# Electronic Supplementary Information

## Type I Strong Acceptor-Weak Acceptor Photosensitizing Assemblies for Regulated Aerobic Oxidative Coupling of Anilines

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## General Experimental Methods and Materials

All the reagents were purchased from Aldrich and were used without further purification. HPLC grade solvents were used in UV-vis and fluorescence studies. UV-vis spectra were recorded on SHIMADZU UV-2450 spectrophotometer, with a quartz cuvette (path length 1 cm). The fluorescence spectra were recorded with HORIBA Scientific FLUOROMAX-4 and HORIBA QM-8075-21-C spectrofluorometer. The electrochemical measurements were performed at room temperature using a computer controlled potentiostat/galvanostat Autolab PGSTAT204 (Netherlands) Metrohm, equipped with FRA (frequency response analyzer) module. The NOVA software was used to collect, plot and analyze the raw data of various CV measurements. The dynamic light scattering (DLS) data were recorded with MALVERN Instruments (Nano-ZS). The melting points were calculated using Cole-Parmer MP 200D-120 Stuart Digital melting point apparatus. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance III HD 500 MHz, Bruker Avance Neo 500MHz and JEOL 400 MHz using $CDCl_3$ as solvent. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad singlet), coupling constants *J* (Hz).

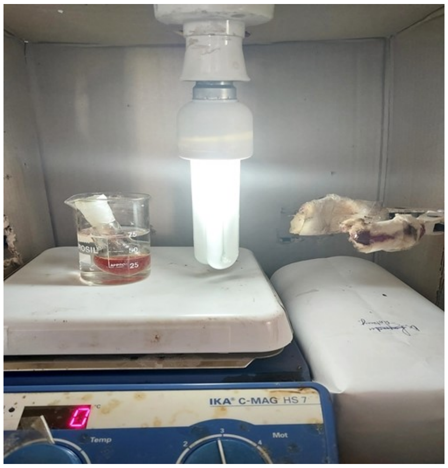
## UV-vis and fluorescence studies.

The stock solution ($10^{-3}$ M) of derivative **3** was prepared by dissolving 8.95 mg in 10.0 mL of DMSO. 15.0 μL of this stock solution further diluted with $H_2O$ and DMSO (1:1) to prepare 3.0 mL solutions of derivatives (5.0 μM) and these solutions were used for each UV-vis and fluorescence experiments.

**Synthesis of phenazine derivative DPZ-TPY**

To a solution of 11, 12-dibromodibenzo [a,c]phenazine (0.40 g, 0.90 mmol) and 4-(2,2′,6′,2″-terpyridine-4′-yl) phenyl boronic acid (0.73 g, 2.09 mmol) in anhydrous dioxane (20 mL), 2 mL aqueous solution of $K_2CO_3$ (1 g, 7.28 mmol) was added followed by addition of $[Pd(PPh_3)_4]$ (0.52 g, 0.45 mmol) under nitrogen atmosphere. The reaction mixture was refluxed overnight and dioxane was then removed under vacuum. The residue so obtained was treated with water and extracted with ethyl acetate, dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and compound was purified by column chromatography using 80:20 (ethylacetate: hexane) as an eluent to give 85% of the derivative **DPZ-TPY** as pale yellow solid; mp: >250°C; $^1$H NMR (400 MHz, $CDCl_3$) δ(ppm) = 9.47-9.44 (m, 2H), 8.78 (s, 4H), 8.70-8.69 (m, 4H), 8.66 (d, *J* = 8Hz, 4H), 8.61 (d, *J* = 8Hz, 2H), 8.49 (s, 2H), 7.93 (d, *J* = 8Hz, 4H), 7.88 (d, *J* = 4 Hz, 1H), 7.86 (d, *J* = 4Hz, 2H), 7.85-7.83 (m, 2H), 7.82-7.80 (m, 2H), 7.78-7.76 (m, 1H), 7.54 (d, *J* = 8Hz, 4H), 7.35-7.31 (m, 4H). $^{13}$C NMR ($CDCl_3$, 125 MHz) δ(ppm) = 156.3, 156.0, 149.6, 149.3, 149.1, 137.4, 136.8, 132.2, 130.7, 130.6, 130.4, 128.0, 127.2, 126.4, 123.7, 123.0, 121.3, 118.9; HRMS (ESI) m/z: $[M+H]^+$ found to be 895.3306, calculated: 895.3298 (Fig. S68-S70).

**General procedure for oxidative coupling of arylamines:** The arylamine (**1a-n**) (1.0 mmol) in is dissolved in DMSO: $H_2O$ (1:1) (3.0 mL) in a 10 mL round-bottom flask with the subsequent addition of KOH (1.5 equiv.) and **DPZ-TPY** assemblies (0.1 mol %) as a photocatalyst. The reaction mixture is allowed to stir continuously for 24 h under aerial condition and visible light irradiations (16 W White LED). The reaction vessel was dipped in water bath and the final temperature of the water bath was maintained between 25°C-28°C. After the completion of the reaction, the organic part was extracted with ethyl acetate and organic layer was dried over anhydrous sodium sulphate and distilled under reduced pressure. The products (**2a-n**) were isolated by chromatography using ethyl acetate and hexane as eluents. The isolated product was air dried overnight and identified by $^1$H NMR spectroscopy (Fig. S19-S45).



Photocatalytic set-up for catalytic reaction.

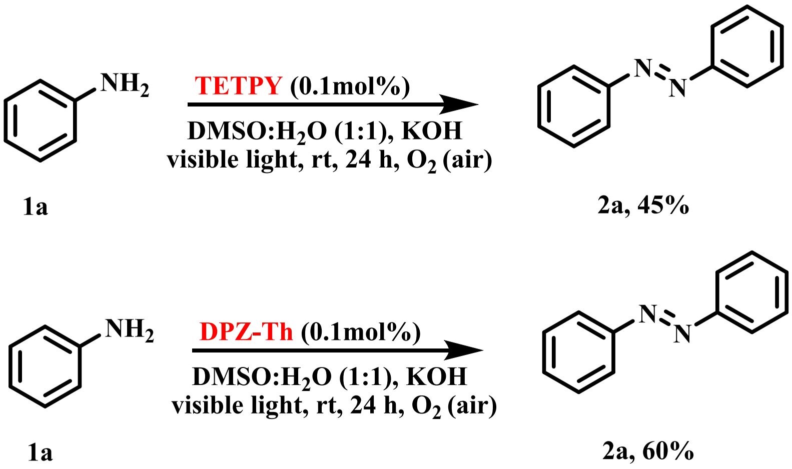
**General procedure for synthesis of azobenzenes from hydroazobenzene:** The hydroazobenzene (1.0 mmol) prepared as per literature procedure[1] in is dissolved in DMSO: $H_2O$ (1:1) (3.0 mL) in a 10 mL round-bottom flask with the subsequent addition of KOH (1.0 equiv.) and **DPZ-TPY** assemblies (0.1 mol %) as a photocatalyst. The reaction mixture is allowed to stir continuously for 10 h under aerial condition and visible light irradiation irradiations (16 W White LED). The reaction vessel was dipped in water bath and the final temperature of the water bath was maintained between 25°C-28°C. After the completion of the reaction, the organic part was extracted with ethylacetate and organic layer was dried over anhydrous sodium sulphate and distilled under reduced pressure. The products (**4a-g**) were isolated by chromatography using ethyl acetate and hexane as eluents. The isolated product was air dried overnight and identified by $^1$H NMR spectroscopy (Fig. S46-S59).

**Table S1**. Comparison table for synthesis of azobenzene from hydrazobenzene.

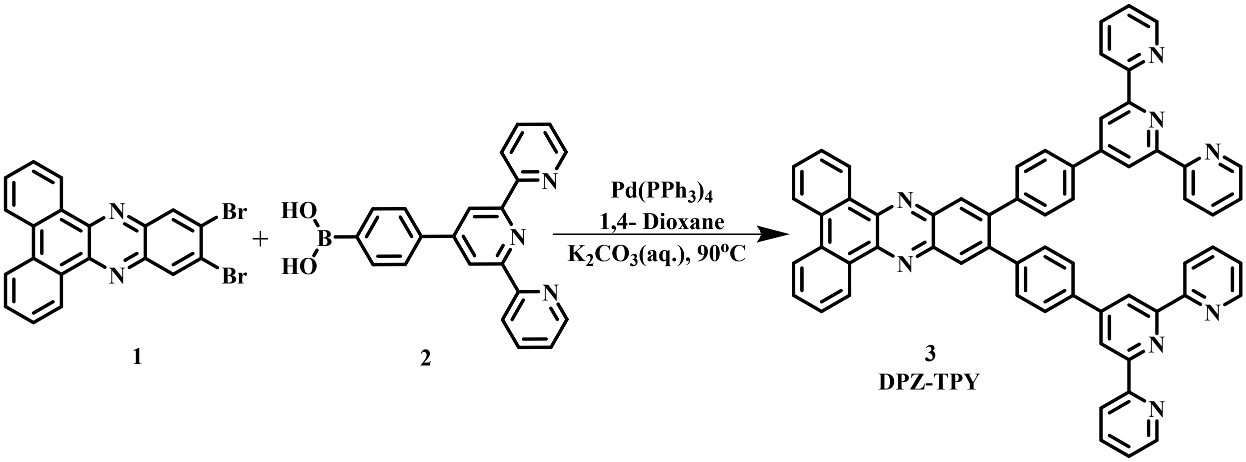
| **Entry** | **Journal** | **Catalyst** | **Catalyst loading** | **Reaction medium** | **Source of light/Temp** | **Atmosphere** | **Base** | **Additive** | **Time (h)** | **Yield (%)** |
|---|---|---|---|---|---|---|---|---|---|---|
| **1.** | **Present Manuscript** | Supramolecular ensemble **DPZ-TPY** | 0.1 mol% | DMSO/$H_2O$ | Visible light | Aerial | KOH | **-** | 24 | 93% |
| **2.** | *J. Am. Chem. Soc.* **2021**, 143, 2938-2943 | Ir(dF-CF$_3$-ppy)$_2$(dtbpy)$^+$ | 5 mol% | ACN | Blue LED | Aerial | $K_3PO_4$ |  | 24 | 94% |
| **3.** | *Angew. Chem. Int. Ed.* **2021,** 60, 6382 – 6385 | Molybdenum based catalyst $[N(C_4H_9)_4]_2[Mo_6O_{19}]$ | 1 mol% | Methanol | 60°C | - | $Na_2S_2O_3$ | $H_2O_2$, | 24 | 95% |
| **4.** | *J.Org.Chem.* ***2017***,82, 9873-9876 | NCS | 2 equiv. | DCM | -78°C to RT | - | DBU | - | 2-10 min | 87% |
| **5.** | *ACS Catal.* **2013**, 3, 478−486 | Ag nanoparticles | 6 mol % | DMSO | RT | Aerial | KOH | - | 24 | 97% |

**Table S2**. Comparison table for synthesis of azobenzene from arylamines

| **Entry** | **Journal** | **Catalyst** | **Catalyst loading** | **Reaction medium** | **Source of light/Temp** | **Atmosphere** | **Base** | **Additive** | **Time (h)** | **Yield (%)** |
|---|---|---|---|---|---|---|---|---|---|---|
| **1.** | **Present Manuscript** | Supramolecular ensemble **DPZ-TPY** | 0.1 mol% | DMSO/$H_2O$ | Visible light | Aerial | KOH | **-** | 10 | 92% |
| **2.** | *Green Chem.,* **2019,** 21, 4189-4193 | Eosin Y | 2 mol% | ACN | CFL | Aerial | - | - | 20 | 95% |
| **3.** | *ACS Catal.,* **2018**, 8, 7727-7733 | Co and Ru photoredox catalyst | 2 mol% | Ethanol | Visible light, 28°C | Argon | - | - | 12 | 93% |
| **4.** | *Angew. Chem. Int.Ed.* **2016**, 55, 1-5 | tBuOK | 20 mol% | Liquid Ammonia | RT | Sealed | - | tBuOK | 0.005 | 100% |



**Scheme S1**. Aerobic oxidative coupling of arylamines using assemblies of **TETPY** and **DPZ-Th**.



**Scheme  S2**. Synthesis of derivative **DPZ-TPY**.

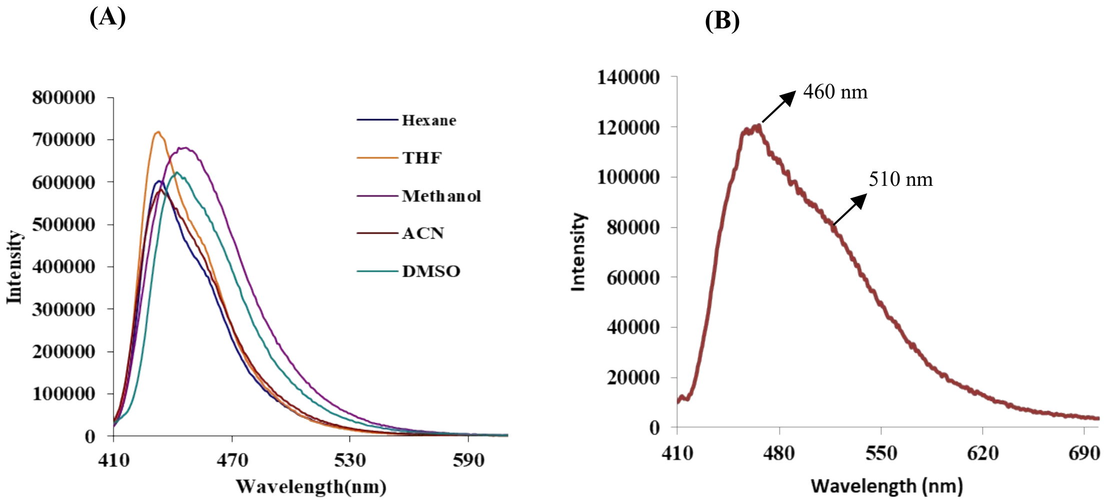


**Fig. S1.** (**A**) Solvent dependent emission studies of **DPZ-TPY** assemblies in various solvents. (**B**) Emission spectrum of **DPZ-TPY** assemblies in DMSO: $H_2O$ (1:1) solvent mixture.

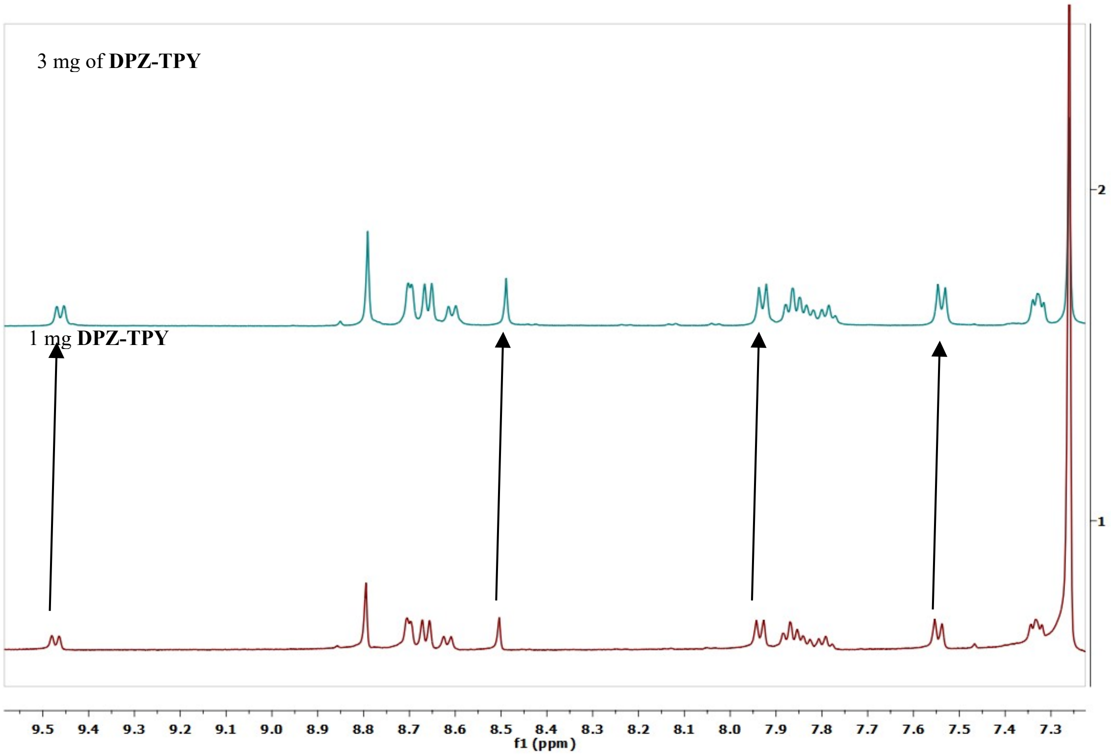


**Fig. S2**. Concentration dependent $^1$H NMR studies of **DPZ-TPY** assemblies showing upfield shift in the signals.

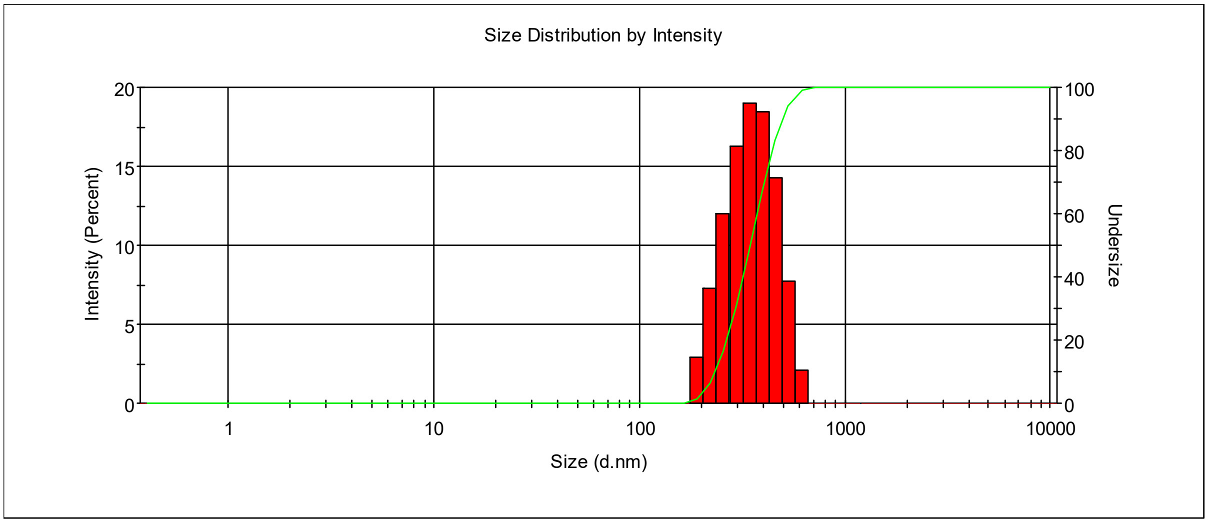


**Fig. S3.** DLS spectra of assemblies of **DPZ-Th** showing the particle size between 200-700 nm.

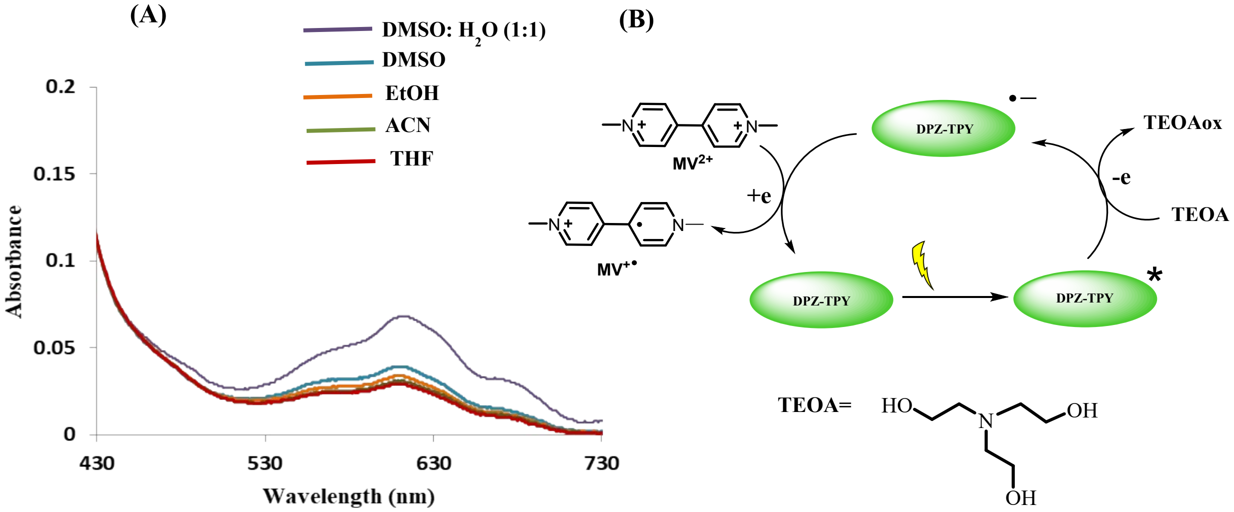


**Fig. S4**. **(A)** Absorption spectra of derivative **DPZ-TPY** (5 µM) in presence of $MV^{2+}$ (0.2 mM) and TEOA (50 mM) under day-light and inert atmosphere. (**B**) **DPZ-TPY** acts as photosensitizer and transports the electron to a sacrificial donor to acceptor under visible-light irradiation and inert atmosphere.

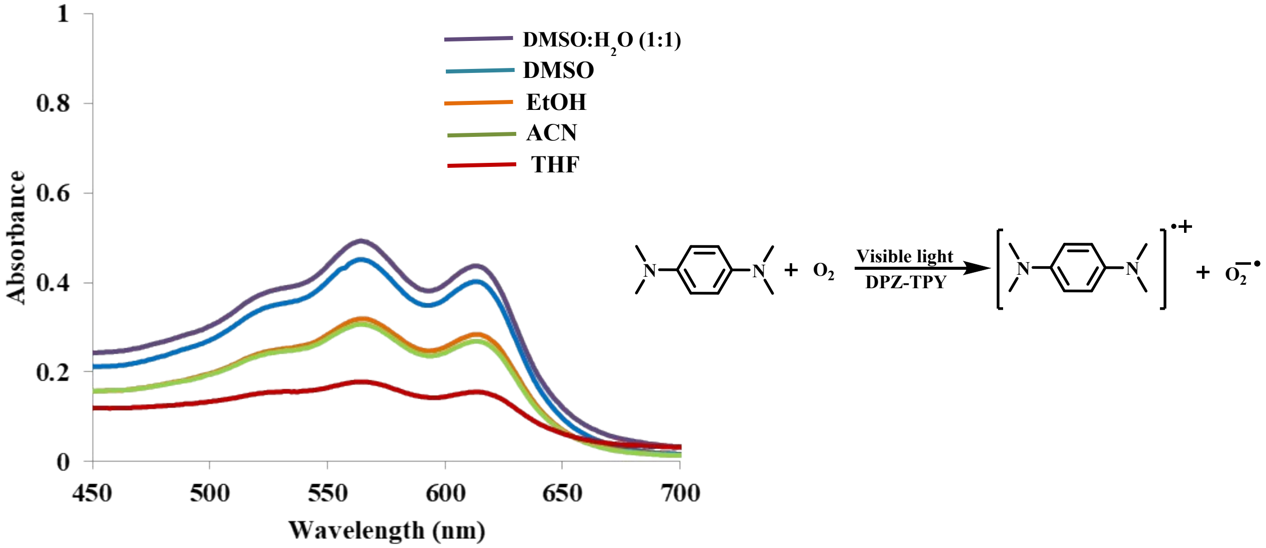


**Fig. S5.** UV-vis absorption spectra and photographs of the cationic radical species of N,N,N′,N′-tetramethyl-p-phenylenediamine generated by assemblies of **DPZ-TPY** (5 μM) in the presence of visible light and oxygen.

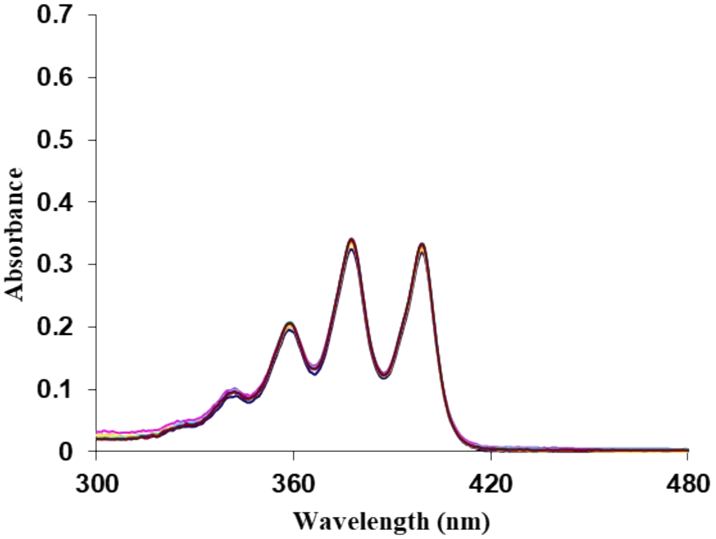


**Fig. S6**. UV-vis spectra of ABDA in the presence of assemblies of **DPZ-TPY** (5μM) under visible light irradiation.

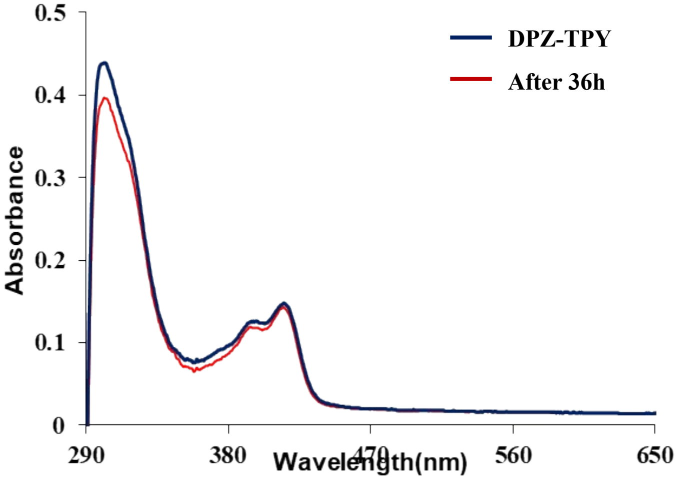


**Fig. S7.** UV-vis spectra of derivative **DPZ-TPY** DMSO: $H_2O$ (1:1) before and after irradiation of 36 h.

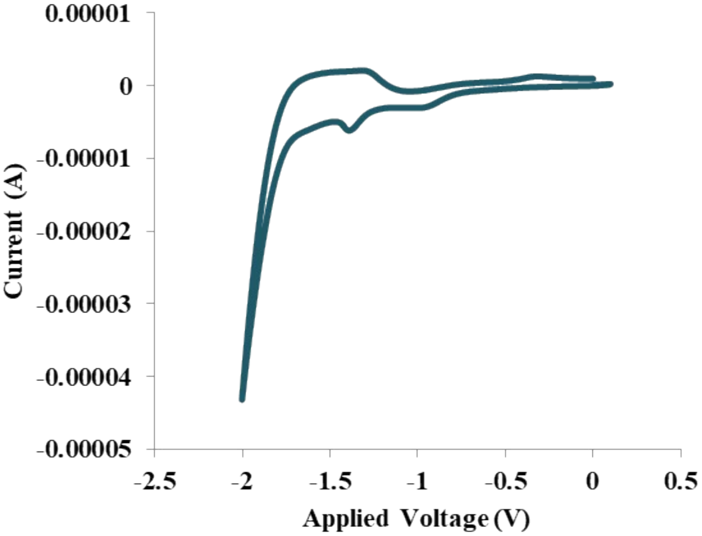


**Fig. S8.** Cyclic voltammogram of **DPZ-TPY** under $N_2$ saturated ACN. The potential was scanned at 100 mV s-1 using platinum (working), Ag/AgCl (reference) and platinum wire (counter) electrodes with (0.1 M) tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as supporting electrolyte in ACN

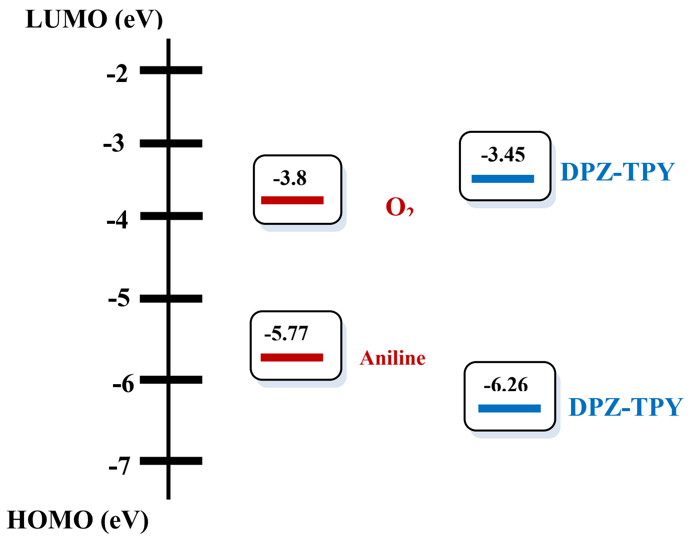


**Fig. S9.** Schematic representation of HOMO/LUMO energy levels of **DPZ-TPY** assemblies**.**

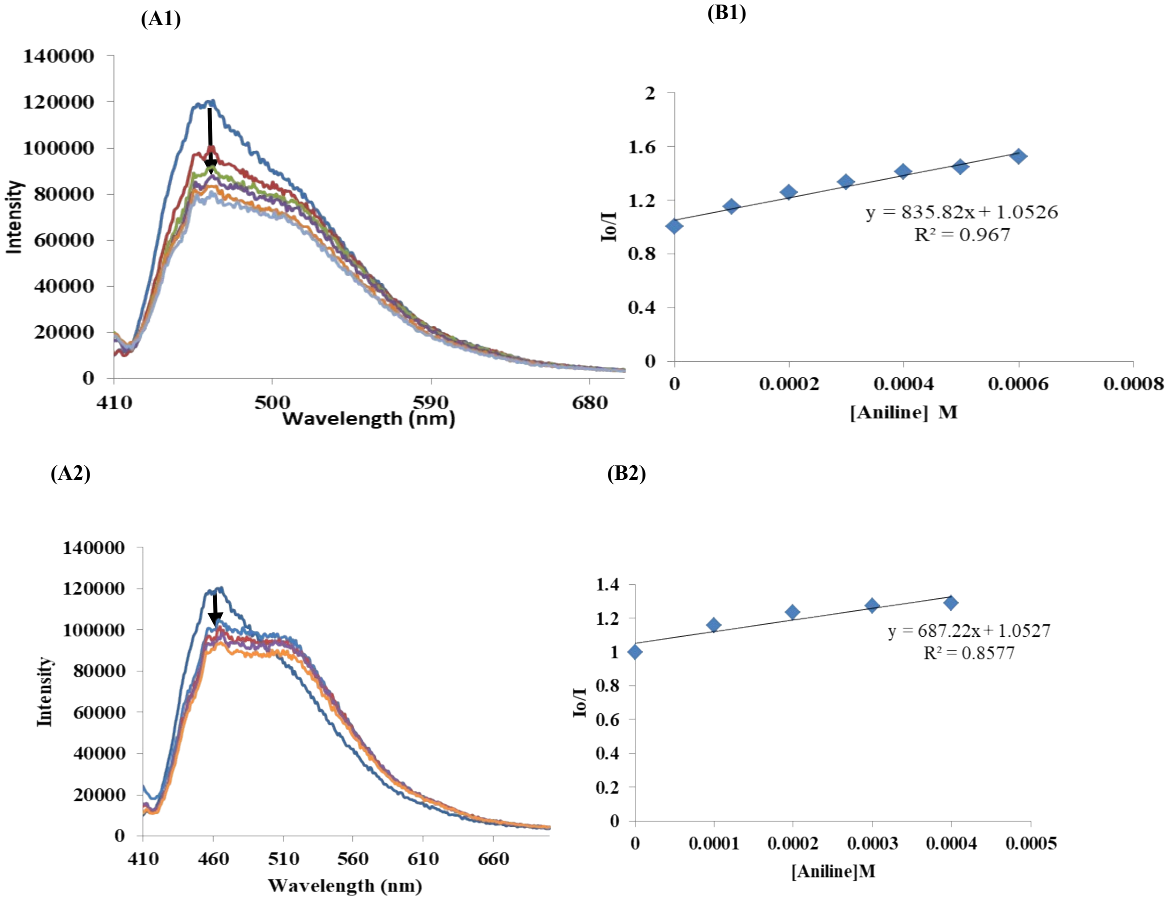


**Fig. S10.** (**A1 and B1**) The fluorescence quenching spectra upon addition of aniline to **DPZ-TPY** assemblies in the absence of base and Stern-Volmer quenching plot. **.** (**A2 and B2**) The fluorescence quenching spectra upon addition of aniline to **DPZ-TPY** assemblies in the presence of base and Stern-Volmer quenching plot.

