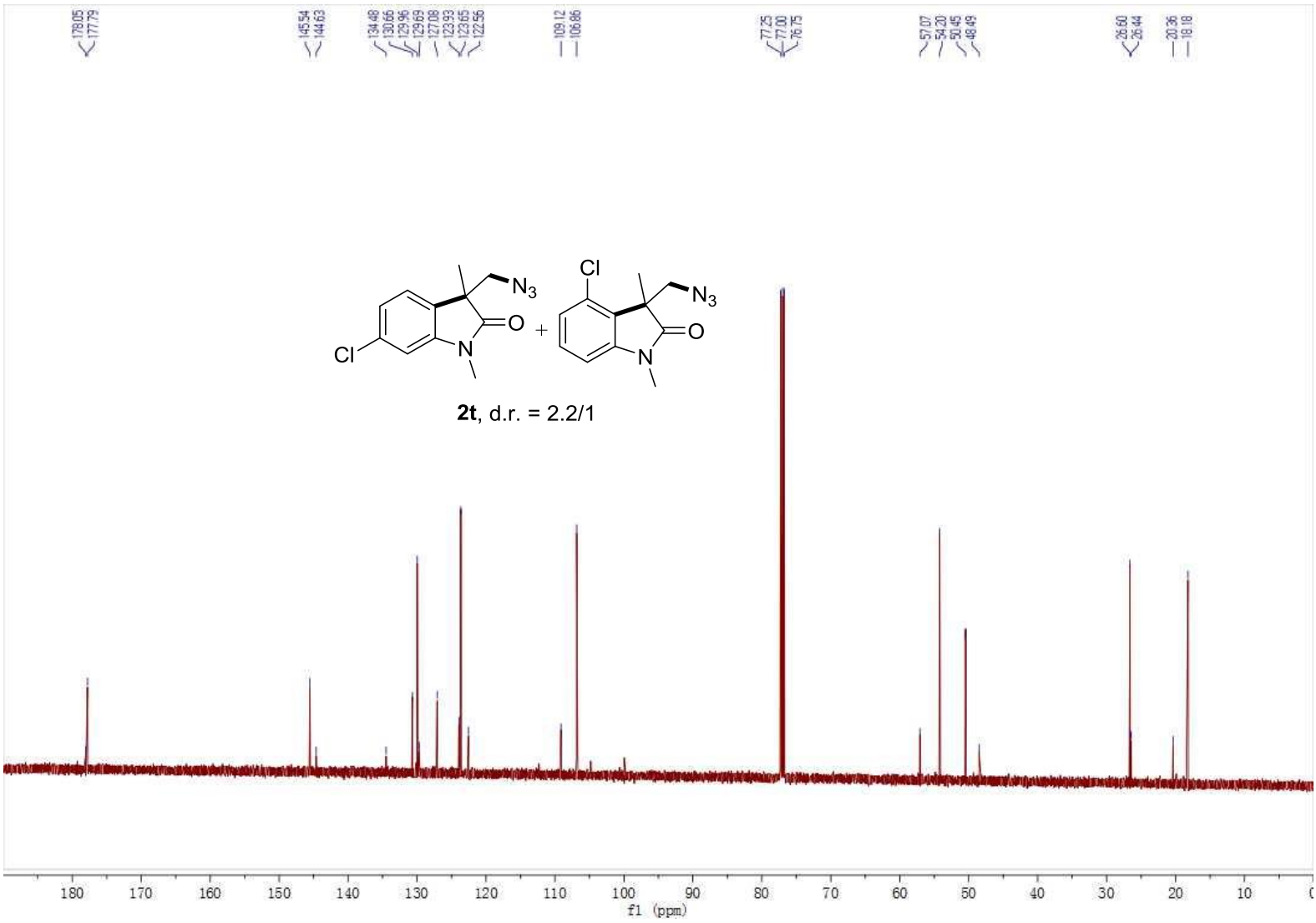

177.88
138.13
135.40
130.32
128.24
122.16
116.12
77.25
77.00
76.75
57.03
46.68
29.67
20.59
Cl
N3
O
N
Cl
2r
f1 (ppm)


OMe
N3
O
N
2s-1
f1 (ppm)

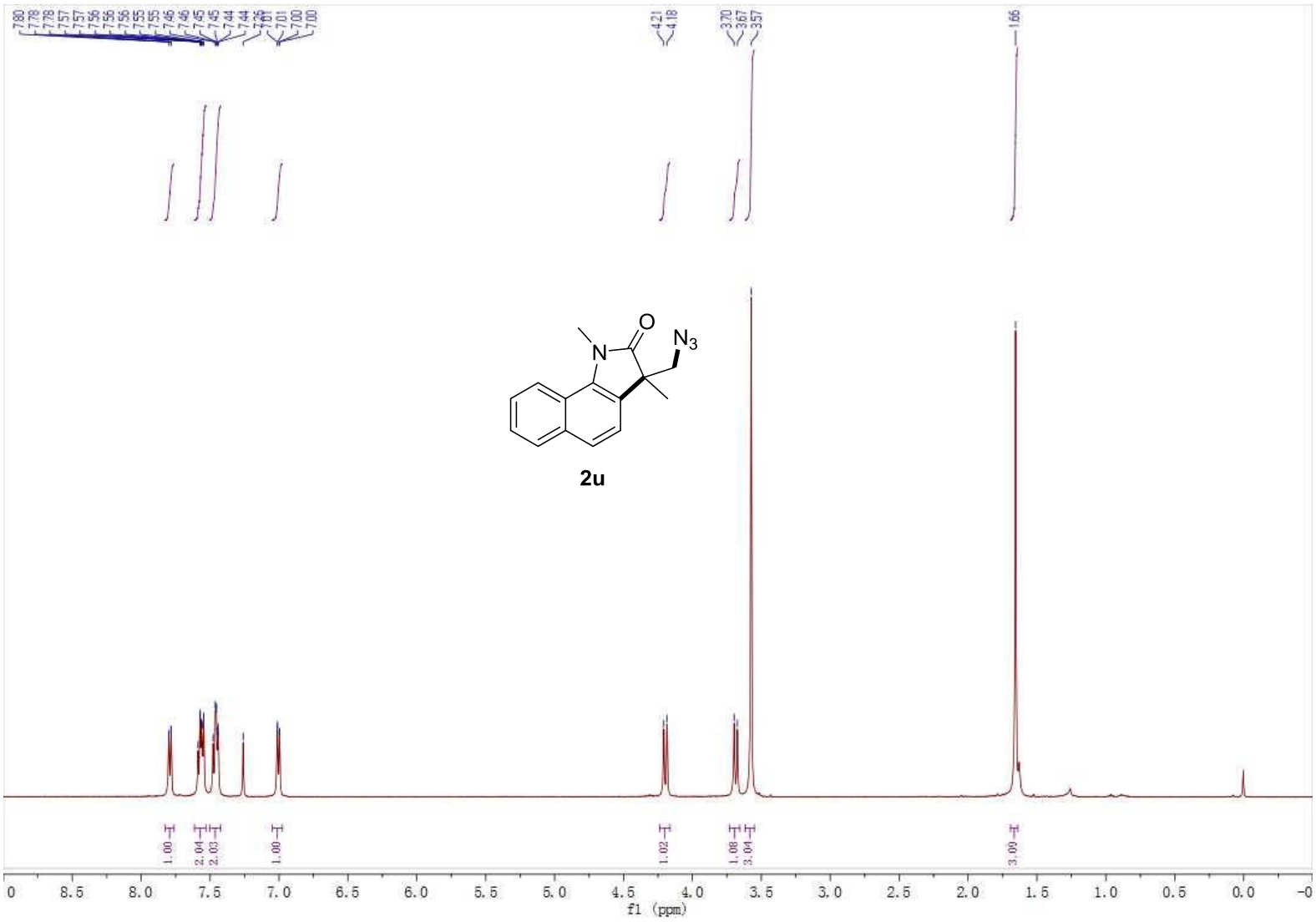

7.26
7.18
7.16
6.61
6.60
6.59
6.59
6.47
6.46
3.84
3.60
3.22
1.35
MeO
N
O
N3
2s-2
1.00
1.03
1.04
3.32
2.11
3.08
2.98
f1 (ppm)
178.75
160.58
144.70
123.61
123.18
106.46
96.47
77.26
77.00
76.75
57.43
55.52
48.32
26.36
20.62
MeO
N
O
N3
2s-2
f1 (ppm)



