Electronic Supplementary Material (ESI) for RSC Advances

Catalysis by Pd Nanoclusters Generated In Situ of High-Efficiency Synthesis of Aromatic Azo Compounds from Nitroaromatics under H_2 Atmosphere

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Figure S1. Optical images of the in-situ formed Pd nanoparticles. (2~3 mg $Pd(acac)_2$, 1 mmol KOH and 2 mL ethanol, at 70 °C for 1 h under 1 atm of hydrogen)

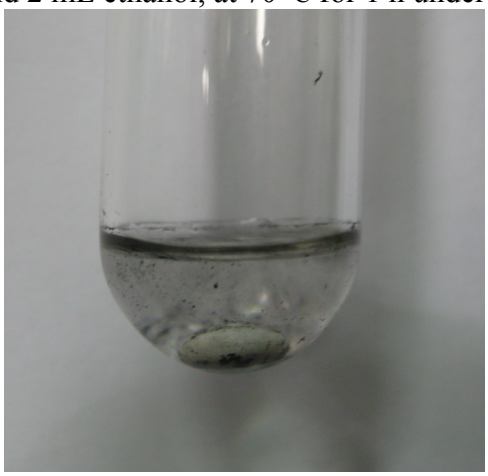


Table S1 Effect of Solvent on Coupling Reactions of Nitrobenzene[a]

Entry	Solvent	Temp. (°C).	Conv. (%)[b]	Select. (%)[b]		
				a	b	c
1	o-xylene	120	>99	78.2	-	21.8
2	m-xylene	120	>99	75.1	-	24.9
3	p-xylene	120	>99	74.7	-	25.3
4	toluene	100	>99	68.6	-	31.4
5	n-heptane	100	76.3	15.0	64.9	20.1
6	dioxane	100	95.6	82.2	6.9	10.9
7	DMF	100	>99	41.0	-	59.0
8[c]	ethanol	70	100	96.8	-	3.2
9	methanol	70	98.0	18.6	2.9	78.5
10	2-propanol	70	97.5	4.0	78.5	17.5
11	acetonitrile	70	28.4	6.6	71.7	21.7
12	H_2O	70	>99	33.6	-	66.4

[a] All reactions were carried out with 2~3 mg of $Pd(acac)_2$ catalyst, 1 mmol nitrobenzene, 1 mmol KOH, and 2 mL solvent at the appropriate temperature for 6 h under 1 atm of hydrogen. [b] GC yield. [c] 1.5 h.

Table S2 Effect of Base on Coupling Reactions of Nitrobenzene[a]

Entry	Base(mmol)	T(h)	Conv. (%)[b]	Select. (%)[b]		
				Azo-	Azoxy-	aniline
1	none	12	100	-	-	100
2	K_2CO_3(1)	12	100	2.5	-	97.5
3	NaOH(1)	1.5	45	84.8	-	15.2
4	NaOH(1)	12	100	78.5	-	21.5
5	KOH(1)	1.5	100	96.8	-	3.2
6	$(CH_3)_3COK$(1)	1.5	100	96.9	-	3.1
7	KOH(0.25)	1.5	100	52.9	-	47.1
8	KOH(0.5)	1.5	100	79.5	-	20.5
9	KOH(2)	1.5	85.7	4.4	92.5	3.1
10	KOH(4)	1.5	64.8	2.8	84.1	13.1

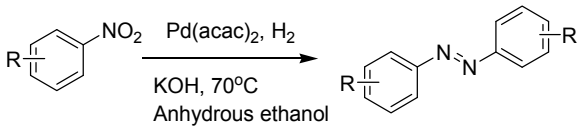
[a] All reactions were carried out with 2~3mg of $Pd(acac)_2$ catalyst, 1 mmol nitrobenzene, base, and 2 mL anhydrous ethanol at 70 °C for the appropriate time under 1 atm of hydrogen. [b] GC yield.

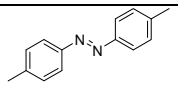
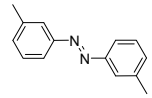
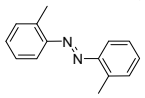
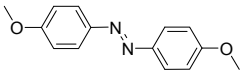
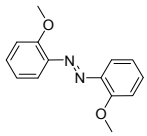
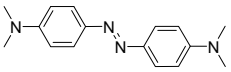
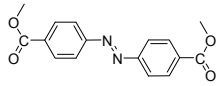
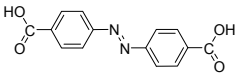
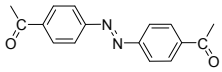
Table S3. The Activity of the Catalysts Using $Pd(acac)_2$ And Fresh In-situ Formed Pd Particles[a]

	T(h)	Conv.(%)[b]	Select.(%)[b]		
			Azo-	Azoxy-	aniline
In-situ formed Pd nanoparticles	25	62.7	4.7	46.3	49.0
$Pd(acac)_2$[c]	2	100	96.6	-	3.4

[a] All reactions were carried out with 1 mmol nitrobenzene, 1 mmol KOH, and 2 mL ethanol at 70 °C for appropriate time under 1 atm of hydrogen. [b] GC yield. [c] 2~3 mg $Pd(acac)_2$ as the catalysts.

