Supporting Information

Atom-dispersed Au combined with Nano-Au on Halloysite Nanotubes with Closo-dodecaborate promotes Synergistic Effects for Enhanced Photocatalysis

Table on content

Results and Discussion

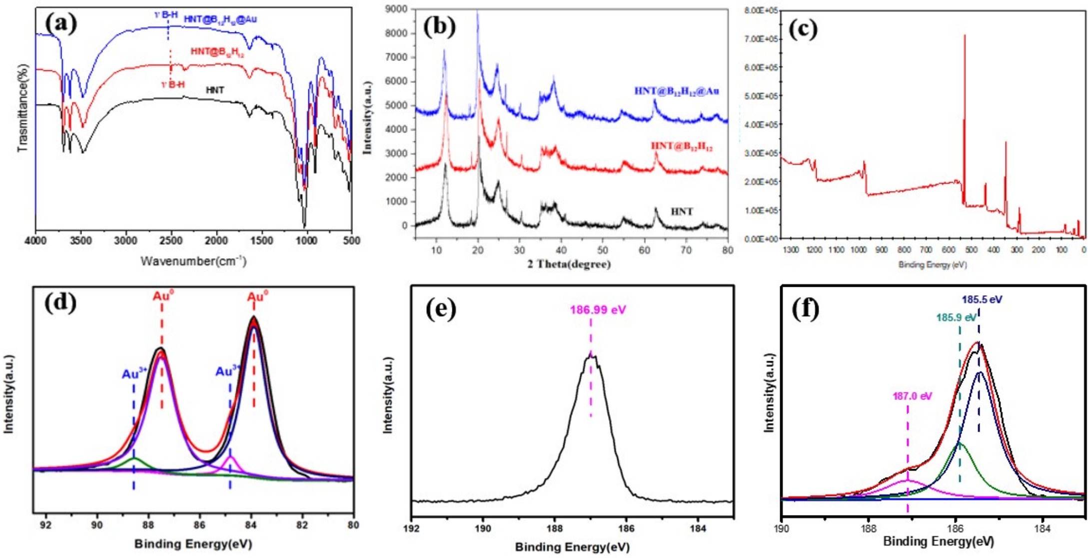


Figure S1. FT-IR spectra of HNT@$B_{12}H_{12}$@Au (a); PXRD spectra of HNT@$B_{12}H_{12}$@Au (b); XPS spectra of HNT@$B_{12}H_{12}$@Au (c, d); and XPS spectra of B before (e) and after (f) Au reduction.

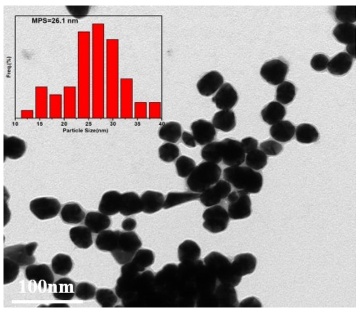


Figure S2. TEM of $Na_2B_{12}H_{12}$@Au.

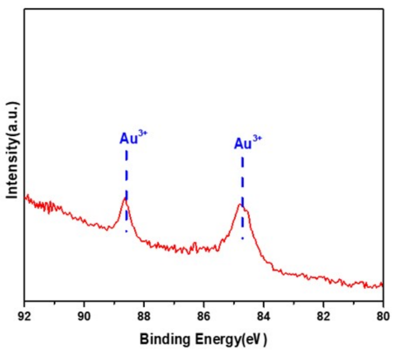


Figure S3. XPS spectra of HNT@Au.

Table S1. pH values before and after reaction and the effect of different solvents on the reducibility of $Na_2B_{12}H_{12}$.

Entry	$Na_2B_{12}H_{12}$	$NaAuCl_4$	Solvent	Time	Solution color	pH
1	-	0.1mmol	H_2O(30 mL)	10 min	yellow	3.63
2	0.5mmol	-	H_2O(30 mL)	10 min	colorless	7.02
3	0.5mmol	0.1mmol	H_2O(30 mL)	10 min	purple black	3.11
4	0.5mmol	0.1mmol	MeOH(30 mL)	10 min	yellow	-
5	0.5mmol	0.1mmol	EtOH(30 mL)	10 min	yellow	-
6	0.5mmol	0.1mmol	CH_2Cl_2(30 mL)	10 min	yellow	-
7	0.5mmol	0.1mmol	Acetone(30 mL)	10 min	yellow	-
8	0.5mmol	0.1mmol	DMF(30 mL)	10 min	yellow	-

Table S2. Catalytic effect of different catalysts on different substrates[a].

Entry	Reactant	Catalyst	Yield(%) of AOB at different Reactin time[b]						Yield(%) of AB at different Reactin time[b]					
			0 h	0.5h	1h	1.5h	2h	2.5h	0 h	0.5h	1h	1.5h	2h	2.5h
1	NB	HNT@Au	-	4.0	7.2	9.4	14	12	-	4.2	5.1	5.4	5.8	6.4
2	NB	$Na_2B_{12}H_{12}$@Au	-	10	22	69	40	4.2	-	-	-	15	38	63
3	NB	HNT@$B_{12}H_{12}$@Au	-	18	29	48	28	-	-	8.1	12	37	69	97
4	NSB	HNT@Au	-	24	49	58	41	-	-	5.7	9.2	14	19	28
5	NSB	$Na_2B_{12}H_{12}$@Au	-	9.9	14	31	44	-	-	3.2	8.5	21	39	57
6	NSB	HNT@$B_{12}H_{12}$@Au	-	31	52	42	28	3.9	-	8.4	17	45	71	98
7	AOB	HNT@Au	-	-	-	-	-	-	-	12	19	24	31	37
8	AOB	$Na_2B_{12}H_{12}$@Au	-	-	-	-	-	-	-	17	29	37	46	54
9	AOB	HNT@$B_{12}H_{12}$@Au	-	-	-	-	-	-	-	25	42	68	82	98

[a] Reaction condition:, reactant 0.5 mmol, photocatalyst 0.5 μmol (base on Au), 5 mL 2-propanol as solvent, 0.75 mmol NaOH as base, 1 atm N_2 atmosphere, room temperature, reaction time from 0-2.5 h, and the light (≈370 nm) intensity was 0.54 W/cm^2. [b] The conversations were analyzed by gas chromatography (GC).

Table S3. Comparison of HNT@$B_{12}H_{12}$@Au with reported solid catalysts for the reduction of nitrobenzene to AB.

Catalyst	Conditions	TON	TOF(h^{-1})	Ref.
BM-Au/TiO_2	2-propanol, KOH, visible-light, 12h, R.T.	43.3	3.61	[1]
Cu/graphene	2-propanol, KOH, 400-800 nm, 12 h, 90°C	36.6	3.05	[2]
g-C_3N_4	2-propanol,KOH, 410 nm LED，5h, R.T.	0.0375	0.0075	[3]
Au@CeO_2	2-propanol,KOH, 4h, 50°C	12.4	3.09	[4]
Au@OC1R	2-propanol,KOH, UV, 2h, 30°C	182	91.0	[5]
SmI_2	THF, n-Bu4NPF6, electrical drive, 2h, 20°C	9.50	4.75	[6]
Ag@ZrO_2	2-propanol,KOH, UV, 2h, 60°C	32.0	2.00	[7]
$Na_2B_{12}H_{12}$@Au	2-propanol,KOH, 370nm, 2.5h, R.T.	7.60	3.10	This work
HNT@$B_{12}H_{12}$@Au	2-propanol,KOH, 370nm, 2.5h, R.T.	218	87.1	This work

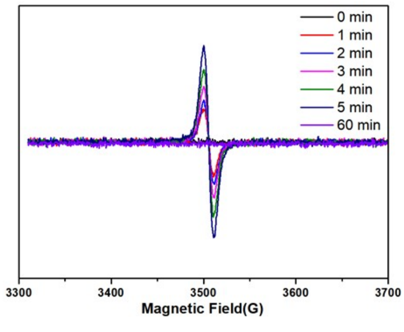
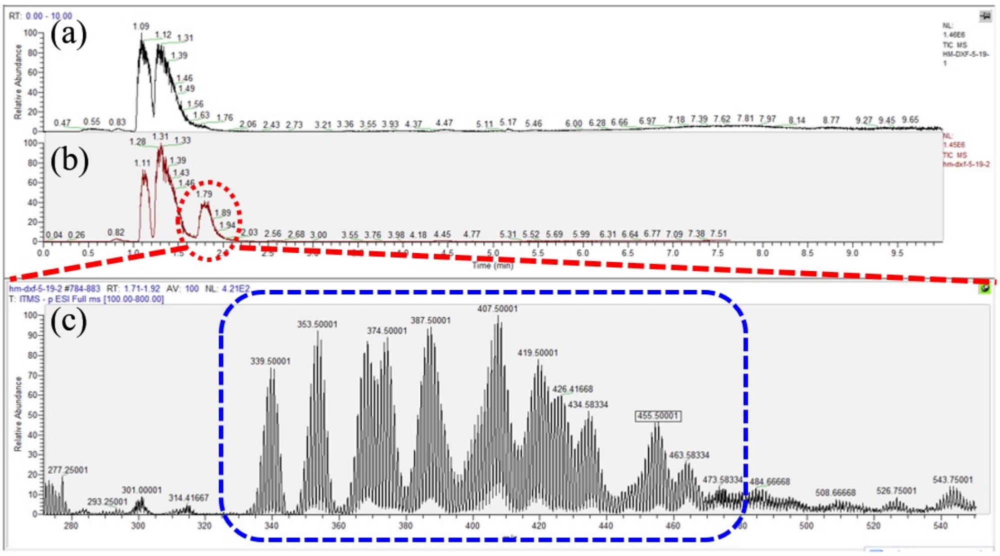


Figure S4. EPR spectra of the $Na_2B_{12}H_{12}$ reduction of Au NPs from 0 to 60 min; 2, 2-dimethyl-3,4-dihydro-2H-pyrrole 1-oxide (DMPO) was added in each period (0, 1, 2, 3, 4, and 60 min).



(1) $$Na_2B_{12}H_{12} \xrightarrow{H_2O} Na^+ + B_{12}H_{12}^{2-}$$

(2) $$3B_{12}H_{12}^{2-} + AuCl_4^- \longrightarrow Au^0 + 3B_{12}H_{12}^{\cdot-} + Cl^-$$

(3) $$B_{12}H_{12}^{\cdot-} + H_2O \longrightarrow H^+ + \begin{cases} B_{24}H_{22}O^- \ m/z=339.50-41.03(CH_3CN)=298.47 \\ B_{24}H_{21}O_2^- \ m/z=353.50-41.03(CH_3CN)=312.47 \\ B_{24}H_{20}O_3^- \ m/z=367.50-41.03(CH_3CN)=326.47 \\ B_{24}H_{24}O_3^- \ m/z=374.50-41.03(CH_3CN)=333.47 \\ B_{24}H_{22}O_4^- \ m/z=387.50-41.03(CH_3CN)=346.47 \\ B_{24}H_{24}O_5^- \ m/z=407.50-41.03(CH_3CN)=366.47 \\ B_{24}H_{22}O_6^- \ m/z=419.50-41.03(CH_3CN)=378.47 \end{cases}$$

Figure S5. LTQ-XL mass spectrometry of $B_{12}H_{12}^{2-}$ before and after reaction (a, b). The detailed *m/z* after the reaction is shown in (c), and the proposed mechanism for Au-NP synthesis by $B_{12}H_{12}^{2-}$ is summarized in (1–3). The *m/z* of $B_{12}H_{12}^{2-}$ derivatives are shown in (3) (because the eluent is acetonitrile, 1–2 molecular weights of acetonitrile should be added when calculating the *m/z* of $B_{12}H_{12}^{2-}$ derivatives).

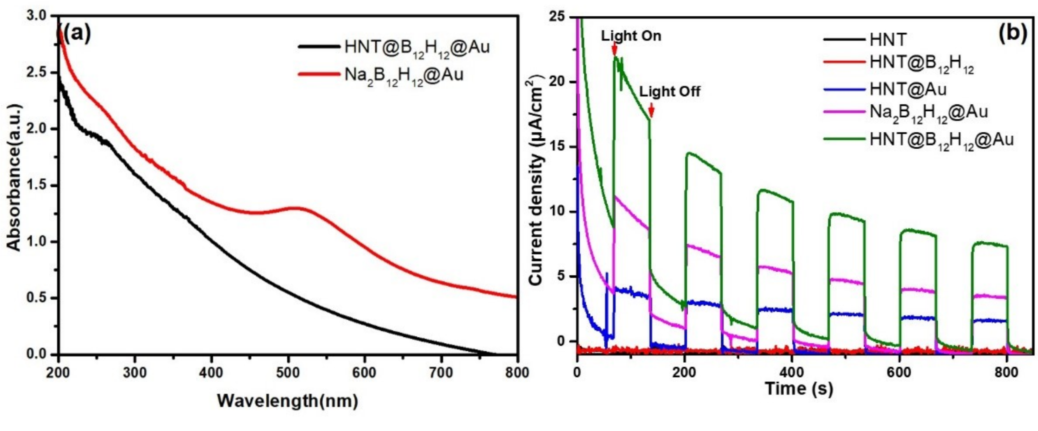


Figure S6. UV-vis spectrometry of HNT@$B_{12}H_{12}$@Au and $Na_2B_{12}H_{12}$@Au (a). The photocurrent density (*I-t* curves) of different materials under UV radiation at 370 nm wavelength (b).

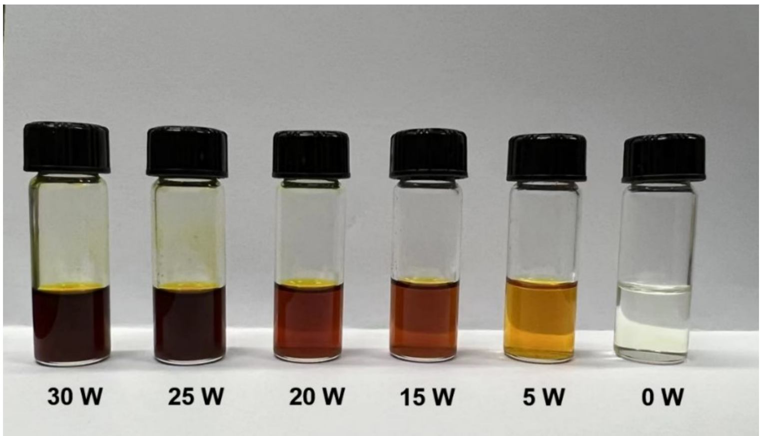


Figure S7. Effect of irradiation density (power) on reaction (The irradiation density corresponding to 25W is 0.54 W/cm^2). Reaction condition: photocatalyst 100 mg, reactant 0.5 mmol, 5 mL 2-propanol as solvent, 0.75 mmol NaOH as base, 1 atm N_2 atmosphere, room temperature, reaction time 2.5 h, and the irradiation (λ≈370 nm), 0, 5, 15, 20, 25 and 30W corresponds to the irradiation density of 0, 0.11, 0.32, 0.54 and 0.65 W/cm^2.

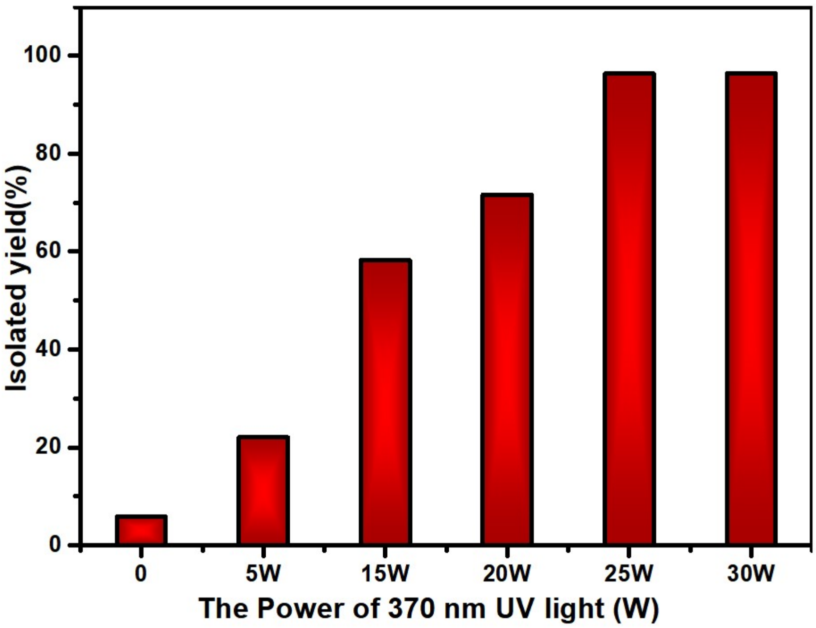


Figure S8. Isolation yields of azobenzene at different irradiation densities. Reaction condition: photocatalyst 100 mg, reactant 0.5 mmol, 5 mL 2-propanol as solvent, 0.75 mmol NaOH as base, 1 atm N_2 atmosphere, room temperature, reaction time 2.5 h, and the irradiation (λ≈370 nm), 0, 5, 15, 20, 25 and 30W corresponds to the irradiation density of 0, 0.11, 0.32, 0.54 and 0.65 W/cm^2.

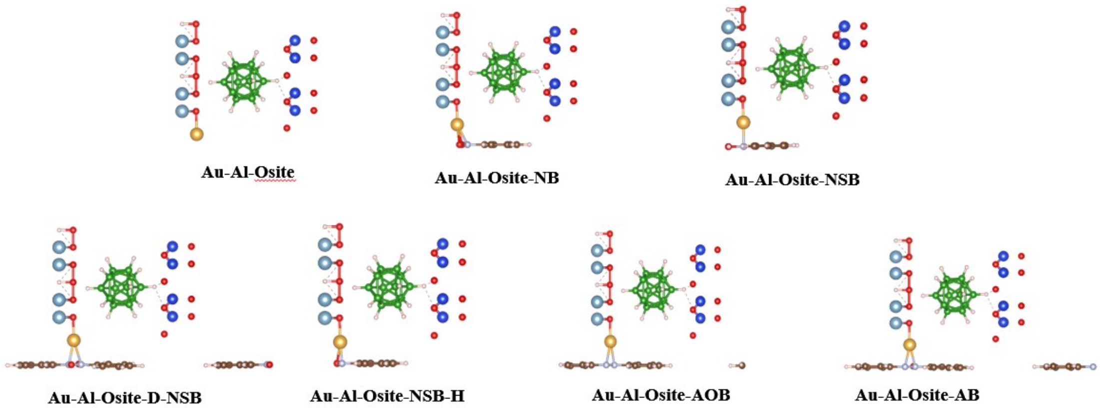


Figure S9. Models of Au-Al-Osite.

