

Supporting Information

Photoactivated Solid-State Self-Assembly: A Mechanochemistry-Free Route to High-Purity Aromatic Amine Crystals

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1. General information.

Solvents and reagents were of reagent grade and were used without purification unless otherwise stated. Column chromatography was performed on silica gel (200 – 300 mesh). All ^1H -NMR (500 MHz) spectra were recorded on a Bruker-DMX 500 using CDCl_3 solution in the presence of tetramethylsilane (TMS), MeOD, D_2O or DMSO- d_6 as internal standard and are reported in ppm (δ). Coupling constants are expressed in Hertz (Hz). Spectral splitting patterns are denoted as s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; m, multiplet; and br, broad. High Resolution Transmission Electron Microscopy (HR-TEM): The particle size of the 12R-Pd-NCs, 0R-Pd-NCs, 16R-Pd-NCs and Pd/C was determined using an FEI Tecnai G2 F20 American FEI. Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES): The Pd content in 12R-Pd-NCs was analyzed by using Agilent inductively coupled Plasma Emission Spectrometer (ICP-OES). X-ray photoelectron spectroscopy (XPS): The measurement of X-ray photoelectron spectroscopy was analyzed through Thermo ESCALAB 250 Xi. X-ray Powder diffractometer (XRD): The measurement of X-ray Powder diffractometer was analyzed through Smart Lab 3 kW. Brunauer-Emmett-Teller (BET) of 12R-Pd-NCs results were performed on Micromeritics/3Flex Chemical adsorption instrument. Fourier transform infrared spectroscopy (FT-IR): FT-IR measurements were performed on a WQF-510 type Fourier Transform infrared spectrometer. The product yield was quantified by means of High-performance liquid chromatography (HPLC) using a Waters-2695 system, which was equipped with a Waters-2998 UV detector. The pulse chemisorption study of CO adsorption on the American Micromeritics Auto Chem II automatic chemical sorbent instrument. The H_2 chemisorption study of H_2 adsorption on the American Micromeritics Auto Chem II automatic chemical sorbent instrument.

2. Synthesis procedures for nanoclusters.

2.1 Synthesis of 0R-Pd-NCs

Step1: Aniline (93.13 mg, 1.0 mmol) and 50% of tetrafluoroboric acid (5 mL) were added to a 25 mL vial at $0\text{ }^\circ\text{C}$, sodium nitrite (0.3 g, 4.5 mmol) in 1.0 mL of H_2O was added slowly to a stirred solution of aniline and HBF_4 , the solution was stirred for 30 minutes, then white solid was obtained, filter with Büchner funnel and washed with H_2O ($2 \times 2.5\text{ mL}$) and aniline diazo salt was

dried under a vacuum desiccator and store at 0 °C.

Step2: Methanol solution of palladium acetate $\text{Pd}(\text{OAc})_2$ (112.3 mg, 0.5 mmol) and tetrahydrofuran solution of aniline diazo salt (96 mg, 0.5 mmol) were mixed and stirred for 30 minutes at 0 °C. Then add the methanol solution of sodium borohydride slowly (2.5 mmol sodium borohydride dissolved in 2.0 mL of MeOH), maintain vigorous stirring at 0 °C for 2 h. After the reaction finished, methanol and tetrahydrofuran were removed with rotary evaporator and dissolved in dichloromethane, washing with 0.5 M H_2SO_4 (3×20 mL), 0.5 M NaHCO_3 (3×20 mL) and H_2O (3×20 mL), dry with anhydrous sodium sulfate, spin dry. The 0R-Pd-NCs were dispersed in absolute ethanol, after the centrifugation treatment could seen significant stratification, abandon the supernatant solvent, and the solid was dried, the nanoclusters stabilized by palladium-carbon covalent bonds was obtained. Black powder: 30 mg, 32.8% (based on Pd).

2.2 Synthesis of 12R-Pd-NCs

4-Dodecylaniline (261.45 mg, 1.0 mmol) and 50% of tetrafluoroboric acid (5 mL) were added to a 25 mL vial at 0 °C, sodium nitrite (0.3 g, 4.5 mmol) in 1.0 mL of H_2O was added slowly to a stirred solution of 4-Dodecylaniline and HBF_4 , the solution was stirred for 30 minutes, then yellow solid was obtained, filter with Büchner funnel and washed with H_2O (2×2.5 mL) and the dodecylaniline diazo salt was dried under a vacuum desiccator and store at 0 °C.

Methanol solution of palladium acetate $\text{Pd}(\text{OAc})_2$ (112.3 mg, 0.5 mmol) and tetrahydrofuran solution of dodecylaniline diazo salt (173 mg, 0.5 mmol) were mixed and stirred for 30 minutes at 0 °C. Then add the methanol solution of sodium borohydride slowly (2.5 mmol sodium borohydride dissolved in 2.0 mL of MeOH), maintain vigorous stirring at 0 °C for 2 h. After the reaction finished, methanol and tetrahydrofuran were removed with rotary evaporator and dissolved in dichloromethane, washing with 0.5 M H_2SO_4 (3×20 mL), 0.5 M NaHCO_3 (3×20 mL) and H_2O (3×20 mL), dry with anhydrous sodium sulfate, spin dry. The 12R-Pd-NCs were dispersed in absolute ethanol, after the centrifugation treatment could seen significant stratification, abandon the supernatant solvent, and the solid was dried, the nanoclusters stabilized by palladium-carbon covalent bonds was obtained. Black powder: 65 mg, 42.3% (based on Pd).

2.3 Synthesis of 16R-Pd-NCs

4-Hexyldecylaniline (317.55 mg, 1.0 mmol) and 50% of tetrafluorooric acid (5 mL) were added to a 25 mL vial at 0 °C, sodium nitrite (0.3 g, 4.5 mmol) in 1.0 mL of H₂O was added slowly to a stirred solution of 4-Hexyldecylaniline and HBF₄, the solution was stirred for 30 minutes, then yellow solid was obtained, filter with Büchner funnel and washed with H₂O (2 × 2.5 mL) and the cetylaniline diazo salt was dried under a vacuum desiccator and store at 0 °C.

Methanol solution of palladium acetate Pd(OAc)₂ (112.3 mg, 0.5 mmol) and tetrahydrofuran solution of cetylaniline diazo salt (159 mg, 0.5 mmol) were mixed and stirred for 30 minutes at 0 °C. Then add the methanol solution of sodium borohydride slowly (2.5 mmol sodium borohydride dissolved in 2.0 mL of MeOH), maintain vigorous stirring at 0 °C for 2 h. After the reaction finished, methanol and tetrahydrofuran were removed with rotary evaporator and dissolved in dichloromethane, washing with 0.5 M H₂SO₄ (3×20 mL), 0.5 M NaHCO₃ (3×20 mL) and H₂O (3×20 mL), dry with anhydrous sodium sulfate, spin dry. The 16R-Pd-NCs were dispersed in absolute ethanol, after the centrifugation treatment could seen significant stratification, abandon the supernatant solvent, and the solid was dried, the nanoclusters stabilized by palladium-carbon covalent bonds was obtained. Black powder: 49 mg, 32.7% (based on Pd).

3. The TOF results were calculated for the catalyst.¹

The 4-chloronitrobenzene (A) conversion is defined by:

$$Conv.A\% = \frac{n_A - n_A'}{n_A} * 100$$

Turnover frequency (TOF, h⁻¹) could be expressed as:

$$TOF = \frac{n_A * C_A}{\left(\frac{m * Pd \text{ Wt.\%}}{M}\right) * t}$$

Where n_A is the initial molar amount of 4-Nitroanisole, mmol; n_A' the molar amount of 4-Nitroanisole at the reaction of t, mmol; C_A is the conversion of substrates at the reaction of t, %; Pd wt.% is the palladium contents in the catalysts; M is the molar mass of Pd, 106.4 g/mol; m is the mass amount of the catalysts at surface active sites, g; t is reaction time, h⁻¹.

Reference:

1. Sun, Y.; Du, B.; Wang, Y.; Zhang, M. K.; Zhang, S. Hydrogen Spillover-Accelerated Selective Hydrogenation on WO₃ with ppm-Level Pd. *ACS Appl. Mater. Interfaces*, **2023**, *15*, 20474-20482.

4. Energy Dispersive Spectroscopy analysis of the 12R-Pd-NCs.

Table S1. HR-TEM-EDS analysis of the 12R-Pd-NCs.

Entry	Element	wt%
1	Pd	25.5

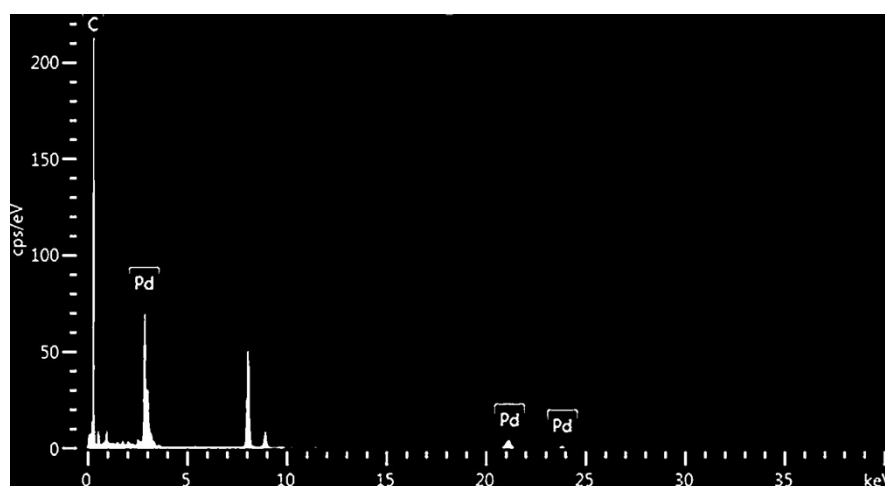


Figure S1. The EDS of 12R-Pd-NCs.

5. The HR-TEM of palladium nanoclusters and Pd/C.

The synthesis of supported Pd nanocluster is conducted under ambient conditions via a surfactant-free process. The reduction of Pd (NO₃)₂ in the presence of a carbon support in alkaline methanol results in the formation of sub 3~5 nm nanocluster **Figure S2 (d)**. For the preparation of Pd/C, please refer to: *RSC Adv.*, 2018, **8**, 33794.

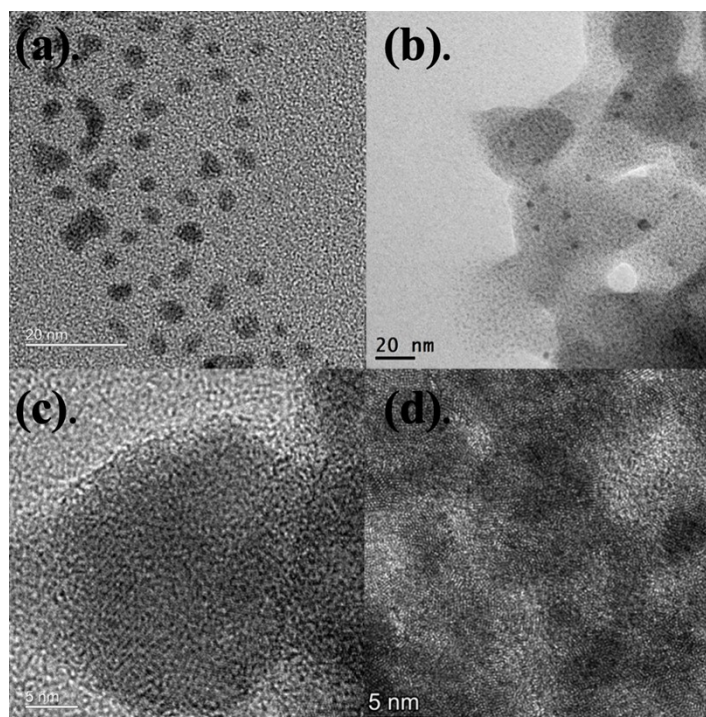


Figure S2. The HR-TEM of (a) 12R-Pd-NCs, (b) 0R-Pd-NCs, (c) 16R-Pd-NCs and (d) Pd/C.

6. Determination of nanoclusters metal content.

Agilent inductively coupled plasma emission spectrometer (ICP-OES) was used to analyze the content of Pd. In the Table S2, 0.0434 g the 12R-Pd-NCs was weighed before digestion, fixed volume was added up to 25 mL, diluted 500 times and measured by machine, and the result obtained by ICP-OES was 2.557 mg/L, after calculation, the metal palladium content in the catalyst was 73.66 wt%.

Table S2. Determination of the palladium content in the 12R-Pd-NCs.

Entry	Sample	Element	Sample WGT (g)	Fixed capacity vol. (mL)	^a Instrument result (mg/L)	^b Final result (wt%)
1 ^a	12R-Pd-NCs	Pd	0.0434	25	2.557	73.66

^a Diluted 500 times; ^b Final result = (Instrument result × Fixed capacity vol. × Dilution ratio)/Sample WGT.

7. Valence bond binding energy calculations for metal nanocluster.

Computational details: Considering the complexity of 12R-Pd-NCs and in order to simplify the computational model, the binding mode of Pd metal and an organic precursor was set to 1:1,

calculation of the 12R-Pd-NCs valence bond binding energy using density functional theory (DFT), the valence bond binding energy of 0 valent palladium in the 12R-Pd NCs prepared by our research group can reach 256.18 kJ/mol. In addition, Pd (2+) valent bond binding energy in the 12R-Pd NCs is 1516.27 kJ/mol. It is evident that the former is more aligned with the findings of our experiments.

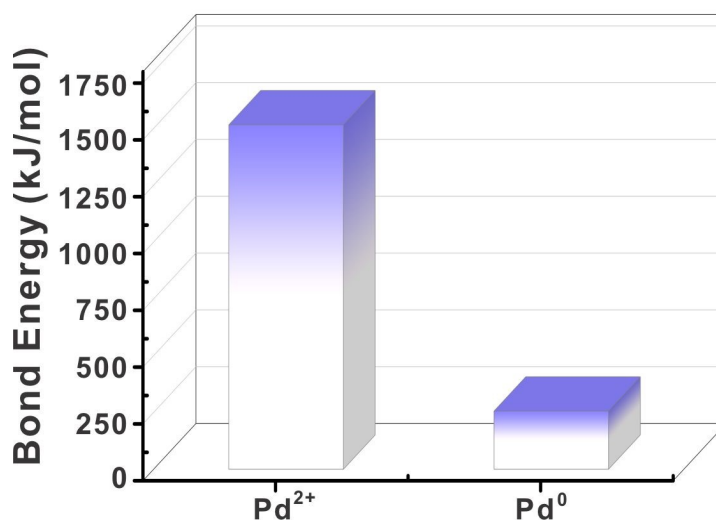


Figure S3. Results of the valence bond binding energies.

All DFT calculations were performed by using Gaussian 09 package.¹ The geometries optimization and frequencies calculations were computed by employing the PBE0 functional.² The def-TZVP basis set was applied to the C and H atoms,³ and the SDD pseudopotential basis set was applied for Pd atoms. The optimized structures discussed are characterized to be local minima without imaginary frequencies. The Grimme's DFT-D3 with BJ-damping method was applied to correct the dispersion interaction.⁴ All single-point calculations were performed by using PBE0 functional in conjunction with the def 2-TZVP basis set. The bond energy (E_b) was calculated by using the following definition:

$$E_b = E_A + E_B - E_{A+B}$$

Where E_A is the electron energy of the A fragment; E_B is the electron energy of the B fragment; E_{A+B} is the total electron energy of the system.

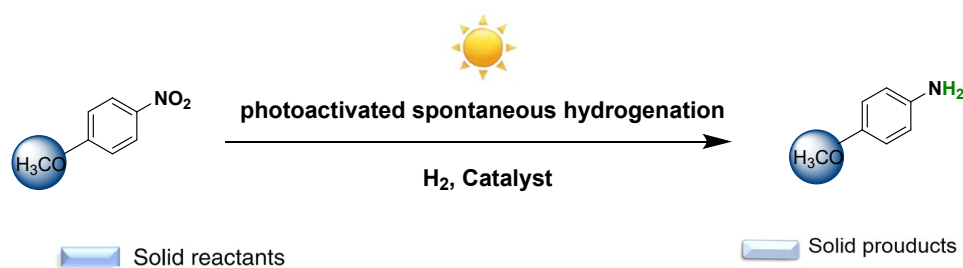
Reference:

1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. E. Gaussian 09 Revision D. 01,

Wallingford: Gaussian Inc., 2014.

2. Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, 77, 3865-3868.
3. Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, 7, 3297-3305.
4. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate *ab initio* parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, 132 (15), 154104.

8. Catalytic evaluation of photoactivated solid-state self-assembly.



Nitroanisole (0.5 mmol, 76.5 mg) and 12R-Pd-NCs (2.0 mg) were each added to a reaction bottle. To avoid introducing mechanical energy into the reaction system, simple shaking mixing of the products and catalysts as well as standing are carried out before the introduction of the necessary reactant hydrogen (H₂, 1 atm). The reaction did not occur at this time. Following a period of standing, the reaction was then allowed to continue under hydrogen balloon (1 atm) as well as static conditions powered by solar energy until the starting material was completely consumed. After dissolving the whole reaction in ethyl acetate, the yield of the whole reaction was monitored by HPLC to avoid the effects caused by local reaction differences in static solid state reactions. The post-treatment purification process can be performed using one of the following methods: a thermal filtration recrystallisation or centrifugation without the presence of organic solvents. The catalyst collected by centrifugation could be recharged into the solid-state catalysis to achieve recycling; The second method: the reaction mixture was washed with EtOAc (10 mL×3). The combined organic extract was washed with brine and dried over anhydrous Na₂SO₄.

The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (5/1) as eluent to afford.

9. Conditional screening of the hydrogenation of nitro toward amines.

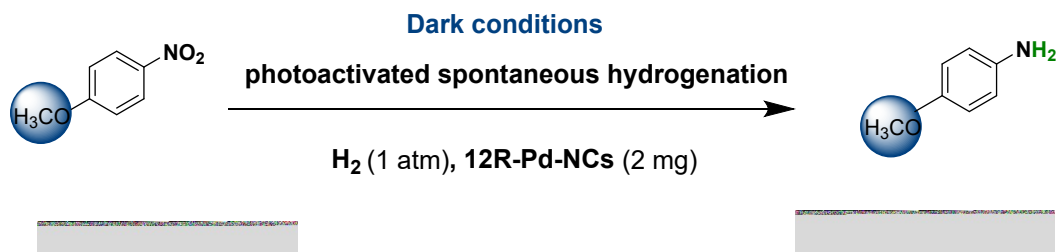


Table S3. Catalytic evaluation of 12R-Pd-NCs under different light intensities.

Entry	Catalyst	Temp.(°C)	Light	Time (h)	Yield (%)	Sel.(%)
1	12R-Pd-NCs	-78	Dark	4	3.7	>99.9
2	12R-Pd-NCs	0	Dark	4	15.1	88.0
3	12R-Pd-NCs	37	Dark	4	74.2	>99.9
4	12R-Pd-NCs	40	Dark	4	52.0	>99.9
5	12R-Pd-NCs	45	Dark	4	54.6	>99.9
6	12R-Pd-NCs	50	Dark	4	56.0	>99.9
7	12R-Pd-NCs	80	Dark	4	39.7	95.0
8	12R-Pd-NCs	100	Dark	4	29.5	89.0

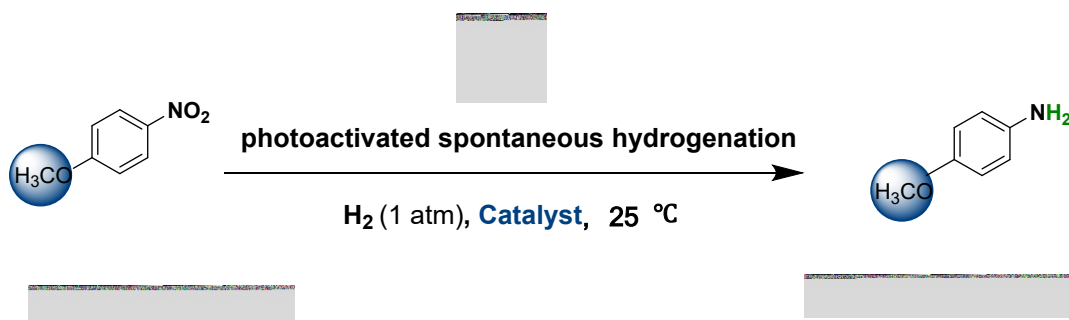


Table S4. Investigation of different palladium catalysts performance in solar.

Entry	Catalyst	Light	Time (h)	Yield (%)	Sel. (%)
1	0R-Pd-NCs	Sun	4	35.0	97
2	12R-Pd-NCs	Sun	4	>99.9	>99.9
3	16R-Pd-NCs	Sun	4	54.0	95
4	Pd(OAc) ₂	Sun	4	55.5	96
5	Pd/C	Sun	4	28.6	98
6	/	Sun	4	0	/

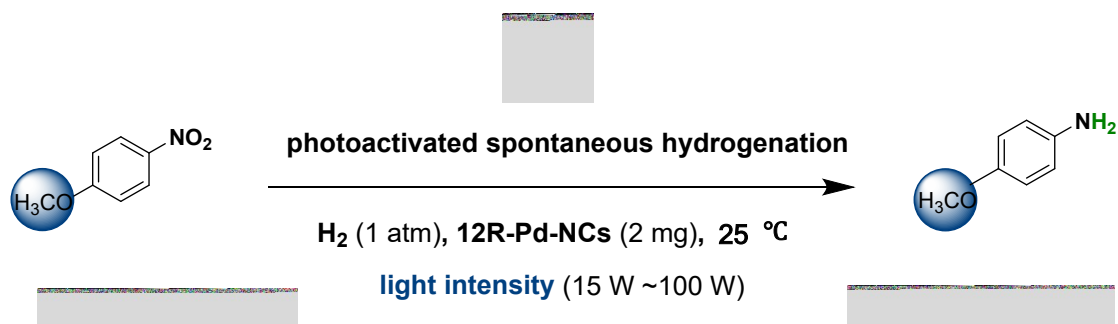


Table S5. Catalytic evaluation of 12R-Pd-NCs under different light intensities

Entry	Catalyst	Light	Time (h)	Yield (%)	Sel. (%)
1	12R-Pd-NCs	10 W	4	41.9	98
2	12R-Pd-NCs	15 W	4	44.9	91
3	12R-Pd-NCs	36 W	4	45	81
4	12R-Pd-NCs	60 W	4	36.8	96
5	12R-Pd-NCs	100 W	4	>99.9	>99.9
6	12R-Pd-NCs	100 W/tempo	4	<10%	99

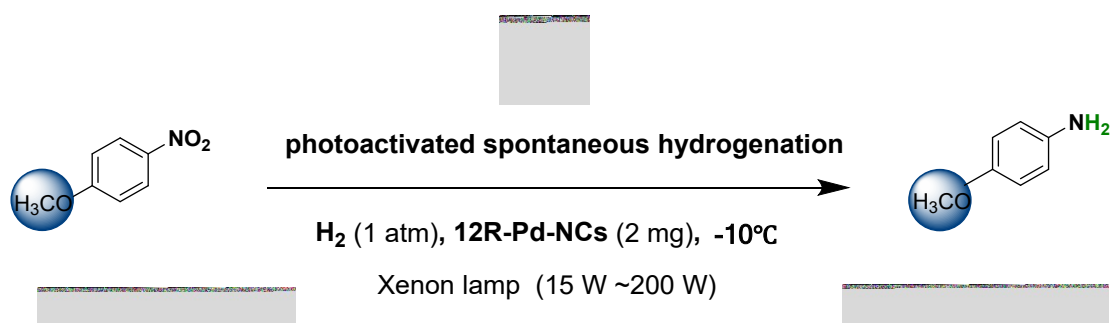


Table S6. Catalytic evaluation of 12R-Pd-NCs under different light intensities at -10 °C

Entry	Catalyst	Light	Time (h)	Yield (%)	Sel. (%)
1	12R-Pd-NCs	15 W	4	5.2%	>99
2	12R-Pd-NCs	60 W	4	4.1%	>99
3	12R-Pd-NCs	100 W	4	4.5%	>99
4	12R-Pd-NCs	200 W	4	4.4%	>99

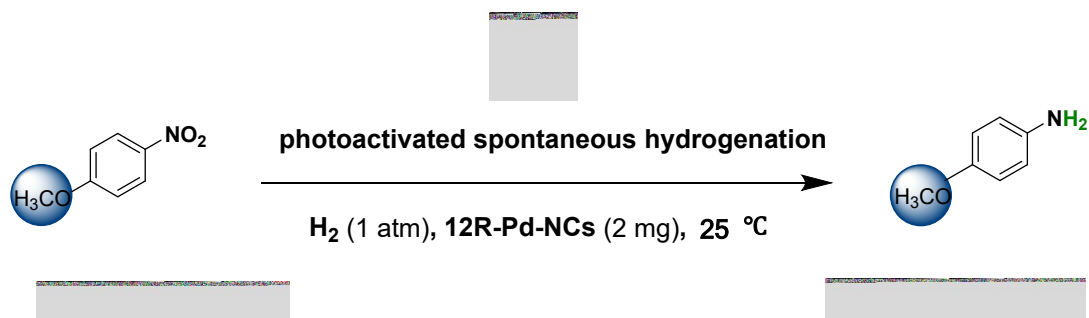


Table S7. Investigation of substrate/catalysts ratio.

Entry	Catalyst	Reactant (mmol)	Light	Time (h)	Yield (%)	Sel. (%)
1	12R-Pd-NCs	0.25	Sun	4	>99.9	>99.9
2	12R-Pd-NCs	0.50	Sun	4	>99.9	>99.9
3	12R-Pd-NCs	0.75	Sun	4	77.1	99
4	12R-Pd-NCs	1.00	Sun	4	47.2	97

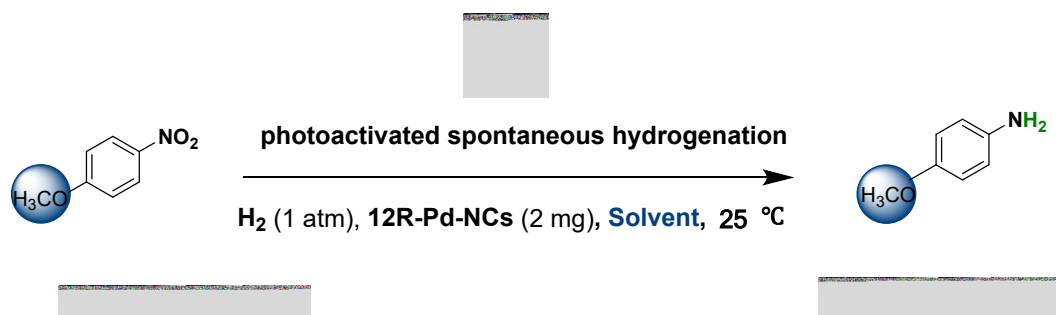


Table S8. Screening of different solvent for the photoactivated self-assembly.

Entry	Catalyst	Solvent	Light	Time (h)	Yield (%)	Sel. (%)
1	12R-Pd-NCs	MeOH	Sun	4	7.08	>99.9
2	12R-Pd-NCs	EtOH	Sun	4	0	/
3	12R-Pd-NCs	1,4-Dioxane	Sun	4	0	/
4	12R-Pd-NCs	THF	Sun	4	16.3	>99.9
5	12R-Pd-NCs	DMSO	Sun	4	0	/
6	12R-Pd-NCs	DMF	Sun	4	1.5	>99.9
7	12R-Pd-NCs	H ₂ O	Sun	4	8.7	89

10. Reaction rates of different palladium catalysts.

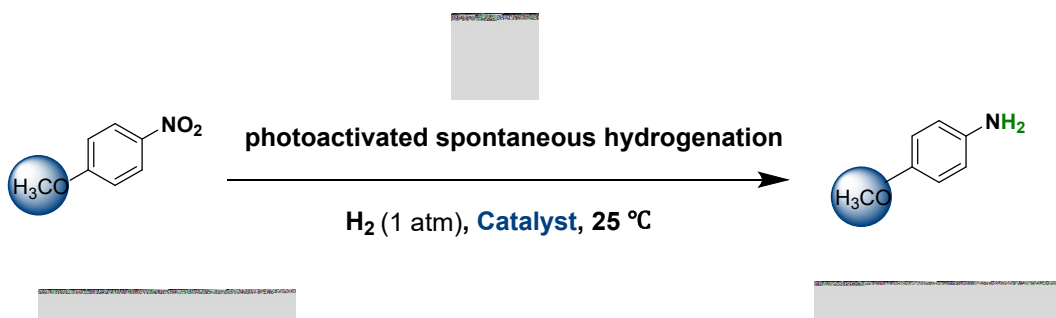


Table S9. 12R-Pd-NCs, Pd(OAc)₂ and Pd/C reaction rates.