2t, d.r. = 2.2/1



2t, d.r. = 2.2/1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7.56
7.56
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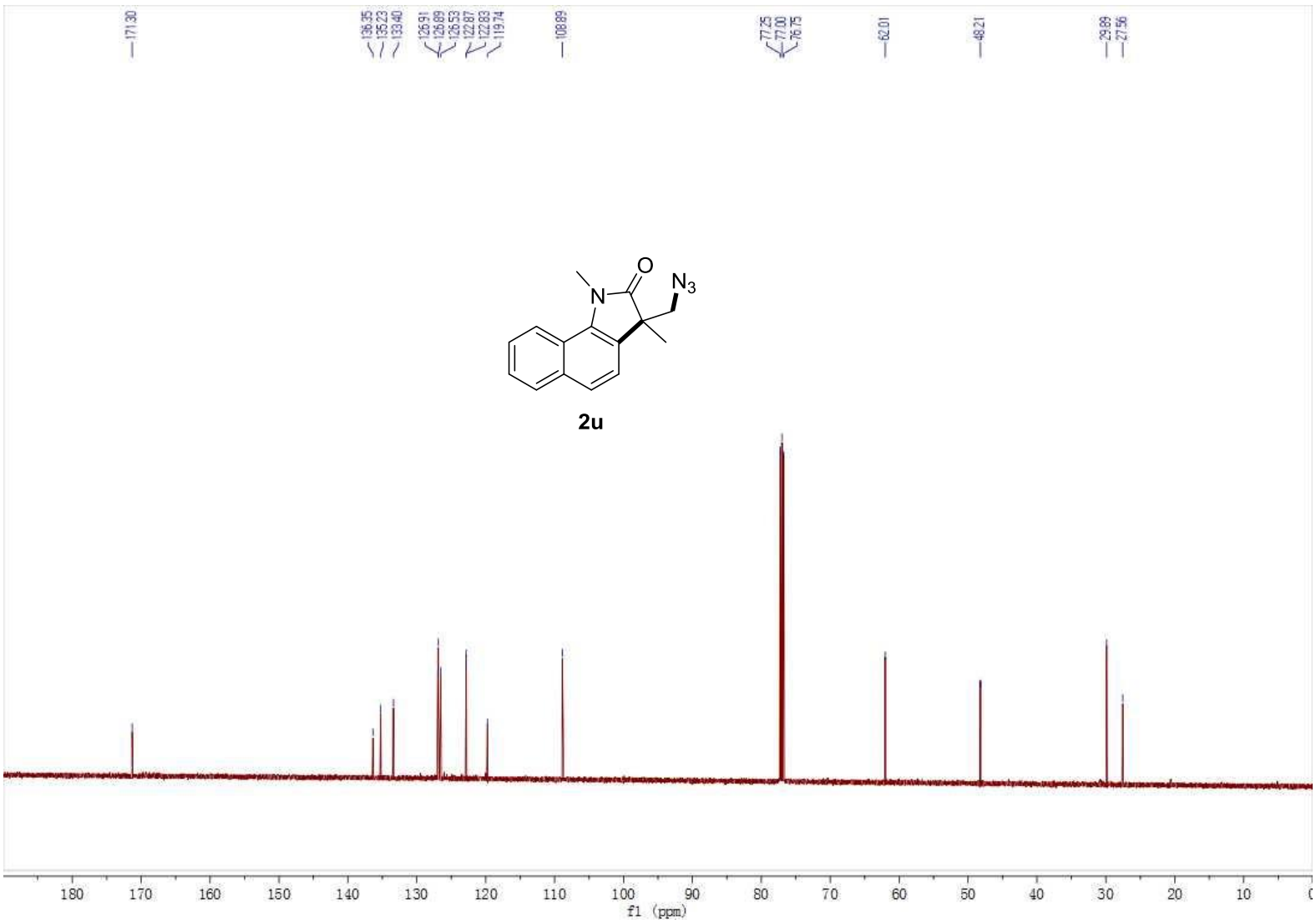
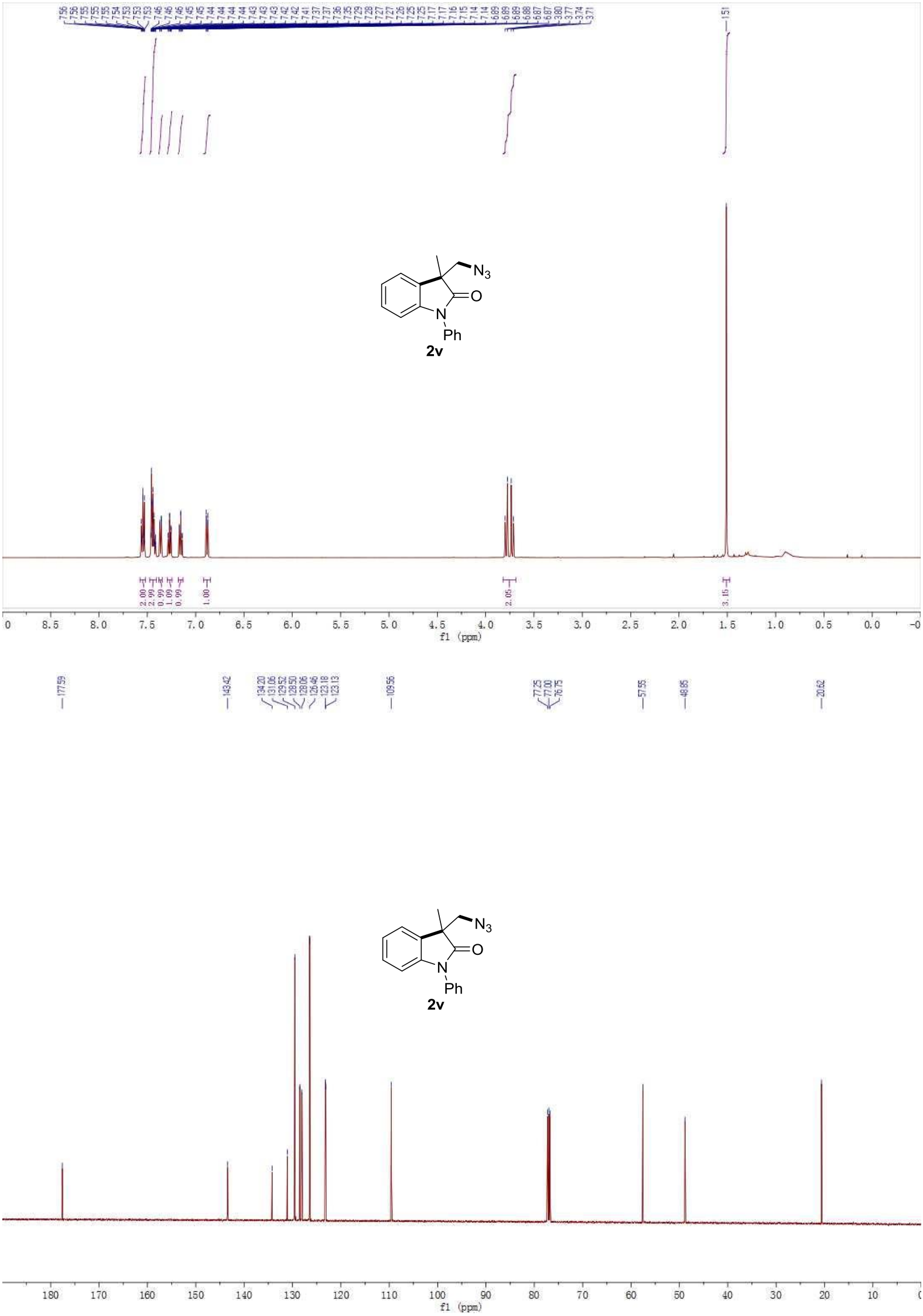
7.55
7.46
7.46
7.45
7.45
7.44
7.44
7.01
7.01
7.00
7.00
4.21
4.18
3.70
3.67
3.57
1.66
O
N
N3
1.00
2.04
2.03
1.00
1.02
1.08
3.04
3.09
f1 (ppm)

