Supporting Information

Construction of Benzimidazole- and Indole-Fused Azabicyclo[3.1.0] hexanes Bearing Cyano-Quaternary Center from Vinylsulfonium Salts through Sequential [3+2]/[2+1] Cyclization

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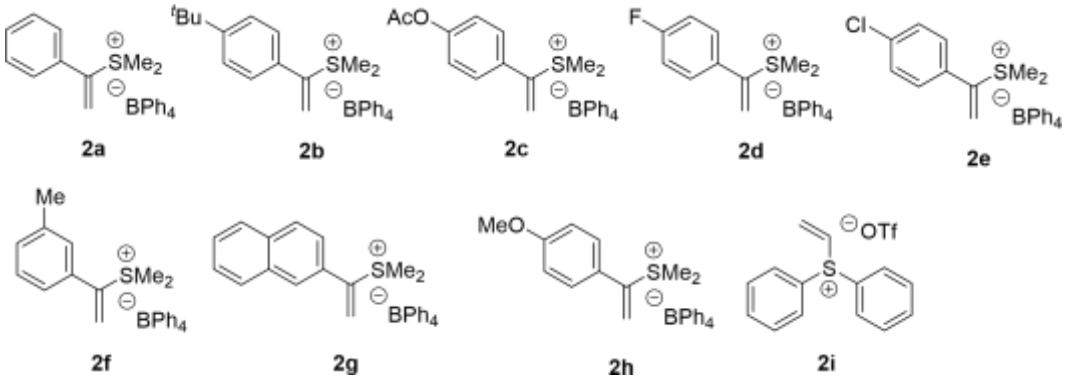
1. General Information

All reactions were performed under air atmospheres in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents were purified and dried according to standard methods prior to use. Organic solutions were concentrated under reduced pressure on a rotary evaporator or an oil pump. The reactions were monitored through thin layer chromatography (TLC) on silica gel-precoated glass plates. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). ^{1}H NMR and ^{13}C NMR were recorded on JEOL ECS–400 spectrometer with $CDCl_3$ as the solvent. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton ($CDCl_3$: δ 7.26 ppm) or DMSO-d_6 (δ: 2.50 ppm), carbon ($CDCl_3$: δ 77.07 ppm) or DMSO-d_6 (δ: 40.0 ppm) and tetramethylsilane (TMS δ 0.00). Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), m (multiplet). Coupling constants *J* are reported in Hz. HRMS data were obtained on LCMS–IT–TOF (Shimadzu, Kyoto, JP) with ESI resource. Single crystal X–ray data were collected on a Bruker APEXII X–ray diffractometer equipped with a CMOS PHOTON 100 detector with a Mo Kα X–ray source (Kα = 0.71073 Å). Melting points were recorded on a Tianjin University of Science and Technology X–4 melting point apparatus.

2. Synthesis of Substrates

Benzimidazole-derived acrylonitriles (**1**),[1] indolaldehyde-derived acrylonitriles (**6**),[2] and α-aryl tetraphenylborate vinylsulfonium salts (**2**),[3] were synthesized according to the previous procedures.



References

(1) C. J. Ni, S. Y. Pan, C. Yuan, S. Y. Qin, Synthesis of 1,2-Fused Benzimidazoles by Amine-Initiated [3 + 3] Annulations of β′-Acetoxy Allenoates with 1C,3N-Bisnucleophiles. *J. Org. Chem.* **2023**, *88*, 8937-8945.

(2) Y. M. Zhou, N. Li, W. Cai, Y. Huang, Asymmetric Sequential Corey-Chaykovsky Cyclopropanation/ Cloke-Wilson Rearrangement for the Synthesis of 2,3-Dihydrofurans. *Org. Lett.* **2021**, *23*, 8755-8760.

(3) J. V. Matlock, S. P. Fritz, S. A. Harrison, D. M. Coe, E. M. McGarrigle, V. K. Aggarwal, Synthesis of α-Substituted Vinylsulfonium Salts and Their Application as Annulation Reagents in the Formation of Epoxide- and Cyclopropane-Fused Heterocycles, *J. Org. Chem.* **2014**, *79*, 10226-10239.

3. Synthesis and Characterization Data of 3a-3z, 3aa-3ac, 5a and 7a-7k

3.1 General Procedure for Synthesis of 3 and 5

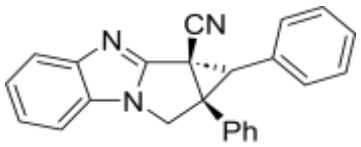
The benzimidazole-derived acrylonitriles **1** (or **4**) (0.2 mmol), vinylsulfonium salts **2** (0.3 mmol, 1.5 equiv.) and THF (2.0 mL) were added to a 10 mL dry sealed tube at air atmosphere. Then Cs_2CO_3 (0.4 mmol, 2.0 equiv.) were added in one portion. This solution was stirred at room temperature for 1-6 hours until the complete consumption of **1** (or **4**) monitored by TLC. The reaction mixture was filtered with Celite,and eluted with dichloromethane. The filtrate was concentrated and the residue was purified by flash column chromatography (petroleum ether: EtOAc = 3:1 or 5:1) on silica gel to afford corresponding products **3** (or **5**).

3.2 General Procedure for Synthesis of 7

The indolaldehyde-derived acrylonitriles **6** (0.2 mmol), vinylsulfonium salts **2** (0.3 mmol, 1.5 equiv.) and DCM (2.0 mL) were added to a 10 mL dry sealed tube at air atmosphere. Then DBU (0.4 mmol, 2.0 equiv.) were added in one portion. This solution was stirred at room temperature for 0.5-2 hours until the complete consumption of **6** monitored by TLC. The reaction mixture was filtered with Celite,and eluted with dichloromethane. The filtrate was concentrated and the residue was purified by flash column chromatography (petroleum ether: EtOAc = 5:1) on silica gel to afford corresponding products **7**

3.3 Characterization Data of 3a-3ac, 5a and 7a-7k

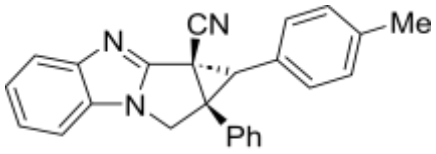
1,8a-Diphenyl-8,8a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazole-1a(1H)-carbonitrile (3a)



3a

Prepared according to the general procedure (reaction time: 1 h) as described above in 98% yield (68.0 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a yellow solid. **M.p.:** 208-210 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 7.3 Hz, 2H), 7.56 – 7.47 (m, 3H), 7.25 – 7.08 (m, 7H), 6.96 (d, *J* = 8.0 Hz, 1H), 4.37 (d, *J* = 11.7 Hz, 1H), 4.21 (d, *J* = 11.7 Hz, 1H), 3.92 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.6, 147.5, 135.2, 131.9, 129.7, 129.7, 129.5, 129.3, 129.0, 128.6, 128.4, 123.0, 122.4, 120.5, 115.3, 109.3, 51.9, 48.4, 41.9, 25.9. **HRMS** (ESI) *m*/*z* calcd for $C_{24}H_{18}N_3^+$ ($[M+H]^+$): 348.1495, found 348.1496.

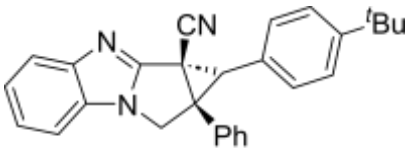
8a-Phenyl-1-(p-tolyl)-8,8a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazole-1a(1H)-carbonitrile (3b)



3b

Prepared according to the general procedure (reaction time: 1 h) as described above in 95% yield (68.6 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a white solid. **M.p.:** 154-156 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 1H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.49-7.39 (m, 3H), 7.14 (t, *J* = 7.7 Hz, 1H), 7.06 (t, *J* = 7.9 Hz, 3H), 6.91 (t, *J* = 8.9 Hz, 3H), 4.30 (d, *J* = 11.7 Hz, 1H), 4.15 (d, *J* = 11.7 Hz, 1H), 3.82 (s, 1H), 2.11 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.7, 147.5, 138.2, 135.3, 132.0, 129.7, 129.7, 129.6, 129.3, 128.4, 126.3, 122.9, 122.4, 120.4, 115.4, 109.4, 52.1, 48.4, 41.8, 25.9, 21.1; **HRMS** (ESI) *m*/*z* calcd for $C_{25}H_{20}N_3^+$ ($[M+H]^+$): 362.1652, found 362.1652.

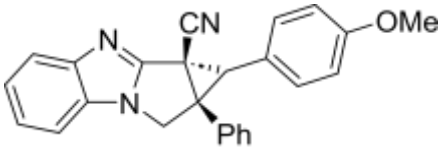
1-(4-(tert-butyl)phenyl)-8a-Phenyl-8,8a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazole-1a(1H)-carbonitrile (3c)



3c

Prepared according to the general procedure (reaction time: 2 h) as described above in 85% yield (68.5 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a yellow solid. **M.p.:** 217-219 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 1H), 7.64 – 7.62 (m, 2H), 7.56 – 7.46 (m, 3H), 7.23 – 7.10 (m, 6H), 7.00 (d, *J* = 7.9 Hz, 1H), 4.37 (d, *J* = 11.7 Hz, 1H), 4.24 (d, *J* = 11.7 Hz, 1H), 3.88 (s, 1H), 1.16 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.8, 151.4, 147.5, 135.4, 132.1, 129.7, 129.6, 129.3, 128.3, 126.4, 125.9, 122.9, 122.4, 120.4, 115.4, 109.4, 52.2, 48.5, 41.8, 34.5, 31.1, 25.9. **HRMS** (ESI) *m*/*z* calcd for $C_{28}H_{26}N_3^+$ ($[M+H]^+$): 404.2121, found 404.2122.

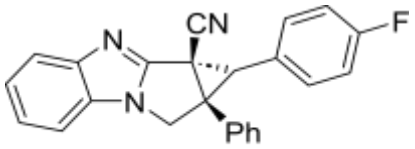
1-(4-methoxyphenyl)-8a-Phenyl-8,8a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazole-1a(1H)-carbonitrile (3d)



3d

Prepared according to the general procedure (reaction time: 1 h) as described above in 97% yield (73.2 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a light-yellow foam. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 1H), 7.63 – 7.61 (m, 2H), 7.55 – 7.46 (m, 3H), 7.22 – 7.10 (m, 4H), 6.99 (d, *J* = 7.9 Hz, 1H), 6.68 (d, *J* = 8.7 Hz, 2H), 4.36 (d, *J* = 11.7 Hz, 1H), 4.21 (d, *J* = 11.7 Hz, 1H), 3.85 (s, 1H), 3.64 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.3, 152.7, 147.5, 135.3, 132.0, 129.8, 129.6, 129.6, 129.3, 122.9, 122.4, 121.2, 120.4, 115.4, 114.4, 109.4, 55.1, 52.1, 48.4, 41.4, 25.9. **HRMS** (ESI) *m*/*z* calcd for $C_{25}H_{20}N_3O^+$ ($[M+H]^+$): 378.1601, found 378.1605.

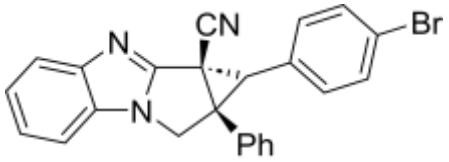
1-(4-fluorophenyl)-8a-Phenyl-8,8a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazole-1a(1H)-carbonitrile (3e)



3e

Prepared according to the general procedure (reaction time: 1 h) as described above in 88% yield (64.3mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a white solid. **M.p.:** 197-199 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 1H), 7.62 (d, *J* = 7.1 Hz, 2H), 7.56 – 7.47 (m, 3H), 7.24 – 7.19 (m, 3H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 7.9 Hz, 1H), 6.86 (t, *J* = 8.6 Hz, 2H), 4.39 (d, *J* = 11.8 Hz, 1H), 4.19 (d, *J* = 11.8 Hz, 1H), 3.86 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.3 (d, *J* = 248.2 Hz), 152.4, 147.4, 134.9, 131.8, 130.4 (d, *J* = 8.4 Hz), 129.7, 129.3, 125.3 (d, *J* = 3.4 Hz), 123.1, 122.6, 120.5, 116.3, 116.0, 115.1, 109.4, 51.8, 48.4, 41.0, 25.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.4 (s). **HRMS** (ESI) *m*/*z* calcd for $C_{24}H_{17}FN_3^+$ ($[M+H]^+$): 366.1401, found 366.1400.

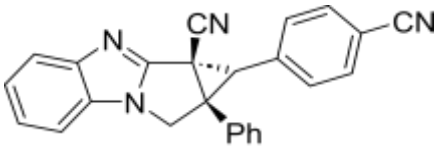
1-(4-bromophenyl)-8a-Phenyl-8,8a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazole-1a(1H)-carbonitrile (3f)



3f

Prepared according to the general procedure (reaction time: 1 h) as described above in 86% yield (73.1 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a yellow solid. **M.p.:**128-130 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 7.1 Hz, 2H), 7.66 – 7.57 (m, 3H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.24 – 7.21 (m, 3H), 7.11 (d, *J* = 7.9 Hz, 1H), 4.49 (d, *J* = 11.8 Hz, 1H), 4.28 (d, *J* = 11.9 Hz, 1H), 3.93 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.2, 147.4, 134.8, 132.3, 131.9, 130.3, 129.8, 129.8, 129.2, 128.6, 123.2, 122.7, 122.6, 120.5, 115.0, 109.5, 51.9, 48.4, 41.2, 25.8. **HRMS** (ESI) *m*/*z* calcd for $C_{24}H_{17}BrN_3^+$ ($[M+H]^+$): 426.0600, found 426.0602.

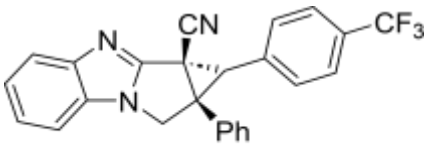
1-(4-cyanophenyl)-8a-Phenyl-8,8a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazole-1 a(1H)-carbonitrile (3g)



3g

Prepared according to the general procedure (reaction time: 1 h) as described above in 79% yield (58.8 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=3:1) to afford a yellow solid. **M.p.:** 170-172 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 7.1 Hz, 2H), 7.58 – 7.52 (m, 3H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 7.9 Hz, 1H), 4.47 (d, *J* = 11.8 Hz, 1H), 4.18 (d, *J* = 11.7 Hz, 1H), 3.96 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.9, 147.3, 135.0, 134.4, 132.7, 131.7, 130.0, 129.8, 129.6, 129.2, 123.5, 122.9, 120.6, 117.9, 114.7, 112.5, 109.5, 51.7, 48.5, 41.2, 25.9. **HRMS** (ESI) *m*/*z* calcd for $C_{25}H_{17}N_4^+$ ($[M+H]^+$): 373.1448, found 373.1448.

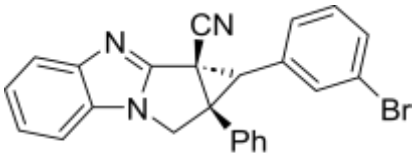
8a-Phenyl-1-(4-(trifluoromethyl)phenyl)-8,8a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazole-1a(1H)-carbonitrile (3h)



3h

Prepared according to the general procedure (reaction time: 2 h) as described above in 87% yield (72.2 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a colorless solid. **M.p.:** 211-213 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 7.3 Hz, 2H), 7.53 – 7.64 (m, 3H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 4.43 (d, *J* = 11.9 Hz, 1H), 4.18 (d, *J* = 11.9 Hz, 1H), 3.94 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.2, 147.4, 134.7, 133.7, 131.9, 130.6 (d, *J* = 32.9 Hz), 129.9, 129.8, 129.2, 129.1, 126.0 (d, *J* = 3.7 Hz), 123.3, 122.7, 120.5, 114.9, 109.5, 51.9, 48.4, 41.3, 25.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.8 (s). **HRMS** (ESI) *m*/*z* calcd for $C_{25}H_{17}F_3N_3^+$ ($[M+H]^+$): 416.1369, found 416.1370.

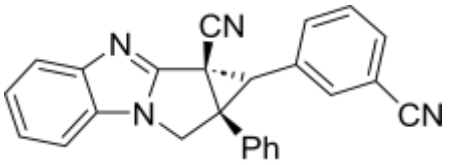
1-(3-bromophenyl)-8a-Phenyl-8,8a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazole-1a(1H)-carbonitrile (3i)



3i

Prepared according to the general procedure (reaction time: 1 h) as described above in 89% yield 75.7 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a light-yellow solid. **M.p.:** 106-108 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 7.1 Hz, 2H), 7.59 – 7.47 (m, 3H), 7.47 (s, 1H), 7.30 – 7.28 (m, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.15 (dd, *J* = 14.0, 7.2 Hz, 2H), 7.04 – 6.99 (m, 2H), 4.43 (d, *J* = 11.9 Hz, 1H), 4.24 (d, *J* = 11.9 Hz, 1H), 3.90 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.7, 144.9, 132.2, 129.3, 129.1, 128.1, 127.3, 127.2, 126.7, 124.8, 120.7, 120.1, 120.1, 117.9, 112.5, 107.0, 49.2, 45.9, 38.5, 23.3. **HRMS** (ESI) *m/z* calcd for $C_{24}H_{17}BrN_3^+$ ($[M+H]^+$): 426.0600, found 426.0603.

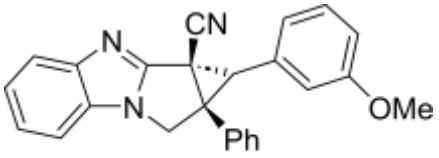
1-(3-cyanophenyl)-8a-Phenyl-8,8a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazole-1a(1H)-carbonitrile (3j)



3j

Prepared according to the general procedure (reaction time: 1 h) as described above in 81% yield (60.3 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=3:1) to afford a white solid. **M.p.:** 235-237 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.67 – 7.64 (m, 3H), 7.60 – 7.52 (m, 3H), 7.46 (dd, *J* = 13.8, 7.4 Hz, 2H), 7.29 – 7.22 (m, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.02 (d, *J* = 7.7 Hz, 1H), 4.48 (d, *J* = 11.6 Hz, 1H), 4.22 (d, *J* = 11.6 Hz, 1H), 3.93 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.9, 147.3, 134.3, 133.2, 132.2, 132.1, 131.7, 131.3, 130.1, 130.0, 129.9, 129.2, 123.4, 122.8, 120.7, 117.8, 114.7, 113.2, 109.4, 51.6, 48.5, 40.7, 25.8. **HRMS** (ESI) *m/z* calcd for $C_{25}H_{17}N_4^+$ ($[M+H]^+$): 373.1448, found 373.1448.

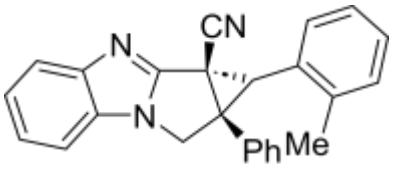
1-(3-methoxyphenyl)-8a-Phenyl-8,8a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazole-1a(1H)-carbonitrile (3k)



3k

Prepared according to the general procedure (reaction time: 1 h) as described above in 97% yield (73.2 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=3:1) to afford a white foam. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 7.1 Hz, 2H), 7.56 – 7.47 (m, 3H), 7.21 (t, *J* = 7.7 Hz, 1H), 7.12 (dd, *J* = 17.5, 8.3 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 7.5 Hz, 1H), 6.67 – 6.66 (m, 2H), 4.37 (d, *J* = 11.7 Hz, 1H), 4.22 (d, *J* = 11.7 Hz, 1H), 3.91 (s, 1H), 3.56 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.8, 152.7, 147.5, 135.1, 131.9, 130.9, 130.0, 129.7, 129.6, 129.3, 123.0, 122.5, 120.8, 120.2, 115.3, 114.6, 113.4, 109.5, 55.2, 51.9, 48.4, 41.8, 25.7. **HRMS** (ESI) *m*/*z* calcd for $C_{25}H_{20}N_3O^+$ ($[M+H]^+$): 378.1601, found 378.1600.

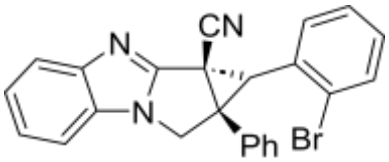
8a-Phenyl-1-(o-tolyl)-8,8a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazole-1a(1H)-carbonitrile (3l)



3l

Prepared according to the general procedure (reaction time: 1 h) as described above in 85% yield (61.4 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=3:1) to afford a light-yellow solid. **M.p.:** 148-150 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 7.4 Hz, 2H), 7.56 – 7.47 (m, 3H), 7.22 – 7.19 (m, 2H), 7.15 – 7.02 (m, 4H), 6.95 (t, *J* = 7.2 Hz, 1H), 4.49 (d, *J* = 11.6 Hz, 1H), 4.35 (d, *J* = 11.6 Hz, 1H), 3.86 (s, 1H), 2.54 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.6, 147.3, 137.9, 135.3, 131.9, 131.0, 129.7, 129.6, 128.9, 128.6, 128.6, 128.3, 126.2, 123.0, 122.4, 120.4, 115.4, 109.4, 51.5, 48.4, 41.2, 27.3, 20.2. **HRMS** (ESI) *m*/*z* calcd for $C_{25}H_{20}N_3^+$ ($[M+H]^+$): 362.1652, found 362.1654.

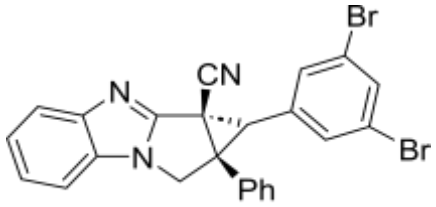
1-(2-bromophenyl)-8a-Phenyl-8,8a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazole-1a(1H)-carbonitrile (3m)



3m

Prepared according to the general procedure (reaction time: 1 h) as described above in 83% yield (70.6mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a colorless solid. **M.p.:** 197-199 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 – 7.74 (m, 3H), 7.55 – 7.45 (m, 4H), 7.21 (t, *J* = 7.9 Hz, 2H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.06 – 6.95 (m, 3H), 4.54 (d, *J* = 12.0 Hz, 1H), 4.29 (d, *J* = 12.0 Hz, 1H), 3.98 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.2, 147.2, 134.7, 133.3, 131.9, 131.4, 130.2, 129.9, 129.5, 129.5, 129.0, 128.0, 124.2, 123.2, 122.6, 120.5, 114.9, 109.5, 52.2, 48.7, 42.6, 27.1. **HRMS** (ESI) *m*/*z* calcd for $C_{24}H_{17}BrN_3^+$ ([M+H]$^+$): 426.0600, found 426.0597.

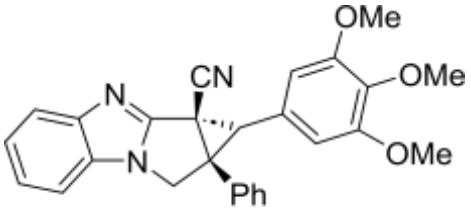
1-(3,5-dibromophenyl)-8a-Phenyl-8,8a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazole-1a(1H)-carbonitrile (3n)



3n

Prepared according to the general procedure (reaction time: 2 h) as described above in 84% yield (84.5 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a light-yellow solid. **M.p.:** 129-131 °C. **^{1}H NMR** (400 MHz, DMSO) δ 7.89 (d, *J* = 7.3 Hz, 2H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.61 (s, 1H), 7.57 – 7.50 (m, 3H), 7.47 (s, 2H), 7.27 (d, *J* = 7.7 Hz, 1H), 7.19 – 7.12 (m, 2H), 4.61 (d, *J* = 12.6 Hz, 1H), 4.50 – 4.34 (m, 2H). **^{13}C NMR** (101 MHz, DMSO) δ 153.0, 147.4, 135.5, 135.3, 133.5, 132.4, 131.2, 130.6, 129.6, 129.5, 123.0, 122.7, 122.4, 119.9, 116.0, 110.9, 52.0, 48.5, 26.0. **HRMS** (ESI) *m*/*z* calcd for $C_{24}H_{16}Br_2N_3^+$ ([M+H]$^+$): 503.9705, found 503.9705.

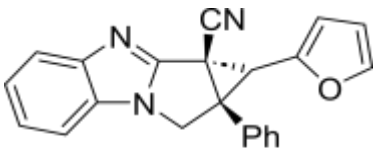
8a-Phenyl-1-(3,4,5-trimethoxyphenyl)-8,8a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazole-1a(1H)-carbonitrile (3o)



3o

Prepared according to the general procedure (reaction time: 1 h) as described above in 91% yield (79.6 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=3:1) to afford a white solid. **M.p.:** 157-159 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 7.0 Hz, 2H), 7.57– 7.47 (m, 3H), 7.24 – 7.20 (m, 1H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 7.9 Hz, 1H), 6.34 (s, 2H), 4.41 (d, *J* = 11.6 Hz, 1H), 4.16 (d, *J* = 11.6 Hz, 1H), 3.88 (s, 1H), 3.69 (s, 3H), 3.62 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.5, 152.5, 147.5, 137.8, 135.0, 131.8, 129.7, 129.7, 129.2, 125.0, 123.2, 122.7, 120.2, 115.2, 109.6, 105.5, 60.8, 56.1, 51.9, 48.5, 41.8, 25.9. **HRMS** (ESI) *m*/*z* calcd for $C_{27}H_{24}N_3O_3^+$ ($[M+H]^+$): 438.1812, found 438.1810.

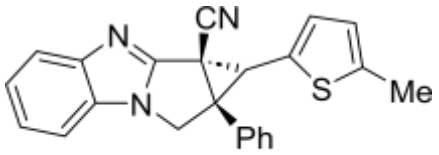
1-(furan-2-yl)-8a-Phenyl-8,8a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazole-1a(1H)-carbonitrile (3p)



3p

Prepared according to the general procedure (reaction time: 1 h) as described above in 88% yield (59.3 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a brown foam. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.9 Hz, 1H), 7.46 (d, *J* = 6.8 Hz, 2H), 7.38 – 7.30 (m, 3H), 7.13 – 7.05 (m, 3H), 7.00 (d, *J* = 7.6 Hz, 1H), 5.90 (dd, *J* = 3.2, 1.8 Hz, 1H), 5.42 (d, *J* = 3.2 Hz, 1H), 4.27 – 4.13 (m, 2H), 3.60 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.8, 147.5, 144.4, 143.2, 134.5, 131.9, 129.7, 129.7, 129.3, 123.4, 122.7, 120.7, 114.6, 110.8, 109.5, 109.2, 51.1, 49.2, 35.5, 25.7. **HRMS** (ESI) *m*/*z* calcd for $C_{22}H_{16}N_3O^+$ ($[M+H]^+$): 338.1288, found 338.1288.

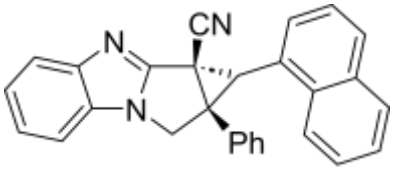
1-(5-methylthiophen-2-yl)-8a-Phenyl-8,8a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazole-1a(1H)-carbonitrile (3q)



3q

Prepared according to the general procedure (reaction time: 1 h) as described above in 91% yield (66.8 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a yellow solid. **M.p.:** 104-106 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.28 (m, 5H), 7.08 – 6.99 (m, 2H), 6.94 (d, *J* = 7.7 Hz, 1H), 6.23 (d, *J* = 3.0 Hz, 1H), 6.16 (d, *J* = 2.7 Hz, 1H), 4.19 (s, 2H), 3.63 (s, 1H), 2.10 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.0, 147.6, 140.9, 134.9, 132.0, 129.7, 129.2, 128.5, 127.7, 125.5, 123.2, 122.6, 120.6, 115.0, 109.6, 52.3, 48.6, 37.8, 26.7, 15.3. **HRMS** (ESI) *m*/*z* calcd for $C_{23}H_{18}N_3S^+$ ([M+H]$^+$): 368.1216, found 368.1214.

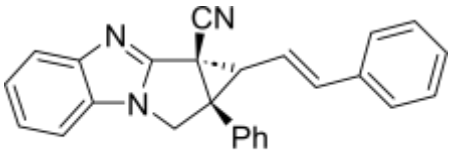
1-(naphthalen-1-yl)-8a-Phenyl-8,8a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazole-1a(1H)-carbonitrile (3r)



3r

Prepared according to the general procedure (reaction time: 1 h) as described above in 73% yield (58.0 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a colorless solid. **M.p.:** 214-216 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.4 Hz, 1H), 7.83-7.79 (m, 3H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.65 – 7.49 (m, 6H), 7.41 (d, *J* = 7.2 Hz, 1H), 7.17 – 7.14 (m, 2H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 4.52 (d, *J* = 11.8 Hz, 1H), 4.30 (s, 1H), 4.14 (d, *J* = 11.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.5, 147.4, 134.9, 133.7, 131.9, 131.7, 129.9, 129.6, 129.4, 129.2, 128.4, 127.8, 127.3, 126.3, 125.8, 125.4, 122.9, 122.4, 120.4, 115.4, 109.4, 51.9, 48.1, 40.7, 27.3. **HRMS** (ESI) *m*/*z* calcd for $C_{28}H_{20}N_3^+$ ([M+H]$^+$): 398.1652, found 398.1655.

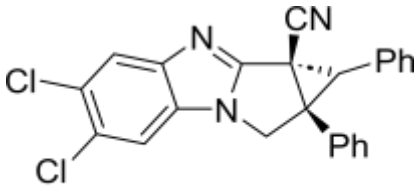
8a-Phenyl-1-((E)-styryl)-8,8a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazole-1a(1H)-carbonitrile (3s)



3s

Prepared according to the general procedure (reaction time: 1 h) as described above in 67% yield (50.0 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a yellow foam. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.3 Hz, 1H), 7.45 – 7.36 (m, 5H), 7.24 – 7.19 (m, 3H), 7.11 – 7.10 (m, 3H), 7.01 (dd, *J* = 6.6, 2.8 Hz, 2H), 6.84 (d, *J* = 15.8 Hz, 1H), 5.20 (dd, *J* = 15.8, 8.2 Hz, 1H), 4.36 (s, 2H), 3.36 (d, *J* = 8.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.7, 147.7, 138.7, 135.5, 135.0, 132.1, 129.6, 129.6, 129.0, 128.7, 128.5, 126.4, 123.4, 122.9, 120.8, 116.7, 115.0, 109.7, 51.1, 48.9, 41.6, 26.3. **HRMS** (ESI) *m*/*z* calcd for $C_{26}H_{20}N_3^+$ ($[M+H]^+$): 374.1652, found 374.1652.

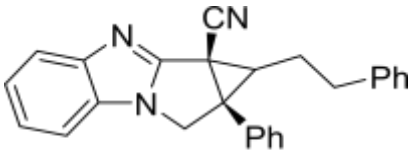
4,5-Dichloro-1,8a-diphenyl-8,8a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazole-1a(1H)-carbonitrile (3t)



3t

Prepared according to the general procedure (reaction time: 1 h) as described above in 84% yield (69.7 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=3:1) to afford a yellow solid. **M.p.:** 185-187 °C.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.60 (s, 1H), 8.00 (d, *J* = 7.0 Hz, 2H), 7.45 – 7.33 (m, 8H), 3.31 (t, *J* = 8.8 Hz, 1H), 2.29 (dd, *J* = 9.2, 5.2 Hz, 1H), 2.14 (dd, *J* = 8.3, 5.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.7, 160.2, 137.2, 135.0, 133.3, 132.7, 132.7, 131.4, 129.7, 129.1, 128.9, 128.5, 128.2, 127.8, 120.6, 117.7, 117.5, 35.1, 25.0, 22.4. **HRMS** (ESI) *m*/*z* calcd for $C_{24}H_{16}Cl_2N_3^+$ ($[M+H]^+$): 416.0716, found 416.0718.

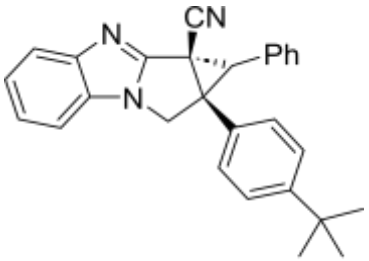
1-Phenethyl-8a-phenyl-8,8a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazole-1a(1H)-carbonitrile (3u)



3u

Prepared according to the general procedure (reaction time: 1 h) as described above in 28% yield (21.0 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=3:1) to afford a light yellow foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (t, *J* = 7.8 Hz, 1H), 7.38 – 7.31 (m, 4H), 7.27 (d, *J* = 7.8 Hz, 1H), 7.23 – 7.08 (m, 7H), 7.04 (d, *J* = 7.2 Hz, 1H), 4.35 – 4.30 (m, 1H), 4.12 – 4.09 (m, 1H), 2.92 – 2.65 (m, 2H), 2.09 – 1.93 (m, 1H), 1.57 – 1.34 (m, 2H). A mixture of diastereoisomer (1:1) ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 152.6, 147.7, 147.5, 140.3, 140.0, 135.4, 132.6, 132.5, 131.9, 129.6, 129.5, 129.3, 129.2, 129.0, 128.8, 128.7, 128.6, 128.4, 126.6, 126.4, 123.3, 123.2, 122.8, 122.7, 120.7, 120.5, 115.5, 114.2, 109.5, 109.4, 52.4, 50.4, 49.5, 48.4 40.9, 38.5, 34.2, 34.1, 30.1, 24.7, 24.5, 24.2. **HRMS** (ESI) *m*/*z* calcd for $C_{26}H_{22}N_3^+$ ([M+H]$^+$): 376.1808, found 376.1809.

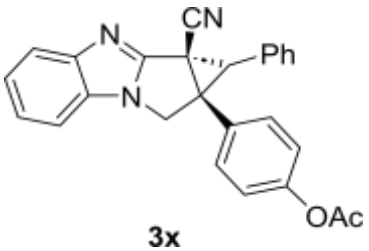
8a-(4-(tert-butyl)phenyl)-1-Phenyl-8,8a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazole-1a(1H)-carbonitrile (3w)



3w

Prepared according to the general procedure (reaction time: 2 h) as described above in 78% yield (62.9 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a light yellow solid. **M.p.:** 166-168 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 1H), 7.61 – 7.56 (m, 4H), 7.29– 7.11 (m, 7H), 6.99 (d, *J* = 8.0 Hz, 1H), 4.39 (d, *J* = 11.7 Hz, 1H), 4.21 (d, *J* = 11.7 Hz, 1H), 3.95 (s, 1H), 1.40 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.8, 152.8, 147.4, 132.1, 131.9, 129.6, 129.0, 129.0, 128.3, 126.6, 122.9, 122.4, 120.4, 115.5, 109.3, 51.7, 48.4, 41.9, 34.9, 31.3, 25.8. **HRMS** (ESI) *m*/*z* calcd for $C_{28}H_{26}N_3^+$ ([M+H]$^+$): 404.2121, found 404.2122.

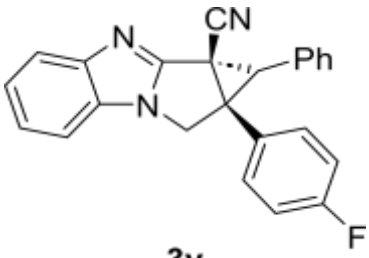
1a-Cyano-1-phenyl-1,1a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazol-8a(8H)-yl)phenyl acetate (3x)



3x

Prepared according to the general procedure (reaction time: 2.5 h) as described above in 73% yield (59.2 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a yellow solid. **M.p.:** 224-226 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.23 – 7.09 (m, 7H), 6.97 (d, *J* = 7.9 Hz, 1H), 4.35 (d, *J* = 11.8 Hz, 1H), 4.20 (d, *J* = 11.8 Hz, 1H), 3.91 (s, 1H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.3, 152.4, 151.5, 147.4, 132.7, 131.9, 130.6, 129.2, 129.0, 128.6, 128.4, 123.0, 123.0, 122.5, 120.4, 115.2, 109.3 , 51.2, 48.4, 41.9, 25.9, 21.2. **HRMS** (ESI) *m/z* calcd for $C_{26}H_{20}N_3O_2^+$ ([M+H]$^+$): 406.1550, found 406.1549.

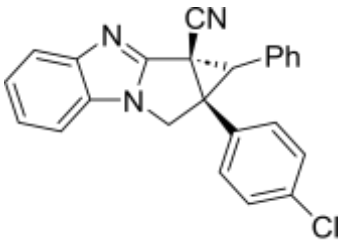
8a-(4-fluorophenyl)-1-Phenyl-8,8a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazole-1a(1H)-carbonitrile (3y)



3y

Prepared according to the general procedure (reaction time: 1 h) as described above in 84% yield (61.3 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a white solid. **M.p.:** 161-163 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 1H), 7.64 (dd, *J* = 8.5, 5.1 Hz, 2H), 7.24 – 7.09 (m, 9H), 6.96 (d, *J* = 7.9 Hz, 1H), 4.34 (d, *J* = 11.8 Hz, 1H), 4.22 (d, *J* = 11.8 Hz, 1H), 3.90 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.2 (d, *J* = 242.0 Hz), 152.4, 147.4, 131.9, 131.3 (d, *J* = 8.7 Hz), 131.2 (d, *J* = 3.2 Hz), 129.2, 129.0, 128.6, 128.5, 123.1, 122.5, 120.4, 116.9, 116.7 115.2, 109.4, 51.1, 48.4, 42.0, 25.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.7 (s). **HRMS** (ESI) *m/z* calcd for $C_{24}H_{17}FN_3^+$ ([M+H]$^+$): 366.1401, found 366.1400.

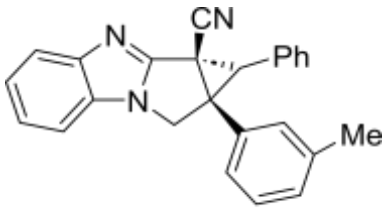
8a-(4-chlorophenyl)-1-Phenyl-8,8a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazole-1a(1H)-carbonitrile (3z)



3z

Prepared according to the general procedure (reaction time: 1 h) as described above in 81% yield (61.7 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a white solid. **M.p.:** 99-101 °C.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.23 – 7.09 (m, 7H), 6.96 (d, *J* = 8.0 Hz, 1H), 4.34 (d, *J* = 11.7 Hz, 1H), 4.22 (d, *J* = 11.7 Hz, 1H), 3.89 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.3, 147.4, 135.8, 133.7, 131.9, 130.7, 130.0, 129.1, 129.0, 128.6, 128.5, 123.1, 122.5, 120.4, 115.2, 109.4, 51.1, 48.2, 41.9, 26.0. **HRMS** (ESI) *m*/*z* calcd for $C_{24}H_{17}ClN_3^+$ ($[M+H]^+$): 382.1106, found 382.1106.

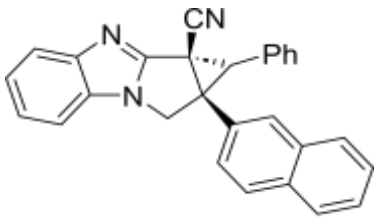
1-Phenyl-8a-(m-tolyl)-8,8a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazole-1a(1H)-carbonitrile (3aa)



3aa

Prepared according to the general procedure (reaction time: 1 h) as described above in 87% yield (62.8 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a yellow solid. **M.p.:** 164-166 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 7.3 Hz, 2H), 7.56 – 7.47 (m, 3H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.07 – 6.98 (m, 4H), 6.93 (d, *J* = 6.9 Hz, 1H), 4.38 (d, *J* = 11.4 Hz, 1H), 4.23 (d, *J* = 11.4 Hz, 1H), 3.90 (s, 1H), 2.17 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.7, 147.5, 138.8, 135.3, 131.9, 129.7, 129.6, 129.4, 129.3, 129.2, 129.1, 128.8, 125.6, 122.9, 122.4, 120.3, 115.4, 109.4, 51.8, 48.4, 41.9, 25.8, 21.2. **HRMS** (ESI) *m*/*z* calcd for $C_{25}H_{20}N_3^+$ ($[M+H]^+$): 362.1652, found 362.1655.

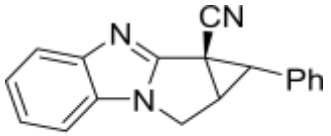
8a-(naphthalen-2-yl)-1-Phenyl-8,8a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazole-1a(1H)-carbonitrile (3ab)



3ab

Prepared according to the general procedure (reaction time: 6 h) as described above in 71% yield (56.4 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a yellow solid. **M.p.:** 185-187 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.96 – 7.91 (m, 2H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.69 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.61 – 7.57 (m, 2H), 7.31 (d, *J* = 7.5 Hz, 2H), 7.23 – 7.10 (m, 5H), 6.99 (d, *J* = 8.0 Hz, 1H), 4.47 (d, *J* = 11.8 Hz, 1H), 4.28 (d, *J* = 11.8 Hz, 1H), 4.06 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.7, 147.5, 133.5, 133.3, 132.4, 132.0, 129.9, 129.5, 129.0, 129.0, 128.7, 128.4, 128.2, 128.0, 127.4, 127.2, 126.1, 123.0, 122.5, 120.4, 115.4, 109.4, 52.1, 48.3, 42.0, 26.0. **HRMS** (ESI) *m/z* calcd for $C_{28}H_{20}N_3^+$ ([M+H]$^+$): 398.1652, found 398.1652.

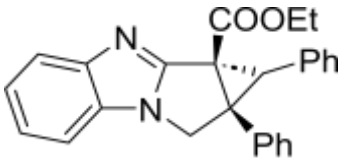
1-phenyl-8,8a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazole-1a(1H)-carbonitrile (3ac)



3ac

Prepared according to the general procedure (reaction time: 1 h) as described above in 32% yield (20.1 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a colorless solid. **M.p.:** 214-216 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.8, 2.2 Hz, 1H), 7.48 – 7.41 (m, 3H), 7.35 (d, *J* = 6.8 Hz, 2H), 7.32 (d, *J* = 3.1 Hz, 3H), 4.55 (dd, *J* = 11.0, 5.7 Hz, 1H), 4.37 (d, *J* = 11.0 Hz, 1H), 3.65 (t, *J* = 5.6 Hz, 1H), 2.91 (d, *J* = 5.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.9, 147.9, 132.5, 132.1, 129.1, 128.8, 127.8, 123.4, 122.8, 120.6, 114.3, 109.5, 44.9, 40.7, 35.2, 22.6. **HRMS** (ESI) *m/z* calcd for $C_{18}H_{14}N_3^+$ ([M+H]$^+$): 272.1182, found 272.1180.

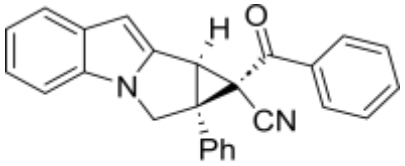
Ethyl-1,8a-diphenyl-8,8a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazole-1a(1H)-carboxylate (5a)



5a

Prepared according to the general procedure (reaction time: 2 h) as described above in 60% yield (47.3 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.89– 7.87 (m, 1H), 7.45 (dd, *J* = 6.3, 2.7 Hz, 1H), 7.35 – 7.33 (m, 2H), 7.28 (s, 1H), 7.19 – 7.15 (m, 5H), 7.05 (d, *J* = 7.4 Hz, 3H), 4.31 (s, 1H), 4.19 (t, *J* = 8.3 Hz, 2H), 3.58 (s, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.9, 147.9, 147.2, 136.2, 135.9, 133.0, 130.9, 130.7, 130.4, 129.0, 127.8, 126.9, 123.0, 122.3, 120.5, 110.2, 61.9, 45.7, 36.0, 32.7, 15.4, 14.3. **HRMS** (ESI) *m*/*z* calcd for $C_{26}H_{23}N_2O_2^+$ ($[M+H]^+$): 395.1754, found 395.1754.

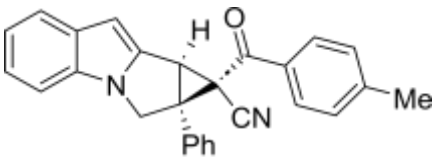
1-Benzoyl-1a-phenyl-1,1a,2,8b-tetrahydrocyclopropa[3,4]pyrrolo[1,2-a]indole-1-carbonitrile (7a)



7a

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 85% yield (63.6 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a yellow solid. **M.p.:** 180 – 182 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.4 Hz, 2H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.31 – 7.16 (m, 6H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.57 (s, 1H), 5.11 (d, *J* = 12.0 Hz, 1H), 4.62 – 4.59 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.4, 137.9, 135.2, 134.1, 133.1, 132.7, 132.0, 129.1, 128.9, 128.7, 128.5, 122.2, 121.6, 120.1, 115.6, 109.5, 96.9, 55.0, 51.6, 40.8, 33.2. **HRMS** (ESI) *m*/*z* calcd for $C_{26}H_{19}N_2O^+$ ($[M+H]^+$): 375.1492, found 375.1492.

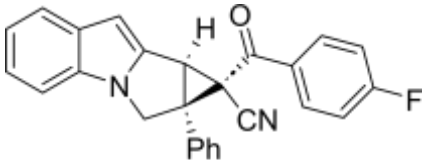
1-(4-methylbenzoyl)-1a-Phenyl-1,1a,2,8b-tetrahydrocyclopropa[3,4]pyrrolo[1,2-a]indole-1-carbonitrile (7b)



7b

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 83% yield (64.4 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a brown solid. **M.p.:** 162 – 164 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.32 – 7.22 (m, 8H), 7.20 – 7.16 (m, 1H), 7.12 – 7.08 (m, 1H), 6.56 (s, 1H), 5.11 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.59 (s, 1H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.8, 145.3, 138.0, 133.1, 132.7, 132.1, 129.4, 129.2, 129.0, 128.9, 128.5, 122.1, 121.5, 120.1, 115.7, 109.4 , 96.8, 54.7, 51.5, 40.7, 32.9, 29.7, 21.8. **HRMS** (ESI) *m/z* calcd for $C_{27}H_{21}N_2O^+$ ($[M+H]^+$): 389.1648, found 389.1648.

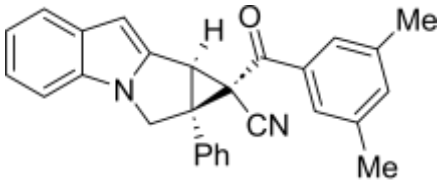
1-(4-fluorobenzoyl)-1a-Phenyl-1,1a,2,8b-tetrahydrocyclopropa[3,4]pyrrolo[1,2-a]indole-1-carbonitrile (7c)



7c

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 61% yield (47.8 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.9, 5.2 Hz, 2H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.29 – 7.27 (m, 4H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.14 – 7.09 (m, 3H), 6.58 (s, 1H), 5.12 (d, *J* = 12.1 Hz, 1H), 4.65 (d, *J* = 12.1 Hz, 1H), 4.60 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 185.8, 166.1 (d, *J* = 257.4 Hz), 137.8, 133.1, 132.7, 131.9 (d, *J* = 9.6 Hz), 131.8, 131.5 (d, *J* = 3.0 Hz), 129.2, 129.0, 128.4, 122.3, 121.6, 120.2, 116.0 (d, *J* = 22.1 Hz), 115.5, 109.5, 96.9, 55.0, 51.5, 40.6, 33.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.4 (s). **HRMS** (ESI) *m/z* calcd for $C_{26}H_{18}FN_2O^+$ ($[M+H]^+$): 393.1398, found 393.1398.

