Supplementary Information for

Asymmetric CoN_3P_1 single-atom catalytic sites for enhanced transfer hydrodehalogenation

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1. Materials and Methods

1.1 Materials

All chemicals were used directly without further purification. Zinc nitrate hexahydrate ($Zn(NO_3)_2\cdot6H_2O$, ≥99.0%), cobalt nitrate hexahydrate ($Co(NO_3)_2\cdot6H_2O$, ≥98.5%), cobalt chloride hexahydrate ($CoCl_2\cdot6H_2O$, ≥99.0%), ammonium hydroxide ($NH_3\cdot H_2O$, 25.0-28.0%), silver nitrate ($AgNO_3$, 99.8%), methanol (MeOH, ≥99.7%), ethanol (EtOH, ≥99.7%), sulfuric acid (H_2SO_4, 98.0%), acetonitrile (MeCN, >99.8%), 1, 4-dioxane (>99.5%), acetone (>99.0%), toluene (>99.5%) and hexane (>97%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Cobalt acetate tetrahydrate ($Co(OAc)_2\cdot4H_2O$, ≥99.9%), 2-methylimidazole (2-MeIm, 98.0%), triphenylphosphine (PPh_3, 99.0%), formic acid (FA, 99.0%), triethylamine (NEt_3, >99.0%), ammonium formate ($HCOONH_4$, AR), potassium formate (HCOOK, 99%), sodium formate (HCOONa, AR), lithium formate (HCOOLi, 98.0%), propylene carbonate (PC, 99.0%), potassium thiocyanate (KSCN, 98.5%), bisphenol A (BPA, >99.0%) and 5,5-dimethyl-1-pyrroline N-oxide (DMPO, 97.0%) were purchased from Aladdin. Platinum on activated carbon (Pt/C, 5% Pt) and palladium on activated carbon (Pd/C, 5% Pd) were purchased from Alfa Aesar. Au/TiO_2 catalyst (average Au particle size ca. 3.5 nm) was purchased from the World Gold Council.

1.2 Catalyst preparation

A) Synthesis of NP-PC and NC

Typically, $Zn(NO_3)_2\cdot6H_2O$ (11.9 g, 40 mmol) and triphenylphosphine (7.9 g, 30 mmol) were dissolved in 600 mL MeOH to form a clear solution and marked as solution A. 2-MeIm (26.3 g, 320.0 mmol) was dissolved in 200 mL MeOH and marked as solution B.

Then solution B was then poured into solution A and stirred at 25 °C for 24 h. The obtained precipitate was collected by centrifugation, wash with MeOH for three times and then dried under vacuum at 25 °C to obtained white precursor. Then 1.1 g precursor was heated to 1000 °C for 4 h with a heating rate of 2 °C/min under the flowing argon atmosphere in a tube furnace. The obtained black powder was named as NP-PC, which stands for N, P-codoped porous carbon. The synthesis of N-PC followed the same procedure as for NP-PC, with the exclusion of PPh_3.

B) Synthesis of CoN_3P_1@NP-PC and CoN_4@N-PC

Typically, $Co(OAc)_2·4H_2O$ (40 mg, 0.16 mmol) was dissolved in 60 mL of absolute ethanol with continuous stirring until complete dissolution. Subsequently, 650 mg of NP-PC was added and stirred at 60 °C for 4 h. The ethanol was then removed by vacuum evaporation. The resulting black powder was further dried at 60 °C and heated to 900 °C for 4 h at a heating rate of 2 °C/min in a tube furnace under a flowing argon atmosphere. After naturally cooling to 25 °C, the powder was stirred in 60 mL of 0.6 M H_2SO_4 solution at 80°C for 3 h and subsequently washed with deionized water until neutral. The obtained black powder was named as CoN_3P_1@NP-PC. The synthesis of CoN_4@N-PC followed the same procedure as for CoN_3P_1@NP-PC, with N-PC as the precursor.

C) Synthesis of CoN_4@N-PC-BMZIF

Typically, $Zn(NO_3)_2·6H_2O$ (11.9 g, 40 mmol) and $Co(NO_3)_2·6H_2O$ (0.23 g, 0.8 mmol) were dissolved in 400 mL of MeOH to form a clear solution, marked as solution A. 2-MeIm (26.8 g, 326 mmol) was dissolved in 400 mL of MeOH, marked as solution B. Solution B was then poured into solution A and stirred at 25 °C for 24 h. The obtained precipitate was collected by centrifugation, washed with MeOH three times, and then dried under vacuum at 25 °C overnight to obtain a white precursor. Subsequently, 1.5 g of the precursor was heated to 900°C for 4 h at a heating rate of 2°C/min in a tube furnace under a flowing argon atmosphere. After naturally cooling to 25 °C the powder was stirred in 60 mL of 0.6 M H_2SO_4 at 80°C for 8 h and subsequently washed with deionized water until neutral. The obtained black powder was named as CoN_4@N-PC-BMZIF.

D) Synthesis of Co NPs@NP-PC

$CoCl_2·6H_2O$ (0.10 g, 0.37 mmol) and 500 mg NP-PC were mixed into 8 mL of deionized water, and the mixture was stirred at 25 °C for 0.5 h. Subsequently, a freshly prepared 37.5 mL solution of NaOH (0.9 wt%) and $NaBH_4$ (0.9 wt%) was added dropwise and stirred for another 0.5 h. After the reaction concluded, the catalyst was washed repeatedly with deionized water until neutral, then vacuum-dried to obtain the Co NPs@NP-PC catalyst.

E) Synthesis of Co@NP-PC-a

Typically, $Co(OAc)_2·4H_2O$ (40 mg, 0.16 mmol) and PPh_3 (210 mg, 0.8 mmol) was dissolved in 60 mL of absolute ethanol. Subsequently, 650 mg of NP-PC was added and stirred at 60 ^oC for 4 h. The ethanol was then removed by vacuum evaporation. The resulting black powder was further dried at 60 ^oC and heated at 900 ^oC for 4 h with a heating rate of 2 ^oC/min under a flowing argon atmosphere in a tube furnace. The obtained black powder was named as Co@NP-PC-a.

F) Synthesis of Co@NP-PC-b

Typically, $Co(OAc)_2·4H_2O$ (40 mg, 0.16 mmol) and PPh_3 (210 mg, 0.8 mmol) was dissolved in 60 mL of absolute ethanol. Subsequently, 650 mg of ZIF-8 was added and stirred at 60 ^oC for 4 h. The ethanol was then removed by vacuum evaporation. The resulting black powder was further dried at 60 ^oC and heated to 900 ^oC for 4 h at a heating rate of 2 ^oC/min in a tube furnace under a flowing argon atmosphere. The obtained black powder was named as Co@NP-PC-b.

2. Catalyst characterization

Elemental analysis: The cobalt contents of the catalysts were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a PerkinElmer Avio 200 (OES) spectrometer. The samples were initially digested by high temperature pyrolysis and then dissolved in hot aqua regia.

X-ray diffraction (XRD) analysis: The crystal structures of the catalysts were characterized with powder X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer using a monochromatic Cu Kα (λ=1.5418 Å) source at 40 kV and 40 mA.

Transmission electron microscopy (TEM) images: TEM images were obtained using a FEI Tecnai G2 F20 S-Twin operating at 200 kV. Atomic-resolution HAADF-STEM images were acquired using a Nion UltraSTEM U100 operated at 60 kV.

X-ray photoelectron spectroscopy (XPS): The XPS measurements were performed using a Thermo Scientific K-Alpha equipped with a monochromatic Al Kα (1486.6 eV) source. The Mg Kα (hν = 1253.6 eV) was operated at 15 kV and 20 mA. The binding energy scale was calibrated taking, as a reference, the adventitious C 1s peak at 284.8 eV.

Brunauer Emmett-Teller (BET) analysis: The BET specific surface areas of the prepared catalysts were determined by adsorption-desorption of nitrogen at liquid nitrogen temperature, using Micromeritics ASAP 2460 equipment. Sample degassing was carried out at 250 °C for 6 h to acquiring the adsorption isotherm.

Raman spectroscopy. Raman spectra were collected on a HORIBA LabRAM HR Evolution high resolution Raman spectrometer. A 514.5 nm Ar^+ laser was used as the excitation source.

X-ray absorption structure (XAS) analysis: XAFS measurements at Co K-edge in transmission mode were performed at the BL14W1 in Shanghai Synchrotron Radiation Facility (SSRF). The electron beam energy was 3.5 GeV and the stored current was 230 mA (top-up). A 38-pole wiggler with the maximum magnetic field of 1.2 T inserted in the straight section of the storage ring was used. XAFS data were collected using a fixed-exit double-crystal Si (111) monochromator. Co foil was used as standard reference materials and the X-ray absorption data were recorded in transmission mode using ion chambers. The raw data analysis was performed using IFEFFIT software package according to the standard data analysis procedures. The spectra were calibrated, averaged, pre-edge background subtracted, and post-edge normalized using Athena program in IFEFFIT software package. After that, the Fourier transformation of k^2 weighted EXAFS oscillations, $k^2 \cdot \chi(k)$, from k space to R space was performed to obtain a radial distribution function. The data fitting was carried out using the Artemis program in IFEFFIT. The wavelet transform (WT) analysis was conducted using the FORTRAN program HAMA S7, developed by H. Funke and M. Chukalina. After running the code, the k-space file for each sample, containing data within the exact Fourier transformation range of k, was processed. This process automatically generated k-space spectra, R-space spectra, and continuous wavelet transform figures.

Electrochemical impedance spectroscopy (EIS): The electrochemical impedance spectroscopy (EIS) measurement was conducted on the Gamry INTERFACE 1010E under the applied potentials of 1.74 V (for $KHCO_3$ electrolyte) and 1.54 V vs RHE (for KF + KBi electrolyte) with the frequency ranging from 102 to 106 Hz.

Electron paramagnetic resonance (EPR): The EPR signals of H radicals (H·) trapped by DMPO were detected by a Bruker-A300 spectrometer. The catalyst was added into the reaction mixture and stirred for a specific duration. Then, the mixture was filtered to eliminate the catalyst, and DMPO was added. The EPR experiment was carried out at 77K under a nitrogen atmosphere.

FA temperature-programmed surface reaction mass spectrometry (TPSR-MS): The FA TPSR-MS were detected by a Microtrac BELCat II spectrometer.

3. Catalyst evaluation

3.1 Catalytic hydrodehalogenation (HDH) of 1-bromonaphthalene

In a typical procedure, **1a** (0.2 mmol, 41.4 mg), a specific amount of catalyst (metal 5.0 mol%) and a given amount of $HCOONH_4$ were mixed in 2 mL of solvent in a 50 mL autoclave. The autoclave was purged with N_2 three times and subsequently maintained at 0.1 MPa. The mixture was then stirred for a specified duration at a given temperature. Upon completion of the reaction, the autoclave was cooled to 25 ^{o}C, and the products were collected through centrifugation and analysed by a Agilent 1260 HPLC system equipped with a C8 column using phenol as internal standard. The C8 column was eluted with the solvent containing 60% acetonitrile and 40% water. In addition, the headspace gas was qualitatively analysed by GC (Agilent 6820 equipped with a TDX-01 column connected to a thermal conductivity detector using helium as carrier gas).

The yield of bromonaphthalene (**1b**) was calculated by the following equation:

$$\text{Yield (\%)} = \frac{\text{number of moles of 1b}}{\text{number of moles of 1a}} \times 100\%$$

3.2 Measurement of kinetic isotope effect

The kinetic isotope effect (KIE) studies were conducted by using deuterated formic acid and NEt_3, owing to the unavailability of deuterated ammonium formate.

In a typical procedure, **1a** (0.2 mmol, 41.4 mg), HCOOH (0.4 mmol, 18.4 mg), NEt_3 (0.4 mmol, 40.5 mg) and CoN_3P_1@NP-PC (or CoN_4@N-PC, Co 5 mol%) were mixed into 2 mL of $EtOH/H_2O$ (1.5 mL/0.5 mL) in a 50 mL autoclave. The autoclave was purged with N_2

three times and subsequently maintained at 0.1 MPa. The mixture was then heated to 120 °C and maintained for a specified duration. Upon completion of the reaction, the autoclave was cooled to 25 °C, and the products were collected through centrifugation. Finally, the yield of obtained product was determined by HPLC using phenol as internal standard. To test the value of KIE, HCOOD or DCOOH was replaced by HCOOH.

The initial TOF was calculated from the reaction rate at below 15% conversion of **1a** based on the total Co loading content in the catalyst. The TOF was calculated by the following equations:

$$\mathrm{TOF} = \frac{n_0 \cdot \mathrm{conv.}}{t \cdot n_{\mathrm{metal}}} \qquad \text{(S1)}$$

The KIE was calculated by the following equations:

$$\mathrm{KIE}_{HCOOH/HCOOD} = \mathrm{TOF}_{HCOOH}/\mathrm{TOF}_{HCOOD} \qquad \text{(S2)}$$

$$\mathrm{KIE}_{HCOOH/DCOOH} = \mathrm{TOF}_{HCOOH}/\mathrm{TOF}_{DCOOH} \qquad \text{(S3)}$$

Where n_0 was the initial molar of **1a**, conv. was the conversion of **1a**, n_{metal} was the molar of Co dosage, t is the reaction time.

3.3 Sole decomposition of formic acid

The sole decomposition of FA over the CoN_3P_1@NP-PC catalyst was assessed in a thermostatically controlled reaction vessel at a specified temperature. The vessel, equipped with a reflux condenser, was connected to an automatic gas burette, enabling the precise measurement of gas evolution volume under constant ambient pressure conditions.

Typically, FA (0.8 mmol, 36.8 mg), NEt_3 (0.8 mmol, 81.0 mg) (if needed), CoN_3P_1@NP-PC (or CoN_4@N-PC, Co 2.5 mol%) and 4 mL PC were added to a 10 mL round bottom flask to stir for a period at 110 ^{o}C. After the reaction, the ground gas passes through the measuring pipe phone to obtain the actual volume of gas generated by the reaction, and the decomposition rate of FA is further calculated. The initial TOF was calculated at below 15% conversion of FA based on the total Co loading content in the catalyst.

3.4 Radical quenching experiment

DMPO was used as selective scavenger for hydrogen radical (H·). **1a** (0.2 mmol, 41.4 mg), $HCOONH_4$ (0.4 mmol, 25.2 mg), DMPO (0.4 mmol, 45.3 mg) and CoN_3P_1@NP-PC (Co 5 mol%) were mixed into 2 mL of EtOH/H_2O (1.5 mL/0.5 mL) solvent in a 50 mL autoclave. The autoclave was purged with N_2 three times and subsequently maintained at 0.1 MPa. The mixture was then heated to 120 °C and stirred for a specified duration. Upon completion of the reaction, the autoclave was cooled to 25 °C, and the products were collected through centrifugation. Finally, the yield of obtained products were determined by HPLC using phenol as internal standard.

3.5 BPA spiking experiment

BPA was used as a selective poisoner for Pyrrolic N site. To prepare BPA-pre-adsorbed sample, CoN_3P_1@NP-PC and 46 mg BPA were mixed into 4 mL of EtOH solvent in a round-bottom flask and stirred at 25 °C for 1 h. The sample was collected by centrifugation and then dried at 25 °C overnight to obtain BPA-pre-adsorbed CoN_3P_1@NP-PC sample. Subsequently, **1a** (0.2 mmol, 41.4 mg), $HCOONH_4$ (0.4 mmol, 25.2 mg) and BPA-pre-adsorbed CoN_3P_1@NP-PC sample (Co 5 mol%) were mixed into 2 mL of EtOH/ H_2O (1.5 mL/0.5 mL) in a 50 mL autoclave. The autoclave was purged with N_2 three times and subsequently maintained at 0.1 MPa. The mixture was then heated to 120 °C and stirred for a specified duration. Upon completion of the reaction, the autoclave was cooled to 25 °C, and the products were collected through centrifugation. Finally, the yield of obtained products were determined by HPLC using phenol as internal standard.

3.6 Procedure for catalyst recycling

Before the next test cycle, the used CoN_3P_1@NP-PC catalyst was regenerated in argon atmosphere at 400 °C for 2 h. Subsequently, **1a** (0.2 mmol, 41.4 mg), catalyst (5.0 mol%), $HCOONH_4$ (0.4 mmol, 25.2 mg) and 2 mL of EtOH/H_2O (1.5 mL/0.5mL) solvent were added into a 50 mL autoclave. The autoclave was purged with N_2 three times and subsequently maintained at 0.1 MPa. The mixture was then heated to 120 °C and stirred for 2 h. At the end of the reaction, the catalyst was separated by centrifugation, washed with alcohol, followed by drying in vacuo before the next test cycle.

3.7 Sole decomposition of $HCOONH_4$

Typically, $HCOONH_4$ (0.4 mmol, 25.2 mg) and CoN_3P_1@NP-PC (Co 2.5 mol%) were mixed in 2 mL of solvent in a 50 mL autoclave. The autoclave was purged with N_2 three times and subsequently maintained at 0.1 MPa. The mixture was then stirred for a specified duration at 120 °C. Upon completion of the reaction, the autoclave was cooled to 25 °C. The conversion of $HCOONH_4$ were analyzed by a Agilent 1260 HPLC system equipped with a Aminex HPX-87 column using propionic acid as internal standard. The Aminex HPX-87 column was eluted with the solvent containing 20% dilute H_2SO_4 and 80% water.

4. Supplementary data (Fig. S1-15/Table S1-7)

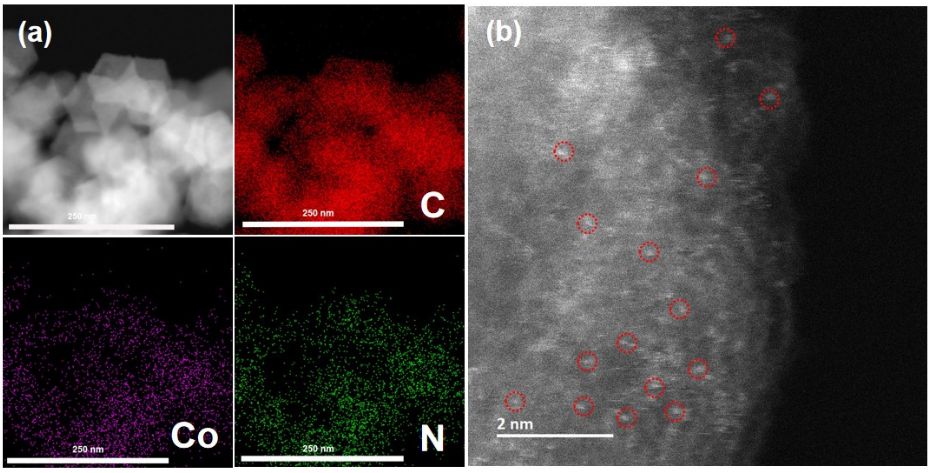


Fig. S1 (a) TEM image of CoN_4@N-PC and the corresponding elemental mappings of C, Co and N. (b) Aberration-corrected HAADF-STEM image of CoN_4@N-PC (single atoms are highlighted by red circles).

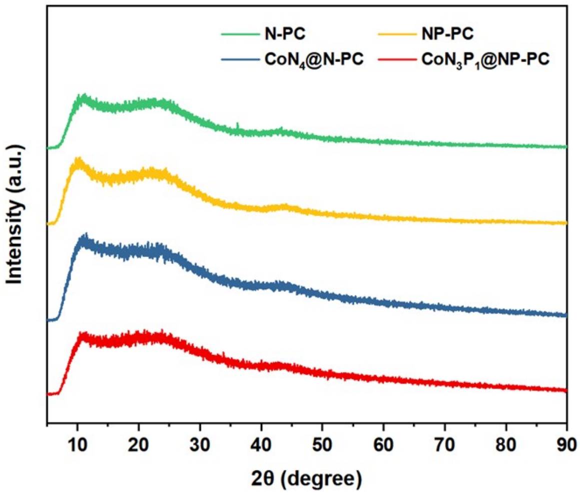


Fig.S2 XRD patterns of N-PC, NP-PC, CoN_4@N-PC and CoN_3P_1@NP-PC.

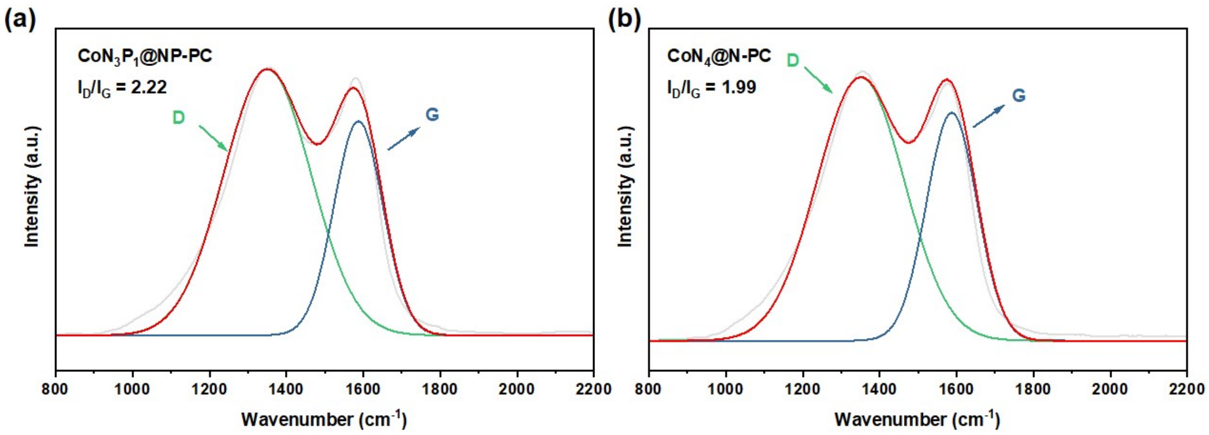


Fig. S3 Raman spectra of the CoN_3P_1@NP-PC (a) and CoN_4@N-PC (b).

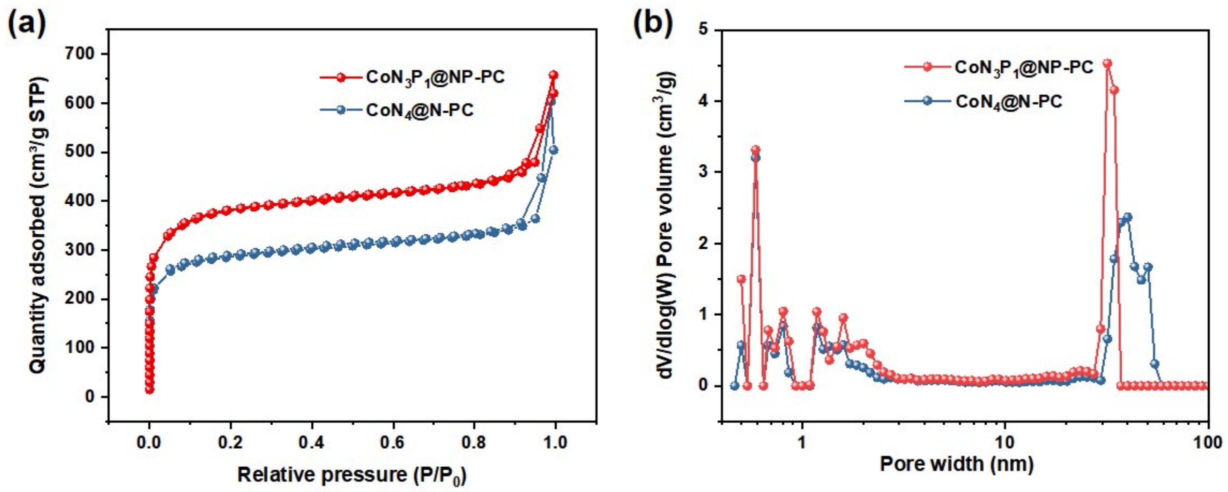


Fig. S4 N_2 adsorption/desorption isotherms (a) and pore distribution curves (b) of the CoN_3P_1@NP-PC and CoN_4@N-PC. The pore size distribution was determined from non-local density functional theory (NLDFT) model of the N_2 adsorption data.