2u


171.30
136.35
135.23
133.40
126.91
126.89
126.53
122.87
122.83
119.74
108.89
77.25
77.00
76.75
62.01
48.21
29.89
27.56
O
N
N3
f1 (ppm)

2u


7.56
7.56
7.55
7.55
7.55
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7.53
7.46
7.46
7.45
7.45
7.44
7.44
7.44
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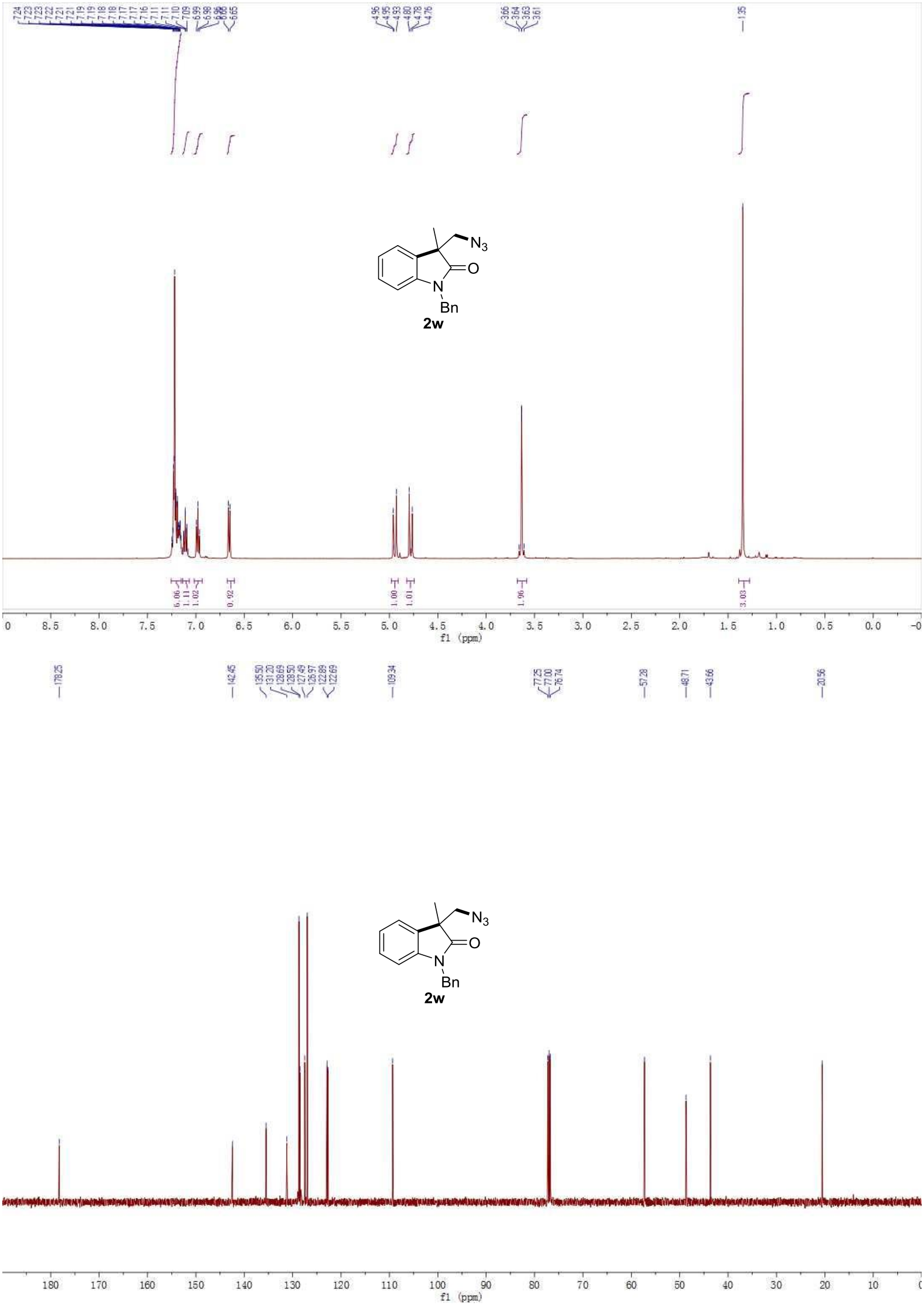
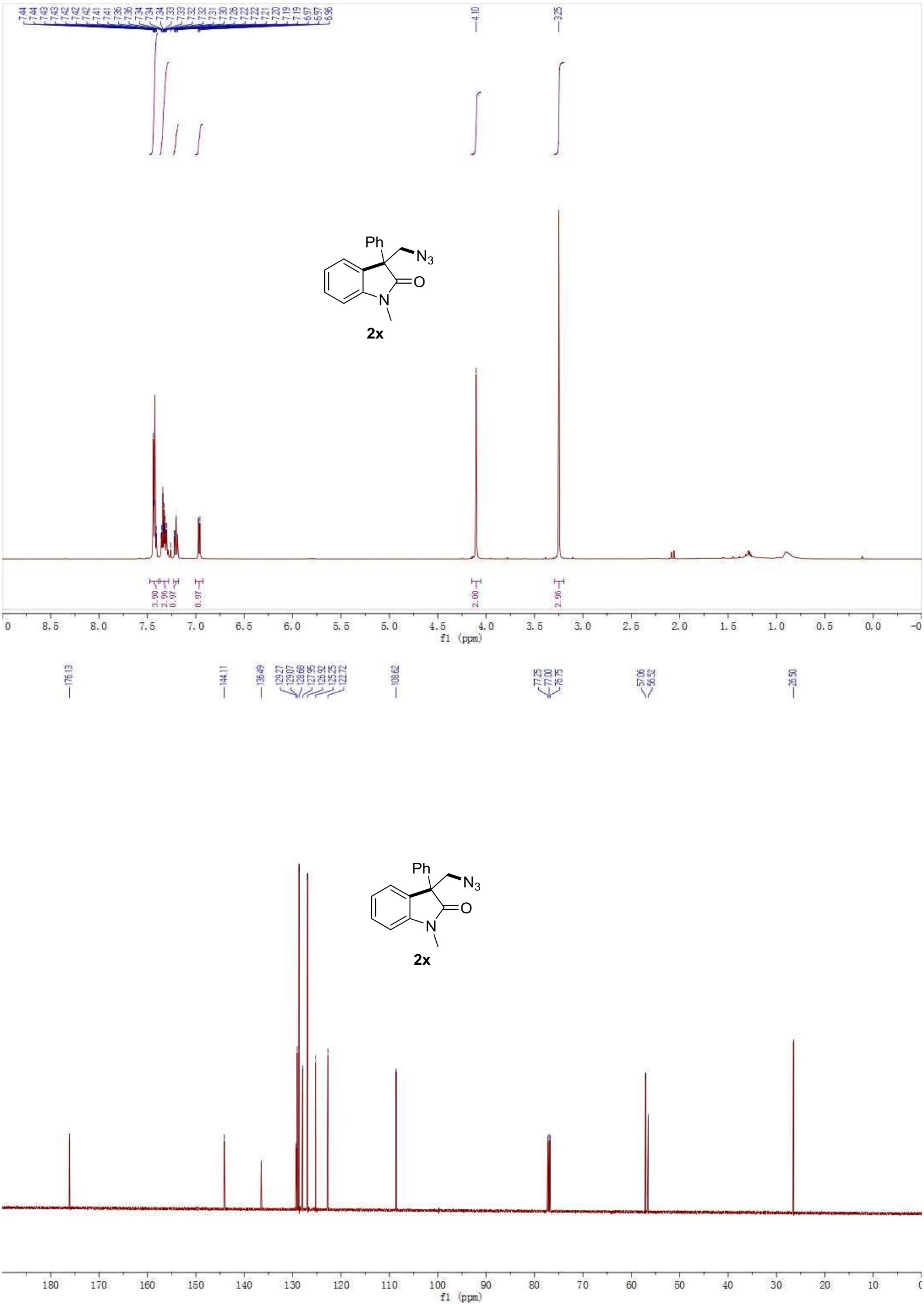
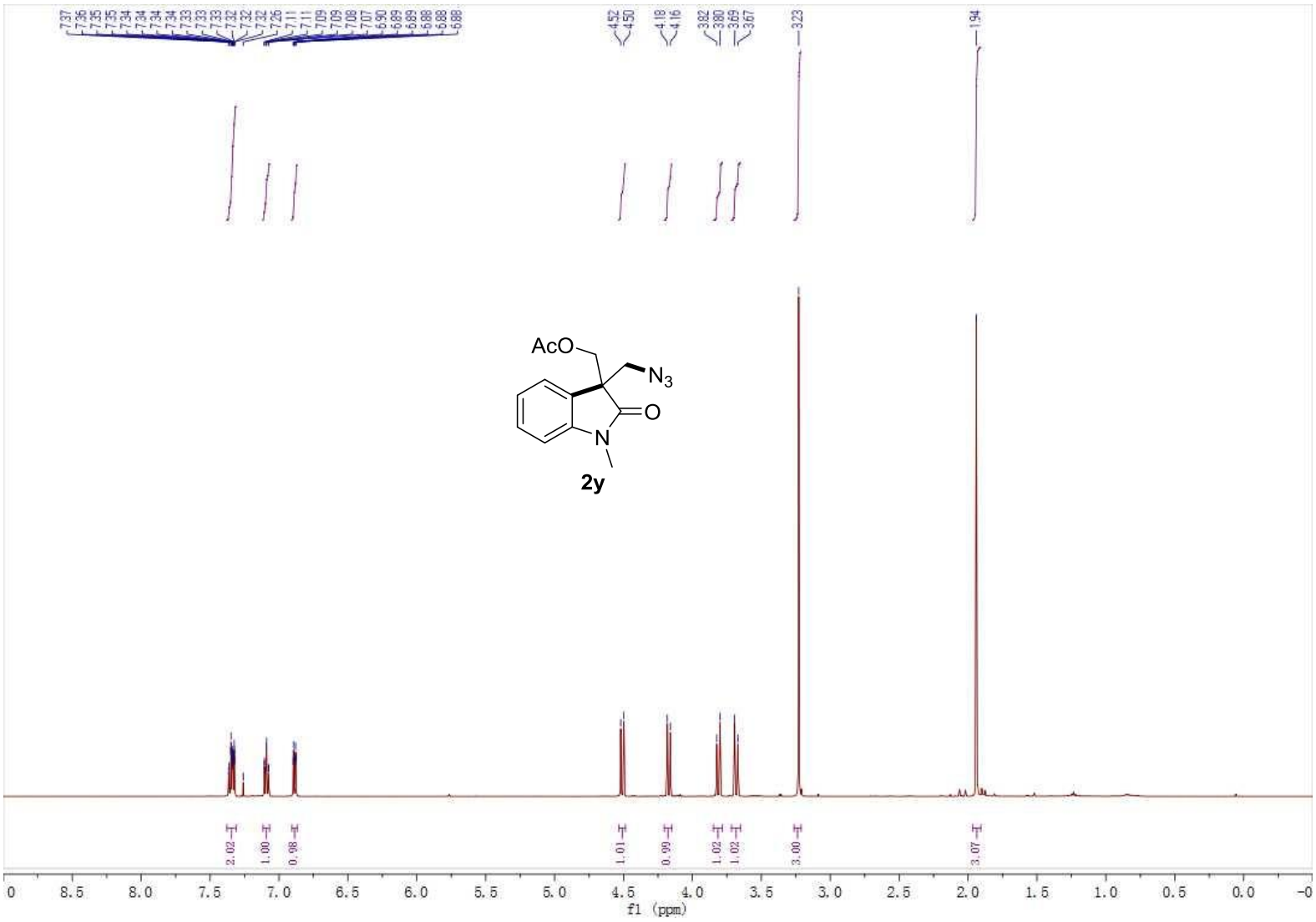
