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Supporting Information

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**Supporting information for**

# New synthesis of pyrazolo[3,4-*b*]pyridine derivatives based on 5-aminopyrazole and azlactones

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# Photophysical properties

**Table S1:** The data of absorption and fluorescence spectra of compounds **5a–i**[a]

| Compound | Ar | UV-VIS | | | | Photoluminescence | |
|---|---|---|---|---|---|---|---|
| | | $^{max}\lambda_{abs}$, nm | ε, $10^3$, $M^{-1}\cdot cm^{-1}$ (λ, nm) | $\lambda_{ex}$, nm | $^{max}\lambda_{em}$, nm | Stokes shift, nm, eV | Quantum yield $\Phi_f$[b] |
| **5a** | $C_6H_5$ | 281, 358 | 18.9 ± 0.6 (358) | 350, 360 | 439 | 81, 0.64 | 0.54 ± 0.01 |
| **5b** | 4-$MeC_6H_4$ | 284, 357 | 19.1 ± 0.5 (357) | 350, 360 | 435 | 78, 0.62 | 0.45 ± 0.01 |
| **5c** | 4-$MeOC_6H_4$ | 247, 289, 359 | 19.9 ± 0.2 (359) | 350, 355 | 428 | 69, 0.56 | 0.52 ± 0.01 |
| **5d** | 3,4-$(MeO)_2C_6H_3$ | 257, 288, 360 | 18.8 ± 0.2 (360) | 350, 355 | 435 | 75, 0.59 | 0.45 ± 0.01 |
| **5e** | 3,4,5-$(MeO)_3C_6H_2$ | 250, 288, 359 | 22.9 ± 0.6 (359) | 350, 355 | 447 | 88, 0.68 | 0.34 ± 0.01 |
| **5f** | 4-$FC_6H_4$ | 281, 359 | 14.5 ± 0.6 (359) | 345, 350 | 438 | 79, 0.62 | 0.54 ± 0.01 |
| **5g** | 4-$ClC_6H_4$ | 282, 360 | 19.9 ± 0.6 (360) | 350, 355 | 451 | 91, 0.69 | 0.56 ± 0.01 |
| **5h** | 2-Th | 250, 290, 367 | - | 350, 360 | 454 | 87, 0.65 | 0.23 ± 0.01 |
| **5i** | 2-Fu | 290, 299, 381, 393 | 19.1 ± 0.4 (393) | 370, 380 | 447 | 54, 0.38 | 0.50 ± 0.01 |

[a]In EtOH solution, $c = 10^{-6}$–$10^{-5}$ mol·$L^{-1}$. [b]Quantum yield determined relative to quinine sulfate standard in 0.5 M $H_2SO_4$ ($\Phi_f = 0.546$).

**Table S2:** The data of absorption and fluorescence spectra of compounds **6a–i**[a]

| Compound | Ar | UV-VIS | | | | Photoluminescence | |
|---|---|---|---|---|---|---|---|
| | | $^{max}\lambda_{abs}$, nm | ε, $10^3$, $M^{-1}\cdot cm^{-1}$ (λ, nm) | $\lambda_{ex}$, nm | $^{max}\lambda_{em}$, nm | Stokes shift, nm; eV | Quantum yield $\Phi_f$[b] |
| **6a** | $C_6H_5$ | 273, 333 | 16.2 ± 0.7 (273) | 330, 350 | 427 | 94; 0.82 | 0.31 ± 0.01 |
| **6b** | 4-$MeC_6H_4$ | 244, 271, 333 | 16.0 ± 0.9 (271) | 325, 335 | 419 | 86; 0.76 | 0.18 ± 0.01 |
| **6c** | 4-$MeOC_6H_4$ | 273, 331 | 22.1 ± 0.7 (273) | 330, 340 | 413 | 82; 0.74 | 0.16 ± 0.01 |
| **6d** | 3,4-$(MeO)_2C_6H_3$ | 277, 331 | 19.6 ± 0.2 (277) | 330, 340 | 415 | 84; 0.76 | 0.17 ± 0.01 |
| **6e** | 3,4,5-$(MeO)_3C_6H_2$ | 272, 331 | 19.6 ± 0.4 (272) | 330, 340 | 427 | 96; 0.84 | 0.26 ± 0.01 |
| **6f** | 4-$FC_6H_4$ | 270, 330 | 17.3 ± 0.4 (270) | 330, 340 | 421 | 91; 0.81 | 0.19 ± 0.01 |
| **6g** | 4-$ClC_6H_4$ | 269, 332 | 17.7 ± 0.6 (269) | 330, 340 | 432 | 100; 0.86 | 0.25 ± 0.01 |
| **6h** | 2-Th | 269, 335 | 17.5 ± 0.5 (269) | 330, 340 | 441 | 106; 0.89 | 0.04 ± 0.00 |
| **6i** | 2-Fu | 273, 344 | 20.7 ± 0.3 (273) | 330, 340 | 434 | 90; 0.75 | 0.14 ± 0.01 |

[a]In EtOH solution, $c = 10^{-6}$–$10^{-5}$ mol·$L^{-1}$. [b]Quantum yield determined relative to quinine sulfate standard in 0.5 M $H_2SO_4$ ($\Phi_f = 0.546$).

# Crystal structure determination

The unit cell parameters and the X-ray diffraction intensities were measured on a Xcalibur Ruby diffractometer (Agilent technologies). The empirical absorption correction was introduced by multi-scan method using SCALE3 ABSPACK algorithm.[1] Using the Olex2,[2] the structures were solved with the SUPERFLIP[3] program and refined by the full-matrix least-squares method in the anisotropic approximation for all non-hydrogen atoms with the SHELXL program.[4] Hydrogen atoms bound to carbon were positioned geometrically and refined using a riding model. The hydrogen atom of OH group was refined independently with isotropic displacement parameters.

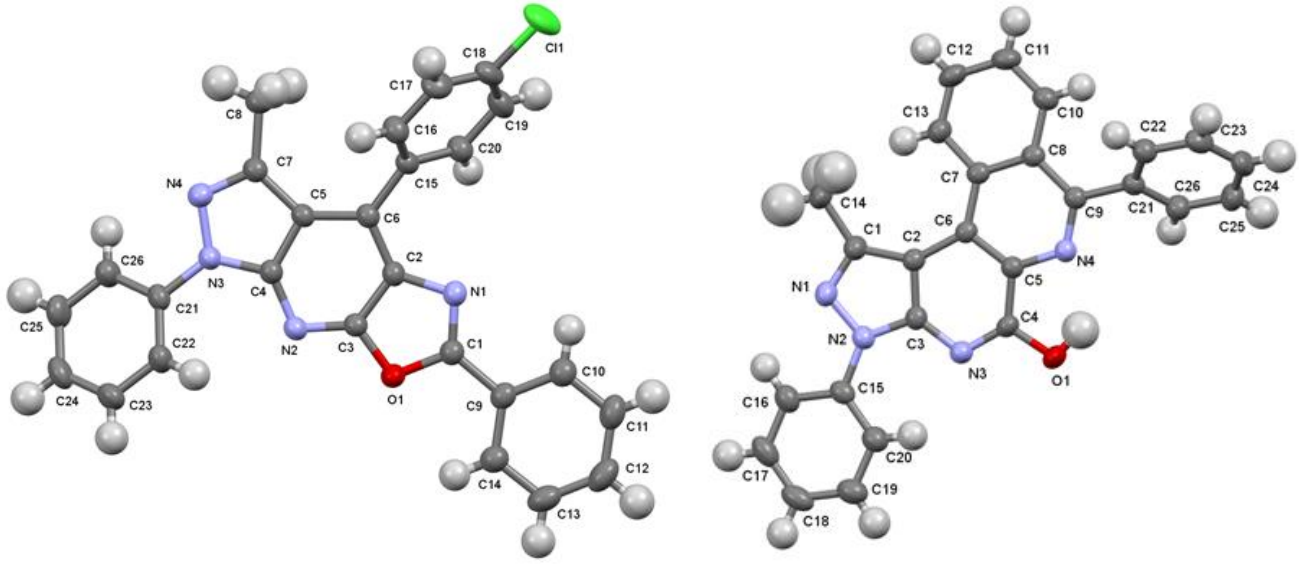



**Figure S1.** The molecular structure of compound **5g** (left) and **7a** (right) with atoms represented as thermal vibration ellipsoids of 50% probability.

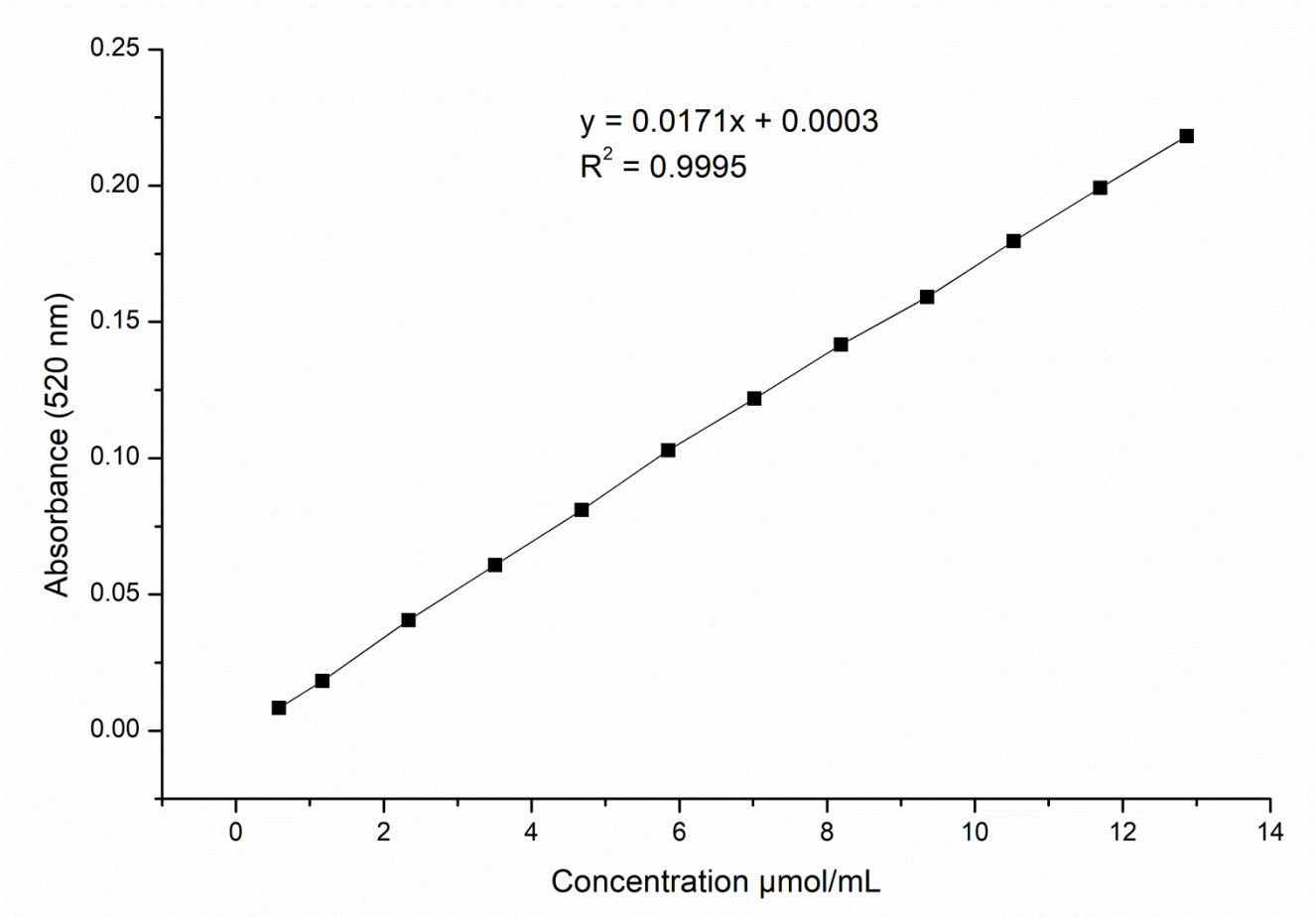
**Table S3.** Crystal data and structure refinement for compounds **5g** (CCDC 2300767) and **7a** (CCDC 2300766).

| **Compound** | **5g** | **7a** |
|---|---|---|
| Empirical formula | $C_{26}H_{17}ClN_4O$ | $C_{26}H_{18}N_4O$ |
| Formula weight | 436.89 | 402.44 |
| Temperature, K | 295(2) | 295(2) |
| Crystal system | triclinic | monoclinic |
| Space group | P-1 | $P2_1/n$ |
| a, Å | 7.6427(11) | 15.381(4) |
| b, Å | 11.5300(18) | 6.900(2) |
| c, Å | 13.554(2) | 19.486(5) |
| α, ° | 108.018(14) | 90 |
| β, ° | 97.654(12) | 108.73(3) |
| γ, ° | 105.703(13) | 90 |
| Volume, $Å^3$ | 1062.3(3) | 1958.5(10) |
| Z | 2 | 4 |

| Continuation of Table S3 | | |
|---|---|---|
| Density (calculated), g/cm$^3$ | 1.366 | 1.365 |
| Absorption coefficient, mm$^{-1}$ | 0.207 | 0.086 |
| F(000) | 452.0 | 840.0 |
| Crystal size, mm$^3$ | 0.6 × 0.35 × 0.15 | 0.55 × 0.08 × 0.07 |
| Radiation | Mo Kα (λ = 0.71073) | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection, ° | 3.936 to 58.53 | 5.594 to 58.558 |
| Index ranges | -9 ≤ h ≤ 10, -15 ≤ k ≤ 13, -16 ≤ l ≤ 18 | -20 ≤ h ≤ 20, -9 ≤ k ≤ 6, -25 ≤ l ≤ 25 |
| Reflections collected | 8948 | 11604 |
| Independent reflections | 4925 [$R_{int}$ = 0.0275, $R_{sigma}$ = 0.0451] | 4662 [$R_{int}$ = 0.0360, $R_{sigma}$ = 0.0487] |
| Data/restraints/parameters | 4925/0/290 | 4662/0/285 |
| Goodness-of-fit on F$^2$ | 1.040 | 1.027 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0478, $wR_2$ = 0.1137 | $R_1$ = 0.0615, $wR_2$ = 0.1371 |
| Final R indexes [all data] | $R_1$ = 0.0665, $wR_2$ = 0.1326 | $R_1$ = 0.0969, $wR_2$ = 0.1675 |
| Largest diff. peak/hole, eÅ$^{-3}$ | 0.20/-0.36 | 0.23/-0.26 |

# Antioxidant activity

Dependences of the optical density of the Fe (III) - 2,2′-bipyridyl indicator systems on the concentration of ascorbic acid (AA):



# References


1. CrysAlisPro, Agilent Technologies, Version 1.171.37.33 (release 27-03-2014 CrysAlis171 .NET).
2. Dolomanov O.V., Bourhis L.J., Gildea R.J., Howard J.A.K., Puschmann H. *J. Appl. Cryst.*, **2009**, *42*, 339.
3. Palatinus L., Chapuis G. *J. Appl. Cryst.* **2007***, 40*, 786.
4. Sheldrick G.M. *Acta Crystallogr., Sect. C: Struct. Chem.*, **2015**, *71*, 3.

