Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Contents

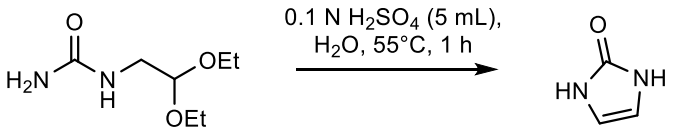
Experimental Section

General methods

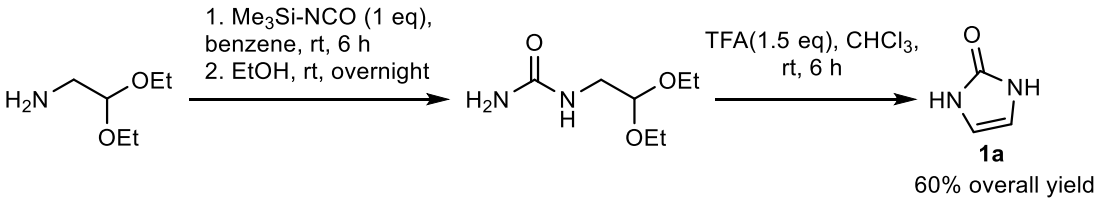
^{1}H spectra were recorded on a Bruker MSL 400 (400 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Bruker MSL 400 (100 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference (proton, $CDCl_3$ δ 7.28, CD_3OD δ 3.32, $(CD_3)_2CO$ δ 2.12, $(CD_3)_2SO$ δ 2.50; carbon, $CDCl_3$ δ 77.7, $(CD_3)_2SO$ δ 40.0). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), td (triplet of doublet), bs (broad singlet). Coupling constants were reported in Hertz (Hz). The IR spectra were recorded on a Vector 22 Fourier spectrometer by Bruker in the range of 400-4000 cm^{-1}. Crystalline samples were studied as a suspension in vaseline oil. The melting points were determined in glass capillaries on a Stuart SMP 10 instrument. Elemental analysis of the compounds was carried out on a high-temperature 2-reactor C, H, Nanalyzer of EuroVector brand EA 3000. The halogen content was determined by the Schöniger method. MALDI-TOF mass spectra were recorded on a Bruker ULTRAFLEX III TOF/TOF instrument (with 2,5-dihydroxybenzoic acid matrix). All commercially available reagents were used as received for the reactions without any purification. All solvents were purified and dried according to standard procedures. 4,4'-bi(imidazole-2-one) **2b** and diimidazoquinoline **4** have been described earlier[4] and were not isolated in pure form.

Synthesis of imidazolinone 1a

The synthesis of imidazolin-2-one **1a** via the acid-catalyzed cyclization of 1-(2,2-diethoxyethyl)urea was first claimed by Marckwald in 1892.[1] Later, Duschinsky and Dolan re-investigated this reaction and stated the formation of imidazolin-2-one **1a** in *ca* 40% yield upon heating of 1-(2,2-diethoxyethyl)urea in the presence of sulfuric acid.[2] Alongside with desired imidazolinone, the unidentified product was obtained, which was believed to be a dimer or a polymer arising from intermolecular condensation of starting acetal. The same procedure was used by Han and Zard, and the yield of 44% of compound **1a** was reported.[3] Duschinsky and Dolan also described the synthesis of compound **1a** in 80% yield by carrying out the reaction in diluted solution of sulfuric acid at room temperature for 72 hours. However, we were unable to reproduce this result, and the yield didn't exceed 30-35%.



We speculated that the low yield of imidazolinone **1a** may be due to the formation of bis(imidazolinone) **2a** in acidic media. According to our observations reported in present paper, this undesired side reaction can be suppressed by the formation of 2-hydroxyimidazolium salt. Indeed, when excess of TFA was employed instead of sulfuric acid and the reaction time was limited to 6 hours, the target imidazolin-2-one **1a** was isolated in 60% overall yield. Still, the formation of the compound **2a** was also observed (*ca* 10-15% according to NMR data). The modified procedure for the synthesis of compound **2a** is given below.

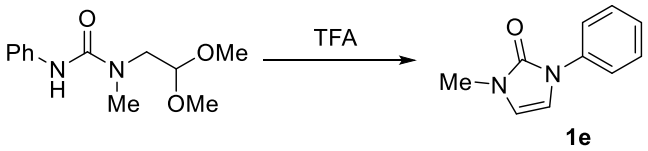


To a solution of trimethylsilylisocyanate (0.54 g, 4.7 mmol, 1.0 equiv.) in benzene (10 mL) 2,2-diethoxyethane-1-amine (0.50 g, 4.7 mmol, 1.0 equiv.) was added. The reaction mixture was stirred at room

temperature for 6 h, and the solvent was evaporated in vacuum. The residue was re-dissolved in ethanol (10 mL) and stirred at room temperature overnight. The volatiles were removed in vacuum; the residue was dissolved in chloroform (5 mL). To this solution, trifluoroacetic acid (0.81 g, 0.54 mL, 7.1 mmol, 1.5 equiv.) was added. The reaction mixture was stirred at room temperature for 6 h and washed with saturated solution of $NaHCO_3$ (3x10 mL). The organic layer was evaporated in vacuum and the residue was recrystallized from small amount of distilled water to give compound **1a** as white crystalline solid. Yield 240 mg (60%). Mp = 248-253°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.67 (br s, 2H, NH), 6.24 (t, *J*=2.0 Hz, 2H, CH). ^{13}C NMR (126 MHz, DMSO-d_6)* δ 155.9, 109.0.

Synthesis of imidazolinones 1e-g[4]

*1-methyl-3-phenylimidazolin-2-one (**1e**)*



1e

To a 25 mL flask a 1-(2,2-dimethoxyethyl)-1-methyl-3-phenylurea[4] (0.50 g, 2.1 mmol, 1.0 equiv.), chloroform (10 mL) and TFA (0.28 mL, 0.353 g, 3.1 mmol, 1.5 equiv.) were added. The reaction mixture was allowed to stir at room temperature for 6 h and concentrated under reduced pressure. To the resulting yellow oily residue distilled water (15 mL) and Na_2CO_3 (0.45 g, 4.2 mmol, 2 equiv.) were added. The precipitate was filtered off, washed with distilled water (3x20 mL) and dried under reduced pressure to give the compound **1e** as yellowish solid (329 mg, yield 90%), which was used without further purification. Mp 105-107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.56 (m, 2H, ArH), 7.43-7.35 (m, 2H, ArH), 7.24-7.18 (m, 1H, ArH), 6.55 (d, 1H, *J* = 3.0 Hz, CH), 6.30 (d, 1H, *J* = 3.1 Hz, CH), 3.29 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.6, 138.0, 129.7, 126.2, 122.0, 113.3, 109.7, 31.0.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.74-7.68 (m, 2H, ArH), 7.45-7.39 (m, 2H, ArH), 7.24-7.18 (m, 1H, ArH), 7.00 (d, 1H, *J* = 3.1 Hz, CH), 6.71 (d, 1H, *J* = 3.1 Hz, CH), 3.28 (s, 3H, CH_3). ^{13}C NMR (126 MHz, DMSO-d_6) δ 152.4, 138.5, 130.0, 126.0, 121.4, 114.6, 109.7, 31.0.

^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.84-7.77 (m, 2H, ArH), 7.50-7.46 (m, 2H, ArH), 7.30-7.25 (m, 1H, ArH), 6.95 (d, 1H, *J* = 3.2 Hz, CH), 6.68 (d, 1H, *J* = 3.1 Hz, CH), 3.31 (s, 3H, CH_3).

^{1}H NMR (400 MHz, CD_3OD) δ 7.62-7.57 (m, 2H, ArH), 7.49-7.42 (m, 2H, ArH), 7.33-7.28 (m, 1H, ArH), 6.84 (d, 1H, *J* = 3.0 Hz, CH), 6.63 (d, 1H, *J* = 3.0 Hz, CH), 3.32 (s, 3H, CH_3).

Anal. Calcd for $C_{10}H_{10}N_2O$: C, 68.95; H, 5.79; N, 16.08. Found: C, 68.80; H, 5.63; N, 16.13. MS (ESI) *m/z* calcd for $C_{10}H_{10}N_2O$: 174.2; found 175.1 $[M+H]^+$, 197.5 $[M+Na]^+$.

*1-(4-chlorophenyl)-3-methylimidazolin-2-one (**1f**)*

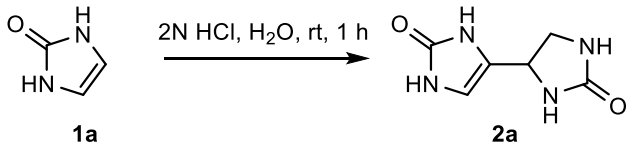
The compound **1f** was obtained using the same procedure as described above from 0.500 g (1.83 mmol) of 1-(2,2-dimethoxyethyl)-1-methyl-3-(4-chlorophenyl)urea[4] and used without additional purification. Yellowish solid, yield 325 mg (85%), mp 70-74°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.46 (m, 2H, ArH), 7.37-7.28 (m, 2H, ArH), 6.51 (d, 1H, *J* = 3.0 Hz, CH), 6.31 (d, 1H, *J* = 3.1 Hz, CH), 3.26 (s, 3H, CH_3). ^{13}C NMR (126 MHz, DMSO-d_6) δ 151.27, 140.58, 132.76, 120.06, 118.02, 113.70, 107.17, 30.02. Anal. Calcd for $C_{10}H_9ClN_2O$: C, 57.57; H, 4.35; Cl, 16.99; N, 13.43. Found: C, 57.45; H, 4.40; Cl, 17.05; N, 13.39. MS (ESI) *m/z* calcd for $C_{10}H_9ClN_2O$: 208.0; found 209.0 $[M+H]^+$.

* The signal of carbon atom of carbonyl group at 155.9 ppm was not observed in proton-decoupled ^{13}C NMR spectrum, thus ^{1}H-^{13}C HMBC spectrum was recorded. The presence of the cross-peak between protons of methyne groups and carbon atom of C=O group confirms the assigned structure (see copies of spectra below).

*1-(4-methoxyphenyl)-3-methylimidazolin-2-one (**1g**)*

The compound **1g** was obtained using the same procedure as described above from 0.50 g (1.86 mmol) of 1-(2,2-dimethoxyethyl)-1-methyl-3-(4-methoxyphenyl)urea[4] and used without additional purification.. Yellowish solid, yield 342 mg (90%), mp 84-88°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.41 (m, 2H, ArH), 6.98-6.89 (m, 2H, ArH), 6.50 (d, 1H, *J* = 3.0 Hz, CH), 6.30 (d, 1H, *J* = 3.1 Hz, CH), 3.83 (s, 3H, CH_3), 3.32 (s, 3H, CH_3). ^{13}C NMR (126 MHz, DMSO-d_6) δ 151.98, 146.60, 125.02, 117.82, 108.72, 106.64, 104.11, 49.88, 24.85. Anal. Calcd for $C_{11}H_{12}N_2O_2$: C, 64.69; H, 5.92; N, 13.72. Found: C, 64.72; H, 5.88; N, 13.78. MS (ESI) *m/z* calcd for $C_{11}H_{12}N_2O_2$: 204.2; found 205.1 $[M+H]^+$, 227.2 $[M+Na]^+$.

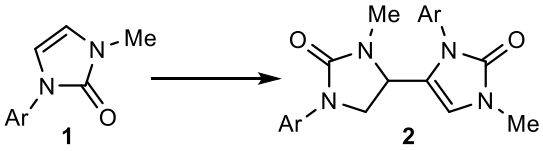
Synthesis of compound 2a



1a **2a**

To a 25 mL flask an imidazolin-2-one **1a** (0.40 g, 4.7 mmol), distilled water (5 mL) and 2N HCl (3.56 mL, 7.1 mmol, 1.5 equiv.) were added. The reaction mixture was stirred at room temperature for 1 h. The solvent was removed under reduced pressure and the solid residue was recrystallized from ethanol to give 418 mg (53%) of the title compound **2a** as beige solid. Mp 50-54 °C. ^{1}H NMR (400 MHz, D_2O) δ 3.42 (dd, *J* = 9.6, 7.1 Hz, 1H, CH), 3.79-3.70 (m, 1H, CH), 4.79 (dd, *J* = 9.4, 7.1 Hz, 1H, CH), 6.44 (s, 1H, CH). ^{13}C NMR (126 MHz, D_2O) δ 165.9, 155.9, 123.4, 110.7, 107.9, 48.9, 46.5. Anal. Calcd for $C_6H_8N_4O_2$: C, 42.86; H, 4.80; N, 33.32. Found: C, 42.98; H, 4.88; N, 33.29. MS (ESI) *m/z* calcd for $C_6H_8N_4O_2$: 168.1, found: 192.2 $[M+Na]^+$.

Dimerization of imidazolin-2-ones in the presence of TsOH

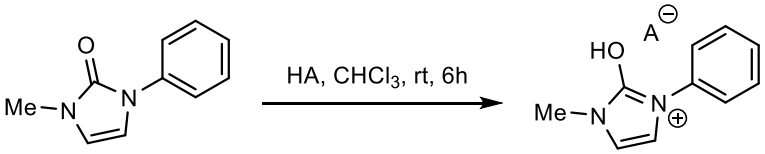


1 **2**

Ar = Ph (**1e, 2b**); 4-Cl-C_6H_4 (**1f, 2c**); 4-MeO-C_6H_4 (**1g, 2d**)

To a 25 mL flask an imidazolin-2-one **1** (2.1 mmol, 1.0 equiv.), chloroform (5 mL) and TsOH (0.072 g, 0.42 mmol, 0.2 equiv.) were added. The reaction mixture was stirred at room temperature for 7 days. The solvent was removed under reduced pressure and the solid residue was analyzed by ^{1}H NMR.

Synthesis of 2-hydroxyimidazolium salts 3a,b



1e **3a,b**

HA = TfOH (a), TFA (b)

To a 25 mL flask an imidazolinone **1e** (0.5 g, 2.1 mmol, 1.0 equiv.) chloroform (5 mL) and appropriate acid (3.1 mmol, 1.5 equiv.) were added. The reaction mixture was stirred at room temperature for 6 h and concentrated under reduced pressure. The residue was washed thoroughly with dry diethyl ether (3x25 mL) and dried under reduced pressure to give the compound **3**.

*2-hydroxy-1-methyl-3-phenylimidazolium triflate (**3a**).* Yellow gum, 0.67 g (98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.47 (m, 3H, ArH), 7.45-7.41 (m, 2H, ArH), 6.92 (d, 1H, *J* = 2.5 Hz, CH), 6.88 (d, 1H, *J* = 2.6 Hz,

CH), 3.70 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.4, 134.2, 130.4, 130.0, 124.9, 117.5, 115.9, 33.4. Anal. Calcd for $C_{11}H_{11}N_2O_4SF_3$: C, 40.74; H, 3.42; F, 17.58; N, 8.64; S, 9.89. Found: C, 40.68; H, 3.51; F, 17.40; N, 8.60; S, 9.81. MS (ESI) *m/z* calcd for $C_{11}H_{11}N_2O_4SF_3$: 324.3; found 175.0 $[M\text{-}CF_3SO_3]^+$.

*2-hydroxy-1-methyl-3-phenylimidazolium trifluoroacetate (**3b**).* Brown hygroscopic gum, 0.60 g (*ca* 100% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.74-7.67 (m, 2H, ArH), 7.45-7.38 (m, 2H, ArH), 7.24-7.17 (m, 1H, ArH), 6.97 (d, 1H, *J* = 3.1 Hz, CH), 6.69 (d, 1H, *J* = 3.1 Hz, CH), 3.20 (s, 3H, CH_3). ^{13}C NMR (126 MHz, DMSO-d_6) δ 158.8 (q, *J* = 38.7 Hz), 151.8, 137.9, 129.4, 125.5, 121.0, 114.0, 109.1, 30.3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.53 (m, 2H, ArH), 7.47-7.39 (m, 2H, ArH), 7.31-7.23 (m, 1H, ArH), 6.60 (d, 1H, *J* = 3.0 Hz, CH), 6.38 (d, 1H, *J* = 3.0 Hz, CH), 3.36 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2 (q, *J* = 40.5 Hz), 152.6, 137.4, 129.8, 127.0, 122.8, 113.6, 110.7, 31.3.

^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 9.04-8.94 (m, 2H, ArH), 8.73-8.64 (m, 2H, ArH), 8.54-8.43 (m, 1H, ArH), 8.16 (d, 1H, *J* = 3.1 Hz, CH), 7.90 (d, 1H, *J* = 3.1 Hz, CH), 4.53 (s, 3H, CH_3).

^{1}H NMR (400 MHz, CD_3OD) δ 7.61-7.56 (m, 2H, ArH), 7.48-7.40 (m, 2H, ArH), 7.32-7.24 (m, 1H, ArH), 6.82 (d, 1H, *J* = 3.0 Hz, CH), 6.61 (d, 1H, *J* = 3.0 Hz, CH), 3.31 (s, 3H, CH_3).

Anal. Calcd for $C_{12}H_{11}N_2O_3F_3$: C, 50.01; H, 3.85; F, 19.77; N, 9.72. Found: C, 49.89; H, 3.89; F, 19.82; N, 9.69. MS (ESI) *m/z* calcd for $C_{12}H_{11}N_2O_3F_3$: 288.23, found: 175.0 $[M\text{-}CF_3COO]^+$.

Synthesis of 2-hydroxyimidazolium salt 3c

To a 25 mL flask an imidazolinone **1a** (0.5 g, 2.1 mmol, 1.0 equiv.) and trifluoroacetic acid (3 mL) were added. The reaction mixture was stirred at room temperature for 10 min and concentrated under reduced pressure to give the compound **3c** as a yellowish gum, which solidifies upon keeping in freezer. NMR spectra of this compound in individual form could not be obtained due to its quick conversion to the bis(imidazolinone) **2a** in a solution.

X-ray data for the compound 3c

X-ray diffraction (XRD) data for the single crystal of **3c** were obtained on a Bruker D8 QUEST automated three-circle diffractometer with a PHOTON III area detector and an IμS DIAMOND microfocus X-ray tube: λ(Mo *K*α) = 0.71073 Å, ω/φ scanning mode with a step of 0.5°. Data collection and indexing, determination and refinement of unit cell parameters were carried out using the *APEX3* software package. Numerical absorption correction based on the crystal shape, additional spherical absorption correction, and systematic error correction were performed using the *SADABS*-2016/2 software.[5] Using *OLEX2*,[6] structures were solved by direct methods using the *SHELXT*-2018/3 program[7] and refined by full-matrix least-squares on F^2 using the *SHELXL*-2018/3 program.[8] Nonhydrogen atoms were refined anisotropically. Positions of H(O/N) hydrogen atom were determined from difference electron density maps and refined isotropically. The remaining hydrogen atoms were refined using a riding model. Most calculations were performed using the *WinGX*-2021.3 software package.[9] The crystallographic data for structure are listed in Table S1.

Compound **3c** crystallizes in the ionic form with the flat imidazolium cation and the anion of trifluoroacetic acid as a counterion. The structure was solved in the triclinic space group $P\bar{1}$ with two independent cation-anion pairs A and B (Z′ = 2), whose geometry is similar. In the cationic part, the lengths of the N1A-C1A and N2A-C1A bonds are equal and constitute an intermediate value between a single and a double bond (1.331(5)), hydrogen atoms on both nitrogen atoms are identified and refined with integer occupancy. This situation corresponds to the delocalization of the positive charge in the triatomic fragment N1A-C1A-N2A. Numerous hydrogen bonds between cations and anions are realized in the crystal.

