Electronic Supplementary Information for

A water-soluble type II photosensitizer for selective photooxidation reactions of hydroazaobenzenes, olefins, and hydrosilanes in water

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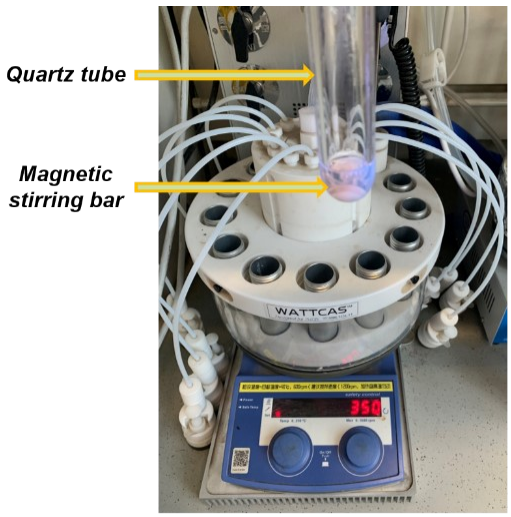
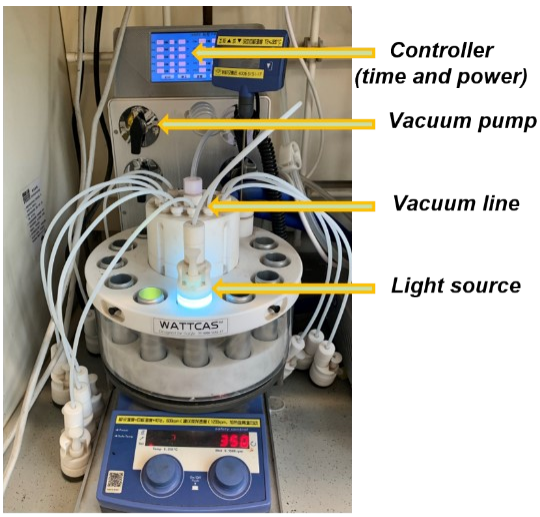
1. Materials and Characterizations.

Unless otherwise stated, the chemicals used are all purchased from reagent companies. ^{1}H NMR spectra was recorded on a Bruker Advance 400 spectrometer (400 MHz) at 298 K, and the chemical shifts (δ) were expressed in ppm and J values were given in Hz. UV-vis absorption spectra were characterized by a Shimadzu UV-2450 spectrophotometer. Fluorescence emission spectra were obtained by fluorescence spectrophotometer F-380A. The photocatalytic reaction was performed on WATTCAS Parallel Photocatalytic Reactor (WP-TEC-HSL) with 10W COB LED.

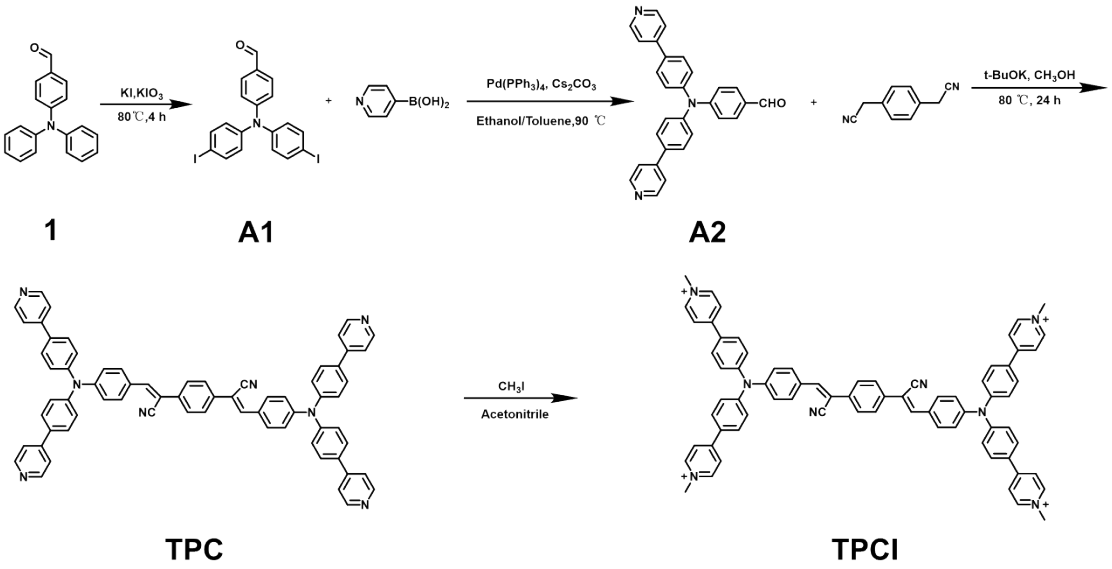


A: Experiment set up without light.