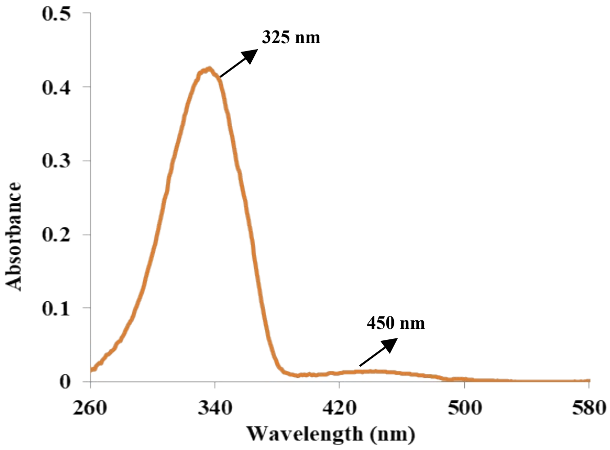
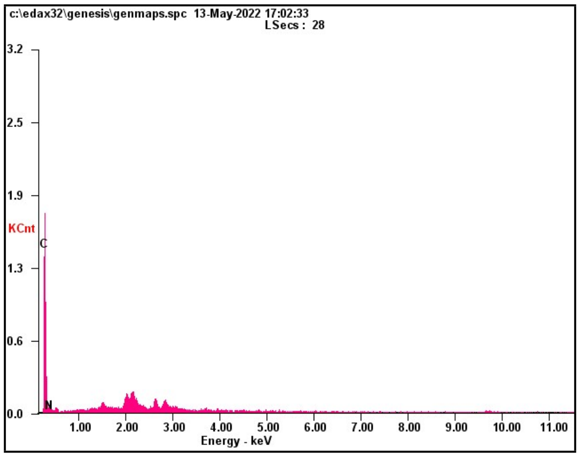


**Fig. S11**. Absorption spectrum of *trans* azobenzene (**2a**).



| *Element* | *Wt%* | *At%* |
|---|---|---|
| ***CK*** | 81.95 | 84.11 |
| ***NK*** | 18.05 | 15.89 |
| ***Matrix*** | Correction | ZAF |

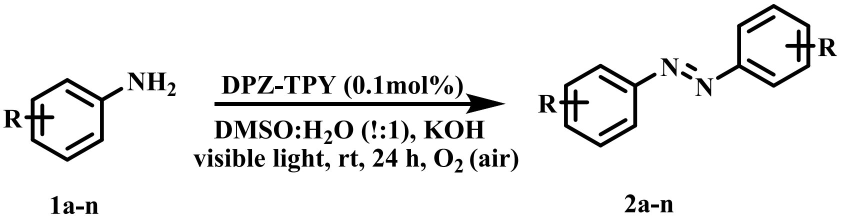
**Fig. S12.** EDX spectra of assemblies of **DPZ-TPY**.

| **Sample** | **Pd** |
|---|---|
| | **ppm** |
| **DPZ-TPY** | **ND** |

**ND MEANS LESS THAN 0.01PPM**

**Fig. S13.** ICP-AES studies of assemblies of **DPZ-TPY**.

**Table S3**. Optimization of reaction conditions for oxidative coupling of arylamines[a]



| Entry | Photocatalyst (supramolecular assemblies) | Base | Solvent system | Yield (%) |
|---|---|---|---|---|
| 1. | **DPZ-TPY** | KOH(1.5 equiv.) | DMSO/$H_2O$ (1:1) | 93% |
| 2[b]. | **DPZ-TPY** | KOH (1.5 equiv.) | DMSO/$H_2O$ (1:1) | 91% |
| 3. | **DPZ-TPY** | KOH(1.5 equiv.) | ACN | 72% |
| 4. | **DPZ-TPY** | KOH(1.5 equiv.) | THF | 70% |
| 5. | **DPZ-TPY** | KOH(1.5 equiv.) | EtOH | 63% |
| 6. | **DPZ-TPY** | KOH(1.5 equiv.) | DMF | 75% |
| 7. | **DPZ-TPY** | Triethylamine(1.5 equiv.) | DMSO/$H_2O$ (1:1) | Traces |
| 8. | **DPZ-TPY** | $K_2CO_3$(1.5 equiv.) | DMSO/$H_2O$ (1:1) | 55% |
| 9. | **DPZ-TPY** | $K_3PO_4$(1.5 equiv.) | DMSO/$H_2O$ (1:1) | 60% |
| 10. | **DPZ-TPY** | KOH (1.0equiv.) | DMSO/$H_2O$ (1:1) | 80% |
| 11[c]. | **DPZ-TPY** | KOH(1.5 equiv.) | DMSO/$H_2O$ (1:1) | 47% |

[a]Reaction conditions (unless otherwise noted): 1a (1.0 mmol), base (1.5 eqv), solvent (3 mL), assemblies of **DPZ-TPY**: 16 W white LED as the irradiation source, room temperature, 24 h, in aerial conditions.[b]50°C. [c]light source turned on for 12 h and turned off for next 12 h.

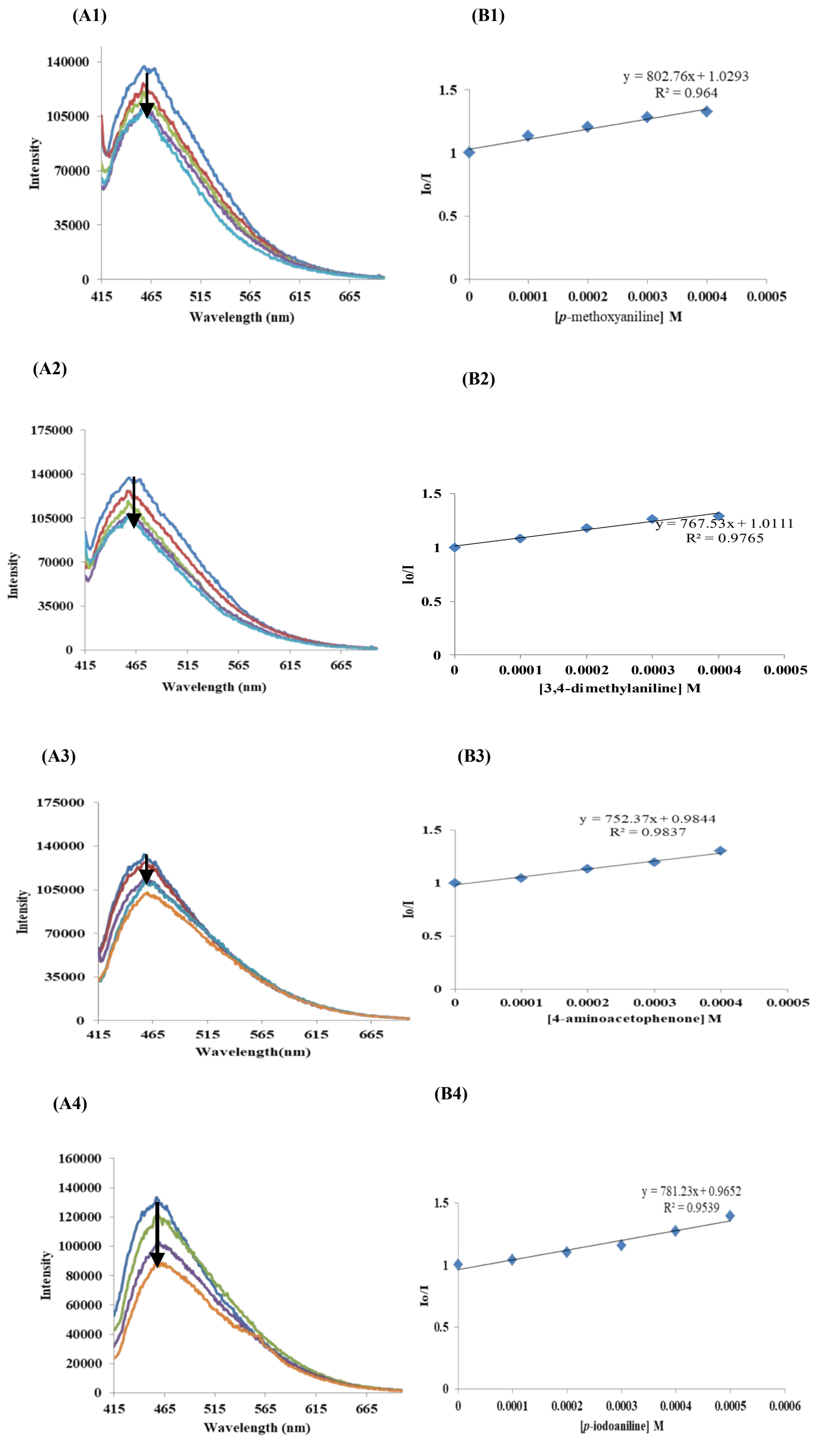


**Fig. S14.** (**A1, A2, A3 and A4**) The fluorescence quenching spectra upon addition of *p*-methoxyaniline (**2d**), 3,4-dimethylaniline (**2l**), 4-aminoacetophenone (**2j**) and *p*-iodoaniline (**2e**) to **DPZ-TPY** assemblies (**B1,B2,B3 and B4)** Stern-Volmer quenching plot.

Table S4. Table showing Stern-Volmer constant values with yields.

| **S.No.** | **Substrate** | **$K_{SV}$ ($M^{-1}$)** | **Yields** |
|---|---|---|---|
| 1. | Aniline (**1a**) | $8.35\times10^2$ | **2a,** 93% |
| 2. | *p*-methoxy aniline (**1d**) | $8.02\times10^2$ | **2d**, 86% |
| 3. | *p*-iodoaniline **(1e)** | $7.81\times10^2$ | **2e,** 85% |
| 4. | 3,4-dimethylaniline (**1l**) | $7.67\times10^2$ | **2l,** 76% |
| 5. | 1-(4-aminophenyl)ethan-1-one (**1j**) | $7.52\times10^2$ | **2j,** 70% |
| 6. | *p*-nitroaniline(**1k**) | No quenching observed | **2k,** 0% |

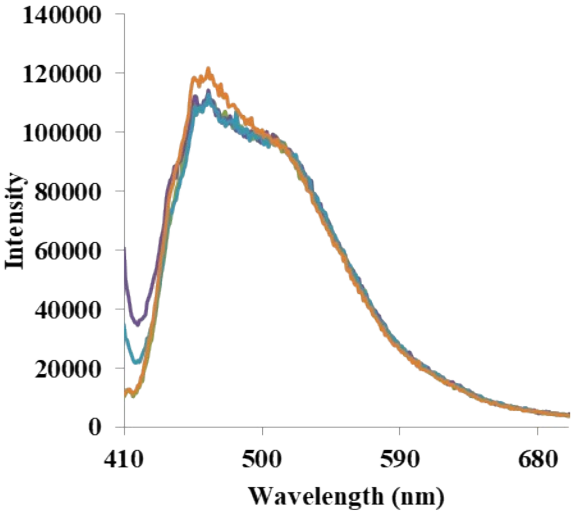


**Fig. S15.** The fluorescence spectra upon addition of *p*-nitroaniline (**1k**) to **DPZ-TPY** assemblies.

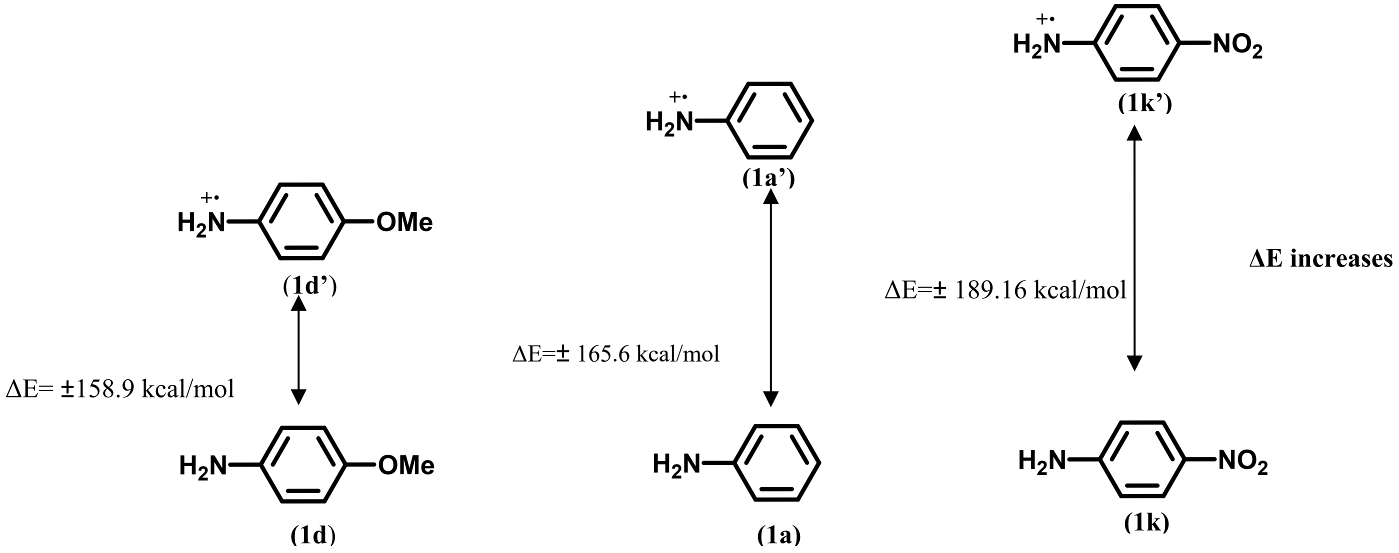


**Fig. S16.** The energy requirement for conversion of reactants into radical cations calculated by B3LYP/6-31G(d,p) methods.

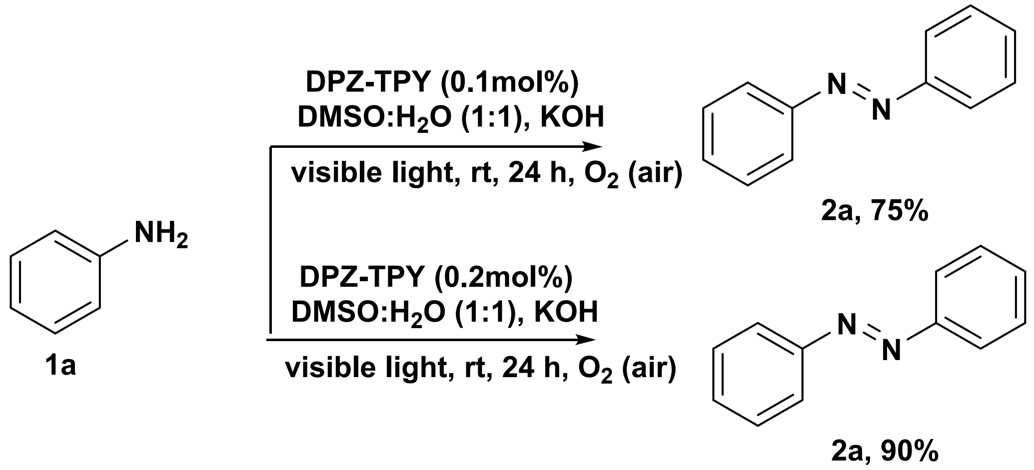


**Fig. S17**. Effect of high catalyst loading and longer time on the gram-scale synthesis.

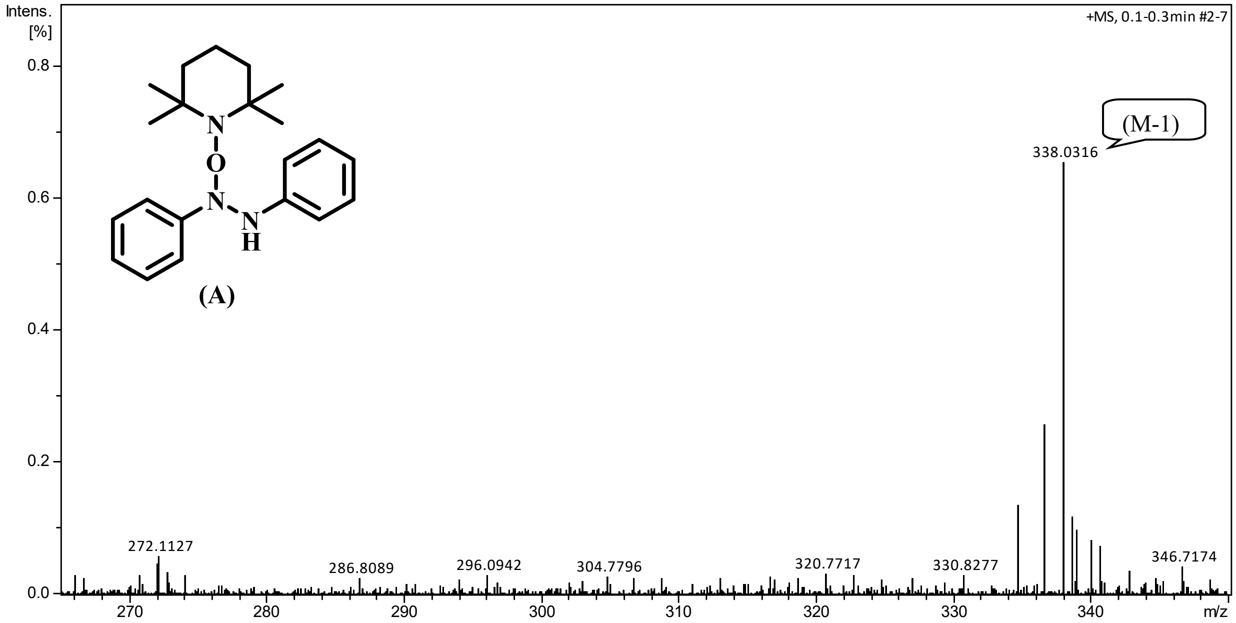


**Fig. S18.** The mass spectra of adduct **(A).**

**$^{1}$H NMR spectra of organic compound**

**1,2-diphenyldiazene (2a).** [1,10] Yellow solid (93%): m.p.: 66-68 °C. $^{1}$H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.94-7.91 (m, 4H), 7.65-7.47 (m, 4H). $^{13}$C NMR ($CDCl_3$, 125 MHz) δ (ppm) = 152.7, 131.0, 129.1, 122.9.

**1,2-di-*p*-tolyldiazene (2b).**[2,11] Yellow solid (90%): m.p.:140-142 °C. $^{1}$H NMR (500 MHz, $CDCl_3$); δ (ppm) = 7.82 (d, *J* = 10 Hz, 4H), 7.31 (d, *J* = 10 Hz, 4H), 2.44 (s, 6H). $^{13}$C NMR ($CDCl_3$, 125 MHz) δ (ppm) = 150.9, 141.2, 129.7, 122.7, 21.5.

**1,2-di-o-tolyldiazene (2c).** [2] Yellow solid (85%): m.p.: 53-54 °C. $^{1}$H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.62 (d, *J* = 8 Hz, 2H), 7.38-7.33 (m, 4H), 7.29-7.27 (m, 2H), 2.74 (s, 6H). $^{13}$C NMR ($CDCl_3$, 125 MHz) δ (ppm) = 151.1, 138.0, 131.3, 130.7, 126.4, 115.9, 17.6.

**1,2-bis(2-methoxyphenyl)diazene (2d).**[3,11] Yellow solid (88%): m.p.: 154.6-156.3 °C. $^{1}$H NMR (500 MHz, $CDCl_3$); δ (ppm) = 7.89 (d, *J* = 10 Hz, 4H), 7.00 (d, *J* = 10 Hz, 4H), 3.89 (s, 6H). $^{13}$C NMR ($CDCl_3$, 125 MHz) δ (ppm) = 161.6, 147.1, 124.4, 114.2, 55.6.

**1,2-bis(2-iodophenyl)diazene (2e)** [3,11] Orange solid (85%): m.p.: 242-244 °C. $^{1}$H NMR (500 MHz, $CDCl_3$); δ (ppm) = 7.86 (d, *J* = 5 Hz, 4H), 7.64 (d, *J* = 10 Hz, 4H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz) δ (ppm) = 151.8, 138.4, 124.5, 98.1.

**1,2-bis(4-bromophenyl)diazene (2f).** [1,11] Yellow solid (82%): m.p.: 205-207 °C. $^{1}$H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.79 (d, *J* = 12 Hz, 4H), 7.65 (d, *J* = 8.0 Hz, 4H). $^{13}$C NMR ($CDCl_3$, 125 MHz) δ (ppm) = 151.2, 132.4, 125.8, 124.4.

**1,2-bis(2-chlorophenyl)diazene (2g).**[1,11] Yellow solid(82%): m.p.: 189-191 °C. $^{1}$H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.87 (d, *J* = 8 Hz, 4H), 7.49 (d, *J* = 8 Hz, 4H). $^{13}$C NMR ($CDCl_3$, 125 MHz) δ (ppm) = 150.8, 137.2, 129.4, 124.2.

**1,2-bis(4-fluorophenyl)diazene (2h).**[1,11-12] Yellow solid (80%): m.p.: 93-95 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ (ppm) = 7.94 -7.91 (m, 4H), 7.21-7.13 (m, 4H). $^{13}$C NMR (CDCl$_3$, 125 MHz) δ (ppm) = 164.4 (d, *J* = 251.2 Hz), 149.0 (d, *J* = 2.5 Hz), 124.8 (d, *J* = 10.0 Hz), 116.07 (d, *J* = 22.5 Hz).

**Dimethyl 4,4'-(diazene-1,2-diyl)-bis(3-methylbenzoate) (2i):** Yellow solid(45%): m.p.: 116-118°C. $^1$H NMR (500 MHz, CDCl$_3$); δ (ppm) = 8.05 (s, 1H), 7.93 (d, *J* =10 Hz, 1H), 7.77-7.73 (m, 2 H), 7.62 (d, *J* =5Hz, 1H), 6.68 (d, *J* = 10 Hz, 1H), 3.95 (s, 3H), 3.85 (s, 3H), 2.78 (s, 3H), 2.20 (s, 3H). $^{13}$C NMR (CDCl$_3$, 125 MHz) δ (ppm) = 167.3, 166.7, 153.5, 148.4, 138.3, 132.8, 132.3, 132.0, 129.3, 127.8, 121.5, 120.2, 115.9, 114.1, 58.3, 51.6, 17.6, 17.2.

**1,2-Bis(4-acetylphenyl)diazene(2j)** [11] Red solid (72%): m.p.: 213-215°C. $^1$H NMR (400 MHz, CDCl$_3$); δ (ppm) = 8.13 (d, *J*= 8Hz, 1H), 8.01 (d, *J*= 12Hz, 1H), 2.68 (s, 6H). $^{13}$C NMR (CDCl$_3$, 125 MHz) δ (ppm) = 197.5, 154.9, 139.0, 129.5, 123.3, 27.0.

**1,2-bis(3,4-dimethylphenyl)diazene (2l).**[7] Yellow solid (76%): m.p.: 157-157 °C. $^1$H NMR (500 MHz, CDCl$_3$); δ (ppm) = 7.69 (s, 2H), 7.65 (d, *J* = 10 Hz, 2H). 7.27 (d, *J* = 10 Hz, 2H), 2.35 (s, 6H), 2.33 (s, 6H). $^{13}$C NMR (CDCl$_3$, 125 MHz) δ (ppm) = 151.2, 139.9, 137.4, 130.2, 123.3, 120.7, 19.9, 19.8.

**1,2-bis(2,5-dimethylphenyl)diazene (2m).**[8] Yellow solid (70%): m.p.: 115-117 °C. $^1$H NMR (500 MHz, CDCl$_3$); δ (ppm) = 7.41 (s, 2H), 7.23-7.16 (m, 4H), 2.69 (s, 6H), 2.38 (s, 6H). $^{13}$C NMR (CDCl$_3$, 125 MHz) δ (ppm) = 151.0, 136.0, 134.8, 131.4, 131.1, 116.2, 21.1, 17.2.

**1,2-bis(3,4-dimethoxyphenyl)diazene (2n)** [9] Yellow solid (72%): m.p.: 190-192°C. $^1$H NMR (500 MHz, CDCl$_3$); δ (ppm) = 7.61-7.59 (m, 2H), 7.52 (d, *J*= 5Hz, 2H), 7.01 (d, *J*= 10Hz, 1H), 6.99 (s, 1H), 3.99 (s, 6H), 3.97 (s, 6H). $^{13}$C NMR (CDCl$_3$, 125 MHz) δ (ppm) = 151.5, 149.6, 146.9, 120.2, 110.5, 102.1, 56.1, 56.0.

**1-phenyl-2-(*p*-tolyl)diazene (4a).** [1,10] orange solid (90%): m.p.: 65-67 °C. $^1$H NMR (400 MHz, CDCl$_3$); δ (ppm) = 7.92-7.83 (m, 4H), 7.54-7.44 (m, 3H), 7.32 (d, *J* = 8Hz, 2H), 2.44 (s, 3H). $^{13}$C NMR (CDCl$_3$, 125 MHz) δ (ppm) = 152.8, 150.9, 141.6, 130.8, 129.8, 129.1, 122.9, 122.8, 21.6.

**1-(4-methoxyphenyl)-2-phenyldiazene (4b).** [1,10] Red solid (92%): m.p.: 52-54 °C. $^1$H NMR (400 MHz, CDCl$_3$); δ (ppm) = 7.93 (d, *J* = 10Hz, 4H), 7.88 (d, *J* = 10Hz, 3H), 7.50 (m, *J*= 15 Hz, 2H), 7.43 (t, *J* = 15Hz, 1H), 7.02 (d, *J* = 10Hz, 2H), 3.89 (s, 3H). $^{13}$C NMR (CDCl$_3$, 125 MHz) δ (ppm) = 162.1, 152.8, 147.0, 130.4, 129.0, 124.8, 122.6, 114.2, 55.6.

**1-(4-iodophenyl)-2-phenyldiazene (4c).**[4,10] Yellow solid (85%): m.p.: 91-93°C. $^1$H NMR (400 MHz, CDCl$_3$); δ (ppm) = 7.91 (m, *J* = 10Hz, 2H), 7.86 (d, *J* = 10Hz, 2H), 7.65 (d, *J* = 10Hz, 2 H), 7.53-7.47 (m, 3H). $^{13}$C NMR (CDCl$_3$, 125 MHz) δ (ppm) = 152.5, 152.0, 138.4, 131.4, 129.2, 124.5, 123.0, 97.6.

**1-(4-bromophenyl)-2-phenyldiazene (4d).**[1,10] Yellow solid (88%): m.p.: 90-92°C. $^1$H NMR (400 MHz, CDCl$_3$); δ (ppm) = 7.93-7.90 (m, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8 Hz, 2 H), 7.55-7.49 (m, 3 H). $^{13}$C NMR (CDCl$_3$, 125 MHz) δ (ppm) = 152.5, 151.4, 132.3, 131.3, 129.2, 125.4, 124.4, 122.9.

**1-(4-chlorophenyl)-2-phenyldiazene (4e).** [1,10] Yellow solid (90%): m.p.: 81-83°C. $^1$H NMR (500 MHz, CDCl$_3$); δ (ppm) = 7.92-7.87 (m, 4H), 7.54-7.44 (m, 5H). $^{13}$C NMR (CDCl$_3$, 125 MHz) δ (ppm) = 152.5, 151.0, 136.9, 131.3, 129.3, 129.1, 124.1, 122.9.

**1-(4-fluorophenyl)-2-phenyldiazene (4f).** [1,10,12] Yellow solid (90%): m.p.: 76-78°C. $^1$H NMR (400 MHz, CDCl$_3$); δ (ppm) = 7.97-7.89 (m, 4H), 7.55-7.47 (m, 3H), 7.23-7.17 (m, 2H). $^{13}$C

NMR ($CDCl_3$, 125 MHz) δ ppm) = 164.3 (d, *J* = 250.0 Hz), 152.5, 149.1 (d, *J* = 2.5 Hz), 131.0, 129.1, 124.8 (d, *J* = 8.7 Hz), 122.8, 116.0 (d, *J* = 22.5 Hz).

**1-(4-nitrophenyl)-2-phenyldiazene (4g).**[5,6] Yellow solid (45%): m.p.: 134-135°C. $^1$H NMR (500 MHz, $CDCl_3$); δ (ppm) = 8.39(d, *J* = 10 Hz , 2H), 8.04 (d, *J* = 10 Hz, 2H), 7.99-7.96 (m, 2H), 7.57-7.54 (m, 3H). $^{13}$C NMR ($CDCl_3$, 125 MHz) δ (ppm) = 155.7, 152.4, 148.7, 132.4, 129.3, 124.7, 123.4.

**1,2-diphenylhydrazine (3a).**[12] Yellow solid (70%).$^1$H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.22 (t, *J*=8 Hz, 4H), 6.86-6.82 (m, 5H), 5.61 (s, 2H).

**1-phenyl-2-(p-tolyl)hydrazine (3b).**[1] Pale yellow solid (70%).$^1$H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.25-7.19 (m, 2H), 7.0-7.01 (m, 2H), 6.86-6.75 (m, 5 H), 5.59 (s, 1H), 5.53 (s, 1H), 2.25 (s, 3H).

**1-(4-methoxyphenyl)-2-phenylhydrazine (3c).**[1] Pale yellow solid (72%).$^1$H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.25-7.20 (m, 2H), 6.86-6.80 (m, 7H), 5.58 (s, 1H), 5.44 (s, 1H), 3.75 (s, 3H).

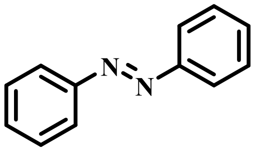
**1-(4-iodophenyl)-2-phenylhydrazine (3d).**[1] Yellow solid (65%).$^1$H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.24-7.20 (m, 4H), 6.87-6.82 (m, 5H), 5.63 (s, 2H)

**1-(4-bromophenyl)-2-phenylhydrazine (3e).**[1] Yellow solid (68%). $^1$H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.31-7.28 (m, 2H), 7.24-7.20 (m, 2H), 6.87-6.75 (m, 5H), 5.64 (s, 2H).

**1-(4-Chlorophenyl)-2-phenylhydrazine (3f).**[1] Yellow solid (62%). $^1$H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.23-7.15 (m, 4H), 6.86-6.79 (m, 5H), 5.64 (s, 2H).

**1-(4-fluorophenyl)-2-phenylhydrazine (3g).**[1] Yellow solid (60%). $^1$H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.24-7.20 (m, 2H), 6.92 (t, *J*= 8Hz, 2H), 6.86-6.79 (m, 5H), 5.63 (s, 1H), 5.55 (s, 1H).

**1-(4-nitrophenyl)-2-phenylhydrazine (3h).**[13] Yellow solid (52%). $^1$H NMR (500 MHz, $CDCl_3$); δ (ppm) = 7.94-7.90 (m, 2H), 7.54-7.48 (m, 1H), 7.24-7.15 (m, 3H), 6.94-6.90 (m, 1H), 6.85-6.80 (m, 4H).



**2a**

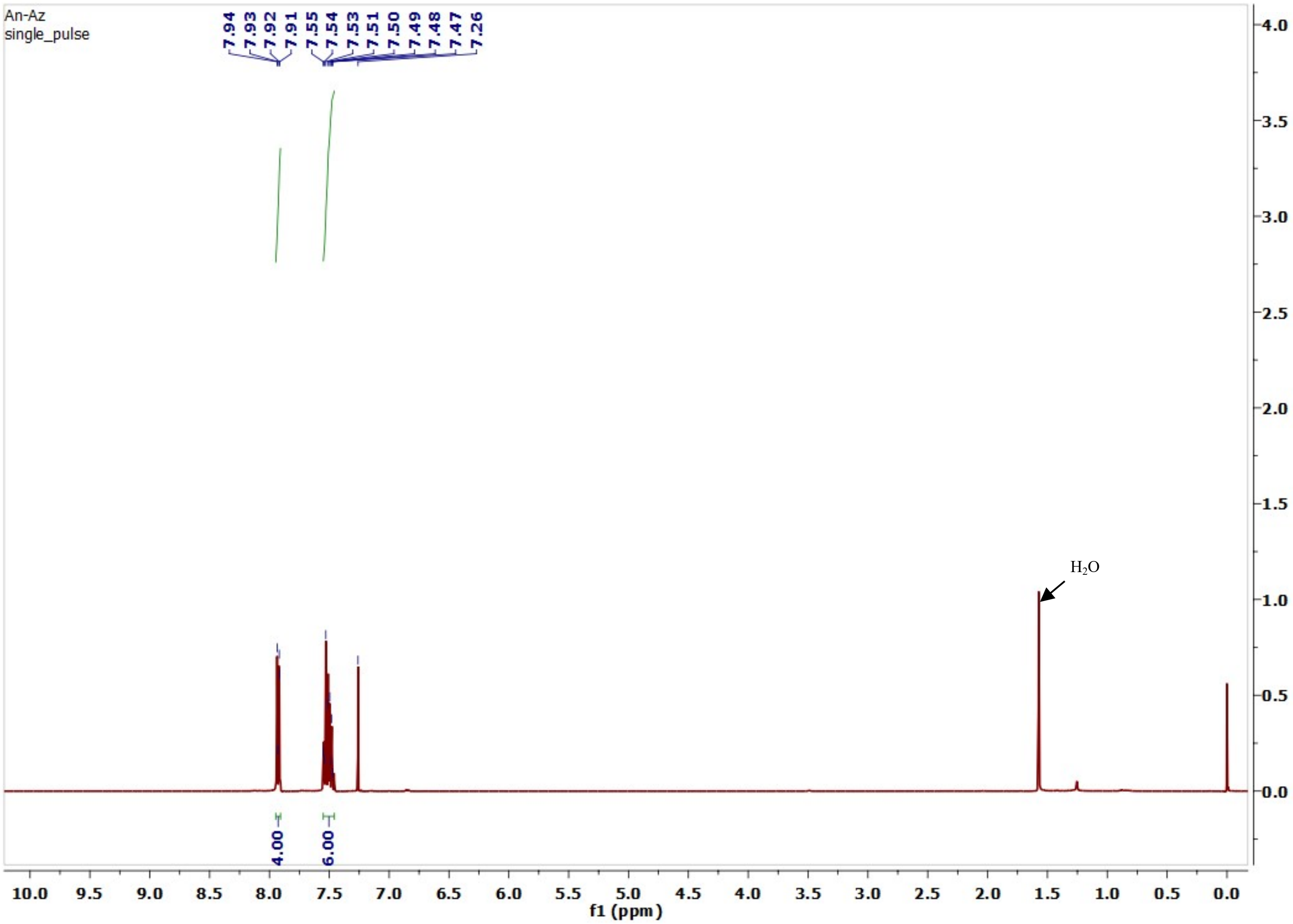
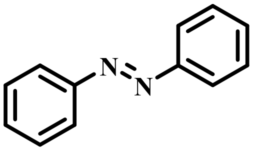


**Fig. S19**. $^1$H NMR (400 MHz, $CDCl_3$) spectrum of **2a**.



**2a**

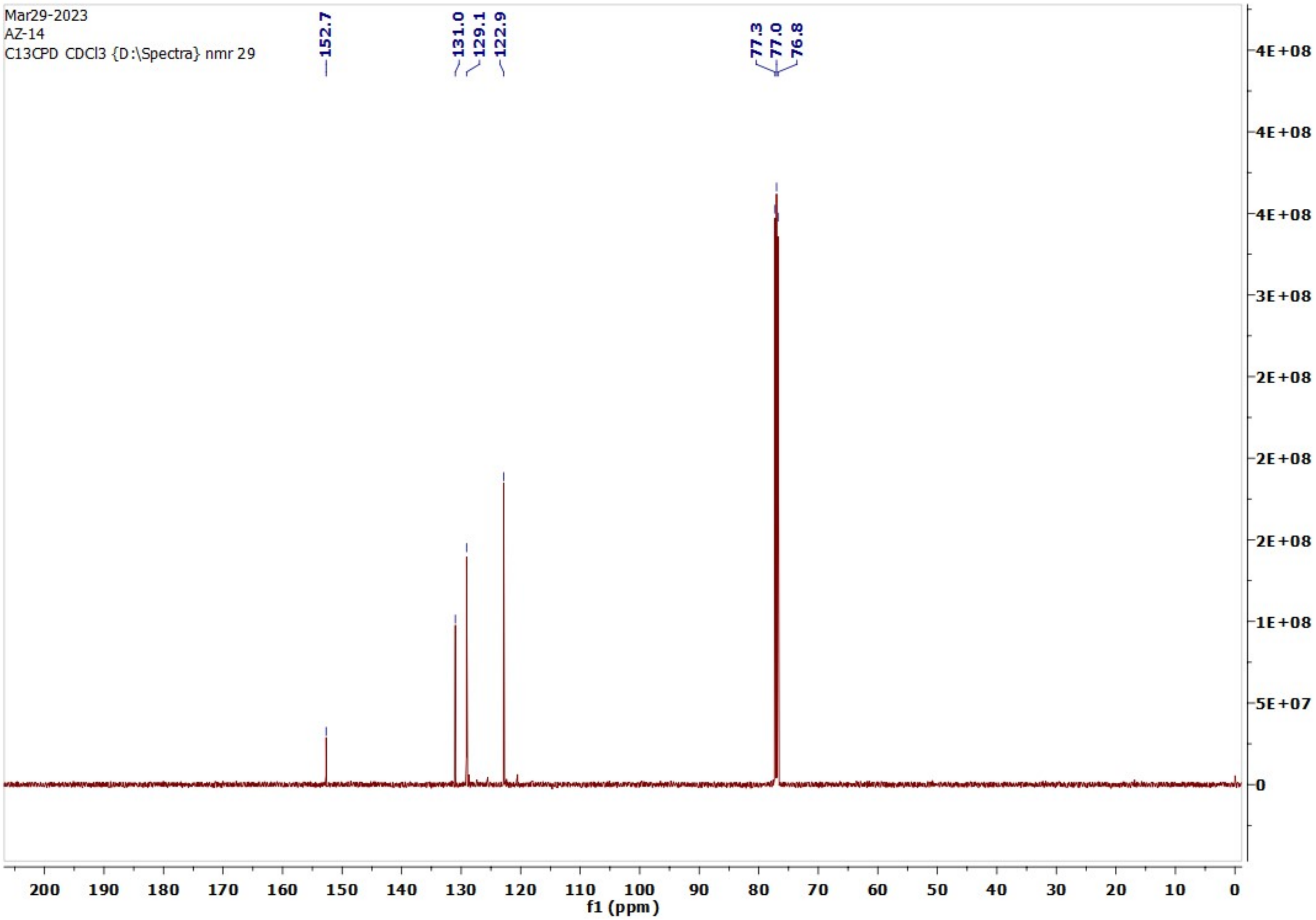
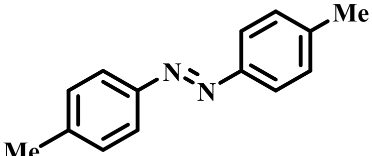


