Supporting Information

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Modified Mesoporous Y Zeolite Catalyzed Nitration of Azobenzene Using NO_2 as Nitro Source Combined with Density Functional Theory Study

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Table S1 The yield of azoxybenzene under mesoporous Y zeolites with different metal modifications [a]

Entry	Catalyst	Time (h)	Solvent	Conversion (%)	Yield (%) [b]
1	Cu-Y	10	DCE	83.6	14.6
2	La-Y	10	DCE	83.9	30.7
3	Ce-Y	10	DCE	82.3	33.5
4	Co-Y	10	DCE	83.0	35.2

[a] Reaction conditions: azobenzene (0.55mmol), NO_2 (6.3mmol), catalyst (0.10 g), DCE (5 mL), 10 °C, O_2 balloon.

[b] HPLC yield using naphthalene as an internal standard. Yield of azoxybenzene.

Table S2 The yield of azoxybenzene under different temperature [a]

Entry	Catalyst	Temperature (℃)	Solvent	Conversion (%)	Yield (%) [b]
1	Fe-Y	25	DCE	94.7	13.3
2	Fe-Y	40	DCE	94.7	22.6
3	Fe-Y	60	DCE	93.9	39.3

[a] Reaction conditions: azobenzene (0.55mmol), NO_2 (6.3mmol), catalyst (0.10 g), DCE (5 mL), 20 h, O_2 balloon.

[b] HPLC yield using naphthalene as an internal standard. Yield of azoxybenzene.

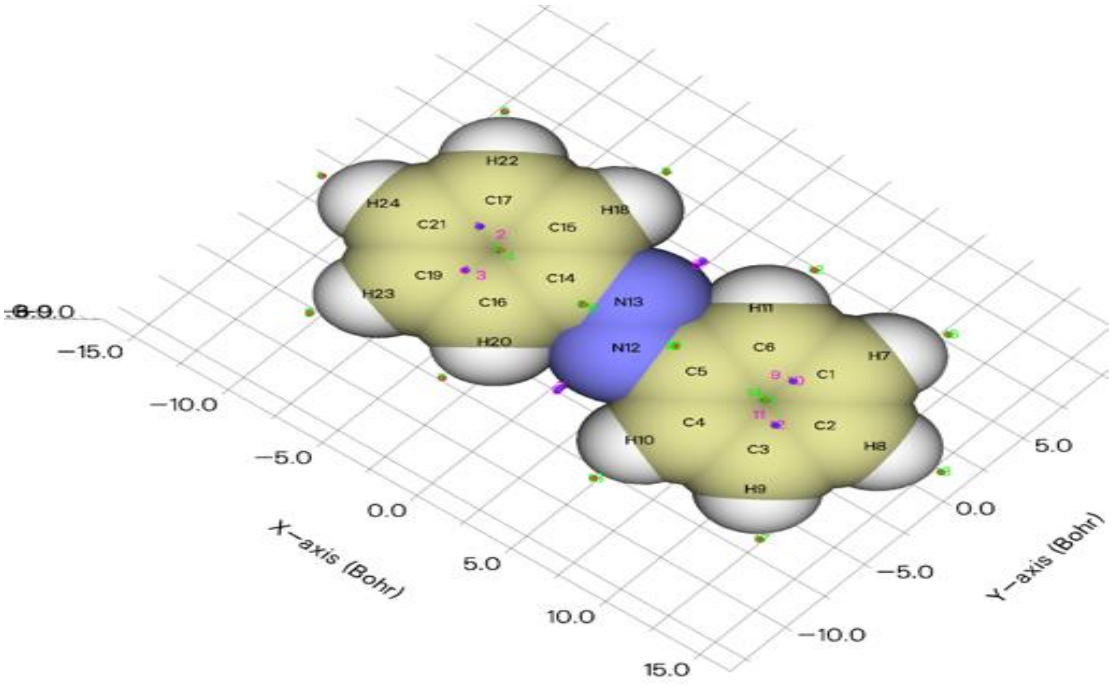


Fig. S1 Maximum and minimum points of the electrostatic potential of azobenzene.

