Supporting Information

Small Far-Red Cationic Benzoquinone Diimine Dyes

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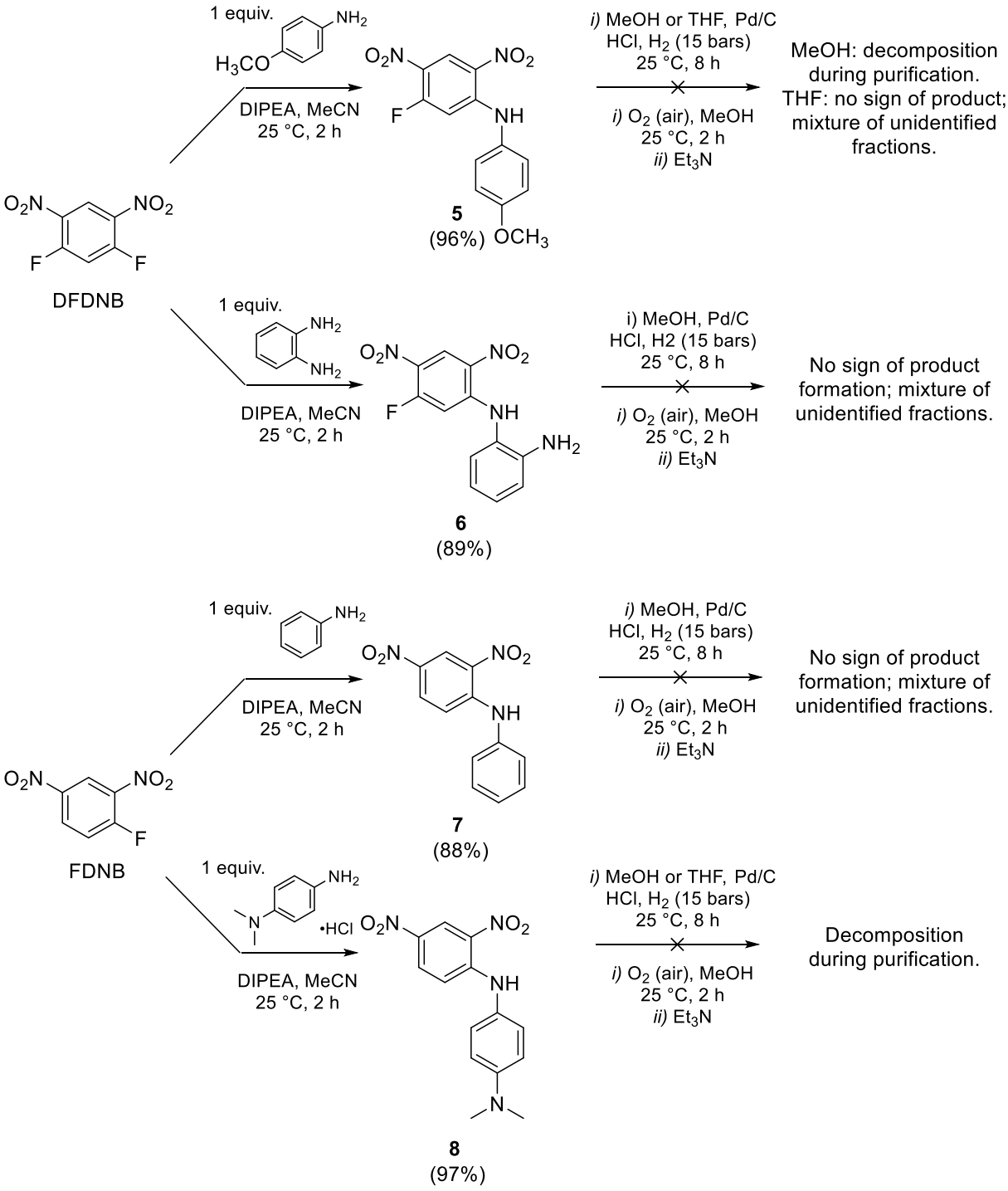
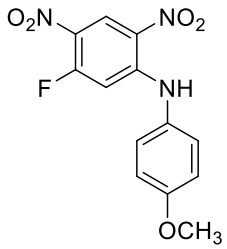
CONTENT

1. ADDITIONAL SYNTHETIC PROTOCOLS AND CHARACTERIZATIONS



Scheme S 1. Attempted reactions to isolate other analogues of **1•H$^+$**.

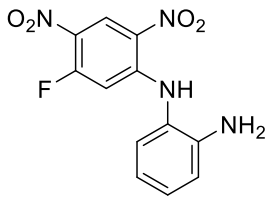
5-Fluoro-*N*-(4-methoxyphenyl)-2,4-dinitroaniline (compound 5)



1,5-Difluoro-2,4-dinitrobenzene (205 mg, 1 mmol, 1 equiv.) was dissolved in 10 mL of acetonitrile and to the solution were added *p*-anisidine (123 mg, 1 mmol, 1 equiv.) and *N,N*-diisopropylethylamine (182 µL, 1.05 mmol, 1.05 equiv.). The reaction was stirred at room temperature and monitored by TLC, until there were no more traces of starting material (after 2 h). Then, the mixture was evaporated, taken in 100 mL of dichloromethane, washed by 200 mL of water and extracted with another 20 mL of dichloromethane. The combined organic layers were collected, dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated, to afford **5** as an orange powder (96% yield, 294 mg, 0.96 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.84 (br s, 1H, NH), 9.17 (d, $^4J_{H\text{-}F}$ = 7.7 Hz, 1H, CH), 7.22 (d, ^3J = 8.5 Hz, 2H, CH), 7.03 (d, ^3J = 8.5 Hz, 2H, CH), 6.70 (d, $^3J_{H\text{-}F}$ = 13.7 Hz, 1H, CH), 3.87 (s, 3H, CH_3). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ = 161.1 (d, $^1J_{C\text{-}F}$ = 270.0 Hz, C), 159.5 (C), 149.3 (C), 149.2 (C), 128.7 (C), 127.9 (CH), 127.5 (CH), 115.6 (CH), 103.2 (d, $^2J_{C\text{-}F}$ = 27.7 Hz, CH), 55.7 (CH_3). One signal corresponding to one of the aromatic quaternary carbon is overlapped. **^{19}F ($CDCl_3$, 376 MHz):** δ = -104.8. **HRMS (ESI+)** calculated for $[M+H]^+$: 308.0677 ($C_{13}H_{11}FN_3O_5^+$), found: 308.0679.

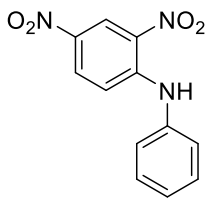
N^1-(5-Fluoro-2,4-dinitrophenyl)benzene-1,2-diamine (compound 6)



1,5-Difluoro-2,4-dinitrobenzene (205 mg, 1 mmol, 1 equiv.) was dissolved in 10 mL of acetonitrile and to the solution were added *o*-phenylenediamine (108 mg, 1 mmol, 1 equiv.) and *N,N*-diisopropylethylamine (182 µL, 1.05 mmol, 1.05 equiv.). The reaction was stirred at room temperature and monitored by TLC, until there were no more traces of starting material (after 2 h). Then, the mixture was evaporated, taken in 100 mL of dichloromethane, washed by 200 mL of water and extracted with another 20 mL of dichloromethane. The combined organic layers were collected, dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated, to afford **6** as a red powder (89% yield, 260 mg, 0.89 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.53 (br s, 1H, NH), 9.18 (d, $^4J_{H\text{-}F}$ = 7.6 Hz, 1H, CH), 7.24 (d, ^3J = 7.8 Hz, 1H, CH), 7.12 (d, ^3J = 7.8 Hz, 1H, CH), 6.91 (m, 2H, CH), 6.53 (d, $^3J_{H\text{-}F}$ = 13.3 Hz, 1H, CH), 3.83 (br s, 2 H, NH_2). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ = 161.3 (d, $^1J_{C\text{-}F}$ = 270.3 Hz, C), 149.0 (d, $^2J_{C\text{-}F}$ = 13.4 Hz, C), 142.9 (C), 130.2 (CH), 128.0 (d, $^2J_{C\text{-}F}$ = 28.6 Hz, CH), 127.9 (C), 127.4 (C), 121.3 (C), 119.6 (CH), 117.0 (CH), 104.0 (CH), 103.7 (CH). **^{19}F ($CDCl_3$, 376 MHz):** δ = -104.62. **HRMS (ESI+)** calculated for $[M+H]^+$: 293.0681 ($C_{12}H_{10}FN_4O_4^+$), found: 293.0678.

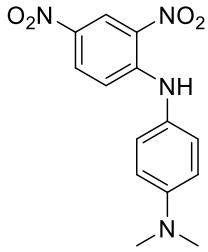
2,4-Dinitro-*N*-phenylaniline (compound 7)



1-Fluoro-2,4-dinitrobenzene (186 mg, 1 mmol, 1 equiv.) was dissolved in 10 mL of acetonitrile and to the solution were added aniline (135 µL, 1.5 mmol, 1.5 equiv.) and *N,N*-diisopropylethylamine (348 µL, 2 mmol, 2 equiv.). The reaction was stirred at room temperature and monitored by TLC, until there were no more traces of starting material (after 2 h). Then, the mixture was evaporated, taken in 50 mL of dichloromethane, washed by 100 mL of water and extracted with another 30 mL of dichloromethane. The combined organic layers were collected, dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated. The residue was purified by a silica gel plug using as eluent dichloromethane/petroleum ether (8:2) to afford **7** as an orange solid (88% yield, 150 mg, 0.88 mmol).

R_f: 0.8 (SiO_2, dichloromethane/petroleum ether, 8:2). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 9.98 (br s, 1H, NH), 9.18 (s, 1H, CH), 8.18 (dd, ^3J = 9.51 Hz, ^4J = 2.14 Hz, 1H, CH), 7.41 (m, 1H, CH), 7.32 (d, ^3J = 8 Hz, 2H, CH), 7.18 (d, ^3J = 9.3 Hz, 1H, CH). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ = 147.2 (C), 137.5 (C), 136.8 (C), 131.2 (C), 130.3 (CH), 130.0 (CH), 127.8 (CH), 125.6 (CH), 124.2 (CH), 116.1 (CH). **HRMS (ESI+)** calculated for $[M+H]^+$: 260.0666 ($C_{12}H_{10}N_3O_4^+$), found: 260.0666.

N^1-(2,4-Dinitrophenyl)-*N*^{4},*N*^{4}-dimethylbenzene-1,4-diamine (compound 8)



1-Fluoro-2,4-dinitrobenzene (186 mg, 1 mmol, 1 equiv.) was dissolved in a mixture of 10 mL acetonitrile and 3 mL dichloromethane and to the solution were added *N*,*N*-dimethyl-*p*-phenylenediamine dihydrochloride (209 mg, 1 mmol, 1 equiv.) and *N,N*-diisopropylethylamine (870 µL, 5 mmol, 5 equiv.). The reaction was stirred at room temperature and monitored by TLC, until there were no more traces of starting material (after 2 h). Then, the mixture was evaporated, taken in 100 mL of dichloromethane, washed by 100 mL of water and extracted with another 30 mL of dichloromethane. The combined organic layers were collected, dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated. The residue was purified by silica gel chromatography using as eluent dichloromethane/petroleum ether (8:2) to afford **8** as a brown solid (97% yield, 295 mg, 0.97 mmol).

R_f: 0.6 (SiO_2, dichloromethane/petroleum ether, 8:2). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 9.86 (br s, 1H, NH), 9.12 (d, ^4J = 2.47 Hz, 1H, CH), 8.10 (dd, ^3J = 9.56 Hz, ^4J = 2.46 Hz, 1H, CH), 7.13 (d, ^3J = 8.6 Hz, 2H, CH), 7.04 (d, ^3J = 9.4 Hz, 1H, CH), 6.77 (d, ^3J = 8.9 Hz, 2H, CH), 3.01 (s, 6H, CH_3). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ = 149.9 (C), 148.4 (C), 136.6 (C), 130.4 (C), 129.7 (CH), 127.0 (CH), 124.8 (C), 124.2 (CH), 116.3 (CH), 113.0 (CH), 40.5 (CH_3). **HRMS (ESI+)** calculated for $[M+H]^+$: 303.1088 ($C_{14}H_{15}N_4O_4^+$), found: 303.1088.

2. NMR SPECTRA

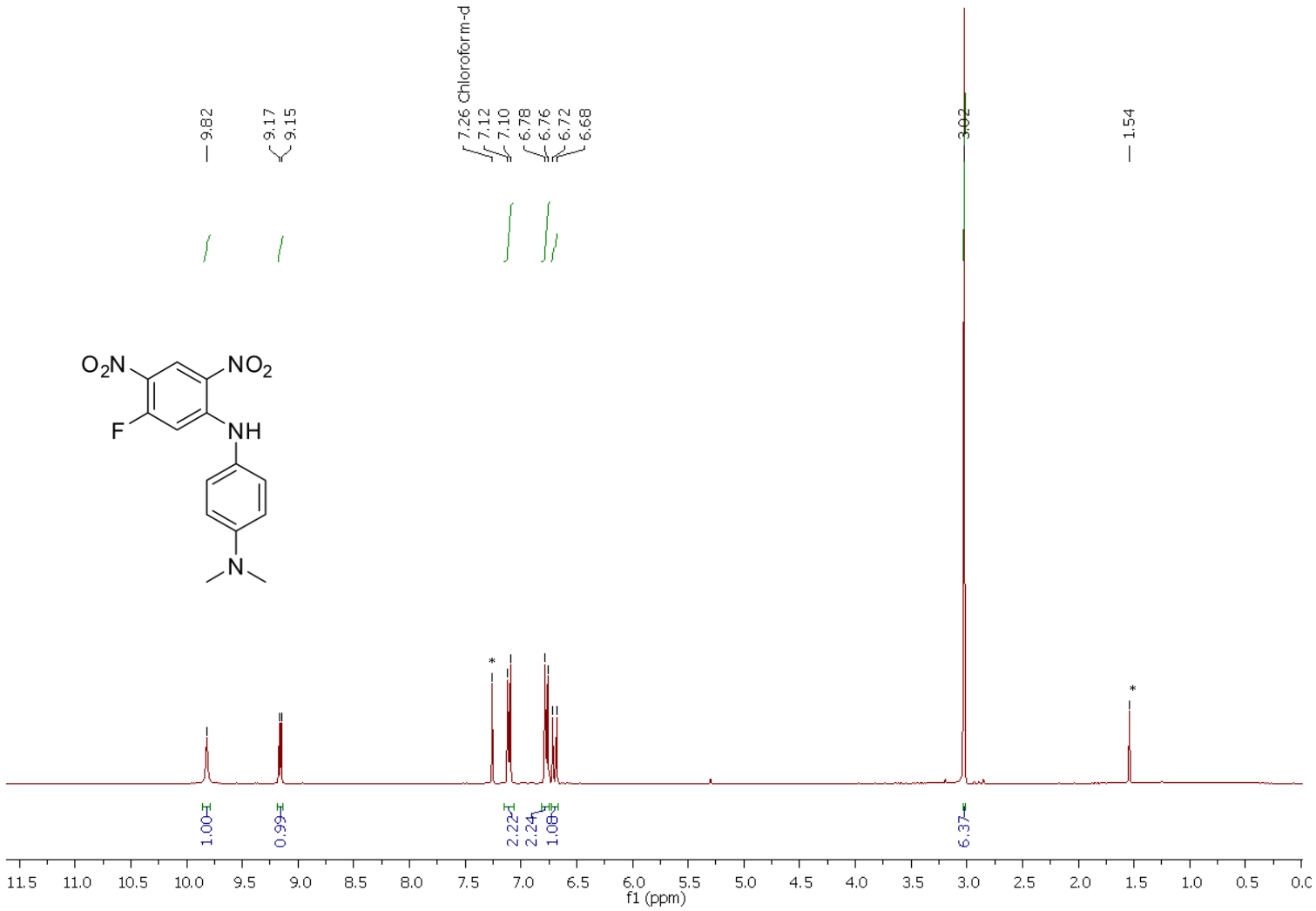


Figure S 1. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) of compound **3**. Asterisks indicate the residual solvent peaks.

