

Highly Efficient Synthesis of Aromatic Azos Catalyzed by Unsupported Ultra-thin Pt Nanowires

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Experiment Section

1. Preparation of the Pt based nanomaterials

1.1. Synthesis of Pt NWs

Ultrathin Pt NWs were achieved by acidic etching of FePt NWs, which was synthesized according to the procedure described by Wang et al.¹ and Li et al.² 200 mg Pt(acac)₂ and 20 mL oleylamine (OAm) were mixed at room temperature under nitrogen atmosphere and this solution was heated to 120°C under stirring. This solution was kept at the temperature of 120°C for 20 minutes. 150 μL Fe(CO)₅ was injected into the hot solution and then the temperature was gradually raised to 160°C. The reaction was kept at this temperature for half an hour without stirring. The black solution was then cooled to room temperature and centrifuged in excess ethanol. The precipitate was redispersed in methanol and washed by ethanol for three times.

100 mg FePt NWs (in 20 mL methanol) were firstly treated by oxygen bubbling at 100°C, and 10 mL HCl/methanol (1:1) solution was added into the above suspension. The solution was heated and stirred at 60°C for 1 hour, the resultant precipitates were obtained following 10 minutes of centrifugation (3000 rpm). The dark solid was washed with methanol for at least two times and stored in hexane.

1.2. Synthesis of Pt nanorods (Pt NRs)

Pt NRs were achieved by acidic etching of FePt NRs. The FePt NRs were synthesized as follow: Pt(acac)₂ (200mg), sodium oleate (150mg) were added to oleylamine (OAm) (20 mL) under vigorous stirring. The mixture was then heated to 120 °C for 15 minutes. As the solution turned clear yellow, a drop of Fe(CO)₅ (~0.005mL) was quickly injected into the hot solution. The solution turned dark in color quickly. The temperature was further heated to 250 °C and kept at this temperature for 30 minutes before it was cooled down to room temperature. The

sample was centrifuged in excess isopropanol to separate the NRs. The NRs were dispersed in 10 mL toluene and precipitated out by adding ethanol. The process was repeated one more time to purify the NRs. The final product was dispersed in 10 mL of methanol for further use.

100 mg FePt NRs (in 20 mL methanol) were firstly treated by oxygen bubbling at 100 °C, and 10 mL HCl/methanol (1:1) solution was added into the above suspension. The solution was heated and stirred at 60 °C for 1 hour, the resultant precipitates were obtained following 10 minutes of centrifugation (5000 rpm). The dark solid was washed with methanol for at least two times and stored in hexane.

1.3. Synthesis of Pt nanoparticles (Pt NPs)

Pt NPs were achieved by acidic etching of FePt NPs. The FePt NPs were synthesized as follow^{3,4}: Pt(acac)₂ (100mg), octadecene (10 mL), oleic acid (1 mL), and OAm (1 mL) were mixed under vigorous stirring. The mixture was then heated to 65 °C to dissolve Pt(acac)₂. The temperature was then raised to about 180 °C. A solution of Fe(CO)₅ in hexane (0.1 mL, prepared by adding 0.1 mL Fe(CO)₅ in 1 mL hexane under argon) was quickly injected into the hot solution. The solution was further heated to 200 °C and kept at this temperature for 1 hour before it was cooled down to room temperature. 40 mL of isopropanol was added and then the suspension was centrifuged to separate the NPs. The NPs were dispersed in 10 mL hexane and precipitated out by adding ethanol. The process was repeated one more time to purify the NPs. The final product was dispersed in 10 mL of methanol for further use.

100 mg FePt NPs (in 20 mL methanol) were firstly treated by oxygen bubbling at 100 °C, and 10 mL HCl/methanol (1:1) solution was added into the above suspension. The solution was heated and stirred at 60 °C for 1 hour, the resultant precipitates were obtained following 10 minutes of centrifugation (8000 rpm). The dark solid was washed with methanol for at least two times and stored in hexane.