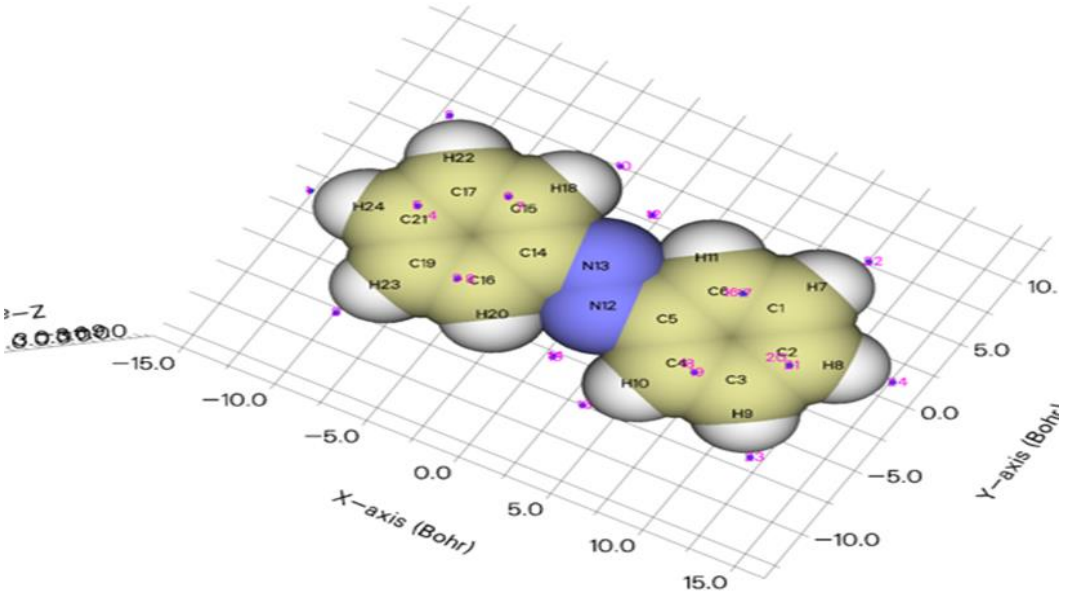
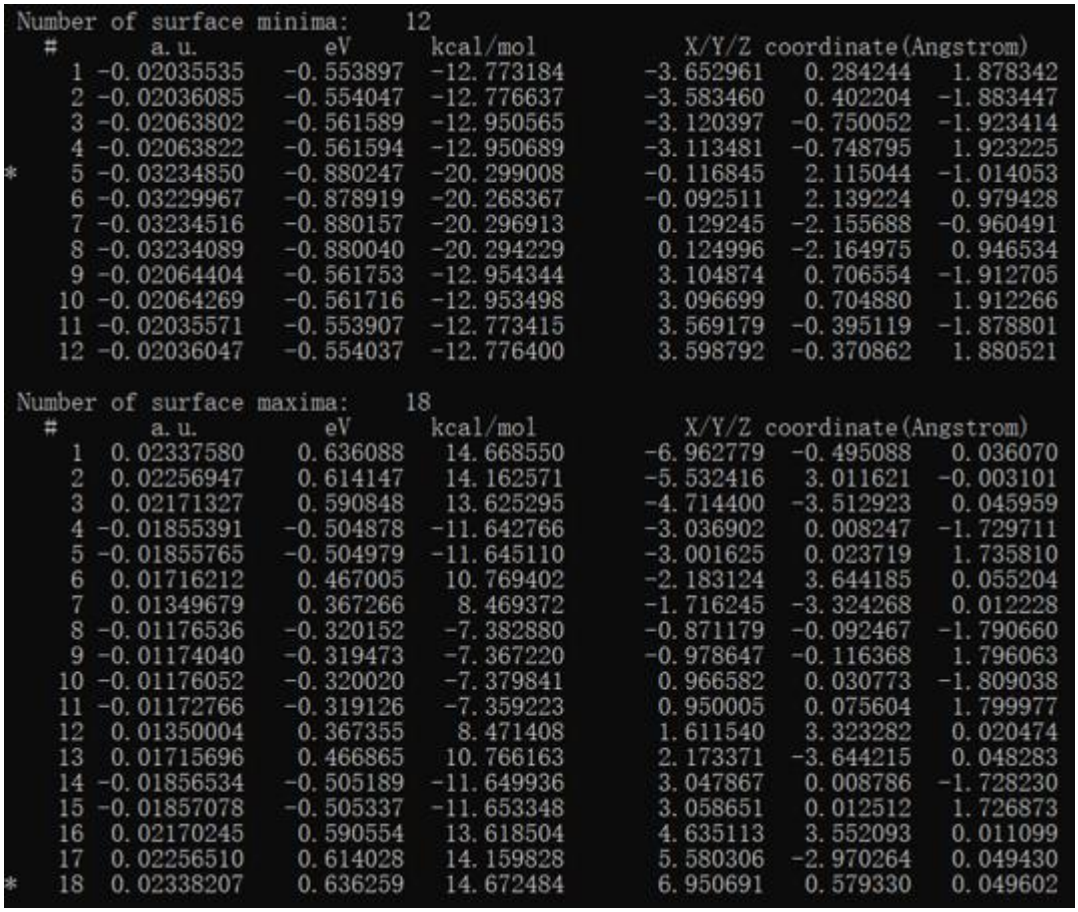