# Copies of NMR spectra

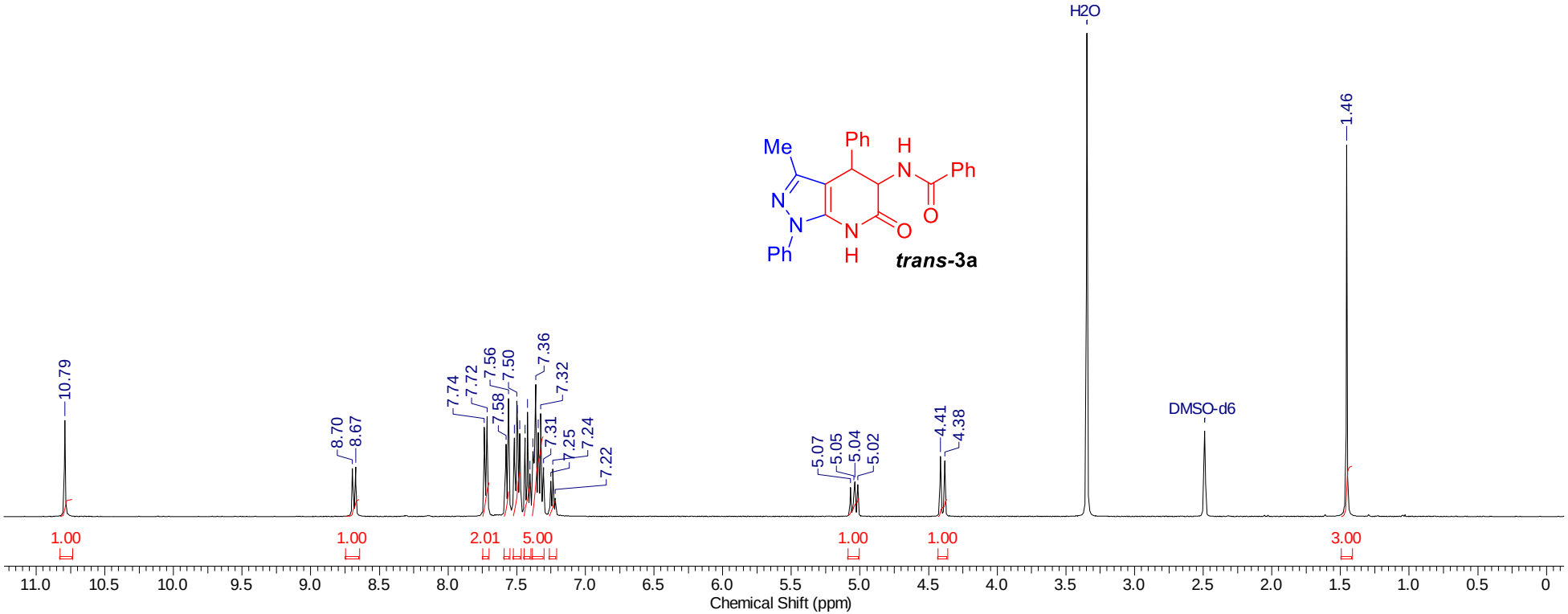



**Figure S2:** $^{1}$H NMR spectrum of compound ***trans*-3a** (DMSO-$d_6$).

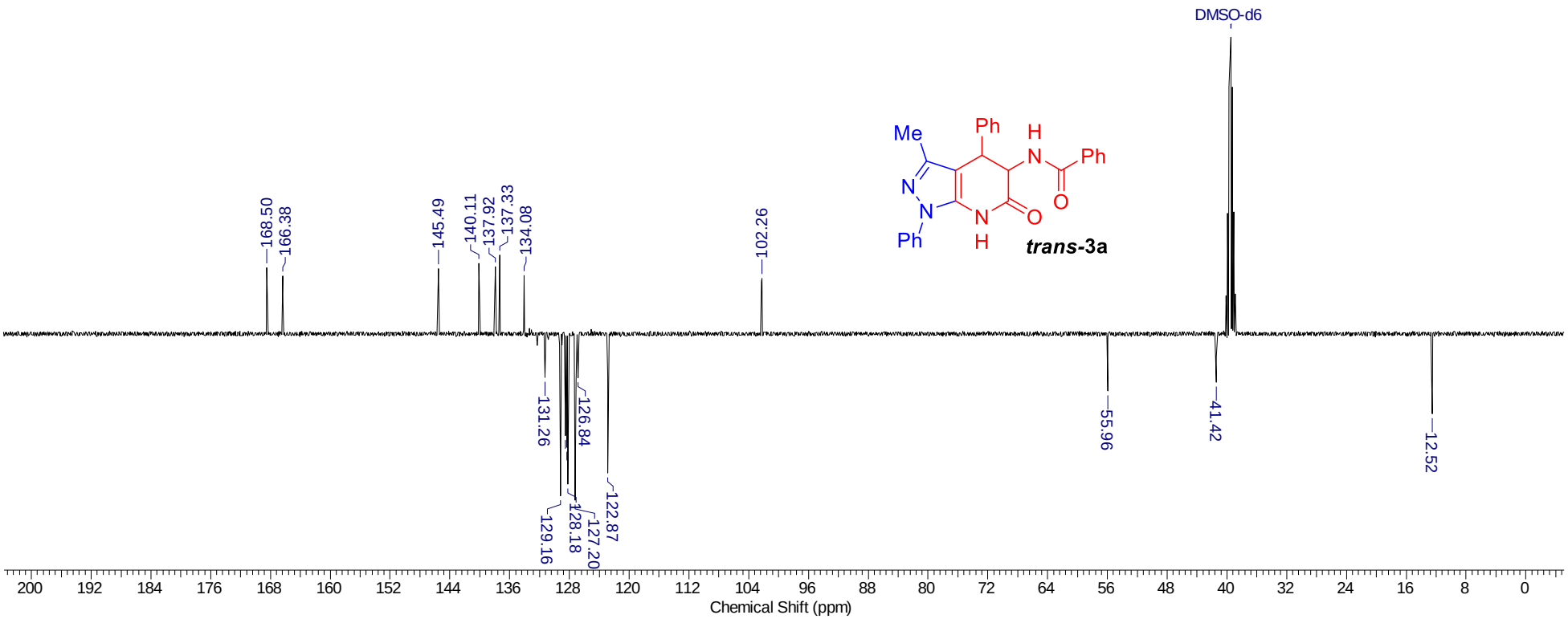



**Figure S3:** $^{13}$C NMR spectrum of compound ***trans*-3a** (DMSO-$d_6$).

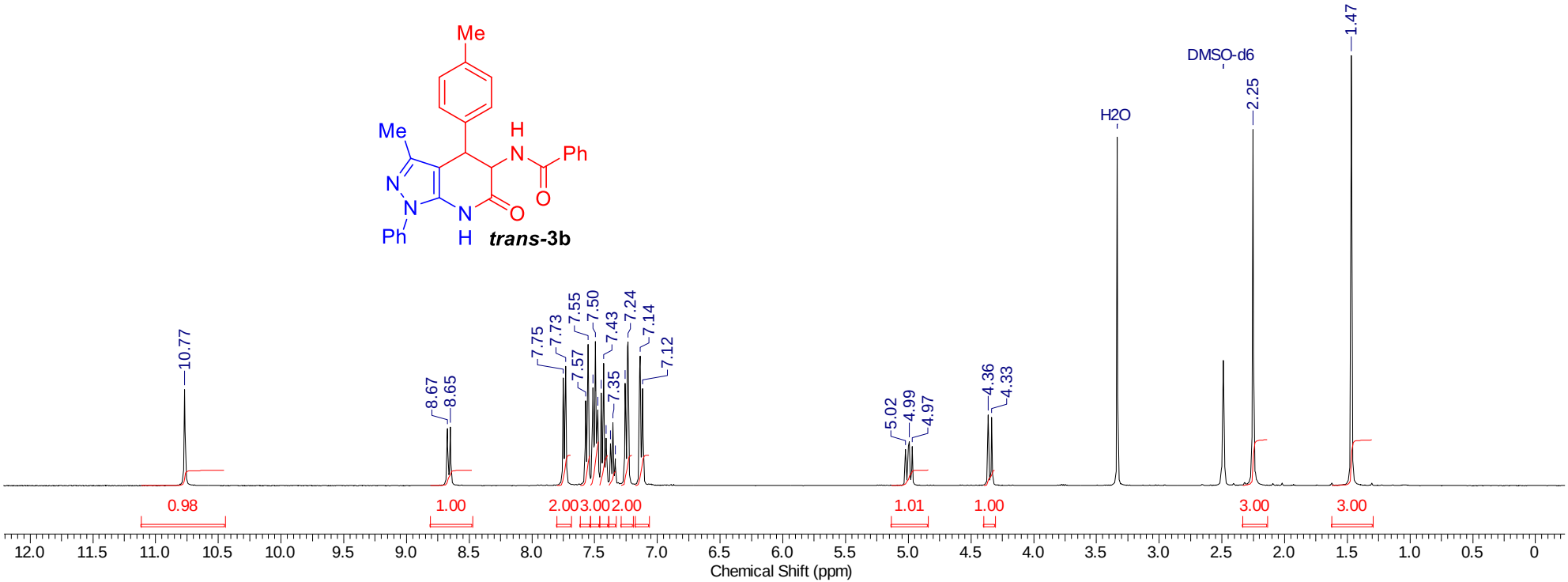



**Figure S4:** $^{1}$H NMR spectrum of compound ***trans*-3b** (DMSO-$d_6$).

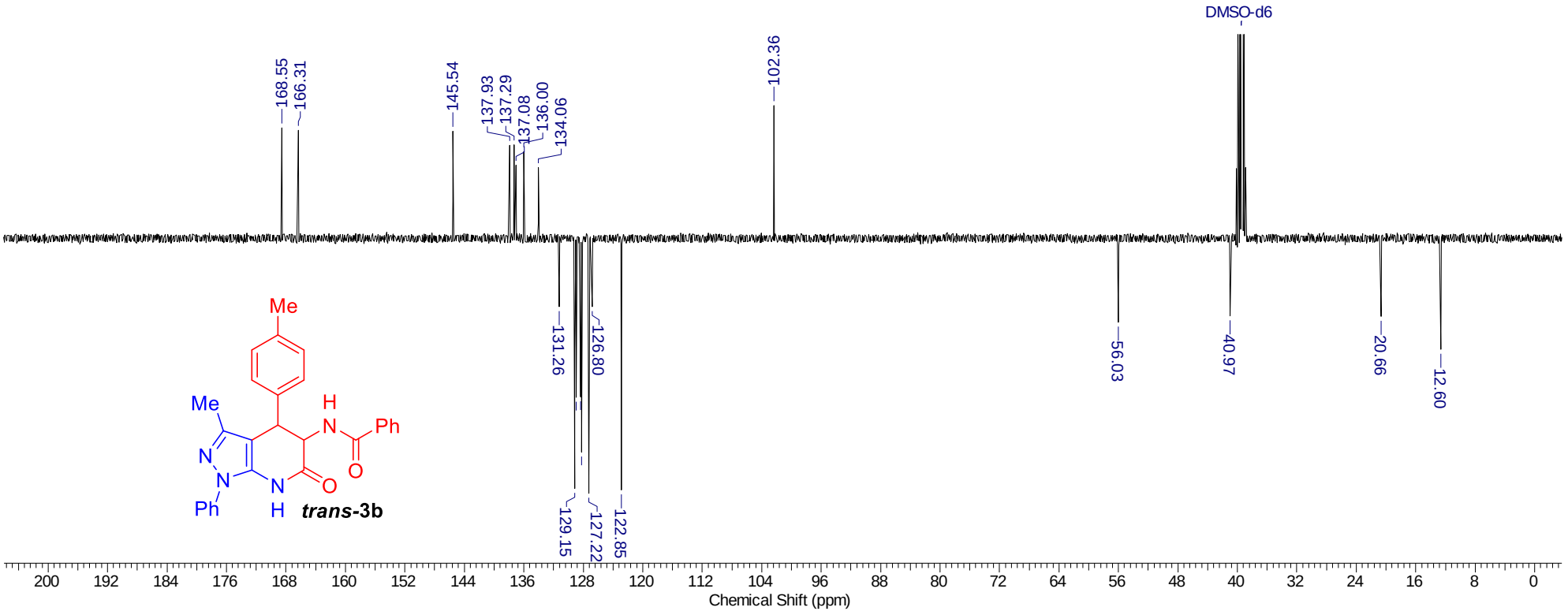



**Figure S5:** $^{13}$C NMR spectrum of compound ***trans*-3b** (DMSO-$d_6$).

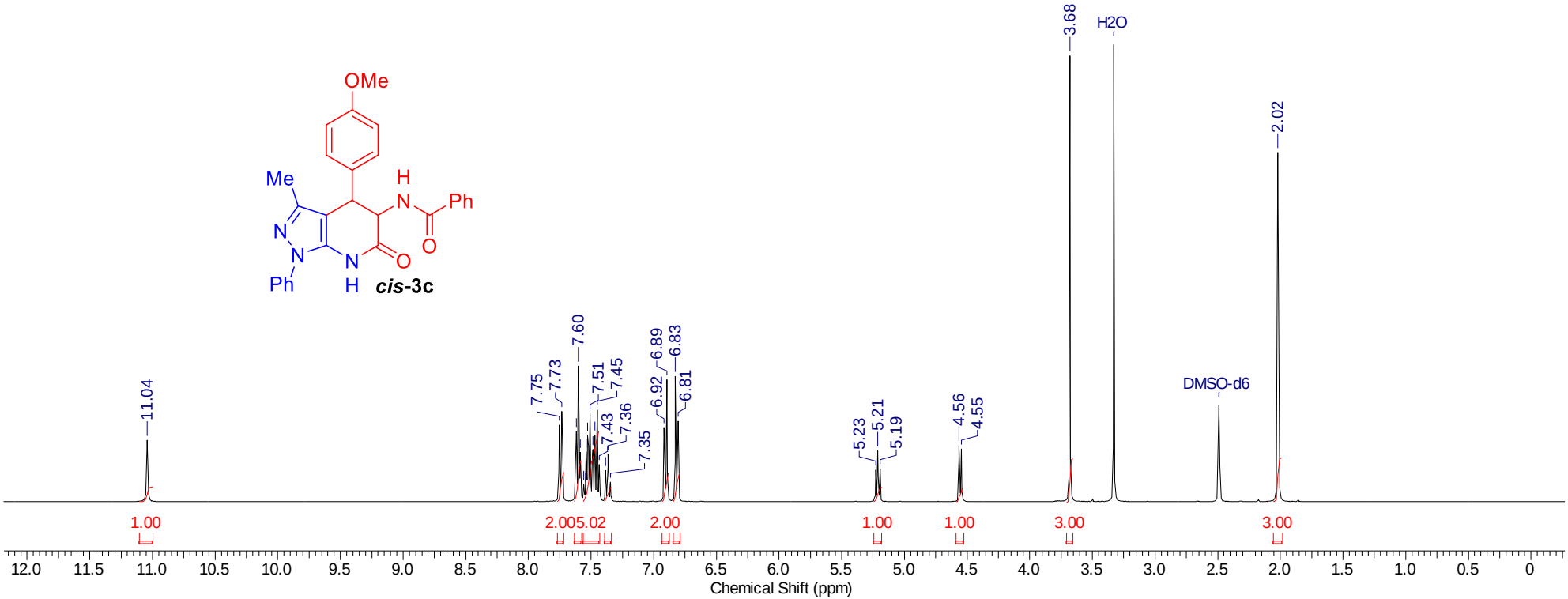



**Figure S6:** $^{1}$H NMR spectrum of compound ***cis*-3c** (DMSO-$d_6$).

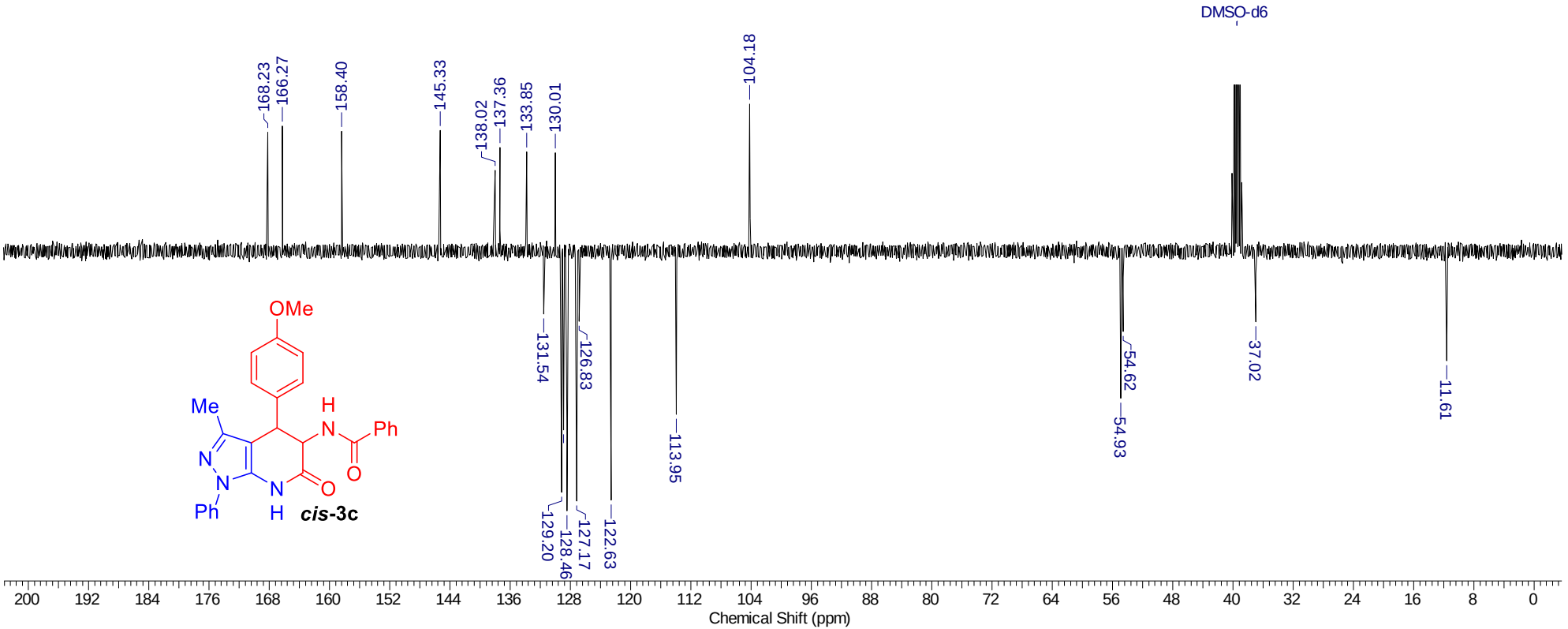



**Figure S7:** $^{13}$C NMR spectrum of compound ***cis*-3c** (DMSO-$d_6$).

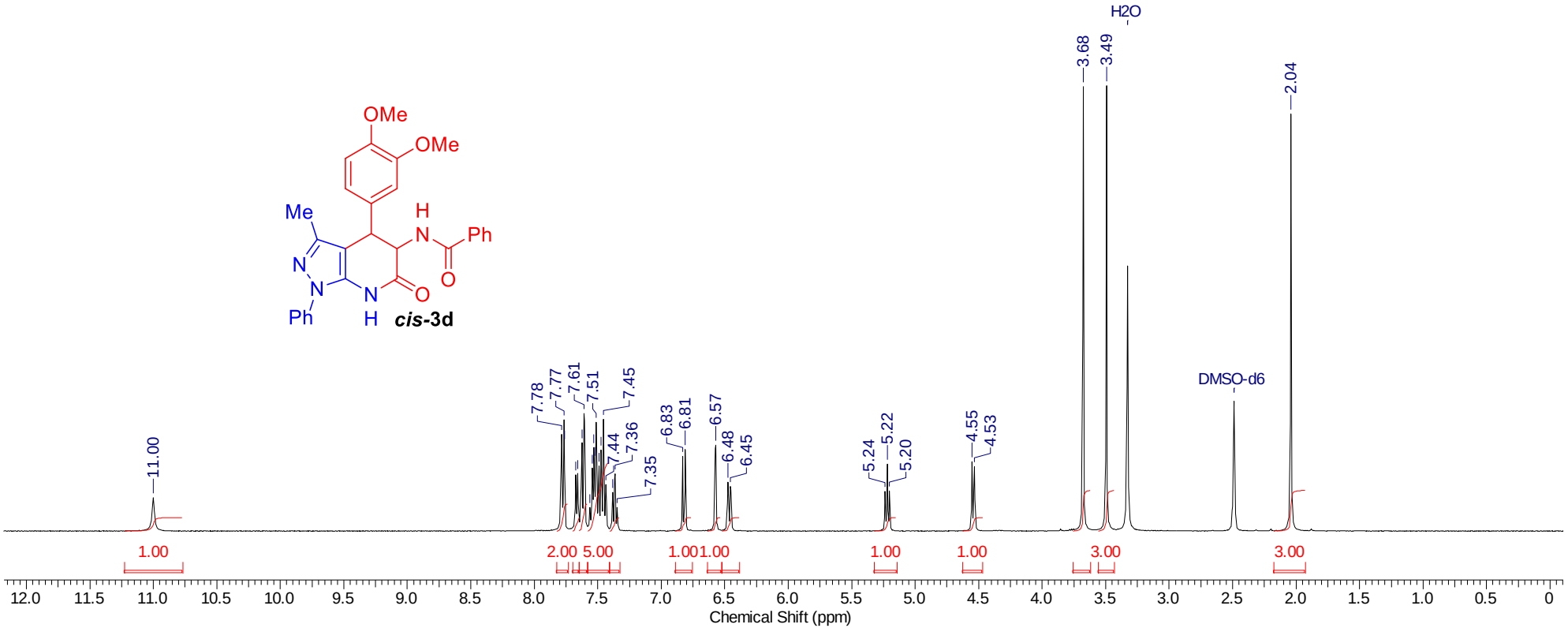



**Figure S8:** $^{1}$H NMR spectrum of compound ***cis*-3d** (DMSO-$d_6$).

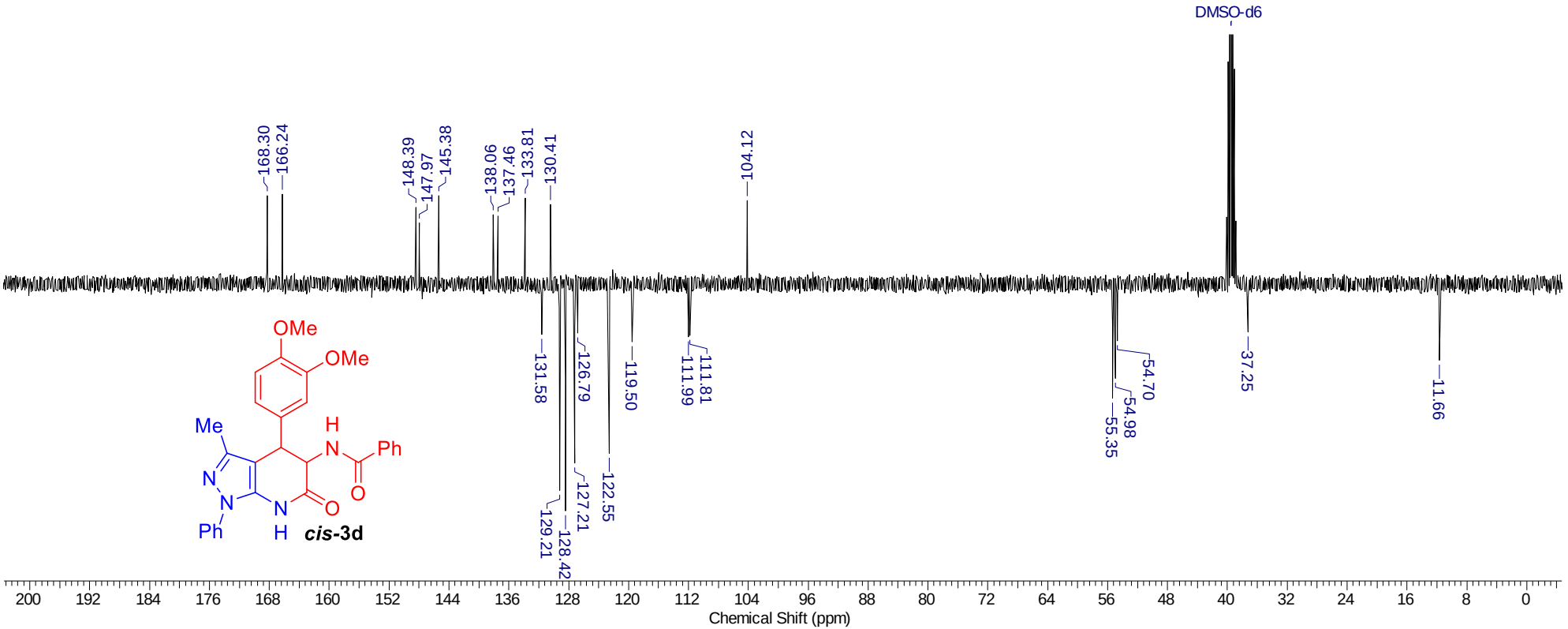



**Figure S9:** $^{13}$C NMR spectrum of compound ***cis*-3d** (DMSO-$d_6$).

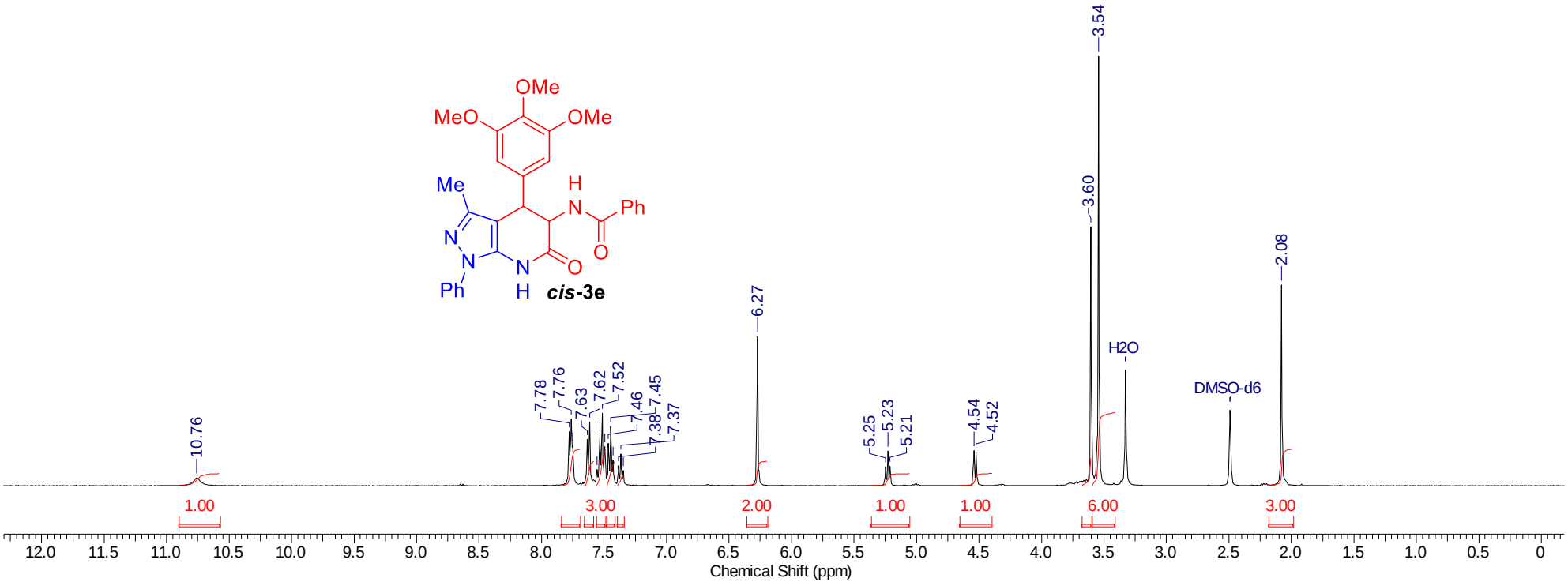



**Figure S10:** $^{1}$H NMR spectrum of compound ***cis*-3e** (DMSO-$d_6$).

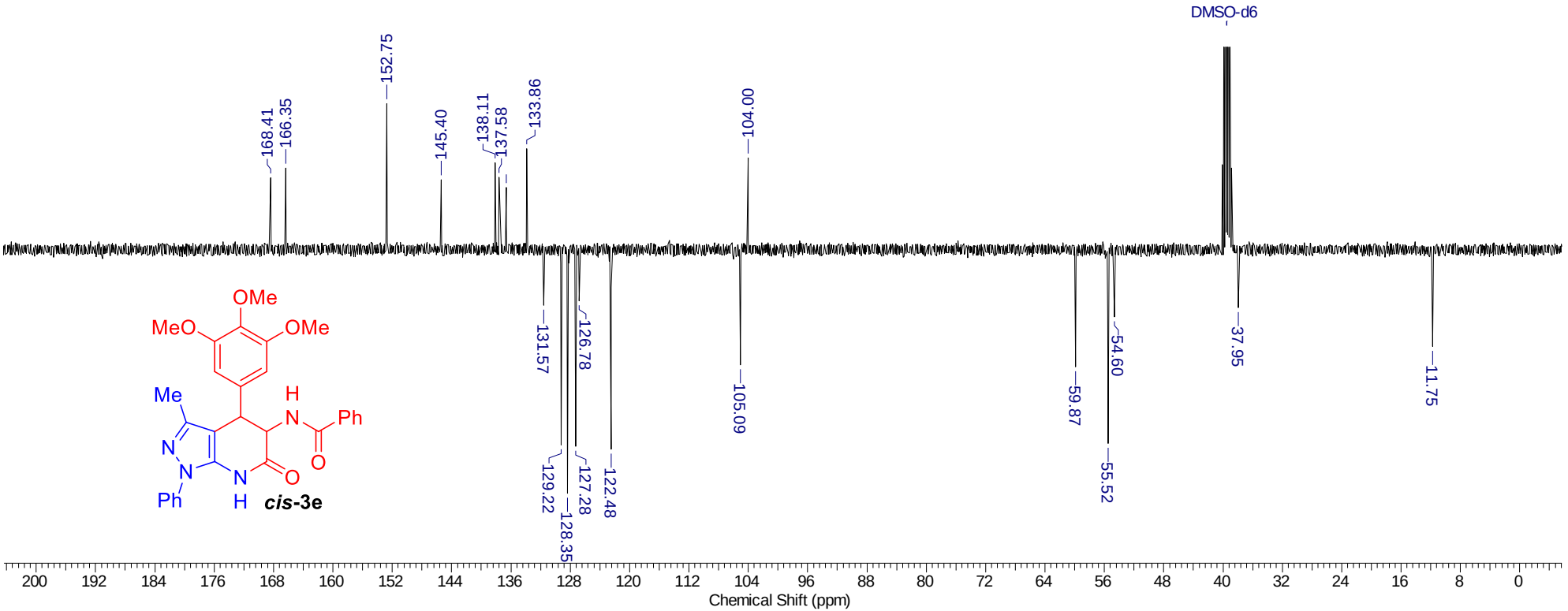



**Figure S11:** $^{13}$C NMR spectrum of compound ***cis*-3e** (DMSO-$d_6$).

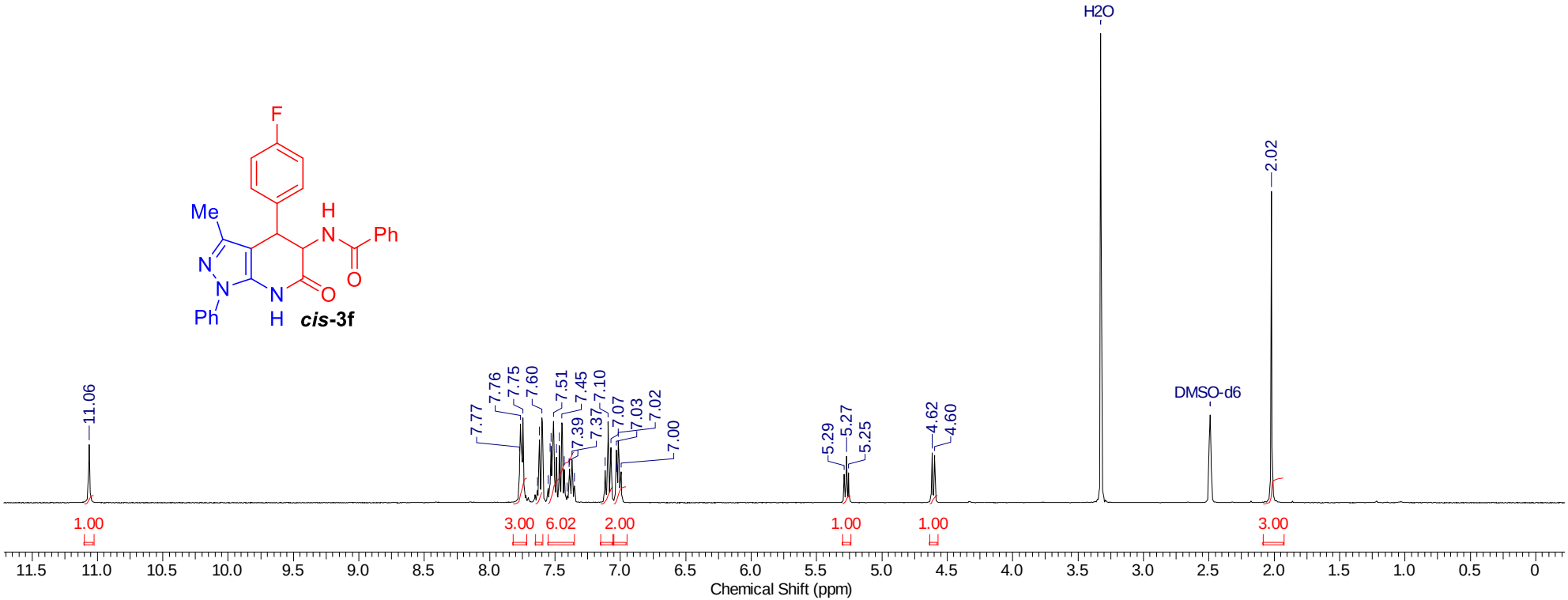



**Figure S12:** $^{1}$H NMR spectrum of compound ***cis*-3f** (DMSO-$d_6$).

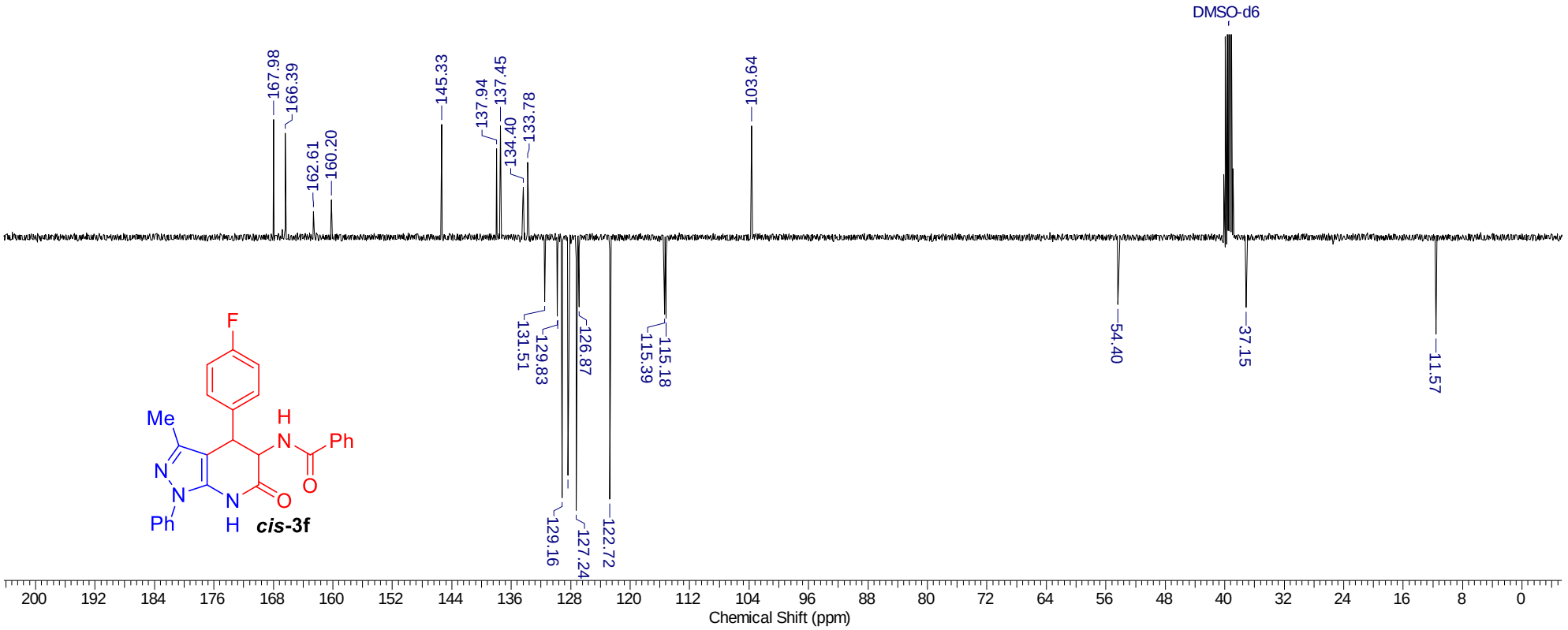



