Electronic Supplementary Material (ESI) for Chemical Science.

Copper-Catalyzed Diastereoselective Aerobic Intramolecular Dehydrogenative Coupling of Hydrazones via sp^3 C-H Functionalization

Xuesong Wu, Mian Wang, Guangwu Zhang, Yan Zhao, Jianyi Wang,* and Haibo Ge*

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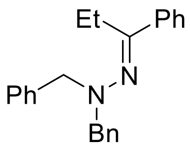
General Information

^{1}H and ^{13}C NMR spectra were recorded on a Bruker 500 MHz NMR Fourier transform spectrometer (500 MHz and 125 MHz, respectively) using tetramethylsilane as an internal reference, and chemical shifts (*δ*) and coupling constants (*J*) were expressed in ppm and Hz, respectively. Infrared spectra were obtained using a Thermo Nicolet IR 330 spectrometer. Mass (MS) analysis were abtained using Agilent 1100 series LC/MSD system with Electrospray Ionization (ESI). All the solvents and commercially available reagents were purchased from commercial sources and used directly. Hydrazone **1h**, **1k**, **1m** and **1n** were prepared according to literature procedures.[1] 1,4-Dioxaspiro[4.5]decan-8-one was prepared from cyclohexane-1,4-dione according to literature procedures.[2]

The relative configuration of **2a-g**, **2i-m**, **2o-p**, **5a**, **5w1**, **5y1**, **5aa1** and **5ab** was assigned by NOESY analysis, and that of the rest of products was assigned by analogy.

Structures of Starting Materials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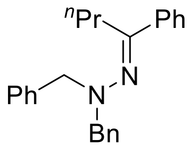
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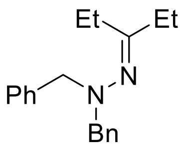
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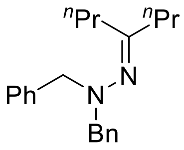
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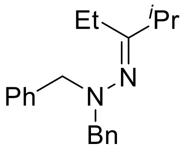
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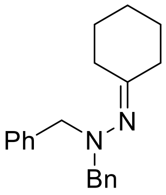
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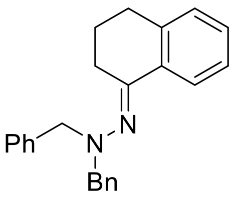
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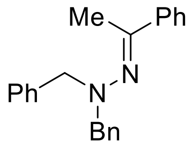
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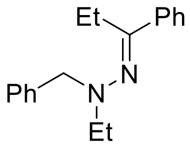
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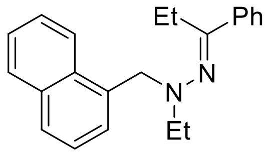
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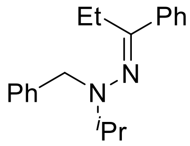
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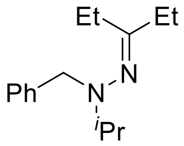
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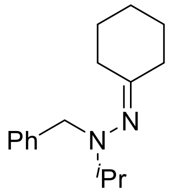
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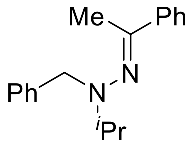
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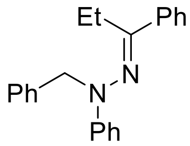
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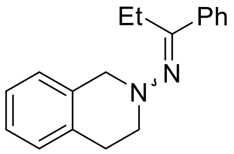
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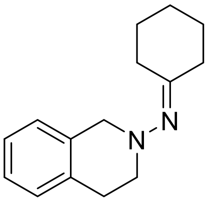
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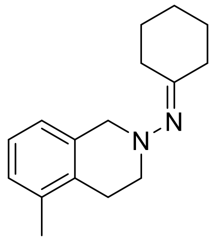
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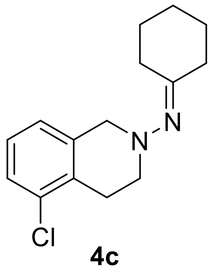
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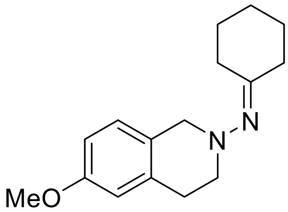
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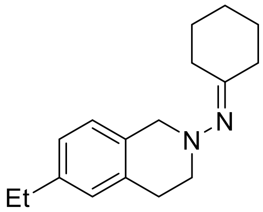
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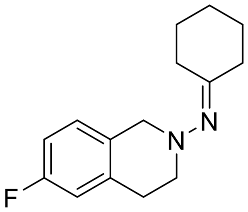
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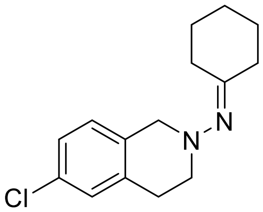
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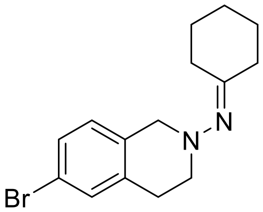
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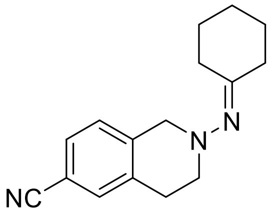
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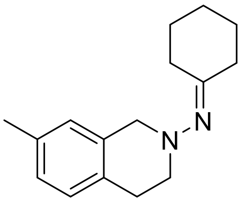
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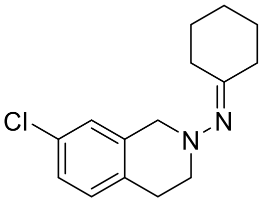
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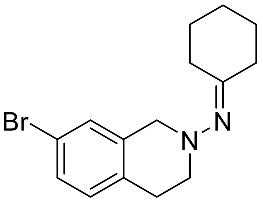
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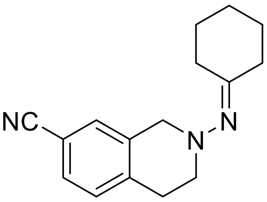

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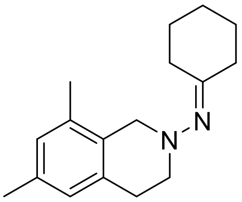

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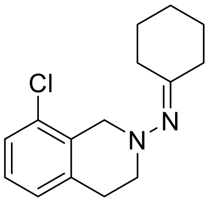

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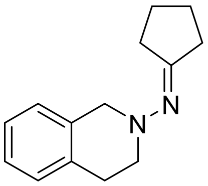

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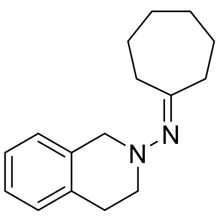

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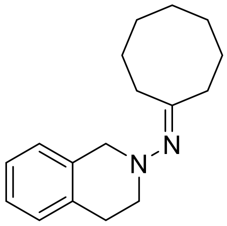

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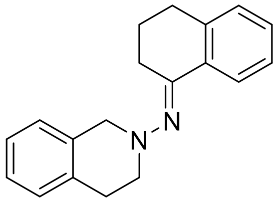

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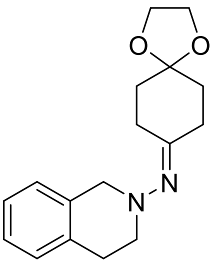

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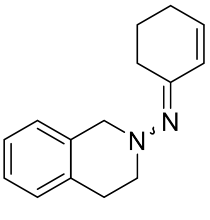

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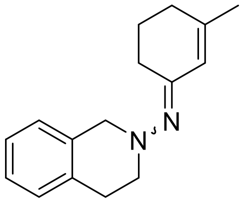

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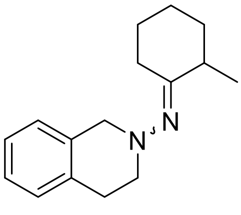

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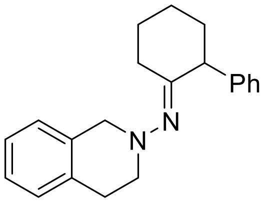

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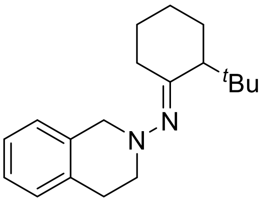

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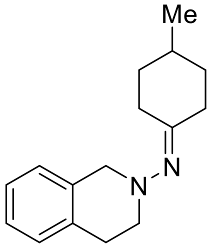

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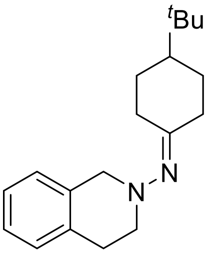

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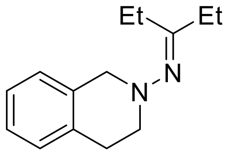

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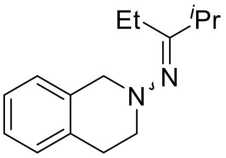
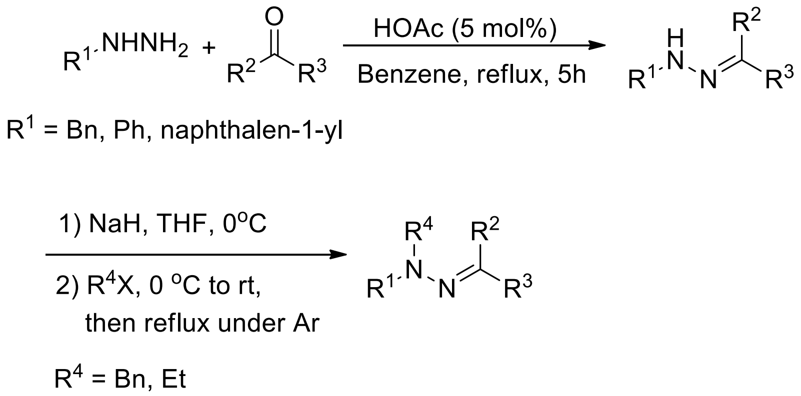


4ac

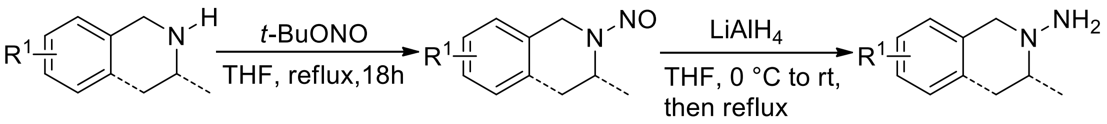
General Procedure for the Preparation of *N,N*-Disubstituted Hydrazones 1a-g, 1i-j, 1o

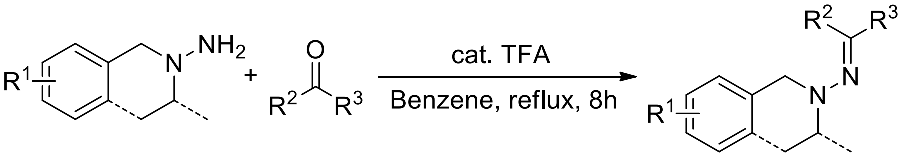


A 100 mL three-necked flask was charged with 30 mL anhydrous benzene, ketone (10 mmol), hydrazine (15 mmol) and acetic acid (28.6 µL, 0.50 mmol) under Ar. The reaction mixture was then refluxed for 5 h. After removal of solvent, the hydrazone, which was usually obtained in nearly quantitative yield, was used directly for the next step without further purification.

To a suspension of NaH (95%, 1.2 g, 48 mmol) in dry THF (20 mL), the solution of hydrazone (5.0 mmol in 5.0 mL dry THF) was added slowly at 0 °C under Ar. The mixture was stirred for 15 min, and then benzyl bromide or alkyl iodide (7.5 mmol) was added dropwise. After stirring at room temperature for 1.5 h, the reaction mixture was refluxed for 8 h. The reaction mixture was cooled to the room temperature, and then the solvent was removed under reduced pressure. The residue was slowly diluted with water (15 mL), extracted with ether (25 mL x 3), and dried over Na_2SO_4. After removal of the solvent, the residue was purified by flash chromatography column on silica gel (gradient eluent of EtOAc/hexanes: 1:100 ~ 1:20, v/v) to yield the product **1** as a yellow oil.

General Procedure for the Preparation of *N*,*N*-Disubstituted Hydrazones 1l, 1p, 4a-h, 4j-l, 4n-z, 4aa, 4ab, 4ac



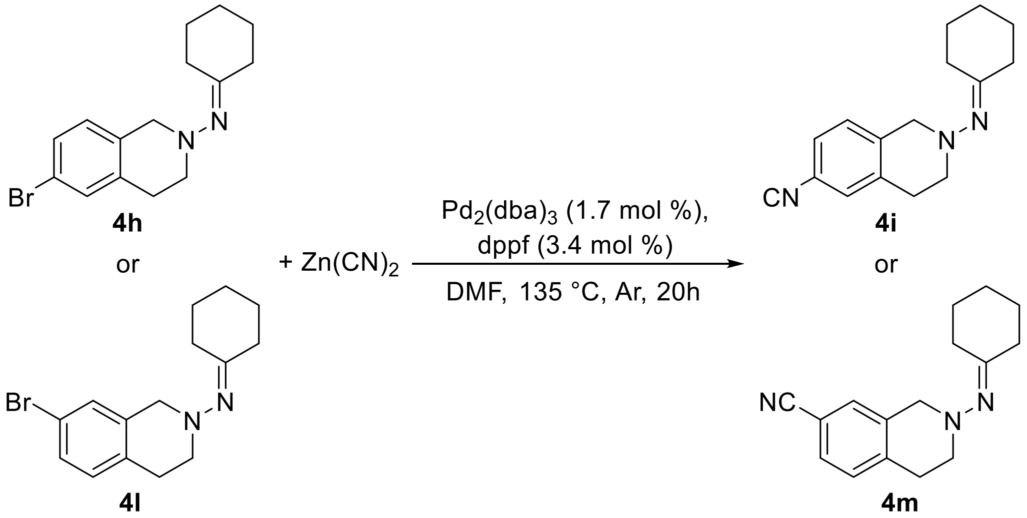


To a solution of 1,2,3,4-tetrahydroisoquinoline or *N*-benzylpropan-2-amine (6.0 mmol) in THF (4.0 mL) was added *tert*-butyl nitrite (1.07 mL, 0.93 g, 9.0 mmol) under Ar. The mixture was heated under reflux for 20 h. Then the solvent and the excess of the *tert*-butyl nitrite were removed in vacuo. The residual oil was dissolved in THF (3.0 mL), and then added dropwise to an ice-cooled, stirred suspension of $LiAlH_4$ (0.32 g, 8.4 mmol) in THF (9.0 mL). After the addition, the suspension was stirred at room temperature for 1 h and then refluxed for 2 h. After cooled to 0 °C, the reaction mixture was added water (1.3 mL) dropwise, the precipitated salts were filtered and washed with THF. The combined filtrate was dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give crude hydrazine as a yellow oil, which was used directly for the next step without further purification.

To a solution of crude hydrazine (5.0 mmol) in anhydrous benzene (6.0 mL) were added ketone (5.0 mmol) and one drop trifluoroacetic acid (no trifluoroacetic acid for **4u** and **4v**) under Ar. The mixture was heated to reflux with Dean-Stark apparatus for 8-16h, and then cooled to room temperature, dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel, eluting with

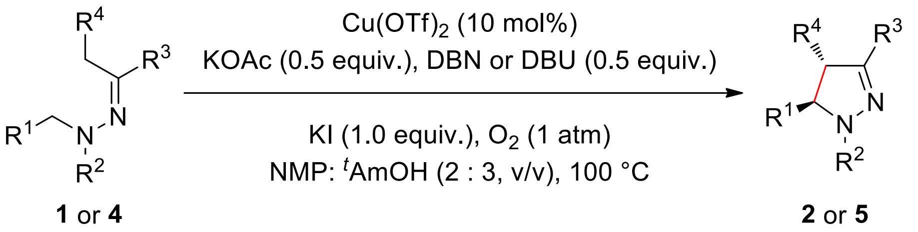
EtOAc/ Et_3N /hexane (1:1:100, v/v), to afford corresponding *N*,*N*-disubstituted hydrazone.

Procedure for the Preparation of Hydrazines 4i and 4m



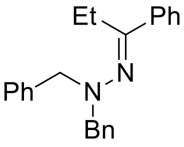
A 50 mL Schlenk tube was charged with $Pd_2(dba)_3$ (9.2 mg, 0.010 mmol), dppf (11.0 mg, 0.020 mmol), and $Zn(CN)_2$ (84.6 mg, 0.72 mmol). Then hydrazine **4h** or **4l** (0.60 mmol) in DMF (6.0 mL) was added, and the vial was degased and filled with argon. After stirring at 135 °C for 20 h, the reaction mixture was cooled to room temperature, diluted with EtOAc (30 mL) and filtered through a pad of Celite. The filtrate was washed with water (3 × 30 mL) to remove the DMF. The organic phase was dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel, eluting with EtOAc/ Et_3N /hexane (1:1:100, v/v), to afford hydrazine **4i** or **4m**.

General Procedure for the Dehydrogenative Cyclization Reactions



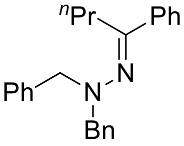
A 50 mL Schlenk tube was charged with hydrazone **1** or **4** (0.30 mmol), $Cu(OTf)_2$ (10.9 mg, 0.030 mmol, 10 mol %), KOAc (14.7 mg, 0.15 mmol), DBN (18.6 mg, 0.15 mmol) or DBU (22.8 mg, 0.15 mmol), KI (49.8 mg, 0.30 mmol), NMP (0.80 mL) and ^{t}AmOH (1.20 mL). The vial was evacuated and filled with O_2 (1 atm), and stirred rigorously at 100 °C for 2-12h (monitored by GC and TLC). The mixture was cooled to room temperature, diluted with EtOAc (20 mL). The organic layer was washed with brine (2 × 10 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel, eluting with EtOAc/hexane (1:100 ~ 1:2, v/v), to afford corresponding product **2** or **5**.

Analytical Data for Starting Materials



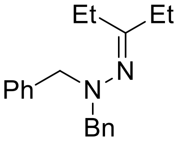
1a

Compound **1a**, yellow solid, yield: 79% (two steps from ketone). ^{1}H NMR (500 MHz, CDCl$_3$, a mixture of (Z/E) isomers in ratio 93:7, the minor one is marked with an *) δ 0.55 (t, J = 7.6 Hz, 3H), 2.61 (q, J = 7.6 Hz, 2H), 3.92 (s, 4H), 7.19-7.24 (m, 2H), 7.27-7.33 (m, 7H), 7.37 (d, J = 7.4 Hz, 4H), 7.42 (d, J = 7.2 Hz, 2H); 0.97* (t, J = 7.5 Hz, 3H), 2.47* (q, J = 7.5 Hz, 1H), 3.70* (s, 4H), 7.10-7.45* (m, 15H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 11.0, 22.5, 62.6, 127.1, 127.2, 128.2, 128.4, 129.3, 129.8, 137.9, 138.9, 174.4; IR (neat) ν 2968, 2935, 2828, 1612, 1494, 1453, 1318, 1028, 950, 737, 696; Ms (ESI): m/z = 329.2 [M+H]$^+$.



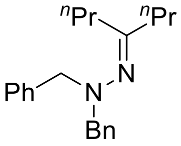
1b

Compound **1b**, yellow solid, yield: 81% (two steps from ketone). ^{1}H NMR (500 MHz, CDCl$_3$, a mixture of (Z/E) isomers in ratio 89:11, the minor one is marked with an *) δ 0.65 (t, J = 7.4 Hz, 3H), 0.92-1.01 (m, 2H), 2.56-2.61 (m, 2H), 3.91 (s, 4H), 7.18-7.24 (m, 3H), 7.27-7.32 (m, 6H), 7.35-7.42 (m, 6H); 0.75* (t, J = 7.4 Hz, 3H), 0.97-1.02* (m, 2H), 2.42-2.46* (m, 2H), 3.69* (s, 4H), 7.15-7.55* (m, 15H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 14.1, 19.9, 31.3, 62.5, 127.0, 127.1, 128.2, 128.4, 129.2, 129.8, 138.3, 128.9, 173.3; 13.5*, 19.8*, 30.7*, 61.6*, 126.9*, 127.0*, 128.0*, 128.5*, 128.7*, 129.7*, 138.0*, 138.8*, 173.3*; IR (neat) ν 2959, 2930, 2871, 1603, 1494, 1453, 1317, 1028, 947, 751, 696; Ms (ESI): m/z = 343.2 [M+H]$^+$.



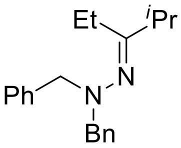
1c

Compound **1c**, colorless oil, yield: 63% (two steps from ketone). ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.58 (t, J = 7.7 Hz, 3H), 0.90 (t, J = 7.5 Hz, 3H), 2.08 (q, J = 7.6 Hz, 2H), 2.15 (q, J = 7.7 Hz, 2H), 3.77 (s, 4H), 7.18-7.22 (m, 2H), 7.24-7.28 (m, 4H), 7.31 (d, J = 7.5 Hz, 4H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 10.3, 11.8, 23.4, 28.4, 62.4, 126.9, 128.1, 129.8, 139.0, 178.8; IR (neat) ν 2969, 2934, 2827, 1635, 1494, 1454, 1374, 1028, 946, 745, 698; Ms (ESI): m/z = 281.2 [M+H]$^+$.



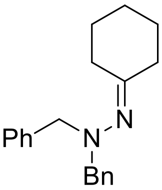
1d

Compound **1d**, colorless oil, yield: 65% (two steps from ketone). ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.71-0.77 (m, 6H), 0.98-1.08 (m, 2H), 1.29-1.38 (m, 2H), 2.03-2.07 (m, 2H), 2.15-2.20 (m, 2H), 3.76 (s, 4H), 7.17-7.22 (m, 2H), 7.24-7.29 (m, 4H), 7.32 (d, J = 7.7 Hz, 4H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 13.9, 14.5, 19.4, 20.6, 32.6, 37.9, 62.4, 127.0, 128.1, 129.7, 139.0, 176.9; IR (neat) ν 2959, 2930, 2871, 1634, 1494, 1453, 1348, 1028, 746, 697; Ms (ESI): m/z = 309.2 [M+H]$^+$.



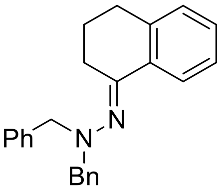
1e

Compound **1e**, colorless oil, yield: 60% (two steps from ketone). ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.37 (d, J = 6.6 Hz, 6H), 0.98 (t, J = 7.8 Hz, 3H), 1.98 (q, J = 7.8 Hz, 2H), 3.50-3.59 (m, 1H), 3.77 (s, 4H), 7.17-7.22 (m, 2H), 7.24-7.28 (m, 4H), 7.31 (d, J = 7.6 Hz, 4H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 12.9, 18.9, 23.7, 29.5, 62.8, 127.0, 128.1, 130.1, 139.1, 181.7; IR (neat) ν 2968, 2933, 2826, 1633, 1495, 1454, 1362, 1028, 946, 745, 698; Ms (ESI): m/z = 295.2 [M+H]$^+$.



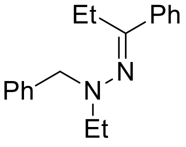
1f

Compound **1f**, colorless oil, yield: 71% (two steps from ketone). ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.93-0.99 (m, 2H), 1.30-1.36 (m, 2H), 1.38-1.44 (m, 2H), 2.06-2.10 (m, 2H), 2.15-2.20 (m, 2H), 3.81 (s, 4H), 7.17-7.22 (m, 2H), 7.24-7.28 (m, 4H), 7.31 (d, J = 7.6 Hz, 4H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 25.9, 26.1, 27.4, 29.6, 35.7, 62.4, 126.9, 128.1, 129.8, 139.0, 176.0; IR (neat) ν 2930, 2856, 1639, 1494, 1452, 1347, 1134, 1028, 745, 697; Ms (ESI): m/z = 293.2 [M+H]$^+$.



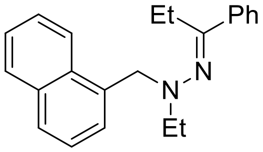
1g

Compound **1g**, yellow solid, yield: 83% (two steps from ketone). ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.57-1.65 (m, 2H), 2.64-2.71 (m, 4H), 3.75-4.05 (m, 4H), 7.05 (d, J = 7.4 Hz, 1H), 7.10-7.30 (m, 8H), 7.33-7.37 (m, 4H), 8.14-8.18 (m, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 22.4, 28.1, 29.9, 61.8, 125.6, 126.2, 126.9, 128.2, 128.6, 129.4, 129.7, 133.0, 139.1, 140.3, 165.9; IR (neat) ν 2933, 2864, 2832, 1616, 1494, 1452, 1349, 1324, 1300, 1027, 952, 752, 730, 697; Ms (ESI): *m*/*z* = 341.2 $[M+H]^+$.



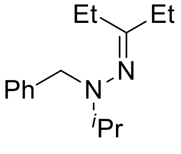
1i

Compound **1i**, yellow oil, yield: 67% (two steps from ketone). ^{1}H NMR (500 MHz, $CDCl_3$, a mixture of (Z/E) isomers in ratio 94:6, the minor one is marked with an *) δ 0.79 (t, *J* = 7.6 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H), 2.77-2.86 (m, 4H), 3.83 (s, 2H), 7.19-7.24 (m, 1H), 7.26-7.37 (m, 7H), 7.56-7.59 (m, 2H); 0.96* (t, *J* = 7.1 Hz, 3H), 1.08* (t, *J* = 7.0 Hz, 3H), 2.53-2.65* (m, 4H), 3.59* (s, 2H), 6.90-6.94* (m, 2H), 7.13-7.46* (m, 7H), 7.48-7.53* (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.3, 13.5, 22.6, 52.3, 63.1, 127.0, 127.2, 128.2, 128.4, 129.3, 129.8, 138.0, 138.9, 173.8; IR (neat) *v* 2970, 2934, 2828, 1611, 1497, 1445, 1378, 1112, 1028, 916, 736, 695; Ms (ESI): *m*/*z* = 267.2 $[M+H]^+$.



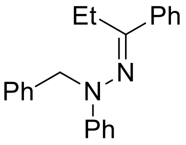
1j

Compound **1j**, yellow oil, yield: 64% (two steps from ketone). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.33 (t, *J* = 7.6 Hz, 3H), 1.10 (t, *J* = 7.2 Hz, 3H), 2.54 (q, *J* = 7.6 Hz, 2H), 2.96 (q, *J* = 7.2 Hz, 2H), 4.30 (s, 2H), 7.26-7.33 (m, 3H), 7.34-7.39 (m, 1H), 7.43-7.53 (m, 5H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 8.34 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.9, 13.5, 22.5, 53.0, 60.8, 124.7, 125.3, 125.5, 125.7, 127.2, 127.9, 128.1, 128.3, 128.5, 129.2, 132.8, 133.8, 134.7, 137.9, 174.7; IR (neat) *v* 2957, 2925, 2852, 1652, 1496, 1464, 1362, 1049, 765, 753, 699, 668; Ms (ESI): *m*/*z* = 317.2 $[M+H]^+$.



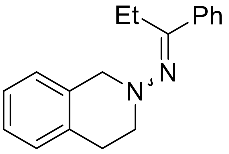
1l

Compound **1l**, colorless oil, yield: 72% (two steps from ketone). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.67 (t, *J* = 7.7 Hz, 3H), 0.97 (t, *J* = 7.6 Hz, 3H), 1.07 (d, *J* = 6.4 Hz, 6H), 2.13-2.24 (m, 4H), 2.84-2.93 (m, 1H), 3.74 (s, 2H), 7.15-7.19 (m, 1H), 7.21-7.27 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.3, 11.9, 19.8, 23.3, 28.4, 55.5, 58.4, 126.6, 127.9, 130.0, 139.8, 178.4; IR (neat) *v* 2967, 2934, 1635, 1456, 1375, 1168, 746, 697; Ms (ESI): *m*/*z* = 233.2 $[M+H]^+$.



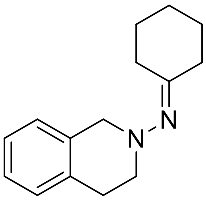
1o

Compound **1o**, yellow oil, yield: 80% (two steps from ketone). ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.78 (t, *J* = 7.6 Hz, 3H), 2.67 (q, *J* = 7.6 Hz, 2H), 4.71 (s, 2H), 6.87-6.91 (m, 1H), 6.95 (d, *J* = 8.4 Hz, 2H), 7.20-7.41 (m, 10H), 7.72-7.75 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 11.1, 22.9, 62.4, 117.0, 120.8, 127.0, 127.3, 128.3, 128.4, 128.5, 129.0, 129.8, 137.1, 139.0, 151.4, 173.7; IR (neat) *v* 2971, 2935, 2876, 1595, 1493, 1452, 1319, 1198, 1028, 916, 753, 694; Ms (ESI): *m*/*z* = 315.2 [M+H]$^+$.



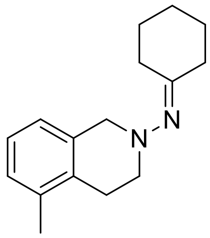
1p

Compound **1p**, yellow oil, yield: 66% (three steps from 1,2,3,4-tetrahydroisoquinoline). ^{1}H NMR (500 MHz, CDCl$_3$, a mixture of (Z/E) isomers in ratio 91:9, the minor one is marked with an *) δ 1.10 (t, *J* = 7.6 Hz, 3H), 2.99 (q, *J* = 7.6 Hz, 2H), 3.05-3.12 (m, 4H), 3.99 (s, 2H), 7.07-7.10 (m, 1H), 7.14-7.21 (m, 3H), 7.38-7.42 (m, 3H), 7.69-7.74 (m, 2H); 1.07* (t, *J* = 7.5 Hz, 3H), 2.61* (q, *J* = 7.5 Hz, 2H), 2.72* (t, *J* = 5.8 Hz, 2H), 2.93* (t, *J* = 5.9 Hz, 2H), 3.92* (s, 2H), 6.92-6.97* (m, 1H), 7.01-7.05* (m, 1H), 7.27-7.32* (m, 1H), 7.33-7.37* (m, 2H), 7.46-7.49* (m, 2H), 7.69-7.74* (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 12.2, 22.2, 29.0, 54.0, 58.0, 125.9, 126.4, 127.0, 127.3, 128.5, 128.6, 129.5, 134.3, 134.6, 137.8, 171.2; 11.9*, 28.8*, 32.4*, 52.6*, 57.3*, 125.7*, 126.1*, 126.9*, 127.3*, 128.3*, 128.3*, 128.4*, 134.5*, 134.9*, 137.4*, 165.7*; IR (neat) *v* 2966, 2929, 2805, 1607, 1496, 1455, 1365, 1017, 938, 770, 744, 694 cm^{-1}; Ms (ESI): *m*/*z* = 265.2 [M+H]$^+$.



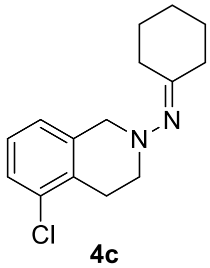
4a

Compound **4a**, pale yellow solid, yield: 60% (three steps from 1,2,3,4-tetrahydroisoquinoline). ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.61-1.77 (m, 6H), 2.32 (t, *J* = 6.5 Hz, 2H), 2.59 (t, *J* = 5.9 Hz, 2H), 2.93-3.03 (m, 4H), 3.86 (s, 2H), 7.04 (d, *J* = 6.9 Hz, 1H), 7.10-7.18 (m, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 26.2, 26.9, 27.7, 29.0, 29.1, 36.2, 53.6, 57.7, 125.8, 126.4, 127.0, 128.5, 134.2, 134.6, 171.8; IR (neat) *v* 2928, 2855, 2803, 1636, 1497, 1468, 1367, 1023, 940, 744 cm^{-1}; Ms (ESI): *m*/*z* = 229.2 [M+H]$^+$.



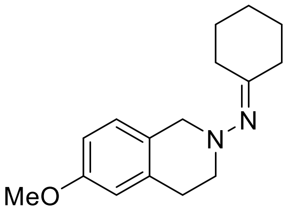
4b

Compound **4b**, yellow oil, yield: 51% (three steps from 1,2,3,4-tetrahydroisoquinoline). ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.61-1.78 (m, 6H), 2.23 (s, 3H), 2.31 (t, J = 6.3 Hz, 2H), 2.59 (t, J = 5.7 Hz, 2H), 2.86 (t, J = 6.0 Hz, 2H), 2.99 (t, J = 6.0 Hz, 2H), 3.84 (s, 2H), 6.90 (d, J = 7.4 Hz, 1H), 7.00-7.08 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 19.2, 26.2, 26.8, 27.1, 27.7, 29.0, 36.2, 53.8, 58.2, 124.7, 125.7, 127.8, 132.8, 134.5, 136.3, 171.7; IR (neat) ν 2926, 2855, 2807, 1635, 1503, 1452, 1366, 1024, 943, 760, 724 cm^{-1}; Ms (ESI): m/z = 243.2 [M+H]$^+$.



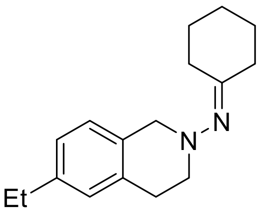
4c

Compound **4c**, yellow oil, yield: 63% (three steps from 1,2,3,4-tetrahydroisoquinoline). ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.61-1.77 (m, 6H), 2.30 (t, J = 6.3 Hz, 2H), 2.56 (t, J = 5.8 Hz, 2H), 2.90-2.96 (m, 4H), 3.80 (s, 2H), 7.01-7.06 (m, 2H), 7.11 (dd, J = 8.2, 1.6 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 26.1, 26.8, 27.6, 28.4, 29.0, 36.1, 53.4, 57.4, 126.5, 126.8, 129.9, 131.4, 132.7, 136.5, 172.1; IR (neat) ν 2928, 2855, 2811, 1636, 1486, 1427, 1362, 1088, 1022, 940, 890, 801cm^{-1}; Ms (ESI): m/z = 263.1 [M+H]$^+$.



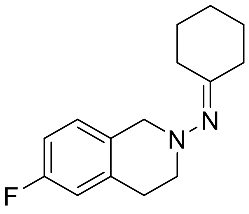
4d

Compound **4d**, yellow solid, yield: 45% (three steps from 1,2,3,4-tetrahydroisoquinoline). ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.60-1.68 (m, 4H), 1.70-1.76 (m, 2H), 2.29-2.33 (m, 2H), 2.56-2.60 (m, 2H), 2.91-2.94 (m, 2H), 2.96-3.00 (m, 2H), 3.77-3.79 (m, 5H), 6.66 (d, J = 2.5 Hz, 1H), 6.71 (dd, J = 8.4, 2.7 Hz, 1H), 6.96 (d, J = 8.4 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 26.2, 26.9, 27.7, 29.0, 29.3, 36.2, 53.6, 55.4, 57.3, 112.2, 113.2, 126.8, 127.9, 135.4, 158.2, 171.6; IR (neat) ν 2930, 2855, 2832, 1615, 1505, 1448, 1270, 1158, 1038, 945, 810 cm^{-1}; Ms (ESI): m/z = 259.2 [M+H]$^+$.



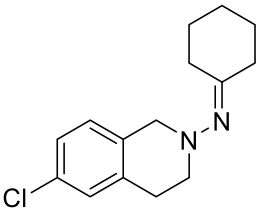
4e

Compound **4e**, yellow oil, yield: 55% (three steps from 1,2,3,4-tetrahydroisoquinoline). ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.22 (t, J = 7.6 Hz, 3H), 1.60-1.77 (m, 6H), 2.28-2.33 (m, 2H), 2.56-2.62 (m, 4H), 2.92-3.02 (m, 4H), 3.81 (s, 2H), 6.94-7.00 (m, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 15.9, 26.2, 26.8, 27.7, 28.7, 29.0, 29.1, 36.2, 53.7, 57.6, 125.5, 126.9, 127.9, 131.8, 134.0, 142.4, 171.6; IR (neat) ν 2929, 2856, 2809, 1636, 1506, 1448, 1366, 1023, 943, 880, 819 cm^{-1}; Ms (ESI): m/z = 257.2 [M+H]$^+$.



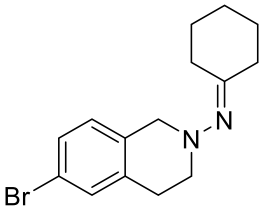
4f

Compound **4f**, yellow oil, yield: 64% (three steps from 1,2,3,4-tetrahydroisoquinoline). ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.61-1.78 (m, 6H), 2.31 (t, J = 6.5 Hz, 2H), 2.57 (t, J = 6.1 Hz, 2H), 2.90-3.01 (m, 4H), 3.80 (s, 2H), 6.80-6.86 (m, 2H), 6.97-7.02 (m, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 26.1, 26.9, 27.6, 29.0, 29.1, 36.2, 53.2, 57.3, 113.0 ($^2J_{\mathrm{CF}}$ = 21.4 Hz), 114.8 ($^2J_{\mathrm{CF}}$ = 20.6 Hz), 128.3 ($^3J_{\mathrm{CF}}$ = 7.9 Hz), 130.2, 136.3, 160.1 ($^1J_{\mathrm{CF}}$ = 242Hz), 171.9; IR (neat) ν 2928, 2855, 2812, 1617, 1501, 1448, 1367, 1238, 1141, 922, 864, 807 cm^{-1}; Ms (ESI): m/z = 247.2 [M+H]$^+$.



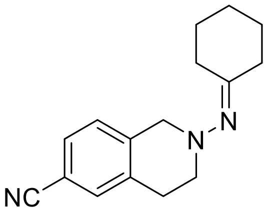
4g

Compound **4g**, yellow oil, yield: 59% (three steps from 1,2,3,4-tetrahydroisoquinoline). ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.61-1.77 (m, 6H), 2.31 (t, J = 6.5 Hz, 2H), 2.57 (t, J = 6.0 Hz, 2H), 2.90-2.99 (m, 4H), 3.80 (s, 2H), 6.97 (d, J = 8.0 Hz, 1H), 7.08-7.13 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 26.1, 26.9, 27.6, 28.8, 29.0, 36.1, 53.2, 57.3, 126.0, 126.2, 128.3, 128.4, 131.9, 136.1, 172.1; IR (neat) ν 2927, 2854, 2813, 1645, 1489, 1448, 1365, 1088, 1022, 942, 877, 808 cm^{-1}; Ms (ESI): m/z = 263.1 [M+H]$^+$.



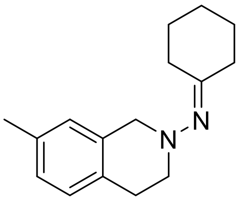
4h

Compound **4h**, yellow oil, yield: 48% (three steps from 1,2,3,4-tetrahydroisoquinoline). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.59-1.76 (m, 6H), 2.30 (t, J = 6.3 Hz, 2H), 2.56 (t, J = 5.7 Hz, 2H), 2.89-2.99 (m, 4H), 3.78 (s, 2H), 6.91 (d, J = 8.1 Hz, 1H), 7.22-7.26 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.1, 26.9, 27.6, 28.8, 29.0, 36.1, 53.1, 57.3, 128.6, 128.6, 128.9, 131.3, 133.6, 136.6, 172.1; IR (neat) ν 2926, 2854, 2813, 1636, 1485, 1447, 1364, 1078, 1022, 941, 866, 806 cm^{-1}; Ms (ESI): m/z = 307.1 [M+H]$^+$.



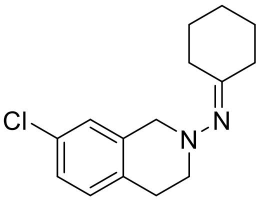
4i

Compound **4i**, yellow oil, yield: 81% (from **4g**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.60-1.78 (m, 6H), 2.28-2.32 (m, 2H), 2.54-2.58 (m, 2H), 2.92-3.03 (m, 4H), 3.89 (s, 2H), 7.13 (d, J = 7.8 Hz, 1H), 7.39-7.43 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.1, 26.9, 27.6, 28.5, 29.0, 36.1, 52.9, 57.6, 110.2, 119.2, 127.9, 129.4, 132.3, 135.8, 140.3, 172.5; IR (neat) ν 2928, 2854, 2815, 2227, 1636, 1499, 1447, 1372, 1080, 1026, 947, 908, 821 cm^{-1}; Ms (ESI): m/z = 254.2 [M+H]$^+$.



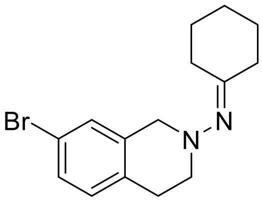
4j

Compound **4j**, yellow oil, yield: 55% (three steps from 1,2,3,4-tetrahydroisoquinoline). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.58-1.77 (m, 6H), 2.28-2.33 (m, 5H), 2.55-2.60 (m, 2H), 2.91-2.97 (m, 4H), 3.81 (s, 2H), 6.86 (s, 1H), 6.96 (d, J = 7.8 Hz, 1H), 7.01 (d, J = 7.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.1, 26.2, 26.9, 27.7, 28.6, 29.0, 36.2, 53.8, 57.8, 127.3, 127.5, 128.4, 131.6, 134.4, 137.3, 171.7; IR (neat) ν 2923, 2854, 2812, 1636, 1506, 1447, 1362, 1083, 1022, 940, 872, 801 cm^{-1}; Ms (ESI): m/z = 243.2 [M+H]$^+$.



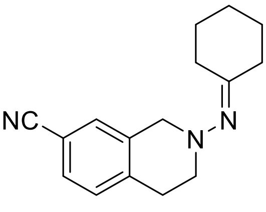
4k

Compound **4k**, yellow oil, yield: 62% (three steps from 1,2,3,4-tetrahydroisoquinoline). ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.58-1.77 (m, 6H), 2.31 (t, J = 6.5 Hz, 2H), 2.57 (t, J = 6.0 Hz, 2H), 2.90-2.97 (m, 4H), 3.80 (s, 2H), 7.01-7.06 (m, 2H), 7.11 (d, J = 8.2 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 26.1, 26.9, 27.6, 28.4, 29.0, 36.1, 53.4, 57.4, 126.5, 126.8, 129.9, 131.4, 132.7, 136.5, 172.1; IR (neat) ν 2927, 2854, 1636, 1486, 1448, 1361, 1088, 1022, 940, 890, 801 cm^{-1}; Ms (ESI): m/z = 263.1 [M+H]$^+$.



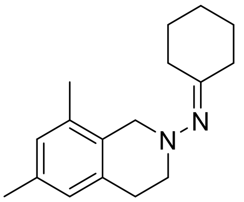
4l

Compound **4l**, yellow oil, yield: 50% (three steps from 1,2,3,4-tetrahydroisoquinoline). ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.59-1.77 (m, 6H), 2.31 (t, J = 6.3 Hz, 2H), 2.56 (t, J = 6.0 Hz, 2H), 2.93 (brs, 4H), 3.80 (s, 2H), 6.99 (d, J = 8.2 Hz, 1H), 7.19 (s, 1H), 7.25 (d, J = 8.2 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 26.1, 26.9, 27.6, 28.4, 29.0, 36.1, 53.3, 57.3, 119.4, 129.4, 129.8, 130.2, 133.3, 136.9, 172.1; IR (neat) ν 2926, 2854, 1635, 1483, 1447, 1362, 1021, 940, 878, 798 cm^{-1}; Ms (ESI): m/z = 307.1 [M+H]$^+$.



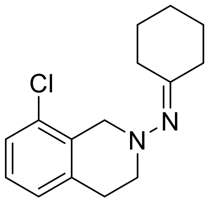
4m

Compound **4m**, yellow oil, yield: 84% (from **4l**). ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.60-1.77 (m, 6H), 2.31 (t, J = 6.0 Hz, 2H), 2.56 (t, J = 6.0 Hz, 2H), 2.95 (t, J = 5.9 Hz, 2H), 3.03 (t, J = 5.9 Hz, 2H), 3.84 (s, 2H), 7.21 (d, J = 7.9 Hz, 1H), 7.34 (s, 1H), 7.41 (d, J = 7.9 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 26.1, 26.8, 27.6, 29.0, 29.1, 36.1, 52.8, 57.1, 109.7, 119.2, 129.4, 129.9, 130.8, 136.1, 140.1, 172.6; IR (neat) ν 2929, 2855, 2227, 1636, 1498, 1448, 1363, 1024, 941, 834, 808 cm^{-1}; Ms (ESI): m/z = 254.2 [M+H]$^+$.



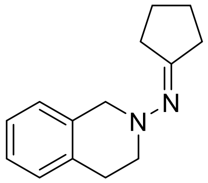
4n

Compound **4n**, yellow oil, yield: 51% (three steps from 1,2,3,4-tetrahydroisoquinoline). ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.62-1.79 (m, 6H), 2.17 (s, 3H), 2.27 (s, 3H), 2.31-2.36 (m, 2H), 2.57-2.62 (m, 2H), 2.87-2.99 (m, 4H), 3.77 (s, 2H), 6.80-6.83 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 18.7, 21.0, 26.2, 26.9, 27.6, 29.0, 29.4, 36.2, 53.2, 55.7, 126.7, 128.3, 130.1, 133.9, 134.9, 135.5, 171.7; IR (neat) ν 2928, 2856, 2809, 1635, 1447, 1363, 1009, 964, 897, 848 cm^{-1}; Ms (ESI): m/z = 257.2 [M+H]$^{+}$.



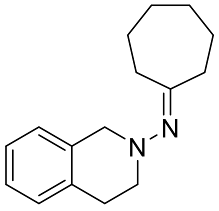
4o

Compound **4o**, yellow oil, yield: 59% (three steps from 1,2,3,4-tetrahydroisoquinoline). ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.59-1.78 (m, 6H), 2.33 (t, J = 6.5 Hz, 2H), 2.58 (t, J = 5.9 Hz, 2H), 2.94 (t, J = 5.8 Hz, 2H), 3.00 (t, J = 5.5 Hz, 2H), 3.86 (s, 2H), 7.03 (d, J = 7.6 Hz, 1H), 7.07-7.11 (m, 1H), 7.18 (d, J = 7.8 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 26.1, 26.9, 27.7, 29.0, 29.2, 36.1, 52.9, 55.4, 126.7, 127.0, 127.1, 132.6, 132.7, 136.8, 172.2; IR (neat) ν 2927, 2854, 2818, 1636, 1447, 1363, 1180, 1026, 956, 769 cm^{-1}; Ms (ESI): m/z = 263.1 [M+H]$^{+}$.



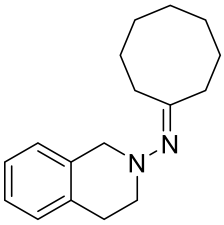
4p

Compound **4p**, yellow oil, yield: 67% (three steps from 1,2,3,4-tetrahydroisoquinoline). ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.73-1.83 (m, 4H), 2.41-2.51 (m, 4H), 2.97-3.06 (m, 4H), 3.92 (s, 2H), 7.04 (d, J = 7.5 Hz, 1H), 7.10-7.17 (m, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 24.3, 25.0, 29.0, 29.8, 33.7, 53.2, 57.1, 125.8, 126.4, 127.0, 128.5, 134.2, 134.6, 177.8; IR (neat) ν 2959, 2887, 2804, 1653, 1497, 1452, 1366, 1026, 939, 744 cm^{-1}; Ms (ESI): m/z = 215.2 [M+H]$^{+}$.



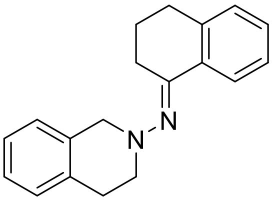
4q

Compound **4q**, yellow oil, yield: 62% (three steps from 1,2,3,4-tetrahydroisoquinoline). ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.53-1.72 (m, 8H), 2.46-2.50 (m, 2H), 2.70-2.74 (m, 2H), 2.92-3.02 (m, 4H), 3.83 (s, 2H), 7.04 (d, J = 7.1 Hz, 1H), 7.10-7.17 (m, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 25.2, 27.4, 29.1, 30.1, 30.6, 31.3, 37.2, 53.2, 57.3, 125.8, 126.4, 127.0, 128.6, 134.3, 134.7, 176.0; IR (neat) ν 2925, 2855, 2823, 1635, 1587, 1454, 1366, 1017, 939, 744 cm^{-1}; Ms (ESI): m/z = 243.2 [M+H]$^+$.



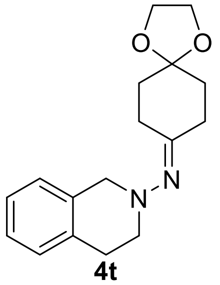
4r

Compound **4r**, yellow oil, yield: 59% (three steps from 1,2,3,4-tetrahydroisoquinoline). ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.43-1.58 (m, 6H), 1.76-1.84 (m, 4H), 2.38-2.42 (m, 2H), 2.55-2.58 (m, 2H), 2.92 (t, J = 5.9 Hz, 2H), 3.01 (t, J = 5.9 Hz, 2H), 3.80 (s, 2H), 7.05 (d, J = 7.2 Hz, 1H), 7.11-7.17 (m, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 24.7, 25.3, 26.9, 27.0, 27.6, 29.1, 30.0, 35.7, 52.9, 57.2, 125.8, 126.3, 127.0, 128.6, 134.4, 134.8, 178.0; IR (neat) ν 2926, 2854, 2804, 1634, 1497, 1455, 1367, 1022, 940, 743 cm^{-1}; Ms (ESI): m/z = 257.2 [M+H]$^+$.



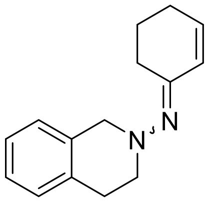
4s

Compound **4s**, yellow solid, yield: 67% (three steps from 1,2,3,4-tetrahydroisoquinoline). ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.90-1.97 (m, 2H), 2.85-2.94 (m, 4H), 3.04-3.15 (m, 4H), 4.06 (s, 2H), 7.08 (d, J = 7.0 Hz, 1H), 7.13-7.24 (m, 5H), 7.27-7.31 (m, 1H), 8.21 (d, J = 7.9 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 22.8, 27.6, 28.9, 30.0, 53.3, 57.5, 125.3, 125.9, 126.3, 126.4, 127.0, 128.6, 128.8, 129.7, 133.1, 134.4, 134.7, 140.1, 162.7; IR (neat) ν 2930, 2830, 2805, 1612, 1585, 1452, 1366, 1020, 939, 762, 746, 730 cm^{-1}; Ms (ESI): m/z = 277.2 [M+H]$^+$.



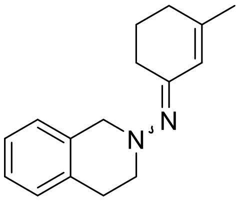
4t

Compound **4t**, white solid, yield: 62% (three steps from 1,2,3,4-tetrahydroisoquinoline). ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.79 (t, J = 6.8 Hz, 2H), 1.88 (t, J = 6.7 Hz, 2H), 2.51 (t, J = 6.8 Hz, 2H), 2.76 (t, J = 6.8 Hz, 2H), 2.94-3.02 (m, 4H), 3.86 (s, 2H), 3.99 (brs, 4H), 7.03 (d, J = 7.4 Hz, 1H), 7.10-7.17 (m, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 32.6, 34.0, 34.1, 34.8, 38.3, 53.6, 57.6, 64.6 (2C), 108.1, 125.8, 126.4, 128.5, 134.1, 134.4, 169.2; IR (neat) v 2953, 2885, 2805, 1717, 1635, 1496, 1436, 1363, 1124, 1087, 1031, 940, 908, 747 cm^{-1}; Ms (ESI): m/z = 287.2 [M+H]$^+$.



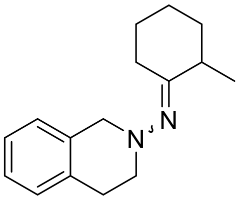
4u

Compound **4u**, yellow oil, yield: 50% (three steps from 1,2,3,4-tetrahydroisoquinoline). ^{1}H NMR (500 MHz, CDCl$_3$, a mixture of (Z/E) isomers in ratio 65:35, the minor one is marked with an *) δ 1.77-1.83 (m, 2H), 2.21-2.29 (m, 2H), 2.71 (t, J = 6.5 Hz, 2H), 2.99-3.06 (m, 4H), 3.93 (s, 2H), 6.22 (d, J = 10.1 Hz, 1H), 6.31-6.36 (m, 1H), 7.02-7.07 (m, 1H), 7.11-7.18 (m, 3H); 1.86-1.92* (m, 2H), 2.21-2.29* (m, 2H), 2.49* (t, J = 6.5 Hz, 2H), 2.99-3.06* (m, 4H), 3.91* (s, 2H) 6.33-6.38* (m, 1H), 6.81* (d, J = 10.3 Hz, 1H), 7.02-7.07* (m, 1H), 7.11-7.18* (m, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 22.0, 25.7, 26.4, 29.0, 53.2, 57.3, 125.8, 126.4, 127.0, 128.5, 128.6, 134.2, 134.5, 138.3, 164.9; 22.7*, 26.6*, 29.0*, 31.9*, 54.0*, 58.1*, 120.6*, 125.8*, 126.4*, 126.9*, 128.5*, 134.3*, 134.6*, 140.8*, 163.1*; IR (neat) v 3023, 2926, 2826, 2804, 1625, 1584, 1497, 1454, 1365, 1026, 938, 744 cm^{-1}; Ms (ESI): m/z = 227.2 [M+H]$^+$.



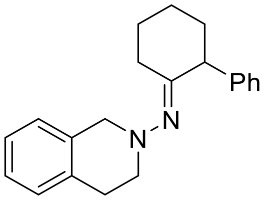
4v

Compound **4v**, yellow oil, yield: 57% (three steps from 1,2,3,4-tetrahydroisoquinoline). ^{1}H NMR (500 MHz, CDCl$_3$, a mixture of (Z/E) isomers in ratio 74:26, the minor one is marked with an *) δ 1.76-1.89 (m, 5H), 2.13-2.18 (m, 2H), 2.65 (t, J = 6.5 Hz, 2H), 2.98-3.02 (m, 4H), 3.90 (s, 2H), 6.04 (s, 1H), 7.02-7.06 (m, 1H), 7.10-7.17 (m, 3H); 1.76-1.89* (m, 5H), 2.17-2.21* (m, 2H), 2.41* (t, *J* = 6.5 Hz, 2H), 3.01-3.04* (m, 4H), 3.89* (s, 2H), 6.62* (s, 1H), 7.02-7.06* (m, 1H), 7.10-7.17* (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.2, 24.3, 25.7, 29.0, 30.9, 53.3, 57.4, 124.1, 125.8, 126.4, 127.0, 128.6, 134.3, 134.6, 148.5, 165.9; 22.8*, 24.6*, 29.1*, 31.4*, 31.8*, 53.9*, 58.0*, 116.8*, 125.8*, 126.4*, 127.0*, 128.6*, 134.4*, 134.8*, 151.6*, 163.8*; IR (neat) ν 2926, 2823, 2804, 1635, 1586, 1455, 1366, 1017, 939, 744 cm^{-1}; Ms (ESI): *m*/*z* = 241.2 [M+H]$^+$.



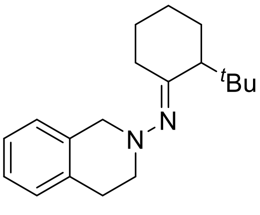
4w

Compound **4w**, yellow oil, yield: 56% (three steps from 1,2,3,4-tetrahydroisoquinoline). ^{1}H NMR (500 MHz, $CDCl_3$, a mixture of (Z/E) isomers in ratio 75:25, the minor one is marked with an *) δ 1.15 (d, *J* = 7.0 Hz, 3H), 1.45-1.80 (m, 5H), 1.83-1.90 (m, 1H), 2.42-2.50 (m, 2H), 2.66-2.73 (m, 1H), 2.90-3.03 (m, 4H), 3.83 (s, 2H), 7.02-7.06 (m, 1H), 7.10-7.17 (m, 3H); 1.16* (d, *J* = 7.0 Hz, 3H), 1.45-1.80* (m, 5H), 2.24-2.30* (m, 1H), 2.35-2.42* (m, 1H), 2.42-2.50* (m, 2H), 2.90-3.03* (m, 4H), 3.85* (s, 2H), 7.02-7.17* (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.0, 23.4, 27.0, 27.2, 29.1, 35.1, 39.1, 53.7, 57.8, 125.8, 126.3, 127.0, 128.5, 134.3, 134.8, 174.2; 17.3*, 21.2*, 28.1*, 29.1*, 30.8*, 32.0*, 33.1*, 54.0*, 58.1*, 125.8*, 126.0*, 126.4*, 128.6*, 134.2*, 134.7*, 177.0*; IR (neat) ν 2926, 2854, 2804, 1635, 1455, 1367, 1022, 940, 743 cm^{-1}; Ms (ESI): *m*/*z* = 243.2 [M+H]$^+$.



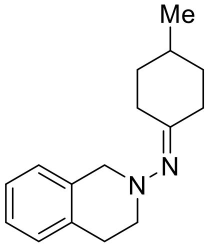
4x

Compound **4x**, yellow solid, yield: 55% (three steps from 1,2,3,4-tetrahydroisoquinoline). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.55-1.84 (m, 5H), 1.95-2.04 (m, 1H), 2.08-2.16 (m, 1H), 2.40-2.48 (m, 1H), 3.00-3.09 (m, 4H), 3.76-3.79 (m, 1H), 3.89-3.97 (m, 2H), 7.06 (d, *J* = 7.3 Hz, 1H), 7.11-7.17 (m, 3H), 7.19-7.25 (m, 1H), 7.31-7.34 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.3, 26.9, 27.2, 29.0, 31.3, 48.1, 53.7, 57.8, 125.8, 126.2, 126.4, 127.0, 127.7, 128.5, 128.6, 134.2, 134.6, 141.1, 172.5; IR (neat) ν 2931, 2858, 2805, 1715, 1634, 1496, 1447, 1366, 1022, 939, 746, 698 cm^{-1}; Ms (ESI): *m*/*z* = 305.2 [M+H]$^+$.



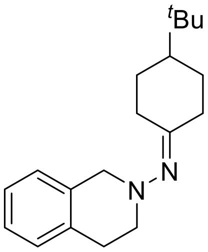
4y

Compound **4y**, yellow oil, yield: 52% (three steps from 1,2,3,4-tetrahydroisoquinoline). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.04 (s, 9H), 1.45-1.53 (m, 1H), 1.57- 1.88 (m, 5H), 2.13 (t, J = 6.2 Hz, 1H), 2.41-2.47 (m, 1H), 2.76-2.82 (m, 1H), 2.95-3.03 (m, 4H), 3.82-3.92 (m, 2H), 7.04 (d, J = 7.1 Hz, 1H), 7.10-7.17 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.3, 26.9, 28.3, 28.9, 29.4 (2C), 33.8, 53.5, 53.8, 58.0, 125.7, 126.3, 127.0, 128.5, 134.3, 134.8, 172.9; IR (neat) ν 2930, 2861, 2804, 1635, 1454, 1365, 1021, 940, 743 cm^{-1}; Ms (ESI): m/z = 285.3 $[M+H]^+$.



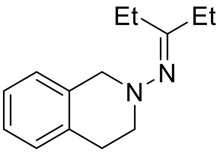
4z

Compound **4z**, yellow oil, yield: 62% (three steps from 1,2,3,4-tetrahydroisoquinoline). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.96 (d, J = 6.6 Hz, 3H), 1.10-1.35 (m, 2H), 1.66-1.76 (m, 1H), 1.81-1.95 (m, 3H), 2.22 (td, J = 13.5, 5.0 Hz, 1H), 2.42-2.49 (m, 1H), 2.93-3.02 (m, 4H), 3.26-3.32 (m, 1H), 3.80-3.90 (m, 2H), 7.04 (d, J = 7.6 Hz, 1H), 7.10-7.17 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.6, 28.1, 29.0, 32.2, 34.8, 35.4, 35.6, 53.6, 57.8, 125.8, 126.4, 127.0, 128.6, 134.2, 134.6, 171.6; IR (neat) ν 2923, 2852, 2805, 1636, 1497, 1455, 1367, 1023, 939, 743 cm^{-1}; Ms (ESI): m/z = 243.2 $[M+H]^+$.



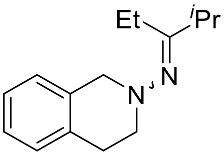
4aa

Compound **4aa**, white solid, yield: 60% (three steps from 1,2,3,4-tetrahydroisoquinoline). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (s, 9H), 1.13-1.36 (m, 3H), 1.80 (td, J = 13.7, 5.4 Hz, 1H), 1.91-2.04 (m, 2H), 2.18 (td, J = 13.5, 5.1 Hz, 1H), 2.51 (dd, J = 13.9, 2.4 Hz, 1H), 2.92-3.03 (m, 4H), 3.41 (dd, J = 14.1, 1.6 Hz, 1H), 3.80-3.90 (m, 2H), 7.04 (d, J = 7.3 Hz, 1H), 7.10-7.17 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.5, 27.7, 28.3, 28.6, 29.1, 32.6, 35.9, 47.8, 53.7, 57.8, 125.8, 126.4, 127.0, 128.5, 134.2, 134.6, 171.7; IR (neat) ν 2950, 2865, 2804, 1636. 1496, 1455, 1365, 1025, 940, 743 cm^{-1}; Ms (ESI): *m*/*z* = 285.2 [M+H]$^+$.



4ab

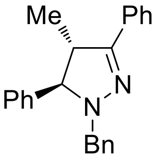
Compound **4ab**, yellow oil, yield: 64% (three steps from 1,2,3,4-tetrahydroisoquinoline). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.07-1.16 (m, 6H), 2.31 (q, *J* = 7.5 Hz, 2H), 2.52 (q, *J* = 7.6 Hz, 2H), 2.92 (t, *J* = 6.0 Hz, 2H), 3.01 (t, *J* = 5.9 Hz, 2H), 3.81 (s, 2H), 7.04 (d, *J* = 7.1 Hz, 1H), 7.10-7.17 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.3, 11.8, 23.0, 29.1 (2C), 53.7, 57.8, 125.8, 126.3, 127.0, 128.5, 134.3, 134.8, 176.1; IR (neat) *v* 2969, 2932, 2804, 1635, 1497, 1456, 1366, 1020, 938, 744 cm^{-1}; Ms (ESI): *m*/*z* = 217.2 [M+H]$^+$.



4ac

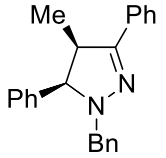
Compound **4ac**, yellow oil, yield: 60% (three steps from 1,2,3,4-tetrahydroisoquinoline). ^{1}H NMR (500 MHz, $CDCl_3$, a mixture of (Z/E) isomers in ratio 77:23, the minor one is marked with an *) δ 1.05-1.18 (m, 9H), 2.43 (q, *J* = 7.5 Hz, 2H), 2.56-2.65 (m, 1H), 2.87-2.92 (m, 2H), 2.98-3.03 (m, 2H), 3.78 (s, 2H), 7.04 (d, *J* = 6.6 Hz, 1H), 7.11-7.18 (m, 3H); 1.05-1.18* (m, 9H), 2.26* (q, *J* = 7.5 Hz, 2H), 2.45-2.50* (m, 1H), 2.87-2.92* (m, 2H), 2.98-3.03* (m, 2H), 3.78* (s, 2H), 7.04* (d, *J* = 6.6 Hz, 1H), 7.11-7.18* (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.1, 20.6, 22.2, 29.1, 35.0, 53.6, 57.8, 125.7, 126.3, 126.9, 128.5, 134.4, 134.9, 179.5; 12.7*, 18.5*, 20.1*, 24.6*, 29.1*, 53.9*, 58.0*, 125.7*, 126.3*, 127.0*, 128.5*, 134.4*, 134.9*, 179.2*; IR (neat) *v* 2964, 2928, 2804, 1635, 1456, 1364, 1018, 939, 742 cm^{-1}; Ms (ESI): *m*/*z* = 231.2 [M+H]$^+$.

Analytical Data for Products



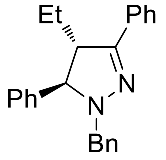
***anti*-2a**

Compound **2a**, yellow oil, yield: 86% (*anti* : *syn* = 6.8 : 1). ***anti*-2a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20 (dd, *J* = 6.9, 0.7 Hz, 3H), 3.35-3.46 (m, 1H), 3.79 (d, *J* = 11.7 Hz, 1H), 3.96 (d, *J* = 14.3 Hz, 1H), 4.53 (d, *J* = 14.3 Hz, 1H), 7.21-7.26 (m, 1H), 7.27-7.39 (m, 10H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.7, 50.2, 56.7, 76.8, 126.4, 127.3, 127.9, 128.0, 128.2, 128.3, 128.5, 128.8, 129.6, 133.3, 137.0, 140.6, 152.7; IR (neat) *v* 2960, 2926, 1494, 1455, 1349, 1051, 758, 697; Ms (ESI): *m*/*z* = 327.2 [M+H]$^+$. The relative configuration was assigned by NOESY analysis of this compound. NOEs between the aromatic proton H_c of ***anti*-2a** and H_b, H_a and H_d were observed. Additionally, there was no observable NOE between H_c and H_d. These results indicate that H_a and H_b of ***anti*-2a** have the *anti* relationship.



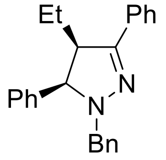
***syn*-2a**

***syn*-2a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.78 (d, *J* = 7.3 Hz, 3H), 3.36-3.44 (m, 1H), 3.97 (d, *J* = 14.2 Hz, 1H), 4.31 (d, *J* = 9.4 Hz, 1H), 4.58 (d, *J* = 14.2 Hz, 1H), 7.22-7.26 (m, 1H), 7.27-7.48 (m, 12H), 7.69 (d, J = 7.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.0, 44.5, 56.3, 72.7, 126.2, 127.3, 127.7, 128.2, 128.5, 128.6, 128.6, 128.6, 129.9, 132.6, 136.6, 136.7, 154.8; IR (neat) *ν* 2969, 2927, 1495, 1455, 1375, 1169, 1028, 761, 699; Ms (ESI): *m*/*z* = 327.2 $[M+H]^+$. The relative configuration was assigned by NOESY analysis of this compound. NOE between the aromatic proton H_c of ***syn*-2a** and H_d was observed. Additionally, there were no observable NOEs between H_a and H_d, or H_b and H_c. Comparing with ***anti*-2a**, these results indicate that H_a and H_b of ***syn*-2a** have the *syn* relationship.



***anti*-2b**

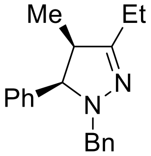
Compound **2b**, yellow oil, yield: 83% (*anti* : *syn* = 7.6 : 1). ***anti*-2b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.67 (t, *J* = 7.5 Hz, 3H), 1.60-1.69 (m, 2H), 3.44-3.49 (m, 1H), 3.98 (d, *J* = 14.4 Hz, 1H), 4.09 (d, J = 9.4 Hz, 1H), 4.62 (d, *J* = 14.4 Hz, 1H), 7.21-7.39 (m, 13H), 7.59 (d, *J* = 7.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.4, 23.5, 56.3, 56.5, 72.0, 126.1, 127.3, 127.8, 127.9, 128.1, 128.2, 128.6, 128.8, 129.5, 133.5, 137.2, 141.9, 150.6; IR (neat) *ν* 2961, 2927, 1494, 1455, 1357, 1166, 1064, 758, 697; Ms (ESI): *m*/*z* = 341.2 $[M+H]^+$. The relative configuration was assigned by NOESY analysis of this compound. NOEs between the aromatic proton H_c of ***anti*-2b** and H_b, H_a and H_d, H_a and H_e were observed. Additionally, there was no observable NOE between H_c and H_d. These results indicate that H_a and H_b of ***anti*-2b** have the *anti* relationship.



***syn*-2b**

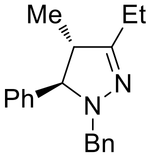
***syn*-2b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.42 (t, *J* = 7.5 Hz, 3H), 1.25-1.33 (m, 1H), 1.41-1.51 (m, 1H), 3.26-3.31 (m, 1H), 3.96 (d, *J* = 14.2 Hz, 1H), 4.35 (d, *J* = 9.6 Hz, 1H), 4.56 (d, *J* = 14.3 Hz, 1H), 7.22-7.41 (m, 11H), 7.44-7.50 (m, 2H), 7.67 (d, *J* = 7.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.2, 20.3, 51.2, 56.4, 72.7, 125.7, 126.4, 127.2, 127.7, 128.2, 128.5, 128.6, 128.6, 129.8, 131.4, 136.6, 138.0, 155.2; IR (neat) *ν* 2958, 2927, 1495, 1456, 1361, 1049, 765, 699; Ms (ESI): *m*/*z* =

341.2 [M+H]$^+$. The relative configuration was assigned by NOESY analysis of this compound. There were no observable NOEs between H_a and H_d, or H_b and H_c. Comparing with ***anti*-2b**, these results indicate that H_a and H_b of ***syn*-2b** have the *syn* relationship.



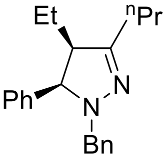
***syn*-2c**

Compound **2c**, yellow oil, yield: 67% (*syn* : *anti* = 3.6 : 1). ***syn*-2c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.66 (d, *J* = 7.4 Hz, 3H), 1.16 (t, *J* = 7.5 Hz, 3H), 2.17-2.26 (m, 1H), 2.33-2.42 (m, 1H), 2.84-2.91 (m, 1H), 3.80 (d, *J* = 14.2 Hz, 1H), 4.09 (d, *J* = 9.5 Hz, 1H), 4.34 (d, *J* = 14.2 Hz, 1H), 7.20-7.25 (m, 1H), 7.26-7.31 (m, 5H), 7.32-7.39 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.5, 12.4, 22.5, 46.6, 56.9, 72.7, 127.1, 127.4, 128.1, 128.4, 128.5, 129.8, 137.3, 137.4, 160.5; IR (neat) *v* 2968, 2928, 1494, 1456, 1374, 1029, 750, 700; Ms (ESI): *m*/*z* = 279.2 [M+H]$^+$. The relative configuration was assigned by NOESY analysis of this compound. NOE between the aromatic proton H_c of ***syn*-2c** and H_d was observed. Additionally, there were no observable NOEs between H_a and H_d, or H_b and H_c. These results indicate that H_a and H_b of ***syn*-2c** have the *syn* relationship.



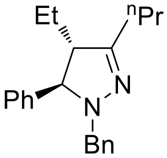
***anti*-2c**

***anti*-2c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.05 (d, *J* = 6.9 Hz, 3H), 1.13 (t, *J* = 7.5 Hz, 3H), 2.14-2.23 (m, 1H), 2.29-2.38 (m, 1H), 2.78-2.87 (m, 1H), 3.45 (d, *J* = 13.5 Hz, 1H), 3.84 (d, *J* = 14.0 Hz, 1H), 4.20 (d, *J* = 14.1 Hz, 1H), 7.17-7.23 (m, 1H), 7.24-7.30 (m, 5H), 7.31-7.35 (m, 2H), 7.41 (d, *J* = 7.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.9, 14.3, 21.9, 51.7, 57.8, 77.9, 127.1, 127.8, 128.0, 128.1, 128.6, 129.7, 137.4, 140.6, 158.7; IR (neat) *v* 2966, 2932, 1494, 1454, 1375, 1154, 1027, 757, 700; Ms (ESI): *m*/*z* = 279.2 [M+H]$^+$. The relative configuration was assigned by NOESY analysis of this compound. NOEs between the aromatic proton H_c of ***anti*-2c** and H_b, H_a and H_d were observed. Additionally, there was no observable NOE between H_c and H_d. Comparing with ***syn*-2c**, these results indicate that H_a and H_b of ***anti*-2c** have the *anti* relationship.



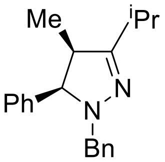
***syn*-2d**

Compound **2d**, yellow oil, yield: 71% (*syn* : *anti* = 2.5 : 1). ***syn*-2d**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.53 (t, *J* = 7.5 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H), 1.18-1.27 (m, 2H), 1.50-1.60 (m, 1H), 1.60-1.70 (m, 1H), 2.16-2.24 (m, 1H), 2.30-2.38 (m, 1H), 2.69-2.74 (m, 1H), 3.77 (d, *J* = 14.2 Hz, 1H), 4.11 (d, *J* = 9.6 Hz, 1H), 4.37 (d, *J* = 14.2 Hz, 1H), 7.21-7.30 (m, 6H), 7.31-7.44 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.2, 14.0, 20.1, 20.4, 32.0, 53.4, 56.8, 72.5, 127.0, 127.5, 128.1, 128.4, 128.6, 129.7, 137.2, 137.3, 158.7; IR (neat) *v* 2958, 2930, 1494, 1454, 1377, 1154, 1028, 742, 700; Ms (ESI): *m*/*z* = 307.2 $[M+H]^+$. The relative configuration was assigned by NOESY analysis of this compound. There were no observable NOEs between H_a and H_d, or H_b and H_c. Comparing with ***anti*-2d**, these results indicate that H_a and H_b of ***syn*-2d** have the *syn* relationship.



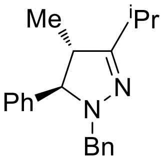
***anti*-2d**

***anti*-2d**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.71 (t, *J* = 7.5 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H), 1.41-1.50 (m, 1H), 1.52-1.66 (m, 3H), 2.12-2.20 (m, 1H), 2.23-2.31 (m, 1H), 2.83-2.89 (m, 1H), 33.67 (d, *J* = 12.8 Hz, 1H), 3.84 (d, *J* = 14.2 Hz, 1H), 4.27 (d, *J* = 14.2 Hz, 1H), 7.17-7.28 (m, 6H), 7.29-7.33 (m, 2H), 7.37 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.0, 14.2, 20.1, 22.1, 30.9, 57.4, 58.1, 73.4, 127.1, 127.6, 128.0, 128.3, 128.6, 129.7, 137.2, 141.7, 155.8; IR (neat) *v* 2960, 2929, 1494, 1454, 1382, 1151, 1028, 756, 700; Ms (ESI): *m*/*z* = 307.2 $[M+H]^+$. The relative configuration was assigned by NOESY analysis of this compound. NOEs between the aromatic proton H_c of ***anti*-2d** and H_b, H_a and H_d were observed. Additionally, there was no observable NOE between H_c and H_d. These results indicate that H_a and H_b of ***anti*-2d** have the *anti* relationship.



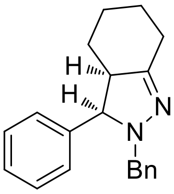
***syn*-2e**

Compound **2e**, yellow oil, yield: 64% (*syn* : *anti* = 1.8 : 1). ***syn*-2e**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.66 (d, *J* = 7.3 Hz, 3H), 1.13 (d, *J* = 7.0 Hz, 3H), 1.22 (d, *J* = 6.8 Hz, 3H), 2.49-2.58 (m, 1H), 2.86-2.93 (m, 1H), 3.81 (d, *J* = 14.2 Hz, 1H), 4.02 (d, *J* = 9.4 Hz, 1H), 4.41 (d, *J* = 14.2 Hz, 1H), 7.19-7.30 (m, 7H), 7.31-7.38 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.9, 20.3, 21.6, 28.8, 45.7, 56.6, 72.5, 127.1, 127.4, 128.0, 128.4, 128.5, 130.0, 137.0, 137.3, 163.8; IR (neat) *v* 2964, 2927, 1494, 1455, 1373, 1167, 1029, 751, 700; Ms (ESI): *m*/*z* = 293.2 $[M+H]^+$. The relative configuration was assigned by NOESY analysis of this compound. NOE between the aromatic proton H_c of ***syn*-2e** and H_d was observed. Additionally, there were no observable NOEs between H_a and H_d, or H_b and H_c. These results indicate that H_a and H_b of ***syn*-2e** have the *syn* relationship.



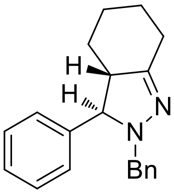
***anti*-2e**

***anti*-2e**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.02 (d, *J* = 6.9 Hz, 3H), 1.09 (d, *J* = 7.0 Hz, 3H), 1.22 (d, *J* = 6.7 Hz, 3H), 2.49-2.59 (m, 1H), 2.81-2.90 (m, 1H), 3.41 (d, *J* = 13.5 Hz, 1H), 3.85 (d, *J* = 14.1 Hz, 1H), 4.31 (d, *J* = 14.1 Hz, 1H), 7.18-7.29 (m, 6H), 7.30-7.35 (m, 2H), 7.38 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 6.72, 14.5, 19.5, 20.4, 28.1, 51.2, 57.5, 127.1, 127.7, 128.0, 128.1, 128.6, 130.0, 136.9, 140.6, 161.2; IR (neat) v 2963, 2927, 1495, 1456, 1377, 1169, 1020, 757, 700; Ms (ESI): *m*/*z* = 293.2 $[M+H]^+$. The relative configuration was assigned by NOESY analysis of this compound. NOEs between the aromatic proton H_c of ***anti*-2e** and H_b, H_a and H_d were observed. Additionally, there was no observable NOE between H_c and H_d. Comparing with ***syn*-2e**, these results indicate that H_a and H_b of ***anti*-2e** have the *anti* relationship.



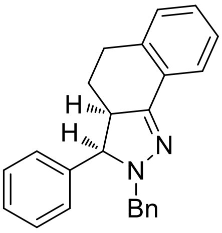
***syn*-2f**

Compound **2f**, yellow oil, yield: 85% (*syn* : *anti* = 5.7 : 1). ***syn*-2f**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.06-1.40 (m, 4H), 1.63-1.70 (m, 1H), 1.86-1.93 (m, 1H), 2.12-2.20 (m, 1H), 2.62-2.68 (m, 1H), 2.81-2.88 (m, 1H), 3.89 (d, *J* = 14.2 Hz, 1H), 4.23 (d, *J* = 10.9 Hz, 1H), 4.37 (d, *J* = 14.2 Hz, 1H), 7.20-7.29 (m, 6H), 7.30-7.39 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.3, 28.5, 29.1, 29.3, 52.9, 57.3, 70.2, 127.2, 127.3, 128.1, 128.2, 128.3, 129.7, 137.3, 137.9, 157.2; IR (neat) v 2931, 2854, 1494, 1454, 1177, 1028, 750, 700; Ms (ESI): *m*/*z* = 291.2 $[M+H]^+$. The relative configuration was assigned by NOESY analysis of this compound. NOE between the aromatic proton H_c of ***syn*-2f** and H_d was observed. Additionally, there were no observable NOEs between H_a and H_d, or H_b and H_c. These results indicate that H_a and H_b of ***syn*-2f** have the *syn* relationship.



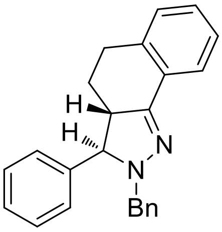
***anti*-2f**

***anti*-2f**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.18-1.33 (m, 2H), 1.35-1.45 (m, 1H), 1.76-1.82 (m, 1H), 1.89-1.95 (m, 1H), 1.98-2.12 (m, 2H), 2.61-2.71 (m, 2H), 3.61 (d, *J* = 12.7 Hz, 1H), 3.84 (d, *J* = 13.9 Hz, 1H), 4.12 (d, *J* = 13.9 Hz, 1H), 7.18-7.22 (m, 1H), 7.24-7.35 (m, 7H), 7.42 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.6, 25.9, 27.8, 31.4, 55.1, 58.3, 77.4, 127.0, 127.6, 127.7, 128.2, 128.7, 129.3, 138.1, 140.1, 156.4; IR (neat) v 2930, 2856, 1493, 1453, 1373, 1166, 1027, 756, 699; Ms (ESI): *m*/*z* = 291.2 $[M+H]^+$. The relative configuration was assigned by NOESY analysis of this compound. NOEs between the aromatic proton H_c of ***anti*-2f** and H_b, H_a and H_d were observed. Additionally, there was no observable NOE between H_c and H_d. Comparing with ***syn*-2f**, these results indicate that H_a and H_b of ***anti*-2f** have the *anti* relationship.



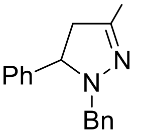
***syn*-2g**

Compound **2g**, yellow oil, yield: 80% (*syn* : *anti* = 3.5 : 1). ***syn*-2g**: ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.22-1.33 (m, 1H), 1.55-1.63 (m, 1H), 2.72-2.78 (m, 1H), 2.81-2.90 (m, 1H), 3.49-3.55 (m, 1H), 4.14 (d, J = 14.1 Hz, 1H), 4.65 (d, J = 10.8 Hz, 1H), 4.77 (d, J = 14.2 Hz, 1H), 7.04-7.31 (m, 13H), 7.97 (d, J = 7.3 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 23.9, 29.9, 49.8, 55.5, 70.1, 124.3, 126.5, 127.2, 127.8, 128.3, 128.4 (2C), 128.5, 128.9, 129.1, 129.6, 132.7, 136.8, 137.8, 152.4; IR (neat) ν 2931, 2849, 1474, 1454, 1359, 1029, 909, 763, 729, 700; Ms (ESI): m/z = 339.2 [M+H]$^+$. The relative configuration was assigned by NOESY analysis of this compound. There were no observable NOEs between H$_a$ and H$_d$, or H$_b$ and H$_c$. Comparing with ***anti*-2g**, these results indicate that H$_a$ and H$_b$ of ***syn*-2g** have the *syn* relationship.



***anti*-2g**

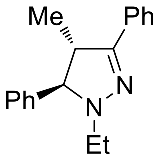
***anti*-2g**: ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.66-1.76 (m, 1H), 2.02-2.09 (m, 1H), 2.79-2.85 (m, 2H), 3.08-3.16 (m, 1H), 3.84 (d, J = 13.7 Hz, 1H), 3.97 (d, J = 14.2 Hz, 1H), 4.41 (d, J = 14.2 Hz, 1H), 7.08-7.13 (m, 1H), 7.18-7.40 (m, 11H), 7.48 (d, J = 7.7 Hz, 2H), 7.93-8.00 (m, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 26.7, 29.4, 54.5, 57.4, 76.7, 124.4, 126.7, 127.2, 127.9, 128.0, 128.2, 128.7, 128.8, 128.9, 129.0, 129.7, 137.3, 138.1, 140.0, 151.7; IR (neat) ν 2928, 2836, 1494, 1453, 1371, 1027, 908, 759, 729, 700; Ms (ESI): m/z = 339.2 [M+H]$^+$. The relative configuration was assigned by NOESY analysis of this compound. NOEs between the aromatic proton H$_c$ of ***anti*-2g** and H$_b$, H$_a$ and H$_d$ were observed. Comparing with ***syn*-2g**, these results indicate that H$_a$ and H$_b$ of ***anti*-2g** have the *anti* relationship.



2h

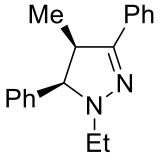
Compound **2h**, yellow oil, yield: 90%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.96 (m, 1H), 3.35 (dd, J = 16.0, 10.4 Hz, 1H), 3.96 (d, J = 14.3 Hz, 1H), 4.26 (dd, J = 14.0, 10.5 Hz, 1H), 4.53 (d, J = 14.3 Hz, 1H), 7.20-7.39 (m, 11H), 7.45 (d, J = 7.9 Hz, 2H), 7.62 (d, J = 8.1 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 43.1, 56.7, 69.1, 125.8, 127.3, 127.8, 127.9, 128.2, 128.5, 128.6, 128.8, 129.7, 133.3, 136.9, 140.8, 149.0; IR (neat) ν 2923, 2840, 1494, 1454, 1362, 1059, 910, 758, 699; Ms

(ESI): *m*/*z* = 313.2 [M+H]$^+$.



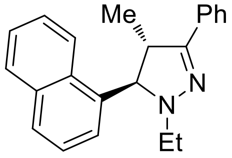
***anti*-2i**

Compound **2i**, yellow oil, yield: 70% (*anti* : *syn* = 8.4 : 1). ***anti*-2i**: ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.20 (t, *J* = 7.1 Hz, 3H), 1.32 (d, *J* = 6.8 Hz, 3H), 2.91-2.99 (m, 1H), 3.02-3.11 (m, 1H), 3.35-3.43 (m, 1H), 3.83 (d, *J* = 12.0 Hz, 1H), 7.27-7.39 (m, 6H), 7.45 (d, *J* = 7.4 Hz, 2H), 7.59 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 12.9, 16.8, 48.1, 50.5, 78.7, 126.4, 127.8, 128.0, 128.2, 128.5, 128.8, 133.4, 141.2, 152.9; IR (neat) ν 2966, 2930, 1496, 1455, 1363, 1166, 1031, 873, 754, 696; Ms (ESI): *m*/*z* = 265.2 [M+H]$^+$. The relative configuration was assigned by NOESY analysis of this compound. NOEs between the aromatic proton H$_c$ of ***anti*-2i** and H$_b$, H$_a$ and H$_d$ were observed. Additionally, there was no observable NOE between H$_c$ and H$_d$. These results indicate that H$_a$ and H$_b$ of ***anti*-2i** have the *anti* relationship.



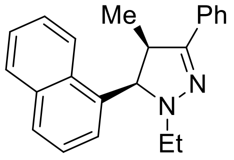
***syn*-2i**

***syn*-2i**: ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.75 (d, *J* = 7.3 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 2.83-2.91 (m, 1H), 3.11-3.19 (m, 1H), 3.47-3.55 (m, 1H), 4.41 (d, *J* = 9.4 Hz, 1H), 7.28-7.33 (m, 2H), 7.34-7.40 (m, 4H), 7.43 (d, *J* = 7.5 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 12.6, 12.8, 44.7, 47.8, 74.4, 126.2, 127.6, 128.3, 128.4, 128.5, 128.7, 132.6, 137.3, 154.9; IR (neat) ν 2969, 2929, 1496, 1456, 1364, 1162, 972, 752, 693; Ms (ESI): *m*/*z* = 265.2 [M+H]$^+$. The relative configuration was assigned by NOESY analysis of this compound. NOE between the aromatic proton H$_c$ of ***syn*-2i** and H$_d$ was observed. Additionally, there were no observable NOEs between H$_a$ and H$_d$, or H$_b$ and H$_c$. Comparing with ***anti*-2i**, these results indicate that H$_a$ and H$_b$ of ***syn*-2i** have the *syn* relationship.



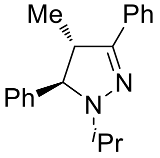
***anti*-2j**

Compound **2j**, yellow oil, yield: 68% (*anti* : *syn* = 9.0 : 1). ***anti*-2j**: ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.17 (t, *J* = 7.1 Hz, 3H), 1.37 (d, *J* = 6.8 Hz, 3H), 3.03-3.16 (m, 2H), 3.72 (brs, 1H), 4.53 (brs, 1H), 7.28-7.32 (m, 1H), 7.34-7.39 (m, 2H), 7.44-7.52 (m, 3H), 7.60-7.70 (m, 3H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.88-7.92 (m, 1H), 8.32-8.43 (m, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 12.9, 18.3, 27.6, 48.6, 72.6, 124.4, 125.6, 125.8, 125.9, 126.4, 128.2, 128.6, 128.7, 129.1, 129.2, 131.8, 133.4, 134.4, 134.5, 152.3; IR (neat) ν 2967, 2928, 2853, 1456, 1378, 1175, 1034, 972, 797, 776, 763, 695; Ms (ESI): *m*/*z* = 315.2 [M+H]$^+$. The relative configuration was assigned by NOESY analysis of this compound. NOEs between the aromatic proton H_c of ***anti*-2j** and H_b, H_a and H_d were observed. These results indicate that H_a and H_b of ***anti*-2j** have the *anti* relationship.



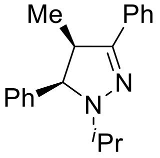
***syn*-2j**

***syn*-2j**: ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 0.61 (d, *J* = 7.3 Hz, 3H), 1.38 (t, *J* = 7.1 Hz, 3H), 2.88-2.96 (m, 1H), 3.21-3.29 (m, 1H), 3.87-3.94 (m, 1H), 5.08 (d, *J* = 9.5 Hz, 1H), 7.30-7.35 (m, 1H), 7.36-7.41 (m, 2H), 7.51-7.59 (m, 3H), 7.78 (d, *J* = 7.7 Hz, 2H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 7.1 Hz, 1H), 7.90-7.97 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 12.7, 12.8, 43.3, 48.2, 70.8, 122.6, 125.7, 125.8 (2C), 126.3, 126.4, 127.9, 128.6, 128.7, 129.2, 131.8, 132.6, 132.9, 133.9, 154.5; IR (neat) *ν* 2969, 2929, 2852, 1448, 1374, 1163, 971, 801, 783, 764, 693; Ms (ESI): *m*/*z* = 315.2 [M+H]$^+$. The relative configuration was assigned by NOESY analysis of this compound. NOE between the aromatic proton H_c of ***syn*-2j** and H_d was observed. Additionally, there was no observable NOE between H_a and H_d. Comparing with ***anti*-2j**, these results indicate that H_a and H_b of ***syn*-2j** have the *syn* relationship.



***anti*-2k**

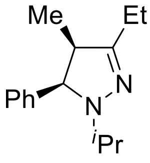
Compound **2k**, yellow oil, yield: 67% (*anti* : *syn* = 3.1 : 1). ***anti*-2k**: ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 1.09 (d, *J* = 6.4 Hz, 3H), 1.29 (d, *J* = 6.6 Hz, 3H), 1.33 (d, *J* = 6.9 Hz, 3H), 3.21 (m, 1H), 3.35 (m, 1H), 4.00 (d, *J* = 11.8 Hz, 1H), 7.27-7.39 (m, 6H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 17.2, 18.0, 21.6, 50.5, 51.9, 75.6, 126.3, 127.6, 127.7, 127.9, 128.5, 128.7, 133.7, 142.5, 151.6; IR (neat) *ν* 2969, 2928, 1494, 1454, 1361, 1176, 1027, 979, 762, 696; Ms (ESI): *m*/*z* = 279.2 [M+H]$^+$. The relative configuration was assigned by NOESY analysis of this compound. NOEs between the aromatic proton H_c of ***anti*-2k** and H_b, H_a and H_d were observed. Additionally, there was no observable NOE between H_c and H_d. These results indicate that H_a and H_b of ***anti*-2k** have the *anti* relationship.



***syn*-2k**

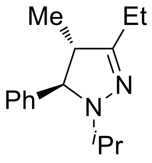
***syn*-2k**: ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 0.74 (d, *J* = 7.3 Hz, 3H), 1.02 (d, *J* = 6.4 Hz, 3H), 1.42 (d, *J* = 6.7 Hz, 3H), 3.13-3.22 (m, 1H), 3.44-3.52 (m, 1H), 4.62 (d, *J* = 9.7 Hz, 1H), 7.27-7.32 (m, 2H), 7.33-7.39 (m, 4H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 13.1, 16.6, 22.2, 44.4, 50.8, 71.5, 126.0, 127.5, 128.1, 128.4, 128.5, 128.6, 133.0, 137.8, 153.6; IR (neat) *ν* 2971, 2929, 1494, 1455, 1375, 1173, 1121, 763, 693; Ms (ESI): *m*/*z* = 279.2 [M+H]$^+$.

The relative configuration was assigned by NOESY analysis of this compound. NOE between the aromatic proton H_c of ***syn*-2k** and H_d was observed. Additionally, there were no observable NOEs between H_a and H_d, or H_b and H_c. Comparing with ***anti*-2k**, these results indicate that H_a and H_b of ***syn*-2k** have the *syn* relationship.



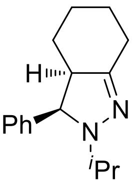
***syn*-2l**

Compound **2l**, yellow oil, yield: 72% (*syn* : *anti* = 2.3 : 1). ***syn*-2l**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.62 (d, J = 7.4 Hz, 3H), 0.96 (d, J = 6.4 Hz, 3H), 1.17 (t, J = 7.5 Hz, 3H), 1.28 (d, J = 6.7 Hz, 3H), 2.19-2.28 (m, 1H), 2.35-2.44 (m, 1H), 2.93-3.07 (m, 2H), 4.36 (d, J = 9.9 Hz, 1H), 7.23-7.27 (m, 1H), 7.30-7.34 (m, 2H), 7.36 (d, J = 7.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.7, 12.7, 16.2, 22.1, 22.5, 46.5, 50.9, 70.7, 127.2, 128.3, 128.4, 138.7, 159.3; IR (neat) v 2969, 2931, 1494, 1453, 1376, 1170, 751, 702; Ms (ESI): m/z = 231.2 $[M+H]^+$. The relative configuration was assigned by NOESY analysis of this compound. NOE between the aromatic proton H_c of ***syn*-2l** and H_d was observed. Additionally, there were no observable NOEs between H_a and H_d, or H_b and H_c. These results indicate that H_a and H_b of ***syn*-2l** have the *syn* relationship.



***anti*-2l**

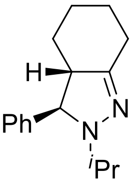
***anti*-2l**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.98 (d, J = 6.5 Hz, 3H), 1.11-1.15 (m, 6H), 1.17 (d, J = 6.7 Hz, 3H), 2.16-2.25 (m, 1H), 2.30-2.39 (m, 1H), 2.74-2.83 (m, 1H), 2.98-3.07 (m, 1H), 3.66 (d, J = 13.2 Hz, 1H), 7.25-7.29 (m, 1H), 7.31-7.35 (m, 2H), 7.42 (d, J = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.0, 14.7, 17.3, 21.4, 22.0, 52.0, 52.1, 75.6, 127.5, 127.8, 128.6, 142.4, 157.5; IR (neat) v 2967, 2930, 1456, 1376, 1162, 995, 750, 700; Ms (ESI): m/z = 231.2 $[M+H]^+$. The relative configuration was assigned by NOESY analysis of this compound. NOEs between H_a and H_d of ***anti*-2l** was observed. Additionally, there was no observable NOE between H_c and H_d. Comparing with ***syn*-2l**, these results indicate that H_a and H_b of ***anti*-2l** have the *anti* relationship.



***syn*-2m**

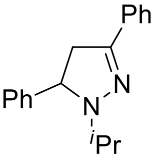
Compound **2m**, yellow oil, yield: 82% (*syn* : *anti* = 3.8 : 1). ***syn*-2m**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95-1.05 (m, 4H), 1.06-1.12 (m, 1H), 1.17-1.27 (m, 4H), 1.29-1.39 (m, 1H), 1.63-1.68 (m, 1H), 1.85-1.91 (m, 1H), 2.14-2.22 (m, 1H), 2.64-2.70 (m, 1H), 2.90-2.97 (m, 1H), 3.09 (hept, J = 6.5 Hz, 1H), 4.46 (d, J = 11.3 Hz, 1H), 7.21-7.25 (m, 1H), 7.28-7.33 (m, 2H), 7.34-7.38 (m, 2H); ^{13}C

NMR (125 MHz, $CDCl_3$) δ 17.7, 21.7, 25.3, 28.1, 29.0, 29.7, 52.2, 52.4, 68.4, 126.9, 128.1 (2C), 139.6, 156.0; IR (neat) v 2928, 2855, 1489, 1455, 1363, 1173, 992, 747, 698 cm^{-1}; Ms (ESI): *m*/*z* = 243.2 $[M+H]^+$. The relative configuration was assigned by NOESY analysis of this compound. NOEs between the aromatic proton H_{11} of ***syn*-2m** and H_{4a}, H_{4b} were observed. Additionally, there was no observable NOE between H_{11} and H_{3a}. These results indicate that H_3 and H_{3a} of ***syn*-2m** have the *syn* relationship.



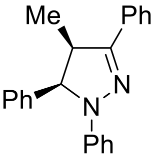
***anti*-2m**

***anti*-2m**: ^1H NMR (500 MHz, $CDCl_3$) δ 1.03 (d, J = 6.4 Hz, 3H), 1.19 (d, J = 6.7 Hz, 3H), 1.25-1.34 (m, 2H), 1.39-1.49 (m, 1H), 1.77-1.85 (m, 1H), 1.91-1.97 (m, 1H), 2.02-2.14 (m, 2H), 2.56-2.67 (m, 2H), 3.02 (hept, J = 6.6 Hz, 1H), 3.79 (d, J = 12.4 Hz, 1H), 7.26-7.29 (m, 1H), 7.30-7.35 (m, 2H), 7.37-7.41 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.2, 21.8, 24.7, 26.2, 27.9, 31.7, 52.0, 55.6, 74.2, 127.3, 127.4, 128.6, 142.7, 155.1; IR (neat) v 2929, 2856, 1494, 1452, 1362, 1166, 990, 748, 700 cm^{-1}; Ms (ESI): *m*/*z* = 243.2 $[M+H]^+$.



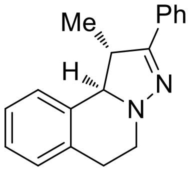
2n

Compound **2n**, yellow oil, yield: 89%.^1H NMR (500 MHz, $CDCl_3$) δ 0.78 (d, J = 7.3 Hz, 3H), 3.36-3.44 (m, 1H), 3.97 (d, J = 14.2 Hz, 1H), 4.31 (d, J = 9.4 Hz, 1H), 4.58 (d, J = 14.2 Hz, 1H), 7.22-7.26 (m, 1H), 7.27-7.48 (m, 12H), 7.69 (d, J = 7.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.0, 44.5, 56.3, 72.7, 126.2, 127.3, 127.7, 128.2, 128.5, 128.6, 128.6, 128.6, 129.9, 132.6, 136.6, 136.7, 154.8; IR (neat) v 2969, 2927, 1495, 1455, 1375, 1169, 1028, 761, 699; Ms (ESI): *m*/*z* = 265.2 $[M+H]^+$.



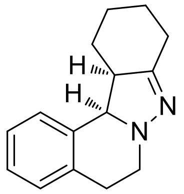
2o

Compound **2o**, yellow oil, yield: 76%. ^1H NMR (500 MHz, $CDCl_3$) δ 1.46 (d, J = 7.1 Hz, 3H), 3.45-3.52 (m, 1H), 4.86 (d, J = 4.5 Hz, 1H), 6.74-6.79 (m, 1H), 7.06 (d, J = 8.5 Hz, 2H), 7.16-7.20 (m, 2H), 7.24-7.27 (m, 3H), 7.28-7.33 (m, 3H), 7.35-7.40 (m, 2H), 7.73 (d, J = 8.1 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.6, 50.9, 72.6, 113.2, 119.0, 125.7, 126.2, 127.8, 128.5, 128.7, 129.1, 129.3, 132.3, 141.7, 144.5, 151.1; IR (neat) v 2963, 2925, 1597, 1503, 1391, 1135, 1069, 763, 691; Ms (ESI): *m*/*z* = 313.2 $[M+H]^+$. The relative configuration was assigned by NOESY analysis of this compound. NOE between the aromatic proton H_c of **2o** and H_d was observed. Additionally, there were no observable NOEs between H_a and H_d, or H_b and H_c. These results indicate that H_a and H_b of **2o** have the *syn* relationship.



2p

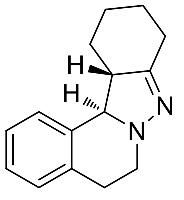
Compound **2p**, yellow oil, yield: 84%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.45 (d, J = 7.2 Hz, 3H), 2.51-2.56 (m, 1H), 3.02-3.11 (m, 1H), 3.34-3.42 (m, 1H), 3.55-3.61 (m, 1H), 4.15 (dd, J = 13.7, 4.8 Hz, 1H), 4.63 (brs, 1H), 7.00 (d, J = 7.6 Hz, 1H), 7.10-7.18 (m, 2H), 7.21-7.26 (m, 2H), 7.30-7.34 (m, 2H), 7.63 (d, J = 8.1 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.7, 26.0, 47.8, 49.6, 69.9, 126.2, 126.4, 126.5, 127.1, 128.5, 128.6, 128.9, 132.0, 135.0, 137.6, 156.5; IR (neat) v 3059, 3020, 2965, 2929, 1494, 1451, 1360, 1159, 1078, 930, 860, 764, 747, 694 cm^{-1}; Ms (ESI): m/z = 263.2 $[M+H]^+$. The relative configuration was assigned by NOESY analysis of this compound. NOE between the aromatic proton H_{10} of **2p** and H_1 was observed. Additionally, there was no observable NOE between H_{10} and H_{11}. These results indicate that H_1 and H_{10b} of **2p** have the *anti* relationship.



5a

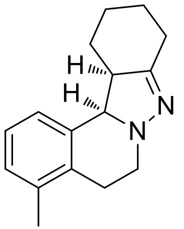
Compound **5a**, yellow oil, yield: 85%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.60-0.70 (m, 1H), 1.10-1.21 (m, 1H), 1.31-1.42 (m, 1H), 1.72-1.79 (m, 1H), 1.80-1.89 (m, 2H), 2.05-2.13 (m, 1H), 2.39 (d, J = 15.6 Hz, 1H), 2.64 (dd, J = 14.9, 4.4 Hz, 1H), 2.90-2.98 (m, 1H), 3.12-3.25 (m, 2H), 3.97 (ddd, J = 13.5, 4.2, 1.7 Hz, 1H), 5.03 (d, J = 11.3 Hz, 1H), 6.92 (d, J = 7.3 Hz, 1H), 7.04 (d, J = 7.2 Hz, 1H), 7.10-7.18 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.9, 25.4, 25.6, 28.1, 29.8, 48.8, 50.7, 63.6, 125.9, 126.2, 128.5, 128.9, 134.4, 137.0, 159.2; IR (neat) v 2931, 2854, 1489, 1448, 1358, 1074, 919, 836, 748 cm^{-1}; Ms (ESI): m/z = 227.2 $[M+H]^+$. The relative configuration was assigned by NOESY analysis of this compound. NOEs between the aromatic proton H_1 of **5a** and H_{12a}, H_{12b} were observed. Additionally, there was no observable NOE between H_1 and H_{13}, or H_{14} and H_{12a} or H_{12b}. These results indicate that H_{13} and H_{14} of **5a** have the *syn* relationship.

To further comfirm the relative stereochemistry of the products, the other diastereoisomer ***anti*-5a** was obtained by using $K_2S_2O_8$ as oxidant instead of O_2, and NOESY analysis of ***anti*-5a** was carried out. NOEs between the aromatic proton H_1 of ***anti*-5a** and H_{13}, H_{14} and H_{12a}, H_{12b} were observed. Comparing with **5a**, these results indicate that H_{13} and H_{14} of ***anti*-5a** have the *anti* relationship.



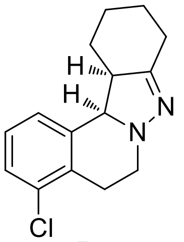
***anti*-5a**

Compound ***anti*-5a**, yellow oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.39-1.50 (m, 2H), 1.64-1.73 (m, 1H), 1.81-1.88 (m, 1H), 1.92-2.02 (m, 1H), 2.07-2.15 (m, 1H), 2.17-2.23 (m, 1H), 2.48-2.53 (m, 1H), 2.57-2.62 (m, 1H), 2.82-2.87 (m, 1H), 2.90-2.98 (m, 1H), 3.22-3.29 (m, 1H), 3.94 (ddd, *J* = 13.5, 4.9, 1.4 Hz, 1H), 4.49 (d, *J* = 3.4 Hz, 1H), 7.02-7.07 (m, 2H), 7.11-7.16 (m, 1H), 7.19-7.24 (m, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 25.6, 25.7, 28.7, 28.8, 33.8, 47.9, 58.4, 66.1, 126.2, 126.3, 127.1, 128.7, 135.3, 138.7, 160.2; IR (neat) *v* 2927, 2853, 1489, 1448, 1363, 1163, 1077, 746 cm^{-1}; Ms (ESI): *m*/*z* = 227.2 [M+H]$^+$.



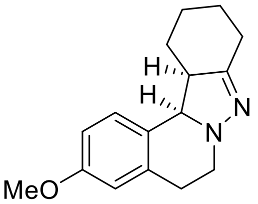
5b

Compound **5b**, yellow oil, yield: 82%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.54-0.66 (m, 1H), 1.10-1.20 (m, 1H), 1.30-1.40 (m, 1H), 1.71-1.87 (m, 3H), 2.05-2.13 (m, 1H), 2.24 (s, 3H), 2.45 (d, J = 16.1 Hz, 1H), 2.60-2.75 (m, 2H), 3.12-3.24 (m, 2H), 3.99 (ddd, *J* = 13.7, 4.4, 1.6 Hz, 1H), 5.03 (d, *J* = 11.2 Hz, 1H), 6.77 (d, *J* = 7.5 Hz, 1H), 6.99-7.08 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 19.4, 21.9, 24.9, 25.5, 28.1, 29.6, 48.5, 50.8, 63.8, 125.2, 126.2, 127.6, 134.2, 135.6, 135.8, 159.0; IR (neat) *v* 2933, 2857, 1463, 1360, 1171, 927, 835, 757 cm^{-1}; Ms (ESI): *m*/*z* = 241.2 [M+H]$^+$.



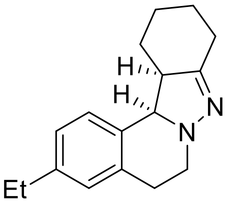
5c

Compound **5c**, yellow oil, yield: 89%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.61-0.71 (m, 1H), 1.10-1.21 (m, 1H), 1.31-1.43 (m, 1H), 1.76-1.92 (m, 3H), 2.05-2.13 (m, 1H), 2.37 (d, *J* = 15.7 Hz, 1H), 2.63 (dd, *J* = 15.1, 4.3 Hz, 1H), 2.83-2.91 (m, 1H), 3.07-3.14 (m, 1H), 3.17-3.25 (m, 1H), 3.94-4.00 (m, 1H), 4.96 (d, *J* = 11.3 Hz, 1H), 6.91-6.93 (m, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 7.10 (dd, *J* = 8.1, 1.9 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 24.8, 24.9, 25.6, 28.0, 29.8, 48.7, 50.5, 63.4, 126.4, 128.2, 130.2, 131.5, 135.4, 136.3, 159.1; IR (neat) *v* 2933, 2856, 1484, 1357, 1177, 1090, 810, 710cm^{-1}; Ms (ESI): *m*/*z* = 261.1 [M+H]$^+$.



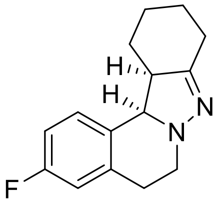
5d

Compound **5d**, yellow oil, yield: 70%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.64-0.74 (m, 1H), 1.10-1.21 (m, 1H), 1.32-1.42 (m, 1H), 1.72-1.88 (m, 3H), 2.04-2.12 (m, 1H), 2.32-2.37 (m, 1H), 2.60-2.65 (m, 1H), 2.88-2.97 (m, 1H), 3.11-3.21 (m, 2H), 3.78 (s, 3H), 3.92-3.97 (m, 1H), 4.98 (d, *J* = 11.1 Hz, 1H), 6.58 (d, *J* = 2.4 Hz, 1H), 6.72-6.75 (m, 1H), 6.83 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 24.9, 25.6, 25.7, 28.1, 29.7, 48.7, 50.8, 55.3, 63.2, 112.5, 113.3, 126.3, 129.6, 138.2, 157.8, 159.1; IR (neat) ν 2932, 2855, 1609, 1500, 1457, 1264, 1041, 860, 836 cm^{-1}; Ms (ESI): *m*/*z* = 257.2 [M+H]$^+$.



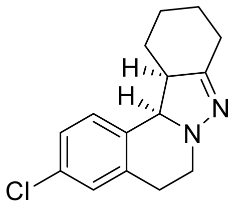
5e

Compound **5e**, yellow oil, yield: 75%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.65-0.74 (m, 1H), 1.12-1.24 (m, 4H), 1.32-1.42 (m, 1H), 1.73-1.90 (m, 3H), 2.05-2.13 (m, 1H), 2.33-2.39 (m, 1H), 2.57-2.67 (m, 3H), 2.88-2.97 (m, 1H), 3.12-3.23 (m, 2H), 3.96 (ddd, *J* = 13.5, 4.4, 1.8 Hz, 1H), 5.00 (d, *J* = 11.2 Hz, 1H), 6.84 (d, *J* = 7.9 Hz, 1H), 6.88 (s, 1H), 7.00 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 15.6, 24.9, 25.5, 25.6, 28.1, 28.5, 29.7, 48.8, 50.7, 63.5, 125.6, 128.2, 128.5, 131.6, 136.8, 142.1, 159.0; IR (neat) ν 2931, 2856, 1498, 1446, 1358, 1074, 885, 838 cm^{-1}; Ms (ESI): *m*/*z* = 255.2 [M+H]$^+$.



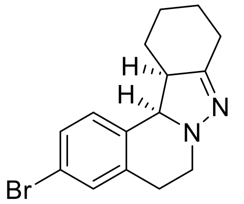
5f

Compound **5f**, yellow oil, yield: 92%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.59-0.68 (m, 1H), 1.09-1.20 (m, 1H), 1.31-1.42 (m, 1H), 1.73-1.86 (m, 3H), 2.04-2.12 (m, 1H), 2.33-2.39 (m, 1H), 2.60-2.66 (m, 1H), 2.88-2.97 (m, 1H), 3.08-3.23 (m, 2H), 3.95 (ddd, *J* = 13.5, 4.3, 1.7 Hz, 1H), 4.98 (d, *J* = 11.2 Hz, 1H), 6.75 (d, *J* = 9.1 Hz, 1H), 6.84-6.89 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 24.9, 25.5, 25.6, 28.0, 29.7, 48.4, 50.6, 63.2, 113.2 ($^2J_{\mathrm{CF}}$ = 21.4 Hz), 115.2 ($^2J_{\mathrm{CF}}$ = 20.4 Hz), 129.9 ($^4J_{\mathrm{CF}}$ = 3.1 Hz), 130.0 ($^3J_{\mathrm{CF}}$ = 8.1 Hz), 139.1 ($^3J_{\mathrm{CF}}$ = 7.4 Hz), 159.0, 161.1 ($^1J_{\mathrm{CF}}$ = 244 Hz); IR (neat) ν 2933, 2857, 1614, 1495, 1447, 1249, 1142, 865, 837 cm^{-1}; Ms (ESI): *m*/*z* = 245.2 [M+H]$^+$.



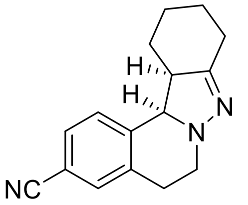
5g

Compound **5g**, yellow oil, yield: 90%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.59-0.69 (m, 1H), 1.09-1.20 (m, 1H), 1.32-1.42 (m, 1H), 1.73-1.88 (m, 3H), 2.05-2.13 (m, 1H), 2.33-2.39 (m, 1H), 2.60-2.66 (m, 1H), 2.87-2.95 (m, 1H), 3.08-3.15 (m, 1H), 3.16-3.24 (m, 1H), 3.95 (ddd, J = 13.6, 4.3, 1.8 Hz, 1H), 4.98 (d, J = 11.2 Hz, 1H), 6.85 (d, J = 8.3 Hz, 1H), 7.05 (s, 1H), 7.13 (dd, J = 8.5, 1.8 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 24.9, 25.2, 25.6, 28.0, 29.8, 48.4, 50.6, 63.2, 126.2, 128.7, 129.8, 131.9, 132.9, 138.9, 159.3; IR (neat) ν 2934, 2857, 1481, 1447, 1357, 1264, 1094, 908, 867, 730 cm^{-1}; Ms (ESI): m/z = 261.1 [M+H]$^+$.



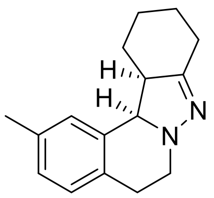
5h

Compound **5h**, yellow oil, yield: 87%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.59-0.70 (m, 1H), 1.09-1.20 (m, 1H), 1.31-1.42 (m, 1H), 1.72-1.88 (m, 3H), 2.04-2.13 (m, 1H), 2.32-2.38 (m, 1H), 2.59-2.66 (m, 1H), 2.87-2.95 (m, 1H), 3.07-3.25 (m, 2H), 3.95 (ddd, J = 13.6, 4.3, 1.7 Hz, 1H), 4.96 (d, J = 11.2 Hz, 1H), 6.79 (d, J = 8.2 Hz, 1H), 7.21 (s, 1H), 7.27 (d, J = 8.3 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 24.9, 25.2, 25.5, 28.0, 29.8, 48.4, 50.5, 63.3, 120.0, 129.1, 130.2, 131.6, 133.5, 139.3, 159.1; IR (neat) ν 2932, 2856, 1478, 1446, 1357, 1084, 861, 838 cm^{-1}; Ms (ESI): m/z = 305.1 [M+H]$^+$.



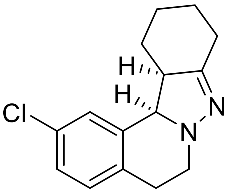
5i

Compound **5i**, yellow oil, yield: 90%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.51-0.61 (m, 1H), 1.09-1.20 (m, 1H), 1.33-1.43 (m, 1H), 1.74-1,90 (m, 3H), 2.05-2.14 (m, 1H), 2.40-2.47 (m, 1H), 2.61-2.67 (m, 1H), 2.90-2.99 (m, 1H), 3.08-3.17 (m, 1H), 3.22-3.30 (m, 1H), 4.00 (ddd, J = 13.7, 4.3, 1.8 Hz, 1H), 5.02 (d, J = 11.4 Hz, 1H), 7.03 (d, J = 8.0 Hz, 1H), 7.36 (s, 1H), 7.44 (d, J = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 24.8, 25.1, 25.5, 28.0, 30.0, 48.3, 50.5, 63.6, 110.2, 119.0, 129.3, 129.4, 132.6, 138.5, 140.5, 159.3; IR (neat) ν 2934, 2857, 2227, 1491, 1446, 1358, 1074, 895, 839, 729 cm^{-1}; Ms (ESI): m/z = 252.1 [M+H]$^+$.



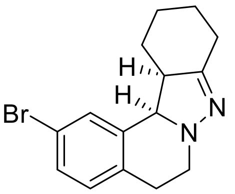
5j

Compound **5j**, yellow oil, yield: 85%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.61-0.71 (m, 1H), 1.11-1.21 (m, 1H), 1.32-1.43 (m, 1H), 1.73-1.89 (m, 3H), 2.05-2.13 (m, 1H), 2.30 (s, 3H), 2.33-2.38 (m, 1H), 2.60-2.66 (m, 1H), 2.84-2.93 (m, 1H), 3.10-3.24 (m, 2H), 3.96 (ddd, *J* = 13.5, 4.1, 1.7 Hz, 1H), 4.98 (d, *J* = 11.3 Hz, 1H), 6.74 (s, 1H), 6.94 (brs, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 21.3, 25.0, 25.1, 25.7, 28.1, 29.9, 49.0, 50.7, 63.6, 127.0, 128.7, 129.0, 133.9, 134.3, 135.3, 159.0; IR (neat) *v* 2930, 2855, 1502, 1446, 1357, 1073, 836, 809 cm^{-1}; Ms (ESI): *m*/*z* = 241.2 [M+H]$^+$.



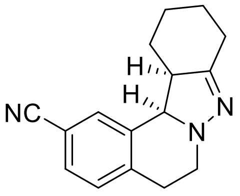
5k

Compound **5k**, yellow oil, yield: 91%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.61-0.71 (m, 1H), 1.10-1.21 (m, 1H), 1.33-1.43 (m, 1H), 1.76-1.92 (m, 3H), 2.05-2.13 (m, 1H), 2.34-2.41 (m, 1H), 2.60-2.67 (m, 1H), 2.81-2.91 (m, 1H), 3.06-3.14 (m, 1H), 3.17-3.25 (m, 1H), 3.97 (ddd, *J* = 13.6, 4.3, 1.7 Hz, 1H), 4.96 (d, *J* = 11.3 Hz, 1H), 6.92 (d, *J* = 1.8 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 7.10 (dd, *J* = 8.2, 2.1 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 24.8, 24.9, 25.6, 28.0, 29.8, 48.6, 50.5, 63.4, 126.4, 128.2, 130.2, 131.5, 135.4, 136.3, 159.1; IR (neat) *v* 2965, 2929, 1494, 1451, 1360, 1159, 1078, 930, 860 cm^{-1}; Ms (ESI): *m*/*z* = 261.1 [M+H]$^+$.



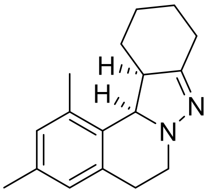
5l

Compound **5l**, yellow oil, yield: 86%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.60-0.70 (m, 1H), 1.10-1.21 (m, 1H), 1.33-1.43 (m, 1H), 1.73-1.92 (m, 3H), 2.05-2.14 (m, 1H), 2.33-2.39 (m, 1H), 2.60-2.67 (m, 1H), 2.80-2.89 (m, 1H), 3.06-3.25 (m, 2H), 3.97 (ddd, *J* = 13.6, 4.2, 1.5 Hz, 1H), 4.96 (d, *J* = 11.3 Hz, 1H), 6.93 (d, *J* = 8.1 Hz, 1H), 7.07 (s, 1H), 7.23-7.26 (m, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 24.9 (2C), 25.6, 28.0, 29.8, 48.6, 50.6, 63.3, 119.4, 129.3, 130.5, 131.2, 136.0, 136.7, 159.2; IR (neat) *v* 2932, 2855, 1481, 1446, 1357, 1176, 1075, 922, 836, 807cm^{-1}; Ms (ESI): *m*/*z* = 305.1 [M+H]$^+$.



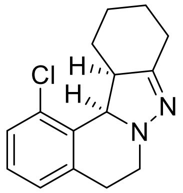
5m

Compound **5m**, yellow oil, yield: 89%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.51-0.61 (m, 1H), 1.06-1.18 (m, 1H), 1.33-1.44 (m, 1H), 1.76-1.91 (m, 3H), 2.05-2.14 (m, 1H), 2.43-2.48 (m, 1H), 2.60-2.66 (m, 1H), 2.93-3.01 (m, 1H), 3.09-3.16 (m, 1H), 3.21-3.28 (m, 1H), 4.00 (ddd, *J* = 13.6, 4.3, 1.4 Hz, 1H), 4.99 (d, *J* = 11.2 Hz, 1H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.23 (s, 1H), 7.40 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 24.8, 25.5, 25.6, 27.9, 29.9, 48.2, 50.4, 63.2, 110.0, 119.0, 129.6, 129.9, 132.2, 136.1, 142.8, 159.2; IR (neat) *v* 2934, 2857, 2227, 1494, 1447, 1358, 1169, 1074, 913, 837, 729 cm^{-1}; Ms (ESI): *m*/*z* = 252.1 [M+H]$^+$.



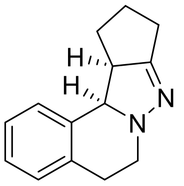
5n

Compound **5n**, yellow oil, yield: 71%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.44-0.53 (m, 1H), 1.19-1.42 (m, 3H), 1.62-1.69 (m, 1H), 1.84-1.90 (m, 1H), 2.09-2.21 (m, 4H), 2.26 (s, 3H), 2.33-2.38 (m, 1H), 2.63-2.69 (m, 1H), 2.71-2.79 (m, 1H), 2.99-3.06 (m, 1H), 3.21-3.29 (m, 1H), 3.90 (ddd, *J* = 13.4, 3.7, 2.2 Hz, 1H), 5.16 (d, *J* = 12.0 Hz, 1H), 6.74 (s, 1H), 6.84 (s, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 19.5, 21.0, 25.1, 26.2, 27.0, 28.6, 30.2, 49.4, 51.3, 60.6, 127.0, 129.3, 130.6, 134.9, 135.6, 137.6, 160.2; IR (neat) *v* 2929, 2856, 1445, 1358, 1182, 1070, 849, 735 cm^{-1}; Ms (ESI): *m*/*z* = 255.2 [M+H]$^+$.



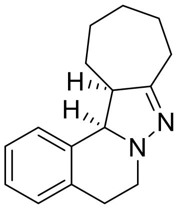
5o

Compound **5o**, yellow oil, yield: 79%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.42-0.52 (m, 1H), 1.20-1.28 (m, 1H), 1.34-1.45 (m, 1H), 1.64-1.92 (m, 3H), 2.09-2.17 (m, 1H), 2.39-2.45 (m, 1H), 2.62-2.68 (m, 1H), 2.76-2.84 (m, 1H), 3.00-3.07 (m, 1H), 3.33-3.41 (m, 1H), 3.95 (ddd, *J* = 13.6, 3.7, 2.0 Hz, 1H), 5.33 (d, *J* = 11.9 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 7.07-7.11 (m, 1H), 7.22 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 25.0, 25.8, 26.9, 28.5, 29.8, 49.1, 51.5, 61.3, 127.2, 127.3, 127.7, 133.0, 133.3, 140.0, 160.5; IR (neat) *v* 2931, 2855, 1457, 1443, 1358, 1187, 1071, 955, 825, 781 cm^{-1}; Ms (ESI): *m*/*z* = 261.1 [M+H]$^+$.



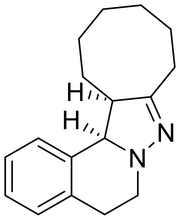
5p

Compound **5p**, yellow oil, yield: 62%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.02-1.13 (m, 1H), 1.86-1.93 (m, 1H), 1.96-2.08 (m, 2H), 2.12-2.21 (m, 1H), 2.28-2.36 (m, 1H), 2.37-2.43 (m, 1H), 3.06-3.15 (m, 1H), 3.16-3.23 (m, 1H), 3.58-3.66 (m, 1H), 3.97-4.03 (m, 1H), 5.01 (d, *J* = 10.3 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 7.10-7.19 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.6, 25.1, 26.8, 27.6, 48.9, 56.7, 66.2, 126.1, 126.2, 128.3, 129.1, 134.1, 136.6, 169.5; IR (neat) ν 2956, 2869, 1490, 1449, 1133, 1066, 916, 748 cm^{-1}; Ms (ESI): m/z = 213.1 $[M+H]^+$.



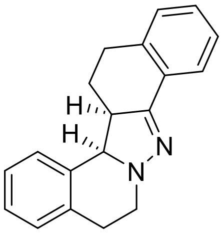
5q

Compound **5q**, yellow oil, yield: 82%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.27-1.37 (m, 3H), 1.42-1.75 (m, 4H), 1.86-1.96 (m, 1H), 2.40-2.56 (m, 3H), 3.03-3.12 (m, 2H), 3.35-3.42 (m, 1H), 3.89-3.96 (m, 1H), 4.79 (d, *J* = 10.0 Hz, 1H), 7.03-7.08 (m, 2H), 7.12-7.18 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.4, 26.7, 27.2, 28.8, 30.5, 30.9, 48.9, 53.4, 66.8, 125.8, 126.3, 128.3, 129.1, 134.0, 137.1, 163.0; IR (neat) ν 2924, 2851, 1489, 1449, 1363, 1142, 1071, 926, 747 cm^{-1}; Ms (ESI): m/z = 241.2 $[M+H]^+$.



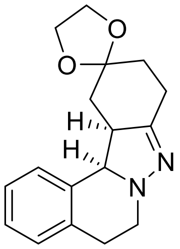
5r

Compound **5r**, yellow oil, yield: 71%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20-1.35 (m, 3H), 1.40-1.59 (m, 4H), 1.65-1.88 (m, 3H), 2.38-2.45 (m, 1H), 2.58-2.65 (m, 2H), 3.00-3.12 (m, 2H), 3.26-3.32 (m, 1H), 3.86-3.94 (m, 1H), 4.60 (d, *J* = 9.8 Hz, 1H), 7.04-7.10 (m, 2H), 7.12-7.18 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.2, 25.4, 25.8, 26.1, 26.9, 28.0, 29.2, 49.4, 50.9, 67.8, 125.8, 126.4, 127.8, 129.0, 134.3, 137.0, 163.0; IR (neat) ν 2925, 2853, 1490, 1457, 1358, 1073, 1017, 926, 746 cm^{-1}; Ms (ESI): m/z = 255.2 $[M+H]^+$.



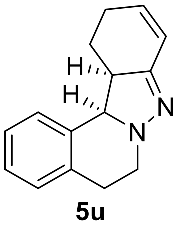
5s

Compound **5s**, yellow oil, yield: 78%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.28-1.38 (m, 1H), 2.22-2.28 (m, 1H), 2.42-2.48 (m, 1H), 2.83-2.90 (m, 1H), 2.93-3.02 (m, 1H), 3.09-3.17 (m, 1H), 3.29-3.36 (m, 1H), 3.57-3.64 (m, 1H), 4.17 (dd, *J* = 13.6, 4.6 Hz, 1H), 5.13 (d, *J* = 10.4 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 2H), 7.08-7.14 (m, 2H), 7.15-7.22 (m, 3H), 7.92 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 25.3, 26.1, 30.0, 48.8, 49.2, 65.5, 124.3, 126.0, 126.4, 126.6, 128.0, 128.7, 128.8, 129.0, 129.2, 133.7, 136.7, 137.7, 154.6; IR (neat) *v* 2932, 2867, 1491, 1461, 1365, 1073, 919, 751, 729 cm^{-1}; Ms (ESI): *m*/*z* = 275.2 [M+H]$^+$.



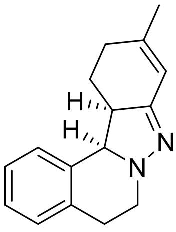
5t

Compound **5t**, yellow oil, yield: 75%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.04 (t, *J* = 12.9 Hz, 1H), 1.45-1.53 (m, 1H), 1.79-1.89 (m, 2H), 2.37-2.45 (m, 2H), 2.63 (dd, *J* = 15.1, 5.0 Hz, 1H), 2.91-2.99 (m, 1H), 3.13-3.20 (m, 1H), 3.53-3.61 (m, 1H), 3.91-4.02 (m, 5H), 5.06 (d, *J* = 11.4 Hz, 1H), 6.87 (d, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 7.3 Hz, 1H), 7.10-7.18 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 24.5, 25.5, 33.3, 37.7, 48.5, 48.9, 64.3, 64.6, 64.8, 109.0, 126.3, 126.4, 128.4, 129.1, 133.9, 137.0, 156.6; IR (neat) *v* 2954, 2930, 2888, 1490, 1455, 1351, 1264, 1116, 1056, 1029, 927, 749 cm^{-1}; Ms (ESI): *m*/*z* = 285.2 [M+H]$^+$.



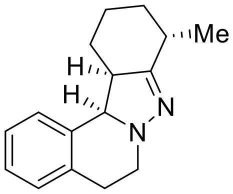
5u

Compound **5u**, yellow oil, yield: 78%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.14-1.24 (m, 1H), 2.10-2.16 (m, 1H), 2.26-2.32 (m, 2H), 2.39-2.45 (m, 1H), 3.03-3.12 (m, 1H), 3.23-3.31 (m, 1H), 3.37-3.44 (m, 1H), 4.05 (dd, *J* = 13.6, 4.7 Hz, 1H), 4.99 (d, *J* = 10.3 Hz, 1H), 6.02-6.07 (m, 1H), 6.31 (d, *J* = 10.2 Hz, 1H), 6.97 (d, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 7.4 Hz, 1H), 7.11-7.19 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 24.8, 25.8, 25.9, 47.9, 48.4, 64.9, 121.2, 125.9, 126.4, 128.0, 129.2, 133.7, 135.2, 136.7, 155.5; IR (neat) *v* 3034, 2930, 2870, 1490, 1449, 1351, 1201, 1132, 1073, 920, 852, 750 cm^{-1}; Ms (ESI): *m*/*z* = 225.1 [M+H]$^+$.



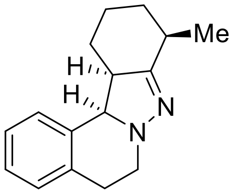
5v

Compound **5v**, yellow oil, yield: 71%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.15-1.25 (m, 1H), 1.79 (s, 3H), 2.07-2.17 (m, 2H), 2.26-2.42 (m, 2H), 3.04-3.12 (m, 1H), 3.21-3.37 (m, 2H), 4.03 (ddd, J = 13.5, 4.6, 1.2 Hz, 1H), 4.96 (d, J = 10.2 Hz, 1H), 6.08 (s, 1H), 6.96 (d, J = 7.4 Hz, 1H), 7.03 (d, J = 7.5 Hz, 1H), 7.10-7.18 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 24.0, 24.9, 25.6, 31.2, 47.6, 48.5, 64.6, 116.9, 125.9, 126.3, 128.1, 129.2, 133.8, 136.7, 145.4, 156.6; IR (neat) ν 3018, 2929, 2868, 1489, 1449, 1385, 1073, 921, 851, 749 cm^{-1}; Ms (ESI): m/z = 239.2 [M+H]$^+$.



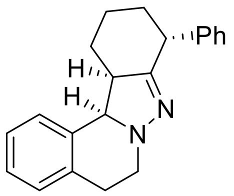
5w1

Compound **5w1**, yellow oil, yield: 61%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.59-0.69 (m, 1H), 1.15 (d, J = 7.3 Hz, 3H), 1.39-1.47 (m, 1H), 1.51-1.66 (m, 3H), 1.80-1.87 (m, 1H), 2.37-2.42 (m, 1H), 2.84-2.98 (m, 2H), 3.12-3.19 (m, 1H), 3.36-3.43 (m, 1H), 3.97 (ddd, J = 13.5, 4.3, 1.8 Hz, 1H), 5.01 (d, J = 11.3 Hz, 1H), 6.93 (d, J = 7.2 Hz, 1H), 7.04 (d, J = 7.2 Hz, 1H), 7.11-7.19 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 18.7, 19.8, 25.5, 30.2, 31.2, 32.0, 47.4, 48.8, 63.6, 125.9, 126.2, 128.6, 128.9, 134.4, 137.0, 162.8; IR (neat) ν 2926, 2854, 1489, 1456, 1374, 1261, 1074, 1024, 804, 746 cm^{-1}; Ms (ESI): m/z = 241.2 [M+H]$^+$. The relative configuration was determined by NOESY analysis of this compound. NOEs between proton H_{13} of **5w1** and H_{15} was observed.



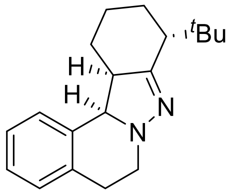
5w2

Compound **5w2**, yellow oil, yield: 17%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.58-0.68 (m, 1H), 0.87-0.95 (m, 1H), 1.19 (d, J = 6.5 Hz, 3H), 1.38-1.48 (m, 1H), 1.71-1.87 (m, 3H), 2.21-2.28 (m, 1H), 2.35-2.41 (m, 1H), 2.89-2.97 (m, 1H), 3.12-3.26 (m, 2H), 4.02 (ddd, J = 13.5, 4.2, 1.9 Hz, 1H), 5.03 (d, J = 11.3 Hz, 1H), 6.93 (d, J = 7.2 Hz, 1H), 7.04 (d, J = 6.5 Hz, 1H), 7.10-7.18 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 17.4, 25.1, 25.3, 30.1, 34.6, 34.9, 48.9, 50.9, 63.8, 125.9, 126.1, 128.6, 128.8, 134.7, 137.2, 162.9; IR (neat) ν 2927, 2853, 1489, 1448, 1374, 1184, 1063, 861, 747 cm^{-1}; Ms (ESI): m/z = 241.2 [M+H]$^+$.



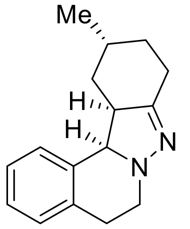
5x1

Compound **5x1**, yellow oil, yield: 71%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.70-0.81 (m, 1H), 1.46-1.71 (m, 3H), 1.73-1.85 (m, 1H), 2.34-2.40 (m, 1H), 2.44-2.50 (m, 1H), 2.97-3.06 (m, 1H), 3.20-3.27 (m, 1H), 3.33-3.40 (m, 1H), 4.03-4.09 (m, 2H), 5.09 (d, J = 11.4 Hz, 1H), 6.92 (d, J = 6.6 Hz, 1H), 7.08 (d, J = 6.5 Hz, 1H), 7.14-7.24 (m, 3H), 7.28-7.35 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.5, 25.7, 30.0, 30.2, 40.6, 48.7, 48.9, 63.8, 126.0, 126.3 (2C), 127.4, 128.5, 128.6, 128.9, 134.3, 137.0, 140.9, 159.9; IR (neat) ν 3058, 3023, 2933, 2860, 1494, 1447, 1355, 1183, 1075, 919, 748, 732, 698 cm^{-1}; Ms (ESI): m/z = 303.2 $[M+H]^+$.



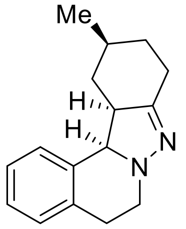
5y1

Compound **5y1**, yellow oil, yield: 55%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.56-0.66 (m, 1H), 1.01 (s, 9H), 1.31-1.40 (m, 1H), 1.46-1.53 (m, 1H), 1.54-1.64 (m, 1H), 1.72-1.78 (m, 1H), 1.96-2.02 (m, 1H), 2.40-2.46 (m, 2H), 2.87-2.95 (m, 1H), 3.18 (ddd, J = 13.5, 12.2, 2.7 Hz, 1H), 3.32-3.40 (m, 1H), 3.99 (ddd, J = 13.4, 4.2, 2.2 Hz, 1H), 5.08 (d, J = 11.5 Hz, 1H), 6.95 (d, J = 7.2 Hz, 1H), 7.05 (d, J = 7.3 Hz, 1H), 7.10-7.18 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.5, 25.9, 26.4, 29.9, 30.3, 34.8, 45.9, 49.0, 50.3, 64.0, 126.0, 126.2, 128.5, 128.8, 134.7, 137.2, 160.7; IR (neat) ν 2942, 2865, 1491, 1451, 1364, 1183, 1076, 923, 747 cm^{-1}; Ms (ESI): m/z = 283.2 $[M+H]^+$. The relative configuration was determined by NOESY analysis of this compound. NOEs between the proton H_{13} of **5y1** and H_{15} was observed.



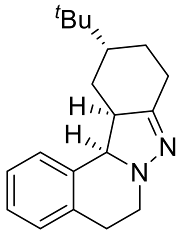
5z1

Compound **5z1**, yellow oil, yield: 43%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87-0.95 (m, 1H), 1.07 (d, J = 7.3 Hz, 3H), 1.39-1.48 (m, 1H), 1.60-1.71 (m, 2H), 2.00-2.10 (m, 1H), 2.28-2.43 (m, 2H), 2.47 (dd, J = 15.4, 4.3 Hz, 1H), 2.91-2.99 (m, 1H), 3.13-3.20 (m, 1H), 3.40-3.48 (m, 1H), 3.98 (dd, J = 13.6, 2.7 Hz, 1H), 5.03 (d, J = 11.2 Hz, 1H), 6.91 (d, J = 7.2 Hz, 1H), 7.04 (d, J = 6.2 Hz, 1H), 7.10-7.18 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.7, 23.0, 25.4, 27.4, 30.6, 34.9, 45.5, 48.9, 63.8, 125.9, 126.2, 128.6, 128.9, 134.3, 137.1, 159.6; IR (neat) ν 2925, 2854, 1490, 1455, 1348, 1154, 1074, 854, 748 cm^{-1}; Ms (ESI): m/z = 241.2 $[M+H]^+$.



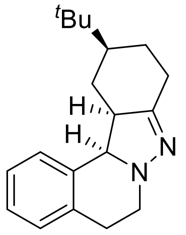
5z2

Compound **5z2**, yellow oil, yield: 38%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.37-0.46 (m, 1H), 0.80-0.95 (m, 4H), 1.55-1.82 (m, 3H), 2.10-2.19 (m, 1H), 2.37-2.43 (m, 1H), 2.62 (dd, *J* = 15.1, 4.4 Hz, 1H), 2.91-2.99 (m, 1H), 3.12-3.20 (m, 1H), 3.25-3.32 (m, 1H), 3.97 (ddd, *J* = 13.5, 4.2, 1.6 Hz, 1H), 5.02 (d, *J* = 11.3 Hz, 1H), 6.93 (d, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 7.3 Hz, 1H), 7.11-7.19 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 22.1, 25.4, 27.5, 31.7, 33.9, 37.9, 48.9, 50.6, 63.9, 126.0, 126.2, 128.6, 128.9, 134.4, 136.9, 159.1; IR (neat) ν 2926, 2855, 1490, 1456, 1357, 1181, 1072, 854, 746 cm^{-1}; Ms (ESI): *m*/*z* = 241.2 [M+H]$^+$.