2. Aazos synthesis from nitroaromatics hydrogenation

2.1. Symmetric Aazos synthesis from the corresponding nitroaromatics

Pt NWs in hexane were added into a Schlenk tube and the hexane was evacuated using pressure reducing valves. 1 mmol Nitroaromatics, 0.25 mmol KOH, 0.1 mL tert-butylbenzene and 2 mL solvent were added into the reaction tube and then sealed. The reaction tube was thrice evacuated and flushed with hydrogen which took place at a certain temperature under a hydrogen atmosphere. After 3 hours reaction, the hydrogen atmosphere was removed and the reactant was heated in air at 120 °C for 2 hours. The resultant product mixtures were analyzed by GC (VARIAN CP-3800 GC, HP-5 capillary column, FID detector) and GC-MS (VARIAN 450-GC &

VARIAN 240-GC) equipped with a CP8944 capillary column (30 m × 0.25 mm) and a flame ionization detector (FID). The Aazos were characterized by ¹H NMR and ¹³C NMR.

2.2. Asymmetric Aazos synthesis from two different nitroaromatics

Pt NWs in hexane were added into a Schlenk tube and the hexane was evacuated using pressure reducing valves. Two nitroaromatics (1 mmol each), 0.25 mmol KOH, 0.1 mL tert-butylbenzene and 2 mL solvent were added into the reaction tube and then sealed. The reaction tube was thrice evacuated and flushed with hydrogen which took place at a certain temperature under a hydrogen atmosphere. After 24 hours reaction, the hydrogen atmosphere was removed and the reactant was heated in air at 120 °C for 2 hours. The resultant product mixtures were analyzed by GC (VARIAN CP-3800 GC, HP-5 capillary column, FID detector) and GC-MS (VARIAN 450-GC & VARIAN 240-GC) equipped with a CP8944 capillary column (30 m × 0.25 mm) and an FID. The asymmetric Aazos were characterized by ¹H NMR and ¹³C NMR.

3. Computational methods

Spin-polarized DFT computations were performed using the Vienna ab initio simulation package (VASP), with projector augmented wave (PAW) functional. We used the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional for the exchange-correlation interaction. Full structural optimizations were performed until the force on each atom was less than 0.02 eV/Å, along with a kinetic energy cutoff of 400 eV for a standard plane wave basis set. The Monkhorst-Pack method for k-points meshes was chosen, with the densities of K-points in actual space less than 0.05×0.05×0.05 Å⁻³ for all calculations.

[1] Wang, C.; Hou, Y. L.; Kim, J.; Sun, S. H. *Angew. Chem. Int. Ed.* **2007**, *46*, 6333-6335.

[2] Li, M.; Hu, L.; Cao, X.; Hong, H.; Lu, J.; Gu, H. *Chem. Eur. J.* **2011**, *17*, 2763-2768.

[3] Wang, C.; Daimon, H.; Onodera, T.; Koda, O.; Sun, S. *Angew. Chem. Int. Ed.* **2008**, *47*, 3588-3591.

[4] Kim, J.; Lee, Y.; Sun, S. *J. Am. Chem. Soc.* **2010**, *132*, 4996-4997.

