Supporting information

Catalytic Selective Oxidation of Aromatic Amines to Azoxy Derivatives with Ultralow Loading Peroxoniobate Salts

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Experimental

Materials

Niobium pentoxide (Nb_2O_5), acetic acid and potassium hydroxide were obtained from Bide Pharmatech Ltd used to prepare niobic acid. Guanidine carbonate (gu_2CO_3), ammonium hydroxide ($NH_3 \cdot H_2O$), tartaric acid (H_4tart) and hydrogen peroxide (30 wt.%) were provided by Aladdin. Tetrabutylammonium hydroxide (TBAOH, 25 wt.% in H_2O) and Tetraethylammonium hydroxide (TEAOH, 25 wt.% in H_2O) were supplied by Bide Pharmatech Ltd. Aniline, N-phenylhydroxylamine and other aromatic amines were purchased from Shanghai Titan Scientific Co., Ltd. Ethanol was supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, People's Republic of China) as reaction solvent. Toluene was supplied by Shanghai Macklin Biochemical Co., Ltd utilized as internal standard in gas chromatography (GC) analysis. Acetonitrile (HPLC) was purchased from Shanghai Macklin Biochemical Co.

Catalyst preparation

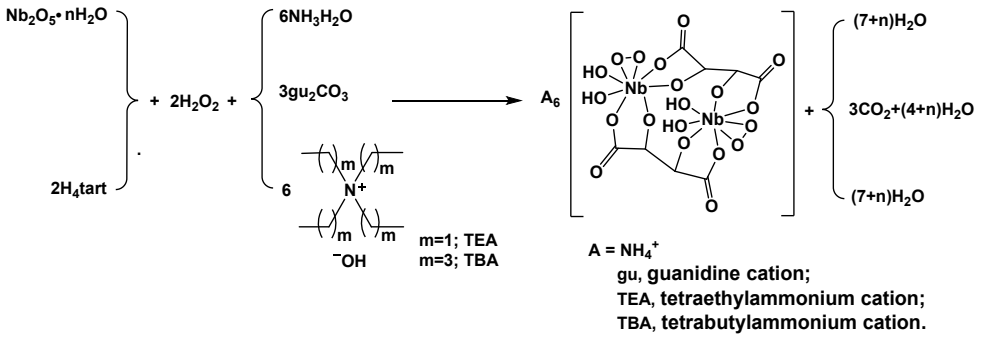
Synthesis of $(NH_4)_3[Nb(O_2)_4]$

$(NH_4)_3[Nb(O_2)_4]$ was a standard niobium-based complex which has been reported and can be easily synthesized according to previous literatures. At first, niobic acid ($Nb_2O_5 \cdot nH_2O$) was prepared according to previously described method.[1] Generally, solid KOH and Nb_2O_5 was sintered at 550 °C for 6 h with a certain molar ratio ($n_{(KOH/Nb2O5)}$ =10) in a nickel crucible. Then the mixture was cooled and dissolved in water. The unreacted Nb_2O_5 was separated by filtration and the filtrate was acetified with acetic acid, adjusting pH to 4 until lots of white precipitate was formed. The precipitate was washed with quantities of water to ensure that acetic acid was removed, which was then dried at 50 °C for 2 h. The water content was measured about 75% in niobic acid. The prepared niobic acid (2 mmol, 2.12 g) was dispersed in distilled water (1 mL). Subsequently, 8 mL of H_2O_2 (30 wt.% in H_2O) was added to the mixture and stirred for 0.5 h at 0 °C adjusting pH of the solution to 9-10 with $NH_3 \cdot H_2O$ until the solution became clear. Ethanol was immediately poured into the solution to generate white precipitate. Then, the precipitate can be collected by suction filtration and washed

with ethanol and dried by air. The resulted white precipitate was $(NH_4)_3[Nb(O_2)_4]$. Anal. Calcd for $H_{12}N_3NbO_8$ (274.97): H, 4.36; N, 15.27; Nb, 33.82. Found: H, 4.35; N, 15.21; Nb, 33.75. Number of peroxide bonds: 3.6 per Nb atom.

Synthesis of $(NH_4)_6[Nb_2(OH)_4(O_2)_2(tart)_2]$ ($(NH_4)_6$-Nb)

The Nb-based catalysts in this work were synthesized according to the following equation:



Scheme S1 Synthetic route of Nb-based salts.

It can be seen that niobic acid was reacted with tartaric acid in the presence of H_2O_2, and then neutralized with base ($NH_3·H_2O$, gu_2CO_3, TEAOH, TBAOH) can afford the corresponding the salts of peroxoniobate anion.

At first, the niobic acid (1 mmol, 1.06 g) was dispersed in distilled water (1 mL). Subsequently, 5 mL of H_2O_2 (30 wt.% in H_2O) was added to the mixture and stirred for 0.5 h at 0 °C until the mixture became clear. Tartaric acid (2 mmol, 0.3g) was added to the clear solution and stirred for 1 h. $NH_3·H_2O$ was added to promote the coordination of tartaric acid and niobium center until that the pH was about 10. Ethanol was immediately poured into the solution to generate white precipitate. Then, the precipitate can be collected by suction filtration and washed with ethanol and dried by air. The resulted white precipitate was $(NH_4)_6[Nb_2(OH)_4(O_2)_2(tart)_2]$. Anal. Calcd for $C_8H_{32}N_6Nb_2O_{20}$ (717.98): C, 13.37; H, 4.46; N, 11.70; Nb, 25.91. Found: C, 13.31; H, 4.49; N, 11.68; Nb, 25.86. Number of peroxide bonds: 0.8 per Nb atom.

Synthesis of $TBA_6[Nb_2(OH)_4(O_2)_2(tart)_2]$ (TBA_6-Nb)

The prepared niobic acid (1 mmol, 1.06 g) was dispersed in distilled water (1 mL). Subsequently, 5 mL of H_2O_2 (30 wt.% in H_2O) was added to the mixture and stirred for 0.5 h at 0 °C until the mixture became clear. Tartaric acid (2 mmol, 0.3g) was added to the clear solution and stirred for 1 h. Then 6 mmol of TBAOH (25 wt.% in H_2O) was added to the solution to benefit coordination of tartaric acid with niobium and the solution was stirred for another 3 h. Finally, the solution was dried vacuum to remove solvent and red-brown viscous liquid was obtained. ^{1}H NMR (600 MHz, D_2O): δ 0.80 (t, 17.73 H), 1.20 (m, 11.83 H), 1.49 (m, 11.86 H), 3.04 (t, 11.59 H), 3.19 (s, 1H), ^{13}C NMR (150 MHz, D_2O): δ 13.15, 18.75, 22.97, 58.06, 73.47, 178.25 (Fig. S2). Anal. Calcd for $C_{104}H_{224}N_6Nb_2O_{20}$ (2063.48): C, 60.48; H, 10.86; N, 4.07; Nb, 9.01. Found: C, 60.35; H, 11.08; N, 3.98; Nb, 8.85. Number of peroxide bonds: 0.9 per Nb atom.

Synthesis of $TEA_6[Nb_2(OH)_4(O_2)_2(tart)_2]$ (TEA_6-Nb)

The $TEA_6[Nb_2(OH)_4(O_2)_2(tart)_2]$ was synthesized by a similar procedure but with TEAOH. Briefly, 1 mmol niobic acid in 1 mL of H_2O was stirred with 5 mL H_2O_2 (30 wt.% in H_2O) for 0.5 h. Then tartaric acid (2 mmol, 0.3g) was added and stirred for 1 h. Whereafter, 6 mmol of TEAOH (25 wt.% in H_2O) was added to the mixture and stirred for 3 h. Finally, the solution was dried vacuum to remove solvent and light-yellow viscous liquid was attained. ^{1}H NMR (600 MHz, D_2O): δ 1.13 (t, 18.12 H), 3.12 (q, 12.01 H), 3.22 (s, 1H), ^{13}C NMR (150 MHz, D_2O): δ 7.56, 52.50, 74.57, 178.67 (Fig. S3). Anal. Calcd for $C_{56}H_{128}N_6Nb_2O_{20}$ (1390.73): C, 48.32; H, 9.20; N, 6.04; Nb, 13.37. Found: C, 48.21; H, 9.31; N, 5.96; Nb, 13.15. Number of peroxide bonds: 0.8 per Nb atom.

Synthesis of $gu_6[Nb_2(OH)_4(O_2)_2(tart)_2]$ (gu_6-Nb)

The $gu_6[Nb_2(OH)_4(O_2)_2(tart)_2]$ was synthesized according to a similar method of $TBA_6[Nb_2(OH)_4(O_2)_2(tart)_2]$ except for replacement of TBAOH with gu_2CO_3. Generally, 1 mmol niobic acid in 1 mL of H_2O was stirred with 5 mL H_2O_2 (30 wt.% in H_2O) for 0.5 h. Then tartaric acid (2 mmol, 0.3g) was added and stirred for 1 h. Then,

3 mmol of gu_2CO_3 was added to the mixture and stirred for 3 h. Finally, the solution was dried vacuum to remove solvent and white viscous liquid was attained. Anal. Calcd for $C_{14}H_{44}N_{18}Nb_2O_{20}$ (970.11): C, 17.32; H, 4.54; N, 25.98; Nb, 19.17. Found: C, 17.15; H, 4.66; N, 25.75; Nb, 18.98. Number of peroxide bonds: 0.8 per Nb atom.

Catalyst characterization

The catalysts were characterized detailed by various techniques such as FT-IR spectra, Elemental analysis, ICP-AES, ^{93}Nb NMR, TGA, ESI-MS, UV-vis and EXAFS. FT-IR spectra were recorded on a Nicolet Magna 550 FT-IR spectrometer. The elemental analysis of C, H and N were recorded using an Elementar Vario EI III CHNOS elemental analyzer and the ICP-AES analysis of Nb was recorded by a Varian 710 instrument respectively. ^{93}Nb NMR spectra were recorded at ambient temperature by a Varian 700 MHz spectrometer in D_2O working at 171.05 MHz with $NbCl_6^-N(Et)_4^+$ as the reference. A PerkinElmer Pyris Diamond were utilized for TGA measurements. The samples were dried under vacuum at 60 °C for 2 h prior to TGA. The samples were heated from 50 to 800 °C (heating rate: 10 °C min^{-1}) under the flow of anhydrous air (flow rate: 20 mL min^{-1}). High-resolution electrospray ionization mass spectrometry (HR ESI-MS) was operated on a micrOTOF II spectrometer with CH_3CN as solvent. The UV-vis spectra were measured with a Varian Cary 500 UV/Vis spectrophotometer. Extended X-ray absorption fine structure (EXAFS) analysis was conducted at the beamline 1W1B of the Beijing Synchrotron Radiation Facility (BSRF), Institute of High Energy Physics (IHEP), Chinese Academy of Sciences (CAS).