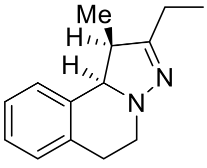
5aa1

Compound **5aa1**, yellow oil, yield: 42%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.73 (s, 9H), 0.95-1.02 (m, 1H), 1.31-1.38 (m, 1H), 1.42-1.50 (m, 1H), 1.61-1.71 (m, 2H), 2.30-2.42 (m, 2H), 2.46-2.53 (m, 1H), 2.93-3.01 (m, 1H), 3.10-3.18 (m, 1H), 3.44-3.51 (m, 1H), 3.96 (ddd, *J* = 13.4, 4.2, 1.9 Hz, 1H), 4.99 (d, *J* = 11.2 Hz, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 7.10-7.19 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 23.1, 24.4, 25.6, 25.8, 27.6, 33.1, 42.5, 47.5, 49.2, 65.6, 126.0, 126.2, 128.8, 129.0, 133.7, 137.3, 160.9; IR (neat) ν 2956, 2867, 1489, 1456, 1364, 1187, 1071, 922, 747 cm^{-1}; Ms (ESI): *m*/*z* = 283.2 [M+H]$^+$. The relative configuration was determined by NOESY analysis of this compound. NOEs between proton H_{13} of **5aa1** and H_{15} was observed.



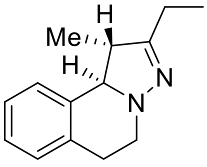
5aa2

Compound **5aa2**, yellow oil, yield: 30%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.38-0.47 (m, 1H), 0.78 (s, 9H), 0.88-0.97 (m, 1H), 1.87-1.95 (m, 2H), 1.96-2.15 (m, 2H), 2.37-2.43 (m, 1H), 2.66-2.70 (m, 1H), 2.92-3.01 (m, 1H), 3.13-3.28 (m, 2H), 3.97 (ddd, *J* = 13.5, 4.3, 1.8 Hz, 1H), 5.03 (d, *J* = 11.1 Hz, 1H), 6.94 (d, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 6.1 Hz, 1H), 7.10-7.19 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 25.4, 26.7, 27.8 (2C), 30.8, 32.7, 47.0, 48.8, 51.0, 64.2, 125.9, 126.2, 128.5, 128.9, 134.3, 136.9, 159.5; IR (neat) *v* 2953, 2867, 1506, 1456, 1365, 1148, 1074, 925, 747 cm^{-1}; Ms (ESI): *m*/*z* = 283.2 [M+H]$^+$.



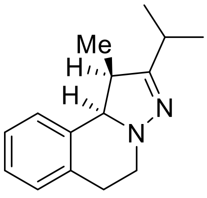
***syn*-5ab**

Compound **5ab**, yellow oil, yield: 64% (*syn* : *anti* = 5.6 : 1). ***syn*-5ab**: ^{1}H NMR (500 MHz, CDCl$_3$) *δ* 0.98 (d, *J* = 7.5 Hz, 3H), 1.13 (t, *J* = 7.5 Hz, 3H), 2.13-2.22 (m, 1H), 2.26-2.36 (m, 1H), 2.45-2.51 (m, 1H), 2.97-3.05 (m, 1H), 3.08-3.15 (m, 1H), 3.33-3.41 (m, 1H), 3.94 (ddd, *J* = 12.6, 4.6, 2.0 Hz, 1H), 4.79 (d, *J* = 10.2 Hz, 1H), 7.01 (d, *J* = 6.9 Hz, 1H), 7.06 (d, *J* = 7.1 Hz, 1H), 7.12-7.19 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) *δ* 11.2, 13.0, 22.0, 26.5, 45.9, 49.0, 65.8, 125.7, 126.3, 128.5, 129.0, 133.7, 137.1, 162.6; IR (neat) *v* 2968, 2932, 1490, 1455, 1375, 1067, 929, 851, 748 cm^{-1}; Ms (ESI): *m*/*z* = 215.2 [M+H]$^+$. The relative configuration was assigned by NOESY analysis of this compound. NOE between the aromatic proton H_{10} of ***syn*-5ab** and H_{11} was observed. Additionally, there was no observable NOE between H_{10} and H_1. These results indicate that H_1 and H_{10b} of ***syn*-5ab** have the *syn* relationship.



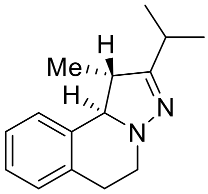
***anti*-5ab**

***anti*-5ab**: ^{1}H NMR (500 MHz, CDCl$_3$) *δ* 1.05 (t, *J* = 7.5 Hz, 3H), 1.35 (d, *J* = 7.3 Hz, 3H), 2.11-2.20 (m, 1H), 2.25-2.34 (m, 1H), 2.43-2.48 (m, 1H), 2.95-3.05 (m, 2H), 3.19-3.26 (m, 1H), 3.99 (dd, *J* = 13.7, 5.0 Hz, 1H), 4.42 (brs, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.7 Hz, 1H), 7.11-7.15 (m, 1H), 7.19-7.23 (m, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) *δ* 11.2, 17.1, 22.1, 25.0, 47.6, 52.5, 68.9, 126.3, 126.4, 127.0, 128.8, 135.2, 138.0, 162.1; IR (neat) *v* 2964, 2927, 1489, 1455, 1374, 1076, 924, 855, 746 cm^{-1}; Ms (ESI): *m*/*z* = 215.2 [M+H]$^+$. The relative configuration was assigned by NOESY analysis of this compound. NOE between the aromatic proton H_{10} of ***anti*-5ab** and H_1 was observed. Additionally, there was no observable NOE between H_{10} and H_{11}. These results indicate that H_1 and H_{10b} of ***anti*-5ab** have the *anti* relationship.



***syn*-5ac**

Compound **5ac**, yellow oil, yield: 70% (*syn* : *anti* = 3.3 : 1). ***syn*-5ac**: ^{1}H NMR (500 MHz, CDCl$_3$) *δ* 0.98 (d, *J* = 7.4 Hz, 3H), 1.12 (d, *J* = 7.0 Hz, 3H), 1.18 (d, *J* = 6.7 Hz, 3H), 2.48-2.54 (m, 2H), 2.99-3.13 (m, 2H), 3.37-3.44 (m, 1H), 3.91-3.96 (m, 1H), 4.70 (d, *J* = 10.0 Hz, 1H), 7.01 (d, *J* = 7.0 Hz, 1H), 7.07 (d, *J* = 7.0 Hz, 1H), 7.12-7.19 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.9, 19.9, 20.9, 26.8, 28.1, 44.9, 49.1, 66.2, 125.7, 126.3, 128.4, 129.0, 133.8, 137.1, 166.2; IR (neat) v 2965, 2929, 1491, 1455, 1360, 1073, 929, 747 cm^{-1}; Ms (ESI): *m/z* = 229.2 [M+H]$^+$.



***anti*-5ac**

***anti*-5ac**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.98 (d, *J* = 7.0 Hz, 3H), 1.11 (d, *J* = 6.8 Hz, 3H), 1.36 (d, *J* = 7.3 Hz, 3H), 2.41-2.55 (m, 2H), 2.96-3.08 (m, 2H), 3.18-3.25 (m, 1H), 3.99 (dd, *J* =13.9, 4.8 Hz, 1H), 4.40 (brs, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.7 Hz, 1H), 7.10-7.14 (m, 1H), 7.18-7.22 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.5, 20.3, 21.3, 25.0, 28.5, 47.6, 51.2, 69.3, 126.2, 126.4, 126.9, 128.7, 135.2, 137.7, 165.7; IR (neat) v 2962, 2927, 1489, 1456, 1362, 1076, 927, 745 cm^{-1}; Ms (ESI): *m/z* = 229.2 [M+H]$^+$.

Scheme S1. Proposed mechanism of stereoselectivity of 2a

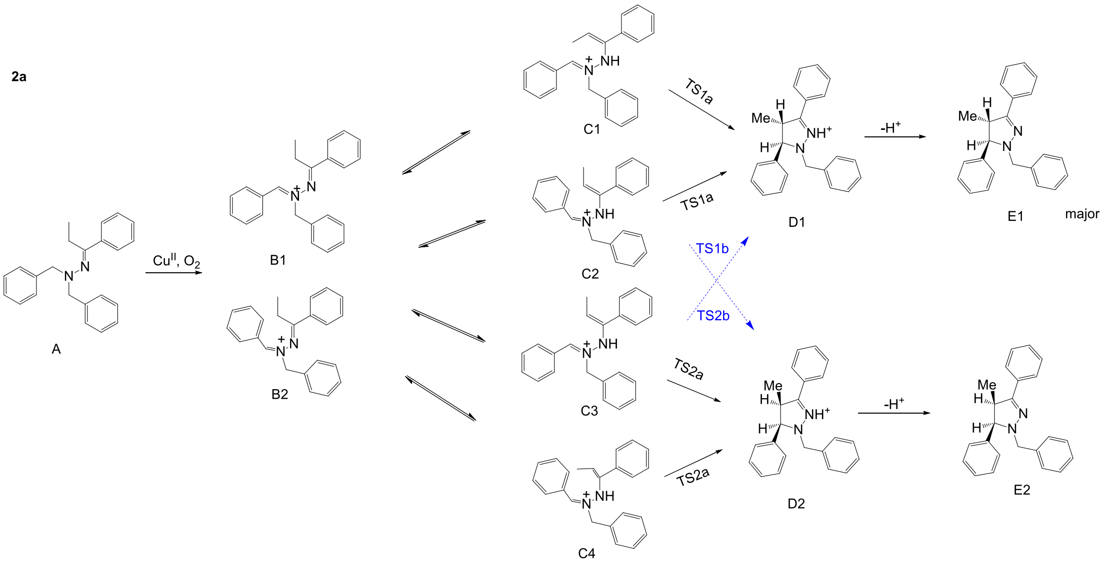
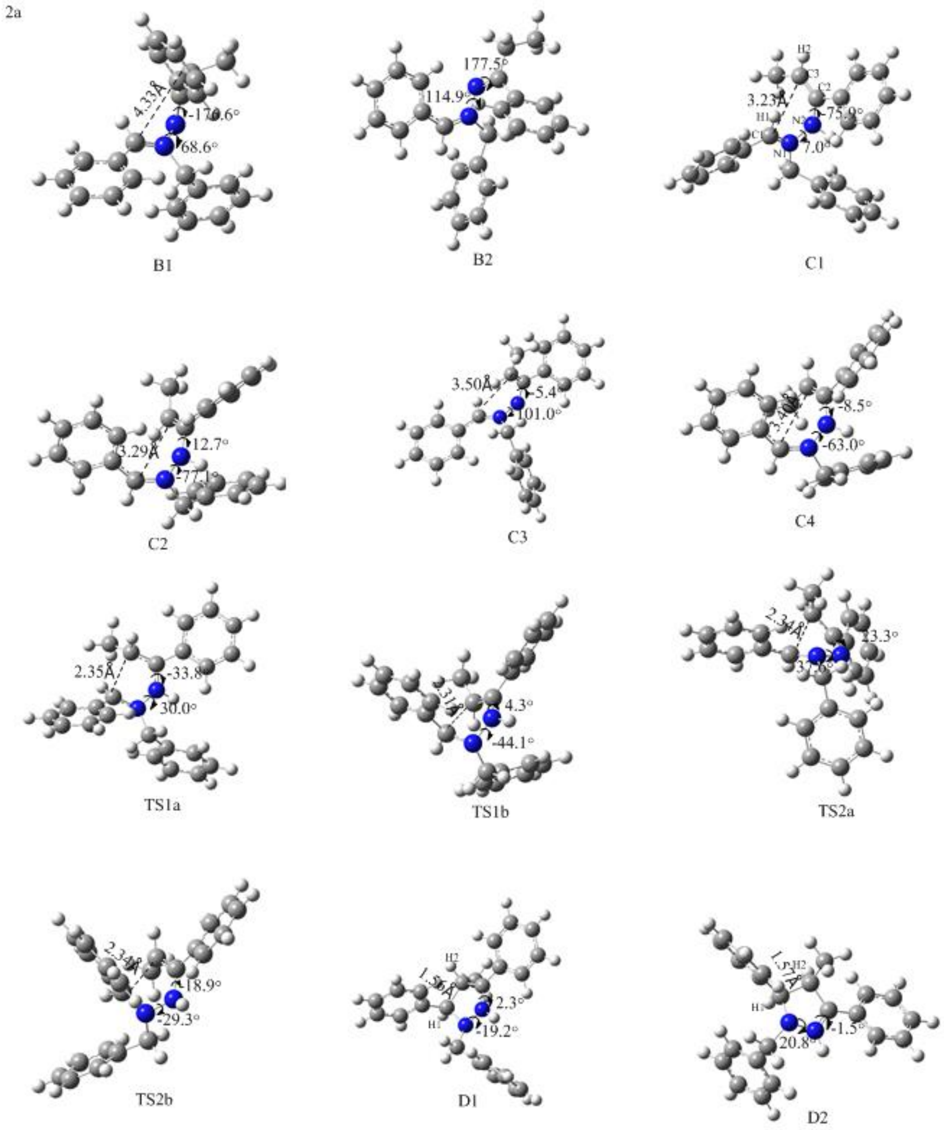


Figure S1. Optimized geometries in 5-center/6-electron cyclization generating 2a



Scheme S2. Proposed mechanism of stereoselectivity of 2f

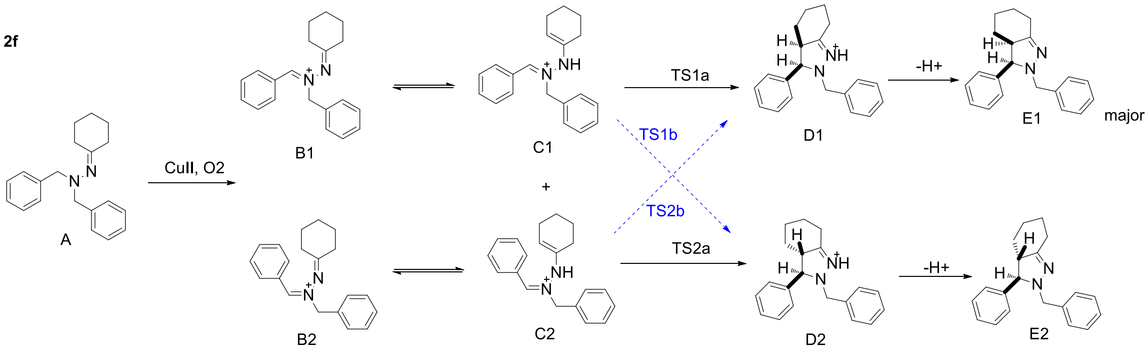


Figure S2. Optimized geometries in 5-center/6-electron cyclization generating 2f

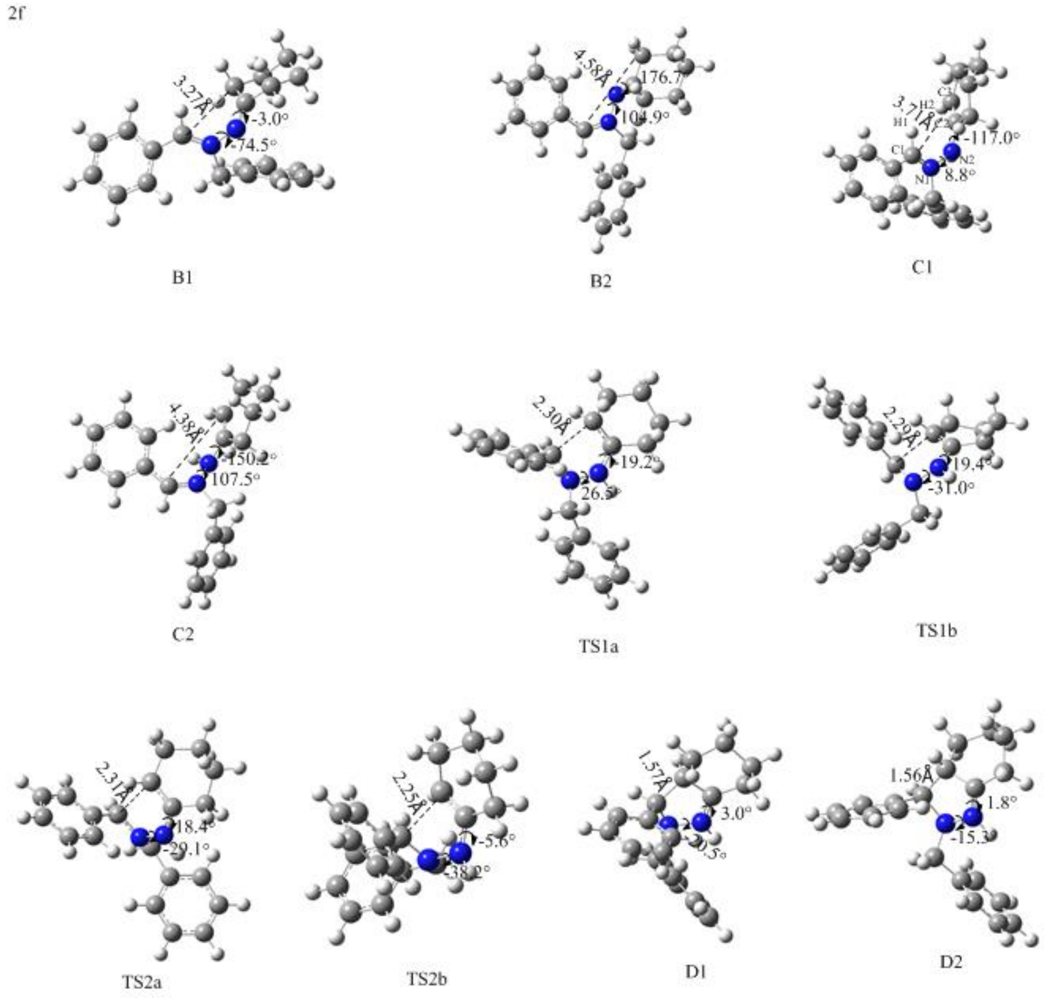
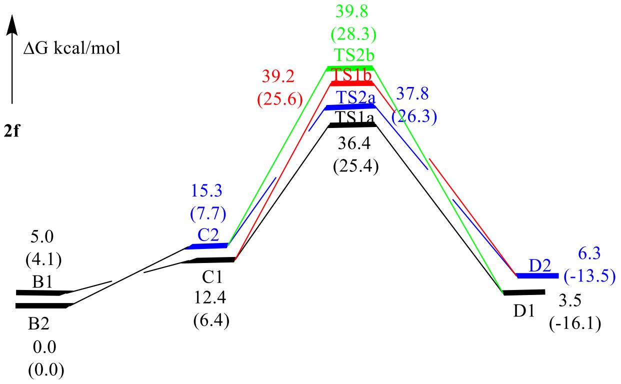


Figure S3. Free energy profiles in 5-center/6-electron cyclization process generating 2f in Scheme 3 in the gas phase. Free energies in the solution phase are given in parentheses.

C1 preferentially goes through disrotatory process (**TS1a**) to give **D1** (to be exothermic by 8.9 kcal/mol with a free energy barrier of 24.0 kcal/mol), rather than conrotatory process (**TS1b**) to afford **D2**. Also, **C2** is more likely to go through disrotatory process (**TS2a**) to give **D2**, rather than conrotatory process (**TS2b**) to afford **D1**. Compared with **C2**, **C1** overcome less free energy barrier, determining the stereoselectivity of this reaction. The overall selective picture is the same as that captured from gas-phase calculations. These are in good agreement with the experimental finding.



Scheme S3. Proposed mechanism of stereoselectivity of 2p

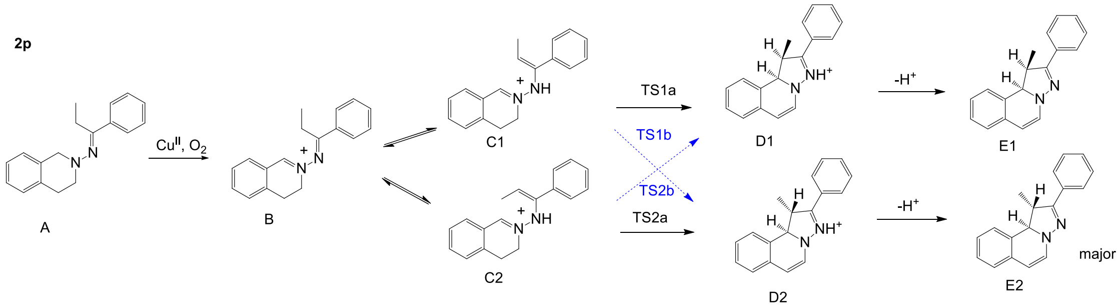
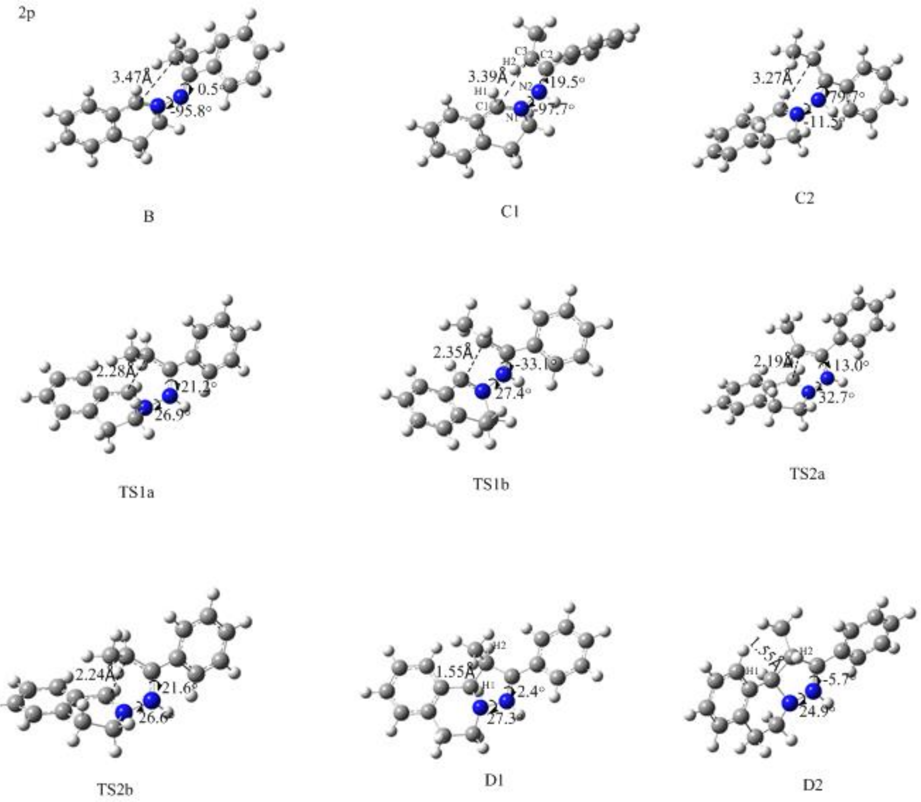


Figure S4. Optimized geometries in 5-center/6-electron cyclization generating 2p.



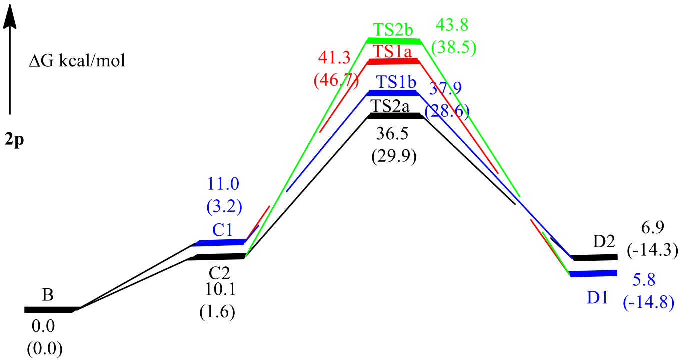
B C1 C2

TS1a TS1b TS2a

TS2b D1 D2

Figure S5. Free energy profiles in 5-center/6-electron cyclization generating 2p in Scheme 3 in the gas phase. Free energies in the solution phase are given in parentheses.

C2 prefers to undergo disrotatory process (**TS2a**) to give **D2** (to be exothermic by 3.2 kcal/mol with a free energy barrier of 26.4 kcal/mol), rather than conrotatory process (**TS2b**) to afford **D1**. However, **C1** is more likely undergo conrotatory process (**TS1b**) to afford **D2**, rather than disrotatory process (**TS1a**) to give **D1**. Compared with **C1**, **C2** overcome less energy barrier, determining the stereoselectivity of this reaction. The overall selective picture is the same as that captured from gas-phase calculations. These are in good agreement with the experimental finding.



Scheme S4. Proposed mechanism of stereoselectivity of 5a

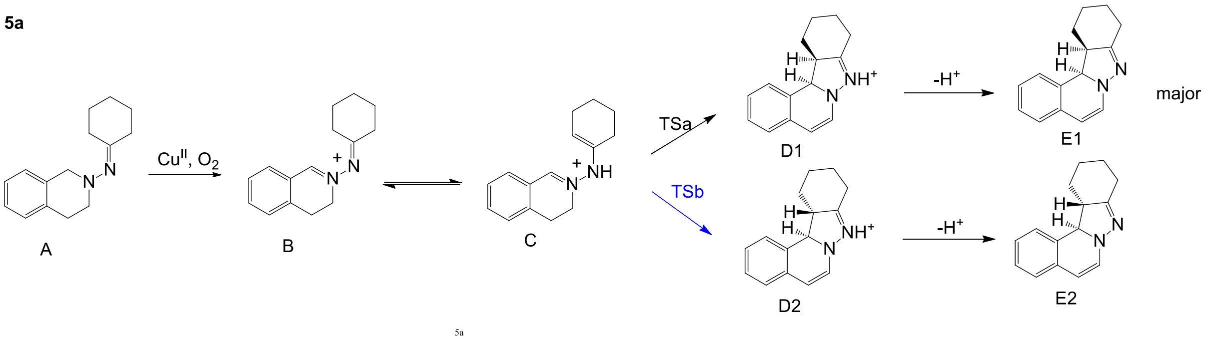
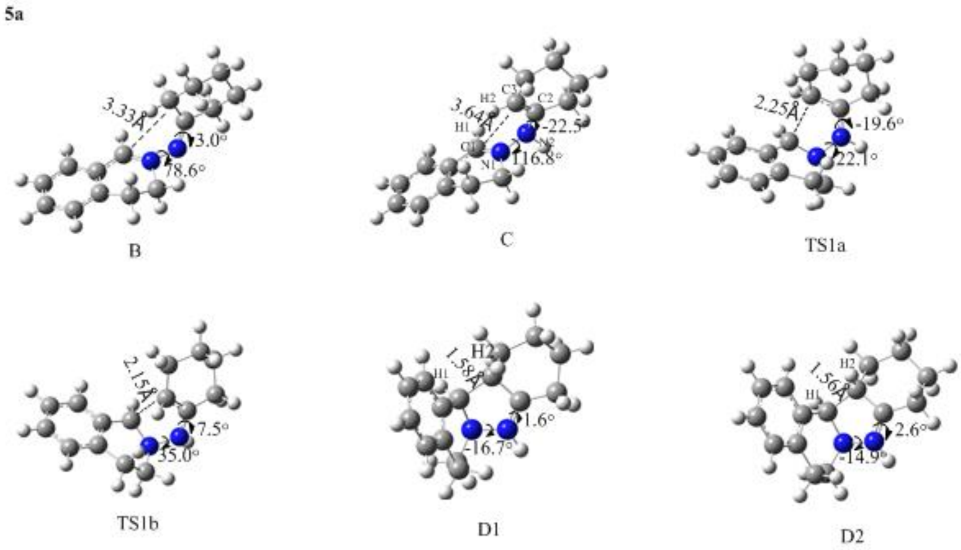


Figure S6. Optimized geometries in 5-center/6-electron cyclization generating 5a



Scheme S5 Proposed mechanism of stereoselectivity of 5ab

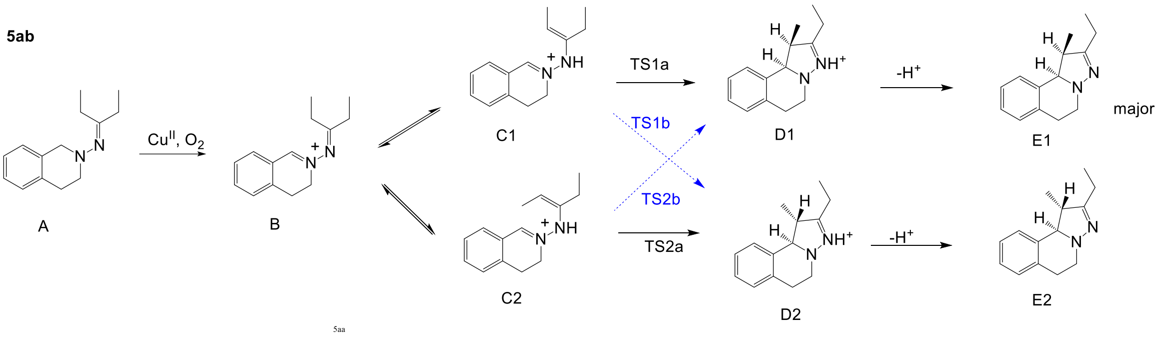


Figure S7. Optimized geometries in 5-center/6-electron cyclization generating 5ab

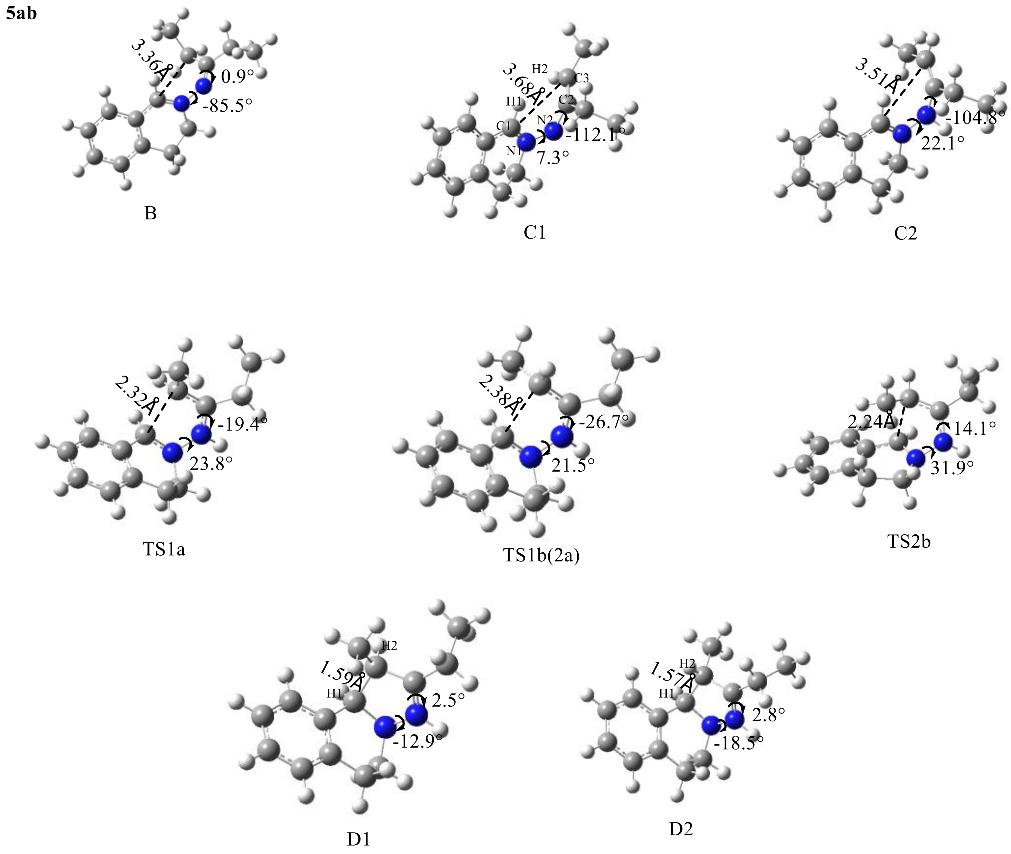


Figure S8. Free energy profiles of the reaction generating 5ab in scheme 3 in the gas phase. Free energies in the solution phase are given in parentheses.

C1 tends to undergo disrotatory process (**TS1a**) to give **D1** (to be exothermic by 2.8 kcal/mol with a free energy barrier of 25.7 kcal/mol), rather than conrotatory process (**TS1b**) to afford **D2**. Also, **C2** is more likely to undergo disrotatory process (**TS2a**) to give **D2**, rather than conrotatory process (**TS2b**) to afford **D1**. However, compared with **C2**, **C1** overcome less free energy barrier, determining the stereoselectivity of this reaction. The overall stereoselective picture is the same as that captured from gas-phase calculations. These are in good agreement with the experimental finding.

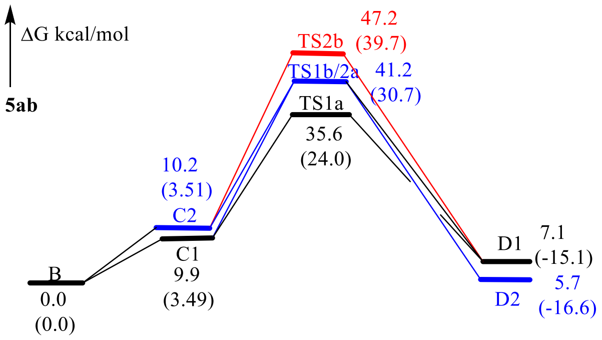


Figure S9. HOMOs of TS1a, TS1b and TS2b generating 5ab

To better understand this point, HOMOs of **TS1a, TS1b(=TS2a) and TS2b** were compared. Seen from **Figure S4**, the under lobe of orbital of C atom in C=N$^+$ bond overlaps with the under lobe of orbital of the terminal C atom in C=C bond, and C=N$^+$-NH-C=C and CH_3 group constitutes a delocalized system in **TS1a**. In **TS1b** the under lobe of orbital of C atom in C=N$^+$ bond overlaps with the under lobe of orbital of the terminal C atom in C=C bond, but the delocalized system is only consisted of C=N$^+$-NH-C=C. The delocalized system in **TS1b** is smaller than **TS1a,** suggesting that **TS1b** is less stable and more difficult to overcome than **TS1a**. Compared with the orbital in **TS2a**, the C=N$^+$-NH-C=C in **TS2b** do not constitute a complete delocalized orbital, and an orbital nodal surface is found between NH and the terminal C atom in C=C bond, also suggesting that **TS2b** is less stable and more difficult to cross than **TS2a**. Therefore, **C1 (C2)** goes through disrotatory process to form **D1(D2)**, instead of conrotatory process to afford **D2 (D1).**

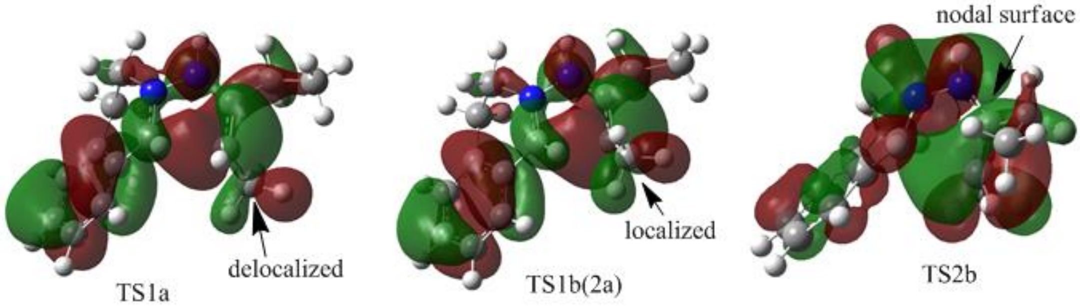


Table S1. Electronic energies (E*elec*), Zero-point energies (E_{zp}), Gibbs free energies (G*gas*), and solvent free energies (ΔG*sol*) of all stationary points. The E*elec* , G*gas* , and E_{zp} energies are in a.u. and ΔG*sol* are in kcal/mol.

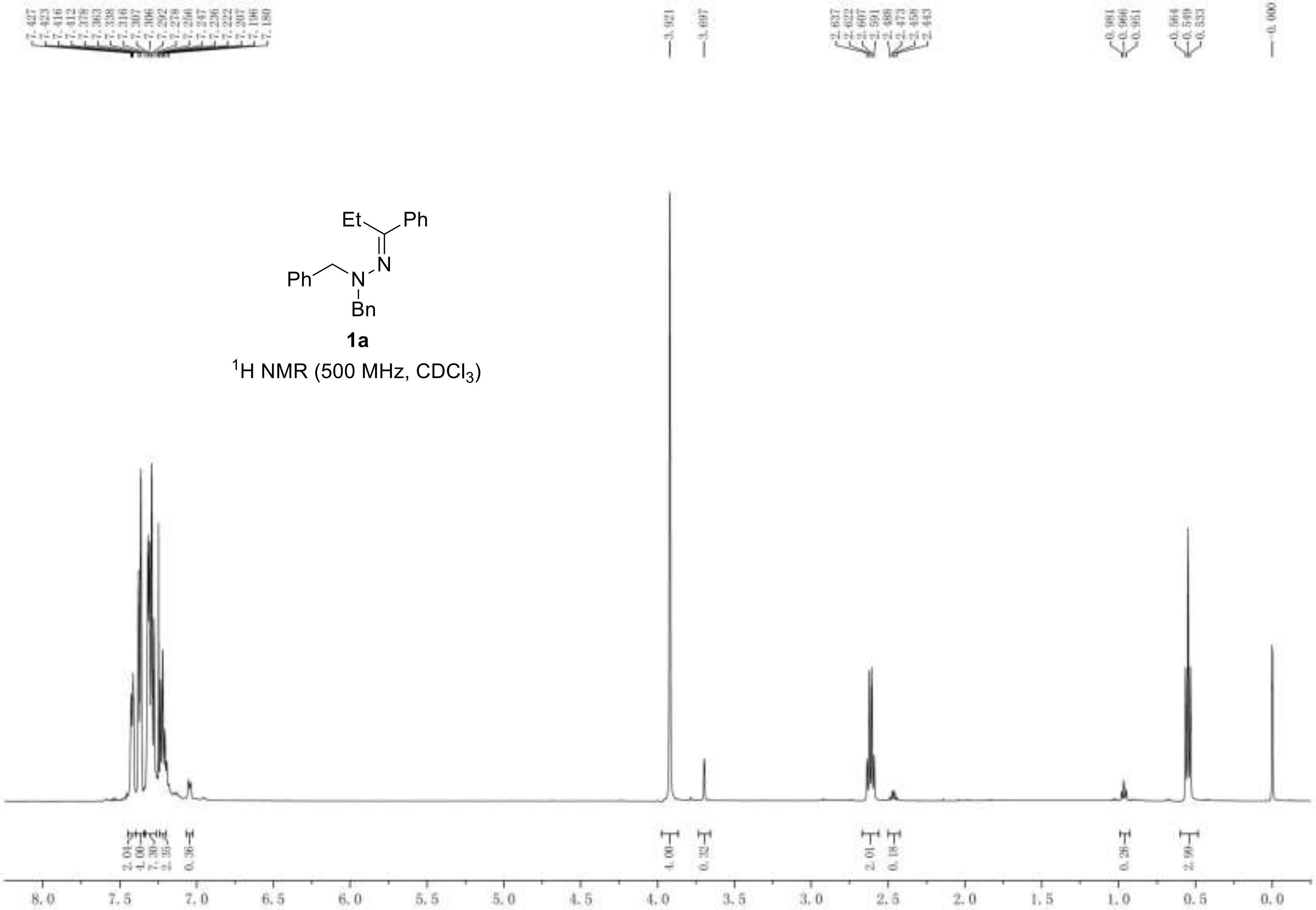
	E_{elec}	E_{ZP}	G_{gas}	ΔG
2a				
B1−2a	−999.6081	0.40334	−999.2607	−63.18
B2−2a	−999.6158	0.4038	−999.2682	−60.1
C1−2a	−999.5989	0.40406	−999.249	−67.41
C2−2a	−999.5977	0.40426	−999.2476	−71.21
C3−2a	−999.5956	0.40417	−999.2455	−55.85
C4−2a	−999.5928	0.40432	−999.2414	−56.12
TS1a−2a	−999.5613	0.40355	−999.2105	−70.43
TS1b−2a	−999.5546	0.40168	−999.2052	−70.16
TS2a−2a	−999.5488	0.40232	−999.1988	−67.9
TS2b−2a	−999.5439	0.4021	−999.1942	−69.51
D1−2a	−999.627	0.40628	−999.2735	−55.54
D2−2a	−999.6245	0.40615	−999.2715	−57.8
2f				
B1−2f	−885.29183	0.388509	−884.953336	−63.0
B2−2f	−885.30011	0.388854	−884.961256	−62.09
C1−2f	−885.28027	0.388834	−884.941425	−68.18
C2−2f	−885.27445	0.388801	−884.936888	−69.65
TS1a−2f	−885.24287	0.388384	−884.903197	−73.14
TS1b−2f	−885.23667	0.387067	−884.898725	−75.68
TS2a−2f	−885.2391	0.387225	−884.900972	−73.59
TS2b−2f	−1770.1337	0.386677	−884.897871	−73.56
D1−2f	−885.29821	0.390767	−884.955698	−81.63
D2−2f	−885.29216	0.390498	−884.951221	−81.92
2p				
B−2p	−806.6697	0.33059	−806.3859	−59.29
C1−2p	−806.6522	0.33052	−806.3684	−67.09
C2−2p	−806.6543	0.33066	−806.3698	−67.79
TS1a−2p	−806.6061	0.3299	−806.32	−64.49
TS1b−2p	−806.6114	0.33025	−806.3254	−68.69
D2−2p	−806.6637	0.33265	−806.3749	−80.47
TS2a−2p	−806.613	0.32932	−806.3277	−65.91
TS2b−2p	−806.6022	0.33	−806.3161	−64.57
D1−2p	−806.6656	0.33285	−806.3767	−79.91
D2−2p	−806.6637	0.33265	−806.3749	−80.47
5a				
B−5a	−692.3511	0.31511	−692.0784	−60.21
C1−5a	−692.3341	0.31535	−692.061	−67.36

TS1a-5a	-692.2921	0.31463	-692.018	-72.35
TS1b-5a	-692.2895	0.31412	-692.0154	-69.41
D1-5a	-692.3348	0.31741	-692.0581	-82.61
D2-5a	-692.3455	0.3176	-692.0679	-82.23
5ab				
B-5ab	-654.2375	0.3059	-653.9758	-59.18
C1-5ab	-654.2225	0.30594	-653.96	-65.57
C2-5ab	-654.222	0.30597	-653.9596	-65.84
TS1a-5ab	-654.1824	0.30528	-653.919	-70.83
TS1b/2a-5ab	-654.1739	0.30558	-653.9101	-69.7
TS2b-5ab	-654.1644	0.30532	-653.9006	-66.62
D1-5ab	-654.2322	0.30879	-653.9645	-81.36
D2-5ab	-654.2336	0.3085	-653.9667	-81.47

References

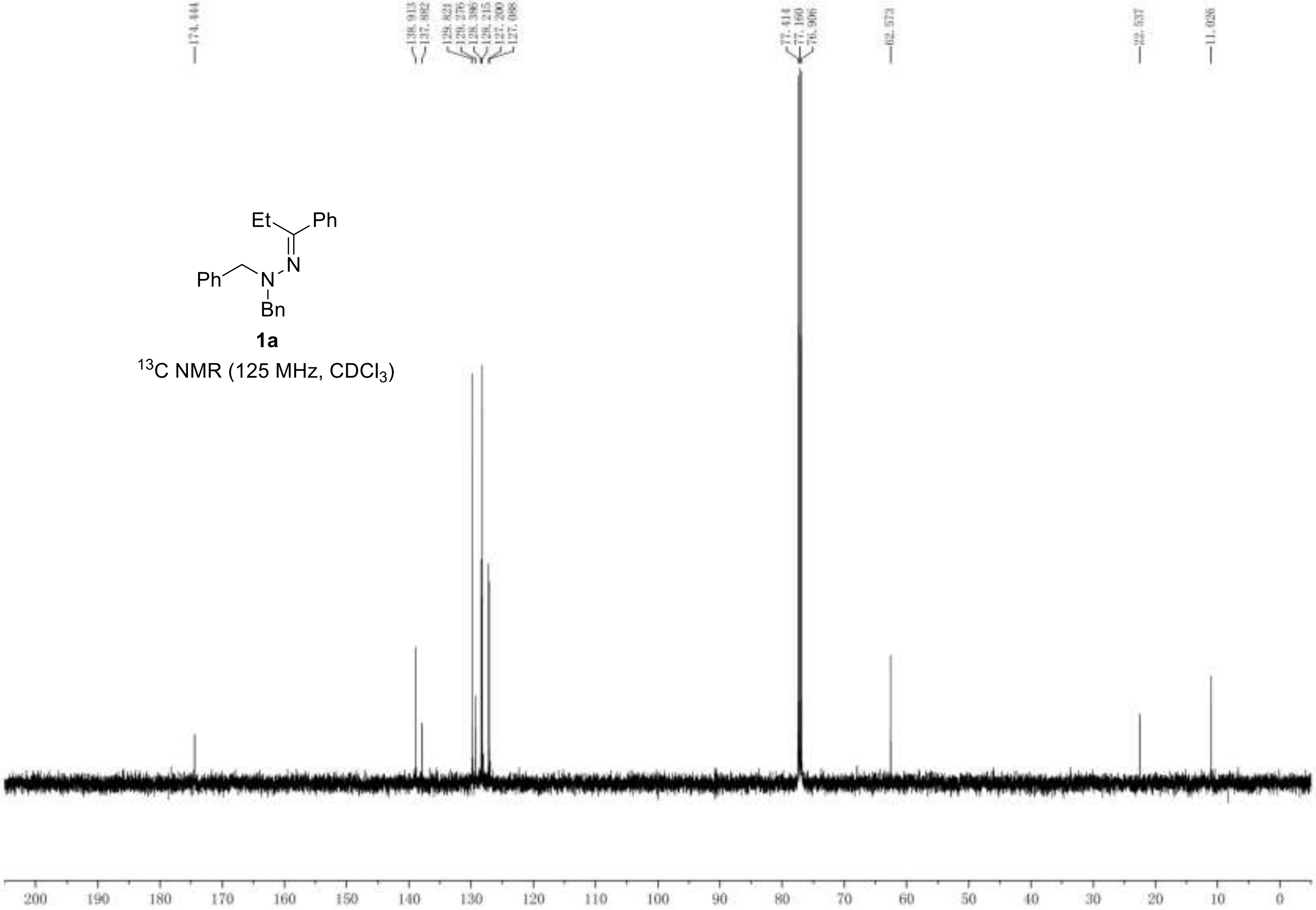
(1) G. Zhang, Y. Zhao and H. Ge, *Angew. Chem., Int., Ed.*, 2013, **52**, 2559.

(2) D. Fischer and E. A. Theodorakis, *Eur. J. Org. Chem.*, 2007, 4193.



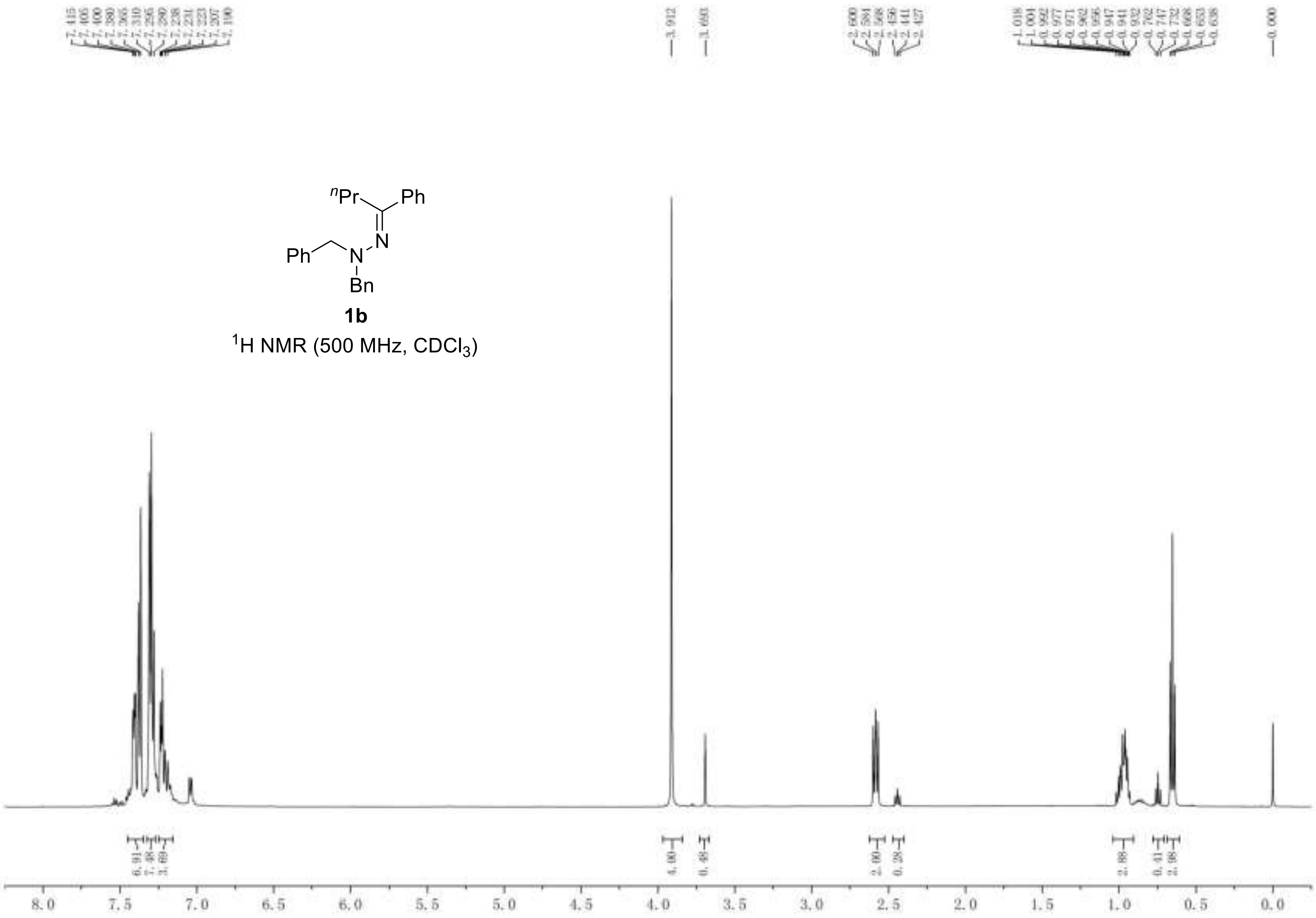
1a

^{1}H NMR (500 MHz, CDCl$_3$)



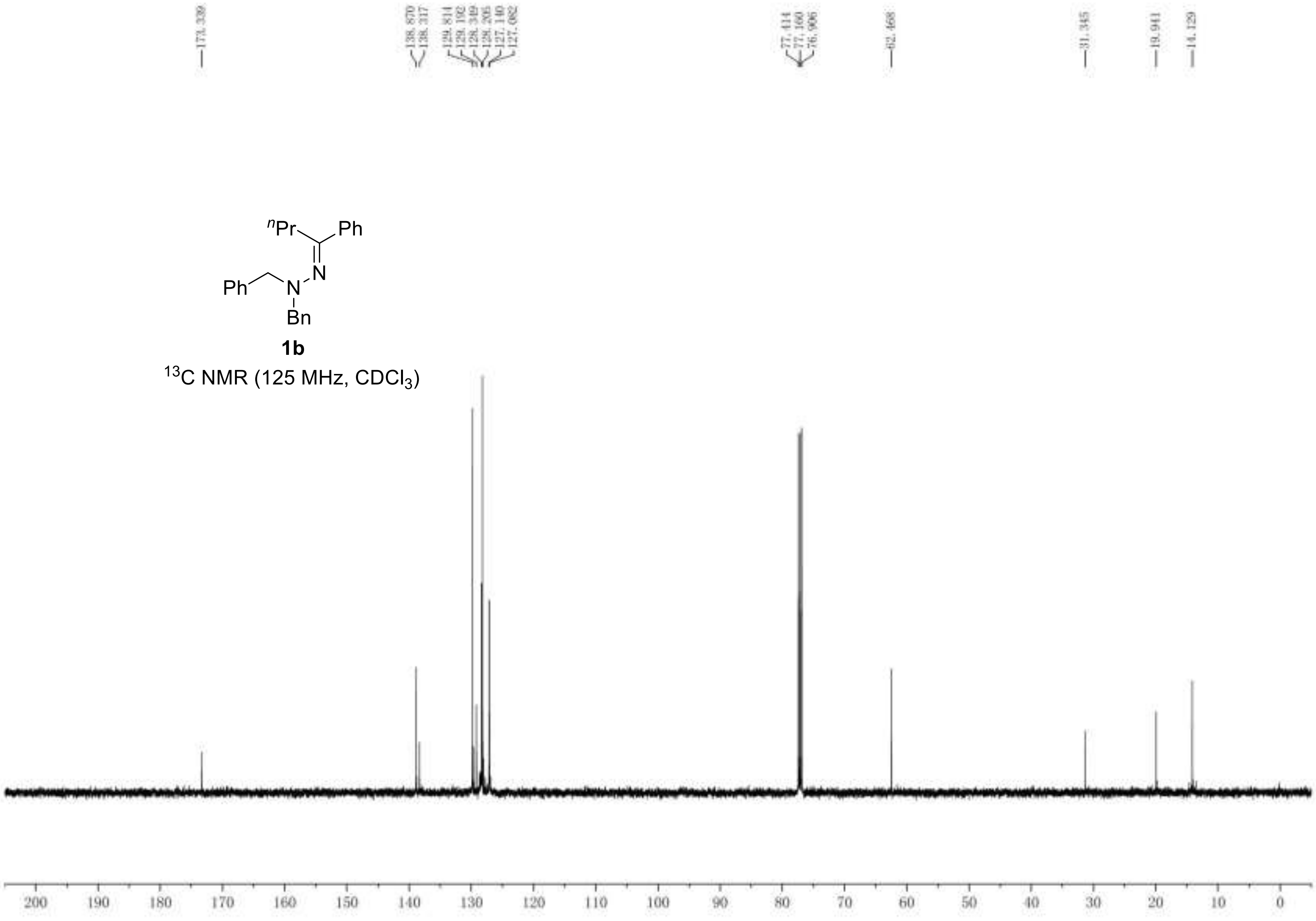
1a

^{13}C NMR (125 MHz, CDCl$_3$)



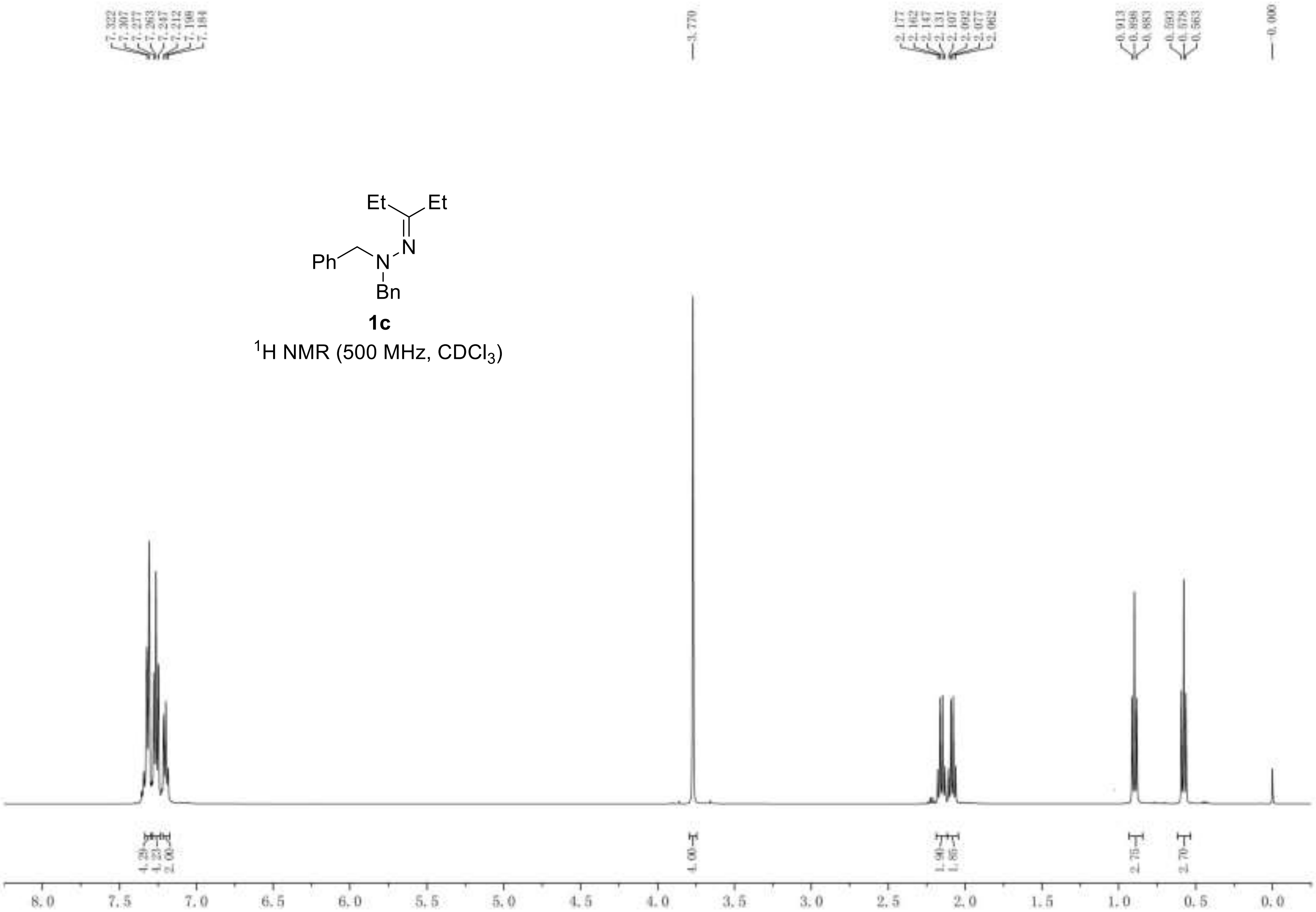
1b

^{1}H NMR (500 MHz, CDCl$_3$)



1b

^{13}C NMR (125 MHz, CDCl$_3$)



1c

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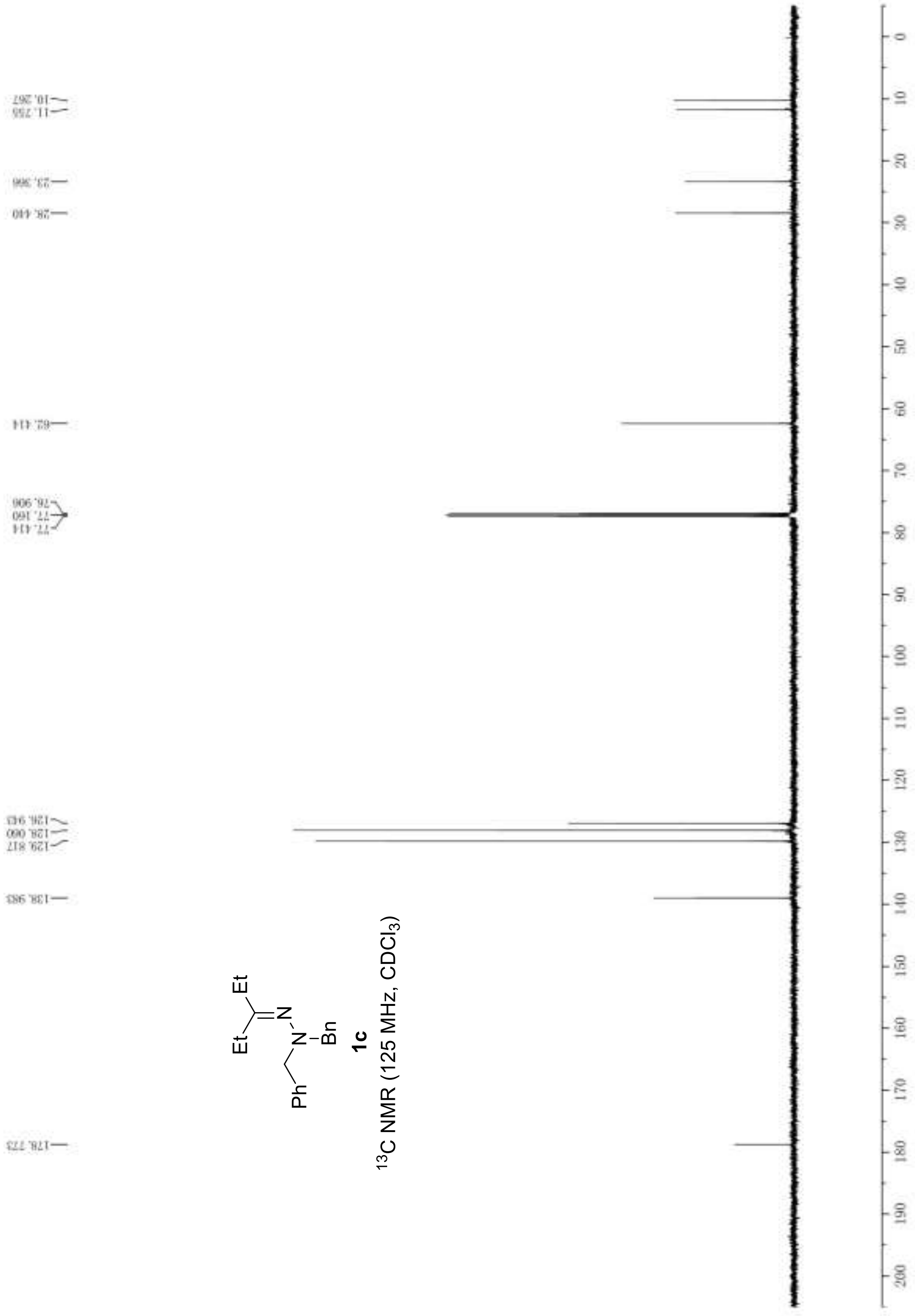
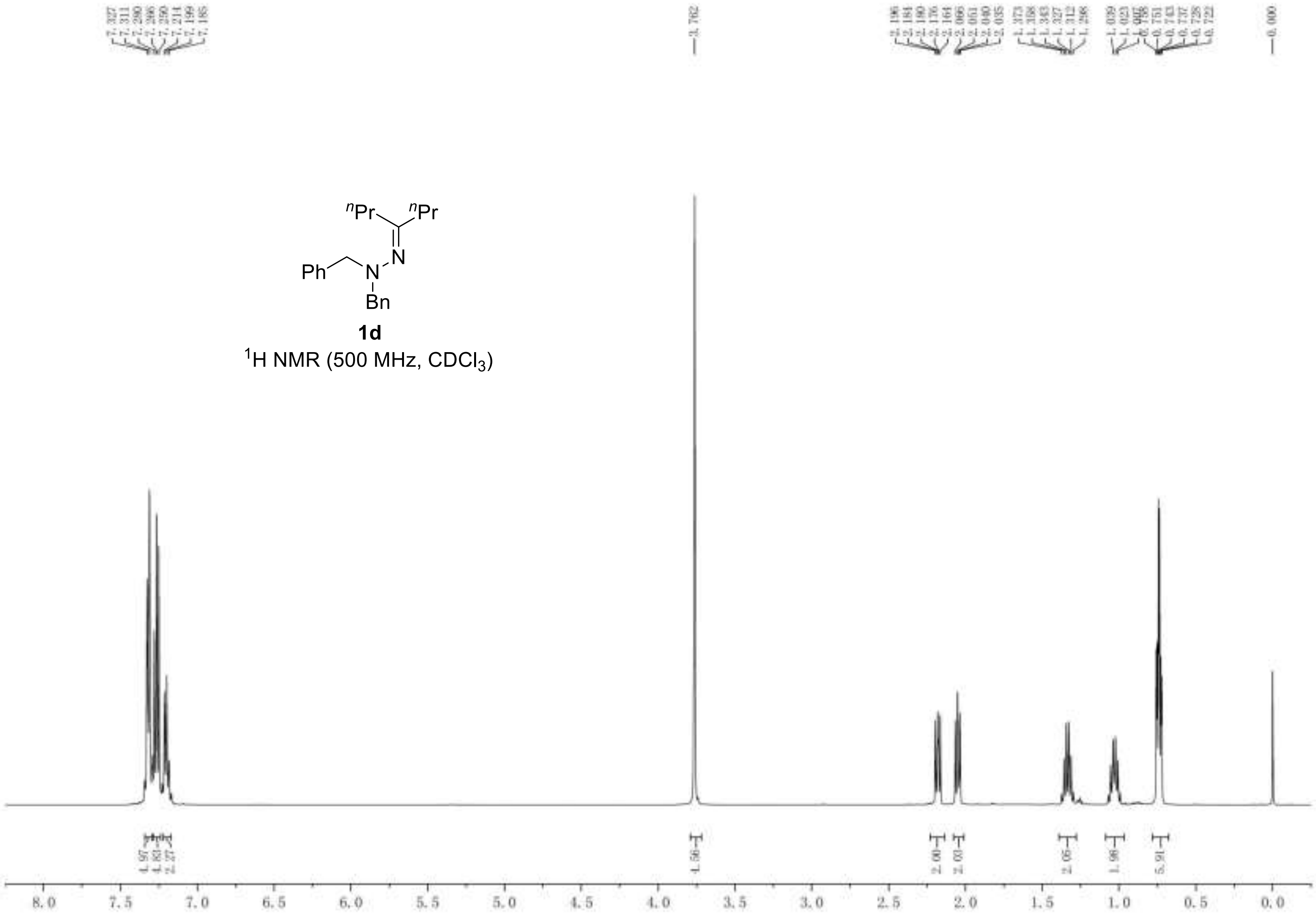


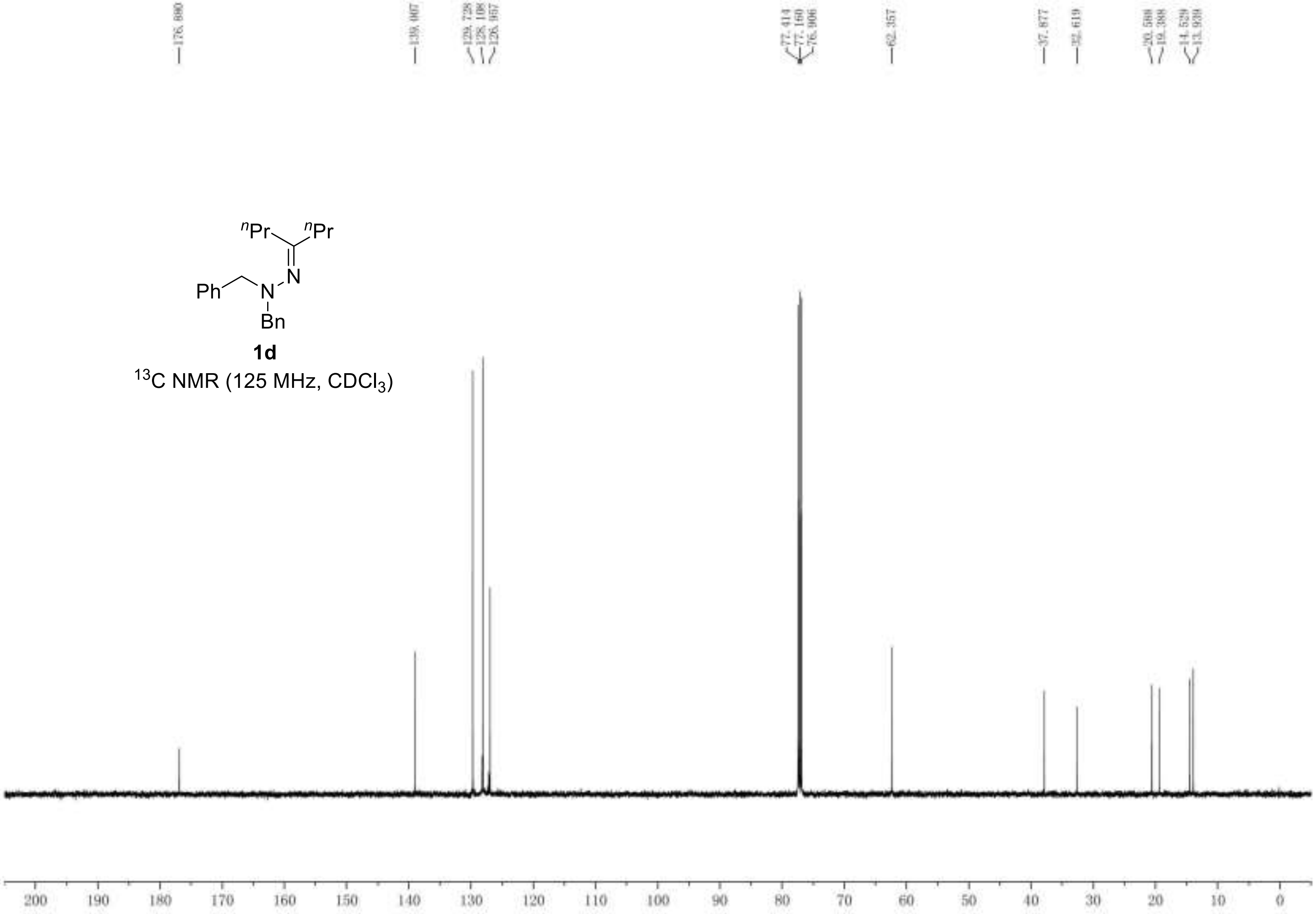
1c

^{13}C NMR (125 MHz, CDCl$_3$)



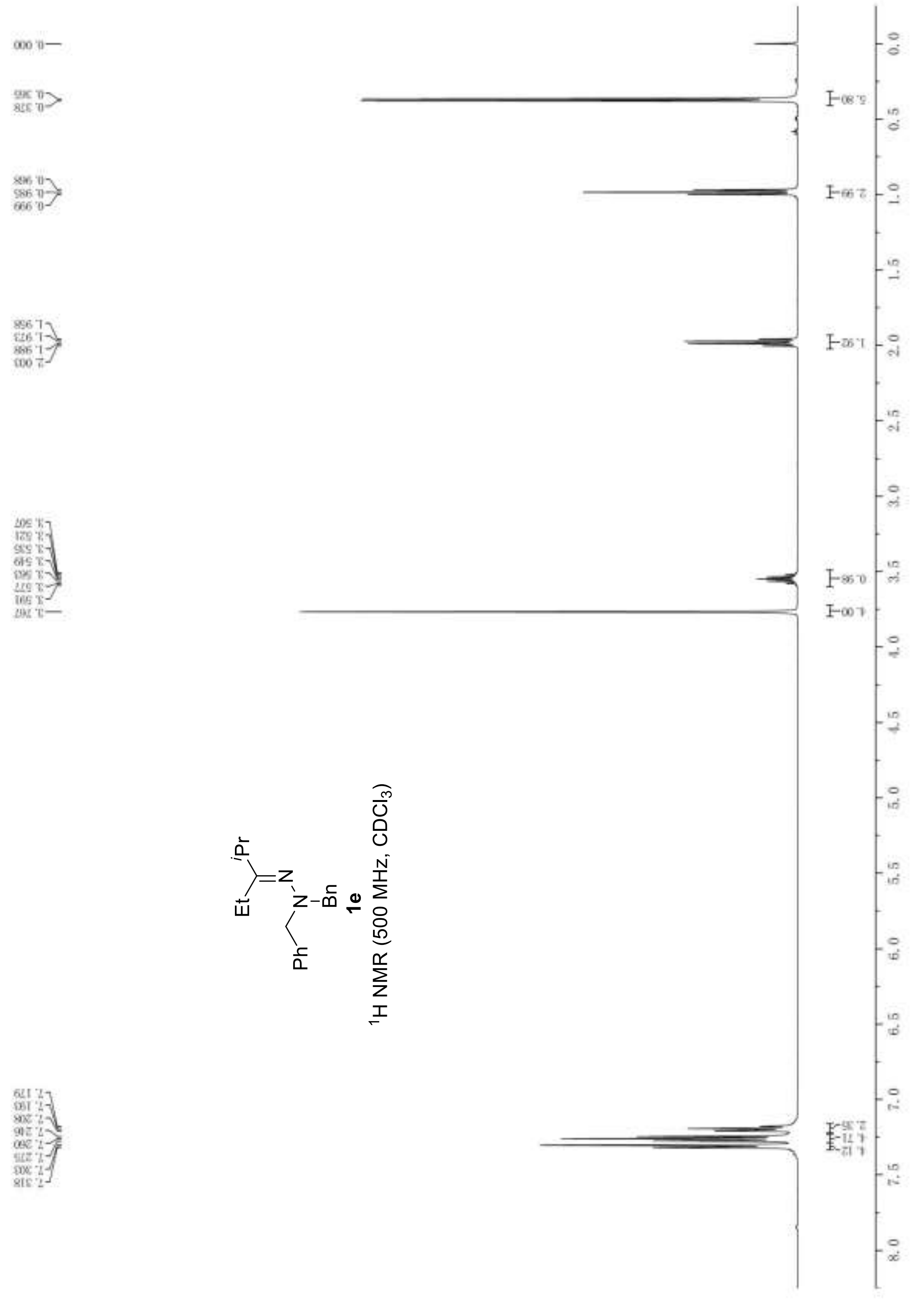
1d

^{1}H NMR (500 MHz, CDCl$_3$)



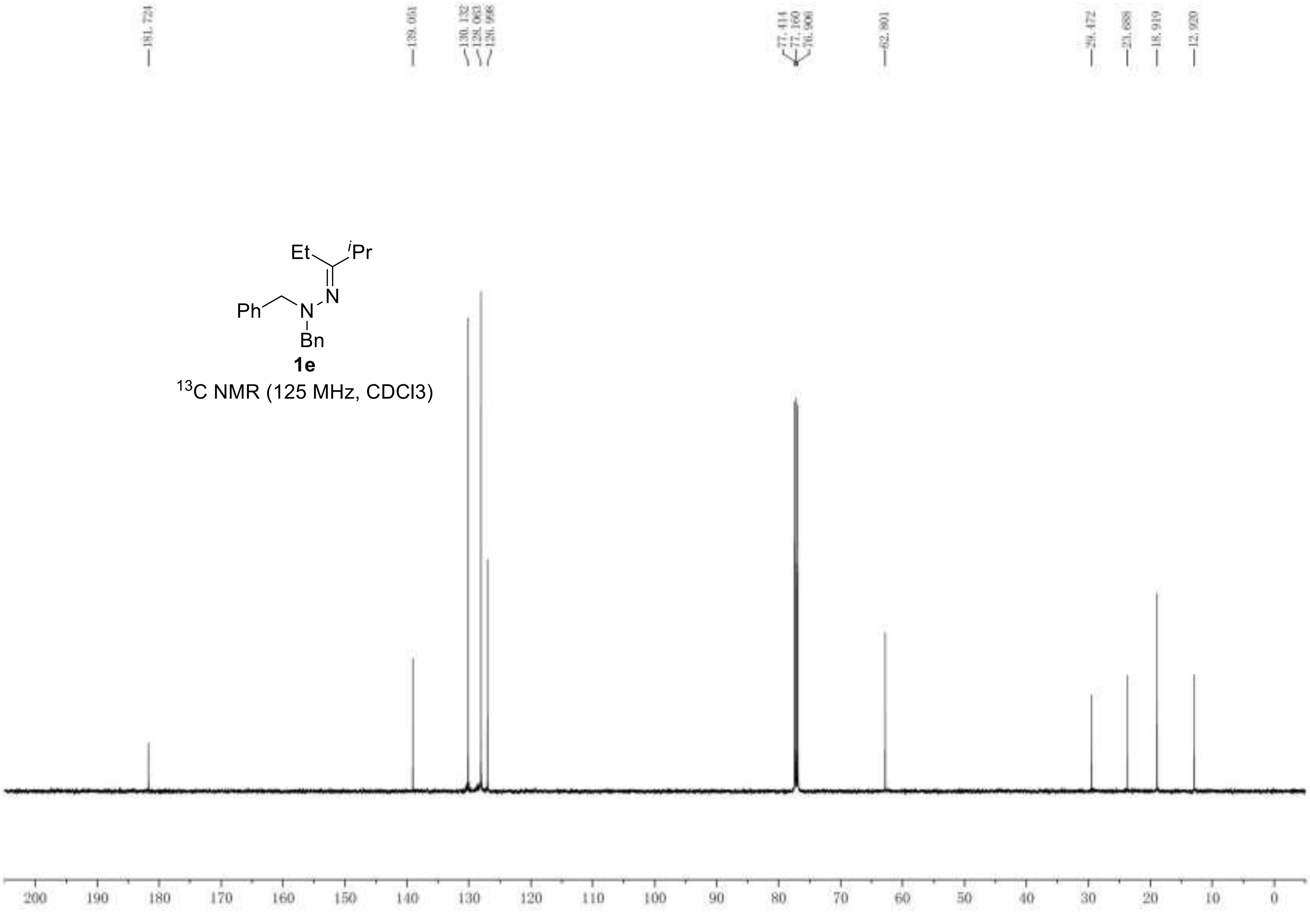
1d

^{13}C NMR (125 MHz, CDCl$_3$)



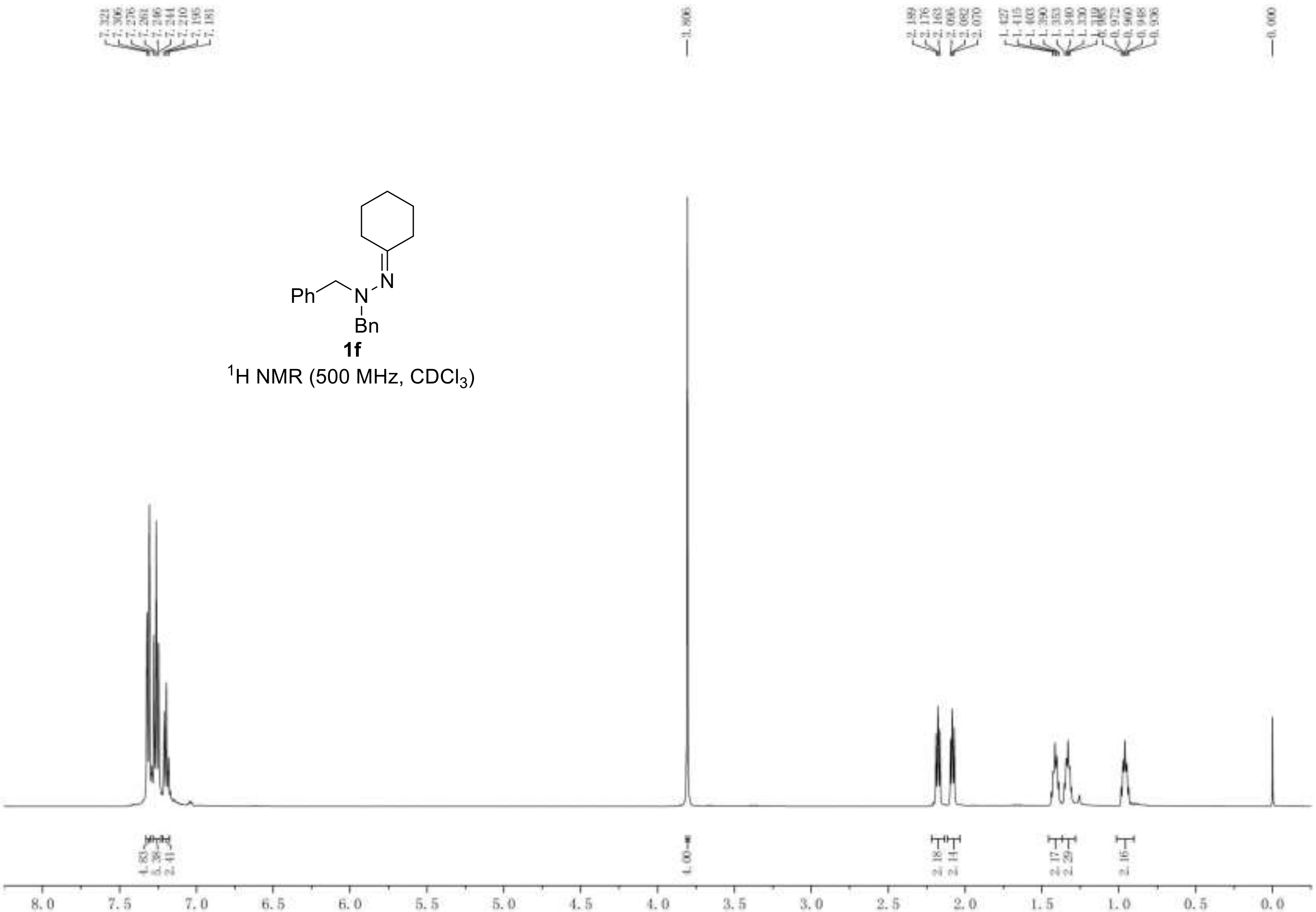
1e

^{1}H NMR (500 MHz, CDCl$_3$)



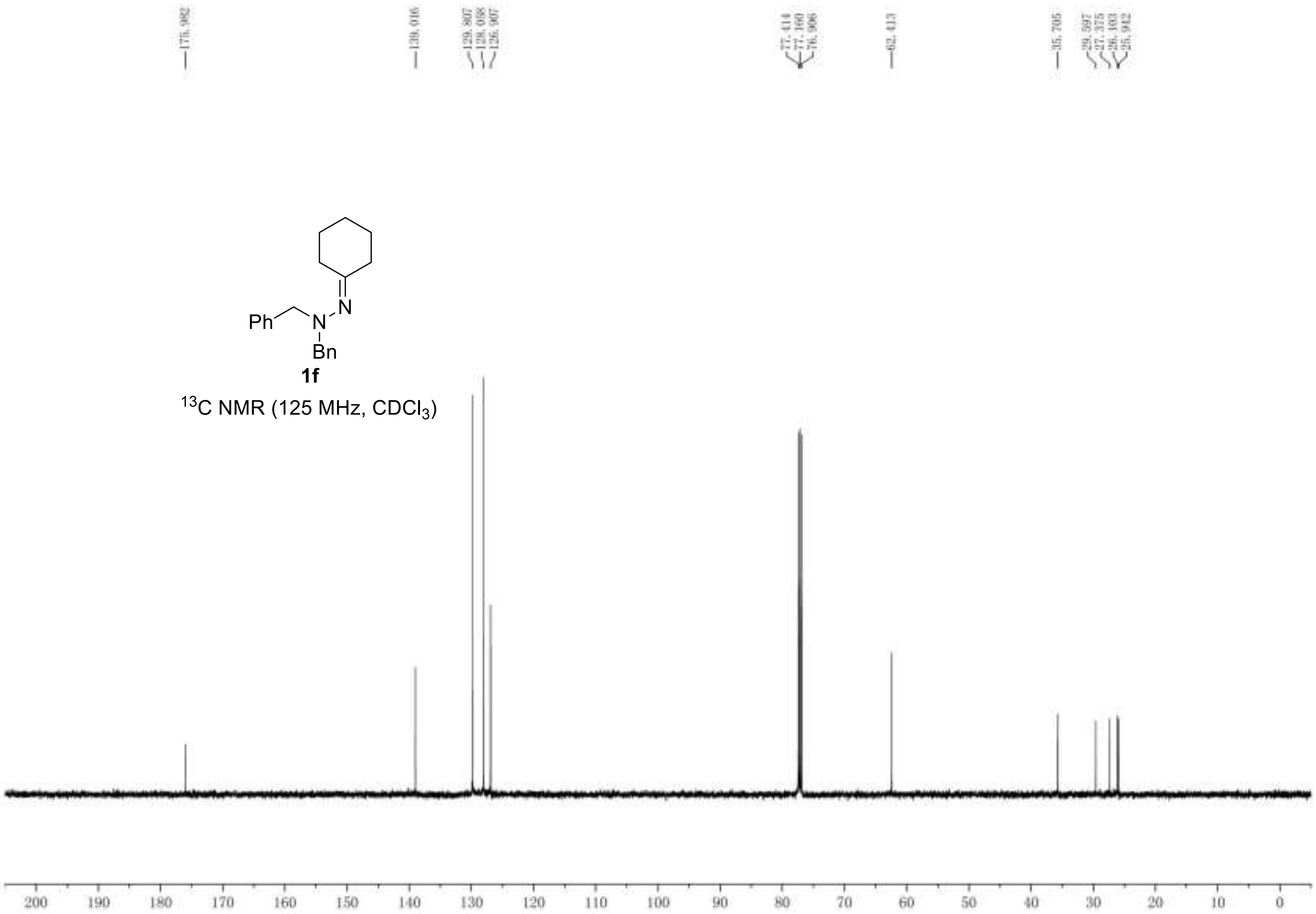
1e

^{13}C NMR (125 MHz, CDCl3)



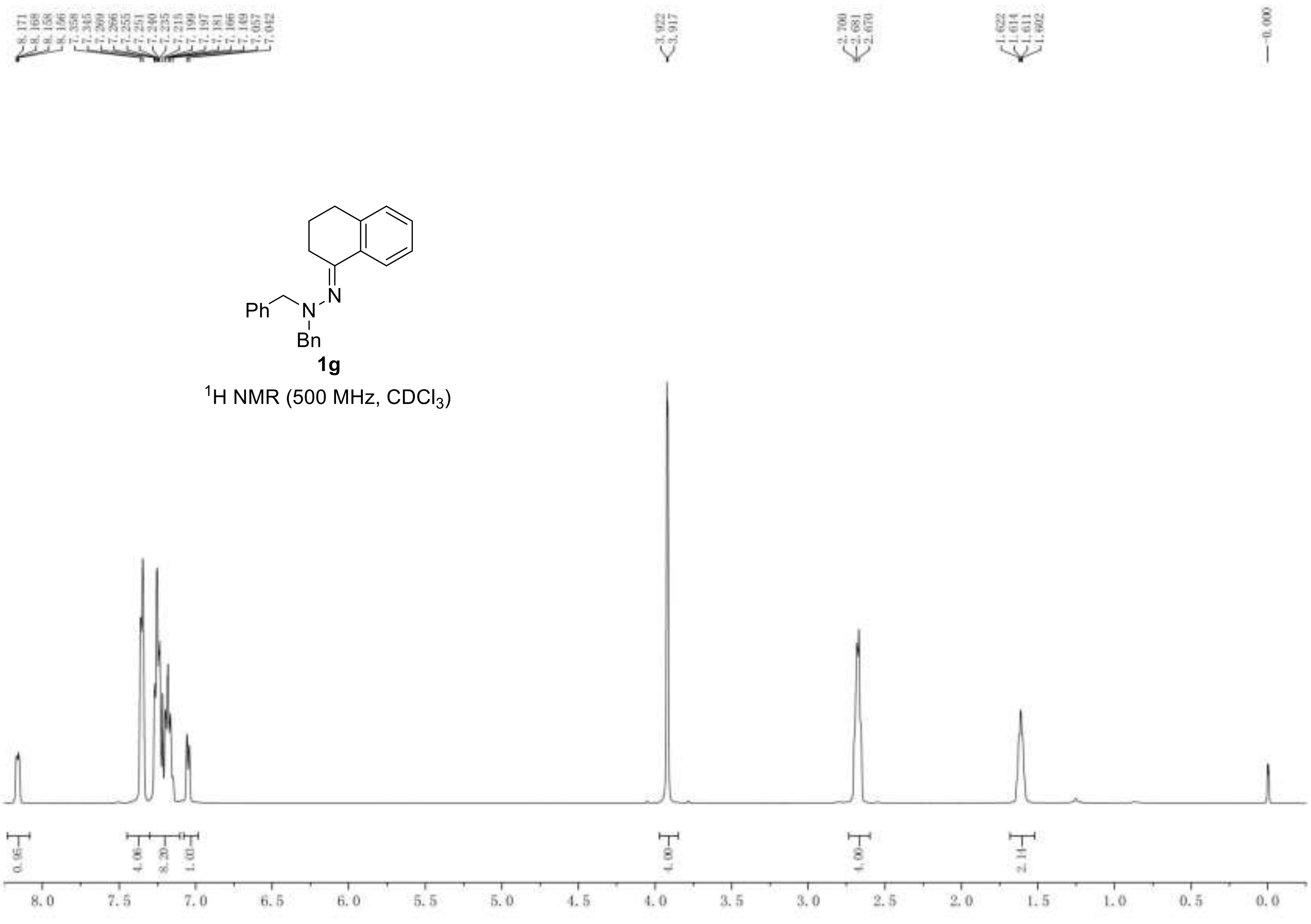
1f

^{1}H NMR (500 MHz, CDCl$_3$)



1f

^{13}C NMR (125 MHz, $CDCl_3$)



1g

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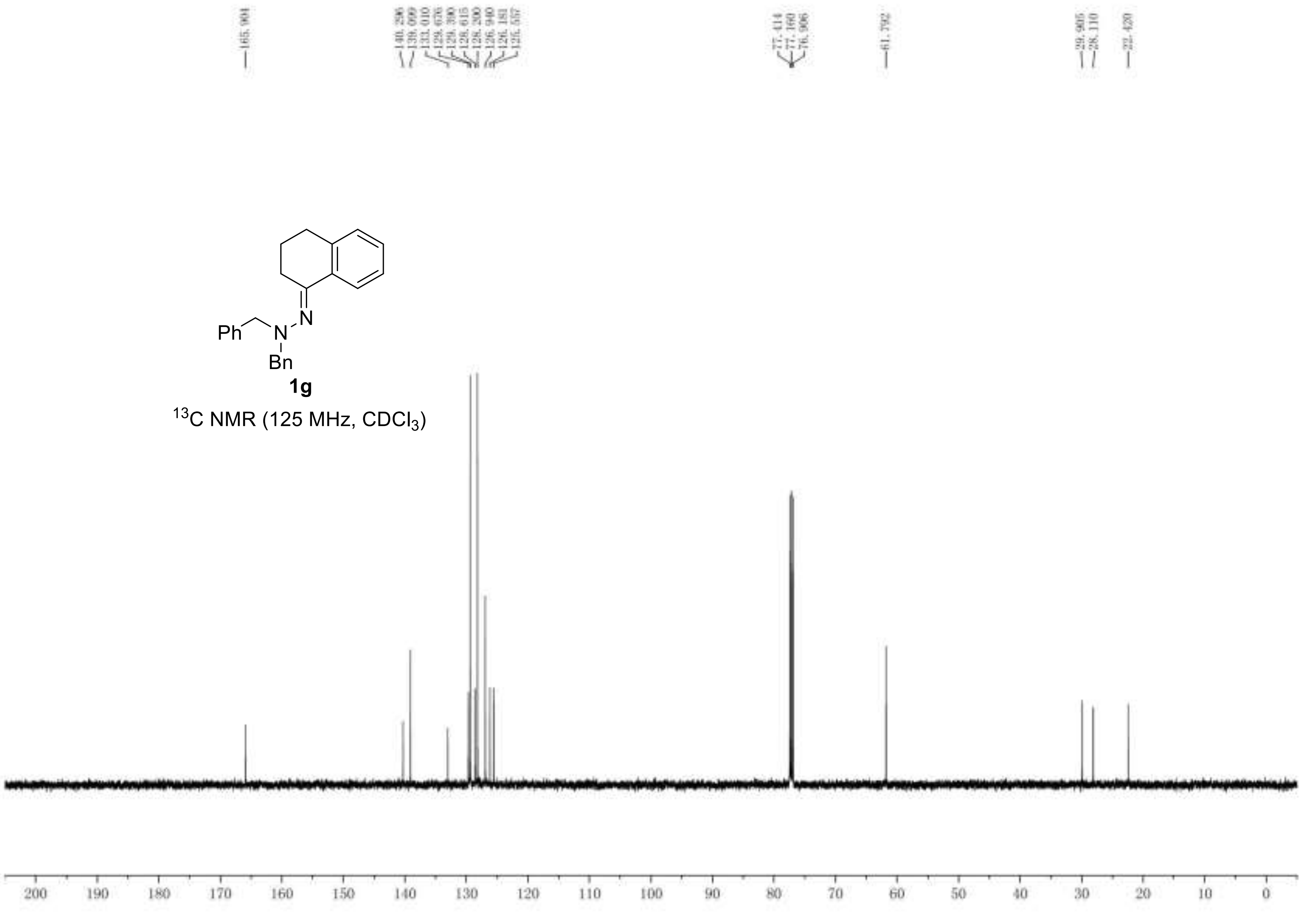
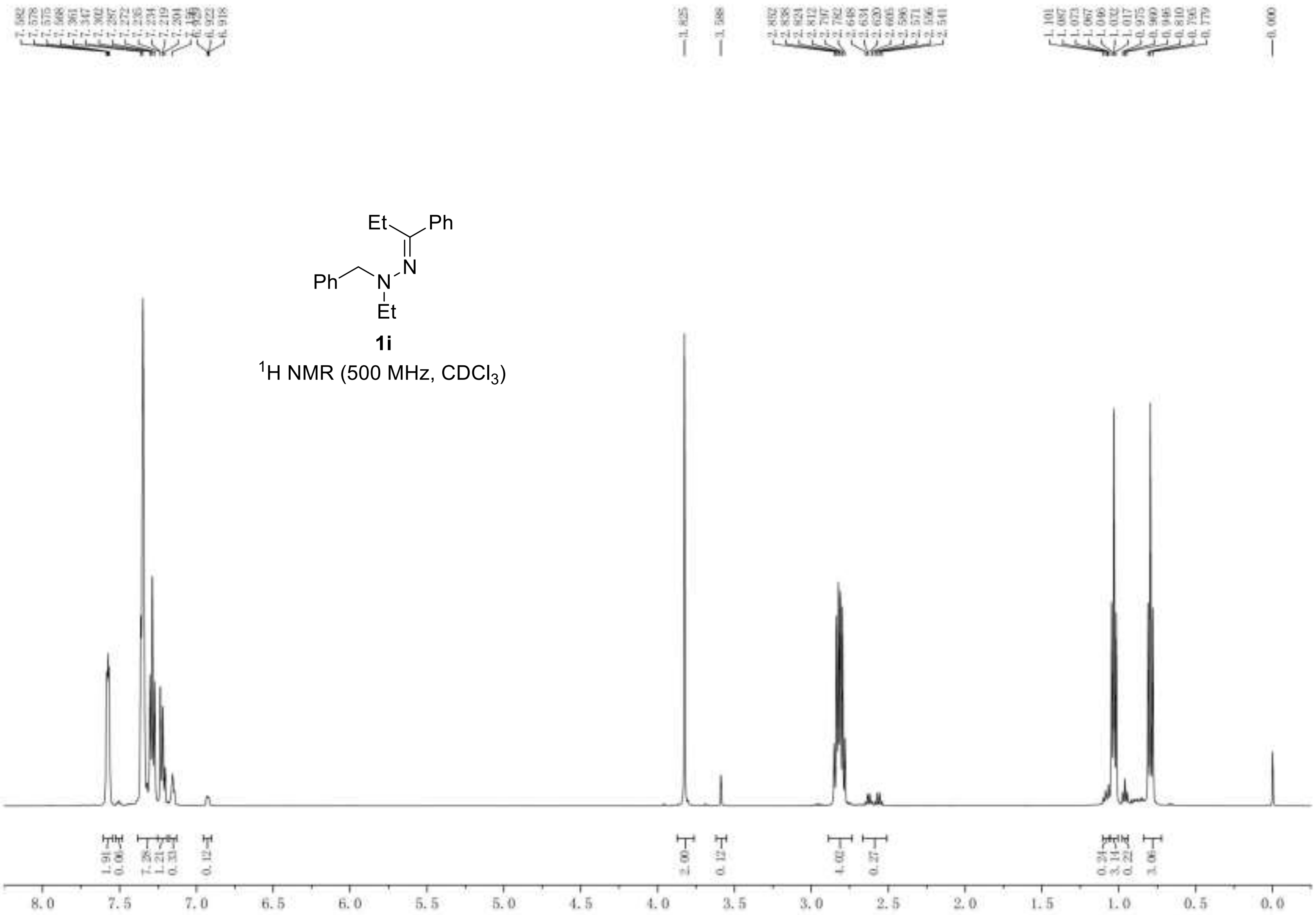


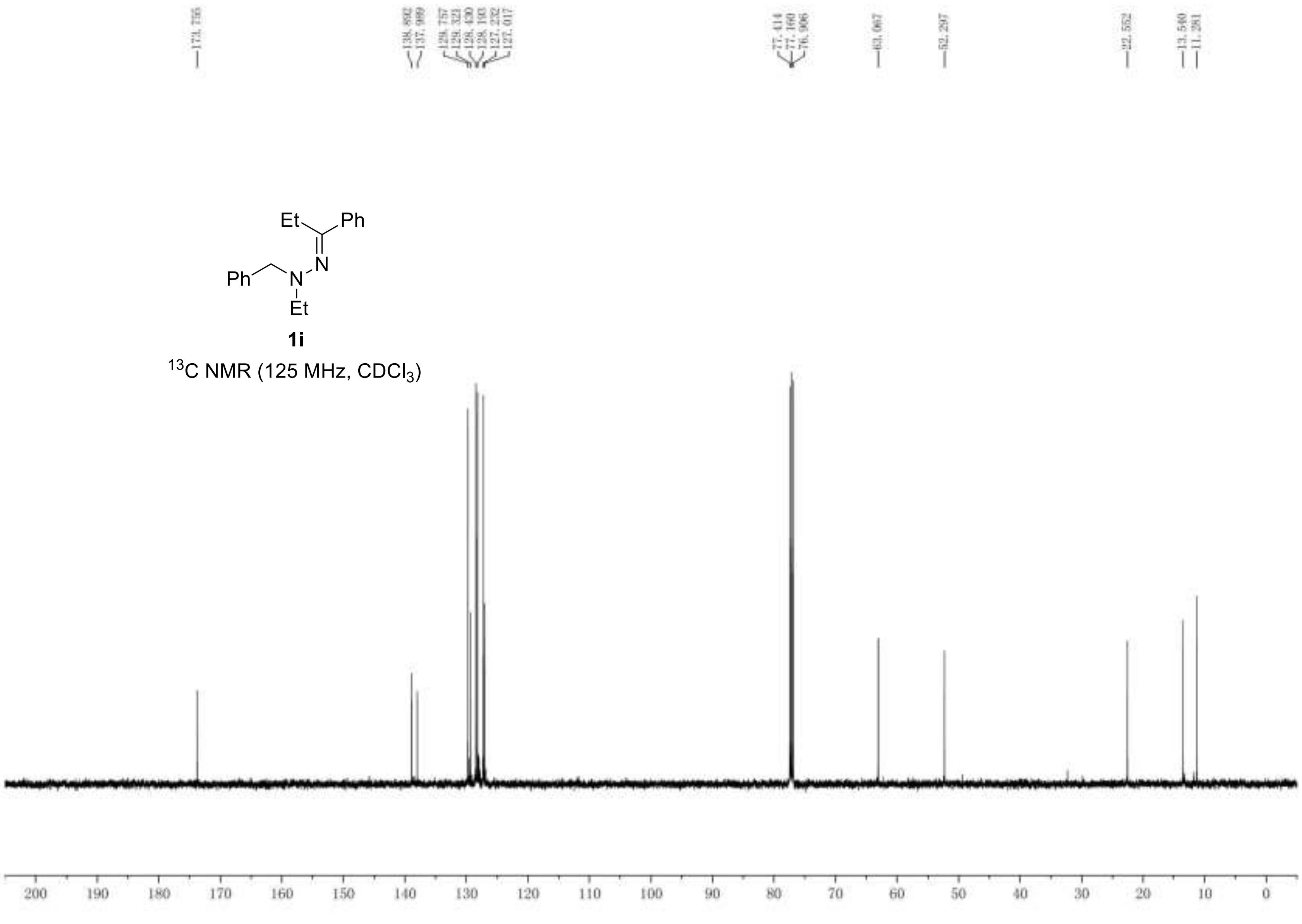
1g

^{13}C NMR (125 MHz, CDCl$_3$)



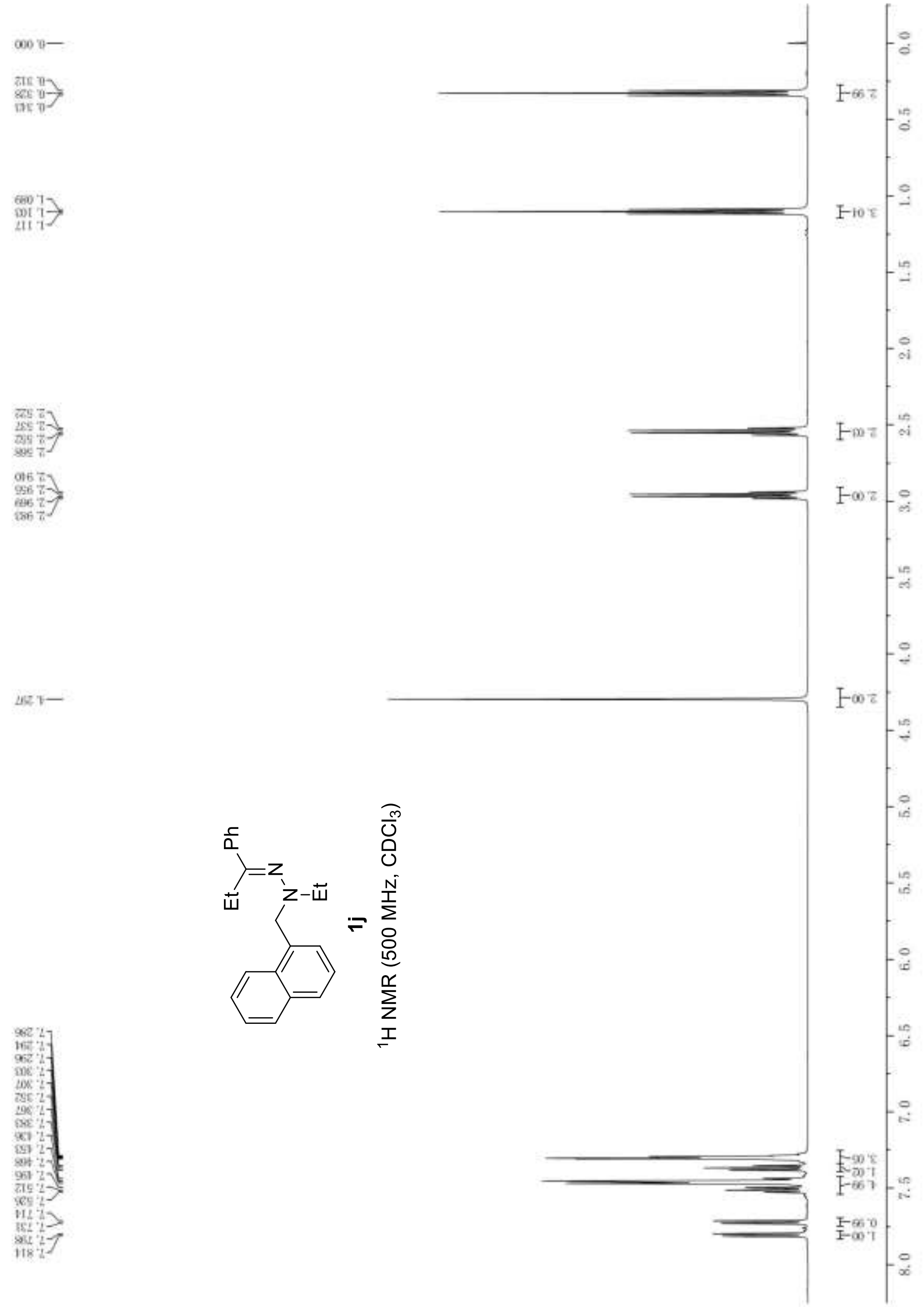
1i

^{1}H NMR (500 MHz, CDCl$_3$)



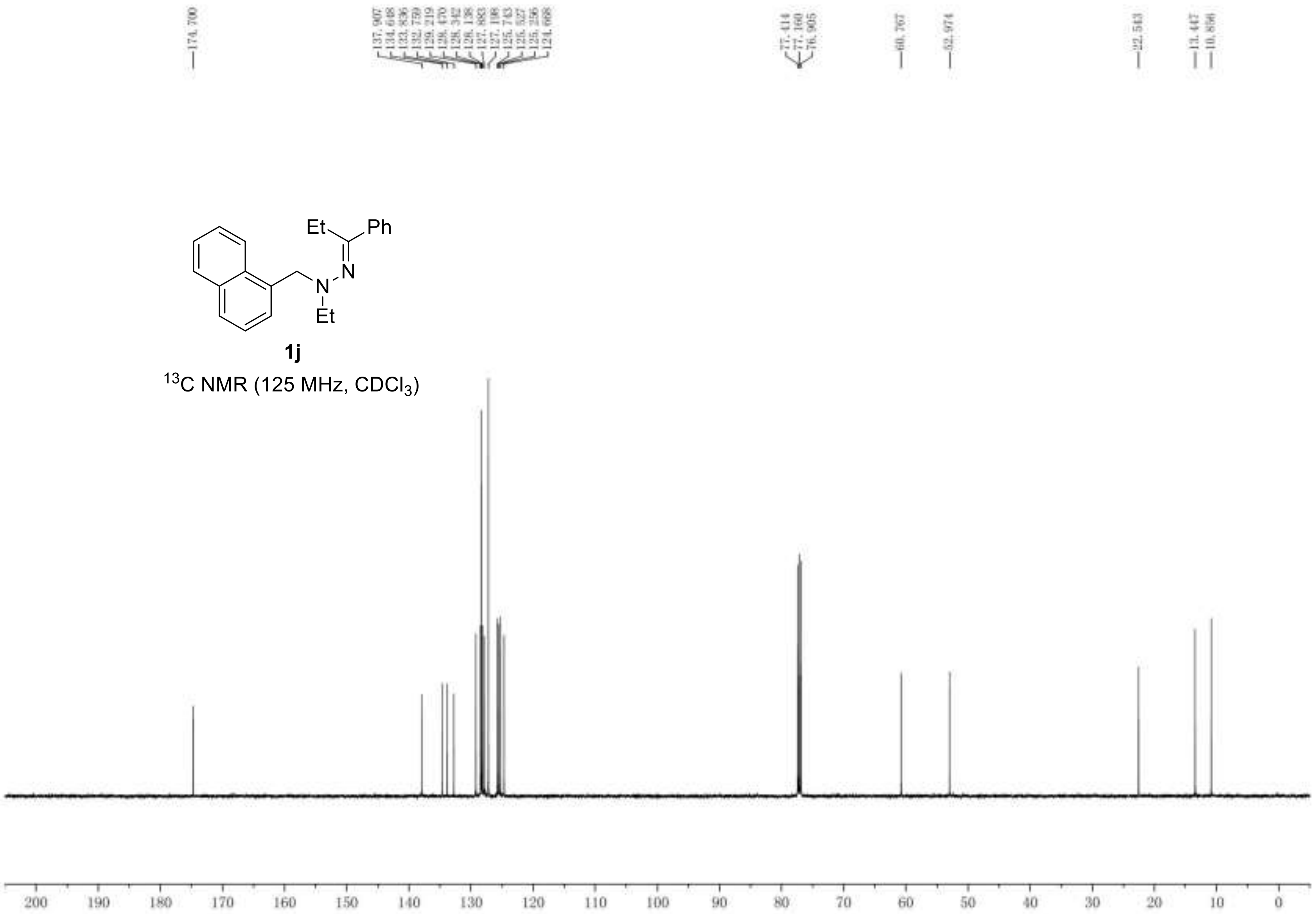
1i

^{13}C NMR (125 MHz, $CDCl_3$)



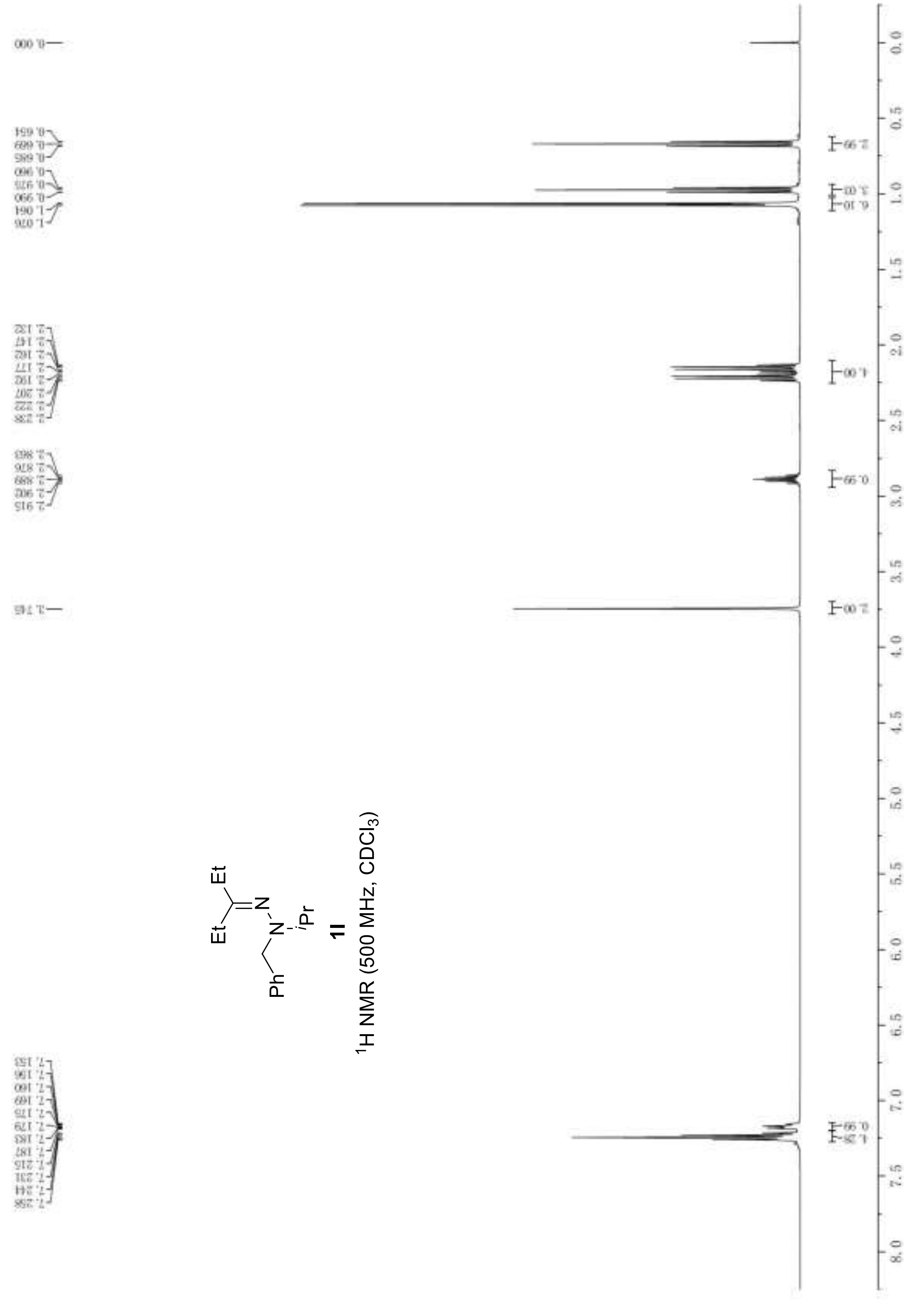
1j

^{1}H NMR (500 MHz, CDCl$_3$)



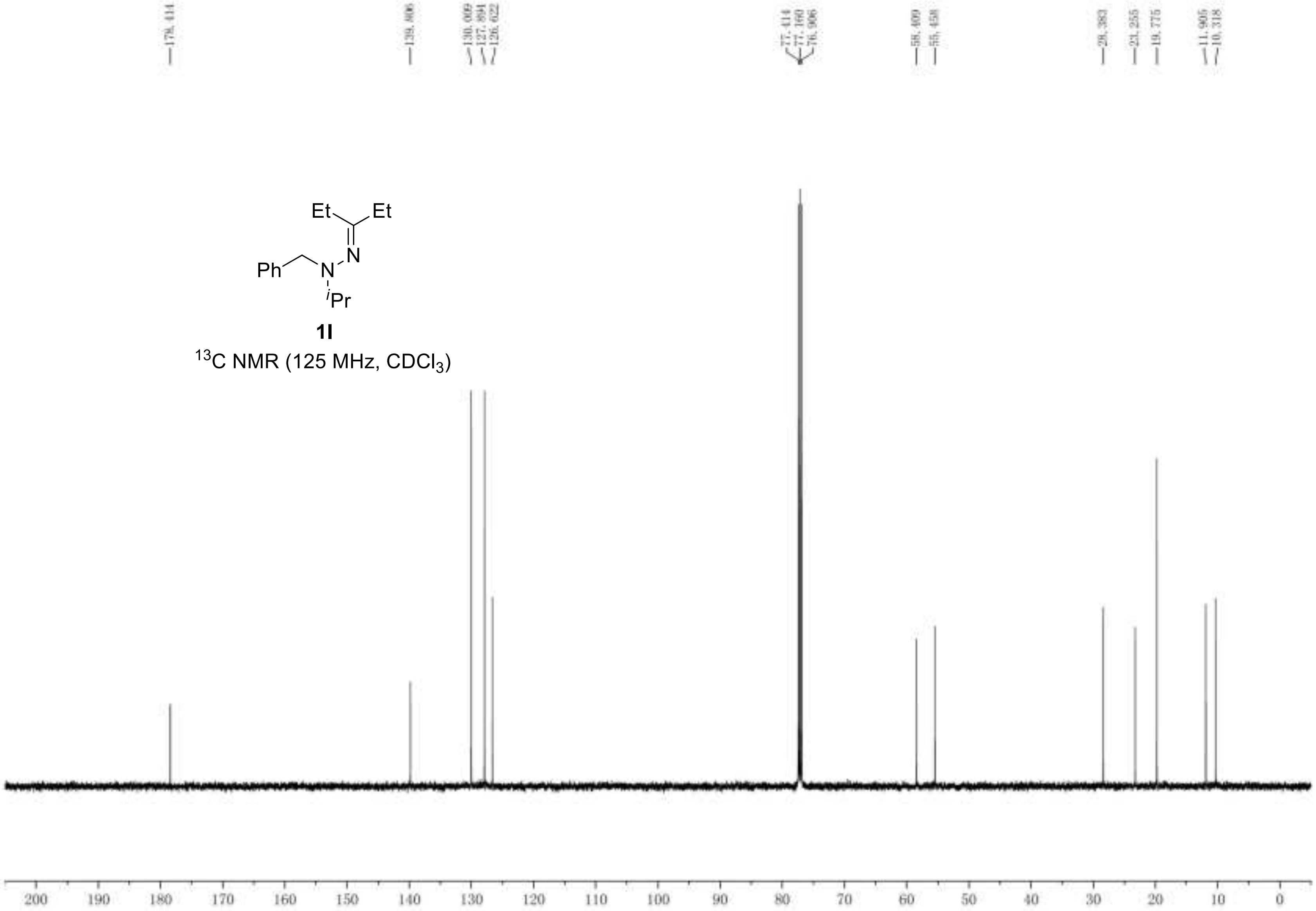
1j

^{13}C NMR (125 MHz, CDCl$_3$)



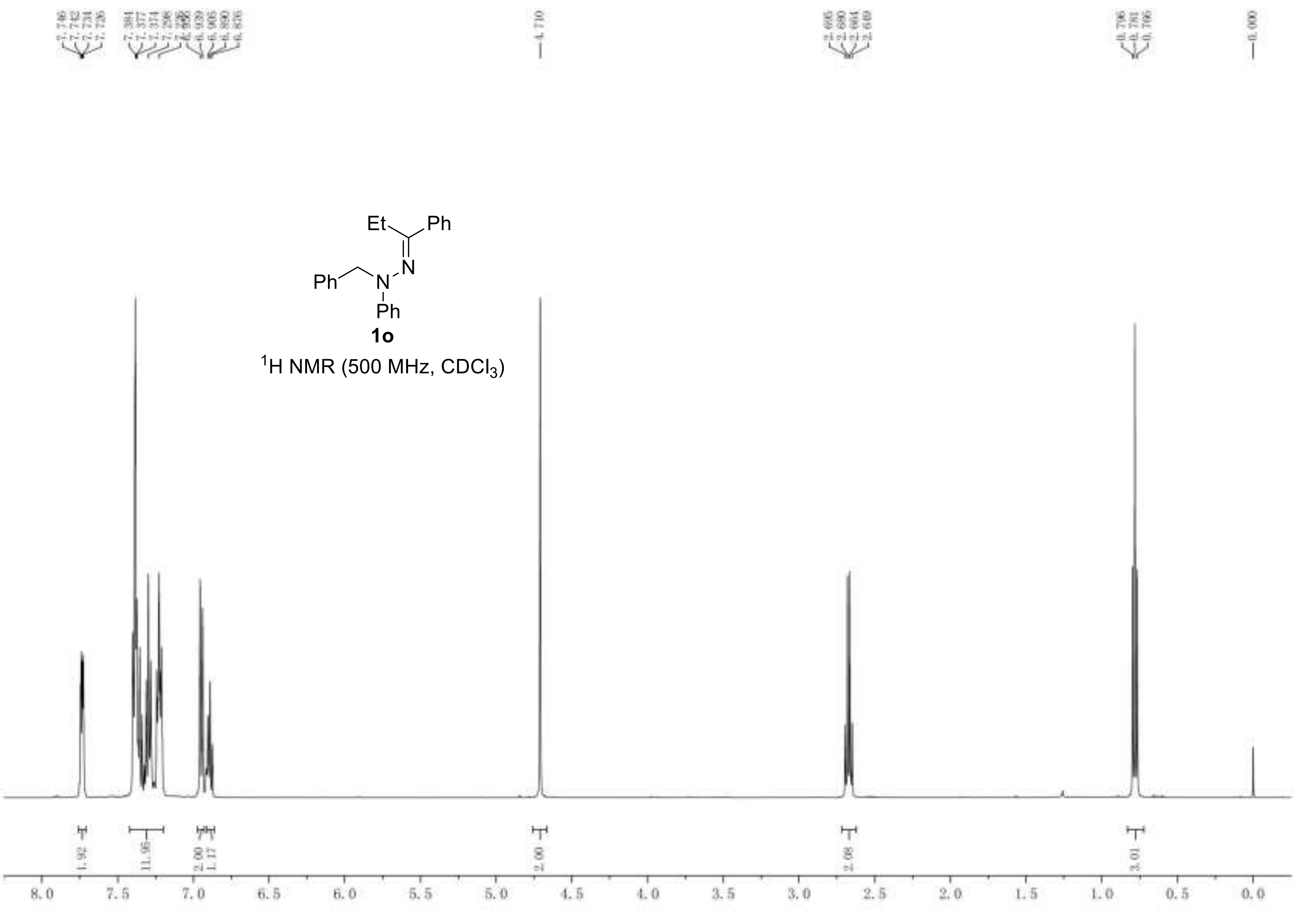
1l

^{1}H NMR (500 MHz, CDCl$_3$)



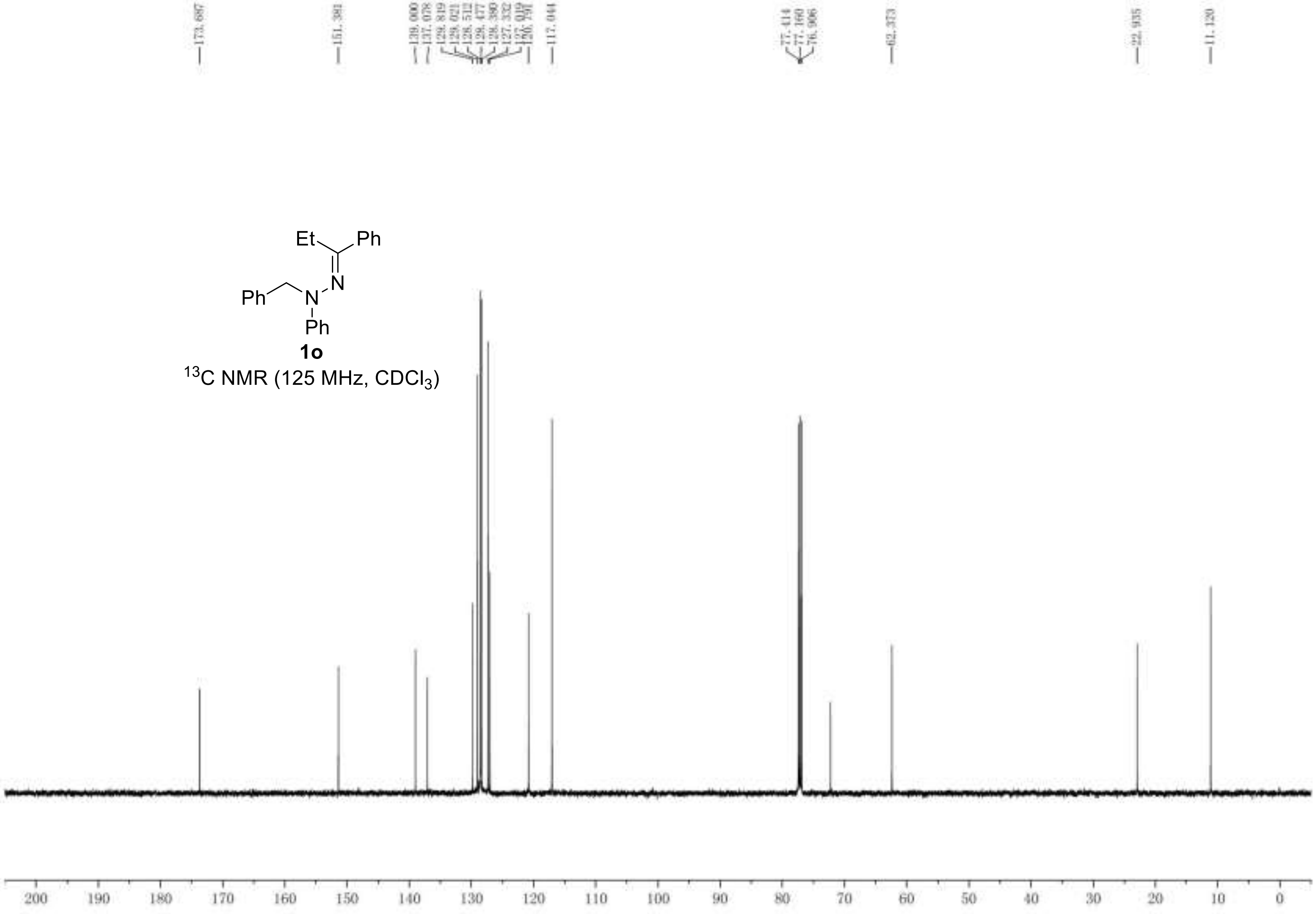
1l

^{13}C NMR (125 MHz, $CDCl_3$)



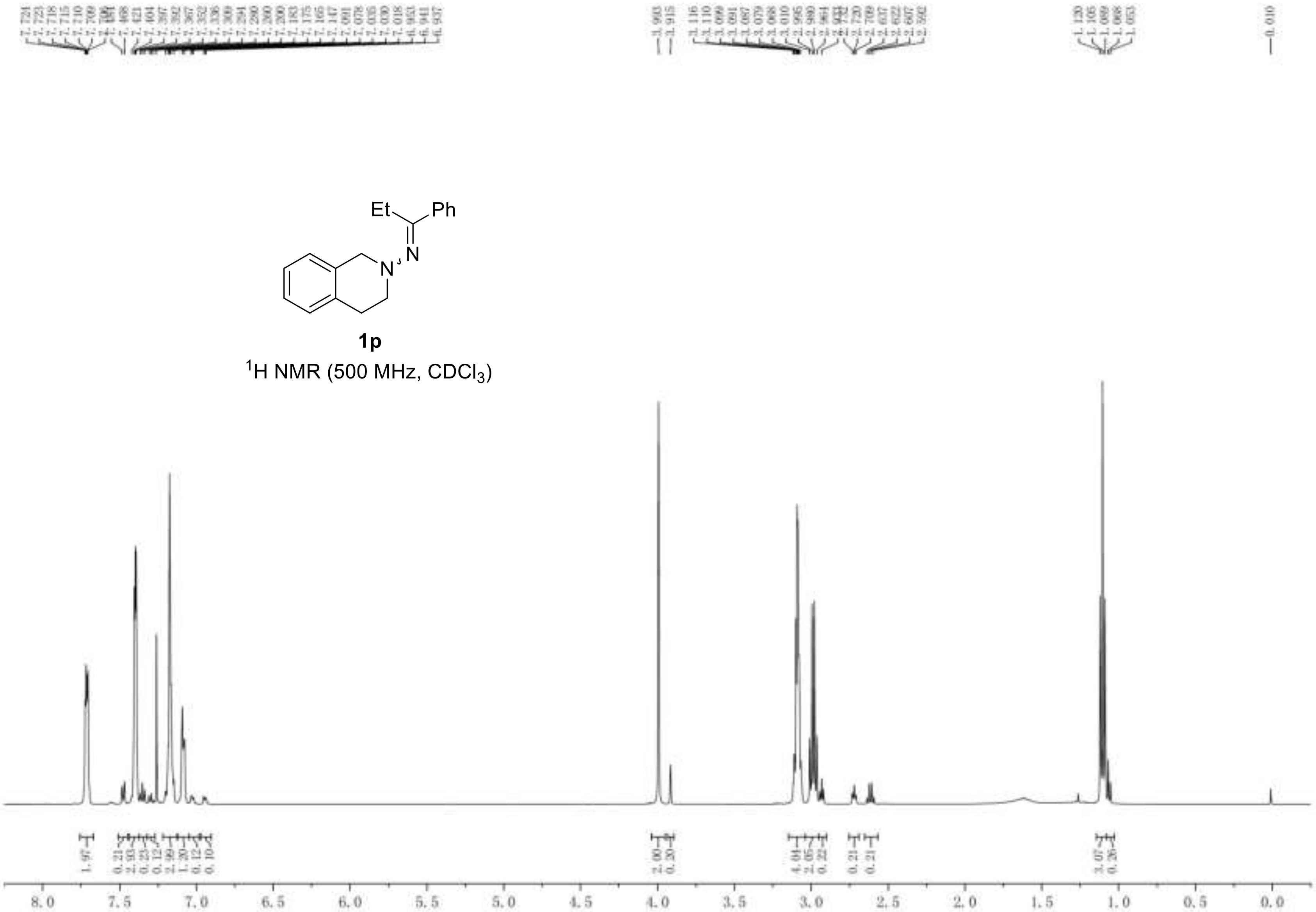
1o

^{1}H NMR (500 MHz, $CDCl_3$)



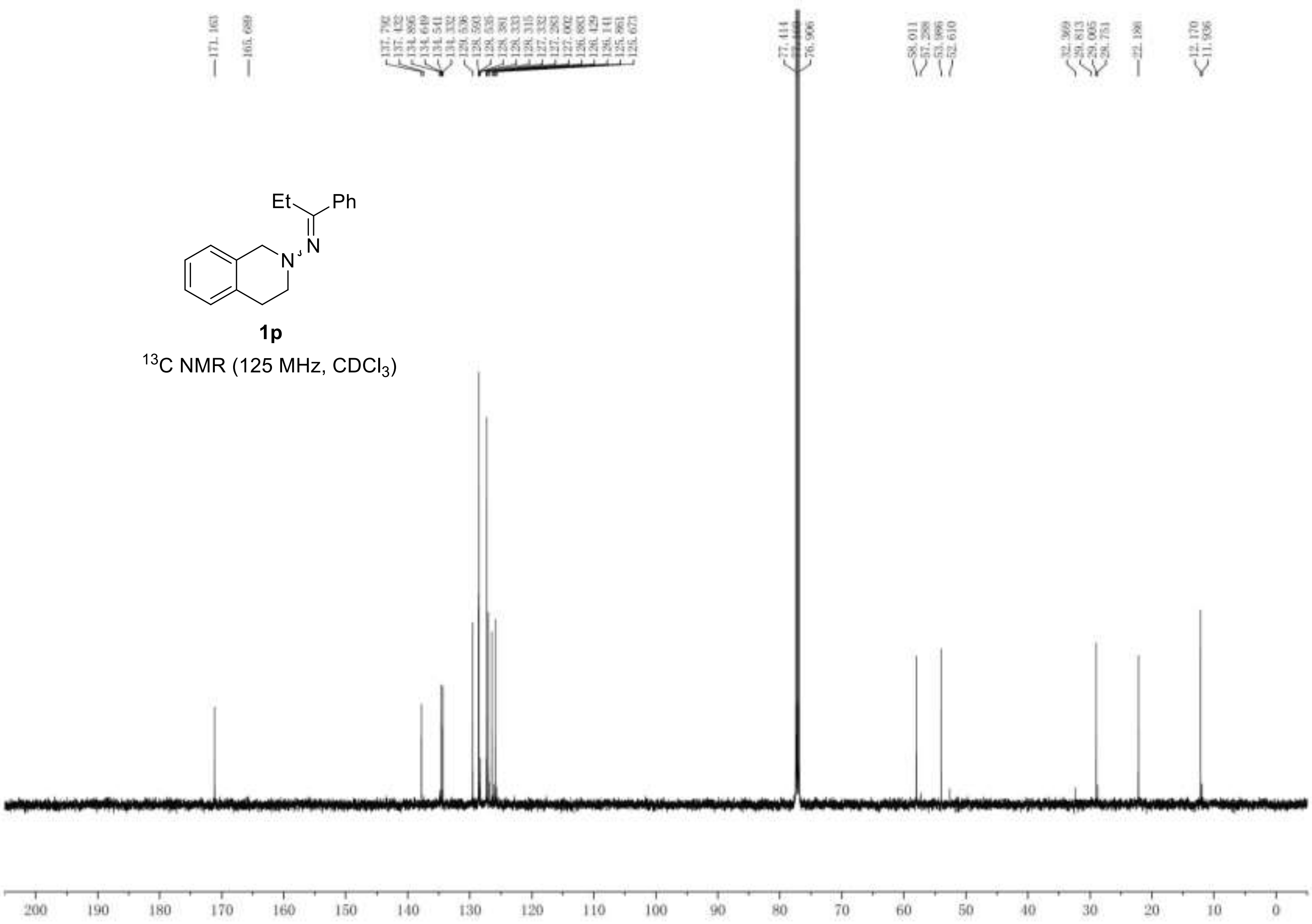
1o

^{13}C NMR (125 MHz, CDCl$_3$)



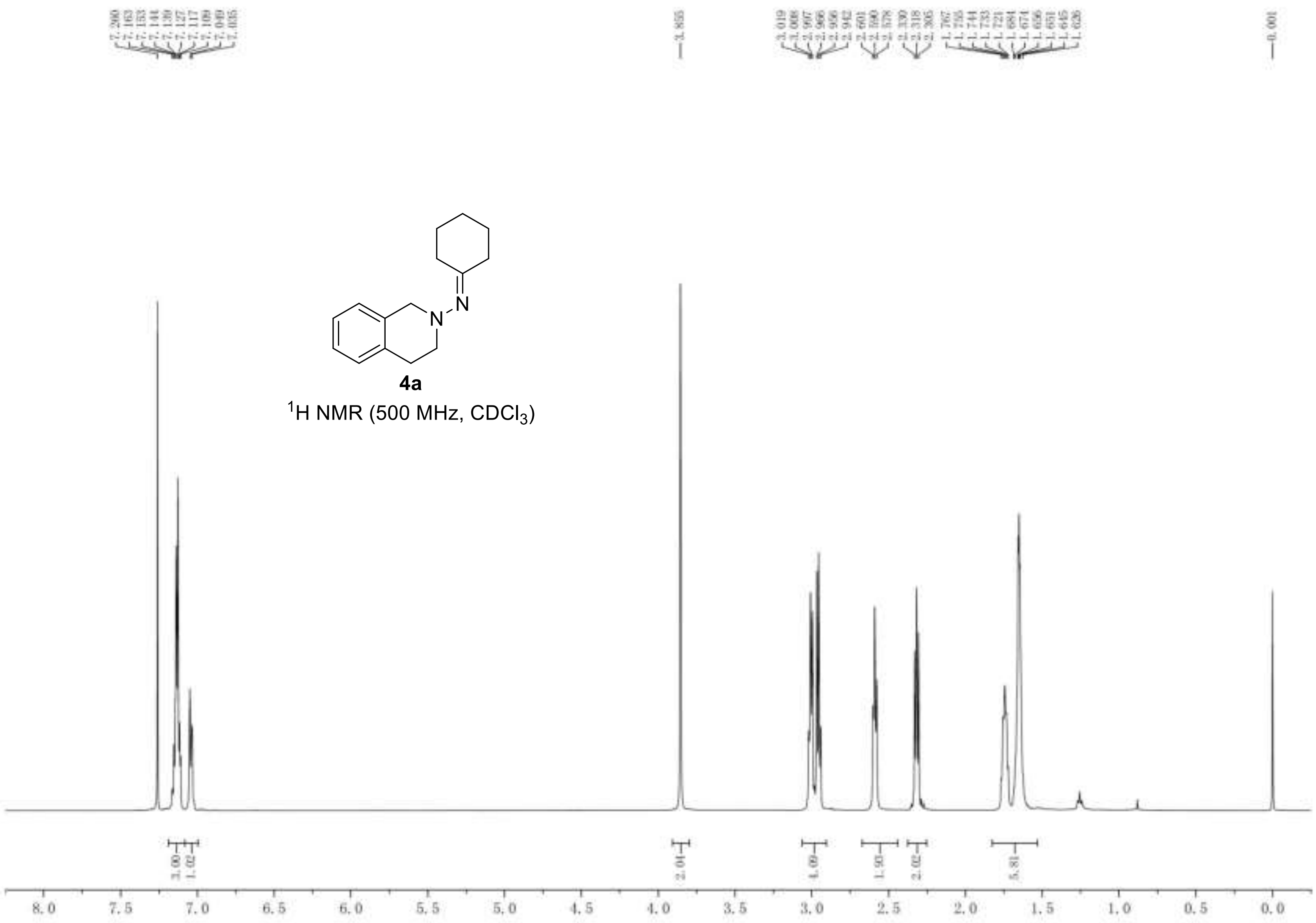
1p

^{1}H NMR (500 MHz, CDCl$_3$)



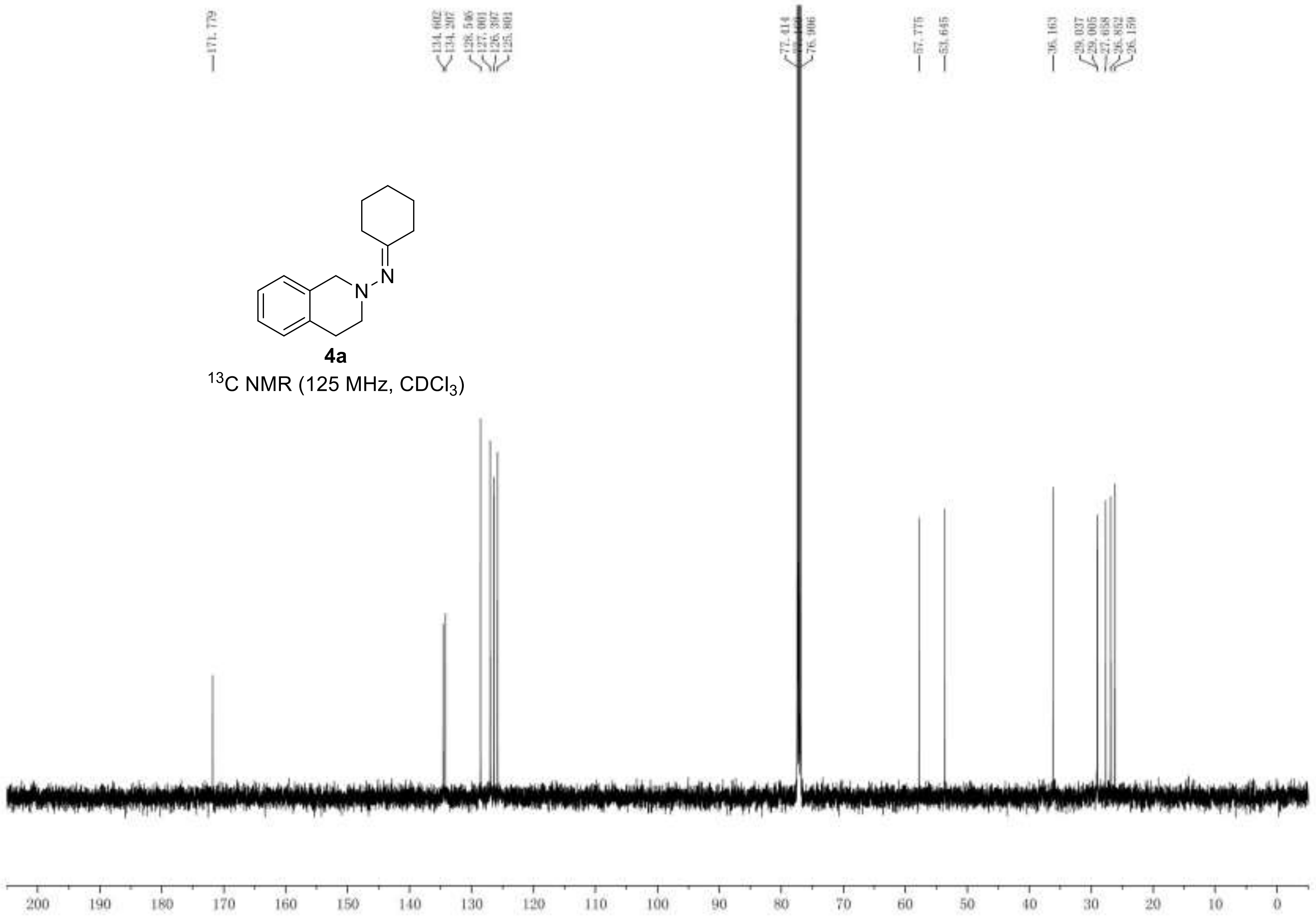
1p

^{13}C NMR (125 MHz, CDCl$_3$)