Entry	Time (min)	12R-Pd-NCs (%)	Pd(OAc) ₂ (%)	Pd/C (%)
1	0.5	3.6	0	0
2	1	4.8	0	0
3	10	64.2	0	10.9
4	40	86.3	2.1	23.3
5	60	97.7	2.2	31.0
6	240	99.9	28.6	55.5

11. Controlled experiments.

In order to explore the experimental mechanism of catalyzing the hydrogenation of nitro toward amines reactions, we performed the single-factor controlled experiments in **Figure S4**: **(a)** 4-Nitroanisole (0.5 mmol, 76.5 mg) and 12R-Pd-NCs (2.0 mg) were each added to a 2 mL vial, add H₂ balloon (1 atm), the reaction was then illuminated for 4 hours under a 100 W tungsten filament at ambient temperature; **(b)** 4-Nitroanisole (0.5 mmol, 76.5 mg) and 12R-Pd-NCs (2.0 mg) were each added to a 2 mL vial, place in 45 °C ambient and add H₂ balloon (1 atm), the reaction was allowed to stay in dark environment react for 4h; **(c)** 4-Nitroanisole (0.5 mmol, 76.5 mg) and 12R-Pd-NCs (2.0 mg) were each added to a 2 mL vial, place in 0 °C ambient temperature and add H₂ balloon (1 atm), the reaction was then illuminate for 4 hours under a 100 W tungsten filament; **(d)** 4-Nitroanisole (0.5 mmol, 76.5 mg) and 12R-Pd-NCs (2.0 mg) were each added to a 2 mL vial, place in 0 °C ambient temperature and add H₂ balloon (1 atm), the reaction was allowed to stay in dark environment react for 4 h; **(e)** 4-Nitroanisole (0.5 mmol, 76.5 mg), 12R-Pd-NCs (2.0 mg) and 1mL H₂O were each added to a 2 mL vial, add H₂ balloon (1 atm), the reaction was then illuminate for 4 hours under a 100W tungsten filament at ambient temperature; **(f)** 4-Nitroanisole (0.5 mmol, 76.5 mg) and 12R-Pd-NCs (2.0 mg) were each added to a 2 mL vial, place in -78 °C environment and add H₂ balloon (1 atm), the reaction was then illuminated for 4 hours under a 100 W tungsten filament.

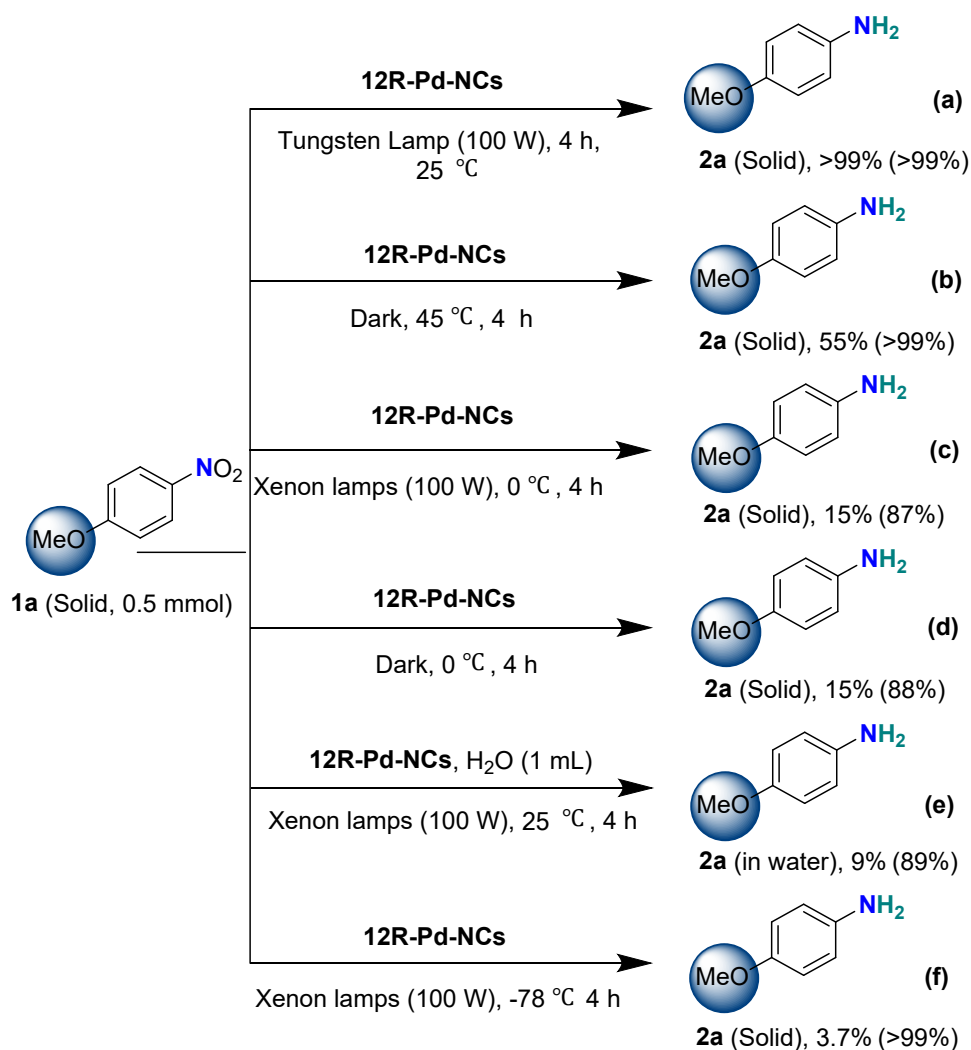


Figure S4. controlled experiments.

12. CO -TPD pulse chemisorption experiments.

The pulse chemisorption study of CO adsorption on the American Micromeritics Auto Chem II automatic chemical sorbent instrument. Place 40 mg of palladium material into a U tube, the PdO_x surface was first reduced at 300 °C for 1 h in 10% H₂/Ar atmosphere, then swept with helium and cooled to 40 °C. Pulse adsorption was performed with 10% CO/He until saturation. The surface areas of two active palladium, the catalyst active surface area (active per gram of the catalyst) and the metal. The active surface area (surface area of active palladium per gram of loaded metal) is calculated in equations a. and b. respectively.

$$A_{\text{metal}} = \frac{V_{\text{chem}} \frac{n}{V_m} N_A \sigma_m}{c} \leftarrow$$

$$c = \frac{mp}{100} \leftarrow$$

A_{metal} : Metal active surface area (corresponding to reduced palladium), m^2/g ; V_{chem} : The CO adsorption volume, cm^3 ; n : Stoichiometric coefficient, 2; V_m : Molar volume of gas under standard conditions, 22.414 L/mol ; N_A : The Avogadro constant, $6.02 \times 10^{23} \text{ mol}^{-1}$; σ_m : Cross-sectional area of the individual palladium species, nm^2 ; m : Catalyst quality, g; c : Mass of the metal palladium loaded on the catalyst, g; p : Palladium actual load, %.

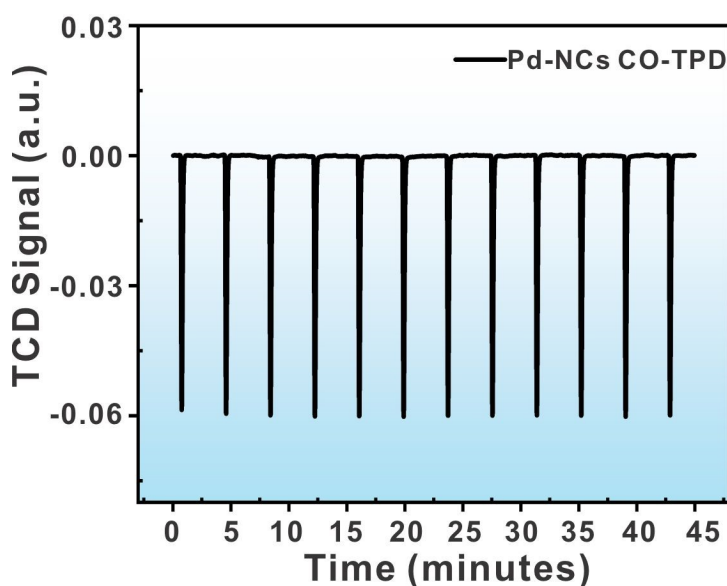


Figure S5. CO -TPD pulse chemisorption experimental data of 12R-Pd NCs.

Index	Pd/C CO -TPD	12R-Pd - NCs CO -TPD
Density (g/cm^3)	12.020	12.020
Atomic Cross-Sectional Area (nm^2)	0.0787	0.0787
Stoichiometry Factor	2.000	2.000
Active loop volume	0.03776 cm^3 STP (111.0 $^{\circ}\text{C}$)	0.03767 cm^3 STP (111.9 $^{\circ}\text{C}$)
Cumulative quantity	2.57734 cm^3/g STP	0.26220 cm^3/g STP
Metal dispersion	24.4694 %	0.3382 %
Metallic surface area (sample)	10.8995 m^2/g	1.1089 m^2/g
Metallic surface area (metal)	108.9952 m^2/g	1.5066 m^2/g
Active particle diameter (hemisphere)	4.5797 nm	331.3210 nm

13. H₂ -TPR pulse chemisorption experiments of 12R-Pd-NCs.

The H₂ chemisorption study of H₂ adsorption on the American Micromeritics Auto Chem II automatic chemical sorbent instrument. There are no peaks available for this experiment.

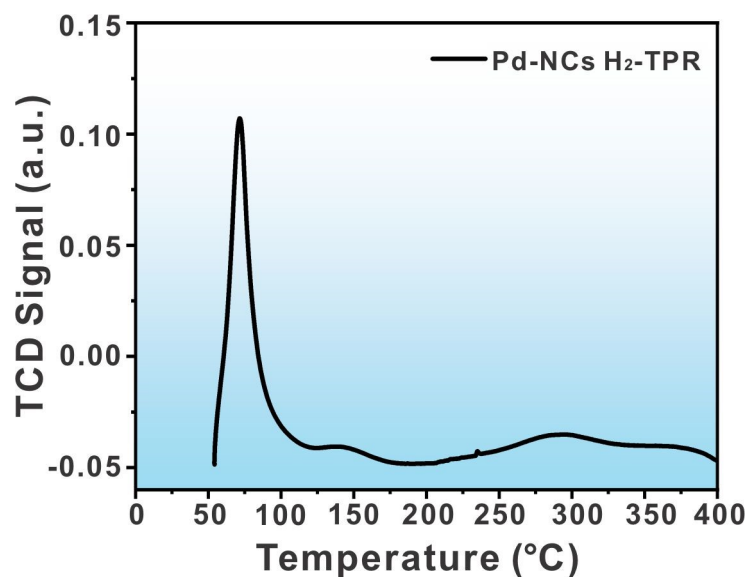


Figure S6. The H₂ -TPR pulse chemisorption of 12R-Pd-NCs.

14. X-ray photoelectron spectroscopy (XPS) of 12R-Pd-NCs.

The measurement of X-ray photoelectron spectroscopy was analyzed through Thermo ESCALAB 250 Xi. 14.

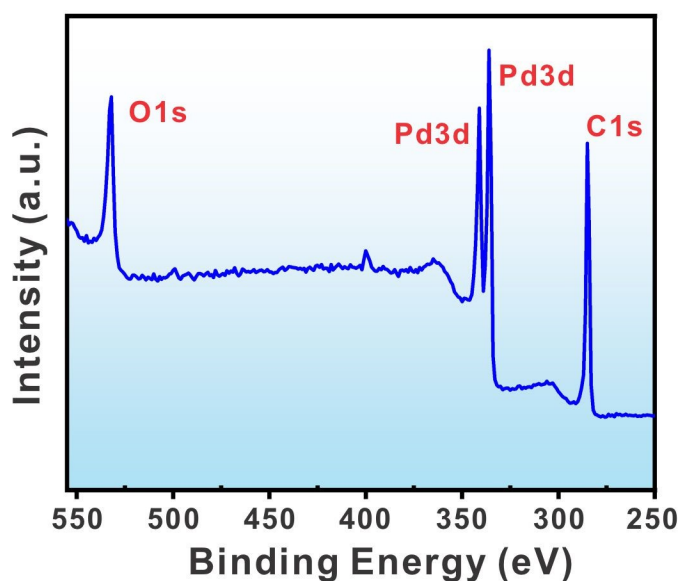


Figure S7. The XPS full-spectrum analysis of 12R-Pd-NCs.

15. Ultraviolet-visible spectroscopy (UV-Vis) of catalyst.

The 12R-Pd-NCs and $\text{Pd}(\text{OAc})_2$ were characterized.

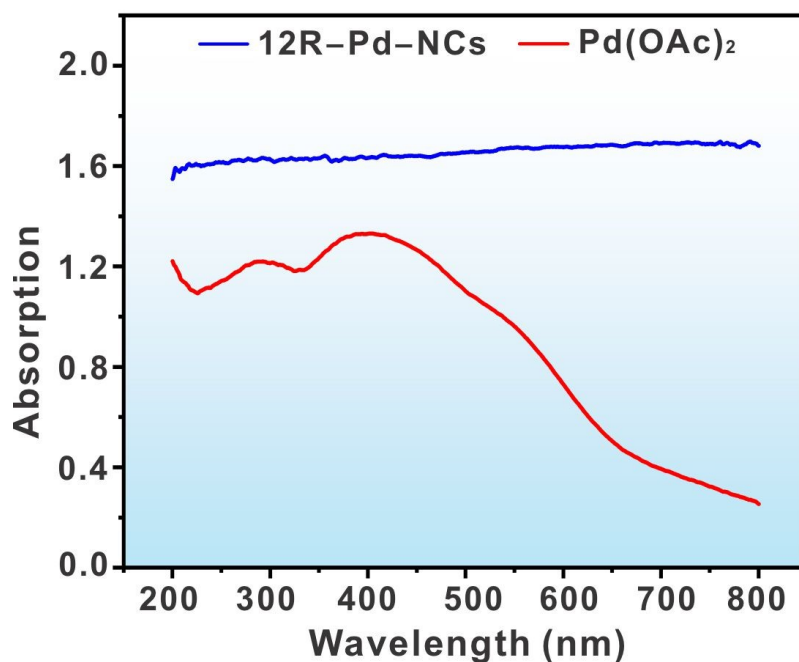


Figure S8. The UV-Vis spectrum analysis of catalyst.

16. Electron paramagnetic resonance (EPR) of 12R-Pd-NCs.

To substantiate our claim about defect structure of 12R-Pd-NCs enhances visible light absorption, the characterization of 12R-Pd-NCs was performed by EPR. The electron paramagnetic resonance (EPR) spectrum of 12R-Pd-NPs exhibits a prominent signal at $g = 2.003$ (Figure S8), characteristic of oxygen vacancy defects.¹ The defect energy levels introduced by oxygen vacancies can narrow the band gap of materials, reduce the energy required for electron transitions, thereby expanding the light absorption range to the visible light region and enhancing the absorption of visible light.²⁻³

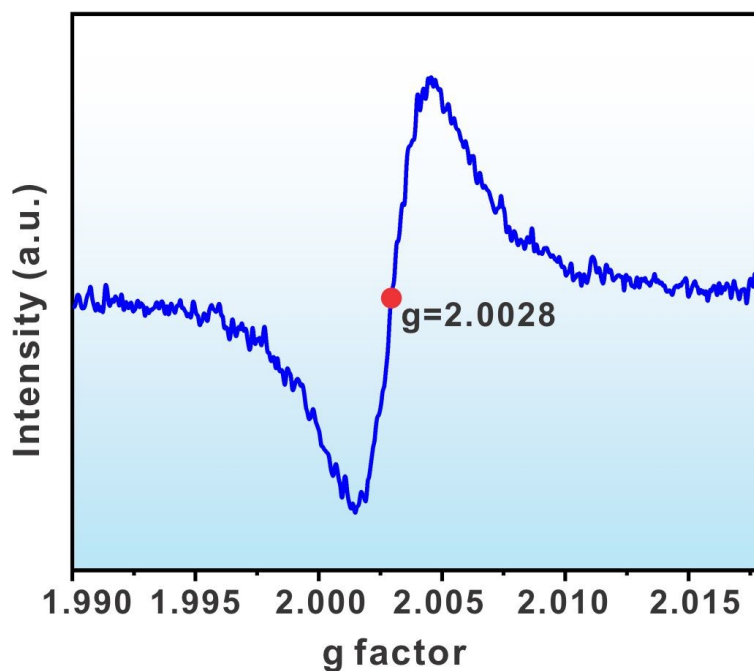


Figure S9. The EPR analysis of 12R-Pd-NCs.

Reference:

1. Zhang, N.; Li, X.; Ye, H.; Chen, S.; Ju, H.; Liu, D.; Lin, Y.; Ye, W.; Wang, C.; Xu, Q.; Zhu, J.; Song, L.; Jiang, J.; Xiong, Y. Oxide Defect Engineering Enables to Couple Solar Energy into Oxygen Activation. *J. Am. Chem. Soc.* **2016**, *138*(28), 8928-8935.
2. Lei, F.; Sun, Y.; Liu, K.; Gao, S.; Liang, L.; Pan, B.; Xie, Y. Oxygen vacancies confined in ultrathin indium oxide porous sheets for promoted visible-light water splitting. *J. Am. Chem. Soc.* **2014**, *136*(19), 6826-6829.
3. Long, R.; Rao, Z.; Mao, K.; Li, Y.; Zhang, C.; Liu, Q.; Wang,.; LI, Z-Y.; Wu, X.; Xiong, Y. Efficient Coupling of Solar Energy to Catalytic Hydrogenation by Using Well-Designed Palladium Nanostructures. *Angew. Chem. Int. Ed.* **2015**, *54*, 2425-2430;
4. Luo, L.; Fu, L.; Liu, H.; Xu, Y.; Xing, J.; Chang, C-R.; Yang, D-Y.; Tang, J. Synergy of Pd atoms and oxygen vacancies on In₂O₃ for methane conversion under visible light. *Nat Commun.* **2022**, *13*, 2930.

17. Identification of Minor Products.

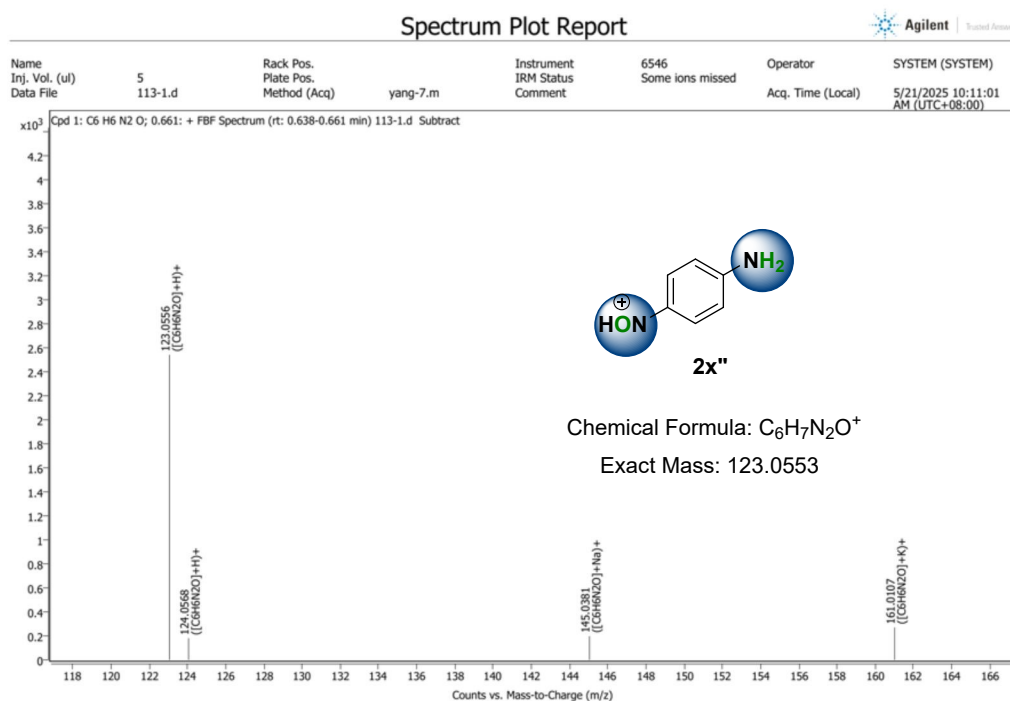
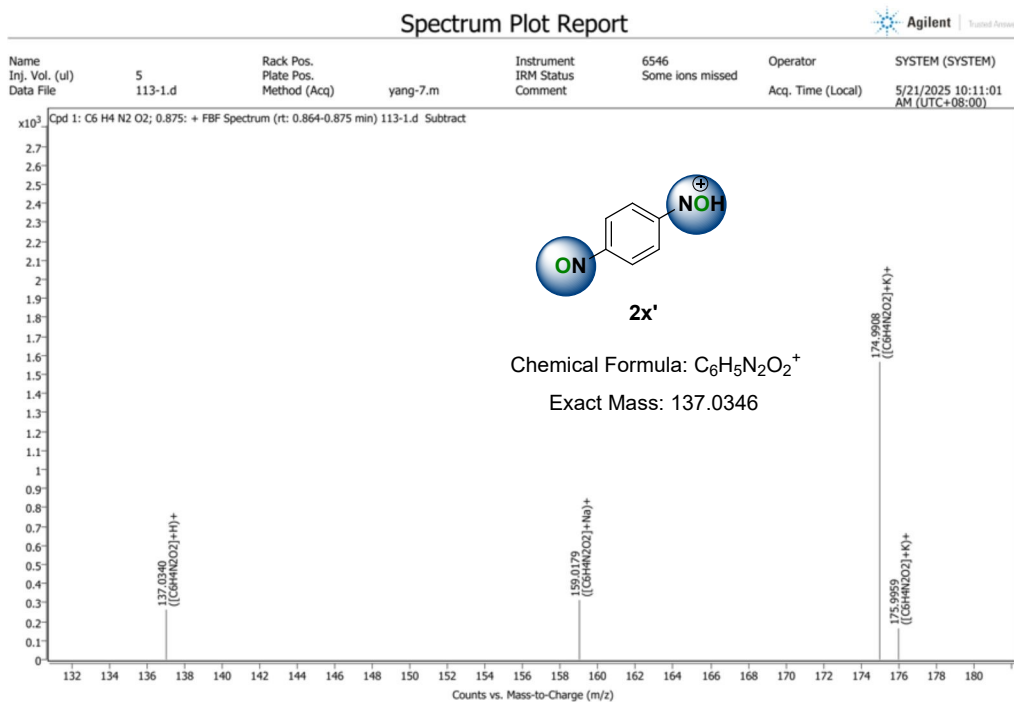
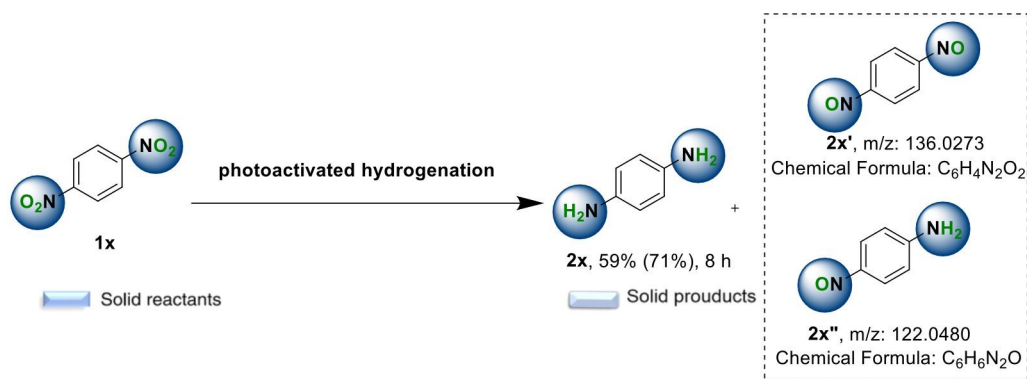


Figure S10. Identification of secondary products for product **2x**.

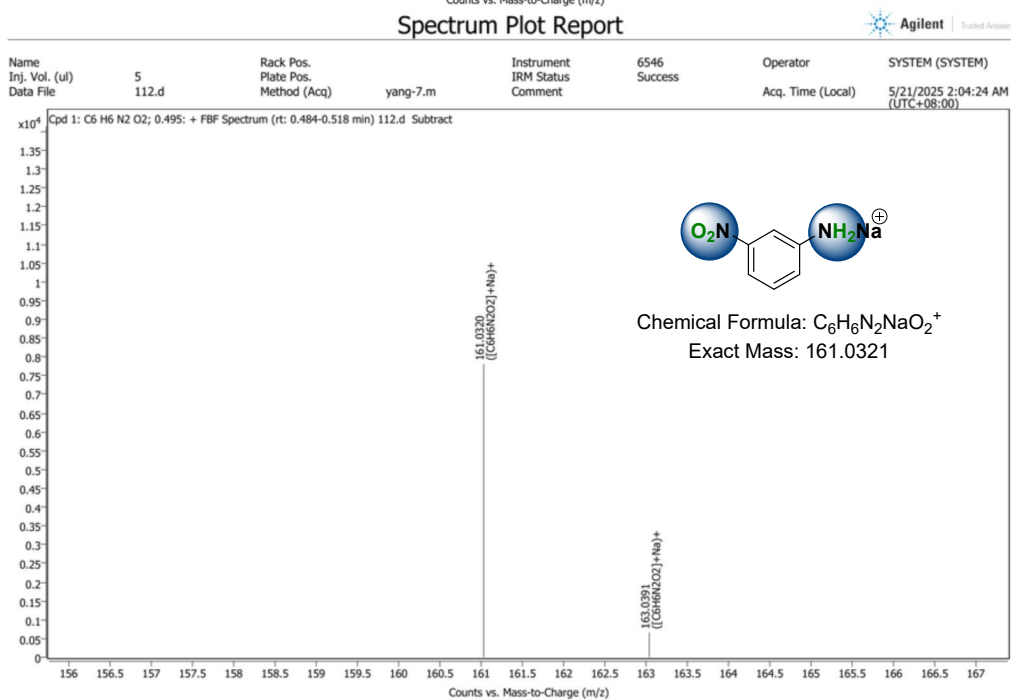
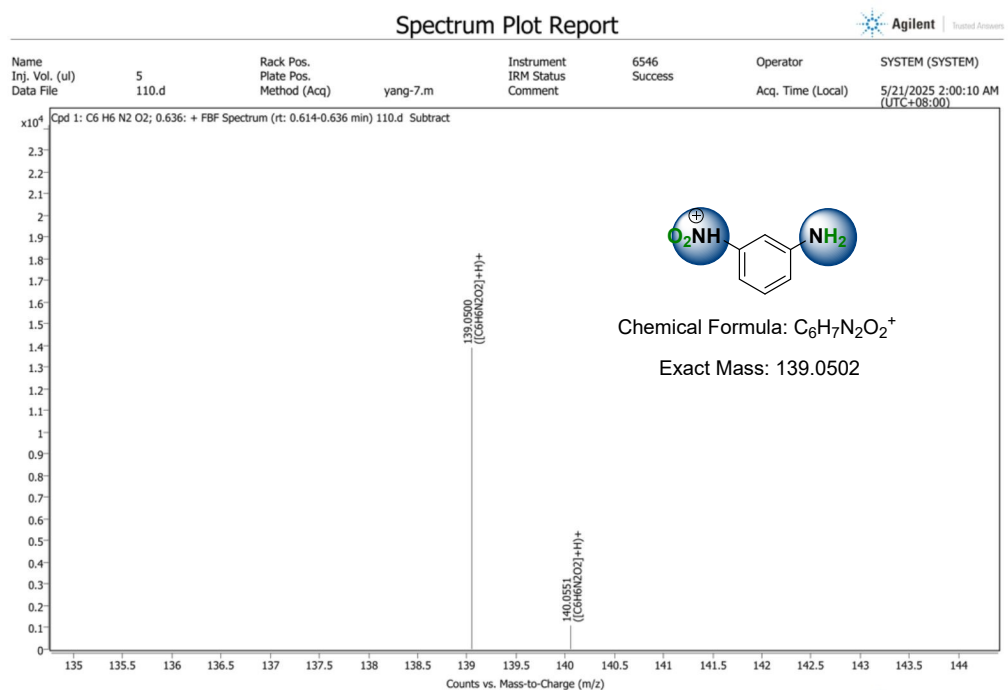
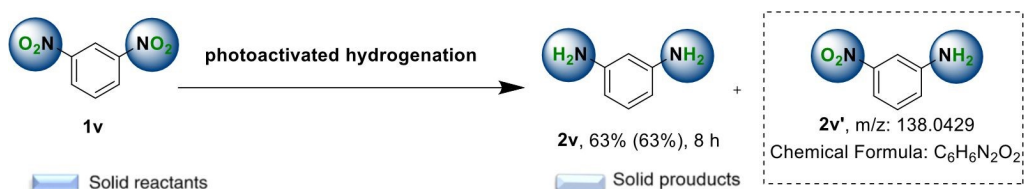


Figure S11. Identification of secondary products for product **2v**.