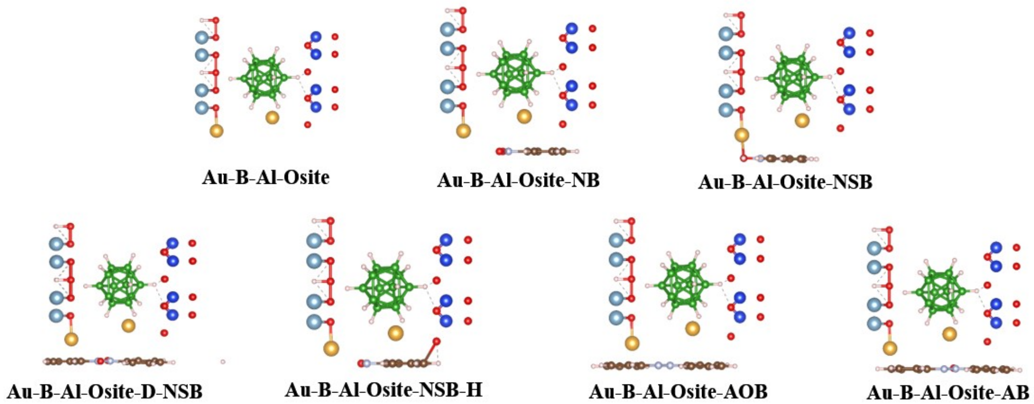


Figure S10. Models of Au-B-Al-Osite.

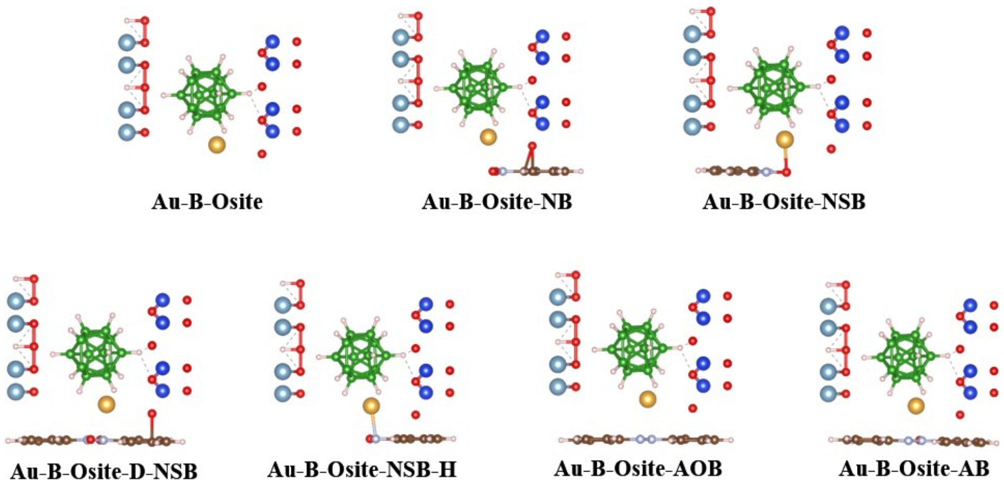


Figure S11. Models of Au-B-Osite.

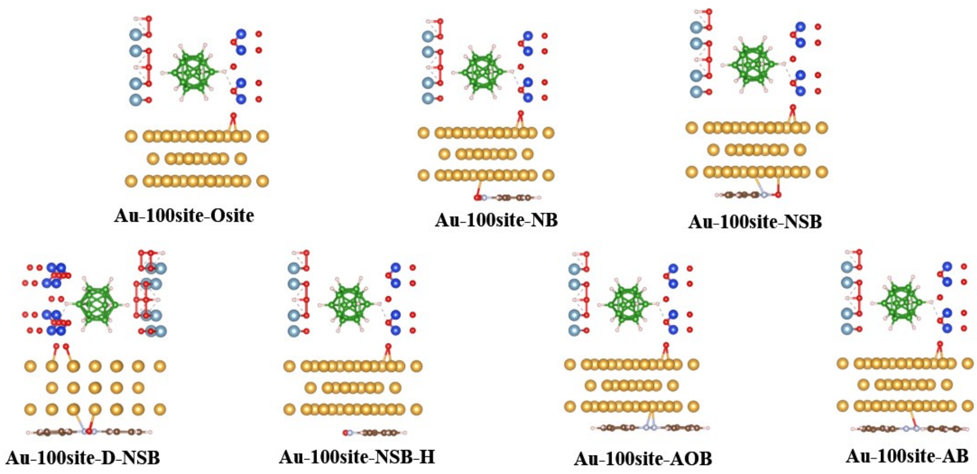


Figure S12. Models of Au-NP site.

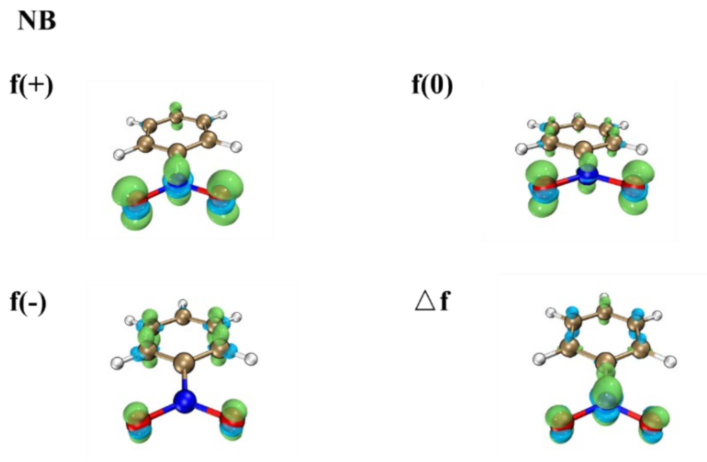


Figure S13. Isodensity contour plot of the Fukui function f (+), f (0), f (-) and delta f for NB.

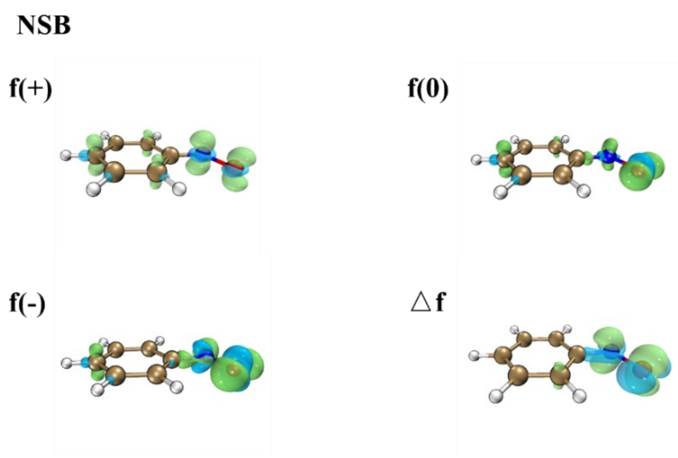


Figure S14. Isodensity contour plot of the Fukui function f (+), f (0), f (-) and delta f for the nitrosobenzene (NSB).

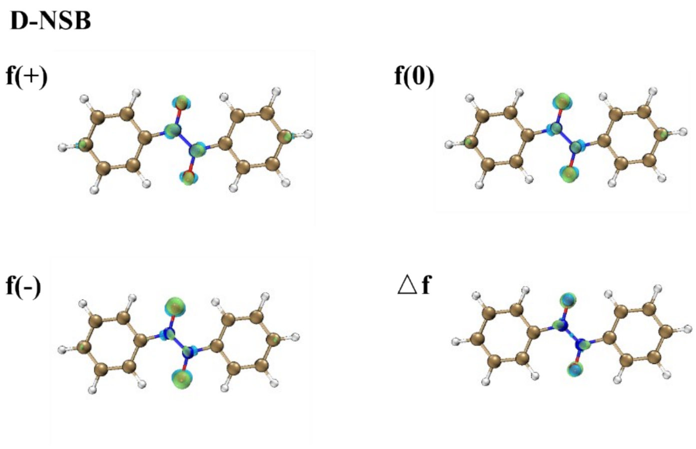


Figure S15. Isodensity contour plot of the Fukui function f (+), f (0), f (-) and delta f for the di-nitrosobenzene (D-NSB).

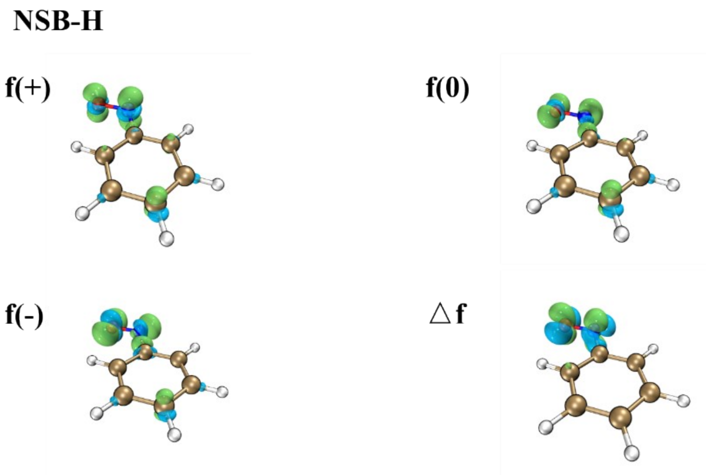


Figure S16. Isodensity contour plot of the Fukui function f (+), f (0), f (-) and delta f for the hydrogenated NSB (NSB-H).

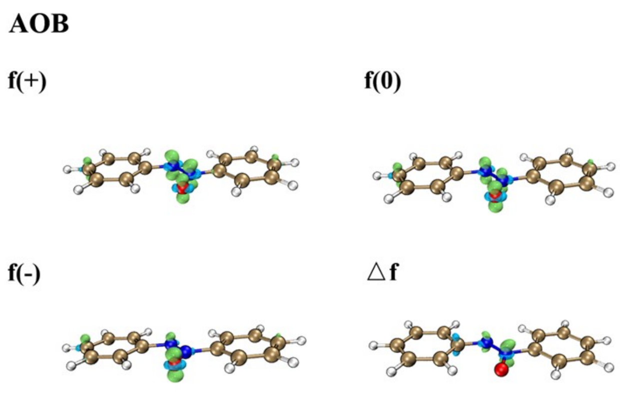


Figure S17. Isodensity contour plot of the Fukui function f (+), f (0), f (-) and delta f for the azoxybenzene (AOB).

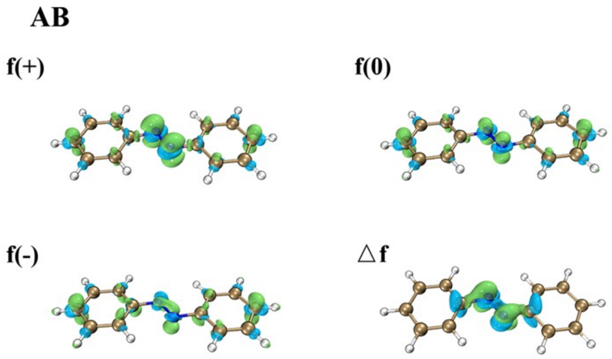


Figure S18. Isodensity contour plot of the Fukui function f (+), f (0), f (-) and delta f for the azobenzene (AB).

Table S4. Mulliken atomic charges of nitrobenzene (NB), azobenzene (AB) and azoxybenzene (AOB) have been calculated using GGA-PBE.

Atomic Populations (Mulliken) of NB							
Species	Ion	s	p	d	f	Total	Charge(e)
H	1	0.67	0.00	0.00	0.00	0.67	0.33
H	2	0.66	0.00	0.00	0.00	0.66	0.34
H	3	0.69	0.00	0.00	0.00	0.69	0.31
H	4	0.69	0.00	0.00	0.00	0.69	0.31
H	5	0.70	0.00	0.00	0.00	0.70	0.30
C	1	1.26	3.00	0.00	0.00	4.26	-0.26
C	2	1.27	2.99	0.00	0.00	4.26	-0.26
C	3	1.26	3.02	0.00	0.00	4.27	-0.27
C	4	1.26	2.97	0.00	0.00	4.24	-0.24
C	5	1.13	2.76	0.00	0.00	3.89	0.11
C	6	1.26	2.98	0.00	0.00	4.24	-0.24
N	1	1.48	3.28	0.00	0.00	4.76	0.24
O	1	1.94	4.40	0.00	0.00	6.33	-0.33
O	2	1.94	4.39	0.00	0.00	6.33	-0.33

Atomic Populations (Mulliken) of NSB							
Species	Ion	s	p	d	f	Total	Charge(e)
H	1	0.76	0.00	0.00	0.00	0.76	0.24
H	2	0.68	0.00	0.00	0.00	0.68	0.32
H	3	0.70	0.00	0.00	0.00	0.70	0.30
H	4	0.70	0.00	0.00	0.00	0.70	0.30
H	5	0.70	0.00	0.00	0.00	0.70	0.30
H	6	0.49	0.00	0.00	0.00	0.49	0.51
C	1	1.19	3.09	0.00	0.00	4.27	-0.27
C	2	1.19	3.10	0.00	0.00	4.29	-0.29
C	3	1.19	3.11	0.00	0.00	4.29	-0.29
C	4	1.19	3.08	0.00	0.00	4.27	-0.27
C	5	1.02	2.85	0.00	0.00	3.88	0.12
C	6	1.16	3.16	0.00	0.00	4.33	-0.33
N	1	1.64	3.49	0.00	0.00	5.13	-0.13
O	1	1.83	4.68	0.00	0.00	6.51	-0.51

Atomic Populations (Mulliken) of D-NSB							
Species	Ion	s	p	d	f	Total	Charge(e)
H	1	0.68	0.00	0.00	0.00	0.68	0.32
H	2	0.68	0.00	0.00	0.00	0.68	0.32
H	3	0.70	0.00	0.00	0.00	0.70	0.30
H	4	0.71	0.00	0.00	0.00	0.71	0.29
H	5	0.71	0.00	0.00	0.00	0.71	0.29
H	6	0.69	0.00	0.00	0.00	0.69	0.31
H	7	0.67	0.00	0.00	0.00	0.67	0.33
H	8	0.71	0.00	0.00	0.00	0.71	0.29
H	9	0.71	0.00	0.00	0.00	0.71	0.29
H	10	0.71	0.00	0.00	0.00	0.71	0.29
C	1	1.26	3.01	0.00	0.00	4.27	-0.27
C	2	1.26	3.01	0.00	0.00	4.27	-0.27
C	3	1.26	3.02	0.00	0.00	4.28	-0.28
C	4	1.26	3.00	0.00	0.00	4.26	-0.26
C	5	1.12	2.76	0.00	0.00	3.88	0.12
C	6	1.25	3.00	0.00	0.00	4.25	-0.25
C	7	1.26	3.01	0.00	0.00	4.27	-0.27

C	8	1.26	3.01	0.00	0.00	4.27	-0.27
C	9	1.26	3.03	0.00	0.00	4.28	-0.28
C	10	1.26	2.99	0.00	0.00	4.25	-0.25
C	11	1.26	3.01	0.00	0.00	3.88	0.12
C	12	1.25	2.99	0.00	0.00	4.25	-0.25
N	1	1.41	3.46	0.00	0.00	4.88	0.12
N	2	1.39	3.45	0.00	0.00	4.84	0.16
O	1	1.93	4.54	0.00	0.00	6.47	-0.47
O	2	1.90	4.54	0.00	0.00	6.45	-0.45

Atomic Populations (Mulliken) of NSB-H							
Species	Ion	s	p	d	f	Total	Charge(e)
H	1	0.68	0.00	0.00	0.00	0.68	0.32
H	2	0.68	0.00	0.00	0.00	0.68	0.32
H	3	0.69	0.00	0.00	0.00	0.69	0.31
H	4	0.69	0.00	0.00	0.00	0.69	0.31
H	5	0.69	0.00	0.00	0.00	0.69	0.31
C	1	1.19	3.10	0.00	0.00	4.29	-0.29
C	2	1.20	3.07	0.00	0.00	4.27	-0.27
C	3	1.19	3.09	0.00	0.00	4.28	-0.28
C	4	1.19	3.09	0.00	0.00	4.28	-0.28
C	5	1.05	2.83	0.00	0.00	3.88	0.12
C	6	1.19	3.07	0.00	0.00	4.27	-0.27
N	1	1.62	3.36	0.00	0.00	4.98	0.02
O	1	1.85	4.46	0.00	0.00	6.31	-0.31

Atomic Populations (Mulliken) of AOB							
Species	Ion	s	p	d	f	Total	Charge(e)
H	1	0.68	0.00	0.00	0.00	0.68	0.32
H	2	0.69	0.00	0.00	0.00	0.69	0.31
H	3	0.70	0.00	0.00	0.00	0.70	0.30
H	4	0.71	0.00	0.00	0.00	0.71	0.29
H	5	0.71	0.00	0.00	0.00	0.71	0.29
H	6	0.70	0.00	0.00	0.00	0.70	0.30
H	7	0.67	0.00	0.00	0.00	0.67	0.33
H	8	0.71	0.00	0.00	0.00	0.71	0.29
H	9	0.71	0.00	0.00	0.00	0.71	0.29
H	10	0.71	0.00	0.00	0.00	0.71	0.29
C	1	1.26	3.01	0.00	0.00	4.27	-0.27
C	2	1.26	3.01	0.00	0.00	4.27	-0.27
C	3	1.26	3.03	0.00	0.00	4.28	-0.28
C	4	1.25	3.00	0.00	0.00	4.26	-0.26
C	5	1.12	2.74	0.00	0.00	3.87	0.13
C	6	1.25	2.99	0.00	0.00	4.24	-0.24
C	7	1.26	3.02	0.00	0.00	4.27	-0.27
C	8	1.26	3.02	0.00	0.00	4.28	-0.28
C	9	1.26	3.03	0.00	0.00	4.28	-0.28
C	10	1.27	2.98	0.00	0.00	4.25	-0.25
C	11	1.13	2.75	0.00	0.00	3.88	0.12
C	12	1.25	3.02	0.00	0.00	4.27	-0.27
N	1	1.43	3.42	0.00	0.00	4.85	0.15
N	2	1.58	3.67	0.00	0.00	5.26	-0.26
O	1	1.92	4.55	0.00	0.00	6.48	-0.48

Atomic Populations (Mulliken) of AB							
Species	Ion	s	p	d	f	Total	Charge(e)
H	1	0.70	0.00	0.00	0.00	0.70	0.30
H	2	0.69	0.00	0.00	0.00	0.69	0.31
H	3	0.71	0.00	0.00	0.00	0.71	0.29
H	4	0.71	0.00	0.00	0.00	0.71	0.29
H	5	0.71	0.00	0.00	0.00	0.71	0.29
H	6	0.70	0.00	0.00	0.00	0.70	0.30
H	7	0.69	0.00	0.00	0.00	0.69	0.31
H	8	0.71	0.00	0.00	0.00	0.71	0.29
H	9	0.71	0.00	0.00	0.00	0.71	0.29
H	10	0.71	0.00	0.00	0.00	0.71	0.29
C	1	1.26	3.02	0.00	0.00	4.27	-0.27
C	2	1.26	3.02	0.00	0.00	4.28	-0.28
C	3	1.26	3.03	0.00	0.00	4.28	-0.28
C	4	1.25	3.00	0.00	0.00	4.26	-0.26
C	5	1.13	2.74	0.00	0.00	3.87	0.13
C	6	1.26	3.01	0.00	0.00	4.26	-0.26
C	7	1.26	3.02	0.00	0.00	4.27	-0.27
C	8	1.26	3.02	0.00	0.00	4.28	-0.28
C	9	1.26	3.03	0.00	0.00	4.28	-0.28
C	10	1.26	3.00	0.00	0.00	4.26	-0.26
C	11	1.13	2.74	0.00	0.00	3.87	0.13
C	12	1.26	3.01	0.00	0.00	4.26	-0.26
N	1	1.60	3.65	0.00	0.00	5.25	-0.25
N	2	1.59	3.66	0.00	0.00	5.25	-0.25