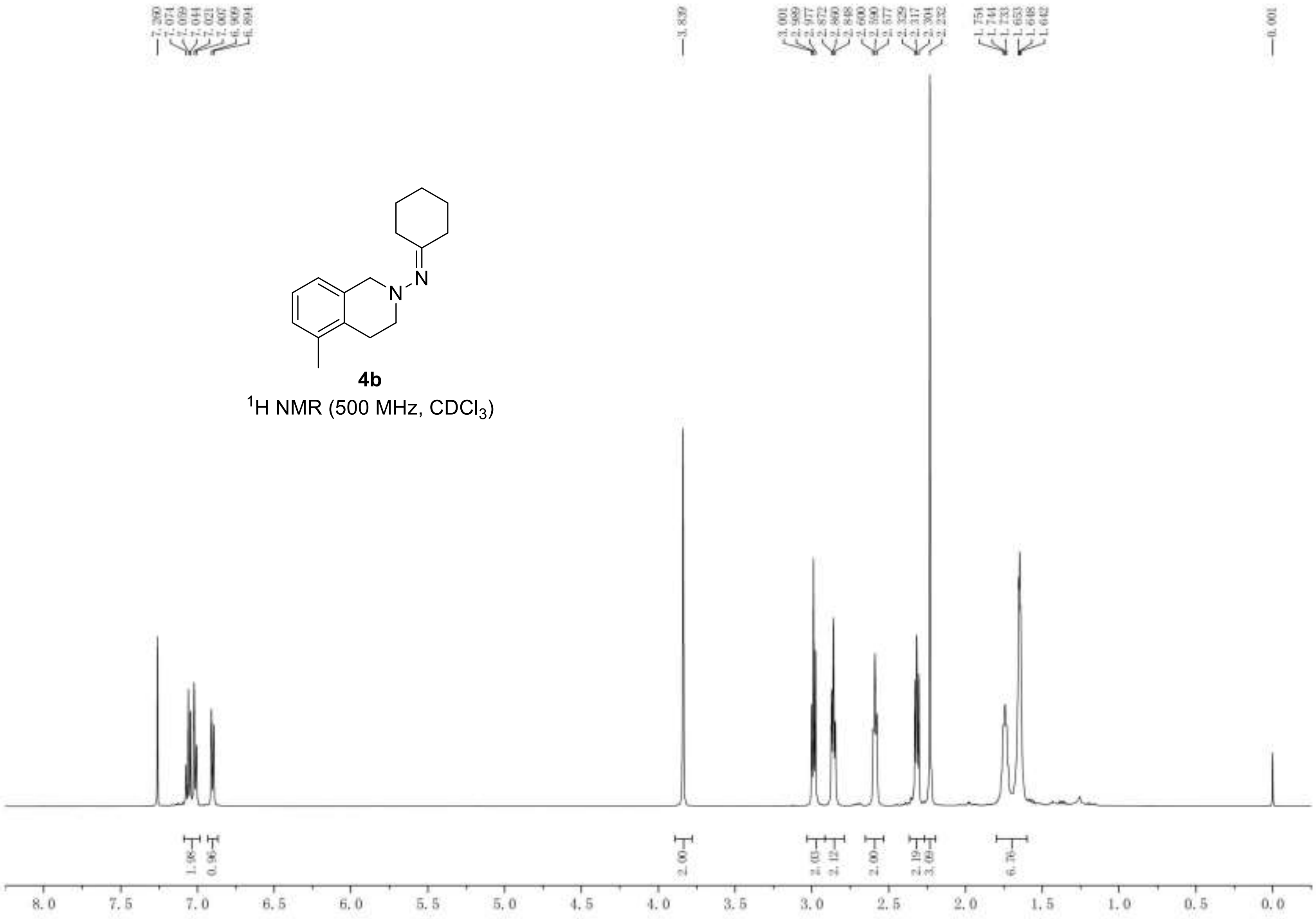
4a

^{1}H NMR (500 MHz, $CDCl_3$)



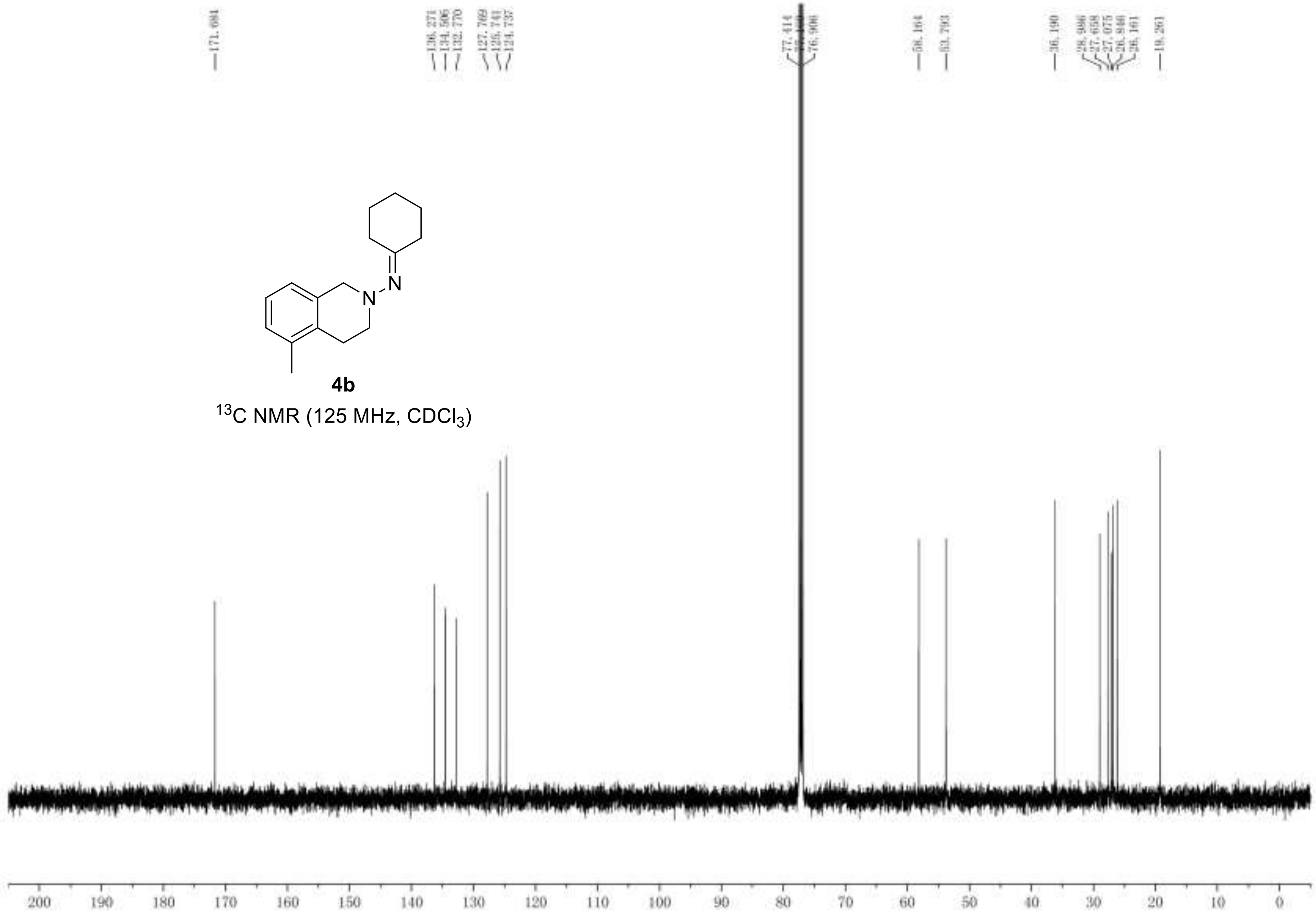
4a

^{13}C NMR (125 MHz, CDCl$_3$)



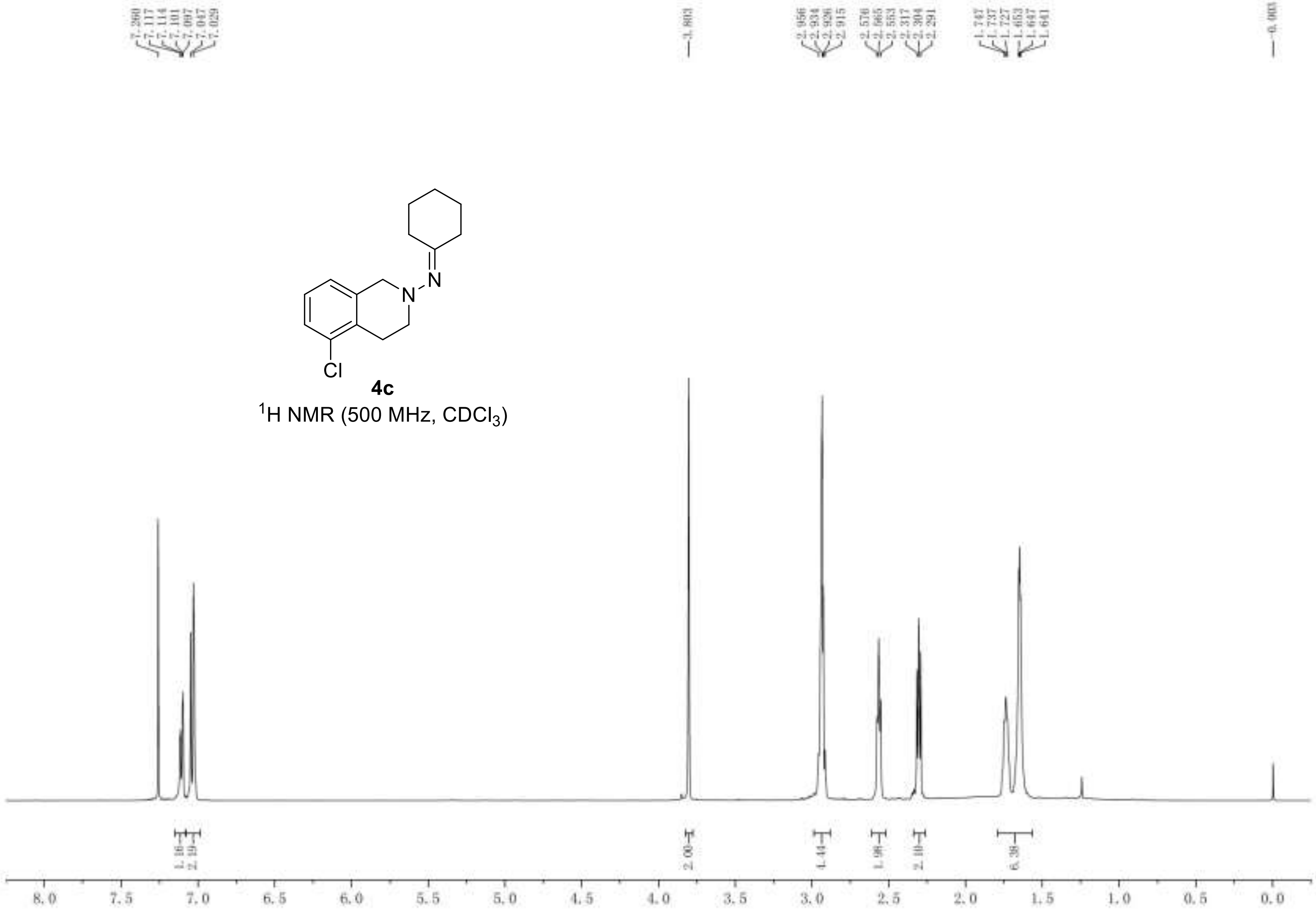
4b

^{1}H NMR (500 MHz, CDCl$_3$)



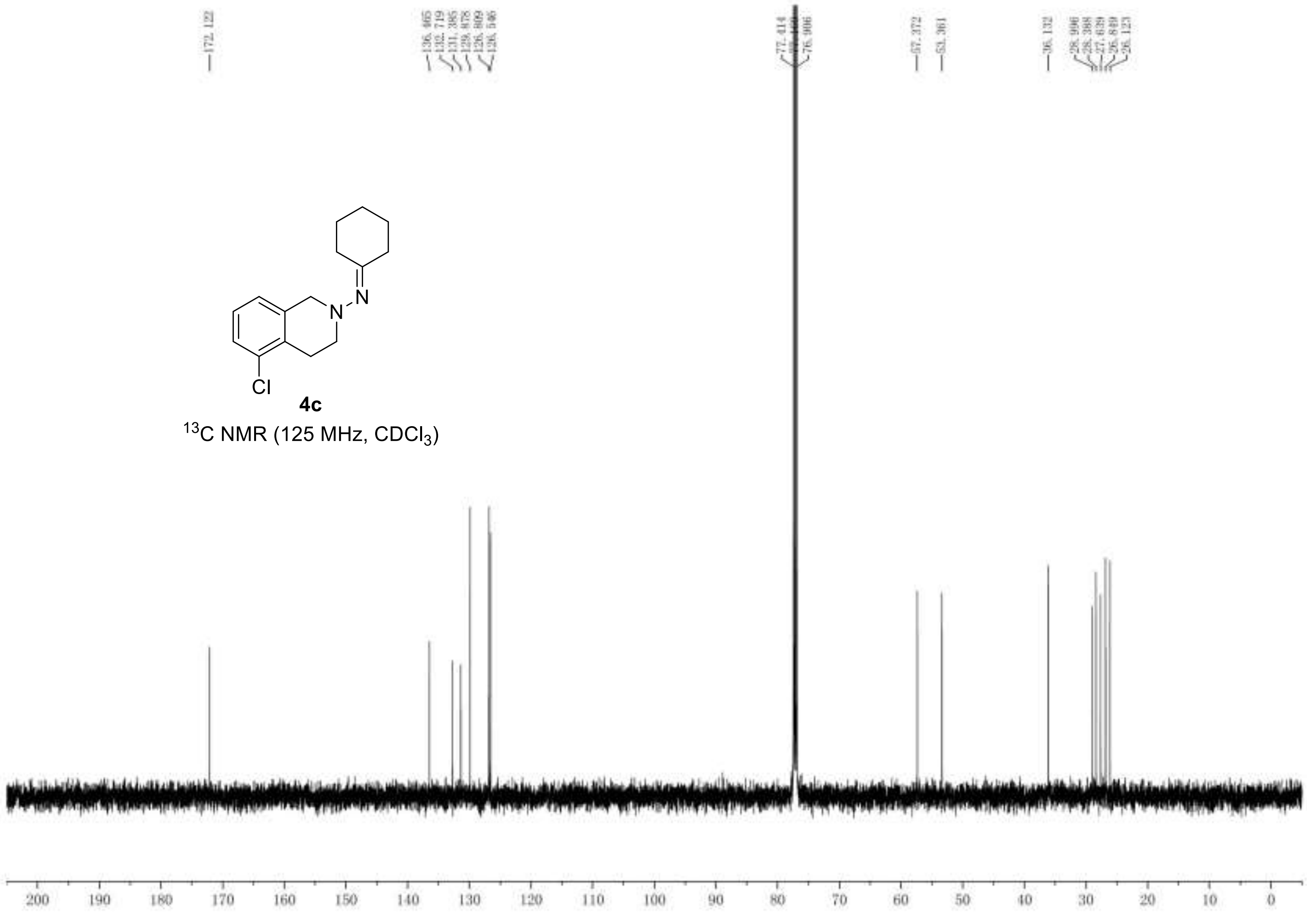
4b

^{13}C NMR (125 MHz, CDCl$_3$)



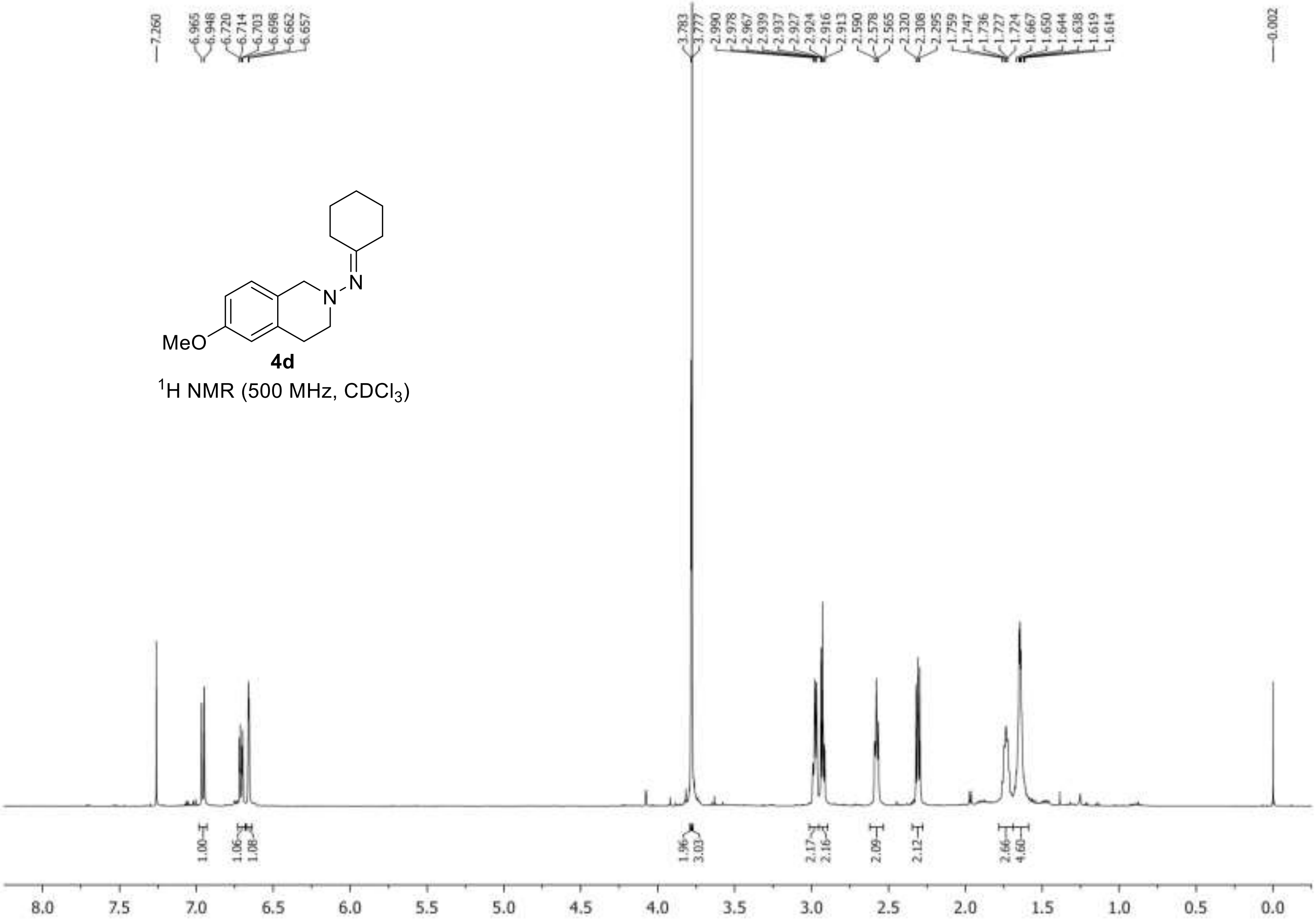
4c

^{1}H NMR (500 MHz, CDCl$_3$)



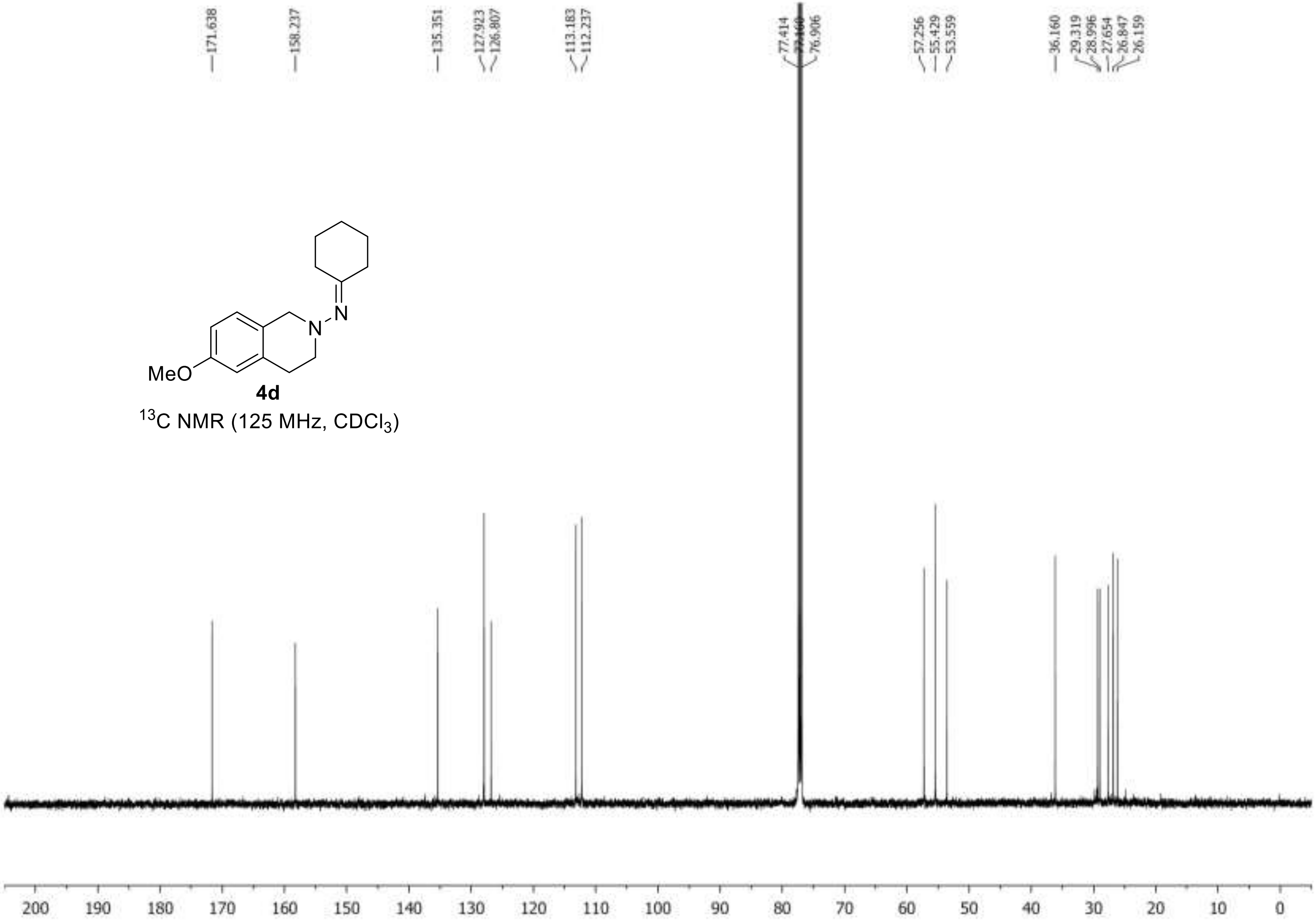
4c

^{13}C NMR (125 MHz, $CDCl_3$)



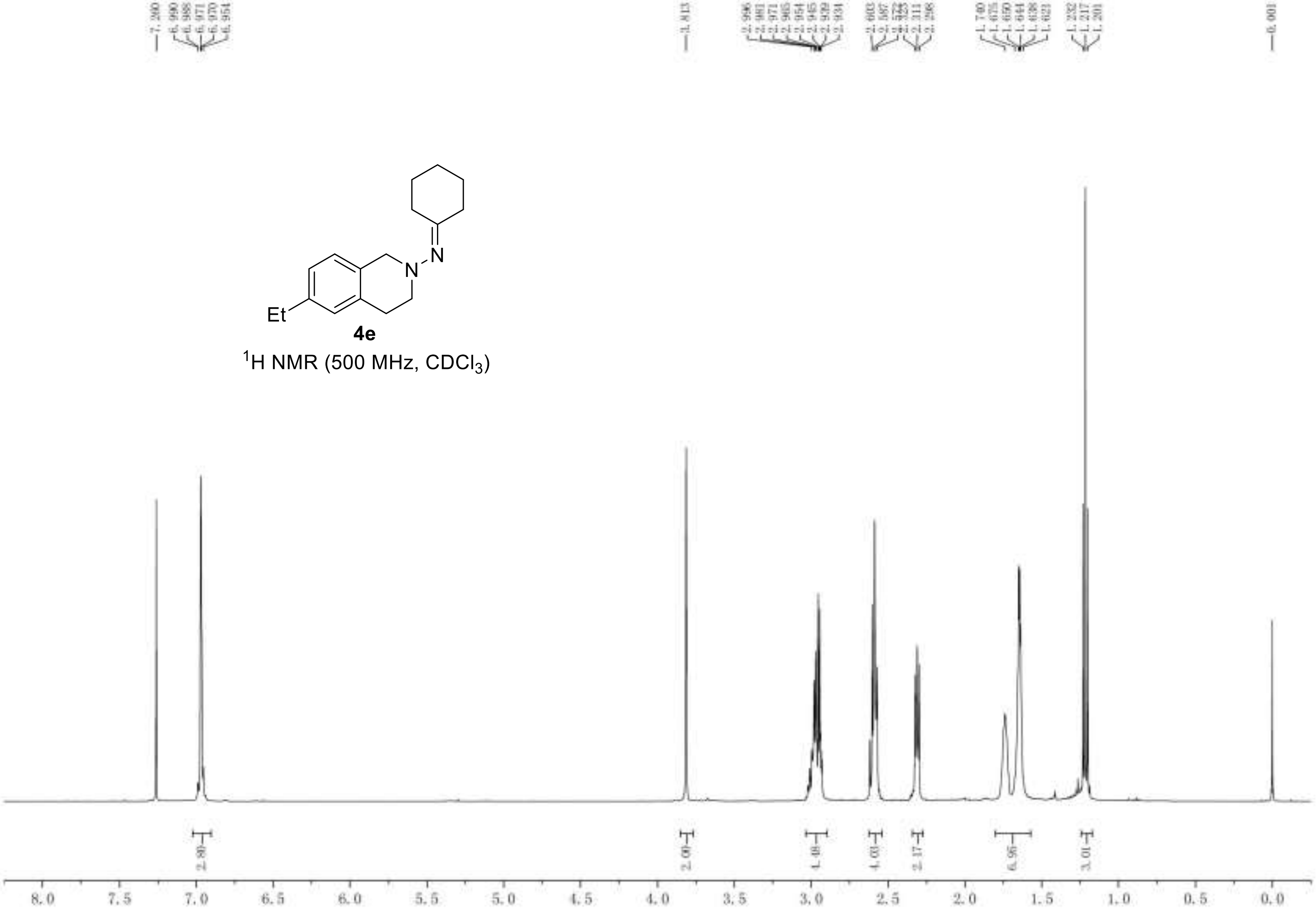
4d

^{1}H NMR (500 MHz, $CDCl_3$)



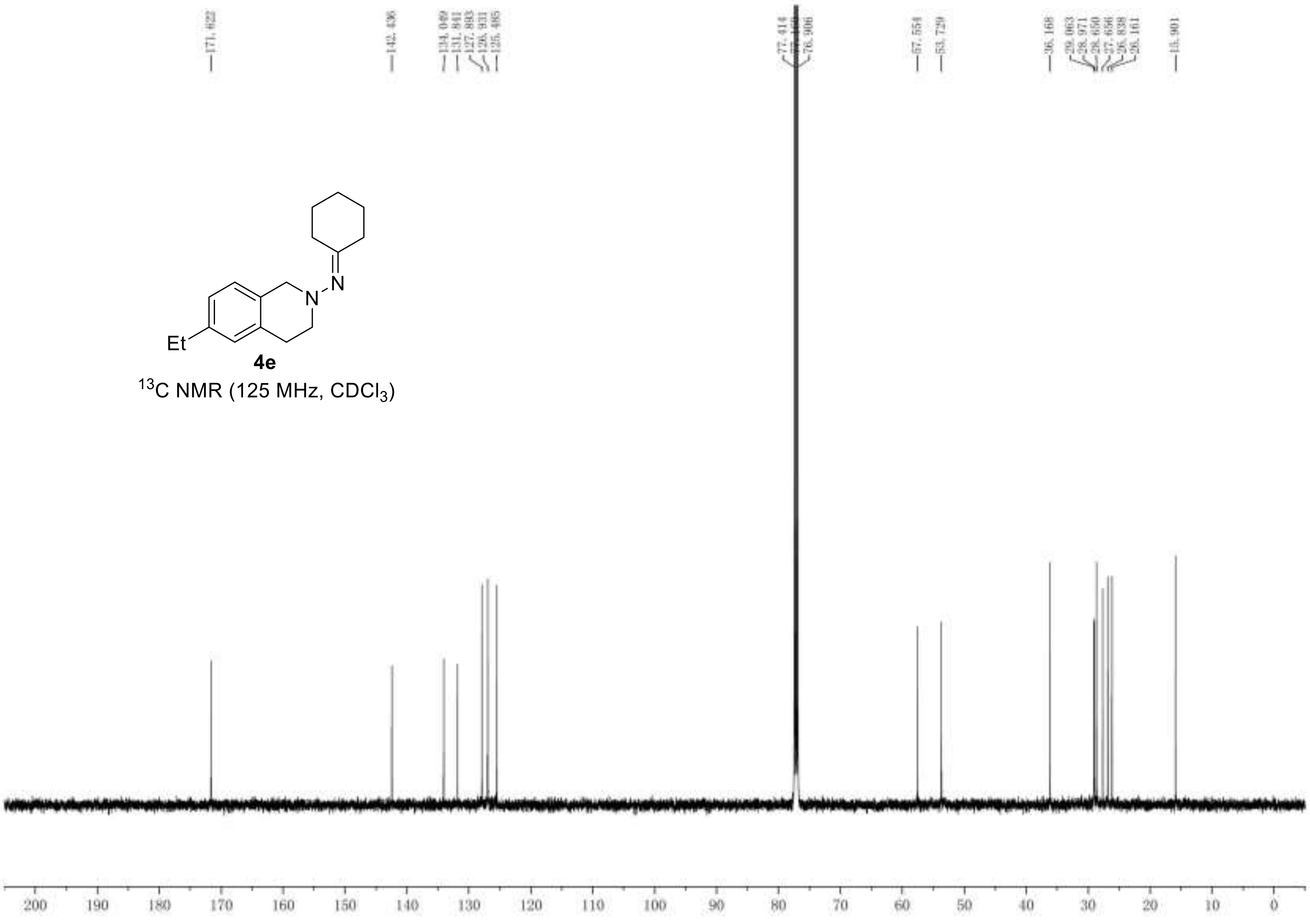
4d

^{13}C NMR (125 MHz, CDCl$_3$)



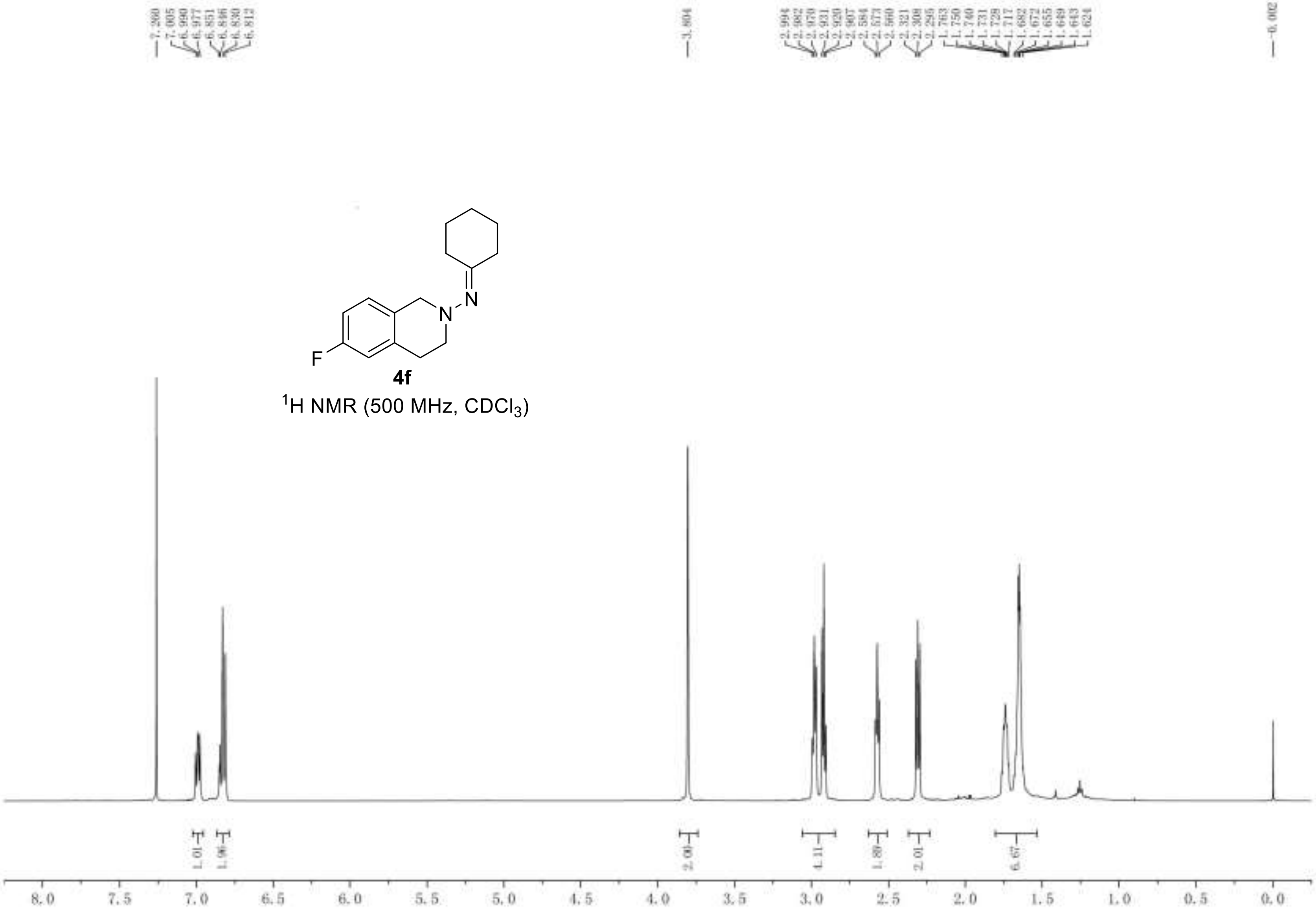
4e

^{1}H NMR (500 MHz, CDCl$_3$)



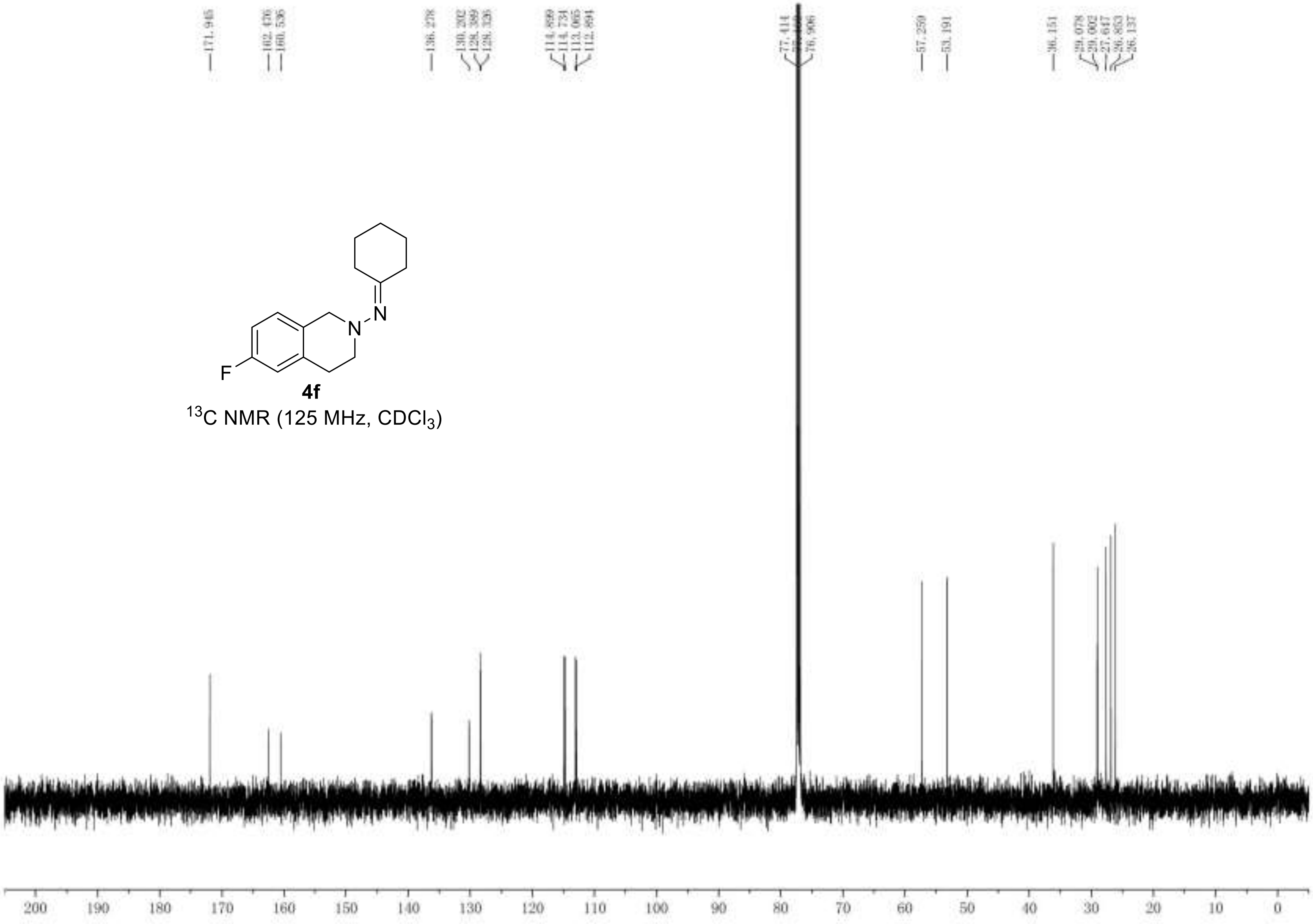
4e

^{13}C NMR (125 MHz, CDCl$_3$)



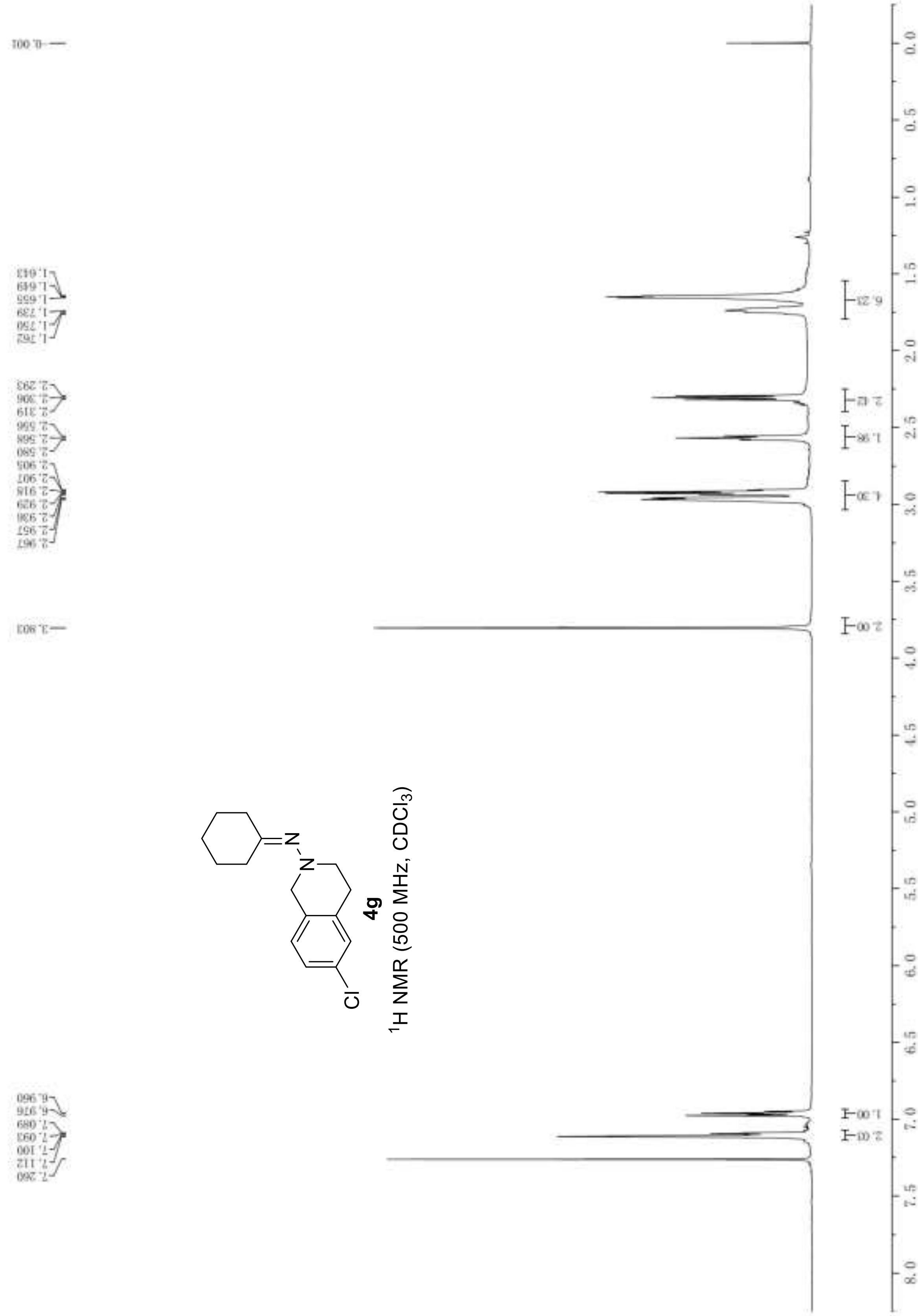
4f

^{1}H NMR (500 MHz, $CDCl_3$)



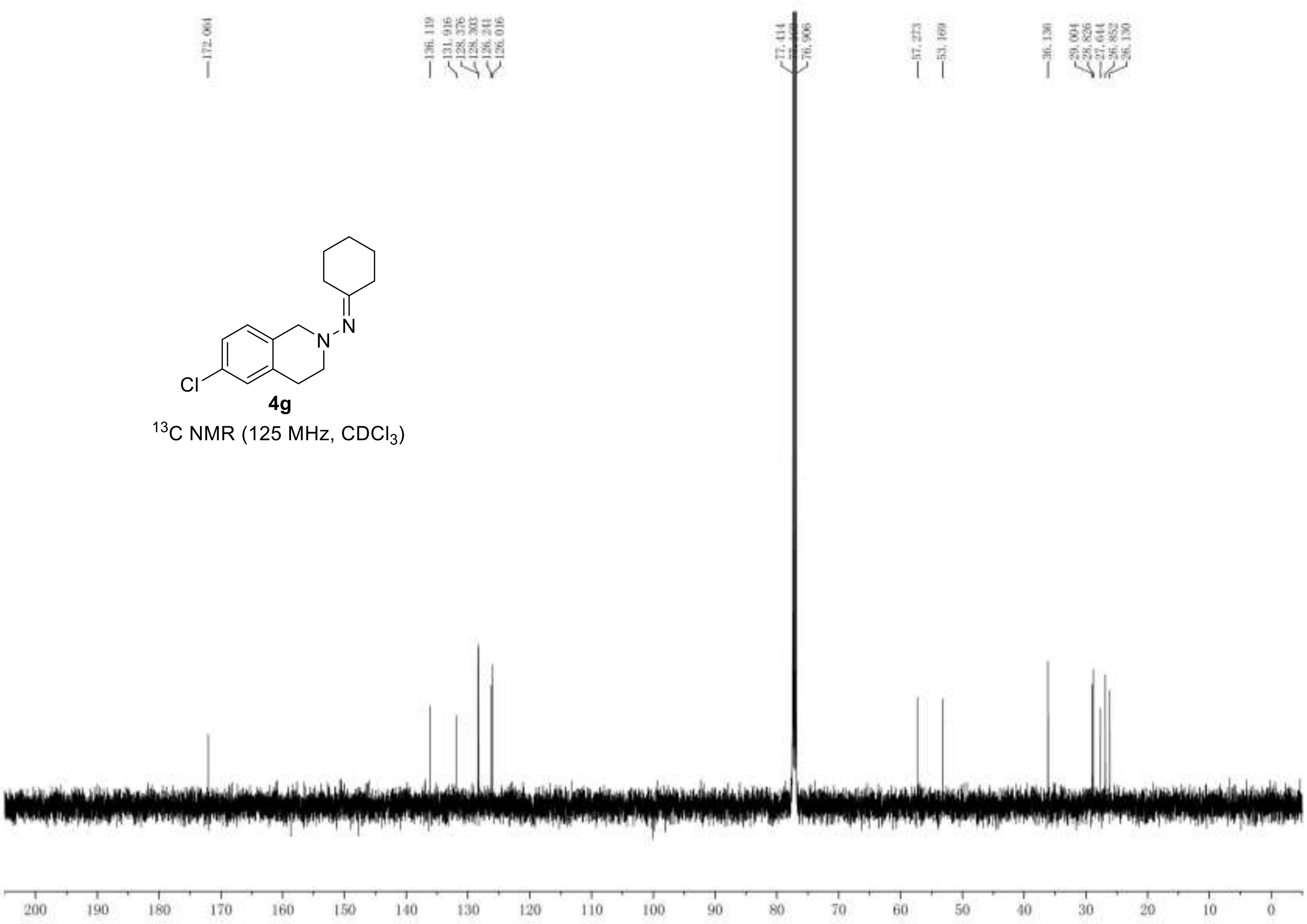
4f

^{13}C NMR (125 MHz, CDCl$_3$)



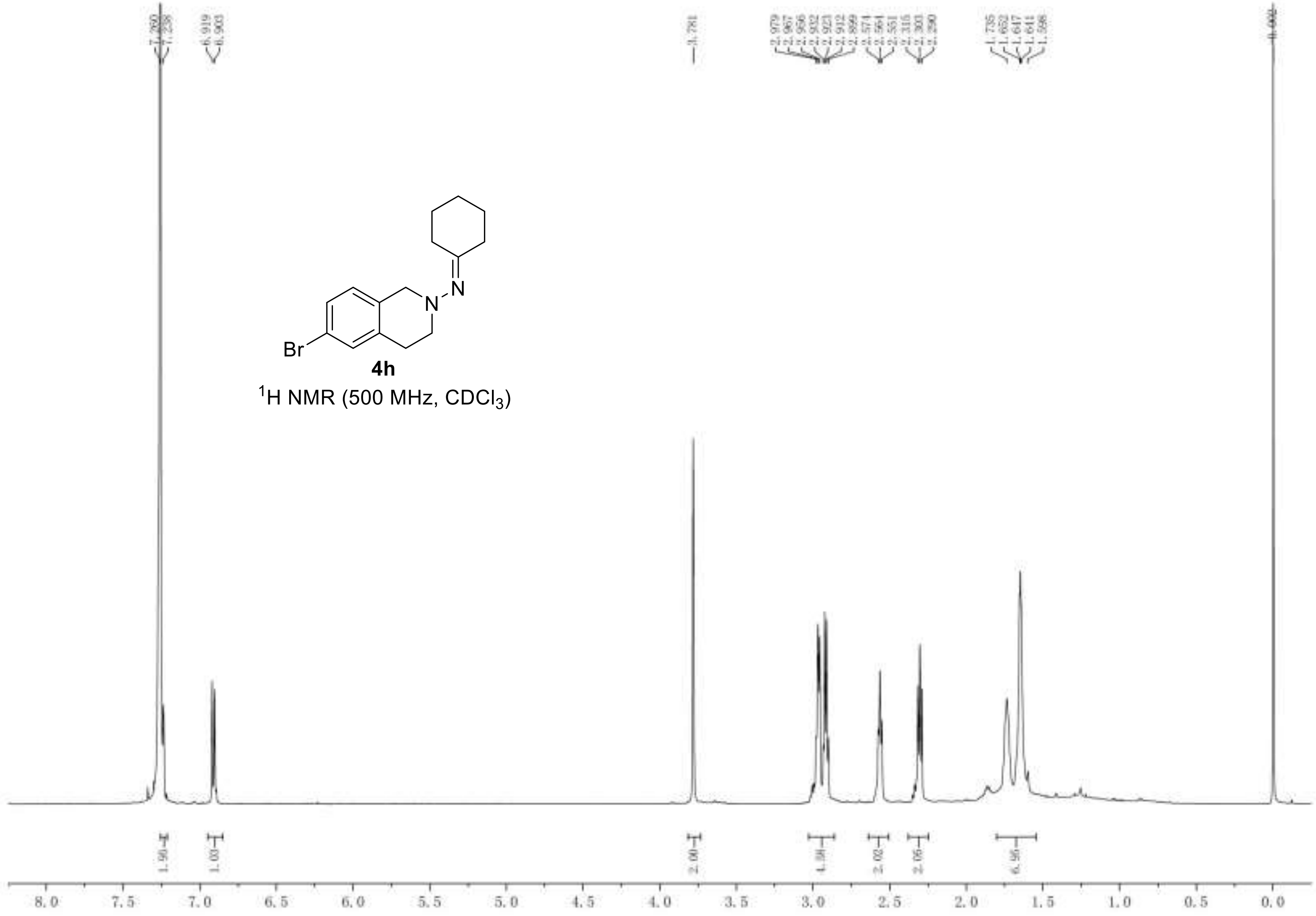
4g

^{1}H NMR (500 MHz, CDCl$_3$)



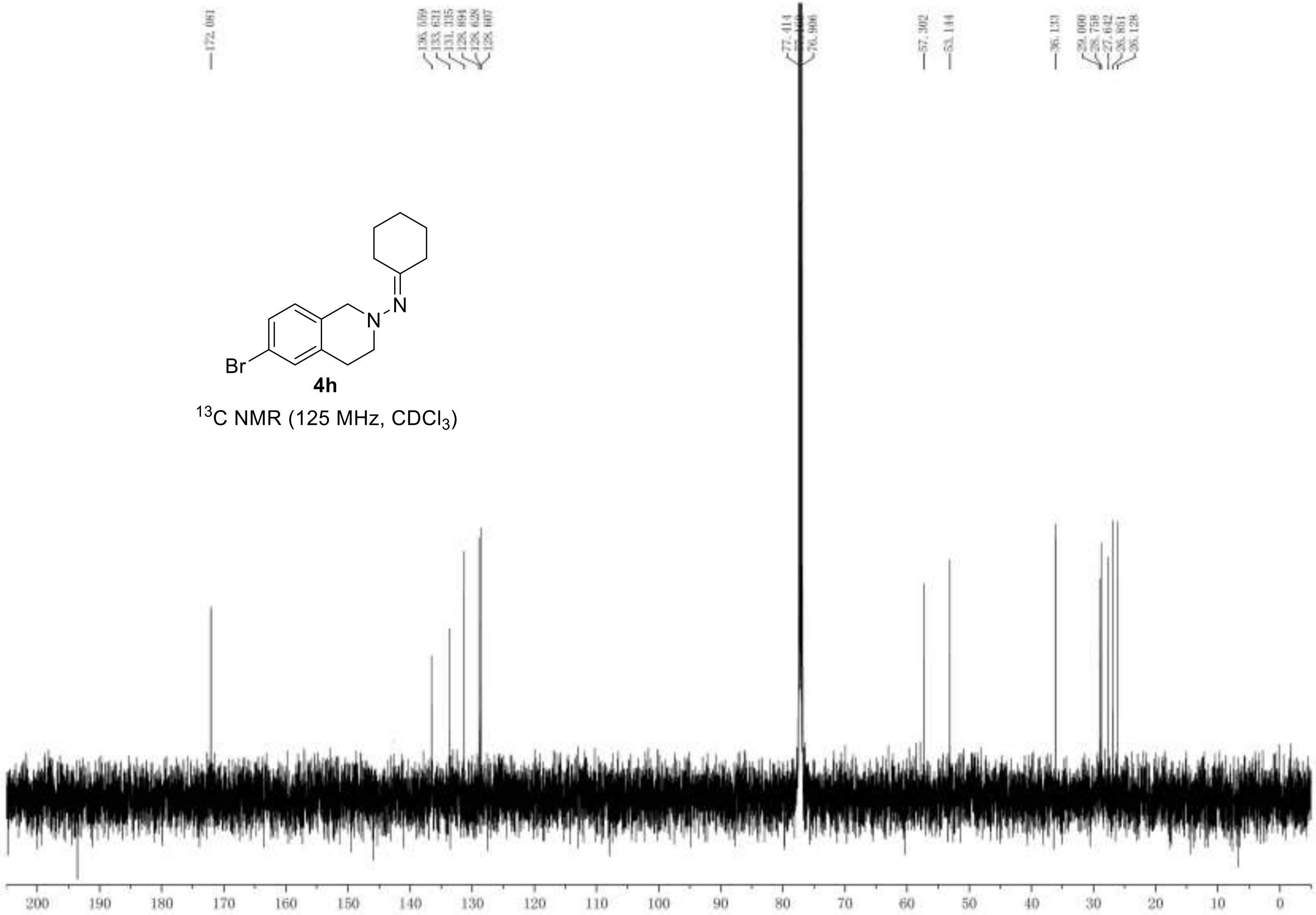
4g

^{13}C NMR (125 MHz, CDCl$_3$)



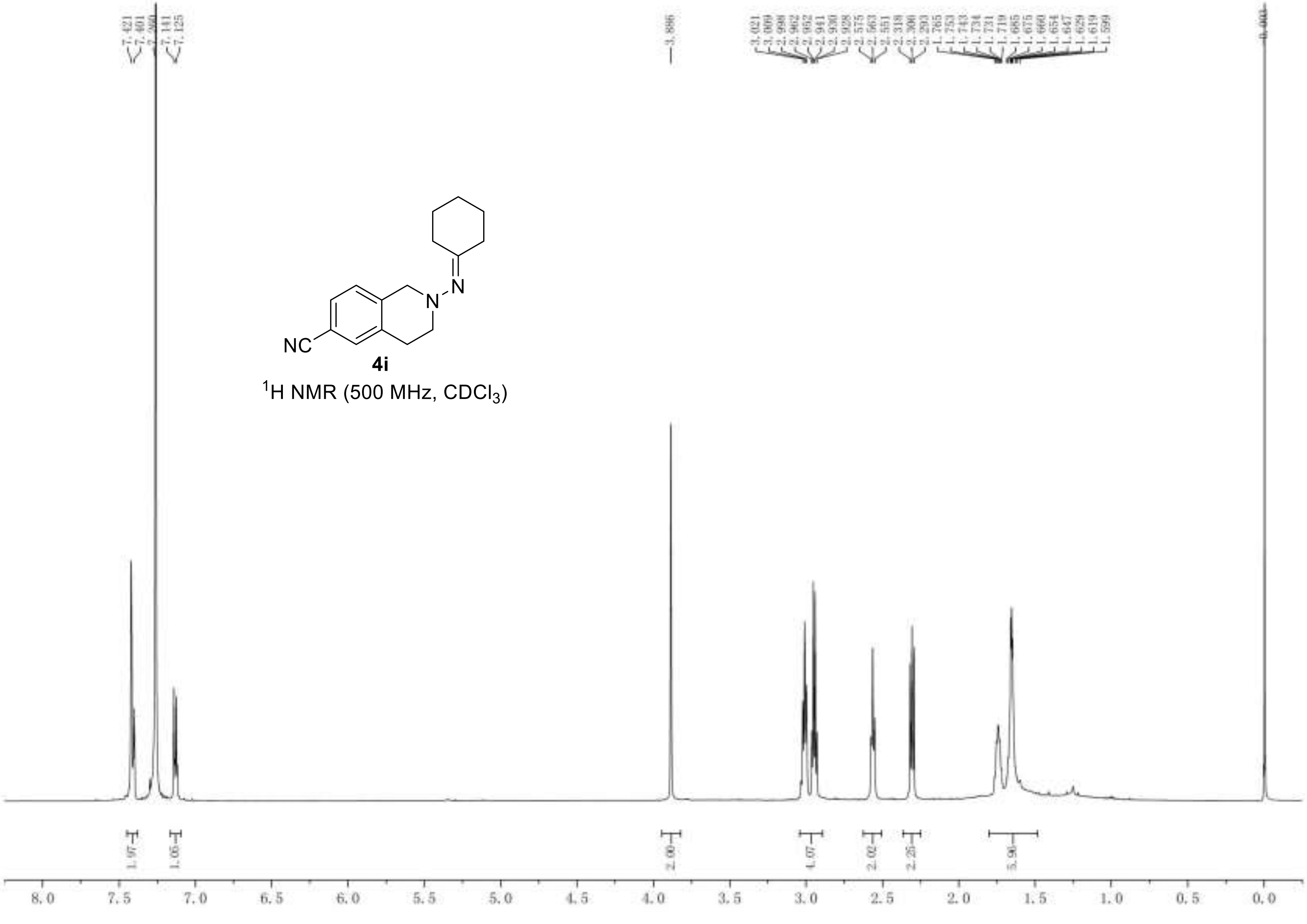
4h

^{1}H NMR (500 MHz, CDCl$_3$)



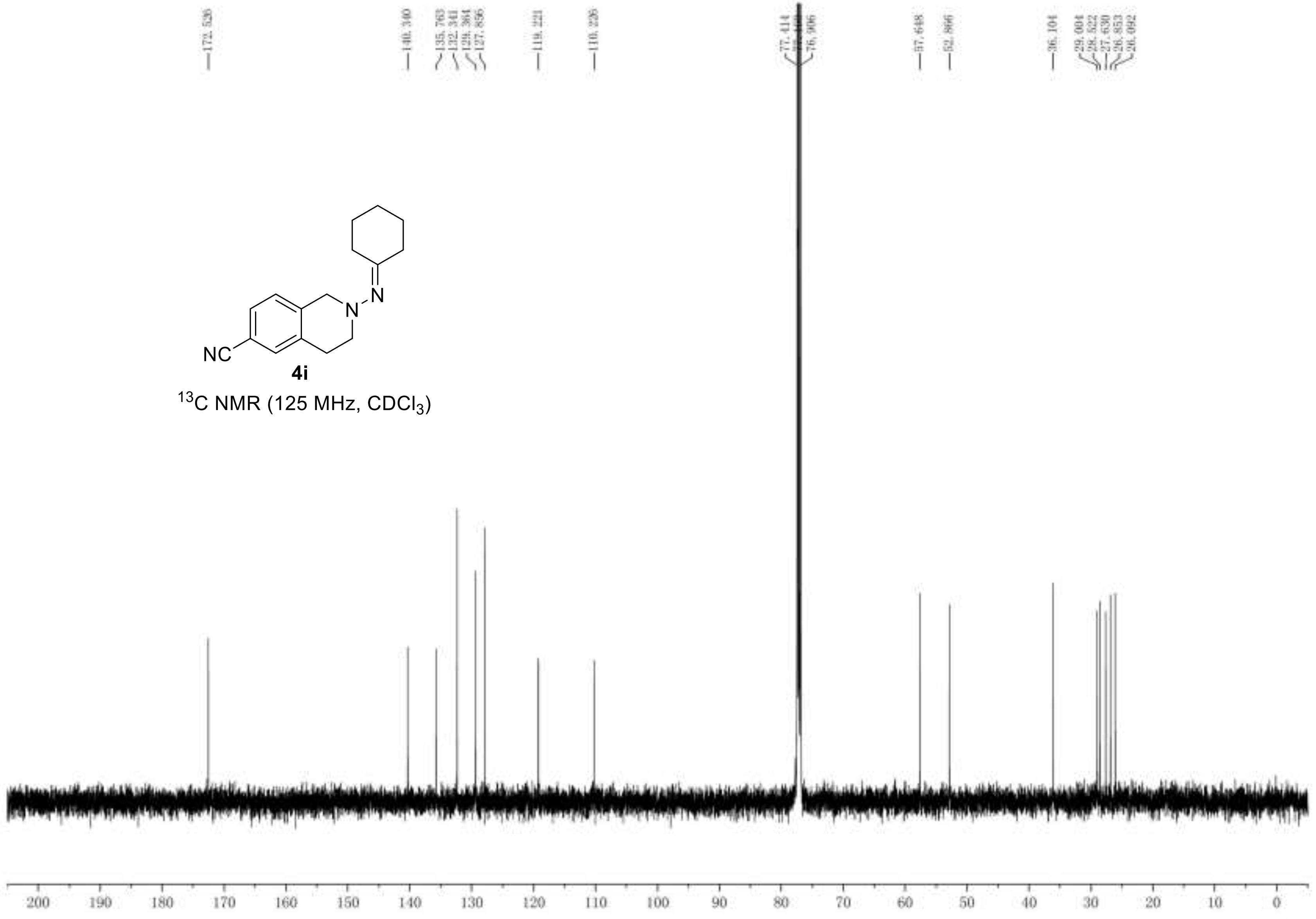
4h

^{13}C NMR (125 MHz, CDCl$_3$)



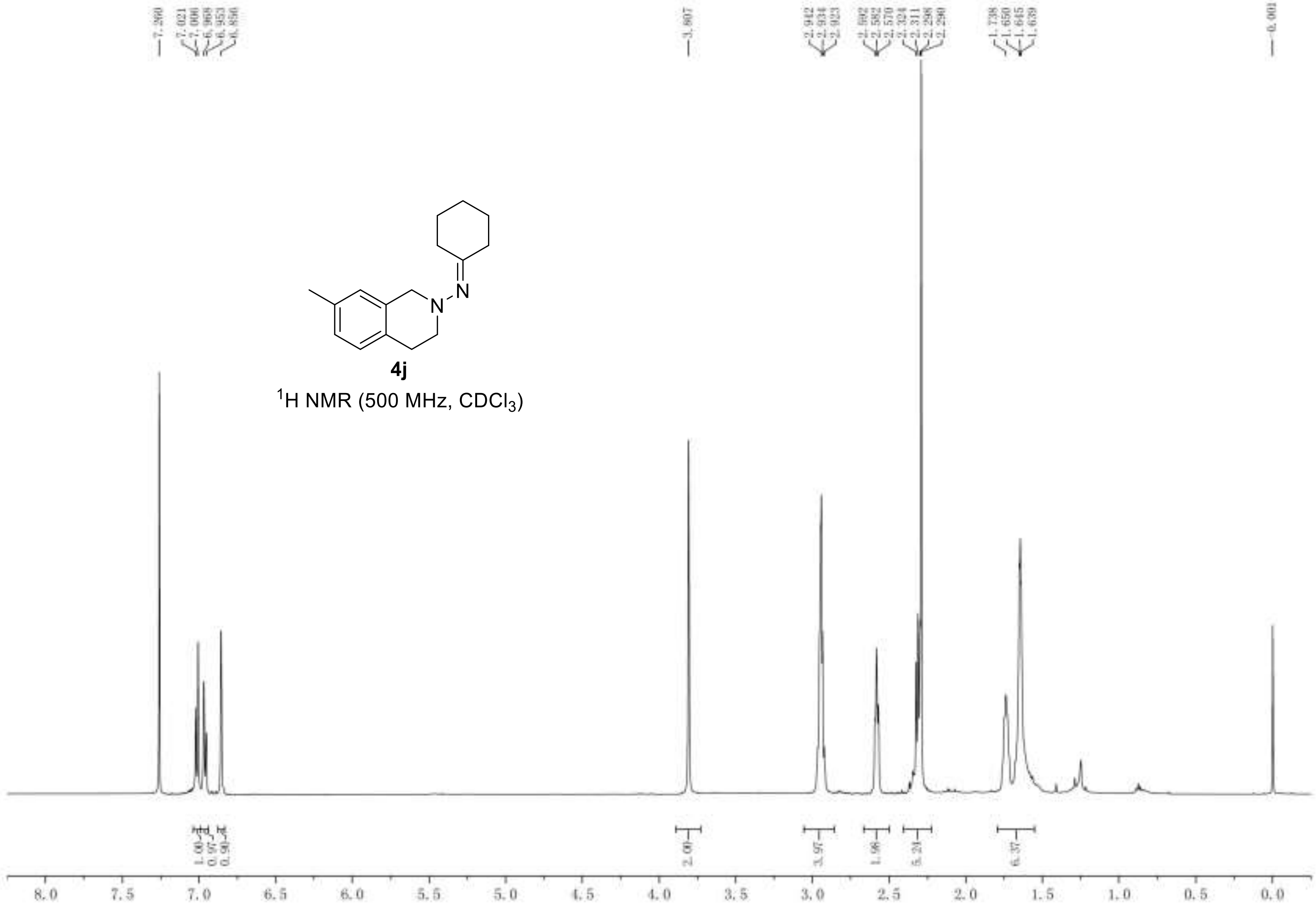
4i

^{1}H NMR (500 MHz, CDCl$_3$)



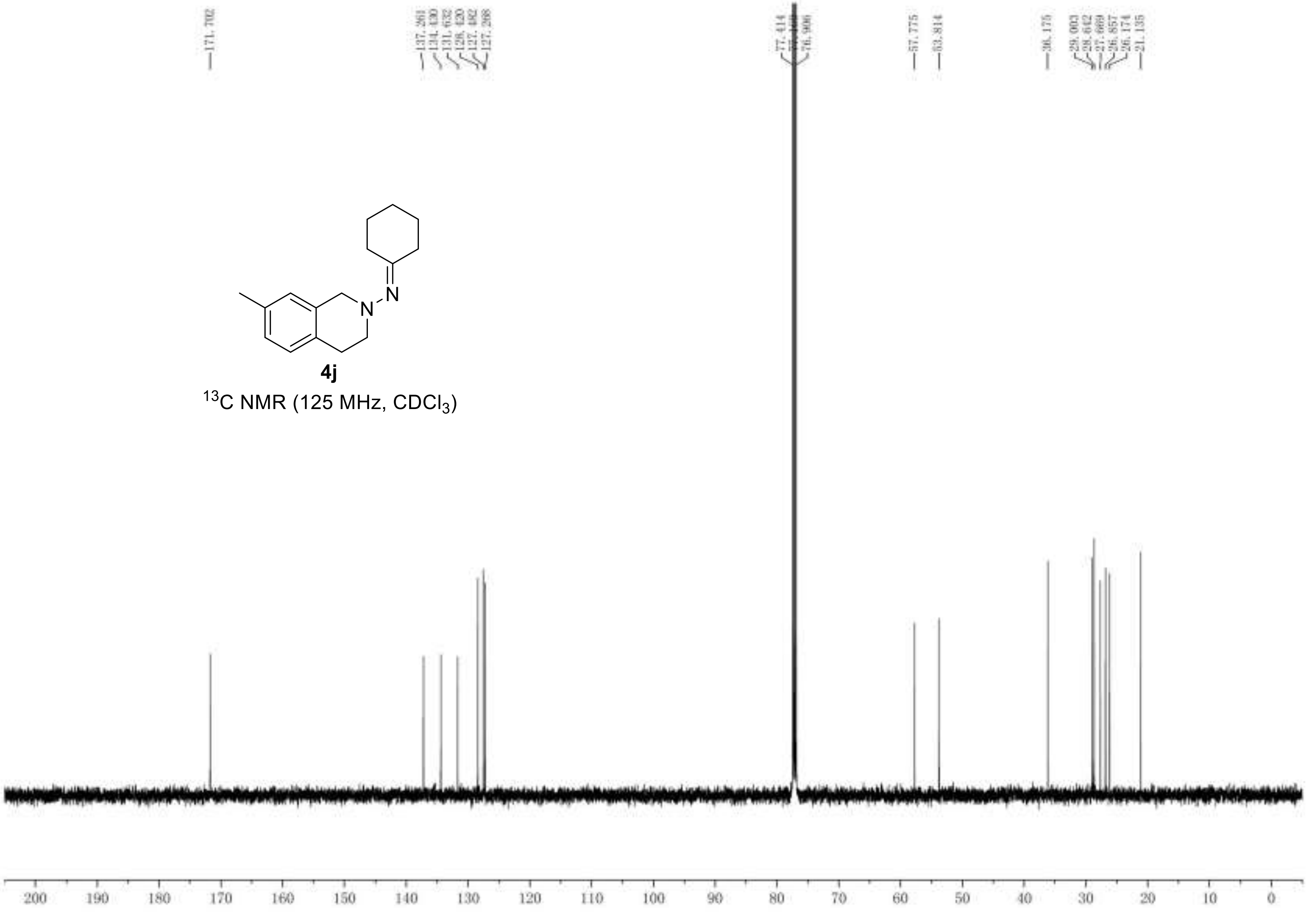
4i

^{13}C NMR (125 MHz, $CDCl_3$)



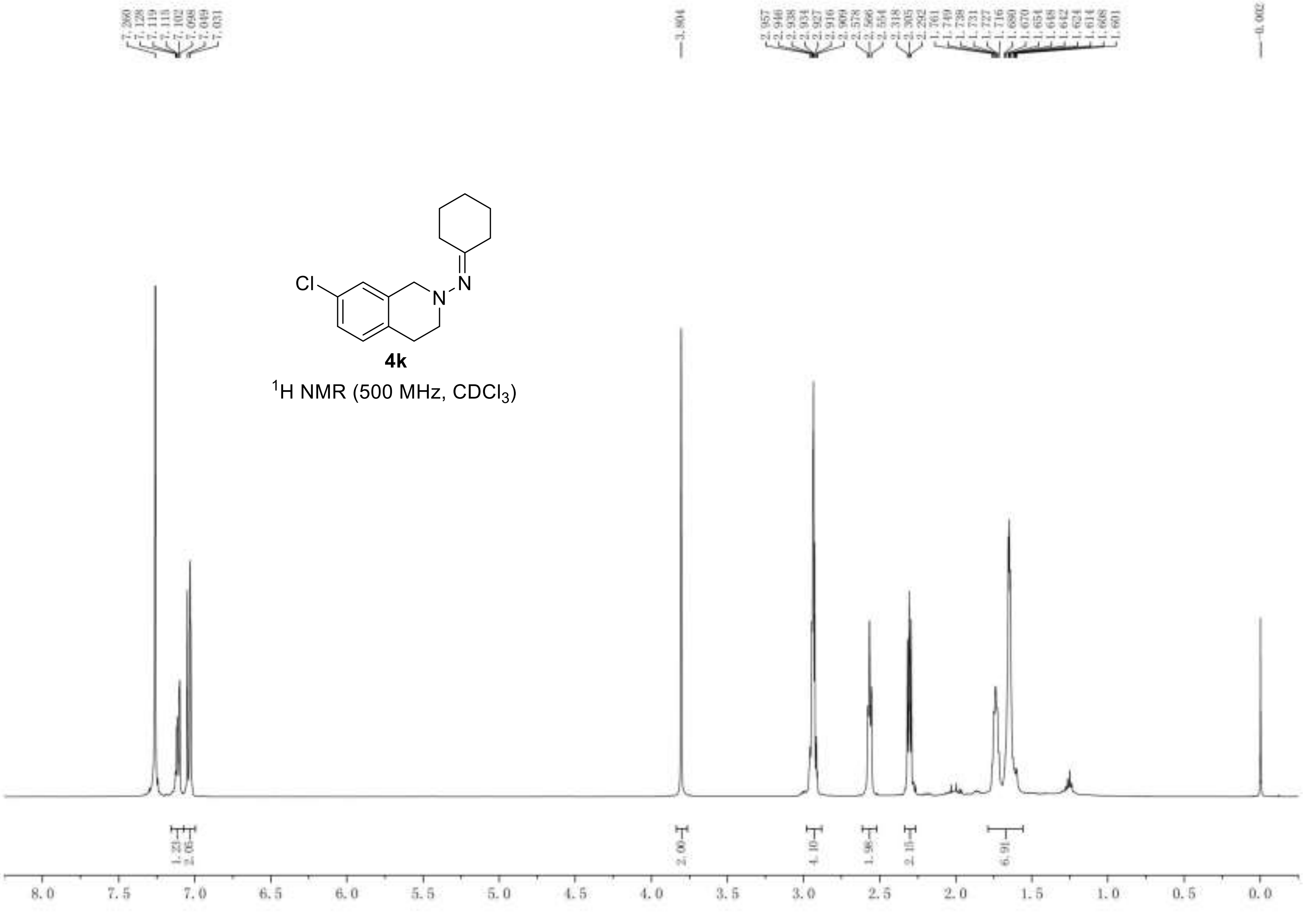
4j

^{1}H NMR (500 MHz, $CDCl_3$)



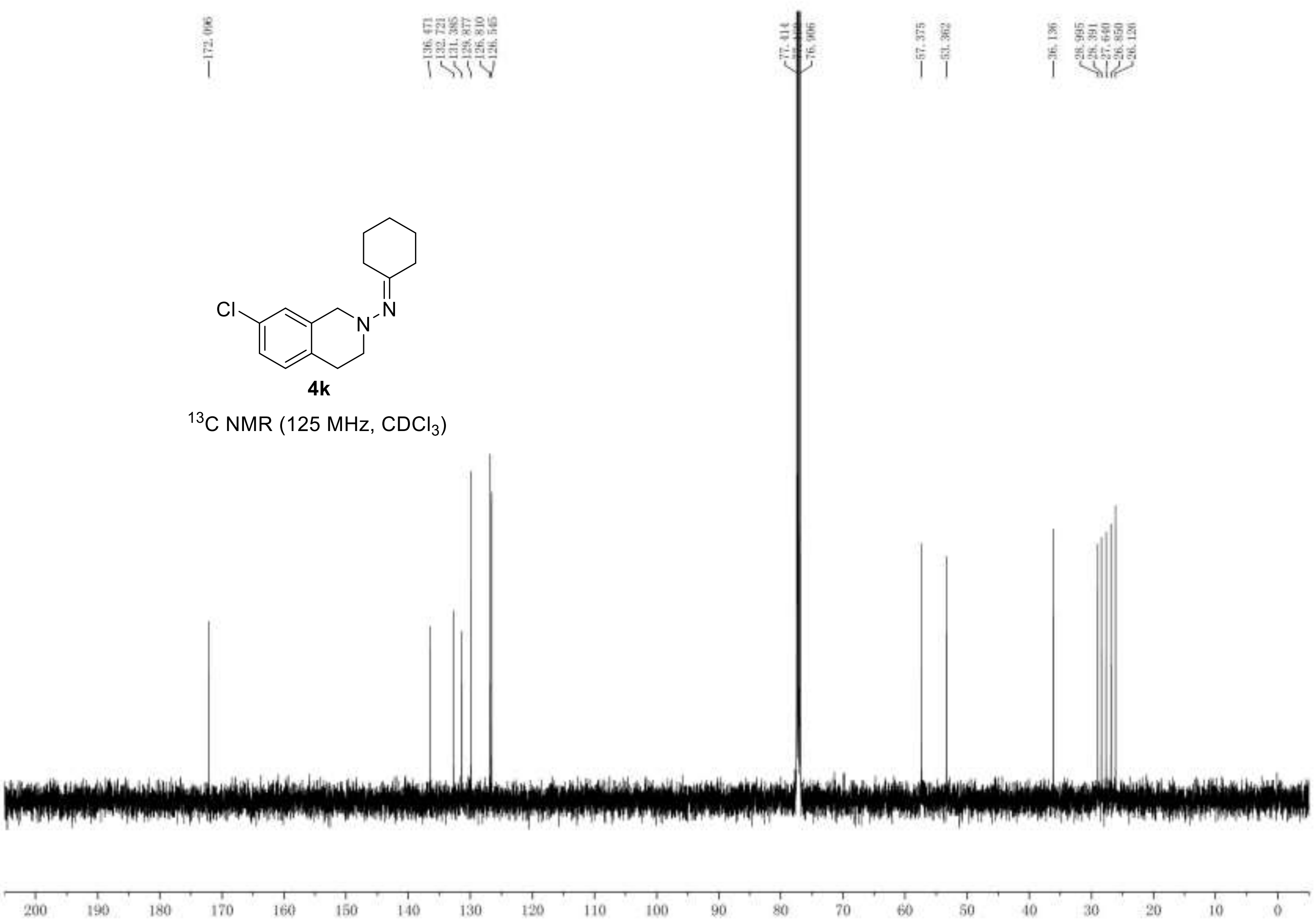
4j

^{13}C NMR (125 MHz, $CDCl_3$)



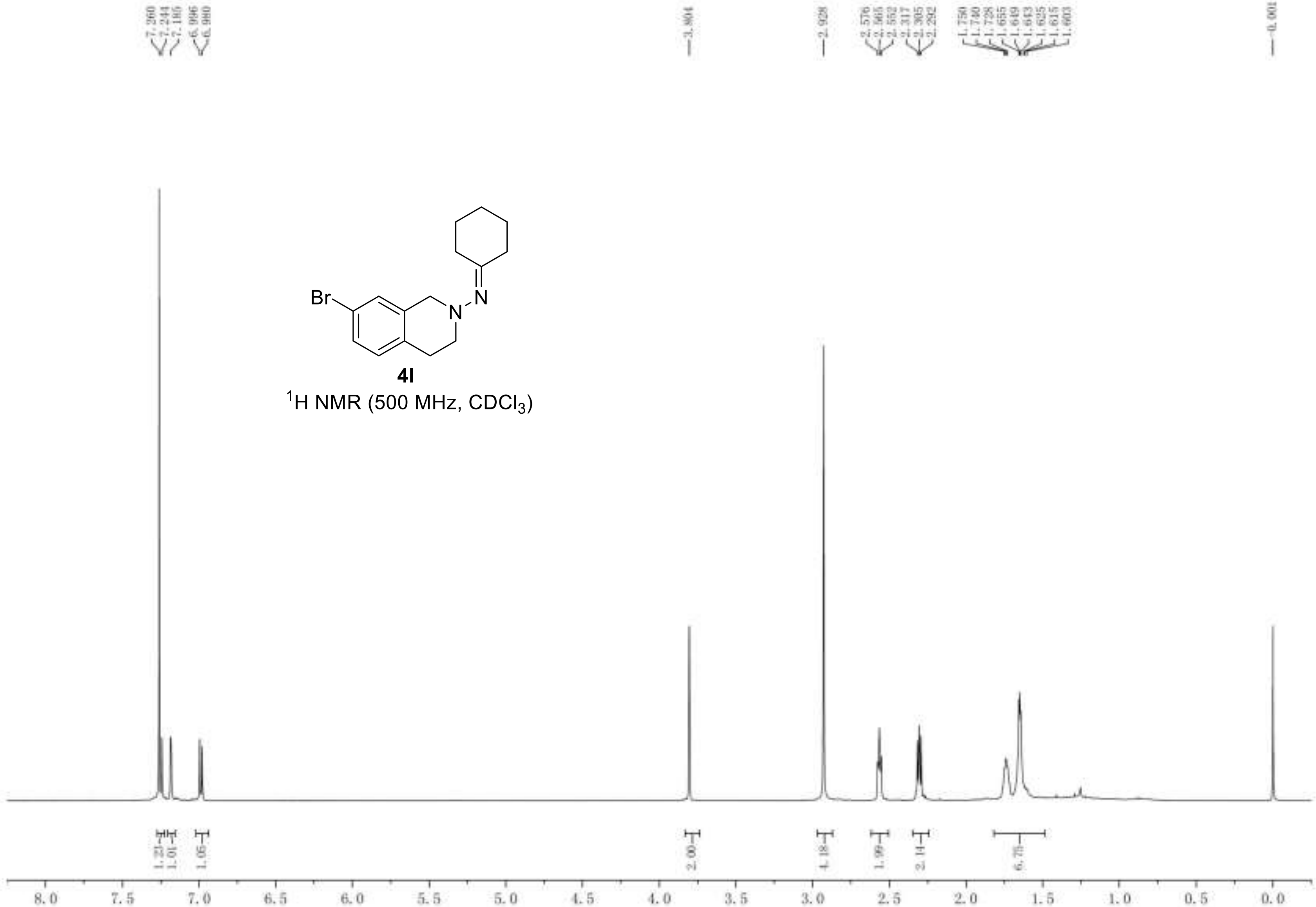
4k

^{1}H NMR (500 MHz, CDCl$_3$)



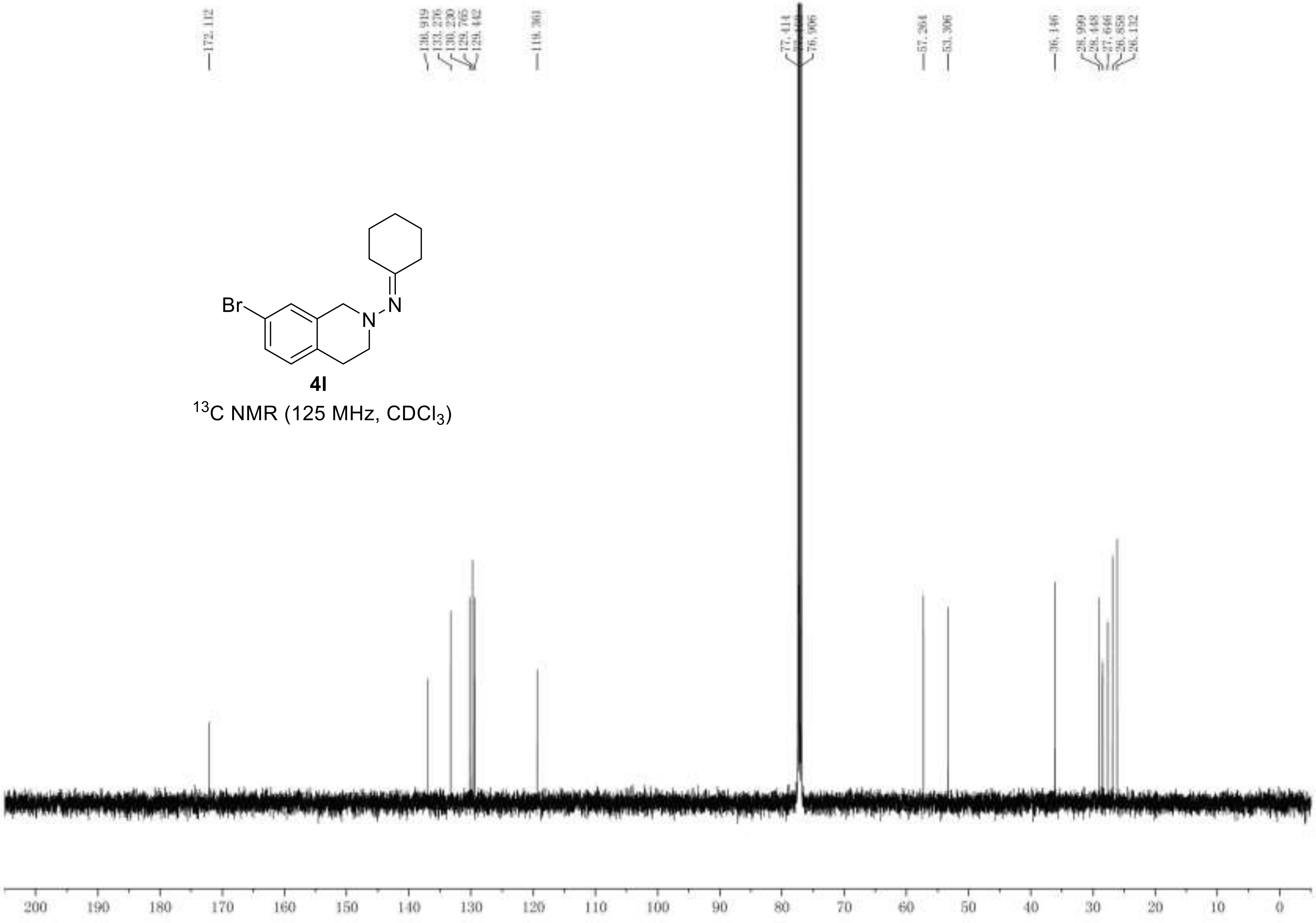
4k

^{13}C NMR (125 MHz, CDCl$_3$)



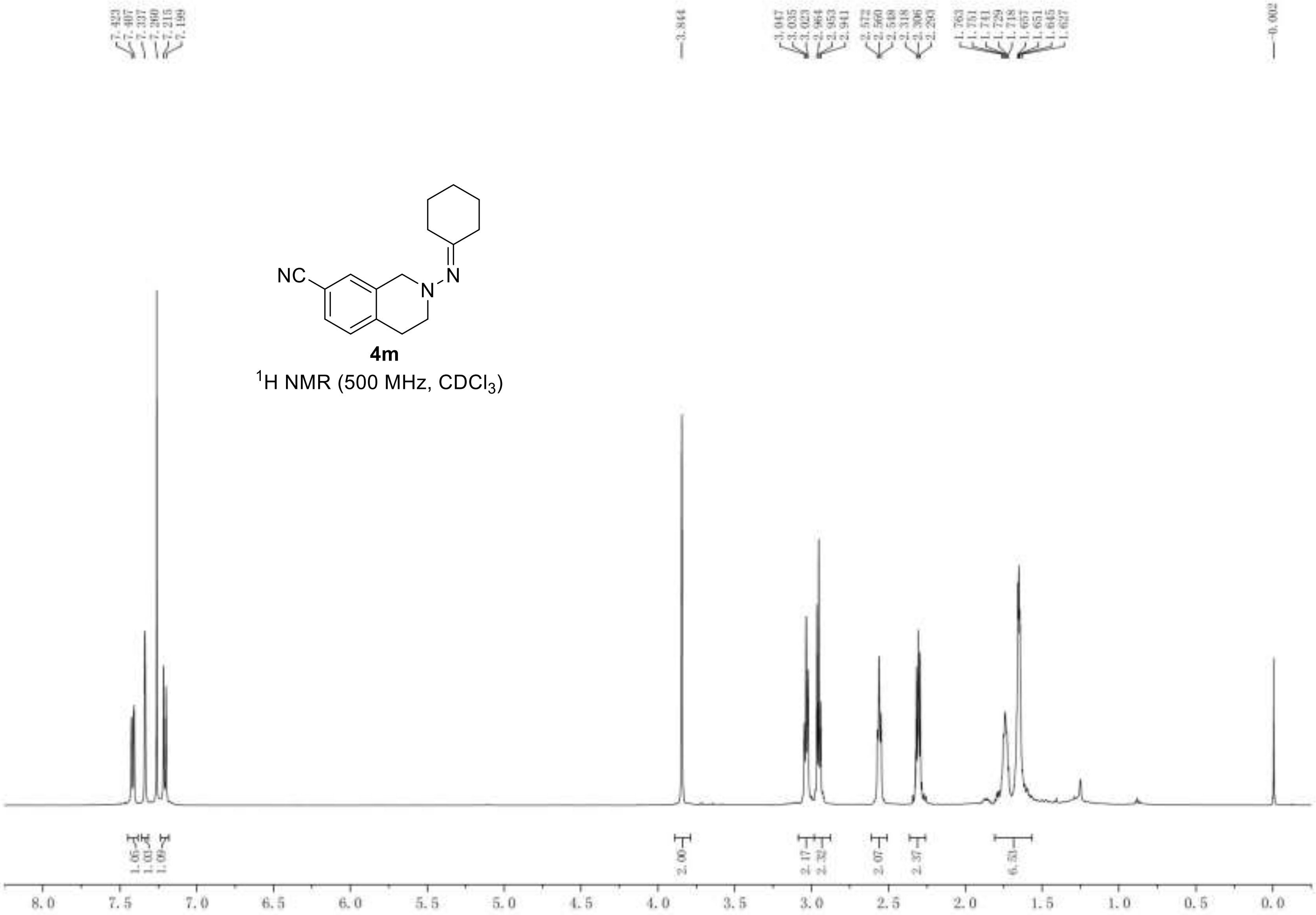
4l

^{1}H NMR (500 MHz, CDCl$_3$)



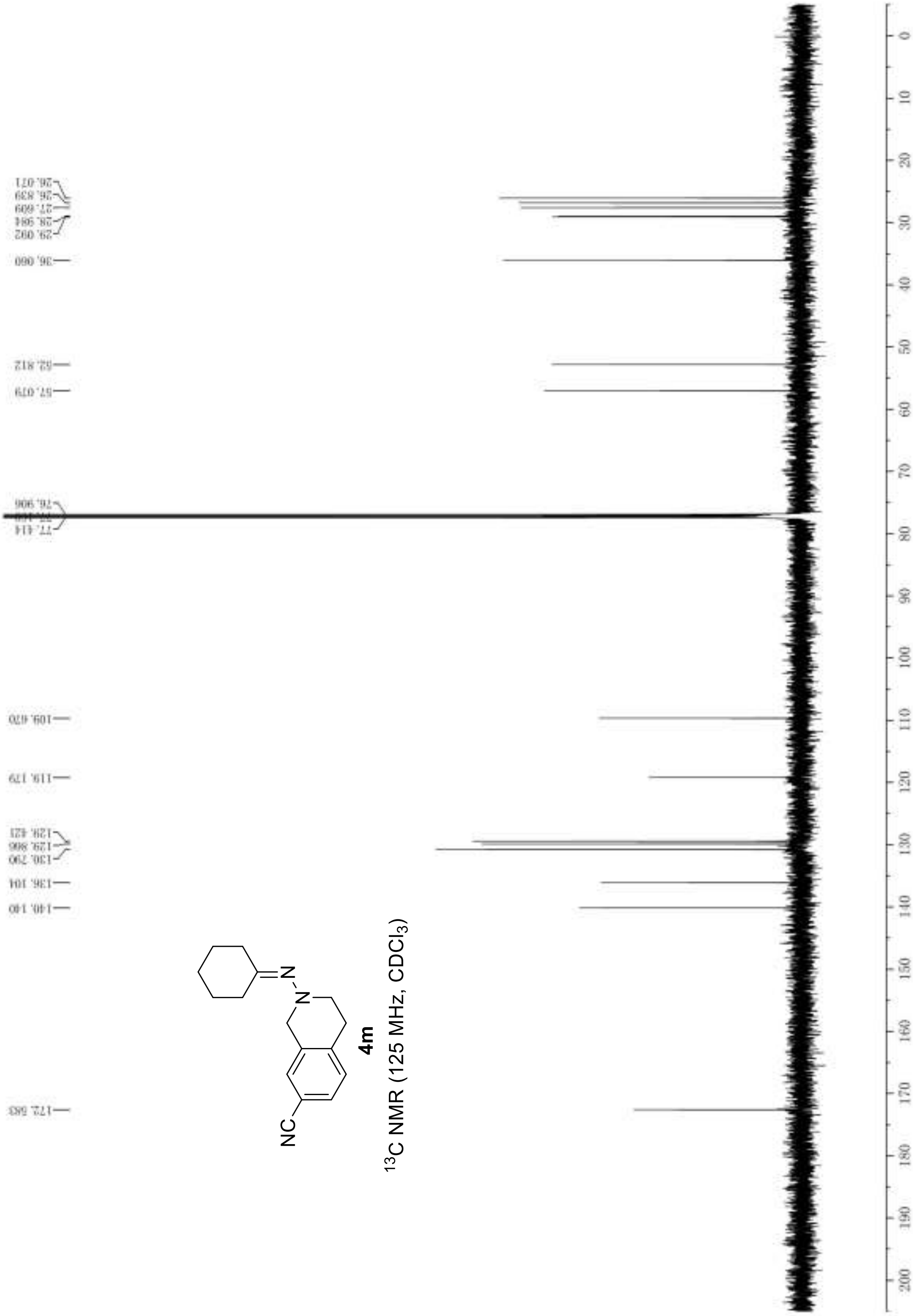
4l

^{13}C NMR (125 MHz, $CDCl_3$)



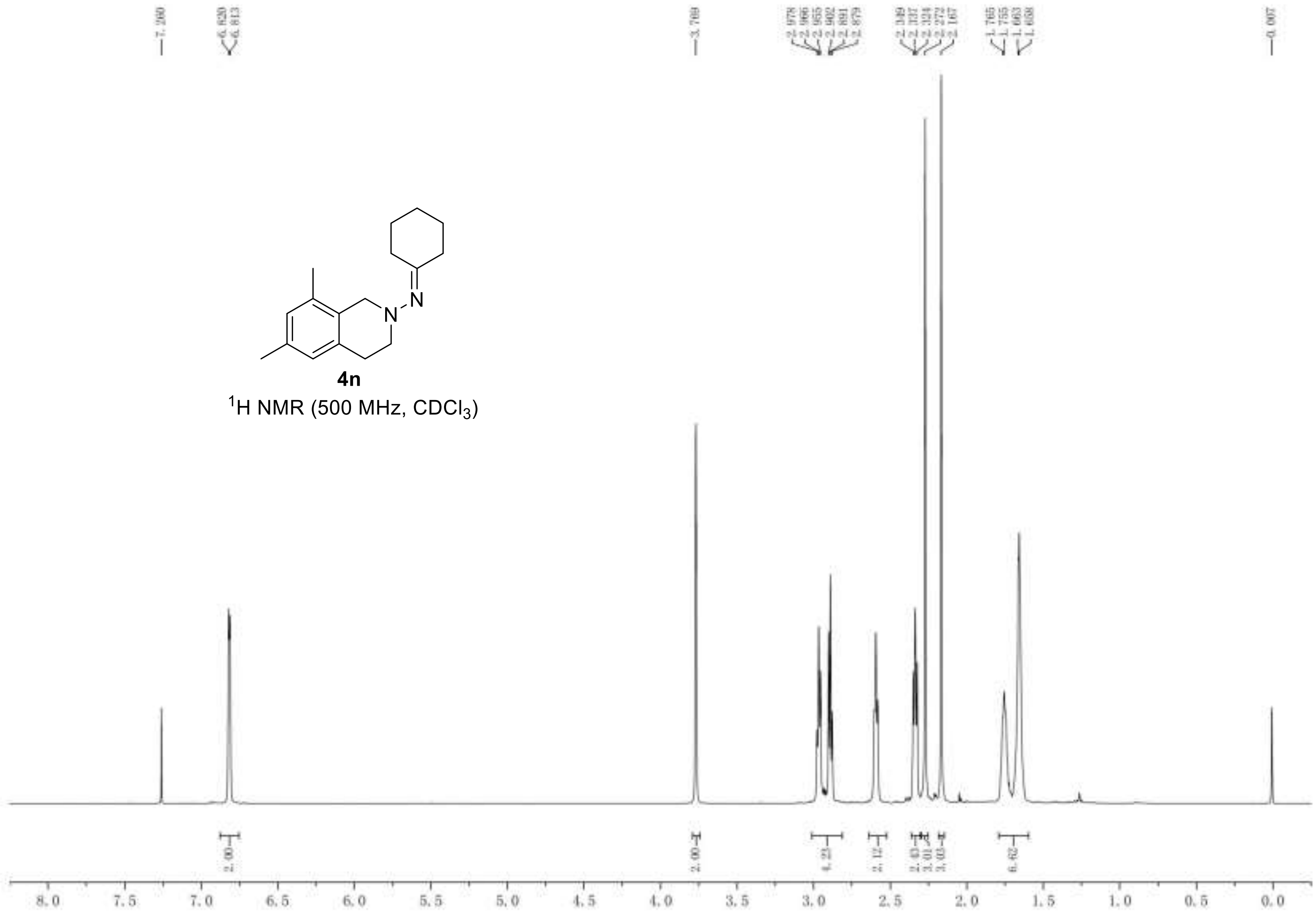
4m

^{1}H NMR (500 MHz, $CDCl_3$)



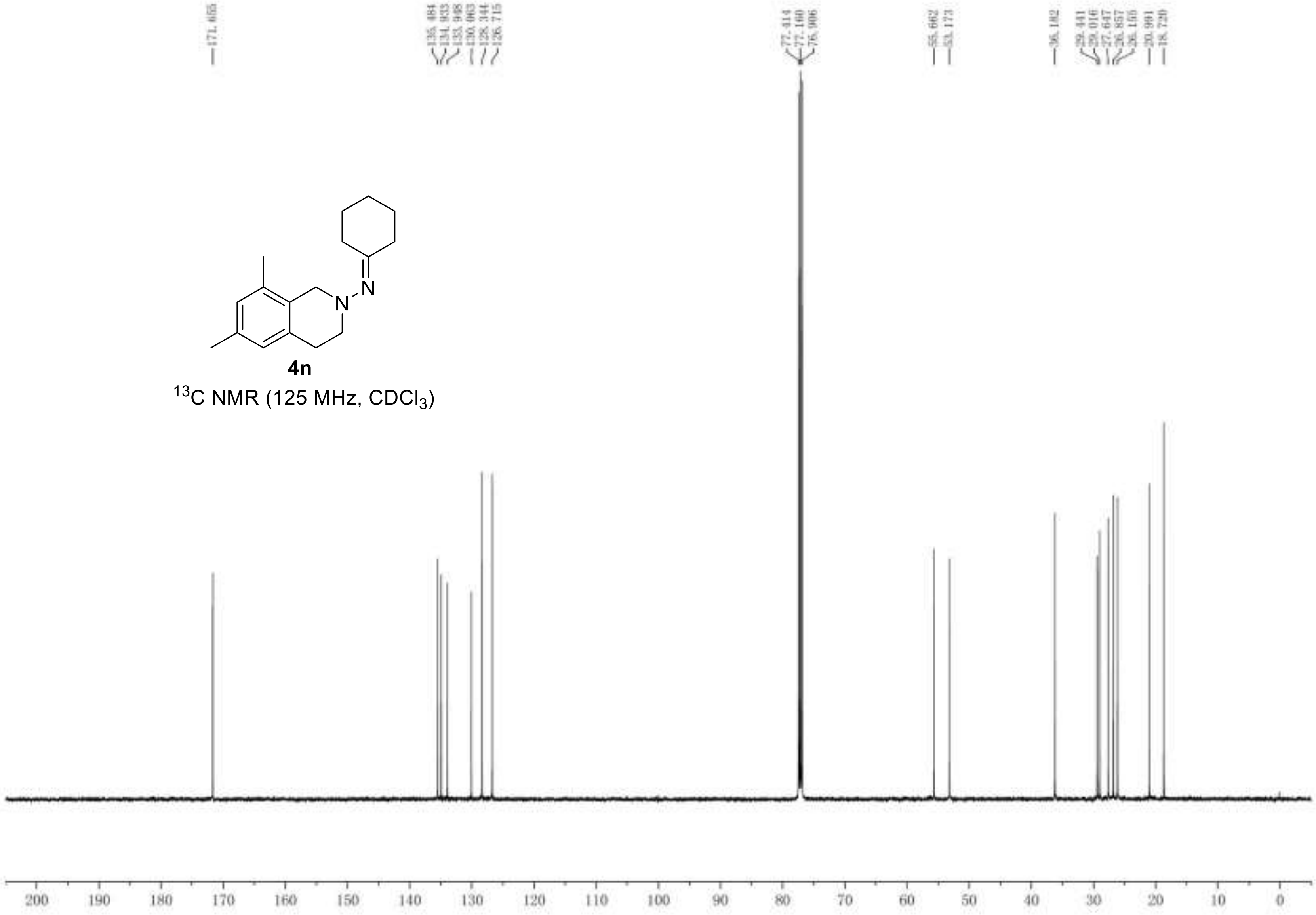
4m

^{13}C NMR (125 MHz, CDCl$_3$)



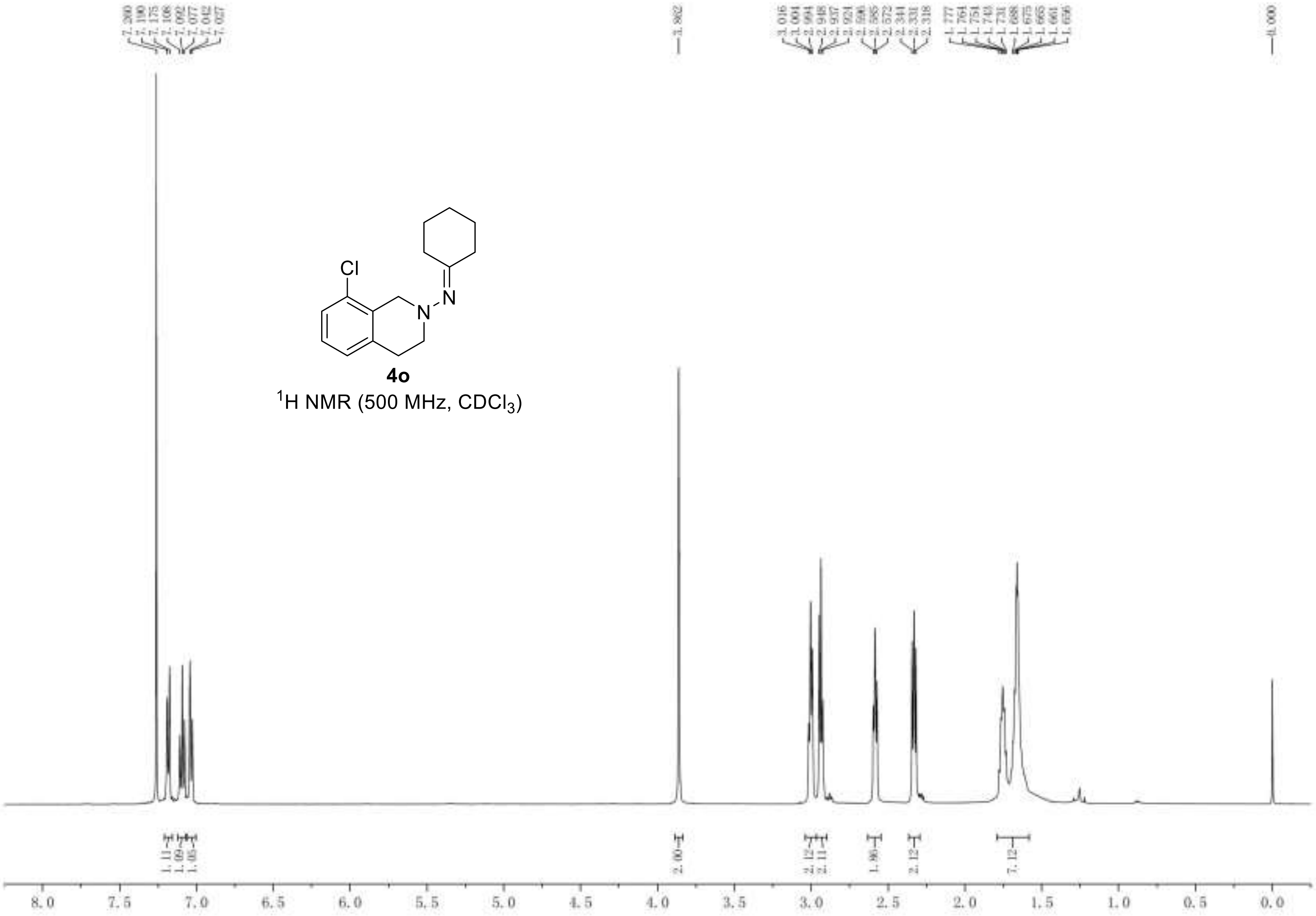
4n

^{1}H NMR (500 MHz, $CDCl_3$)



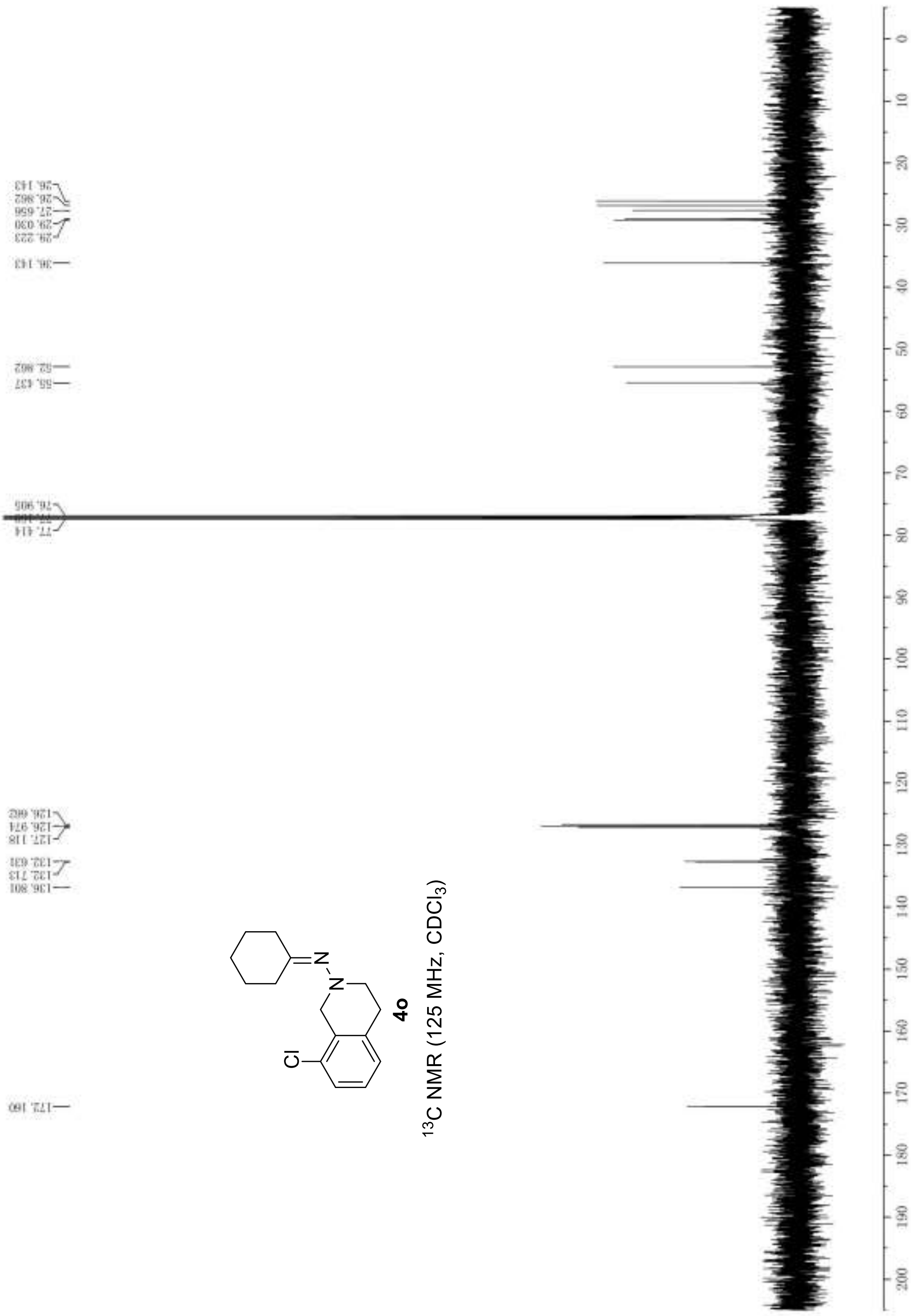
4n

^{13}C NMR (125 MHz, CDCl$_3$)



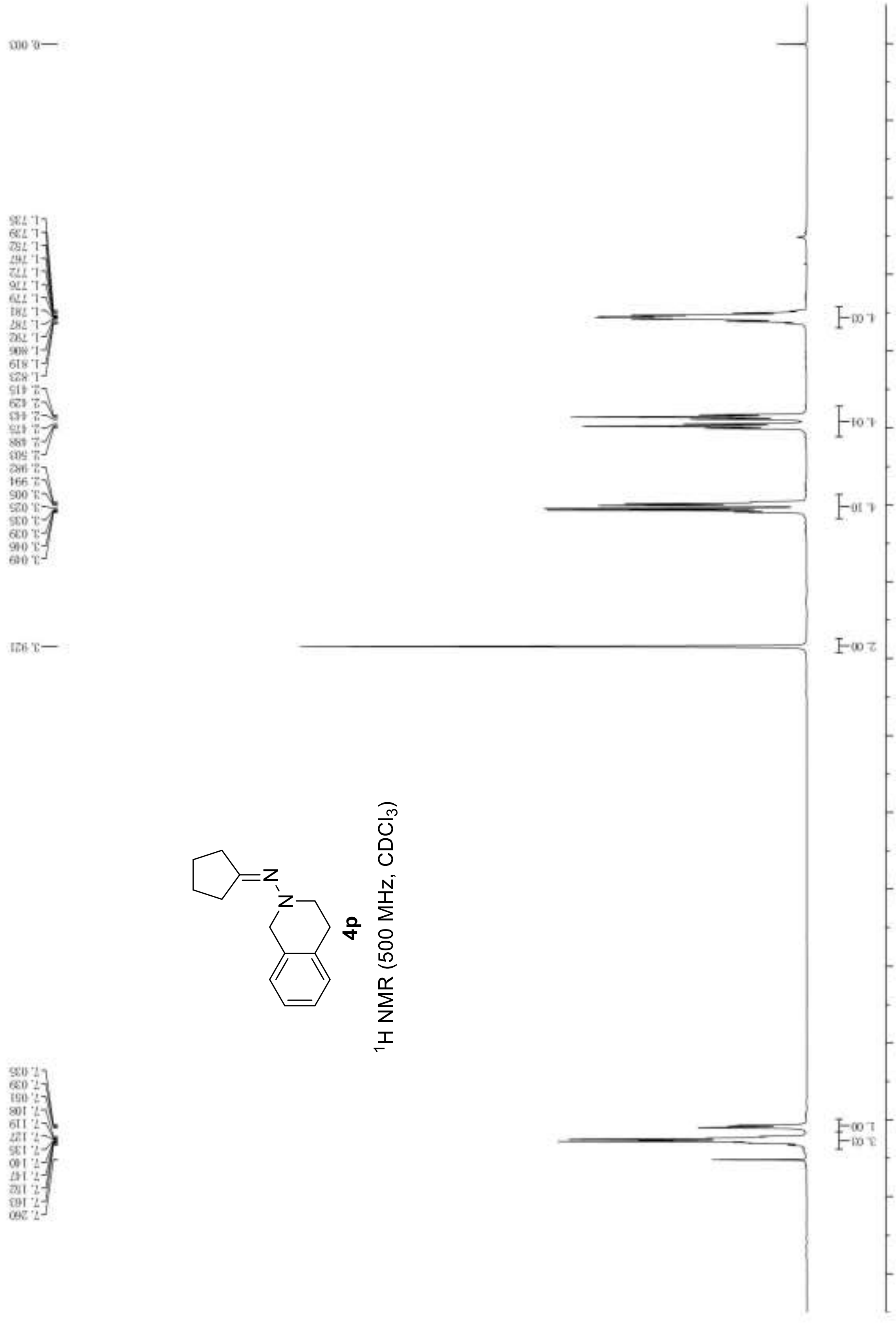
4o

^{1}H NMR (500 MHz, CDCl$_3$)



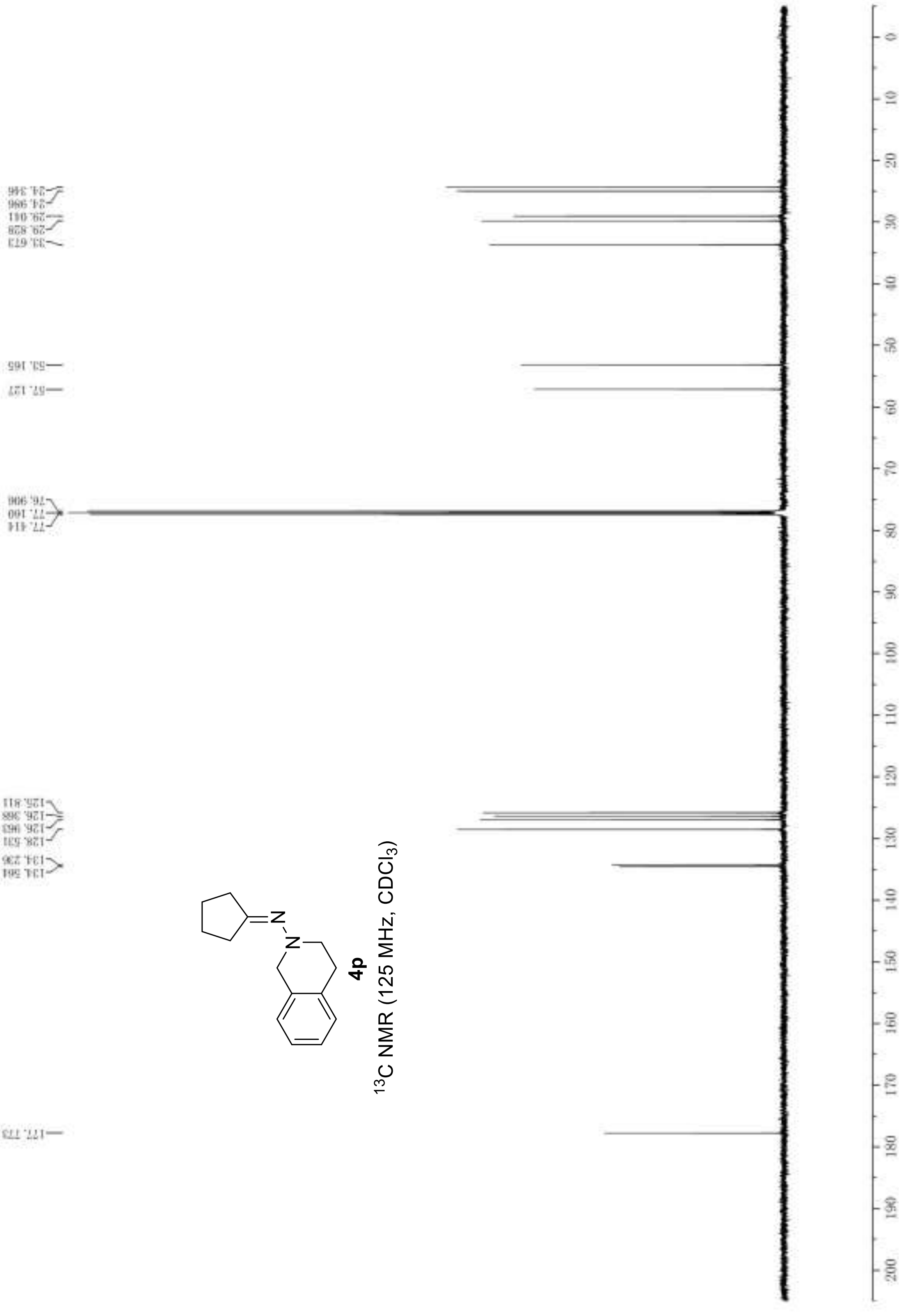
4o

^{13}C NMR (125 MHz, CDCl$_3$)



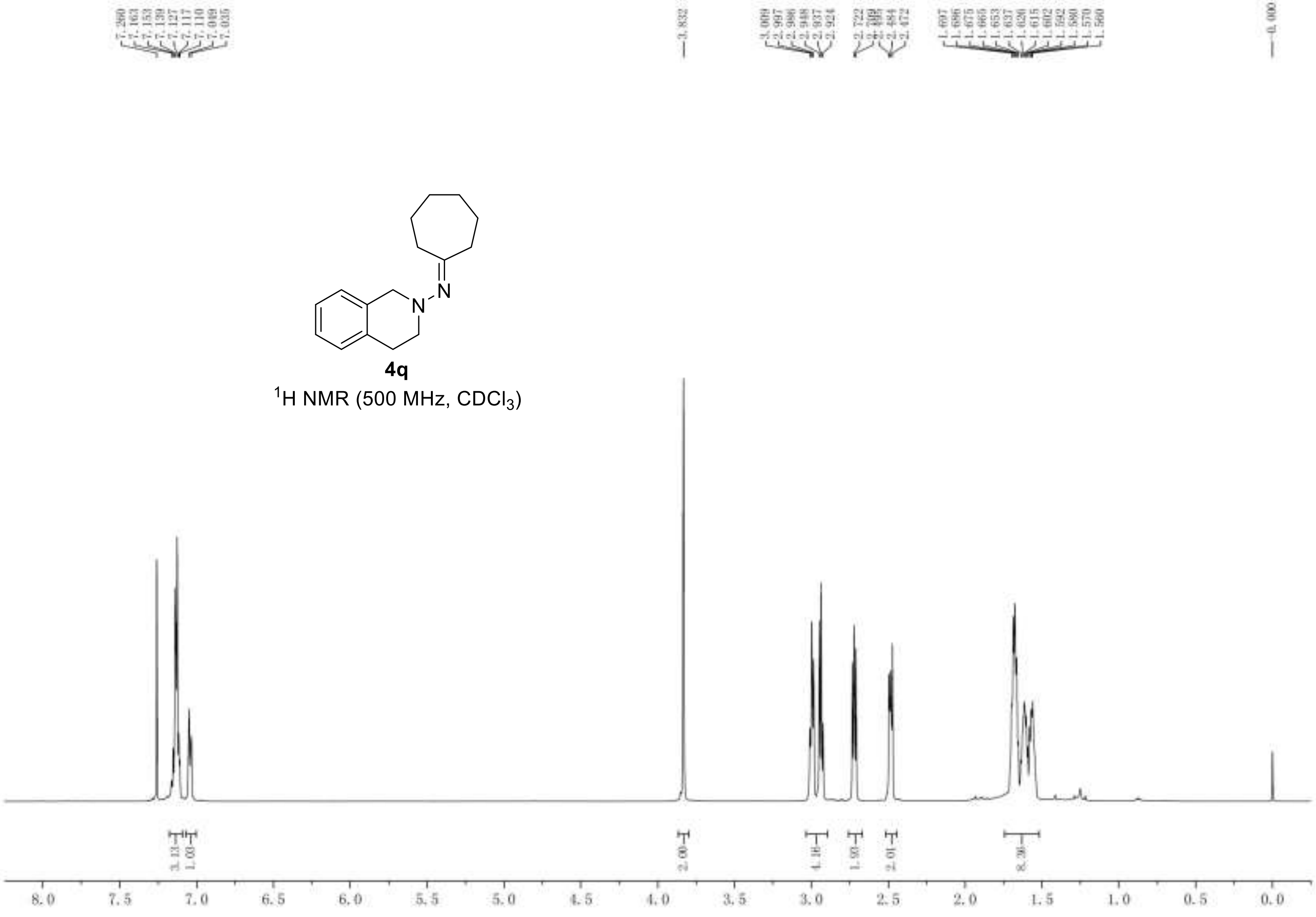
4p

^{1}H NMR (500 MHz, CDCl$_3$)



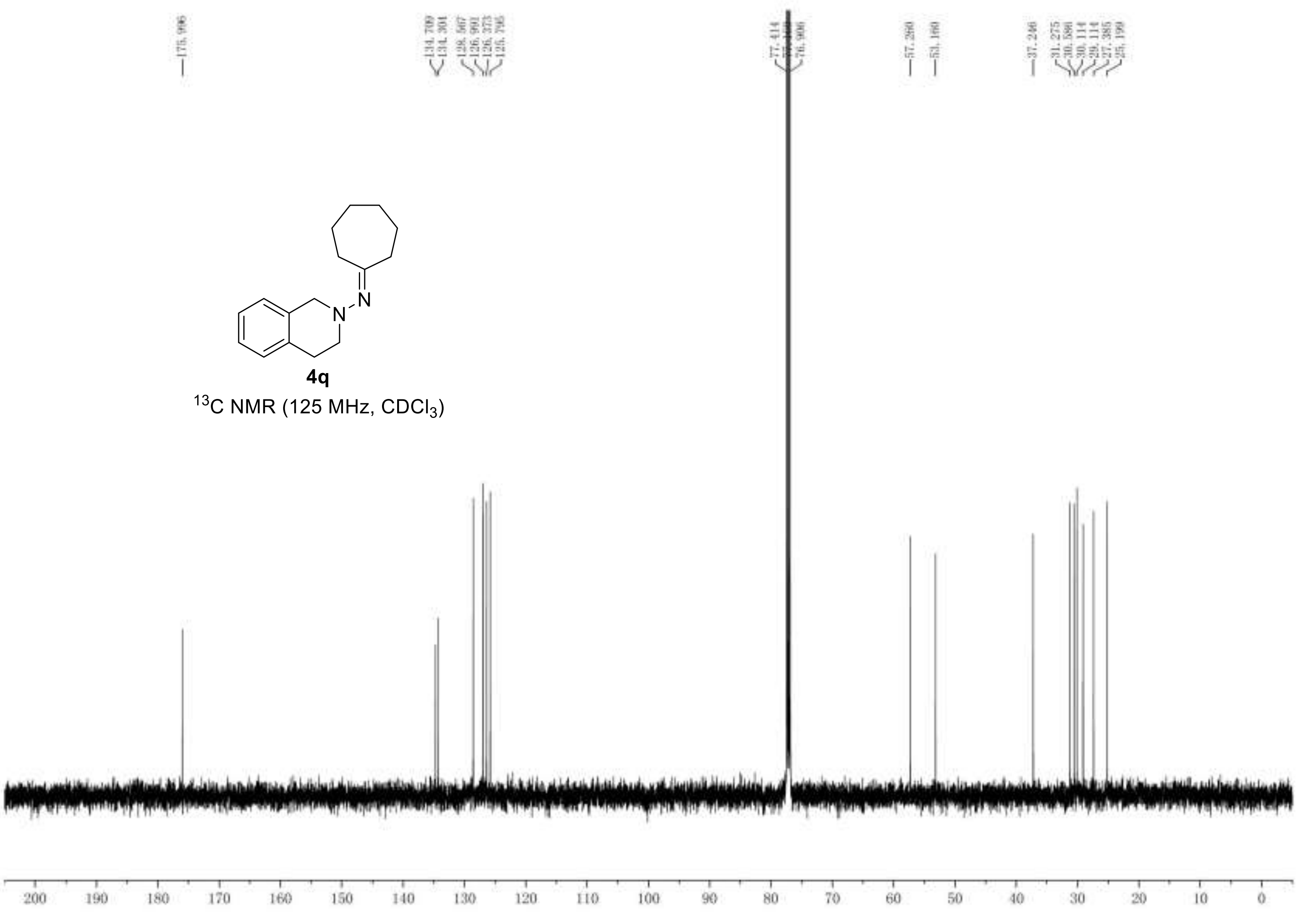
4p

^{13}C NMR (125 MHz, CDCl$_3$)



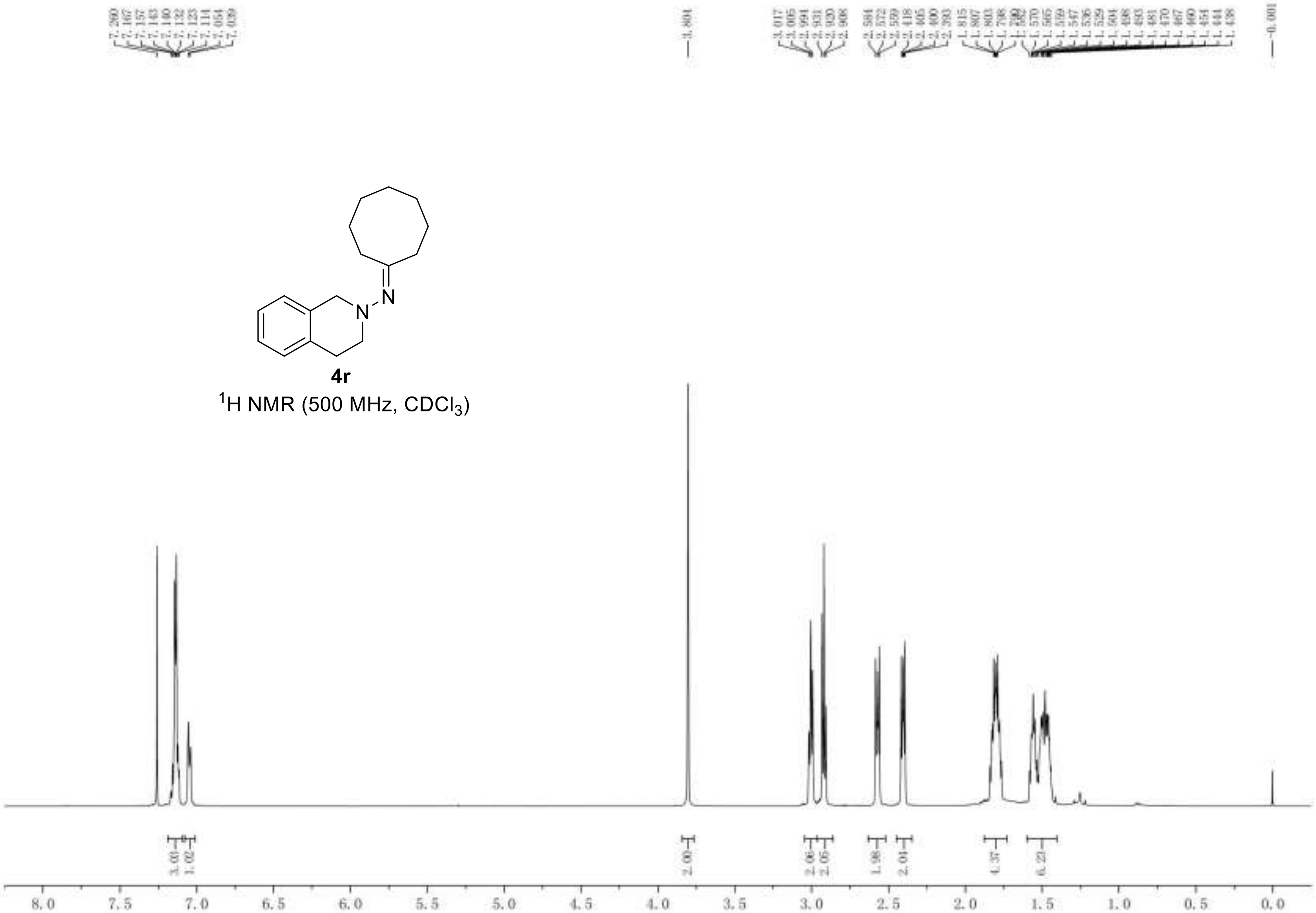
4q

^{1}H NMR (500 MHz, CDCl$_3$)



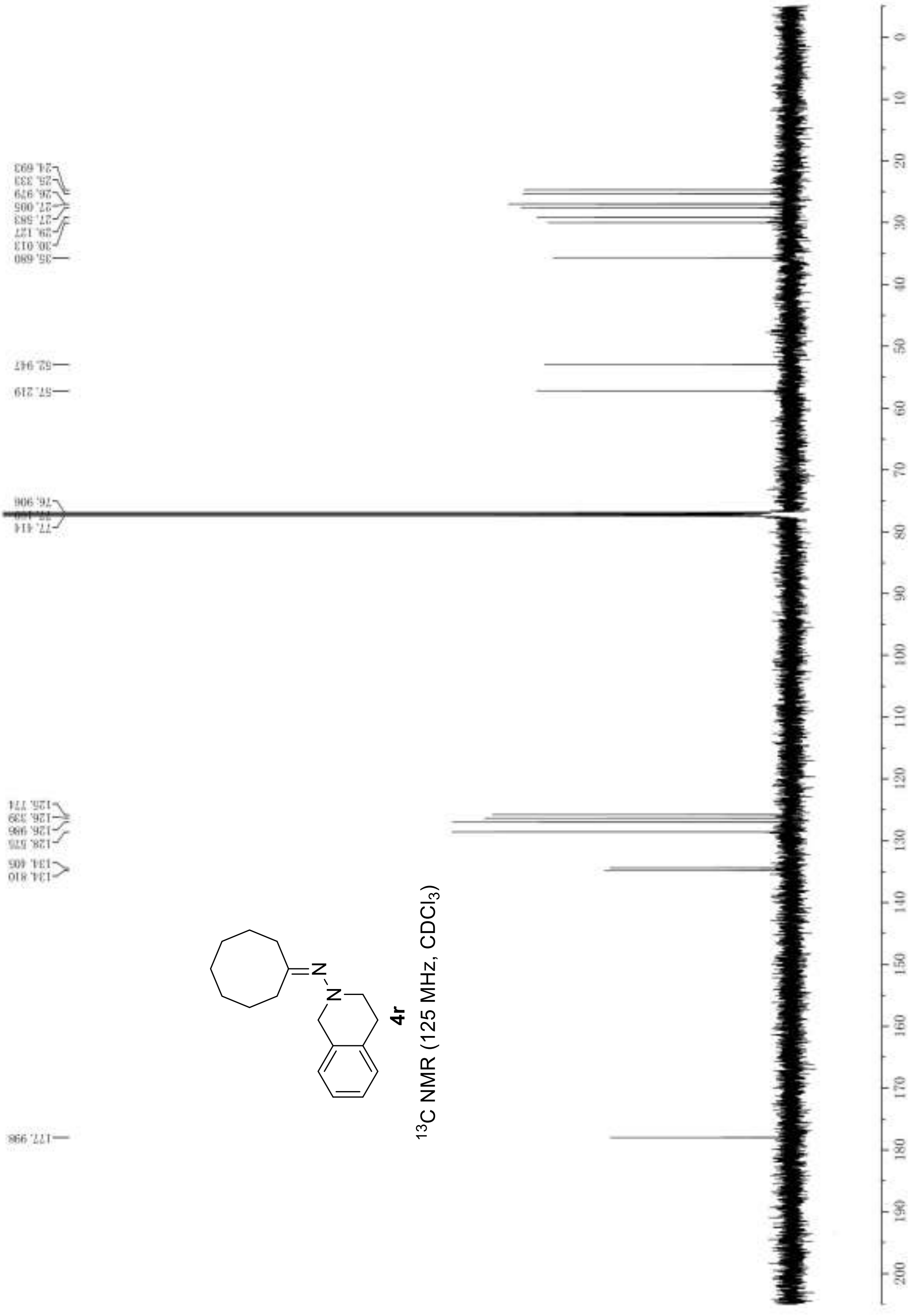
4q

^{13}C NMR (125 MHz, CDCl$_3$)



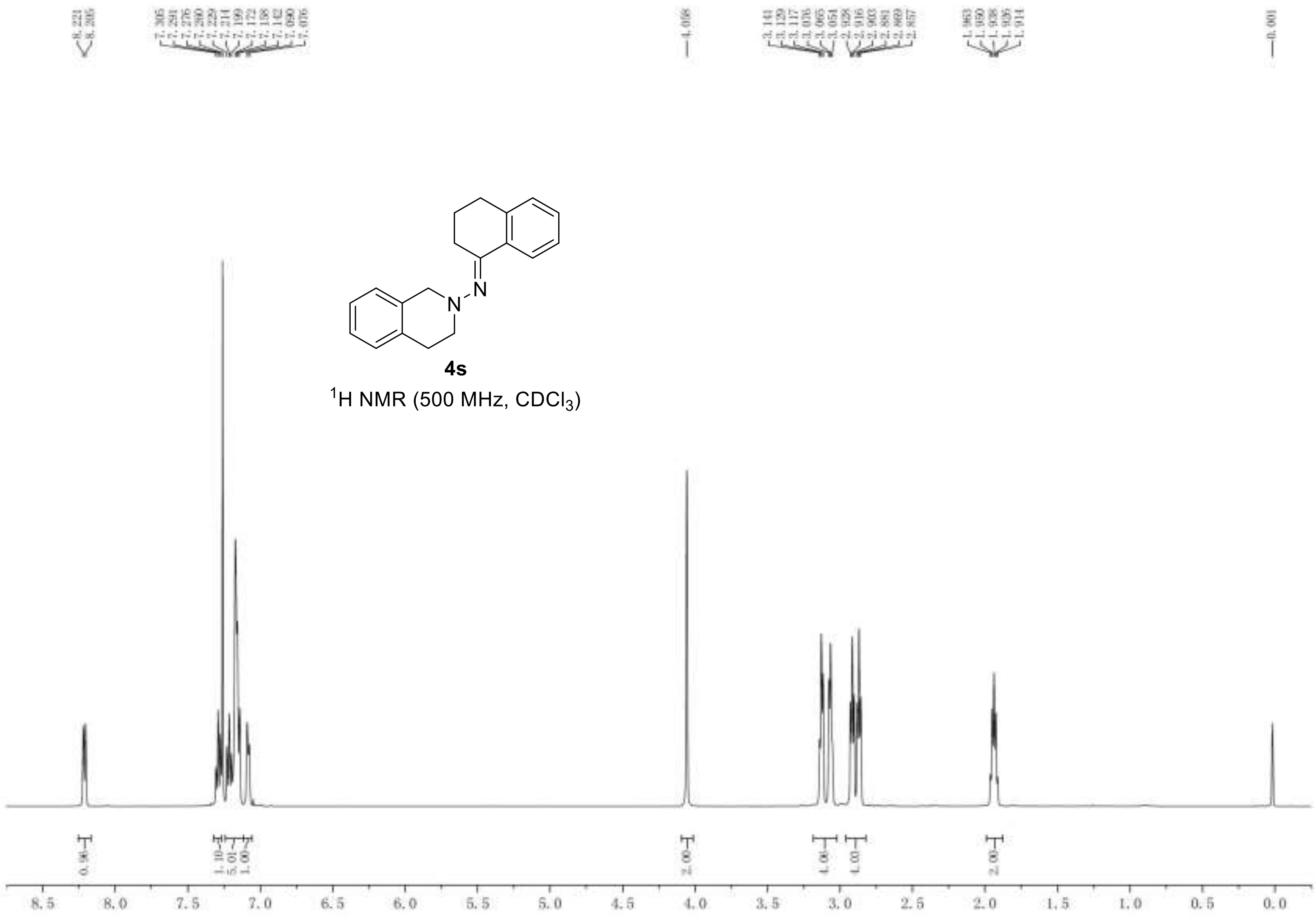
4r

^{1}H NMR (500 MHz, $CDCl_3$)