18. Cycle experiments.

Nitroanisole (0.5 mmol, 76.5 mg) and 12R-Pd-NCs (2.0 mg) were each added to a reaction bottle. To avoid introducing mechanical energy into the reaction system, simple shaking mixing of the products and catalysts as well as standing are carried out before the introduction of the necessary reactant hydrogen (H_2 , 1 atm). Repeat the above operation 5 times. We conducted HR-TEM and ICP analyses on the catalyst after five cycles, which revealed that aggregation and decomposition are likely the primary causes of catalyst deactivation.

The HR-TEM images of the recycled catalyst (5th cycle) clearly show significant agglomeration of Pd nanoparticles. TEM Analysis (**Figure S12**): Post-recycling HR-TEM images reveal significant agglomeration of Pd nanoparticles, with average particle size increasing from 3.2 ± 0.8 nm (fresh catalyst) to 6.7 ± 2.1 nm (after 5 cycles).

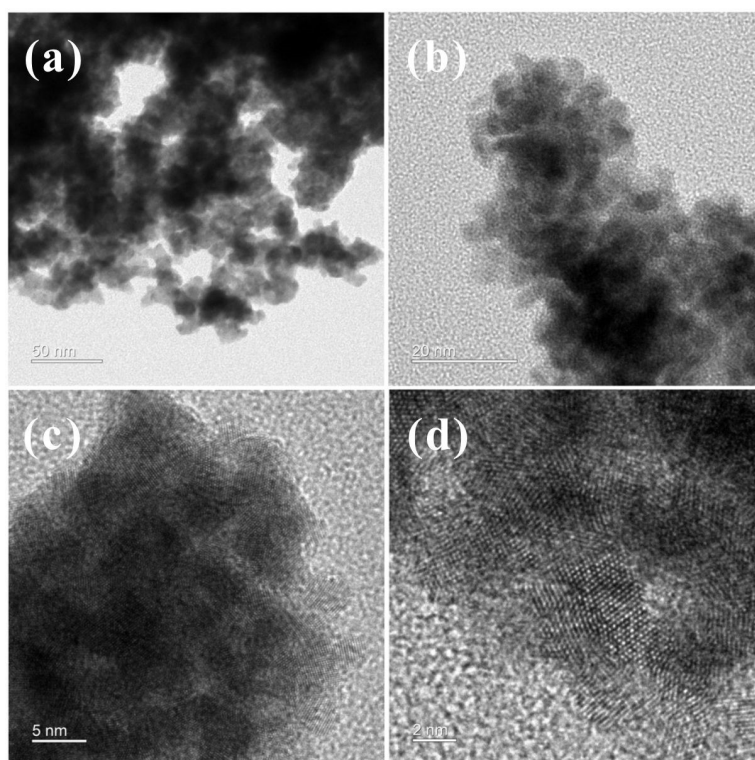


Figure S12. The HR-TEM of catalyst after five cycles.

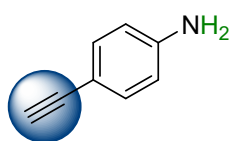
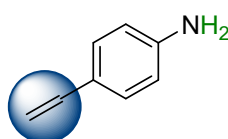
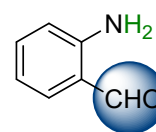
ICP results indicate a decrease in Pd content from 73.66 wt% (fresh catalyst) to 56.1 wt% (after 5 cycles), suggesting partial decomposition of the clusters. ICP-OES Quantification (**Table S10**), this corresponds to a metal loss of 76 wt% (calculated via mass-balance analysis).

Table S10. Determination of the palladium content in the 12R-Pd-NCs after five cycles.

Entry	Sample	Element	Sample WGT (g)	Fixed capacity vol. (mL)	^a Instrument result (mg/L)	^b Final result (wt%)
1 ^a	12R-Pd-NCs	Pd	0.0092	25	4.1280	56.0870%

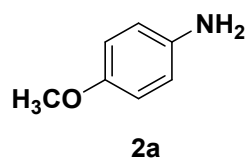
^a Diluted 50 times; ^b Final result = (Instrument result × Fixed capacity vol. × Dilution ratio)/Sample WGT; 10000 mg/kg=1 wt%.

19. Experiments of sensitive groups.

**3a**, 25% (61%)**3b**, 79% (95%)**3c**, trace

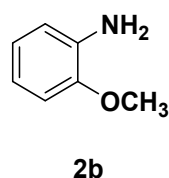
20. Characterizations of products.

4-Nitroanisol (2a) ¹



Light yellow solid, > 99% yield. ¹H NMR (500 MHz, CDCl₃) δ 6.76 (d, *J* = 10.0 Hz, 2H), 6.65 (d, *J* = 10.0 Hz, 2H), 3.75 (s, 3H), 3.44 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 153.04, 140.29, 116.70, 115.08, 56.02.

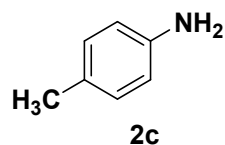
2-Nitroanisol (2b) ³



Light yellow liquid, 85% yield. ¹H NMR (500 MHz, CDCl₃) δ 6.86 – 6.81 (m, 2H), 6.79 – 6.74 (m, 2H), 3.87 (s, 3H), 3.76 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 147.61, 136.42, 121.36,

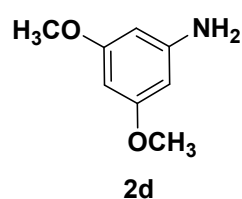
118.54, 115.33, 110.70, 55.70.

***p*-Toluidine (2c)**¹



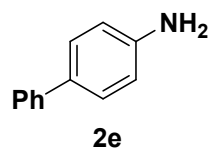
Colourless oil, > 99% yield. ¹H NMR (500 MHz, DMSO) δ 7.28 – 7.14 (m, 2H), 6.98 – 6.88 (m, 2H), 5.21 (s, 2H), 2.48 (s, 3H). ¹³C NMR (126 MHz, DMSO) δ 135.76, 120.67, 118.92, 107.19, 10.78.

3, 5-Dimethylaniline (2d)²



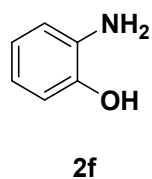
Colourless oil, 91% yield. ¹H NMR (500 MHz, CDCl₃) δ 6.46 (s, 1H), 6.36 (s, 2H), 3.56 (s, 2H), 2.26 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 146.19, 138.84, 120.29, 112.90, 21.16.

[1,1'-biphenyl]-4-Amine (2e)²



White solid, 79% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.60 (d, *J* = 5.0 Hz, 2H), 7.51 – 7.42 (m, 4H), 7.32 (t, *J* = 5.0 Hz, 1H), 6.80 – 6.77 (m, 2H), 3.74 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 146.19, 141.47, 131.83, 129.01, 128.33, 126.73, 126.60, 115.72.

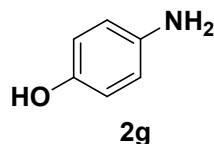
2-Aminophenol (2f)⁴



White needle-like crystals, 89% yield. ¹H NMR (500 MHz, MeOD) δ 6.75 – 6.73 (m, 1H), 6.71 –

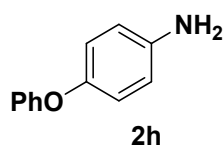
6.69 (m, 1H), 6.66 – 6.62 (m, 1H), 6.60 – 6.67 (m, 1H), 4.94 (s, 3H). ^{13}C NMR (126 MHz, MeOD) δ 146.54, 135.91, 121.02, 120.30, 117.55, 115.54.

4-Aminophenol (2g) ⁵



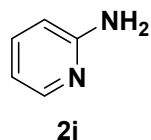
White solid, 92% yield. ^1H NMR (500 MHz, MeOD) δ 6.64 – 6.59 (m, 4H), 4.90 (s, 3H). ^{13}C NMR (126 MHz, MeOD) δ 151.26, 140.20, 118.53, 116.73.

Phenoxyaniline (2h) ⁶



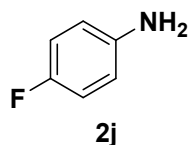
Brown solid, 89% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.30 – 7.23 (m, 2H), 7.00 (t, J = 5.0 Hz, 1H), 6.92 (d, J = 5.0 Hz, 2H), 6.88 – 6.82 (m, 2H), 6.70 – 6.60 (m, 2H), 3.51 (s, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 159.22, 148.81, 143.05, 129.63, 122.39, 121.23, 117.71, 116.29.

Pyridin-2-amine (2i) ⁷



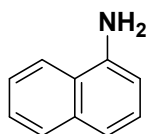
A yellow liquid, 91% yield. ^1H NMR (500 MHz, CDCl_3) δ 8.04 (d, J = 5.0 Hz, 1H), 7.95 (d, J = 5.0 Hz, 1H), 7.03 – 7.00 (m, 1H), 6.95 – 6.88 (m, 1H), 3.73 (s, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 143.01, 140.01, 137.64, 124.03, 121.72.

4-Fluoroaniline (2j) ¹



Colourless oil, 91% yield. ^1H NMR (500 MHz, CDCl_3) δ 6.95 – 6.82 (m, 2H), 6.65 – 6.56 (m, 2H), 3.56 (s, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 157.06, 155.19, 142.29, 115.45 (q, J = 16 Hz).

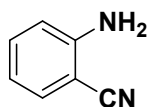
Naphthalen-1-amine (2k) ²



2k

White solid, 43% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.79 – 7.76 (m, 2H), 7.53 – 7.38 (m, 2H), 7.30 – 7.26 (m, 2H), 6.73 (d, J = 10 Hz, 1H), 4.08 (s, 2H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 141.91, 134.21, 128.39, 126.19, 125.69, 124.69, 123.47, 120.64, 118.79, 109.51.

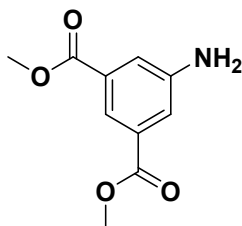
2-Aminobenzonitrile (2l) ⁸



2l

Pale yellow crystals, 51% yield. $^1\text{H NMR}$ (500 MHz, MeOD) δ 7.34 – 7.28 (m, 2H), 6.81 (d, J = 10.0 Hz, 1H), 6.71 – 6.60 (m, 1H), 4.87 (s, 2H). $^{13}\text{C NMR}$ (126 MHz, MeOD) δ 153.19, 135.58, 133.81, 119.39, 118.31, 116.84, 96.26.

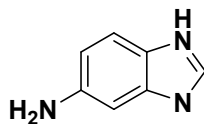
Dimethyl 5-aminoisophthalate (2m) ⁹



2m

Light yellow solid, 50% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.04 (s, 1H), 7.51 (d, J = 5.0 Hz, 2H), 3.86 (s, 8H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 166.65, 146.87, 131.55, 120.72, 119.87, 52.43.

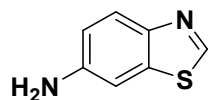
5-Aminobenzimidazole (2n) ¹⁰



2n

Brown oily liquid, 87% yield. $^1\text{H NMR}$ (500 MHz, D_2O) δ 7.53, (s, 1H), 6.89 – 6.86 (m, 1H), 6.39 (s, 1H), 6.34 – 6.21, (m, 1H). $^{13}\text{C NMR}$ (126 MHz, D_2O) δ 141.71, 140.10, 135.55, 130.99, 115.55, 113.66, 99.75.

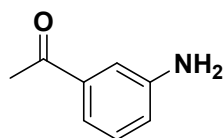
Benzo[b]thiophene-6-amine (2o) ⁷



2o

An orange solid, 49% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.67 (s, 1H), 7.86 (d, $J = 10.0$ Hz, 1H), 7.11 (s, 1H), 6.83 (d, $J = 10.0$ Hz, 1H), 3.87 (s, 2H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 149.83, 146.68, 144.93, 135.50, 123.89, 115.99, 105.63.

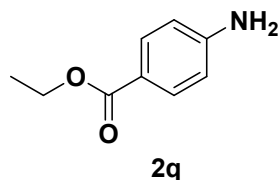
1-(3-aminophenyl) ethan-1-one (2p)¹¹



2p

White solid, 88% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.35 – 7.23 (m, 3H), 6.90 – 6.87 (m, 1H), 3.71 (s, 2H), 2.57 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 198.32, 146.50, 137.89, 129.06, 119.42, 118.55, 113.73, 26.46.

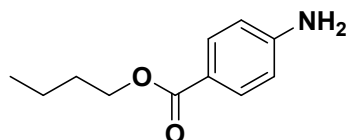
Ethyl 4-aminobenzoate (2q)¹²



2q

White solid, 90% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.84 – 7.82 (m, 2H), 6.78 – 6.41 (m, 2H), 4.32 – 4.26 (m, 2H), 4.22 (s, 1H), 1.33 (t, $J = 8.0$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 167.16, 151.44, 131.79, 119.85, 113.98, 60.61, 14.68.

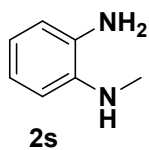
Butyl 4-aminobenzoate (2r)¹



2r

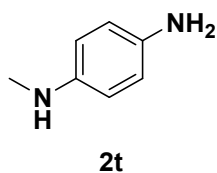
White solid, 80% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.86 – 7.84 (m, 2H), 6.64 – 6.62 (m, 2H), 4.26 (t, $J = 10.0$ Hz, 2H), 4.03 (s, 1H), 1.74 – 1.68 (m, 2H), 1.49 – 1.42 (m, 2H), 0.96 (t, $J = 10.0$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 167.16, 151.11, 132.10, 120.34, 114.13, 64.57, 31.21, 19.78, 19.65.

N¹-Methylbenzene-1,2-diamine (2s) ¹³



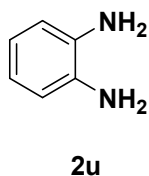
Brown liquid, 99% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.00 – 6.98 (m, 1H), 6.84 – 6.76 (m, 3H), 3.45 (s, 3H), 2.92 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 138.54, 133.78, 120.35, 118.03, 115.86, 110.53, 30.57.

N¹-Methylbenzene-1,4-diamine (2t) ¹⁴



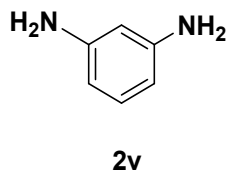
A dark gray solid, 88% yield. ¹H NMR (500 MHz, CDCl₃) δ 6.63 (d, *J* = 10.0 Hz, 2H), 6.53 (d, *J* = 10.0 Hz, 2H), 3.35 (s, 3H), 2.78 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 142.56, 137.68, 116.84, 114.01, 31.73.

Benzene-1, 2-diamine (2u) ¹⁵



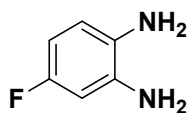
White solid, 75% yield. ¹H NMR (500 MHz, CDCl₃) δ 6.76 – 6.70 (m, 4H), 3.41(s, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 134.53, 120.03, 116.51.

Benzene-1, 3-diamine (2v) ¹⁵



A yellow solid, 63% yield. ¹H NMR (500 MHz, CDCl₃) δ 6.97 – 6.93 (m, 1H), 6.13 (d, *J* = 5.0 Hz, 2H), 6.00 (s, 1H), 3.59 (s, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 147.32, 129.91, 105.65, 101.72.

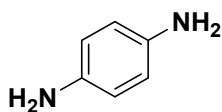
4-Fluorobenzene-1, 2-diamine (2w) ¹



2w

A yellow solid, 52% yield. $^1\text{H NMR}$ (500 MHz, DMSO) δ 6.44 – 6.41 (m, 1H), 6.31 – 6.29 (m, 1H), 6.14 – 6.10 (m, 1H), 4.76 (s, 2H), 4.28 (s, 2H). $^{13}\text{C NMR}$ (126 MHz, DMSO) δ 156.19, 154.37, 136.44, 130.54, 114.07, 100.47 (q, J = 58 Hz).

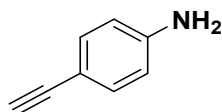
Benzene-1, 4-diamine (2x) ¹⁵



2x

A yellow solid, 59% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.57 (s, 4H), 3.33 (s, 4H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 138.94, 117.07.

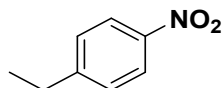
4-Ethynylaniline (3a) ⁶



3a

Yellow powder, 25% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.30 (d, J = 8.7 Hz, 2H), 6.59 (d, J = 8.5 Hz, 2H), 3.82 (s, 2H), 2.96 (s, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 147.39, 133.84, 114.96, 111.66, 84.76, 75.29.

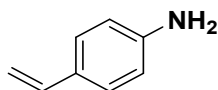
4-Ethynylaniline (3a') ¹⁶



3a'

Yellow powder, 16% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.14 (d, J = 8.9 Hz, 2H), 7.34 (d, J = 8.7 Hz, 2H), 2.76 (q, J = 7.6 Hz, 2H), 1.28 (t, J = 7.6 Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 152.45, 146.61, 129.06, 124.05, 29.27, 15.49.

4-Ethynylaniline (3b) ¹⁷



3b

Yellow powder, 79% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.32 (d, *J* = 8.4 Hz, 2H), 6.72 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 2H), 5.66 (d, *J* = 17.5 Hz, 1H), 5.15 (d, *J* = 11.0 Hz, 1H), 3.74 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 146.24, 136.51, 128.08, 127.28, 114.93, 109.90.

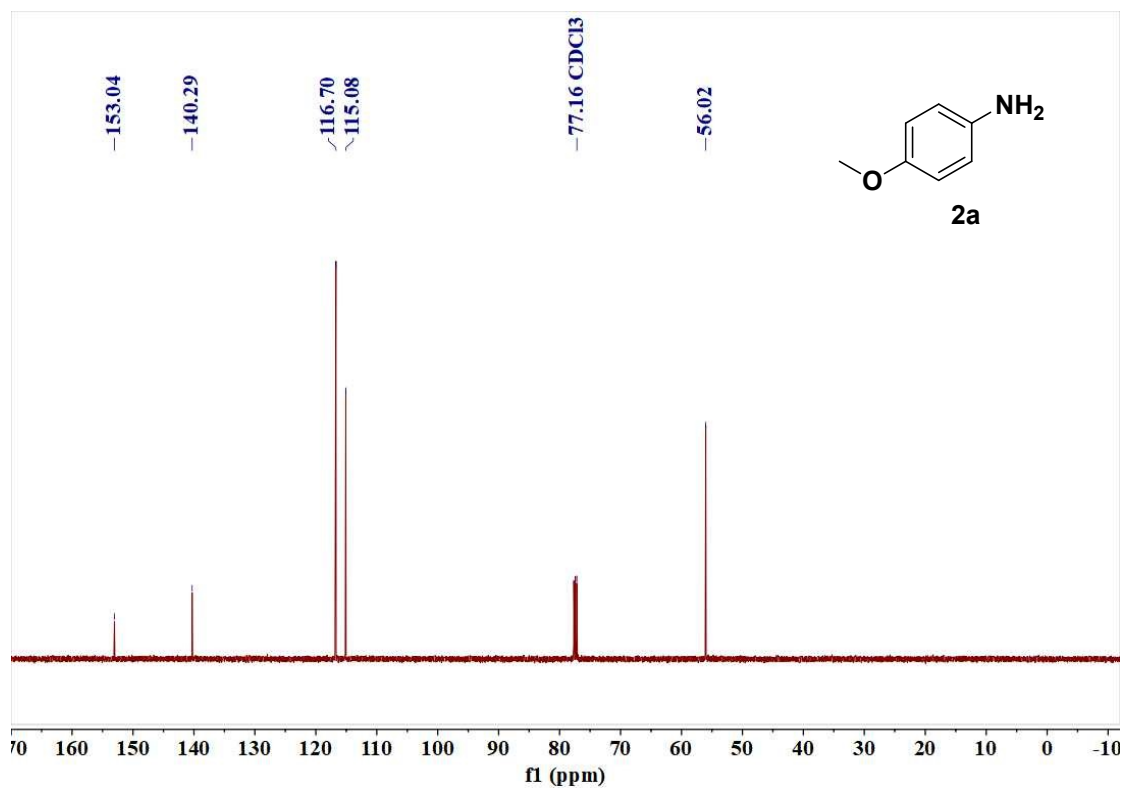
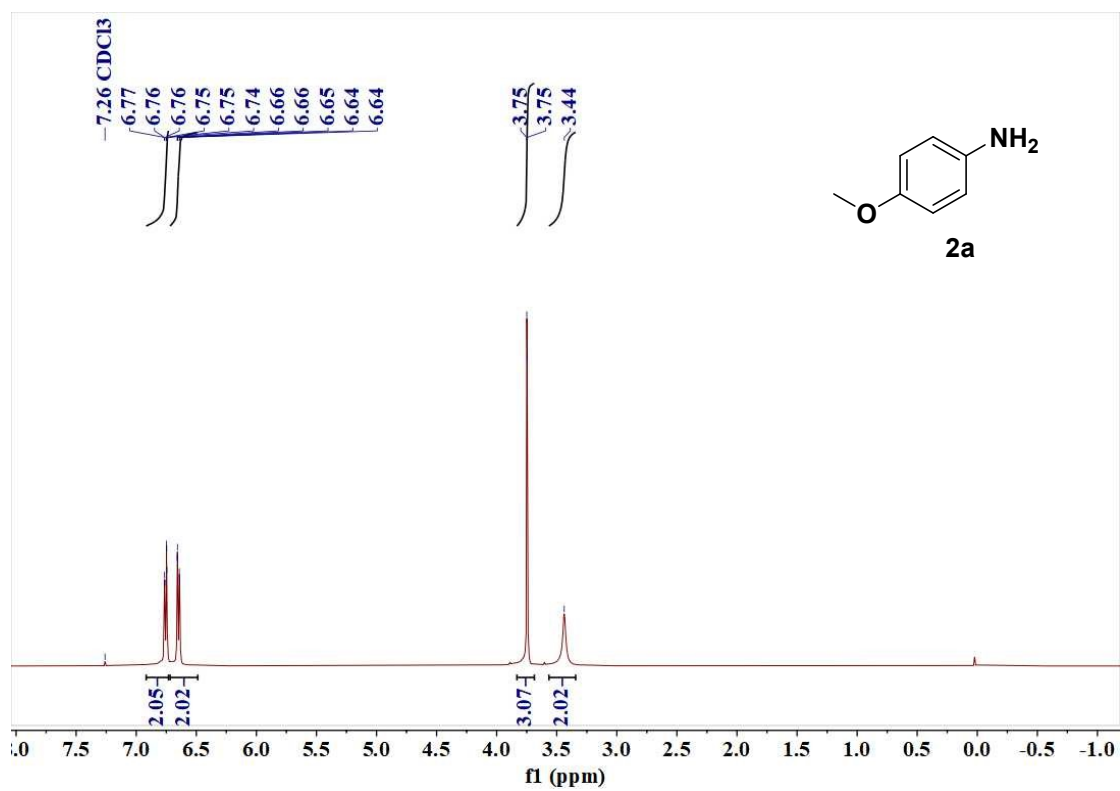
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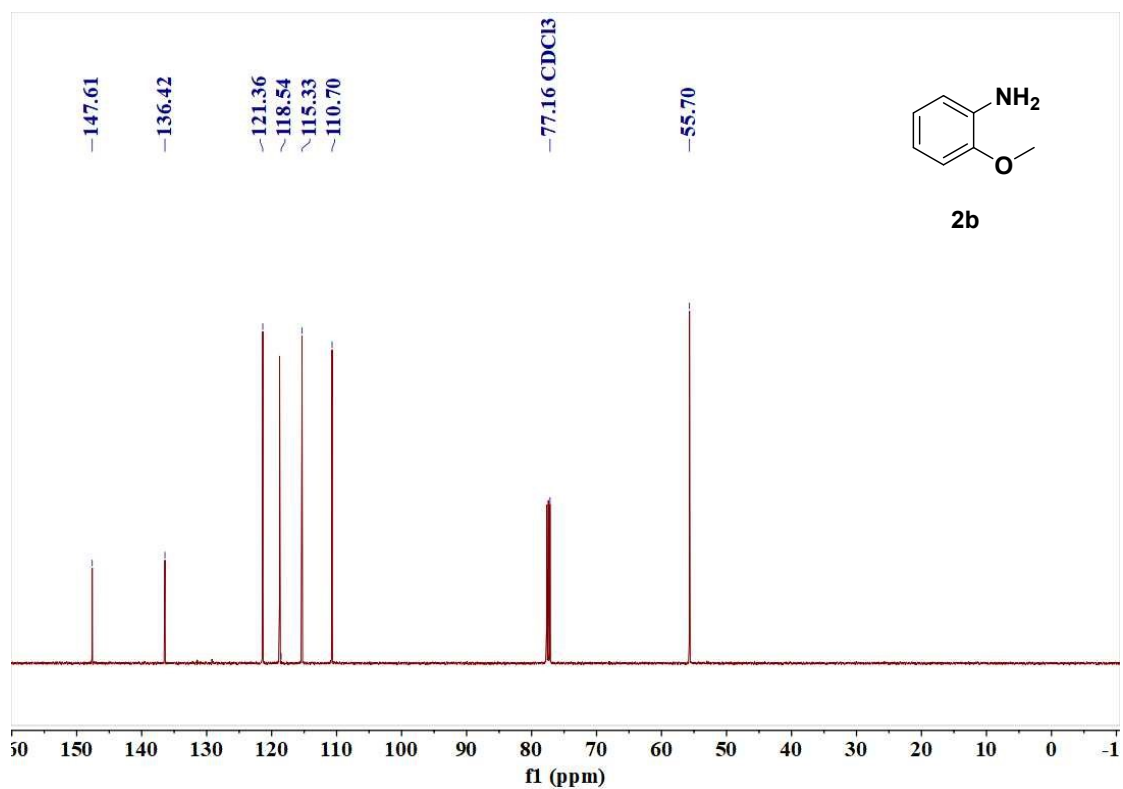
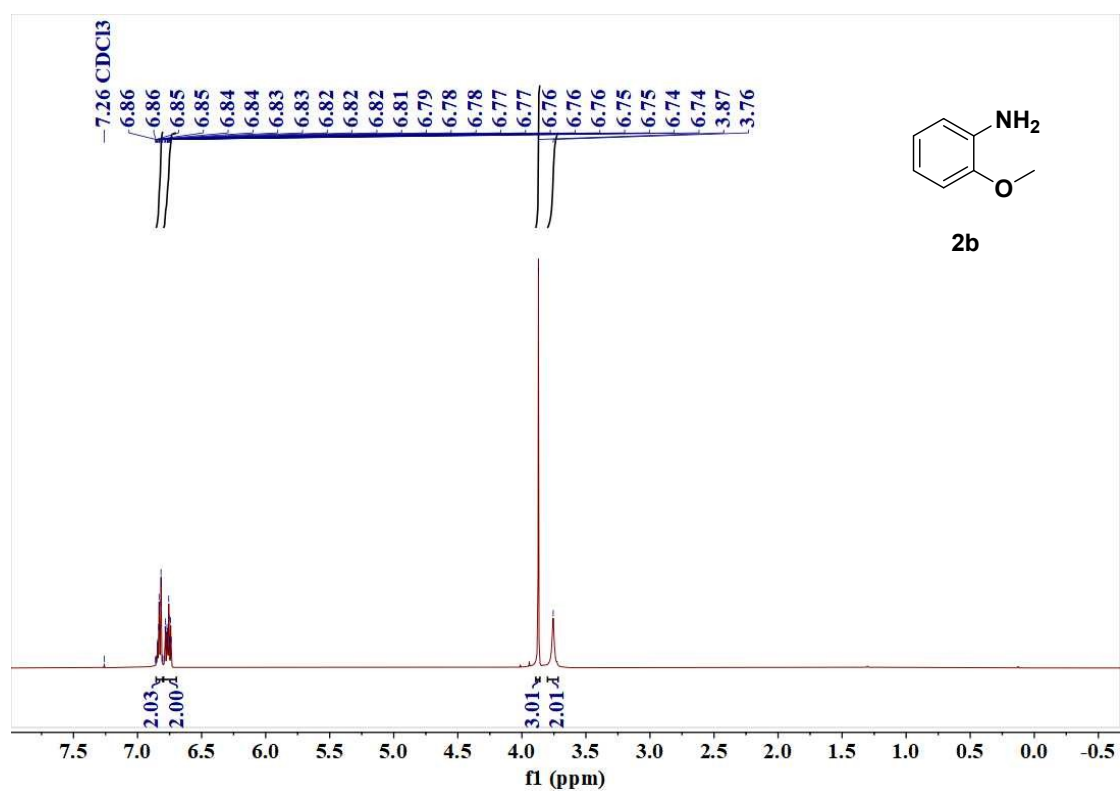
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21. ^1H -NMR and ^{13}C -NMR spectra.