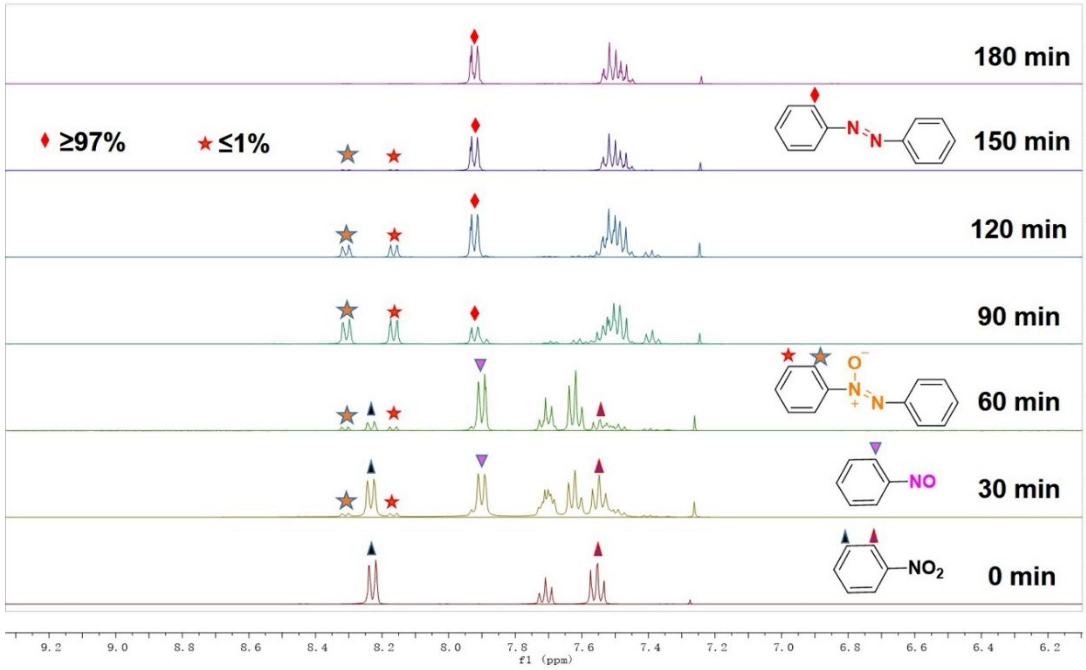


Figure S19. [1]H NMR analysis of the crude products during different reaction time recorded in $CDCl_3$ for mechanistic study**.**

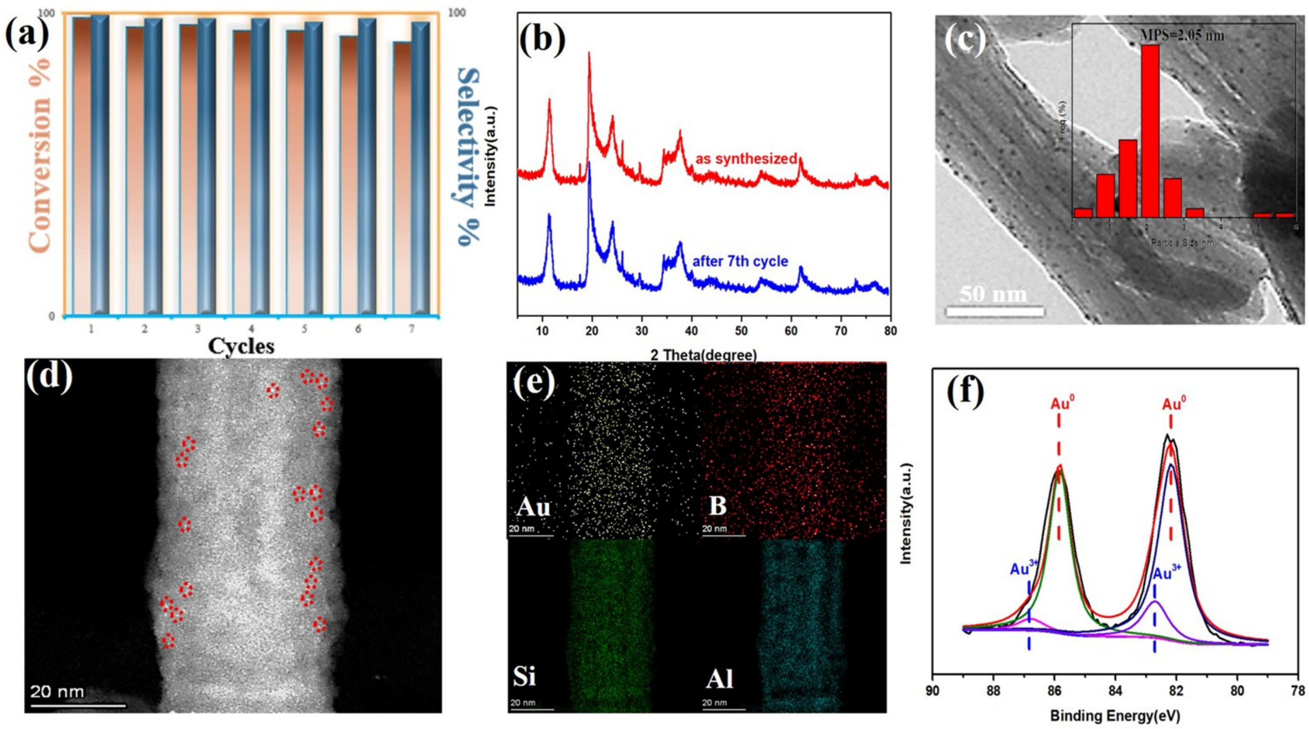
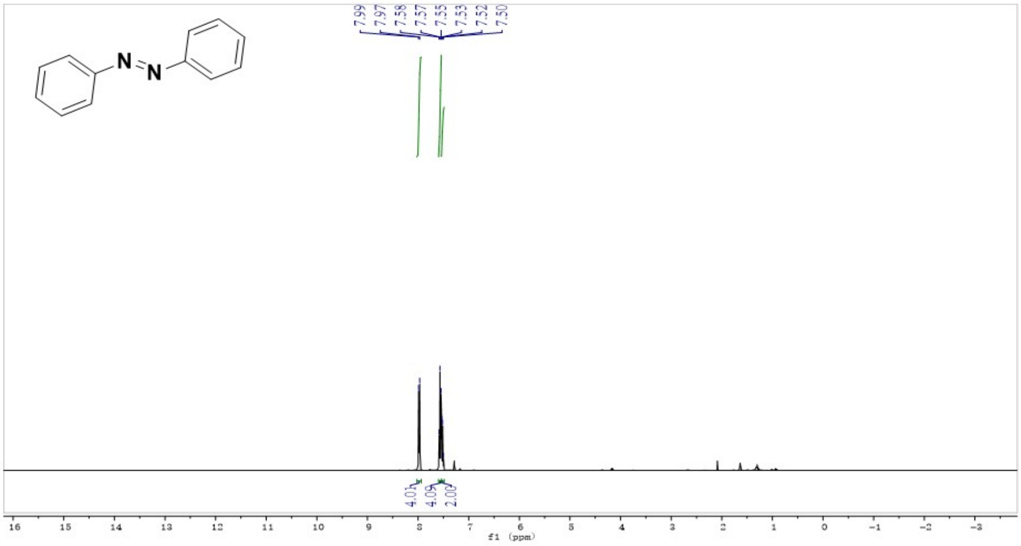
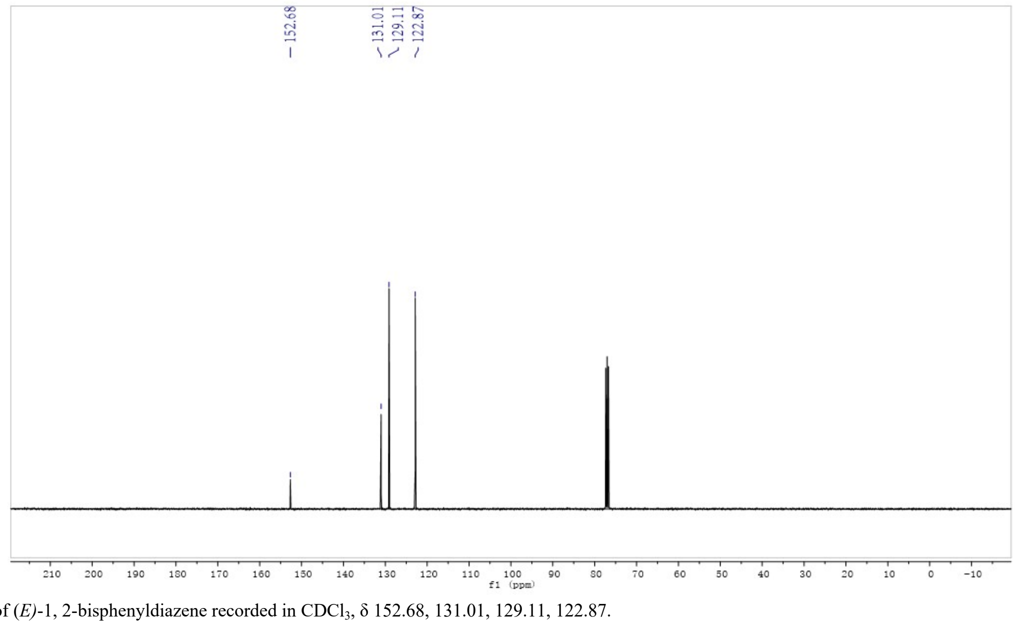


Figure S20. (a) Reusability of HNT@$B_{12}H_{12}$@Au (conversions and selectivity are based on GC), (b) PXRD of recycled HNT@$B_{12}H_{12}$@Au after seven cycles, (c) HRTEM of recycled HNT@$B_{12}H_{12}$@Au after seven cycles, (d) HAADF-STEM image of HNT@$B_{12}H_{12}$@Au after 7th use, and representative B, Au, Al, Si elemental mapping of (e), (f) XPS spectra of Au on the recycled HNT@$B_{12}H_{12}$@Au.

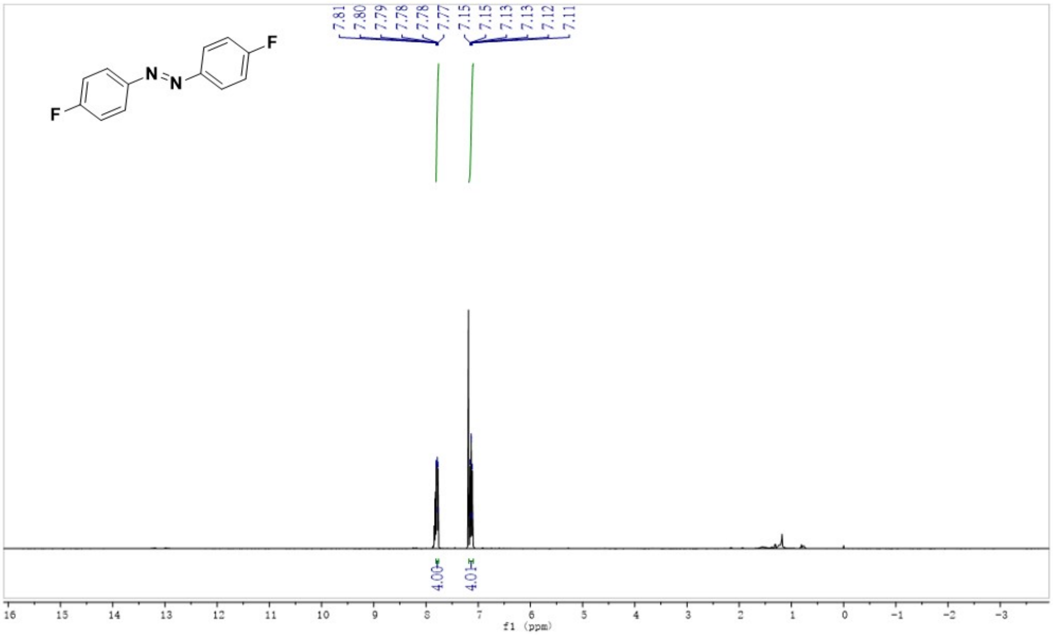
Spectroscopic characterizations of the azo products



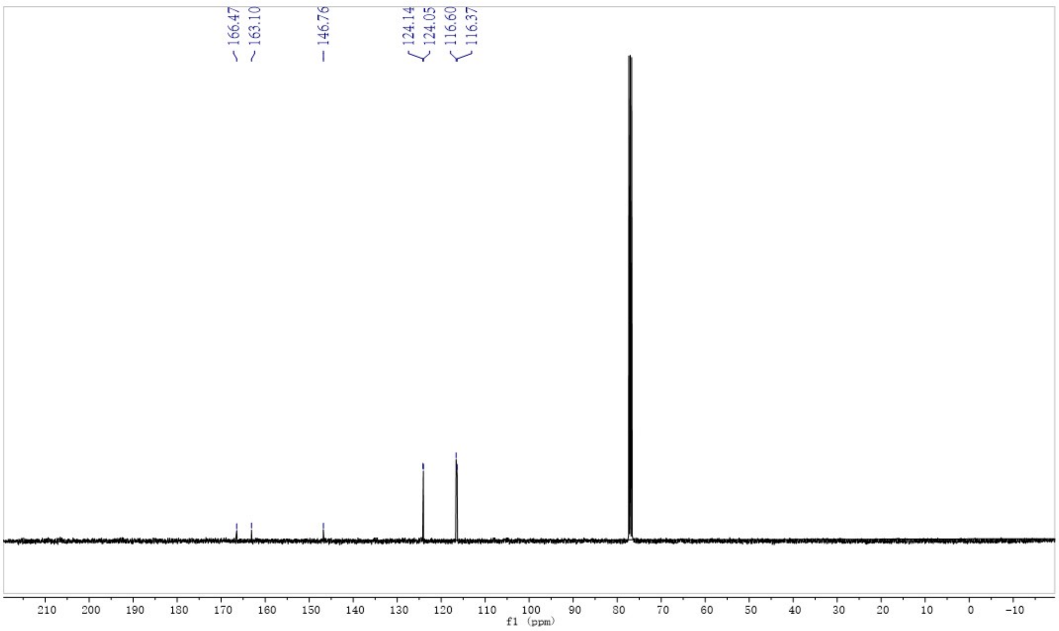
[1]H NMR spectrum of (*E*)-1, 2-bisphenyldiazene recorded in $CDCl_3$, δ 7.99-7.97 (m, 4H), 7.58-7.50 (m, 6H).



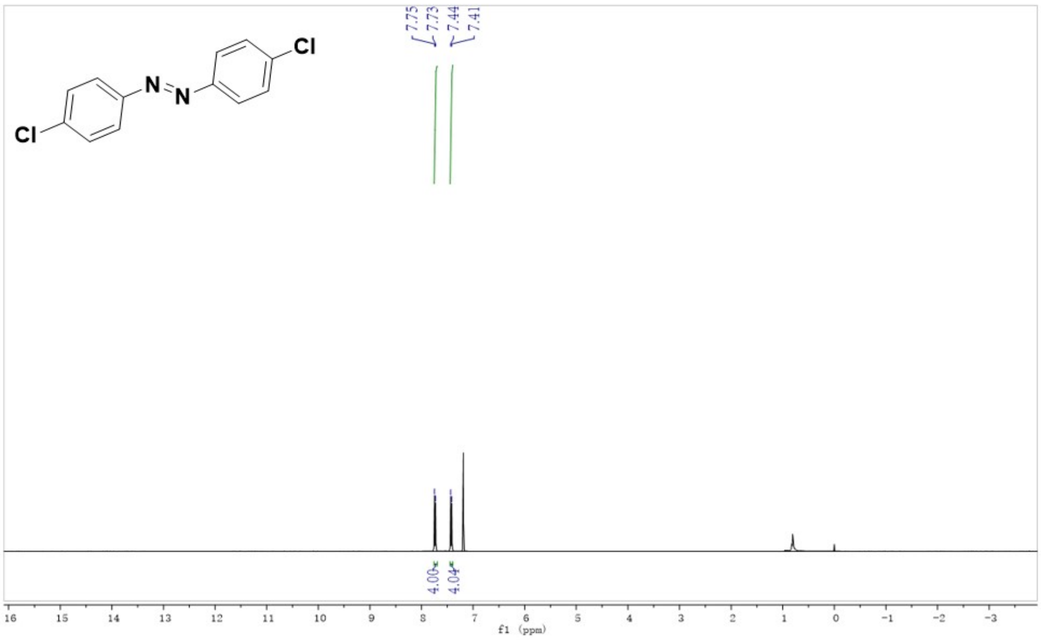
[13]C NMR spectrum of (*E*)-1, 2-bisphenyldiazene recorded in $CDCl_3$, δ 152.68, 131.01, 129.11, 122.87.



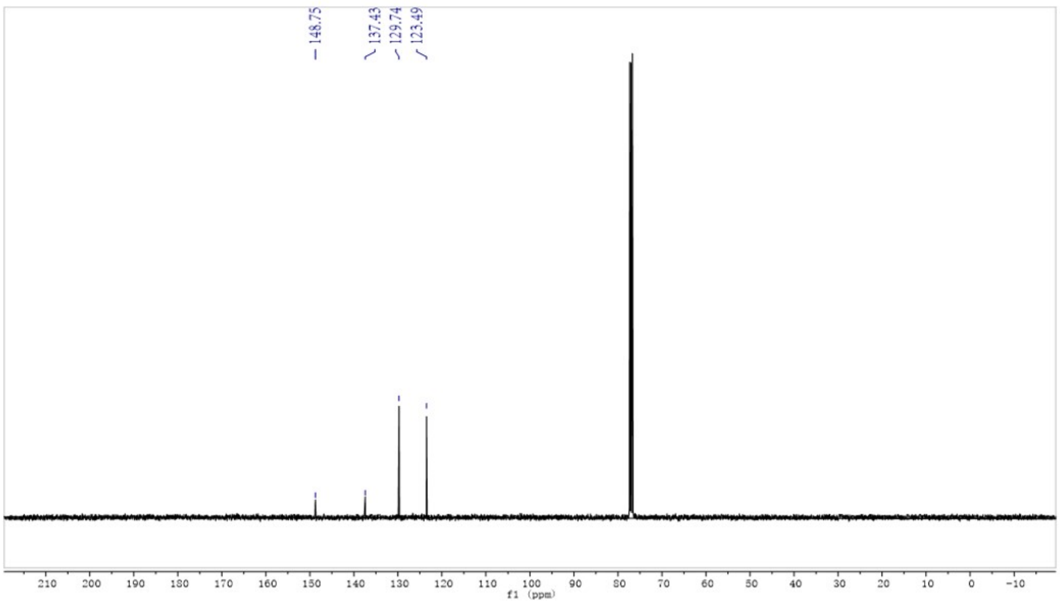
[1]H NMR spectrum of *(E)*-1, 2-bis (4-fluorophenyl)diazene recorded in $CDCl_3$, δ 7.81-7.77 (m, 4H), 7.15-7.11 (m, 4H).