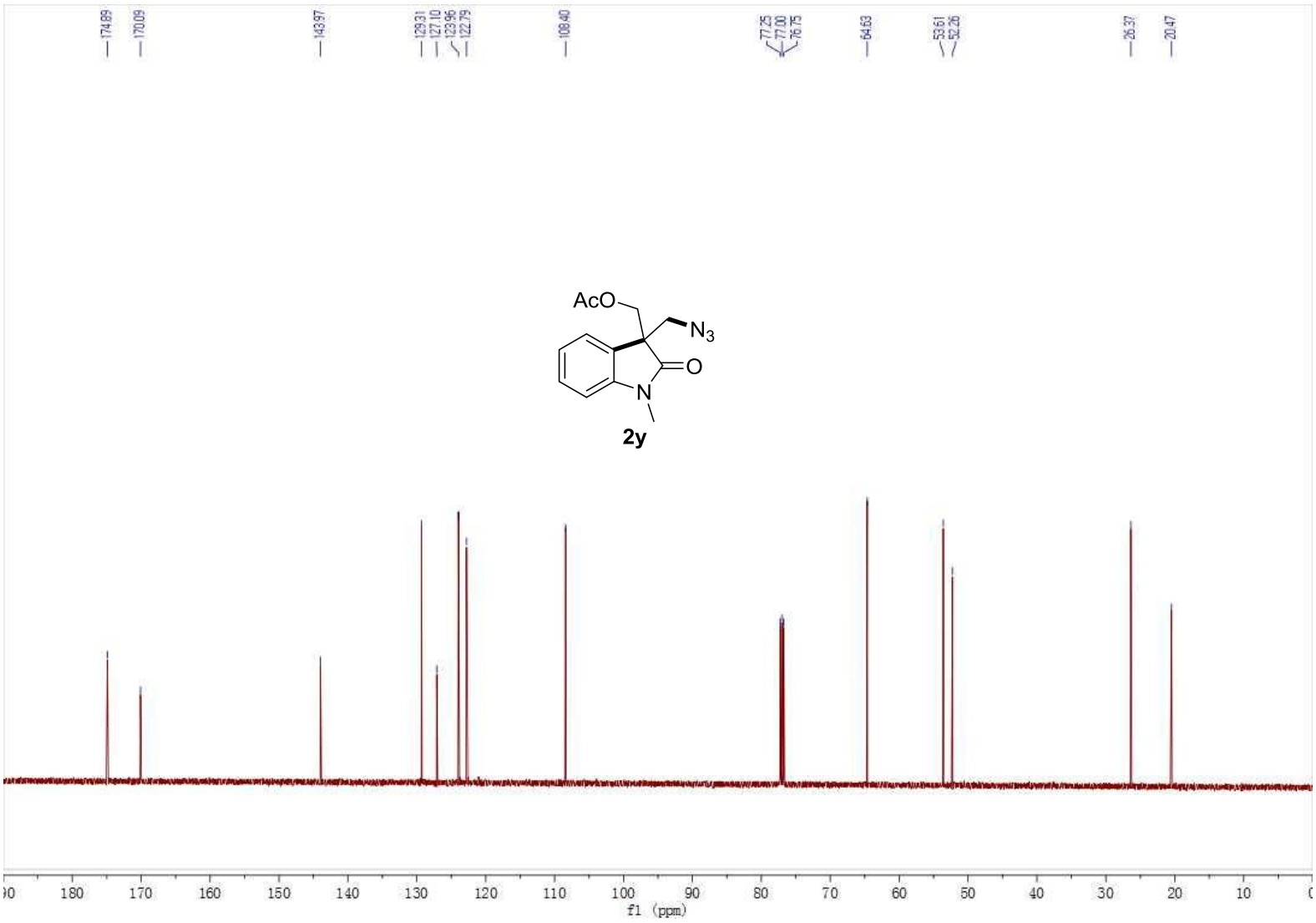
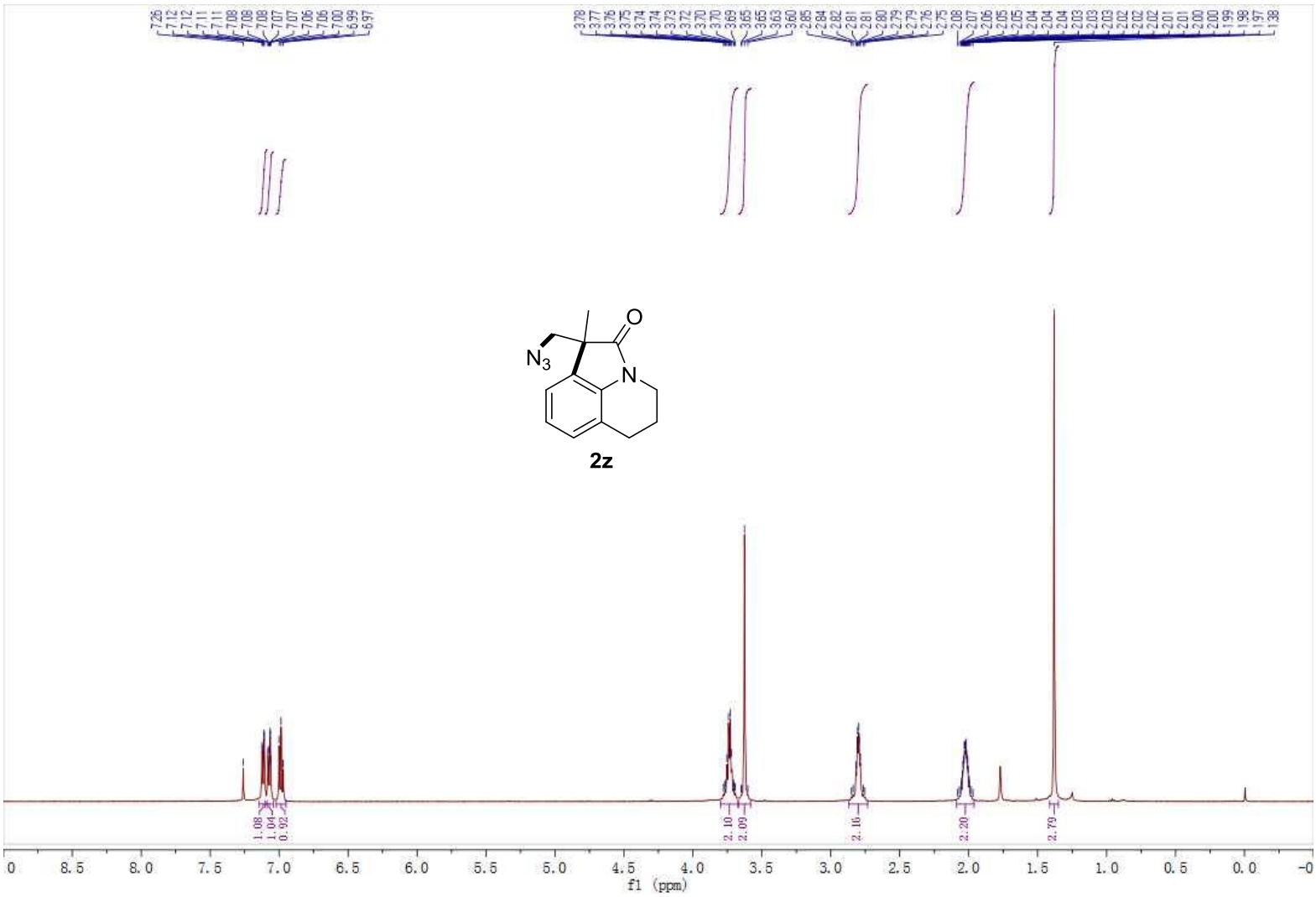
7.43
7.43
7.42
7.42
7.41
7.37
7.37
7.36
7.35
7.29
7.28
7.27
7.27
7.26
7.25
7.25
7.17
7.17
7.16
7.15
7.14
7.14
6.89
6.89
6.88
6.87
6.87
3.80
3.77
3.74
3.71
1.51
N3
O
N
Ph
2v
2.00
2.99
0.99
1.09
0.99
1.00
2.05
3.15
f1 (ppm)
177.59
143.42
134.20
131.06
129.52
128.50
128.06
126.46
123.18
123.13
109.56
77.25
77.00
76.75
57.55
48.85
20.62
N3
O
N
Ph
2v
f1 (ppm)