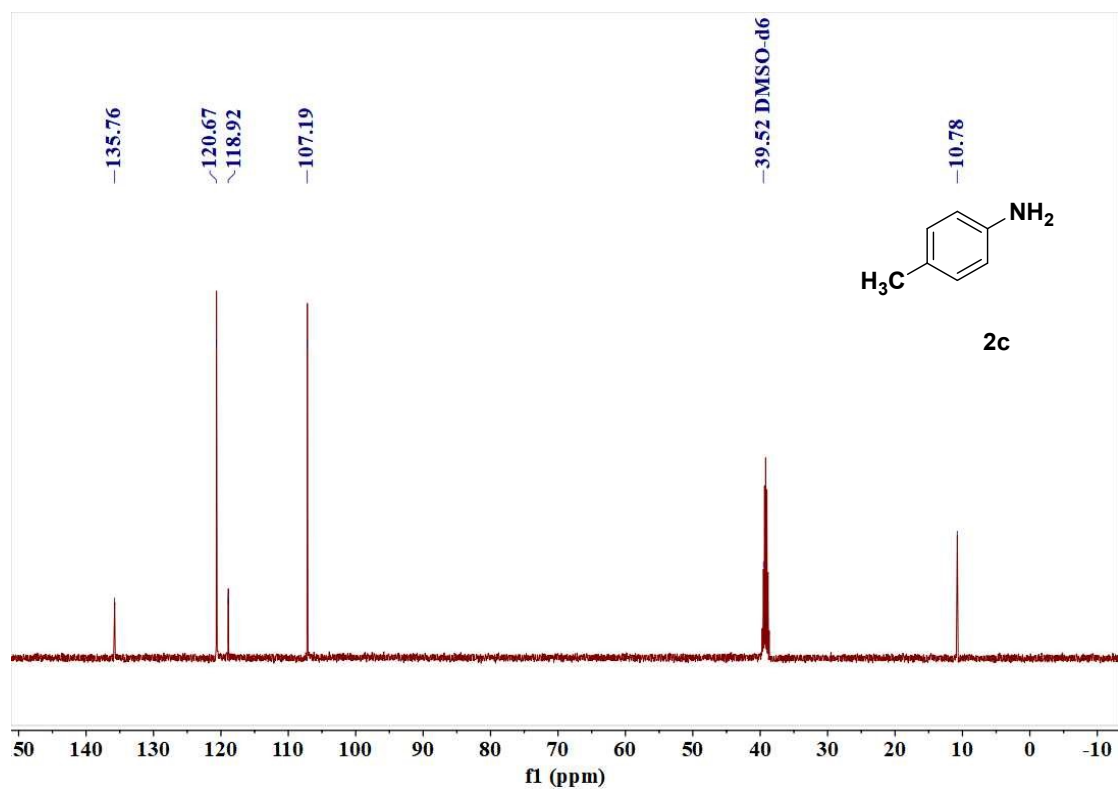
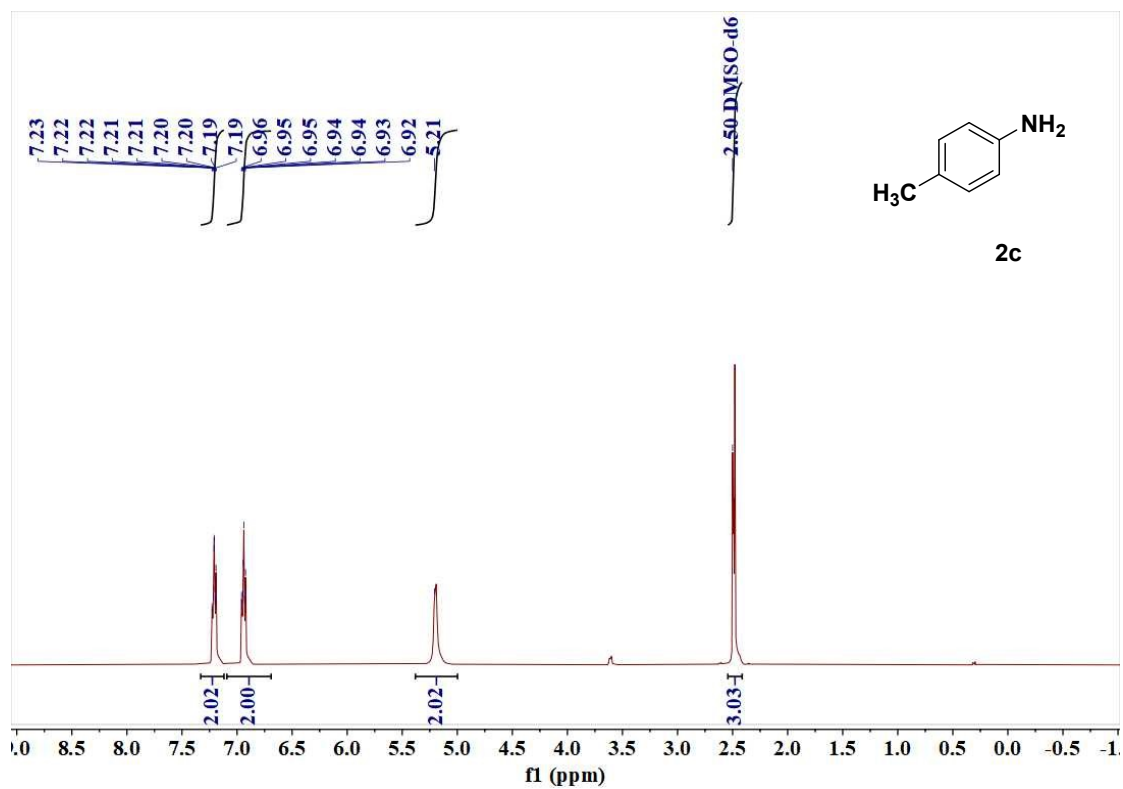
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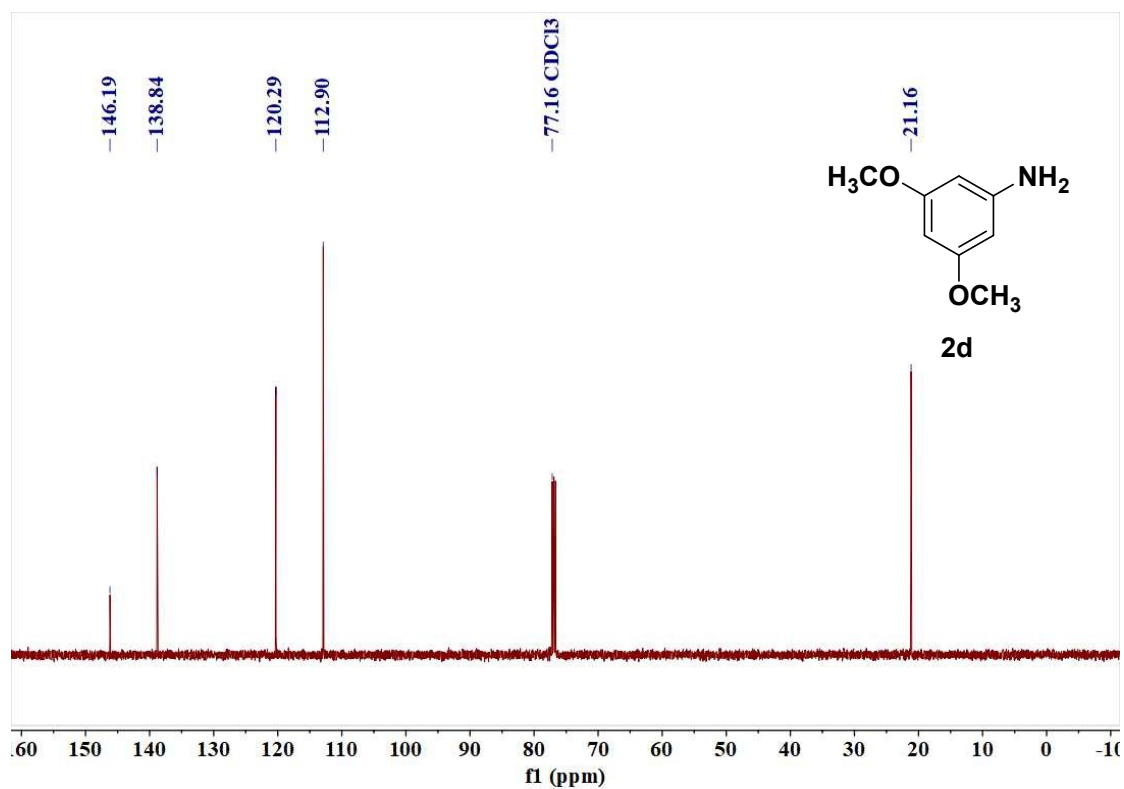
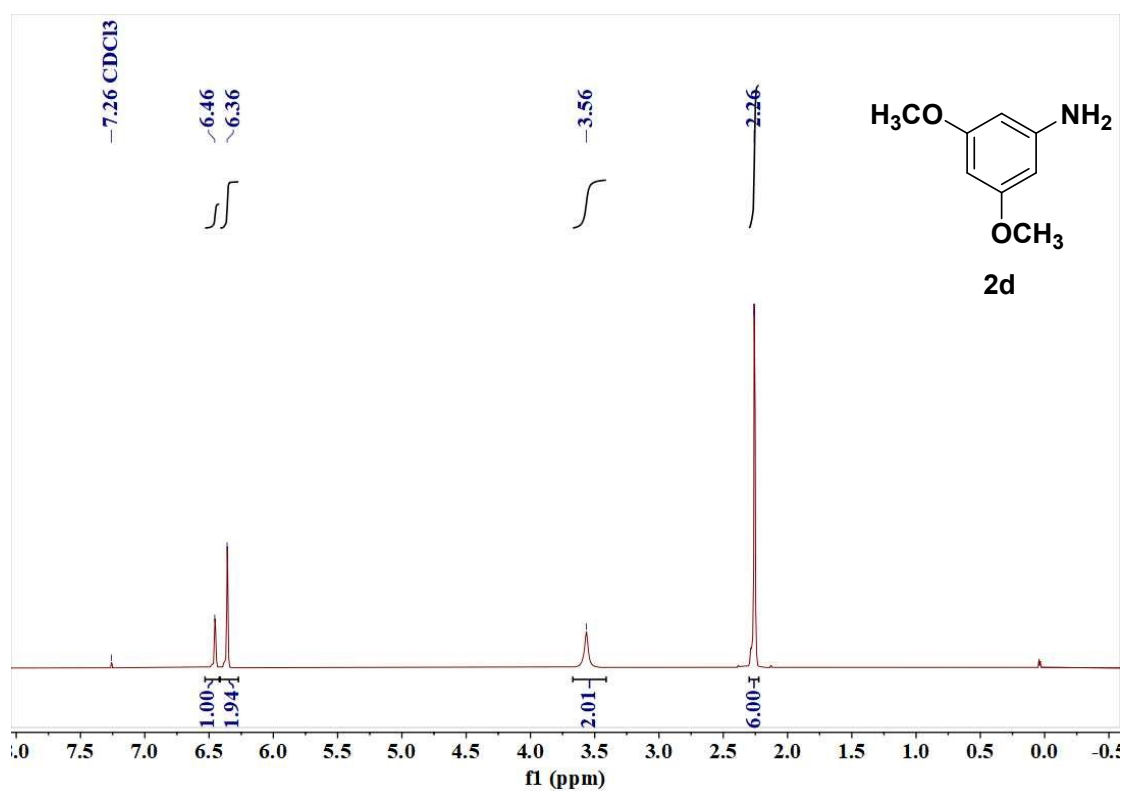
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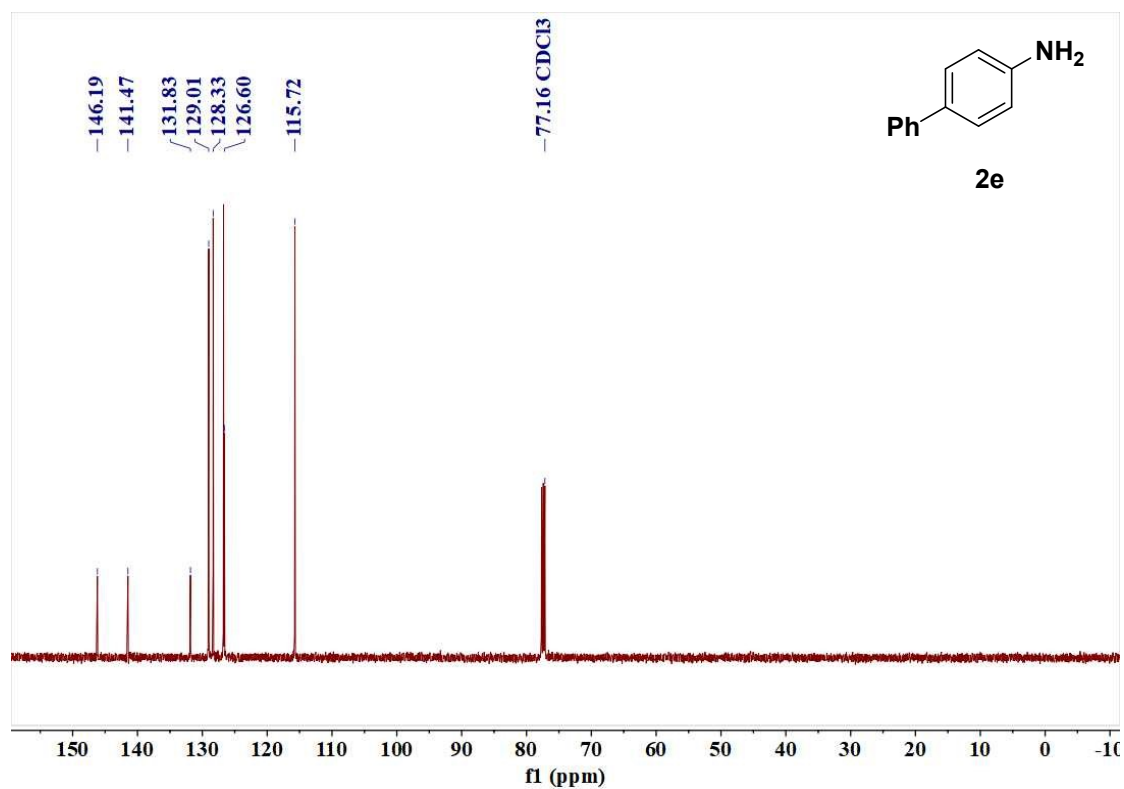
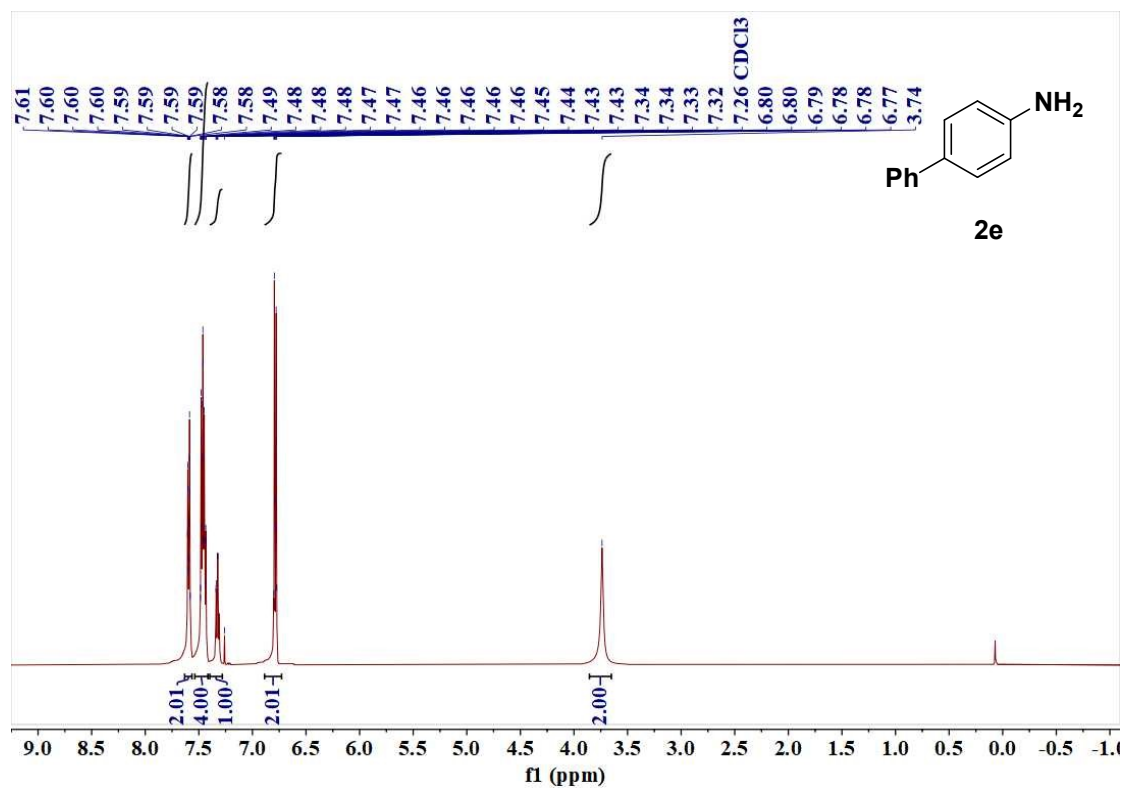
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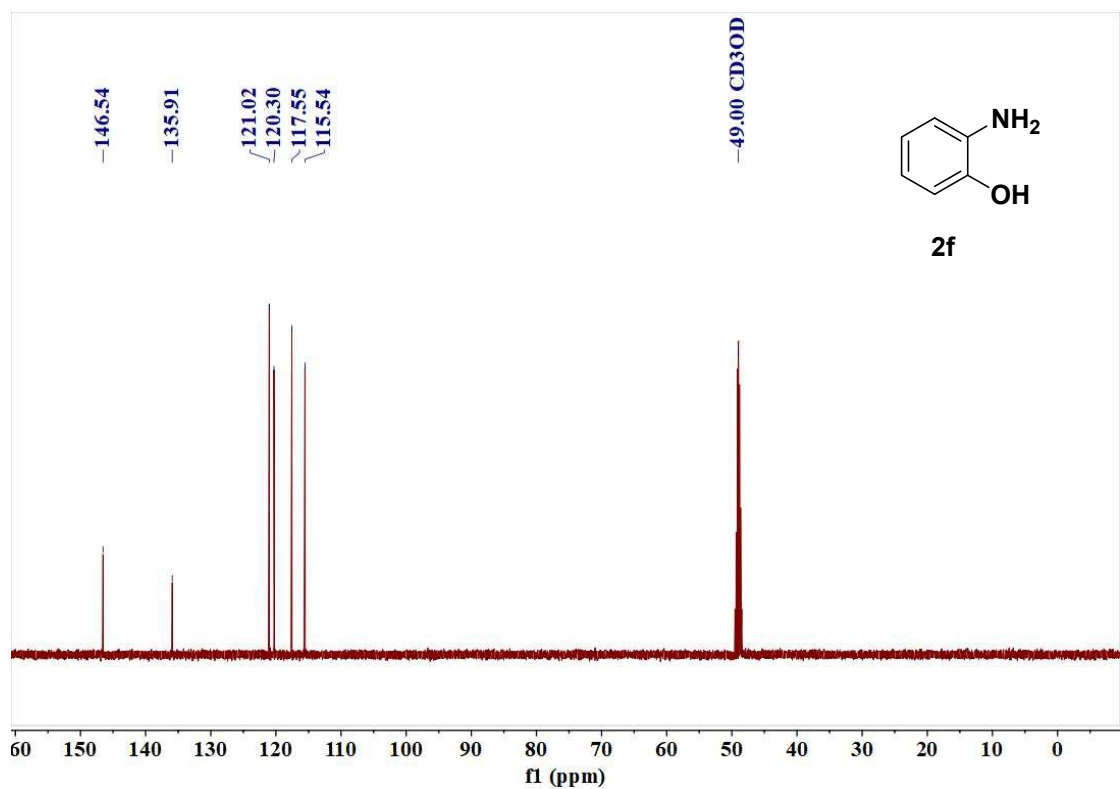
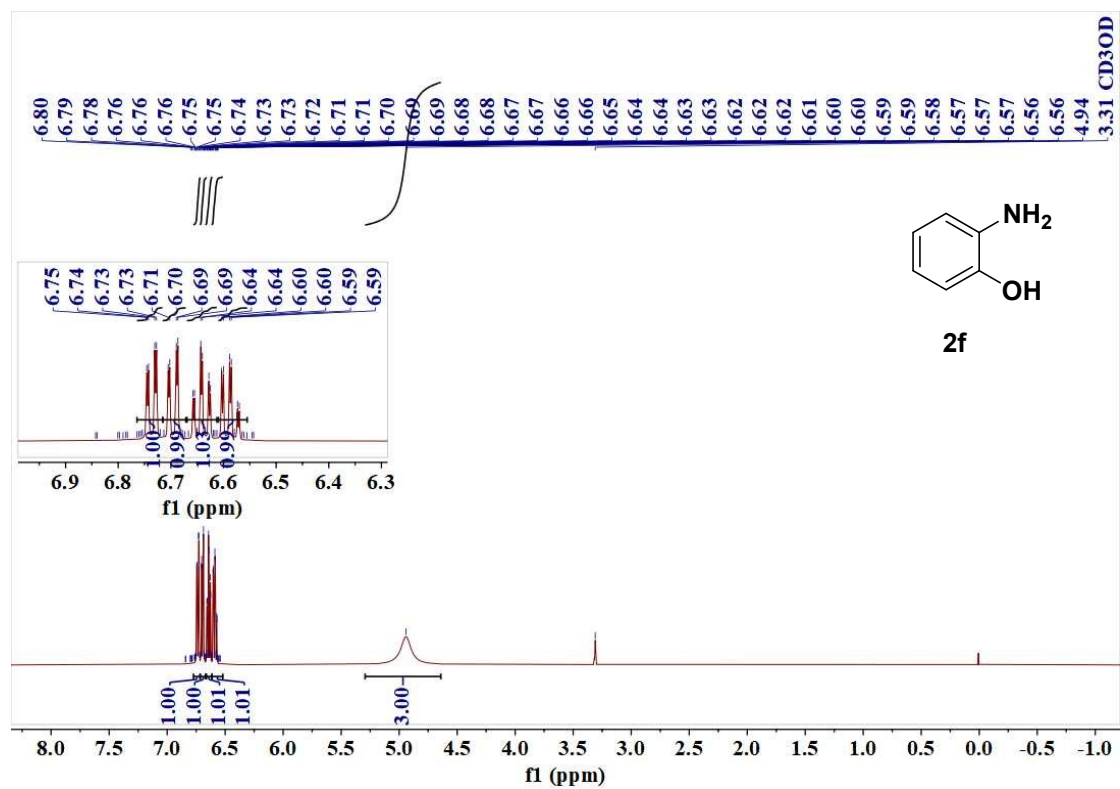
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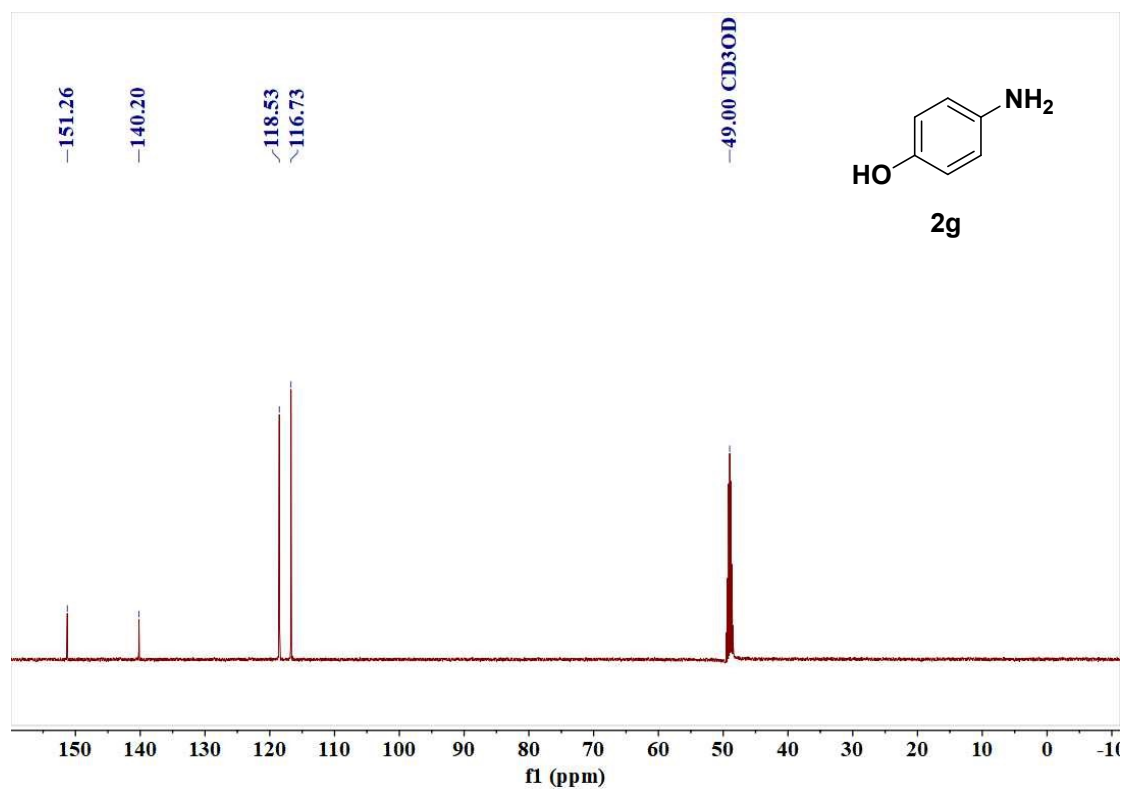
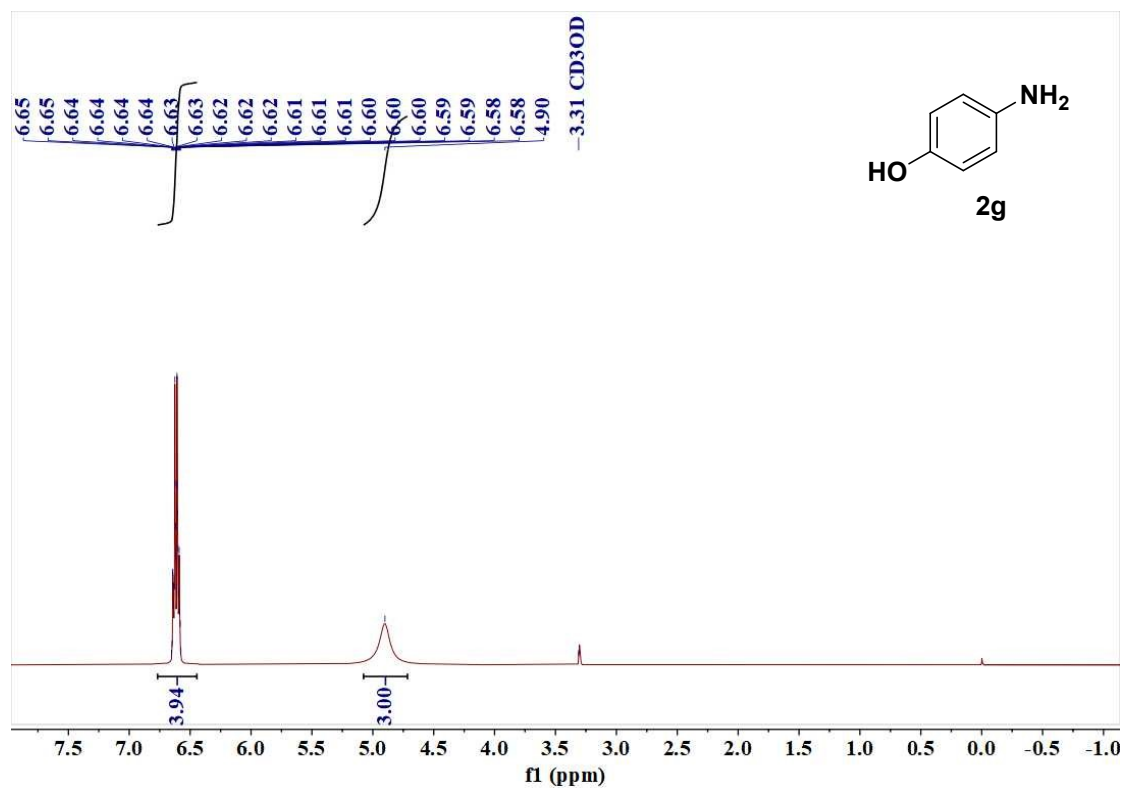
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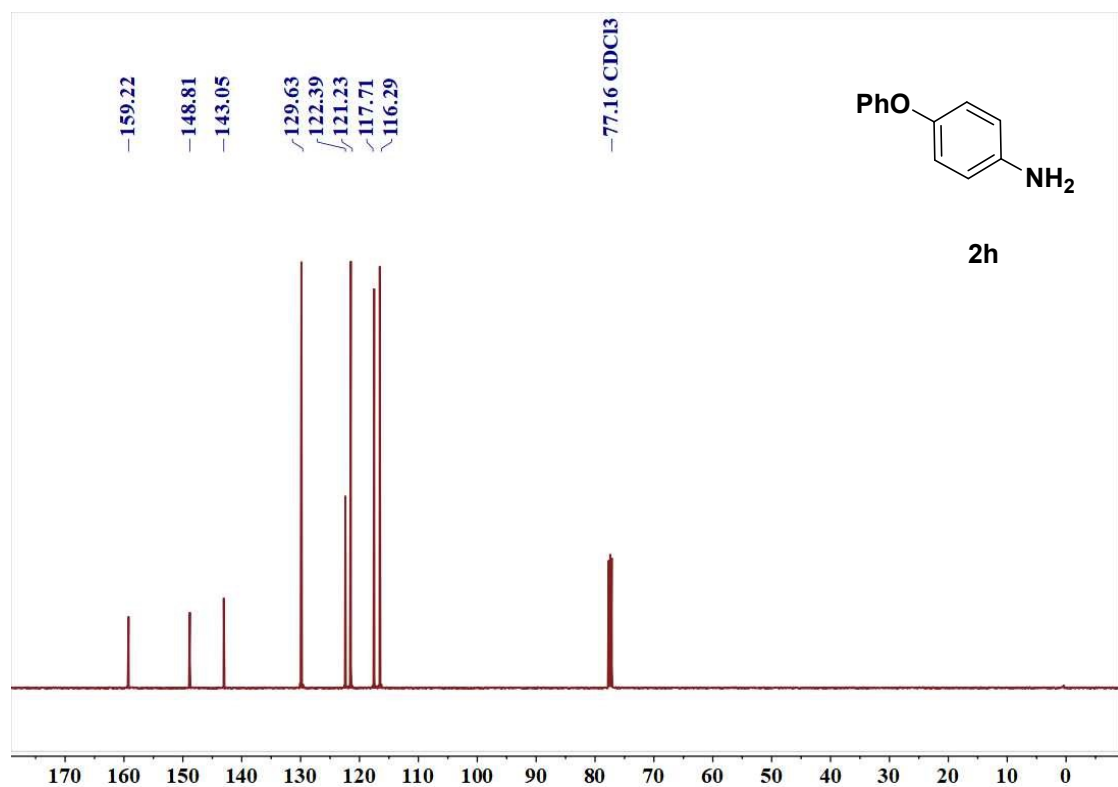
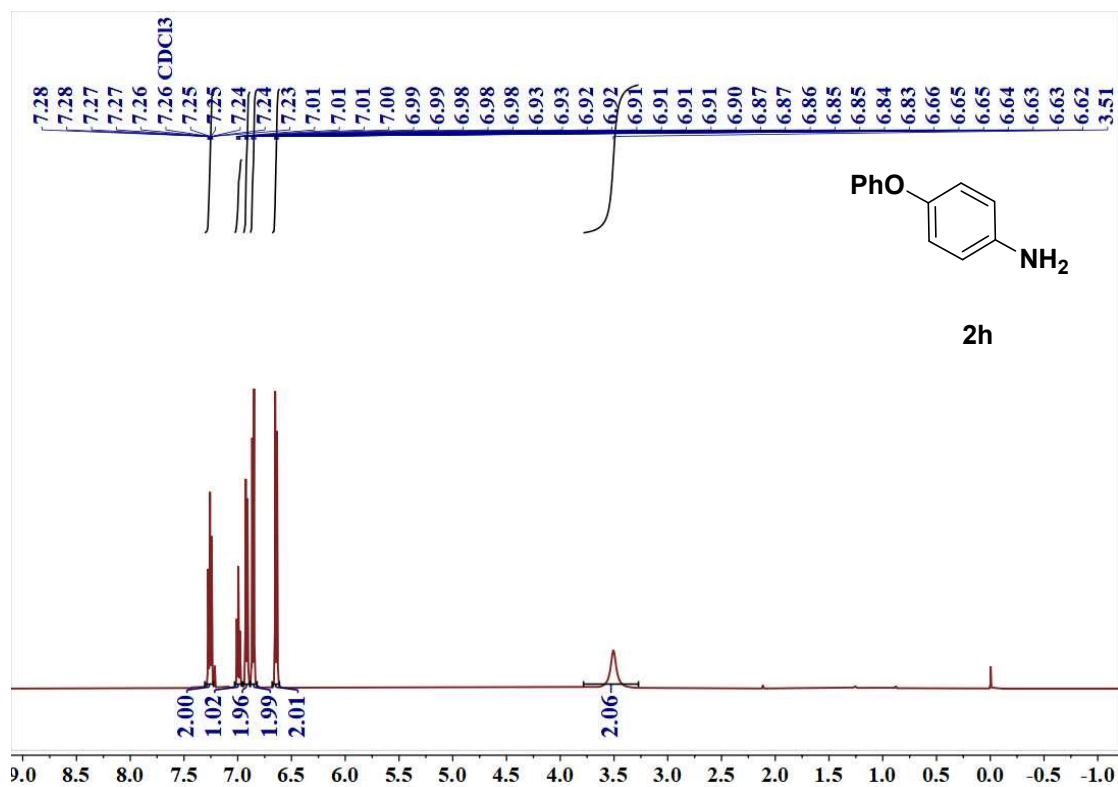
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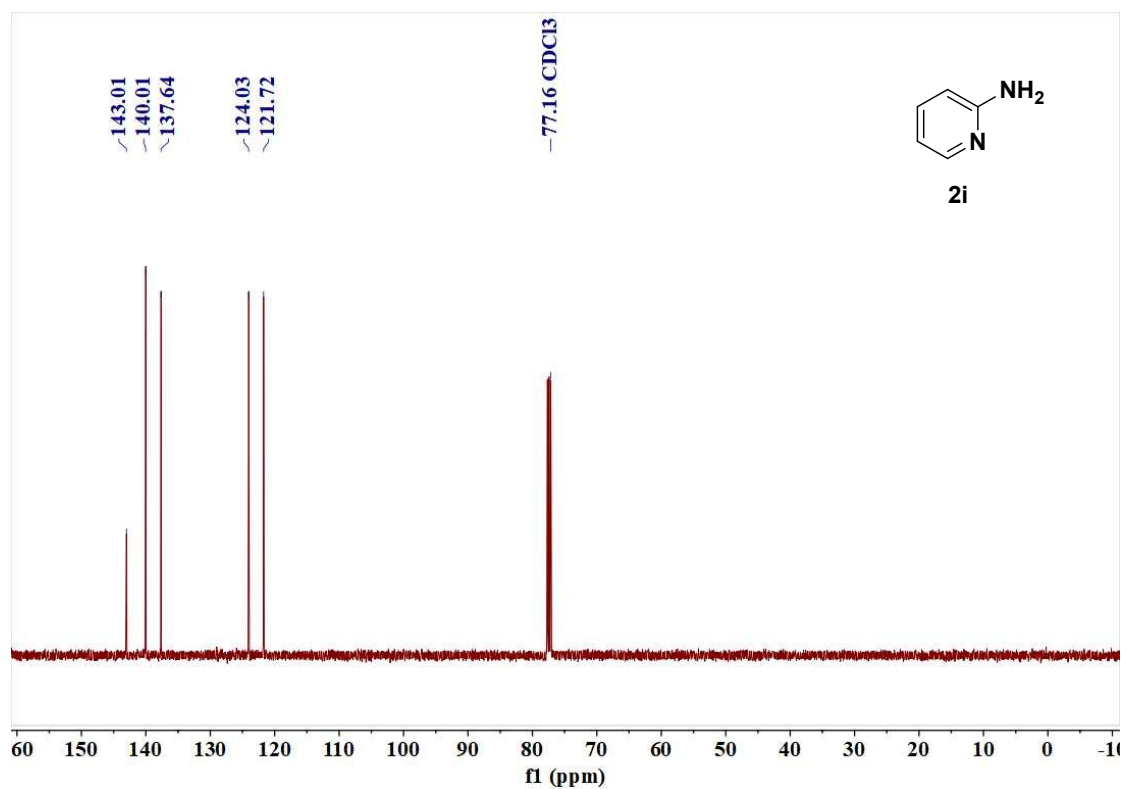
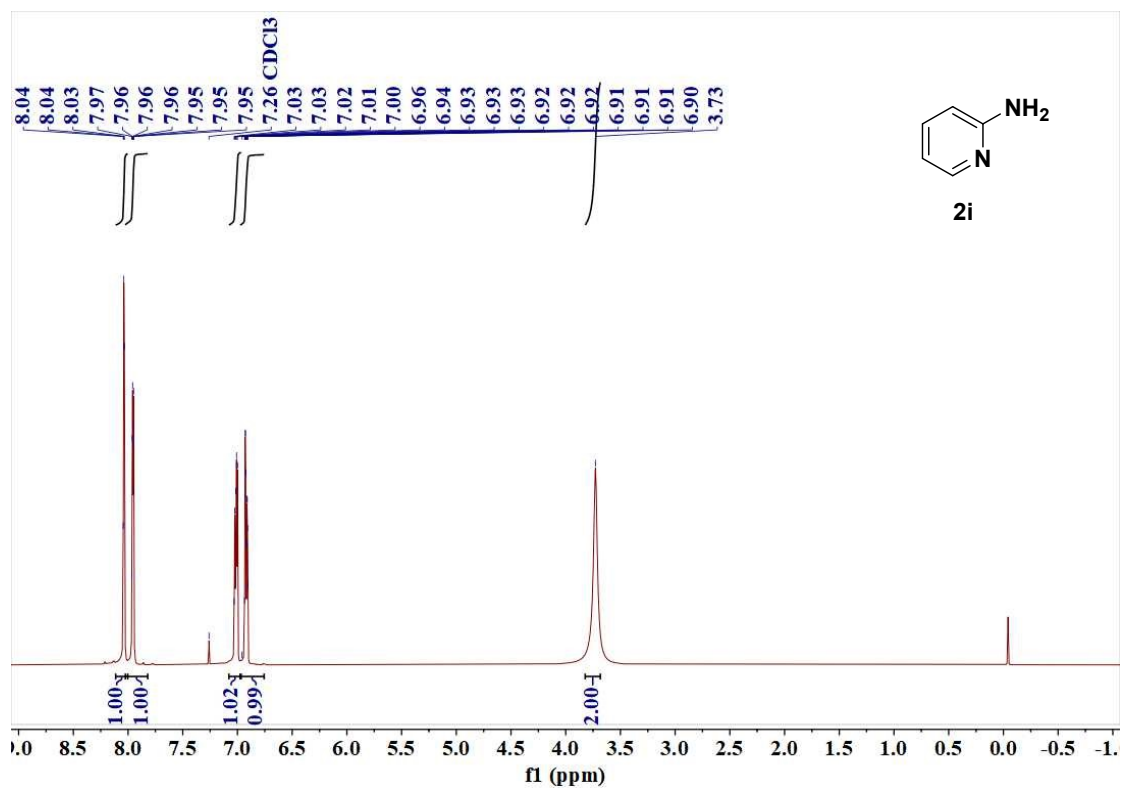
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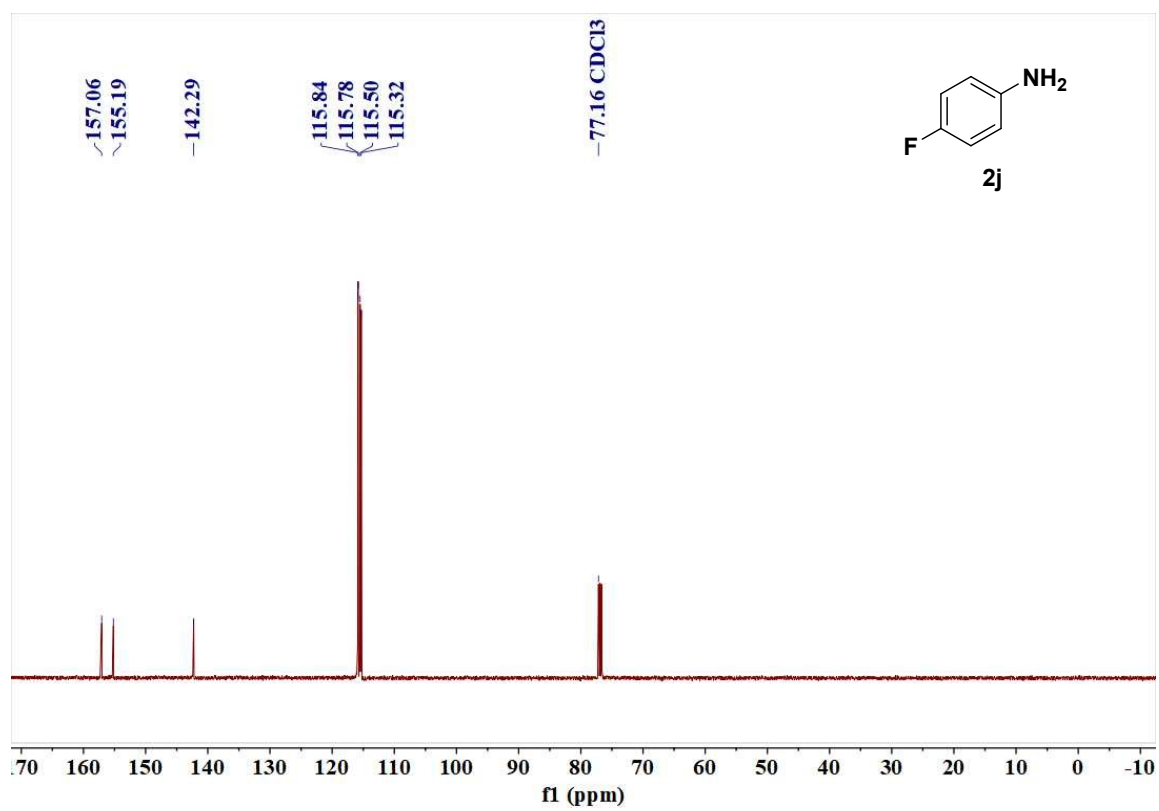
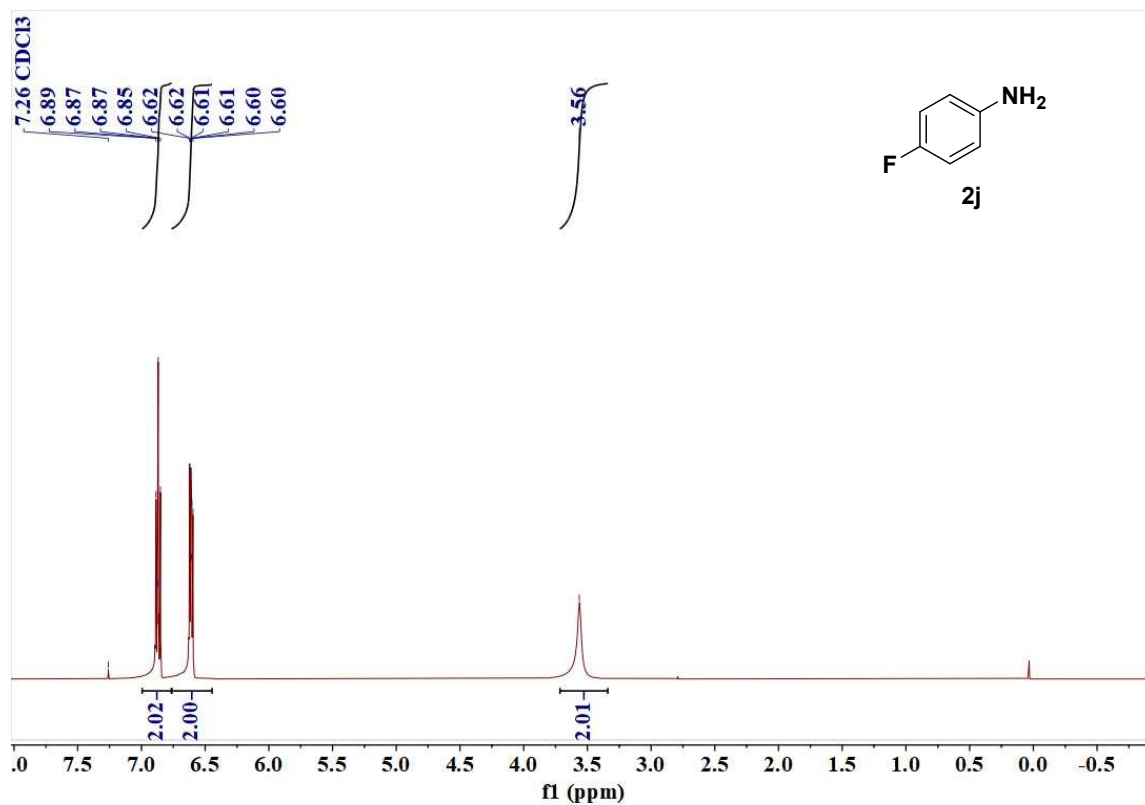
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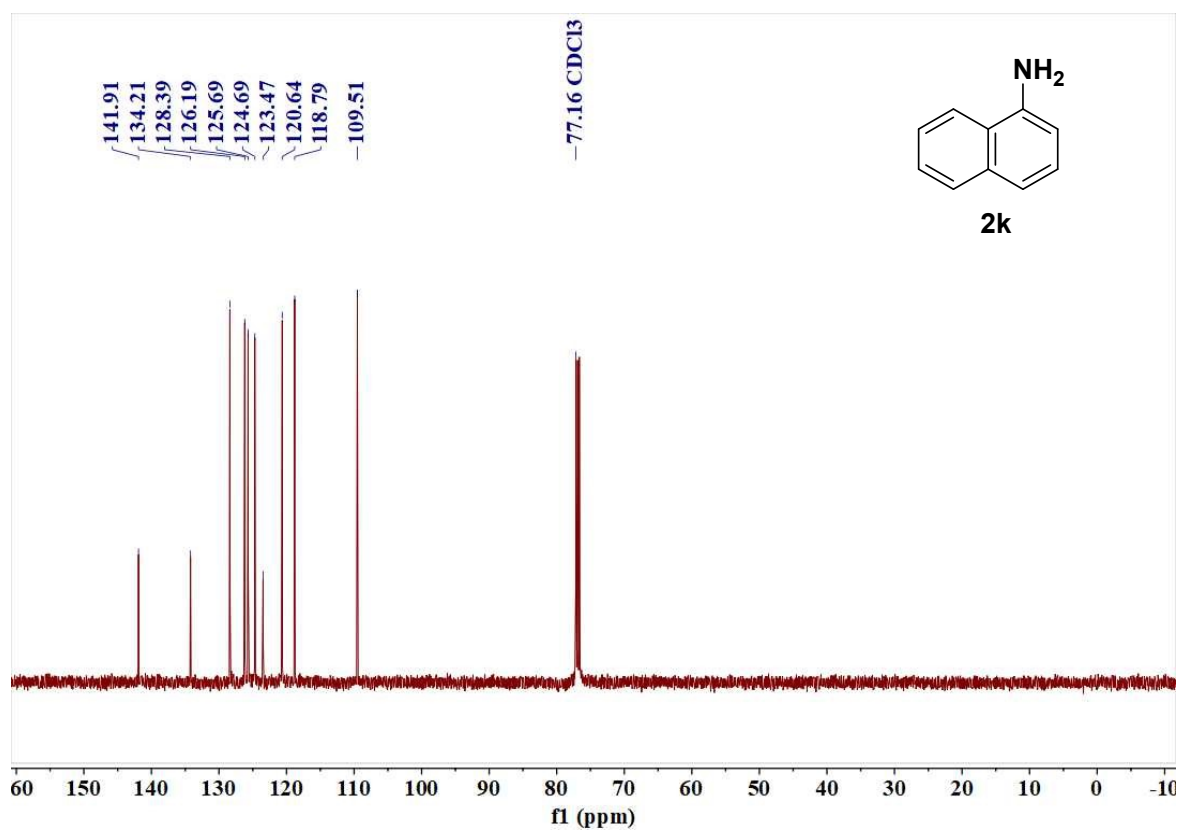
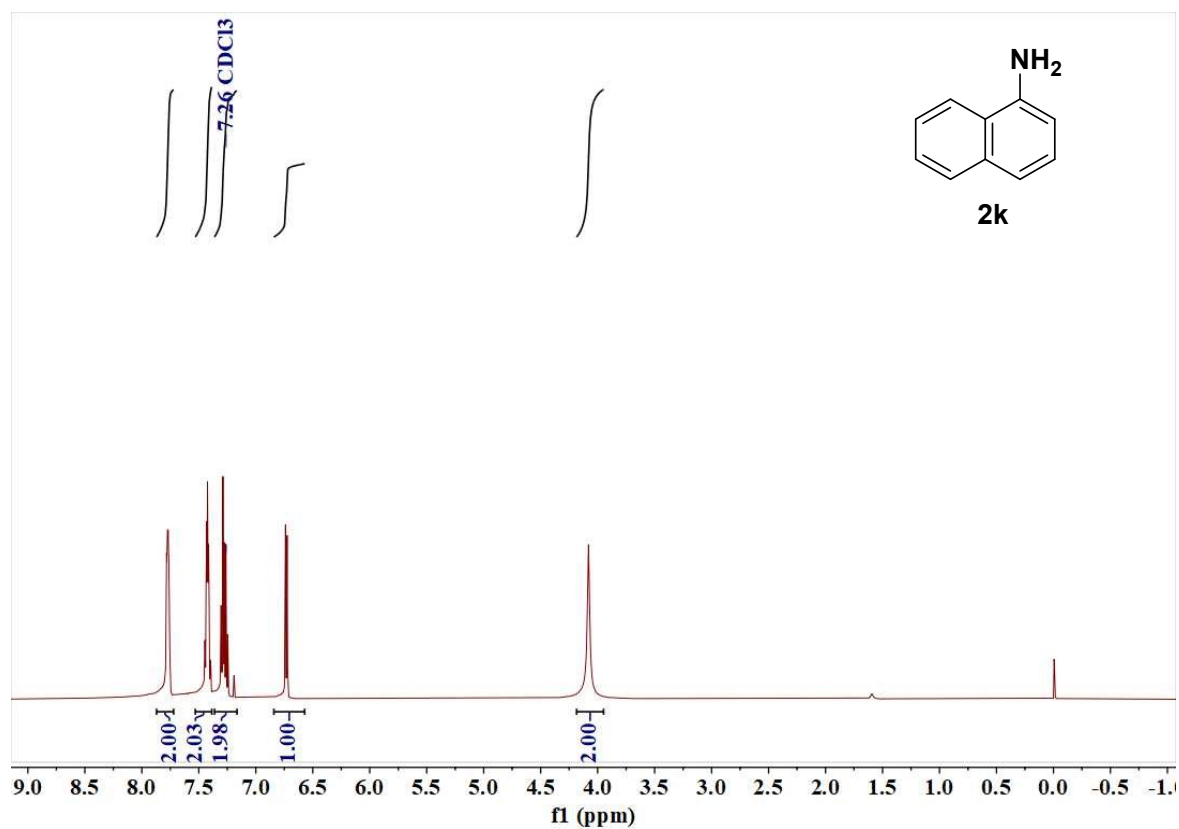
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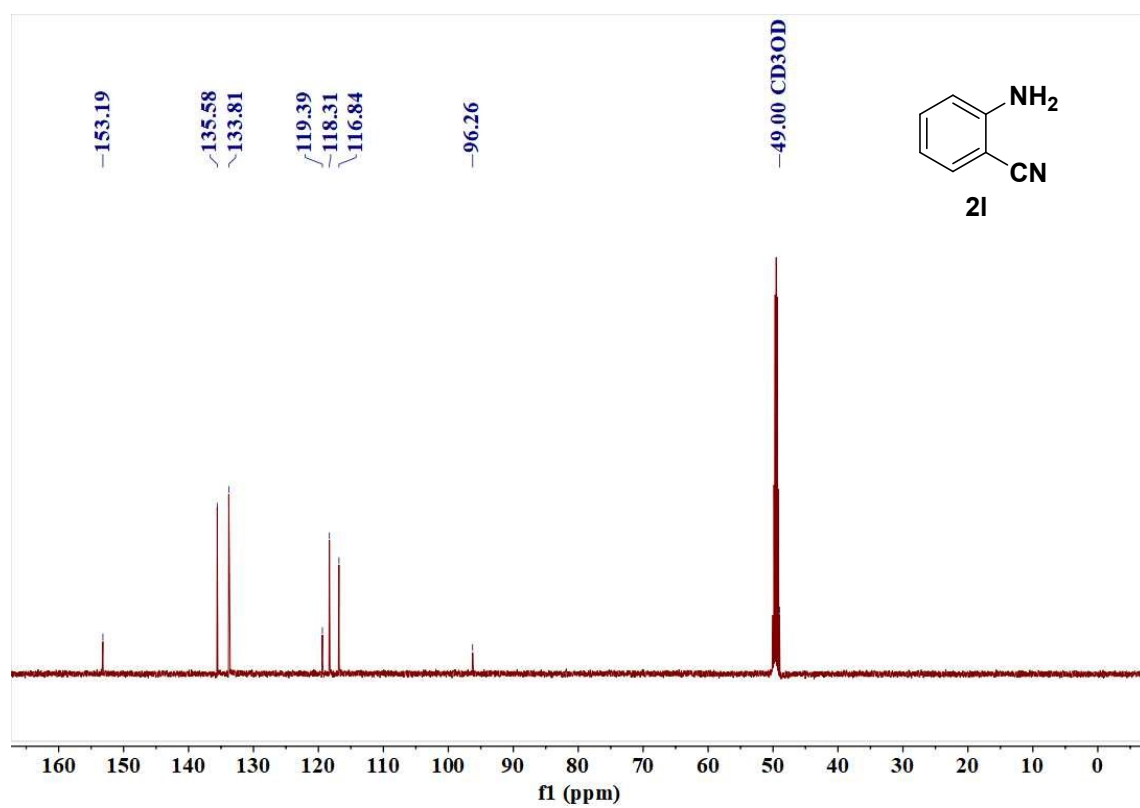
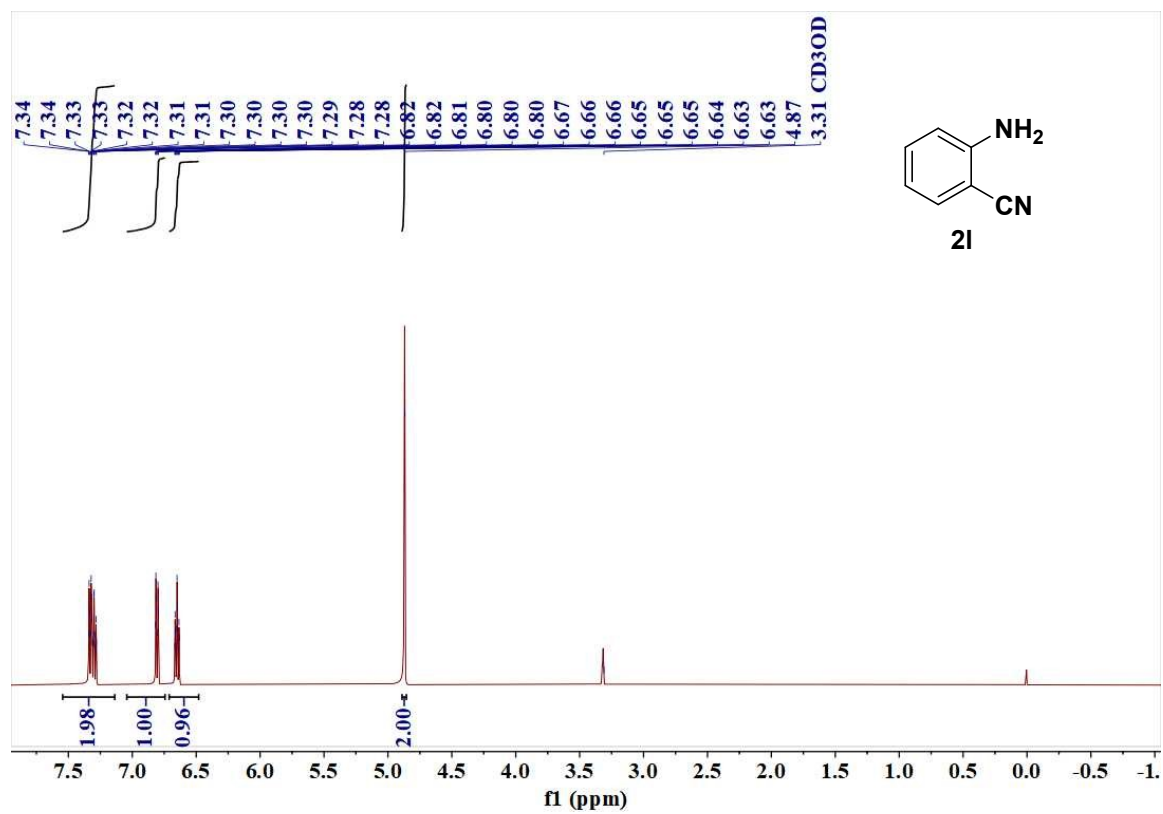