Fig. S2 Minimum points of the average local ionization energy of azobenzene.



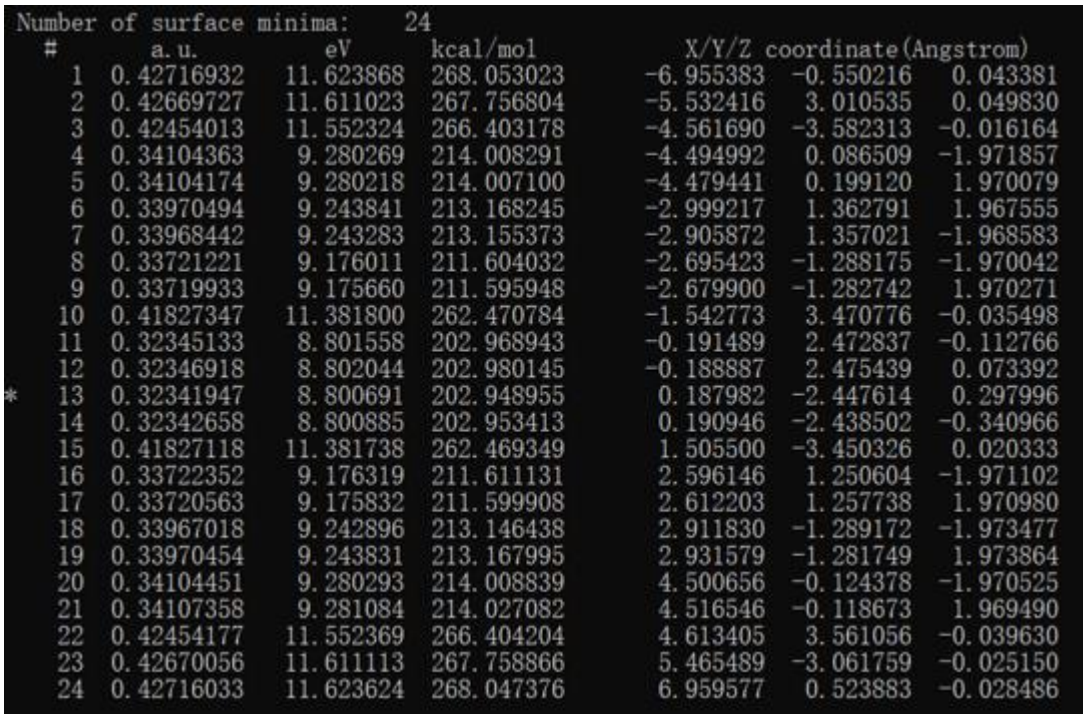
Number of surface minima: 12

#	a.u.	eV	kcal/mol	X/Y/Z coordinate(Angstrom)		
1	-0.02035535	-0.553897	-12.773184	-3.652961	0.284244	1.878342
2	-0.02036085	-0.554047	-12.776637	-3.583460	0.402204	-1.883447
3	-0.02063802	-0.561589	-12.950565	-3.120397	-0.750052	-1.923414
4	-0.02063822	-0.561594	-12.950689	-3.113481	-0.748795	1.923225
* 5	-0.03234850	-0.880247	-20.299008	-0.116845	2.115044	-1.014053
6	-0.03229967	-0.878919	-20.268367	-0.092511	2.139224	0.979428
7	-0.03234516	-0.880157	-20.296913	0.129245	-2.155688	-0.960491
8	-0.03234089	-0.880040	-20.294229	0.124996	-2.164975	0.946534
9	-0.02064404	-0.561753	-12.954344	3.104874	0.706554	-1.912705
10	-0.02064269	-0.561716	-12.953498	3.096699	0.704880	1.912266
11	-0.02035571	-0.553907	-12.773415	3.569179	-0.395119	-1.878801
12	-0.02036047	-0.554037	-12.776400	3.598792	-0.370862	1.880521