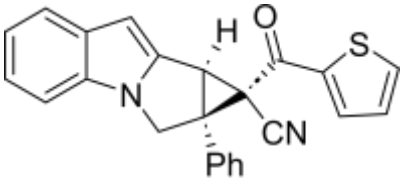
1-(3,5-dimethylbenzoyl)-1a-Phenyl-1,1a,2,8b-tetrahydrocyclopropa[3,4]pyrrolo[1,2-a]indole-1-carbonitrile (7d)



7d

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 80% yield 64.4 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a yellow solid. **M.p.:** 170 – 172 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.8 Hz, 1H), 7.47 (s, 2H), 7.33 – 7.28 (m, 3H), 7.25– 7.23 (m, 3H), 7.20 – 7.16 (m, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.57 (s, 1H), 5.14 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.58 (s, 1H), 2.35 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.7, 138.3, 138.0, 135.8, 135.4, 133.1, 132.7, 132.2, 129.0, 128.9, 128.5, 126.8, 122.1, 121.5, 120.1 , 115.6, 109.4, 96.8, 54.9, 51.6, 40.9, 33.3, 21.3. **HRMS** (ESI) *m*/*z* calcd for $C_{28}H_{23}N_2O^+$ ($[M+H]^+$): 403.1805, found 403.1803.

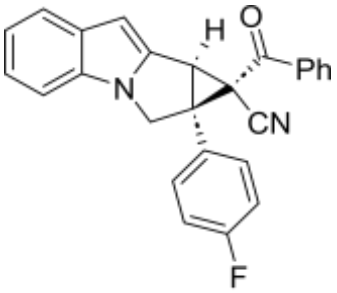
1a-Phenyl-1-(thiophene-2-carbonyl)-1,1a,2,8b-tetrahydrocyclopropa[3,4]pyrrolo[1,2-a]indole -1-carbonitrile (7e)



7e

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 84% yield (63.8 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a brown solid. **M.p.:** 192 – 194 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 3.9, 0.8 Hz, 1H), 7.67 (dd, *J* = 4.9, 0.8 Hz, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.26 – 7.22 (m, 5H), 7.21 – 7.09 (m, 4H), 6.58 (s, 1H), 5.03 (d, *J* = 12.1 Hz, 1H), 4.58 (d, *J* = 12.1 Hz, 1H), 4.55 (s, 1H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.6, 141.9, 137.8, 136.0, 134.3, 133.1, 132.7, 132.0, 129.0, 128.9, 128.5, 122.2, 121.6, 120.1, 115.8, 109.5 , 96.9, 54.9, 51.8, 40.0, 33.8, 29.7. **HRMS** (ESI) *m*/*z* calcd for $C_{24}H_{17}N_2OS^+$ ($[M+H]^+$): 381.1056, found 381.1058.

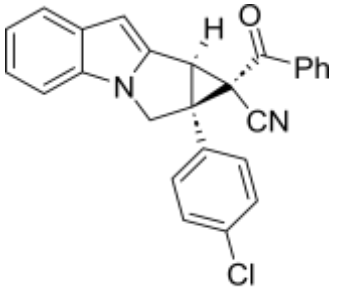
1-Benzoyl-1a-(4-fluorophenyl)-1,1a,2,8b-tetrahydrocyclopropa[3,4]pyrrolo[1,2-a]indole-1-carbonitrile (7f)



7f

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 44% yield (34.6 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a brown solid. **M.p.:** 199 – 201 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.4 Hz, 2H), 7.62 – 7.56 (m, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.30 (dd, *J* = 8.7, 5.1 Hz, 2H), 7.24 – 7.17 (m, 2H), 7.11 (dd, *J* = 10.8, 3.9 Hz, 1H), 6.96 (t, *J* = 8.5 Hz, 2H), 6.58 (s, 1H), 5.10 (d, *J* = 12.0 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.57 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.3, 162.8 (d, *J* = 249.4 Hz), 137.7, 135.2, 134.2, 133.1, 132.6, 130.4 (d, *J* = 8.6 Hz), 129.0, 128.7, 127.9 (d, *J* = 3.3 Hz), 122.0 (d, *J* = 66.8 Hz), 120.2 , 116.2, 116.0, 115.4, 109.4, 97.0, 54.3, 51.6, 40.8, 33.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.4 (s). **HRMS** (ESI) *m*/*z* calcd for $C_{26}H_{18}FN_2O^+$ ($[M+H]^+$): 393.1398, found 393.1398.

1-Benzoyl-1a-(4-chlorophenyl)-1,1a,2,8b-tetrahydrocyclopropa[3,4]pyrrolo[1,2-a]indole-1-carbonitrile (7g)

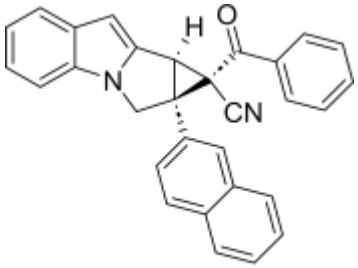


7g

Prepared according to the general procedure (reaction time: 2 h) as described above in 39% yield (31.8mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a yellow solid. **M.p.:** 125 – 127 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.7 Hz, 2H), 7.62 – 7.56 (m, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.25 – 7.17 (m, 6H), 7.11 (t, *J* = 7.3 Hz, 1H), 6.58 (s, 1H), 5.10 (d, *J* = 12.0 Hz, 1H), 4.60 – 4.57 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.3, 137.5, 135.2, 135.1, 134.3, 133.0,

132.6, 130.6, 129.8, 129.2, 129.0, 128.8, 122.3, 121.6, 120.2, 115.3, 109.4, 97.1, 54.3, 51.4, 40.8, 33.5. **HRMS** (ESI) *m/z* calcd for $C_{26}H_{18}ClN_2O^+$ ($[M+H]^+$): 409.1102, found 409.1102.

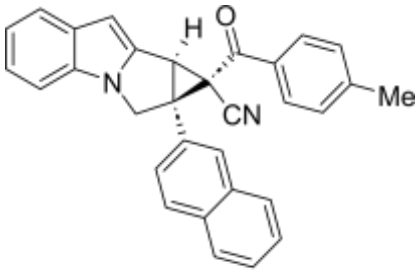
1-Benzoyl-1a-(naphthalen-2-yl)-1,1a,2,8b-tetrahydrocyclopropa[3,4]pyrrolo[1,2-a]indole-1-carbonitrile (7h)



7h

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 88% yield (74.6 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a brown oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.4 Hz, 2H), 7.76 – 7.71 (m, 4H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.46 – 7.38 (m, 5H), 7.25 – 7.17 (m, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.60 (s, 1H), 5.20 (d, *J* = 12.1 Hz, 1H), 4.72 (s, 1H), 4.66 (d, *J* = 12.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.4, 138.0, 135.3, 134.1, 133.1, 132.9, 132.7, 129.2, 129.1, 129.0, 128.6, 128.2, 128.1, 127.7, 127.0, 126.9, 125.4, 122.2, 121.6, 120.2, 115.6, 109.5, 96.9, 55.3, 51.7, 41.0, 33.5. **HRMS** (ESI) *m/z* calcd for $C_{30}H_{21}N_2O^+$ ($[M+H]^+$): 425.1648, found 425.1648.

1-(4-methylbenzoyl)-1a-(naphthalen-2-yl)-1,1a,2,8b-Tetrahydrocyclopropa[3,4]pyrrolo[1,2-a]indole-1-carbonitrile (7i)

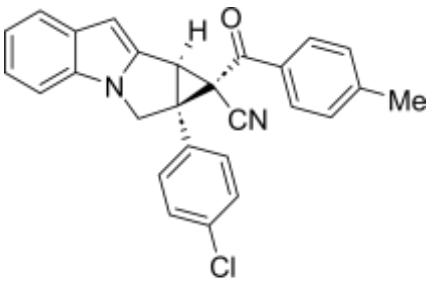


7i

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 95% yield (83.2 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a brown oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.75 – 7.72 (m, 4H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.47 – 7.40 (m, 3H), 7.25 – 7.19 (m, 4H), 7.10 (t, *J* = 7.1 Hz, 1H), 6.60 (s, 1H), 5.19 (d, *J* = 12.0 Hz,

1H), 4.71 (s, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.8, 145.3, 138.1, 133.1, 132.9, 132.7, 132.7, 129.4, 129.3, 129.3, 129.0, 128.2, 128.1, 127.7, 126.9, 126.9, 125.5, 122.2, 121.6, 120.1, 115.8, 109.5, 96.9, 54.9, 51.7, 40.9, 33.2, 29.8, 21.8. **HRMS** (ESI) *m/z* calcd for $C_{31}H_{23}N_2O^+$ ($[M+H]^+$): 439.1805, found 439.1805.

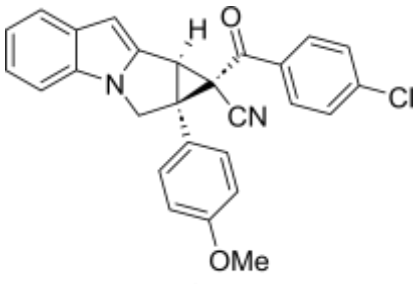
1a-(4-chlorophenyl)-1-(4-methylbenzoyl)-1,1a,2,8b-Tetrahydrocyclopropa[3,4]pyrrolo[1,2-a] indole-1-carbonitrile (7j)



7j

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 75% yield (63.4 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a yellow solid. **M.p.:** 99 – 101 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.25 – 7.22 (m, 7H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.12 – 7.18 (m, 1H), 6.56 (s, 1H), 5.08 (d, *J* = 12.0 Hz, 1H), 4.58 – 4.55 (m, 2H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.6, 145.5, 137.7, 135.1, 133.0, 132.7, 132.6, 130.7, 129.8, 129.5, 129.2, 122.3, 121.6, 120.2, 115.5, 109.4, 97.0, 53.9, 51.4, 40.7, 33.1, 29.7, 21.8. **HRMS** (ESI): *m/z* calcd for $C_{27}H_{20}ClN_2O^+$ ($[M+H]^+$): 423.1259, found 423.1259.

1-(4-chlorobenzoyl)-1a-(4-methoxyphenyl)-1,1a,2,8b-Tetrahydrocyclopropa[3,4]pyrrolo[1,2-a]indole-1-carbonitrile (7k)



7k

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 54% yield (47.4 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a yellow oil. **^{1}H NMR**

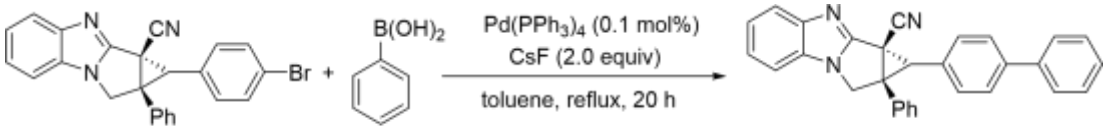
(400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.24 – 7.17 (m, 4H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 8.7 Hz, 2H), 6.56 (s, 1H), 5.09 (d, *J* = 12.1 Hz, 1H), 4.60 (d, *J* = 12.1 Hz, 1H), 4.56 (s, 1H), 3.73 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.4, 160.0, 140.7, 137.8, 133.5, 133.0, 132.6, 130.4, 129.6, 129.1, 123.6, 122.2, 121.6, 120.1, 115.5, 114.4, 109.4, 96.8, 55.3, 55.0, 51.7, 40.8, 33.4. **HRMS** (ESI): *m*/*z* calcd for $C_{27}H_{20}ClN_2O^+_2$ ($[M+H]^+$): 439.1208, found 439.1208.

4. Scaled-up Synthesis of the Products 3f and 7a

The compound **1f** (1.13 g, 3.5 mmol), vinylsulfonium salt **2a** (2.54 g, 5.25 mmol.) and THF (40.0 mL) were added to a 100 mL dry sealed tube. Then Cs_2CO_3 (2.28 g, 7.0 mmol) were added in one portion. The system was stirred at room temperature for 1 hour until the complete consumption of compound **1f** monitored by TLC. The reaction mixture was filtered with Celite, and eluted with dichloromethane. The filtrate was concentrated and the residue was purified by flash column chromatography (petroleum ether: EtOAc = 5:1) on silica gel to afford corresponding product **3f** with a yellow solid 1.2 g (83% yield).

The compound **6a** (953 mg, 3.5 mmol), vinylsulfonium salt **2a** (2.54 g, 5.25 mmol.) and DCM (40.0 mL) were added to a 100 mL dry sealed tube. Then DBU (1.1 g, 7.0 mmol) were added in one portion. The solution was stirred at room temperature for half an hour until the complete consumption of compound **6a** monitored by TLC. The reaction mixture was filtered with Celite, and eluted with dichloromethane. The filtrate was concentrated and the residue was purified by flash column chromatography (petroleum ether: EtOAc = 5:1) on silica gel to afford corresponding product **7a** with a yellow solid 1.0 g (80% yield).

5. Transformations of the Product 3f



3f **8**

Under nitrogen atmosphere, compound **3f** (85.0 mg, 0.2 mmol), phenylboric acid (29.2 mg, 0.24 mmol), CsF (60.7 mg, 0.4 mmol), and $Pd(PPh_3)_4$ (0.23 mg, 0.1 mol%) were successively added to a 10 mL dried sealed tube, followed by the addition of 2.0 mL of toluene. The resulting mixture

was stirred at 100 °C in an oil bath for 20 hours, and then the reaction mixture was directly subjected to flash column chromatography on silica gel (eluting with PE : EA = 5:1) to afford the corresponding product **8** as a yellow solid (66.0 mg, 78% yield), **M.p.:** 201 – 203 °C.

1-([1,1'-biphenyl]-4-yl)-8a-Phenyl-8,8a-dihydrobenzo[d]cyclopropa[3,4]pyrrolo[1,2-a]imidazole-1a(1H)-carbonitrile (8)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 1H), 7.67 (d, *J* = 7.1 Hz, 2H), 7.58 – 7.50 (m, 3H), 7.45 – 7.34 (m, 6H), 7.30 (d, *J* = 7.5 Hz, 3H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 7.9 Hz, 1H), 4.42– 4.25 (m, 2H), 3.96 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 147.5, 141.0, 139.8, 135.2, 132.0, 129.7, 129.7, 129.3, 129.1, 128.8, 128.5, 127.7, 127.6, 126.9, 123.0, 122.5, 120.5, 115.3, 109.4, 52.1, 48.5, 41.7, 25.9.; HRMS (ESI): *m*/*z* calcd for $C_{30}H_{22}N_3^+$ $[M+H]^+$ 424.1808, found 424.1810.

6. X-Ray Single Crystal Data of Products 3f and 7e

Sample preparation for single crystal 3f or 7e: Pure **3f** (20 mg) was dissolved in 1.0 mL of ethyl acetate with a 10 mL of test tube, and then 4.0 mL of *n*-hexane was added to the test tube slowly. The test tube was sealed with a parafilm and kept standing for 3-5 days, and the single crystal **3f** appeared at the bottom of the test tube.

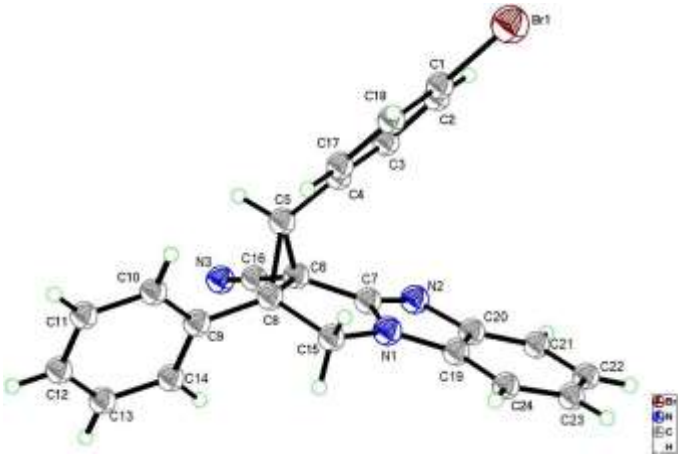


Figure 1. X-Ray structure of **3f** with the ellipsoid contour 80% probability levels

Table S1 Crystal data and structure refinement for 3f.

CCDC number	2375873
Identification code	240615LU_LGPZ305045_0m
Empirical formula	$C_{24}H_{16}BrN_3$
Formula weight	426.31
Temperature/K	295.30
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.132(3)
b/Å	17.534(3)
c/Å	12.433(2)
α/°	90
β/°	114.296(7)
γ/°	90
Volume/Å^3	2410.5(9)
Z	4
ρcalcg/cm^3	1.175
μ/mm^{-1}	1.717
F(000)	864.0
Crystal size/mm^3	0.12 × 0.11 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.28 to 50.736
Index ranges	-11 ≤ h ≤ 14, -18 ≤ k ≤ 21, -14 ≤ l ≤ 14
Reflections collected	18458
Independent reflections	4389 [R_{int} = 0.0614, R_{sigma} = 0.0596]
Data/restraints/parameters	4389/0/241
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0547, wR_2 = 0.1317
Final R indexes [all data]	R_1 = 0.1032, wR_2 = 0.1529
Largest diff. peak/hole / e Å^{-3}	0.36/-0.42

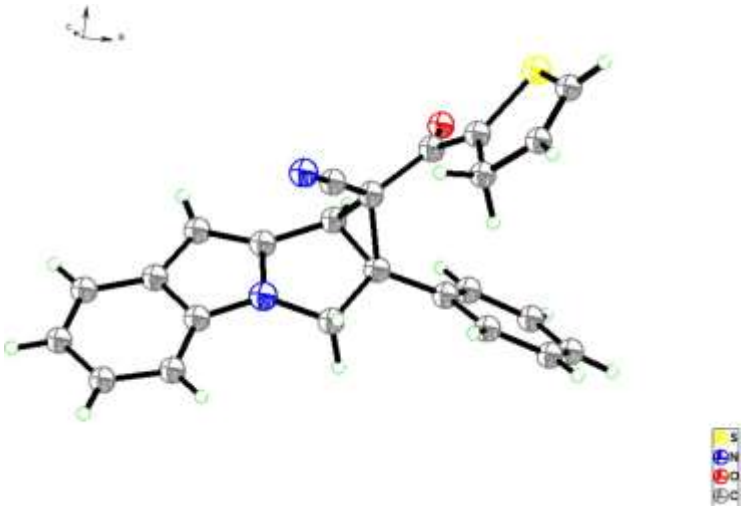


Figure 2. X-Ray structure of **7e** with the ellipsoid contour 80% probability levels

Table S2 Crystal data and structure refinement for 7e.

CCDC number	2346296
Identification code	20240407
Empirical formula	$C_{24}H_{17}N_2OS$
Formula weight	381.45
Temperature/K	293.0
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	19.8487(19)
b/Å	11.0122(12)
c/Å	8.5823(8)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1875.9(3)
Z	4
ρ_{calc}g/cm^3	1.351
μ/mm^{-1}	0.190
F(000)	796.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.23 to 52.762
Index ranges	$-24 \le h \le 24$, $-13 \le k \le 11$, $-10 \le l \le 10$
Reflections collected	15262
Independent reflections	3814 [R_{int} = 0.0654, R_{sigma} = 0.0603]
Data/restraints/parameters	3814/1/253
Goodness-of-fit on F^2	1.076
Final R indexes [I>=2σ (I)]	R_1 = 0.0639, wR_2 = 0.1583
Final R indexes [all data]	R_1 = 0.0952, wR_2 = 0.1803
Largest diff. peak/hole / e Å^{-3}	0.38/-0.47
Flack parameter	0.06(6)

7. NMR Spectra of Products 3a-3ac, 5a,7a-7k and 8

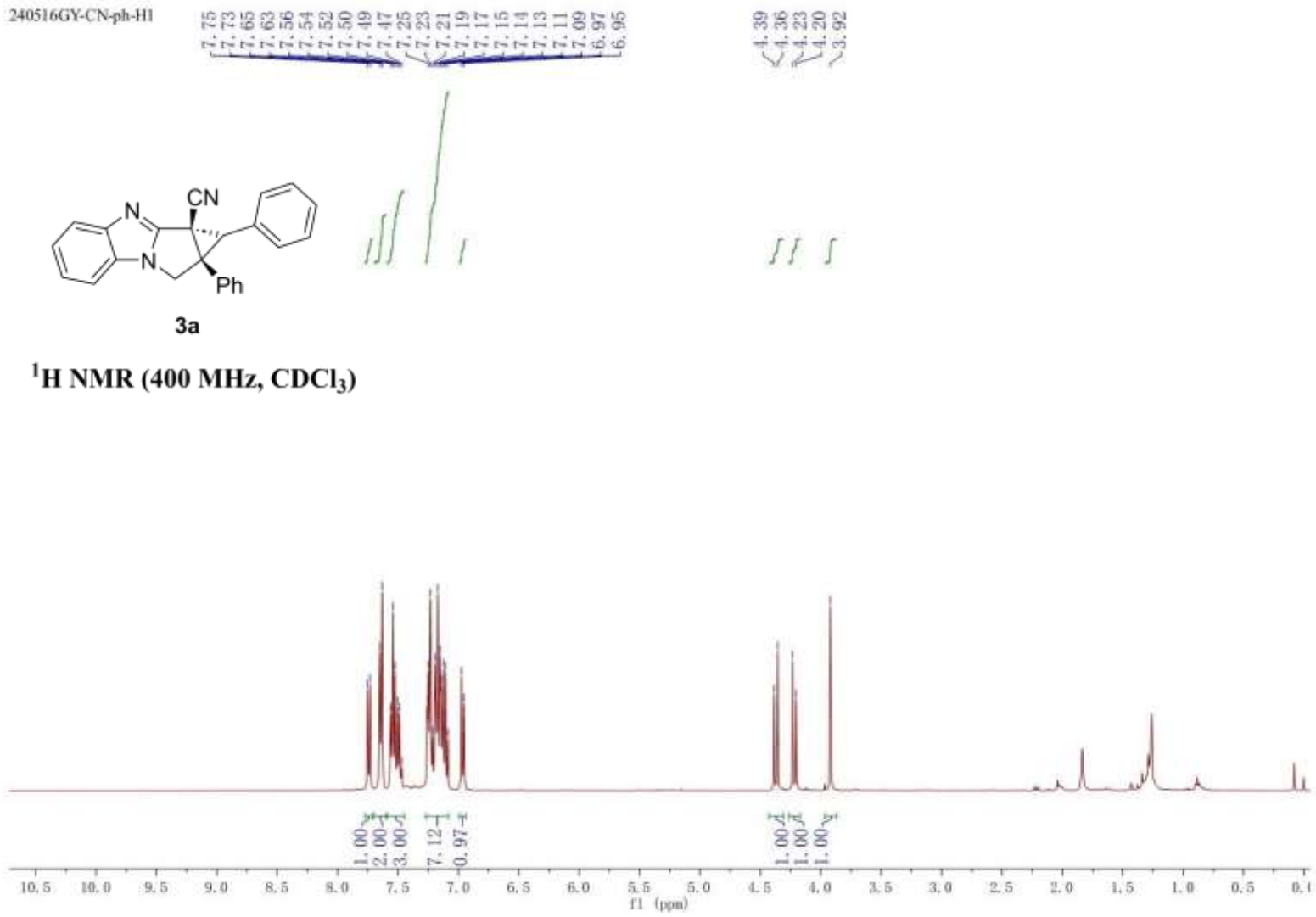


Figure 3. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3a**

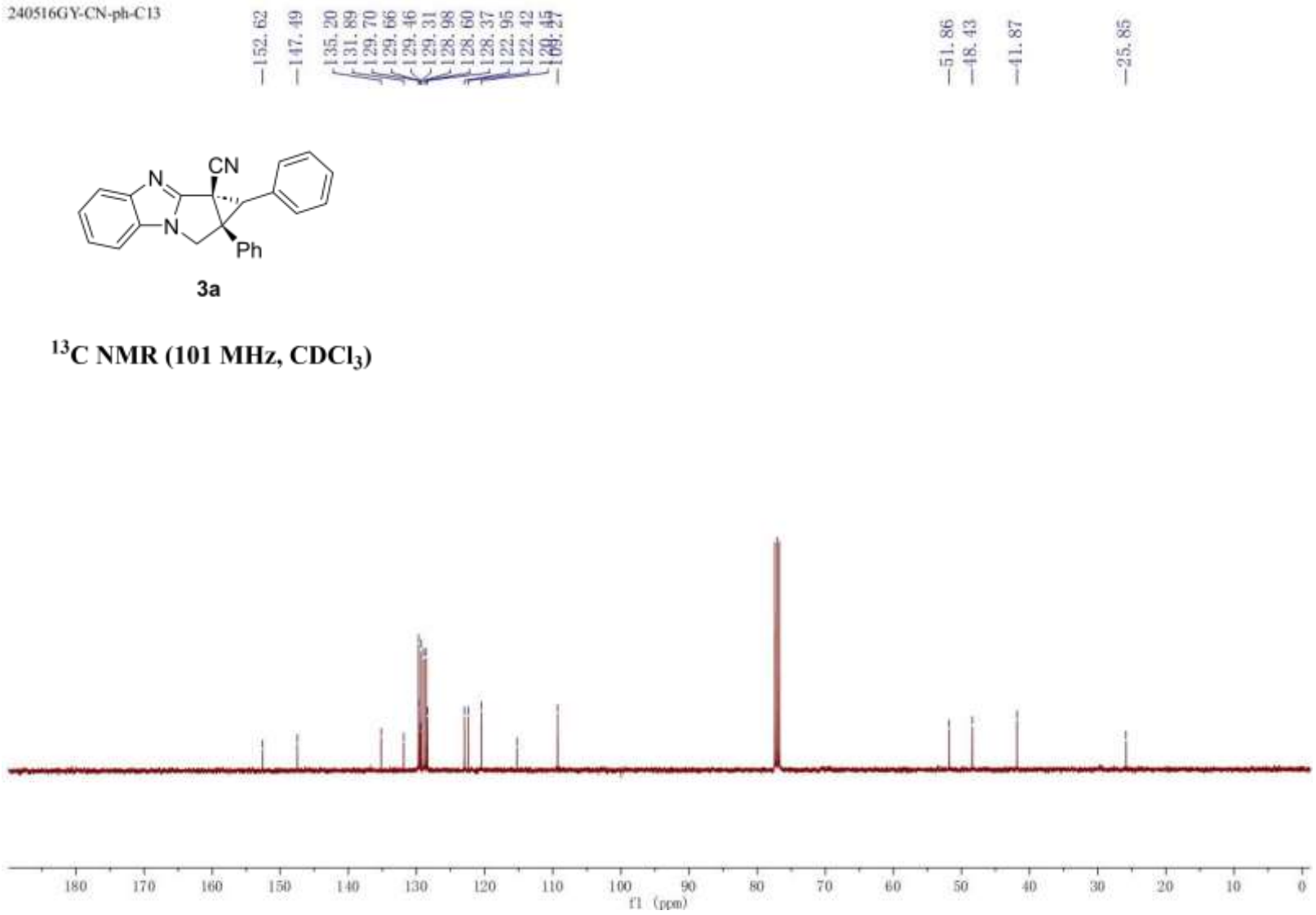


Figure 4. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **3a**

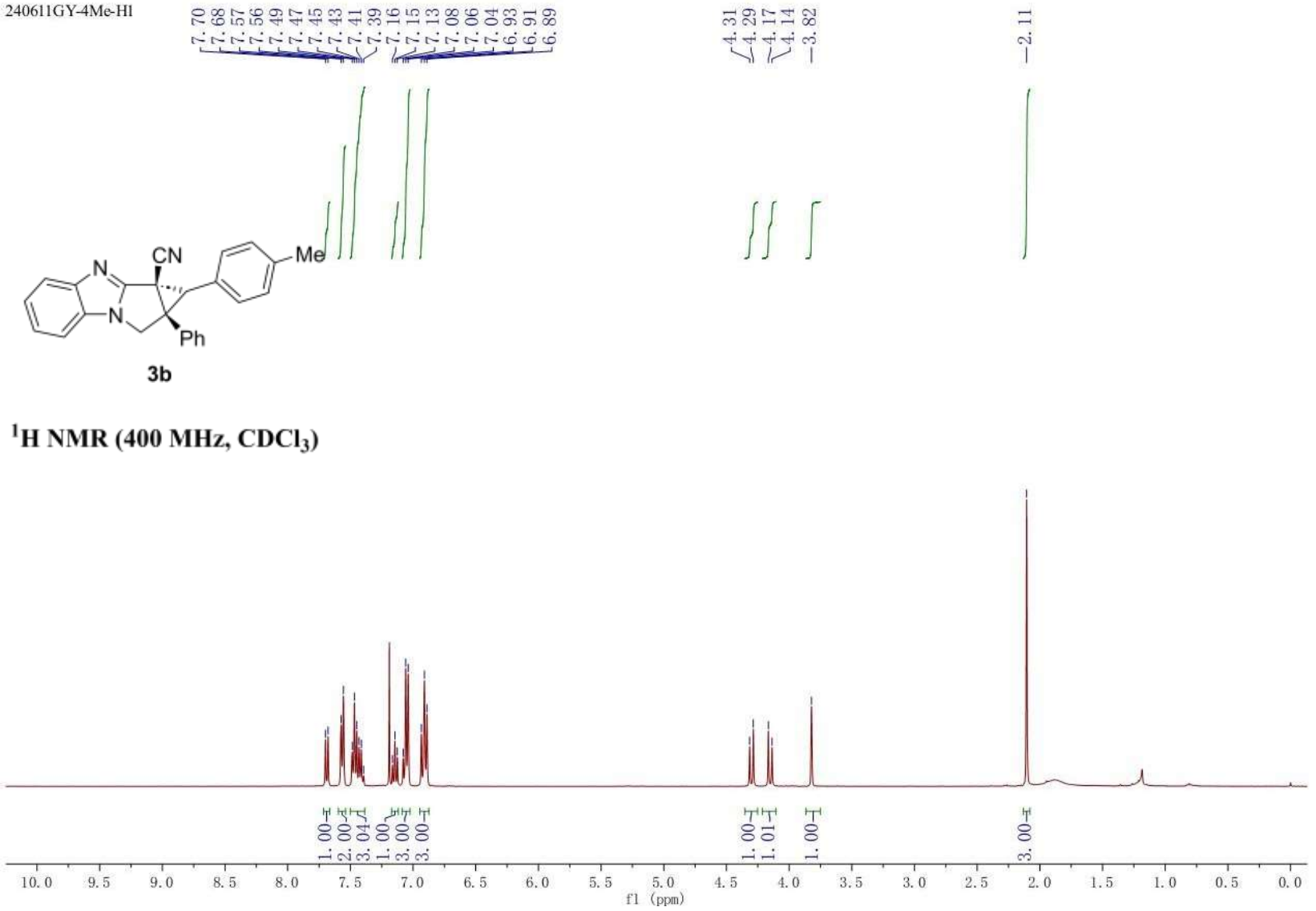


Figure 5. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3b**

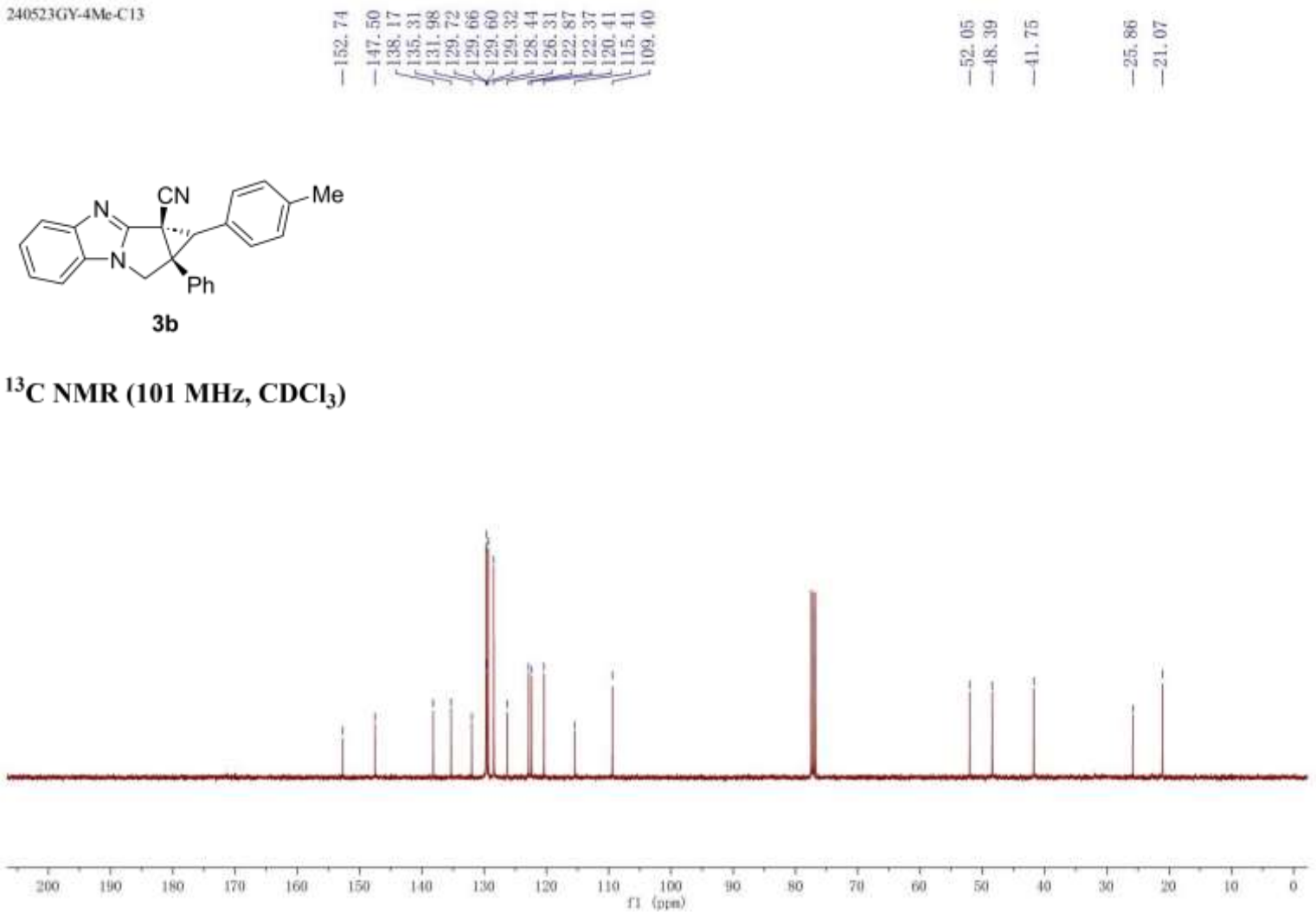


Figure 6. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **3b**

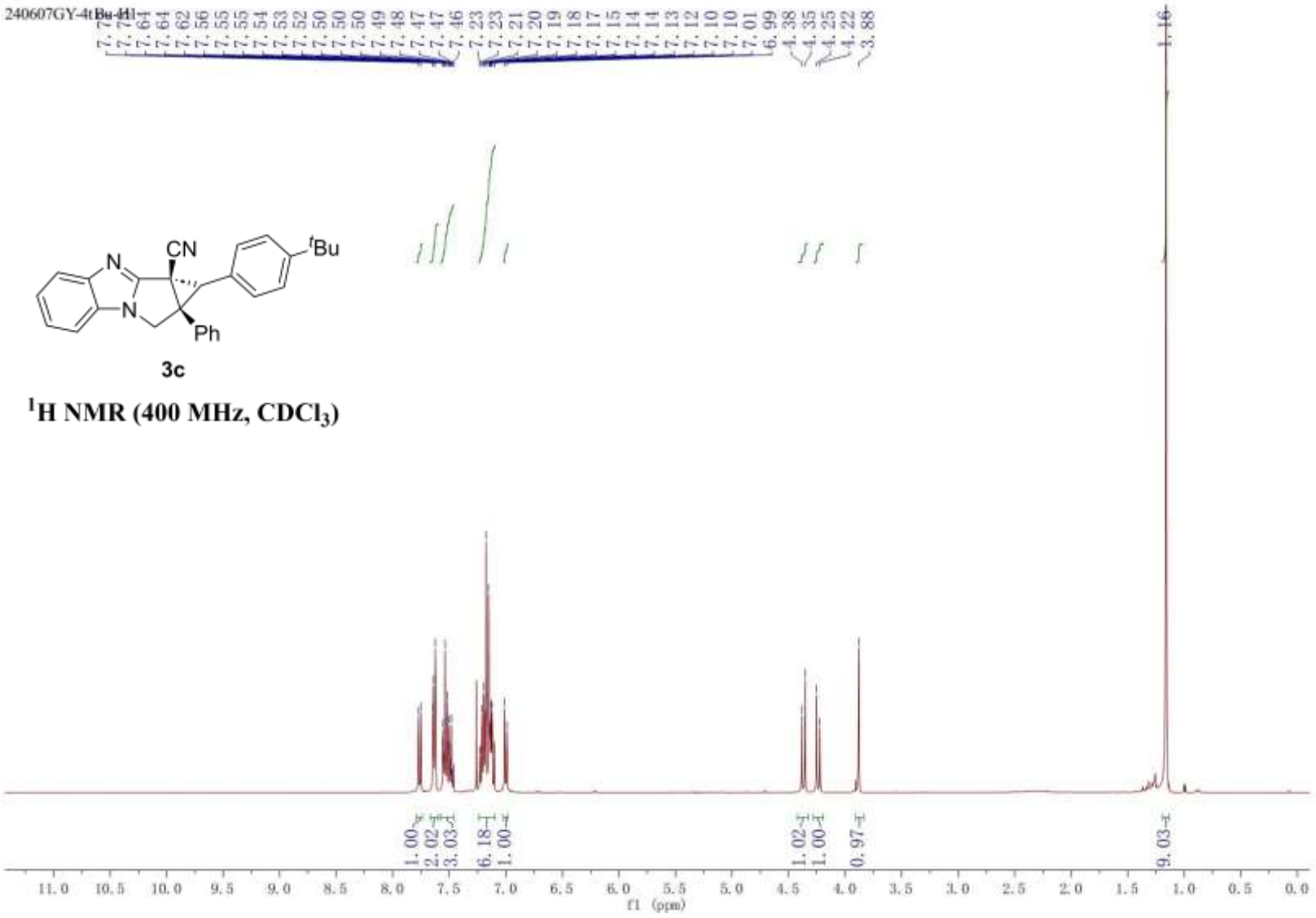


Figure 7. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3c**

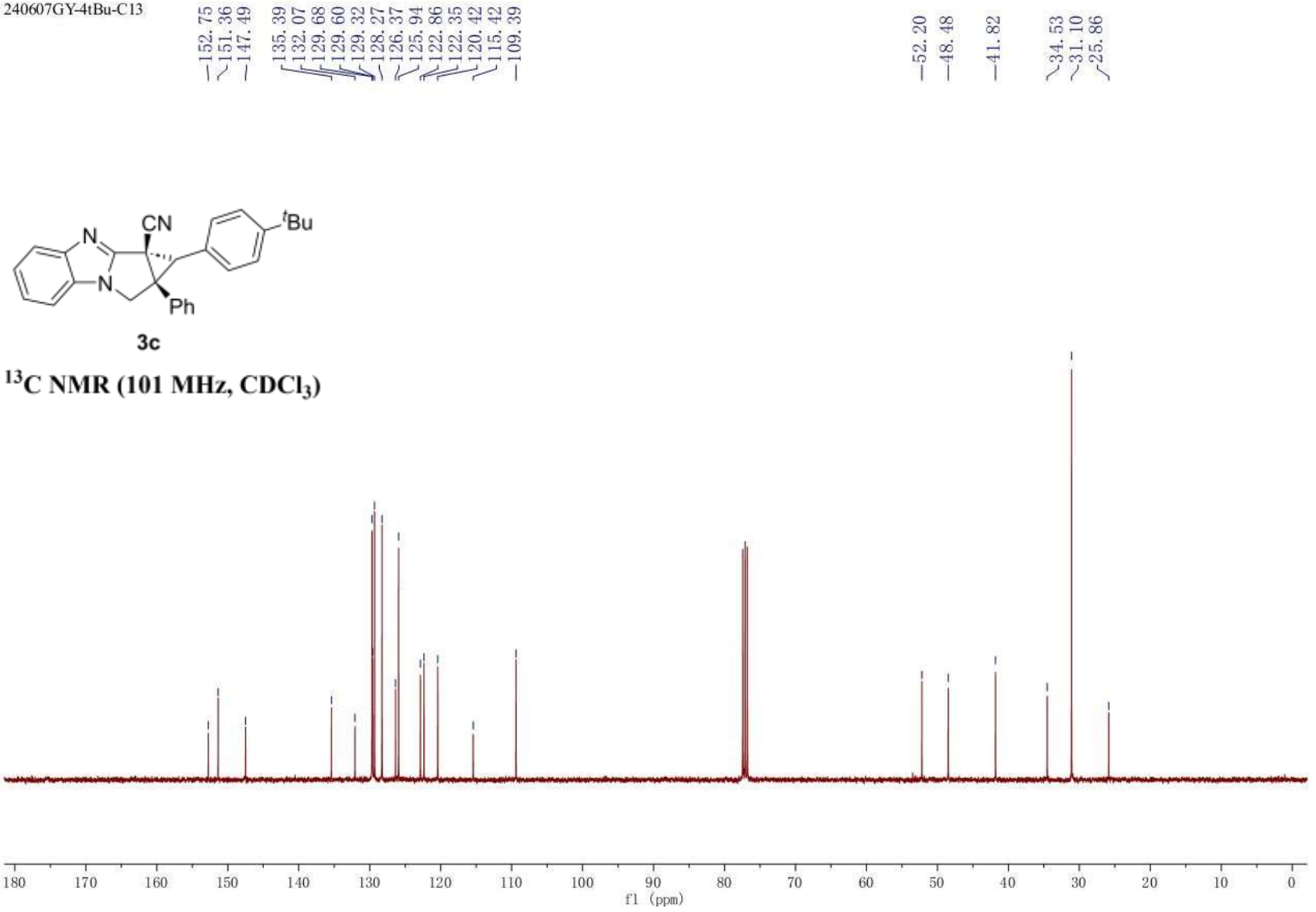


Figure 8. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **3c**

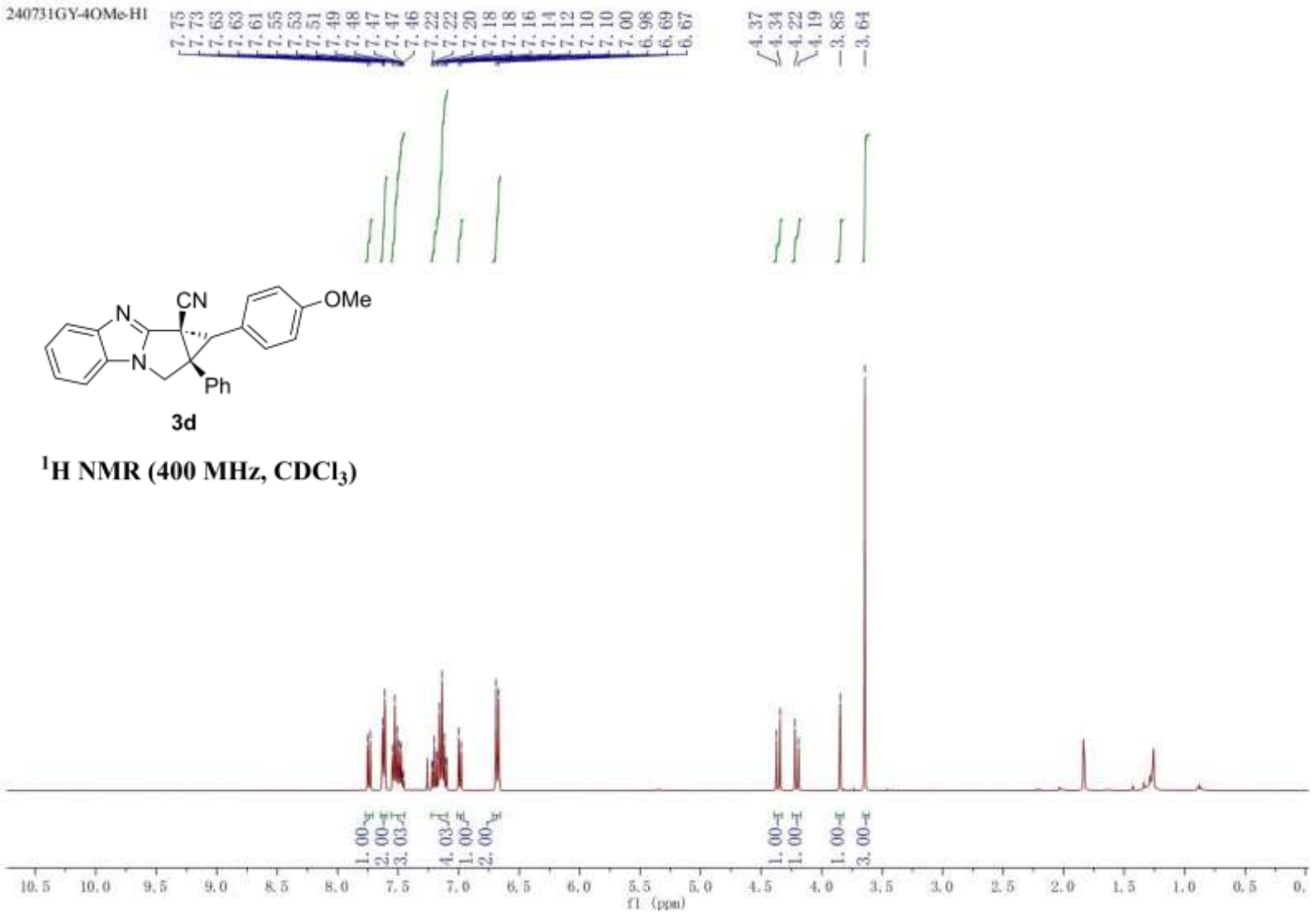


Figure 9. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3d**

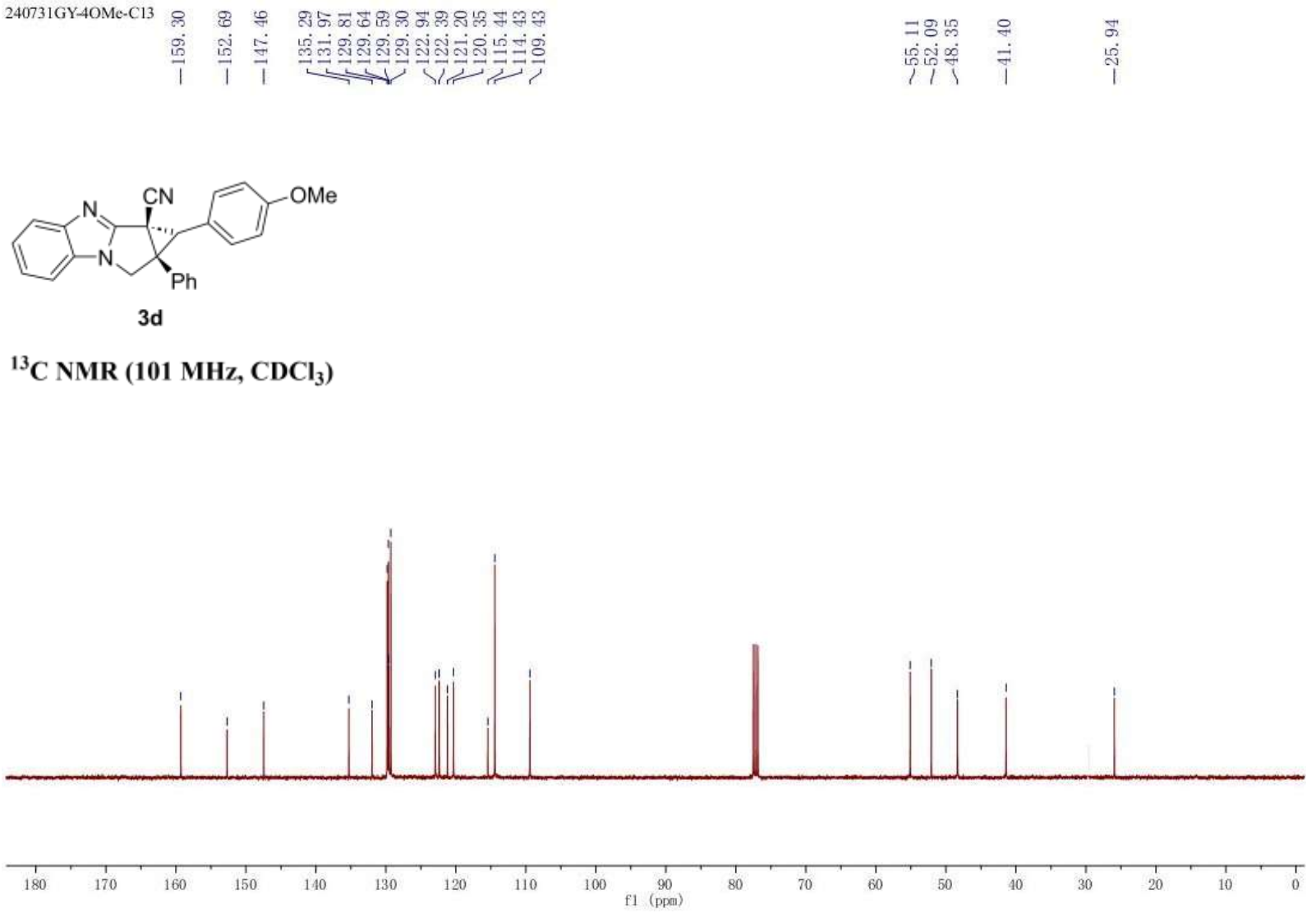
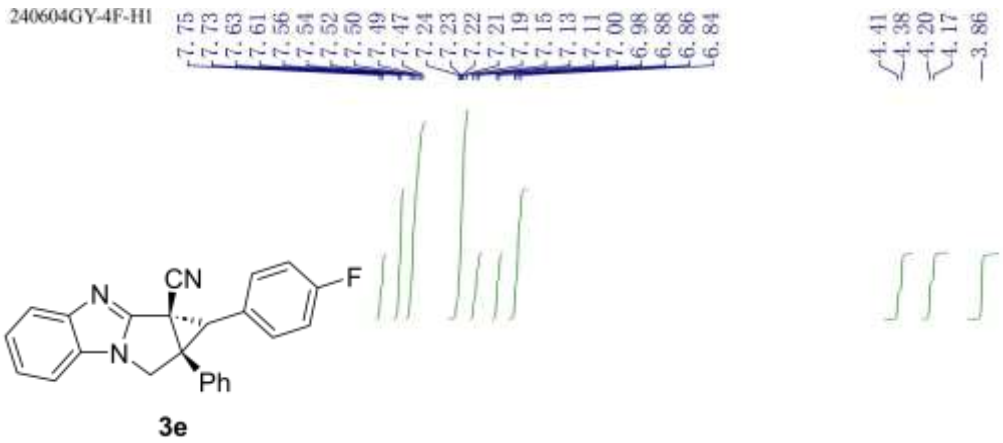