B: Experiment set up with light.

2. Synthesis of TPCI



Scheme S1 The synthetic route of the TPCI.

Synthesis of compound A1: A1 was synthesized based on the literature reports.[1,2] A modified version of a previously reported method was used. In a 500 mL three-necked round-bottom flask, 4-(*N,N*-diphenylamine) benzaldehyde (2.8 g, 10.25 mmol), potassium iodide (2.3 g, 13.8 mmol), acetic acid (100 mL), and water (10 mL) were heated to 80 ℃. After stirring for 1 h, potassium iodate (2.1 g, 10.25 mmol) was added and the reaction was stirred at 80 ℃ for 4 h. The solution was allowed to cool and the solid was collected. Then, washed with water, and recrystallized from DCM/ethanol (1:5) giving the product as a yellow powder (4.01 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (s, 1H), 7.73-7.70 (m, 2H), 7.65-7.61 (m, 4H), 7.08-7.04 (m, 2H), 6.92-6.87 (m, 4H).

Synthesis of compound A2: Under a nitrogen atmosphere, a mixture of compound A1 (2.1 g, 4.0 mmol), cesium carbonate (2.61 g, 8.0 mmol), and $Pd(PPh_3)_4$ (46.2 mg, 0.04 mmol) in toluene (50 mL) was stirred and heated to 60 °C, and then a solution of pyridine-4-boronic acid (1.48 g, 12.0 mmol) in 20 mL ethanol was injected slowly and the mixture was heated to reflux for 8 h. After it was cooled, 50 mL water was added to quench the reaction and the raw product was extracted three times using dichloromethane (DCM) and water. The organic layers were combined and dried by

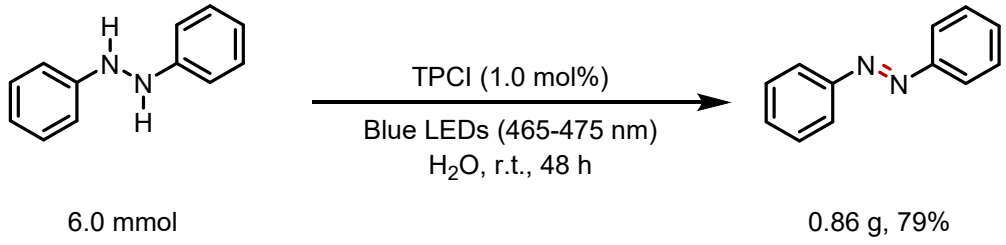
anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure, and the residue was purified by chromatography on a silica gel column with DCM/ethanol (v/v 50:1) to give compound A2 as a yellow solid (1.575 g, yield: 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 8.67 (d, *J* = 5.2 Hz, 4H), 7.78 (d, *J* = 8.7 Hz, 2H), 7.64 (d, *J* = 8.6 Hz, 4H), 7.51 (d, *J* = 6.2 Hz, 4H), 7.30 (d, *J* = 8.6 Hz, 4H), 7.20 (d, *J* = 8.7 Hz, 2H).

Synthesis of compound TPC: A mixture of compound A2 (855 mg, 2 mmol), 1,4-phenylenediacetonitrile (312.4 mg, 0.66 mmol), and potassium tert-butoxide (1.12 g, 10 mmol) were dissolved in 50 mL methanol. This mixture was stirred for 24 h at reflux temperature under an atmosphere of nitrogen. After cooling down to room temperature, the solvent was removed under reduced pressure. The raw product was extracted three times using DCM and water. The organic layers were combined and dried by anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure, and the residue was purified by chromatography on a silica gel column with DCM/ethanol (volume = 20:1) to give compound TPC as an orange solid (420 mg, yield: 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69-8.64 (m, 8H), 7.87 (dd, *J* = 14.1, 8.8 Hz, 4H), 7.68 (d, *J* = 8.5 Hz, 4H), 7.65-7.59 (m, 8H), 7.53-7.47 (m, 10H), 7.30 (t, *J* = 3.2 Hz, 8H), 7.23-7.18 (m, 4H).