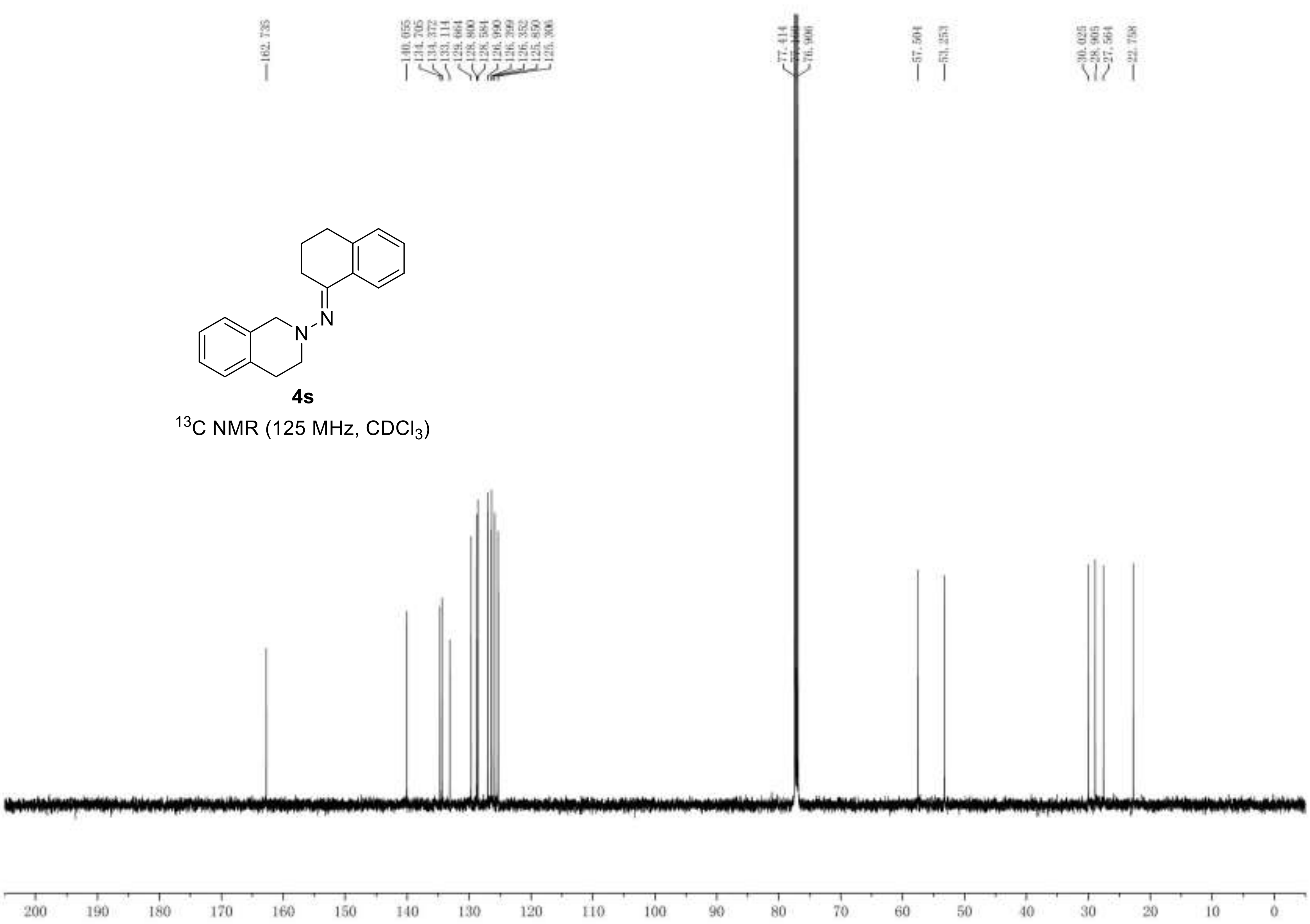
4r

^{13}C NMR (125 MHz, CDCl$_3$)



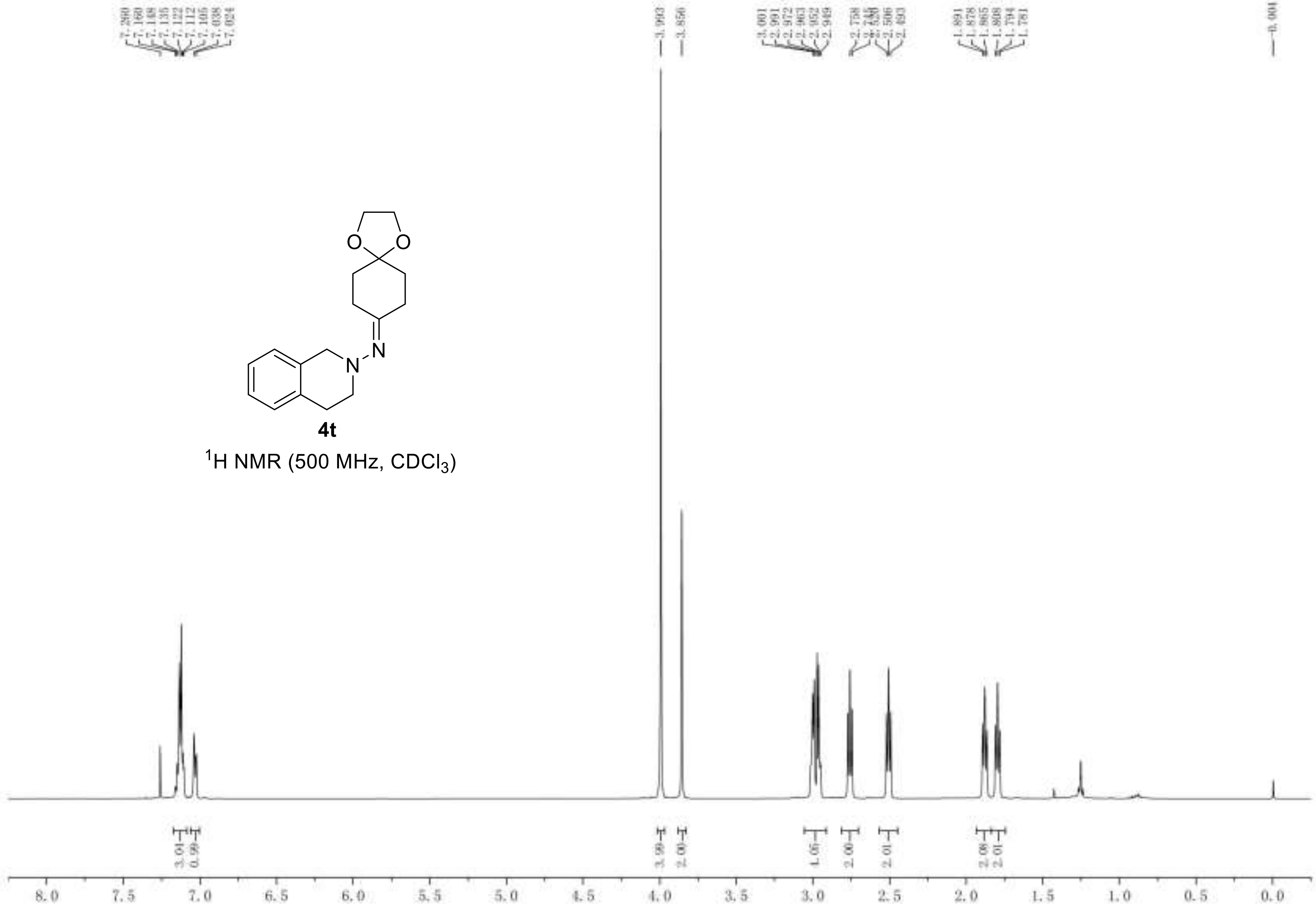
4s

^{1}H NMR (500 MHz, CDCl$_3$)



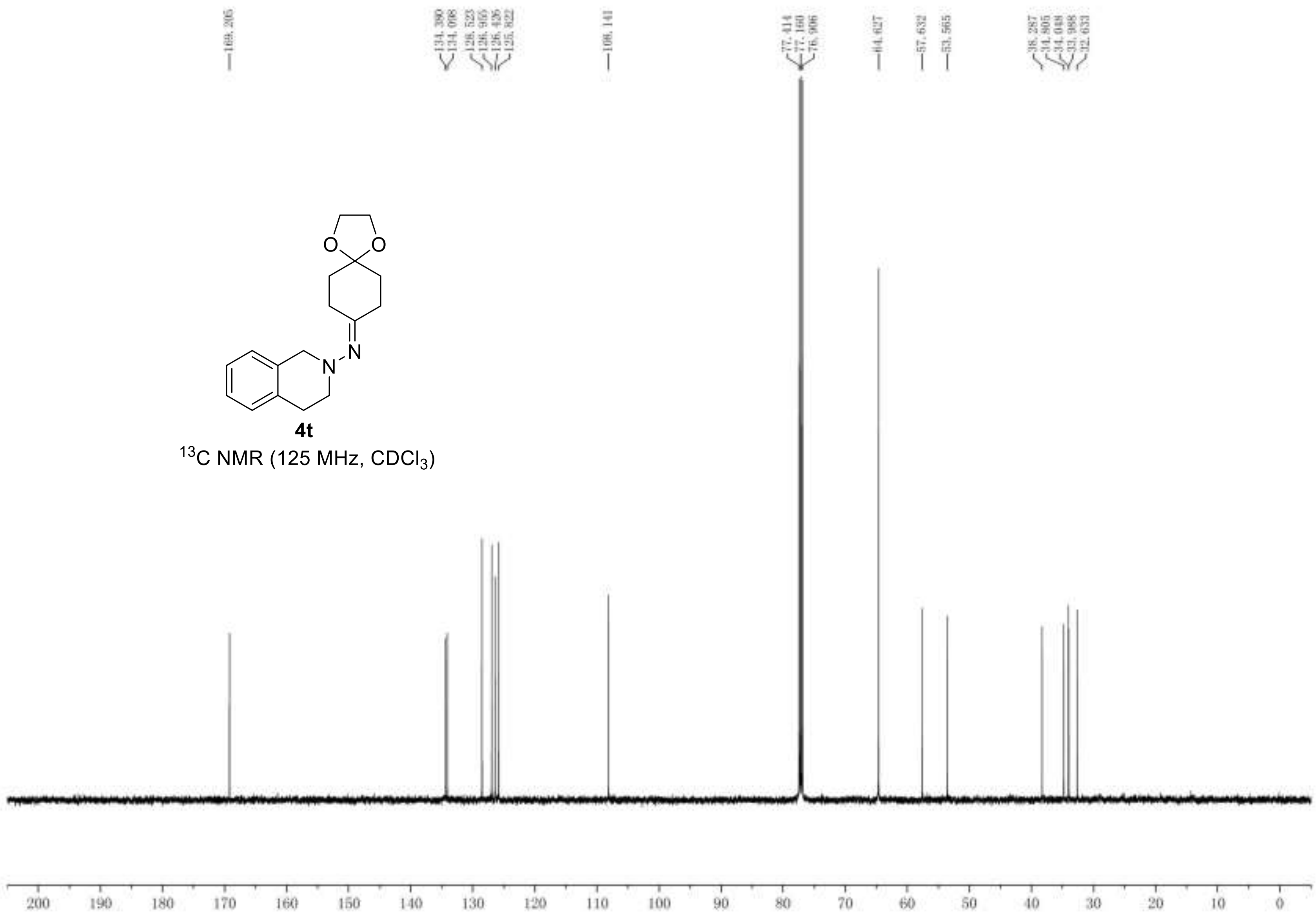
4s

^{13}C NMR (125 MHz, CDCl$_3$)



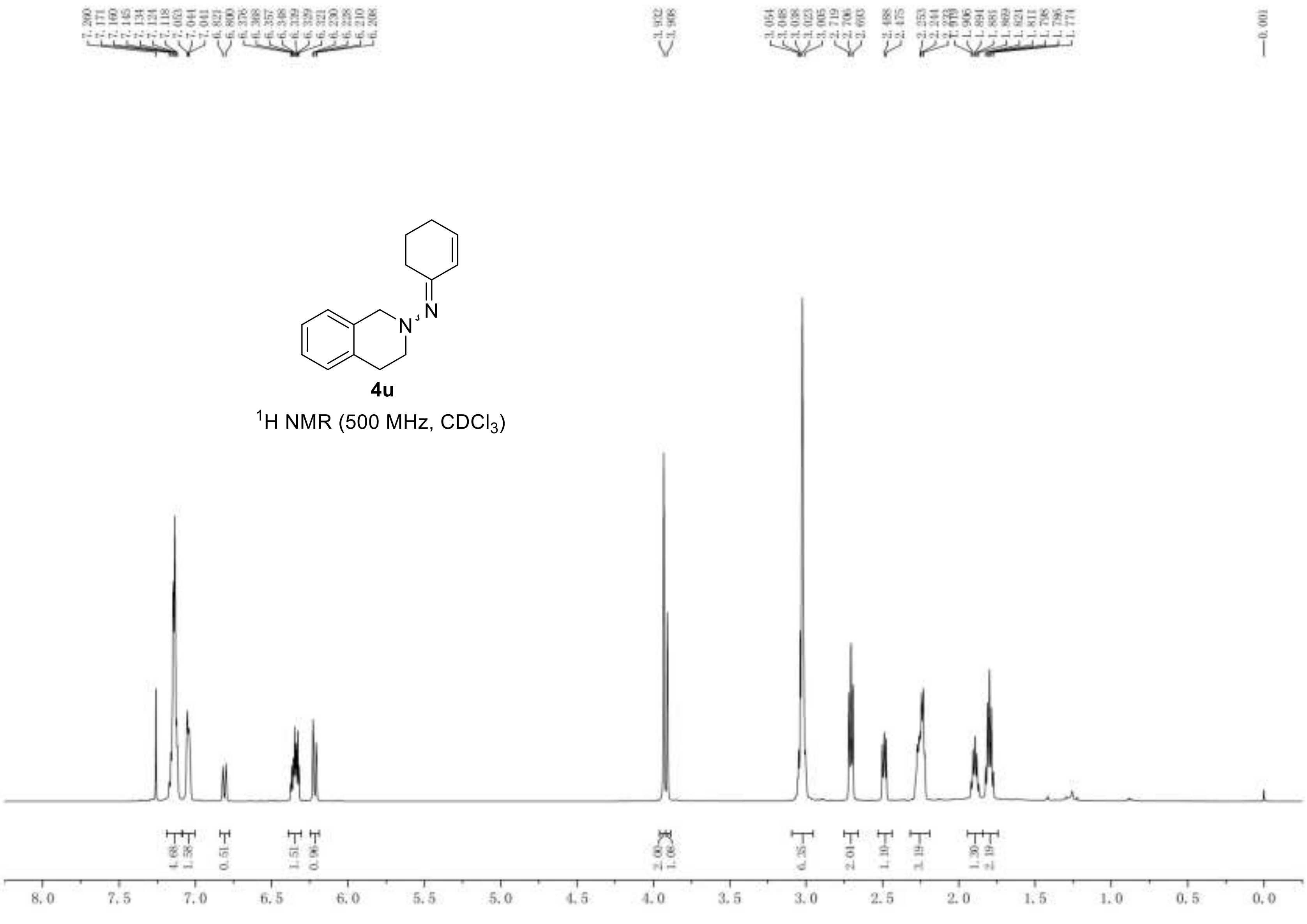
4t

^{1}H NMR (500 MHz, CDCl$_3$)



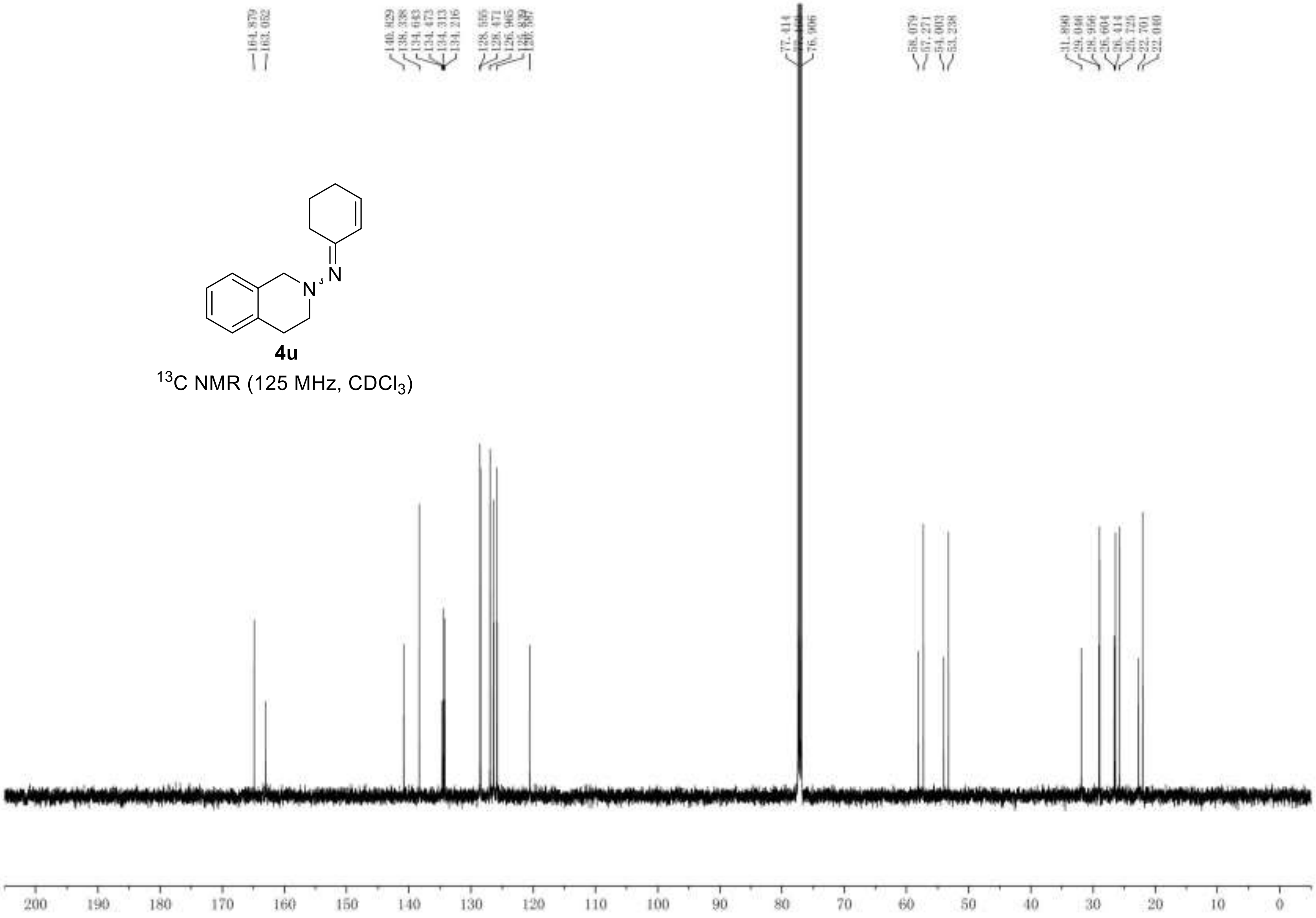
4t

^{13}C NMR (125 MHz, CDCl$_3$)



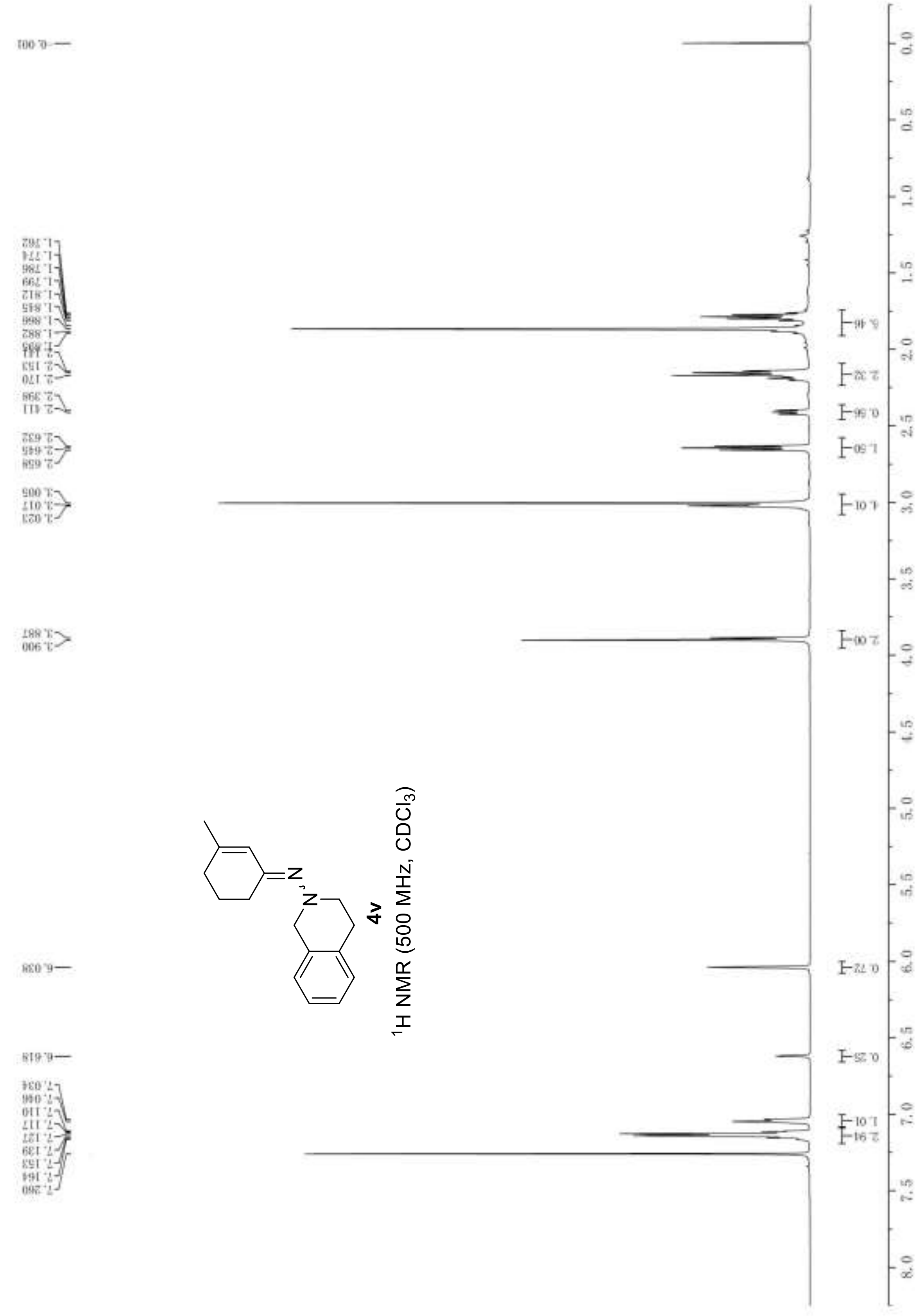
4u

^{1}H NMR (500 MHz, $CDCl_3$)



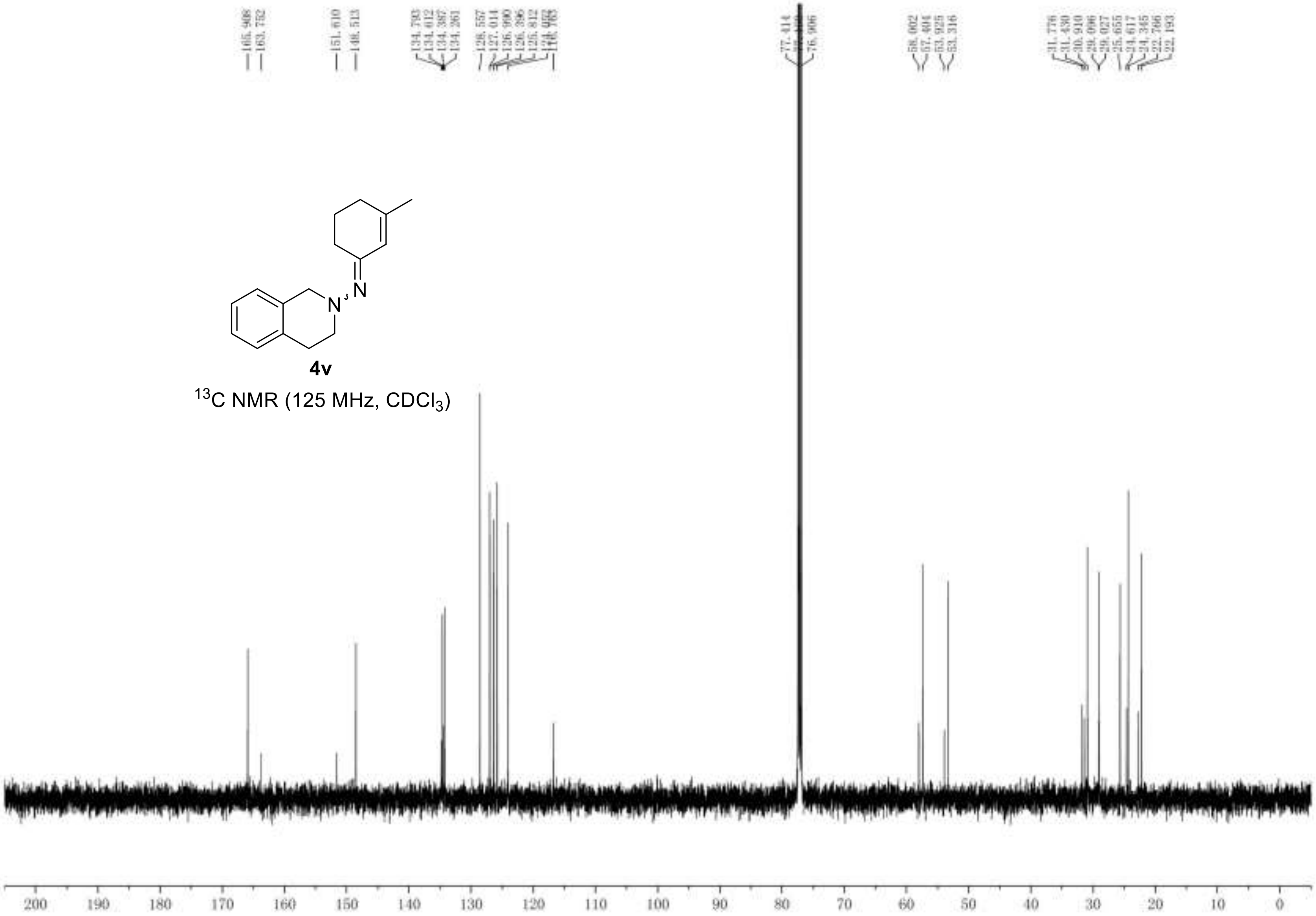
4u

^{13}C NMR (125 MHz, CDCl$_3$)



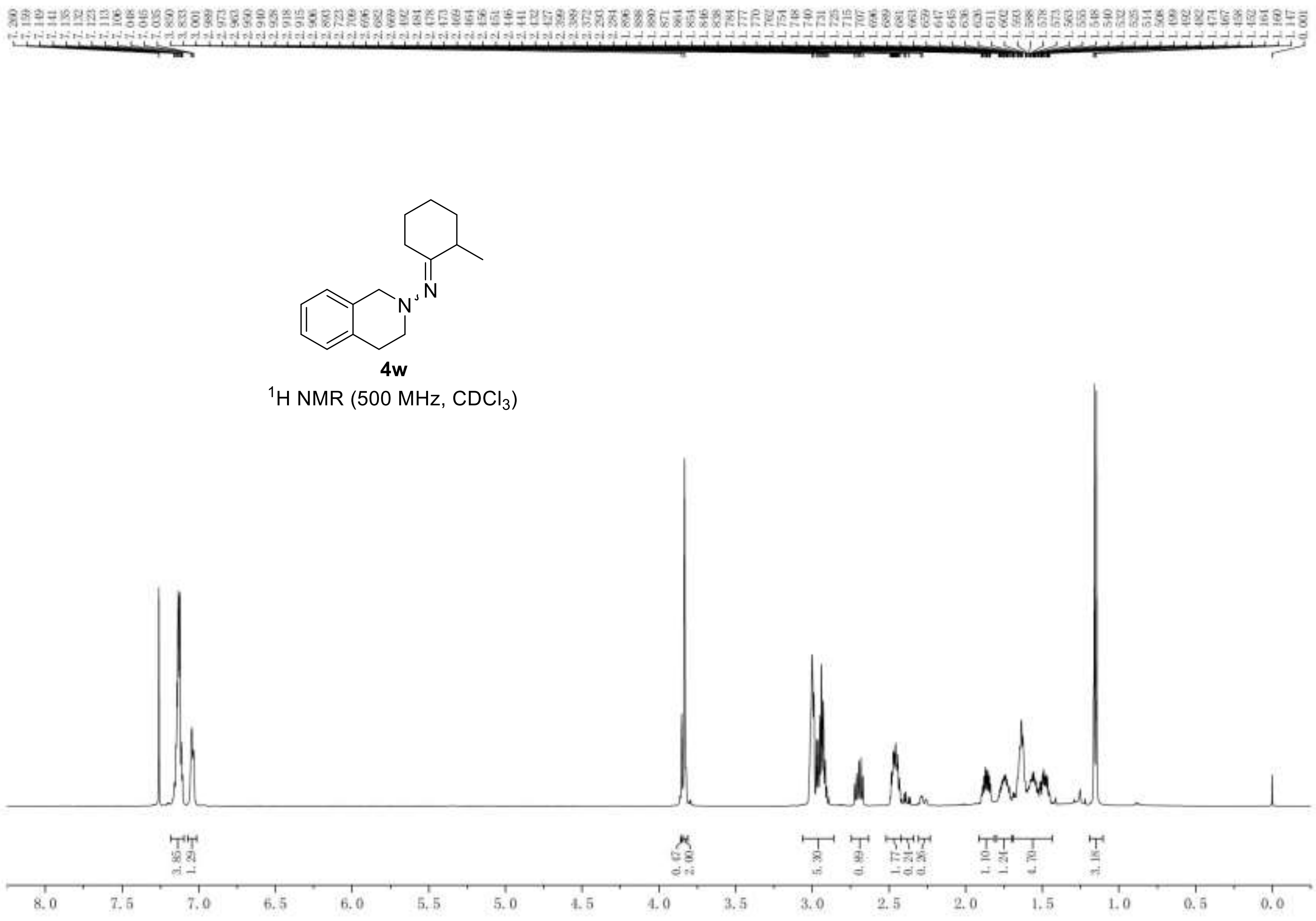
4v

^{1}H NMR (500 MHz, CDCl$_3$)



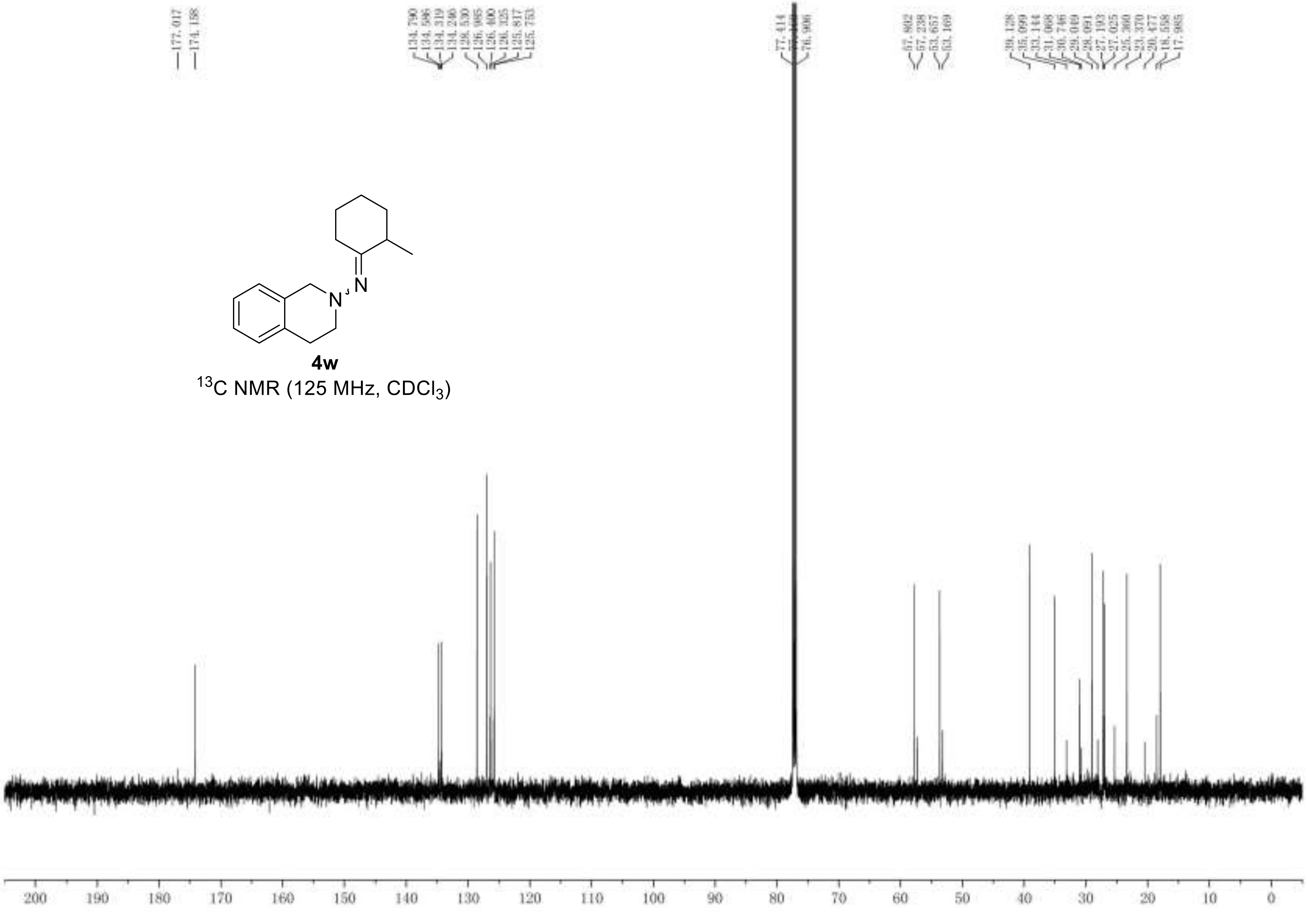
4v

^{13}C NMR (125 MHz, CDCl$_3$)



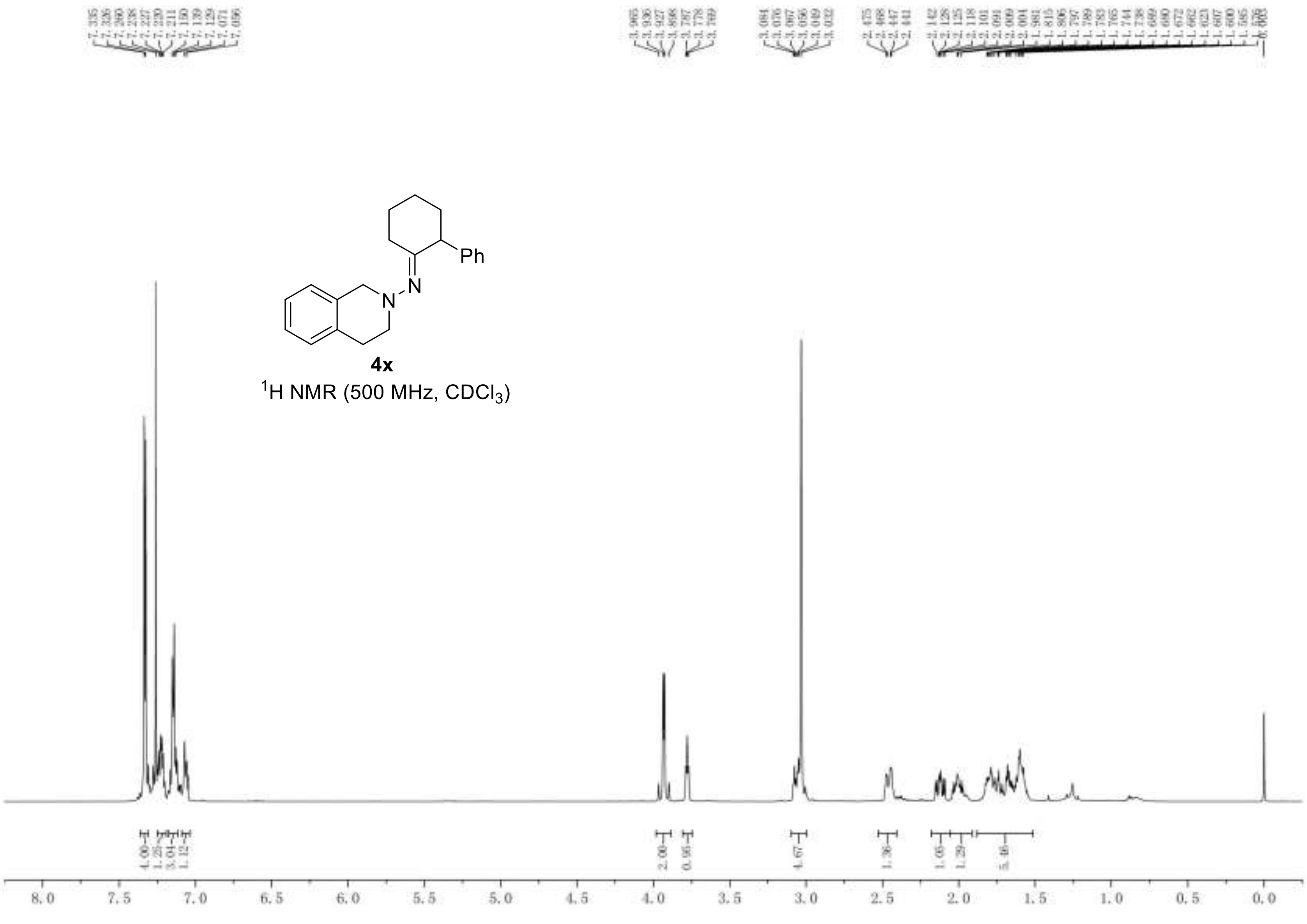
4w

^{1}H NMR (500 MHz, CDCl$_3$)



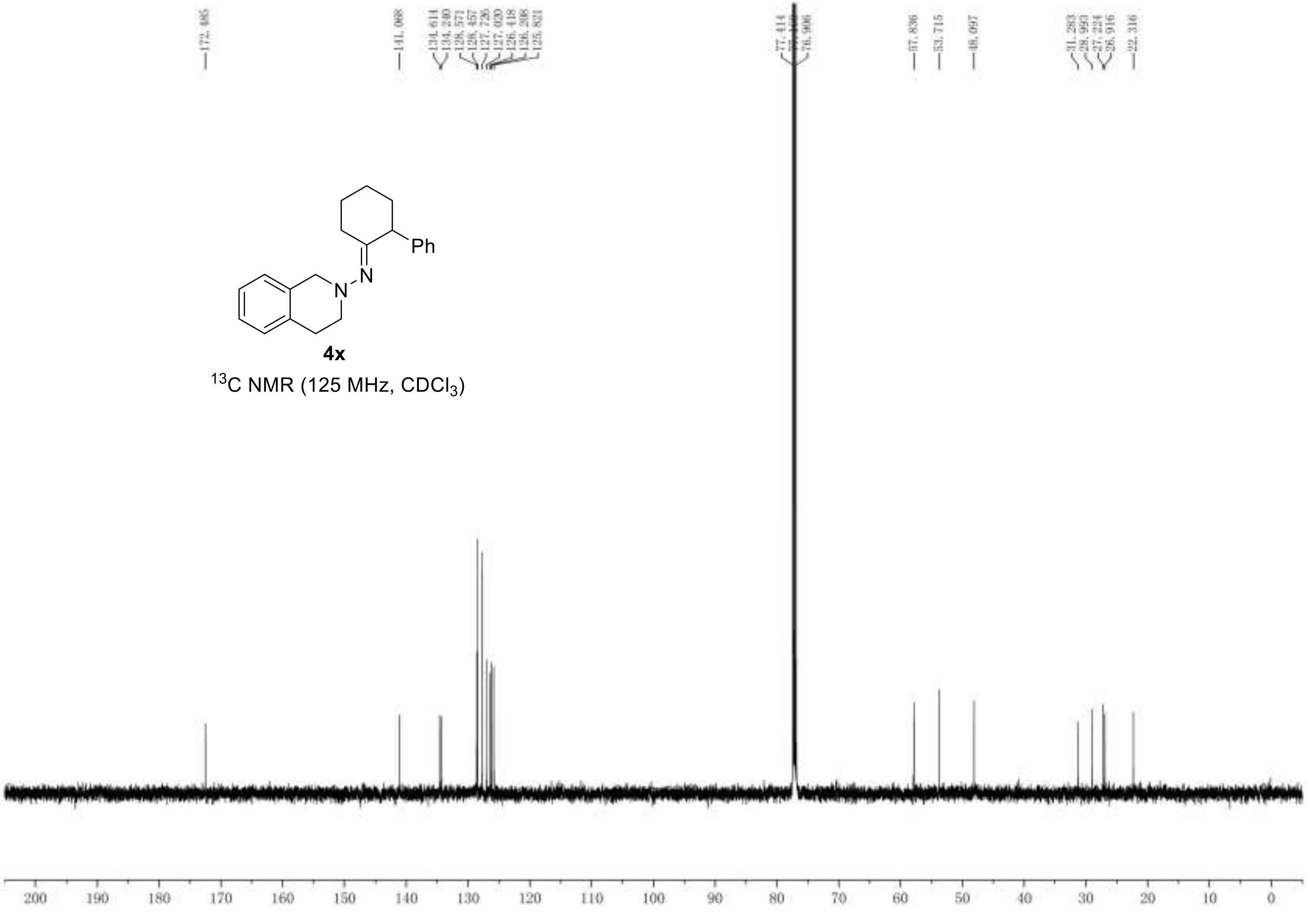
4w

^{13}C NMR (125 MHz, CDCl$_3$)



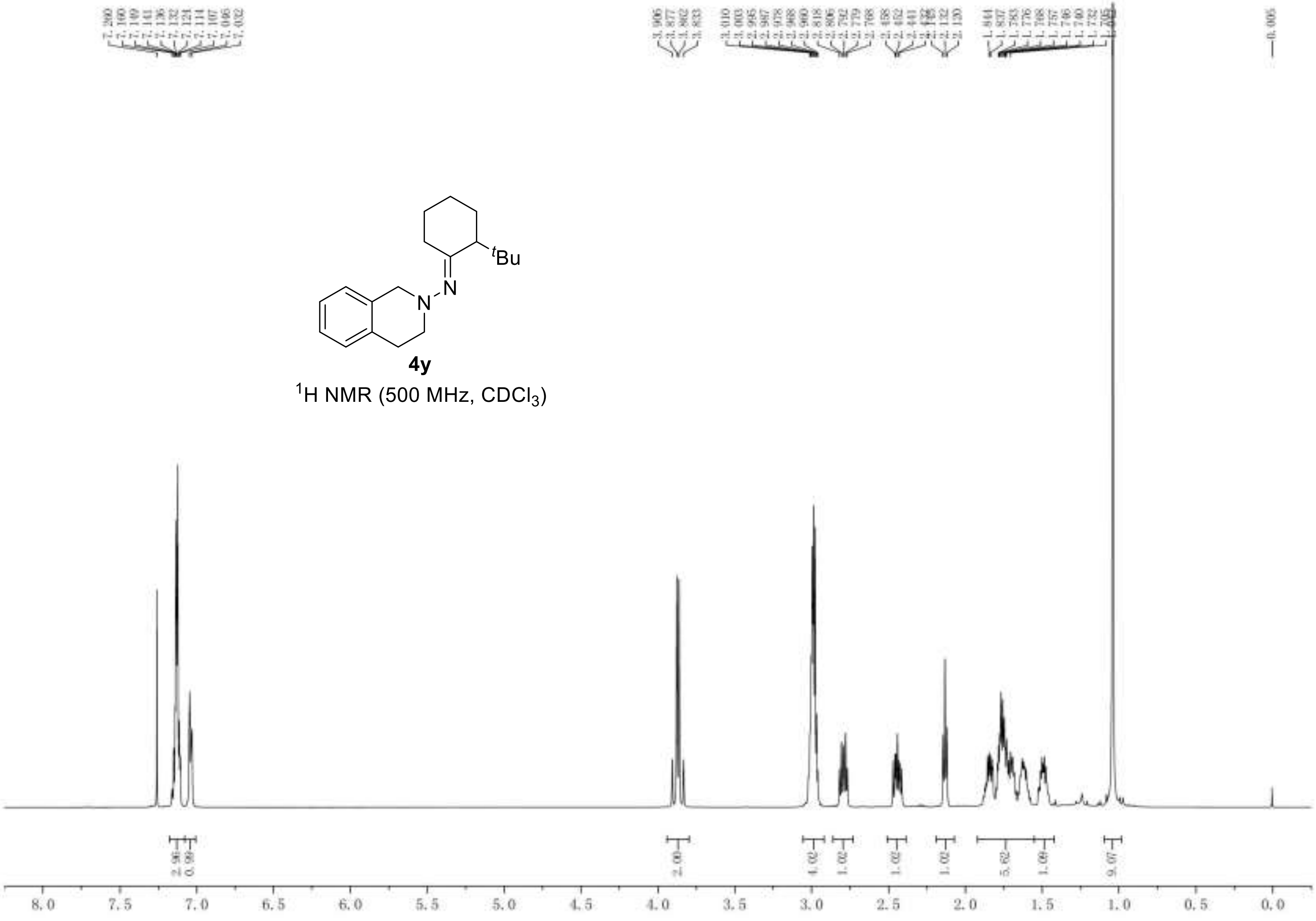
4x

^{1}H NMR (500 MHz, CDCl$_3$)



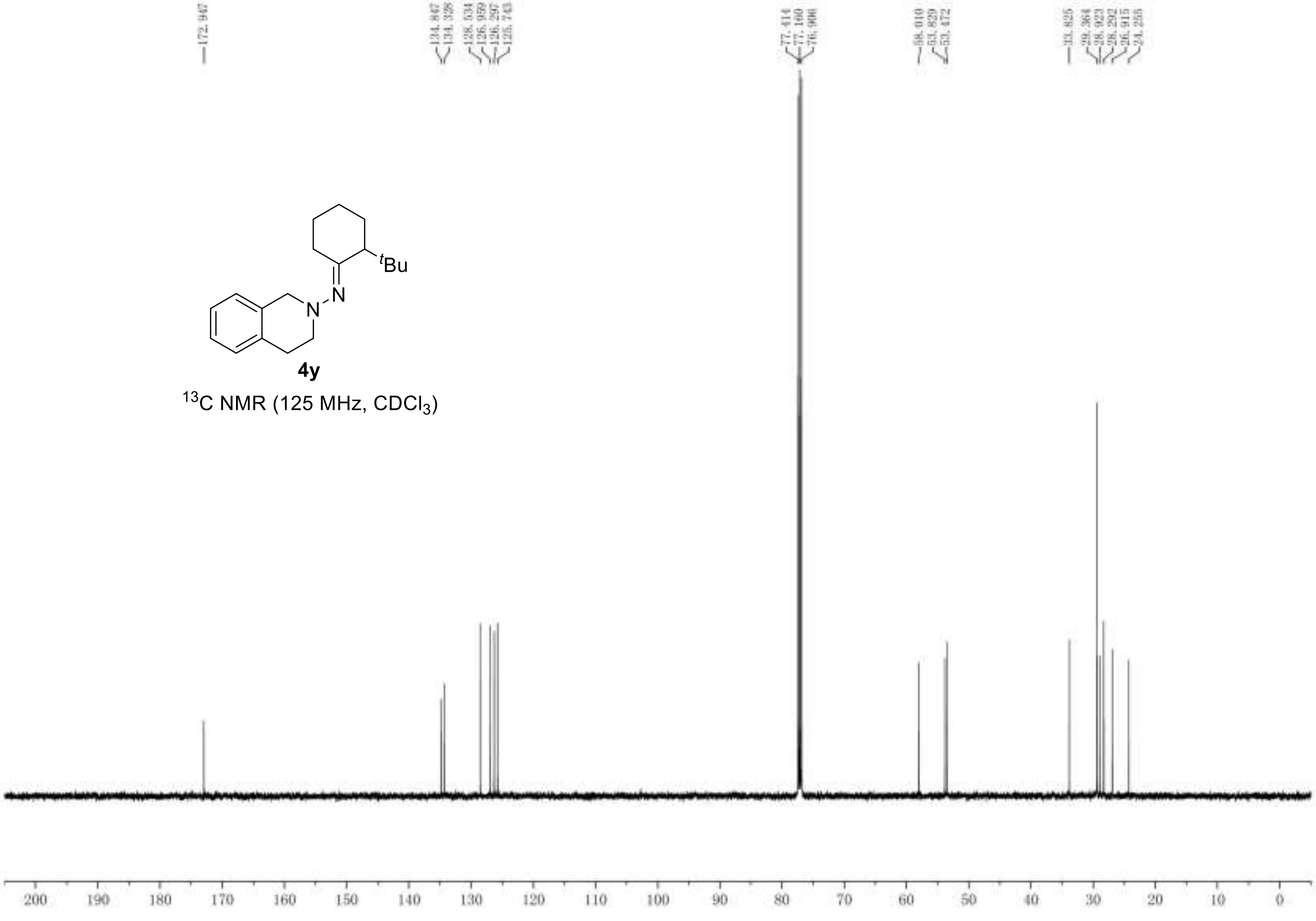
4x

^{13}C NMR (125 MHz, CDCl$_3$)



4y

^{1}H NMR (500 MHz, CDCl$_3$)



4y

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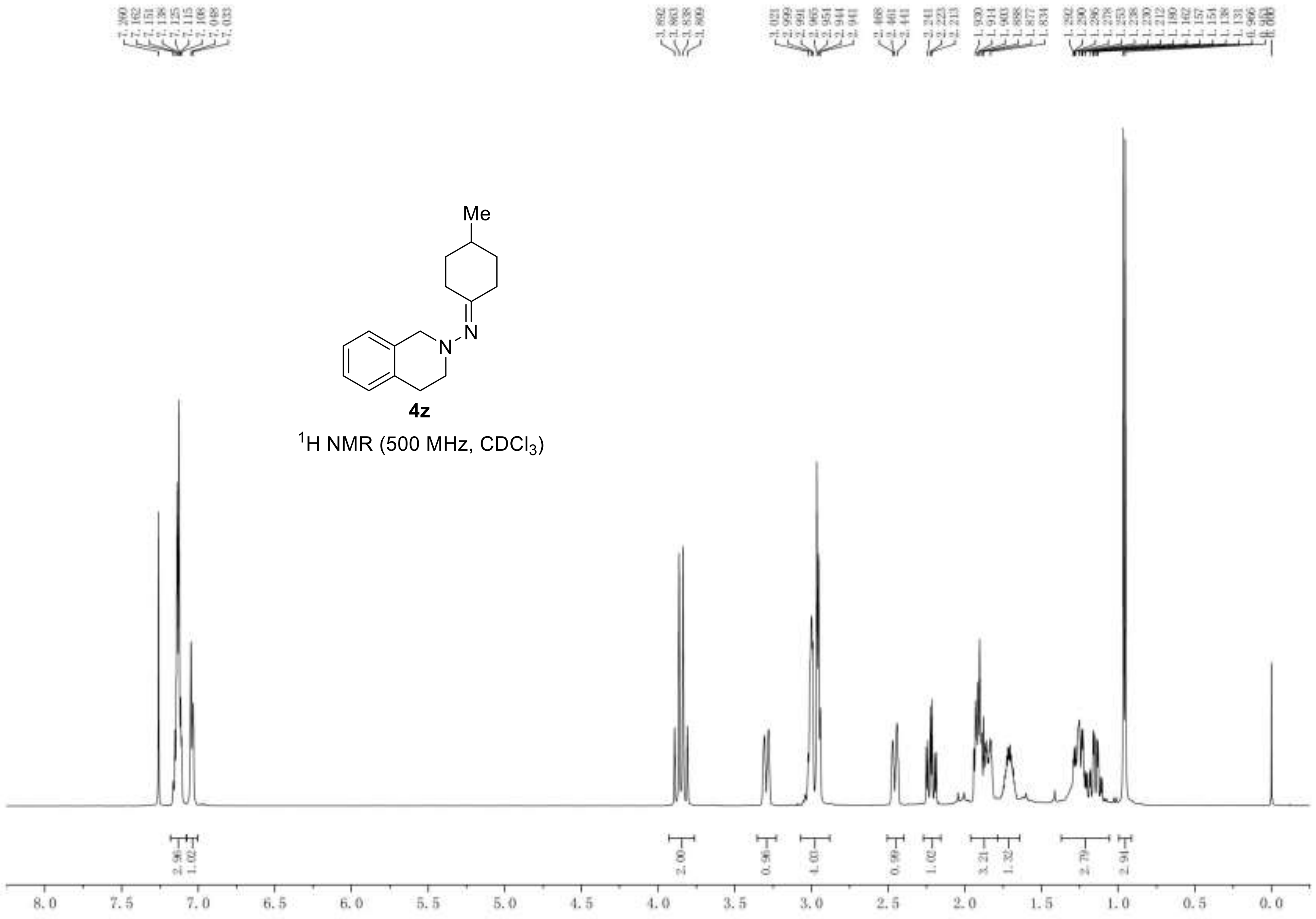
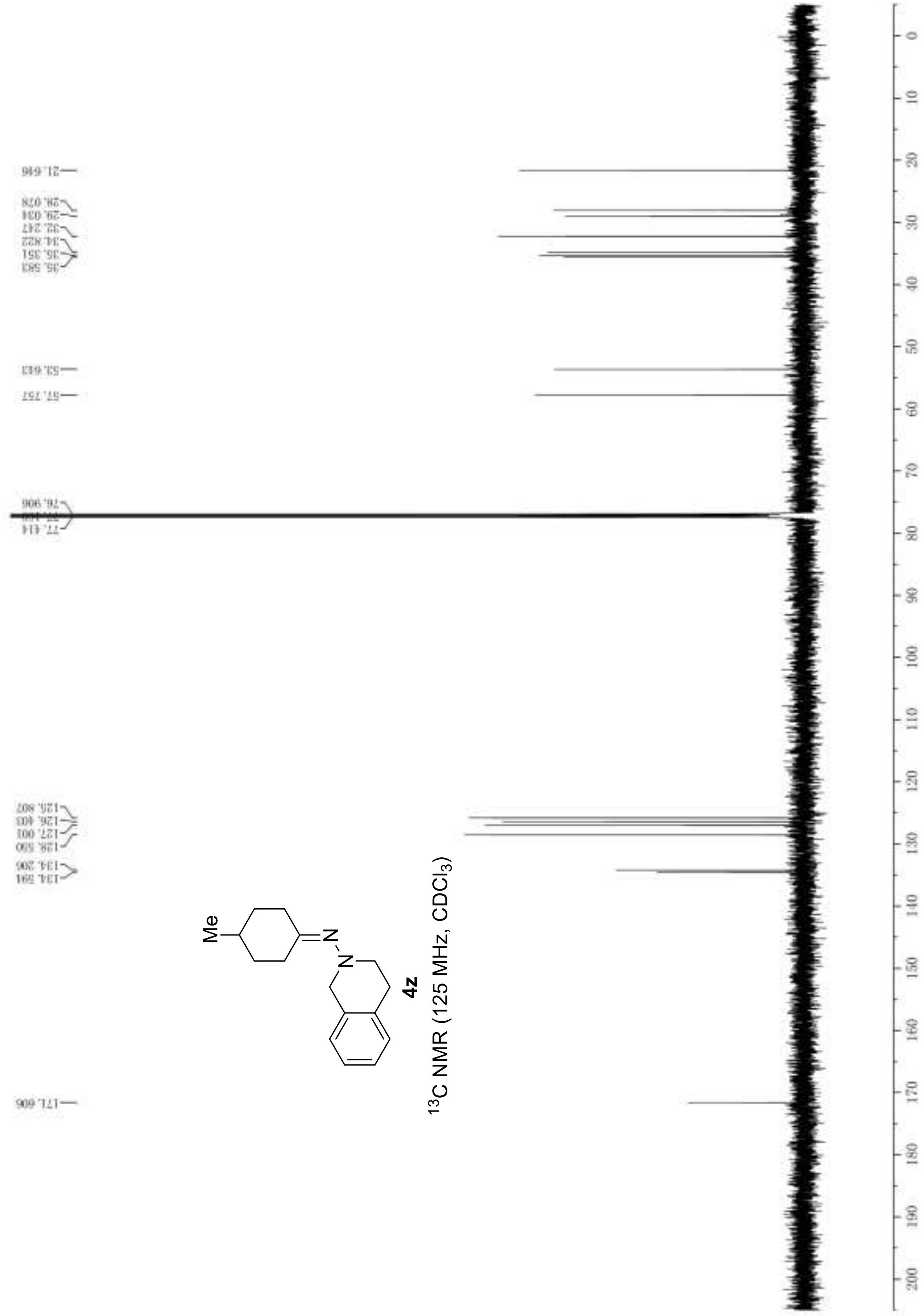


4z

^{1}H NMR (500 MHz, CDCl$_3$)



4z

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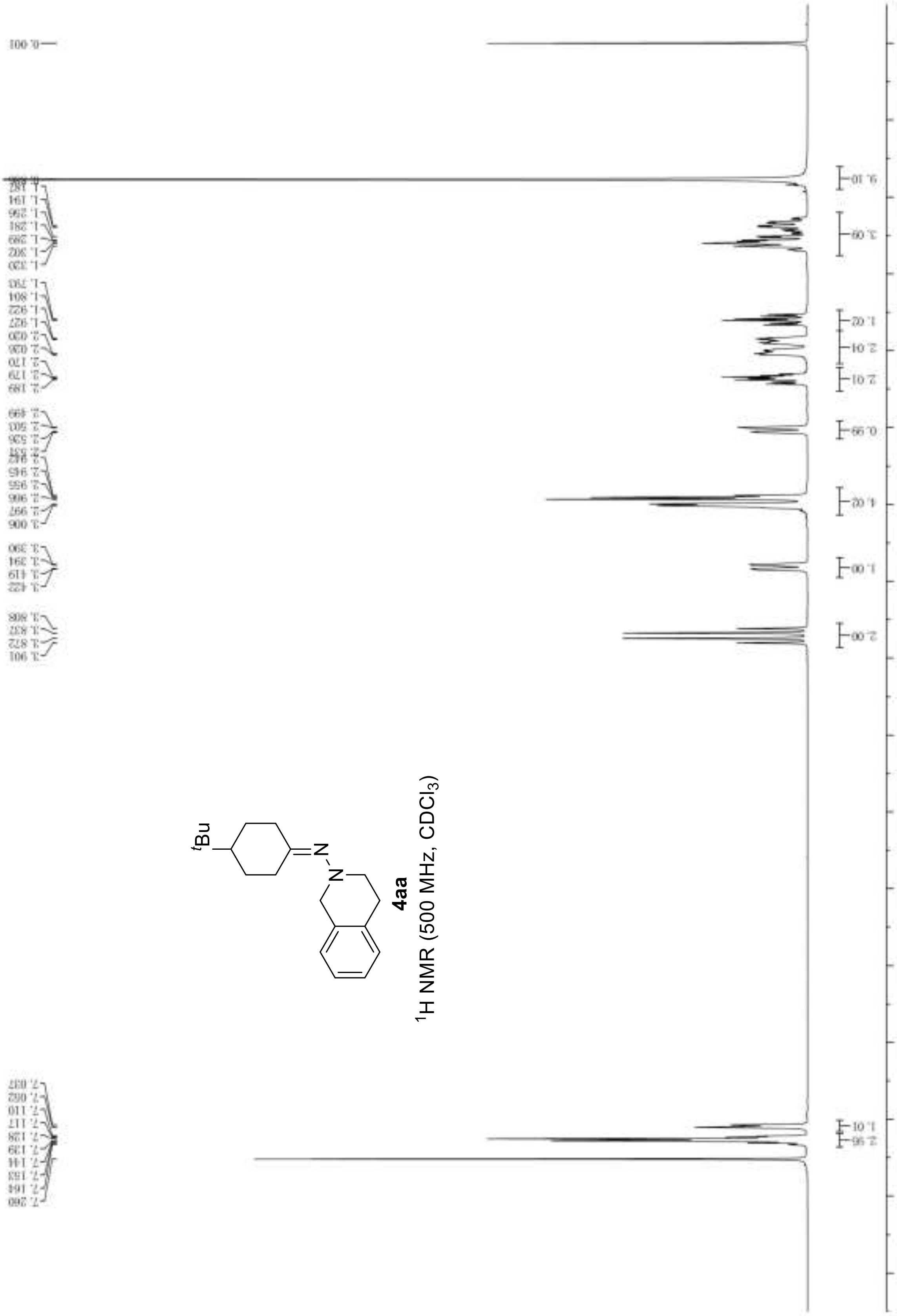

4aa

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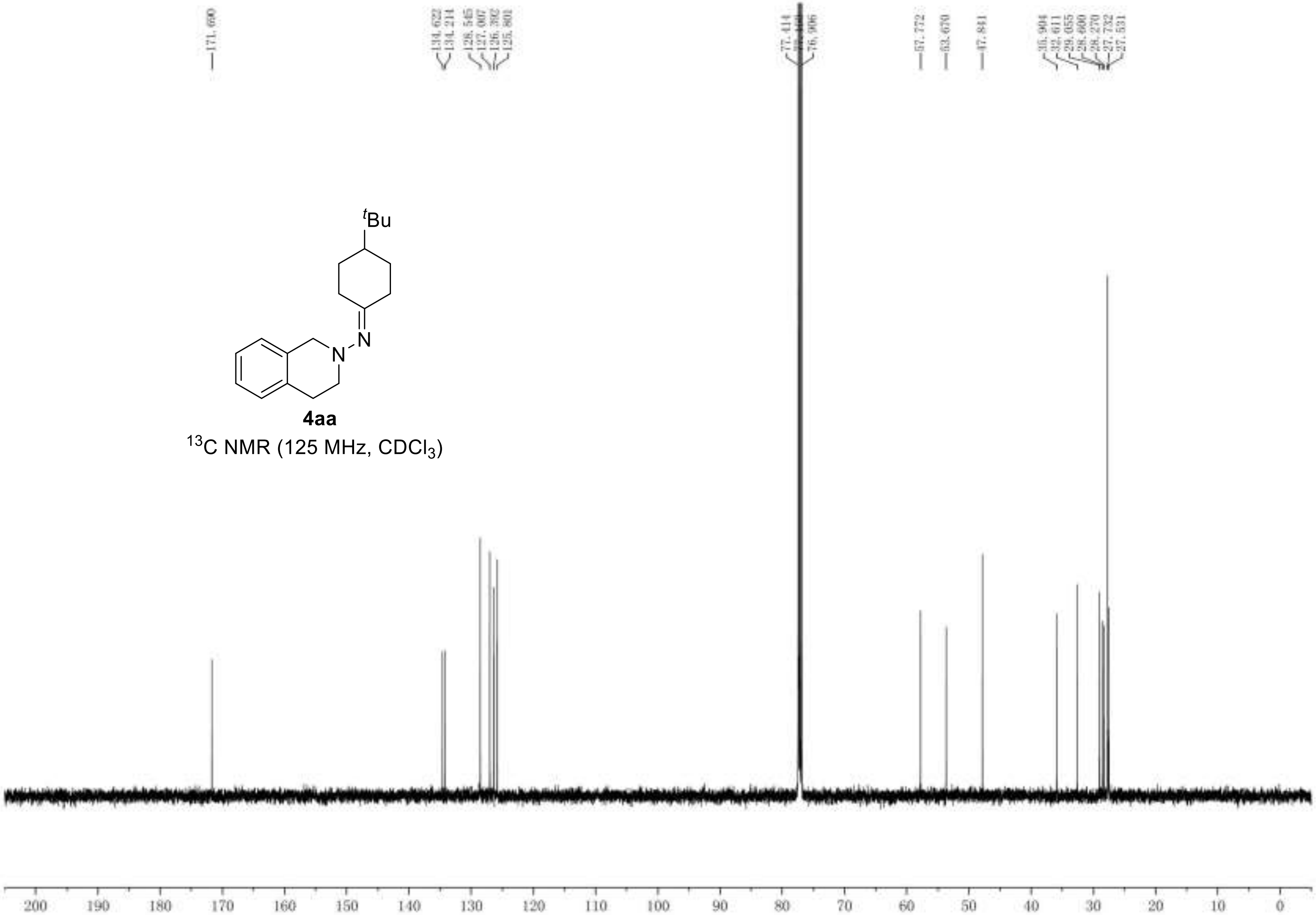
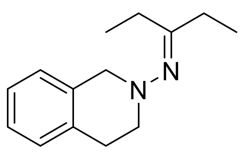


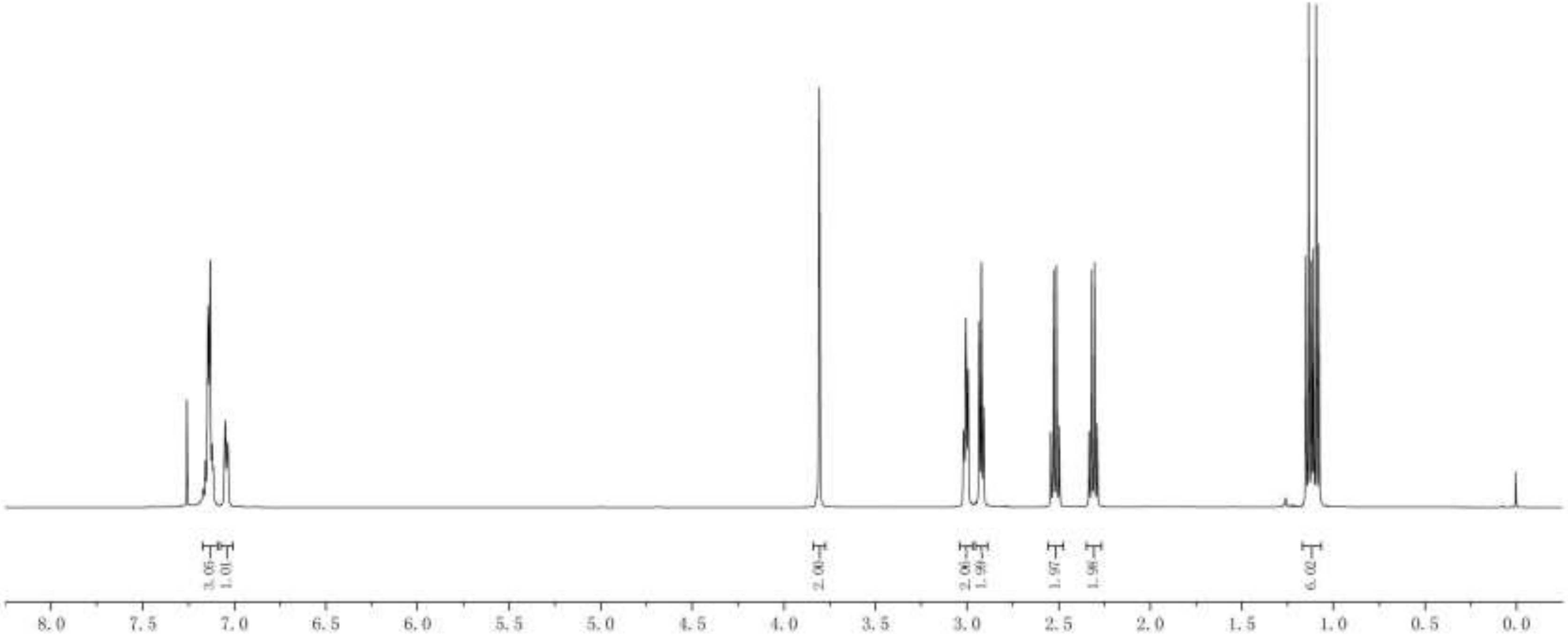
4aa

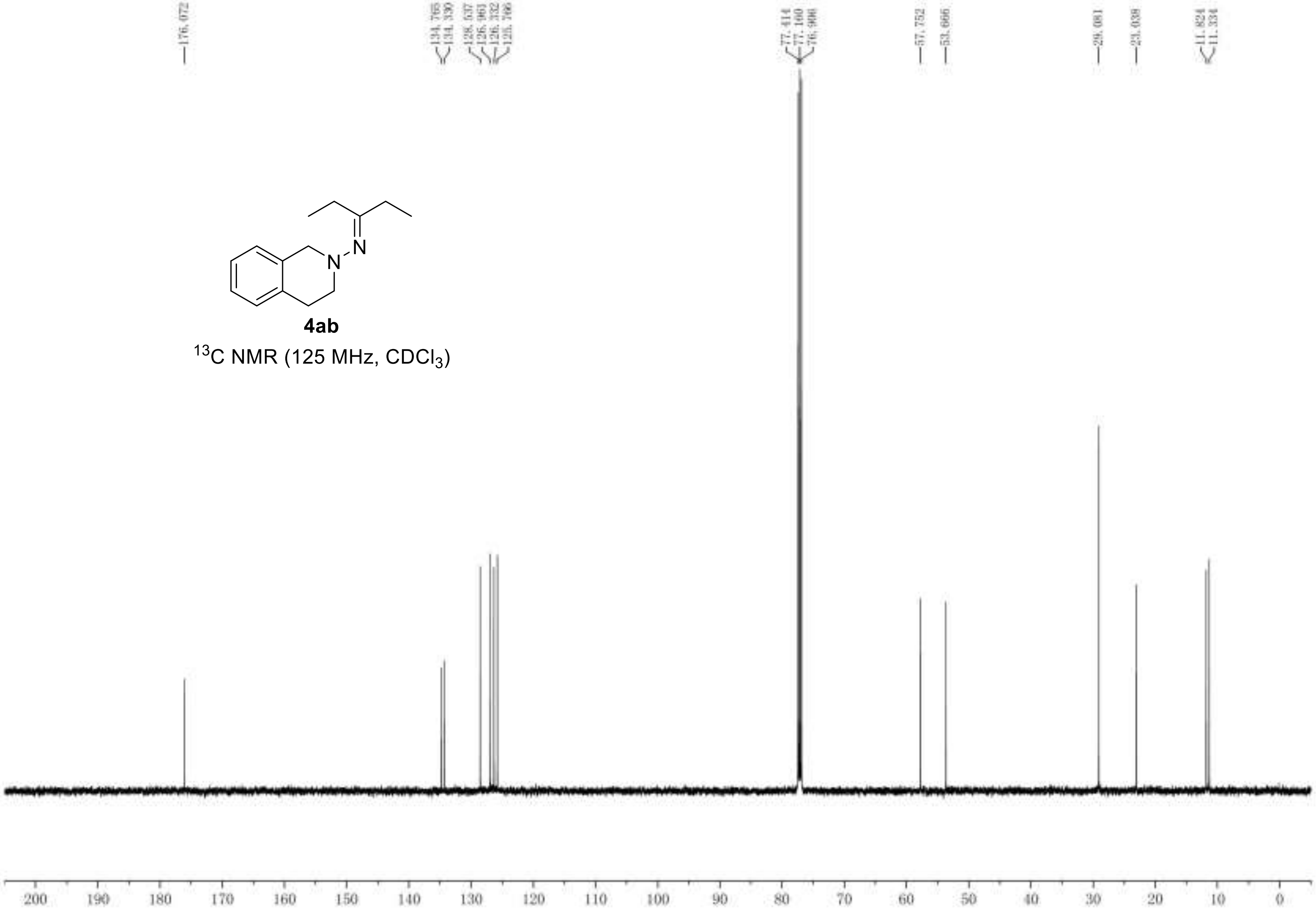
^{13}C NMR (125 MHz, CDCl$_3$)



4ab

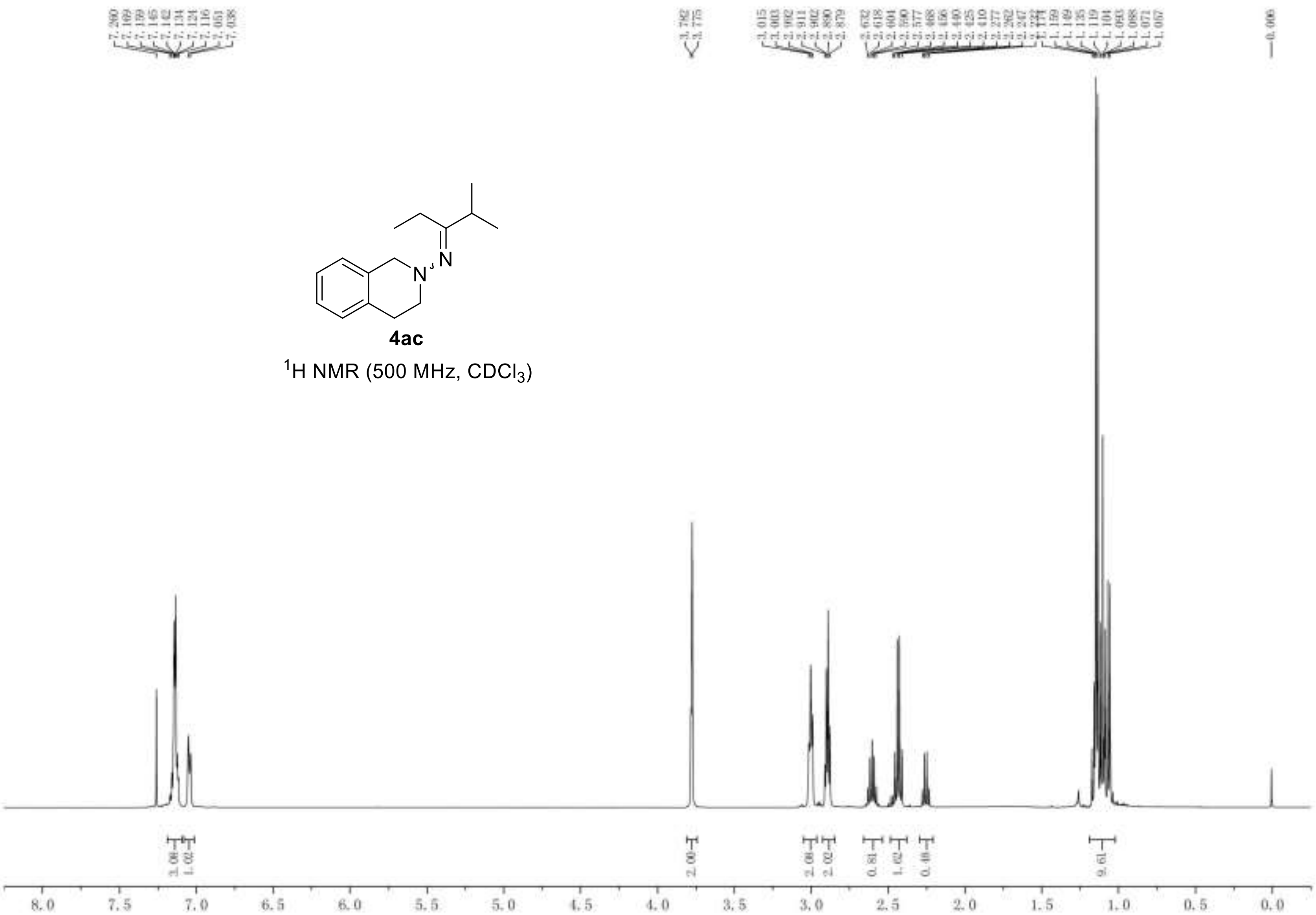
^{1}H NMR (500 MHz, CDCl$_3$)





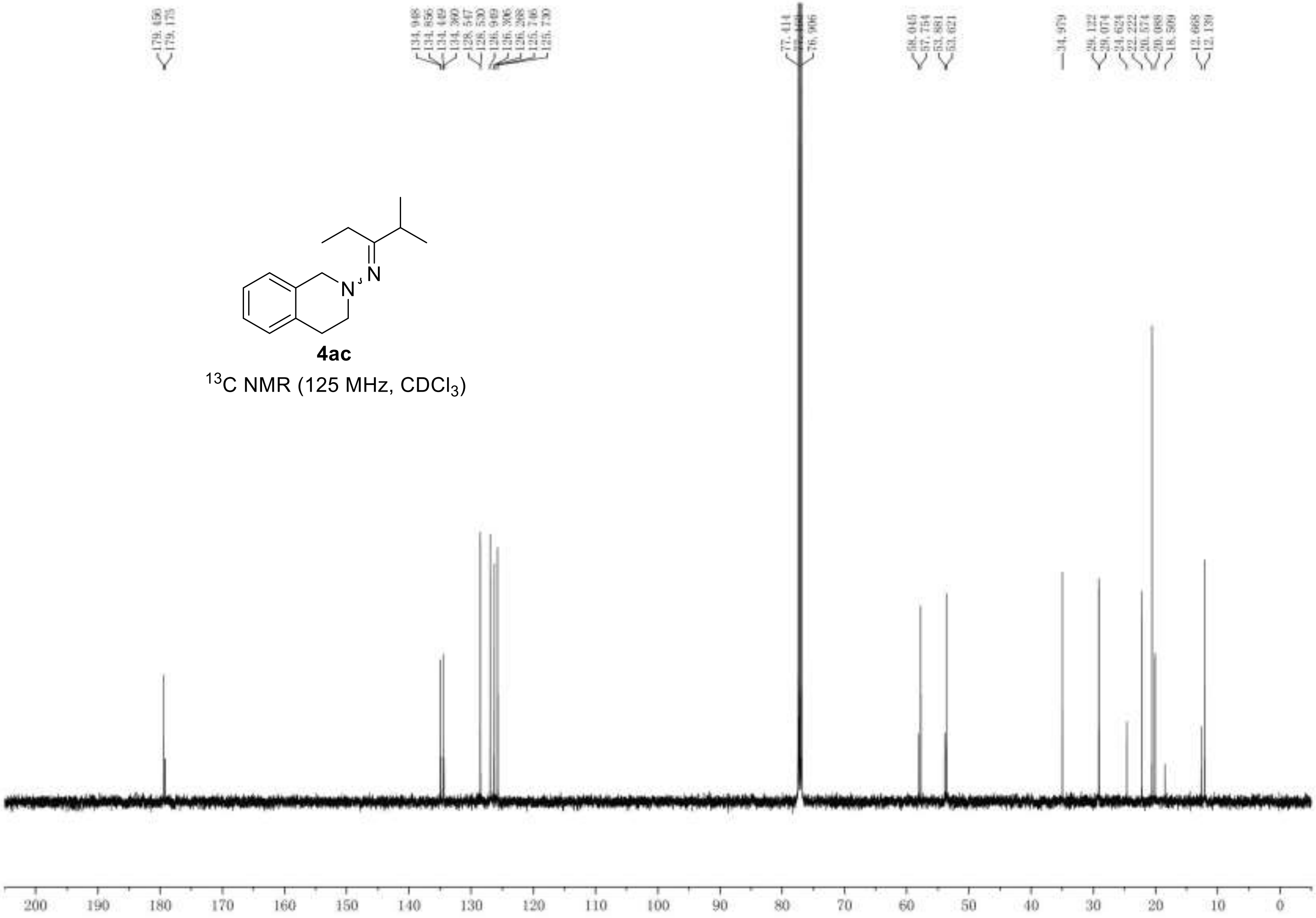
4ab

^{13}C NMR (125 MHz, CDCl$_3$)



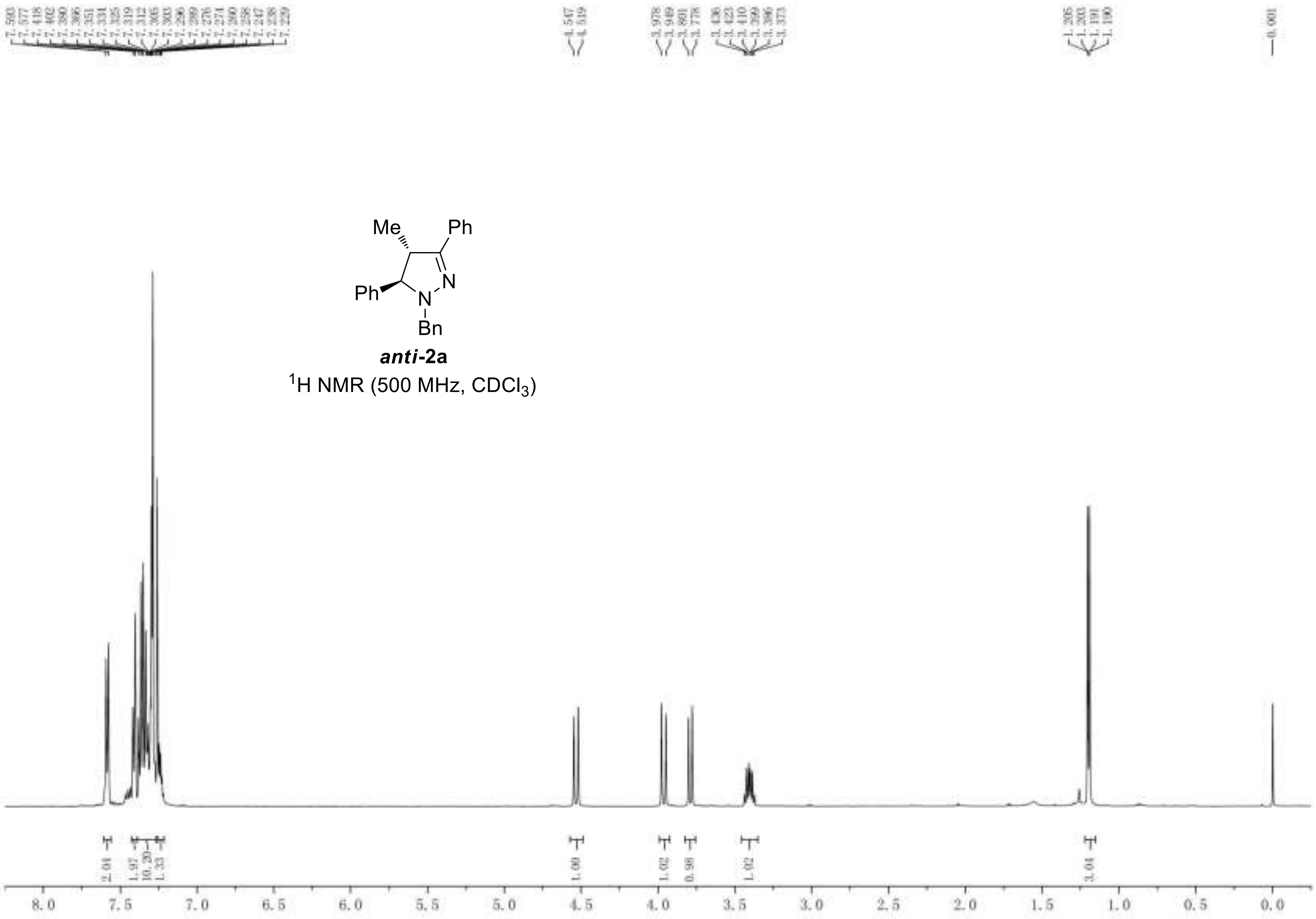
4ac

^{1}H NMR (500 MHz, CDCl$_3$)



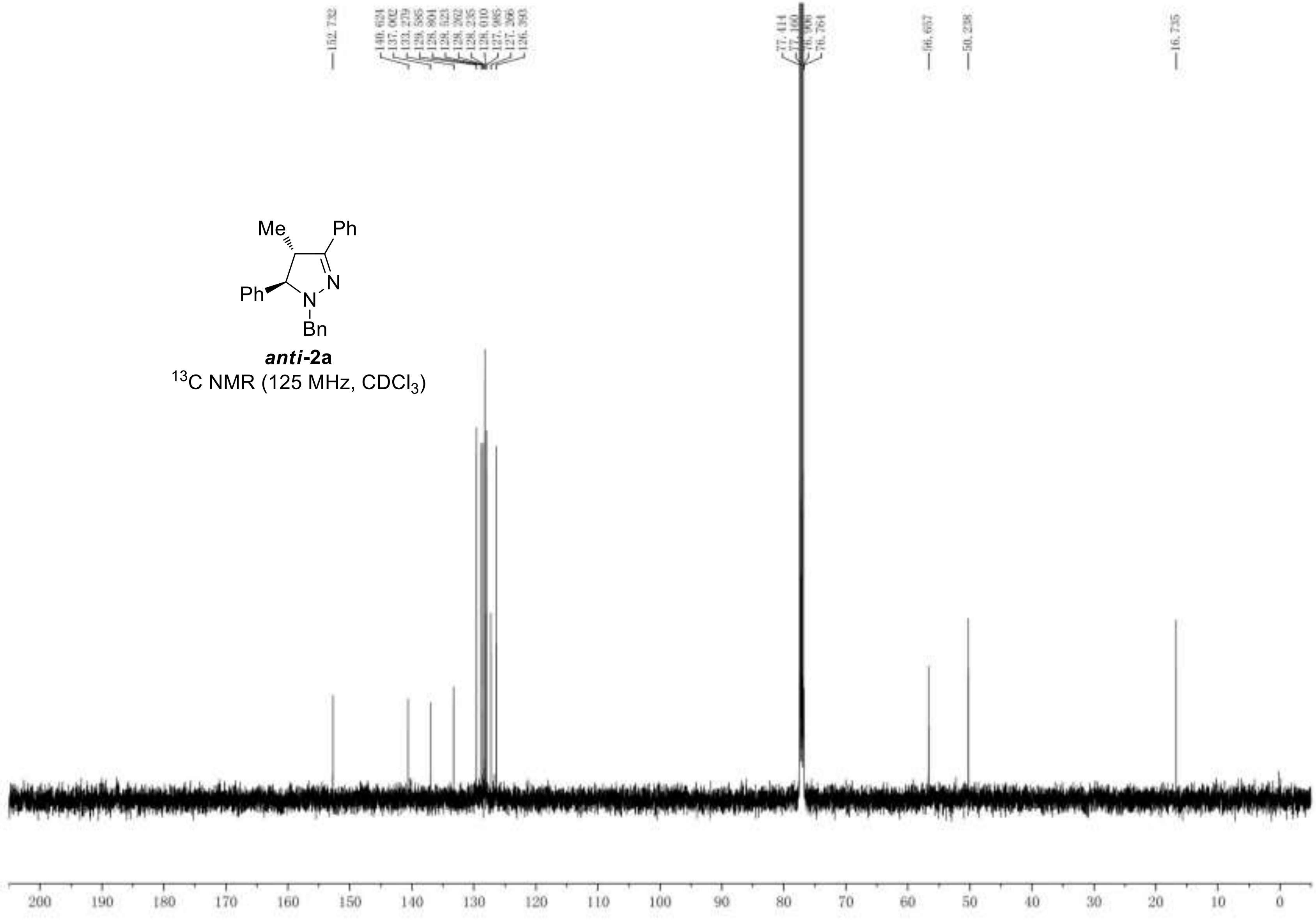
4ac

^{13}C NMR (125 MHz, CDCl$_3$)



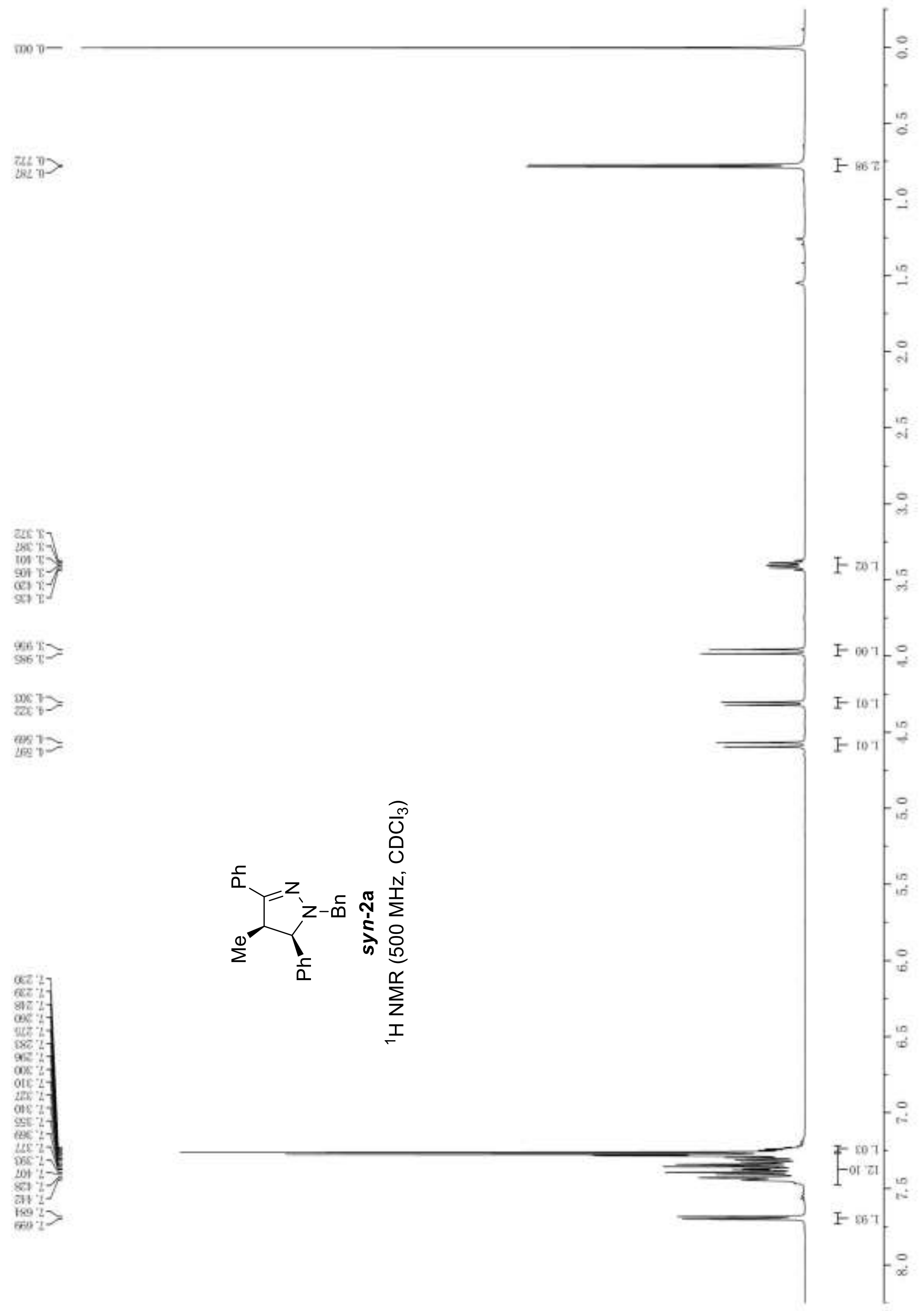
***anti*-2a**

^{1}H NMR (500 MHz, CDCl$_3$)



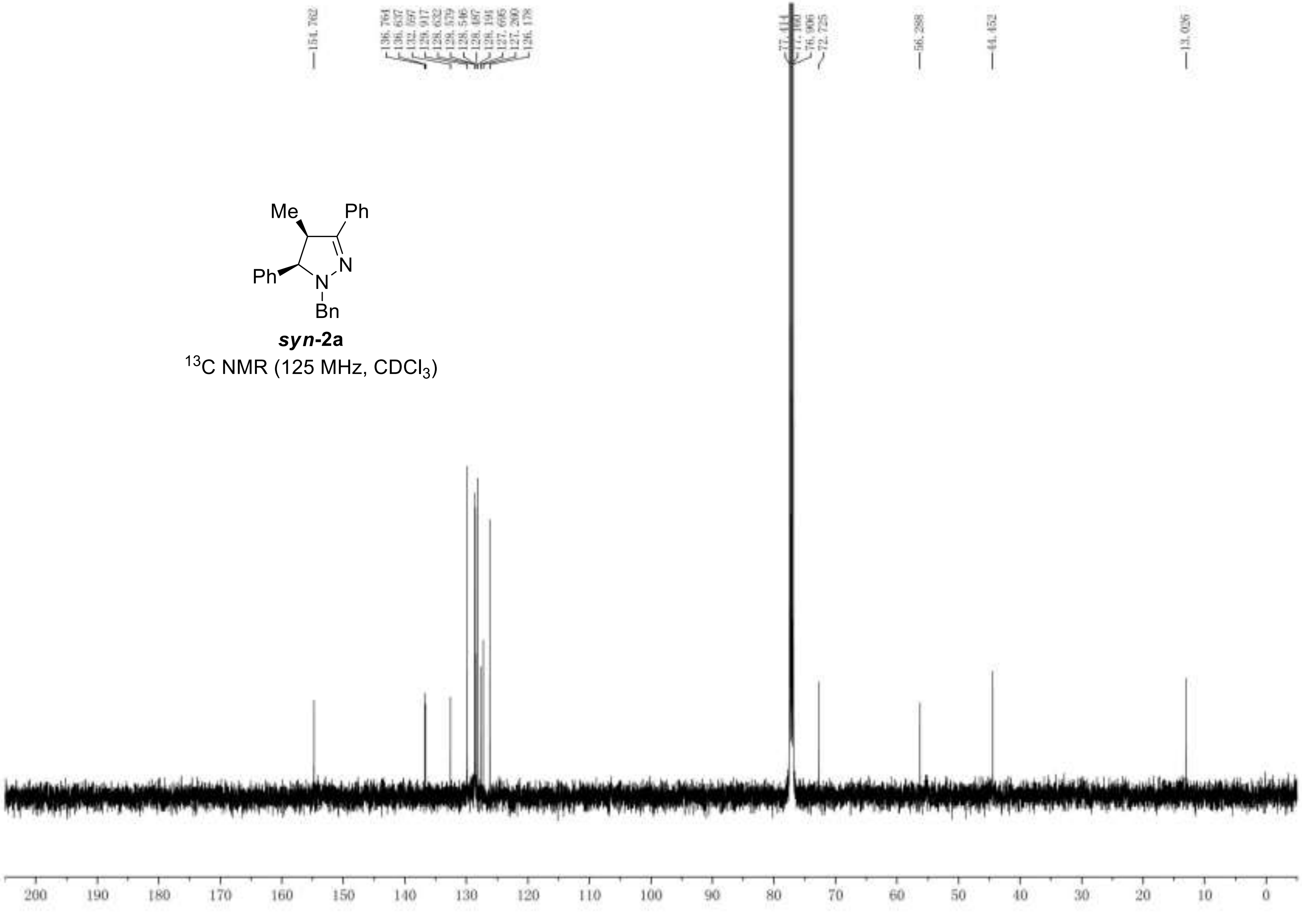
***anti*-2a**

^{13}C NMR (125 MHz, $CDCl_3$)



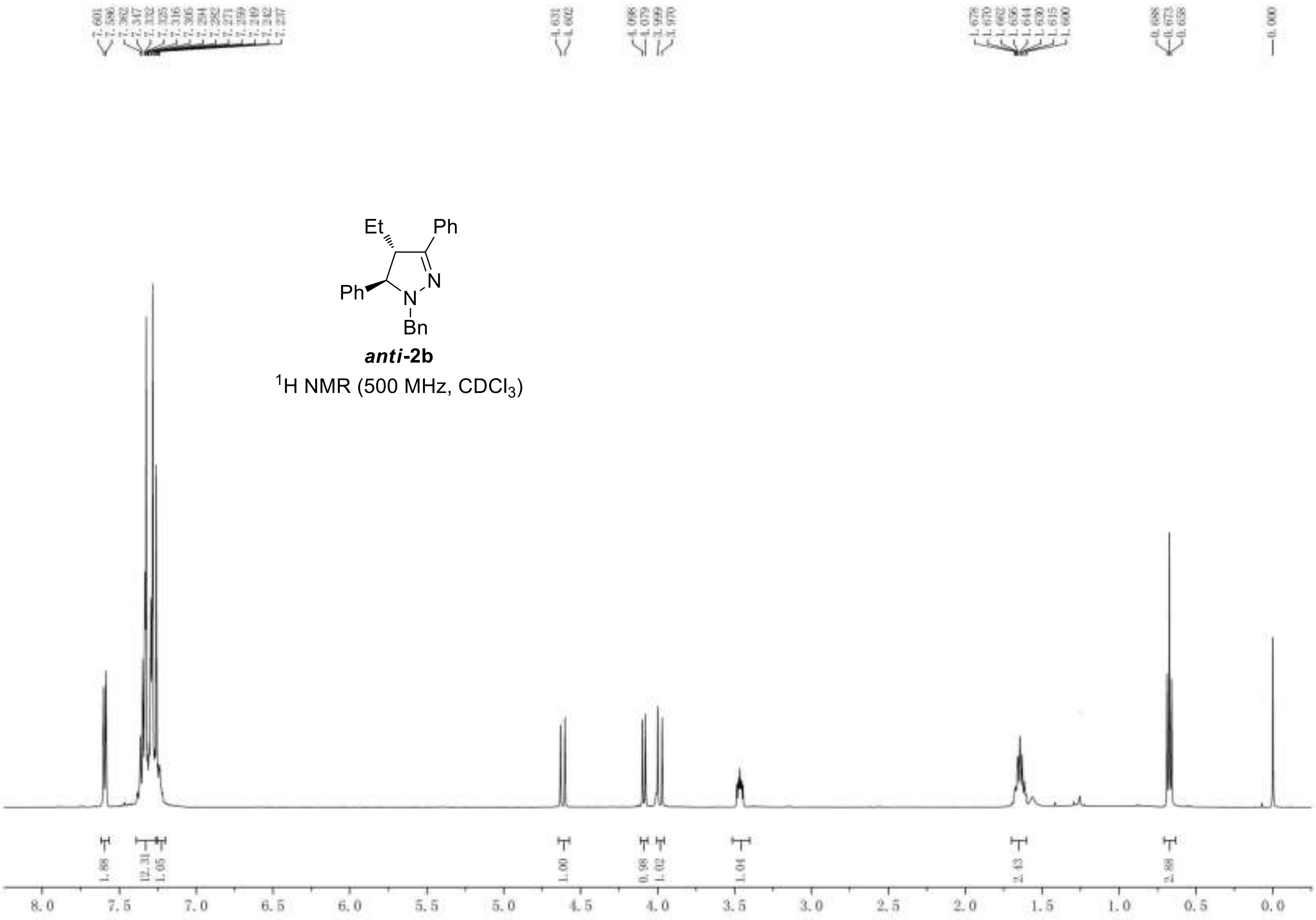
***syn*-2a**

^{1}H NMR (500 MHz, CDCl$_3$)



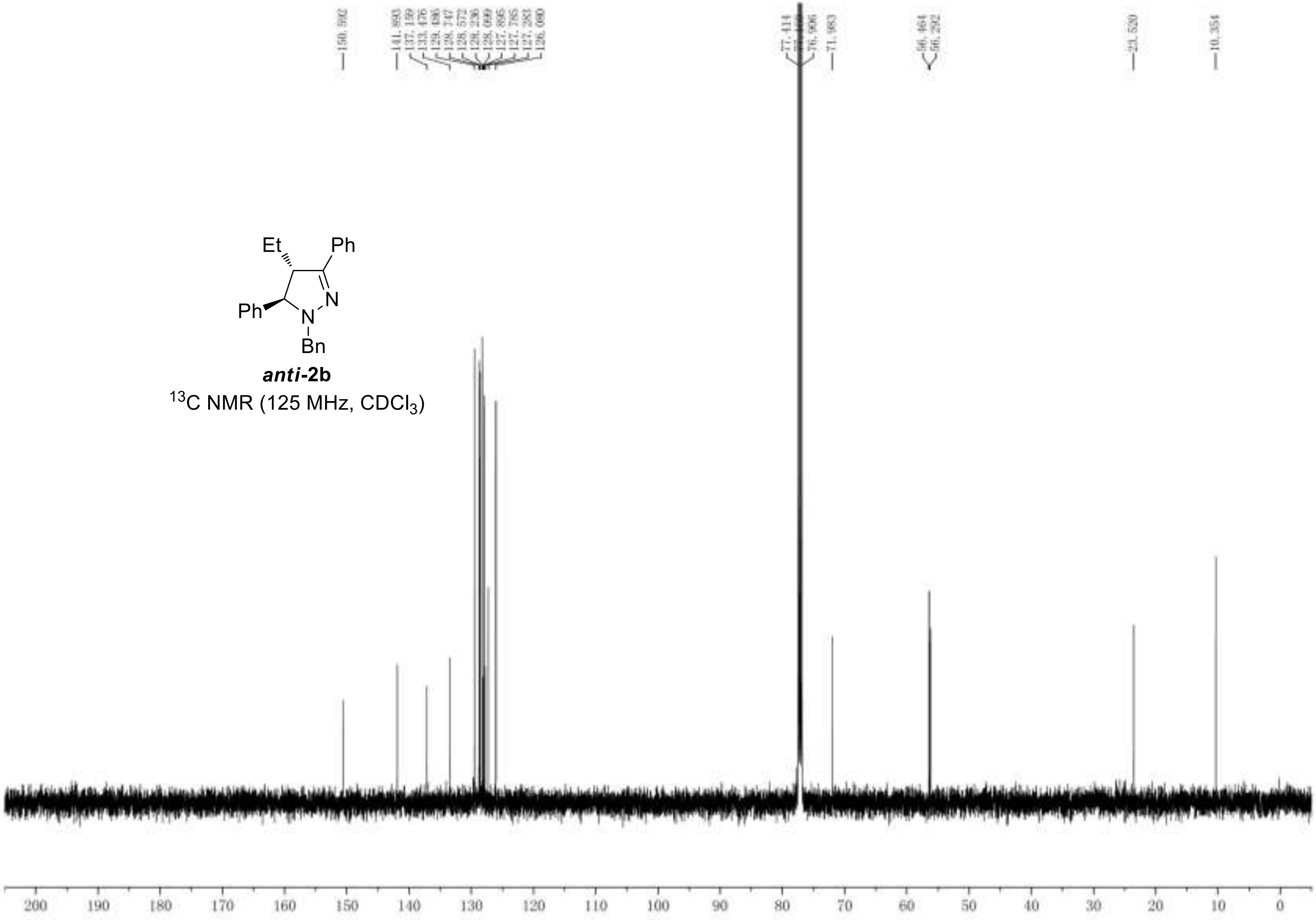
***syn*-2a**

^{13}C NMR (125 MHz, $CDCl_3$)



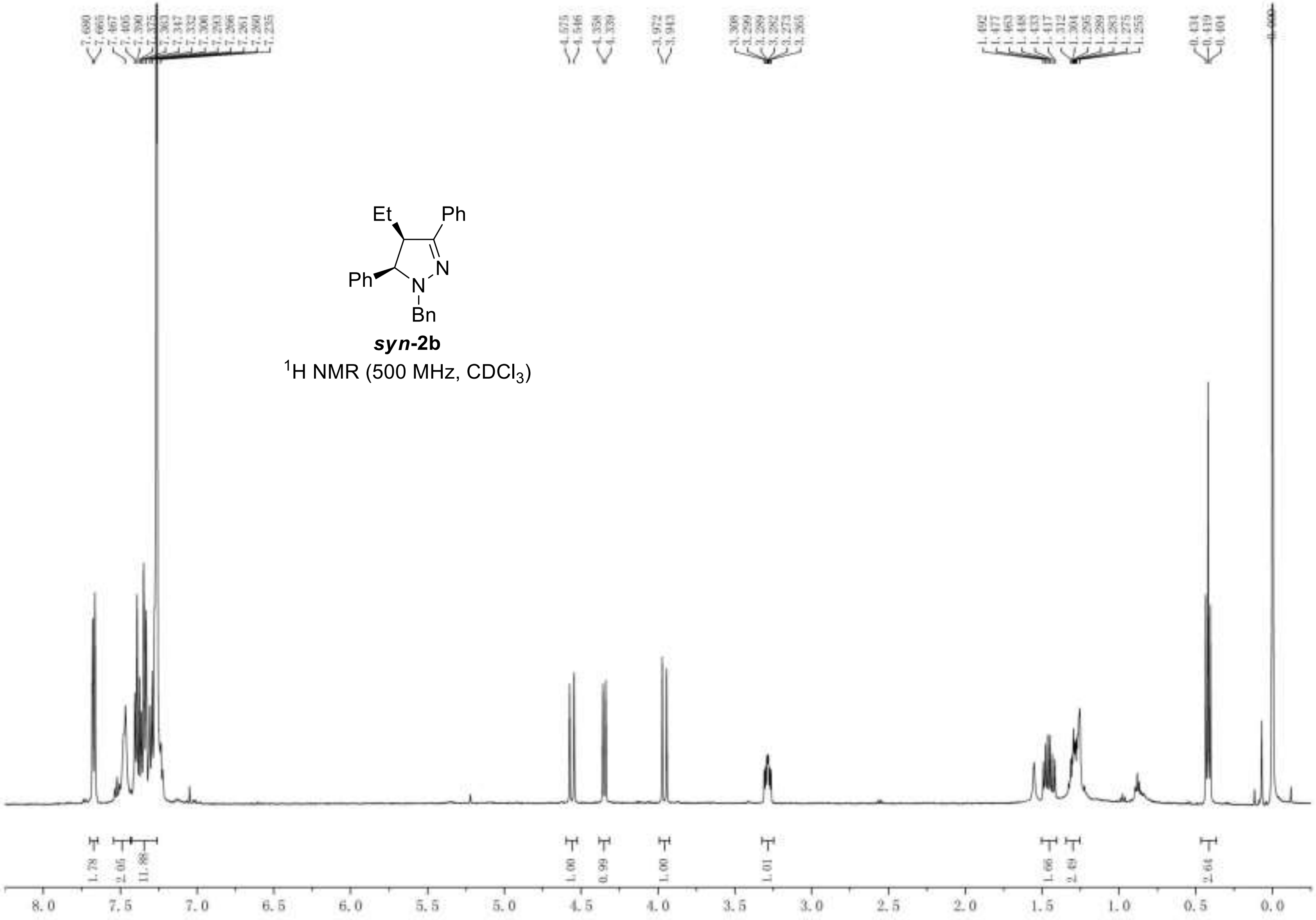
***anti*-2b**

^{1}H NMR (500 MHz, $CDCl_3$)



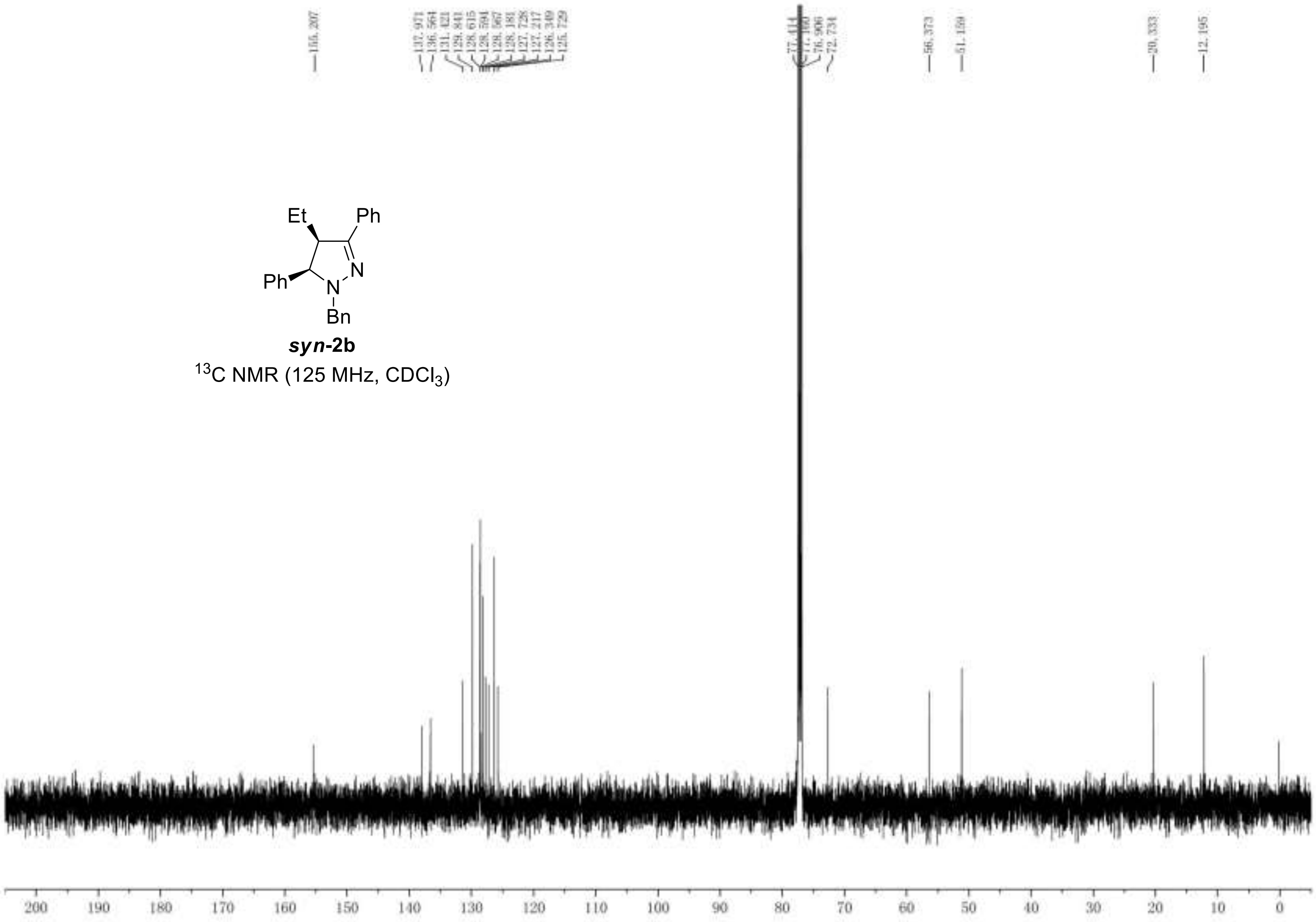
***anti*-2b**

^{13}C NMR (125 MHz, $CDCl_3$)



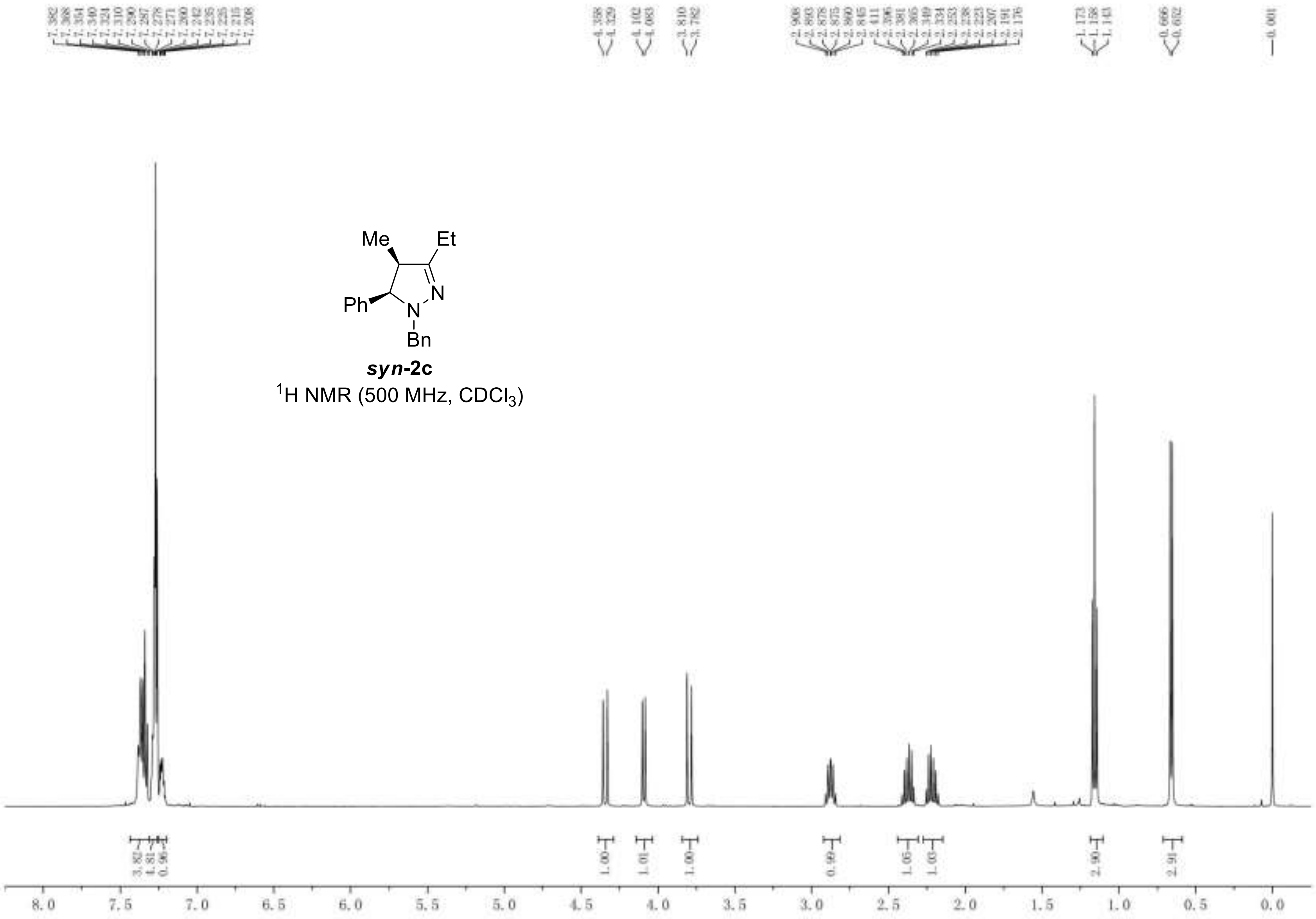
***syn*-2b**

^{1}H NMR (500 MHz, CDCl$_3$)



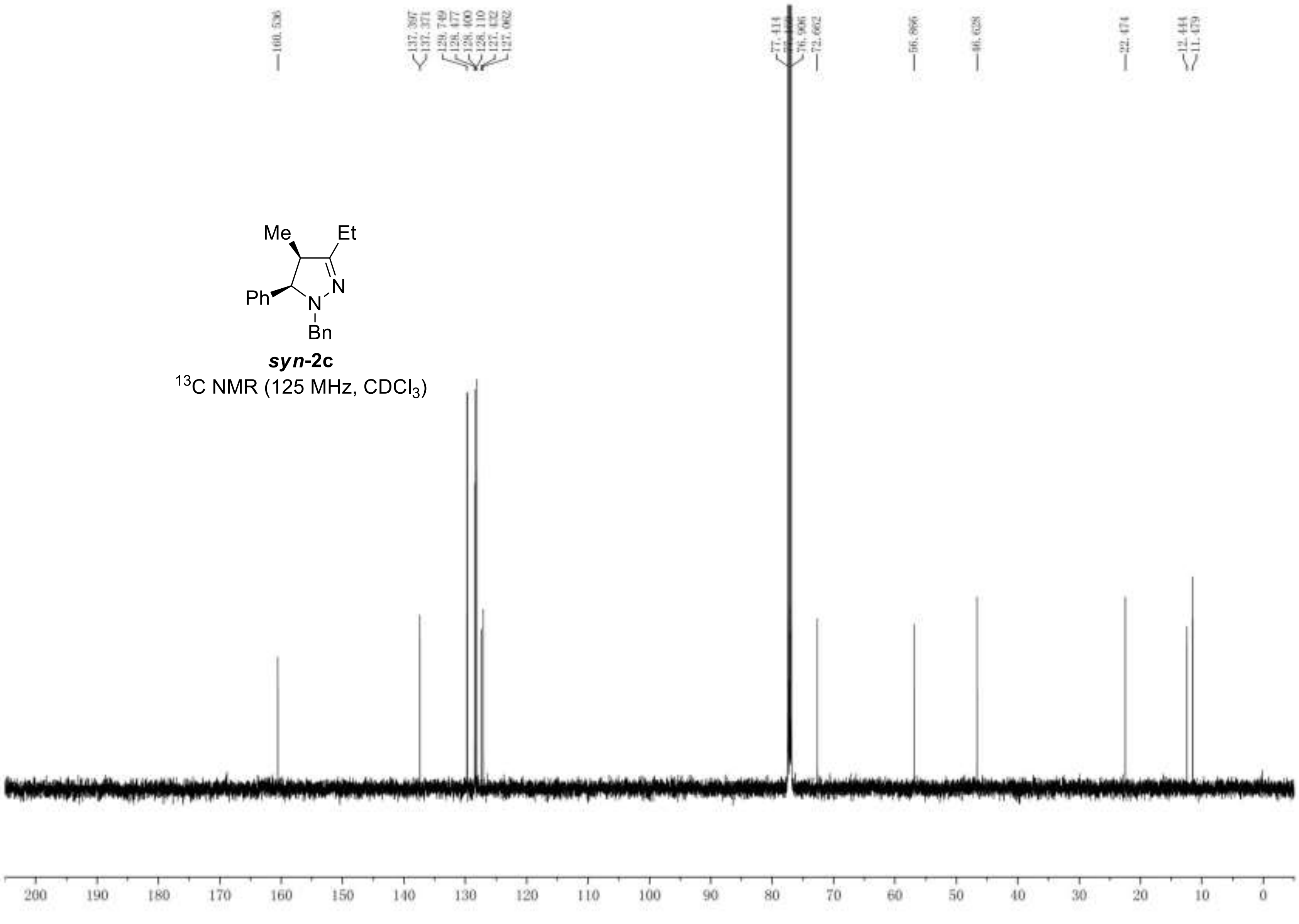
***syn*-2b**

^{13}C NMR (125 MHz, $CDCl_3$)



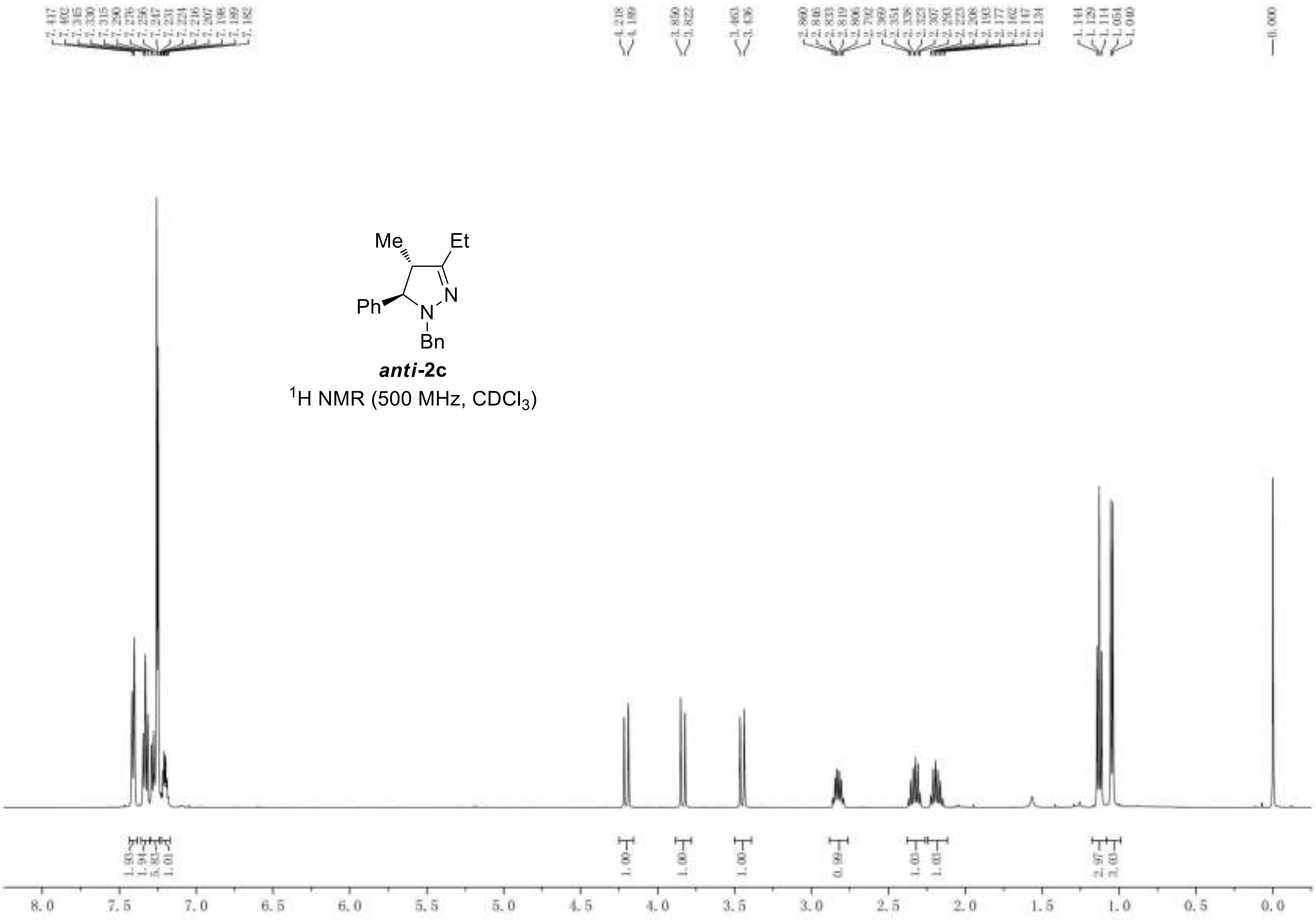
***syn*-2c**

^{1}H NMR (500 MHz, $CDCl_3$)



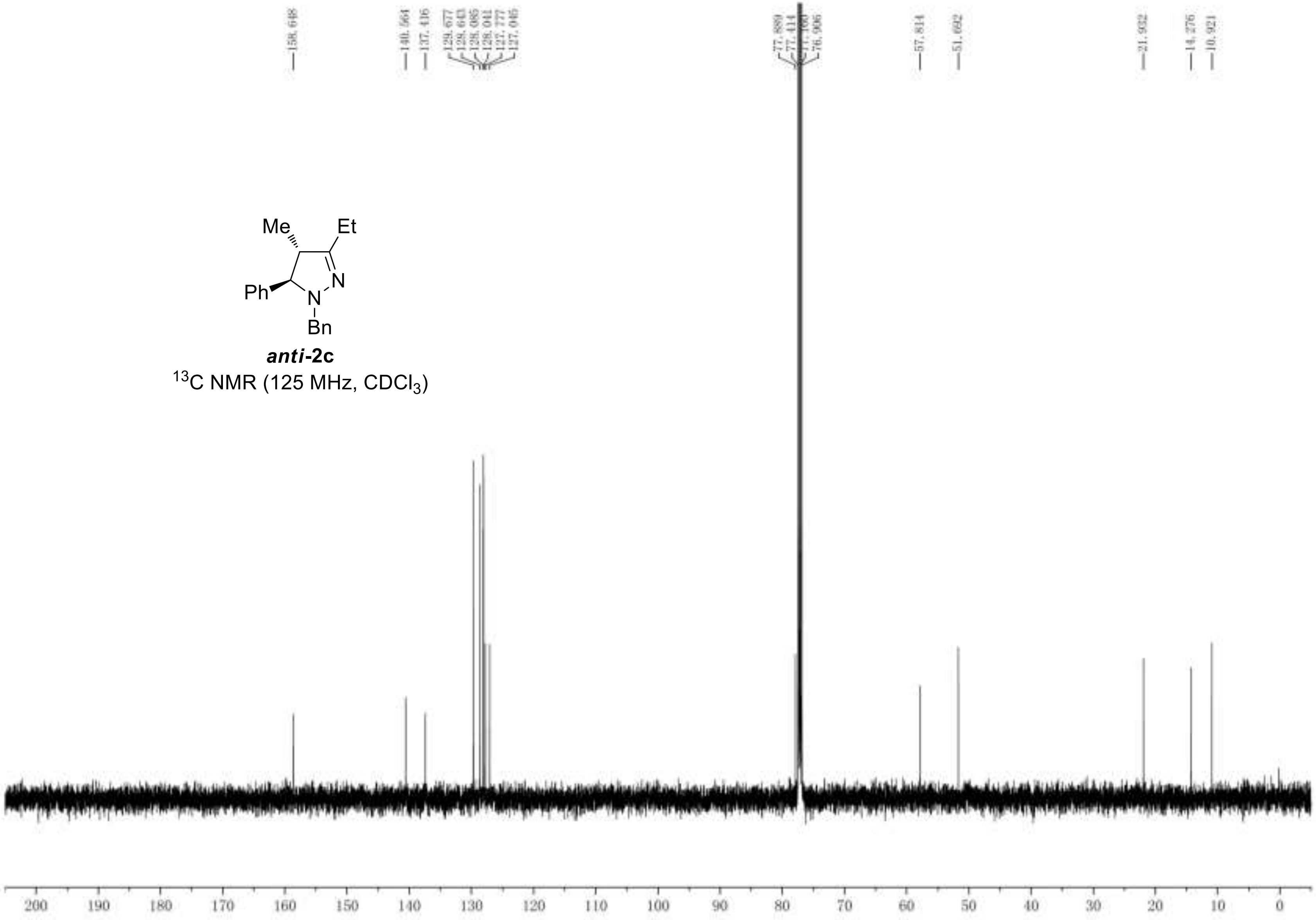
***syn*-2c**

^{13}C NMR (125 MHz, CDCl$_3$)



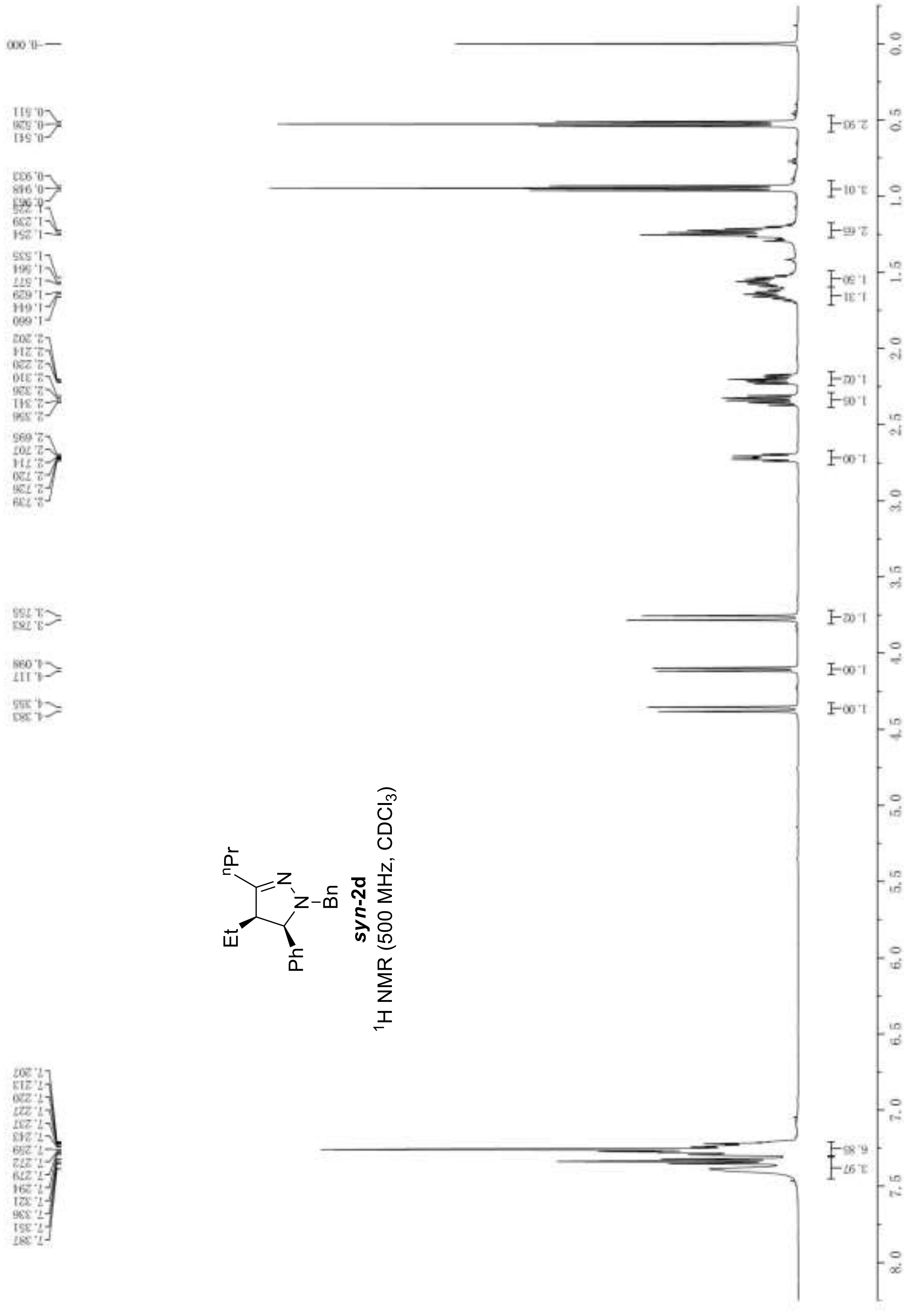
***anti*-2c**

^{1}H NMR (500 MHz, CDCl$_3$)



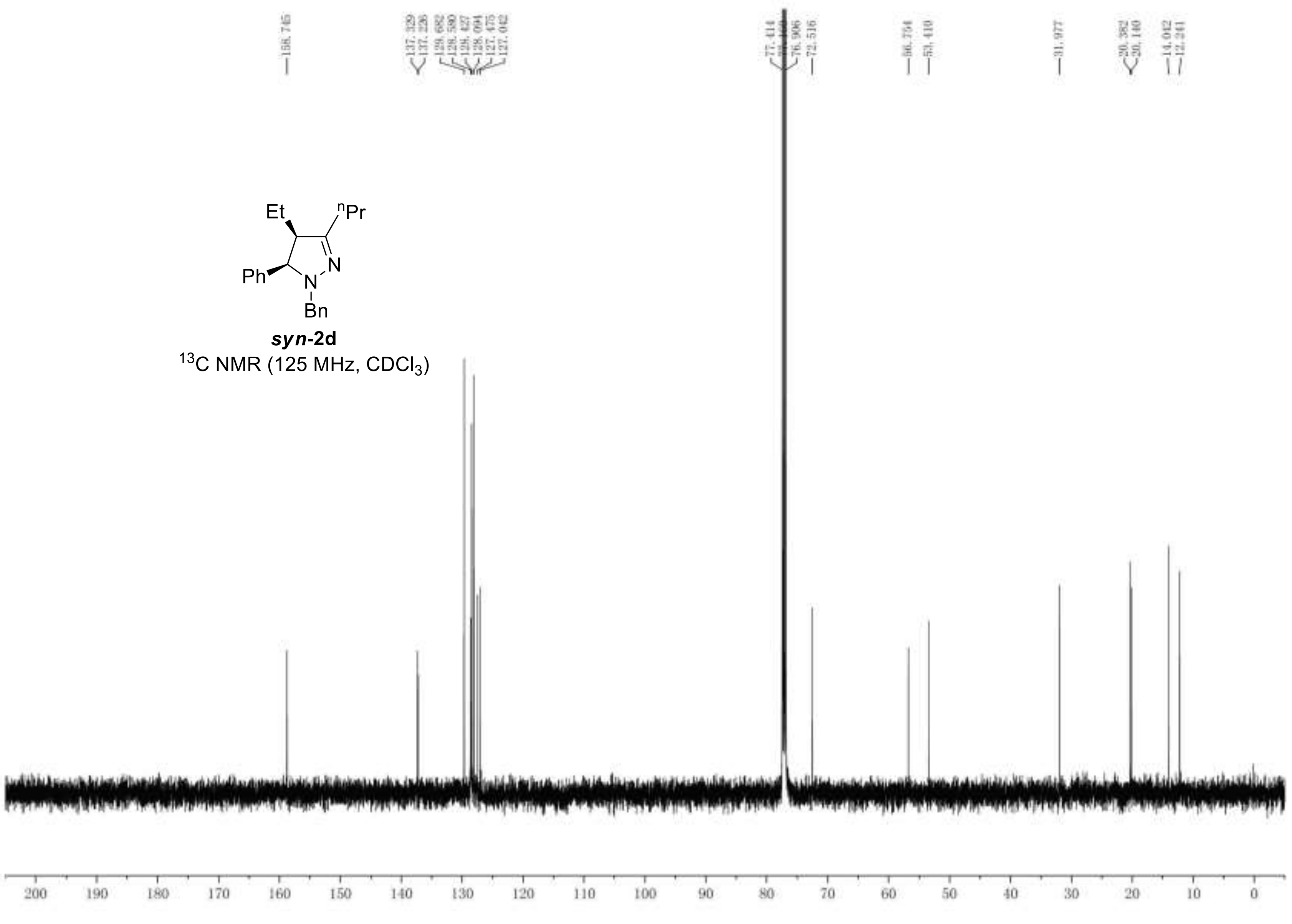
***anti*-2c**

^{13}C NMR (125 MHz, $CDCl_3$)



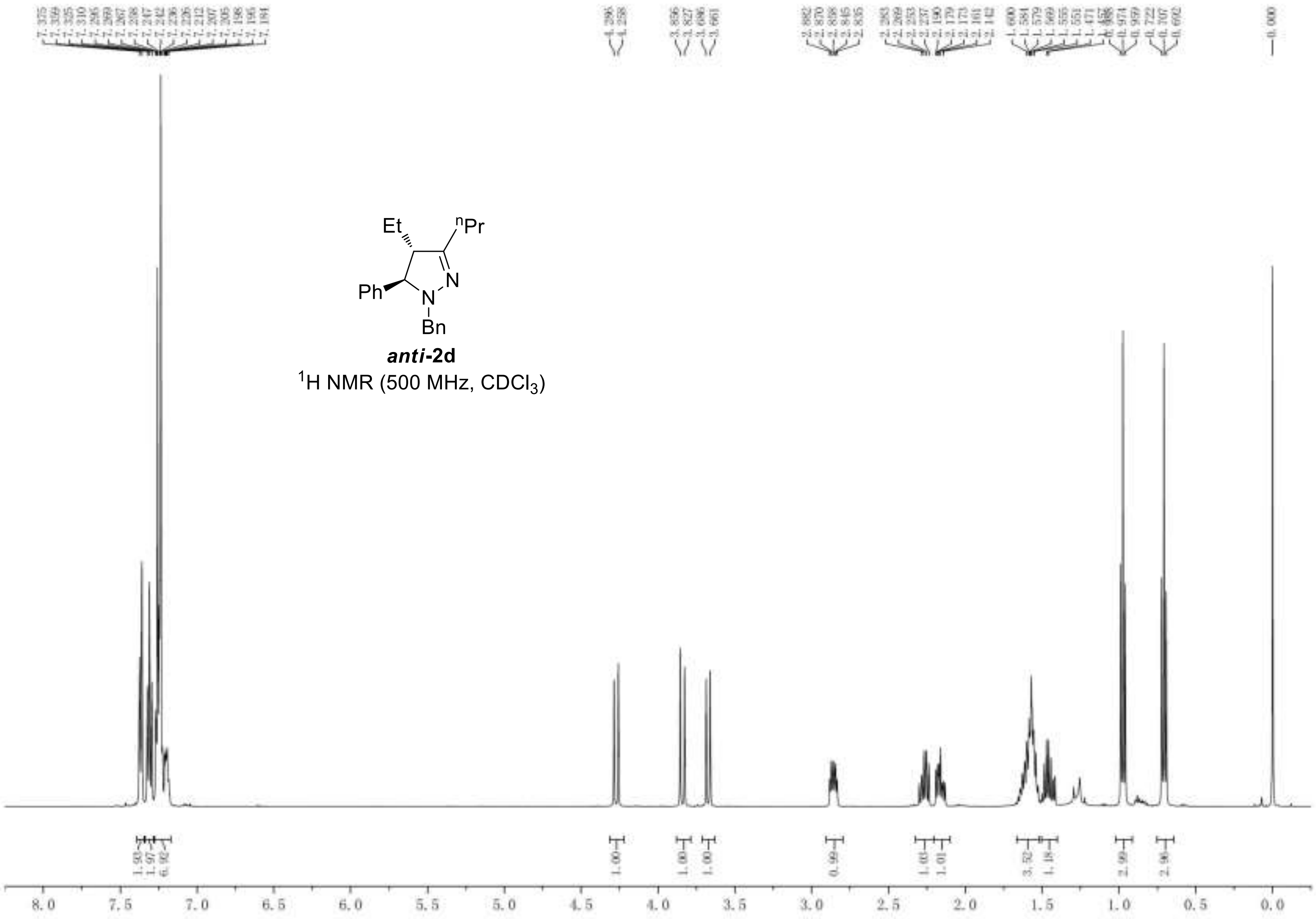
***syn*-2d**

^{1}H NMR (500 MHz, $CDCl_3$)



