Supplementary Information for

# Biomimetic photoredox anthraquinone platform for efficient hydrogen peroxide production

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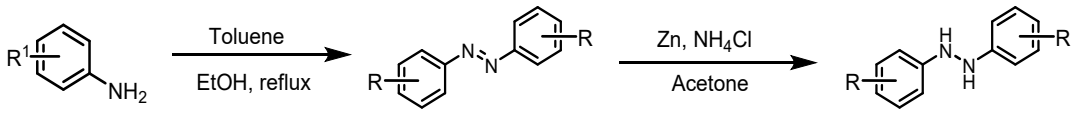
## Contents

## 1. General Information

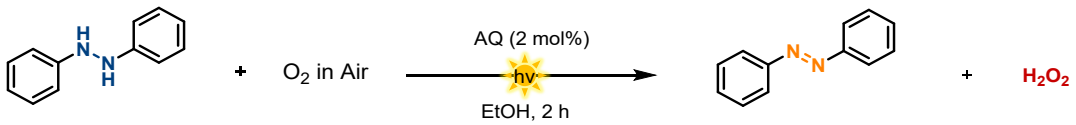
Unless otherwise stated, the chemicals used are all purchased from reagent companies. $^1$H NMR spectra was recorded on a Bruker Advance 400 spectrometer (400 MHz) at 298 K, and the chemical shifts (δ) were expressed in ppm and J values were given in Hz. UV-vis absorption spectra were characterized by a Shimadzu UV-2450 spectrophotometer. Conversion was monitored by thin layer chromatography (TLC). Flash column chromatography was performed over silica gel (100-200 mesh). LED (395 nm, 10W) was purchased from Taobao.com. Quantum Yield Meter (Model C11347-11; Manufacturer: Hamamatsu).

## 2. Preparation of 1,2-diphenyldiazene



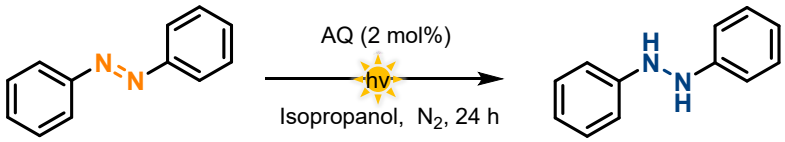

Dissolve the amine (1.0 g) in toluene (60 mL), then add activated manganese dioxide (10 equivalents). The mixture was refluxed at 110 °C for 11 hours. Subsequently, the reaction mixture was filtered. The filtrate was subjected to vacuum treatment to obtain the crude product, which was purified by flash column chromatography to afford the pure azobenzene compound. Dissolve the azobenzene compound (0.8 g) and zinc powder (4.0 g) in acetone (50 mL) and saturated aqueous ammonium chloride solution (5.0 mL), followed by stirring at room temperature for 4 hours. After completion of the reaction, the reaction mixture was filtered and extracted, then dried over anhydrous sodium sulfate. The product was finally obtained via vacuum treatment.

## 3. General procedure for the photochemical reaction



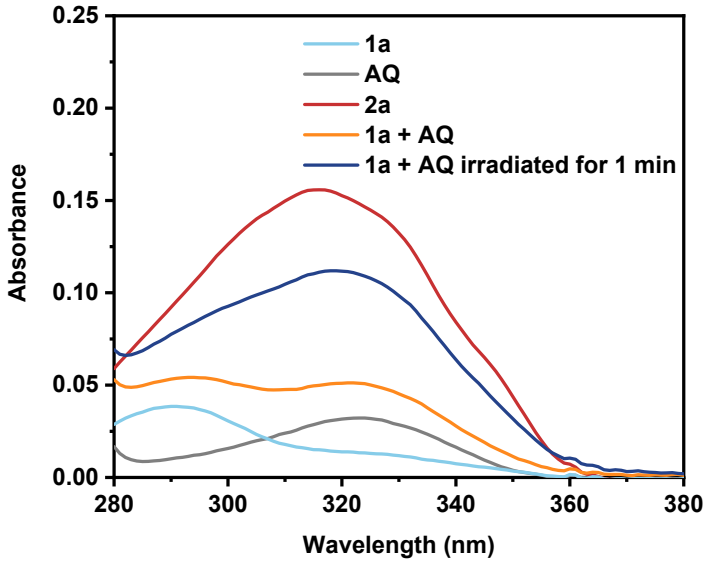

1,2-Diphenylhydrazine (36.8 mg, 0.2 mmol), anthraquinone (0.8 mg, 2 mol%), and ethanol (EtOH, 2.0 mL) were added to a 10 mL screw-cap vial equipped with a magnetic stir bar, with a pipette tip fitted at the vial mouth to act as a gas exchange port.

The reaction vial was positioned 2 cm away from a 10 W purple LED lamp (395 nm). Under ambient air (without inert gas protection), the reaction mixture was irradiated at 25 °C for 2 hours. Upon completion of the reaction, the reaction solution was transferred to a 25 mL round-bottom flask, and the solvent was removed via vacuum concentration. The residue was purified by silica gel flash column chromatography to afford the target pure product.



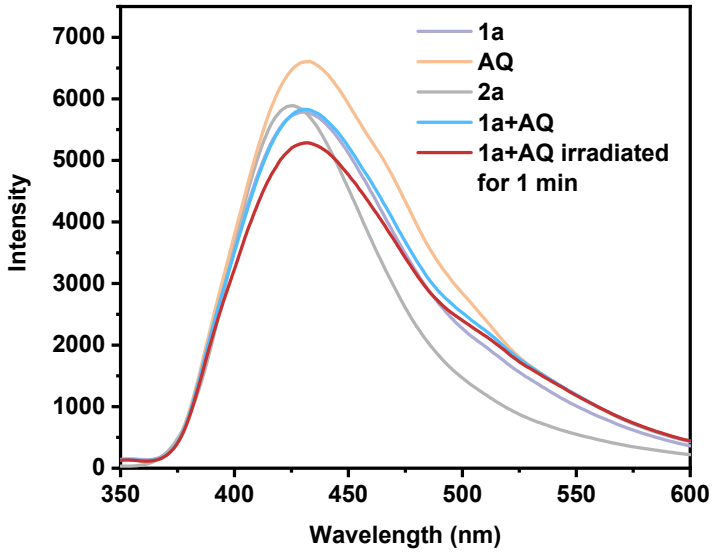

1,2-Diphenylhydrazine (36.4 mg, 0.2 mmol), anthraquinone (0.8 mg, 2 mol%), and isopropanol (2.0 mL) were added to a 10 mL screw-cap vial equipped with a magnetic stir bar. The reaction vial was positioned 2 cm away from a 10 W purple LED lamp (395 nm). Under a nitrogen atmosphere, the reaction mixture was irradiated at 25 °C for 24 hours. Upon completion of the reaction, the reaction solution was transferred to a 25 mL round-bottom flask, and the solvent was removed via vacuum concentration. The residue was purified by silica gel flash column chromatography to afford the target pure product.

## 4. UV−*vis* absorption spectrum



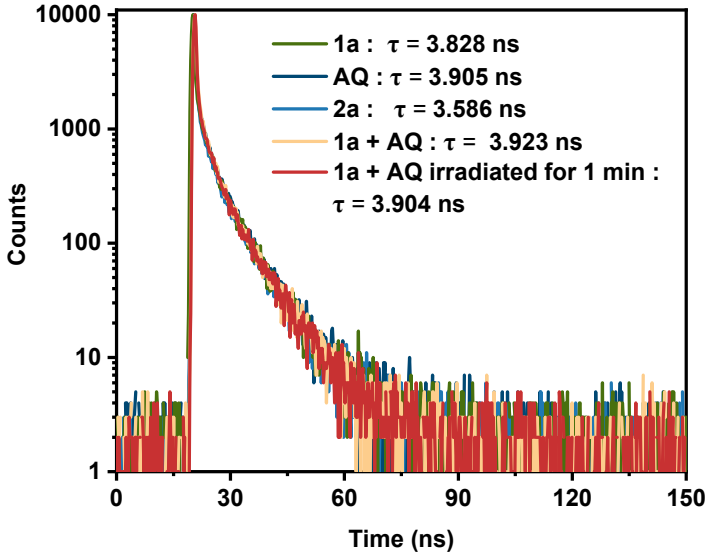

Absorption spectra for 1,2-diphenylhydrazine (**1a**, $1\times10^{-5}$ M in EtOH), anthraquinone ($1\times10^{-5}$ M in EtOH), product (*E*)-1,2-diphenyldiazene (**2a**, $1\times10^{-5}$ M in EtOH), mixture of **1a** and **AQ** ($1\times10^{-5}$ M in EtOH) and mixture of **1a** and **AQ** ($1\times10^{-5}$ M in EtOH) irradiated from one purple 10 W LEDs (395 nm) for 1 min.

## 5. Fluorescence spectrum



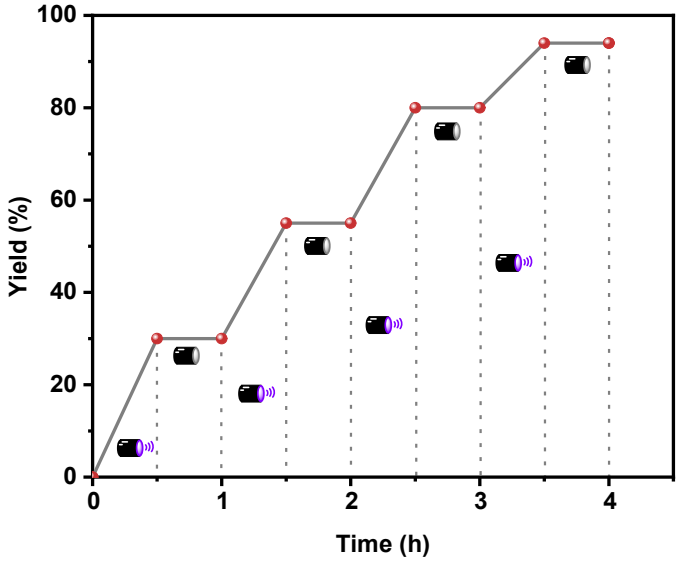

Fluorescence emission spectra for 1,2-diphenylhydrazine (**1a**, $1\times10^{-5}$ M in EtOH), anthraquinone ($1\times10^{-5}$ M in EtOH), product (*E*)-1,2-diphenyldiazene (**2a**, $1\times10^{-5}$ M in EtOH), mixture of **1a** and **AQ** ($1\times10^{-5}$ M in EtOH) and mixture of **1a** and **AQ** ($1\times10^{-5}$ M in EtOH) irradiated from one purple 10 W LEDs (395 nm) for 1 min.

## 6. Fluorescence lifetime spectra



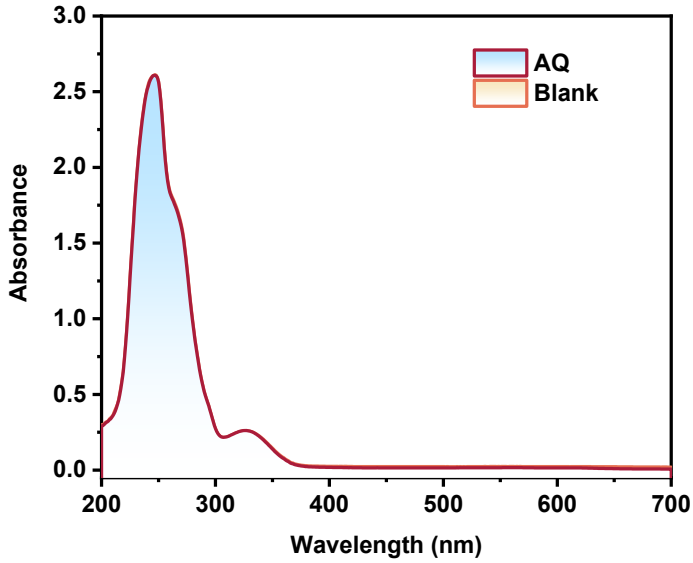

Fluorescence lifetime spectra of 1,2-diphenylhydrazine (**1a**, $1\times10^{-5}$ M in EtOH), anthraquinone ($1\times10^{-5}$ M in EtOH), product (*E*)-1,2-diphenyldiazene (**2a**, $1\times10^{-5}$ M in EtOH), mixture of **1a** and **AQ** ($1\times10^{-5}$ M in EtOH) and mixture of **1a** and **AQ** ($1\times10^{-5}$ M in EtOH) irradiated from one purple 10 W LEDs (395 nm) for 1 min.

## 7. Light on/off experiment



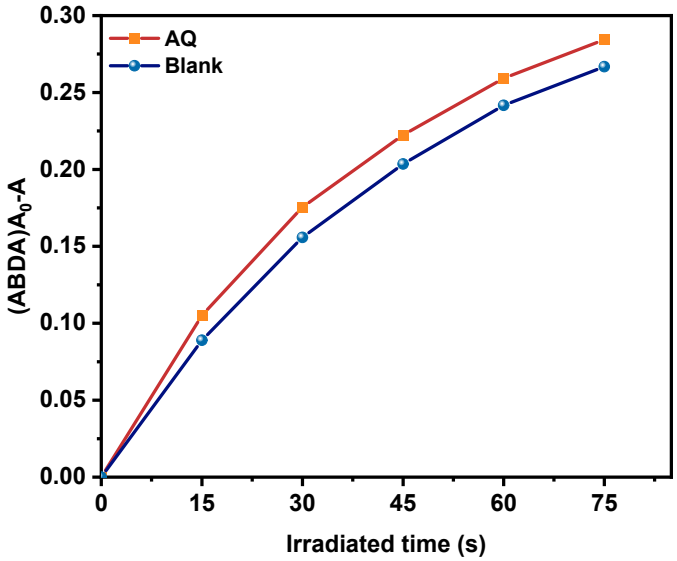

1,2-Diphenylhydrazine (36.8 mg, 0.2 mmol), anthraquinone (0.8 mg, 2 mol%), and ethanol (EtOH, 2.0 mL) were all added to an oven-dried quartz tube equipped with a magnetic stir bar. The reaction vessels were placed 2 cm away from one side of two 10 W purple LED lamps (395 nm), and the mixtures were stirred and irradiated at room temperature. After 0.5 hours, the light source was turned off, and one vial was removed from the irradiator for analysis. Subsequently, the remaining mixtures were continuously stirred under light-free conditions for another 0.5 hours, and one vial was taken out for analysis. The light source was then turned back on to irradiate the remaining two mixtures; after another 0.5 hours, the light source was shut down, and one vial was removed for analysis. The last vial was additionally stirred under light-free conditions for 0.5 hours before analysis. The product yield was determined by $^1$H NMR spectroscopy using dibromomethane as the internal standard.

## 8. UV–*vis* absorption spectra of the cationic radical formed from TMPD



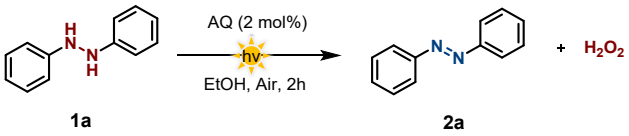

UV-*vis* absorption spectra of the cationic radical of TMPD generated in the presence of blank and AQ ($1\times10^{-5}$ M in EtOH). Blank: TMPD without any additive.

## 9. Rate of $^1O_2$ generation in the presence of AQ




Rate of $^1O_2$ generation in the presence of AQ ($1\times10^{-5}$ M in EtOH). Blank: ABDA without any additive.

## 10. Control experiments

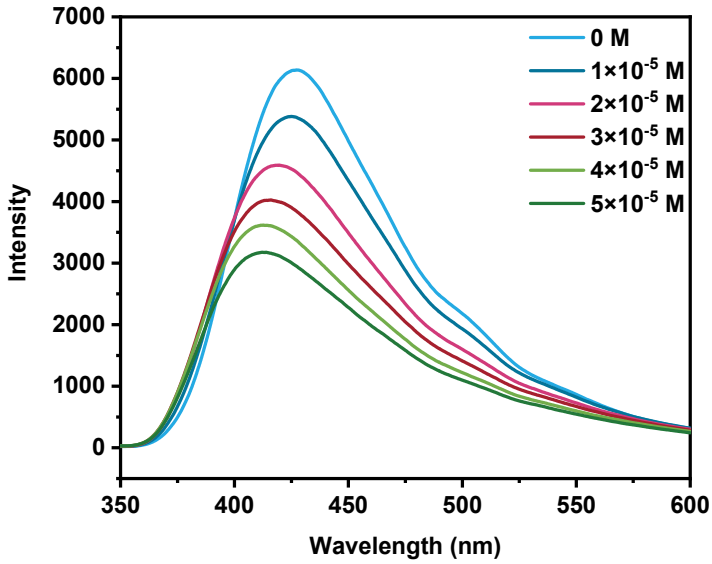



1a 2a

| Additive (2equiv.) | Yield (%) | Additive (2equiv.) | Yield (%) | Additive (2equiv.) | Yield (%) |
|---|---|---|---|---|---|
| standard conditions | 99 | $HO^{\cdot}$ scavenger (TEA) | 95 | $^1O_2$ scavenger ($NaN_3$) | 93 |
| radical scavenger (TEMPO) | 96 | radical scavenger (BHT) | 60 | $O_2^{-\cdot}$ scavenger (Benzoquinone) | 98 |

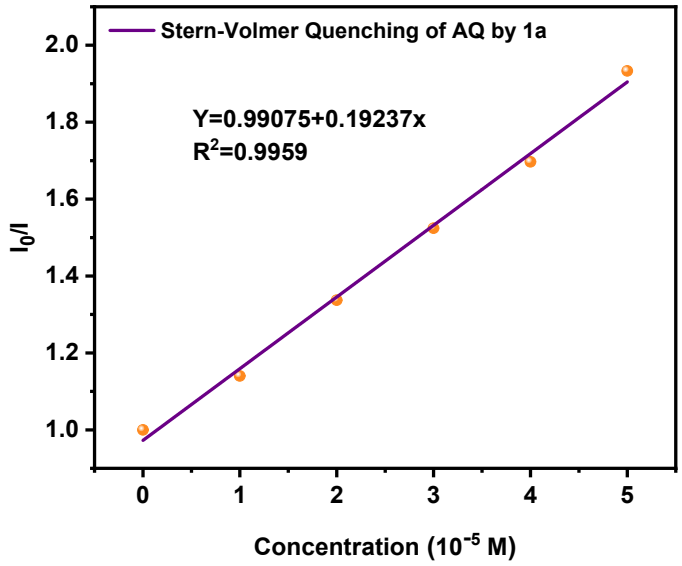
Active species quenchers such as TOMPO and BHT were added to the standard reaction system containing 1,2-diphenylhydrazine (36.8 mg, 0.2 mmol), anthraquinone (0.8 mg, 2 mol%), and ethanol (EtOH, 2.0 mL). The reaction vial was placed 2 cm away from a 10 W purple LED lamp (395 nm). Under ambient air (without inert gas protection), the reaction mixture was irradiated at 25 °C for 2 hours. Upon completion of the reaction, the reaction progress was observed, and the reaction solution was transferred to a 25 mL round-bottom flask. The solvent was removed by vacuum concentration, and the residue was purified by silica gel flash column chromatography to afford the target pure product.

## 11. Stern–Volmer quenching experiment

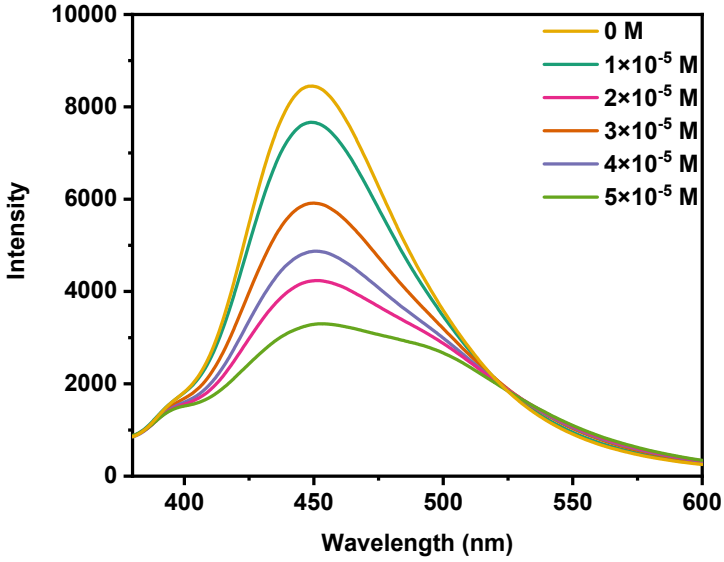



Fluorescence emission spectra for **AQ** ($1\times10^{-5}$ M in EtOH) with the addition of

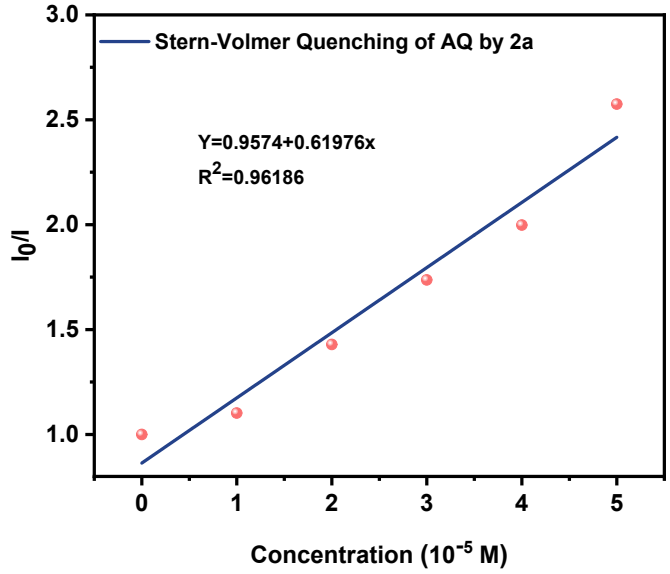
different concentrations of **1a** ($1\times10^{-5}$ M in EtOH) excited at 350 nm.




Stern-Volmer plot

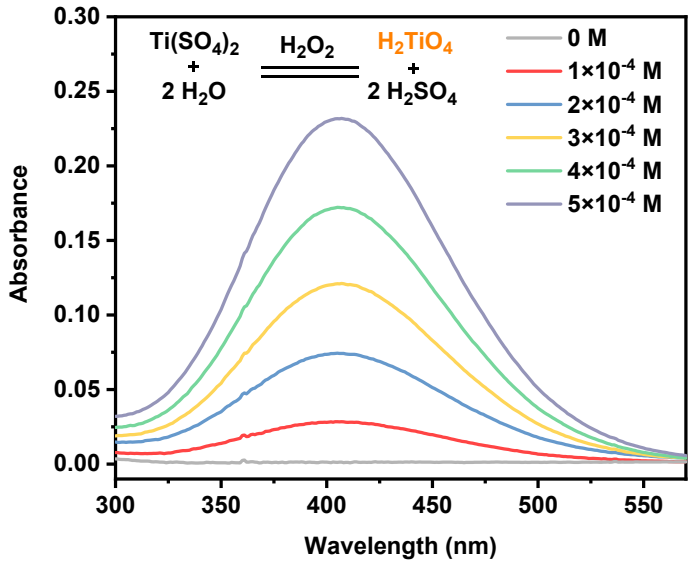



Fluorescence emission spectra for **AQ** ($1\times10^{-5}$ M in isopropanol) with the addition of different concentrations of **2a** ($1\times10^{-5}$ M in isopropanol) excited at 350 nm.



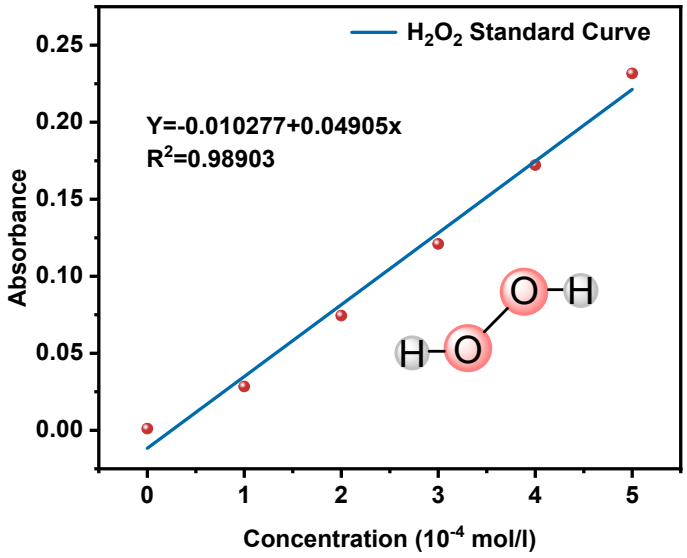

Stern-Volmer plot

## 12. Quantitative determination of hydrogen peroxide using titanium sulfate

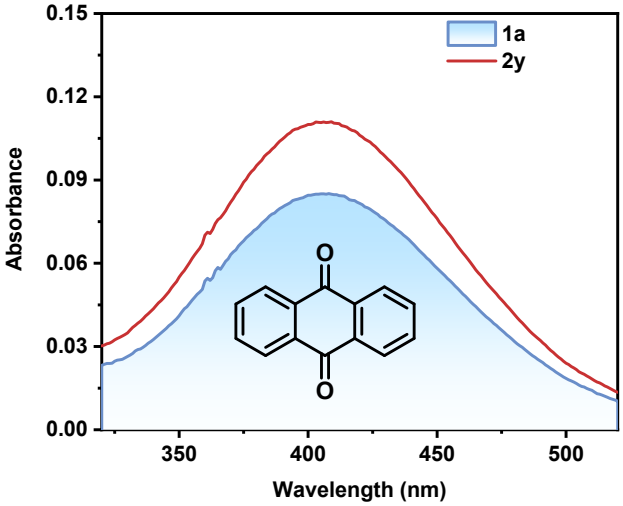



Firstly, the required experimental reagents were prepared. A $5.0\times10^{-2}$ mol/L sulfuric acid solution was prepared using ultrapure water as the solvent, serving as the acidic reaction medium. An appropriate amount of titanium sulfate solid was accurately weighed, dissolved in the aforementioned sulfuric acid solution, and diluted to volume to prepare a $1.0\times10^{-2}$ mol/L titanium sulfate standard solution. A calibrated 30% $H_2O_2$

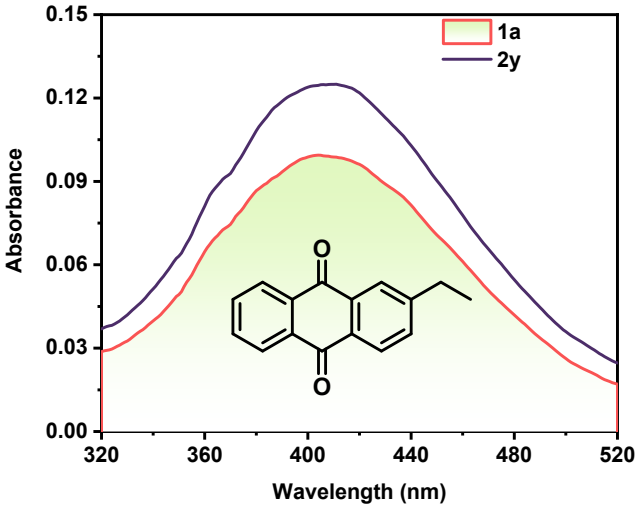
standard sample was used to prepare a $1.0\times10^{-2}$ mol/L $H_2O_2$ standard stock solution, which was stored refrigerated in a brown bottle at 4 ℃ (to be used within 24 hours). Subsequently, a standard curve was constructed: six 10 mL stoppered colorimetric tubes were taken, and different volumes of the $H_2O_2$ standard stock solution were added to each tube respectively. Each tube was diluted to volume with the $5.0\times10^{-2}$ mol/L sulfuric acid solution to prepare a series of $H_2O_2$ standard solutions. The prepared titanium sulfate solution was added to each colorimetric tube at a 1:1 volume ratio. After thorough mixing, the solutions were allowed to stand at room temperature for 5 minutes. Using a blank solution (sulfuric acid solution without $H_2O_2$) as the reference, the absorbance of each tube was measured at the characteristic absorption wavelength of 407 nm using a UV-visible spectrophotometer, and the regression equation of the standard curve was obtained.




Regression equation of the standard curve

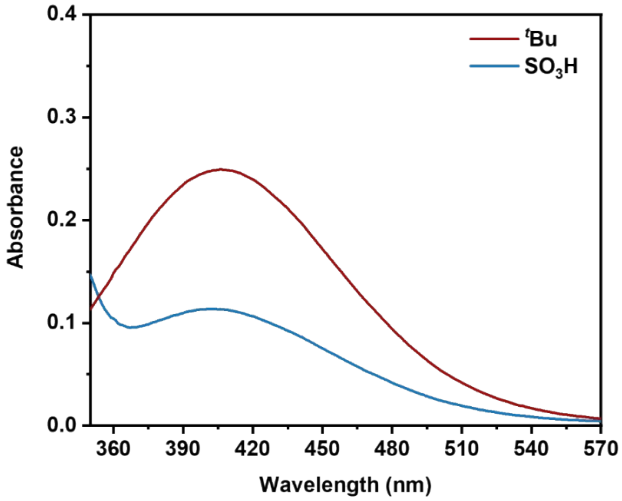



UV absorption spectrum of $H_2O_2$ determined by the titanium sulfate method in the reaction system of 1a and 2y with Anthraquinone as the catalyst.




UV absorption spectrum of $H_2O_2$ determined by the titanium sulfate method in the reaction system of 1a and 2y with Ethylanthraquinone as the catalyst.