Number of surface maxima: 18

#	a.u.	eV	kcal/mol	X/Y/Z coordinate(Angstrom)		
1	0.02337580	0.636088	14.668550	-6.962779	-0.495088	0.036070
2	0.02256947	0.614147	14.162571	-5.532416	3.011621	-0.003101
3	0.02171327	0.590848	13.625295	-4.714400	-3.512923	0.045959
4	-0.01855391	-0.504878	-11.642766	-3.036902	0.008247	-1.729711
5	-0.01855765	-0.504979	-11.645110	-3.001625	0.023719	1.735810
6	0.01716212	0.467005	10.769402	-2.183124	3.644185	0.055204
7	0.01349679	0.367266	8.469372	-1.716245	-3.324268	0.012228
8	-0.01176536	-0.320152	-7.382880	-0.871179	-0.092467	-1.790660
9	-0.01174040	-0.319473	-7.367220	-0.978647	-0.116368	1.796063
10	-0.01176052	-0.320020	-7.379841	0.966582	0.030773	-1.809038
11	-0.01172766	-0.319126	-7.359223	0.950005	0.075604	1.799977
12	0.01350004	0.367355	8.471408	1.611540	3.323282	0.020474
13	0.01715696	0.466865	10.766163	2.173371	-3.644215	0.048283
14	-0.01856534	-0.505189	-11.649936	3.047867	0.008786	-1.728230
15	-0.01857078	-0.505337	-11.653348	3.058651	0.012512	1.726873
16	0.02170245	0.590554	13.618504	4.635113	3.552093	0.011099
17	0.02256510	0.614028	14.159828	5.580306	-2.970264	0.049430
* 18	0.02338207	0.636259	14.672484	6.950691	0.579330	0.049602

Fig. S3 Maximum and minimum values of the electrostatic potential of azobenzene.



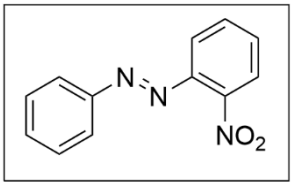
Number of surface minima: 24

#	a.u.	eV	kcal/mol	X/Y/Z coordinate(Angstrom)		
1	0.42716932	11.623868	268.053023	-6.955383	-0.550216	0.043381
2	0.42669727	11.611023	267.756804	-5.532416	3.010535	0.049830
3	0.42454013	11.552324	266.403178	-4.561690	-3.582313	-0.016164
4	0.34104363	9.280269	214.008291	-4.494992	0.086509	-1.971857
5	0.34104174	9.280218	214.007100	-4.479441	0.199120	1.970079
6	0.33970494	9.243841	213.168245	-2.999217	1.362791	1.967555
7	0.33968442	9.243283	213.155373	-2.905872	1.357021	-1.968583
8	0.33721221	9.176011	211.604032	-2.695423	-1.288175	-1.970042
9	0.33719933	9.175660	211.595948	-2.679900	-1.282742	1.970271
10	0.41827347	11.381800	262.470784	-1.542773	3.470776	-0.035498
11	0.32345133	8.801558	202.968943	-0.191489	2.472837	-0.112766
12	0.32346918	8.802044	202.980145	-0.188887	2.475439	0.073392
* 13	0.32341947	8.800691	202.948955	0.187982	-2.447614	0.297996
14	0.32342658	8.800885	202.953413	0.190946	-2.438502	-0.340966
15	0.41827118	11.381738	262.469349	1.505500	-3.450326	0.020333
16	0.33722352	9.176319	211.611131	2.596146	1.250604	-1.971102
17	0.33720563	9.175832	211.599908	2.612203	1.257738	1.970980
18	0.33967018	9.242896	213.146438	2.911830	-1.289172	-1.973477
19	0.33970454	9.243831	213.167995	2.931579	-1.281749	1.973864
20	0.34104451	9.280293	214.008839	4.500656	-0.124378	-1.970525
21	0.34107358	9.281084	214.027082	4.516546	-0.118673	1.969490
22	0.42454177	11.552369	266.404204	4.613405	3.561056	-0.039630
23	0.42670056	11.611113	267.758866	5.465489	-3.061759	-0.025150
24	0.42716033	11.623624	268.047376	6.959577	0.523883	-0.028486

Fig. S4 Minimum values of the average local ionization energy of azobenzene.