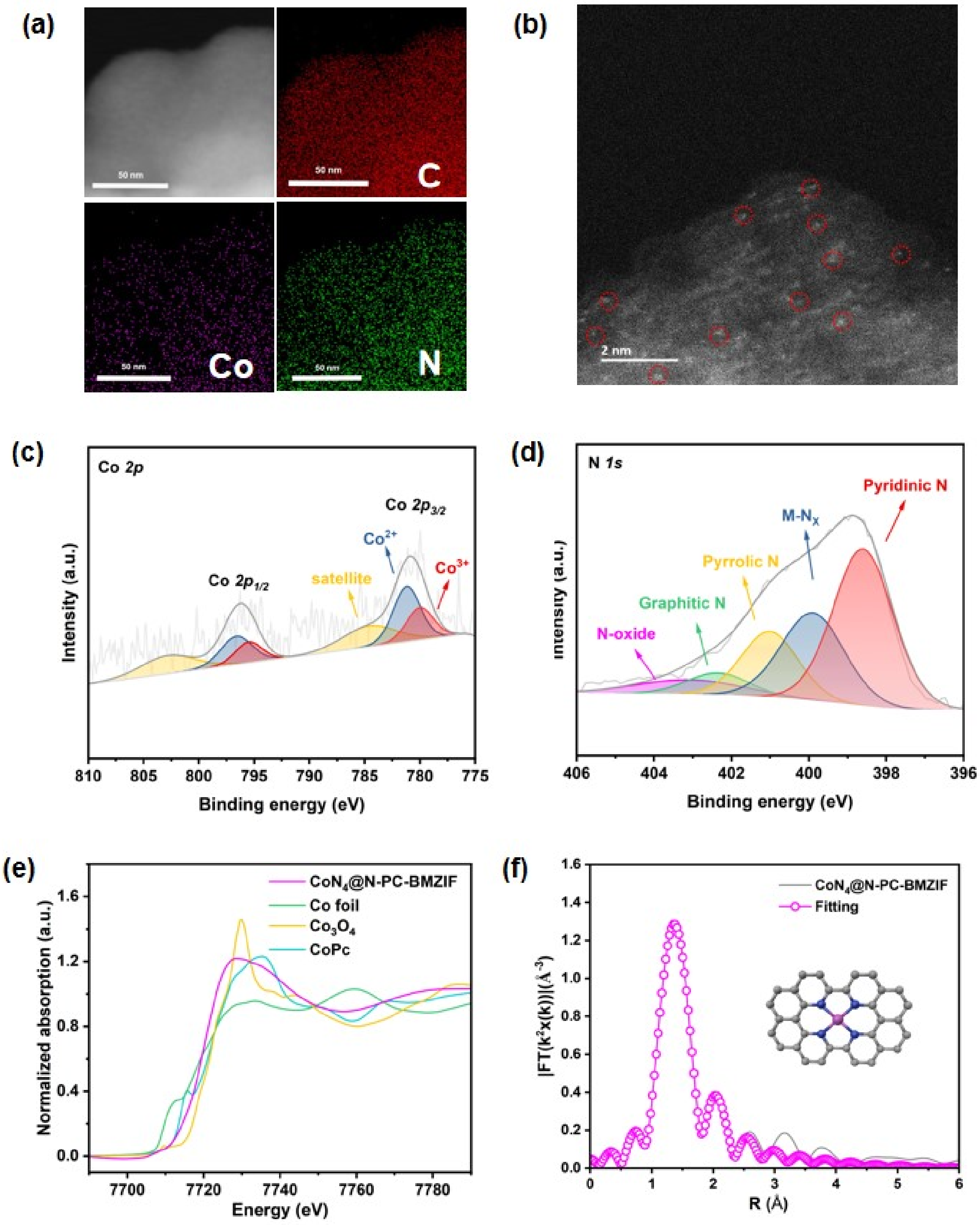


Fig. S5 Characterizations of CoN_4@N-PC-BMZIF. (a) TEM images and corresponding elemental mapping images of C, Co and N. (b) Aberration-corrected HAADF-STEM image of CoN_4@N-PC-BMZIF (single atoms are highlighted by red circles). (c) Co 2p XPS spectrum. (d) N 1s XPS spectrum. (e) Co K-edge XANES spectra of CoN_4@N-PC-BMZIF and reference samples. (f) R-space Co K-edge EXAFS spectrum and fitting of CoN_4@N-PC-BMZIF. The fitting results are listed in Table S3.

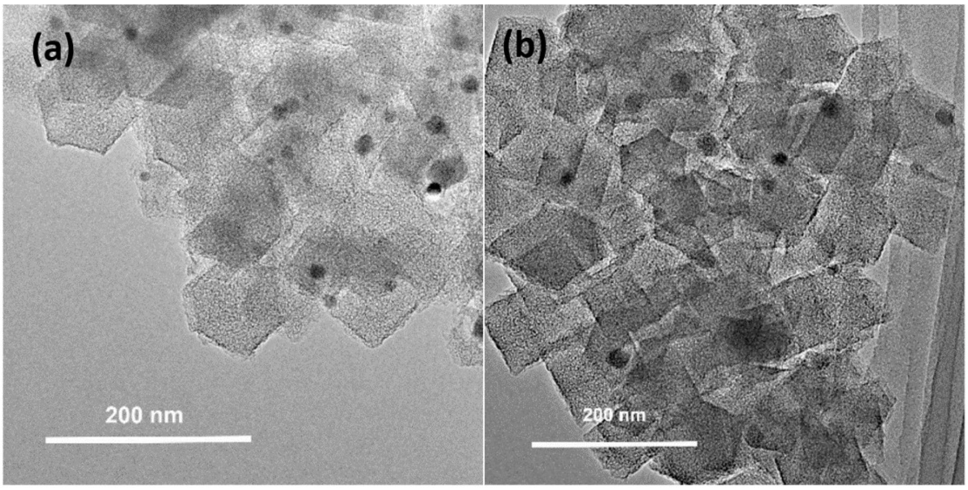


Fig. S6 TEM images of Co@NP-PC-a (a) and Co@NP-PC-b (b).

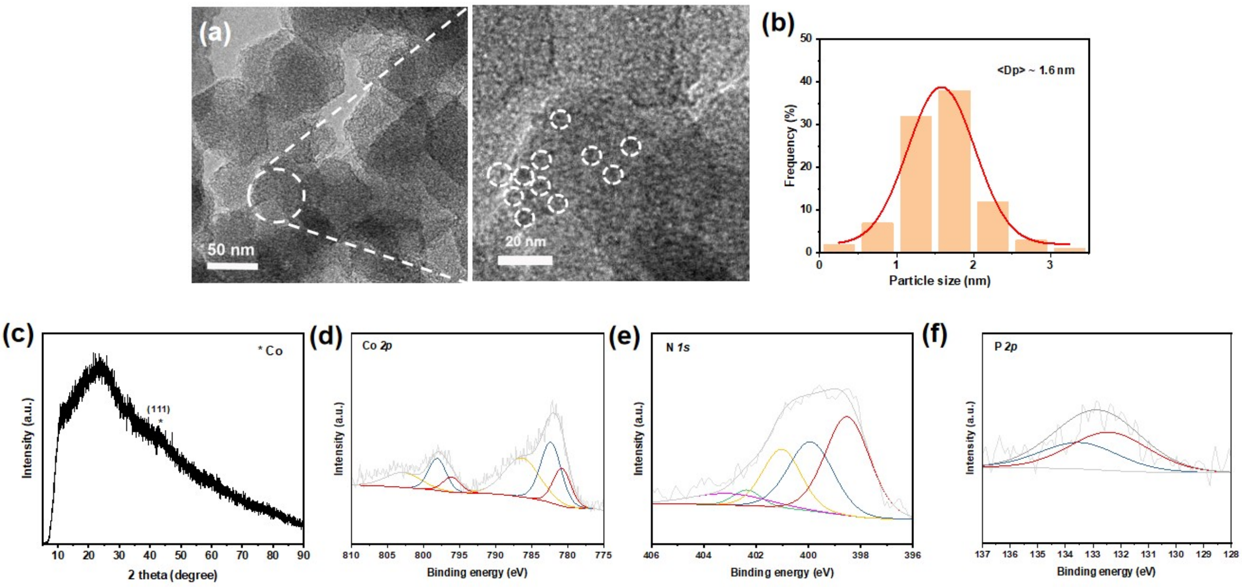


Fig. S7 Characterizations of Co NPs@NP-PC. (a) STEM images. (b) Particle size distribution diagram based on STEM images. The average size of Co particles is about 1.6 nm. (c) XRD pattern. (d) Co 2p XPS spectrum. (e) N 1s XPS spectrum. (f) P 2p XPS spectrum**.**

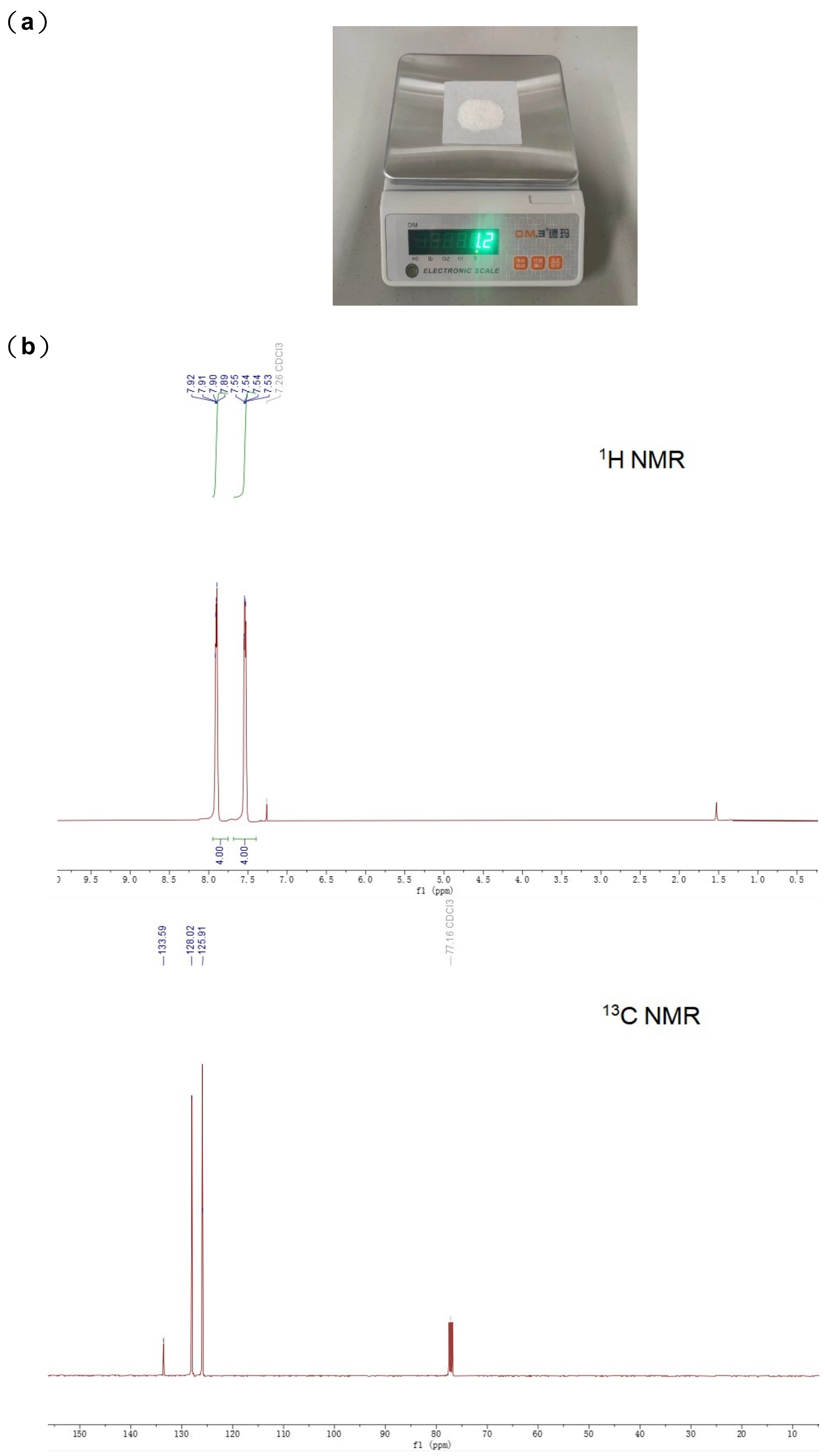


Fig. S8 Gram-scale experiment. (a) Isolated **1b** yield. (b) ^{1}H NMR and ^{13}C NMR spectra of isolated **1b** in $CDCl_3$.

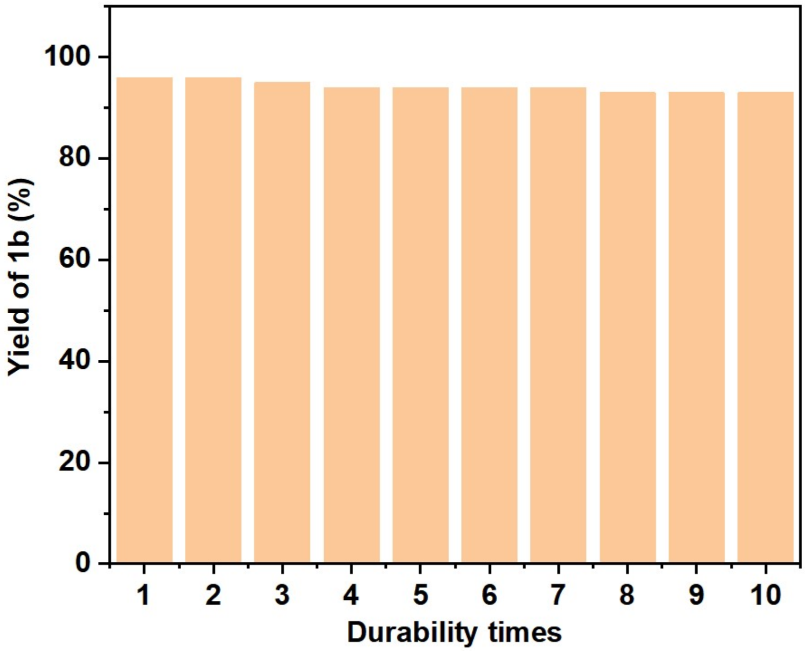


Fig. S9 Large-scale durability of CoN_3P_1@NP-PC catalyst for HDH of **1a**. Reaction conditions: **1a** 10 mmol, $HCOONH_4$ 2 equiv., CoN_3P_1@NP-PC (Co 1 mol%), EtOH/H_2O (75 mL/25 mL), N_2 0.1 MPa, 120 ^oC, 48 h.

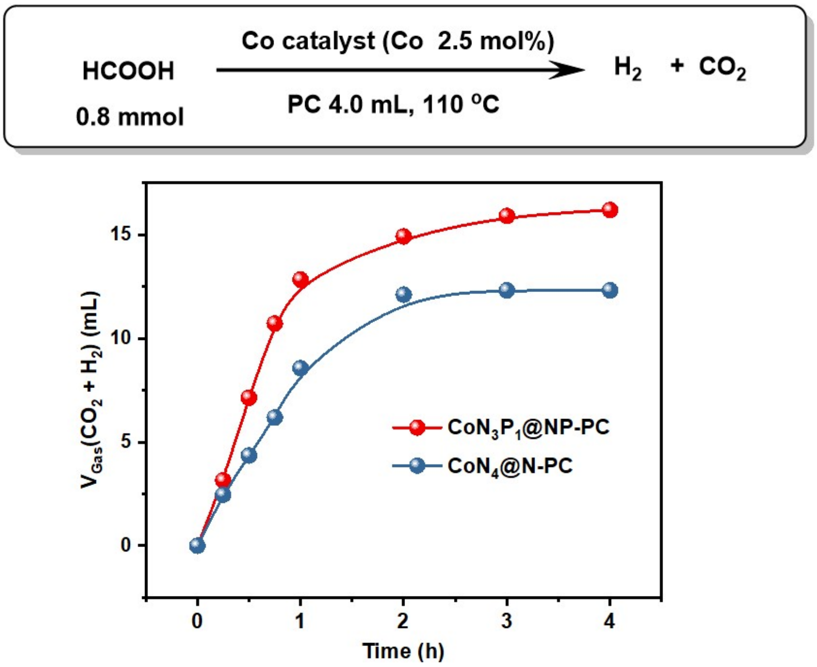


Fig. S10 Time-course of gas volume formed from FA decomposition over CoN_3P_1@NP-PC and CoN_4@N-PC. Reaction conditions: FA 0.8 mmol, Co catalyst (Co 2.5 mol%), PC 4 mL, 110 °C.

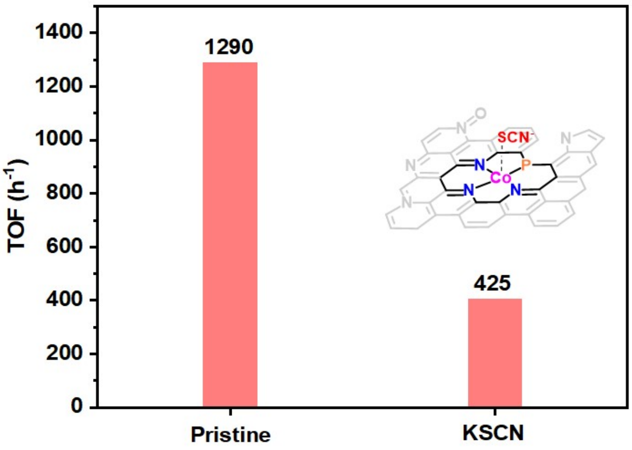


Fig. S11 KSCN poisoning experiment. Reaction conditions: FA 0.8 mmol, CoN_3P_1@NP-PC (Co 2.5 mol%), KSCN 20 equiv. of Co sites, PC 4 mL, 110 °C. The initial TOF was calculated at below 15% conversion of FA based on the total Co loading content in the catalyst.

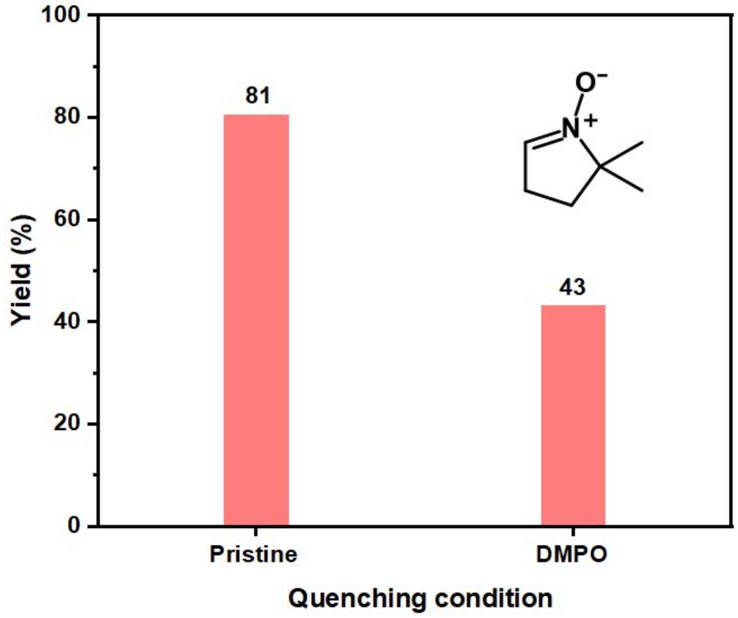


Fig. S12 Effect of DMPO (**H**· scavenger) on HDH of **1a**. Reaction conditions:**1a** 0.2 mmol, $HCOONH_4$ 2 equiv., Co 5 mol%, DMPO 2 equiv., EtOH/H_2O (1.5 mL/0.5 mL), N_2 0.1 MPa, 120 ^oC, 1.5 h. The yield was determined by HPLC with phenol as internal standard substance.

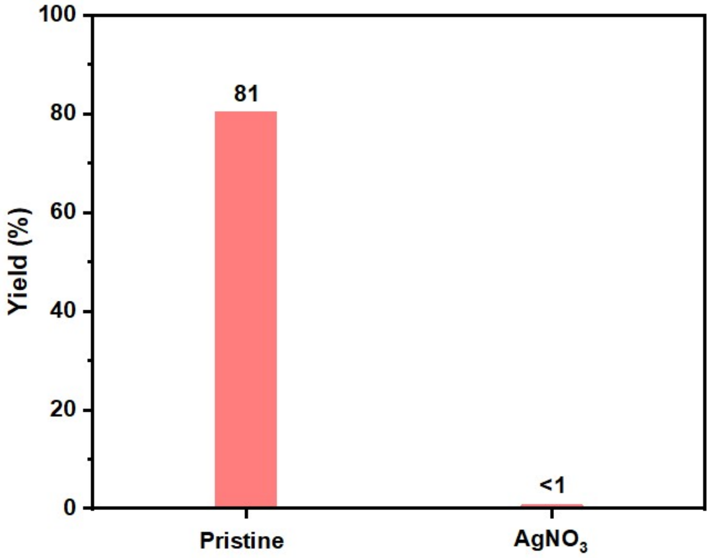


Fig. S13 Effect of $AgNO_3$ (electron trapping agent) on HDH of **1a**. Reaction conditions: **1a** 0.2 mmol, $HCOONH_4$ 2 equiv., Co 5 mol%, $AgNO_3$ 2 equiv., EtOH/H_2O (1.5 mL/0.5 mL), N_2 0.1 MPa, 120 ^oC, 1.5 h. The yield was determined by HPLC with phenol as internal standard substance.

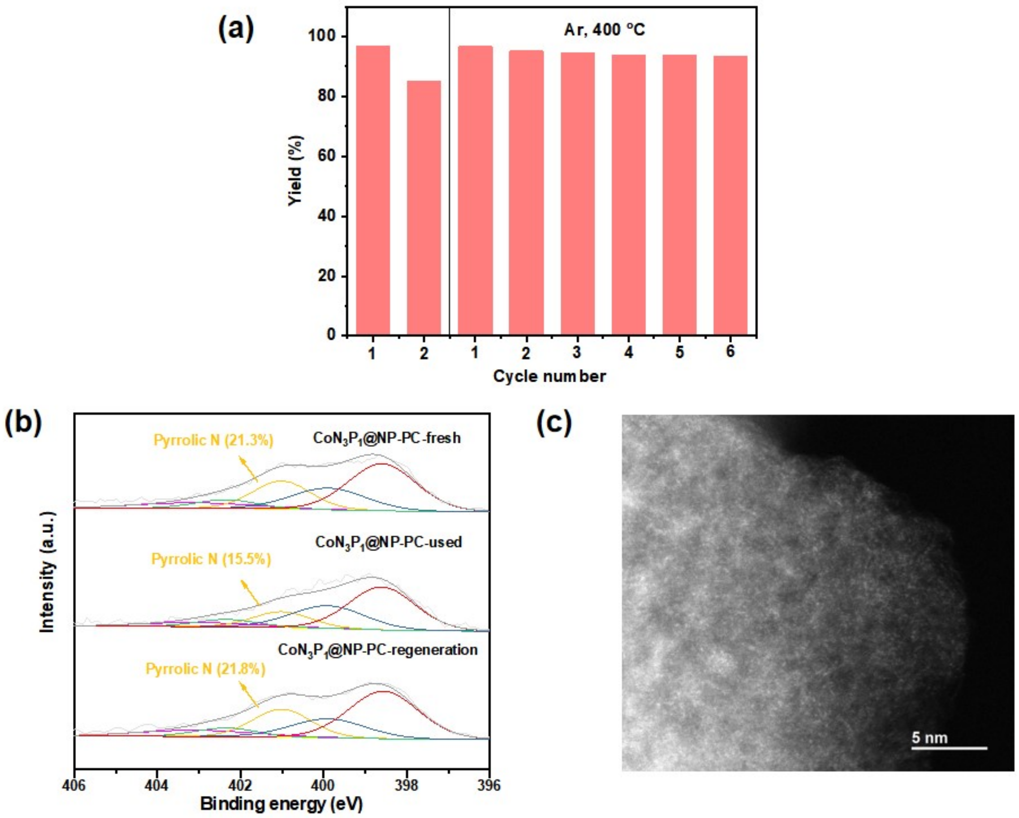


Fig. S14 (a) The reuse of CoN$_3$P$_1$@NP-PC catalyst in the HDH of **1a**. Reaction conditions: **1a** 0.2 mmol, HCOONH$_4$ 2 equiv., CoN$_3$P$_1$@NP-PC (Co 5 mol%), EtOH/H$_2$O (1.5 mL/0.5 mL), N$_2$ 0.1 MPa, 120 ^{o}C, 2 h. Regeneration pretreatment was repeated before each recycling test; regeneration conditions: Ar, 400 ^{o}C, 2 h. (b) High-resolution XPS spectra of N 1s for CoN$_3$P$_1$@NP-PC before, after the reaction, and after regeneration. (c) Aberration-corrected HAADF-STEM image of CoN$_3$P$_1$@NP-PC after regeneration.