Table S4 Aromatic Azos Formation from Different Corresponding Nitroaromatic Compounds[a]

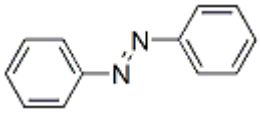


Entry	Product	T(h)	Yield(%)[b]
1		6	90.1
2		6	96.4
3[c]		24	96.6
4[d]		24	64.4
5[d]		24	45.7
6[e]		3	83.5
7[f]		24	18.7
8[g]		24	81.3
9[h]		3	18.3

[a] All reactions were carried out with 2~3mg of $Pd(acac)_2$ catalyst, 1 mmol nitroaromatic compounds, 1 mmol KOH, and 2 mL ethanol at 70°C for the appropriate time under 1 atm of hydrogen, [b] Isolated yield. [c] 5 atm of H_2. [d] 100°C, toluene as the solvent. [e] 1 atm of mixture of H_2 and N_2. [f] 100°C, pyridine as the solvent. [g] 80°C, water as the solvent. [h] 5 atm of H_2. All reactions were exposed to air at the appropriate temperature for 2 h.

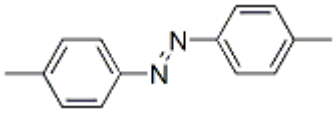
NMR data of the Azos:

1. Azobenzene



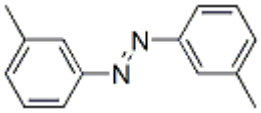
^{1}H NMR(400 MHz, $CDCl_3$):δ=7.95-7.93(d, 4H), 7.54-7.47(m, 6H).
^{13}C NMR(100 MHz, $CDCl_3$): δ=123.07, 129.31, 131.22, 152.85.

2. 1,2-dip-tolyldiazene



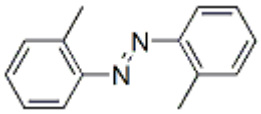
^{1}H NMR(400 MHz, $CDCl_3$):δ=7.83-7.81(d,4H), 7.32-7.30(d,4H),2.44(s,6H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.71, 122.92, 129.91, 141.43, 150.99.

3. 1,2-dim-tolyldiazene



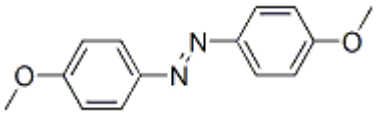
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (s, 4H), 7.43-7.39 (m, 2H), 7.31-7.26 (d, 2H), 2.47 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.61, 120.70, 123.04, 129.11, 131.91, 139.19, 152.97.

4. 1,2-dio-tolyldiazene



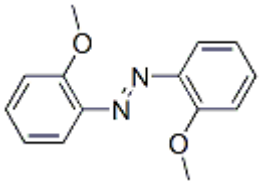
^{1}H NMR (400 MHz,$CDCl_3$): δ = 7.62-7.60(d,2H),7.33-7.30(m, 4H),7.24-7.22(m, 2H),2.72(s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.88, 116.07, 126.60, 130.92, 138.26, 151.31.

5. 1,2-bis(4-methoxyphenyl)diazene



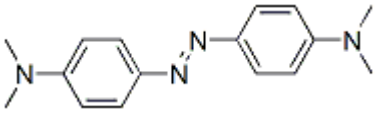
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89-7.87 (d, 4H), 7.01-6.99 (d, 4H), 3.89 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.78, 114.37, 124.55, 147.26, 161.81.

6. 1,2-bis(2-methoxyphenyl)diazene



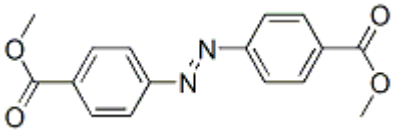
^{1}H NMR (400 MHz, $CDCl_3$): δ=7.65-7.61 (m, 2H), 7.42-7.39 (m, 2H), 7.09-7.06 (m, 2H), 7.03-6.98 (m, 2H), 4.02 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$): δ =56.28, 112.43, 116.96, 120.78, 125.26, 132.20, 145.24.

7. 4,4’-azobis(N,N-dimethylaniline)



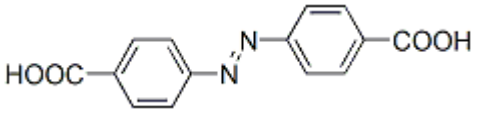
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83-7.80 (d, 4H), 6.77-6.75 (d, 4H), 3.06 (s, 12H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 40.50, 110.42, 126.34, 142.92, 154.42.

8. DimethylAzobenzene-4,4'-dicarboxylate



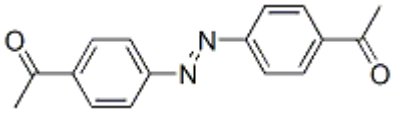
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23-8.20 (d, 4H), 7.99-7.97 (d, 4H), 3.97 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.85, 123.15, 130.91, 131.82, 154.23, 166.30.

9. Azobenzene-4,4'-dicarboxylic acid



^{1}H NMR (400 MHz, D_2O): δ = 8.02-7.99 (d, 4H), 7.89-7.86 (d, 4H).
^{13}C NMR (100 MHz, D_2O): δ =122.44, 130.06, 139.25, 153.67, 174.86.

10. 4,4'-diacethylazobenzene



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14-8.12 (d, 4H), 8.03-8.00 (d, 4H), 2.68(s, 3H).
^{13}C NMR (100 MHz, CDCl3): δ = 27.13, 123.42, 129.63, 140.12, 154.50, 197.69.