**Figure S13:** $^{13}$C NMR spectrum of compound ***cis*-3f** (DMSO-$d_6$).

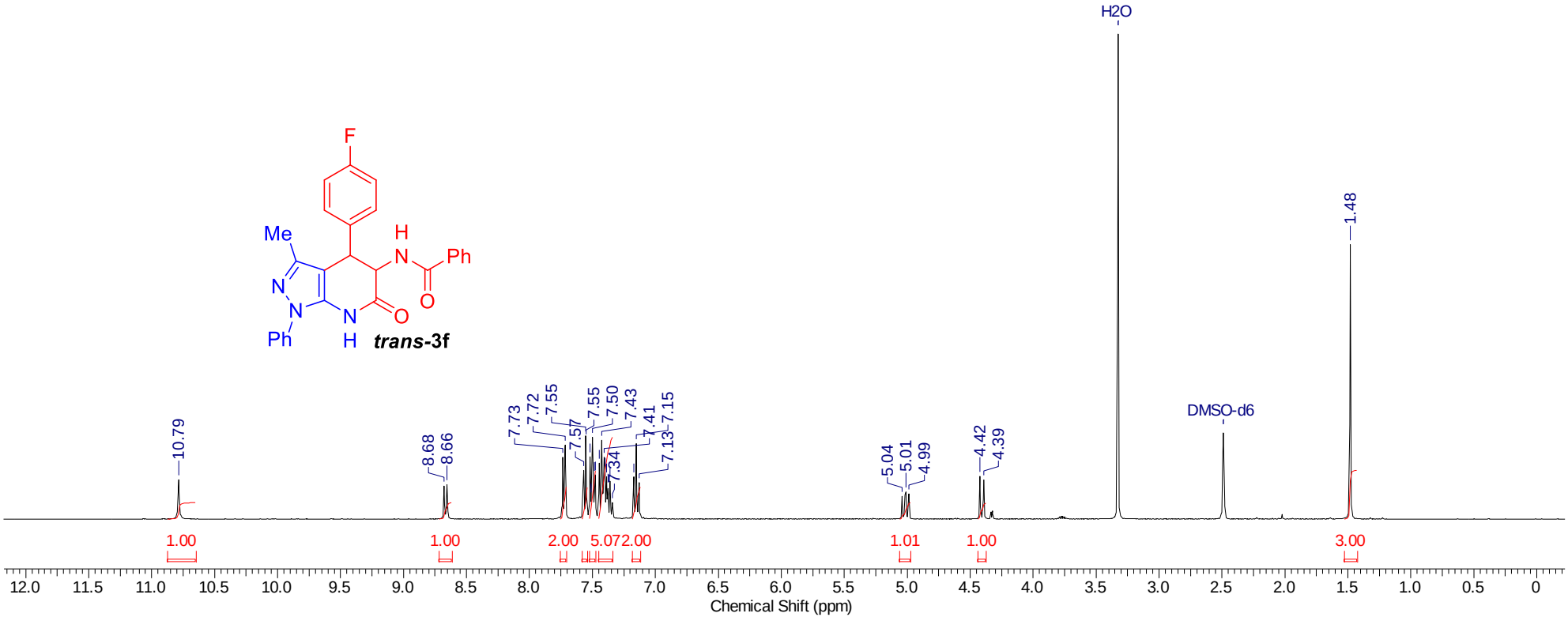



**Figure S14:** $^{1}$H NMR spectrum of compound ***trans*-3f** (DMSO-$d_6$).

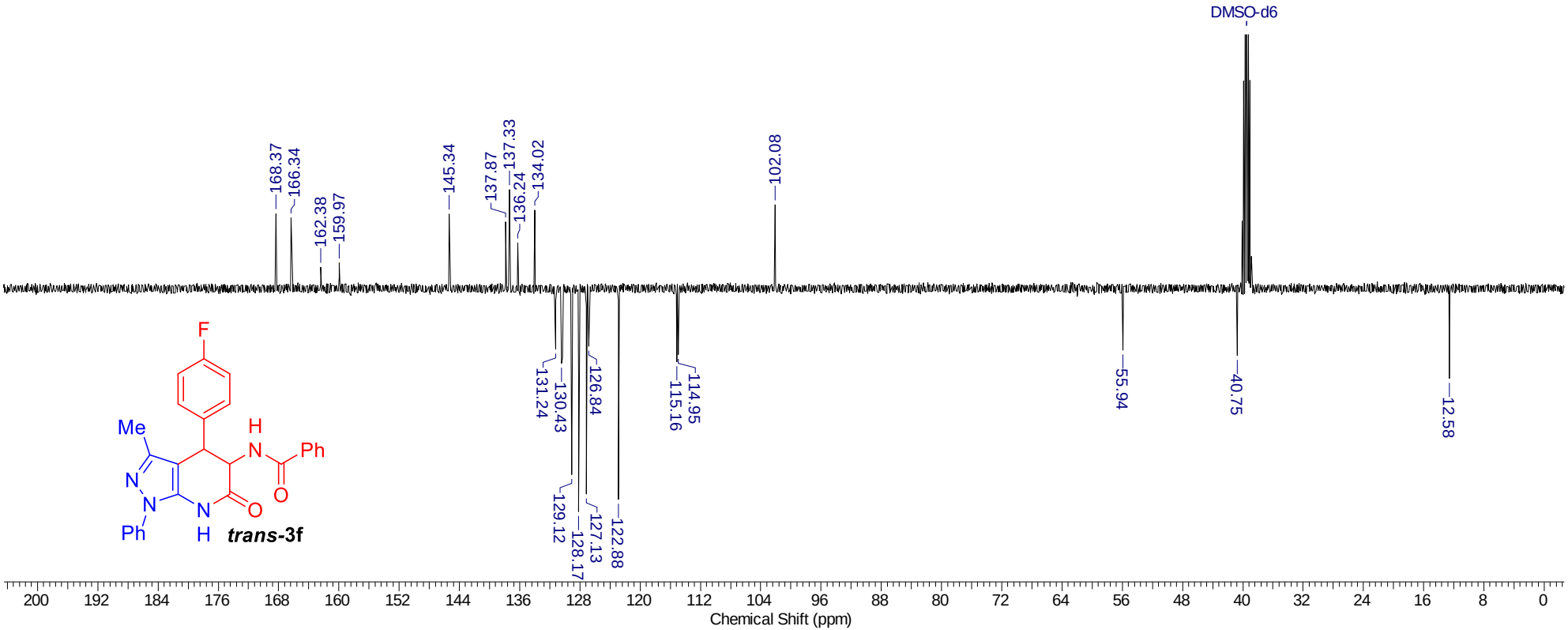



**Figure S15:** $^{13}$C NMR spectrum of compound ***trans*-3f** (DMSO-$d_6$).

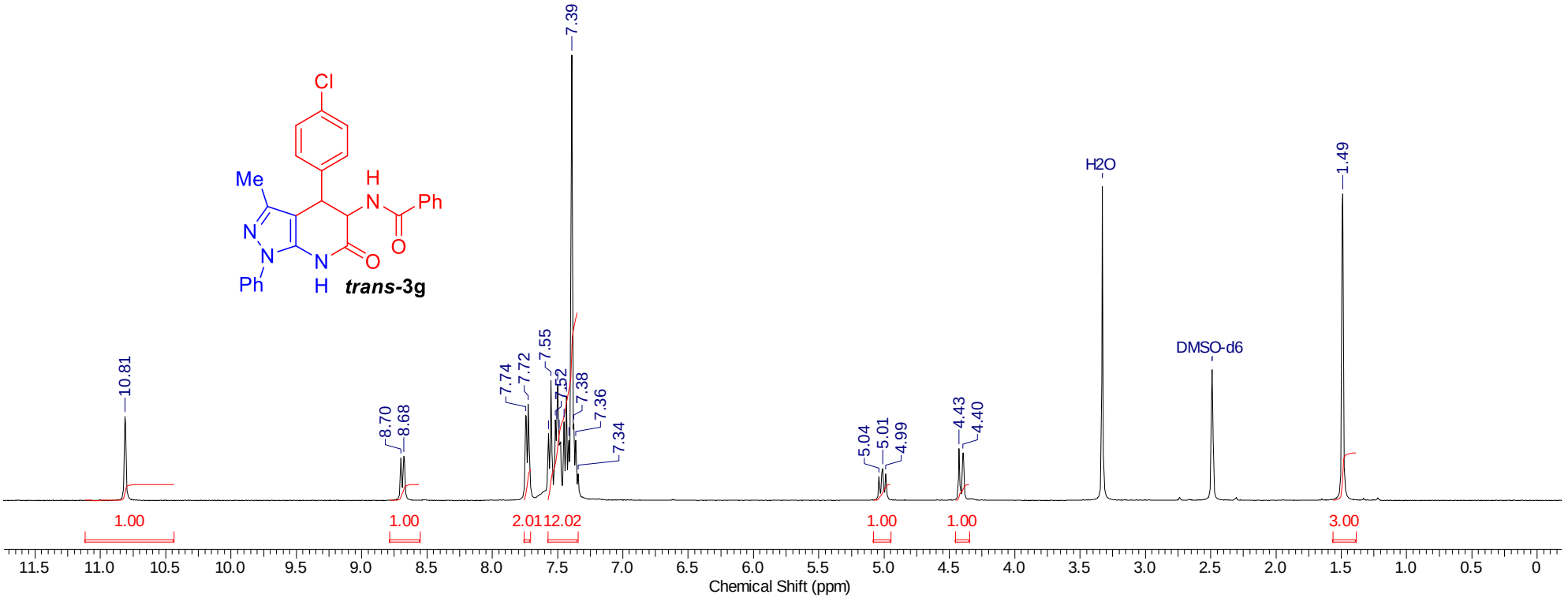



**Figure S16:** $^{1}$H NMR spectrum of compound ***trans*-3g** (DMSO-$d_6$).

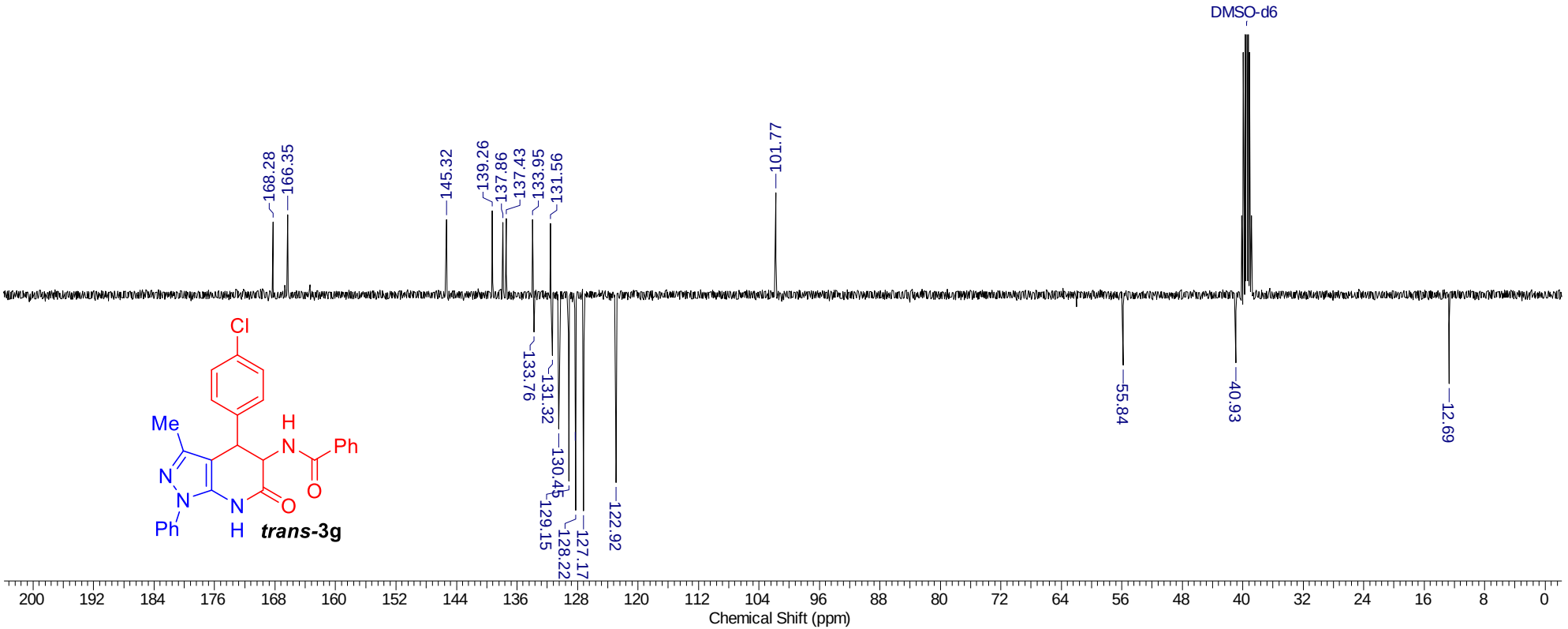



**Figure S17:** $^{13}C$ NMR spectrum of compound ***trans*-3g** (DMSO-$d_6$).

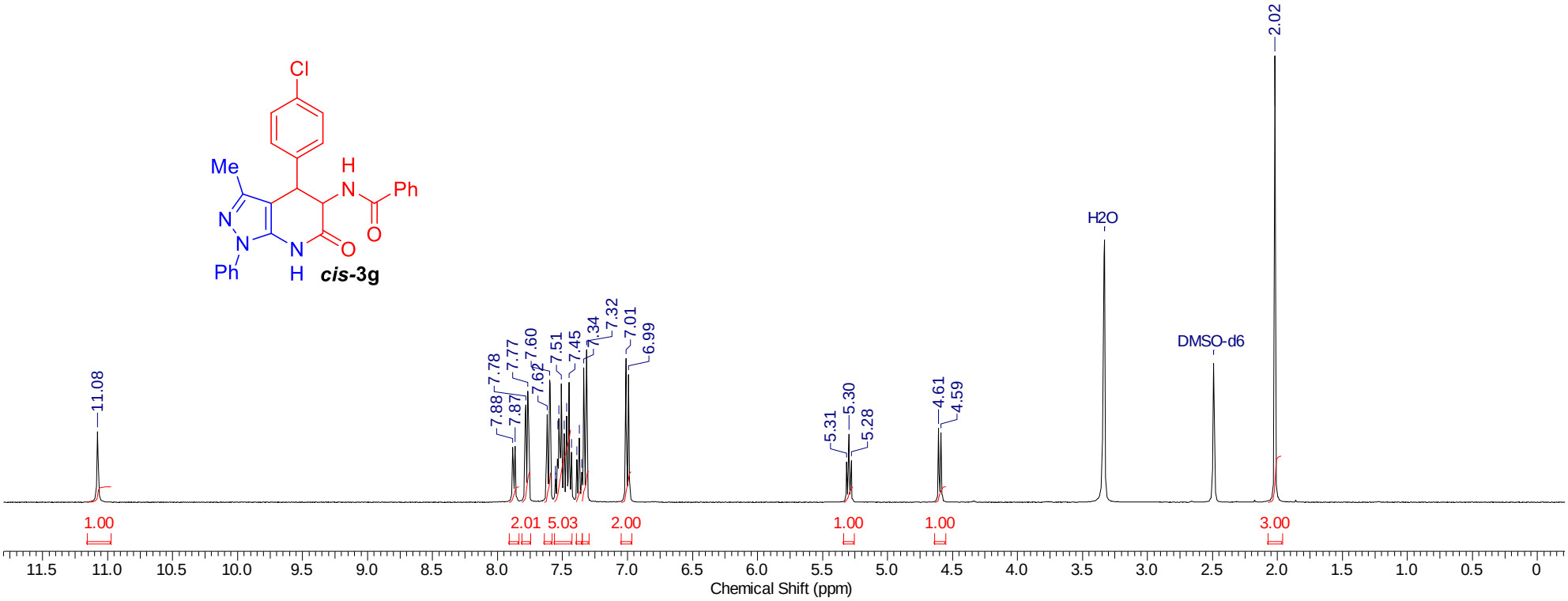



**Figure S18:** $^{1}$H NMR spectrum of compound ***cis*-3g** (DMSO-$d_6$).

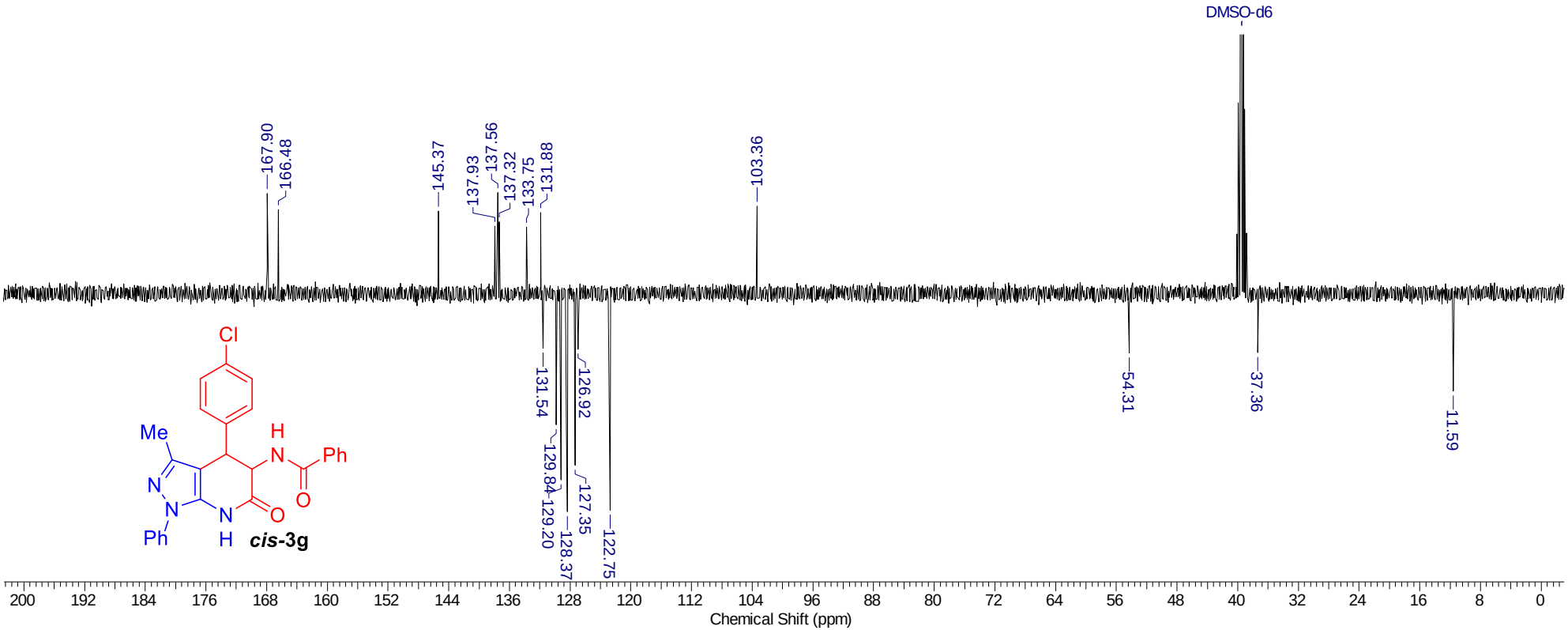



**Figure S19:** $^{13}$C NMR spectrum of compound ***cis*-3g** (DMSO-$d_6$).

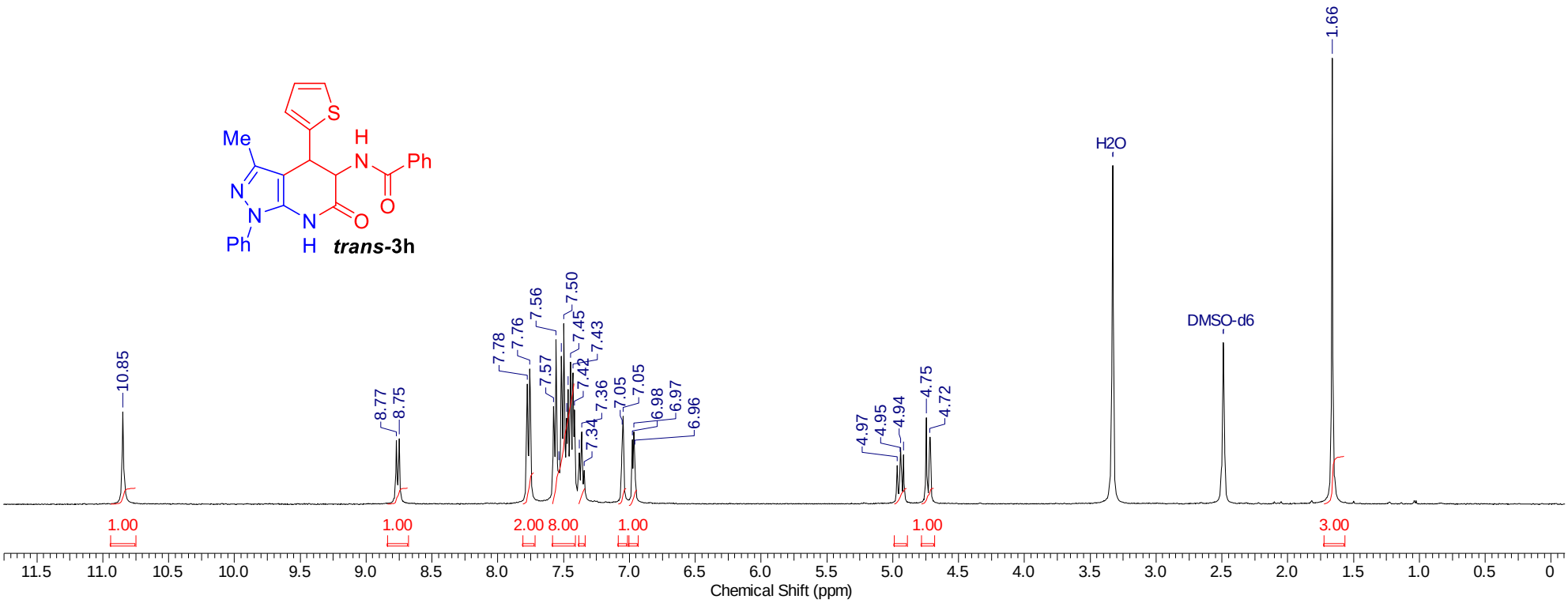



**Figure S20:** $^{1}$H NMR spectrum of compound ***trans*-3h** (DMSO-$d_6$).

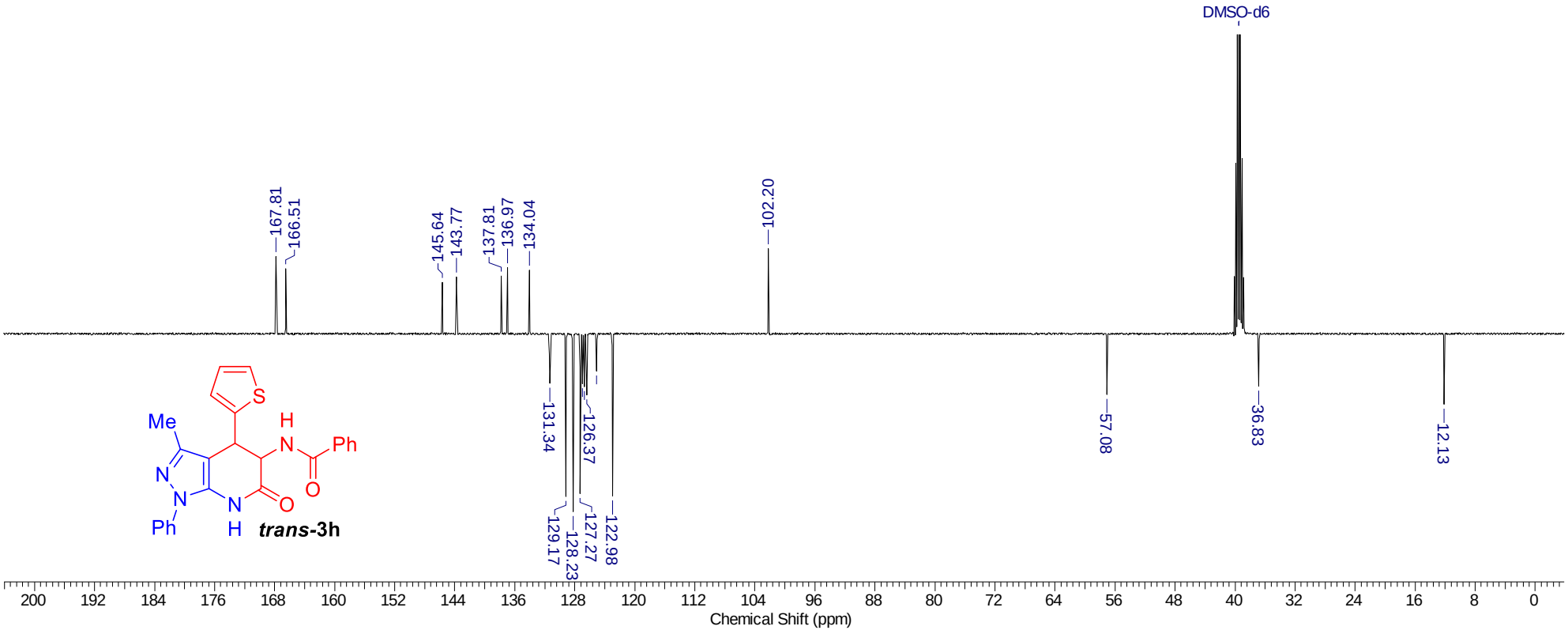



**Figure S21:** $^{13}C$ NMR spectrum of compound ***trans*-3h** (DMSO-$d_6$).

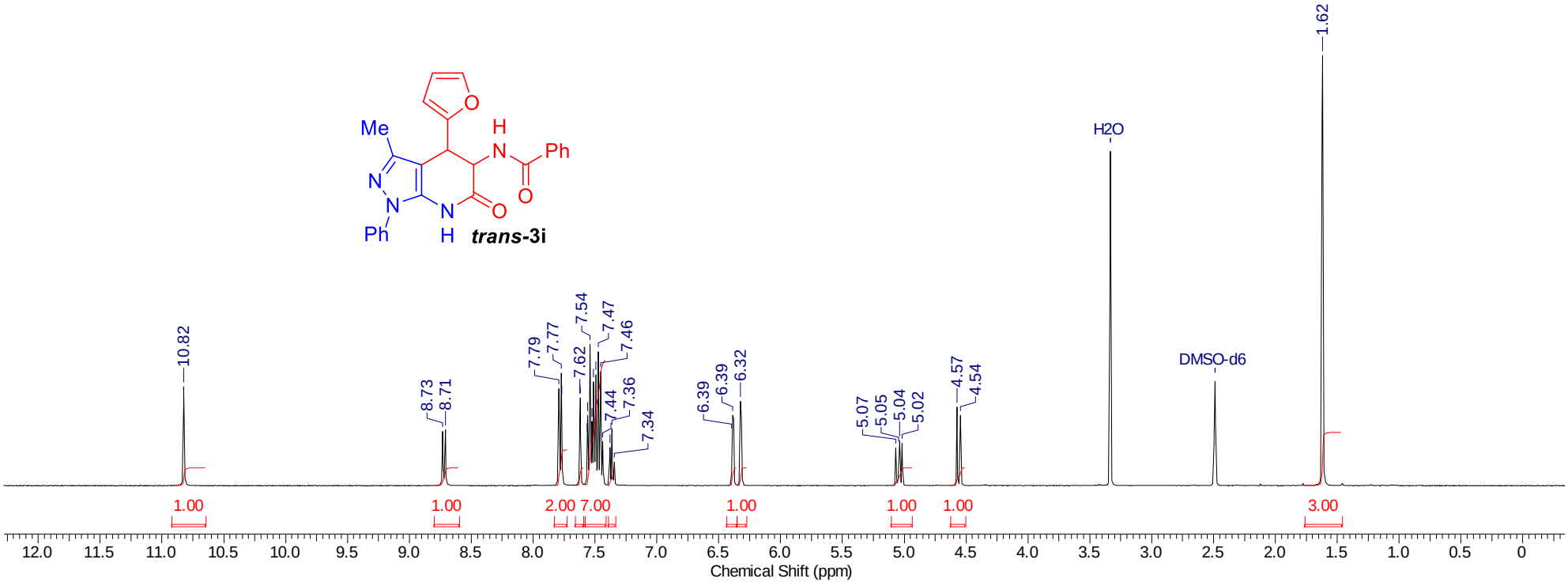



**Figure S22:** $^{1}$H NMR spectrum of compound ***trans*-3i** (DMSO-$d_6$).

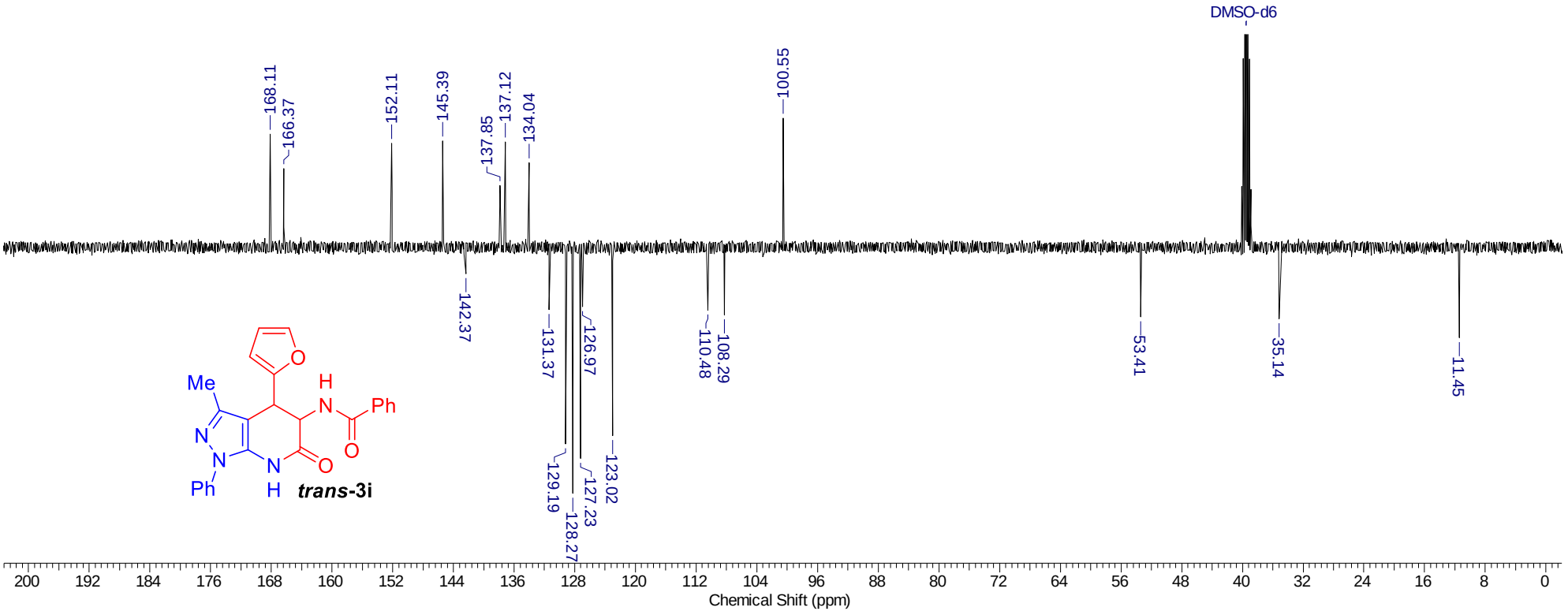



**Figure S23:** $^{13}$C NMR spectrum of compound ***trans*-3i** (DMSO-$d_6$).

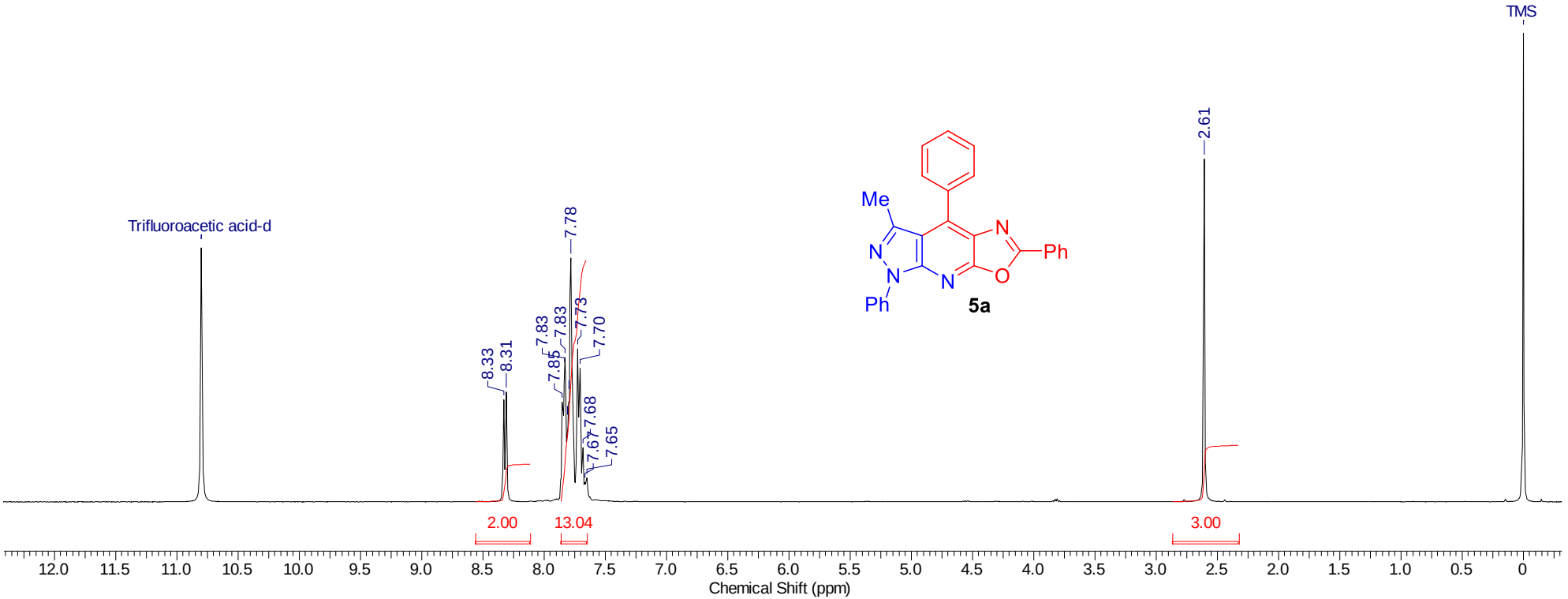