3. General procedure for photooxidation reactions of 1,2-diphenylhydrazine and its derivatives.

The 1,2-diphenylhydrazine and its derivatives were dissolved in freshly prepared TPCI solution in H_2O (3.0 mL, [TPCI]=5.0 × 10^{-4} M). The mixture was subsequently irradiated with a blue light (465-475 nm) for 24 h at room temperature. Afterward, the organic product was extracted with ethyl acetate, and the mixed organic layer was dried with anhydrous Na_2SO_4, the solvent removed by reduced pressure distillation. The oil fractions were separated by chromatographic column (PE:EA = 10:1), and the target compounds were analyzed by ^1H NMR and ^{13}C NMR. 1a (0.2 mmol), PC (1.0 mol%) in H_2O (3.0 mL) were irradiated with Blue LEDs (465 - 475 nm) for 24 h at room temperature

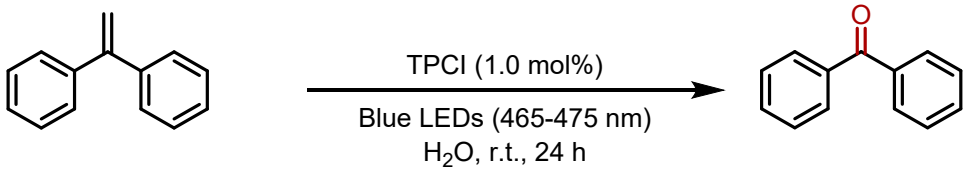
For gram-scale reaction, 1,2-diphenylhydrazine (1.11 g, 6 mmol, 1.0 equiv.), freshly prepared TPCI solution in H_2O (90.0 mL, [TPCI]=5.0 × 10^{-4} M) was added to a round bottle (100 mL) with magnetic stirring bar. The vessel placed 2 cm away from four Blue LEDs (465-475 nm). The reaction mixture was irradiated with for 48 h under air atmosphere. Afterward, the organic product was extracted with ethyl acetate, and the mixed organic layer was dried with anhydrous Na_2SO_4, the solvent removed by reduced pressure distillation. The pure product was obtained by flash column chromatography on silica gel (PE:EA = 10:1) to get the desired product as a yellow solid 0.86 g in 79% yield.



4. General procedure for photooxidation reactions of 1,1-diphenylethylene and its derivatives.

The 1,1-diphenylethylene and its derivatives were dissolved in freshly prepared TPCI solution in H_2O (3.0 mL, [TPCI]=5.0 × 10^{-4} M). The mixture was subsequently irradiated with a blue light (465-475 nm) for 24 h at room temperature. Afterward, the organic product was extracted with ethyl acetate, and the mixed organic layer was dried with anhydrous Na_2SO_4, the solvent removed by reduced pressure distillation. The oil fractions were separated by chromatographic column (PE:EA = 20:1), and the target compounds were analyzed by ^1H NMR.

For gram-scale reaction, 1,1-diphenylethylene (1.1 mL, 6 mmol, 1.0 equiv.), freshly prepared TPCI solution in H_2O (90.0 mL, [TPCI]=5.0 × 10^{-4} M) was added to a round bottle (100 mL) with magnetic stirring bar. The vessel placed 2 cm away from four Blue LEDs (465-475 nm). The reaction mixture was irradiated with for 24 h under air atmosphere. Afterward, the organic product was extracted with ethyl acetate, and the mixed organic layer was dried with anhydrous Na_2SO_4, the solvent removed by reduced pressure distillation. The pure product was obtained by flash column chromatography on silica gel (PE:EA = 20:1) to get the desired product as a colorless oil 1.0 g in 91% yield.



