Supplementary information

Sustainable synthesis of azobenzenes, quinolines and quinoxalines *via* oxidative dehydrogenative couplings catalysed by reusable transition metal oxide–Bi(III) cooperative catalysts

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SECTION S1.

Supporting results and comparative data

Table S1 The compositions of the as-prepared bismutite supported composites.

| Composites	Bulk composition*	Specific surface area (m²/g)**
$Bi_2O_2CO_3$	$(BiO)_2(CO_3)_{0.93}(OH)_{0.28}$	32
$CoBi_2O_2CO_3$	$Co_{0.16}(BiO)_2(CO_3)_{1.04}(OH)_{1.04}$	48
$MnBi_2O_2CO_3$	$Mn_{0.28}(BiO)_2(CO_3)_{1.02}(OH)_{0.36}$	38
$NiBi_2O_2CO_3$	$Ni_{0.69}(BiO)_2(CO_3)_{1.02}(OH)_{3.94}$	44

*Determined by the combination of ICP-MS and TG measurement
**Determined by BET measurements

Table S2 Optimisation procedure of the bismutite-based catalysts promoted oxidative dehydrogenative homocoupling of aniline. Reaction conditions: 0.5 ml solvent, T = 64–175 °C for 12–72h and 10 mol% catalyst; c (aniline) = 0.6 M (when using other solvents than aniline).

Numbers	Composites	Solvent	Temperature (°C)	Catalyst loading (mol%)	Reaction time (h)	Aniline conversion (mol%)	Azobenzene selectivity (mol%)	Azobenzene yield (mol%)
1	—	DMSO	150	—	72	3	—	—
2	$Bi_2O_2CO_3$	DMSO	150	10	72	7	90	6
3	$MnBi_2O_2CO_3$	DMSO	150	10	72	29	100	29
4	$CoBi_2O_2CO_3$	DMSO	150	10	72	19	100	19
5	$NiBi_2O_2CO_3$	DMSO	150	10	72	14	100	14
6	$MnBi_2O_2CO_3$*	DMSO	150	10	72	2	100	2
7	$MnBi_2O_2CO_3$	DMSO	110	10	72	9	100	12
8	$MnBi_2O_2CO_3$	DMSO	175	10	72	30	100	30
9	$MnBi_2O_2CO_3$	methanol	reflux	10	72	5	100	5
10	$MnBi_2O_2CO_3$	toluene	reflux	10	72	20	75	15
11	$MnBi_2O_2CO_3$	acetonitrile	reflux	10	72	—	—	—
12	$MnBi_2O_2CO_3$	γ-valerolactone	reflux	10	72	15	100	15
13	$MnBi_2O_2CO_3$	—	150	10	72	71	100	71
14	$MnBi_2O_2CO_3$	—	reflux	10	72	73	96	70
15	$MnBi_2O_2CO_3$	—	110	10	72	35	80	28
16	$MnBi_2O_2CO_3$	—	150	5	72	49	90	44
17	$MnBi_2O_2CO_3$	—	150	20	72	79	97	77
18	$MnBi_2O_2CO_3$	—	150	10	48	34	100	34
19	$MnBi_2O_2CO_3$	—	150	10	24	16	100	16
20	$CoBi_2O_2CO_3$	—	150	10	48	75	100	75
21	$CoBi_2O_2CO_3$	—	150	10	24	51	100	51
22	$CoBi_2O_2CO_3$	—	150	10	12	23	100	23
23	$CoBi_2O_2CO_3$	—	150	5	72	48	100	48
24	$CoBi_2O_2CO_3$	—	150	2.5	72	12	100	12