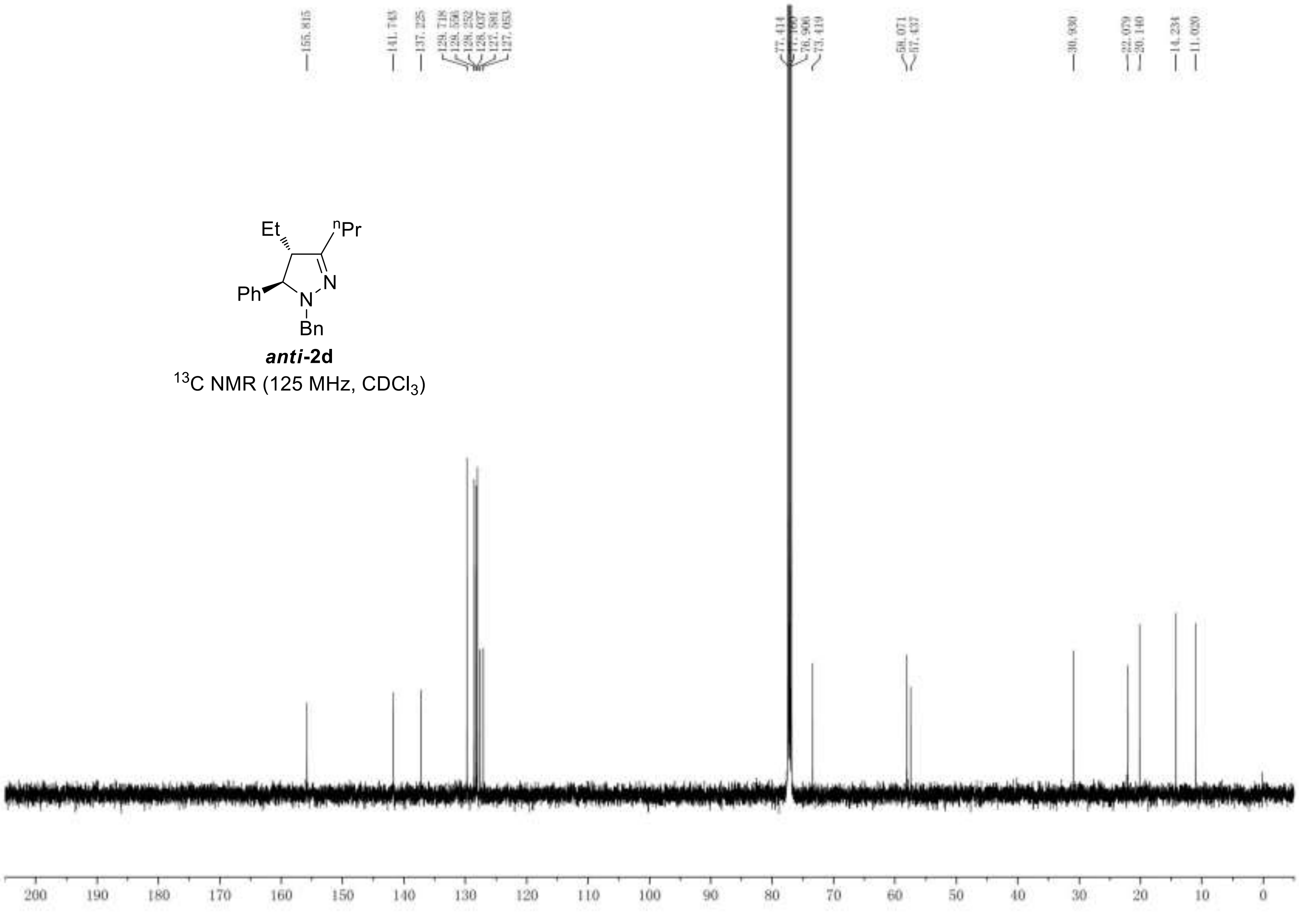
***syn*-2d**

^{13}C NMR (125 MHz, CDCl$_3$)



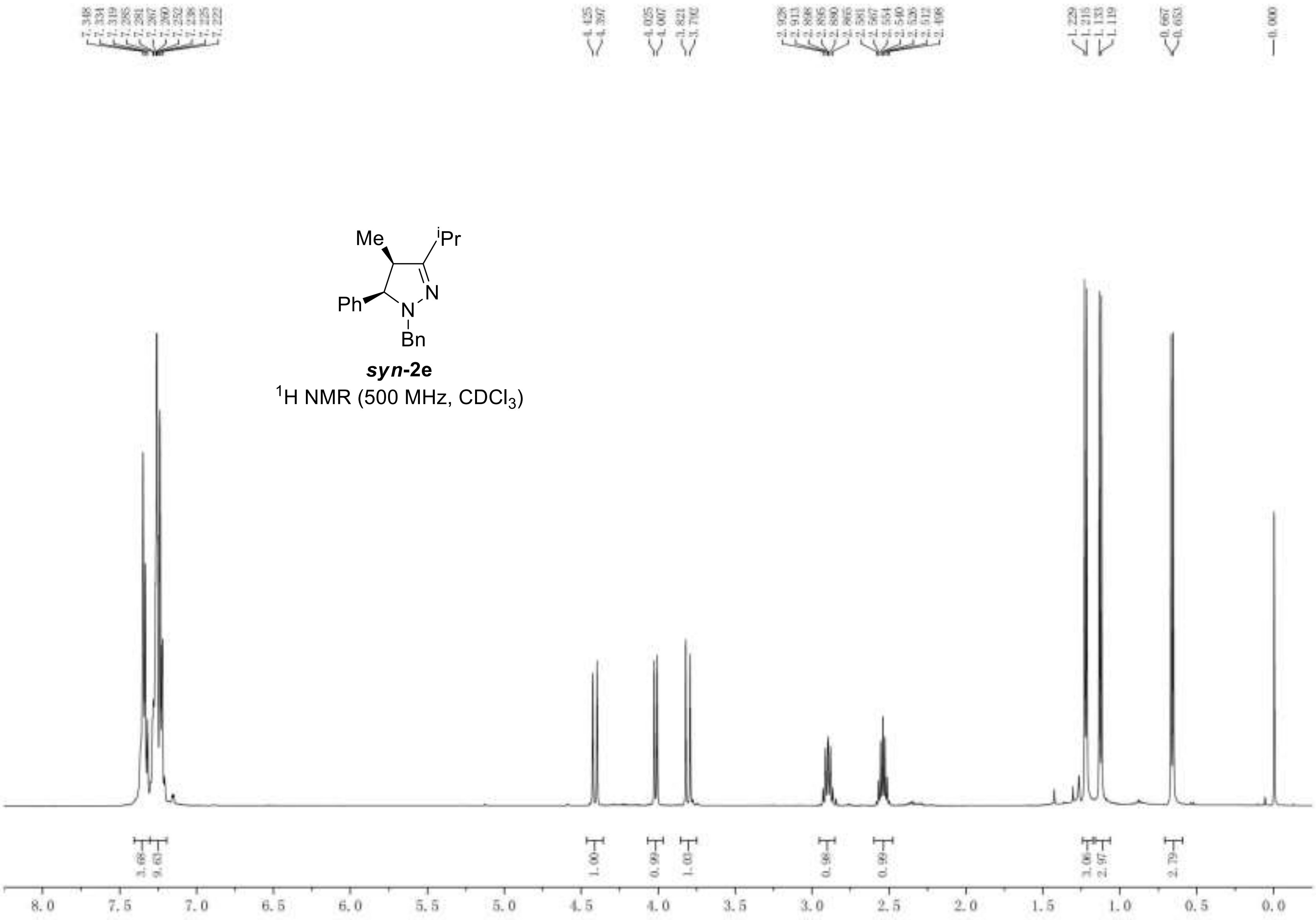
***anti*-2d**

^{1}H NMR (500 MHz, $CDCl_3$)



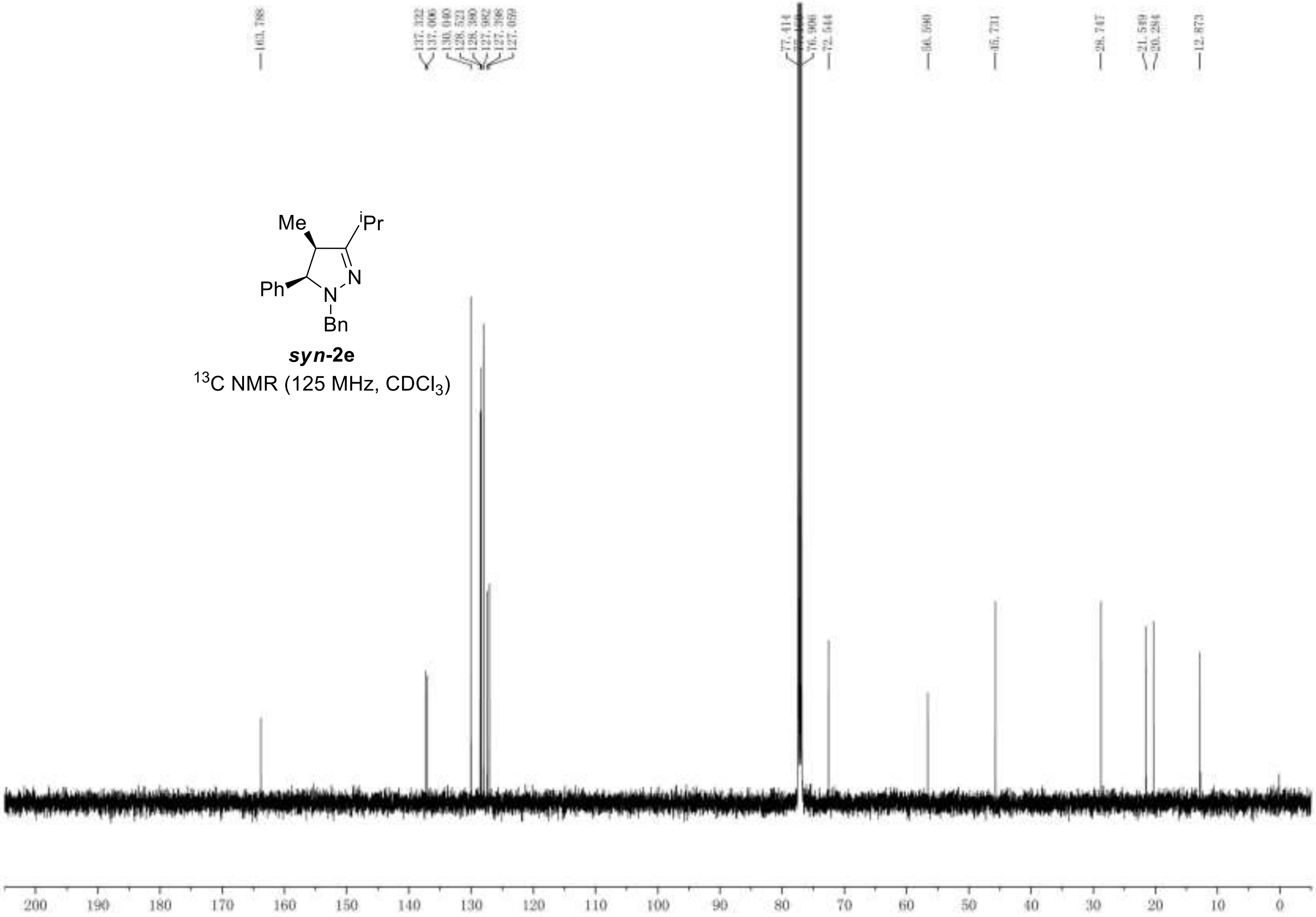
***anti*-2d**

^{13}C NMR (125 MHz, CDCl$_3$)



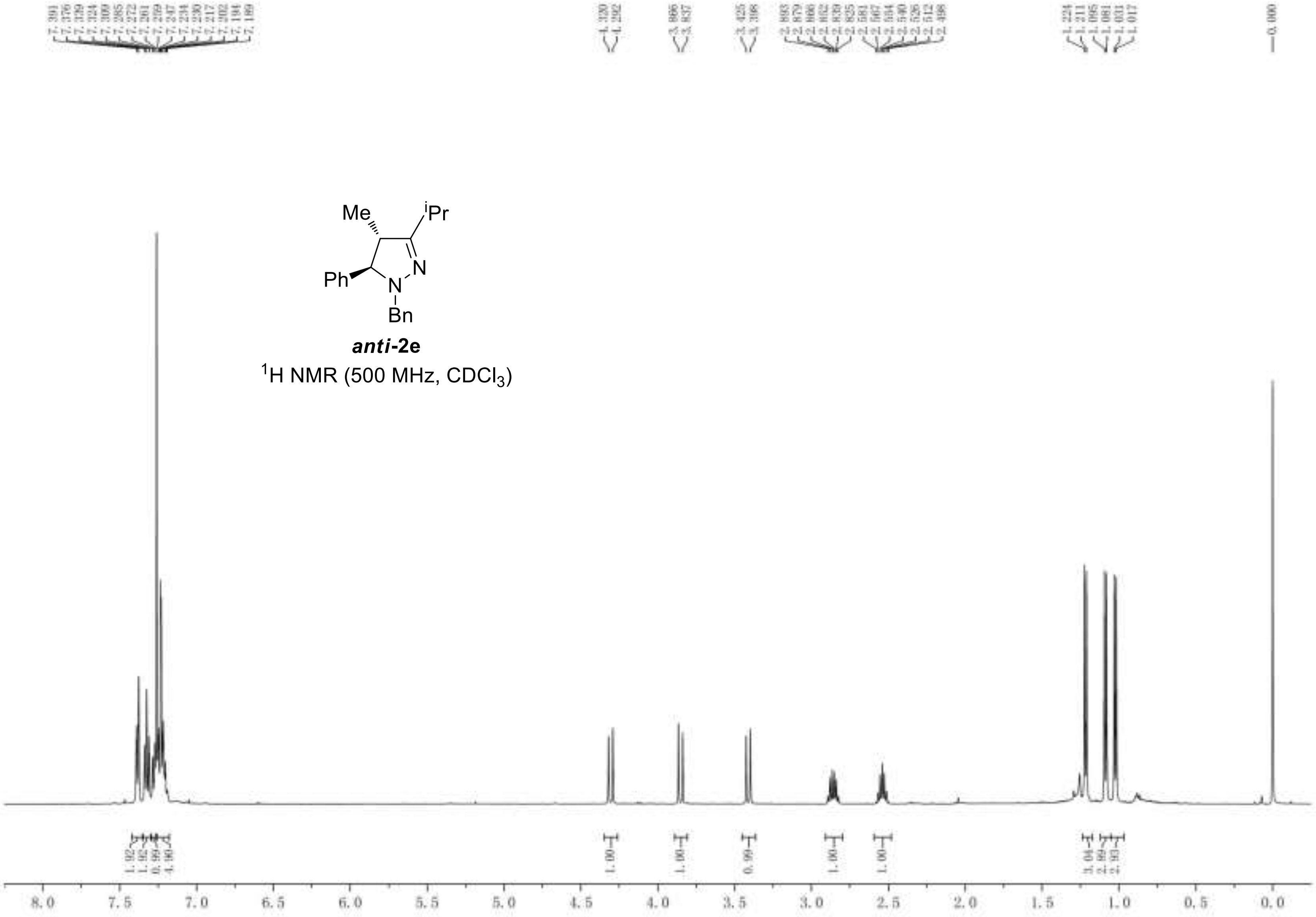
***syn*-2e**

^{1}H NMR (500 MHz, CDCl$_3$)



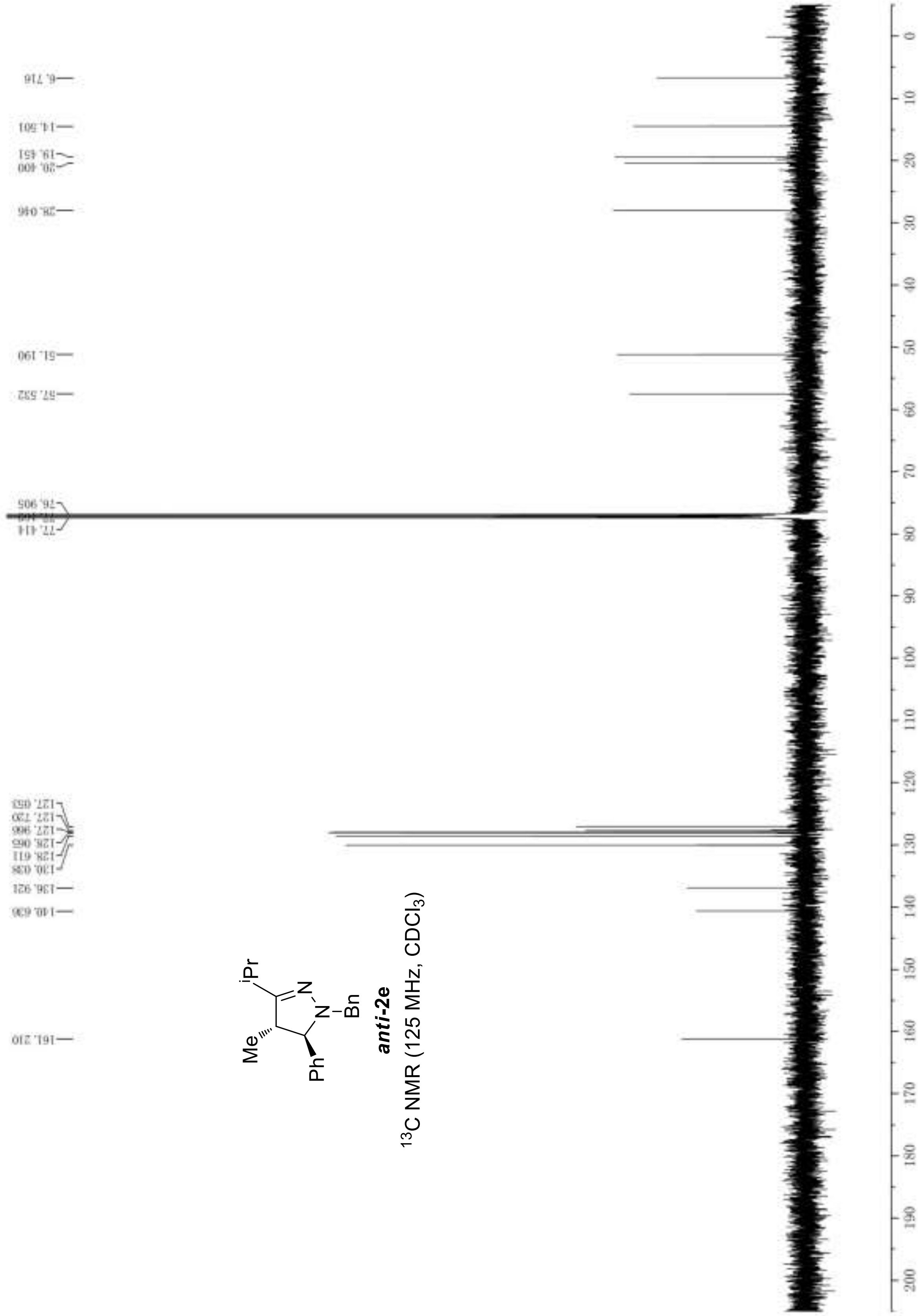
***syn*-2e**

^{13}C NMR (125 MHz, $CDCl_3$)



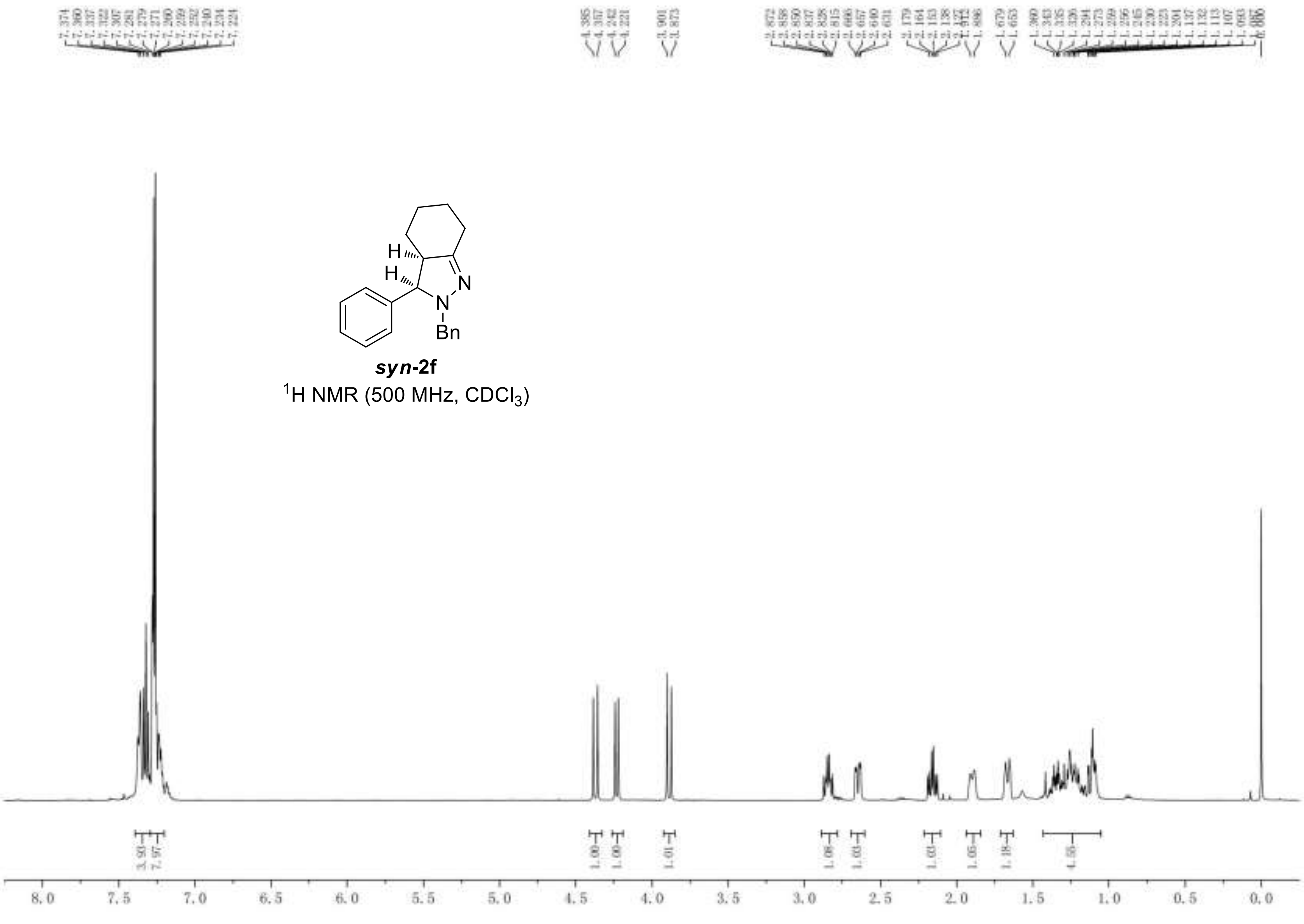
***anti*-2e**

^{1}H NMR (500 MHz, CDCl$_3$)



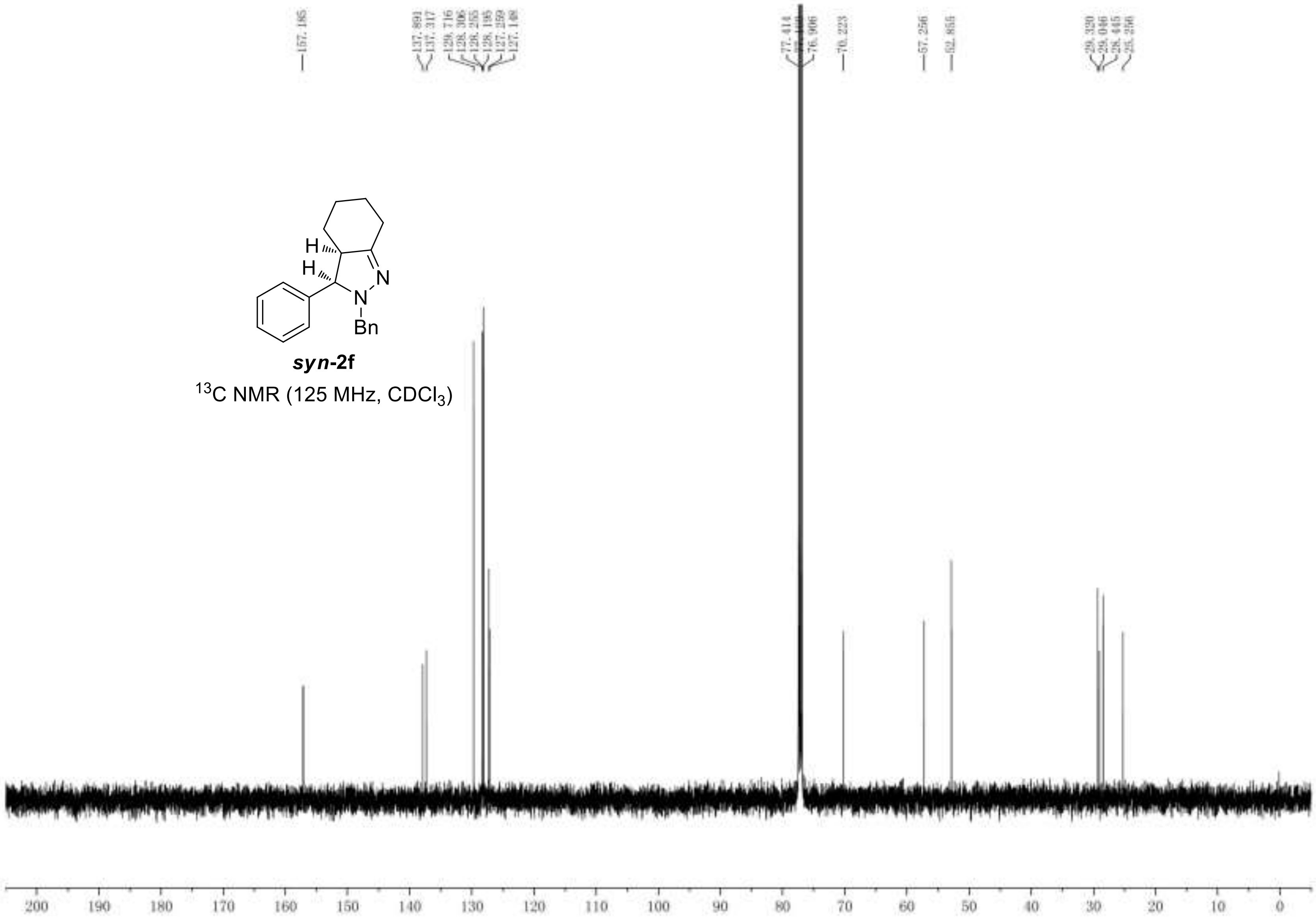
***anti*-2e**

^{13}C NMR (125 MHz, CDCl$_3$)



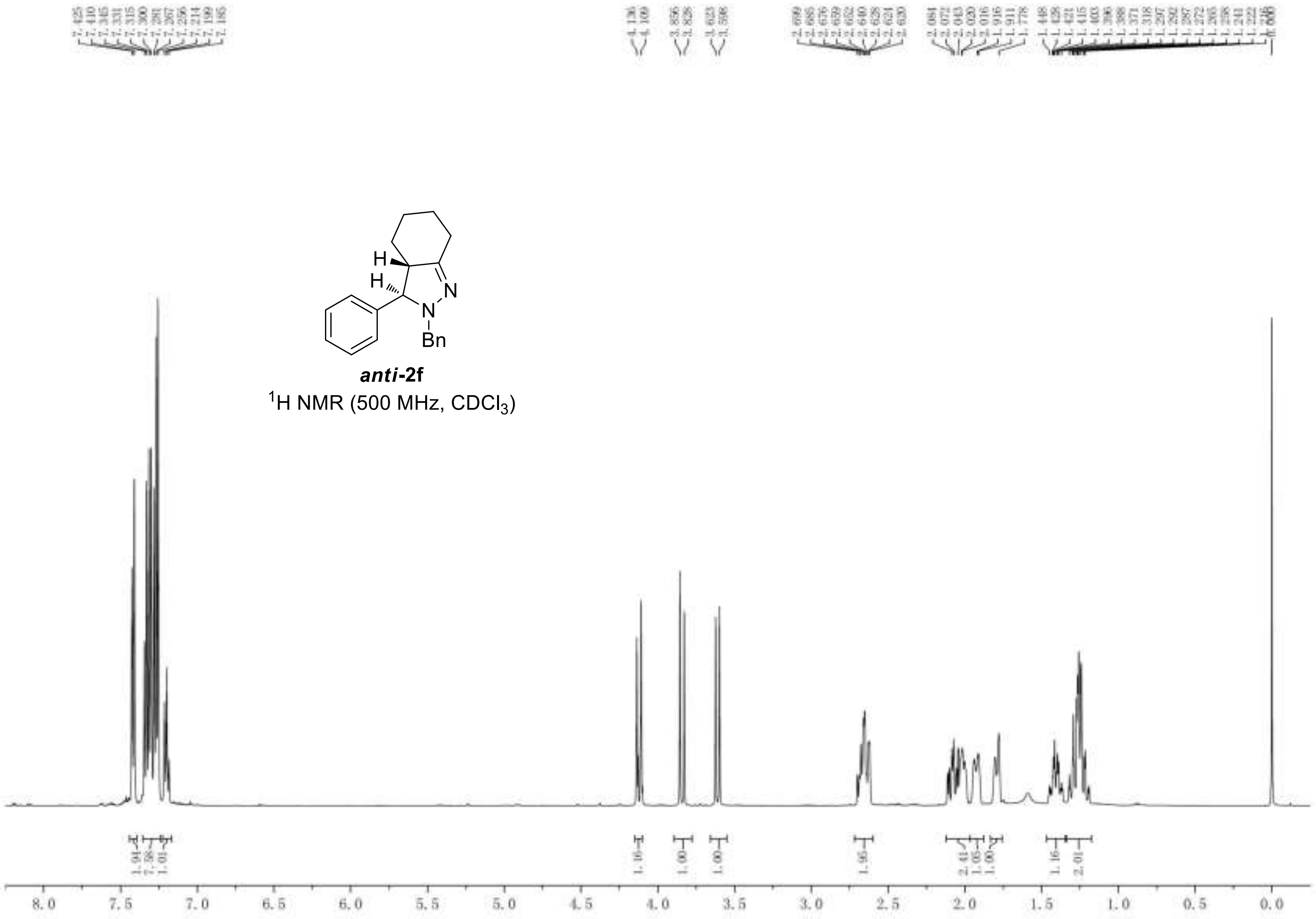
***syn*-2f**

^1H NMR (500 MHz, $CDCl_3$)



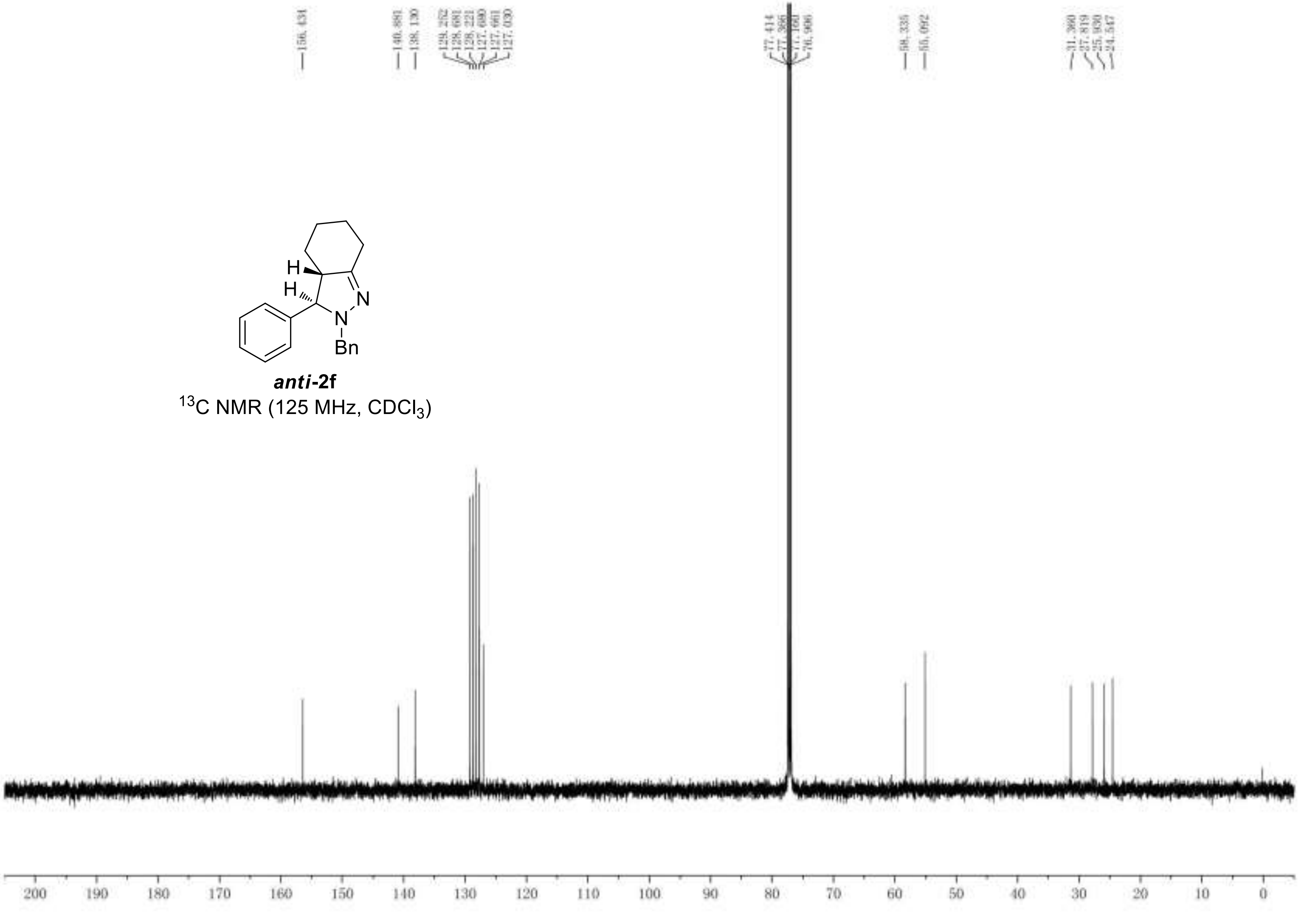
syn-2f

^{13}C NMR (125 MHz, CDCl$_3$)



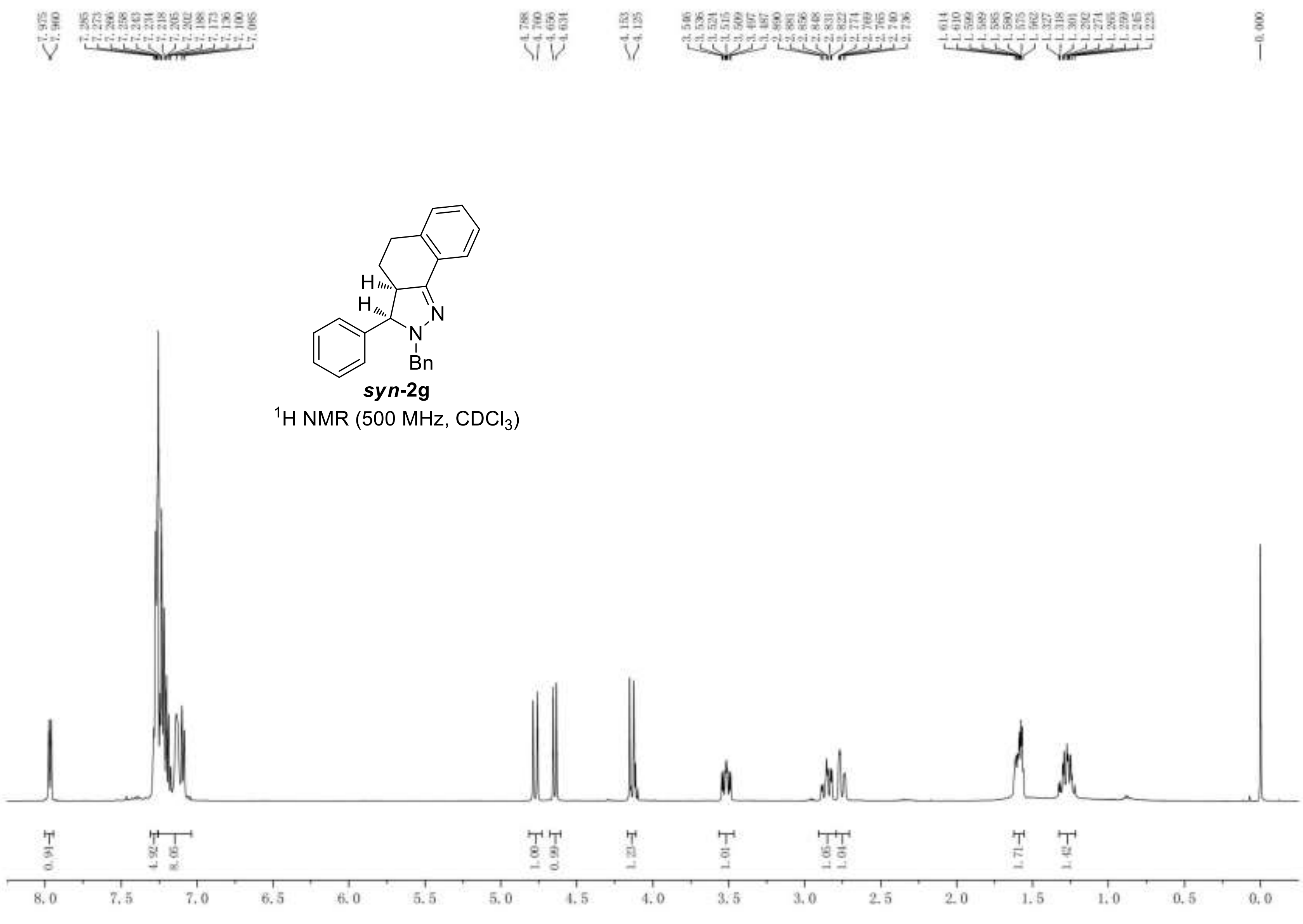
***anti*-2f**

^{1}H NMR (500 MHz, CDCl$_3$)



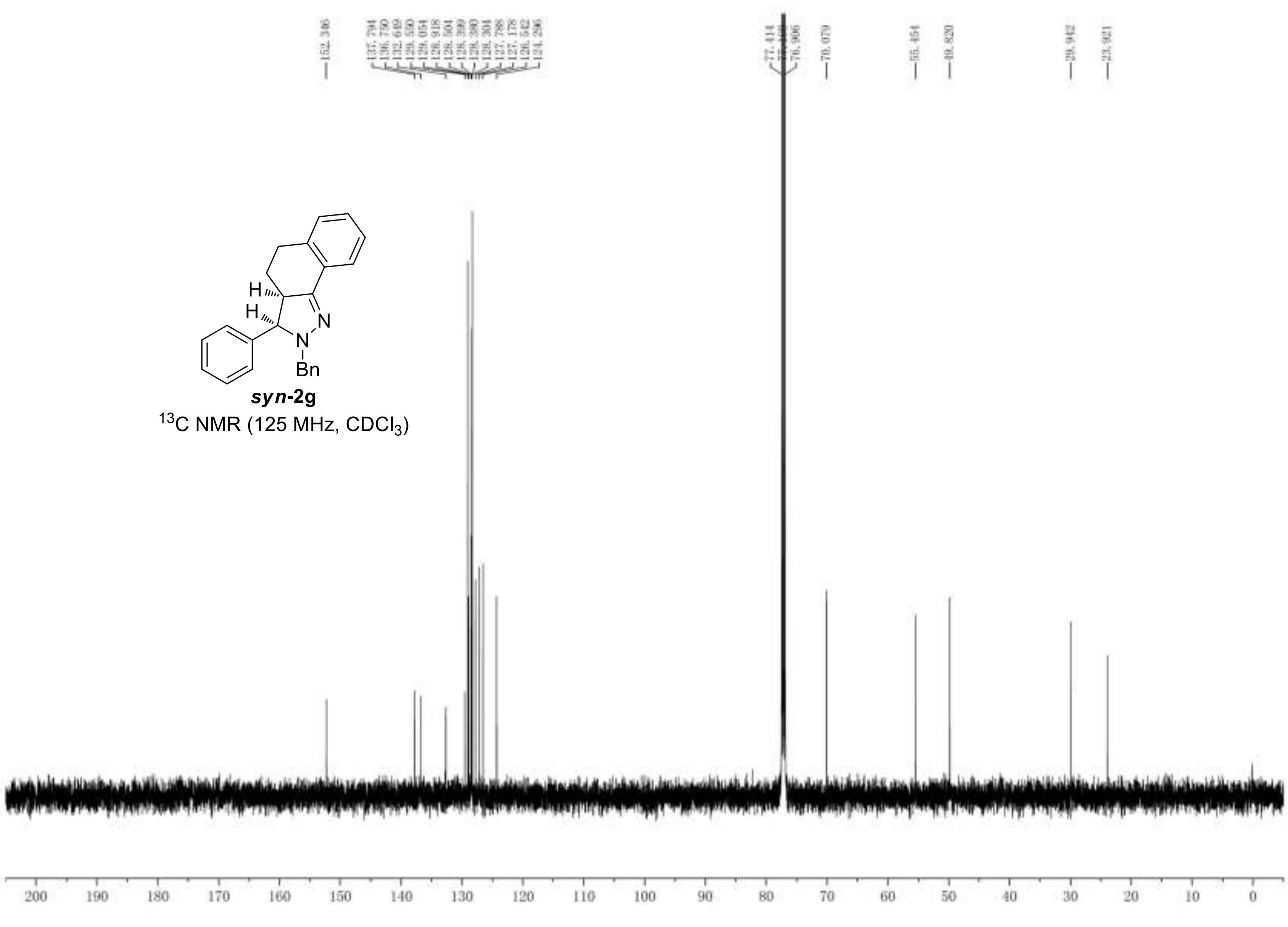
***anti*-2f**

^{13}C NMR (125 MHz, CDCl$_3$)



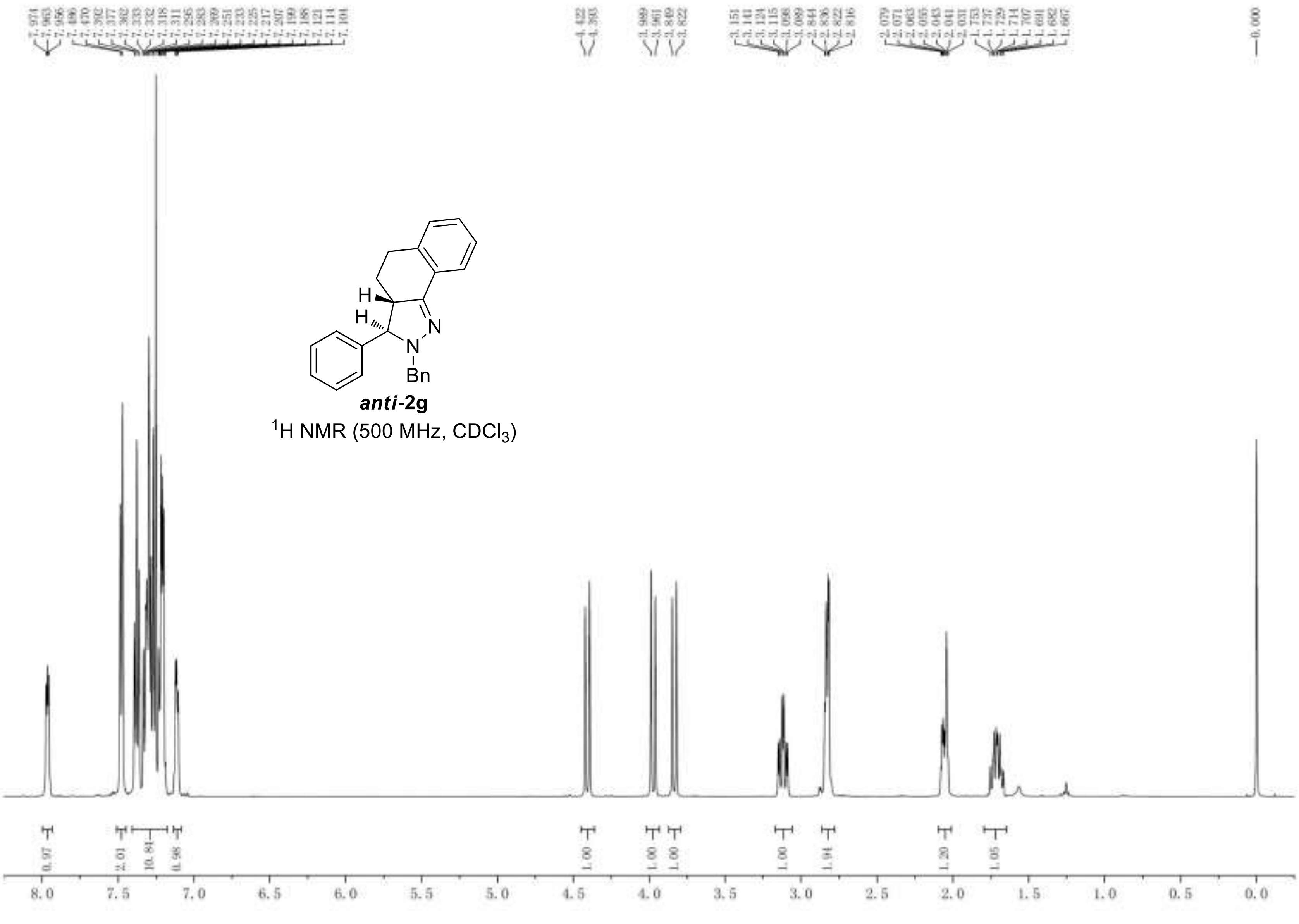
***syn*-2g**

^{1}H NMR (500 MHz, $CDCl_3$)



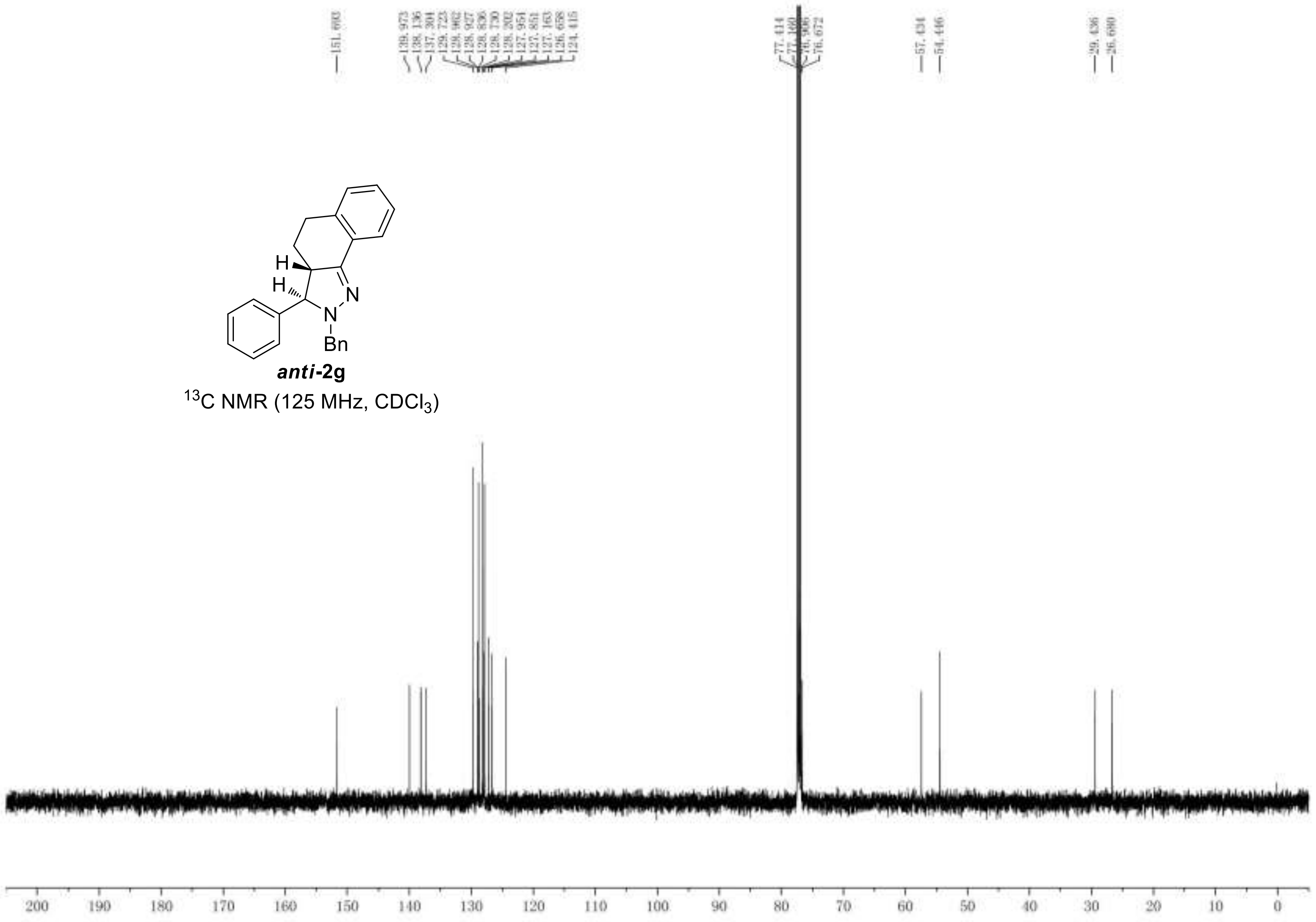
***syn*-2g**

^{13}C NMR (125 MHz, $CDCl_3$)



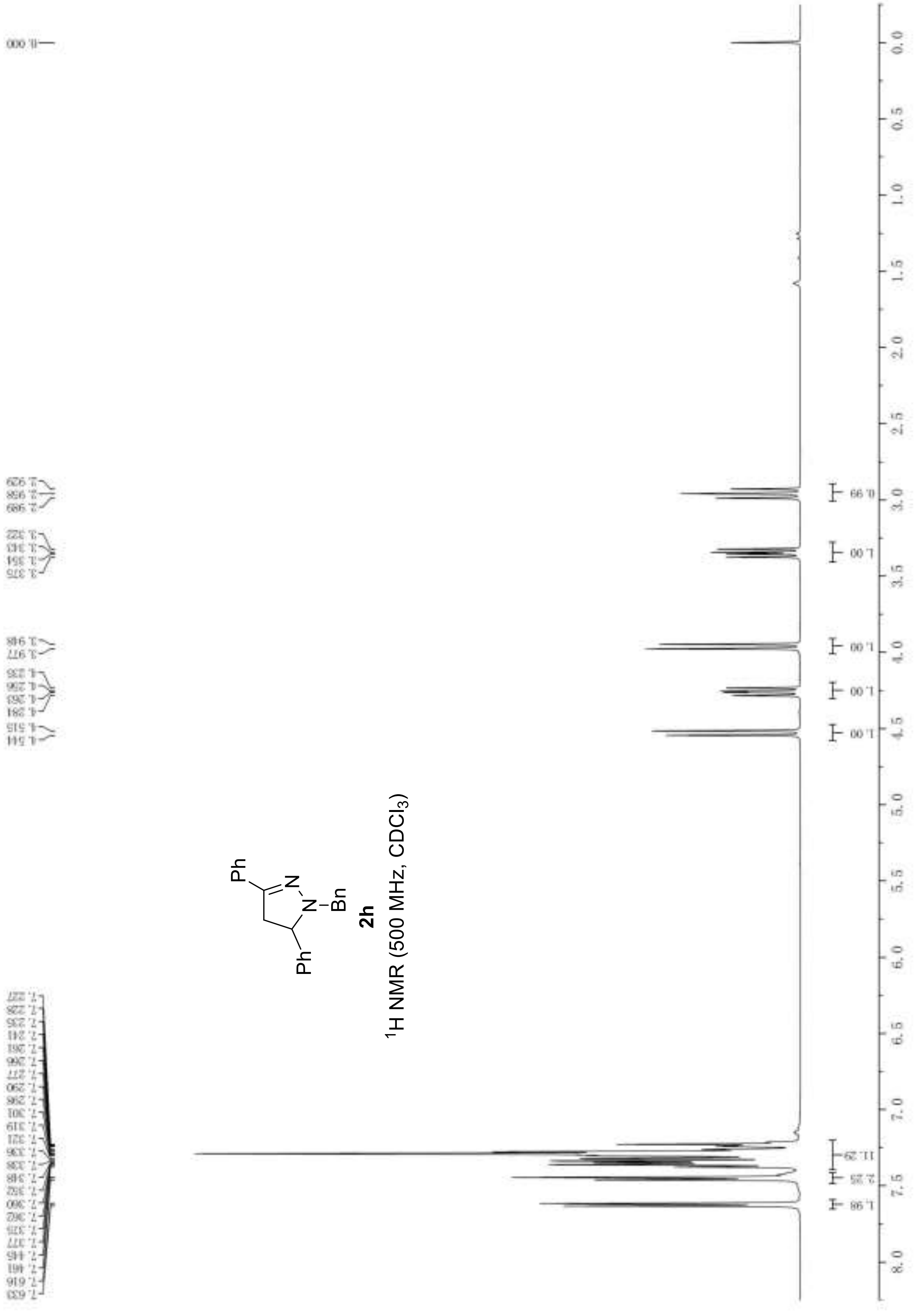
***anti*-2g**

^{1}H NMR (500 MHz, $CDCl_3$)



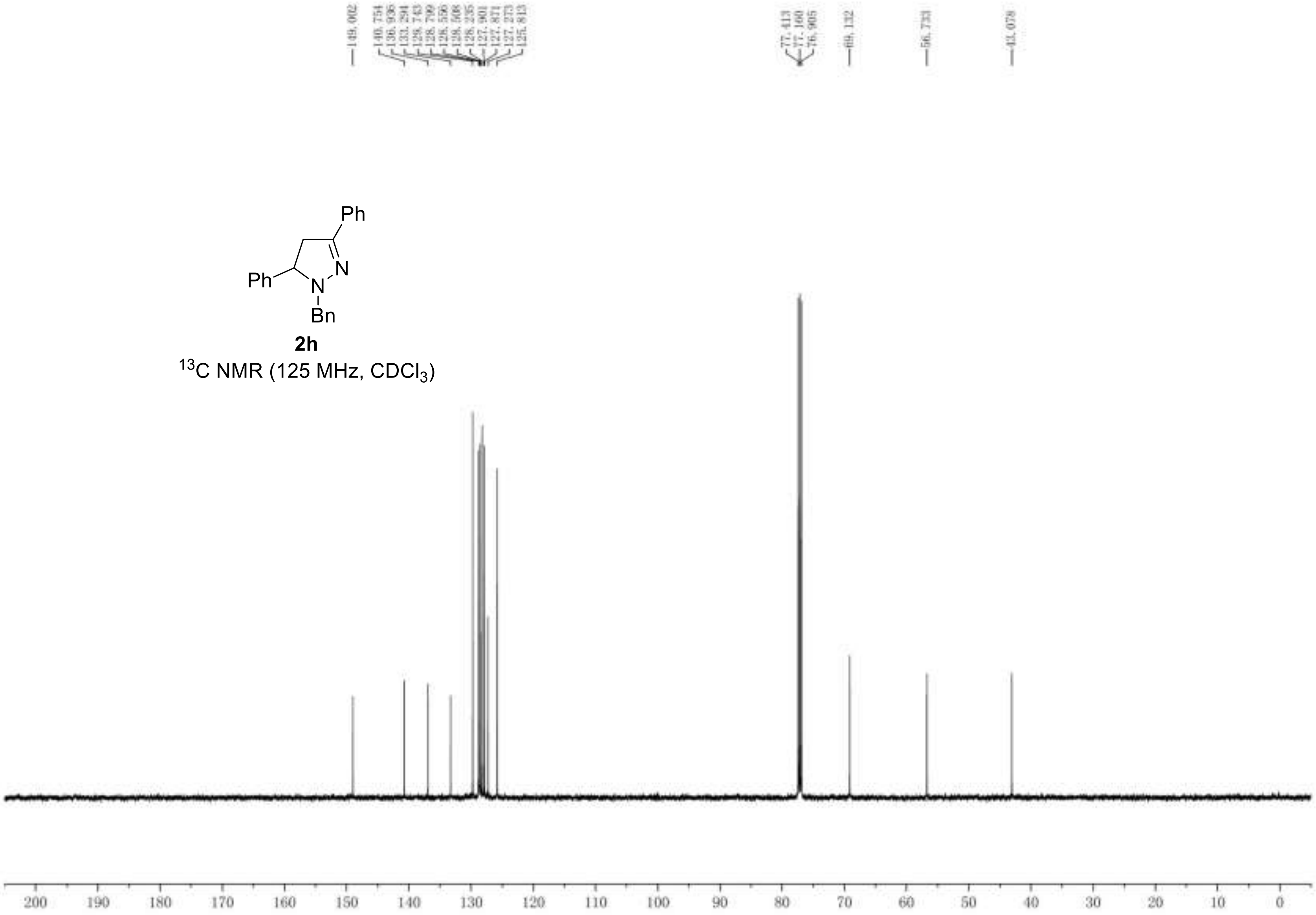
***anti*-2g**

^{13}C NMR (125 MHz, CDCl$_3$)



2h

^{1}H NMR (500 MHz, $CDCl_3$)

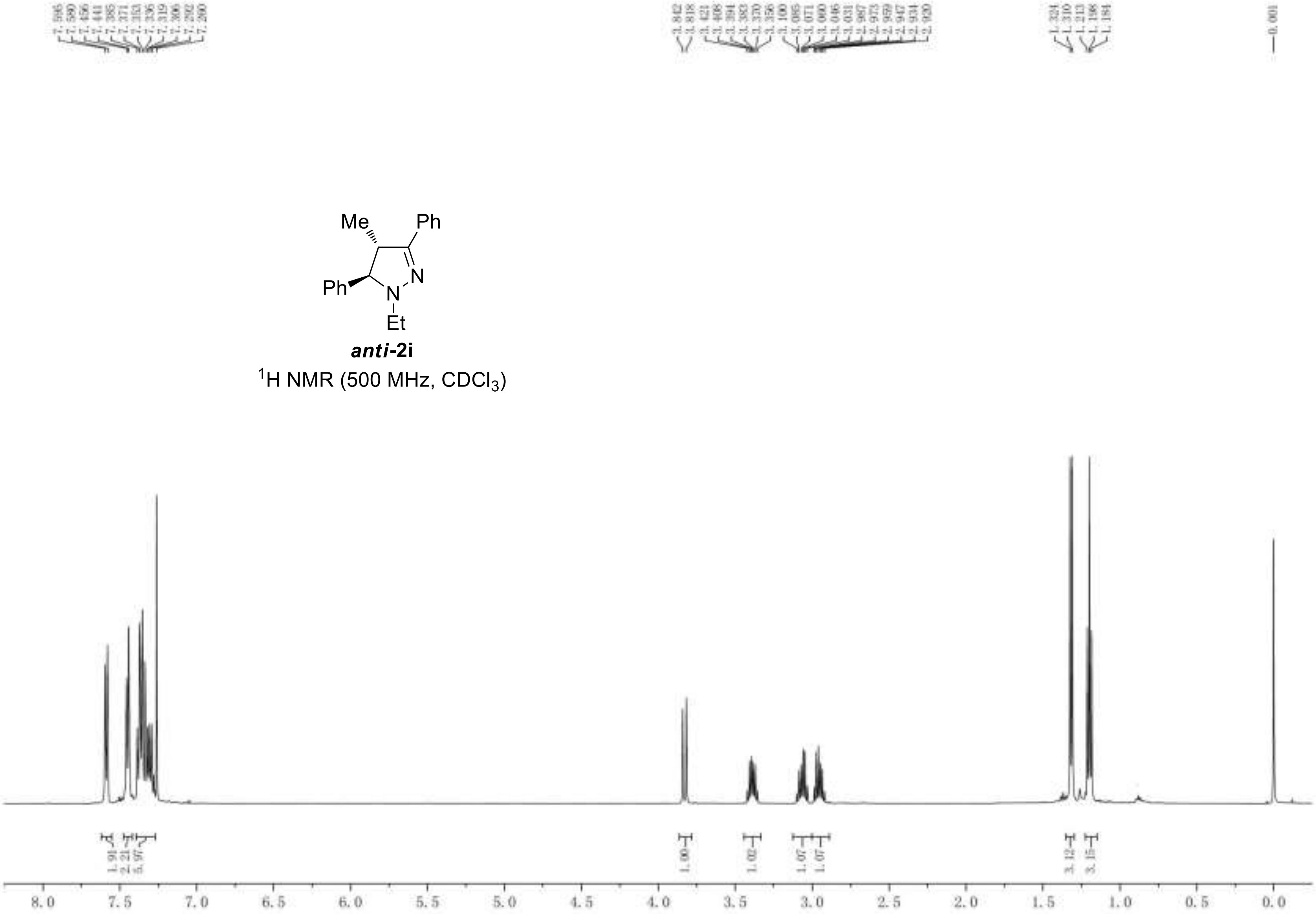


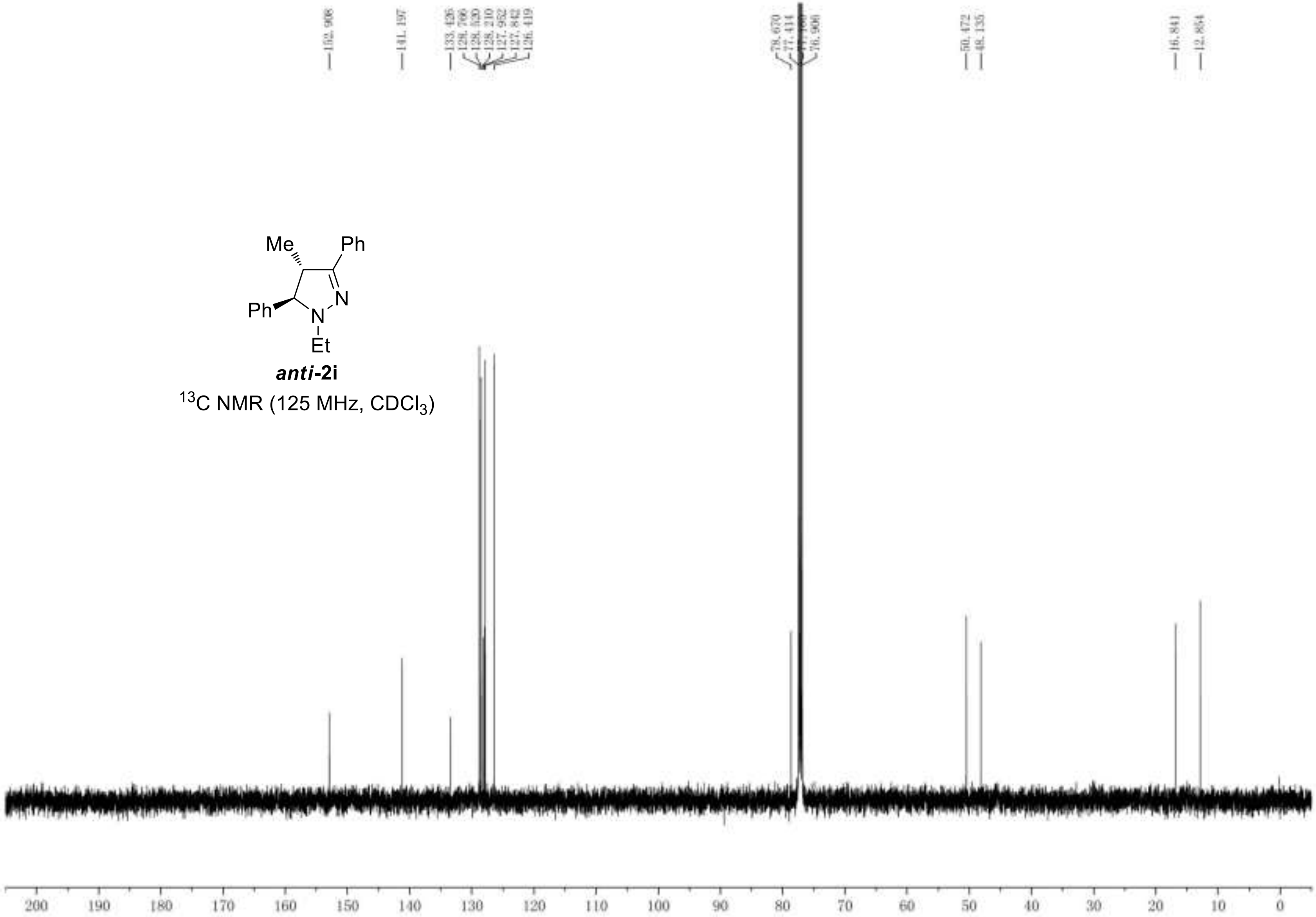
2h

^{13}C NMR (125 MHz, CDCl$_3$)

***anti*-2i**

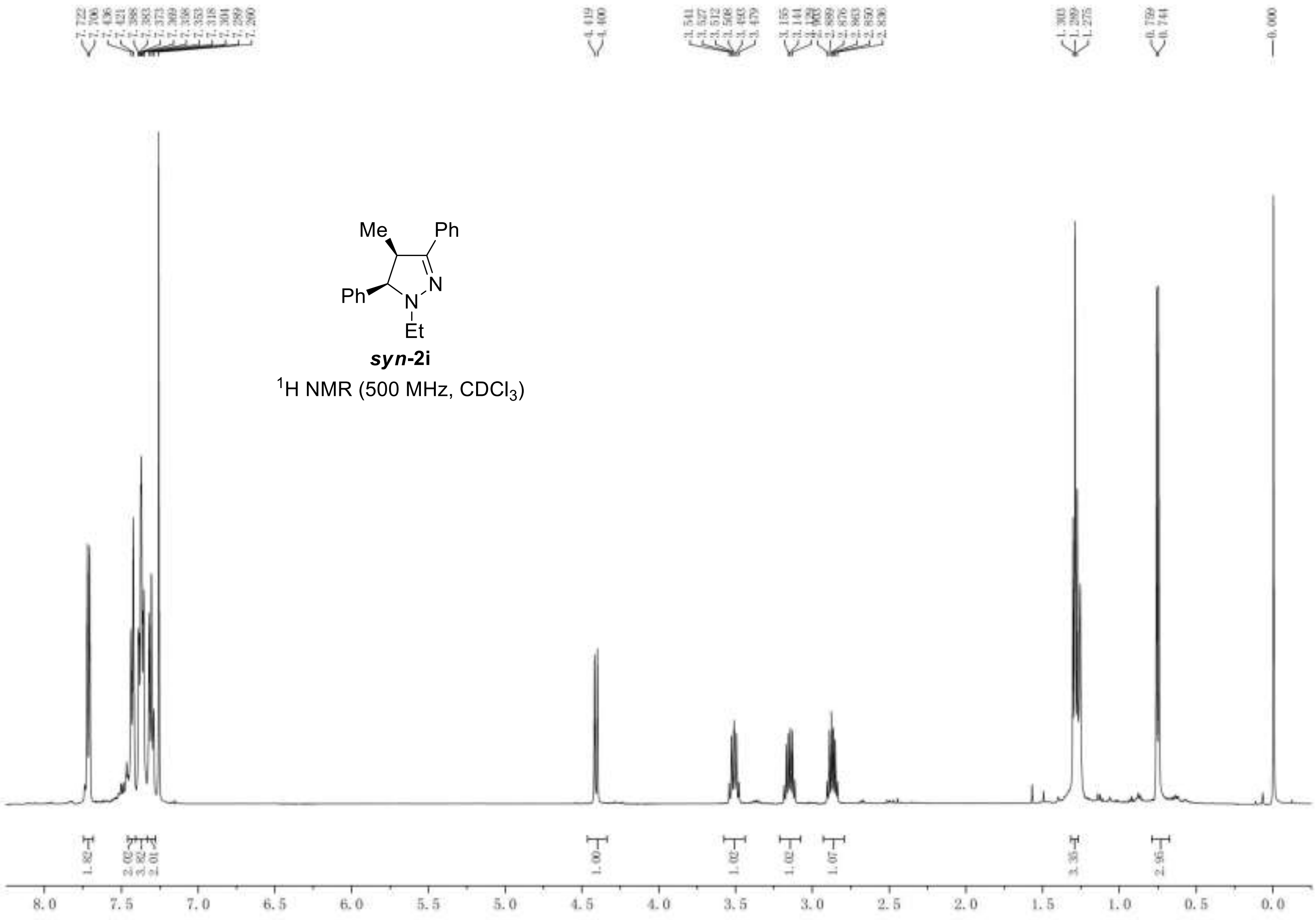
^{1}H NMR (500 MHz, $CDCl_3$)





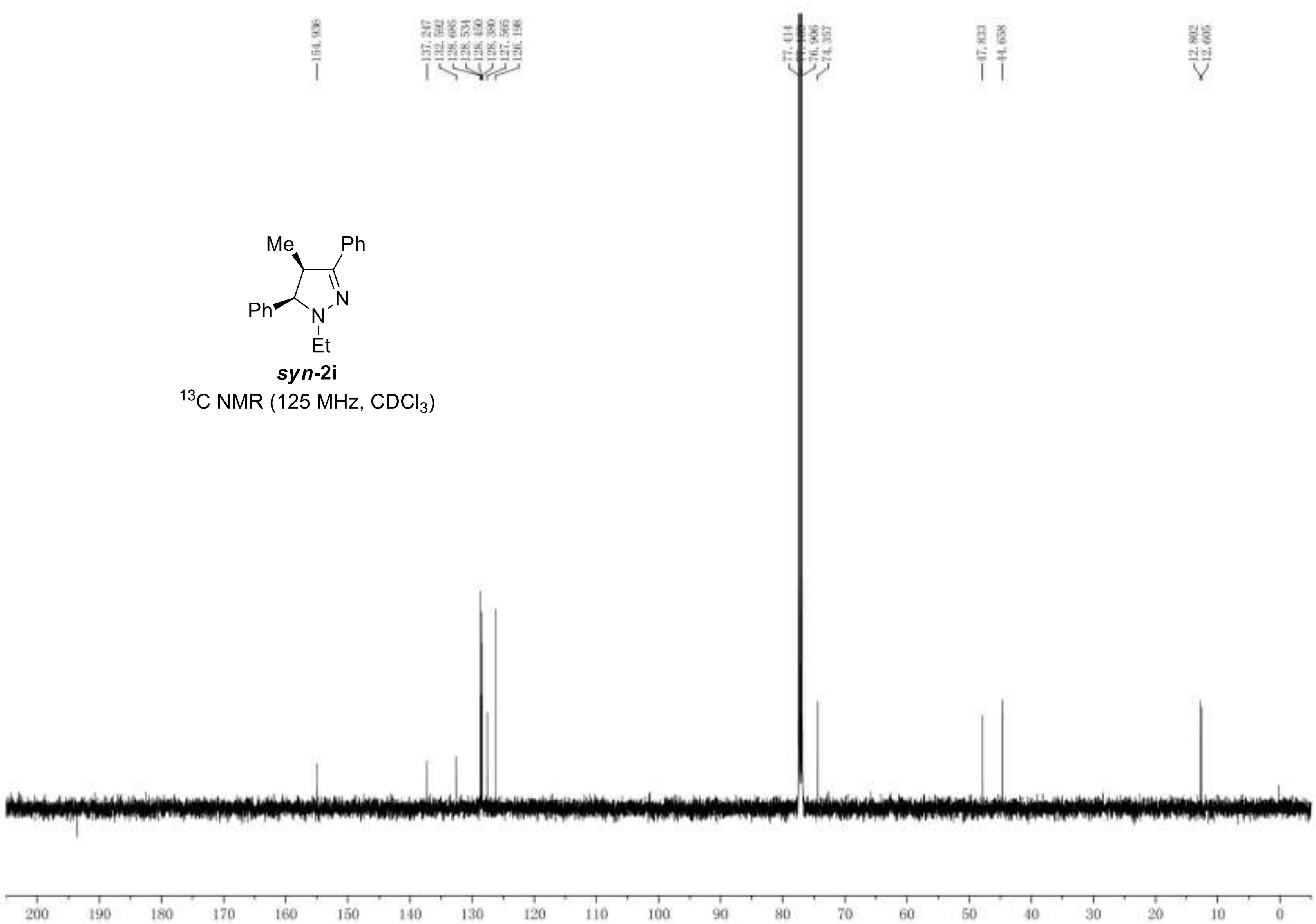
***anti*-2i**

^{13}C NMR (125 MHz, CDCl$_3$)



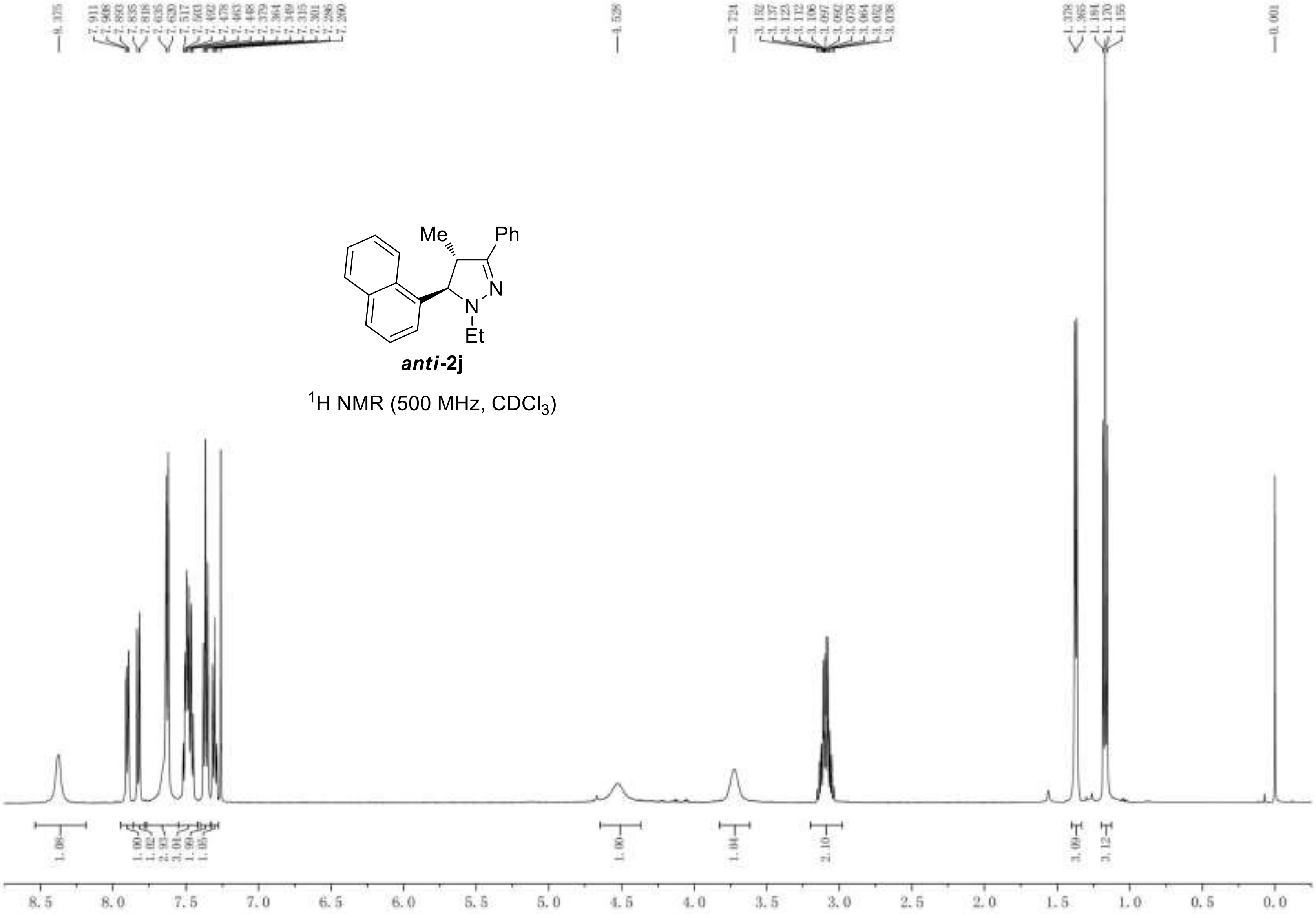
***syn*-2i**

^{1}H NMR (500 MHz, $CDCl_3$)



***syn*-2i**

^{13}C NMR (125 MHz, $CDCl_3$)



***anti*-2j**

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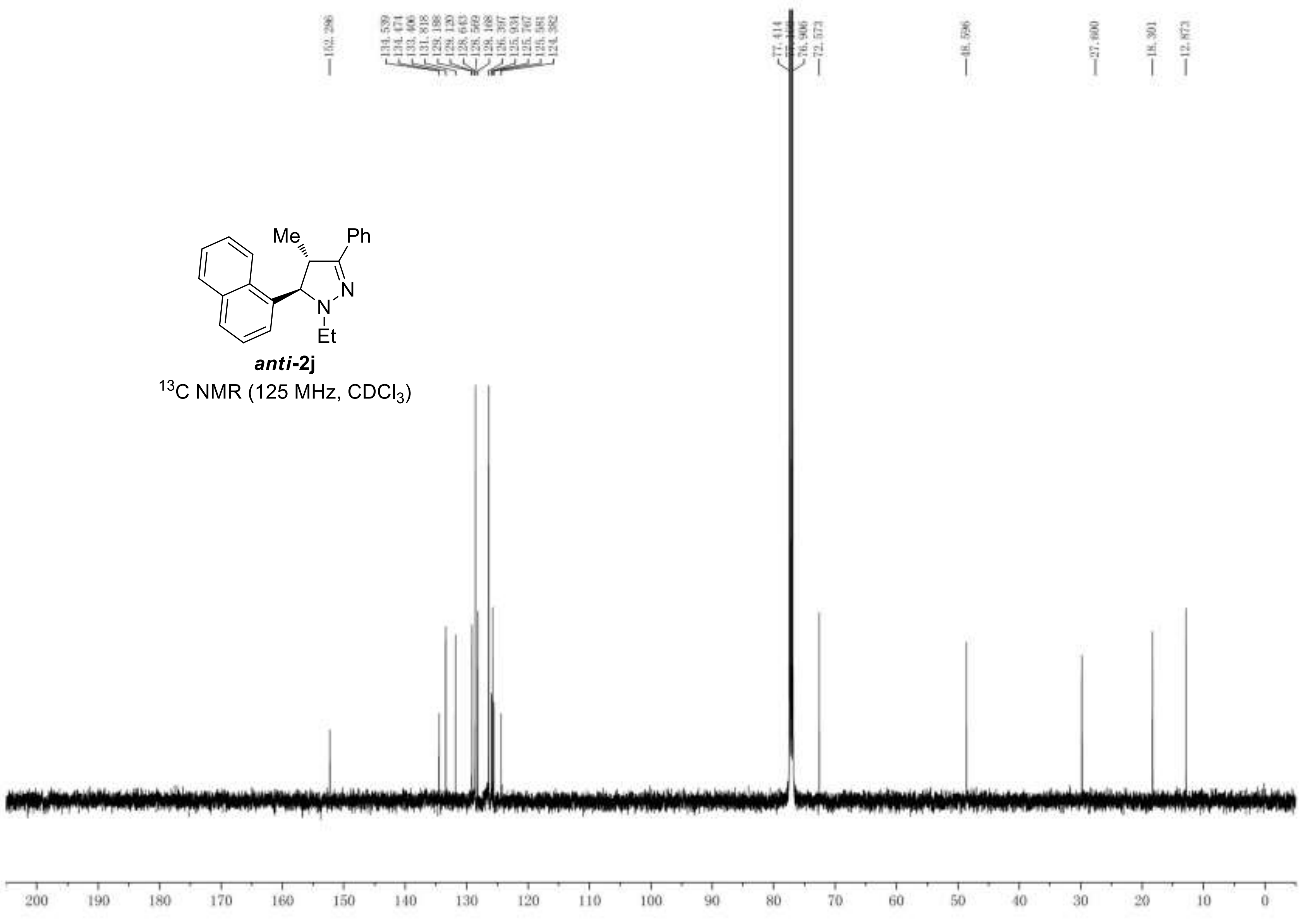
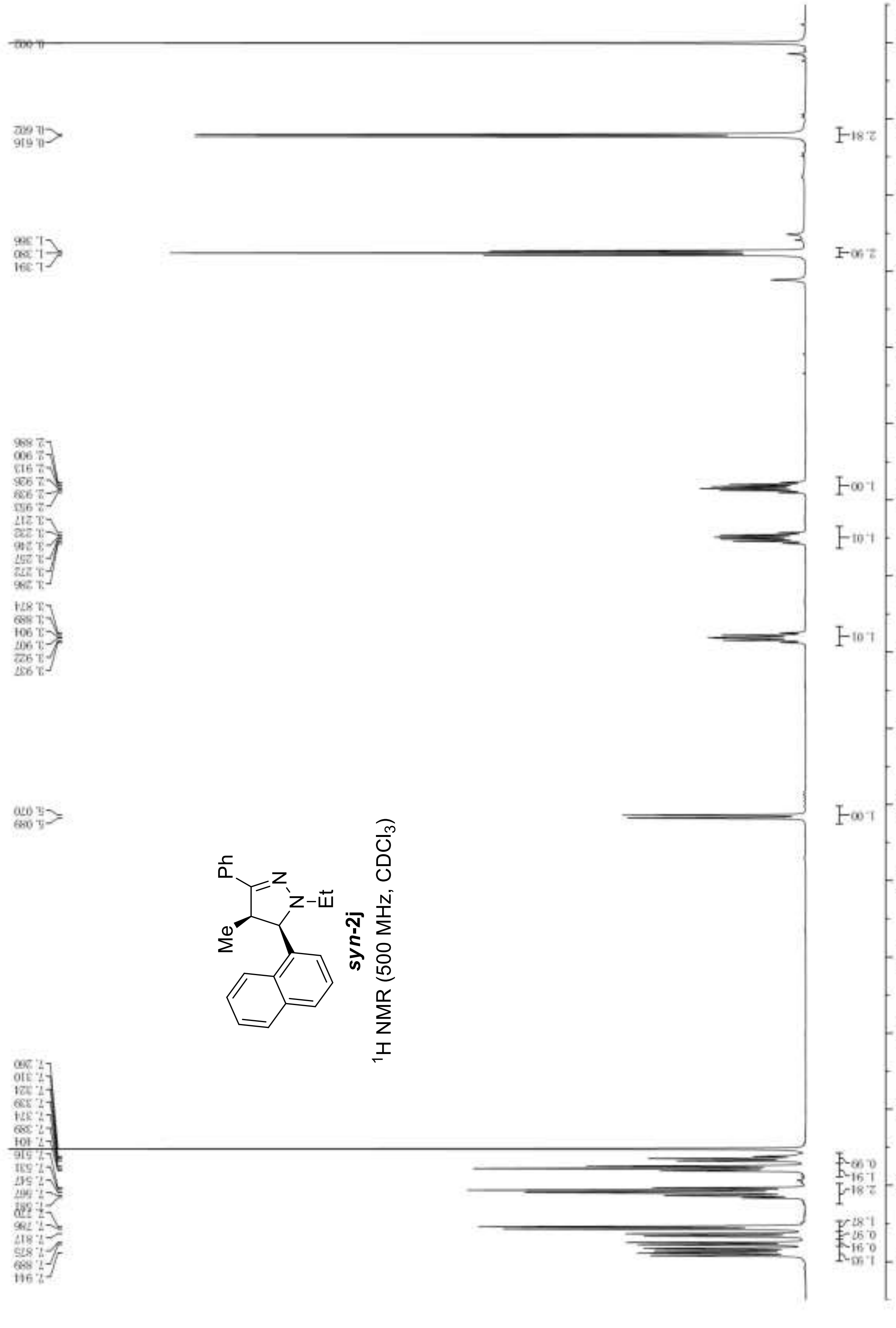


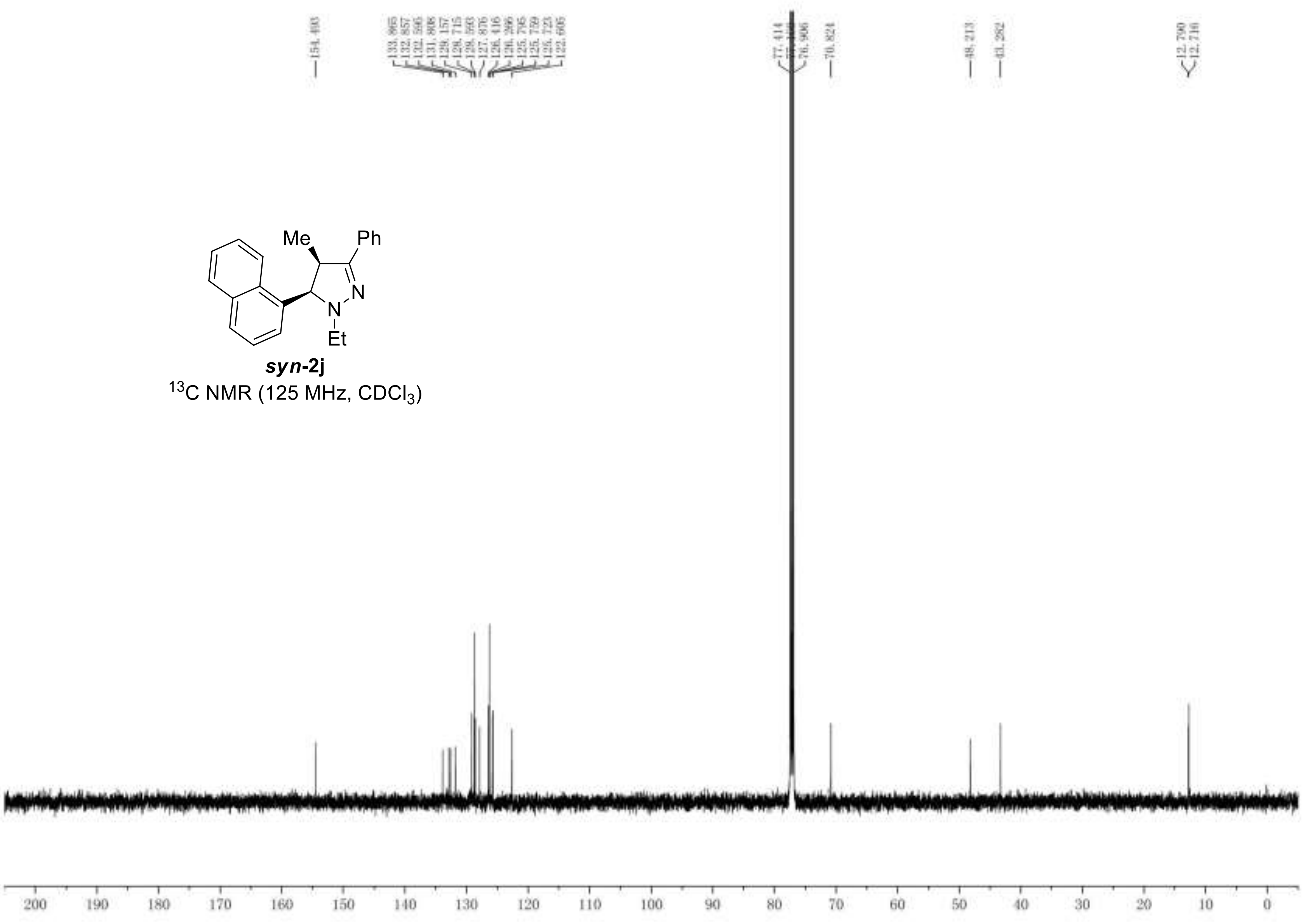
***anti*-2j**

^{13}C NMR (125 MHz, $CDCl_3$)



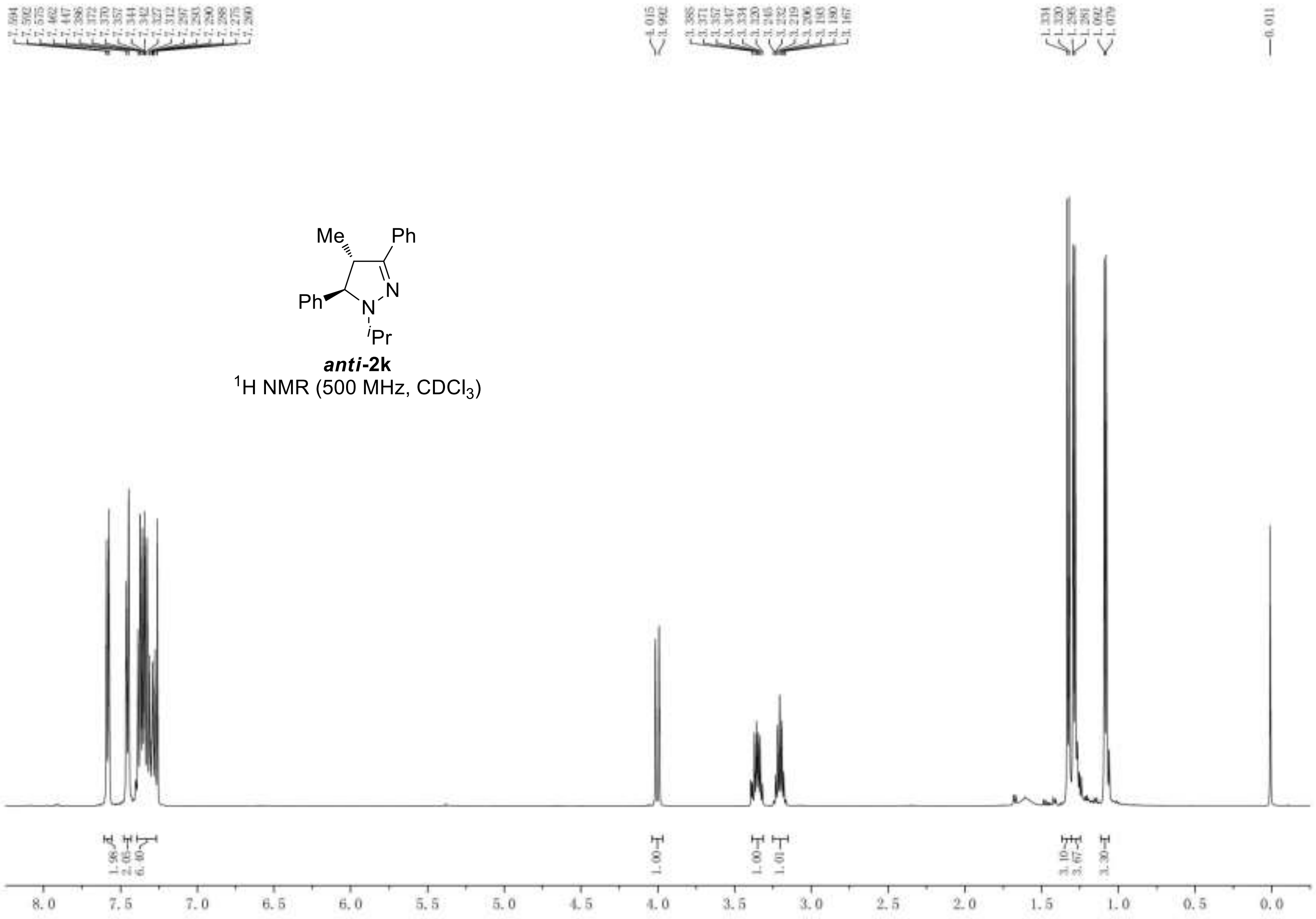
***syn*-2j**

^{1}H NMR (500 MHz, CDCl$_3$)



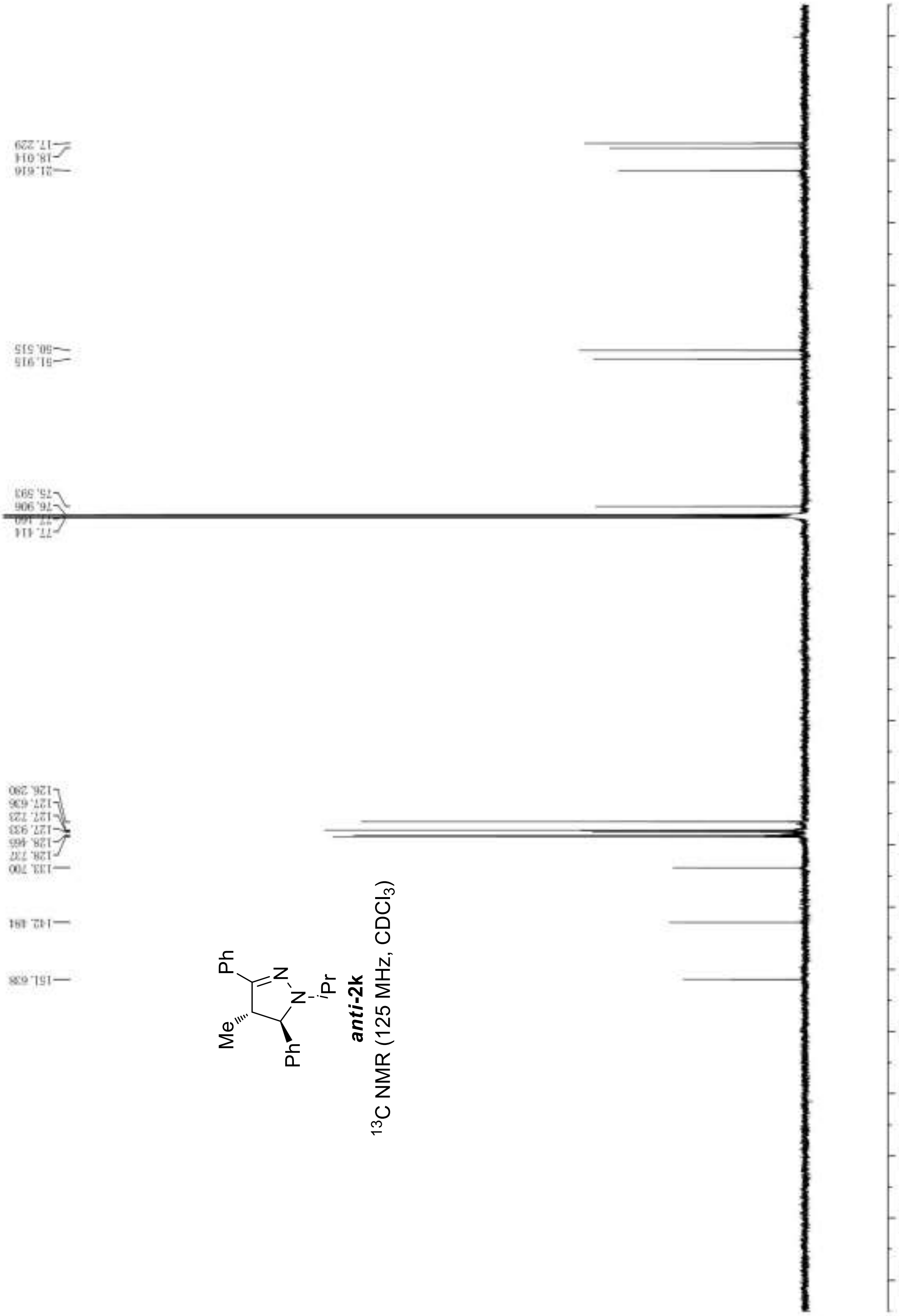
***syn*-2j**

^{13}C NMR (125 MHz, $CDCl_3$)



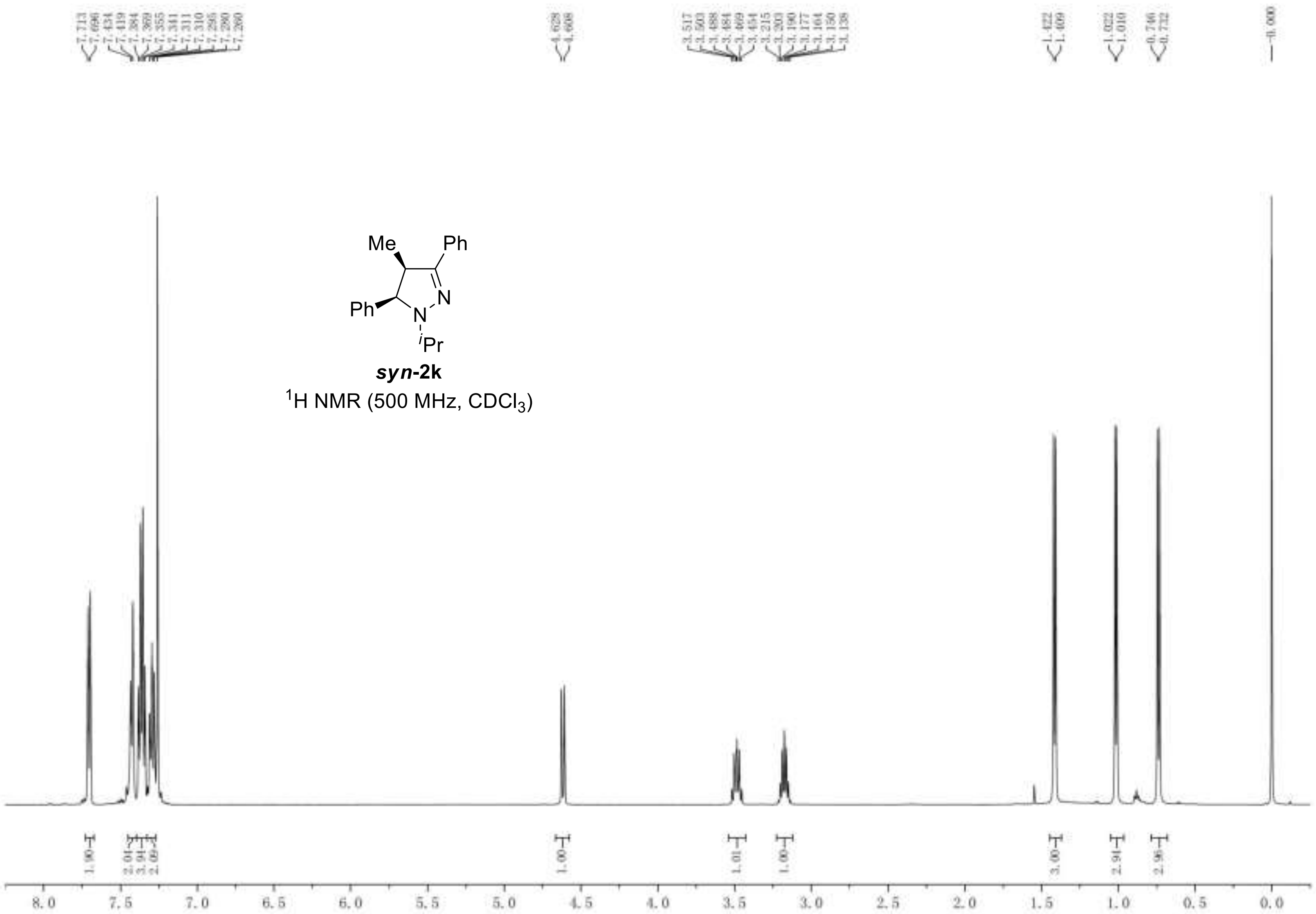
***anti*-2k**

^{1}H NMR (500 MHz, $CDCl_3$)



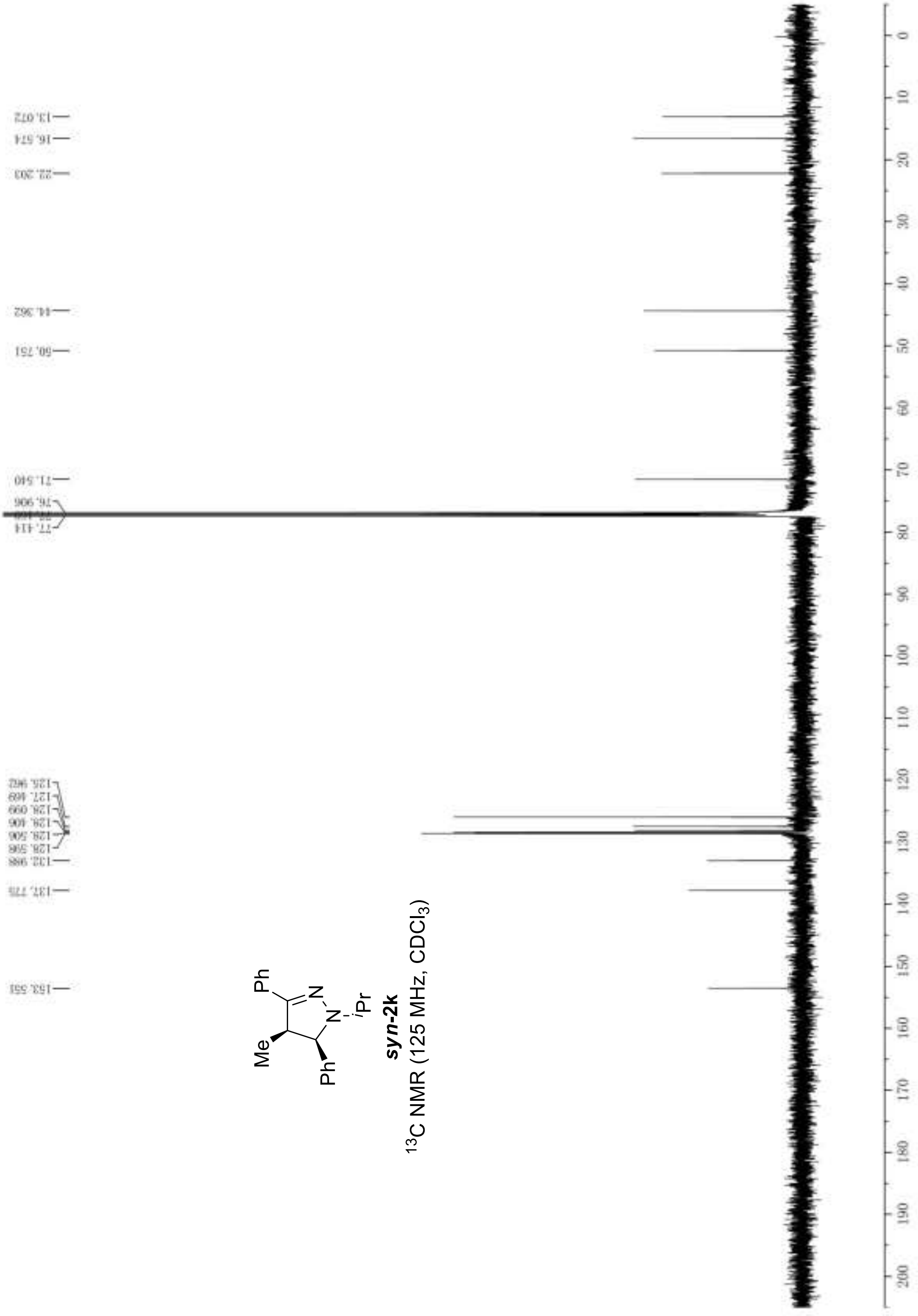
***anti*-2k**

^{13}C NMR (125 MHz, CDCl$_3$)



***syn*-2k**

^{1}H NMR (500 MHz, CDCl$_3$)

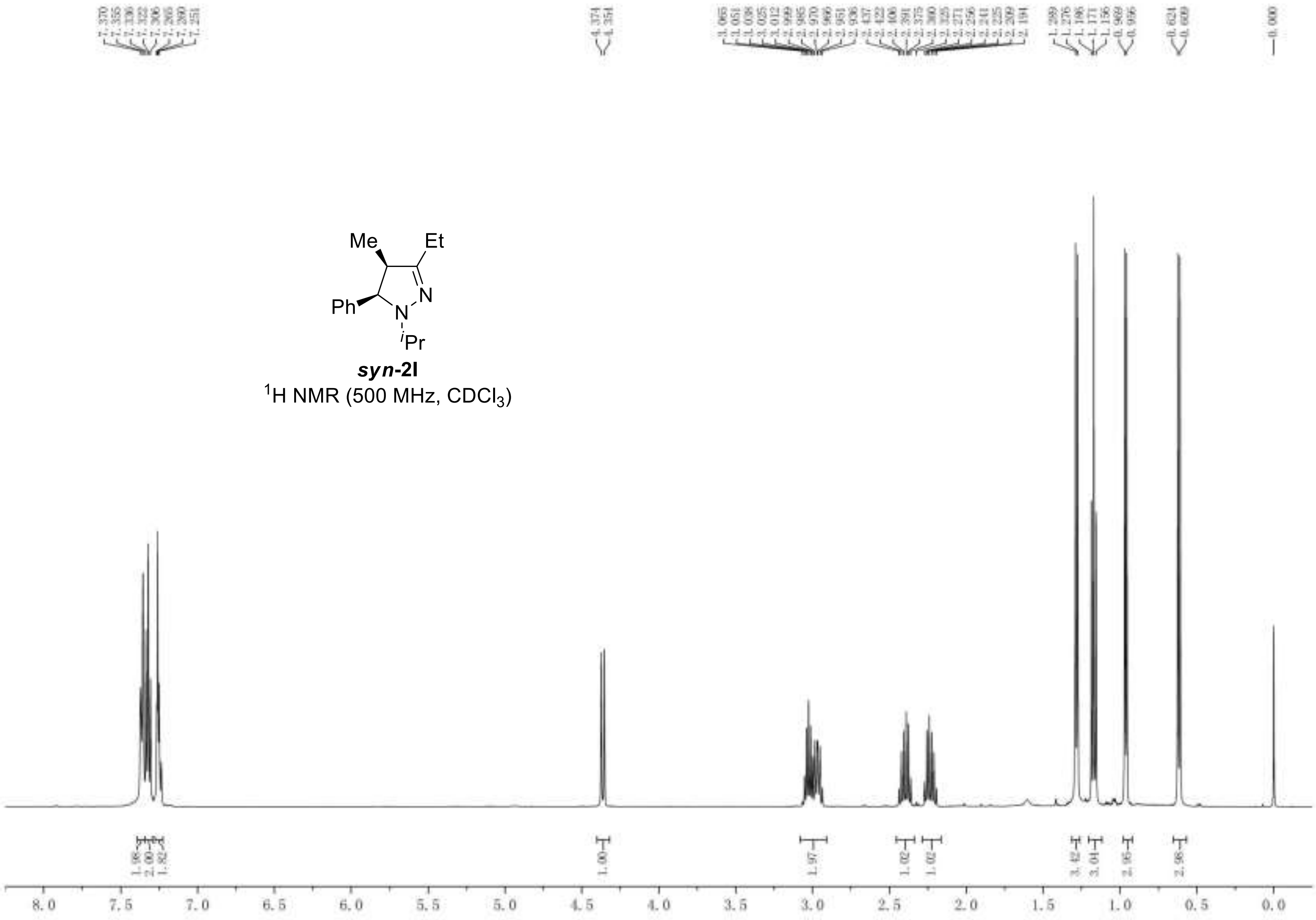


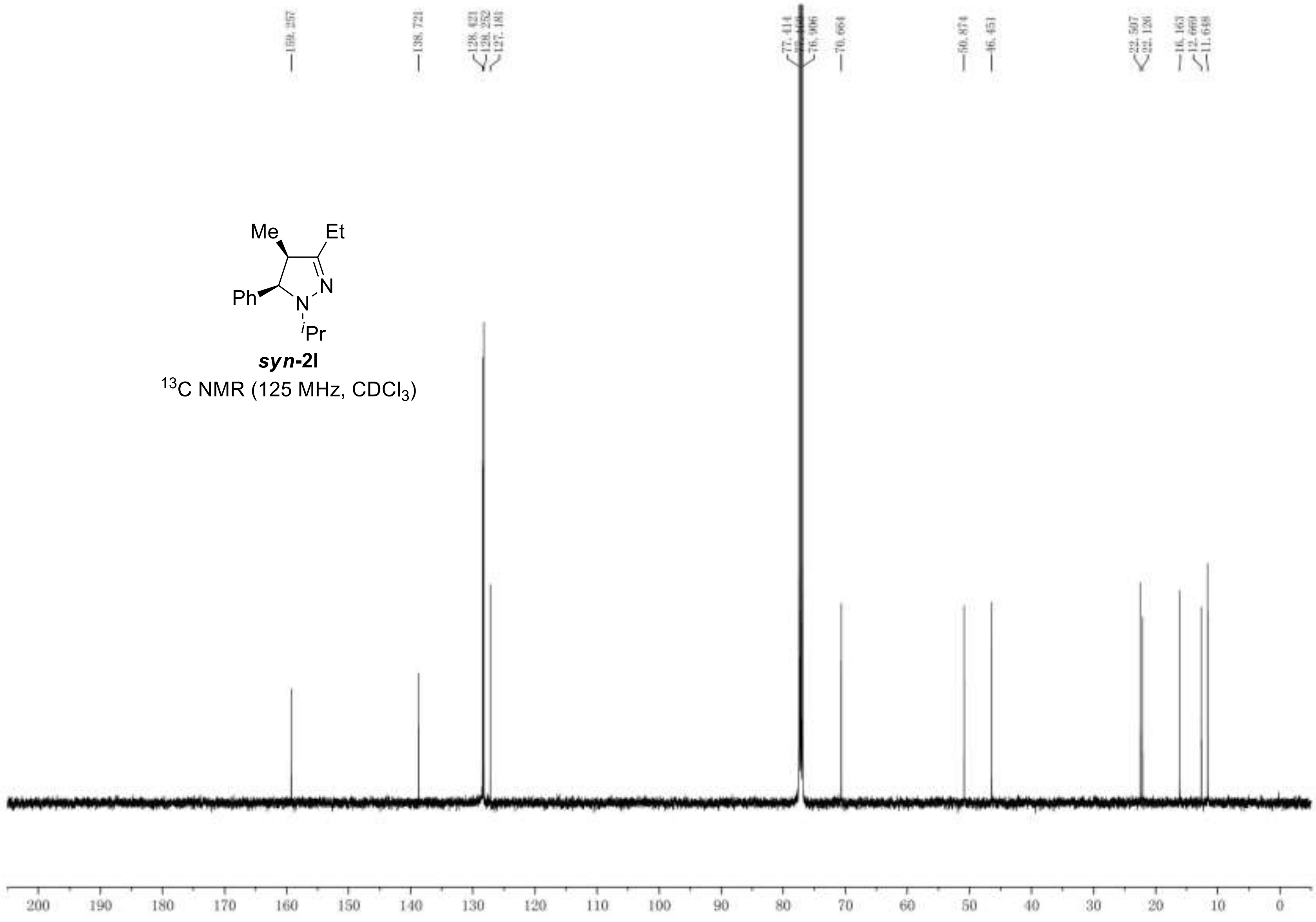
syn-2k

^{13}C NMR (125 MHz, $CDCl_3$)

***syn*-2l**

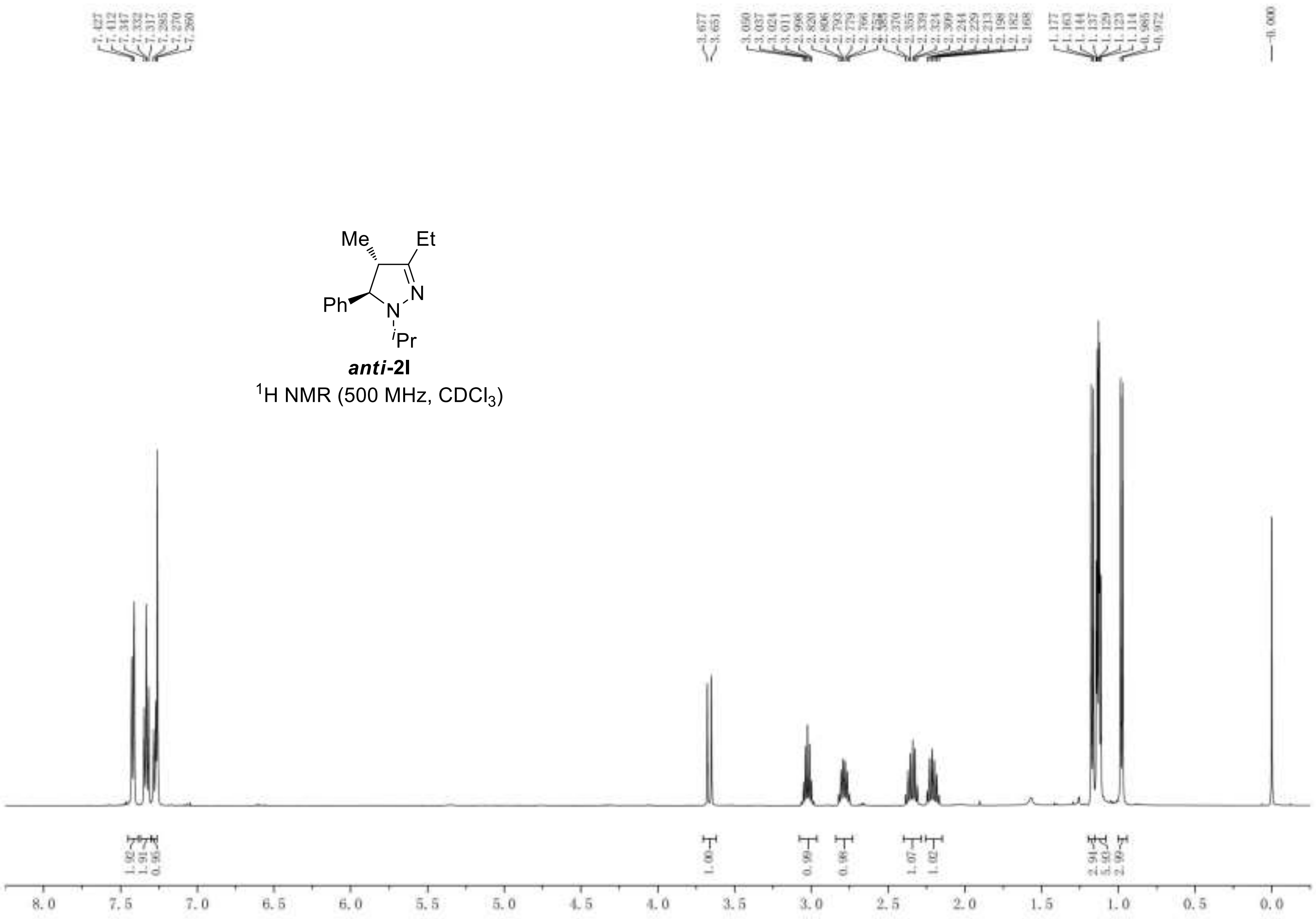
^{1}H NMR (500 MHz, $CDCl_3$)





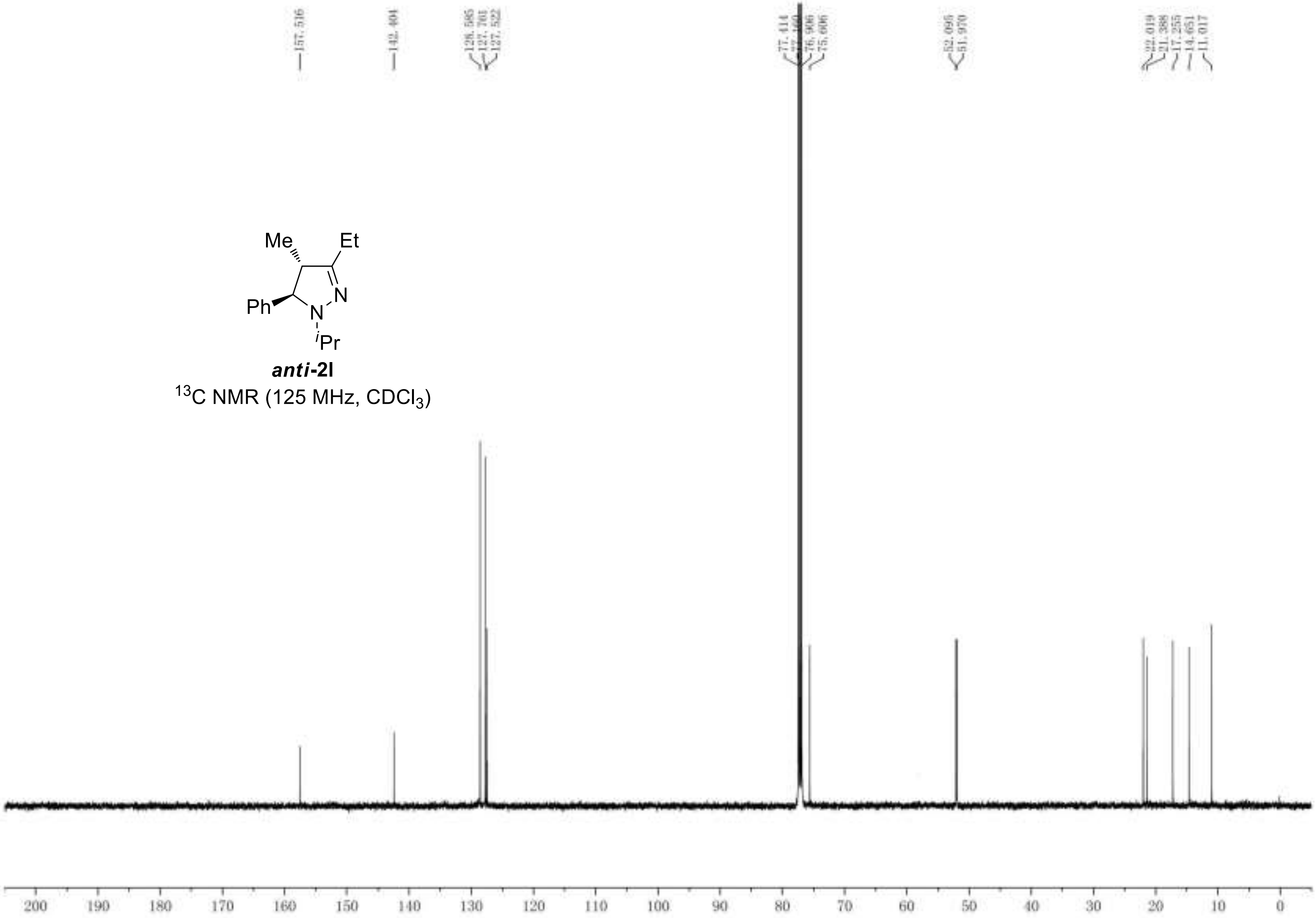
***syn*-2l**

^{13}C NMR (125 MHz, CDCl$_3$)



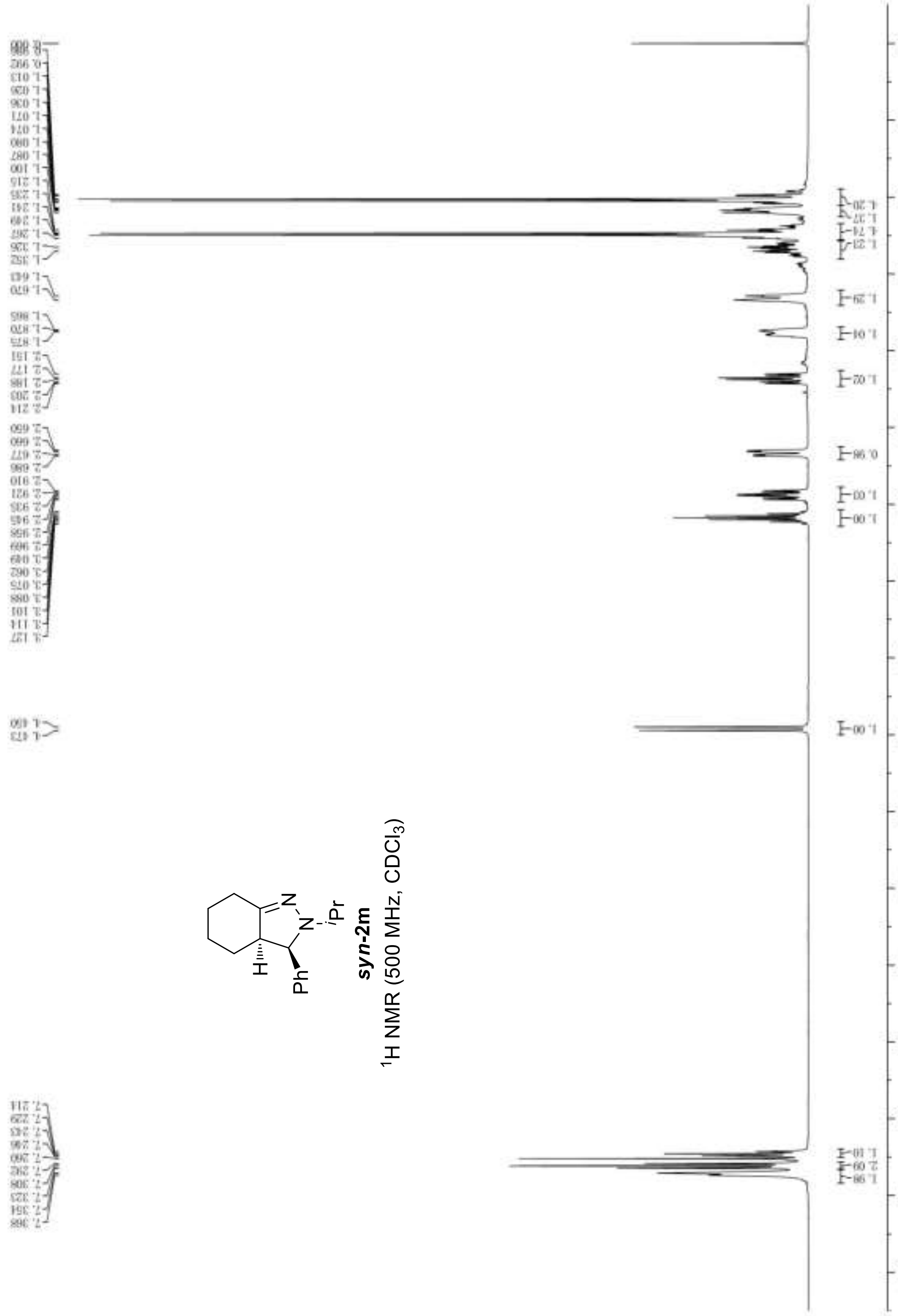
***anti*-2l**

^{1}H NMR (500 MHz, CDCl$_3$)



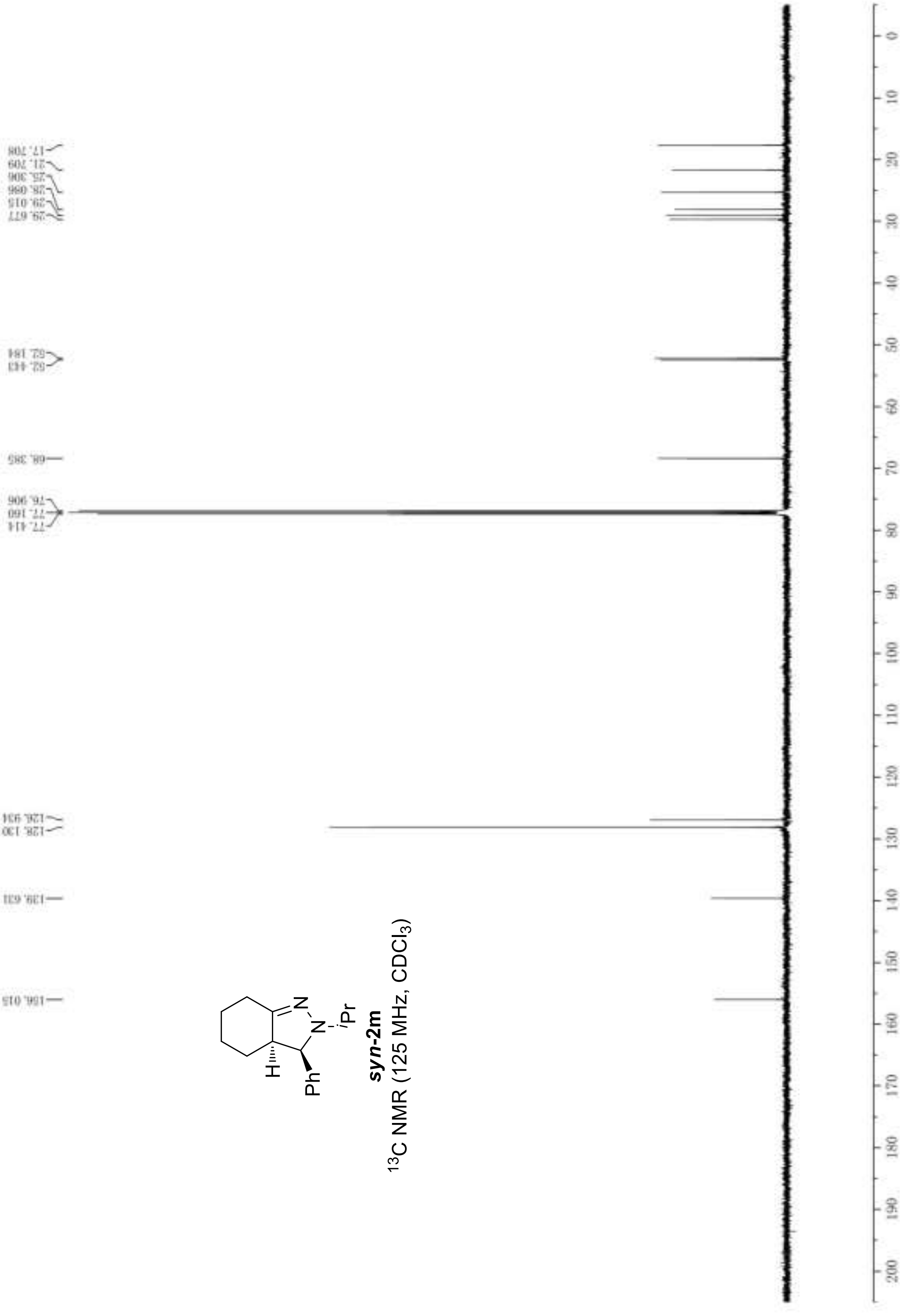
***anti*-2l**

^{13}C NMR (125 MHz, CDCl$_3$)



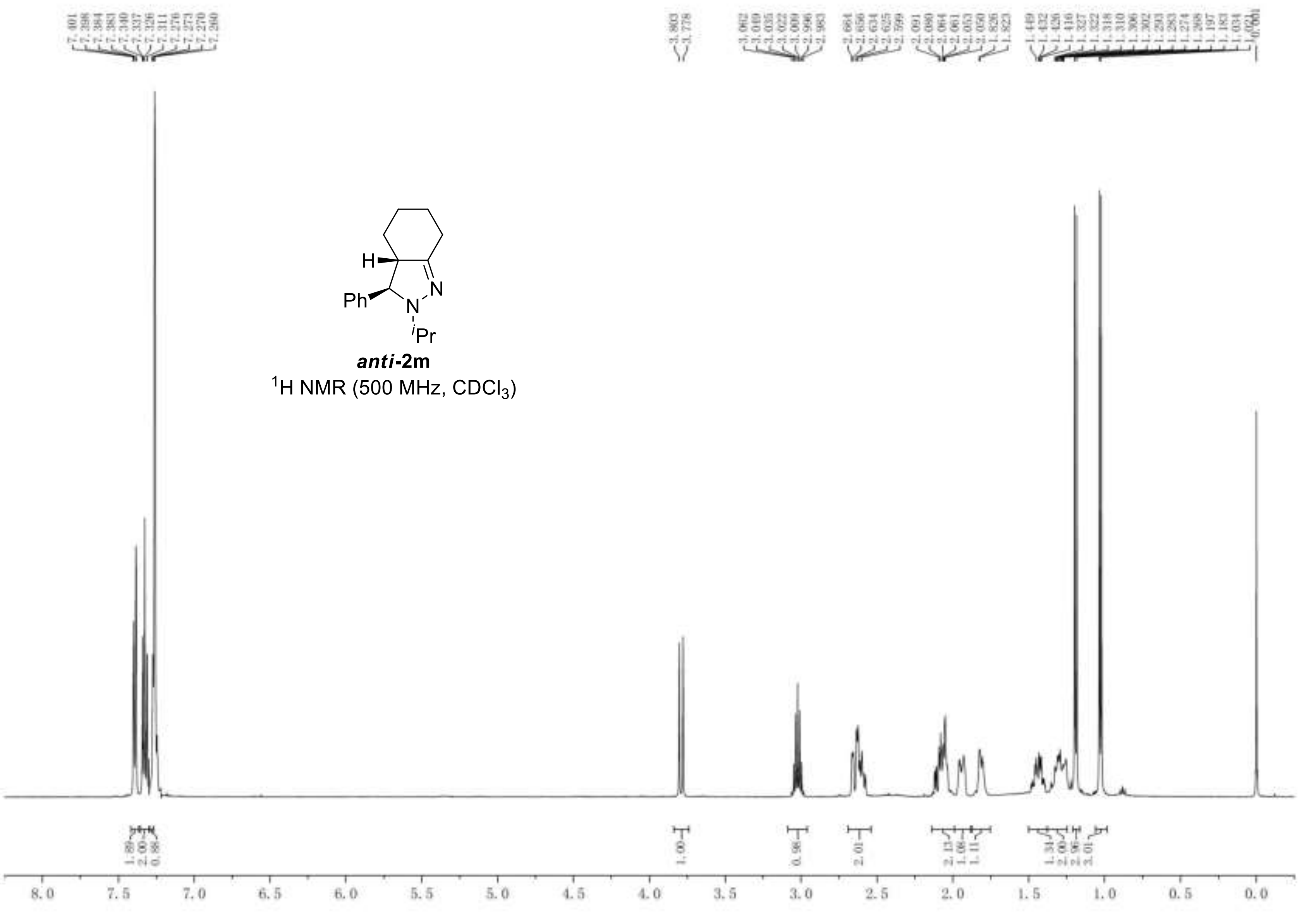
***syn*-2m**

^{1}H NMR (500 MHz, $CDCl_3$)



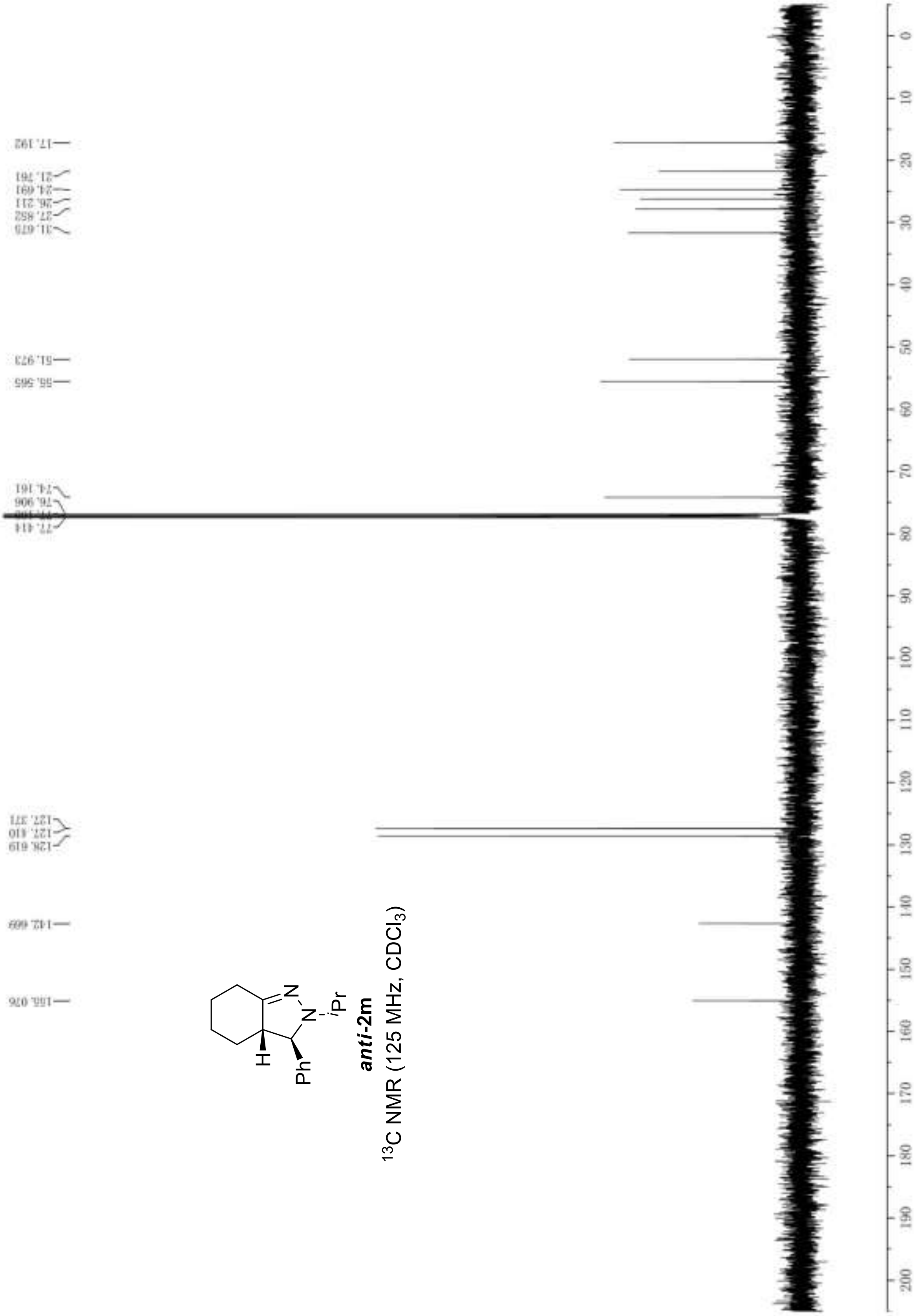
syn-2m

^{13}C NMR (125 MHz, $CDCl_3$)



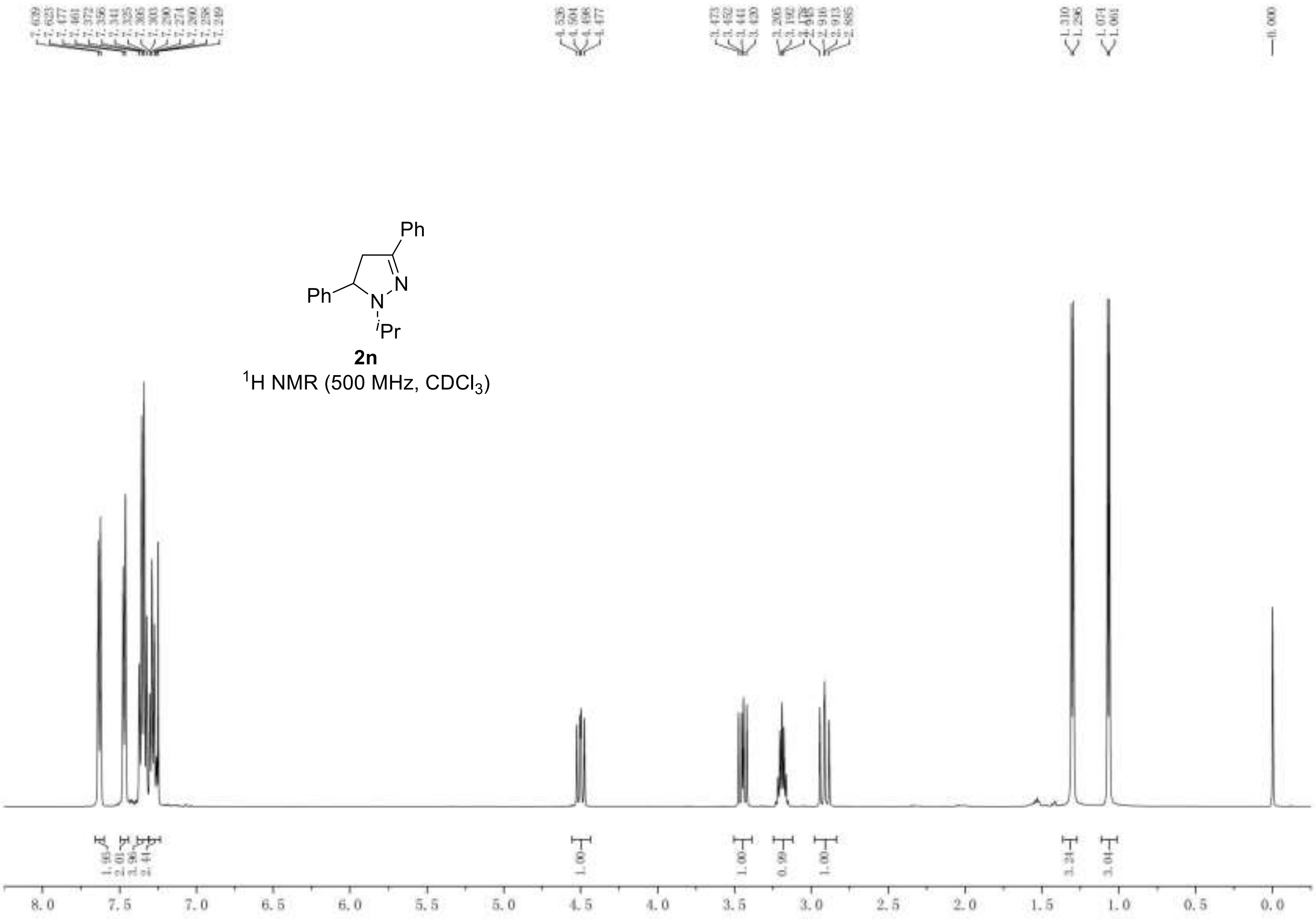
***anti*-2m**

^{1}H NMR (500 MHz, CDCl$_3$)