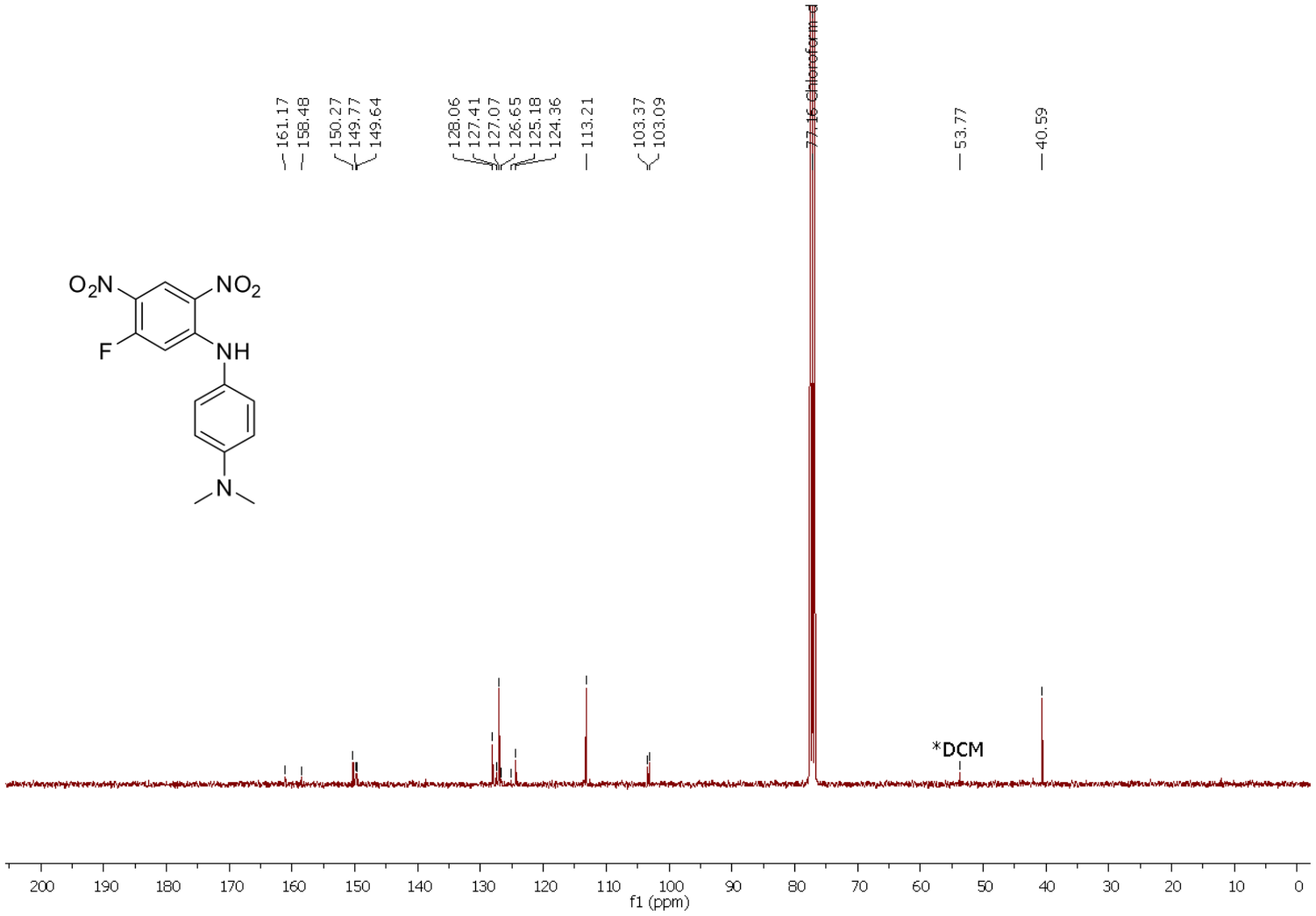


Figure S 2. ^{13}C NMR (101 MHz, 298 K, $CDCl_3$) of compound **3**. Asterisks indicate the residual solvent peaks.

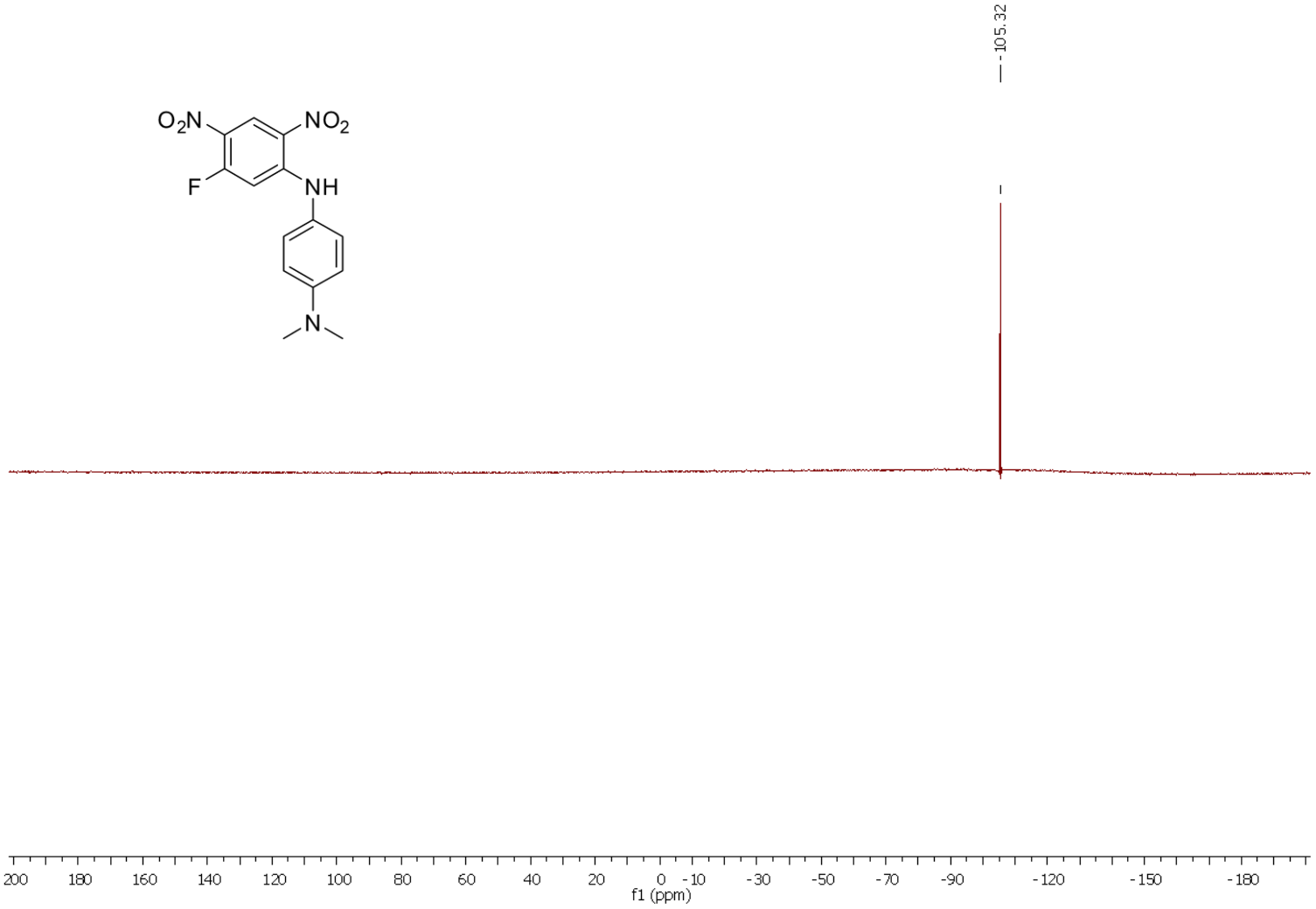


Figure S 3. ^{19}F NMR (376 MHz, 298 K, $CDCl_3$) of compound **3**.

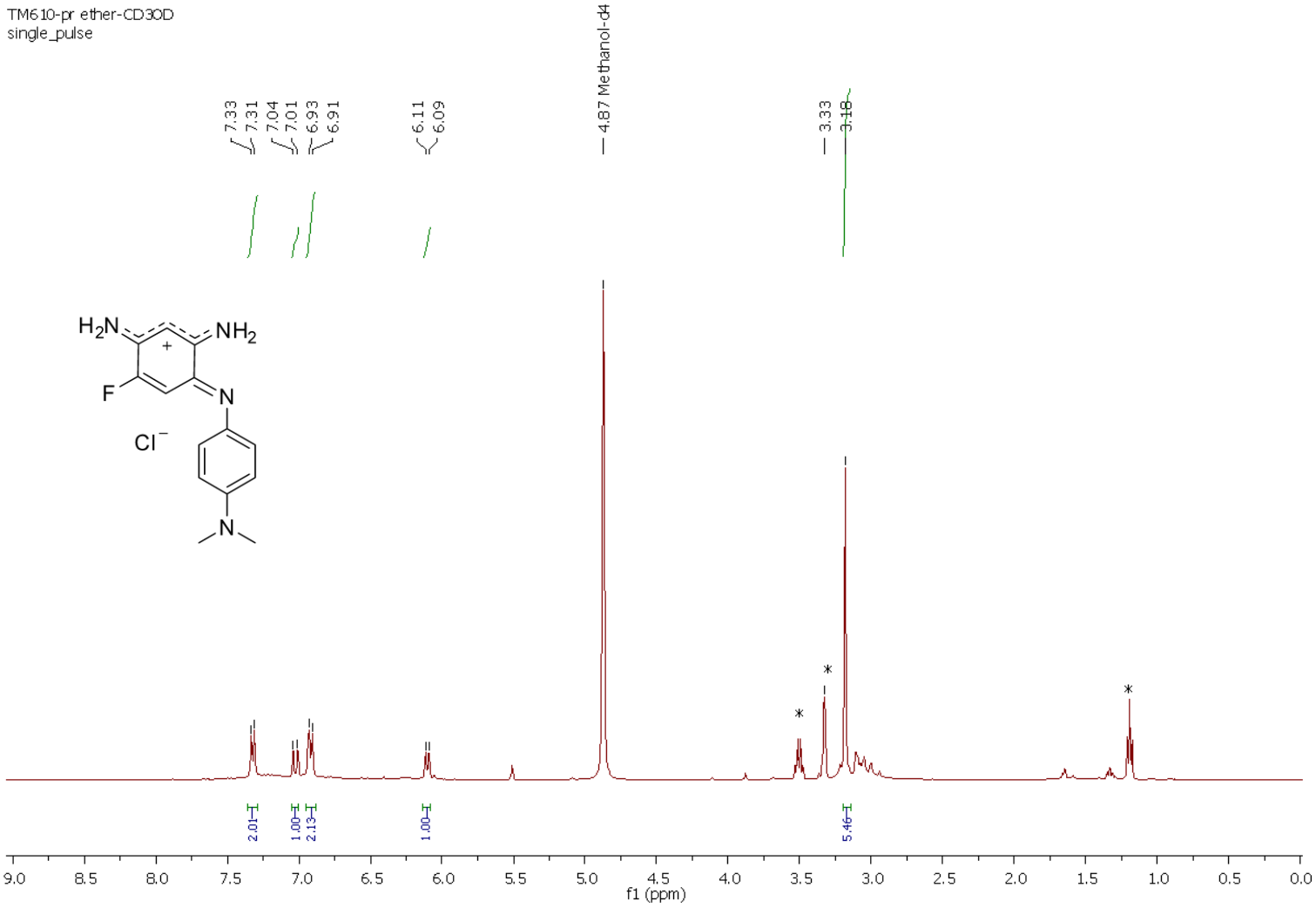


Figure S 4. ^{1}H NMR (400 MHz, 298 K, CD_3OD) of compound **1•H$^+$**. Asterisks indicate the residual solvent peaks.

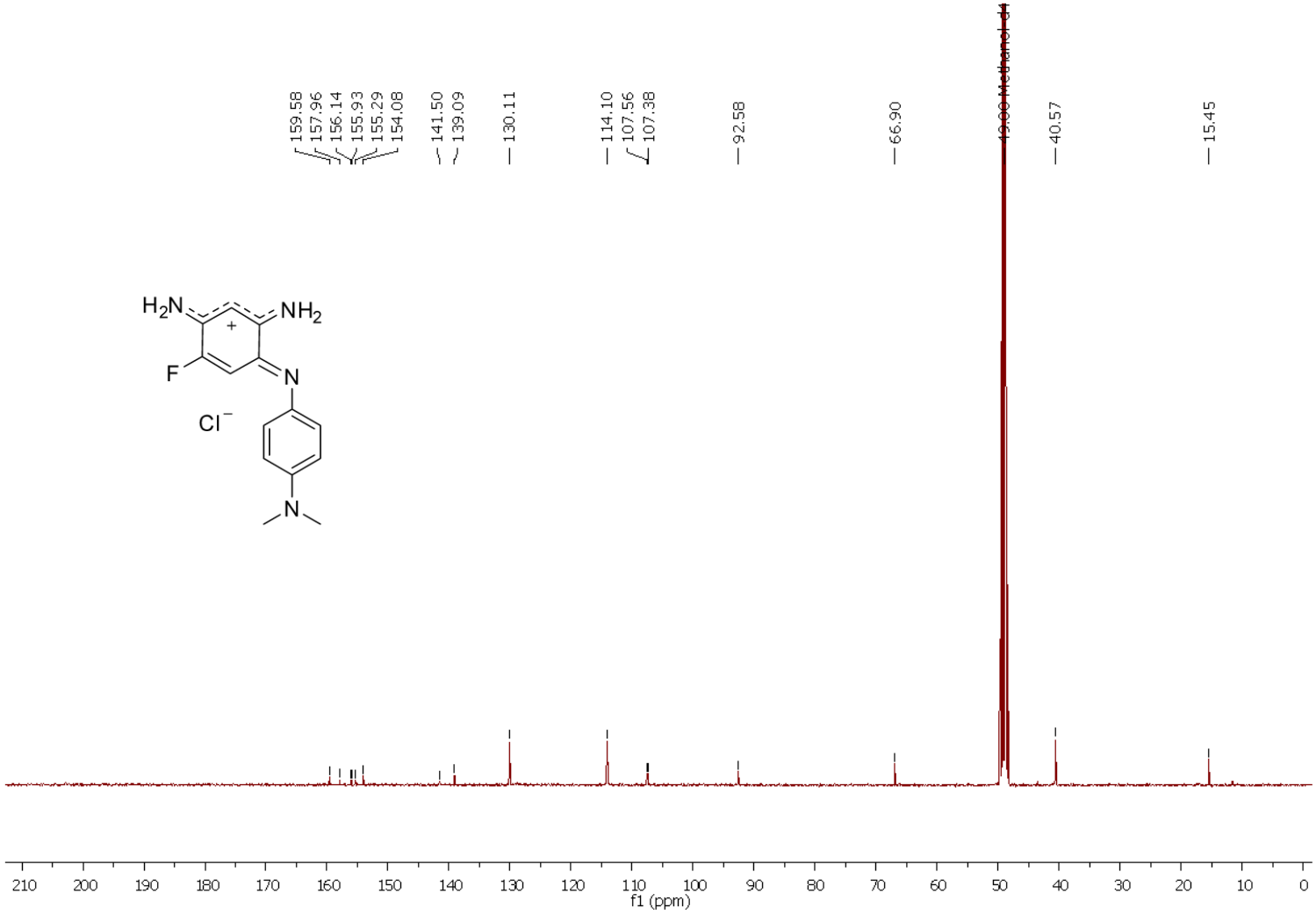


Figure S 5. ^{13}C NMR (101 MHz, 298 K, CD_3OD) of compound **1•H⁺**. Asterisks indicate the residual solvent peaks.

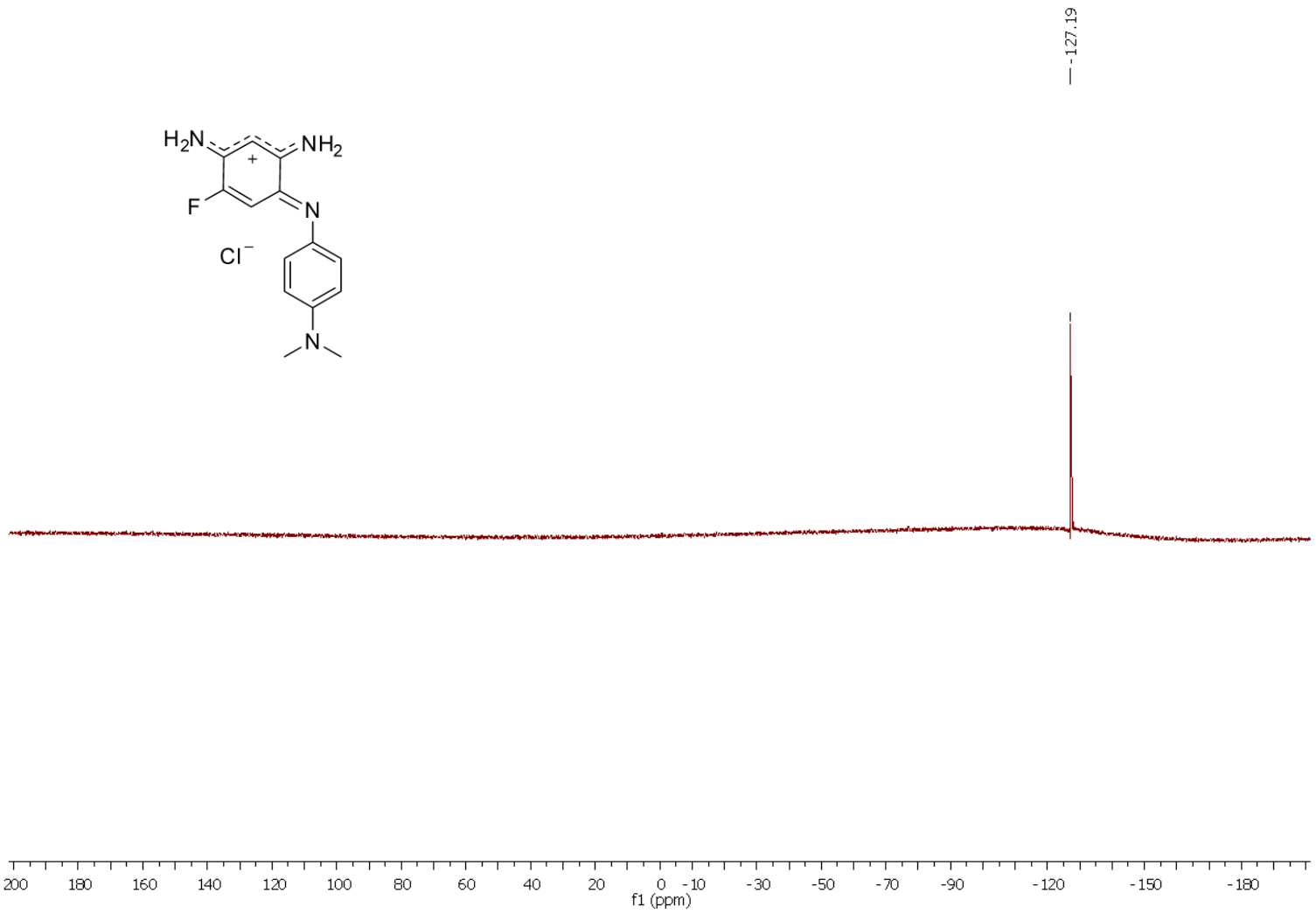


Figure S 6. ^{19}F NMR (376 MHz, 298 K, CD_3OD) of compound **1•H$^+$**.