Catalytic oxidation test

The selective oxidation of aromatic amines was performed in liquid phase with a 50 mL Schlenk flask equipped with a magnetic stirrer. In a typical experiment, 10 mmol arylamines, 15 mmol H_2O_2, 7.8×10^{-3} mol% of Nb-based salt and toluene (an internal standard) were dissolved in 10 mL ethanol at 30 °C. The reaction solution was withdrawn periodically for analysis using gas chromatography (GC). The N-phenylhydroxylamine and 4-aminophenol cannot detectable by GC and thus were

detected by a high-performance liquid chromatography (WuFen LC100) equipped with an ultraviolent detector. A SilGreen GH0515046C18A column (150 mm × 4.6 mm) was utilized for product separation with acetonitrile and H_2O ($v_{actonitrile}/v_{H2O}$=7/3) as the mobile phase at a flow rate of 0.5 mL min^{-1}. All the reaction products were recrystallized from ethanol and verified by HPLC and NMR spectra.

$$\text{Conversion}=\frac{moles_{aniline.\,init}-moles_{aniline.\,end}}{moles_{aniline.\,init}}\times 100\%$$

where $moles_{aniline.init}$ represented the molar amount of aniline prior to reaction while $moles_{aniline.end}$ denoted that of aniline after after a set reaction time.

$$\text{Yield}=\frac{n\times moles\ of\ products\ x}{moles_{aniline.init}}\times 100\%$$

(n=1 for N-phenylhydroxyamine, nitrosobenzene and nitrobenzene, n=2 for azoxybenzene).

$$\text{TOF}=\frac{moles_{aniline\ converted}\ (mol)}{moles_{Nb}\ (mol)\times reaction\ time\ (h)}$$ (at initial conversion < 20%)

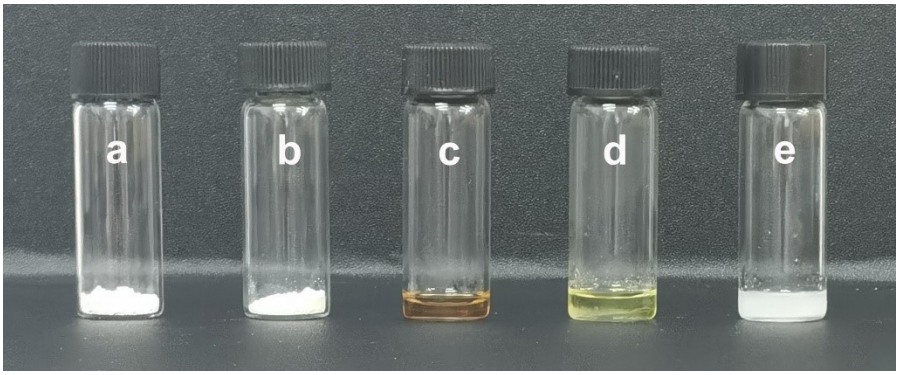


Fig. S1 Photographs of a) $(NH_4)[Nb(O_2)_4]$, b) $(NH_4)_6$-Nb, c) TBA_6-Nb, d) TEA_6-Nb, e) gu_6-Nb under room temperature.

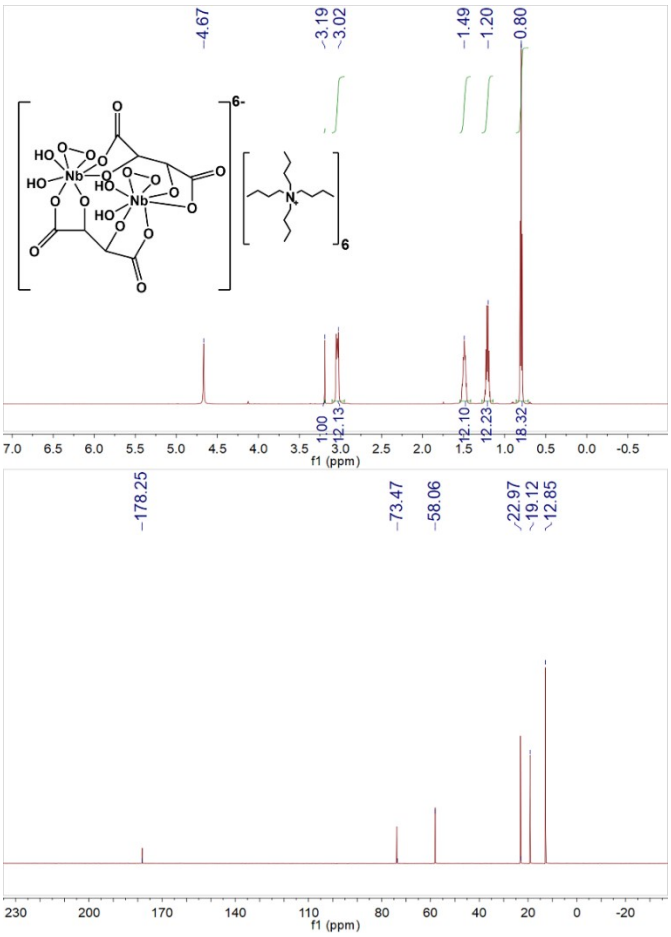


Fig. S2 ^{1}H NMR and ^{13}C NMR of TBA_6-Nb in D_2O.

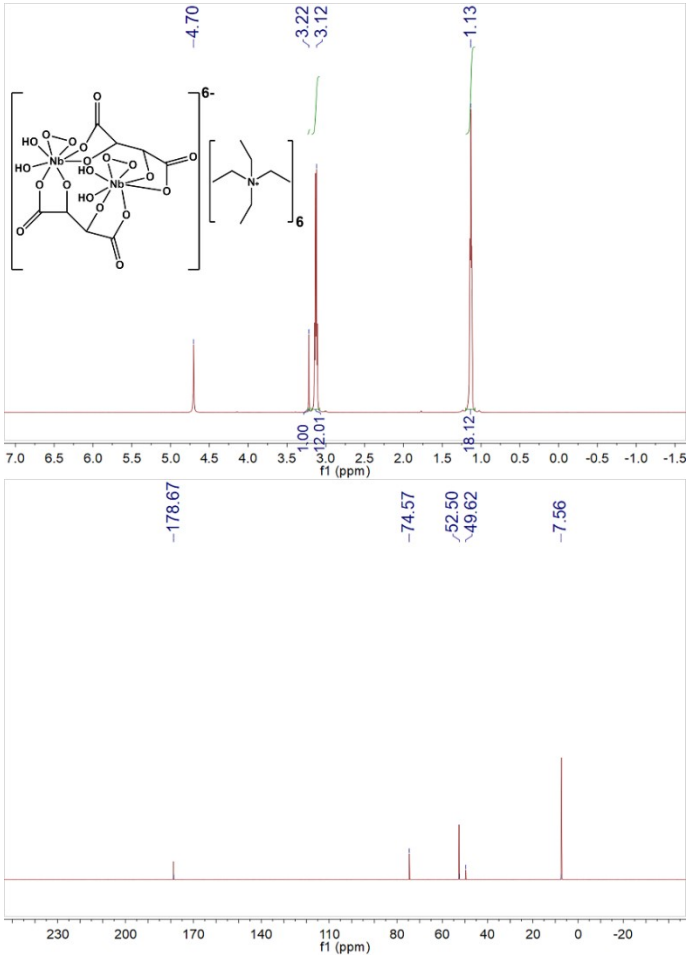


Fig. S3 ^{1}H NMR and ^{13}C NMR of TEA_6-Nb in D_2O.

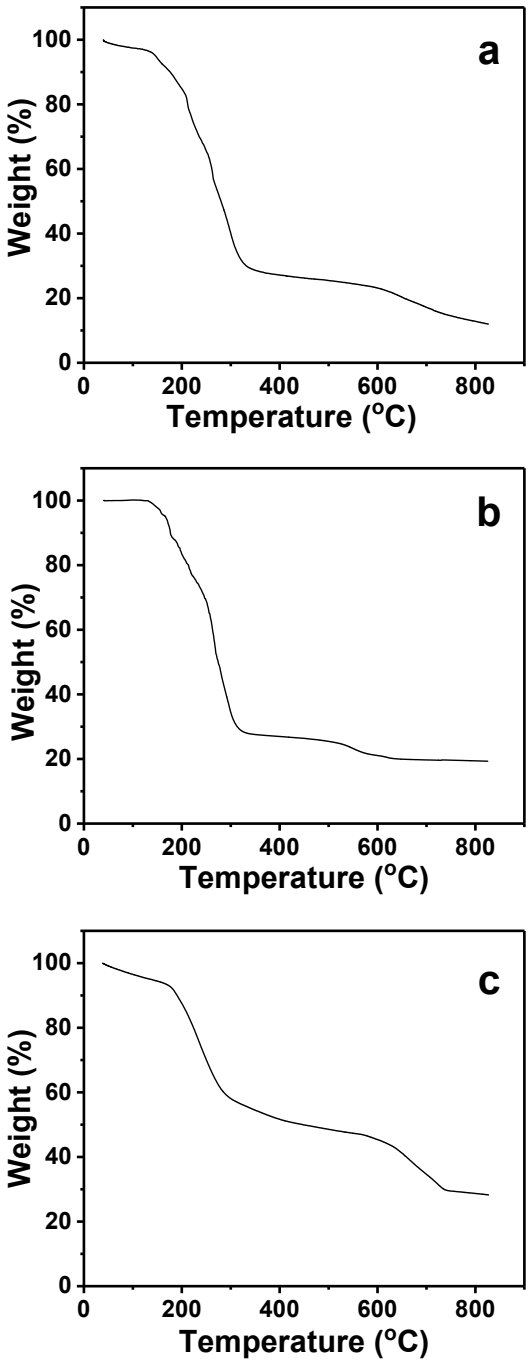


Fig. S4 TGA patterns of a) TBA_6-Nb; b) TEA_6-Nb; c) gu_6-Nb.

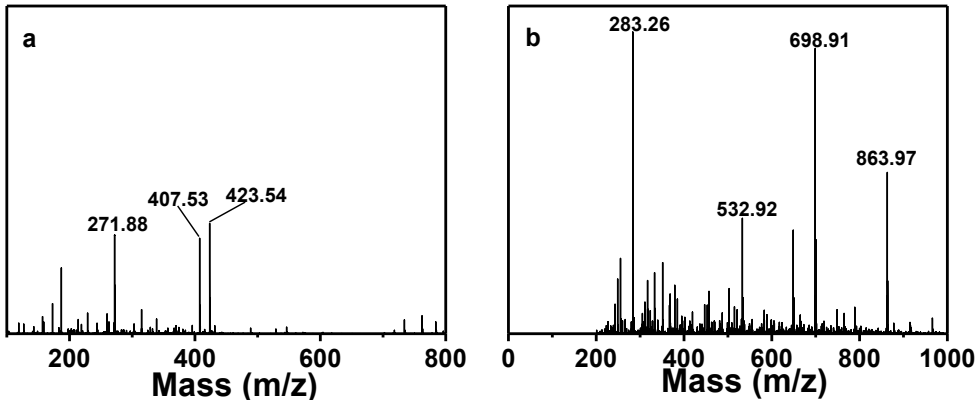


Fig. S5 ESI-MS of a) TBA_6-Nb; b) gu_6-Nb.

Table S1 The identification of anion species in CH_3CN solution of TBA_6-Nb.