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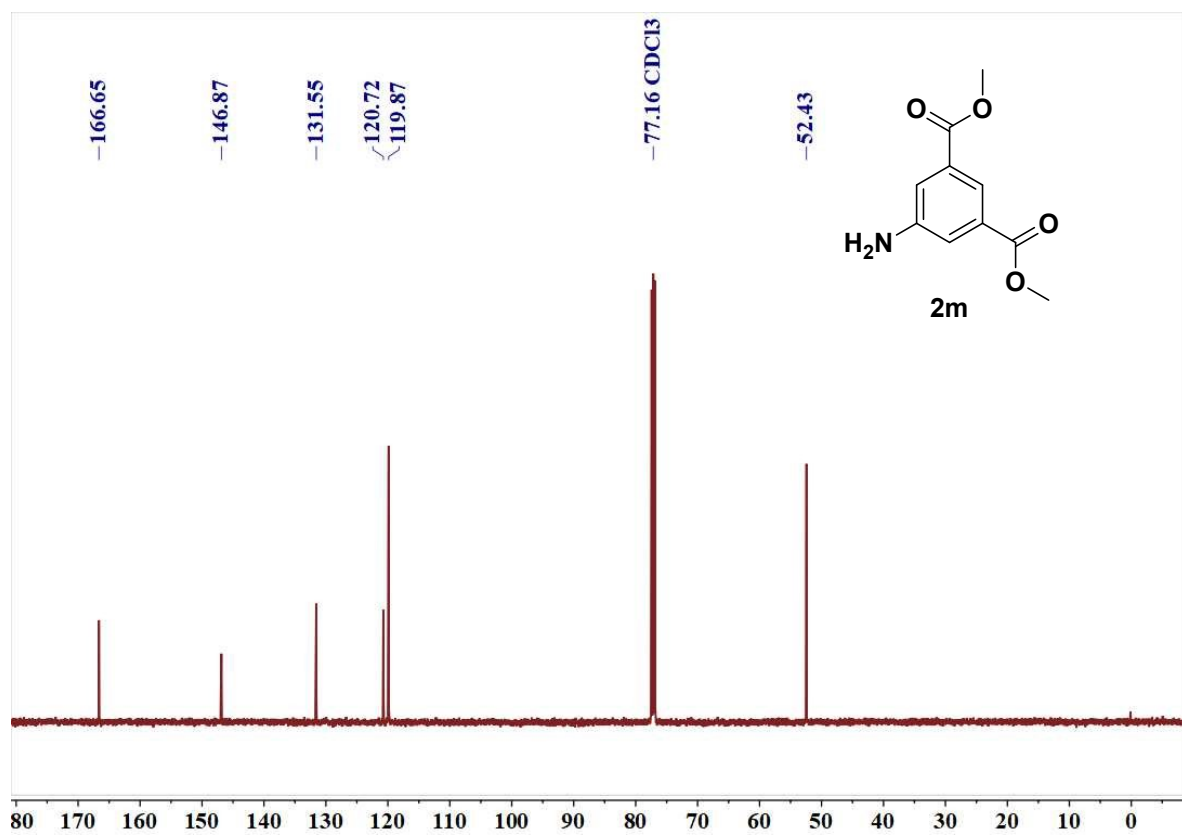
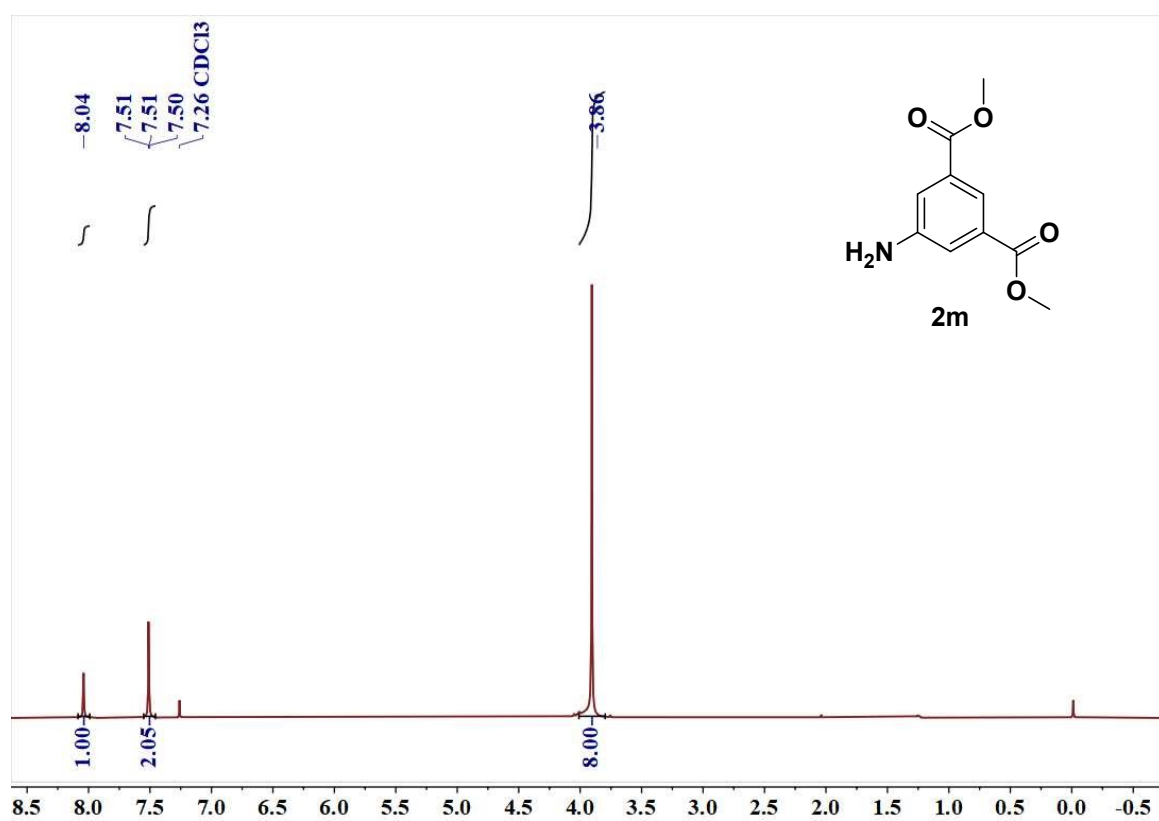