**Fig. S20**. $^{1}$C NMR (125 MHz, CDCl$_3$) spectrum of **2a**.



**2b**

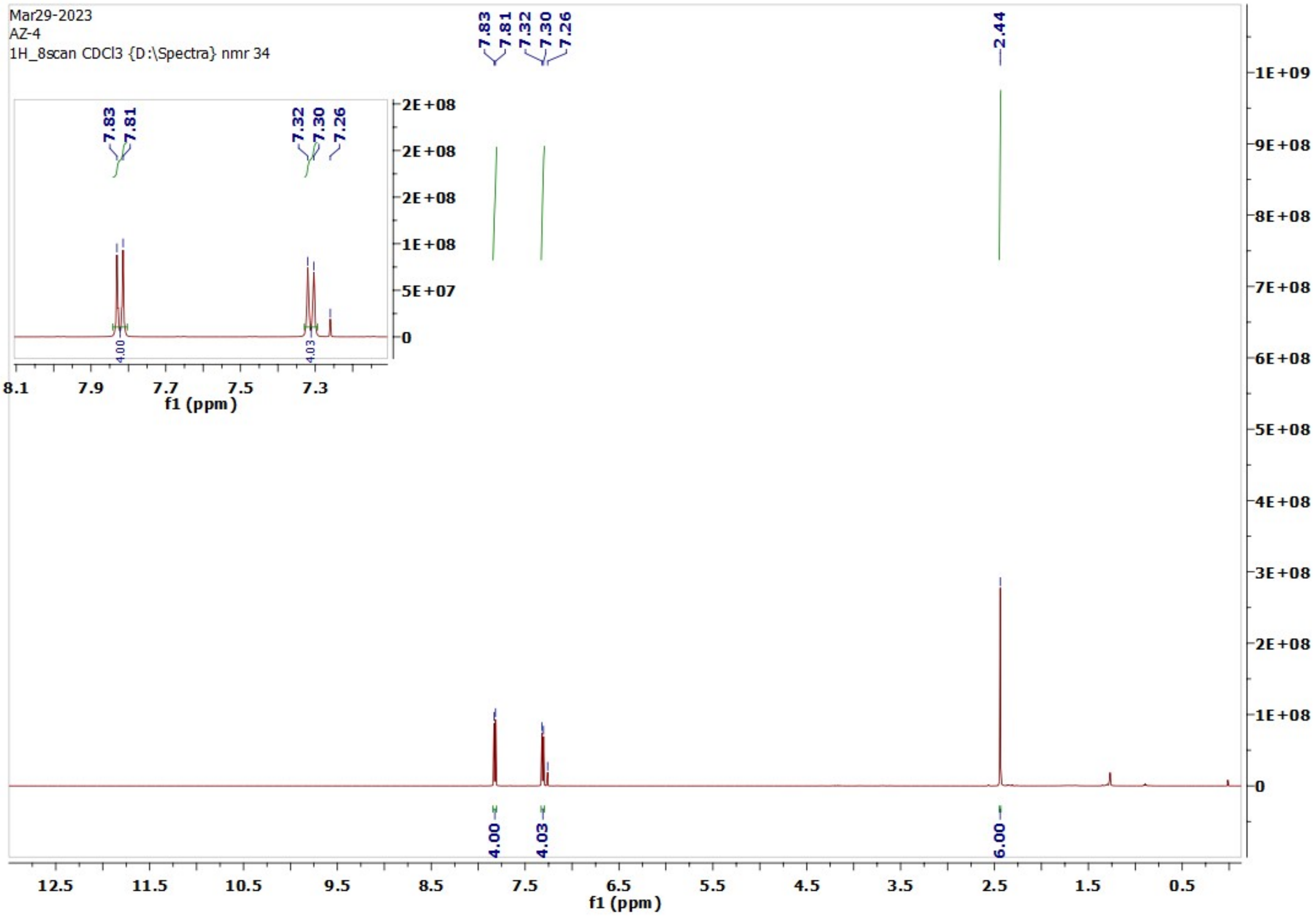
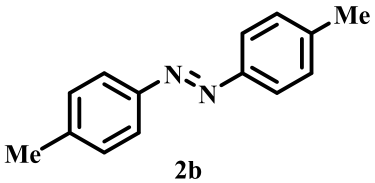


**Fig. S21**. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of **2b**.



**2b**

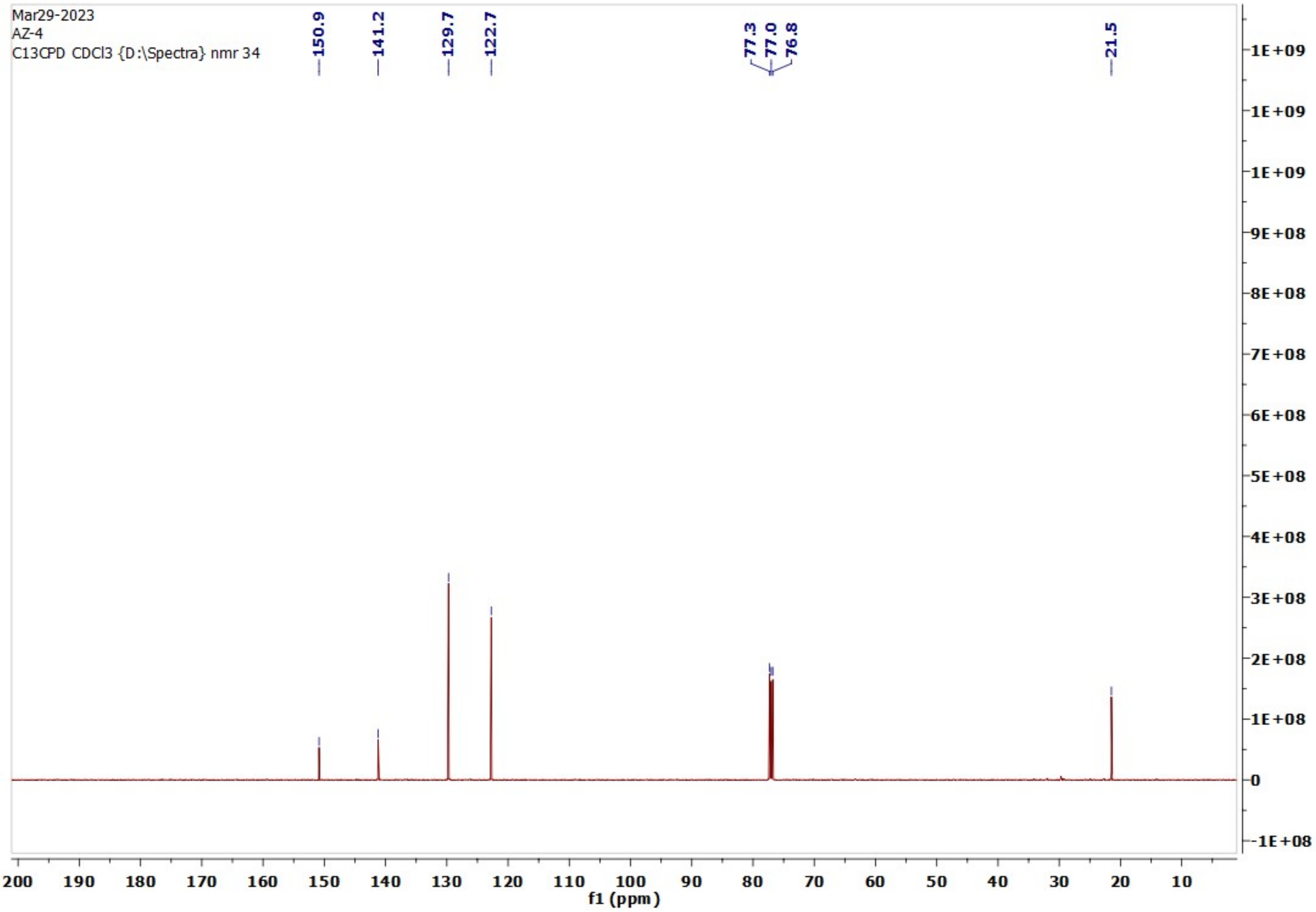
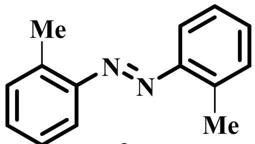


**Fig. S22**. $^{1}$C NMR (125 MHz, $CDCl_3$) spectrum of **2b**.



**2c**

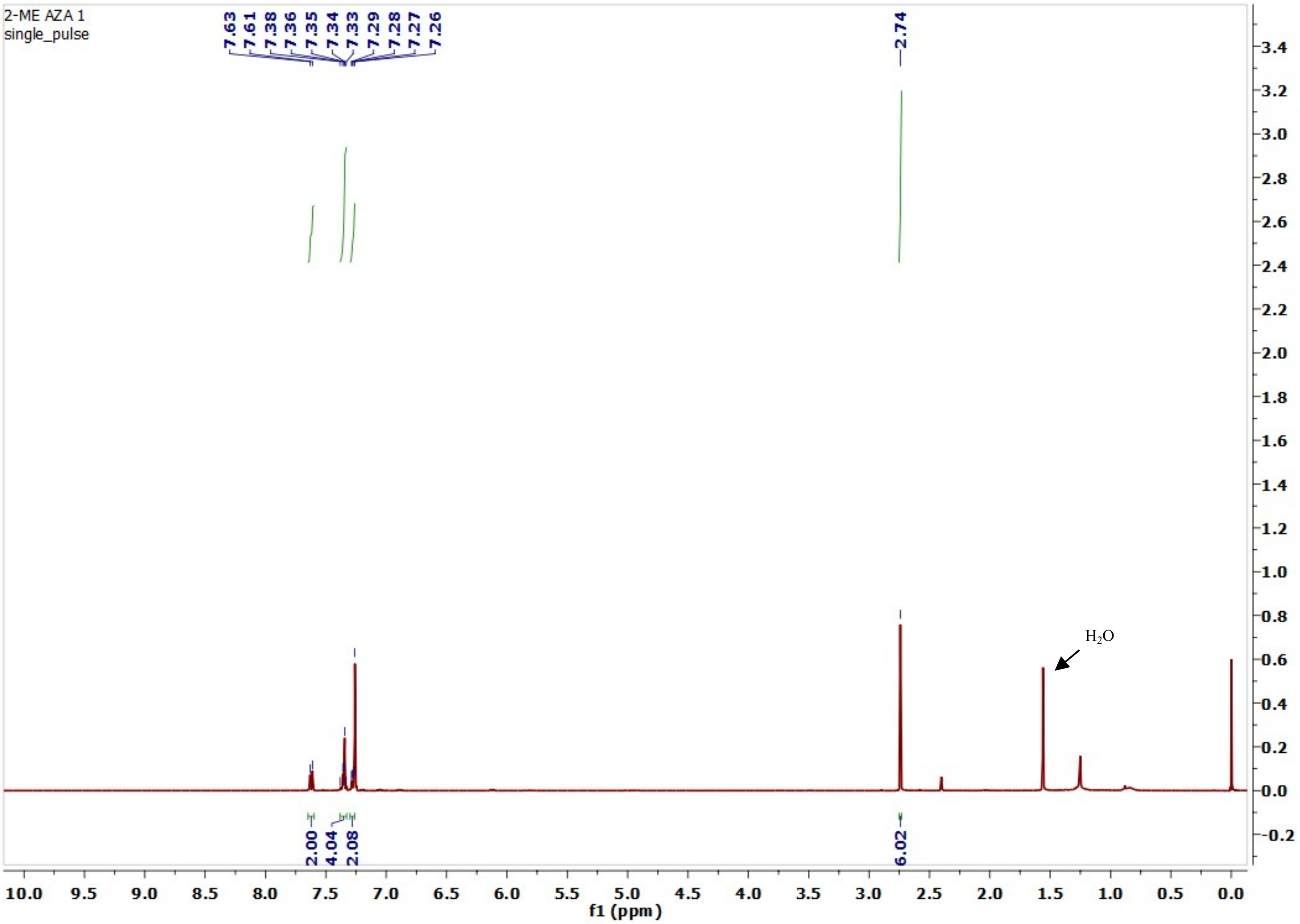
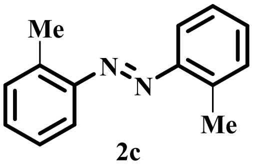


**Fig. S23**. $^1$H NMR (400 MHz, $CDCl_3$) spectrum of **2c**.



**2c**

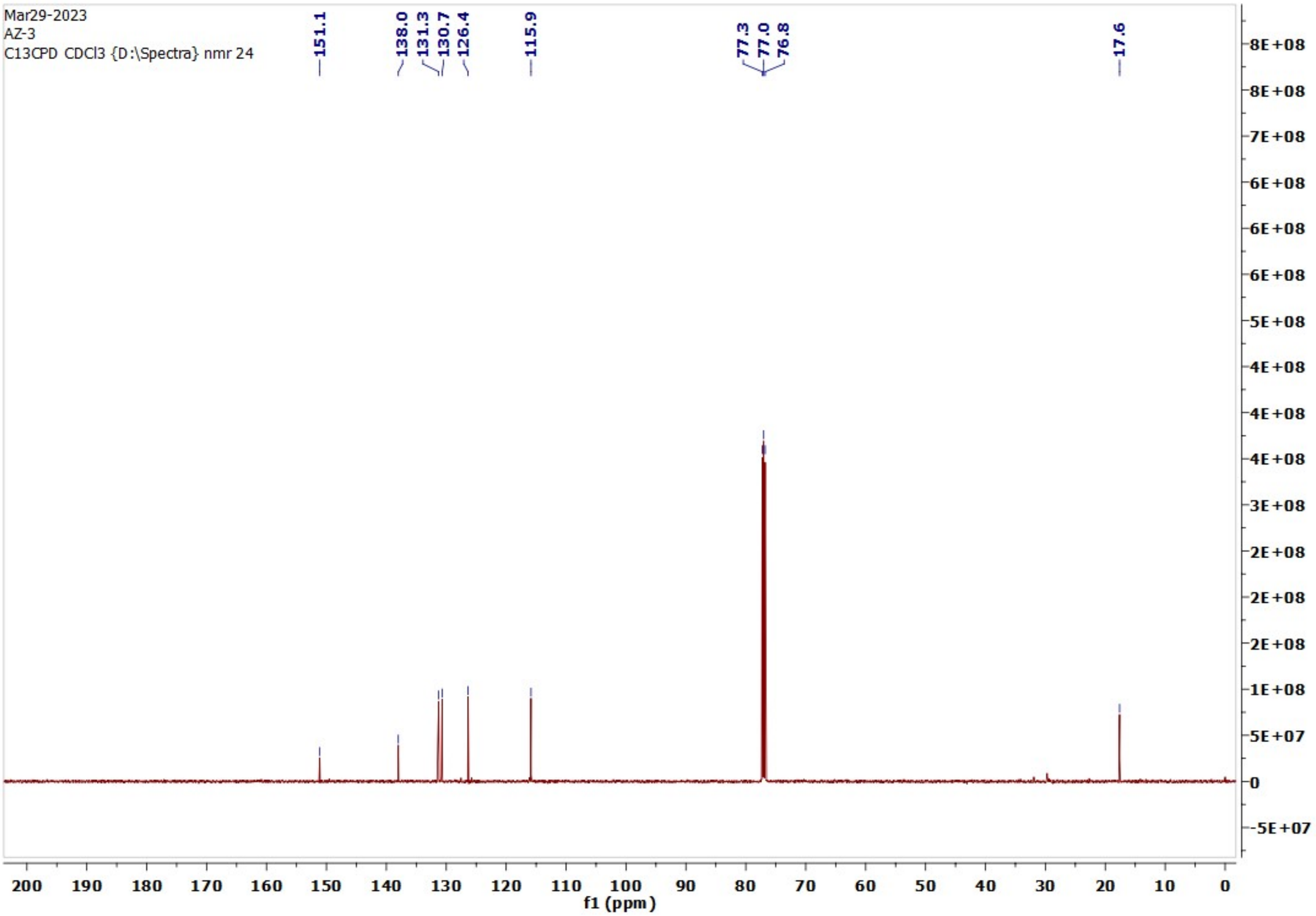
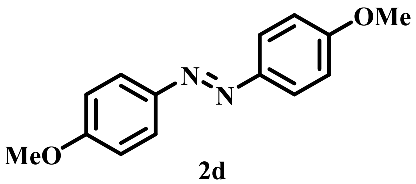


**Fig. S24**. $^{1}$C NMR (125 MHz, CDCl$_3$) spectrum of **2c**.



**2d**

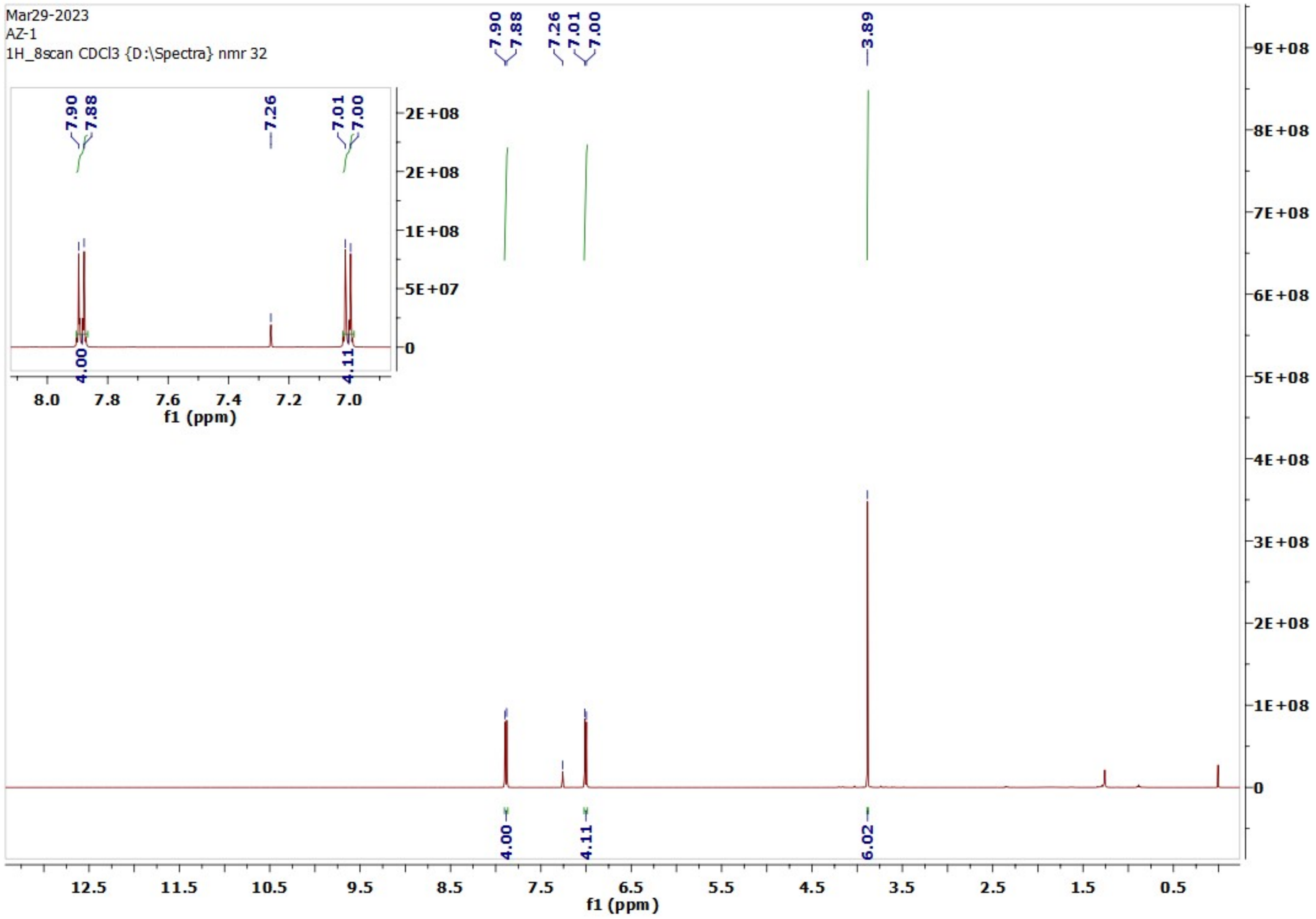
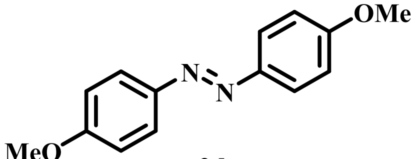


**Fig. S25**. $^1$H NMR (500 MHz, $CDCl_3$) spectrum of **2d**.



**2d**

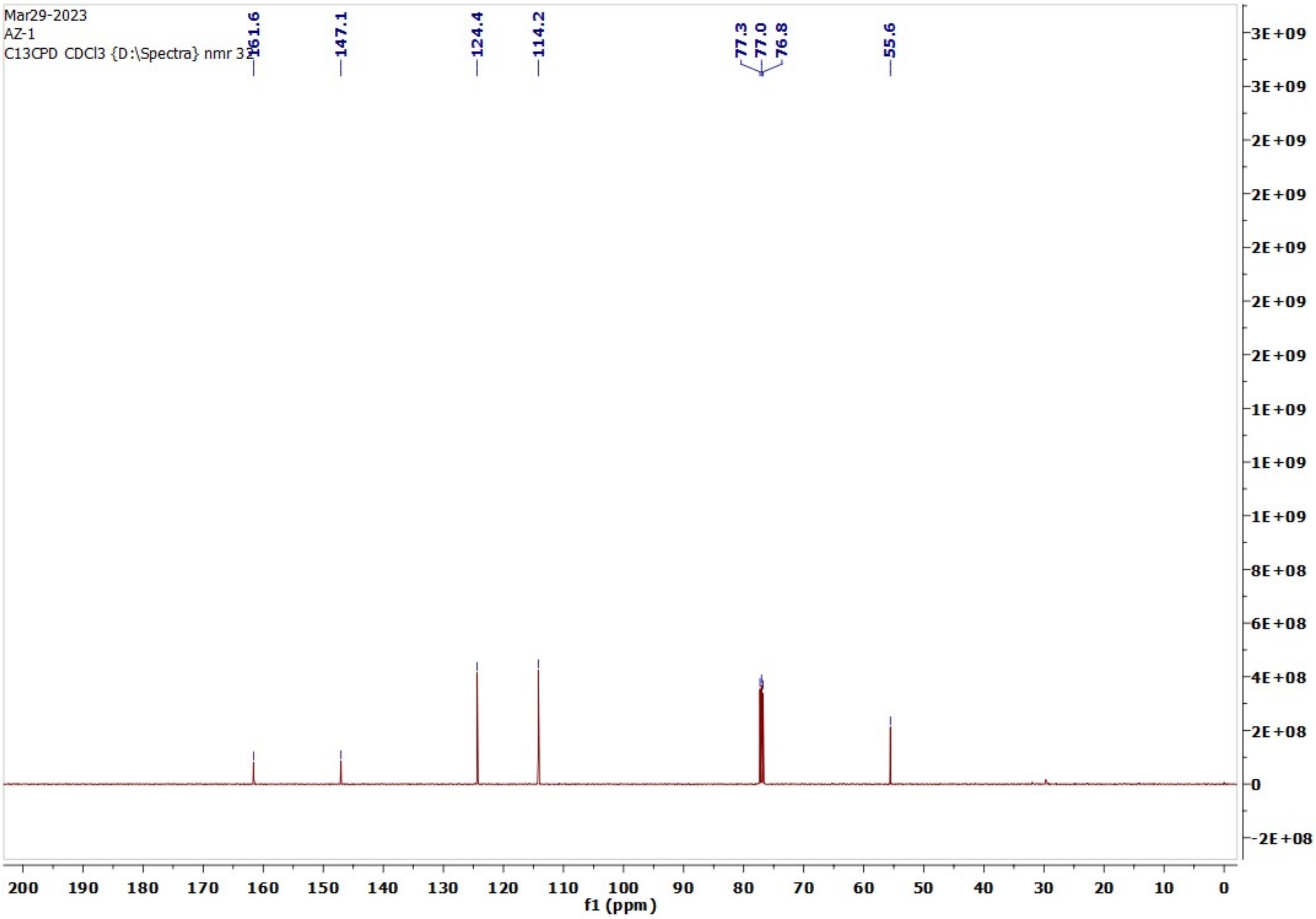
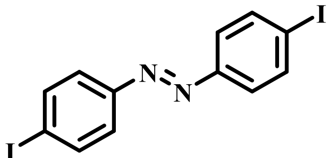


**Fig. S26**. $^{1}$C NMR (125 MHz, CDCl$_3$) spectrum of **2d**.



**2e**

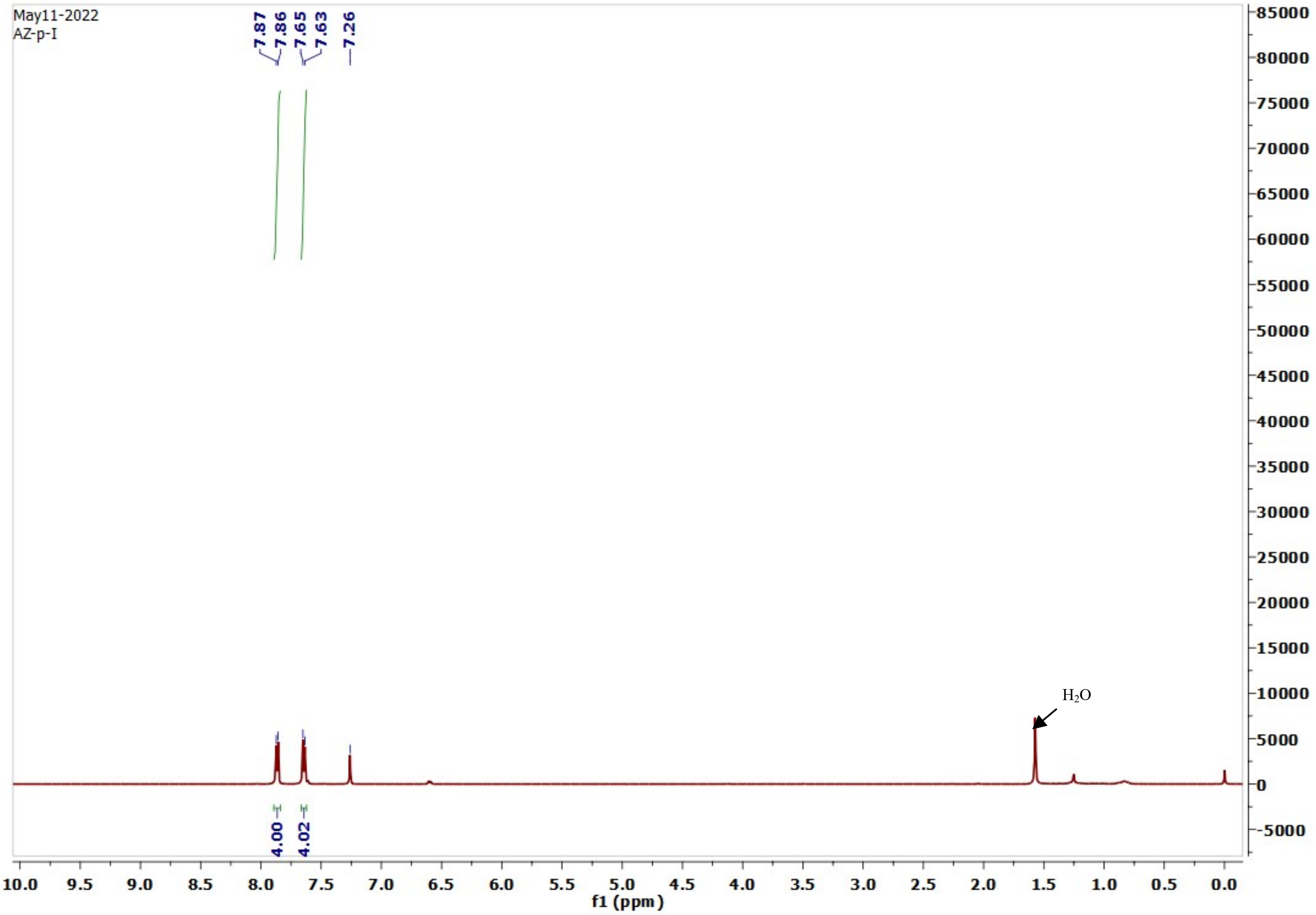
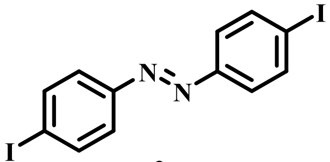


**Fig. S27**. $^1$H NMR (500 MHz, $CDCl_3$) spectrum of **2e**.



**2e**

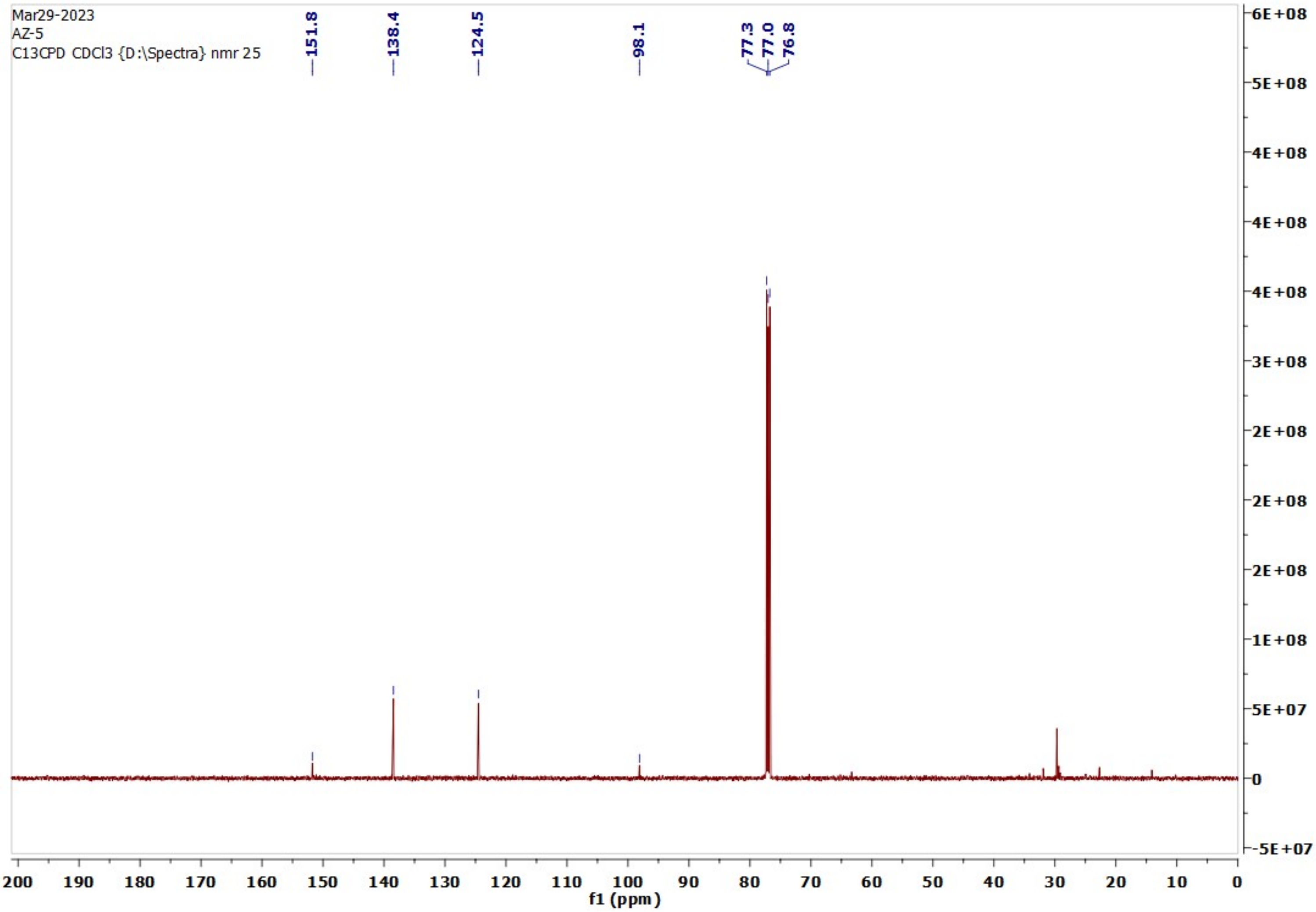
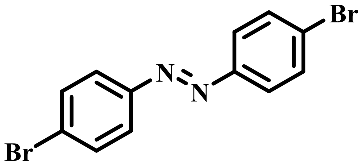