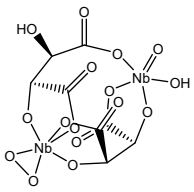
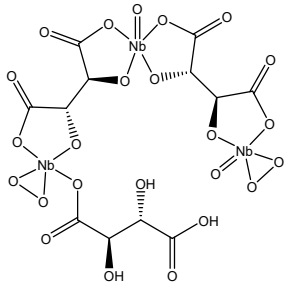
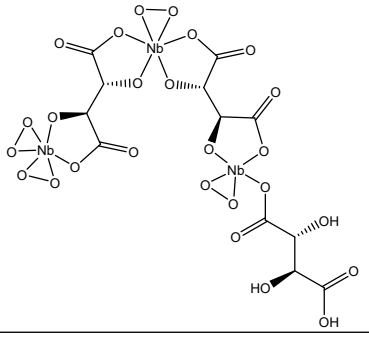
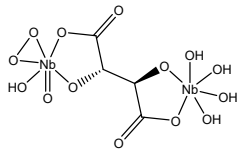
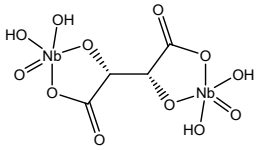
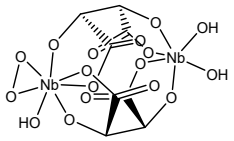
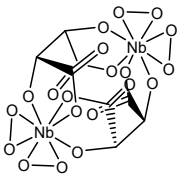
Entry	Mass (m/z)	Formula	Possible structure
1	271.88	$[Nb_2O(O_2)(OH)(tart)_2]^{2-}$	
2	407.53	$[Nb_3(O_2)_2O_2(tart)_2(Htart)]^{2-}$	
3	423.54	$[Nb_3(O_2)_4(tart)_2(Htart)]^{2-}$	

Table S2 The identification of anion species in CH_3CN solution of gu_6-Nb.

Entry	Mass (m/z)	Formula	Possible anion structure
1	283.26	$\{(gu)(CH_3CN)[Nb_2O(OH)_5(O_2)(tart)]\}^{2-}$	
2	532.92	$\{(gu)(CH_3CN)[Nb_2O_2(OH)_4(tart)]\}^{-}$	
3	698.91	$[(gu)_2Nb_2(OH)_3(O_2)(tart)_2(H_2O)]^{-}$	
4	863.97	$\{(gu)_4H[Nb_2(O_2)_4(H_2O)(tart)_2]\}^{-}$	

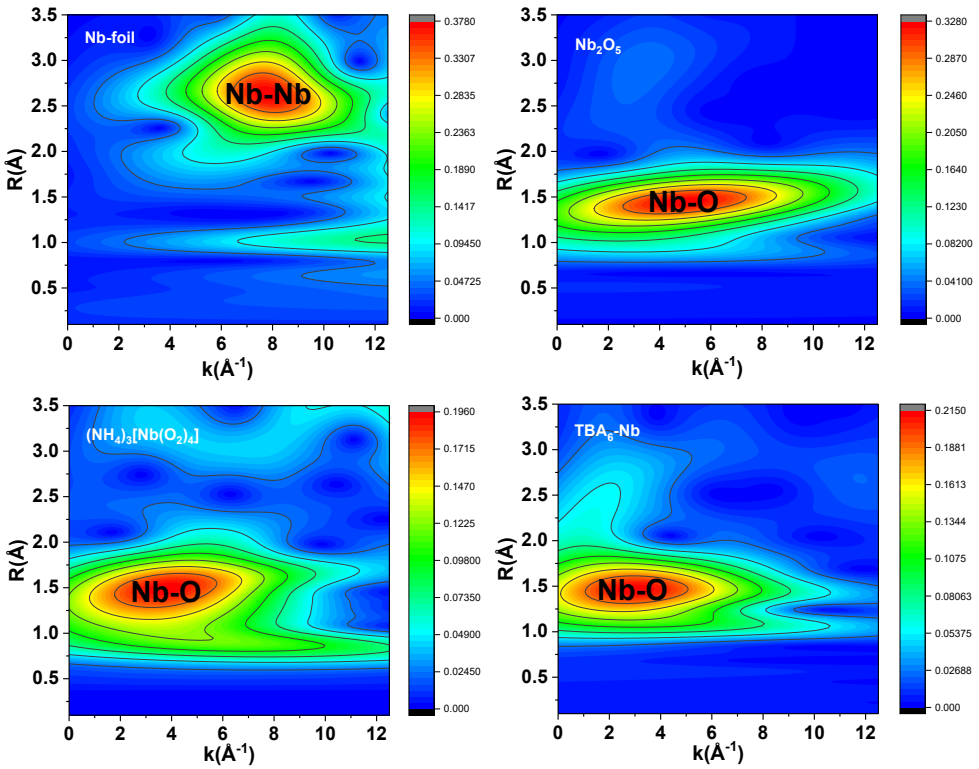


Fig. S6 Experimental 2D WT EXAFS plots for *x*(k) EXAFS data of Nb foil, Nb_2O_5, $(NH_4)_3[Nb(O_2)_4]$ and TBA_6-Nb.

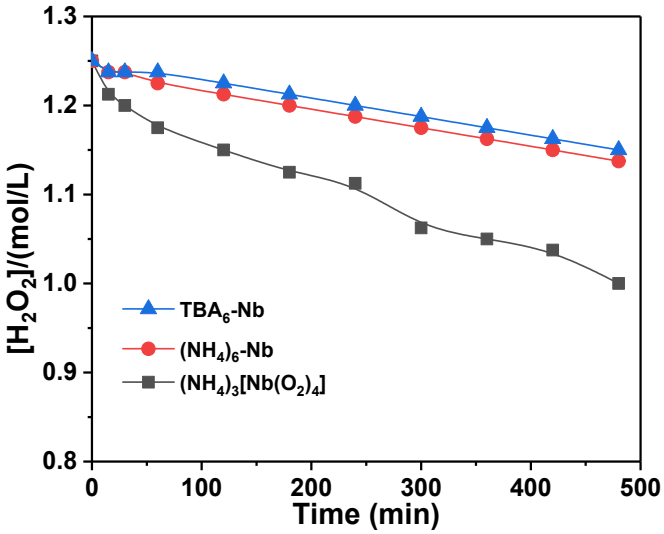
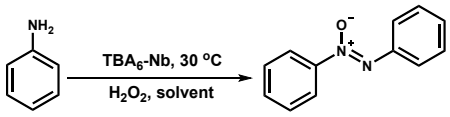


Fig. S7 Dependence of H_2O_2 concentration [H_2O_2] in ethanol on time in the presence of the different catalysts. Conditions: H_2O_2 (15 mmol, 30 wt%), ethanol (10 mL), T = 30 °C. The residual amount of H_2O_2 was measured by potential difference titration of Ce^{3+}/Ce^{4+}.

Table S3 Oxidative coupling of aniline to azoxybenzene in different solvents[a].



			Sel. (%)	
Entries	Solvents	Con. (%)[b]	Azoxybenzene	Others[c]
1	None	5	51	49
2	H_2O	2	1	-
3	dichloromethane	1	1	-
4	acetonitrile	94	93	7
5	acetone	91	96	4
6	methanol	98	97	3
7	ethanol	98	97	3

[a]Reaction conditions: 10 mmol aniline, 10 mL solvent, 7.8×10^{-3} mol% TBA_6-Nb, 1.5 equiv H_2O_2, 30 °C, 5 h. [b]GC conversion with toluene as an internal standard. [c]Others include nitrosobenzene, nitrobenzene, N-phenylhydroxylamine and 4-aminophenol.

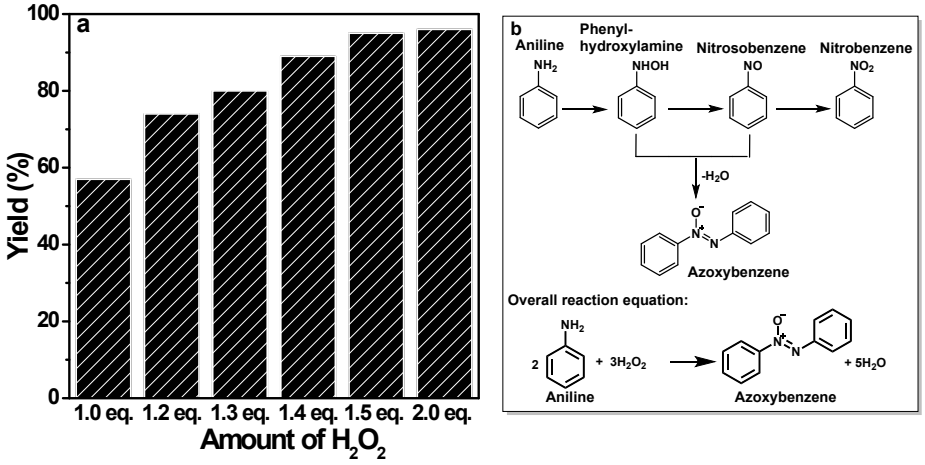


Fig. S8 a) Effect of the molar ratio of H_2O_2 to aniline on yield of azoxybenzene. Reaction conditions: 10 mmol aniline, 10 mL ethanol, TBA_6-Nb (7.8×10^{-3} mol%), 30 ^{o}C, 5 h. b) Reaction pathways for the synthesis of azoxybenzene through the oxidation of aniline

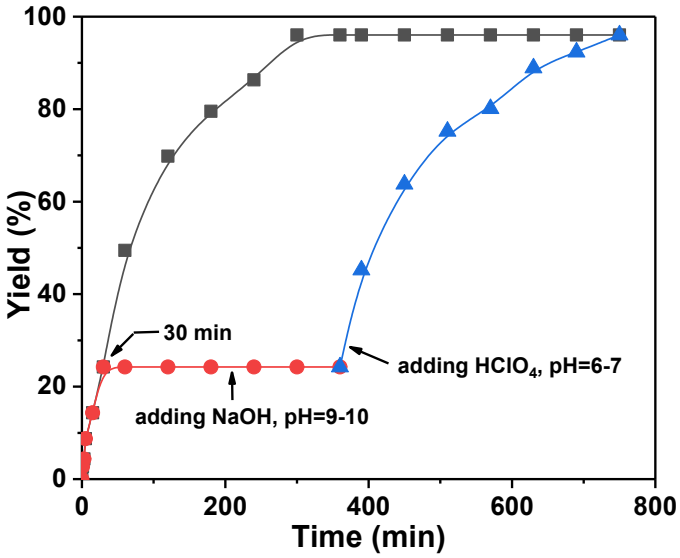


Fig. S9 Time profile of the oxidative coupling of aniline in the presence of different additives adjusting the pH of the solution. Reaction conditions: 10 mmol aniline, 10 mL ethanol, 7.8×10^{-3} mol% TBA_6-Nb, 1.5 equiv H_2O_2, 30 °C. After reaction for 30min, the reaction solution was equally divided into two parts. One part was continued to stir for reaction (black line) and another part was added by NaOH solution until the pH of the solution was adjusted to pH=9-10 (red line). Subsequently, $HClO_4$ was added to the part and the pH was adjusted again from 9-10 to 6-7 (blue line).