**Figure S24:** $^{1}H$ NMR spectrum of compound **5a** ($CF_3CO_2D$ + TMS).

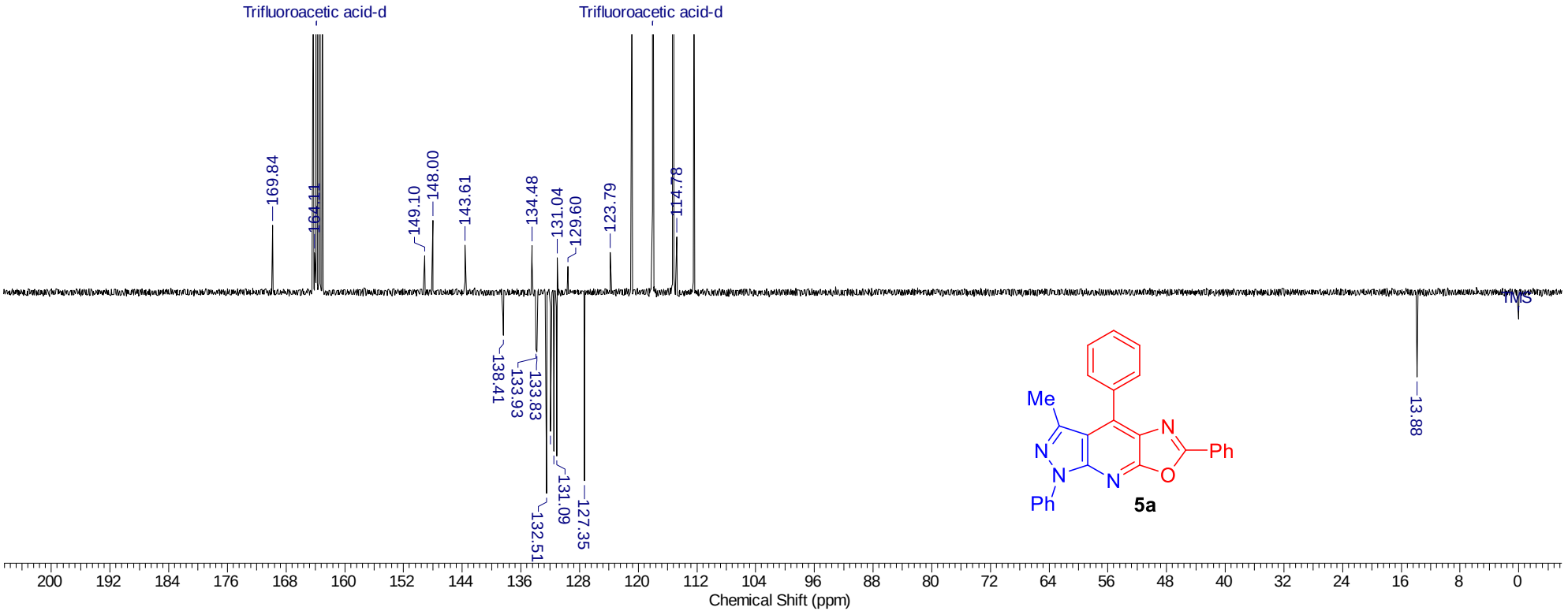



**Figure S25:** $^{13}C$ NMR spectrum of compound **5a** ($CF_3CO_2D$ + TMS).

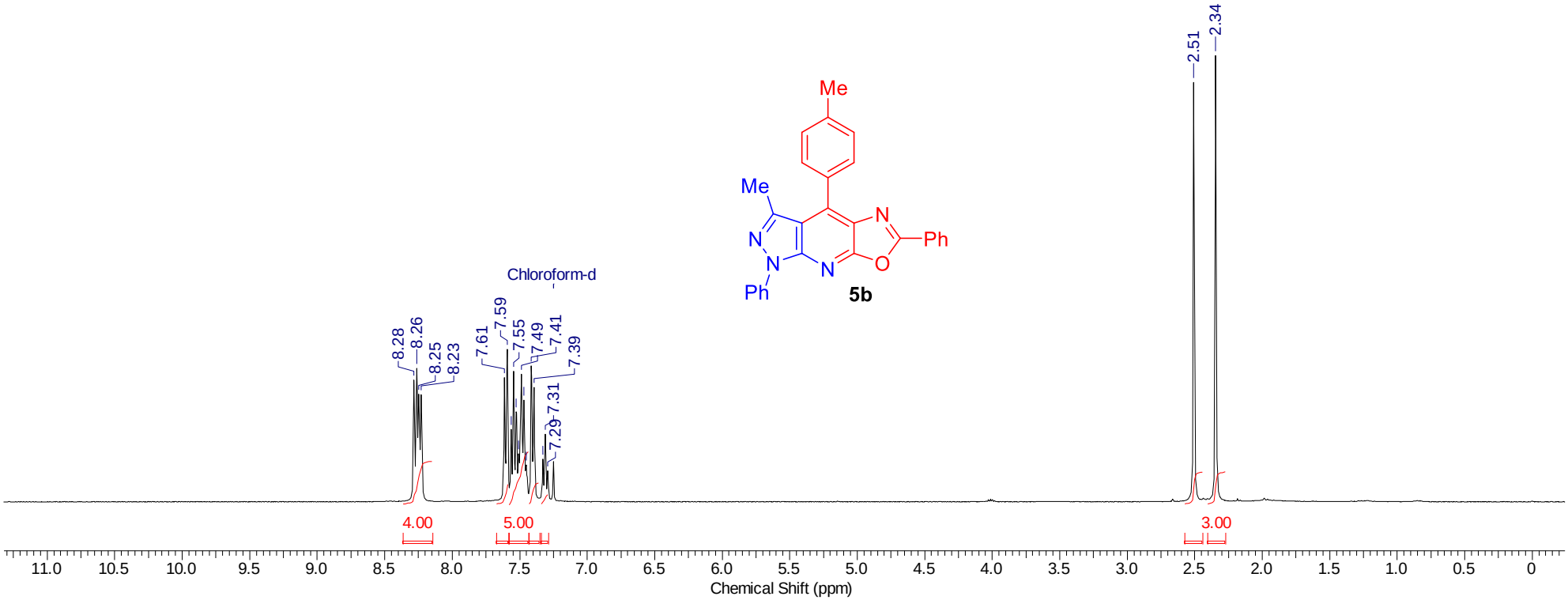



**Figure S26**: $^{1}$H NMR spectrum of compound **5b** ($CDCl_3$).

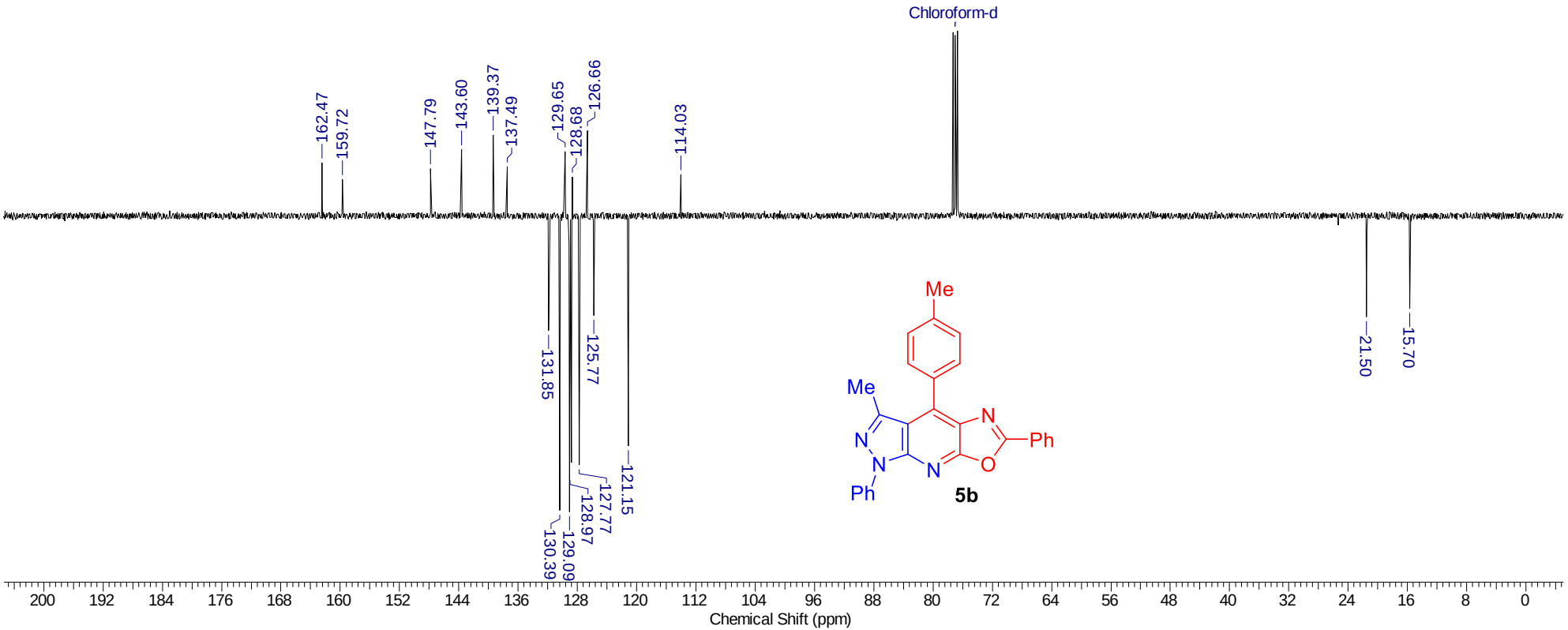



**Figure S27:** $^{13}C$ NMR spectrum of compound **5b** ($CDCl_3$).

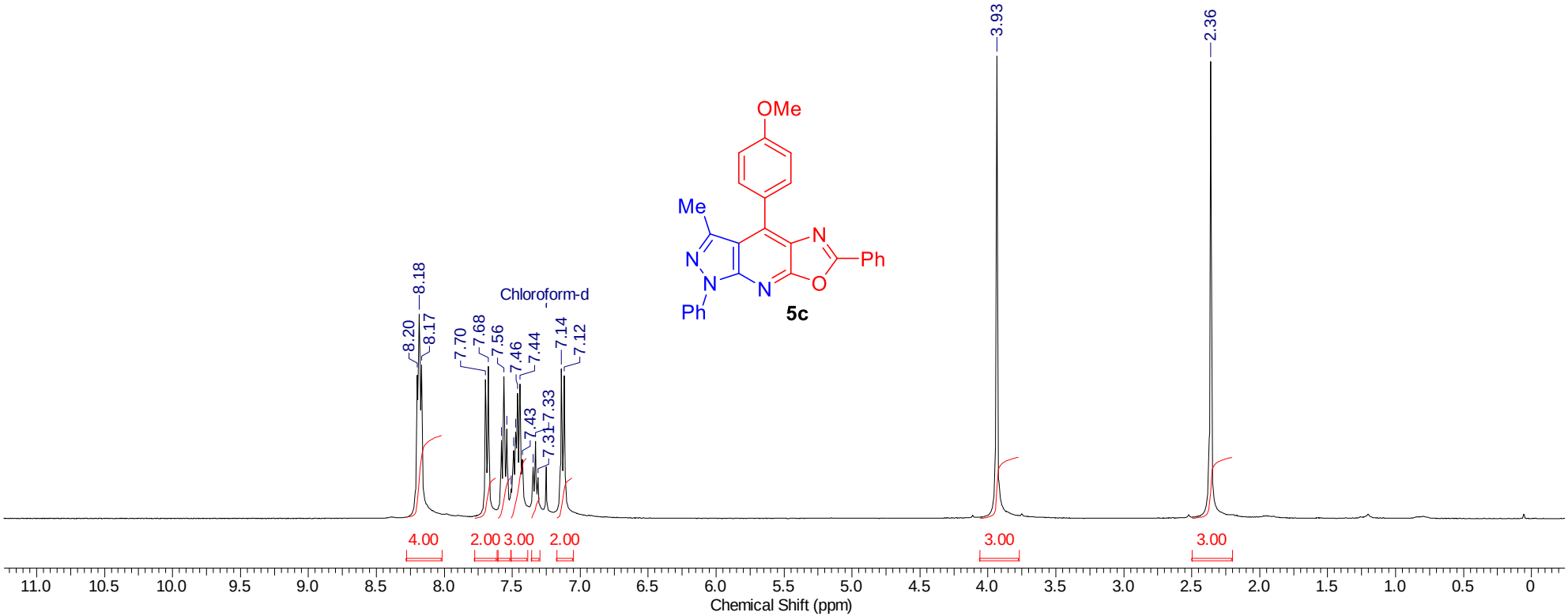



**Figure S28**: $^{1}H$ NMR spectrum of compound **5c** ($CDCl_3$).

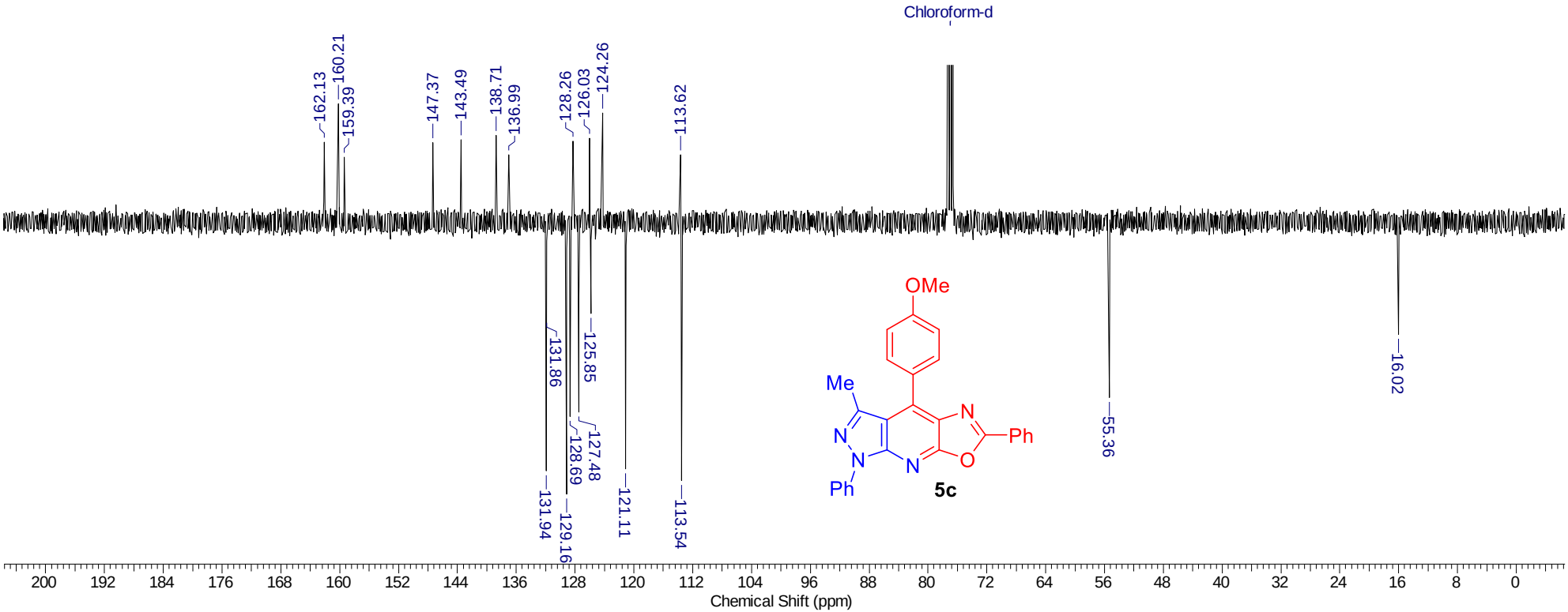



**Figure S29:** $^{13}C$ NMR spectrum of compound **5c** ($CDCl_3$).

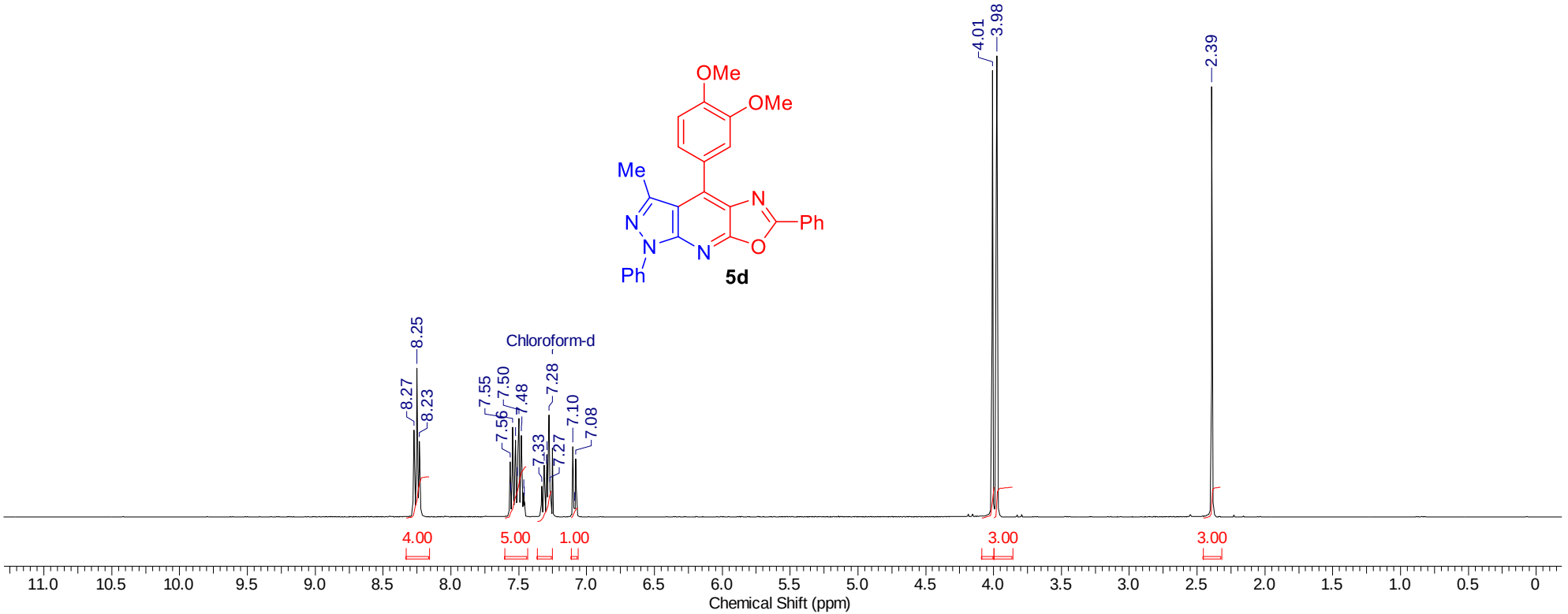



**Figure S30**: $^{1}$H NMR spectrum of compound **5d** ($CDCl_3$).

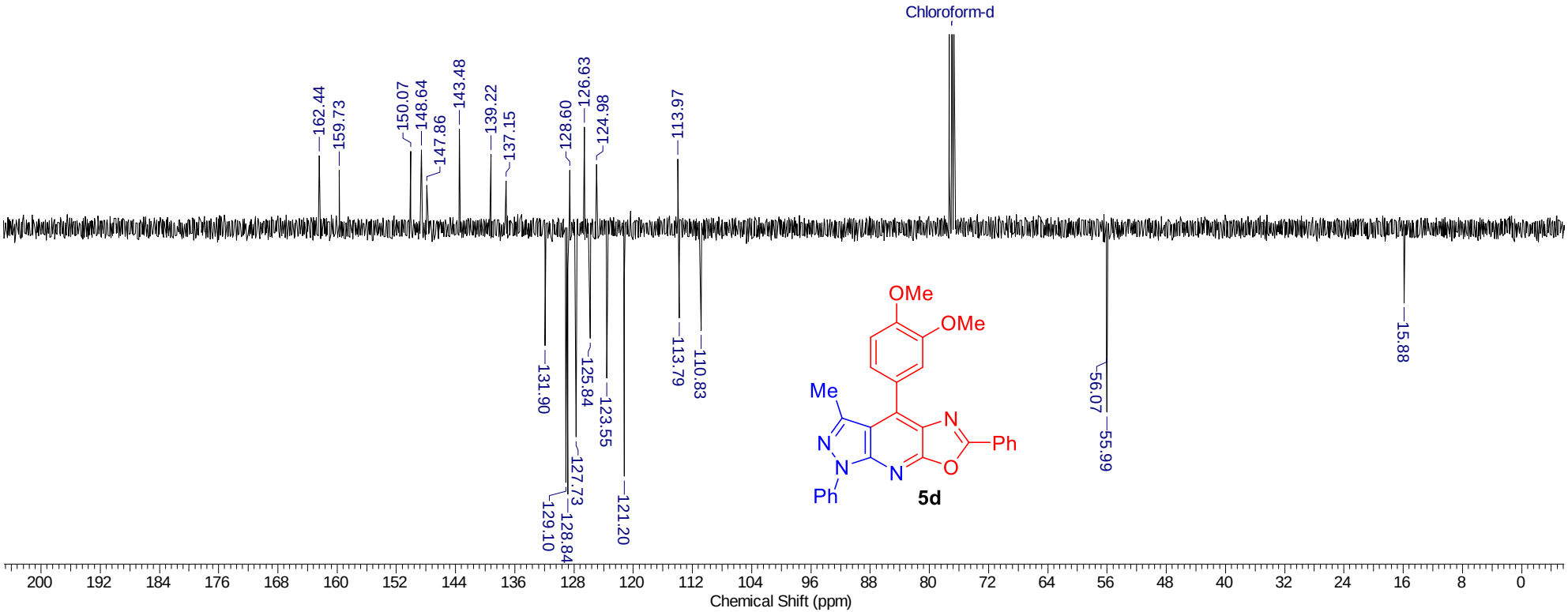



**Figure S31:** $^{13}C$ NMR spectrum of compound **5d** ($CDCl_3$).

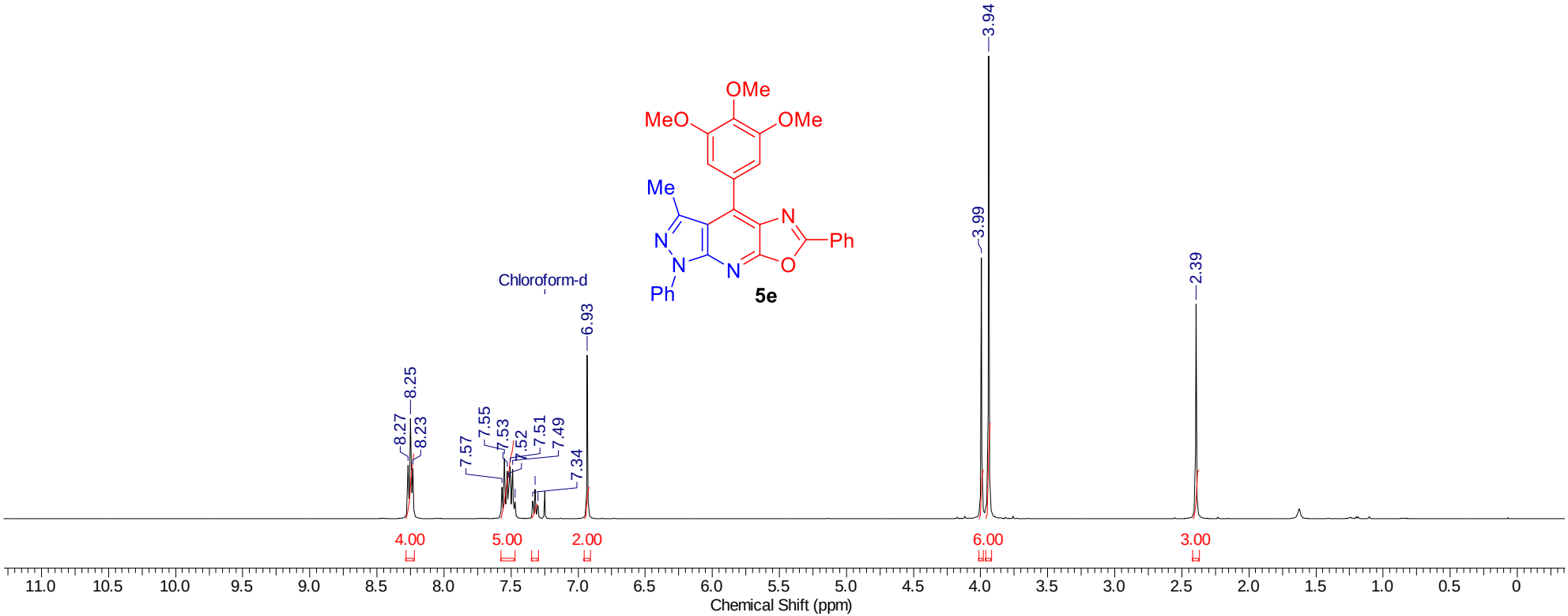



**Figure S32**: $^{1}H$ NMR spectrum of compound **5e** ($CDCl_3$).

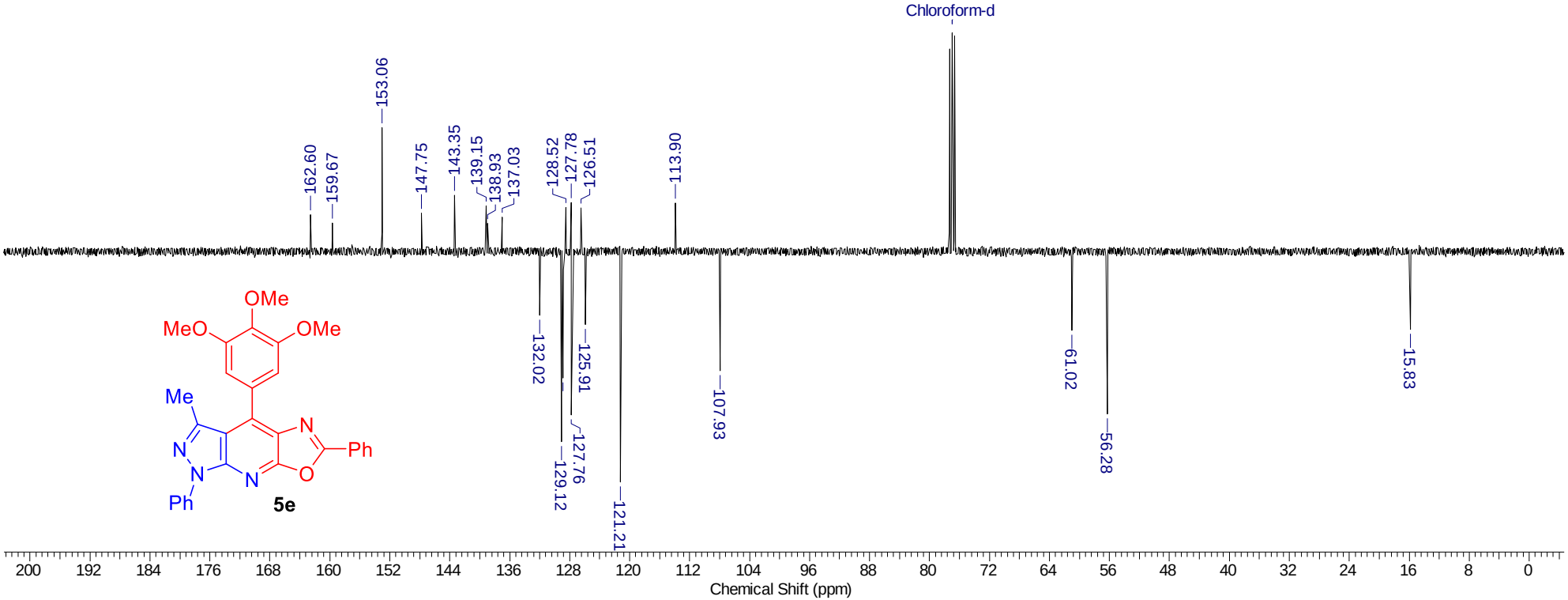



**Figure S33:** $^{13}C$ NMR spectrum of compound **5e** ($CDCl_3$).

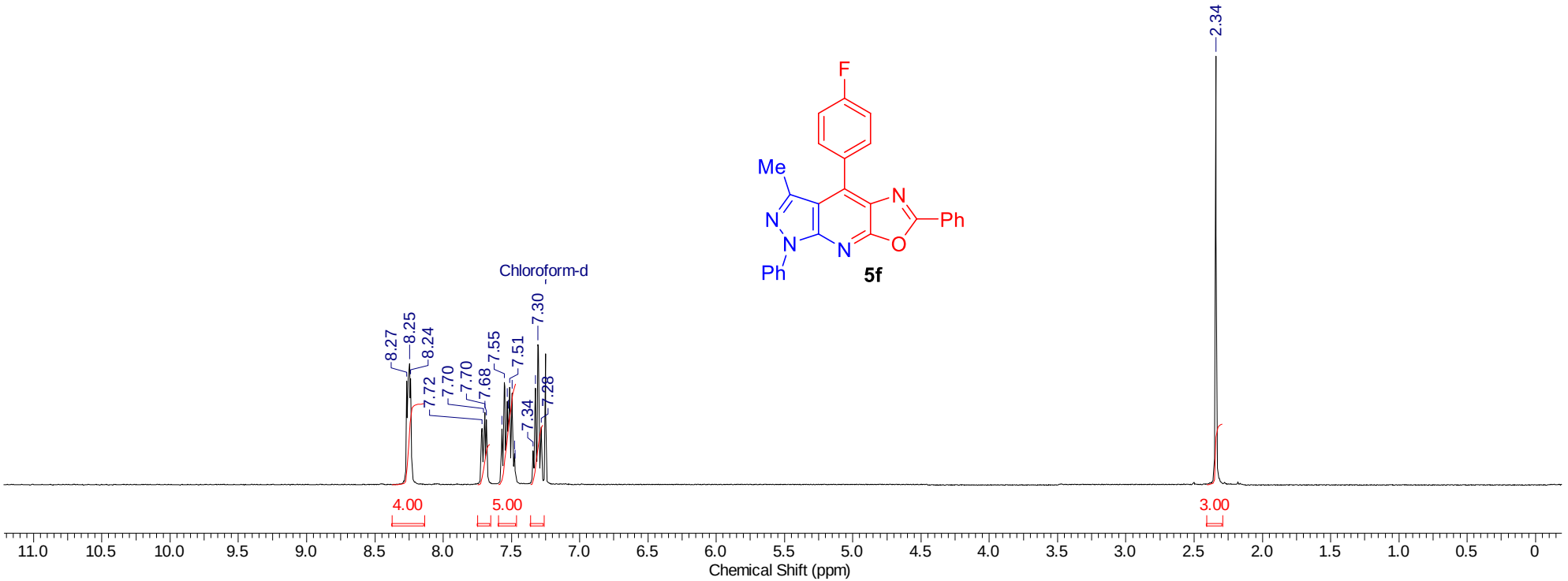



**Figure S34**: $^{1}H$ NMR spectrum of compound **5f** ($CDCl_3$).

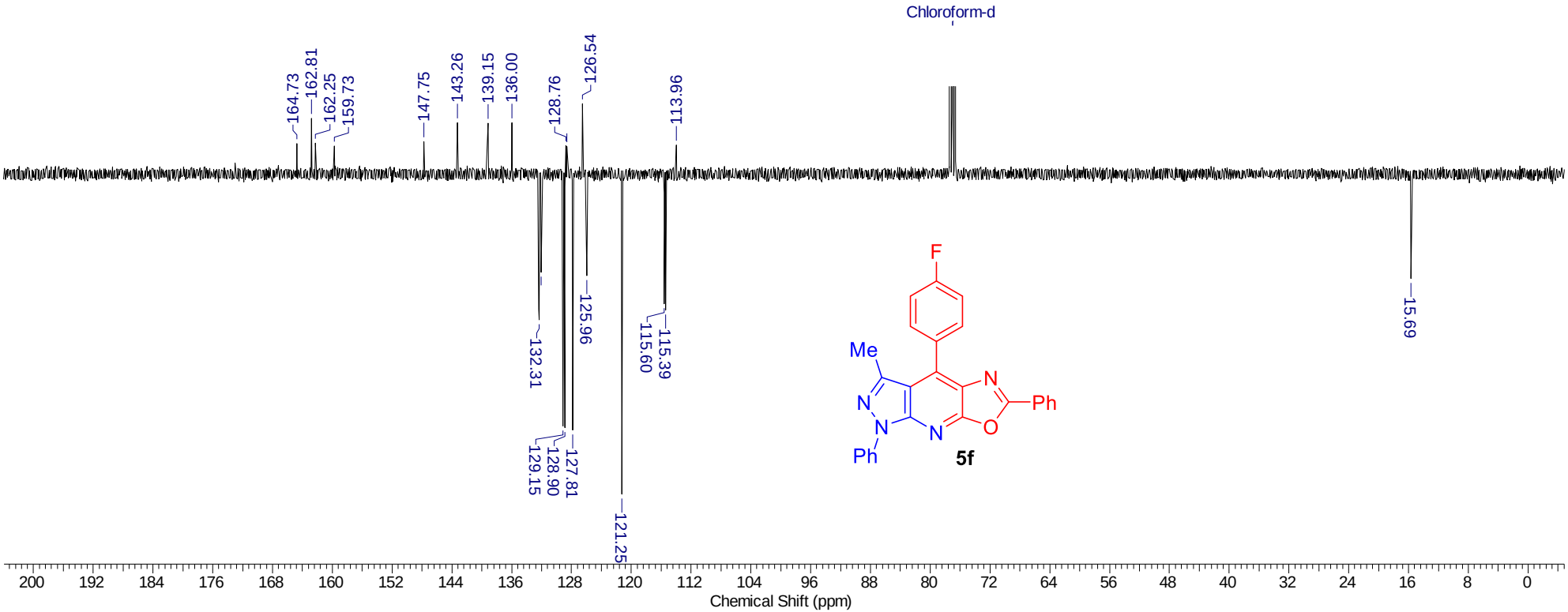



**Figure S35:** $^{13}C$ NMR spectrum of compound **5f** ($CDCl_3$).

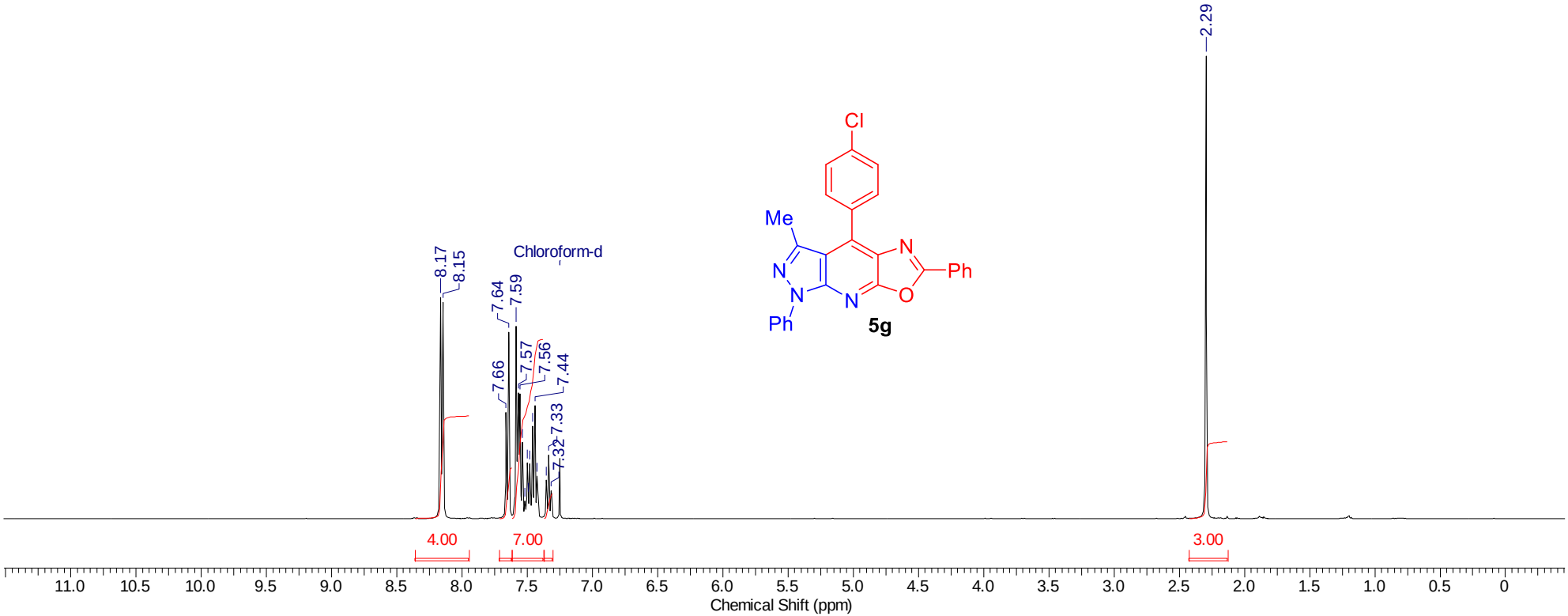



**Figure S36**: $^{1}$H NMR spectrum of compound **5g** ($CDCl_3$).

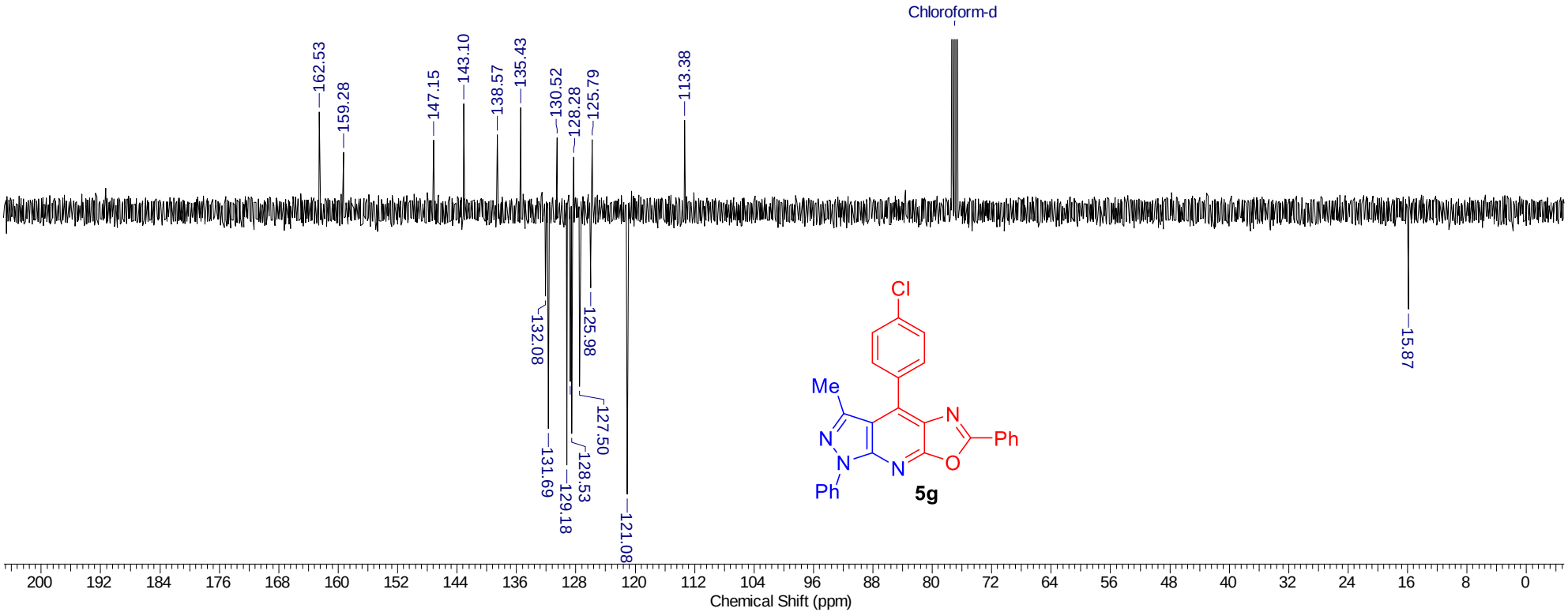