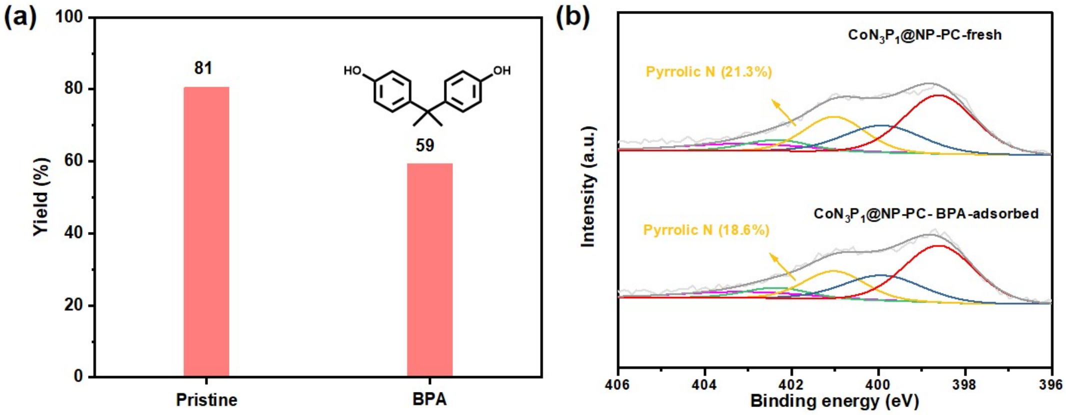


Fig. S15 (a) Effect of BPA (Pyrrolic N blocker) on HDH of **1a**. Reaction conditions: **1a** 0.2 mmol, HCOONH$_4$ 2 equiv., BPA-soaked CoN$_3$P$_1$@NP-PC (Co 5mol%), EtOH/H$_2$O (1.5 mL/0.5 mL), N$_2$ 0.1 MPa, 120 ^{o}C, 1.5 h. The yield was determined by HPLC with phenol as internal standard substance. (b) High-resolution XPS spectra of N 1s for CoN$_3$P$_1$@NP-PC before and after adsorption of BPA.

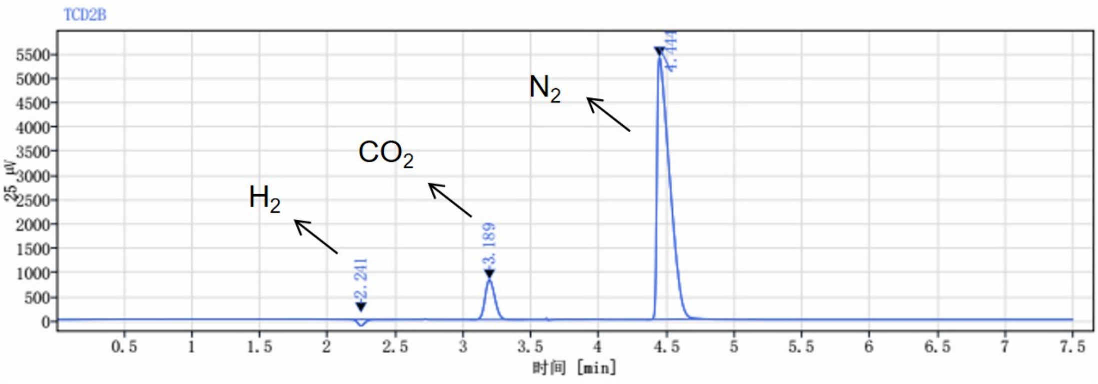


Fig. S16 Gas chromatogram of the headspace gas at the end of the reaction.

Table S1. The texture properties of the different Co catalysts.

Sample	SBET ($m^2 \cdot g^{-1}$) [a]	Pore volume ($cm^3 \cdot g^{-1}$)	V_{micro} ($cm^3 \cdot g^{-1}$)	V_{meso} ($cm^3 \cdot g^{-1}$)	Average pore size (nm) [b]
CoN_3P_1@NP-PC	1415	0.96	0.48	0.55	7.50
CoN_4@N-PC	1083	0.78	0.35	0.57	11.27
CoN_4@N-PC-BMZIF	893	0.71	0.31	0.40	11.11
Co NPs@NP-PC	1156	1.01	0.43	0.63	11.38

[a] Specific surface areas were determined by the BET multipoint method. [b] Average pore sizes were obtained by the BJH method.

Table S2. The elements atomic contents in different Co catalysts.

Sample	XPS analysis						ICP-OES
	C (at%)	N (at%)	O (at%)	Co (at%)	P (at%)	Zn (at%)	Co (wt%)
CoN_3P_1@NP-PC	85.99	5.15	7.84	0.30	0.32	0.40	1.49
CoN_4@N-PC	87.16	4.82	7.40	0.28	---	0.34	1.51
CoN_4@N-PC-BMZIF	79.60	7.11	12.72	0.10	---	0.47	1.45
Co NPs@NP-PC	79.44	9.68	9.02	0.64	0.44	0.78	3.11

Table S3. EXAFS fitting parameters for various samples.

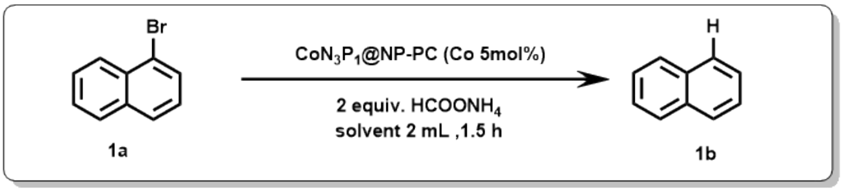
Sample	**Shell**	**CN**^{a}	**R[Å]**^{b}	**σ^{2}** ^{c}	**ΔE_0**^{d}	**R facto**^{e}
Co-foil	Co-Co	12	2.49	0.0063	7.2	0.001
CoO	Co-O	6	2.12	0.0125	-3.1	0.007
	Co-Co	12	3.00	0.0088		
CoPc	Co-N	4	1.91	0.0023	6.4	0.012
CoP	Co-P1	3	2.24	0.0020	1.4	0.015
	Co-P2	3	2.39	0.0026		
Co_2O_3	Co-O	5.5	1.91	0.0034	-5.9	0.004
	Co-Co1	5	2.86	0.0049		
	Co-Co2	8	3.37	0.0067		
CoN_3P_1@NP-PC	Co-N	2.8	1.93	0.0060	-5.3	0.003
	Co-P	1.0	2.29	0.0074		
CoN_4@N-PC	Co-N	4.3	1.89	0.0070	-10.3	0.011
CoN_4@N-PC-BMZIF	Co-N	4.5	1.91	0.0030	-9.1	0.005

^{a} CN: coordination numbers; ^{b} R: the average bond distance; ^{c} σ^2: Debye-Waller factors; ^{d} ΔE_0: the inner potential correction. ^{e} R factor: the fitting quality.

Table S4. CoN_3P_1@NP-PC catalyst compared with reported representative heterogeneous catalytic systems for HDH of 1-bromonaphthalene or 2-bromonaphthalene.

Entry	Catalyst	Substrate	Metal amount (mol%)	H-Source	Additive	Temp. (°C)	t (h)	Yield (%)	TON	$TOF_{Avg.}$	Ref.
1	Co-Co_3O_4@Chitosan-700	2-bromonaphthalene	6.0	H_2 (3 MPa)	NEt_3 (2 equiv.)	120	48	90	15	0.3	1
2	PANI/Fe^0-2	1-bromonaphthalene	2.5	*t*-BuMgCl (4 equiv.)	---	40	7	78	31	4.5	2
3	CuO/ZrO_2	1-bromonaphthalene	7.9	1-octanol (solvent）	*t*-BuOK (1.2 equiv.)	140	15	95.6	6	0.4	3
4	Ni-Phen@TiO_2-800	1-bromonaphthalene	3	H_2 (2 MPa)	NEt_3 (1.25 equiv.)	45	20	92	31	1.5	4
5	CoN_3P_1@NP-PC	1-bromonaphthalene	5	$HCOONH_4$ (2 equiv.)	---	120	2	96	19	10	This work
		2-bromonaphthalene	5	$HCOONH_4$ (2 equiv.)	---	120	3	96	19	6.4	This work

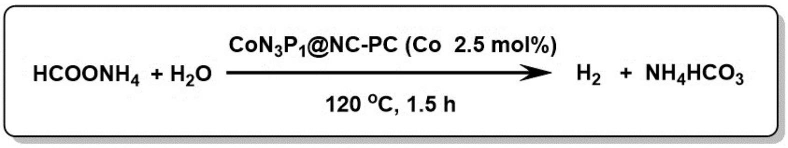
Table S5. Reaction conditions optimization for HDH of **1a**.[a]



Entry	Catalyst	Organic solvent	Temp. (°C)	Yield (%) [b]
1	CoN_3P_1@NP-PC	EtOH	120	81
2	CoN_3P_1@NP-PC	MeCN	120	72
3	CoN_3P_1@NP-PC	1, 4-dioxane	120	58
4	CoN_3P_1@NP-PC	acetone	120	51
5	CoN_3P_1@NP-PC	toluene	120	16
6	CoN_3P_1@NP-PC	hexane	120	12
7	CoN_3P_1@NP-PC	EtOH	80	17
8	CoN_3P_1@NP-PC	EtOH	100	39
9	CoN_3P_1@NP-PC	EtOH	140	85
10 [c]	CoN_3P_1@NP-PC	EtOH	120	70

[a] Reaction conditions: **1a** 0.2 mmol, $HCOONH_4$ 2 equiv., CoN_3P_1@NP-PC (Co 5 mol%), organic solvent/H_2O (1.5 mL/0.5 mL), N_2 0.1 MPa, 1.5 h. [b] The yield was determined by HPLC with phenol as internal standard substance. [c] $HCOONH_4$ 1 equiv., 2 h.

Table S6. The effect of solvent for decomposition of ammonium formate. [a]



Entry	Catalyst	Solvent	Conv. (%) [b]
1	CoN_3P_1@NP-PC	EtOH/H_2O (2.0/0)	70
2	CoN_3P_1@NP-PC	EtOH/H_2O (1.5/0.5)	89
3	CoN_3P_1@NP-PC	EtOH/H_2O (1.0/1.0)	63
4	CoN_3P_1@NP-PC	EtOH/H_2O (0.5/1.5)	44
5	CoN_3P_1@NP-PC	EtOH/H_2O (0/2.0)	37
6	CoN_3P_1@NP-PC	MeCN/H_2O (1.5/0.5)	77
7	CoN_3P_1@NP-PC	1, 4-dioxane/H_2O (1.5/0.5)	60
8	CoN_3P_1@NP-PC	acetone/H_2O (1.5/0.5)	53
9	CoN_3P_1@NP-PC	toluene/H_2O (1.5/0.5)	18
10	CoN_3P_1@NP-PC	hexane/H_2O (1.5/0.5)	22

[a] Reaction conditions: $HCOONH_4$ 0.4 mmol, CoN_3P_1@NC-PC (Co 2.5 mol%), organic solvent/H_2O (1.5 mL/0.5 mL), 120 °C, N_2 0.1 MPa, 1.5 h. [b] The conversation was determined by HPLC with propionic acid as internal standard substance.

Table S7. Kinetic isotope effect study for HDH of **1a** over $\mathrm{CoN_3P_1}$@NP-PC and $\mathrm{CoN_4}$@N-PC catalysts.[a]

Entry [a]	**Catalyst**	**FA**	**TOF (h^{-1})** [b]	**KIE** [c]
1	$\mathrm{CoN_3P_1}$@NP-PC	HCOOH	30.5	---
2		HCOOD	29.3	1.04
3		DCOOH	20.7	1.47
4	$\mathrm{CoN_4}$@N-PC	HCOOH	23.5	---
5		HCOOD	21.4	1.10
6		DCOOH	11.6	2.03

Reaction conditions: **1a** 0.2 mmol, FA 2 equiv., Co 5 mol%, NEt_3 2 equiv., EtOH/H_2O (1.5mL/0.5 mL), N_2 0.1 MPa, 120 °C. [b] TOF was measured at **1a** conversion below 15% based on total Co atoms. [c] KIE = TOF (entry 1)/TOF (entry 2) or TOF (entry 1)/TOF (entry 3) or TOF (entry 4)/TOF (entry 5) or TOF (entry 4)/TOF (entry 6).

Table S8 The relative contents of different N species based on XPS of $\mathrm{CoN_3P_1}$@NP-PC and reference samples.

Sample	**Relative concentrations of different N species**					**Total N (at %)**
	Pyridinic N (%)	**Co-N_X (%)**	**Pyrrolic N (%)**	**Graphitic N(%)**	**N-oxide (%)**	
$\mathrm{CoN_3P_1}$@NP-PC-fresh	41.7	21.1	21.3	7.1	8.8	5.15
$\mathrm{CoN_3P_1}$@NP-PC-used	43.9	22.9	15.5	8.3	9.4	4.80
$\mathrm{CoN_3P_1}$@NP-PC-**1a**-adsorped	43.2	23.6	16.1	8.0	9.1	4.55
$\mathrm{CoN_3P_1}$@NP-PC-BPA-adsorped	41.8	22.6	18.6	7.8	9.2	4.74
$\mathrm{CoN_3P_1}$@NP-PC-regeneration	42.0	21.0	21.8	7.0	8.2	5.10

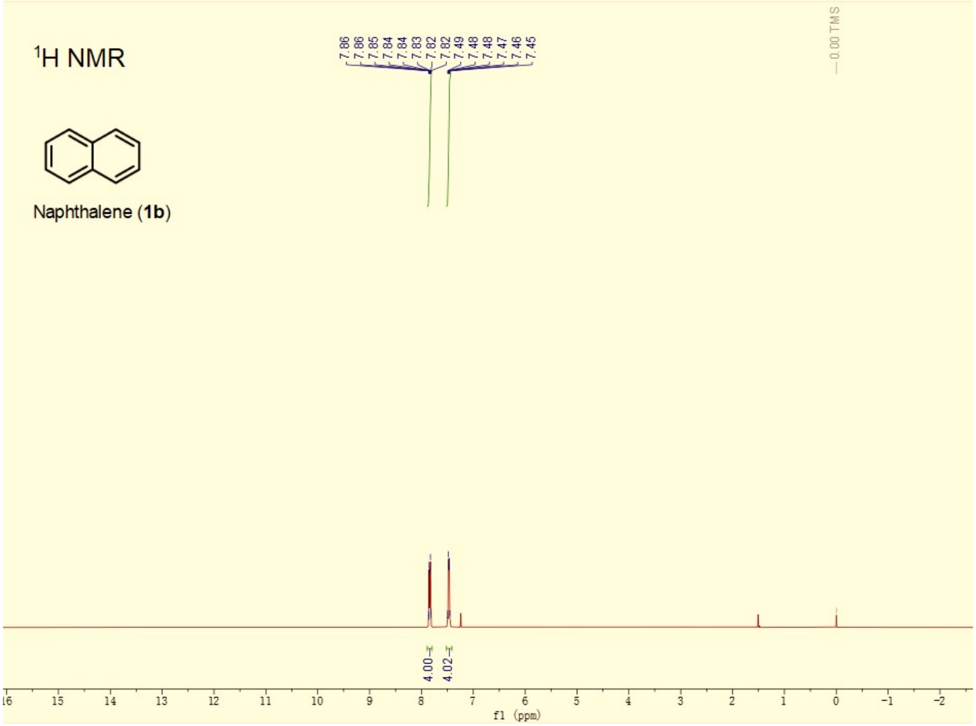
Table S9 The decomposition of ammonium formate under optimal condition. [a]

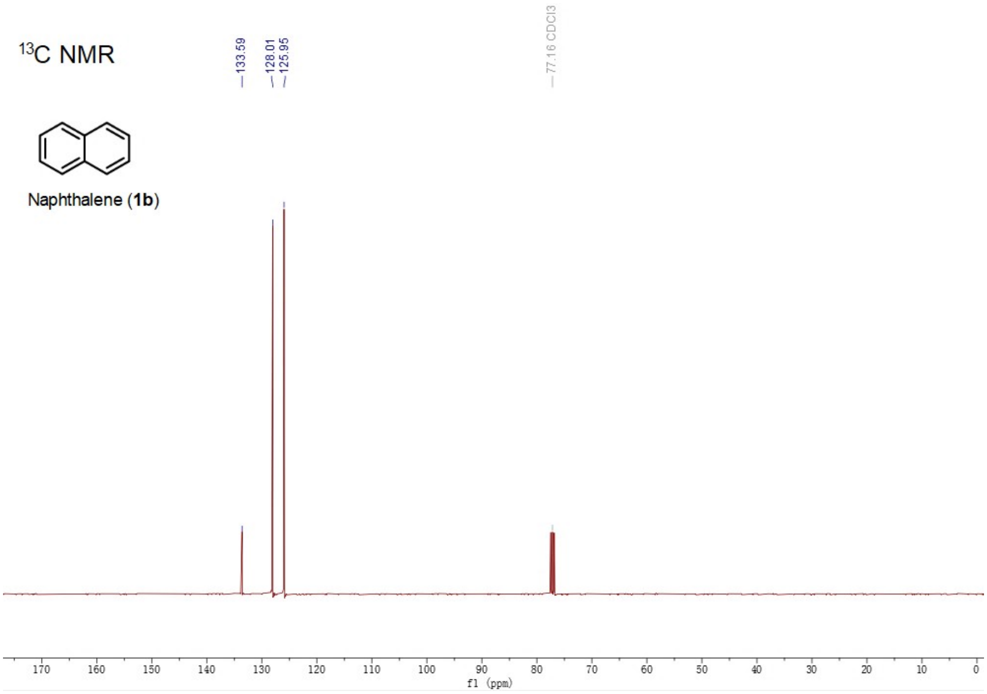
Entry	Initial $HCOONH_4$ (mmol)	Residual $HCOONH_4$ (mmol)
1	0.4	N.D.

[a] Reaction conditions: $HCOONH_4$ 0.4 mmol, **1a** 0.2 mmol, CoN_3P_1@NC-PC (2.5 mol% Co based on $HCOONH_4$), EtOH/H_2O (1.5 mL/0.5 mL), 120 ^oC, N_2 0.1 MPa, 2 h. [b] Residual $HCOONH_4$ at the end of the reaction was determined using potentiometric titration (titration end at pH = 2.4) with 0.5 M HCl. [5,6] Titrations of standard showed that the error of this method was determined to be ±15%.

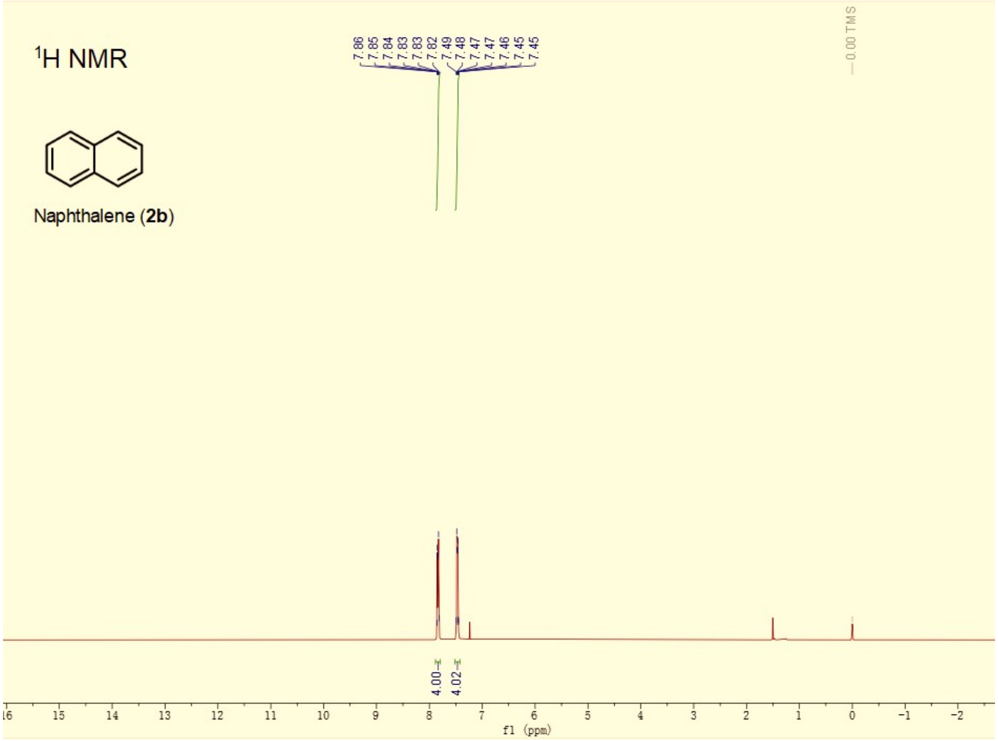
5. Characterization data of isolated products