**Fig. S28**. $^1$C NMR (125 MHz, CDCl$_3$) spectrum of **2e**.



**2f**

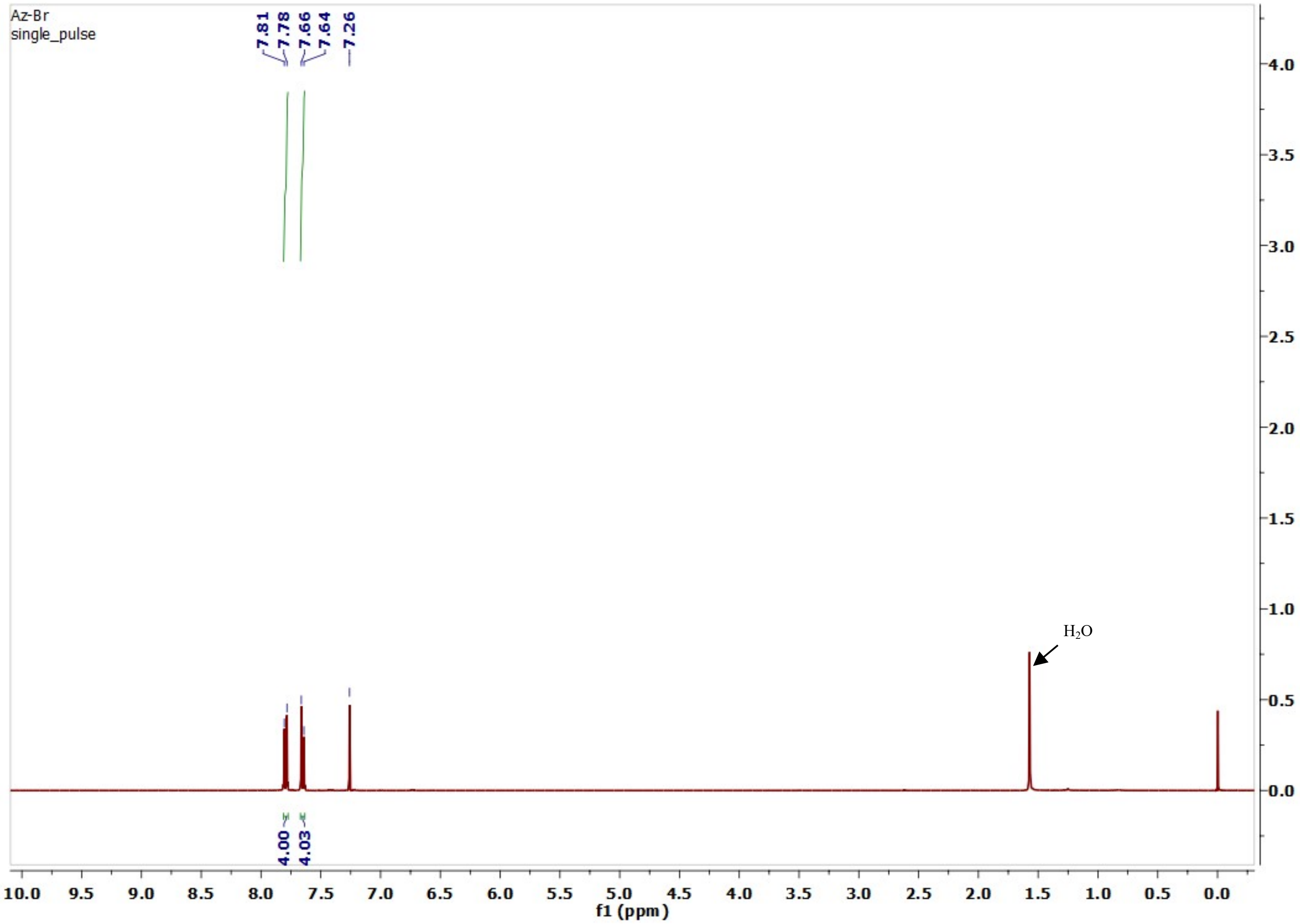
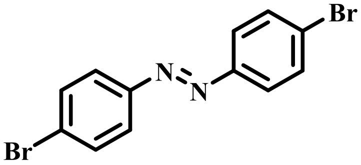


**Fig. S29**. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of **2f**.



**2f**

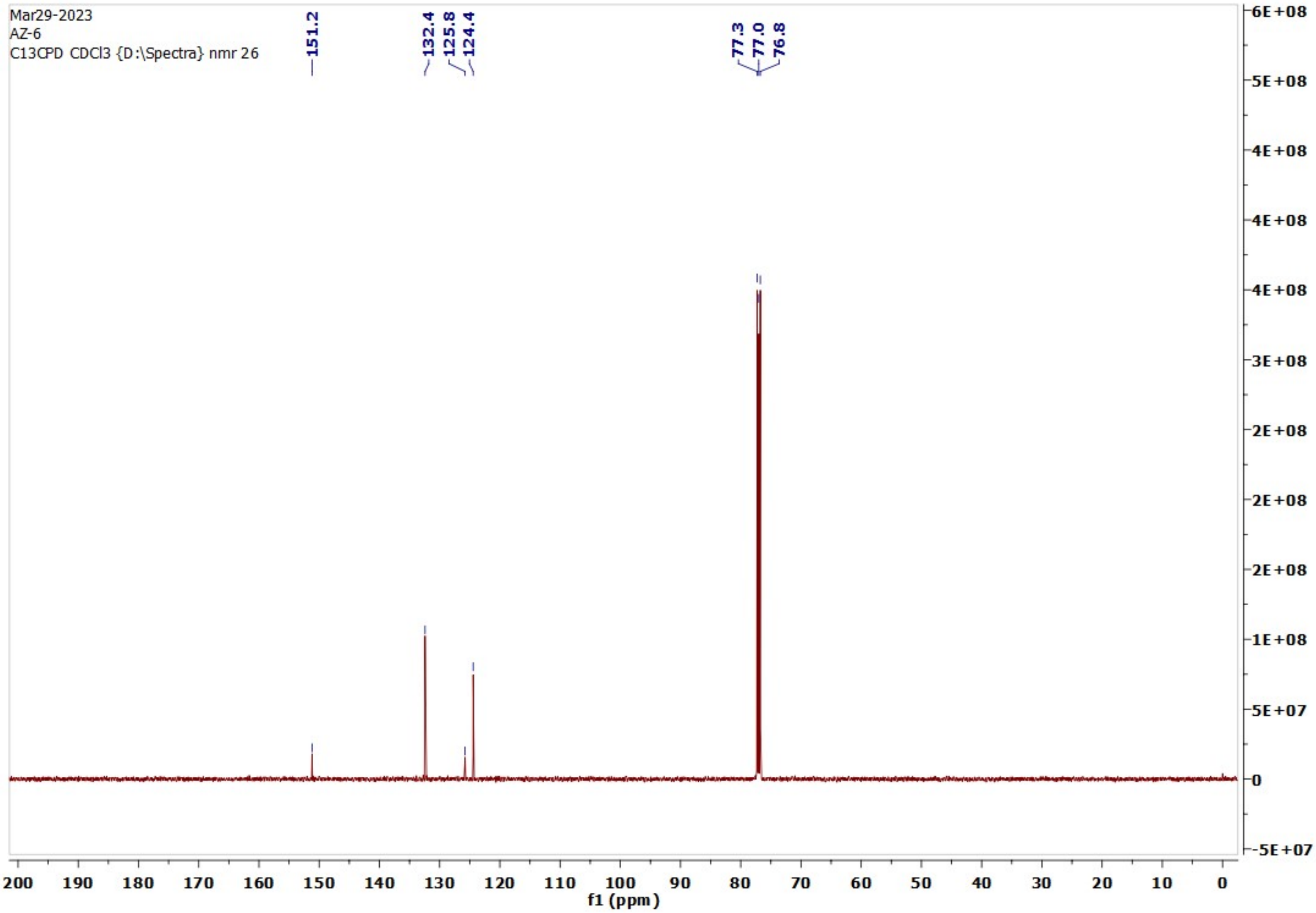
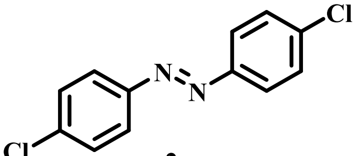


**Fig. S30**. $^{1}$C NMR (125 MHz, $CDCl_3$) spectrum of **2f**.



**2g**

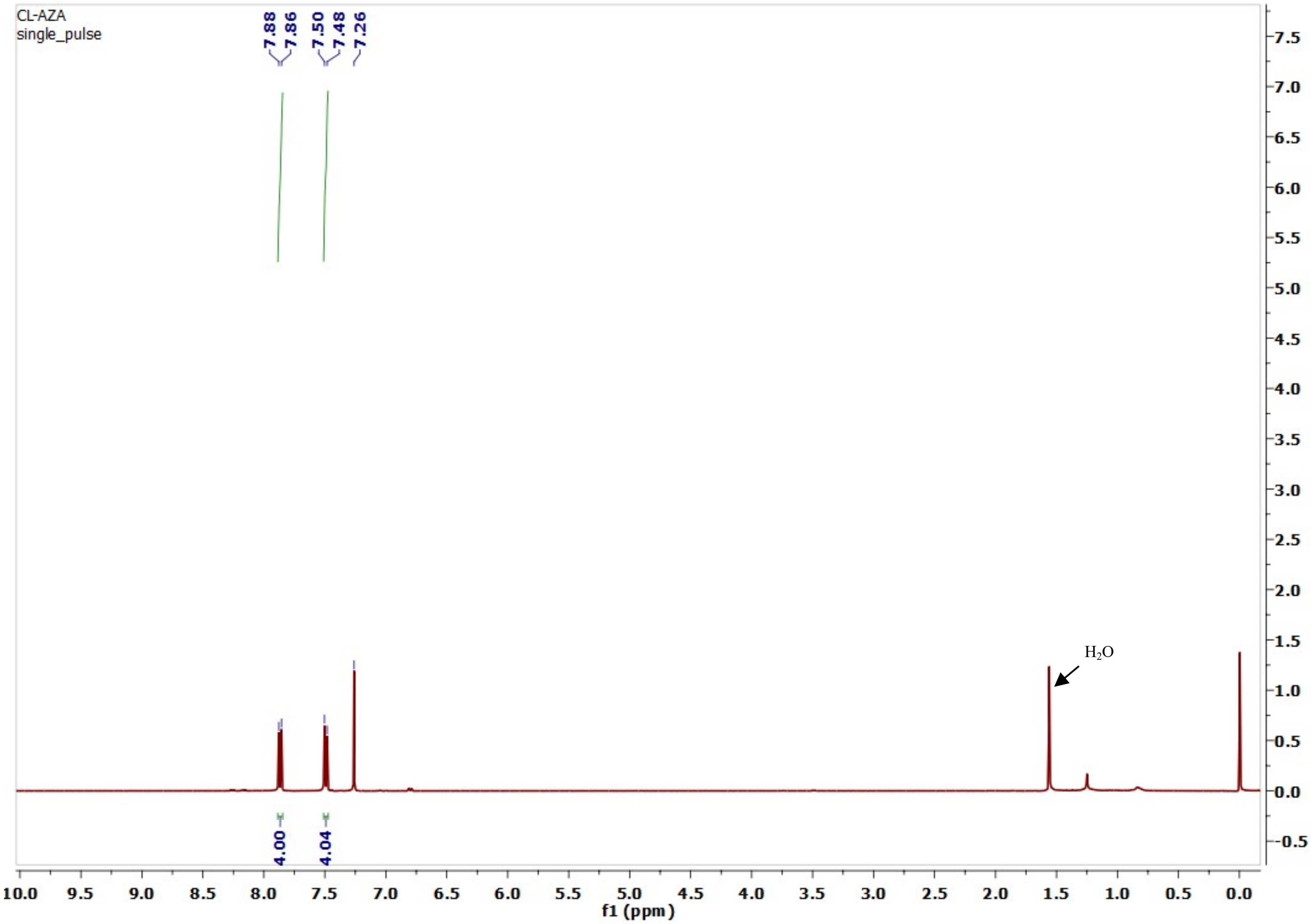
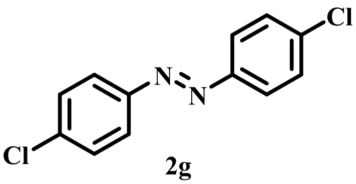


**Fig. S31**. $^1$H NMR (400 MHz, $CDCl_3$) spectrum of **2g**.



**2g**

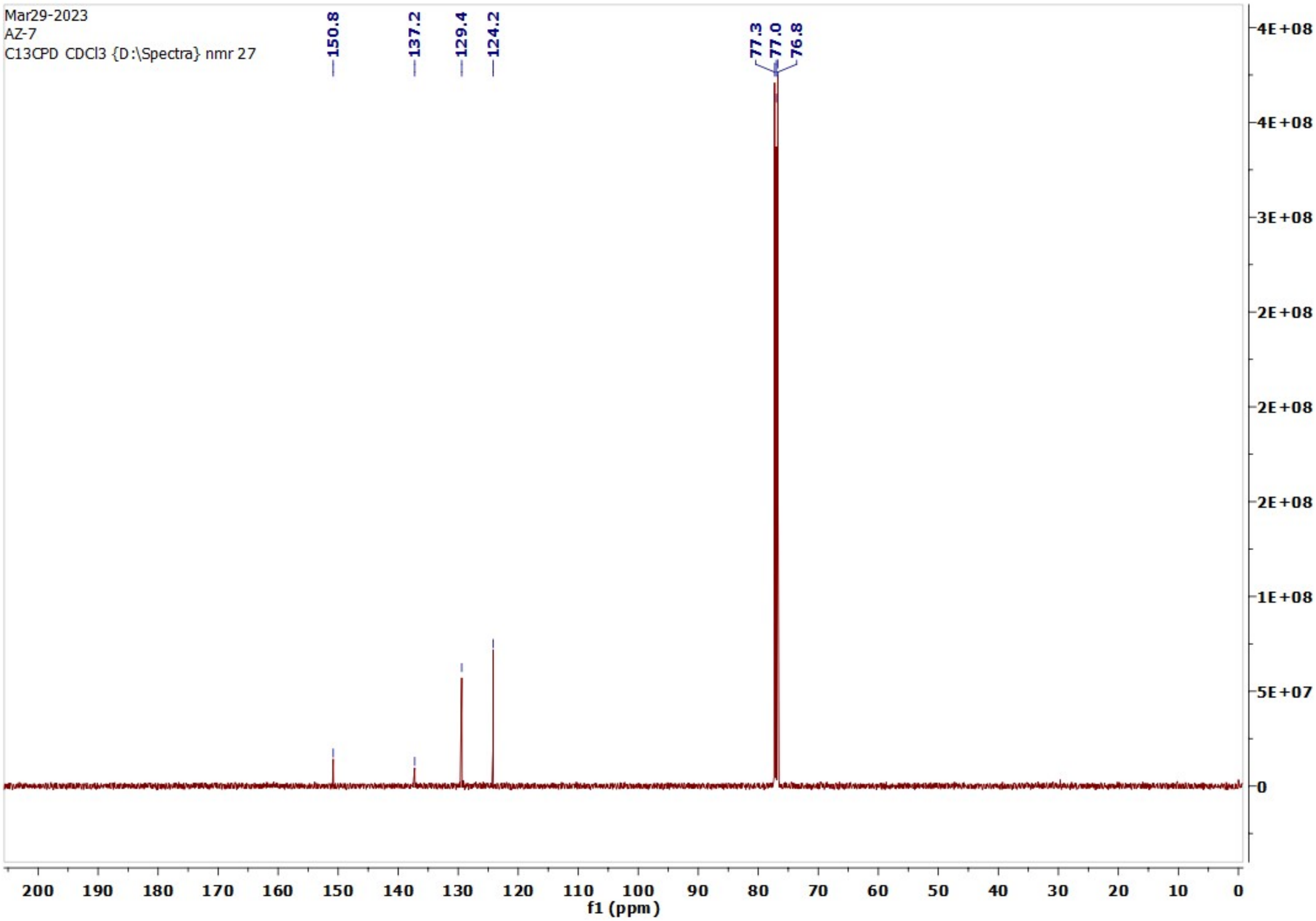
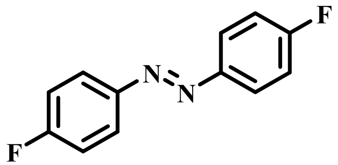


**Fig. S32**. $^{1}$C NMR (125 MHz, $CDCl_3$) spectrum of **2g**.



**2h**

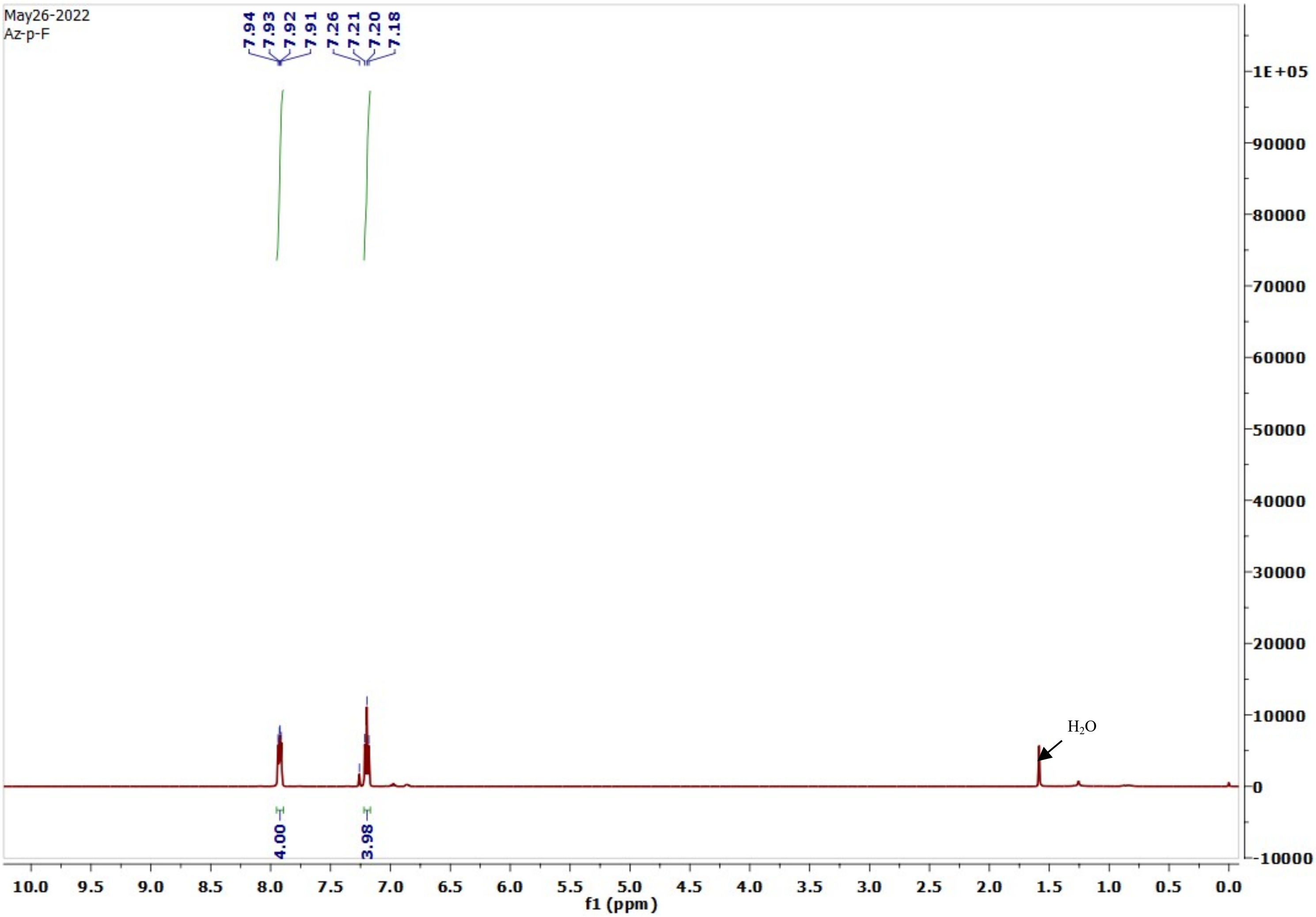
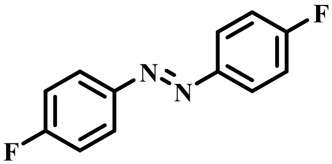


**Fig. S33**. $^1$H NMR (500 MHz, $CDCl_3$) spectrum of **2h**.



**2h**

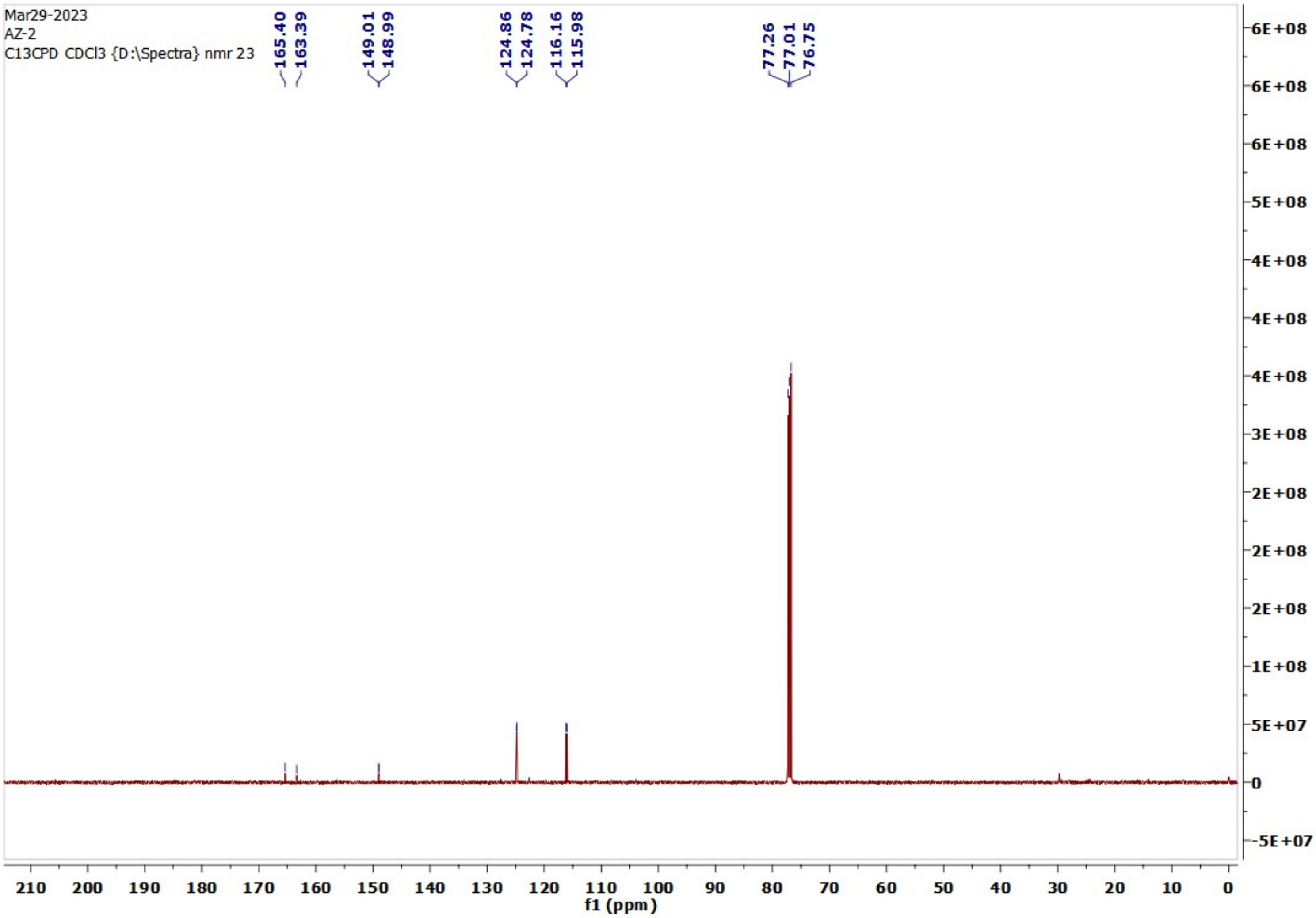
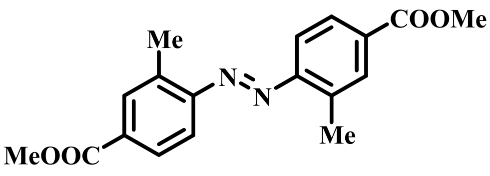


**Fig. S34**. $^{1}$C NMR (125 MHz, CDCl$_3$) spectrum of **2h**.



**2i**

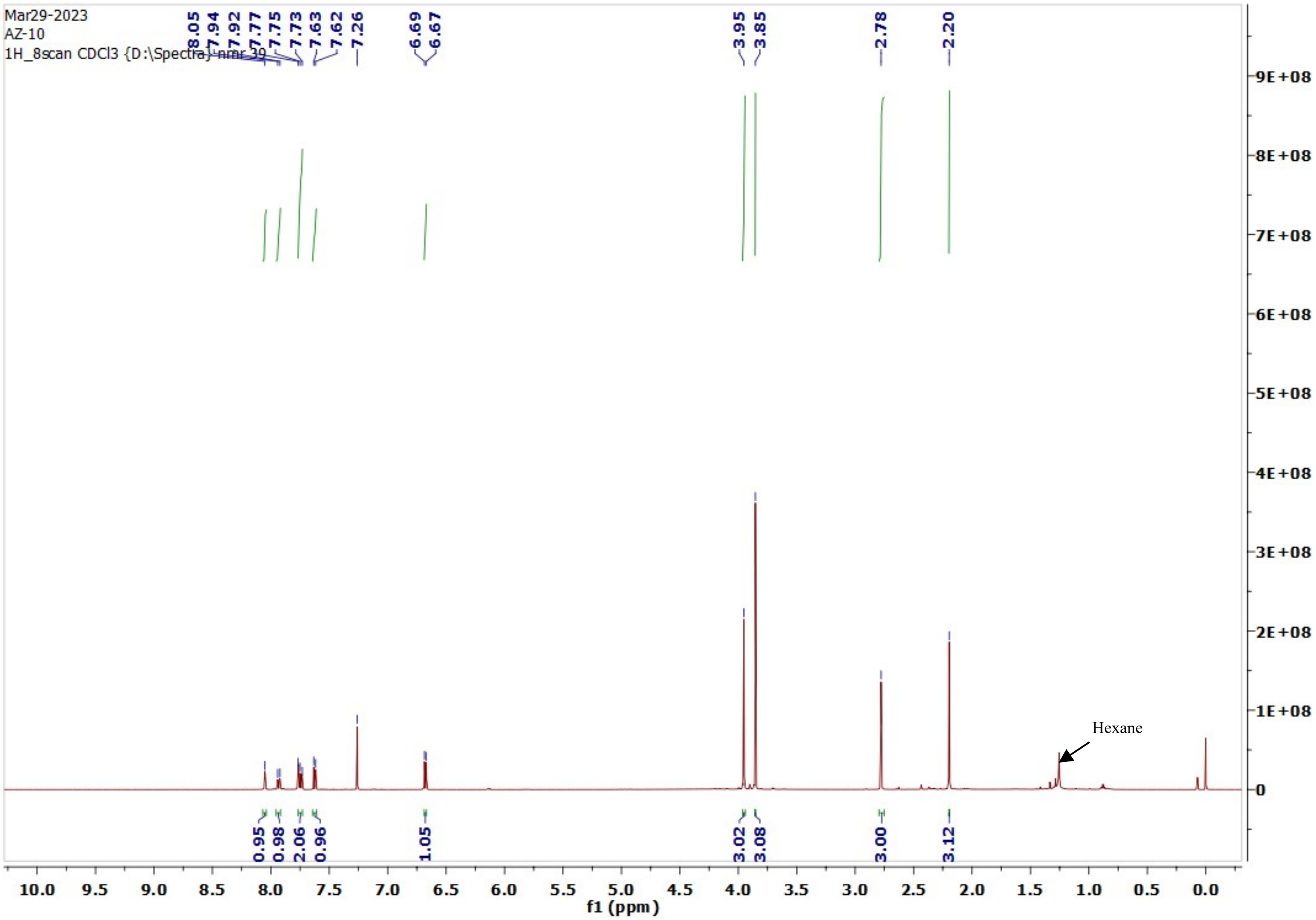
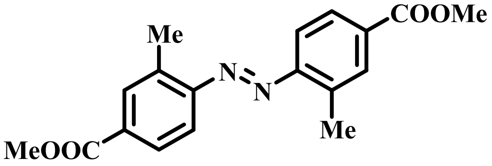


**Fig. S35**. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of **2i**.



**2i**

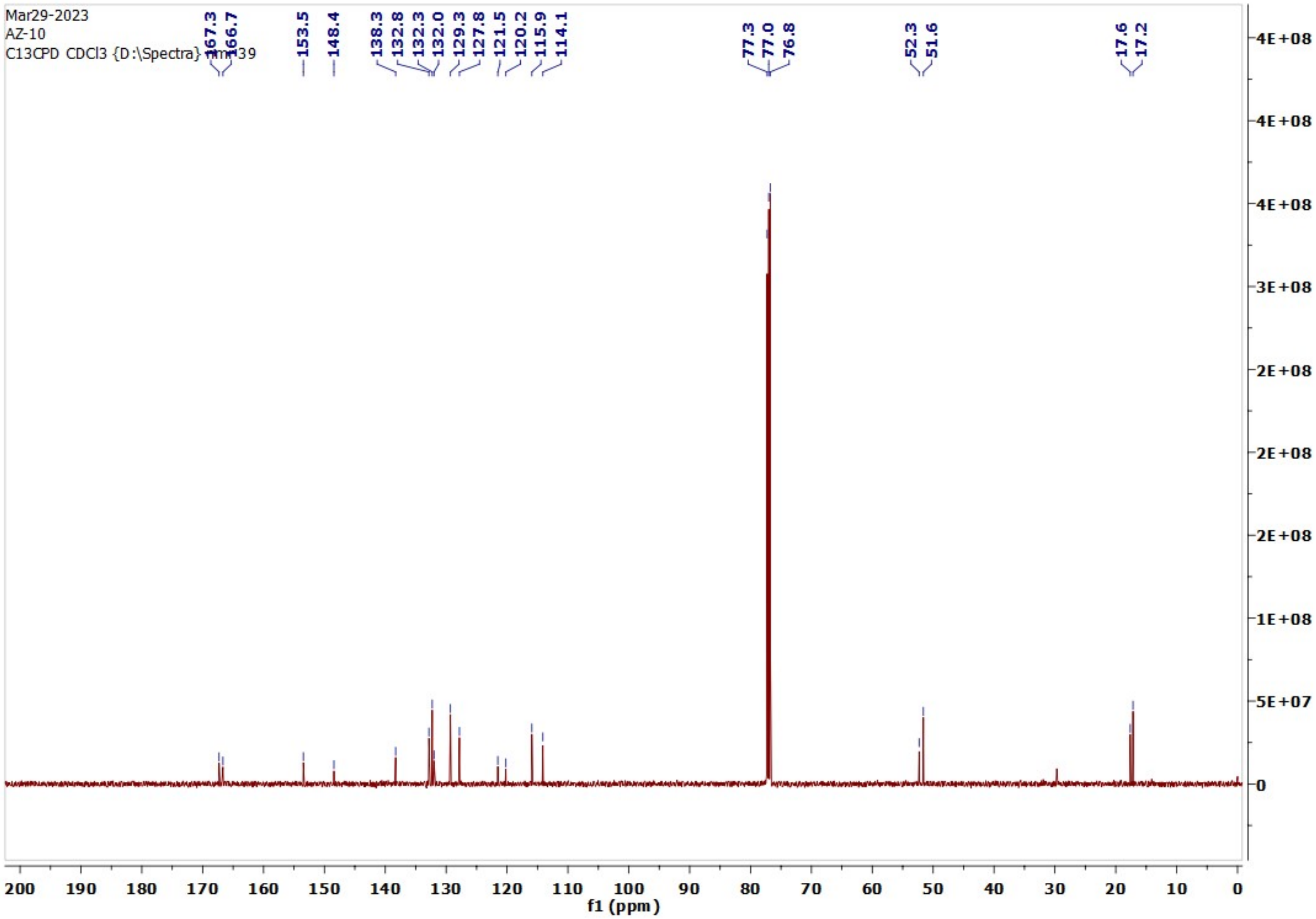


**Fig. S36**. $^{1}$C NMR (125 MHz, $CDCl_3$) spectrum of **2i**.

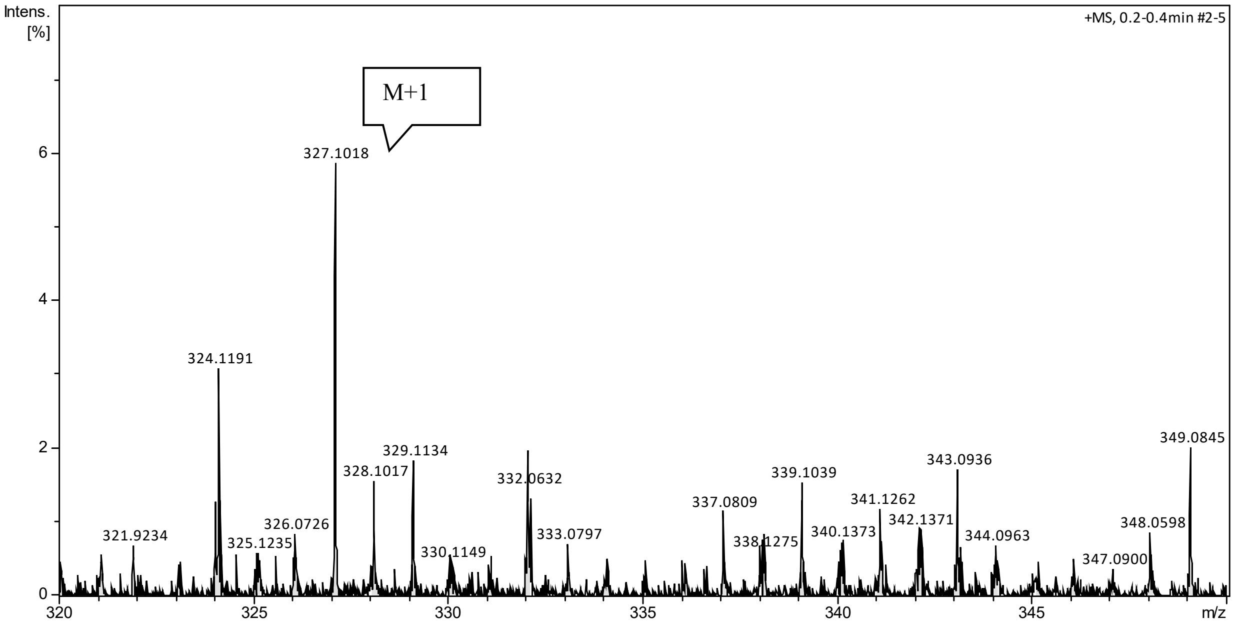
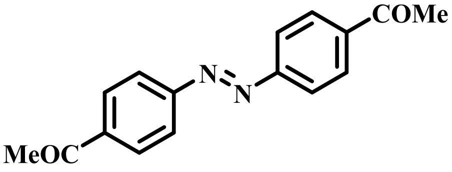