**Figure S37:** $^{13}C$ NMR spectrum of compound **5g** ($CDCl_3$).

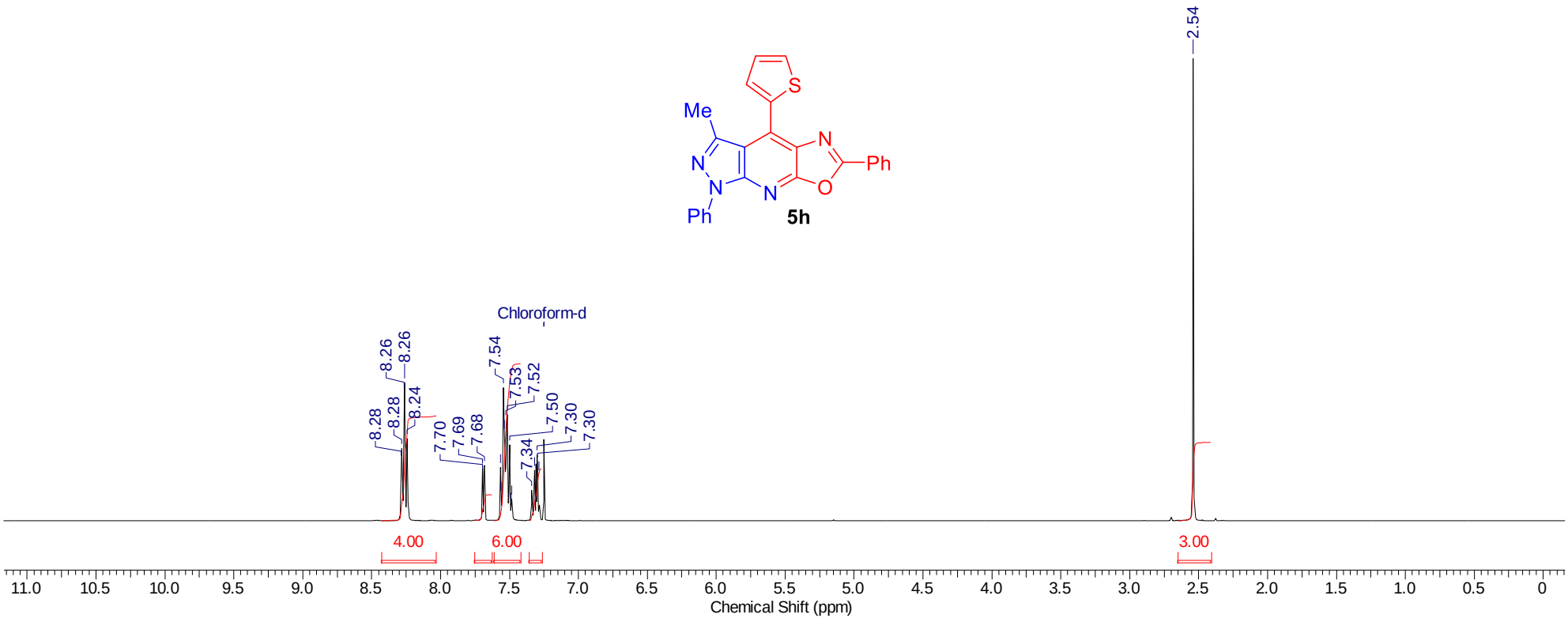



**Figure S38**: $^{1}$H NMR spectrum of compound **5h** ($CDCl_3$).

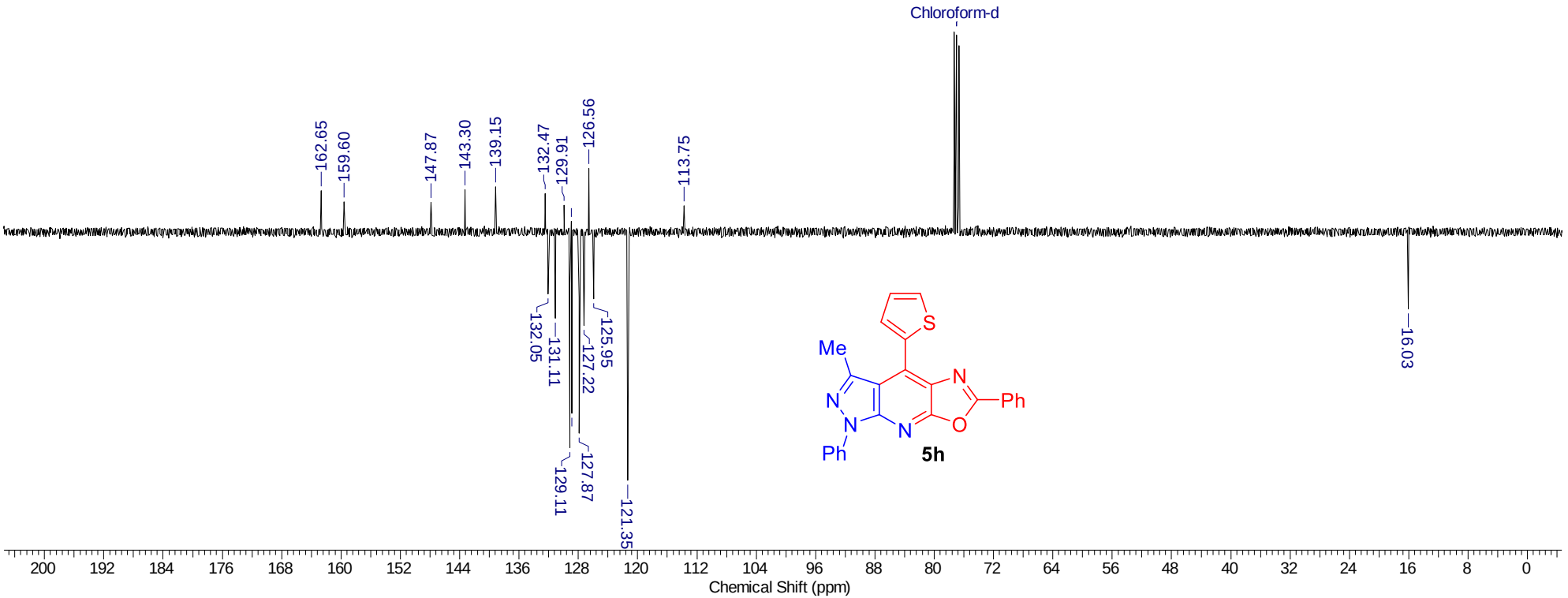



**Figure S39:** $^{13}C$ NMR spectrum of compound **5h** ($CDCl_3$).

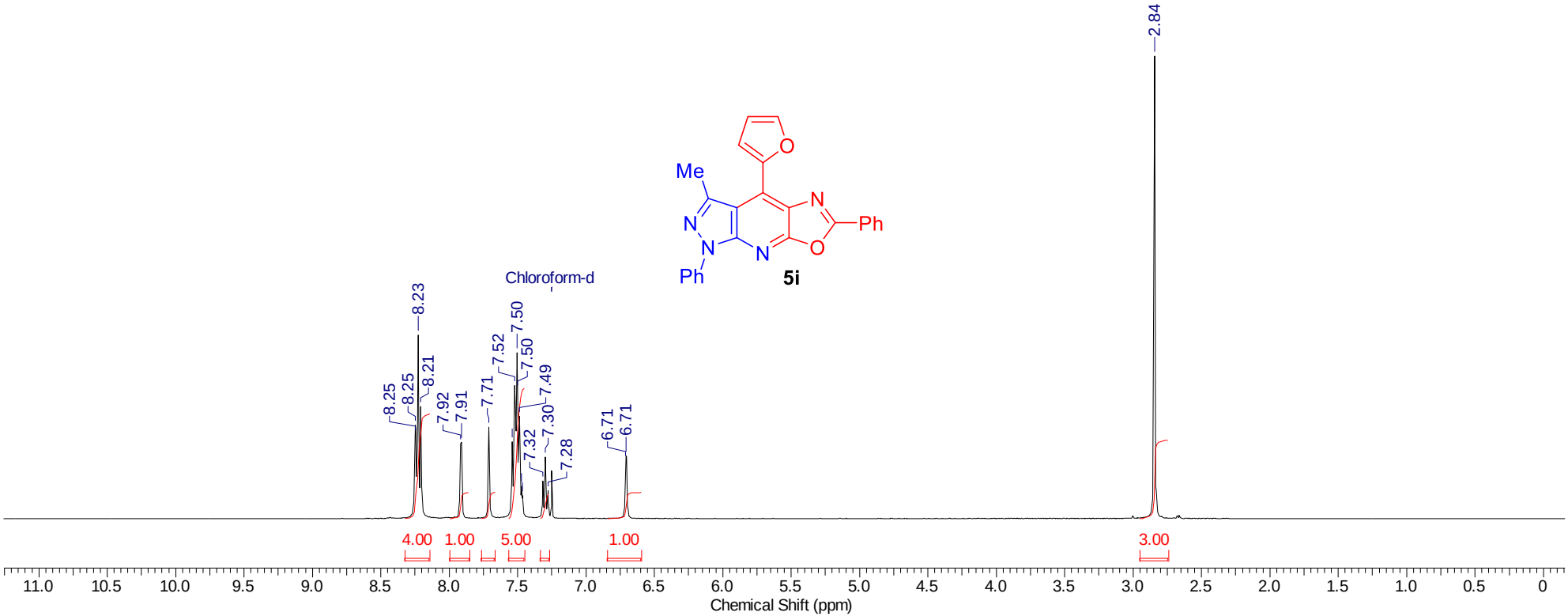



**Figure S40**: $^{1}H$ NMR spectrum of compound **5i** ($CDCl_3$).

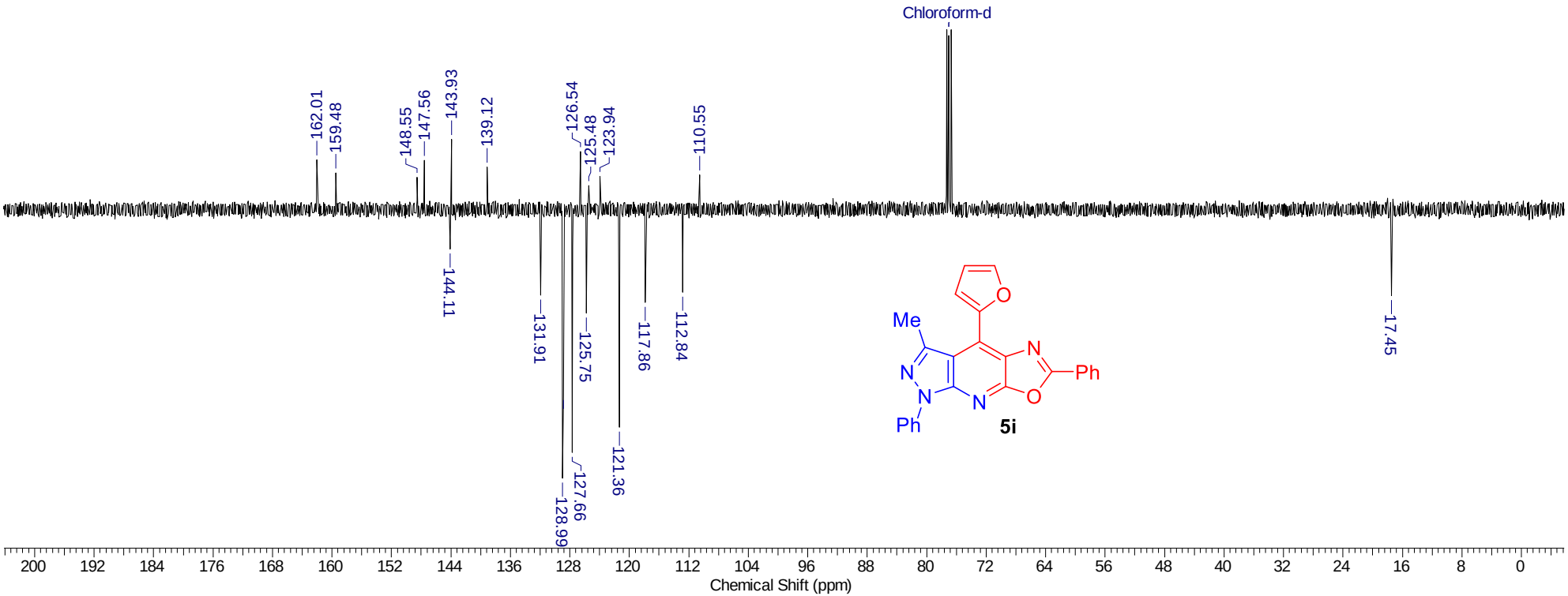



**Figure S41:** $^{13}C$ NMR spectrum of compound **5i** ($CDCl_3$).

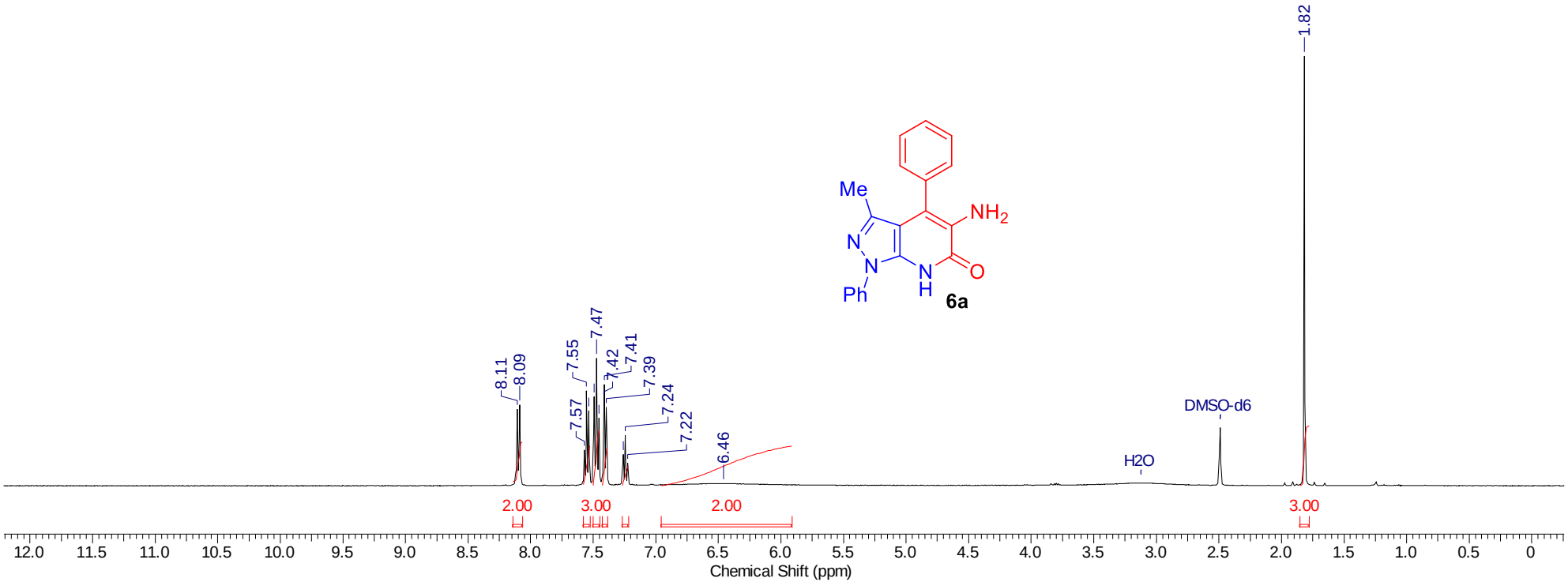



**Figure S42:** $^{1}$H NMR spectrum of compound **6a** (DMSO-$d_6$).

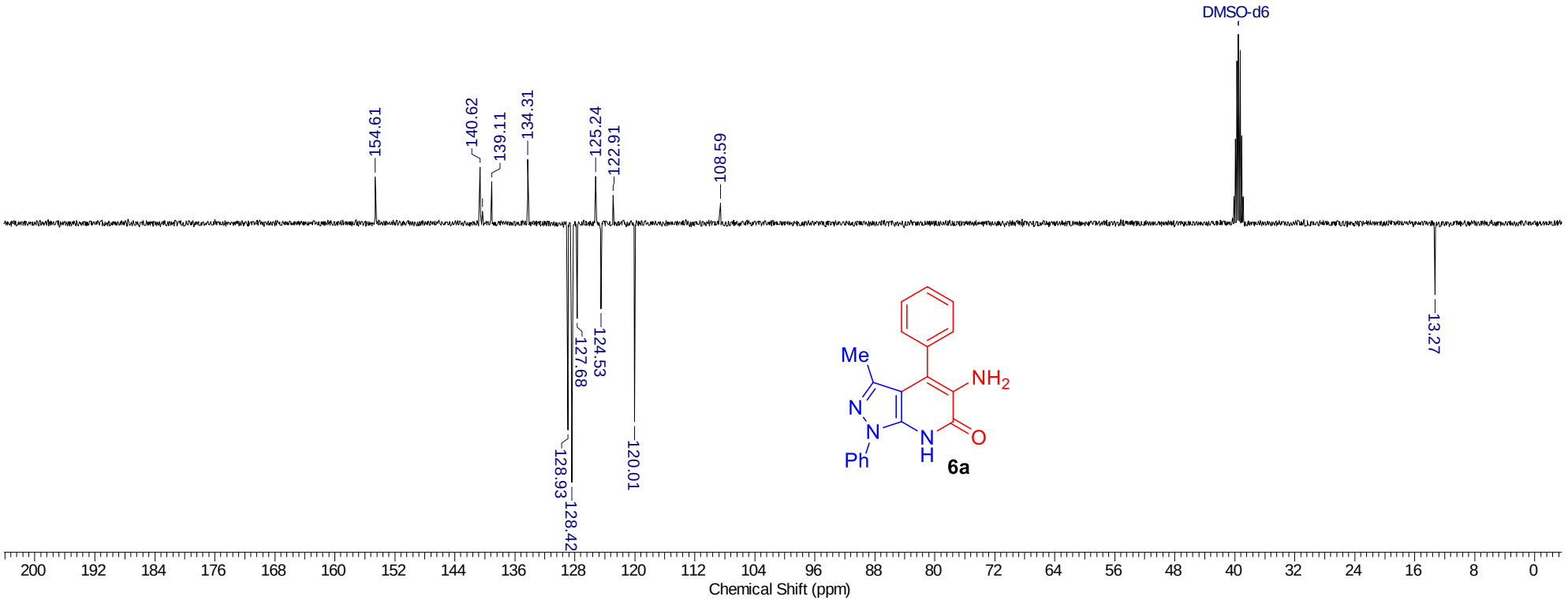



**Figure S43:** $^{13}$C NMR spectrum of compound **6a** (DMSO-$d_6$).

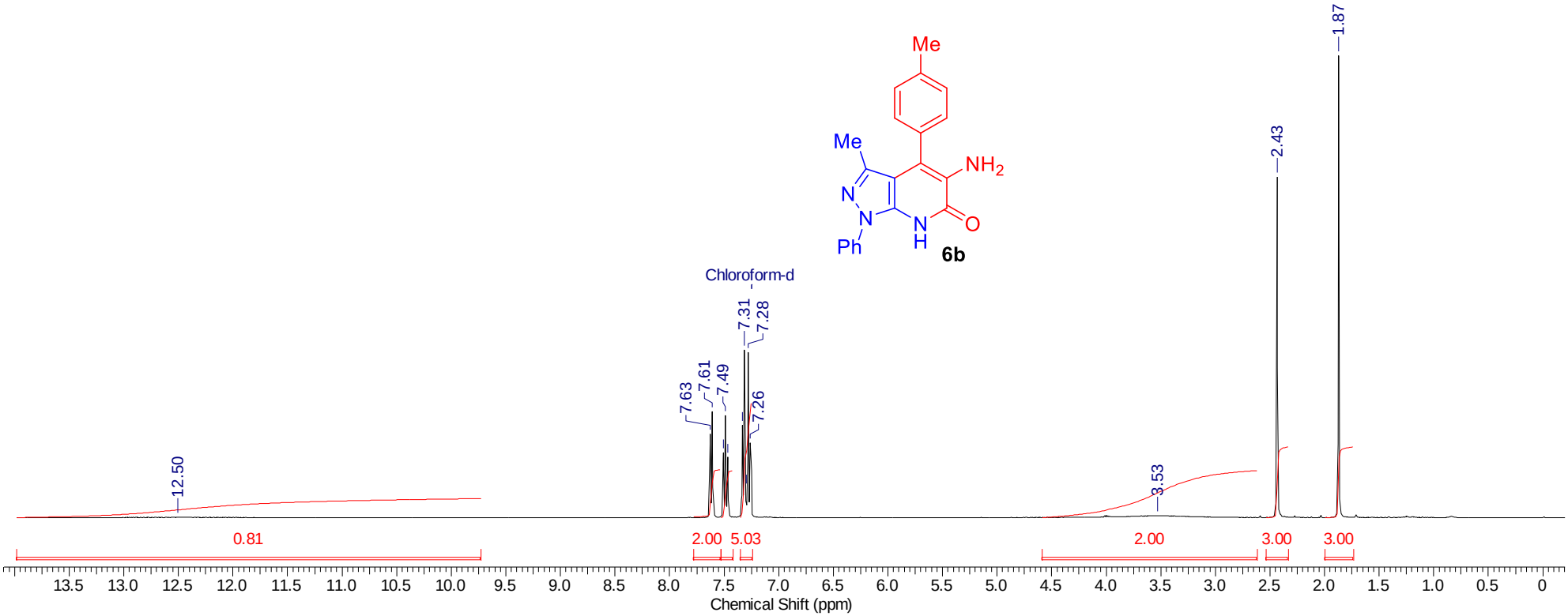



**Figure S44:** $^{1}H$ NMR spectrum of compound **6b** ($CDCl_3$).

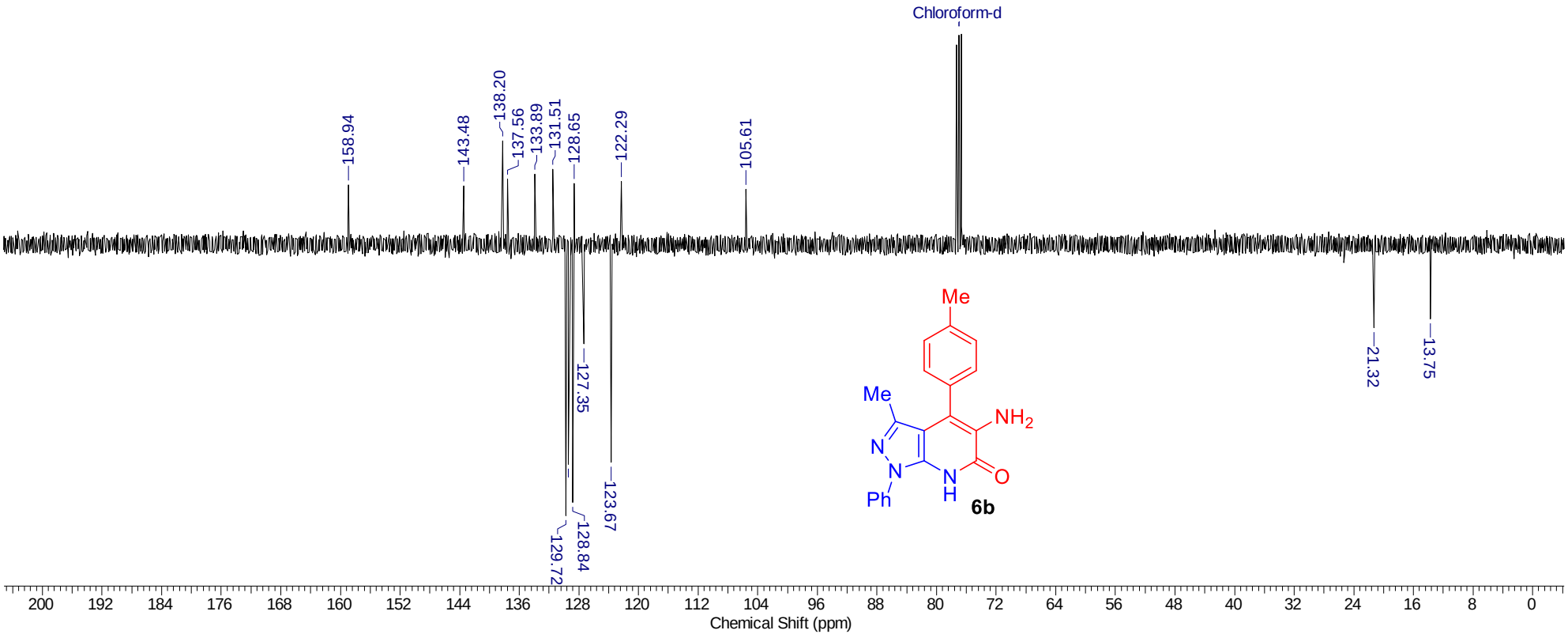



**Figure S45:** $^{13}C$ NMR spectrum of compound **6b** ($CDCl_3$).

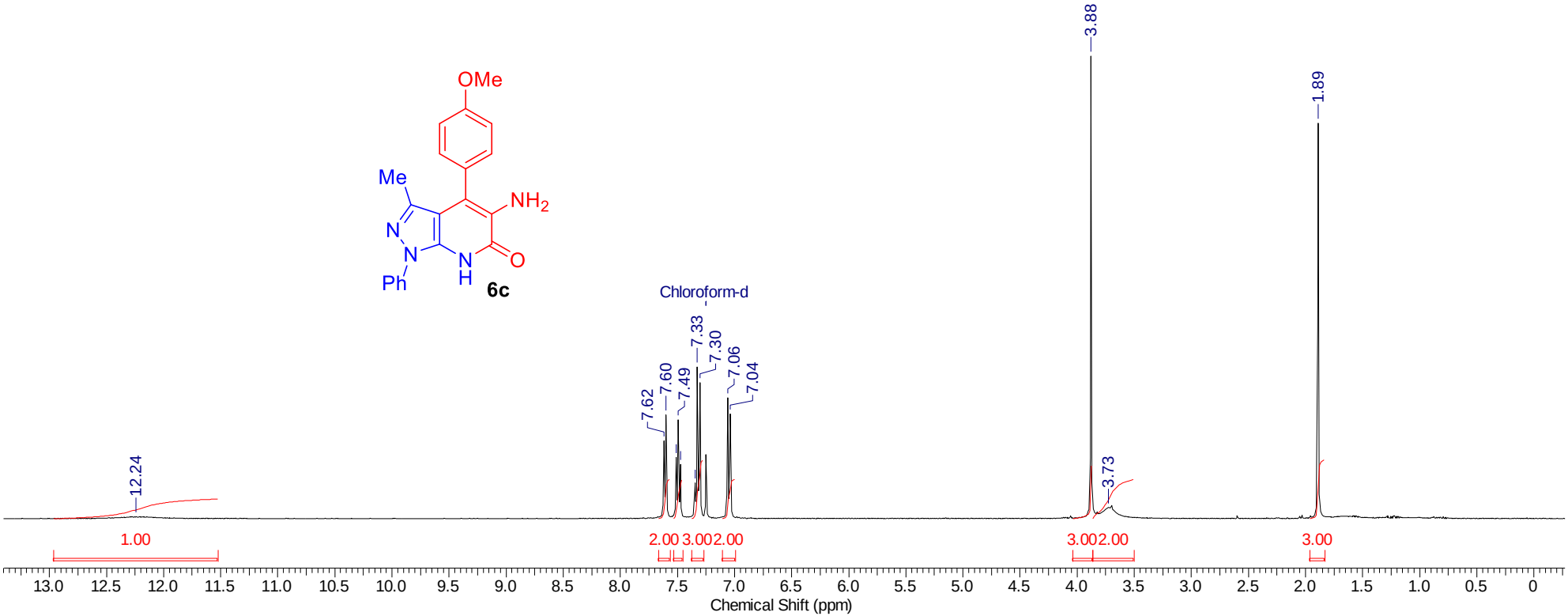



**Figure S46:** $^{1}$H NMR spectrum of compound **6c** ($CDCl_3$).

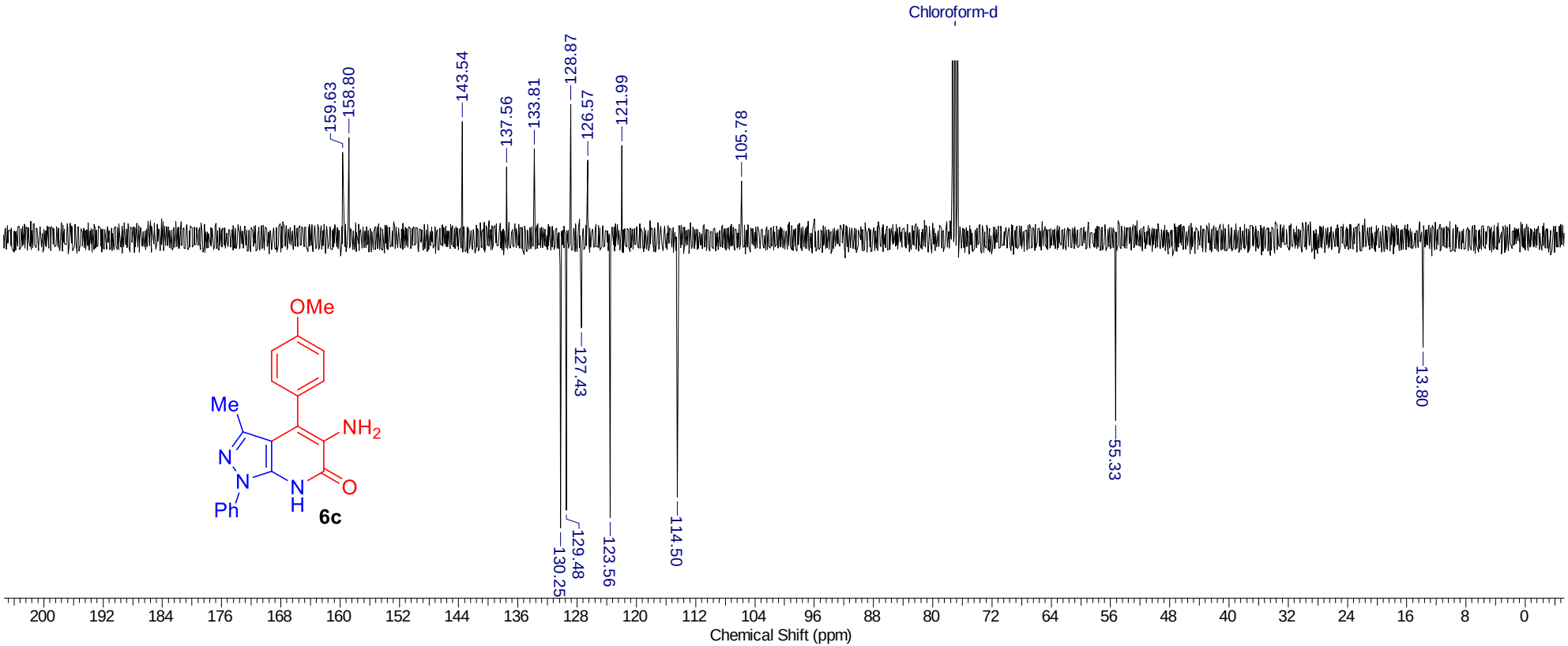



**Figure S47:** $^{13}C$ NMR spectrum of compound **6c** ($CDCl_3$).

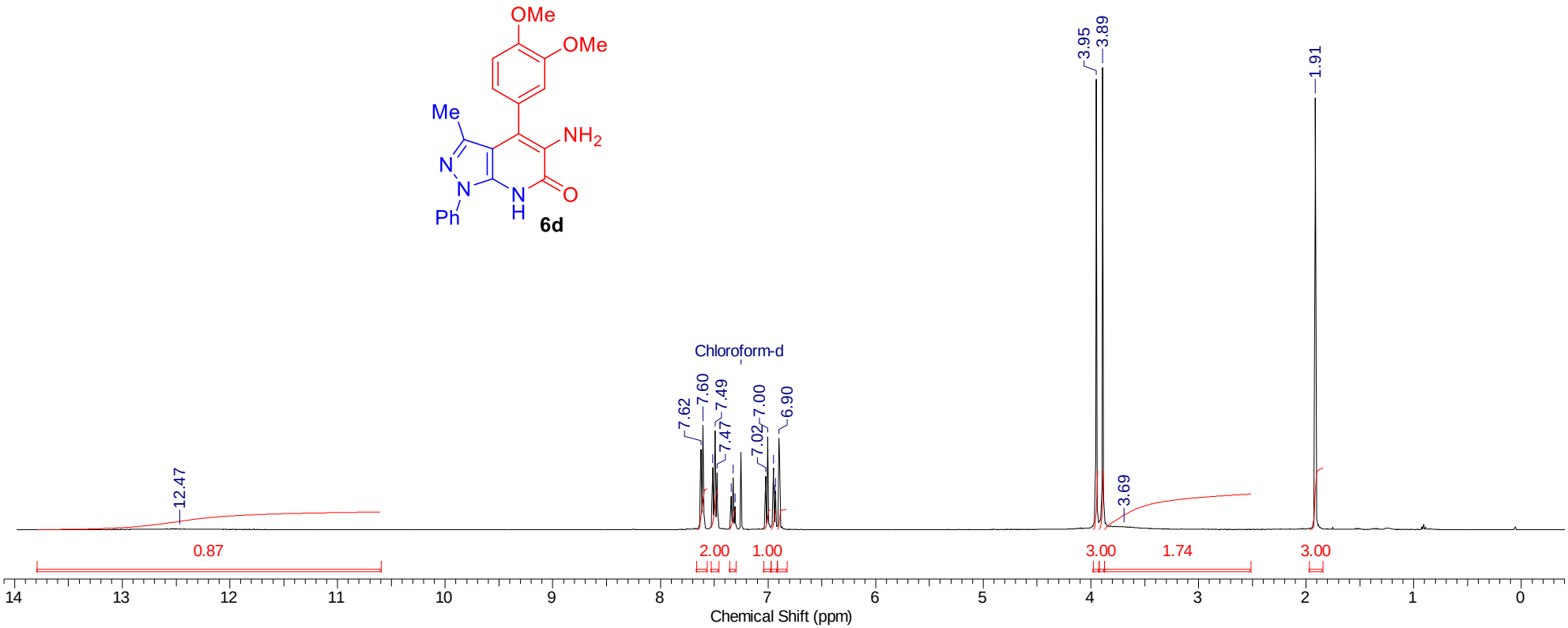



**Figure S48:** $^{1}$H NMR spectrum of compound **6d** ($CDCl_3$).

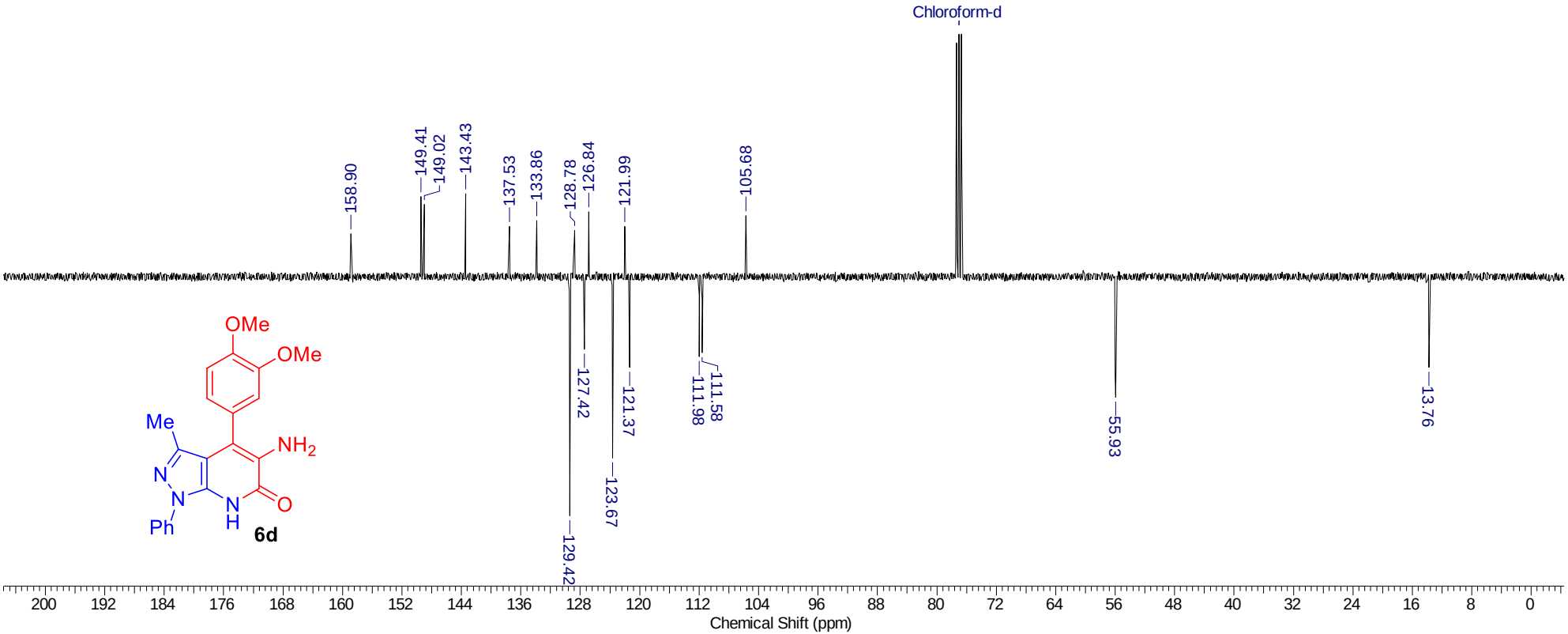