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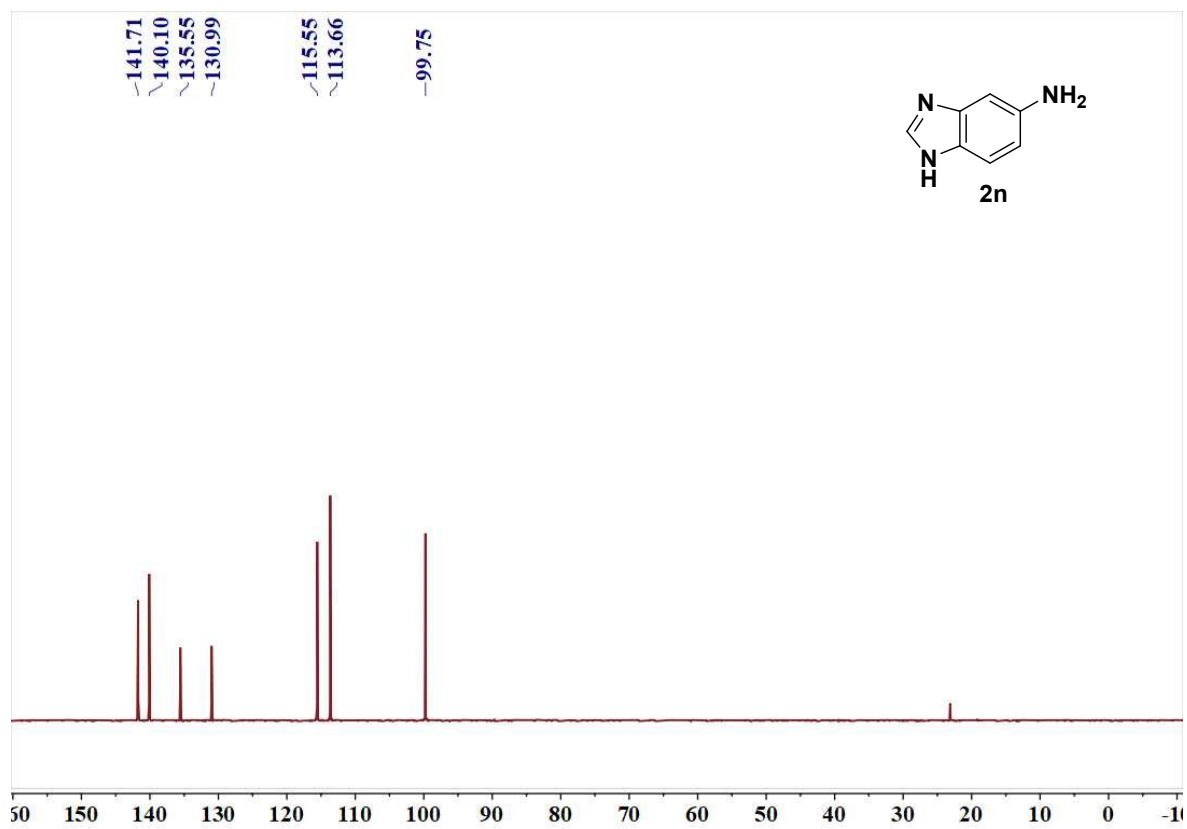
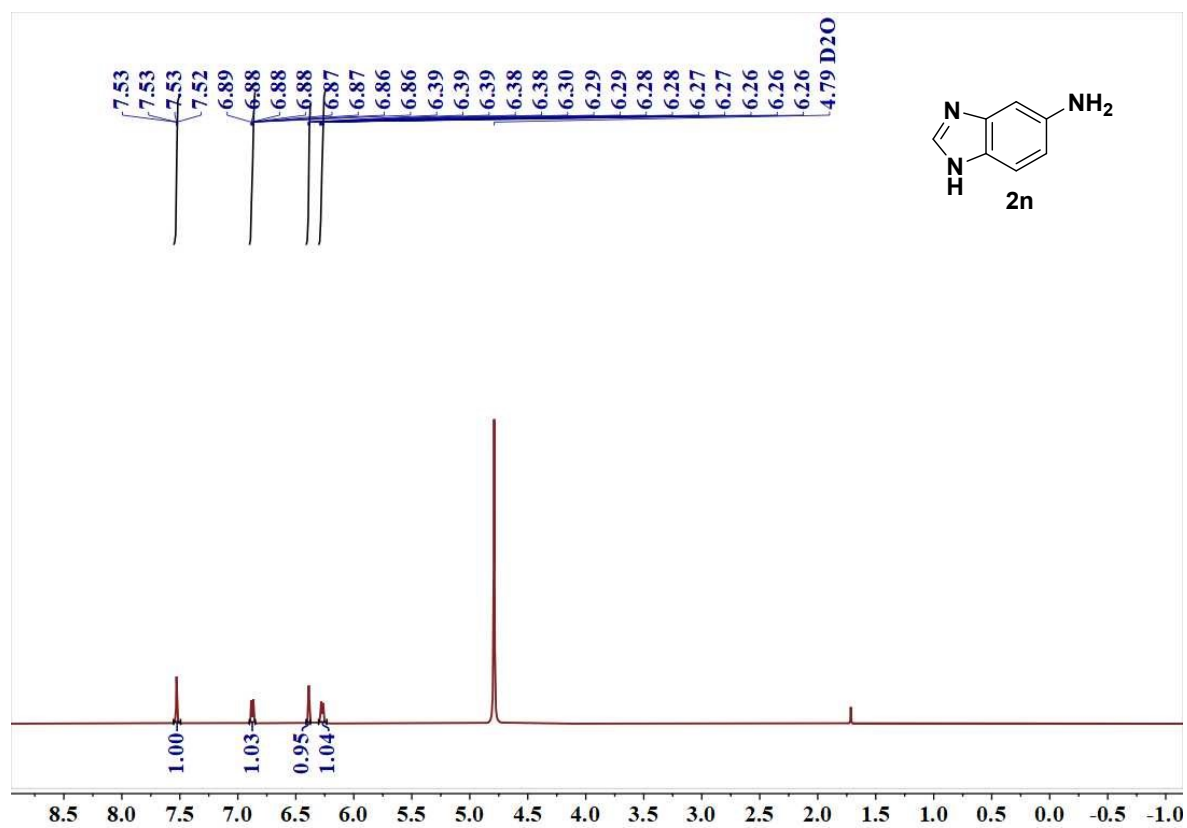




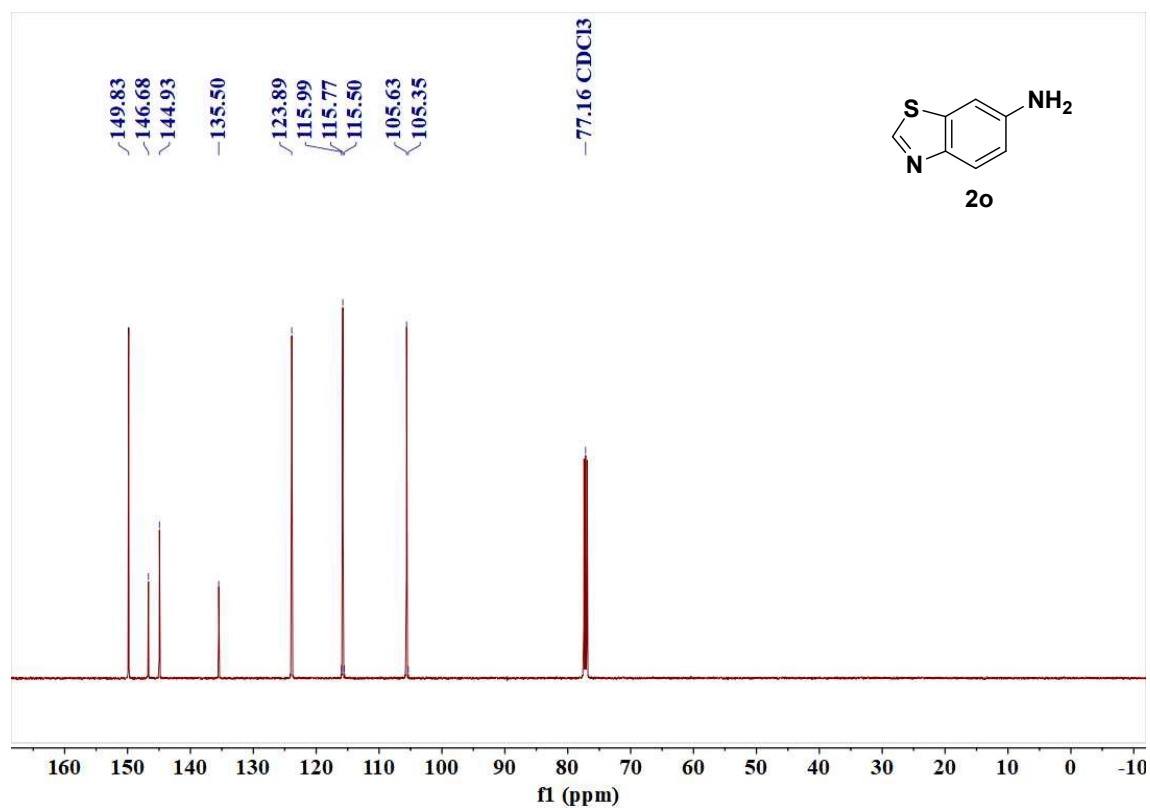
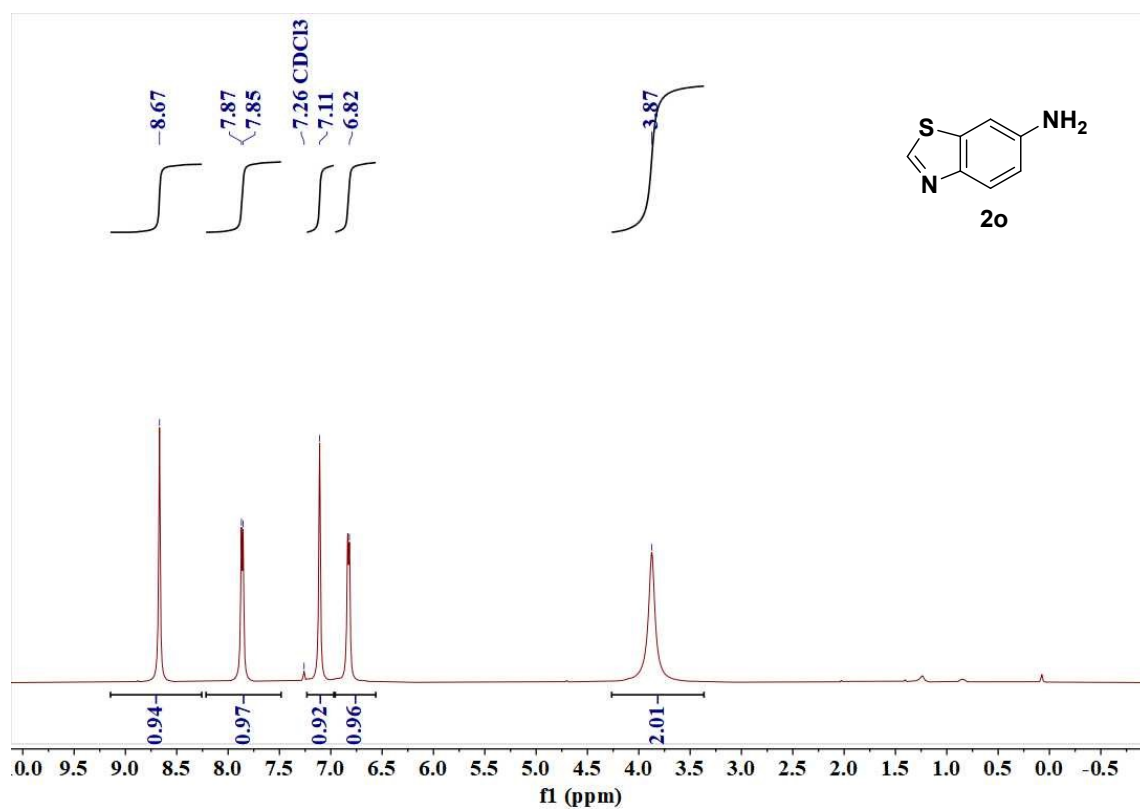
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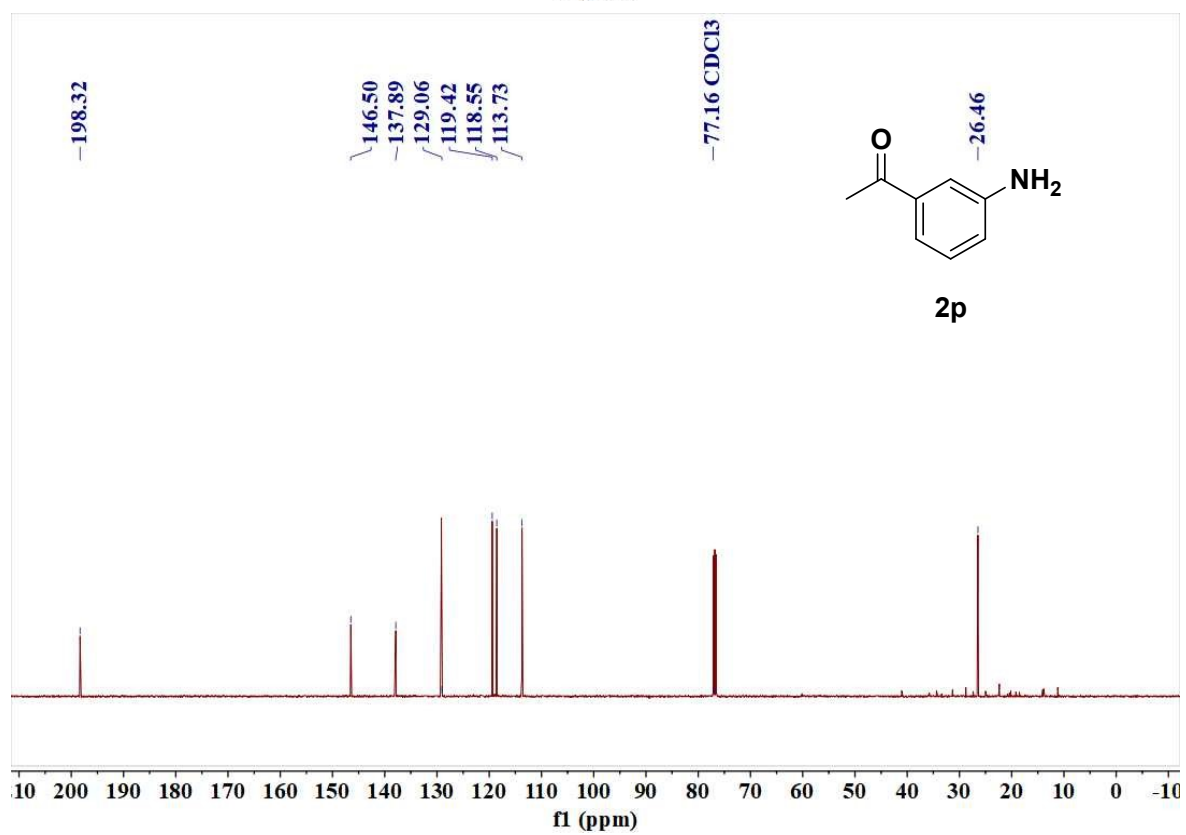
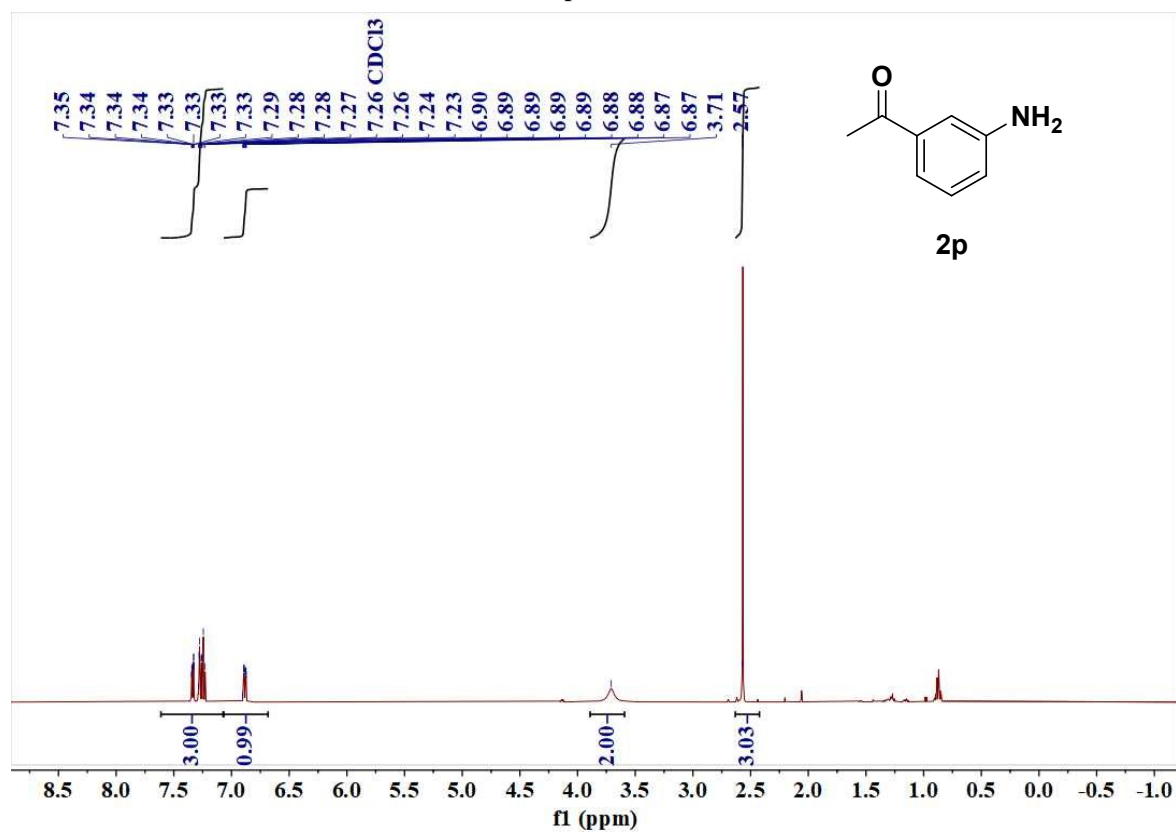
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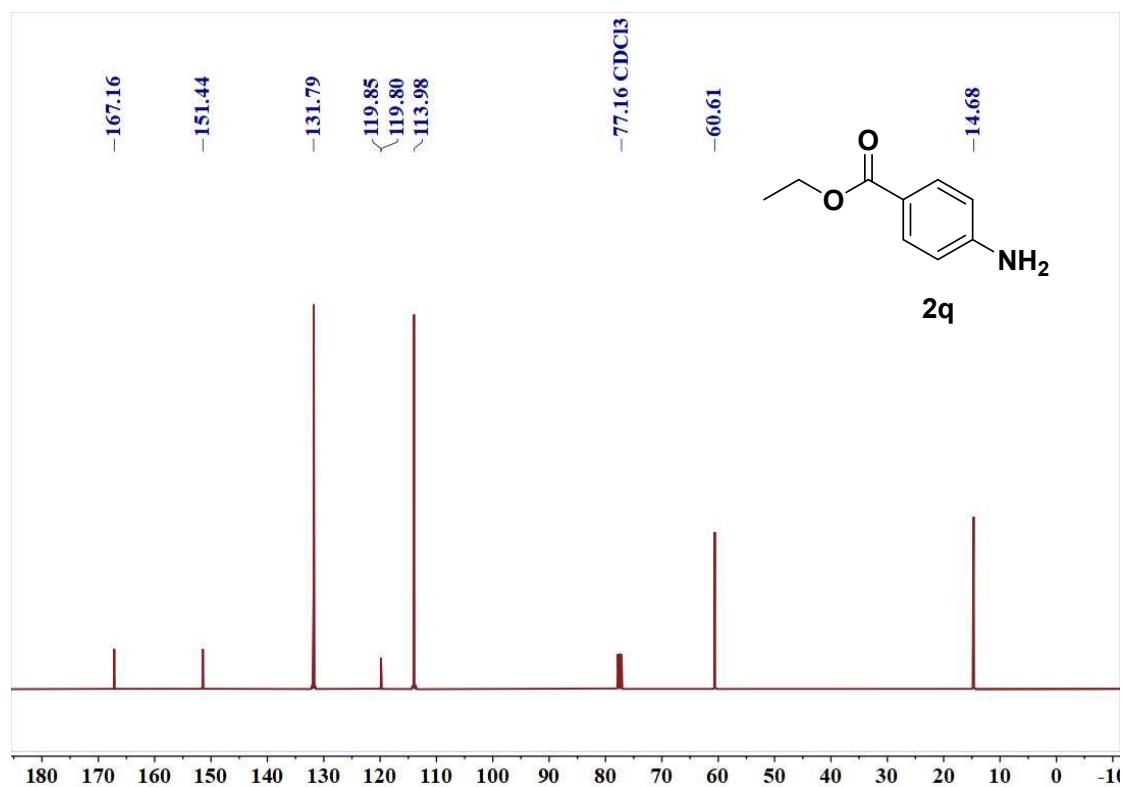
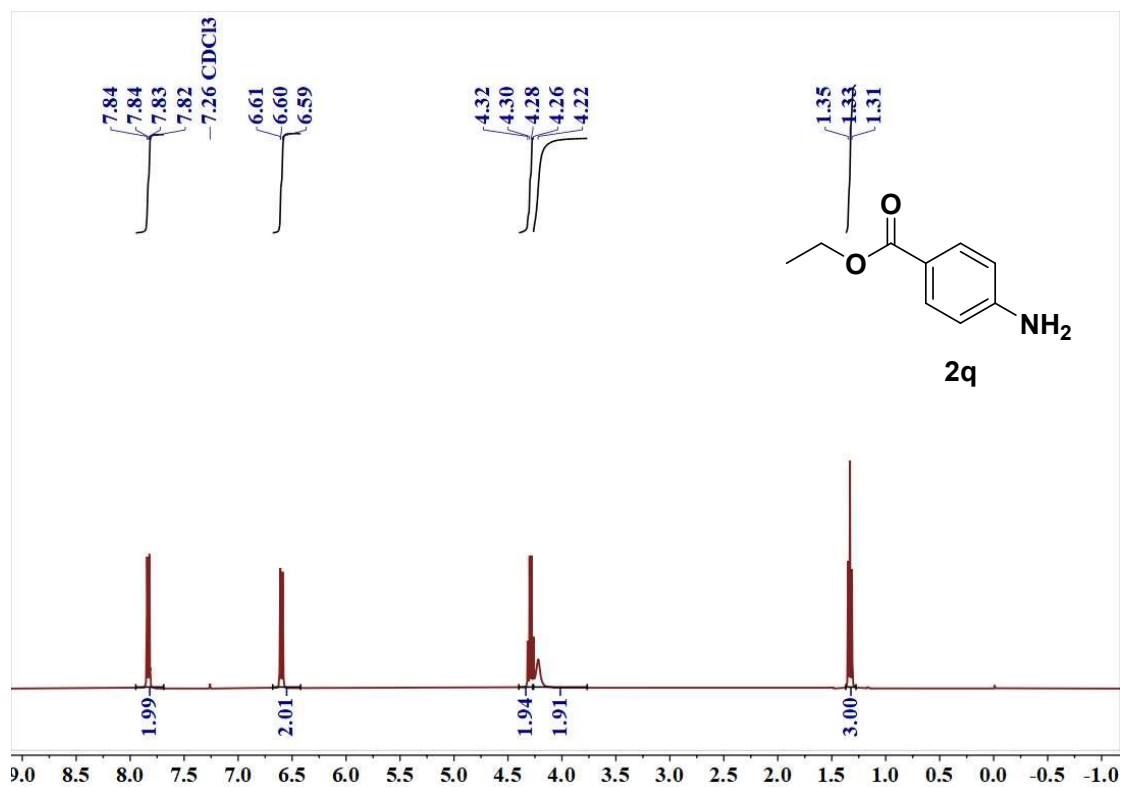
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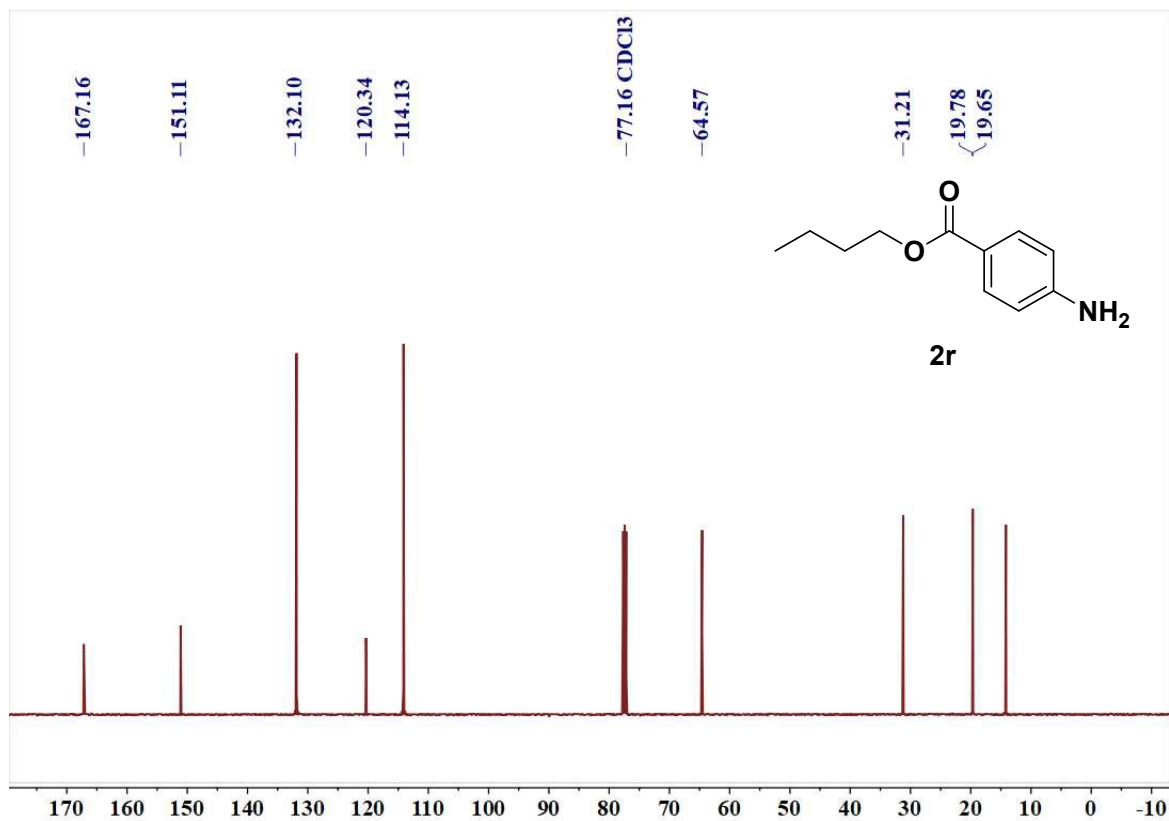
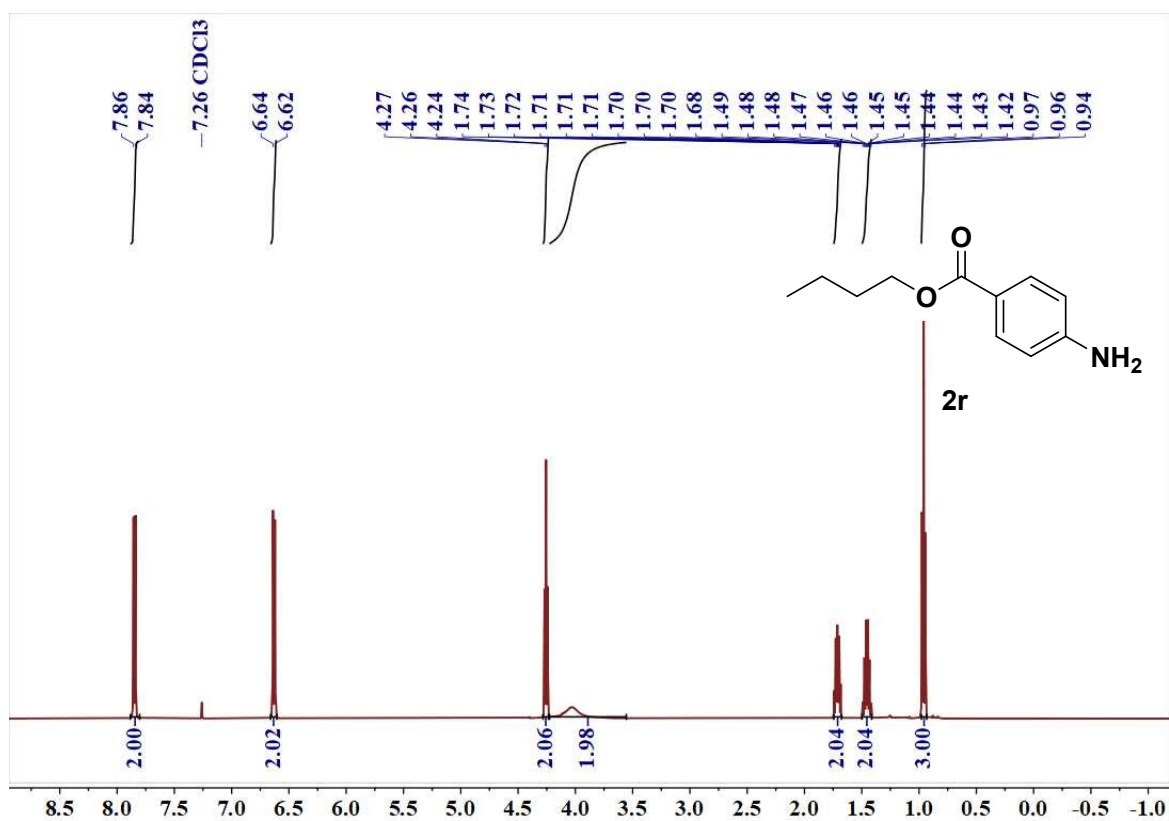
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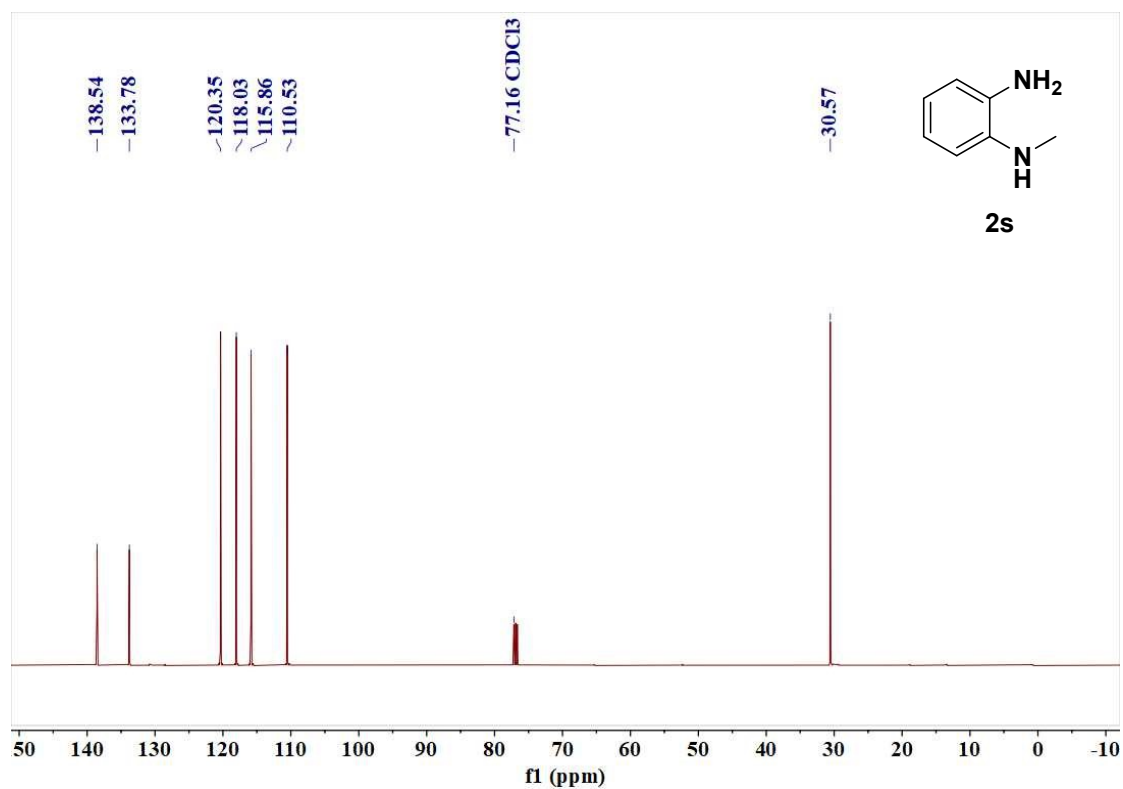
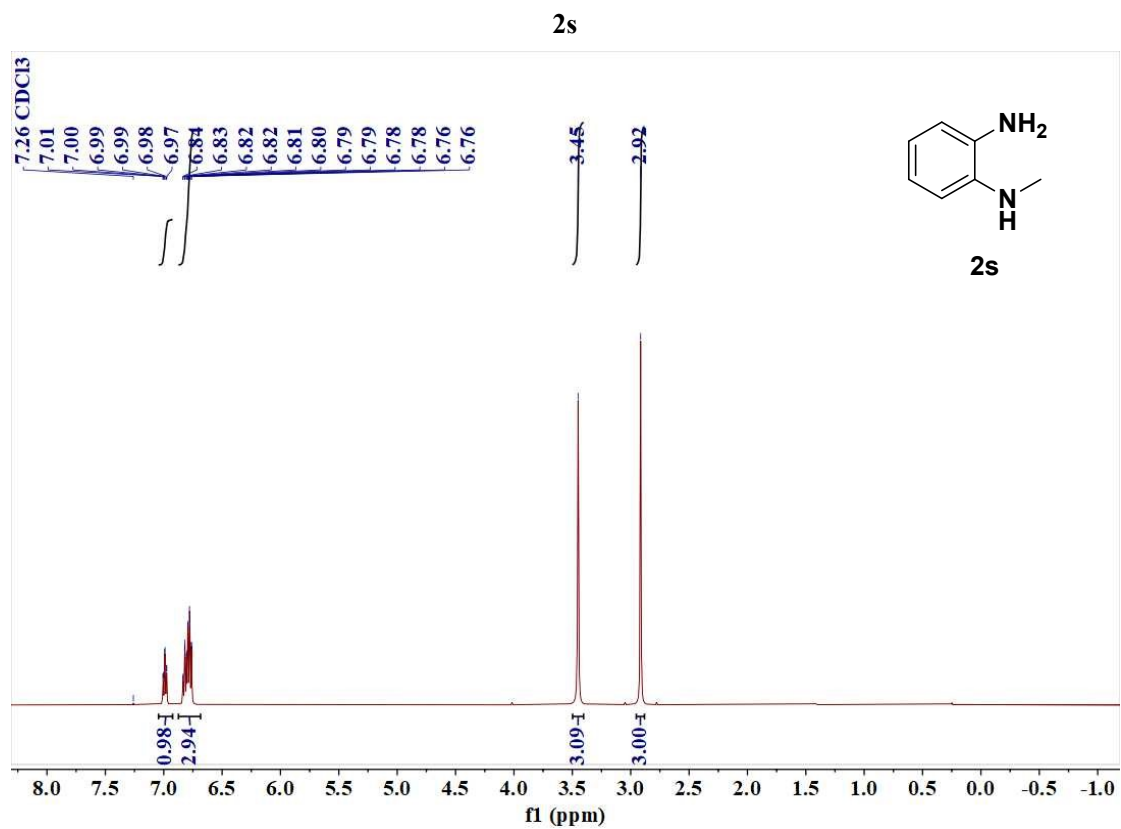