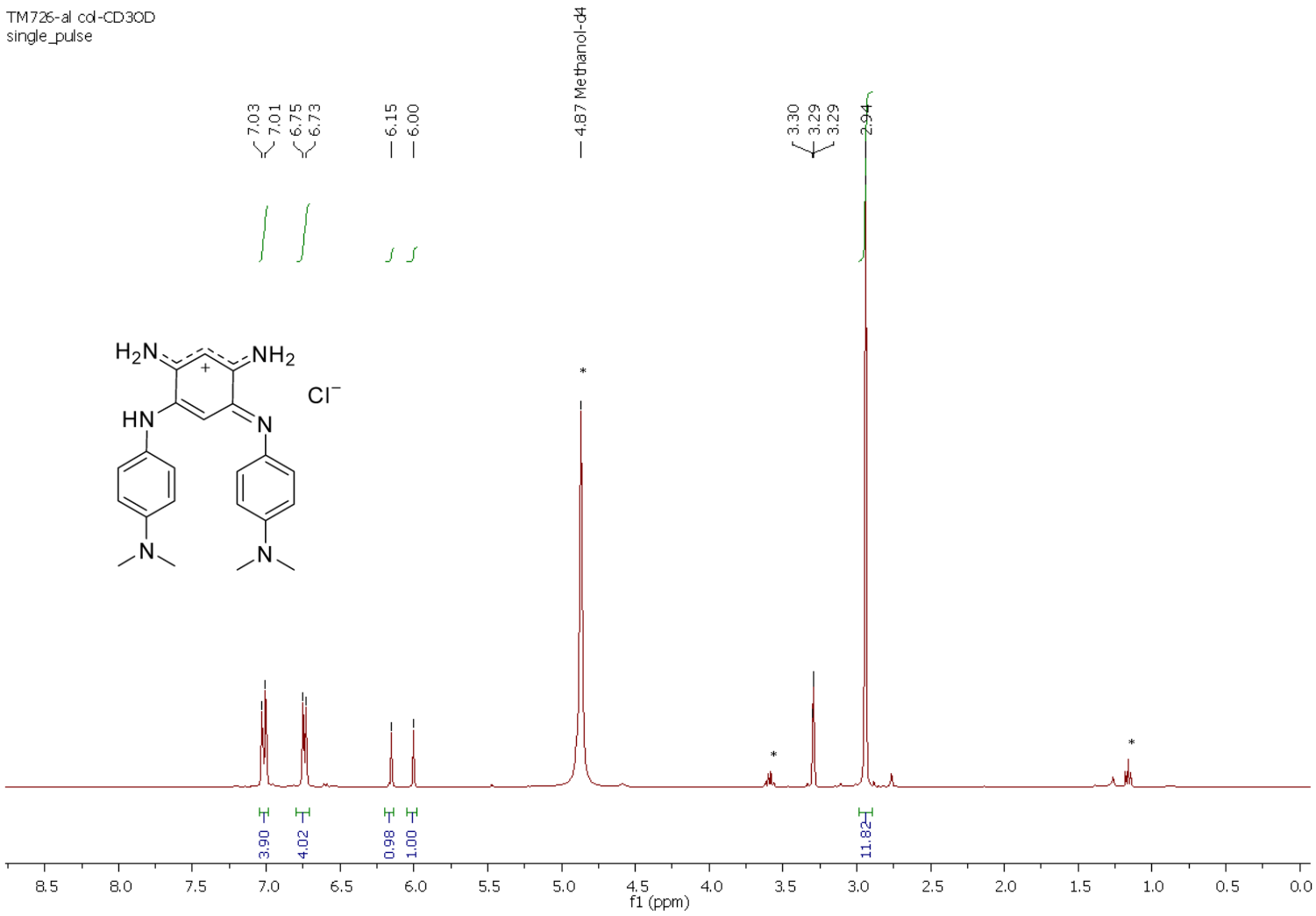


Figure S 7. ^{1}H NMR (400 MHz, 298 K, CD_3OD) of compound **2•H$^+$**. Asterisks indicate the residual solvent peaks.

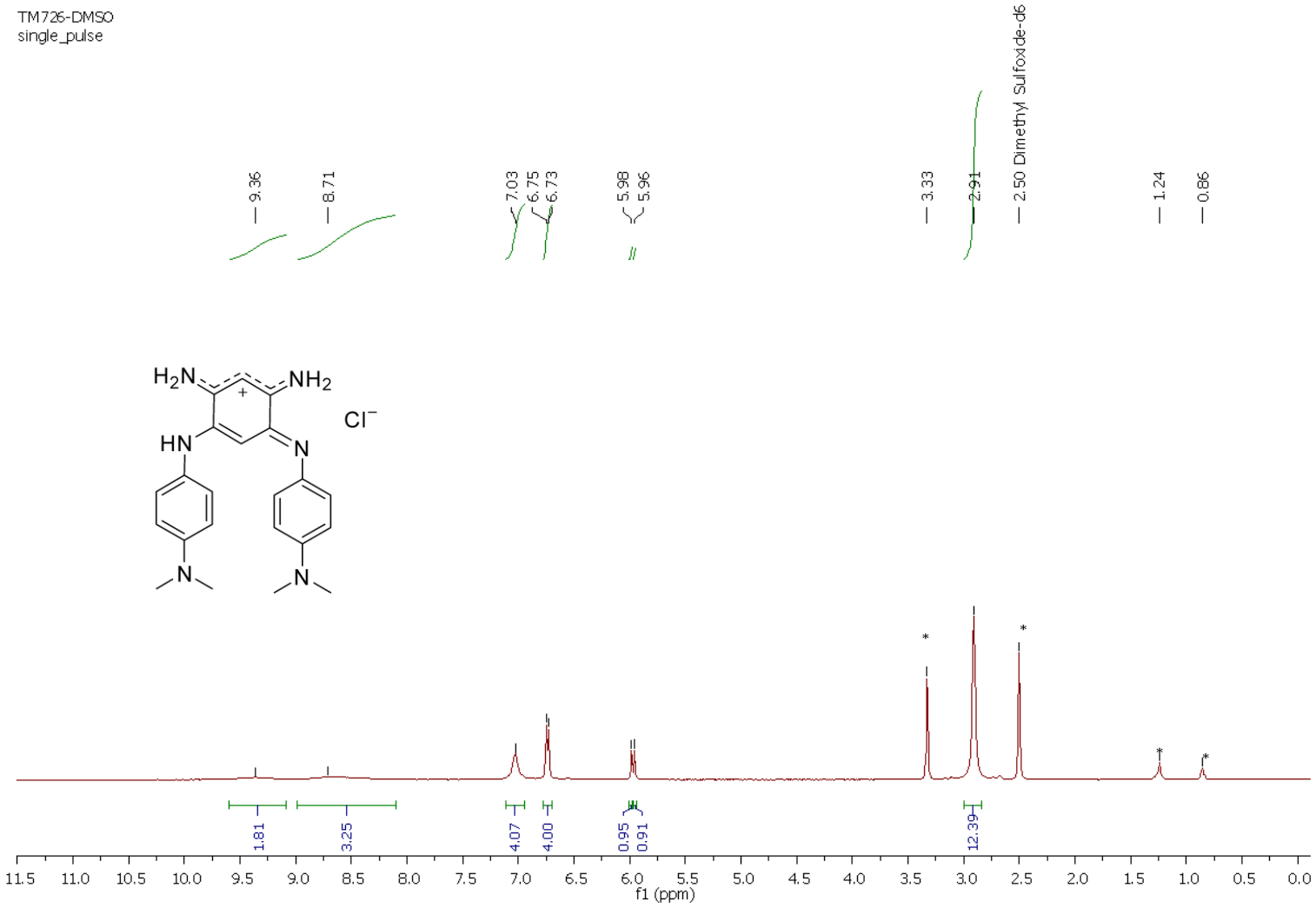


Figure S 8. ^{1}H NMR (400 MHz, 298 K, DMSO-d_6) of compound **2•H$^+$**. Asterisks indicate the residual solvent peaks.

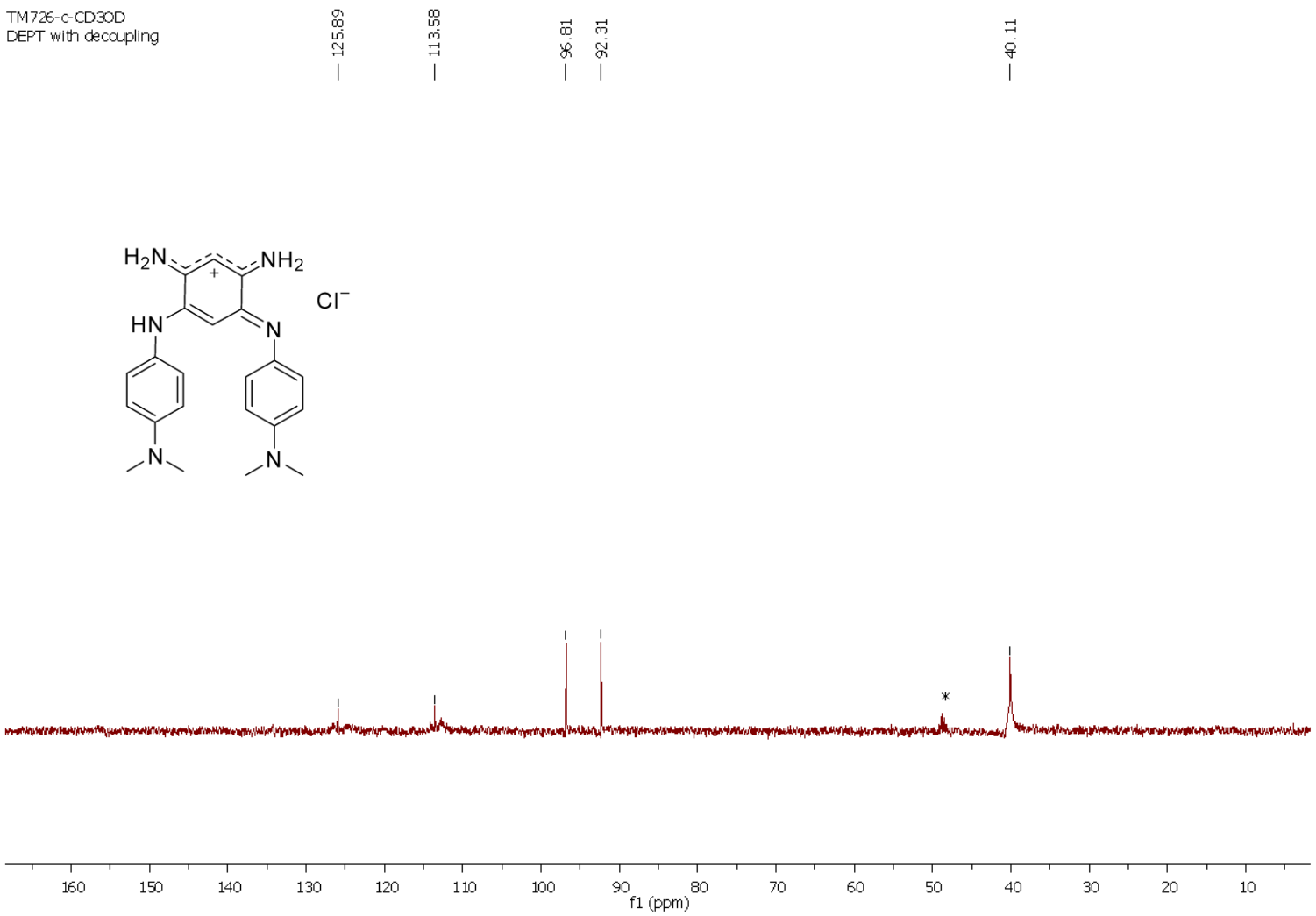


Figure S 9. ^{13}C NMR (101 MHz, 298 K, CD_3OD, DEPT135) of compound **2•H$^+$**. Asterisk indicates the residual solvent peaks.

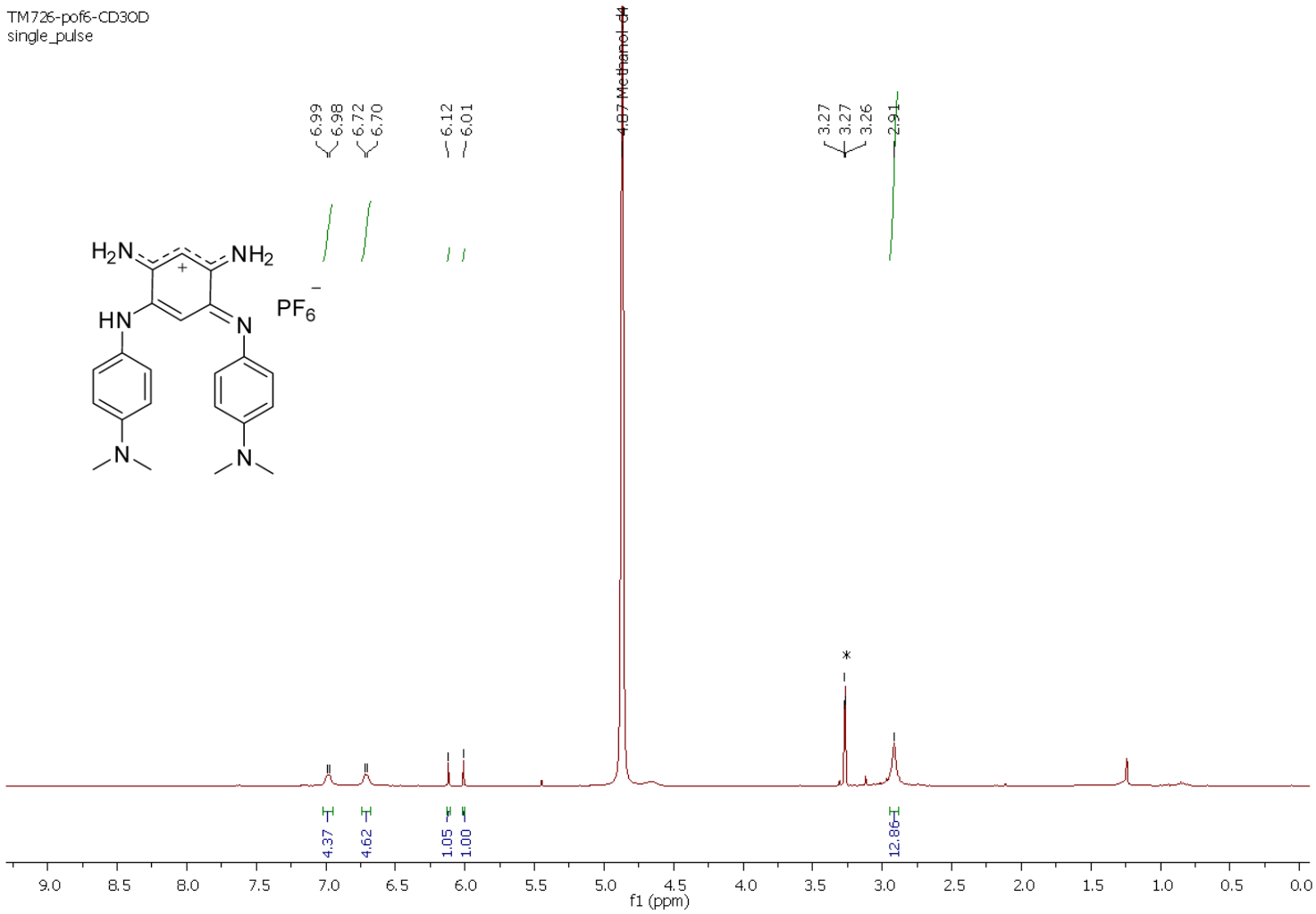


Figure S 10. ^{1}H NMR (400 MHz, 298 K, CD_3OD) of compound **2•H$^+$ PF$_6^-$**. Asterisks indicate the residual solvent peaks.