Figure 10. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **3d**



3e

^{1}H NMR (400 MHz, $CDCl_3$)

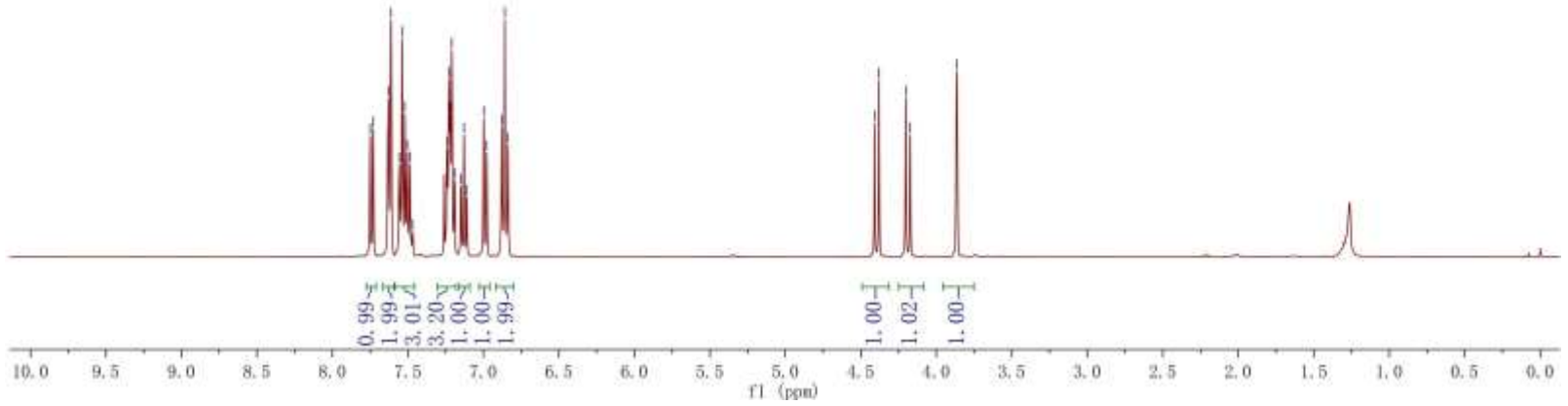


Figure 11. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3e**

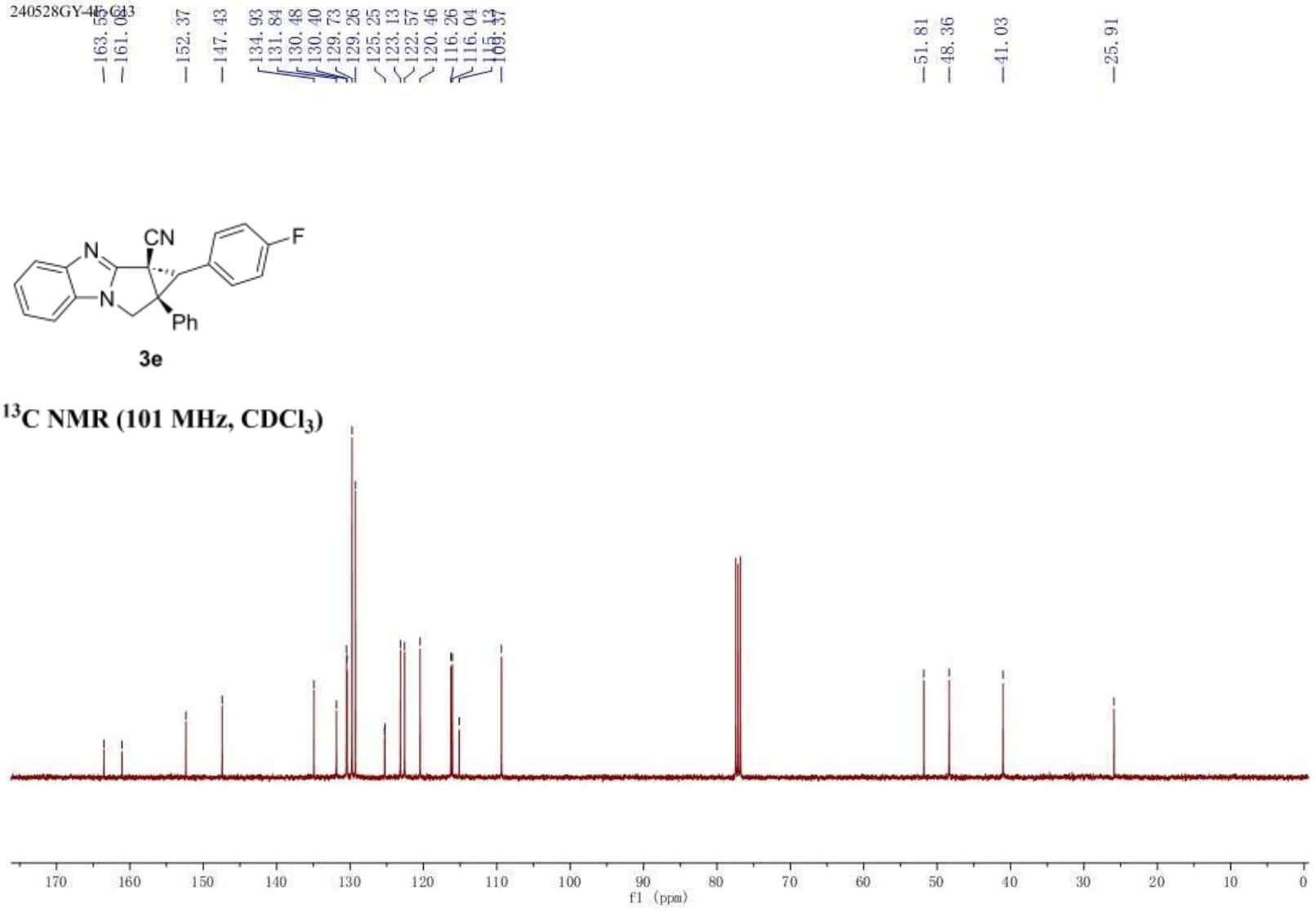
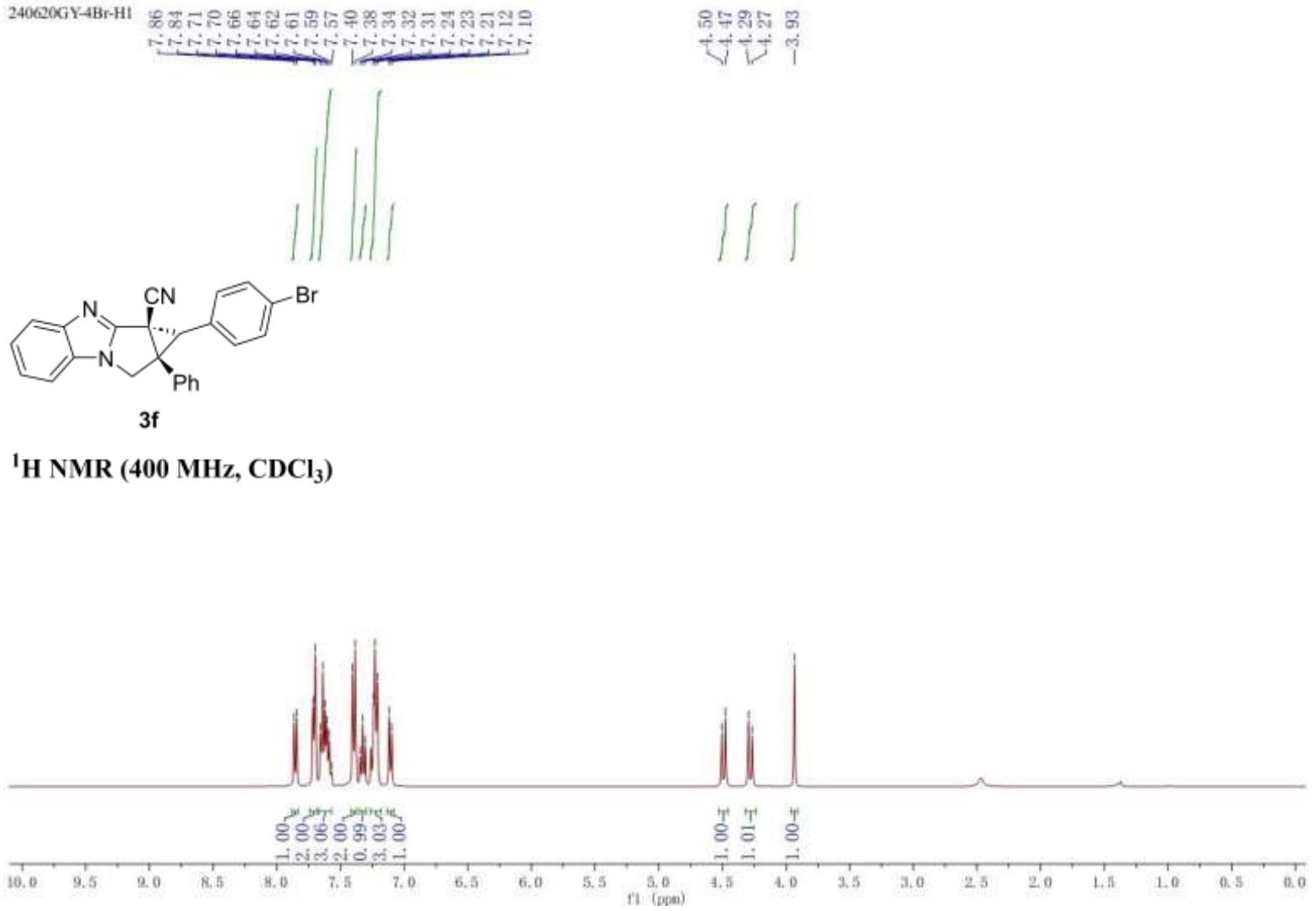


Figure 12. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **3e**



3f

^{1}H NMR (400 MHz, $CDCl_3$)

