

Electronic supplementary information

Photosensitizer-free singlet oxygen generation via charge transfer transition involving molecular O₂ toward highly efficient oxidative coupling of arylamines to azoaromatics

Shivendra Singh and Tushar Kanti Mukherjee*

Department of Chemistry, Indian Institute of Technology (IIT) Indore, Simrol, Indore 453552, Madhya Pradesh, India

* Corresponding author Email: tusharm@iiti.ac.in

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Experimental Section

1. Materials

Milli-Q water was obtained from a Millipore water purifier system (Milli-Q integral). *p*-chloroaniline, 5,5-dimethyl-1-pyrroline N-oxide (DMPO), *p*-toluidine, 2,2,6,6-tetramethylpiperidine (TEMP), and 2,4,6-trimethylaniline were procured from TCI. H₂O₂ test strips (MQuant test peroxide) were purchased from Supelco, Sigma-Aldrich. 1,4-diazabicyclo[2.2.2]octane (DABCO), and piperidine were purchased from SRL, India. Aniline hydrochloride, potassium phosphate (K₃PO₄), potassium carbonate (K₂CO₃), *p*-anisidine, acetonitrile (ACN), methanol (MeOH), benzene, mesitylene, 3,4-dimethylaniline, 2,4-dimethylaniline, and *p*-nitroaniline were purchased from Merck. 3-bromo-4-methylaniline, 3-fluoro-4-methylaniline, 3-chloro-4-methylaniline, 5,6,7,8-tetrahydro-2-naphthylamine, and 2-methoxyaniline hydrochloride were procured from BLD Pharmatech, India.

2. Methods

2.1. Procedure for synthesis of azo compounds

Initially, 0.05 mmol amine substrate was added to 5 ml Milli-Q water in a 15 ml glass vial. Subsequently, 2 equiv. K₃PO₄ was added to the above solution. The solution was then stirred for 3-5 minutes in the dark before illuminating the reaction mixture with 370 nm Kessil LED. The reaction mixture was irradiated for 90 min inside a homemade photocatalytic reactor equipped with Kessil LED and a portable fan under ambient conditions. The product was extracted with ethyl acetate, washed several times with water, and dried using anhydrous sodium sulfate. The solvent was evaporated using a rotary evaporator, and then the residue obtained was characterized using GC-MS. The obtained product was further purified using a silica gel column and was air-dried overnight for NMR analysis. For NMR analysis, the reaction was scaled up by three times.

2.2. Gas chromatography-mass spectrometry measurements

Gas chromatography-mass spectrometry (GC-MS) spectra were recorded using a Shimadzu GC-MS, QP2010 mass spectrometer with a 30 m long Rxi-5Sil MS separation column with a 0.25 mm diameter and 0.25 μm thickness. Ethyl acetate was used as a solvent for the GC-MS analysis of the reaction mixture. The column oven temperature was set at 40 °C for 5 min, followed by a 20 °C/min ramp to 280 °C and held for 8 min.

2.3. Nuclear magnetic resonance measurements

AVANCE NEO Ascend 500 Bruker BioSpin, a 500 MHz spectrometer, was used to record ¹H and ¹³C nuclear magnetic resonance (NMR) spectra. Data for ¹H NMR spectra are reported as chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (*J* Hz), and integration. The assignment data for ¹³C NMR spectra are reported as chemical shifts.

2.4. H₂O₂ detection

The H₂O₂ detection experiment was carried out under the standard optimized reaction conditions. Briefly, *p*-toluidine (0.05 mmol) and K₃PO₄ (2 equiv.) were added to 5 ml Milli-Q and stirred for 5 min. Subsequently, the above solution was irradiated with 370 nm Kessil LED for 90 min. Finally, 10-20 µl of the reaction mixture was dropped over the H₂O₂ test strips (MQuant test peroxide) to check the presence of H₂O₂.

2.5. Scalability experiments

The scalability of the present synthesis approach was estimated by simply increasing the substrate (*p*-toluidine) concentration from 0.05 mmol to 5 mmol and 10 mmol. The 5 mmol reaction was carried out at standard reaction conditions under irradiation of one 370 nm Kessil LED (44 W), while to carry out the reaction with 10 mmol substrate, two 370 nm Kessil LEDs (44 W) were utilized.

2.6. Radical trapping experiment

Briefly, 0.05 mmol *p*-toluidine and 2 equiv. K₃PO₄ was added to a 1:1 mixture of methanol and water. The solution was then irradiated with a 370 nm Kessil LED and 1 equiv. 2,6-Di-*tert*-butyl-4-methylphenol (BHT) was added to the above reaction mixture to trap the radicals. The above mixture was irradiated for 90 min before conducting the HR-MS and GC-MS analysis.

2.7. Electron paramagnetic resonance experiment

Electron paramagnetic resonance (EPR) spectra were recorded on a JEOL EPR spectrometer (JES-FA200) to confirm the presence of reactive oxygen species (ROS). Initially, to check the presence of singlet oxygen in the aqueous solution, 5 ml Milli-Q was taken in a 15 ml glass vial and irradiated with a 370 nm Kessil LED. Subsequently, 5 equiv. TEMP was added to the above solution as a singlet oxygen scavenger. Next, 500 µL aliquot of this solution was collected after 30 min and transferred in a quartz tube for EPR analysis at 298 K.

Similarly, to check the presence of superoxide radicals in the reaction mixture, 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was used as a radical scavenger. Briefly, 0.05 mmol *p*-toluidine and 2 equiv. K₃PO₄ was added to a 1:1 mixture of methanol and water. The solution was then irradiated with a 370 nm Kessil LED and 5 equiv. DMPO was added to the reaction mixture to trap the superoxide radical. Subsequently, 500 µL aliquot of this solution was collected after 30 min and transferred in a quartz tube for EPR analysis at 298 K.

2.8. Calculation of internal quantum yield for oxidative coupling of arylamines to azoaromatics

The internal quantum yield (ϕ_{int}) was calculated as per the formula given below,¹

$$\phi_{int} = \frac{\text{moles of product formed}}{\text{moles of photons absorbed}} \times 100$$

The moles of the product formed were estimated using the conversion yield of *p*-toluidine to its corresponding azo compound while the moles of photons absorbed were estimated by multiplying photon flux (q_p) with the total irradiation time (t). The photon flux was calculated using the following equation,

$$\text{moles of photons absorbed} = q_p \times t \text{ (s)} = \frac{P_{\text{abs}} \times \lambda \text{ (m)}}{hc \times (6.023 \times 10^{23})} \times t \text{ (s)}$$

Where P_{abs} ($\text{J}\cdot\text{s}^{-1}$) is the power of light absorbed by the reaction mixture, λ is the wavelength (m) of the LED light source, h is the Planck's constant ($\text{J}\cdot\text{s}$), and c is the speed of light ($\text{m}\cdot\text{s}^{-1}$).

The P_{abs} was calculated indirectly from the difference between incident light (P_0) and transmitted light (P_f) using the following Beers's law,

$$A_{370} \times b = \log \frac{P_0}{P_f}$$

$$P_0 - P_f = P_{\text{abs}}$$

Where ' b ' is the path length of the optical cell.

The calculated quantum yield is ~ 0.15 for the conversion of *p*-toluidine to its corresponding azo compound under standard reaction conditions.

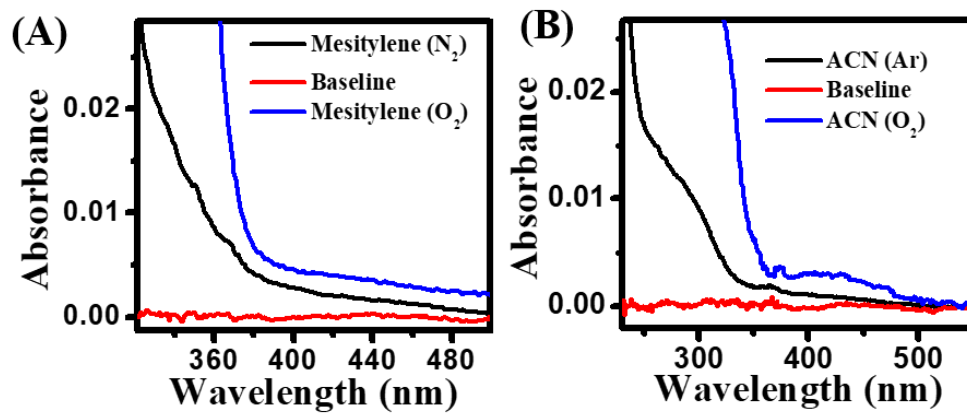


Figure S1. UV-vis spectra of (A) mesitylene and (B) acetonitrile (ACN) under N_2 and O_2 atmospheres.

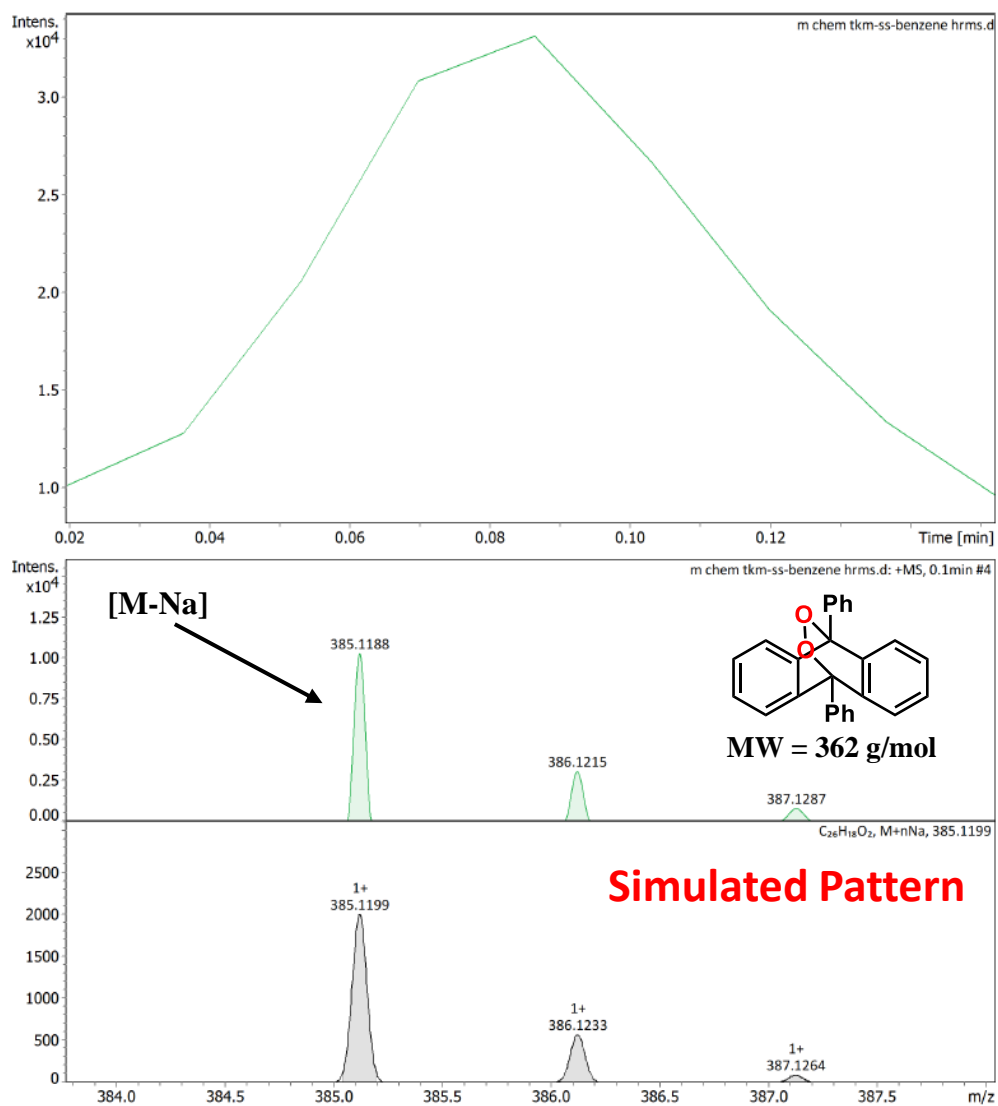


Figure S2. HR-MS spectrum of 9,10-diphenyl-9,10-epidioxyanthracene.

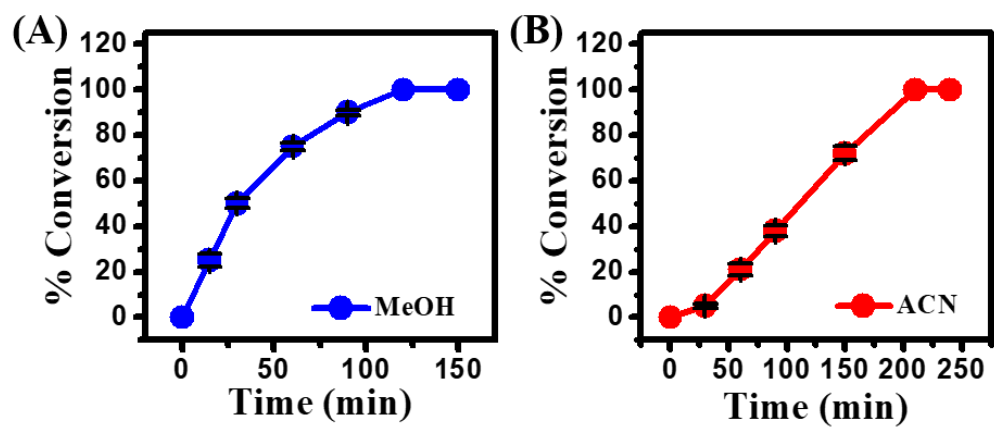


Figure S3. Time-dependent conversion yields for the oxidative coupling of 0.05 mmol *p*-toluidine in the presence of 2 equiv. K_3PO_4 in (A) methanol and (B) acetonitrile under the irradiation of 370 nm LED.

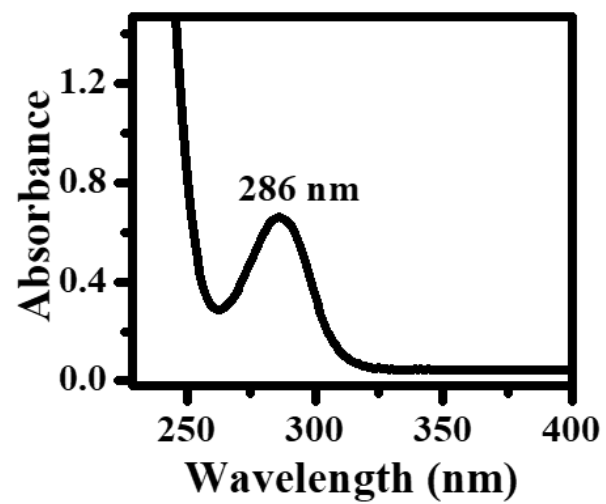
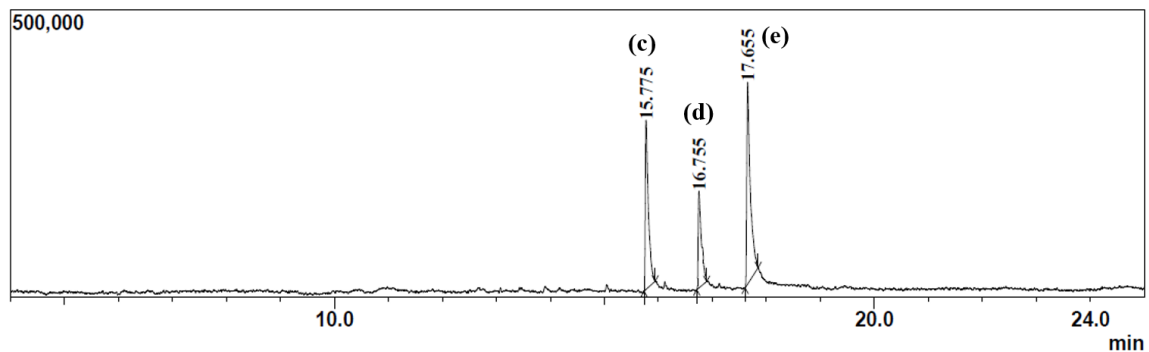
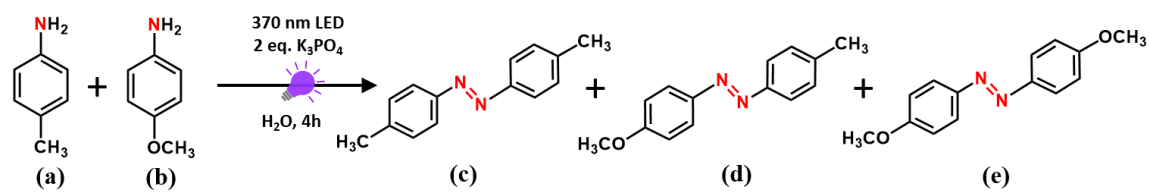


Figure S4. UV-vis spectrum of *p*-toluidine in water.



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Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	15.775	1107777	33.39	288571	36.15	3.84	Diazene, 1,2-bis(4-methylphenyl)-
2	16.755	671009	20.23	164904	20.66	4.07	Diazene, 1-(4-methoxyphenyl)-2-(4-methylphenyl)-
3	17.655	1538430	46.38	344803	43.19	4.46	Diazene, 1,2-bis(4-methoxyphenyl)-
		3317216	100.00	798278	100.00		

Figure S5. GC-MS spectrum for the oxidative coupling of *p*-toluidine and *p*-anisidine.

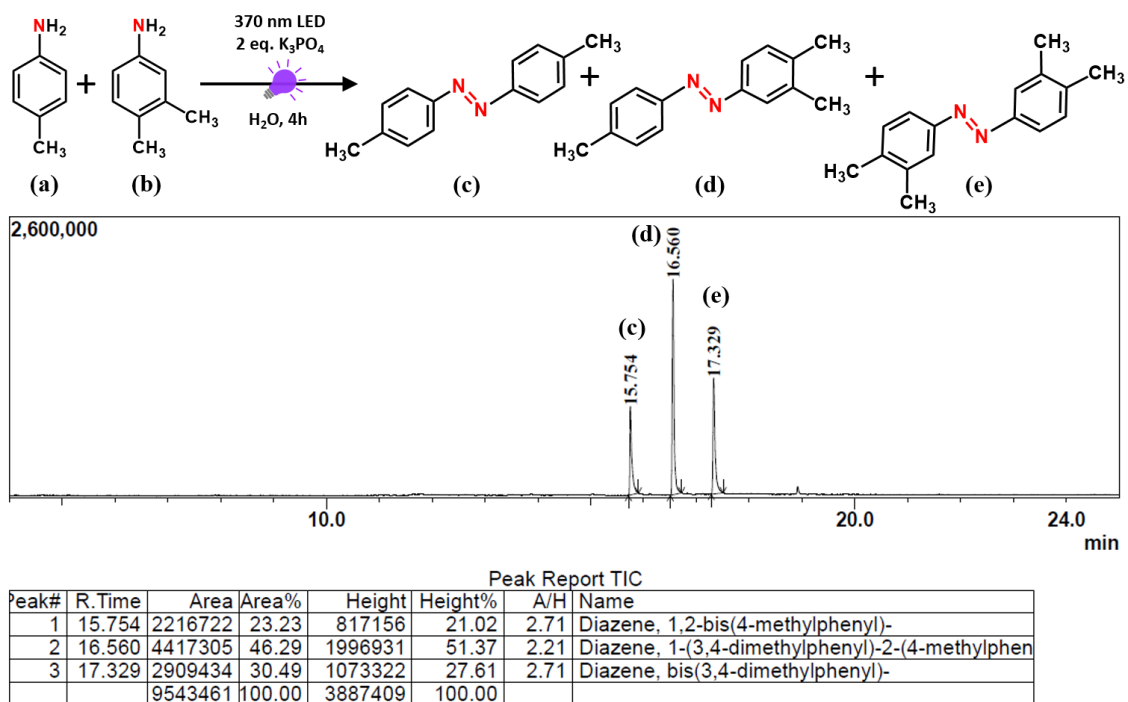
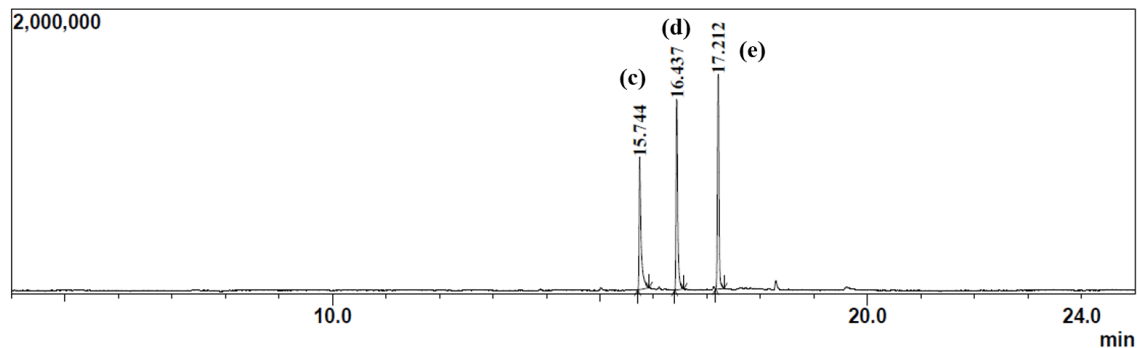
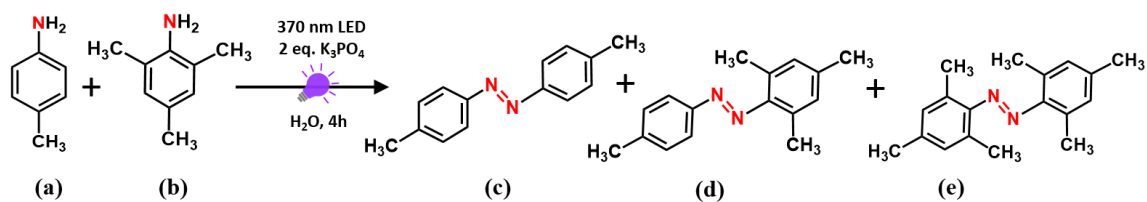


Figure S6. GC-MS spectrum for the oxidative coupling of *p*-toluidine and 3,4-dimethylaniline.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	15.744	2499848	30.56	932769	24.62	2.68	Diazene, 1,2-bis(4-methylphenyl)-
2	16.437	2779268	33.97	1343184	35.45	2.07	Diazene, 1-(4-methylphenyl)-2-(2,4,6-trimethylphenyl)-
3	17.212	2901436	35.47	1512945	39.93	1.92	Diazene, 1,2-bis(4-2,4,6-trimethylphenyl)-
		8180552	100.00	3788898	100.00		

Figure S7. GC-MS spectrum for the oxidative coupling of *p*-toluidine and 2,4,6-trimethylaniline.