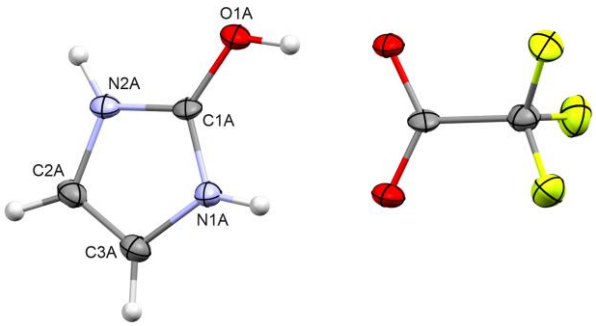


Figure S1 Molecular geometry of **3c** in the crystal (molecule A). Thermal ellipsoids for non-H atoms are set at the 50% probability level

Table S1 Crystallographic data for the compound **3c**

Compound	**3c**
Empirical formula	$C_3H_5N_2O^+$, $C_2F_3O_2^-$
Formula weight	198.11
Radiation, wavelength	Mo *K*α, 0.71073 Å
Temperature	100(2)
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
Unit cell dimensions	*a* = 8.243(2) Å, *b* = 8.488(3) Å, *c* = 11.355(3) Å, α = 80.218(8)°, β = 73.432(8)°, γ = 78.498(8)°
Volume	740.9(4) Å^3
***Z* and *Z*′**	4 and 2
Calculated density	1.776 g cm^{-3}
Absorption coefficient	0.190 mm^{-1}
***F*(000)**	400
Crystal size	0.451 x 0.110 x 0.100 mm^3
θ range for data collection	1.885° to 25.998°
Index ranges	$-10 \le h \le 10$, $-10 \le k \le 10$, $-14 \le l \le 14$
Reflections collected	20109
Independent reflections	2895
R_{int}	0.1088
Rσ	0.0700
Observed Data [$I > 2\sigma(I)$]	1973
Completeness to θ = 25.242°	100.0
Max. and min. transmission	0.7460 and 0.5961
Data / restraints / parameters	2895 / 0 / 259
Goodness-of-fit on F^2	1.022
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0553, *wR*2 = 0.1299
***R* indices (all data)**	*R*1 = 0.0935, *wR*2 = 0.1512
Largest diff. peak and hole	0.400 and –0.389 e Å^{-3}
CCDC number	2253122

Tautomers of imidazolin-2-ones

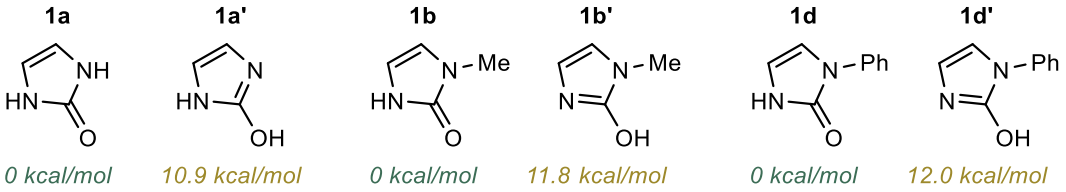
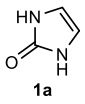
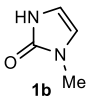
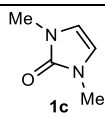
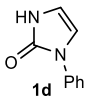
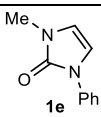


Figure S2 Relative energies of imidazolin-2-ones and their 2-hydroxyimidazole tautomers as obtained from quantum chemistry calculations (B3PW91/def2-TZVPD // PBE/def2-TZVPD, Orca 5.0.3)

Energies of orbitals

Table S2 Energies of oxygen's lone pair and bonding π-orbital of C=C bond for the compounds **1a-d**[a]

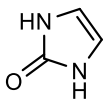
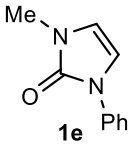
	 1a	 1b	 1c	 1d	 1e
$E_{LP(O)}$, eV	-0.213	-0.208	-0.203	-0.212	-0.208
$E_{\pi(C=C)}$, eV	-0.342	-0.338	-0.334	-0.356	-0.354

[a] *As obtained from NBO analysis (B3PW91/def2-TZVPD // PBE/def2-TZVPD, Orca 5.0.3, Janpa 2.02)*

Comparison of quantum chemistry calculations at different levels of theory

The functional for the quantum chemistry calculations was chosen based on the reproducibility of the experimental data for proton affinities of model compounds. As seen from the Table S3, both (B3PW91/def2-TZVPD // PBE/def2-TZVPD) methods combination and higher-level (ωB97X-V/def2-TZVPD) method give essentially the same results (the maximum difference between calculated values is 1.5 kcal/mol, the average difference is *ca* 0.5 kcal/mol). Notably, for both urea and pyridine, the predicted proton affinity fitted the experimental values perfectly (within the experimental error). Moreover, PBE/B3PW91 combination succeeded in correct prediction of proton affinity of ethylene (within 0.4 kcal/mol), whereas ωB97X-V performed considerably worse (the geometry optimization resulted in three-centre two-electron cation instead of ethyl cation in this case). Based on this, (B3PW91/def2-TZVPD // PBE/def2-TZVPD) was the method of choice due to much less computational cost.

Table S3 Comparison of proton affinities and gas-phase basicities calculated at different levels of theory.[a]

	 1a		 1e			**Urea**	**Pyridine**	**Ethylene**
Protonation site	O	C	O	C-NMe	C-NPh	O	N	C
PA (kcal/mol)	-211.6 (-211.5)	-198.6 (-199.3)	-222.3 (-222.6)	-211.7 (-211.7)	-209.7 (-210.9)	-209.1 (-208.3) -208.6[b]	-222.9 (-222.2) -222.1[b]	156.3 (-164.2) -155.9[b]
GB (kcal/mol)	-206.9 (-206.9)	-194.0 (-194.7)	-217.7 (-218.3)	-207.2 (-207.2)	-205.1 (-206.6)	-204.7 (-204.1) -201.0[b]	-217.8 (-217.6) -214.5[b]	159.0 (-160.1) 162.8[b]

[a] *values for (B3PW91/def2-TZVPD // PBE/def2-TZVPD), values for (ωB97X-V/def2-TZVPD) are given in parentheses;* [b] *experimental values (taken from paper by Abboud[10] (GB, urea), Cooks[11] (PA, urea), Lias[12] (GB and PA, pyridine; GB and PA, ethylene); Poutsma[13] gives value of 223.8±2.0 kcal/mol for PA of pyridine)*

The results of NBO analysis on the lower- and higher-level geometries are provided on the Figure S3. Despite the changes in the absolute values, the trends remain the same. E.g., the low-level calculation suggests that the LP(N^3)->π*(C=C) interaction energies in compounds **1e** and **1e** differ by 1.2 kcal/mol (34.5-33.3 = 1.2 kcal/mol). The higher-level method gives 1.5 kcal/mol difference (48.2-46.7 = 1.5 kcal/mol). The same is true for the LP(N^1)->π*(C=C) interaction (2.0 kcal/mol *vs* 2.3 kcal/mol), LP(N^3)->π*(C=O) interaction (1.4 kcal/mol vs 1.5 kcal/mol). The difference for the LP(N^3)->π*(C=O) interaction is somewhat higher (4.7 kcal/mol vs 7.6 kcal/mol). Nonetheless, this also doesn't change the observed trend. Again, this suggests that (B3PW91/def2-TZVPD // PBE/def2-TZVPD) combination is suitable for the performed analysis.

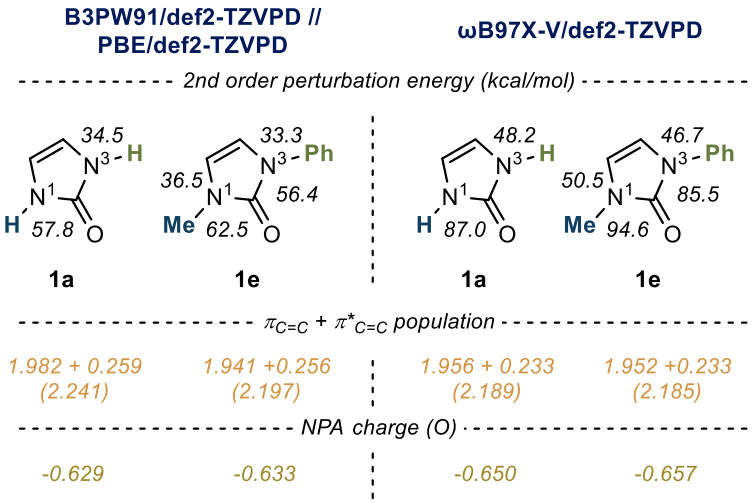


Figure S3 Comparison of NBO data at different levels of theory

Energy profiles for the reactions of imidazolinones

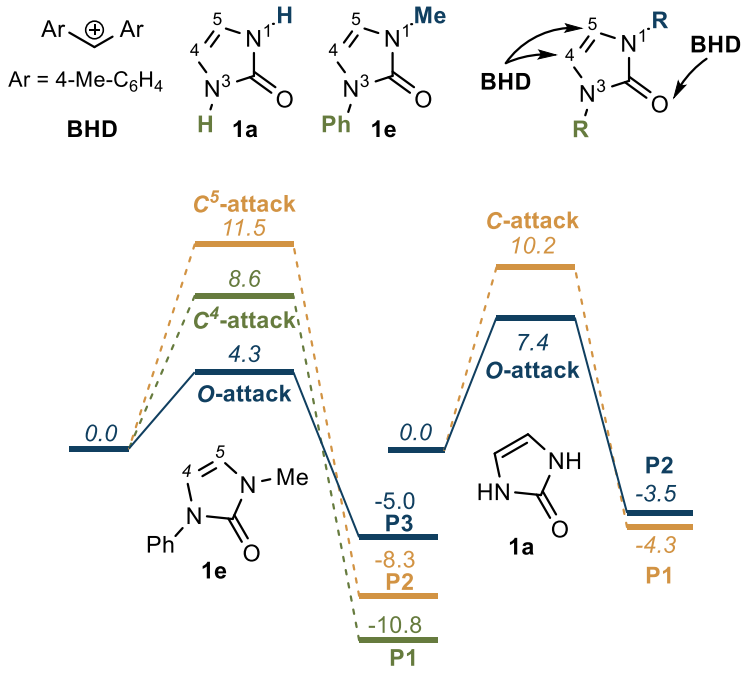
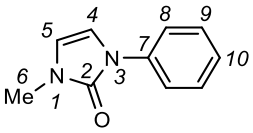


Figure S4 Energy profiles (kcal/mol) for the reactions of imidazolinones **1a,e** with benzhydrilium cation (ωB97X-V/def2-TZVPD, PCM (chloroform) solvation, Orca 5.0.3)

NMR studies of imidazolinone 1e

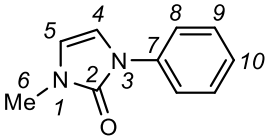
Table S4 Chemical shifts of signals in NMR spectra of imidazolinone **1e** in the presence of acids ($CDCl_3$, 400 MHz, 303 K)



Atom	1e, δ, ppm	1e + HA (1 equiv), δ (Δδ),[a] ppm	
		TFA	TfOH
	^{1}H NMR		
C^5H	6.31	6.38 (+0.07)	6.88 (+0.57)
C^4H	6.56	6.60 (+0.04)	6.92 (+0.36)
C^6H	3.30	3.37 (+0.07)	3.70 (+0.40)
C^8H	7.60	7.57 (-0.03)	7.43 (-0.17)
C^9H	7.40	7.46 (+0.04)	7.52 (+0.12)
$C^{10}H$	7.23	7.29 (+0.06)	7.51 (+0.28)
	^{13}C NMR		
C^2	152.6	152.6 (+0.0)	148.4 (-4.2)
C^4	109.7	110.7 (+1.0)	117.5 (+7.8)
C^5	113.3	113.6 (+0.3)	115.9 (+2.6)
C^6	31.0	31.3 (+0.3)	33.4 (+2.4)
C^7	138.0	137.4 (-0.6)	134.2 (-3.8)
C^8	122.0	122.8 (+0.8)	124.9 (+2.9)
C^9	129.7	129.8 (+0.1)	130.4 (+0.7)
C^{10}	126.2	127.0 (+0.8)	130.0 (+3.8)

[a] *Δδ is calculated as δ_H(**1e** + HA) – δ_H(**1e**)*

Table S5 Chemical shifts of signals in ^{1}H NMR spectra of imidazolinone **1e** in the presence of TFA in various solvents (400 MHz, 303 K)

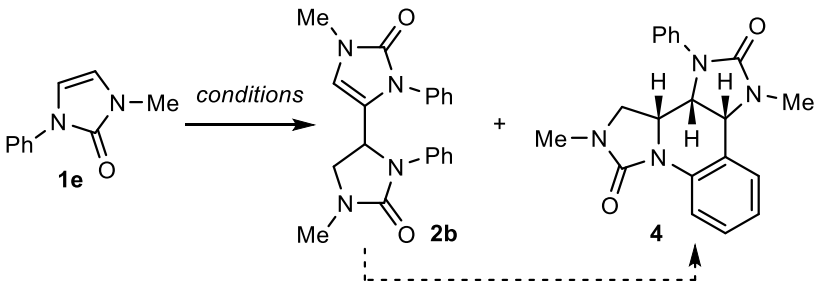


Atom	1e, δ, ppm				1e + TFA (1 equiv), δ (Δδ),[a] ppm			
	$CDCl_3$	CD_3OD	$(CD_3)_2CO$	$(CD_3)_2SO$	$CDCl_3$	CD_3OD	$(CD_3)_2CO$	$(CD_3)_2SO$
C^5H	6.31	6.63	6.68	6.72	6.38 (+0.07)	6.61 (-0.02)	6.70 (+0.03)	6.68 (-0.04)
C^4H	6.56	6.84	6.95	7.01	6.60 (+0.04)	6.82 (-0.02)	6.96 (+0.01)	6.96 (-0.03)
C^6H	3.30	3.32	3.31	3.19	3.37 (+0.07)	3.31 (-0.01)	3.33 (+0.02)	3.19 (0)
C^8H	7.60	7.59	7.82	7.71	7.57 (-0.03)	7.58 (-0.01)	7.80 (-0.02)	7.69 (-0.02)
C^9H	7.40	7.46	7.48	7.43	7.44 (+0.04)	7.45 (-0.01)	7.49 (+0.01)	7.41 (-0.02)
$C^{10}H$	7.23	7.30	7.28	7.23	7.29 (+0.06)	7.29 (-0.01)	7.30 (+0.02)	7.21 (-0.02)

[a] *Δδ is calculated as δ_H(**1e** + HA) – δ_H(**1e**)*

Reaction conditions optimization

Table S6 Optimization of catalyst and solvent for the self-condensation of imidazolinone **1e**[a]



Entry	Solvent	Catalyst	Yield of 2b, %[b]	Yield of 4, %[b]
1	$CDCl_3$	TFA (0.1 eqiv.)	0	0
2	CD_3OD	TFA (0.1 eqiv.)	0	0
3	$(CD_3)_2CO$	TFA (0.1 eqiv.)	0	0
4	$(CD_3)_2SO$	TFA (0.1 eqiv.)	0	0
5	$CDCl_3$	TfOH (0.1 eqiv.)	0	0
6	$(CD_3)_2SO$	TfOH (0.1 eqiv.)	0	0
7	$(CD_3)_2SO$	TsOH (0.1 eqiv.)	5	0
8	$CDCl_3$	TsOH (1.0 eqiv.)	0	92
9	$CDCl_3$	TsOH (0.2 eqiv.)	21	5
10[c]	$CDCl_3$	TsOH (0.2 eqiv.)	64	16

*[a] Reaction conditions: imidazolinone **1e** (1 equiv), catalyst, solvent, rt, 2 days; [b] according to NMR data; [c] after 7 days*