Figure 13. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3f**

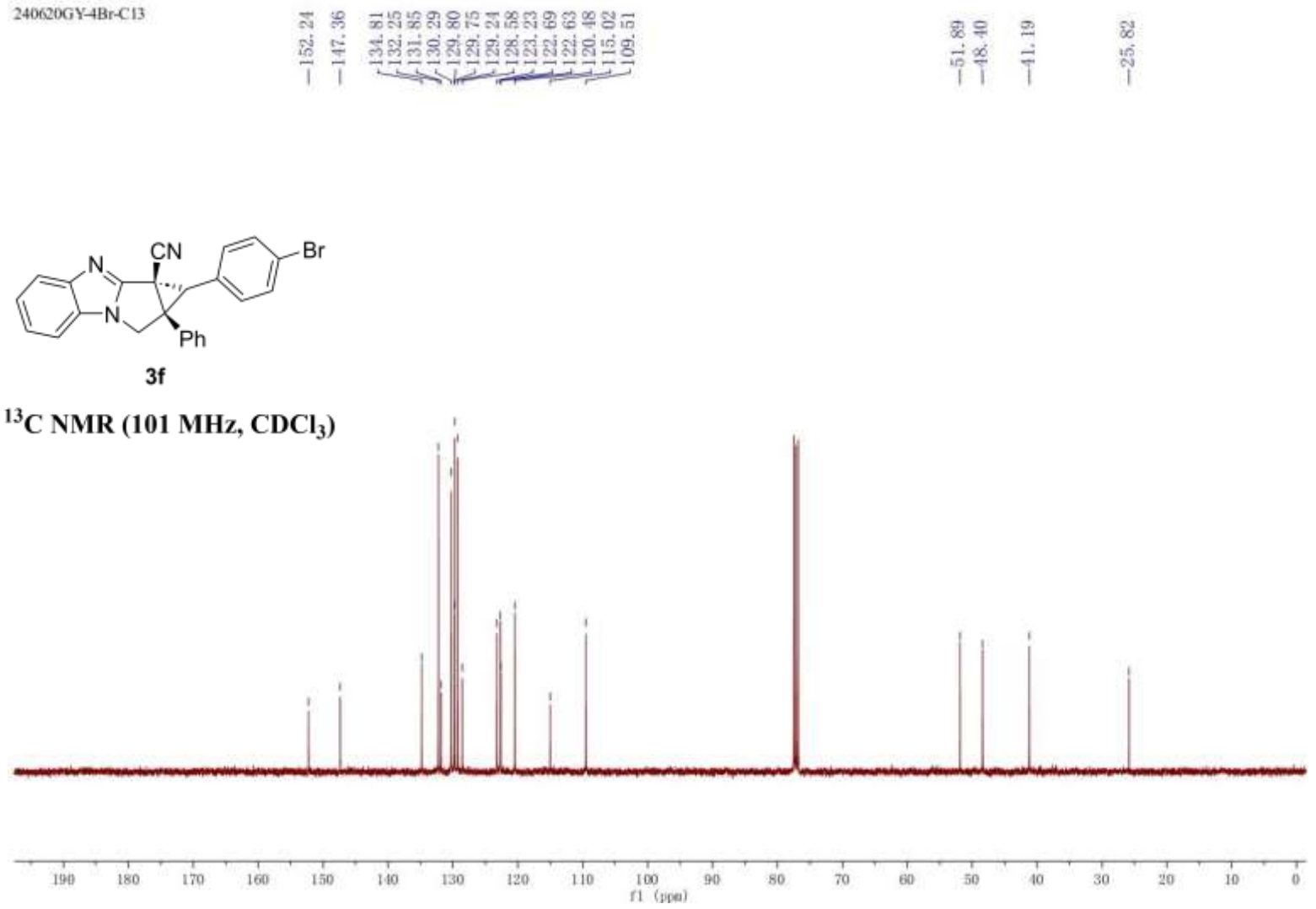


Figure 14. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **3f**

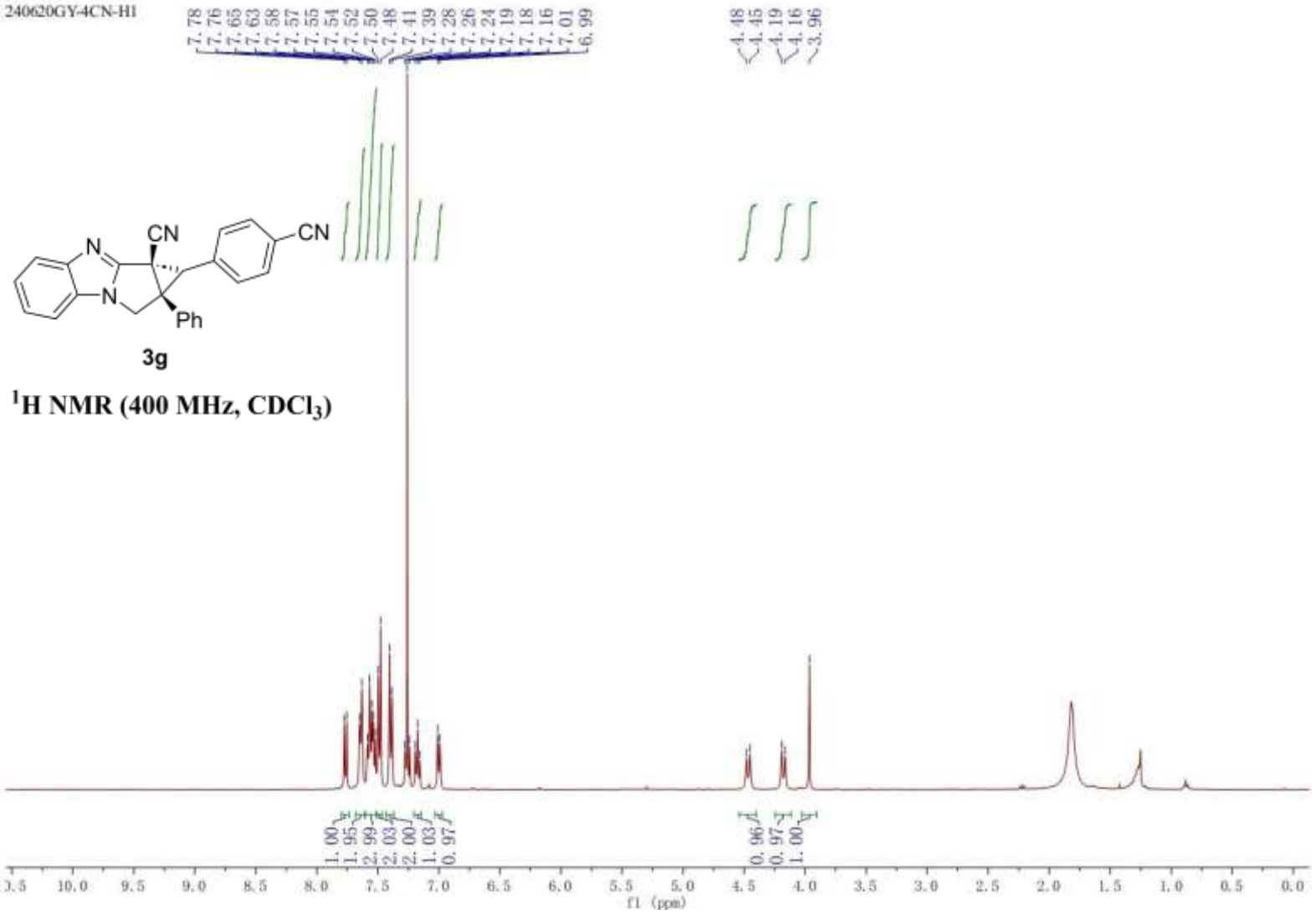


Figure 15. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3g**

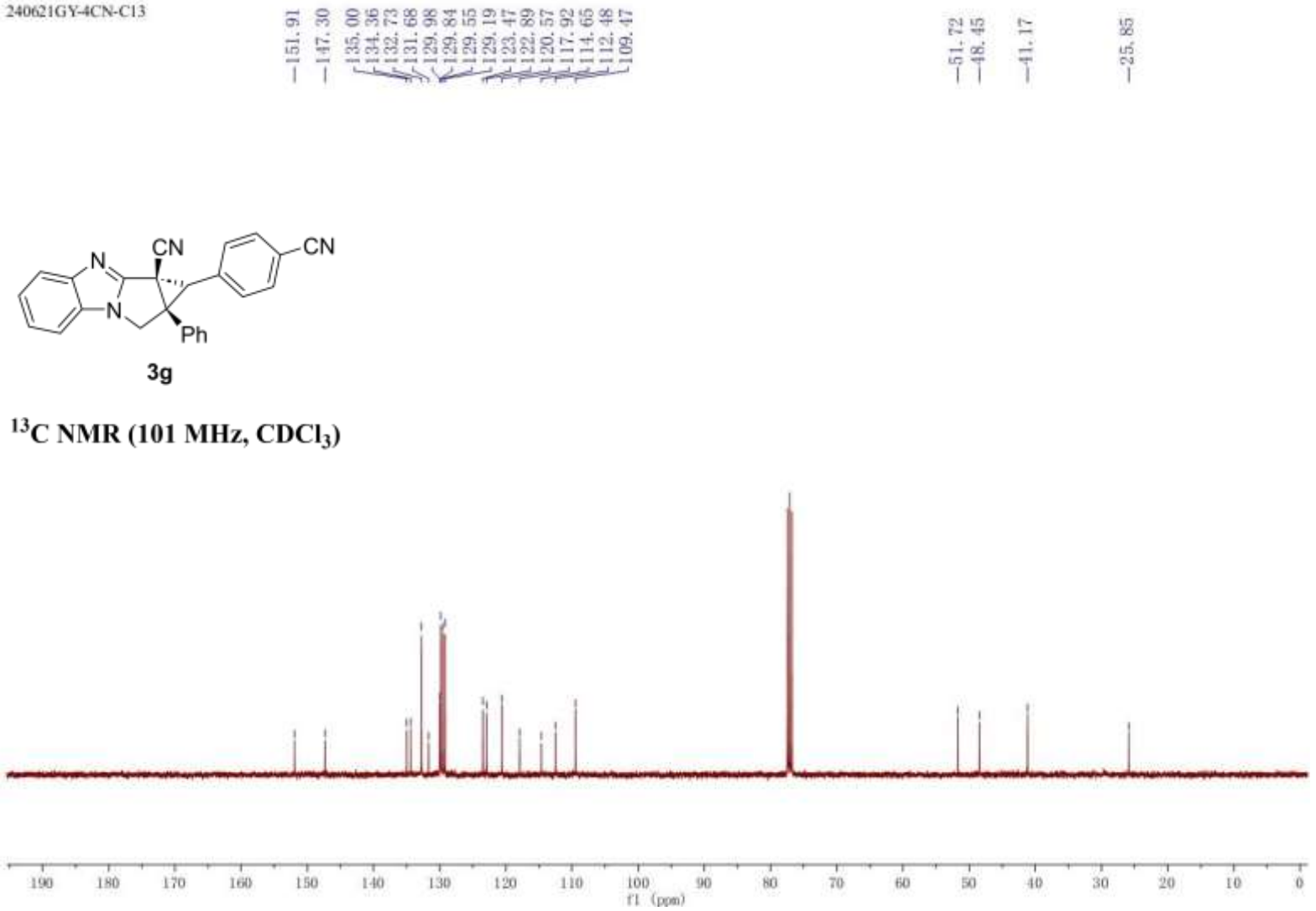


Figure 16. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **3g**

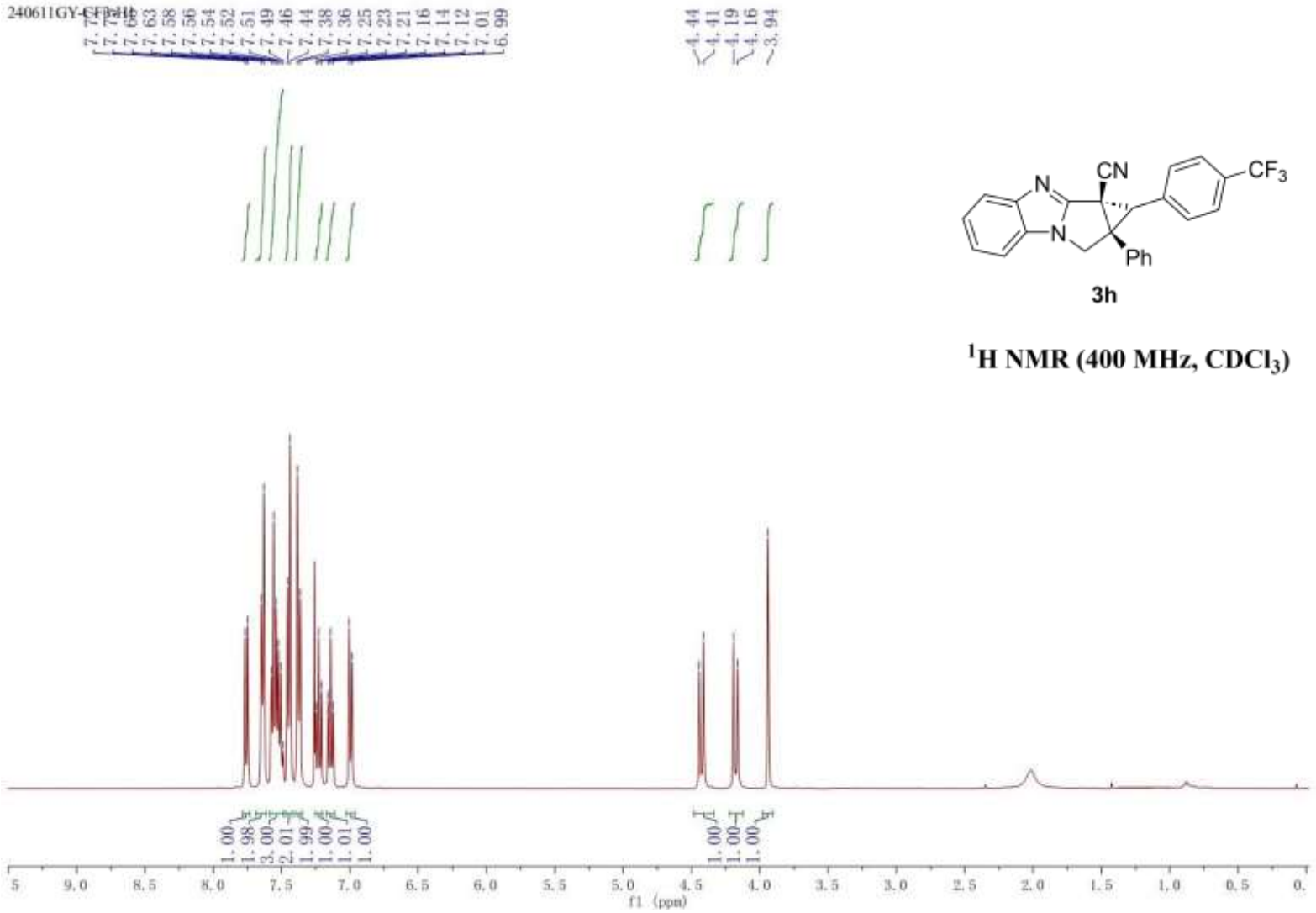


Figure 17. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3h**

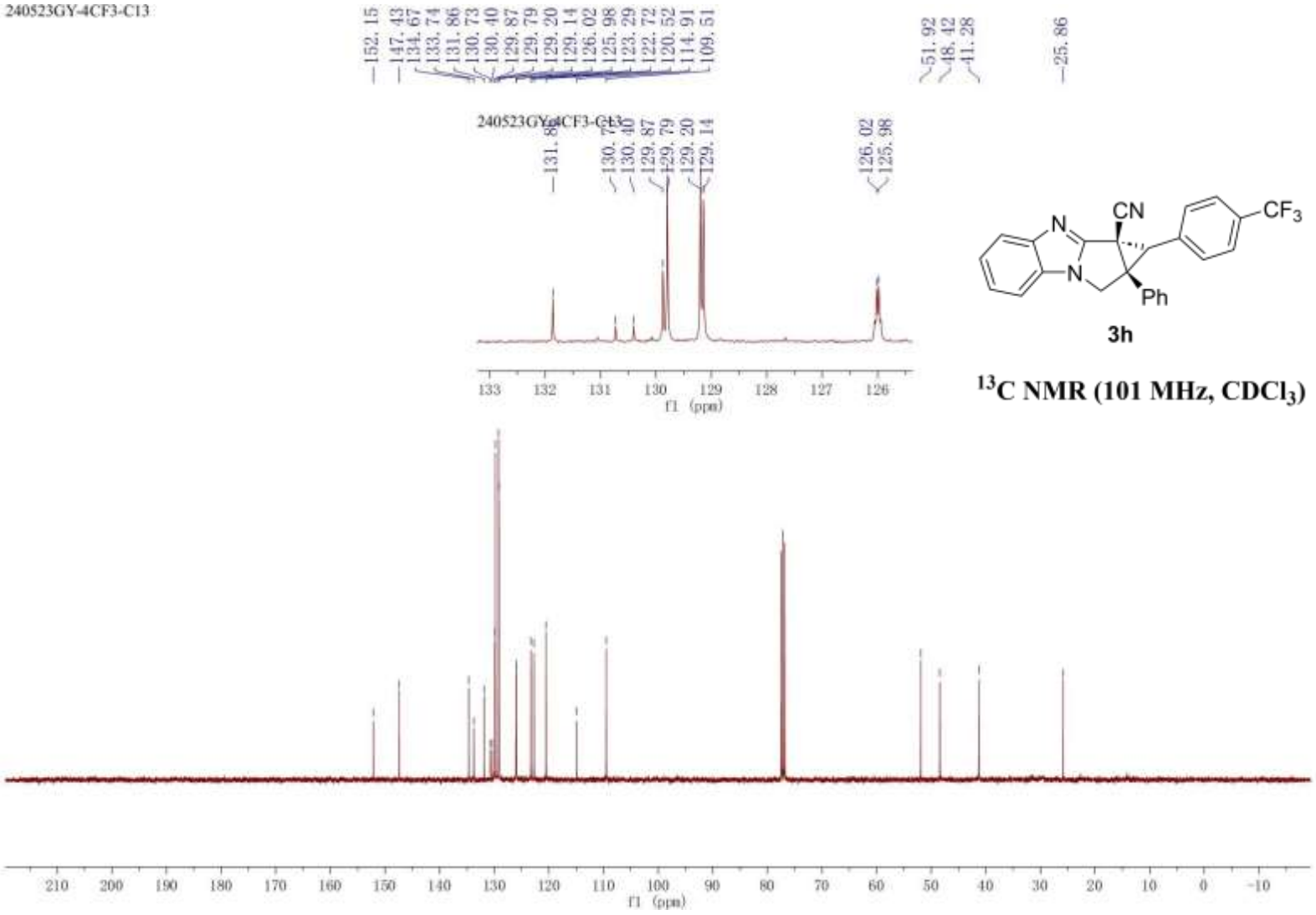


Figure 18. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **3h**

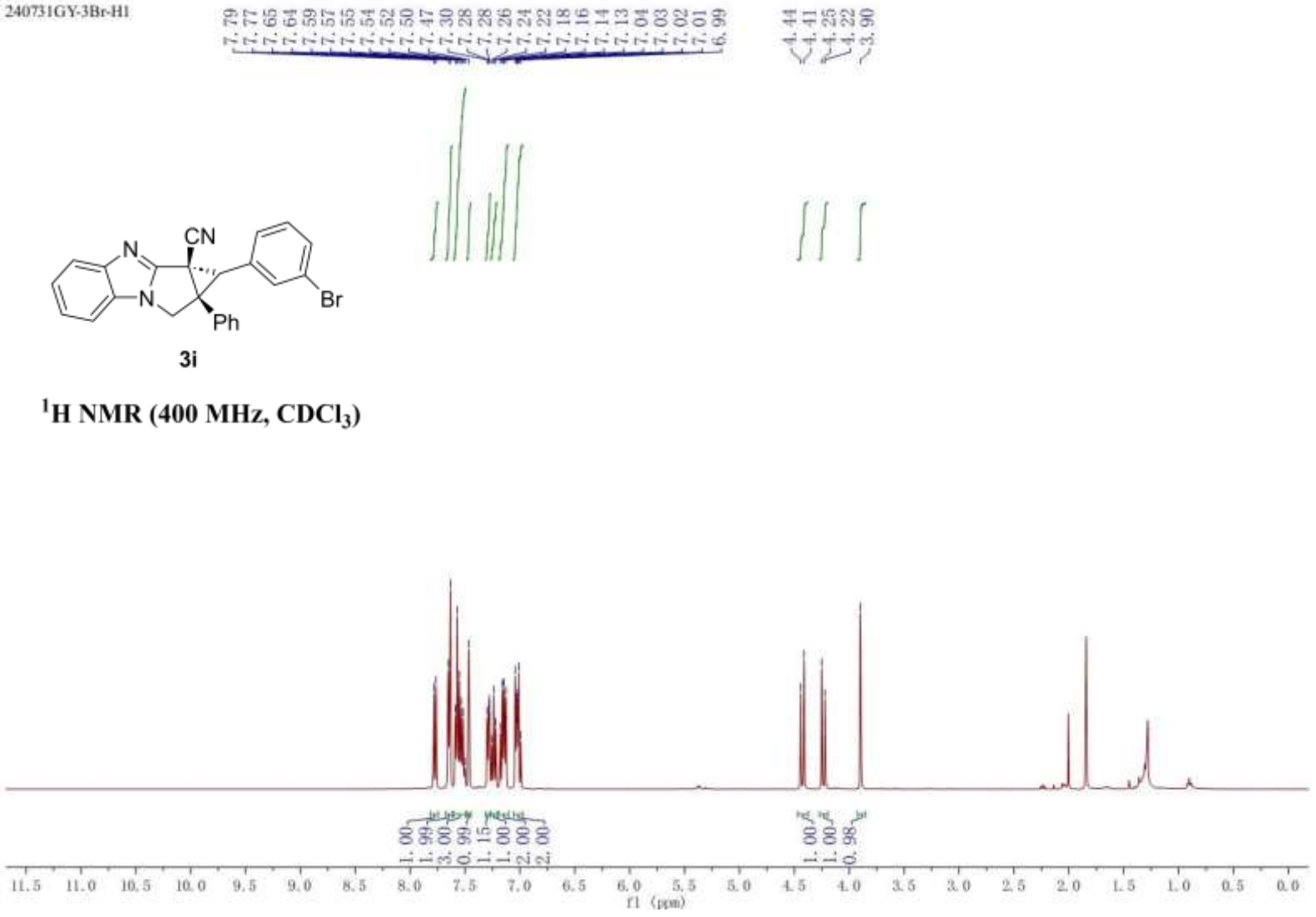


Figure 19. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3i**

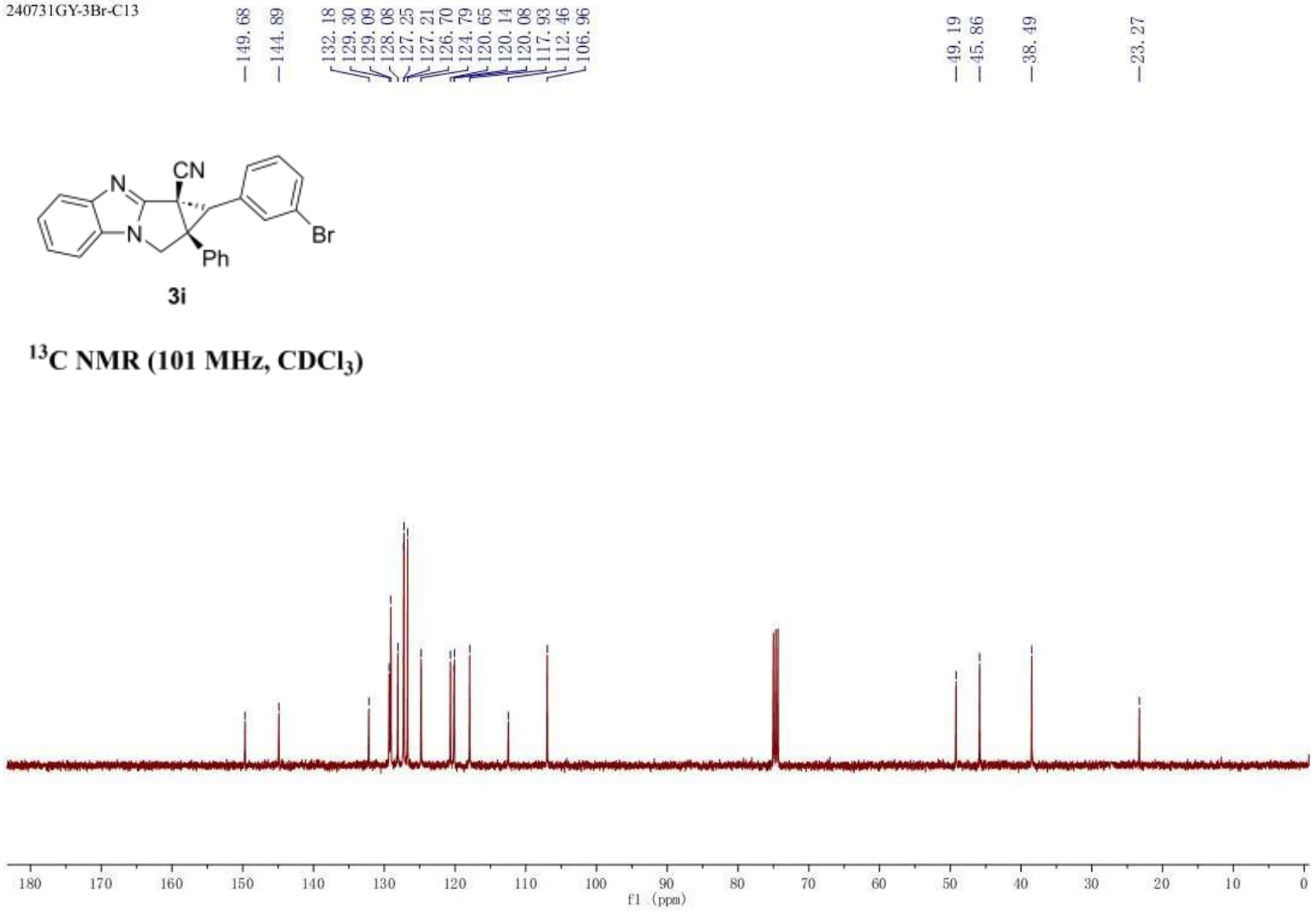


Figure 20. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **3i**

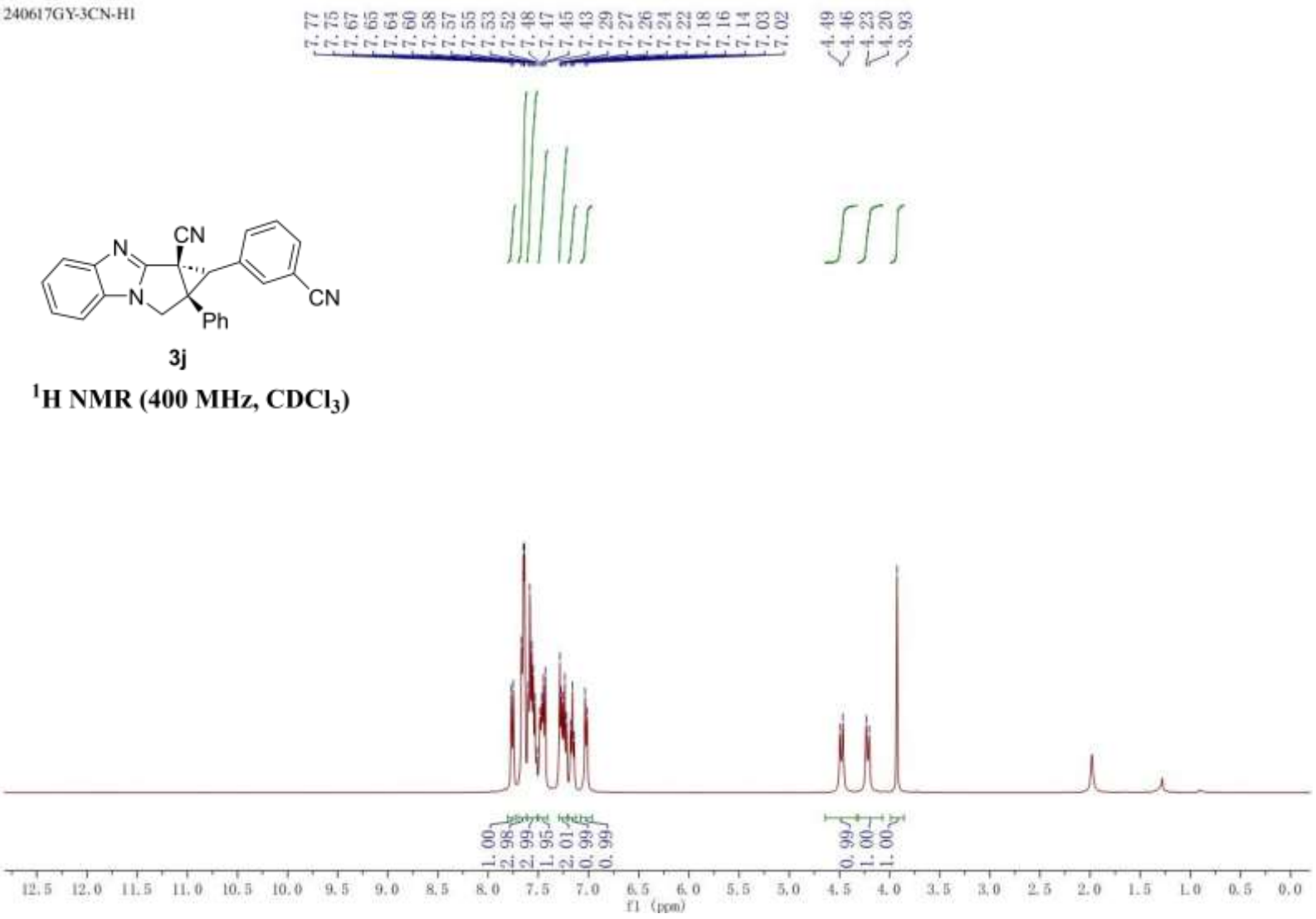


Figure 21. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3j**

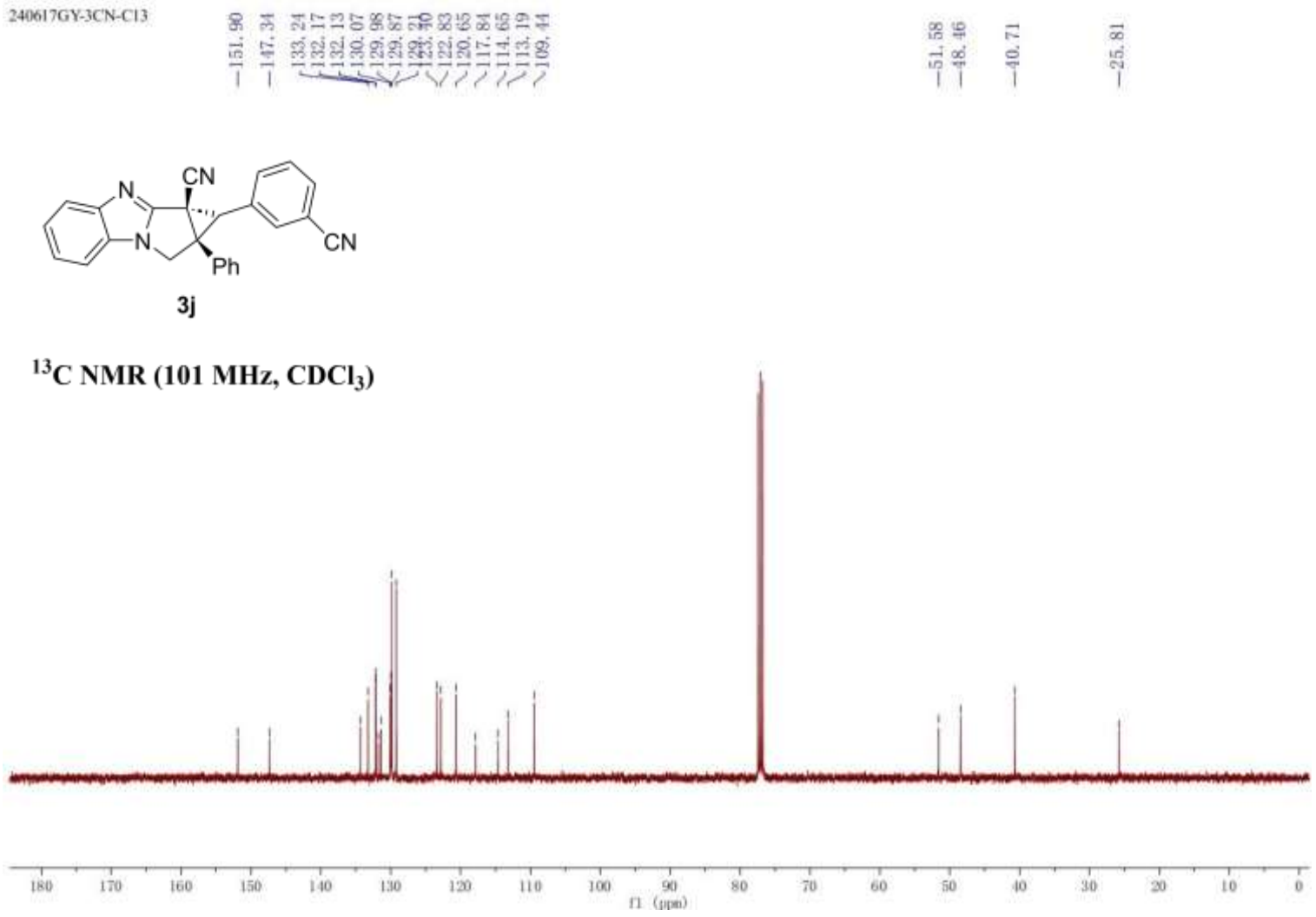


Figure 22. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **3j**

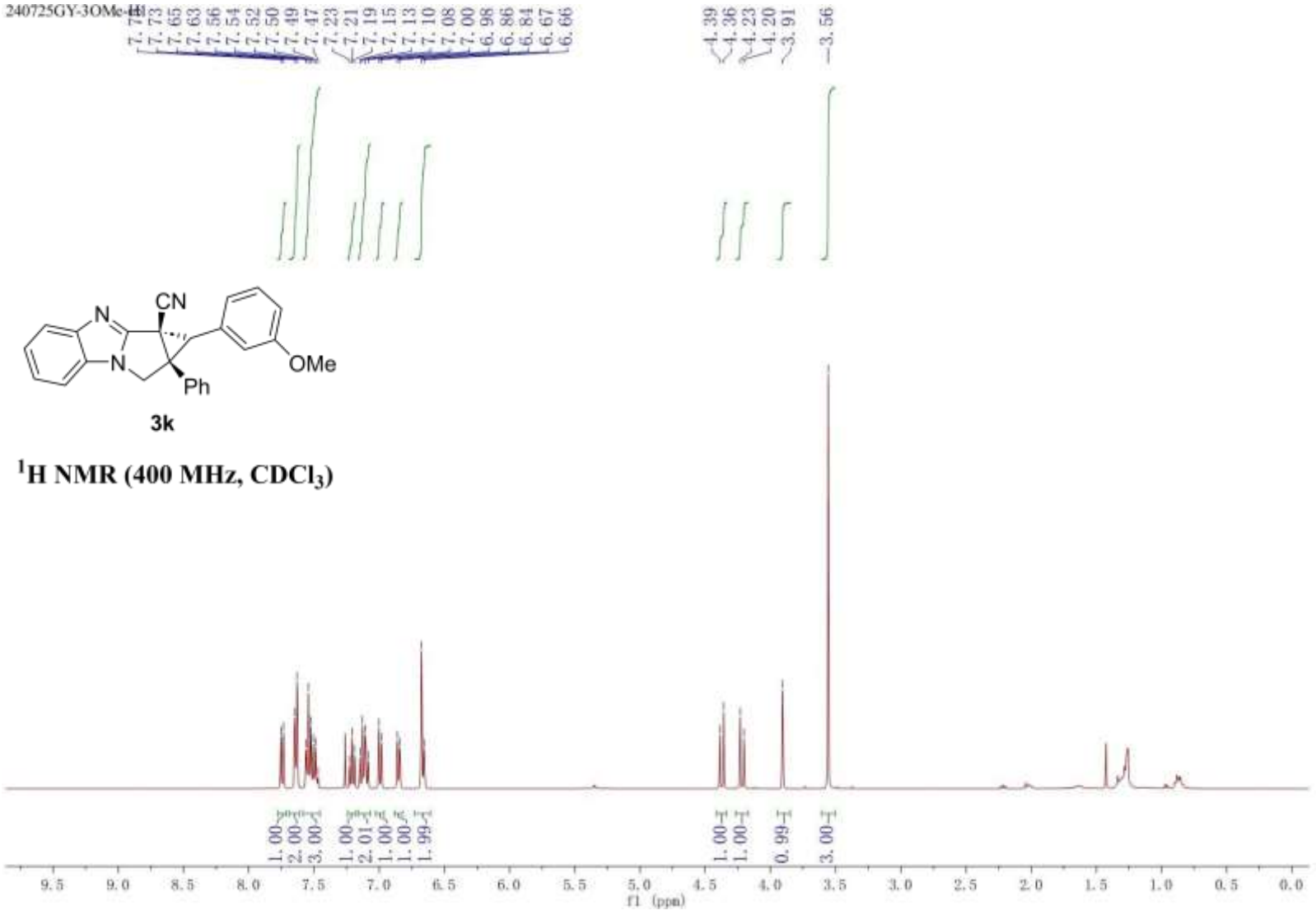


Figure 23. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3k**

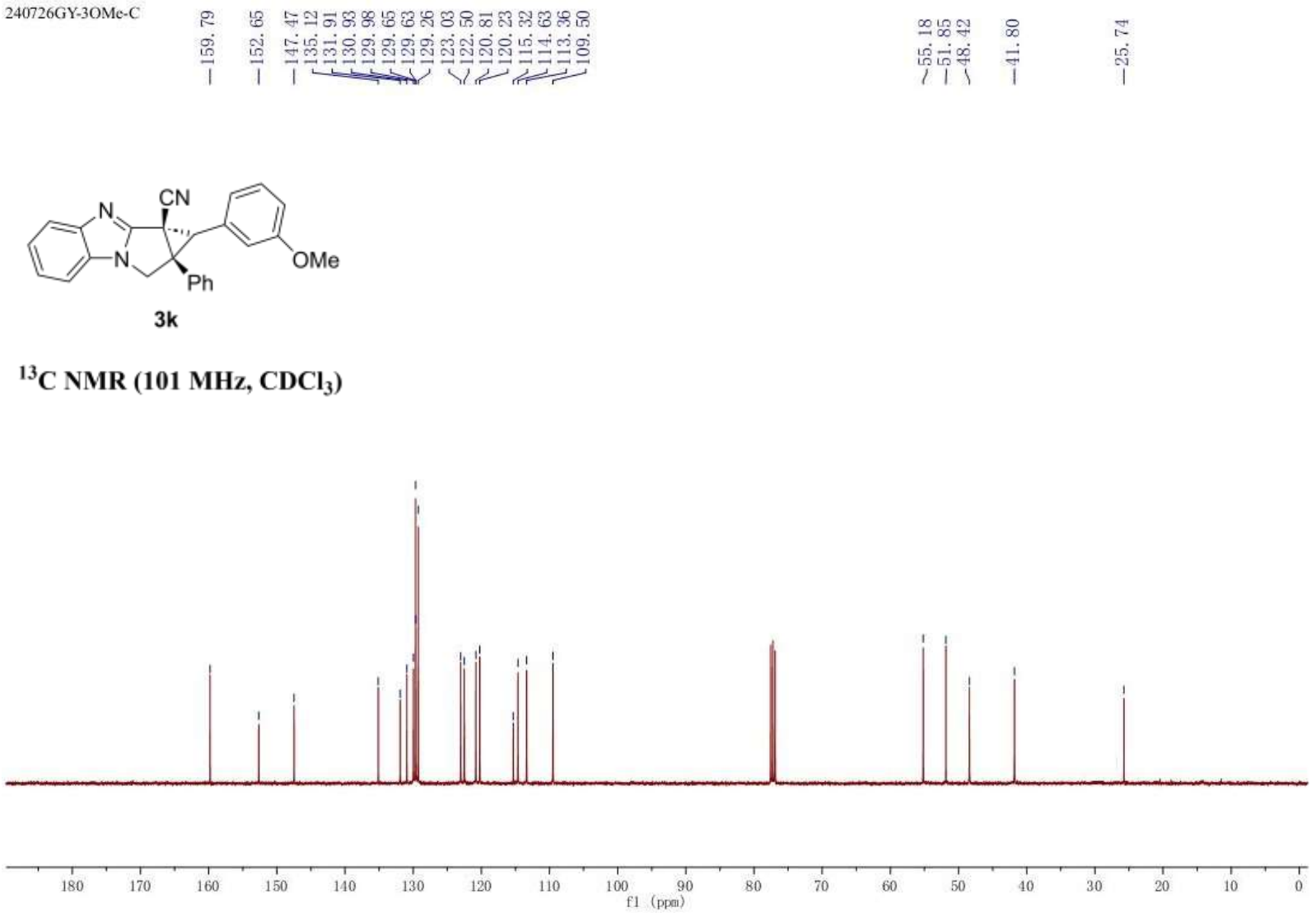


Figure 24. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **3k**

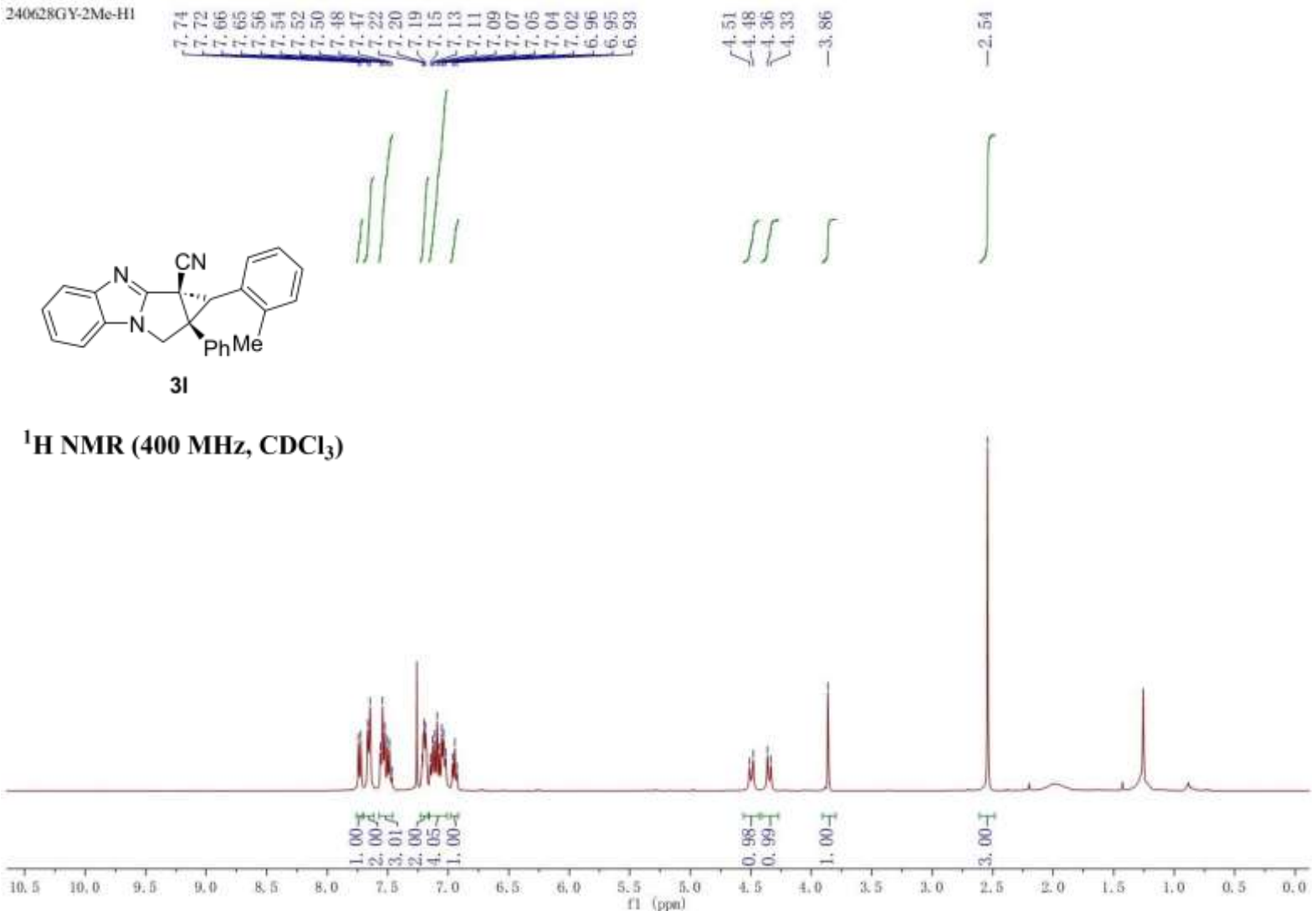


Figure 25. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3l**

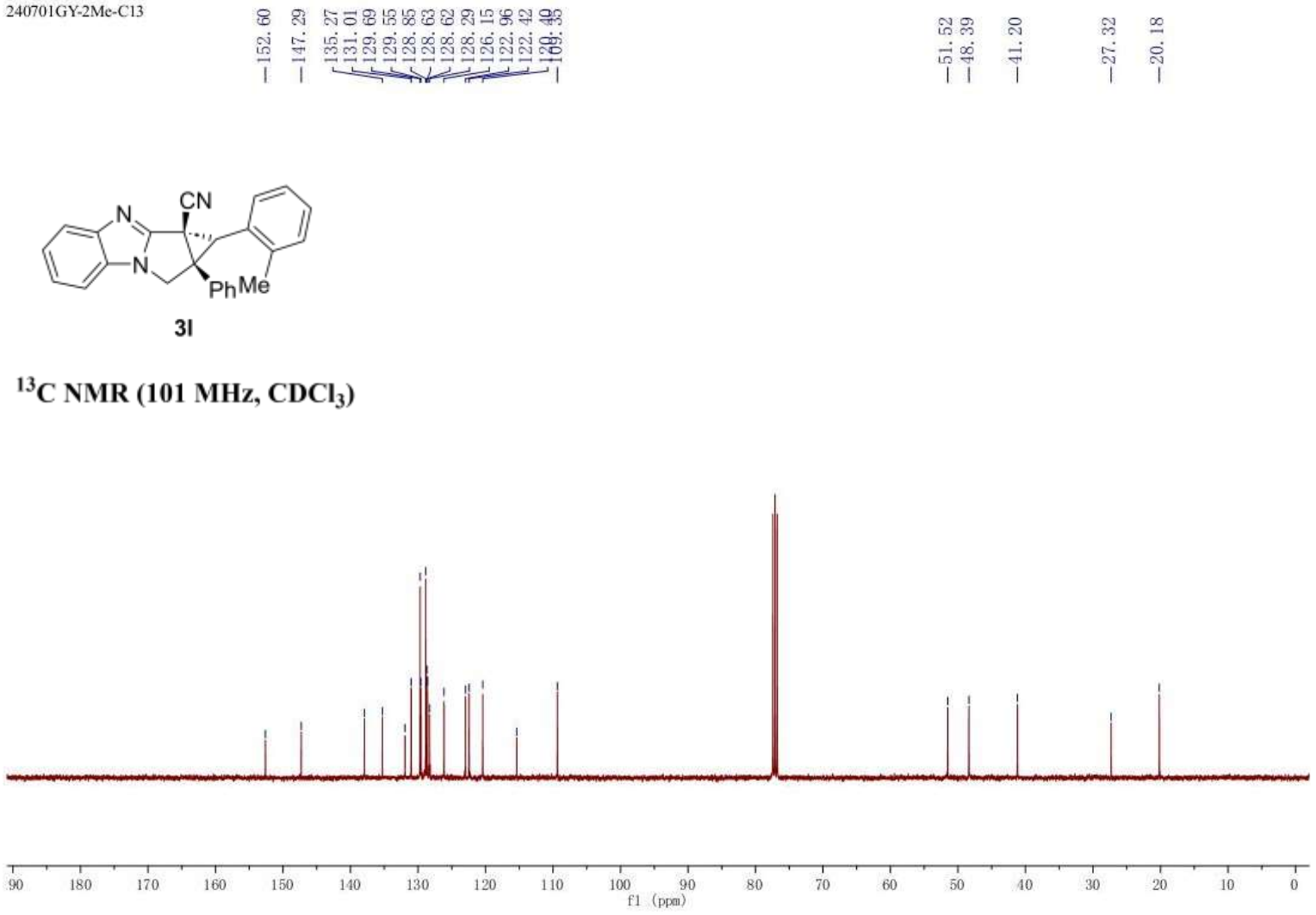


Figure 26. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **3l**

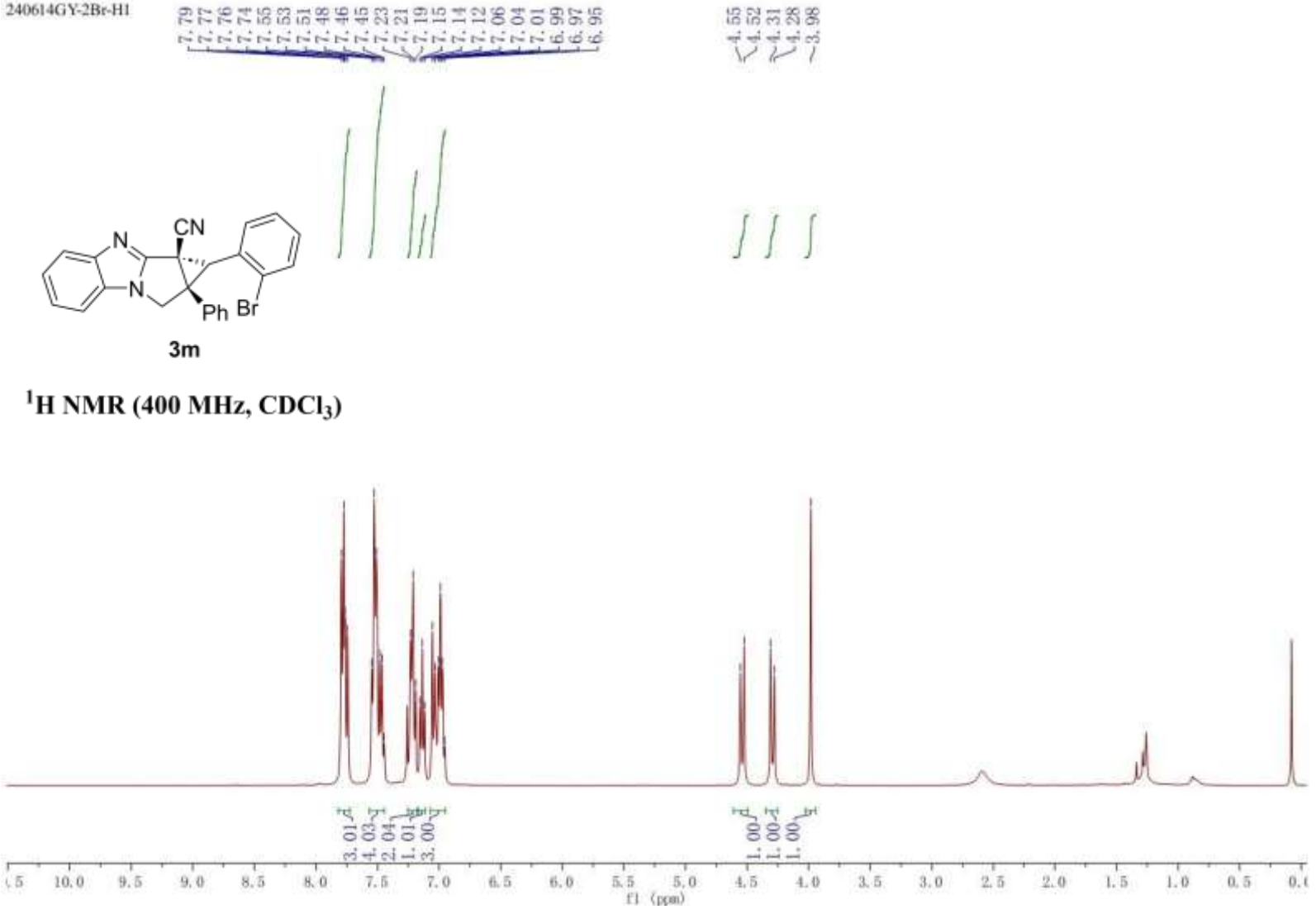


Figure 27. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3m**

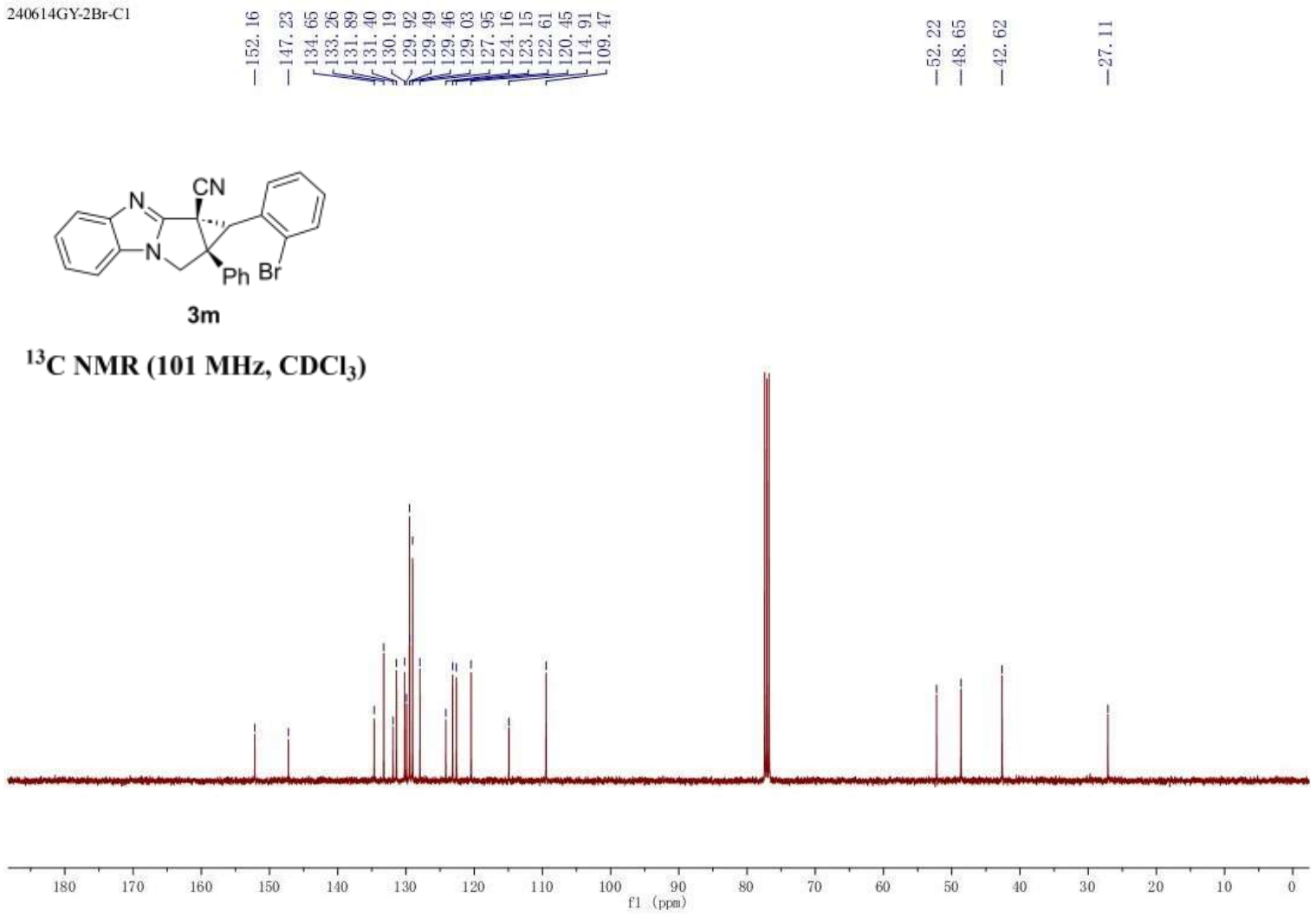


Figure 28. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **3m**

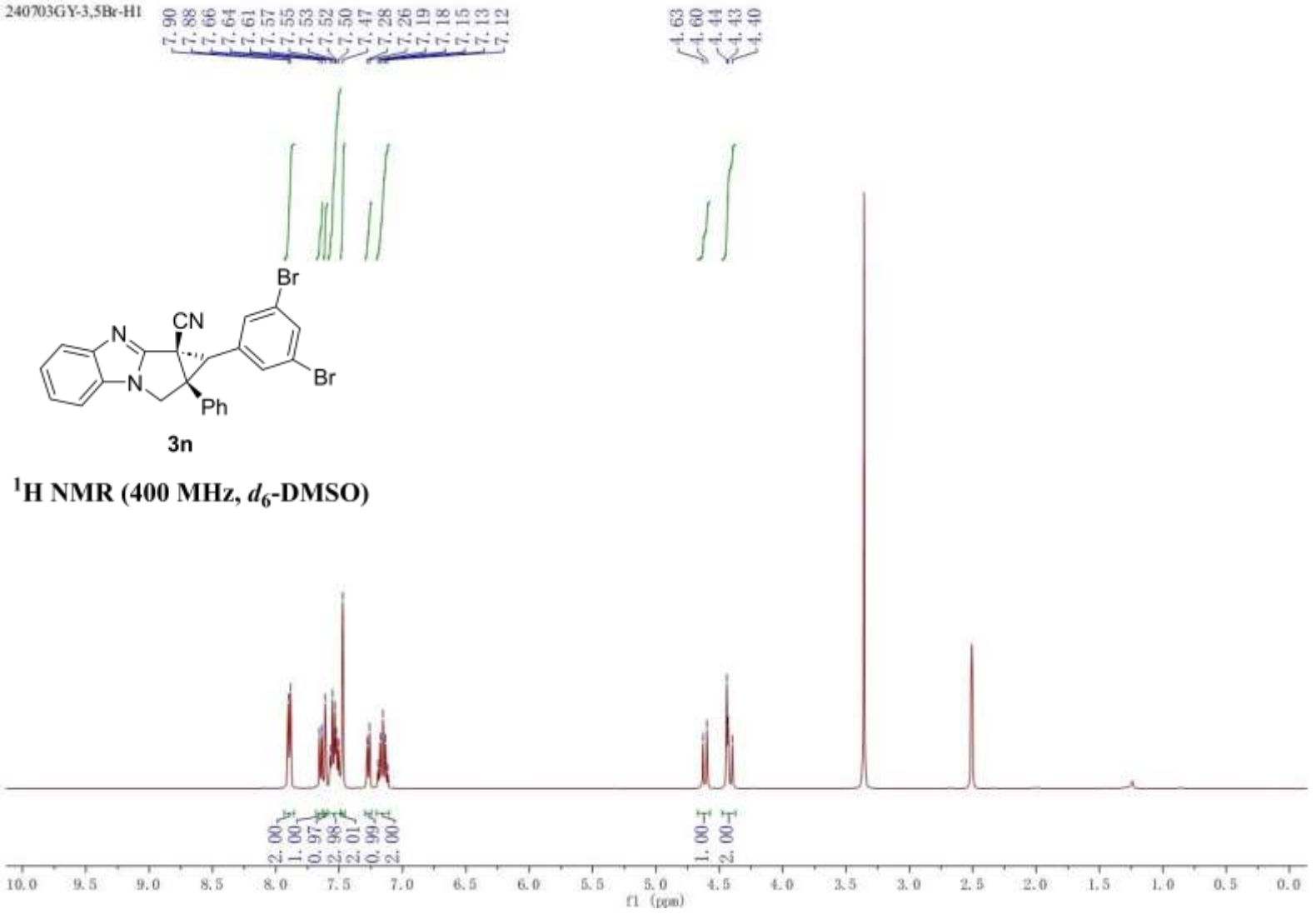


Figure 29. [1]H NMR (400 MHz, d_6-DMSO) spectra of compound **3n**

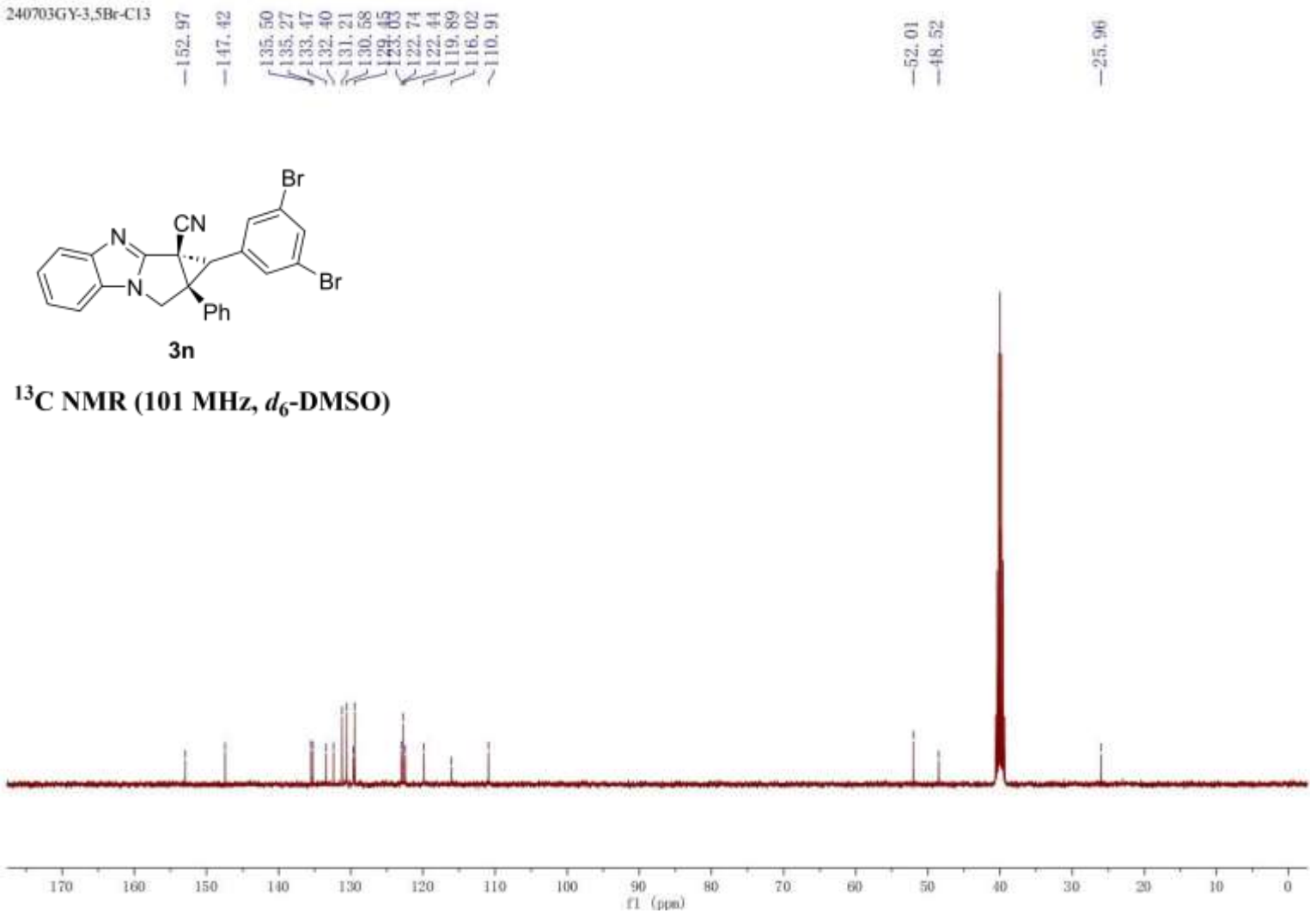


Figure 30. ^{13}C NMR (101 MHz, d_6-DMSO) spectra of compound **3n**

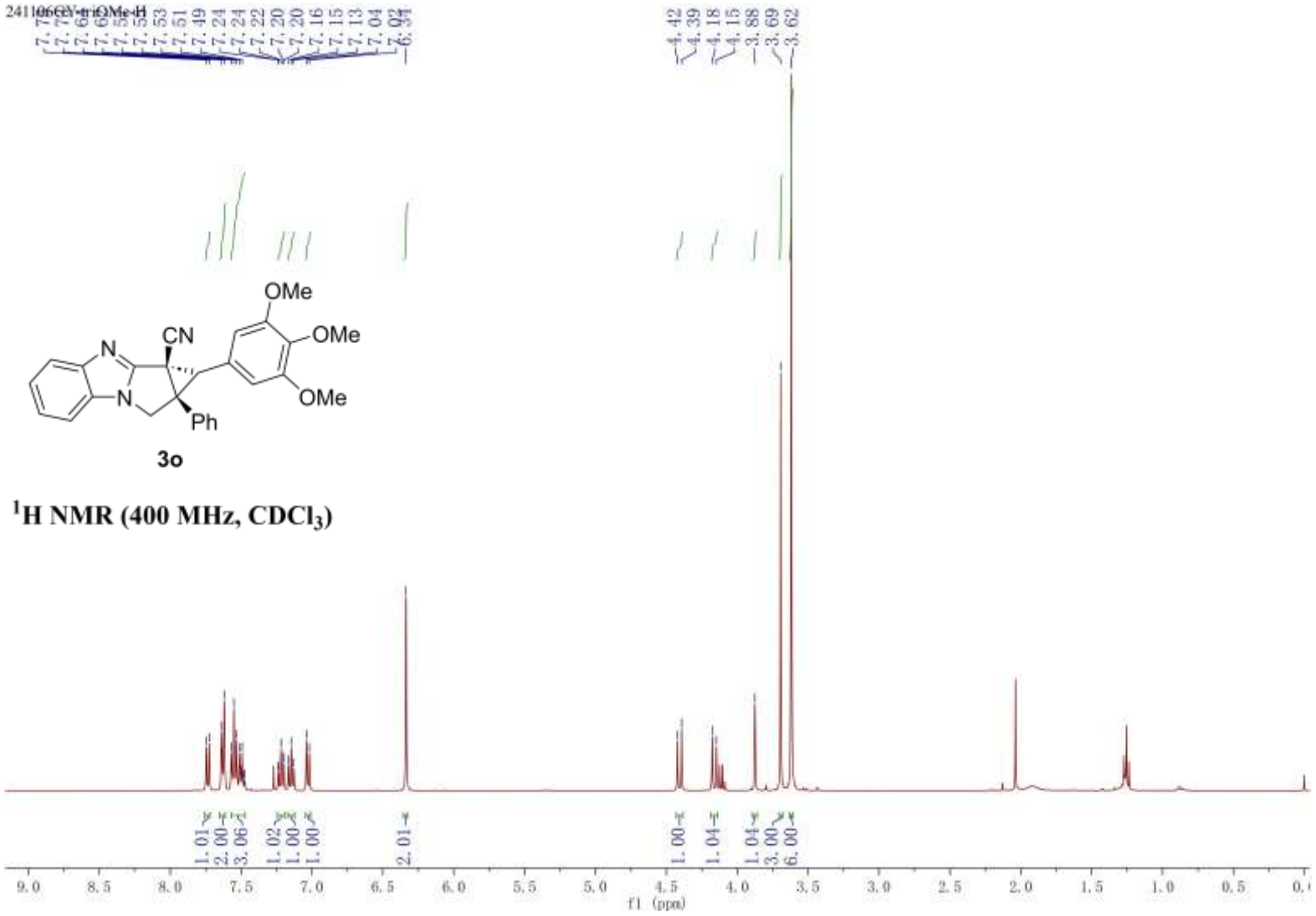


Figure 31. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3o**

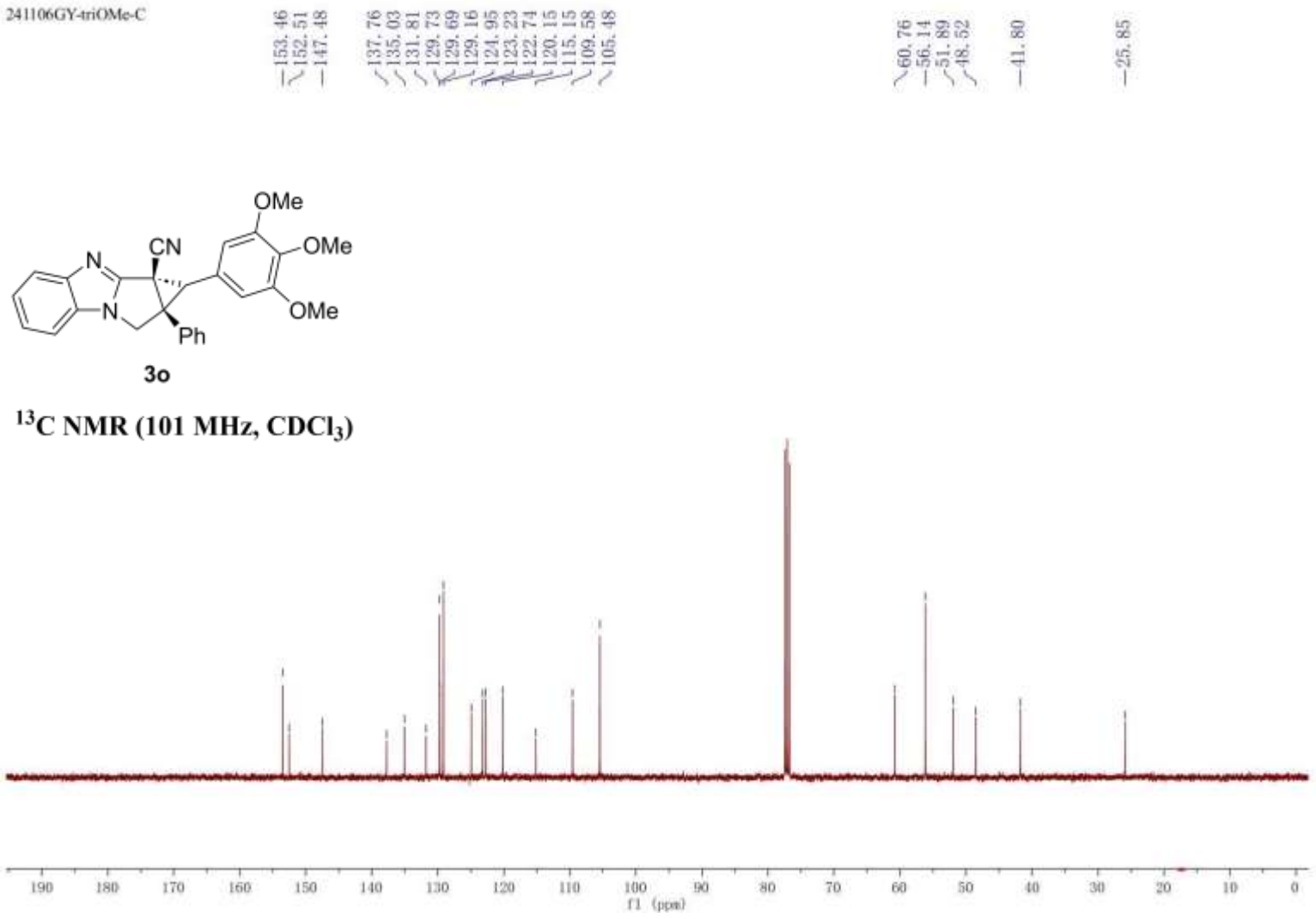
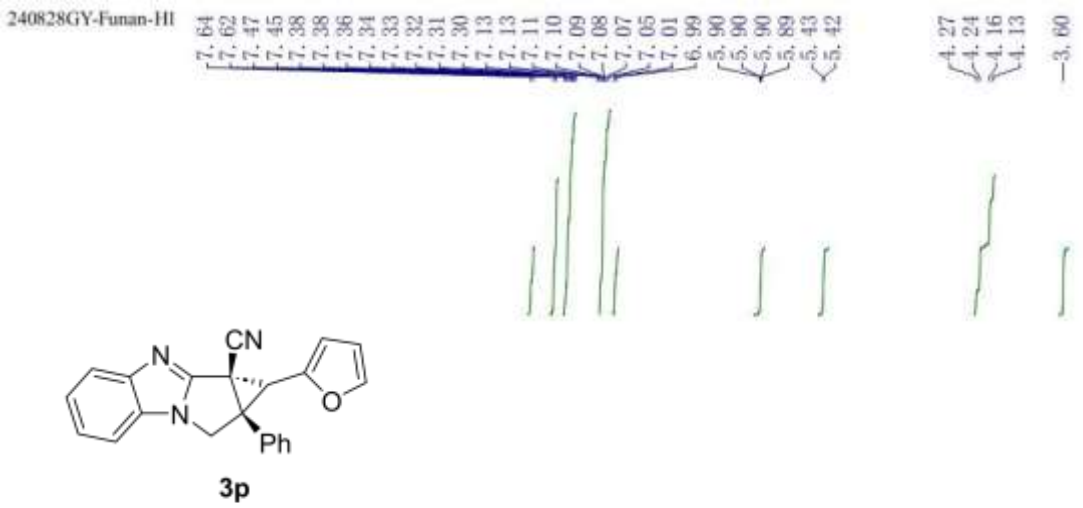


Figure 32. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **3o**



3p

^{1}H NMR (400 MHz, $CDCl_3$)