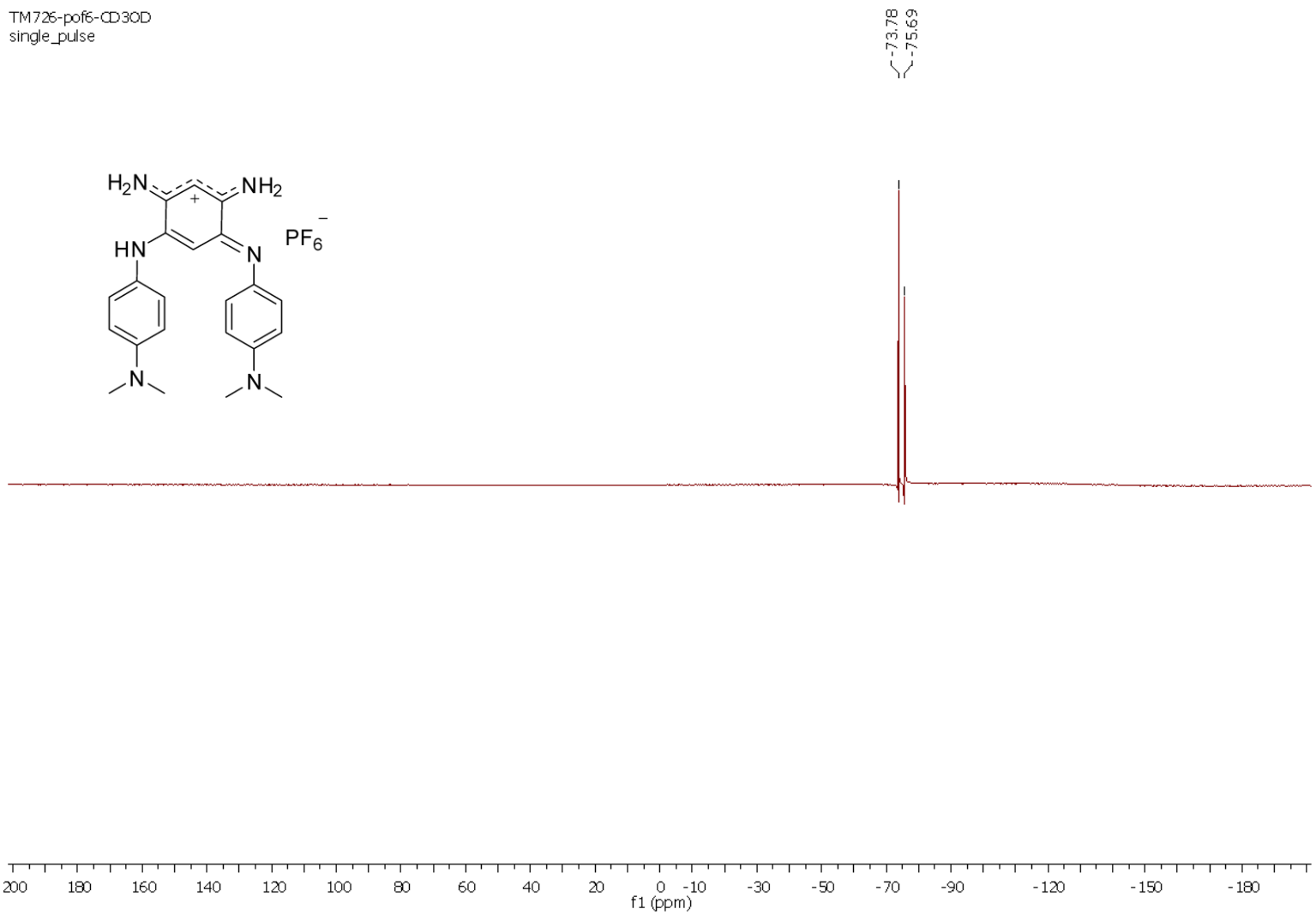


Figure S 11. ^{19}F NMR (376 MHz, 298 K, CD_3OD) of compound **2•H$^+$ PF$_6^-$**.

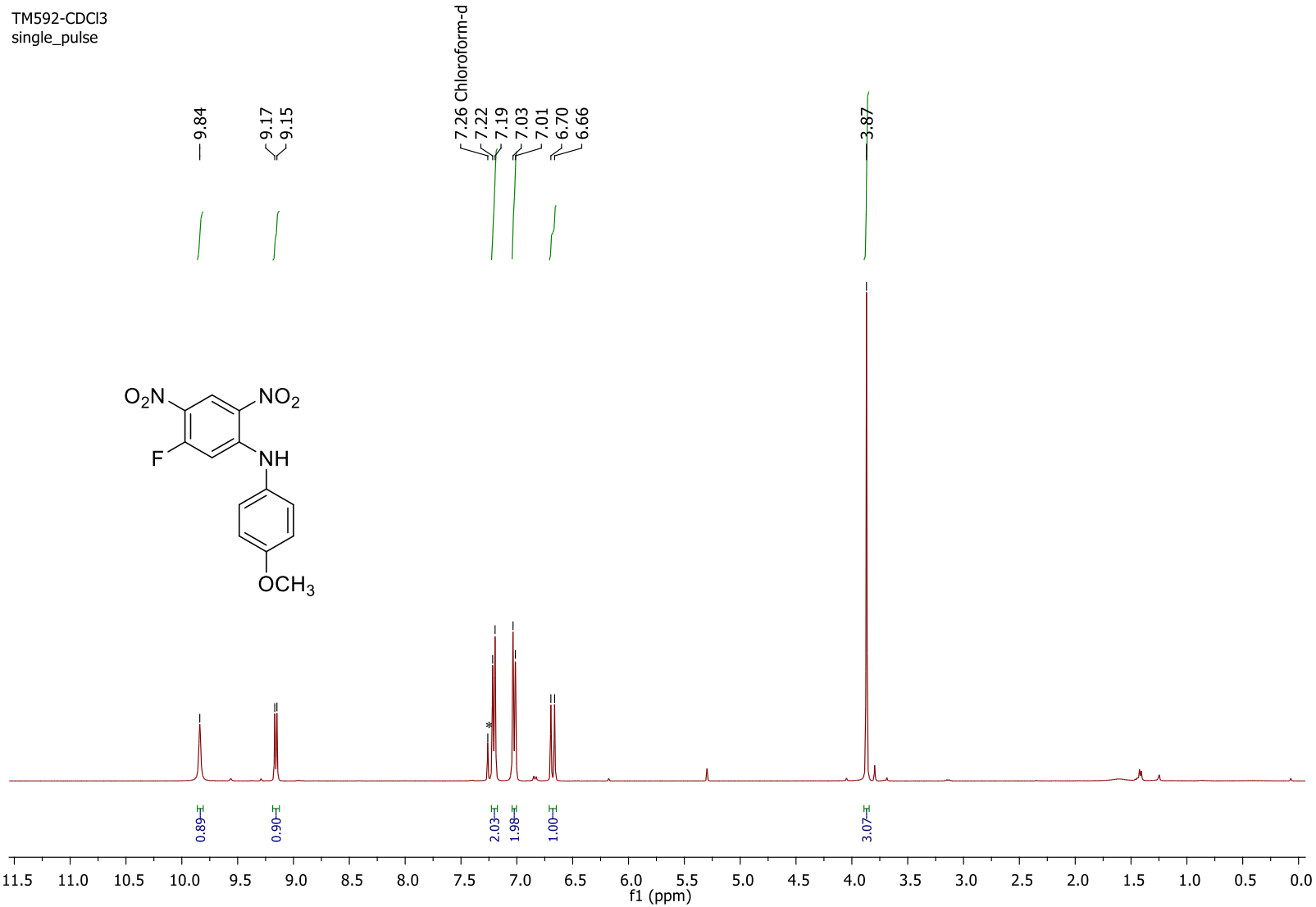


Figure S 12. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) of compound **5**. Asterisks indicate the residual solvent peaks.

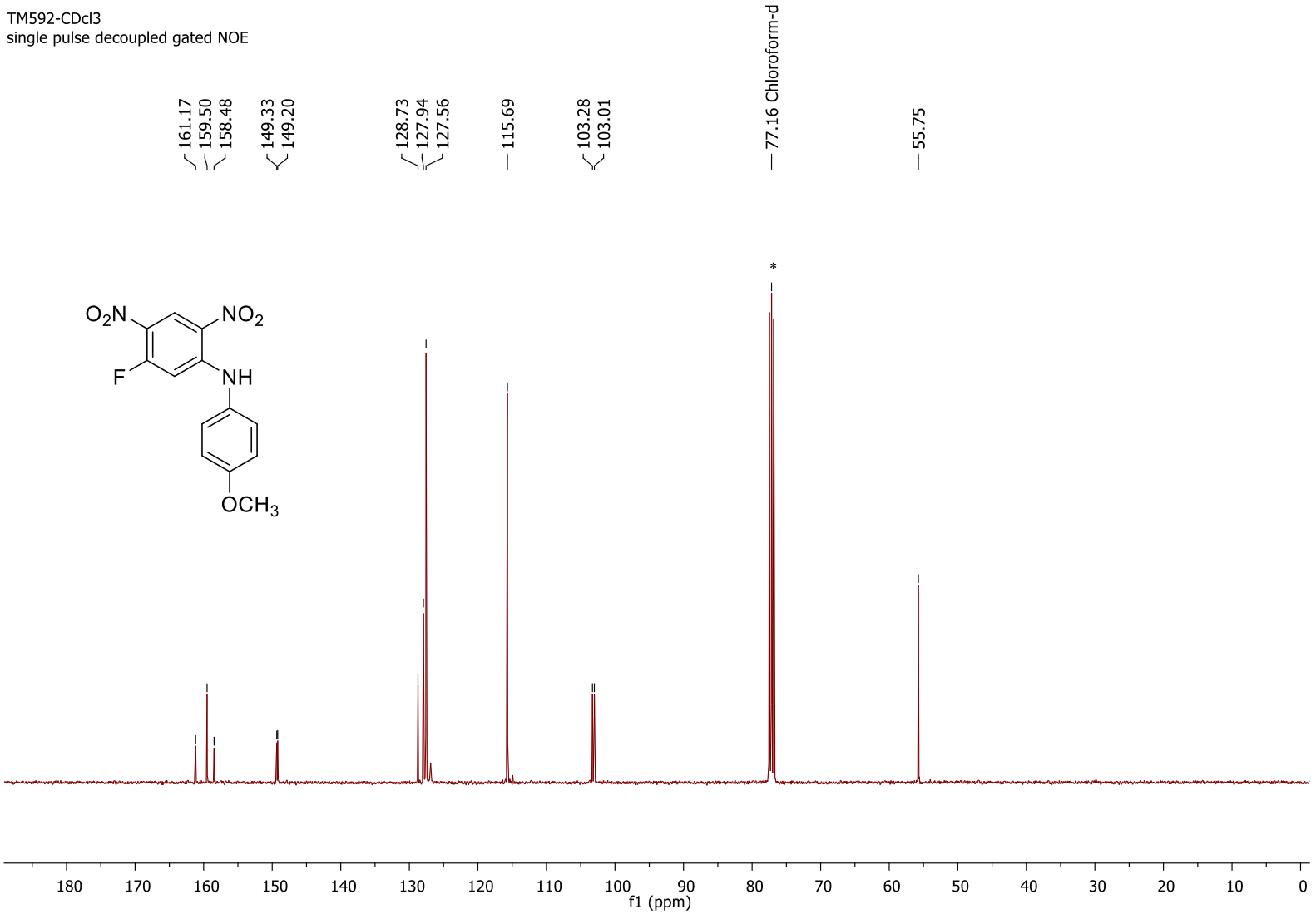


Figure S 13. ^{13}C NMR (101 MHz, 298 K, $CDCl_3$) of compound **5**. Asterisks indicate the residual solvent peaks.

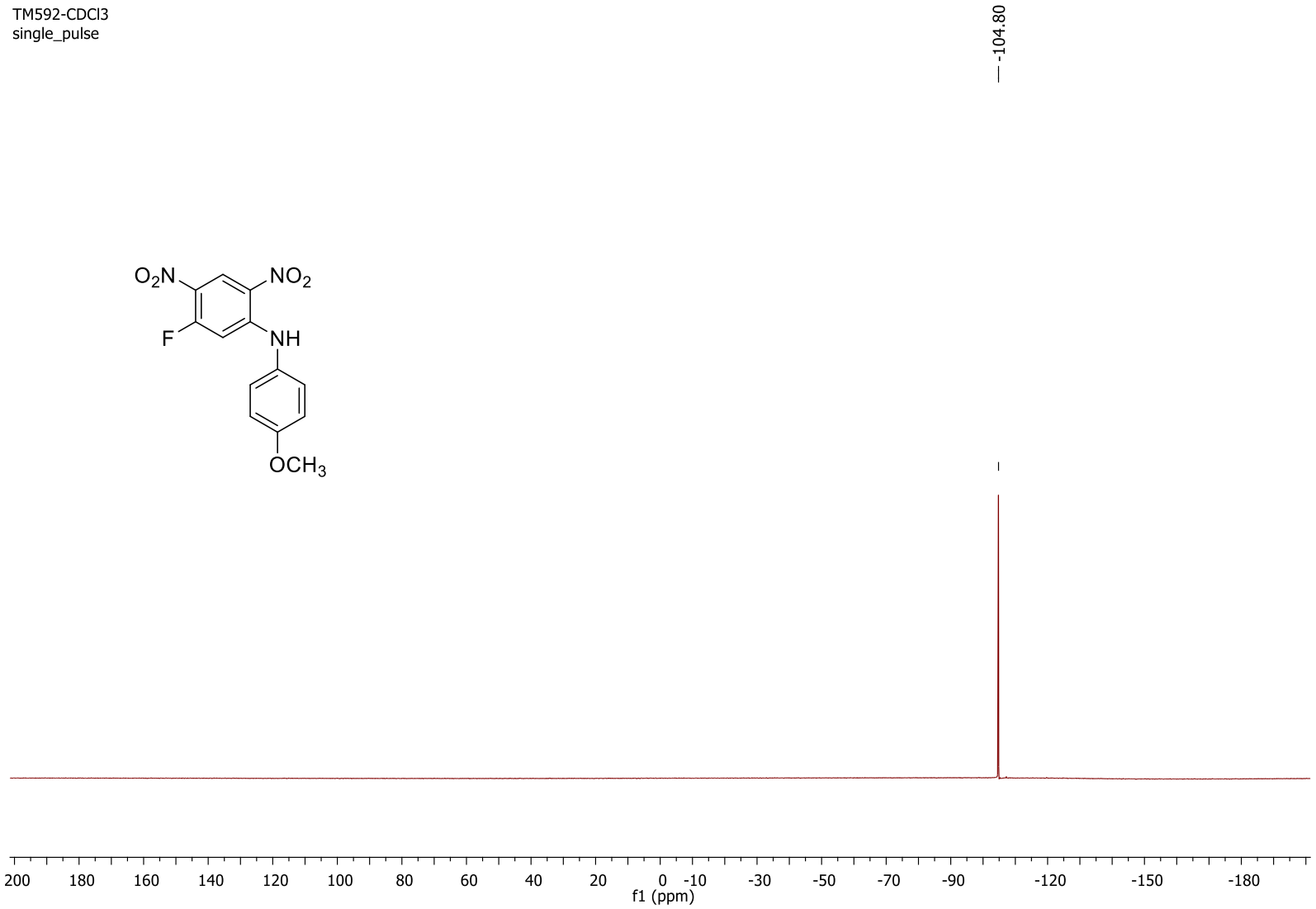


Figure S 14. ^{19}F NMR (376 MHz, 298 K, $CDCl_3$) of compound **5**.