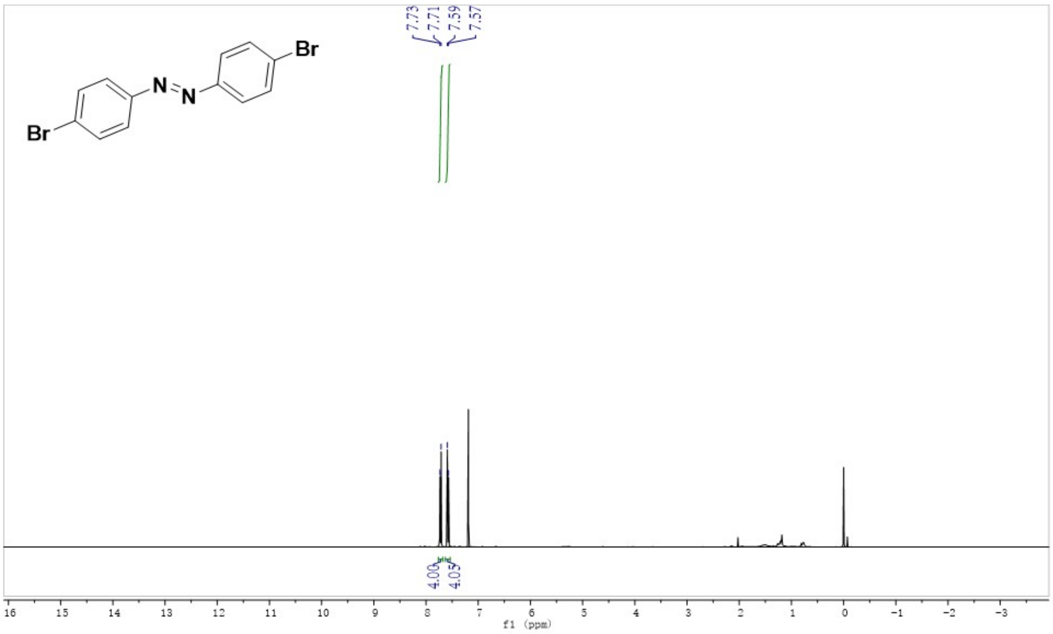
[13]C NMR spectrum of *(E)*-1, 2-bis (4-fluorophenyl)diazene recorded in $CDCl_3$, δ 166.47(d, *J* = 337Hz), 146.76, 124.14(d, *J* = 9 Hz), 116.60(d, *J* = 23 Hz).



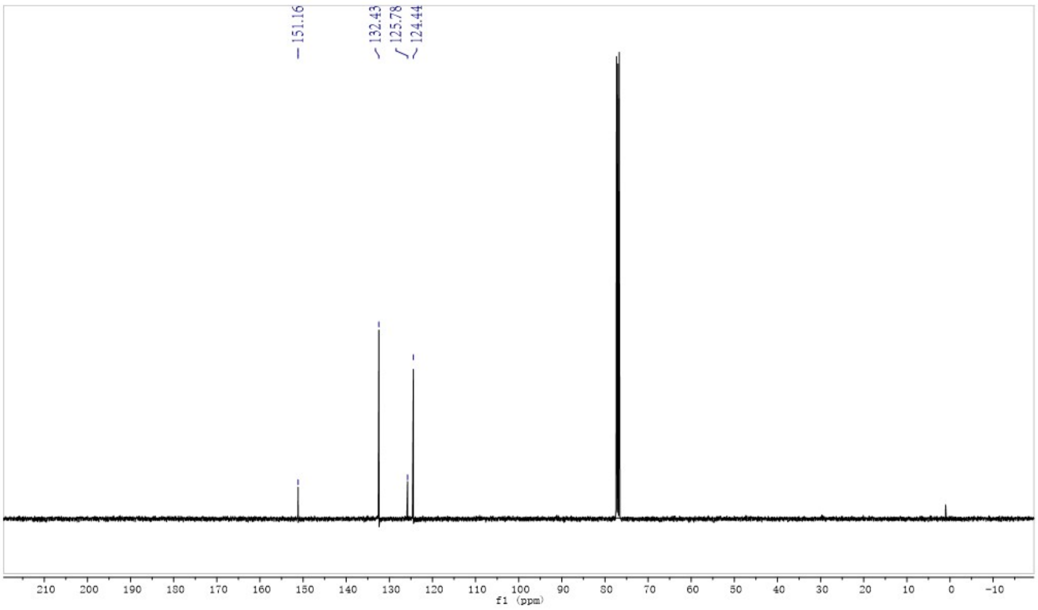
[1]H NMR spectrum of *(E)*- 1, 2-bis(4-chlorophenyl)diazene recorded in $CDCl_3$, δ 7.75-7.73 (d, *J*=8 Hz, 4H), 7.44-7.41 (d, *J*=12 Hz,4H).



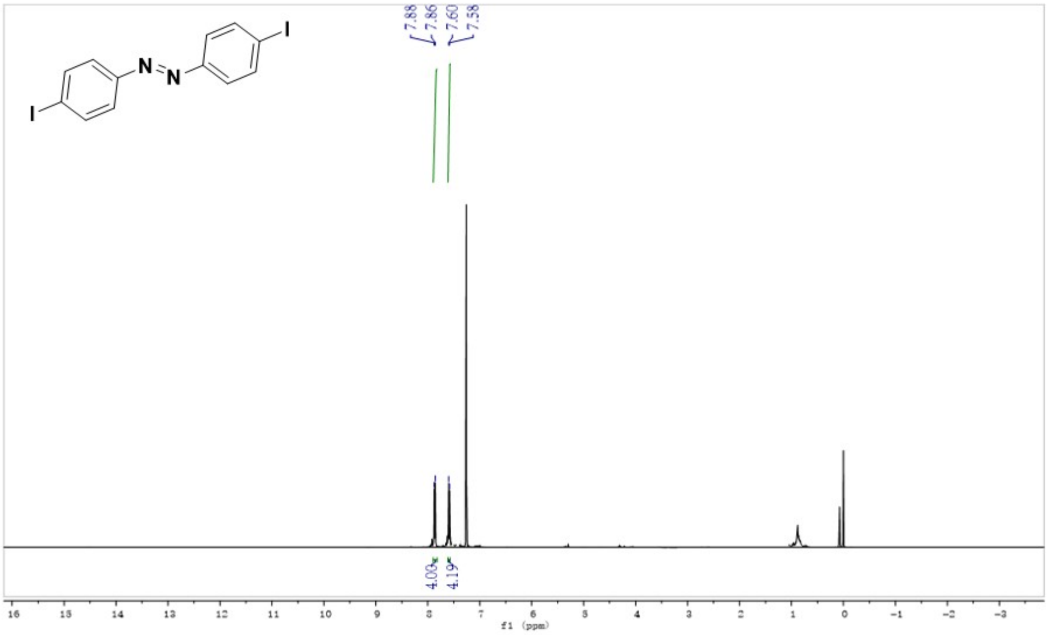
[13]C NMR spectrum of *(E)*- 1, 2-bis(4-chlorophenyl)diazene recorded in $CDCl_3$, δ 148.85, 137.43, 129.74, 123.49.



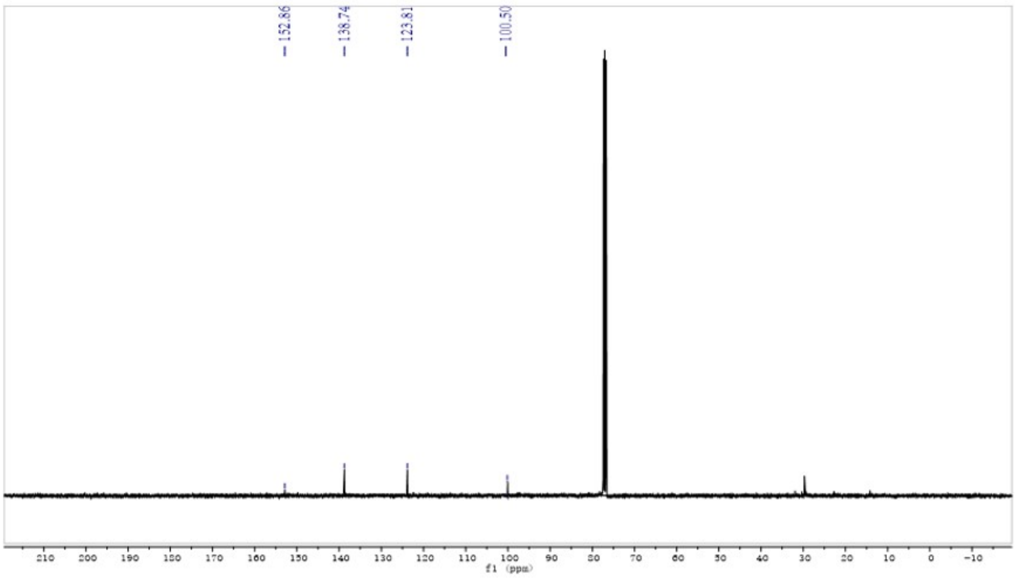
[1]H NMR spectrum of *(E)* -1,2-bis(4-bromophenyl)diazene recorded in $CDCl_3$, δ 7.73-7.71 (d, *J*=8 Hz, 4H), 7.59-7.57 (d, *J*=8 Hz, 4H).



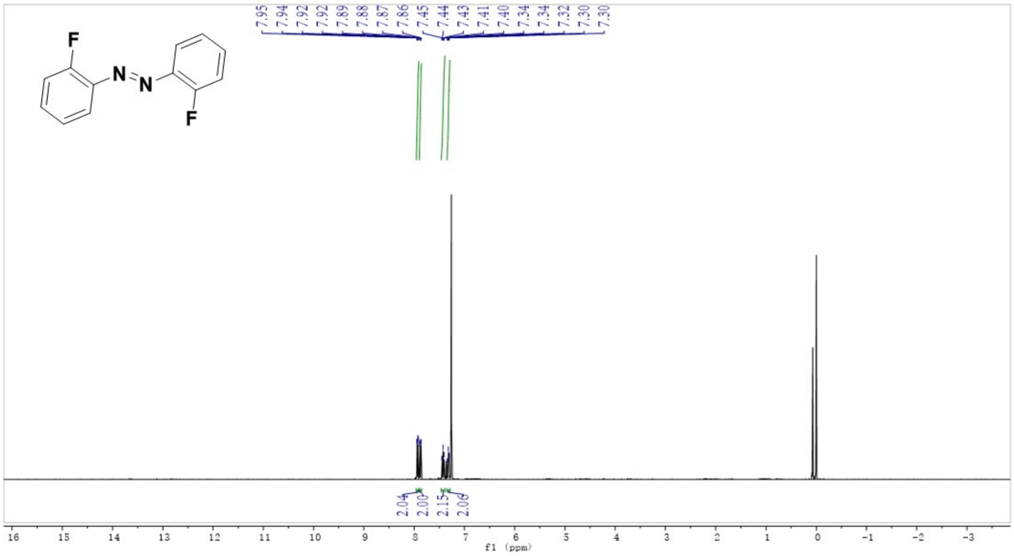
[13]C NMR spectrum of *(E)* -1,2-bis(4-bromophenyl)diazene recorded in $CDCl_3$, δ 151.16, 132.43, 125.78, 124.44.



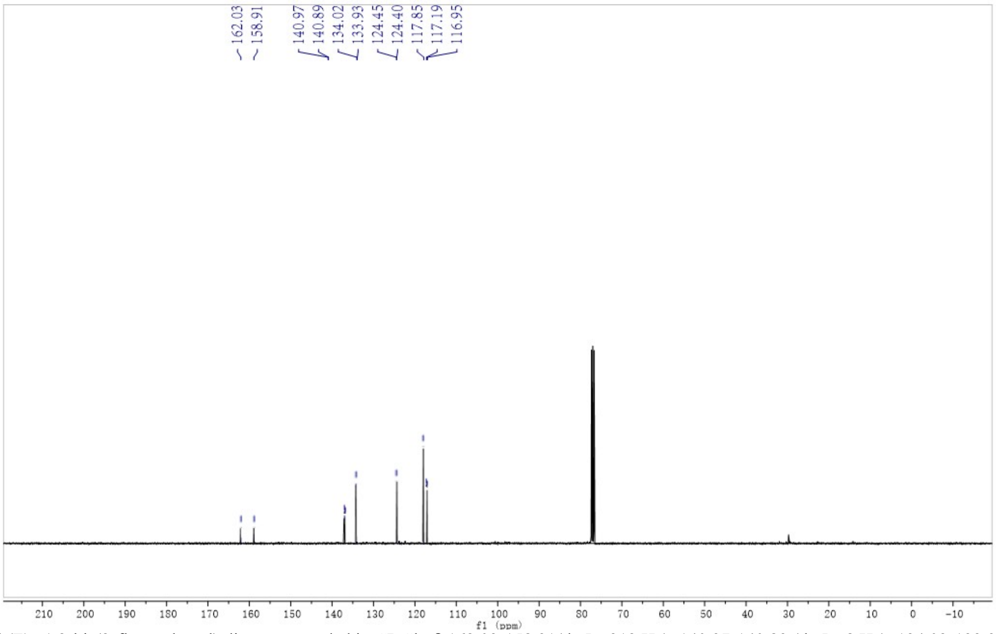
[1]H NMR spectrum of *(E)* - 1,2-bis(4-iodophenyl) diazene recorded in $CDCl_3$, δ 7.88-7.86 (d, *J*=8 Hz, 4H), 7.60-7.58 (d, *J*=8 Hz, 4H).



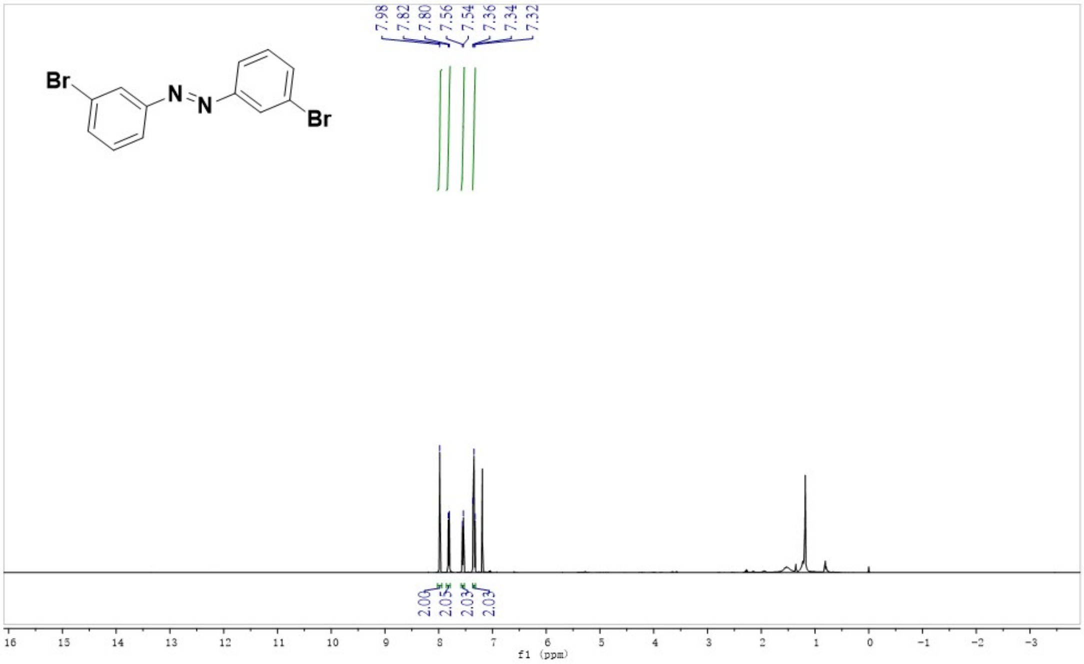
[13]C NMR spectrum of *(E)* - 1,2-bis(4-iodophenyl) diazene recorded in $CDCl_3$, δ 152.86, 128.74, 123.81, 100.50.



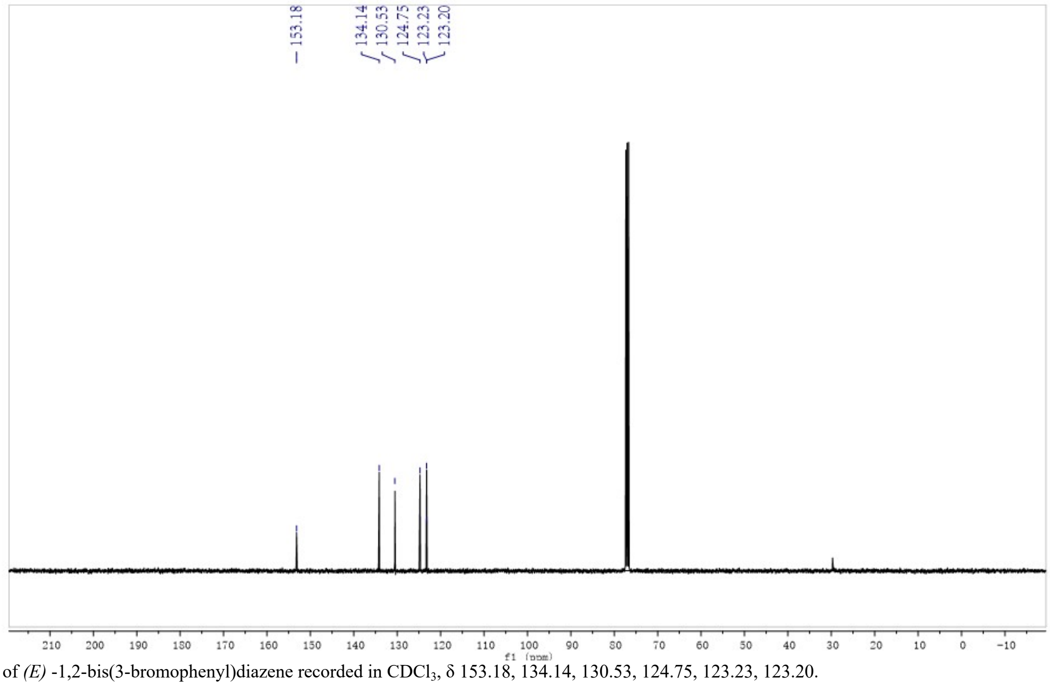
^{1}H NMR spectrum of *(E)* - 1,2-bis(2-fluorophenyl) diazene recorded in $CDCl_3$, δ 7.95-7.92 (m, 2H), 7.89-7.86 (m, 2H), 7.45-7.40(m, 2H), 7.34-7.30(m, 2H).