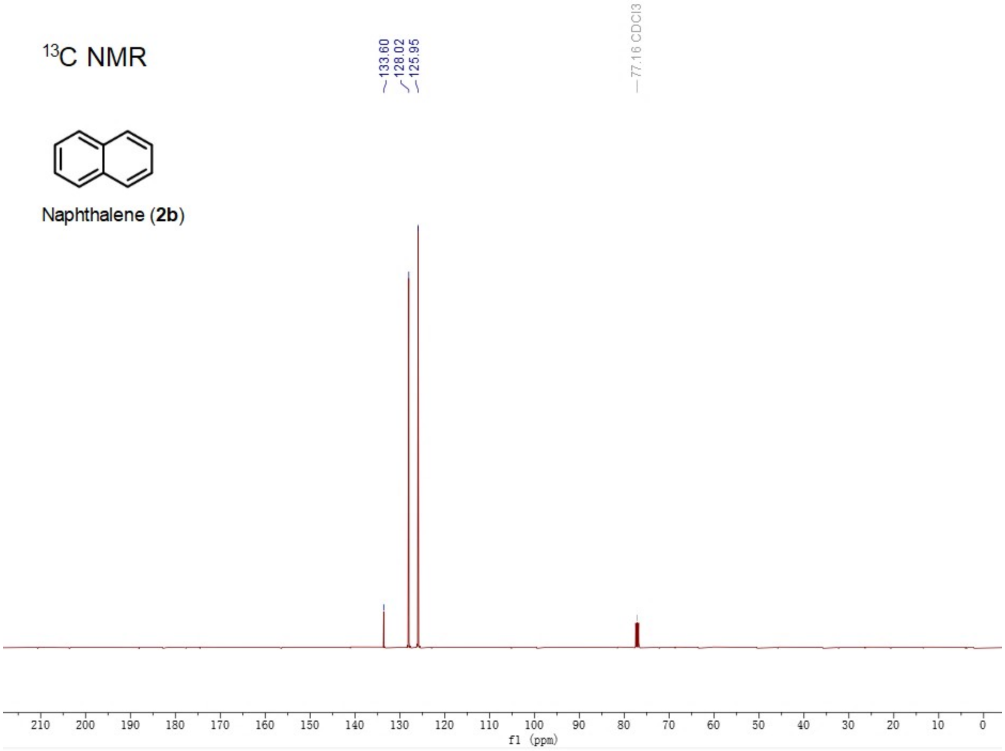
5.1 NMR spectra



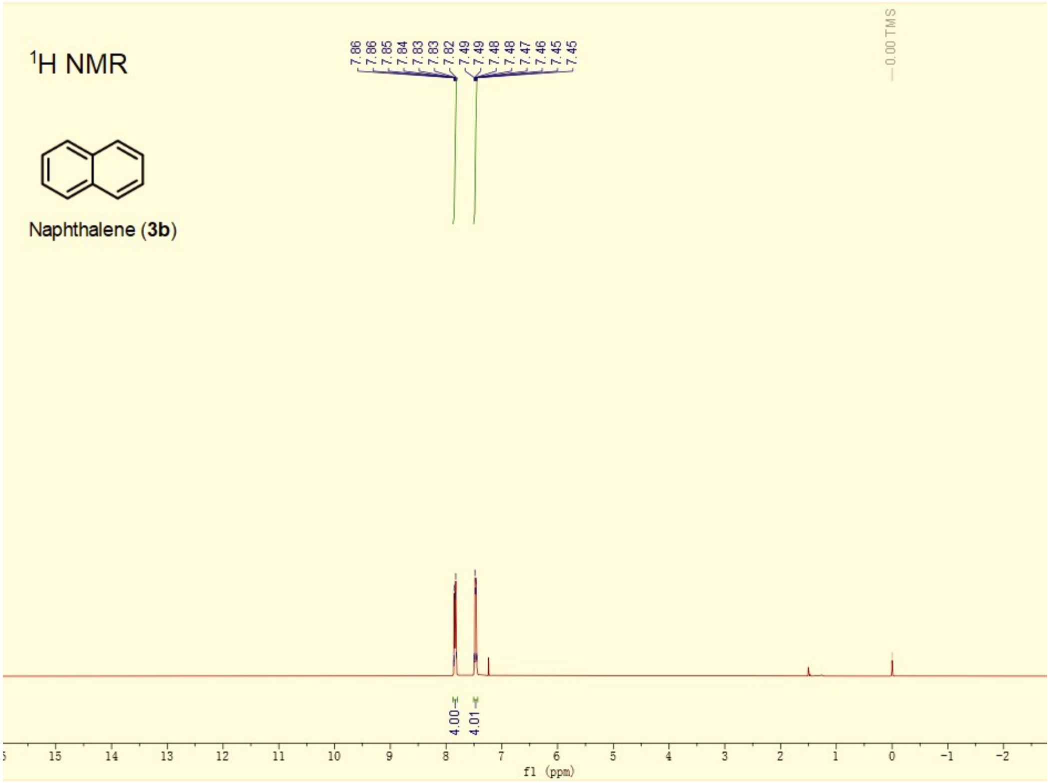


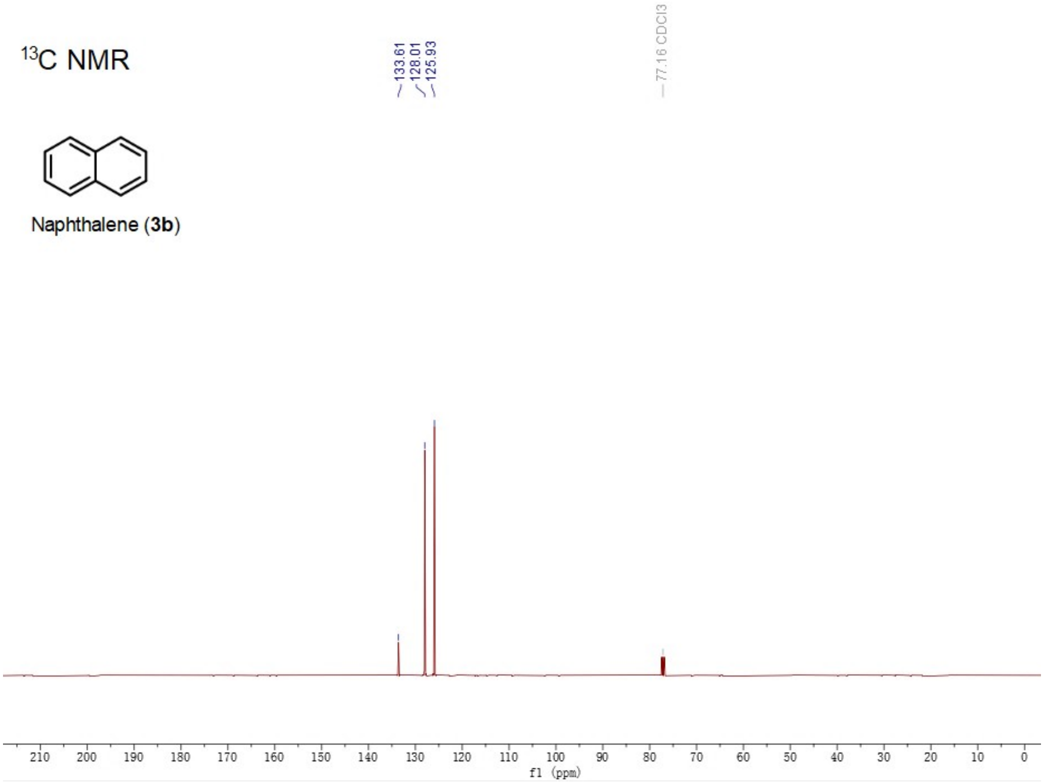
Naphthalene (**1b**). **^{1}H NMR (400 MHz, CDCl$_3$):** δ (ppm) = 7.87-7.81 (m, 4H), 7.50-7.44 (m, 4H); **^{13}C NMR (101 MHz, CDCl$_3$)**：δ (ppm) = 133.59, 128.01, 125.95.



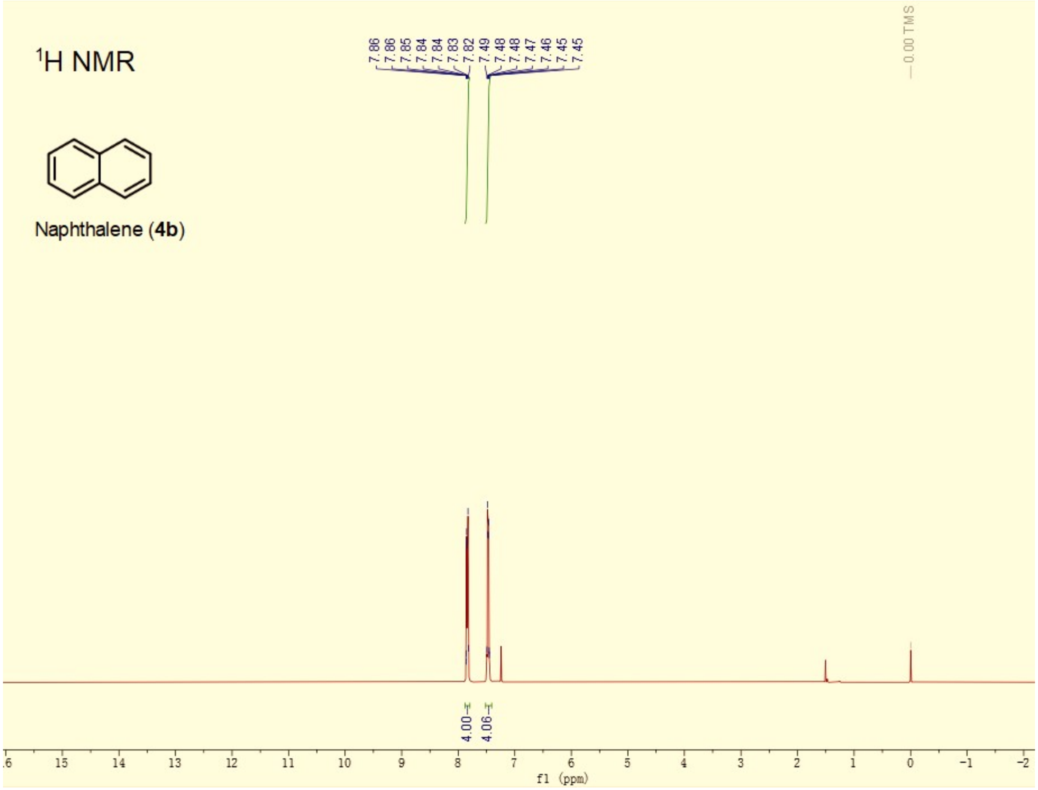


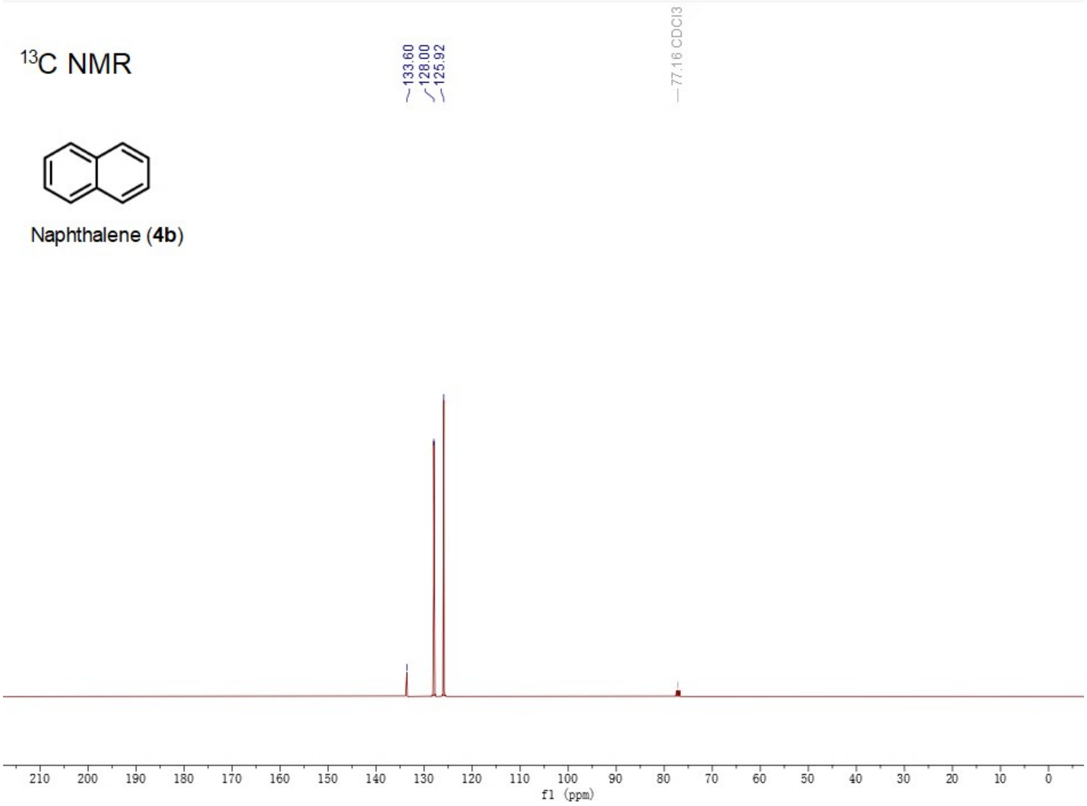
Naphthalene (**2b**). **^{1}H NMR (400 MHz, CDCl$_3$):** δ (ppm) = 7.87-7.81 (m, 4H), 7.50-7.44 (m, 4H); **^{13}C NMR (101 MHz, CDCl$_3$)**: δ (ppm) = 133.60, 128.02, 125.95.



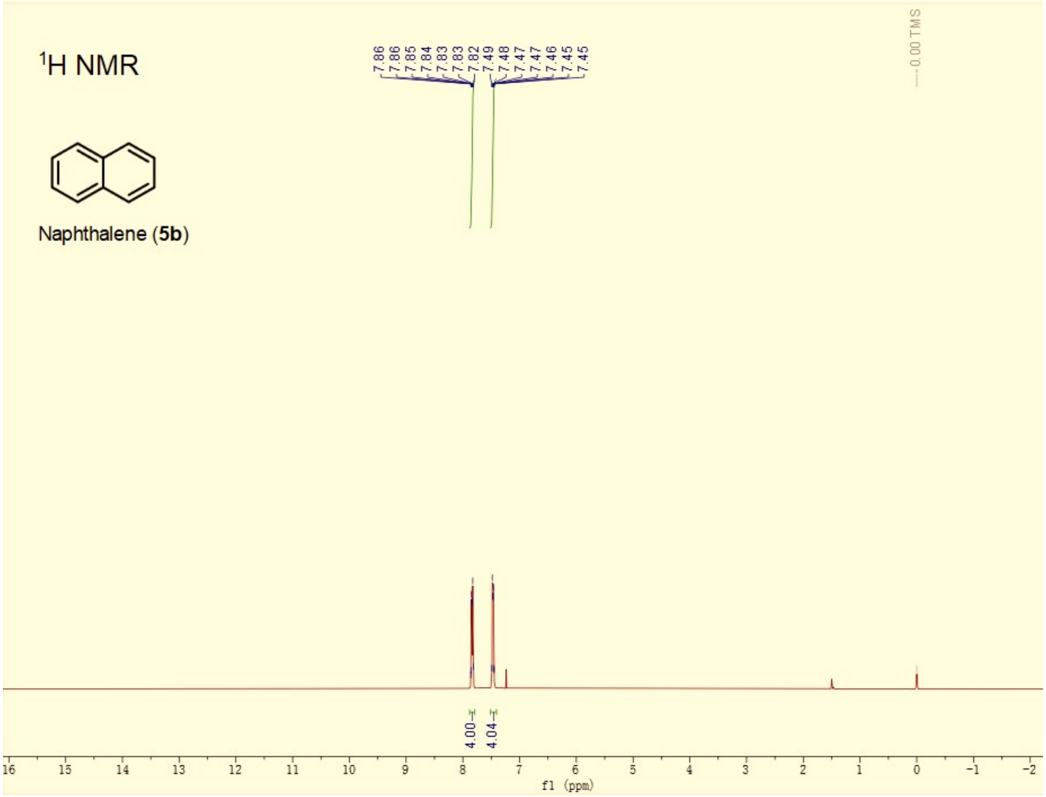


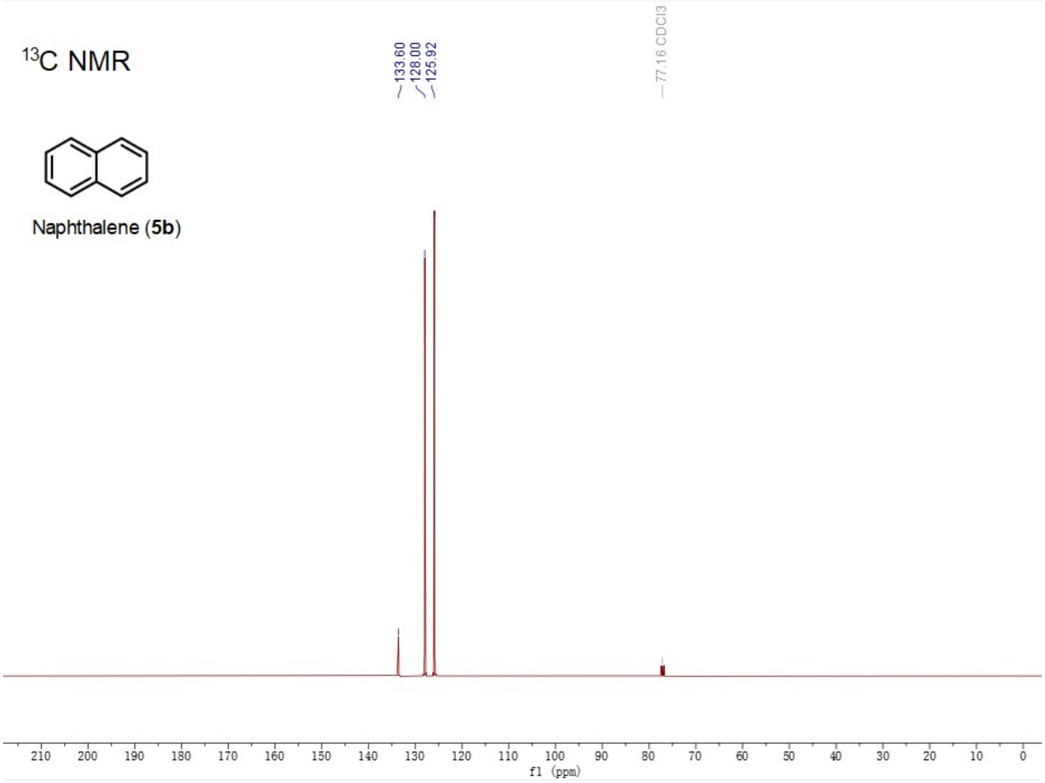
Naphthalene (**3b**). **^{1}H NMR (400 MHz, CDCl$_3$):** δ (ppm) = 7.88-7.80 (m, 4H), 7.51-7.43 (m, 4H); **^{13}C NMR (101 MHz, CDCl$_3$)**: δ (ppm) = 133.61, 128.01, 125.93.



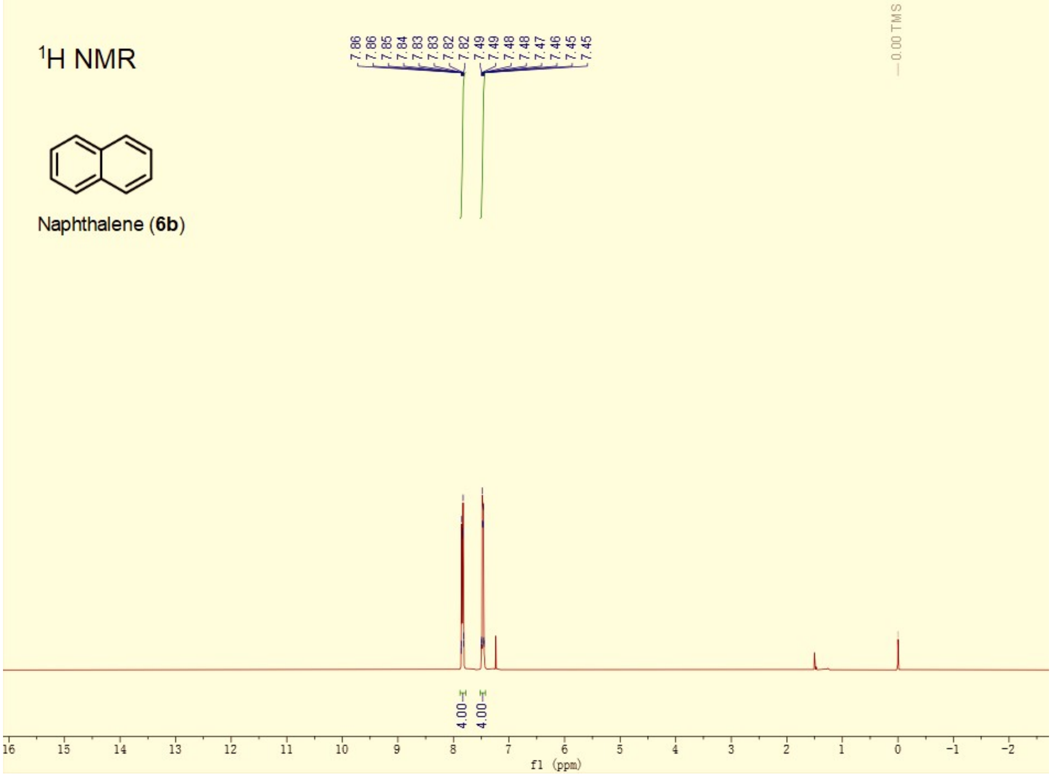


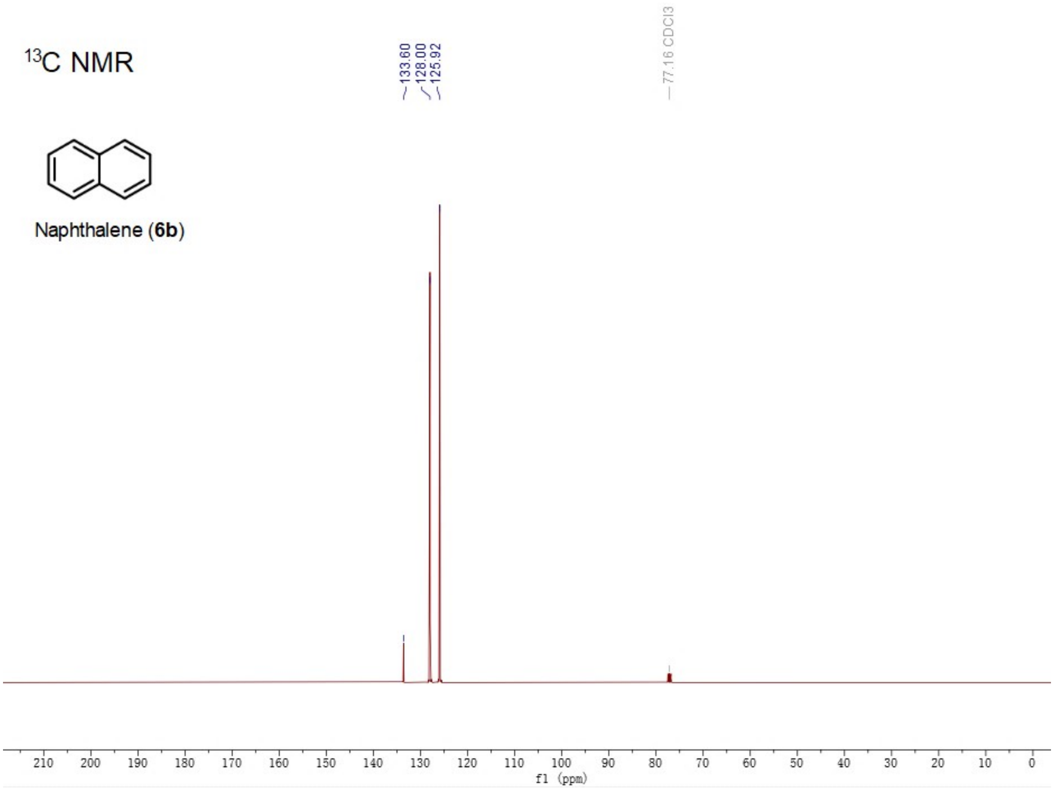
Naphthalene (**4b**). **^{1}H NMR (400 MHz, CDCl$_3$):** δ (ppm) = 7.87-7.80 (m, 4H), 7.50-7.44 (m, 4H); **^{13}C NMR (101 MHz, CDCl$_3$)**: δ (ppm) = 133.60, 128.00, 125.92.