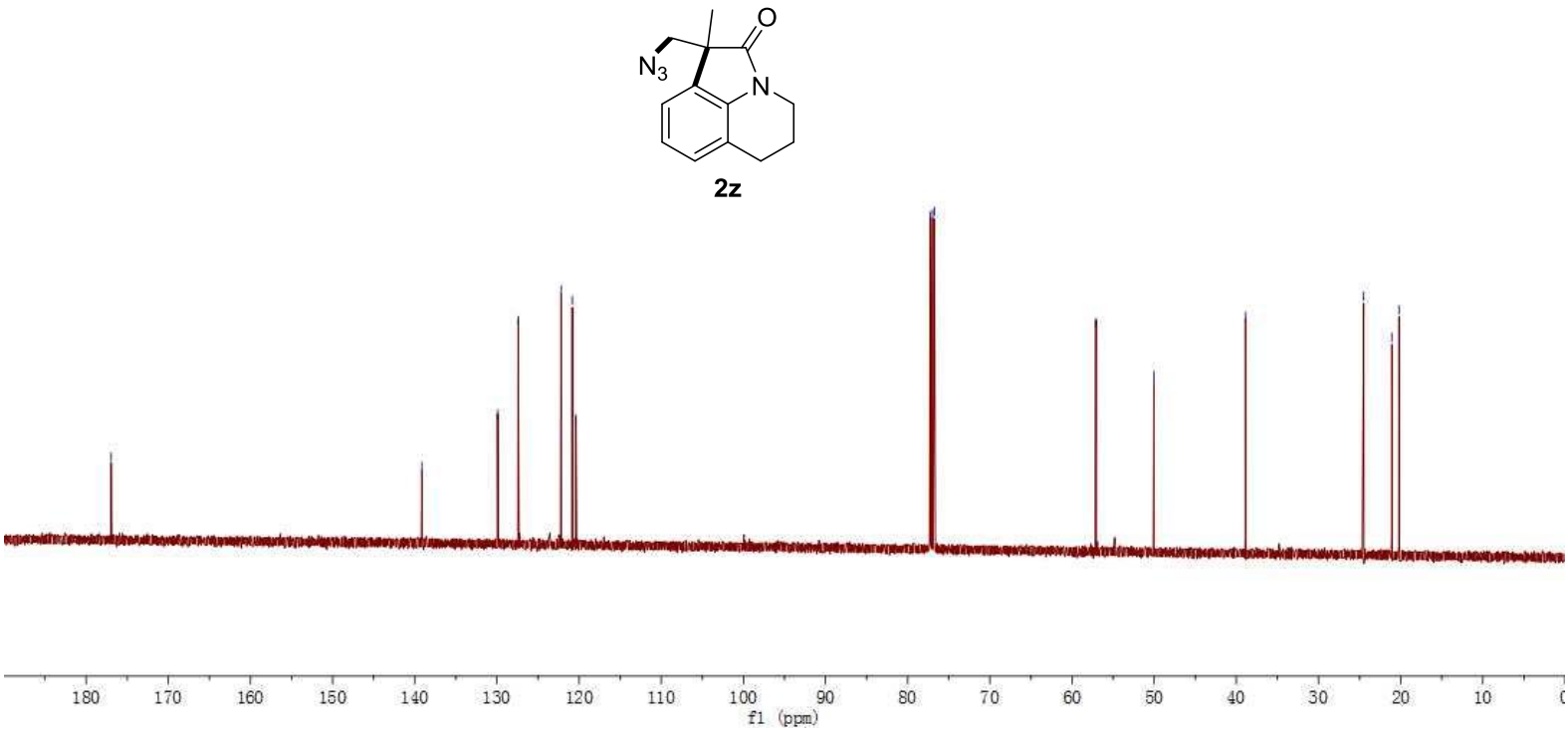

N3
O
N
Bn
2w
f1 (ppm)