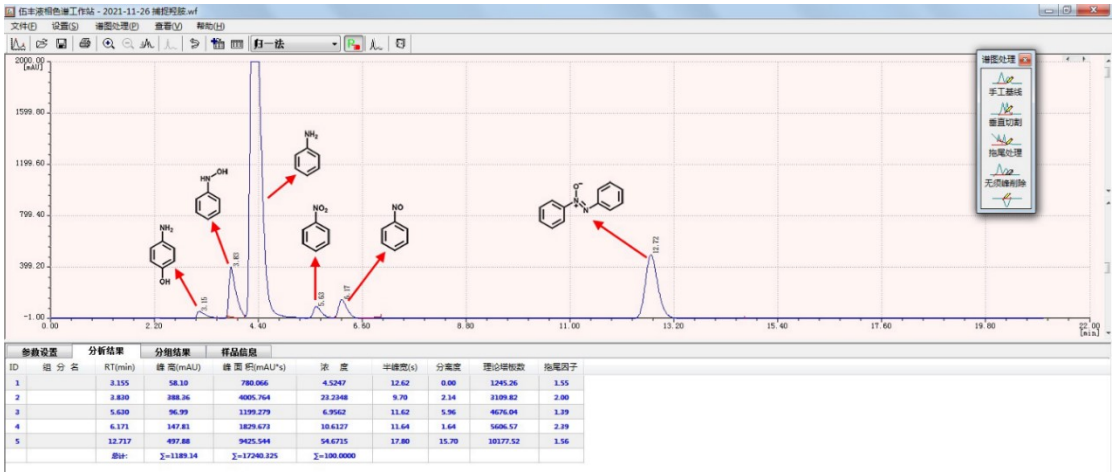


Fig. S10 HPLC chromatogram of the initial reaction solution. Reaction conditions: 10 mmol aniline, 10 mL ethanol, 1.5 equiv H_2O_2, 7.8×10^{-3} mol% TBA_6-Nb, -5 °C, 15 min.

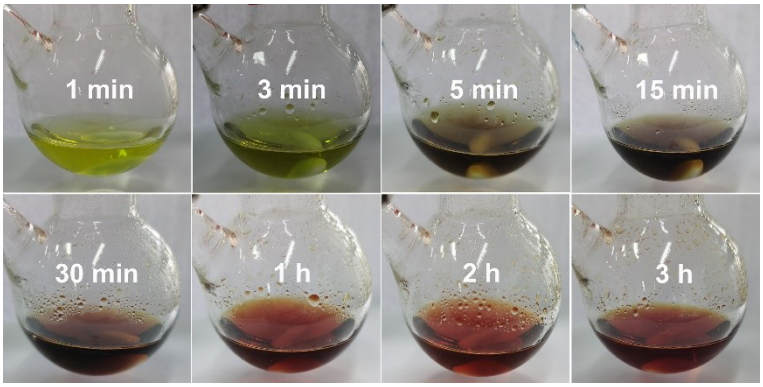


Fig. S11 The color of aniline oxidation solution varies with time. Reaction conditions: 10 mmol aniline, 10 mL ethanol, 7.8×10^{-3} mol% TBA_6-Nb, 1.5 equiv H_2O_2, 30 °C.

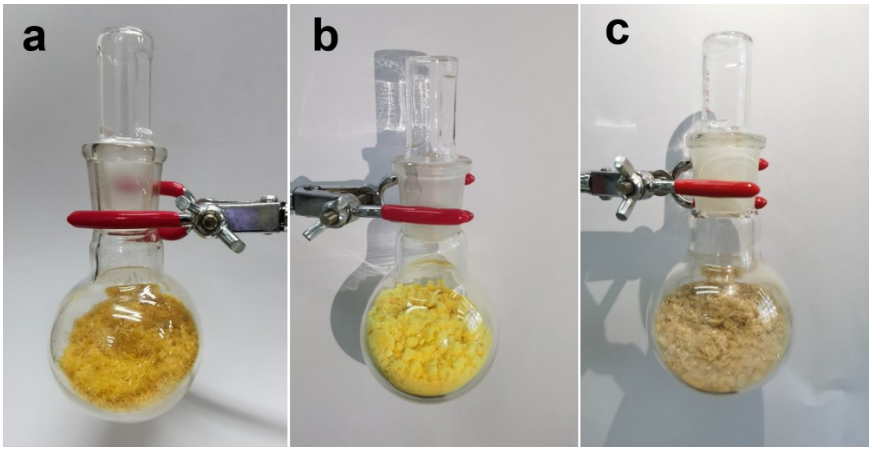


Fig. S12 Crystalline products of a) Azoxybenzene; b) 4,4'-Azoxytoluene; c) 4,4'-Azoxychlorobenzene in a large-scale study (*ca*. 10 g).

Table S4 Comparison of the TBA_6-Nb with the previous reports in the oxidative coupling of aniline to azoxybenzene.

Catalyst	Aniline :H_2O_2	t (^oC)	Solvent	Yield[a] (%)	TOF (h^{-1})	Ref.
TiO_2	1:3	50	Methanol	98	2.3	2
P25	1:1.7	60	-	51	50	3
TS-1	1:0.8	70	t-Butanol	20	1.2	4
Ti-MCM-48	1:3	50	Methanol	90	2.0	5
Ti-Beta	1:0.2	70	Acetonitrile	8	0.2	6
Co-Si-oxide	1:2	80	Acetonitrile	99	16	7
$CuCr_2O_4$	1:5	70	1,4-Dioxane	72	0.7	8
Ag-WO_3	1:3	RT	Acetonitrile	79	0.3	9
Cu-CeO_2	1:3	50	Acetonitrile	87	1.4	10
Nb-Zn-Al-oxide[c]	1:2	RT	Methanol	90	0.2	11
$TBA_2[Mo_6O_{19}]$	1:2	50	MTBE	93	12	12
$Zr(OH)_4$	1:3	RT	H_2O	92	10	13
NbOOH-FeOOH	1:11	RT	Propanol	80	0.3	14
Nb_2O_5-$scCO_2$	1:1.4	RT	Ethanol	79	305	15
TBA_6-Nb	1:1.5	RT	Ethanol	97	4358	This work

[a]Refer to yield of azoxybenzene

Azoxybenzene: Crude product was purified by recrystallization from ethanol. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.41 (m 1H), 7.47-7.58 (m, 5H), 8.11-8.21 (d, 2H), 8.25-8.35 (d, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.39, 125.58, 128.75, 128.84, 129.66, 131.63, 144.05, 148.39. HPLC analysis conditions: mobile phase: $V_{acetonitrile}/V_{H2O}$) =7/3; flow rate: 0.5 mL min^{-1}.

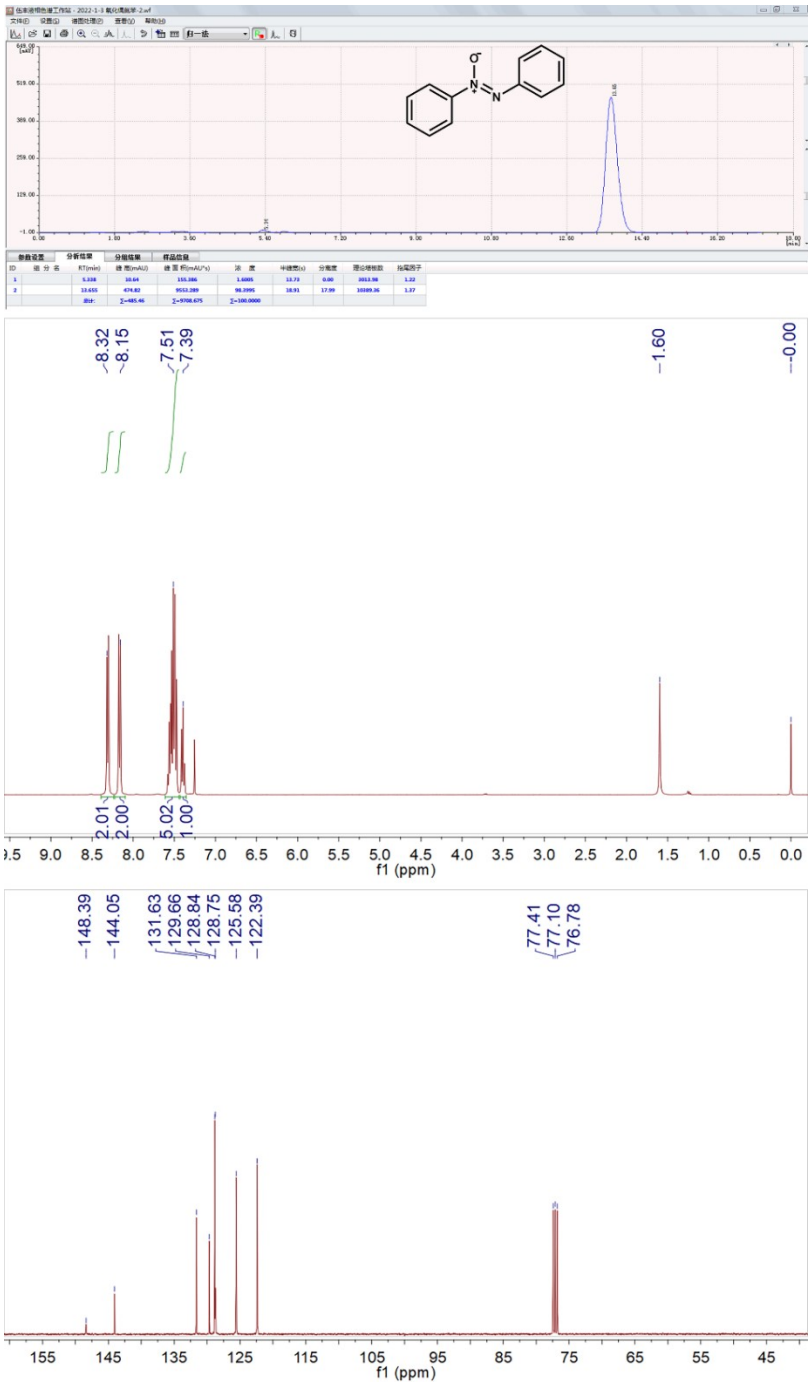


Fig. S13 HPLC chromatogram ^{1}H NMR and ^{13}C NMR spectra of azoxybenzene.

2,2'-Azoxytoluene: Crude product was purified by recrystallization from ethanol. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 2.51 (s, 3H), 7.21-7.31 (m, 5H), 7.36 (m, 1H), 7.67 (d, 1H), 8.03 (d, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.45, 18.54, 121.59, 123.62, 126.11, 126.64, 128.64, 130.07, 130.83, 131.24, 131.83, 134.16, 142.82, 149.49. HPLC analysis conditions: mobile phase: $V_{acetonitrile}/V_{H2O}$) =7/3; flow rate: 0.5 mL min^{-1}.

