Supplementary Information

Mild palladium-catalysed highly efficient hydrogenation of C=N,

C-NO₂ and C=O bonds using H_2 of 1atm in H_2O

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1. General

All chemicals are commercially available and were purchased from Aladdin (Shanghai, China), and used as received without any further purification. All chemicals used were of analytical grade. ¹H NMR and ¹³C NMR spectrum were recorded on a Bruker Avance-400 instrument, 400 MHz for ¹H NMR and 100 MHz for ¹³C NMR, with CDCl₃ or DMSO-d6 or CD₃OD-d4 as solvent in all cases. All chemical shifts (δ) were quoted in parts per million (ppm) and reported relative to an internal tetramethylsilicane (TMS, δ 0.00) standard. The following abbreviations were used to explain the multiplicities: *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *m* = multiplet. Yields of some products were measured by HPLC analysis using a SHIMADZU instrument equipped with a Wonda Sil C18-WR column (5µm). Yields of some other products were measured by GC analysis using FULI 9790II instrument equipped with a DB-624 capillary column (30 m1.4 um × 0.25 mm). High-resolution mass spectrometry (HRMS) spectra was recorded on a SHIMADZU liquid chromatography/mass spectrometry ion-trap time-of-flight (LCMS-IT-TOF) instrument.

The High-Resolution Transmission Electron Microscope (HRTEM) measurements were performed using a JEM 2100F microscope. The samples were dispersed in ethanol with ultrasonic for 5min and then dropped onto a carbon film on copper grid. And the instrument was operated at 200 kV. Inductively coupled plasma-optical emission spectrometer (ICP-OES) from Perkin Elmer Nexion 300 was used to identify the Pd content of the nanoparticles. Samples were prepared by digesting 10 mg of nanoparticles in 2.0 mL of H₂O₂ and 8ml aqua regia using constant temperature drying oven for 3 hours. The solutions was made up to 50 mL in standard flask and start to detect Pd.

X-ray diffraction (XRD) patterms was collected from 5° to 90° with a step of 0.02 on a Bruker D 8 Advance diffractometer with Cu K α radiation (λ = 1.5418 Å) and a Lynxeye one-dimensional detector. Elemental analysis (EA) measurement was performed using the Flash 2000. X-Ray photoelectron spectroscopy (XPS) measurements were obtained in ultra-high vacuum (base pressure of 1 × 10⁻¹⁰ mbar) equipped with an Al source (K α radiation of 1486.6 eV) and an Escalab 250Xi analyser at 53° detection angle. The number of active atoms were determined by chemisorption analysis of hydrogen under 50°C using AutoChem II 2920.

2. General procedure for the preparation of Pd-L6

To a mixed solution of the 4-nitrobenzene-1,2-diamine (15.3 mg, 0.1 mmol) and HBF₄ (40%,1ml), sodium nitrite (13.8mg, 0.2mmol) dissolved in ultrapure water (1ml) was added dropwise, with light-yellow solid 2'-(4-nitro-1,2-phenylene)bis(1-(trifluoro- λ^5 -boranylidene)diazen-1-ium) fluoride generated. After being stirred at 0°C for 1 h, the light-yellow solid was obtained, reacting subsequently with toluene (1ml), ultrapure water(2ml) and potassium tetrachloropalladate (K₂PdCl₄, 26.0mg, 0.08mmol) in another new reaction system, which was stirred with a magnetic bar for another 1 h. NaBH₄ (22.6mg, 0.6mmol) dissolved in ultrapure water(1ml) was dropped at room temperature to the previous solution and incubated at room temperature for 2 h. After that, the mixed solution was transferred to a 10 ml centrifuge tube and centrifuged, the aqueous phase was separated and the rest of solid phase was washed with diluted H₂SO₄ (0.5M) three times, following three times washing with a solution of

NaHCO₃(0.5M). The resulted suspension was centrifuged again, its solid phase was washed with ethanol and sonicated for 5 minutes, and centrifuged to remove ethanol. The resulted solid was dried to provide Pd-L6.

3. The behavior of selectivity and pH tolerance of Pd-L6

The selectivity of Pd-L6 with reaction time towards the model substrate benzonitrile for the desired product benzylamine under varied pH conditions were evaluated employing Pd-L6 at the loading of 4mol%, and the results were listed in **Figure S1** and **Figure S2**. Results indicated that with increased pH of reaction medium, though conversions of the substrate benzonitrile decreased from >99% at pH 1.0 to 5% at pH 11.0, the catalyst Pd-L6 still maintained its selectivity at about 99.9%, we did not observe any obvious differences in the selectivity under varied pH conditions during the whole course of the hydrogenation (**Figure S1**). As to the selectivity with reaction time, results indicated that the conversions of the model substrate almost reached an ideal one of 100% within 3h from about 40% at 0.5h after reaction started, the same was with the yields, we did not find any obvious vibration in the selectivity as during the whole reaction, Pd-L6 always kept its selectivity at about >99.9% (**Figure S2**). The above results proved that the selectivity of the catalyst Pd-L6 was pH tolerant, though there was an obvious loss in its activity under strong acidic conditions.