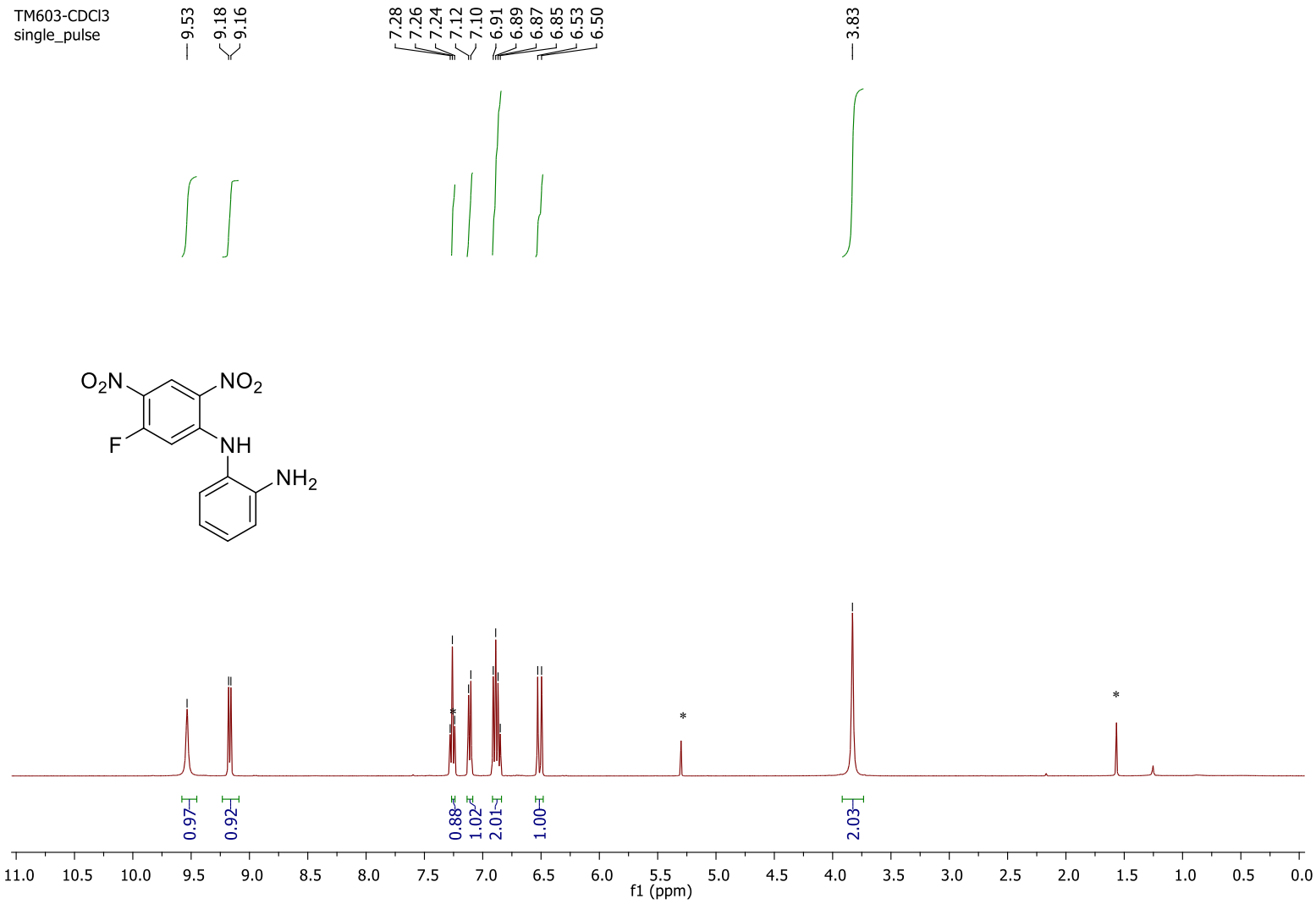


Figure S 15. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) of compound **6**. Asterisks indicate the residual solvent peaks.

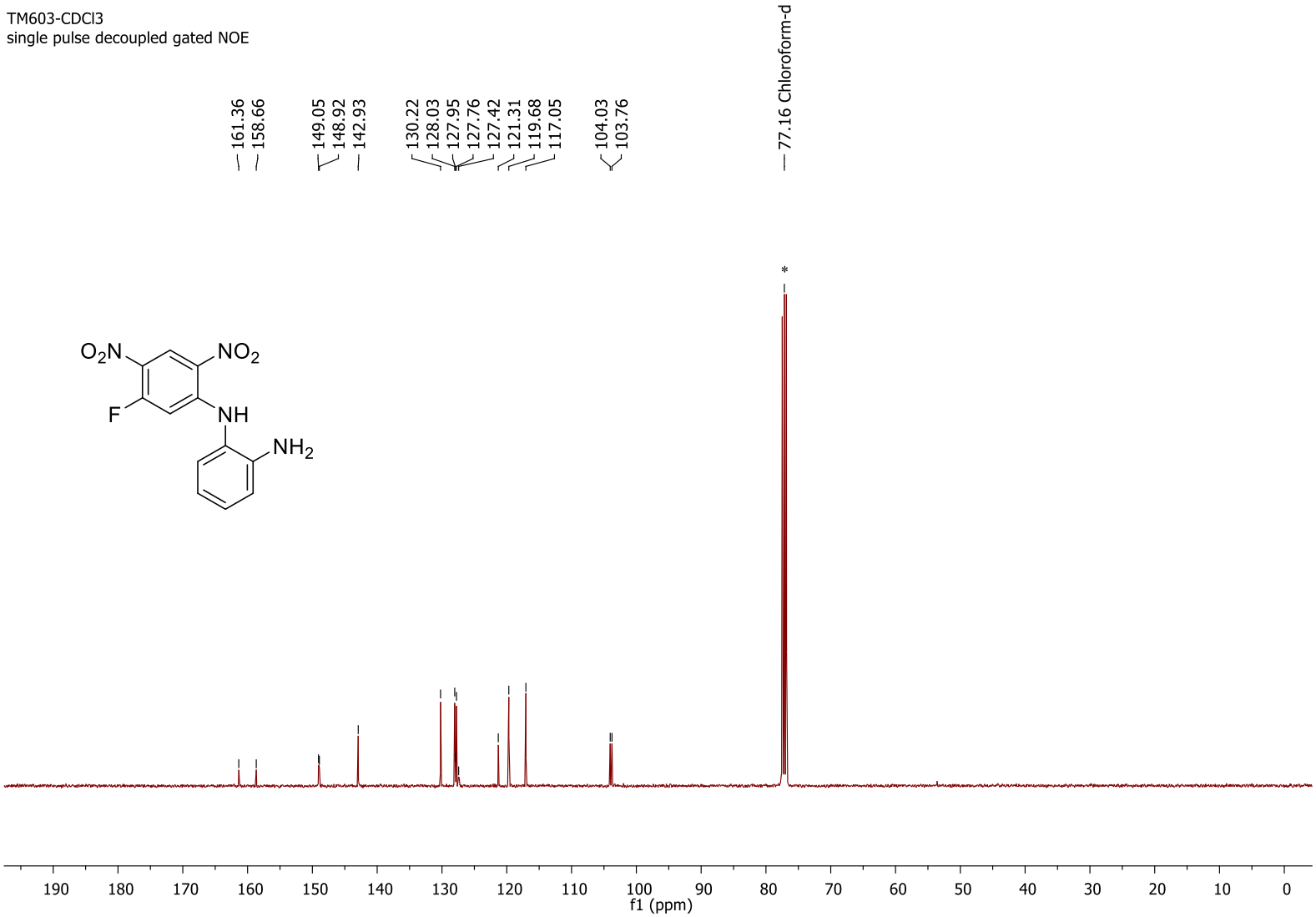


Figure S 16. ^{13}C NMR (101 MHz, 298 K, $CDCl_3$) of compound **6**. Asterisks indicate the residual solvent peaks.

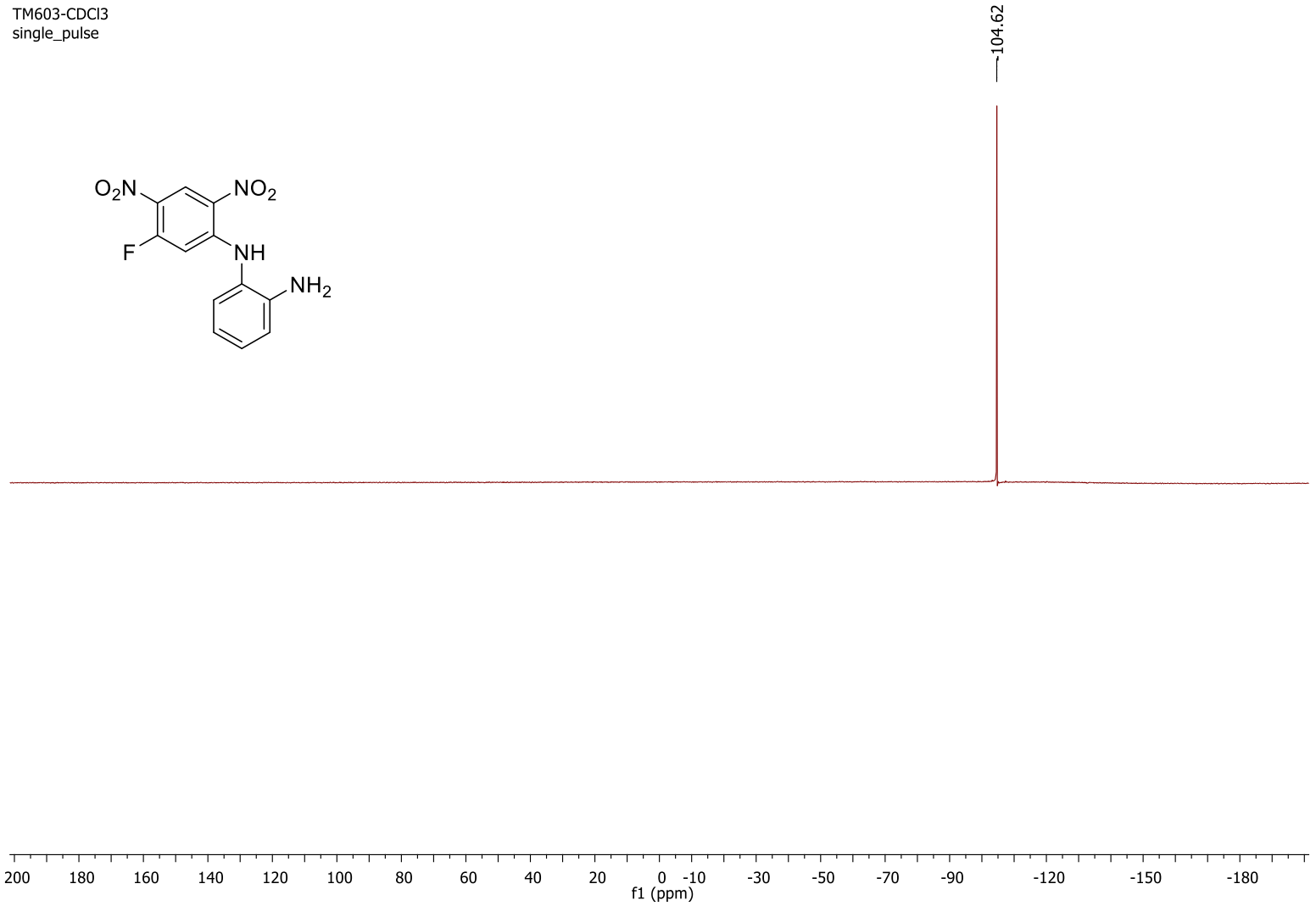


Figure S 17. ^{19}F NMR (376 MHz, 298 K, $CDCl_3$) of compound **6**.

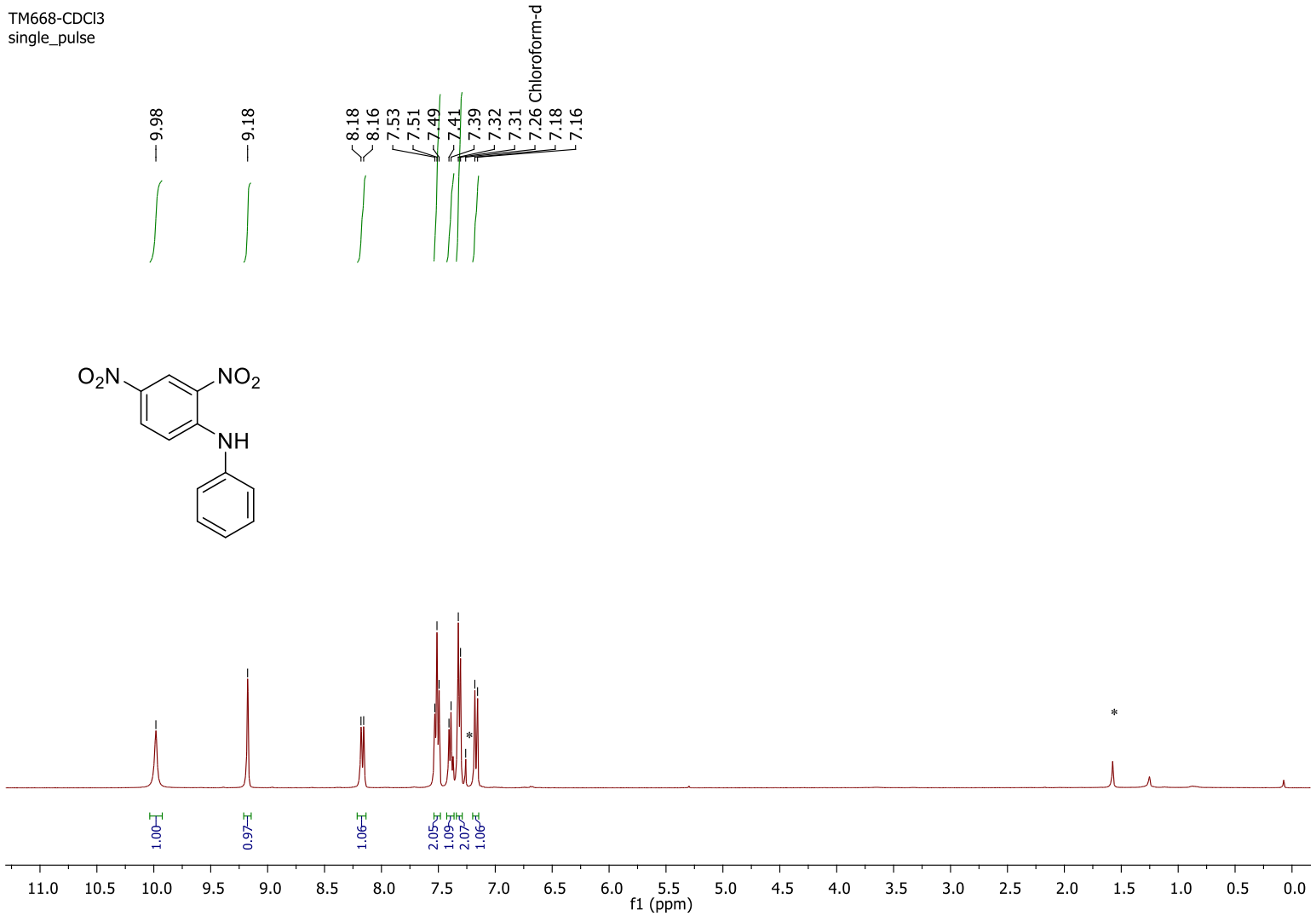


Figure S 18. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) of compound **7**. Asterisks indicate the residual solvent peaks.

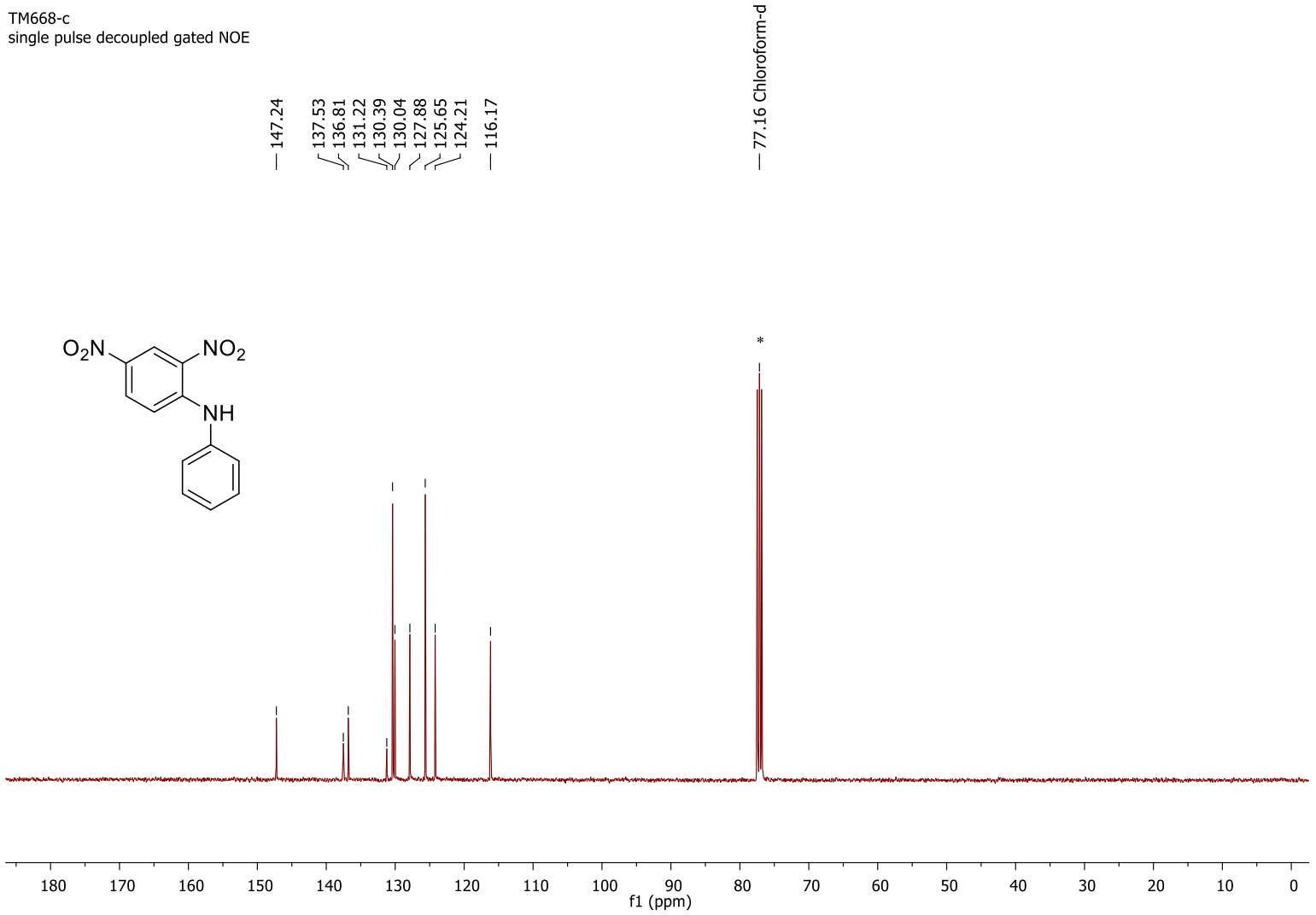


Figure S 19. ^{13}C NMR (101 MHz, 298 K, $CDCl_3$) of compound **7**. Asterisks indicate the residual solvent peaks.