**Fig. S37**. ESI-MS of **2i.**



**2j**

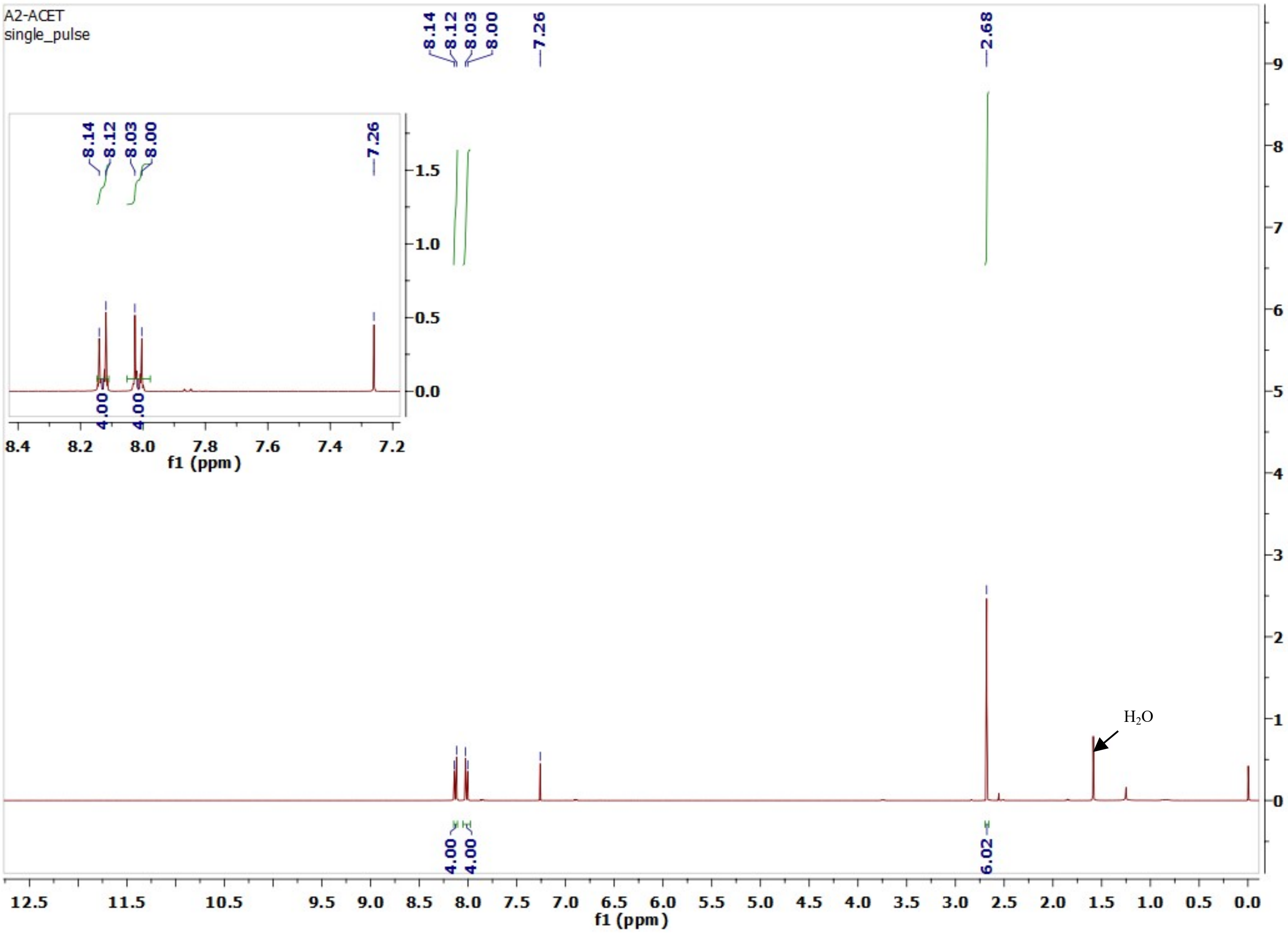
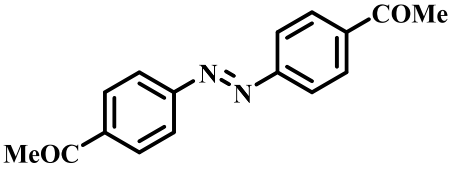


**Fig. S38**. ${}^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **2j.**



**2j**

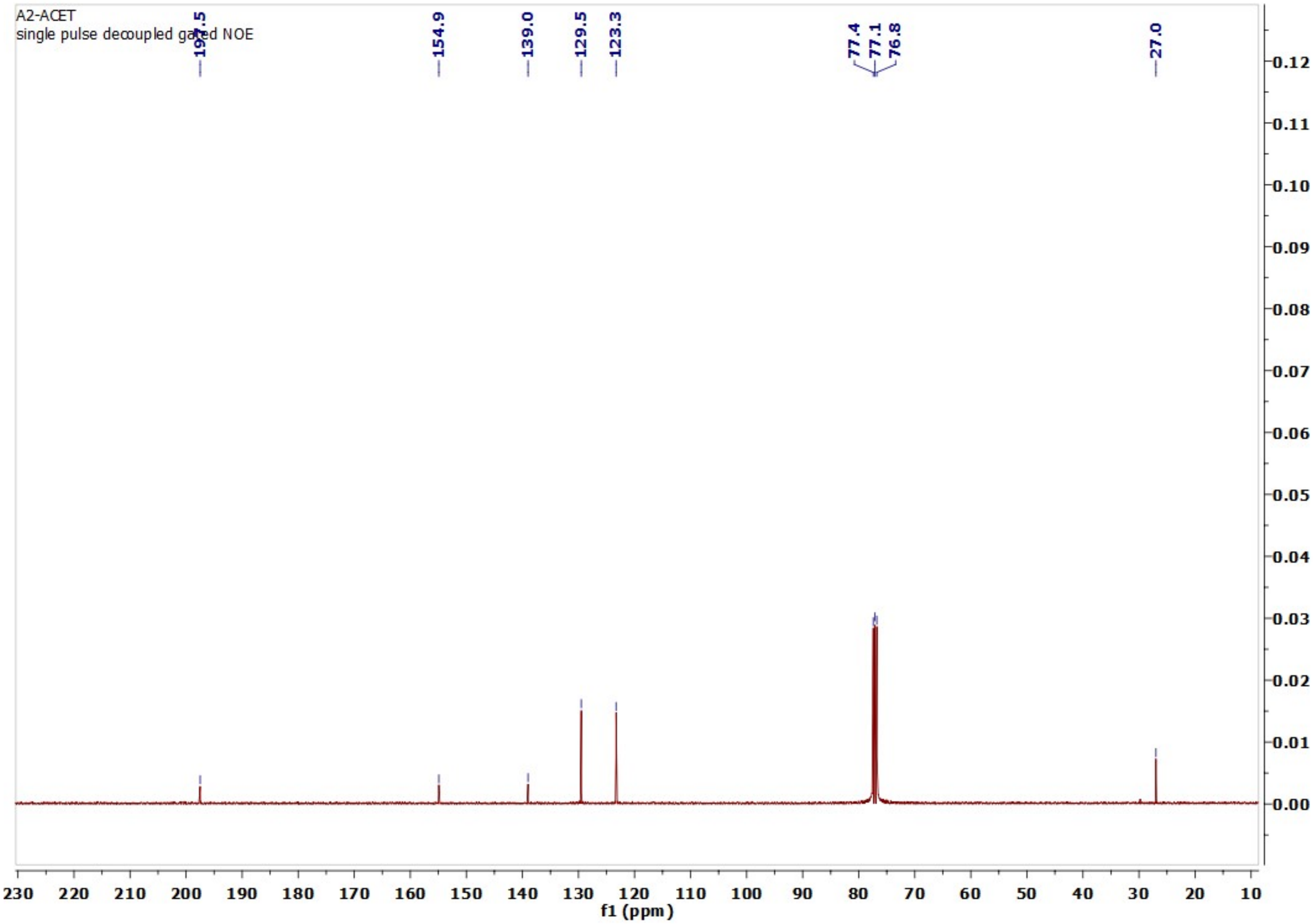
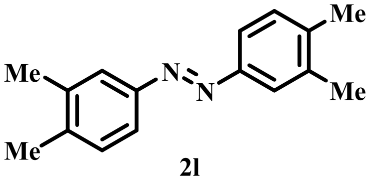


**Fig. S39**. $^{1}$C NMR (100 MHz, CDCl$_3$) spectrum of **2j.**



**2l**

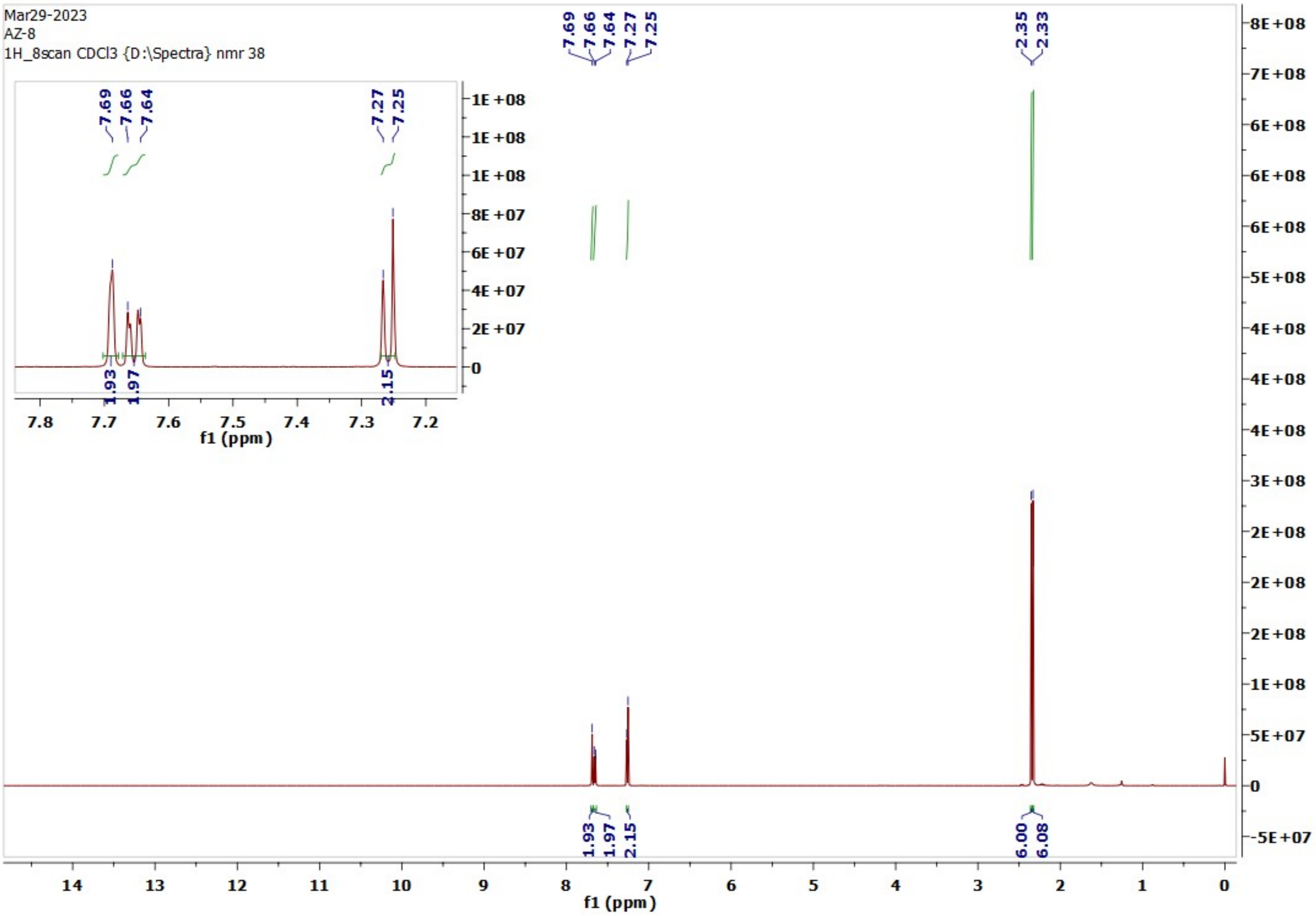
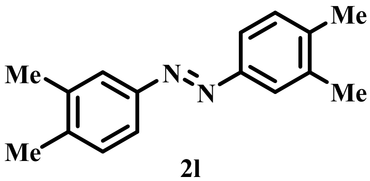


**Fig. S40**. $^1H$ NMR (500 MHz, $CDCl_3$) spectrum of **2l**.



**2l**

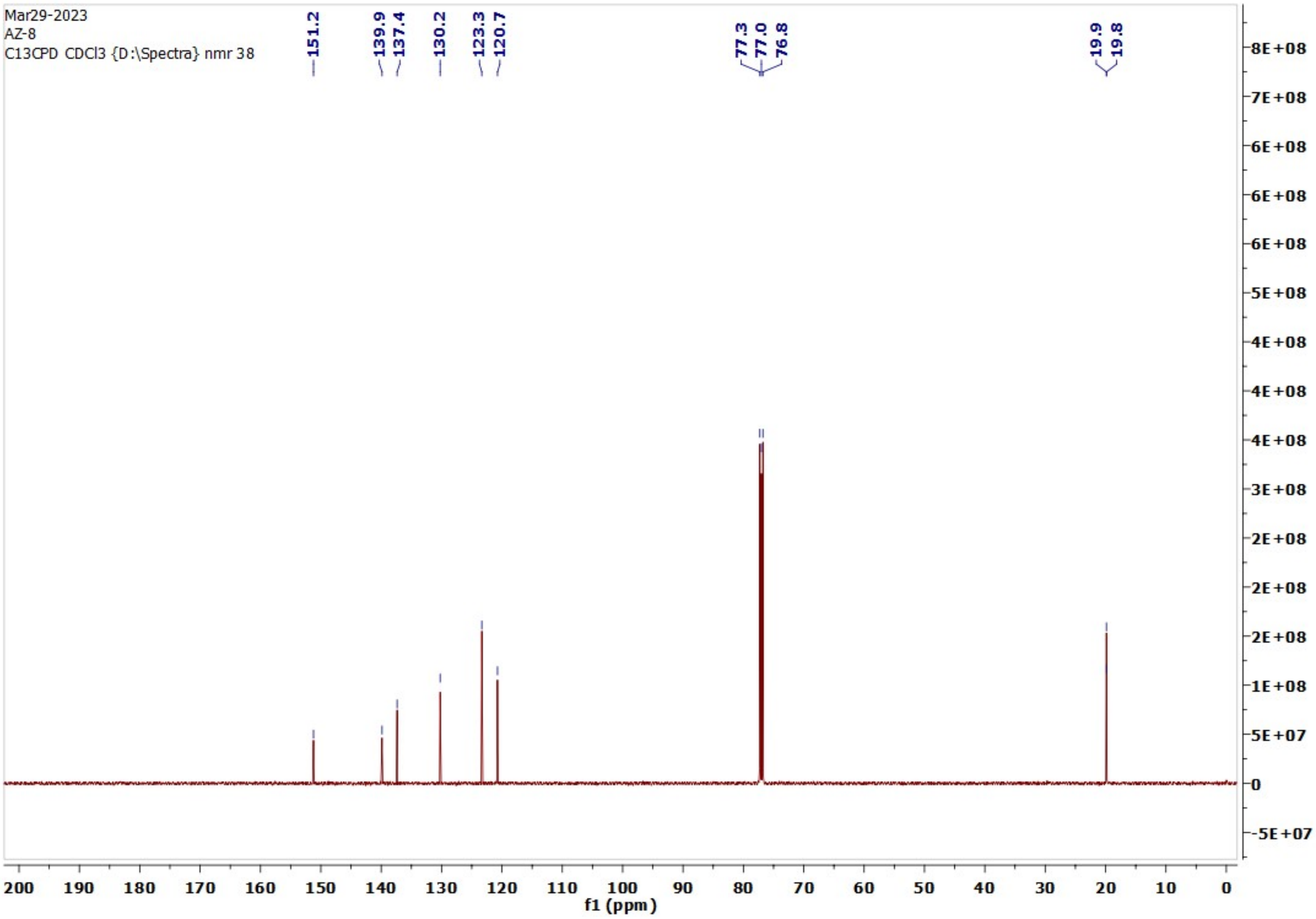
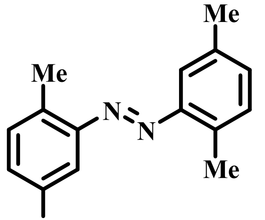


**Fig. S41**. $^{1}$C NMR (125 MHz, $CDCl_3$) spectrum of **2l**.



**2m**

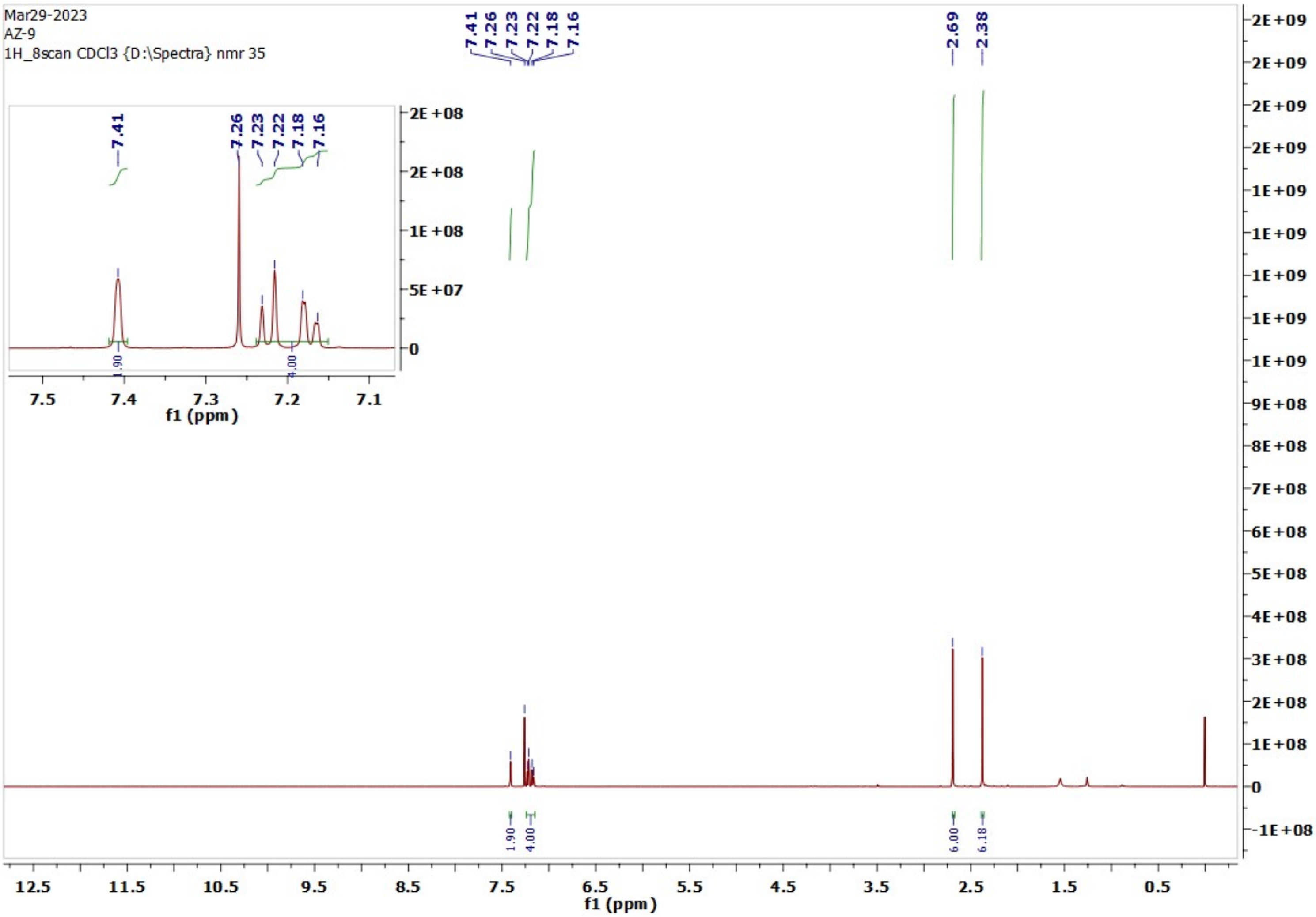
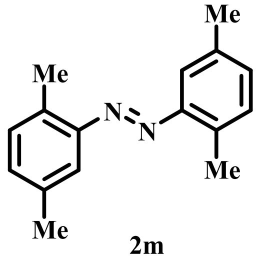


**Fig. S42**. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of **2m**.



**2m**

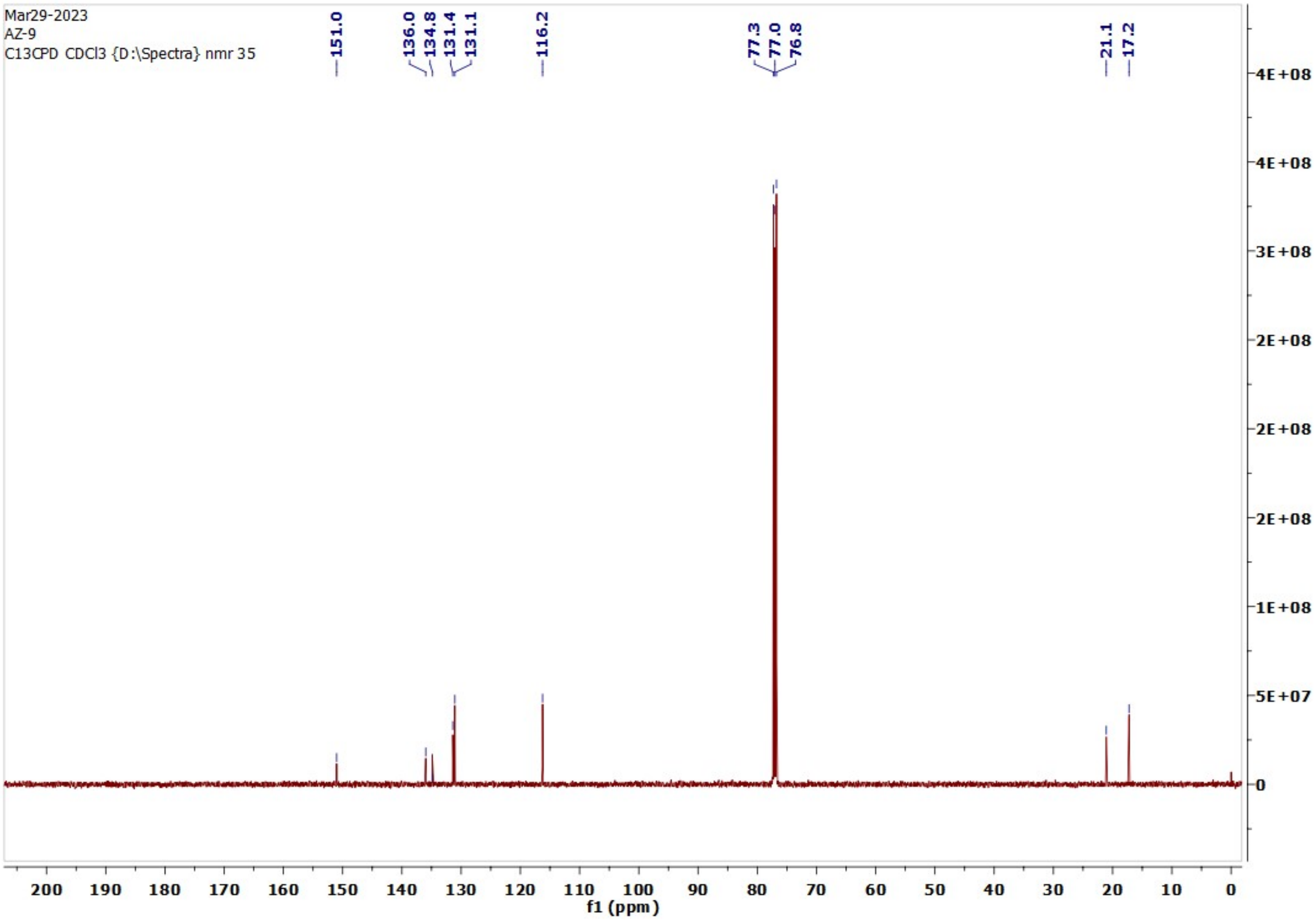
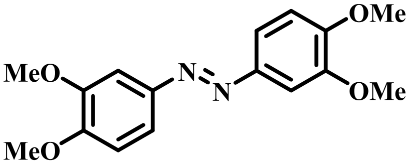


**Fig. S43**. $^{1}$C NMR (125 MHz, $CDCl_3$) spectrum of **2m**.



**2n**

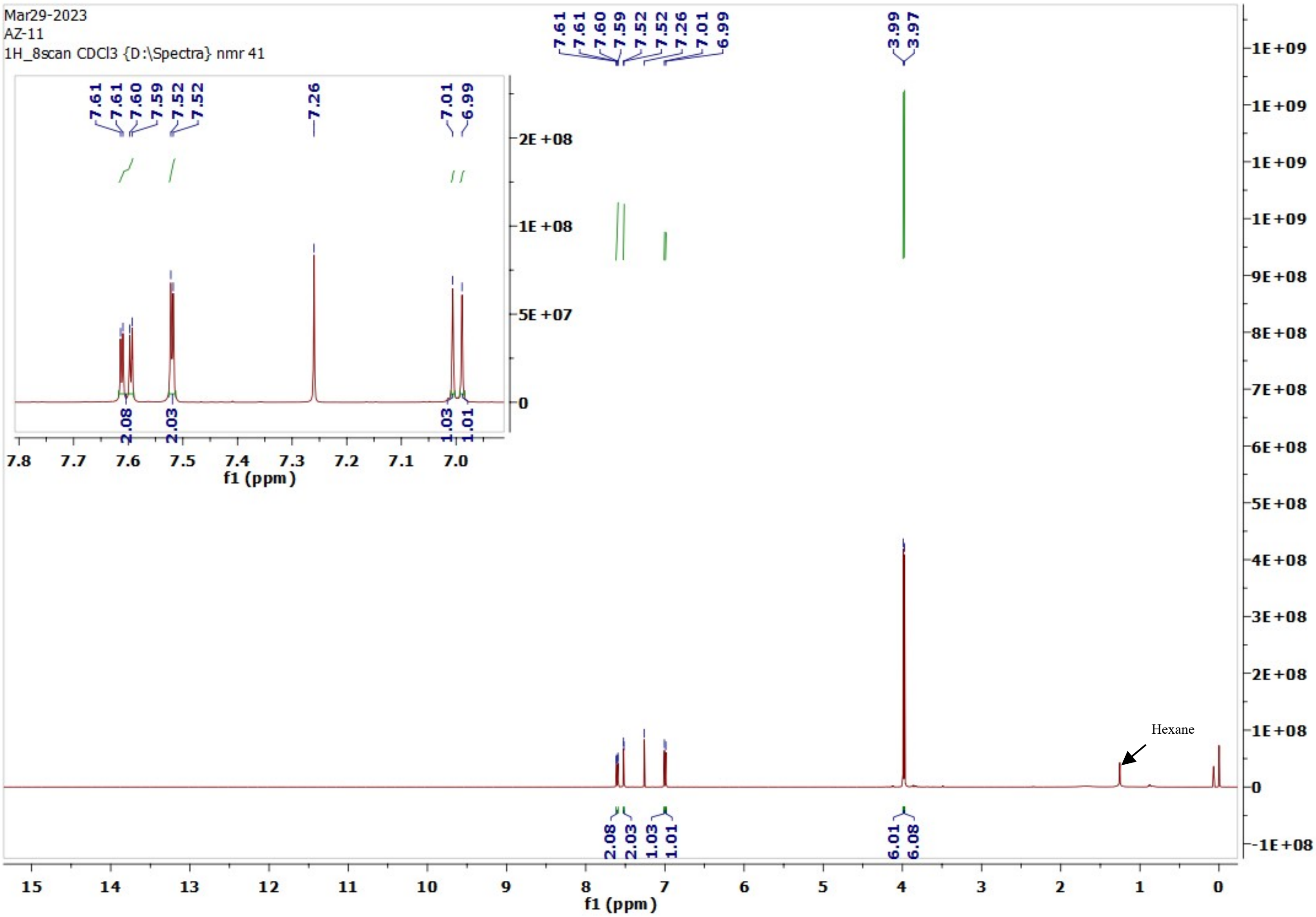
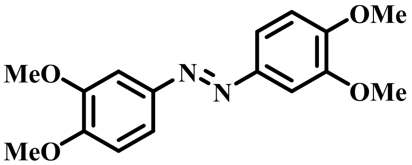


**Fig. S44**. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of **2n**.



**2n**

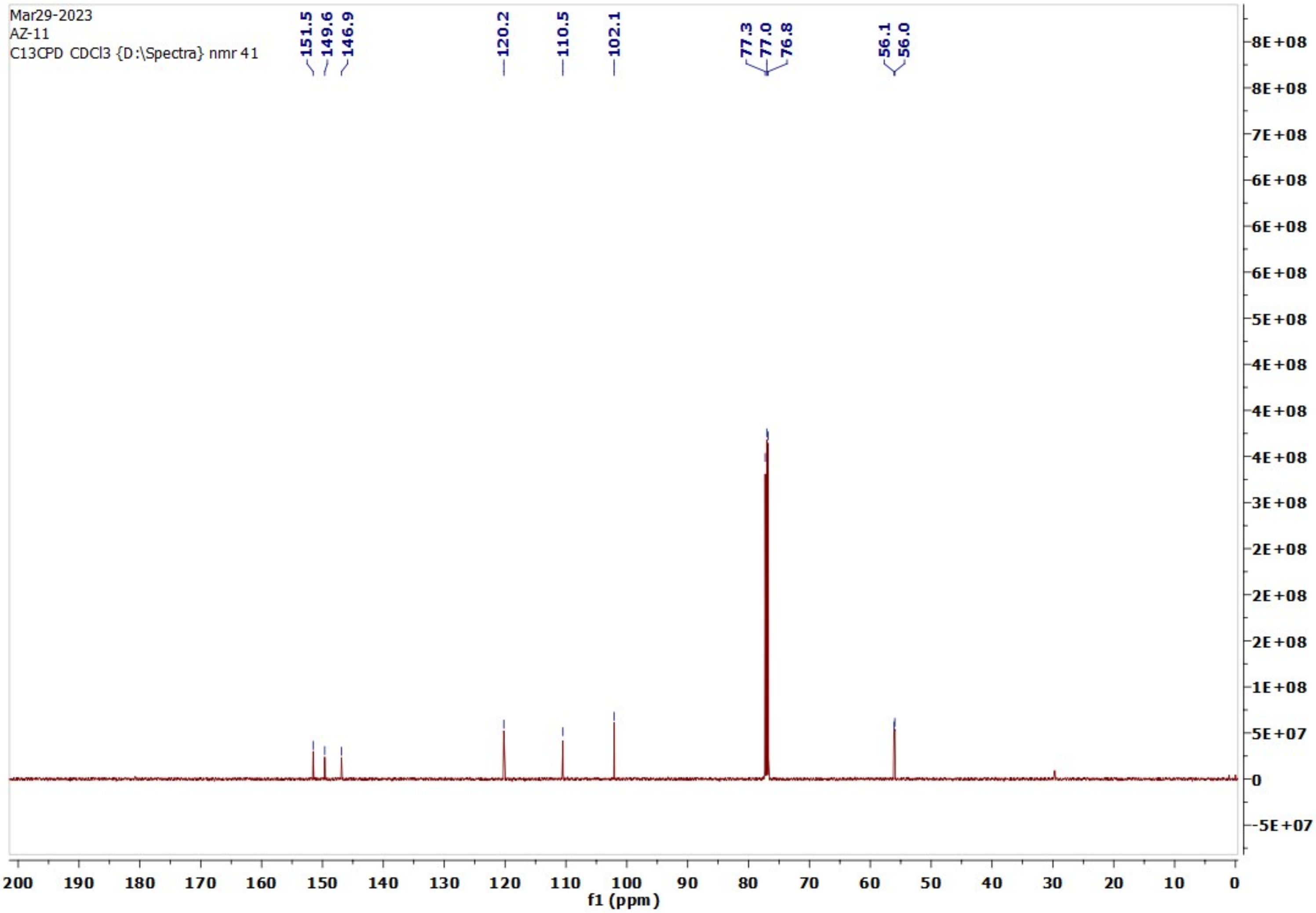
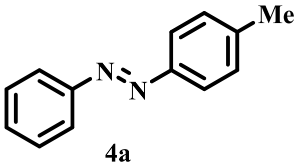


**Fig. S45**. $^{1}$C NMR (125 MHz, CDCl$_3$) spectrum of **2n.**



**4a**

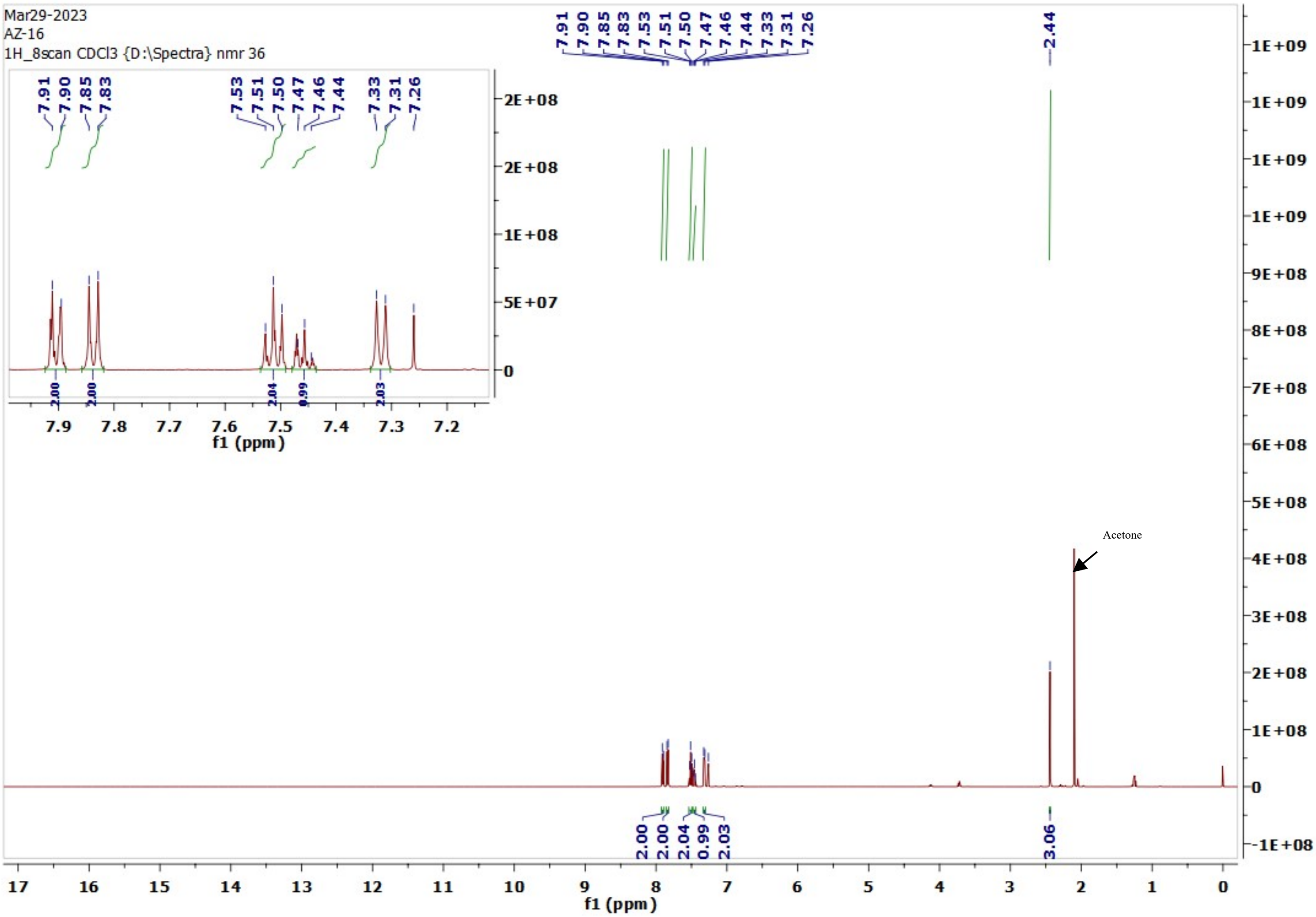
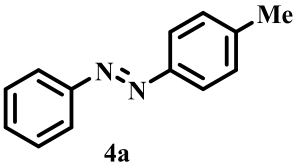