## 13. Test spectrum of tert-butyl-substituted and sulfonic acid-substituted anthraquinones

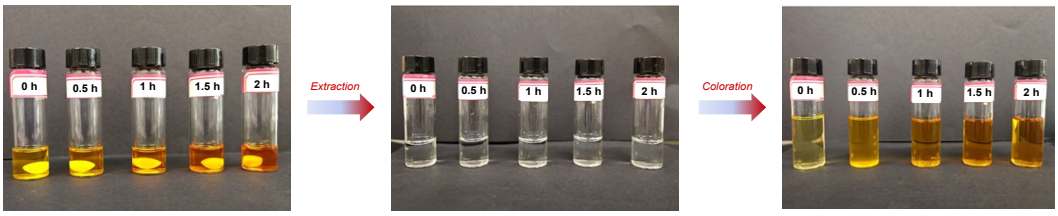



The titanium sulfate method was employed to determine the ultraviolet absorption spectra of hydrogen peroxide in the reaction system when tert-butyl-substituted anthraquinone and sulfonic acid-substituted anthraquinone served as catalysts.

## 14. Quantum yield experiment

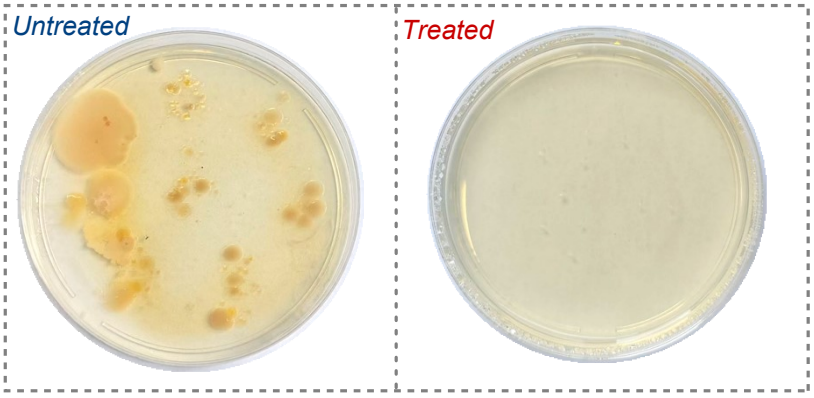

The fluorescence quantum yield of the mixture of 1,2-diphenylhydrazine (**1a**, $1\times10^{-3}$ M in EtOH), **AQ** ($1\times10^{-3}$ M in EtOH) was measured by Quantum Yield Meter (*Model C11347-11; Manufacturer: Hamamatsu, Japan*) with an excitation wavelength of 315 nm.

## 15. Determination of hydrogen peroxide by the titanium sulfate method




1,2-Diphenylhydrazine (36.8 mg, 0.2 mmol), anthraquinone (0.8 mg, 2 mol%), and ethanol (EtOH, 2.0 mL) were added to a 10 mL screw-cap vial equipped with a magnetic stir bar, and a pipette tip was fitted at the vial mouth to serve as a gas exchange port. The reaction vial was positioned 2 cm away from a 10 W purple LED lamp (395 nm). Under ambient air (without inert gas protection), the reaction mixture was irradiated at 25 °C for 2 hours. Upon completion of the reaction, water and dichloromethane (DCM) were added to the reaction vial for extraction, affording a colorless aqueous solution containing $H_2O_2$. Subsequently, a titanium sulfate solution in sulfuric acid was added to the reaction vial, and it was observed that the solution turned yellow.

## 16. Lake-water disinfection experimen




Bacterial disinfection effect of water samples collected from lake water taken from Shandong University of Technology campus (Ji Xia Lake: 118°0′E, 36°48′N)

## 17. Comparison of $H_2O_2$ Production Rates over photocatalysis and electrocatalysis

**Table S1. Comparison of electrocatalytic $H_2O_2$ production**

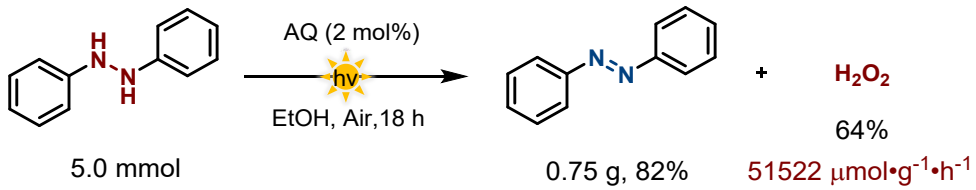
| Catalyst | Electrolyte/PH | $H_2O_2$ production rate | Ref. |
|---|---|---|---|
| Pdδ+⁻OCNT | 0.1 M $HClO_4$ | / | **1** |
| Pt SA/HSC | 0.1 M $HClO_4$ | ~1950 mmol·$g_{cat}^{-1}$·$h^{-1}$ | **2** |
| Pt-Hg | 0.1 M $HClO_4$ | / | **3** |
| Au-Pd-Ni | 0.1 M KOH | 0.0591 mmol·$L^{-1}$·$h^{-1}$ | **4** |
| Pt (0.2wt%)/TiC | 0.1 M $HClO_4$ | / | **5** |
| h-Pt1-$CuS_x$ | 0.1 M $HClO_4$ | ~546 mmol·$g_{cat}^{-1}$·$h^{-1}$ | **6** |
| $Mo_1$/OSG-H | 0.1 M KOH | / | **7** |
| Co-N-C | 0.1 M $HClO_4$ | 80 mmol·$g_{cat}^{-1}$·$h^{-1}$ (0.5 $V_{RHE}$) | **8** |
| FPC | pH = 1 | 112.6~792.6 mmol·$g_{cat}^{-1}$·$h^{-1}$ | **9** |
| F-mrGO | 0.1 M KOH | 430.8 mmol·$g_{cat}^{-1}$·$h^{-1}$ (0.685 $V_{RHE}$) | **10** |
| CNTs | 0.1 M KOH | / | **9** |
| oxo-G/$NH_3H_2O$ | 0.1 M KOH | 224.8 mmol·$g_{cat}^{-1}$·$h^{-1}$ (0.2 $V_{RHE}$) | **11** |
| HPC | 0.1 M $HClO_4$ | 395.7~110.2 mmol·$g_{cat}^{-1}$·$h^{-1}$ | **12** |
| CMK-3 | 0.1 M KOH | 0.3 wt% (2 h) (1.6 V, 46 mA) | **13** |

**Table S2. Comparison of photocatalytic $H_2O_2$ production**

| Photocatalysts | Sacrificial agent | Light source | $H_2O_2$ Yield ($\mu mol \cdot g^{-1} \cdot h^{-1}$) | Ref. |
|---|---|---|---|---|
| TAPT–DHA | / | Xe lamp | 1629 | **14** |
| CKCN | IPA | 300 W Xe lamp | 9000 | **15** |
| ZnO/$WO_3$ | Ethanol | 300 W Xe lamp | 6788 | **16** |
| COF-2CN | / | 300 W Xe lamp (λ≥420 nm) | 1601 | **17** |
| KPCN | IPA | 300 W Xe lamp (λ>420 nm) | 7740 | **18** |
| Sb-SAPC | / | 300 W Xe lamp (λ=420～500 nm) | 196 | **19** |
| NiSAPs-PuCN | / | 300 W Xe lamp (λ≥420 nm) | 342.2 | **20** |
| Nv–CN–CN | / | 300 W Xe lamp (λ≥420 nm) | 3093 | **21** |
| ZnPPC-NBCN | / | 300 W Xe lamp (λ=400～800 nm) | 114 | **22** |
| CPN | / | 300 W Xe lamp (λ≥420 nm) | 1968 | **23** |
| Co/AQ/$C_3N_4$ | / | Xe lamp AM 1.5G | 124 | **24** |
| 5Cv@g-$C_3N_4$ | / | Xe lamp AM 1.5G | 1650 | **25** |
| TfpBpy (COF) | / | Xe lamp (λ=420～700 nm) | 694.7 | **26** |
| TZ-COF (COF) | | Xe lamp (λ>420 nm) | 268 | **27** |
| JNM-24 (MOF) | / | 300 W Xe lamp | 168 | **28** |
| CNIO-GaSA | / | Visible light (λ≥420 nm) | 331.7 | **29** |
| $Ni_1Zn_1$-PCN | / | 300 W Xe lamp | 1205.4 | **30** |
| **AQ**-PAFs | / | 300 W Xe lamp (λ>420nm) | 7124 | **31** |
| **AQ**TEE-COP | / | Visible light (λ≥420nm) | 3204 | **32** |
| PS-TAA-**AQ**-Ru | furfuryl alcohol | 300 W Xe lamp (λ>400nm) | 1550±50 | **33** |

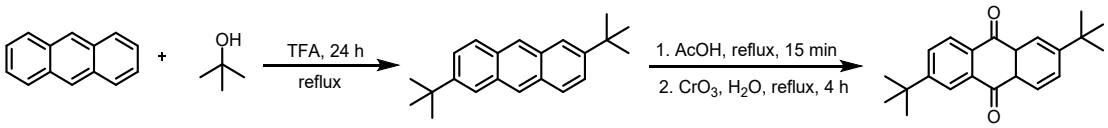
| | | | | |
|---|---|---|---|---|
| PEI/$C_3N_4$ | / | Xe lamp AM 1.5G | 208.1 | **34** |
| TBTN-COF (COF) | / | 300 W Xe lamp (λ>420nm) | 11013 | **35** |
| TpDz | / | 300 W Xe lamp (λ>420nm) | 7327 | **36** |
| PS-Ru-**AQ**-TAA | / | 300 W Xe lamp (λ≥420nm) | 1111 | **33** |
| AQ | / | Visible light (λ=395 nm LED) | 97500 | **This work** |

## 18. Gram scale preparation




Add 1,2-diphenylhydrazine (920.5 mg, 5 mmol), anthraquinone (20.8 mg, 0.1 mmol) and ethanol (50 mL) to an oven-dried quartz tube equipped with a magnetic stirring bar. Irradiate the mixture with four 10W purple LED lamps (395 nm) at 25 °C for 18 hours under ambient air without inert gas protection. Subsequently, concentrate the residual solvent under vacuum and purify by flash column chromatography on silica gel to obtain the product 1,2-diphenyldiazene (746.5 mg, 82% yield) and $H_2O_2$ (51522 μmol·$g^{-1}$·$h^{-1}$, 64% yield).

## 19. Synthesis of 2,6-Di-tert-butylanthraquinone

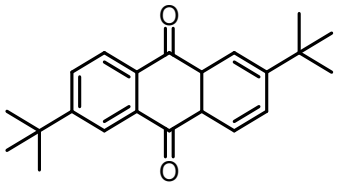



The target compound was synthesized based on the previously published reference[37]. In a 100 mL round-bottom flask, prepare a mixture containing 5.78 mmol (1.03 g) of anthracene, 16.73 mmol (1.24 g) of tert-butanol, and 7.5 mL of trifluoroacetic acid. Heat the mixture to 120°C and reflux for 24 hours. After reaction completion, the mixture was cooled to room temperature. Reaction was terminated by adding 1 mL ice water and 1 mL petroleum ether. The entire system was transferred to a 50 mL beaker and 13 mL distilled water was added. Excess acid was neutralized by adding sodium

bicarbonate in portions. The mixture was then transferred to a separatory funnel, and the organic layer was washed repeatedly with distilled water and saturated salt solution. After washing, the organic phase was filtered under reduced pressure through a Büchner funnel. The filter cake was washed with ice-cold petroleum ether to yield a white solid powder. The cake was transferred to a watch glass and dried in a vacuum oven at 50°C for 12 hours. The final white powdery product, 2,6-di-tert-butylanthracene, was obtained in 0.80 g, corresponding to an overall yield of 45%.

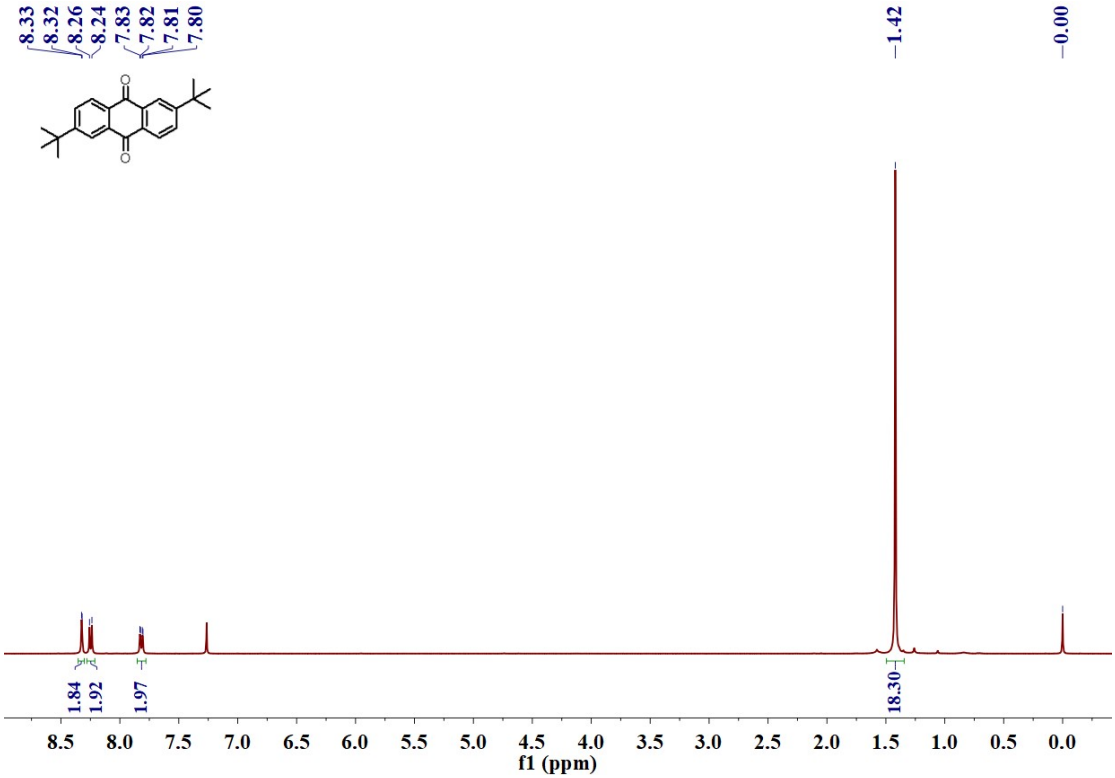
In a 100 mL round-bottom flask, mix 5.5 mmol (1.60 g) of 2,6-di-tert-butylanthraquinone with 16 g of glacial acetic acid. The reaction mixture was heated to 124°C, maintained at this temperature for 15 minutes, then cooled to room temperature. A solution containing 2.4 mL distilled water and 15.4 mmol (15.4 g) chromium trioxide ($CrO_3$) was added to the flask. The reaction system was refluxed at 110°C for 4 hours. After heating cessation, allow the reaction mixture to cool to room temperature before adding 80 mL ice water to quench the reaction. Filter the mixture through a Büchner funnel to isolate green crystals. Wash the crystals sequentially with hot water and 1 M NaOH solution in batches; the solid color changes from green to pale yellow. After final washing with ice water, the solid was transferred to a Petri dish and dried in a vacuum oven at 50°C for 12 hours. This yielded 1.5 g of yellow crystalline 2,6-di-tert-butylanthraquinone with an 87% yield. The spectral data of the product correspond to those previously reported.

**2,6-di-tert-butyl-4a,9a-dihydroanthracene-9,10-dione AQ1**

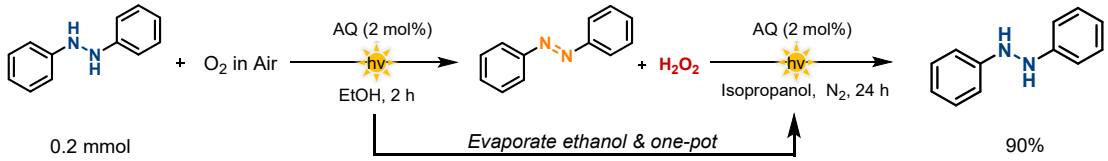


$^1$H NMR (400 MHz, Chloroform-*d*) δ 8.32 (d, *J* = 2.1 Hz, 2H), 8.25 (d, *J* = 8.2 Hz, 2H), 7.82 (dd, *J* = 8.2, 2.1 Hz, 2H), 1.42 (s, 18H). The spectrum is consistent with the reference literature[37].

$^1$H NMR (400 MHz, Chloroform-*d*) spectrum of compound **AQ1**

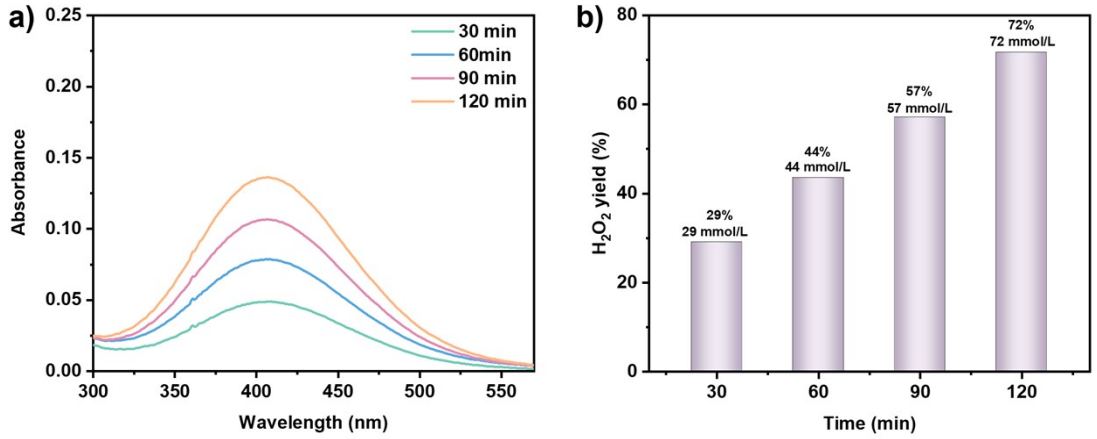



## 20. One-pot experiment




Add 1,2-diphenylhydrazine (36.8 mg, 0.2 mmol), anthraquinone (0.8 mg, 2 mol%), and ethanol (EtOH, 2.0 mL) to a 10 mL screw-cap vial equipped with a magnetic stir bar. Use a pipette tip as the gas exchange port at the vial opening. The reaction flask was placed 2 cm below a 10W violet LED lamp (395 nm). Under ambient air conditions (without inert gas protection), the reaction mixture was irradiated at 25 °C for 2 hours. After the reaction, the solvent was removed by vacuum concentration. Add isopropanol (2.0 mL) to the reaction flask and place it 2 cm below a 10W violet LED lamp (395 nm). Under a nitrogen atmosphere, the reaction mixture was irradiated at 25°C for 24 hours. After the reaction, the reaction solution was transferred to a 25 mL round-bottom flask and the solvent was removed by vacuum concentration. The residue was purified by silica gel flash chromatography, yielding the target pure compound in 90% yield.

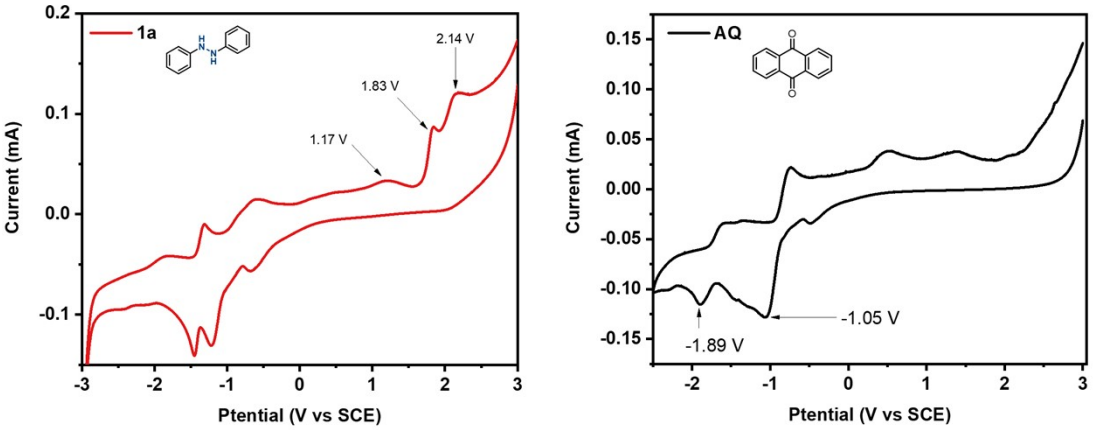
## 21. The variation of hydrogen peroxide yield/concentration over time




**a)** The curve of ultraviolet absorption of titanium sulfate method over time; **b)** The yield/concentration of hydrogen peroxide varies with time.

When using the titanium sulfate method to determine the ultraviolet absorption spectrum of hydrogen peroxide in the reaction system with anthraquinone as a catalyst, four parallel reactions with different reaction times were first conducted under standard reaction conditions. After reaction completion, the reaction mixture was extracted with dichloromethane, and the upper aqueous layer was collected. The extracted aqueous layer was diluted for later use. Subsequently, a $5\times10^{-2}$ concentration sulfuric acid solution and a $1\times10^{-2}$ titanium sulfate solution was prepared for later use. UV testing was then conducted. A 100 μL aliquot of the test solution and a sulfuric acid peptide solution were diluted to 3 mL in sulfuric acid solution. The UV absorption of the hydrogen peroxide-sulfuric acid peptide reaction was measured at different reaction times. Subsequently, calculations were performed using the standard curve obtained from the hydrogen peroxide-sulfuric acid titanium method to determine the concentration and yield.

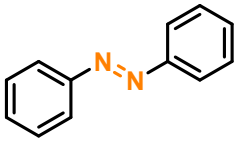
## 22.CV experiment




Solvent: acetonitrile solution containing tetrabutylammonium hexafluorophosphate (0.1M); Scan rate: 200 mV/s

## 23. Characterization data for products

**1,2-diphenyldiazene 2a**

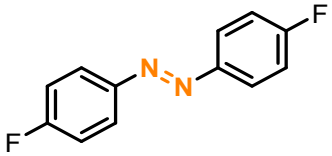


Following the general procedure. The crude material was purified by flash column chromatography (Petroleum ether /EtOAc = 20:1) to give **2a** as a colorless oil (36.0 mg, 99% yield).

$^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.87 (m, 4H), 7.53 – 7.41 (m, 6H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 152.7, 131.1, 129.2, 122.9.

**1,2-bis(4-fluorophenyl)diazene 2b**

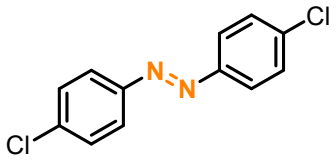


Following the general procedure. The crude material was purified by flash column chromatography (Petroleum ether /EtOAc = 20:1) to give **2b** as a colorless oil (41.4 mg, 95% yield).

$^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.90 (m, 4H), 7.21 (dd, *J* = 9.0, 8.2 Hz, 4H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 165.6, 163.1, 149.0 (d, *J* = 2.6 Hz), 124.8 (d, *J* = 9.1 Hz), 116.1 (d, *J* = 23.1 Hz).

**1,2-bis(4-chlorophenyl)diazene 2c**

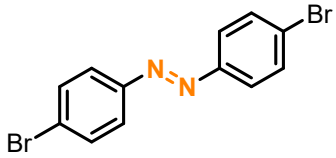



Following the general procedure. The crude material was purified by flash column chromatography (Petroleum ether /EtOAc = 20:1) to give **2c** as a colorless oil (45.0 mg, 90% yield).

$^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.84 (m, 4H), 7.52 – 7.47 (m, 4H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 150.7, 137.2, 129.4, 124.2.

**1,2-bis(4-bromophenyl)diazene 2d**

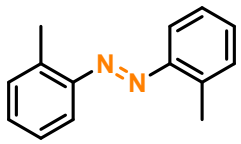



Following the general procedure. The crude material was purified by flash column chromatography (Petroleum ether /EtOAc = 20:1) to give **2d** as a colorless oil (69.5 mg, 92% yield).

$^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.77 – 7.70 (m, 4H), 7.63 – 7.58 (m, 4H).

$^{3}$C NMR (101 MHz, Chloroform-*d*) δ 151.1, 132.4, 125.8, 124.4.

**1,2-di-o-tolyldiazene 2e**

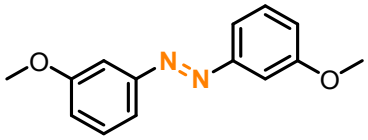



Following the general procedure. The crude material was purified by flash column chromatography (Petroleum ether /EtOAc = 20:1) to give **2e** as a colorless oil (36.6 mg, 87% yield).

$^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.58 (m, 2H), 7.38 – 7.32 (m, 4H), 7.26 (ddd, *J* = 10.3, 5.5, 2.3 Hz, 2H), 2.74 (s, 6H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 151.1, 138.1, 131.3, 130.7, 126.4, 115.9, 17.7.

**1,2-bis(3-methoxyphenyl)diazene 2f**

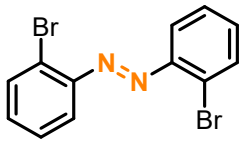


Following the general procedure. The crude material was purified by flash column chromatography (Petroleum ether /EtOAc = 20:1) to give **2f** as a colorless oil (41.2 mg, 85% yield).

$^1$H NMR (400 MHz, Chloroform-*d*) δ 7.56 (ddd, *J* = 7.8, 1.8, 1.0 Hz, 2H), 7.47 – 7.40 (m, 4H), 7.05 (ddd, *J* = 8.2, 2.7, 1.0 Hz, 2H), 3.90 (s, 6H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 160.3, 153.8, 129.8, 117.9, 117.2, 105.7, 55.5.

**1,2-bis(2-bromophenyl)diazene 2g**

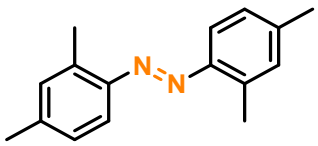


Following the general procedure. The crude material was purified by flash column chromatography (Petroleum ether /EtOAc = 20:1) to give **2g** as a colorless oil (61.5 mg, 91% yield).

$^1$H NMR (400 MHz, Chloroform-*d*) δ 7.76 (ddd, *J* = 7.9, 4.1, 1.6 Hz, 4H), 7.41 (td, *J* = 7.6, 1.5 Hz, 2H), 7.34 (td, *J* = 7.6, 1.8 Hz, 2H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 149.5, 133.8, 132.5, 128.1, 126.4, 118.5.

**1,2-bis(2,4-dimethylphenyl)diazene 2h**

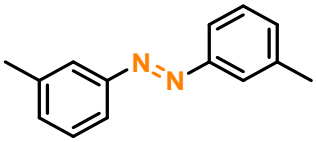


Following the general procedure. The crude material was purified by flash column chromatography (Petroleum ether /EtOAc = 20:1) to give **2h** as a colorless oil (39.5 mg, 83% yield).

$^1$H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 1.9 Hz, 2H), 7.03 (dd, *J* = 8.2, 1.9 Hz, 2H), 2.67 (s, 6H), 2.35 (s, 6H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 149.2, 140.7, 137.9, 131.8, 127.1, 115.7, 21.4, 17.6.

**1,2-di-m-tolyldiazene 2i**

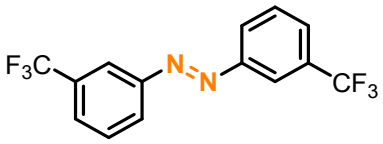


Following the general procedure. The crude material was purified by flash column chromatography (Petroleum ether /EtOAc = 20:1) to give **2i** as a colorless oil (37.0 mg, 88% yield).

$^1$H NMR (400 MHz, Chloroform-*d*) δ 7.72 (dd, *J* = 6.5, 1.6 Hz, 4H), 7.38 (dd, *J* = 8.6, 7.5 Hz, 2H), 7.26 (d, *J* = 7.5 Hz, 2H), 2.43 (s, 6H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 152.8, 139.0, 131.8, 129.0, 122.9, 120.6, 21.5.

**1,2-bis(3-(trifluoromethyl)phenyl)diazene 2j**

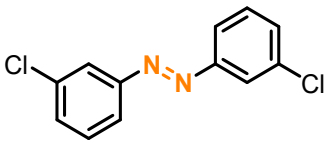


Following the general procedure. The crude material was purified by flash column chromatography (Petroleum ether /EtOAc = 20:1) to give **2j** as a colorless oil (52.2 mg, 82% yield).

$^1$H NMR (400 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 1.9 Hz, 2H), 8.14 (dt, *J* = 7.9, 1.5 Hz, 2H), 7.77 (d, *J* = 7.7 Hz, 2H), 7.68 (t, *J* = 7.8 Hz, 2H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 152.2, 131.9 (q, *J* = 33.0 Hz), 129.8, 127.9 (q, *J* = 3.7 Hz), 126.5, 125.1, 122.4, 119.7 (q, *J* = 3.8 Hz).

**1,2-bis(3-chlorophenyl)diazene 2k**

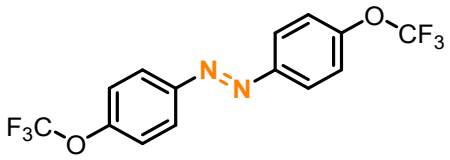


Following the general procedure. The crude material was purified by flash column chromatography (Petroleum ether /EtOAc = 20:1) to give **2k** as a colorless oil (40.0 mg, 80% yield).

$^1$H NMR (400 MHz, Chloroform-*d*) δ 7.88 (q, *J* = 1.5 Hz, 2H), 7.82 (ddt, *J* = 6.8, 4.3, 2.4 Hz, 2H), 7.49 – 7.41 (m, 4H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 153.1, 135.2, 131.2, 130.2, 122.7, 121.9.

**1,2-bis(4-(trifluoromethoxy)phenyl)diazene 2l**

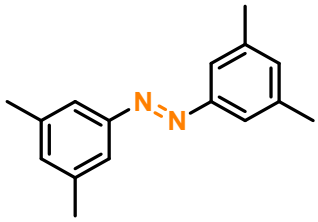


Following the general procedure. The crude material was purified by flash column chromatography (Petroleum ether /EtOAc = 20:1) to give **2l** as a colorless oil (63.0 mg, 90% yield).

$^1$H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.90 (m, 4H), 7.35 (dq, *J* = 7.9, 1.1 Hz, 4H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 151.2 (q, *J* = 1.9 Hz), 150.5, 124.5, 121.7, 121.29, 117.9 (d, *J* = 258.1 Hz).