Table S3 Selectivity test of the as-prepared $CoBi_2O_2CO_3$ catalyst in oxidative dehydrogenative heterocoupling of aniline derivatives. Reaction conditions: 0.5 ml solvent, T = 150 °C for 72h and 10 mol% catalyst; c (aniline) = 0.6 M, c (substituted aniline) = 0.5 M.
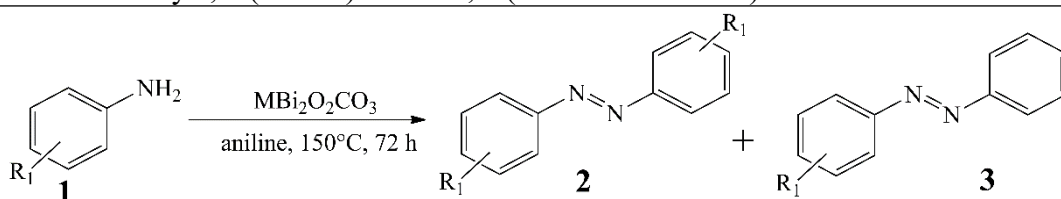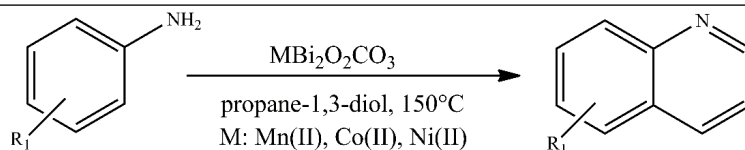

	Solvent	Temperature (°C)	Catalyst loading (mol%)	Reaction time (h)	Conversion of 1 (mol%)	Selectivity of 3 (mol%)	Yield of 3 (mol%)
R= *o*-OMe	DMSO	150	10	72	17	88	15
R= *p*-Br	DMSO	150	10	72	28	96	27
R= *p*-Me	DMSO	150	10	72	25	95	24
R= *o*-OMe	toluene	reflux	10	72	51	90	46
R= *p*-Br	toluene	reflux	10	72	54	96	52
R= *p*-Me	toluene	reflux	10	72	54	92	50

Table S4 Comparative table of the catalytic ability of the as-prepared $CoBi_2O_2CO_3$ catalyst and the benchmark catalysts for the oxidative dehydrogenative homo- and heterocoupling of different anilines.
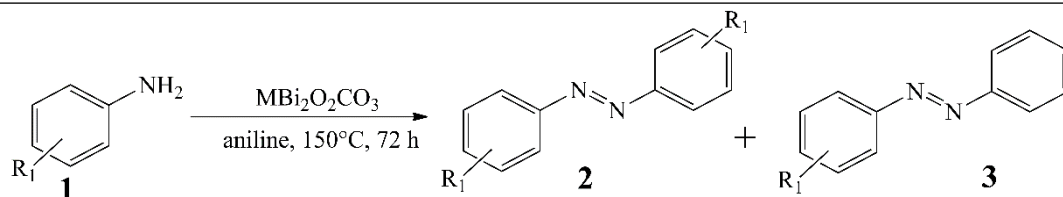
Catalyst	Solvent	Temperature (°C)	Catalyst loading (mol%)	Reaction time (h)	Additive	Atmosphere	Aniline conversion (mol%)	Selectivity of 3 (mol%)	Yield of 3 (mol%)	References
$CoBi_2O_2CO_3$	—	150	10	72	—	air	35–100	75–100	34–95	This work
$CuBr_2$	toluene	60	20	24	60 mol% pyridine	1 bar O_2	60–100	50–100	42–69	1
meso-Mn_2O_3	toluene	110	32	12	—	air	80–100	28–92	28–87	2

Table S5 Comparative table of the catalytic ability of the as-prepared $CoBi_2O_2CO_3$ catalyst and the benchmark catalysts for the oxidative dehydrogenative couplings for the synthesis of quinolines.

$$\text{aniline (}R_1\text{)} \xrightarrow[\substack{\text{propane-1,3-diol, 150°C} \\ \text{M: Mn(II), Co(II), Ni(II)}}]{MBi_2O_2CO_3} \text{quinoline (}R_1\text{)}$$