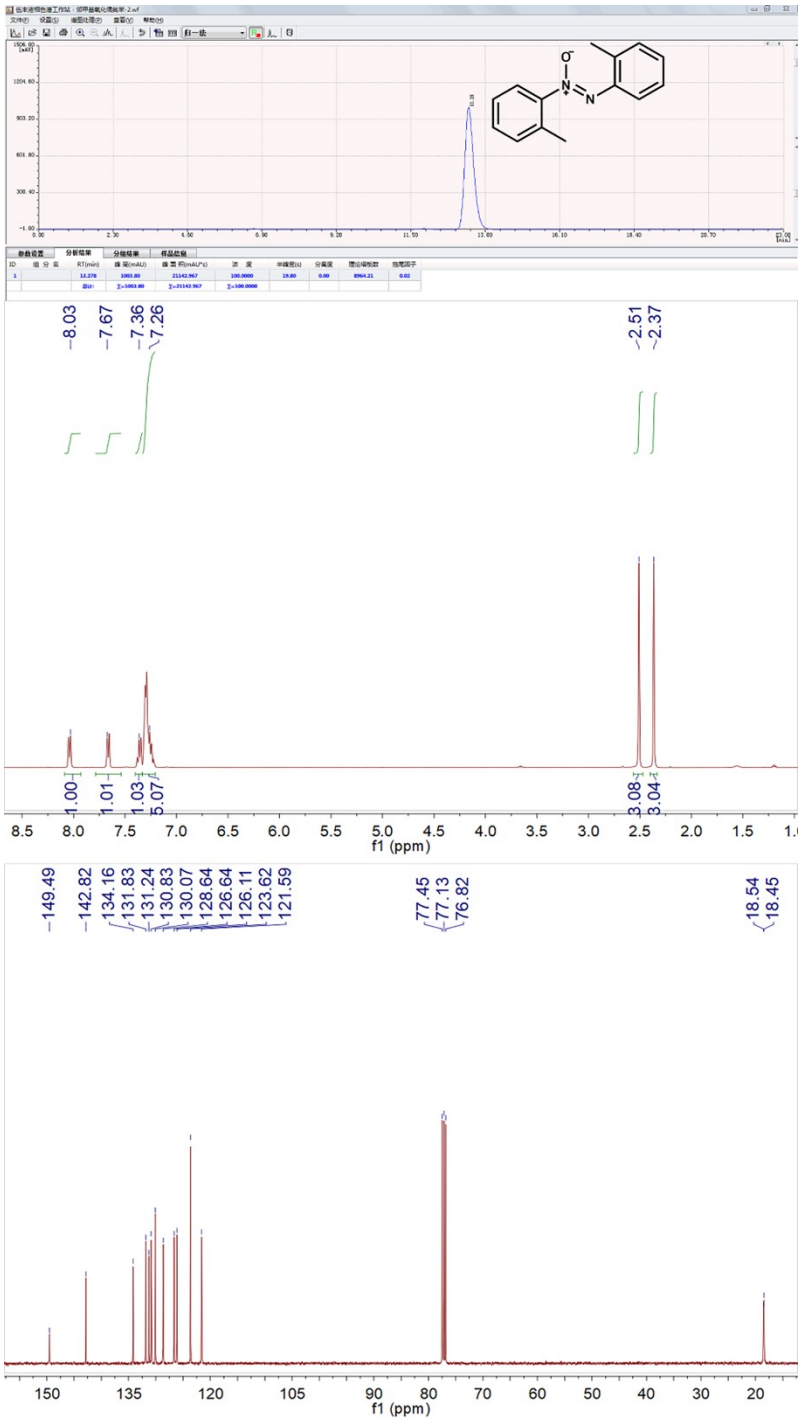


Fig. S14 HPLC chromatogram, ^{1}H NMR and ^{13}C NMR spectra of 2,2'-azoxytoluene.

2,2'-Azoxychlorobenzene: Crude product was purified by recrystallization from ethanol. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (m, 1H), 7.35-7.46 (m, 3H), 7.51-7.54 (m, 2H), 7.74 (m, 1H), 7.99 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.41, 125.21, 126.82, 127.10, 127.64, 129.65, 129.77, 130.32, 131.09, 131.23, 140.86, 147.27. HPLC analysis conditions: mobile phase: acetonitrile; flow rate: 0.5 mL min^{-1}.

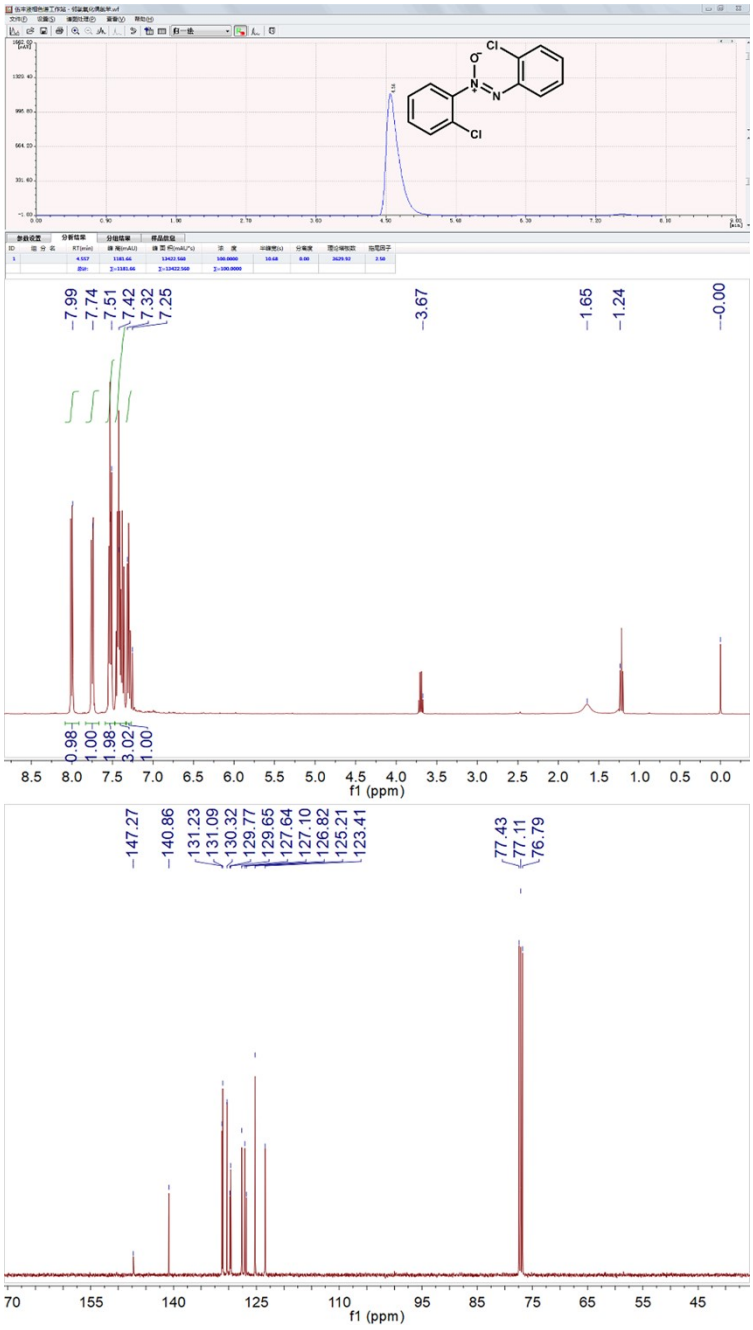


Fig. S15 HPLC chromatogram, ^{1}H NMR and ^{13}C NMR spectra of 2,2'-Azoxychlorobenzene.

2,2'-Azoxyanisole: Crude product was purified by recrystallization from ethanol. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.89 (s, 3H), 3.90 (s, 3H), 6.99-7.10 (m, 4H), 7.32 (t, 1H), 7.40 (t, 1H),7.62 (d, 1H), 8.11 (d, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.01, 56.34, 111.73, 113.03, 120.29, 120.48, 123.16, 124.82, 129.83, 131.12, 133.52, 139.73, 151.92, 153.47. HPLC analysis conditions: mobile phase: $V_{acetonitrile}/V_{H2O}$) =7/3; flow rate: 0.5 mL min^{-1}.

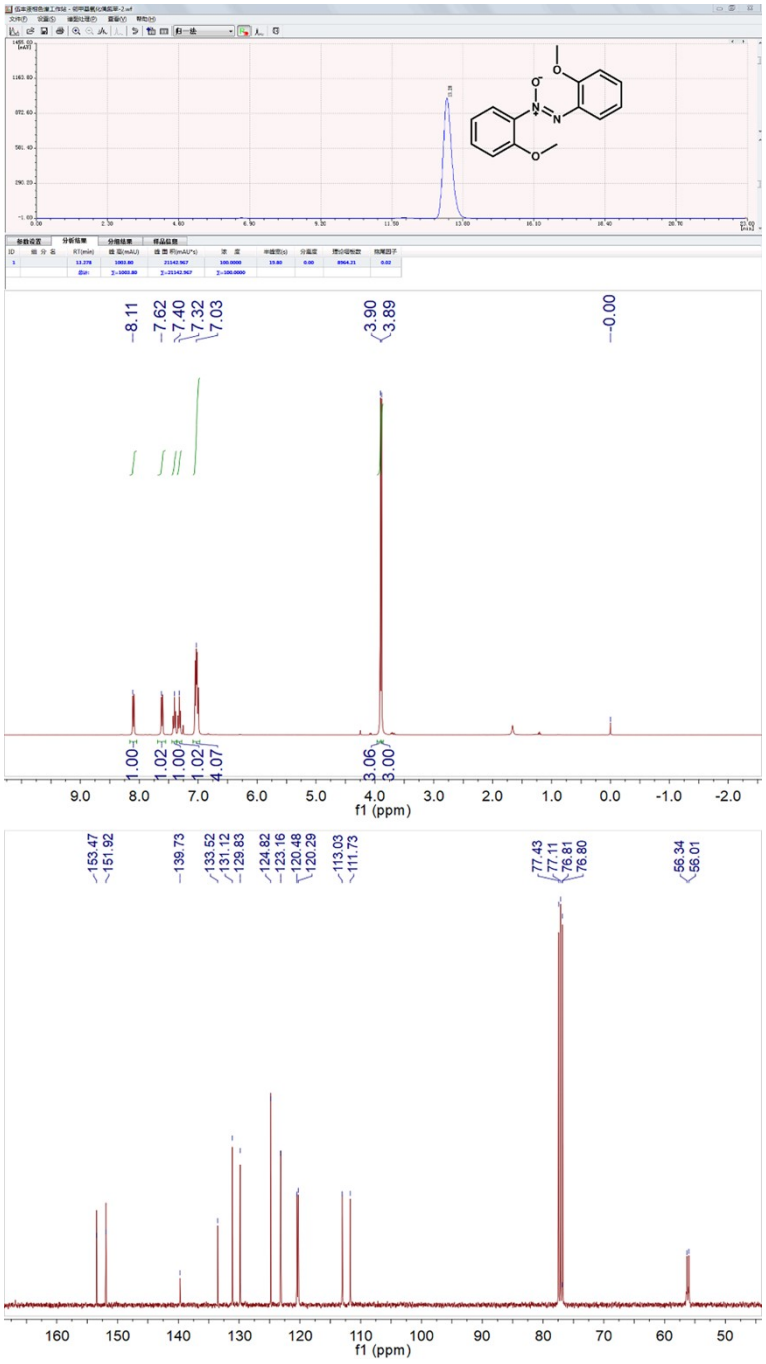


Fig. S16 HPLC chromatogram, ^{1}H NMR and ^{13}C NMR spectra of 2,2'-azoxyanisole.

3,3'-Azoxytoluene: Crude product was purified by recrystallization from ethanol. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H), 2.43 (s, 3H), 7.17-7.19 (m, 1H), 7.30-7.37 (m, 3H), 7.96-7.98 (m, 2H), 8.06-8.09 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.47, 21.52, 119.54, 122.57, 122.81, 126.09, 128.54, 128.62, 130.42, 132.32, 138.47, 144.08, 148.43. HPLC analysis conditions: mobile phase: $V_{acetonitrile}/V_{H2O}$) =7/3; flow rate: 0.5 mL min^{-1}.