**Fig. S46**. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of **4a.**



**4a**

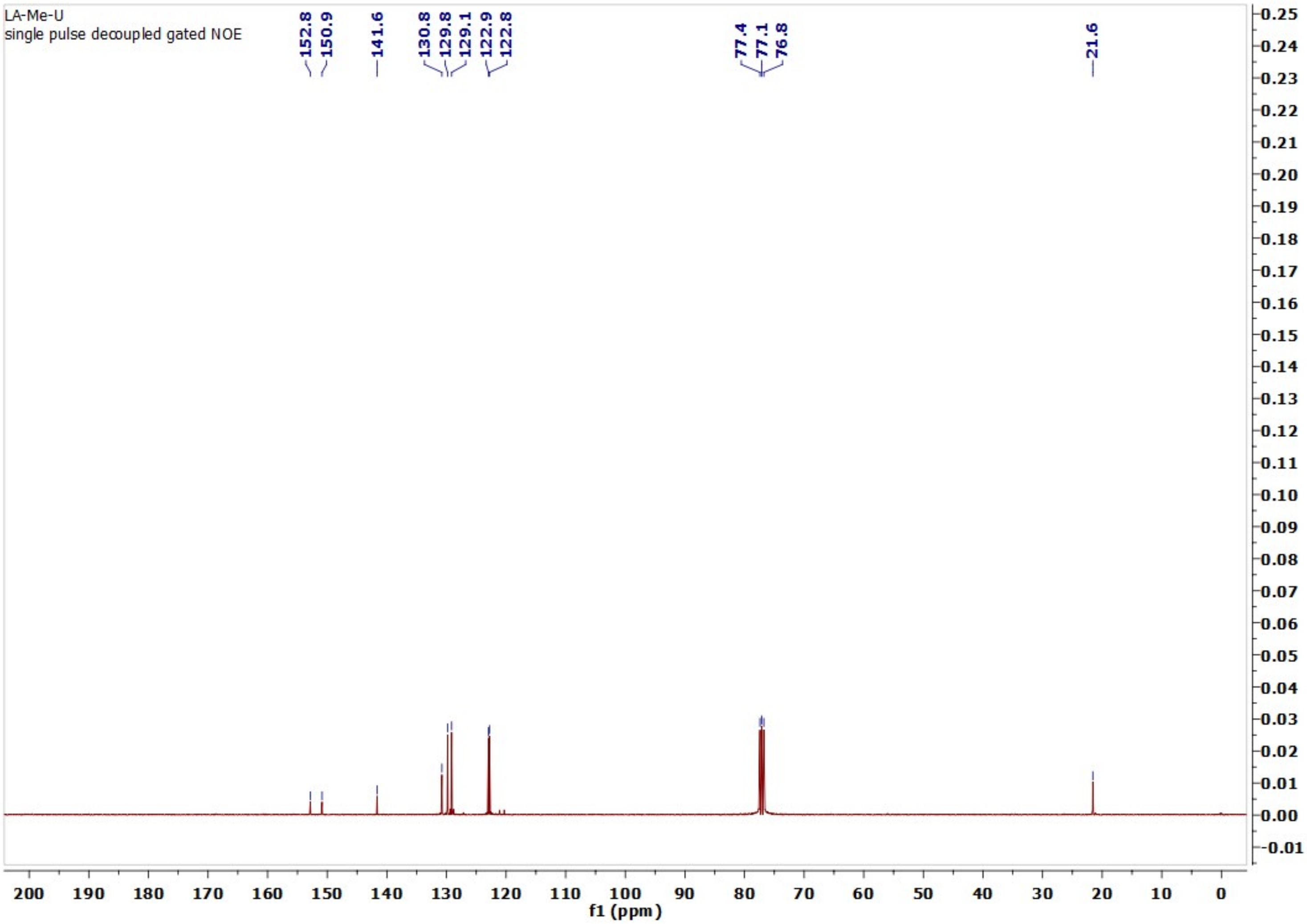
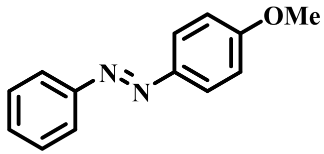


**Fig. S47**. $^{1}$C NMR (125 MHz, CDCl$_3$) spectrum of **4a.**



**4b**

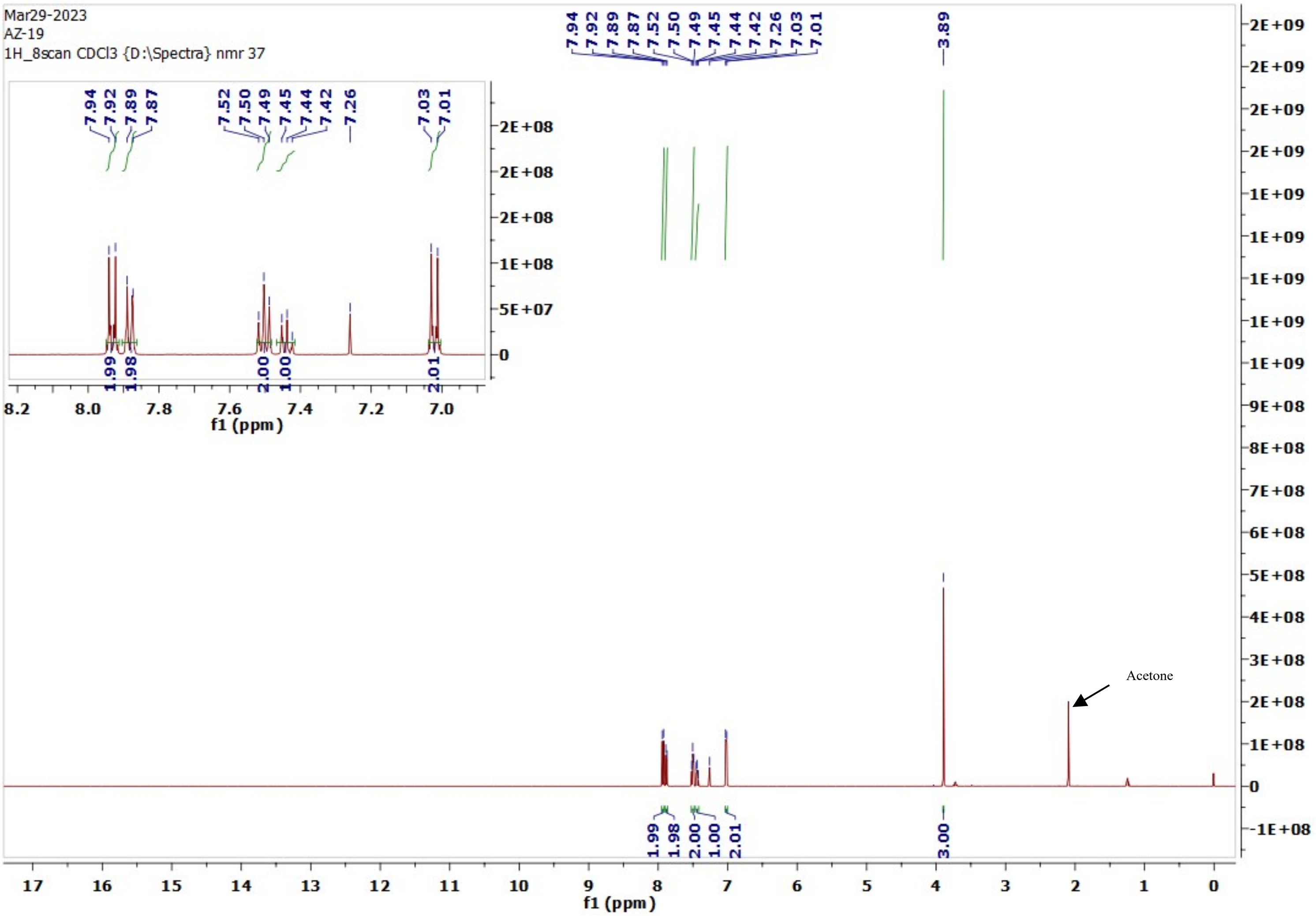
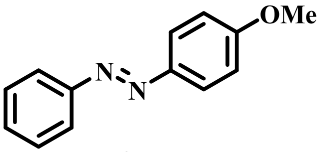


**Fig. S48**. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of **4b.**



**4b**

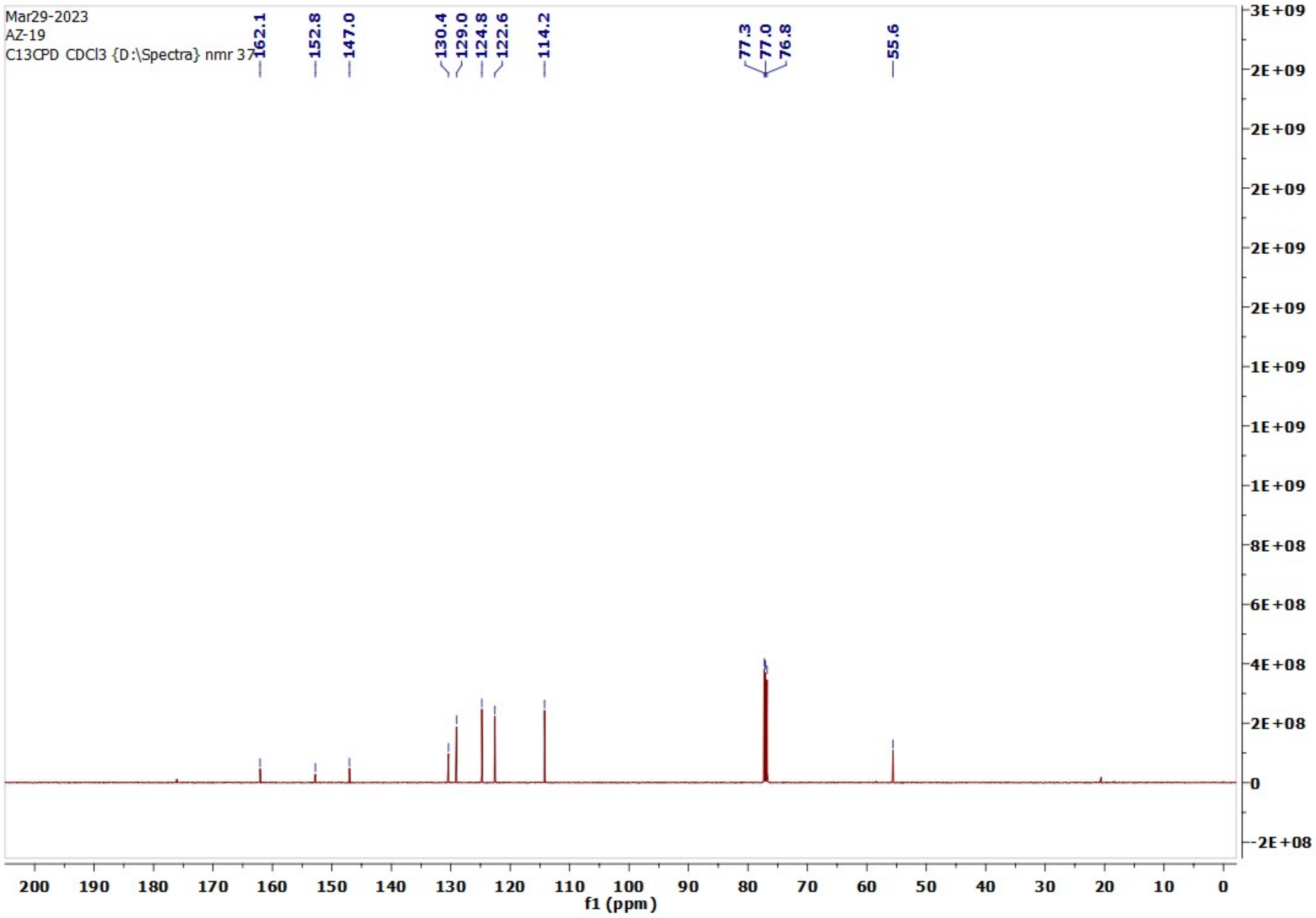
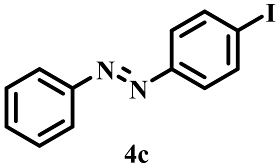


**Fig. S49**. $^{1}$C NMR (125 MHz, CDCl$_3$) spectrum of **4b.**



**4c**

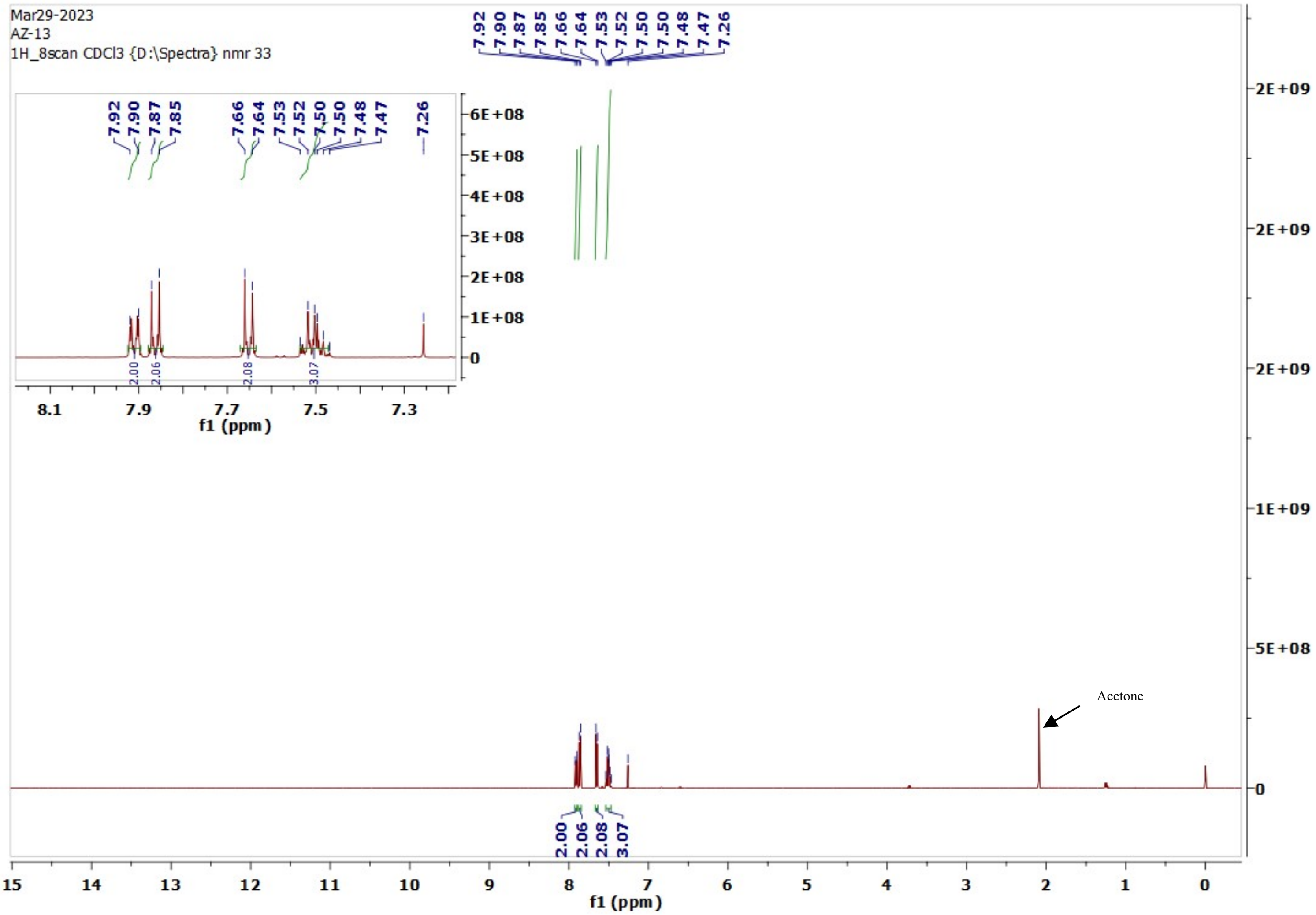
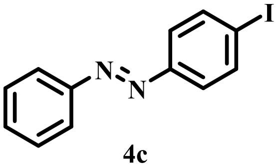


**Fig. S50**. ${}^{1}$H NMR (400 MHz, CDCl$_3$) spectrum of **4c**.



**4c**

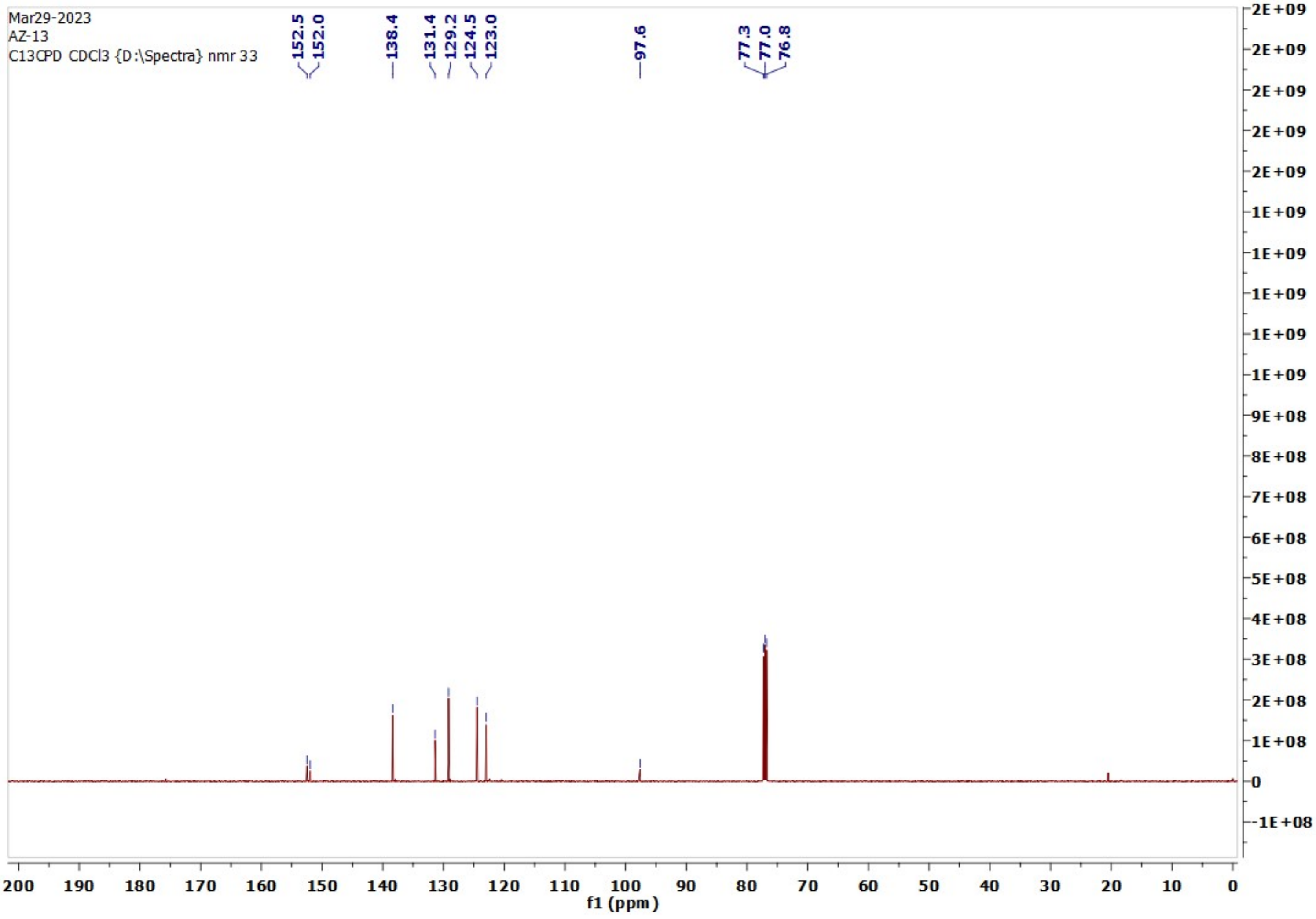
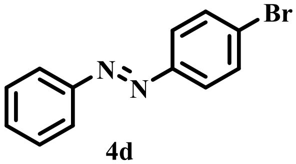


**Fig. S51**. $^{1}$C NMR (125 MHz, CDCl$_3$) spectrum of **4c**.



**4d**

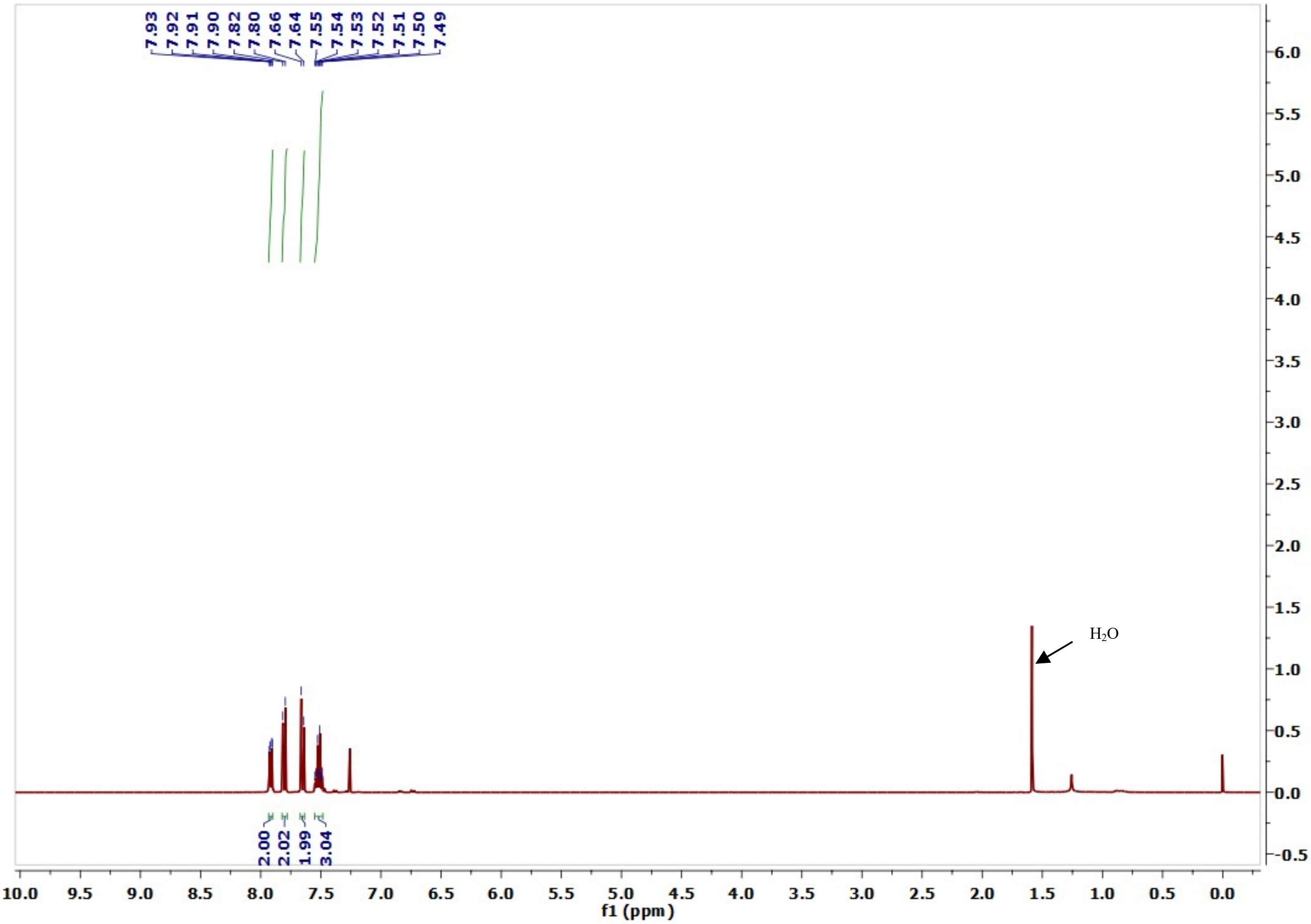
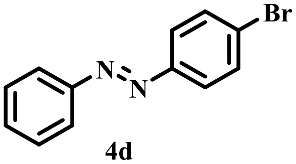


**Fig. S52**. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of **4d**.



**4d**

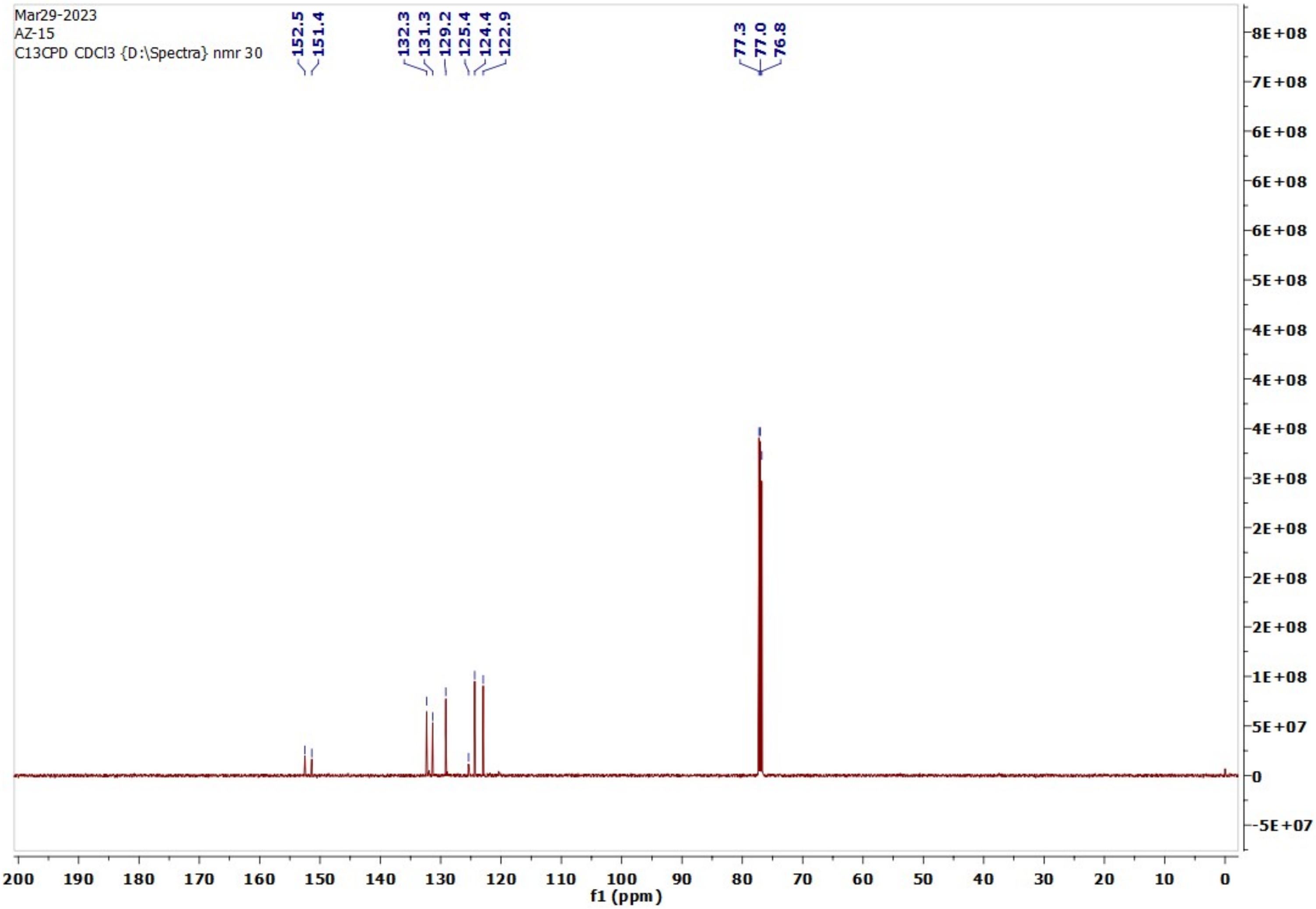
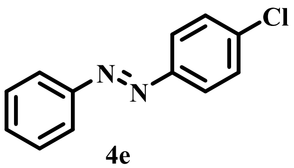


**Fig. S53**. $^{1}$C NMR (125 MHz, CDCl$_3$) spectrum of **4d**.



**4e**

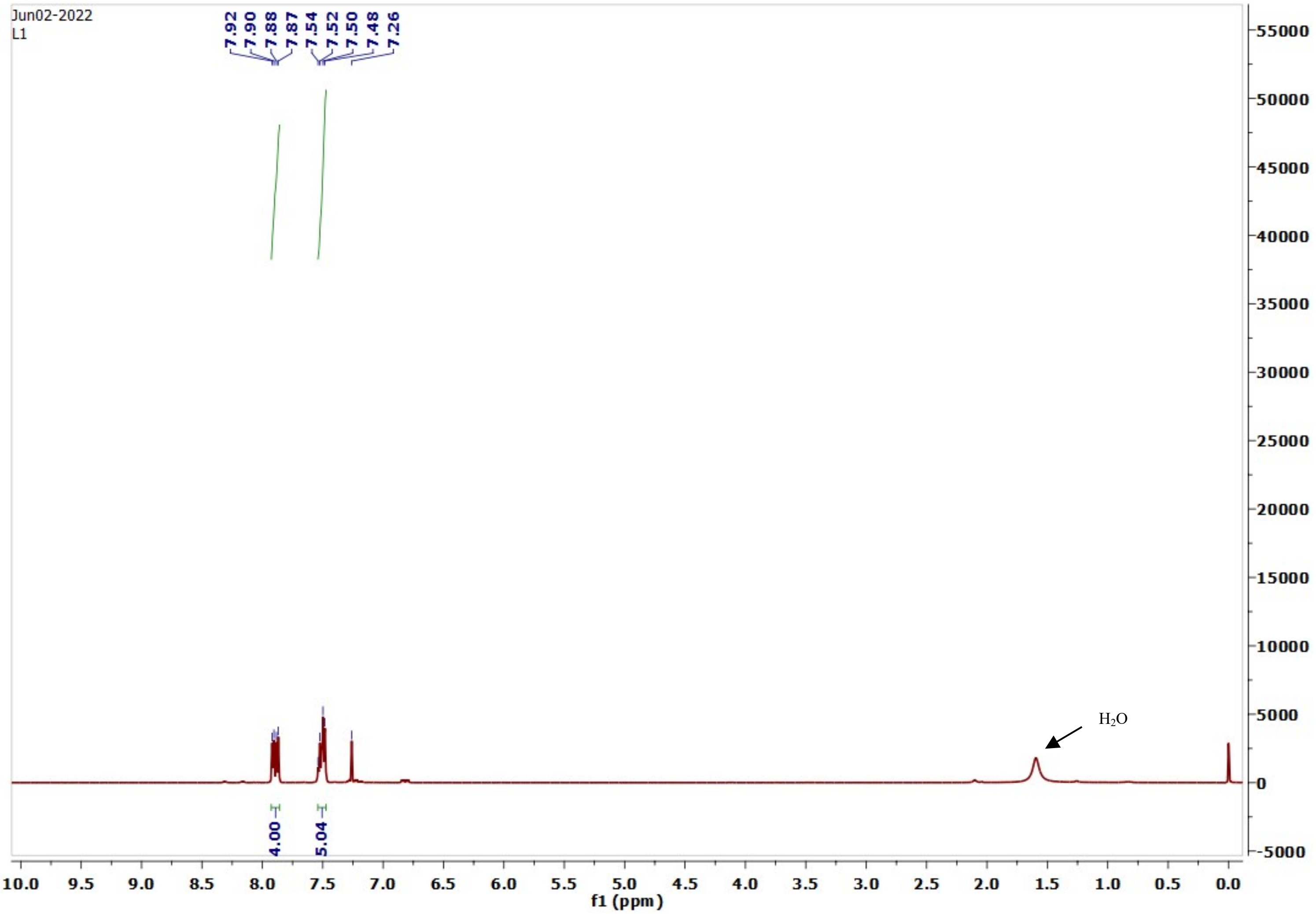
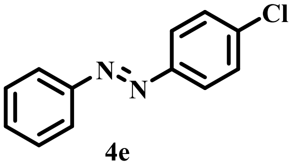


**Fig. S54**. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of **4e.**



**4e**

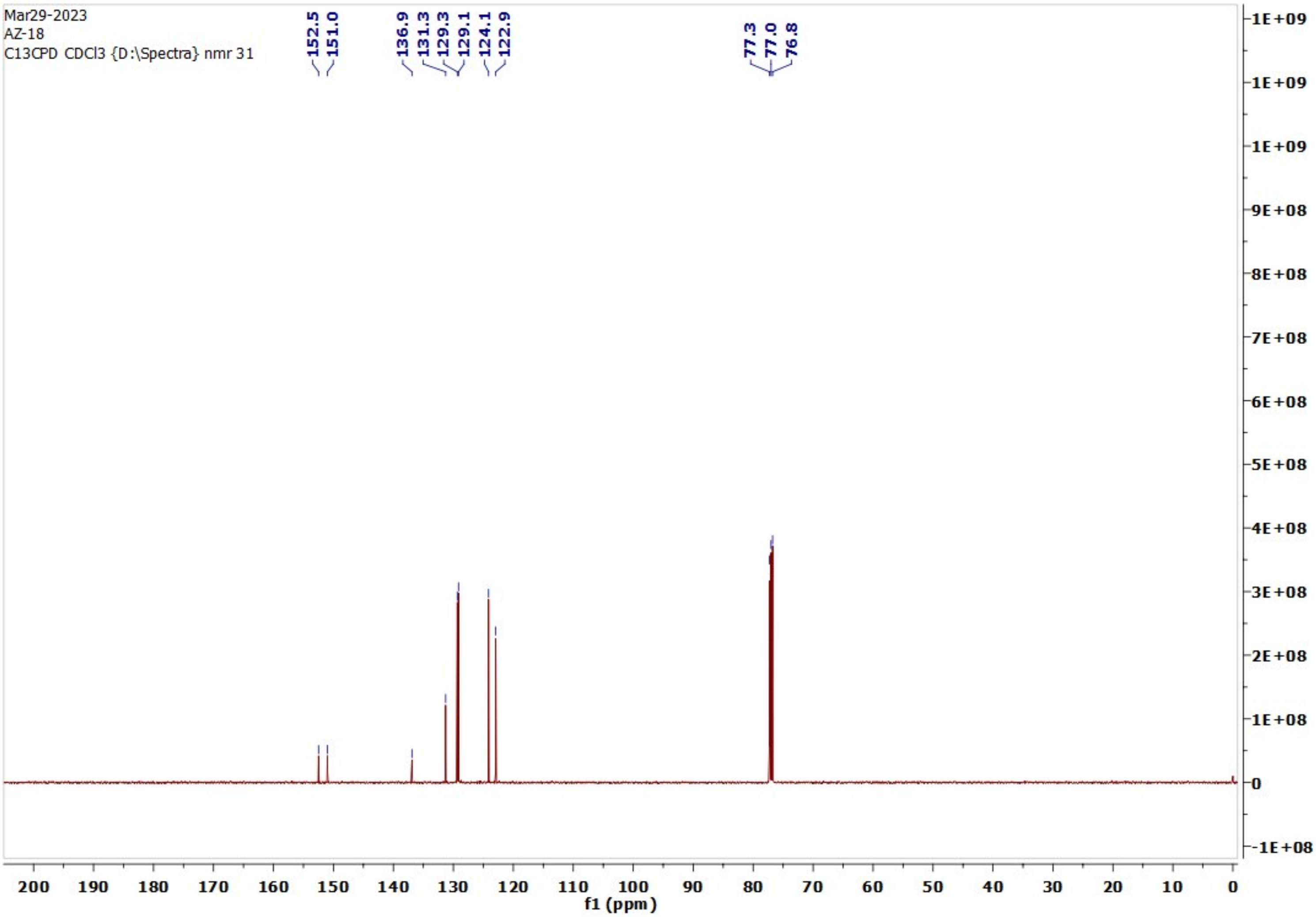
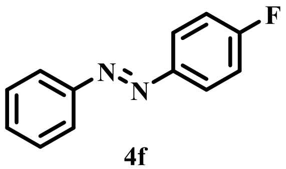