Figure S1 Schematic profile of selectivity and conversions with varied pH



Figure S2 Schematic profile of selectivity and conversions with reaction time

4. Experimental Procedures

4.1 General procedure for synthesis of primary amines from nitrile

Nitrile (0.05 mmol), and Pd-NPs (0.5 mg, 4mmol %) were taken in an oven dried reaction bottle (25 ml) equipped with magnetic pellet. H_2O (10 ml, pH = 1.0) were added to the reaction tube and the reaction mixture was stirred at room temperature with H_2 balloon. The reaction was monitored by TLC. The reaction conversions and yields were determined by HPLC analysis equipped with a C18 column. When the substrate completely consumed, the reaction was stopped, Adjust the pH value of the reaction solution to be weakly alkaline using NaHCO₃ solution and then the solution was extracted with saturated salt water and ethyl acetate (3X10ml). The organic phase was dried by using Na₂SO₄ and concentrated in vacuum. The crude product was purified by column chromatography using silica gel. The products were characterized with NMR (Due to the small scales of the reactions, we combined the products of several runs to get higher concentration samples.)

4.2 General procedure for synthesis of primary amines from nitro compound

Nitro compound (0.05 mmol), and Pd-NPs (0.5 mg, 4mmol %) were taken in an oven dried reaction bottle (25 ml) equipped with magnetic pellet. H₂O (10 ml, pH = 8.0) were added to the reaction tube and the reaction mixture was stirred at room temperature with H₂ balloon. The reaction was monitored by TLC. The reaction conversions and yields were determined by HPLC analysis equipped with a C18 column. When the substrate completely consumed, the reaction was stopped and then the solution was extracted with saturated salt water and ethyl acetate (3X10ml). The organic phase was dried by using Na₂SO₄ and concentrated in vacuum. The crude product was purified by column chromatography using silica gel. The products were characterized with NMR (Due to the small scales of the reactions, we combined the products of several runs to get higher concentration samples.)

4.3 General procedure for synthesis of alcohol from ketone and aldehyde

Ketone or aldehyde (0.05 mmol), and Pd-NPs (0.5 mg, 4mmol %) were taken in an oven dried reaction bottle (25 ml) equipped with magnetic pellet. H₂O (10 ml, pH = 8.0) were added to the reaction tube and the reaction mixture was stirred at room temperature with H₂ balloon. The reaction was monitored by TLC. The reaction conversions and yields were determined by HPLC analysis equipped with a C18 column. When the substrate completely consumed, the reaction was stopped and then the solution was extracted with saturated salt water and ethyl acetate (3X10ml). The organic phase was dried by using Na₂SO₄ and concentrated in vacuum. The crude product was purified by column chromatography using silica gel. The products were characterized with NMR (Due to the small scales of the reactions, we combined the products of several runs to get higher concentration samples.)



5. ¹H NMR spectrum analysis of diazonium salt and Pd-NPs.

Figure S3. 1H NMR spectrum of 4-nitrobenzene-1,2-diamine







Figure S6 Catalytic recycles of Pd-NPs for the catalytic hydrogenation of benzonitrile.

After the successful application of the heterogeneous catalyst Pd-NPs for mild and efficient hydrogenation of an army of nitriles, ketones, aldehydes and nitro-compounds in water at room temperature, the recyclability and recoverability of Pd-NPs were then evaluated on hydrogenation of benzonitrile. When reaction was accomplished, the reaction mixture was placed stationary for 1 hour, and the solution was removed. The resulting solid was washed using ethanol and dried under vacuum. The recycled Pd-NPs were then employed to further cycles of reactions and the results were summarized in **Figure S6**. Results indicated that the Pd-NPs could be repeat reused for ten times without any obvious loss in its catalytic activity, nor in its selectivity.

For recyclability, the reaction was repeated with benzonitrile as substrate (0.05 mmol) and the same conditions as described above, except using the recovered catalyst. When the reaction was accomplished, the reaction mixture was allowed to settle down in 1 hour, and the liquid was moved out. The resulting solid was washed using ethanol(6ml) and dried under vacuum. The recovered Pd-NPs were applied to further cycles experiment.



Figure S7. HRTEM image of Pd-NPs after ten catalytic cycles.

The HRTEM analysis of the recovered Pd-NPs(**Figure S7**) showed that the catalyst had a similar average particle size of 4.4 nm, it was consistent with the fresh nano-particle Pd-NPs, no detectable aggregation of recovered Pd-NPs occurred, and no obvious loss in catalytic performace was observed, indicating that stable performance performed by Pd-NPs in high-efficiency hydrogenation of nitrile, ketone, aldehyde, nitro compound, and the reason why high catalytic behaviours were maintained even for recovered ones after many cycles.

7. Elemental analysis and ICP-OES of Pd-NPs

Table S1 Elemental analysis and ICP-OES of Pd-NPs

Content (wt %)									
Cª	Hª	Oª	N ^a	Pd⁵					
13.33	1.66	9.96	8.29	43.51					

^a measured by elemental analysis (EA). ^b measured by inductively coupled plasma-optical emission spectrometer (ICP-OES).