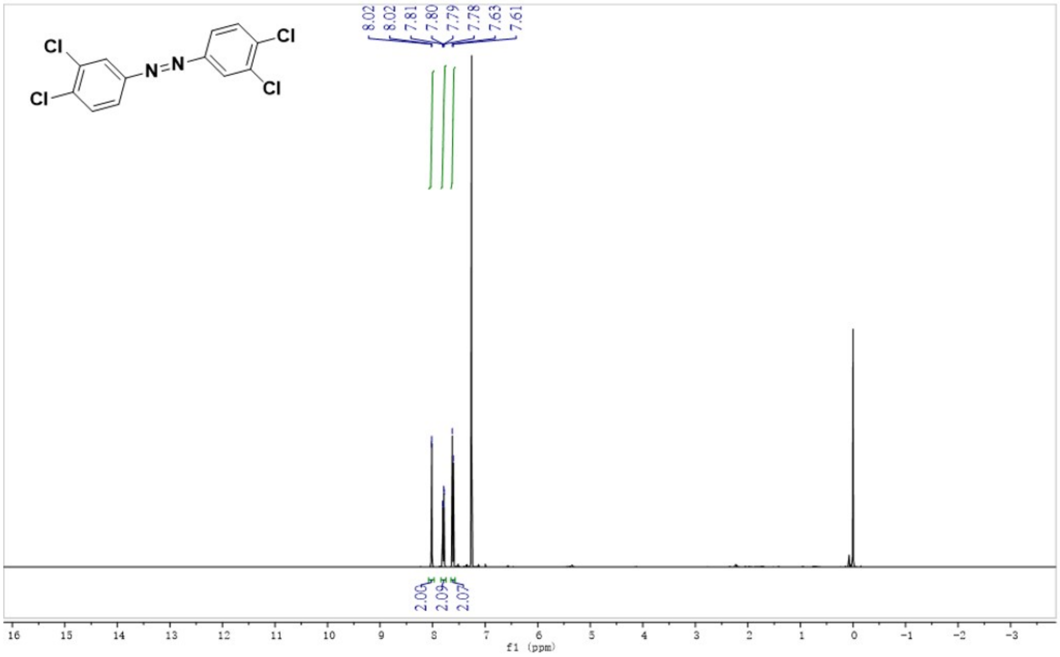
^{13}C NMR spectrum of *(E)* - 1,2-bis(2-fluorophenyl) diazene recorded in $CDCl_3$, δ 162.03-158.91(d, *J* = 312 Hz), 140.97-140.89 (d, *J* = 8 Hz), 134.02-133.93 (d, *J*= 9 Hz), 124.45-124.40 (d, *J* = 5Hz), 117.85, 117.19-116.95 (d, *J* = 24 Hz).



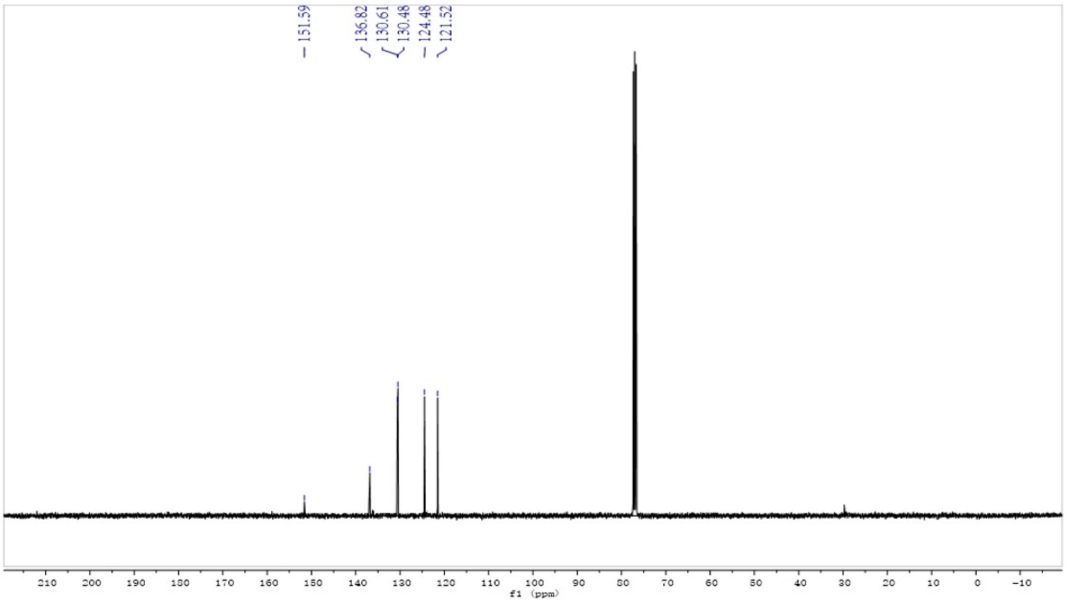
[1]H NMR spectrum of *(E)* -1,2-bis(3-bromophenyl)diazene recorded in $CDCl_3$, δ 7.98 (s, 2H), 7.82-7.80 (d, *J*=8 Hz, 2H), 7.56-7.54(d, *J*=8 Hz, 2H), 7.36-7.32(t, *J*=16 Hz, 2H).



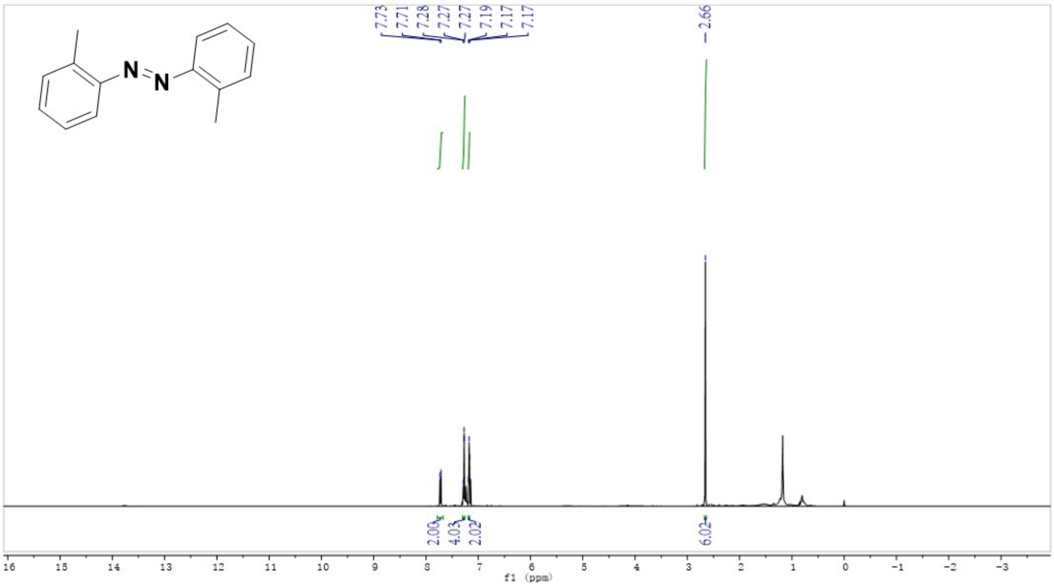
[13]C NMR spectrum of *(E)* -1,2-bis(3-bromophenyl)diazene recorded in $CDCl_3$, δ 153.18, 134.14, 130.53, 124.75, 123.23, 123.20.



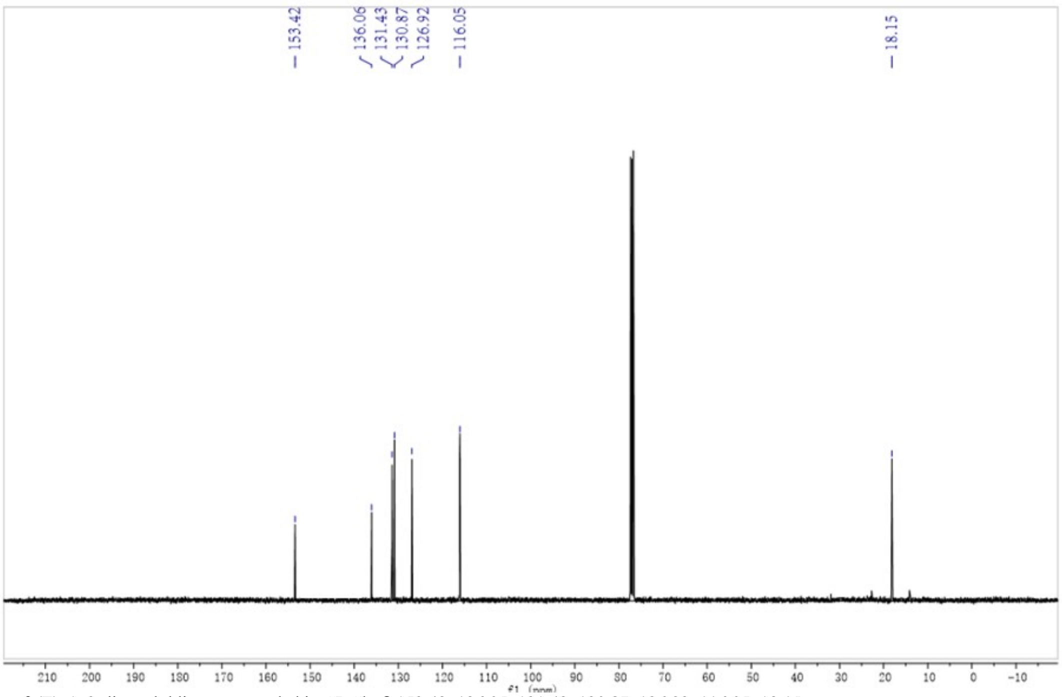
[1]H NMR spectrum of *(E)* -1,2-bis(3,4-dichlorophenyl)diazene recorded in $CDCl_3$, δ 8.02 (s, 2H), 7.81-7.78 (d, *J*=12 Hz, 2H), 7.63-7.61(d, *J*=8 Hz, 2H).



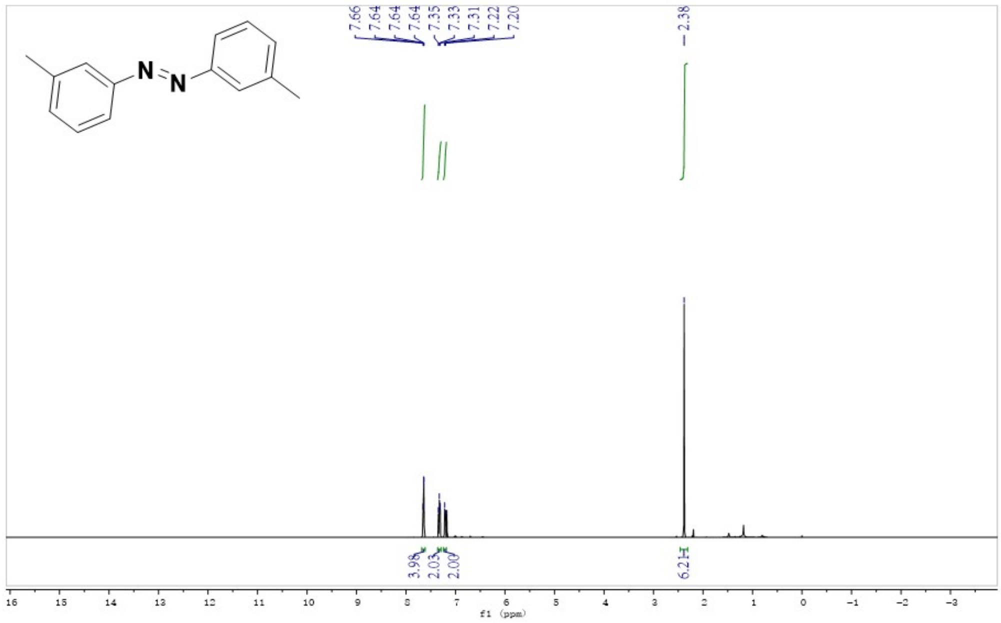
[13]C NMR spectrum of *(E)* -1,2-bis(3,4-dichlorophenyl)diazene recorded in $CDCl_3$, δ 151.59, 136.82, 130.61, 130.48, 124.48, 121.52.



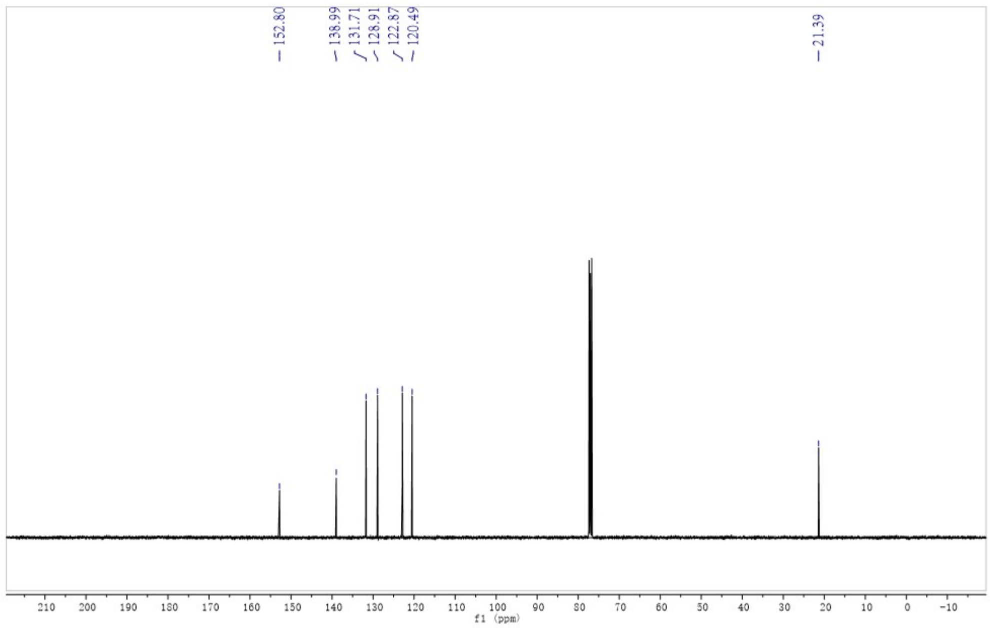
^{1}H NMR spectrum of *(E)* -1, 2-di-o-tolyldiazene recorded in $CDCl_3$, δ 7.73-7.71 (m, 2H), 7.28-7.27 (m, 4H), 7.19-7.17(m, 2H), 2.66(s, 6H).



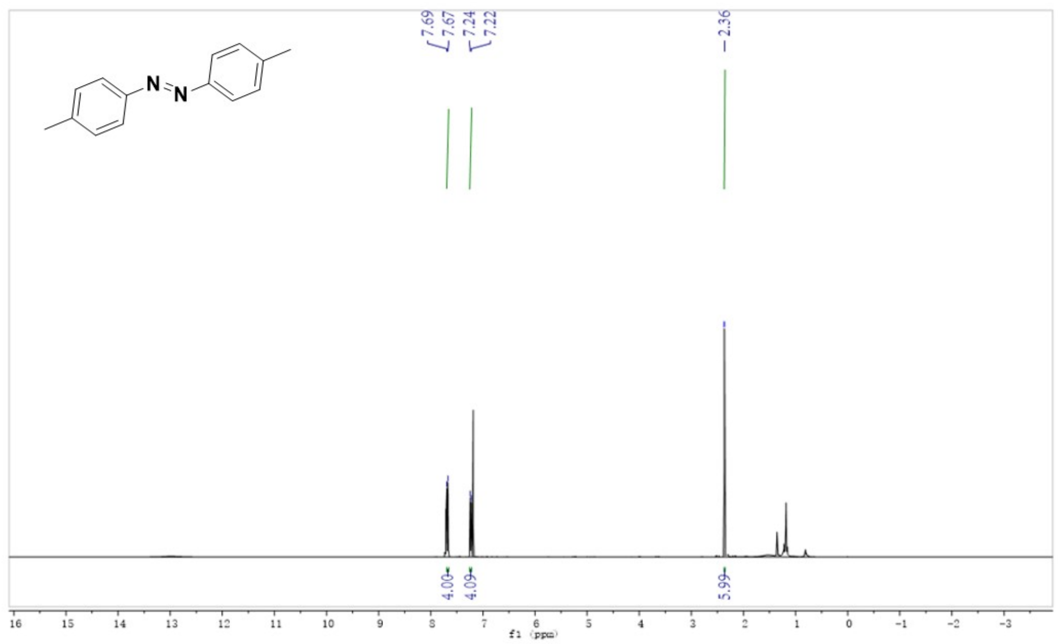
^{13}C NMR spectrum of *(E)* -1, 2-di-o-tolyldiazene recorded in $CDCl_3$, δ 153.42, 136.05, 131.43, 130.87, 126.92, 116.05, 18.15.



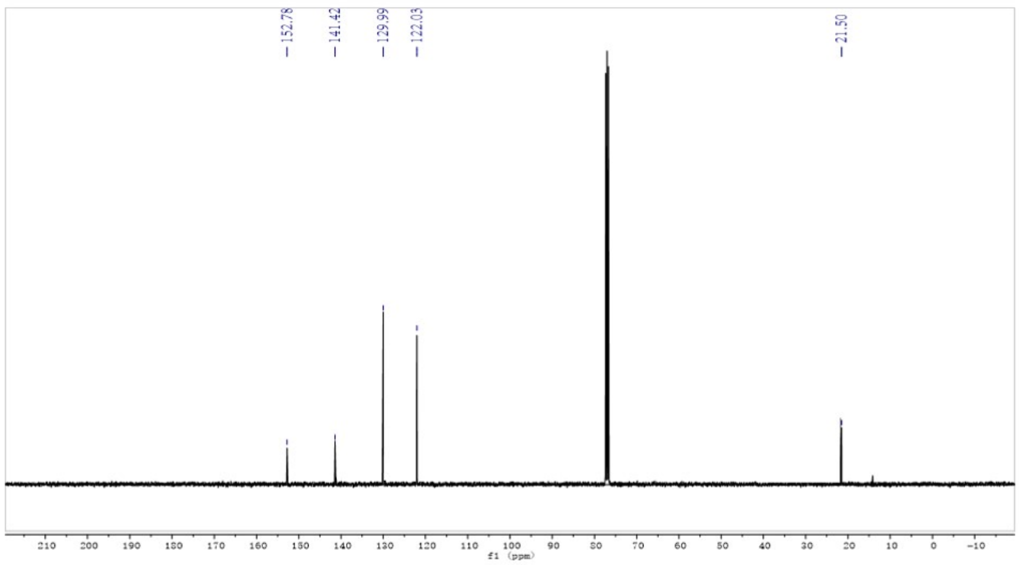
[1]H NMR spectrum of *(E)* -1, 2-di-m-tolyldiazene recorded in $CDCl_3$, δ 7.66-7.64 (m, 4H), 7.35- 7.31(t, *J*=16 Hz, 2H), 7.22-7.20(d, *J*=8 Hz, 2H), 2.38(s, 6H).



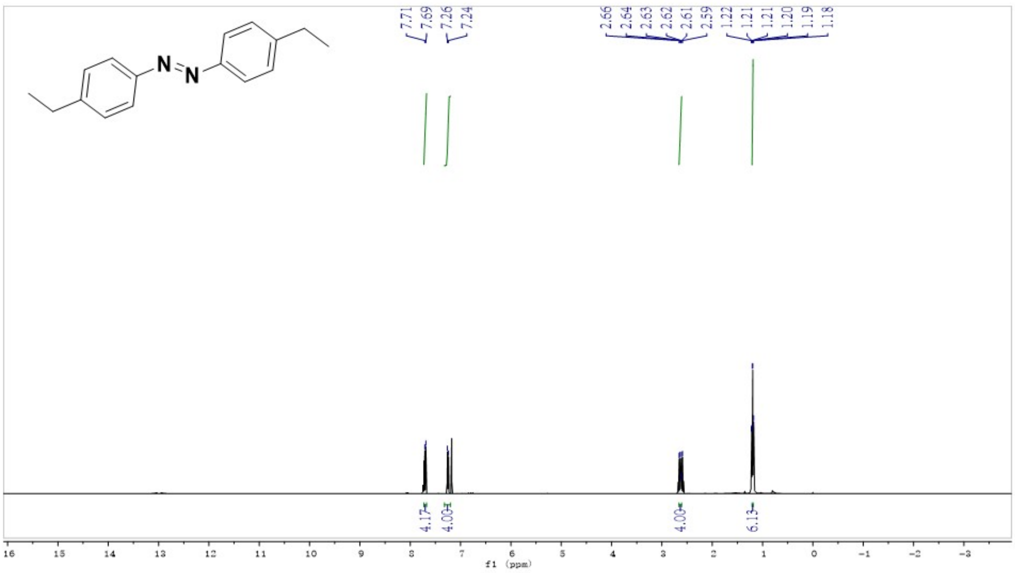
[13]C NMR spectrum of *(E)* -1, 2-di-m-tolyldiazene recorded in $CDCl_3$, δ 152.80, 138.99, 131.71, 128.91, 122.87, 120.49, 21.39.