**1,2-bis(3,5-dimethylphenyl)diazene 2m**

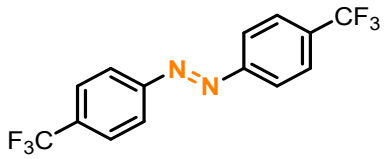


Following the general procedure. The crude material was purified by flash column chromatography (Petroleum ether /EtOAc = 20:1) to give **2m** as a colorless oil (45.2 mg, 95% yield).

$^1$H NMR (400 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 1.6 Hz, 4H), 7.10 (s, 2H), 2.40 (s, 12H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 152.9, 138.8, 132.6, 120.6, 21.3.

**1,2-bis(4-(trifluoromethyl)phenyl)diazene 2n**



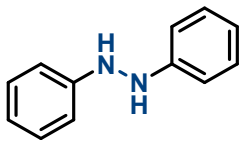
Following the general procedure. The crude material was purified by flash column chromatography (Petroleum ether /EtOAc = 20:1) to give **2n** as a colorless oil (54.7 mg, 86% yield).

$^1$H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.2 Hz, 4H), 7.80 (d, *J* = 8.3 Hz, 4H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 154.0 (d, *J* = 1.5 Hz), 133.0 (q, *J* = 32.6 Hz),

127.9, 126.4 (q, $J$ = 3.8 Hz), 125.2, 123.3, 122.4, 119.7.

**1,2-diphenylhydrazine 1a**

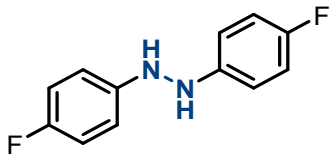


Following the general procedure. The crude material was purified by flash column chromatography (Petroleum ether /EtOAc = 10:1) to give **1a** as a colorless oil (35.0 mg, 95% yield).

$^1$H NMR (400 MHz, Chloroform-*d*) δ 7.19 (dd, $J$ = 8.8, 7.1 Hz, 4H), 6.87 – 6.76 (m, 6H), 5.50 (s, 2H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 148.9, 129.4, 119.9, 112.4.

**1,2-bis(4-fluorophenyl)hydrazine 2o**

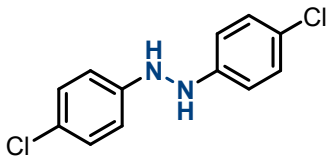


Following the general procedure. The crude material was purified by flash column chromatography (Petroleum ether /EtOAc = 10:1) to give **2o** as a colorless oil (40.5 mg, 92% yield).

$^1$H NMR (400 MHz, Chloroform-*d*) δ 6.90 (td, $J$ = 8.8, 4.5 Hz, 4H), 6.75 (dt, $J$ = 8.8, 4.4 Hz, 4H), 5.56 – 5.46 (m, 2H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 158.4, 156.0, 144.9 (d, $J$ = 2.1 Hz), 115.9 (d, $J$ = 22.4 Hz), 113.4 (d, $J$ = 7.6 Hz).

**1,2-bis(4-chlorophenyl)hydrazine 2p**

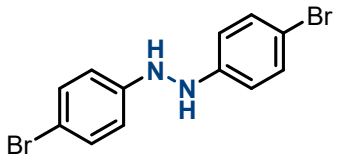


Following the general procedure. The crude material was purified by flash column chromatography (Petroleum ether /EtOAc = 10:1) to give **2p** as a colorless oil (44.9 mg, 89% yield).

$^1$H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.09 (m, 4H), 6.80 – 6.69 (m, 4H), 5.59 (s, 2H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 147.1, 129.3, 124.7, 113.5.

**1,2-bis(4-bromophenyl)hydrazine 2q**

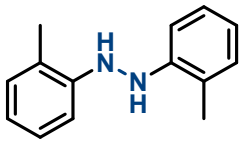



Following the general procedure. The crude material was purified by flash column chromatography (Petroleum ether /EtOAc = 10:1) to give **2q** as a colorless oil (59.1 mg, 87% yield).

$^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.25 (m, 4H), 6.72 – 6.68 (m, 4H), 5.61 (s, 2H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 147.4, 132.2, 124.5, 114.0.

**1,2-di-o-tolylhydrazine 2r**

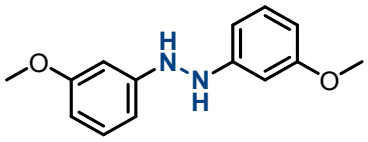



Following the general procedure. The crude material was purified by flash column chromatography (Petroleum ether /EtOAc = 10:1) to give **2r** as a colorless oil (39.5 mg, 93% yield).

$^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.12 – 7.04 (m, 4H), 6.88 (dd, *J* = 8.0, 1.2 Hz, 2H), 6.77 (td, *J* = 7.3, 1.3 Hz, 2H), 5.50 (s, 2H), 2.24 (s, 6H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 146.3, 130.4, 127.3, 121.2, 119.4, 111.0, 17.2.

**1,2-bis(3-methoxyphenyl)hydrazine 2s**

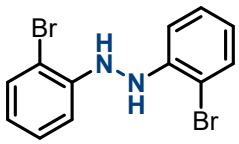



Following the general procedure. The crude material was purified by flash column chromatography (Petroleum ether /EtOAc = 10:1) to give **2s** as a colorless oil (41.0 mg, 84% yield).

$^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.13 – 7.05 (m, 2H), 6.43 – 6.34 (m, 6H), 5.55 (s, 2H), 3.72 (s, 6H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 160.9, 150.5, 130.2, 105.2, 105.1, 98.4, 55.2.

**1,2-bis(2-bromophenyl)hydrazine 2t**

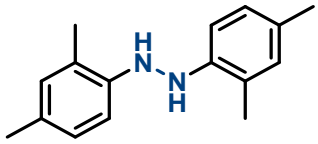


Following the general procedure. The crude material was purified by flash column chromatography (Petroleum ether /EtOAc = 10:1) to give **2t** as a colorless oil (59.8 mg, 88% yield).

$^1$H NMR (400 MHz, Chloroform-*d*) δ 7.45 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.15 (ddd, *J* = 8.5, 7.5, 1.4 Hz, 2H), 6.91 (dd, *J* = 8.2, 1.6 Hz, 2H), 6.71 (td, *J* = 7.6, 1.6 Hz, 2H), 6.20 (s, 2H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 144.7, 132.6, 128.7, 120.8, 113.1, 107.5.

**1,2-bis(2,4-dimethylphenyl)hydrazine 2u**

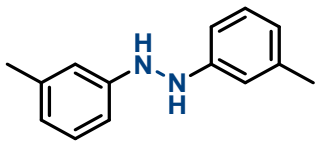


Following the general procedure. The crude material was purified by flash column chromatography (Petroleum ether /EtOAc = 10:1) to give **2u** as a colorless oil (38.9 mg, 81% yield).

$^1$H NMR (400 MHz, Chloroform-*d*) δ 6.90 (d, *J* = 2.0 Hz, 2H), 6.86 (dd, *J* = 8.2, 2.0 Hz, 2H), 6.76 (d, *J* = 8.1 Hz, 2H), 5.35 (s, 2H), 2.23 (s, 6H), 2.17 (s, 6H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 142.1, 131.2, 127.9, 127.4, 122.6, 115.2, 20.6, 17.4.

**1,2-di-m-tolylhydrazine 2v**

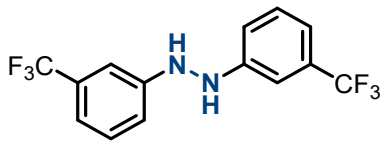


Following the general procedure. The crude material was purified by flash column chromatography (Petroleum ether /EtOAc = 10:1) to give **2v** as a colorless oil (32.7 mg, 77% yield).

$^1$H NMR (400 MHz, Chloroform-*d*) δ 7.07 (t, *J* = 7.9 Hz, 2H), 6.68 – 6.56 (m, 6H), 5.41 (s, 2H), 2.25 (s, 6H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 149.2, 139.3, 129.3, 120.8, 113.1 109.6, 21.7.

**1,2-bis(3-(trifluoromethyl)phenyl)hydrazine 2w**

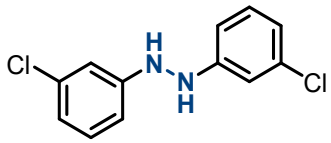


Following the general procedure. The crude material was purified by flash column chromatography (Petroleum ether /EtOAc = 10:1) to give **2w** as a colorless oil (49.9mg, 78% yield).

$^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.30 (t, *J* = 7.9 Hz, 2H), 7.12 – 7.06 (m, 4H), 7.00 – 6.95 (m, 2H), 5.80 (s, 2H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 148.7, 131.8 (q, *J* = 32.2 Hz), 130.0, 128.2, 125.5, 122.8, 120.1, 116.8 (q, *J* = 3.9 Hz), 115.3 (d, *J* = 1.4 Hz), 108.8 (q, *J* = 3.9 Hz).

**1,2-bis(3-chlorophenyl)hydrazine 2x**

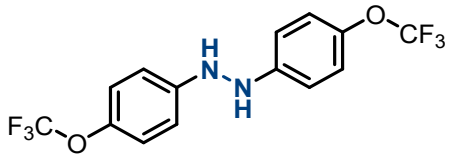


Following the general procedure. The crude material was purified by flash column chromatography (Petroleum ether /EtOAc = 10:1) to give **2x** as a colorless oil (42.3 mg, 84% yield).

$^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.13 (t, *J* = 8.0 Hz, 2H), 6.85 – 6.79 (m, 4H), 6.68 (ddd, *J* = 8.2, 2.3, 0.9 Hz, 2H), 5.65 (s, 2H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 149.6, 135.3, 130.5, 120.2, 112.3, 110.5.

**1,2-bis(4-(trifluoromethoxy)phenyl)hydrazine 2y**

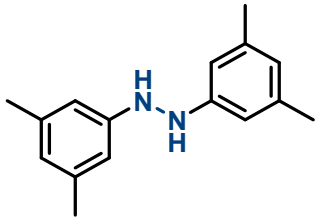


Following the general procedure. The crude material was purified by flash column chromatography (Petroleum ether /EtOAc = 10:1) to give **2y** as a colorless oil (45.8 mg, 65% yield).

$^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.11 – 7.04 (m, 4H), 6.83 – 6.78 (m, 4H), 5.81 (s, 2H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 147.3, 142.3 (q, *J* = 2.1 Hz), 124.5, 122.5, 121.91, 119.4, 116.8, 112.8.

**1,2-bis(3,5-dimethylphenyl)hydrazine 2z**

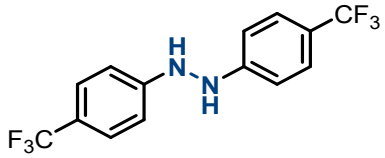


Following the general procedure. The crude material was purified by flash column chromatography (Petroleum ether /EtOAc = 10:1) to give **2z** as a colorless oil (35.1 mg, 73% yield).

$^{1}$H NMR (400 MHz, Chloroform-*d*) δ 6.46 (dd, *J* = 6.8, 1.5 Hz, 6H), 5.42 (s, 2H), 2.22 (s, 12H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 149.4, 139.1, 121.7, 110.1, 21.5.

**1,2-bis(4-(trifluoromethyl)phenyl)hydrazine 3a**



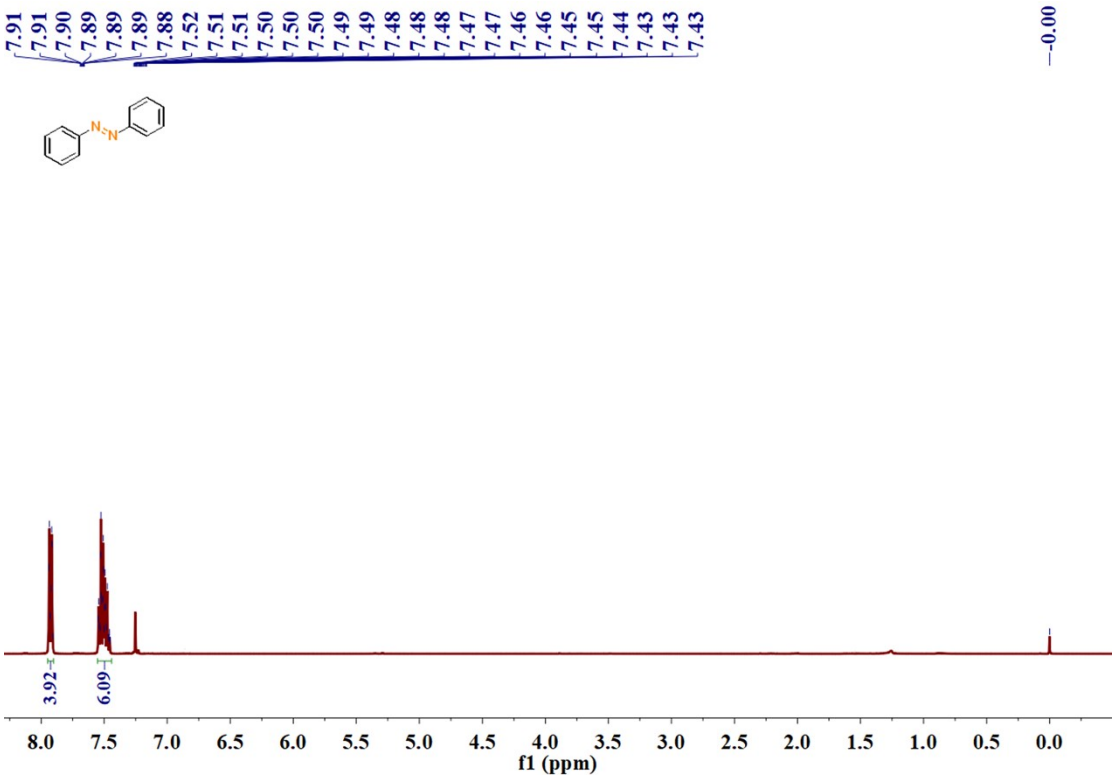
Following the general procedure. The crude material was purified by flash column chromatography (Petroleum ether /EtOAc = 10:1) to give **3a** as a colorless oil (57.0 mg, 89% yield).

$^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.5 Hz, 4H), 6.85 (d, *J* = 8.5 Hz, 4H), 6.05 (s, 2H).

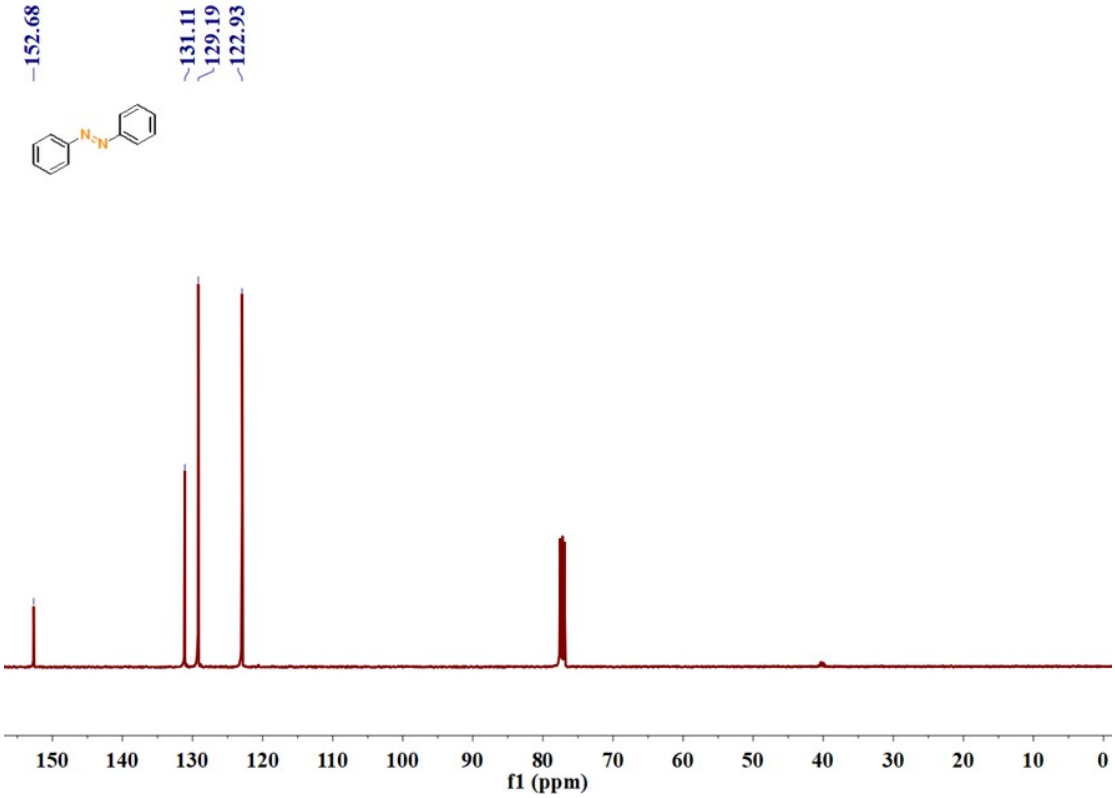
$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 150.9, 128.7, 126.8 (q, *J* = 3.9 Hz), 126.0, 123.3, 121.9 (q, *J* = 32.6 Hz), 120.6, 111.6.

## 24. Spectra of prepared compounds

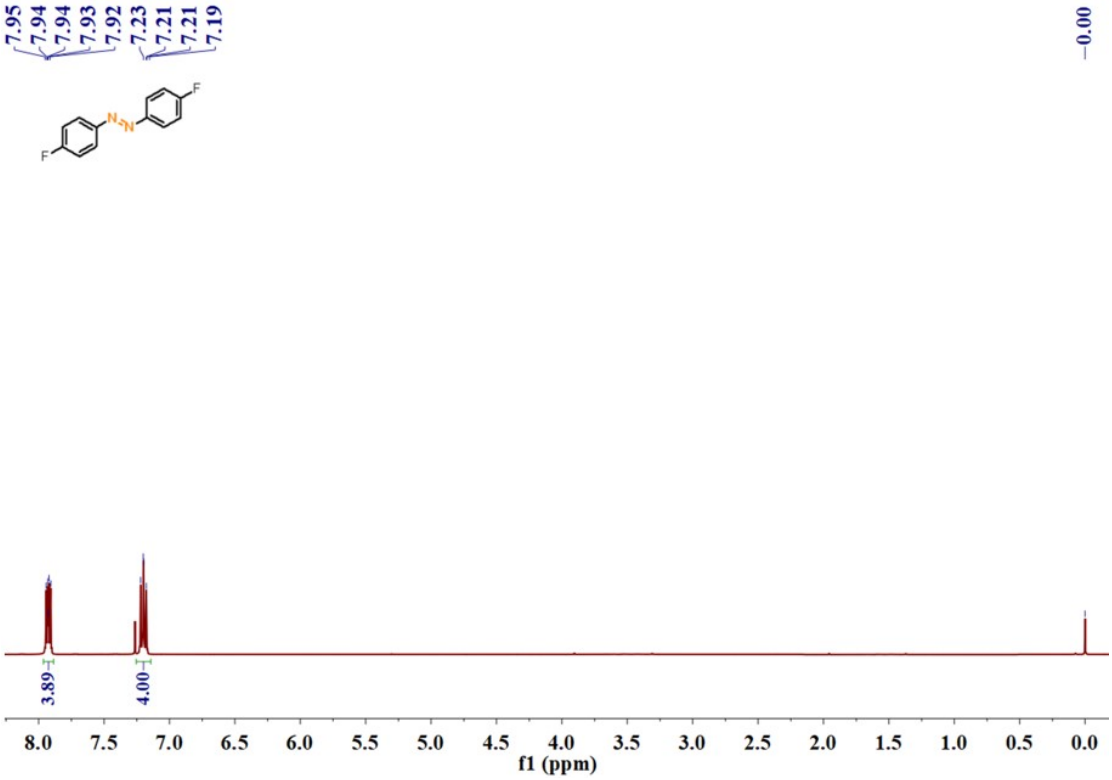
$^{1}$H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2a**



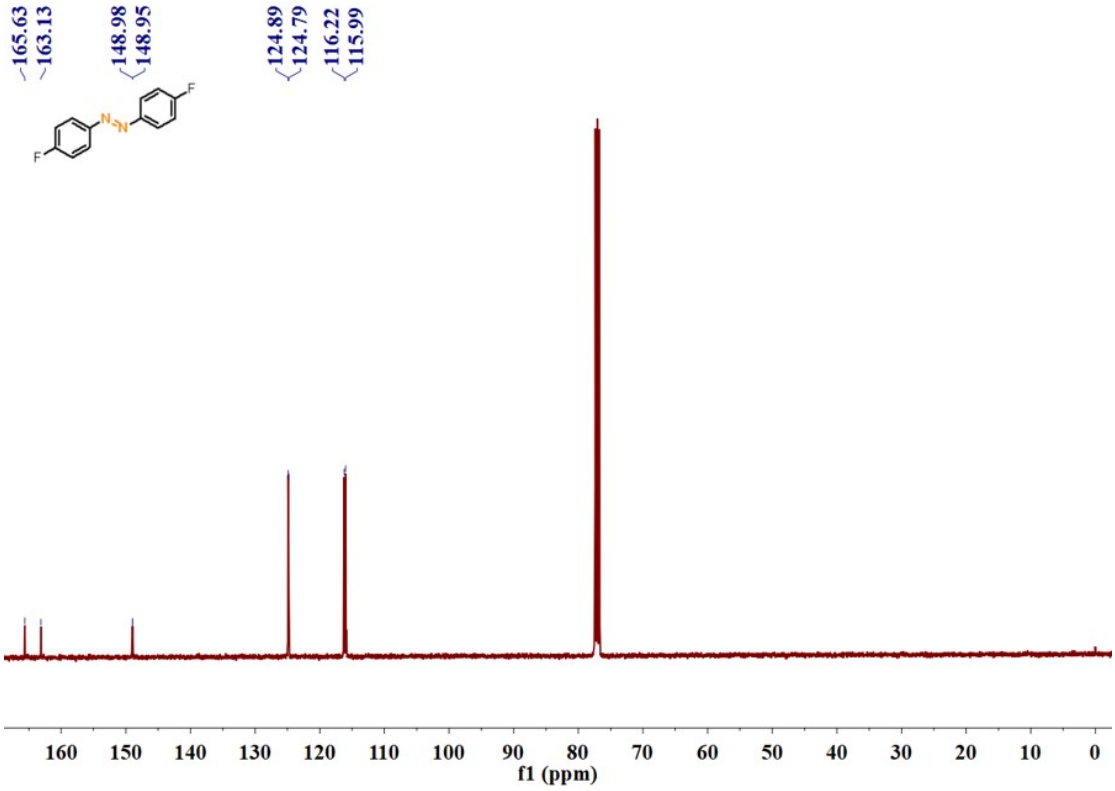

$^{13}$C NMR (101 MHz, Chloroform-d) spectrum of compound **2a**



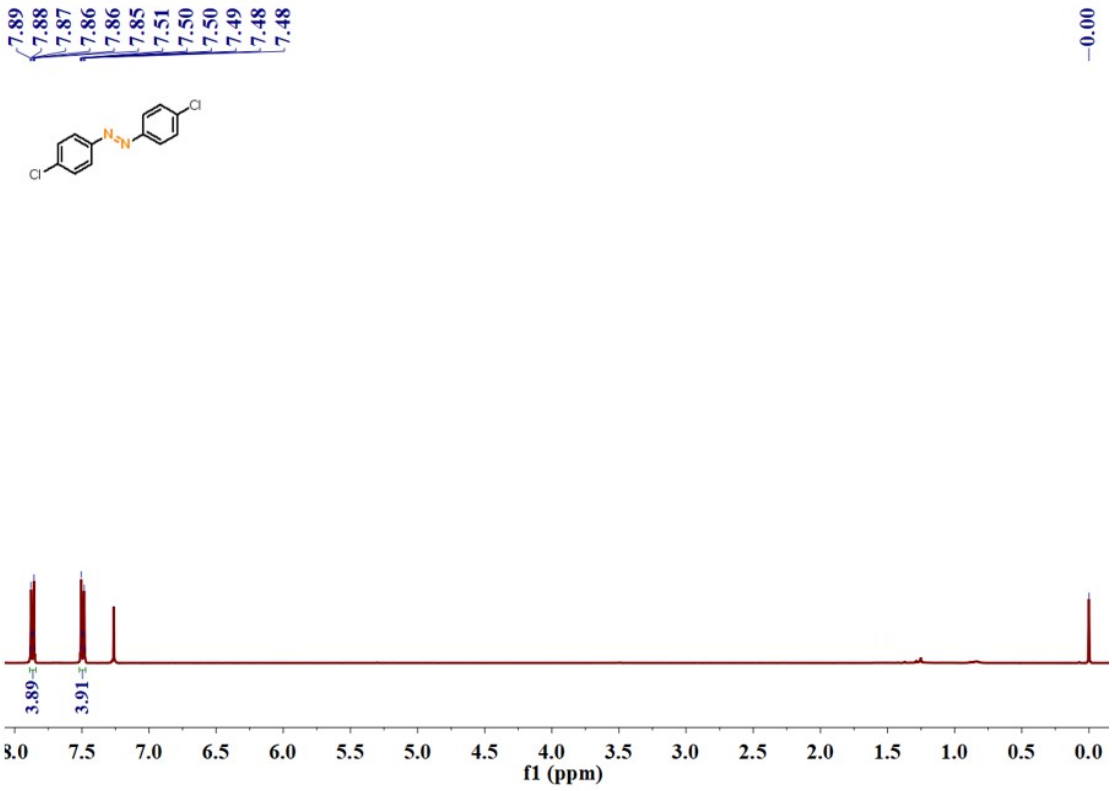
$^{1}$H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2b**



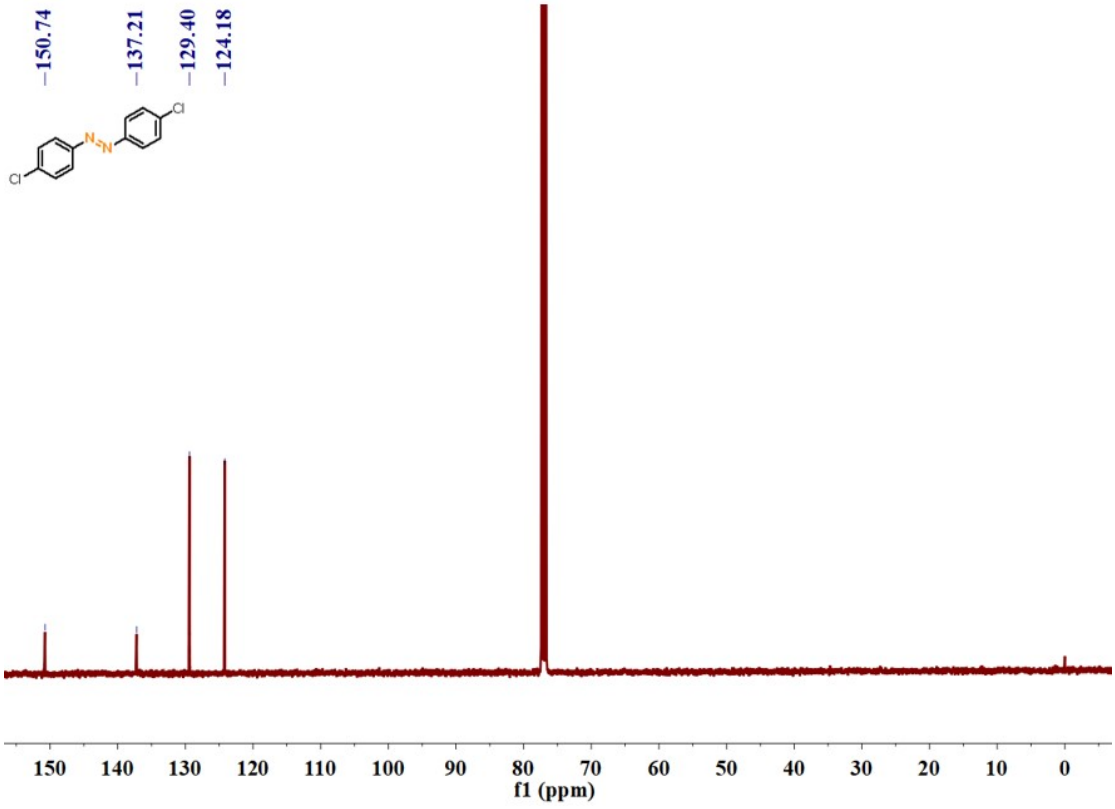

$^{13}$C NMR (101 MHz, Chloroform-d) spectrum of compound **2b**



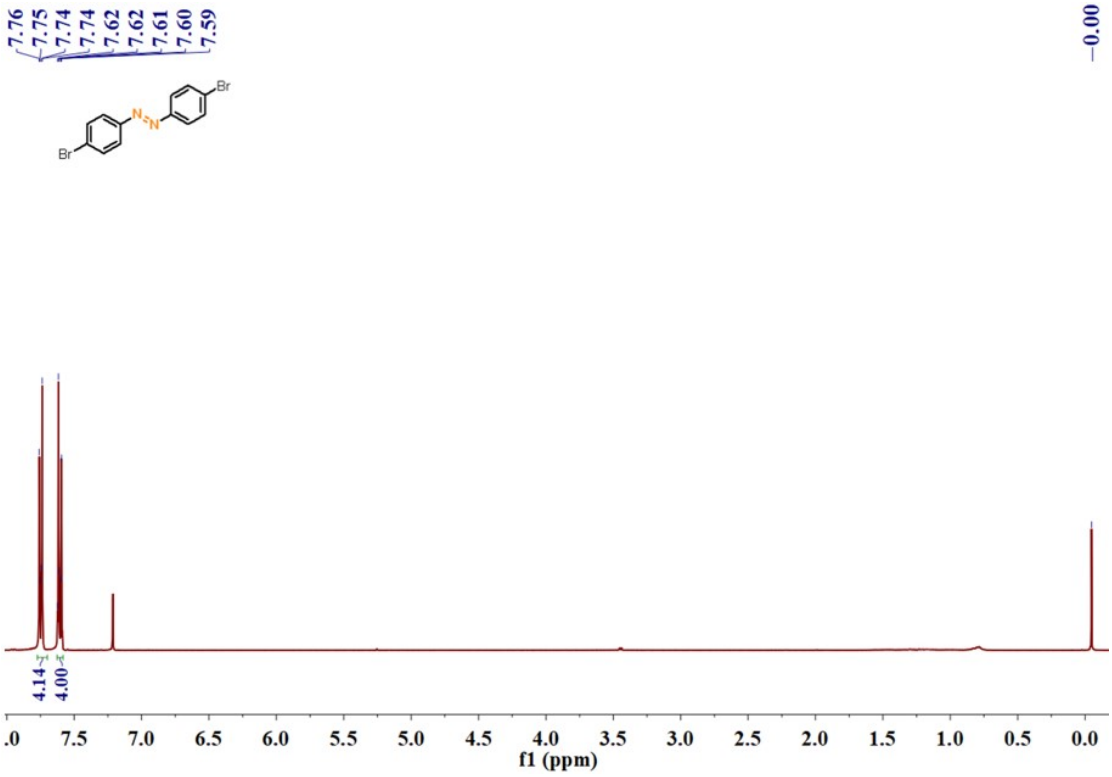
$^{1}$H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2c**