8. Calculation of TON and TOF

Table S2. Hydrogenation of nitriles assisted by Pd-NPs^a

				R-(C≡N <u>Pd-N</u>	<u>Ps (4mol</u> H ₂ O, pH :	<u>%), H₂ (1</u> = 1.0, <i>r.t.</i>	latm) >	H R- <mark>Ċ-NH</mark> 2 H				
Entry	R-C≡N	l	Time (h)	Conv. (%) ^b	ТОF (h ⁻¹) с	TON ^d	Entry	R-C≡N		Time (h)	Conv. (%) ^b	$TOF(\mathbf{h}^{-1})^{c}$	TON ^d
1		R = Br	3.0	99.3	1898	5694	10		R = F	8.0	98.8	708	5665
2		R = F	6.0	98.8	944	5665	11	N	$R = OCH_3$	3.0	98.9	1890	5671
3		$R = CH_3$	3.0	98.6	1884	5653	12		$R = NH_2$	3.0	99.1	1894	5682
4	Z	$R = OCH_3$	3.0	99.1	1894	5682	13	K	$R = CH_3$	3.0	98.6	1884	5653
5	\bigcirc	$R = NH_2$	3.0	99.8	1907	5722	14	R.	$R = CH_3$	3.0	99.5	1901	5705
6	R	R = CN	8.0	99.2	711	5688	15	Ŭ	$R = OCH_3$	3.0	99.6	1903	5611
7		$R = CF_3$	1.5	99.0	3784	5676	16			3.0	99.0	1892	5676
8		R = Cl	3.0	98.7	1886	5659	17			3.0	62.0	1185	3555
9		R = H	3.0	99.3	1899	5694							

^a Unless otherwise stated, all reactions were carried out under conditions: nitrile, 0.05 mmol; H₂O as the solvent, 10 ml proceeded at r.t., H₂ of 1 atm filled in a balloon; reaction time, 1h. ^b Conversions and yields were determined by high performance liquid chromatography (HPLC) analysis equipped with a C18 reverse column ^cTOF was calculated by mmol of product formed per mmol of the available active sites of Pd (as determined by the chemisorption analysis) for the used catalyst. ^dTON=TOF*Times.

Table S3. Hydrogenation of nitro aromatic substrates^a

$R_{\parallel}^{\mu} \xrightarrow{\text{NO}_2} \frac{\text{Pd-NPs}(4\text{mol}\%), \text{H}_2(1\text{atm})}{\text{H}_2\text{O}, r.t.} R_{\parallel}^{\mu} \xrightarrow{\text{NH}_2}$										
Entry		Ar-NO ₂	Time (h)	TON $(h^{-1})^{c}$	Conv. (%) ^b	TOF ^d				
1		R = H	1.5	3776	98.8	5665				
2		R = F	2.0	2847	99.3	5694				
3	NOa	R = Cl	2.0	2855	99.6	5711				
4	B	R = Br	2.0	2835	98.9	5671				
5		R = OH	2.0	2838	99.0	5676				
6		R = CH ₃	2.0	2844	99.2	5688				
7		R = OCH ₃	2.0	2858	99.7	5717				
8		$R = NH_2$	1.5	3788	99.1	5682				

^a Unless otherwise stated, all reactions were carried out under conditions: nitro compound, 0.05 mmol, 10 ml H ₂ O, proceeded at r.t., H ₂ of 1 atm filled in a
balloon; ^b Conversions and yields were determined by high performance liquid chromatography (HPLC) analysis equipped with a C18 reverse column ^c TOF was
calculated by mmol of product formed per mmol of the available active sites of Pd (as determined by the chemisorption analysis) for the used catalyst. ^d
TON=TOF*Times.

$\begin{array}{c} O \\ Ar \\ H \end{array} \xrightarrow{Pd-NPs (4mol\%), H_2 (1atm)} \xrightarrow{OH} \\ Ar \\ H_2O, r.t. \xrightarrow{Ar} \\ H \end{array}$													
Entry	ArCHO		TON	Conv. (%) ^b	Time (h)	TON ^d	Entry	ArCHO		TOF	Conv. (%) ^b	Time (h)	TON ^d
1		R = F	2844	99.2	2.0	5688	10	СНО	R = OCH ₃	3769	98.6	1.5	5653
2		R = OCH ₃	2858	99.7	2.0	5717	11	R	R = OH	1894	99.1	3.0	5682
3		R = Cl	2847	99.3	2.0	5694	12		R = CH ₃	2844	99.2	2.0	5688
4	СНО	R = Br	2826	98.6	2.0	5653		Ţ					
5	R	$R = CH_3$	2838	99.0	2.0	5676	13			1630	99.5	3.5	5707
6		R = CHO	1892	98.8	3.0	5676		сно					
7		R = CF ₃	2838	98.9	2.0	5676	14	Сно		1900	00.2	2.0	E604
8		R = OH	1896	99.2	3.0	5688	14	\bigcirc		1099	55.5	5.0	5054
9		$R = CH(CH_3)_2$	2855	99.6	2.0	5711	15	Сно		2844	99.2	2.0	5688

^a Unless otherwise stated, all reactions were carried out under conditions: aldehyde, 0.05 mmol; H₂O as the solvent, 10 ml; proceeding at r.t., H₂ of 1 atm filled in a balloon. ^b Conversions and yields were determined by high performance liquid chromatography (HPLC) analysis equipped with a C18 reverse column ^cTOF was calculated by mmol of product formed per mmol of the available active sites of Pd (as determined by the chemisorption analysis) for the used catalyst. ^dTON=TOF*Times.