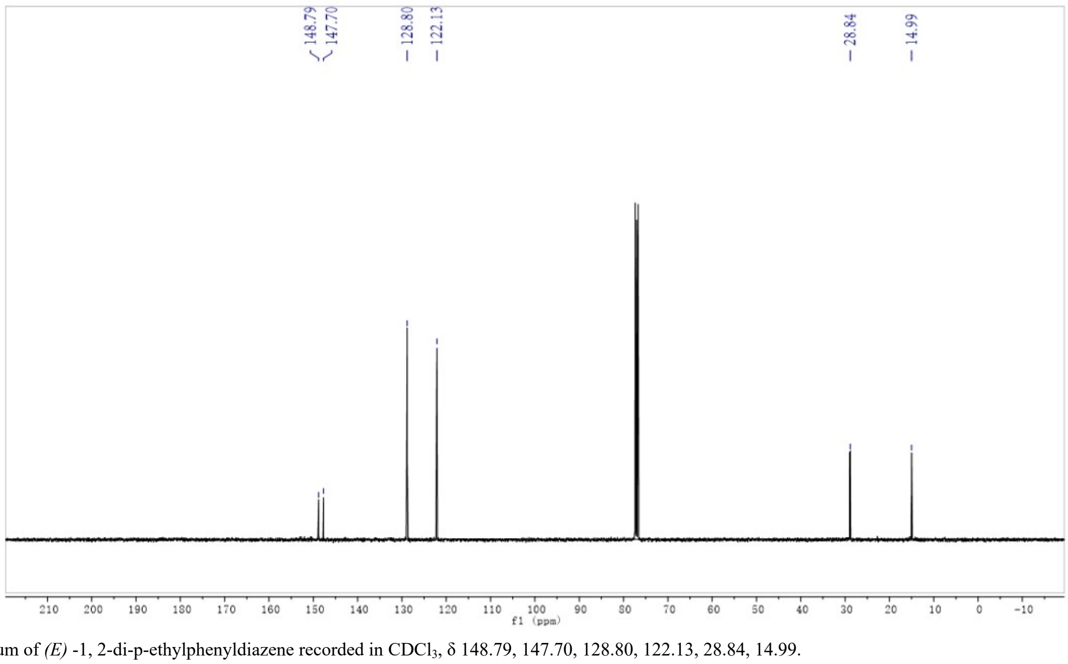
[1]H NMR spectrum of *(E)* -1, 2-di-p-tolyldiazene recorded in $CDCl_3$, δ 7.69-7.67 (d, *J*=8 Hz, 4H), 7.24- 7.22(d, *J*=8 Hz, 4H), 2.36(s, 6H).



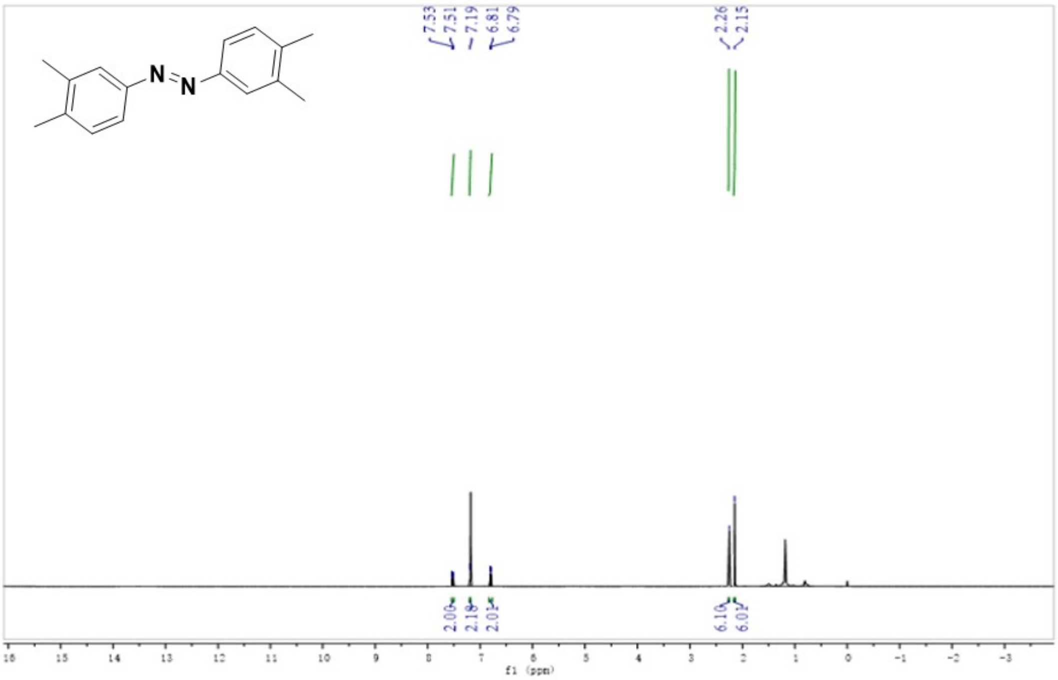
[13]C NMR spectrum of *(E)* -1, 2-di-p-tolyldiazene recorded in $CDCl_3$, δ 152.78, 141.42, 129.99, 122.03, 21.50.



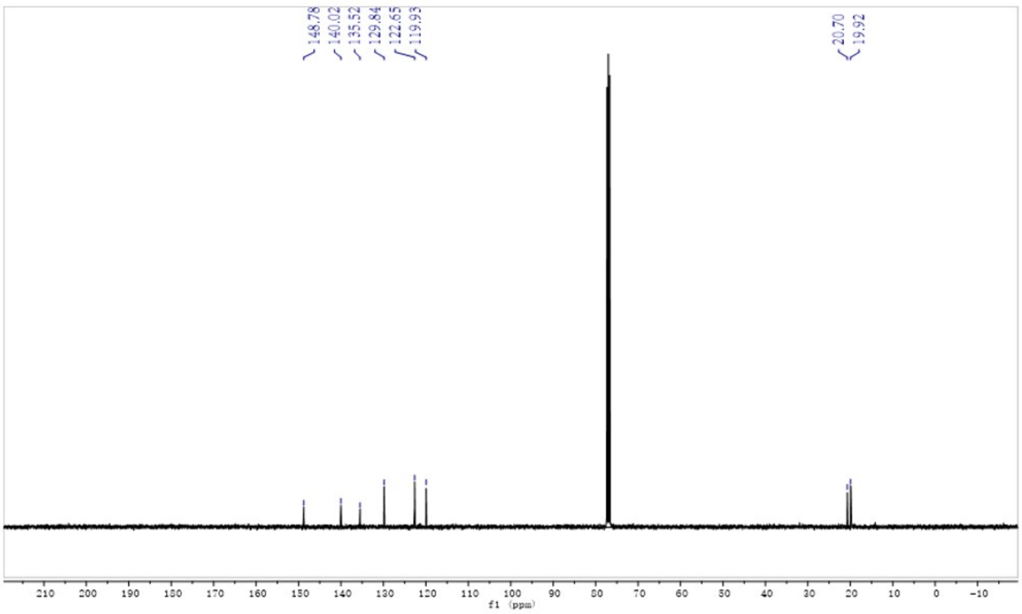
[1]H NMR spectrum of *(E)* -1, 2-di-p-ethylphenyldiazene recorded in $CDCl_3$, δ 7.71-7.69 (d, *J*=8 Hz, 4H), 7.26- 7.24(d, *J*=8 Hz, 4H), 2.66-2.59(m, 4H), 1.22-1.18(t, *J*=16 Hz, 6H).



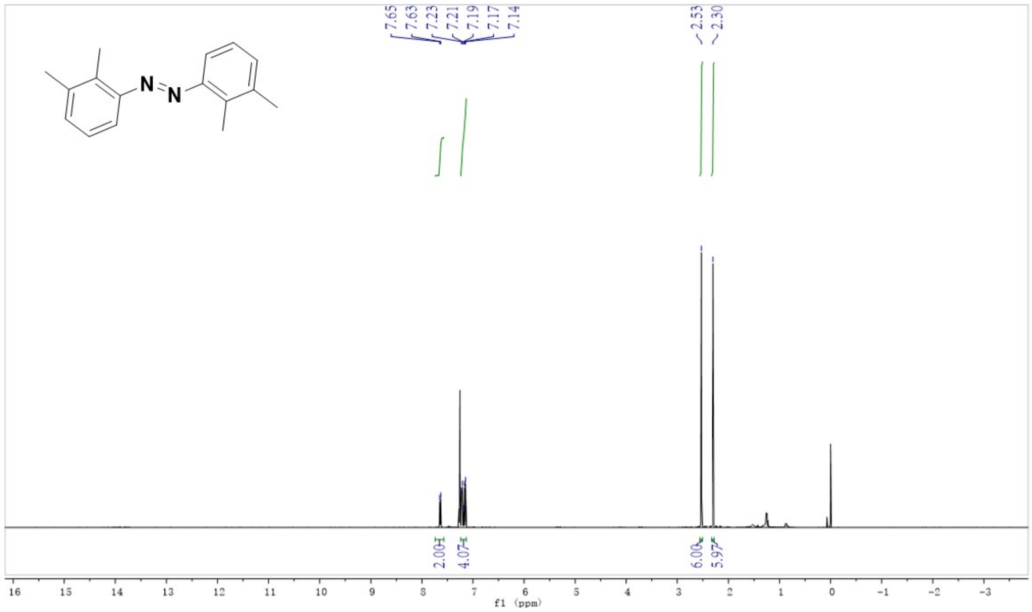
[13]C NMR spectrum of *(E)* -1, 2-di-p-ethylphenyldiazene recorded in $CDCl_3$, δ 148.79, 147.70, 128.80, 122.13, 28.84, 14.99.



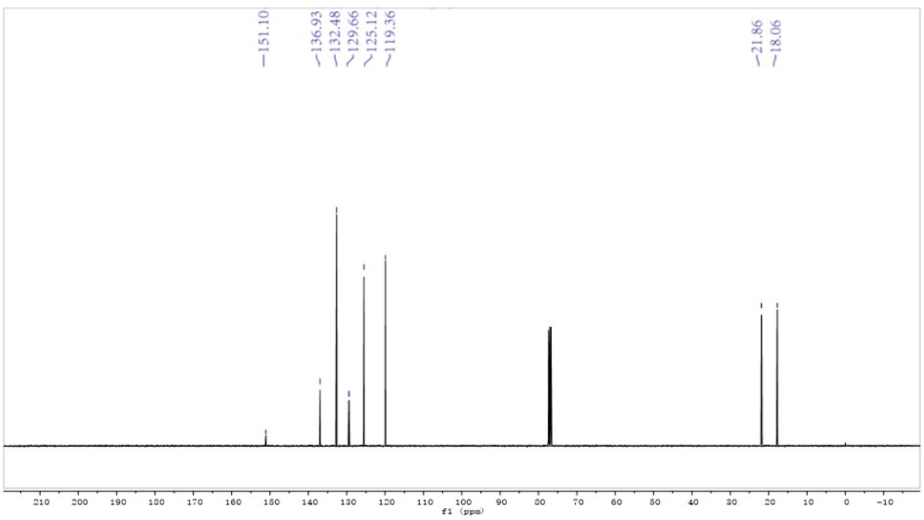
[1]H NMR spectrum of *(E)* - 1, 2-bis(3,4-dimethylphenyl)diazene recorded in $CDCl_3$, δ 7.53-7.41 (d, *J*=8 Hz, 2H), 7.19(s, 2H), 6.81-6.79(d, *J*=8 Hz, 2H), 2.26(s, 6H), 2.15(s, 6H).



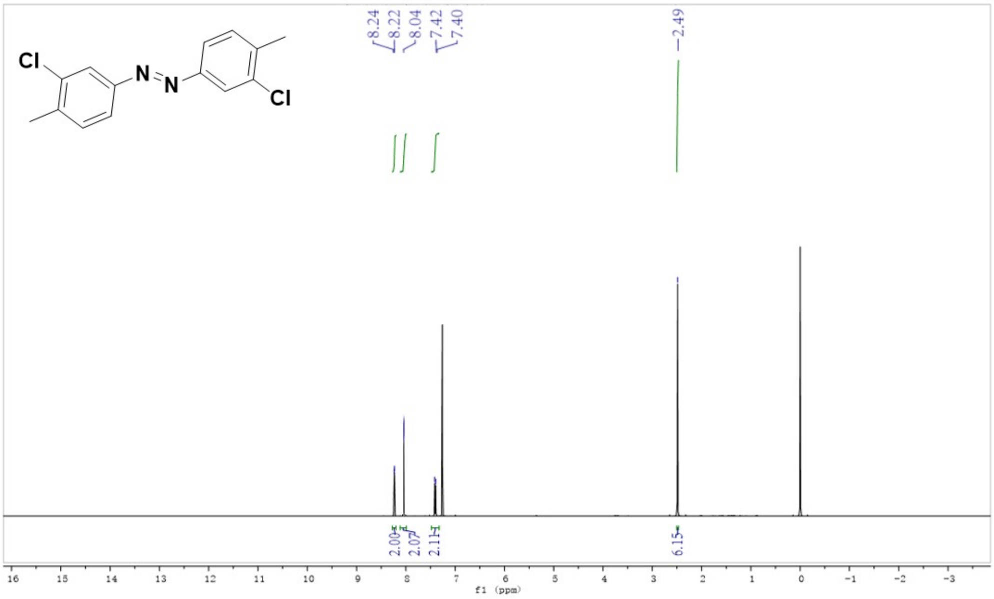
[13]C NMR spectrum of *(E)* - 1, 2-bis(3,4-dimethylphenyl)diazene recorded in $CDCl_3$, δ 148.78, 140.02, 135.52, 129.84, 122.65, 119.93, 20.70, 19.92.



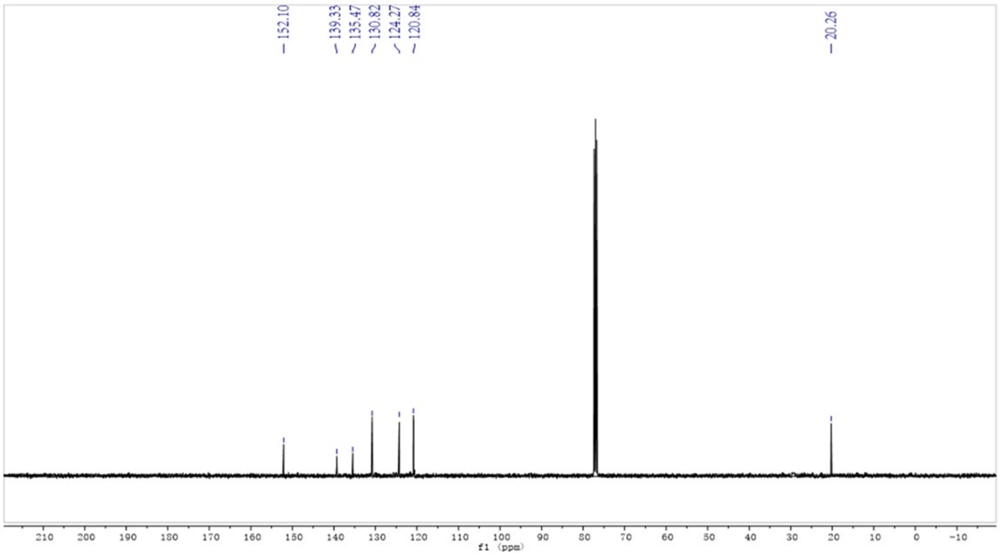
[1]H NMR spectrum of *(E)* - 1, 2-bis(2, 3-dimethylphenyl)diazene recorded in $CDCl_3$, δ 7.65-7.63 (d, *J*=8 Hz, 2H), 7.23-7.14(m, 4H), 2.53(s, 6H), 2.30(s, 6H).



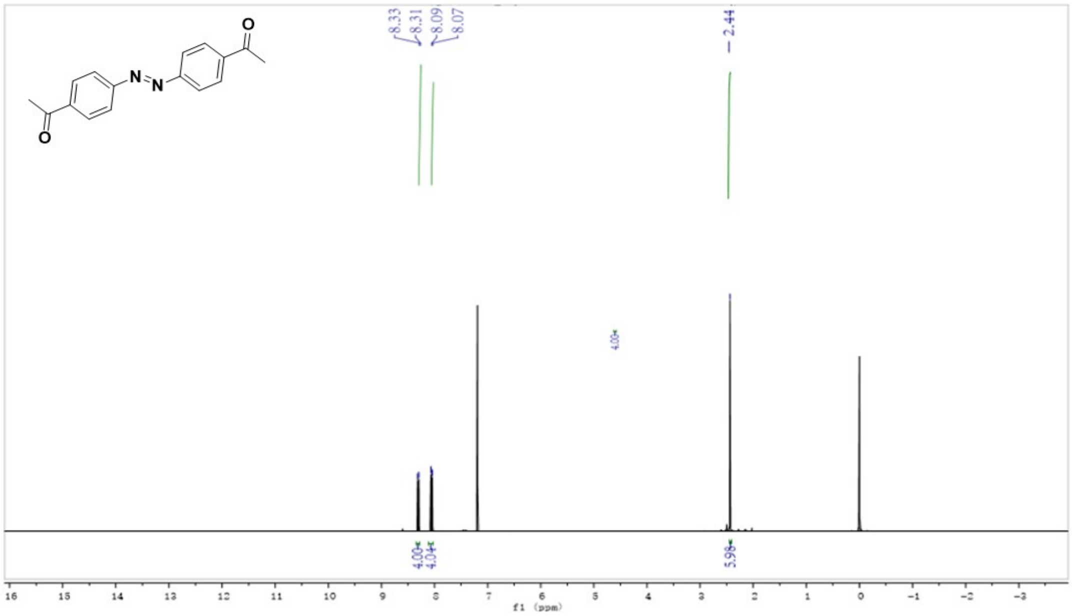
[13]C NMR spectrum of *(E)* - 1, 2-bis(2, 3-dimethylphenyl)diazene recorded in $CDCl_3$, δ 151.10, 136.93, 132.48, 129.99, 125.12, 119.36, 21.86, 18.06.