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Copies of NMR spectra

Copies of NMR spectra

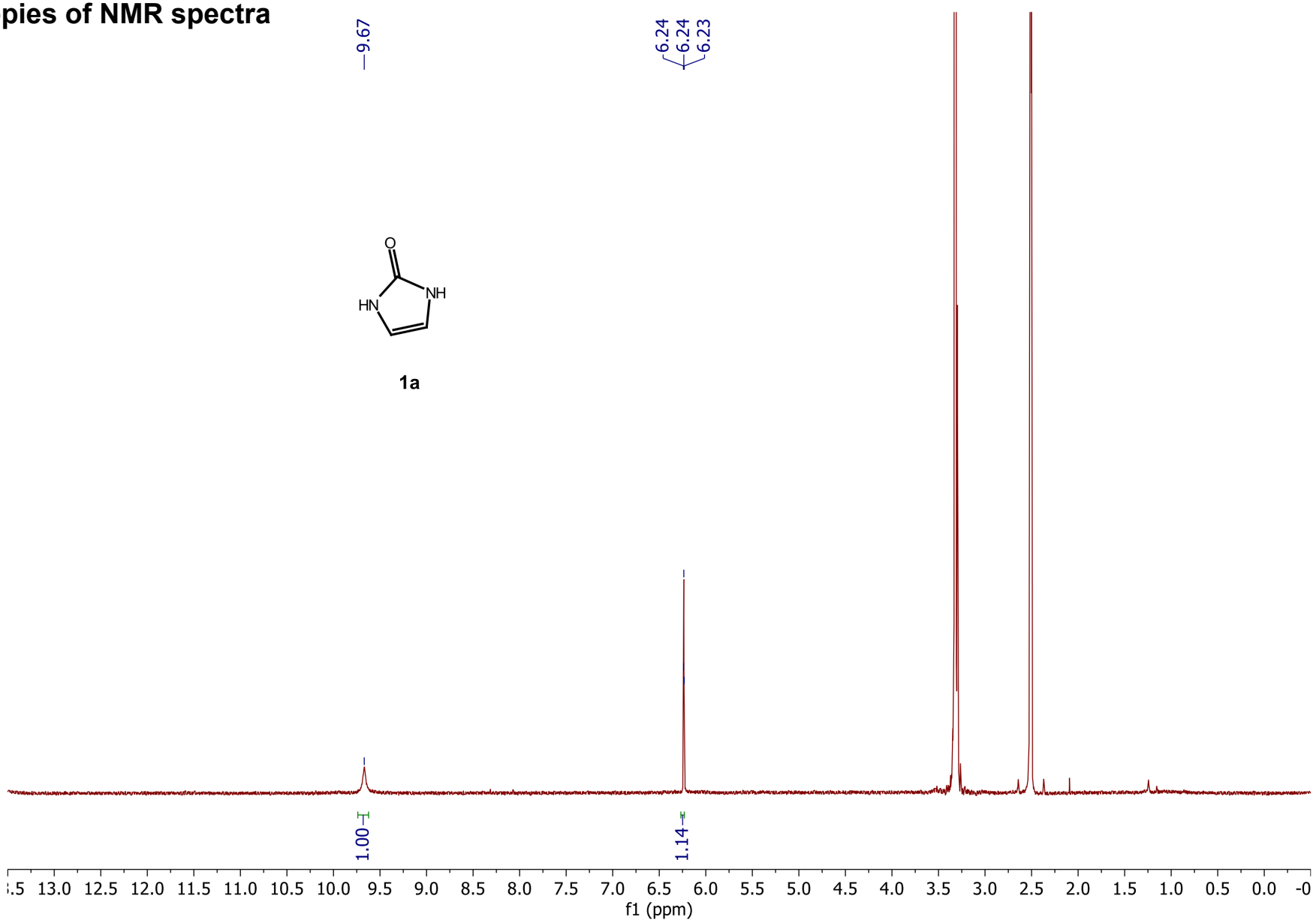


Figure S5. ^{1}H NMR spectrum ($(CD_3)_2SO$, 400MHz) of the compound **1a**

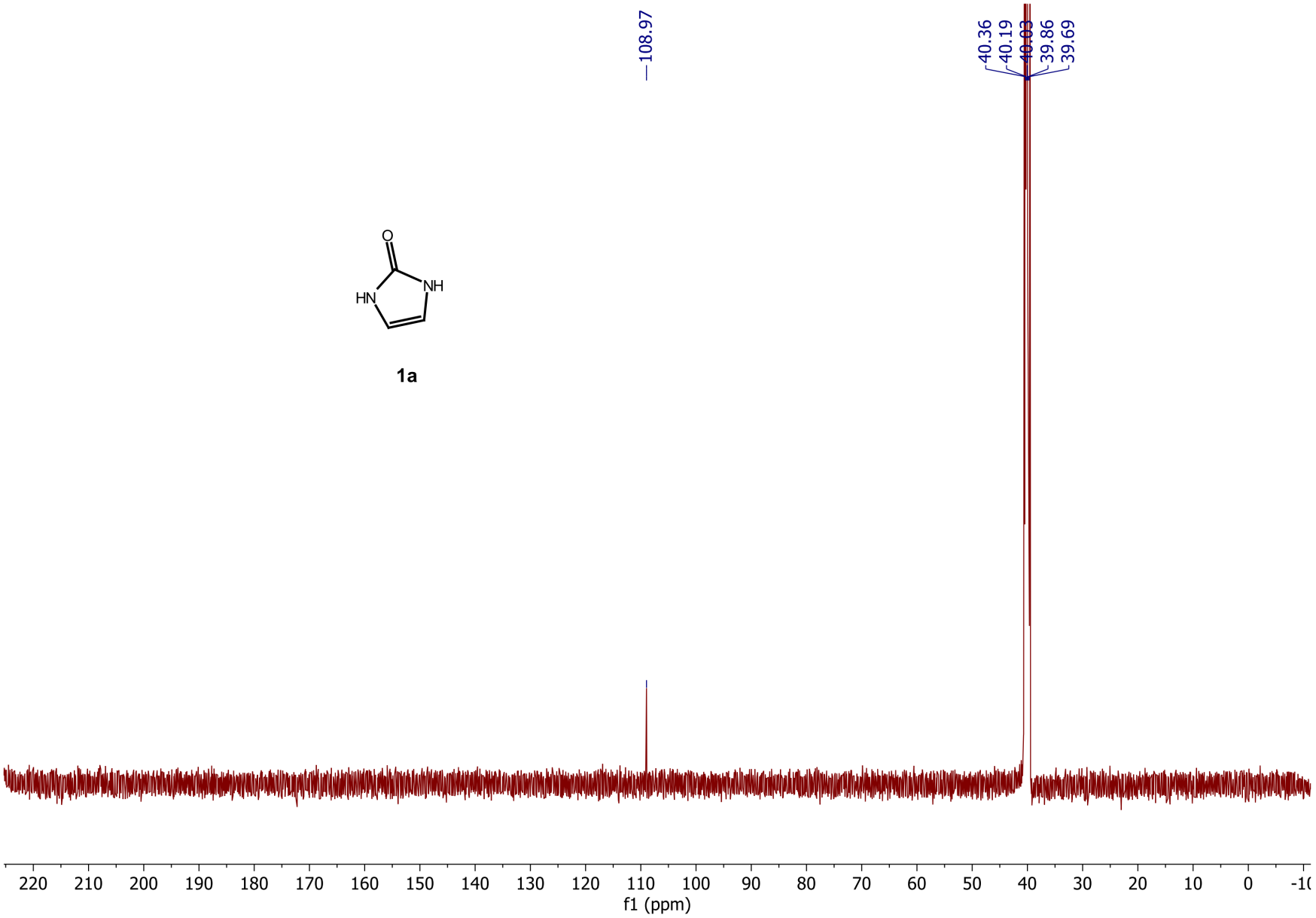


Figure S6. ^{13}C NMR spectrum ($(CD_3)_2SO$, 126MHz) of the compound **1a**

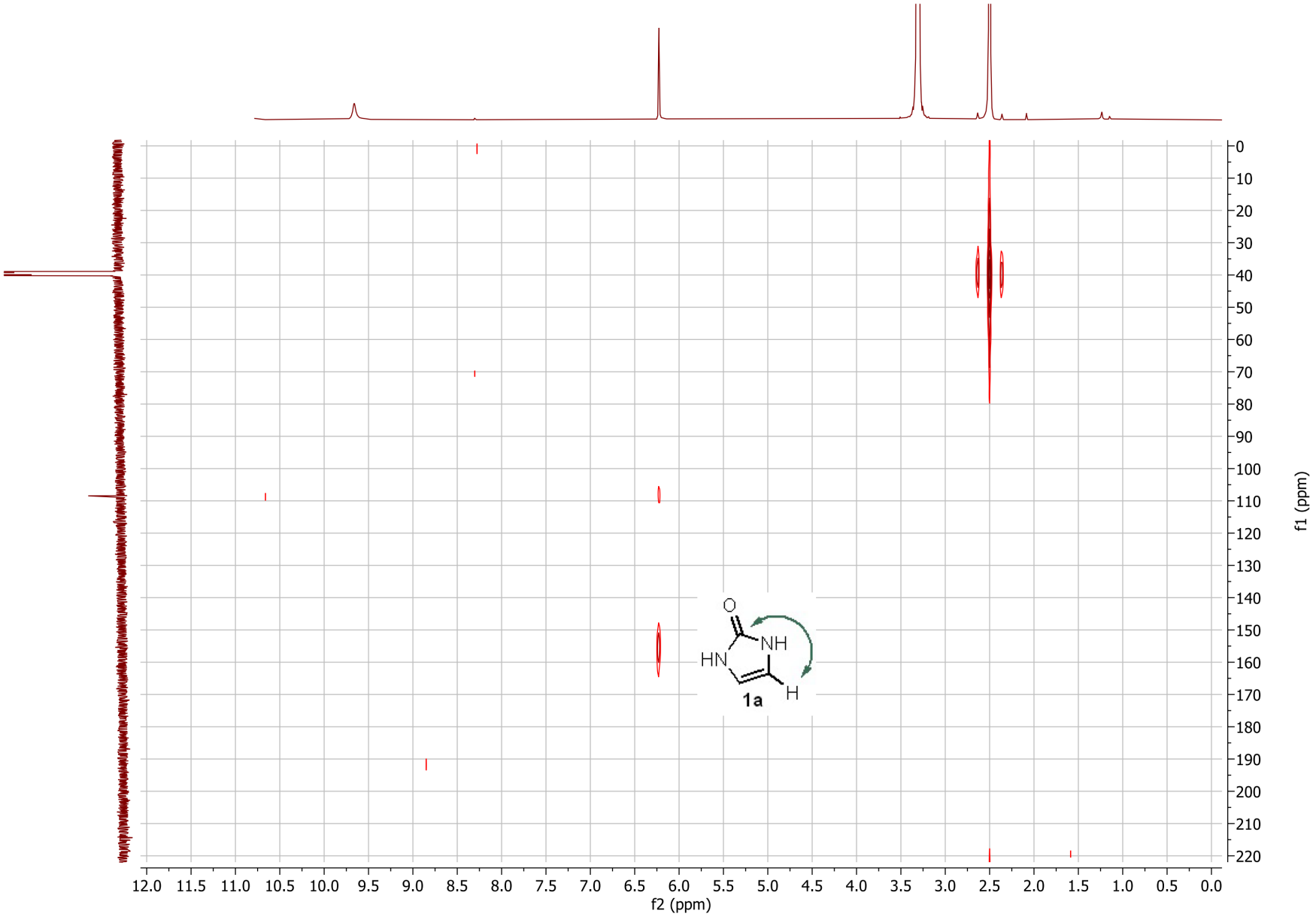


Figure S7. ^{1}H-^{13}C HMBC spectrum ($(CD_3)_2SO$) of the compound **1a**

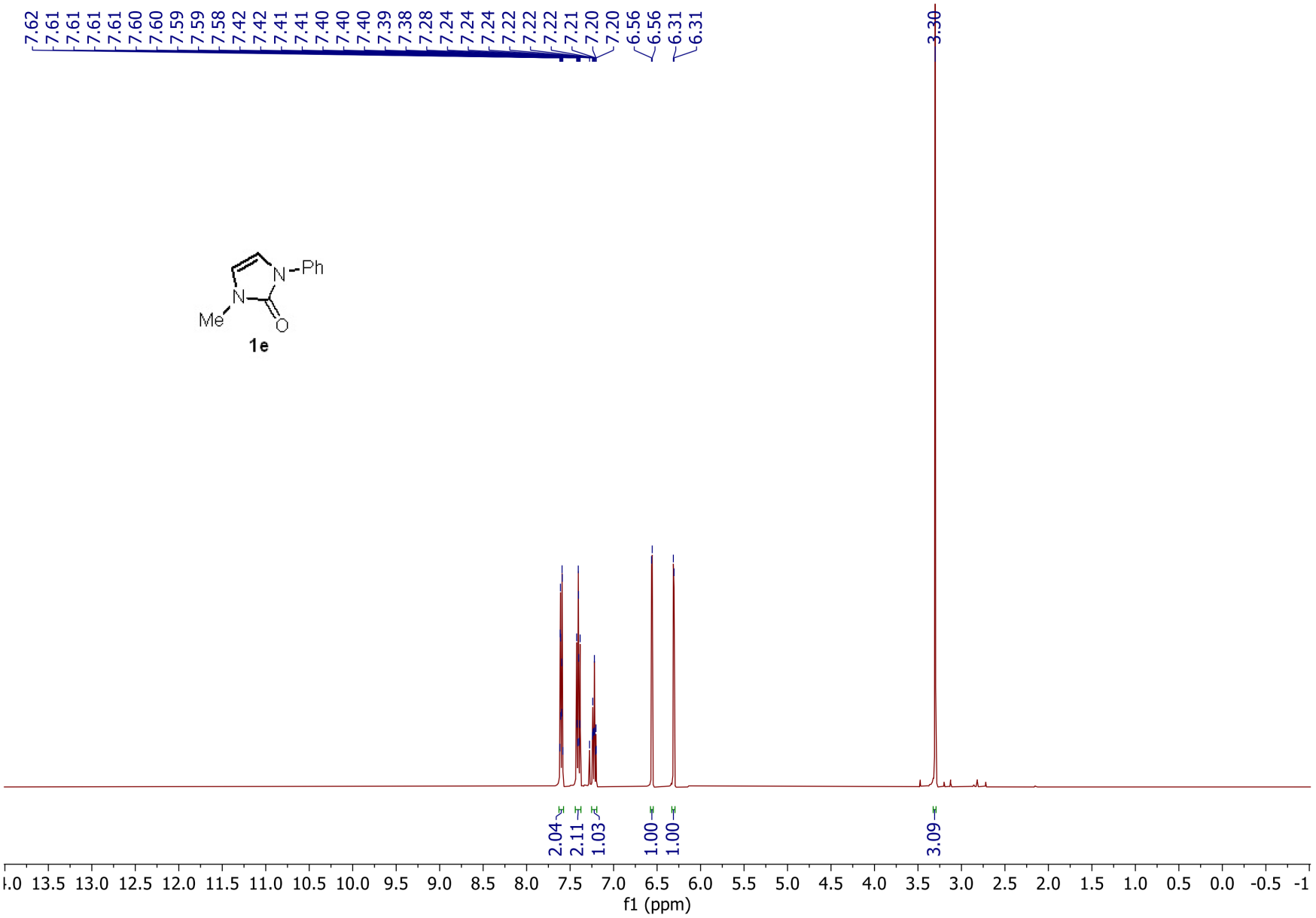


Figure S8. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of the compound **1e**

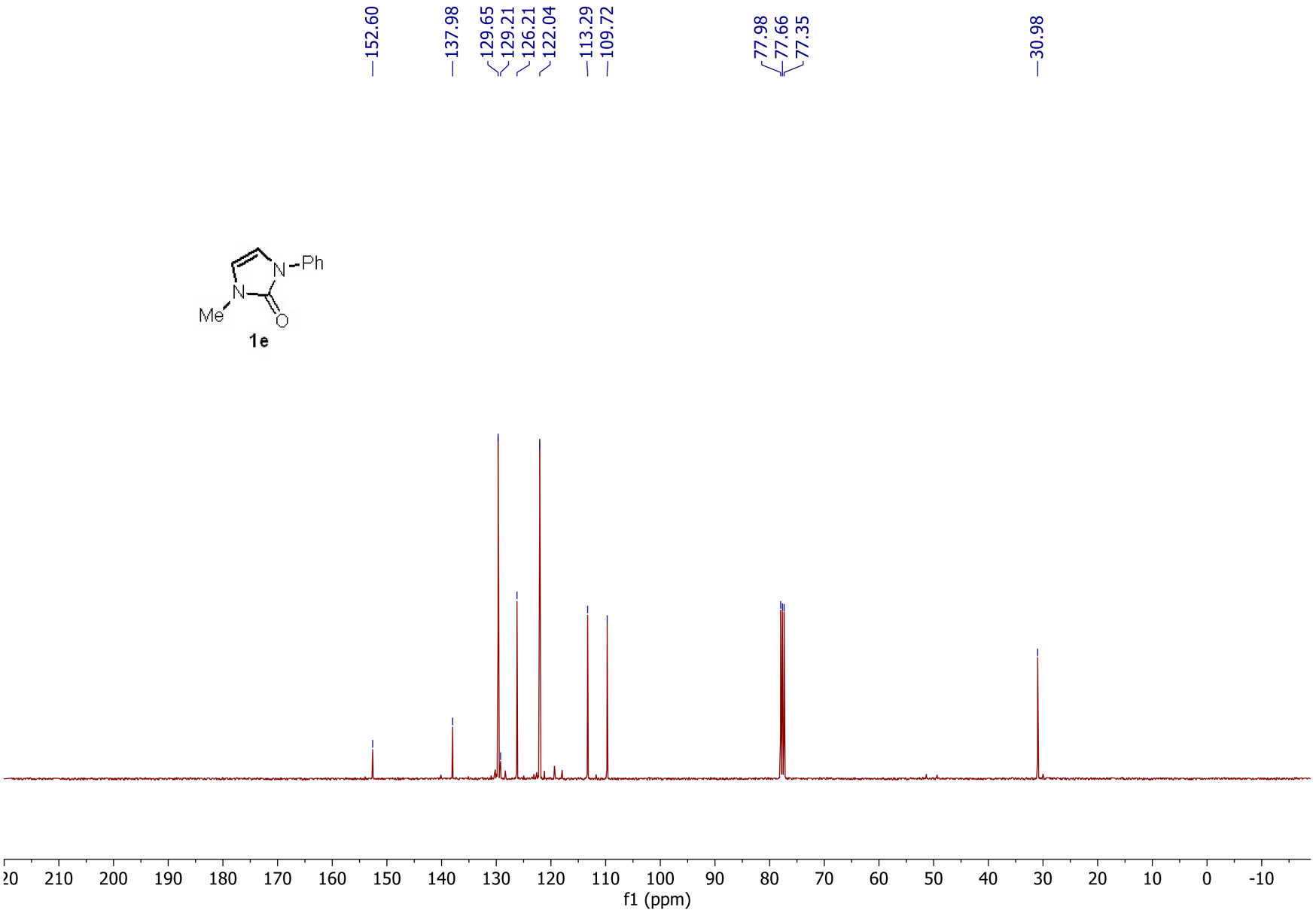


Figure S9. ^{13}C NMR spectrum ($CDCl_3$, 126MHz) of the compound **1e**

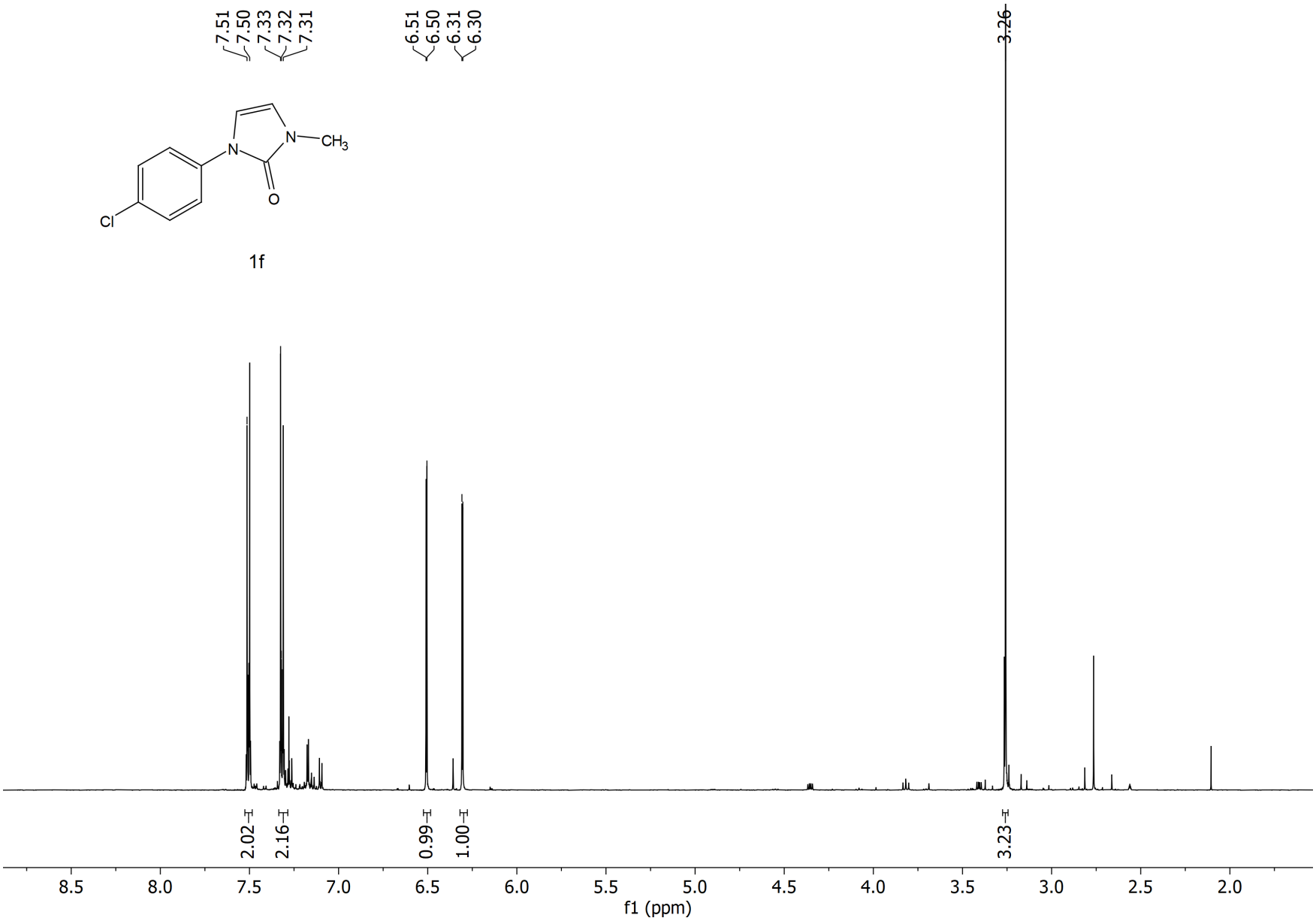


Figure S10. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of the compound **1f**