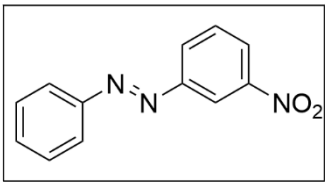
^{1}H NMR data for products

(E)-1-(2-nitrophenyl)-2-phenyldiazene



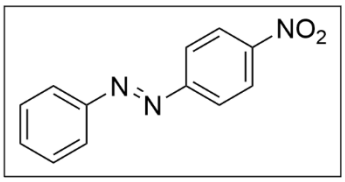
Orange solid, m. p. 66-68 ℃ (lit.[1] 67-68 ℃**) ^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ 8.28 – 8.22 (m, 2H), 8.20 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.91 (td, *J* = 7.8, 1.4 Hz, 1H), 7.80 – 7.73 (m, 1H), 7.66 (dddd, *J* = 11.3, 9.1, 7.2, 1.6 Hz, 4H).

(E)-1-(3-nitrophenyl)-2-phenyldiazene



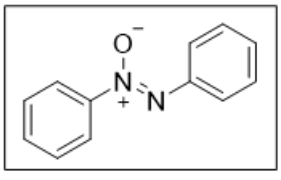
Yellow solid, m. p. 94-95 ℃ (lit.[2] 95-96 ℃) **^{1}H NMR (500 MHz, Chloroform-*d*):** δ 8.75 (t, *J* = 2.1 Hz, 1H), 8.34 (ddd, *J* = 8.2, 2.3, 1.1 Hz, 1H), 8.27 (ddd, *J* = 8.0, 1.9, 1.1 Hz, 1H), 8.03 – 7.93 (m, 2H), 7.72 (t, *J* = 8.0 Hz, 1H), 7.61 – 7.51 (m, 3H).

(E)-1-(4-nitrophenyl)-2-phenyldiazene



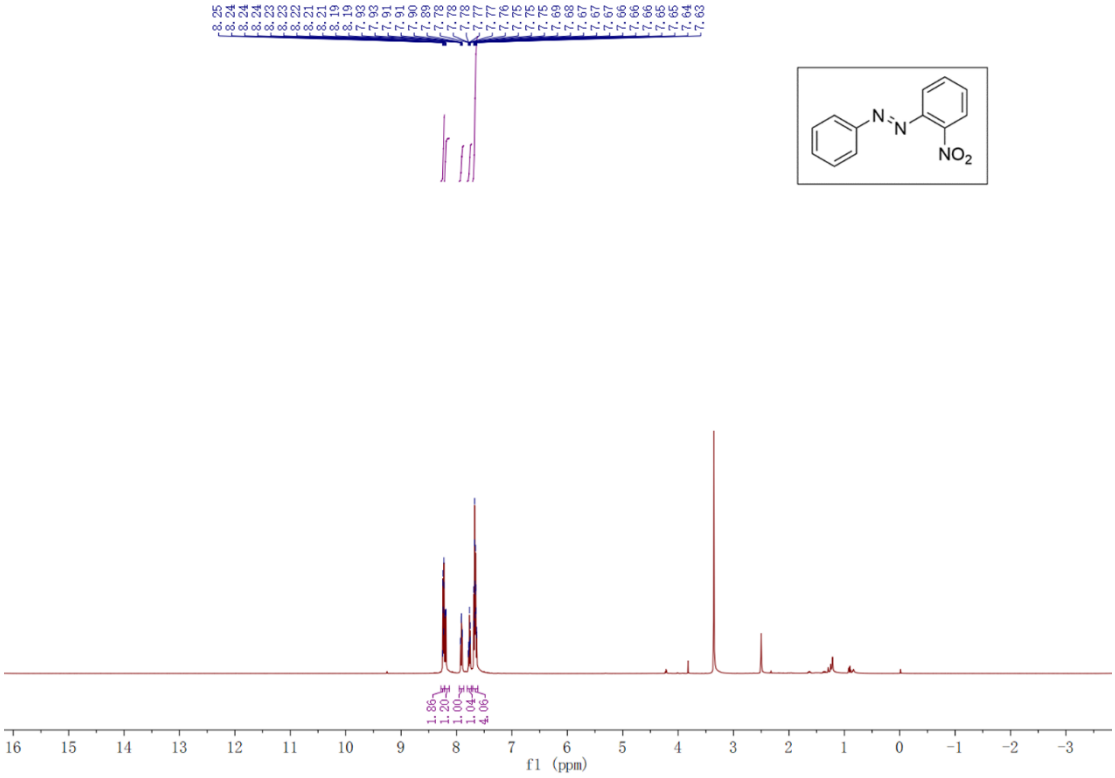
Orange solid**,** m. p. 130-131 ℃ (lit.[2] 132-133 ℃) **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ 8.37 (d, *J* = 9.0 Hz, 2H), 8.28 (d, *J* = 8.0 Hz, 2H), 8.13 (d, *J* = 9.0 Hz, 2H), 7.74 (t, *J* = 7.3 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 2H).