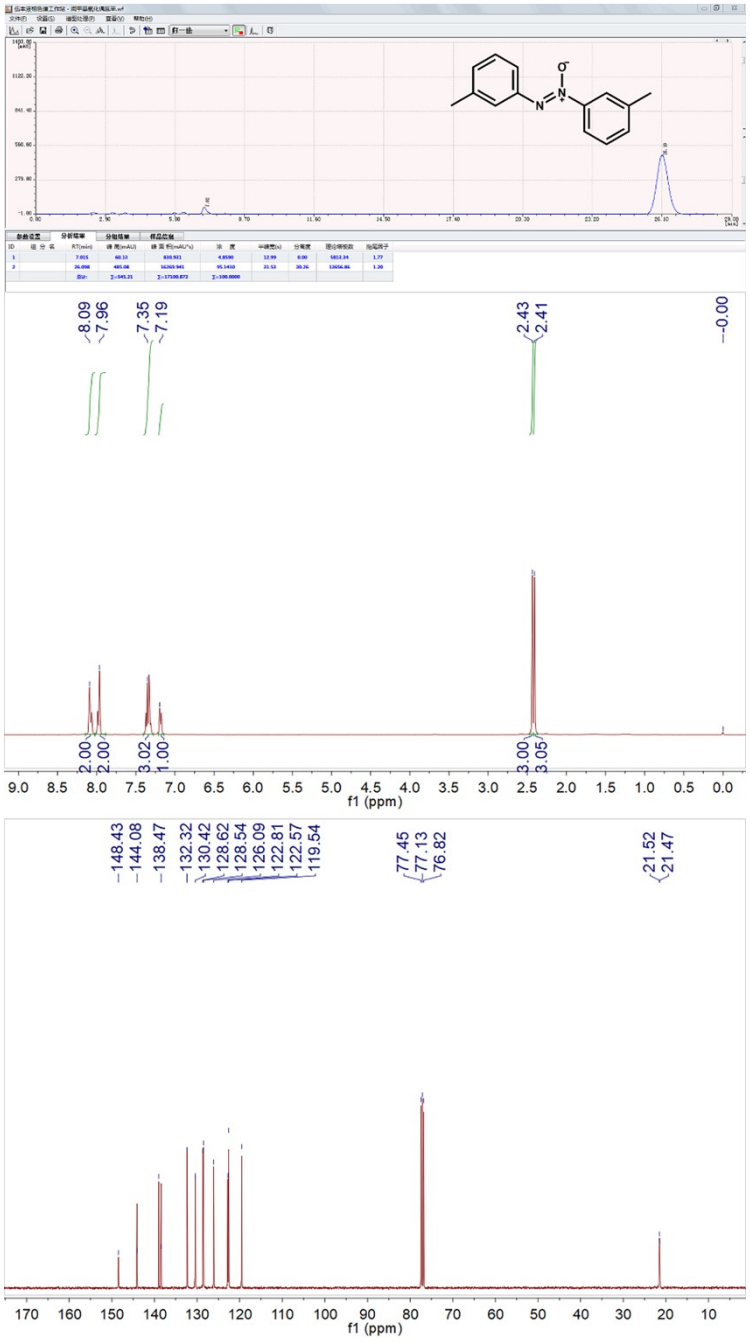


Fig. S17 HPLC chromatogram, ^{1}H NMR and ^{13}C NMR spectra of 3,3'-azoxytoluene.

3,3'-Azoxychlorobenzene: Crude product was purified by recrystallization from ethanol. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.54 (m, 4H), 7.99 (d, 1H), 8.19 (d, 1H), 8.24-8.29 (d, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.63, 122.84, 124.12, 125.42, 129.75, 132.03, 134.42, 134.83, 144.53, 148.82. HPLC analysis conditions: mobile phase: acetonitrile; flow rate: 0.5 mL min^{-1}.

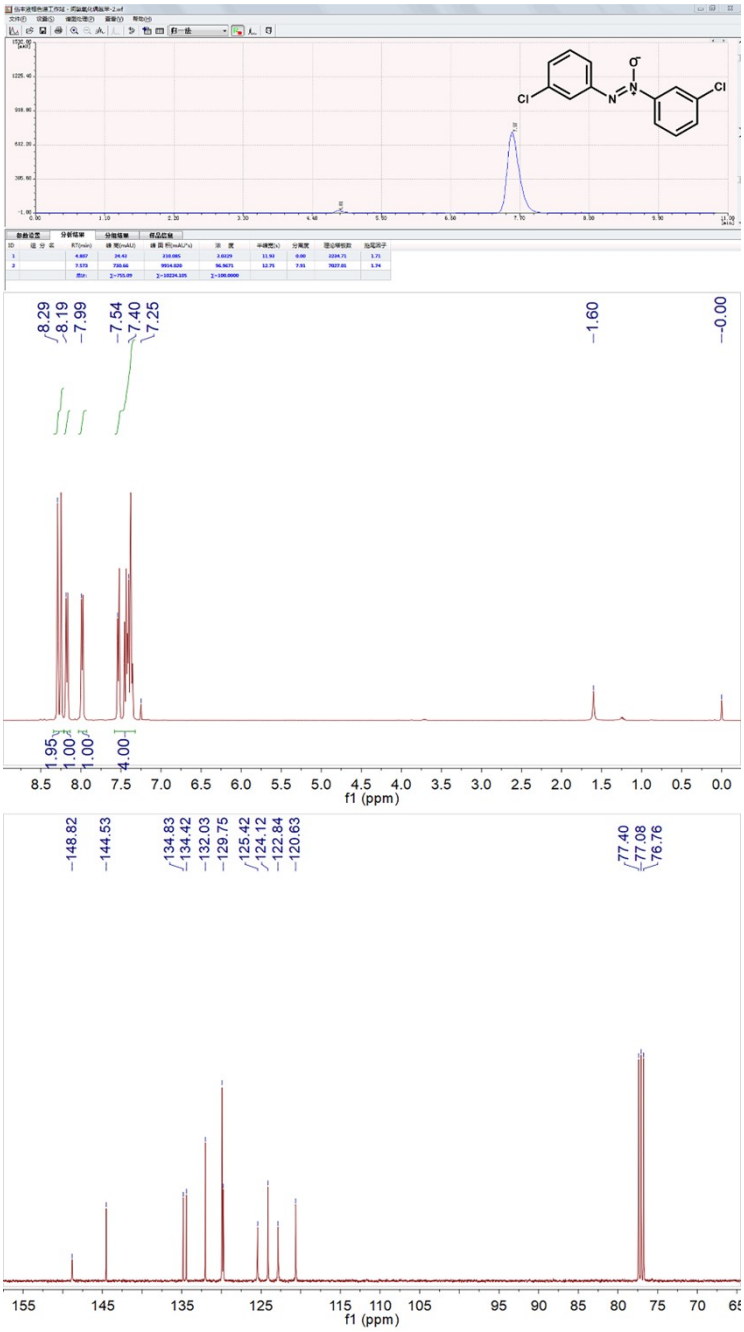


Fig. S18 HPLC chromatogram, ^{1}H NMR and ^{13}C NMR spectra of 3,3'-Azoxychlorobenzene.

4,4'-Azoxytoluene: Crude product was purified by recrystallization from ethanol. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H), 2.44 (s, 3H), 7.27-7.30 (d, 4H), 8.10 (d, 2H), 8.17 (d, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.06, 16.36, 116.90, 116.95, 120.45, 120.49, 124.04, 124.13, 134.80, 136.65, 136.71, 141.01. HPLC analysis conditions: mobile phase: $V_{acetonitrile}/V_{H2O}$) =7/3; flow rate: 0.5 mL min^{-1}.

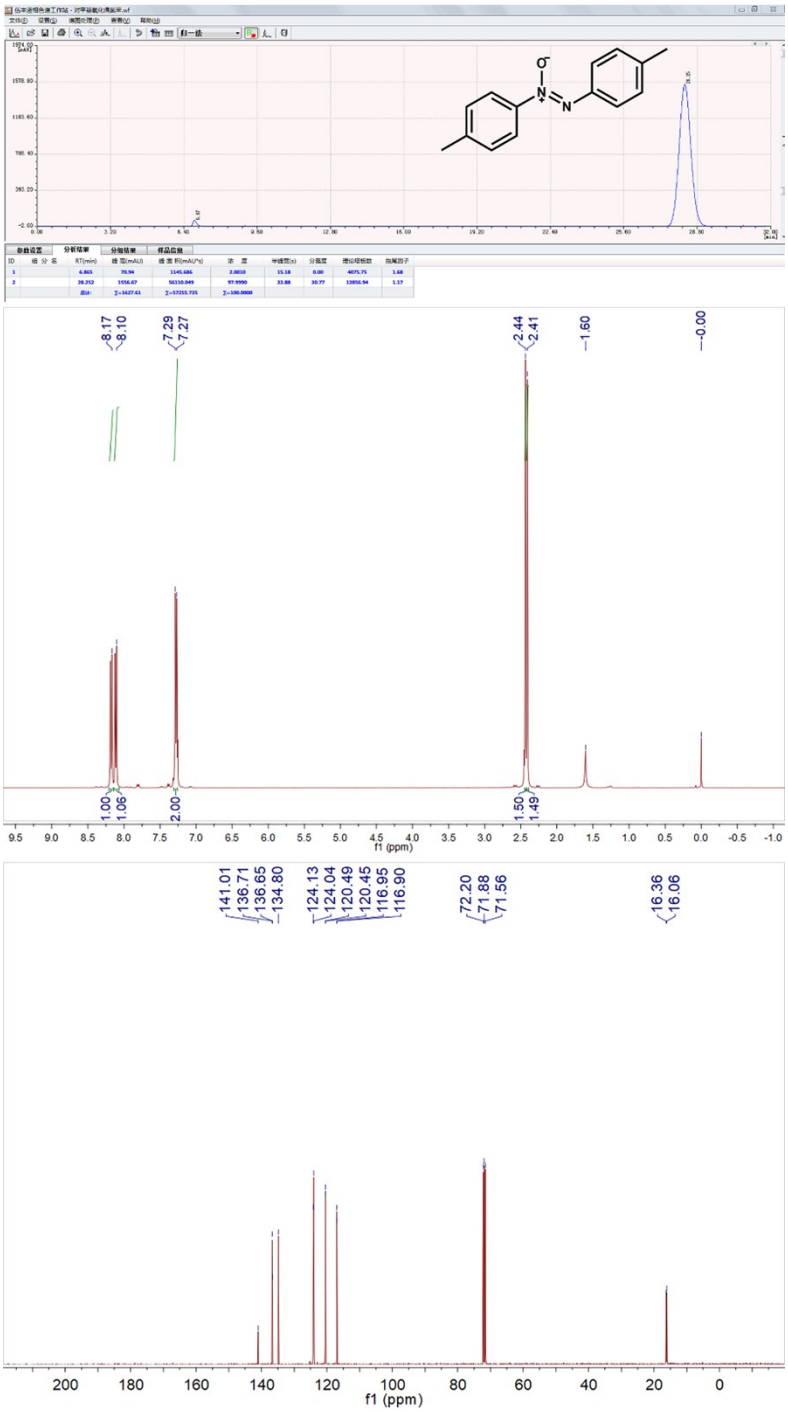


Fig. S19 HPLC chromatogram, ^{1}H NMR and ^{13}C NMR spectra of 4,4'-Azoxytoluene.

4,4'-Azoxychlorobenzene: Crude product was purified by recrystallization from ethanol. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.52 (m, 4H), 8.14 (d, 2H), 8.23 (d, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.69, 127.08, 128.95, 129.01, 135.25, 138.06, 142.19, 146.50. HPLC analysis conditions: mobile phase: acetonitrile; flow rate: 0.5 mL min^{-1}.