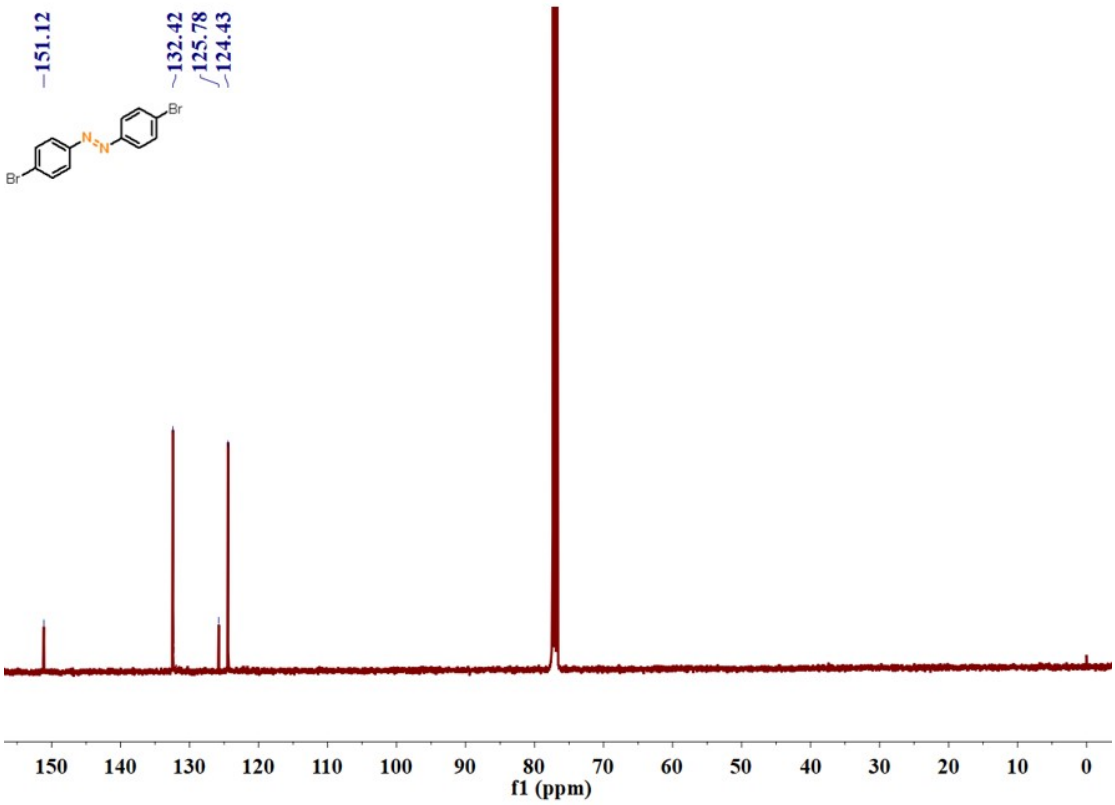

$^{13}$C NMR (101 MHz, Chloroform-d) spectrum of compound **2c**



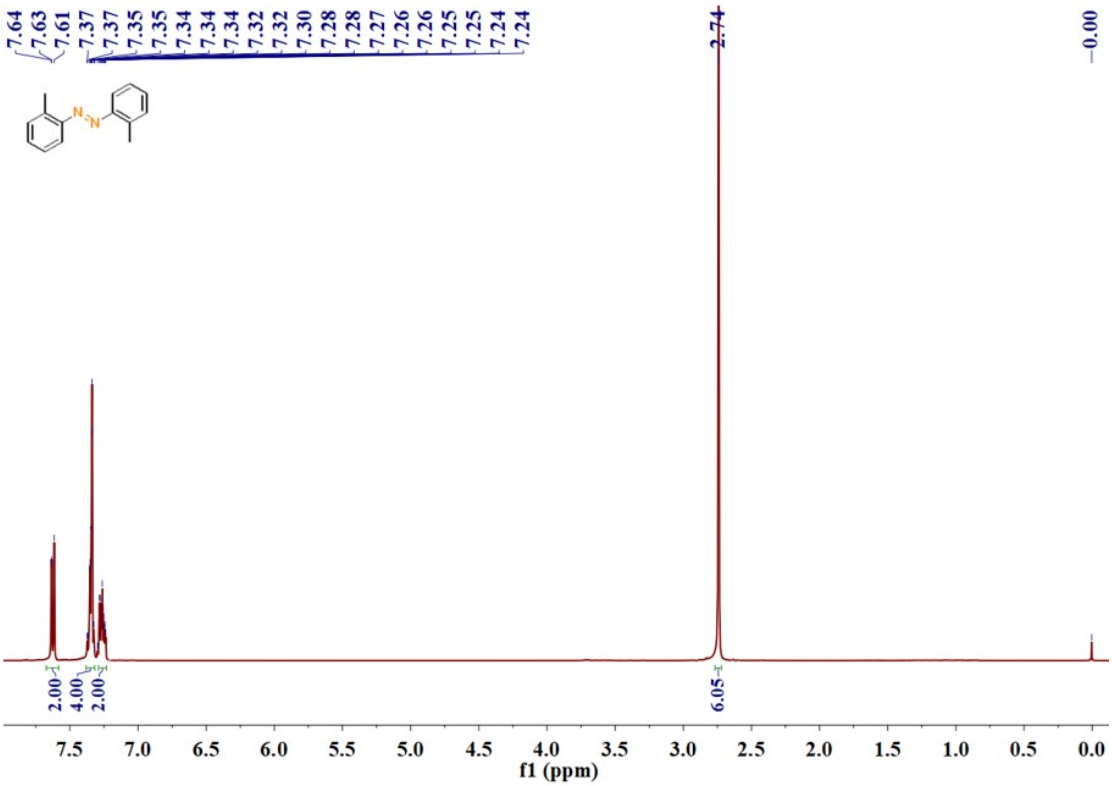
$^{1}$H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2d**



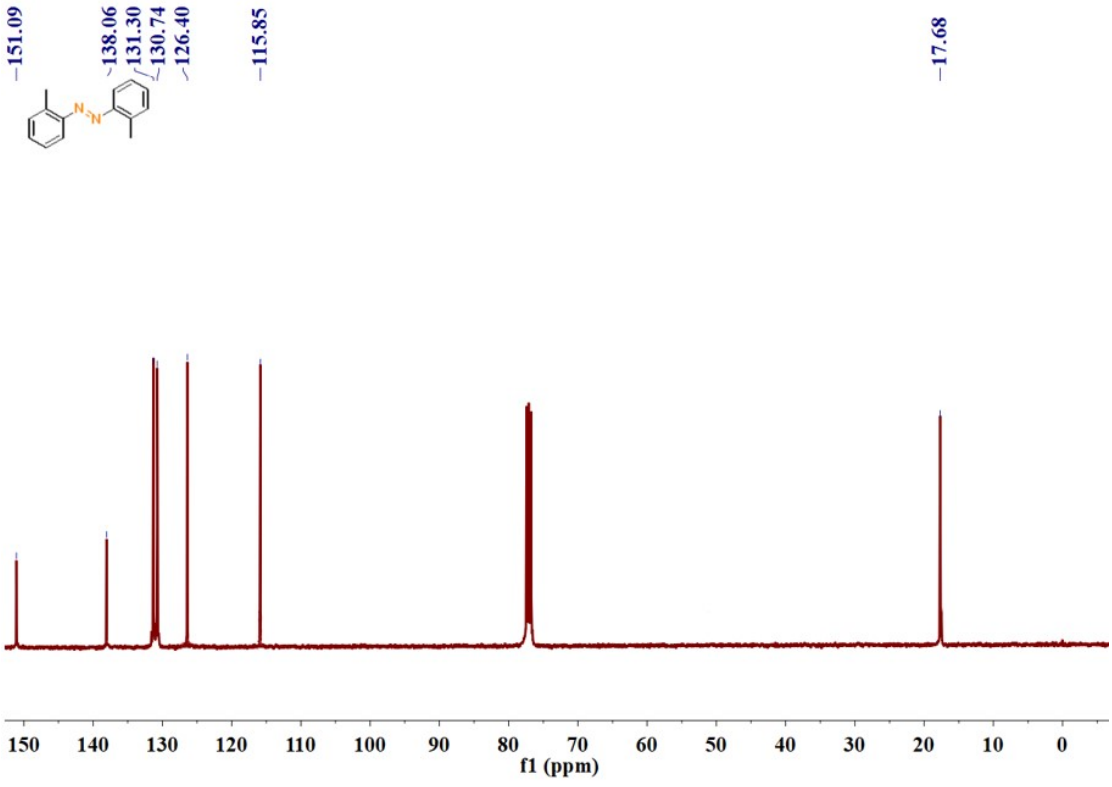

$^{13}$C NMR (101 MHz, Chloroform-d) spectrum of compound **2d**



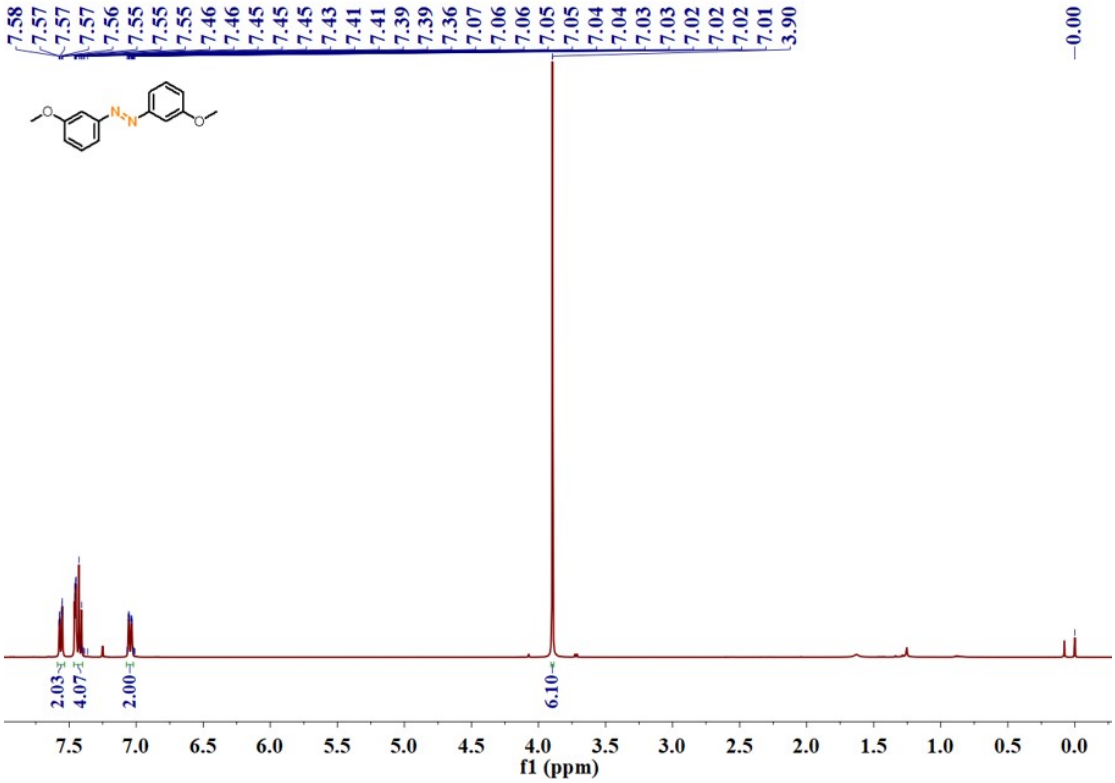
[1]H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2e**



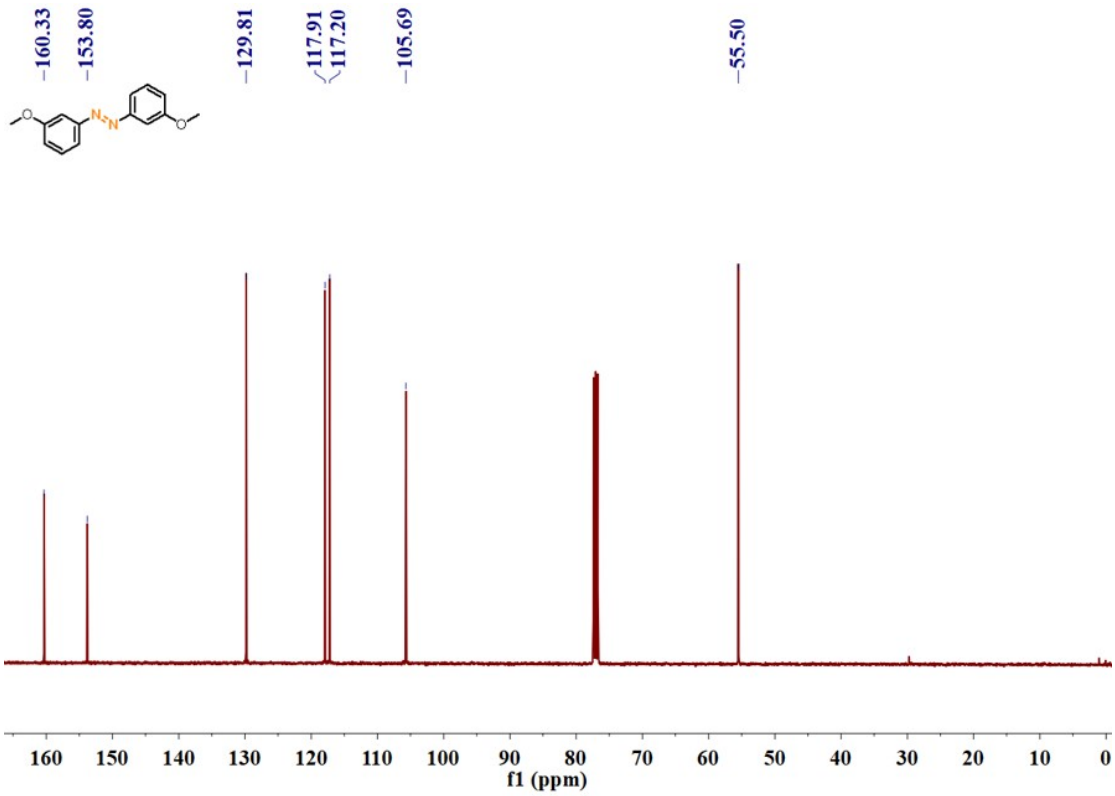

[13]C NMR (101 MHz, Chloroform-d) spectrum of compound **2e**



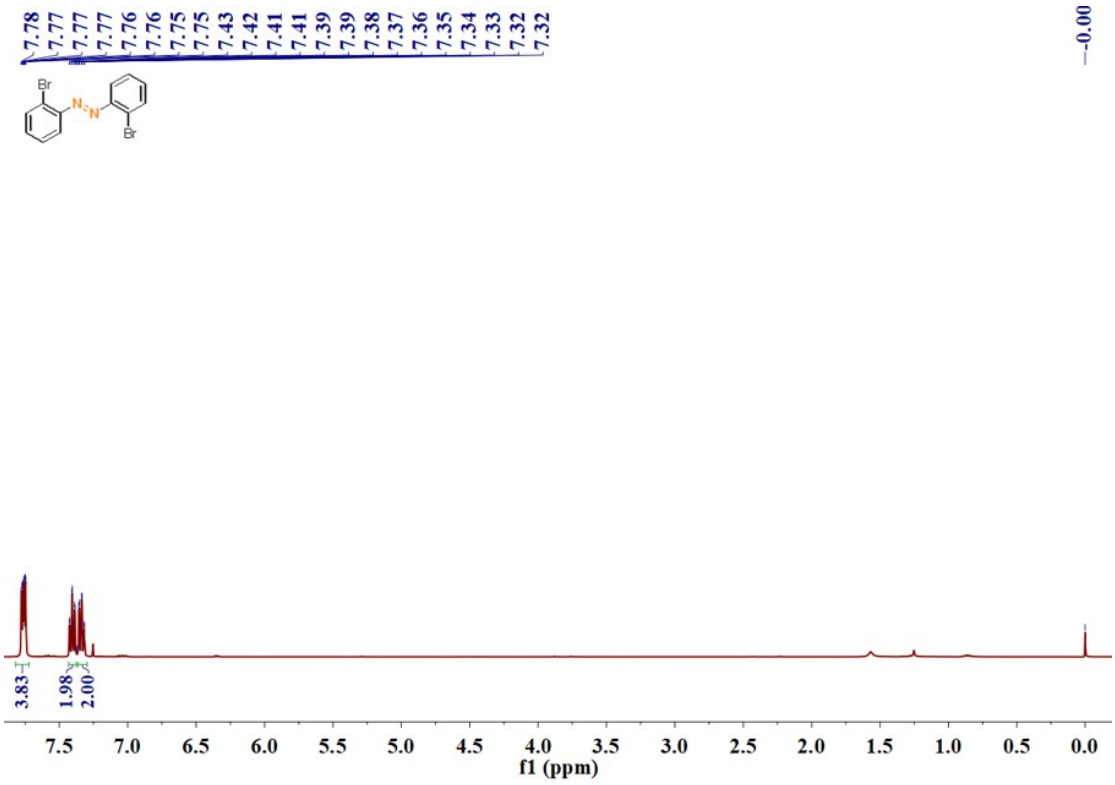
$^{1}$H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2f**



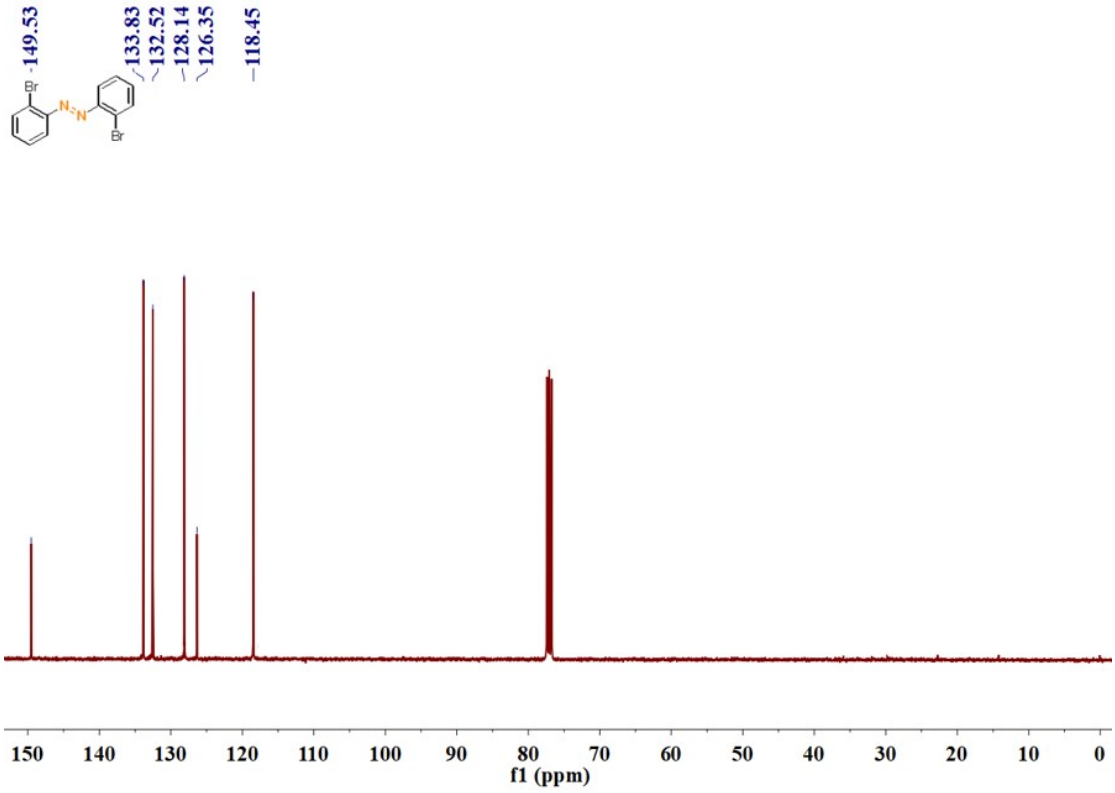

$^{13}$C NMR (101 MHz, Chloroform-d) spectrum of compound **2f**



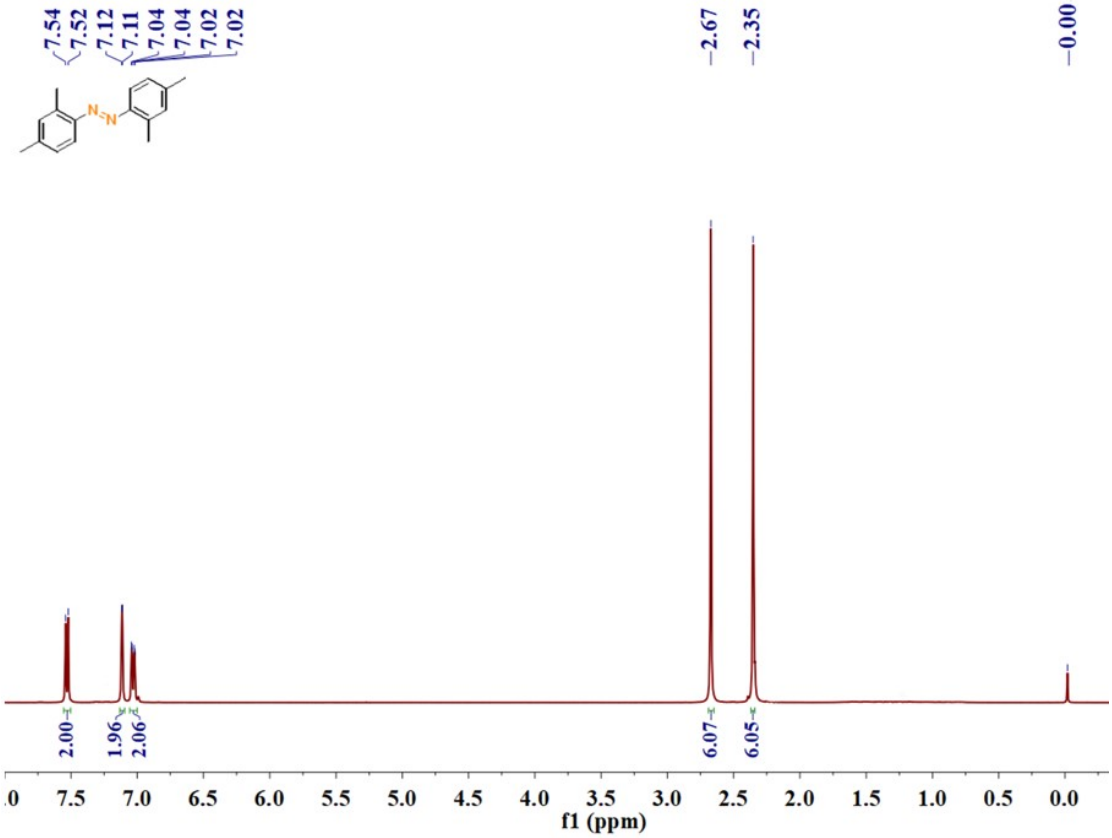
[1]H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2g**



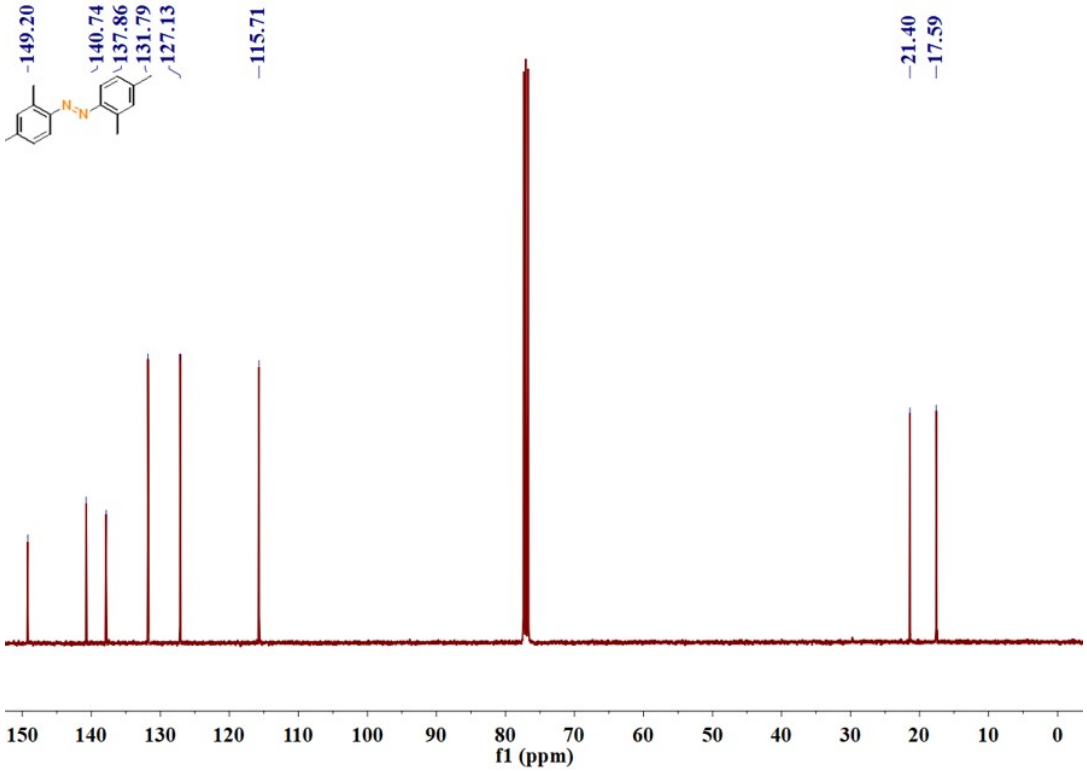

[13]C NMR (101 MHz, Chloroform-d) spectrum of compound **2g**



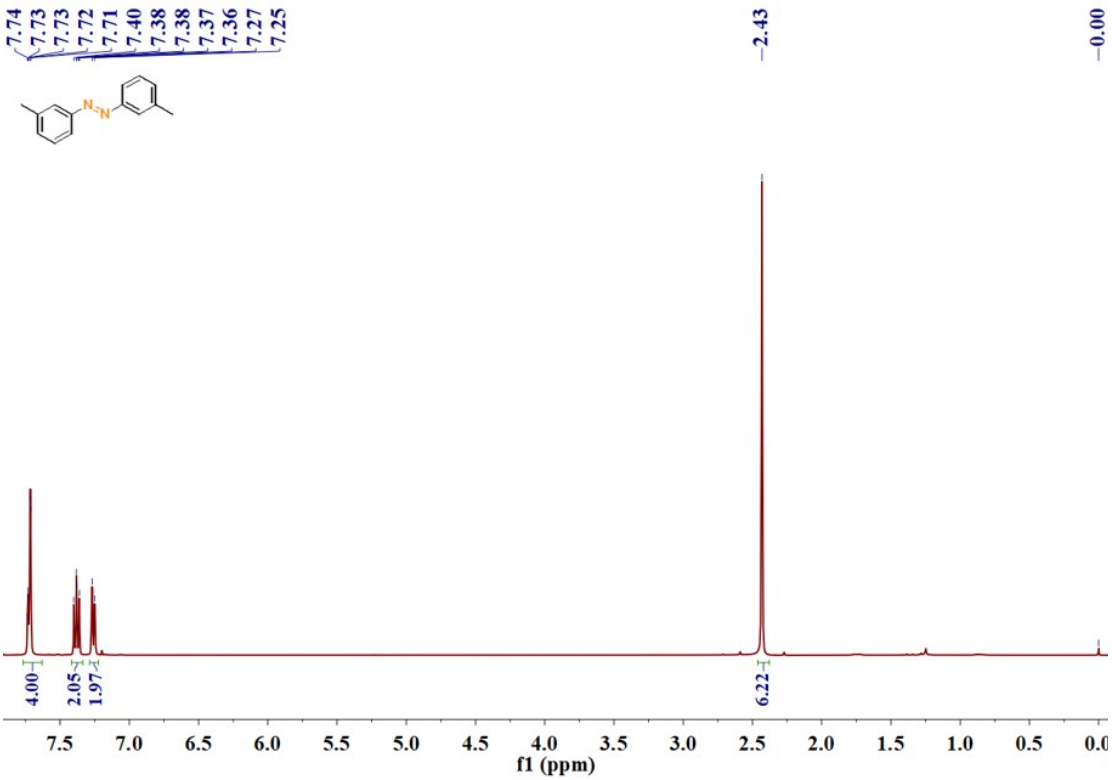
$^{1}$H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2h**