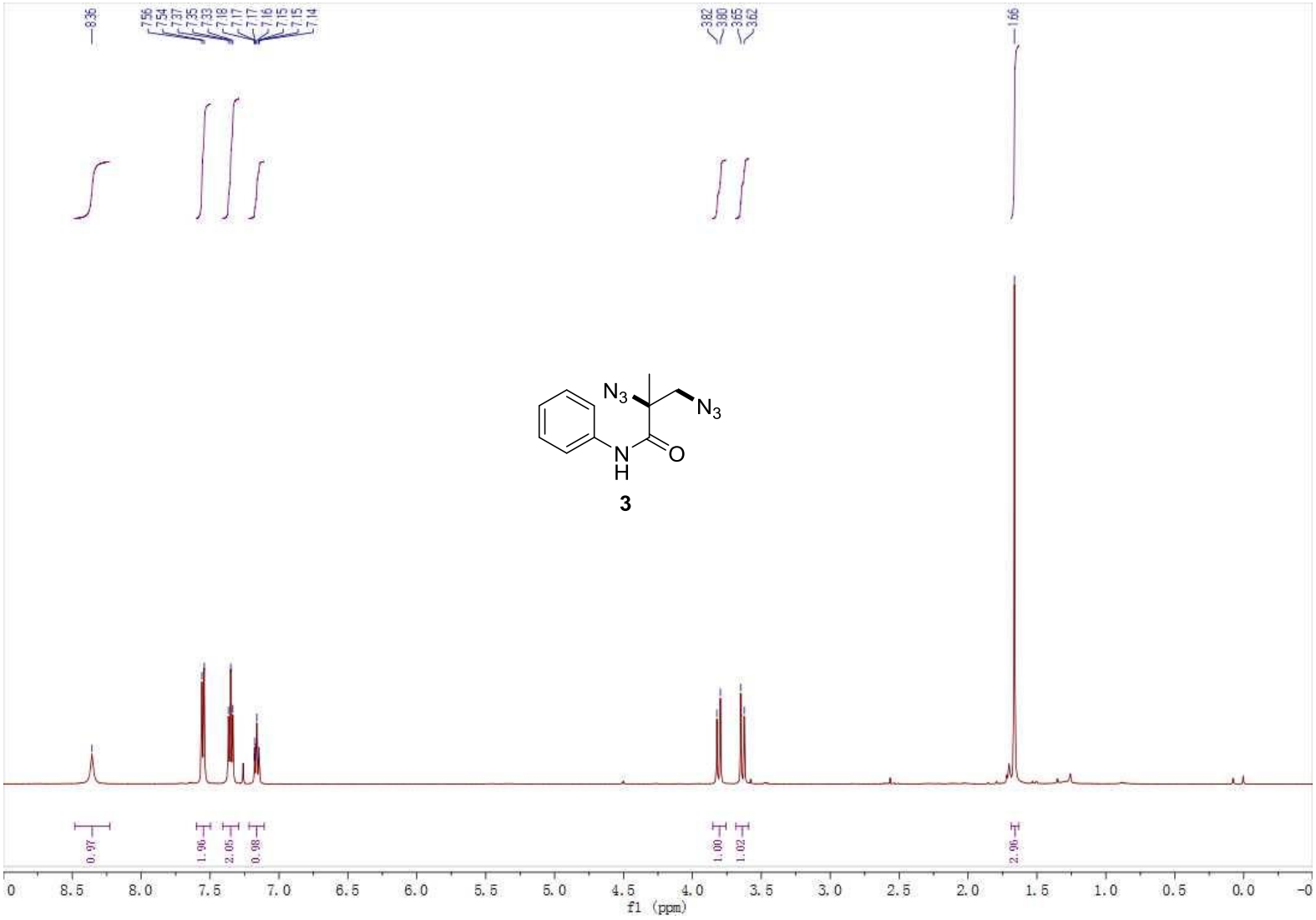

Ph
N3
O
N
2x
f1 (ppm)

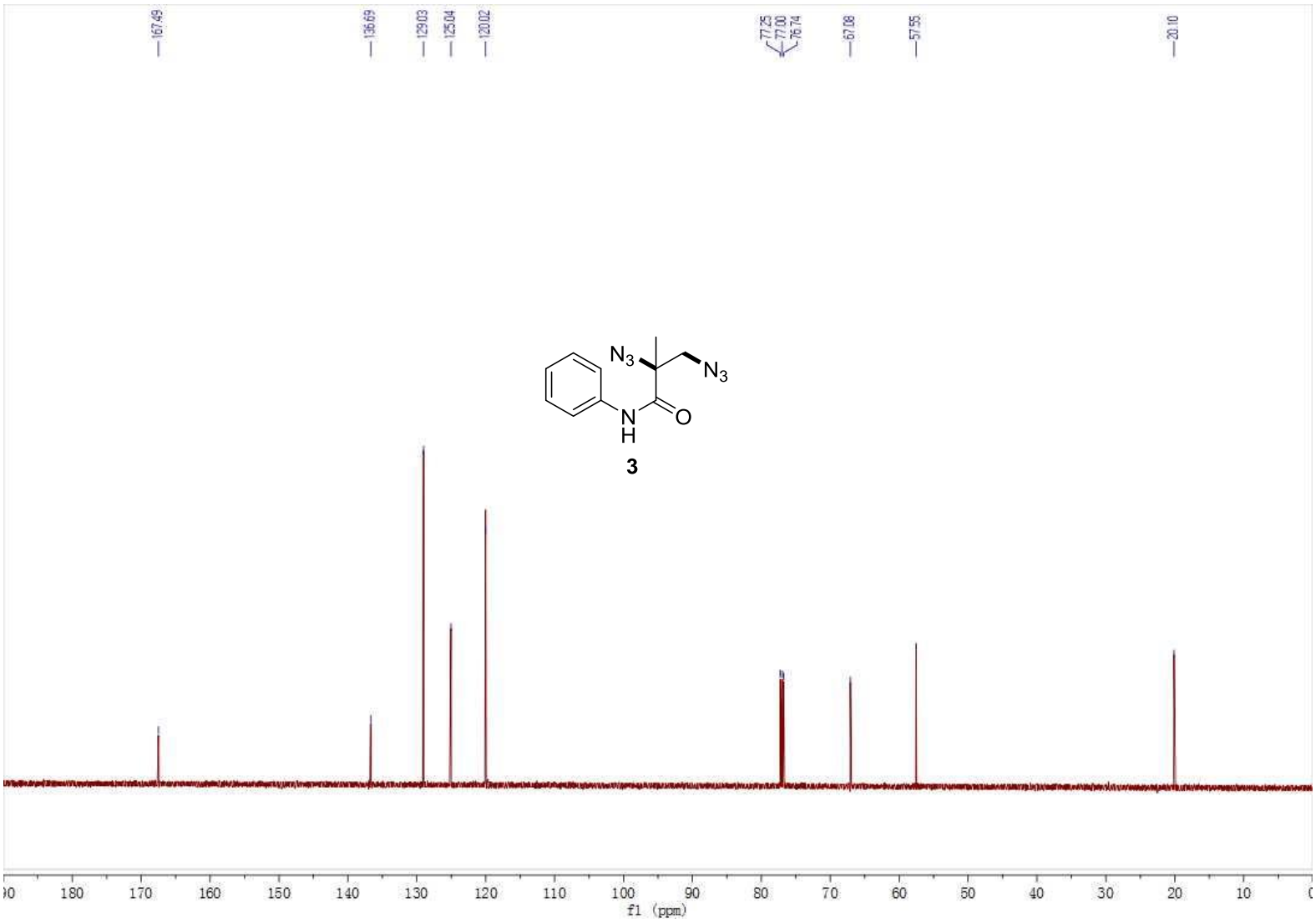

AcO
N3
O
N
2y
f1 (ppm)