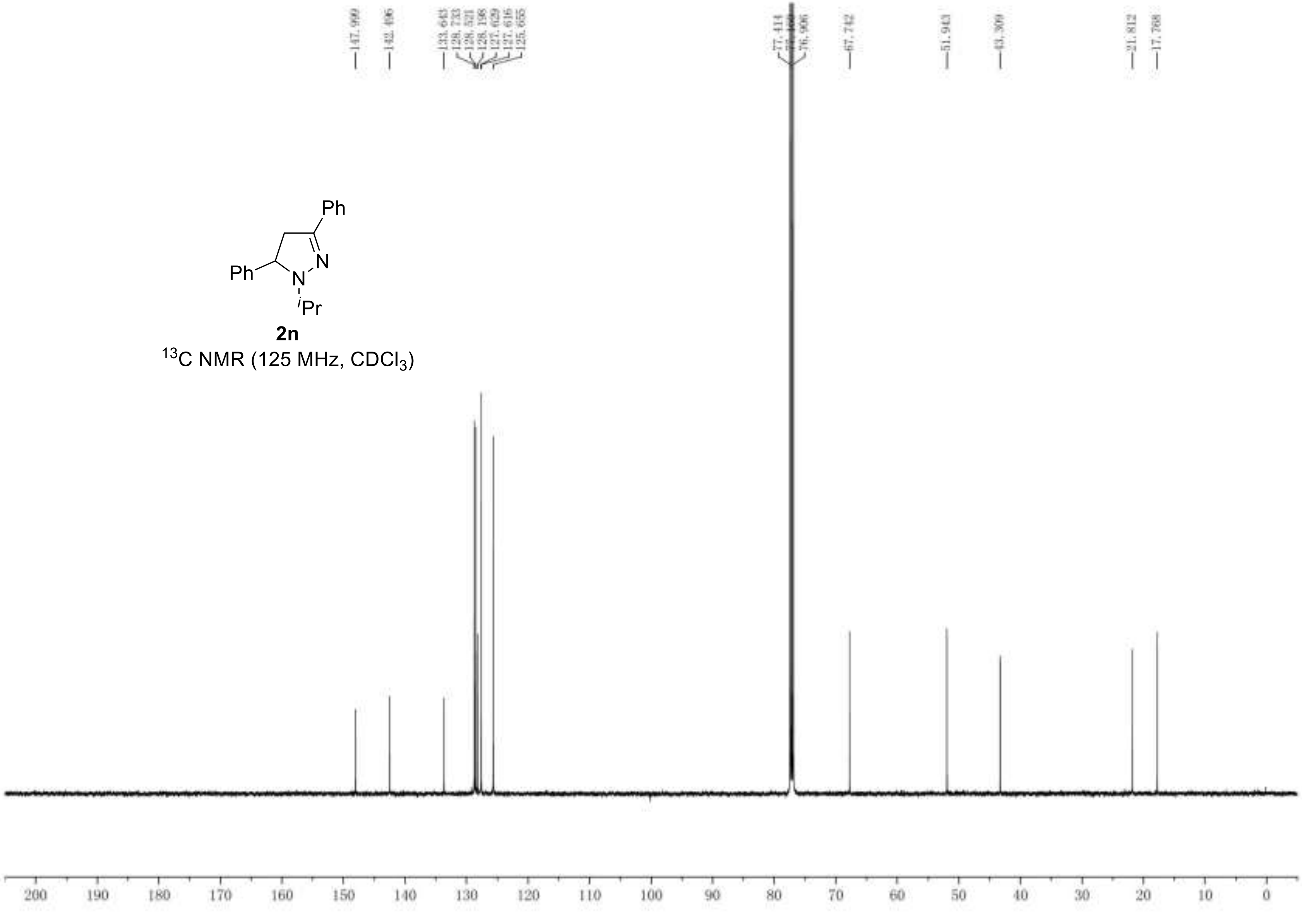
***anti*-2m**

^{13}C NMR (125 MHz, CDCl$_3$)



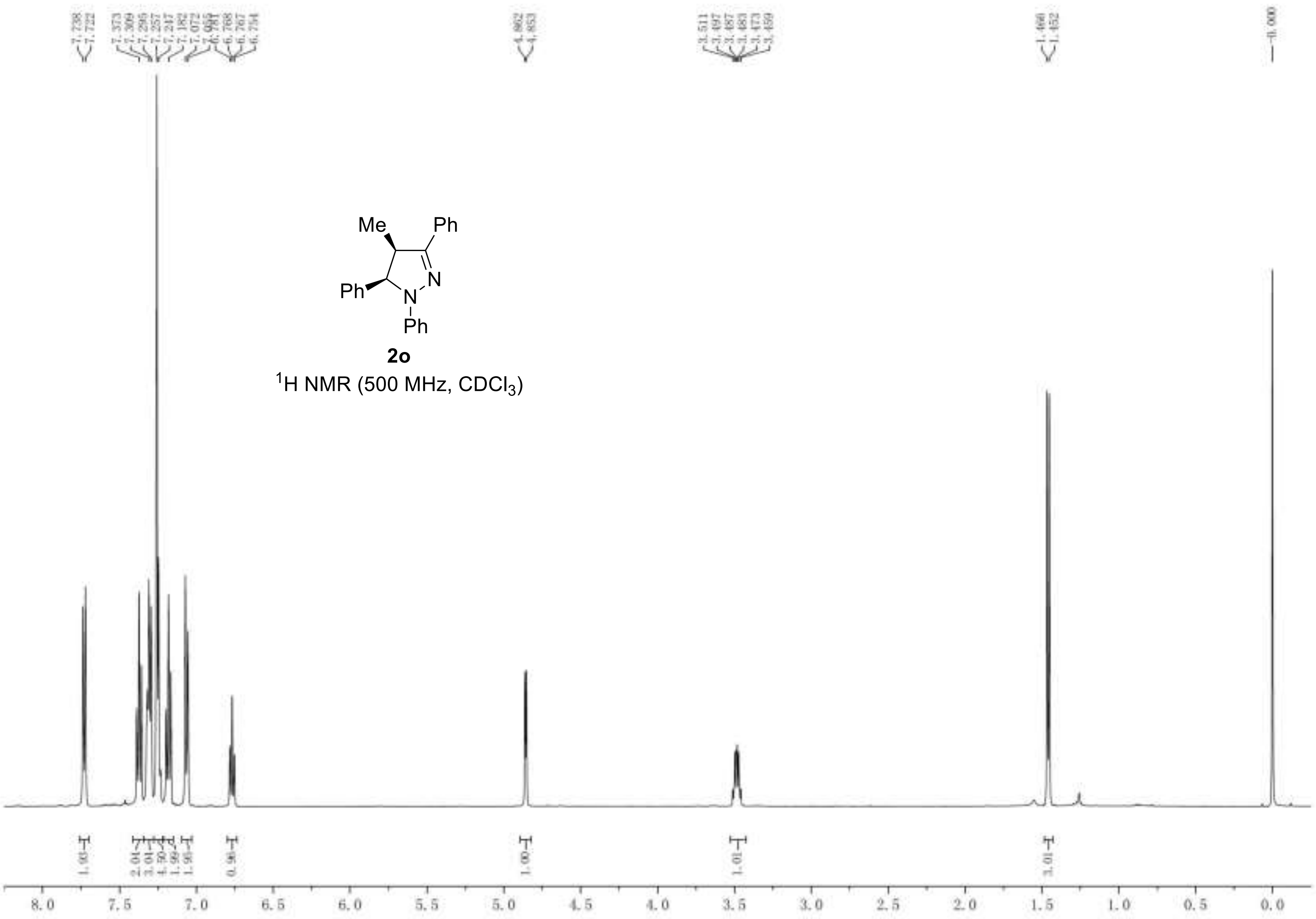
2n

^1H NMR (500 MHz, $CDCl_3$)



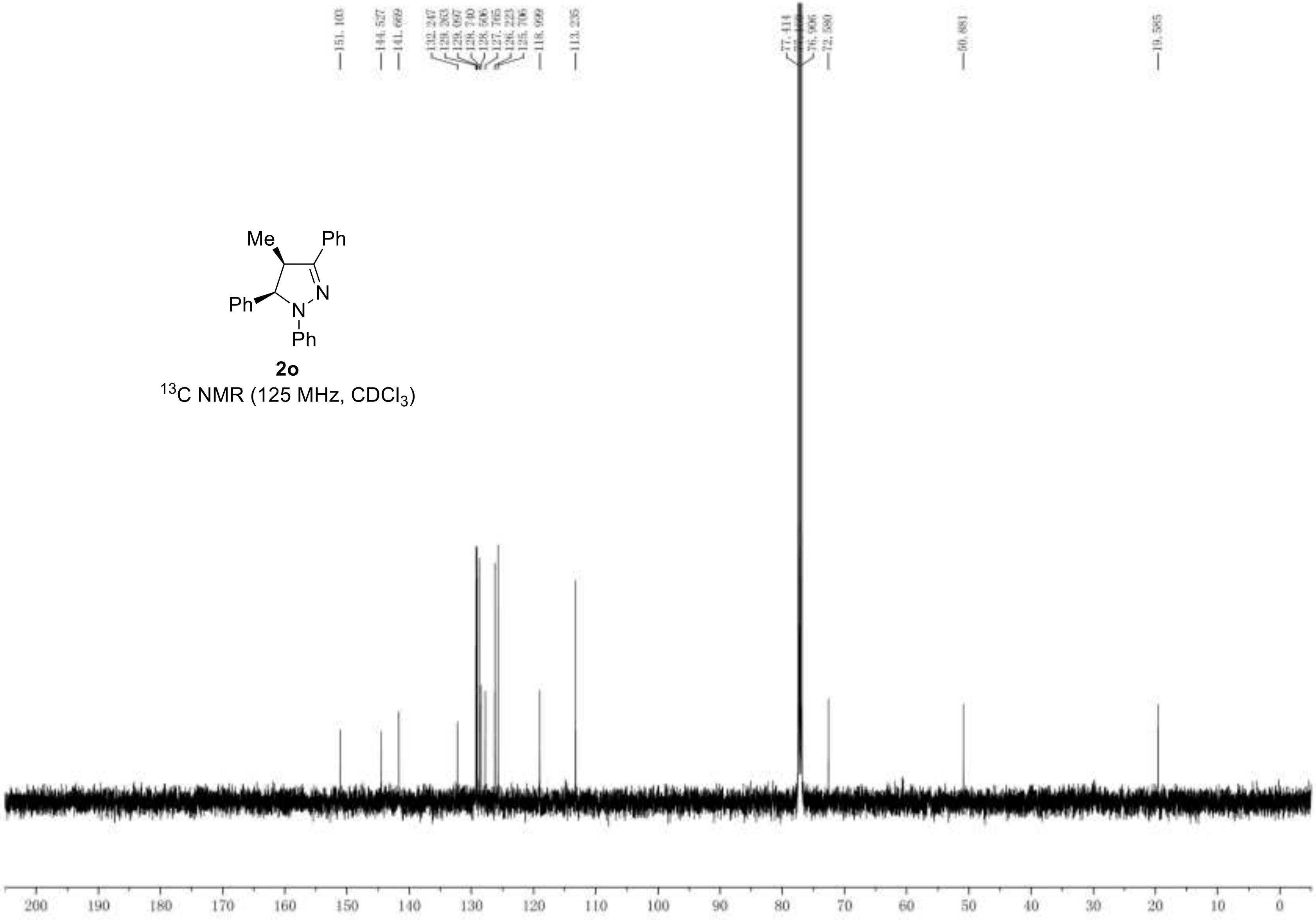
2n

^{13}C NMR (125 MHz, CDCl$_3$)



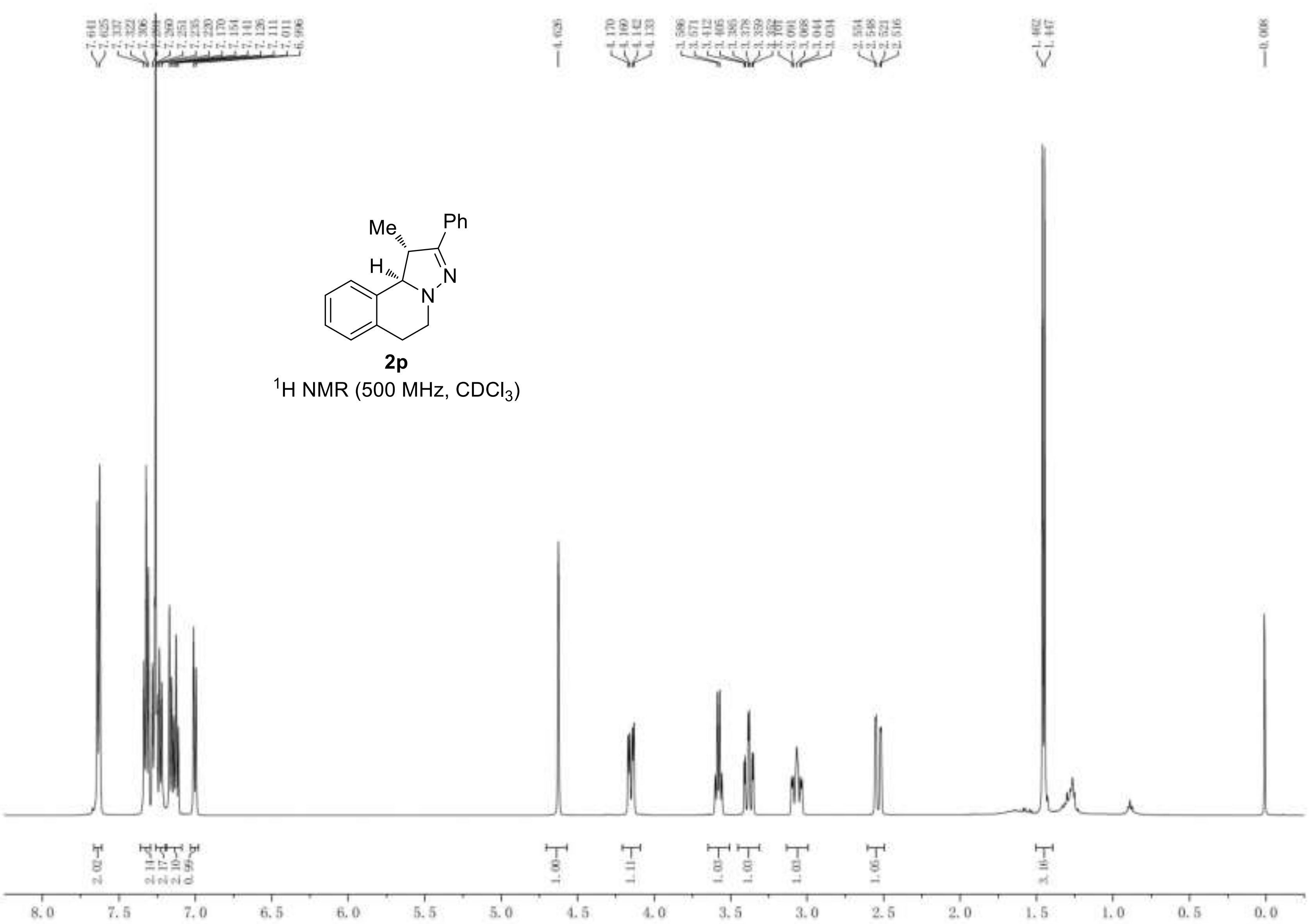
2o

^1H NMR (500 MHz, $CDCl_3$)



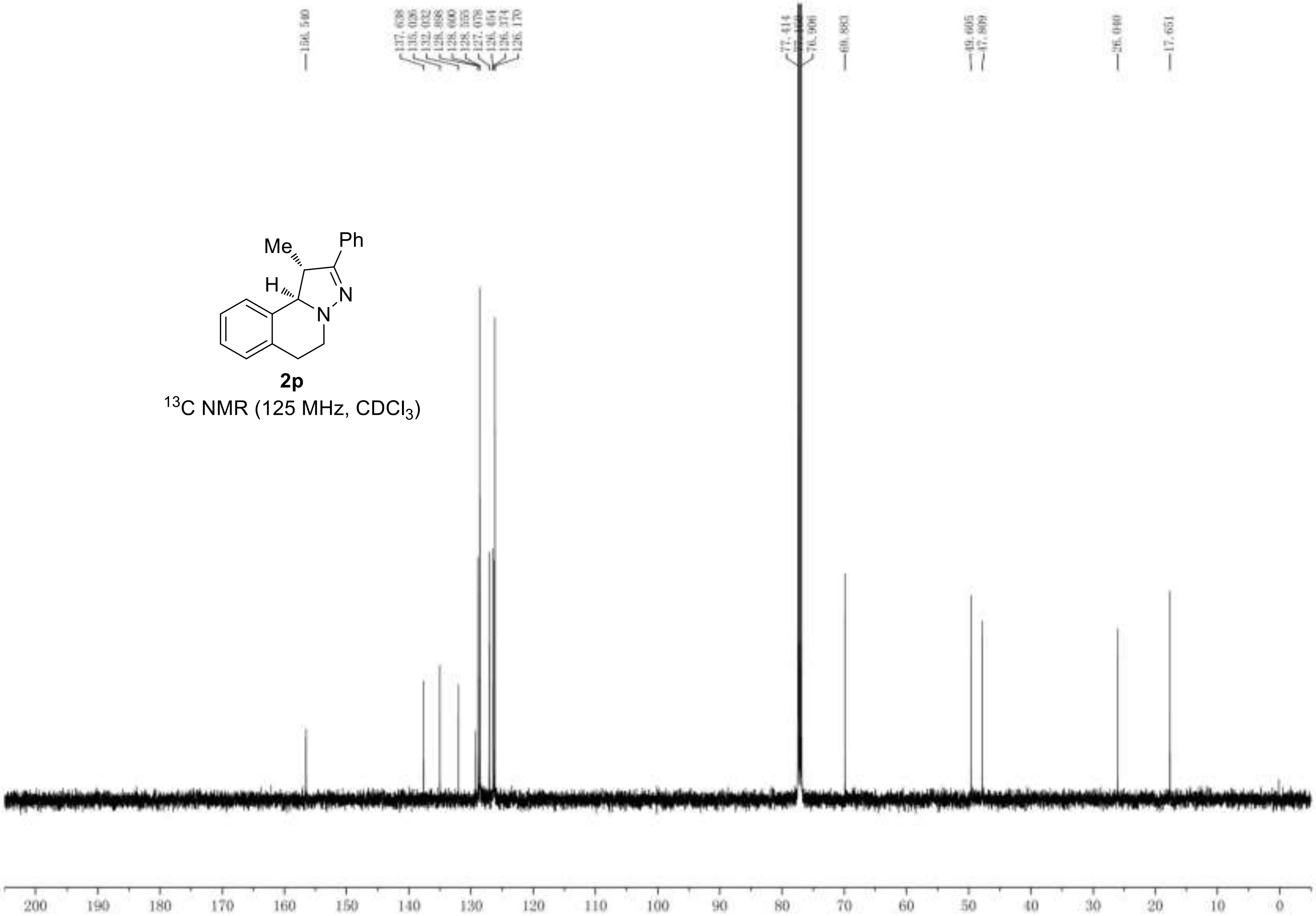
2o

^{13}C NMR (125 MHz, CDCl$_3$)



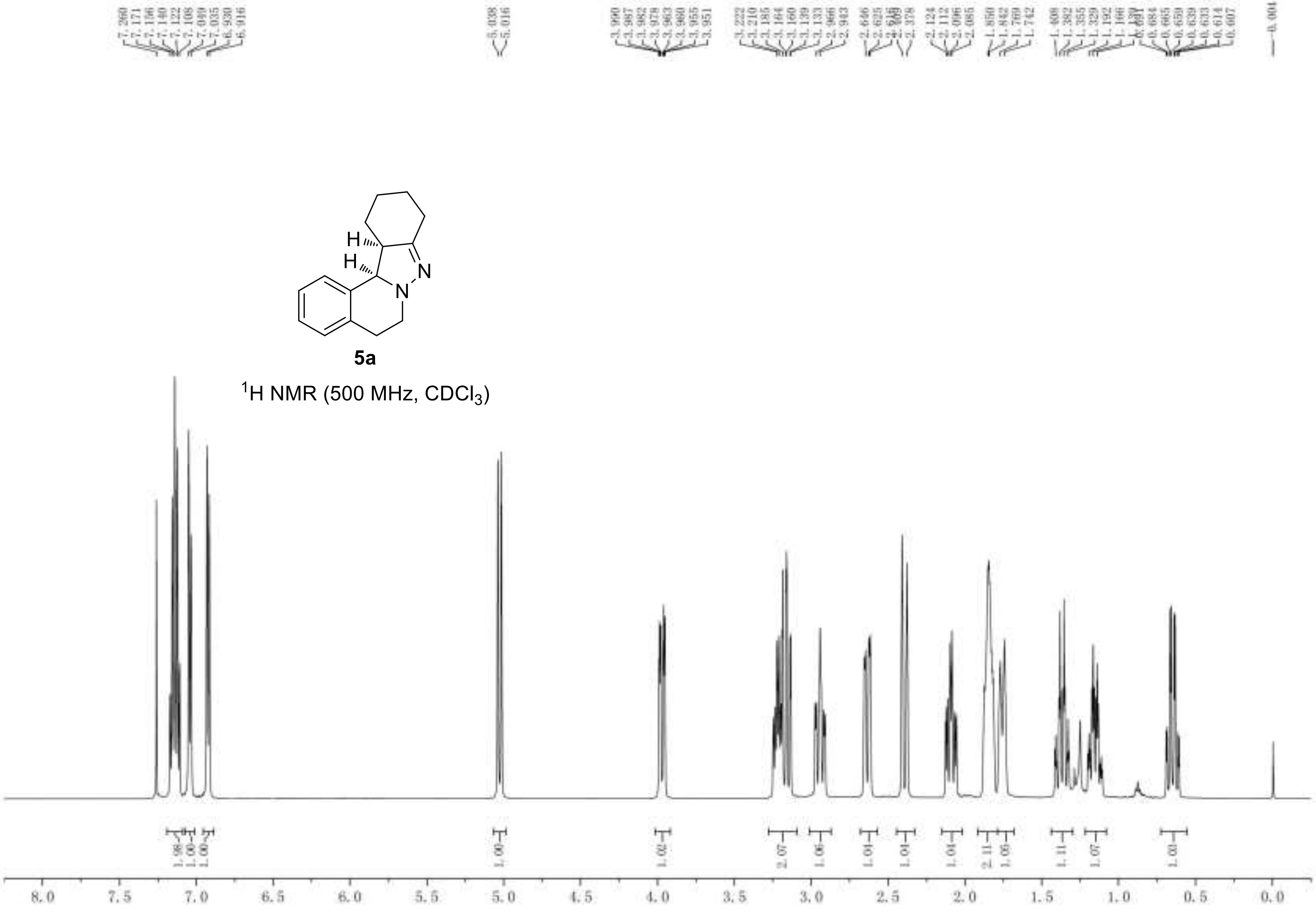
2p

^{1}H NMR (500 MHz, CDCl$_3$)



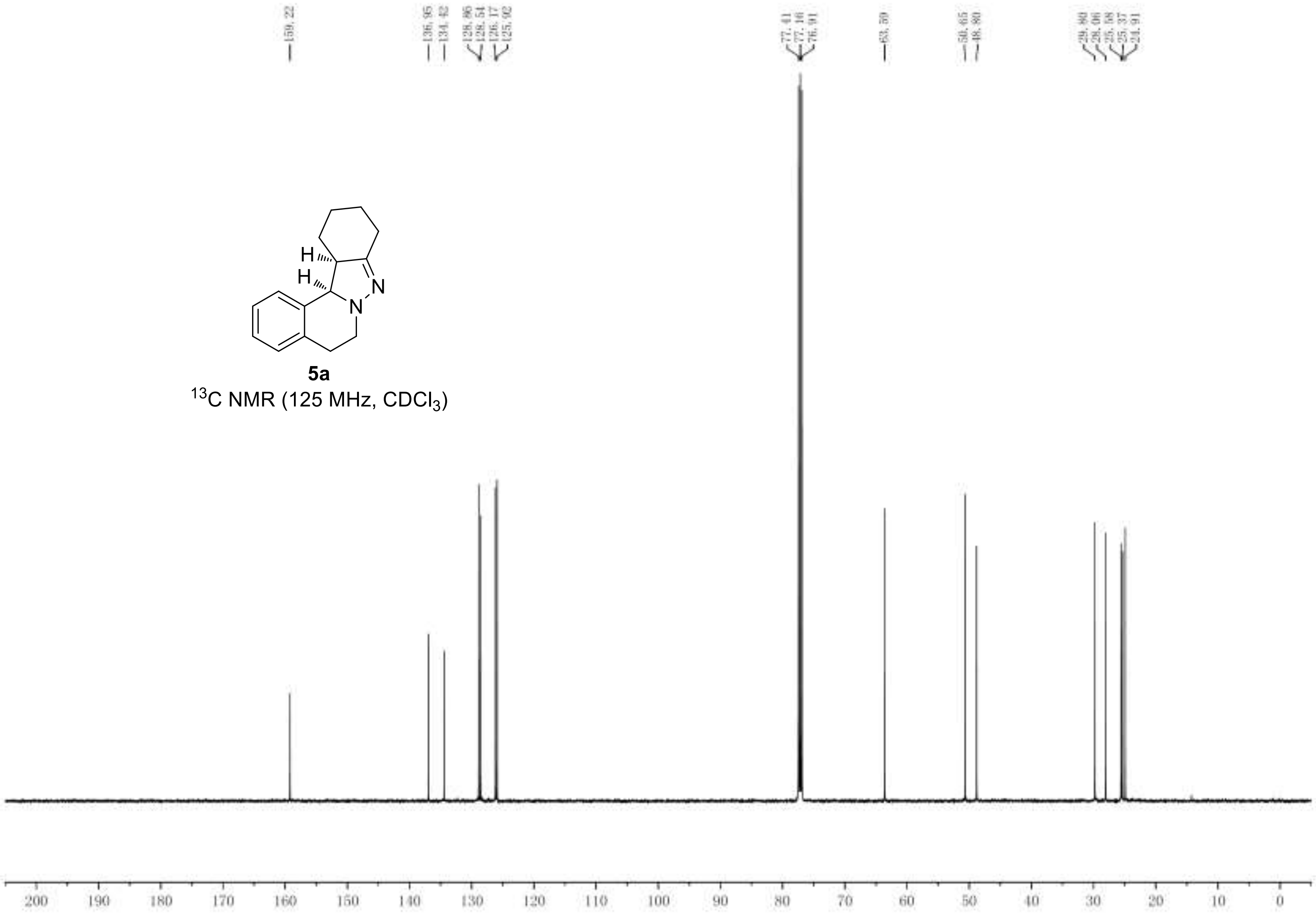
2p

^{13}C NMR (125 MHz, $CDCl_3$)



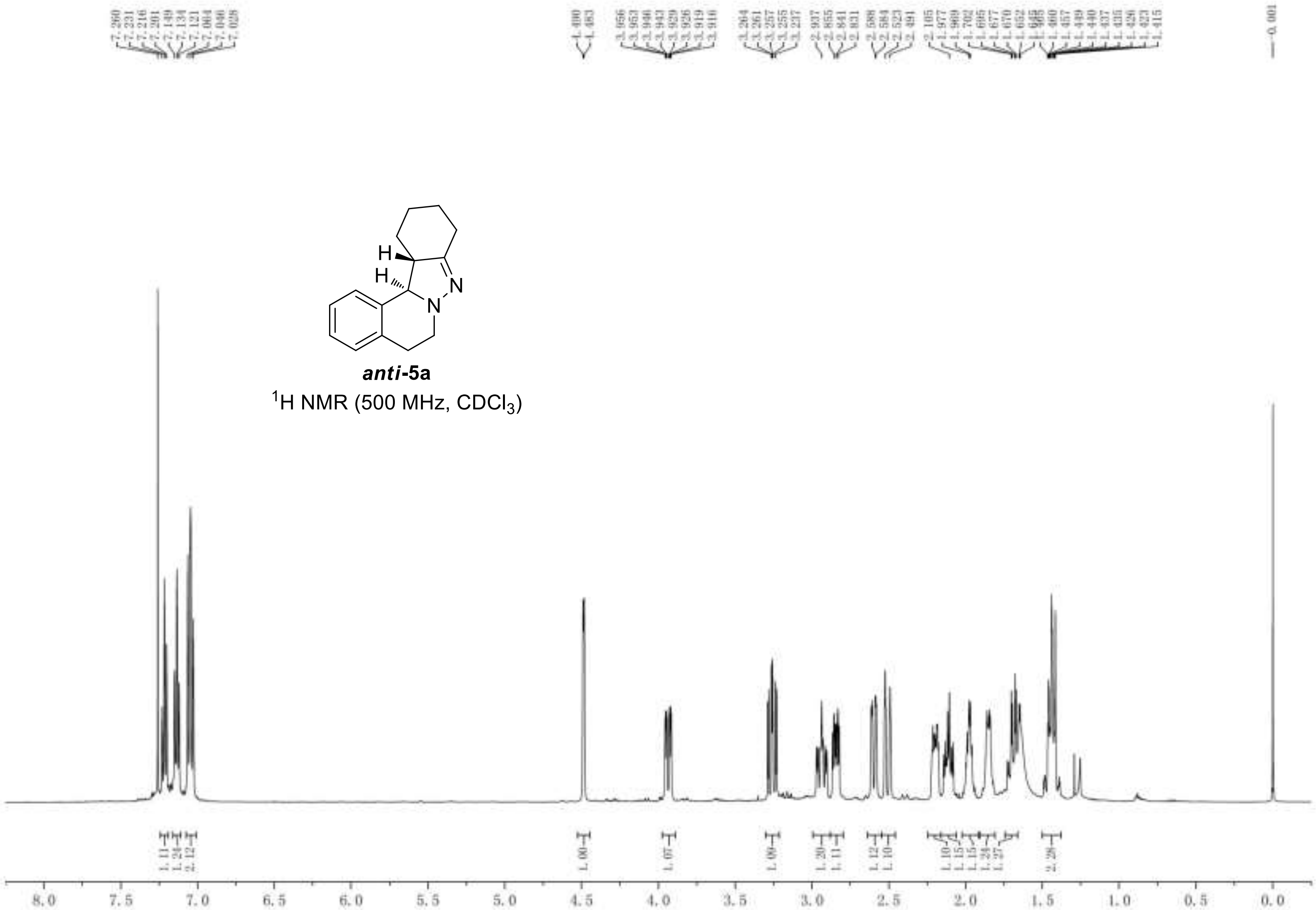
5a

^{1}H NMR (500 MHz, CDCl$_3$)



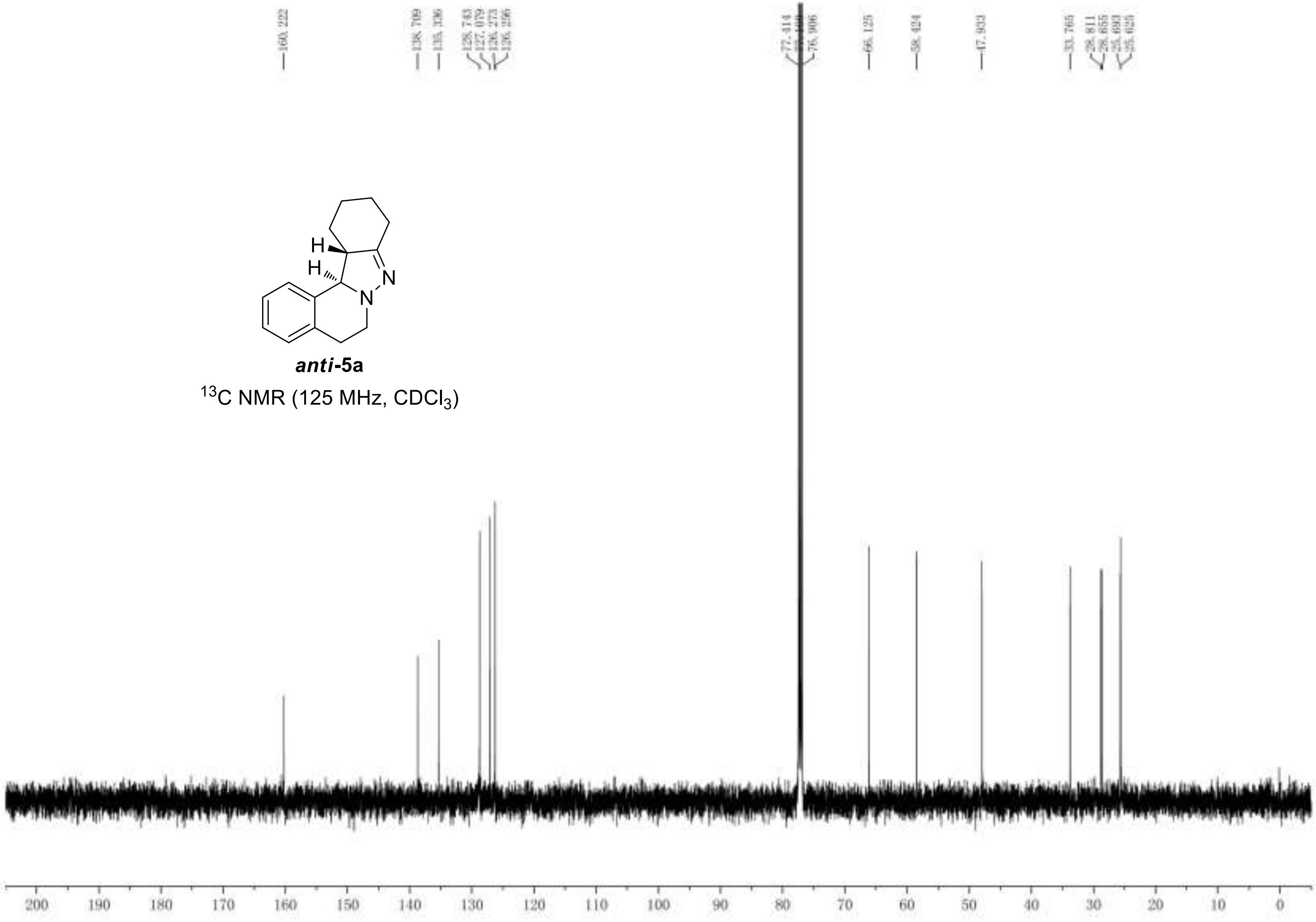
5a

^{13}C NMR (125 MHz, CDCl$_3$)



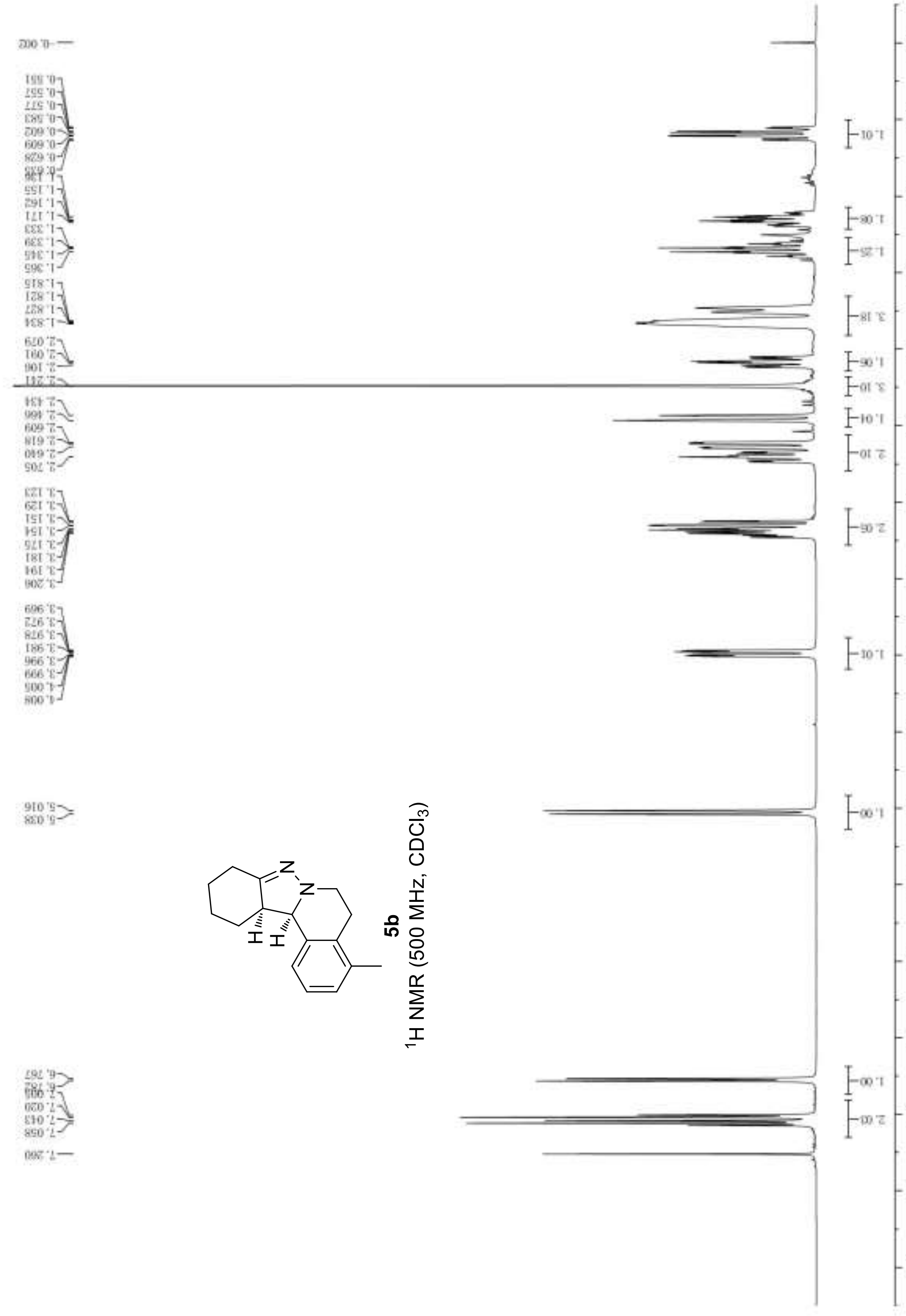
***anti*-5a**

^{1}H NMR (500 MHz, CDCl$_3$)



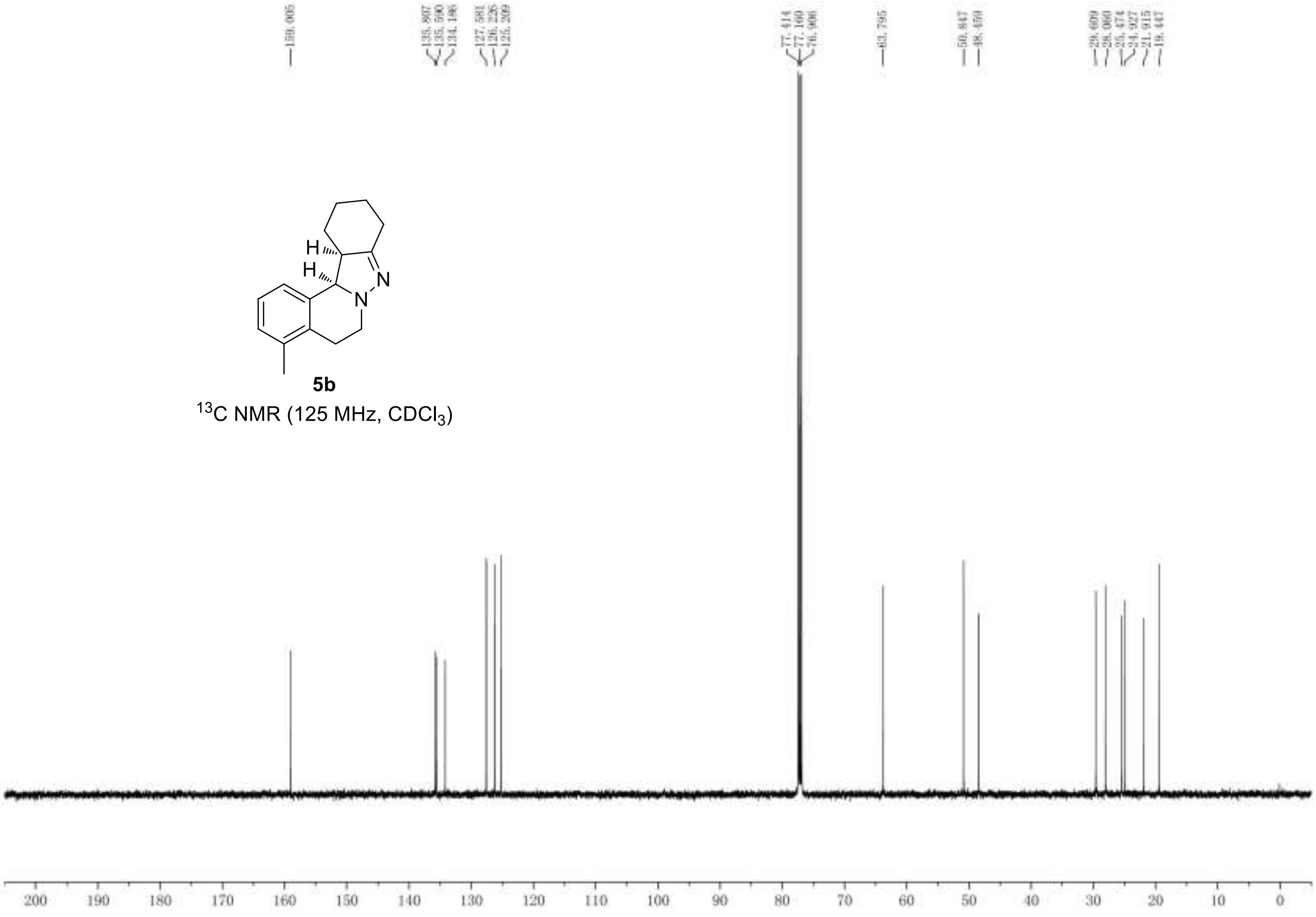
***anti*-5a**

^{13}C NMR (125 MHz, CDCl$_3$)



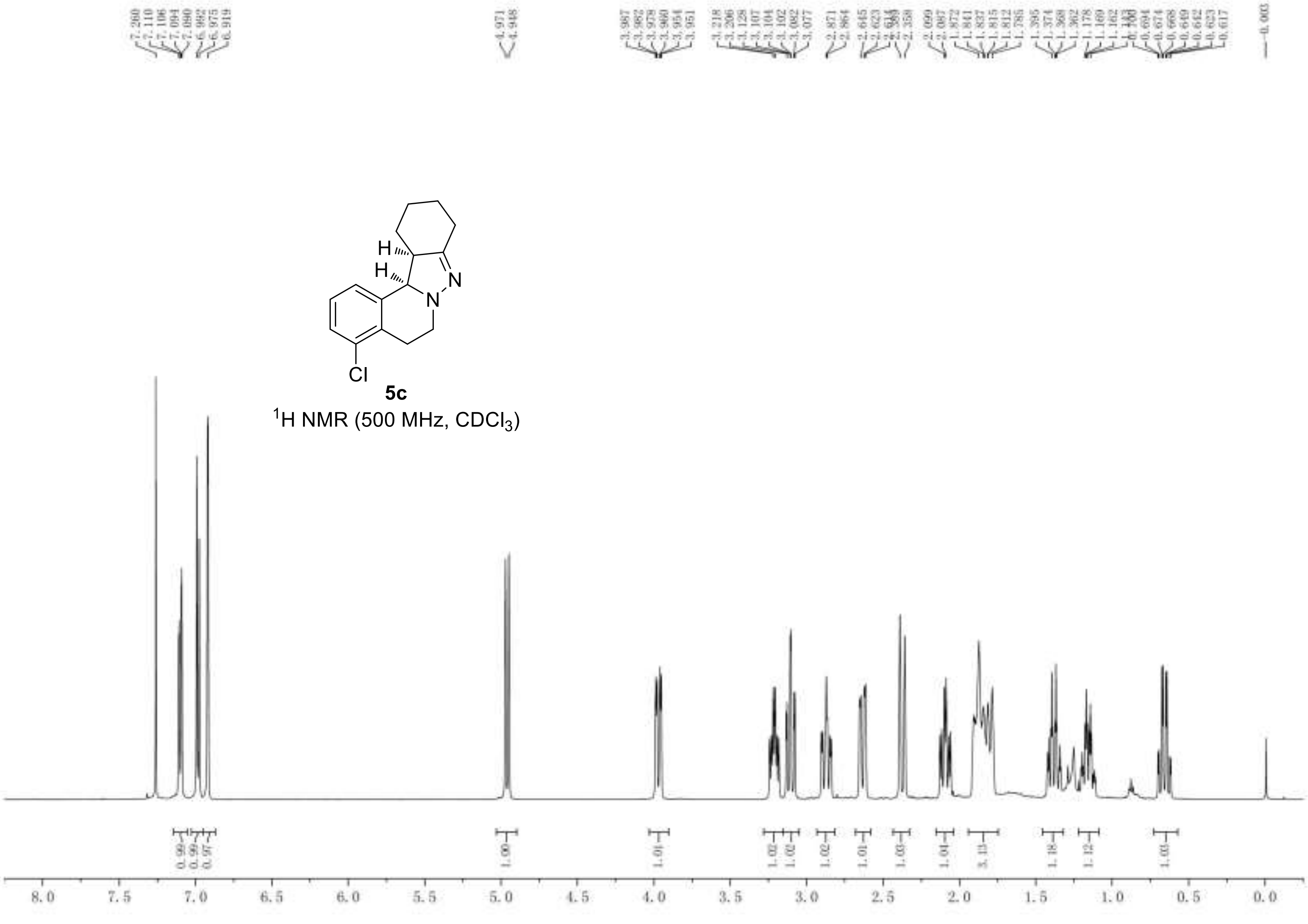
5b

^1H NMR (500 MHz, $CDCl_3$)



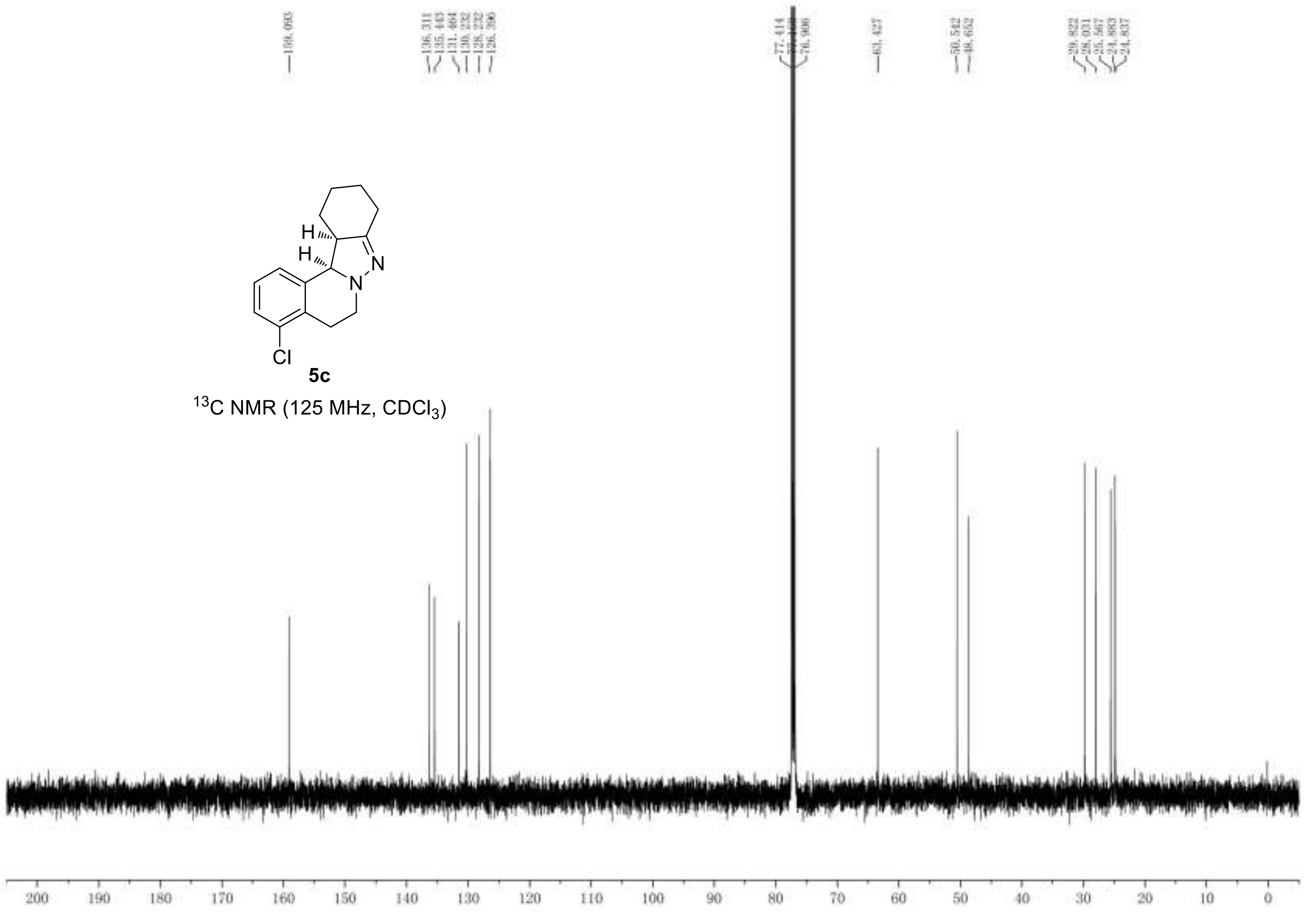
5b

^{13}C NMR (125 MHz, CDCl$_3$)



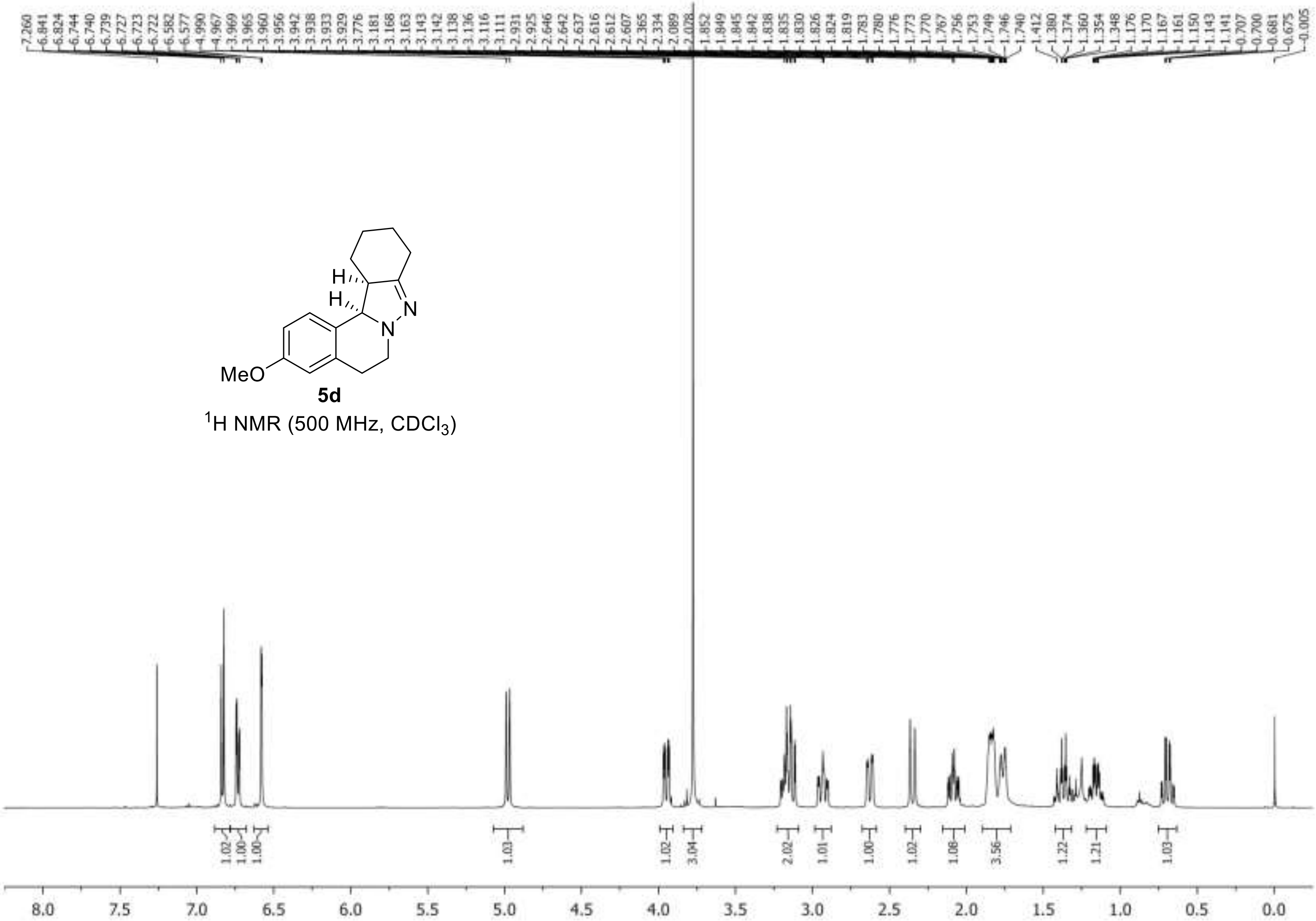
5c

^{1}H NMR (500 MHz, CDCl$_3$)



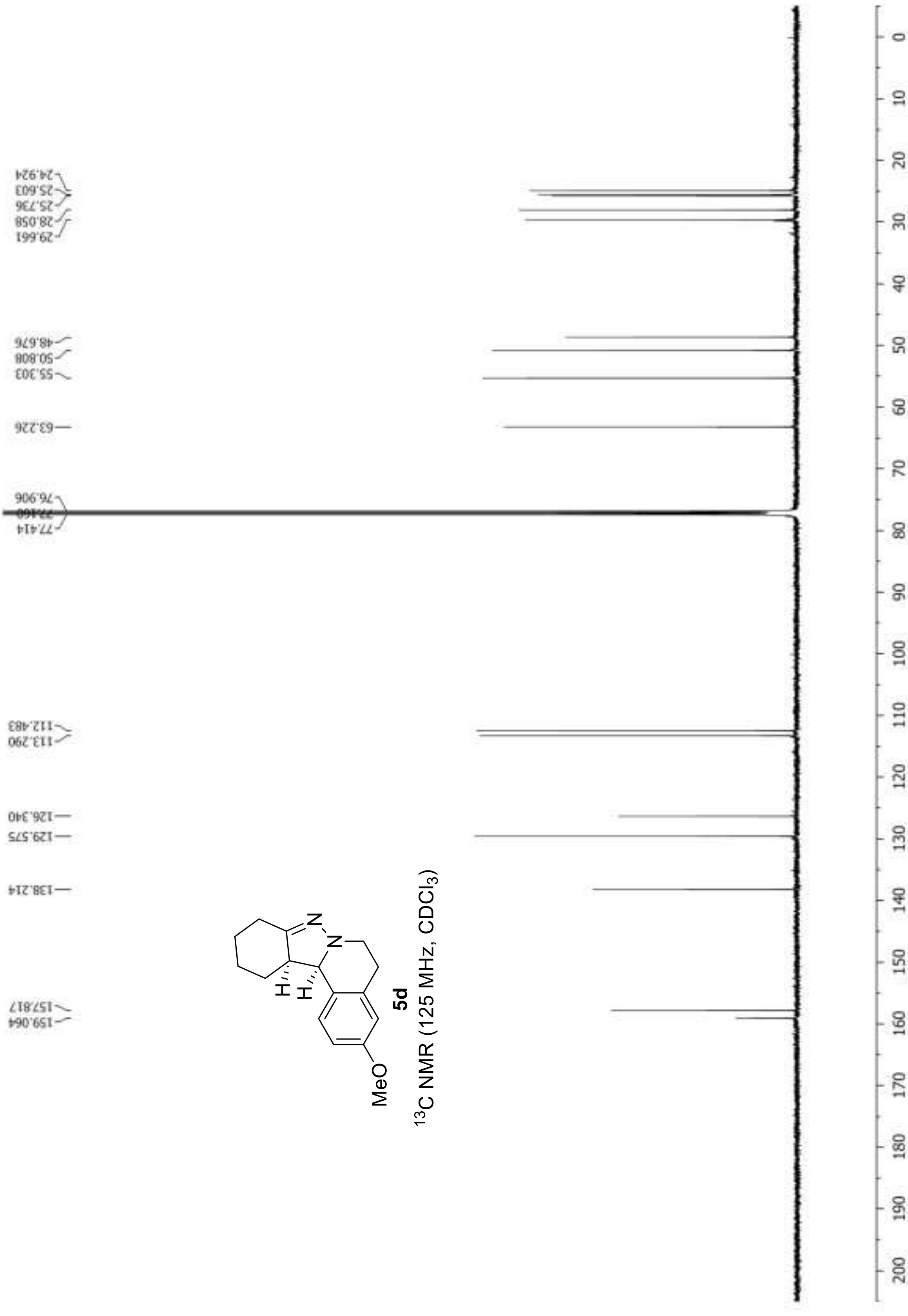
5c

^{13}C NMR (125 MHz, CDCl$_3$)



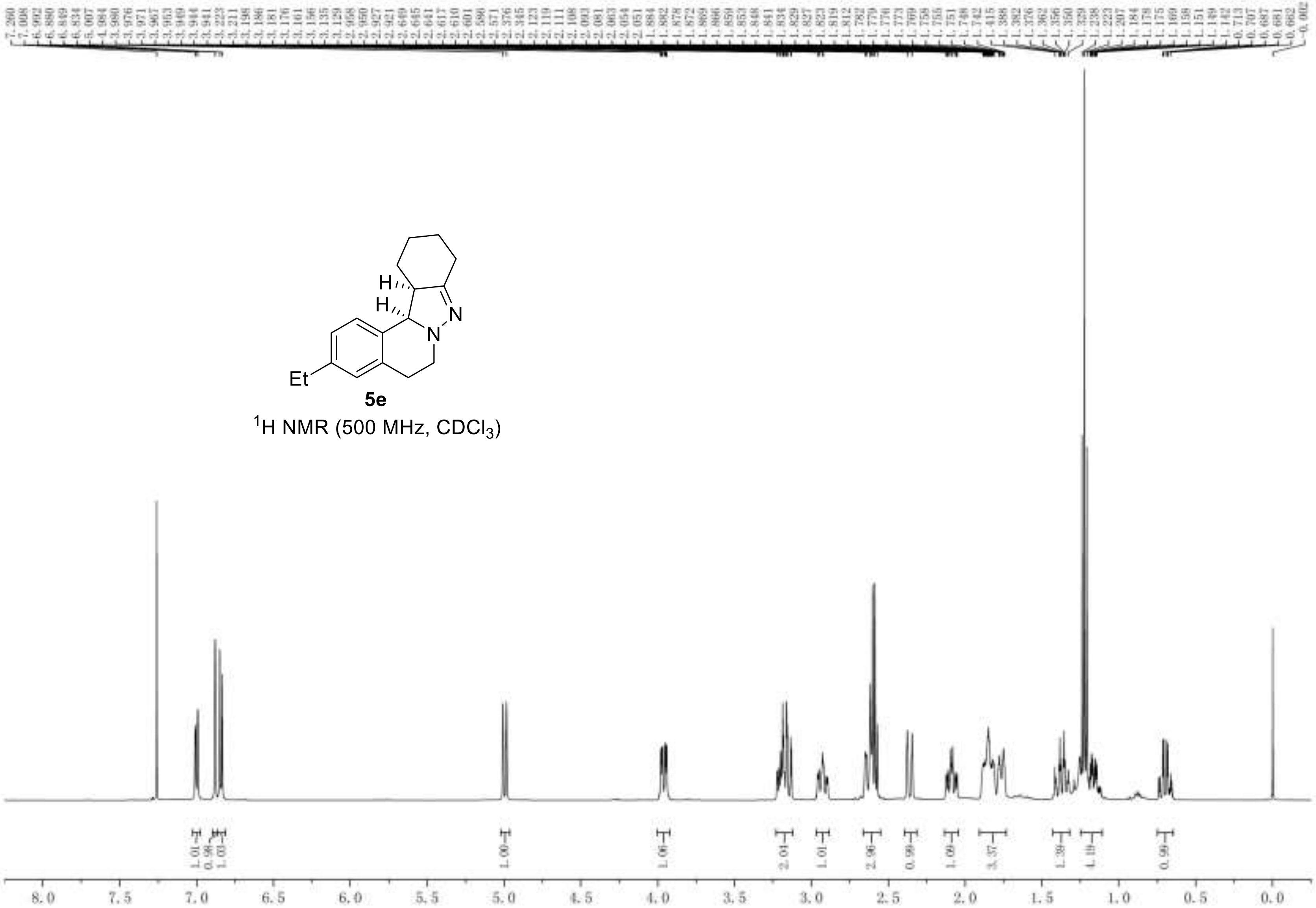
5d

^{1}H NMR (500 MHz, $CDCl_3$)



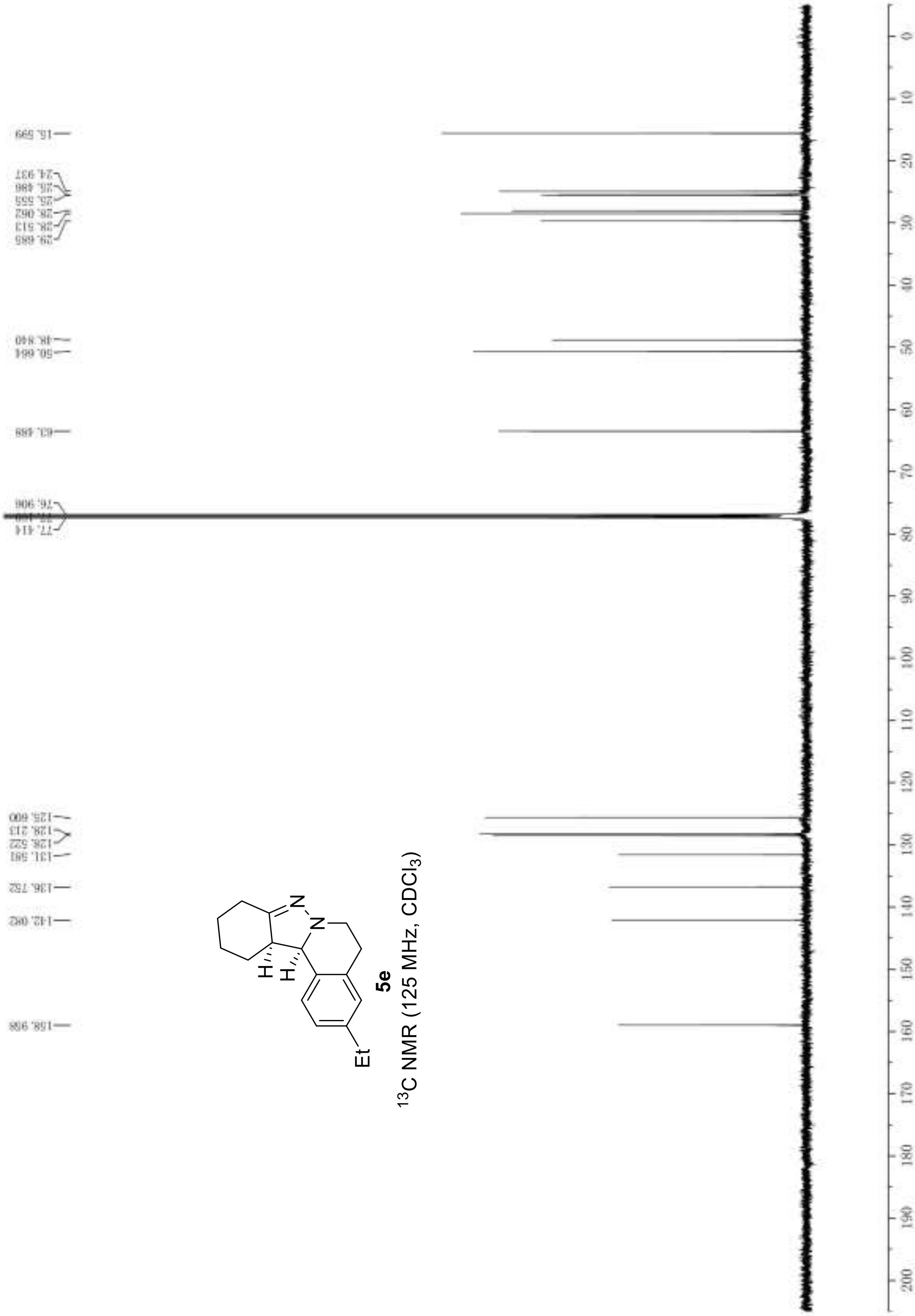
5d

^{13}C NMR (125 MHz, CDCl$_3$)



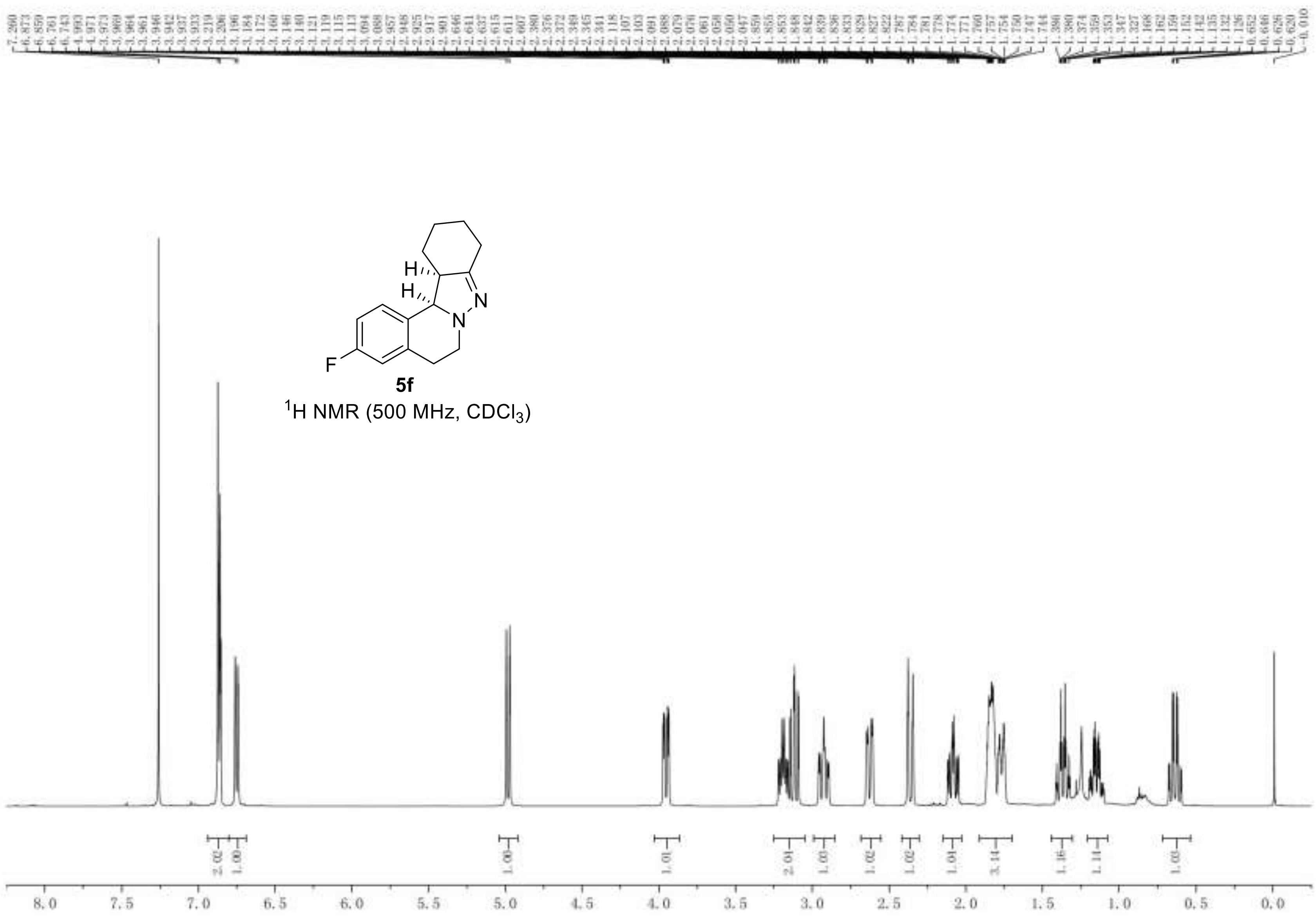
5e

^{1}H NMR (500 MHz, CDCl$_3$)



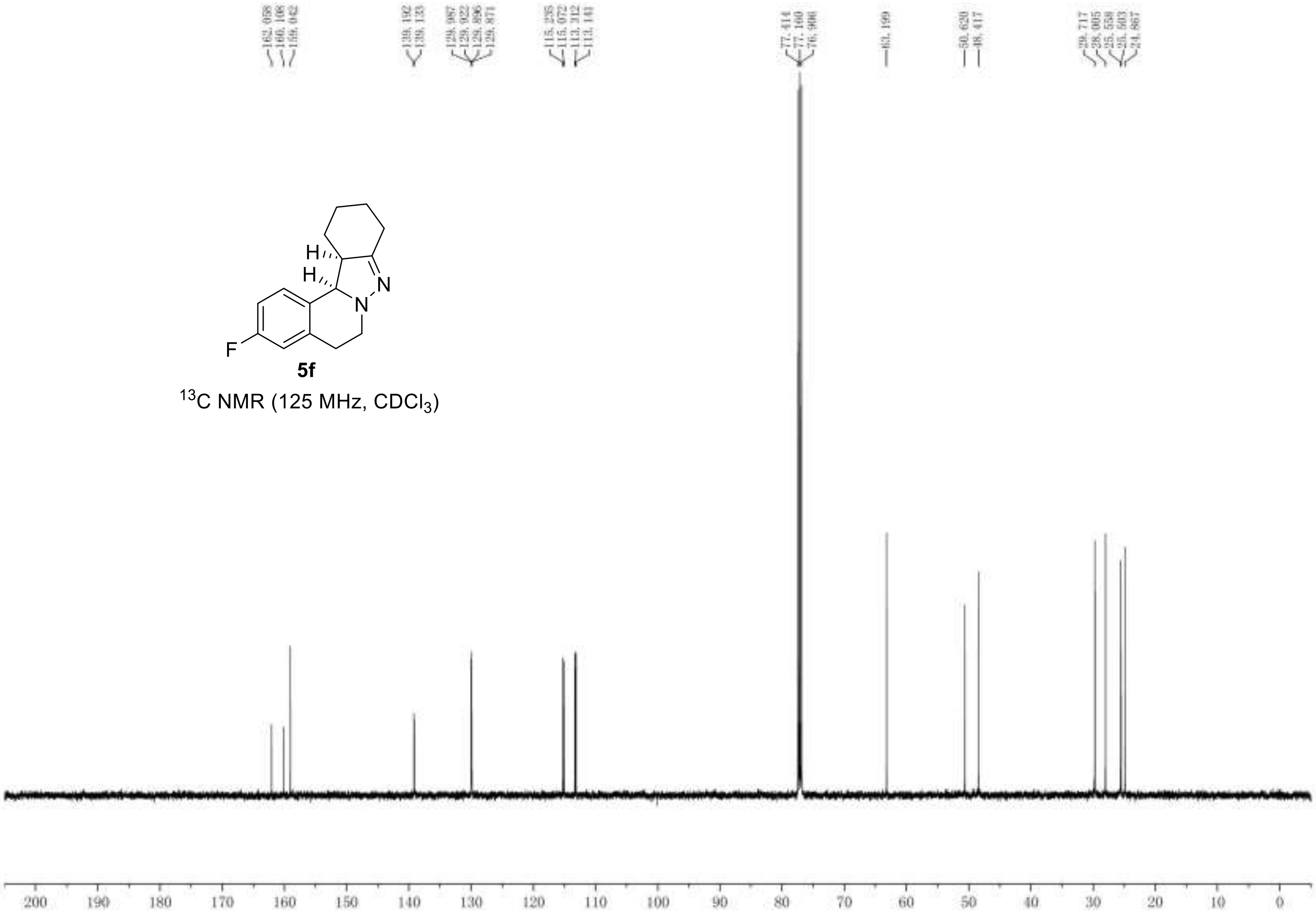
5e

^{13}C NMR (125 MHz, CDCl$_3$)



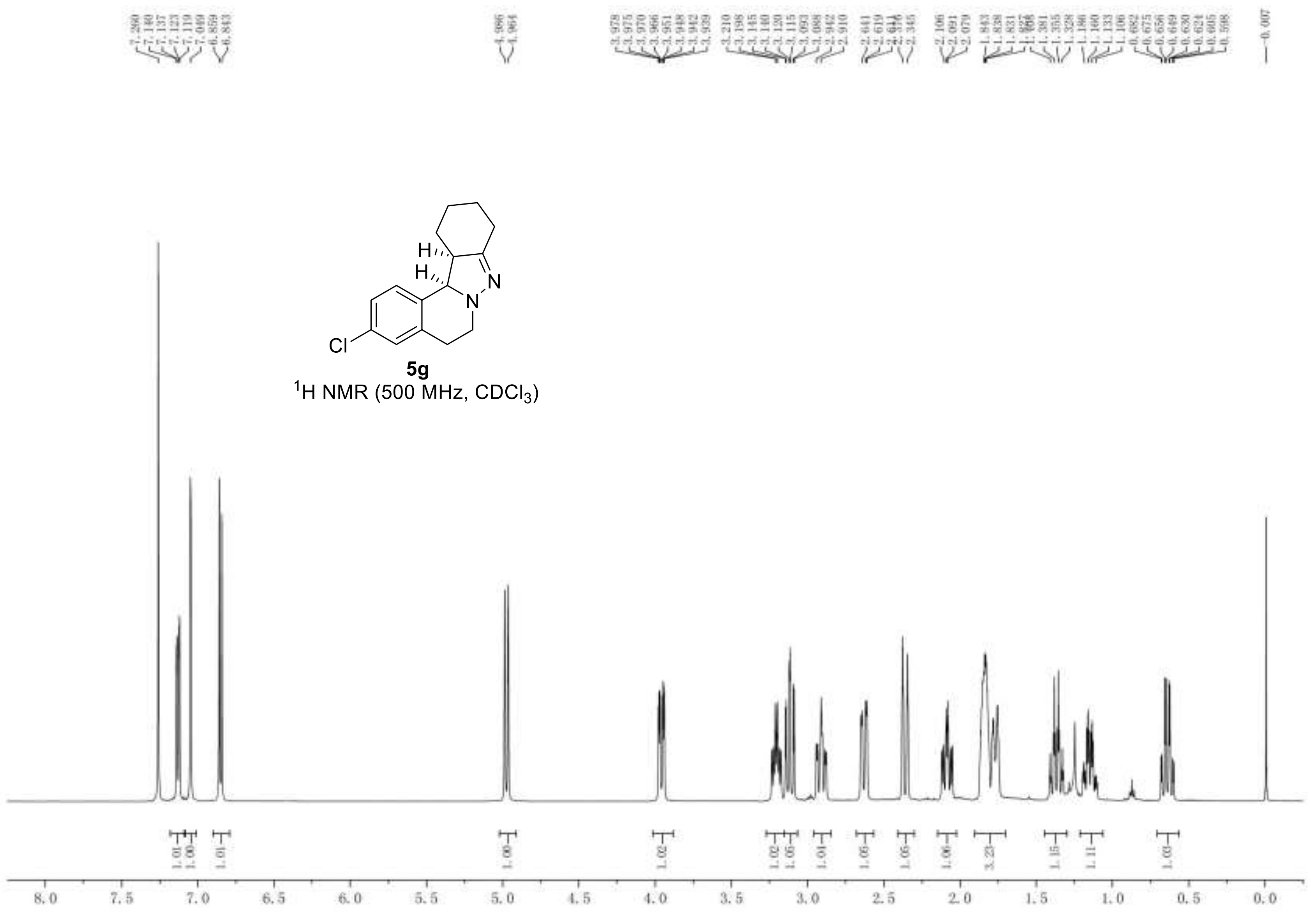
5f

^{1}H NMR (500 MHz, CDCl$_3$)



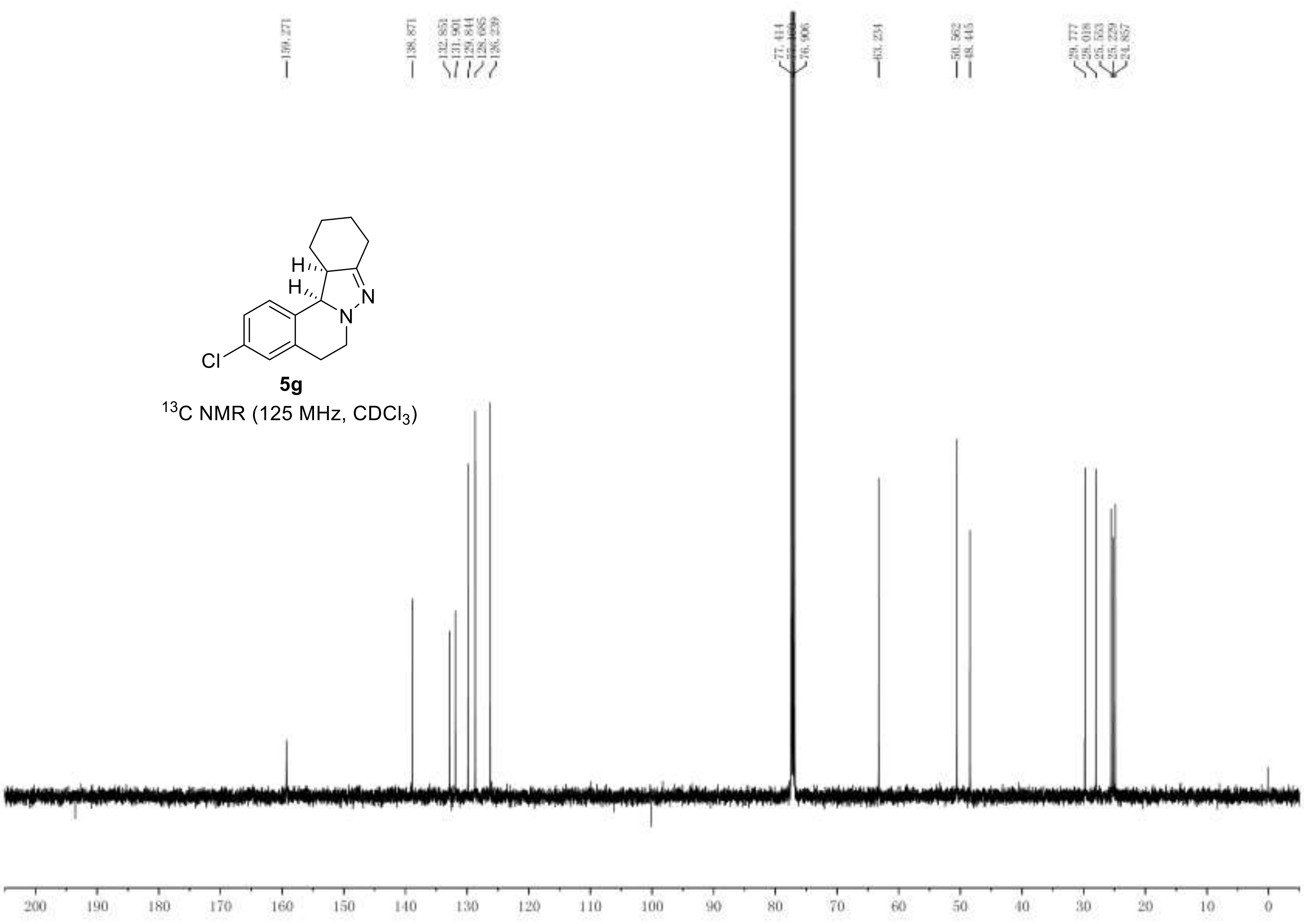
5f

^{13}C NMR (125 MHz, CDCl$_3$)



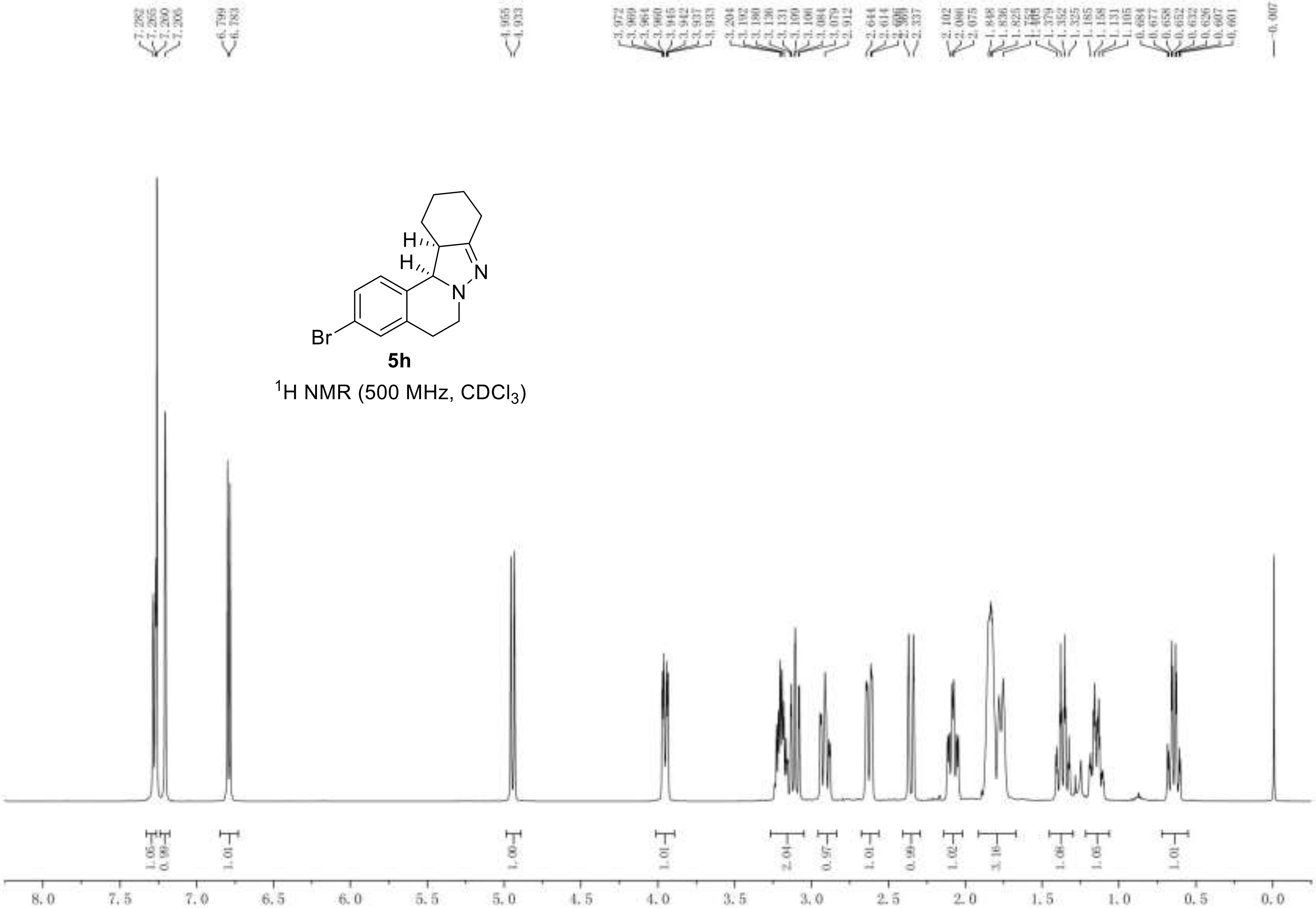
5g

^{1}H NMR (500 MHz, CDCl$_3$)



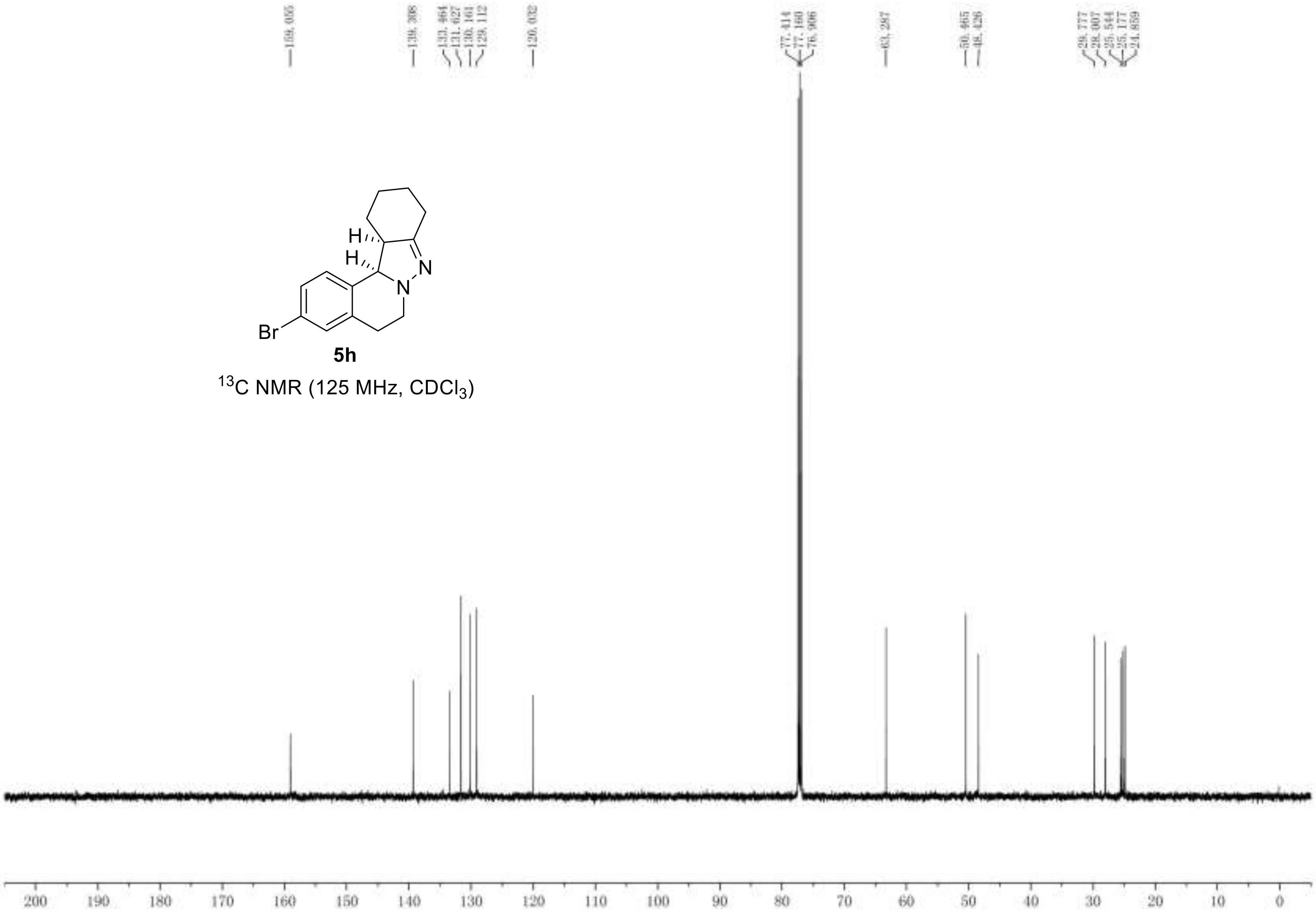
5g

^{13}C NMR (125 MHz, $CDCl_3$)



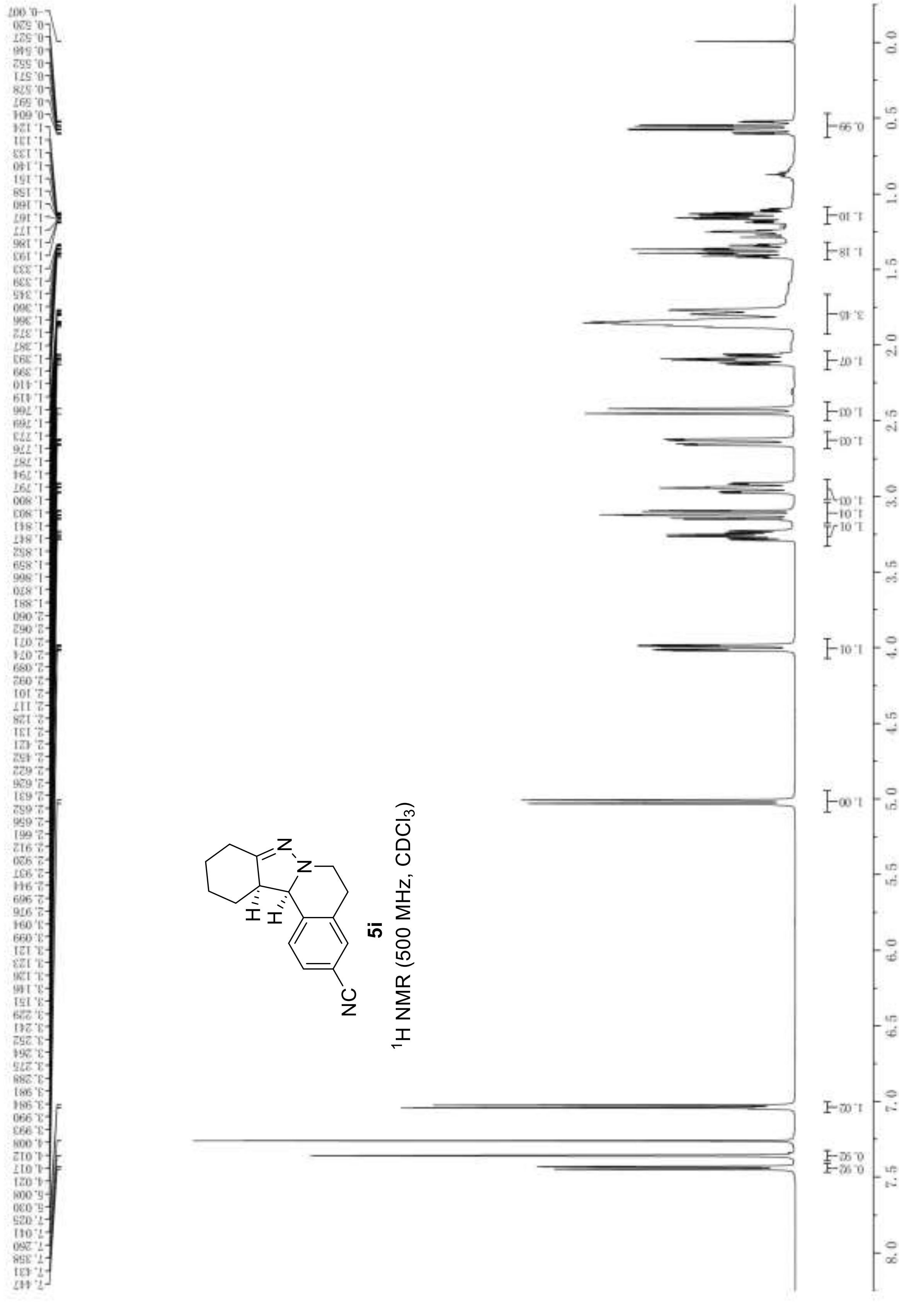
5h

^{1}H NMR (500 MHz, CDCl$_3$)



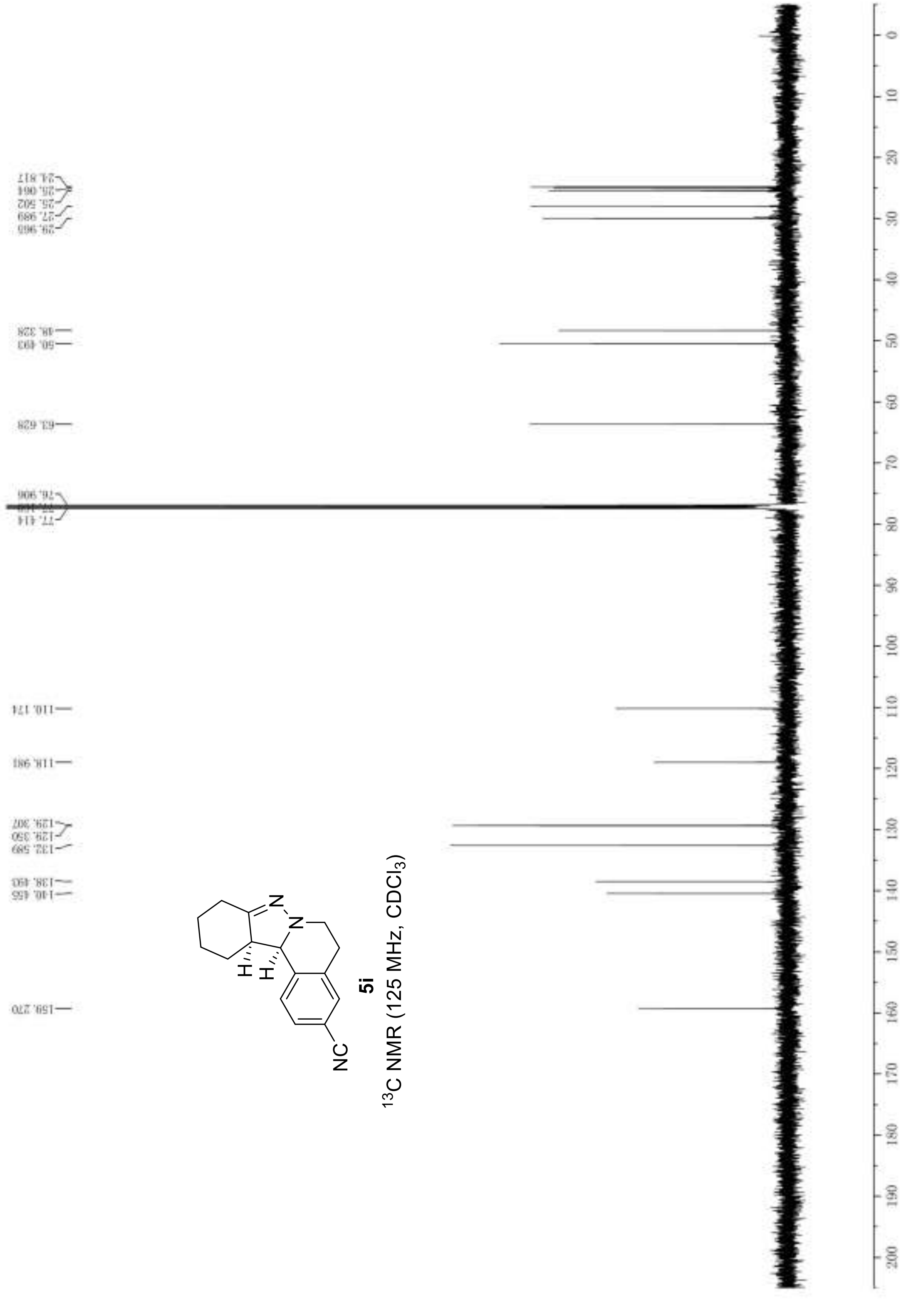
5h

^{13}C NMR (125 MHz, CDCl$_3$)



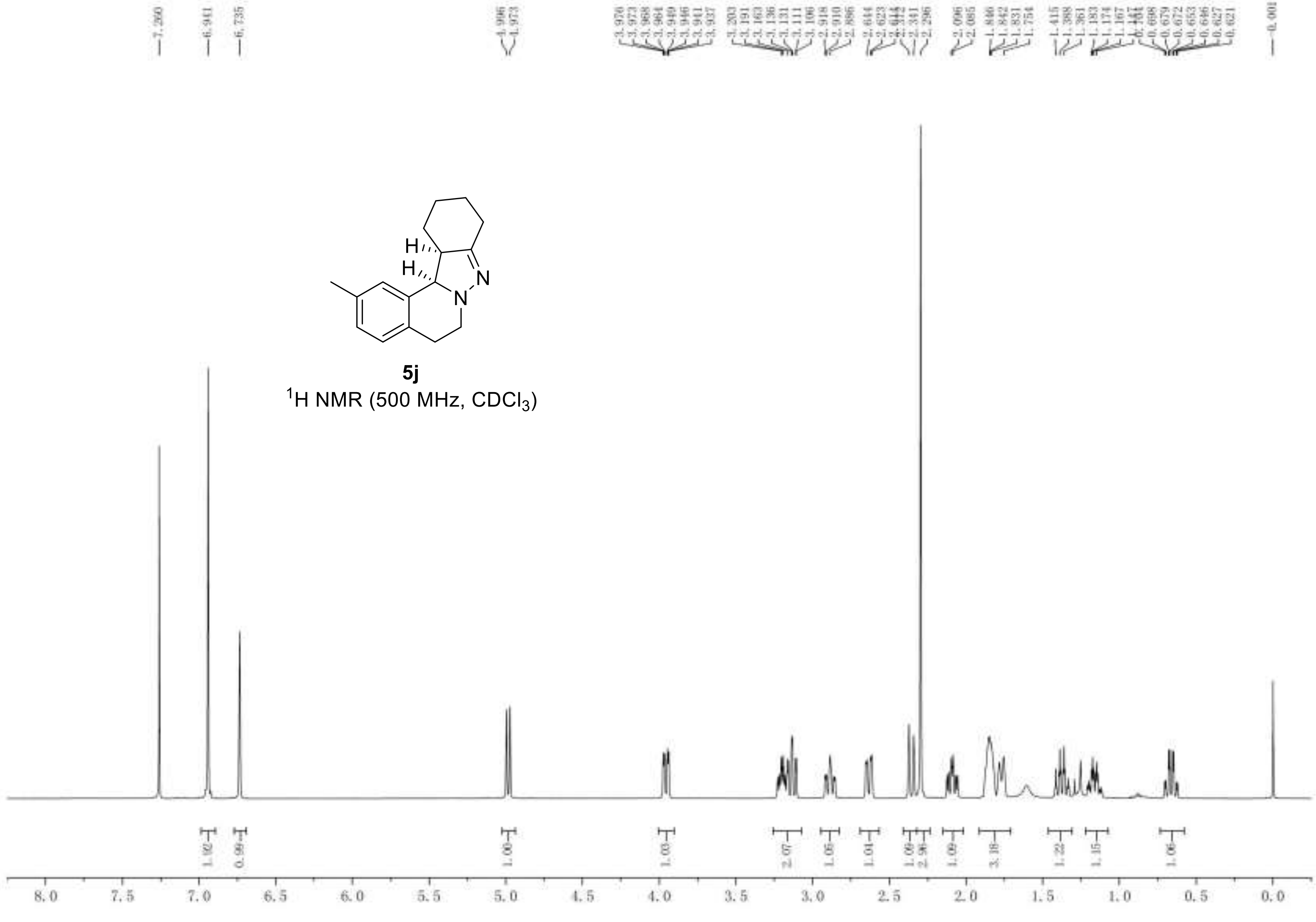
5i

^{1}H NMR (500 MHz, CDCl$_3$)



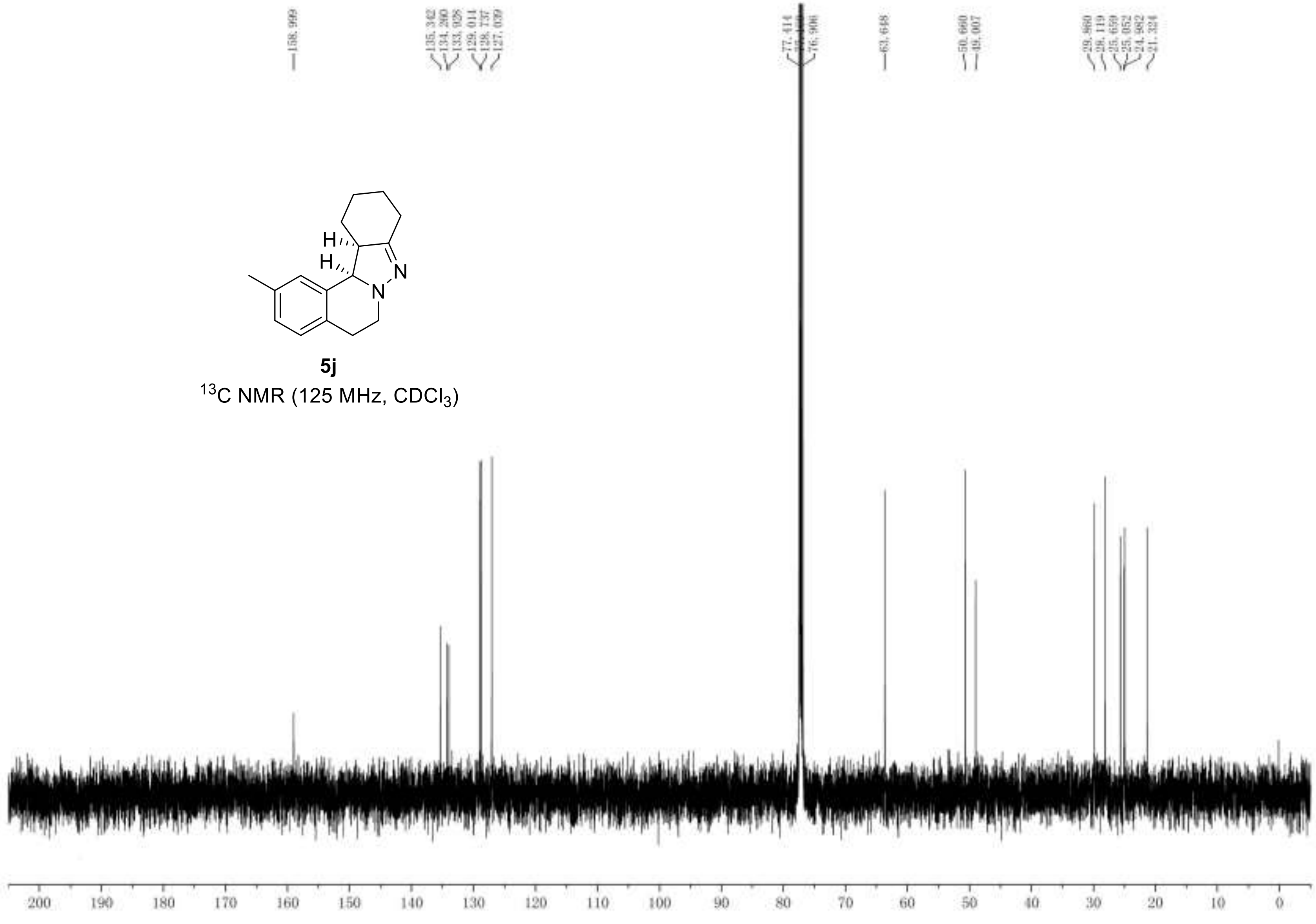
5i

^{13}C NMR (125 MHz, CDCl$_3$)



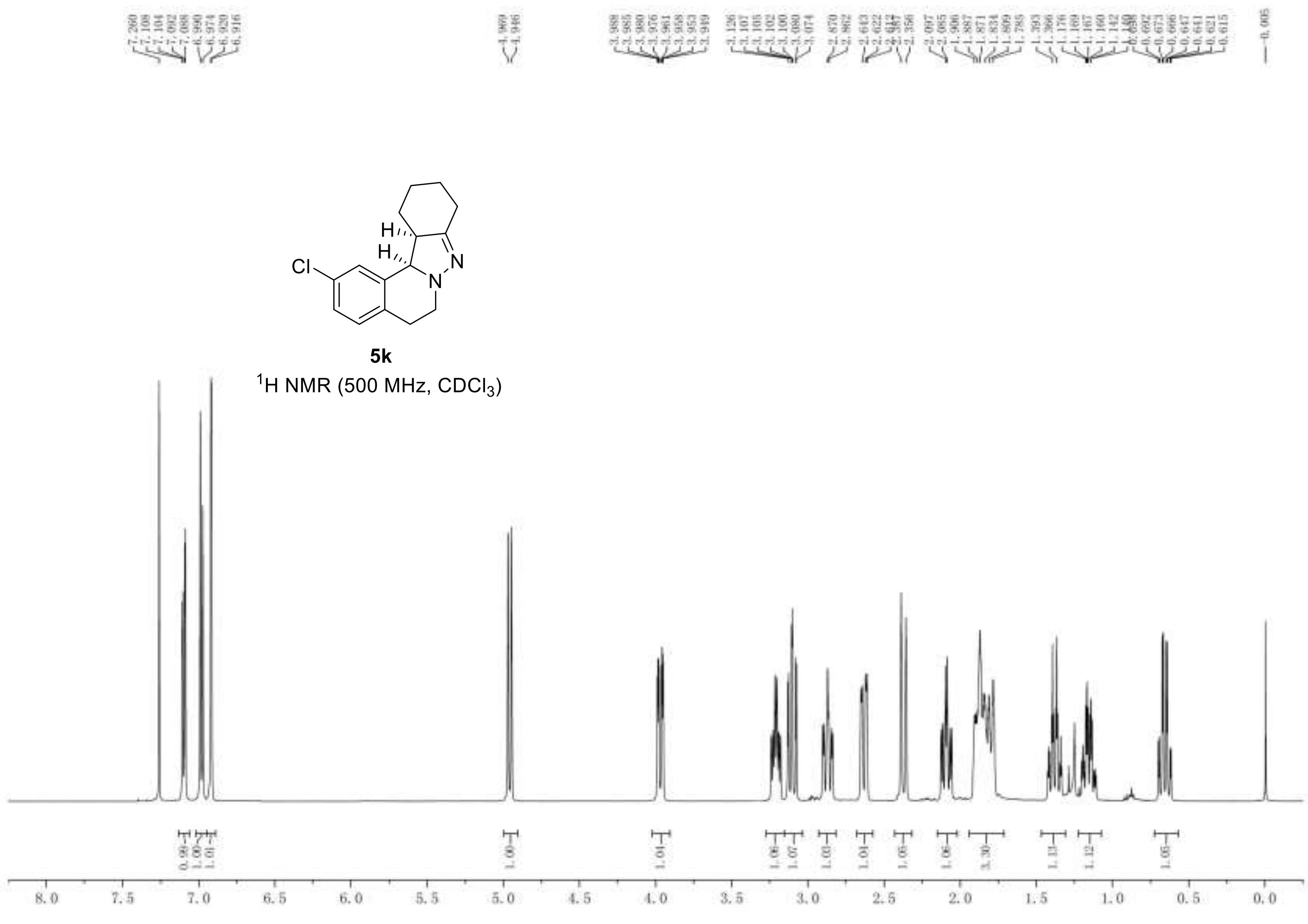
5j

^{1}H NMR (500 MHz, CDCl$_3$)



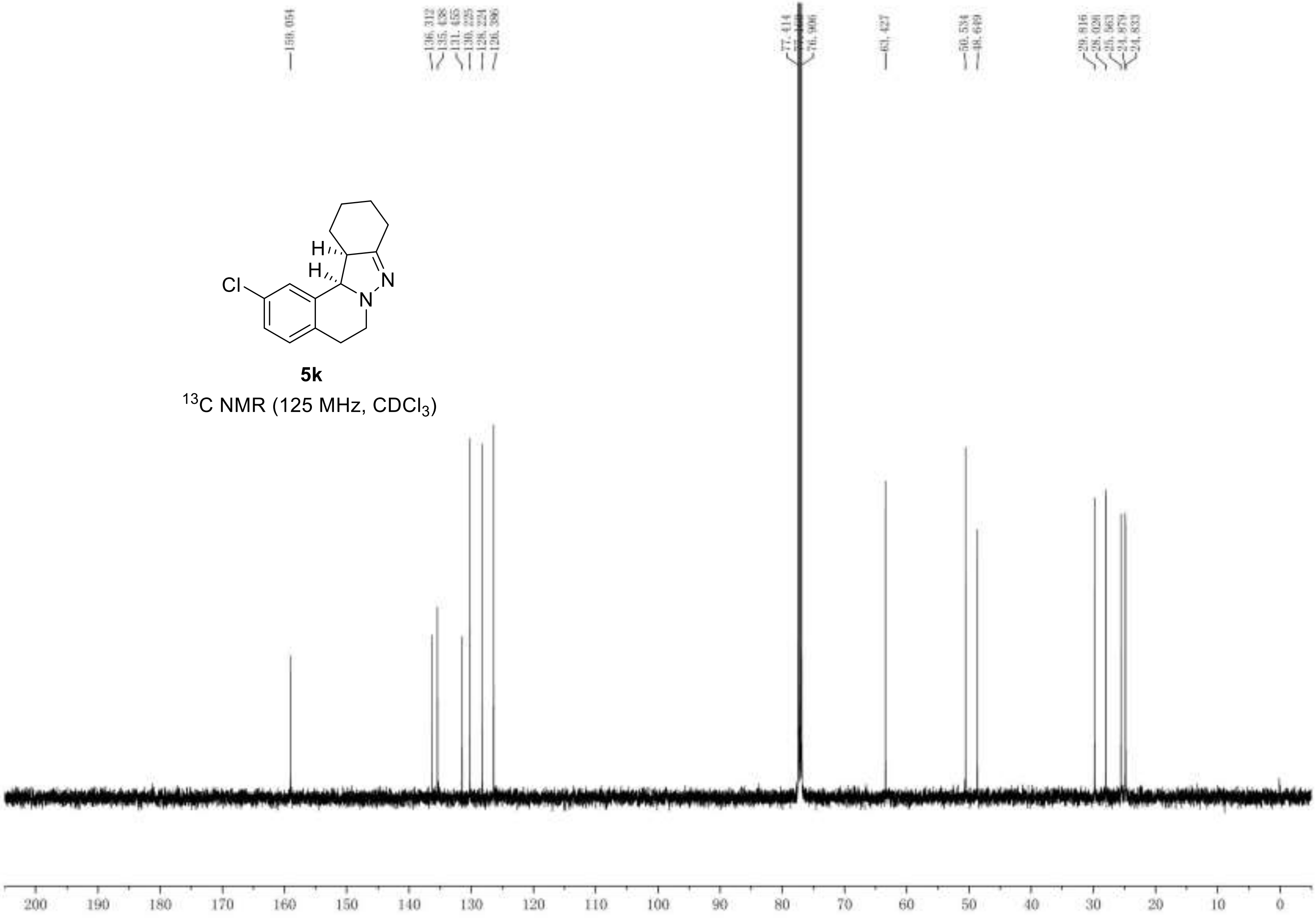
5j

^{13}C NMR (125 MHz, $CDCl_3$)



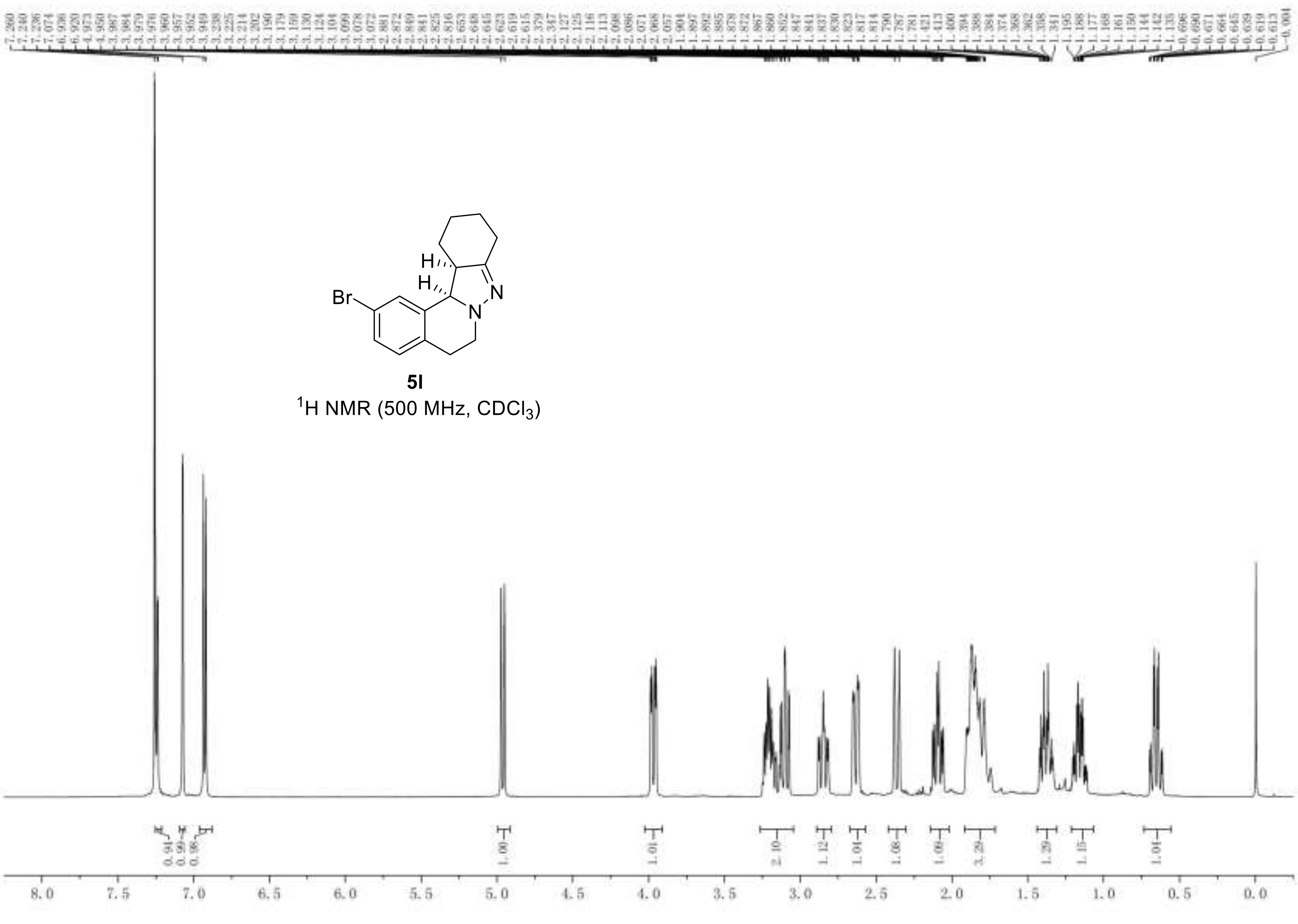
5k

^{1}H NMR (500 MHz, CDCl$_3$)



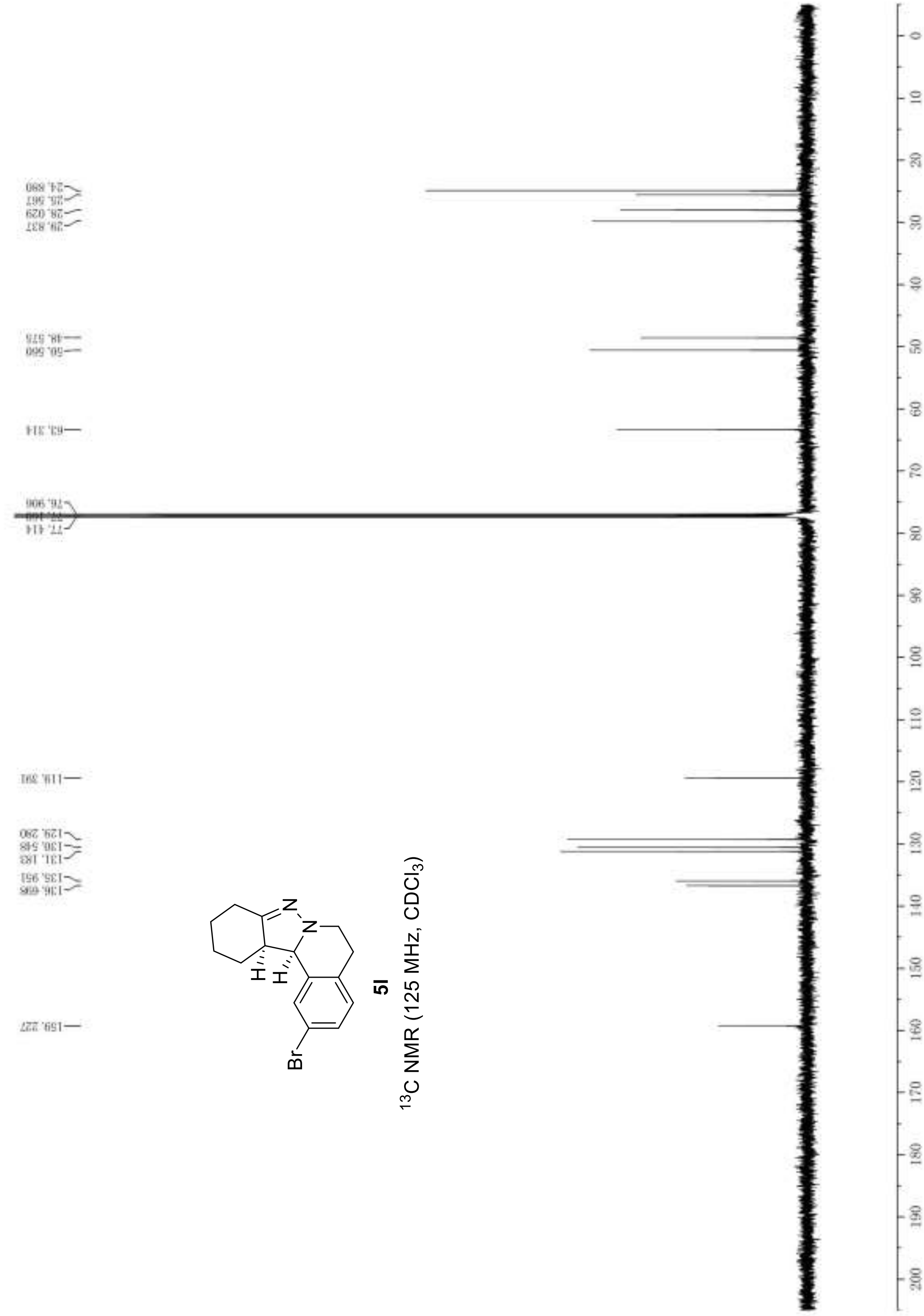
5k

^{13}C NMR (125 MHz, CDCl$_3$)



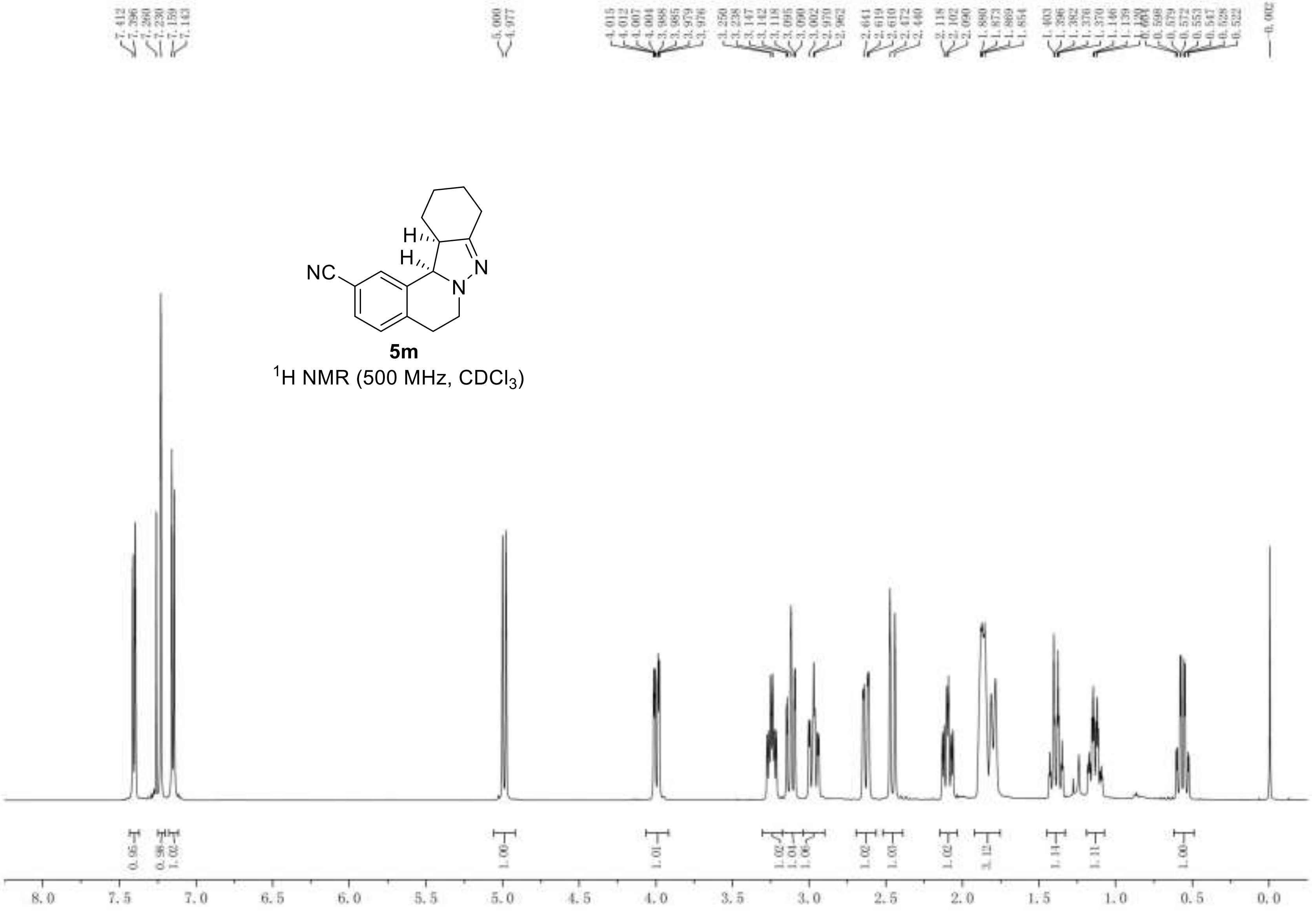
5l

^{1}H NMR (500 MHz, CDCl$_3$)



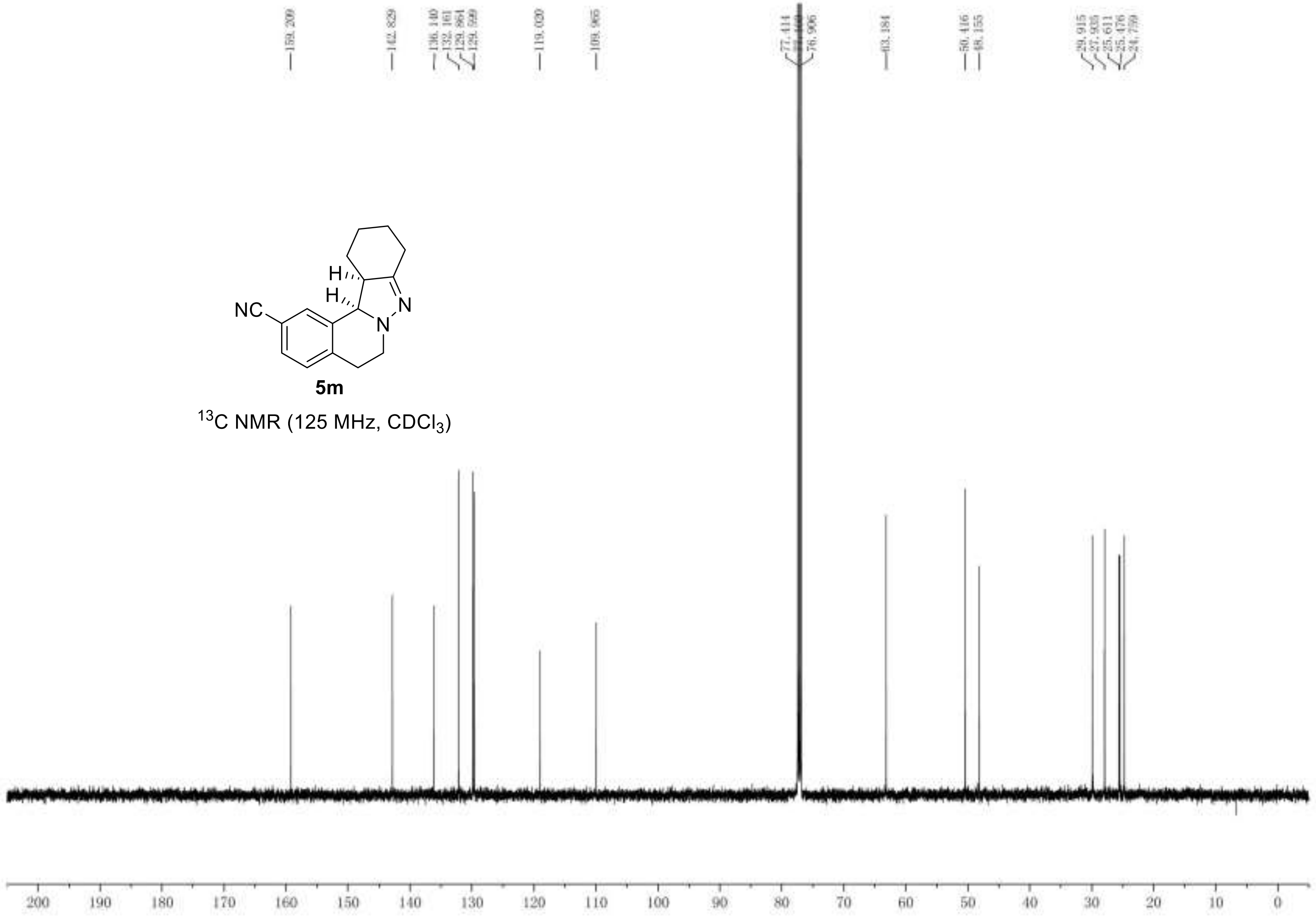
5l

^{13}C NMR (125 MHz, CDCl$_3$)



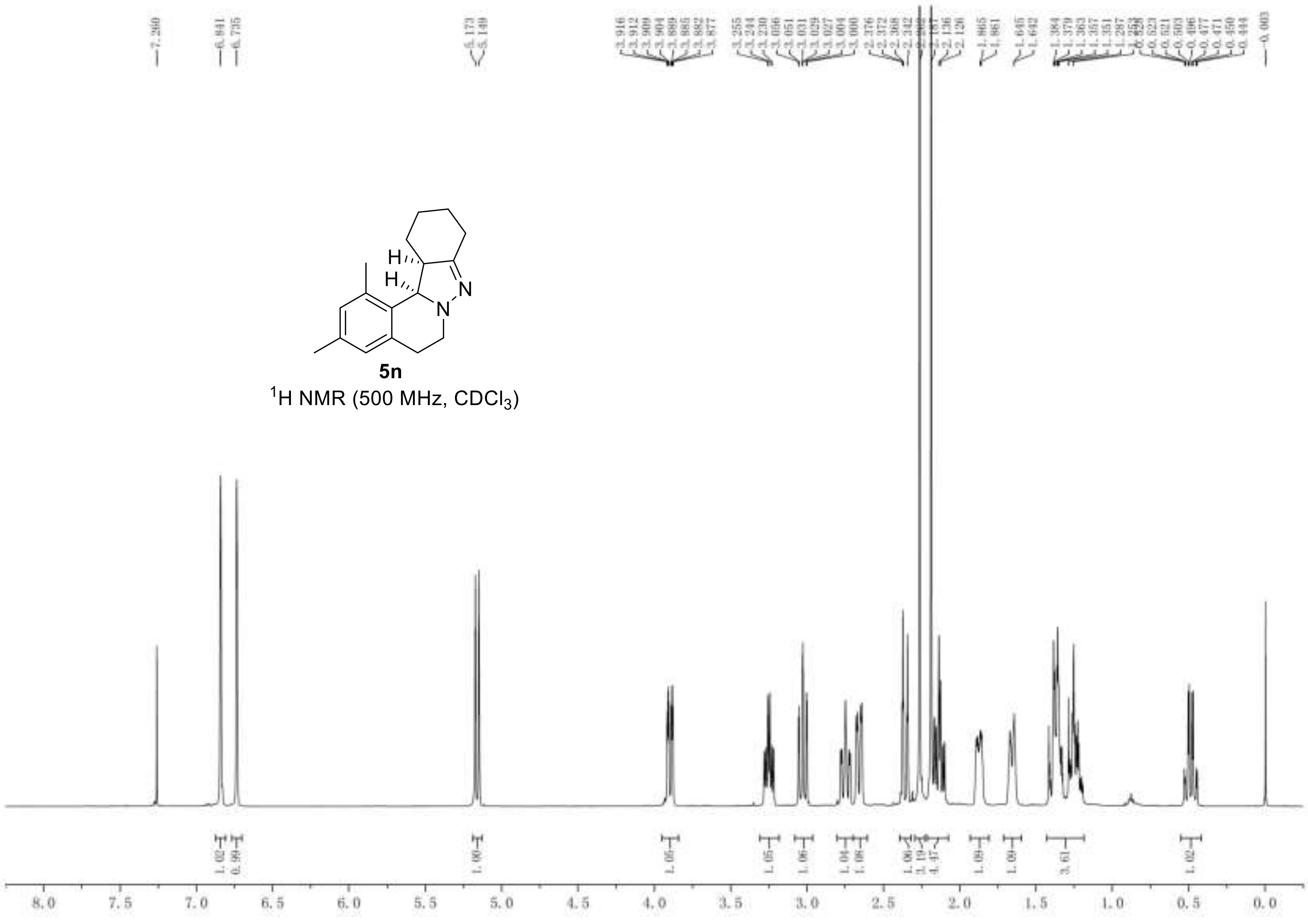
5m

^{1}H NMR (500 MHz, CDCl$_3$)



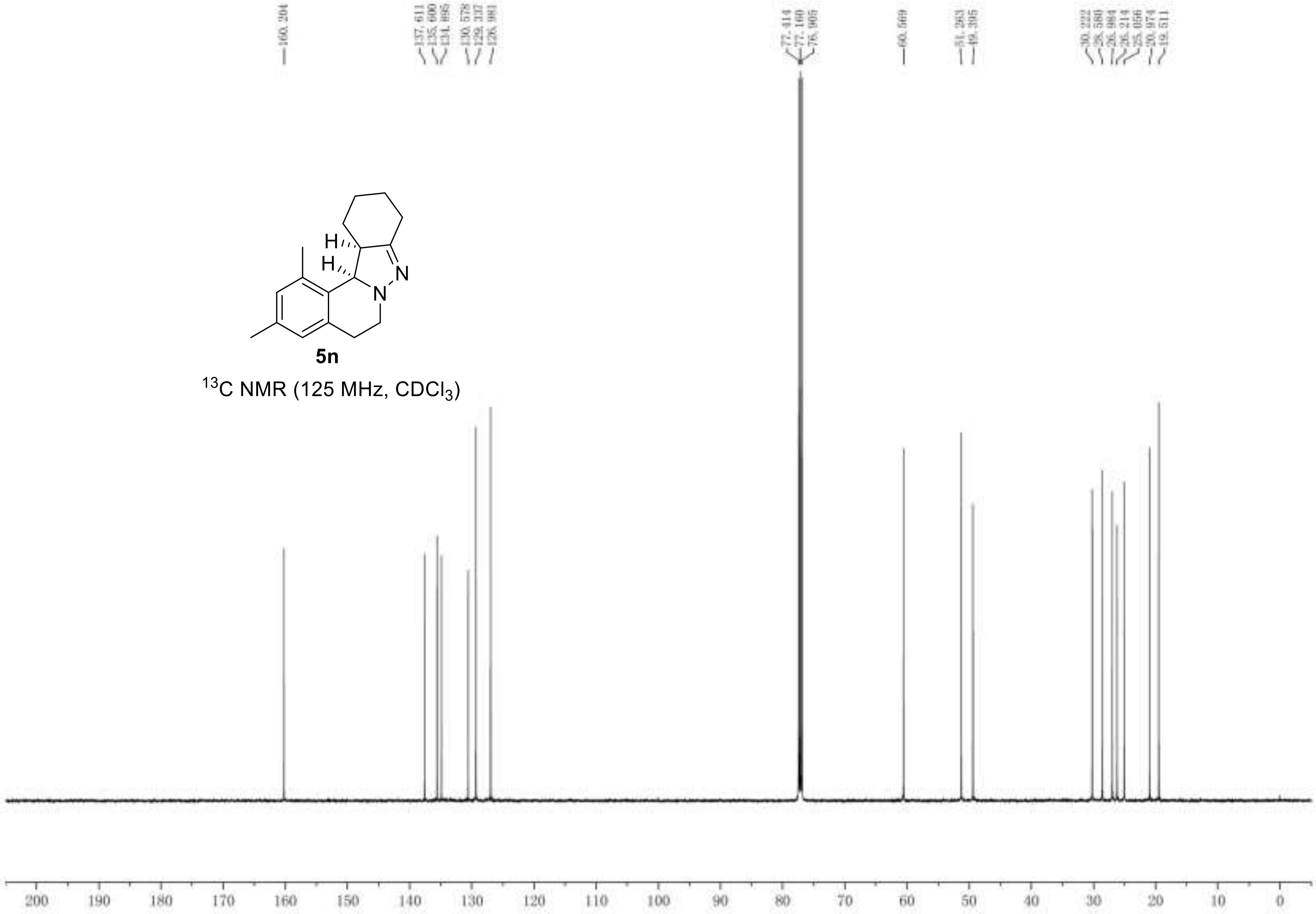
5m

^{13}C NMR (125 MHz, $CDCl_3$)



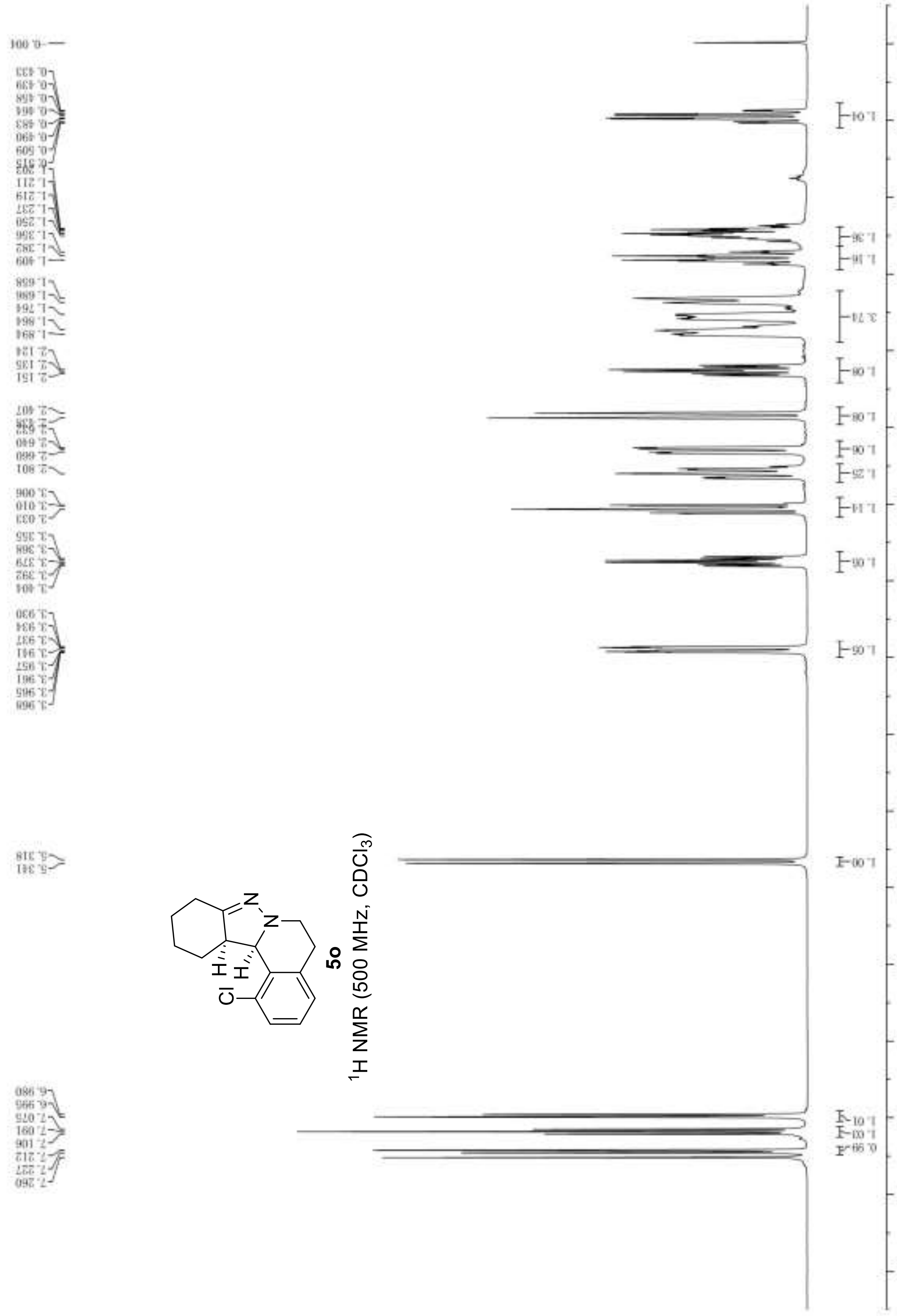
5n

^{1}H NMR (500 MHz, CDCl$_3$)