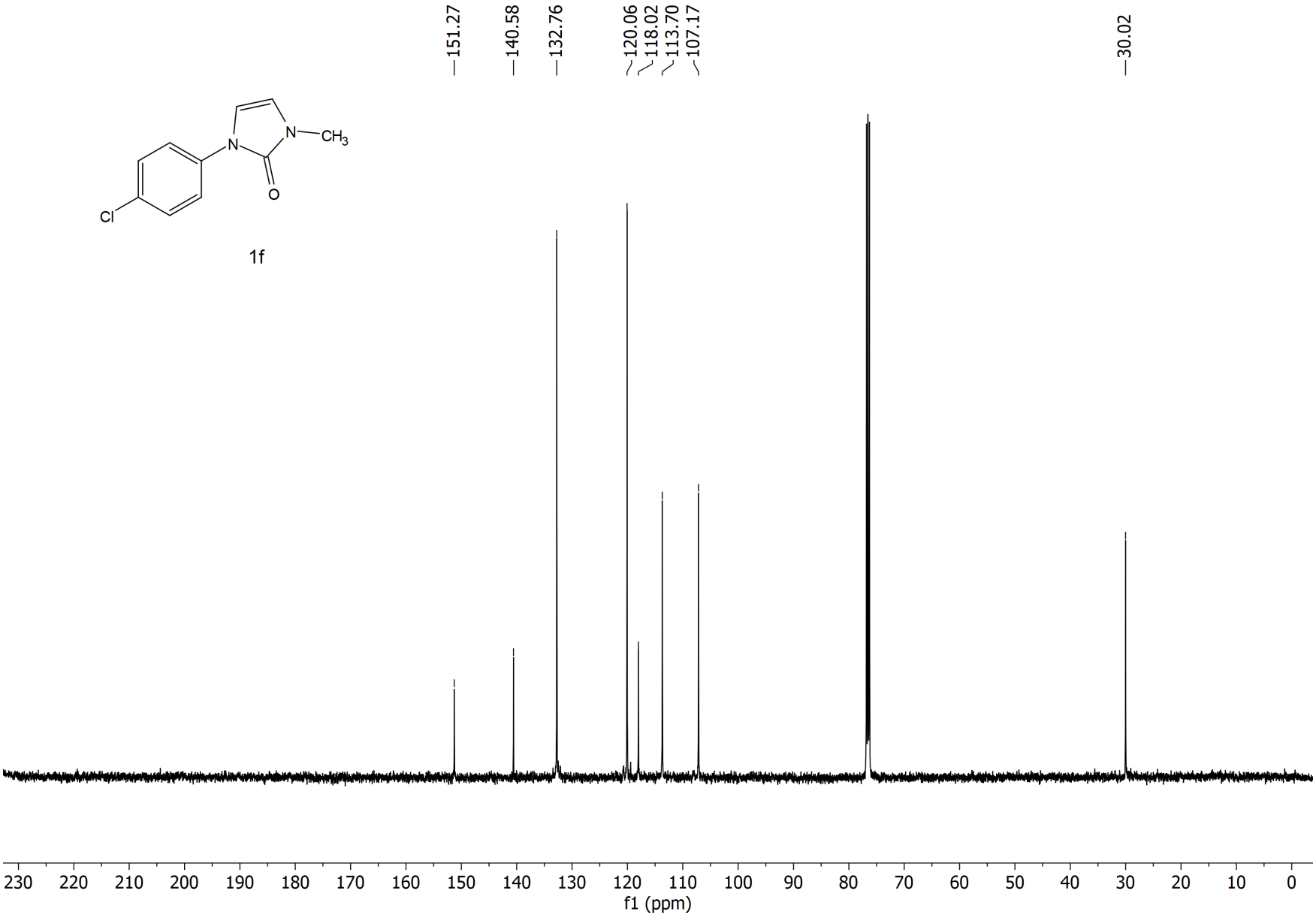


Figure S11. ^{13}C NMR spectrum ($CDCl_3$, 126MHz) of the compound **1f**

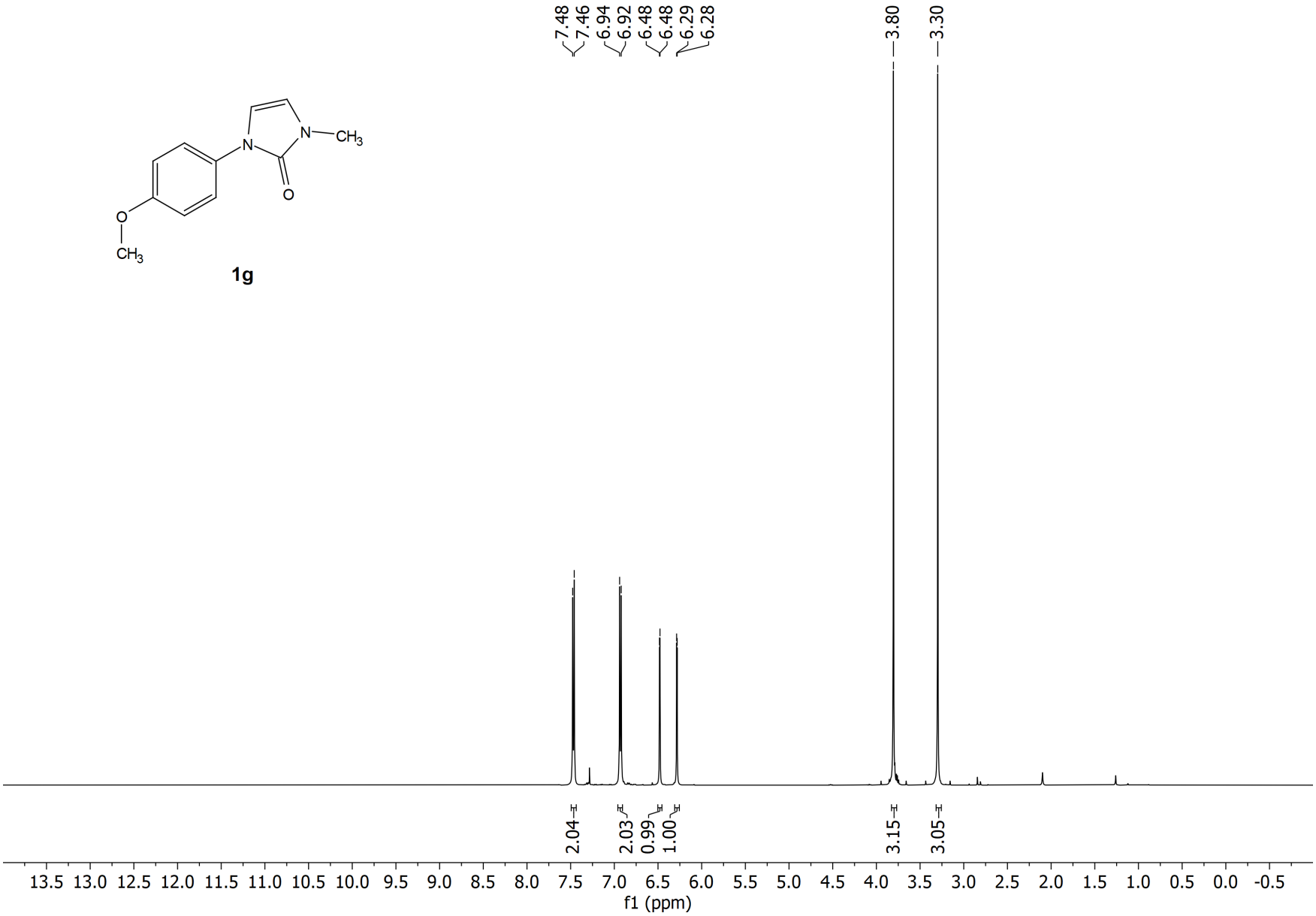


Figure S12. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of the compound **1g**