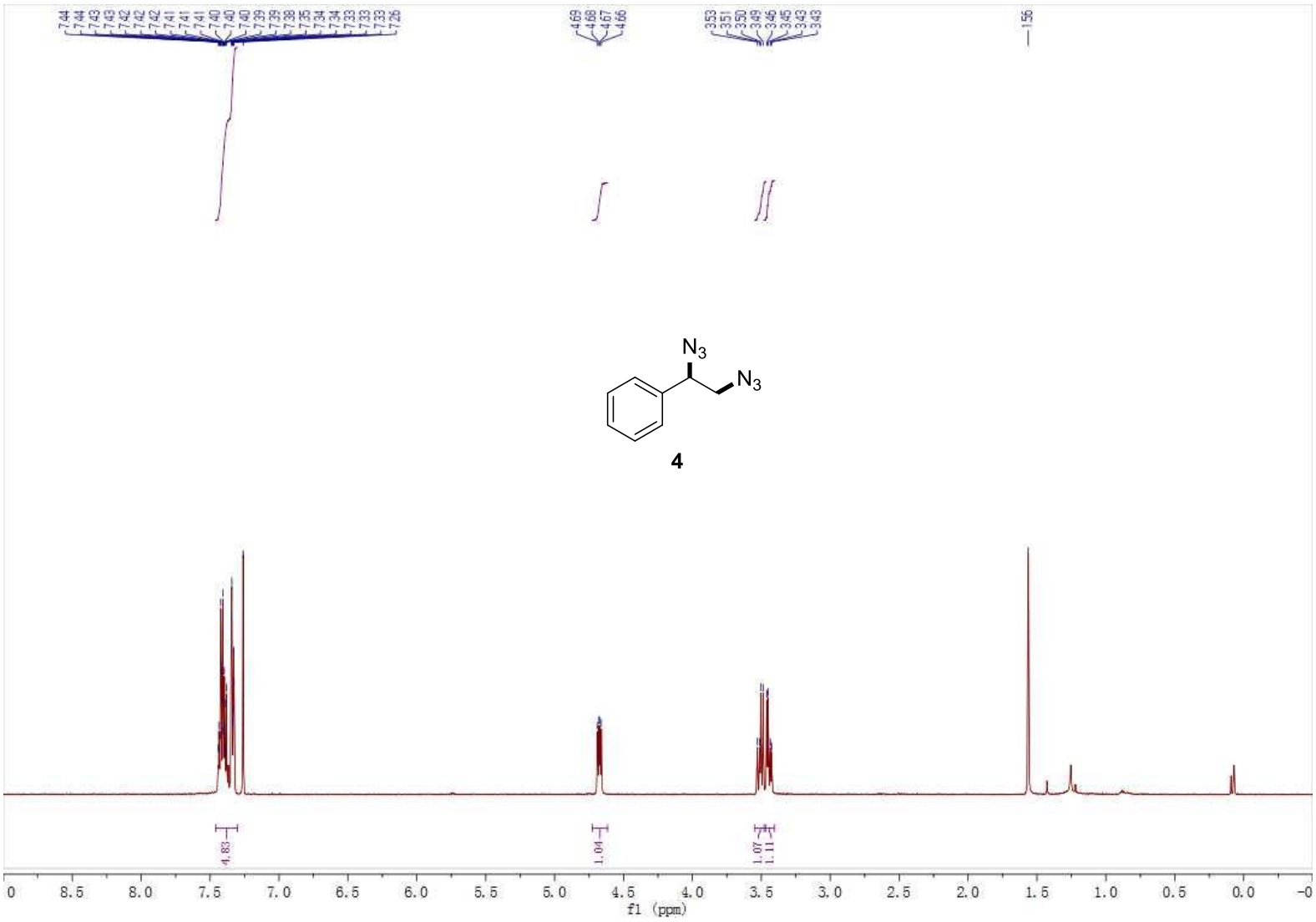

AcO
N3
O
N
2y
f1 (ppm)

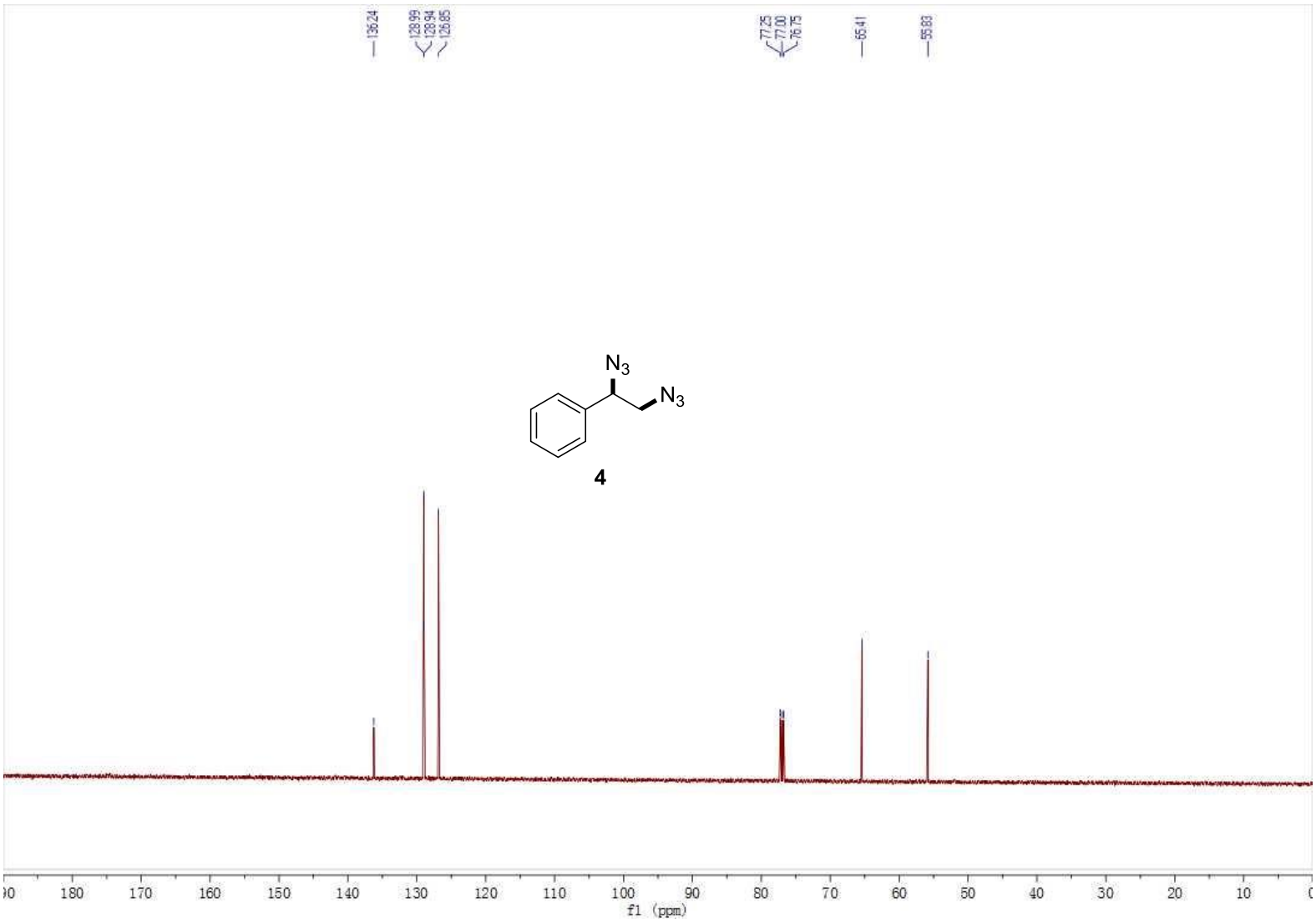

2z
f1 (ppm)