Table S5. Hydrogenation of	ketones to the	e formation of alcohols ^a
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0		ОН
Ŭ	Pd-NPs (4mol%), H ₂ (1atm)	
R	H ₃ H ₂ O, <i>r.t.</i>	R CH₃

Entry	RC(O)CH₃	TOF (h ⁻¹) ^c	Conv. (%) ^b	Time (h)	TON ^d	Entry	RC(O)CH₃	TOF (h ⁻¹) ^C	Conv. (%) ^b	Time (h)	TON ^d
1	R = OCH	1900	99.4	3.0	5700	10	R = OCH ₃	1890	98.9	3.0	5671
2	R = Cl	2832	98.8	2.0	5665	11	R = F	1898	99.3	3.0	5694
3	O CH ₃ R = Br	2827	98.6	2.0	5654	12	R = OH	1901	99.5	3.0	5705
4	R = CH ₃	1892	99.0	3.0	5676	13	$R = CH_3$	1884	98.6	3.0	5653
5	$R = C_2H_5$	1886	98.7	3.0	5660		CH3				
6	R = CH(C	H ₃) ₂ 1896	99.2	3.0	5688	14		2864	99.9	2.0	5728
7	R = F	2861	99.8	2.0	5722	15		1904	00.1	2.0	5693
8		1903	99.6	3.0	5711	15	CF3	1894	99.1	3.0	5082
9	OCH ₃	1333	93.0	4.0	5332						

^a Unless otherwise stated, all reactions were carried out under conditions: ketone, 0.05 mmol, H₂O as the solvent, 10 ml, proceeded at r.t., H₂ of 1 atm filled in a balloon; ^b Conversions and yields were determined by high performance liquid chromatography (HPLC) analysis equipped with a C18 reverse column. ^cTOF was calculated by mmol of product formed per mmol of theavailable active sites of Pd (as determined by the chemisorption analysis) for the used catalyst. ^dTON=TOF*Times.

9. Characterization data for all products

NH₂

phenylmethanamine ¹H NMR (400MHz CDCl₃): δ (ppm) 7.31-7.18 (m 5H); 3.79 (s 2H); 1.43 (brs 2H); ¹³C NMR (100MHz CDCl₃): δ (ppm) 143.42, 128.53, 127.09, 126.76, 46.51

(4-fluorophenyl)methanamine ¹H NMR (400MHz CDCl₃): δ (ppm) 7.25-7.22 (q *J* = 4.0 Hz 2H); 6.97 (t *J* = 8.0Hz 2H); 3.78 (s 2H); 1.55 (brs 2H); ¹³C NMR (100MHz CDCl₃): δ (ppm) 161.68 (d *J* = 242.0 Hz), 138.97 (d *J* = 3.0 Hz), 128.5 7 (d *J* = 8.0 Hz), 115.10 (d *J* = 21.0 Hz), 45.61

p-tolylmethanamine ¹H NMR(400MHz DMSO-d6): δ (ppm) 7.21 (d J = 8.0Hz 2H); 7.10(d J = 8.0 Hz 2H); 3.68 (s 2H); 2.27 (s 3H); 1.72 (brs 2H); ¹³C NMR (100MHz DMSO-d6): δ (ppm) 141.76, 135.46, 129.08, 127.39, 45.93, 21.12

(4-methoxyphenyl)methanamine ¹H NMR (400MHz DMSO-d6): δ (ppm) 7.24 (d *J* = 8.0 Hz 2H); 6.86 (d *J* = 8.0 Hz 2H); 3.72 (s 3H); 3.65 (s 2H); 1.68 (brs 2H); ¹³C NMR (100MHz DMSO-d6): δ (ppm) 158.25, 136.82, 128.56, 113.91, 55.41, 45.60

4-(aminomethyl)aniline ¹H NMR (400MHz CDCl₃): δ (ppm) 7.06 (d *J* = 8.0Hz 2H); 6.61 (d *J* = 8.0Hz 2H); 3.70 (s 2H); 1.48 (brs 2H); ¹³C NMR (100MHz CDCl₃): δ (ppm) 145.36, 133.47, 128.21,115.19, 46.04

1,4-phenylenedimethanamine ¹H NMR (400MHz DMSO-d6): δ (ppm) 7.25 (s 4H); 3.68 (s 4H); 2.21 (brs 4H); ¹³C NMR (100MHz, DMSO-d6): δ (ppm) 142.59, 127.24, 45.95