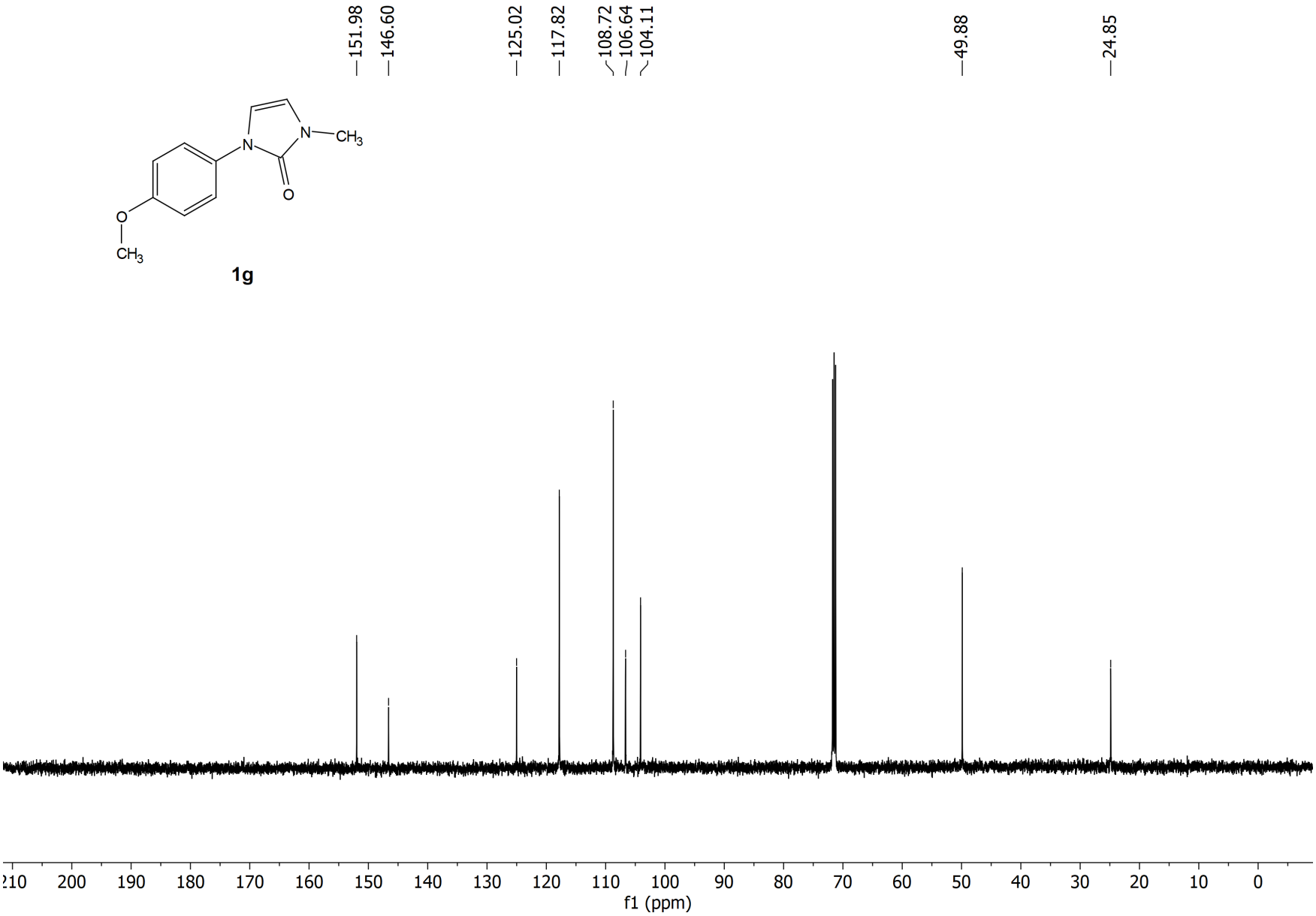


Figure S13. ^{13}C NMR spectrum ($CDCl_3$, 126MHz) of the compound **1g**

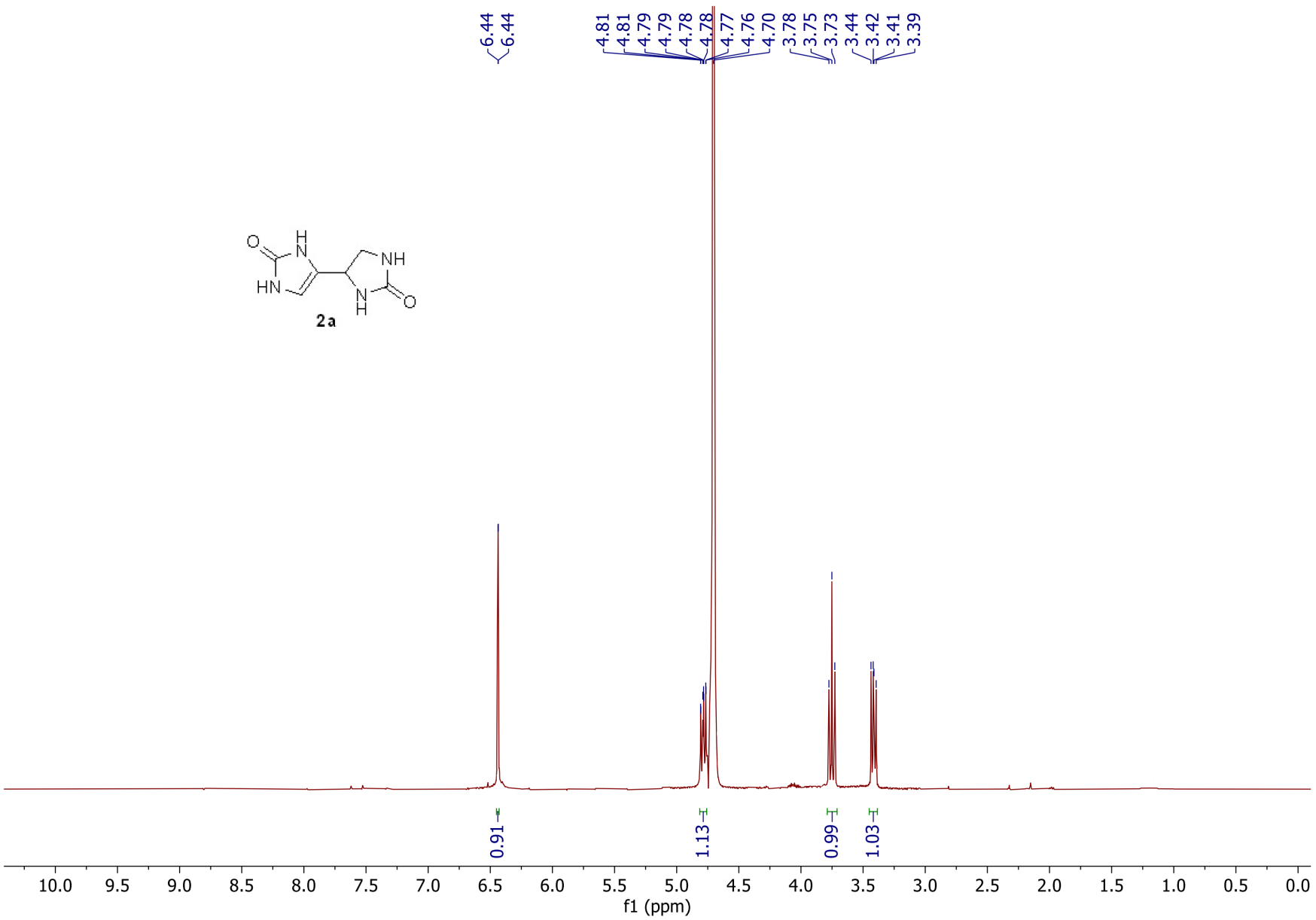


Figure S14. ^{1}H NMR spectrum (D_2O, 400MHz) of the compound **2a**

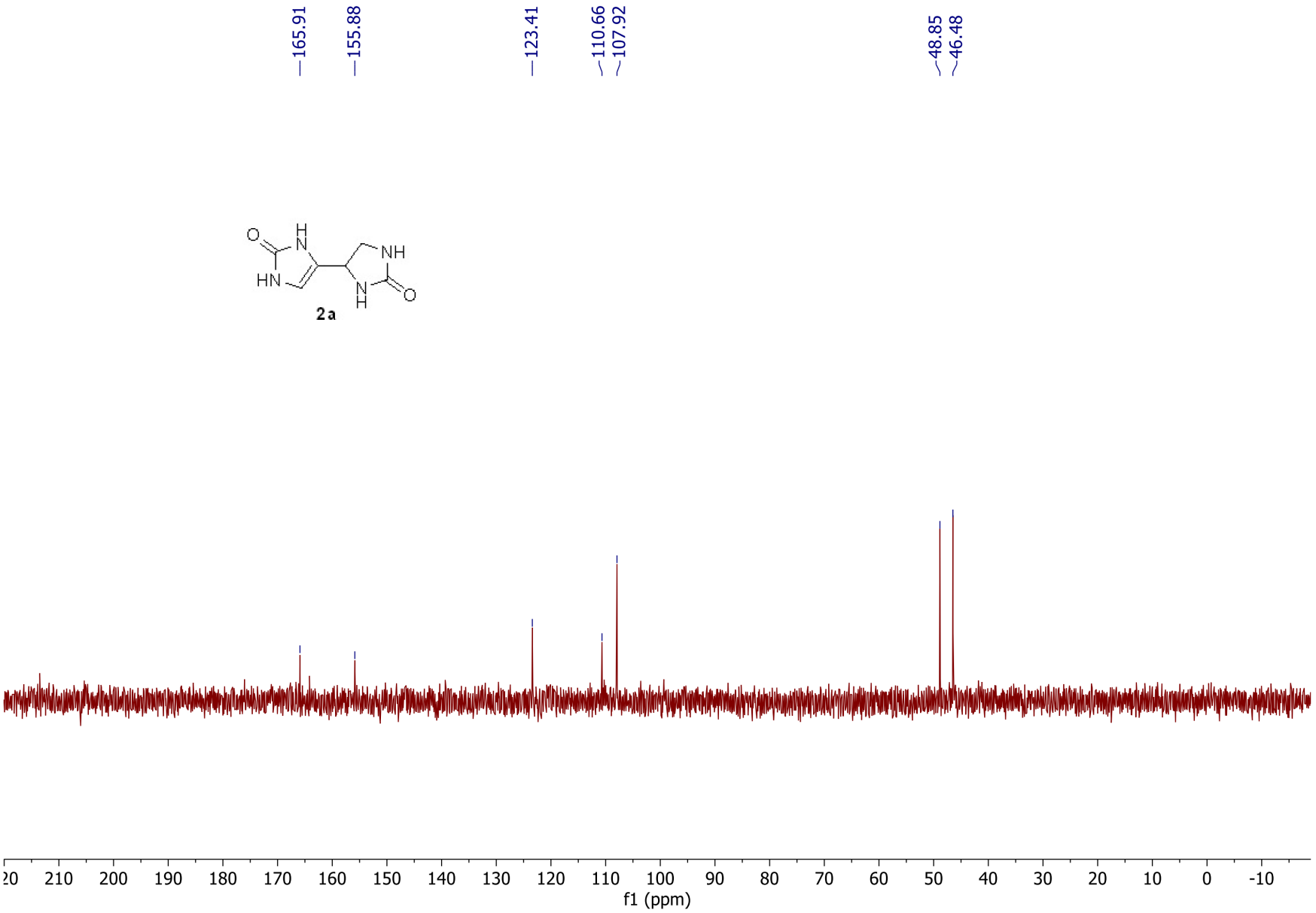


Figure S15. ^{13}C NMR spectrum (D_2O, 126MHz) of the compound **2a**

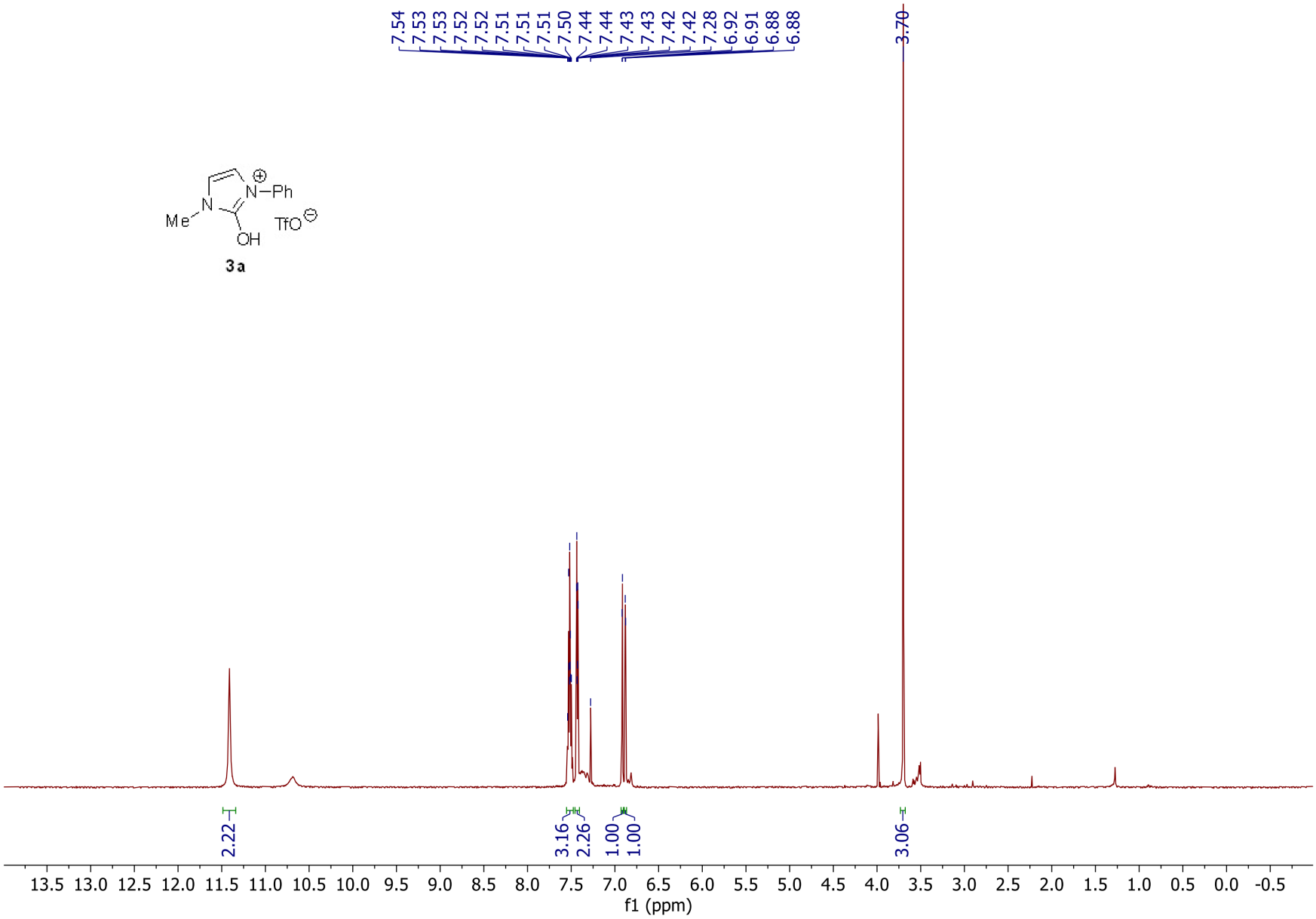


Figure S16. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of the compound **3a**

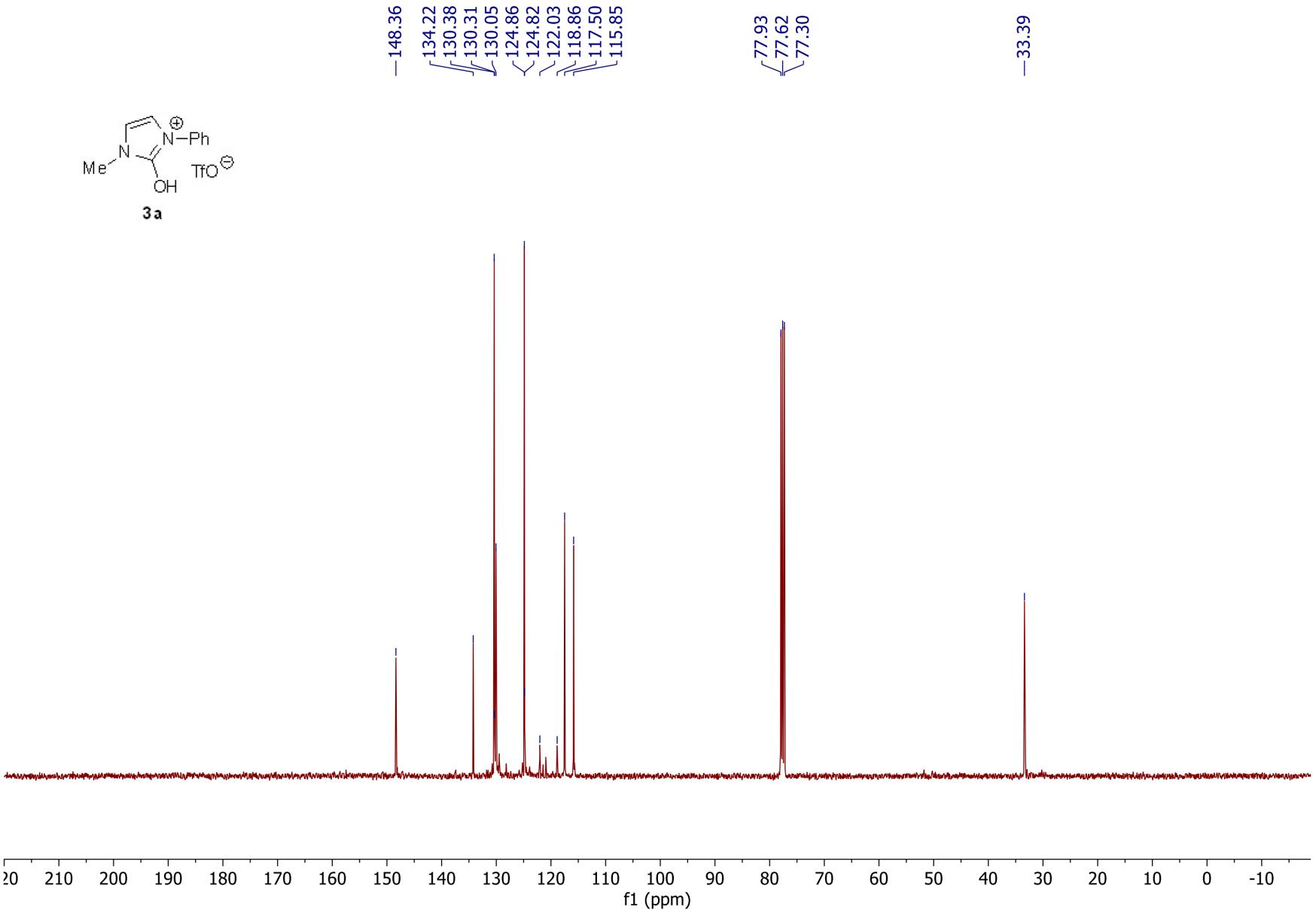


Figure S17. ^{13}C NMR spectrum ($CDCl_3$, 126MHz) of the compound **3a**

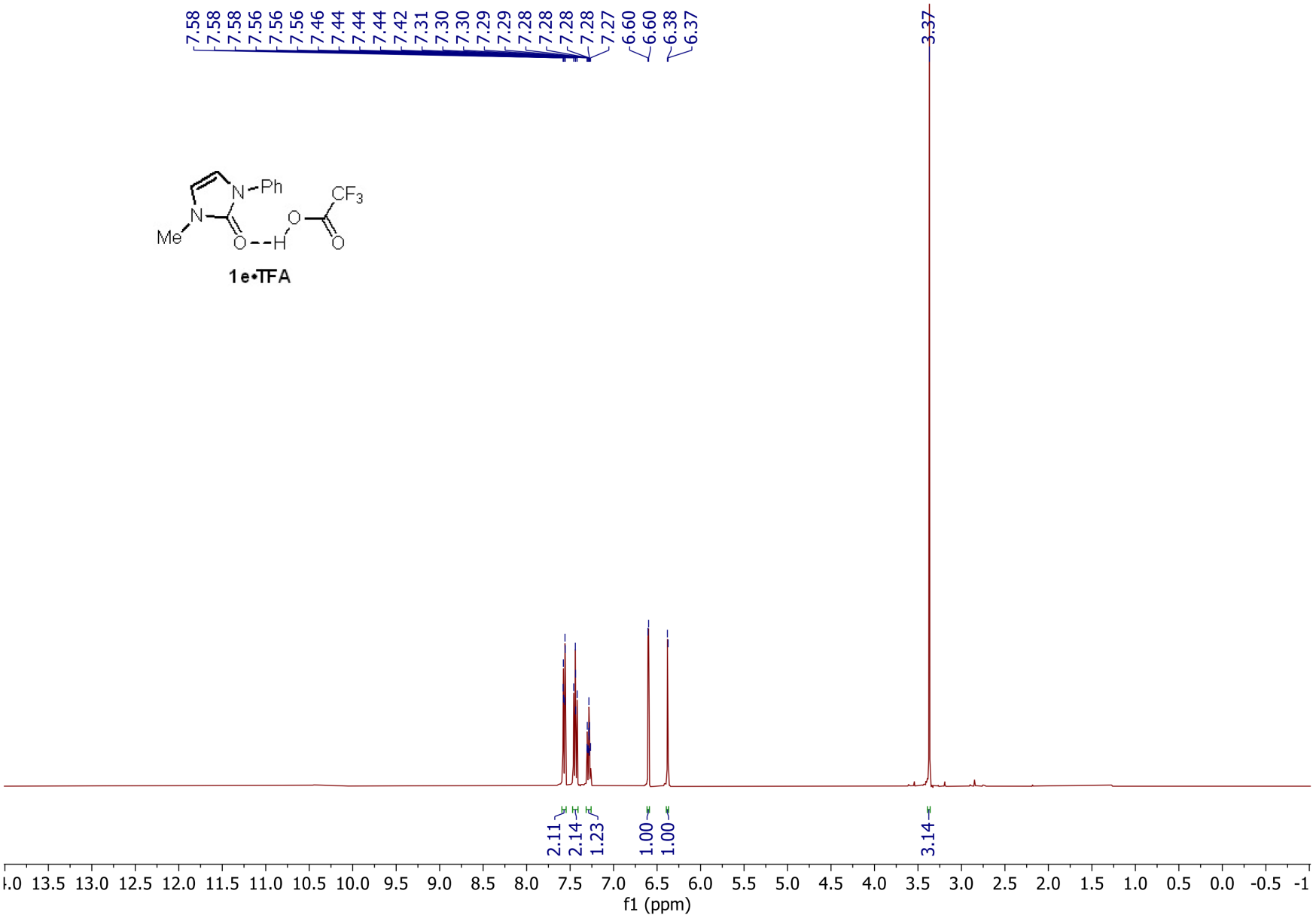


Figure S18. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of the compound **3b** (**1e•TFA**)

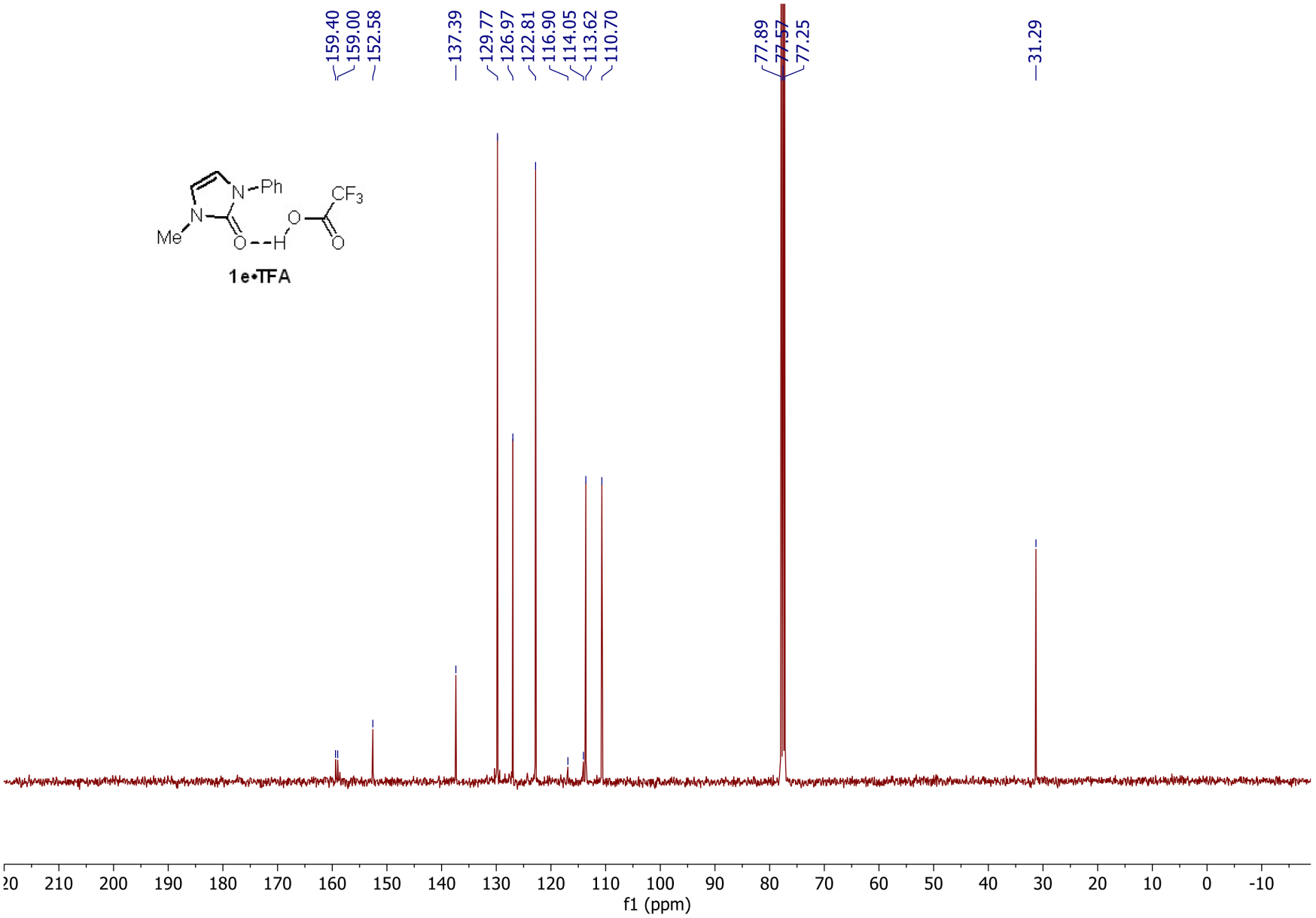


Figure S19. ^{13}C NMR spectrum ($CDCl_3$, 126MHz) of the compound **3b** (**1e•TFA**)

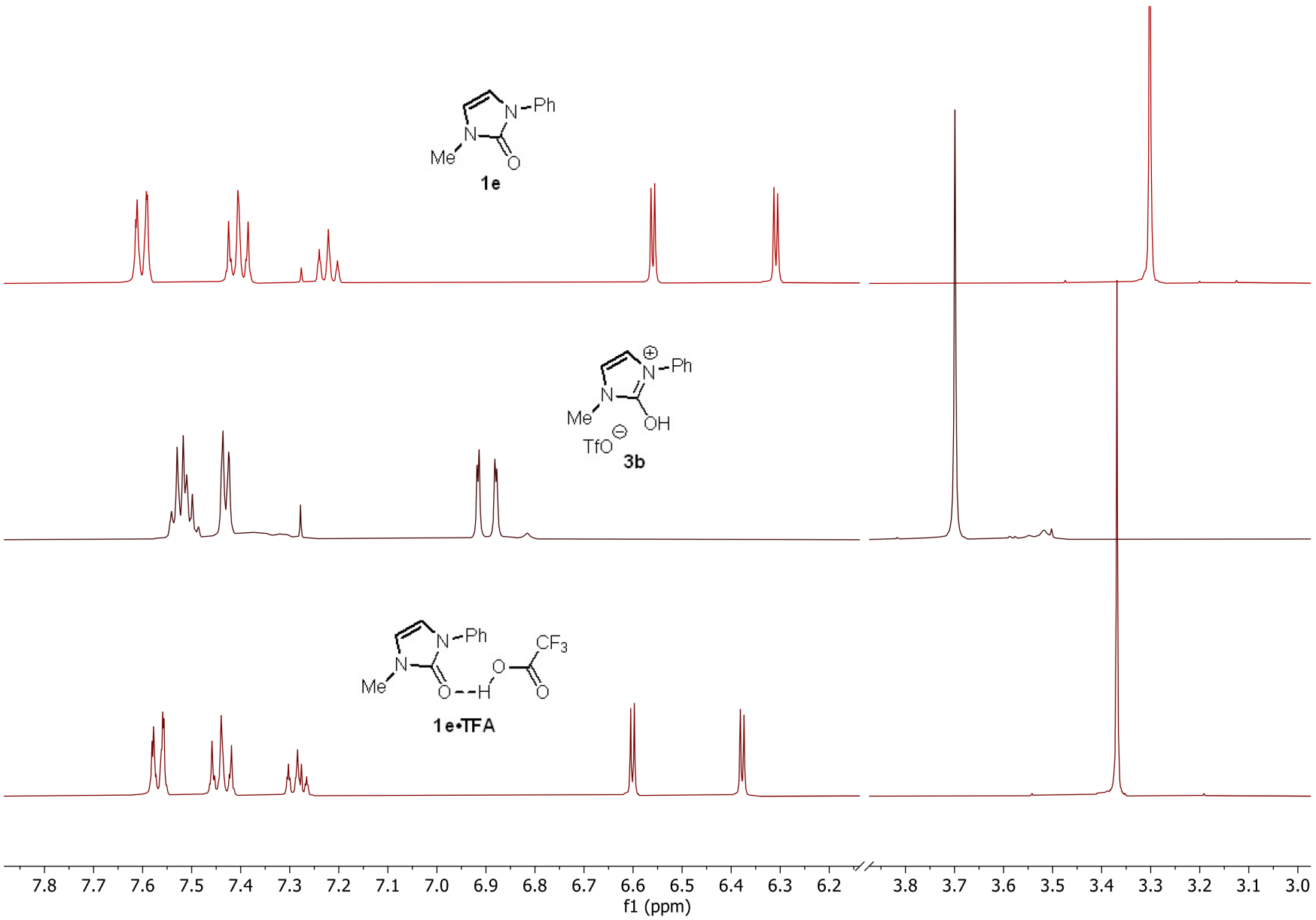


Figure S20. Comparison of ^{1}H NMR spectra ($CDCl_3$, 400MHz) of the compounds **1e**, **3a** and **3b** (**1e•TFA**)