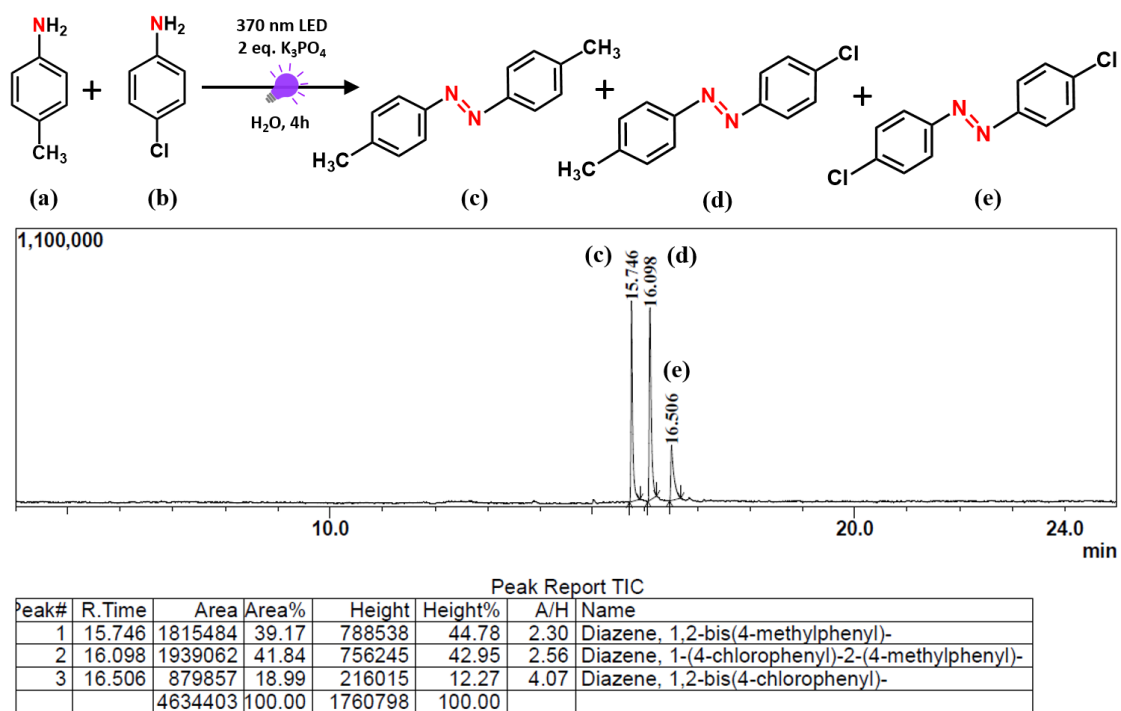
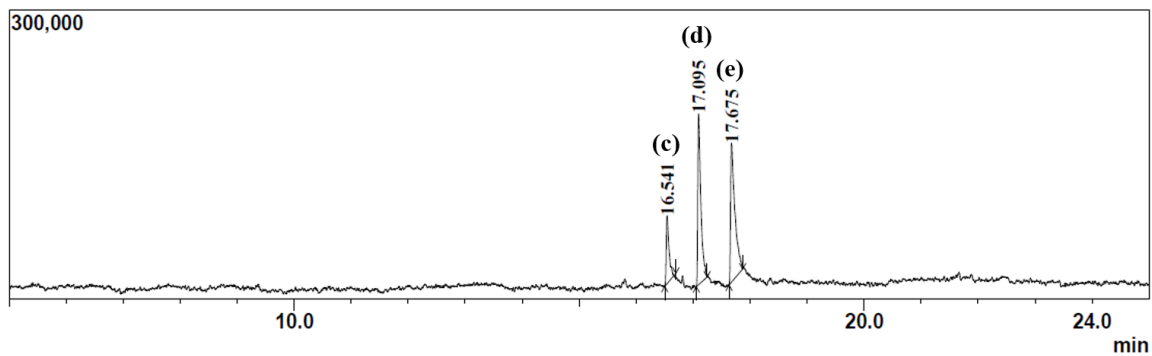
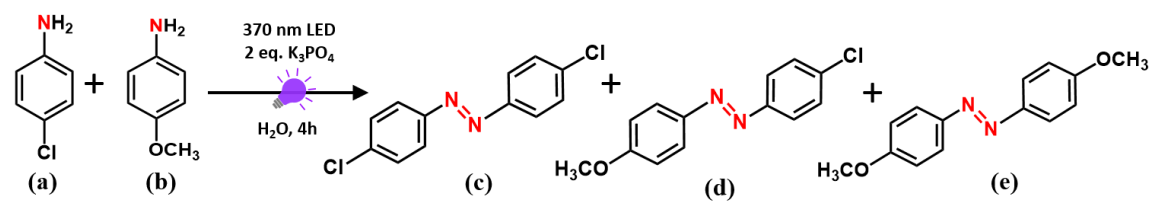


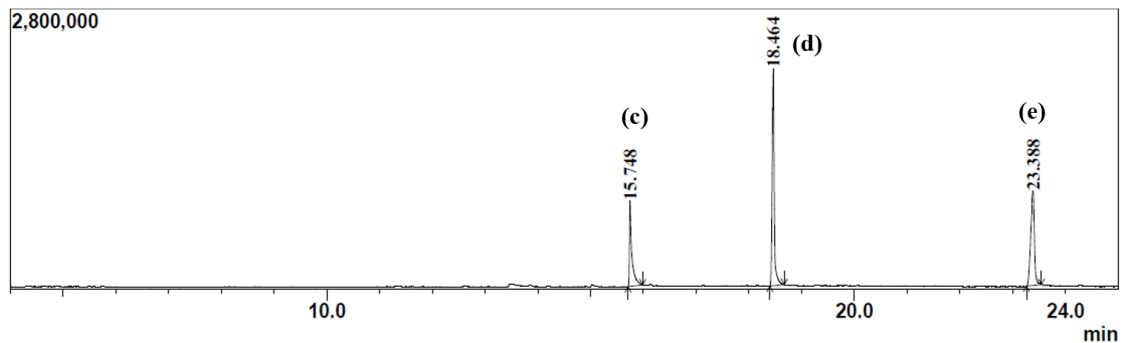
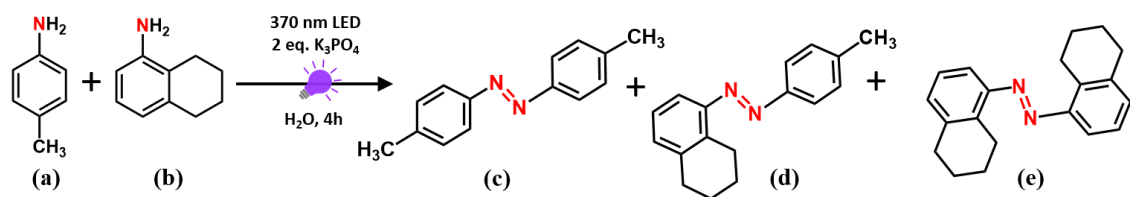
Figure S8. GC-MS spectrum for the oxidative coupling of *p*-toluidine and *p*-chloroaniline.



Peak Report TIC

Peak#	R. Time	Area	Area%	Height	Height%	A/H	Name
1	16.541	226893	14.07	68163	17.97	3.33	Diazenes, 1,2-bis(4-chlorophenyl)-
2	17.095	644465	39.97	171457	45.21	3.76	Diazenes, 1-(4-chlorophenyl)-2-(4-methoxyphenyl)-
3	17.675	740942	45.96	139622	36.82	5.31	Diazenes, 1,2-bis(4-methoxyphenyl)-
		1612300	100.00	379242	100.00		

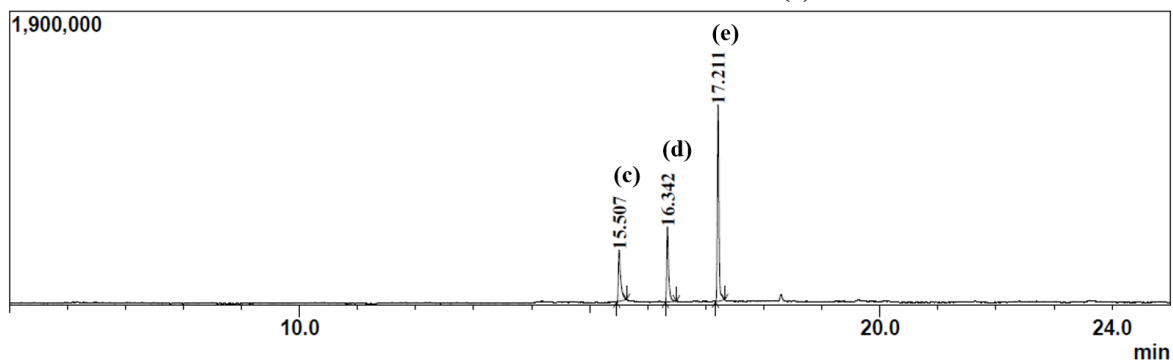
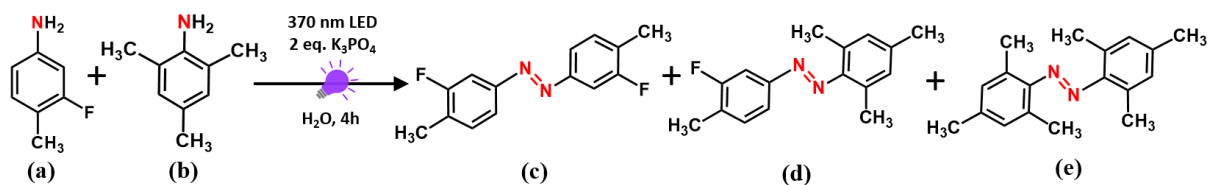
Figure S9. GC-MS spectrum for the oxidative coupling of *p*-chloroaniline and *p*-anisidine.



Peak Report TIC

Peak#	R. Time	Area	Area%	Height	Height%	A/H	Name
1	15.748	2808529	20.56	860170	21.55	3.27	Diazeno, 1,2-bis(4-methylphenyl)-
2	18.464	6241883	45.69	2179020	54.60	2.86	Diazeno, 1-(4-methylphenyl)-2-(5,6,7,8-tetrahydro-
3	23.388	4609915	33.75	951797	23.85	4.84	Diazeno, 1,2-bis(5,6,7,8-tetrahydronaphthalen-1-yl)-
		3660327	100.00	3990987	100.00		

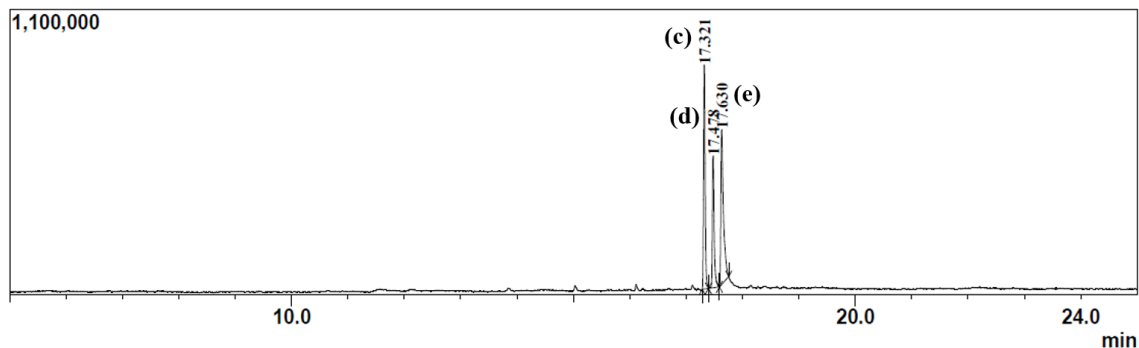
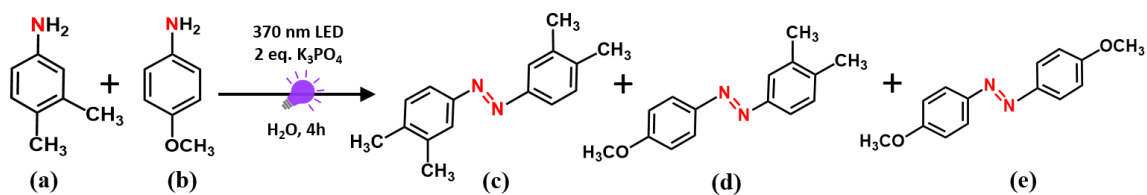
Figure S10. GC-MS spectrum for the oxidative coupling of *p*-toluidine and 5,6,7,8-tetrahydronaphthalene-1-amine.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	15.507	913616	20.64	330522	15.82	2.76	Diazeno, 1,2-bis(3-fluoro-4-methylphenyl)-
2	16.342	1084686	24.51	486321	23.28	2.23	Diazeno, 1-(3-fluoro-4-methylphenyl)-2-(2,4,6-trimethylphenyl)-
3	17.211	2427542	54.85	1272270	60.90	1.91	Diazeno, 1,2-bis(2,4,6-trimethylphenyl)-
		4425844	100.00	2089113	100.00		

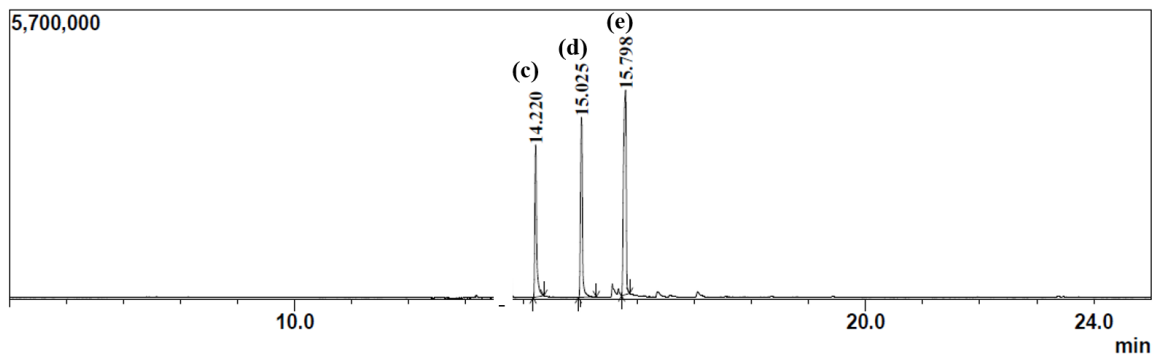
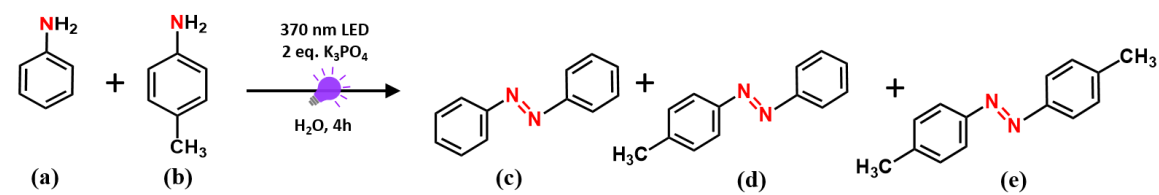
Figure S11. GC-MS spectrum for the oxidative coupling of 3-fluoro-4-methylaniline and 2,4,6-trimethylaniline.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	17.321	1677180	35.87	861313	43.90	1.95	Diazeno, 1,2-bis(3,4-dimethylphenyl)-
2	17.478	1104074	23.61	505968	25.79	2.18	Diazeno, 1-(3,4-dimethylphenyl)-2-(4-methoxyphenyl)-
3	17.630	1894960	40.52	594735	30.31	3.19	Diazeno, 1,2-bis(4-methoxyphenyl)-
		4676214	100.00	1962016	100.00		

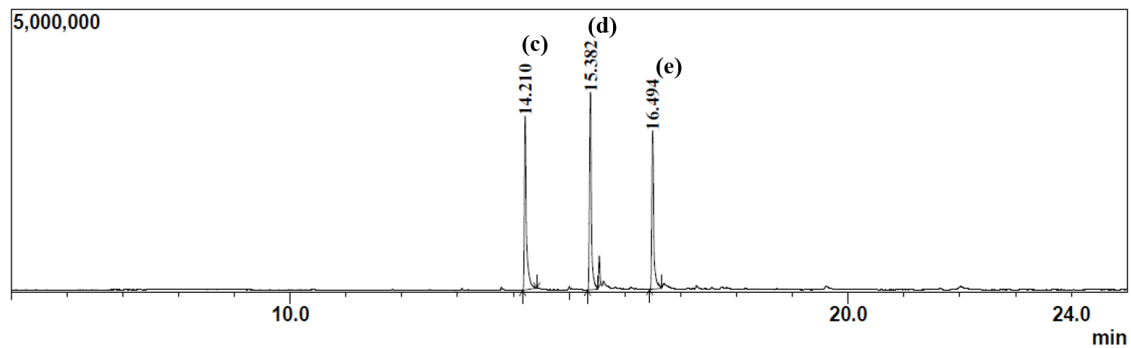
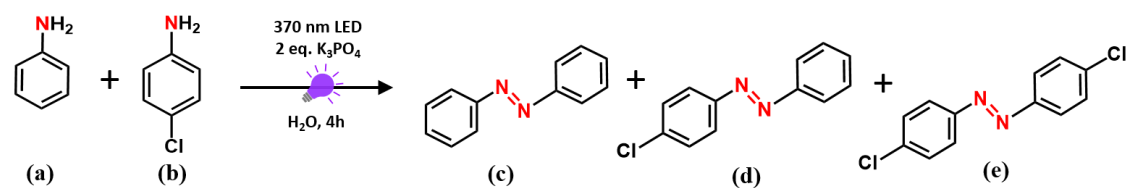
Figure S12. GC-MS spectrum for the oxidative coupling of 3,4-dimethylaniline and *p*-anisidine.