(4-(trifluoromethyl)phenyl)methanamine ¹H NMR (400MHz CDCl₃): δ (ppm) 7.58 (d *J* = 8.0Hz 2H); 7.43 (d *J* = 8.0Hz 2H); 3.93 (s 2H); 1.64 (brs 2H); ¹³C NMR (100MHz CDCl₃): δ (ppm) 147.07, 128.66 (q *J* = 40.0Hz), 127.30, 125.41 (q *J* = 4.0Hz), 122.91, 45.93

 NH_2

(3-fluorophenyl)methanamine ¹H NMR (400MHz CDCI₃): δ (ppm) 7.31-7.25 (m 1H); 7.08-6.90 (m 3H); 3.86 (s 2H); 1.61 (brs 2H); ¹³C NMR (100MHz CDCI₃): δ (ppm) 164.29, 161.84, 145.88 (d *J* = 7.0Hz), 129.96 (d *J* = 8.0Hz), 122.53, 113.72 (q *J* = 21.0Hz), 45.95 (d *J* = 2.0Hz)

(3-methoxyphenyl)methanamine ¹H NMR (400MHz CDCl₃): δ (ppm) 7.24 (t *J* = 16.0Hz 1H); 6.89-6.76 (m 3H); 3.82 (s 2H); 3.79 (s 3H); 1.50 (brs 2H); ¹³C NMR (100MHz CDCl₃): δ (ppm) 159.85, 145.08, 129.55, 119.32, 112.59, 112.21, 55.18, 46.50



3-(aminomethyl)aniline ¹H NMR (400MHz CDCl₃): δ (ppm) 7.07 (t *J* = 8.0Hz 1H); 6.64-6.49 (m 3H); 3.70 (s 2H); 1.73 (brs 2H); ¹³C NMR (100MHz CDCl₃): δ (ppm) 146.92, 144.62, 129.44, 117.05, 113.73, 113.54, 46.43



m-tolylmethanamine ¹H NMR (400MHz CDCl₃): δ (ppm) 7.24-7.20 (m 1H); 7.12-7.04 (m 3H); 3.81 (s 2H); 2.34 (s 3H); 1.51 (brs 2H); ¹³C NMR (100MHz CDCl₃): δ (ppm) 143.34, 138.18, 128.48, 127.89, 127.53, 124.11, 46.51, 21.42



o-tolylmethanamine ¹H NMR (400MHz CDCl₃): δ (ppm) 7.29-7.14 (m 4H); 3.83 (s 2H); 2.32 (s 3H); 1.48 (brs 2H); ¹³C NMR (100MHz CDCl₃): δ (ppm) 141.15, 135.49, 130.29, 127.03, 126.82, 126.20, 44.12, 18.81



(2-methoxyphenyl)methanamine ¹H NMR (400MHz CDCl₃): δ (ppm) 7.24-7.19 (m 2H); 6.92-6.84 (m 2H); 3.83 (s 3H); 3.80 (s 2H); 1.77 (brs 2H); ¹³C NMR (100MHz CDCl₃): δ (ppm) 157.43, 131.78, 128.49, 128.07, 120.54, 110.22, 55.14, 42.62

NH₂

naphthalen-1-ylmethanamine ¹H NMR (400MHz DMSO-d6): δ (ppm) 8.12 (t *J* = 12.0Hz 1H); 7.93-7.91 (m 1H); 7.78 (d *J* = 8.0Hz 1H); 7.59-7.45 (m 4H); 4.21 (s 2H); 1.94 (brs 2H); ¹³C NMR (100MHz DMSO-d6): δ (ppm) 140.07, 133.74, 131.42, 128.90, 127.17, 126.31, 126.02, 125.99, 124.62, 124.02, 43.56

NH2

butan-1-amine ¹H NMR (400MHz CDCl₃): δ (ppm) 2.69 (t *J* = 12.0Hz 2H); 1.43-1.32 (m 4H); 1.15 (brs 2H); 0.92 (t *J* = 16.0Hz 3H); ¹³C NMR (100MHz CDCl₃): δ (ppm) 41.82, 35.93, 19.85, 13.77



aniline ¹H NMR (400MHz CDCl₃): δ (ppm) 7.31-7.27 (m 2H); 6.91-6.88 (m 1H); 6.78-6.76 (m 2H); 3.71 (brs 2H); ¹³C NMR (100MHz CDCl₃): δ (ppm) 146.64, 129.43, 118.60, 115.25



4-fluoroaniline ¹H NMR (400MHz CDCl₃): δ(ppm) 6.83 (t *J* = 8.0Hz 2H); 6.58-6.54 (m 2H); 3.52 (brs 2H); ¹³C NMR (100MHz CDCl₃): δ (ppm) 156.41 (d *J* = 234.0Hz), 142.61 (d *J* = 2.0Hz), 116.11 (d *J* = 8.0Hz), 115.68 (d *J* = 22.0Hz)