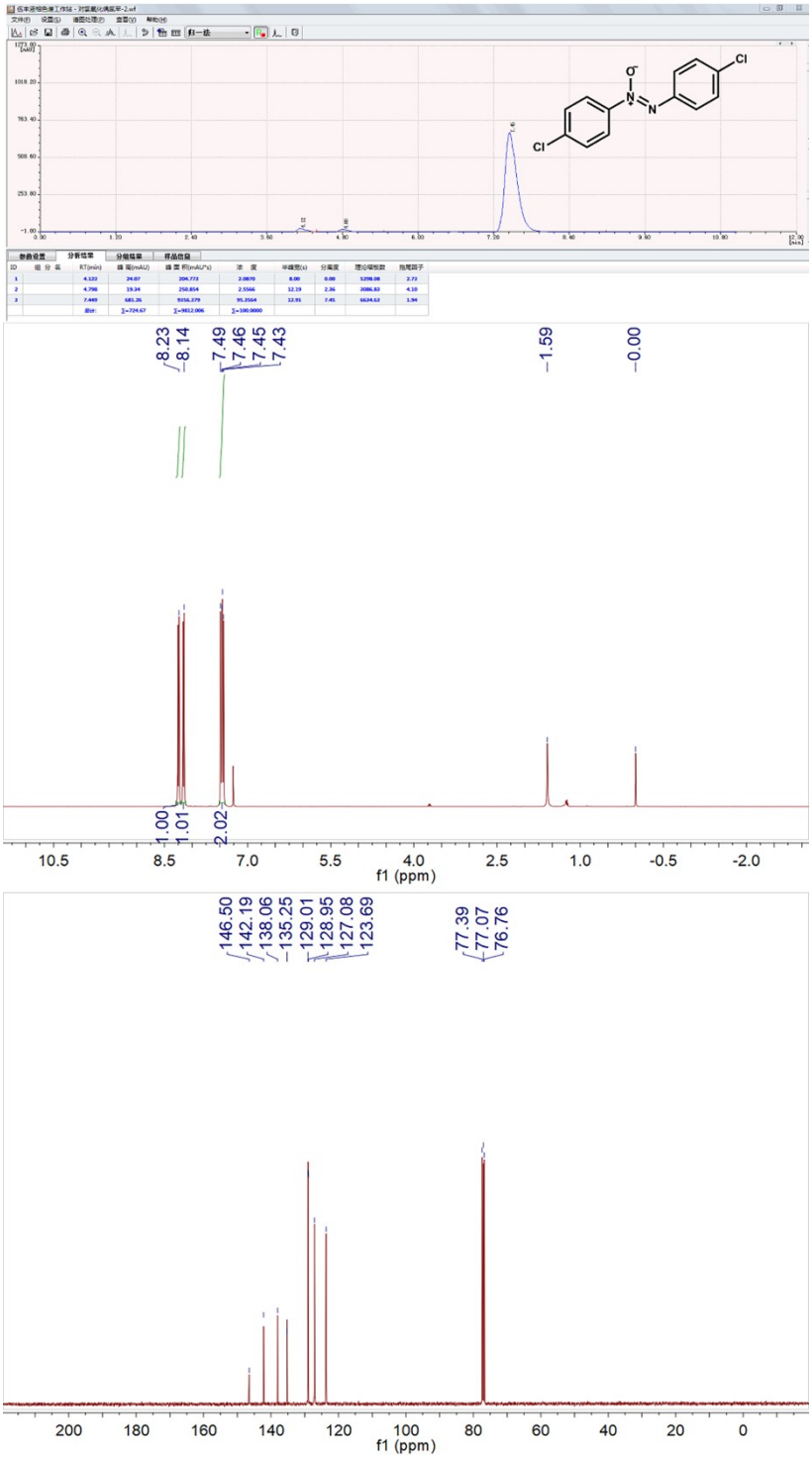


Fig. S20 HPLC chromatogram, ^{1}H NMR and ^{13}C NMR spectra of 4,4'-Azoxychlorobenzene.

4,4'-bis(hydroxymethl)azoxybenzene: Crude product was purified by recrystallization from ethanol. ^{1}H NMR (400 MHz, DMSO-d_6) δ 4.59 (s, 2H), 4.64 (s, 2H), 5.47 (s, 2H), 7.51 (d, 2H), 7.57 (d, 2H), 8.13 (d, 2H), 8.22 (d, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 62.57, 62.97, 122.27, 125.50, 127.07, 127.21, 142.63, 145.15, 146.74, 147.53. HPLC analysis conditions: mobile phase: acetonitrile; flow rate: 0.5 mL min^{-1}.

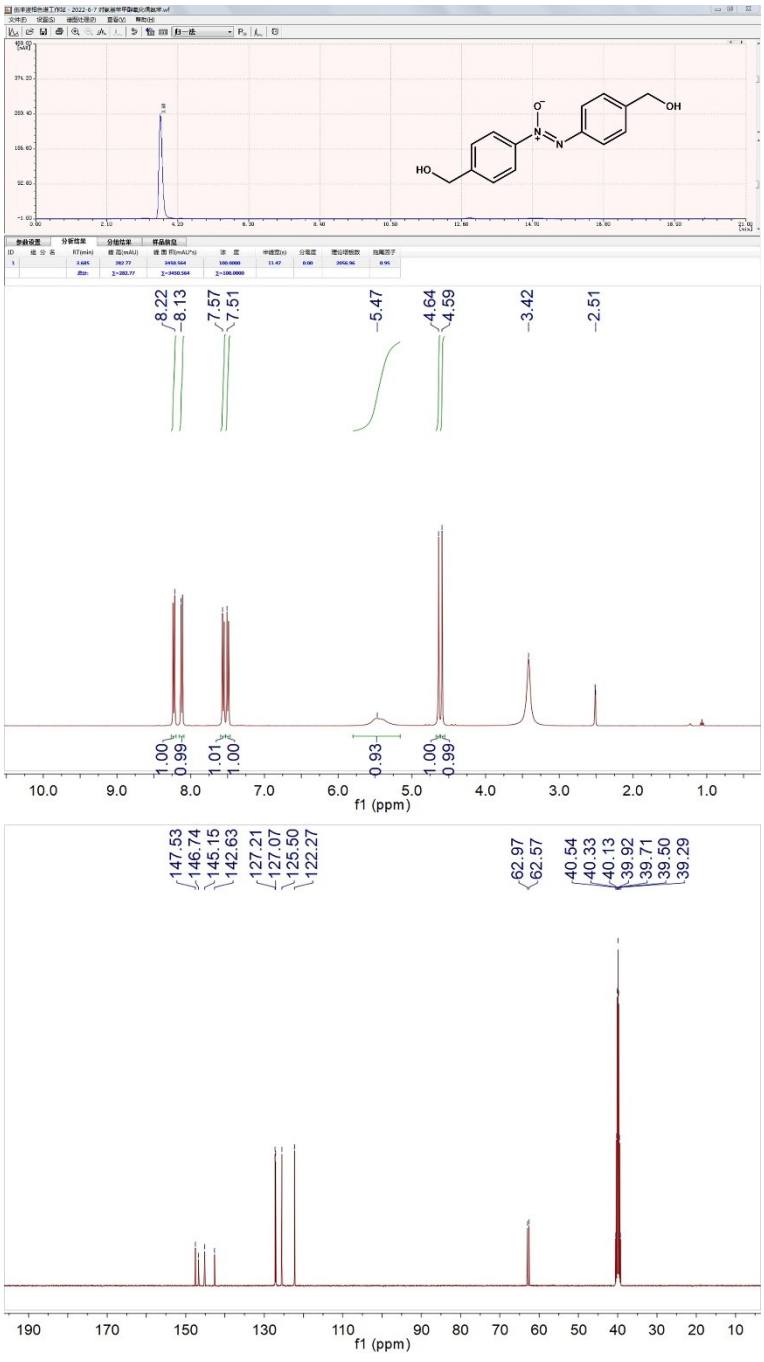


Fig. S21 HPLC chromatogram, ^{1}H NMR and ^{13}C NMR spectra of 4,4'-bis(hydroxymethl)azoxybenzene.

1,2-Di(pyridine-3-yl)diazene oxide: Crude product was purified by recrystallization from ethanol. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.59 (m, 1H), 7.70 (m, 1H), 8.63 (m, 3H), 8.87 (m, 1H), 9.16 (d, 1H), 9.44 (d, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 124.43, 124.69, 130.65, 140.01, 143.96, 144.15, 147.38, 150.85, 153.69. HPLC analysis conditions: mobile phase: acetonitrile; flow rate: 0.5 mL min^{-1}.

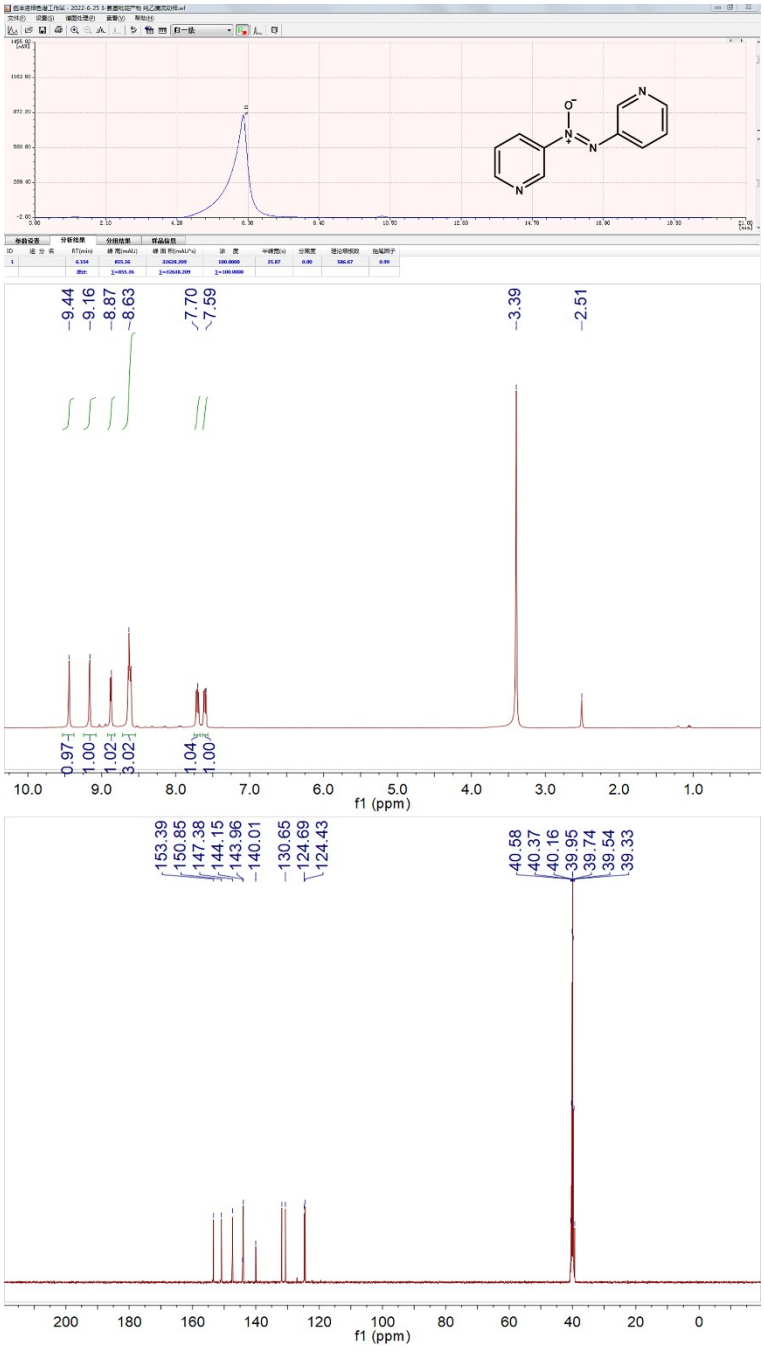


Fig. S22. HPLC chromatogram, ^{1}H NMR and ^{13}C NMR spectra of 1,2-Di(pyridine-3-yl)diazene oxide.