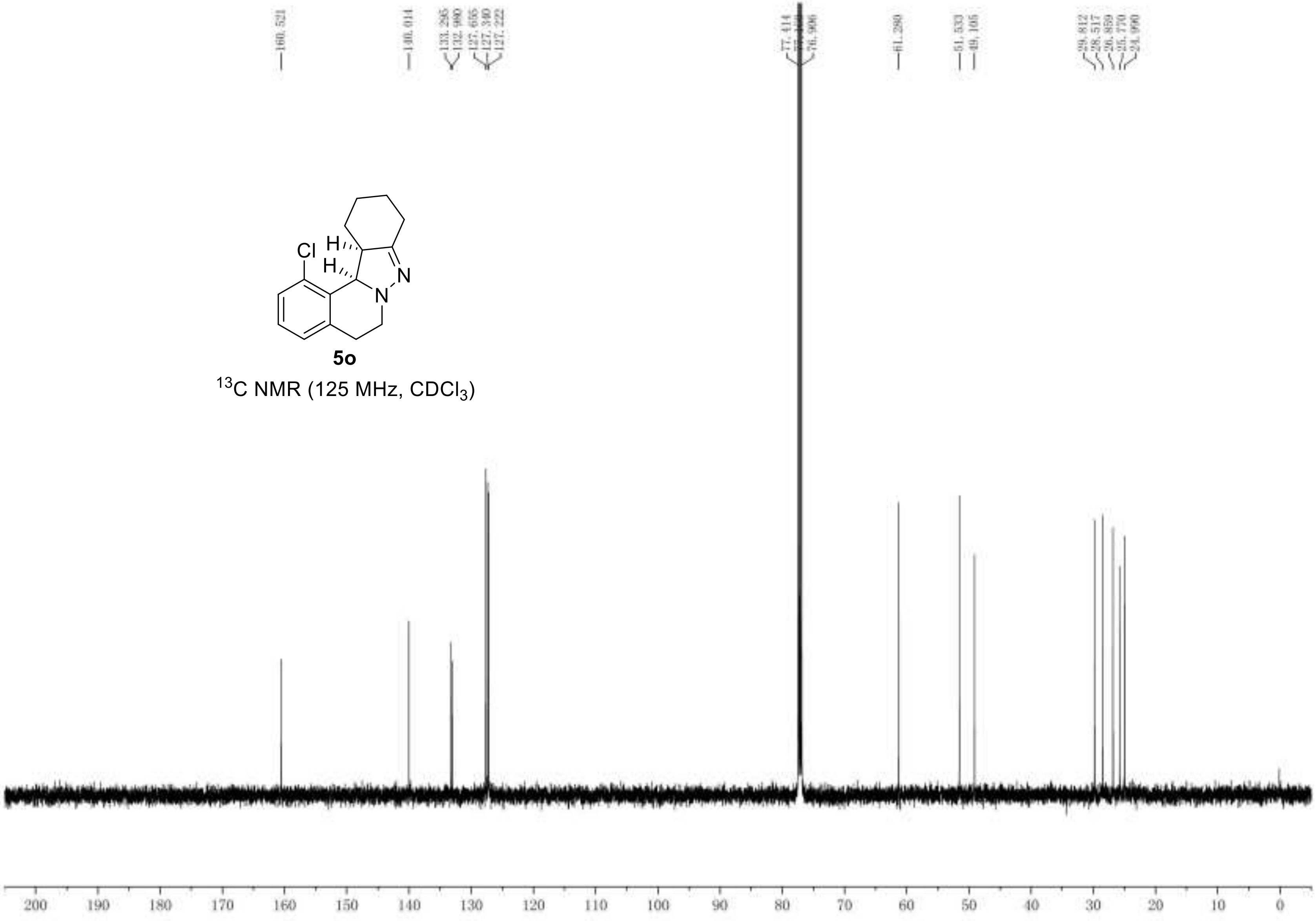
5n

^{13}C NMR (125 MHz, CDCl$_3$)



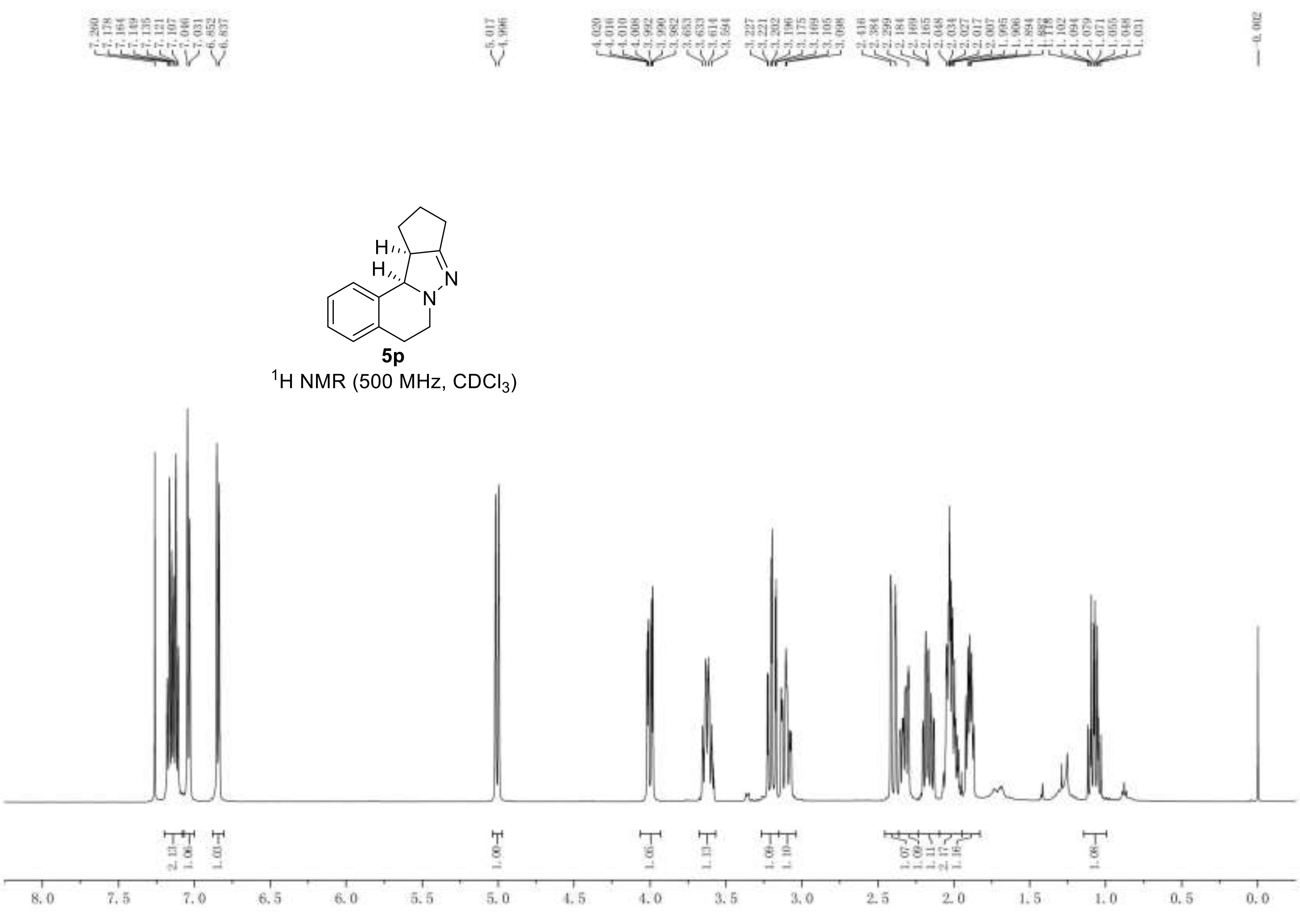
5o

^{1}H NMR (500 MHz, CDCl$_3$)



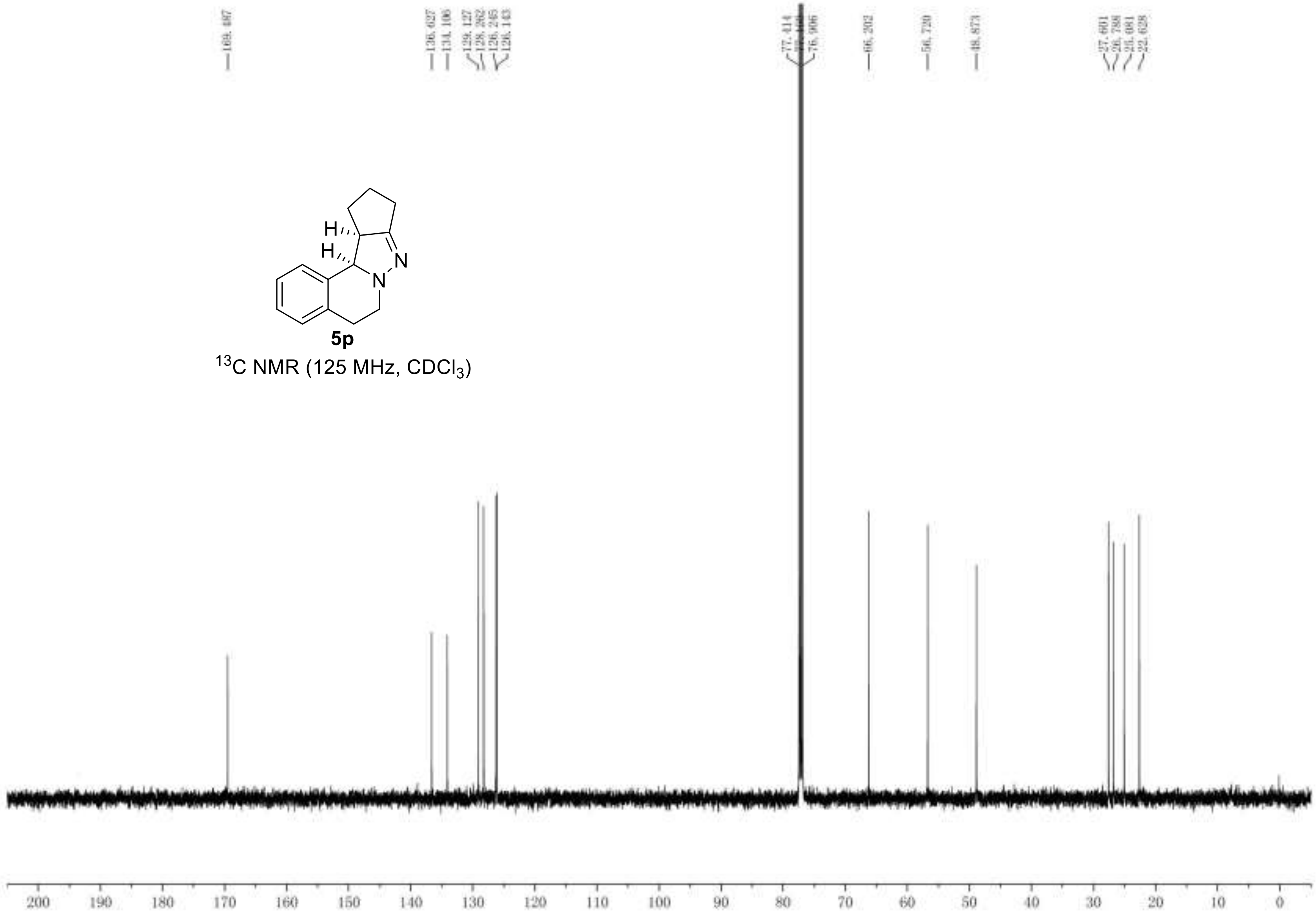
5o

^{13}C NMR (125 MHz, CDCl$_3$)



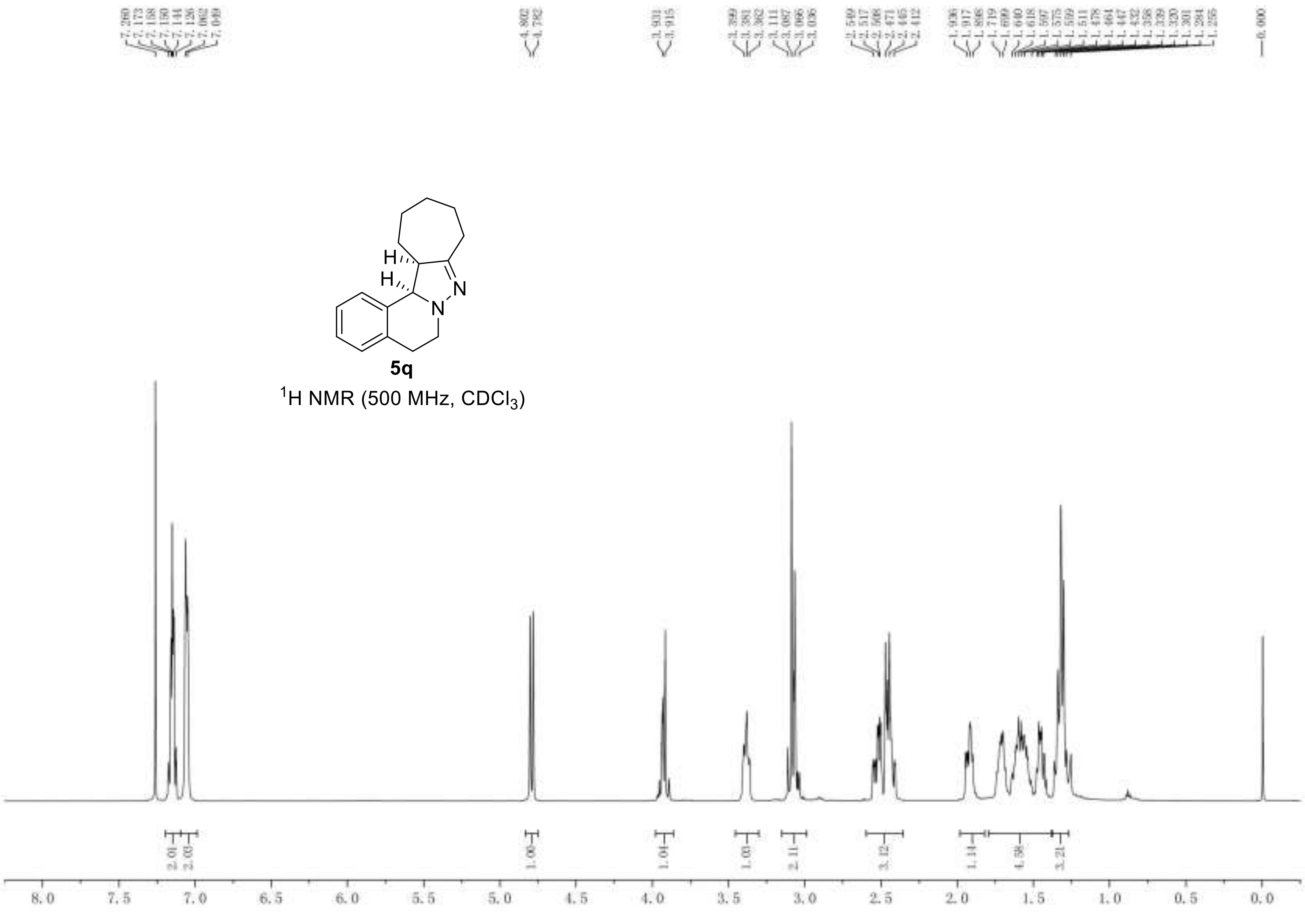
5p

^{1}H NMR (500 MHz, CDCl$_3$)



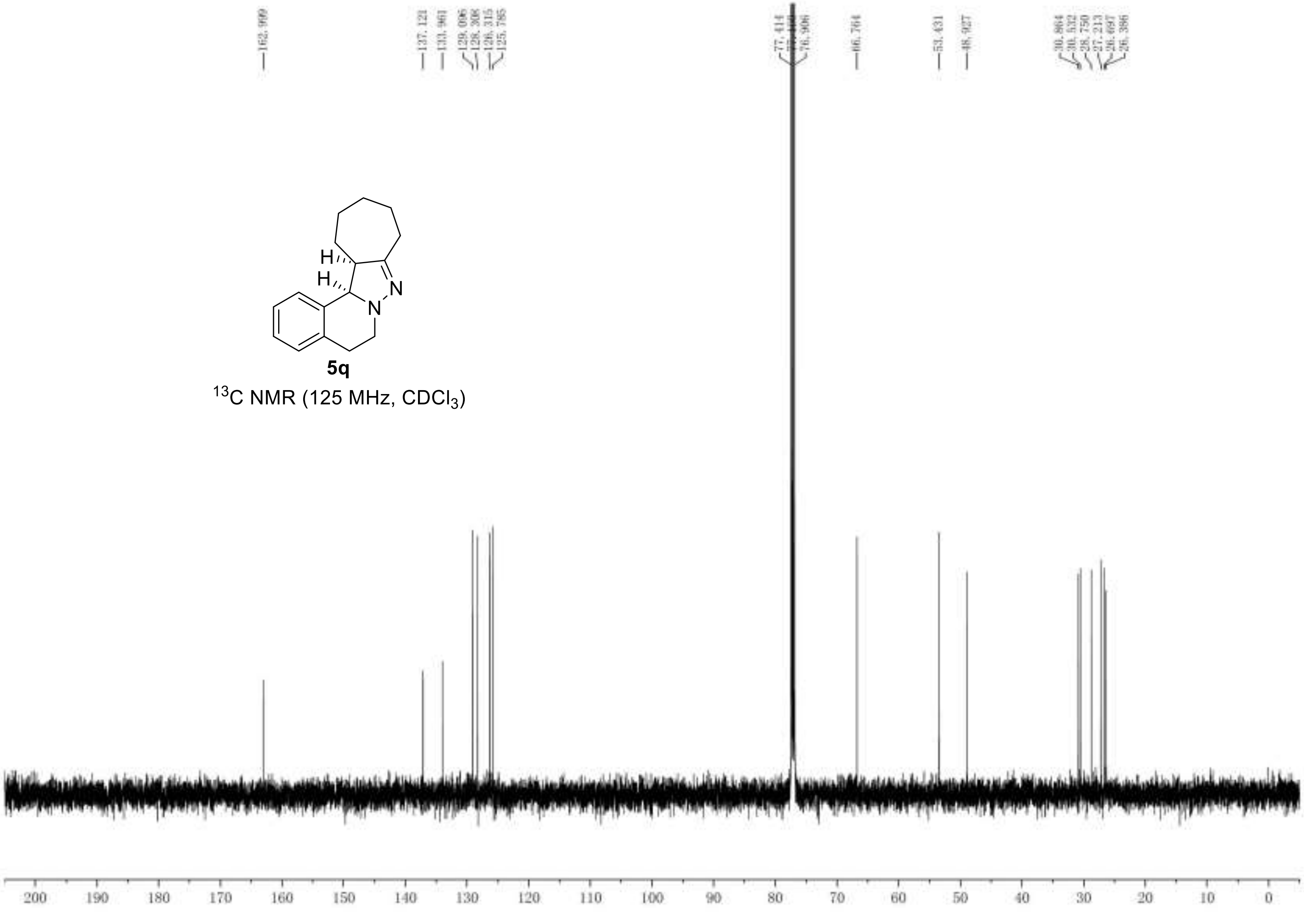
5p

^{13}C NMR (125 MHz, CDCl$_3$)



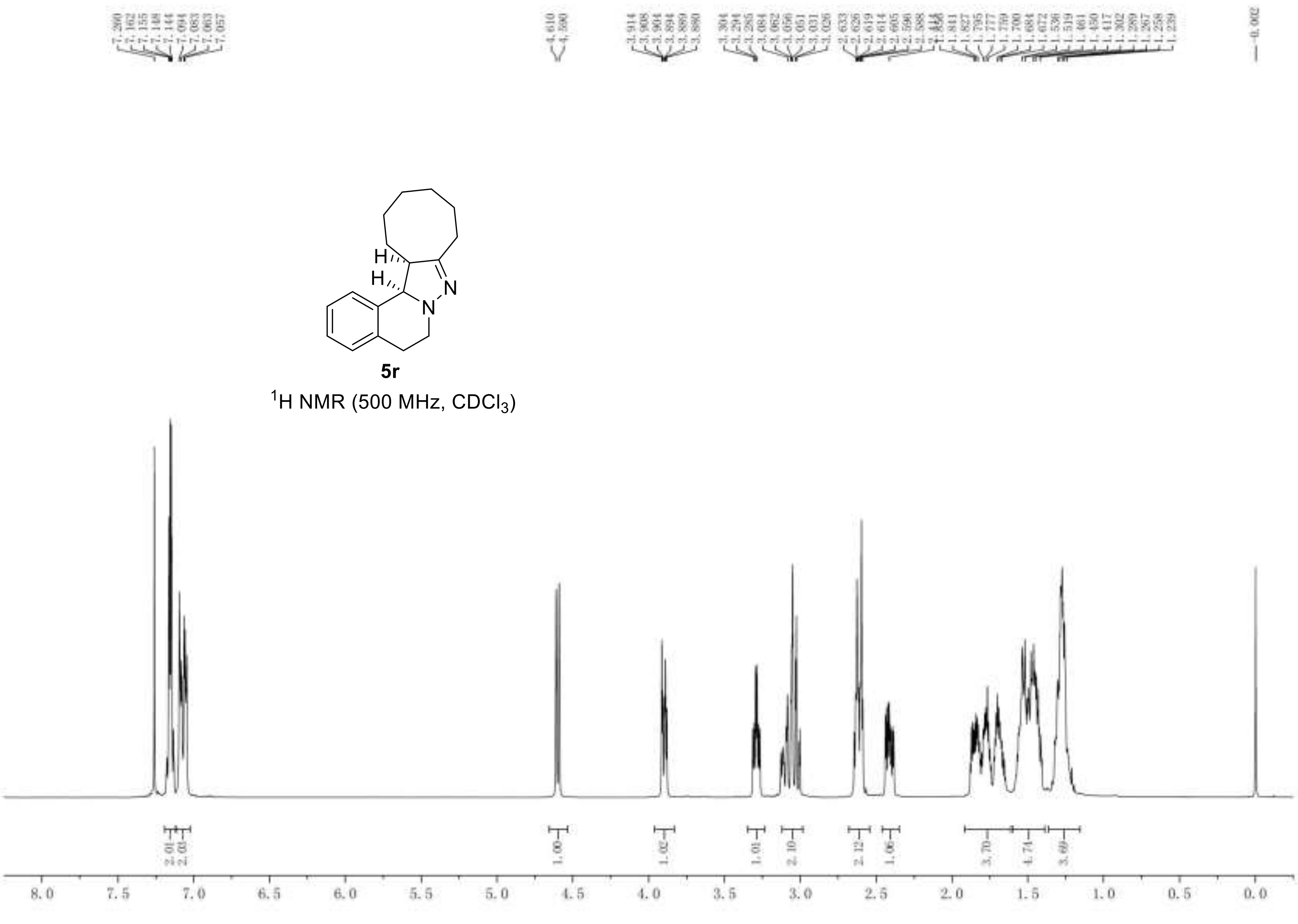
5q

^{1}H NMR (500 MHz, CDCl$_3$)



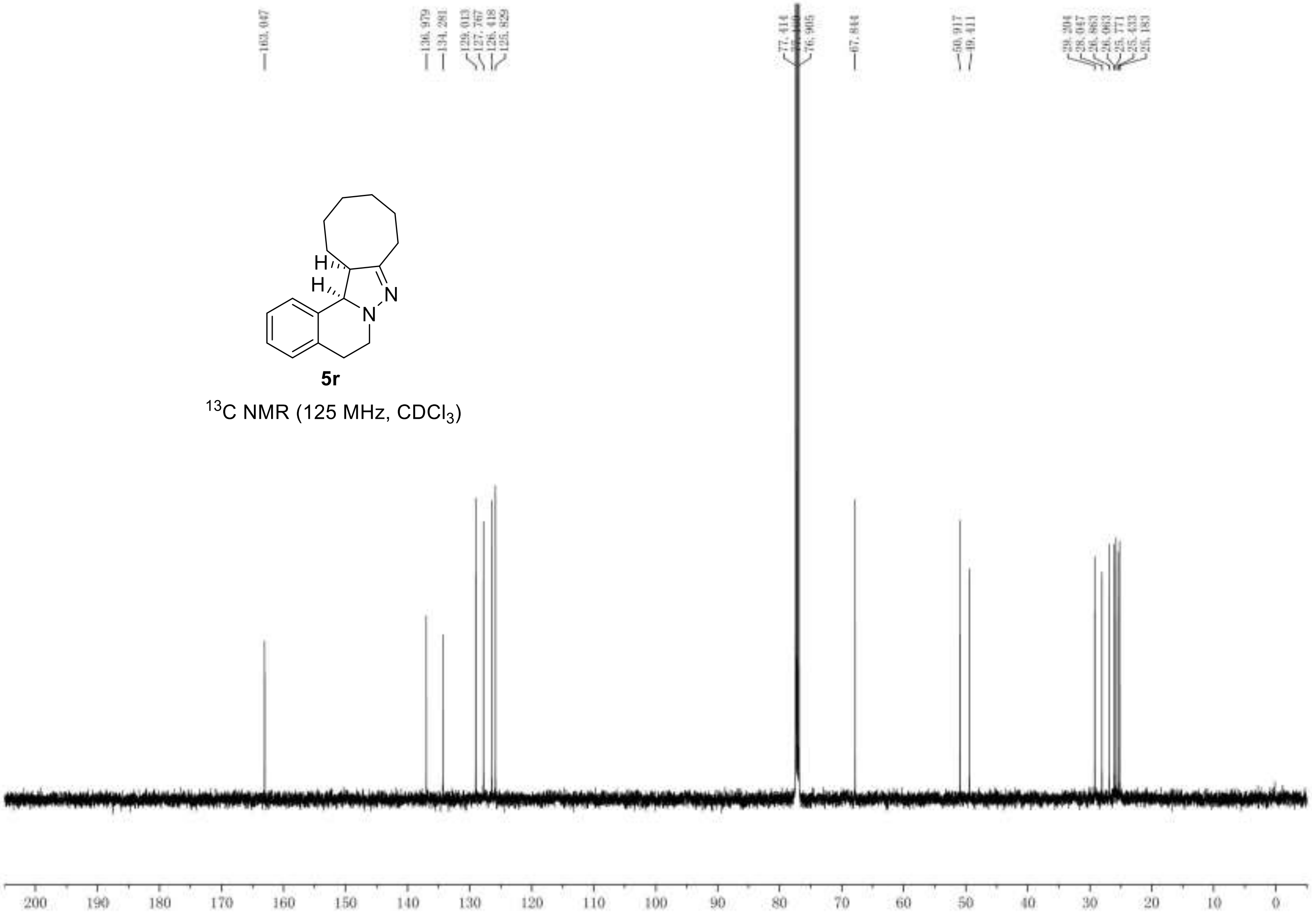
5q

^{13}C NMR (125 MHz, CDCl$_3$)



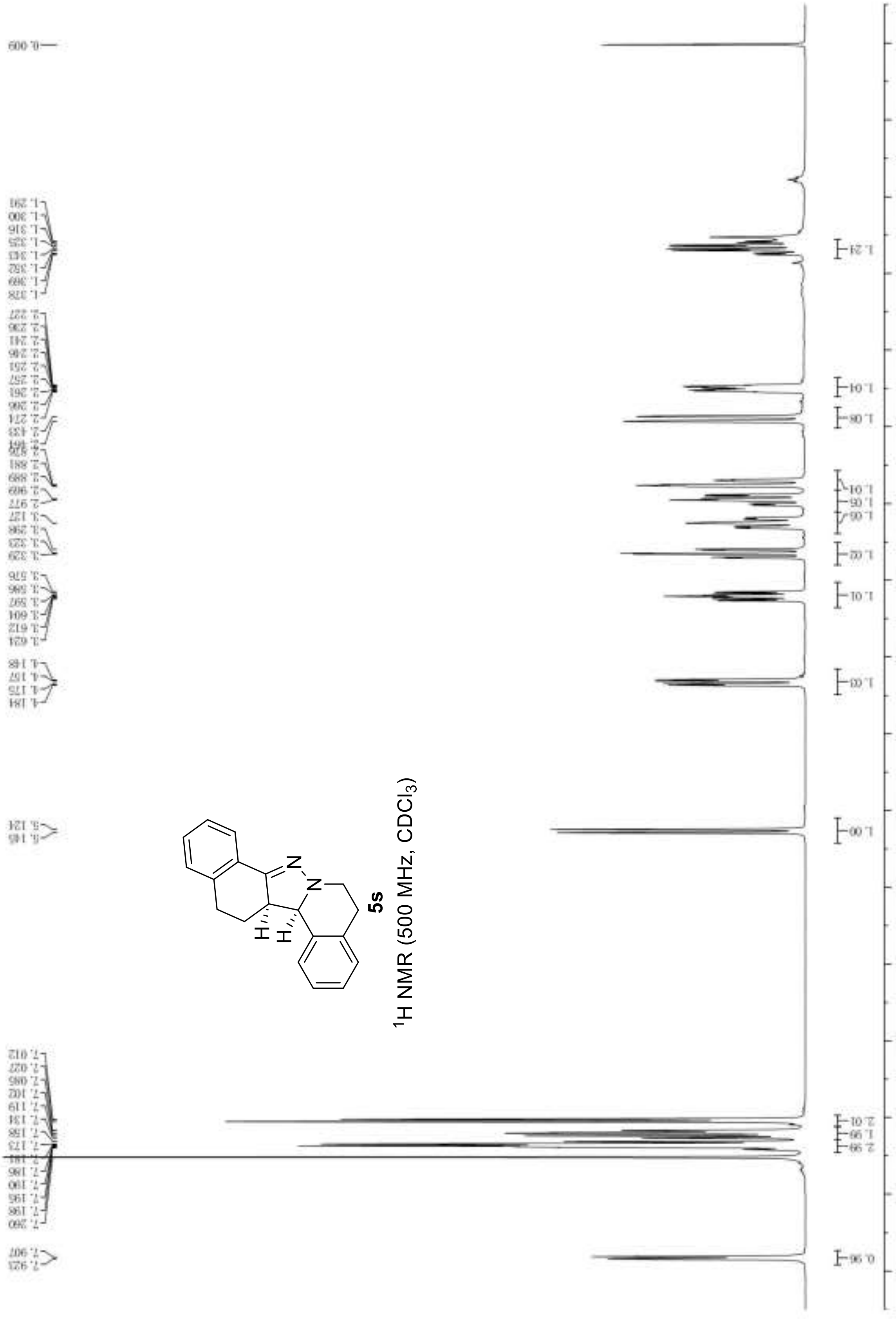
5r

^{1}H NMR (500 MHz, CDCl$_3$)



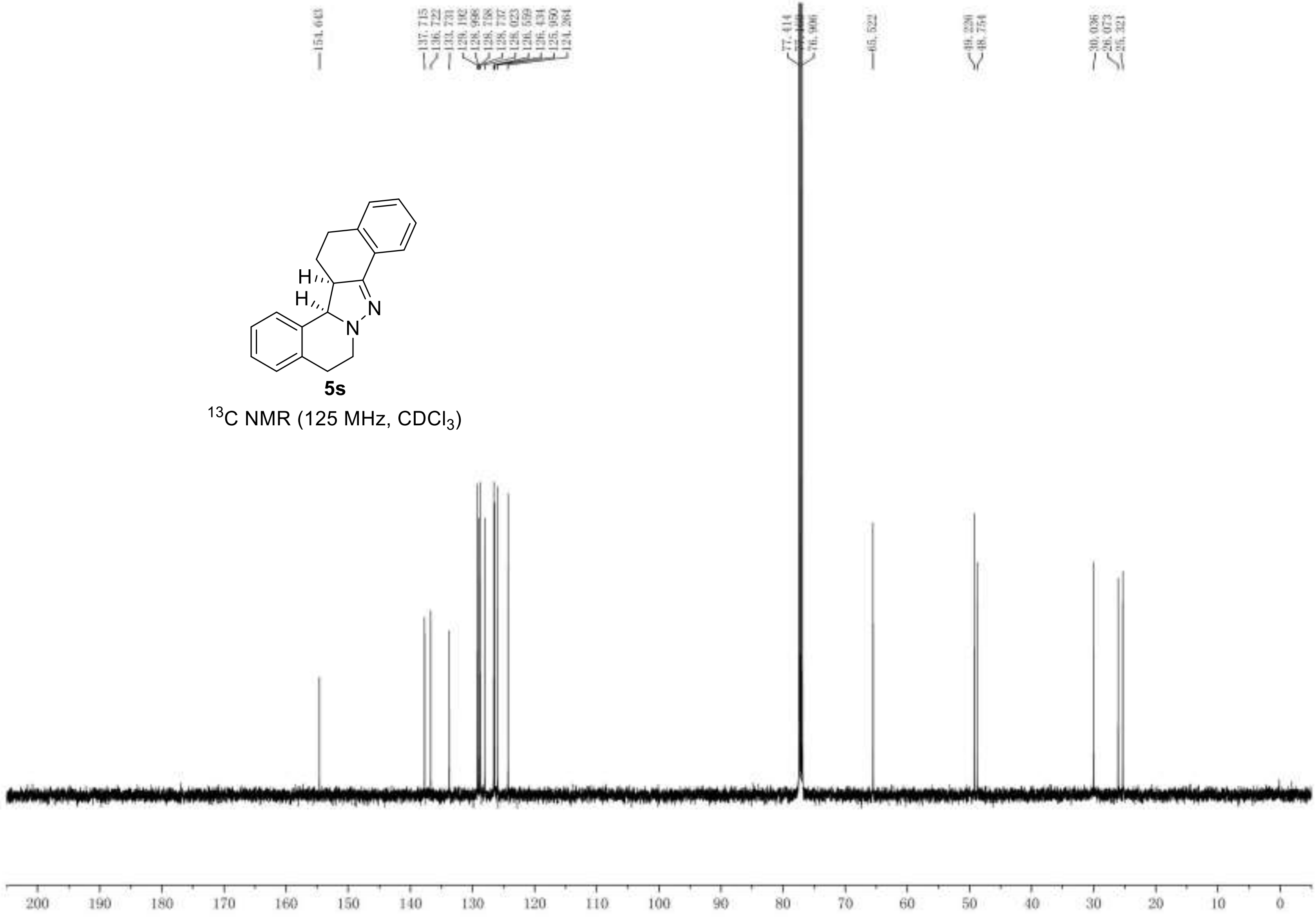
5r

^{13}C NMR (125 MHz, $CDCl_3$)



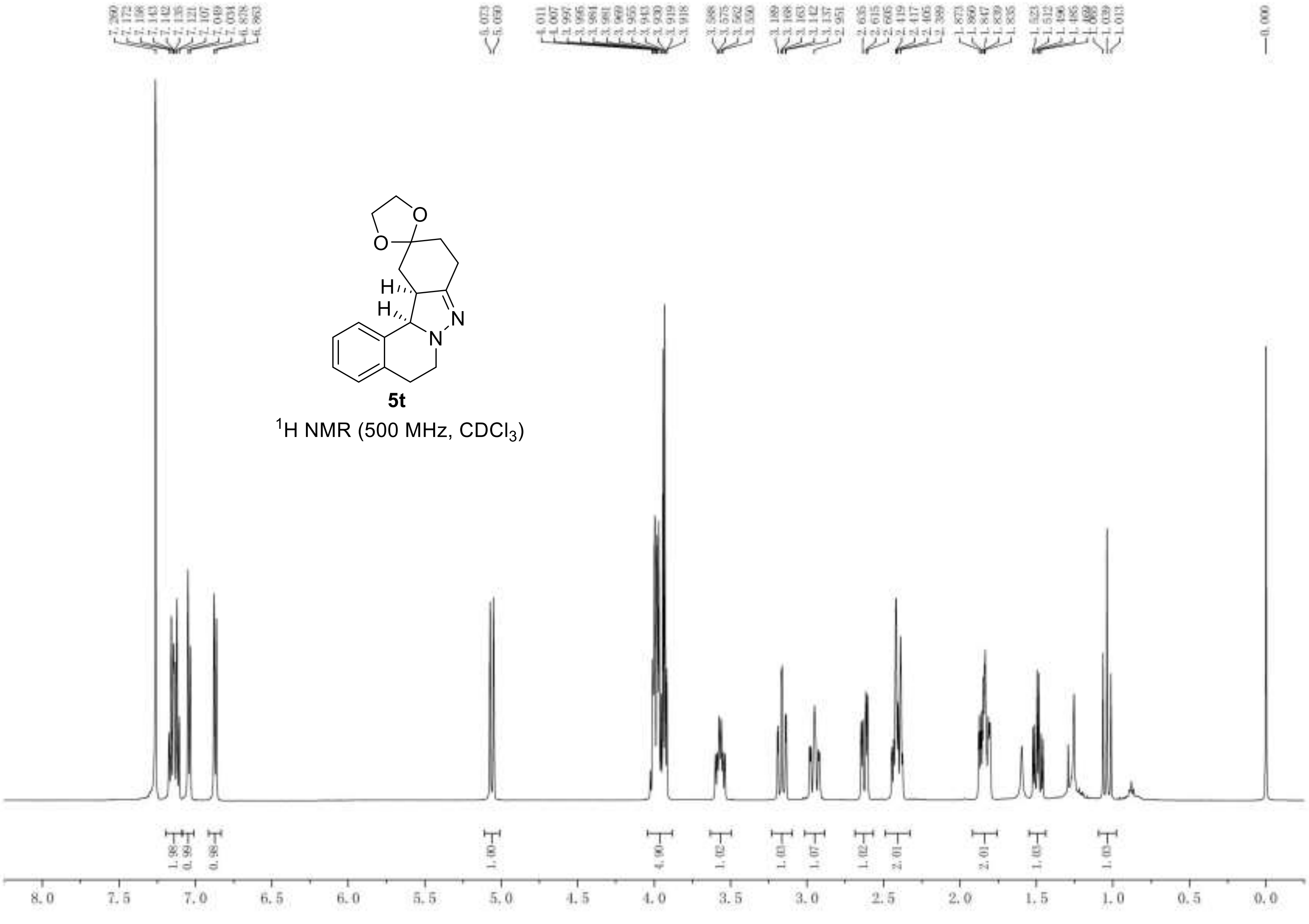
5s

^{1}H NMR (500 MHz, CDCl$_3$)



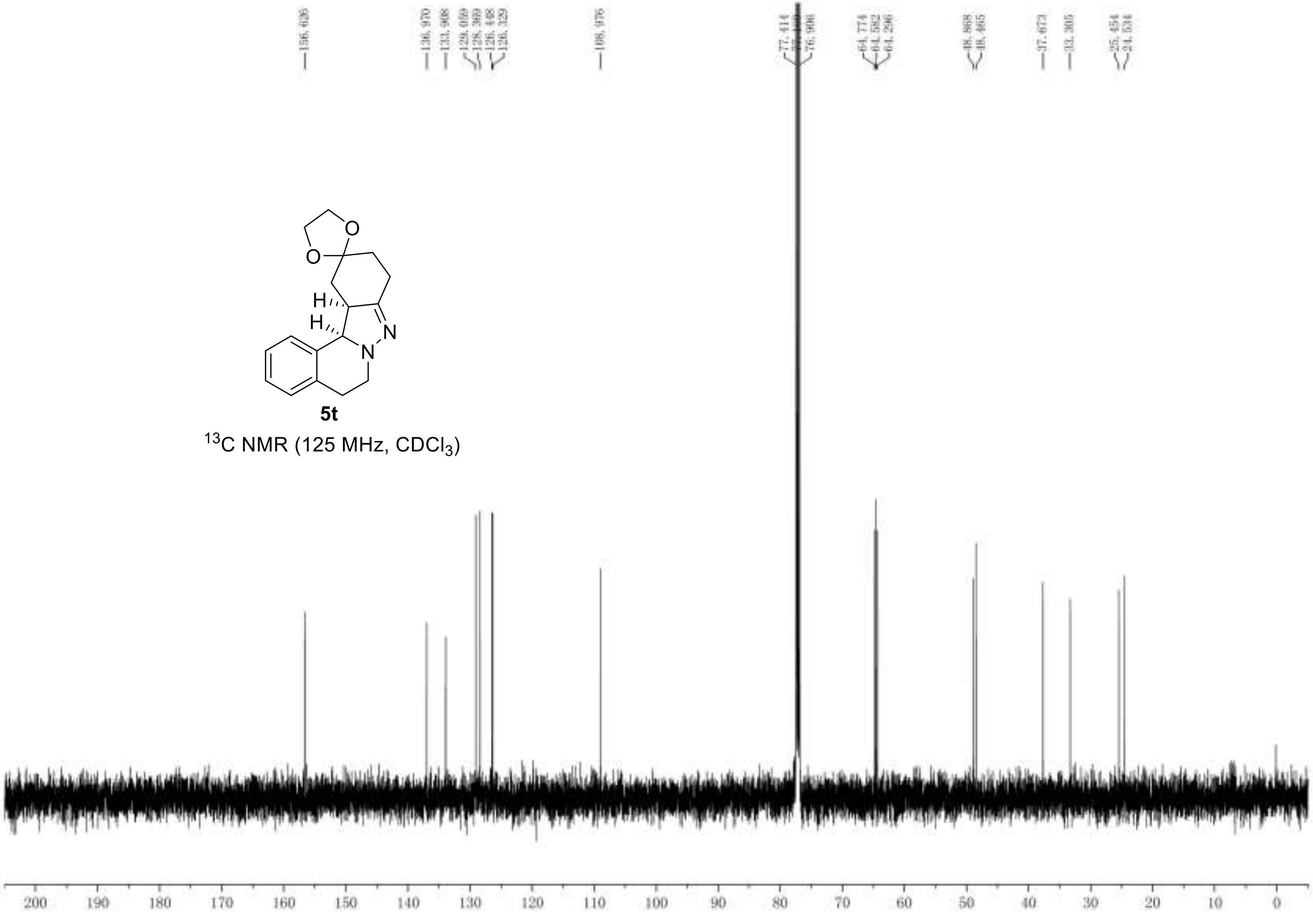
5s

^{13}C NMR (125 MHz, CDCl$_3$)



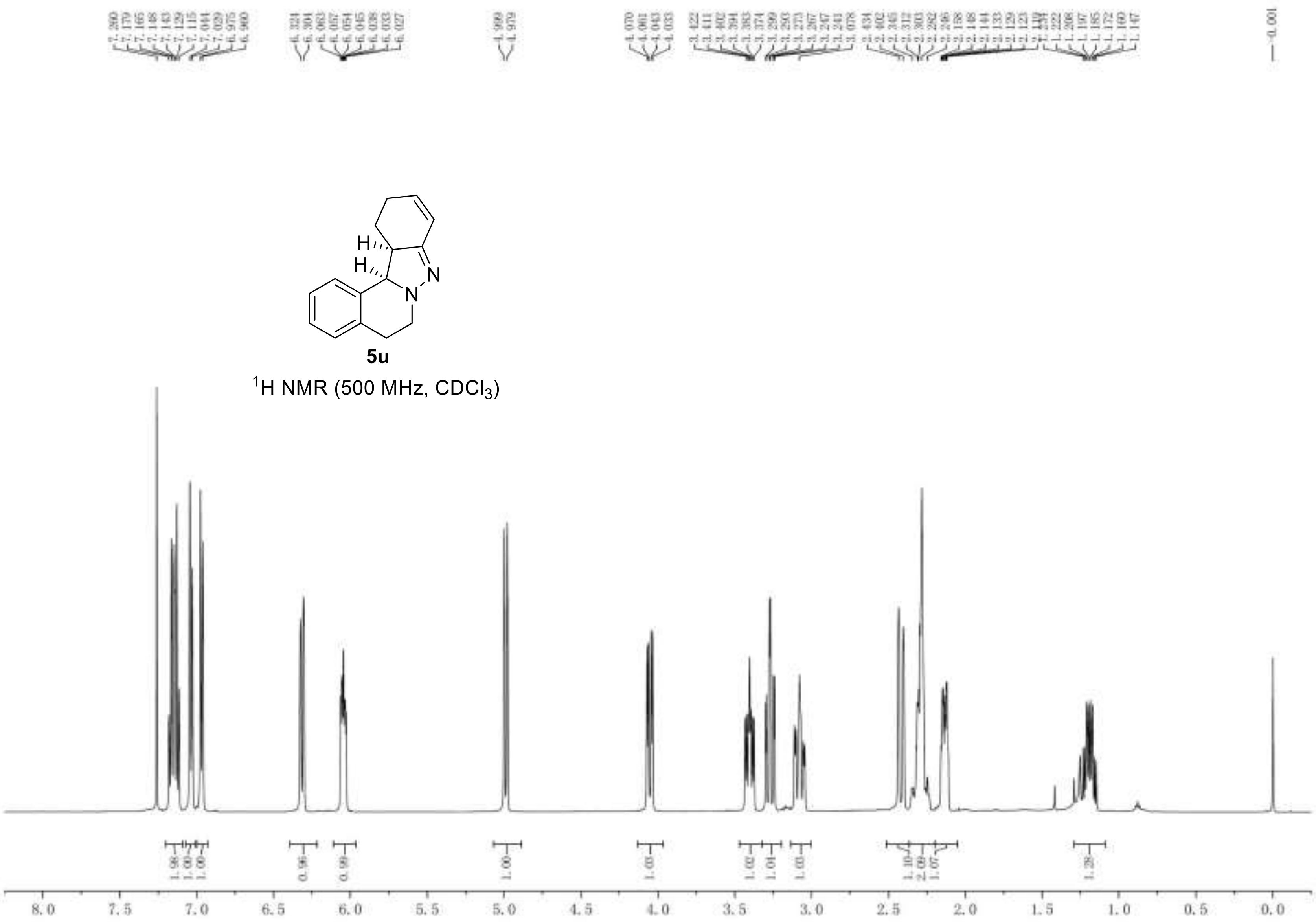
5t

^{1}H NMR (500 MHz, CDCl$_3$)



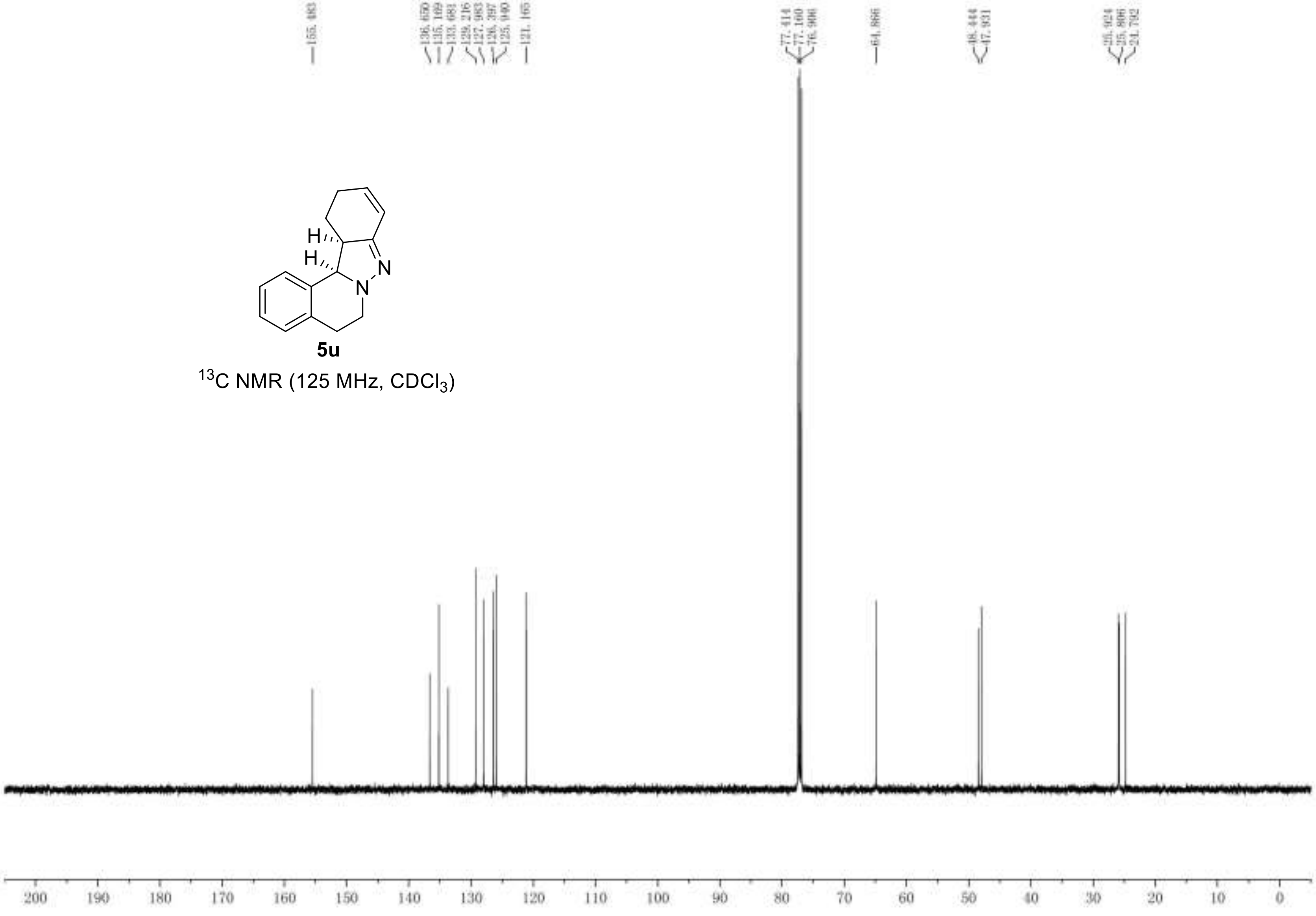
5t

^{13}C NMR (125 MHz, CDCl$_3$)



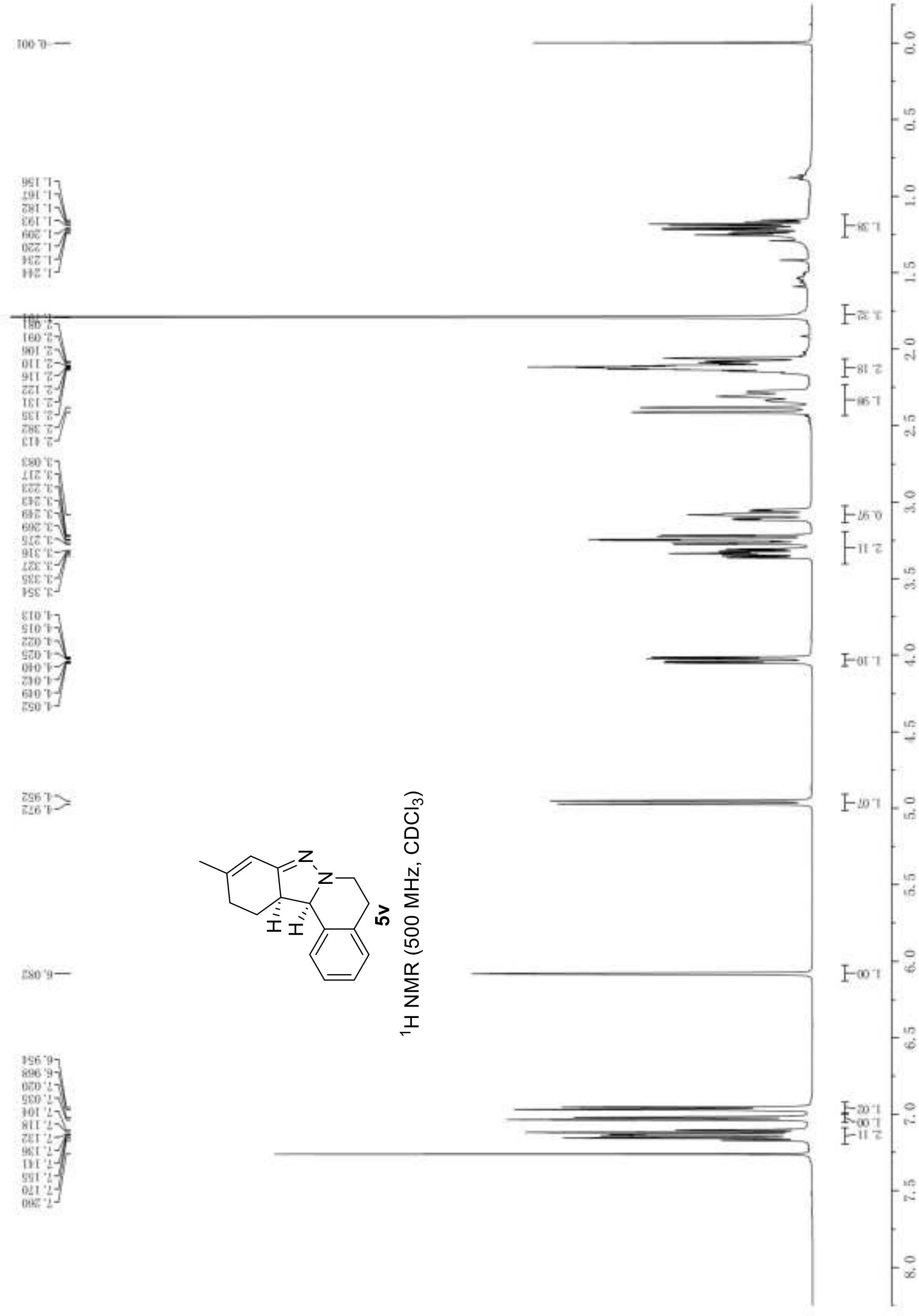
5u

^{1}H NMR (500 MHz, CDCl$_3$)



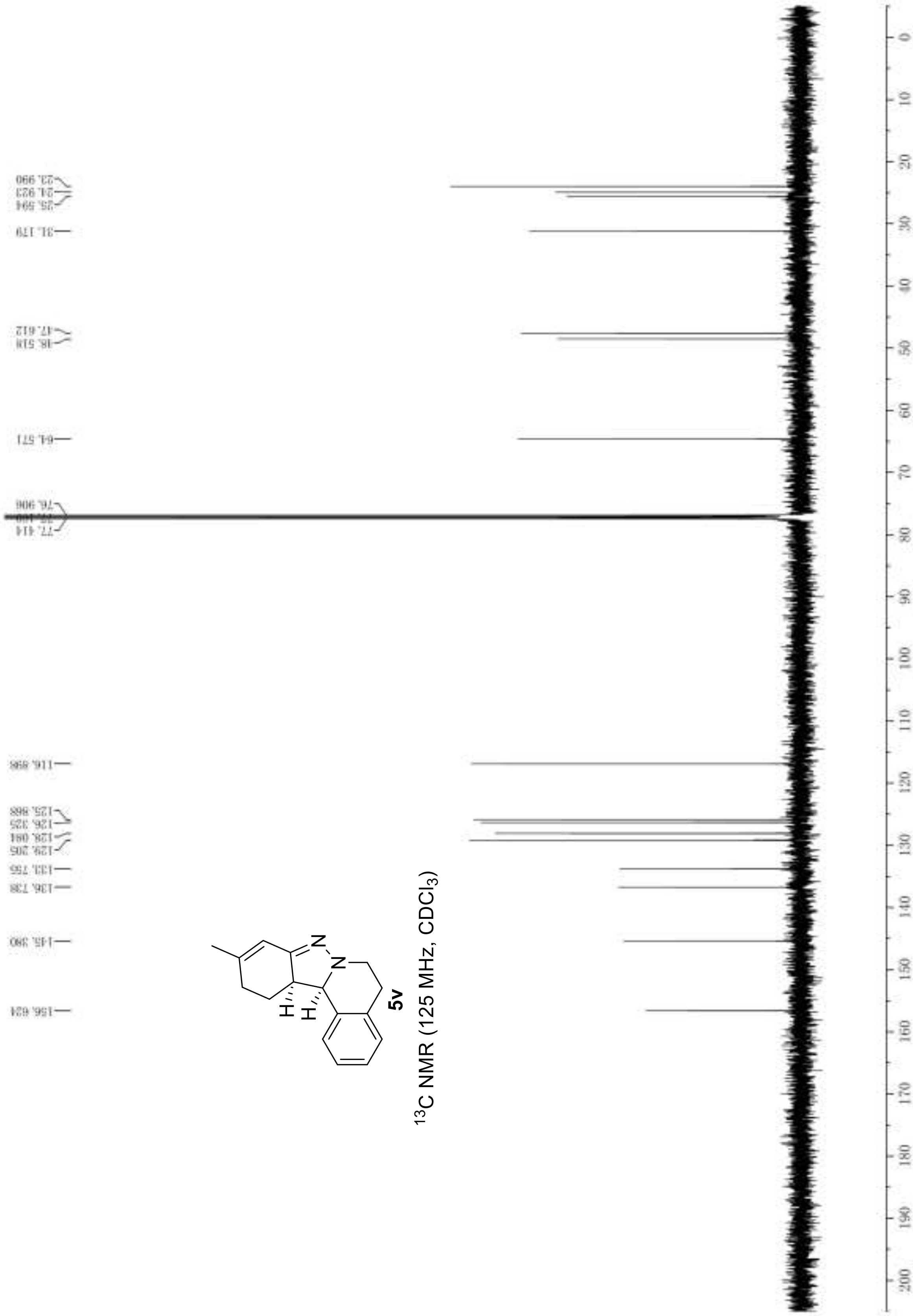
5u

^{13}C NMR (125 MHz, CDCl$_3$)



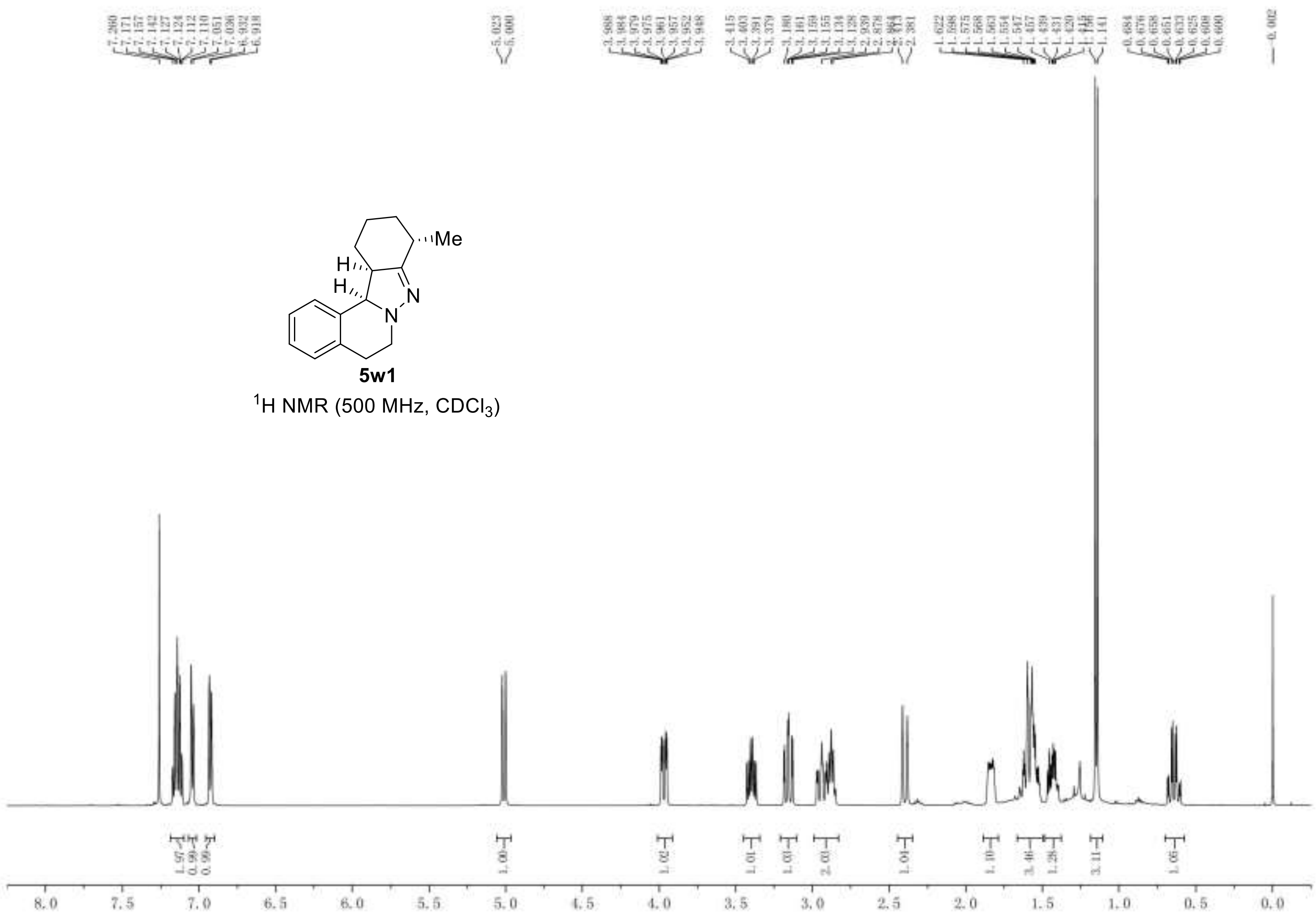
5v

^{1}H NMR (500 MHz, CDCl$_3$)



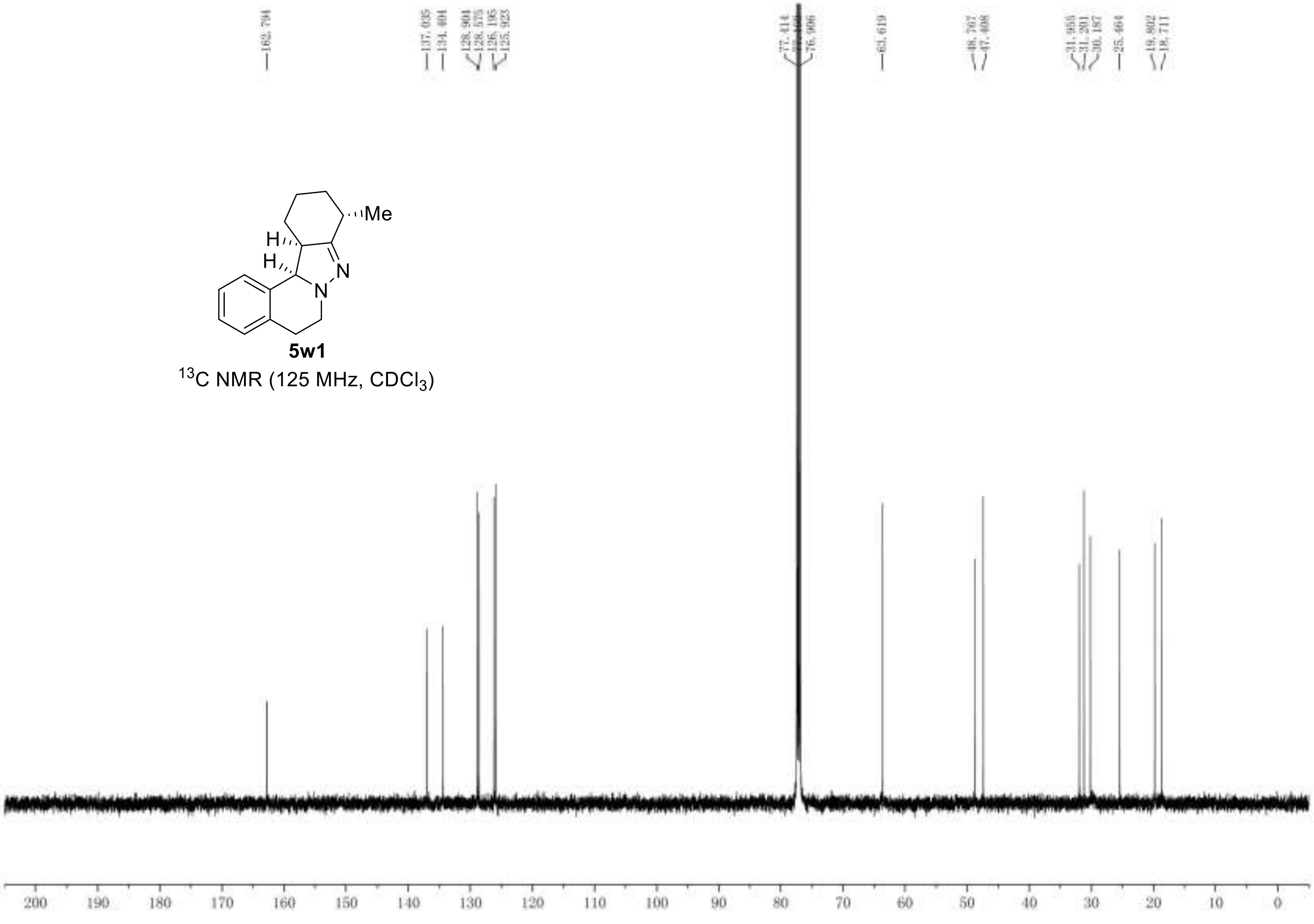
5v

^{13}C NMR (125 MHz, CDCl$_3$)



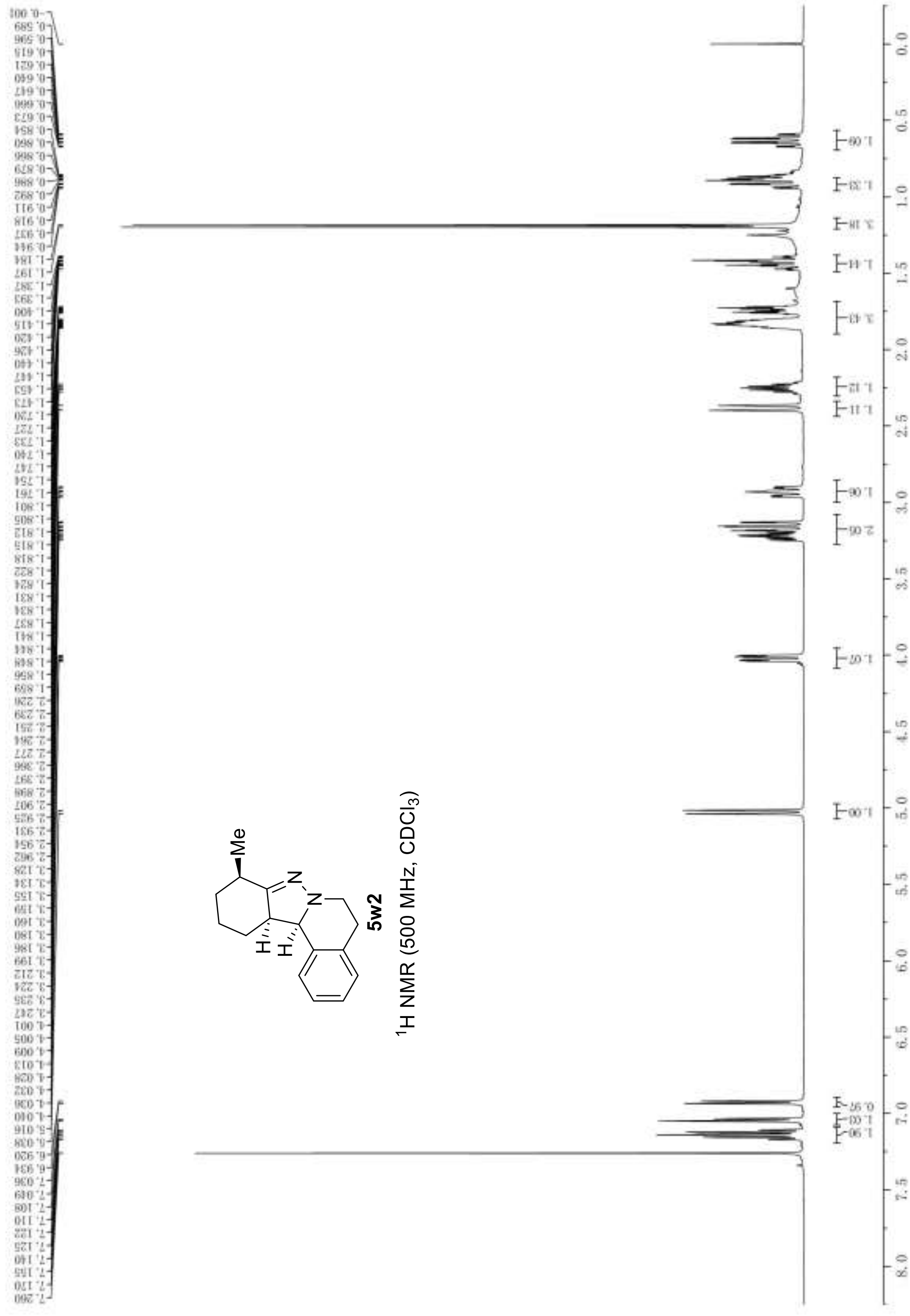
5w1

^{1}H NMR (500 MHz, $CDCl_3$)



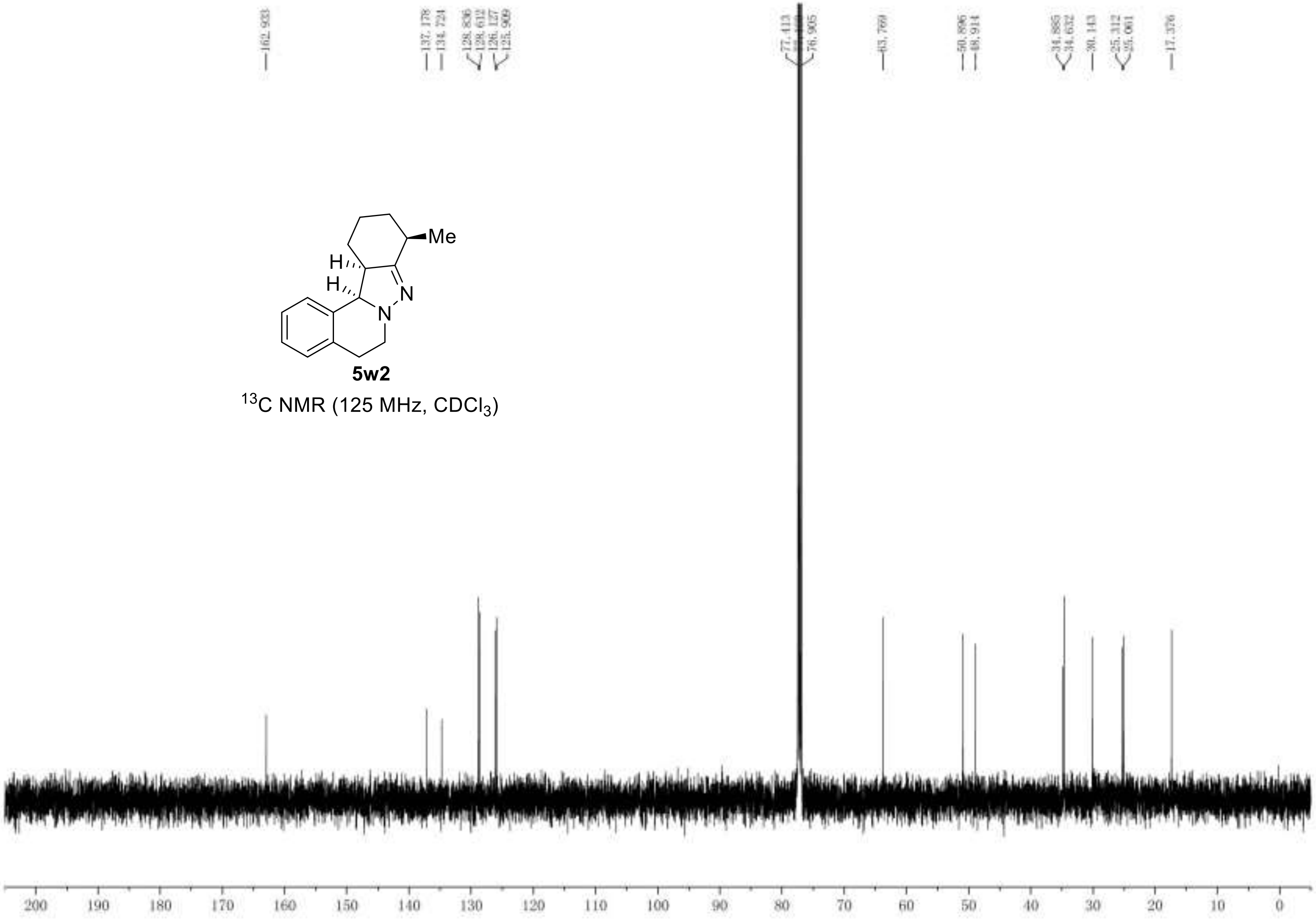
5w1

^{13}C NMR (125 MHz, $CDCl_3$)



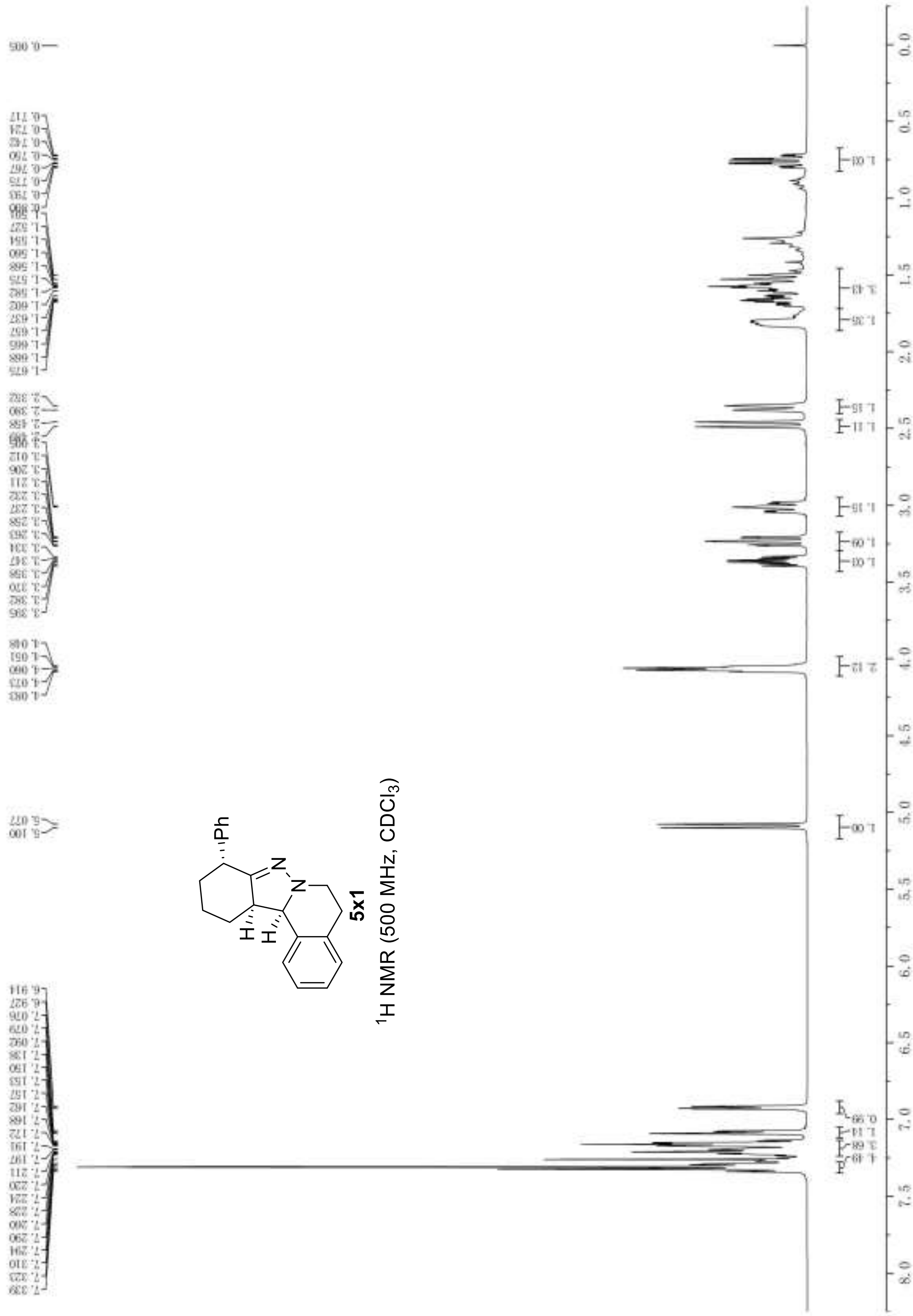
5w2

^{1}H NMR (500 MHz, CDCl$_3$)



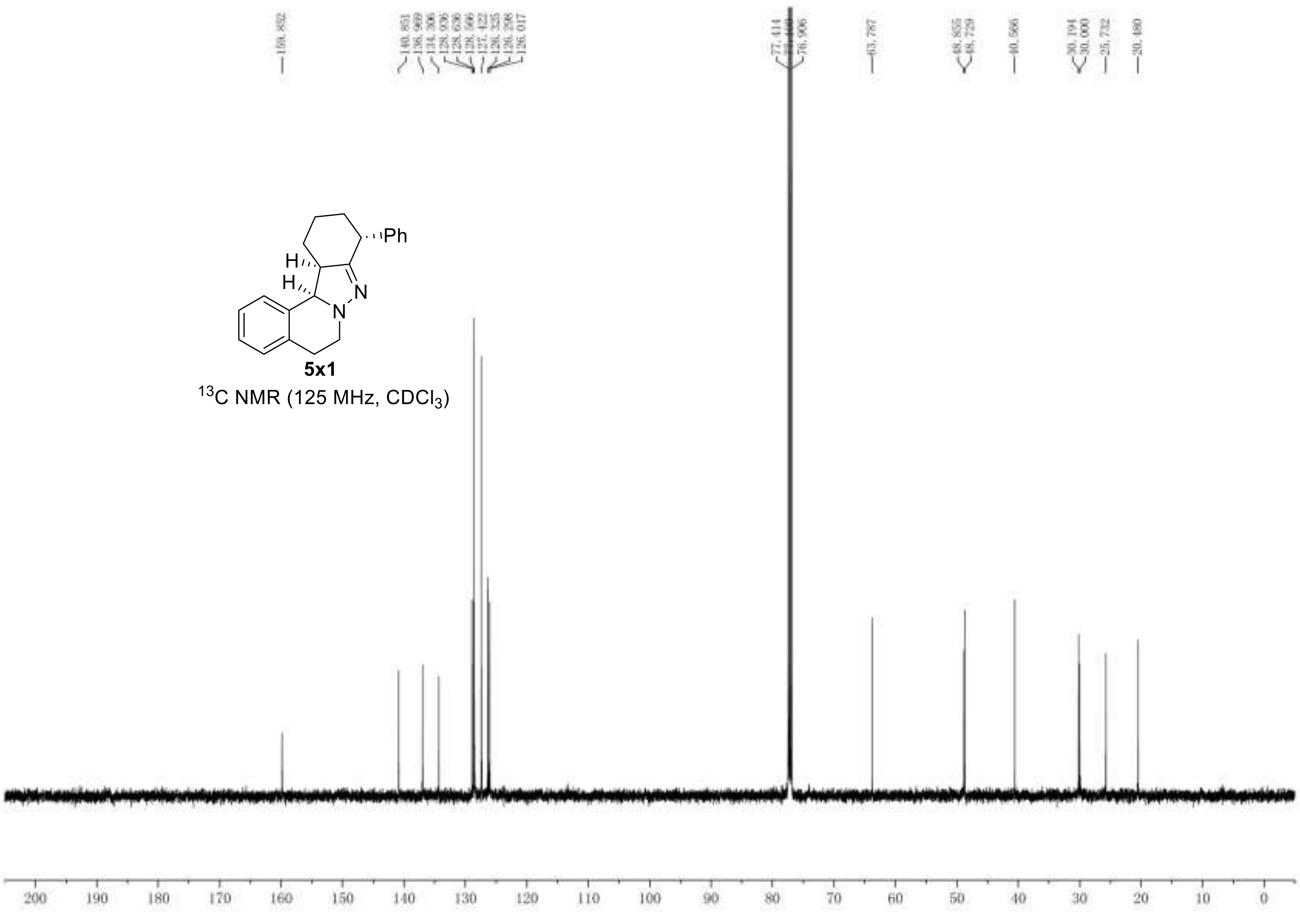
5w2

^{13}C NMR (125 MHz, $CDCl_3$)



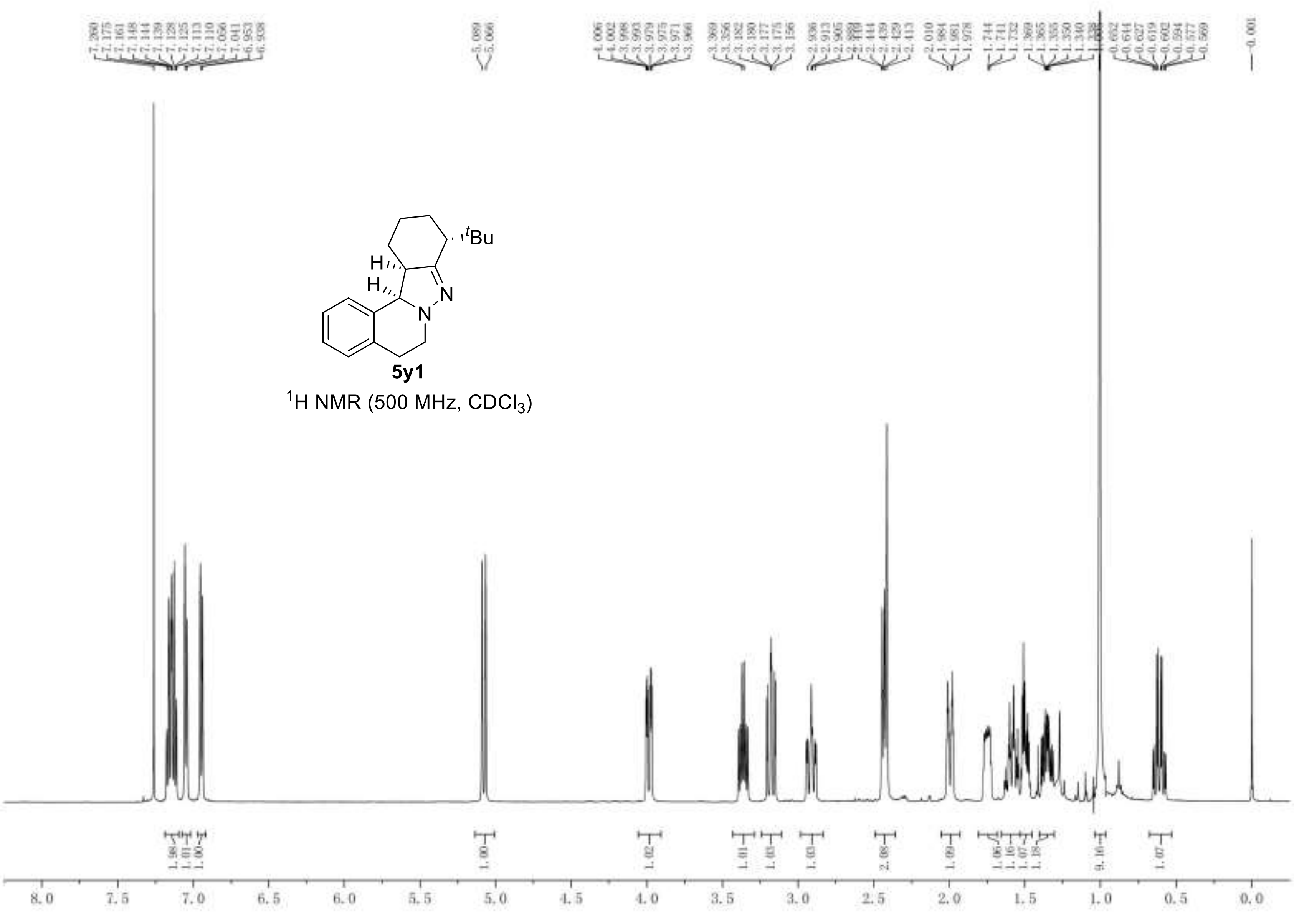
5x1

^{1}H NMR (500 MHz, CDCl$_3$)



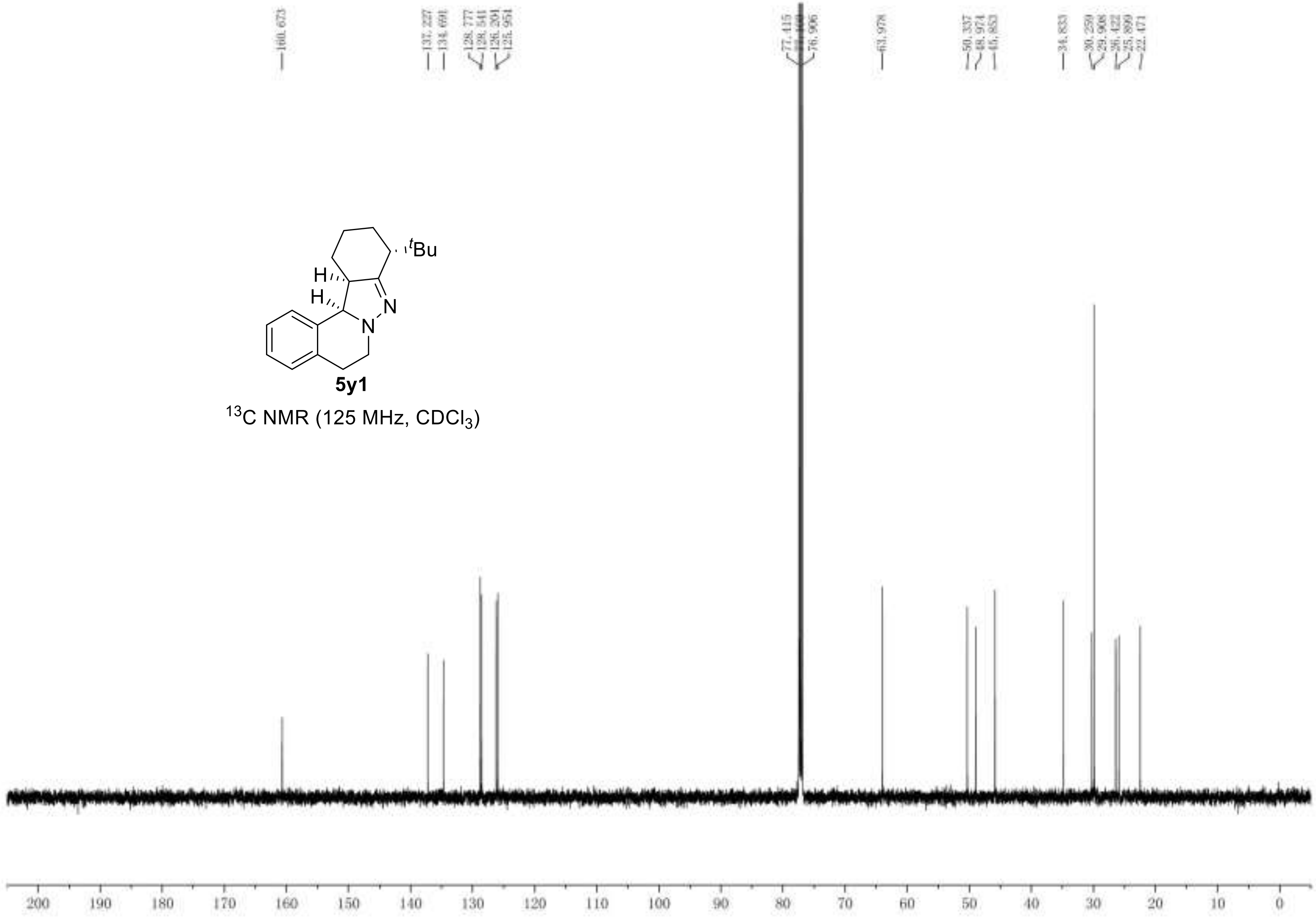
5x1

^{13}C NMR (125 MHz, CDCl$_3$)



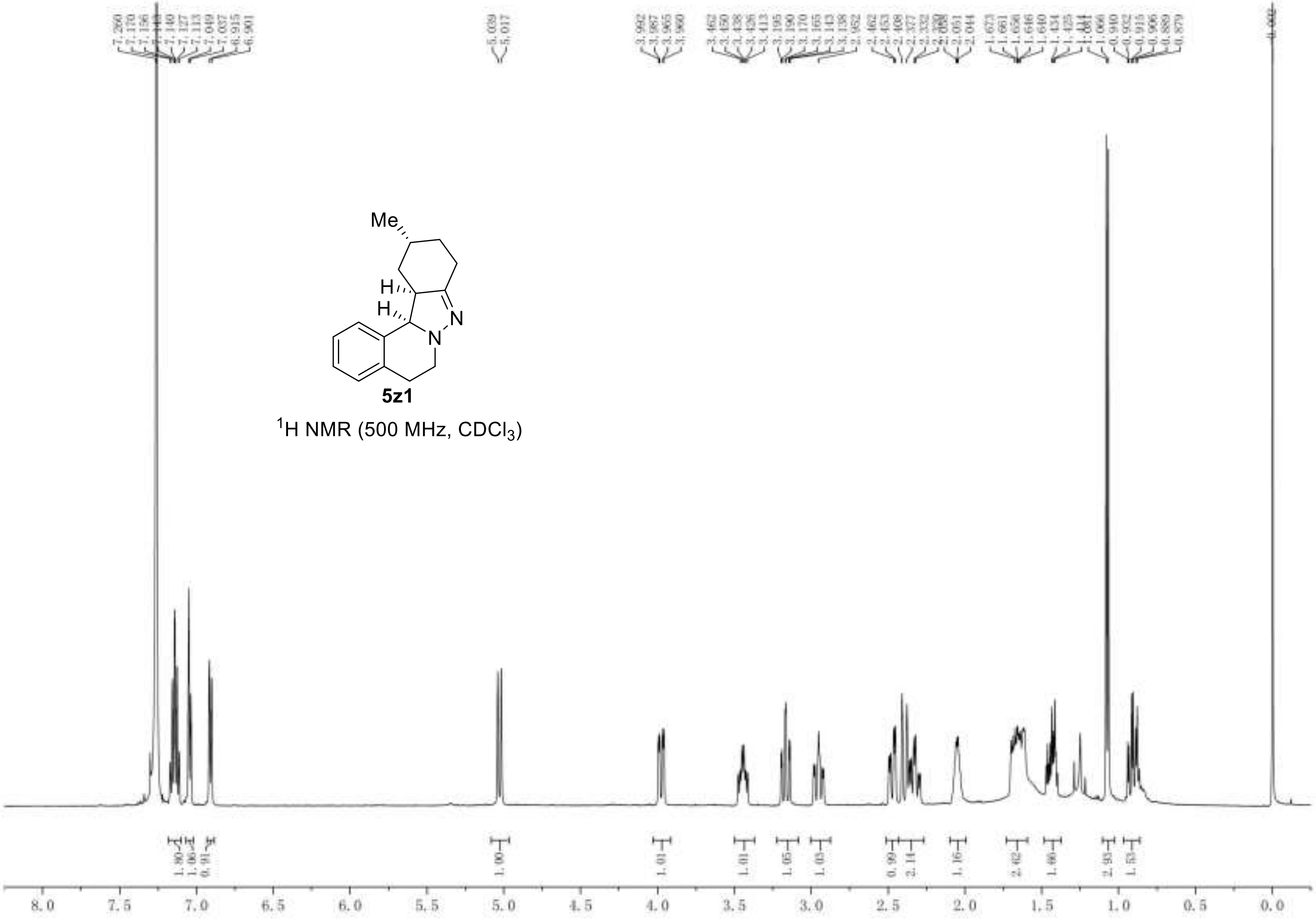
5y1

^{1}H NMR (500 MHz, CDCl$_3$)



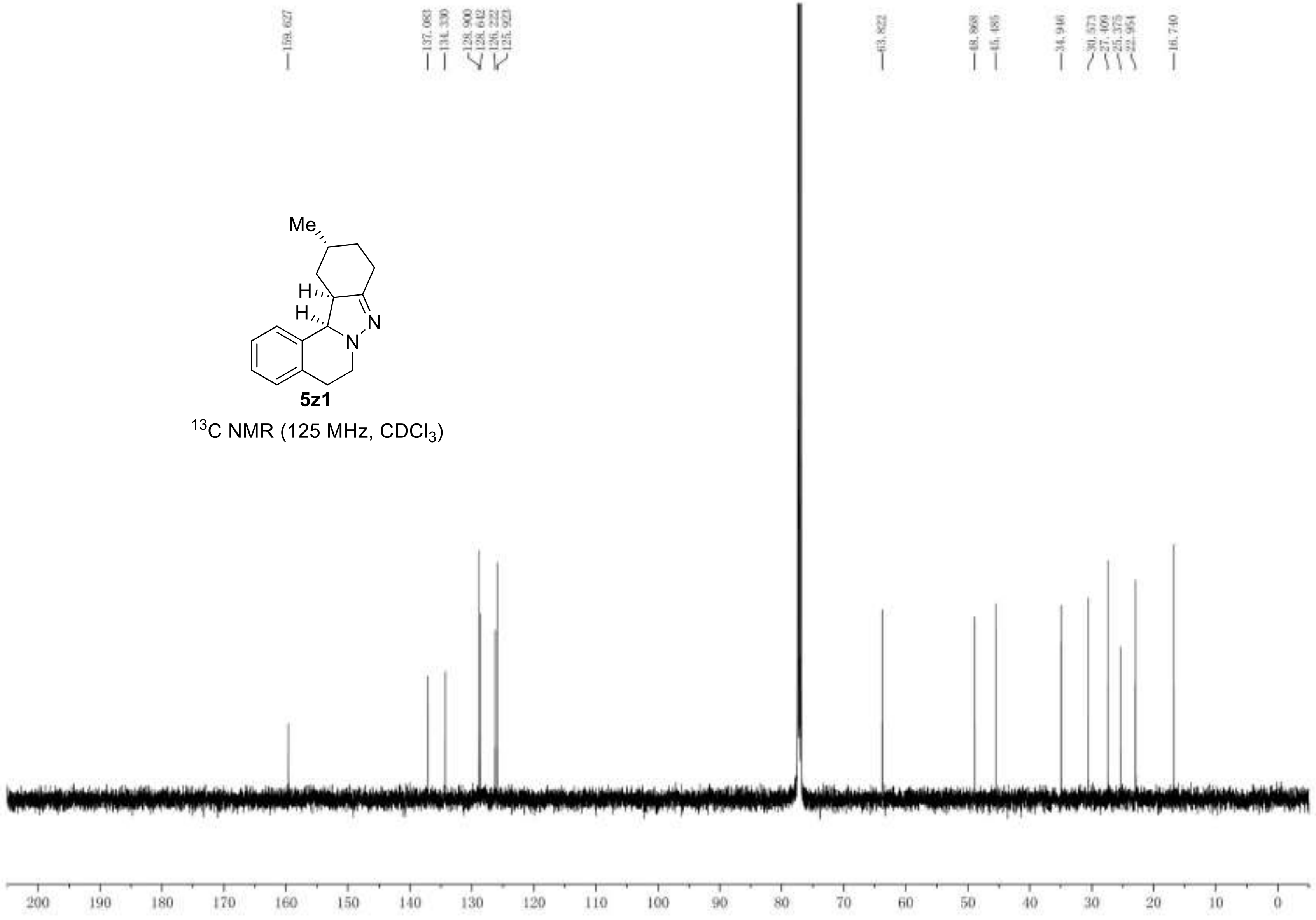
5y1

^{13}C NMR (125 MHz, CDCl$_3$)



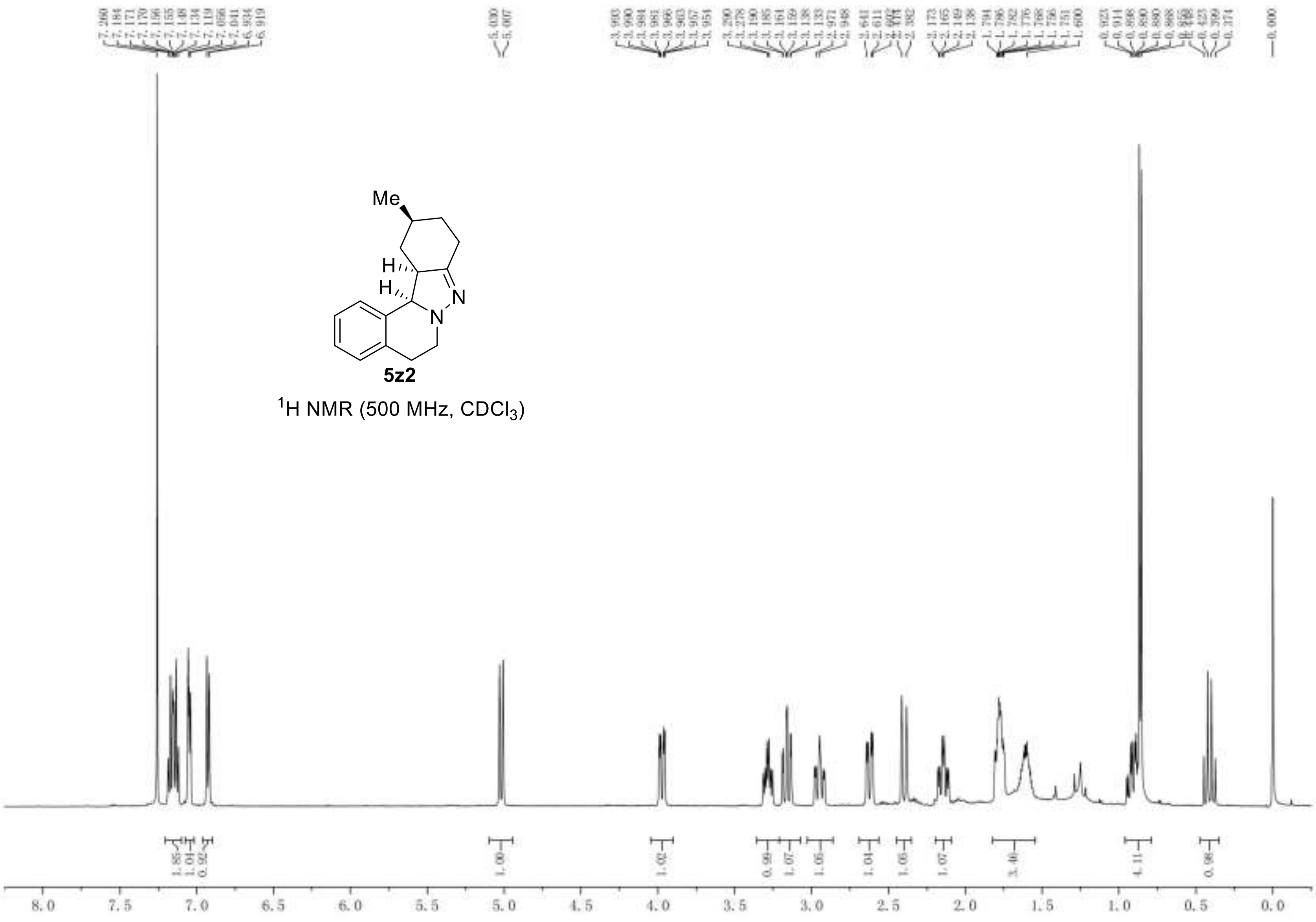
5z1

^{1}H NMR (500 MHz, $CDCl_3$)



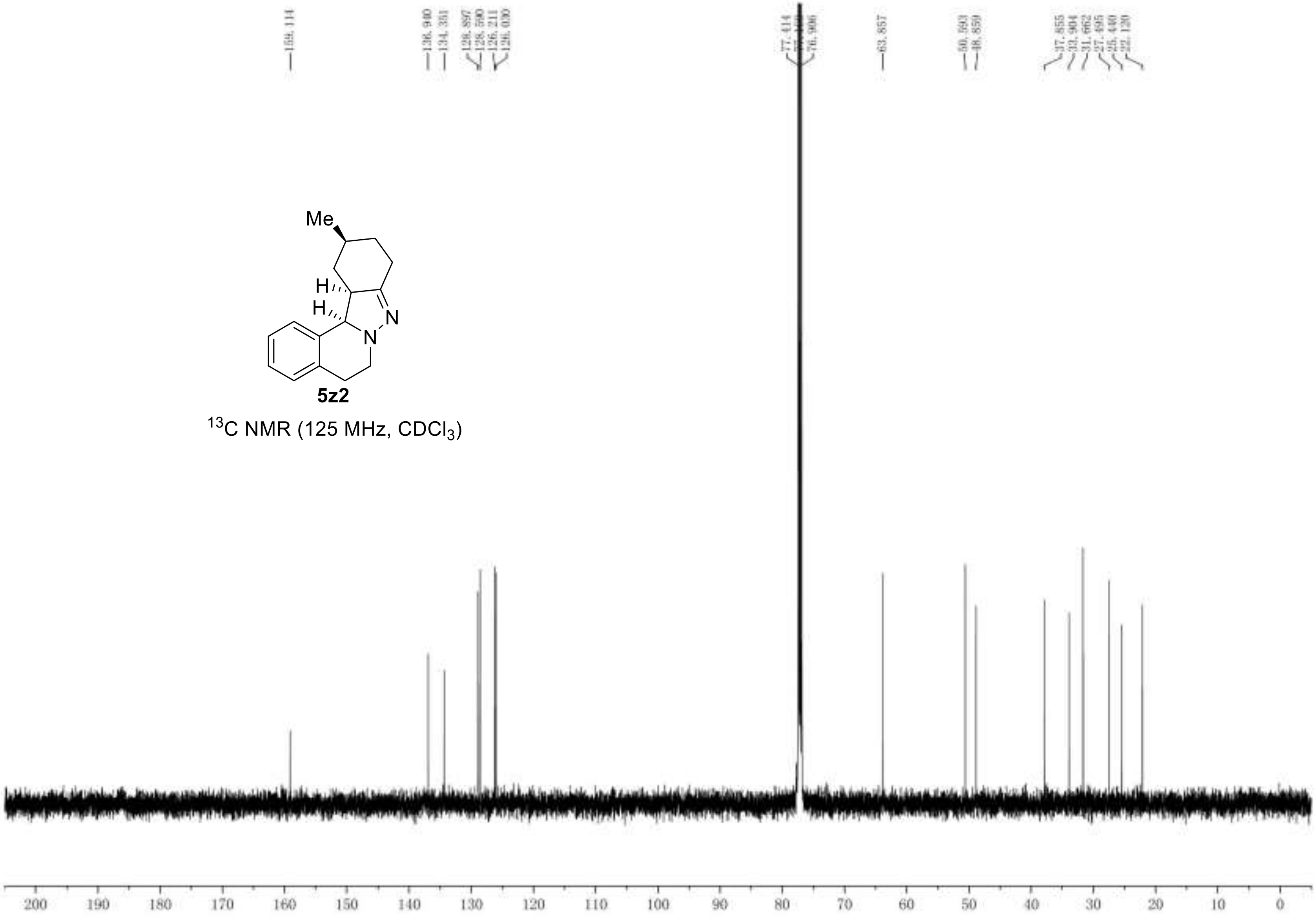
5z1

^{13}C NMR (125 MHz, CDCl$_3$)



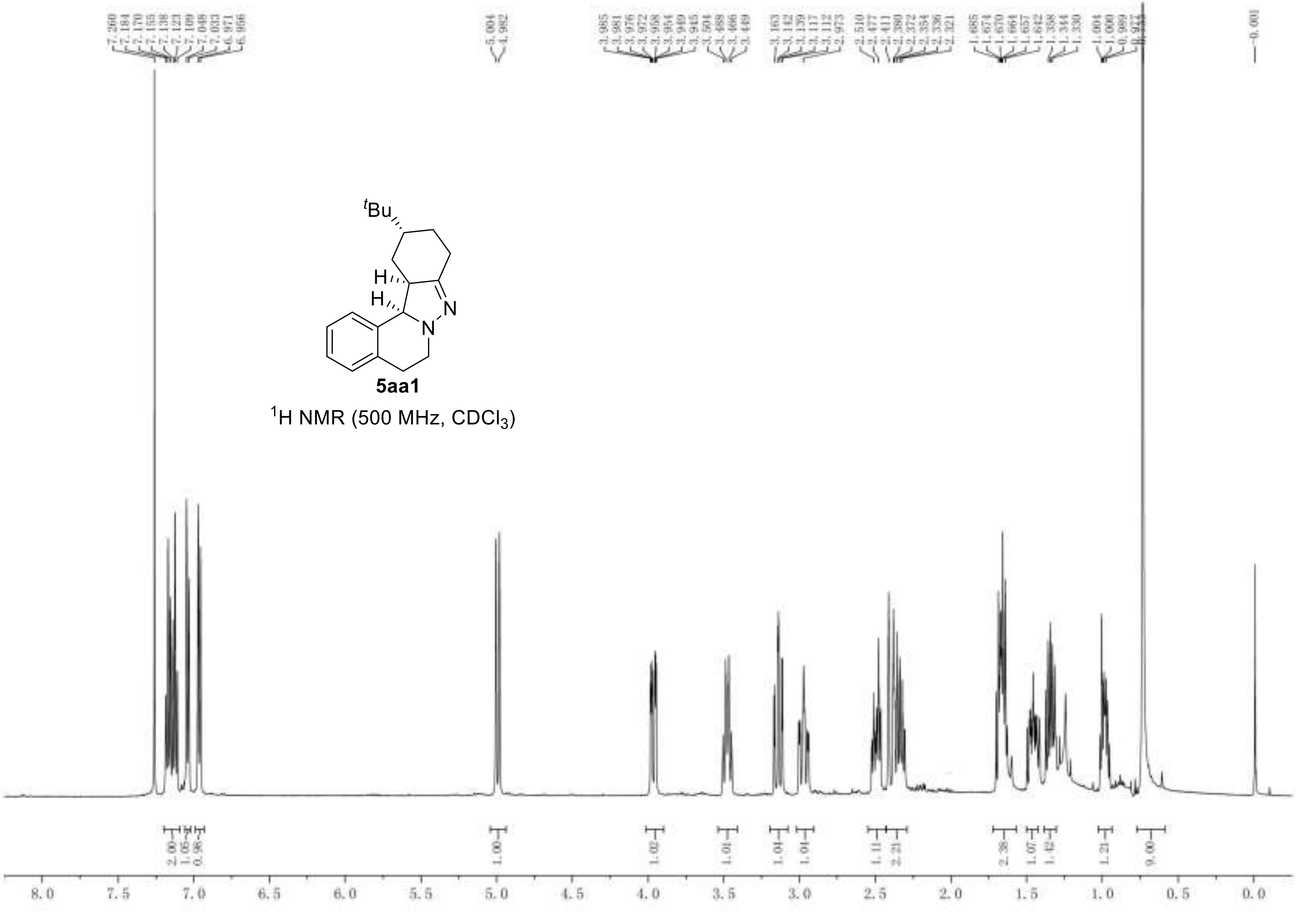
5z2

^{1}H NMR (500 MHz, CDCl$_3$)



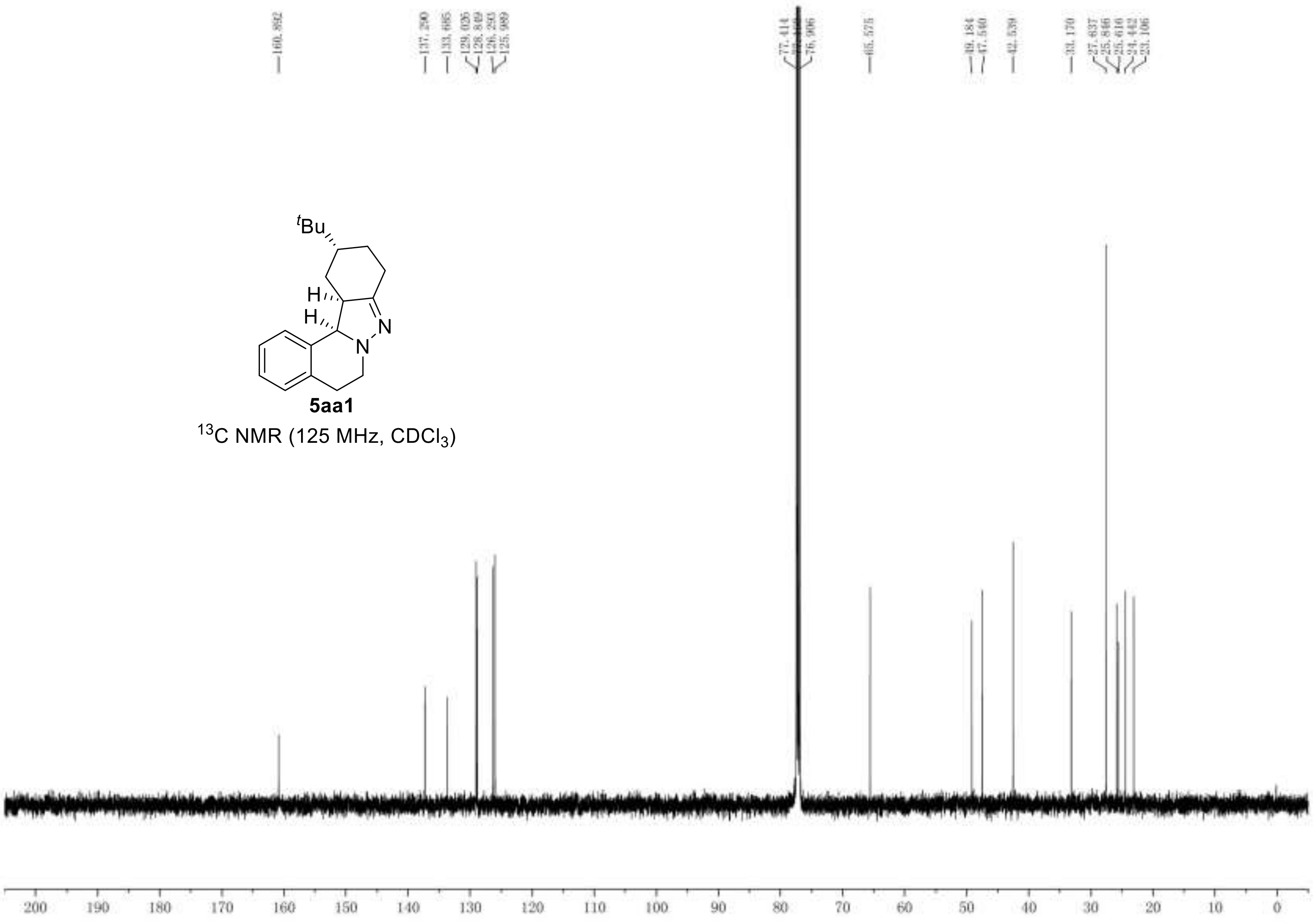
5z2

^{13}C NMR (125 MHz, CDCl$_3$)



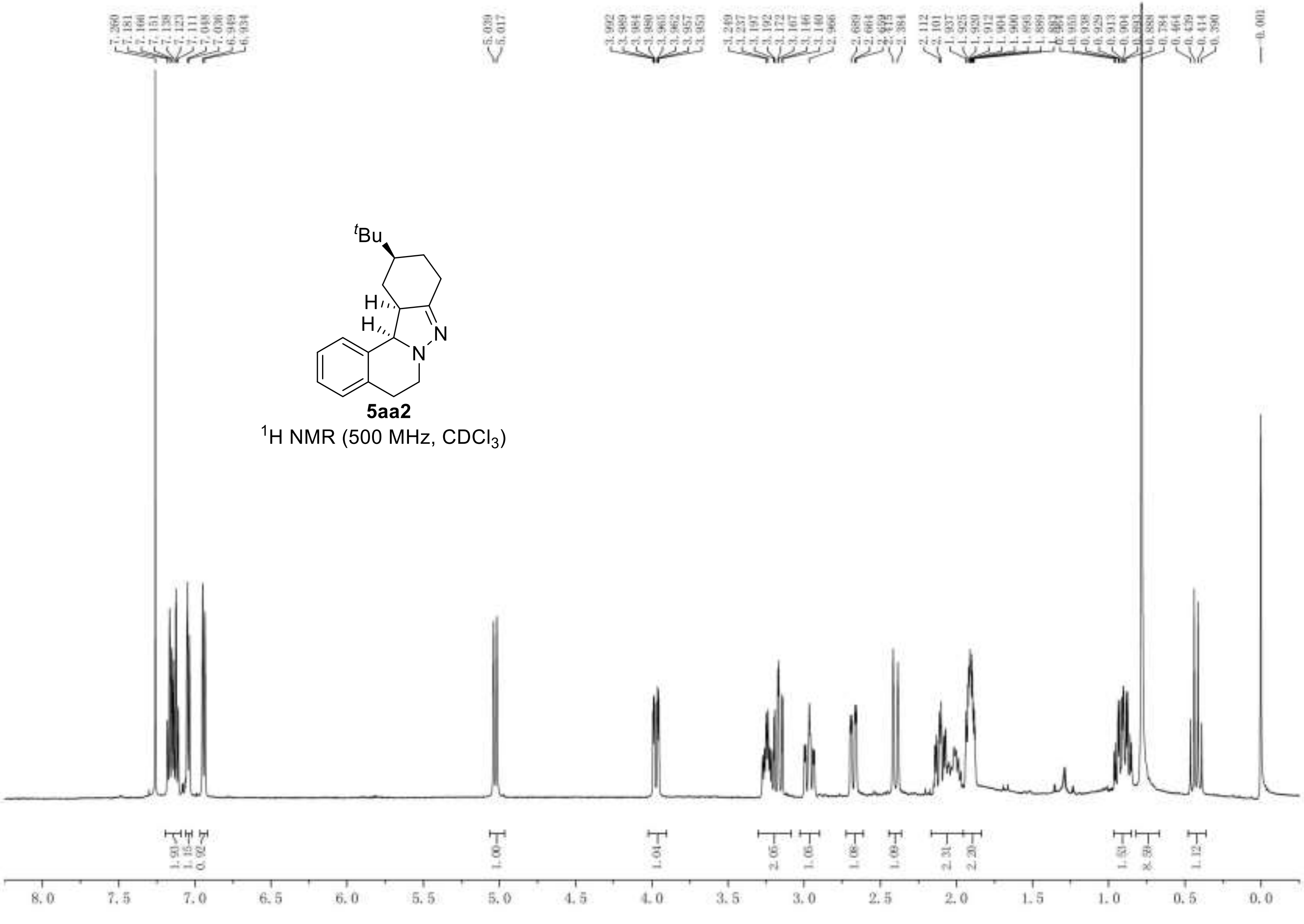
5aa1

^{1}H NMR (500 MHz, CDCl$_3$)



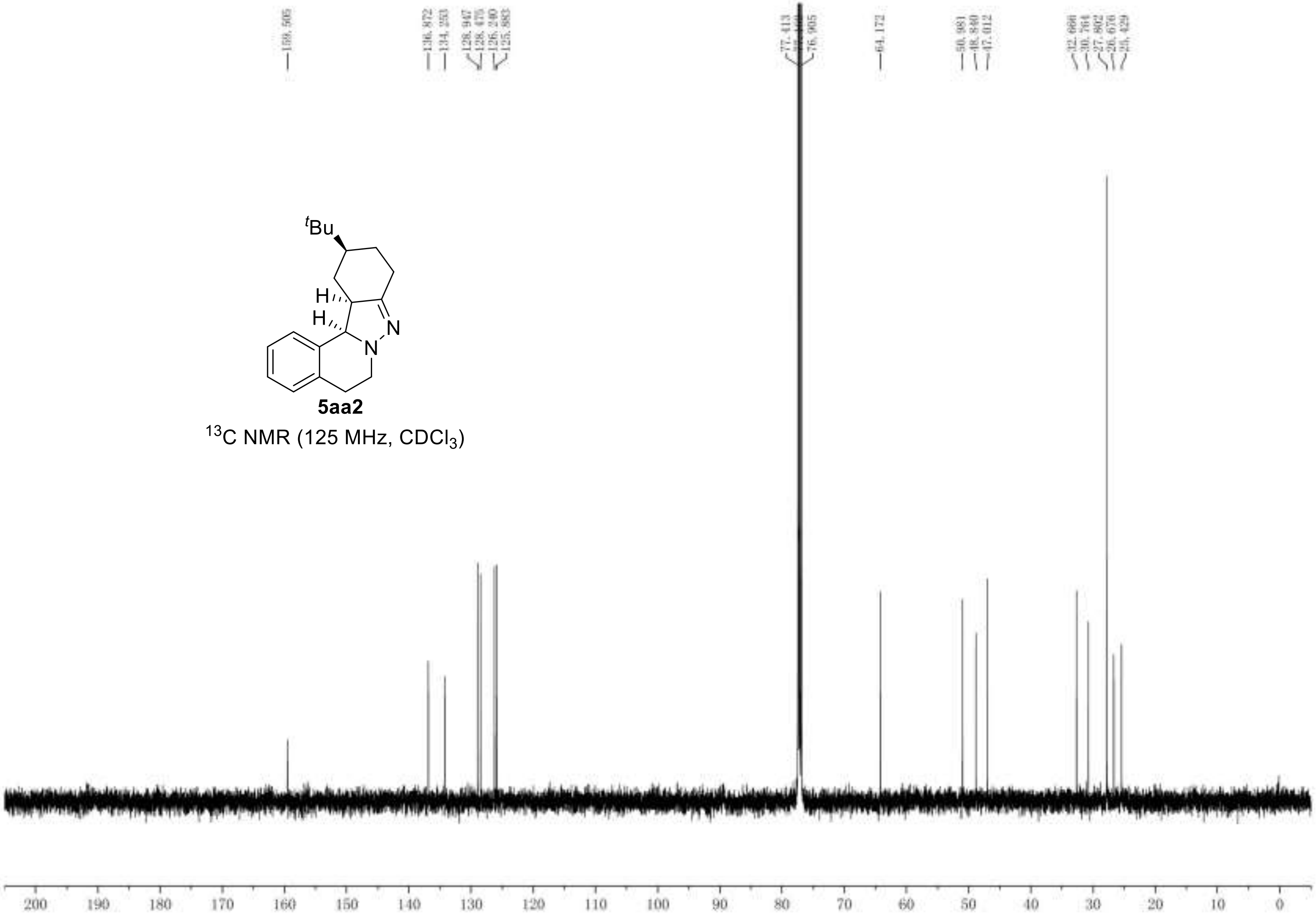
5aa1

^{13}C NMR (125 MHz, CDCl$_3$)



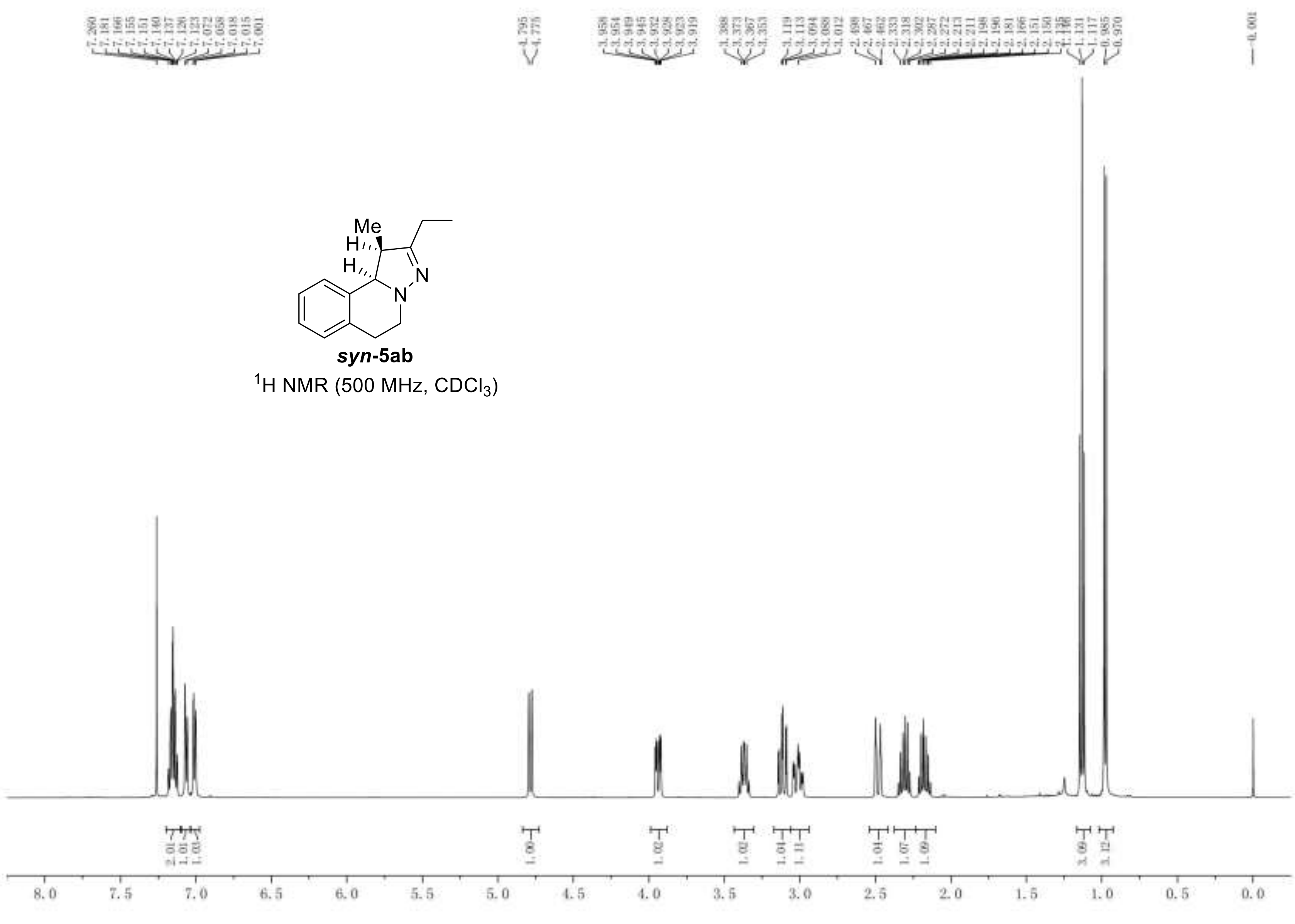
5aa2

^{1}H NMR (500 MHz, $CDCl_3$)



5aa2

^{13}C NMR (125 MHz, CDCl$_3$)

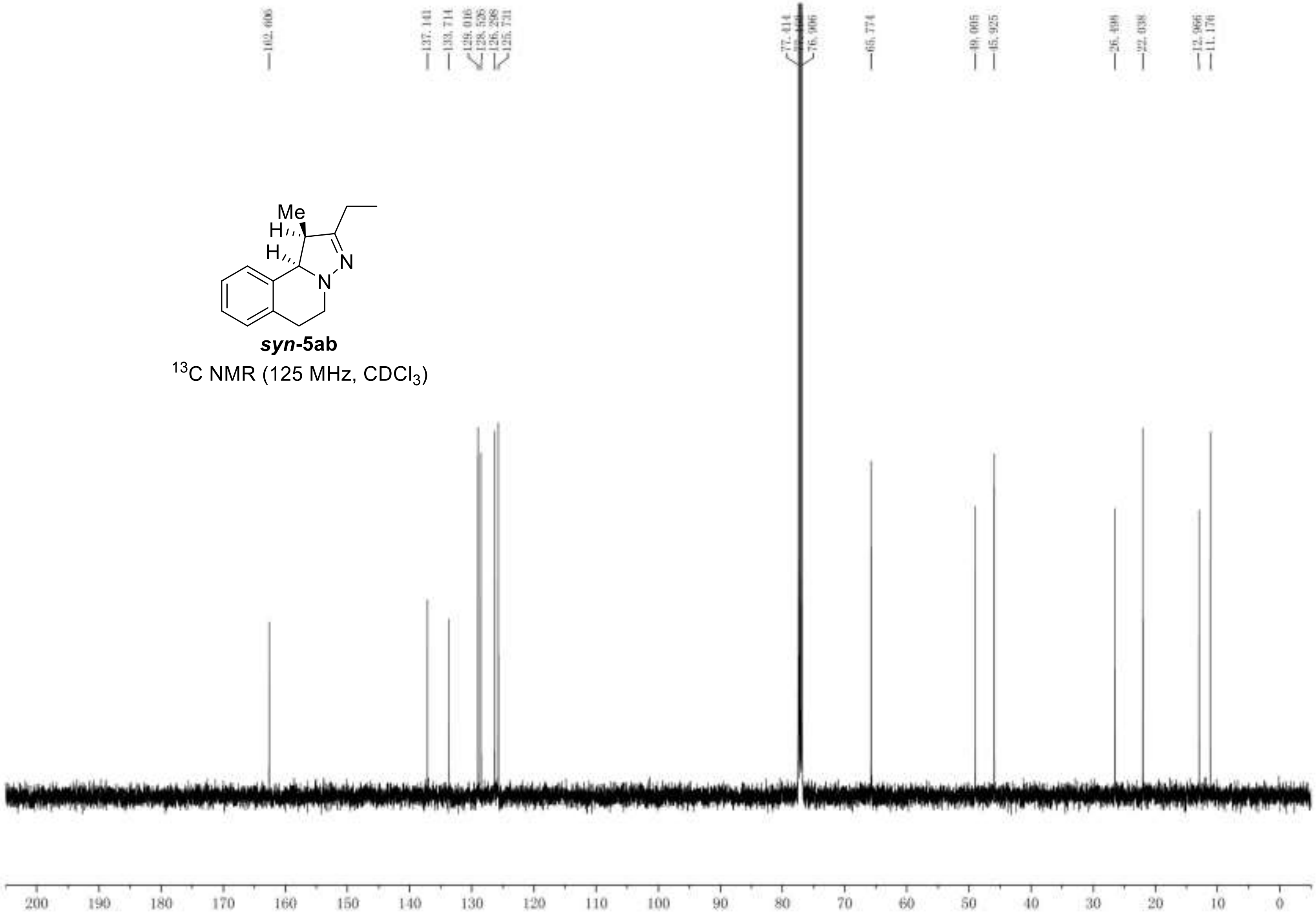


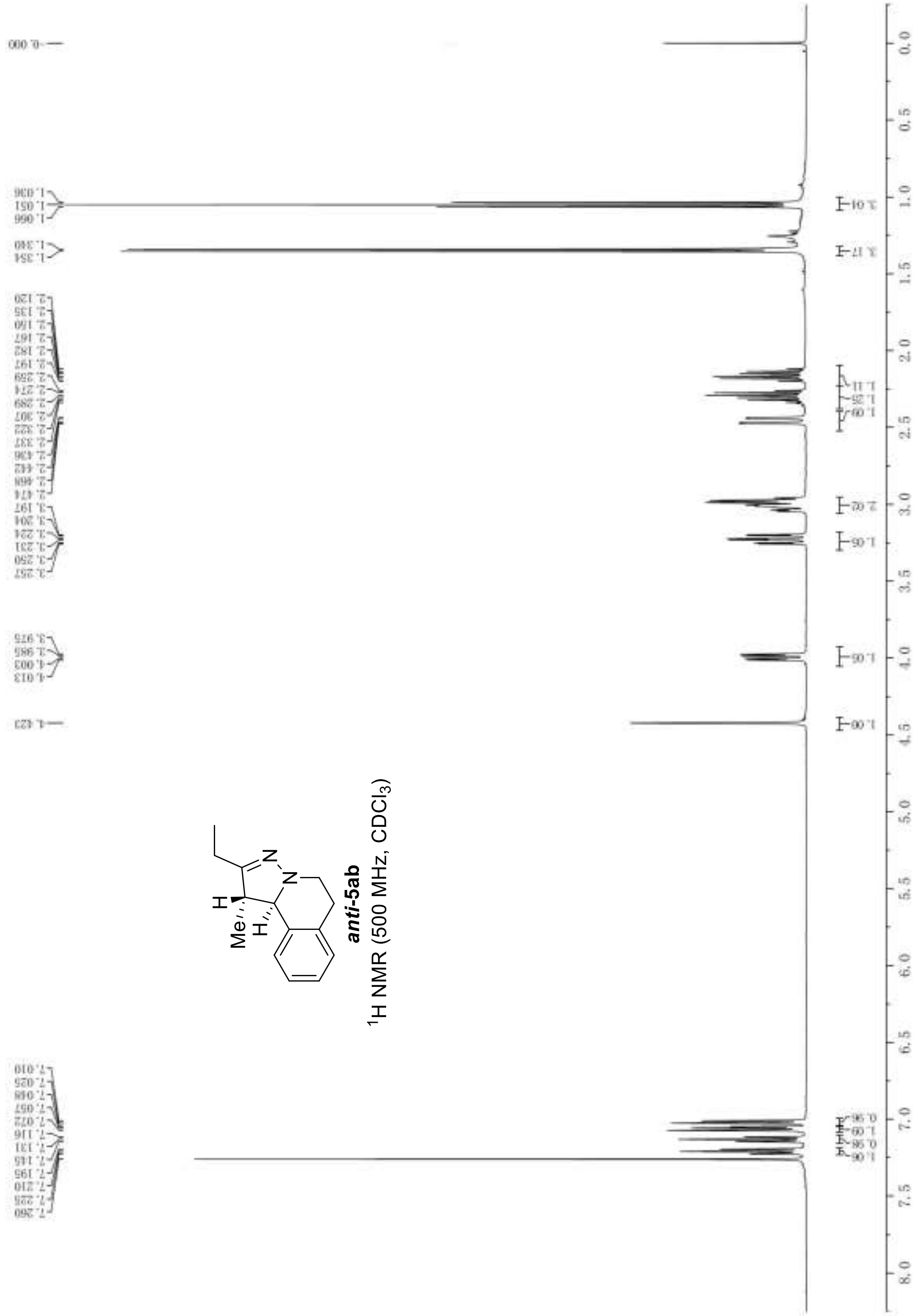
***syn*-5ab**

^{1}H NMR (500 MHz, $CDCl_3$)

***syn*-5ab**

^{13}C NMR (125 MHz, $CDCl_3$)



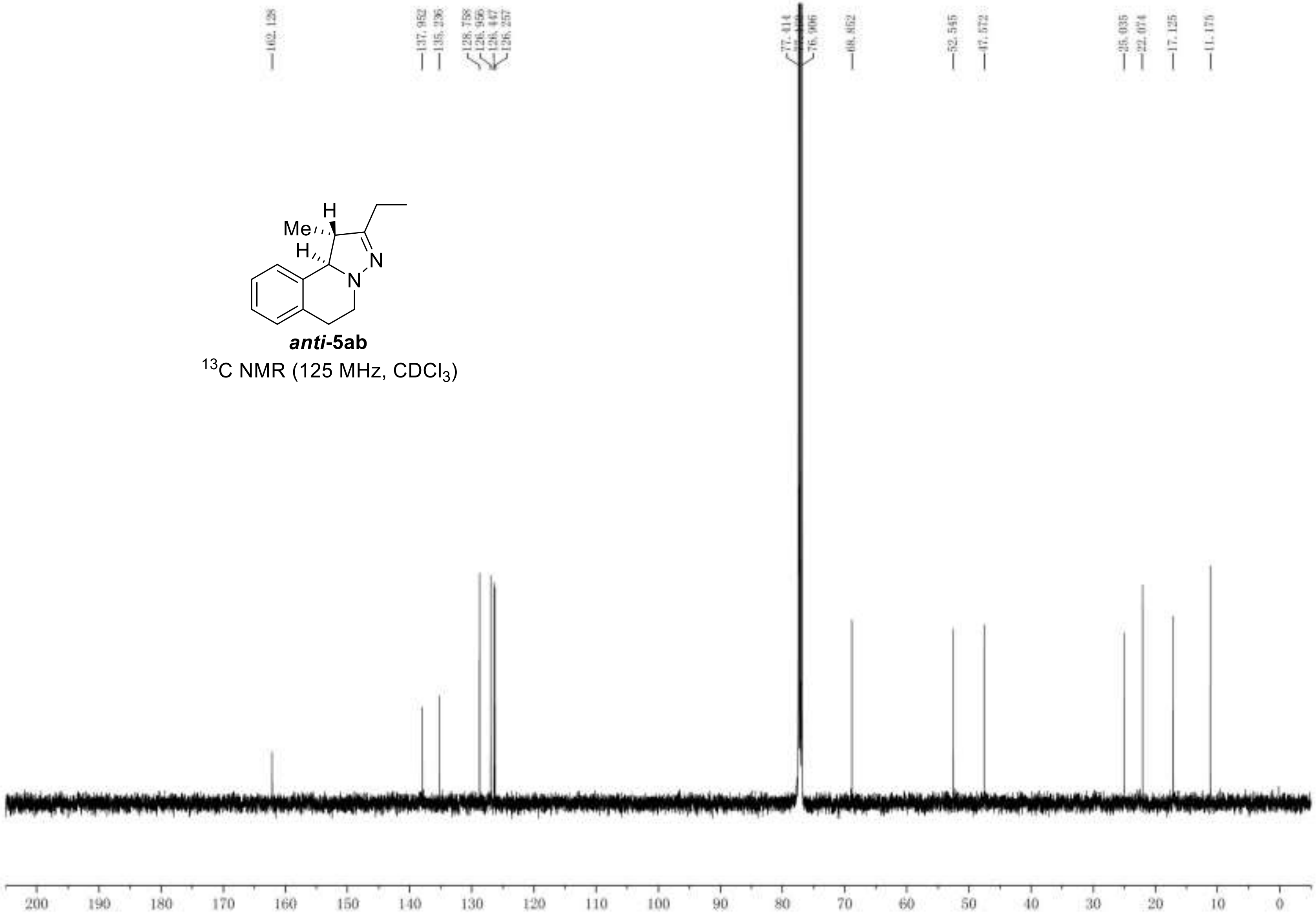


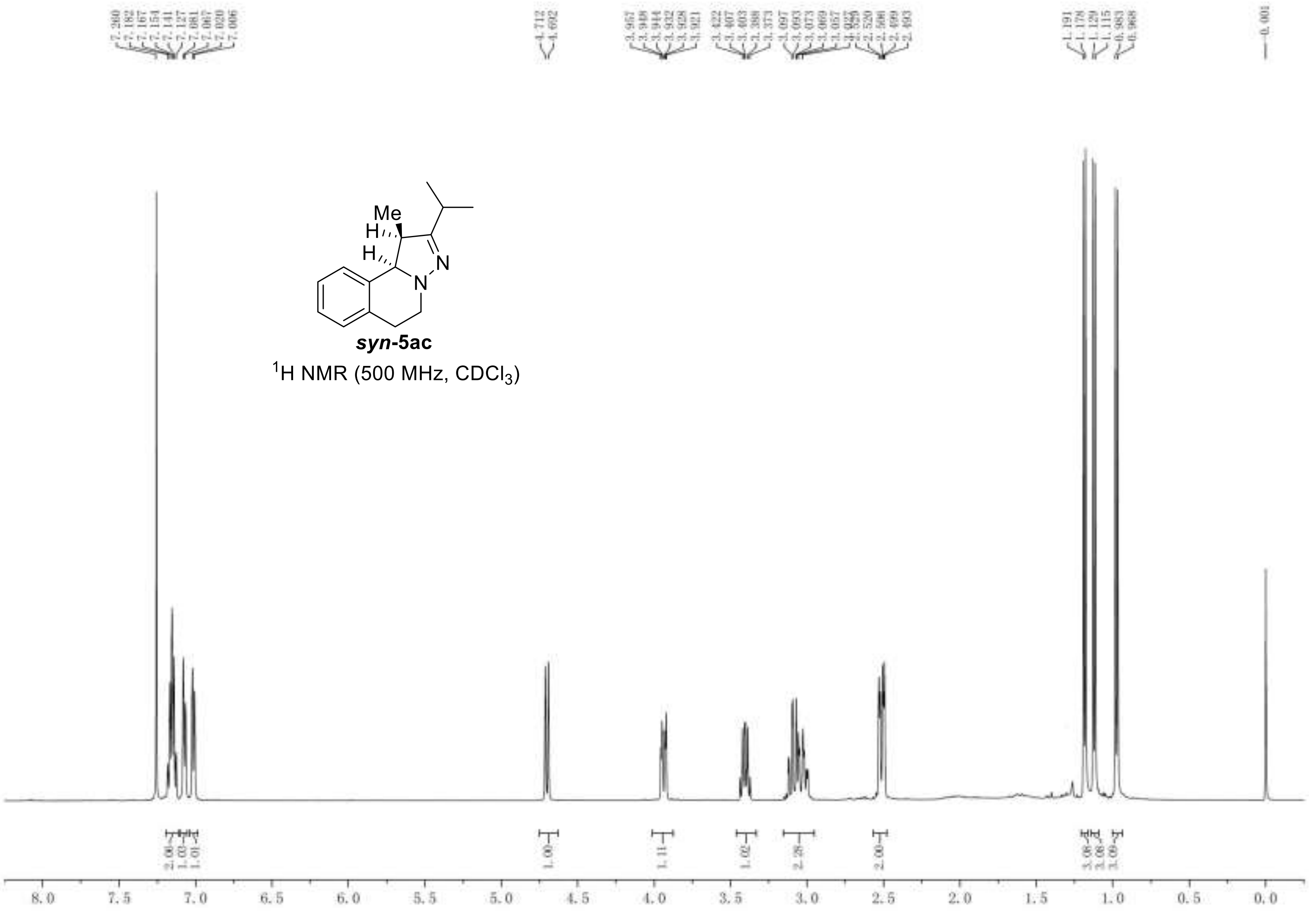
***anti*-5ab**

^{1}H NMR (500 MHz, CDCl$_3$)