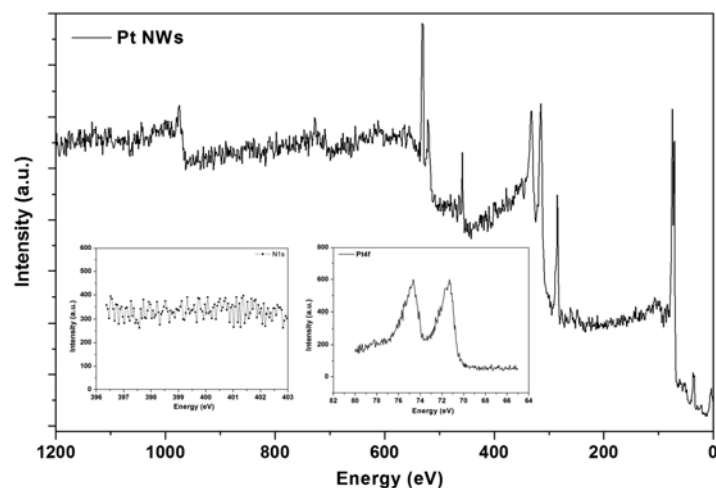
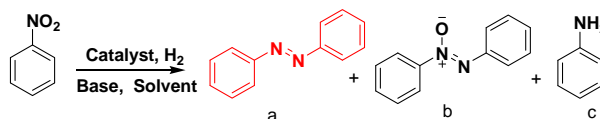


Figure S1. XPS spectrum of Pt nanowires catalysts (insert: N 1s peak and Pt 4f peak).

Table S1. Hydrogenation of Nitrobenzene in different reaction conditions to obtain the azobenzene.^a



Entry	Solvent	Base (mmol)	T (°C)	t (h)	Conv. ^b (%)	Select. (%) ^b		
						a	b	c
1 ^c	p-xylene	KOH/1	80	24	trace	-	-	-
2 ^d	p-xylene	KOH/1	80	24	trace	-	-	-
3	p-xylene	KOH/0.125	80	3.5	100	90.3	-	9.7
4	p-xylene	KOH/0.25	80	3.5	100	92.7	-	7.3
5	p-xylene	KOH/0.5	80	3.5	100	87.8	-	12.2
6	p-xylene	KOH/1	80	3.5	100	86.0	-	14.0
7	p-xylene	KOH/2	80	3.5	100	85.3	-	14.7
8	o-xylene	KOH/0.25	120	18	100	83.4	-	16.1
9	m-xylene	KOH/0.25	120	18	100	84.2	-	15.8
10	toluene	KOH/0.25	100	24	99.8	90.0	-	10.0
11	n-heptane	KOH/0.25	100	24	100	19.3	72.0	8.5
12	dioxane	KOH/0.25	100	24	88.1	6.0	88.3	5.7
13	ethanol	KOH/0.25	80	24	100	11.6	74.5	13.9
14	acetonitrile	KOH/0.25	80	24	47.3	5.8	79.3	14.8
15	2-propanol	KOH/0.25	80	24	100	56.0	27.4	15.7
16	H ₂ O	KOH/0.25	80	12	100	65.4	-	34.6
25 ^e	p-xylene	KOH/0.25	80	0.7	100	89.7	-	10.3
26 ^f	p-xylene	KOH/0.25	80	3.5	100	40.5	43.1	4.1
27 ^f	p-xylene	KOH/0.25	80	24	100	44.3	-	55.7
28 ^g	p-xylene	KOH/0.25	80	3.5	100	42.8	-	57.2
29 ^g	p-xylene	KOH/0.25	80	24	100	69.7	-	30.3

^a Reaction conditions: nitrobenzene (1.0 mmol), KOH and solvent (2 mL) at 1 bar H₂ with 0.005 mmol Pt NW catalyst. ^b Determined by GC using tert-butylbenzene as an internal standard. ^c No catalyst. ^d No hydrogen. ^e 4 bar H₂. ^f Pt nanoparticles as catalyst. ^g Pt nanorods as catalyst.

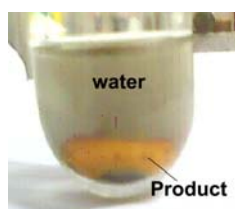


Figure S2. Optical images of the nitrobenzene hydrogenation in water using Pt NWs as the catalyst.