Peak Report TIC

Peak#	R. Time	Area	Area%	Height	Height%	A/H	Name
1	14.220	6723953	23.86	3009729	28.38	2.23	Azobenzene
2	15.025	8325630	29.54	3557350	33.55	2.34	Diazene, 1-(4-methylphenyl)-2-(phenyl)-
3	15.798	3135427	46.60	4037559	38.07	3.25	Diazene, 1,2-bis(4-methylphenyl)-
		8185010	100.00	10604638	100.00		

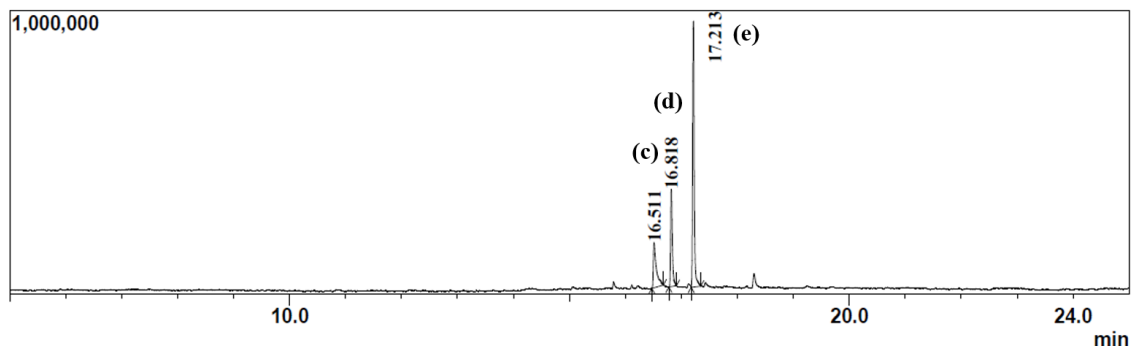
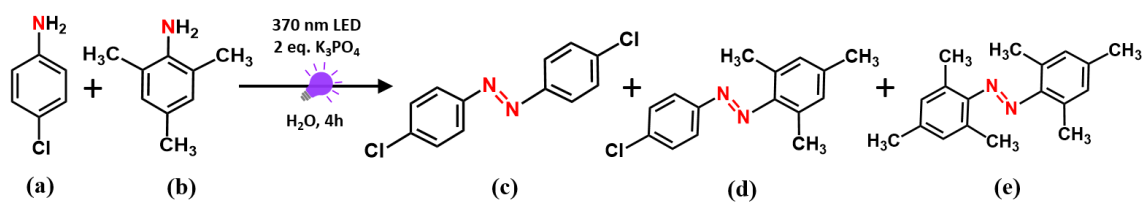
Figure S13. GC-MS spectrum for the oxidative coupling of aniline and *p*-toluidine.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	14.210	7795987	33.83	3083051	32.77	2.53	Azobenzene
2	15.382	8432944	36.60	3508546	37.30	2.40	Diazene, 1-(4-chlorophenyl)-2-(phenyl)-
3	16.494	6814732	29.57	2815920	29.93	2.42	Diazene, 1,2-bis(4-chlorophenyl)-
		3043663	100.00	9407517	100.00		

Figure S14. GC-MS spectrum for the oxidative coupling of aniline and *p*-chloroaniline.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	16.511	583356	18.70	158479	11.05	3.68	Diazene, 1,2-bis(4-chlorophenyl)-
2	16.818	718306	23.02	341830	23.84	2.10	Diazene, 1-(4-chlorophenyl)-2-(2,4,6-trimethylphe
3	17.213	1818548	58.28	933757	65.11	1.95	Diazene, 1,2-bis(2,4,6-trimethylphenyl)-
		3120210	100.00	1434066	100.00		

Figure S15. GC-MS spectrum for the oxidative coupling of *p*-chloroaniline and 2,4,6-trimethylaniline.

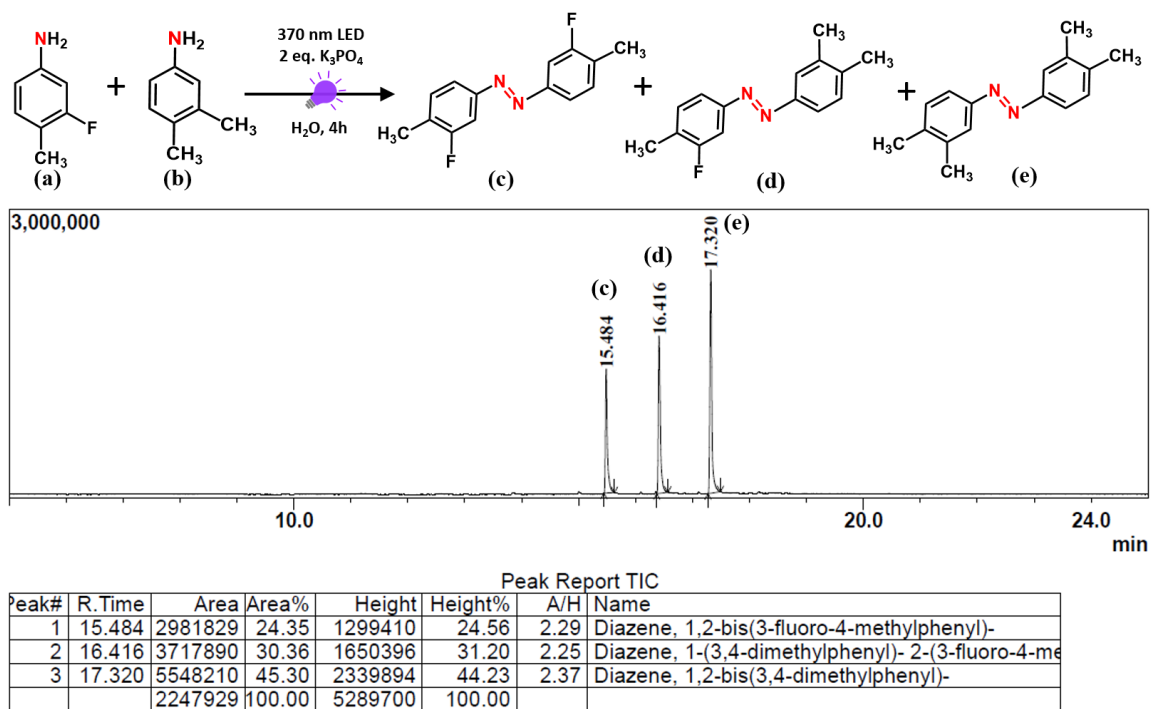
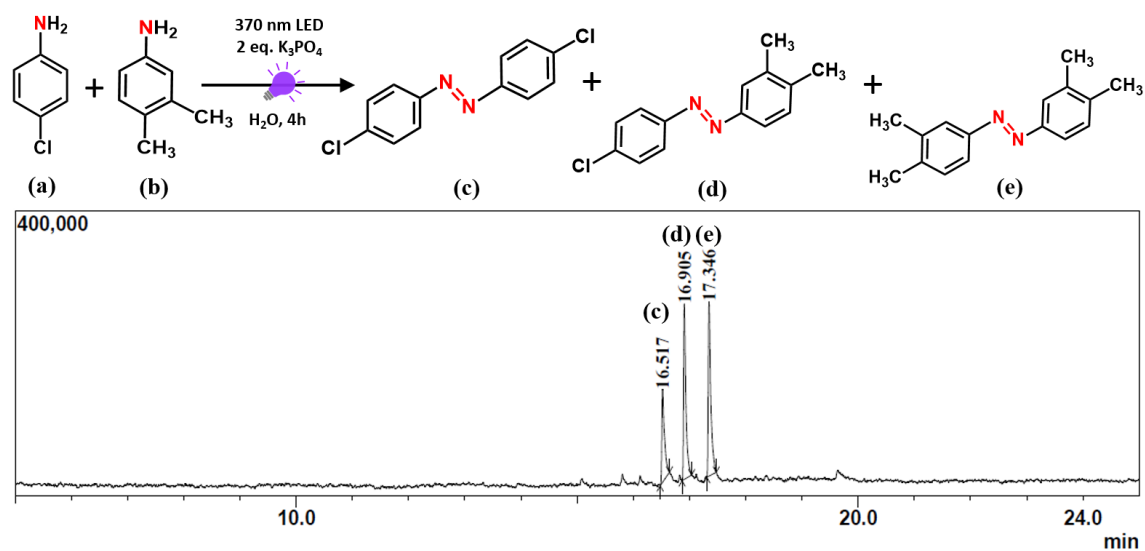


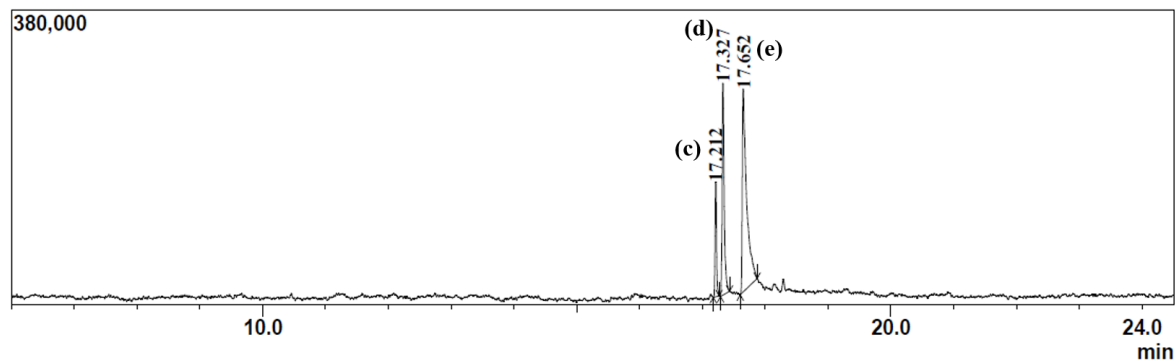
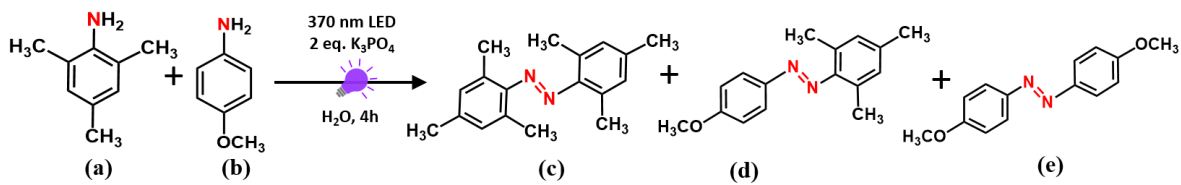
Figure S16. GC-MS spectrum for the oxidative coupling of 3-fluoro-4-methylaniline and 3,4-dimethylaniline.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	16.517	419312	22.46	128891	20.98	3.25	Diazenes, 1,2-bis(4-chlorophenyl)-
2	16.905	695156	37.24	243488	39.63	2.85	Diazenes, 1-(4-chlorophenyl)-2-(3,4-dimethylphenyl)-
3	17.346	752375	40.30	242034	39.39	3.11	Diazenes, 1,2-bis(3,4-dimethylphenyl)-
		1866843	100.00	614413	100.00		

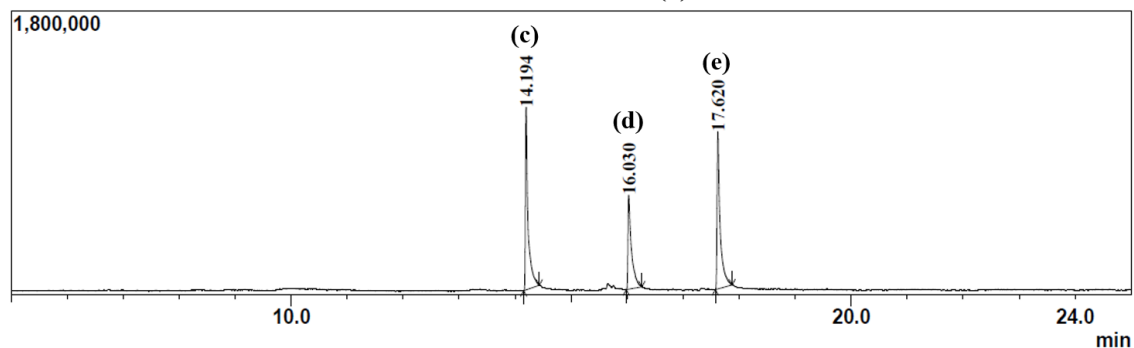
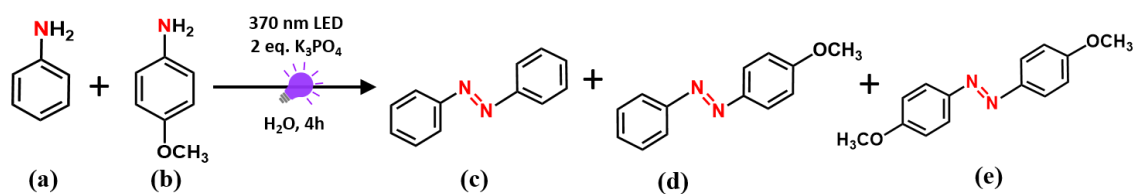
Figure S17. GC-MS spectrum for the oxidative coupling of *p*-chloroaniline and 3,4-dimethylaniline.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	17.212	254829	12.06	144339	21.68	1.77	Diazene, 1,2-bis(2,4,6-trimethylphenyl)-
2	17.327	625702	29.60	266421	40.01	2.35	Diazene, 1-(4-methoxyphenyl)-2-(2,4,6-trimethylp
3	17.652	1232971	58.34	255109	38.31	4.83	Diazene, 1,2-bis(4-methoxyphenyl)-
		2113502	100.00	665869	100.00		

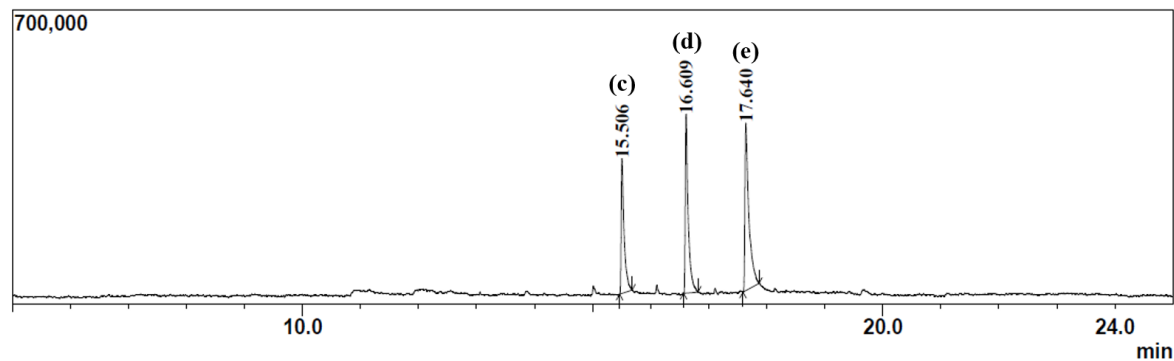
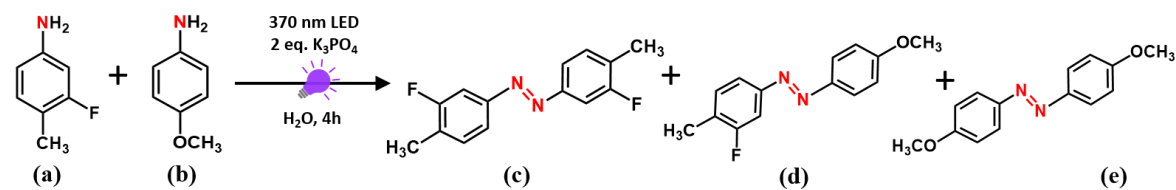
Figure S18. GC-MS spectrum for the oxidative coupling of 2,4,6-trimethylaniline and *p*-anisidine.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	14.194	3804310	37.32	1163312	42.12	3.27	Azobenzene
2	16.030	2574878	25.26	597665	21.64	4.31	Diazene, 1-(4-methoxyphenyl)-2-(phenyl)-
3	17.620	3814836	37.42	1001171	36.25	3.81	Diazene, bis(4-methoxyphenyl)-
		0194024	100.00	2762148	100.00		

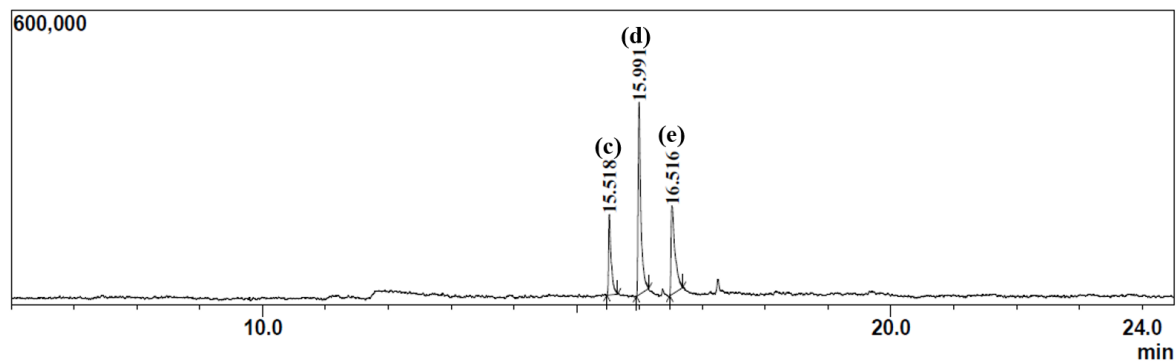
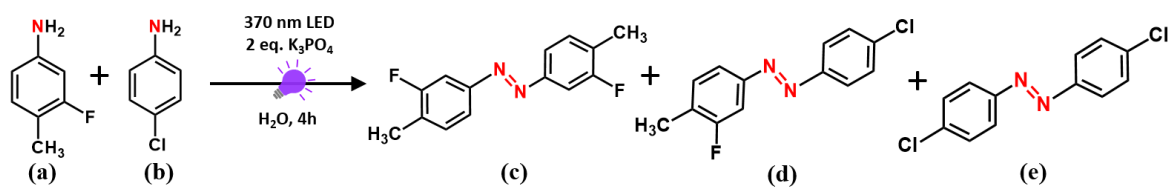
Figure S19. GC-MS spectrum for the oxidative coupling of aniline and *p*-anisidine.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	15.506	1119850	25.00	321100	28.03	3.49	Diazeno, 1,2-bis(3-fluoro-4-methylphenyl)-
2	16.609	1480757	33.05	426368	37.22	3.47	Diazeno, 1-(4-methoxyphenyl)-2-(3-fluoro-4-meth
3	17.640	1879653	41.95	397974	34.74	4.72	Diazeno, 1,2-bis(4-methoxyphenyl)-
		4480260	100.00	1145442	100.00		

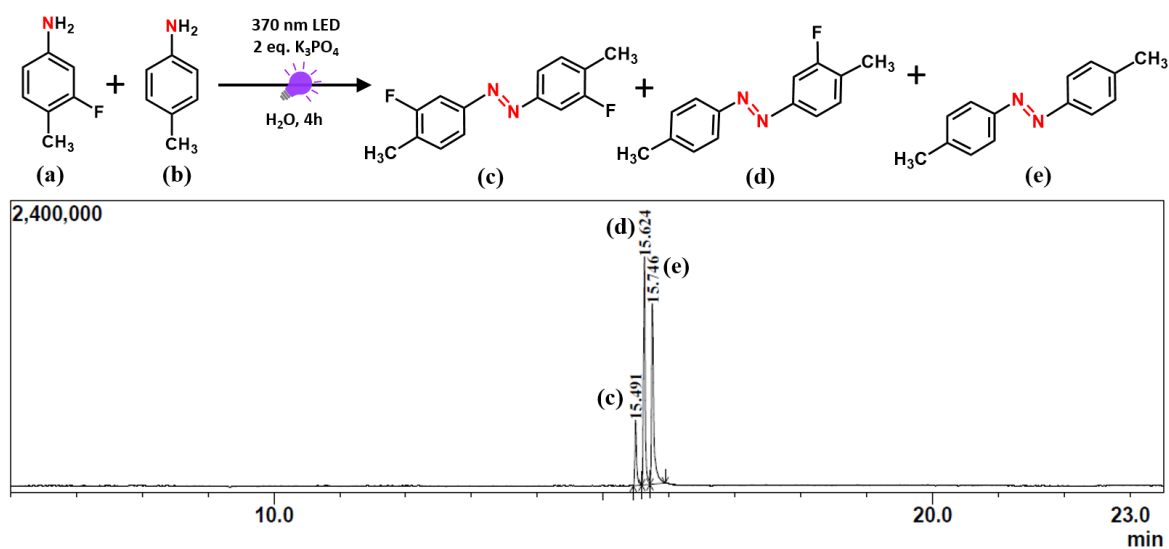
Figure S20. GC-MS spectrum for the oxidative coupling of 3-fluoro-4-methylaniline and *p*-anisidine.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	15.518	468070	19.44	162423	22.22	2.88	Diazene, 1,2-bis(3-fluoro-4-methylphenyl)-
2	15.991	1164998	48.38	389234	53.25	2.99	Diazene, 1-(4-chlorophenyl)-2-(3-fluoro-4-methylphenyl)-
3	16.516	775193	32.19	179324	24.53	4.32	Diazene, 1,2-bis(4-chlorophenyl)-
		2408261	100.00	730981	100.00		