4-aminophenol ¹H NMR (400MHz DMSO-d6): δ (ppm) 8.39 (brs 1H); 6.52-6.44 (m 4H); 4.37 (brs 2H); ¹³C NMR (100MHz DMSO-d6): δ (ppm) 148.75, 141.05, 116.06, 115.81



p-toluidine ¹H NMR (400MHz CDCl₃): δ (ppm) 6.95 (d *J* = 8.0Hz 2H); 6.58 (d *J* = 8.0Hz 2H); 3.49 (brs 2H); 2.23 (s 3H); ¹³C NMR (100MHz CDCl₃): δ (ppm) 143.90, 129.81, 127.80, 115.32, 20.50



4-methoxyaniline ¹H NMR (400MHz CDCI₃): δ (ppm) 6.74-6.70 (m 2H); 6.63-6.59 (m 2H); 3.71 (s 3H); 3.42 (brs 2H); ¹³C NMR (100MHz CDCI₃): δ (ppm) 152.78, 140.12, 116.44, 114.86, 55.75

 $.NH_2$ H₂N

benzene-1,4-diamine ¹H NMR (400MHz CDCI₃): δ (ppm) 6.37 (s 4H); 4.18 (brs 4H); ¹³C NMR (100MHz CDCI₃): δ (ppm) 139.39, 115.92



(4-fluorophenyl)methanol¹H NMR (400MHz DMSO-d6): δ (ppm) 7.39-7.36 (m 2H); 7.16-7.11 (m 2H); 5.25 (brs 1H); 4.52 (s 2H); ¹³C NMR (100MHz DMSO-d6): δ (ppm) 162.63 (d *J* = 241.0Hz), 139.11 (d *J* = 3.0Hz), 128.79 (d *J* = 8.0Hz), 115.14 (d *J* = 21.0Hz), 62.73

(4-methoxyphenyl)methanol ¹H NMR (400MHz DMSO-d6): δ (ppm) 7.25 (d *J* = 8.0Hz 2H); 6.88 (d *J* = 8.0Hz 2H); 5.09 (t *J* = 4.0Hz 1H); 4.44 (d *J* = 4.0Hz 2H); **3.72**(s 3H); ¹³C NMR (100MHz DMSO-d6): δ (ppm) 158.67, 134.99, 128.41, 113.90, 63.11, 55.40

phenylmethanol ¹H NMR (400MHz DMSO-d6): δ (ppm) 7.35-7.20(m 5H); 5.24(t *J* = 4.0Hz 1H); 4.52(d *J* = 4.0Hz 2H); ¹³C NMR (100MHz DMSO-d6): δ (ppm) 143.01, 128.52,127.11, 126.92, 63.47

p-tolylmethanol ¹H NMR (400MHz DMSO-d6): δ (ppm) 7.20 (d *J* = 8.0Hz 2H); 7.12 (d *J* = 8.0Hz 2H); 5.10 (q *J* = 4.0Hz 1H); 4.46 (d *J* = 4.0Hz 2H); 2.27 (s 3H); ¹³C NMR (100MHz DMSO-d6): δ (ppm) 139.98, 136.05, 129.05, 126.96, 63.26, 21.17



1,4-phenylenedimethanol ¹H NMR (400MHz DMSO-d6): δ (ppm) 7.26 (s 4H); 5.14 (t *J* = 8.0Hz 2H); 4.48 (d *J* = 4.0Hz 4H); ¹³C NMR (100MHz DMSO-d6): δ (ppm) 141.34, 126.71, 63.26

(4-(trifluoromethyl)phenyl)methanol ¹H NMR (400MHz CDCI₃): δ (ppm) 7.55 (d *J* = 8.0Hz 2H); 7.36 (d *J* = 8.0Hz 2H); 4.63 (s 2H); 3.39 (brs 1H); ¹³C NMR (100MHz CDCI₃): δ (ppm) 144.64, 129.69 (q *J* = 33.0Hz), 126.78, 125.53, 125.37 (q *J* = 4.0Hz), 122.82, 64.13

4-(hydroxymethyl)phenol ¹H NMR (400MHz CD3OD): δ(ppm) 7.16 (d *J* = 8.0Hz 2H); 6.75 (d *J* = 8.0Hz 2H); 4.98 (brs 2H); 4.48 (s 2H); ¹³C NMR (100MHz CD3OD): δ (ppm) 154.71, 130.34, 126.77, 113.01, 62.03

(4-isopropylphenyl)methanol ¹H NMR (400MHz CDCl₃): δ (ppm) 7.27 (d *J* = 8.0Hz 2H); 7.20 (d *J* = 8.0Hz 2H); 4.61 (s 2H); 2.93-2.87 (m 1H); 2.01 (brs 1H); 1.24 (d *J* = 8.0Hz 6H); ¹³C NMR (100MHz CDCl₃): δ (ppm) 148.46, 138.35, 127.22, 126.64, 65.20, 33.89, 24.04

(3-methoxyphenyl)methanol ¹H NMR (400MHz CDCl₃): δ (ppm) 7.21 (q *J* = 4.0Hz 1H); 6.87-6.77 (m 3H); 4.55 (s 2H); 3.75 (d *J* = 8.0Hz 3H); 3.16 (brs 1H); ¹³C NMR (100MHz CDCl₃): δ (ppm) 159.74, 142.67, 129.54, 119.18, 113.12, 112.29, 64.85, 55.20