Catalyst	Solvent	Temperature (°C)	Catalyst loading (mol%)	Reaction time (h)	Additive	Atmosphere	Aniline conversion (mol%)	Selectivity of dp (mol%)	Yield of dp (mol%)	References
CoBi₂O₂CO₃	—	*150*	*10*	*48*	—	*air*	*92–100*	*65–100*	*65–100*	*This work*
RuCl₃×nH₂O	mesitylene	164	5	16	10 mol% phosphine, 5% MgBr₂*OEt₂	argon	20–61	100	20–61	3
Pt/Al₂O₃ + ZnO	NMP	175	1.7 + 4.5	16–45	5% p-TSA*H₂O	argon	15–70	80–100	18–62	4
(Pd(OAc)₂)	—	150	5	16	10 mol% ligand + 20 mol% acid	oxygen	55–82	100	55–82	5
Mn(I)-PNP	toluene	140*	5	24	210 mol% t-BuOK; 100 mol% KOH	pressured gas + argon	61–91	100	61–91	6
Co(II)-PNP	toluene	120*	2	24	5 mol% t-BuOK	pressured gas + argon	38–65	100	38–65	7
Knölker–Fe	toluene	140*	2	48	2 mol% PPh₃ + 10–30 mol% t-BuOK	pressured gas	55–67	100	55–67	8
Mn(I)–NNN	toluene	130*	2	20	100 mol% t-BuOK	pressured gas + nitrogen	60–75	100	60–75	9
[Ni(II)(MeTAA)],	toluene	90	8	36	200 mol% t-BuOK	air	32–83	100	32–83	10
Ni(II)–NNNN	toluene	135*	2	24	100 mol% t-BuOK	pressured gas + argon	46–88	100	46–88	11
Ni(II)–NNNN	toluene	80	4	10–30	50 mol% t-BuOK	air	49–90	100	49–90	12
Cu(II)–NNN**	toluene	85	1	18	50 mol% NaOH	air	40–96	100	40–96	13
SNS–Co(II)	m-xylene	139	2.5	24	110 mol% t-BuOK	argon	63–57	100	63–87	14
Co(II)–NNN	toluene	150*	5	12	100 mol% CsOH×H₂O	pressured gas + argon	55–93	100	55–93	15
Mn(II)–NNN	toluene	120*	5	24	75 mol% KOH	pressured gas	35–90	100	35–90	16
Ru(II)-PCy₃	1.4-dioxane	80	1	1	100 mol% KOH	argon	22–100	100	22–100	17
Re(I)–PN(H)P	toluene	150*	1	24	10 mol% t-BuOK	pressured gas + argon	87–98	90–96	87–96	18
Organo-Ru(II)–NNN	toluene	100	0.01	6	15 mol% KOH	argon	72–98	100	72–98	19

*over boiling point; ** H₂O₂ waste; dp: desired product
yellow background: amino benzyl alcohols + ketones/alcohols
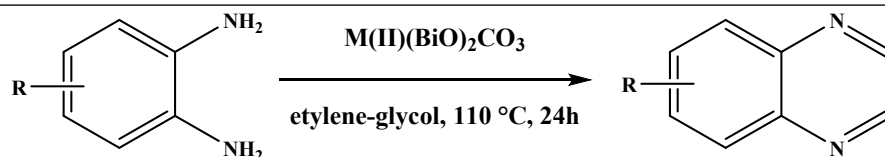orange background: anilines + diols (alcohols)

Table S6 Some variations in the reaction conditions of oxidative dehydrogenative heterocoupling of o-phenylenediamines and ethylene-glycol. Applied reaction conditions: 1 equiv. (0.25 M) o-phenylenediamines or its derivatives, ethylene-glycol of 2 ml, 110 °C for 24h and 10 mol% catalyst.

R-group	Composites	Temperature (°C)	Catalyst loading (mol%)	Reaction time (h)	Aniline conversion (mol%)	Selectivity of dp (mol%)	Yield of dp (mol%)
H					100	100	100
p-Br					60	100	60
p-Cl	$MnBi_2O_2CO_3$	110	10	24	73	41	30
p-nitro					11	100	11
p-COOH					100	19	19
p-Me					58	100	58
H					100	100	100
p-Br					66	100	66
p-Cl	$CoBi_2O_2CO_3$	110	2.5	24	45	76	34
p-nitro					99	100	99
p-COOH					100	50	50
p-Me					55	100	55
H					100	100	100
p-Br					93	100	93
p-Cl	$CoBi_2O_2CO_3$	110	10	24	86	86	74
p-nitro					100	100	100
p-COOH					100	78	78
p-Me					95	100	95
H					100	89	89
p-Br					93	80	75
p-Cl	$CoBi_2O_2CO_3$	90	10	24	79	65	51
p-nitro					100	85	85
p-COOH					95	60	57
p-Me					90	82	74