**Figure S49:** $^{13}C$ NMR spectrum of compound **6d** ($CDCl_3$).

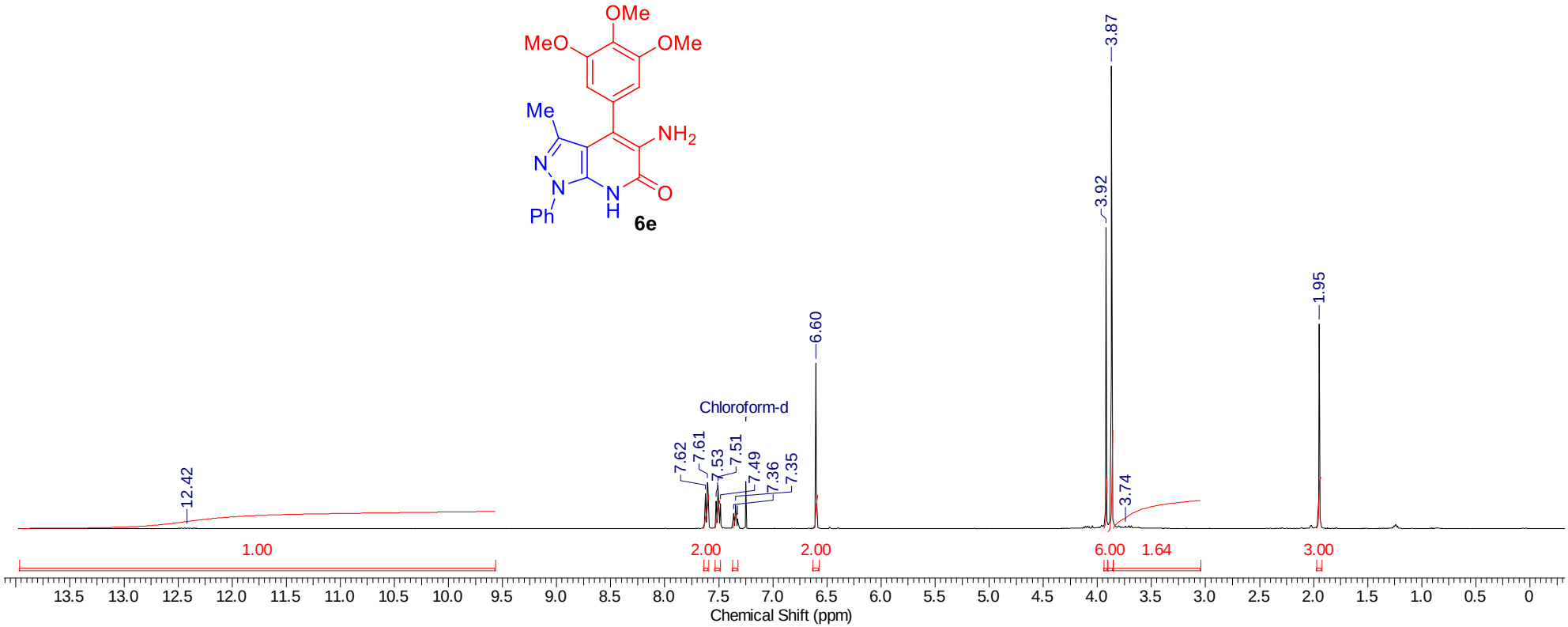



**Figure S50:** $^{1}H$ NMR spectrum of compound **6e** ($CDCl_3$).

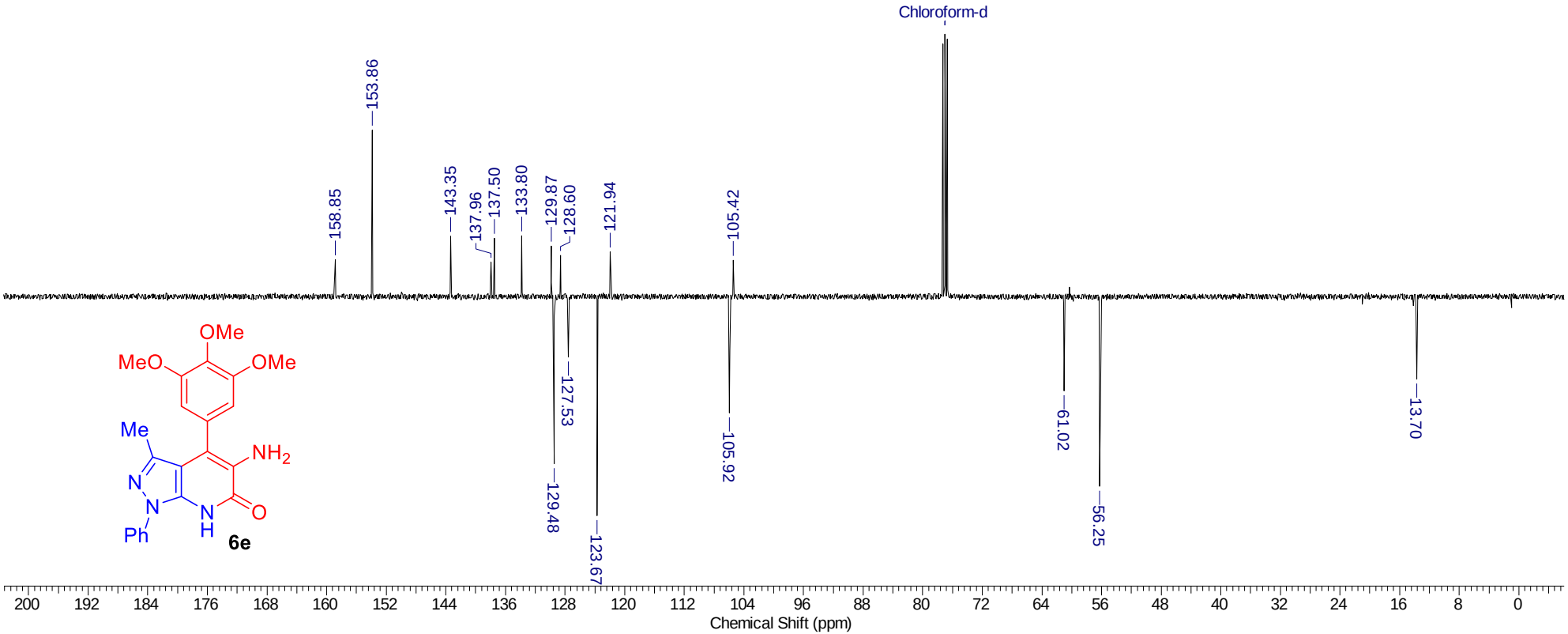



**Figure S51:** $^{13}C$ NMR spectrum of compound **6e** ($CDCl_3$).

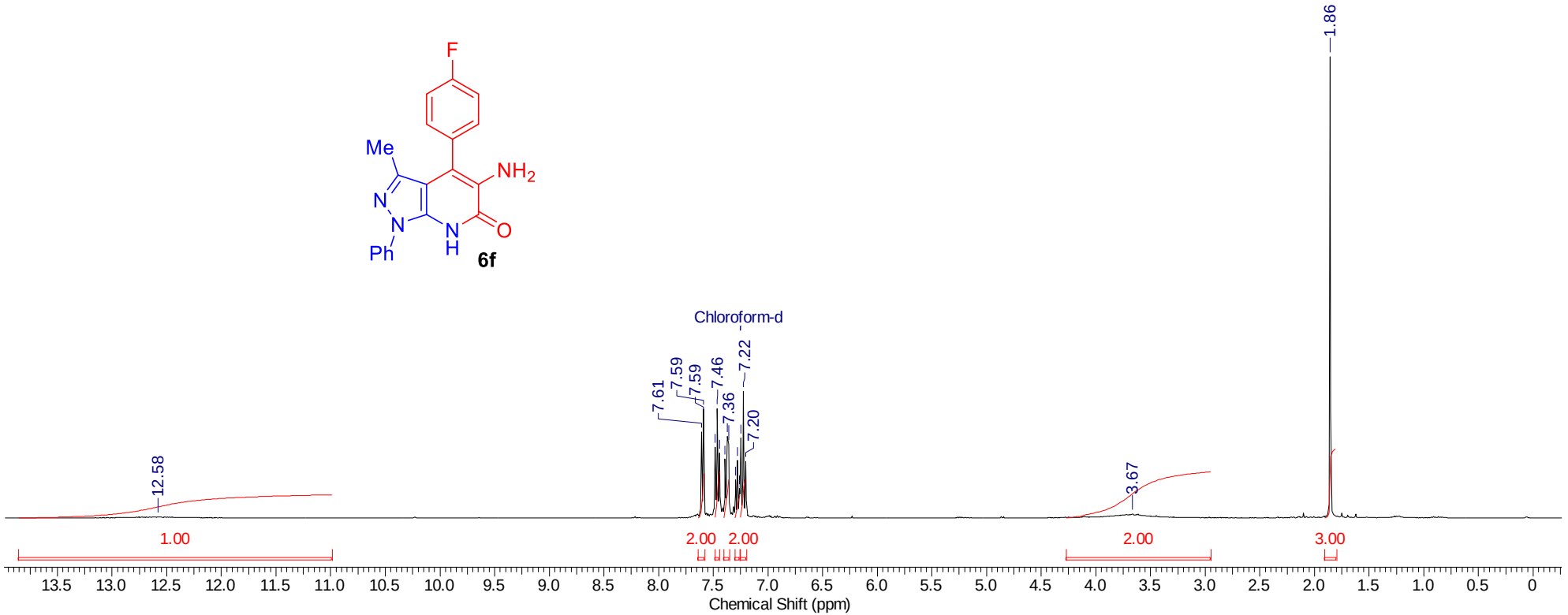



**Figure S52:** $^{1}$H NMR spectrum of compound **6f** ($CDCl_3$).

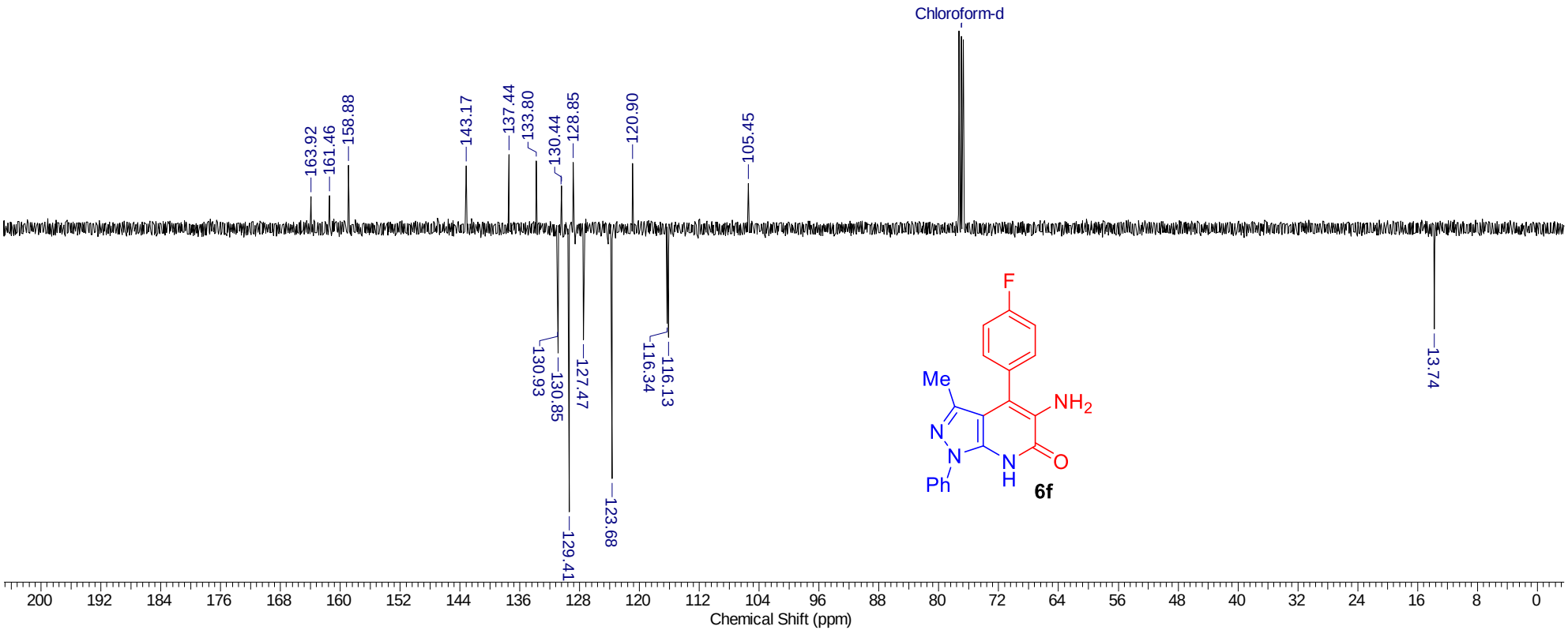



**Figure S53:** $^{13}C$ NMR spectrum of compound **6f** ($CDCl_3$).

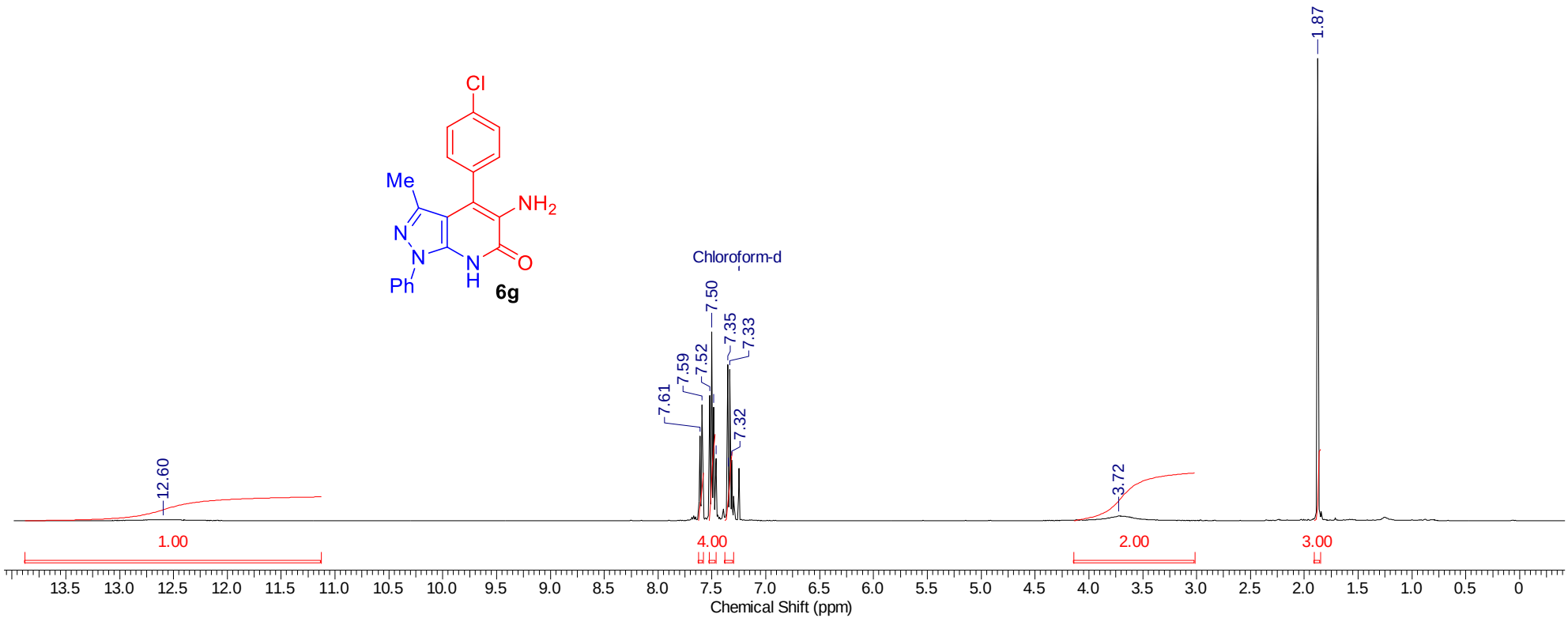



**Figure S54:** $^{1}$H NMR spectrum of compound **6g** ($CDCl_3$).

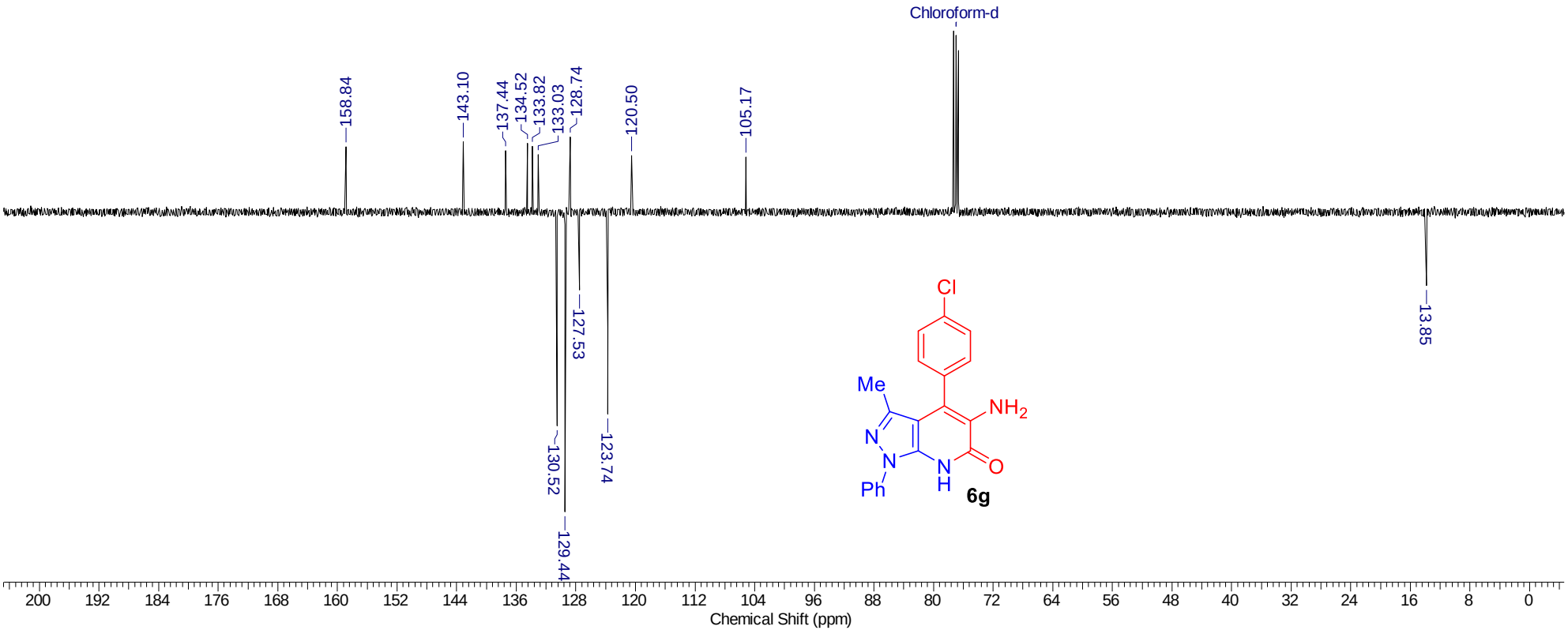



**Figure S55:** $^{13}C$ NMR spectrum of compound **6g** ($CDCl_3$).

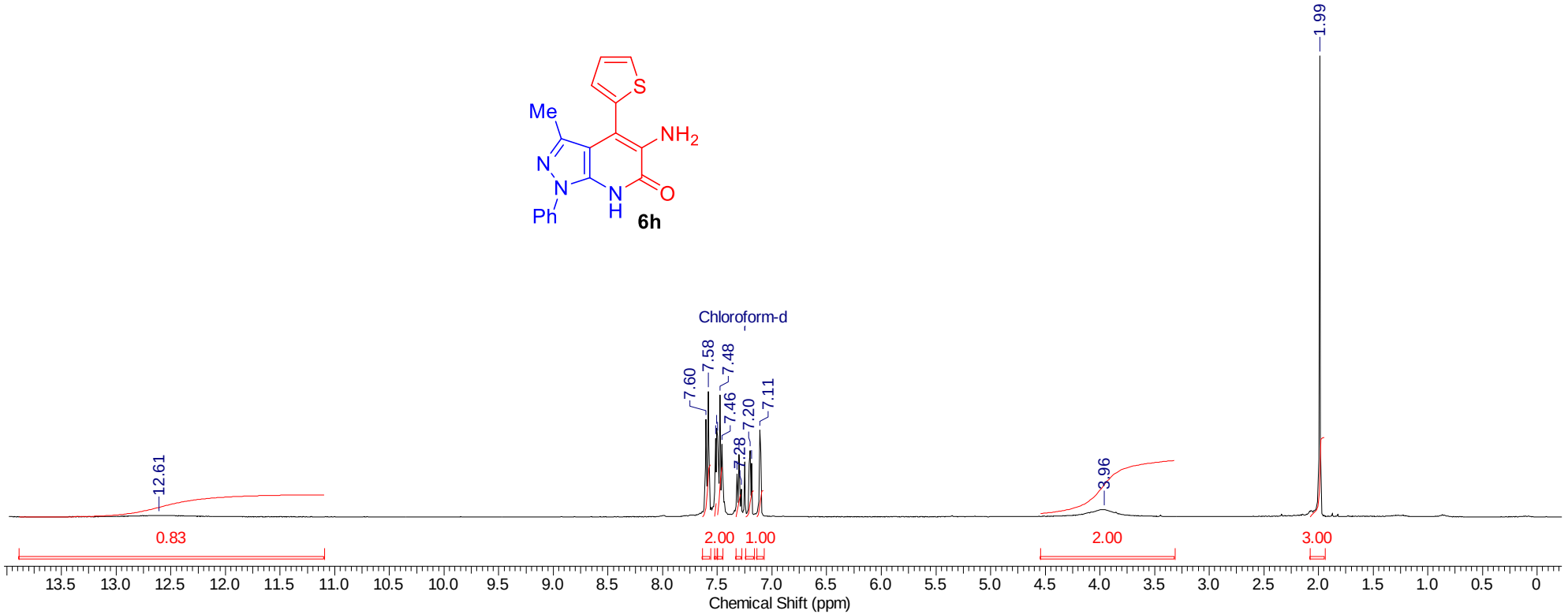



**Figure S56:** $^{1}$H NMR spectrum of compound **6h** ($CDCl_3$).

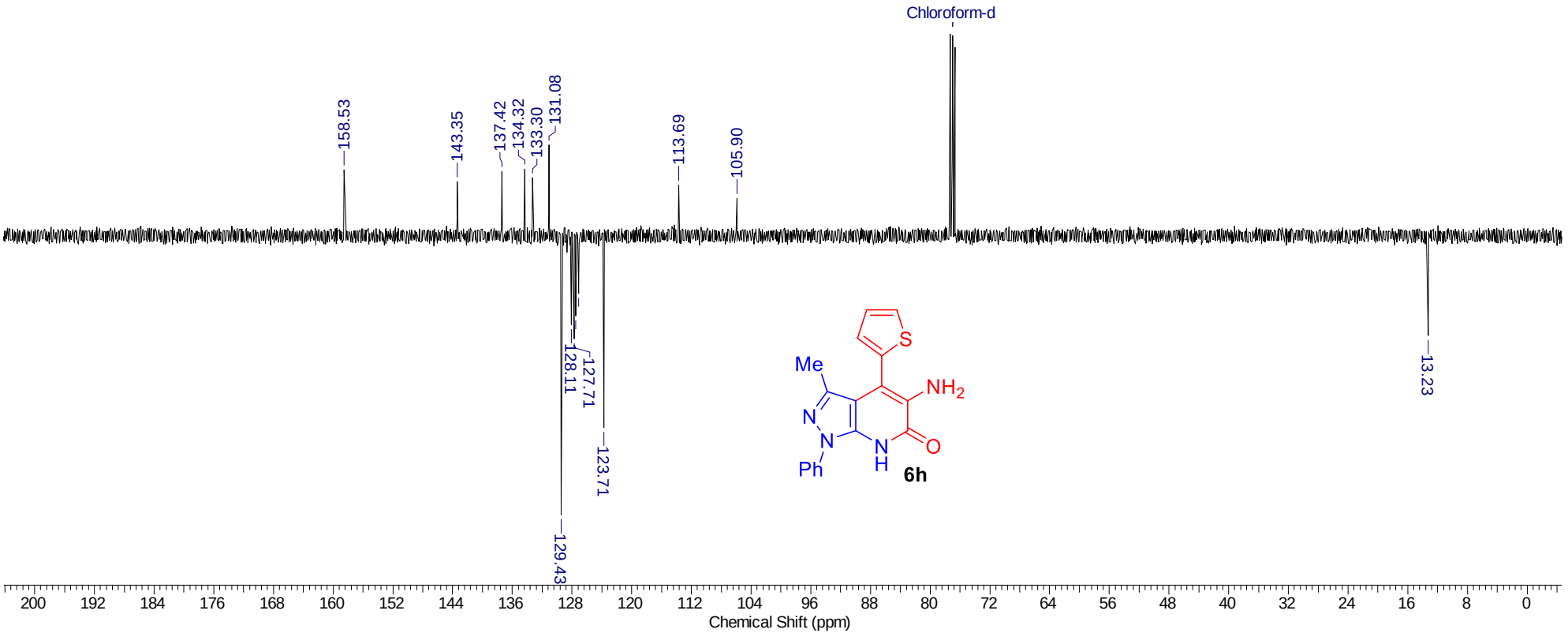



**Figure S57:** $^{13}C$ NMR spectrum of compound **6h** ($CDCl_3$).

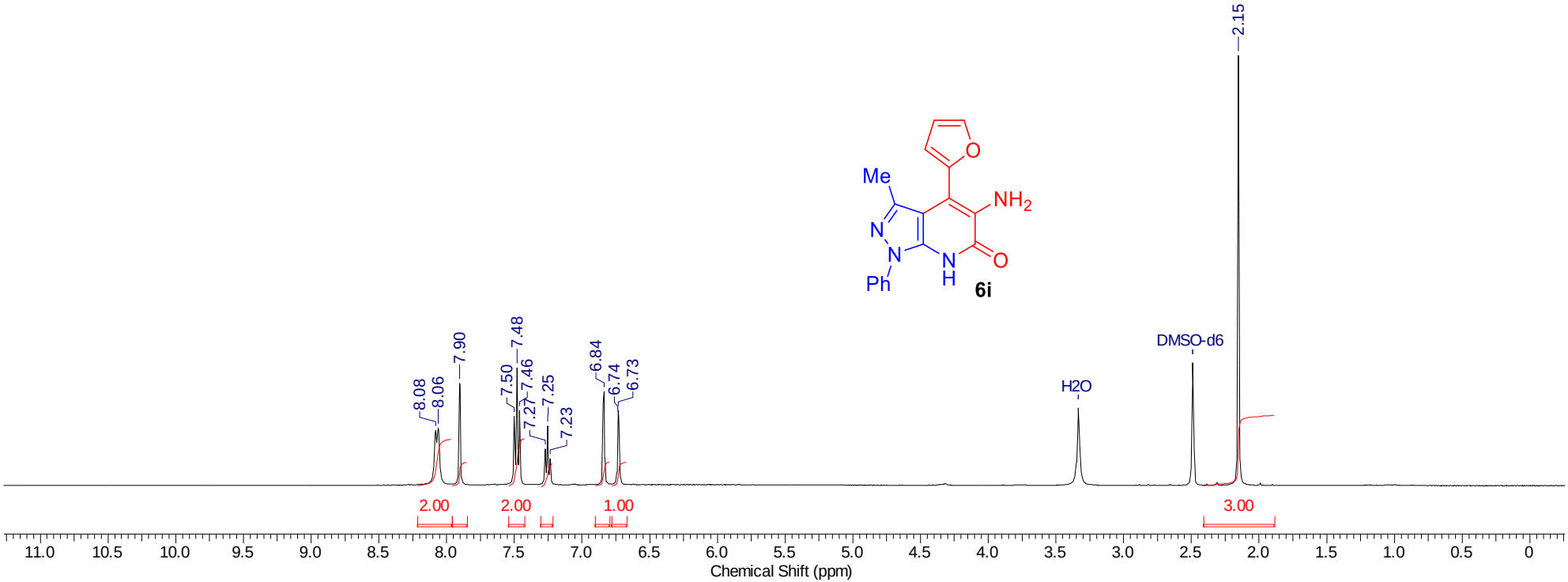



**Figure S58:** $^{1}$H NMR spectrum of compound **6i** (DMSO-$d_6$).

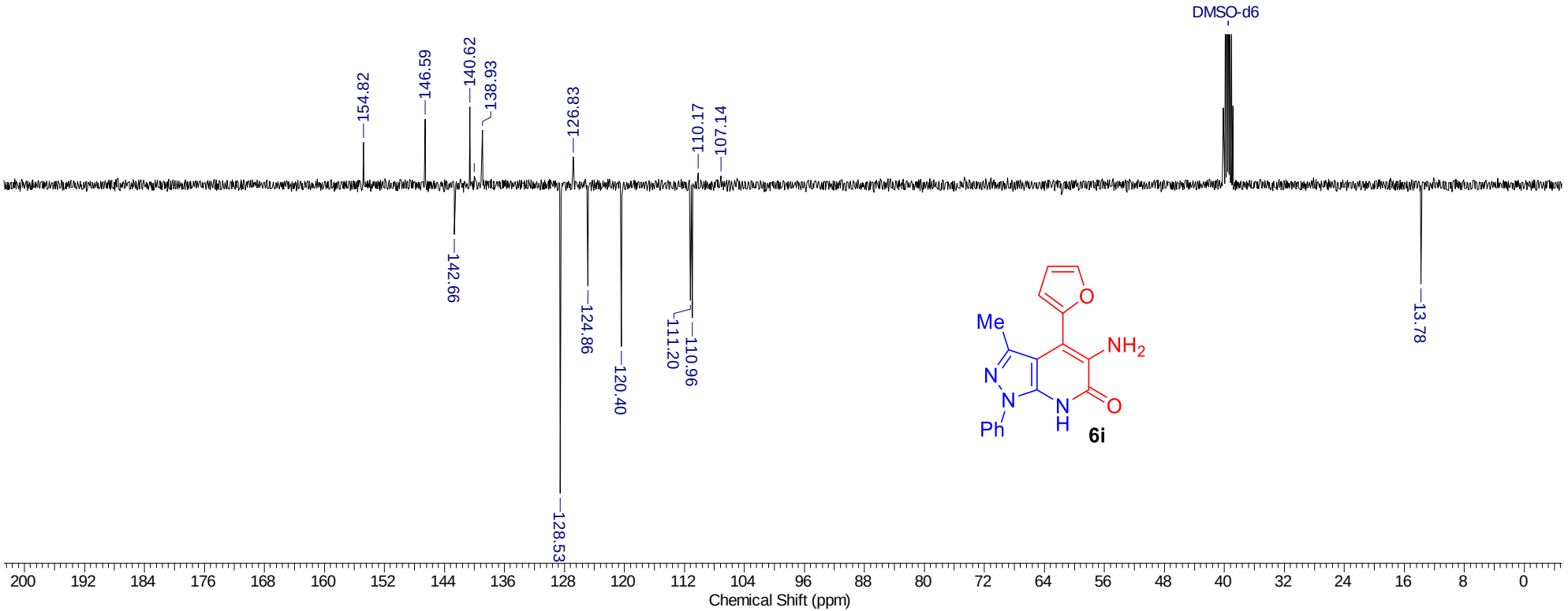



**Figure S59:** $^{13}$C NMR spectrum of compound **6i** (DMSO-$d_6$).

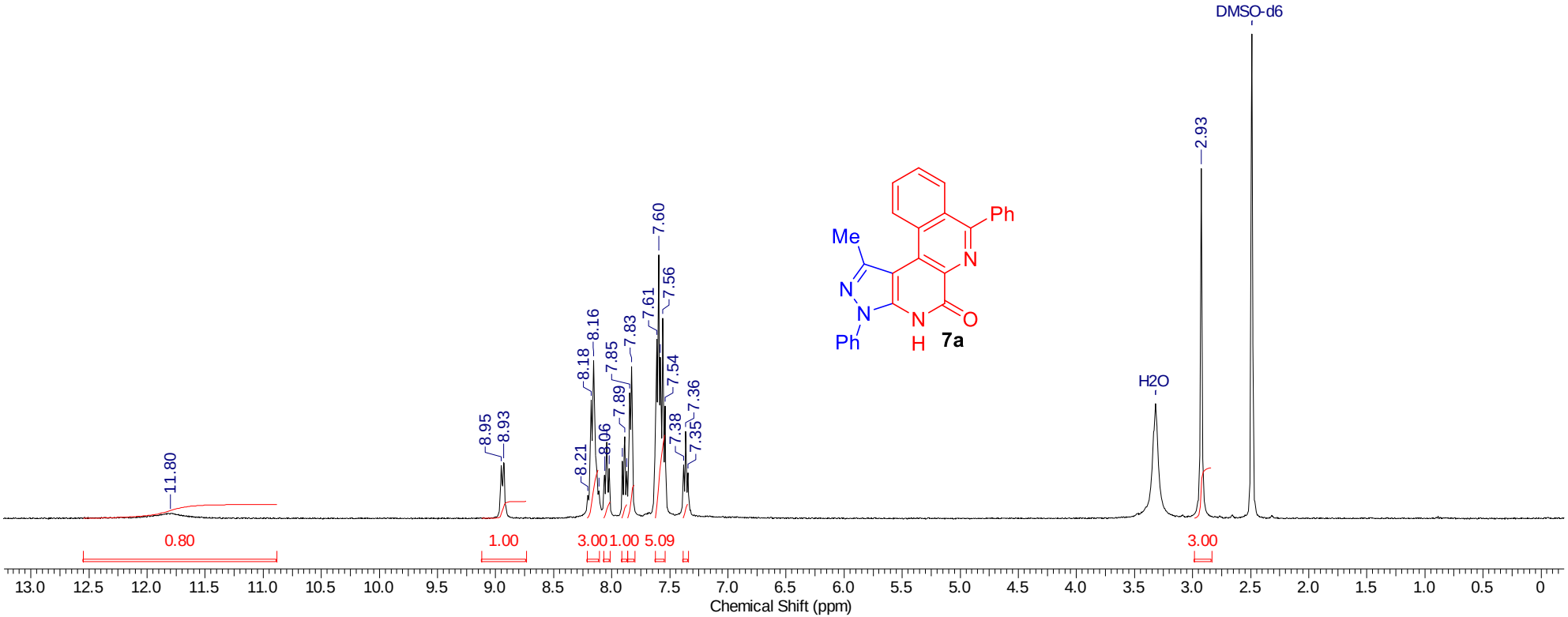



**Figure S60:** $^{1}$H NMR spectrum of compound **7a** (DMSO-$d_6$).

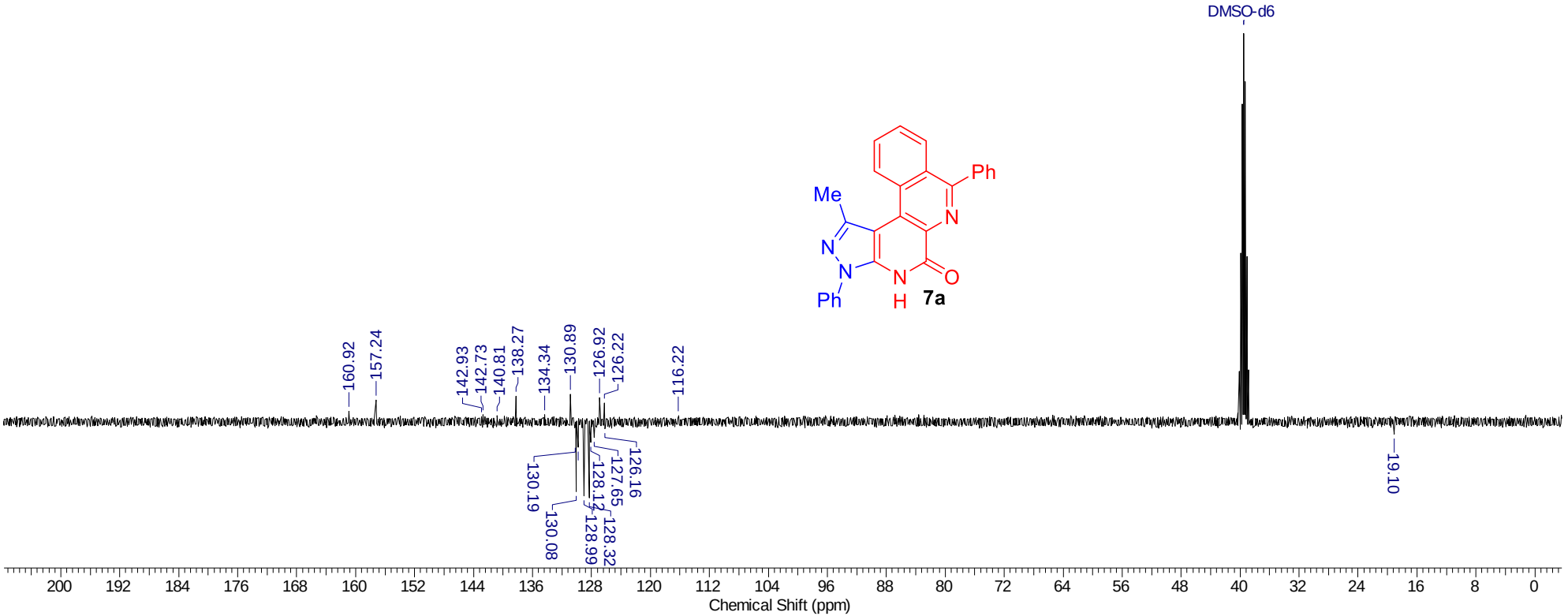