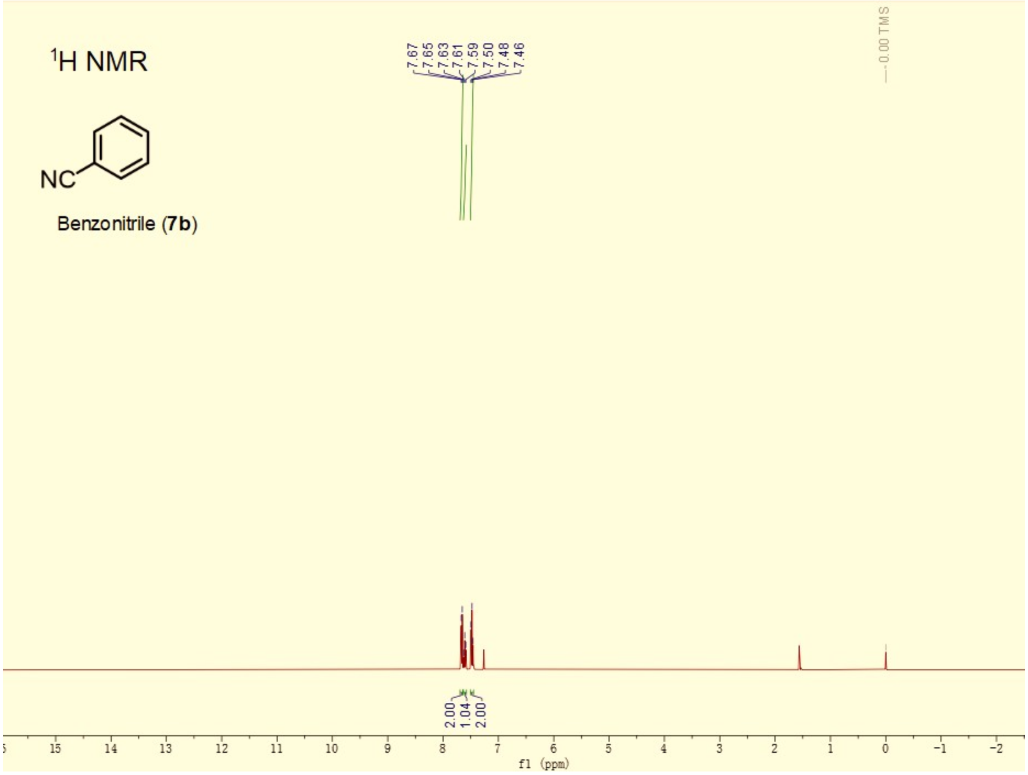


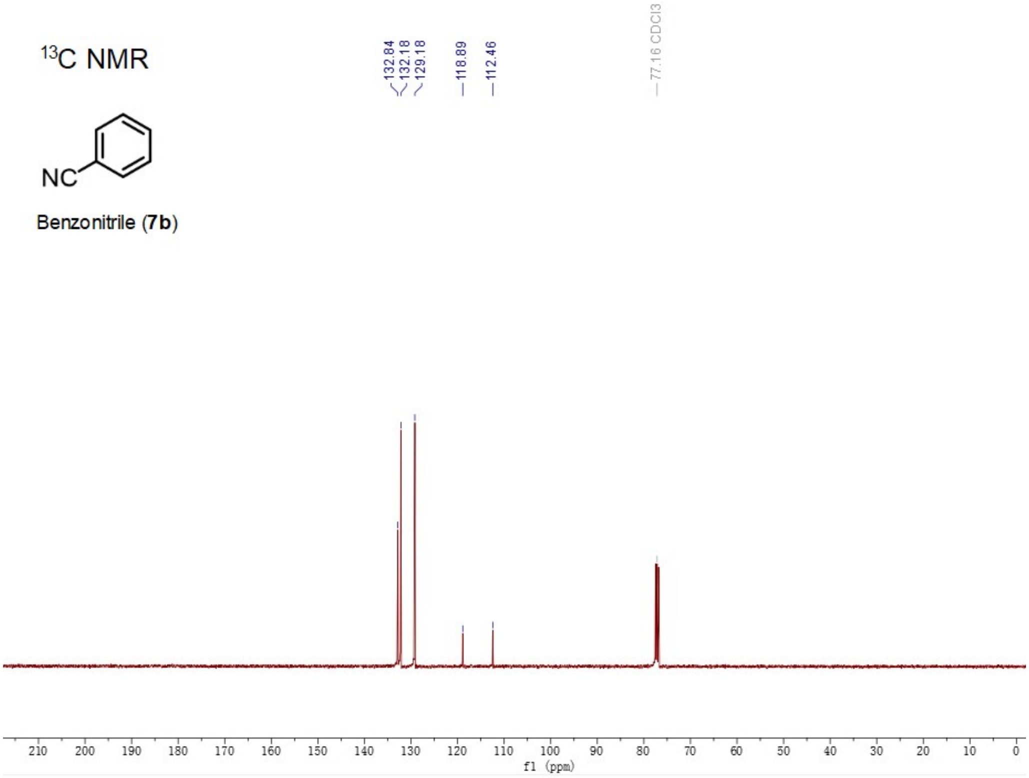
Naphthalene (**5b**). **^{1}H NMR (400 MHz, CDCl$_3$):** δ (ppm) = 7.87-7.81 (m, 4H), 7.50-7.44 (m, 4H); **^{13}C NMR (101 MHz, CDCl$_3$)**: δ (ppm) = 133.60, 128.00, 125.92.



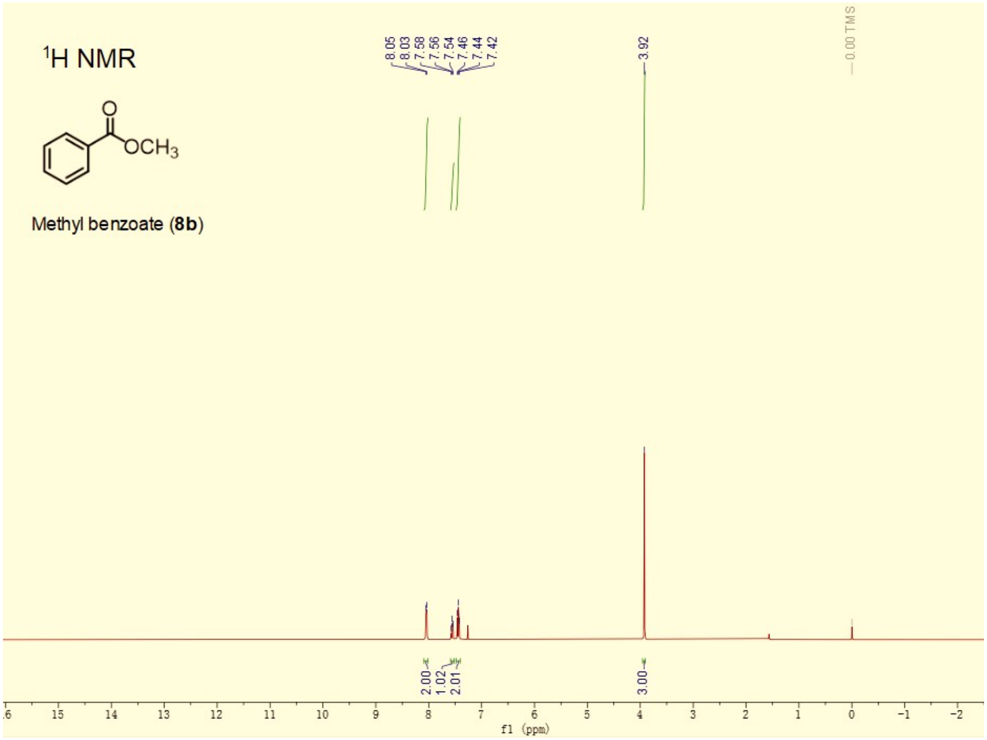


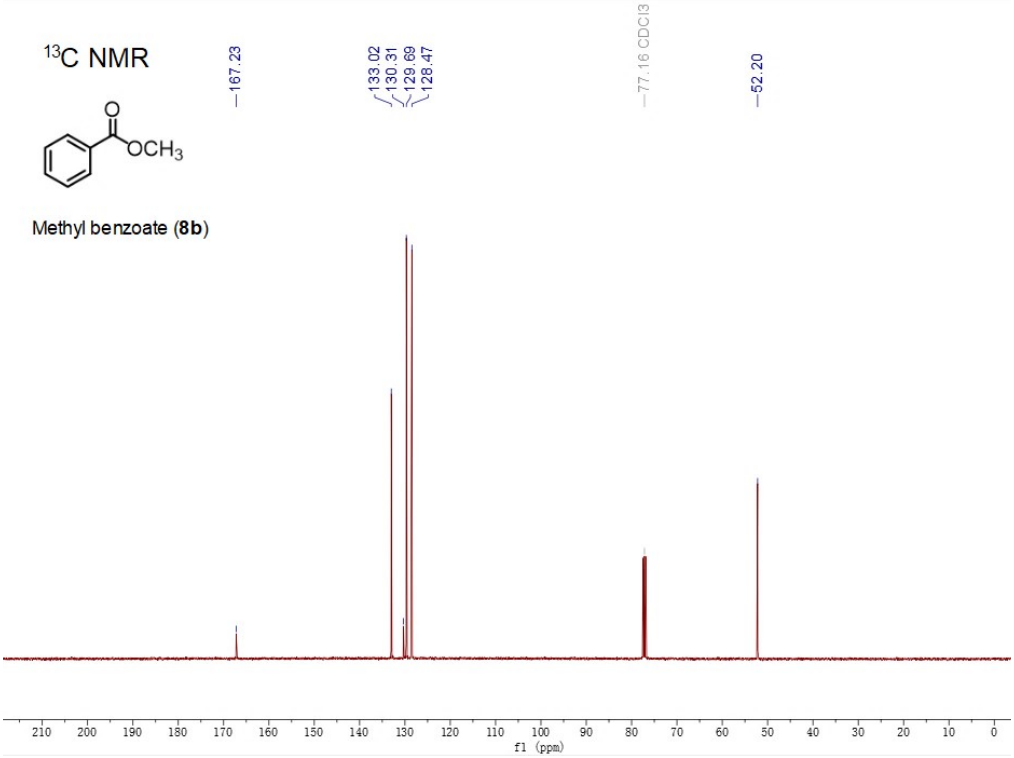
Naphthalene (**6b**). ^{1}**H NMR (400 MHz, CDCl$_3$):** δ = 7.88-7.80 (m, 4H), 7.50-7.44 (m, 4H); ^{13}**C NMR (101 MHz, CDCl$_3$)**: δ = 133.60, 128.00, 125.92.



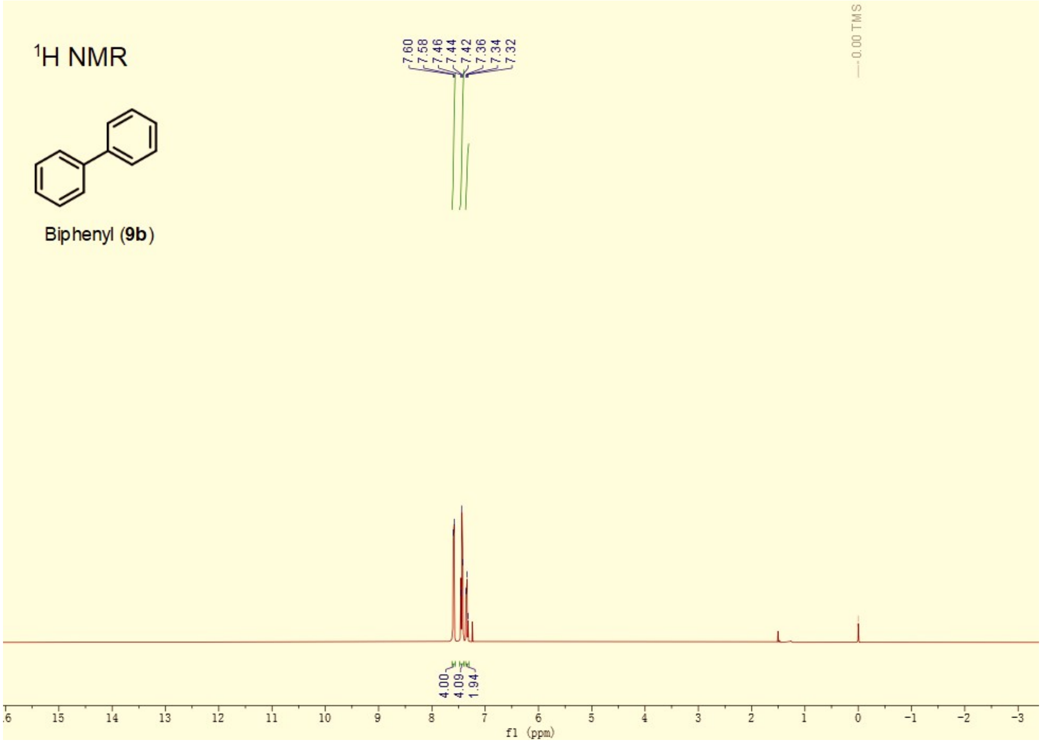


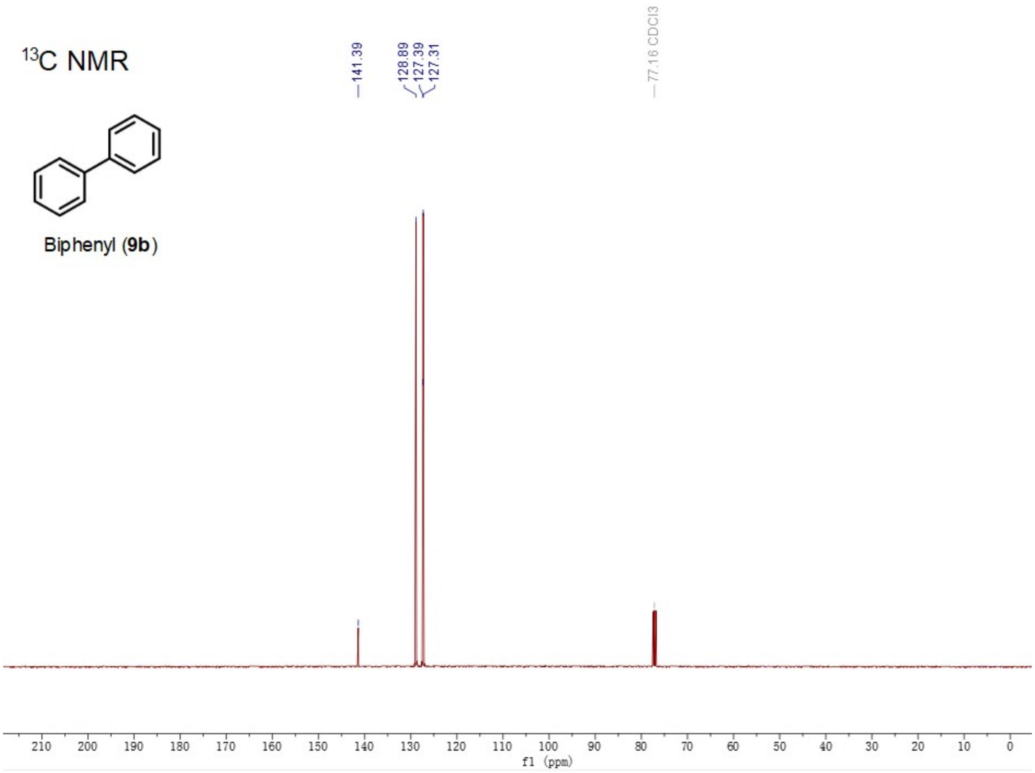
Benzonitrile (**7b**). **^{1}H NMR (400 MHz, CDCl$_3$):** δ (ppm) = 7.66 (d, *J* = 7.9 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H);**^{13}C NMR (101 MHz, CDCl$_3$):** δ (ppm) = 132.84, 132.18, 129.18, 118.89, 112.46.



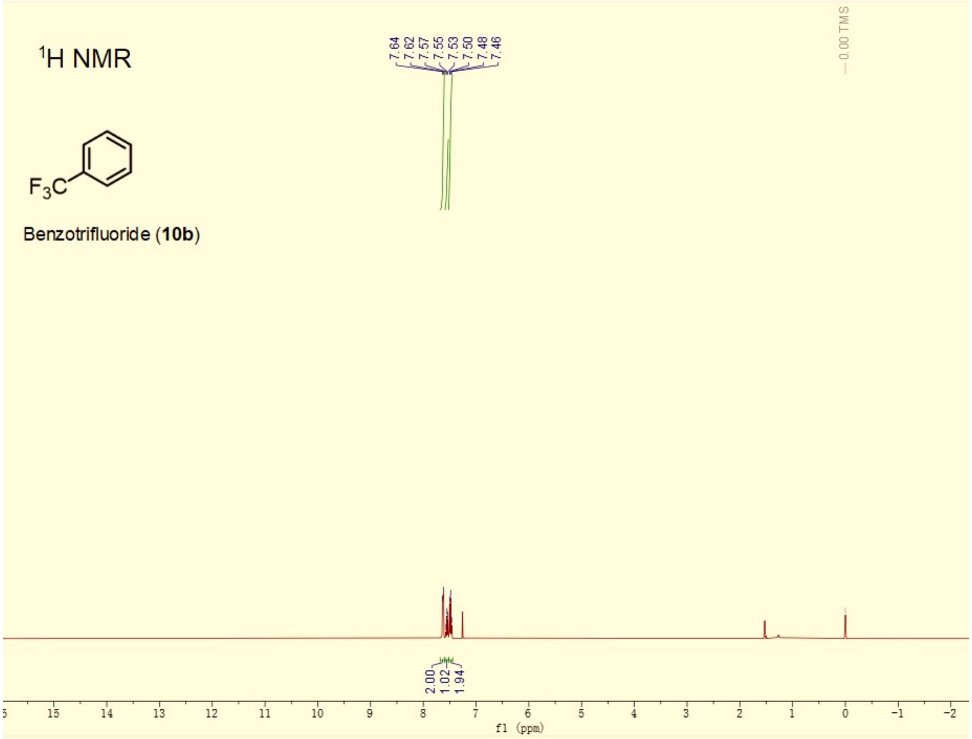


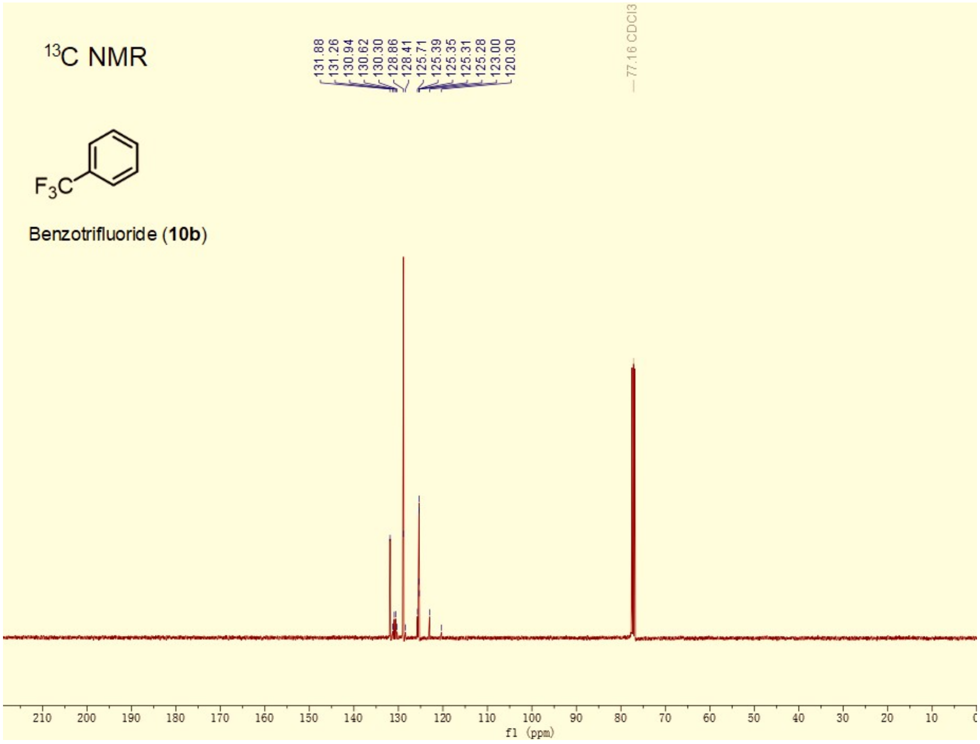
Methyl benzoate (**8b**). **^{1}H NMR (400 MHz, CDCl$_3$):** δ (ppm) = 8.04 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 3.92 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$):** δ (ppm) =167.23, 133.02, 130.31, 129.69, 128.47, 52.20.



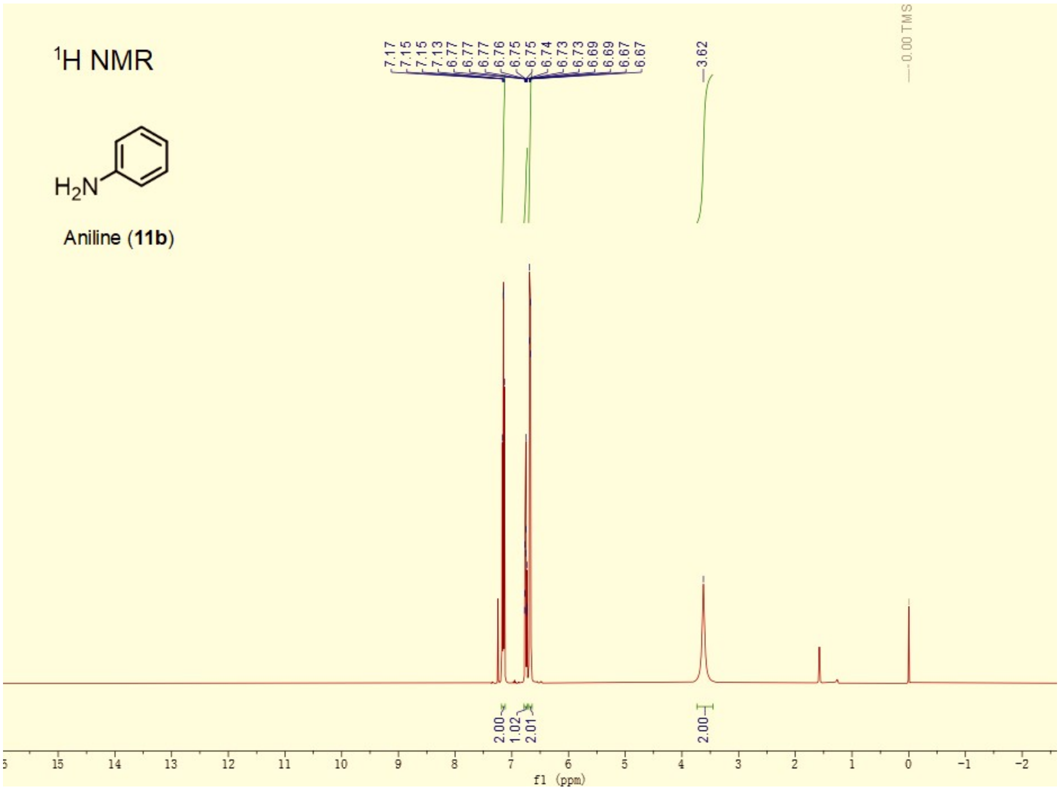


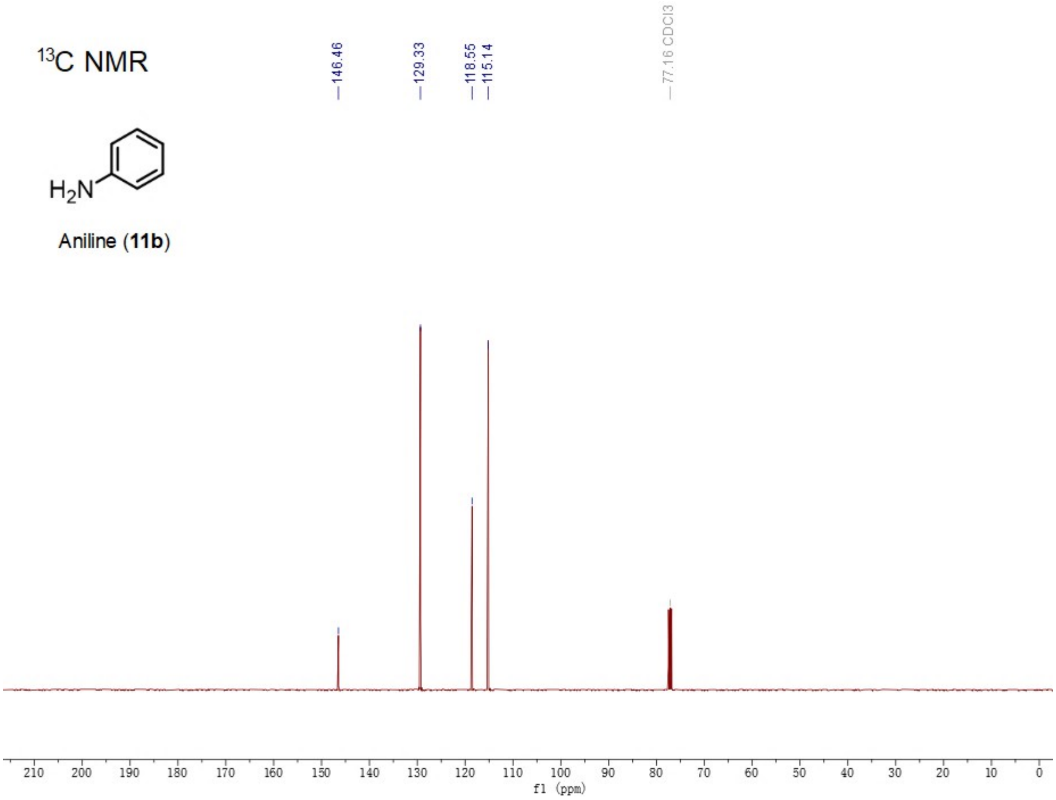
Biphenyl (**9b**).**^{1}H NMR (400 MHz, CDCl$_3$):** δ (ppm) = 7.59 (d, *J* = 7.5 Hz, 4H), 7.44 (t, *J* = 7.6 Hz, 4H), 7.34 (t, *J* = 7.3 Hz, 2H); **^{13}C NMR (101 MHz, CDCl$_3$):** δ (ppm) = 141.39, 128.89, 127.39, 127.31.