dp: desired product

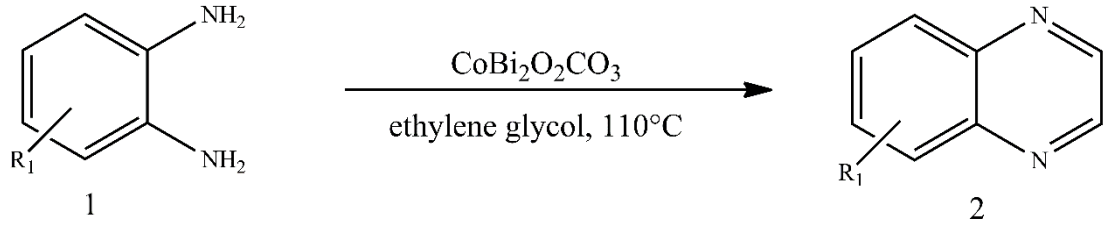**Table S7** Comparative table of the catalytic ability of the as-prepared CoBi$_2$O$_2$CO$_3$ catalyst and the benchmark catalysts for the oxidative dehydrogenative couplings for the synthesis of quinoxalines.

Catalyst	Solvent	Temperature (°C)	Catalyst loading (mol%)	Reaction time (h)	Additive	Atmosphere	Aniline conversion (mol%)	Selectivity of dp (mol%)	Yield of dp (mol%)	References
CoBi$_2$O$_2$CO$_3$	—	*110*	*10*	*24*	—	*air*	*86–100*	*78–100*	*78–100*	*This work*
Mn(I)–PNP	toluene	150*	2	36	3–100 mol% KH	argon	45–99	50–98	35–95	20
Mn(I)–NNS	—	140	4	20	27 mol% KOH	argon	53–82	100	53–82	21
Mn(I)(CO)$_5$Br	toluene	130*	2	36	3 mol% ligand + 40 mol% t-BuOK	argon	43–83	100	43–83	22
Co(OAc)$_2$-Phen/Carbon-800	toluene	150*	1.5	24–36	25–75 mol% CsOH×H$_2$O	argon	64–96	100	64–96	23
NiBr$_2$	toluene	110	5	24	50 mol% Cs$_2$CO$_3$ + 5 mol% ligand	argon	79–98	90–100	70–98	24
Ni(II)–NNOO	toluene	80	5	8	50 mol% t-BuOK	oxygen	70–92	100	70–92	25
Co(II)–NNN	toluene	150*	5	24	120 mol% CsOH×H$_2$O	pressured gas + argon	70–93	100	75–93	15
RuCl$_2$(PPh$_3$)$_3$	diglyme	162	4	20	400 mol% KOH	air	63–82	100	63–82	26
Ir–P^N^P	THF	90*	0.06	24	200 mol% t-BuOK	pressured gas + nitrogen	61–89	100	61–89	27
Re(I)–PNP	toluene	120*	0.05	6	50 mol% t-BuOK	argon	67–85	100	67–85	28
organo-Ir–NNO	H$_2$O	120*	2.5	24	150 mol% KOH	argon	69–88	90–98	65–84	29
Ru$_3$(CO)$_{12}$	toluene	150*	1	8	50 mol% CsOH×H$_2$O + 3 mol% DPPH	nitrogen	36–84	100	36–84	30
Au/CeO$_2$	diglyme	140	1	24–30	—	air	94–99	35–92	35–91	31

*over boiling point; green background: reusable; **dp:** desired product

Table S8 Oxidative dehydrogenative heterocoupling of o-phenylenediamines and ethylene glycol. Reaction conditions: 1 equiv. (0.25 M) o-phenylenediamine or its substituted derivative, 2 mL ethylene glycol, 110 °C for 24h and 10 mol% catalyst.

Desired product	Yield of 2 (mol%)	Isolated yield (%)	E-factor
R_1 = H	100*	85	2.1
R_1 = 4-Br	93	80	2.9
R_1 = 4-Cl	74	63	5.6
R_1 = 4-COOH	78	64	4.9
R_1 = 4-Me	95	84	3.4
R_1 = 4-nitro	99*	85	2.1