**Fig. S55**. $^{1}$C NMR (125 MHz, $CDCl_3$) spectrum of **4e.**



**4f**

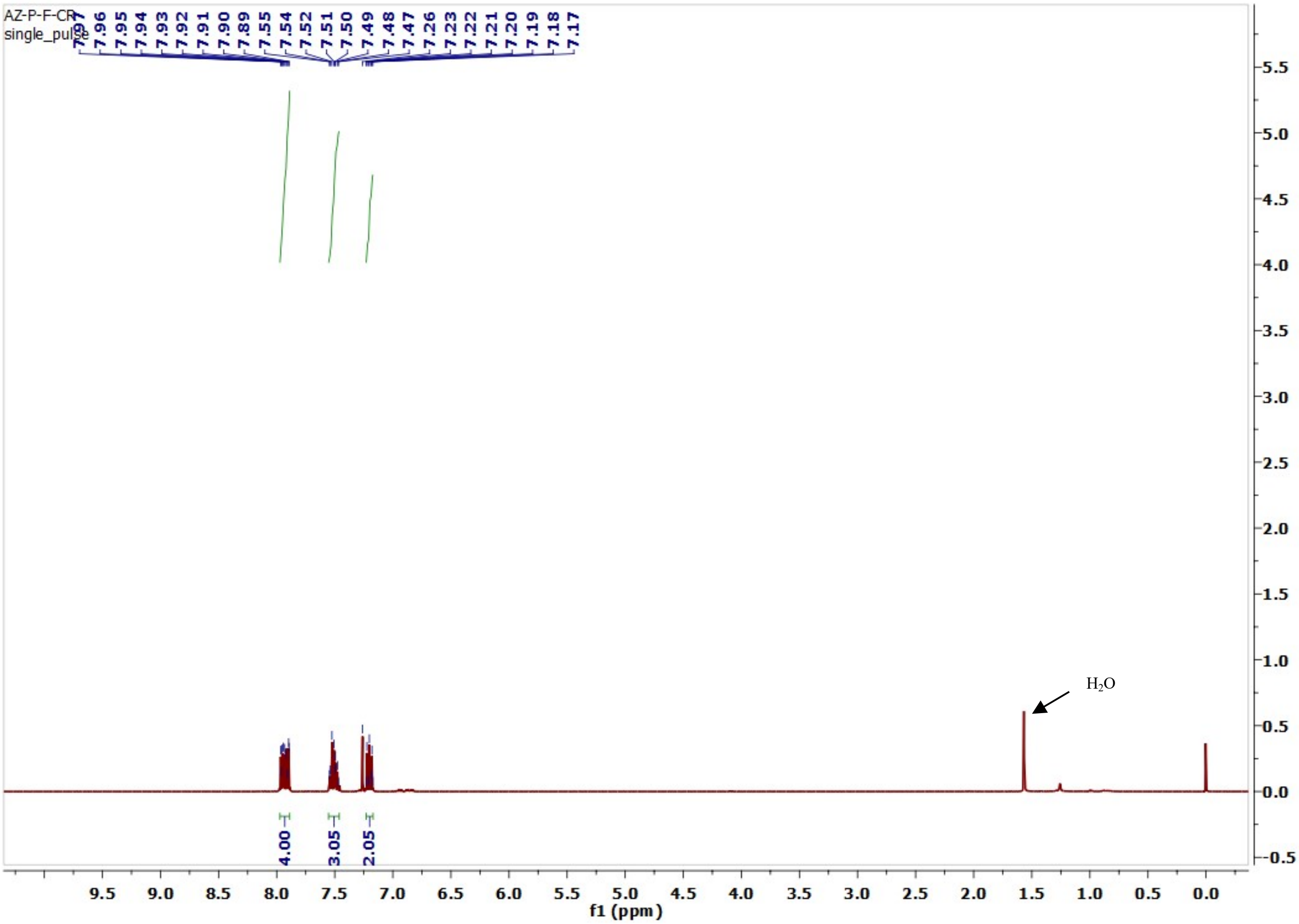
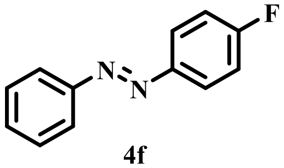


**Fig. S56**. $^1$H NMR (400 MHz, $CDCl_3$) spectrum of **4f**.



**4f**

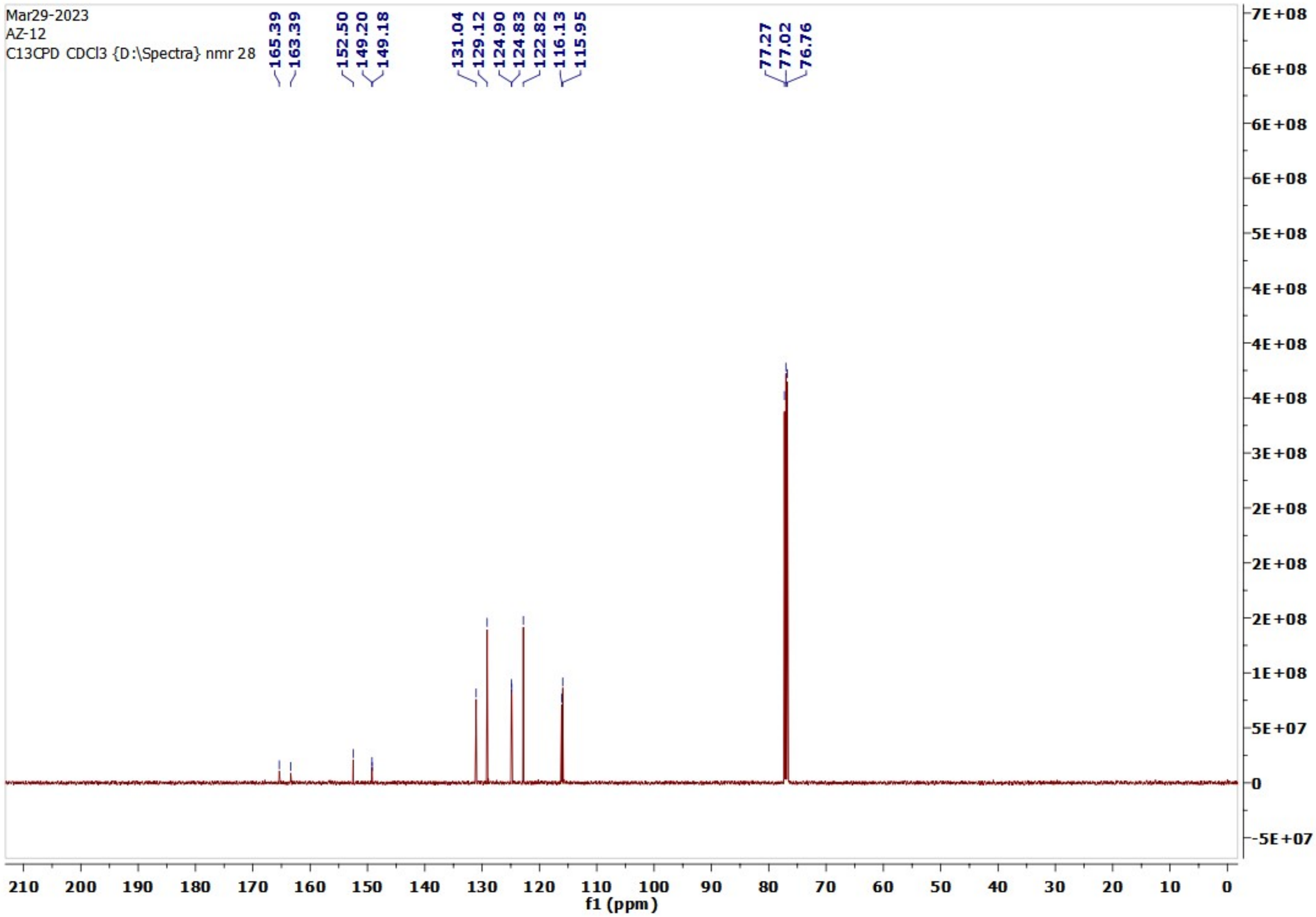
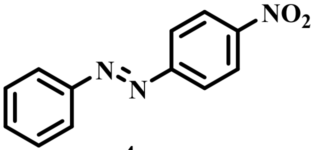


**Fig. S57**. $^{1}$C NMR (125 MHz, CDCl$_3$) spectrum of **4f**.



**4g**

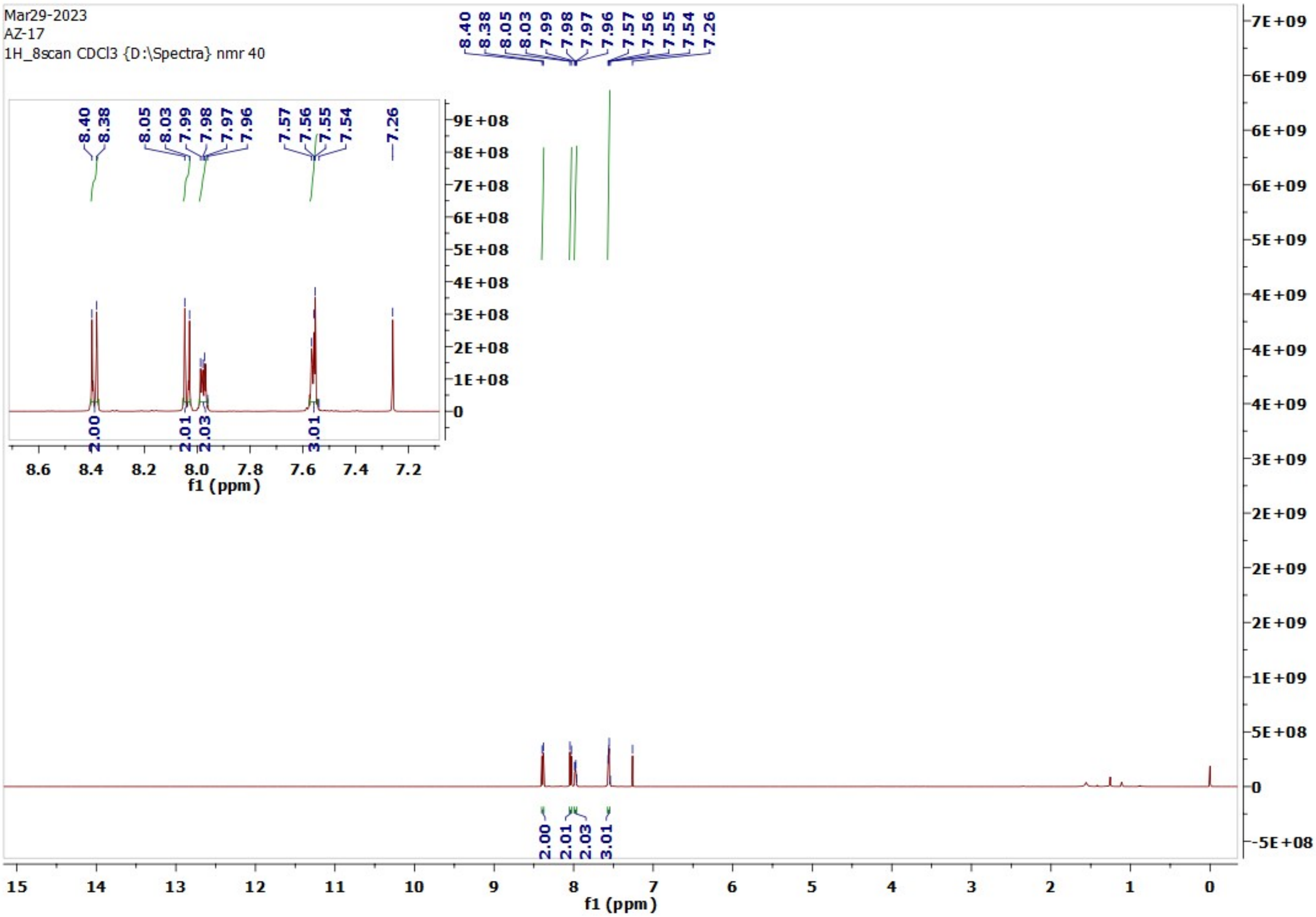
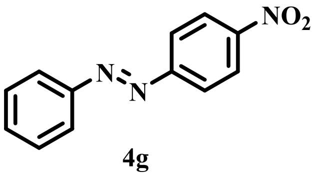


**Fig. S58**. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of **4g.**



**4g**

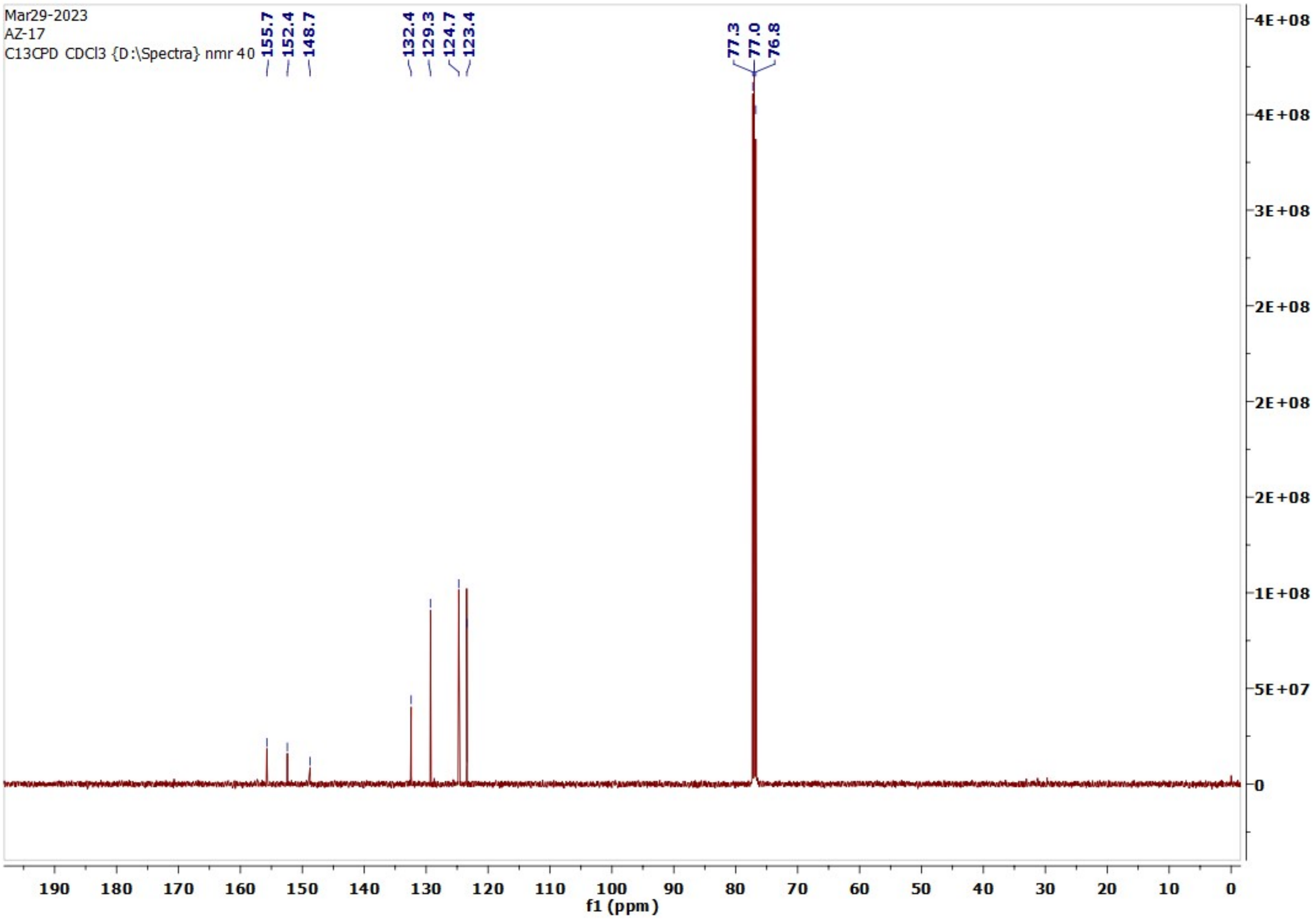
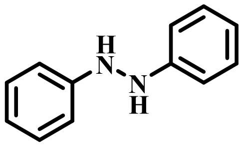


**Fig. S59**. $^{1}$C NMR (125 MHz, $CDCl_3$) spectrum of **4g.**



**3a**

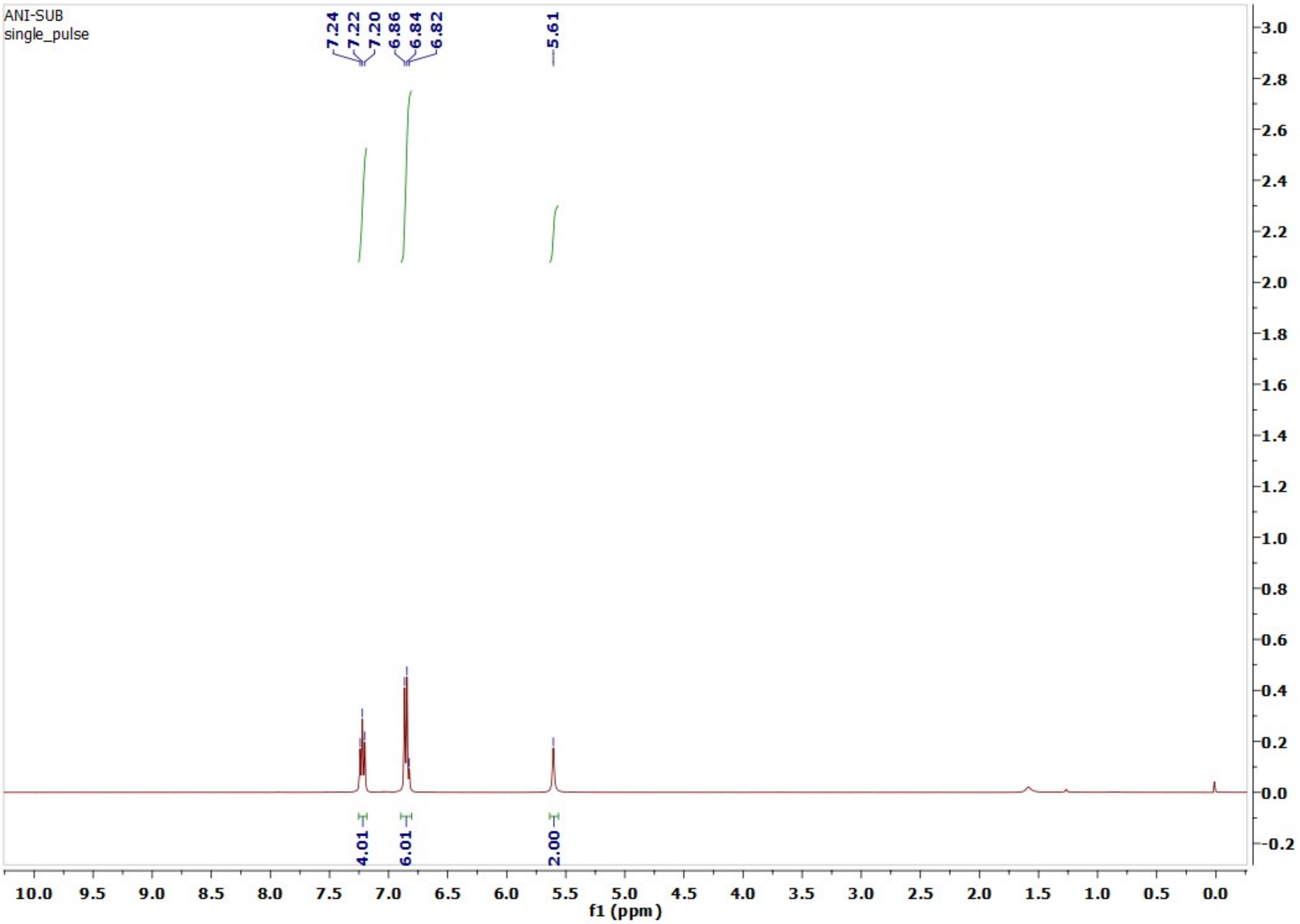
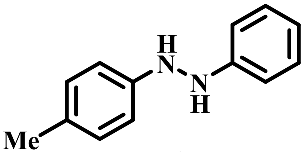


**Fig. S60**. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of **3a**.



**3b**

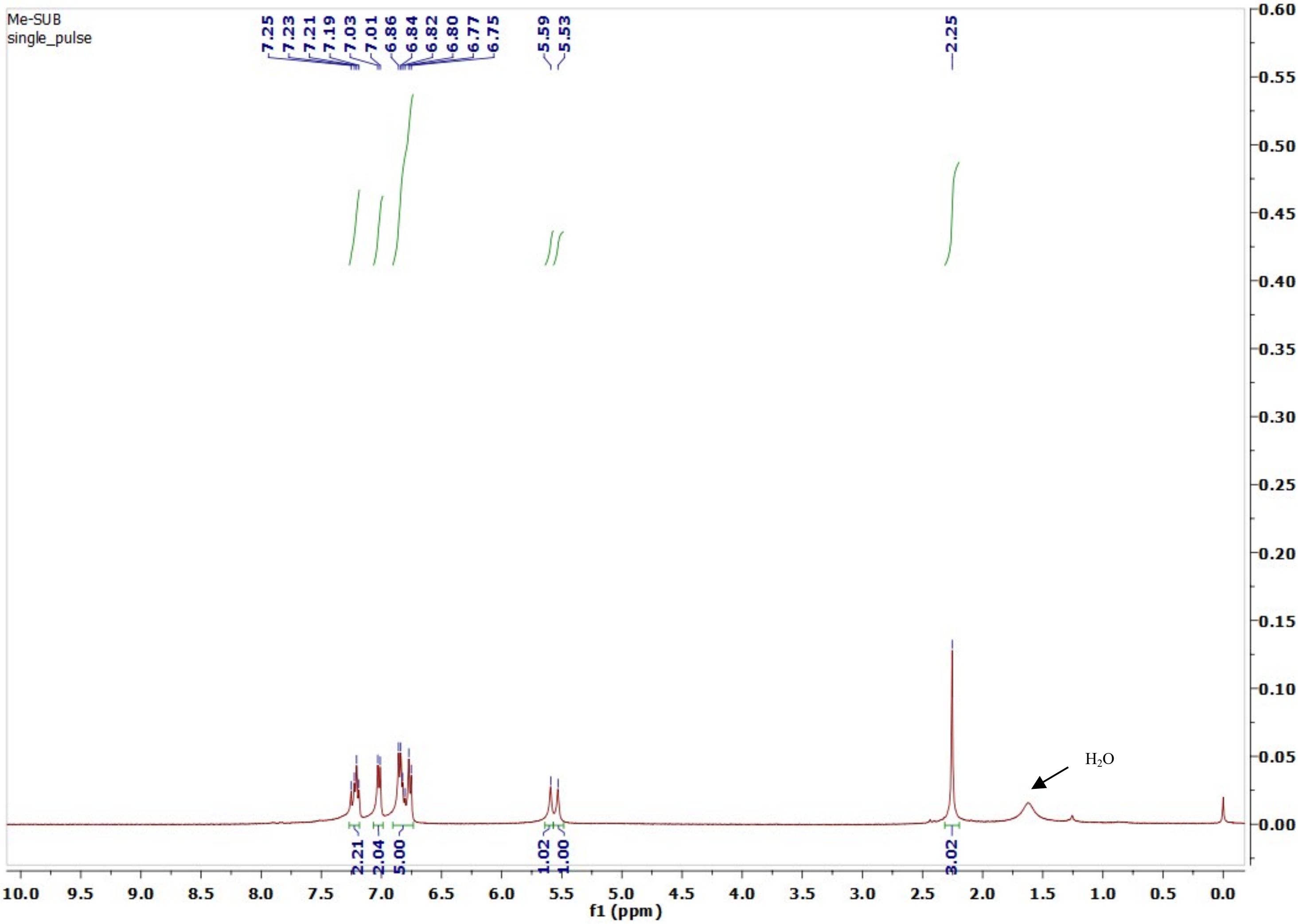
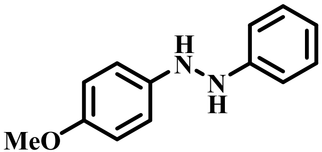


**Fig. S61**. $^1$H NMR (400 MHz, $CDCl_3$) spectrum of **3b**.



**3c**

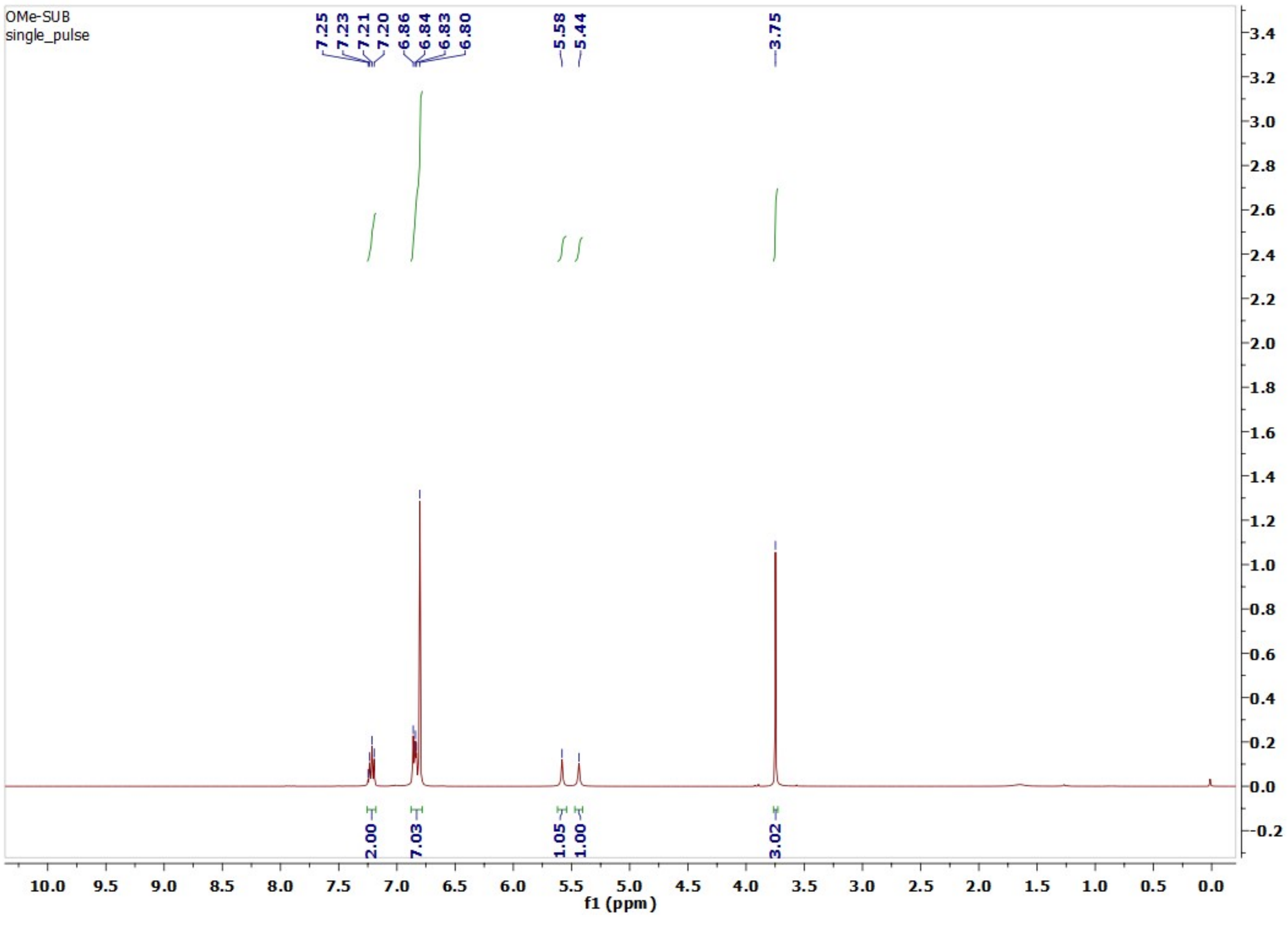
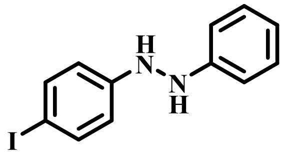


**Fig. S62**. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of **3c**.



**3d**

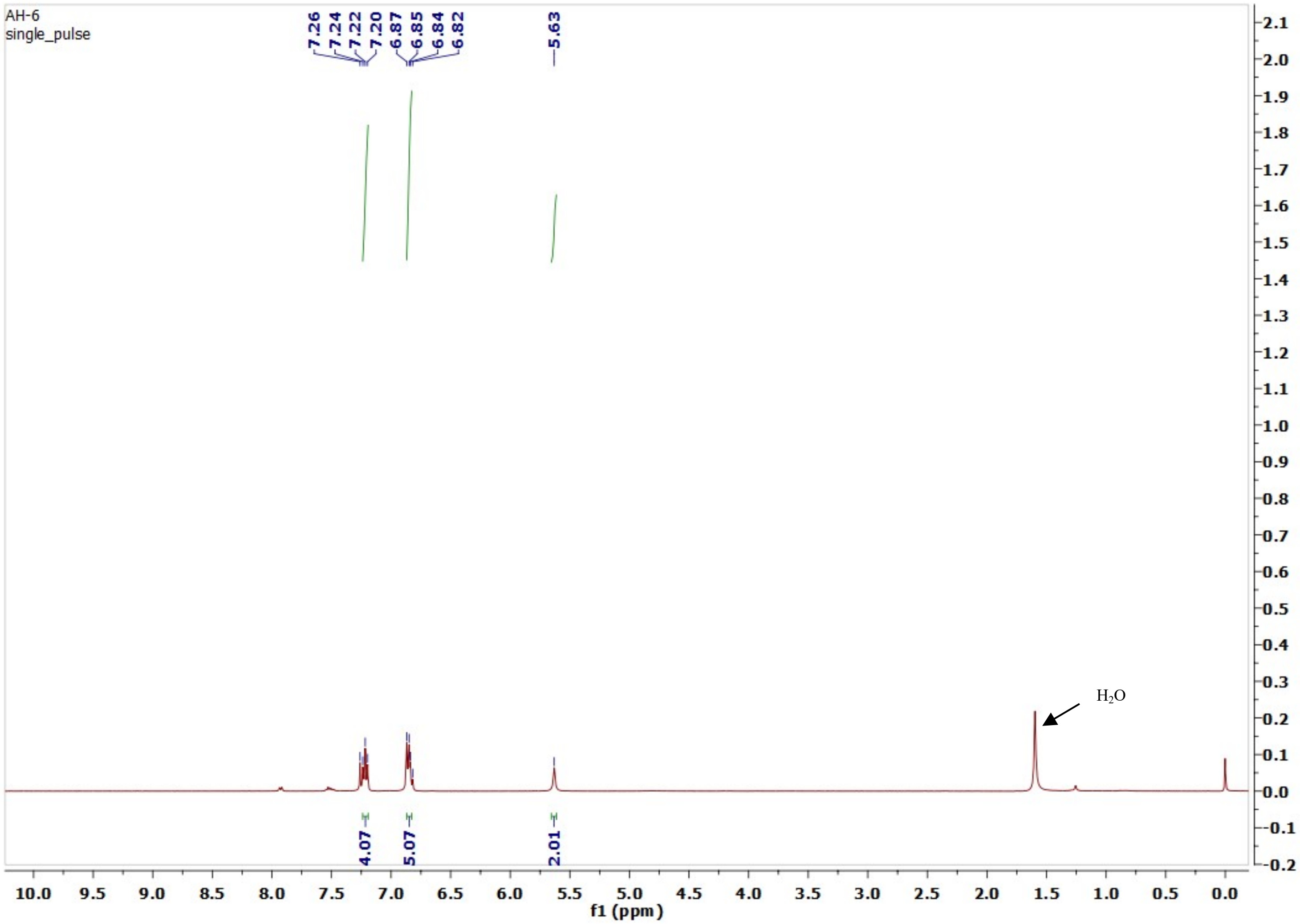
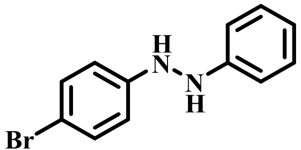