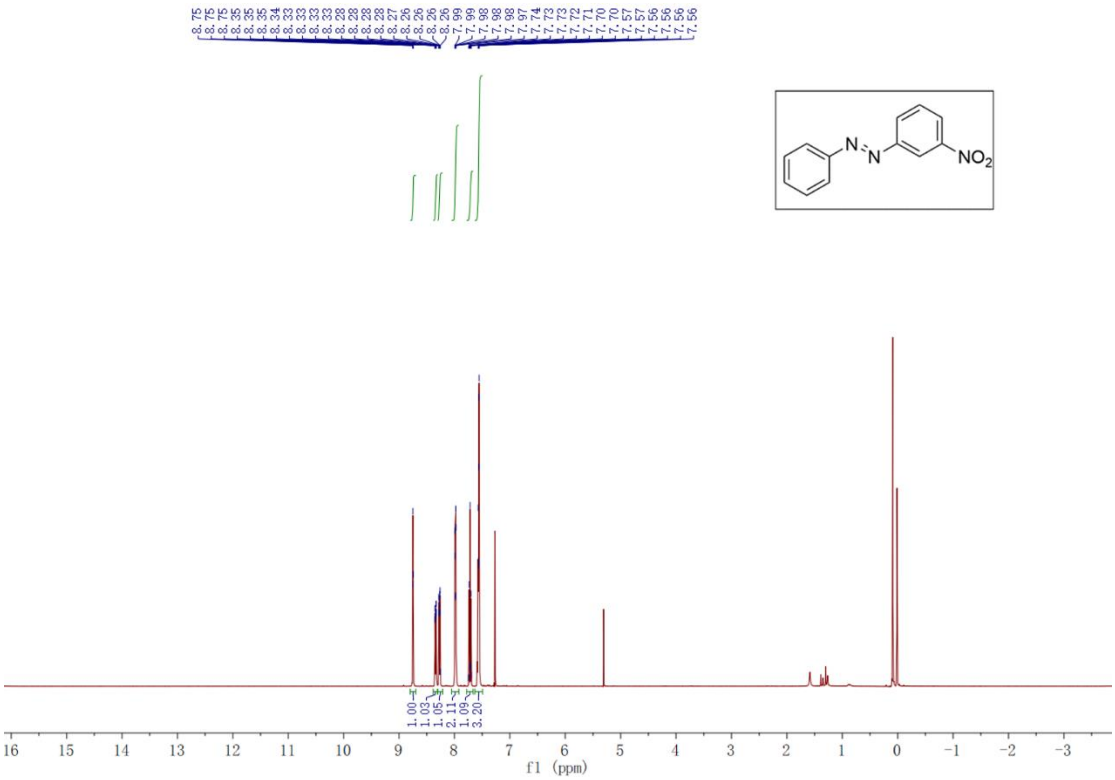
Azoxybenzene

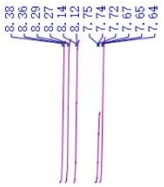


Yellow solid, m. p. 35-36 ℃ (lit.[3] 36-37 ℃) **^{1}H NMR (500 MHz, Chloroform-*d*):** δ 8.32 (dd, *J* = 7.8, 2.0 Hz, 2H), 8.25 – 8.10 (m, 2H), 7.63 – 7.45 (m, 5H), 7.41 (dd, *J* = 8.3, 6.5 Hz, 1H).