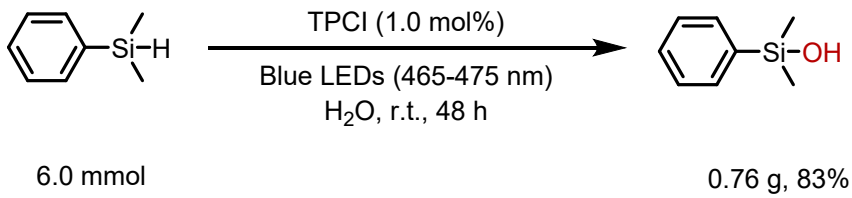
6.0 mmol

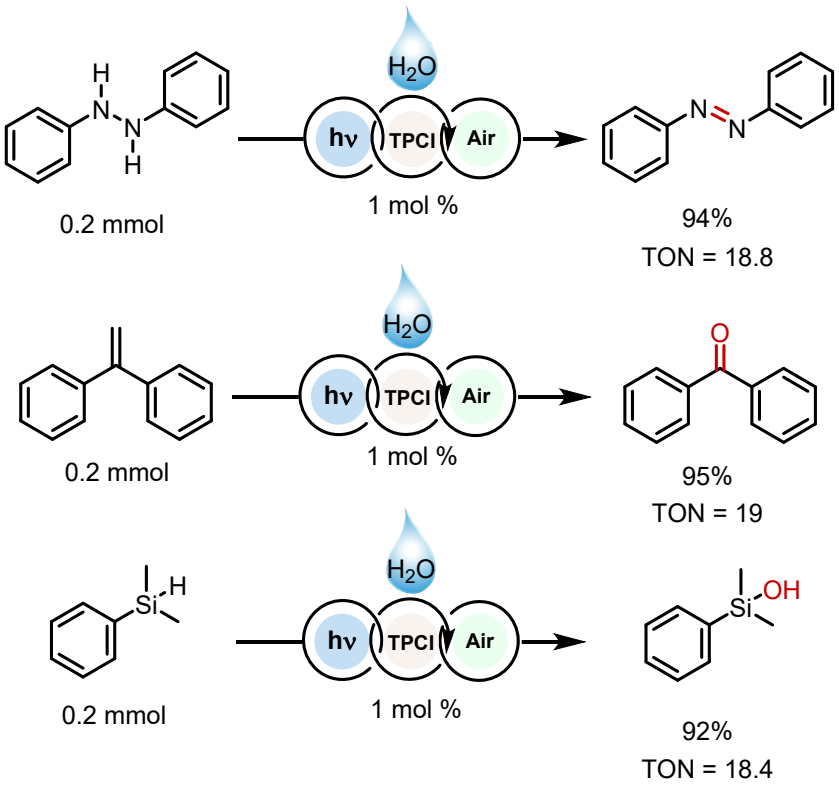
1.00 g, 91%

5. General procedure for photooxidation reactions of dimethyl(phenyl)silane and its derivatives.

The dimethyl(phenyl)silane and its derivatives were dissolved in freshly prepared TPCI solution in H_2O (3.0 mL, [TPCI]=5.0 × 10^{-4} M). The mixture was subsequently irradiated with a blue light (465-475 nm) for 24 h at room temperature. Afterward, the organic product was extracted with ethyl acetate, and the mixed organic layer was dried with anhydrous Na_2SO_4, the solvent removed by reduced pressure distillation. The oil fractions were separated by chromatographic column (PE: EA = 20:1), and the target compounds were analyzed by ^1H NMR and ^{13}C NMR.

For gram-scale reaction, dimethyl(phenyl)silane (0.82 g, 6 mmol, 1.0 equiv.), freshly prepared TPCI solution in H_2O (90.0 mL, [TPCI]=5.0 × 10^{-4} M) was added to a round bottle (100 mL) with magnetic stirring bar. The vessel placed 2 cm away from four Blue LEDs (465-475 nm). The reaction mixture was irradiated with for 24 h under air atmosphere. Afterward, the organic product was extracted with ethyl acetate, and the mixed organic layer was dried with anhydrous Na_2SO_4, the solvent removed by reduced pressure distillation. The pure product was obtained by flash column chromatography on silica gel (PE:EA = 20:1) to get the desired product as a white solid 0.76 g in 91% yield.