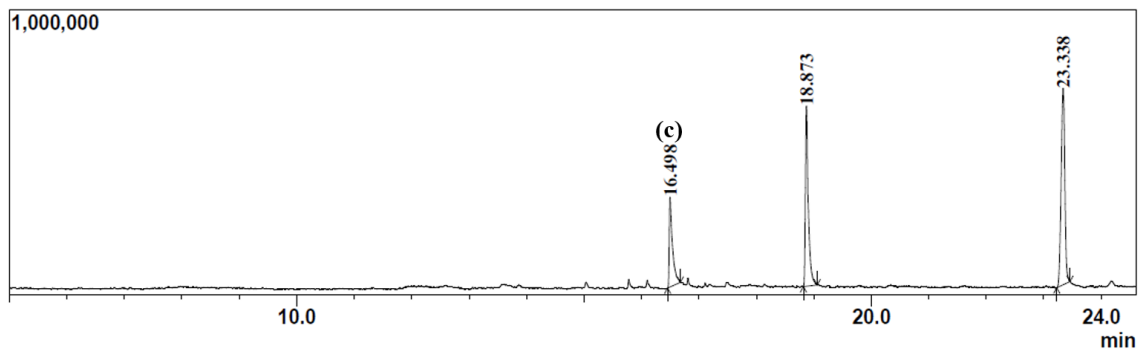
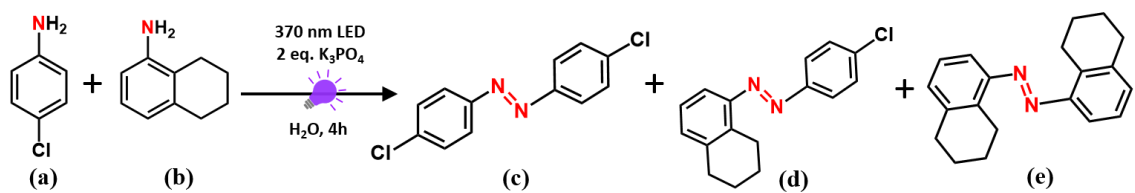
Figure S21. GC-MS spectrum for the oxidative coupling of 3-fluoro-4-methylaniline and *p*-chloroaniline.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	15.491	994175	12.43	547839	13.81	1.81	Diazenes, 1,2-bis(3-fluoro-4-methylphenyl)-
2	15.624	3482851	43.55	1907617	48.09	1.83	Diazenes, 1-(3-fluoro-4-methylphenyl)-2-(4-methylphenyl)-
3	15.746	3521011	44.02	1511037	38.10	2.33	Diazenes, 1,2-bis(4-methylphenyl)-
		7998037	100.00	3966493	100.00		

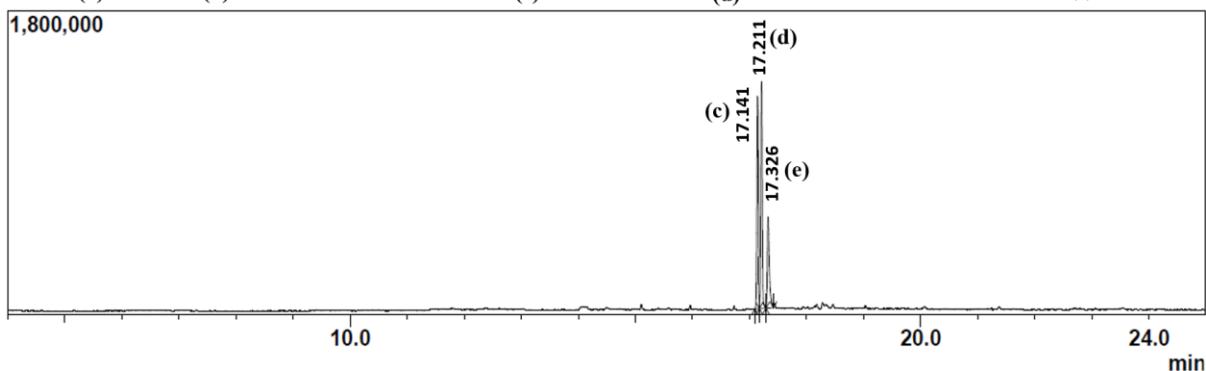
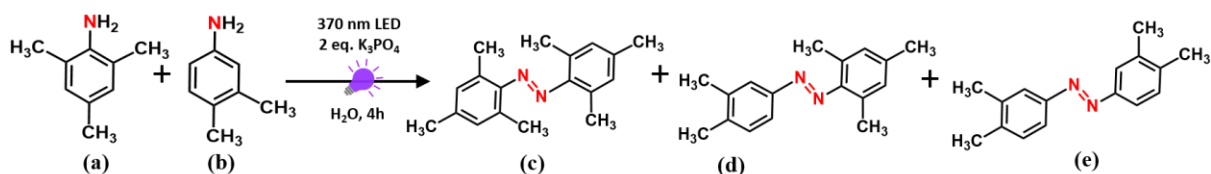
Figure S22. GC-MS spectrum for the oxidative coupling of 3-fluoro-4-methylaniline and *p*-toluidine.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	16.498	1248440	18.90	316913	19.23	3.94	Diazene, 1,2-bis-(4-chlorophenyl)-
2	18.873	2191671	33.19	636747	38.64	3.44	Diazene, 1-(4-chlorophenyl)-2-(5,6,7,8-tetrahydro
3	23.338	3163978	47.91	694279	42.13	4.56	Diazene, 1,2-bis(5,6,7,8-tetrahydronaphthalen-1-
		6604089	100.00	1647939	100.00		

Figure S23. GC-MS spectrum for the oxidative coupling of *p*-chloroaniline and 5,6,7,8-tetrahydronaphthalene-1-amine.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	17.141	2172087	37.39	1268114	40.07	1.71	Diazene, 1-(3,4-dimethylphenyl)-2-(2,4,6-trimethylphenyl)-
2	17.211	2351810	40.48	1353725	42.77	1.74	Diazene, 1,2-bis(2,4,6-trimethylphenyl)-
3	17.326	1285572	22.13	543292	17.16	2.37	Diazene, 1,2-bis(3,4-dimethylphenyl)-
		5809469	100.00	3165131	100.00		

Figure S24. GC-MS spectrum for the oxidative coupling of 2,4,6-trimethylaniline and 3,4-dimethylaniline.

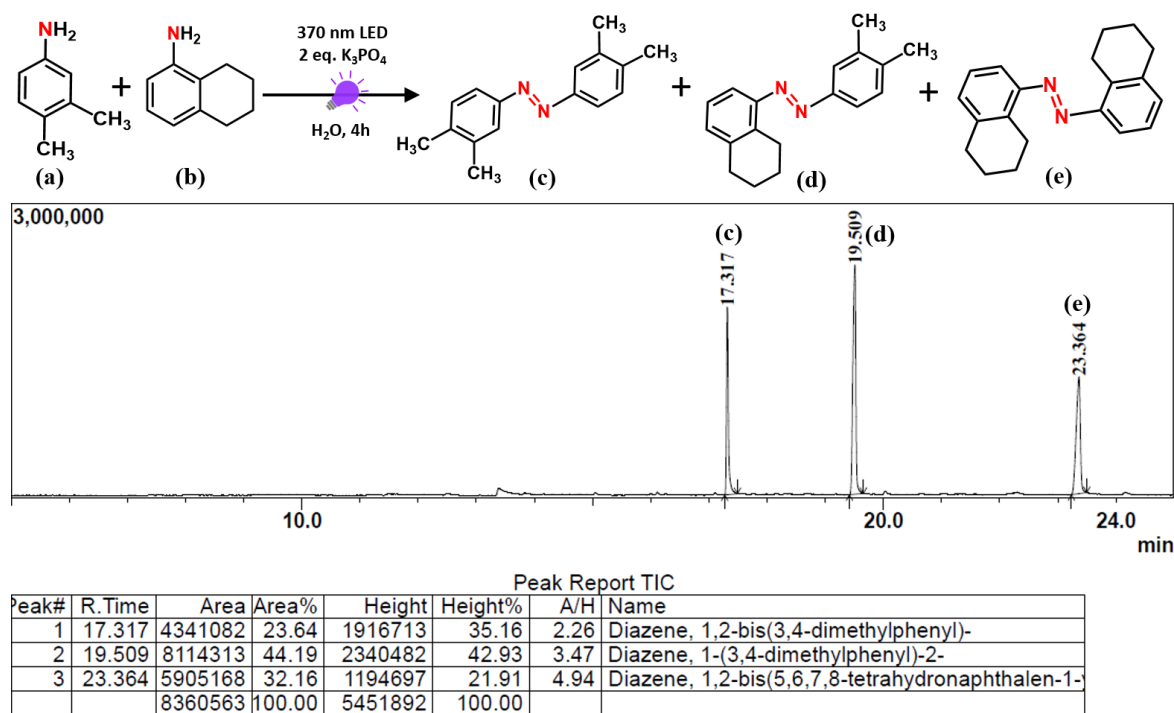


Figure S25. GC-MS spectrum for the oxidative coupling of 3,4-dimethylaniline and 5,6,7,8-tetrahydronaphthalene-1-amine.

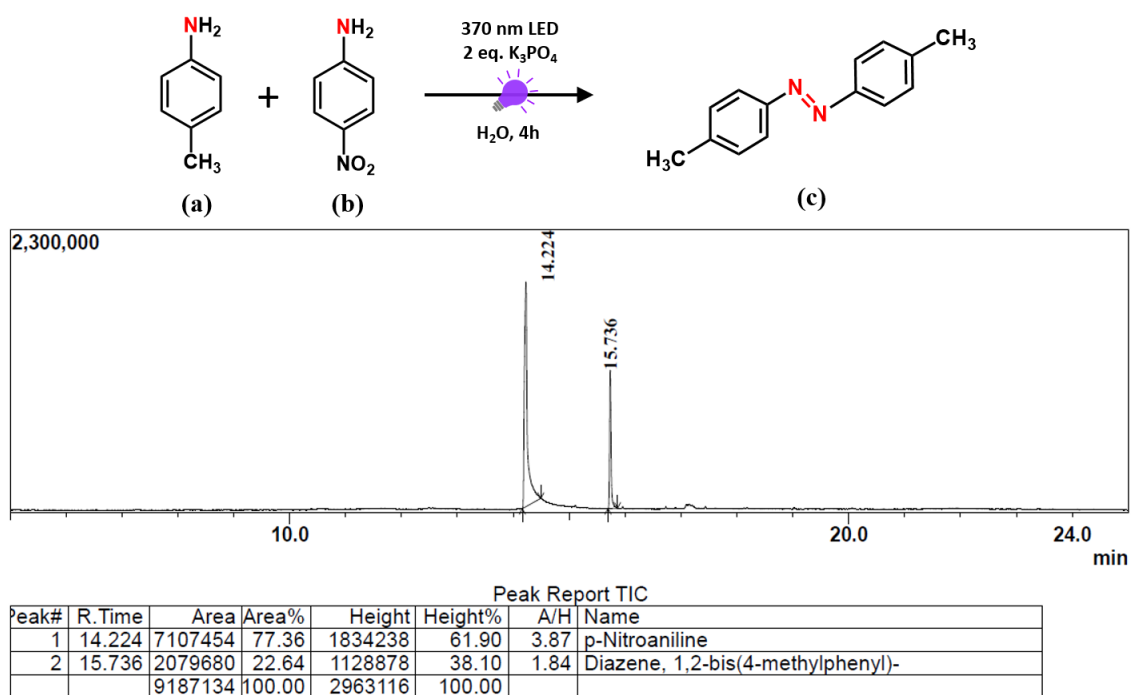
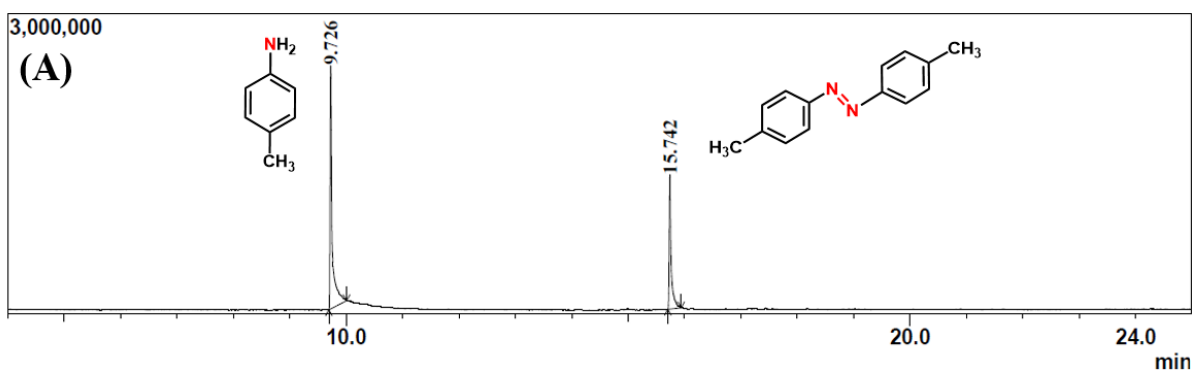
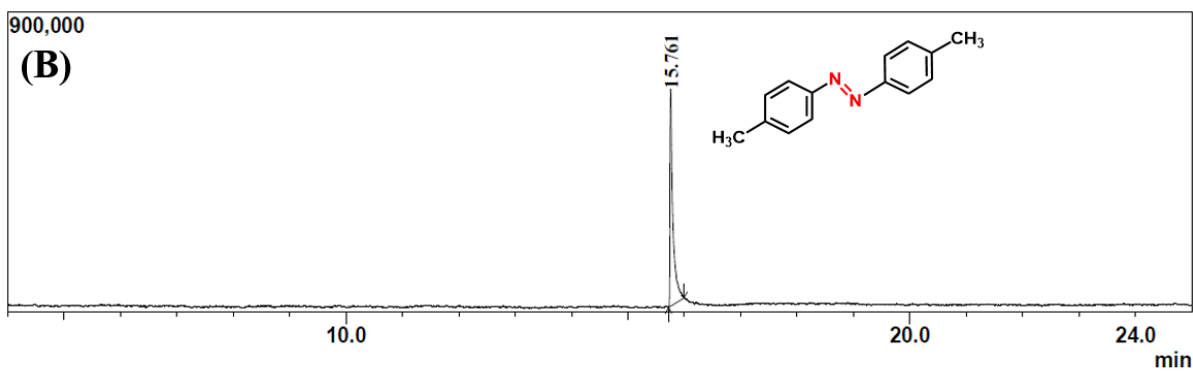


Figure S26. GC-MS spectrum for the oxidative coupling of *p*-toluidine and *p*-nitroaniline.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	9.726	6363907	65.14	2447939	64.35	2.60	p-Toluidine
2	15.742	3405936	34.86	1355952	35.65	2.51	Diazene, 1,2-bis(4-methylphenyl)-
		9769843	100.00	3803891	100.00		



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	15.761	2278179	100.00	648531	100.00	3.51	Diazene, 1,2-bis(4-methylphenyl)-
		2278179	100.00	648531	100.00		

Figure S27. GC-MS spectra of the oxidative coupling of 0.05 mmol *p*-toluidine under standard reaction conditions after (A) 15 and (B) 90 min of irradiation under 370 nm LED.

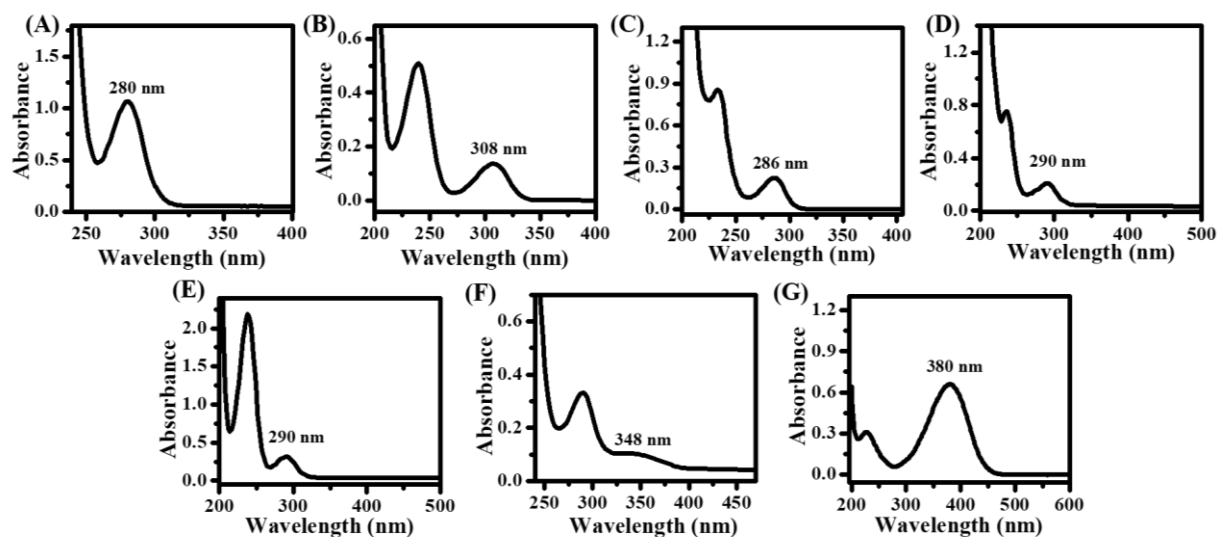


Figure S28. UV-vis spectra of different amine substrates (100 μM) in aqueous medium. (A) Aniline, (B) *p*-anisidine, (C) 2,4,6-trimethylaniline, (D) 3-chloro-4-methylaniline, (E) *p*-chloroaniline, (F) 5,6,7,8-tetrahydronaphthalen-1-amine, and (G) *p*-nitroaniline.

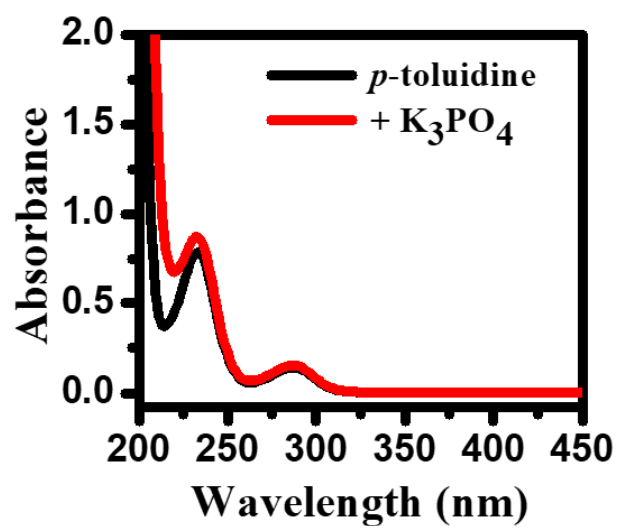


Figure S29. Changes in the UV-vis spectra of *p*-toluidine (100 μ M) in the absence and presence of K₃PO₄ in aqueous medium.

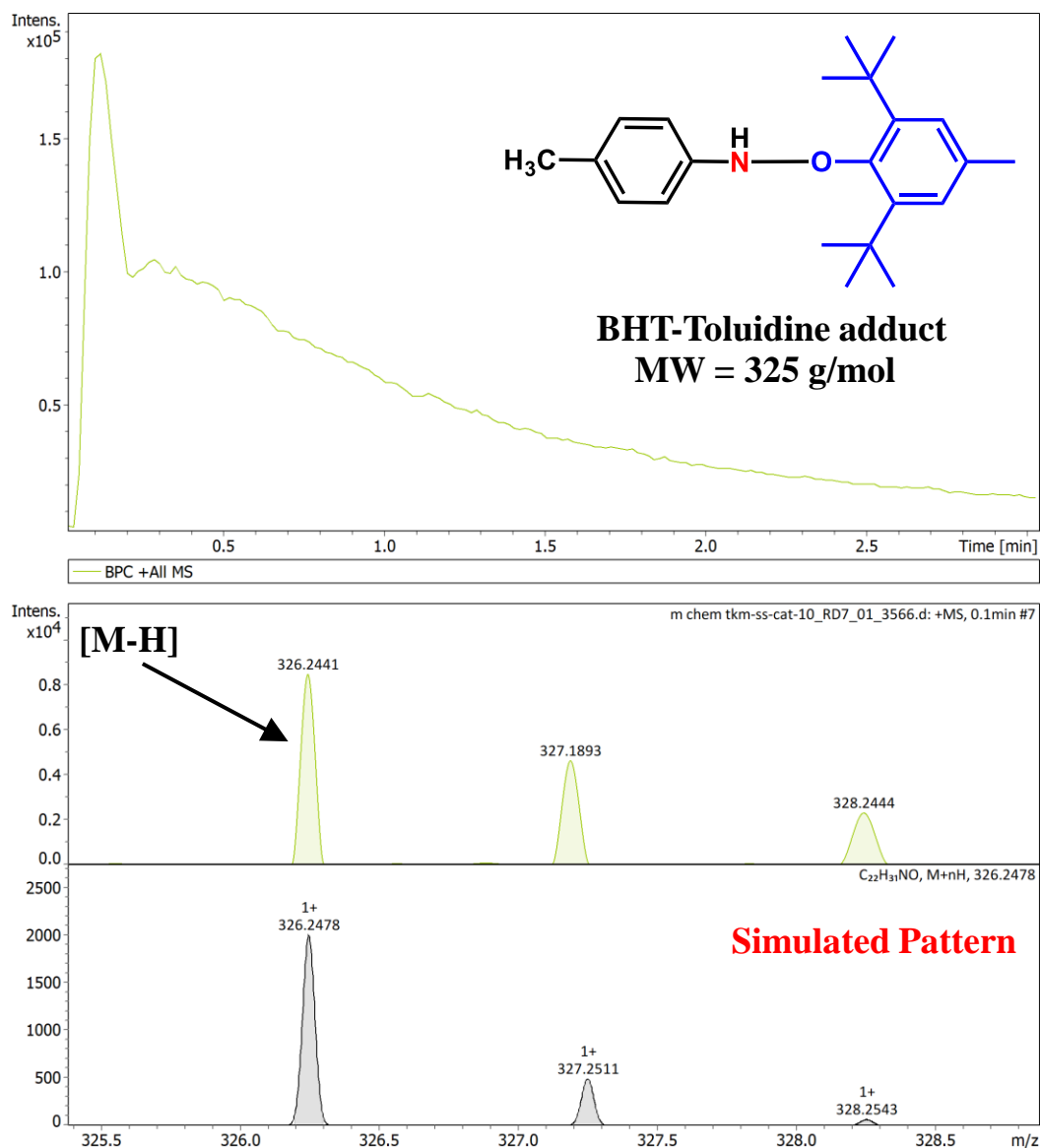


Figure S30. HR-MS spectrum of BHT-*p*-toluidine adduct obtained after radical trap experiment with 1 equiv. BHT under standard reaction conditions in a 1:1 methanol-water mixture.