^{1}H NMR Spectra



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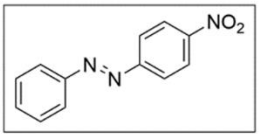
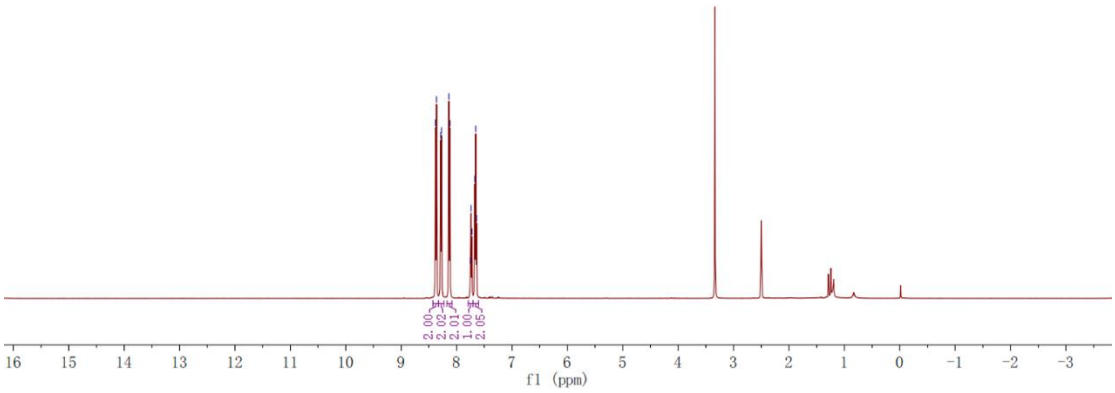
7.75
7.74
7.72
7.67
7.65
7.64


NO2
N
N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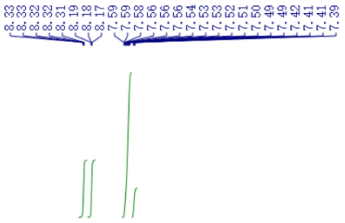
2.02
2.01
1.00
2.05
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)


8.33
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8.32
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8.18
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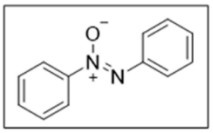
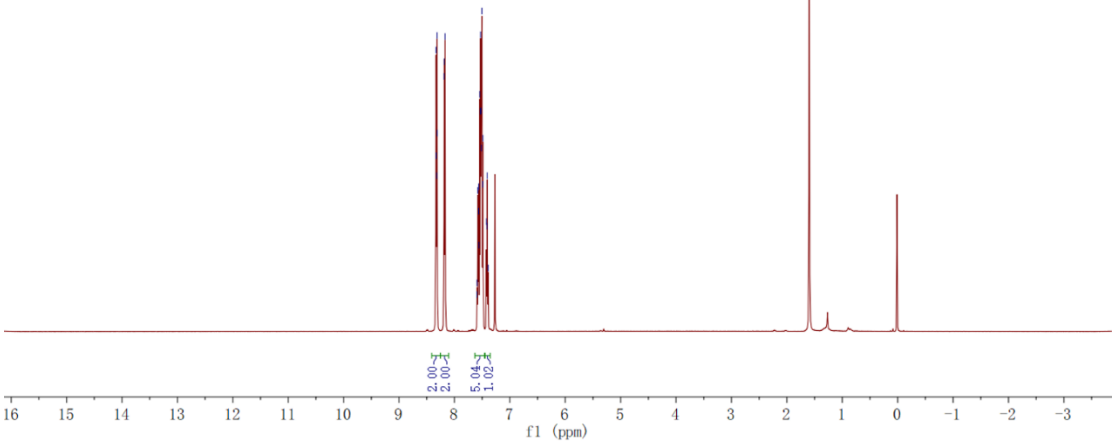
7.41
7.39


O
N
N


2.00
2.00
5.04
1.02
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)

References

1. J. Dong, B. Jin and P. Sun, *Org. Lett.*, 2014, **16**, 4540-4542.
2. M. Barbero, S. Cadamuro, S. Dughera and C. Giaveno, *Eur. J. Org. Chem.*, 2006, **2006**, 4884-4890.
3. J. H. Boyer and S. E. Ellzey, *J. Am. Chem. Soc.*, 1960, **82**, 2525-2528.