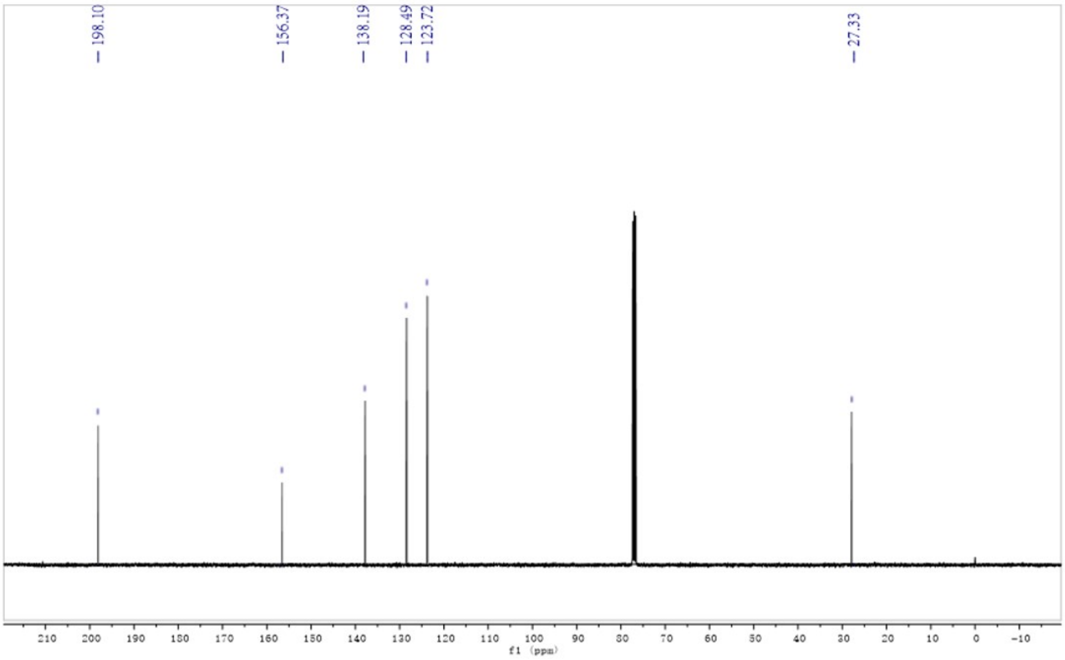
[1]H NMR spectrum of *(E)* - 1, 2-bis(3- chloro, 4-methylphenyl)diazene recorded in $CDCl_3$, δ 8.24-8.22 (d, *J*=8 Hz, 2H), 8.04(s, 2H), 7.42-7.40(d, *J*=8 Hz, 2H), 2.49(s, 6H).



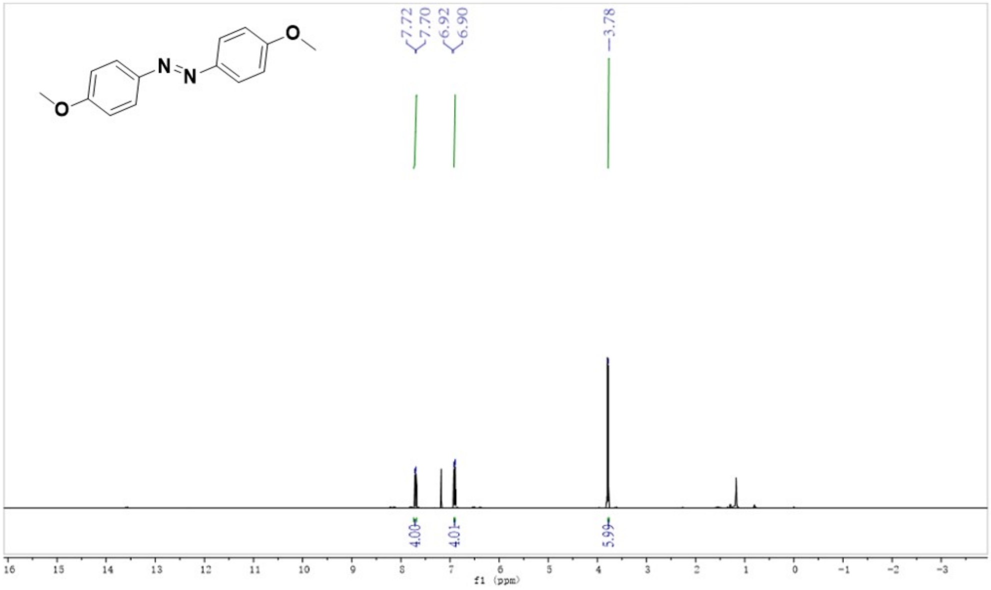
[13]C NMR spectrum of *(E)* - 1, 2-bis(3- chloro, 4-methylphenyl)diazene recorded in $CDCl_3$, δ 152.10, 139.33, 135.47, 130.82, 124.27, 120.84, 20.26.



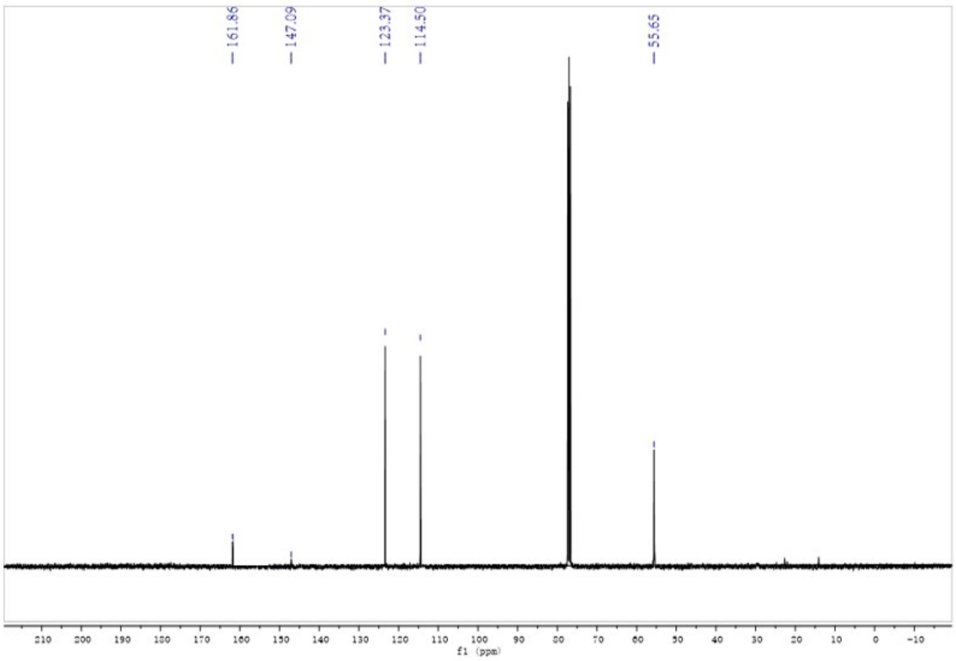
[1]H NMR spectrum of *(E)* - 1, 2-bis(4-acetophenyl))diazene recorded in $CDCl_3$, δ 8.33-8.31 (d, *J*=8 Hz, 2H), 8.09-8.07(d, *J*=8 Hz, 2H), 2.44(s, 6H).



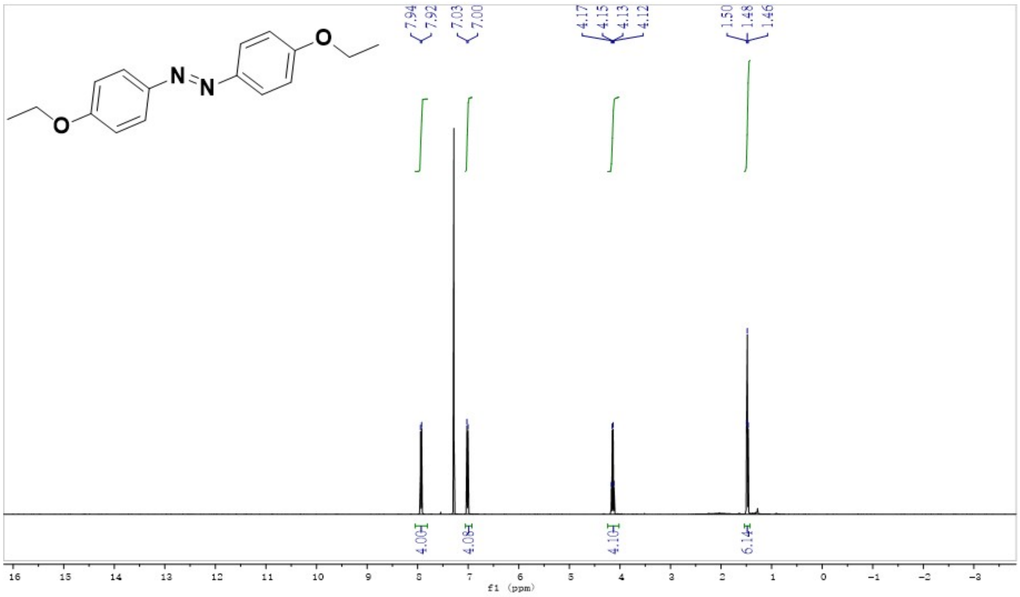
[13]C NMR spectrum of *(E)* - 1, 2-bis(4-acetophenyl))diazene recorded in $CDCl_3$, δ 198.10, 156.37, 138.19, 128.49, 123.72, 27.33.



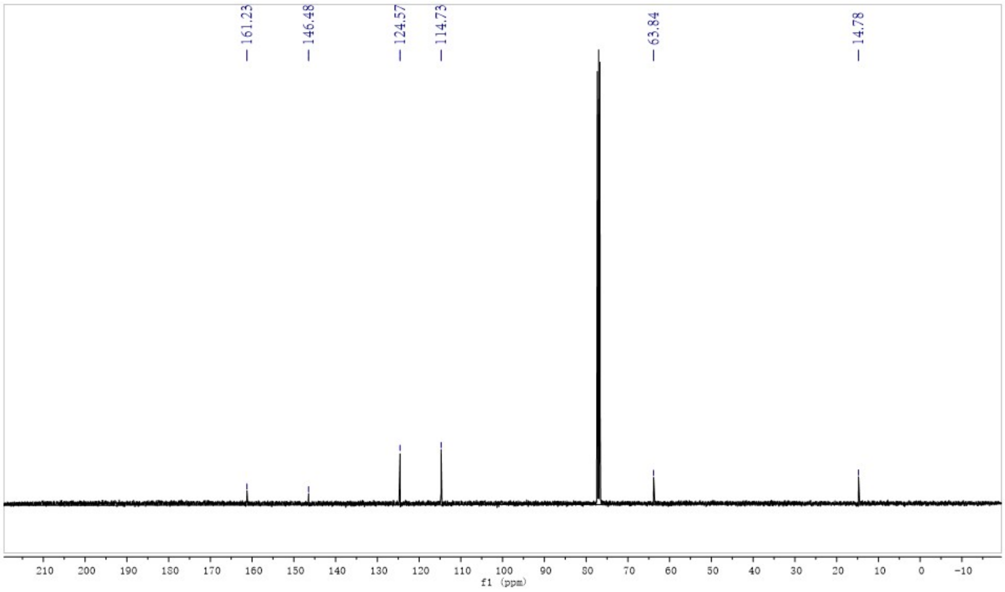
^{1}H NMR spectrum of *(E)* - 1, 2-bis(4-methoxylphenyl)diazene recorded in $CDCl_3$, δ 7.72-7.70 (d, *J*=8 Hz, 4H), 6.92-6.90(d, *J*=8 Hz, 2H), 3.78(s, 6H).



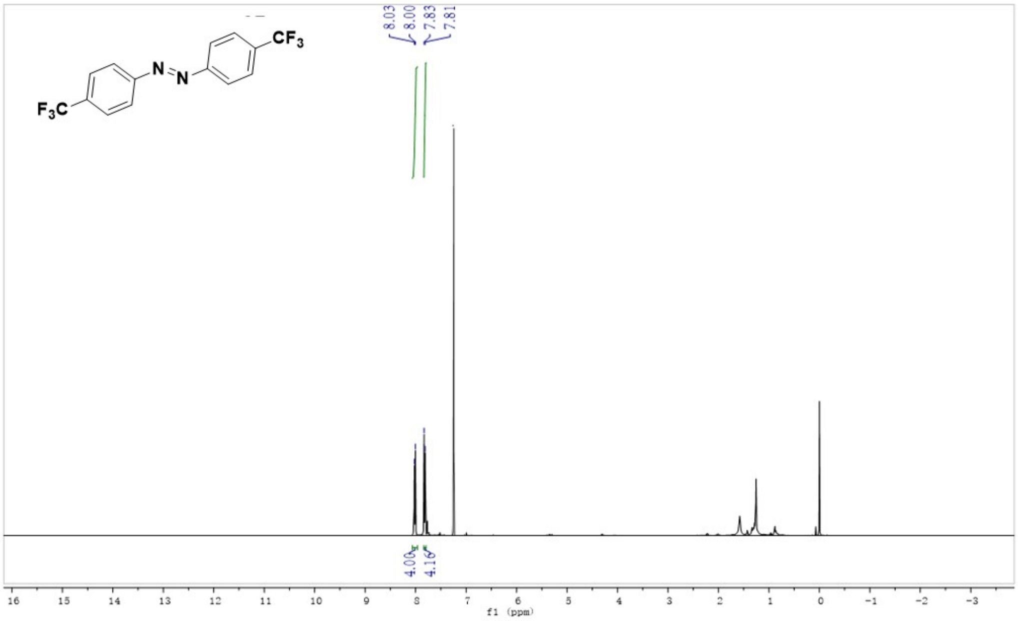
^{13}C NMR spectrum of *(E)* - 1, 2-bis(4-methoxylphenyl)diazene recorded in $CDCl_3$, 161.85, 147.09, 123.37, 114.50, 55.65.



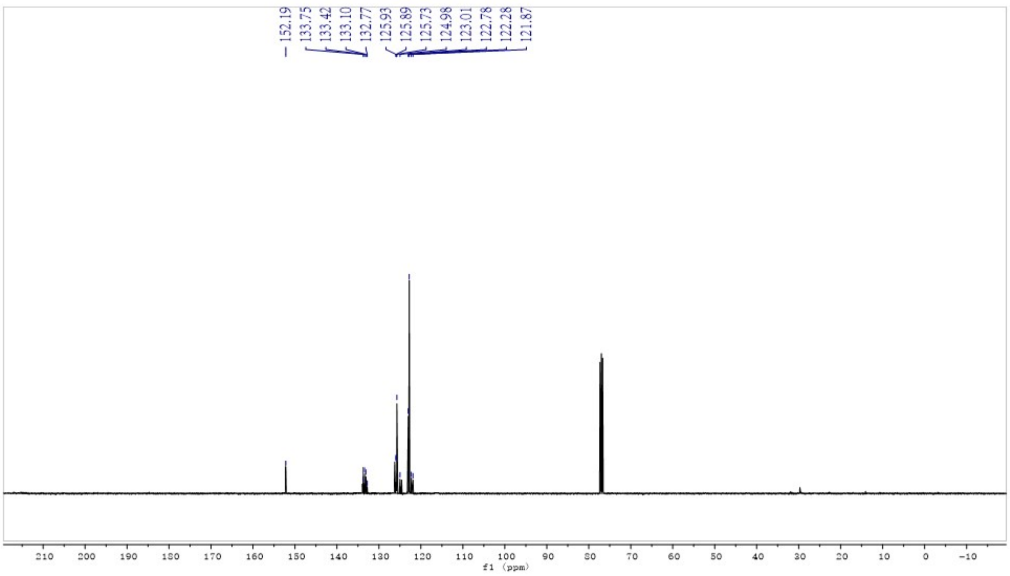
[1]H NMR spectrum of *(E)* - 1, 2-bis(4-methoxylphenyl)diazene recorded in $CDCl_3$, δ 7.94-7.92 (d, *J*=8 Hz, 4H), 7.03-7.00(d, *J*=8 Hz, 4H), 4.17-4.12(m, 4H), 1.50-1.46(t, *J*=16 Hz, 6H).



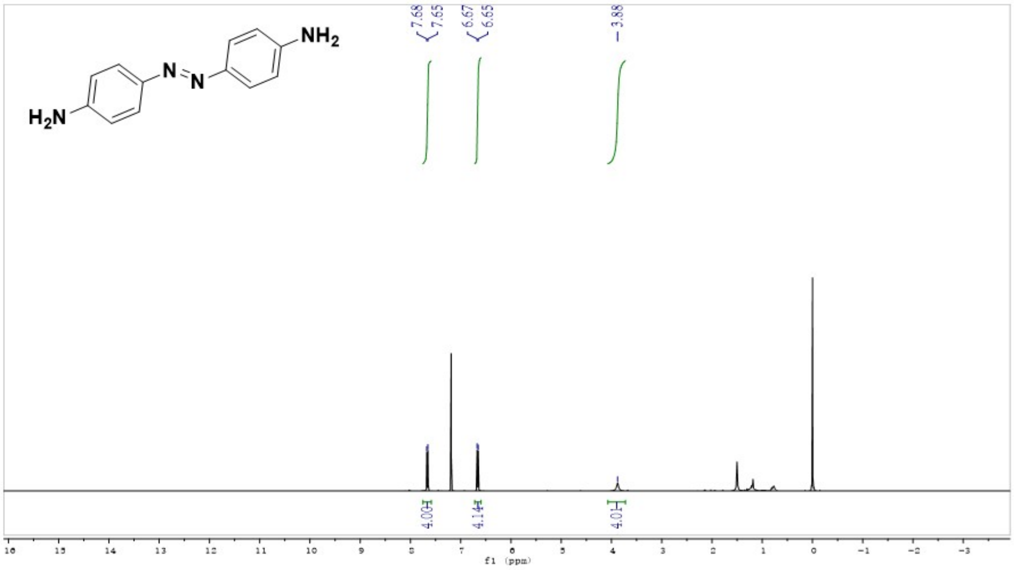
[13]C NMR spectrum of *(E)* - 1, 2-bis(4-methoxylphenyl)diazene recorded in $CDCl_3$, δ 161.23, 146.48, 124.57, 114.73, 63.84, 14.78.



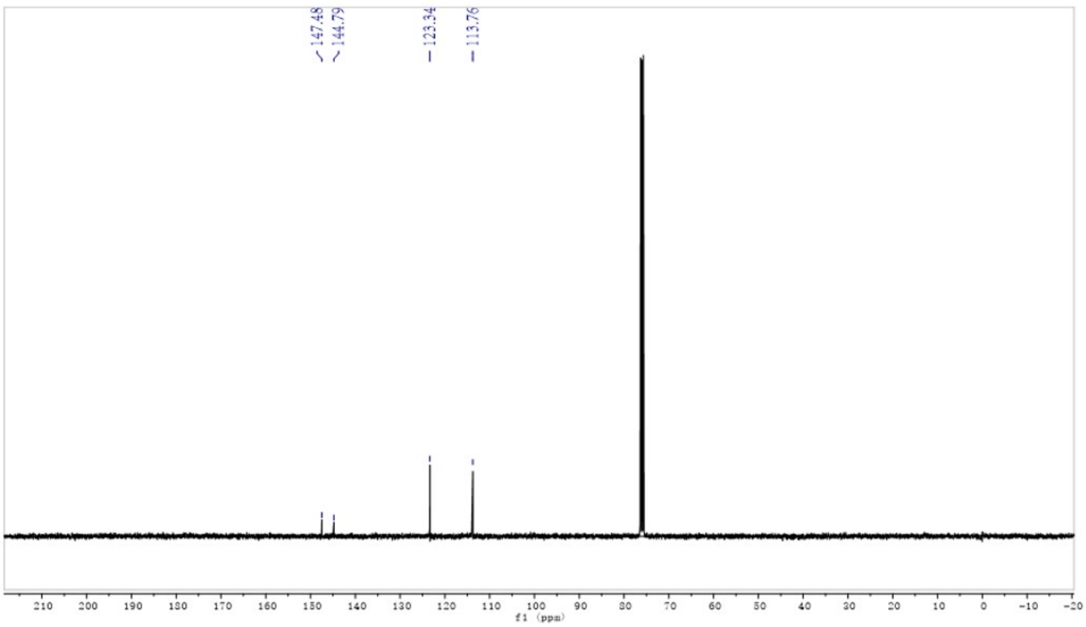
^{1}H NMR spectrum of *(E)* - 1, 2-bis (4-(trifluoromethyl) phenyl)diazene recorded in $CDCl_3$, δ 8.03-8.00 (d, *J*=8 Hz, 4H), 7.83-7.81(d, *J*=8 Hz, 4H).