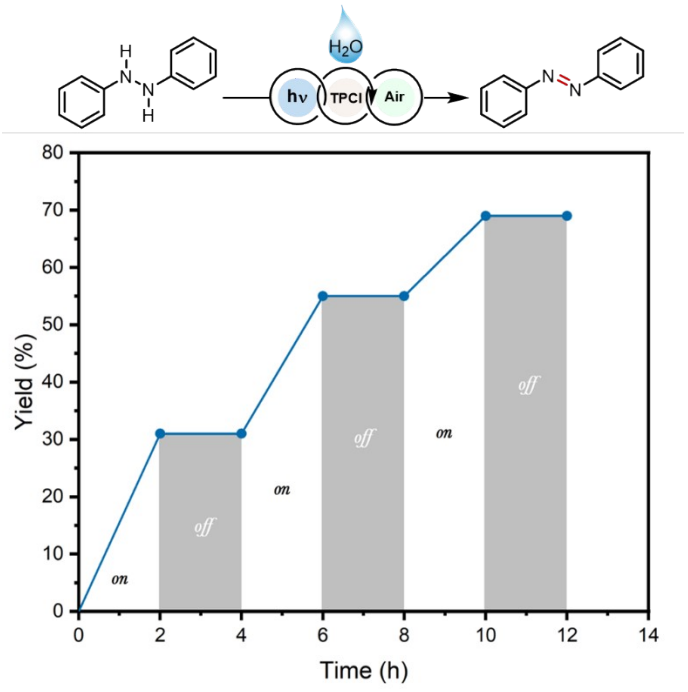




Scheme S2 TON of the photochemical oxidation reactions catalyzed by TPCI.

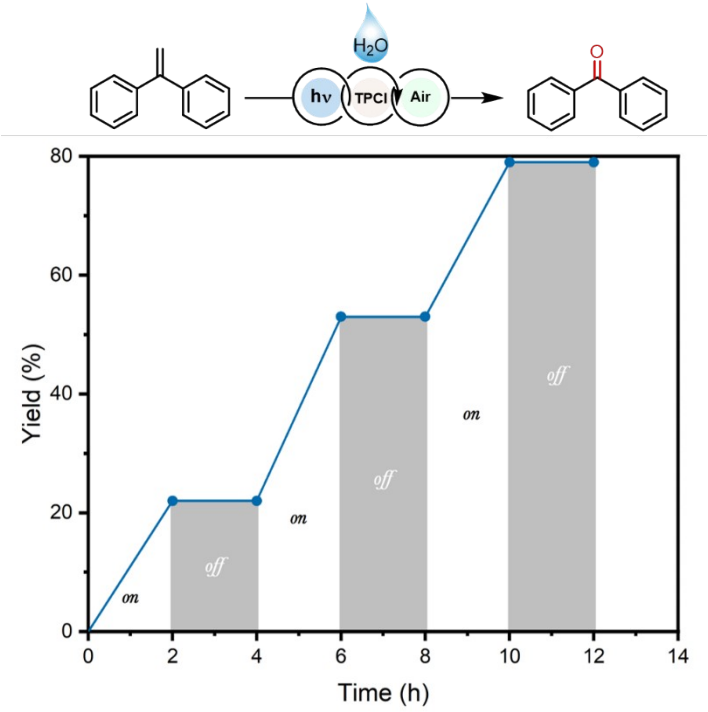
6. Light on/off experiment

Six standard reaction mixtures in an oven-dried 10 mL quartz tube were charged with 1,2-diphenylhydrazine (36.8 mg, 0.2 mmol, 1.0 equiv.), freshly prepared TPCI solution in H_2O (3.0 mL, [TPCI]=5.0 × 10^{-4} M). The mixtures were then stirred and irradiated with blue light (465-475 nm) at room temperature. After 2 h, the light was turned off, and one vial was removed from the irradiation setup for analysis. The remaining five vials were stirred in the absence of light for an additional 2 h. Then, one vial was removed for analysis, and the light was turned back on to irradiate the remaining four four mixtures. After an additional 2 h of irradiation, the light was turned off, and one vial was removed for analysis. The remaining three vials were stirred in the absence of light for an additional 2 h. Then, a vial was removed for analysis, and the LED was turned back on to irradiate the remaining two reaction mixtures. After 1 h, the light was turned off, and one vial was removed for analysis. The remaining one vial were stirred in the absence of light for an additional 2 h and then it was analyzed. The yield was determined by ^{1}H NMR spectroscopy using dibromomethane as the internal standard. The operational procedures of additional two oxidation reactions align with the above mentioned.