* 2.5 mol% catalyst, E - factor = the mass of waste (mg)/the mass of product (mg)

waste = by-product (mg) + leftover reactant (mg)+ solvent losses (mg)
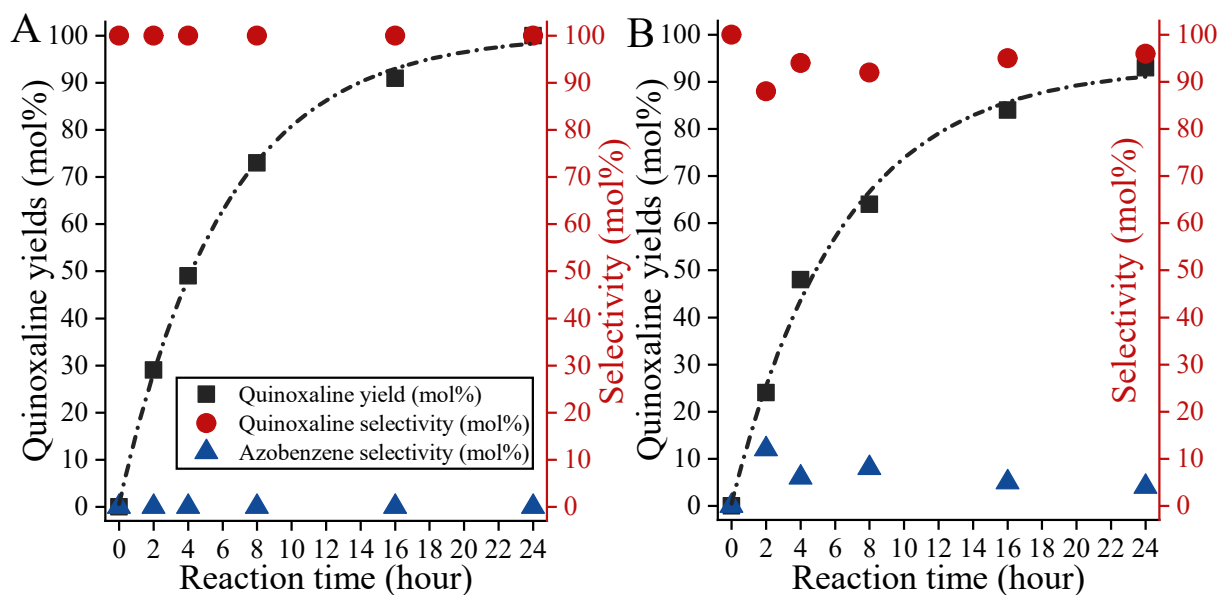
Fig. S1 Catalytic stability test of the $CoBi_2O_2CO_3$ composite. Quinoxaline yields, quinoxaline selectivity and azobenzene selectivity as a function of time in a catalytic reaction of o-phenylenediamine and ethylene glycol catalysed by $CoBi_2O_2CO_3$ in first (A) and fifth (B) reaction cycle. Reaction conditions: 1 equiv. (0.25 M) o-phenylenediamine, 2 mL ethylene glycol and 2.5 mol% catalyst at 110°C.
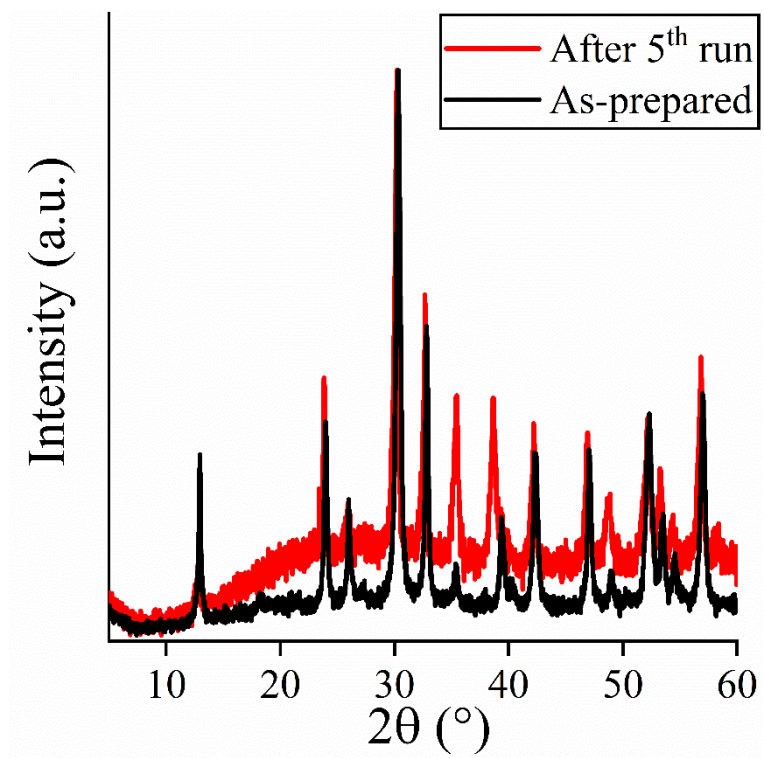
Fig. S2 XRD patterns of $CoBi_2O_2CO_3$ composite before and after the recycling test.