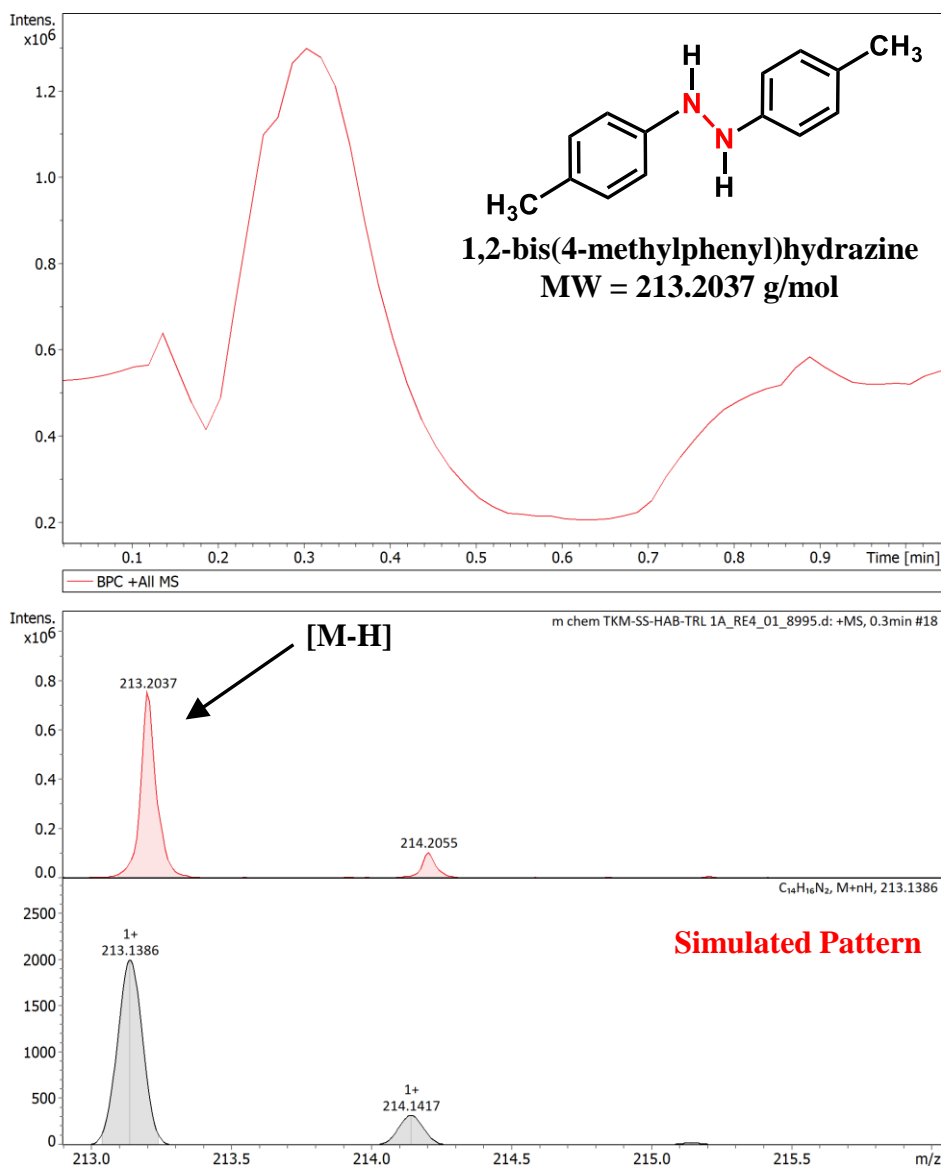
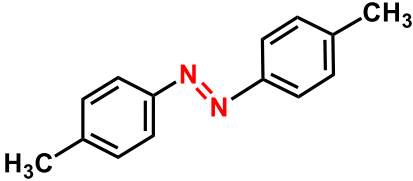
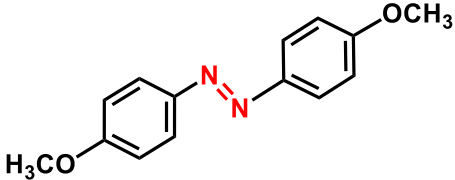
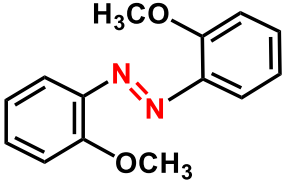
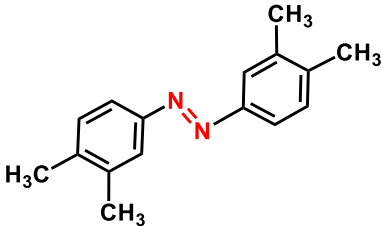
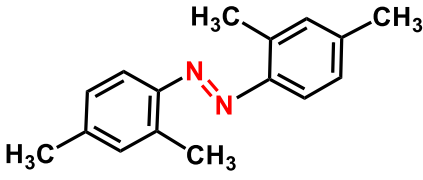
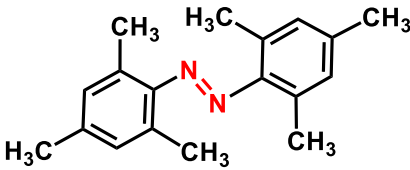
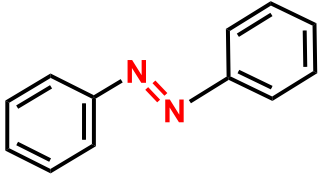
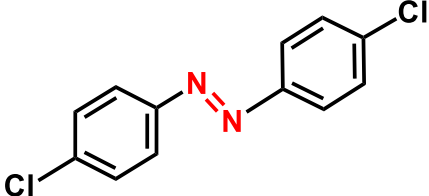
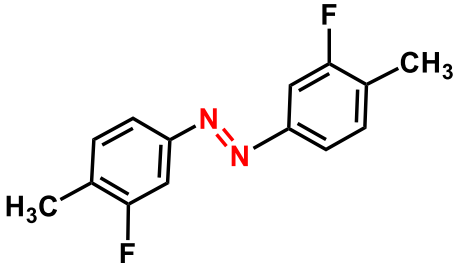
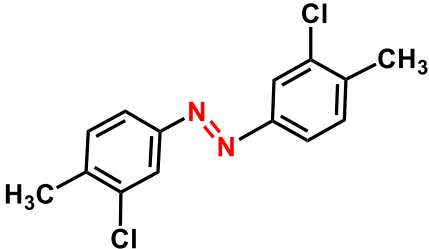
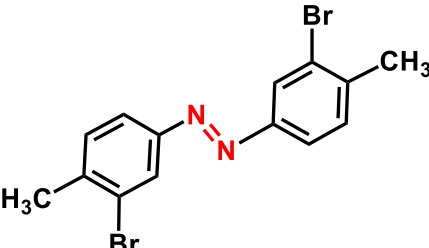
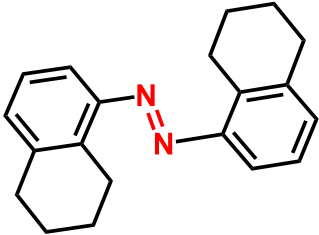


Figure S31. LC-MS spectrum of the hydrazobenzene intermediate obtained during the oxidative coupling of 0.05 mmol *p*-toluidine under standard reaction conditions after 10 min of irradiation under 370 nm LED.

List of ^1H and ^{13}C NMR data	
	<p>The isolated product was yellow solid, 15.7 mg, 98% yield. ^1H NMR (500 MHz, CDCl_3) δ 2.44 (s, 6H), 7.31 (d, J = 8.3 Hz, 4H), 7.82 (d, J = 8.2 Hz, 4H). ^{13}C NMR (126 MHz, CDCl_3) δ 21.62, 76.91, 77.41, 122.86, 129.84, 141.34, 150.96.</p>
	<p>The isolated product was red solid, 16.3 mg, 88% yield. ^1H NMR (500 MHz, CDCl_3) δ 3.88 (s, 6H), 7.00 (d, J = 9.1 Hz, 4H), 7.88 (d, J = 9.0 Hz, 4H). ^{13}C NMR (126 MHz, CDCl_3) δ 55.69, 114.30, 124.47, 147.21, 161.69.</p>
	<p>The isolated product was red solid, 15.7 mg, 85% yield. ^1H NMR (500 MHz, CDCl_3) δ 4.02 (s, 6H), 7.00 (t, J = 7.7 Hz, 2H), 7.08 (d, J = 8.3 Hz, 2H), 7.42 (t, J = 7.8, 7.8 Hz, 2H), 7.63 (d, J = 7.9 Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 56.48, 76.91, 77.41, 112.69, 117.70, 120.96, 132.32, 143.13, 157.00.</p>
	<p>The isolated product was orange solid, 17.8 mg, 98% yield. ^1H NMR (500 MHz, CDCl_3) δ 2.26 (s, 6H), 2.28 (s, 6H), 7.18 (d, J = 7.6 Hz, 2H), 7.58 (d, J = 8.0 Hz, 2H), 7.61 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 19.75, 76.65, 77.16, 120.60, 123.20, 130.10, 137.23, 139.72, 151.10.</p>
	<p>The isolated product was orange solid, 16.5 mg, 91% yield. ^1H NMR (500 MHz, CDCl_3) δ 2.38 (s, 6H), 2.70 (s, 6H), 7.06 (d, J = 7.6 Hz, 2H), 7.14 (s, 2H), 7.55 (d, J = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 17.44, 21.25, 115.59, 126.99, 131.65, 137.71, 140.60, 149.09.</p>
	<p>The isolated product was yellow solid, 17.6 mg, 88% yield. ^1H NMR (500 MHz, CDCl_3) δ 2.34 (s, 6H), 2.42 (s, 12H), 6.97 (s, 4H). ^{13}C NMR (126 MHz, CDCl_3) δ 20.15, 21.17, 130.21, 131.78, 138.48, 149.26.</p>

	<p>The isolated product was orange solid, 13.2 mg, 95% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.46 – 7.51 (m, 2H), 7.51 – 7.56 (m, 4H), 7.94 (d, <i>J</i> = 8.5 Hz, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 123.24, 129.48, 131.38, 153.06.</p>
	<p>The isolated product was yellow solid, 13.3 mg, 70% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.49 (d, <i>J</i> = 8.5 Hz, 4H), 7.86 (d, <i>J</i> = 8.5 Hz, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 76.91, 77.41, 124.34, 129.56, 137.38, 150.94.</p>
	<p>The isolated product was orange solid, 18.4 mg, 98% yield. ¹H NMR (500 MHz, CDCl₃) δ 2.36 (s, 6H), 7.33 (t, <i>J</i> = 7.9 Hz, 2H), 7.56 (d, <i>J</i> = 10.4 Hz, 2H), 7.66 (d, <i>J</i> = 7.7 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 14.98, 107.61, 107.80, 120.64, 131.75, 152.23, 162.75.</p>
	<p>The isolated product was yellow solid, 18.7 mg, 88% yield. ¹H NMR (500 MHz, CDCl₃) δ 2.45 (s, 6H), 7.37 (d, <i>J</i> = 8.0 Hz, 2H), 7.73 (d, <i>J</i> = 8.0 Hz, 2H), 7.90 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 20.36, 76.91, 77.41, 122.39, 122.60, 131.44, 135.34, 139.49, 151.59.</p>
	<p>The isolated product was orange solid, 16.2 mg, 58% yield. ¹H NMR (500 MHz, CDCl₃) δ 2.48 (s, 6H), 7.38 (d, <i>J</i> = 8.0 Hz, 2H), 7.78 (d, <i>J</i> = 7.9 Hz, 2H), 8.09 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 23.18, 76.91, 77.41, 123.06, 125.63, 125.84, 131.27, 141.32, 151.55.</p>
	<p>The isolated product was reddish-orange solid, 16.7 mg, 75% yield. ¹H NMR (500 MHz, CDCl₃) δ 1.82–1.86 (m, 8H), 2.85 (d, <i>J</i> = 17.3 Hz, 8H), 7.19 (d, <i>J</i> = 8.0 Hz, 2H), 7.62 (s, 2H), 7.64 (d, <i>J</i> = 8.2 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 23.19, 29.67, 76.91, 77.41, 120.00, 123.42, 129.86, 138.02, 140.59, 150.96.</p>

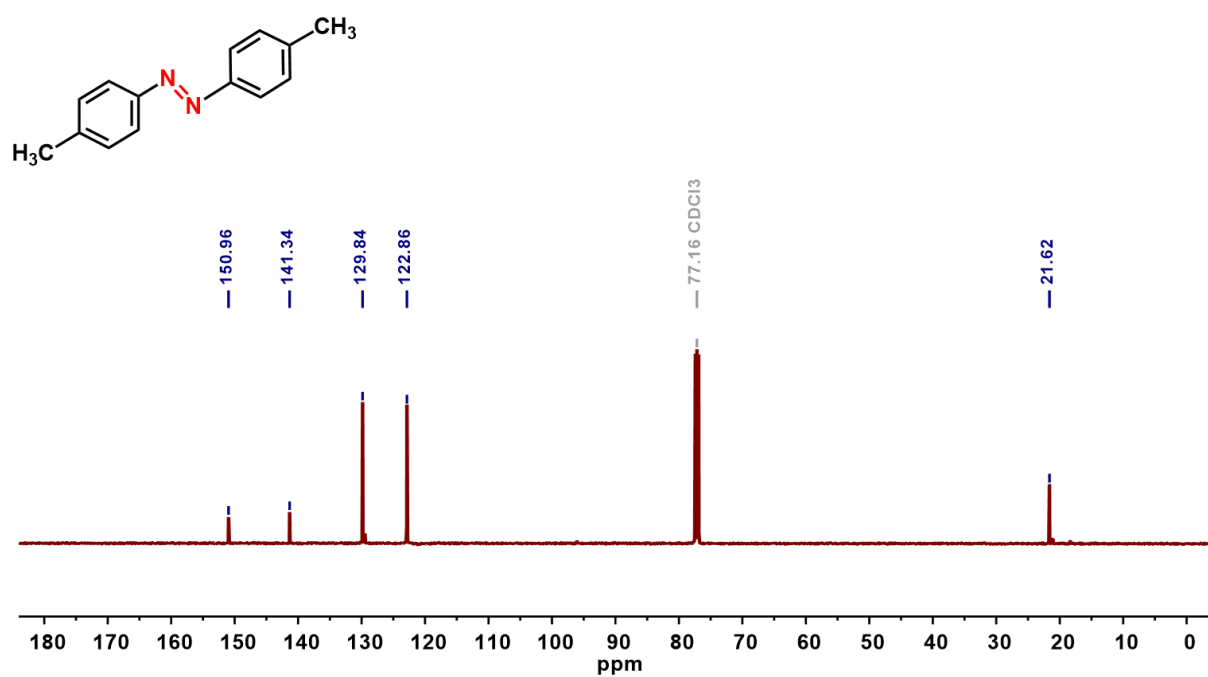
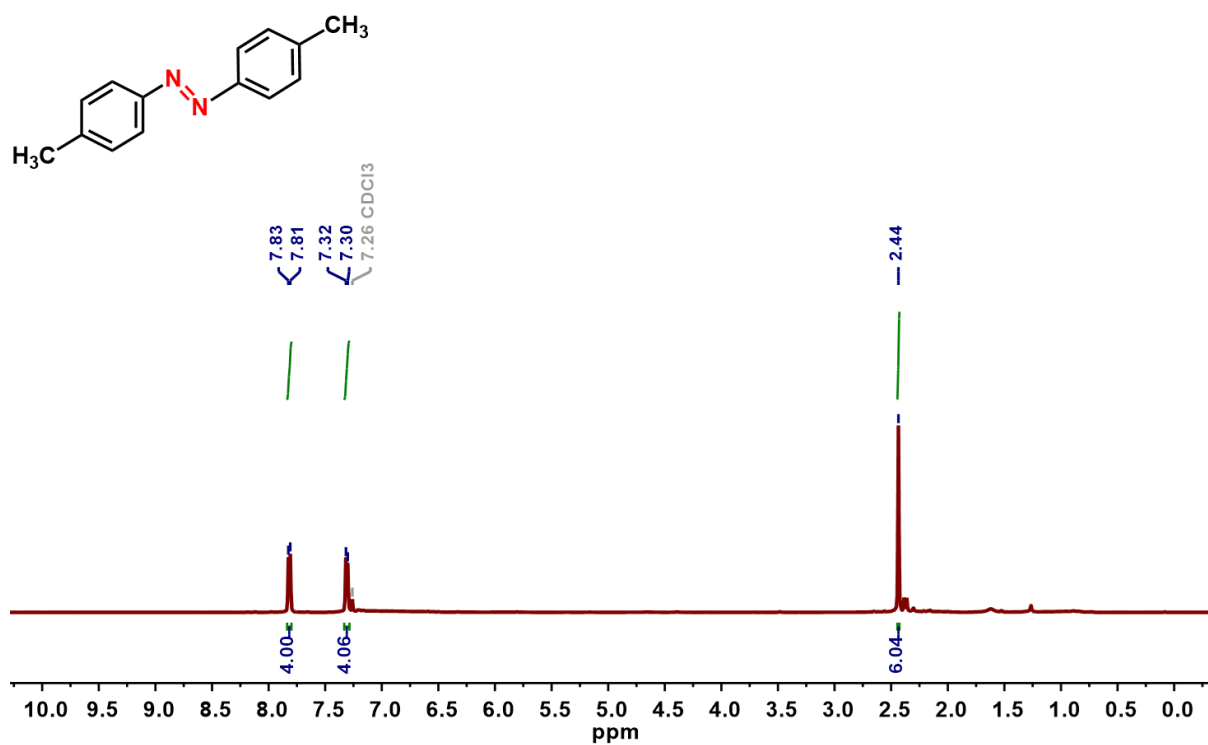


Figure S32. ¹H and ¹³C NMR spectra of 1,2-bis(4-methylphenyl)diazene.