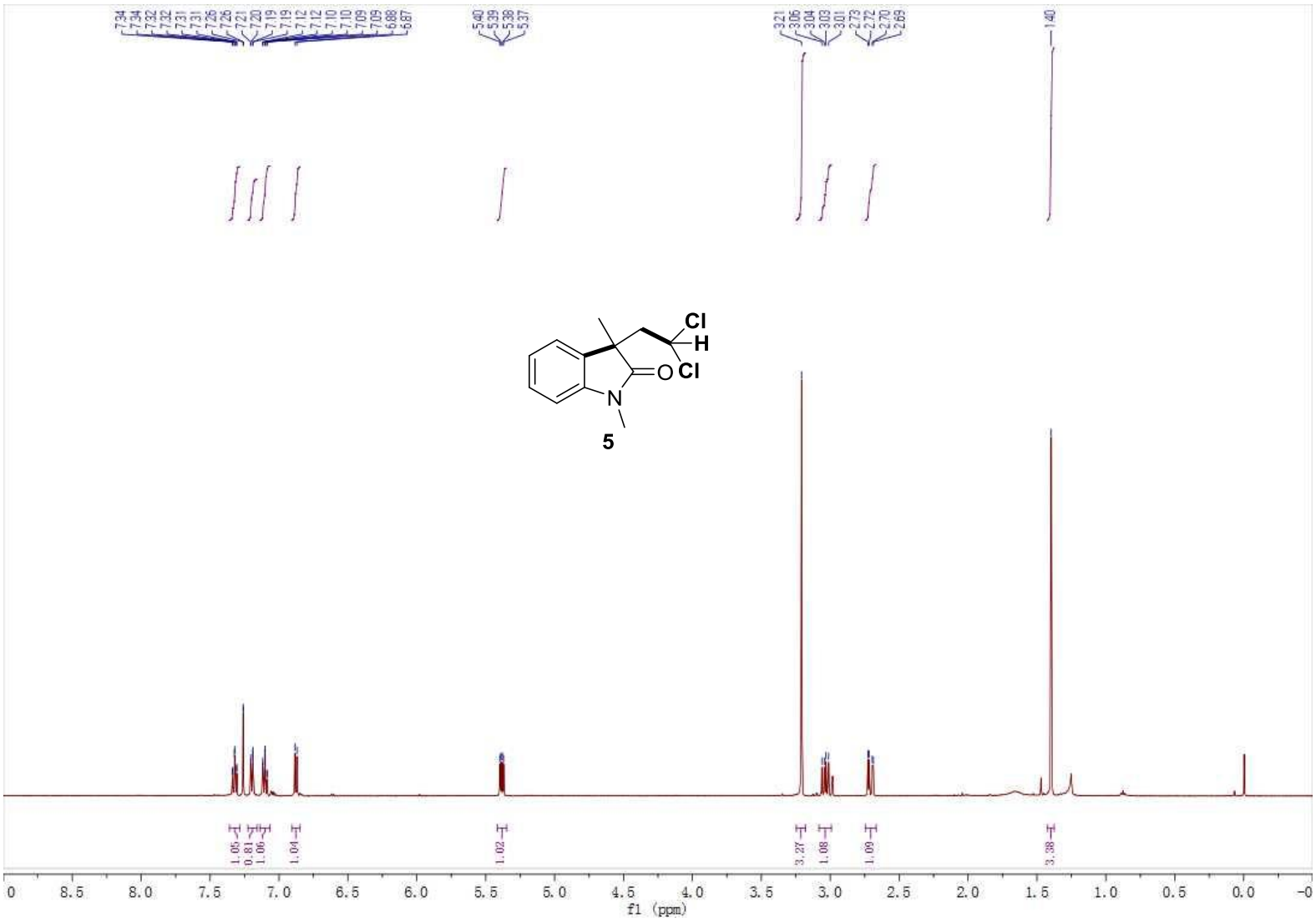

2z
f1 (ppm)

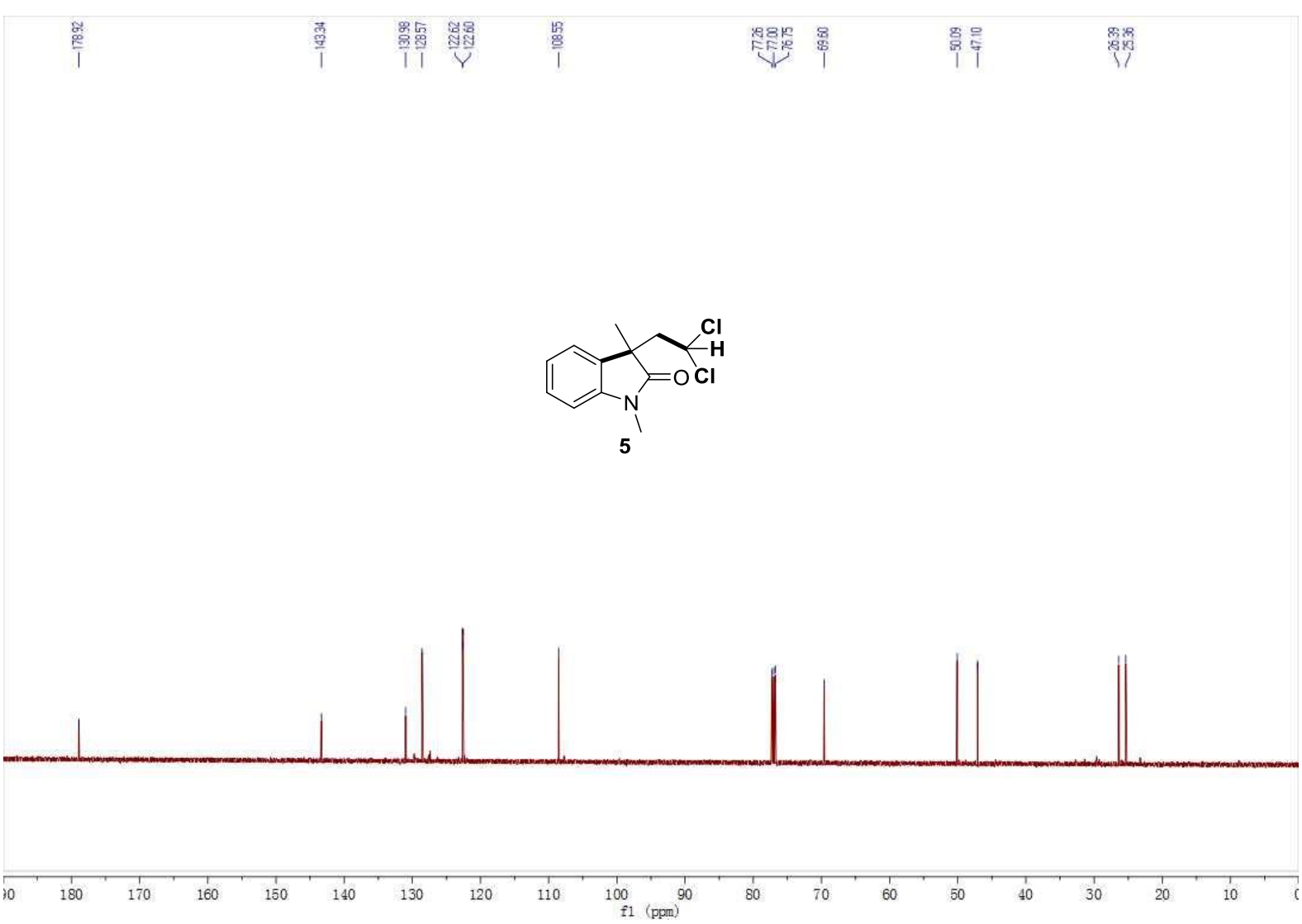

8.36
7.56
7.54
7.37
7.35
7.33
7.18
7.17
7.17
7.16
7.15
7.15
7.14
3.82
3.80
3.65
3.62
1.66
N3
N3
N
H
O
3
0.97
1.96
2.05
0.98
1.00
1.02
2.96
f1 (ppm)


167.49
136.69
129.03
125.04
120.02
77.25
77.00
76.74
67.08
57.55
20.10
N3
N3
N
H
O
3
f1 (ppm)


7.44
7.44
7.43
7.43
7.42
7.42
7.42
7.41
7.41
7.41
7.40
7.40
7.40
7.39
7.39
7.38
7.35
7.34
7.34
7.33
7.33
7.26
4.69
4.68
4.67
4.66
3.53
3.51
3.50
3.49
3.46
3.45
3.43
3.43
1.56
N3
N3
4
4.83
1.04
1.07
1.11
f1 (ppm)


136.24
128.99
128.94
126.85
77.25
77.00
76.75
65.41
55.83
N3
N3
4
f1 (ppm)


7.34
7.34
7.32
7.32
7.31
7.31
7.26
7.26
7.21
7.20
7.19
7.19
7.12
7.12
7.10
7.10
7.09
7.09
6.88
6.87
5.40
5.39
5.38
5.37
3.21
3.06
3.04
3.03
3.01
2.73
2.72
2.70
2.69
1.40
Cl
H
O
Cl
N
5
1.05
0.81
1.06
1.04
1.02
3.27
1.08
1.09
3.38
f1 (ppm)


178.92
143.34
130.98
128.57
122.62
122.60
108.55
77.26
77.00
76.75
69.60
50.09
47.10
26.39
25.36
Cl
H
O
Cl
N
5
f1 (ppm)