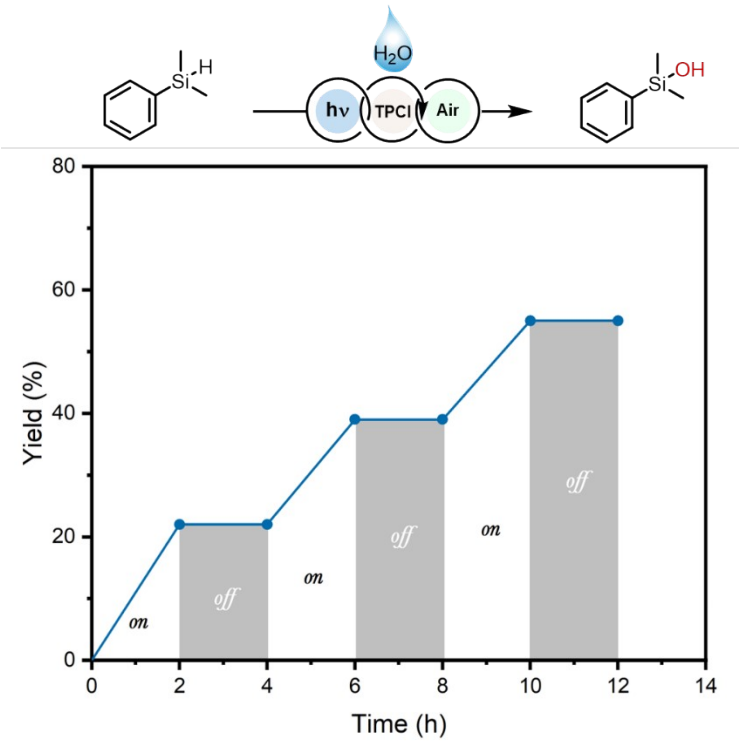


Scheme S3 Light on/off experiment for photooxidation reaction of 1,2-

diphenylhydrazine.



Scheme S4 Light on/off experiment for photooxidation reaction of 1,1-diphenylethylene.



Scheme S5 Light on/off experiment for photooxidation reaction of dimethyl(phenyl)silane.

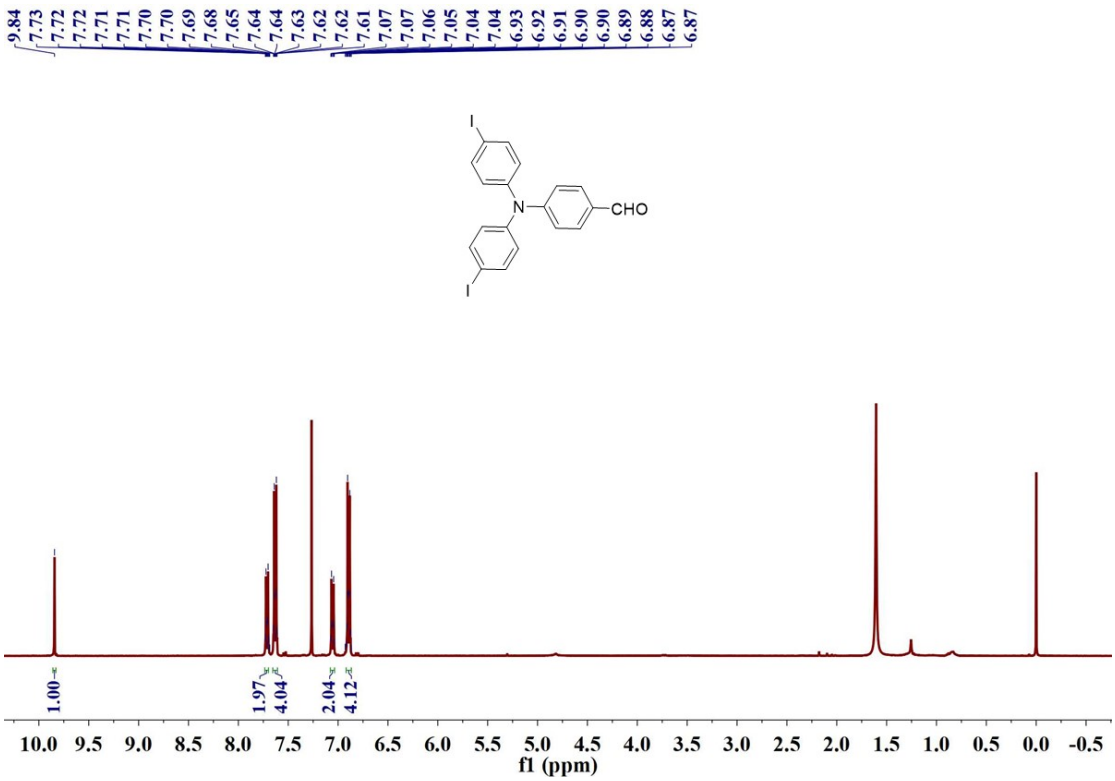


Fig. S1 ^{1}H NMR spectra of A1 in $CDCl_3$.