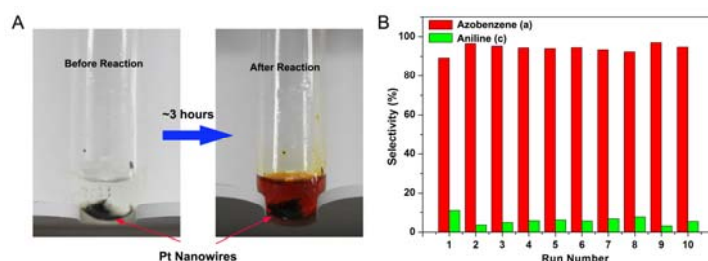


Figure S3. (A), Optical images of the nanowire catalysts before and after the reactions; (B), Catalytic stabilities of Pt nanowire catalysts.

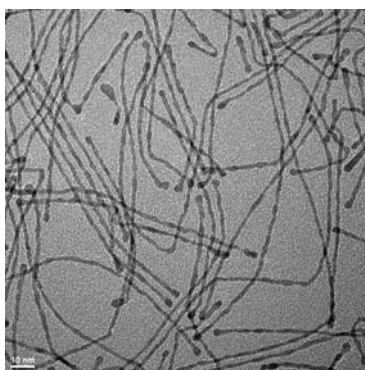


Figure S4. TEM image of Pt nanowires after 10 cycles.

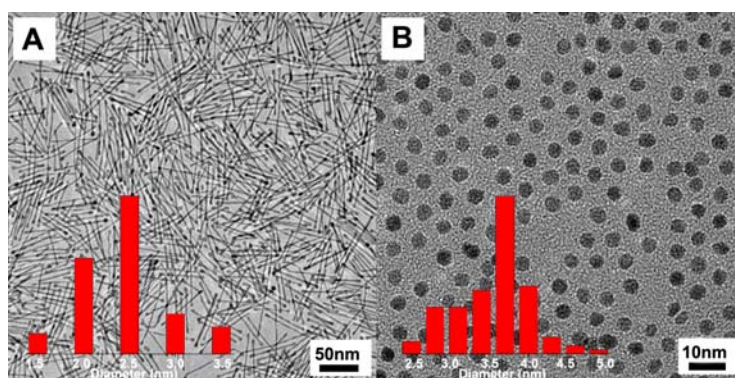


Figure S5. TEM images of Pt Nanorods (A) and Nanoparticles (B).

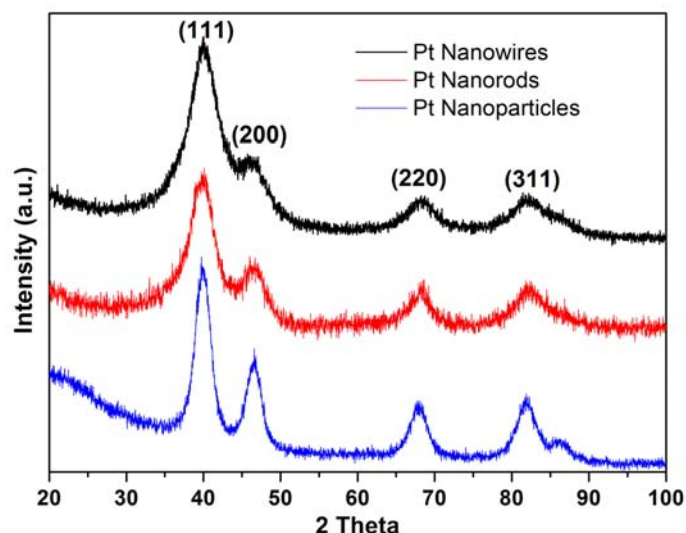


Figure S6. XRD results of Pt Nanowires, Nanorods and Nanoparticles.

Table S2. Compare the catalytic activity and selectivity of Pt catalysts^a.