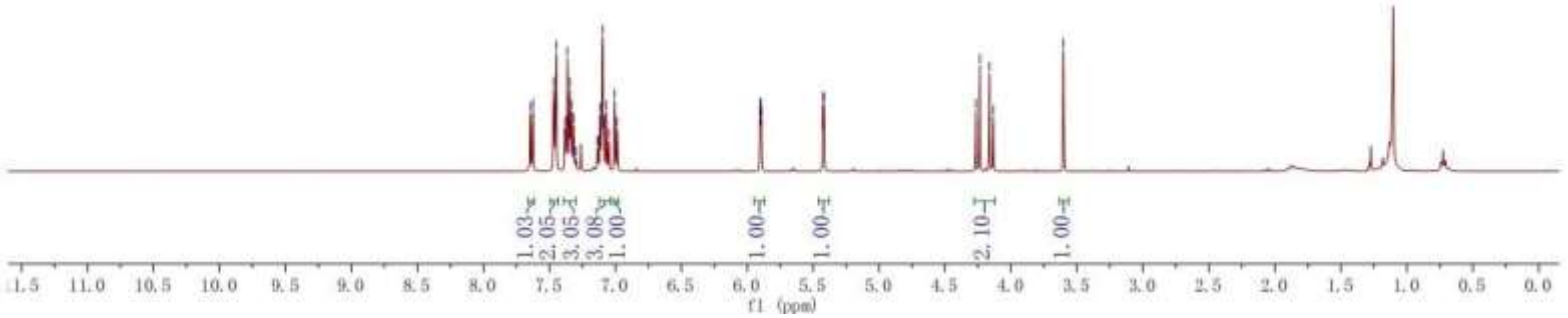


Figure 33. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3p**

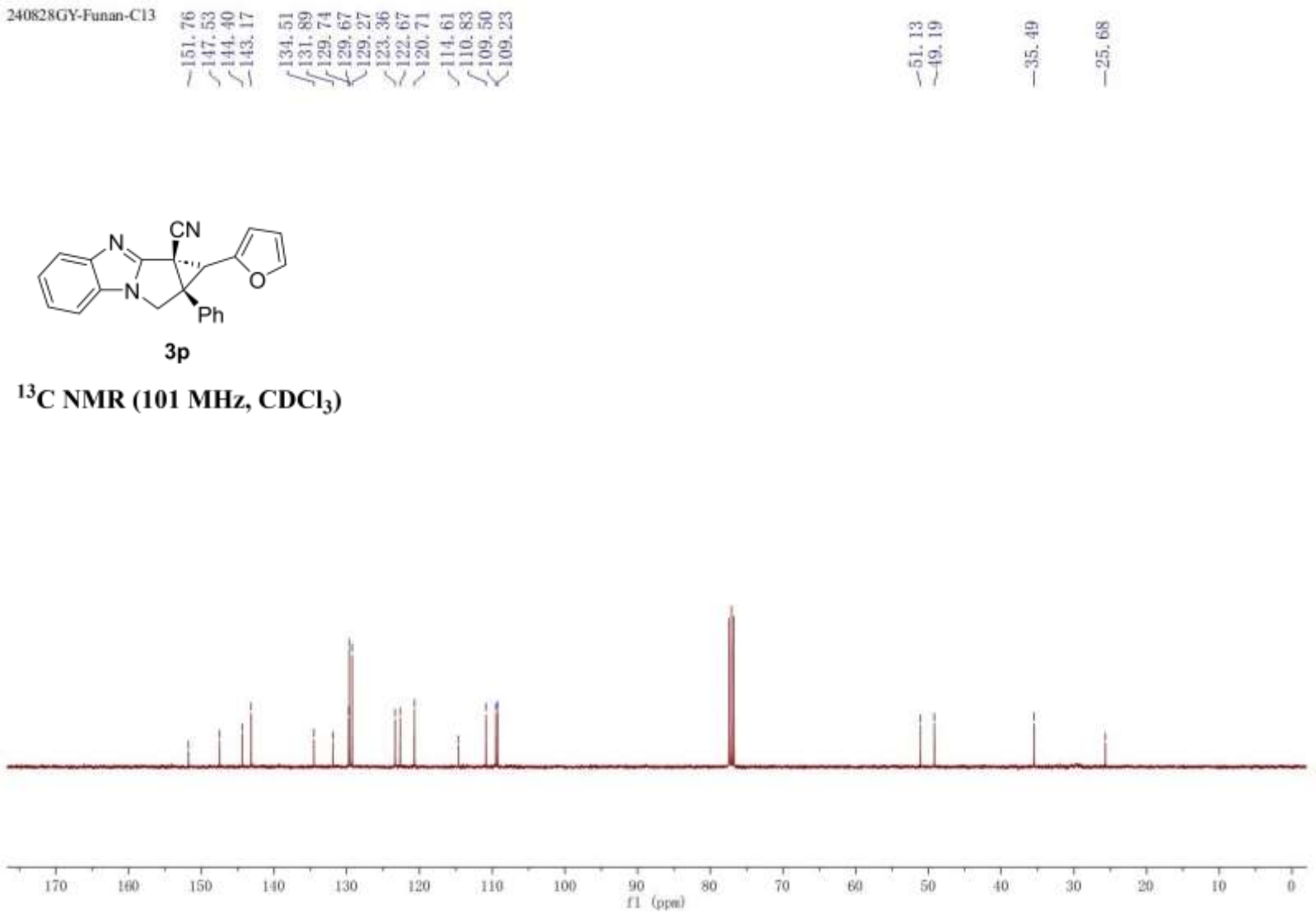


Figure 34. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **3p**

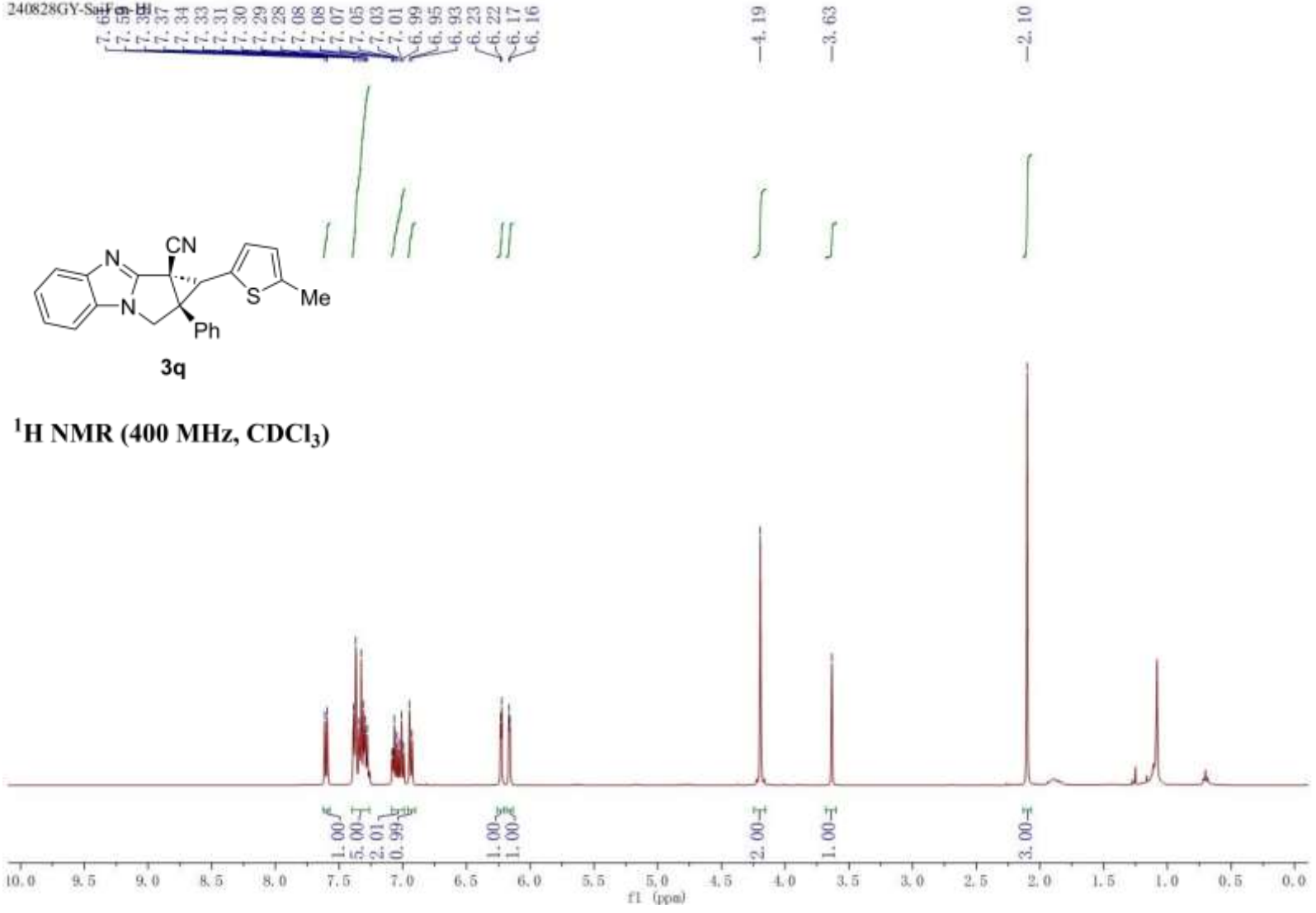


Figure 35. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3q**

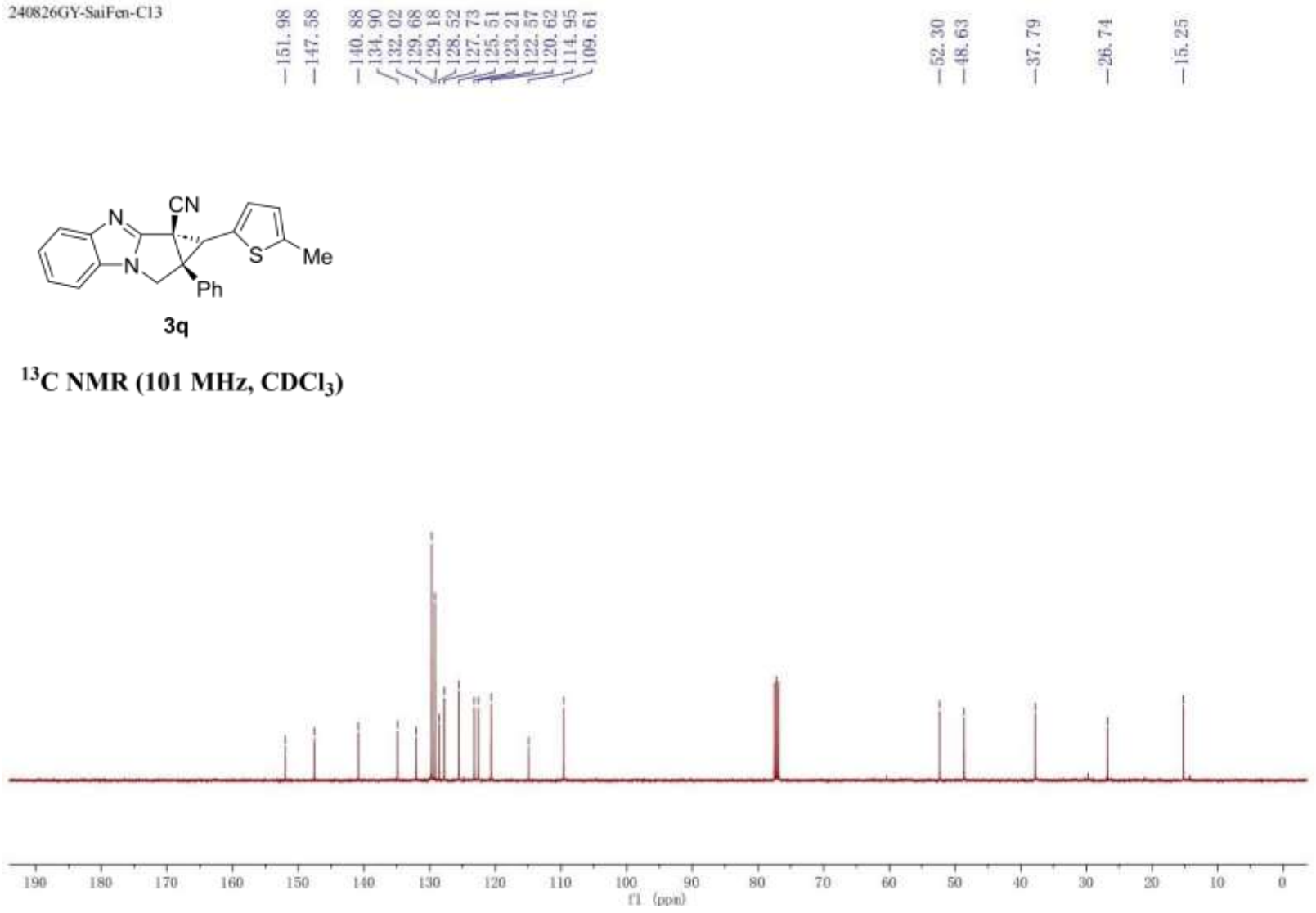


Figure 36. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **3q**

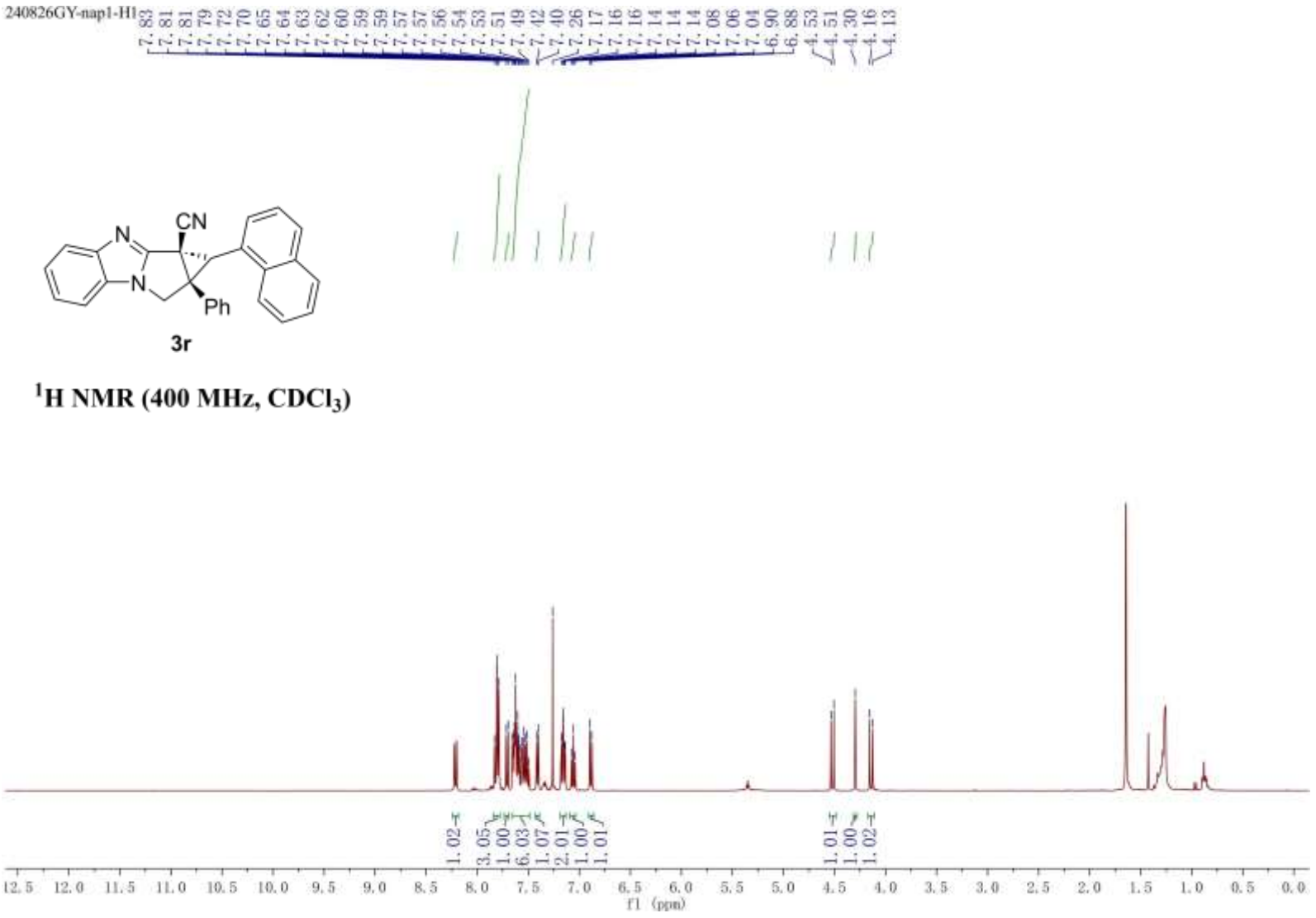


Figure 37. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3r**

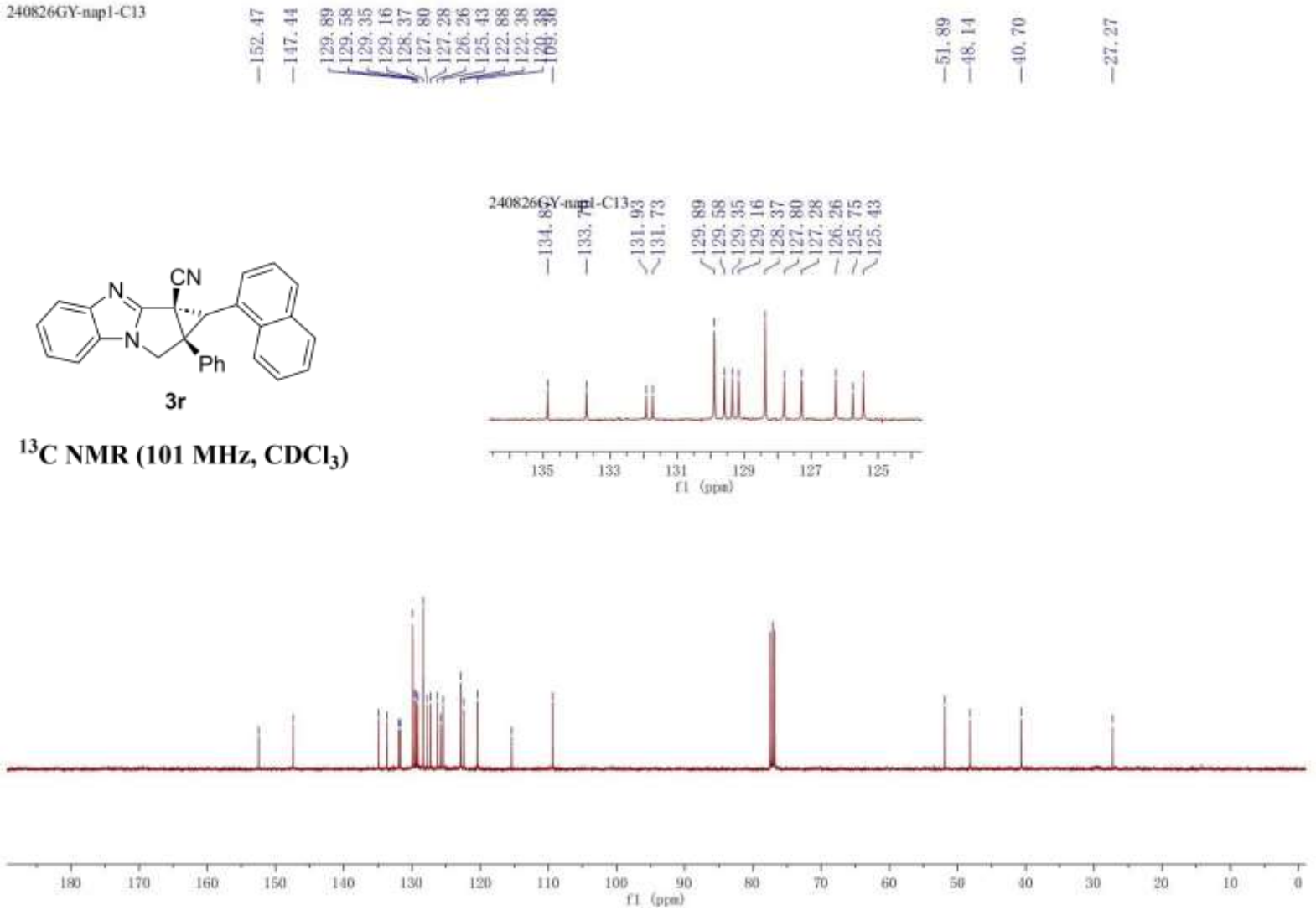


Figure 38. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **3r**

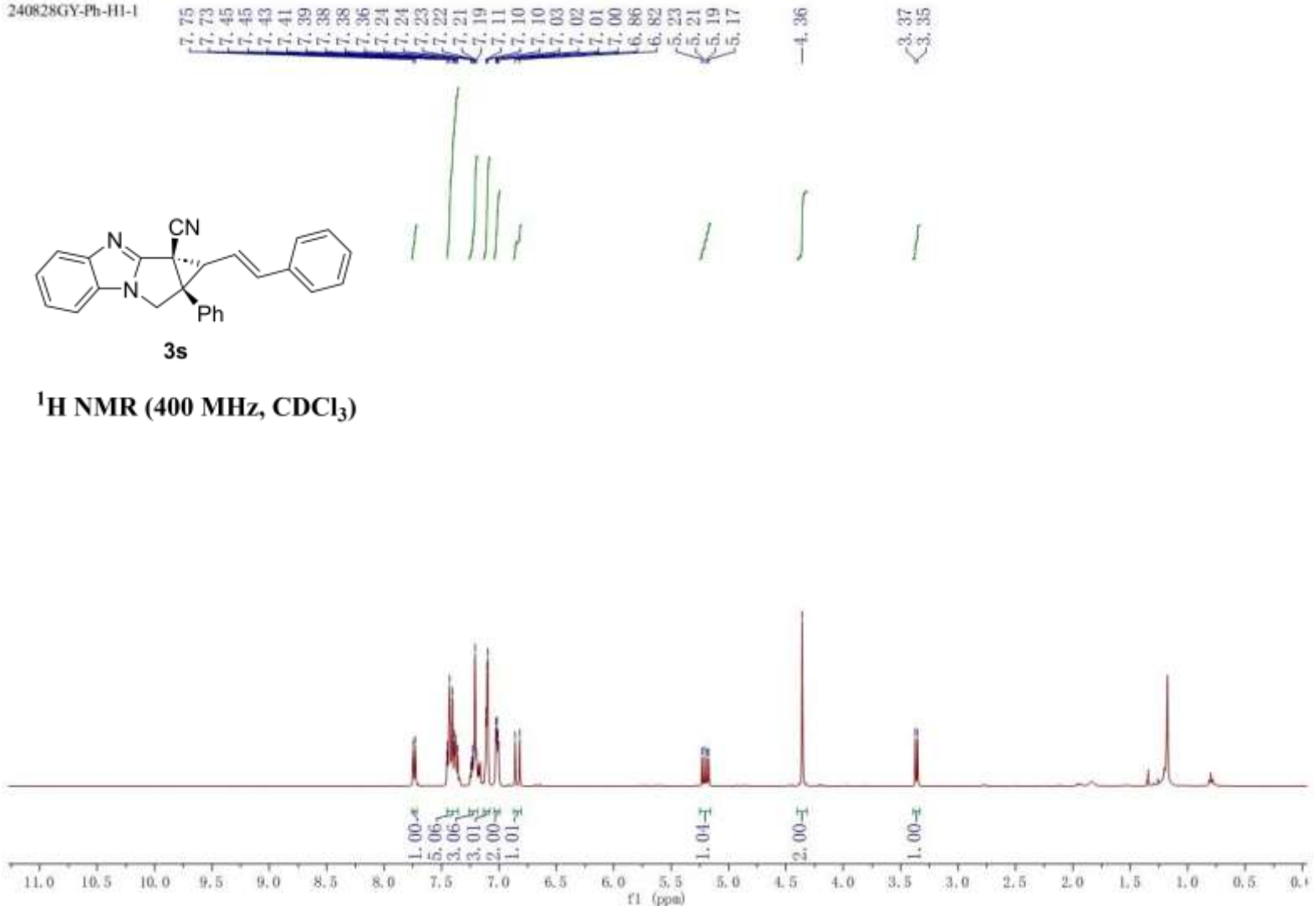


Figure 39. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3s**

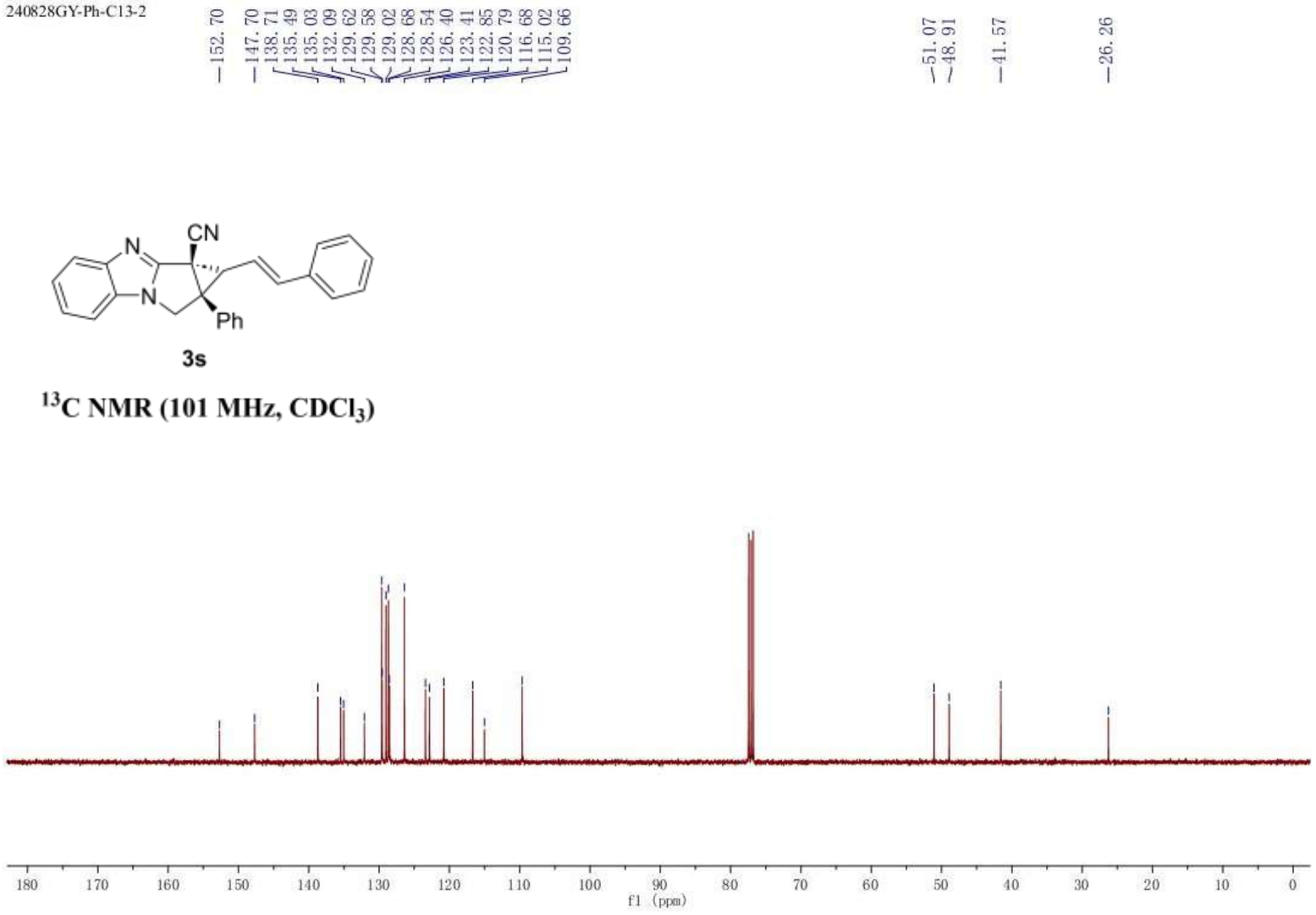


Figure 40. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **3s**

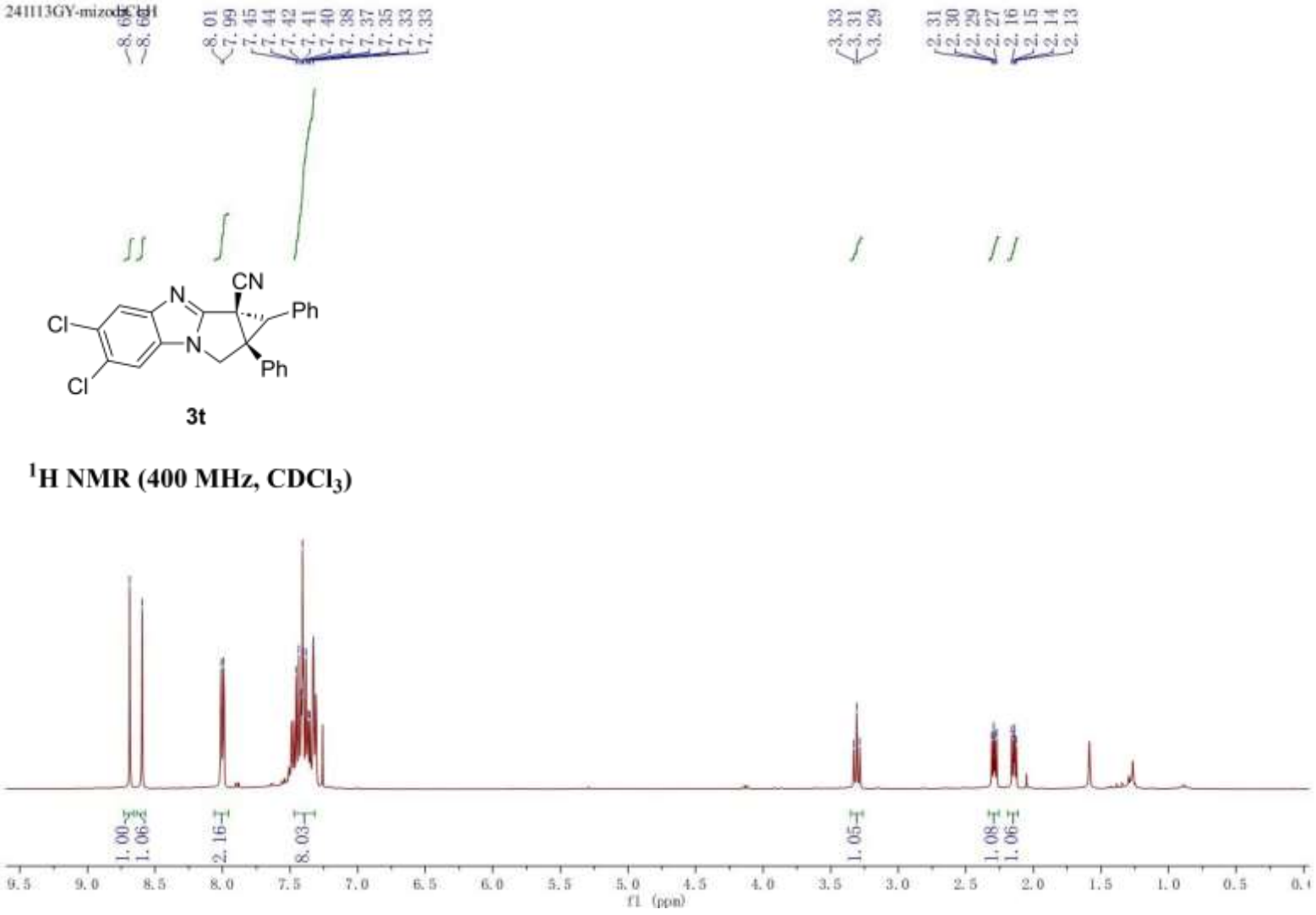


Figure 41. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3t**

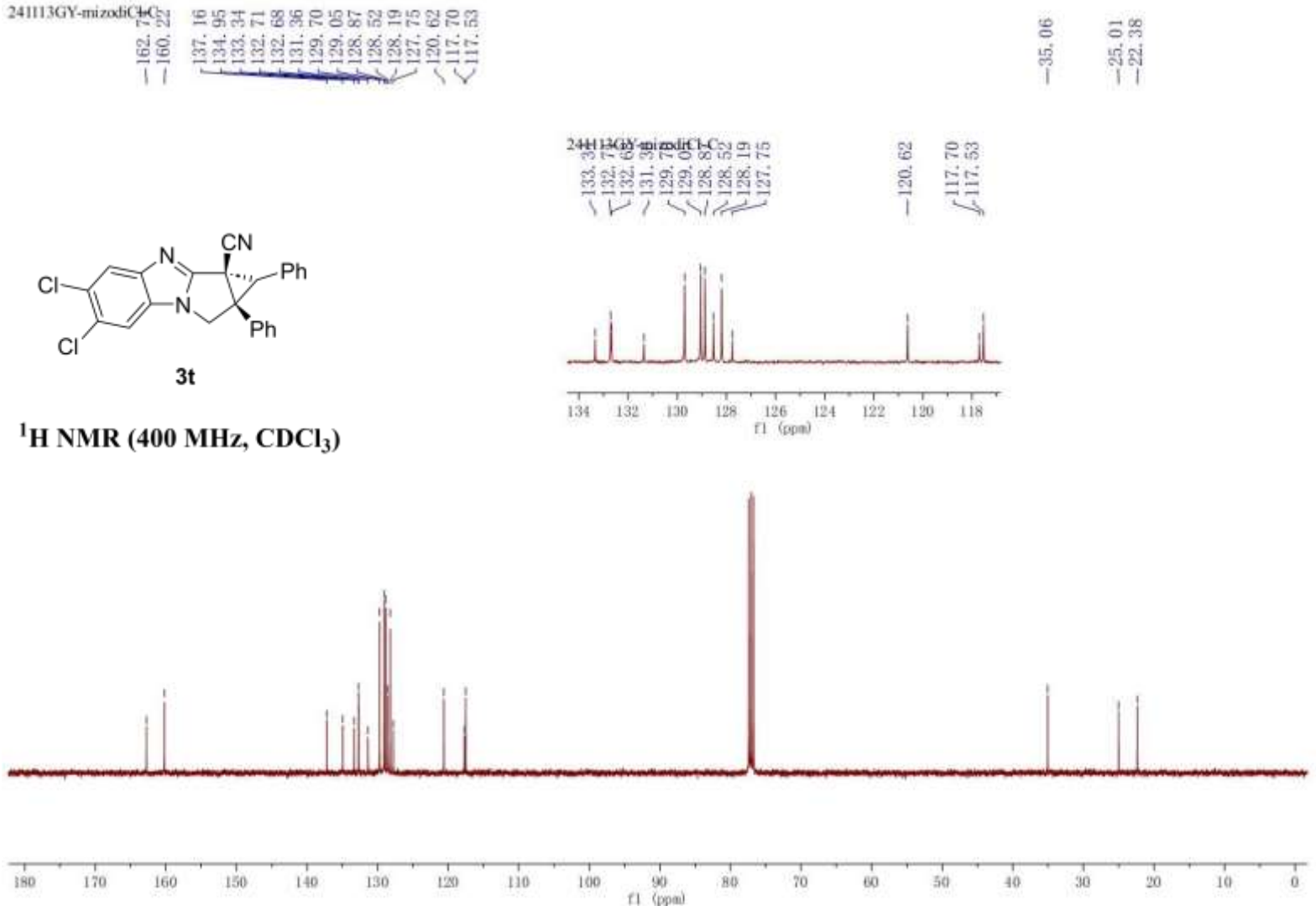


Figure 42. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **3t**

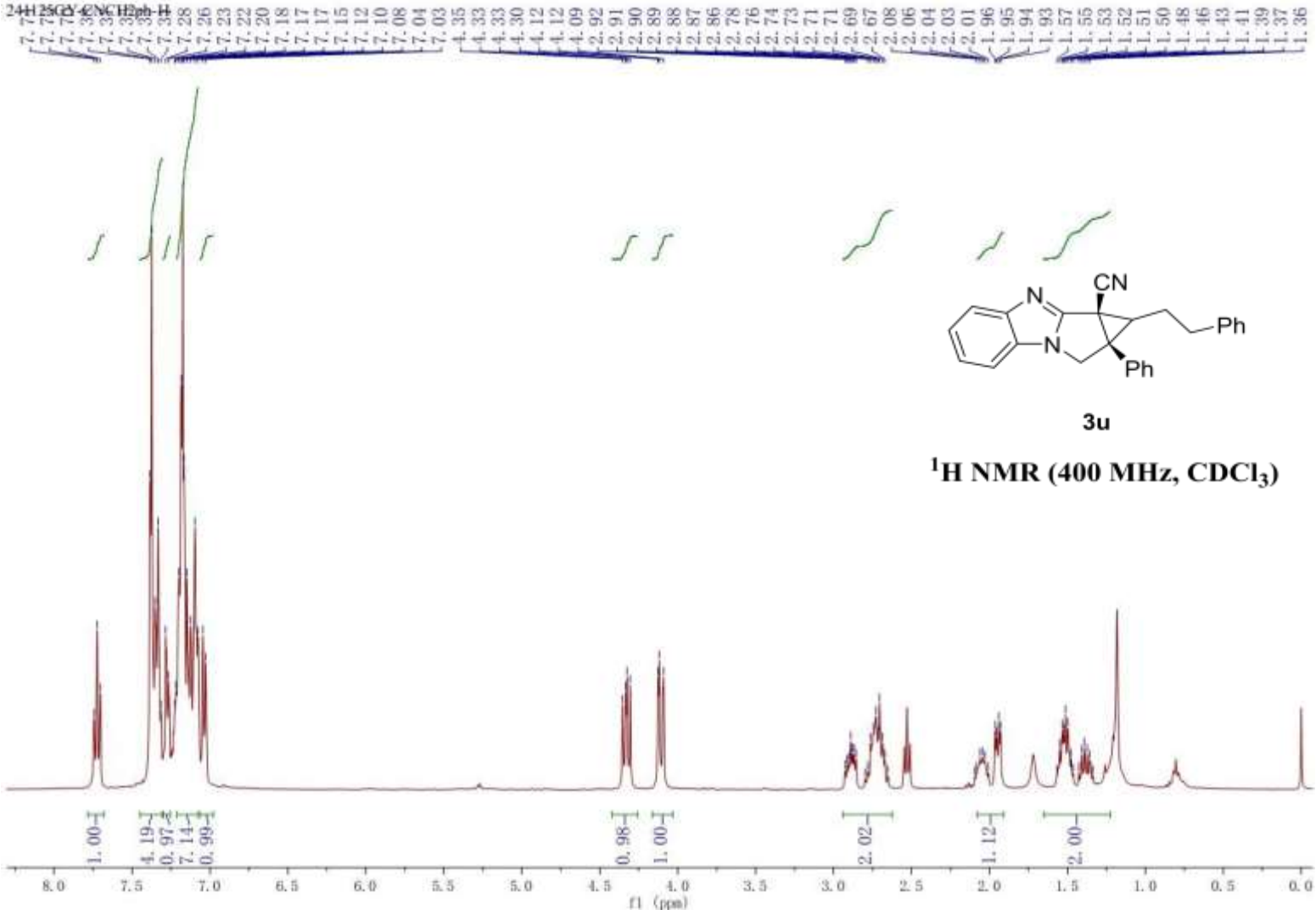


Figure 43. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3u**

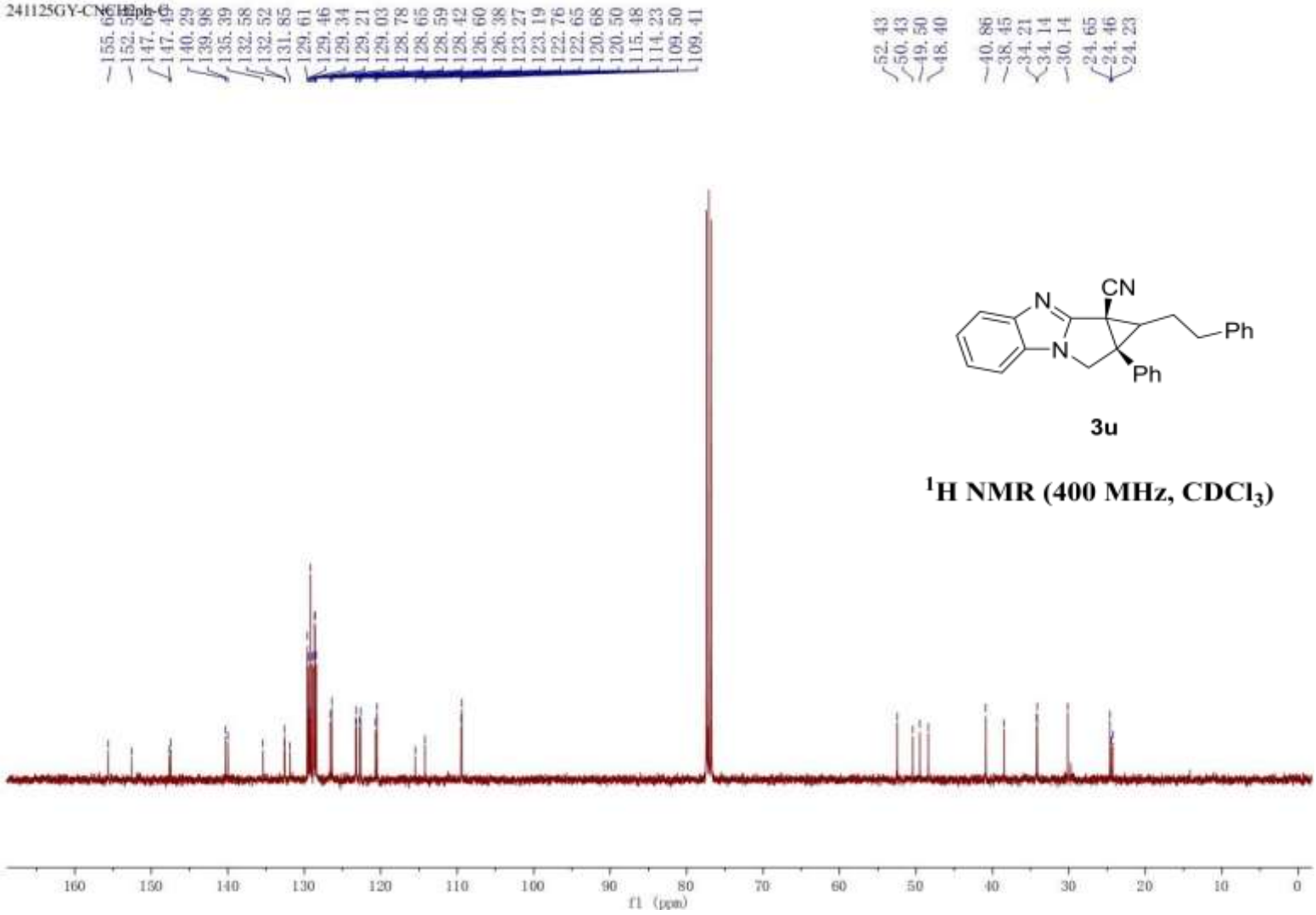


Figure 44. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **3u**

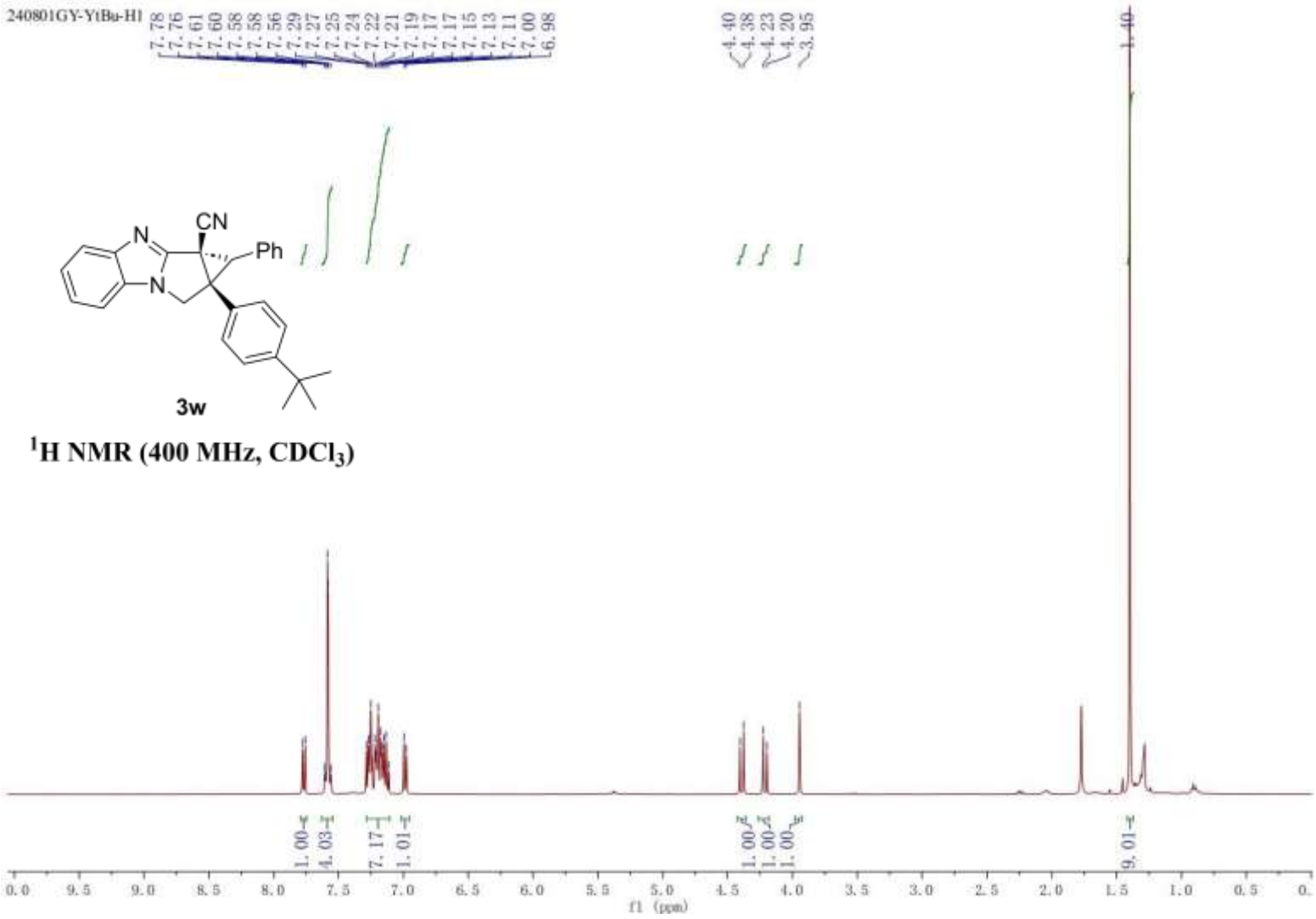


Figure 45. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3w**

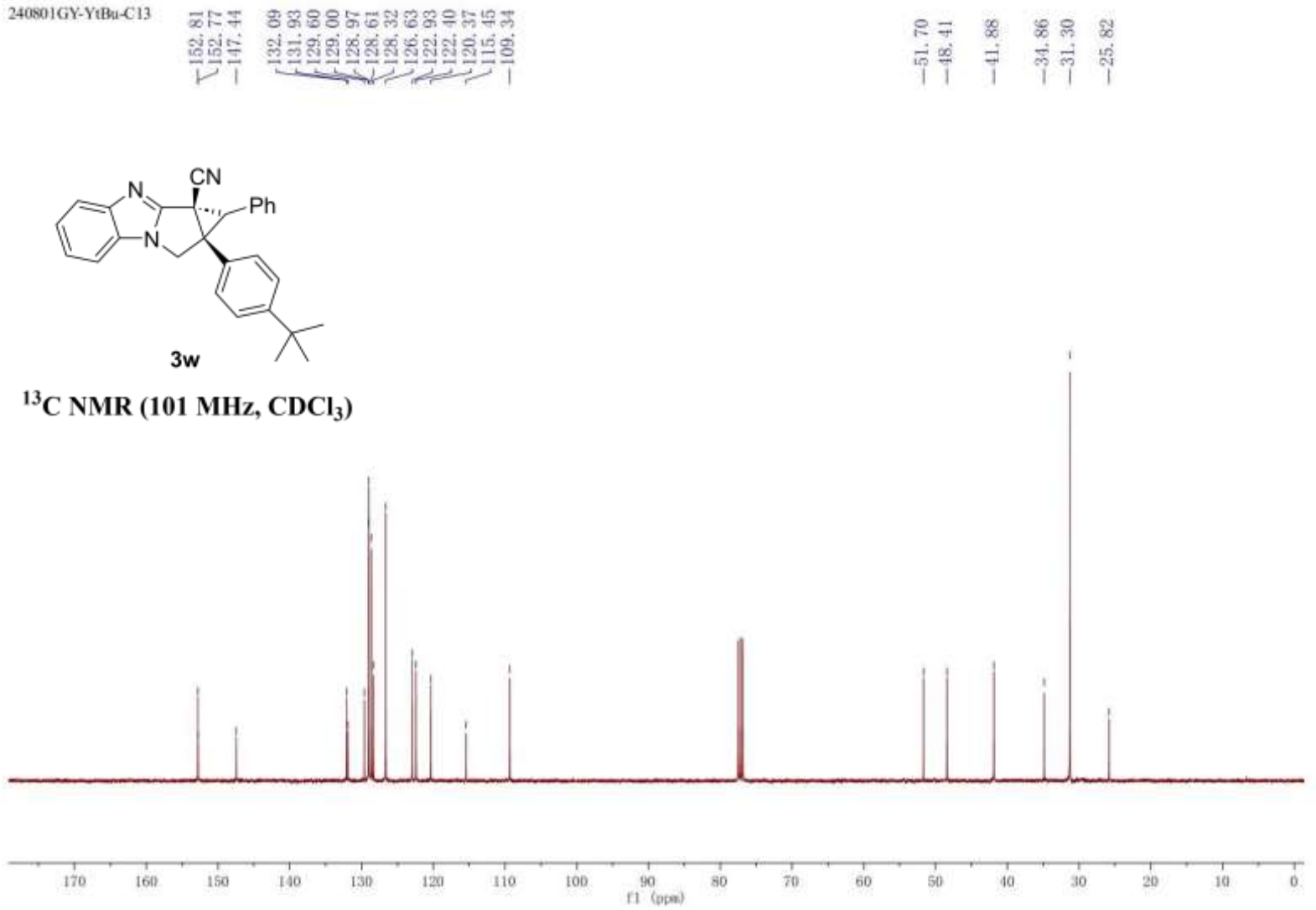