**Fig. S63**. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of **3d**.



**3e**

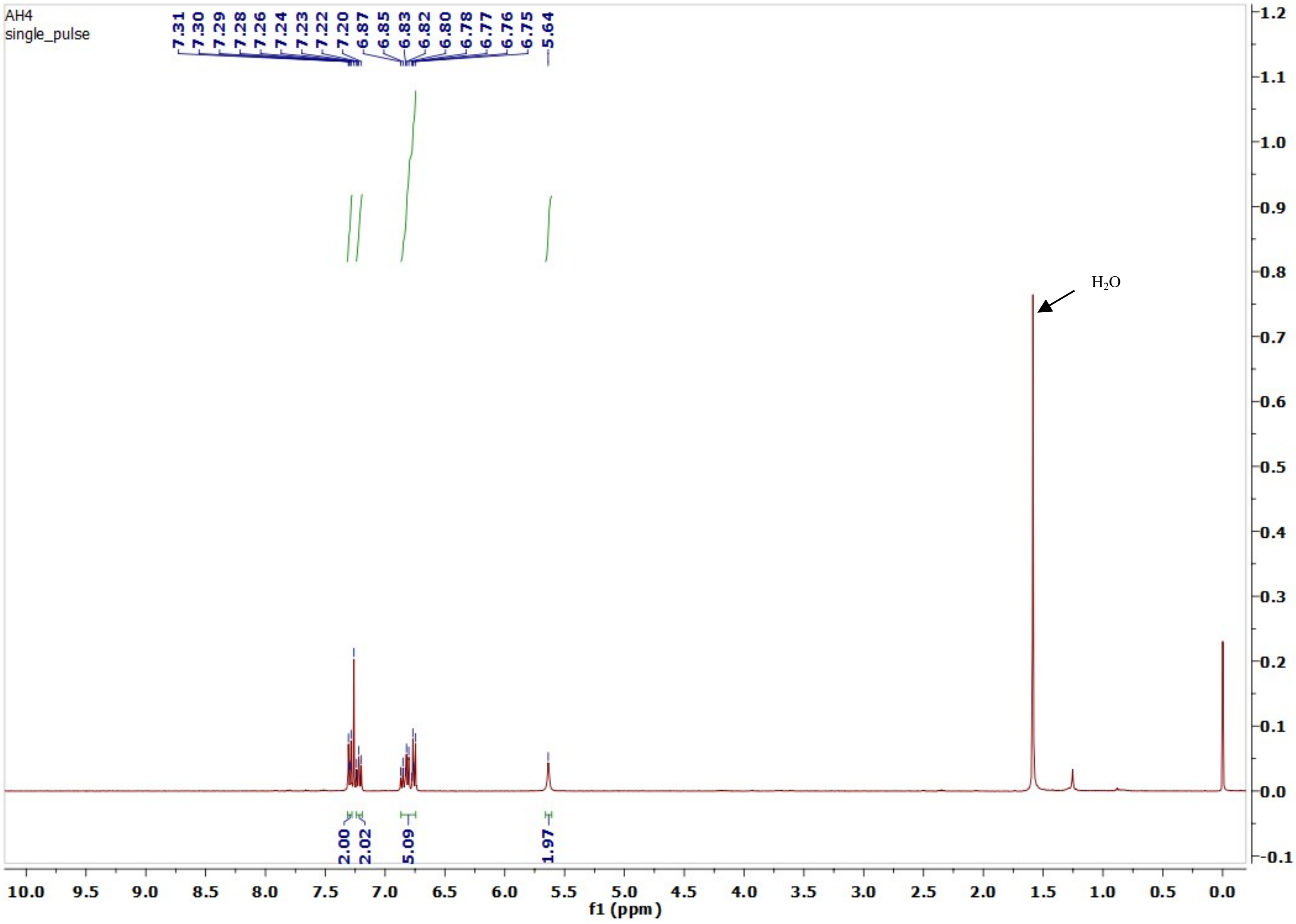
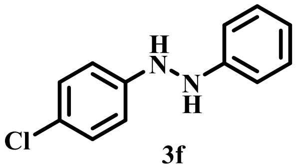


**Fig. S64**. $^1$H NMR (400 MHz, $CDCl_3$) spectrum of **3e**.



**3f**

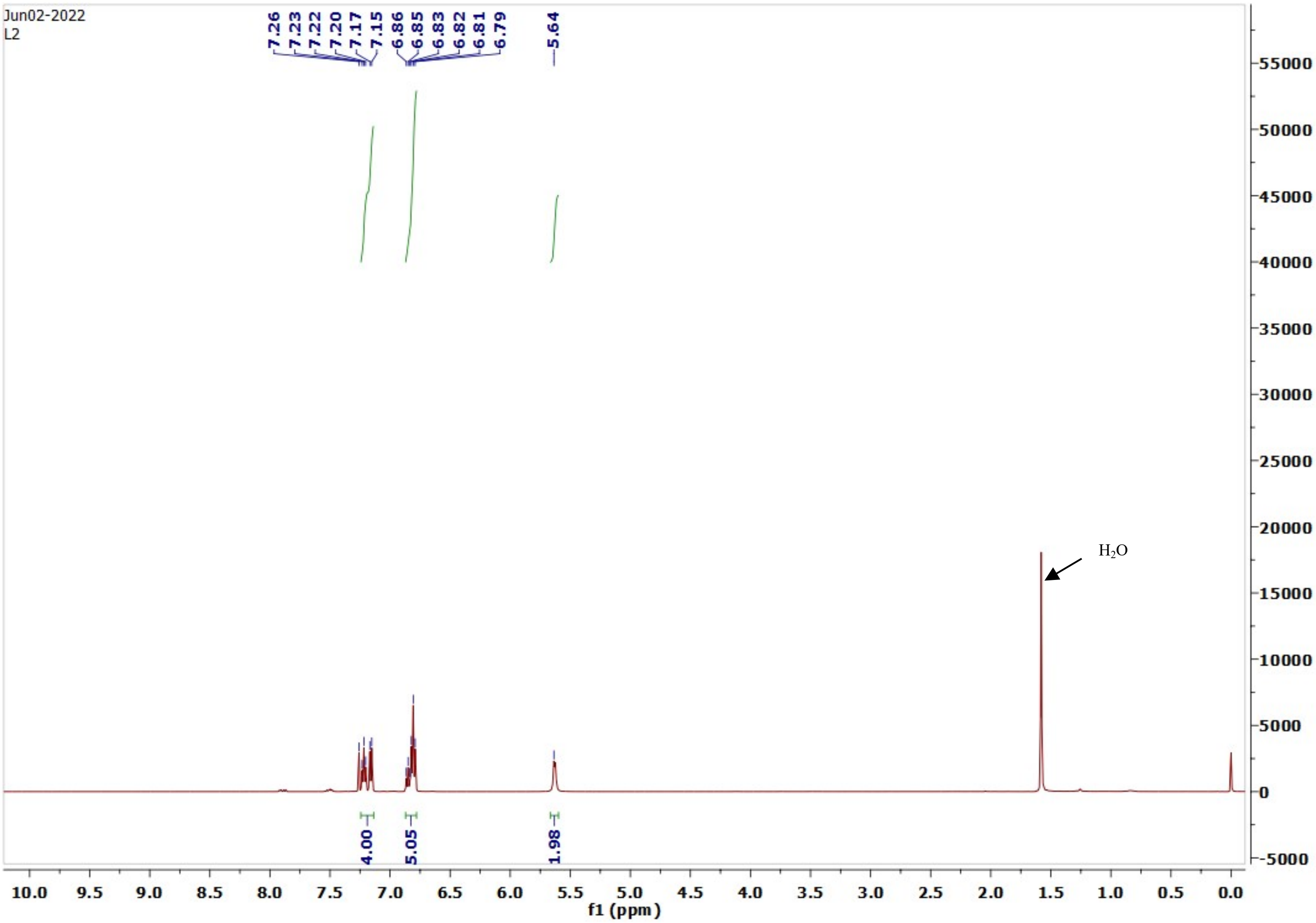
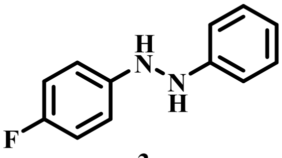


**Fig. S65**. $^1$H NMR (400 MHz, $CDCl_3$) spectrum of **3f.**



**3g**

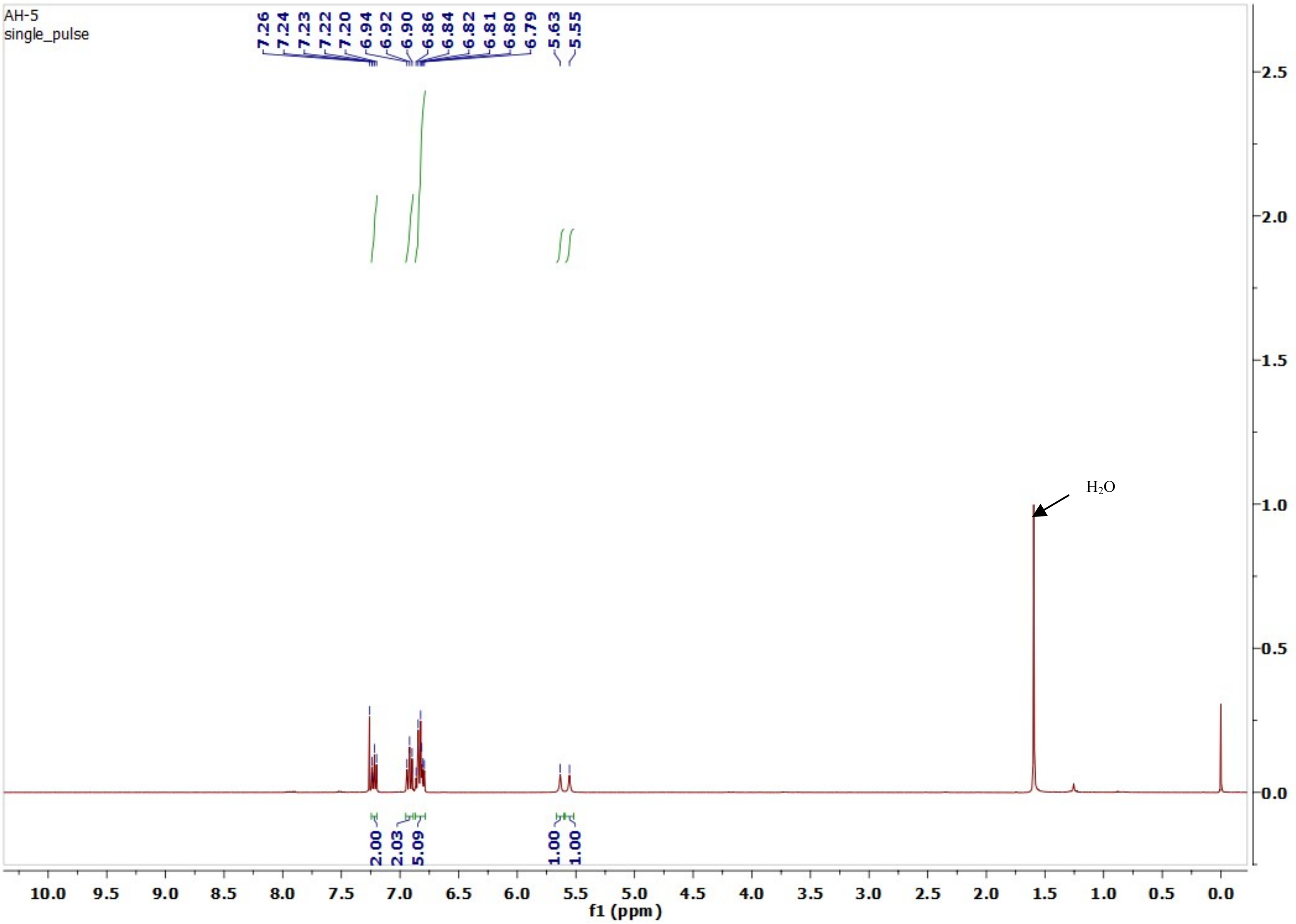
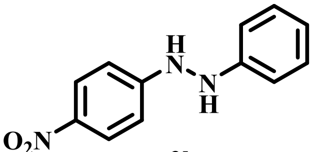


**Fig. S66**. $^1$H NMR (400 MHz, $CDCl_3$) spectrum of **3g.**



**3h**

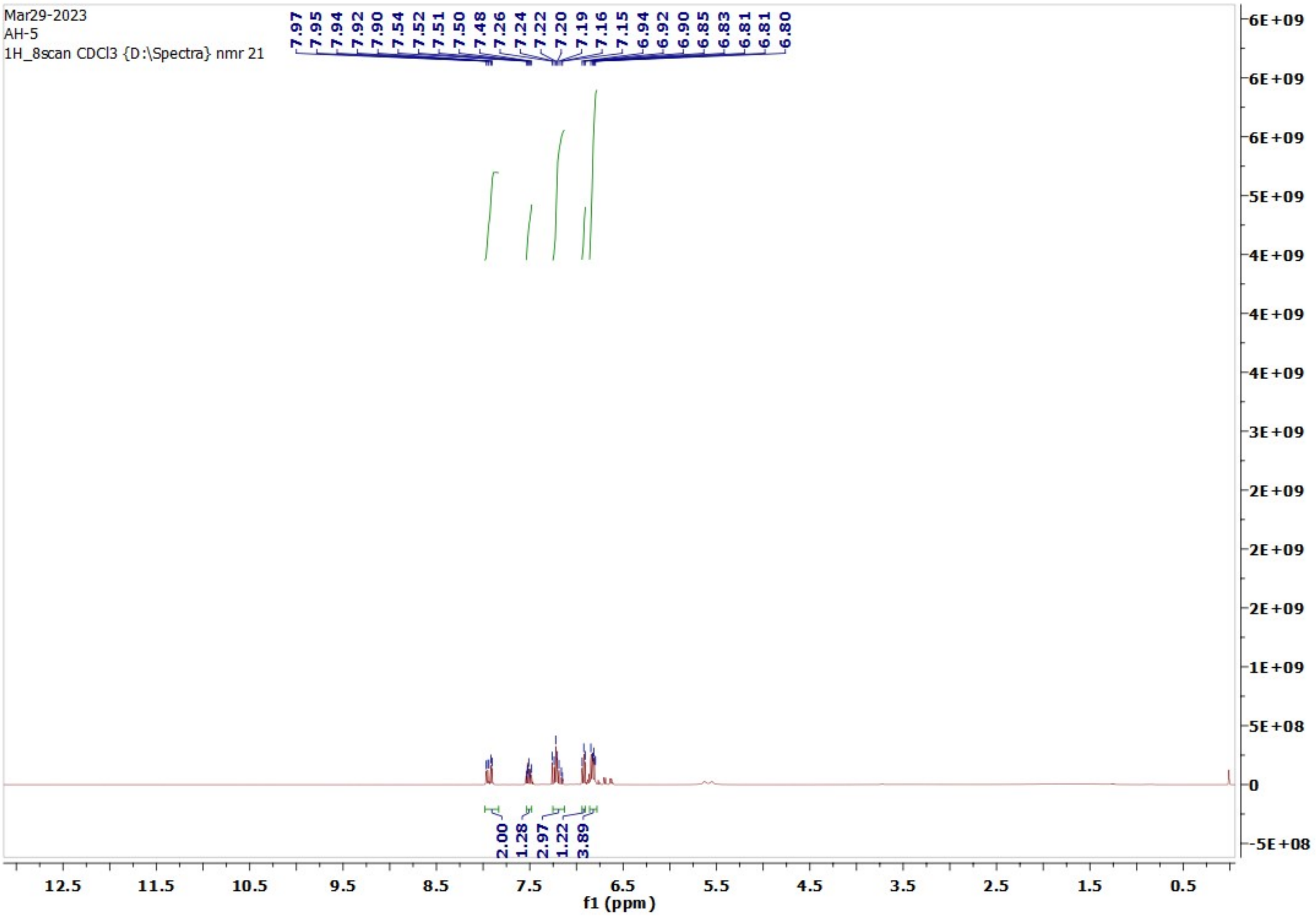
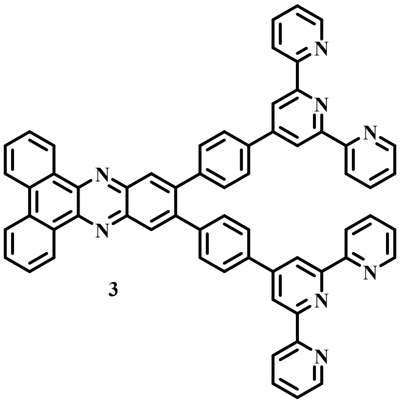


**Fig. S67**. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of **3h** (crude).



3

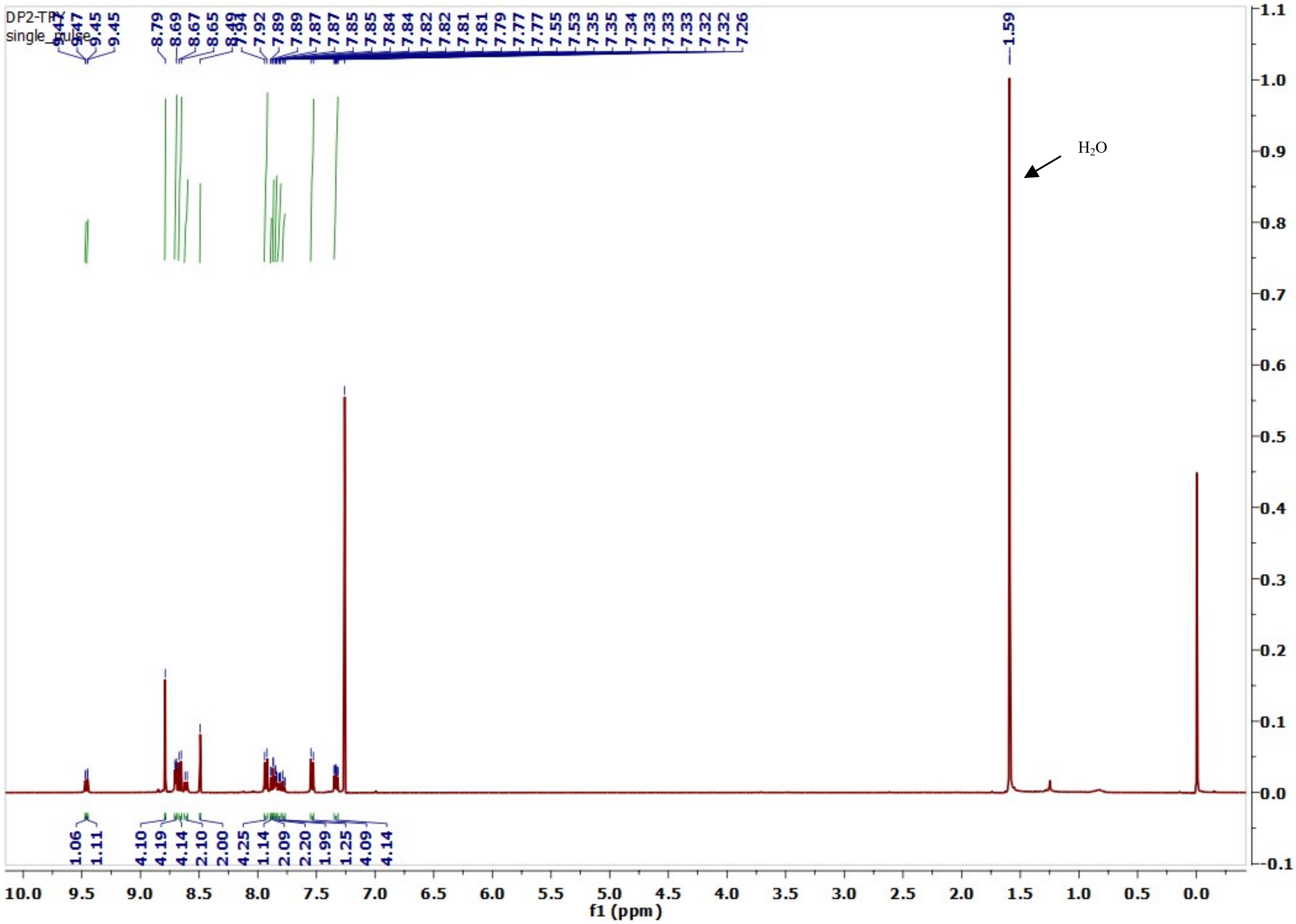
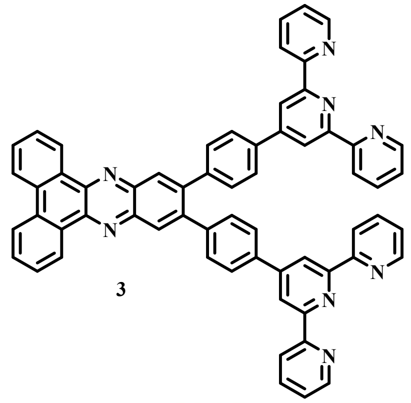


**Fig. S68**. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of derivative **3**.



**3**

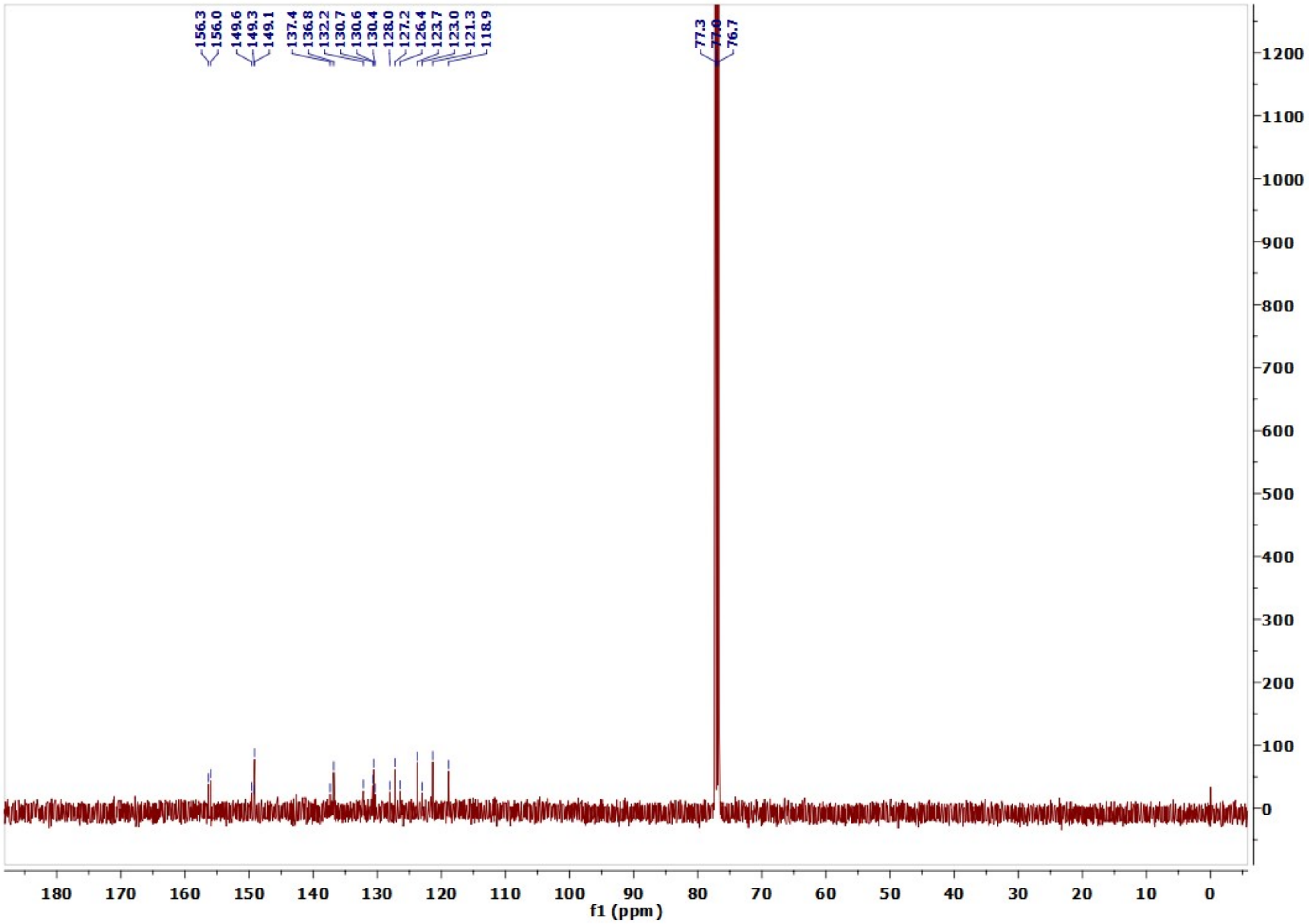
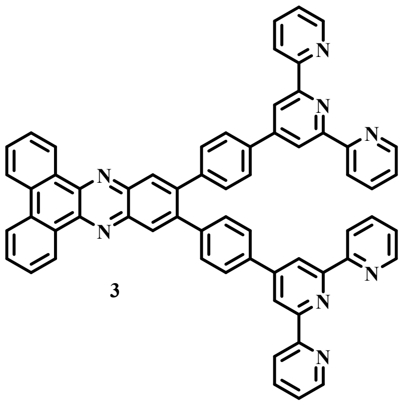
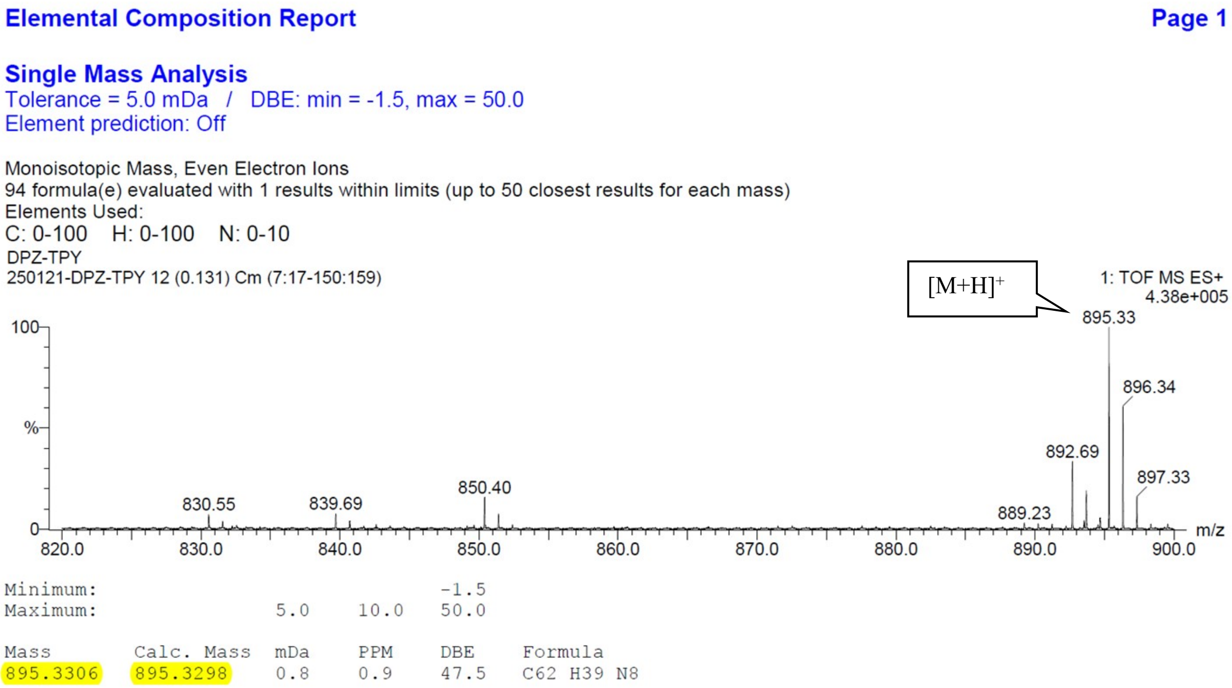


**Fig. S69**. $^{13}$C NMR (125 MHz, $CDCl_3$) spectrum of derivative **3.**



**3**



Elemental Composition Report  Page 1

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Even Electron Ions
94 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-100 H: 0-100 N: 0-10
DPZ-TPY
250121-DPZ-TPY 12 (0.131) Cm (7:17-150:159)

```
Minimum:                                -1.5
Maximum:                 5.0     10.0   50.0

Mass         Calc. Mass  mDa     PPM    DBE     Formula
895.3306     895.3298    0.8     0.9    47.5    C62 H39 N8
```

**Fig. S70**. HRMS spectrum of derivative **3.**

**Computational methods:**

Structure optimization and harmonic frequencies at ground-state were calculated employing DFT at the Becke’s three parameter functional in combination with the Lee-Yang-Parr correlation functional (B3LYP) and 6-311g (d,p) basis set. All computational studies were performed using the Gaussian 09 program suite.[14]

**Ground state optimized coordinates of aniline derivatives at B3LYP/6-311g(d,p) level of theory.**

**Aniline (1a)**: E(B3LYP/6-311g(d,p)) = -287.6726629 hartrees, G = -287.585229 hartrees, H = -287.550159 hartrees.

| | | | |
|---|---|---|---|
| C | -1.15228000 | 1.22049100 | 0.00000400 |
| C | 0.24015200 | 1.19058700 | -0.00000600 |
| C | 0.92624300 | -0.02906800 | 0.00000100 |
| C | 0.19289100 | -1.21602100 | -0.00001400 |
| C | -1.20077700 | -1.18832100 | -0.00001100 |
| C | -1.87682300 | 0.02946500 | 0.00001600 |
| H | -1.67140100 | 2.17270700 | 0.00001100 |
| H | 0.80547000 | 2.11749000 | 0.00000000 |
| H | 0.73698800 | -2.15290500 | -0.00003000 |
| H | -1.75773000 | -2.11880000 | -0.00001400 |
| H | -2.96076500 | 0.05188500 | 0.00002500 |
| N | 2.36719700 | -0.11744800 | -0.00002300 |
| H | 2.75031200 | 0.35471800 | -0.81379400 |
| H | 2.75031100 | 0.35424200 | 0.81402300 |

**Aniline radical cation (1a’)**: E(B3LYP/6-311g(d,p)) = -287.408764 hartrees, G = -287.321278 hartrees, H = -287.284822 hartrees.

| | | | |
|---|---|---|---|
| C | -1.15184500 | 1.22850900 | 0.00006400 |
| C | 0.21860400 | 1.24263000 | 0.00019100 |
| C | 0.93521900 | -0.00010400 | 0.00001600 |
| C | 0.21872500 | -1.24263500 | 0.00023100 |
| C | -1.15175300 | -1.22849500 | -0.00000900 |
| C | -1.84907700 | -0.00001200 | -0.00021900 |

| | | | |
|---|---|---|---|
| H | -1.70434900 | 2.15959000 | 0.00012900 |
| H | 0.77042800 | 2.17567900 | 0.00037000 |
| H | 0.77041500 | -2.17575400 | 0.00060200 |
| H | -1.70427600 | -2.15957200 | 0.00006700 |
| H | -2.93243900 | -0.00016800 | -0.00061300 |
| N | 2.26892900 | 0.00007500 | -0.00033800 |
| H | 2.79907900 | 0.86332600 | 0.00015900 |
| H | 2.79940500 | -0.86298600 | 0.00000800 |

**4-Methoxy aniline (1d)**: E(B3LYP/6-311g(d,p)) = -362.921315 hartrees, G = -362.831591 hartrees, H = -362.792645 hartrees.

| | | | |
|---|---|---|---|
| C | -0.70237300 | 1.21371900 | -0.00026600 |
| C | 0.68629800 | 1.19919500 | -0.00582100 |
| C | 1.40070900 | -0.00792000 | -0.00648400 |
| C | 0.67017700 | -1.20125400 | -0.00541700 |
| C | -0.72282300 | -1.18921900 | -0.00005600 |
| C | -1.41968500 | 0.01756900 | 0.00214900 |
| H | -1.24722900 | 2.15016700 | 0.00216800 |
| H | 1.22762400 | 2.14007600 | -0.01435000 |
| H | 1.19403100 | -2.15183400 | -0.01384800 |
| H | -1.26541500 | -2.13061100 | 0.00299400 |
| N | 2.80387600 | -0.01603600 | -0.07952000 |
| H | 3.24084600 | 0.81157800 | 0.30116000 |
| H | 3.23194300 | -0.85031100 | 0.29667100 |
| O | -2.79123900 | 0.09357200 | 0.00939500 |
| H | -3.15283900 | -0.79794000 | 0.00205400 |

**4-Methoxy aniline radical cation (1d')**: E(B3LYP/6-311g(d,p)) = -362.668071 hartrees, G = -362.577042 hartrees, H = -362.538190 hartrees.

| | | | |
|---|---|---|---|
| C | 0.69108100 | -1.23933400 | -0.00007300 |
| C | -0.67265100 | -1.23449100 | -0.00007200 |
| C | -1.38801300 | 0.00480400 | 0.00009800 |
| C | -0.65851500 | 1.23549200 | -0.00006200 |
| C | 0.70843300 | 1.22568800 | -0.00009100 |
| C | 1.40648800 | -0.01032000 | -0.00015600 |
| H | 1.25632400 | -2.16267500 | -0.00005100 |

| | | | |
|---|---|---|---|
| H | -1.22367600 | -2.16776200 | -0.00014800 |
| H | -1.19839200 | 2.17525300 | -0.00017300 |
| H | 1.26131600 | 2.15869800 | -0.00006800 |
| N | -2.72601700 | 0.01376400 | 0.00012900 |
| H | -3.25970600 | -0.84503800 | 0.00020600 |
| H | -3.25023100 | 0.87827300 | -0.00015200 |
| O | 2.72695200 | -0.09891800 | 0.00011600 |
| H | 3.15992900 | 0.76721400 | 0.00068000 |

**4-nitro aniline (1k)** : E(B3LYP/6-311g(d,p)) = -492.242834 hartrees, G = -492.156949 hartrees, H = -492.114289 hartrees.

| | | | |
|---|---|---|---|
| C | -1.36274800 | -1.21217100 | -0.00412800 |
| C | -2.08173500 | 0.00010400 | -0.00377900 |
| C | -1.36281200 | 1.21223500 | -0.00410500 |
| C | 0.01989500 | 1.21260100 | -0.00273700 |
| C | 0.70736300 | 0.00002600 | -0.00201100 |
| H | 0.58175500 | -2.13628900 | -0.00101100 |
| H | -1.90176200 | -2.15333700 | -0.00842400 |
| H | -1.90162000 | 2.15352100 | -0.00842900 |
| H | 0.58169700 | 2.13631800 | -0.00097700 |
| N | -3.45759700 | -0.00007000 | -0.05190400 |
| H | -3.93712800 | -0.84759900 | 0.20597800 |
| H | -3.93742300 | 0.84730800 | 0.20592000 |
| N | 2.17005800 | 0.00000000 | 0.00254700 |
| O | 2.74298700 | -1.08546600 | 0.00435500 |
| O | 2.74305900 | 1.08541100 | 0.00433000 |

**4-nitro aniline radical cation (1k')**: E(B3LYP/6-311g(d,p)) = -491.941380 hartrees, G = -491.856554 hartrees, H = -491.812982 hartrees.

| | | | |
|---|---|---|---|
| C | -0.01886800 | -1.22959500 | -0.13735400 |
| C | 1.35055300 | -1.23641500 | -0.14308200 |
| C | 2.06705300 | 0.00002900 | 0.00000100 |
| C | 1.35057800 | 1.23649300 | 0.14296200 |
| C | -0.01881200 | 1.22962200 | 0.13720000 |
| C | -0.68868300 | -0.00002600 | -0.00004300 |
| H | -0.59526400 | -2.14122700 | -0.22537100 |

|  |  |  |  |
|---|---|---|---|
| H | 1.90000500 | -2.16430100 | -0.25185600 |
| H | 1.89999500 | 2.16440500 | 0.25172500 |
| H | -0.59521100 | 2.14124500 | 0.22522300 |
| N | 3.39837200 | -0.00004300 | 0.00006400 |
| H | 3.92986600 | 0.85800300 | 0.09495900 |
| H | 3.92980600 | -0.85817000 | -0.09444700 |
| N | -2.16907200 | 0.00001700 | 0.00003600 |
| O | -2.70775000 | -1.01936600 | 0.39032100 |
| O | -2.70790200 | 1.01931300 | -0.39020100 |

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