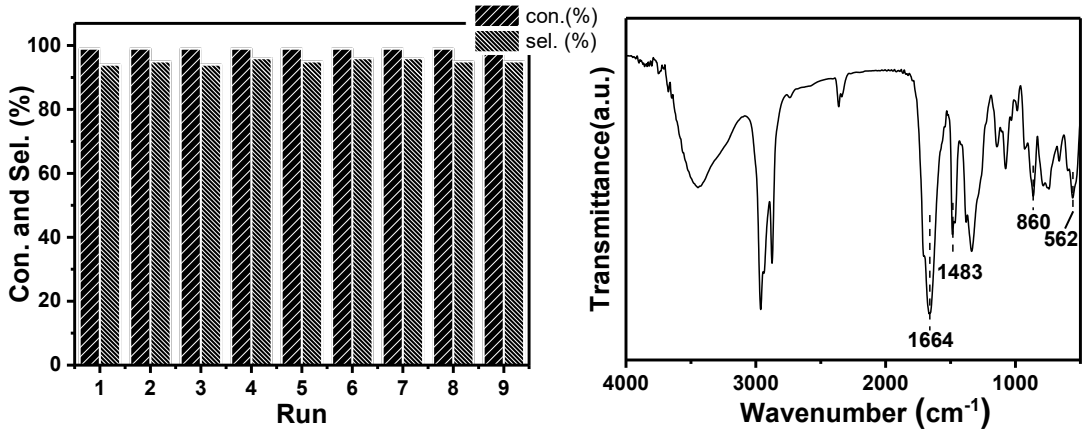


Fig. S23 Left: Recyclability of TBA_6-Nb for oxidative coupling of aniline. Reaction conditions: 10 mmol aniline, 0.2 g TBA_6-Nb, 1.5 equiv H_2O_2, 30 °C, 5 h, 10 mL ethanol. Right: FT-IR spectra of the reused TBA_6-Nb.

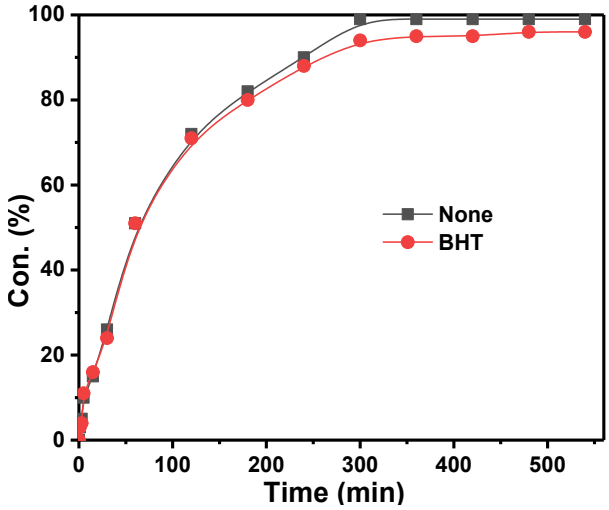


Fig. S24 Time profile of the oxidative coupling of aniline in the presence of and without adding BHT as radical scavenger. Reaction conditions: 10 mmol aniline, 10 mL ethanol, 7.8×10^{-3} mol% TBA_6-Nb, 1.5 equiv H_2O_2, 30 °C.

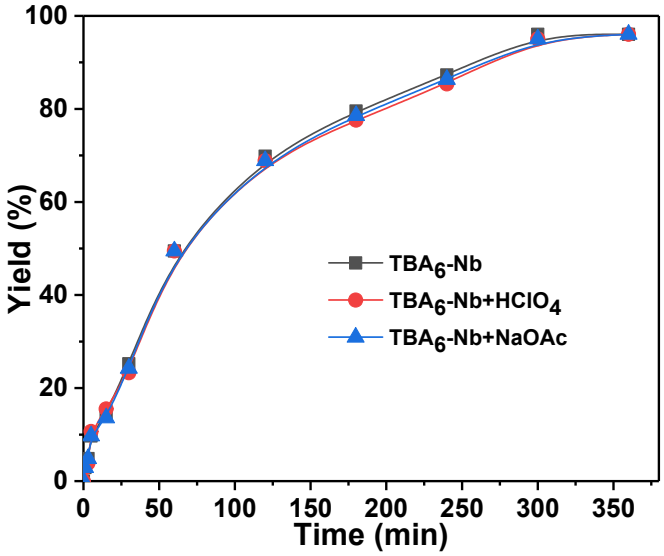


Fig. S25 Time profile of the oxidative coupling of aniline in the presence of additives. Reaction conditions: 10 mmol aniline, 10 mL ethanol, 7.8×10^{-3} mol% TBA_6-Nb, 1.5 equiv H_2O_2, 30 °C, n_{HClO4}/n_{Nb}=1.2/1 or n_{NaOAc}/n_{Nb}=1.2/1.

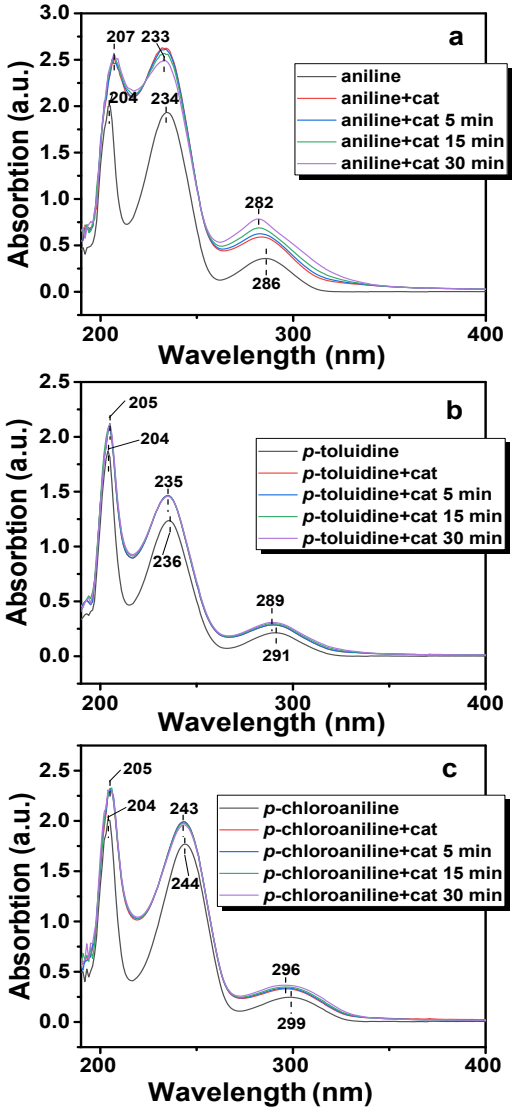


Fig. S26 UV-vis spectra of aniline, *p*-toluidine and *p*-chloroaniline in ethanol ($5x10^{-4}$ mol/L) with TBA_6-Nb catalyst. Cat. refers to the TBA_6-Nb (7.8×10^{-3} mol%).

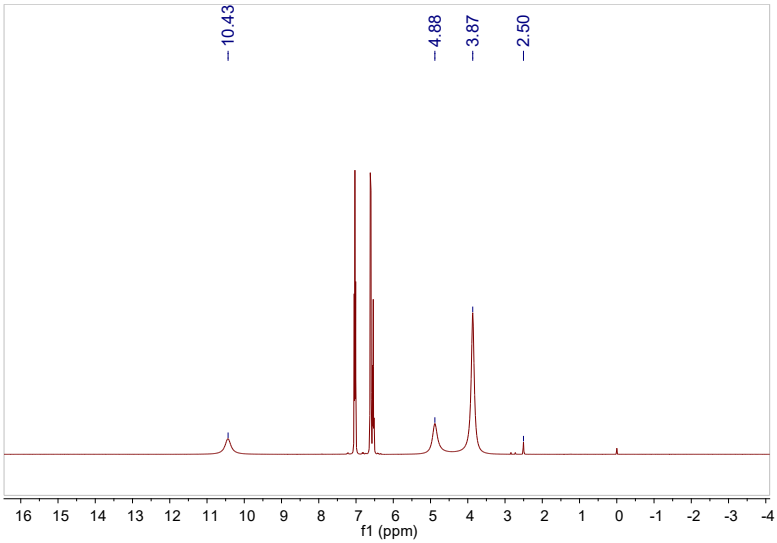
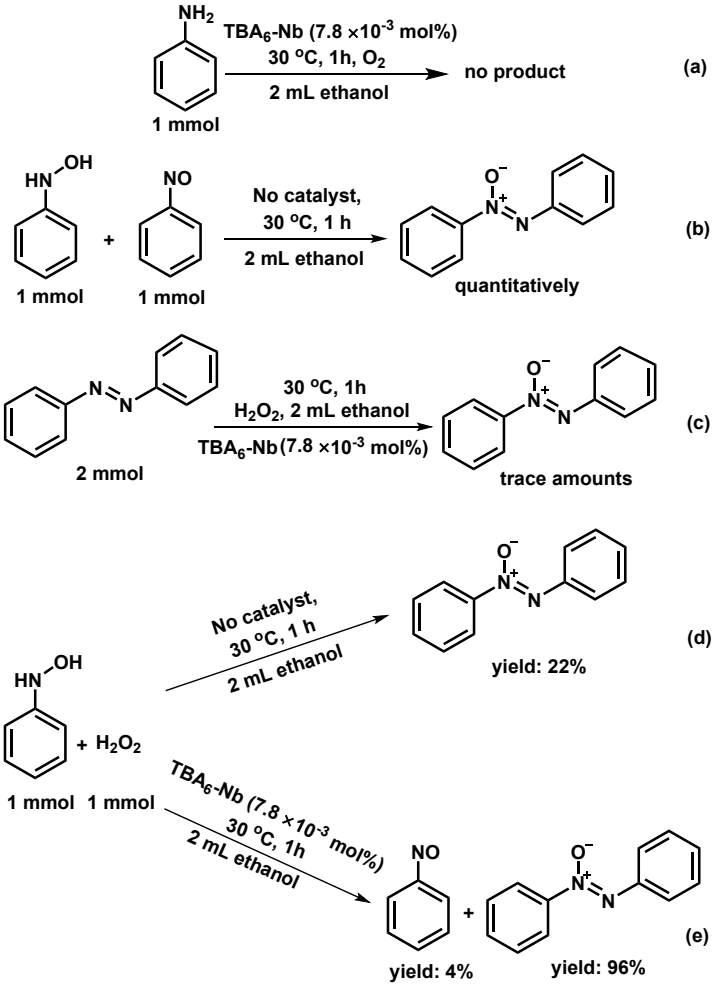


Fig. S27 ^{1}H NMR spectra of aniline in the presence of H_2O_2 in DMSO- d_6.



Scheme S2 Control experiments.

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