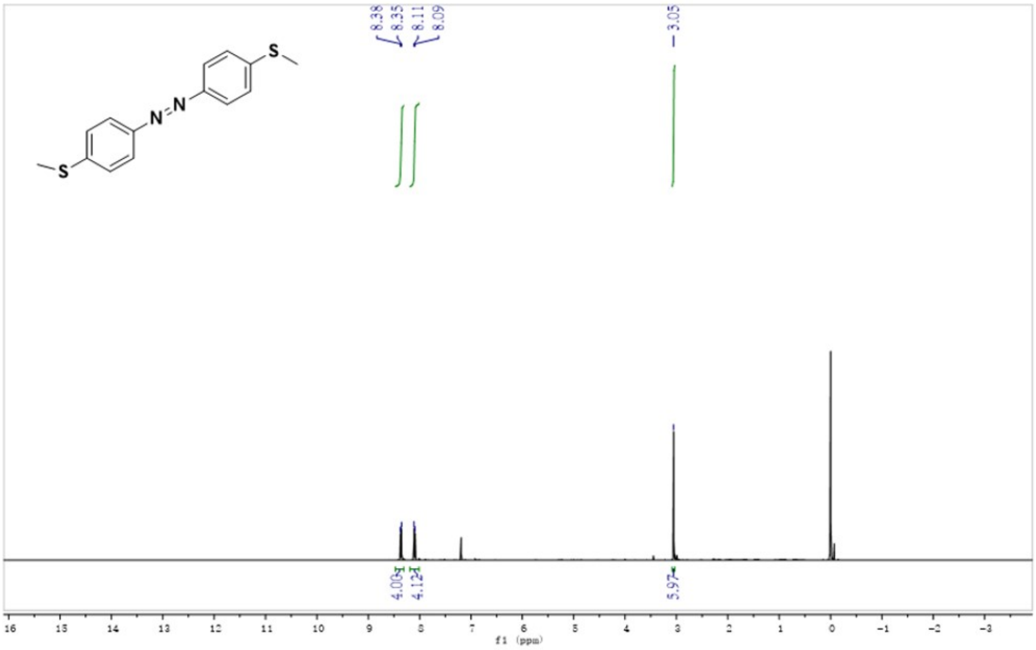
^{13}C NMR spectrum of *(E)* - 1, 2-bis (4-(trifluoromethyl) phenyl)diazene recorded in $CDCl_3$, δ 152.19, 133.75-132.77 (q, *J*=32.7 Hz), 125.93-125.89(d, *J*=4.0 Hz), 125.73-122.28(d, *J*=345 Hz)121.873.



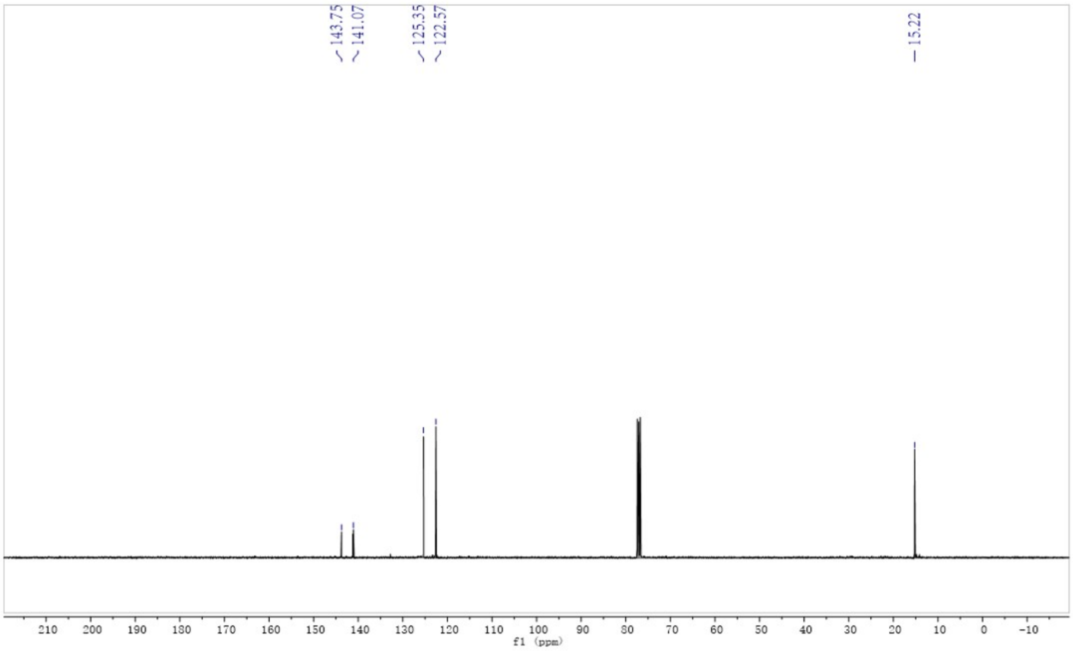
[1]H NMR spectrum of *(E)* - -4, 4'-(diazene-1,2-diyl)dianiline recorded in $CDCl_3$, δ 7.68-7.65 (d, *J*=8 Hz, 4H), 6.67-6.65 (d, *J*=8 Hz, 4H), 3.88(s, 4H).



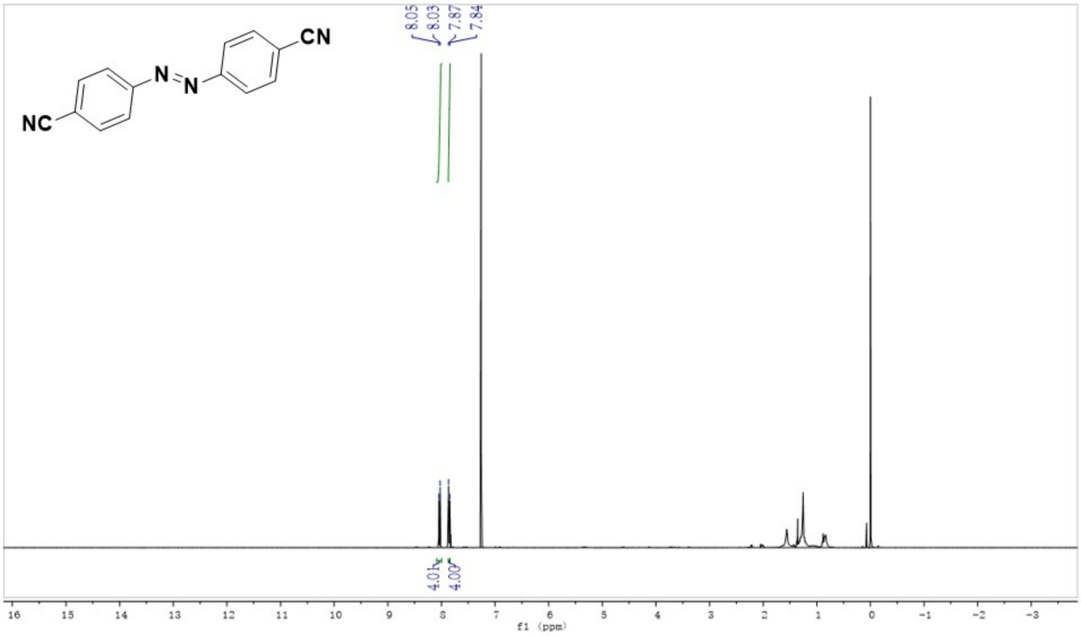
[13]C NMR spectrum of *(E)* - -4, 4'-(diazene-1,2-diyl)dianiline recorded in $CDCl_3$, δ 147.48, 144.79, 123.34, 113.76.



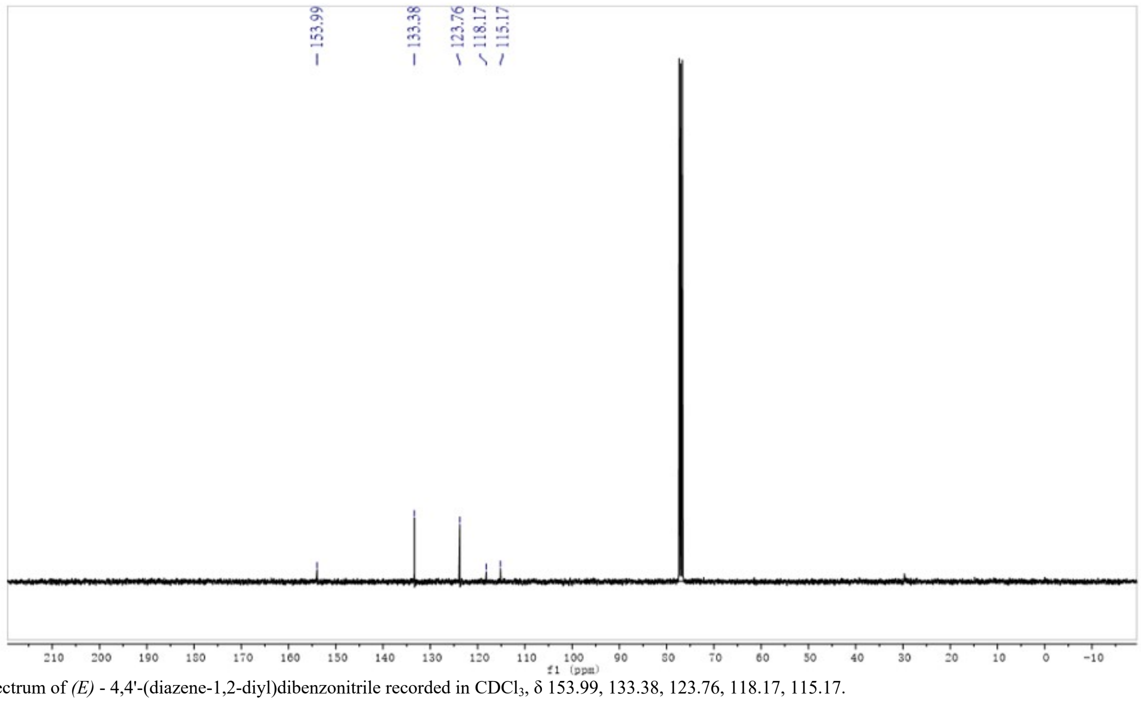
[1]H NMR spectrum of *(E)* - 1, 2-bis (4-(methylthio)phenyl) diazene recorded in $CDCl_3$, δ 8.38-8.35 (d, *J*=8 Hz, 4H), 8.11-8.09(d, *J*=8 Hz, 4H), 3.05(s, 4H).



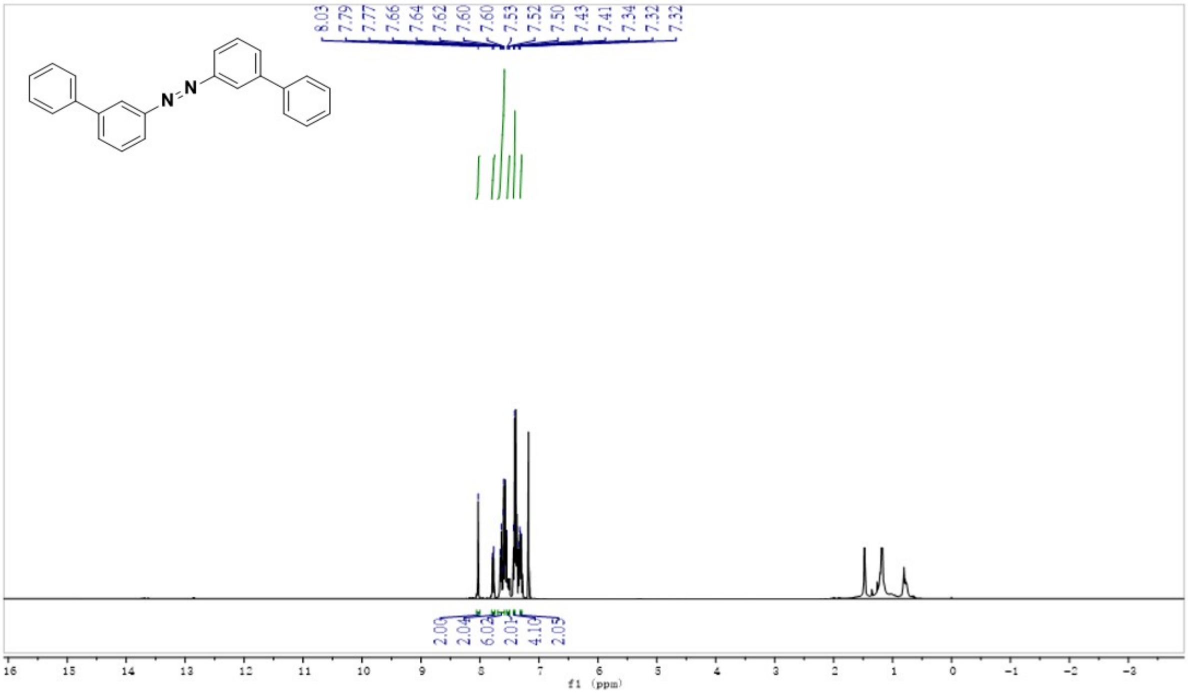
[13]C NMR spectrum of *(E)* - 1, 2-bis (4-(methylthio)phenyl) diazene recorded in $CDCl_3$, δ 143.75, 141.07, 125.35, 122.57, 15.22.



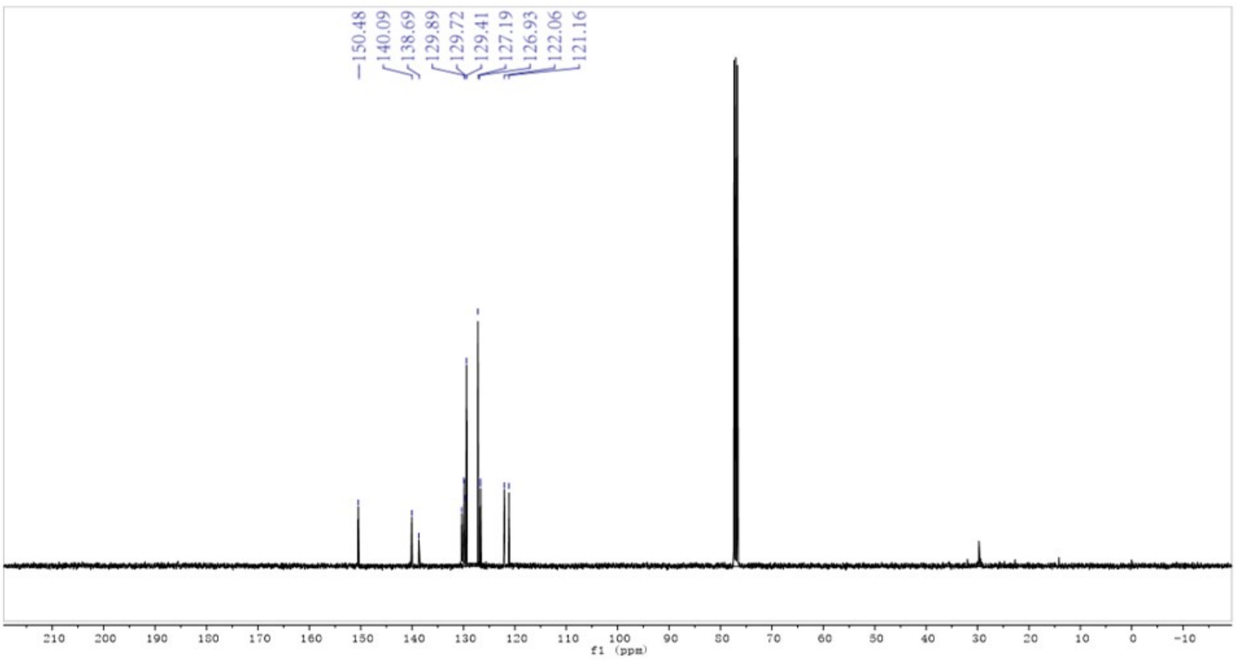
^{1}H NMR spectrum of *(E)* - 4,4'-(diazene-1,2-diyl)dibenzonitrile recorded in $CDCl_3$, δ 8.05-8.03 (d, *J*=8 Hz, 4H), 7.87-7.84(d, *J*=8 Hz, 4H).



^{13}C NMR spectrum of *(E)* - 4,4'-(diazene-1,2-diyl)dibenzonitrile recorded in $CDCl_3$, δ 153.99, 133.38, 123.76, 118.17, 115.17.



[1]H NMR spectrum of *(E)* - 1,2-bis([1,1'-biphenyl]-3-yl)diazene recorded in $CDCl_3$, δ 8.03 (s, 2H), 7.79-7.77(m, 2H), 7.66-7.60(m, 6H), 7.53-7.50(t,2H), 7.43-7.41(m,4H), 7.34-7.32(t, 2H).



[13]C NMR spectrum of *(E)* - 1,2-bis([1,1'-biphenyl]-3-yl)diazene recorded in $CDCl_3$, δ 150.48, 140.09, 138.69, 129.89, 129.72, 129.41, 127.19, 126.93, 122.06, 121.16.

References

[1] S.-i. Naya, T. Niwa, T. Kume, H. Tada, **2014**, *53*, 7305-7309.
[2] X. Guo, C. Hao, G. Jin, H. Y. Zhu, X. Y. Guo, *Angew Chem Int Ed Engl* **2014**, *53*, 1973-1977.
[3] Y. Dai, C. Li, Y. Shen, T. Lim, J. Xu, Y. Li, H. Niemantsverdriet, F. Besenbacher, N. Lock, R. Su, *Nature communications* **2018**, *9*, 60.
[4] J. Li, S. Song, Y. Long, L. Wu, X. Wang, Y. Xing, R. Jin, X. Liu, H. Zhang, *Adv Mater* **2018**, *30*.
[5] B. Mondal, P. S. Mukherjee, *Journal of the American Chemical Society* **2018**, *140*, 12592-12601.
[6] Y.-F. Zhang, M. Mellah, *ACS Catalysis* **2017**, *7*, 8480-8486.
[7] Z. Liu, Y. Huang, Q. Xiao, H. Zhu, *Green Chemistry* **2016**, *18*, 817-825.