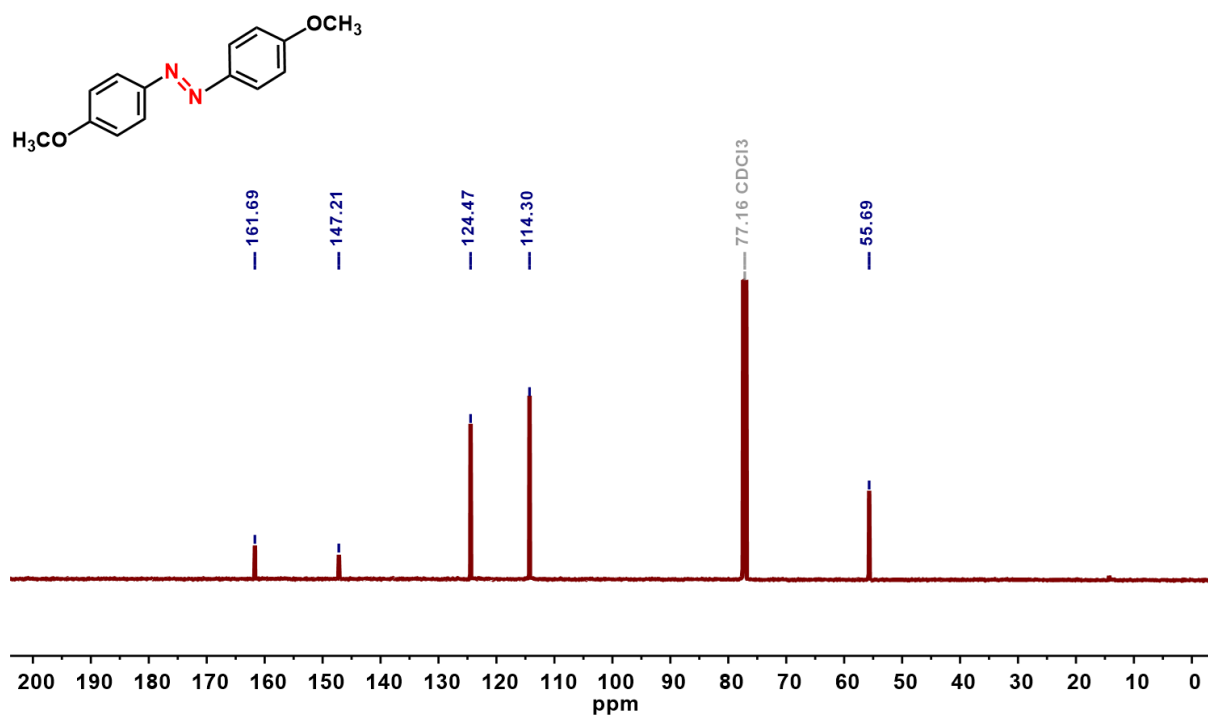
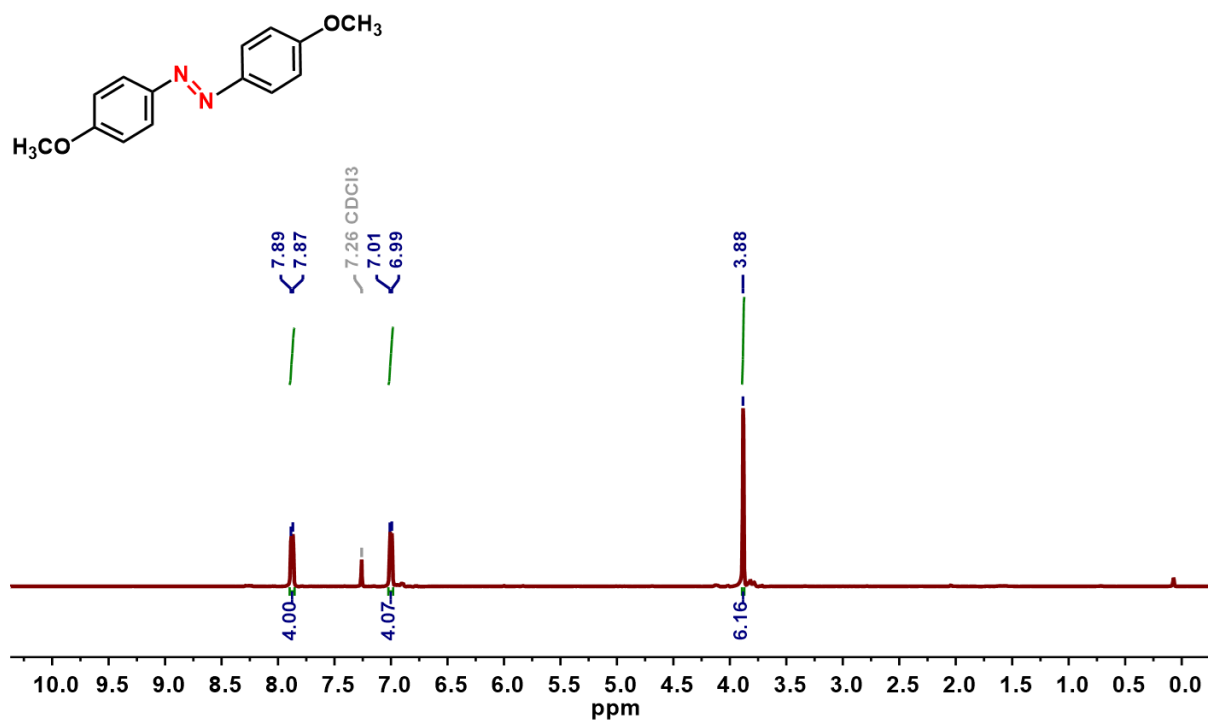


Figure S33. ¹H and ¹³C NMR spectra of 1,2-bis(4-methoxyphenyl)diazene.

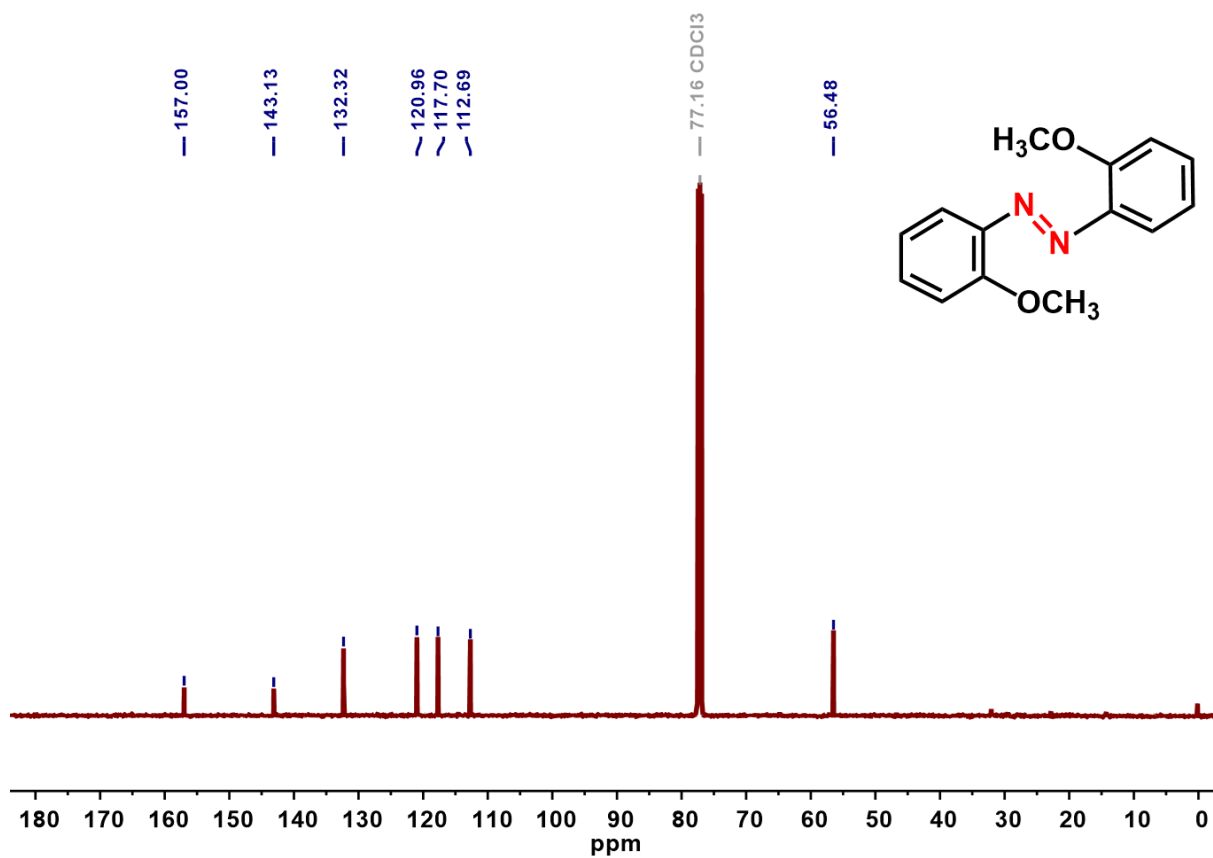
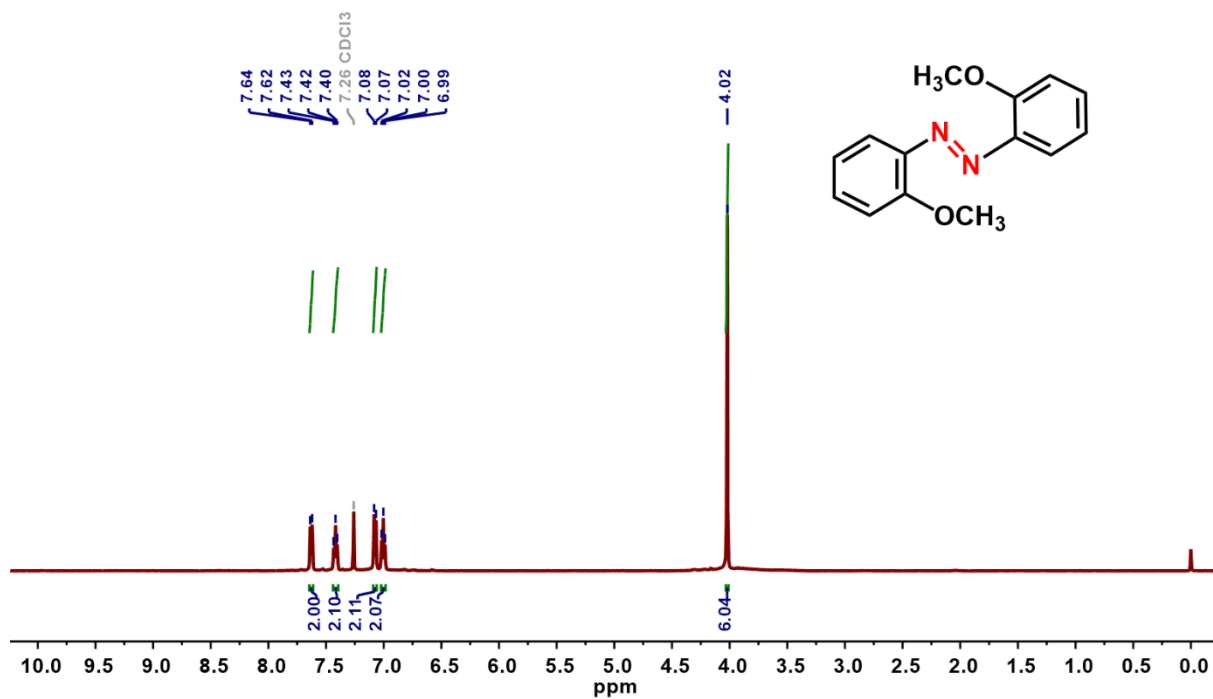


Figure S34. ¹H and ¹³C NMR spectra of 1,2-bis(2-methoxyphenyl)diazene.

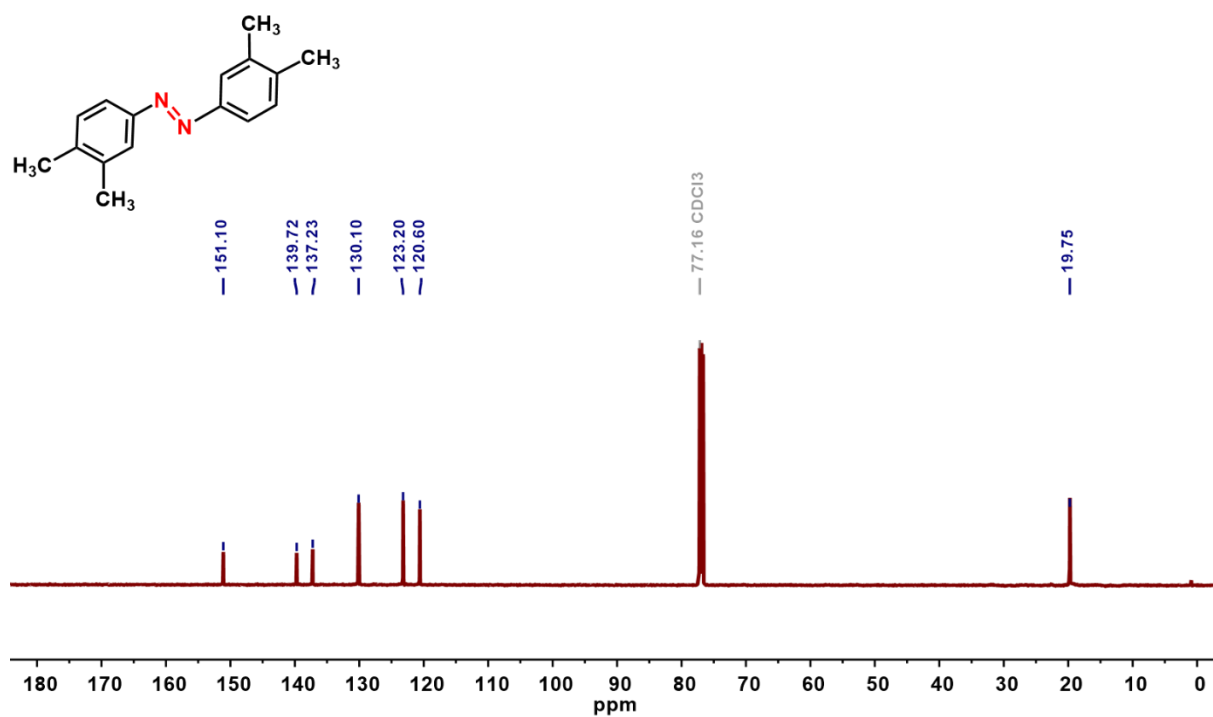
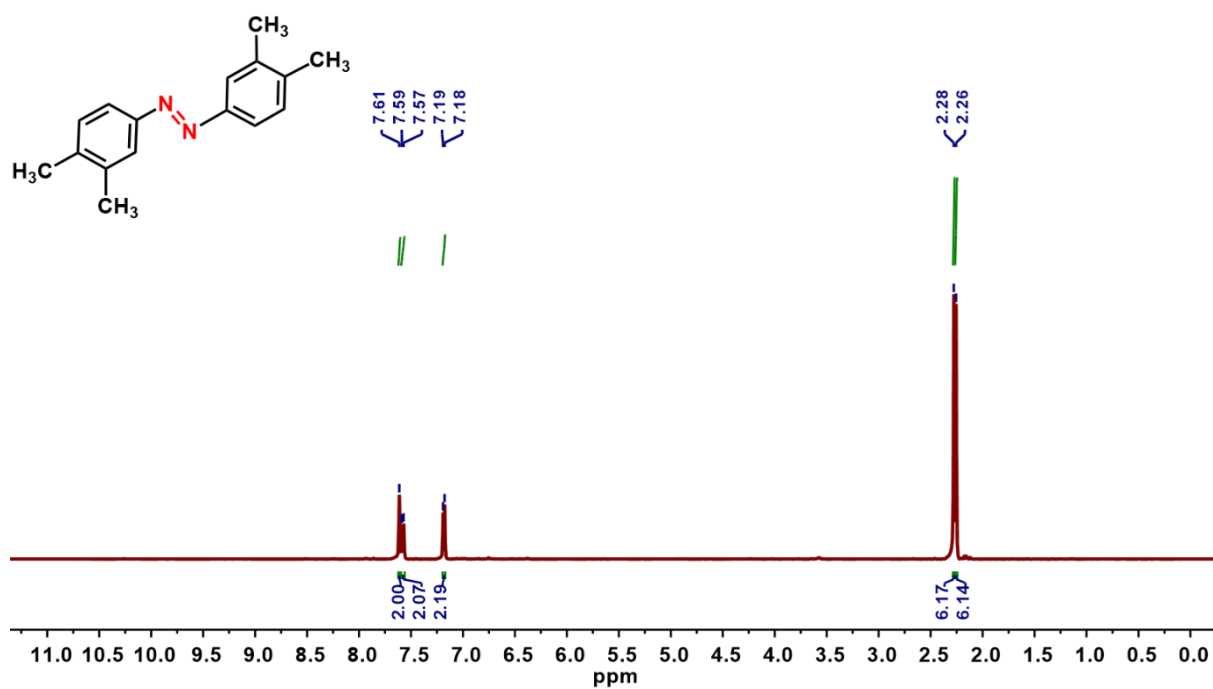


Figure S35. ¹H and ¹³C NMR spectra of 1,2-bis(3,4-dimethylphenyl)diazene.

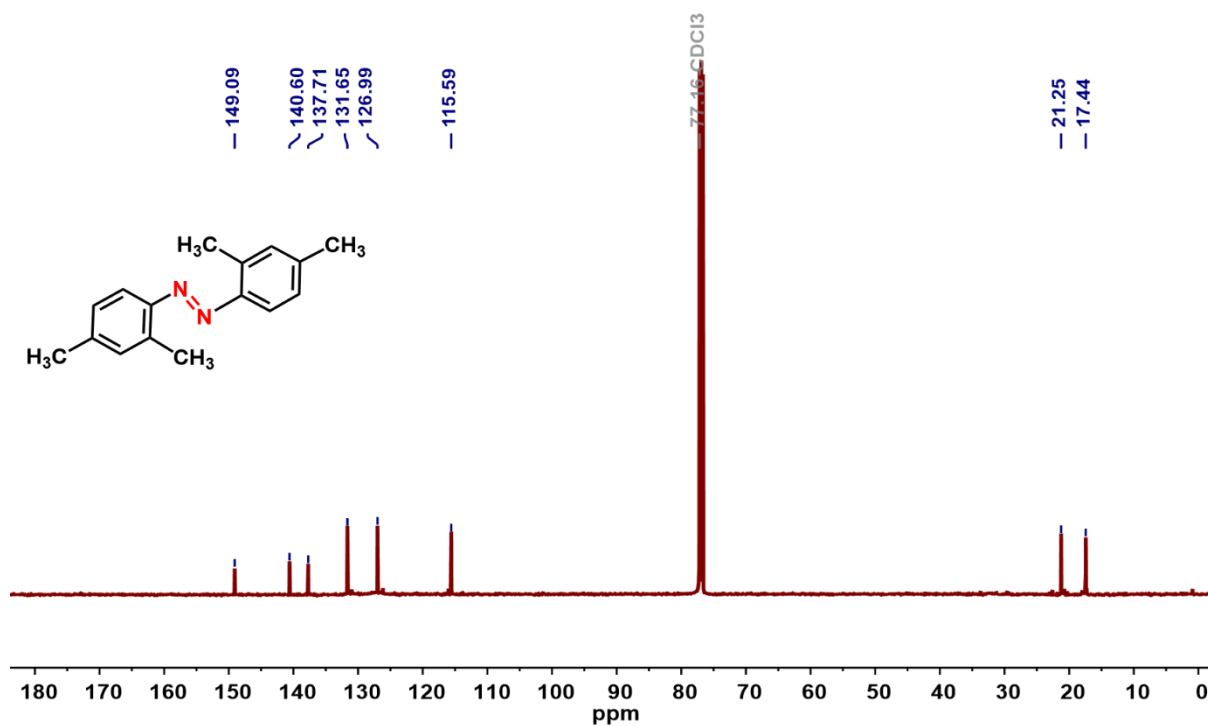
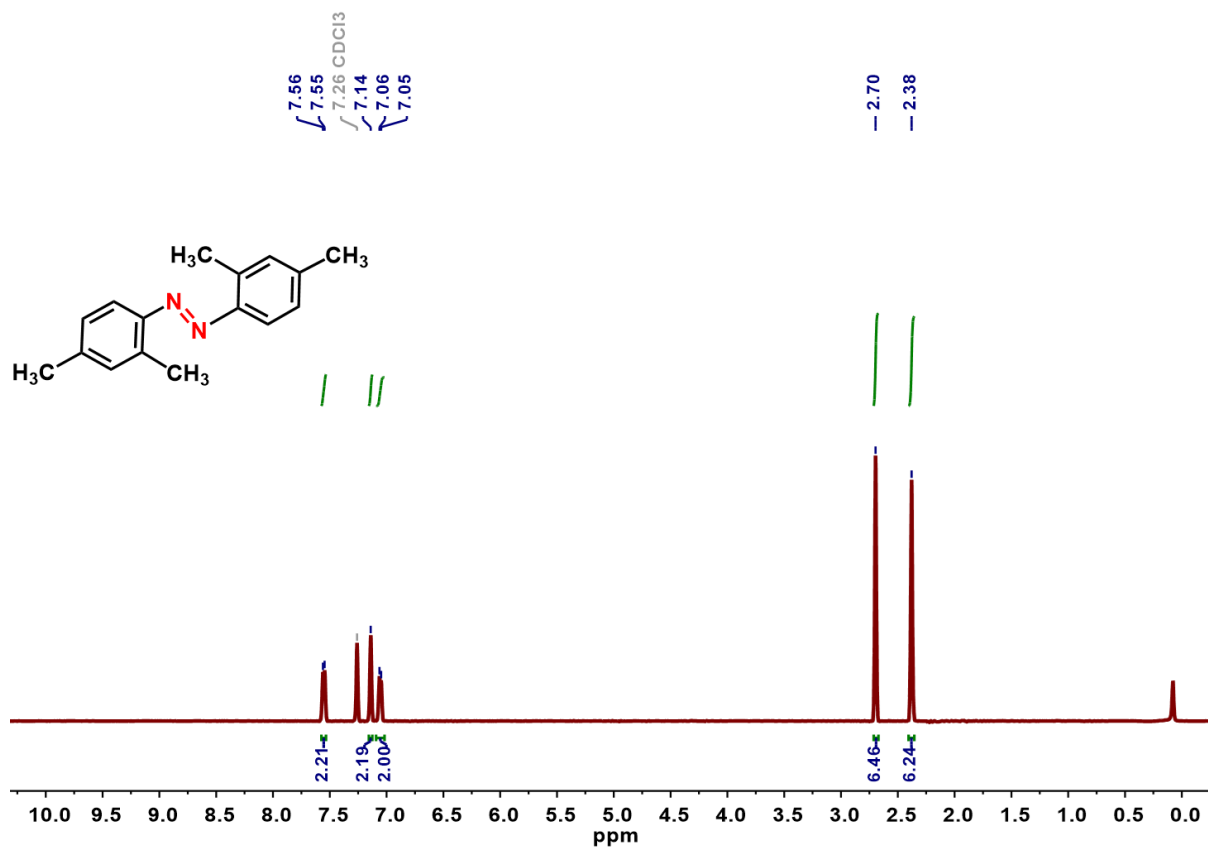


Figure S36. ¹H and ¹³C NMR spectra of 1,2-bis(2,4-dimethylphenyl)diazene.