3-(hydroxymethyl)phenol ¹H NMR (400MHz DMSO-d6): δ (ppm) 9.28 (brs 1H); 7.10 (t *J* = 8.0Hz 1H); 6.76-6.61 (m 3H); 5.11 (brs 1H); 4.42 (s 2H); ¹³C NMR (100MHz DMSO-d6): δ (ppm) 157.72, 144.54, 129.45, 117.39, 113.99, 113.72, 63.33



m-tolylmethanol ¹H NMR (400MHz CDCl₃): δ (ppm) 7.22-7.05 (m 4H); 4.53 (s 2H); 2.85 (brs 1H); 2.31 (s 3H); ¹³C NMR (100MHz CDCl₃): δ (ppm) 140.92, 138.18, 128.32, 127.81, 124.10, 65.08, 21.41



(3,4,5-trimethoxyphenyl)methanol ¹H NMR (400MHz DMSO-d6): δ (ppm) 6.65 (s 2H); 5.20 (t *J* = 8.0Hz 1H); 4.46 (d *J* = 4.0Hz 2H); 3.78 (s 6H); 3.66 (s 3H); ¹³C NMR (100MHz DMSO-d6): δ (ppm) 153.20, 138.78, 136.56, 103.86, 63.50, 60.39, 56.10



naphthalen-1-ylmethanol ¹H NMR (400MHz CDCl₃): δ (ppm) 8.04 (t *J* = 4.0Hz 1H); 7.85-7.75 (m 2H); 7.50-7.37 (m 4H); 5.03 (s 2H); 2.29 (brs 1H); ¹³C NMR (100MHz CDCl₃): δ (ppm) 136.30, 133.80, 131.24, 128.69, 128.55, 126.35, 125.90, 125.44, 125.32, 123.68, 63.53

QН СH H₃CO²

1-(4-methoxyphenyl)ethan-1-ol ¹H NMR (400MHz CDCl₃): δ (ppm) 7.25 (d J = 8.0Hz 2H); 6.84 (d J = 8.0Hz 2H); 4.78 (q J = 8.0Hz 1H); 3.76 (s 3H); 2.55 (brs 1H); 1.42 (d J = 4.0Hz 3H); ¹³C NMR (100MHz CDCl₃): δ (ppm) 158.88, 138.14, 126.70, 113.81, 69.82, 55.28, 25.04

1-phenylethan-1-ol ¹**H NMR (400MHz DMSO-d6)**: δ (ppm) 7.36-7.18 (m 5H); 5.17 (d *J* = 4.0Hz 1H); 4.76-4.70 (m 1H); 1.33 (d *J* = 8.0Hz 3H); ¹³**C NMR (100MHz DMSO-d6)**: δ (ppm) 147.88, 128.44, 126.96, 125.76, 68.62, 26.47

1-(p-tolyl)ethan-1-ol ¹**H NMR (400MHz CDCl₃)**: δ (ppm) 7.29 (d *J* = 8.0Hz 2H); 7.20 (d *J* = 8.0Hz 2H); 4.87 (q *J* = 8.0Hz 1H); 2.39 (s 3H); 2.31 (brs 1H); 1.51 (q (d *J* = 4.0Hz 3H); ¹³**C NMR (100MHz CDCl₃)**: δ (ppm) 142.97, 137.08, 129.16, 125.41, 70.19, 25.10, 21.11

1-(4-ethylphenyl)ethan-1-ol ¹**H NMR (400MHz CDCl**₃): δ (ppm) 7.17 (d *J* = 8.0Hz 2H); 7.08 (d *J* = 8.0Hz 2H); 4.72 (q *J* = 8.0Hz 1H); 2.55 (q *J* = 8.0Hz 2H); 2,17 (brs 1H); 1.36 (d *J* = 4.0Hz 3H); 1.14 (t *J* = 8.0Hz 3H); ¹³**C NMR (100MHz CDCl**₃): δ (ppm) 143.50, 143.19, 127.97, 125.49, 70.20, 28.56, 25.05, 15.65

1-(4-isopropylphenyl)ethan-1-ol ¹**H NMR (400MHz CDCl₃)**: δ (ppm) 7.28 (d *J* = 8.0Hz 2H) ; 7.20 (d *J* = 8.0Hz 2H); 4.84 (q *J* = 4.0Hz 1H); 2.93-2.86 (m 1H); 2.03 (brs 1H); 1.47 (d *J* = 8.0Hz 3H); 1.24 (d *J* = 8.0Hz 6H); ¹³**C NMR (100MHz CDCl₃)**: δ (ppm) 148.17, 143.27, 126.54, 125.47, 70.22, 33.83, 24.98, 24.03

1-(4-fluorophenyl)ethan-1-ol ¹**H NMR (400MHz CDCI₃)**: δ (ppm) 7.33 (q *J* = 4.0Hz 2H); 7.03 (t *J* = 8.0Hz 2H); 4.88 (q *J* = 8.0Hz 1H); 1.89 (brs 1H); 1.48 (d *J* = 4.0Hz 3H); ¹³**C NMR (100MHz CDCI₃)**: δ (ppm) 162.13 (d *J* = 244.0Hz), 141.53 (d *J* = 3.0Hz), 127.05 (d *J* = 8.0Hz), 115.26 (d *J* = 21.0Hz), 69.78, 25.30