***anti*-5ab**

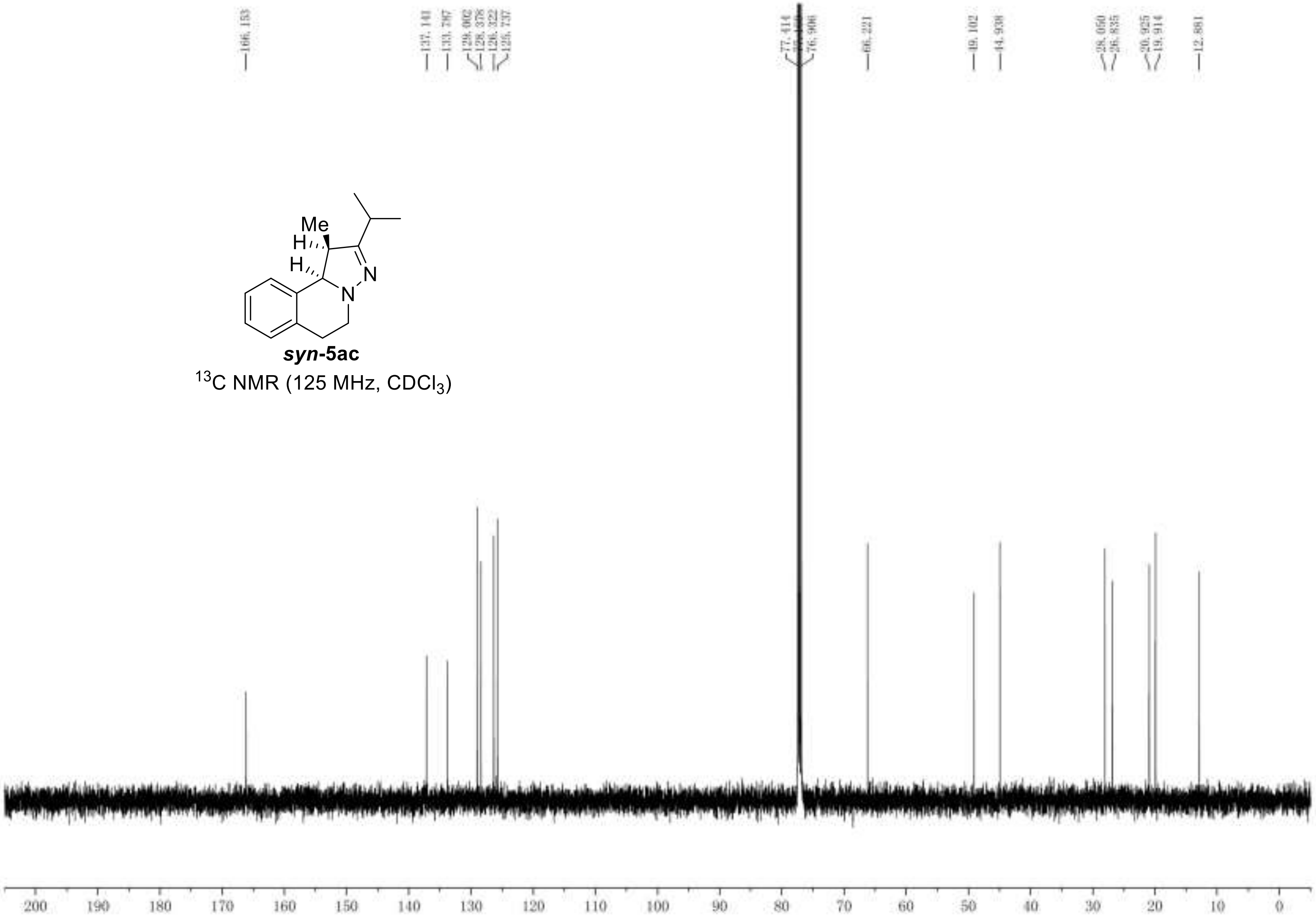
^{13}C NMR (125 MHz, CDCl$_3$)





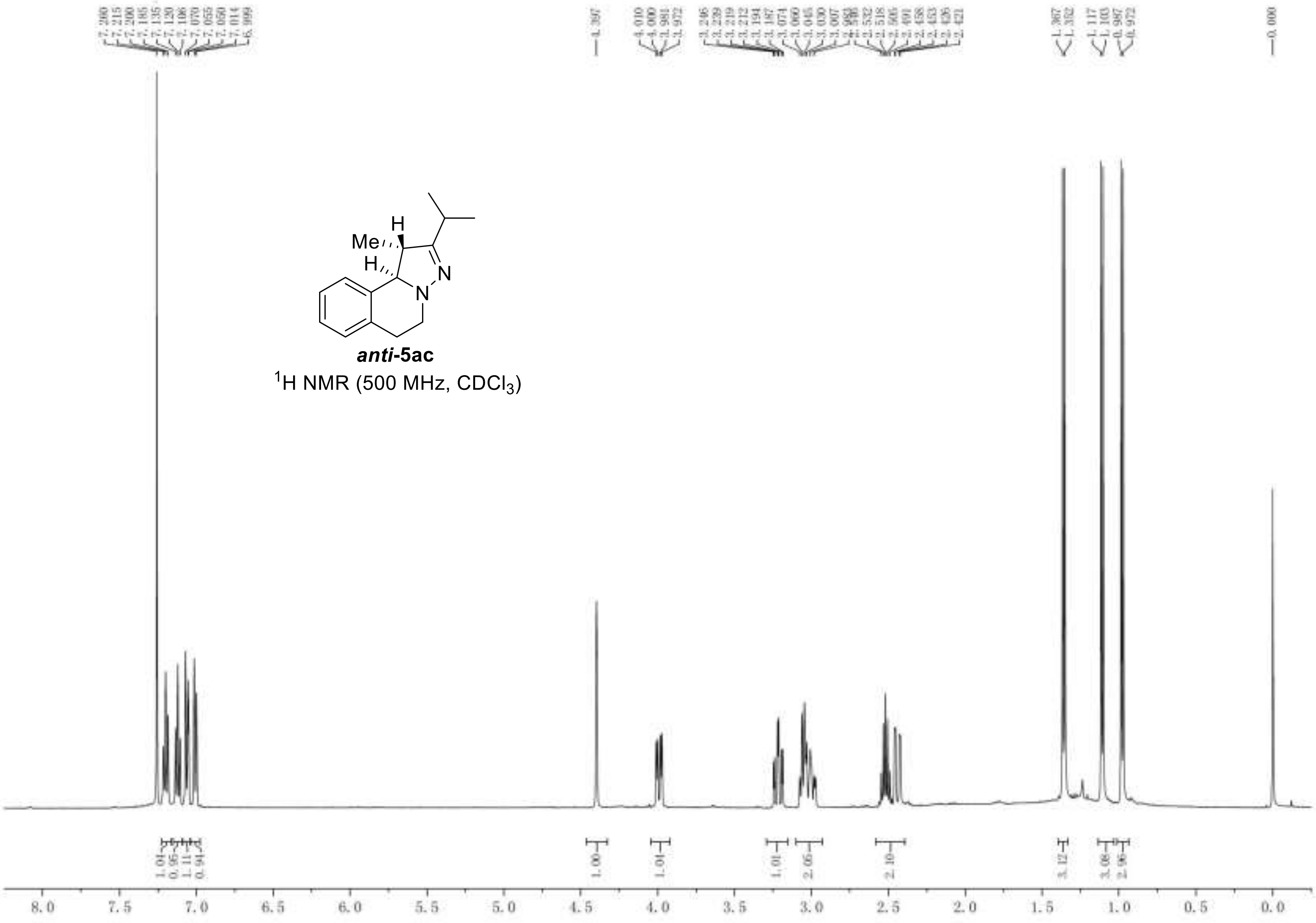
***syn*-5ac**

^{1}H NMR (500 MHz, CDCl$_3$)



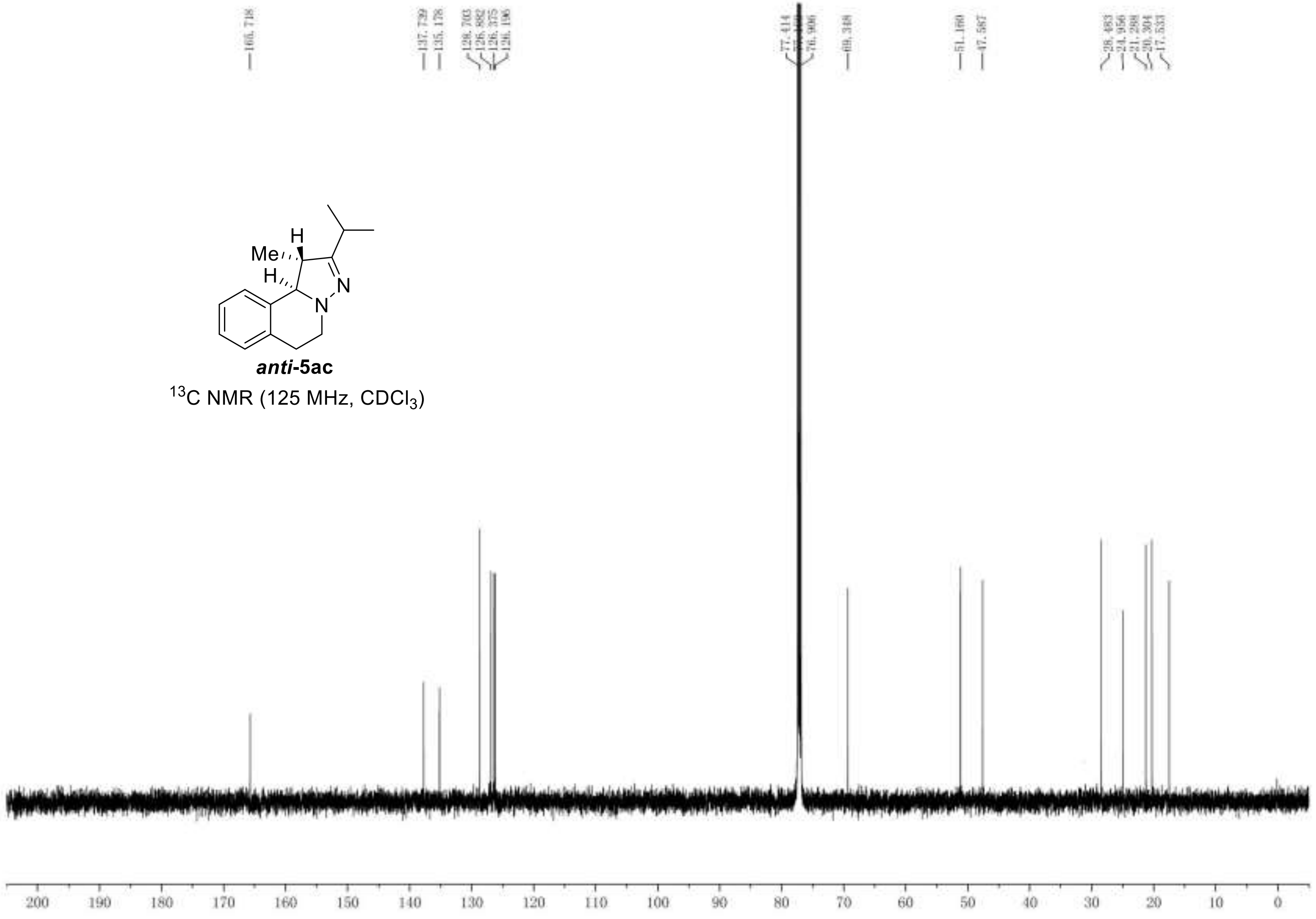
syn-5ac

^{13}C NMR (125 MHz, $CDCl_3$)



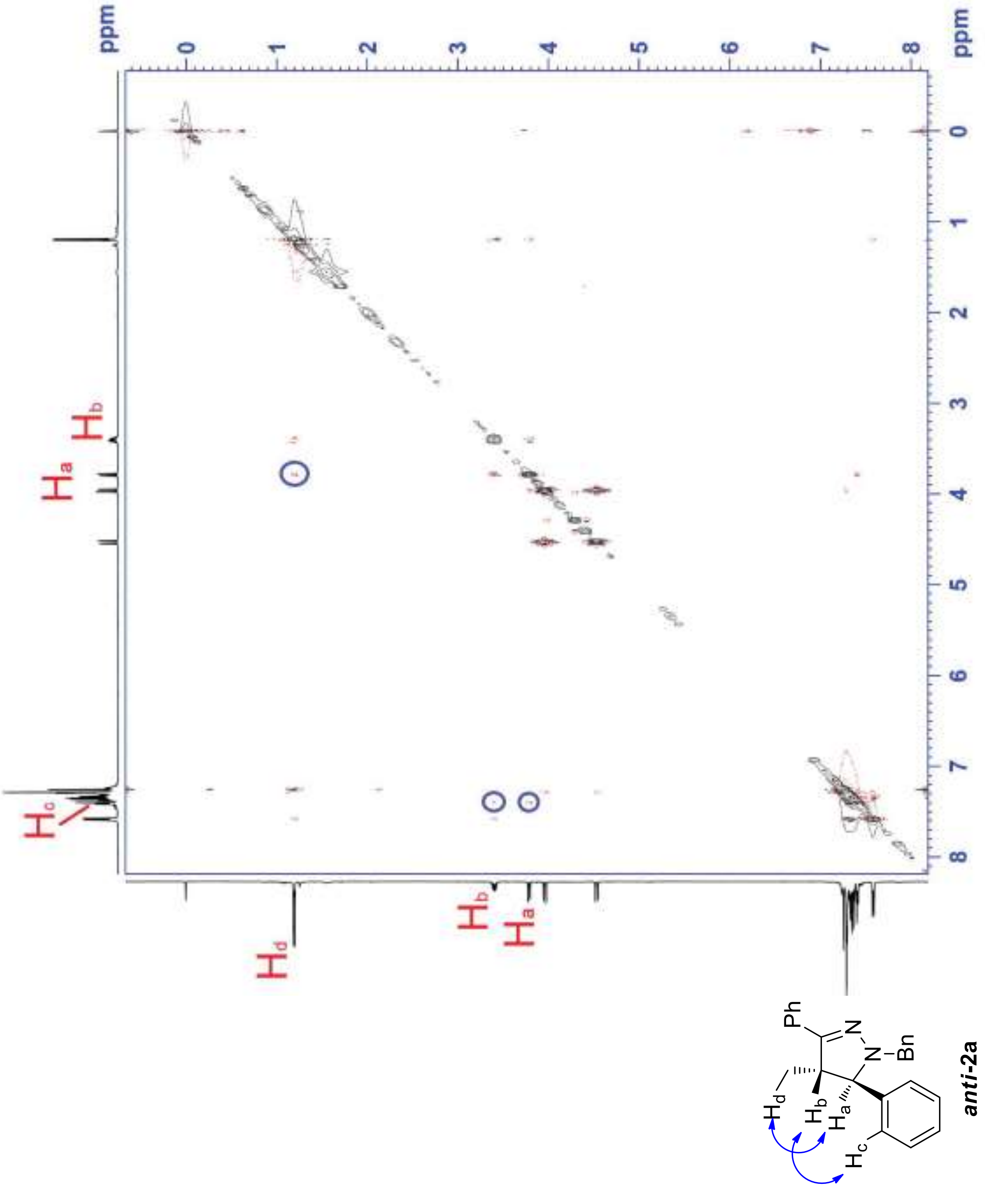
***anti*-5ac**

^{1}H NMR (500 MHz, CDCl$_3$)

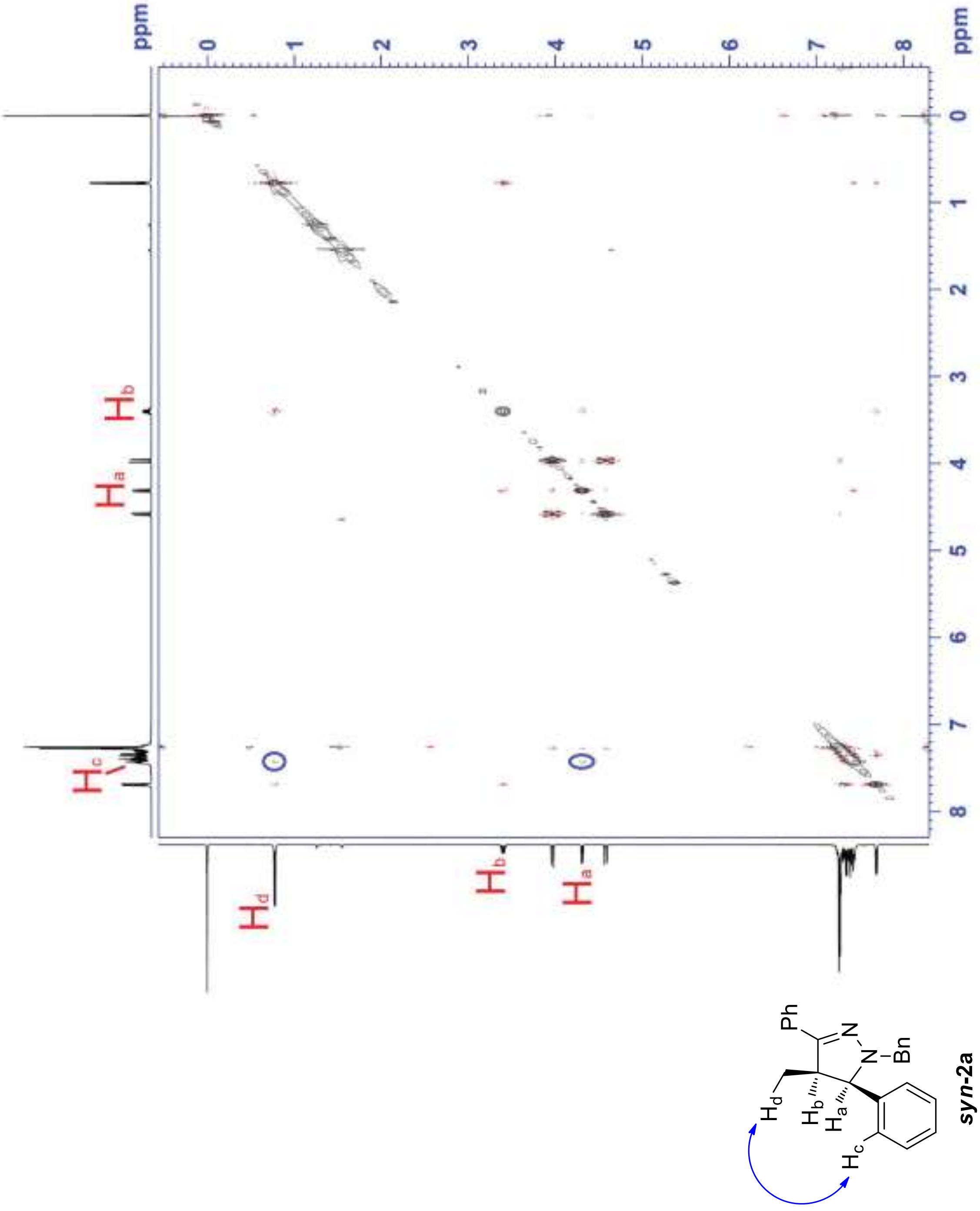


***anti*-5ac**

^{13}C NMR (125 MHz, $CDCl_3$)



anti-2a



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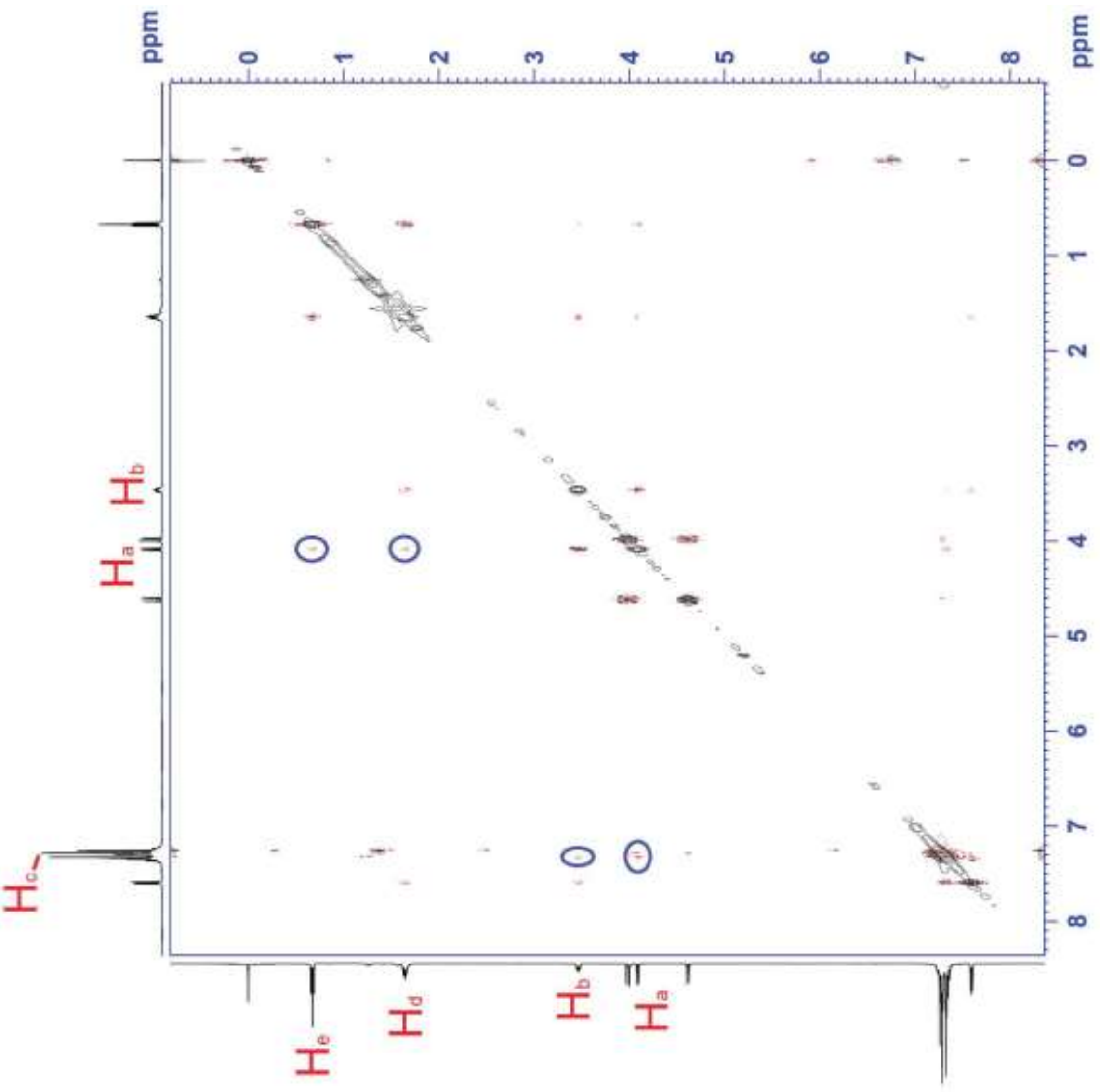

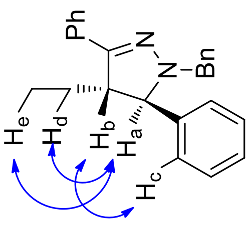

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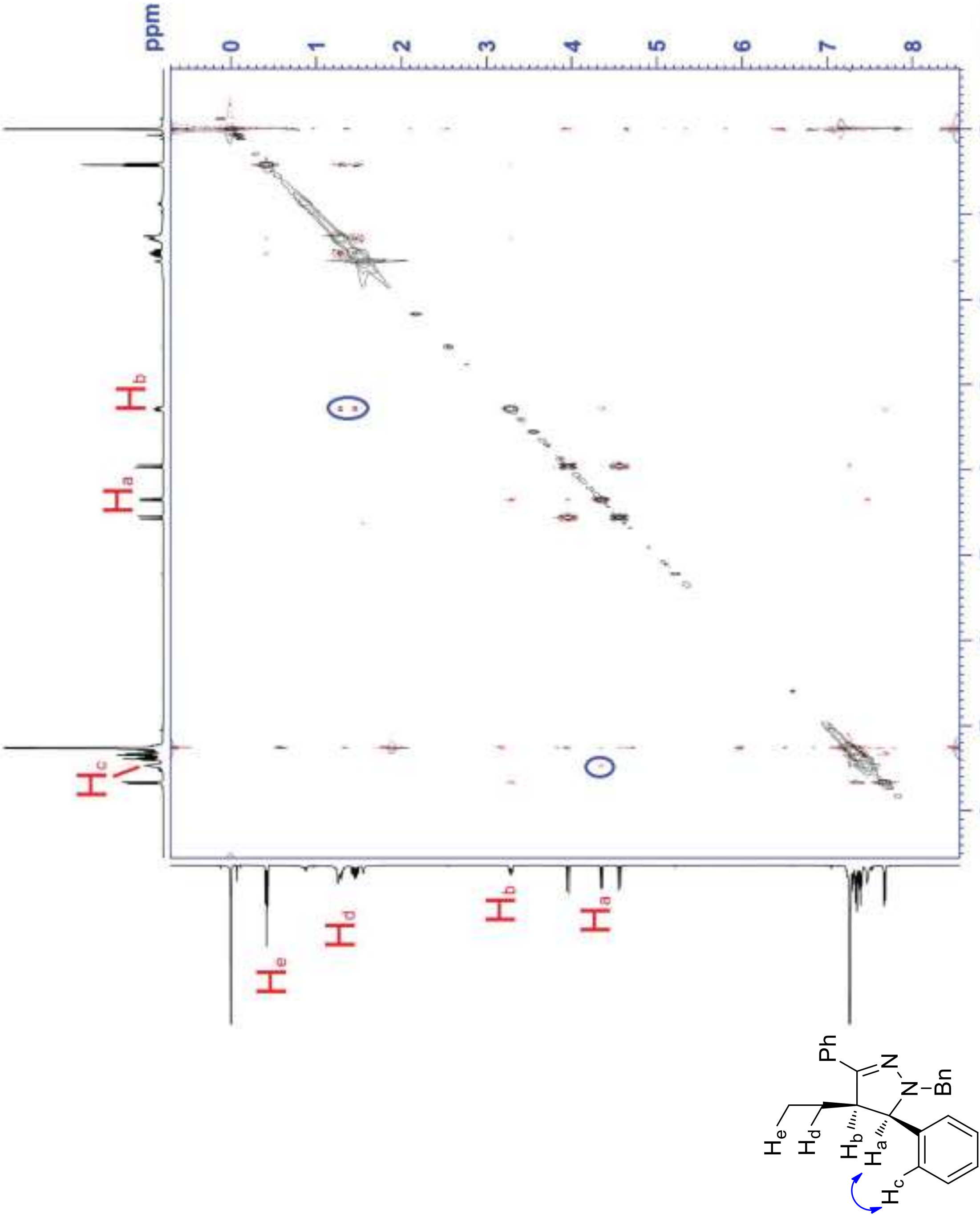
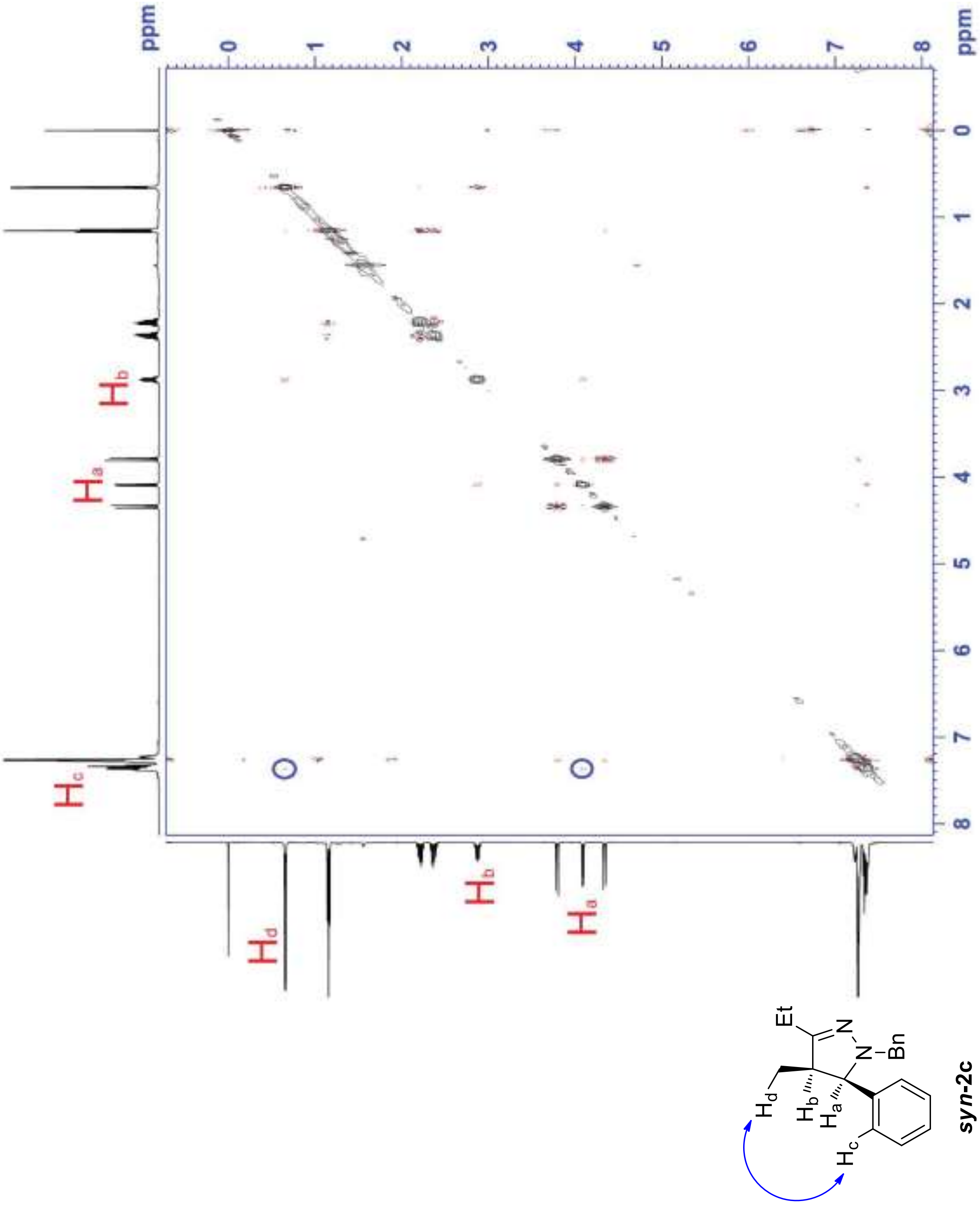


syn-2b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Hd
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Hc
Et
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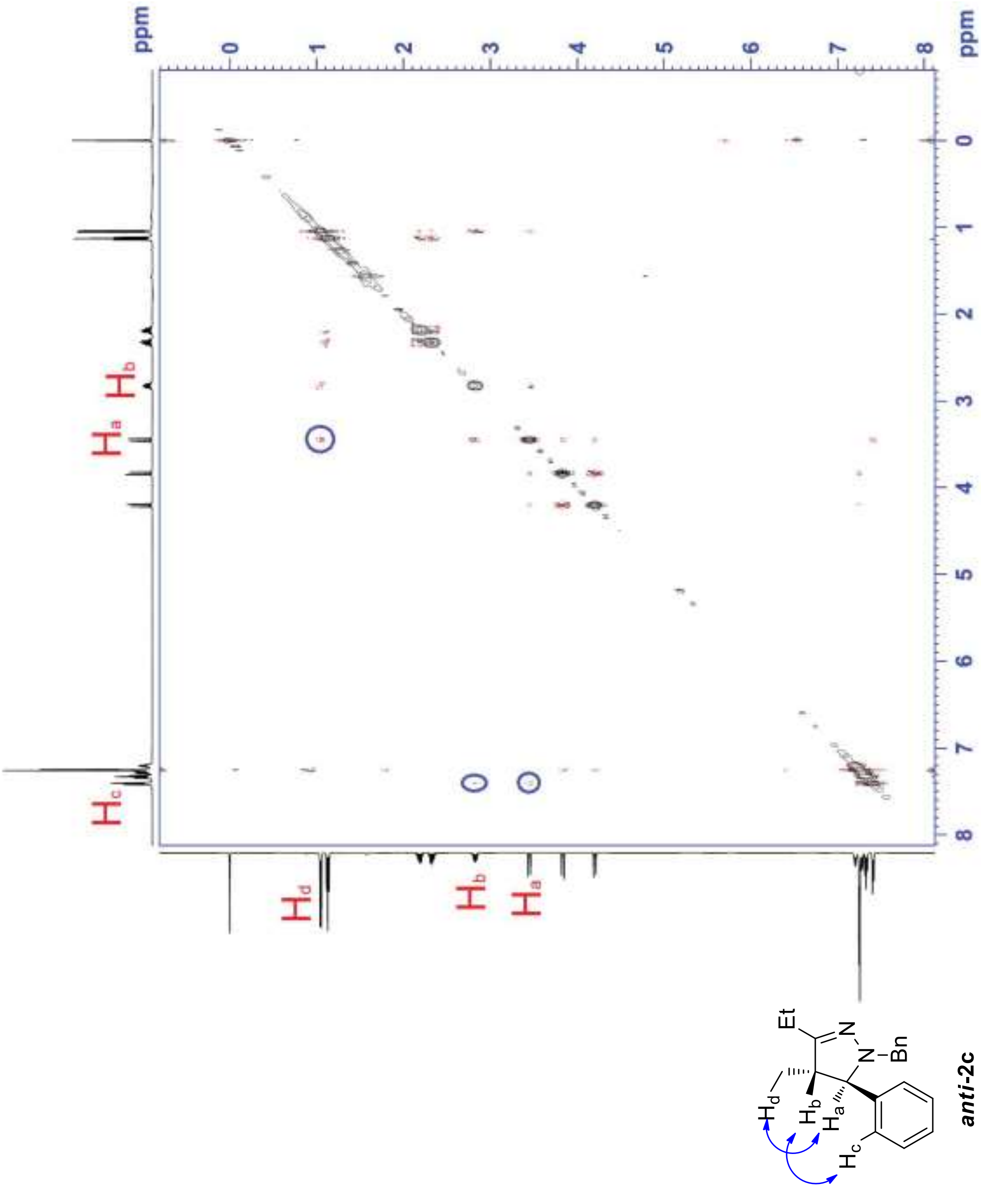
N
Bn

***syn*-2c**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ppm
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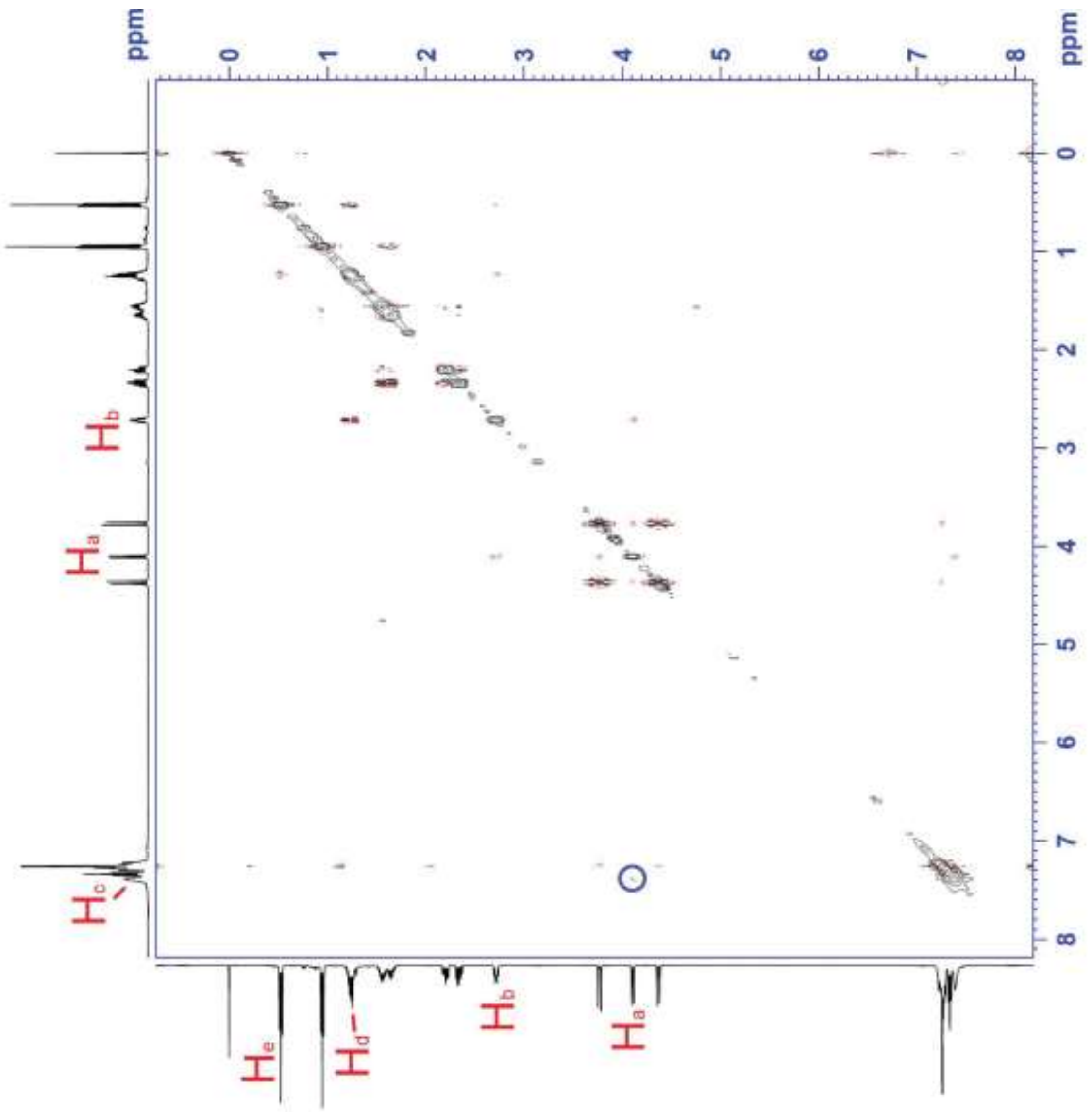
Bn
Hd
Hb
Ha
Hc

***anti*-2c**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Hb
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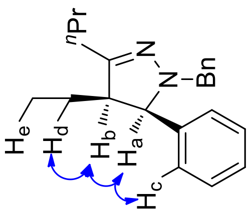
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Bn

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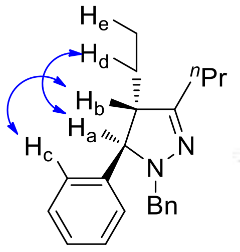

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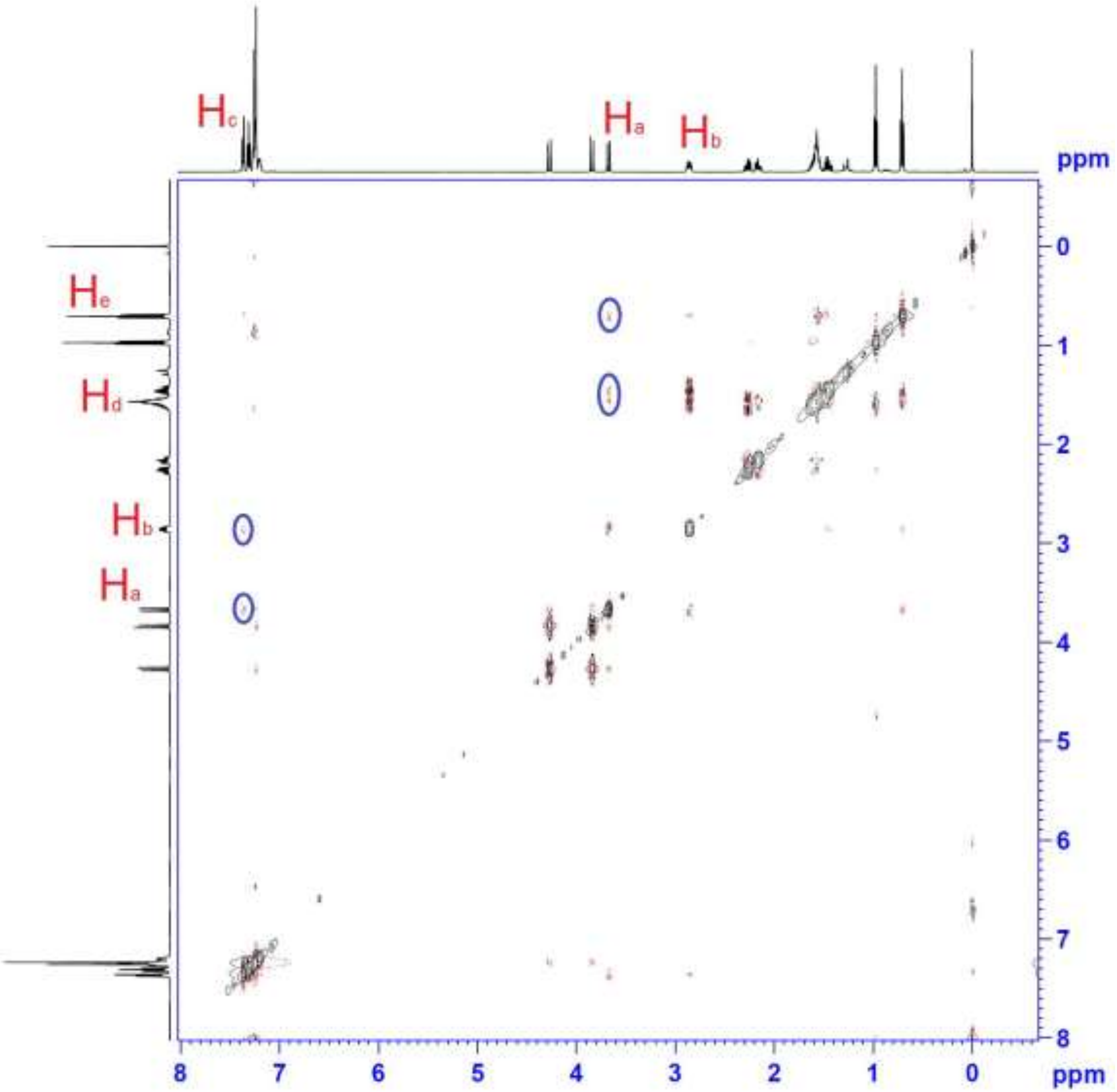

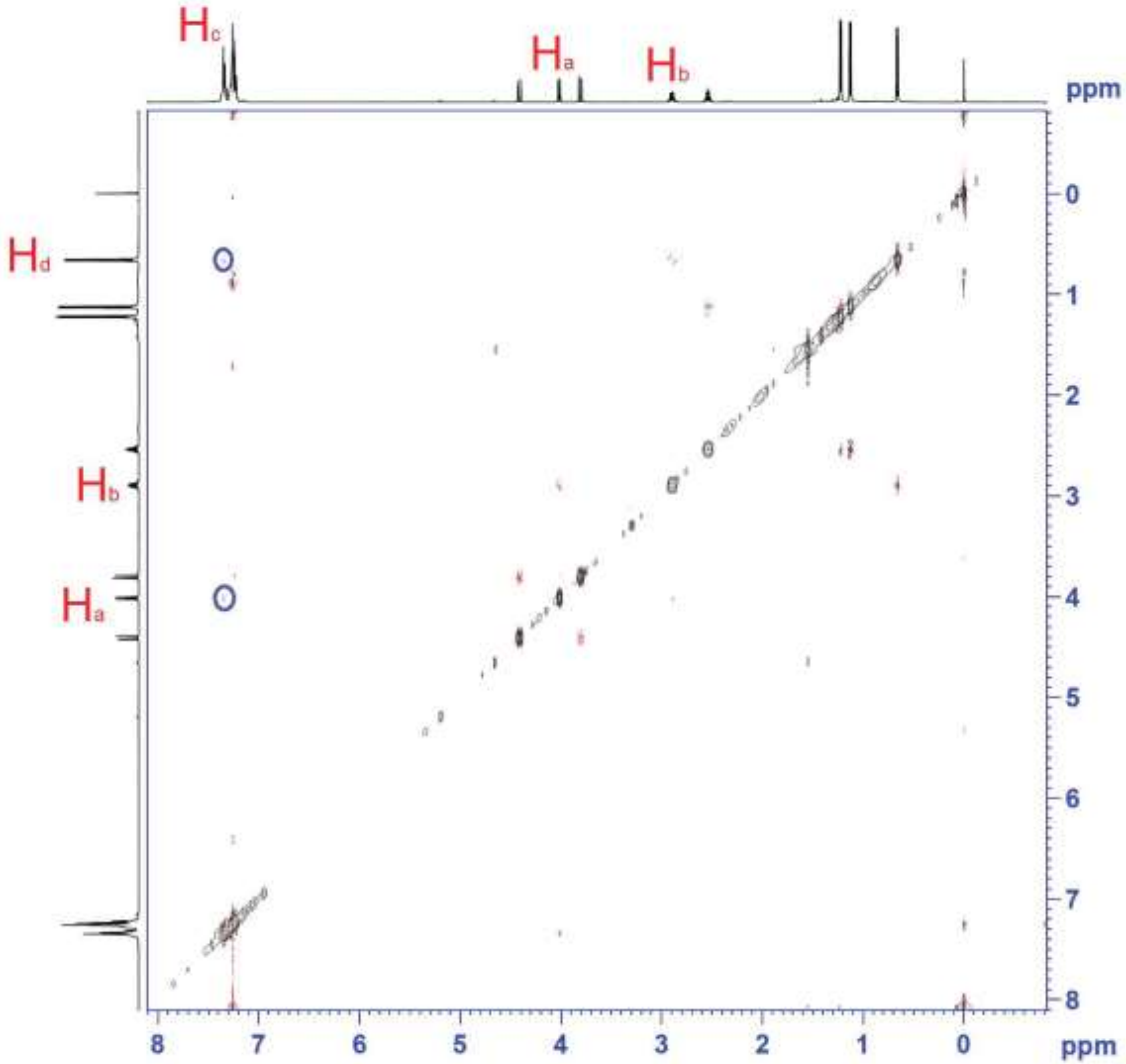
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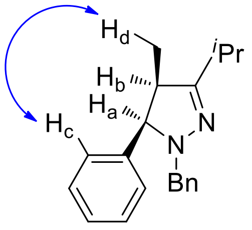
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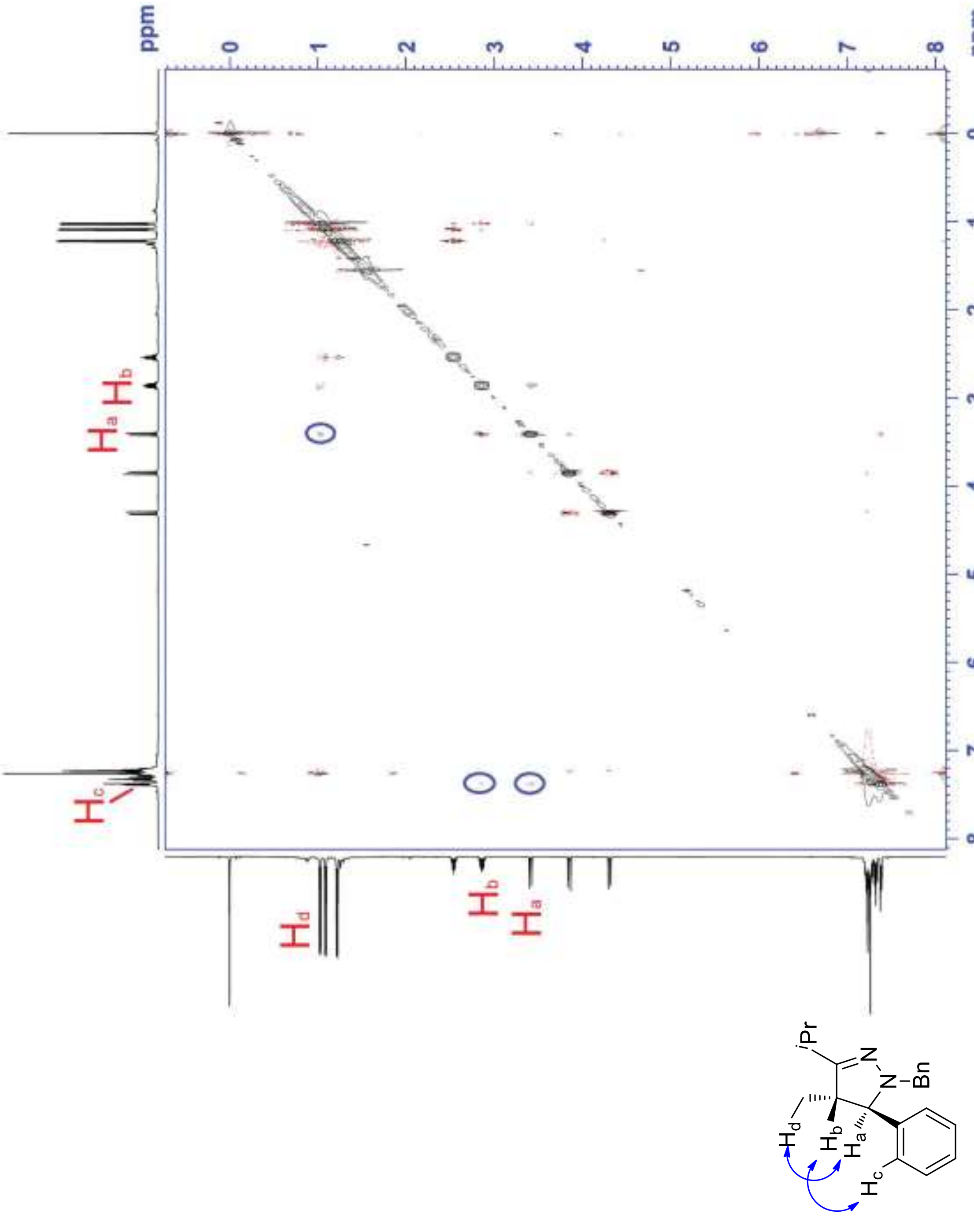
Bn

***syn*-2e**



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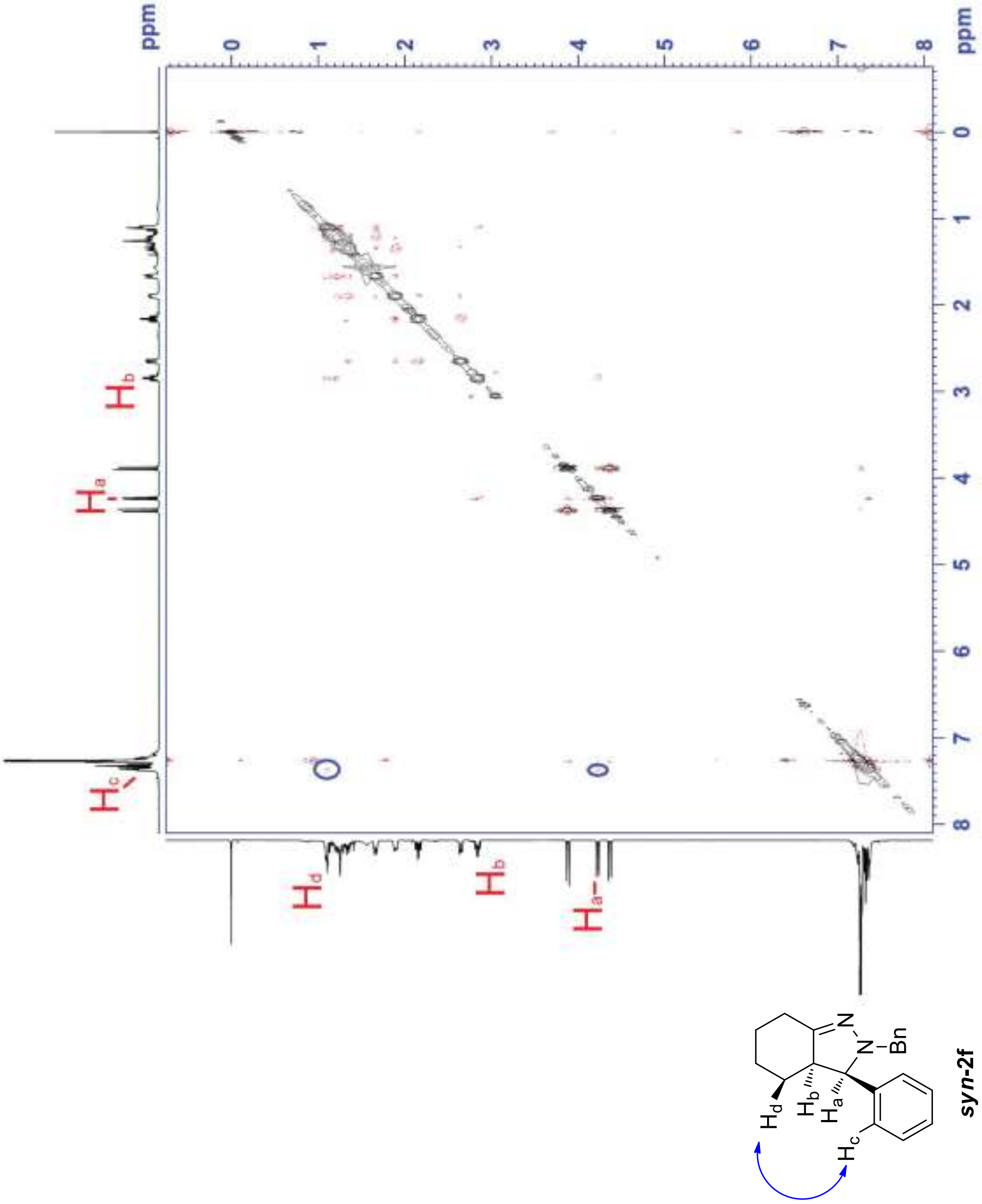

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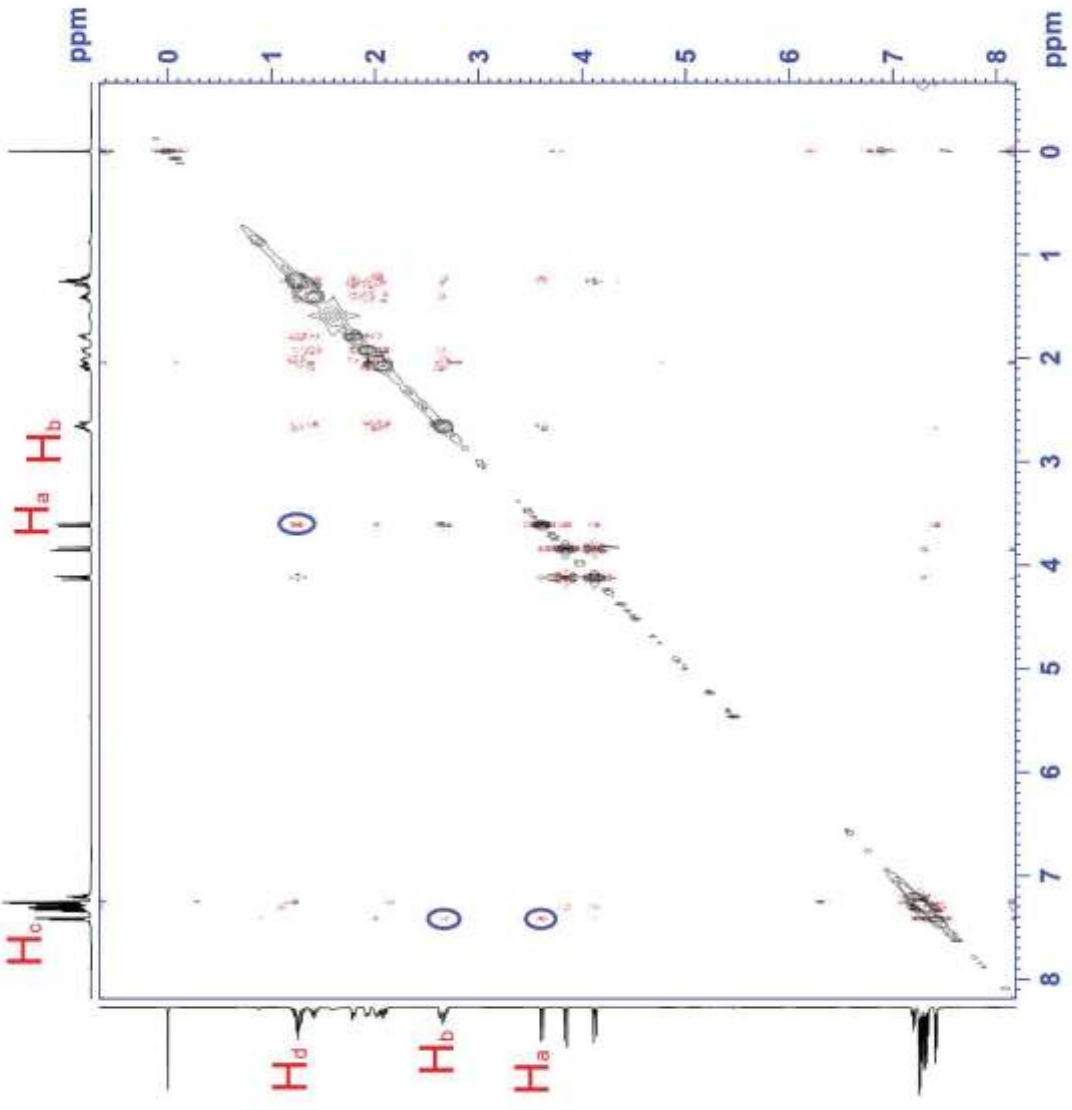

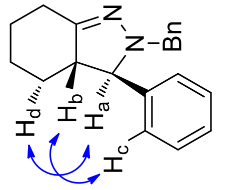

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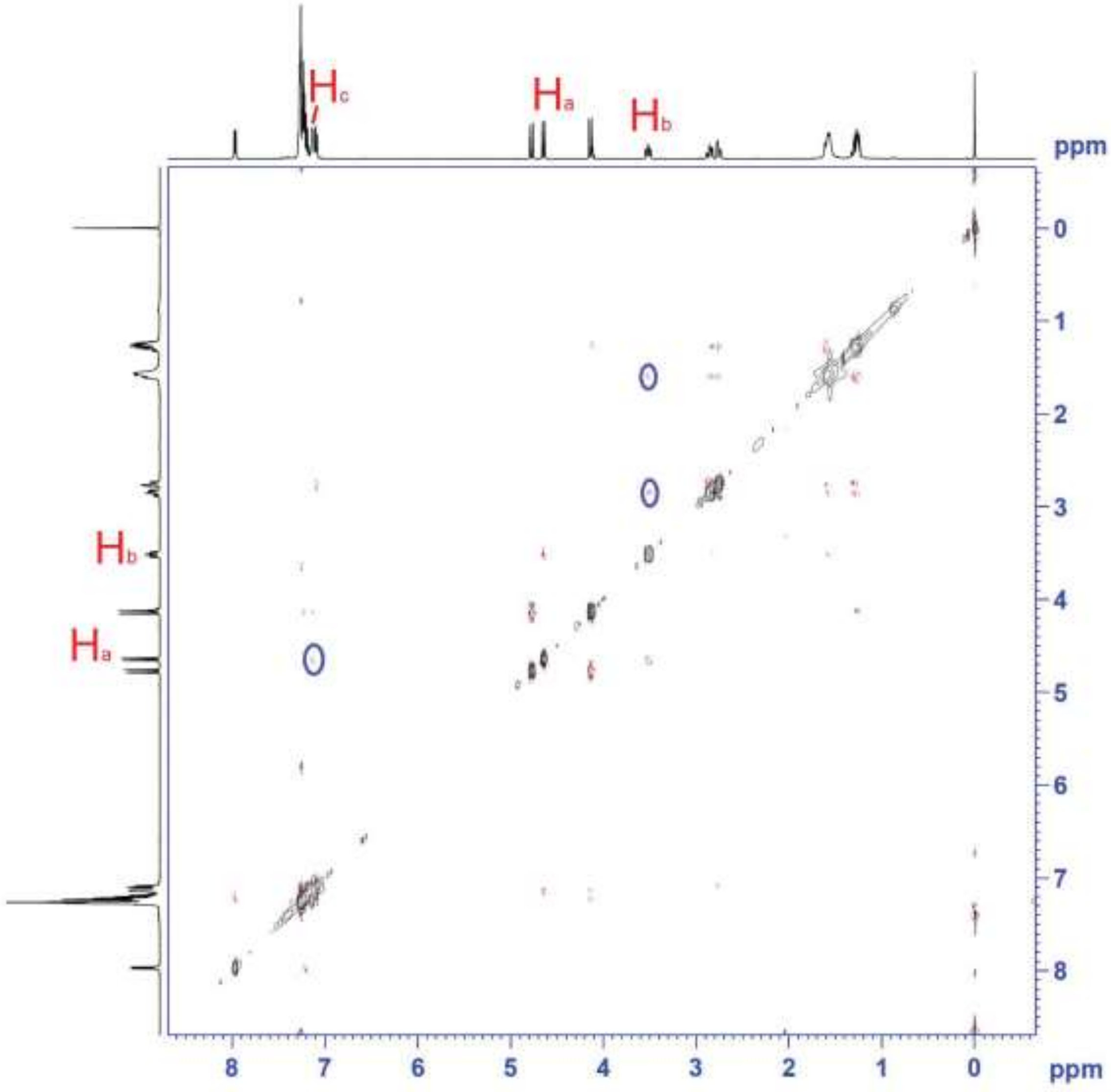
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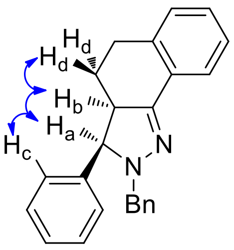
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N
Bn

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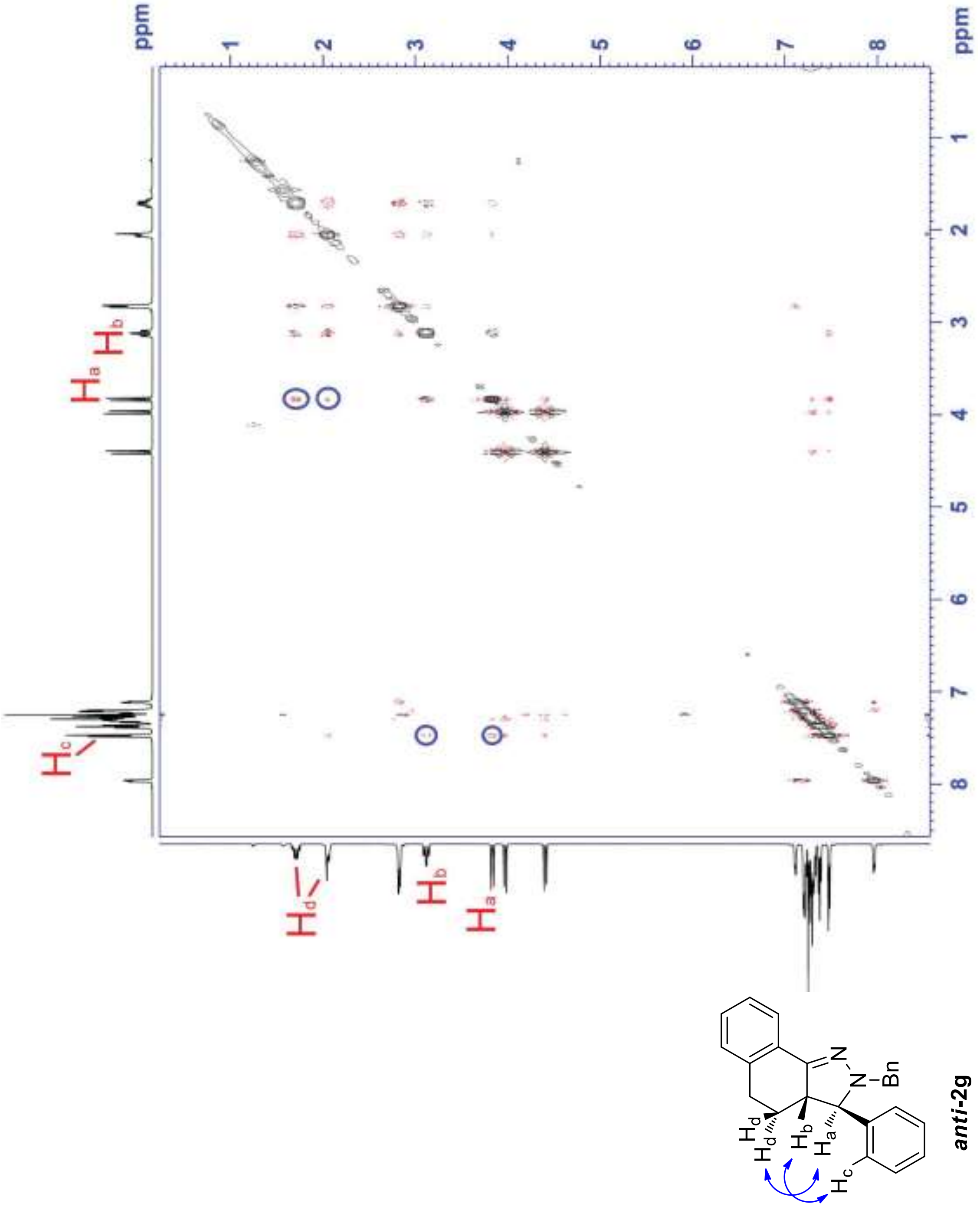

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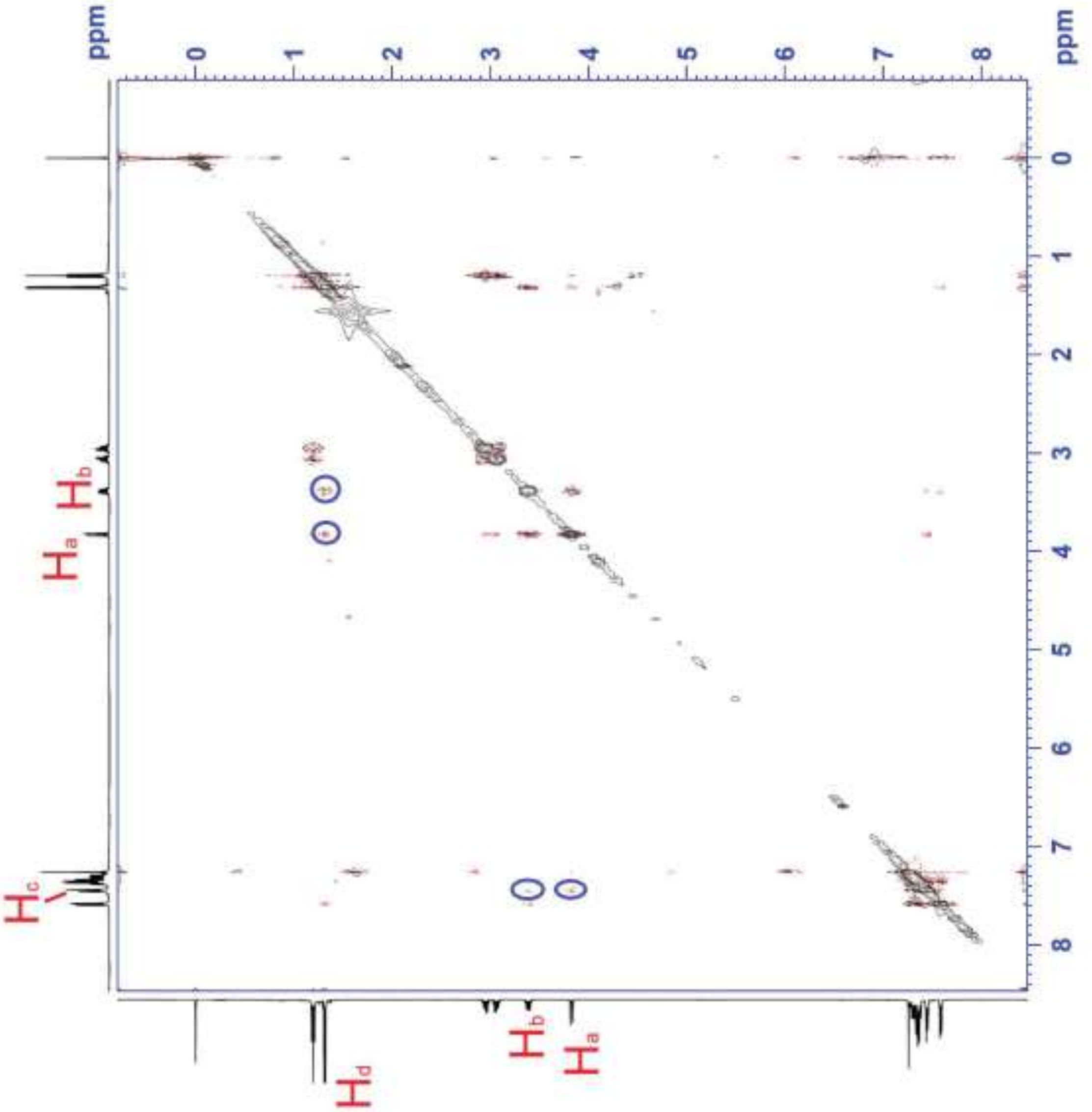

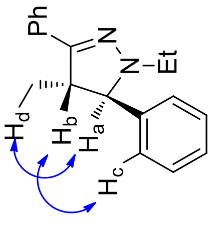

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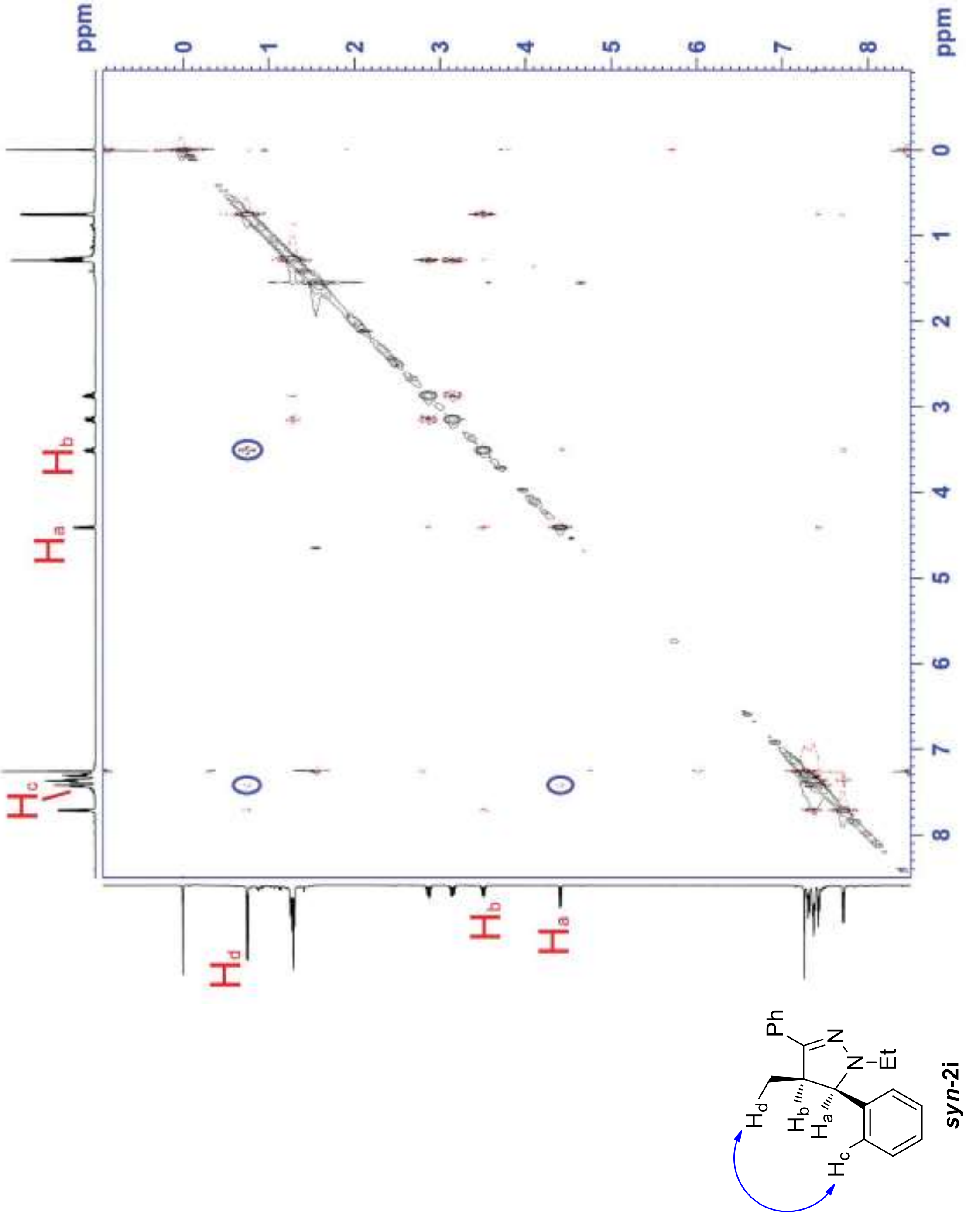

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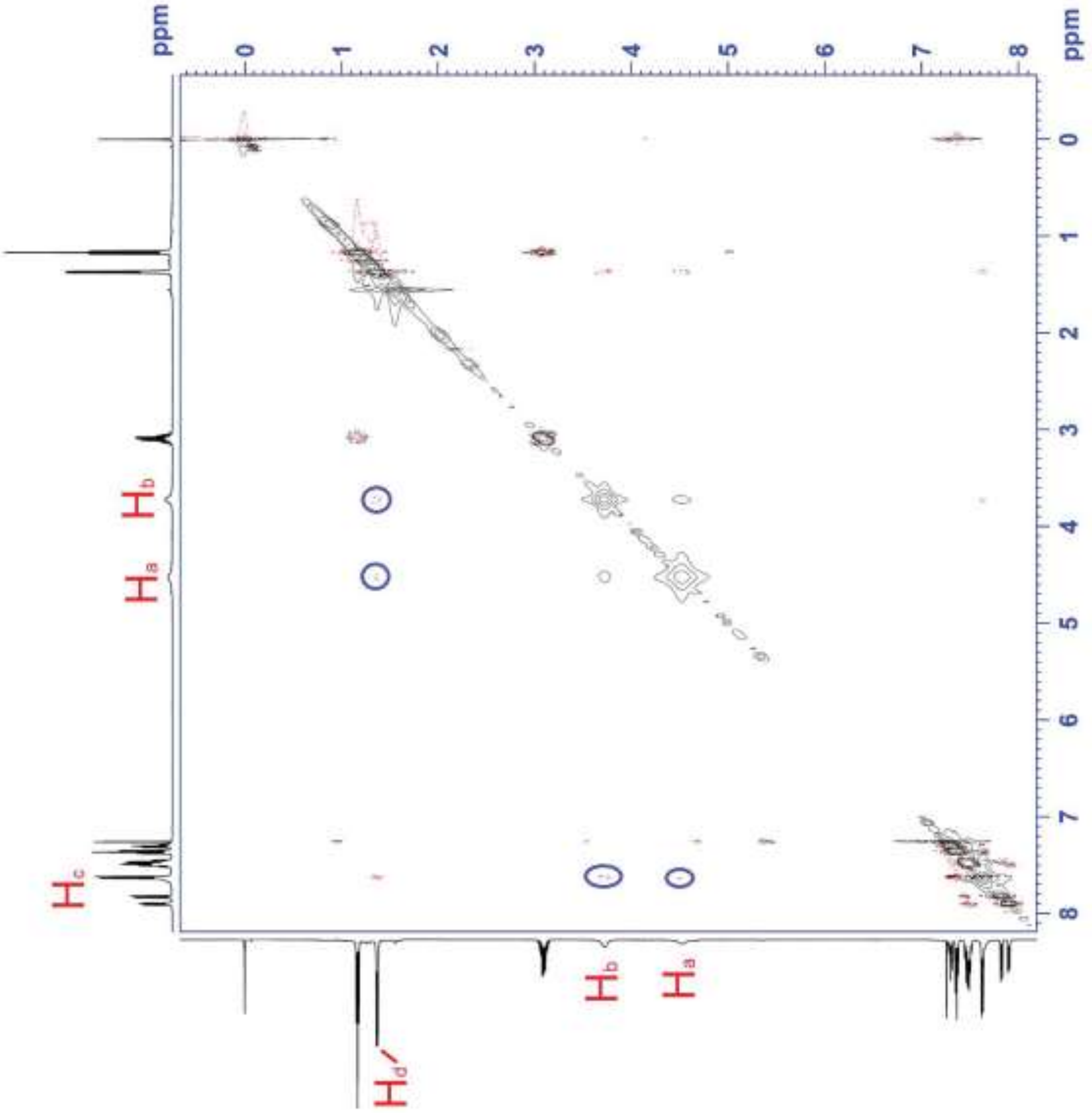

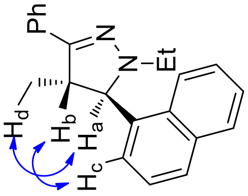

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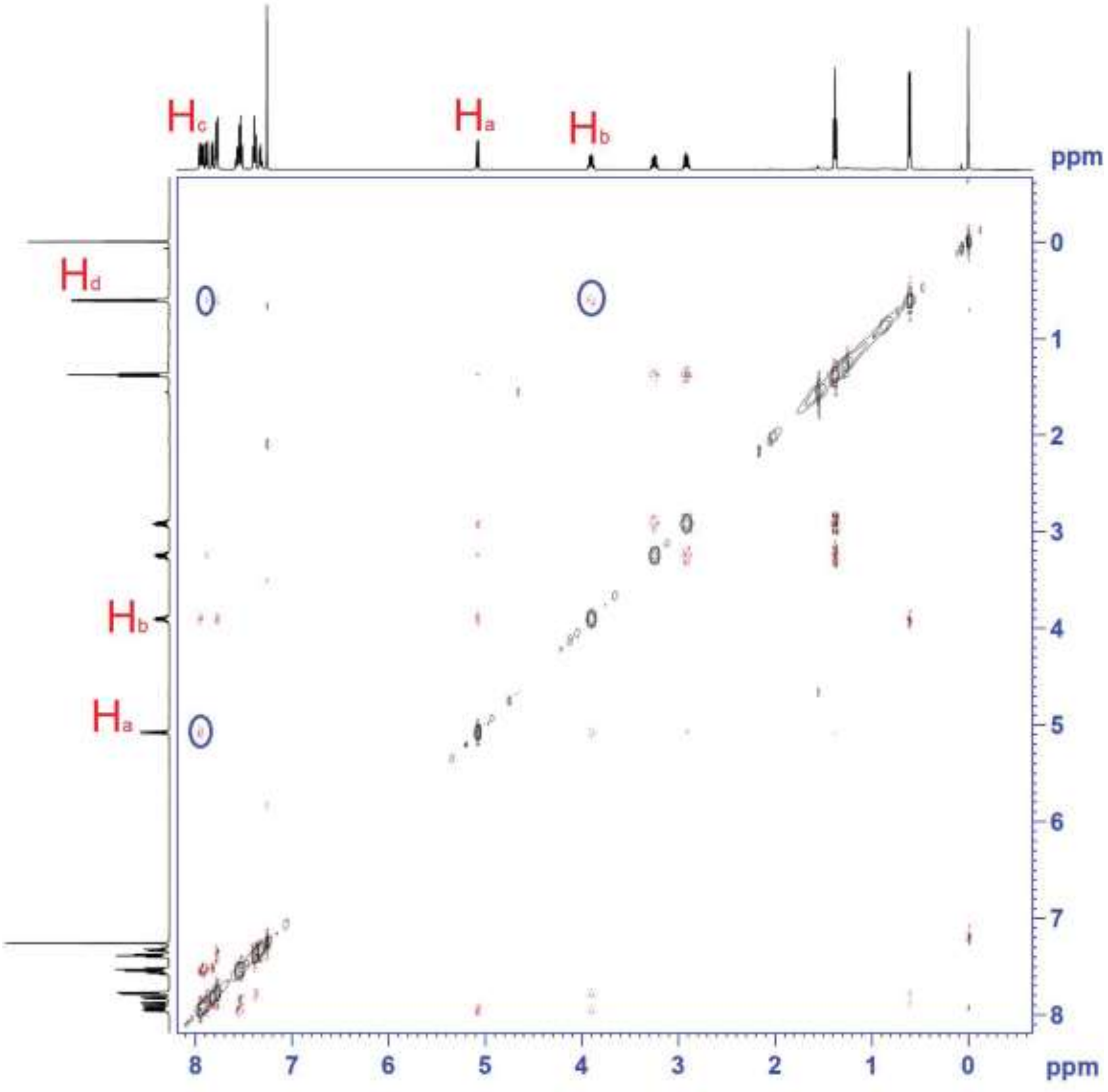
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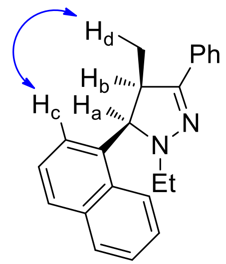
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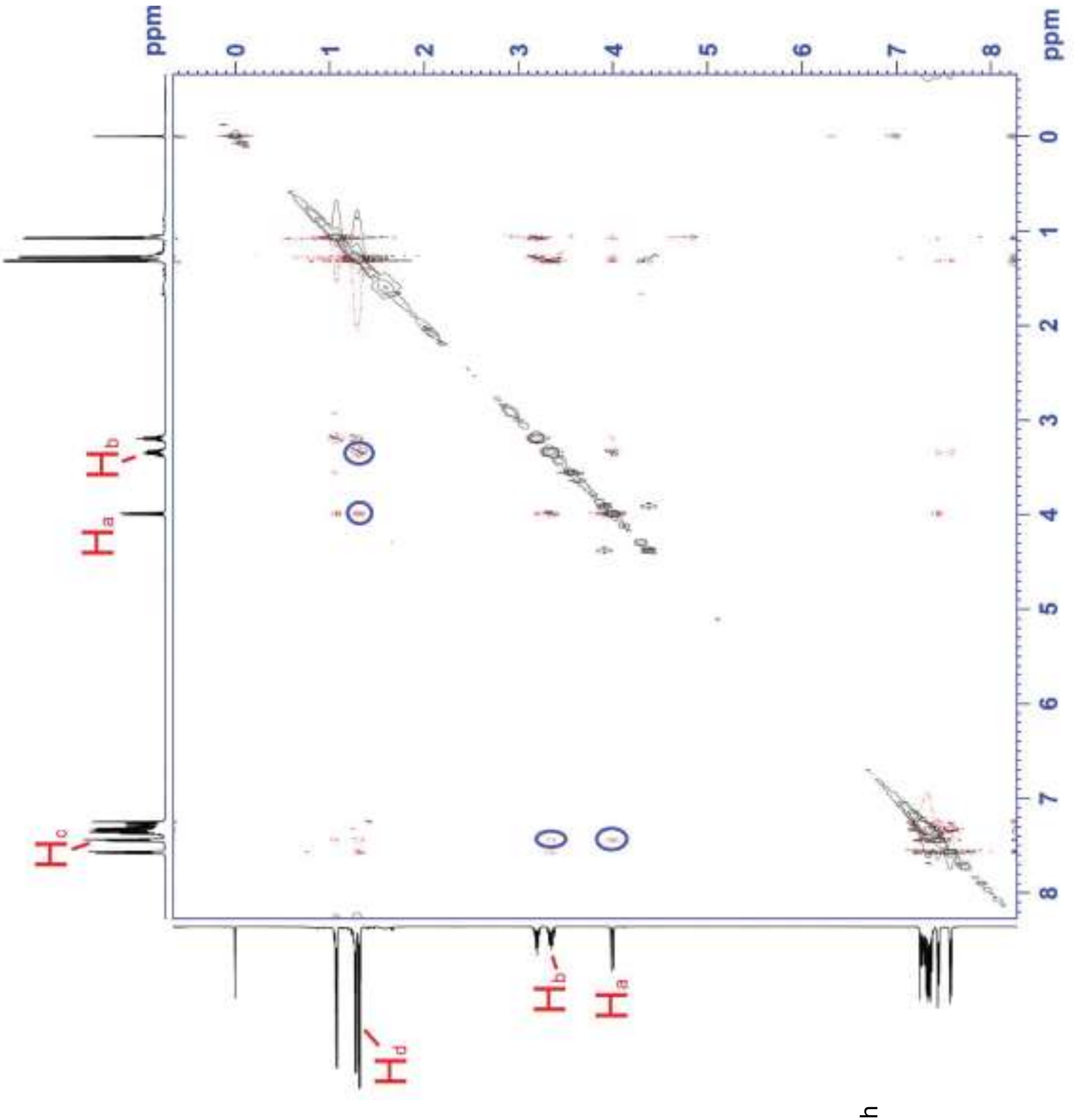
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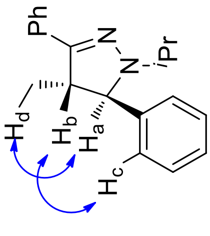
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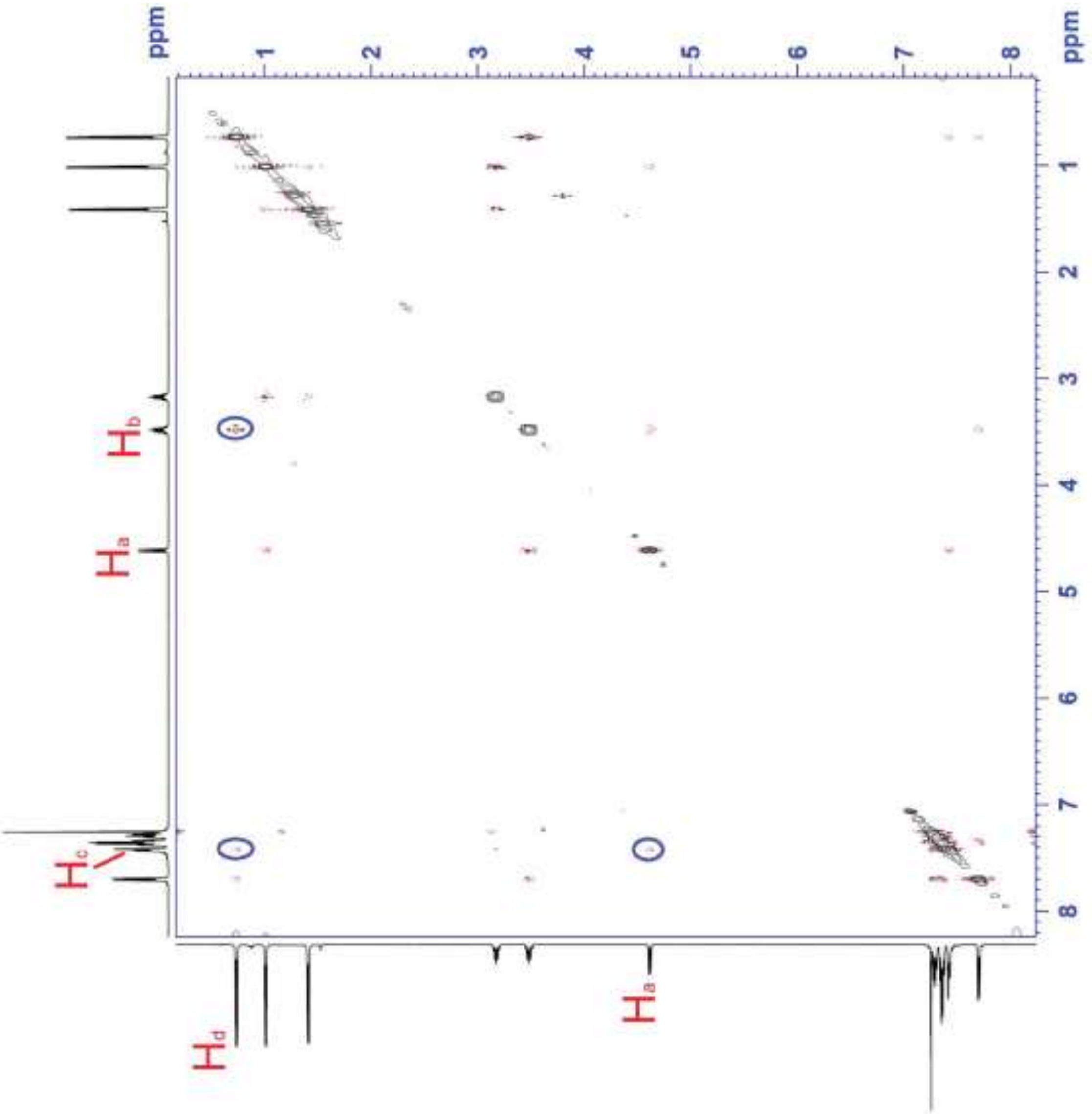
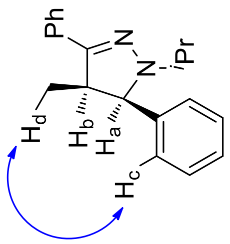
***anti*-2k**





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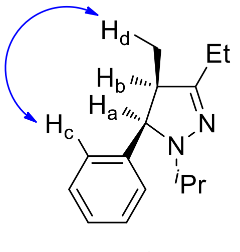
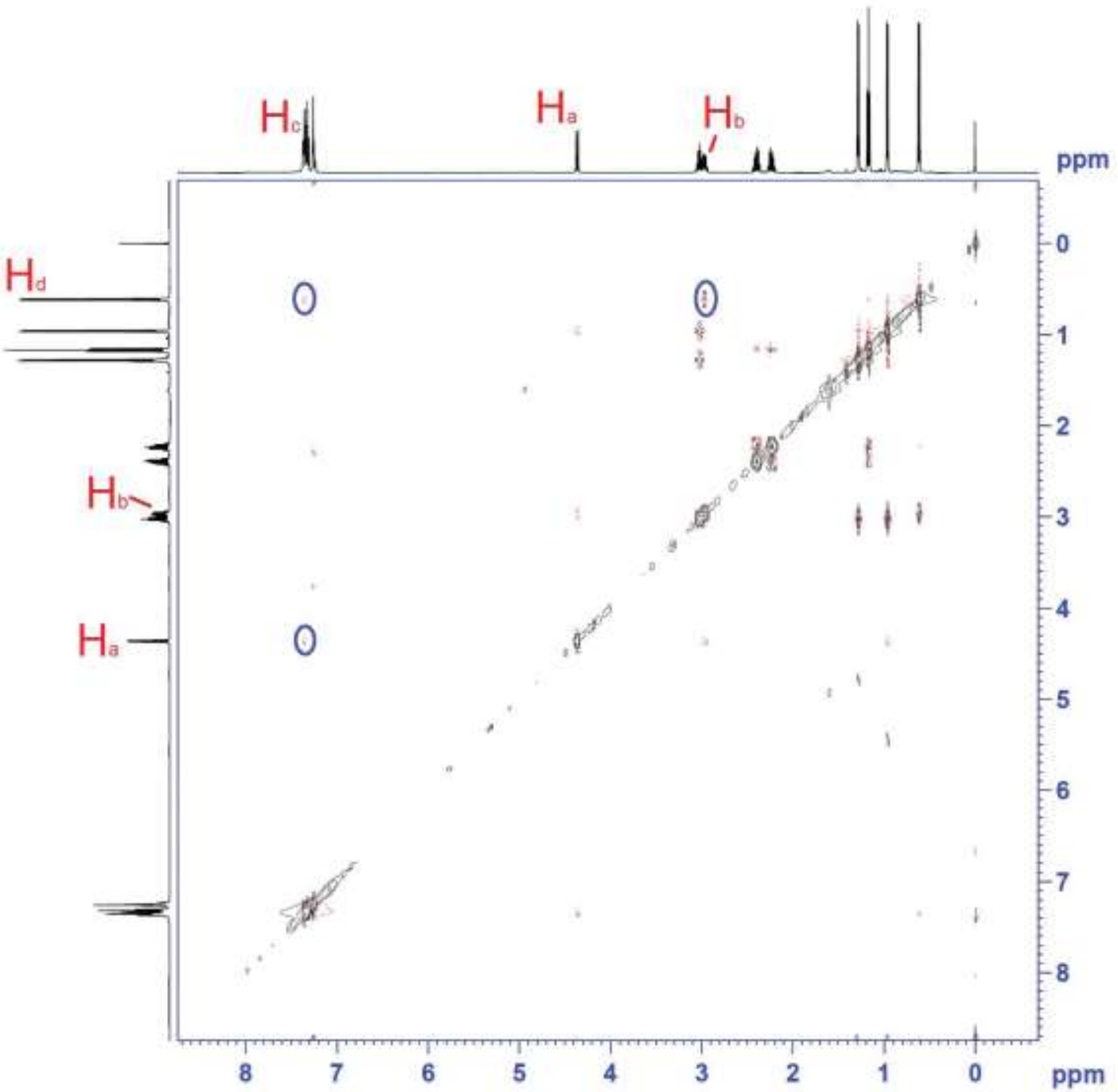
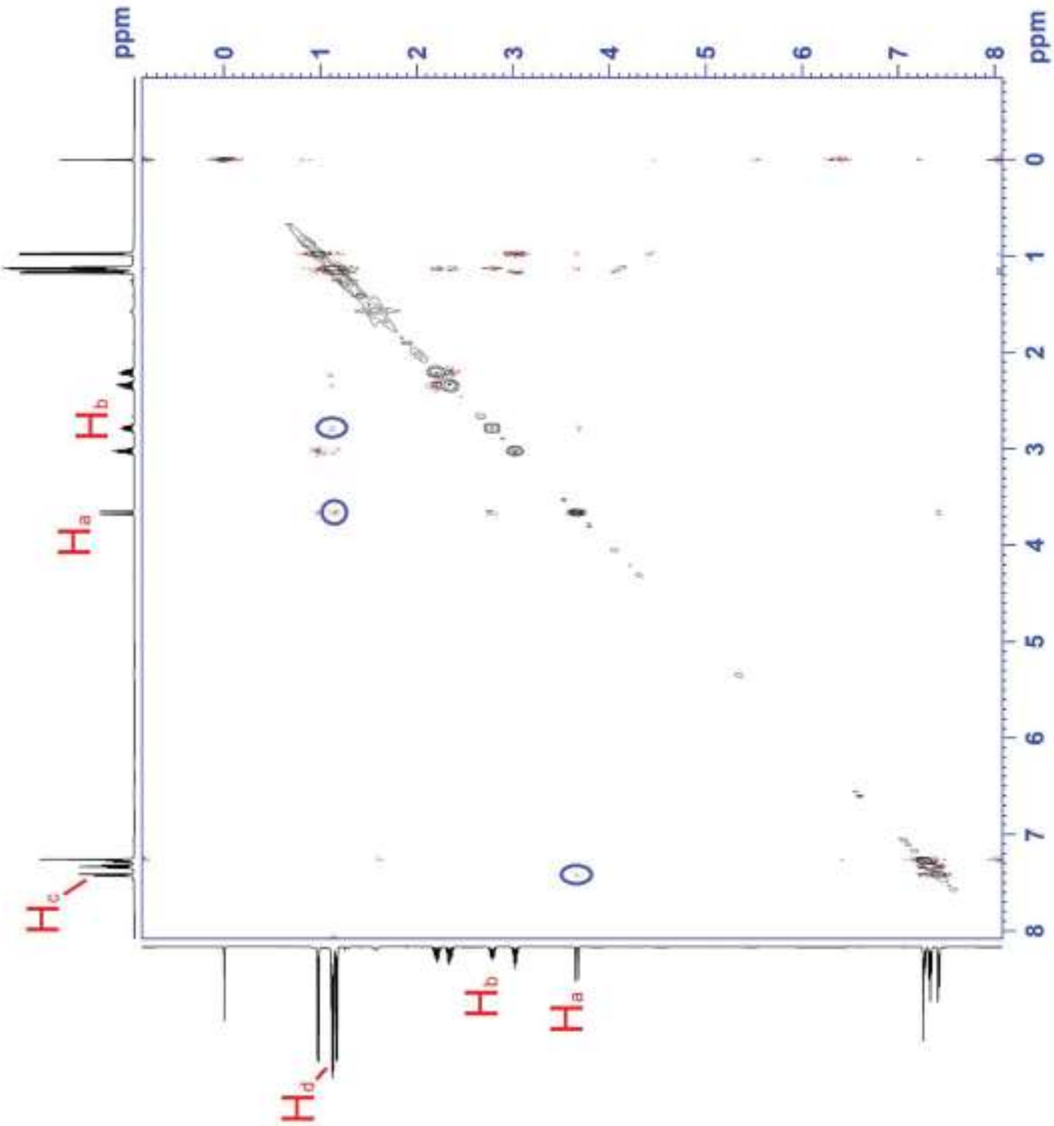
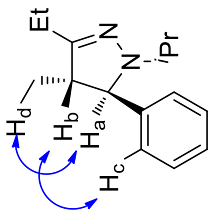


syn-2l







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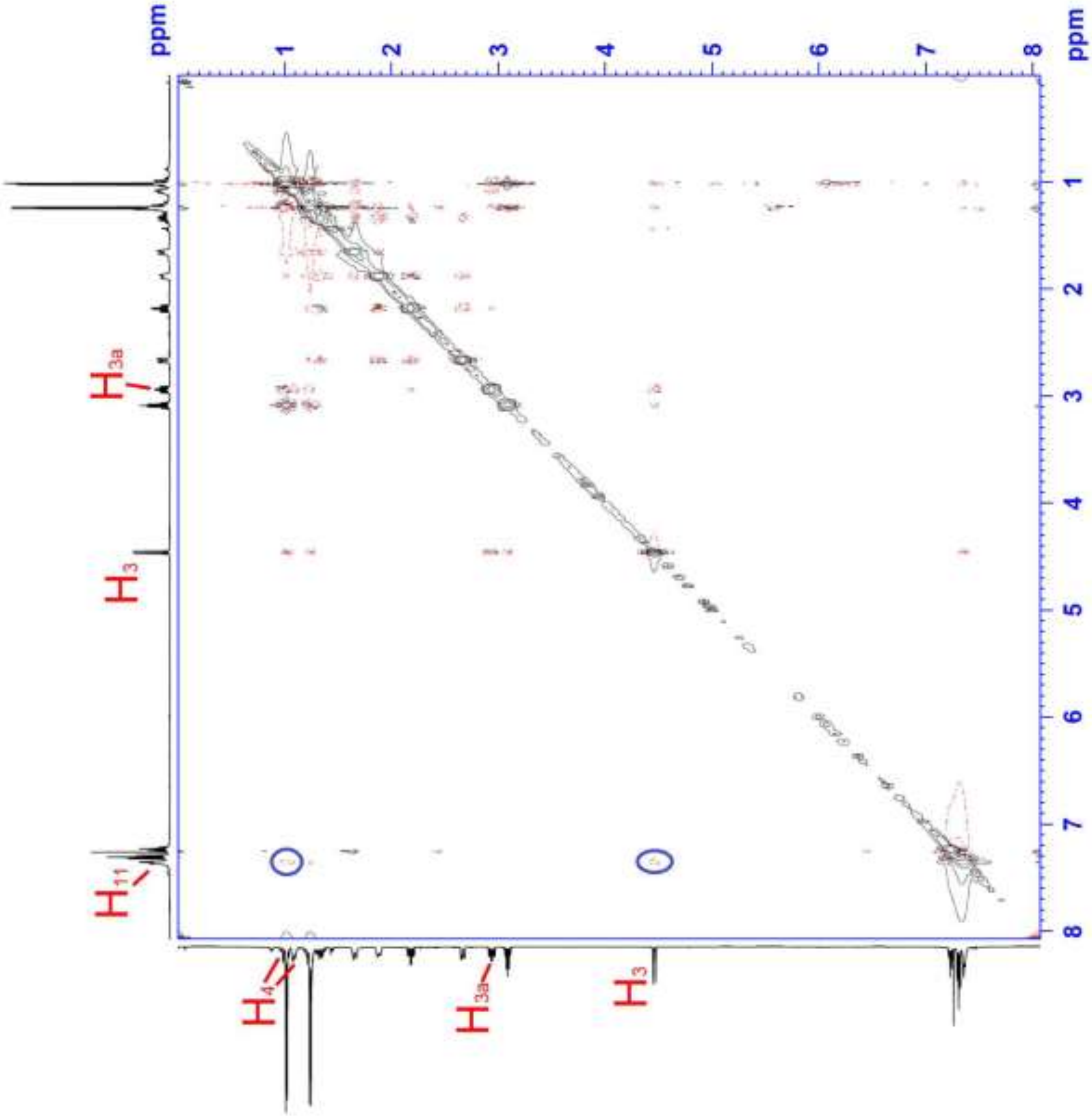

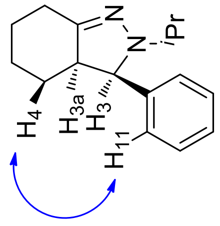

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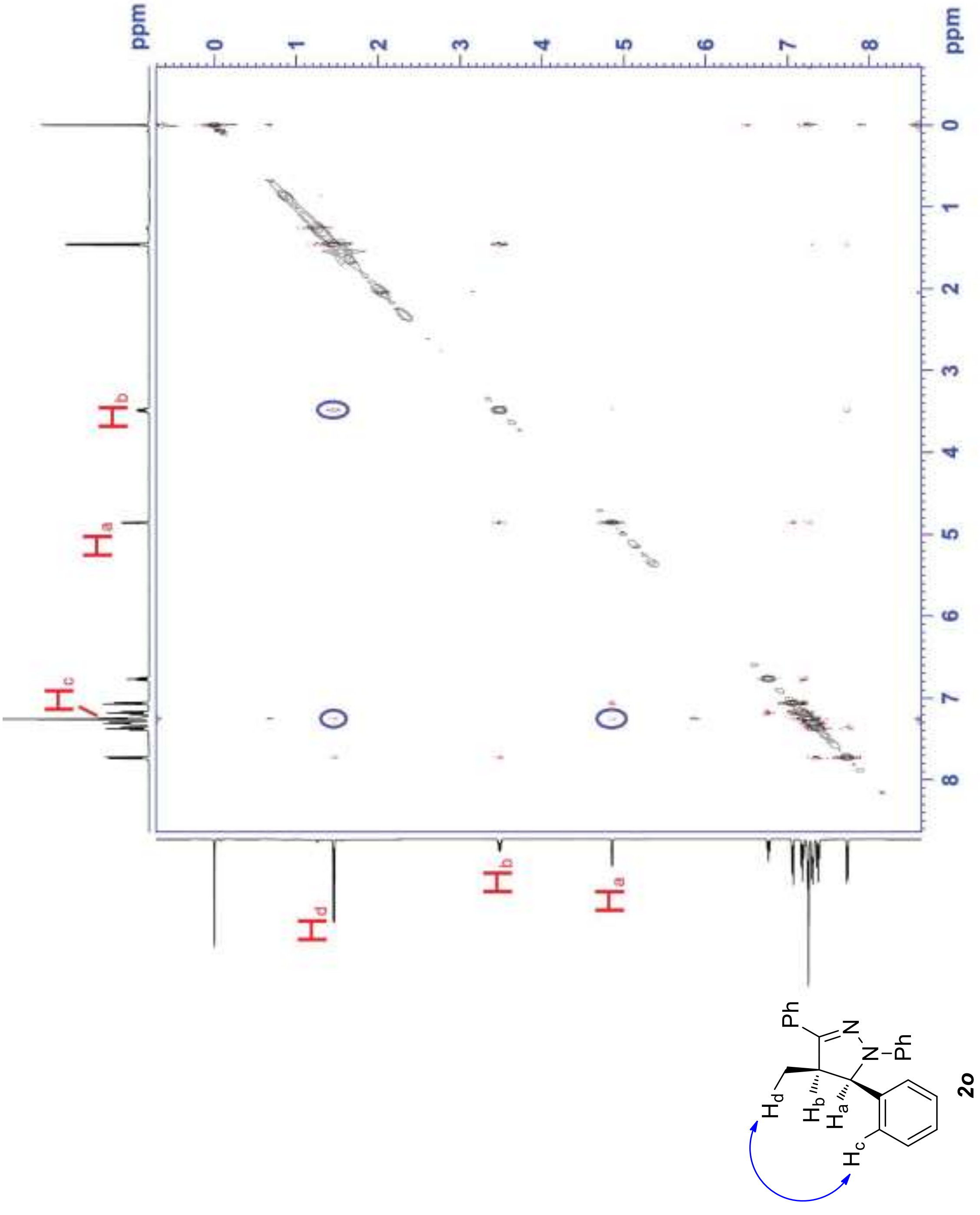
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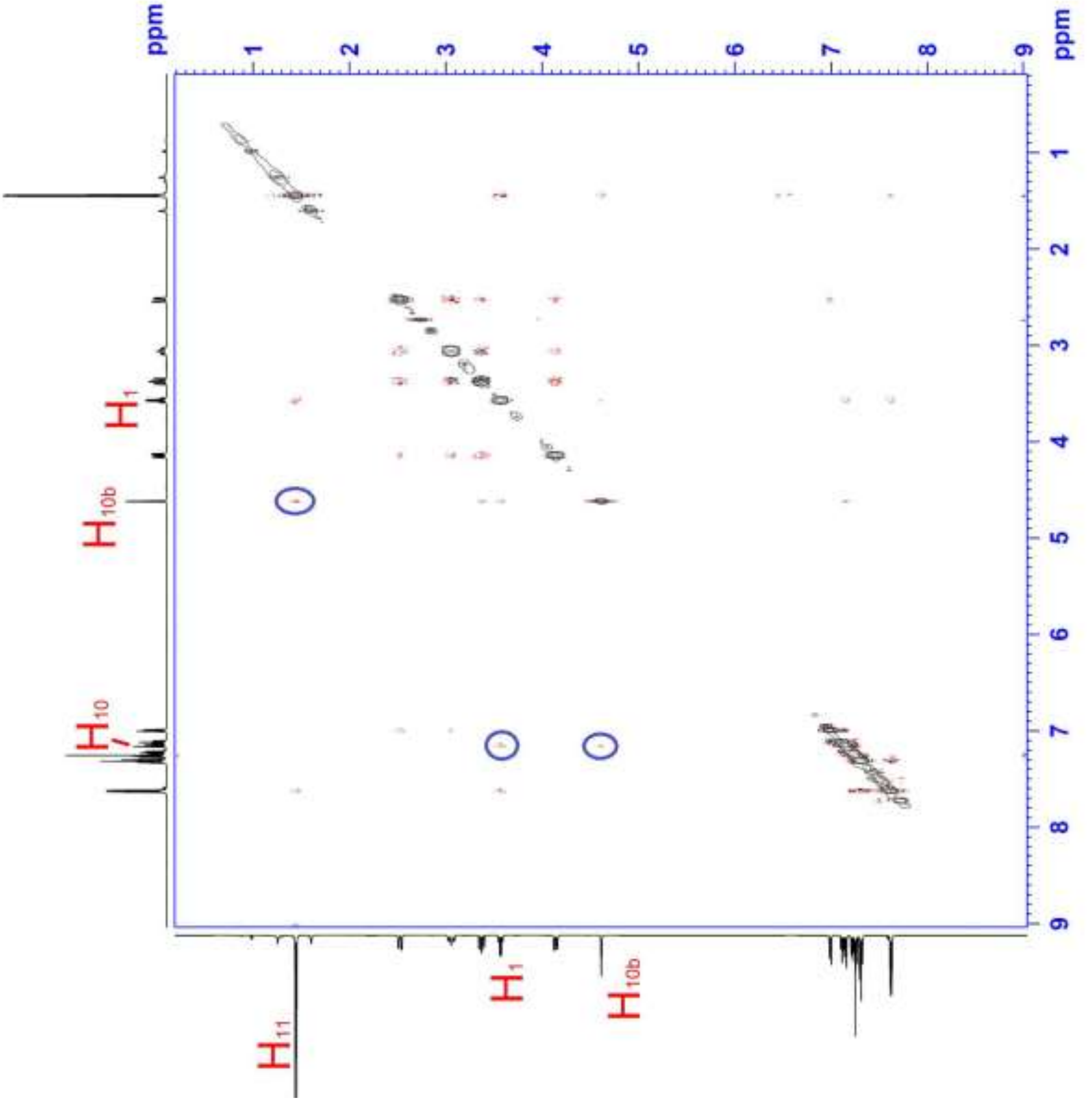
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H10b
H10
H1
H10b
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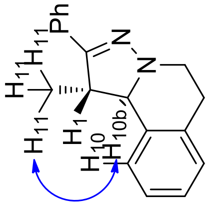
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H11
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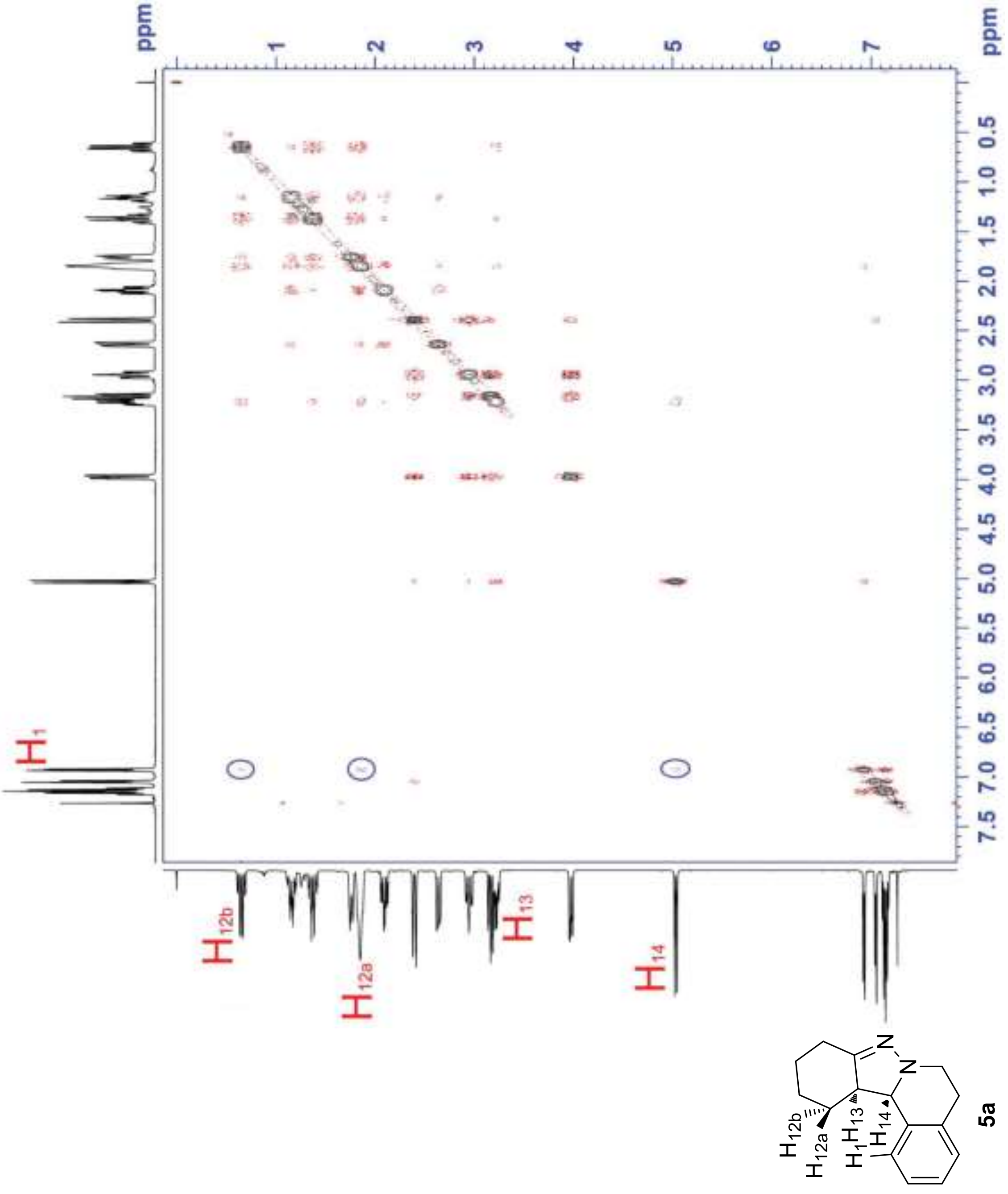
N
H1
H10
H10b

2p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H₁₂b
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H₁₃
H₁₄
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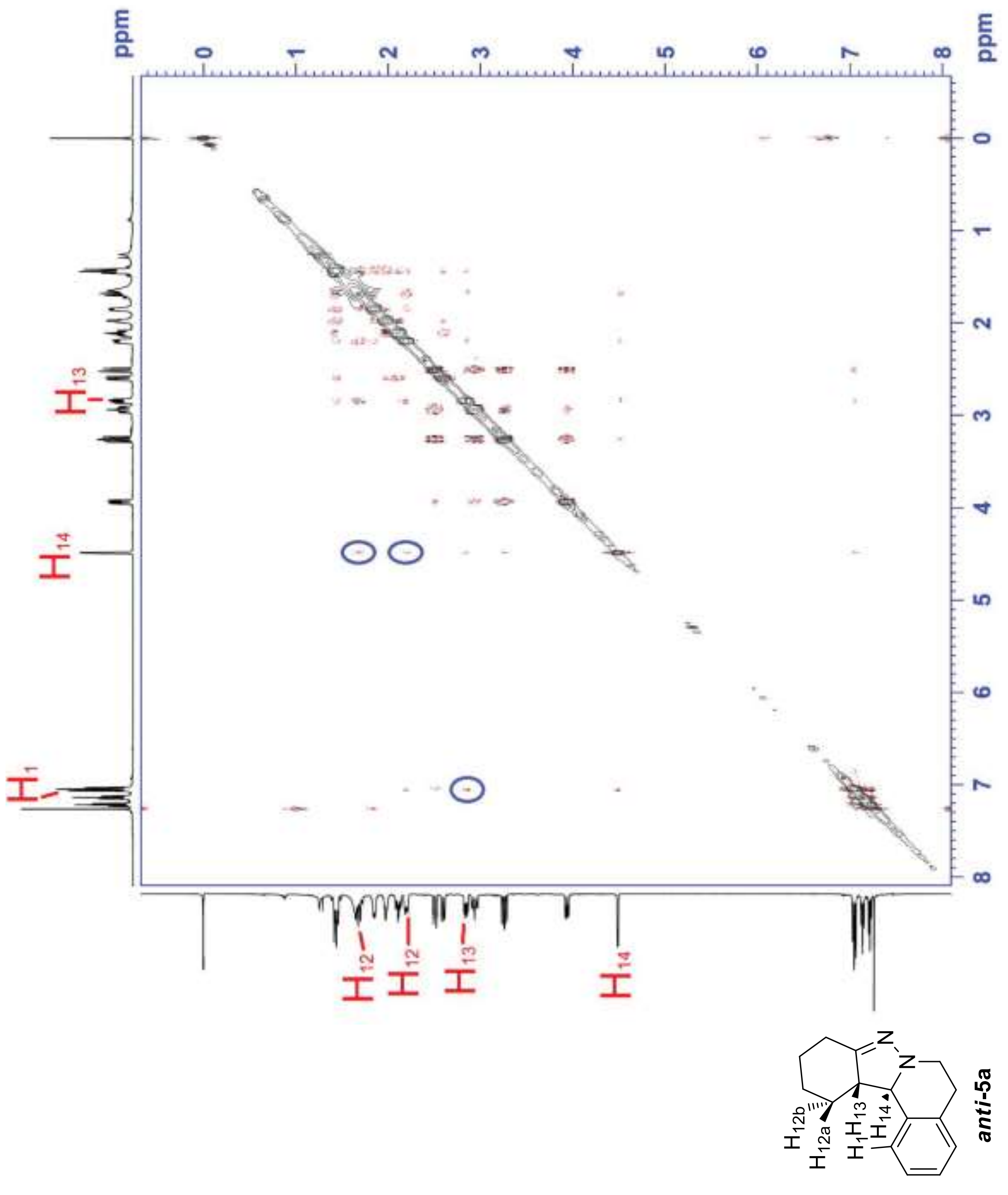
N

5a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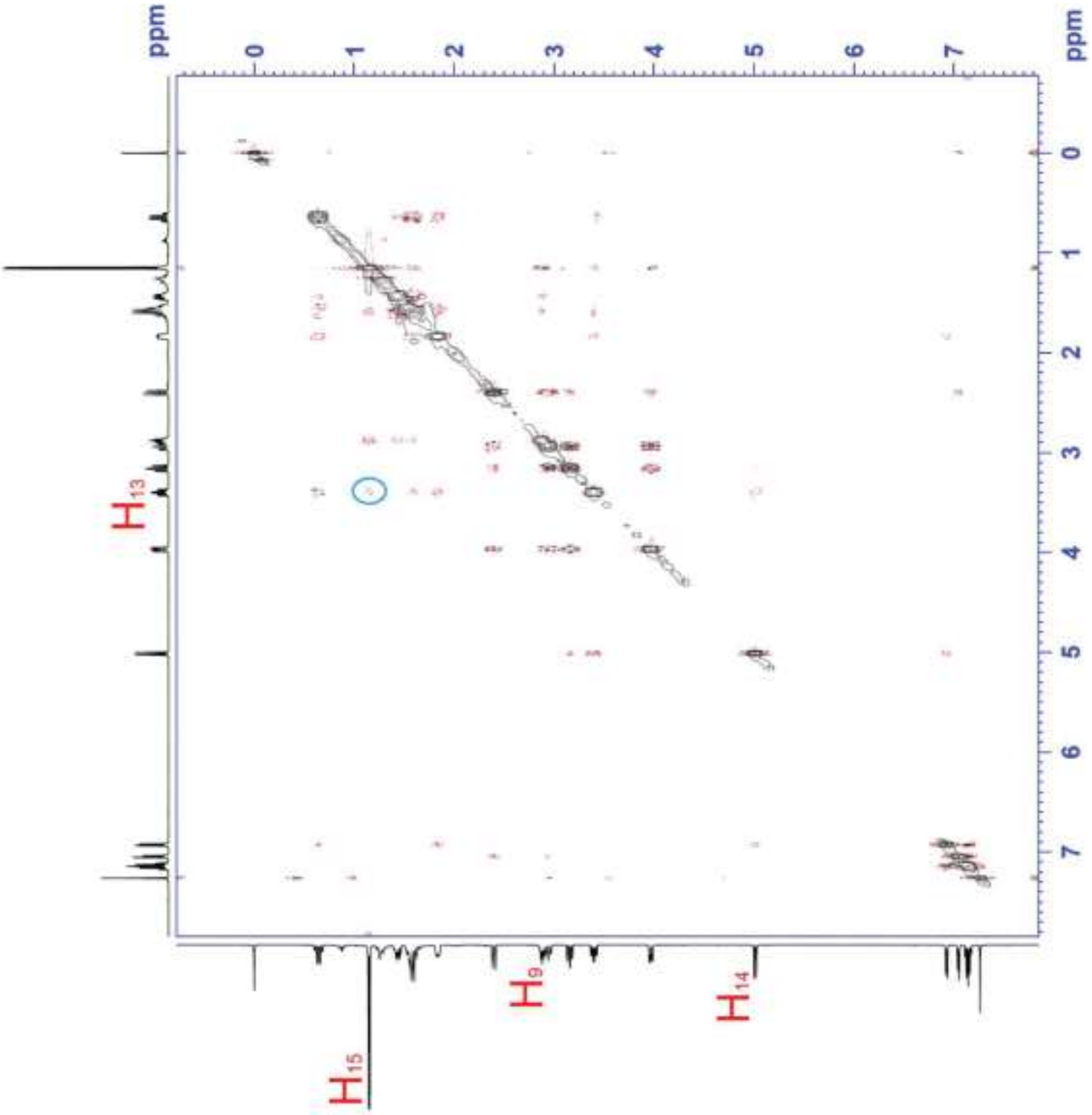
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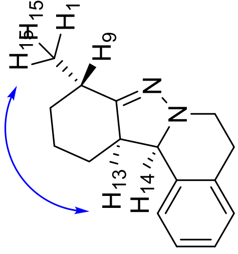
H14
H15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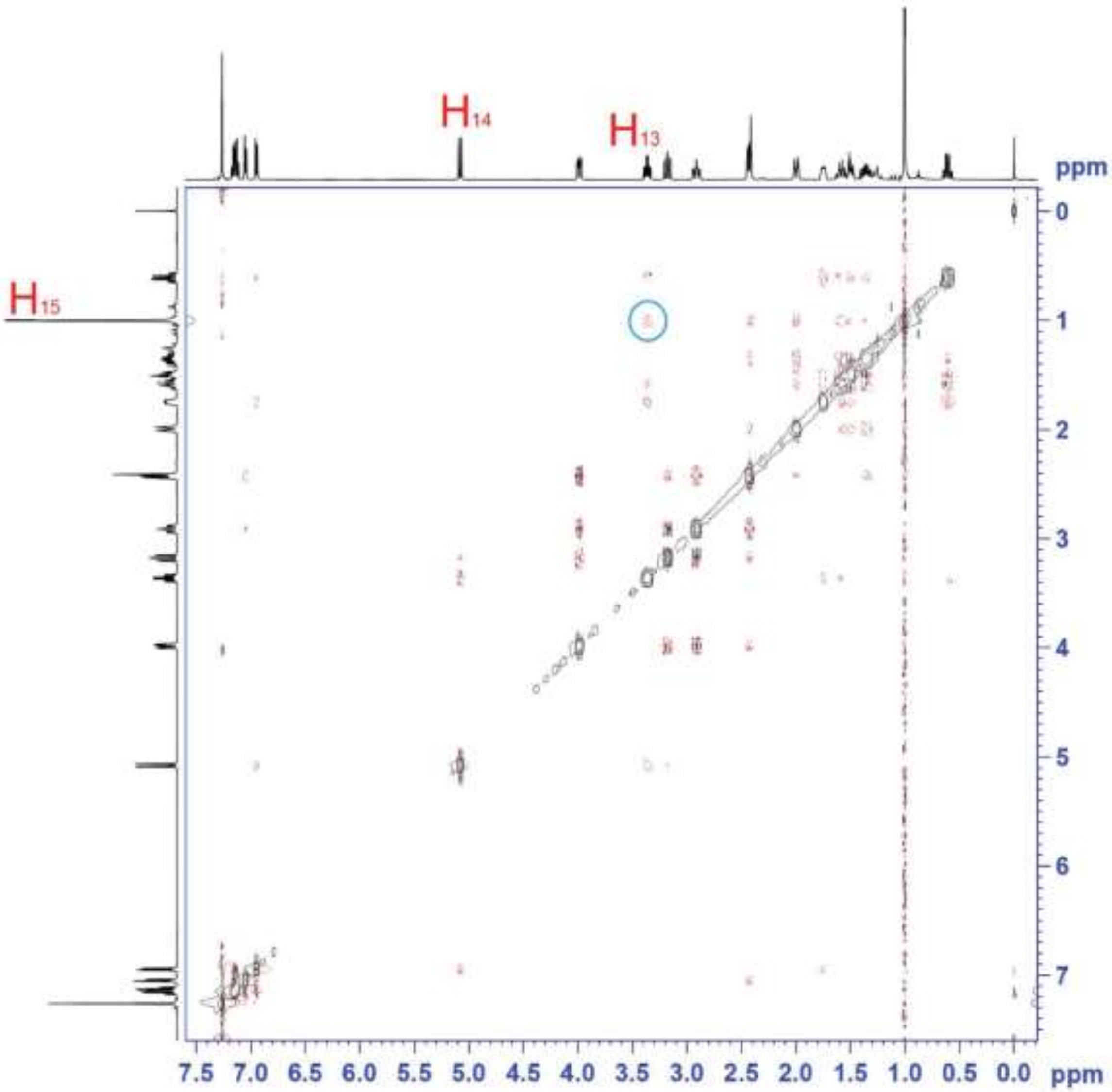
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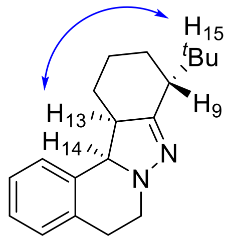
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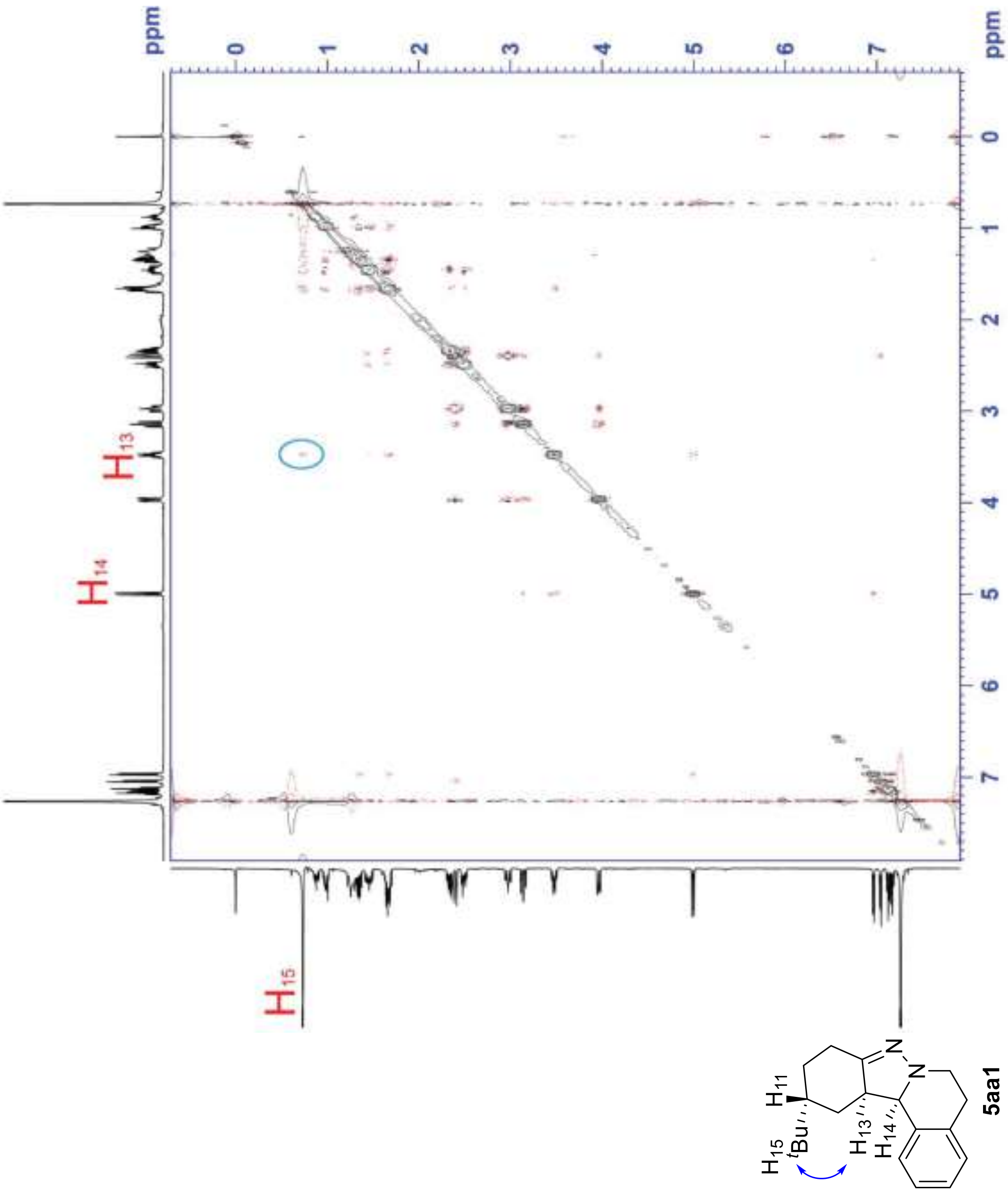

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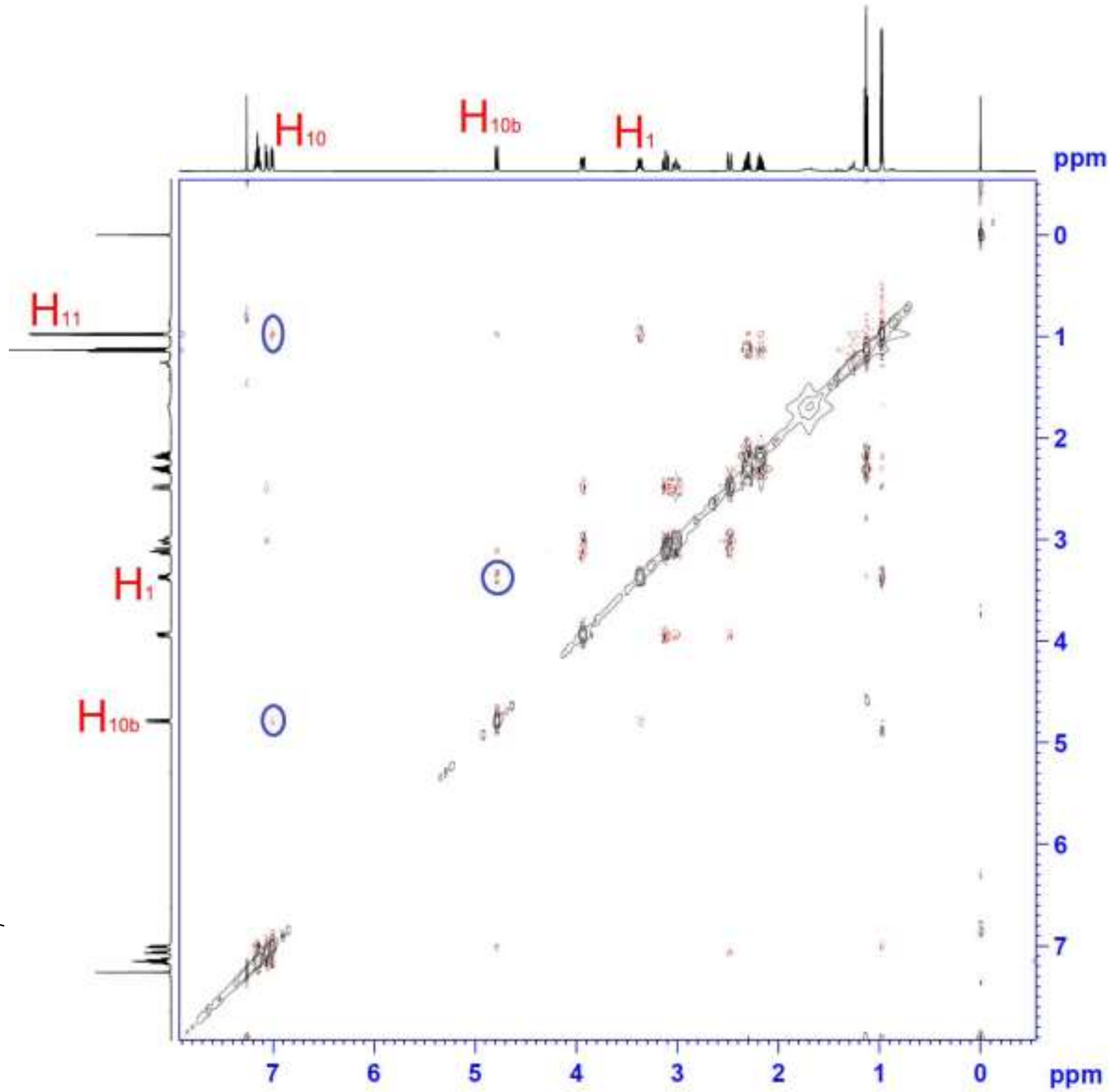
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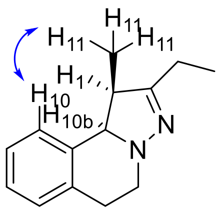
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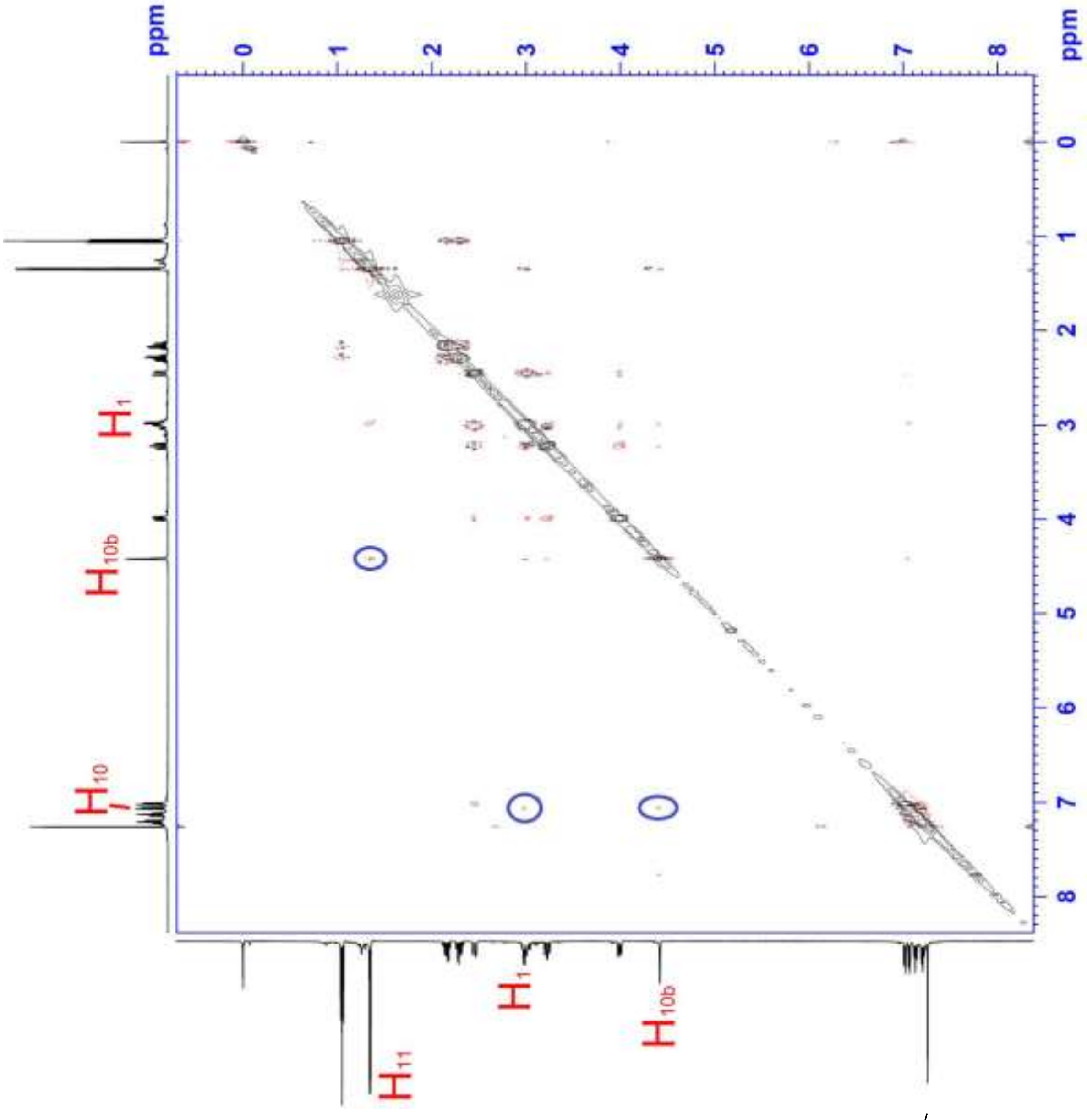
N

***syn*-5ab**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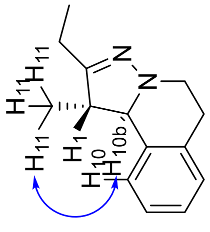
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H10b
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N

***anti*-5ab**