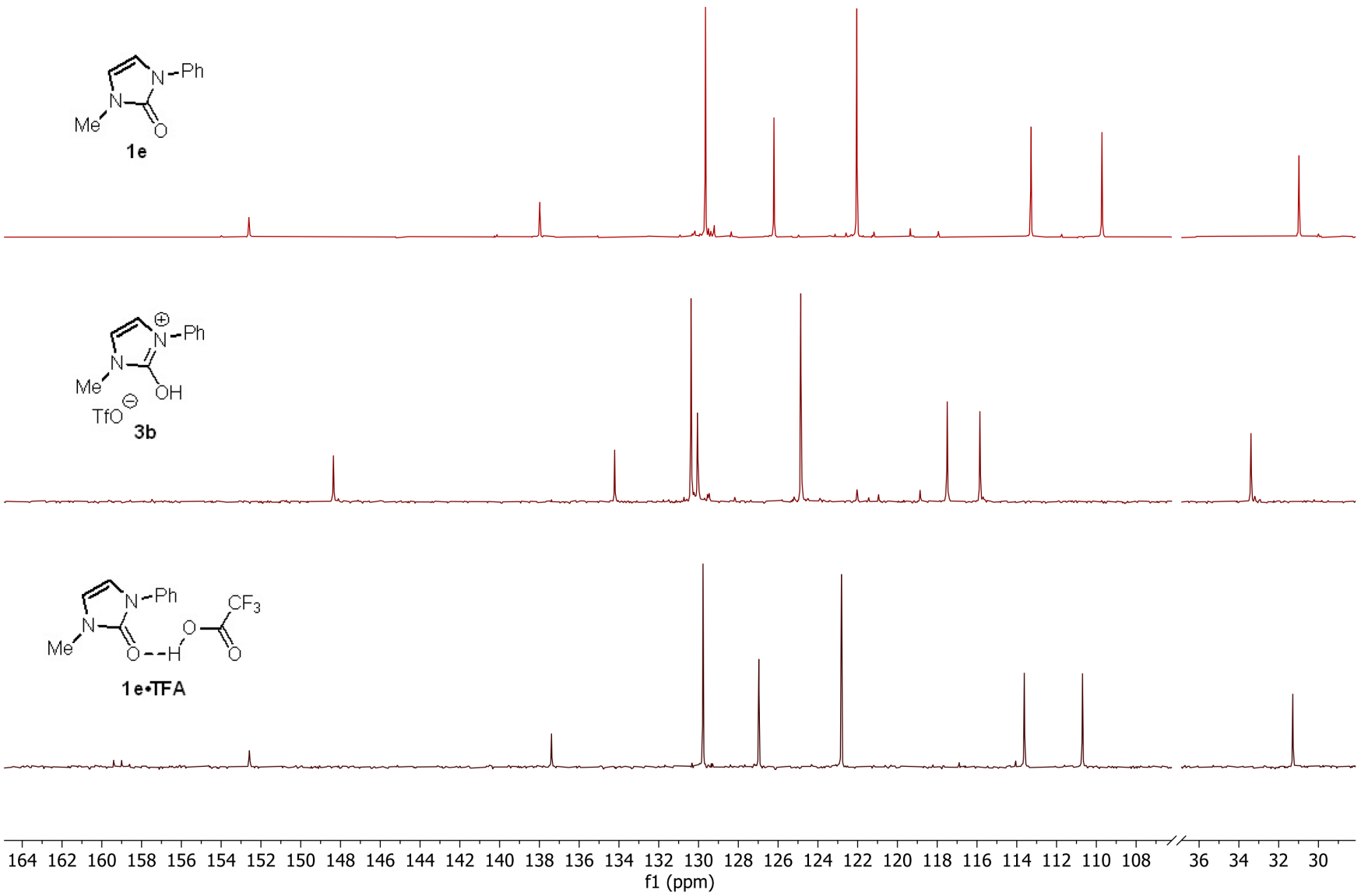


Figure S21. Comparison of ^{13}C NMR spectra ($CDCl_3$, 400MHz) of the compounds **1a**, **3a** and **3b** (**1e•TFA**)

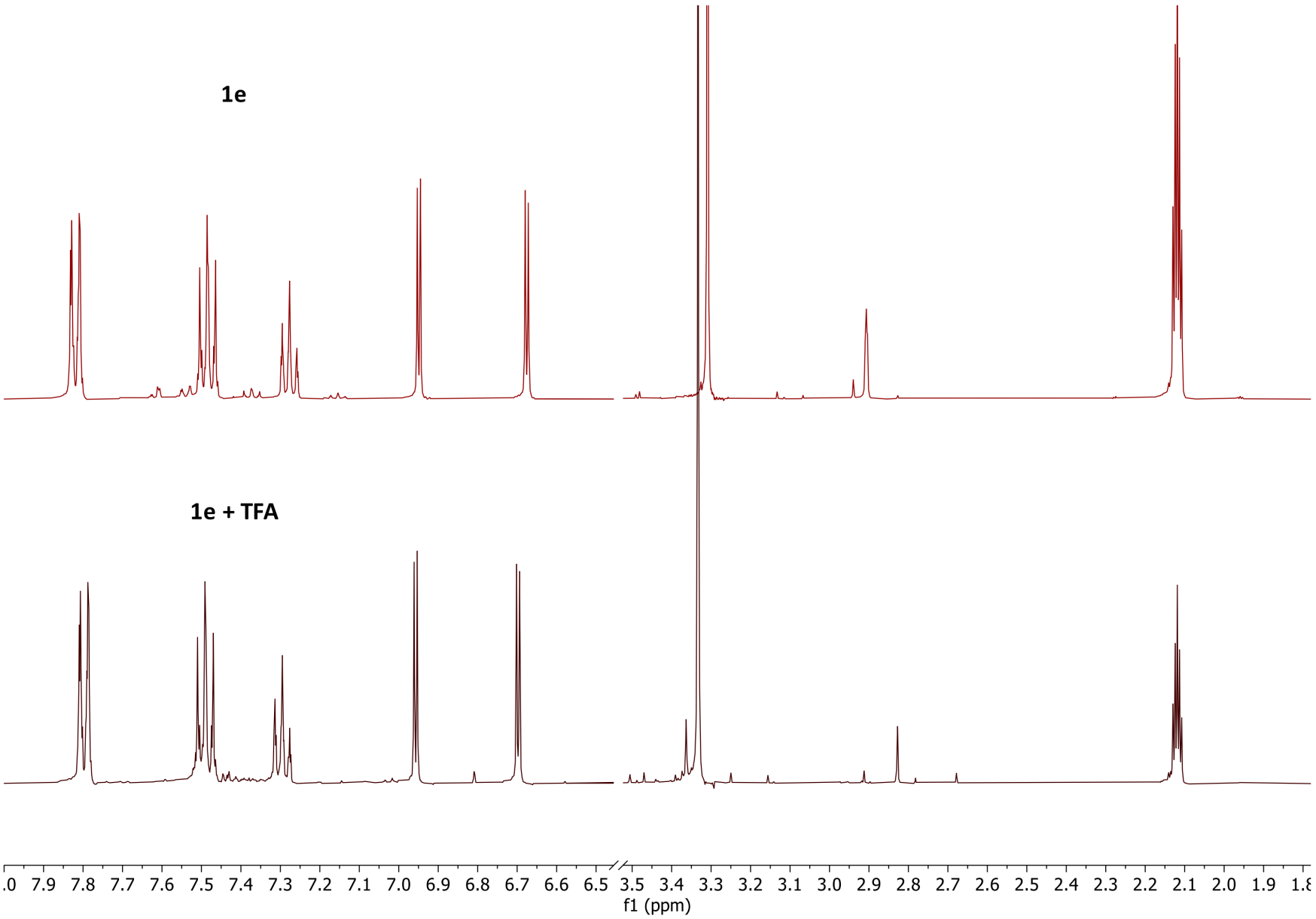


Figure S22. ^{1}H NMR spectra of the compound **1e** (upper) and of the compound **1e** in the presence of 1 equivalent of TFA (lower), ($(CD_3)_2CO$, 400MHz)

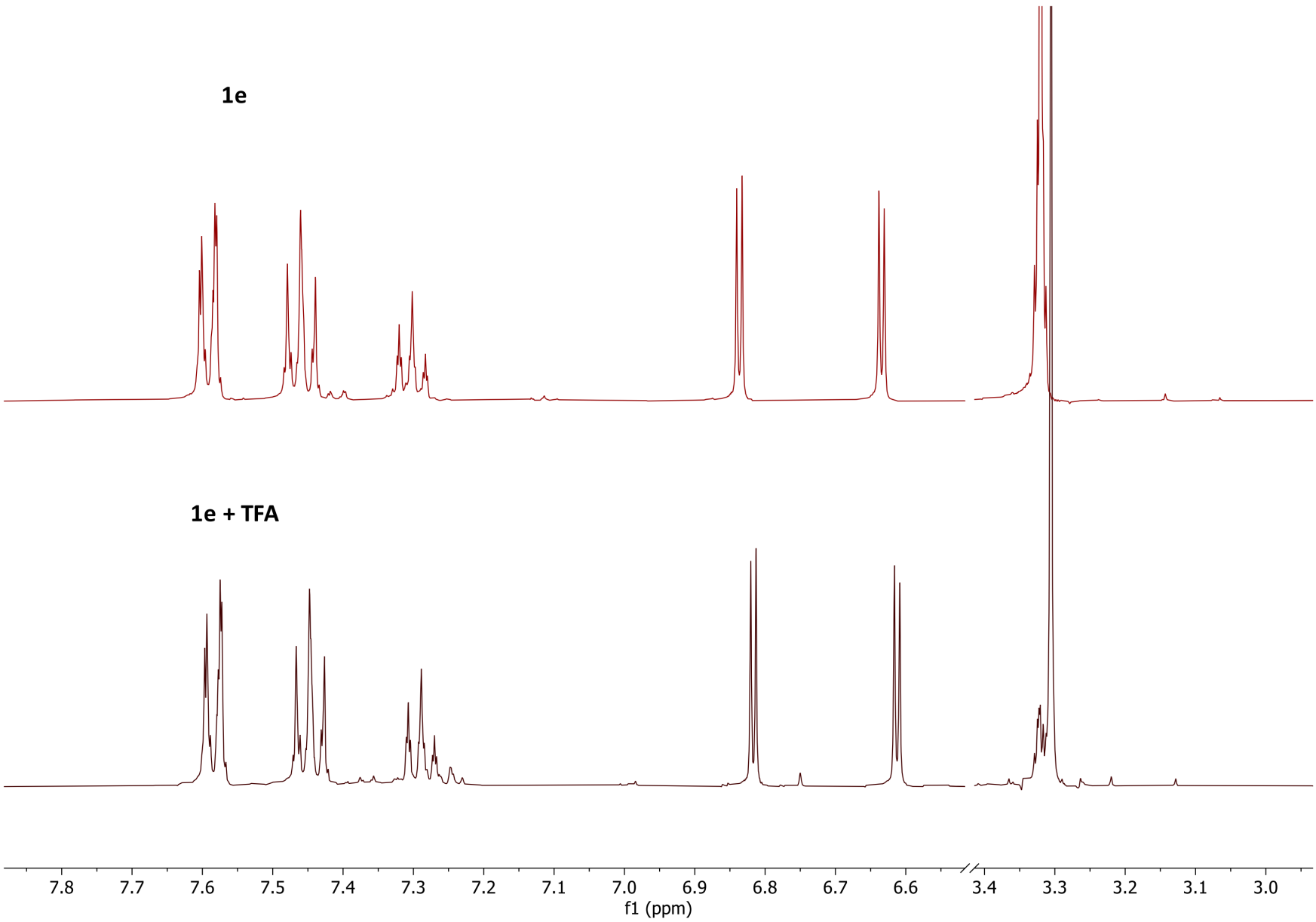


Figure S23. ^{1}H NMR spectra of the compound **1e** (upper) and of the compound **1e** in the presence of 1 equivalent of TFA (lower), (CD_3OD, 400MHz)

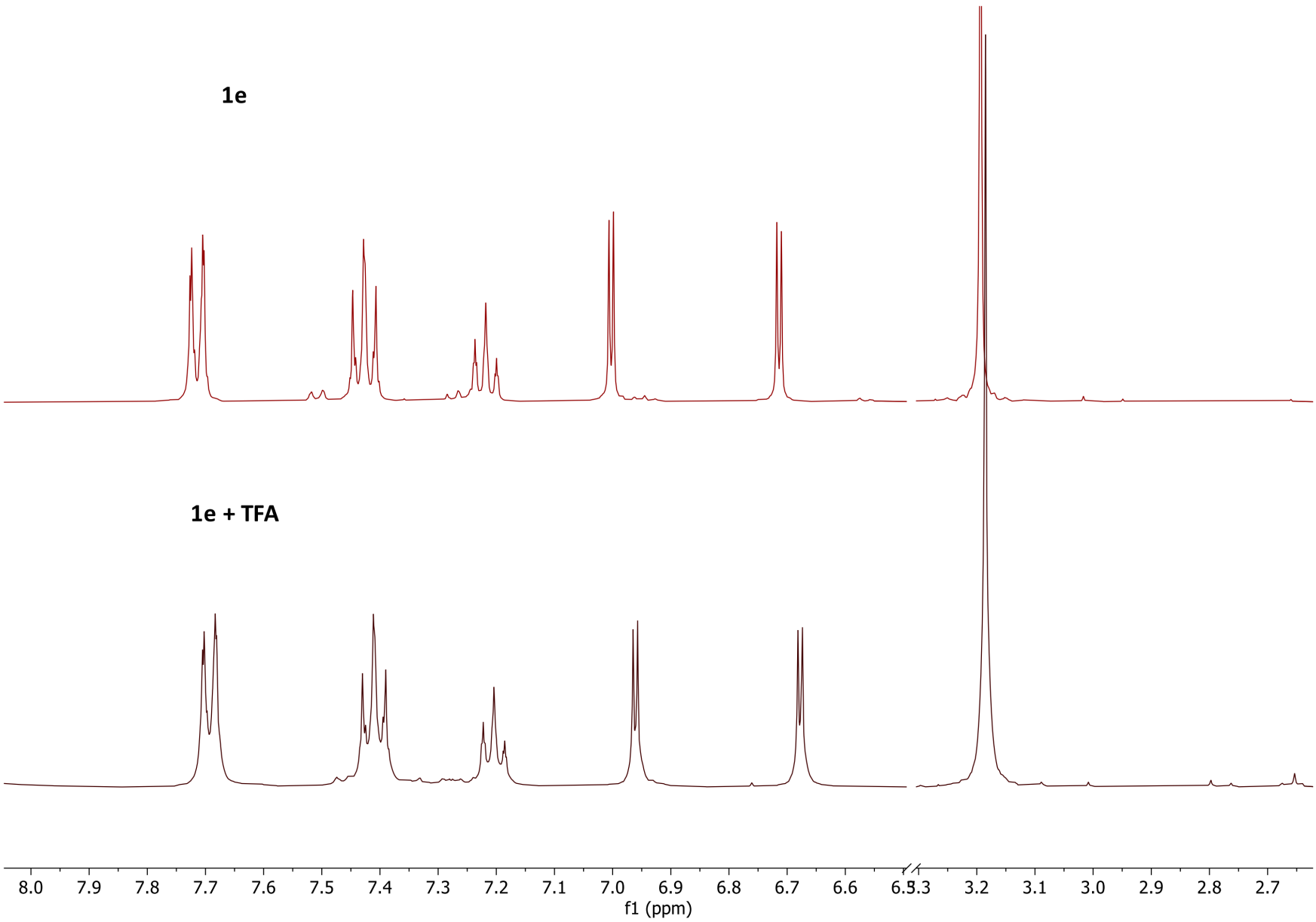
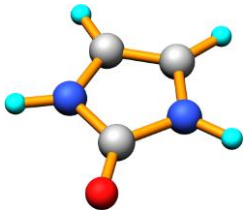
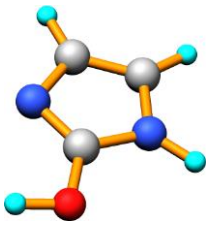
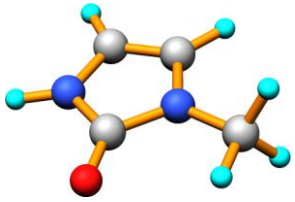
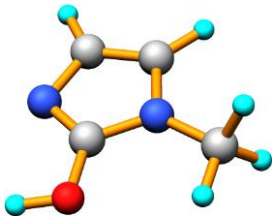


Figure S24. ^{1}H NMR spectra of the compound **1e** (upper) and of the compound **1e** in the presence of 1 equivalent of TFA (lower), ($(CD_3)_2SO$, 400MHz)

Coordinates of stationary points for studied compounds

IMIDAZOLES 1a-e and 2-HYDROXYIMIDAZOLES 1a',b'd', B3PW91/def2-TZVPD // PBE/def2-TZVPD				
Molecule: **1a**  Energy = -301.408770 Hartree	10			
	C	-0.29819	1.71476	-0.02459
	O	0.86742	2.09506	-0.00362
	N	-1.46487	2.47773	-0.10316
	N	-0.79237	0.40982	0.02405
	C	-2.60230	1.67555	-0.10190
	C	-2.18316	0.38687	-0.02267
	H	-3.60482	2.08075	-0.15662
	H	-2.75503	-0.53209	0.00389
	H	-1.43576	3.48772	-0.15280
	H	-0.17492	-0.38917	0.08543
Molecule: **1a'**  Energy = -301.160571 Hartree	10			
	C	-0.38909	1.65513	-0.04273
	O	0.86575	2.15709	-0.03593
	N	-1.45907	2.49304	-0.10756
	N	-0.73322	0.38875	0.00816
	C	-2.59625	1.68640	-0.09648
	C	-2.12169	0.40134	-0.02542
	H	-3.59550	2.10351	-0.13920
	H	-2.69281	-0.52122	0.00427
	H	-1.42525	3.50465	-0.15515
	H	1.46012	1.38430	0.01203
Molecule: **1b**  Energy = -340.695728 Hartree	13			
	C	-0.31864	1.72287	0.11168
	O	0.83527	2.11651	0.26816
	N	-1.46845	2.48844	-0.11032
	N	-0.79889	0.41499	0.11070
	C	-2.58527	1.66722	-0.23795
	C	-2.17273	0.38033	-0.10176
	H	-3.57704	2.06619	-0.41397
	H	-2.73693	-0.54294	-0.13801
	H	-0.18526	-0.37766	0.24585
	C	-1.43377	3.93064	-0.18480
	H	-0.38871	4.23576	-0.04971
	H	-1.79039	4.28513	-1.16317
	H	-2.04719	4.38352	0.60830

Molecule: **1b'**

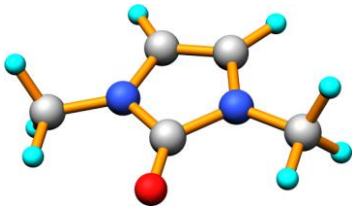


Energy = -340.400740 Hartree

13

C	-0.39760	1.66693	0.03998
O	0.85001	2.17679	0.17306
N	-1.45997	2.50304	-0.13241
N	-0.72731	0.39402	0.05742
C	-2.57877	1.67491	-0.23326
C	-2.10353	0.39336	-0.11465
H	-3.57298	2.08336	-0.37632
H	-2.66634	-0.53456	-0.14321
C	-1.43396	3.95180	-0.18993
H	-0.39184	4.28633	-0.15116
H	-1.88747	4.30698	-1.12598
H	-1.97904	4.38640	0.66063
H	1.43779	1.40464	0.27583