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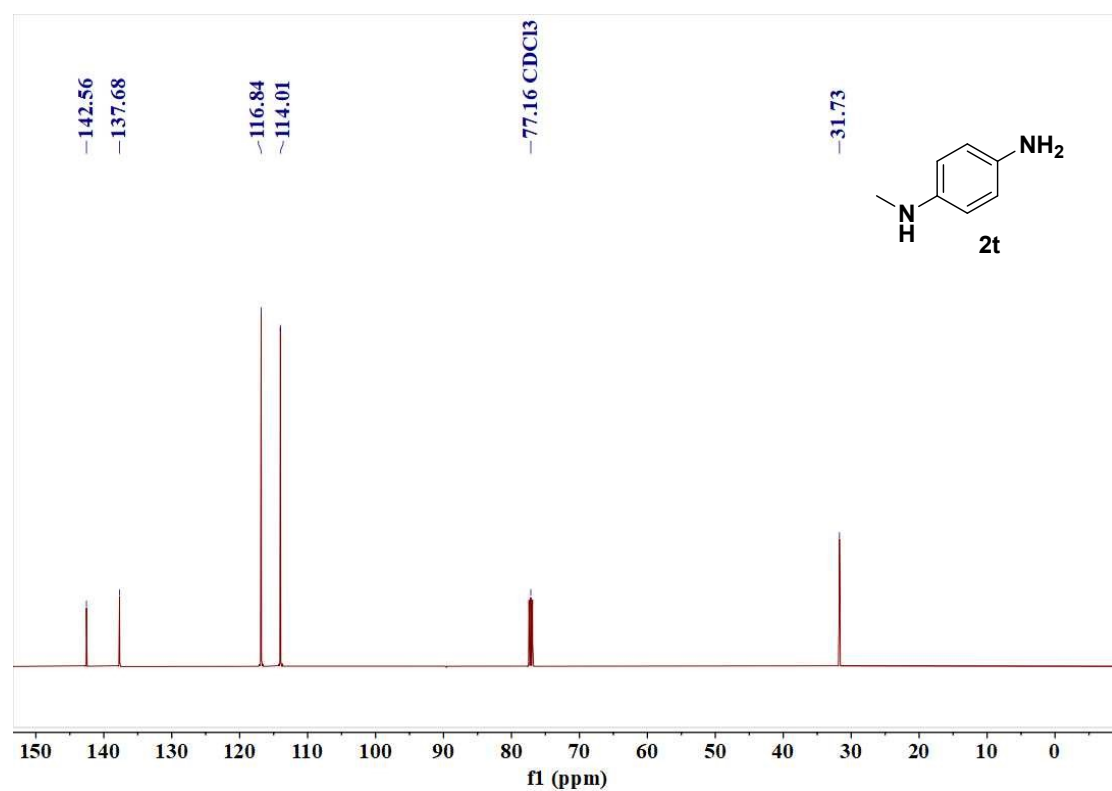
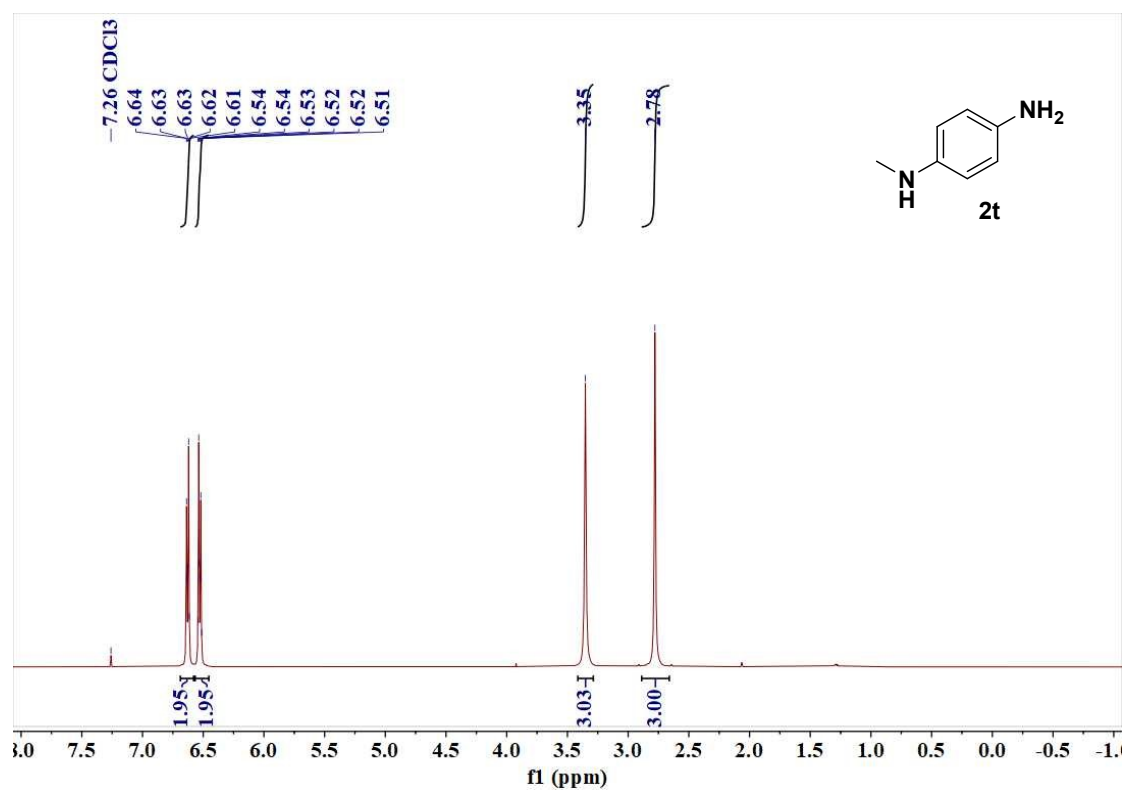


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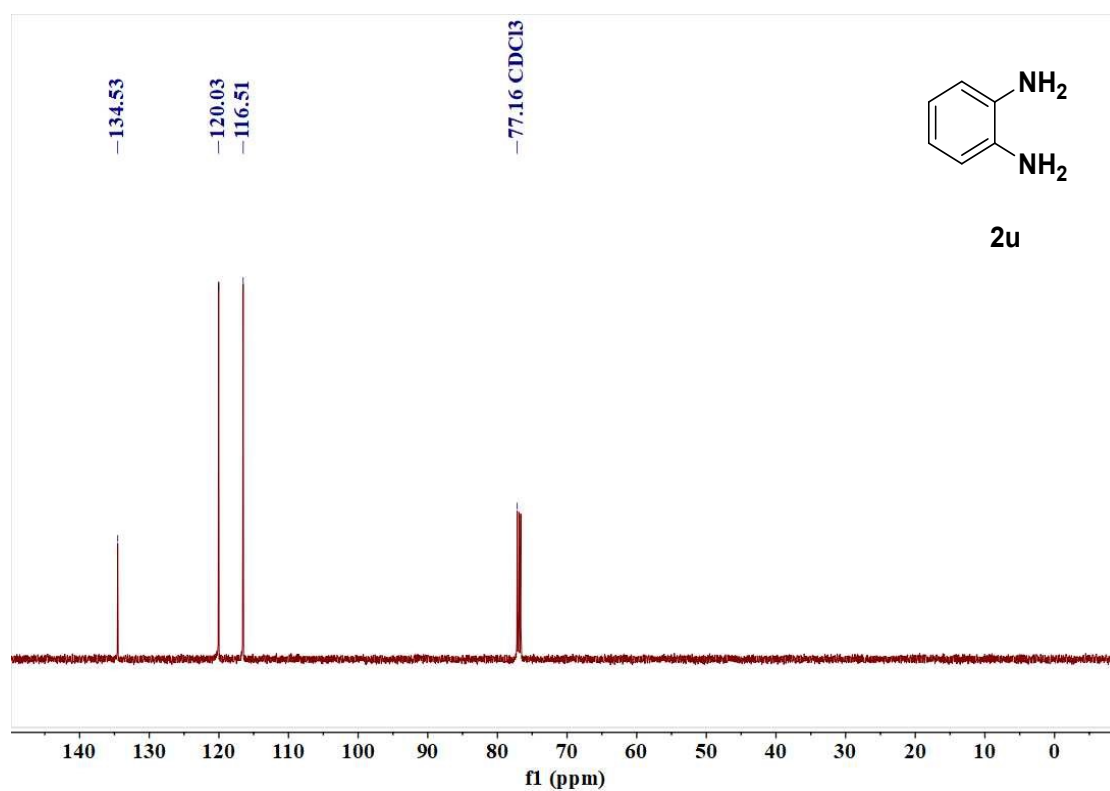
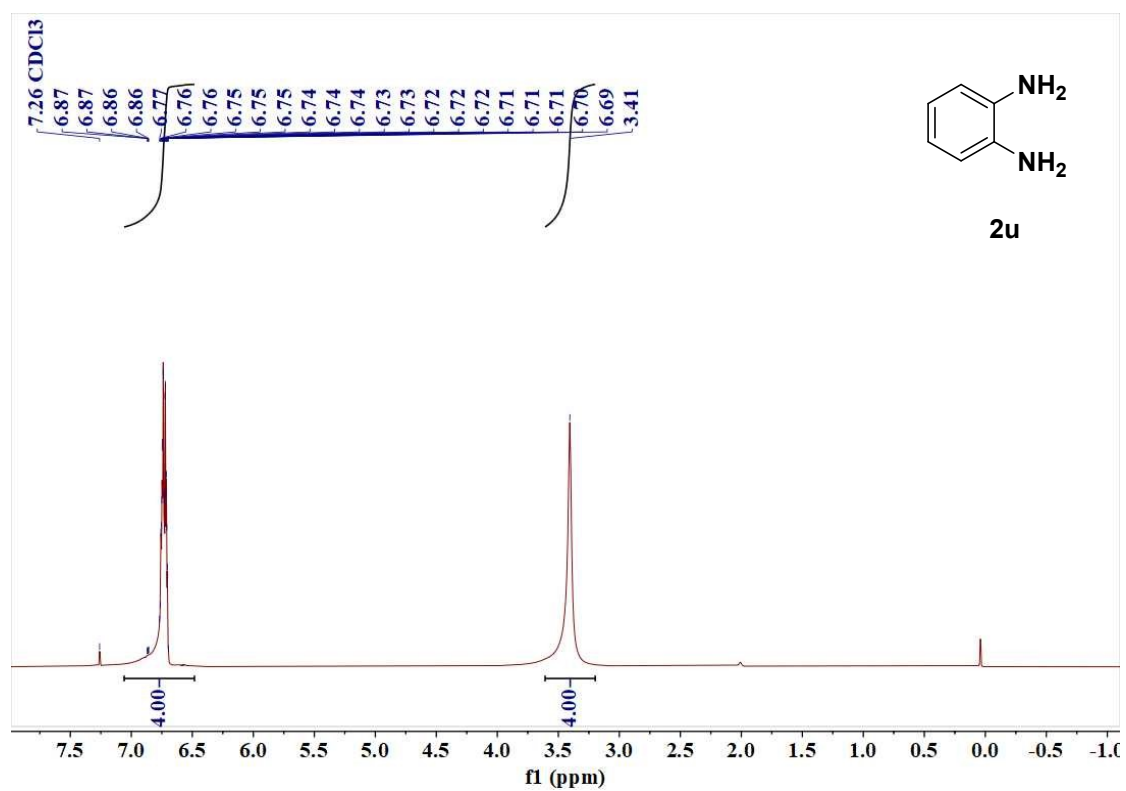