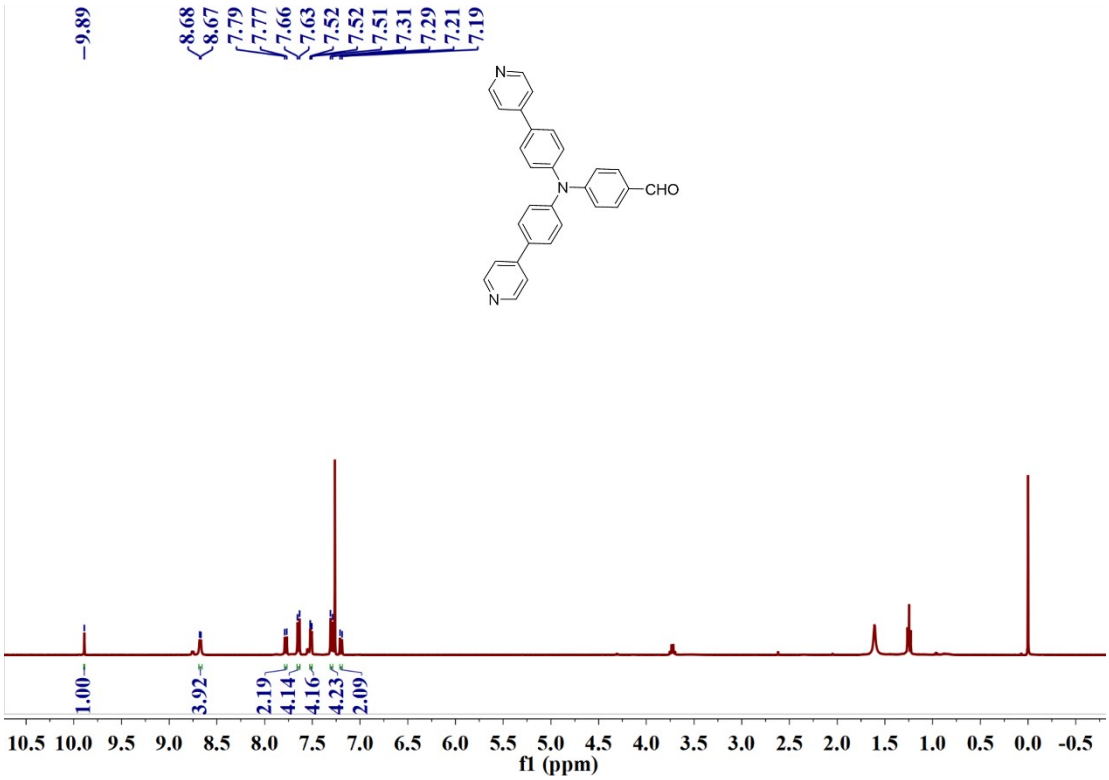


Fig. S2 ^{1}H NMR spectra of A2 in $CDCl_3$.