Pt	Diameter (nm)	Length (nm)	t (h)	Yield (%)		TOF (h ⁻¹)
				azobenzen e	anilin e	
Nanowires	1.5	>1000	3.5	92.7	7.3	57.1
Nanorods	2.5	10-20	4.5	69.7	30.3	44.4
Nanoparticles	3.7	-	8	44.3	55.7	25

^a Reaction conditions: nitrobenzene (1.0 mmol), 0.25 equiv. KOH and *p*-xylene (2 mL) at 1 bar H₂ with 0.005 mmol Pt catalyst.

To understand the difference of above three nanocatalysts expect the morphology, we used X-ray diffraction (XRD) to detect these Pt based nanomaterials (Figure S6) and found the ratio of Pt (111) to Pt (100) was as the following: nanowires > nanorods > nanoparticles. Many groups have demonstrated that the catalytic activity of Pt (100) is higher than Pt (111) in hydrogenation or oxidation¹⁻⁵. We ascribed the good selectivity of the nanowire to the high ratio of (111) plane. There are two competing reactions in the azobenzene formation process: N-phenylhydroxylamine to aniline and N-phenylhydroxylamine condensate with nitrosobenzene to obtain N, N'-dihydroxy intermediate. On the surface of Pt (100), N-phenylhydroxylamine will be quickly reduced to aniline; on the surface of Pt (111), the nitrosobenzene and N-phenylhydroxylamine will be obtained. The free nitrosobenzene and N-phenylhydroxylamine will be catalyzed by active KOH to form N, N'-dihydroxy intermediate and then azobenzene.

[1] Grozovski, V.; Solla-Gullón, J.; Climent, V.; Herrero, E.; Feliu, J. M. *J. Phys. Chem. C* **2010**, *114*, 13802-13812.

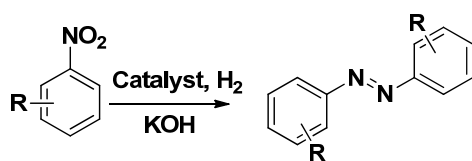
[2] Chen, J.; Lim, B.; Lee, E. P.; Xia, Y. *Nano Today* **2009**, *4*, 81-95.

[3] Tsung, C. K.; Kuhn, J. N.; Huang, W.; Aliaga, C.; Hung, L. I.; Somorjai, G. A.; Yang, P. *J. Am. Chem. Soc.* **2009**, *131*, 5816-5822.

[4] Schmidt, E.; Vargas, A.; Mallat, T.; Baiker, A. *J. Am. Chem. Soc.* **2009**, *131*, 12358-12367.

[5] Kliewer, C. J.; Aliaga, C.; Bieri, M.; Huang, W.; Tsung, C. K.; Wood, J. B.; Komvopoulos, K.; Somorjai, G. A. *J. Am. Chem. Soc.* **2010**, *132*, 13088-13095.

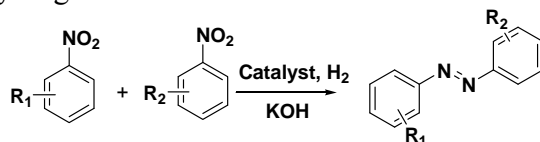
Table S3. Hydrogenation of substituted Nitrobenzenes using Pt NWs as the catalyst.^a



Entry	R	t (h)	Yield (%) ^b
1 ^c	<i>p</i> -Cl	24	56.1
2	<i>p</i> -CH ₃	3.5	90.7
3	<i>m</i> -CH ₃	3	94.5
4	<i>o</i> -CH ₃	24	trace
5 ^d	<i>o</i> -CH ₃	4	71.4
6	<i>p</i> -N(CH ₃) ₂	24	82.6
7	<i>p</i> -OCH ₃	24	64.6
8 ^e	<i>m</i> -N(CH ₂ CH ₂)CH ₂	24	74.9
9	<i>p</i> -COOCH ₃	24	trace
10 ^f	<i>p</i> -COOCH ₃	5	70.7
11 ^d	<i>p</i> -COCH ₃	5	56.8
12 ^g	<i>p</i> -COOH	24	52.3

^a Substituted nitrobenzene (1 mmol), KOH (0.25 mmol) and *p*-xylene (2 mL) at 1 bar H₂ with 0.005 mmol Pt catalyst; ^b Determined by GC using *tert*-butylbenzene as an internal standard; ^c Byproduct: aniline (4.2%) and 2-(4-chlorophenyl)-1-phenyldiazene (4.4%); ^d 4 atm H₂, 80°C; ^e isolated yield; ^f CHCl₃ as solvent, 4 atm H₂, 40°C; ^g water as the solvent.