**Figure S61:** $^{13}C$ NMR spectrum of compound **7a** (DMSO-$d_6$).

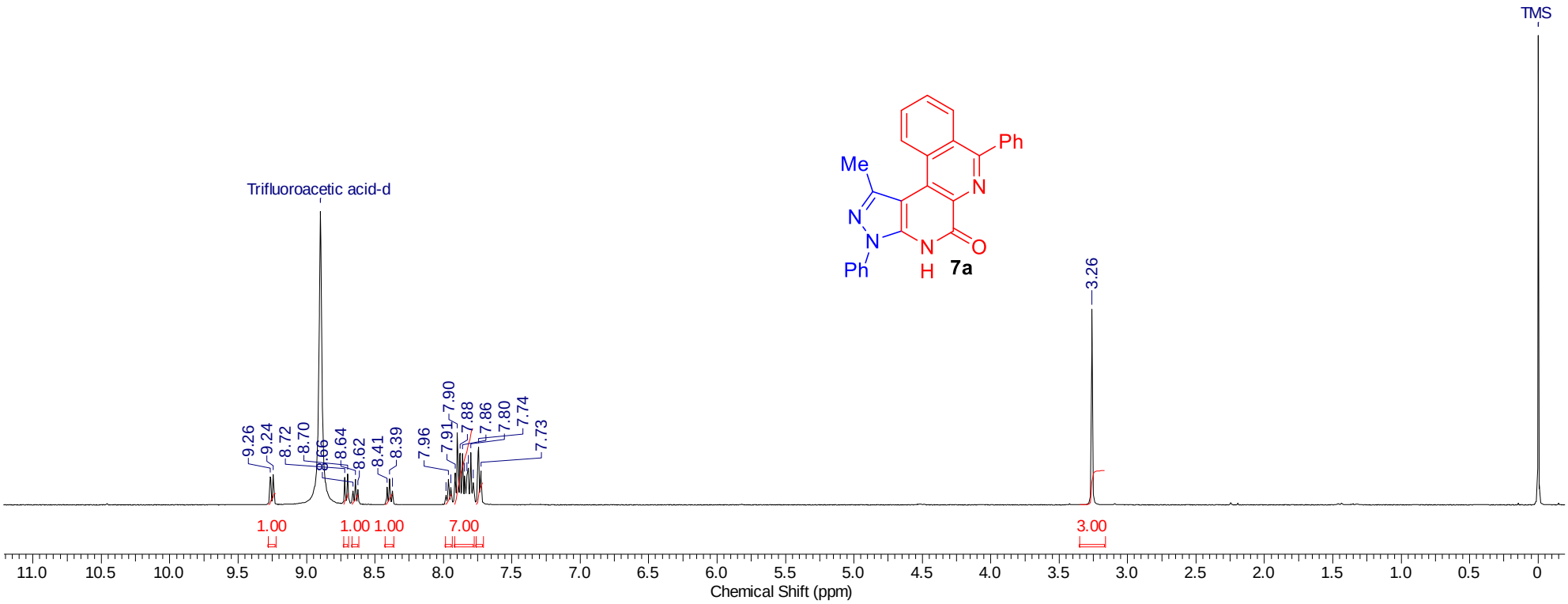



**Figure S62:** $^{1}H$ NMR spectrum of compound **7a** ($CF_3CO_2D$ + TMS).

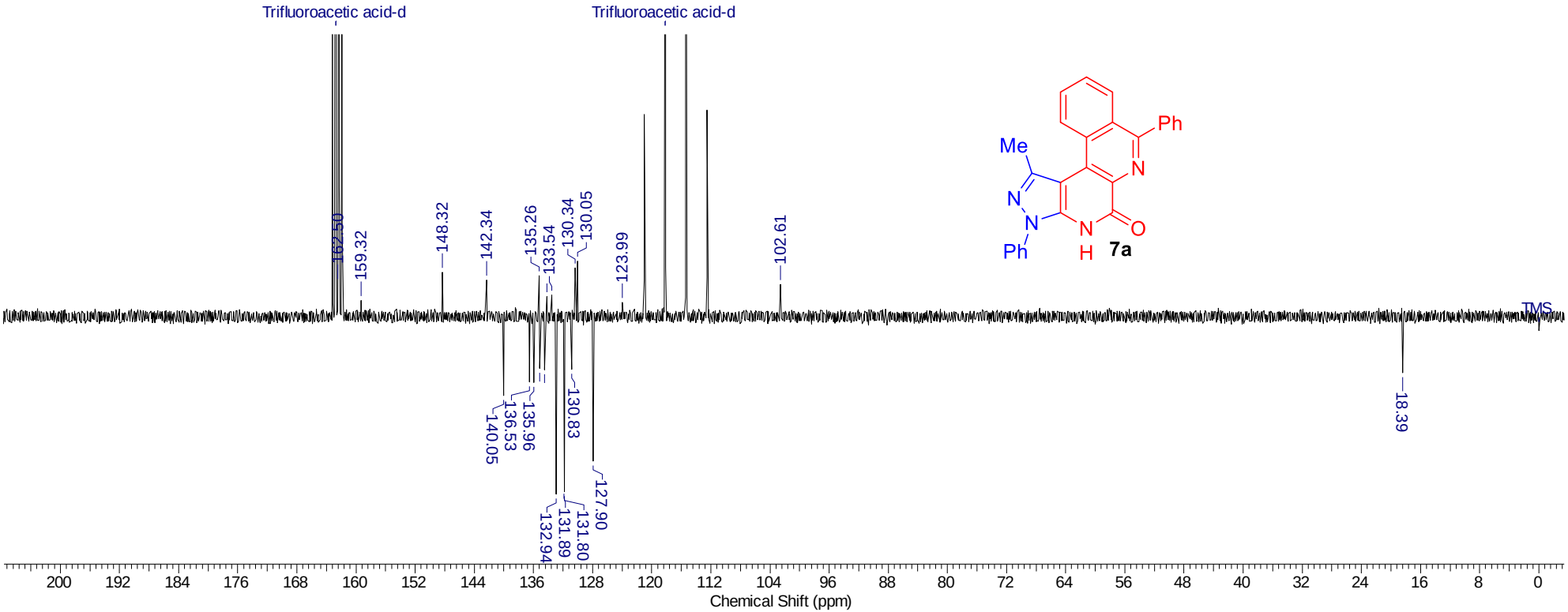



**Figure S63:** $^{13}C$ NMR spectrum of compound **7a** ($CF_3CO_2D$ + TMS).

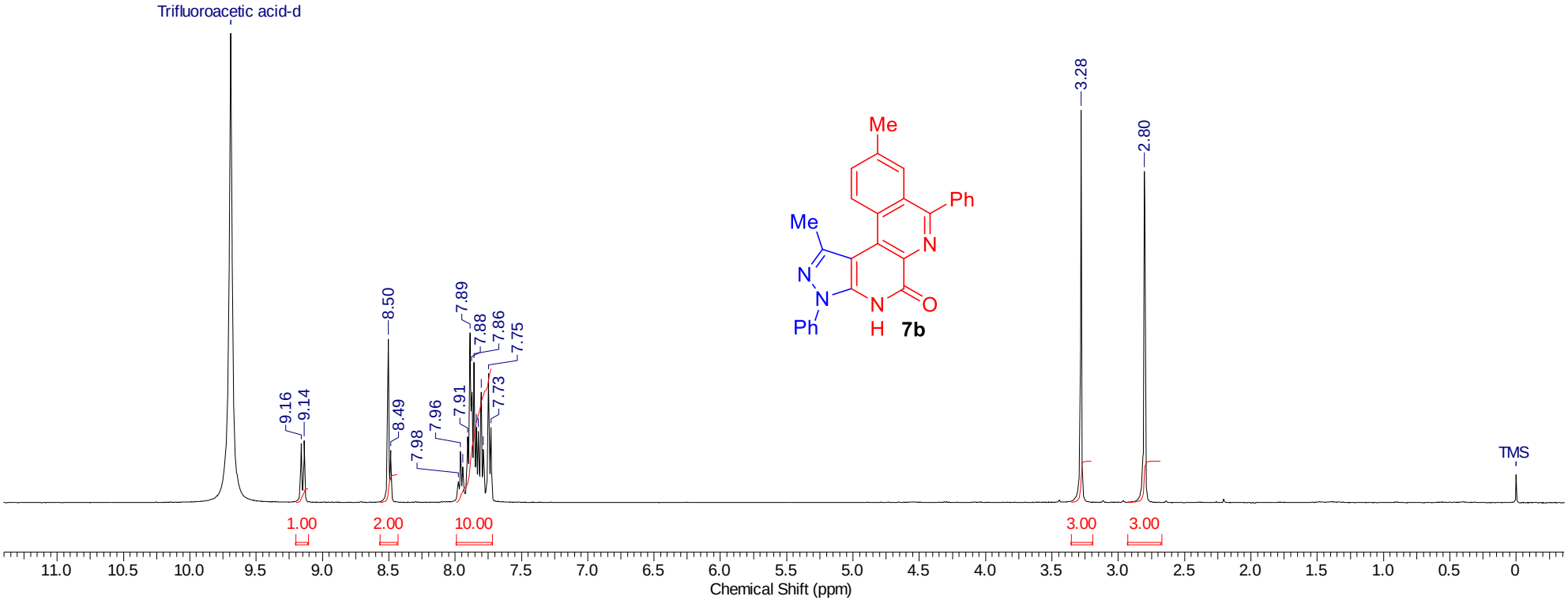



**Figure S64:** $^{1}H$ NMR spectrum of compound **7b** ($CF_3CO_2D$ + TMS).

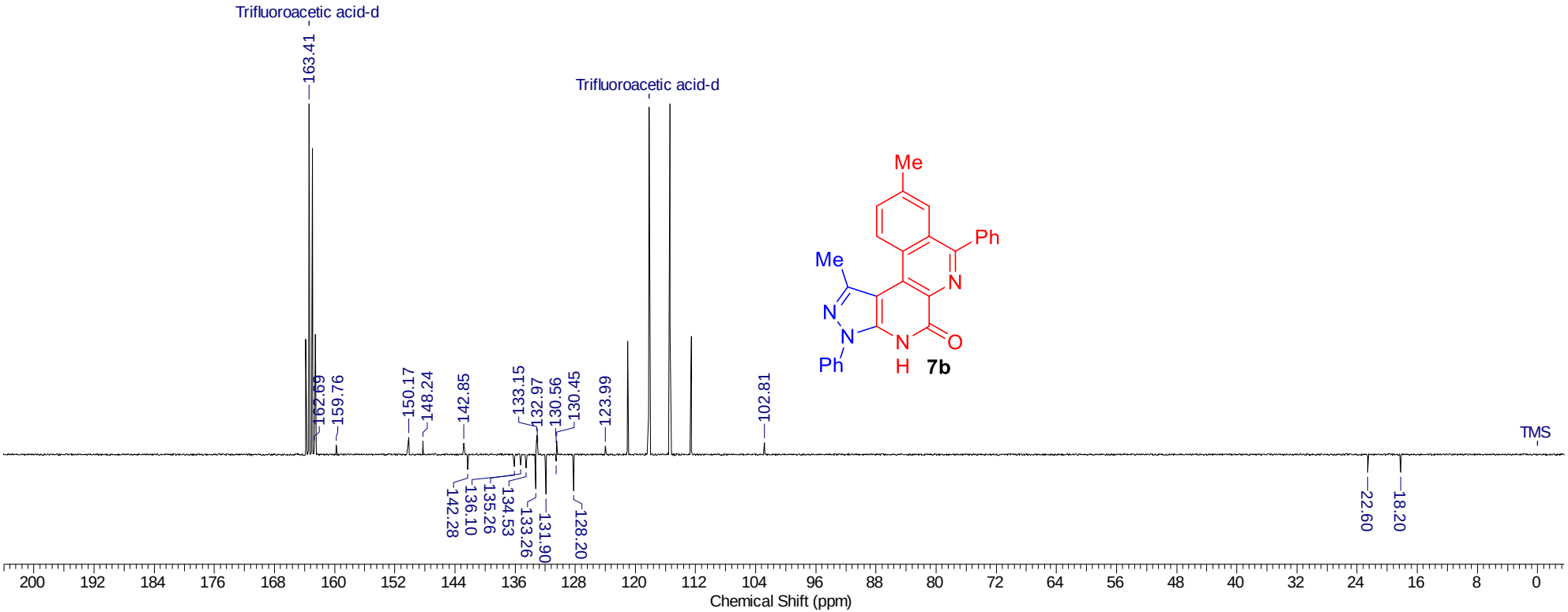



**Figure S65:** $^{13}C$ NMR spectrum of compound **7b** ($CF_3CO_2D$ + TMS).

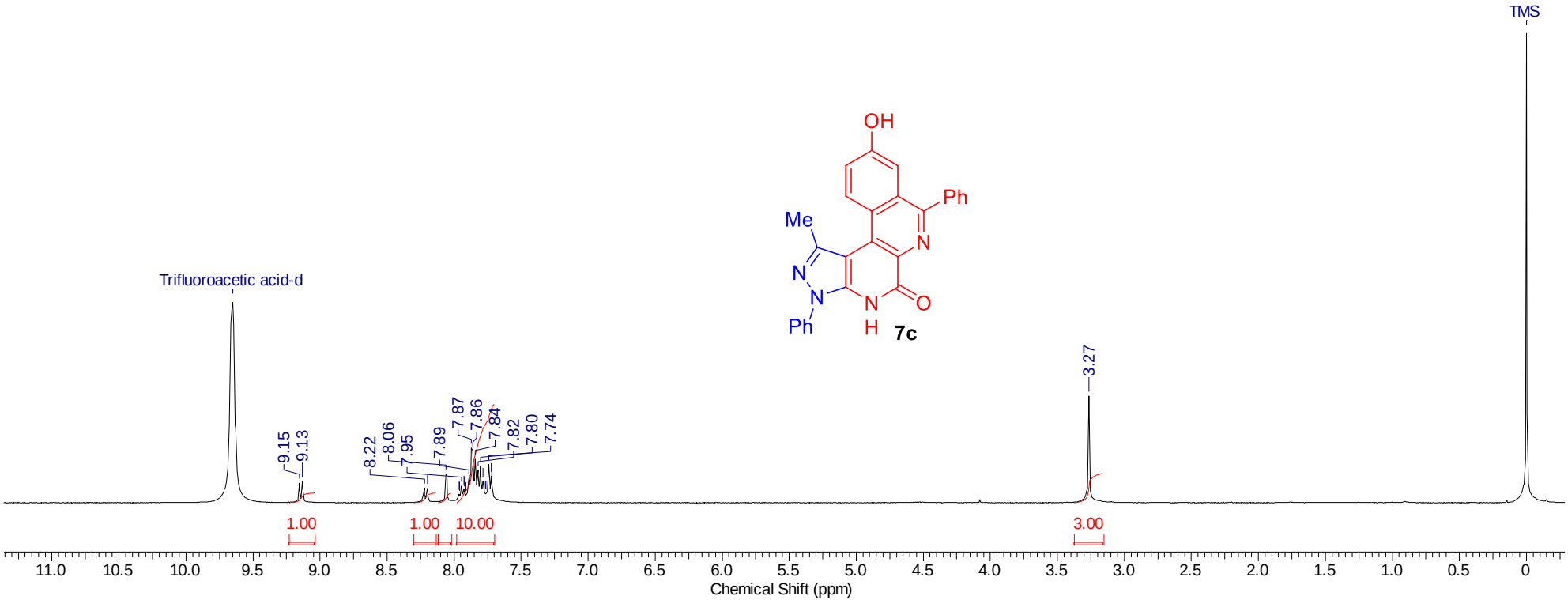



**Figure S66:** $^{1}$H NMR spectrum of compound **7c** ($CF_3CO_2D$ + TMS).

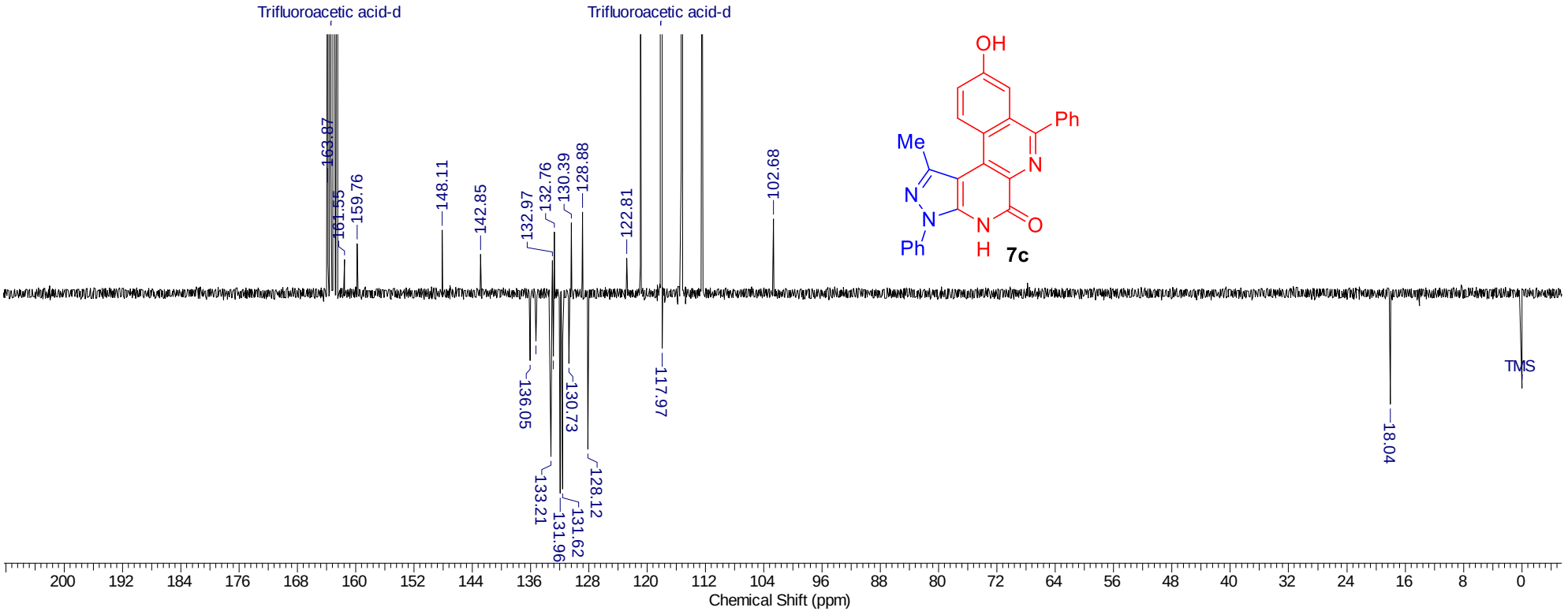



**Figure S67:** $^{13}C$ NMR spectrum of compound **7c** ($CF_3CO_2D$ + TMS).

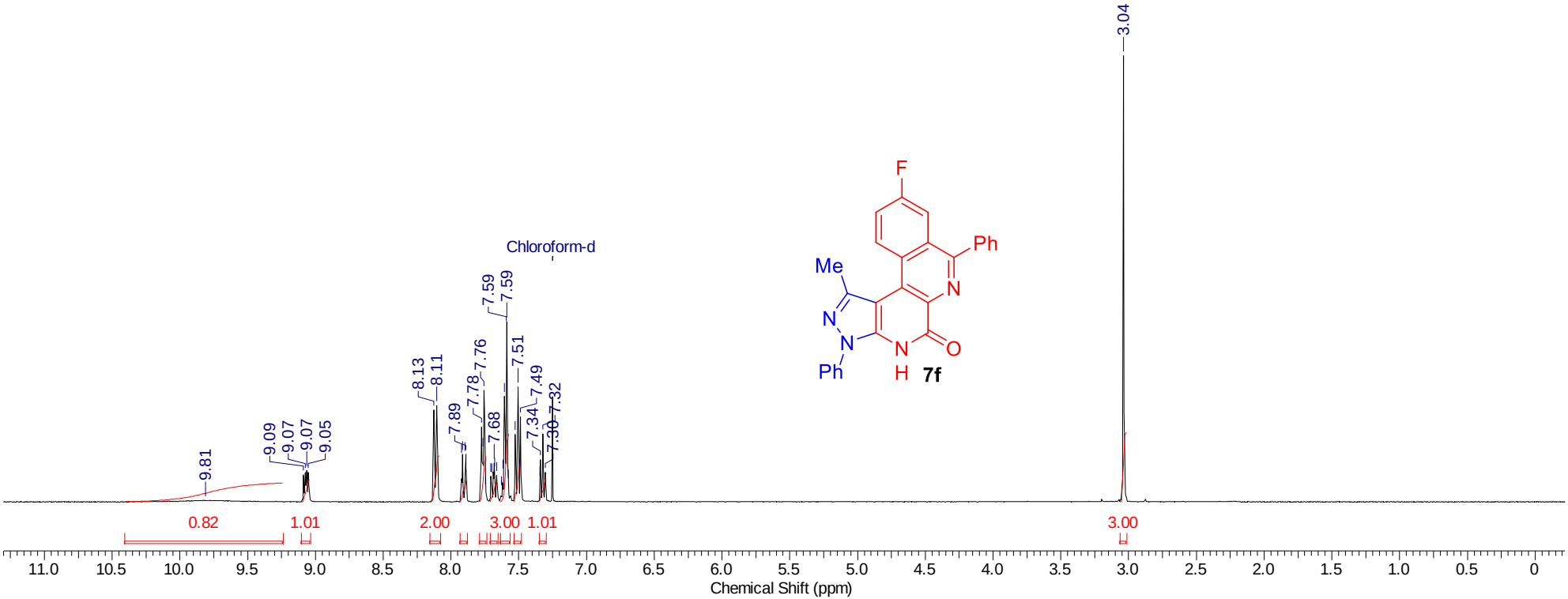



**Figure S68:** $^{1}H$ NMR spectrum of compound **7f** ($CDCl_3$).

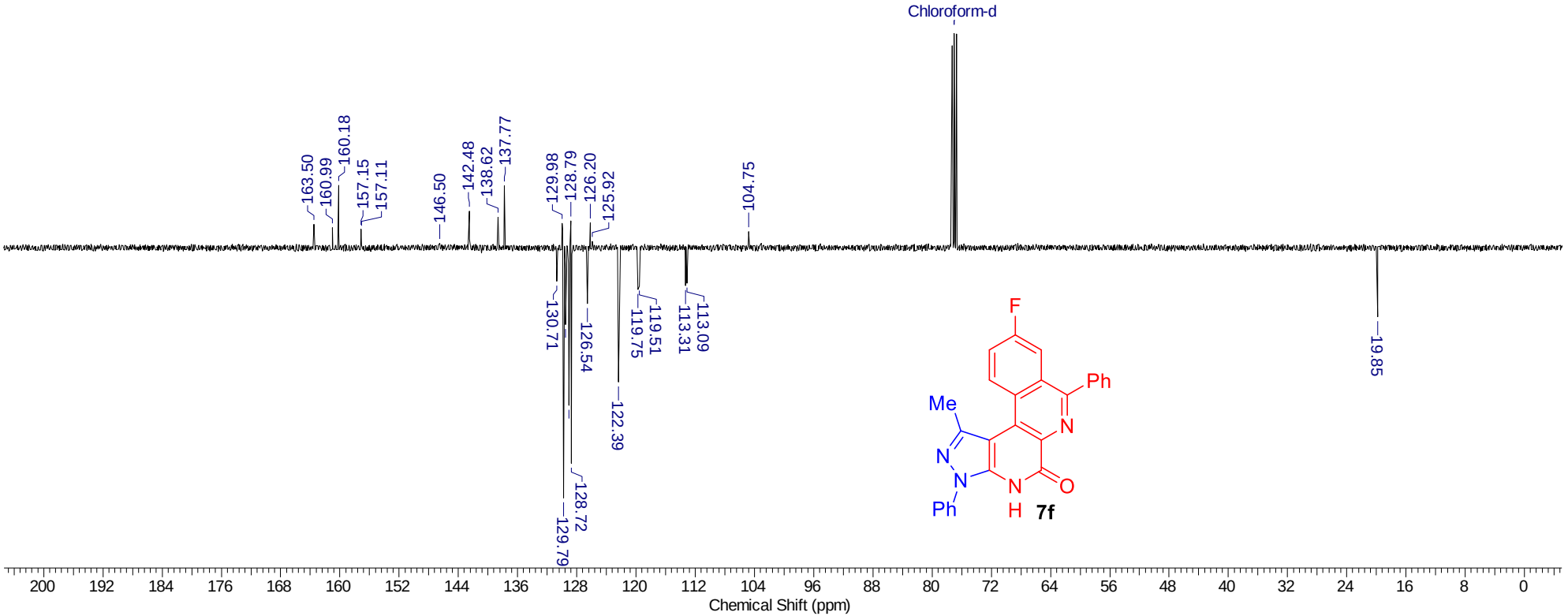



**Figure S69:** $^{13}C$ NMR spectrum of compound **7f** ($CDCl_3$).

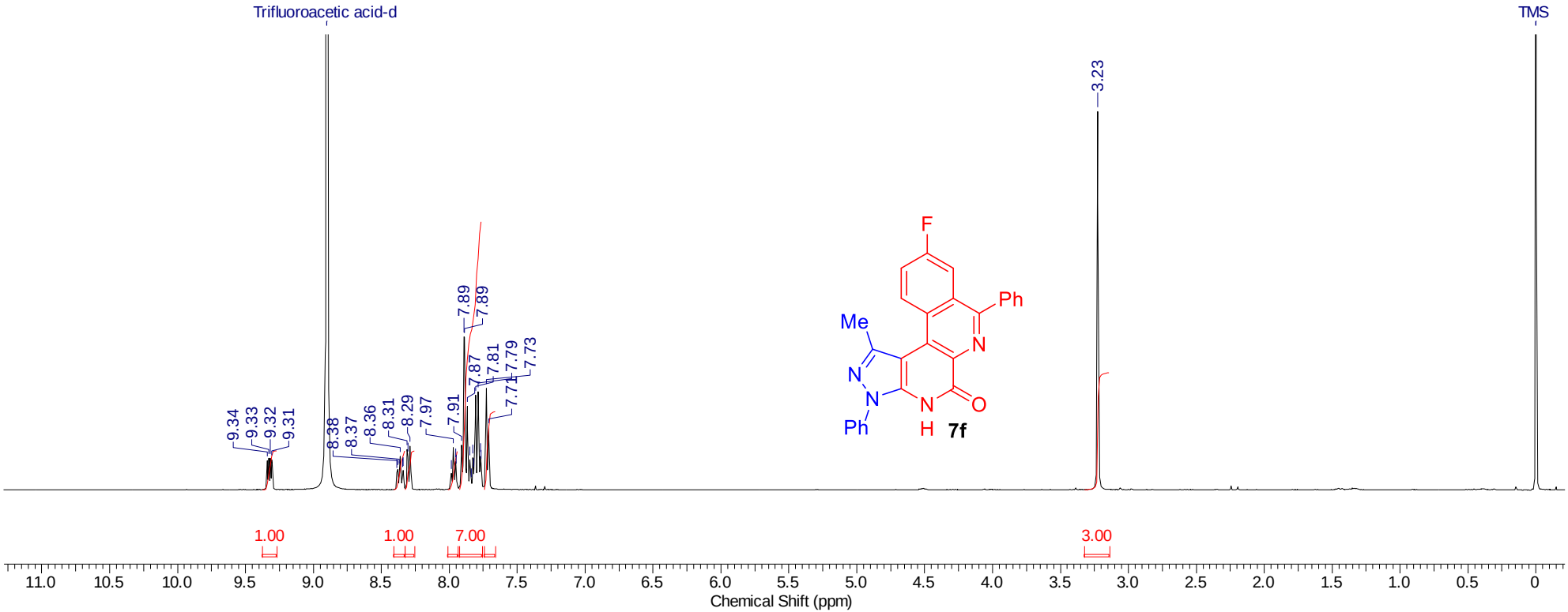



**Figure S70:** $^{1}H$ NMR spectrum of compound **7f** ($CF_3CO_2D$ + TMS).

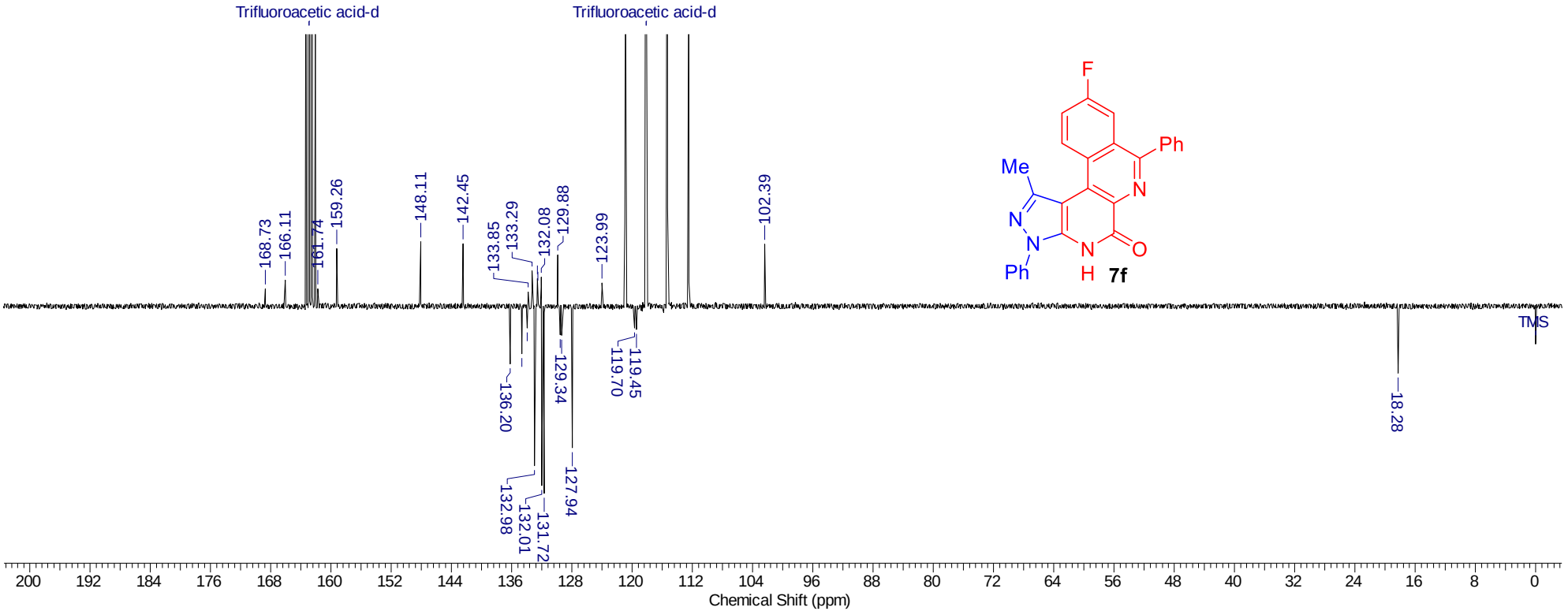



**Figure S71:** $^{13}C$ NMR spectrum of compound **7f** ($CF_3CO_2D$ + TMS).

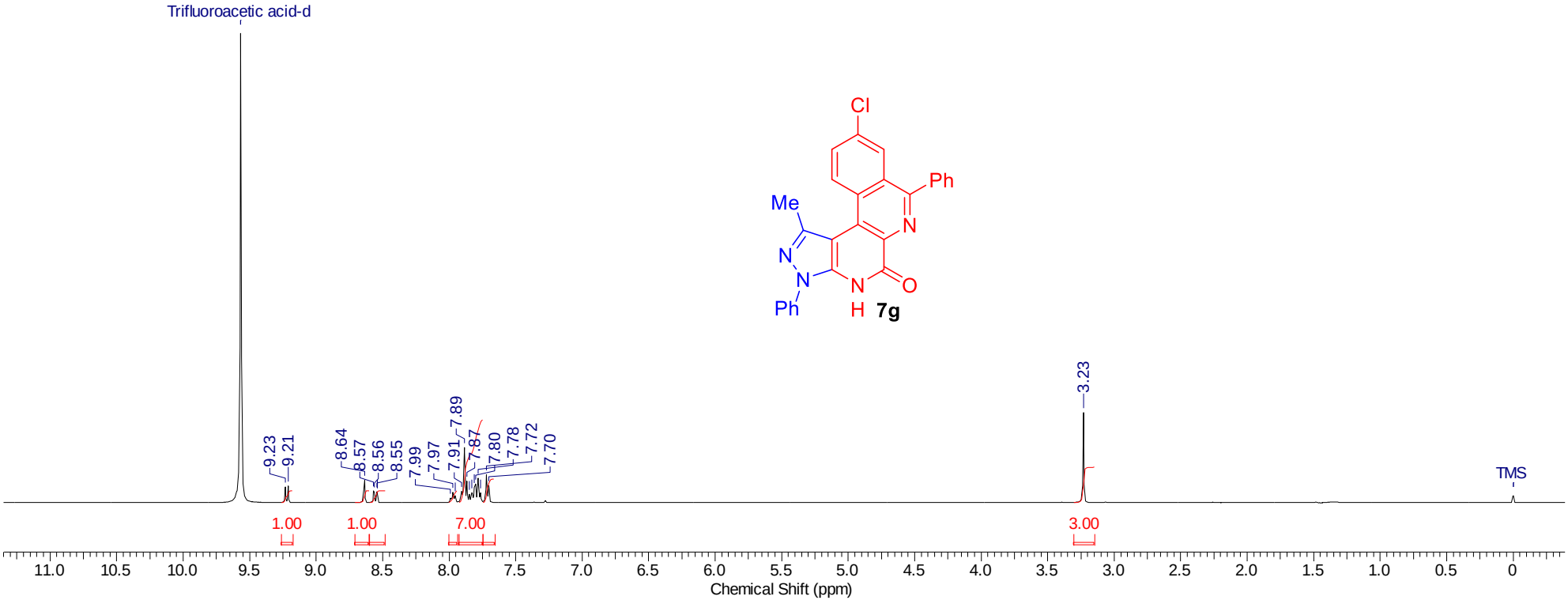



**Figure S72:** $^{1}$H NMR spectrum of compound **7g** ($CF_3CO_2D$ + TMS).

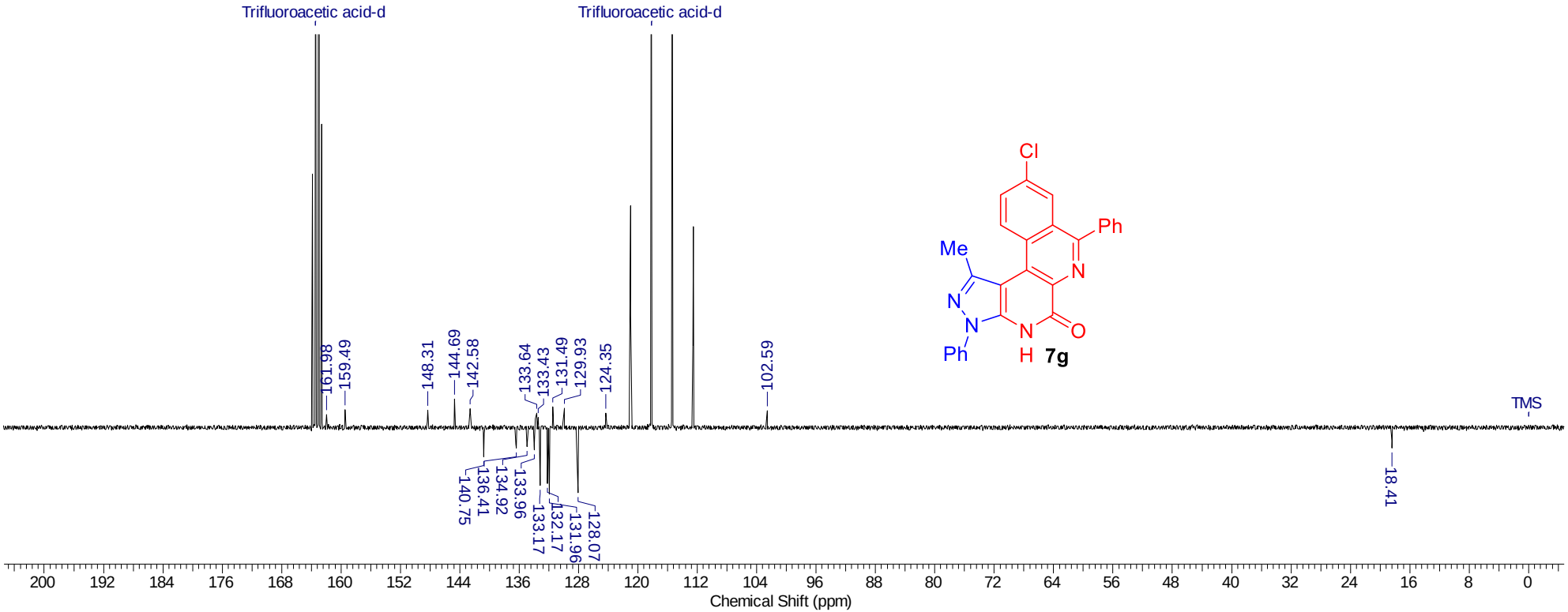