OH |

pentan-2-ol ¹H NMR (400MHz CDCl₃): δ (ppm) 3.83-3.75 (m 1H); 2.28 (brs 1H); 1.43-1.35 (m 4H); 1.17 (d *J* = 4.0Hz 3H); 0.92 (t *J* = 8.0Hz 3H); ¹³C NMR (100MHz CDCl₃): δ (ppm) 67.65, 41.45, 23.31, 18.89, 13.99



1-(3-methoxyphenyl)ethan-1-ol ¹**H NMR (400MHz CDCl**₃): δ (ppm) 7.21 (q *J* = 8.0Hz 1H); 6.89-6.88 (t *J* = 4.0Hz 2H); 6.78-6.75(m 1H); 4.77 (q *J* = 8.0Hz 1H); 3.76 (s 3H);2.97 (brs 1H); 1.41(d *J* = 4.0Hz 3H); ¹³**C NMR (100MHz CDCl**₃): δ (ppm) 159.68, 147.75, 129.47, 117.79, 112.77, 110.99, 70.11, 55.18, 25.14



1-(3-fluorophenyl)ethan-1-ol ¹**H NMR (400MHz CDCI**₃): δ (ppm) 731-7.26 (m 1H); 7.08 (t J = 12.0Hz 2H); 6.96-6.91 (m 1H); 4.84 (t J = 8.0Hz 1H); 2.44 (brs 1H); 1.45 (d J = 8.0Hz 3H); ¹³**C NMR (100MHz CDCI**₃): δ (ppm) 162.98 (d J = 245.0Hz), 148.54 (d J = 7.0Hz), 129.98 (d J = 8.0Hz), 120.96 (d J = 3.0Hz), 114.18 (d J = 21.0Hz), 112.31 (d J = 21.0Hz) 69.76, 25.20



3-(1-hydroxyethyl)phenol ¹H NMR (400MHz DMSO-d6): δ (ppm) 9.23 (brs 1H); 7.08 (t *J* = 8.0Hz 1H); 6.77-6.72 (m 2H); 6.61-6.58 (m 1H); 5.05 (d *J* = 4.0Hz 1H); 4.62 (q *J* = 4.0Hz 1H); 1.28 (d *J* = 8.0Hz 3H); ¹³C NMR (100MHz DMDO-d6): δ (ppm) 157.62, 149.47, 129.34, 116.42, 113.83, 112.65, 68.51, 26.40



1-(m-tolyl)ethan-1-ol ¹H NMR (400MHz CDCl₃): δ (ppm) 7.20-7.02 (m 4H); 4.74 (q *J* = 8.0Hz 1H); 2.84 (brs 1H); 2.31 (s 3H); 1.40 (d *J* = 8.0Hz 3H); ¹³C NMR (100MHz CDCl₃): δ (ppm) 145.96, 138.05, 128.14, 126.21, 122.54, 70.26, 25.15, 21.50

1-(o-tolyl)ethan-1-ol ¹H NMR (400MHz CDCl₃): δ (ppm) 7.46 (d *J* = 8.0Hz 1H); 7.21-7.08 (m 3H); 5.04 (q J = 8.0Hz 1H); 2.39 (s 1H); 2.29 (s 3H); 1.41 (d J = 4.0Hz 3H); ¹³C NMR (100MHz CDCl₃): δ (ppm) 143.94, 134.23, 130.39, 127.17, 126.40, 124.59, 66.76, 23.97, 18.96

2,2,2-trifluoro-1-phenylethan-1-ol ¹H NMR (400MHz CDCl₃): δ (ppm) 7.50-7.43 (m 5H); 5.01 (q *J* = 8.0Hz 1H); 3.26 (brs 1H); ¹³C NMR (100MHz CDCl₃): δ (ppm) 134.06, 129.54, 128.63, 127.48, 125.71, 72.79 (q *J* = 32.0Hz)

$$O_2N$$
 $N_2^+BF_4^-$

2,2'-(4-nitro-1,2-phenylene)bis(1-(trifluoro- λ 5-boranylidene)diazen-1-ium) fluoride ¹H NMR (400MHz DMSO-d6): δ (ppm) 8.86 (d *J* = 2.0Hz 1H); 8.26-8.24 (m 1H); 8.02 (d *J* = 4.0Hz 1H); ¹³C NMR (100MHz DMSO-d6): δ (ppm) 145.04, 140.76, 139,18, 121.47, 114.75, 114.42

10. ¹H NMR and ¹³C NMR spectra of products















S21



S22



























S30



S31







S33









¹³C NMR of benzene-1,4-diamine

¹³C NMR of 1-(3-methoxyphenyl)ethan-1-ol

¹³C NMR of 2,2'-(4-nitro-1,2-phenylene)bis(1-(trifluoro-λ⁵-boranylidene)diazen-1-ium) fluoride