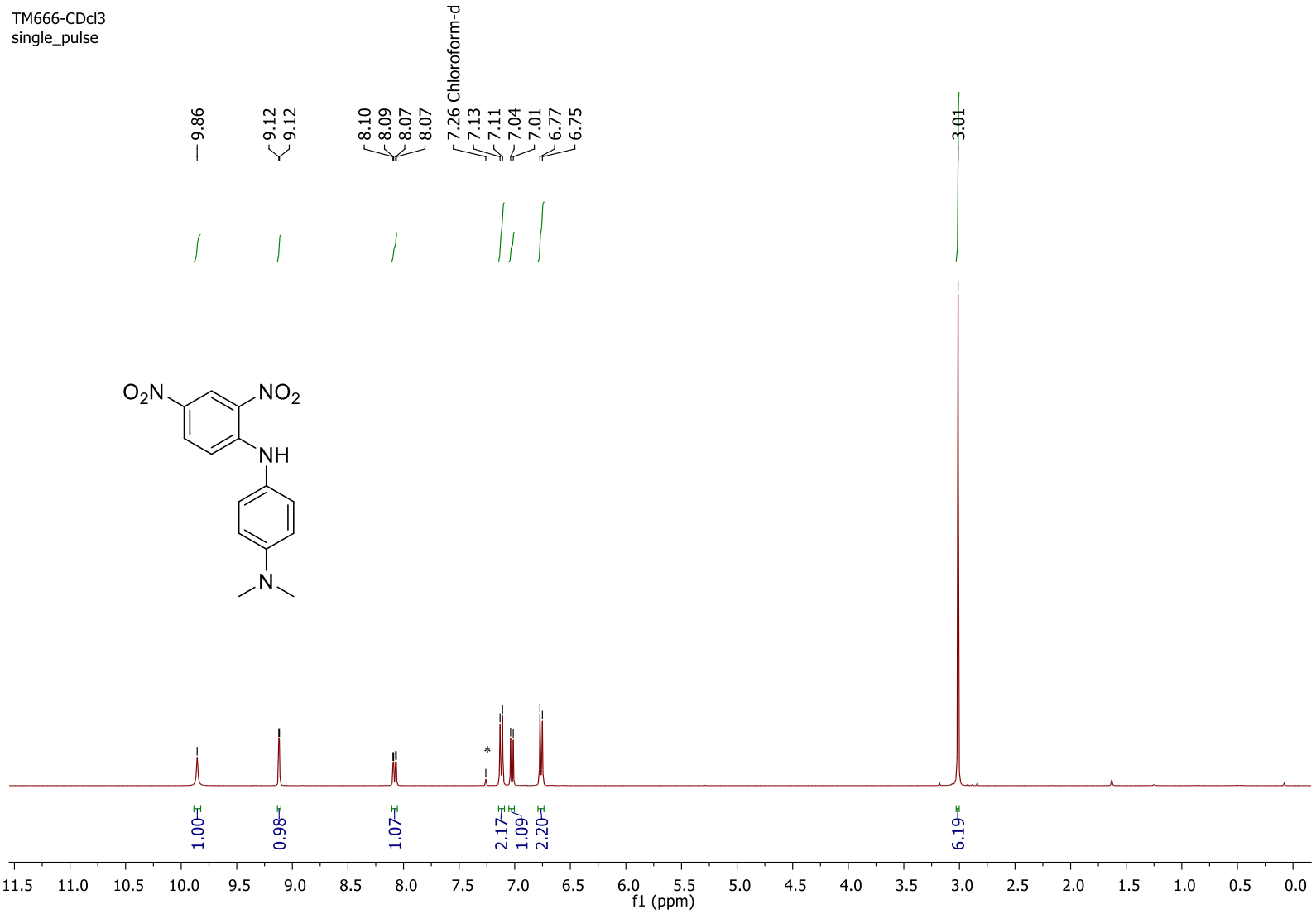


Figure S 20. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) of compound **8**. Asterisks indicate the residual solvent peaks.

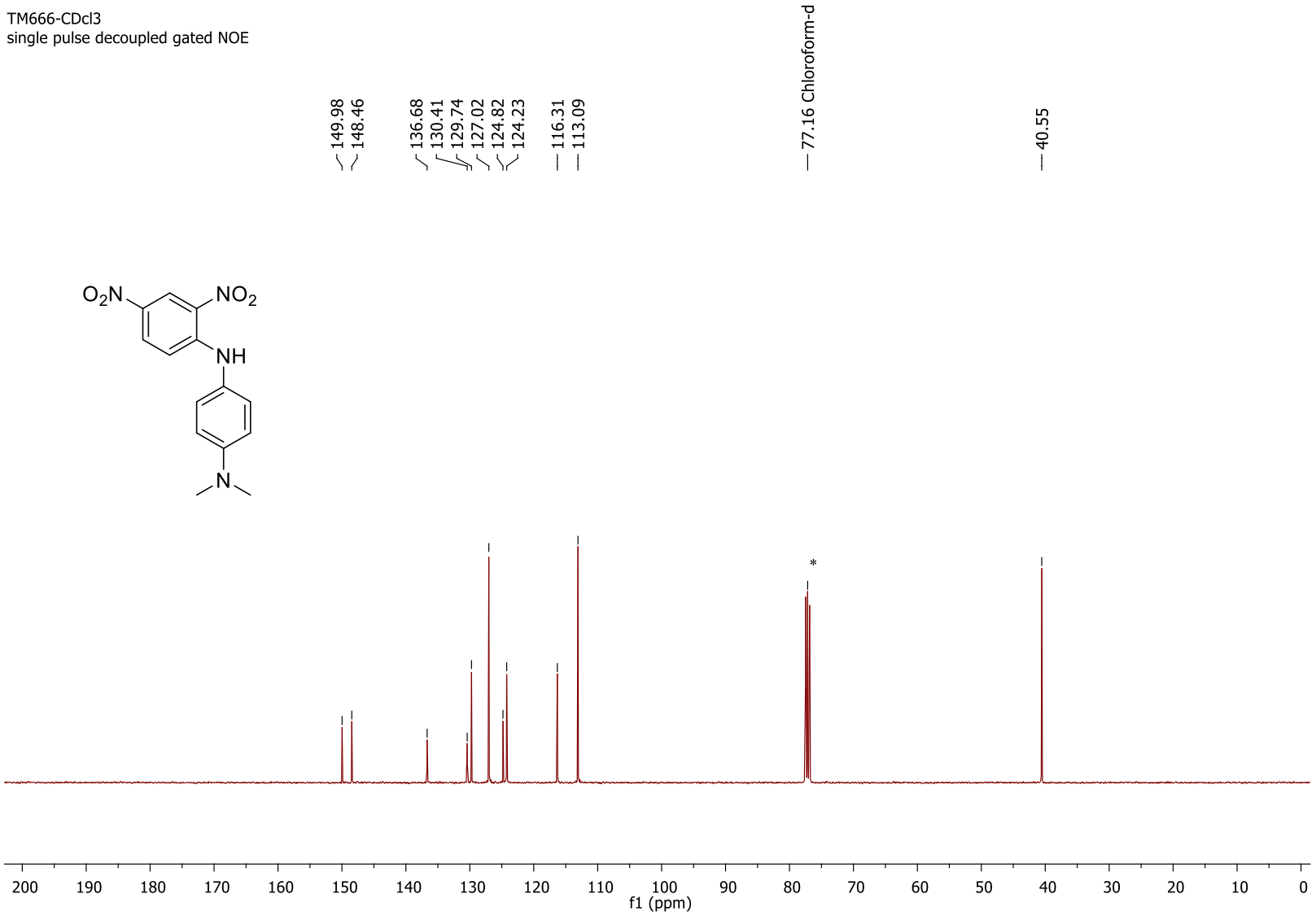


Figure S 21. ^{13}C NMR (101 MHz, 298 K, $CDCl_3$) of compound **8**. Asterisks indicate the residual solvent peaks.

3. HRMS SPECTRA

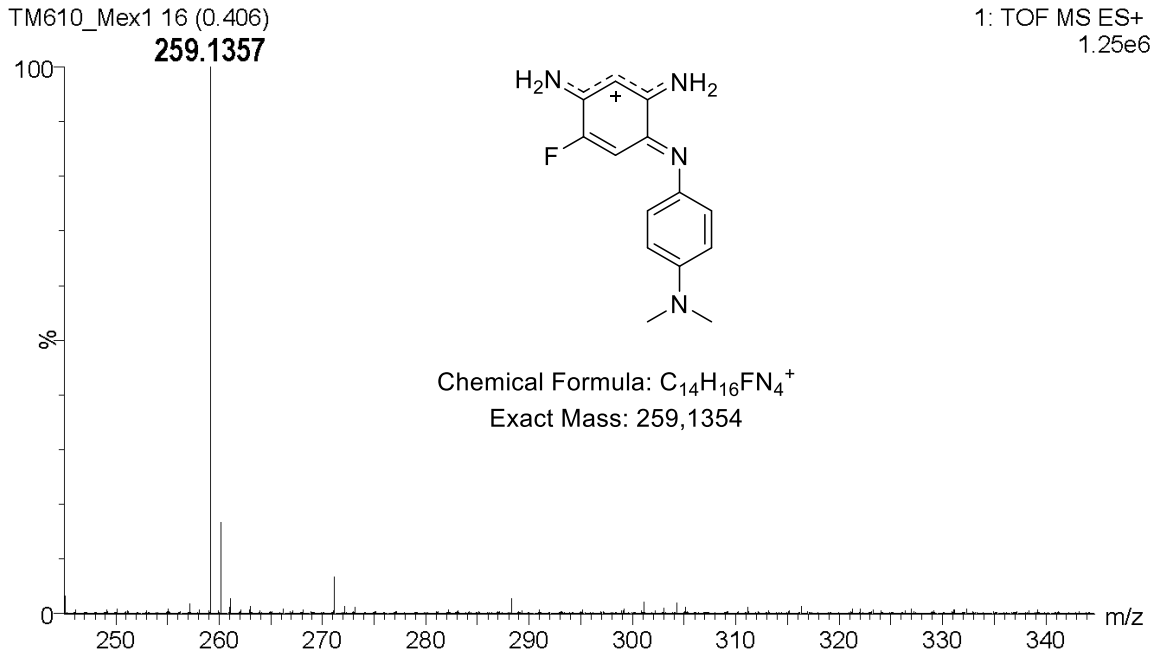


Figure S 22. HRMS (ES+) of compound **1•H⁺**.

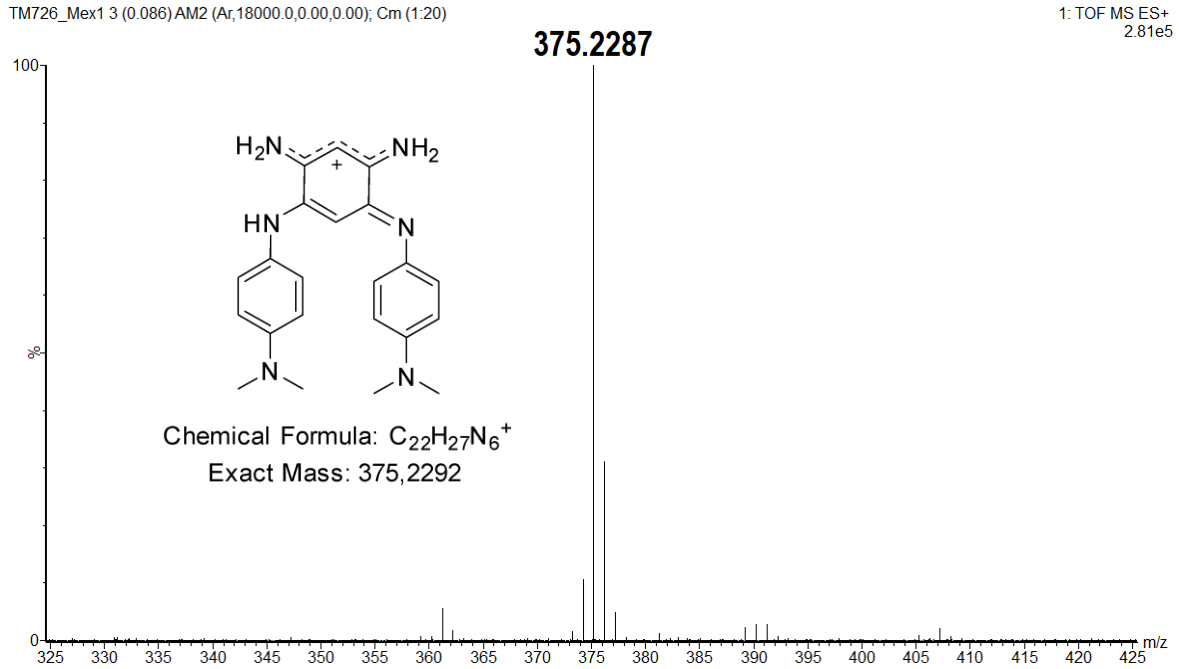


Figure S 23. HRMS (ES+) of compound **2•H⁺**.

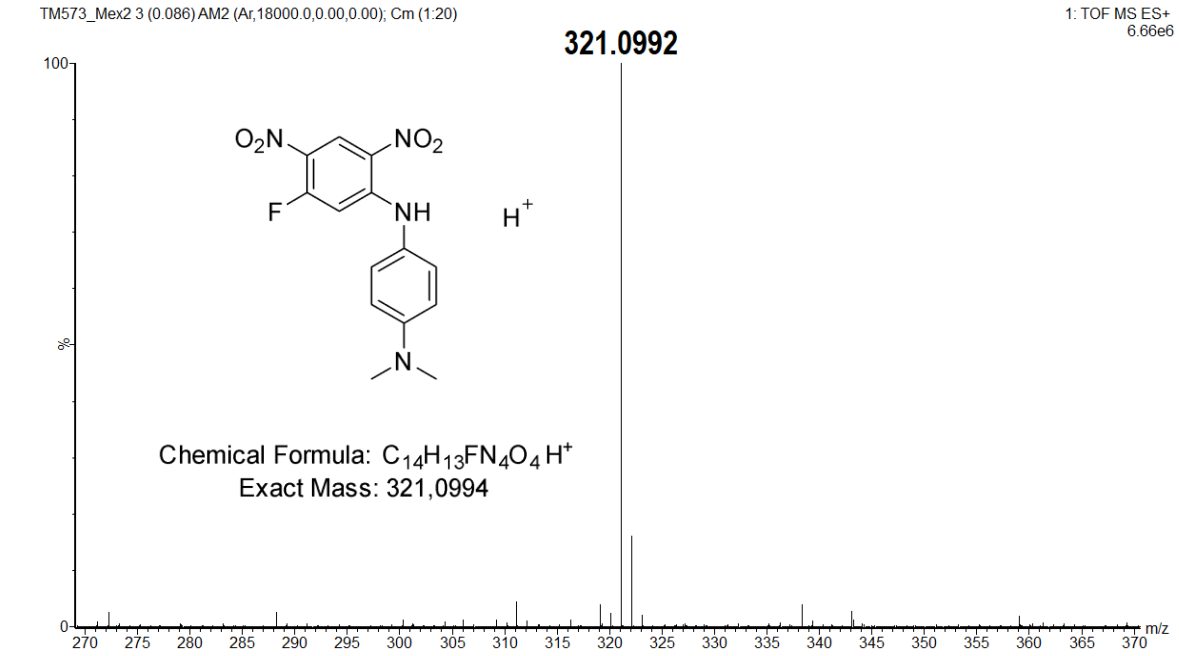


Figure S 24. HRMS (ES+) of compound **3**.