**Figure S73:** $^{13}C$ NMR spectrum of compound **7g** ($CF_3CO_2D$ + TMS).

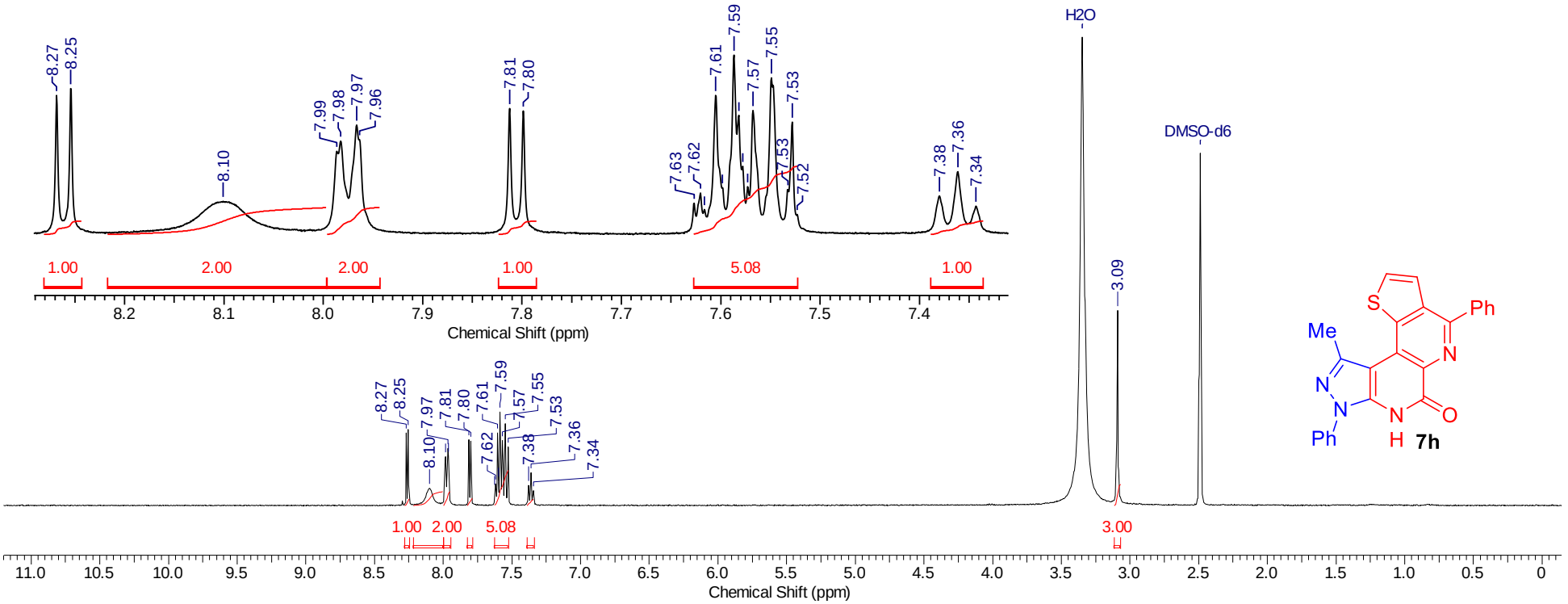



**Figure S74:** $^{1}$H NMR spectrum of compound **7h** (DMSO-$d_6$, 25°C).

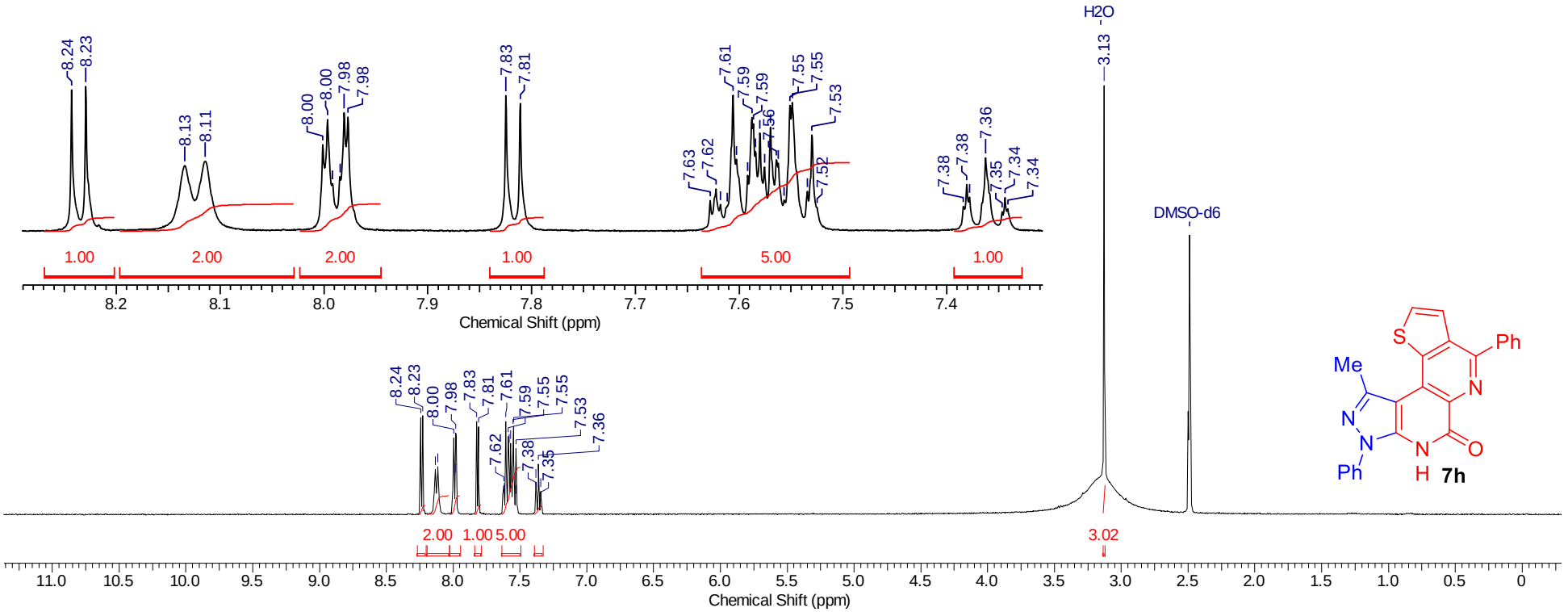



**Figure S75:** $^{13}$C NMR spectrum of compound **7h** (DMSO-$d_6$, 80°C).

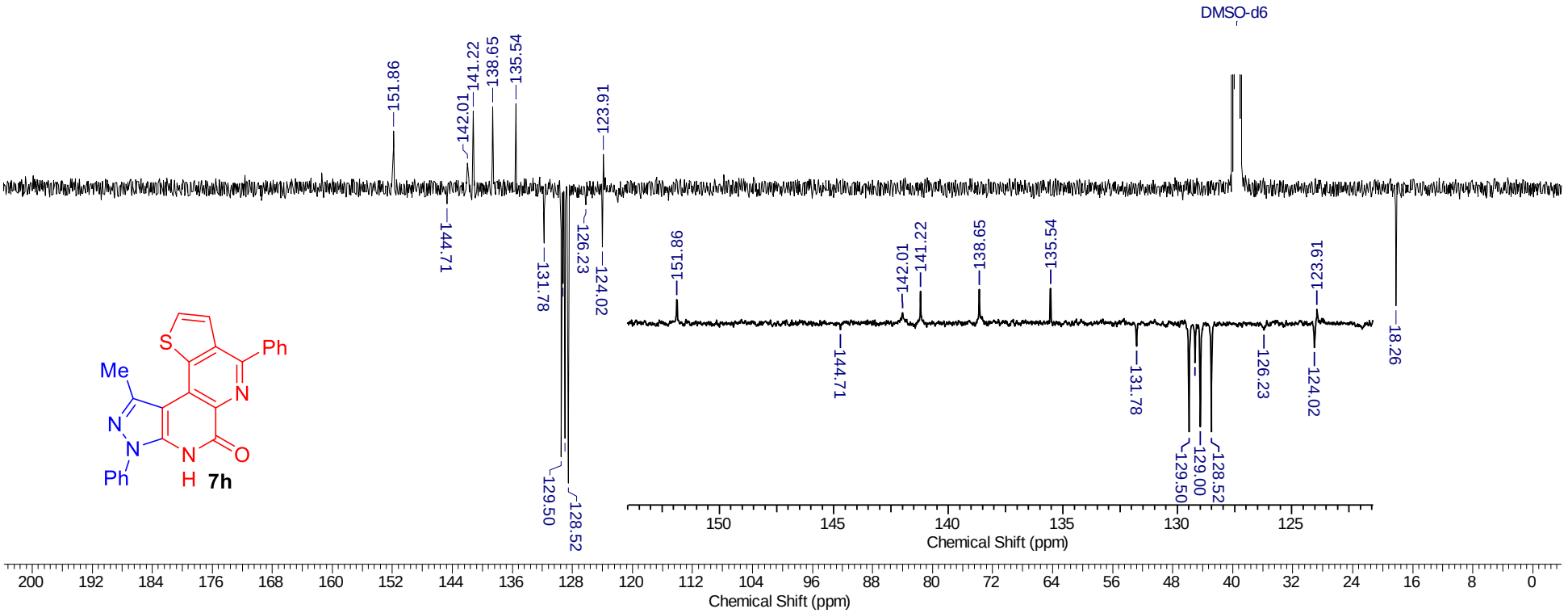



**Figure S76:** $^{13}$C NMR spectrum of compound **7h** (DMSO-$d_6$, 25°C).

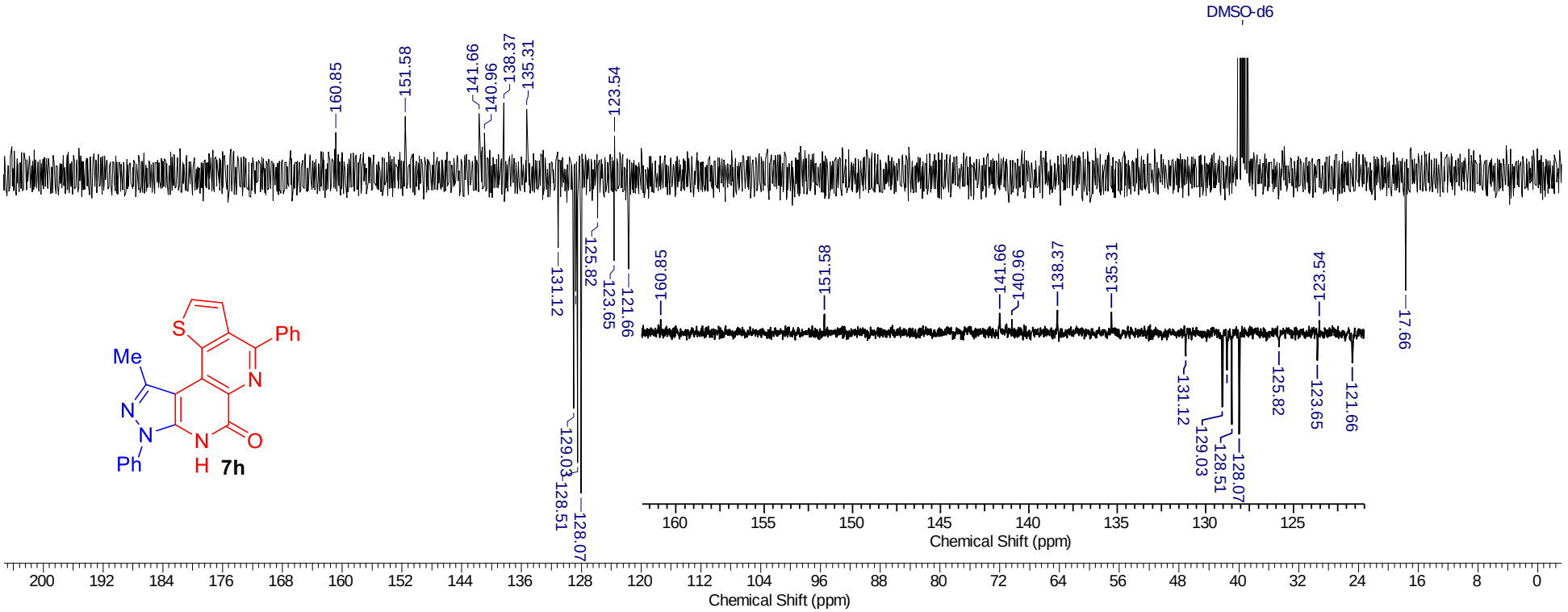



**Figure S77:** $^{13}$C NMR spectrum of compound **7h** (DMSO-$d_6$, 80°C).

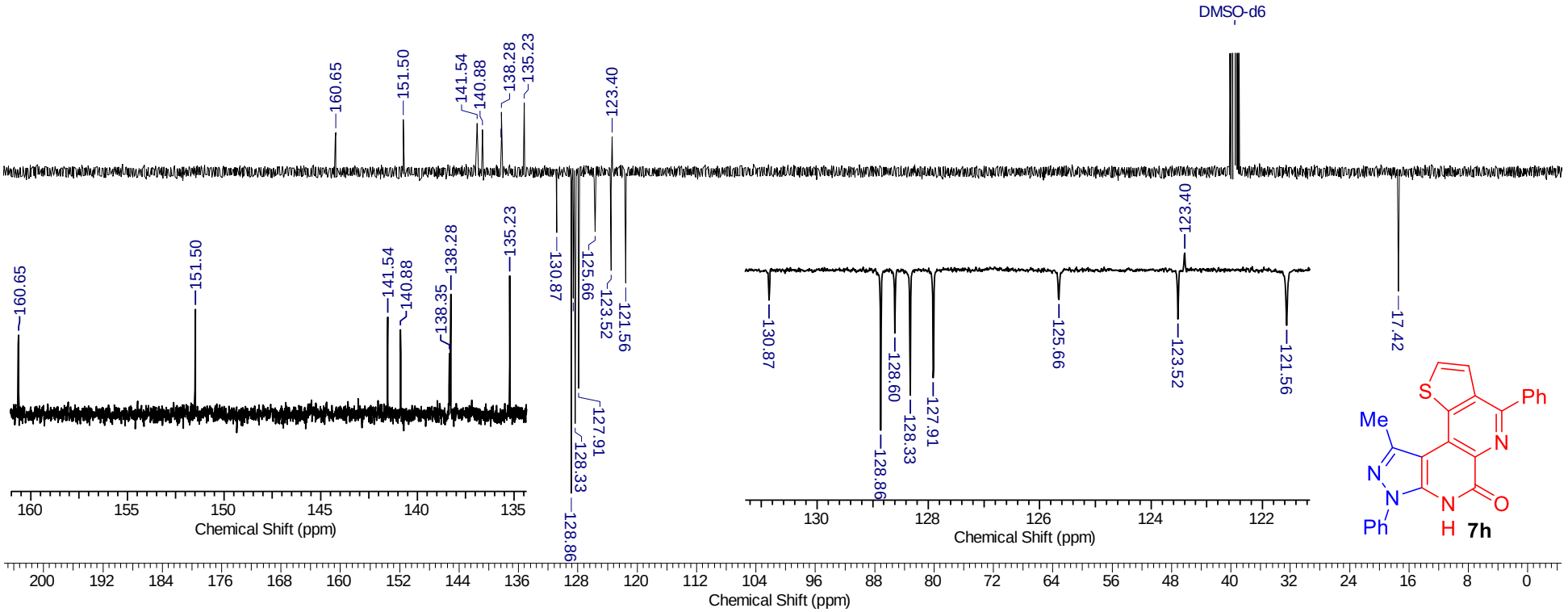



**Figure S78:** $^{13}$C NMR spectrum of compound **7h** (DMSO-$d_6$, 100°C).

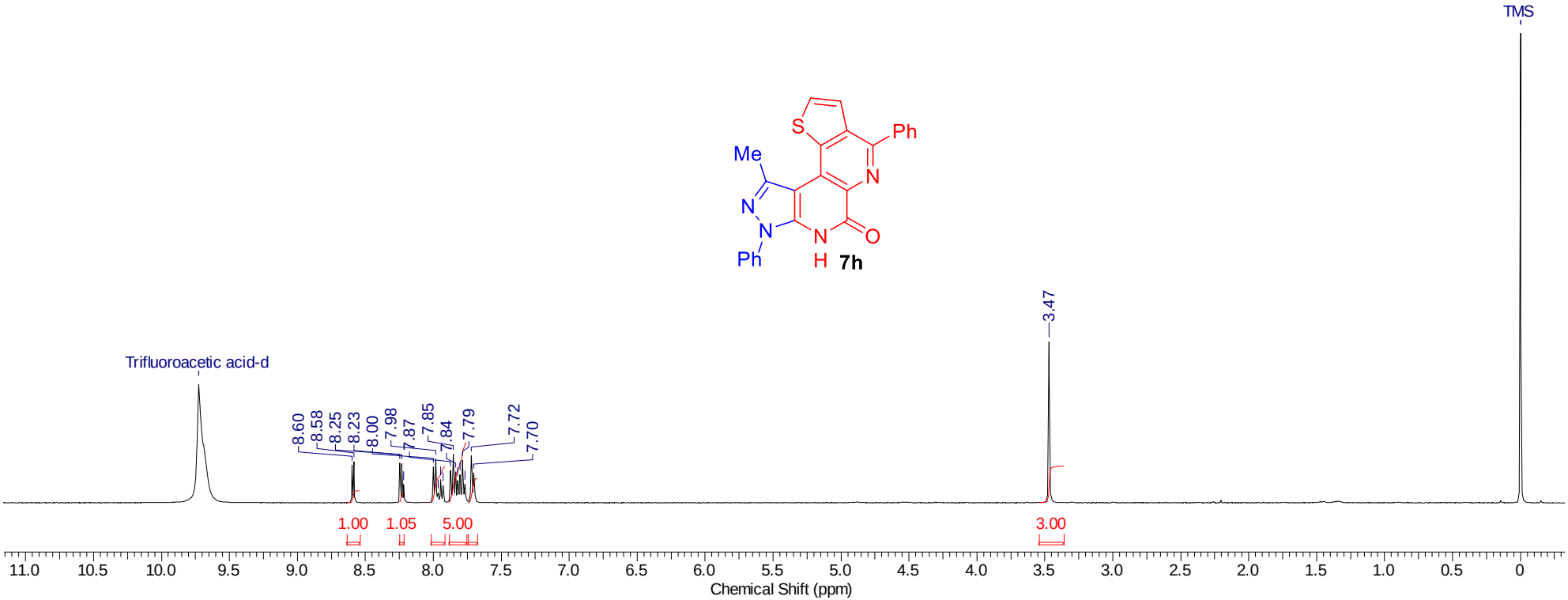



**Figure S79:** $^{1}H$ NMR spectrum of compound **7h** ($CF_3CO_2D$ + TMS).

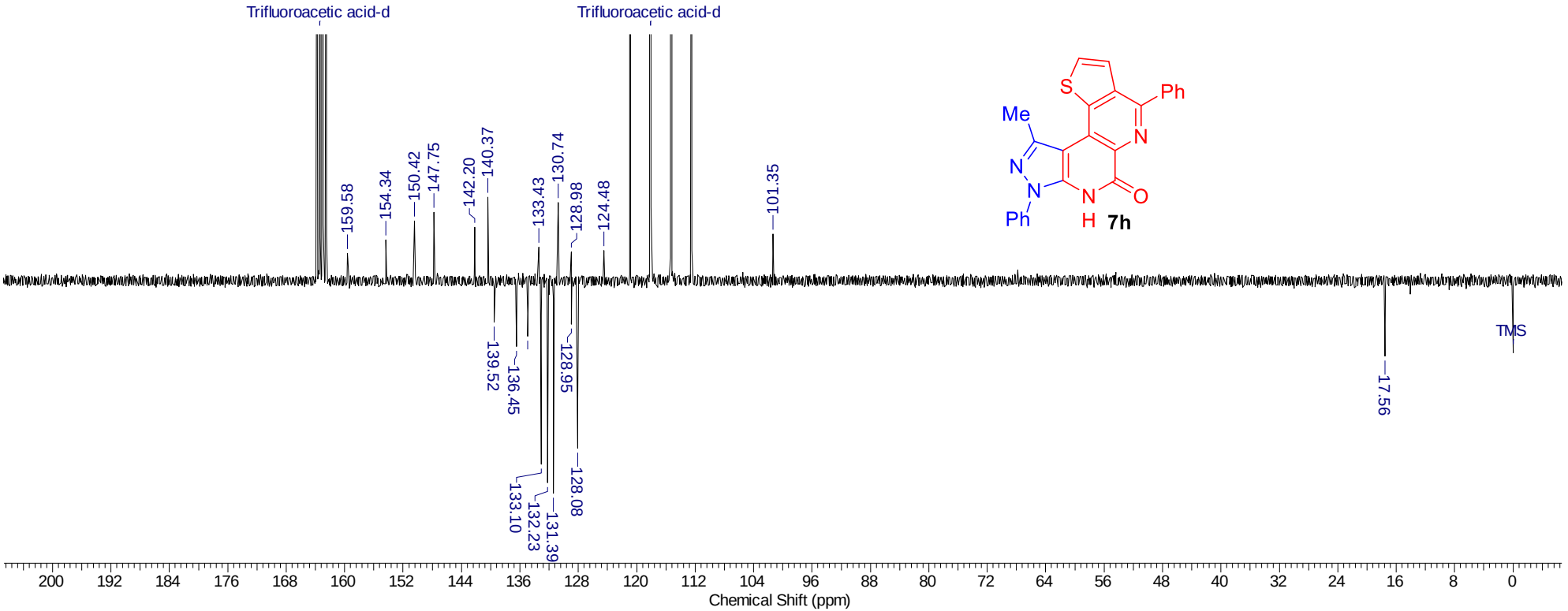



**Figure S80:** $^{13}C$ NMR spectrum of compound **7h** ($CF_3CO_2D$ + TMS).

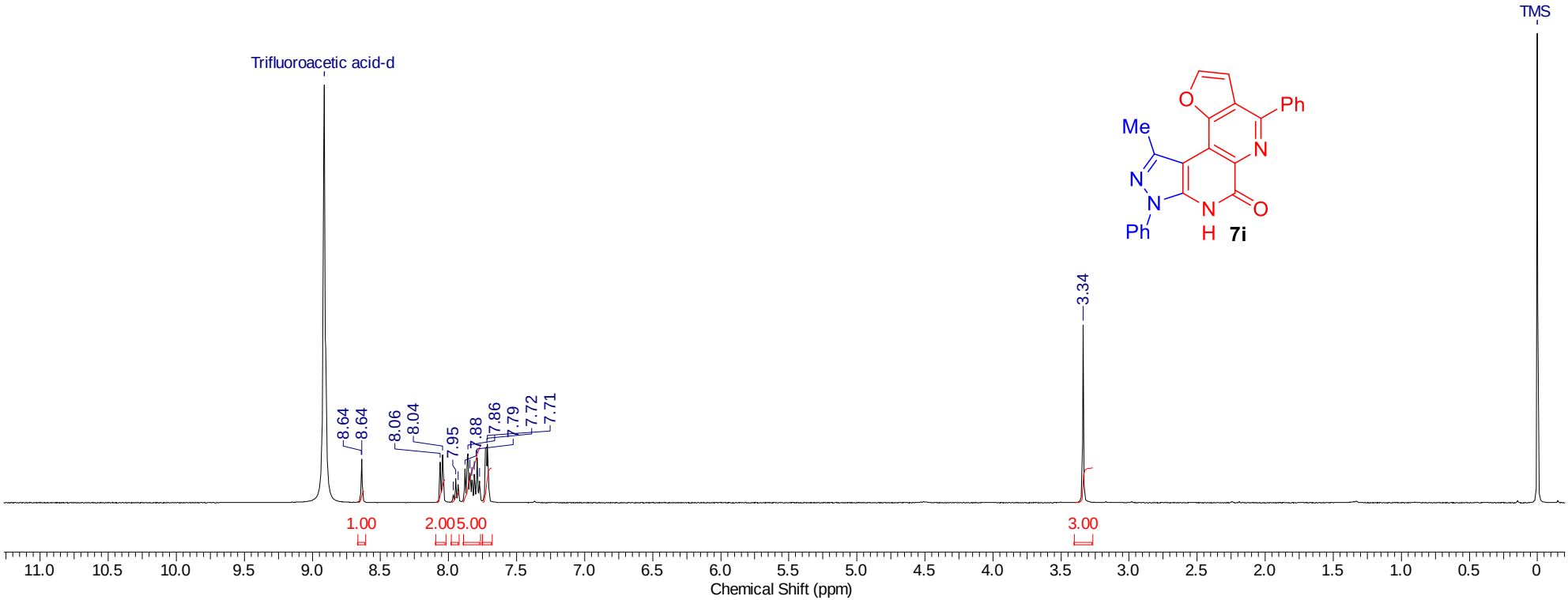



**Figure S81:** $^{1}H$ NMR spectrum of compound **7i** ($CF_3CO_2D$ + TMS).

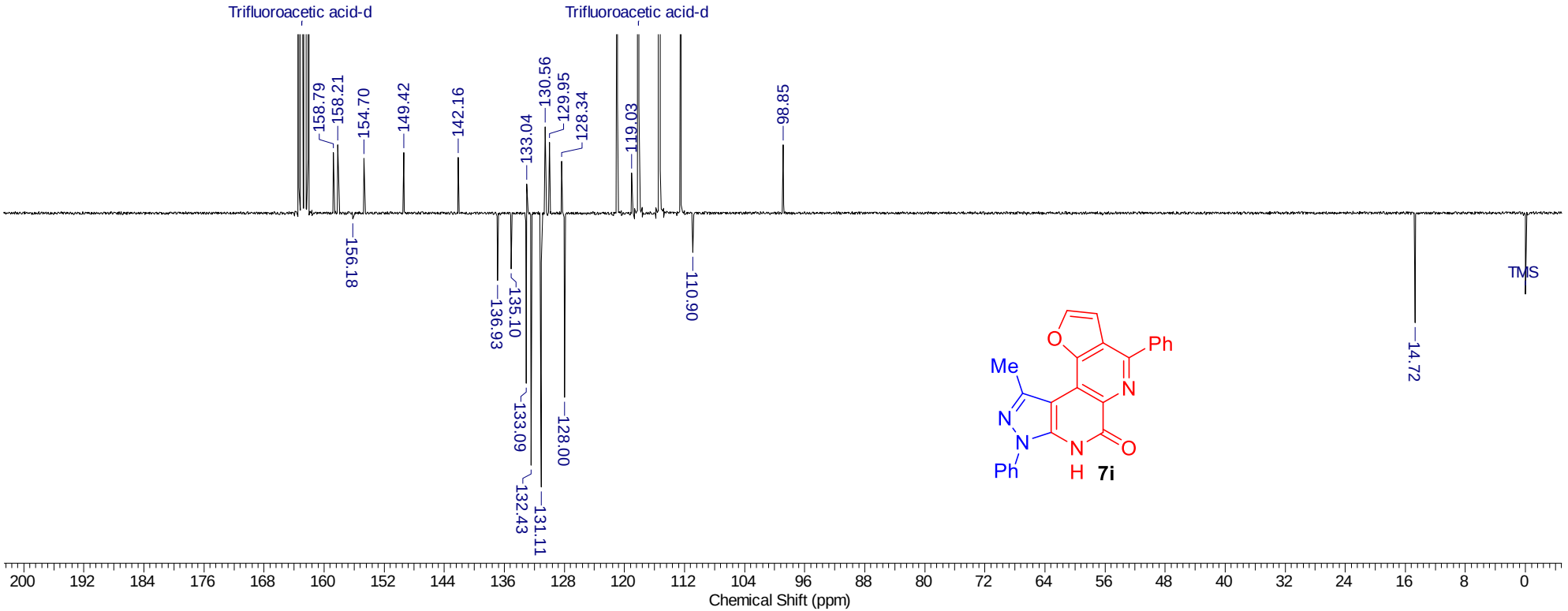



**Figure S82:** $^{13}C$ NMR spectrum of compound **7i** ($CF_3CO_2D$ + TMS).

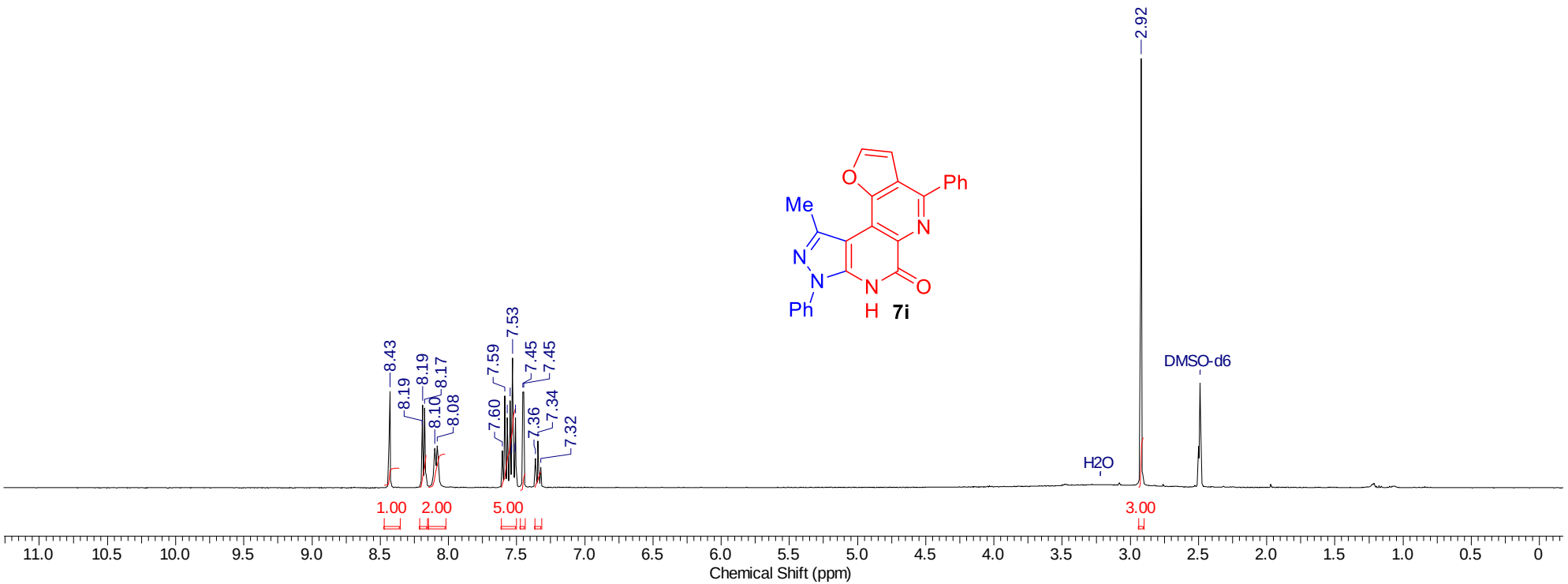



**Figure S83:** $^{1}$H NMR spectrum of compound **7i** (DMSO-$d_6$).

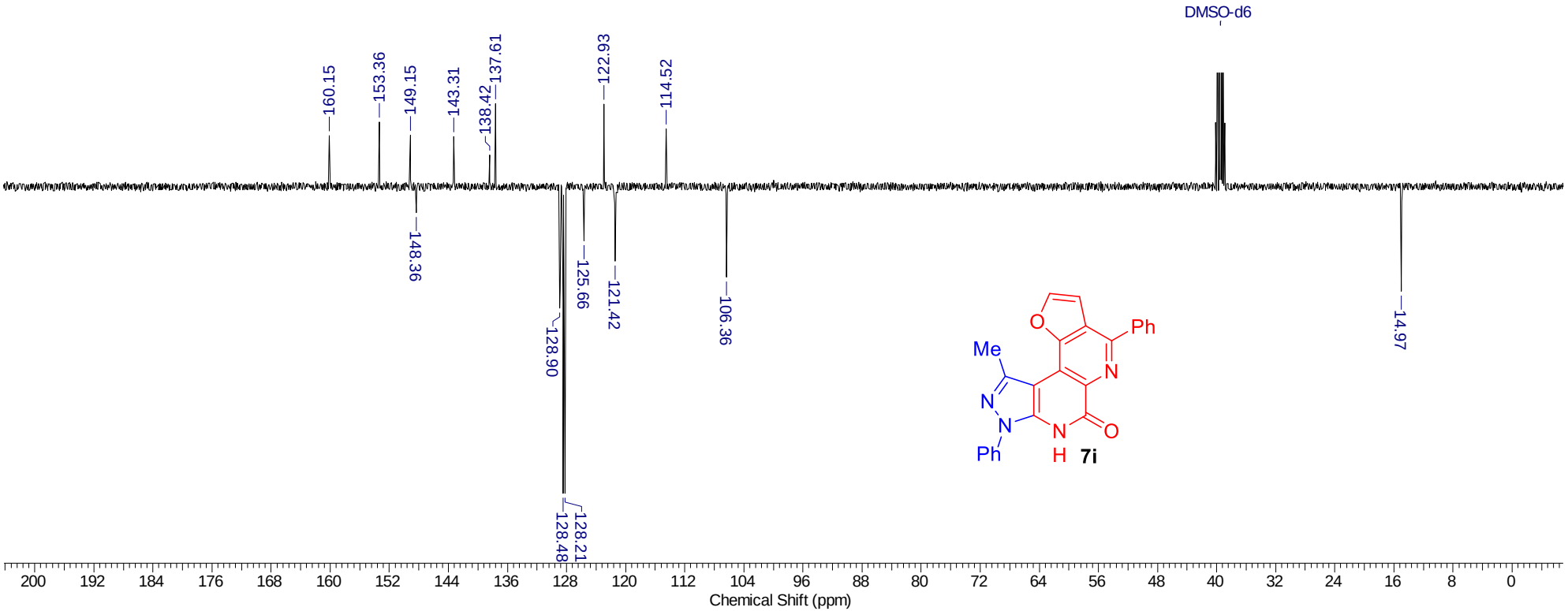



**Figure S84:** $^{13}$C NMR spectrum of compound **7i** (DMSO-$d_6$).