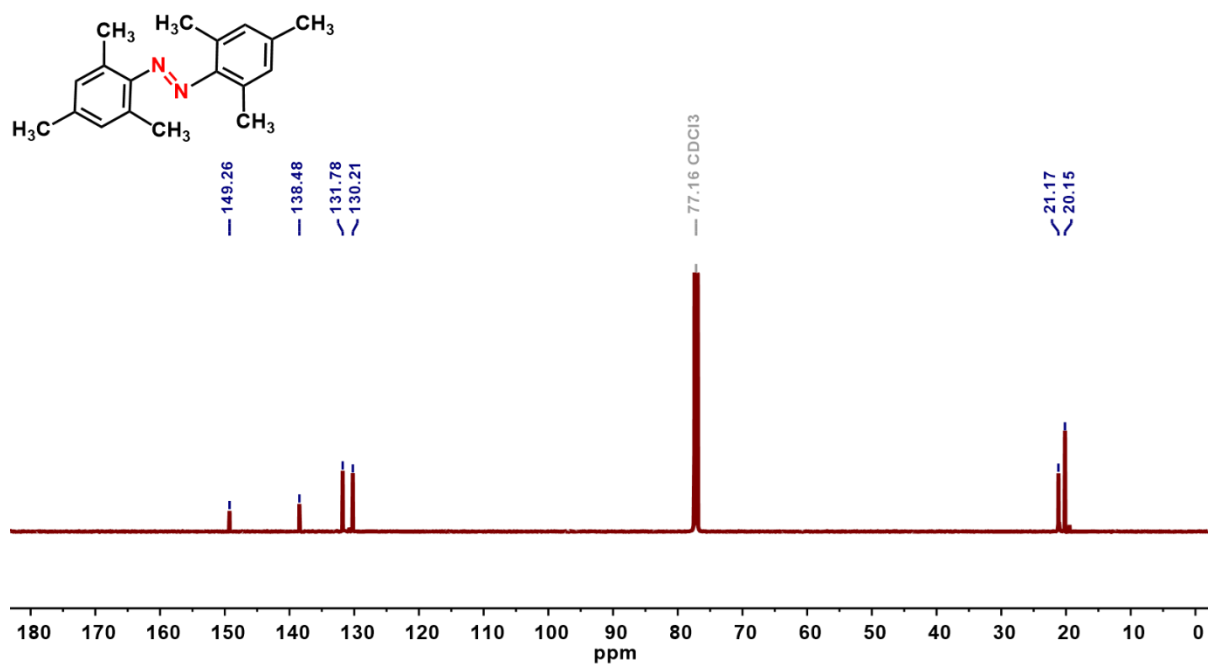
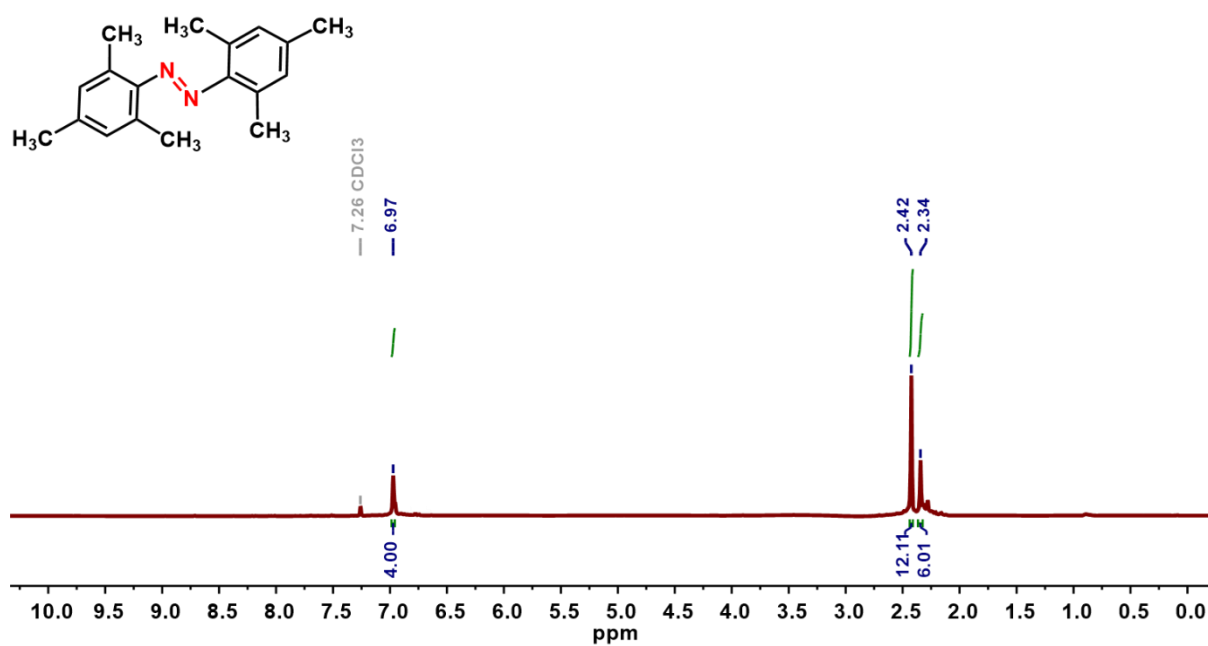


Figure S37. ¹H and ¹³C NMR spectra of 1,2-bis(2,4,6-trimethylphenyl)diazene.

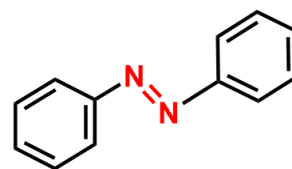
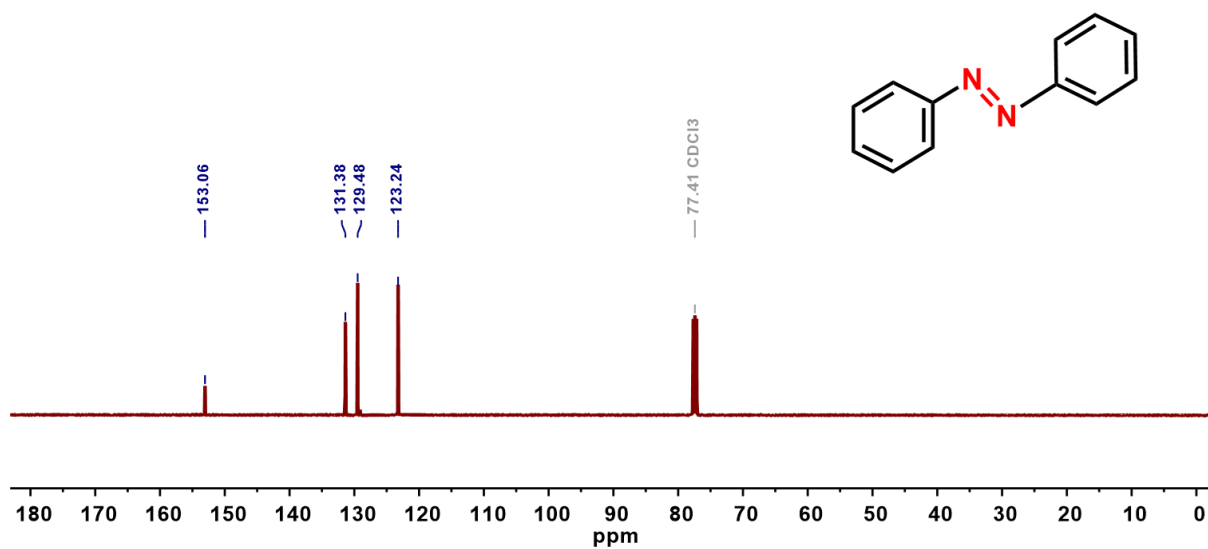
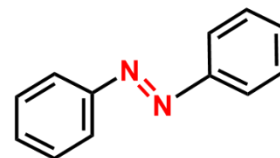
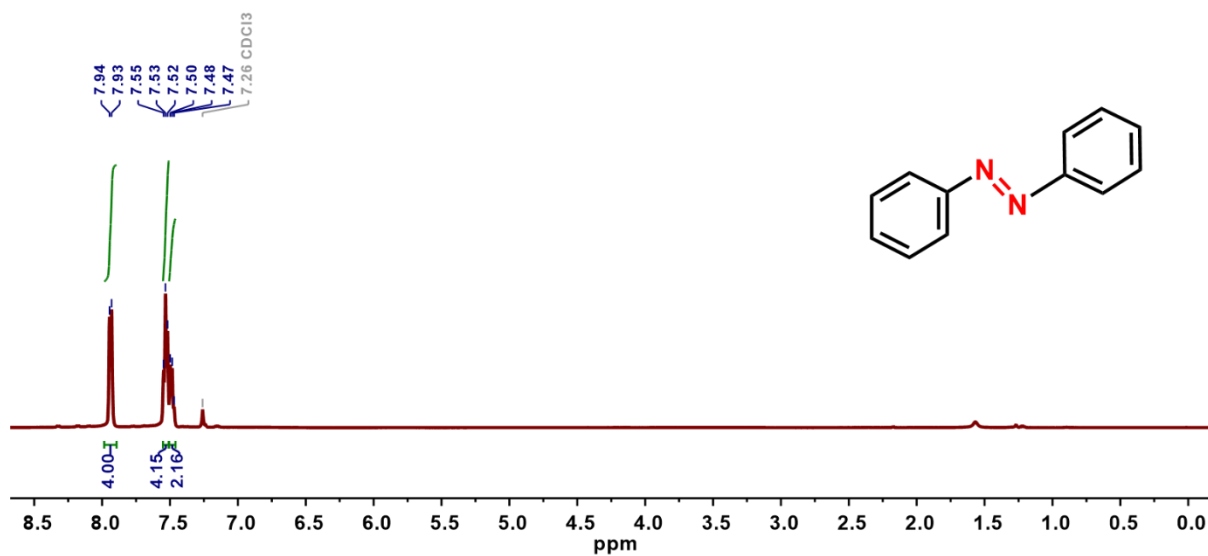


Figure S38. ¹H and ¹³C NMR spectra of azobenzene.

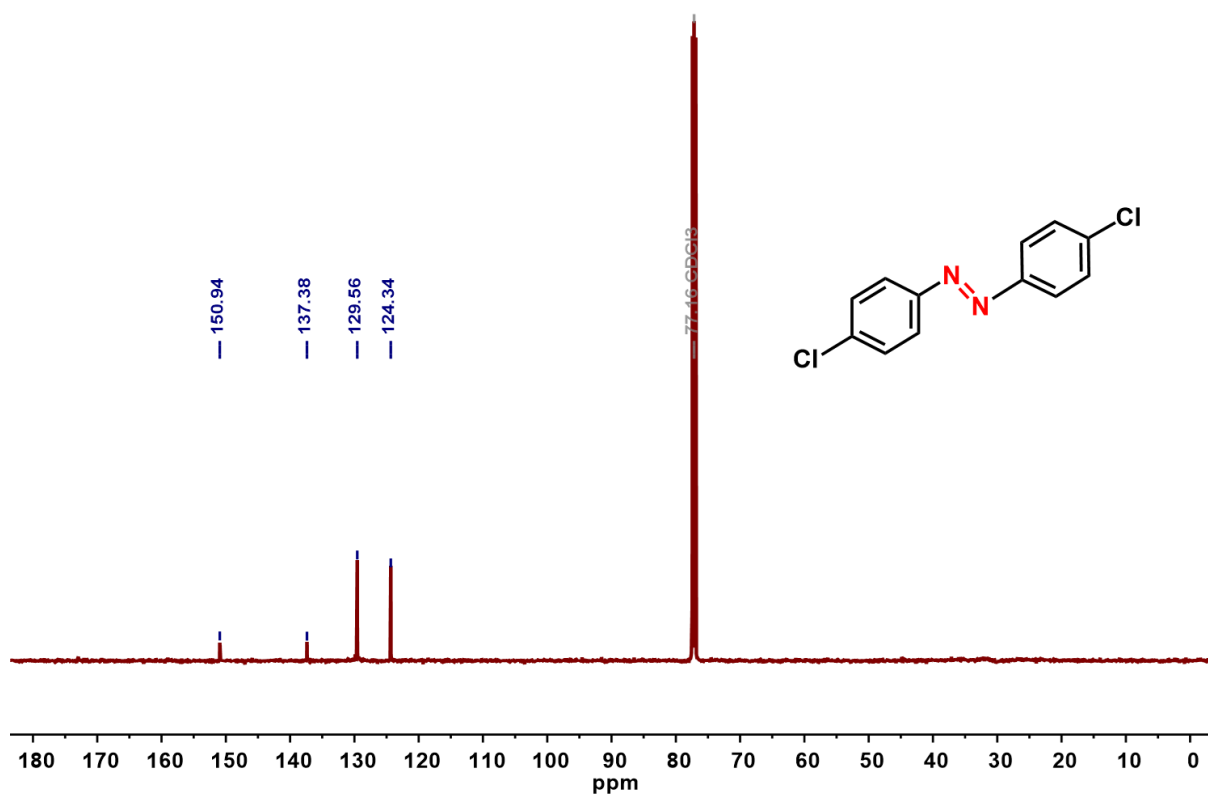
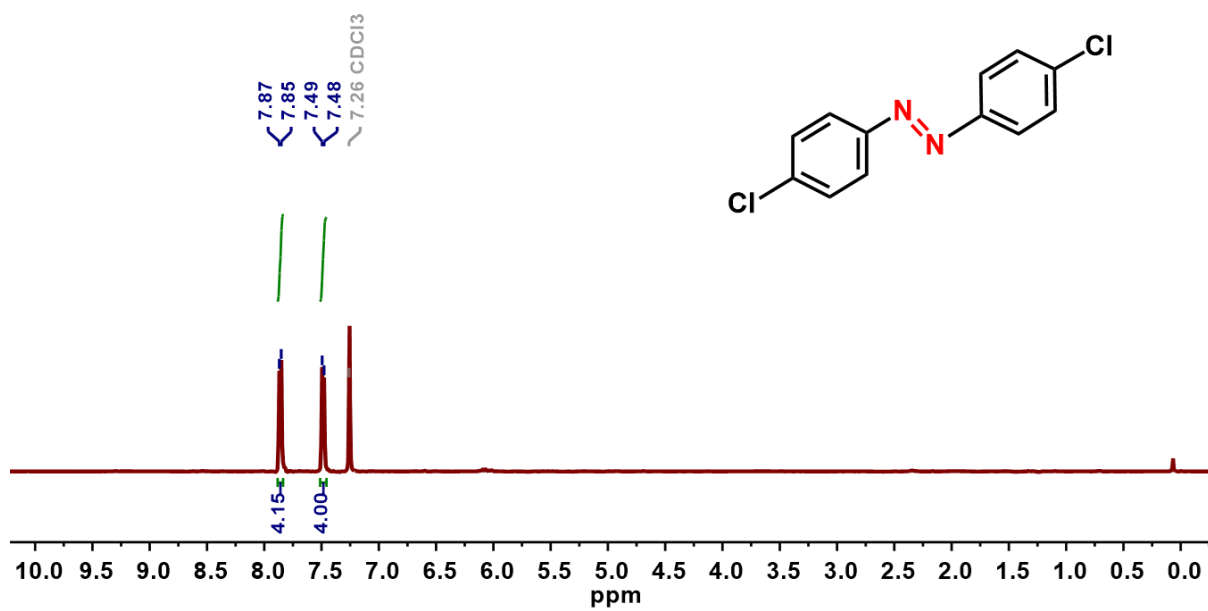


Figure S39. ¹H and ¹³C NMR spectra of 1,2-bis(4-chlorophenyl)diazene.

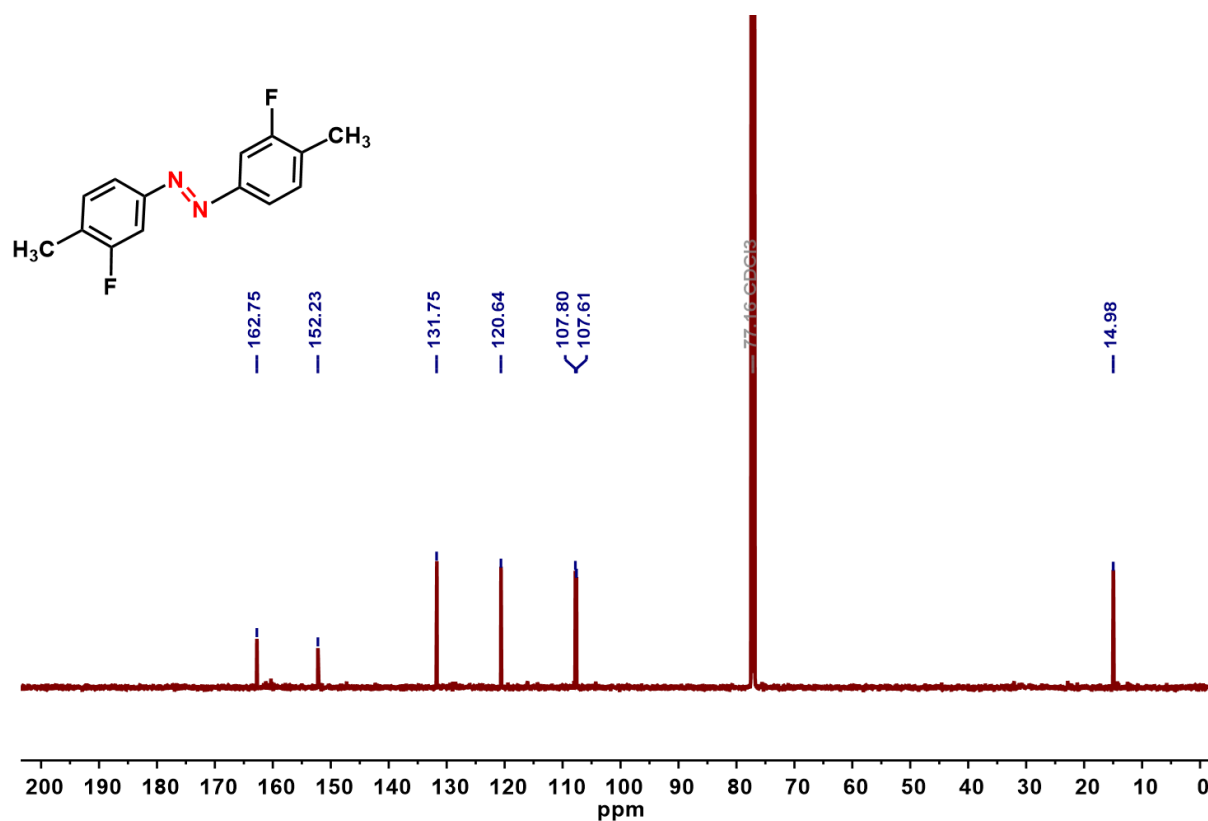
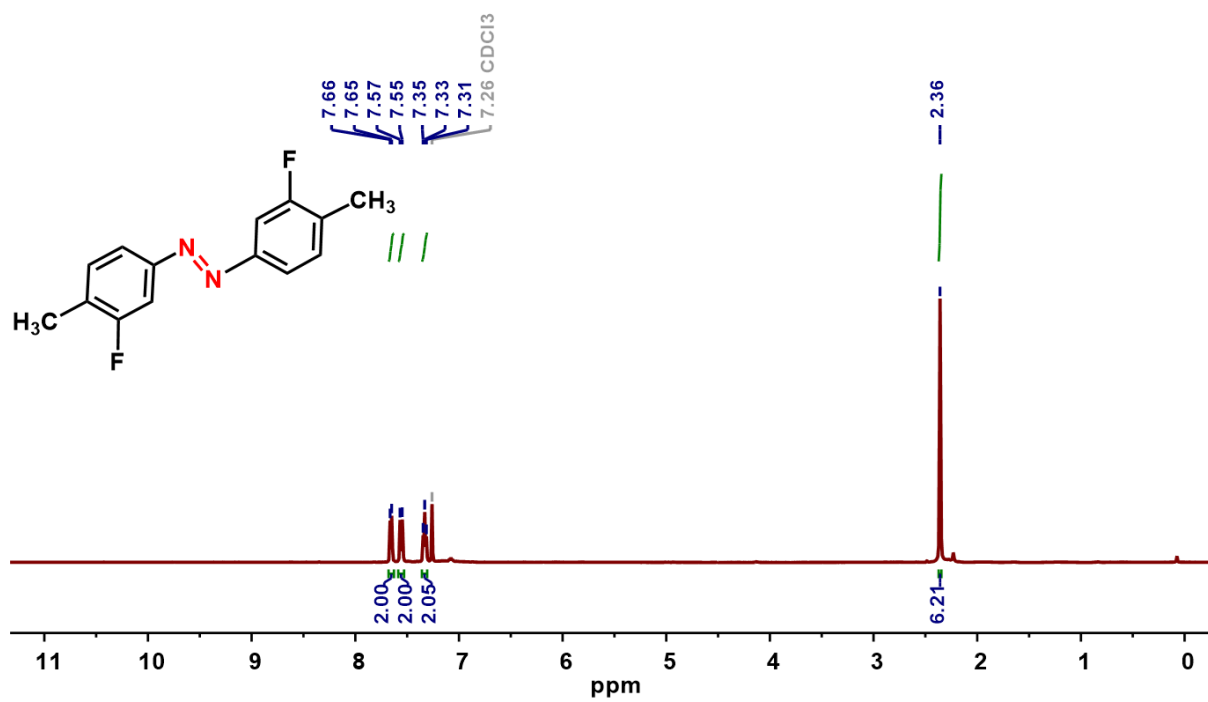


Figure S40. ¹H and ¹³C NMR spectra of 1,2-bis(3-fluoro-4-methylphenyl)diazene.