Table S4. Hydrogenation of two different substituted Nitrobenzenes.^a



Entry	R ₁	R ₂	Conv. (%)	Yield (%) ^b
13	<i>p</i> -H	<i>p</i> -COOH	100	72.5
14	<i>p</i> -H	<i>p</i> -COCH ₃	100	58.1
15	<i>p</i> -CH ₃	<i>p</i> -OCH ₃	100	38.2

^a Substituted nitrobenzene (1 mmol), KOH (0.25 mmol) and *p*-xylene (2 mL) at 4 bar H₂, 80°C with 0.005 mmol Pt catalyst for 24 h; ^b Determined by GC using *tert*-butylbenzene as an internal standard.

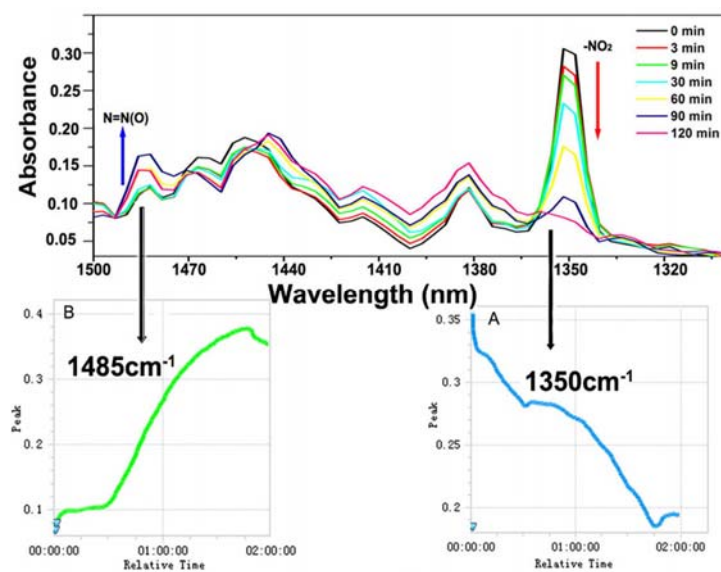


Figure S7. ReactIR results of nitrobenzene hydrogenation in the first two hours.

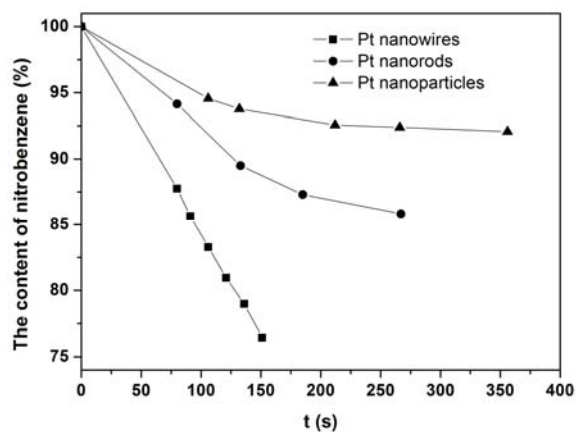


Figure S8. The initial conversion speeds of the different Pt catalysts from In-suit IR analysis (Pt nanowires, Pt nanorods and Pt nanoparticles).