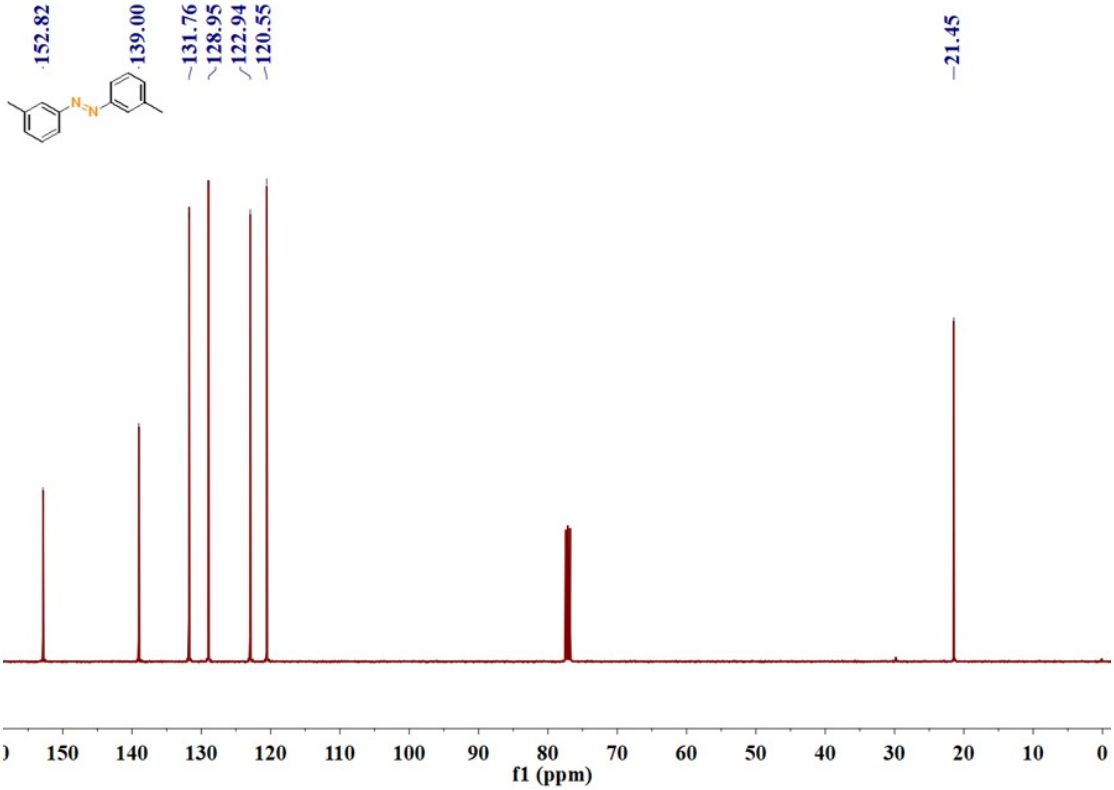

$^{13}$C NMR (101 MHz, Chloroform-d) spectrum of compound **2h**



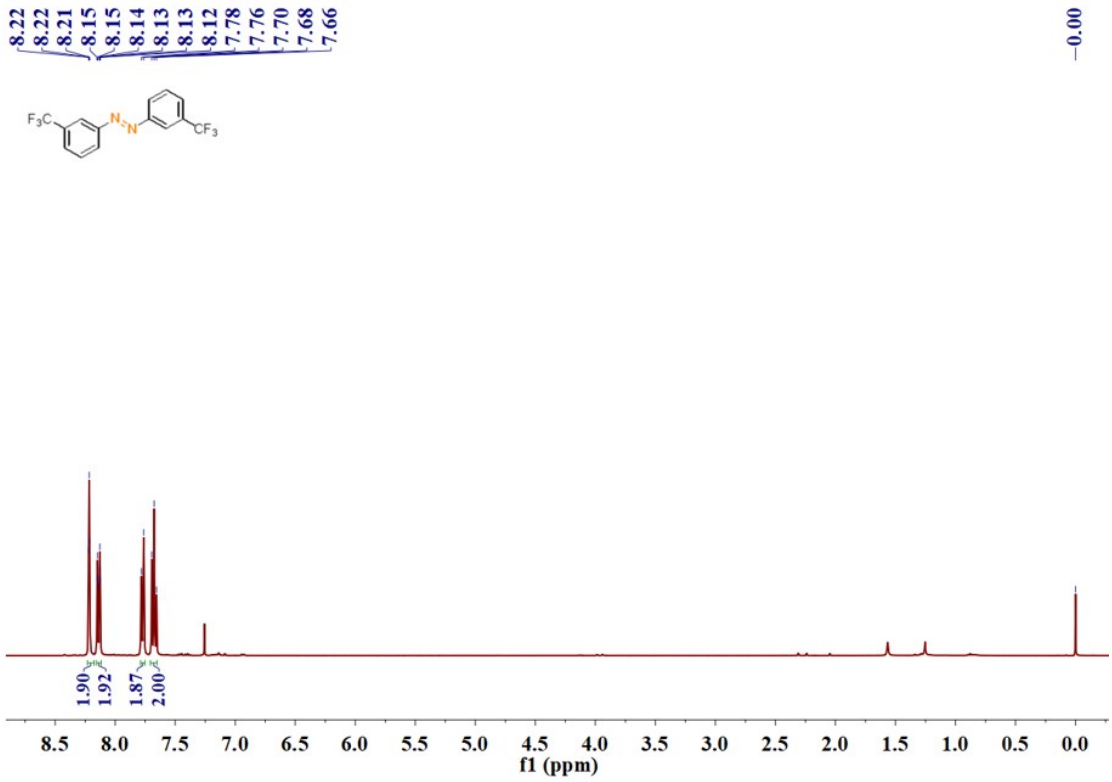
$^{1}$H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2i**



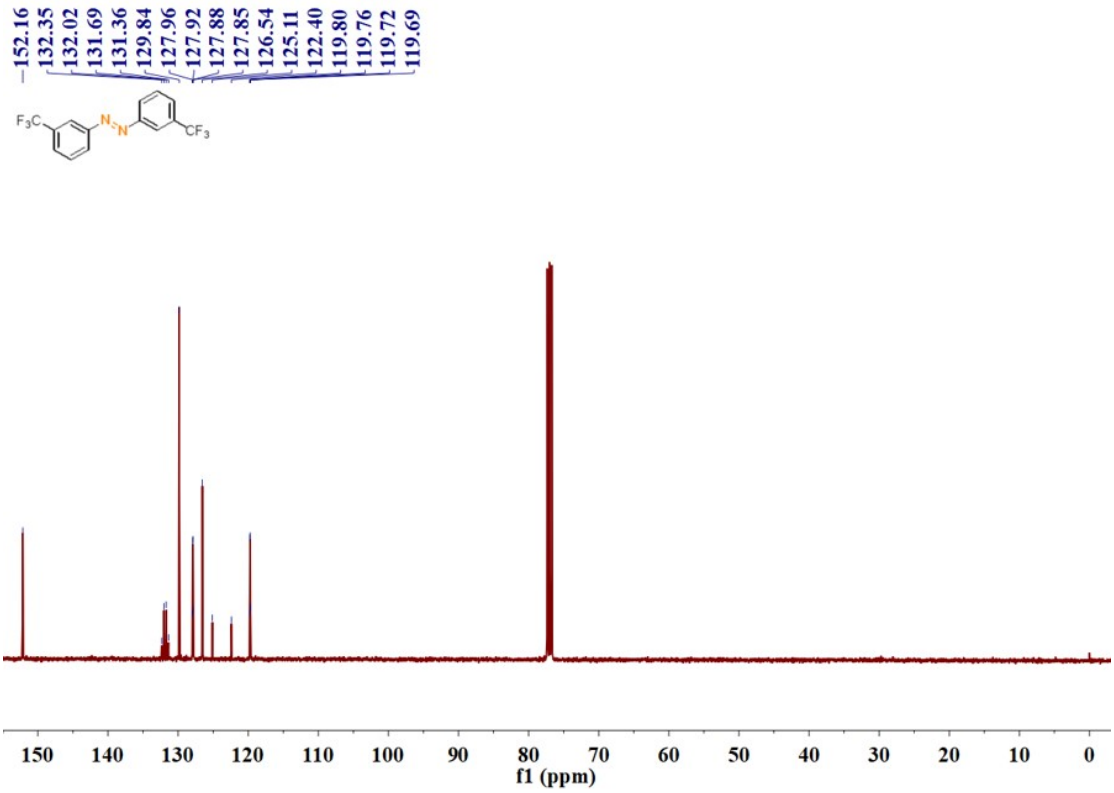

$^{13}$C NMR (101 MHz, Chloroform-d) spectrum of compound **2i**



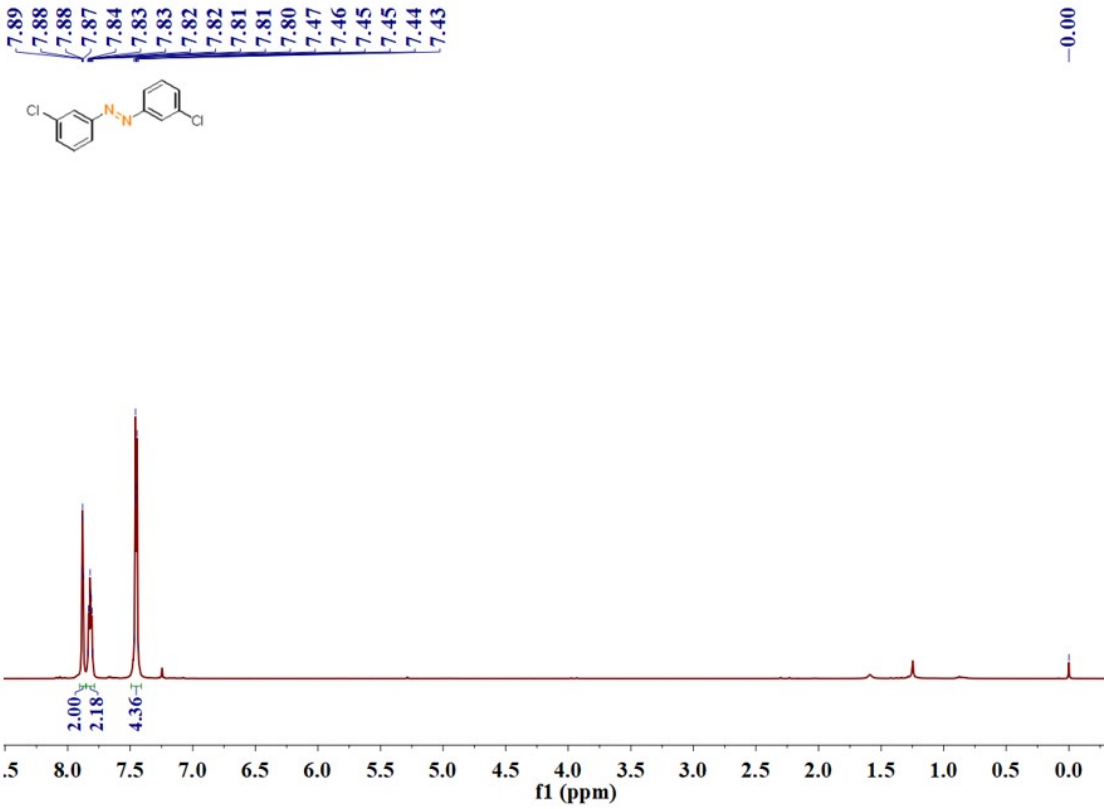
[1]H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2j**



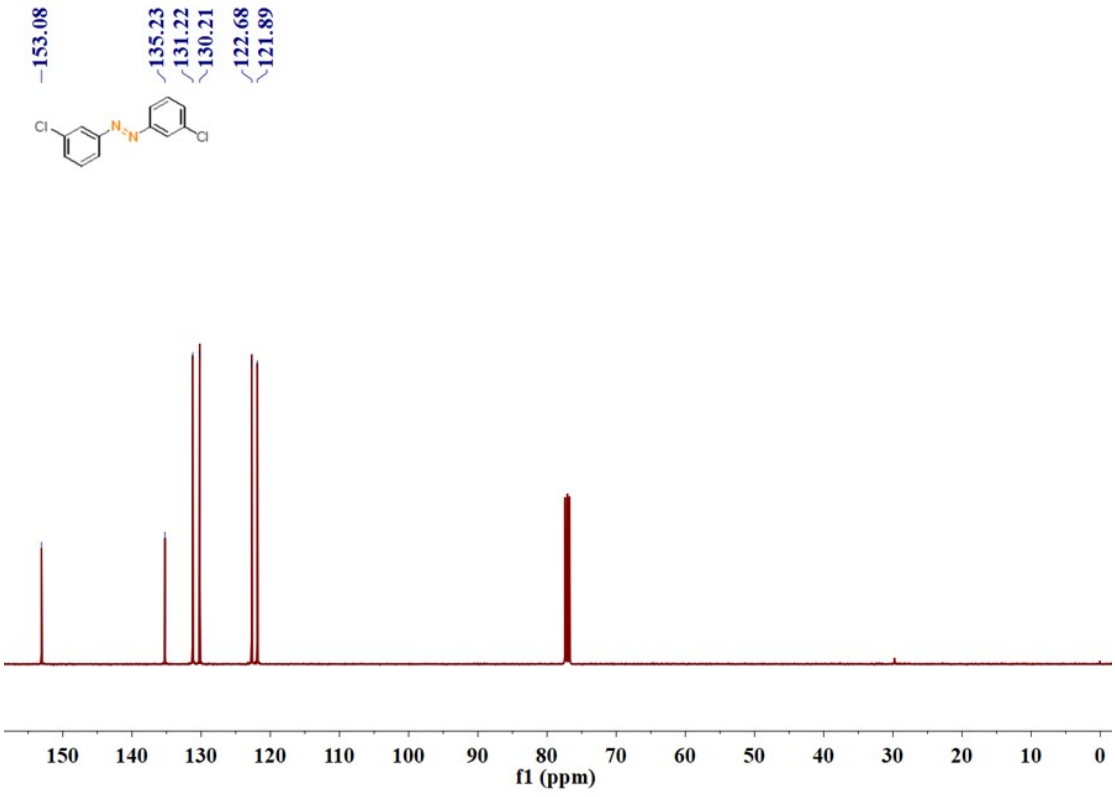

[13]C NMR (101 MHz, Chloroform-d) spectrum of compound **2j**



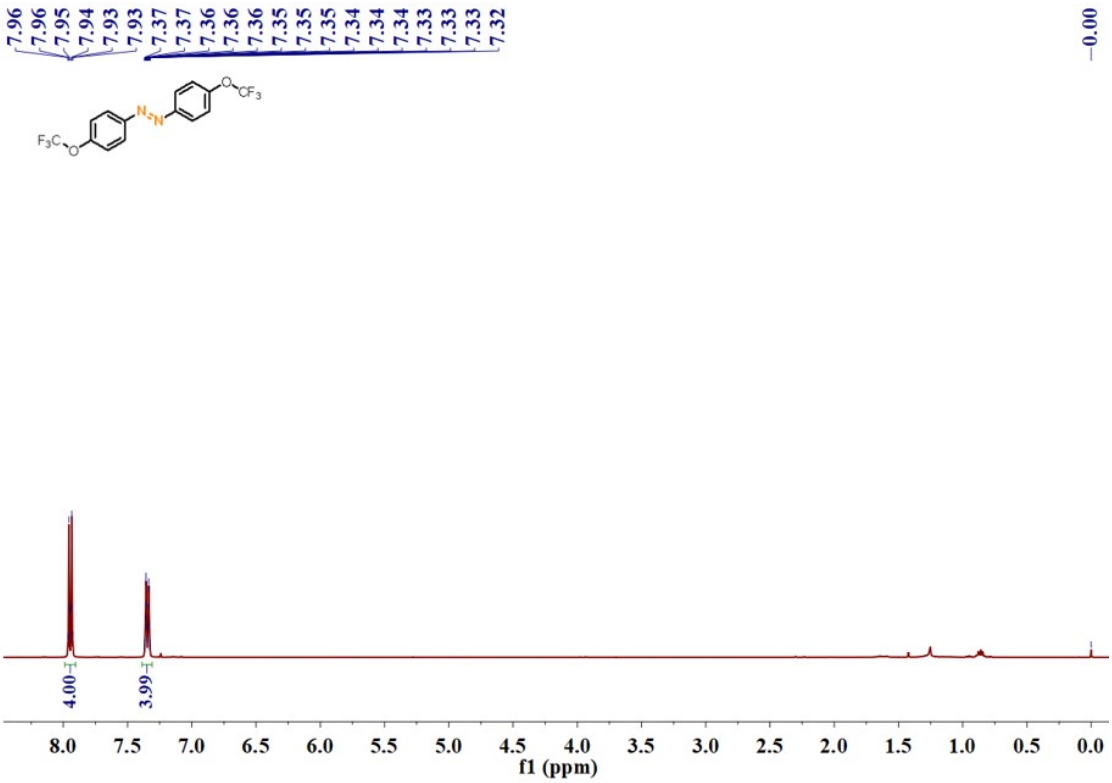
$^{1}$H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2k**



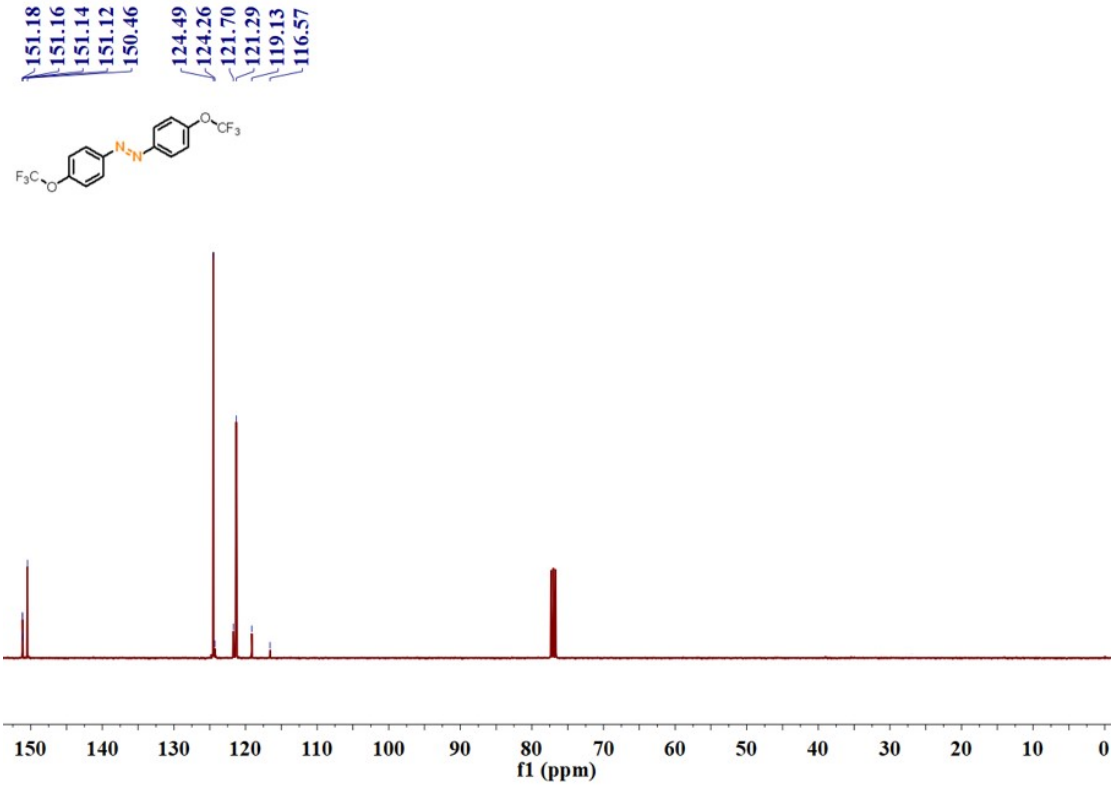

$^{13}$C NMR (101 MHz, Chloroform-d) spectrum of compound **2k**



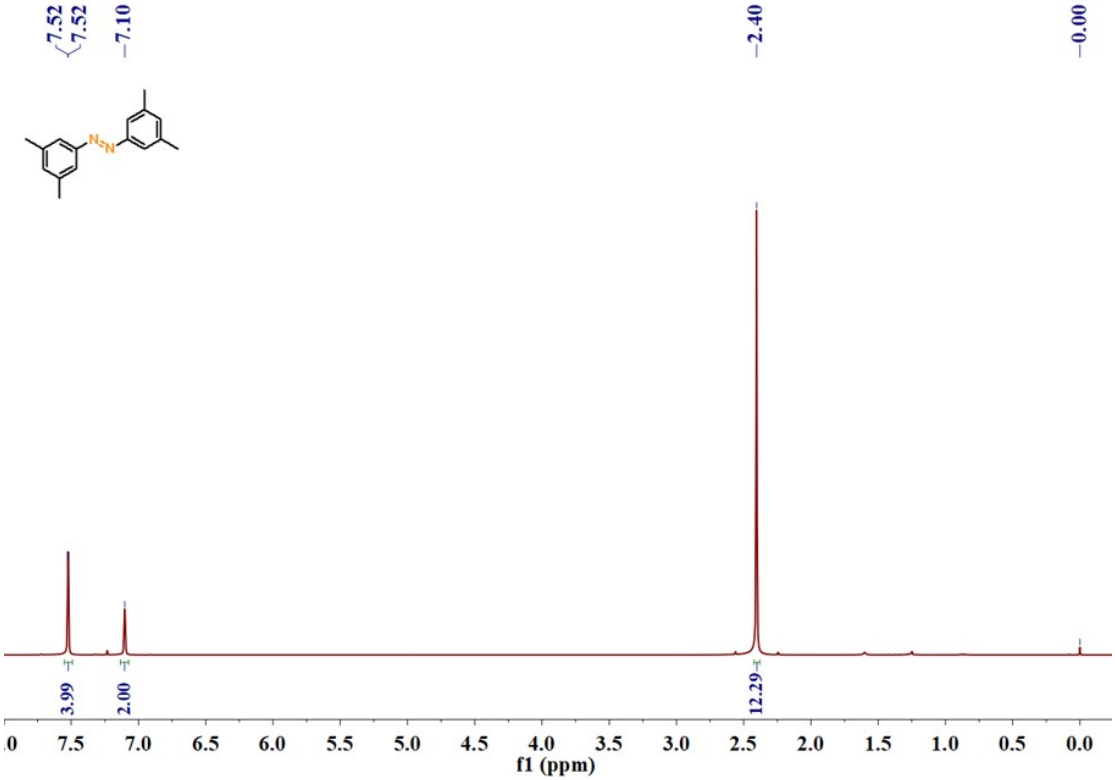
$^{1}$H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2l**



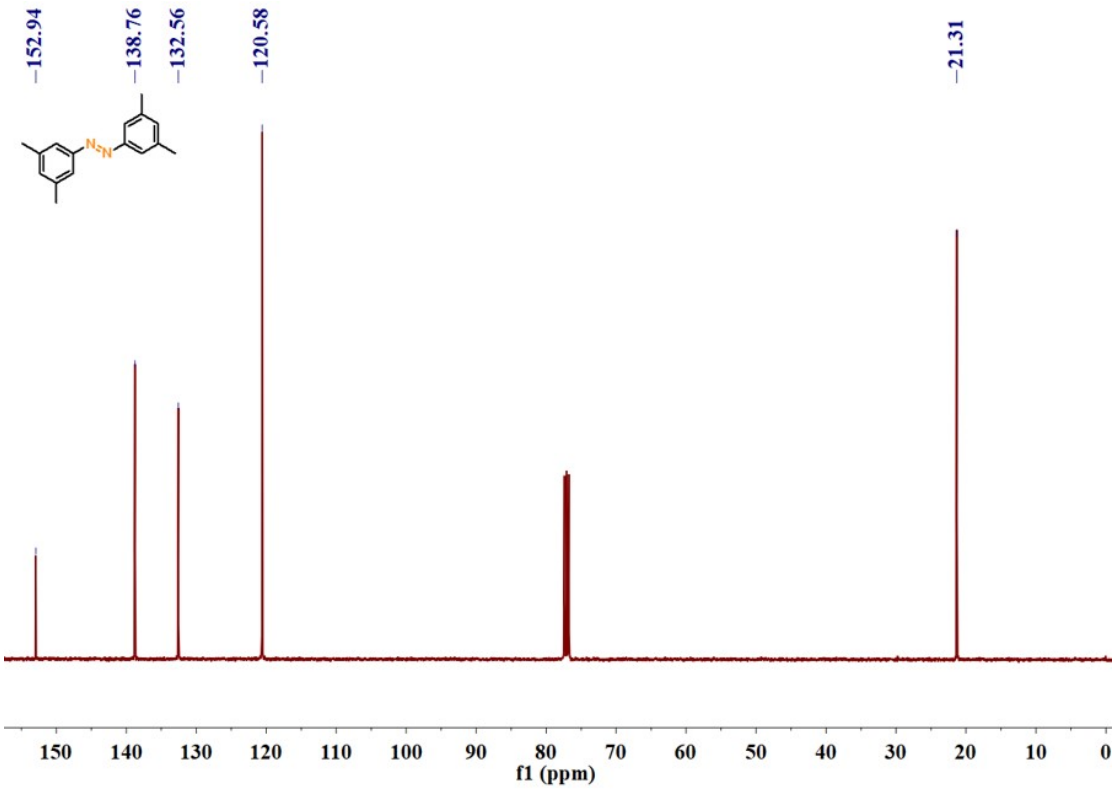

$^{13}$C NMR (101 MHz, Chloroform-d) spectrum of compound **2l**



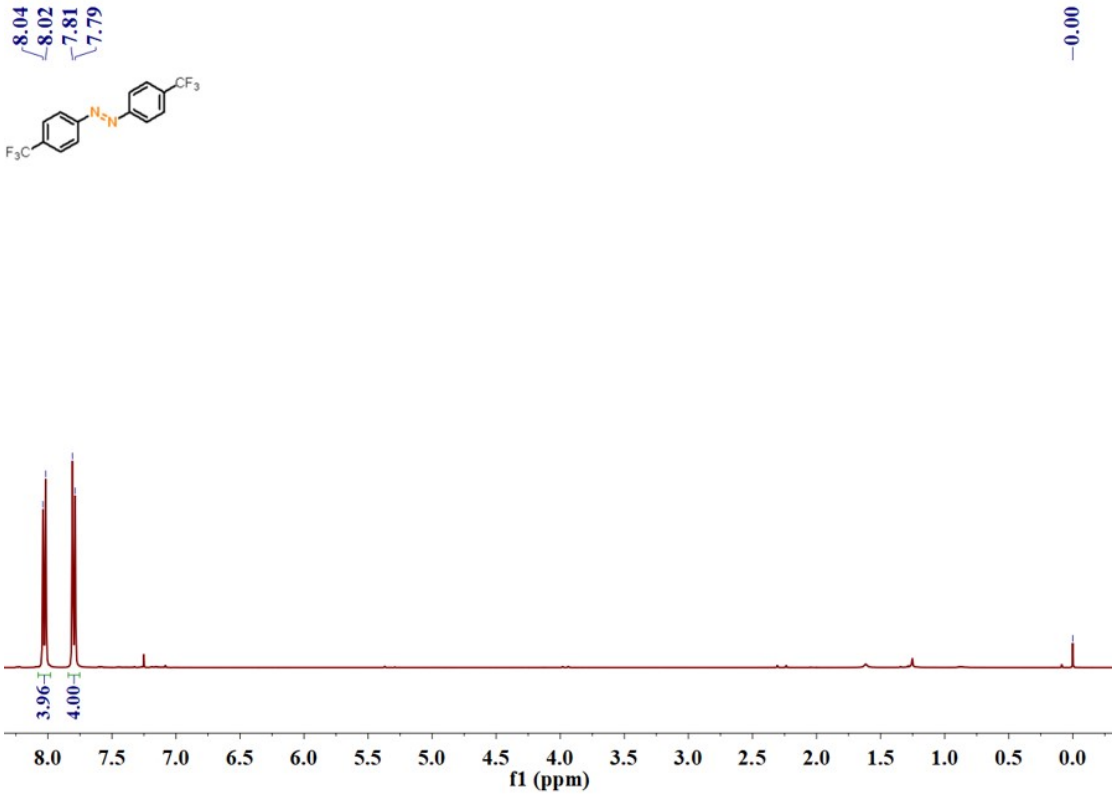
$^{1}$H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2m**