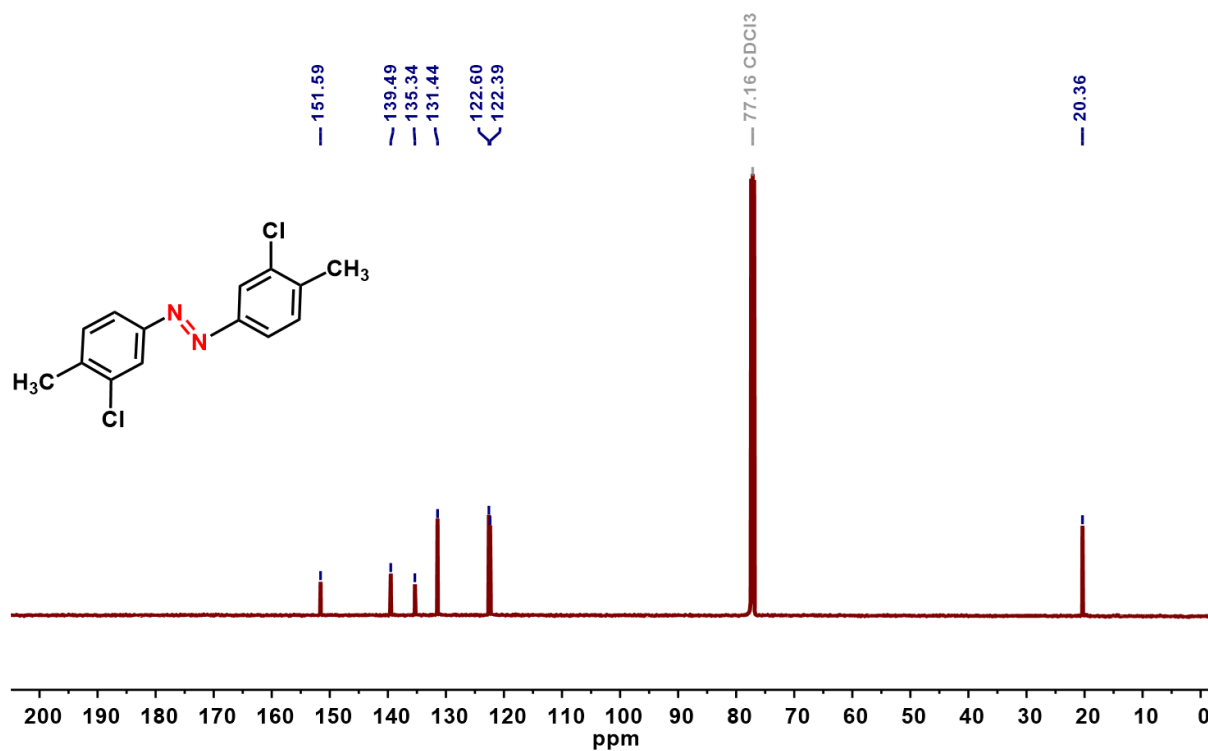
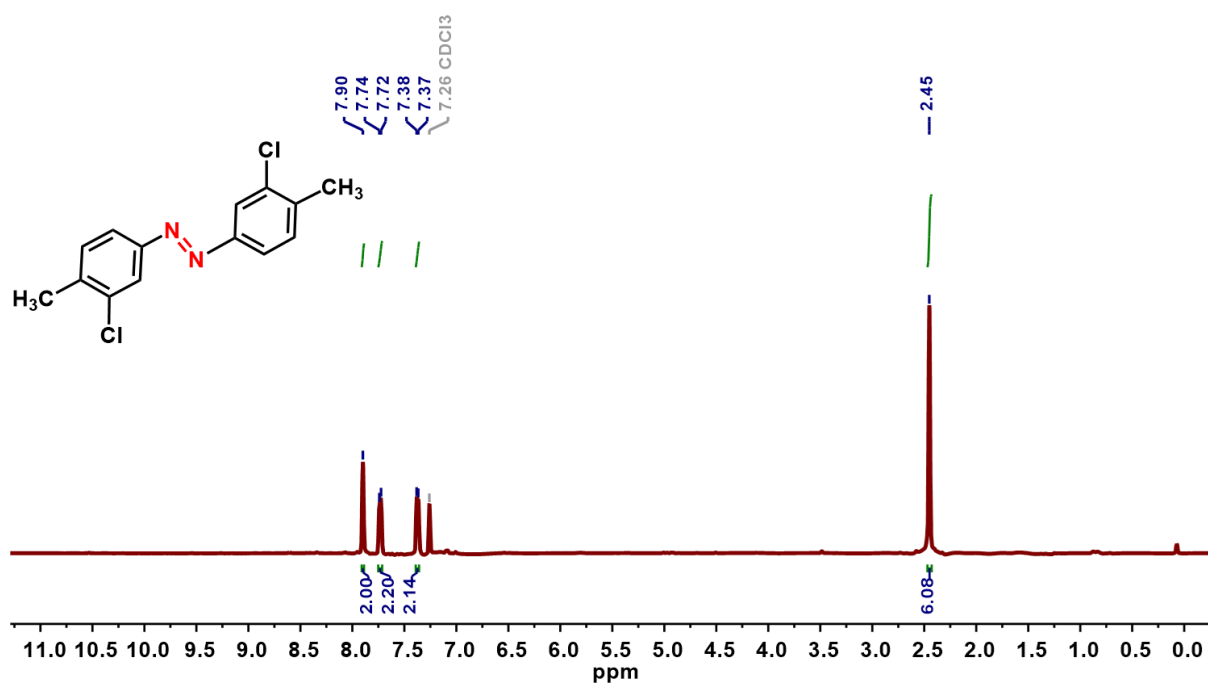


Figure S41. ¹H and ¹³C NMR spectra of 1,2-bis(3-chloro-4-methylphenyl)diazene.

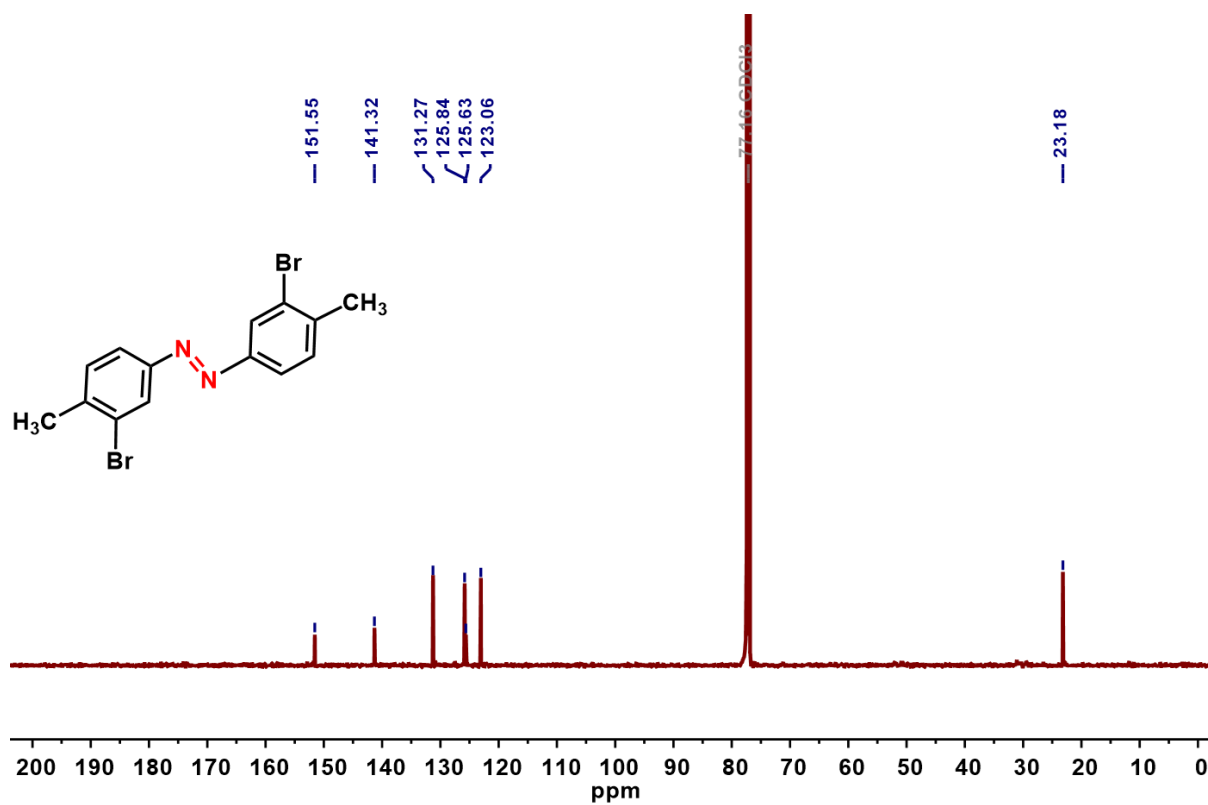
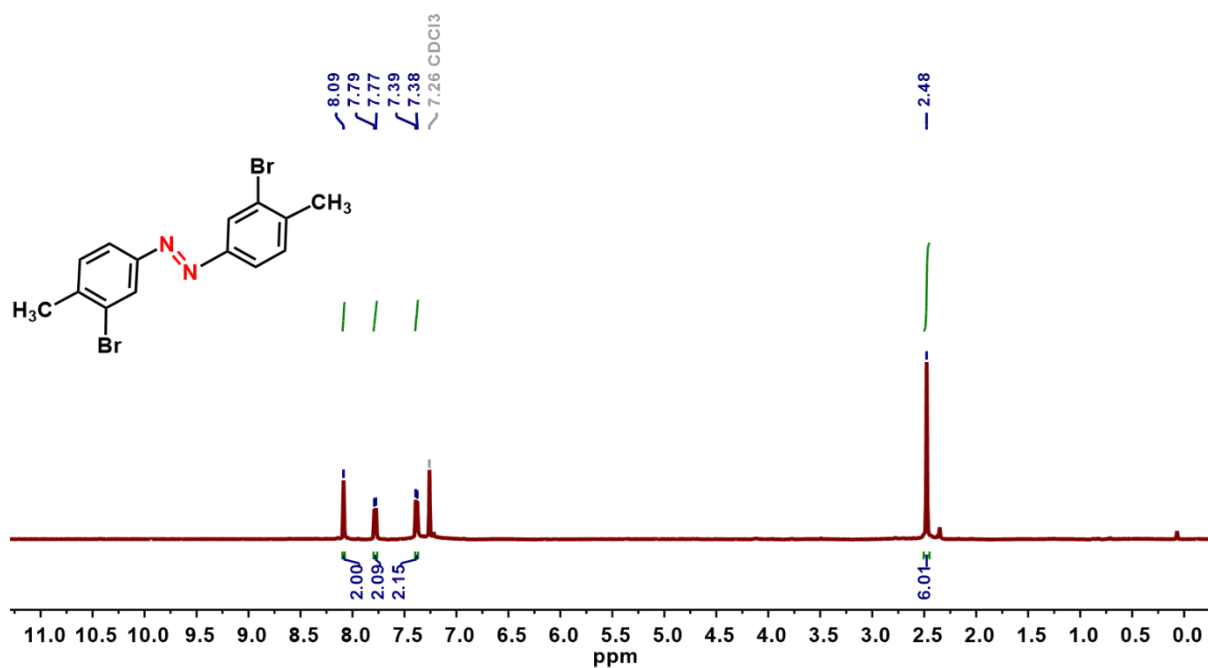


Figure S42. ¹H and ¹³C NMR spectra of 1,2-bis(3-bromo-4-methylphenyl)diazene.

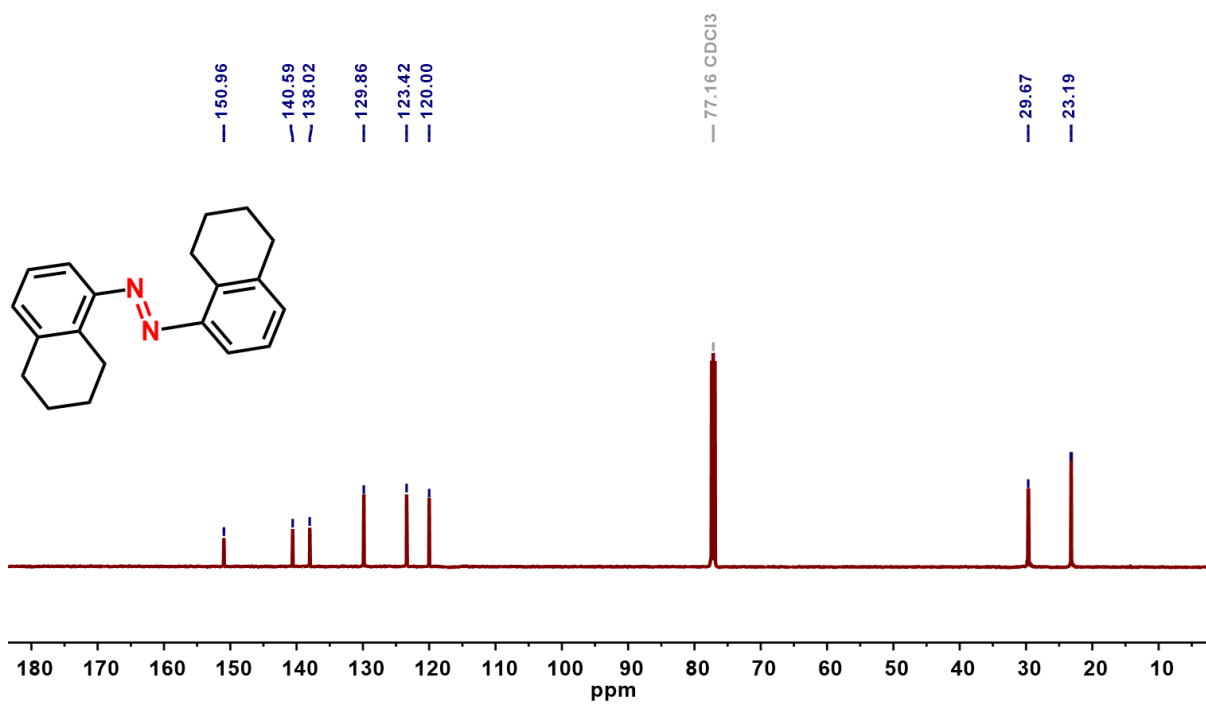
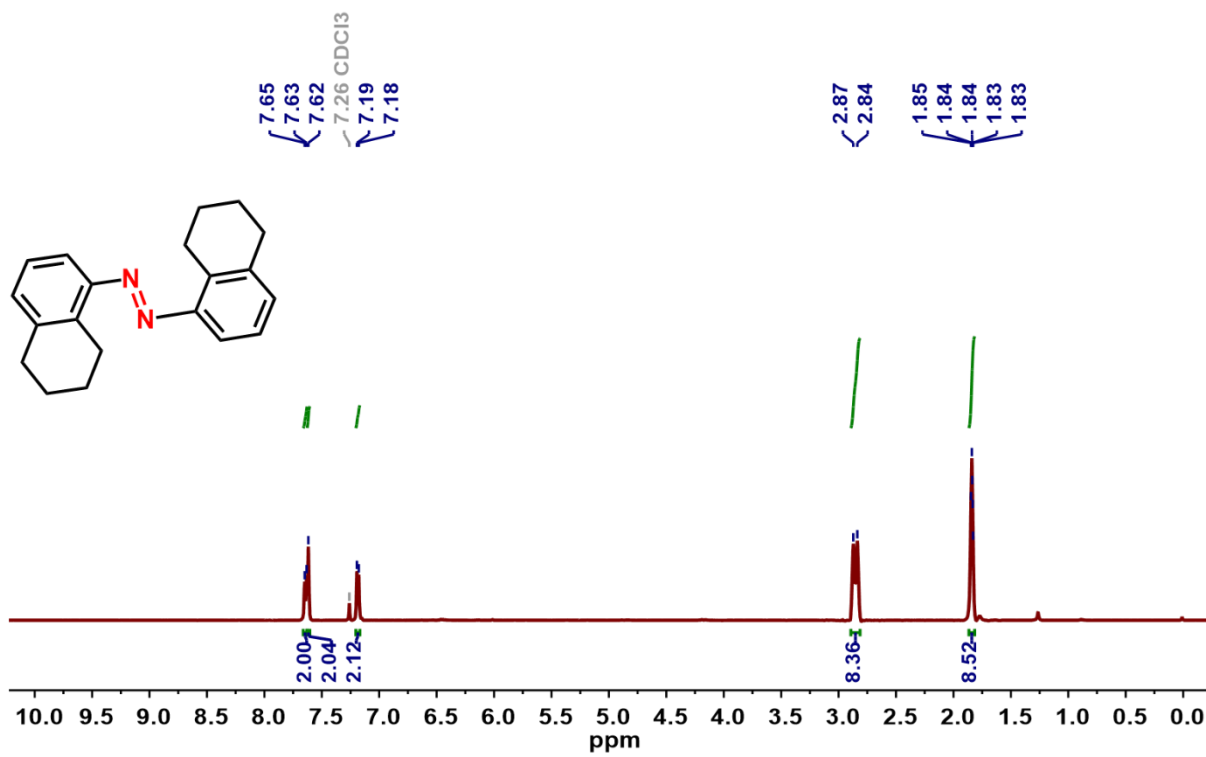


Figure S43. ¹H and ¹³C NMR spectra of 1,2-bis(5,6,7,8-tetrahydronaphthalen-1-yl)diazene.

Table S1 Recent literatures on the synthesis of azo compounds

Entry	Catalyst	Solvent	Time (h)	Standard conditions	Ref.
1.	Au/TiO ₂ (1.5 wt%)	Toluene	3	100 °C, O ₂ (5 bar)	[2]
2.	CuBr (6 mol%),	Toluene	20	Pyridine (18 mol%), 60 °C	[3]
3.	Ag NPs/C (6 mol%)	DMSO	24	KOH (1 eq.), 60 °C	[4]
4.	Meso-Mn ₂ O ₃ (32 mol%)	Toluene	8	110 °C, air balloon	[5]
5.	OMS-2 (20 mg)	Chlorobenzene	24	160 °C, O ₂	[6]
6.	Cu/graphene (5 wt%)	Isopropyl alcohol	5	300 W Xe lamp, 90 °C, KOH, Ar	[7]
7.	Au@OC1 ^R (0.5 mol% Au)	Isopropyl alcohol	2	30 °C, UV light, NaOH (0.2 eq.), N ₂	[8]
8.	g-C ₃ N ₄ (50 mg)	Isopropyl alcohol	20	Blue LED ($\lambda = 410$ nm), 40 mM KOH, deaerated conditions.	[9]
9.	Meso- RuO ₂ /Cu ₂ O NPs (50 mg)	Acetonitrile	16	85 °C	[10]
10.	NT-MnOOH (20 mg)	Toluene	11	60 °C	[11]
11.	Mo oxide molecular catalyst (0.5 mol%)	Methanol	24	30% H ₂ O ₂ (2 eq.), Na ₂ SO ₃ (0.1 eq.), 60 °C, O ₂	[12]
12.	Zr(OH) ₄ (10 wt% substrate)	Mesitylene	12	100 °C, O ₂	[13]
13.	Ir Complex (5 mol%)	Acetonitrile	24	Blue LED ($\lambda = 450$ nm), K ₃ PO ₄ (3 eq.)	[14]
14.	EY@CTAB (0.06 mol%)	Water	4	Green LED ($\lambda = 525$ nm), K ₃ PO ₄ (2 eq.)	[15]
15.	HNT@B ₁₂ H ₁₂ @A u (100 mg)	2-propanol	2.5 h	$\lambda = 370$ nm, NaOH (1.5 eq.), N ₂	[16]
16.	Catalyst-free	Water	90 min (40 min)	$\lambda = 370$ nm, K₃PO₄ (2 eq.), open atm (O₂ atm)	This work

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