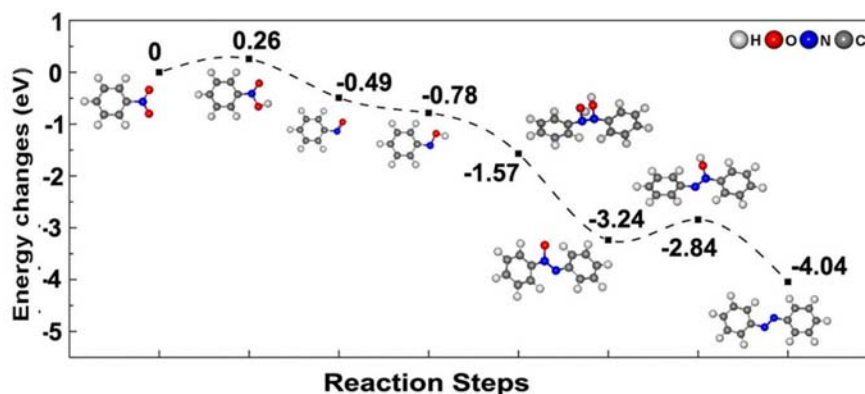
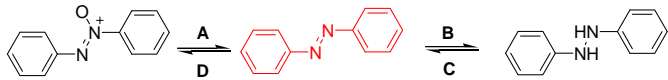


Figure S9. DFT results of the azobenzene formation (seven steps).

Table S5. The Hydrogenation and oxidation of azobenzene^a and oxidation of aniline^b.

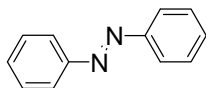


Entry	t (h)	Yield (%)	T (°C)	Cat.	KOH	atmosphere
A	2	>99	80	Pt NWs	Y	H ₂
B1	5	98.1	80	Pt NWs	Y	H ₂
B2	18	90.2	80	Pt NWs	N	H ₂
B3	12	trace	80	-	Y	H ₂
C1	5	>99	100	Pt NWs	Y	air
C2	12	96.8	100	Pt NWs	N	air
C3	12	95.5	100	-	Y	air
D	12	trace	100	Pt NWs	Y	O ₂

^aAzobenzene (1 mmol), KOH (0.25 mmol), p-xylene (2 mL) and 0.005 mmol Pt NWs. ^bAniline (1 mmol), KOH (1 mmol), p-xylene (2 mL) and 0.005 mmol Pt NWs.

NMR results of the Aazo compounds.

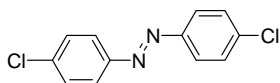
1. Azobenzene



^1H 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.

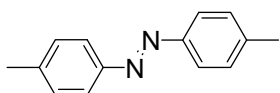
2. 1,2-bis(4-chlorophenyl)diazene



^1H NMR (400 MHz, CDCl_3): δ = 7.88-7.85 (d, 4H), 7.50-7.48 (d, 4H).

^{13}C NMR (100 MHz, CDCl_3): δ = 124.41, 129.63, 137.45, 150.92.

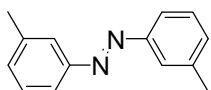
3. 1,2-dip-tolyldiazene



^1H 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.

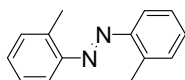
4. 1,2-dim-tolyldiazene



^1H 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.

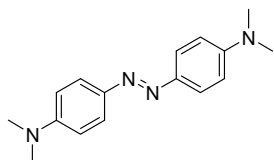
5. 1,2-dio-tolyldiazene



^1H 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.

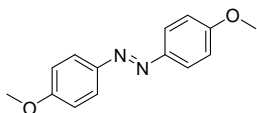
6. 4-4'-azobis(N,N-dimethylaniline)



¹H NMR (400 MHz, CDCl₃): δ = 7.83-7.80 (d, 4H), 6.77-6.75 (d, 4H), 3.06 (s, 12H).

¹³C NMR (100 MHz, CDCl₃): δ = 40.50, 110.42, 126.34, 142.92, 154.42.