SECTION S2.

Identification of the produced azobenzene, quinoline, quinoxaline and their derivatives by NMR spectroscopy

Azobenzene
^{1}H NMR (500 MHz, DMSO-d_6) δ 7.63-7.57 (m, 1H), 7.52-7.45 (m, 1H), 7.45-7.38 (m, 1H).
^{13}C NMR (125 MHz, DMSO-d_6) δ 153.03, 129.94, 129.12, 122.06.

1,2-bis(4-methoxyphenyl)diazene
^{1}H NMR (500 MHz, DMSO-d_6) δ 7.66-7.60 (m, 1H), 7.04-6.98 (m, 1H), 3.76 (s, 6H).
^{13}C NMR (100 MHz, DMSO-d_6) δ 160.73, 147.10, 124.02, 114.57, 55.33.

1-(4-methoxyphenyl)-2-phenyldiazene
^{1}H NMR (500 MHz, DMSO-d_6) δ 7.66-7.57 (m, 4H), 7.52-7.45 (m, 2H), 7.45-7.38 (m, 1H), 7.04 – 6.98 (m, 2H), 3.76 (s, 3H).
^{13}C NMR (100 MHz, DMSO-d_6) δ 160.73, 152.32, 147.10, 129.94, 129.12, 124.02, 122.09, 114.57, 55.33.

1,2-bis(2-methoxyphenyl)diazene
^{1}H NMR (500 MHz, DMSO-d_6) δ 7.73 (dd, 1H), 7.35 (dd, 1H), 7.13 (q, 2H), 3.85 (s, 3H).
^{13}C NMR (100 MHz, DMSO-d_6) δ 153.01, 143.50, 128.22, 125.05, 122.30, 114.39, 56.15.

1-(2-methoxyphenyl)-2-phenyldiazene
^{1}H NMR (500 MHz, DMSO-d_6) δ 7.77 (dd, 1H), 7.63-7.57 (m, 2H), 7.52-7.45 (m, 2H), 7.45-7.38 (m, 1H), 7.33 (t, 1H), 7.14 (t, 1H), 7.10 (dd, 1H), 3.85 (s, 3H).
^{13}C NMR (100 MHz, DMSO-d_6) δ 152.92, 151.96, 143.22, 129.94, 129.55, 128.22, 124.08, 122.30, 122.18, 114.39, 56.15.

1,2-bis(3-nitrophenyl)diazene
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.64 (t, 1H), 8.32-8.26 (m, 1H), 7.81-7.75 (m, 1H), 7.69 (dd, 1H).
^{13}C NMR (100 MHz, DMSO-d_6) δ 152.16, 147.25, 129.06, 127.30, 123.00, 116.59.

1-(3-nitrophenyl)2-phenyldiazene
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.63 (t, 1H), 8.32- 8.26 (m, 1H), 7.80-7.75 (m, 1H), 7.72 - 7.65 (m, 1H), 7.63-7.57 (m, 2H), 7.52-7.45 (m, 2H), 7.45-7.38 (m, 1H).
^{13}C NMR (100 MHz, DMSO-d_6) δ 152.60, 152.13, 147.25, 129.94, 129.12, 129.06, 127.30, 123.00, 122.65, 116.58.

1,2-bis(4-bromophenyl)diazene
^{1}H NMR (500 MHz, DMSO-d_6) δ 7.73-7.67 (m, 1H), 7.63-7.57 (m, 1H).
^{13}C NMR (125 MHz, DMSO-d_6) δ 151.90, 132.06, 123.25, 122.26.