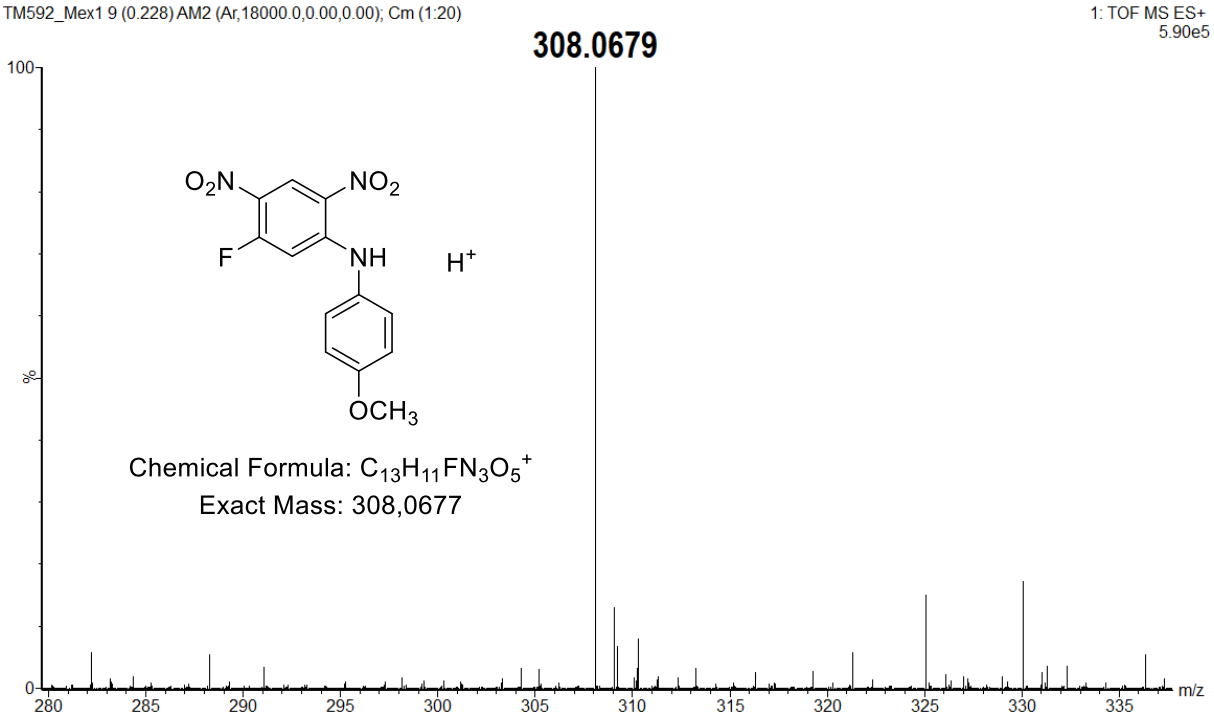


Figure S 25. HRMS (ES+) of compound **5**. The peaks at m/z = 325 and m/z = 315 were attributed to the ammonium and respectively sodium adduct of compound **5**.

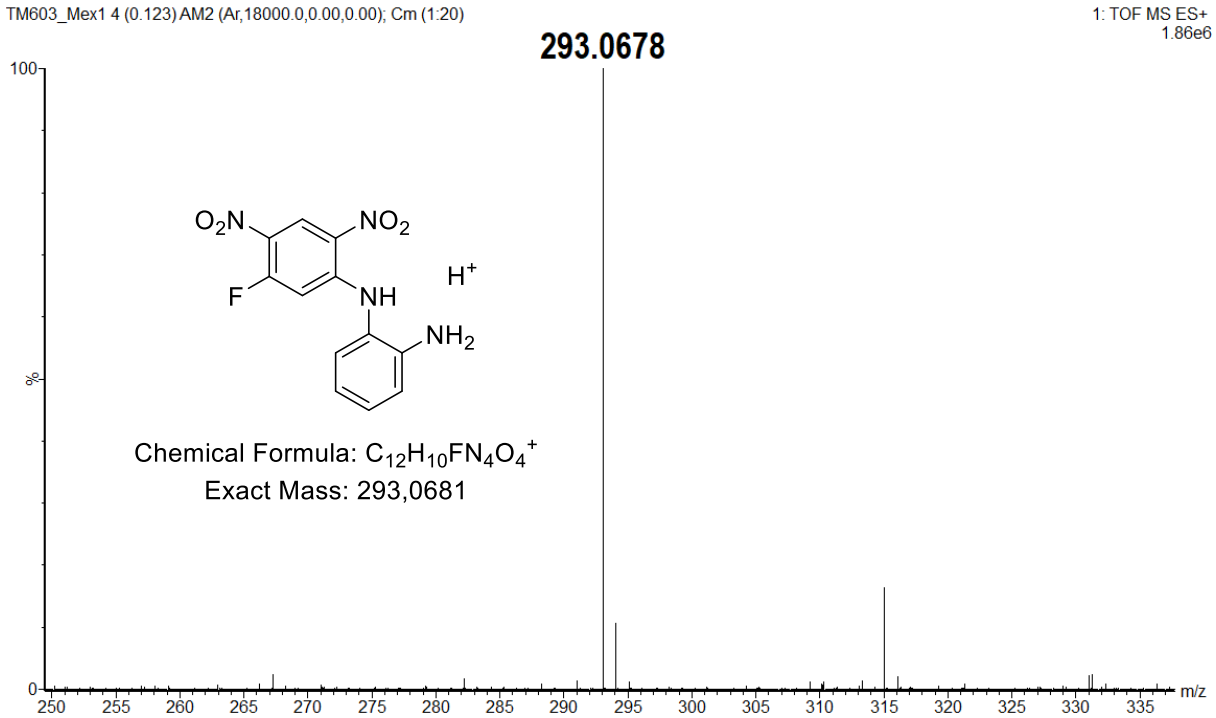


Figure S 26. HRMS (ES+) of compound **6**. The peak at m/z = 315 was attributed to the sodium adduct of compound **6**.

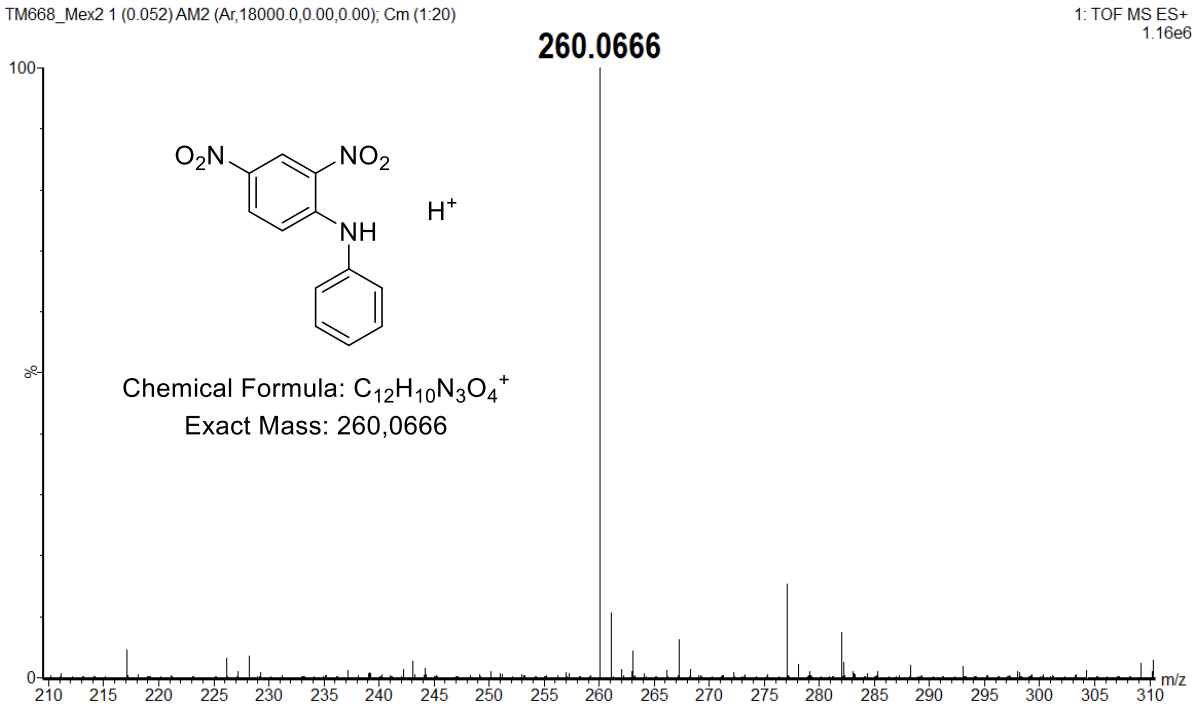


Figure S 27. HRMS (ES+) of compound **7**. The peaks at m/z = 277 and m/z = 282 were attributed to the ammonium and sodium adduct of compound **7**, respectively.

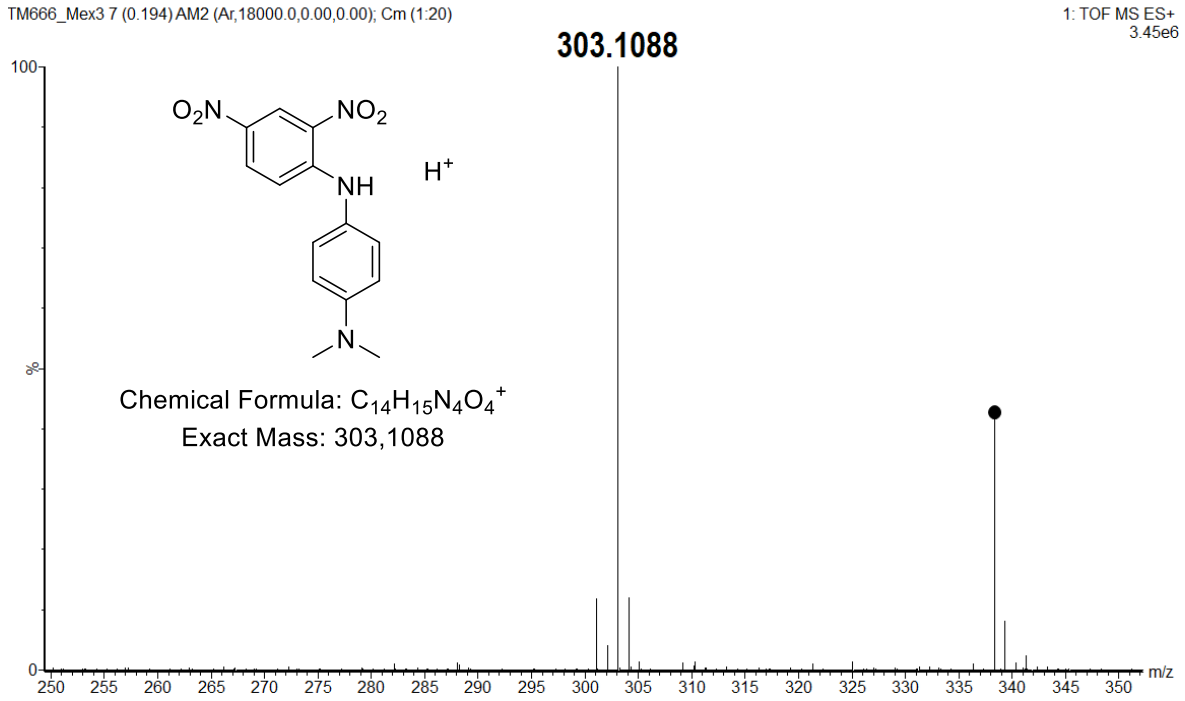


Figure S 28. HRMS (ES+) of compound **8**. The signal annotated by a black circle is an ion present in the mass spectrum of the analytical blank and is therefore not specific to the sample.

4. ADDITIONAL ELECTRONIC ABSORPTION SPECTRA

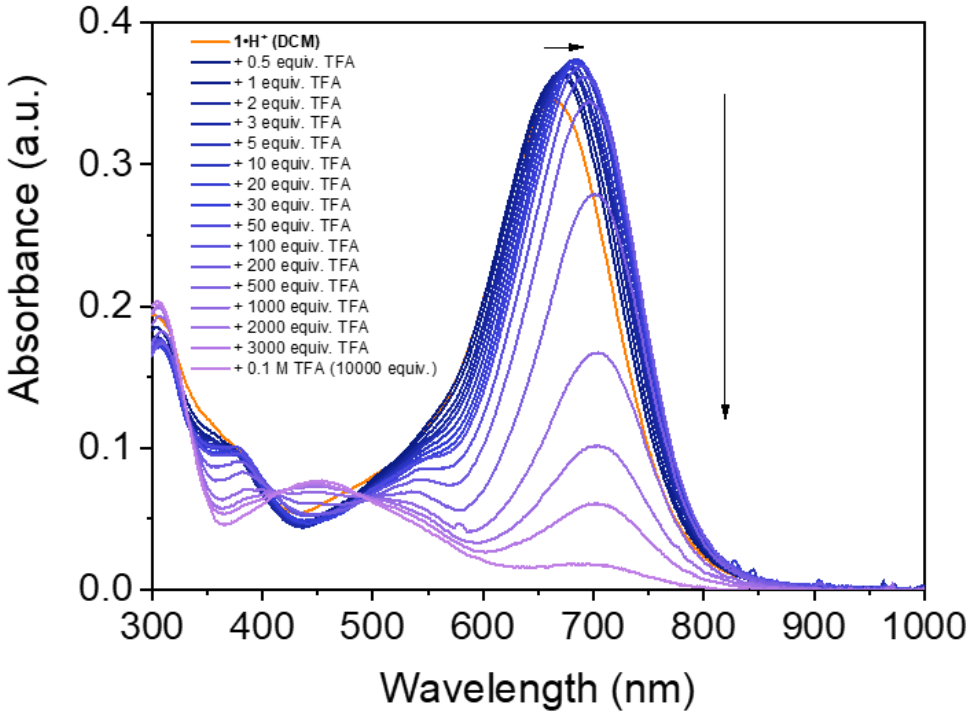


Figure S 29. Electronic absorption spectra of **1•H⁺** in dichloromethane and its stepwise protonation with TFA (c = 3.774×10^{-5} M).

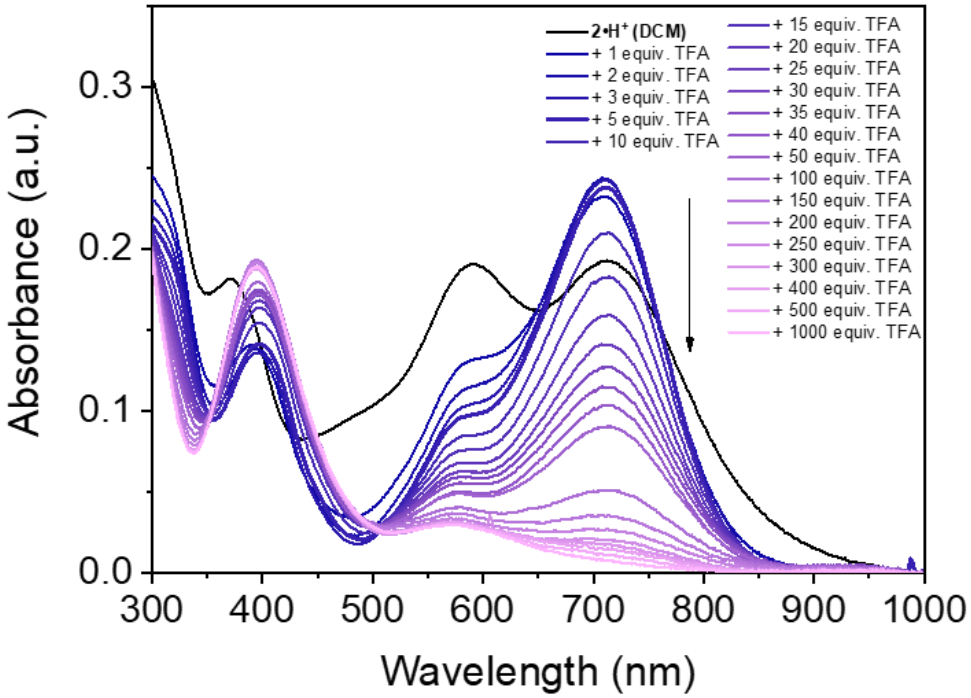


Figure S 30. Electronic absorption spectra of **2•H⁺** in dichloromethane and its stepwise protonation with TFA (c = 1.927×10^{-5} M).