Figure 46. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **3w**

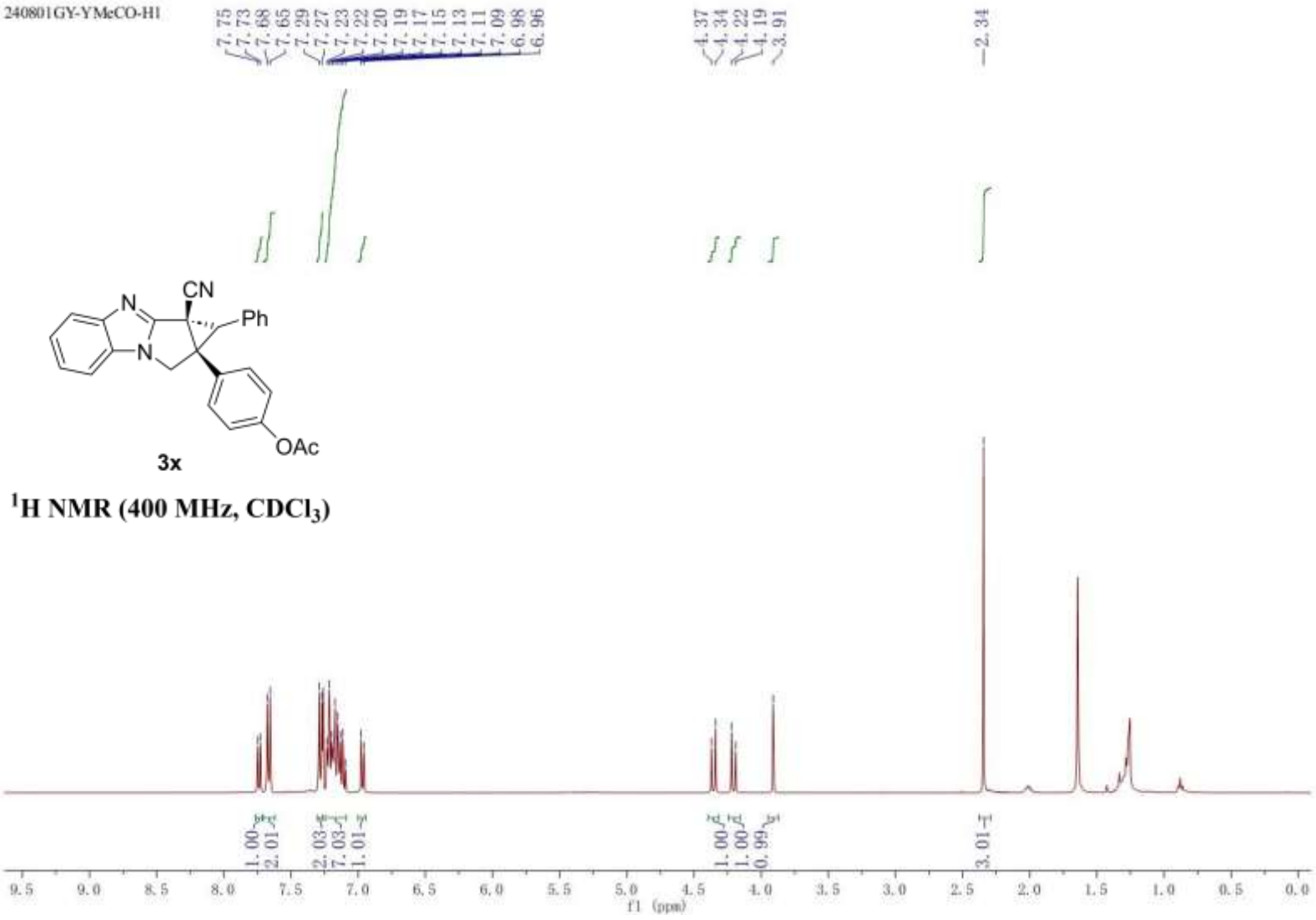


Figure 47. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3x**

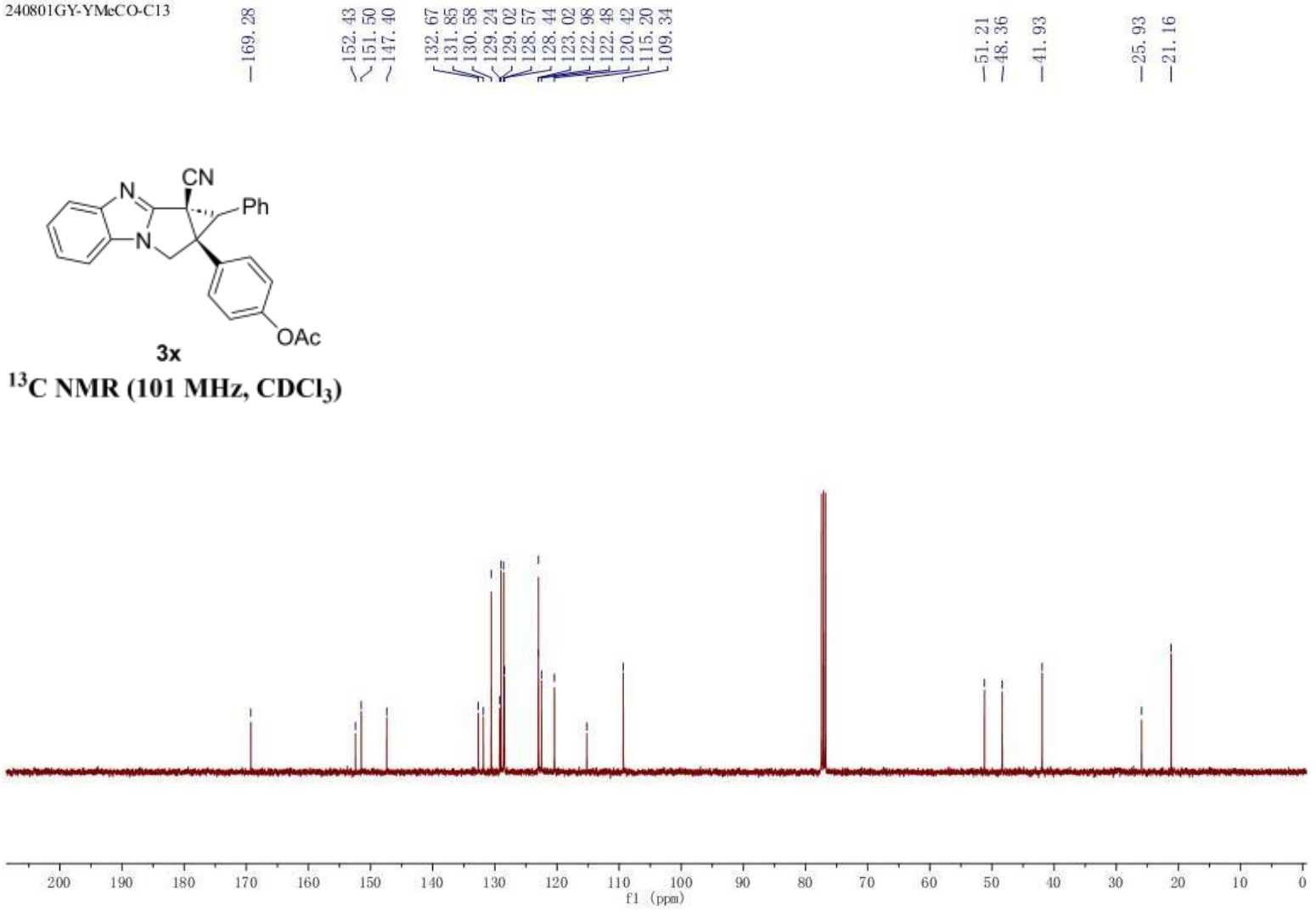


Figure 48. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **3x**

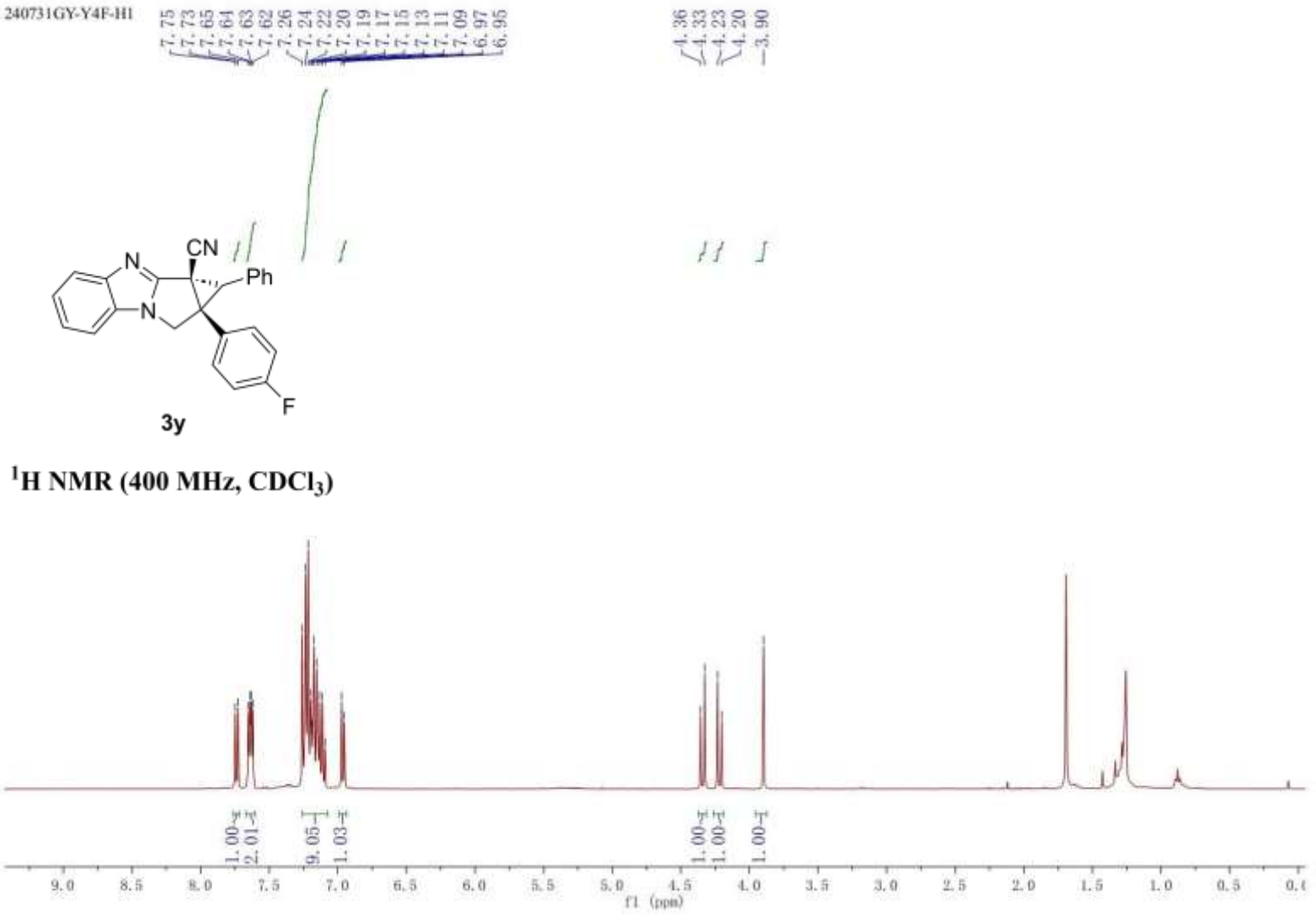


Figure 49. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3y**

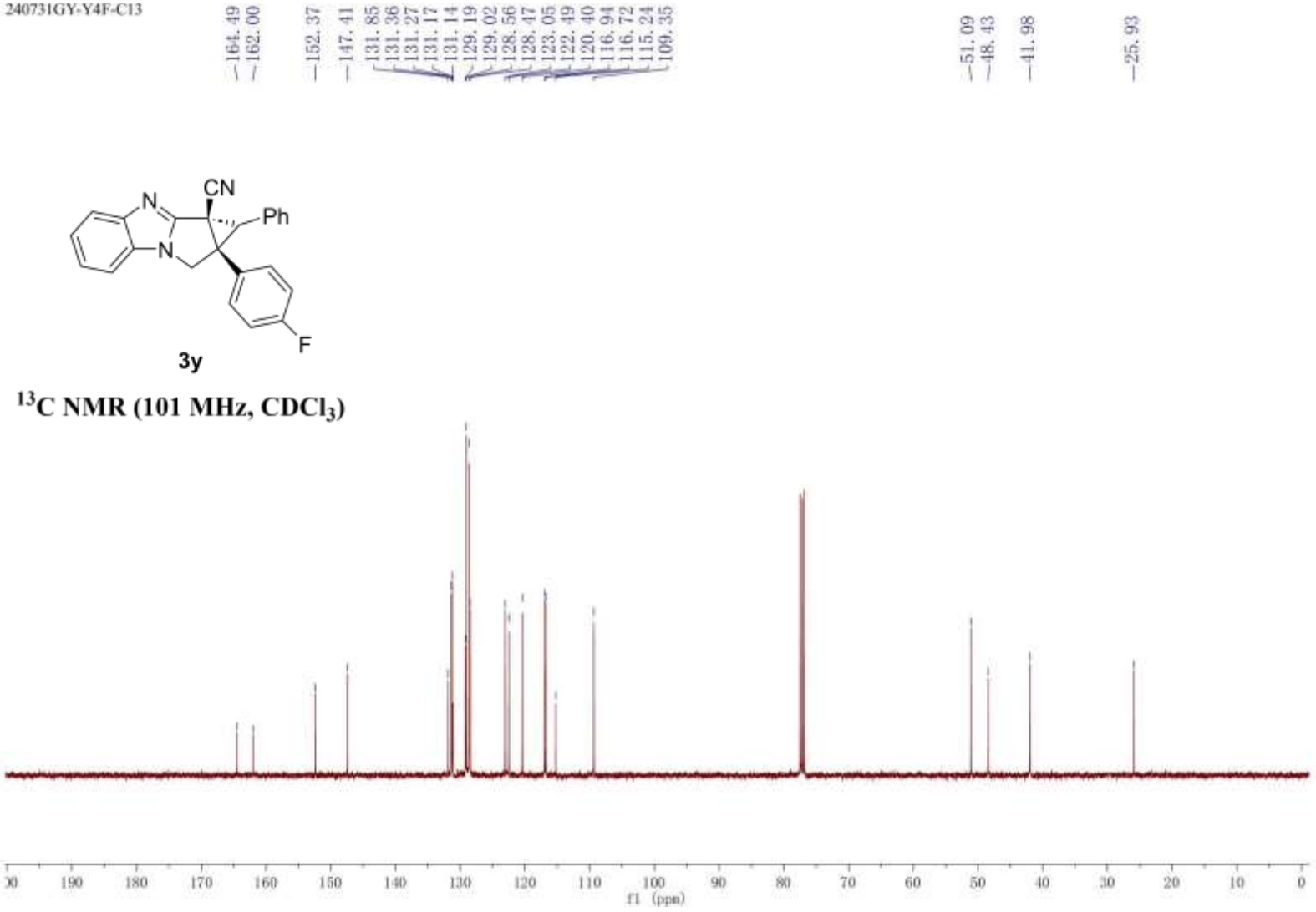


Figure 50. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **3y**

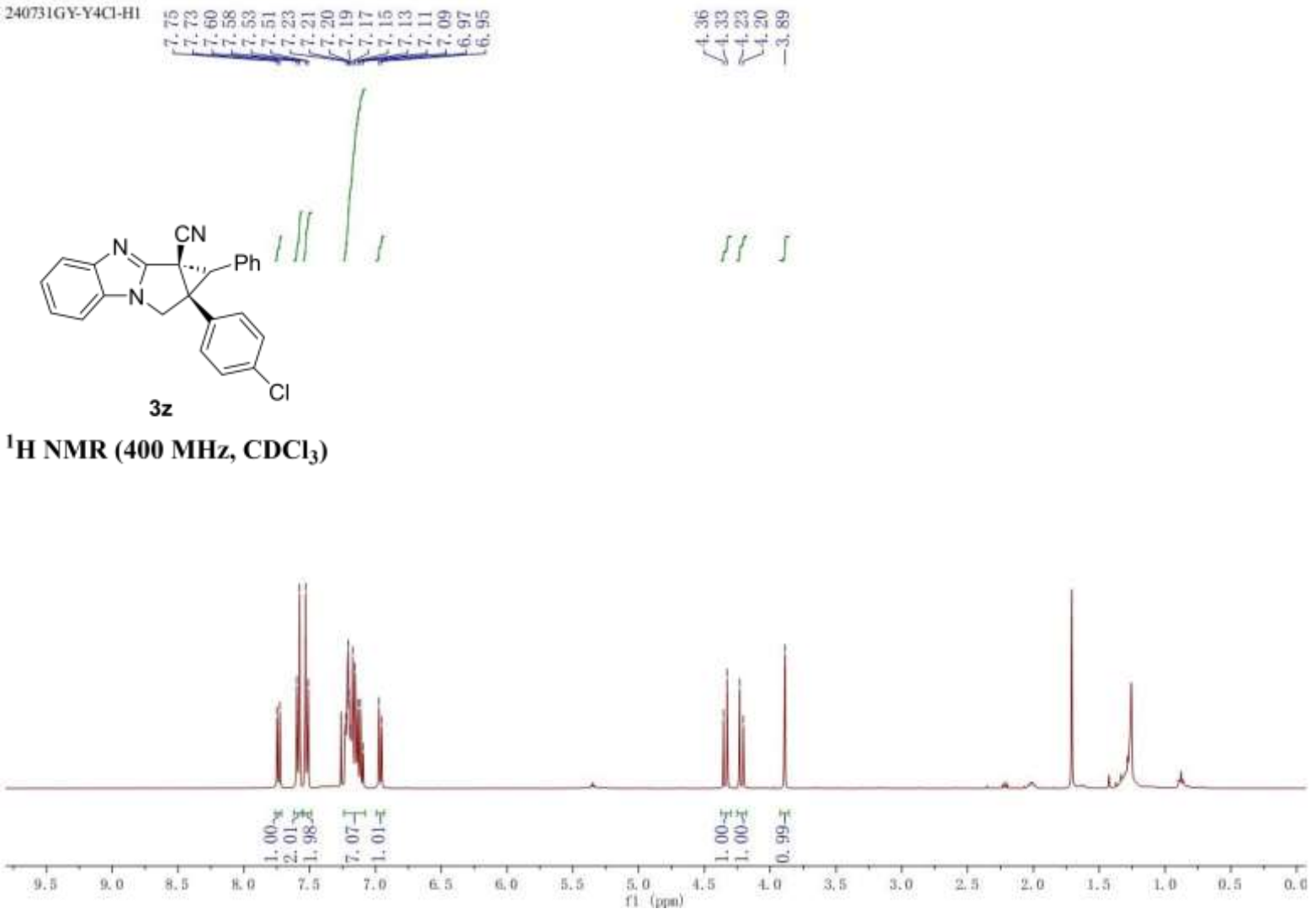


Figure 51. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3z**

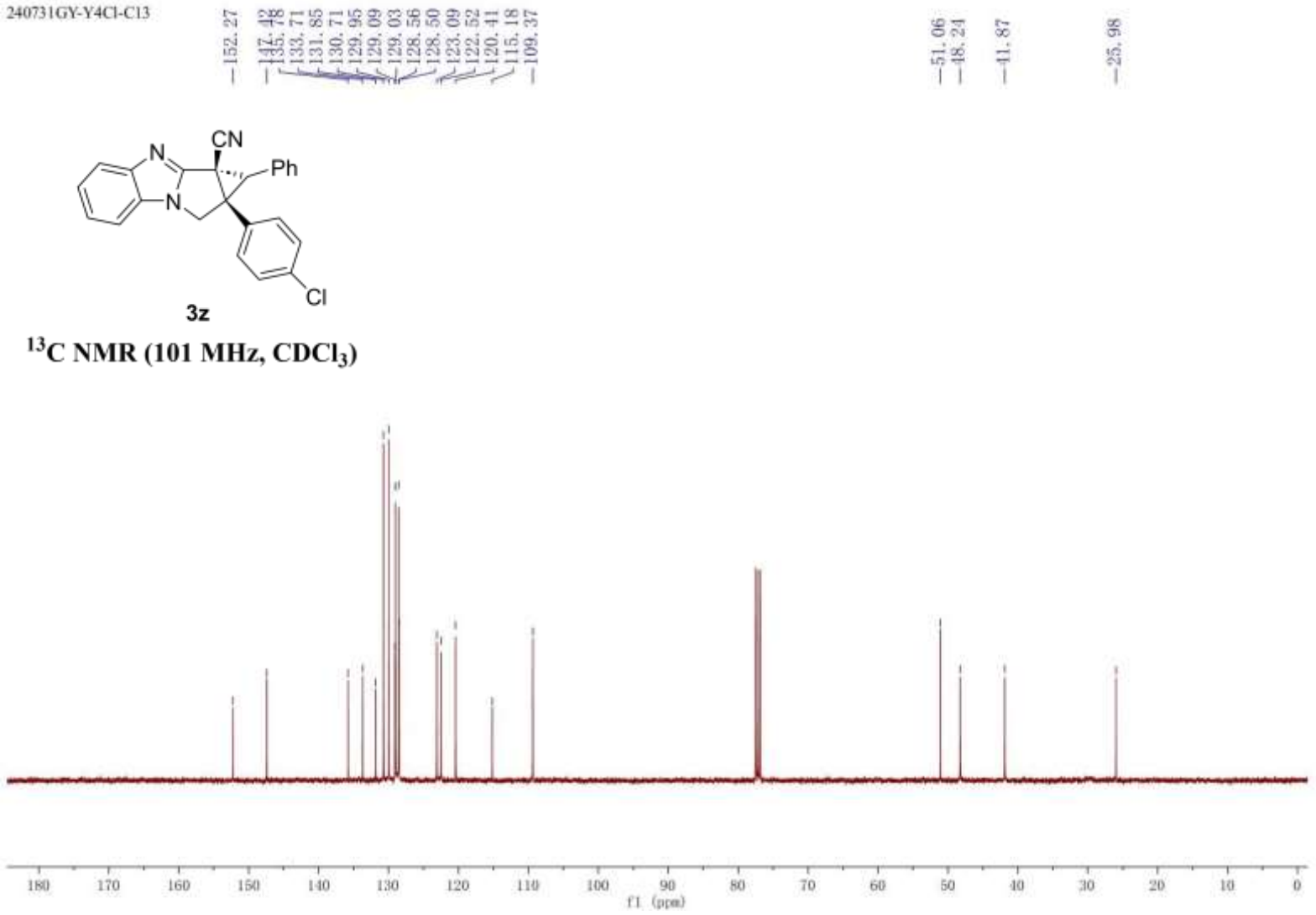


Figure 52. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **3z**

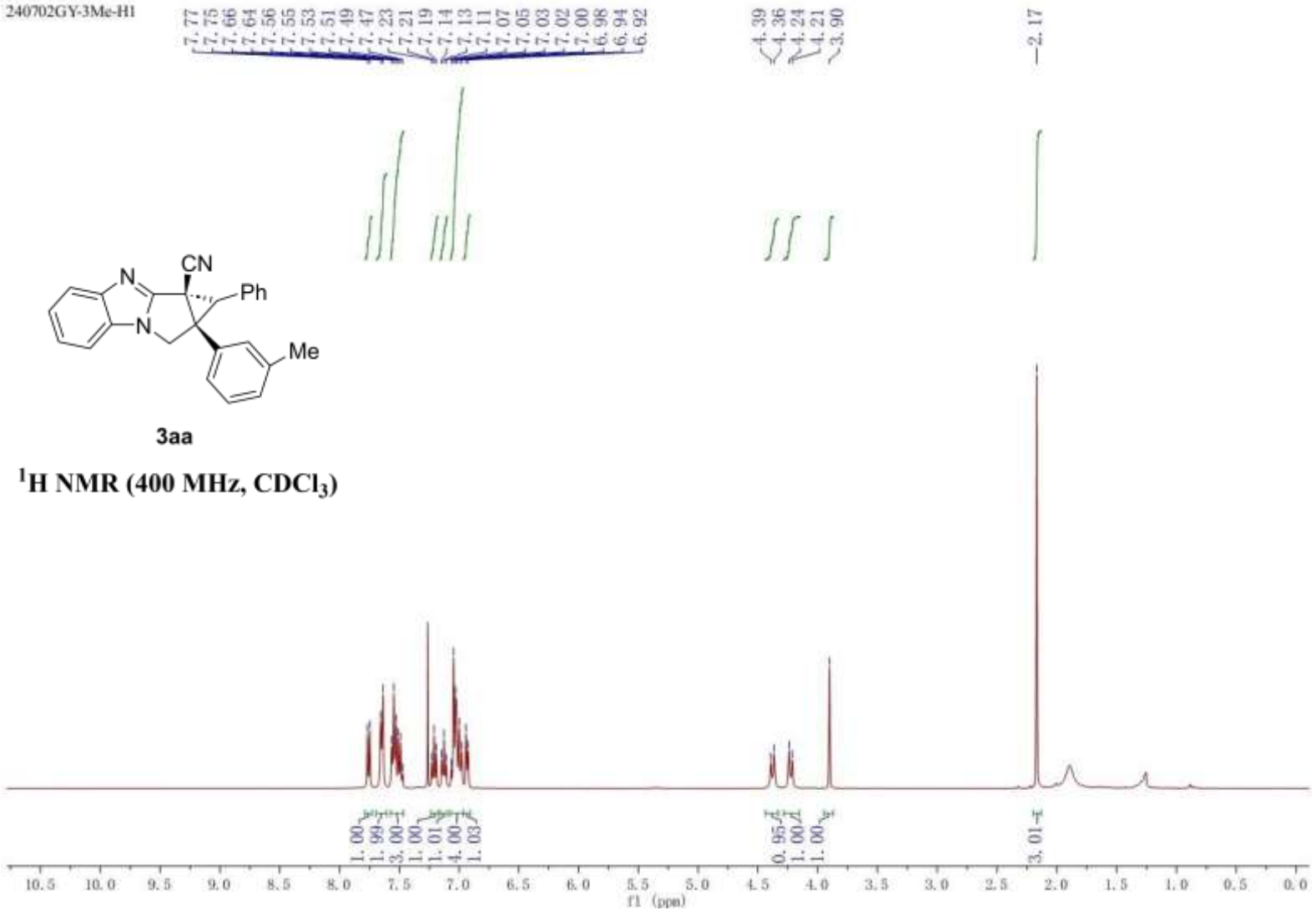


Figure 53. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3aa**

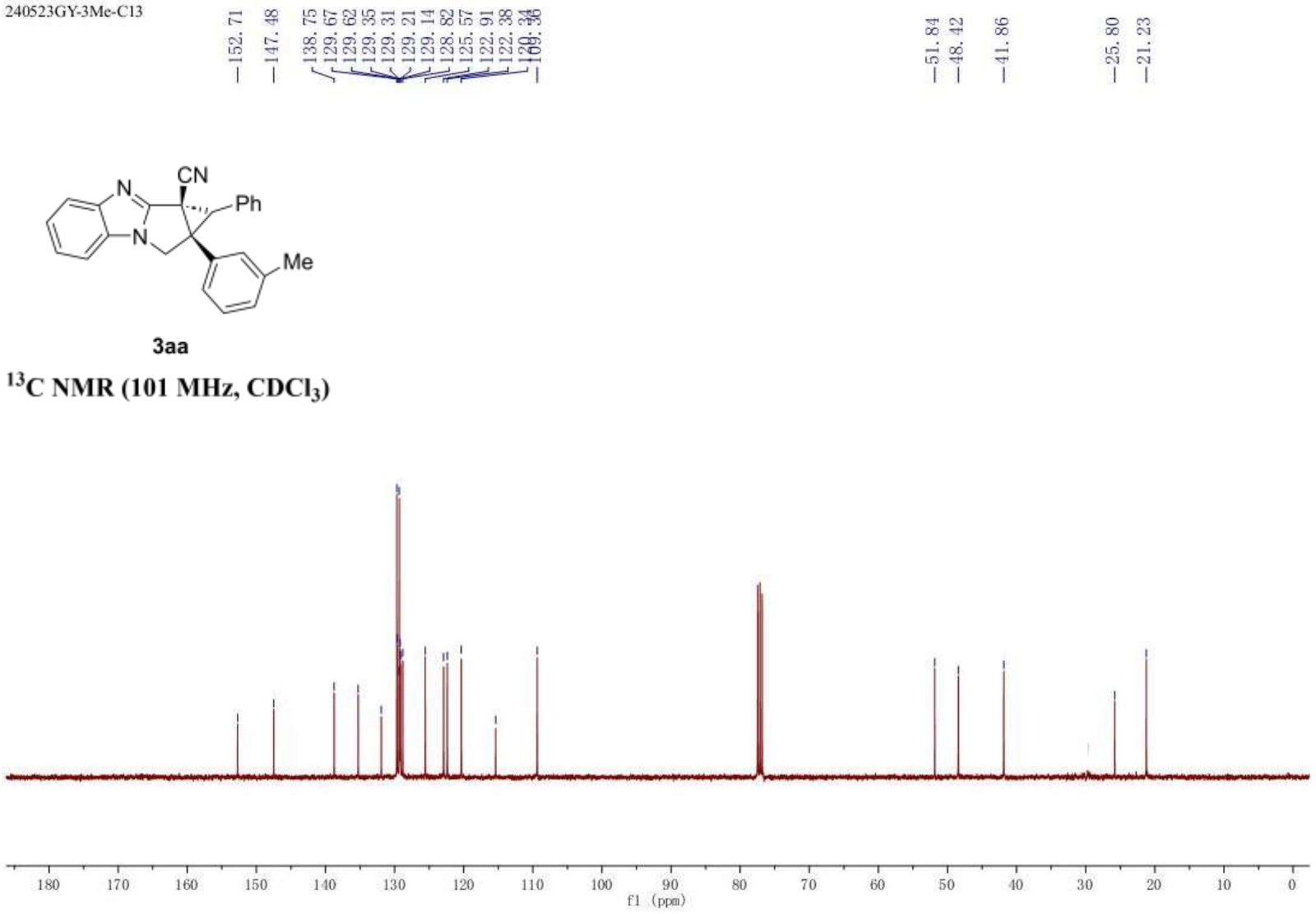


Figure 54. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **3aa**

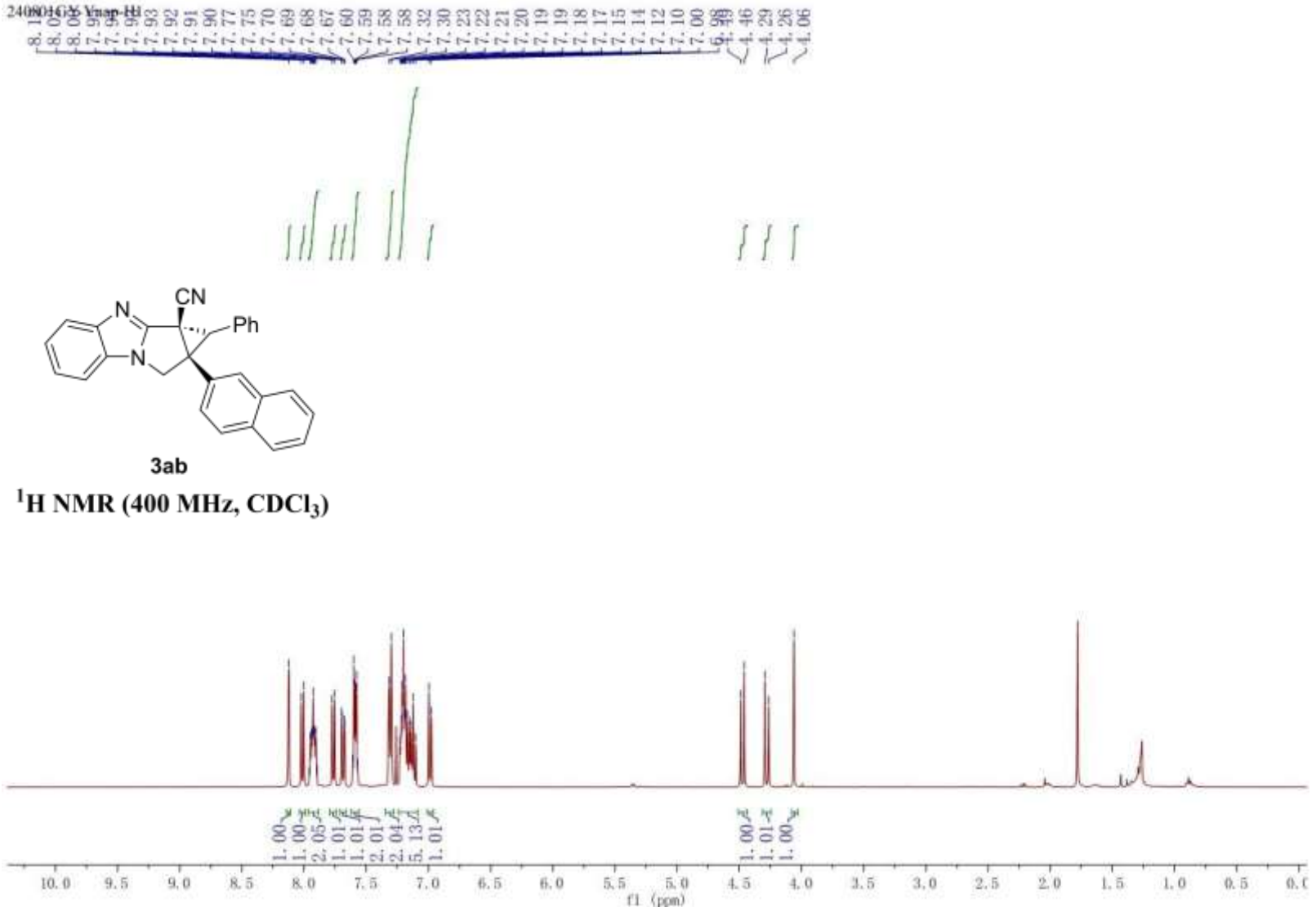


Figure 55. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3ab**

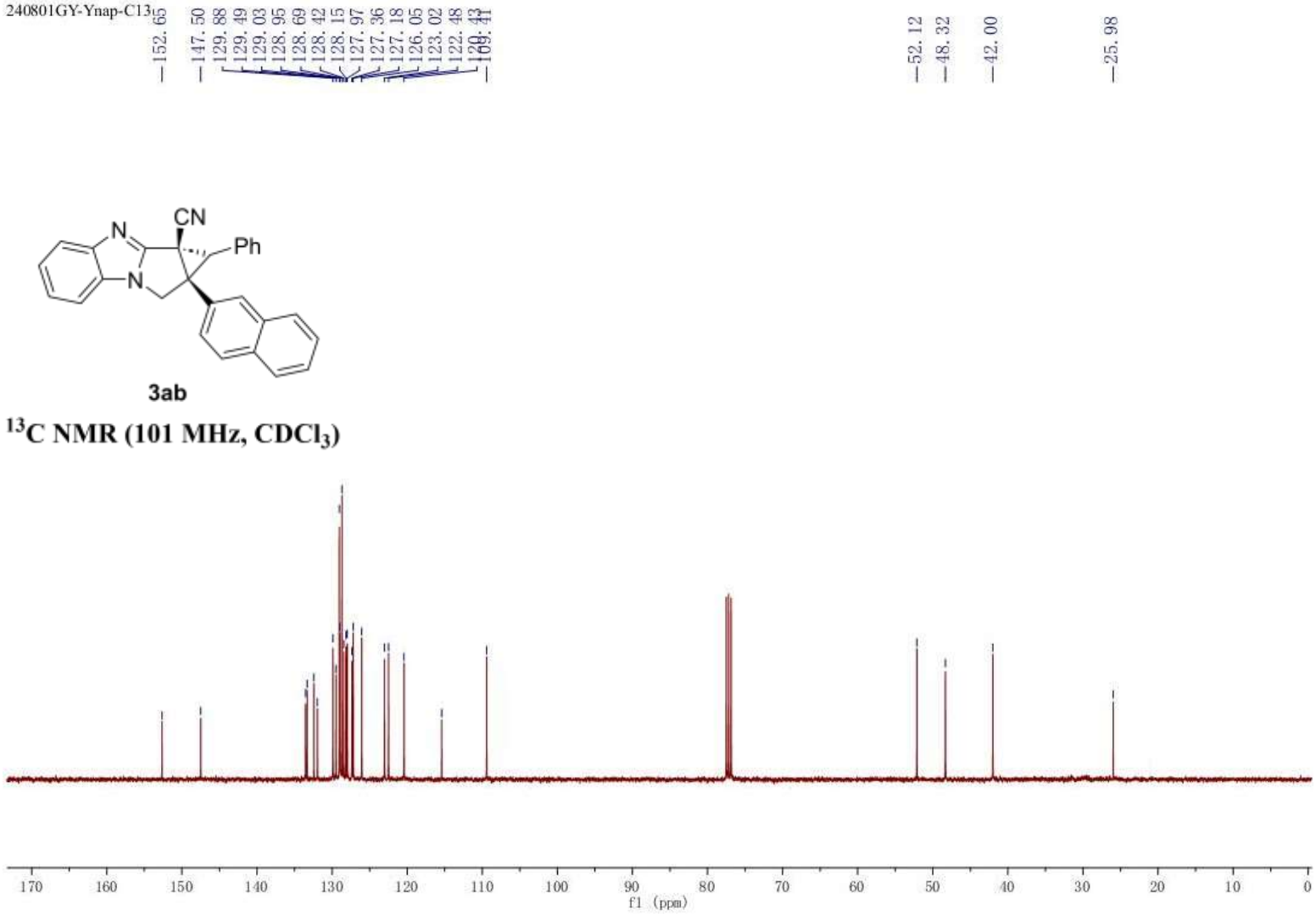


Figure 56. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **3ab**

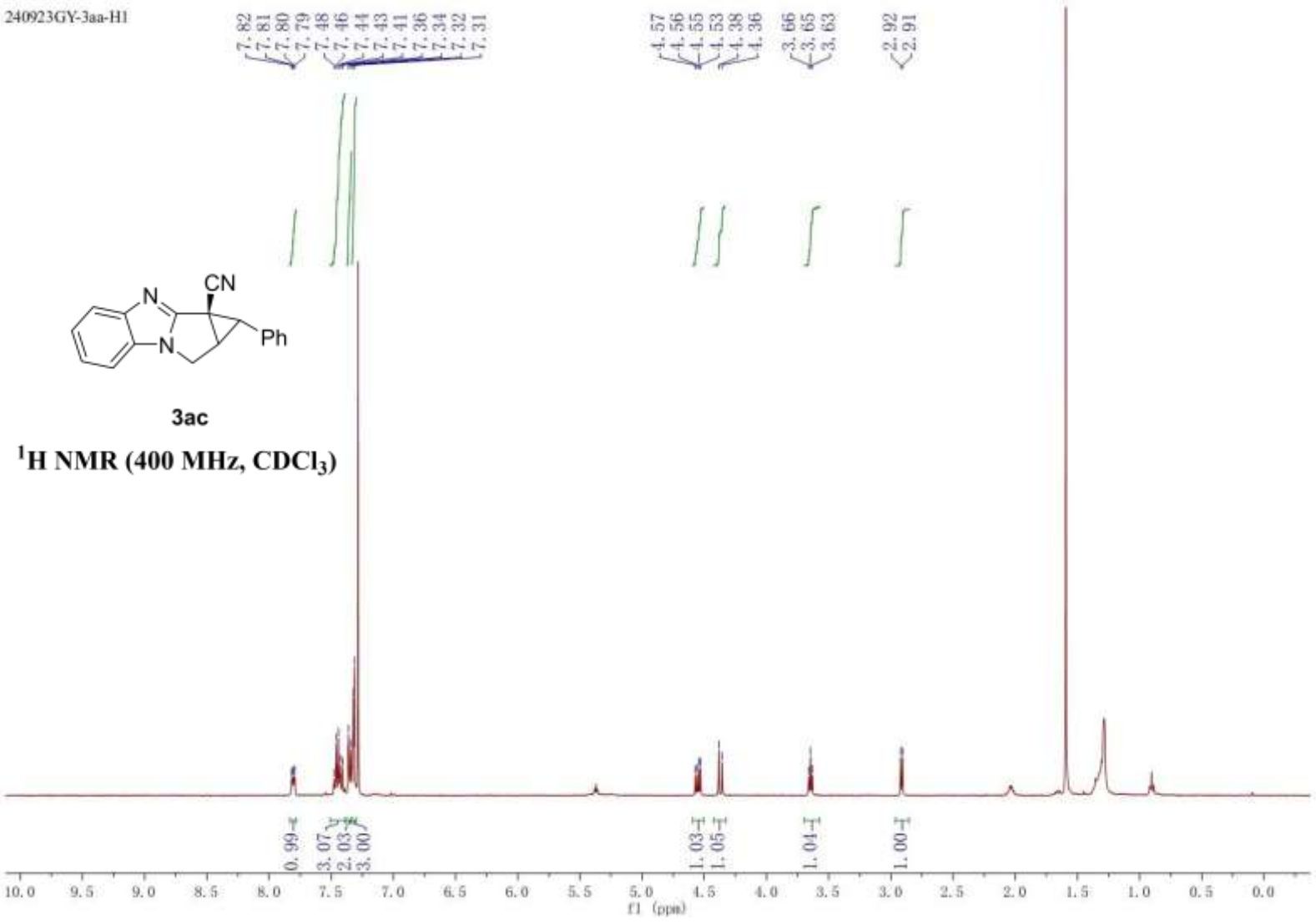


Figure 57. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3ac**

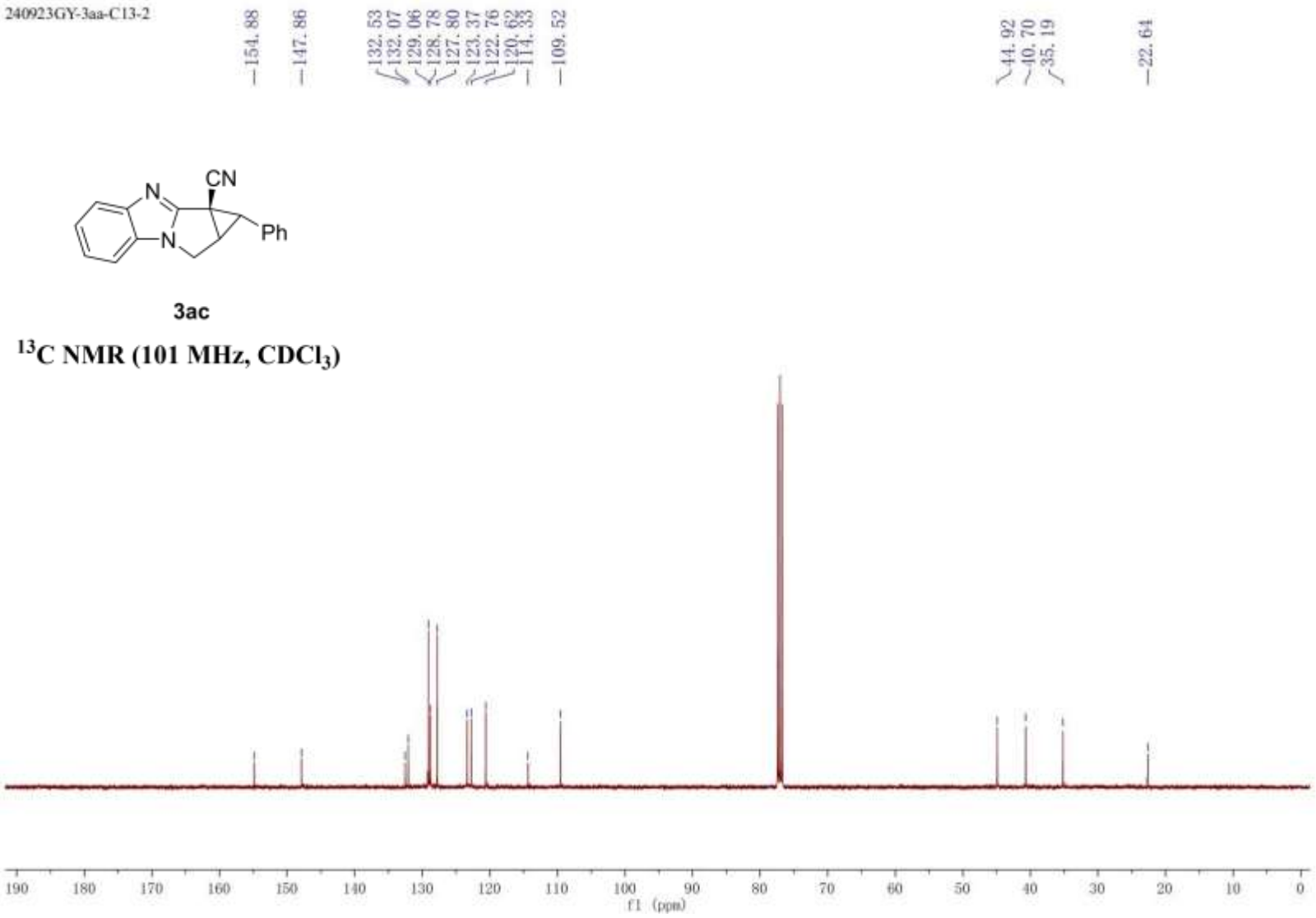


Figure 58. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **3ac**

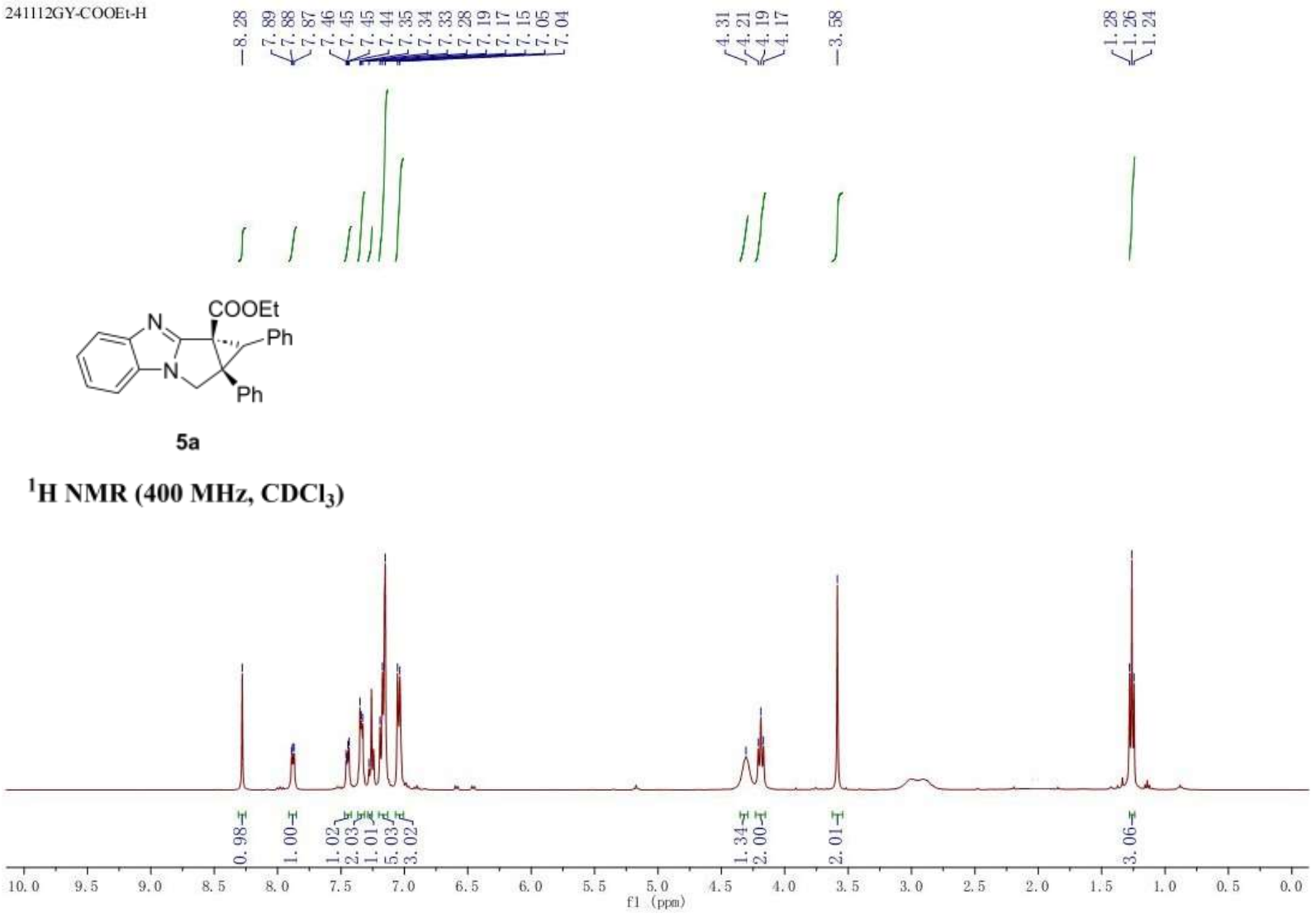
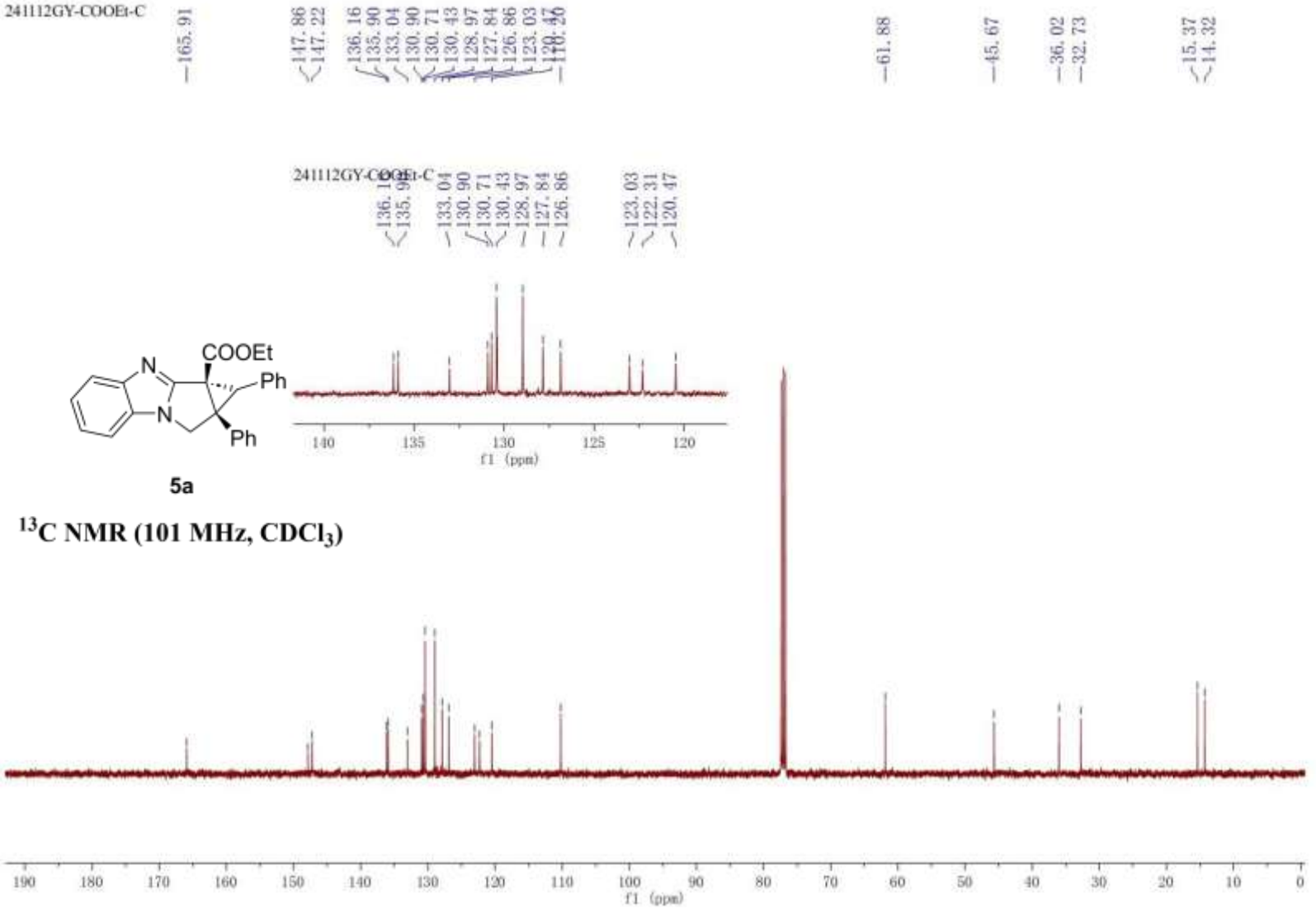