Molecule: **1c**

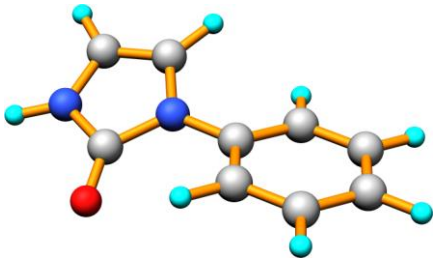


Energy = -379.982620 Hartree

16

C	-0.31447	1.71118	-0.00658
O	0.85499	2.09511	0.04226
N	-1.46917	2.48703	-0.12890
N	-0.79132	0.39975	0.04724
C	-2.59745	1.67474	-0.14742
C	-2.17889	0.38605	-0.03896
H	-3.59807	2.08022	-0.23664
H	-2.74866	-0.53505	-0.01581
C	-1.42974	3.92833	-0.21730
H	-0.37446	4.22540	-0.17382
H	-1.86539	4.27883	-1.16486
H	-1.97065	4.39151	0.62145
C	0.08632	-0.74046	0.17420
H	1.11281	-0.35530	0.21658
H	-0.12662	-1.30361	1.09516
H	-0.01123	-1.41372	-0.69060

Molecule: **1d**

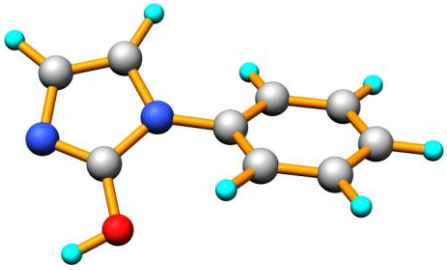


Energy = -532.391294 Hartree

20

C	-0.87659	1.25066	-1.11717
O	-0.27791	1.27253	-2.18652
N	-1.79100	2.18165	-0.63729
N	-0.80118	0.29810	-0.07186
C	-2.26133	1.83561	0.62229
C	-1.65012	0.67890	0.97421
H	-3.00374	2.41998	1.15112
H	-1.78059	0.06809	1.85735
C	0.05711	-0.82608	-0.05673
C	0.49140	-1.35037	1.17005
C	0.47007	-1.42670	-1.25548
C	1.31456	-2.47524	1.19625
H	0.20464	-0.86732	2.10442
C	1.30252	-2.54436	-1.21263
H	0.14753	-1.00382	-2.20415
C	1.72551	-3.07889	0.00638
H	1.64598	-2.87240	2.15704
H	1.61923	-3.00446	-2.15007
H	2.37442	-3.95526	0.02925
H	-2.04551	2.99640	-1.18044

Molecule: **1d'**

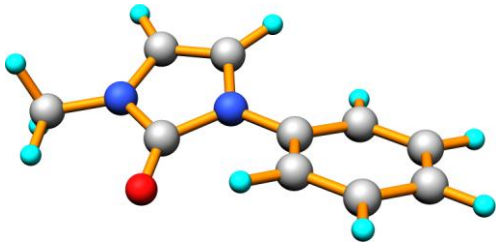


Energy = -531.924818 Hartree

20

C	-0.92270	1.19546	-1.01725
O	-0.37641	1.12534	-2.25114
N	-0.30635	0.93942	0.11199
N	-2.24772	1.52560	-0.85314
C	-1.27617	1.11190	1.08995
C	-2.47374	1.46354	0.53003
H	-1.04282	0.98370	2.14233
H	-3.43744	1.72036	0.95248
C	-3.22260	1.80549	-1.84618
C	-4.53639	1.35520	-1.66157
C	-2.88834	2.53876	-2.99143
C	-5.51083	1.64664	-2.61526
H	-4.78439	0.76369	-0.77982
C	-3.86833	2.81093	-3.94532
H	-1.86788	2.89222	-3.12895
C	-5.18156	2.37222	-3.76199
H	-6.53159	1.29209	-2.46459
H	-3.60175	3.38175	-4.83609
H	-5.94409	2.59344	-4.50979
H	0.54009	0.81927	-2.10827

Molecule: **1e**

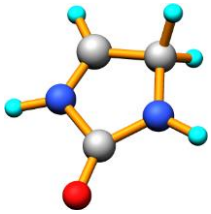
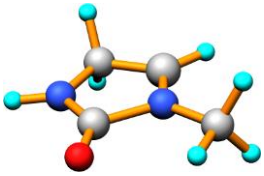
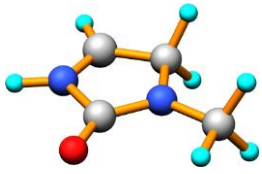


Energy = -571.678472 Hartree

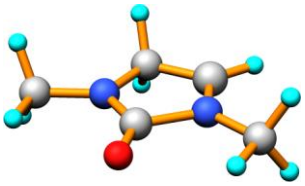
23

C	-0.88022	1.24666	-1.11729
O	-0.28374	1.26450	-2.19115
N	-1.79543	2.18807	-0.64934
N	-0.79677	0.29892	-0.07208
C	-2.25435	1.83748	0.61333
C	-1.64206	0.68300	0.97366
H	-2.99639	2.42480	1.14089
H	-1.77110	0.07757	1.86054
C	-2.16789	3.35342	-1.41888
H	-1.90024	4.27820	-0.88680
H	-1.61376	3.30805	-2.36445
H	-3.24735	3.35683	-1.63068
C	0.06030	-0.82595	-0.05722
C	0.49001	-1.35350	1.16997
C	0.47657	-1.42544	-1.25558
C	1.31119	-2.47996	1.19687
H	0.20127	-0.87226	2.10464
C	1.30688	-2.54484	-1.21198
H	0.15830	-0.99997	-2.20454
C	1.72507	-3.08257	0.00738
H	1.63868	-2.87913	2.15822
H	1.62569	-3.00369	-2.14938
H	2.37232	-3.96019	0.03087

IMINIUM CATIONS (*C*-PROTONATED IMIDAZOLES 1a-e), B3PW91/def2-TZVPD // PBE/def2-TZVPD

Molecule: **1a_C**  Energy = -301.493367 Hartree	11 C -0.23819 1.66811 -0.02052 O 0.85518 2.14145 -0.00686 N -1.51098 2.49577 -0.10575 N -0.74134 0.40367 0.02612 C -2.56611 1.76085 -0.10496 C -2.17817 0.33361 -0.01981 H -3.58486 2.15002 -0.15946 H -2.63218 -0.13155 0.87760 H -1.47238 3.51912 -0.15589 H -0.12874 -0.40536 0.08762 H -2.57123 -0.22067 -0.89509
Molecule: **1b_C1**  Energy = -340.748250 Hartree	14 C -0.27257 1.67765 0.12331 O 0.80752 2.16792 0.26454 N -1.53115 2.51045 -0.12136 N -0.75105 0.40886 0.11996 C -2.55847 1.74327 -0.24008 C -2.17127 0.31901 -0.09923 H -3.56987 2.11256 -0.42014 H -2.71812 -0.14849 0.74197 H -0.13805 -0.38961 0.25958 C -1.43453 3.96664 -0.18732 H -0.37641 4.22355 -0.05955 H -1.79579 4.31571 -1.16235 H -2.03198 4.41122 0.61820 H -2.44125 -0.24674 -1.01150
Molecule: **1b_C2**  Energy = -340.740161 Hartree	14 C -0.29896 1.78142 0.11022 O 0.85458 2.05290 0.27475 N -1.42558 2.51317 -0.10591 N -0.82725 0.36294 0.10745 C -2.60814 1.70284 -0.24331 C -2.09791 0.32187 -0.08711 H -3.37949 1.91623 0.52380 H -2.68402 -0.59806 -0.12672 H -0.19861 -0.43412 0.24948 C -1.42024 3.97092 -0.18494 H -0.38625 4.30818 -0.05250 H -1.78849 4.29938 -1.16607 H -2.04755 4.39734 0.60941 H -3.10908 1.81798 -1.22557

Molecule: **1c_C**

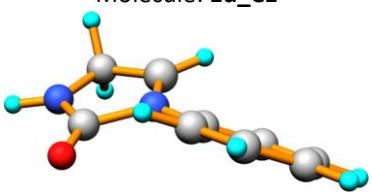


Energy = -379.994646 Hartree

17

C	-0.27524	1.67292	-0.00045
O	0.82110	2.15761	0.03776
N	-1.53766	2.51525	-0.13412
N	-0.74467	0.40304	0.05106
C	-2.57886	1.75793	-0.15172
C	-2.18094	0.33514	-0.03592
H	-3.59919	2.13493	-0.24052
H	-2.64764	-0.12873	0.85487
C	-1.43452	3.96979	-0.22093
H	-0.36738	4.21690	-0.17523
H	-1.86446	4.31264	-1.16994
H	-1.96698	4.42690	0.62210
C	0.12151	-0.76391	0.17768
H	1.15730	-0.40975	0.22268
H	-0.11539	-1.31580	1.09738
H	-0.00069	-1.42422	-0.69156
H	-2.53527	-0.24065	-0.91313

Molecule: **1d_C1**

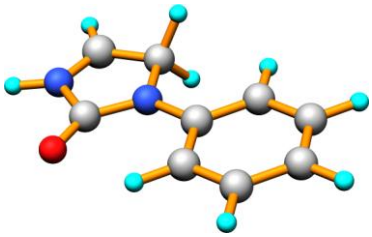


Energy = -532.277952 Hartree

21

C	-0.77583	1.35793	-1.09094
O	-0.04214	1.34233	-2.03303
N	-1.71797	2.23011	-0.65751
N	-0.81481	0.25976	-0.01013
C	-2.35623	1.85669	0.57787
C	-1.70127	0.56466	0.88726
H	-3.45060	1.72604	0.48312
H	-1.92702	-0.07874	1.73700
C	0.06445	-0.85755	-0.02057
C	0.58293	-1.31844	1.19915
C	0.37877	-1.47711	-1.23793
C	1.41663	-2.43057	1.19668
H	0.37355	-0.78596	2.12858
C	1.21082	-2.59386	-1.21664
H	-0.02987	-1.10511	-2.17483
C	1.72762	-3.07010	-0.00889
H	1.84100	-2.78844	2.13471
H	1.45590	-3.09440	-2.15331
H	2.38734	-3.93826	-0.00568
H	-1.90704	3.08858	-1.16688
H	-2.18724	2.58945	1.38998

Molecule: **1d_C2**

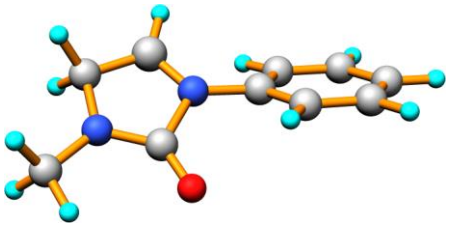


Energy = -532.266538 Hartree

21

C	-1.08446	1.05229	-1.21485
O	-0.79066	1.00337	-2.37755
N	-1.98810	2.10796	-0.66199
N	-0.77434	0.30156	-0.10710
C	-2.17834	1.98713	0.60669
C	-1.41655	0.81516	1.08577
H	-2.80318	2.65148	1.20430
H	-2.09902	0.08292	1.55702
C	0.07575	-0.84711	-0.08622
C	0.28149	-1.51113	1.13135
C	0.69428	-1.30218	-1.26070
C	1.10816	-2.63167	1.17115
H	-0.18979	-1.17434	2.05475
C	1.51773	-2.42560	-1.19846
H	0.53691	-0.79025	-2.20622
C	1.72927	-3.09336	0.00808
H	1.26535	-3.14486	2.11999
H	1.99761	-2.77766	-2.11185
H	2.37526	-3.97054	0.04476
H	-2.38193	2.82361	-1.28081
H	-0.69242	1.12226	1.86388

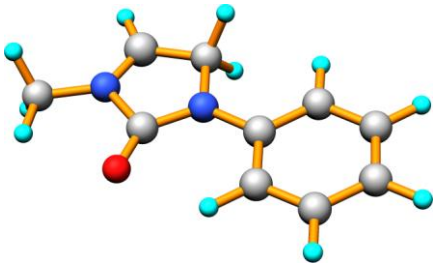
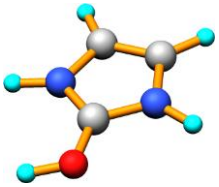
Molecule: **1e_C1**

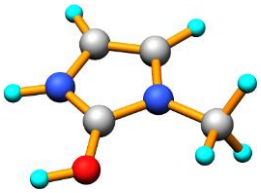
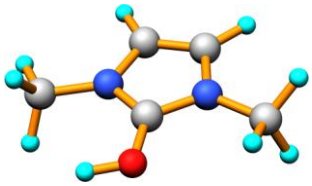


Energy = -571.523822 Hartree

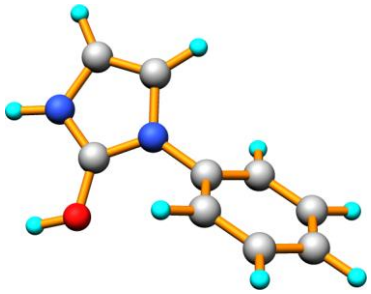
24

C	-0.82790	1.31994	-1.10895
O	-0.10822	1.29339	-2.06713
N	-1.76678	2.20029	-0.68719
N	-0.83262	0.24205	-0.01417
C	-2.37629	1.82852	0.56414
C	-1.70727	0.55024	0.89286
H	-3.47182	1.69004	0.48575
H	-1.91152	-0.08135	1.75658
C	-2.09053	3.41974	-1.41693
H	-1.87803	4.30200	-0.79763
H	-1.46675	3.44901	-2.31700
H	-3.15015	3.41980	-1.70661
C	0.05810	-0.86652	-0.02196
C	0.60086	-1.30377	1.19564
C	0.35941	-1.50143	-1.23439
C	1.44545	-2.40788	1.19668
H	0.40072	-0.75958	2.12028
C	1.20295	-2.60959	-1.20985
H	-0.06667	-1.14540	-2.16965
C	1.74362	-3.06268	-0.00376
H	1.88801	-2.74736	2.13315
H	1.43844	-3.12147	-2.14286
H	2.41182	-3.92432	0.00190
H	-2.20786	2.58234	1.35811

Molecule: **1e_C2**  Energy = -571.520468 Hartree	24 C -0.97105 1.13541 -1.16461 O -0.64347 1.11504 -2.32116 N -1.87211 2.21995 -0.61706 N -0.71354 0.34190 -0.08316 C -2.08766 2.04190 0.64070 C -1.37504 0.83373 1.10800 H -2.70964 2.69917 1.24955 H -2.08791 0.10301 1.53202 C -2.36214 3.26990 -1.50694 H -2.01467 4.24637 -1.14836 H -1.95154 3.06141 -2.50158 H -3.45825 3.24504 -1.53466 C 0.10308 -0.83248 -0.07622 C 0.23929 -1.54964 1.12041 C 0.75731 -1.25942 -1.24093 C 1.03206 -2.69529 1.14894 H -0.26120 -1.23488 2.03608 C 1.54579 -2.40837 -1.19077 H 0.65386 -0.70658 -2.17069 C 1.68802 -3.12928 -0.00468 H 1.13430 -3.24944 2.08216 H 2.05363 -2.73824 -2.09735 H 2.30710 -4.02600 0.02248 H -0.66121 1.09182 1.91185
2-HYDROXYIMIDAZOLIUM CATIONS (*O*-PROTONATED IMIDAZOLES 1a-e), B3PW91/def2-TZVPD // PBE/def2-TZVPD	
Molecule: **1a_OH**  Energy = -301.748381 Hartree	11 C -0.35704 1.67393 -0.03397 O 0.86366 2.16701 -0.01207 N -1.44103 2.46070 -0.10490 N -0.78900 0.39987 0.01754 C -2.59138 1.67605 -0.09814 C -2.18537 0.38259 -0.02277 H -3.58269 2.10943 -0.14827 H -2.74644 -0.54337 0.00552 H -1.39977 3.47677 -0.15658 H -0.19572 -0.42360 0.08392 H 1.56278 1.48463 -0.02328

Molecule: **1b_OH**  Energy = -341.040669 Hartree	14 C -0.36638 1.68051 0.00523 O 0.86026 2.16822 0.06866 N -1.44139 2.47549 -0.11246 N -0.78922 0.40007 0.02973 C -2.58095 1.67176 -0.16945 C -2.17882 0.37819 -0.07840 H -3.57091 2.10110 -0.26584 H -2.73976 -0.54817 -0.07686 H -0.19301 -0.41931 0.10978 C -1.41294 3.93830 -0.19275 H -0.42629 4.29423 0.11905 H -1.61111 4.25686 -1.22373 H -2.17765 4.34478 0.47846 H 1.54116 1.48396 0.21457
Molecule: **1c_OH**  Energy = -380.332365 Hartree	17 C -0.37424 1.68897 0.01439 O 0.85413 2.17306 0.11532 N -1.44969 2.48567 -0.10373 N -0.77405 0.40085 0.00089 C -2.57866 1.67563 -0.20173 C -2.16248 0.38365 -0.13350 H -3.57111 2.09682 -0.30678 H -2.71739 -0.54614 -0.16370 C -1.42068 3.94859 -0.16121 H -0.49302 4.30678 0.29630 H -1.47094 4.28425 -1.20474 H -2.27745 4.33941 0.39815 C 0.11008 -0.75726 0.11597 H 0.86272 -0.74494 -0.68449 H 0.59486 -0.77801 1.10187 H -0.49334 -1.66351 0.00618 H 1.52027 1.47118 0.24779

Molecule: **1d_OH**

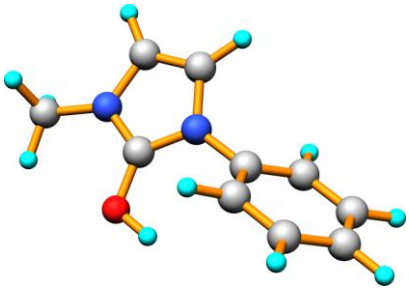


Energy = -532.737539 Hartree

21

C	-0.75831	1.34675	-0.92946
O	0.14908	1.43039	-1.88634
N	-1.73718	2.21421	-0.59969
N	-0.82587	0.29917	-0.08645
C	-2.44707	1.71212	0.49036
C	-1.87996	0.52017	0.80627
H	-3.28584	2.24391	0.92187
H	-2.12657	-0.21056	1.56632
C	0.05711	-0.84211	-0.07599
C	0.70991	-1.16505	1.11468
C	0.21663	-1.60057	-1.23589
C	1.54520	-2.28184	1.13833
H	0.57789	-0.54619	2.00340
C	1.06269	-2.70886	-1.19772
H	-0.31864	-1.33987	-2.14918
C	1.72325	-3.04960	-0.01495
H	2.06336	-2.54597	2.06030
H	1.19634	-3.31327	-2.09502
H	2.37961	-3.91983	0.00872
H	-1.93817	3.08791	-1.07850
H	0.15955	2.30308	-2.32407