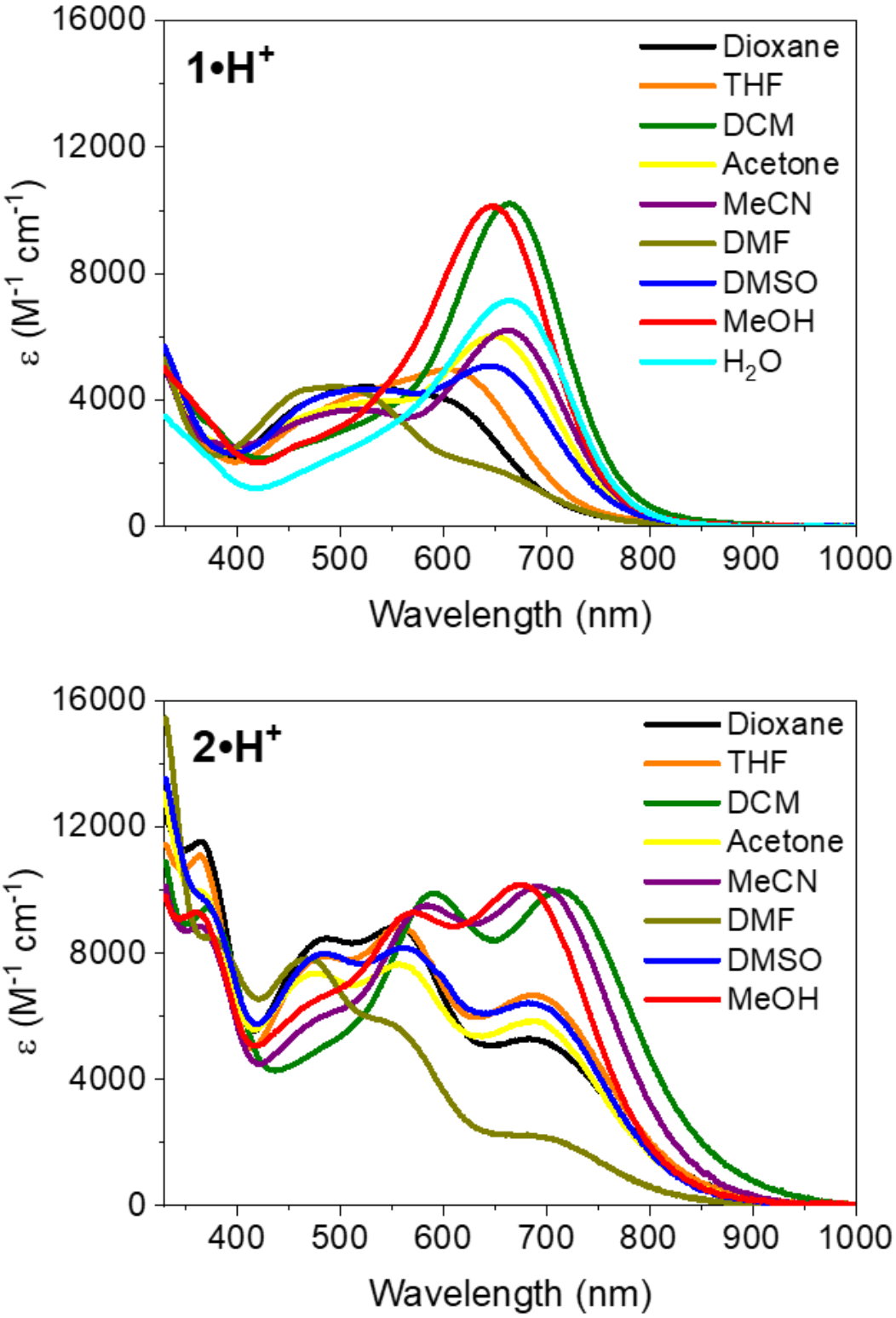


Figure S 31. Electronic absorption solvatochromism of **1•H⁺** and **2•H⁺**.

5. THEORETICAL DATA

Conformational Analysis

Table S 1. Summary of the three most significant isomers and tautomers of compound **1** and its corresponding mono- and di-cations, as identified in the study. The table presents the relative Gibbs free energy (ΔG) in kcal/mol with respect to the lowest-energy isomer, along with the percentage contribution of each isomer according to the Boltzmann law. For further details on the computational methods used, refer to the Computational Details section.

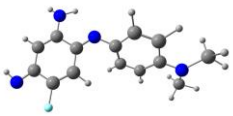
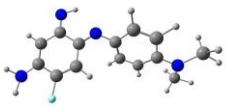
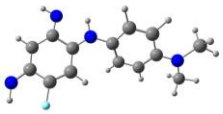
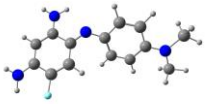
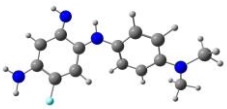
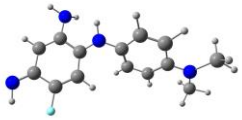
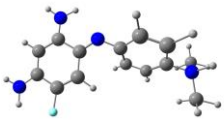
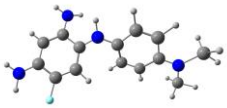
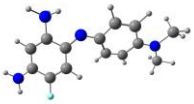
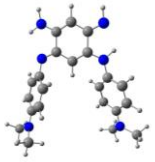
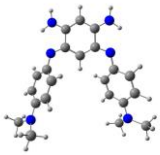
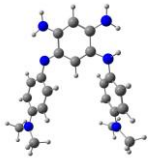
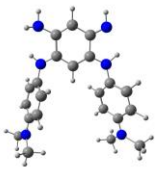
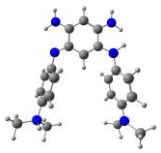
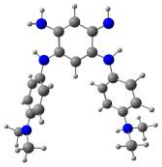
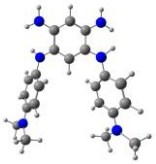
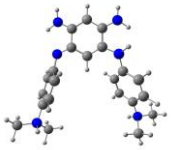
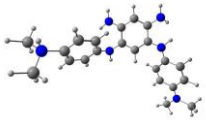
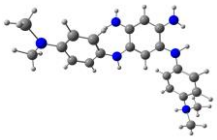
1			
ΔG [Kcal/mol] (%)	**0.0 (99.7)**	3.6 (0.3)	20.1 (0.0)
1•H^{+}			
ΔG [Kcal/mol] (%)	**0.0 (100.0)**	13.0 (0.0)	17.5 (0.0)
1•2H^{2+}			
ΔG [Kcal/mol] (%)	**0.0 (100.0)**	10.8 (0.0)	10.9 (0.0)

Table S 2. Summary of the three most significant isomers and tautomers of compound **2** and its corresponding cations, as identified in the study. See caption of Table S 1 for more details.

2			
ΔG [Kcal/mol] (%)	**0 (100.0)**	8.1 (0.0)	8.3 (0.0)
2•H$^+$			
ΔG [Kcal/mol] (%)	**0.0 (73.0)**	**0.6 (26.8)**	3.6 (0.2)
2•2H^{2+}			
ΔG [Kcal/mol] (%)	**0.0 (99.8)**	3.8 (0.2)	6.5 (0.0)
2•3H^{3+}			
ΔG [Kcal/mol] (%)	0.0 (100.0)	6.7 (0.0)	9.5 (0.0)

Excited states calculations

Table S 3. Vertical excitation wavelengths and oscillator strengths of relevant transitions, computed using the protocol outlined in the computational details. The composition of each excited state is also included, where H identifies the HOMO orbital and L identifies the LUMO, and the quantity into parentheses represents the percentage contribution of such transition into the excitation.

Molecule	State	λ^{clr2}[nm]	$\lambda^{clr2+cc2}$[nm]	f^{TD-DFT}	Orbital contibution (%)
1	1	468	497	0.5	H→L (90)
1•H^{+}	1	597	699	0.8	H→L (90)
1•H^{2+}	1	428	449	0.1	H→L (90)
2	1	471	503	0.2	H→L (84)
	2	400	427	0.3	H-1→L (68), H-2→L (20)
	3	339	356	0.3	H-2→L (66), H-1→L (-16)
2•H^{1+} (1)	1	615	732	0.7	H→L (82)
	2	539	641	0.1	H-1→L (76)
	3	409	438	0.1	H-2→L (84)
2•H^{1+} (2)	1	624	763	0.5	H→L (90)
	2	530	619	0.1	H-1→L (88)
	3	428	464	0.1	H-2→L (82)
2•H^{2+}	1	626	777	0.1	H→L (80)
	2	448	480	0.1	H-1→L (72)
	3	395	409	0.1	H-2→L (72)
2•H^{3+}	1	493	520	0.1	H→L (88)
	2	410	452	0.1	H-1→L (50), H-2→L (36)
	3	355	379	0.4	H-2→L (-42), H-1→L (40)

Orbitals involved in the relevant excited states

Table S 4. HOMO and LUMO orbital representations for compound **1** and the corresponding cations. All plots were generated using an isosurface value of 0.1.

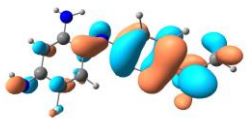
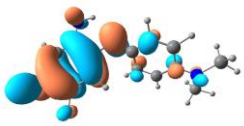
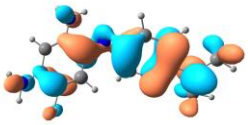
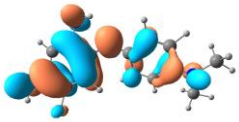
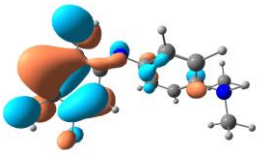
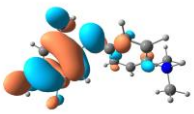
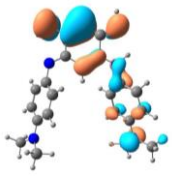
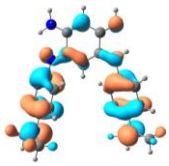
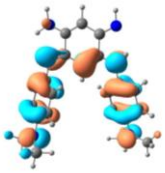
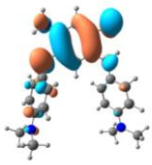
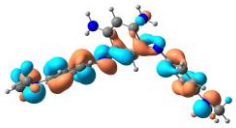
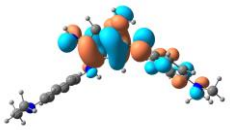
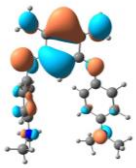
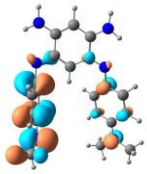
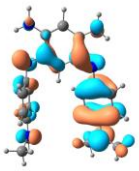
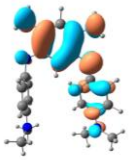
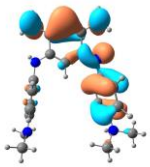
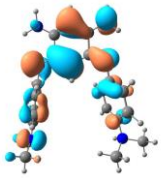
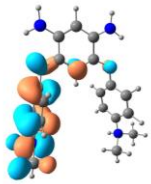
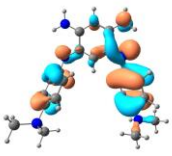
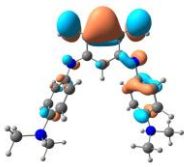
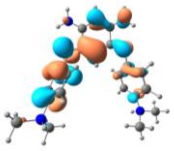
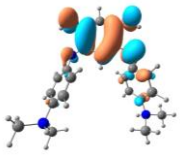
1		
	HOMO	LUMO
1•H^{1+}		
	HOMO	LUMO
1•2H^{2+}		
	HOMO	LUMO

Table S 5. HOMO-2, HOMO-1, HOMO and LUMO orbital representations for compound **2** and the corresponding cations. All plots were generated using an isosurface value of 0.1.

2				
	HOMO-2	HOMO-1	HOMO	LUMO
2•H^{1+} (1)				
	HOMO-2	HOMO-1	HOMO	LUMO
2•H^{1+} (2)				
	HOMO-2	HOMO-1	HOMO	LUMO
2•2H^{2+}				
	HOMO-2	HOMO-1	HOMO	LUMO
2•3H^{3+}				
	HOMO-2	HOMO-1	HOMO	LUMO

Further electronic density difference plots

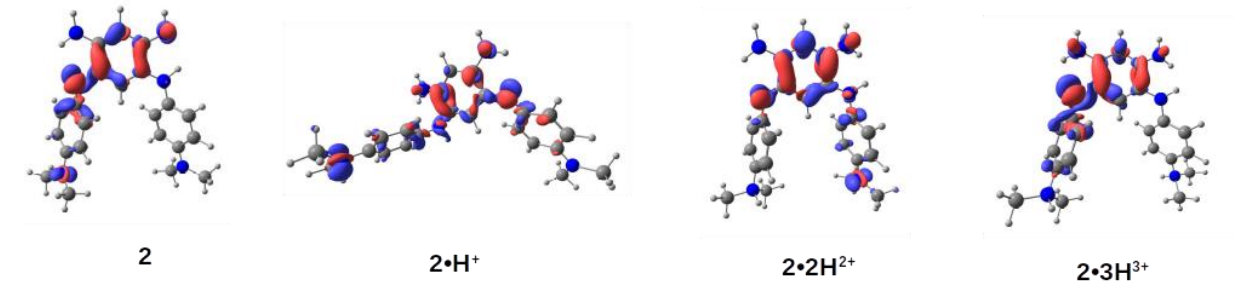


Figure S 32. Electronic density differences (EDD (2)) between the ground (S_0) and the second excited state (S_2) for molecule **2**, and its corresponding cationic forms. Zones in red indicate an increase in electronic density between S_0 to S_2, while blue regions indicate a decrease. The isosurfaces are visualized with an isovalue of 0.003.

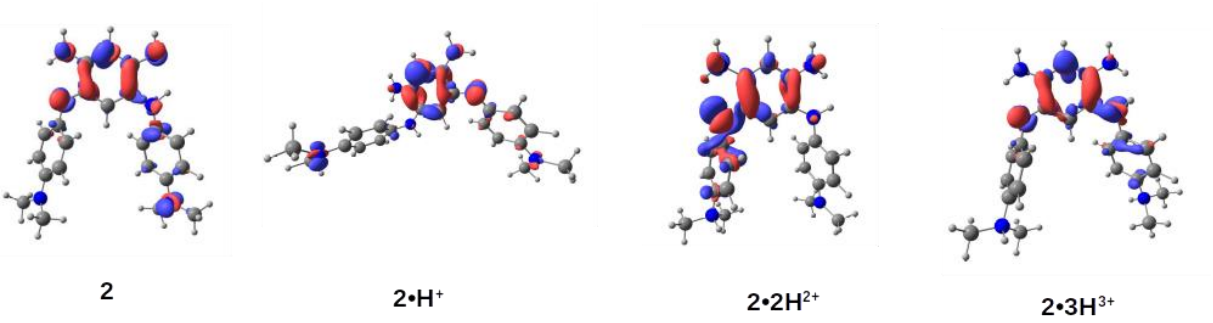


Figure S 33. Electronic density differences (EDD (3)) between the ground (S_0) and the third excited state (S_3) for molecule **2**, and its corresponding cationic forms. See caption of Figure S 32 for more details.

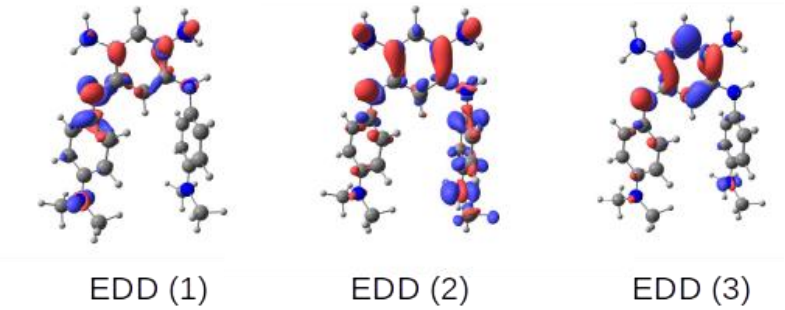


Figure S 34. Electronic density differences (EDD) between the ground (S_0), the first (S_1), the second (S_2), and the third (S_3) excited states for molecule **2•H^{1+} (2)**. See caption of Figure S 32 for more details.

Vibrationally resolved spectra of molecule 2•H$^+$

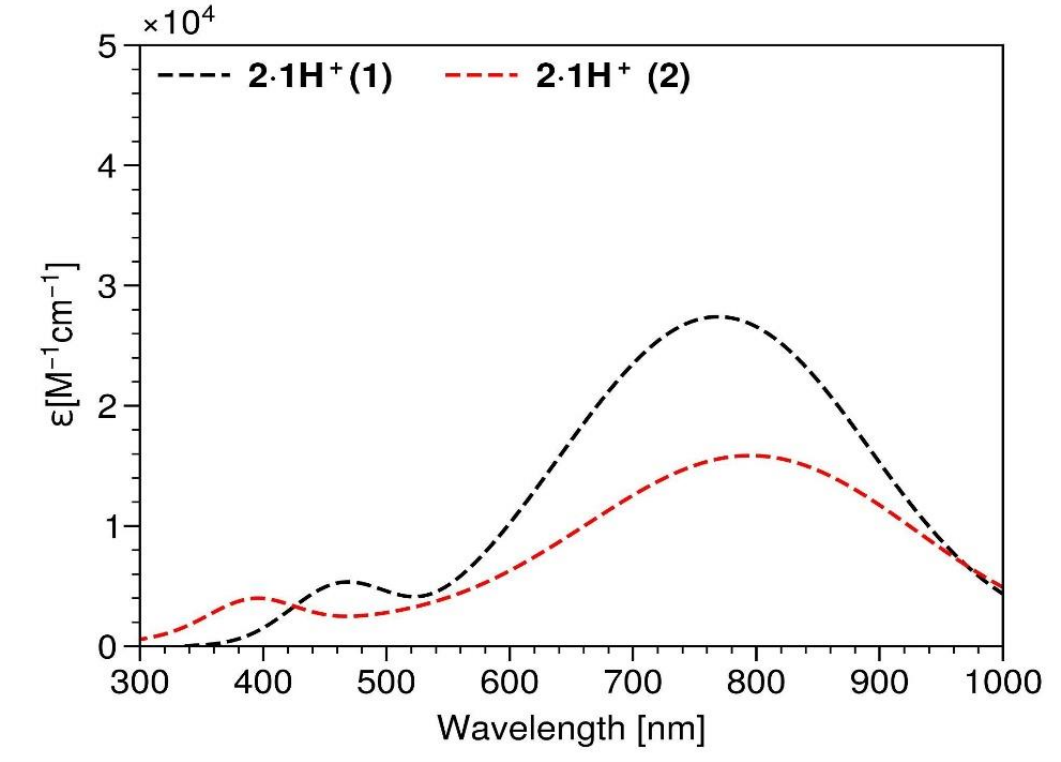


Figure S 35. Theoretical absorption spectra of the two conformers **2•H^{1+} (1)** and **(2)**.