1-(4-bromophenyl)-2-phenyldiazene
^{1}H NMR (500 MHz, DMSO-d_6) δ 7.73-7.67 (m, 2H), 7.63- 7.57 (m, 4H), 7.52- 7.45 (m, 2H), 7.45- 7.38 (m, 1H).
^{13}C NMR (125 MHz, DMSO-d_6) δ 152.32, 151.90, 132.06, 129.94, 129.12, 123.25, 122.26, 122.06.

1,2-bis(4-chlorophenyl)diazene
^{1}H NMR (500 MHz, DMSO-d_6) δ 7.79- 7.73 (m, 1H), 7.50- 7.44 (m, 1H).
^{13}C NMR (100 MHz, DMSO-d_6) δ 151.15, 133.73, 128.90, 122.63.

1-(4-clorophenyl)-2-phenyldiazene
^{1}H NMR (500 MHz, DMSO-d_6) δ 7.79-7.73 (m, 1H), 7.63-7.57 (m, 1H), 7.52- 7.38 (m, 2H).
^{13}C NMR (100 MHz, DMSO-d_6) δ 152.32, 151.15, 133.73, 129.94, 129.12, 128.90, 122.60, 122.09.

1,2-di-p-tolyldiazene
^{1}H NMR (500 MHz, DMSO-d_6) δ 7.61-7.55 (m, 1H), 7.28- 7.22 (m, 1H), 2.36 (s, 6H).
^{13}C NMR (100 MHz, DMSO-d_6) δ 149.94, 138.49, 131.06, 116.25, 21.18.

1-phenyl-2-(p-tolyl)diazene
^{1}H NMR (500 MHz, DMSO-d_6) δ 7.59 (t, 4H), 7.52-7.45 (m, 2H), 7.45-7.38 (m, 1H), 7.28-7.22 (m, 2H), 2.36 (s, 3H).
^{13}C NMR (100 MHz, DMSO-d_6) δ 152.32, 149.94, 138.49, 131.06, 129.94, 129.12, 122.06, 116.25, 21.18.

4,4'-(diazene-1,2-diyl)dibenzonitrile
^{1}H NMR (500 MHz, DMSO-d_6) δ 7.85-7.76 (m, 1H).
^{13}C NMR (100 MHz, DMSO-d_6) δ 155.72, 133.54, 123.23, 118.45, 112.27.

4-(phenyldiazenyl)benzonitrile
^{1}H NMR (500 MHz, DMSO-d_6) δ 7.85 – 7.76 (m, 4H), 7.63 – 7.57 (m, 2H), 7.52 – 7.45 (m, 2H), 7.45 – 7.38 (m, 1H).
^{13}C NMR (100 MHz, DMSO-d_6) δ 155.72, 152.32, 133.54, 129.94, 129.12, 123.23, 122.09, 118.45, 112.27.

Quinoline
^{1}H NMR (500 MHz, DMSO-d_6) δ:8.90 (dd, 1H), 8.36 (dd, 1H), 8.02-7.99 (d, 1H), 7.98-7.97 (d, 1H), 7.63-7.61 (t, 1H), 7.63, 7.52-7.49 (m, 2H)
^{13}C NMR (100 MHz, DMSO-d_6) δ:148.77, 148.05, 131.52, 130.14, 129.36, 128.58, 127.43, 126.15, 121.32.

8-methoxyquinoline
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.83 (dd, 2H), 8.29 (dd, 2H), 7.97-7.91 (m, 2H), 7.51 (dd, 2H), 7.32 (t, 2H), 7.18 (dd, 2H), 3.83 (s, 3H)
^{13}C NMR (100 MHz, DMSO-d_6) δ 154.53, 148.72, 139.39, 130.00, 129.75, 128.73, 126.29, 122.48, 113.75, 55.69.

6-methoxyquinoline
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.73 (dd, 2H), 8.24 (d, 2H), 7.91 (d, 2H), 7.51-7.43 (m, 2H), 7.38 (t, 2H), 7.11 (dd, 2H), 3.79 (s, 3H).
^{13}C NMR (100 MHz, DMSO-d_6) δ 157.52, 148.24, 143.70, 130.13, 129.96, 128.26, 122.15, 115.12, 105.51, 55.28.