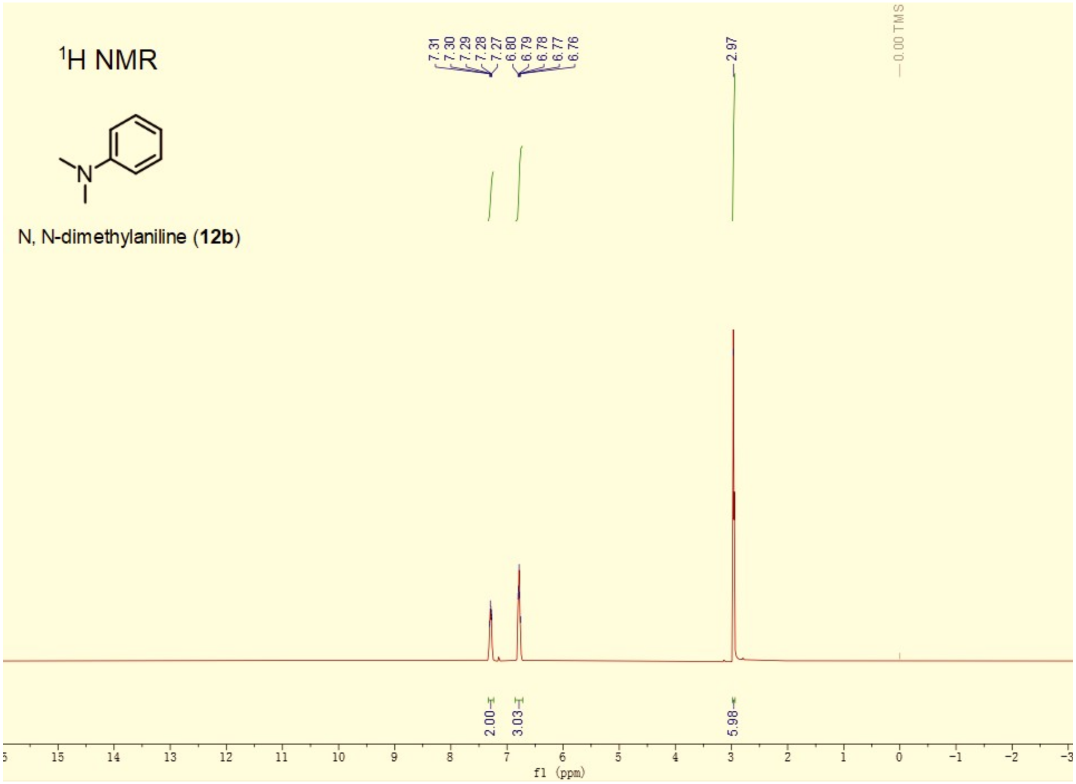


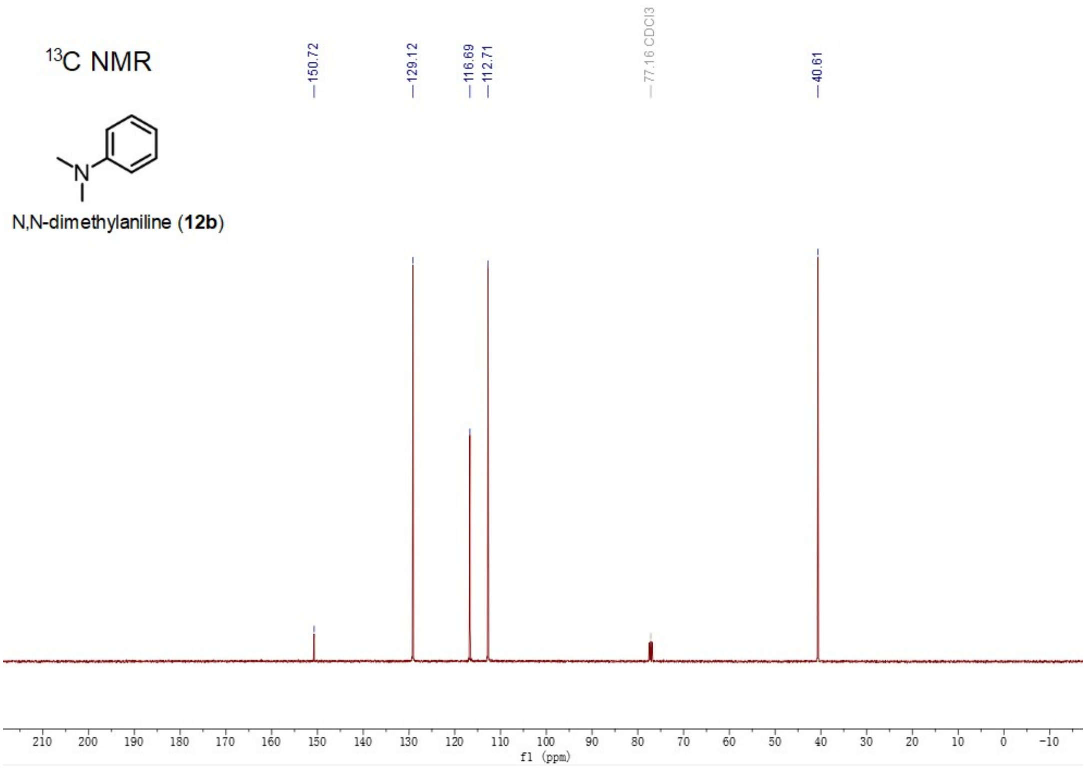
Benzotrifluoride (**10b**). **^{1}H NMR (400 MHz, CDCl$_3$):** δ (ppm) = 7.63 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H); **^{13}C NMR (101 MHz, CDCl$_3$):** δ (ppm) = 131.88, 130.78 (q, J^2= 32.2 Hz), 128.86, 125.33 (q, J^3= 3.8 Hz), 124.35 (q, J^1 = 272.2 Hz).



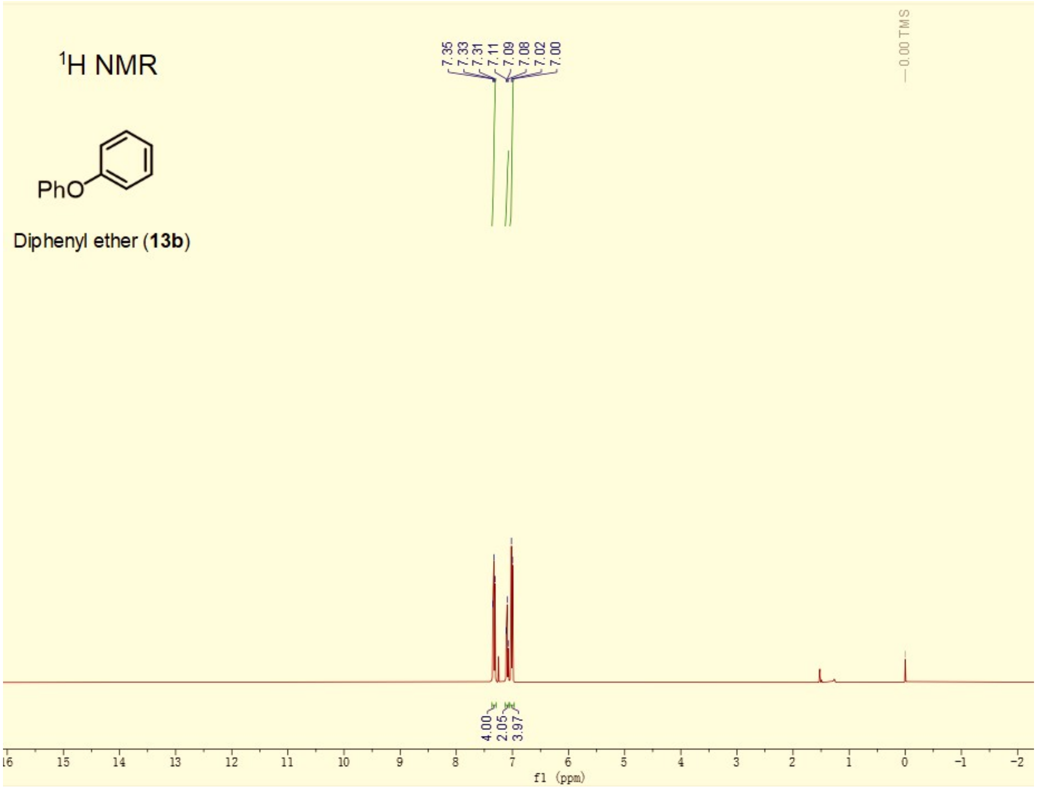


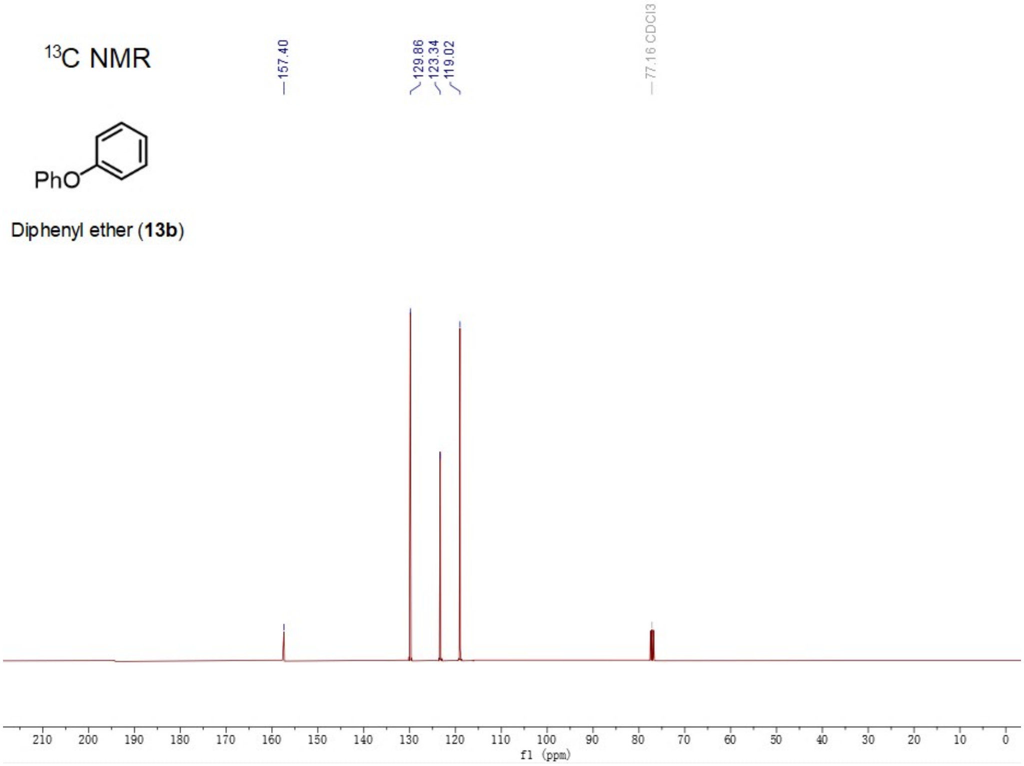
Aniline (**11b**). **^{1}H NMR (400 MHz, $CDCl_3$):** δ (ppm) =7.15 (dd, *J* = 8.4, 7.3 Hz, 2H), 6.75 (tt, *J* = 7.4, 1.2 Hz, 1H), 6.68 (dd, *J* = 8.5, 1.1 Hz, 2H), 3.62 (s, 2H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ (ppm) = 146.46, 129.33, 118.55, 115.14



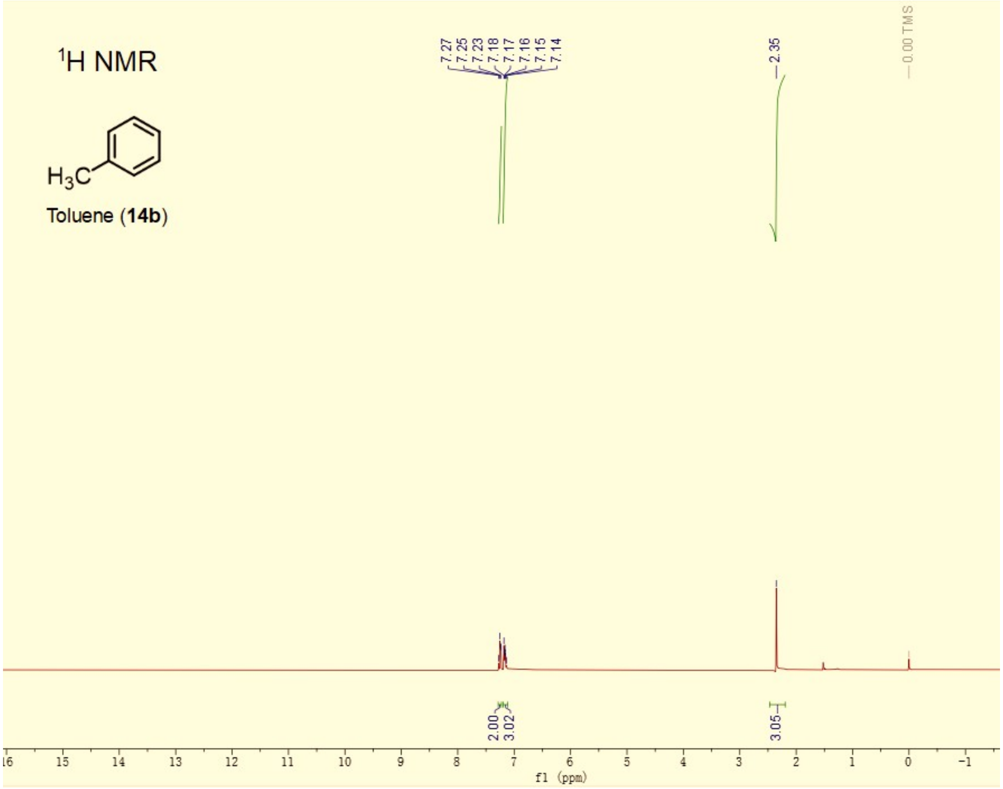


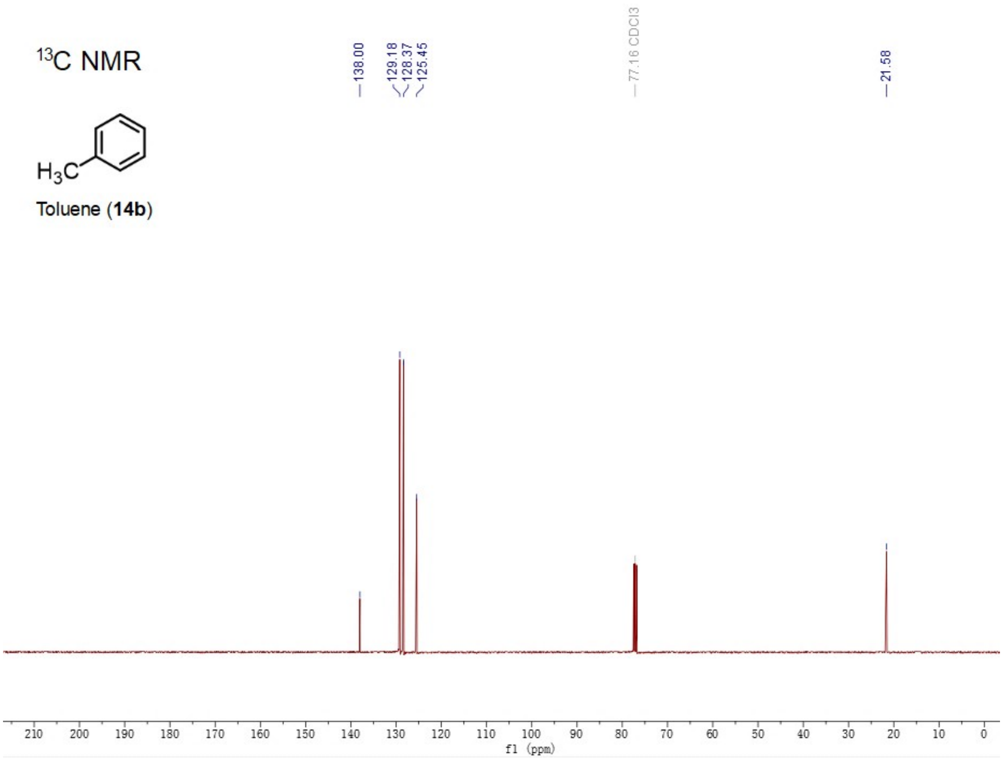
N, N-dimethylaniline (**12b**). **^{1}H NMR (400 MHz, $CDCl_3$):** δ (ppm) = 7.32-7.26 (m, 2H), 6.81-6.75 (m, 3H), 2.97 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ (ppm) = 150.72, 129.12, 116.69, 112.71, 40.61.



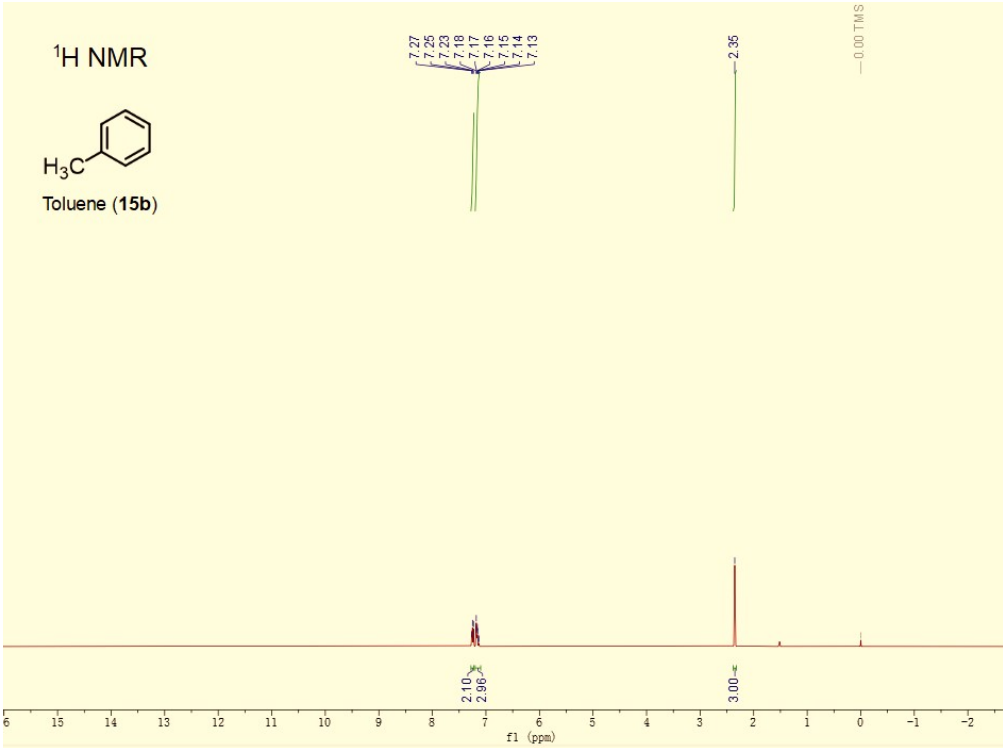


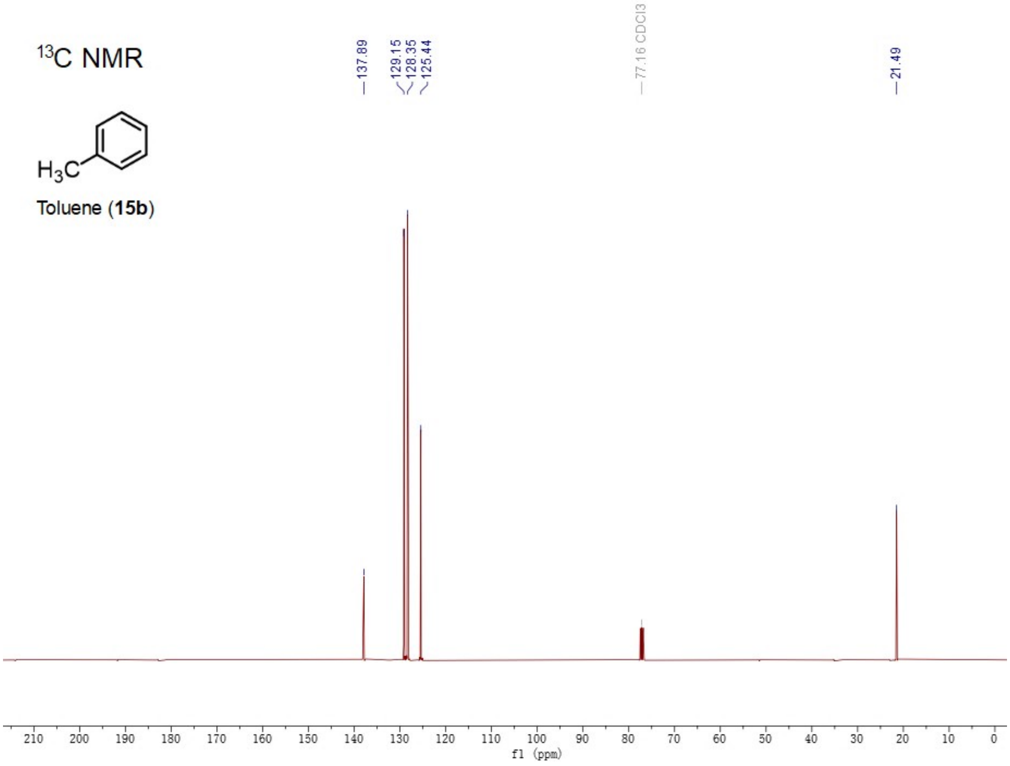
Diphenyl ether (**13b**). **^{1}H NMR (400 MHz, CDCl$_3$)** δ (ppm) = 7.33 (t, *J* = 8.0 Hz, 4H), 7.09 (t, *J* = 7.4 Hz, 2H), 7.01 (d, *J* = 7.7 Hz, 4H).; **^{13}C NMR (101 MHz, CDCl$_3$):** δ (ppm) = 157.40, 129.86, 123.34, 119.02.