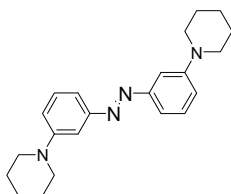
7. 1,2-bis(4-methoxyphenyl)diazene



¹H NMR (400 MHz, CDCl₃): δ = 7.89-7.87 (d, 4H), 7.01-6.99 (d, 4H), 3.89 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ = 55.78, 114.37, 124.55, 147.26, 161.81.

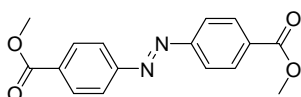
8. 1,2-bis(3-(piperidin-1-yl)phenyl)diazene



¹H NMR (400 MHz, CDCl₃): δ = 7.49 (s, 2H), 7.38-7.37 (d, 4H), 7.07-7.04 (m, 2H), 3.28-3.25 (m, 8H), 1.77-1.72 (m, 8H), 1.64-1.58 (m, 4H).

¹³C NMR (100 MHz, CDCl₃): δ = 24.51, 25.97, 50.63, 110.27, 114.10, 119.11, 129.62, 153.01, 153.91.

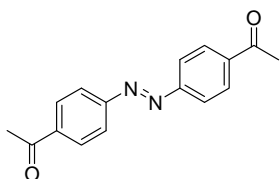
9. DimethylAzobenzene-4,4'-dicarboxylate



¹H NMR (400 MHz, CDCl₃): δ = 8.23-8.20 (d, 4H), 7.99-7.97 (d, 4H), 3.97 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ = 51.85, 123.15, 130.91, 131.82, 154.23, 166.30.

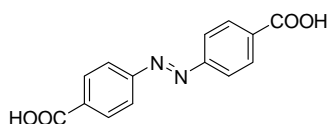
10. 4,4'-diacetylazobenzene



¹H NMR (400 MHz, CDCl₃): δ = 8.14-8.12 (d, 4H), 8.03-8.00 (d, 4H), 2.68(s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ = 27.13, 123.42, 129.63, 140.12, 154.50, 197.69.

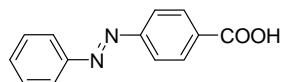
11. Azobenzene-4,4'-dicarboxylic acid



$^1\text{H NMR}$ (400 MHz, D_2O): $\delta = 8.02\text{-}7.99$ (d, 4H), $7.89\text{-}7.86$ (d, 4H).

$^{13}\text{C NMR}$ (100 MHz, D_2O): $\delta = 122.44, 130.06, 139.25, 153.67, 174.86$.

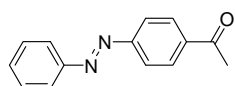
12. 4-(Phenylazo)benzoic Acid



$^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 13.23$ (brs, 1H), $8.17\text{-}8.14$ (d, 4H), $8.0\text{-}7.88$ (d, 4H), 7.61 (s, 1H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 123.49, 131.35, 134.06, 136.08, 154.82, 167.25, 171.01$.

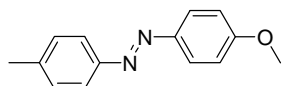
13. 4'-acethylazobenzene



$^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 8.13\text{-}8.10$ (d, 2H), $7.99\text{-}7.95$ (m, 54H), $7.55\text{-}7.53$ (m, 3H), 2.67 (s, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 31.16, 120.73, 123.06, 127.57, 128.92, 129.31, 131.21, 152.86$.

14. 1-(4-Methoxyphenyl)-2-*p*-tolylidiazene



$^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.91\text{-}7.88$ (d, 2H), $7.79\text{-}7.77$ (d, 2H), $7.30\text{-}7.28$ (d, 2H), $7.02\text{-}6.99$ (d, 2H), 3.89 (s, 3H), 2.42 (s, 3H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 21.4, 55.6, 114.2, 122.5, 124.6, 129.7, 140.8, 147.1, 150.9, 161.8$.