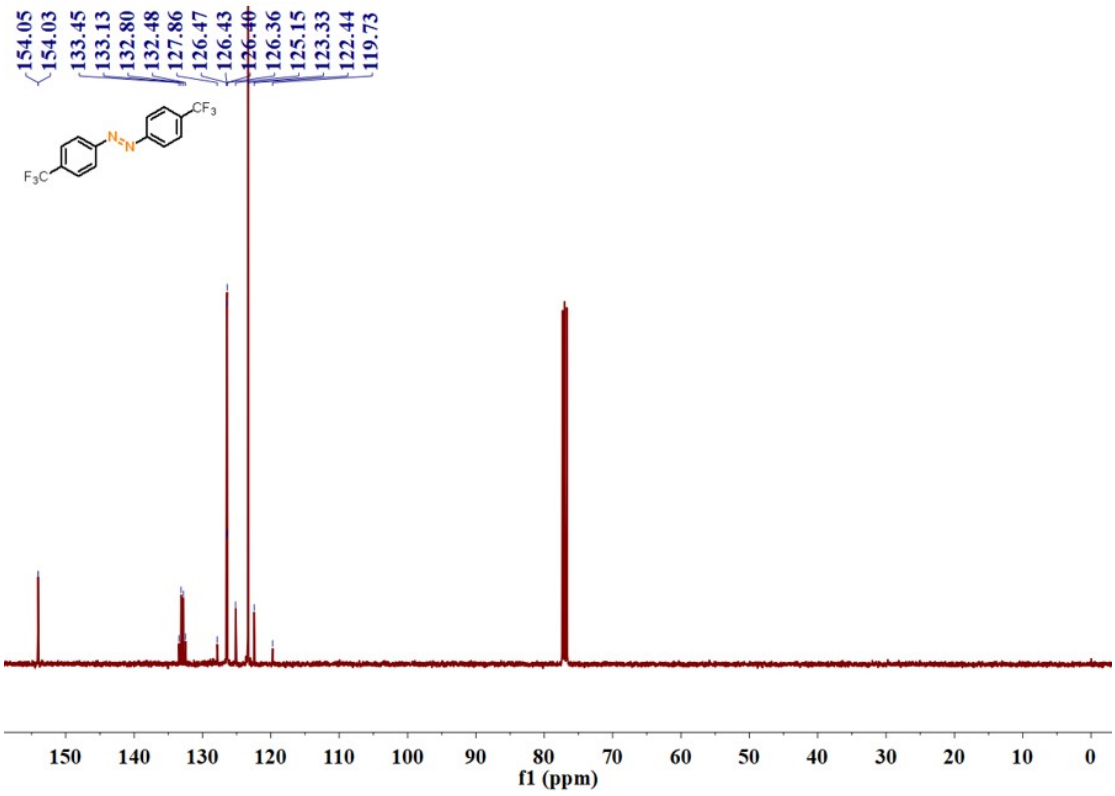

$^{13}$C NMR (101 MHz, Chloroform-d) spectrum of compound **2m**



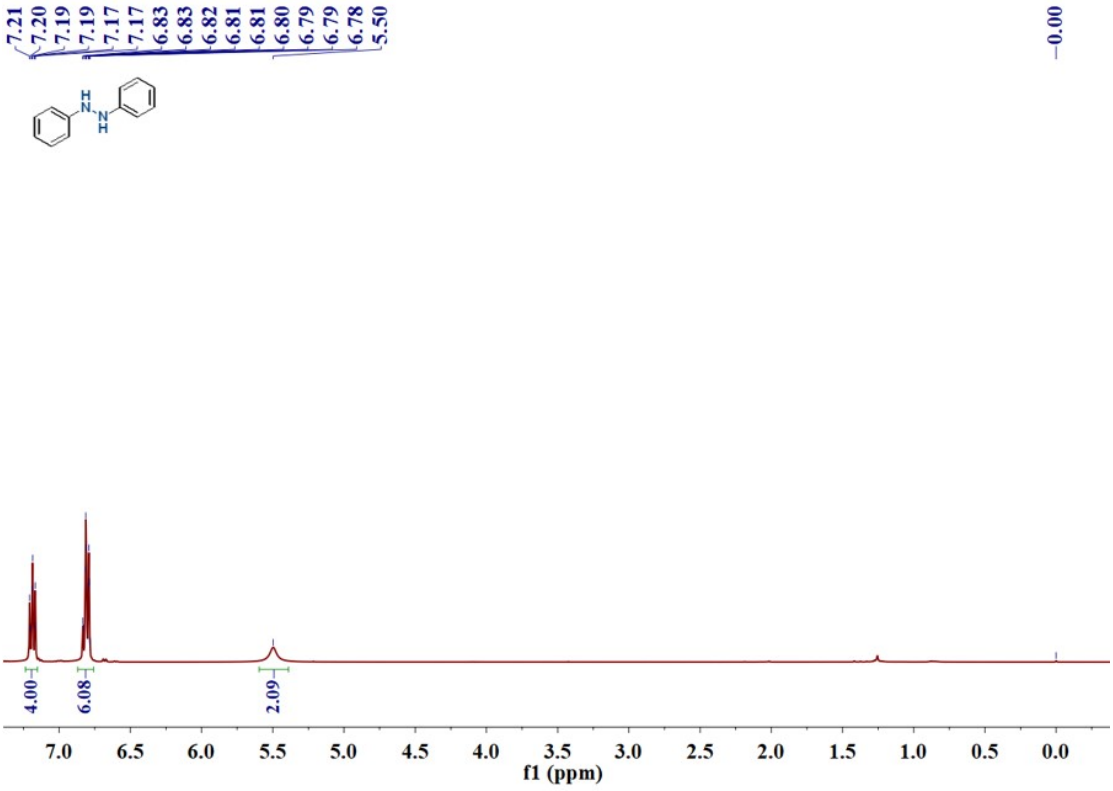
$^{1}$H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2n**



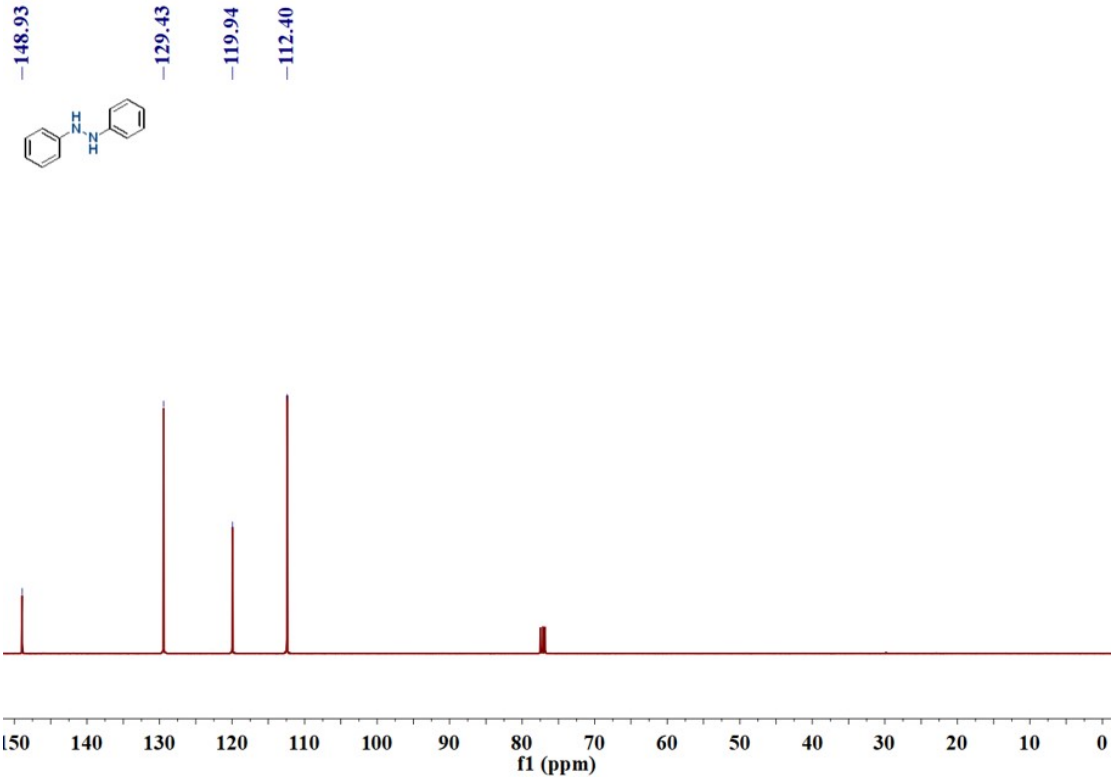

$^{13}$C NMR (101 MHz, Chloroform-d) spectrum of compound **2n**



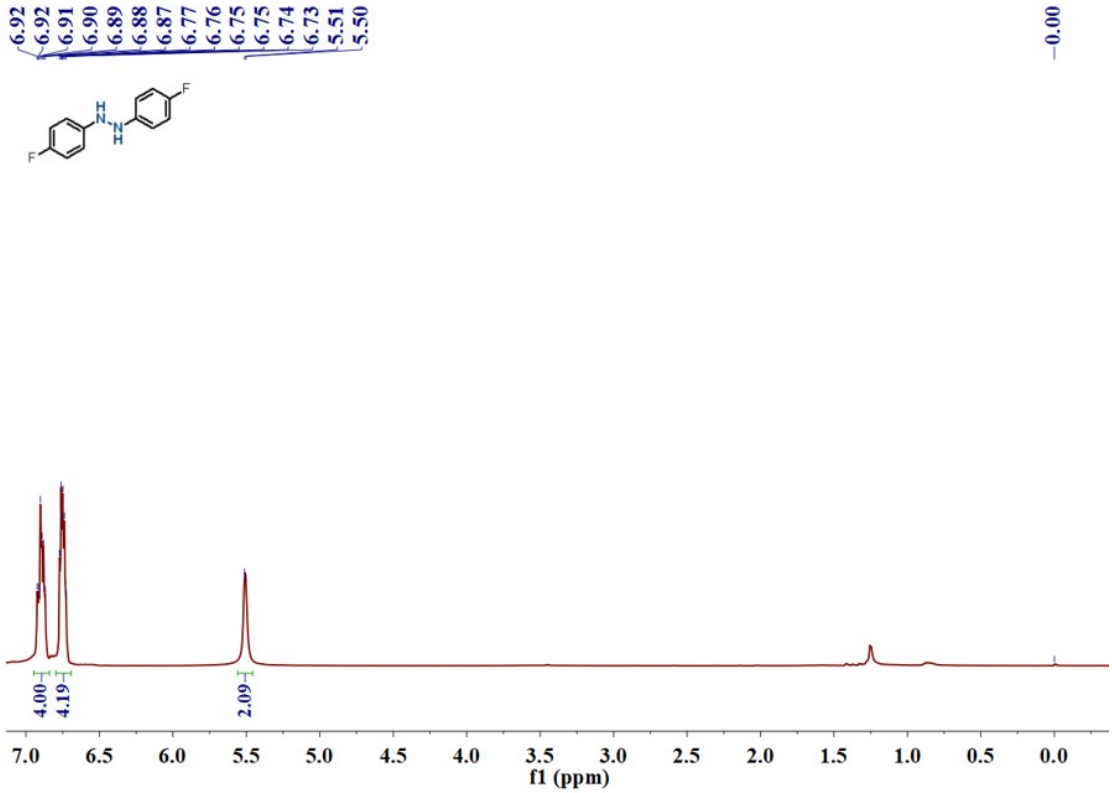
$^{1}$H NMR (400 MHz, Chloroform-*d*) spectrum of compound **1a**



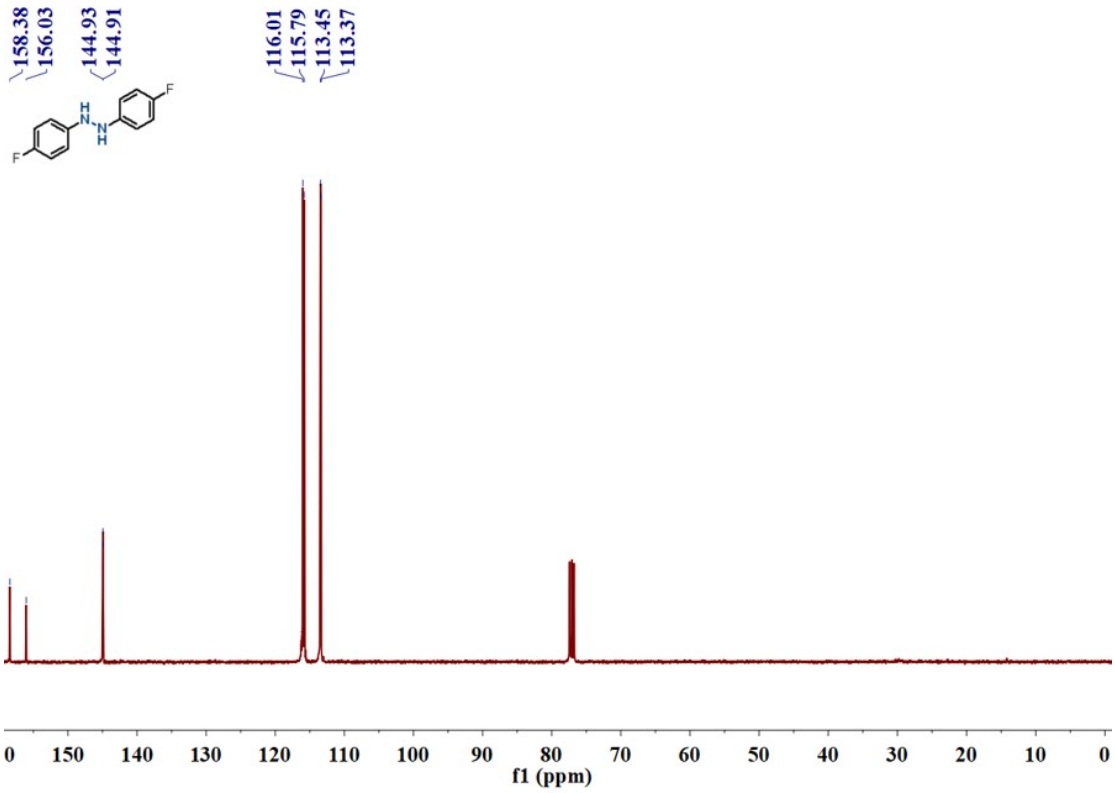

$^{13}$C NMR (101 MHz, Chloroform-d) spectrum of compound **1a**



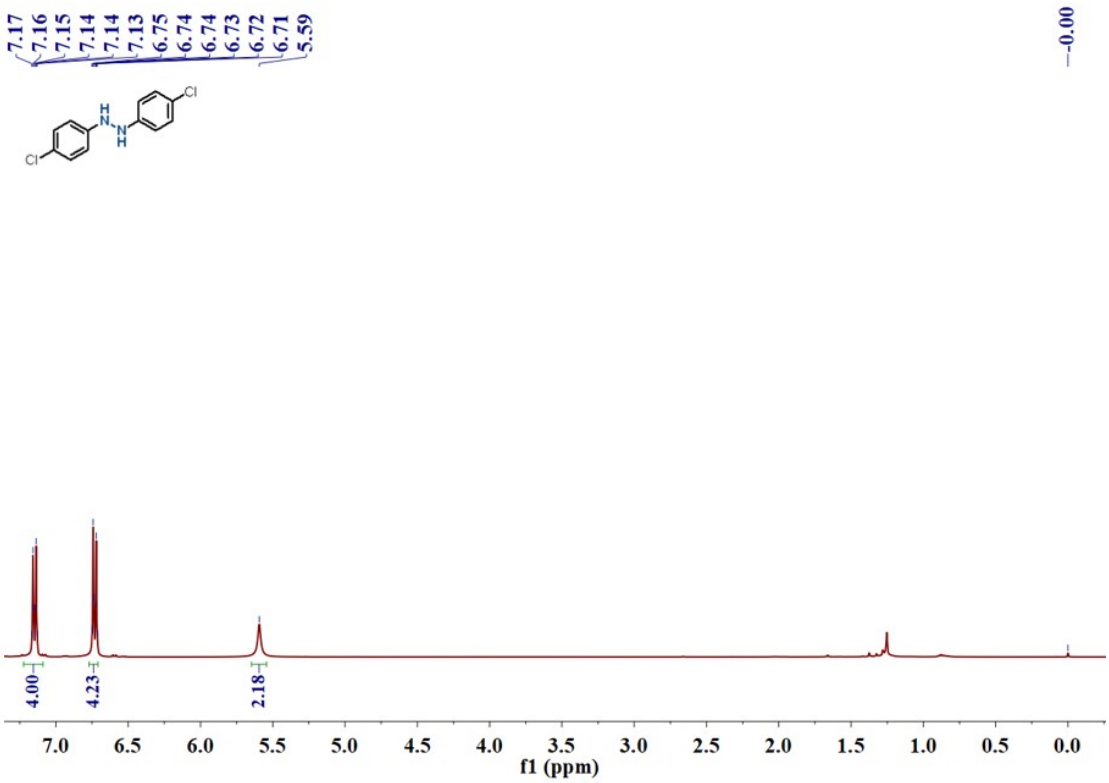
$^{1}$H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2o**



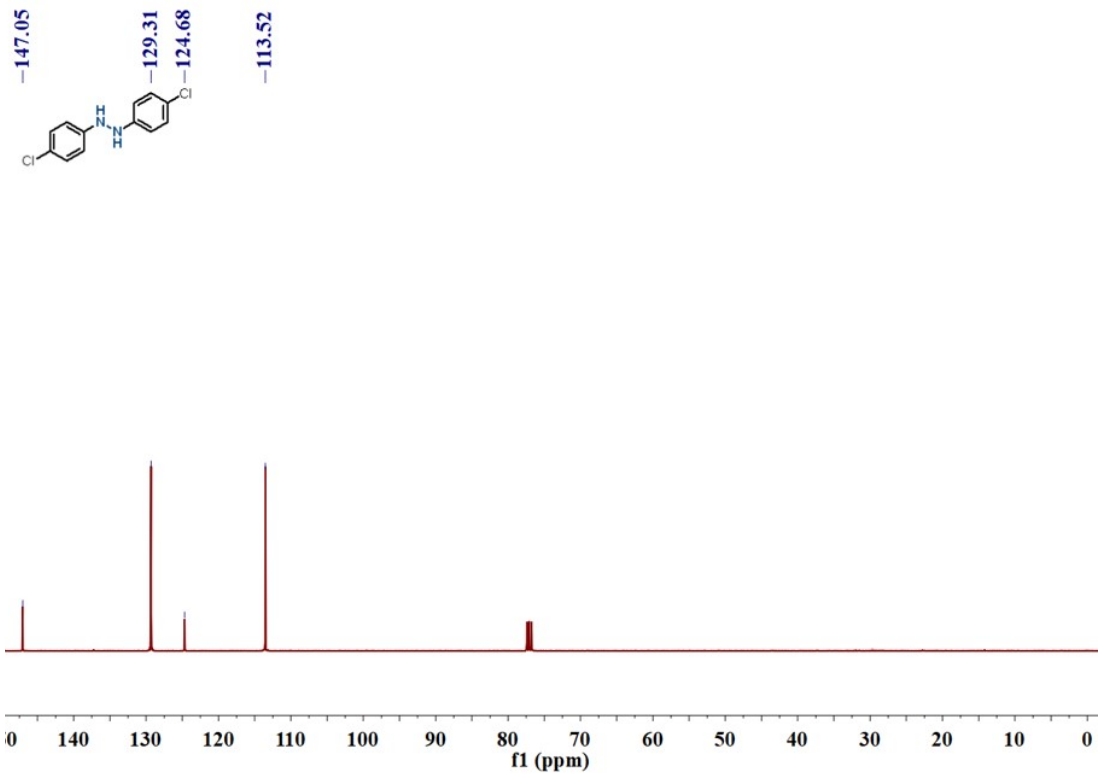

$^{13}$C NMR (101 MHz, Chloroform-d) spectrum of compound **2o**



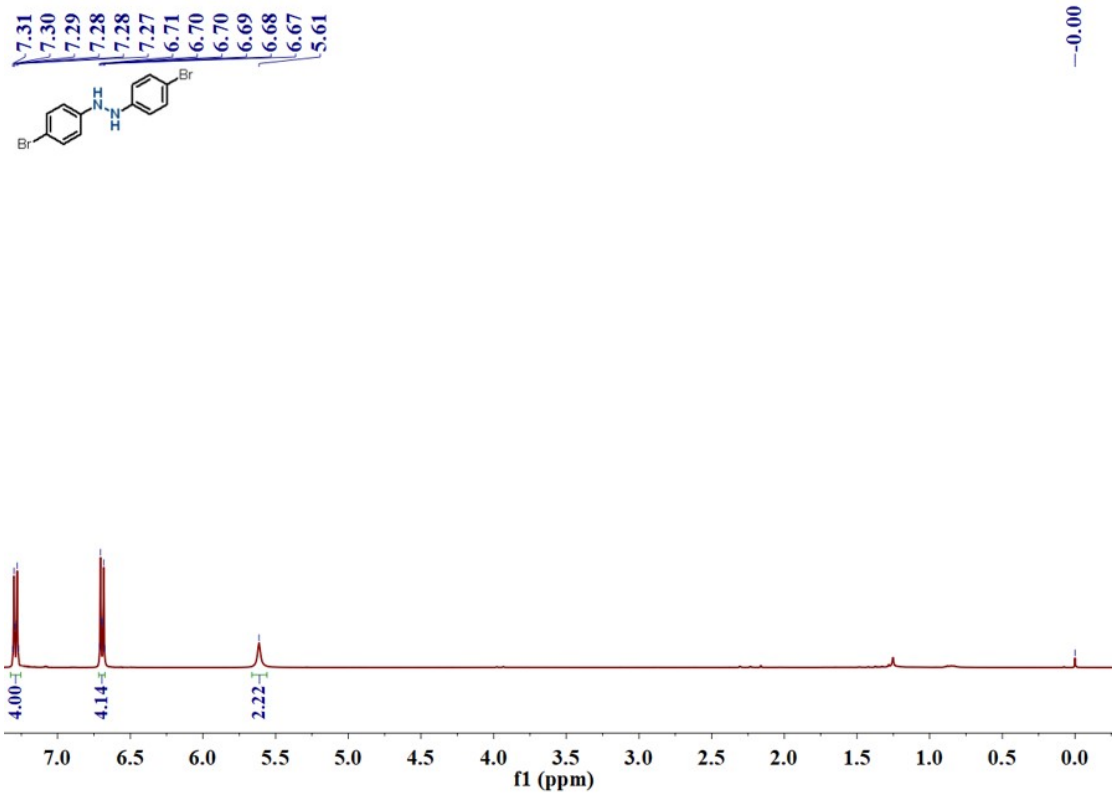
$^{1}$H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2p**



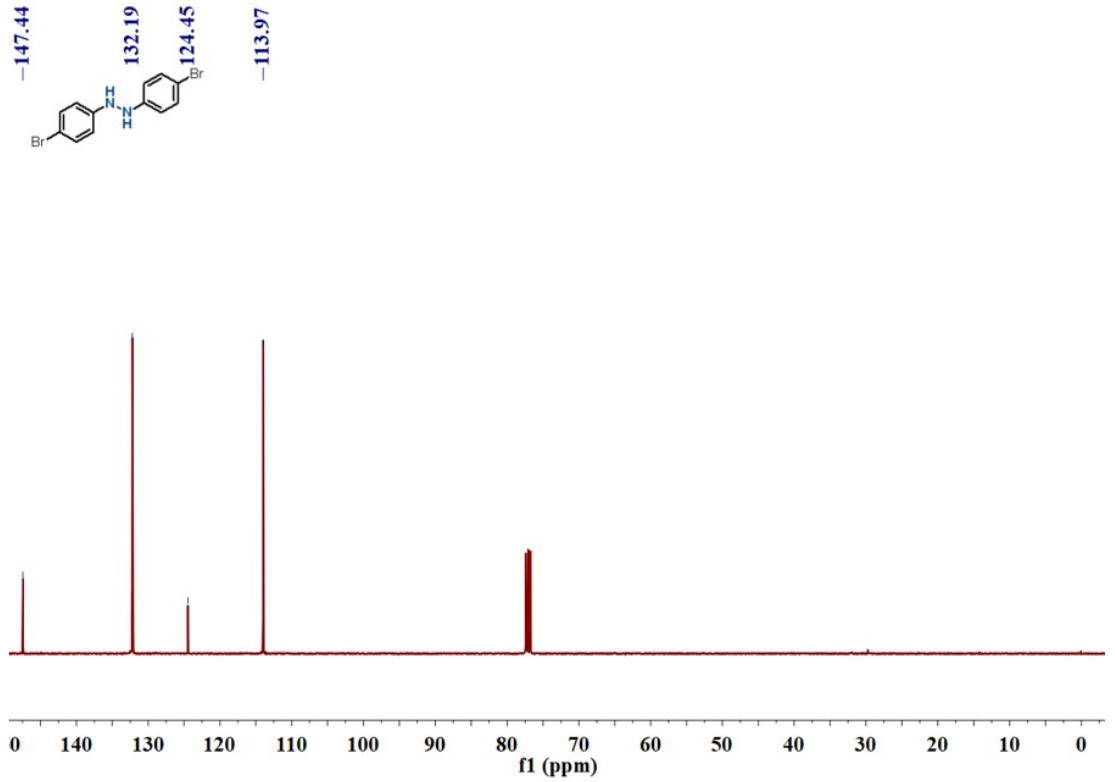

$^{13}$C NMR (101 MHz, Chloroform-d) spectrum of compound **2p**



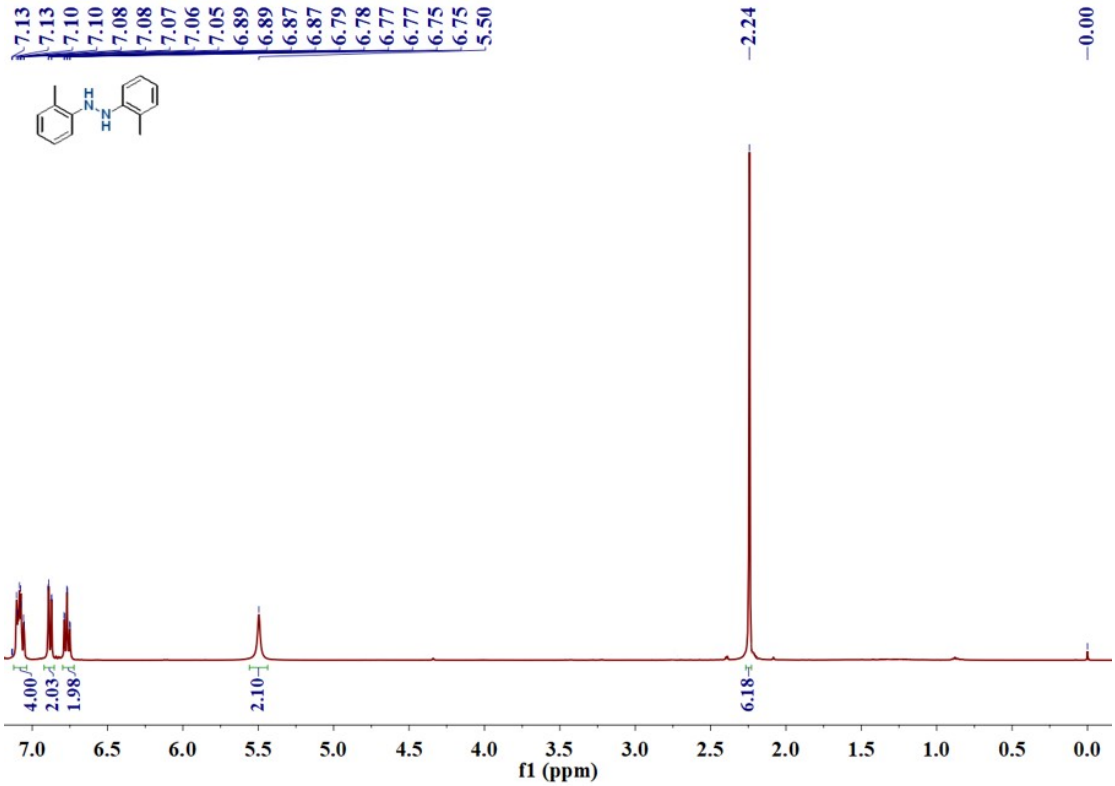
$^{1}$H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2q**