7-nitroquinoline

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.87 (d, 1H), 8.61 (dd, 1H), 8.20 (dd, 1H), 8.16-8.07 (m, 2H), 7.51 (dd,1H).
^{13}C NMR (100 MHz, DMSO-d_6) δ 151.01, 148.14, 148.05, 131.61, 128.54, 127.26, 124.39, 122.52, 120.70.

6-cloroquinoline
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.93 (dd, 1H), 8.36 (d, 1H), 8.04 (d, 1H), 7.78 (dd, 1H), 7.63 – 7.7.56 (m, 2H).
^{13}C NMR (100 MHz, DMSO-d_6) δ 147.83, 146.61, 131.83, 129.90, 129.72, 129.42, 126.34, 123.91, 121.68.

8-methylquinoline
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.93 (dd, 1H), 8.33 (dd, 1H), 7.80 (d, 1H), 7.63 (dd, 2H), 7.50 (t, 1H), 2.73 (s, 3H)
^{13}C NMR (00 MHz, DMSO-d_6) δ 148.24, 147.03, 132.78, 130.63, 130.30, 129.90, 128.42, 125.74, 121.07, 17.02.

6-methlquinoline
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.82 (dd, 1H), 8.23 (dt, 1H), 7.94 (d, 1H), 7.73 (t, 1H), 7.50 – 7.43 (m, 2H), 2.47 (s, 3H).
^{13}C NMR (100 MHz, DMSO-d_6) δ 149.29, 147.07, 135.26, 130.63, 130.03, 128.52, 128.05, 127.97, 121.11, 21.55.

Quinoxaline
^{1}H NMR (500 MHz, DMSO-d_6) δ:8.96 (s, 2H), 8.11-8.10 (dd, 2H), 7.88-7.86 (dd, 2H).
^{13}C NMR (100MHz, DMSO-d_6) δ:145.55, 144.04, 130.05, 127.01.

6-bromoquinoxaline
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.98 (d, 1H), 8.34 (d, 1H), 8.20 (d, 1H), 8.06-8.04, (m 1H) 8.00 (dd, 1H).
^{13}C NMR (100 MHz, DMSO-d_6) δ 145.88, 145.33, 142.40, 141.34, 133.71, 129.10, 128.66, 122.32.

6-cloroquinoxaline
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.98 (d, 1H), 8.20 (d, 1H), 7.92 (m, 2H) 6.9 (d, 1H)
^{13}C NMR (100 MHz, DMSO-d_6) δ:145.52, 144.95, 143.61, 142.30, 134.30, 130.36, 130.32, 125.51.

6-nitroquinoxaline
^{1}H NMR (500 MHz, DMSO-d_6) δ 9.16 (d, 1H), 8.97, (d, 1H), 8.93 (d, 1H), 8.42-8.27 (m, 2H).
^{13}C NMR (100 MHz, DMSO-d_6) δ:147.50, 147.08, 146.90, 144.71, 142.41, 130.89, 123.85, 123.79.

quinoxaline-6-carboxylic acid
^{1}H NMR (500 MHz, DMSO-d6) δ:9.34 (d, 1H), 8.88 (d, 1H), 8.38 (m, 1H) 8.18-8.12 (m, 2H).
^{13}C NMR (100 MHz, DMSO-d_6) δ:167.26, 146.12, 145.33, 145.05, 140.72, 131.47, 128.28, 127.18, 124.81.

6-methylquinoxaline

^{1}H NMR (500 MHz, DMSO-d_6) δ 9.00 (d, 1H), 8.87 (d, 1H), 7.97 (d, 1H) 7.87 (d, 1H), 7.71 (d, 1H) 2.56. (s, 3H)
^{13}C NMR (100 MHz, DMSO-d_6) δ:144.75, 144.08, 142.32, 141.92, 138.45, 130.48, 127.68, 126.70, 21.05.

7H-dibenzo[c,g][1,2,6]triazonine
^{1}H NMR (DMSO-d_6) δ:8.81 (s, 1H), 8.03-7.99 (m, 2H), 7.53-7.50 (m, 2H), 7.46-7.39 (m, 3H), 7.33- 7.31, (t, 1H), 5.20 (s, 1H).
^{13}C NMR (100 MHz, DMSO-d_6) δ:158.24, 152.72, 143.62, 131.56, 130.04, 130.02, 128.68, 128.49, 127.65, 126.77, 126.73, 125.29, 123.60, 61.79.

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