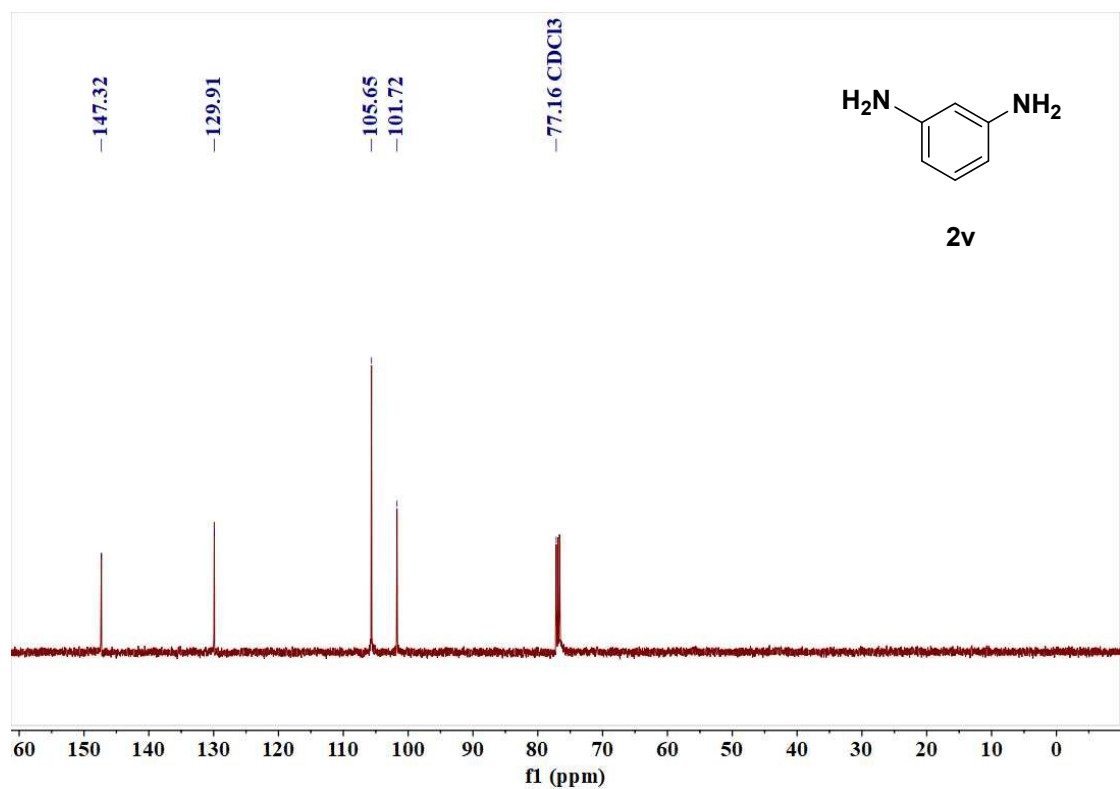
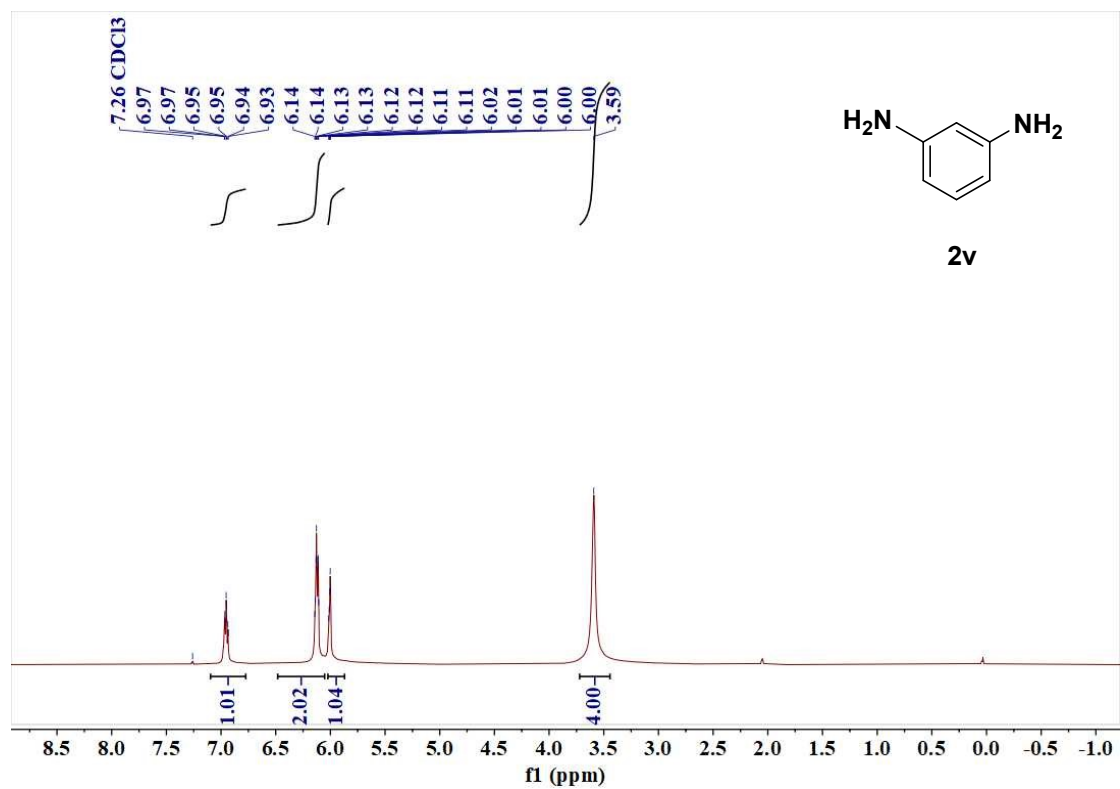
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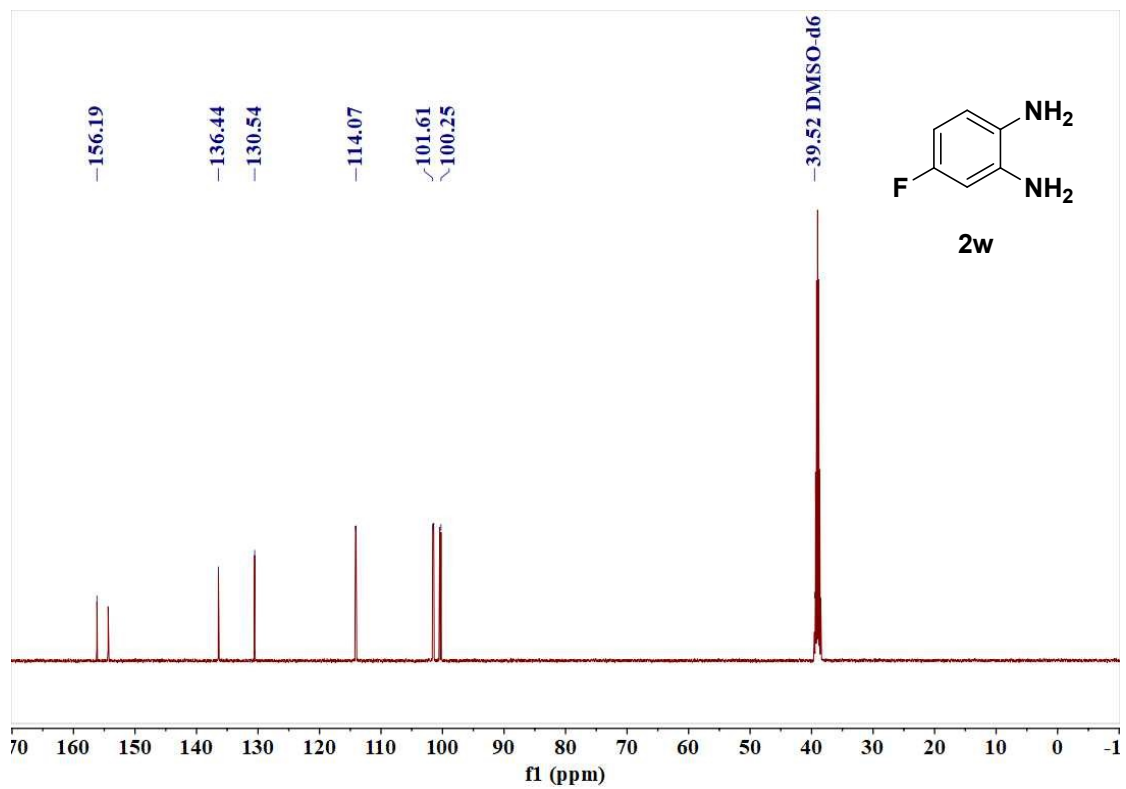
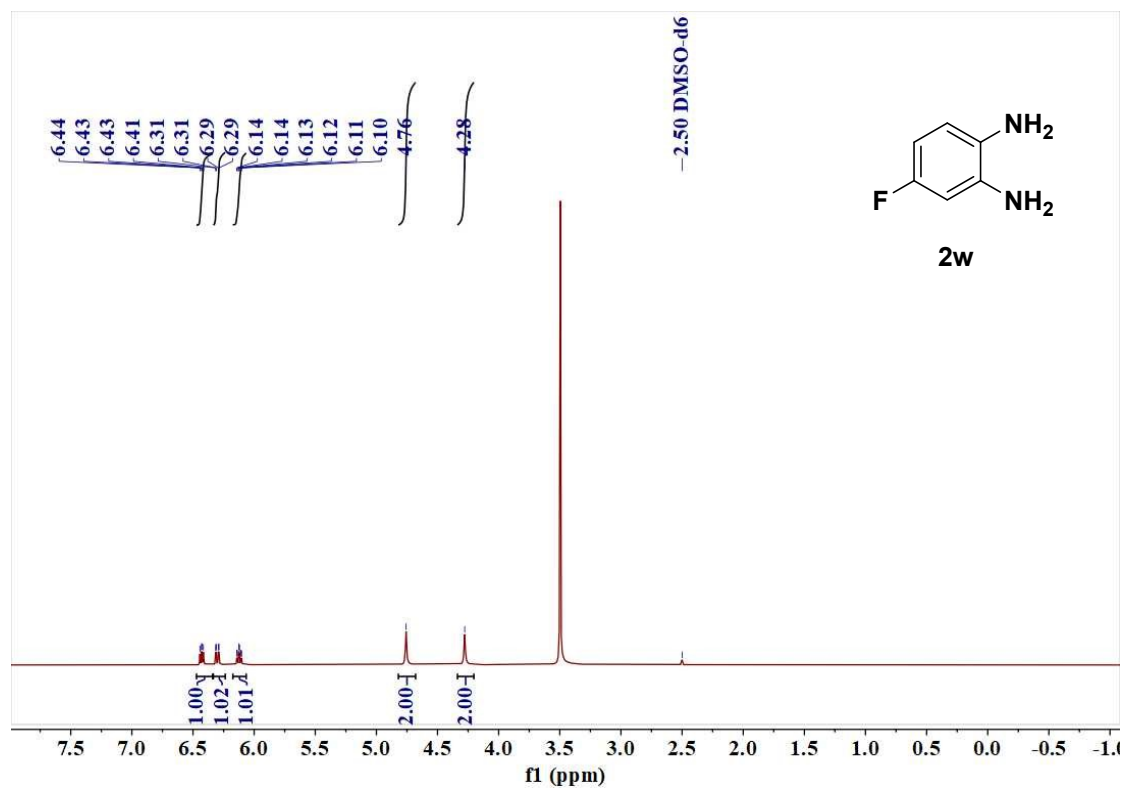
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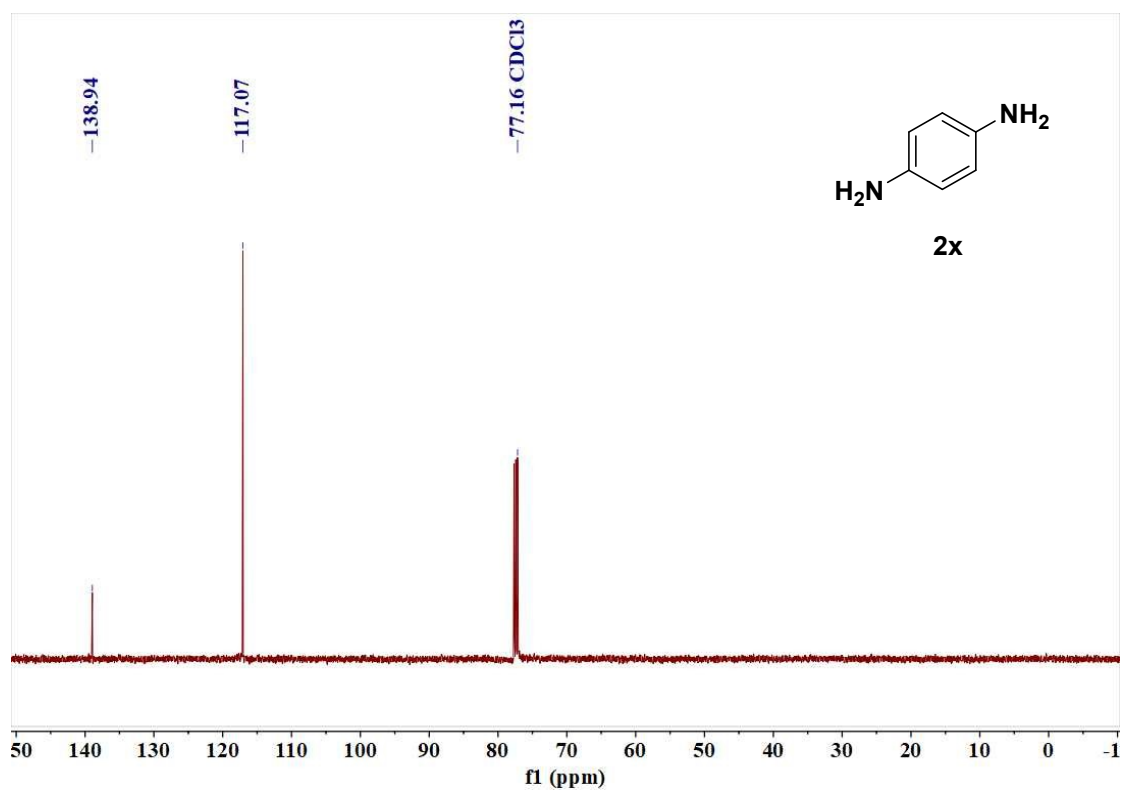
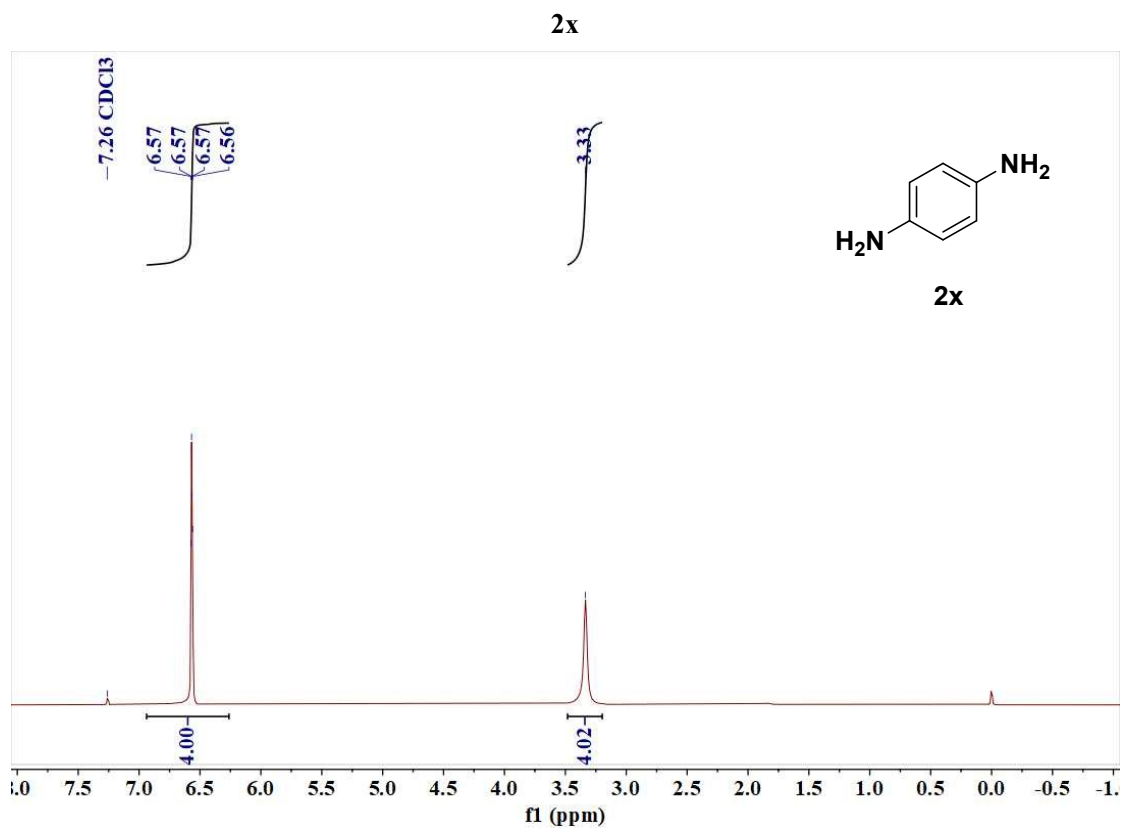


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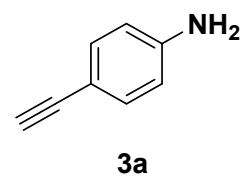
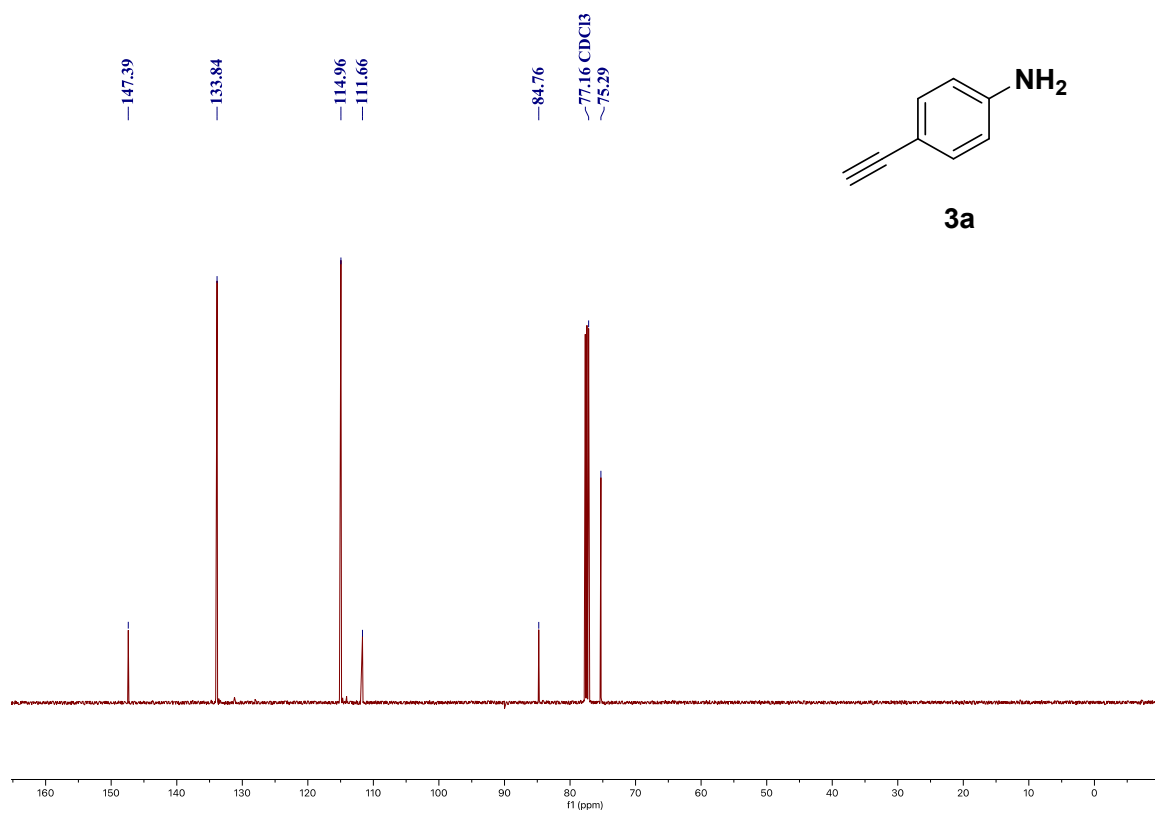
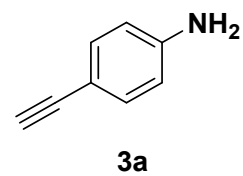
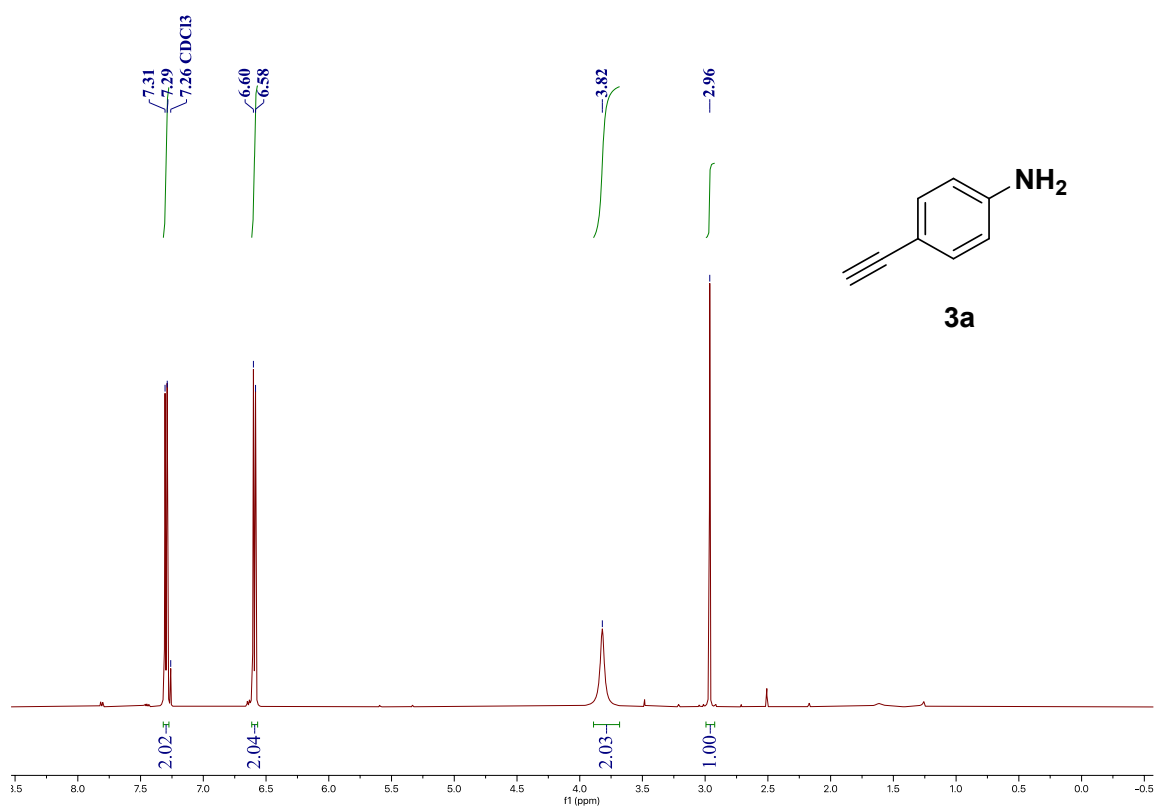


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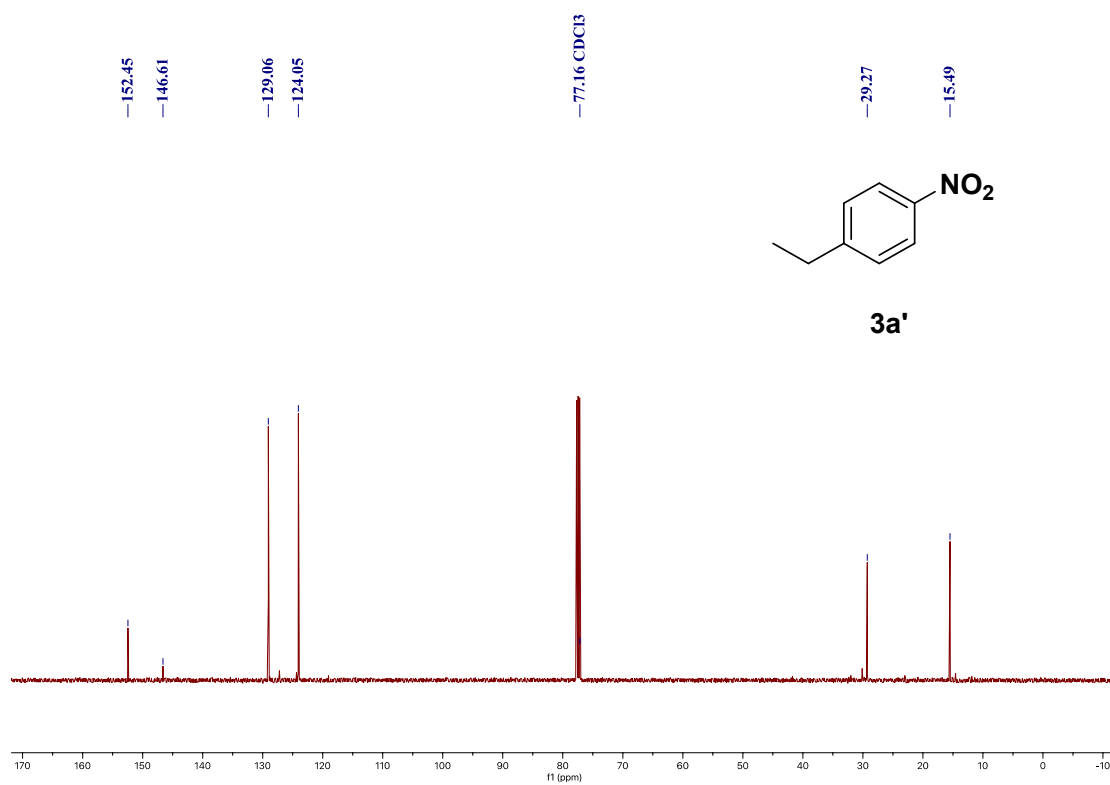
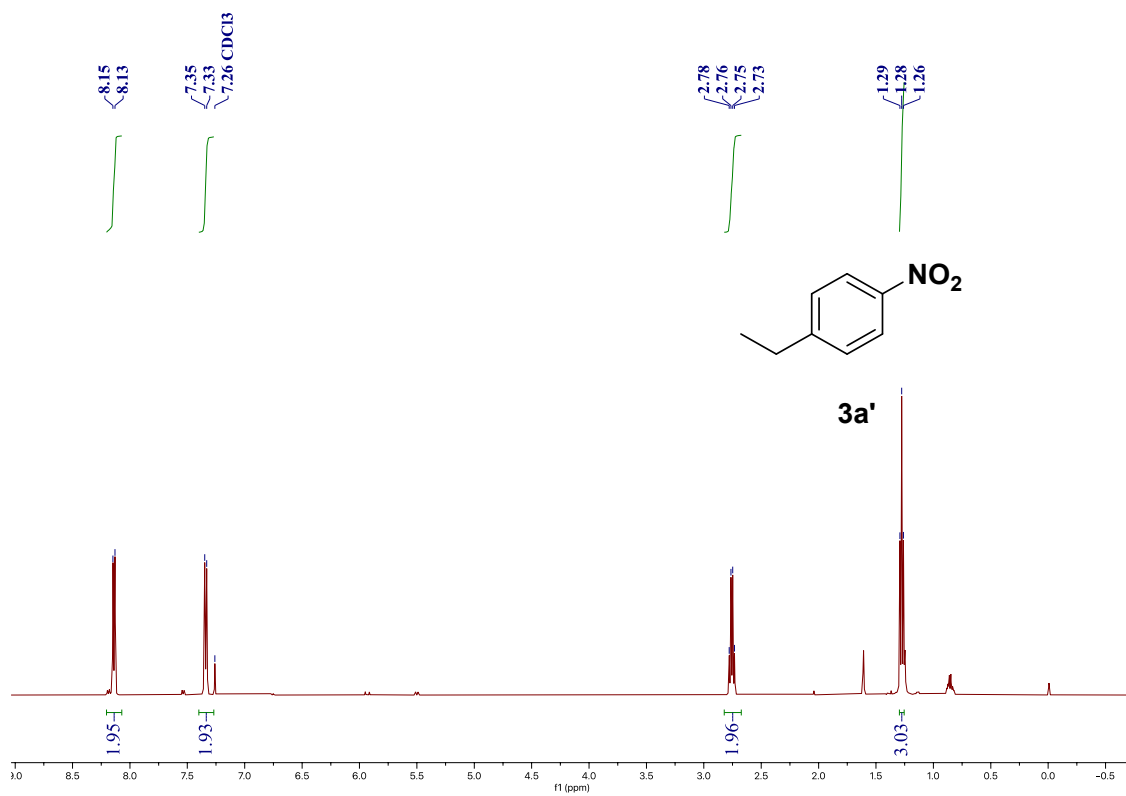




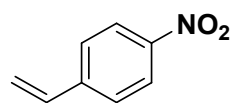
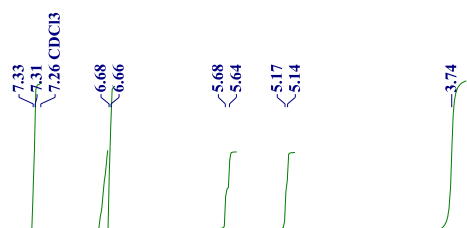
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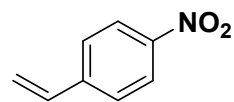
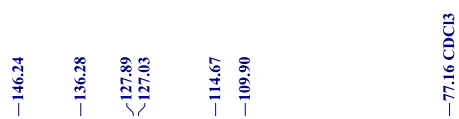
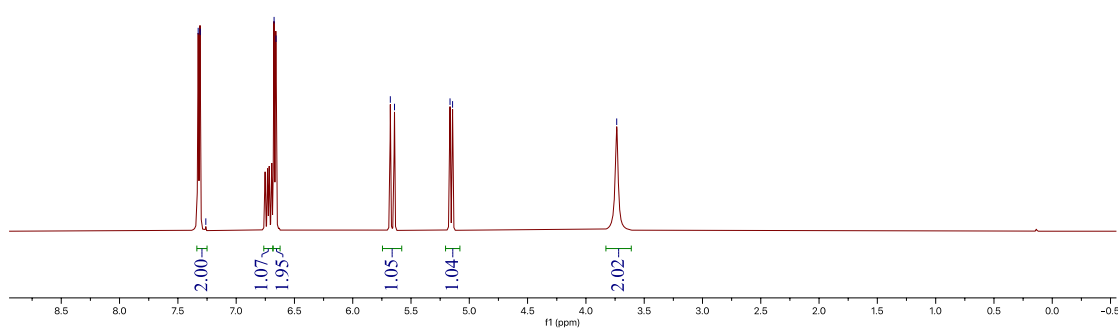
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3b



3b



3b