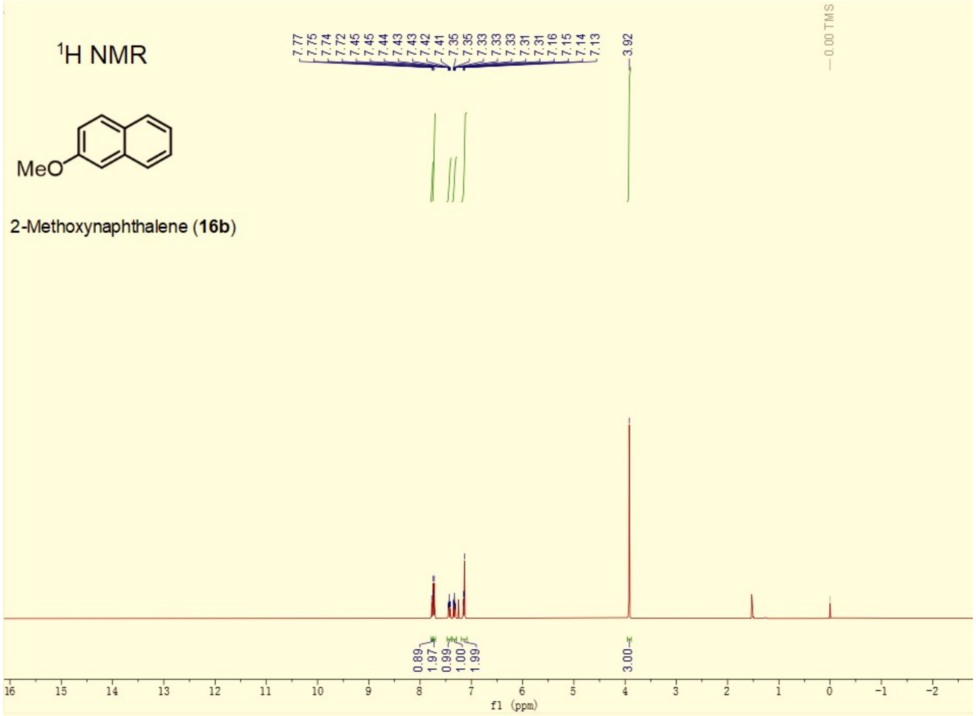


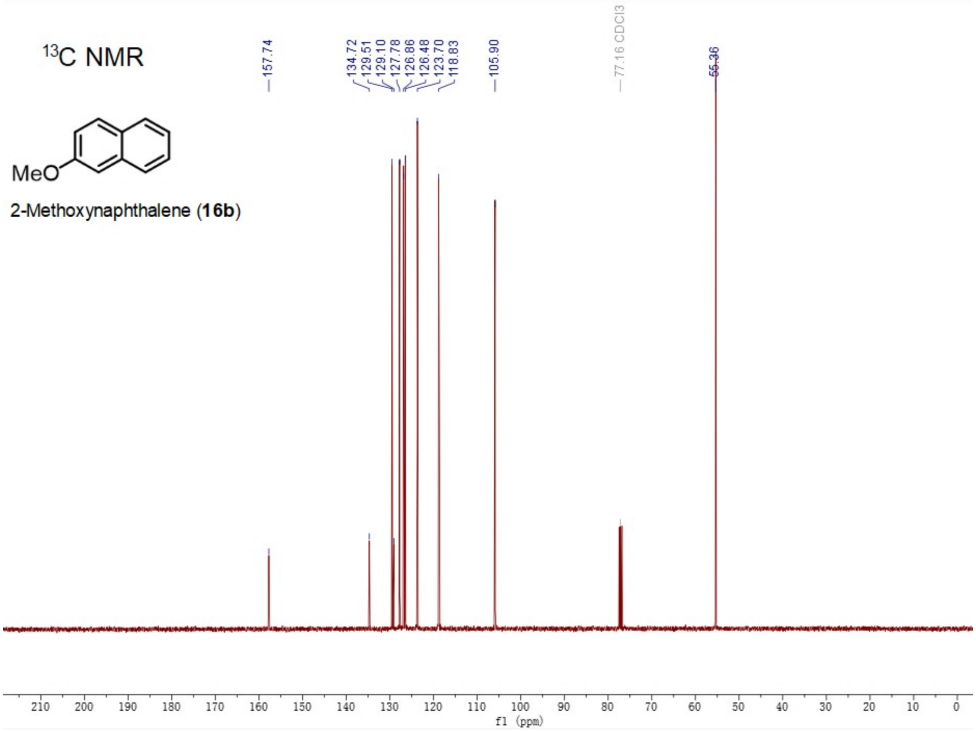
Toluene (**14b**). **^{1}H NMR (400 MHz, CDCl$_3$):** δ (ppm) = 7.25 (t, *J* = 7.4 Hz, 2H), 7.21-7.11 (m, 3H), 2.35 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$):** δ (ppm) = 138.00, 129.18, 128.37, 125.45, 21.58.



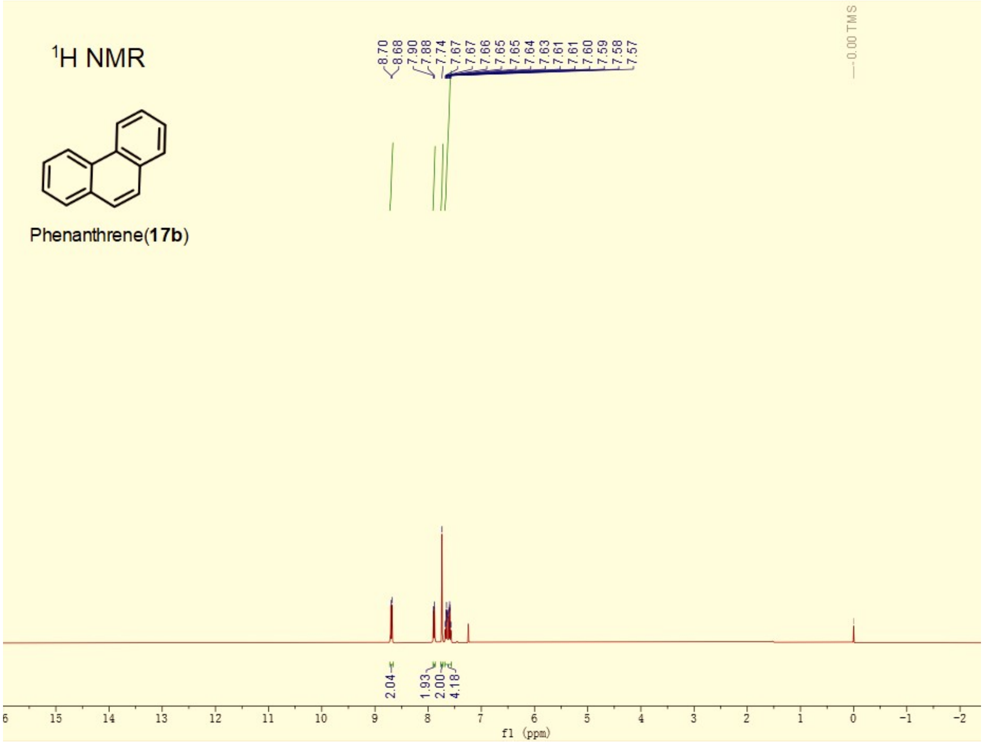


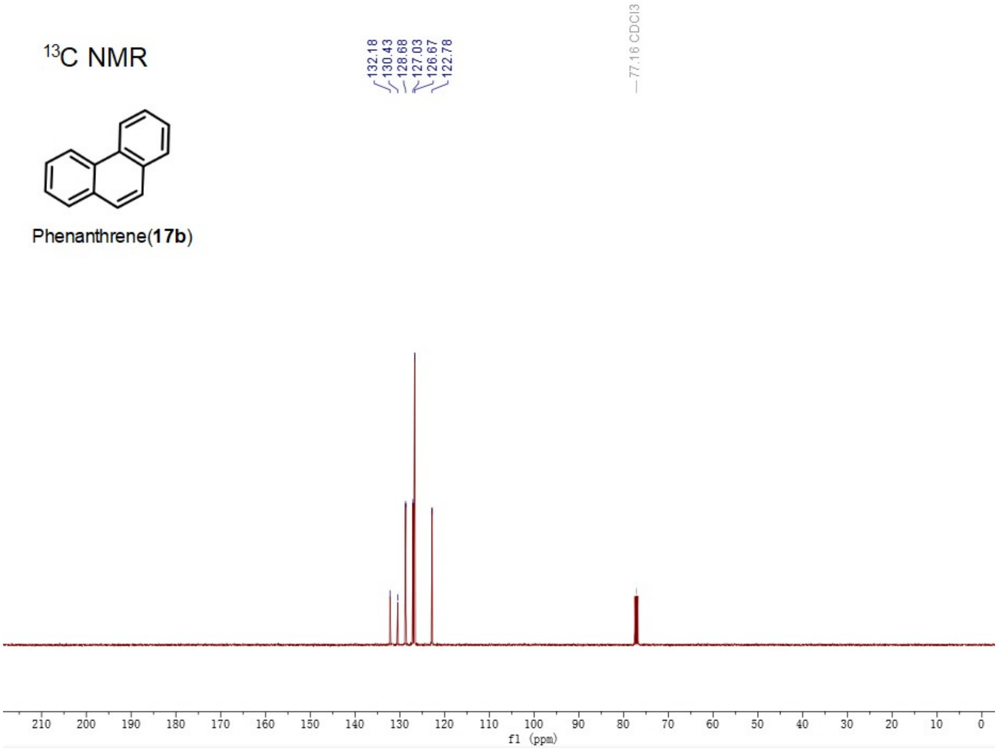
Toluene (**15b**). **^{1}H NMR (400 MHz, CDCl$_3$):** δ (ppm) = 7.25 (t, *J* = 7.4 Hz, 2H), 7.20-7.12 (m, 3H), 2.35 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$):** δ (ppm) = 137.89, 129.15, 128.35, 125.44, 21.49.



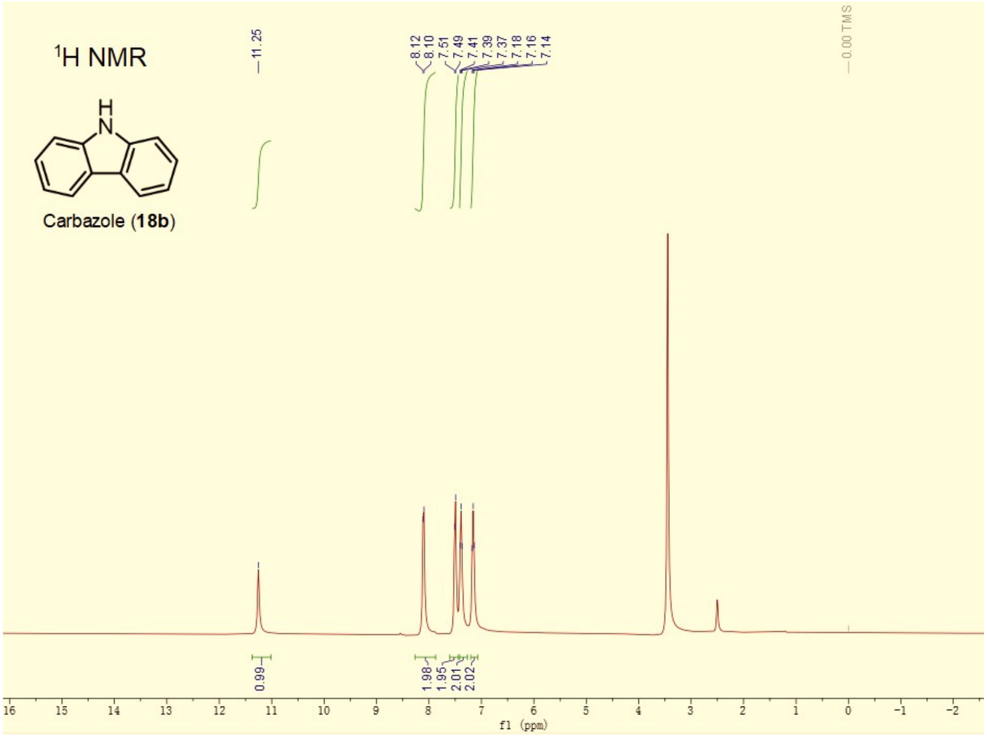


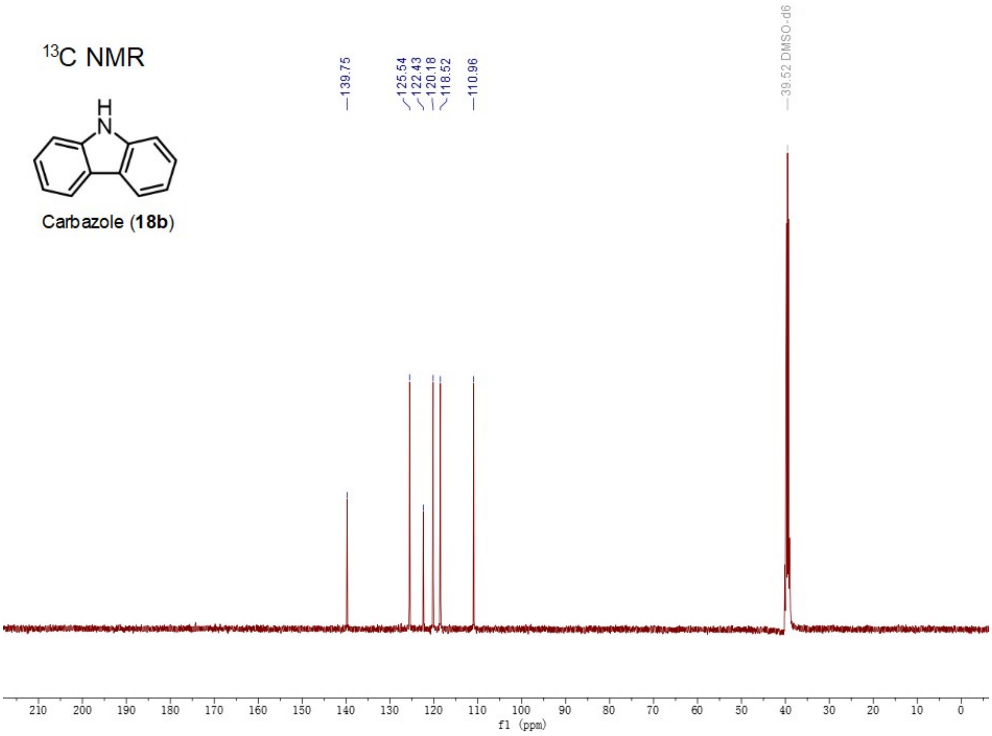
2-Methoxynaphthalene (**16b**). **^{1}H NMR (400 MHz, CDCl$_3$):** δ (ppm) = 7.76 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.43 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.33 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.19-7.10 (m, 2H), 3.92 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$):** δ (ppm) = 157.74, 134.72, 129.51, 129.10, 127.78, 126.86, 126.48, 123.70, 118.83, 105.90, 55.36.



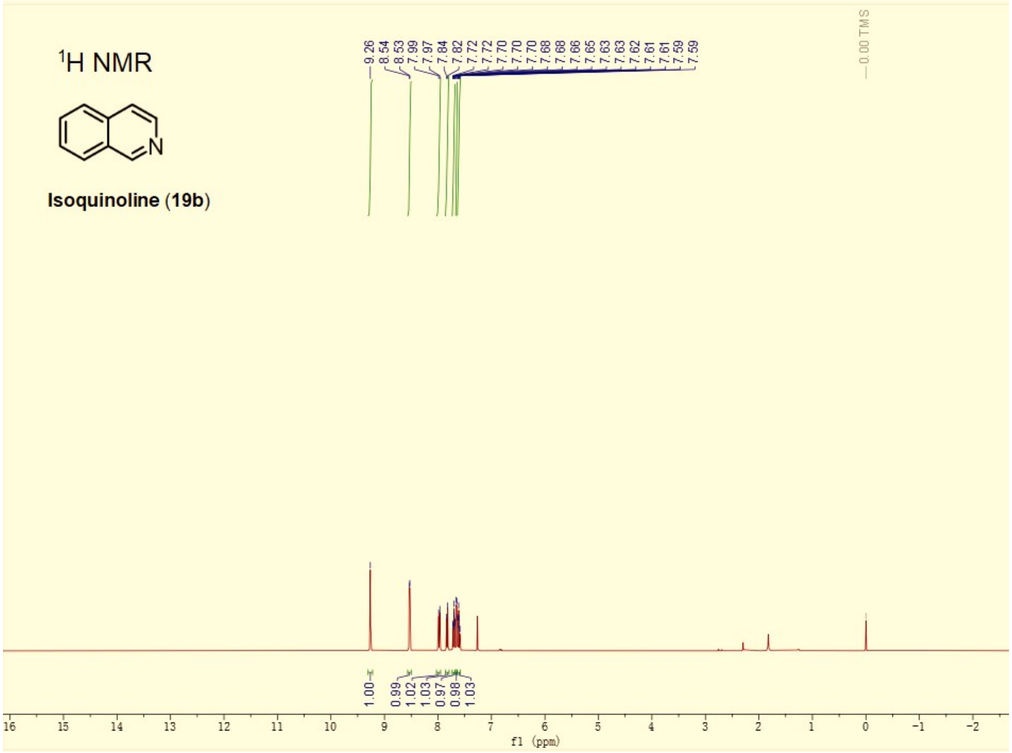


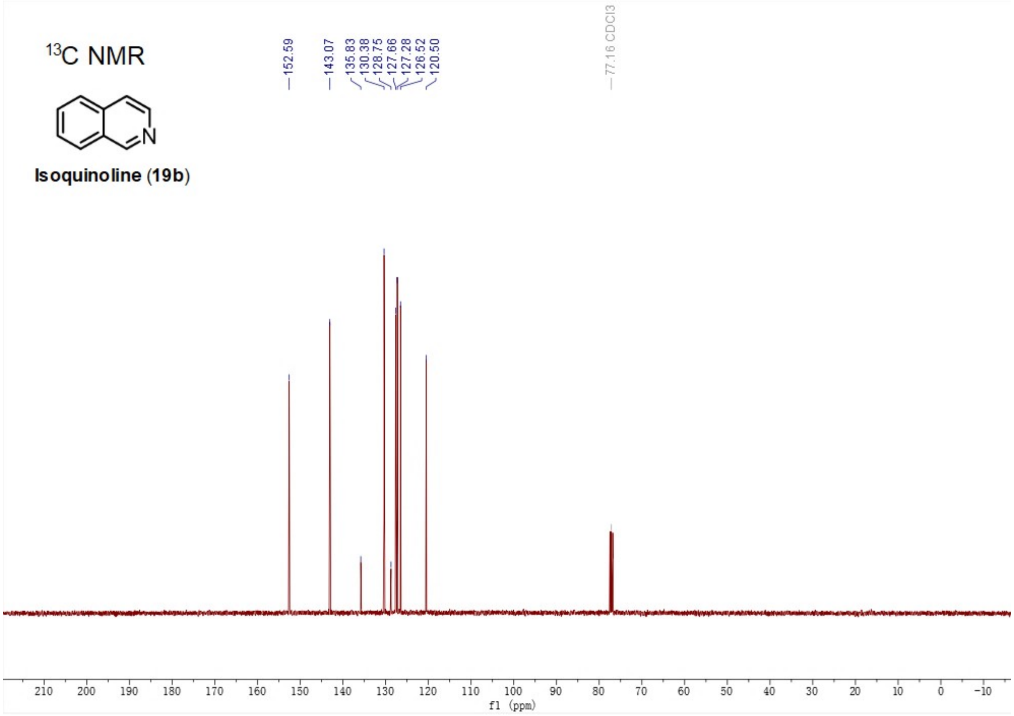
Phenanthrene (**17b**). **^{1}H NMR (400 MHz, CDCl$_3$)**: δ (ppm) = 8.69 (d, *J* = 7.6 Hz, 2H), 7.89 (d, *J* = 7.8 Hz, 2H), 7.74 (s, 2H), 7.70-7.56 (m, 4H); **^{13}C NMR (101 MHz, CDCl$_3$):** δ (ppm) = 132.18, 130.43, 128.68, 127.03, 126.67 (2C), 122.78.



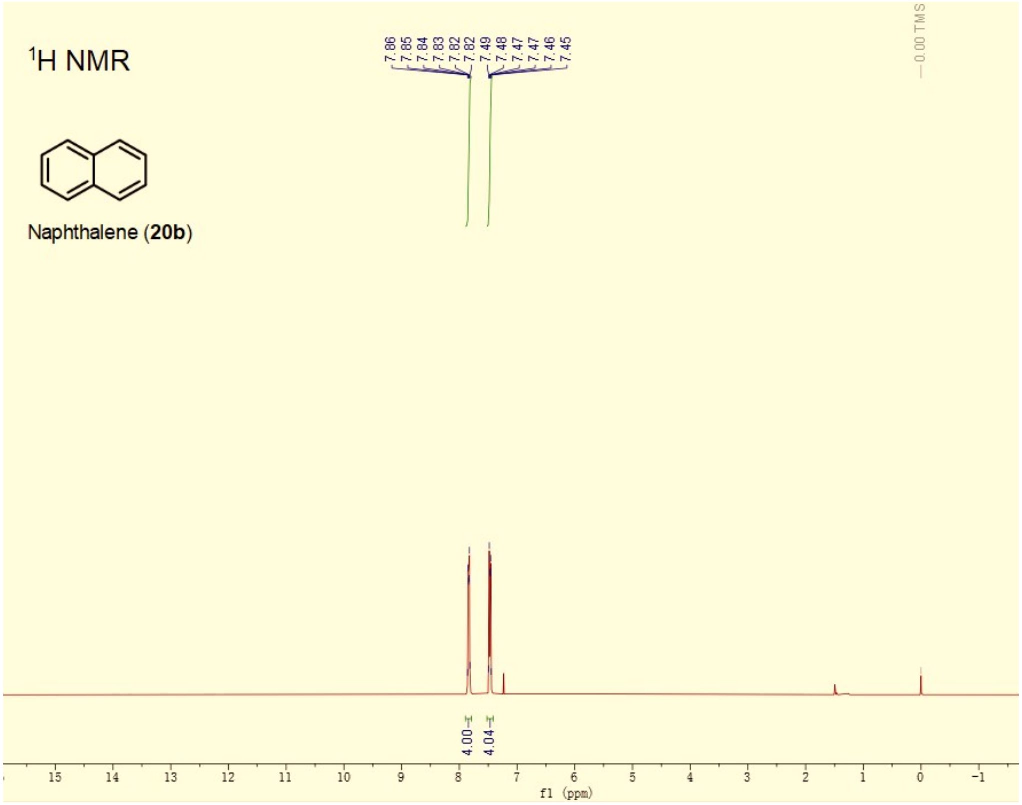


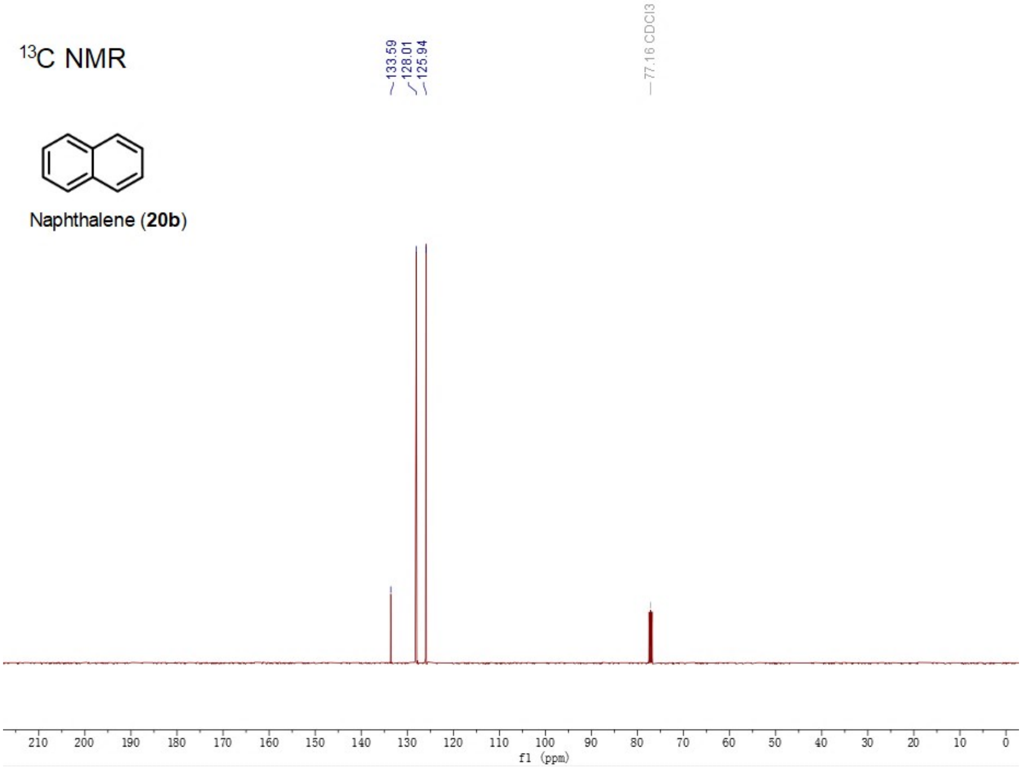
Carbazole (**18b**). **^{1}H NMR (400 MHz, DMSO-*d_6*):** δ (ppm) = 11.25 (s, 1H), 8.11 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.16 (t, *J* = 7.7 Hz, 2H); **^{13}C NMR (101 MHz, DMSO-*d_6*):** δ (ppm) =139.75, 125.54, 122.43, 120.18, 118.52, 110.96.