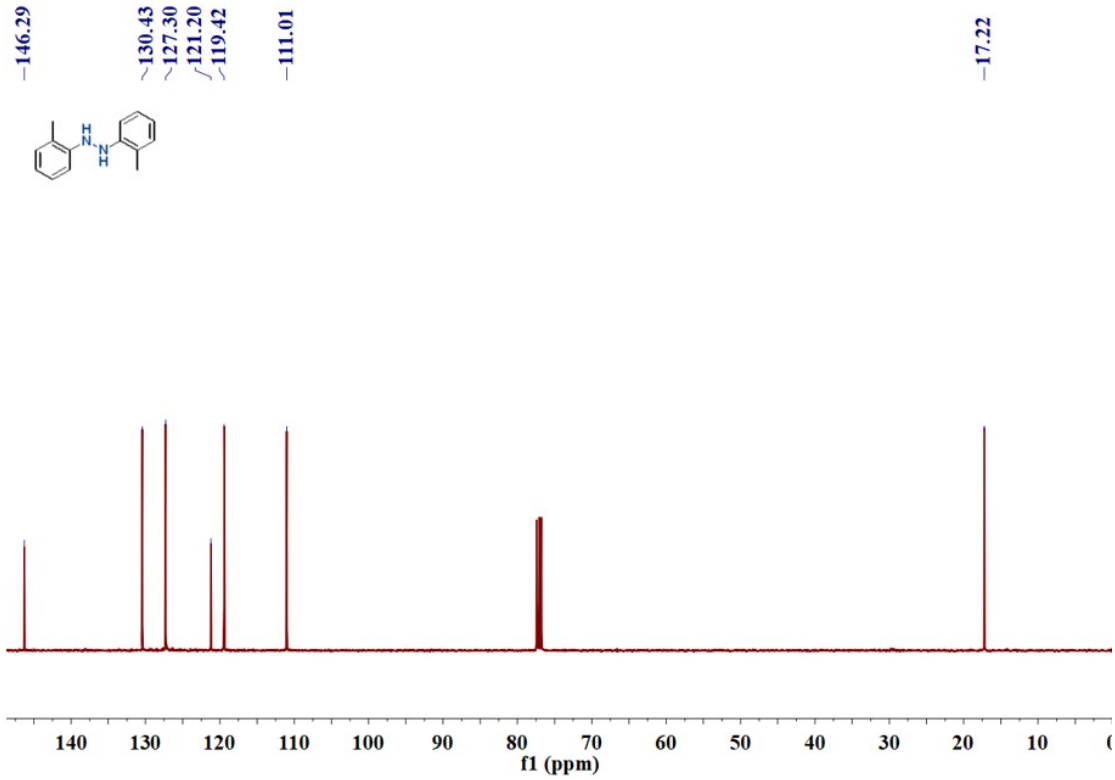

$^{13}$C NMR (101 MHz, Chloroform-d) spectrum of compound **2q**



$^{1}$H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2r**




$^{13}$C NMR (101 MHz, Chloroform-d) spectrum of compound **2r**



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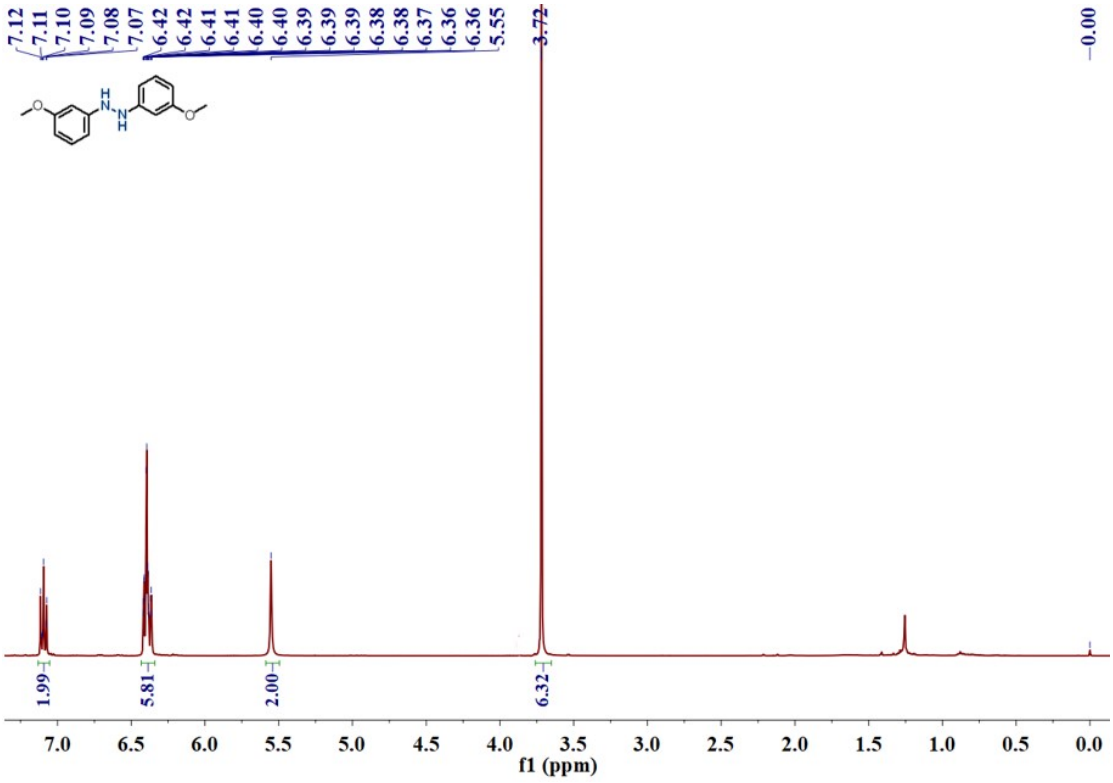
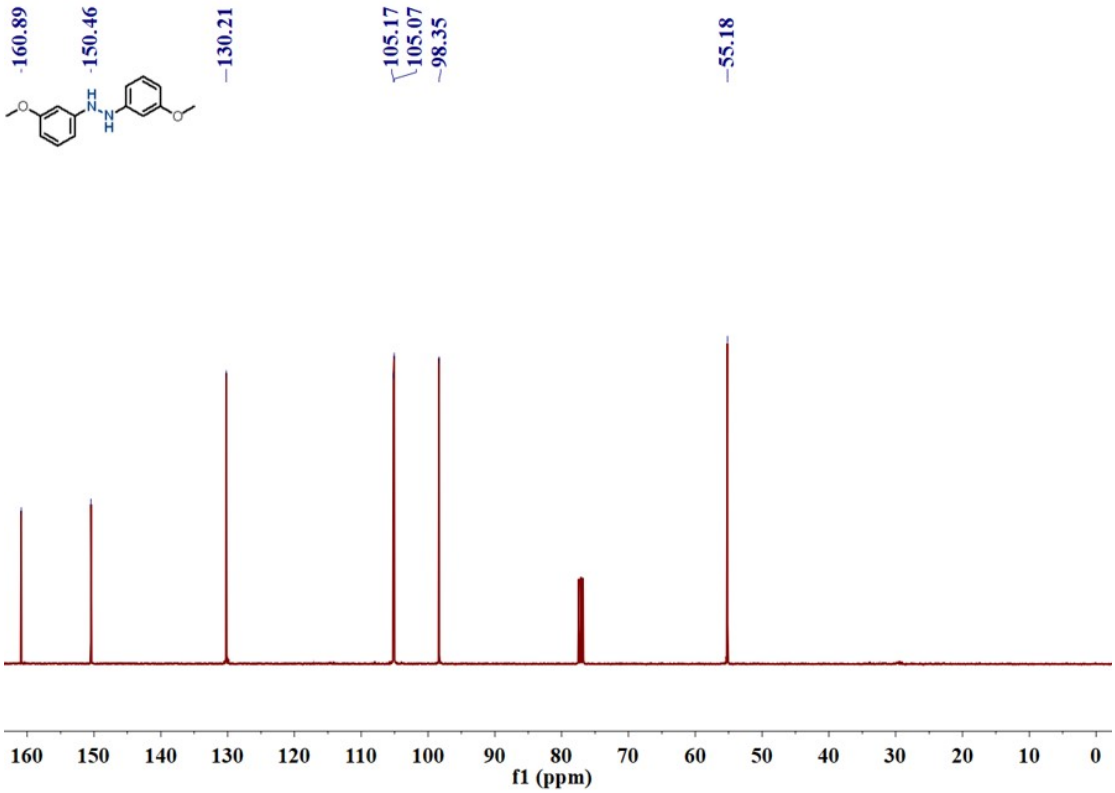
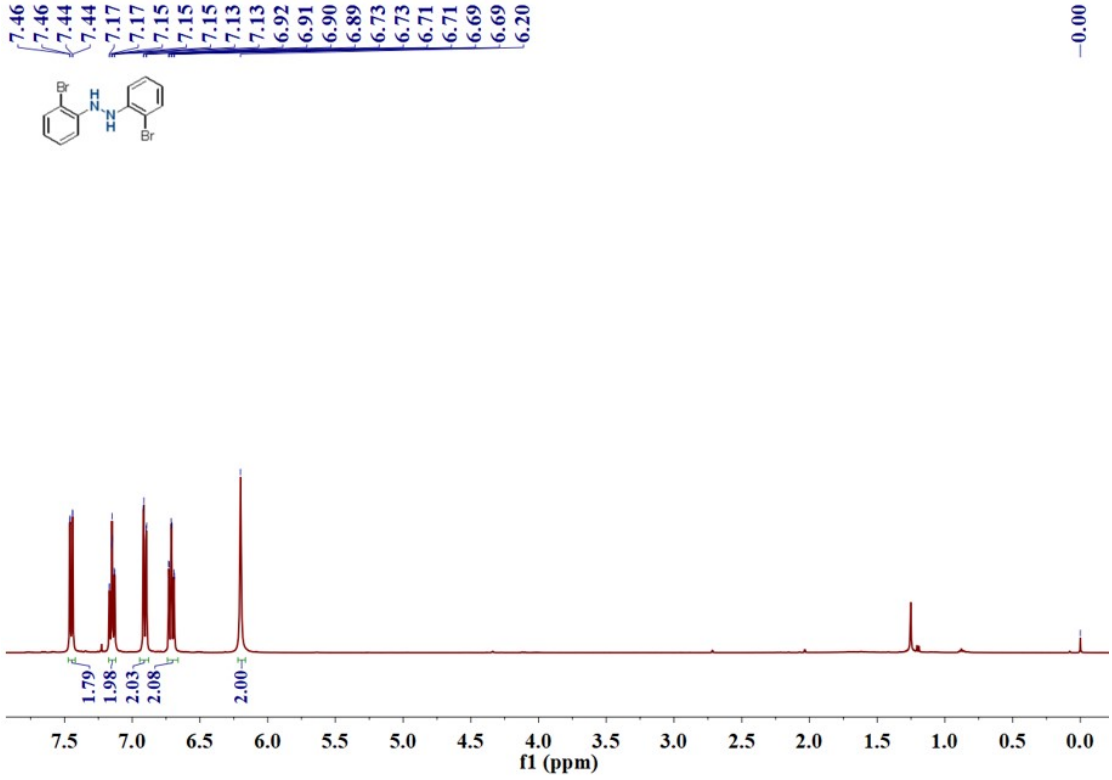


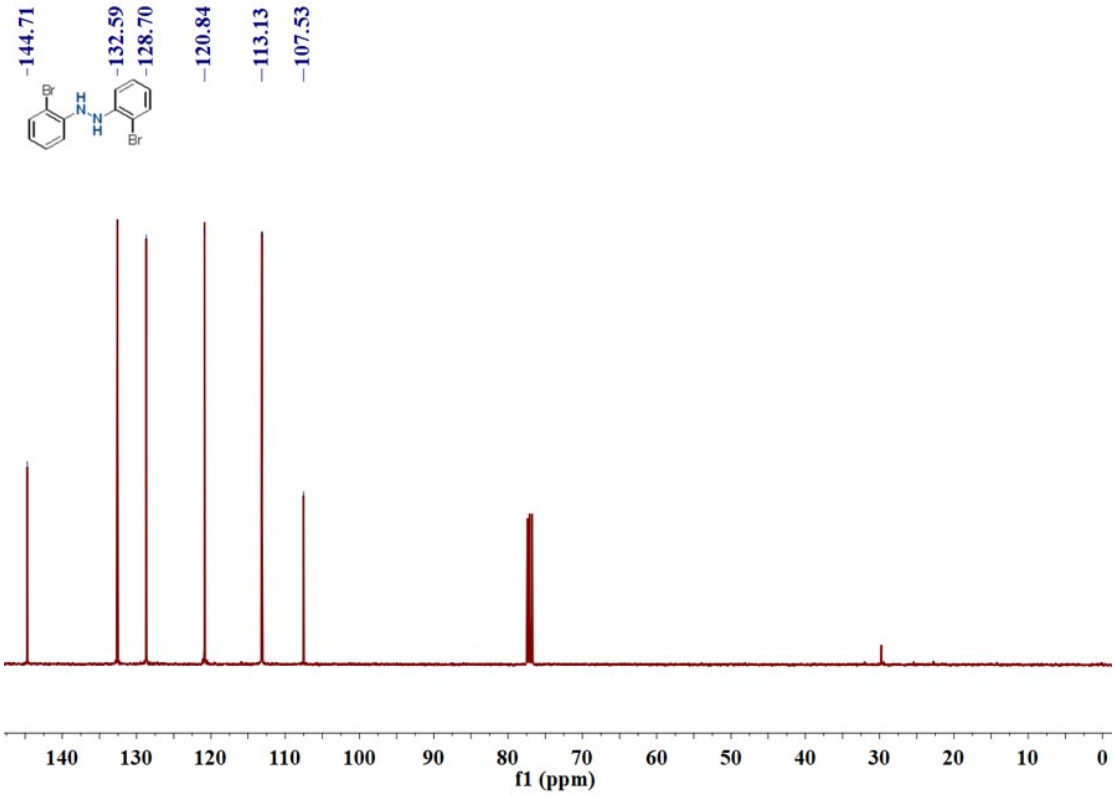

$^{13}$C NMR (101 MHz, Chloroform-d) spectrum of compound **2s**



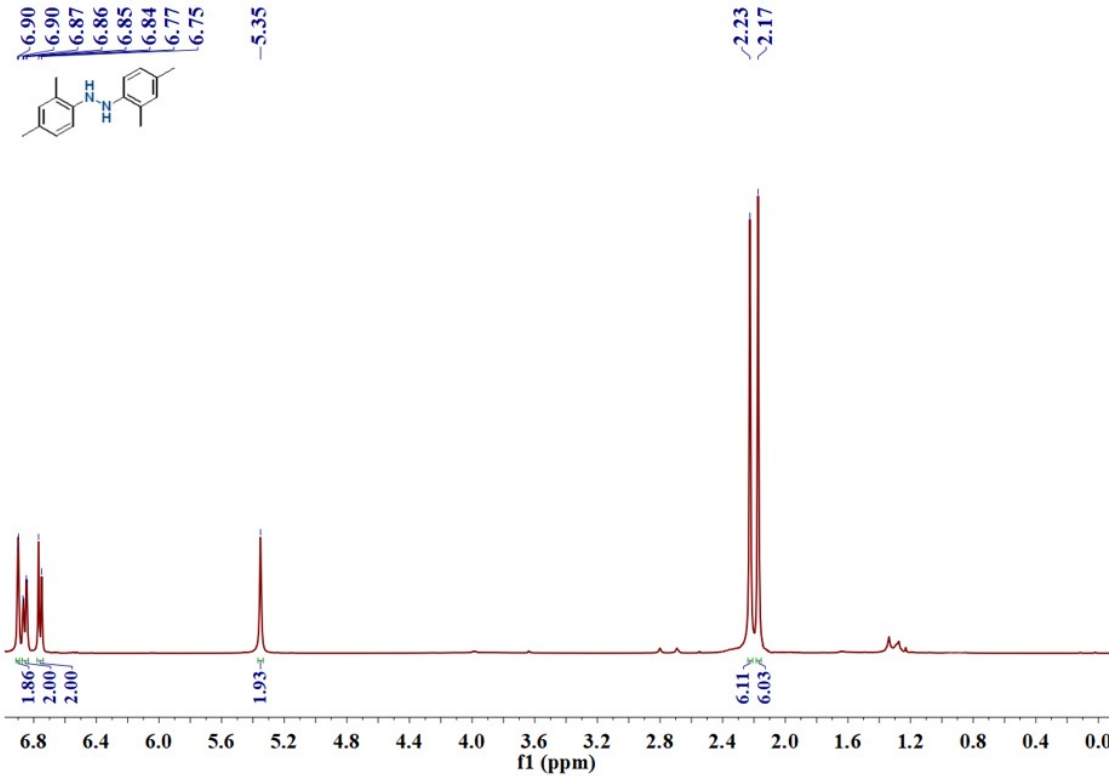
$^{1}$H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2t**



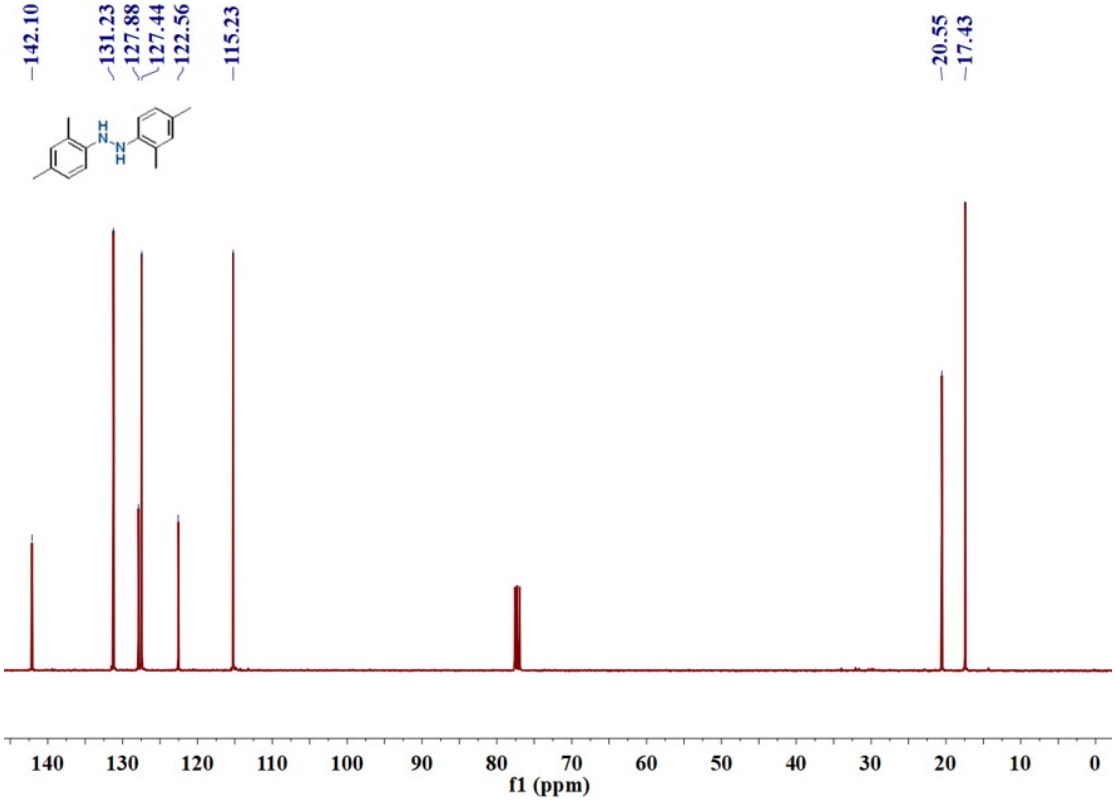

$^{13}$C NMR (101 MHz, Chloroform-d) spectrum of compound **2t**



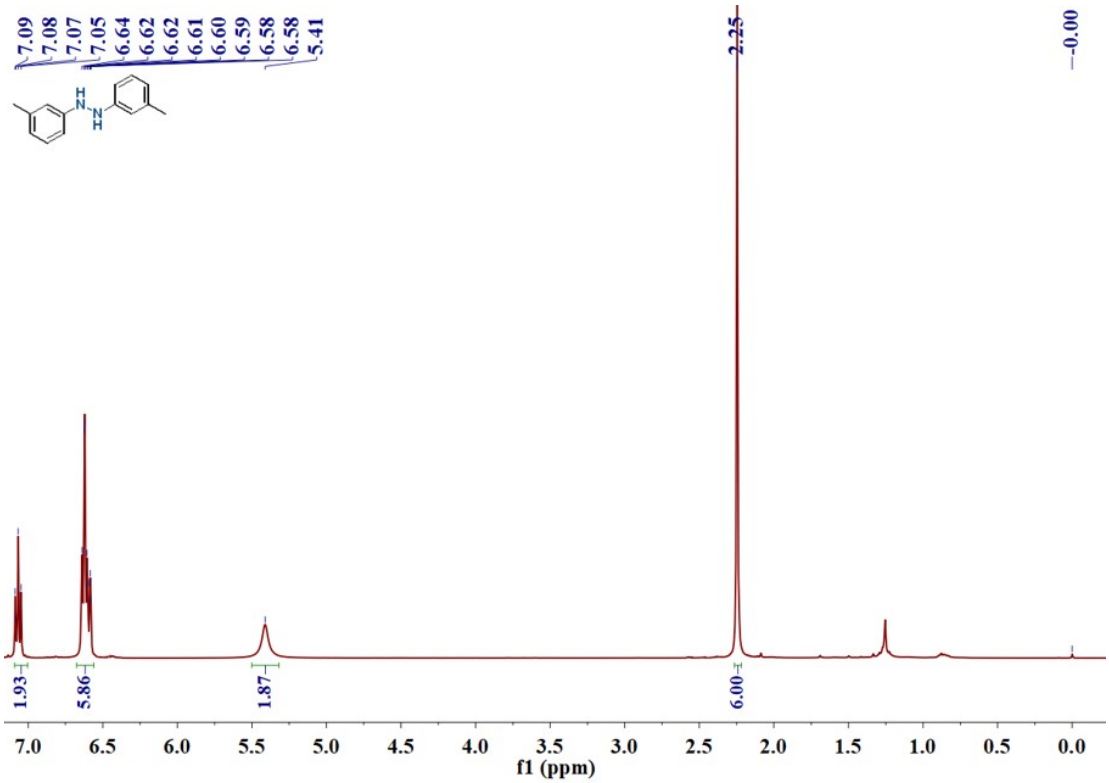
$^{1}$H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2u**



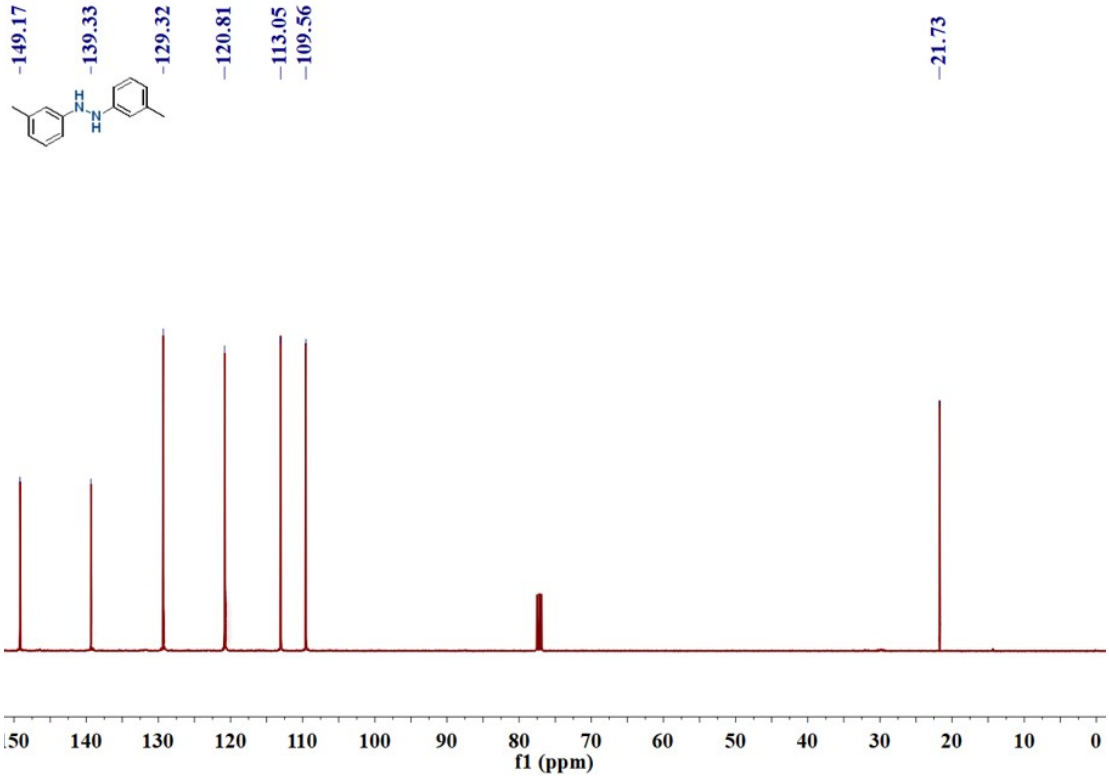

$^{13}$C NMR (101 MHz, Chloroform-d) spectrum of compound **2u**



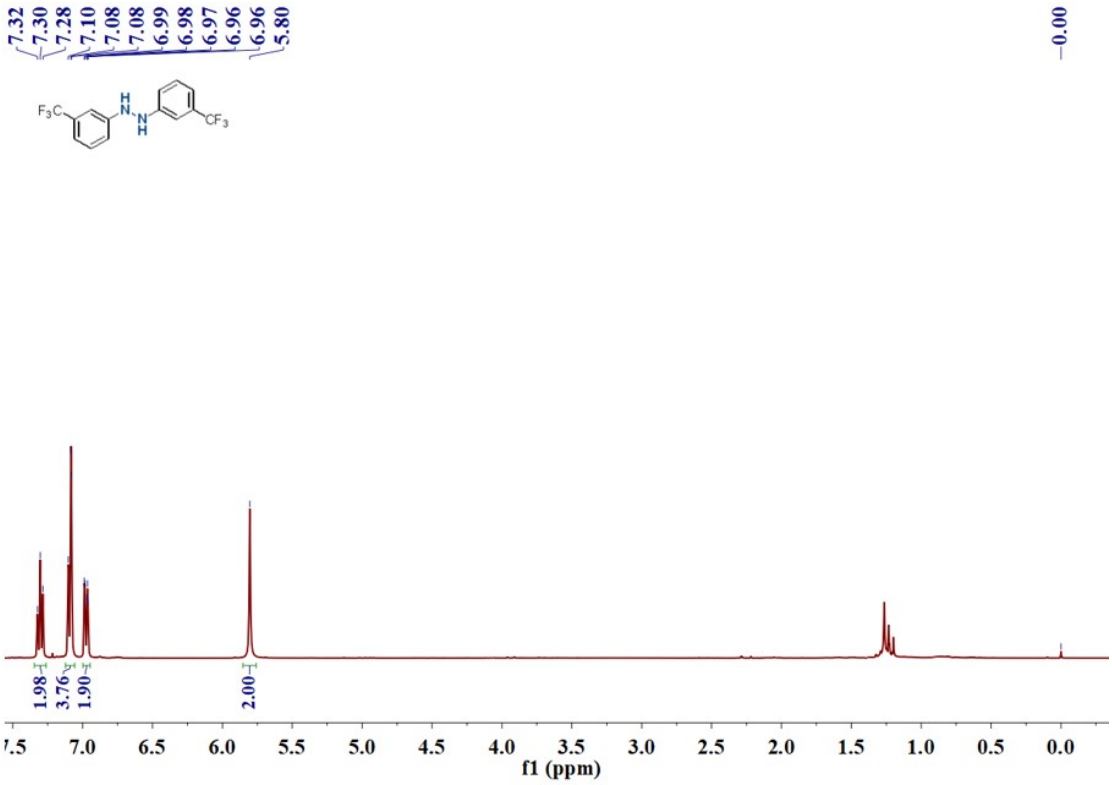
$^{1}$H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2v**



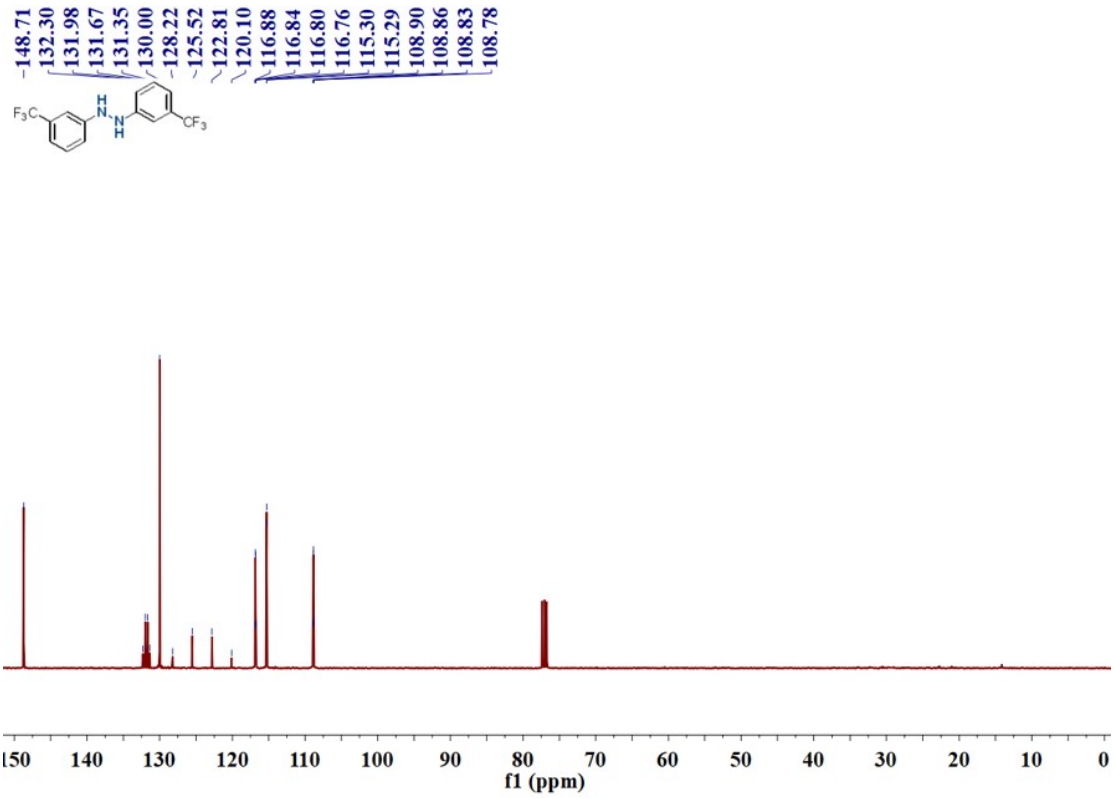

$^{13}$C NMR (101 MHz, Chloroform-d) spectrum of compound **2v**



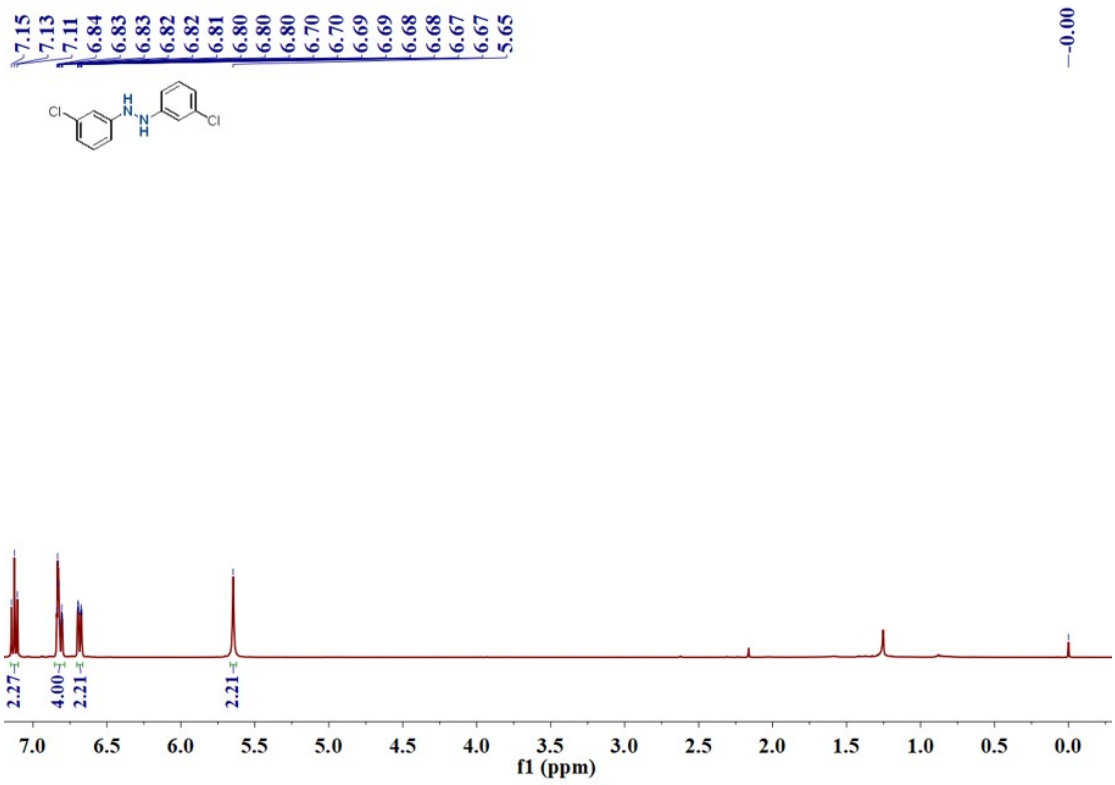
$^{1}$H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2w**