Molecule: **1e_OH**



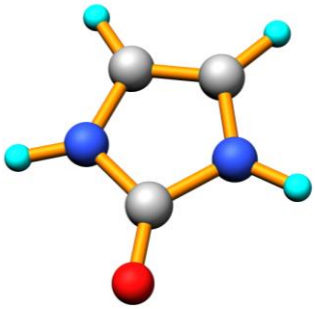
Energy = -572.035220 Hartree

24

C	-0.78914	1.31440	-0.91583
O	0.11273	1.50012	-1.86188
N	-1.76228	2.19706	-0.63871
N	-0.88548	0.26987	-0.06228
C	-2.50455	1.70160	0.43445
C	-1.96231	0.50954	0.79587
H	-3.35568	2.24280	0.82948
H	-2.24245	-0.20436	1.56035
C	-1.99665	3.45800	-1.34347
H	-1.96024	4.28755	-0.62740
H	-1.21582	3.59336	-2.09811
H	-2.97809	3.42927	-1.83235
C	0.02086	-0.84527	-0.04919
C	0.73472	-1.13287	1.11610
C	0.17711	-1.60618	-1.21327
C	1.62096	-2.20987	1.11102
H	0.60400	-0.51746	2.00720
C	1.08377	-2.66895	-1.20727
H	-0.43405	-1.40248	-2.09540
C	1.80111	-2.97030	-0.04800
H	2.18114	-2.44829	2.01539
H	1.21060	-3.27320	-2.10574
H	2.50073	-3.80643	-0.04481
H	0.73303	0.73712	-1.88514

TRANSITION STATE CALCULATIONS, ωB97X-V/def2-TZVPD, PCM(chloroform)

Molecule: **1a**

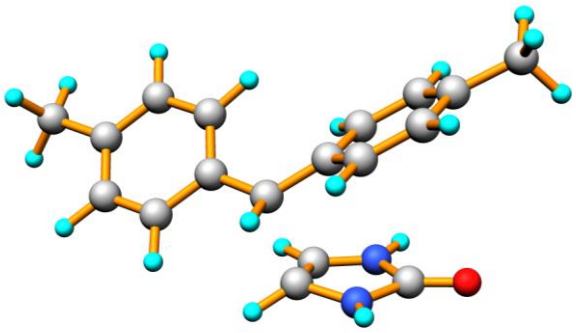


Energy = -301.620280 Hartree

10

C	-0.30608	1.35031	-0.32001
C	0.67121	1.48323	-1.24115
C	1.24414	-0.29437	0.09872
N	0.03615	0.27325	0.49313
H	-1.20718	1.92453	-0.17658
N	1.61451	0.49064	-0.98911
O	1.83271	-1.24585	0.58636
H	0.77569	2.19485	-2.04425
H	2.45600	0.31358	-1.50877
H	-0.48313	-0.07718	1.27867

Molecule: **1a_TS1** (*C*-attack)



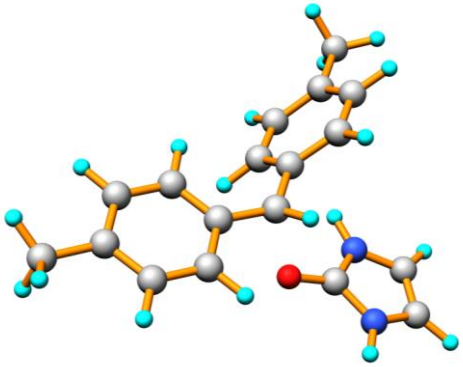
Energy = -882.303588 Hartree

Imag. Freq. = -467.6800 cm^{-1}

40

C	0.69628	1.90746	-0.26818
C	1.99611	2.26215	-0.67969
C	1.93061	-0.02048	-0.50088
N	0.66717	0.50655	-0.33173
H	-0.17835	2.47478	-0.56215
N	2.72487	1.16168	-0.77097
O	2.33718	-1.14733	-0.45982
H	2.39401	3.26149	-0.80469
C	1.01271	3.93089	1.70187
C	0.77557	2.47879	1.66217
C	1.61584	1.47340	2.30155
C	0.10775	4.78449	1.04571
C	0.28480	6.15638	1.05208
C	1.35933	6.74127	1.73499
C	2.23485	5.89570	2.42221
C	2.07213	4.51780	2.40898
C	3.02412	1.49137	2.26921
C	3.75945	0.47488	2.85368
C	3.13009	-0.61167	3.47472
C	1.73016	-0.63753	3.50066
C	0.98972	0.37471	2.91790
H	-0.28643	2.24165	1.76320
H	-0.75585	4.37024	0.52918
H	2.74059	3.90297	3.00050
H	3.54773	2.30456	1.77530
H	-0.09670	0.33549	2.96056
H	4.84519	0.51257	2.82194
H	1.21995	-1.46615	3.98361
H	3.05164	6.32655	2.99522
H	-0.42778	6.79089	0.53167
C	1.52598	8.23026	1.77184
H	0.88915	8.66361	2.55309
H	2.55755	8.51453	1.99272
H	1.23090	8.68787	0.82349
C	3.93362	-1.73084	4.06089
H	3.39018	-2.23909	4.86109
H	4.15605	-2.47799	3.28846
H	4.88896	-1.37414	4.45484
H	-0.09263	-0.07542	-0.01484
H	3.72151	1.10165	-0.93439

Molecule: **1a_TS3** (*O*-attack)



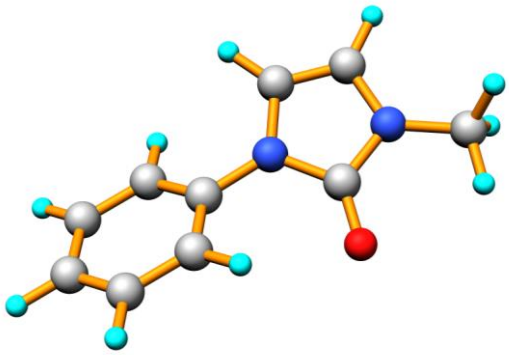
Energy = -882.307712 Hartree

Imag. Freq. = -256.3600 cm^{-1}

40

C	-0.30512	1.35015	-0.31678
C	0.67610	1.48301	-1.23902
C	1.22457	-0.25916	0.09167
N	0.03730	0.27548	0.49085
H	-1.21099	1.91654	-0.17209
N	1.61892	0.50183	-0.96837
O	1.84002	-1.26492	0.56070
H	0.77961	2.17642	-2.05822
C	3.06798	-2.48107	2.49806
C	2.45828	-1.17496	2.36778
C	1.28024	-0.74926	3.10737
C	4.17202	-2.79431	1.68212
C	4.79453	-4.02131	1.78005
C	4.35978	-4.97720	2.71127
C	3.28734	-4.65003	3.54841
C	2.64353	-3.42878	3.44476
C	0.13197	-1.55640	3.20073
C	-1.00093	-1.08608	3.84336
C	-1.02665	0.18942	4.43198
C	0.11352	0.99188	4.32369
C	1.24349	0.53958	3.65708
H	3.15730	-0.37260	2.13401
H	4.51874	-2.06584	0.95461
H	1.84513	-3.18779	4.13785
H	0.12051	-2.52946	2.71772
H	2.11352	1.18553	3.56994
H	-1.88678	-1.71408	3.89517
H	0.11066	1.98693	4.76011
H	2.96258	-5.36244	4.30163
H	5.63836	-4.25077	1.13506
C	5.02576	-6.31543	2.79808
H	4.57052	-7.00742	2.07787
H	6.08985	-6.24951	2.55590
H	4.91619	-6.75720	3.79141
C	-2.23993	0.66471	5.17222
H	-2.20667	0.31113	6.21036
H	-2.29412	1.75571	5.20021
H	-3.16041	0.27565	4.72848
H	2.45481	0.30892	-1.49837
H	-0.48192	-0.07490	1.28464

Molecule: **1e**

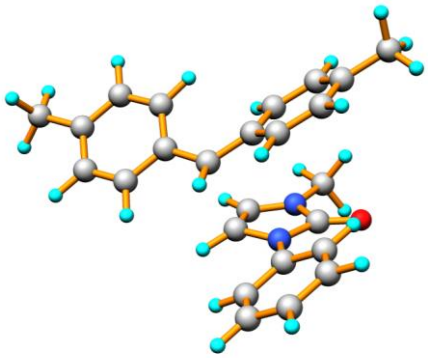


Energy = -572.095715 Hartree

23

C	0.35714	1.76721	-0.55038
C	1.59778	2.26731	-0.71847
C	1.83580	0.03086	-0.33301
N	0.47704	0.39619	-0.30566
H	-0.59442	2.27174	-0.52416
C	-0.60101	-0.50419	-0.15505
C	-0.46727	-1.64437	0.64140
C	-1.81209	-0.24001	-0.80001
C	-1.54885	-2.50400	0.78773
H	0.47855	-1.85199	1.12589
C	-2.88876	-1.10211	-0.63057
H	-1.90543	0.62294	-1.45189
C	-2.76366	-2.23848	0.16201
H	-1.43878	-3.38946	1.40701
H	-3.82583	-0.88912	-1.13666
H	-3.60410	-2.91431	0.28666
N	2.50137	1.22076	-0.59140
O	2.33029	-1.07713	-0.18119
C	3.94166	1.29948	-0.71820
H	4.34222	0.29944	-0.53624
H	4.22996	1.62354	-1.72501
H	4.36031	1.99500	0.01813
H	1.91707	3.28370	-0.88892

Molecule: **1e_TS1** (*C*[4]-attack)



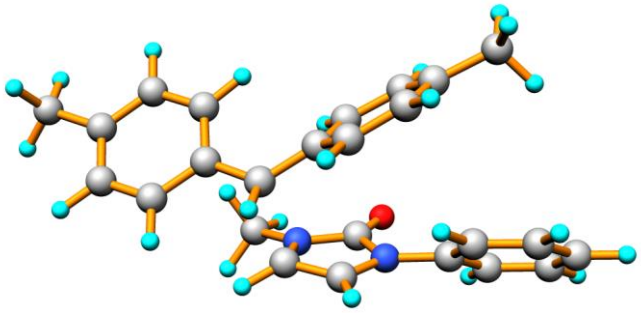
Energy = -1152.783373 Hartree

Imag. Freq. = -338.6200 cm^{-1}

53

C	0.77530	1.91262	-0.39773
C	2.10448	2.20650	-0.69947
C	1.92427	-0.05136	-0.51318
N	0.66131	0.51960	-0.39019
H	-0.06280	2.54396	-0.64655
C	-0.54988	-0.19369	-0.14736
C	-0.52295	-1.44533	0.46962
C	-1.76269	0.38451	-0.52512
C	-1.72212	-2.10510	0.71095
H	0.42089	-1.89613	0.74821
C	-2.95282	-0.28421	-0.26346
H	-1.79177	1.33327	-1.05175
C	-2.93780	-1.52964	0.35505
H	-1.70083	-3.08184	1.18435
H	-3.89348	0.16648	-0.56357
H	-3.86822	-2.05347	0.54873
N	2.79525	1.06893	-0.72356
O	2.28850	-1.20135	-0.47385
C	4.22575	0.86980	-0.91194
H	4.60879	0.25161	-0.09534
H	4.40255	0.34767	-1.85667
H	4.72408	1.84066	-0.92171
H	2.55791	3.18194	-0.81662
C	1.01544	3.93807	1.73281
C	0.79130	2.50017	1.69481
C	1.62362	1.48235	2.29833
C	0.07568	4.78418	1.11148
C	0.23296	6.15712	1.11886
C	1.32217	6.75383	1.76879
C	2.23403	5.91808	2.42300
C	2.09068	4.54025	2.40985
C	3.03272	1.50452	2.28512
C	3.76240	0.47850	2.85784
C	3.12618	-0.61845	3.45581
C	1.72621	-0.65297	3.45415
C	0.99038	0.36548	2.87878
H	-0.26651	2.22977	1.68285
H	-0.79522	4.35379	0.62102
H	2.78434	3.93312	2.97975
H	3.55816	2.31963	1.79655
H	-0.09506	0.31268	2.88205
H	4.84853	0.51602	2.83784
H	1.21150	-1.49751	3.90457
H	3.06202	6.36014	2.97098
H	-0.50481	6.78489	0.62620
C	1.46929	8.24404	1.81188
H	0.89892	8.65617	2.65396
H	2.51225	8.54143	1.94647
H	1.08482	8.71064	0.90093
C	3.91846	-1.71689	4.09378
H	3.97735	-1.55613	5.17781
H	3.44690	-2.69090	3.93692
H	4.94054	-1.75445	3.70994

Molecule: **1e_TS2** (C^5-attack)



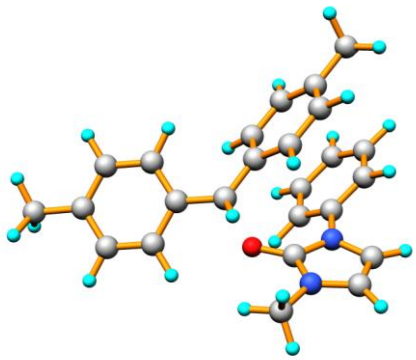
Energy = -1152.778906 Hartree

Imag. Freq. = -392.0800 cm^{-1}

53

C	0.30671	0.90910	0.66011
C	0.24182	2.28756	0.44090
C	1.69751	1.40611	-1.07651
N	1.21089	0.37609	-0.16889
H	-0.21156	0.32557	1.40850
C	1.70599	-0.95835	-0.15019
C	2.03416	-1.59421	-1.34749
C	1.83875	-1.61054	1.07539
C	2.49667	-2.90324	-1.30211
H	1.92690	-1.07738	-2.29283
C	2.29376	-2.92171	1.10014
H	1.62566	-1.08654	2.00133
C	2.62625	-3.56942	-0.08668
H	2.75015	-3.40760	-2.22901
H	2.39966	-3.43361	2.05163
H	2.98709	-4.59286	-0.06427
N	1.02889	2.54078	-0.67934
O	2.50891	1.26464	-1.95764
C	1.11448	3.79944	-1.41339
H	1.70017	3.61312	-2.31581
H	0.11098	4.13474	-1.69302
H	1.75545	1.20797	4.14835
H	-0.61975	2.90593	0.65167
C	1.46660	4.38314	1.89715
C	1.36082	2.96651	2.20223
C	2.49009	2.05949	2.30390
C	0.30254	5.17926	1.92802
C	0.35398	6.53054	1.65458
C	1.57333	7.16000	1.35554
C	2.73550	6.38123	1.36574
C	2.69181	5.02217	1.63126
C	3.51383	1.98028	1.34098
C	4.52060	1.03435	1.45715
C	4.56897	0.15544	2.54356
C	3.56560	0.25365	3.51777
C	2.53106	1.16216	3.38708
H	0.54053	2.72782	2.87980
H	-0.65402	4.72251	2.17431
H	3.61846	4.46238	1.67799
H	3.51070	2.63854	0.47872
H	1.60379	4.57273	-0.81479
H	5.28433	0.97578	0.68641
H	3.59520	-0.40397	4.38291
H	3.69521	6.85485	1.17712
H	-0.55826	7.12071	1.68208
C	5.63918	-0.88819	2.64209
H	6.57651	-0.54437	2.19688
H	5.82720	-1.17539	3.67969
H	5.33254	-1.79134	2.09788
C	1.62791	8.63289	1.09311
H	0.75589	8.96980	0.52532
H	1.62724	9.18455	2.04193
H	2.53332	8.91289	0.54976

Molecule: **1e_TS3** (*O*-attack)



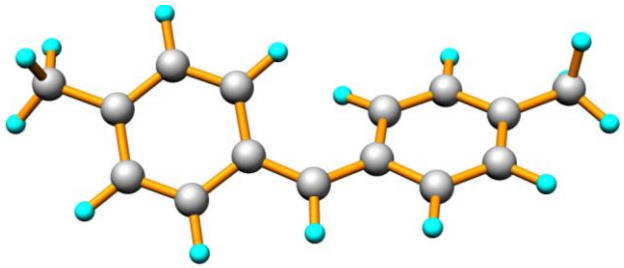
Energy = -1152.790086 Hartree

Imag. Freq. = -267.3200 cm^{-1}

53

C	-0.23849	1.38711	-0.55375
C	1.01157	1.78576	-0.88523
C	1.17958	-0.25269	0.04823
N	-0.13911	0.13197	0.03106
H	-1.19150	1.86252	-0.72075
C	-1.24726	-0.62480	0.52058
C	-1.30670	-1.99926	0.30576
C	-2.26961	0.04676	1.18489
C	-2.40623	-2.70505	0.77870
H	-0.50784	-2.50604	-0.22348
C	-3.37237	-0.67038	1.63366
H	-2.19623	1.11427	1.36930
C	-3.44025	-2.04611	1.43865
H	-2.46296	-3.77600	0.61022
H	-4.17748	-0.14923	2.14236
H	-4.30307	-2.60348	1.78986
N	1.88131	0.77808	-0.51005
O	1.66432	-1.33948	0.49325
C	3.32064	0.76405	-0.74153
H	3.68680	-0.24765	-0.56182
H	3.52773	1.03968	-1.77896
H	3.82796	1.46537	-0.07151
H	1.35063	2.68273	-1.37990
C	2.99020	-2.52589	2.41977
C	2.35771	-1.22261	2.26899
C	1.21210	-0.79225	3.04110
C	3.92421	-2.96123	1.46239
C	4.57921	-4.16698	1.61070
C	4.35453	-4.97815	2.73345
C	3.45580	-4.52765	3.70272
C	2.77628	-3.32789	3.55188
C	0.17054	-1.67446	3.38402
C	-0.92520	-1.21905	4.08877
C	-1.03691	0.12792	4.46420
C	-0.01671	1.01090	4.09530
C	1.08702	0.56220	3.38722
H	3.03940	-0.41913	1.99013
H	4.10598	-2.35425	0.58134
H	2.12100	-2.98512	4.34499
H	0.20990	-2.70630	3.05046
H	1.87588	1.26032	3.11576
H	-1.72916	-1.90805	4.33281
H	-0.09049	2.05971	4.37017
H	3.29404	-5.12104	4.59836
H	5.28498	-4.49241	0.85092
C	5.06100	-6.29194	2.87699
H	4.58313	-7.05070	2.24488
H	6.10480	-6.21812	2.55752
H	5.03527	-6.65348	3.90742
C	-2.22344	0.60187	5.24661
H	-2.06516	0.42641	6.31811
H	-2.39531	1.67290	5.11242
H	-3.12906	0.05833	4.96204

Molecule: **BHD**



Energy = -580.677158 Hartree

30

C	1.11471	4.18858	2.07786
C	0.74844	2.83258	2.19005
C	1.52864	1.71133	2.53579
C	0.24043	5.05254	1.36348
C	0.56079	6.37605	1.16990
C	1.73205	6.91907	1.72612
C	2.57064	6.08289	2.49144
C	2.28007	4.75180	2.66657
C	2.94815	1.67489	2.46614
C	3.63162	0.54236	2.83713
C	2.95121	-0.60202	3.30141
C	1.54587	-0.58537	3.33648
C	0.84706	0.53031	2.93860
H	-0.30042	2.61835	1.97833
H	-0.67115	4.64576	0.93386
H	2.90261	4.14799	3.31740
H	3.48999	2.51329	2.04276
H	-0.23938	0.52828	2.96215
H	4.71393	0.51353	2.74809
H	1.01022	-1.47059	3.66650
H	3.44842	6.50982	2.96868
H	-0.10175	7.01489	0.59344
C	2.05469	8.36552	1.56790
H	1.71986	8.91680	2.45780
H	3.13303	8.52740	1.48218
H	1.55174	8.80270	0.70277
C	3.71258	-1.80778	3.73441
H	4.03550	-1.68022	4.77739
H	3.10379	-2.71336	3.68848
H	4.61765	-1.94738	3.13691