Figure 59. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **5a**



5a

^{13}C NMR (101 MHz, $CDCl_3$)

Figure 60. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **5a**

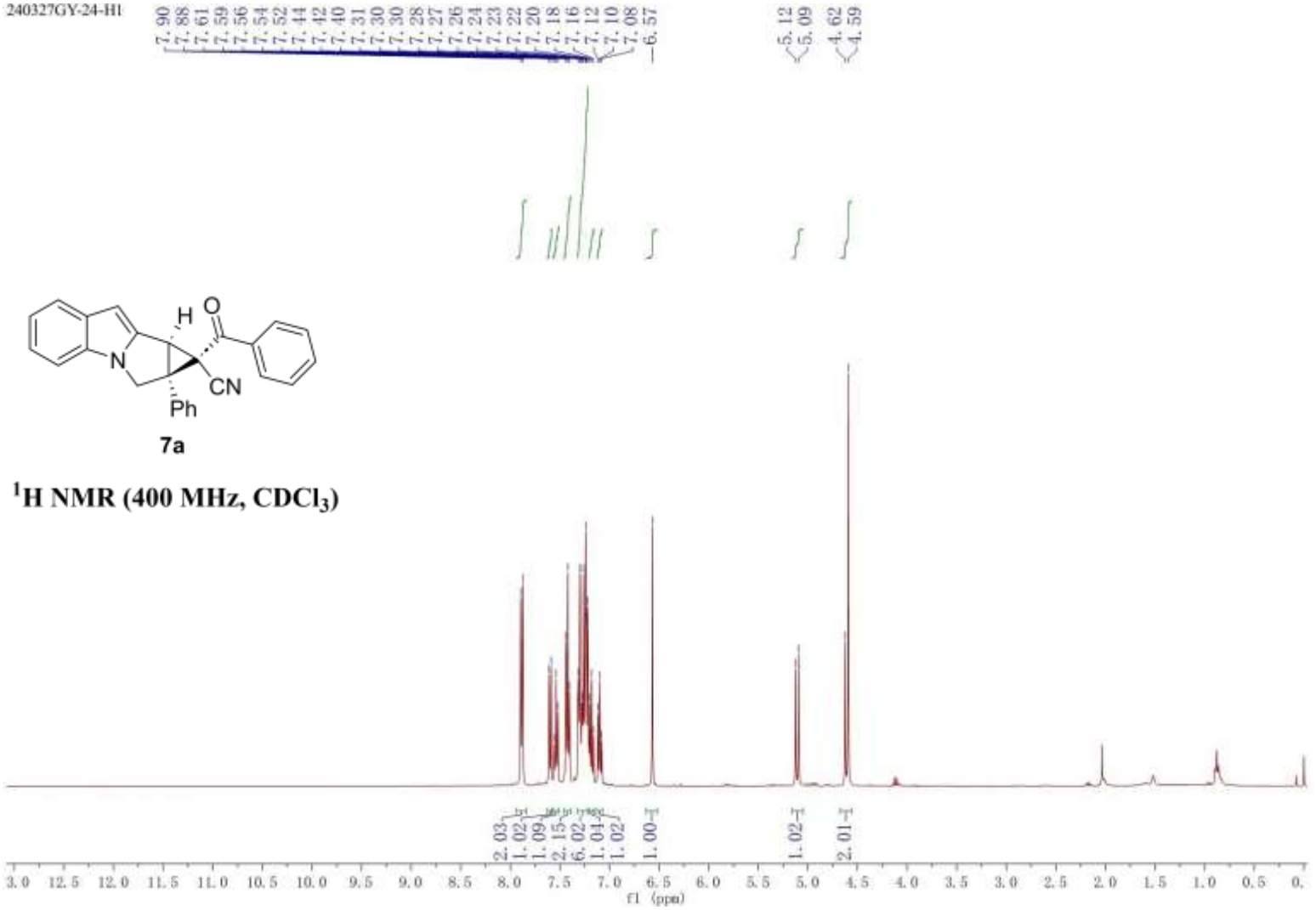


Figure 61. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **7a**

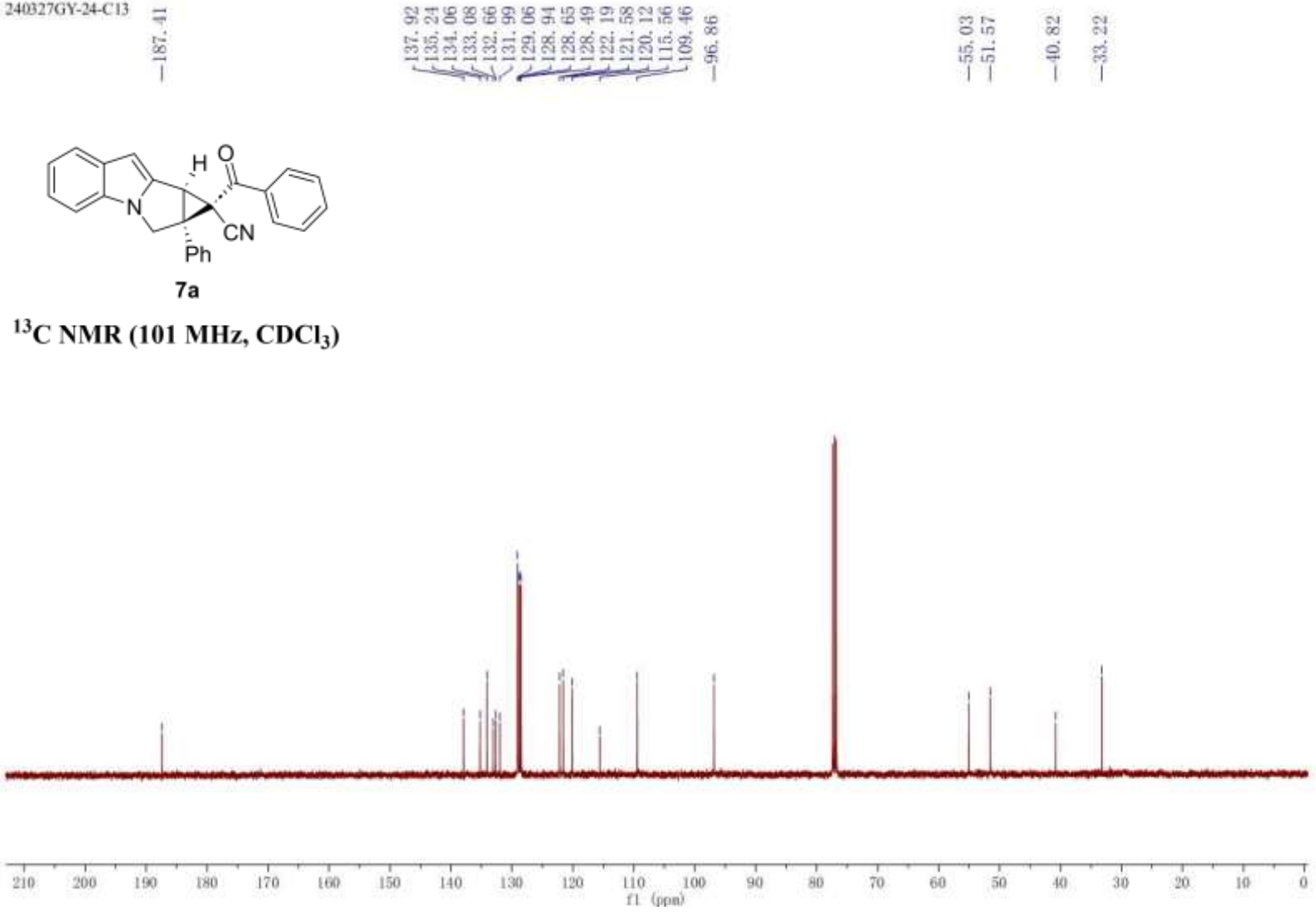


Figure 62. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **7a**

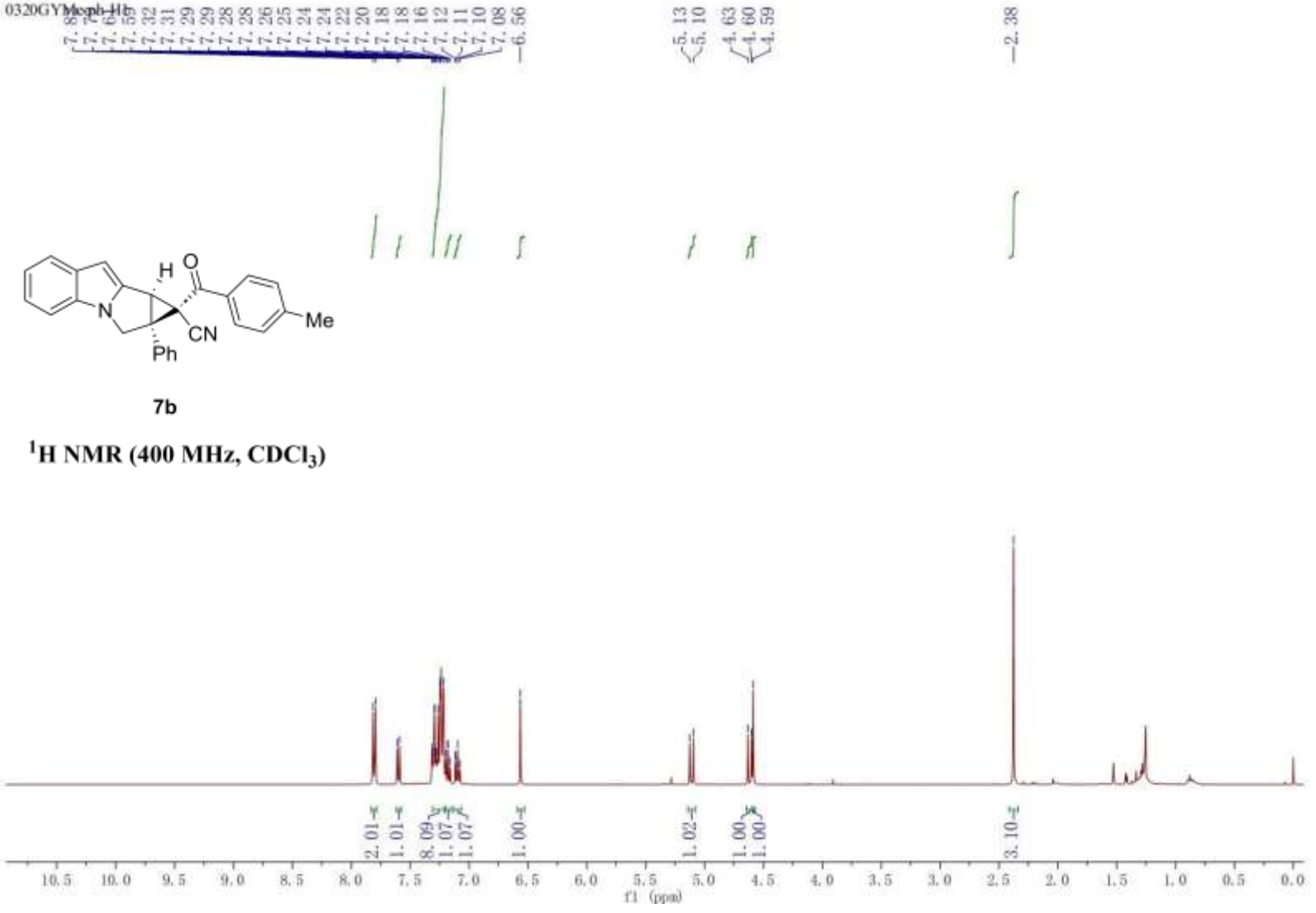


Figure 63. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **7b**

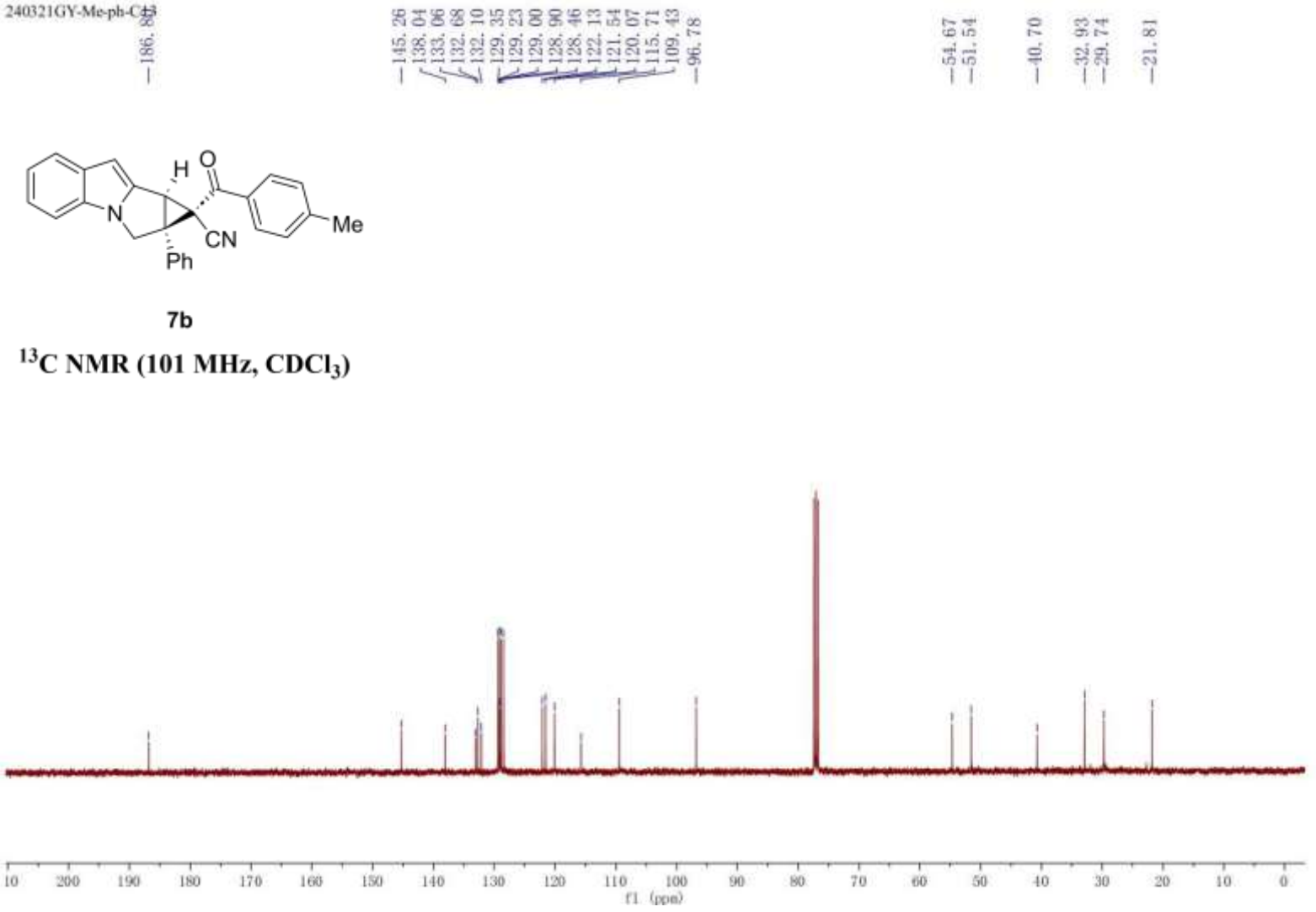


Figure 64. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **7b**

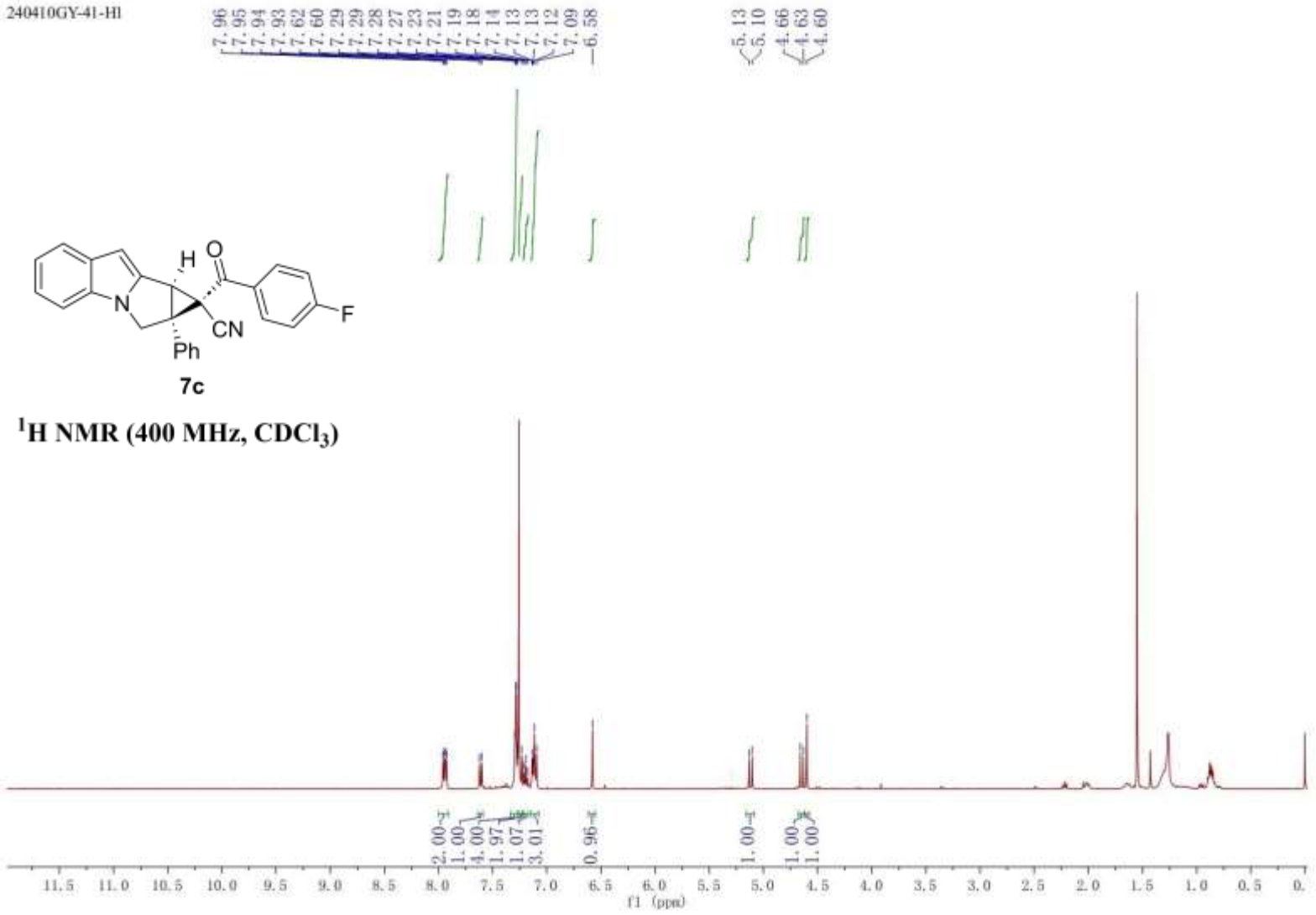


Figure 65. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **7c**

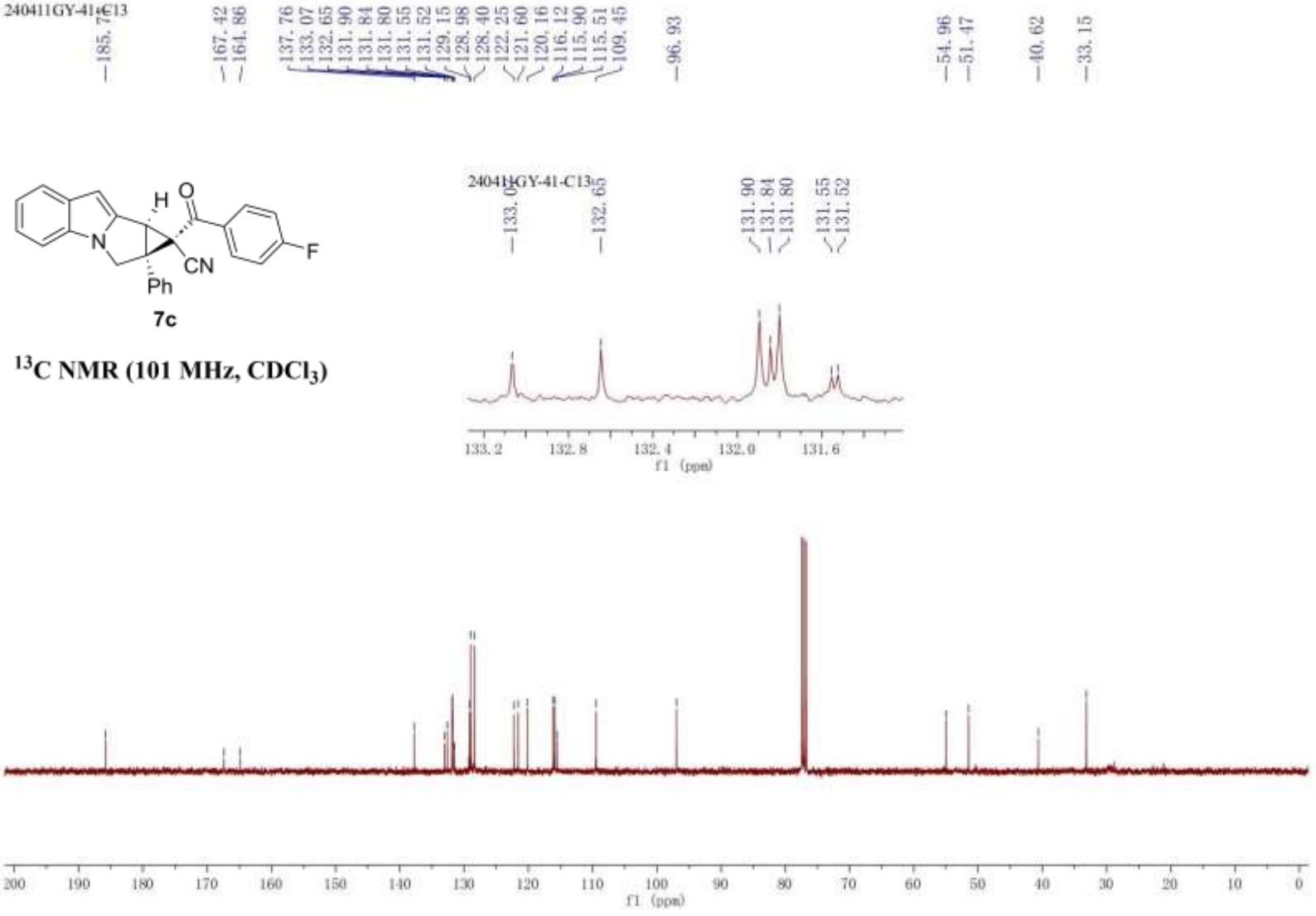


Figure 66. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **7c**

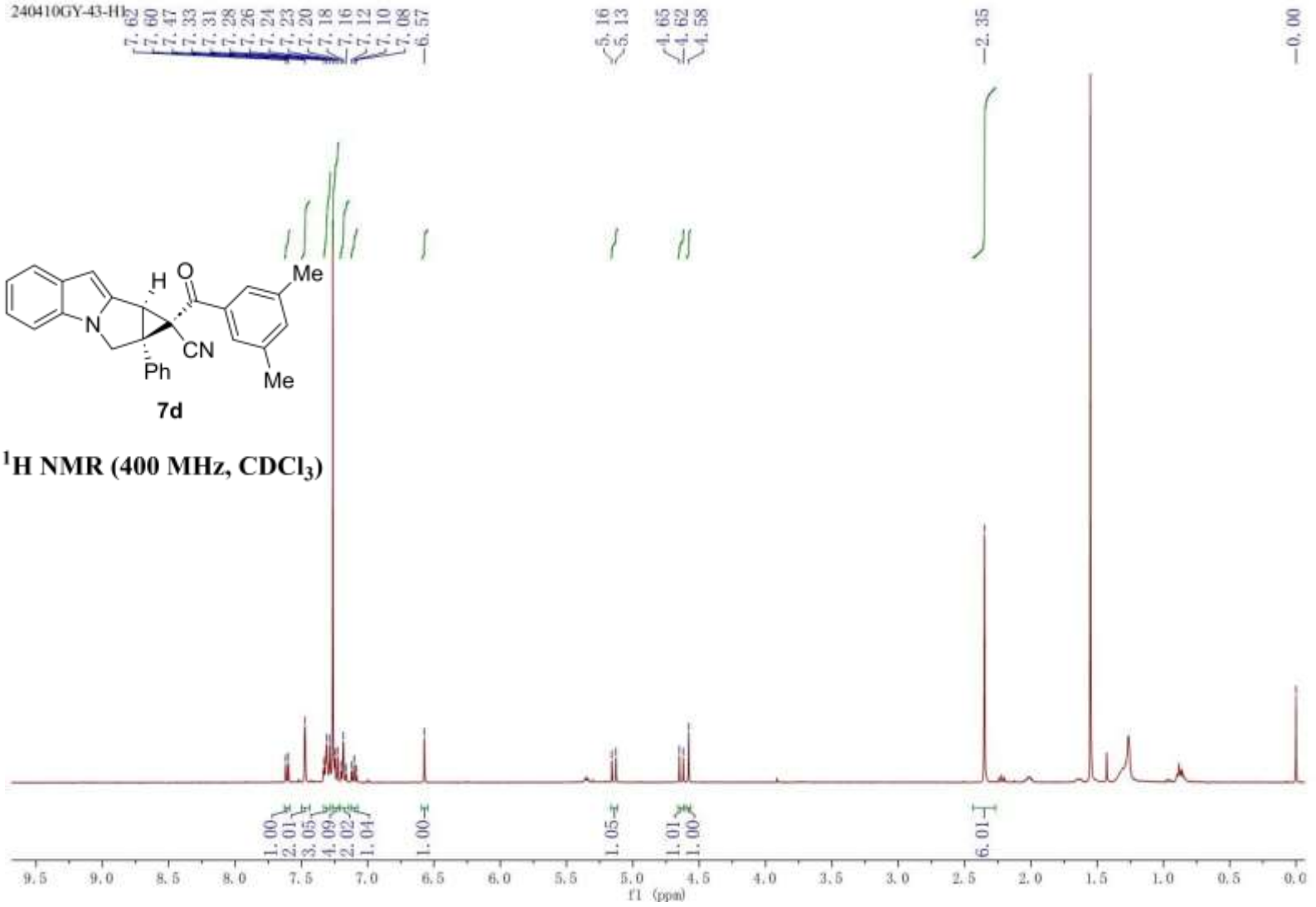


Figure 67. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **7d**

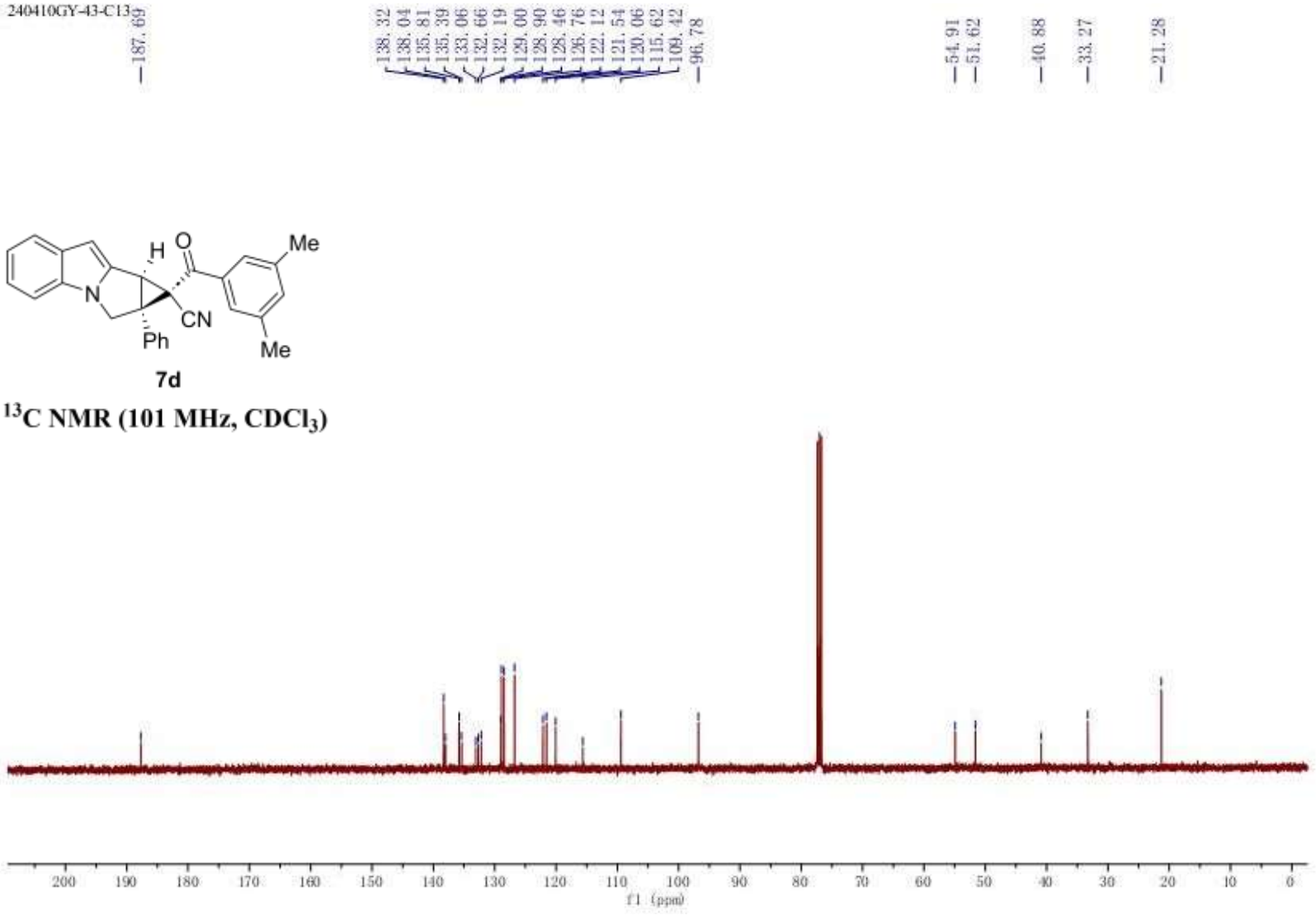


Figure 68. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **7d**

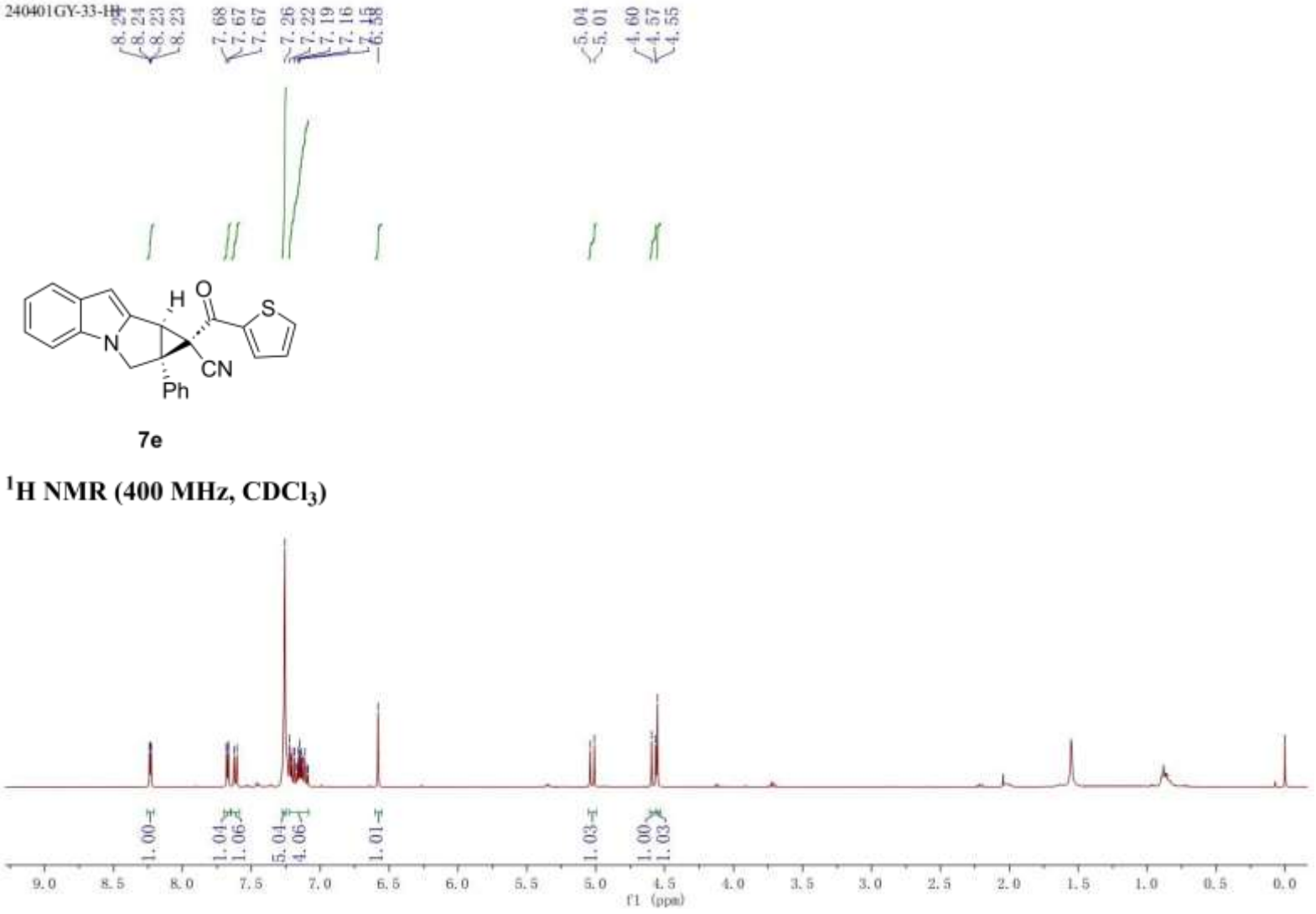


Figure 69. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **7e**

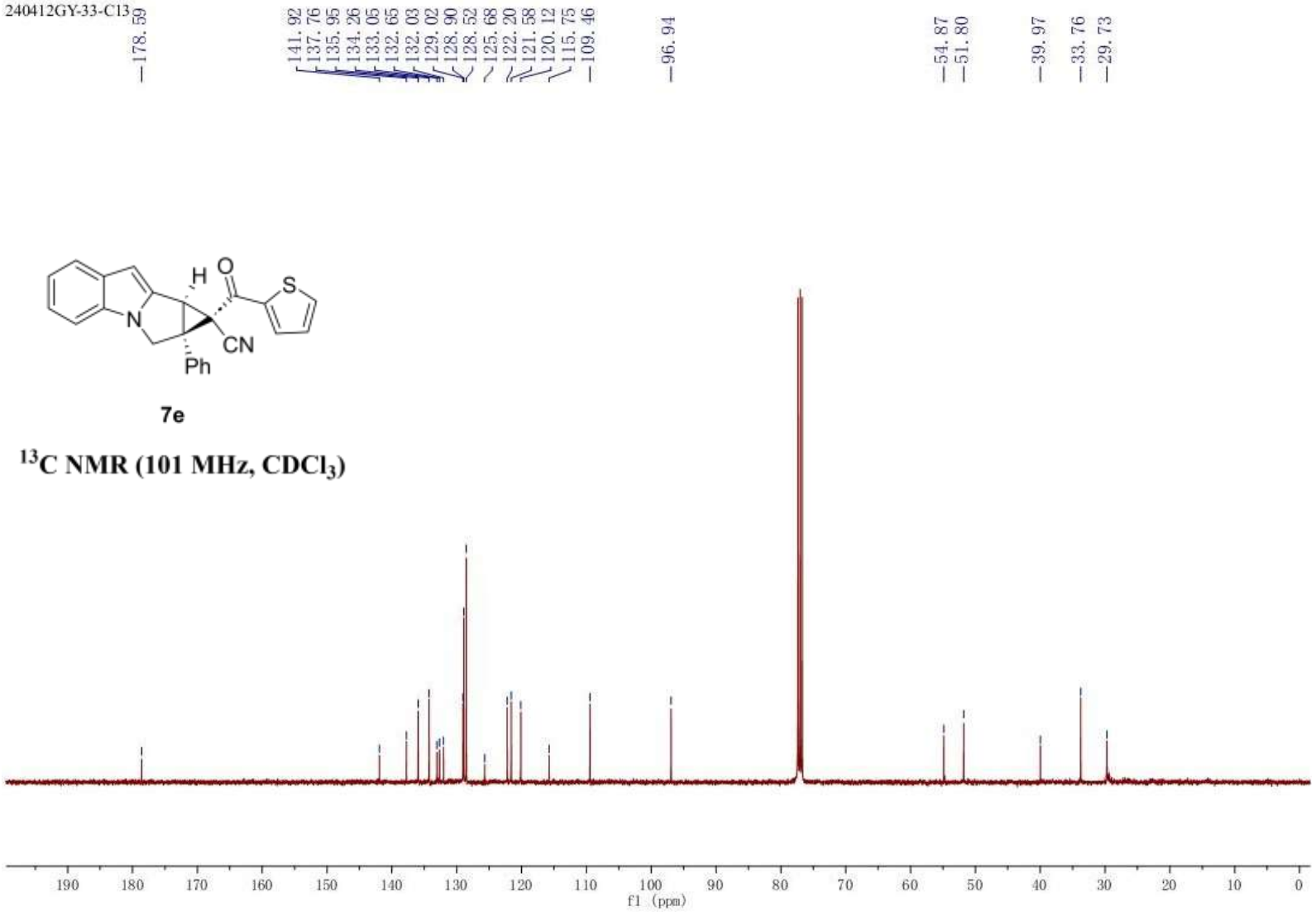
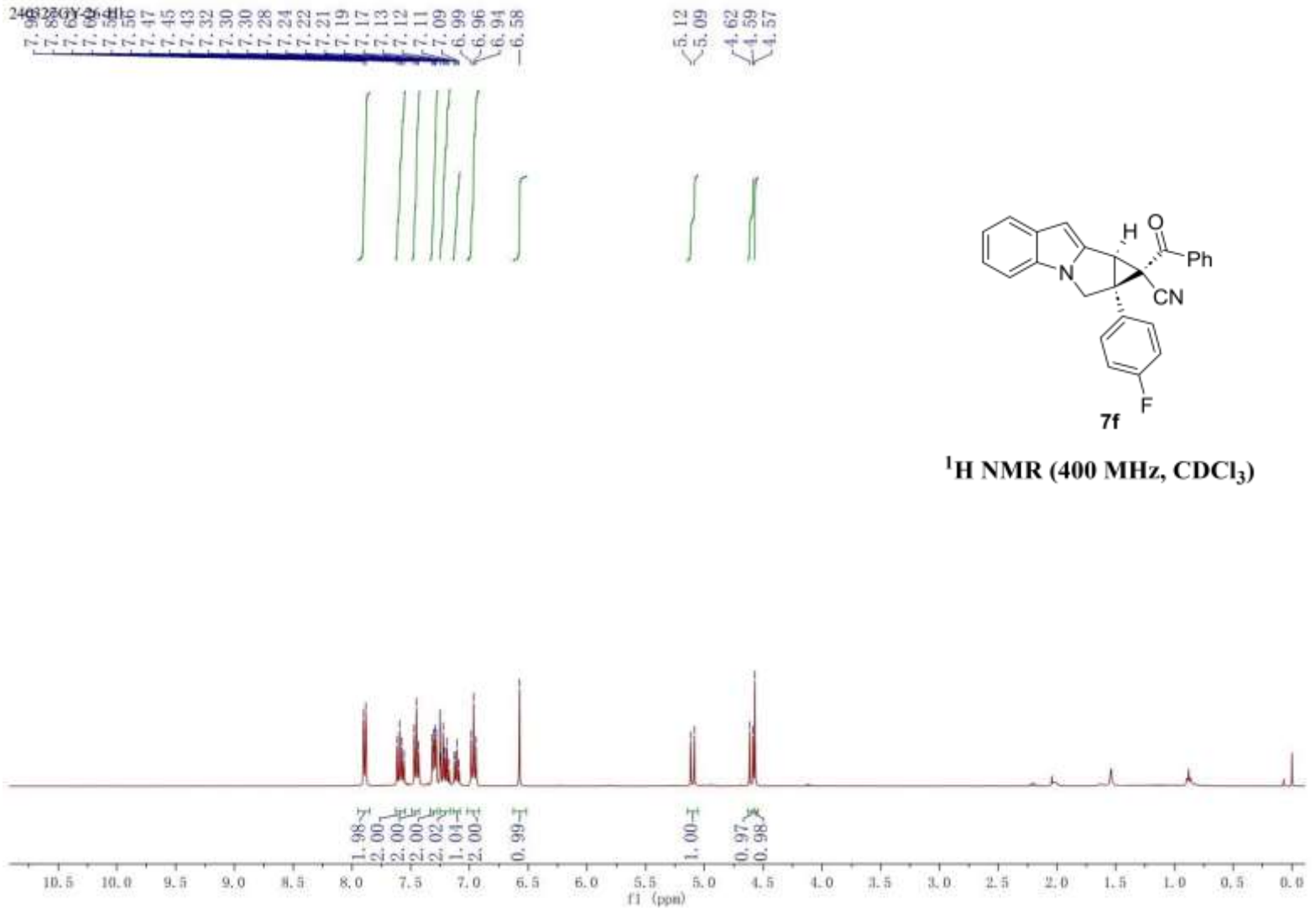


Figure 70. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **7e**



^{1}H NMR (400 MHz, $CDCl_3$)