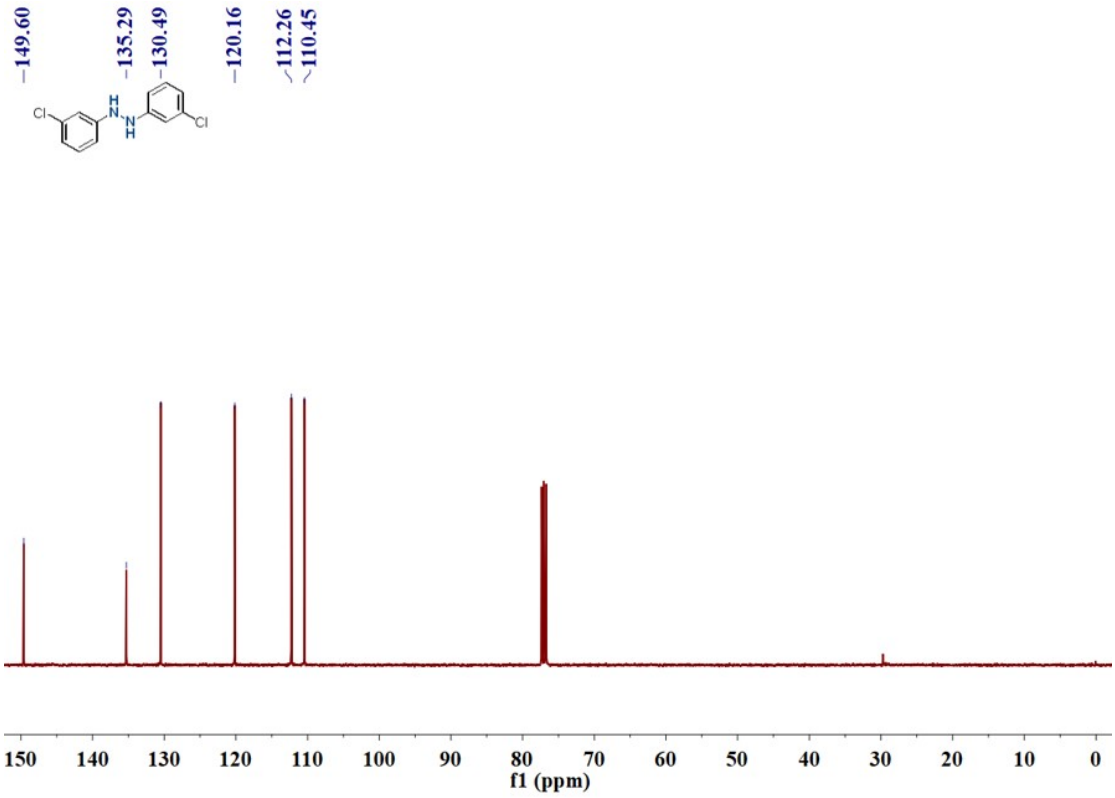

$^{13}$C NMR (101 MHz, Chloroform-d) spectrum of compound **2w**



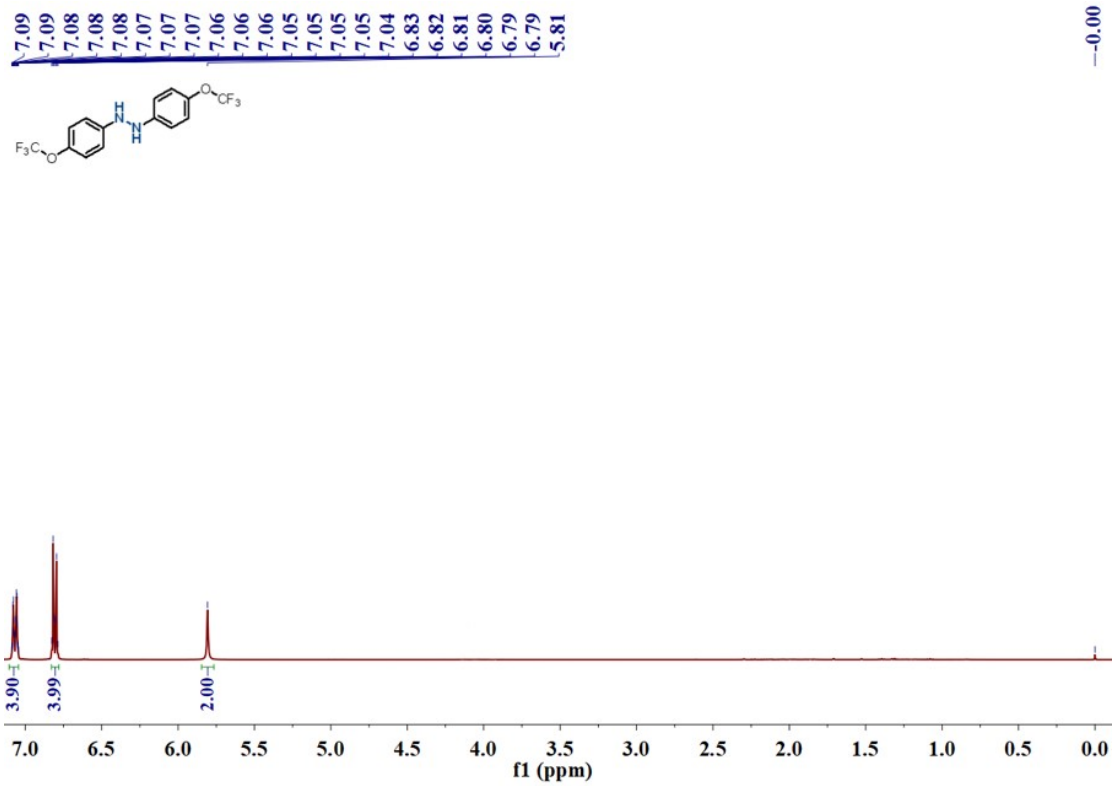
$^{1}$H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2x**




$^{13}$C NMR (101 MHz, Chloroform-d) spectrum of compound **2x**



$^{1}$H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2y**

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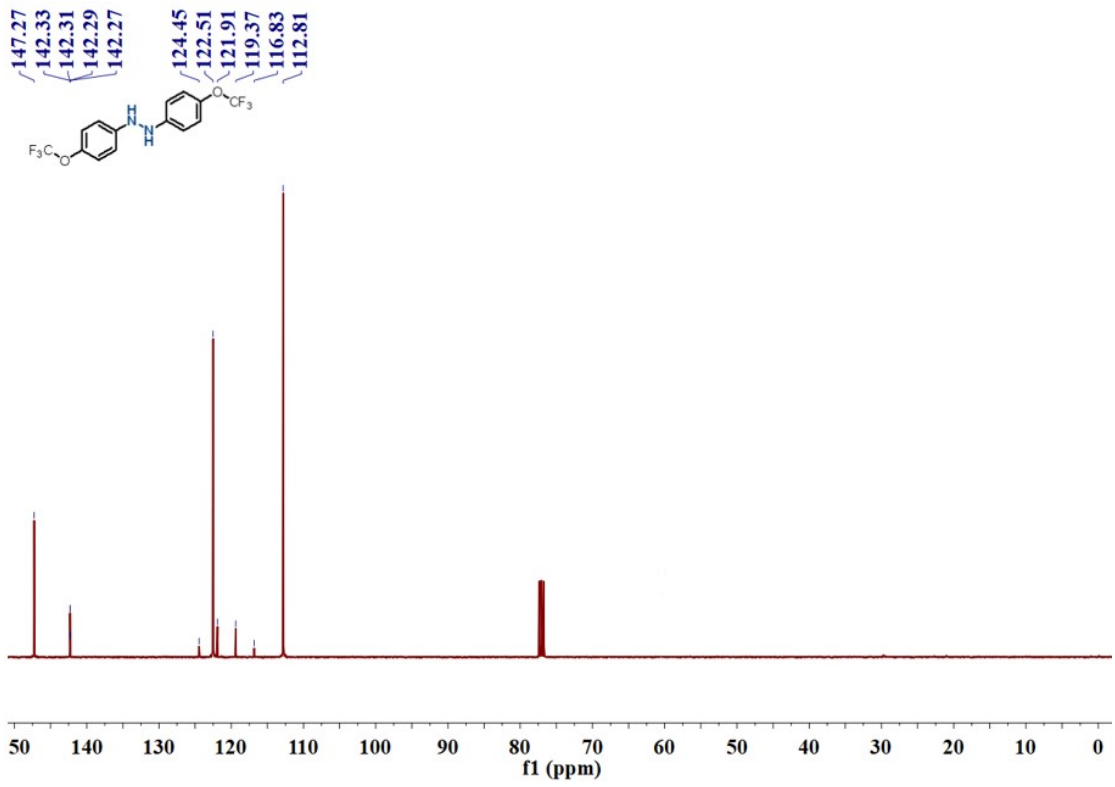
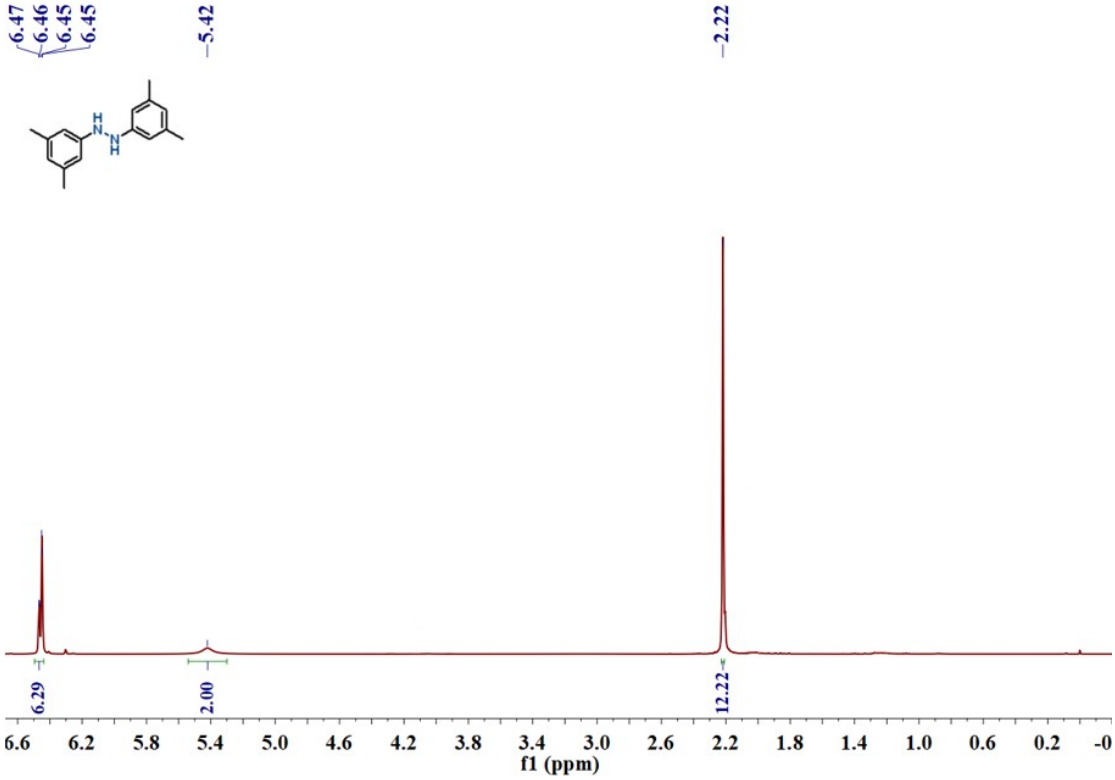
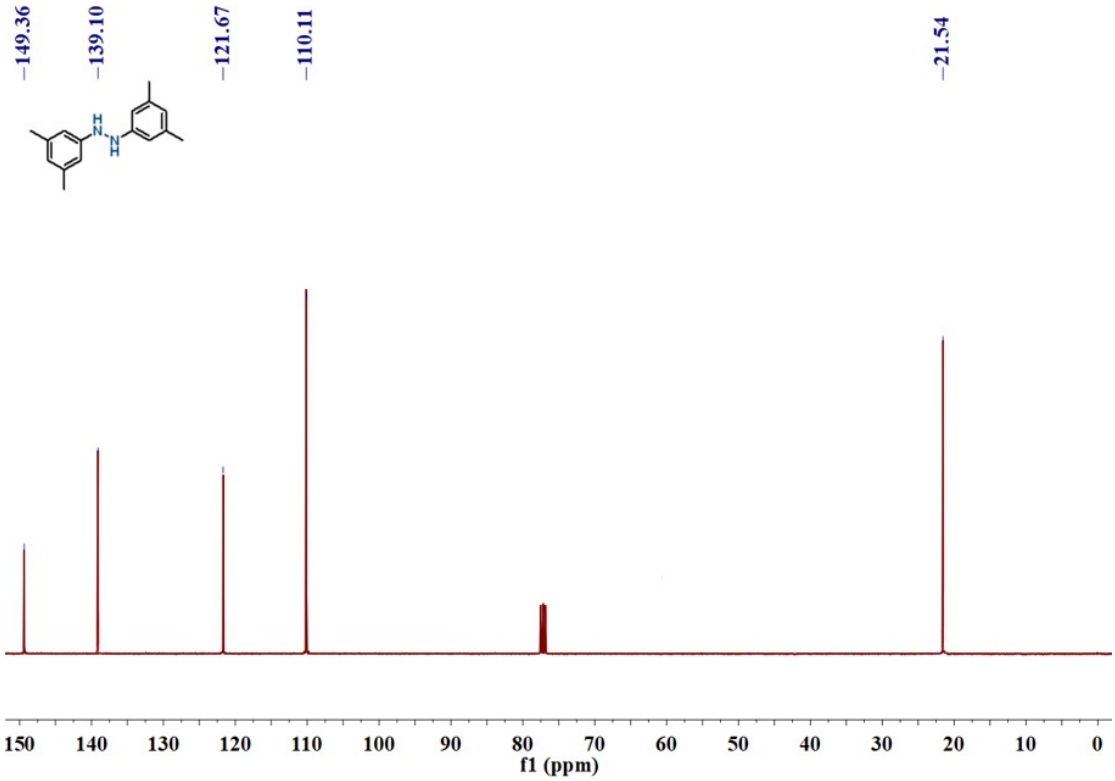


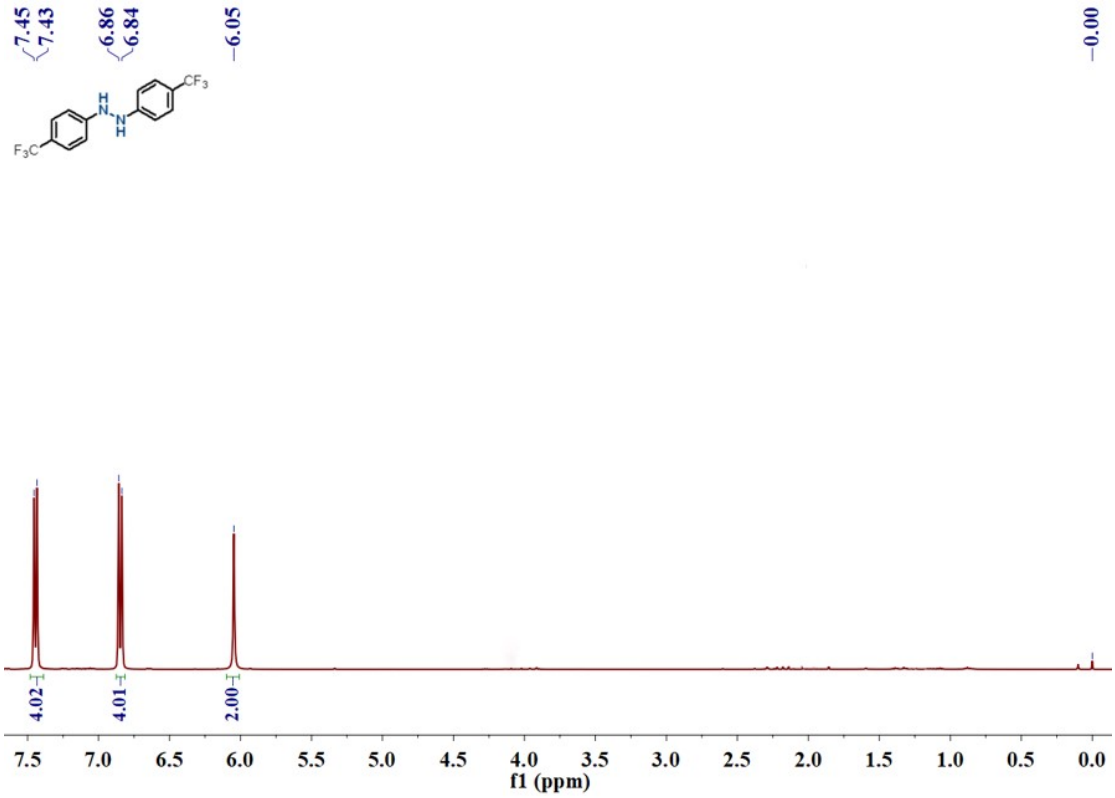
$^{1}$H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2z**



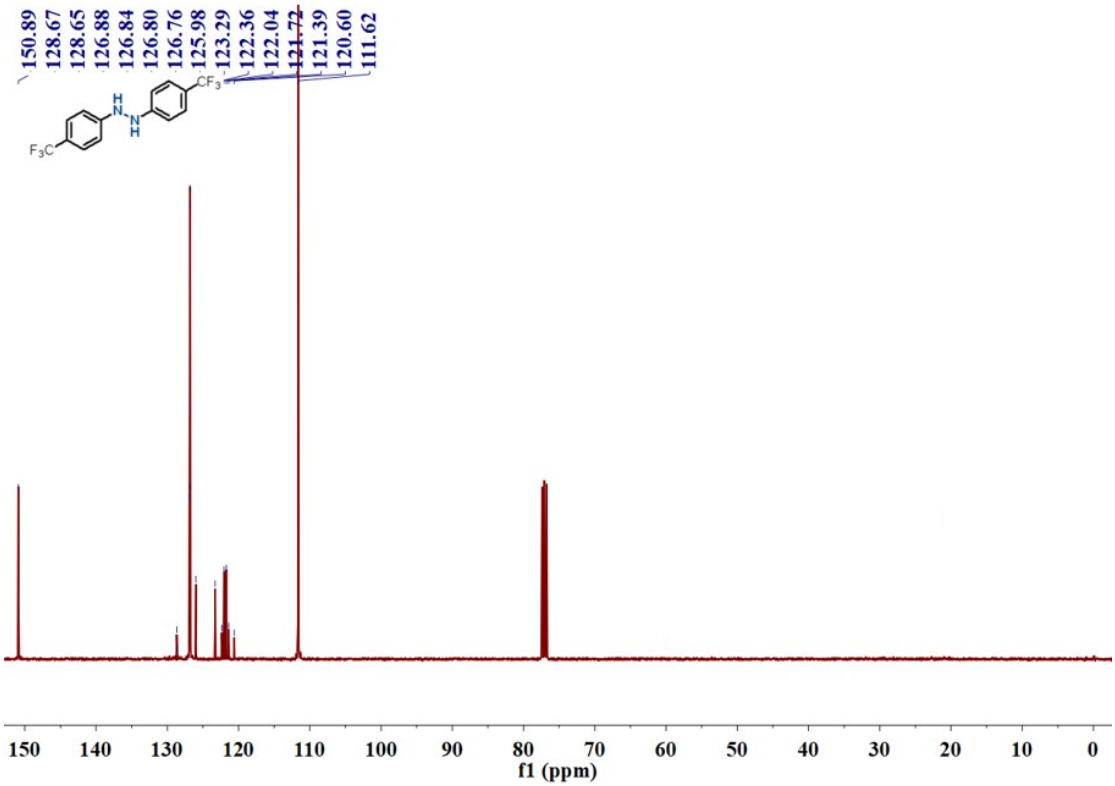

$^{13}$C NMR (101 MHz, Chloroform-d) spectrum of compound **2z**



$^{1}$H NMR (400 MHz, Chloroform-*d*) spectrum of compound **3a**




$^{13}$C NMR (101 MHz, Chloroform-d) spectrum of compound **3a**



## 25. References


1. Q. Chang, P. Zhang, A. H. B. Mostaghimi, X. Zhao, S. R. Denny, J. H. Lee, H. Gao, Y. Zhang, H. L. Xin, S. Siahrostami, J. G. Chen and Z. Chen, *Nat. Commun.*, 2020, **11**, 2178.
2. C. H. Choi, M. Kim, H. C. Kwon, S. J. Cho, S. Yun, H.-T. Kim, K. J. J. Mayrhofer, H. Kim and M. Choi, *Nat. Commun.*, 2016, **7**, 10922.
3. S. Siahrostami, A. Verdaguer-Casadevall, M. Karamad, D. Deiana, P. Malacrida, B. Wickman, M. Escudero-Escribano, E. A. Paoli, R. Frydendal, T. W. Hansen, I. Chorkendorff, I. E. L. Stephens and J. Rossmeisl, *Nat. Mater.*, 2013, **12**, 1137-1143.
4. Z. Zheng, Y. H. Ng, D.-W. Wang and R. Amal, Adv. Mater., 2016, **28**, 9949-9955.
5. S. Yang, Y. J. Tak, J. Kim, A. Soon and H. Lee, *ACS Catal.*, 2017, **7**, 1301-1307.
6. R. Shen, W. Chen, Q. Peng, S. Lu, L. Zheng, X. Cao, Y. Wang, W. Zhu, J. Zhang, Z. Zhuang, C. Chen, D. Wang and Y. Li, *Chem*, 2019, **5**, 2099-2110.
7. C. Tang, Y. Jiao, B. Shi, J.-N. Liu, Z. Xie, X. Chen, Q. Zhang and S.-Z. Qiao, *Angew Chem. Int. Edit.*, 2020, 59, 9171-9176.
8. E. Jung, H. Shin, B.-H. Lee, V. Efremov, S. Lee, H. S. Lee, J. Kim, W. Hooch Antink, S. Park, K.-S. Lee, S.-P. Cho, J. S. Yoo, Y.-E. Sung and T. Hyeon, *Nat. Mater.*, 2020, **19**, 436-442.
9. Z. Lu, G. Chen, S. Siahrostami, Z. Chen, K. Liu, J. Xie, L. Liao, T. Wu, D. Lin, Y. Liu, T. F. Jaramillo, J. K. Nørskov and Y. Cui, *Nat. Catal.*, 2018, **1**, 156-162.
10. H. W. Kim, M. B. Ross, N. Kornienko, L. Zhang, J. Guo, P. Yang and B. D. McCloskey, *Nat. Catal.*, 2018, **1**, 282-290.
11. L. Han, Y. Sun, S. Li, C. Cheng, C. E. Halbig, P. Feicht, J. L. Hübner, P. Strasser and S. Eigler, *ACS Catal.*, 2019, **9**, 1283-1288.
12. Y. Liu, X. Quan, X. Fan, H. Wang and S. Chen, *Angew Chem. Int. Edit.*, 2015, **127**, 6941-6945.
13. S. Chen, Z. Chen, S. Siahrostami, D. Higgins, D. Nordlund, D. Sokaras, T. R. Kim, Y. Liu, X. Yan, E. Nilsson, R. Sinclair, J. K. Nørskov, T. F. Jaramillo and Z. Bao, *J. Am. Chem. Soc.*, 2018, **140**, 7851-7859.

14. X. Bai, L. Guo, T. Jia, Z. Hu, *J. Mater. Chem. A*, 2024, **12**, 13116-13126.

15. R. Mandal, S. Bhattacharyya, *J. Phys. Chem. Lett.*, 2024, **128**, 17342-17352.

16. Z. Jiang, B. Cheng, Y. Zhang, S. Wageh, A. A. Al-Ghamdi, J. Yu, L. Wang, *J. Mater. Sci. Technol.*, 2022, **124**, 193-201.

17. Y. Hou, P. Zhou, F. Liu, Y. Lu, H. Tan, Z. Li, M. Tong, J. Ni, *Angew. Chem. Int. Ed.*, 2024, **136**, e202318562.

18. R. Li, J. Qu, Y. Zhang, X. Liang, Y. Li, Z. Cao, J. Ren, C. Lin, Y. Zheng, X. Guo, *Mat. Sci. Semicon. Proc.,* 2024, **179**, 108520.

19. Z. Teng, Q. Zhang, H. Yang, K. Kato, W. Yang, Y.-R. Lu, S. Liu, C. Wang, A. Yamakata, C. Su, B. Liu and T. Ohno, *Nat Catal*, 2021, **4**, 374-384.

20. X. Zhang, H. Su, P. Cui, Y. Cao, Z. Teng, Q. Zhang, Y. Wang, Y. Feng, R. Feng, J. Hou, X. Zhou, P. Ma, H. Hu, K. Wang, C. Wang, L. Gan, Y. Zhao, Q. Liu, T. Zhang and K. Zheng, *Nat Commun*, 2023, **14**, 7115.

21. X. Zhang, P. Ma, C. Wang, L. Gan, X. Chen, P. Zhang, Y. Wang, H. Li, L. Wang, X. Zhou and K. Zheng, *Energ. Environ. Sci.*, 2022, **15**, 830-842.

22. Y.-X. Ye, J. Pan, F. Xie, L. Gong, S. Huang, Z. Ke, F. Zhu, J. Xu and G. Ouyang, *Proc. Natl. Acad. Sci.*, 2021, **118**, e2103964118.

23. J. Cao, H. Wang, Y. Zhao, Y. Liu, Q. Wu, H. Huang, M. Shao, Y. Liu and Z. Kang, *J. Mater. Chem. A*, 2020, **8**, 3701-3707.

24. C. Chu, Q. Zhu, Z. Pan, S. Gupta, D. Huang, Y. Du, S. Weon, Y. Wu, C. Muhich, E. Stavitski, K. Domen and J.-H. Kim, *Proc. Natl. Acad. Sci.*, 2020, **117**, 6376-6382.

25. L. Chen, C. Chen, Z. Yang, S. Li, C. Chu and B. Chen, *Adv. Funct. Mater.*, 2021, **31**, 2105731.

26. M. Kou, Y. Wang, Y. Xu, L. Ye, Y. Huang, B. Jia, H. Li, J. Ren, Y. Deng, J. Chen, Y. Zhou, K. Lei, L. Wang, W. Liu, H. Huang and T. Ma, *Angew. Chem. Int. Ed.*, 2022, **61**, e202200413.

27. Y. Mou, X. Wu, C. Qin, J. Chen, Y. Zhao, L. Jiang, C. Zhang, X. Yuan, E. Huixiang Ang and H. Wang, *Angew. Chem. Int. Ed.*, 2023, **62**, e202309480.

28. Y.-Y. Tang, X. Luo, R.-Q. Xia, J. Luo, S.-K. Peng, Z.-N. Liu, Q. Gao, M. Xie, R.-J. Wei, G.-H. Ning and D. Li, *Angew. Chem. Int. Ed.*, 2024, **63**, e202408186.

29. H. Tan, P. Zhou, M. Liu, Q. Zhang, F. Liu, H. Guo, Y. Zhou, Y. Chen, L. Zeng, L. Gu, Z. Zheng, M. Tong and S. Guo, *Nat. Synth.*, 2023, **2**, 557-563.

30. J.-R. Huang, H.-Y. Chen, H.-L. Zhu, P.-Q. Liao and X.-M. Chen, *J. Am. Chem. Soc.*, 2025, **147**, 37167-37175.

31. H. Wang, L. Cao, X. Tao and G. J. A. C. Zhu, *Angew. Chem. Int. Ed.*, 2025, **137**, e202502943.

32. X. Xu, R. Sa, W. Huang, Y. Sui, W. Chen, G. Zhou, X. Li, Y. Li and H. Zhong, *ACS Catal.*, 2022, **20**, 12954-12963.

33. X. Song, J. Peng, X. Li, P. Zhao, X. Zhao and L. Wang, *Green Chem.*, 2025, **27**, 12333-12340.

34. X. Zeng, Y. Liu, Y. Kang, Q. Li, Y. Xia, Y. Zhu, H. Hou, M. H. Uddin, T. R. Gengenbach, D. Xia, C. Sun, D. T. McCarthy, A. Deletic, J. Yu and X. Zhang, *ACS Catal.*, 2020, **10**, 3697-3706.

35. E. Zhou, F. Wang, X. Zhang, Y. Hui and Y. Wang, *Angew. Chem. Int. Ed.*, 2024, **63**, e202400999.

36. Q. Liao, Q. Sun, H. Xu, Y. Wang, Y. Xu, Z. Li, J. Hu, D. Wang, H. Li and K. Xi, *Angew. Chem. Int. Ed.*, 2023, **62**, e202310556.

37. Z. Yu, S. Li, Y. Wu, C. Ma, J. Li, L. Duan, Z. Liu, H. Sun, G. Zhao, Y. Lu, Q. Liu, Q. Meng and J. Zhao, *Green Chem.*, 2024, **26**, 9310-9319.