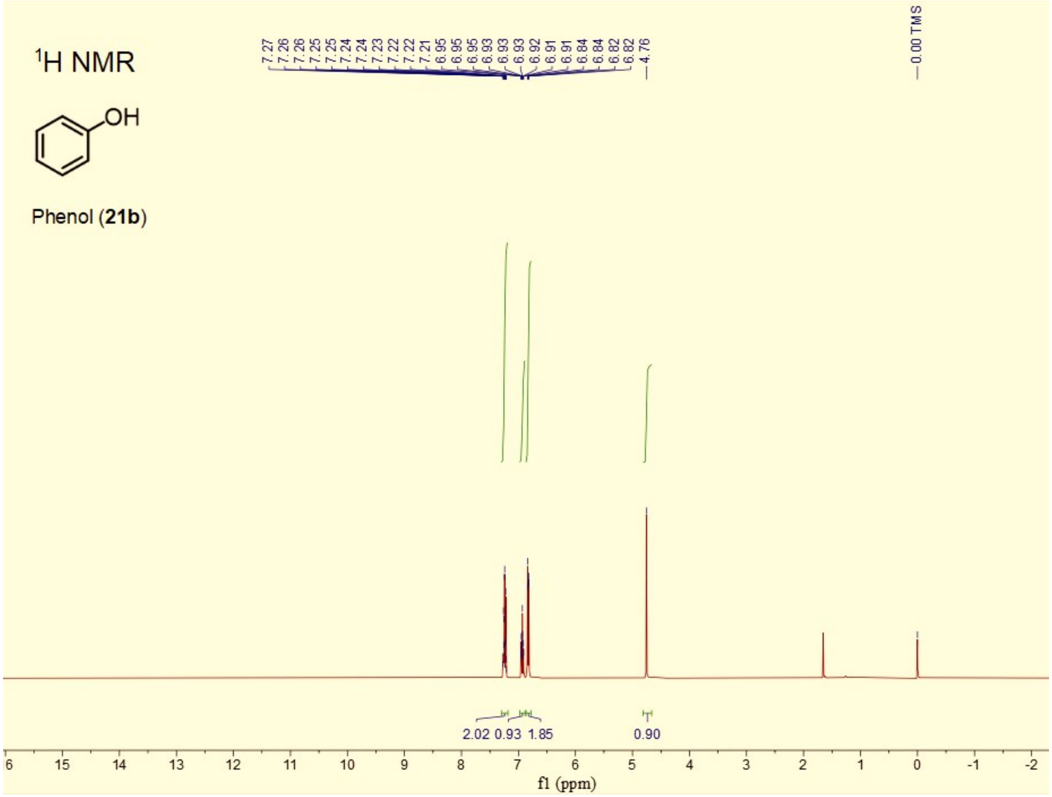


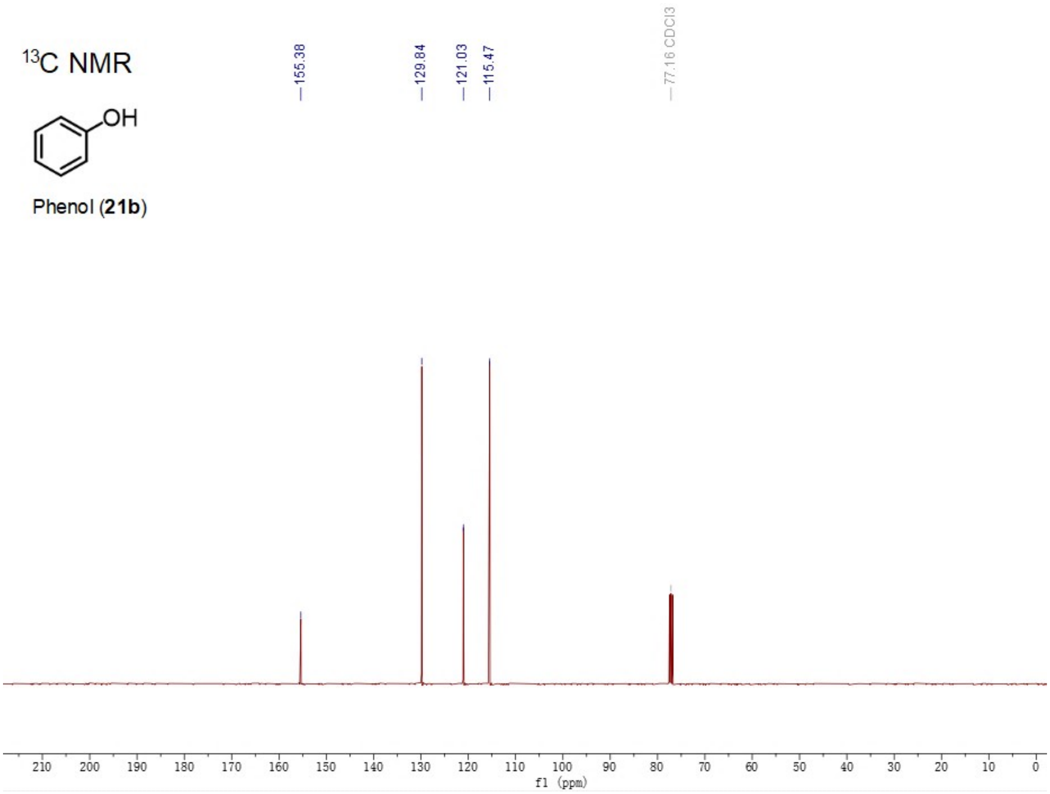
Isoquinoline (**19b**). **^{1}H NMR (400 MHz, CDCl$_3$):** δ (ppm) = 9.26 (s, 1H), 8.53 (d, *J* = 5.7 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.70 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.65 (d, *J* = 5.8 Hz, 1H), 7.61 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H); **^{13}C NMR (101 MHz, CDCl$_3$) :** δ (ppm) = 152.59, 143.07, 135.83, 130.38, 128.75, 127.66, 127.28, 126.52, 120.50.



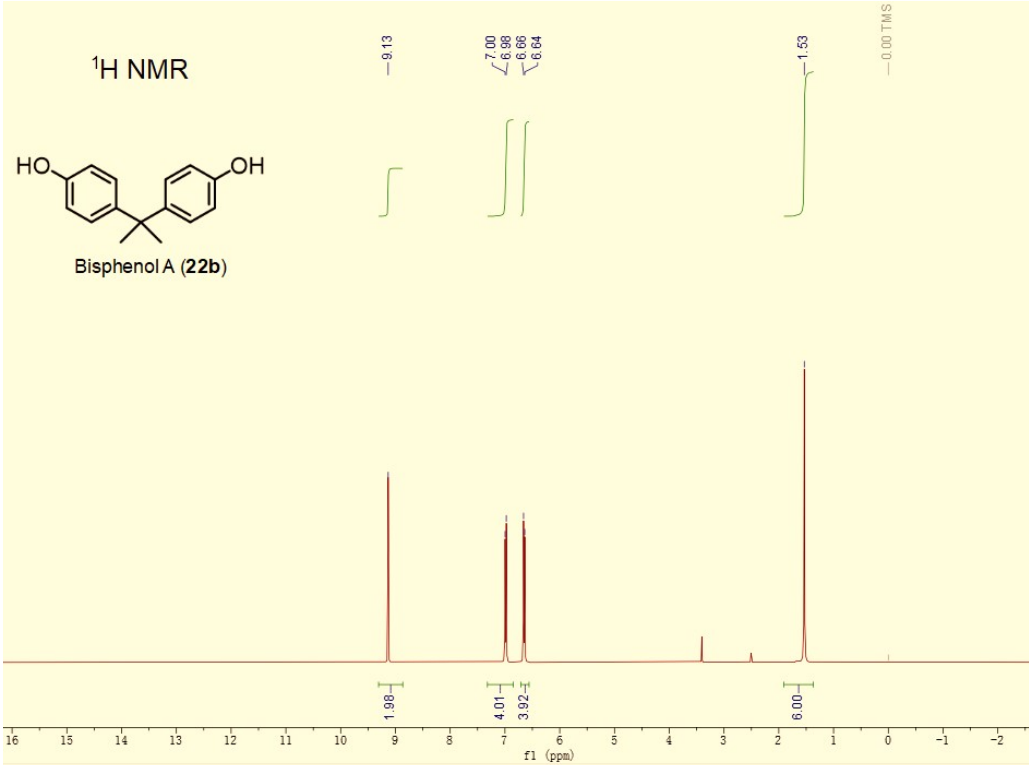


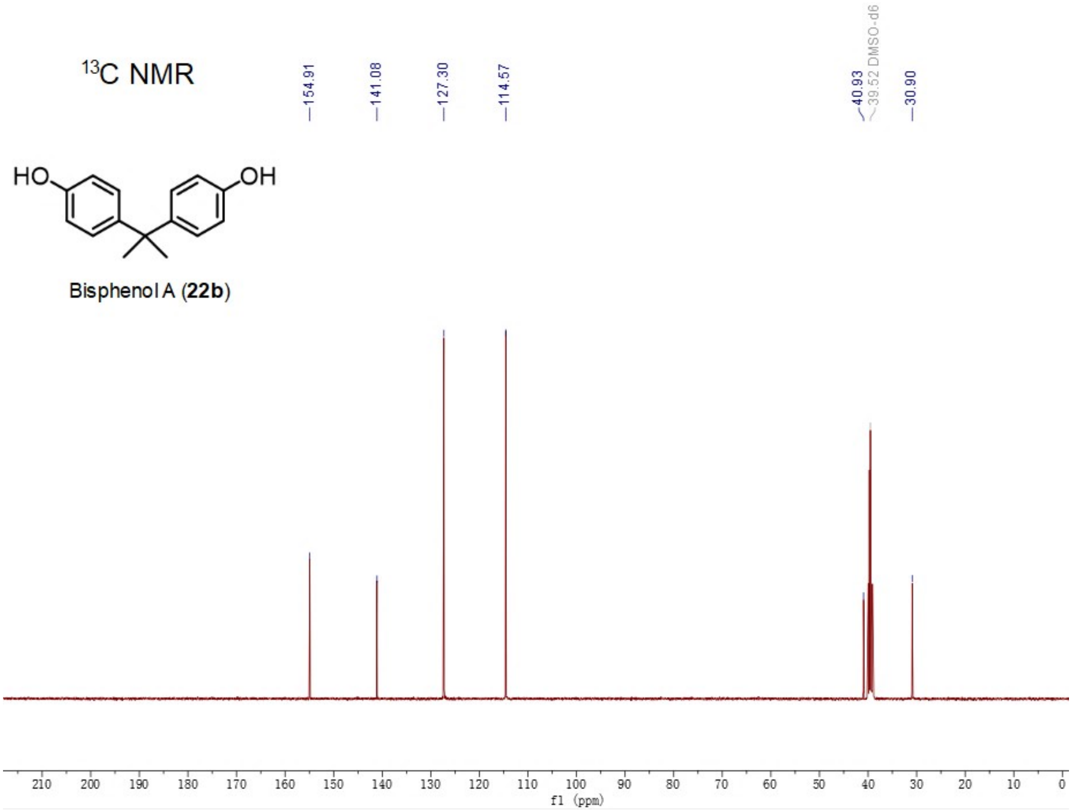
Naphthalene (**20b**).^{1}**H NMR (400 MHz, CDCl$_3$):** δ (ppm) = 7.87-7.81 (m, 4H), 7.50-7.44 (m, 4H); ^{13}**C NMR (101 MHz, CDCl$_3$)**：δ (ppm) = 133.59, 128.01, 125.94.





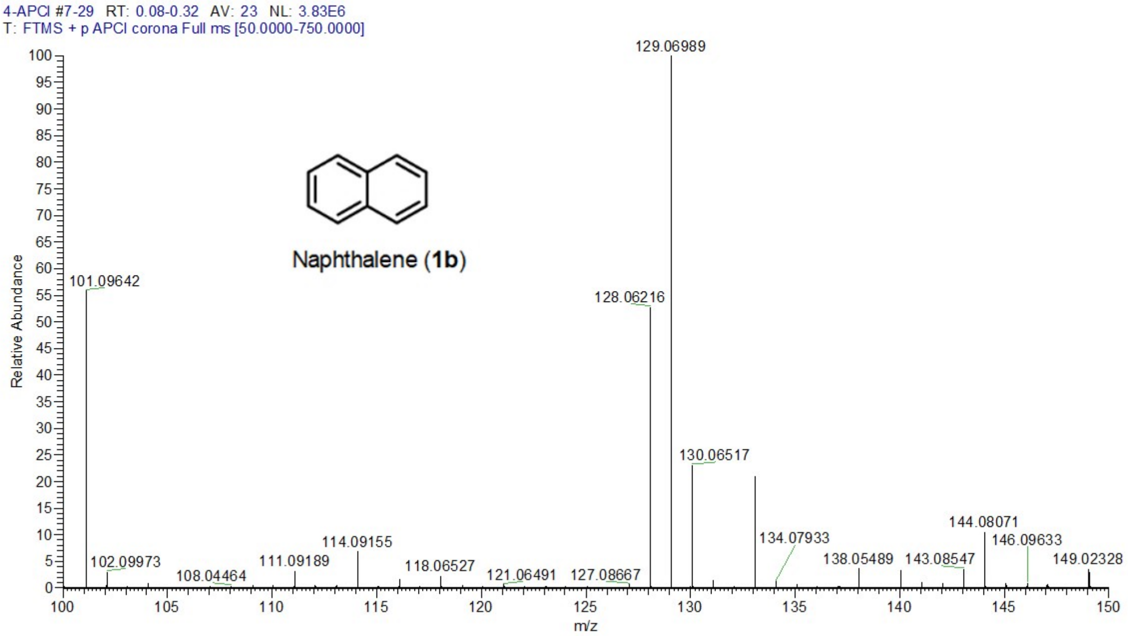
Phenol (**21b**). **^{1}H NMR (400 MHz, CDCl$_3$):** δ (ppm) = 7.30-7.19 (m, 2H), 6.93 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.83 (dd, *J* = 8.6, 1.1 Hz, 2H), 4.76 (s, 1H); **^{13}C NMR (101 MHz, CDCl$_3$):** δ (ppm) = 155.38, 129.84, 121.03, 115.47.



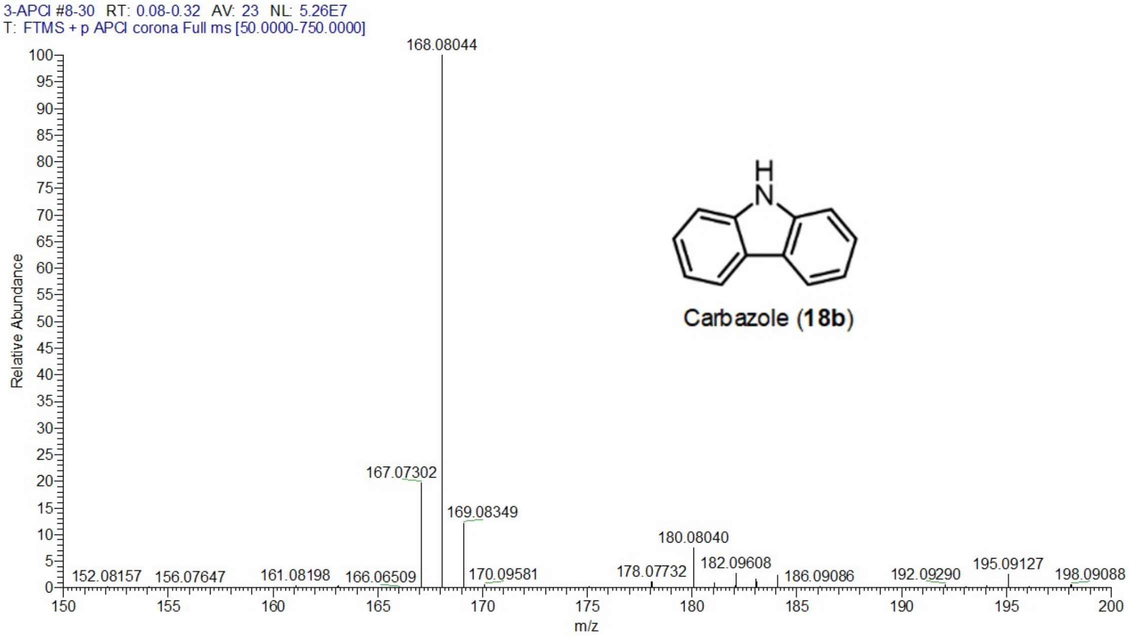


Bisphenol A (**22b**). **^{1}H NMR (400 MHz, DMSO-d_6):** δ (ppm) = 9.13 (s, 2H), 6.99 (d, J = 8.6 Hz, 4H,), 6.65 (d, J = 8.6 Hz, 4H), 1.53 (s, 6H); **^{13}C NMR (101 MHz, DMSO-d_6):** δ (ppm) =154.91, 141.08, 127.30, 114.57, 40.93, 30.90.

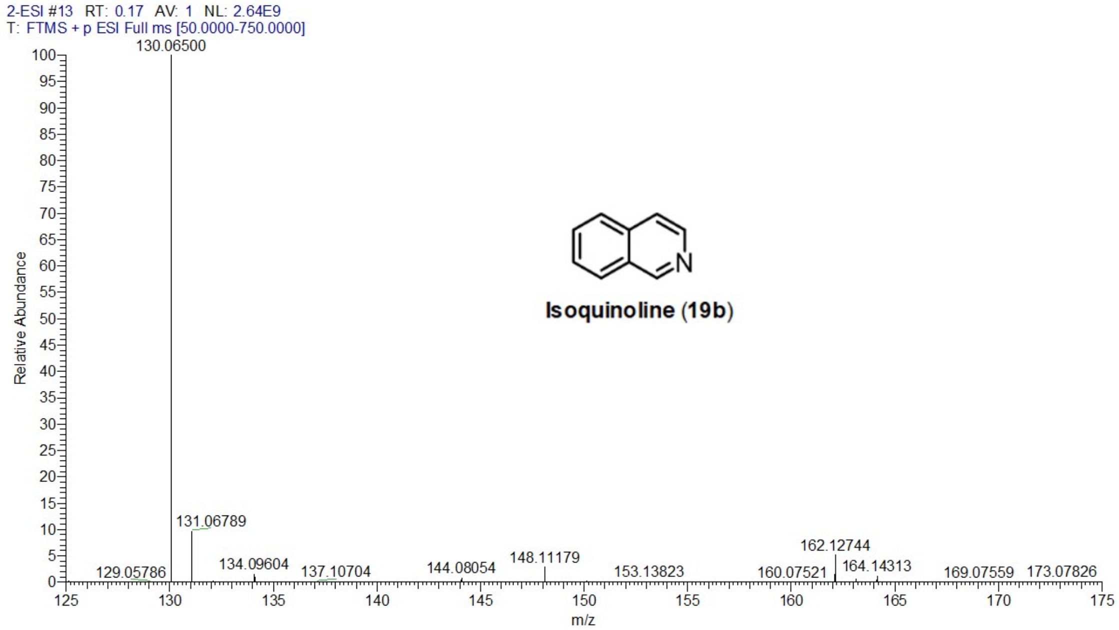
5.2 HR-MS spectra.



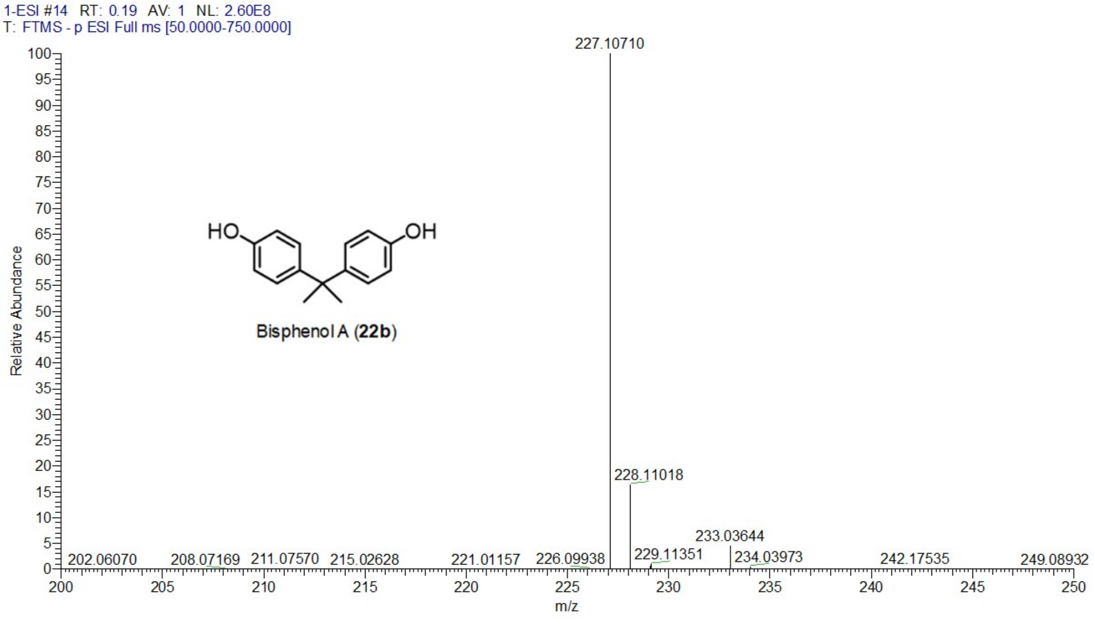
HR-MS (APCI): *m/z* calculated for[$C_{10}H_8$] ([M]): 128.0626, found: 128.0622



HR-MS (APCI): *m/z* calculated for [$C_{12}H_9N$] ([M]): 167.0735, found: 167.0730



HR-MS (ESI): *m/z* calculated for $[C_9H_8N]^+$ ($[M+H]^+$): 130.0657, found: 130.0650



HR-MS (ESI): *m/z* calculated for $[C_{15}H_{16}O_2]$ (M)**:** 228.1150, found: 228.1102

References

1 B. Sahoo, A.-E. Surkus, M.-M. Pohl, J. Radnik, M. Schneider, S. Bachmann, M. Scalone, K. Junge and M. Beller, *Angew. Chem. Int. Ed.*, 2017, **56**, 11242–11247.

2 S. Giri, M. Bhaumik, R. Das, V. K. Gupta and A. Maity, *Appl. Catal. B Environ.*, 2017, **202**, 207–216.

3 J. Jiang, L. Du and Y. Ding, *ChemistrySelect*, 2021, **6**, 1372–1377.

4 D. K. Leonard, P. Ryabchuk, M. Anwar, S. Dastgir, K. Junge and M. Beller, *Chem. Sci.*, 2022, **15**, e202102315.

5. O. Arkad, H. Wiener, N. Garti and Y. Sasson. *JAOCS*, 1987, **64**, 1529-1532.

6. Z. DOBROVOLNA and L. CERVENY. *Res. Chem. Intermed.*, 1999, **26**, 489-497.