Figure 71. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **7f**

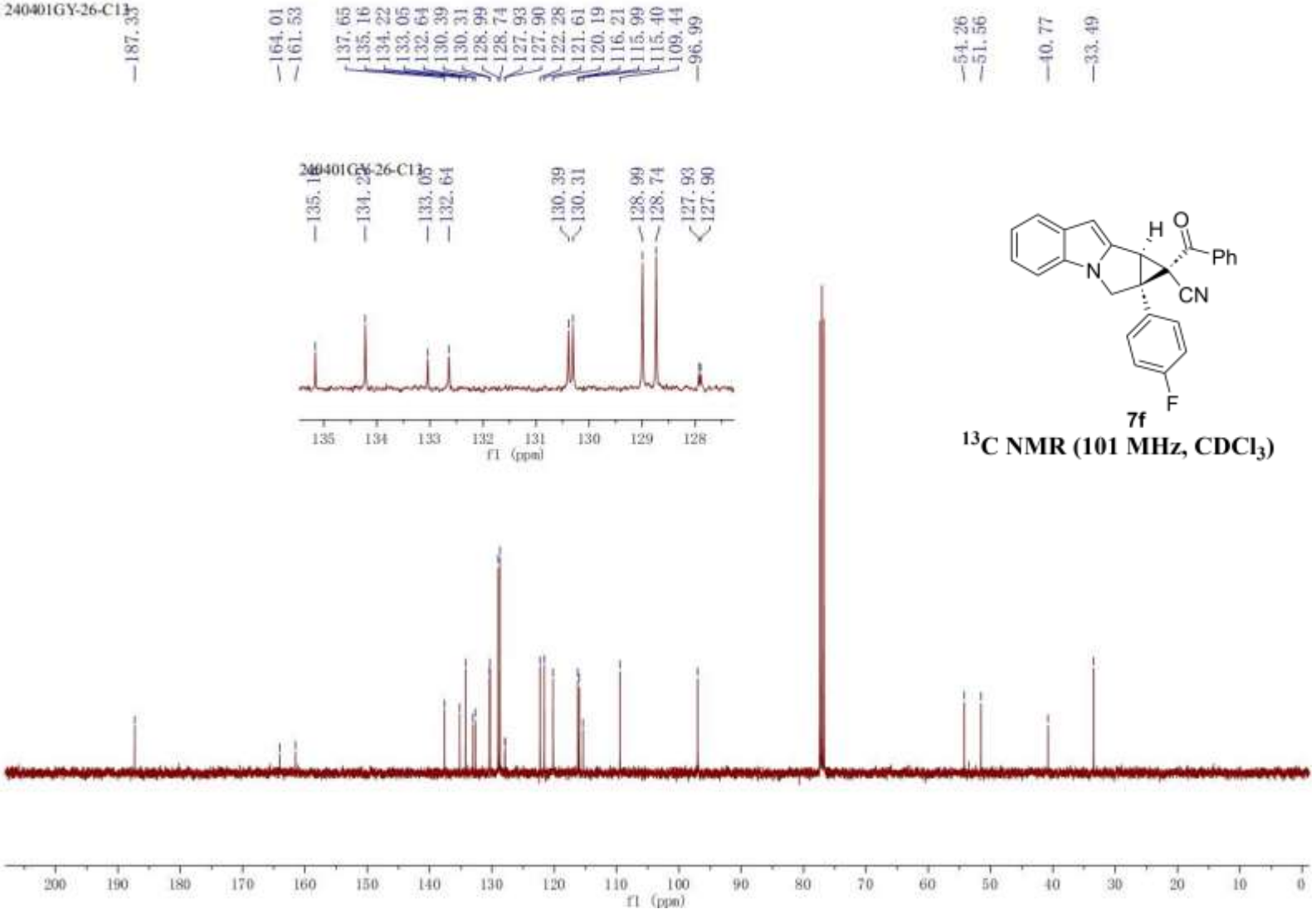


Figure 72. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **7f**

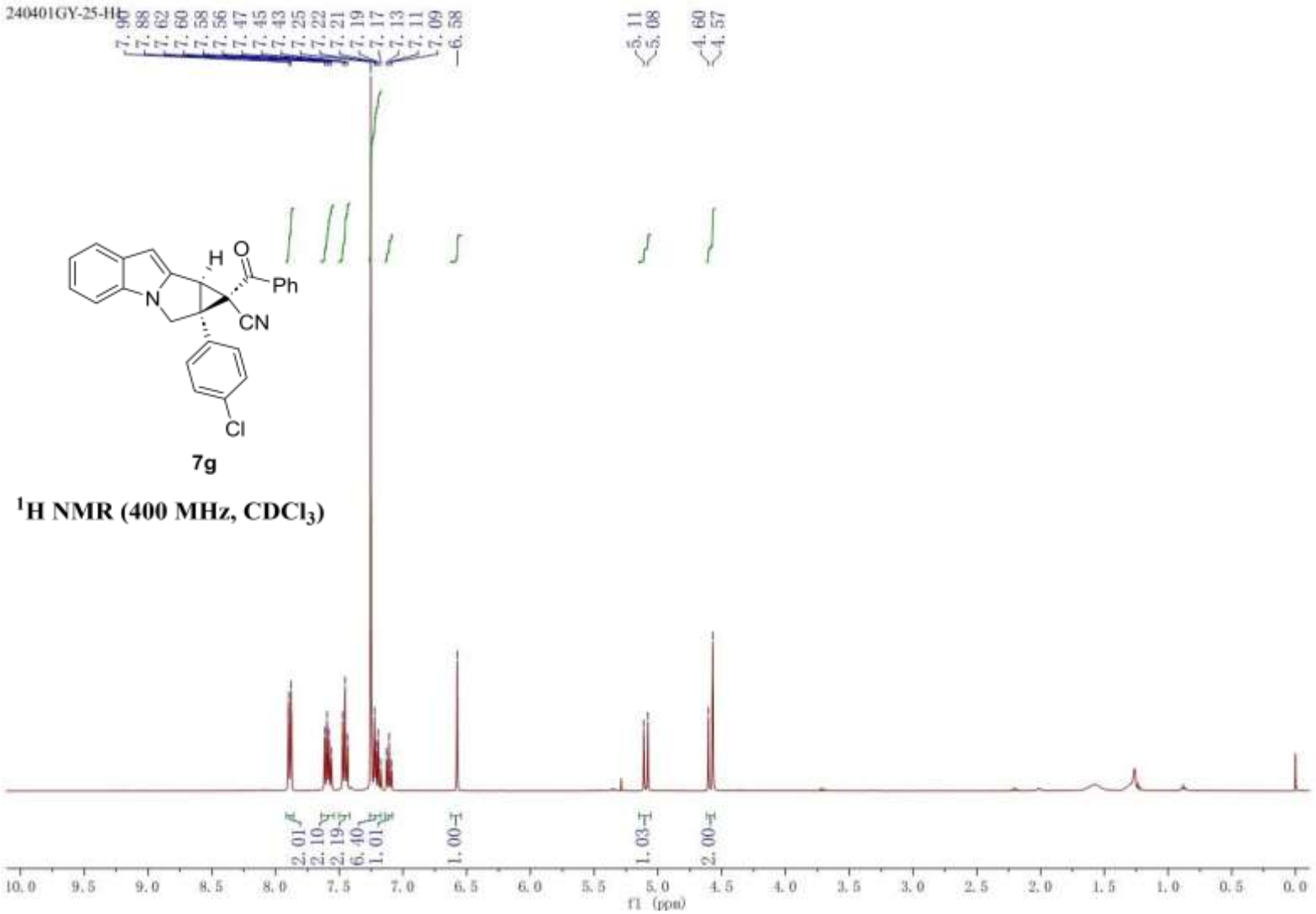


Figure 73. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **7g**

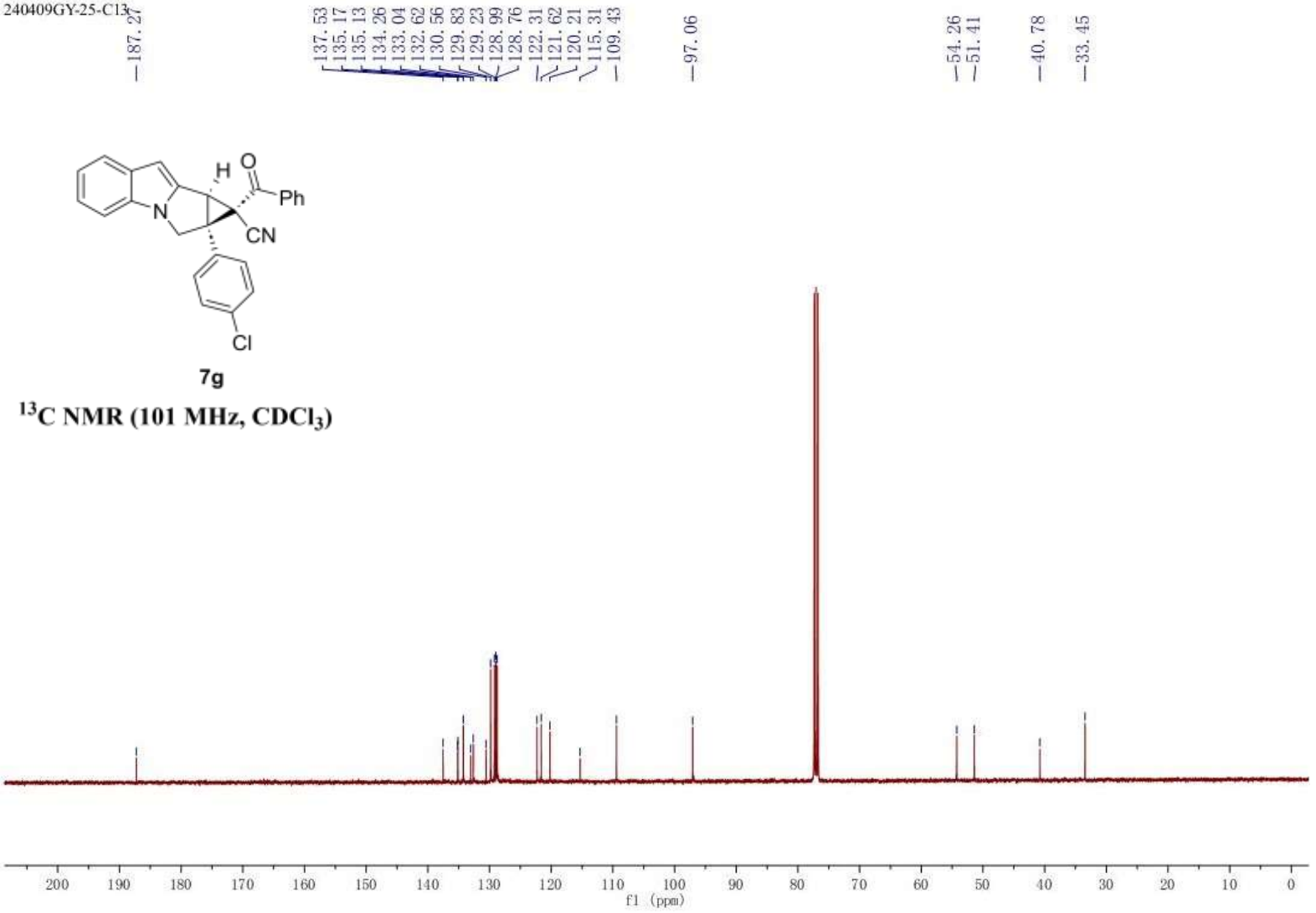
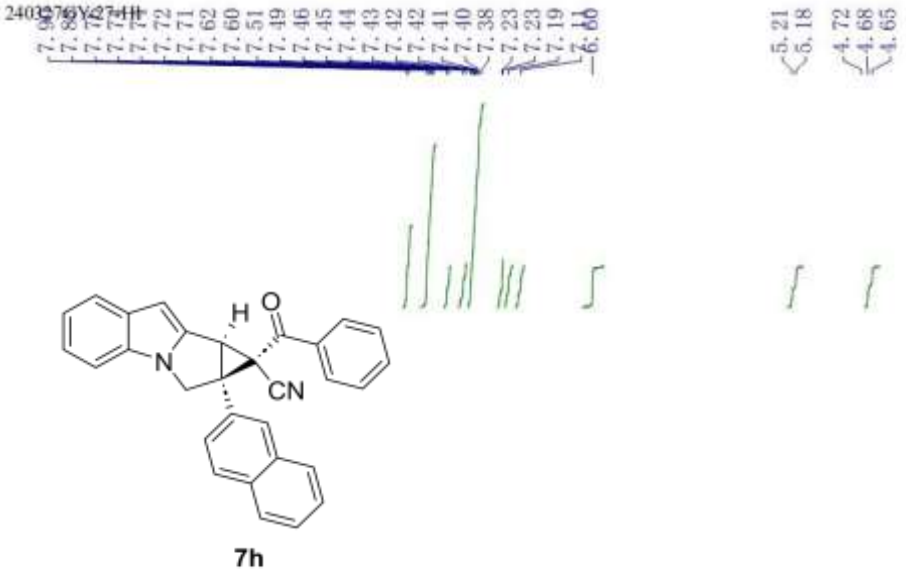


Figure 74. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **7g**



7h

^{1}H NMR (400 MHz, $CDCl_3$)

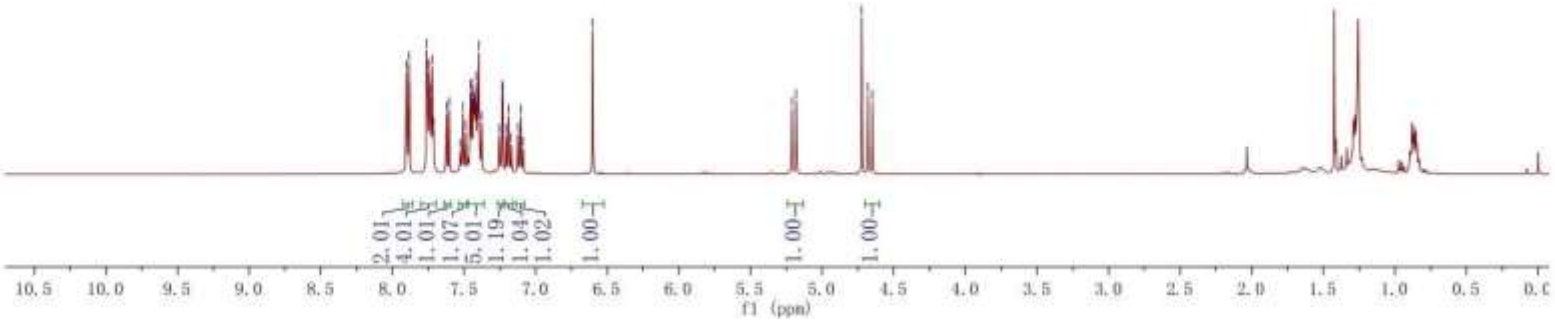


Figure 75. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **7h**

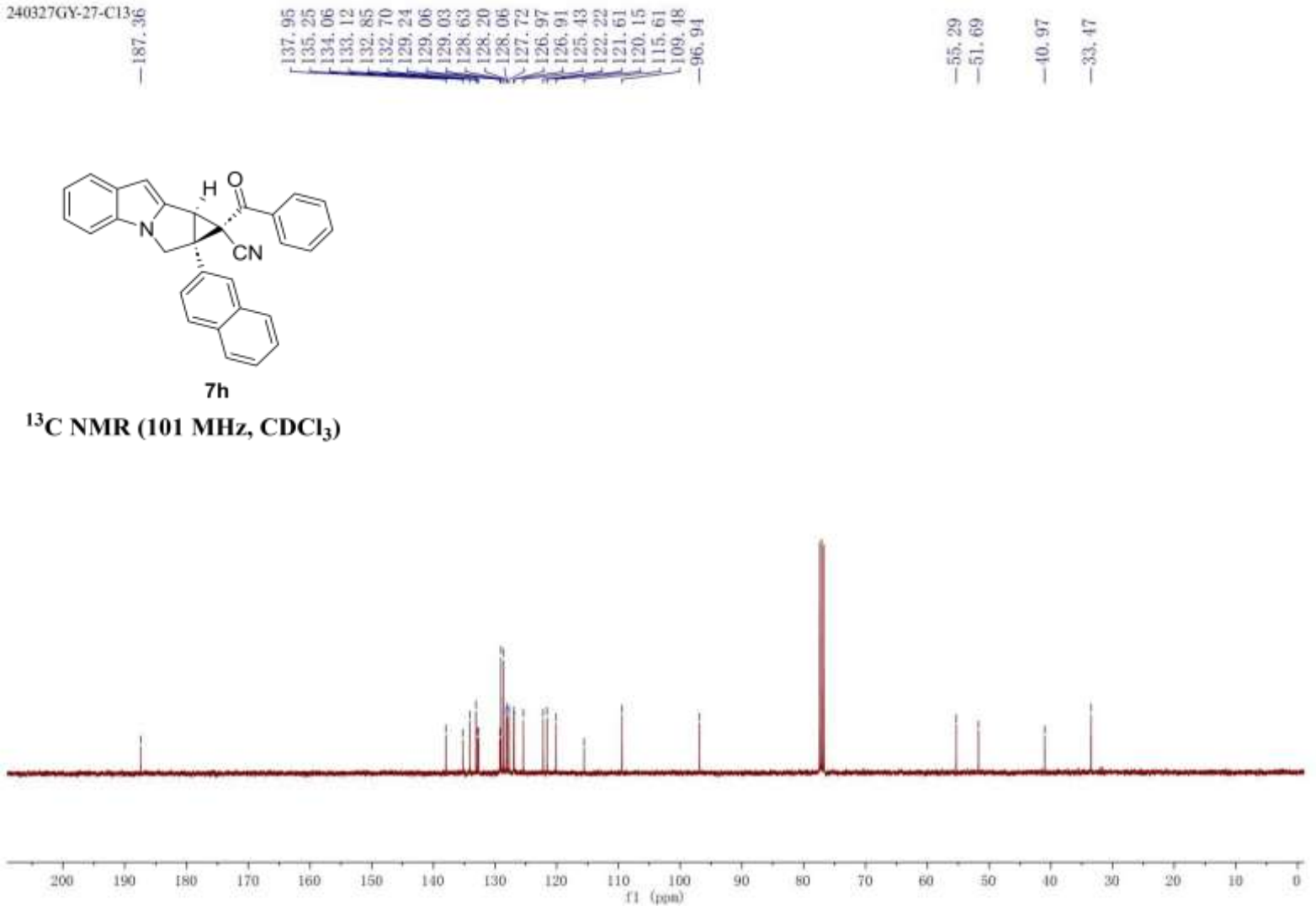


Figure 76. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **7h**

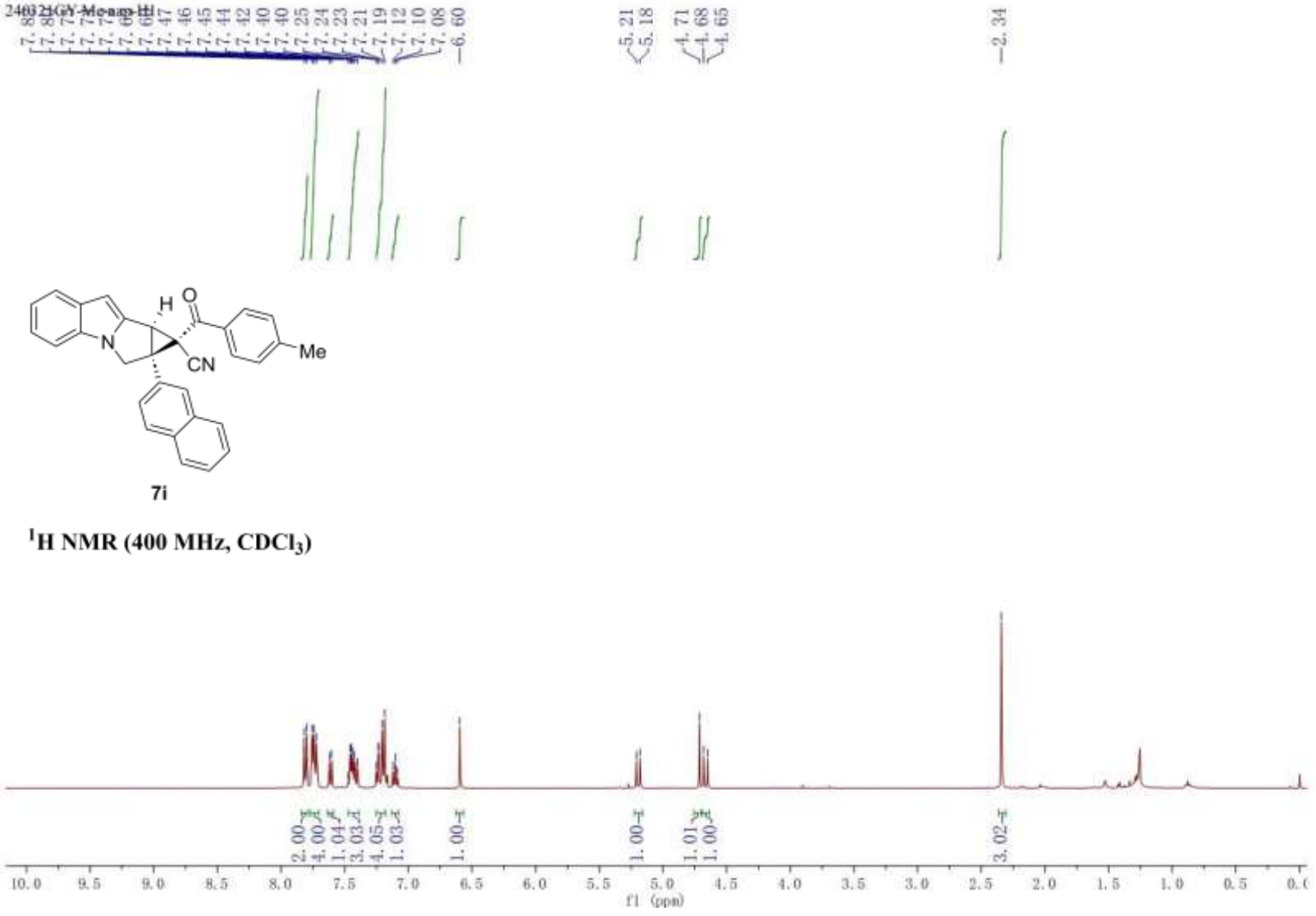


Figure 77. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **7i**

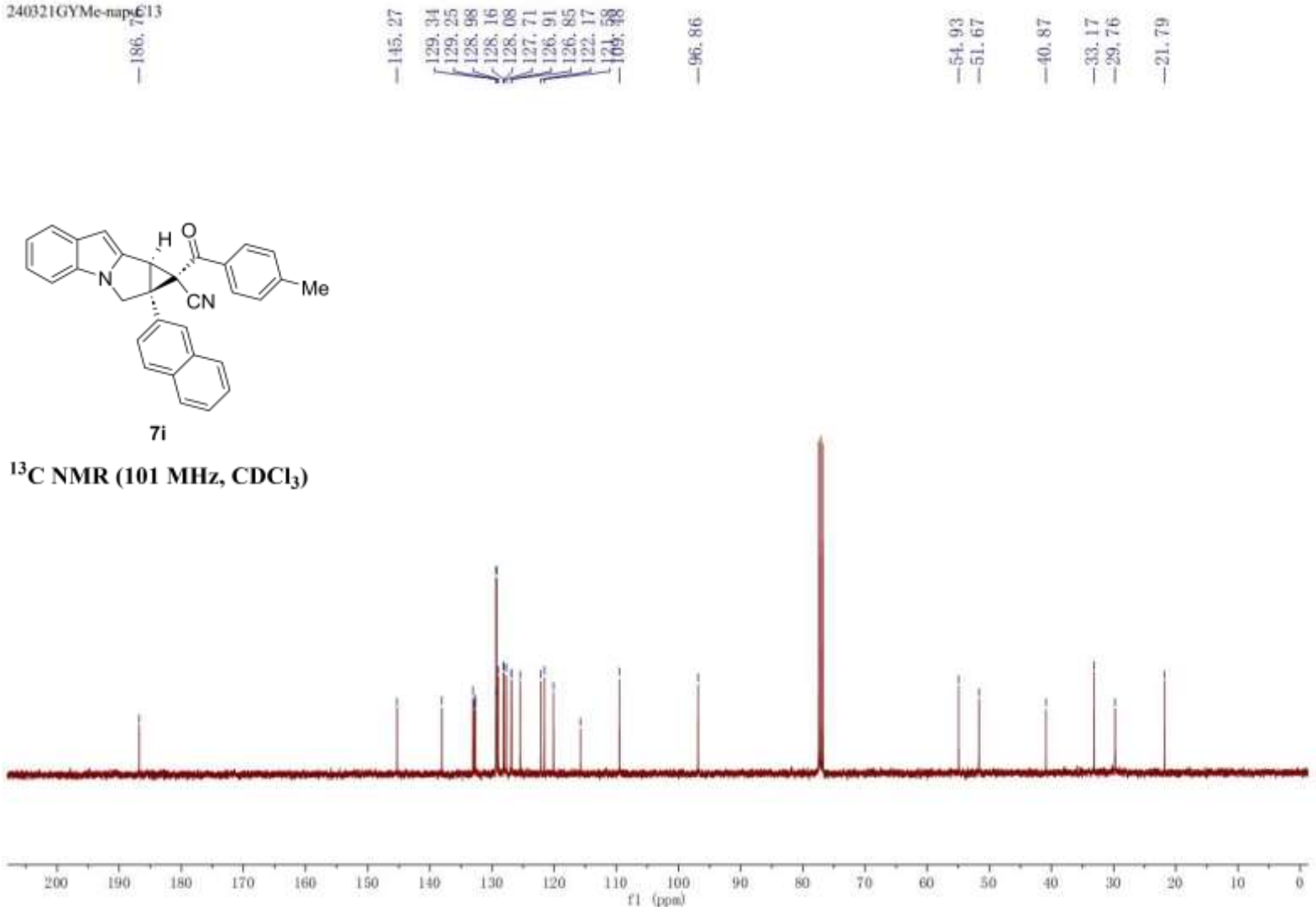


Figure 78. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **7i**

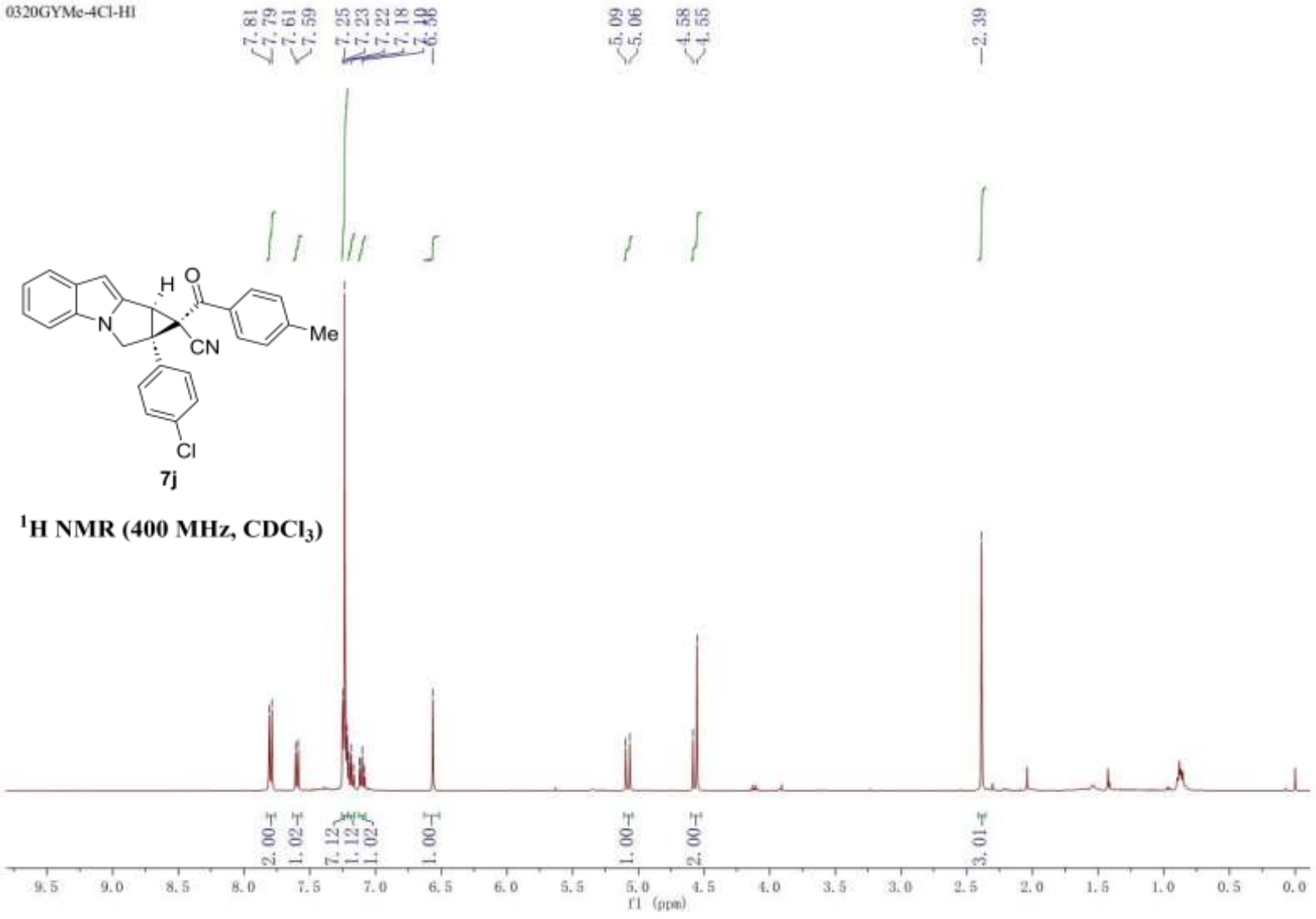


Figure 79. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **7j**

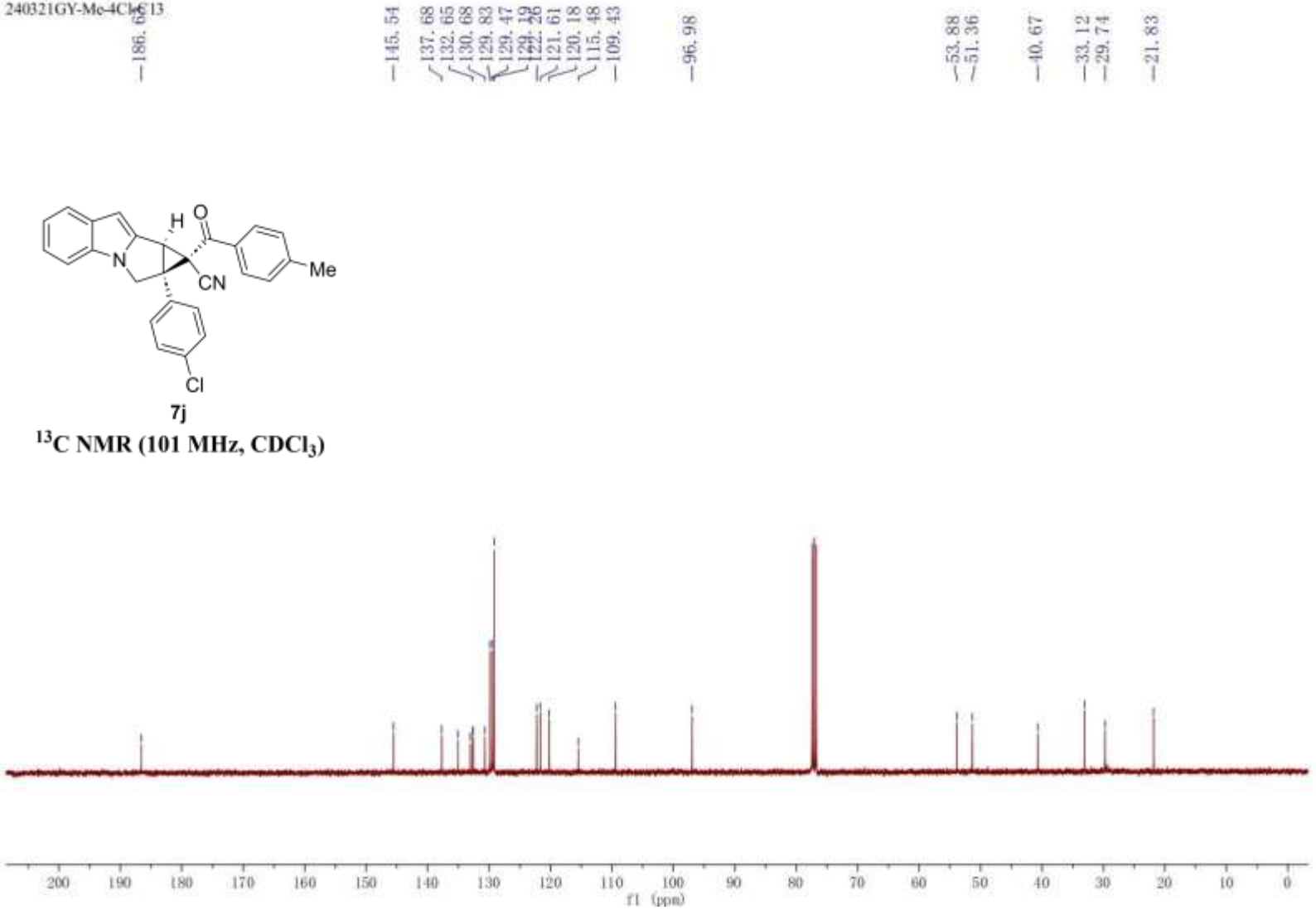


Figure 80. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **7j**

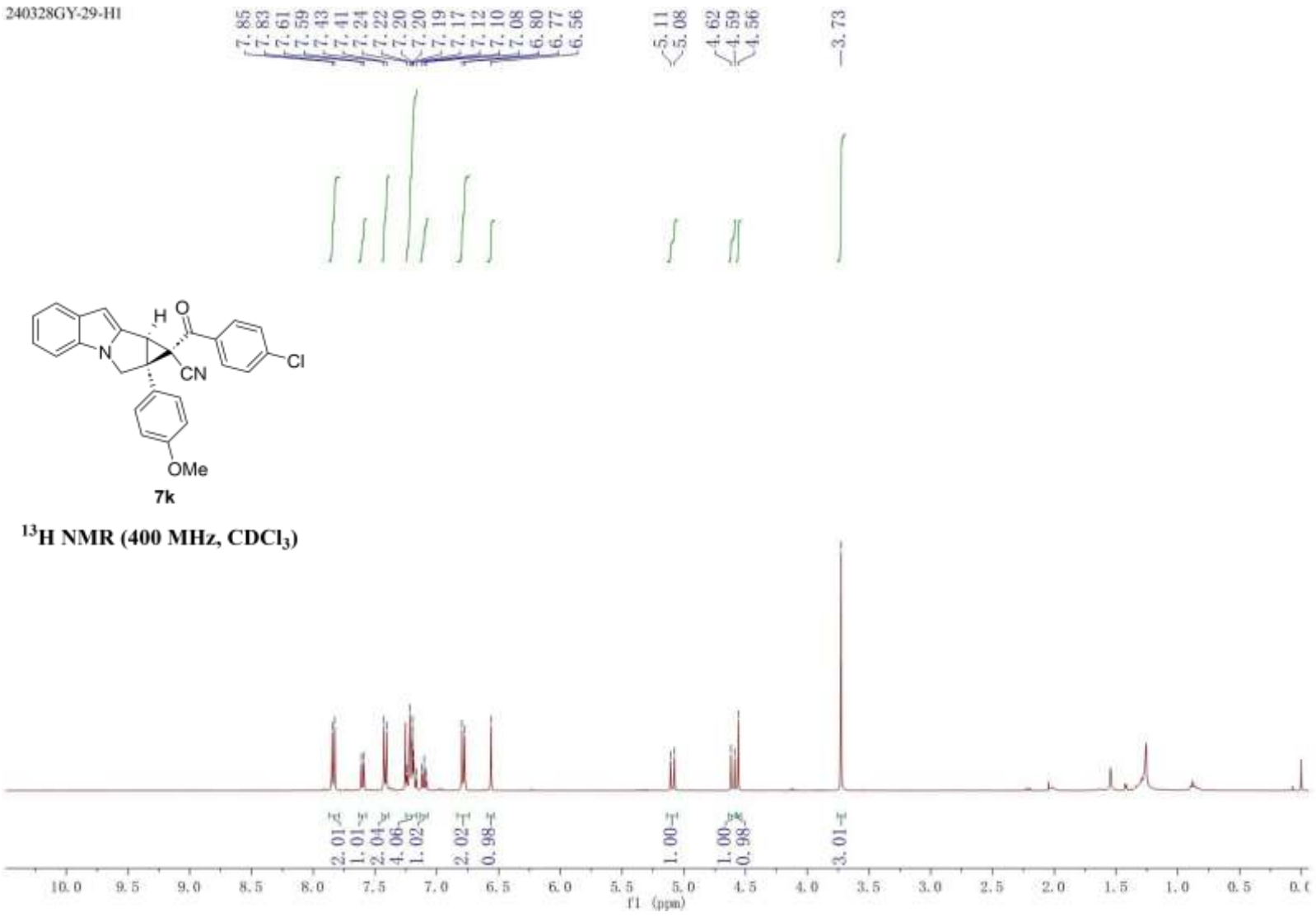


Figure 81. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **7k**

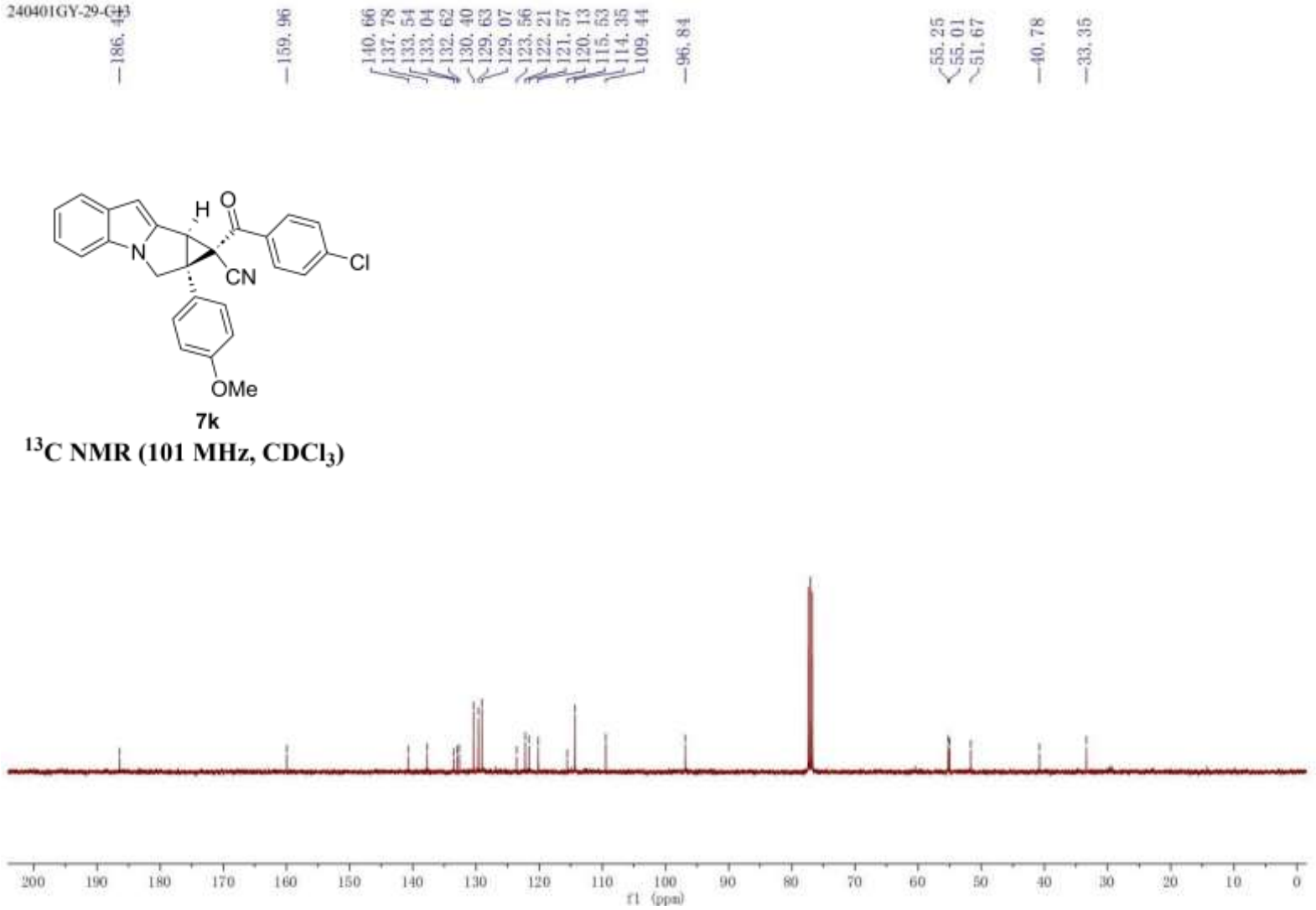


Figure 82. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **7k**

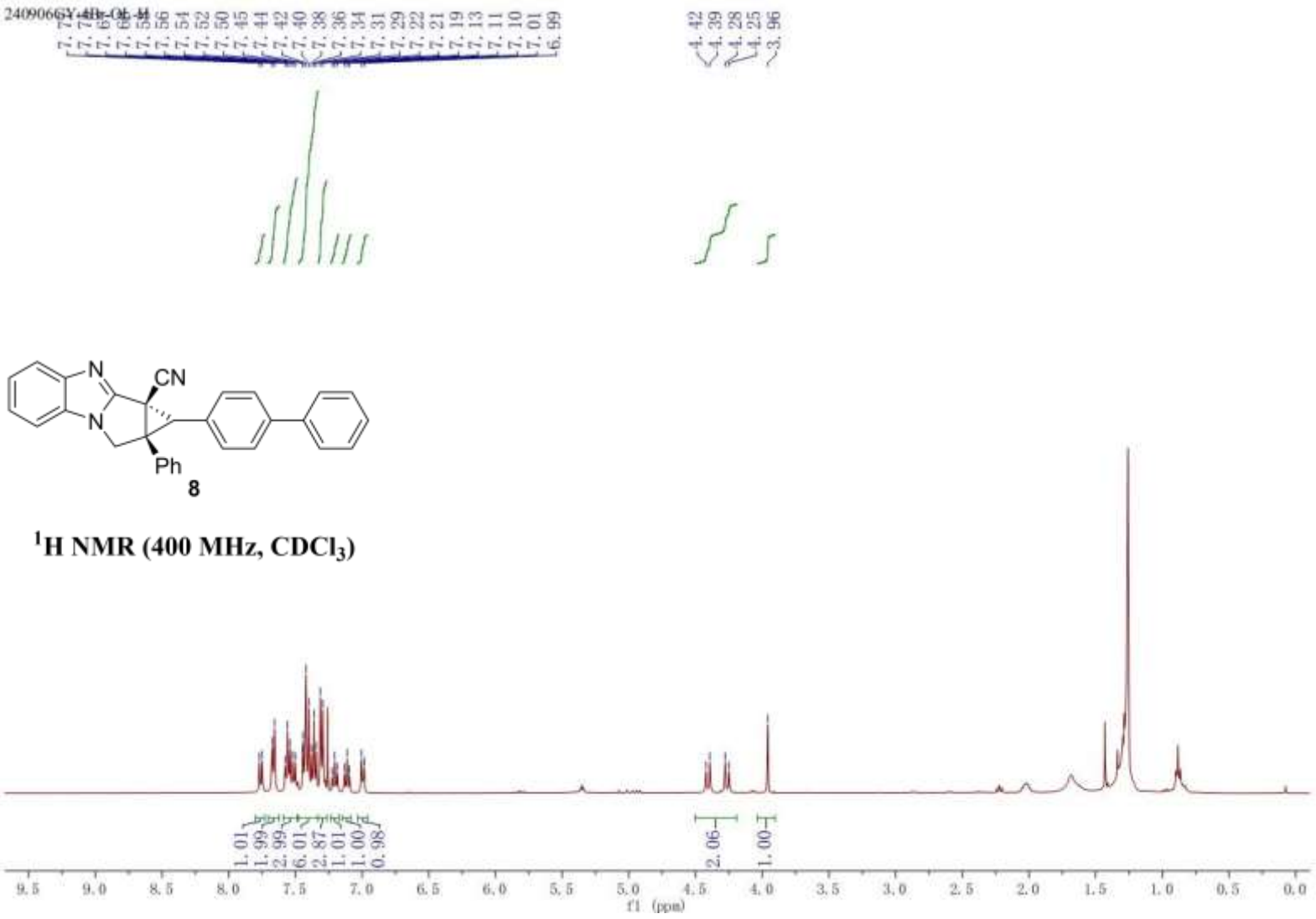


Figure 83. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **8**

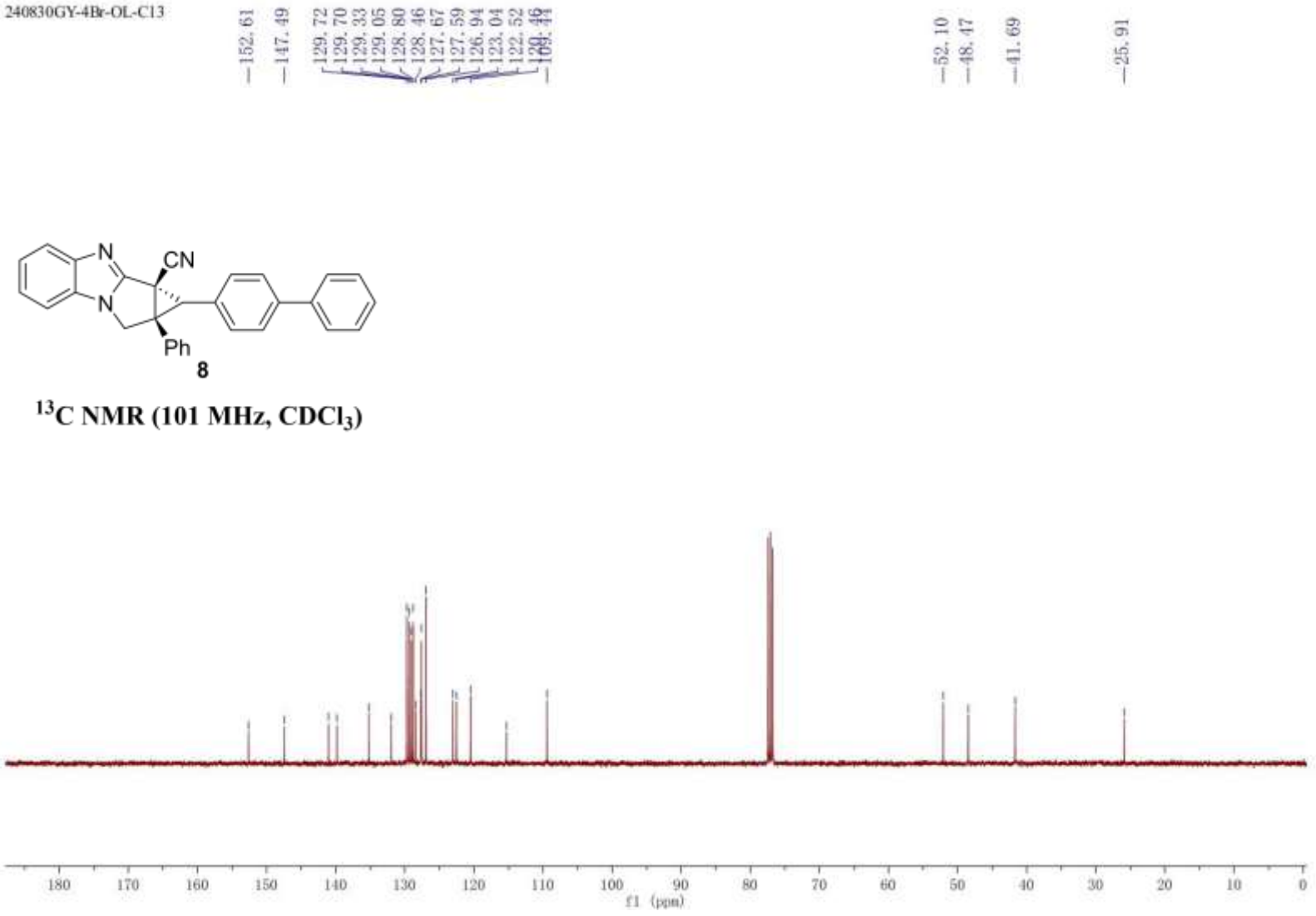


Figure 84. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of compound **8**