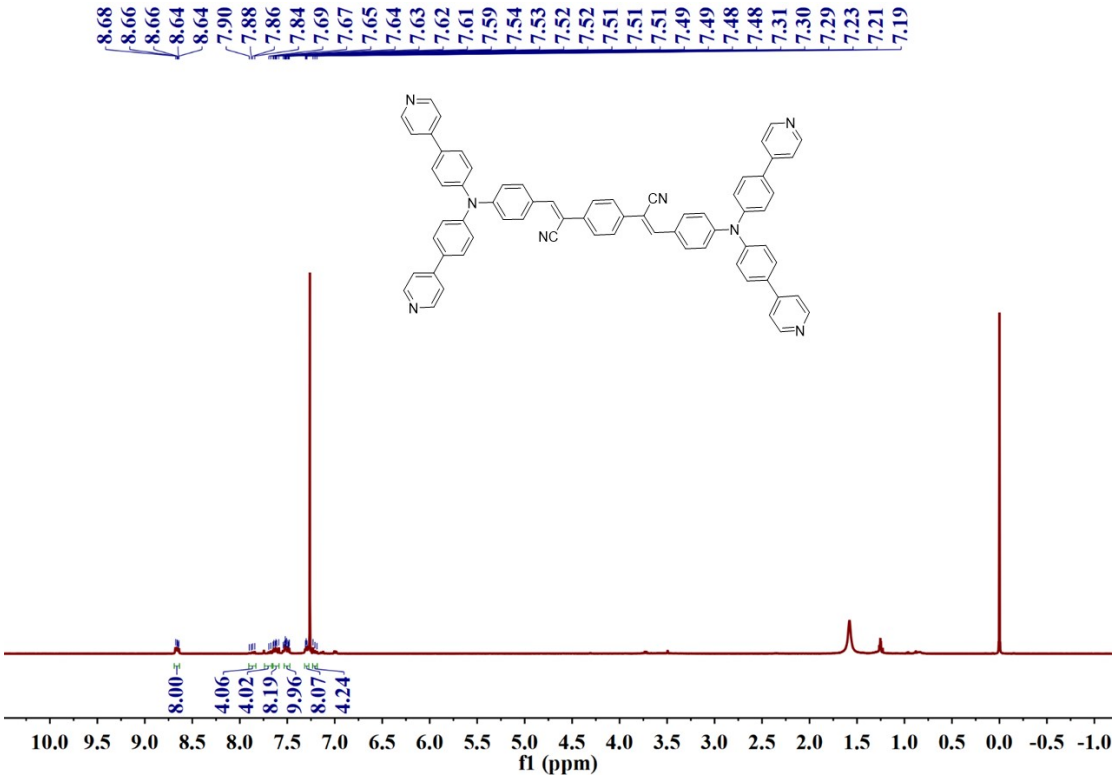


Fig. S3 ^{1}H NMR spectra of TPC in $CDCl_3$.

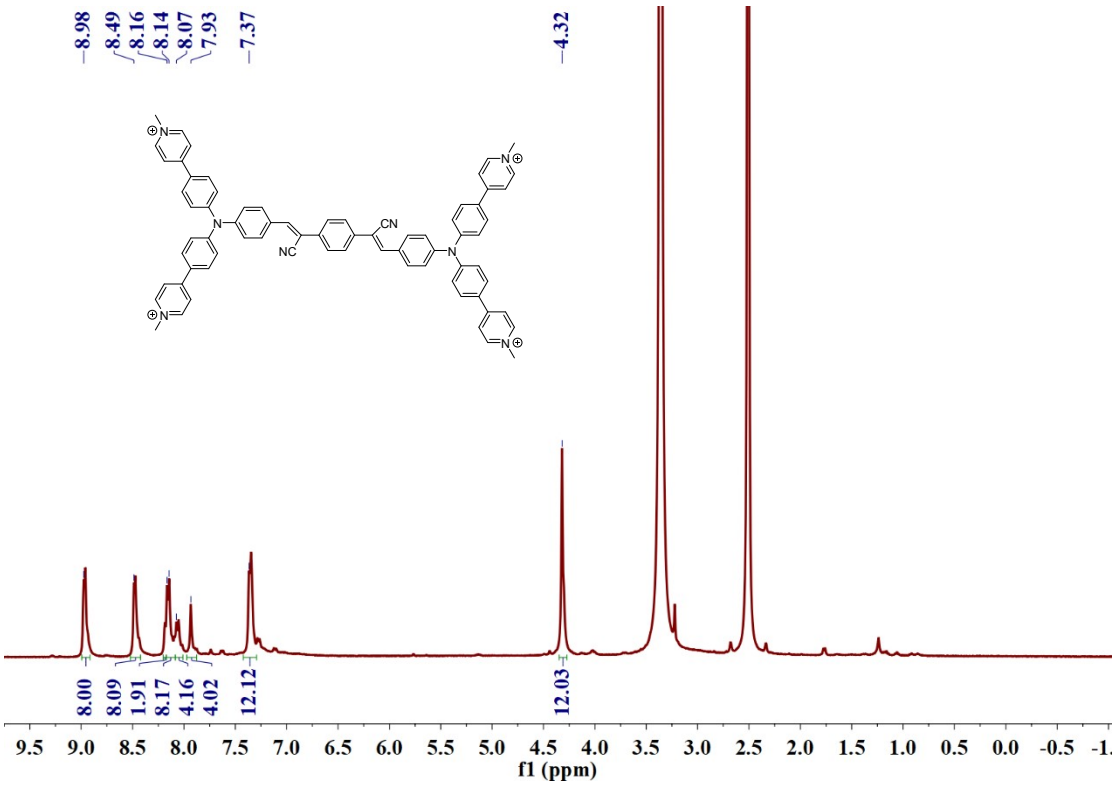


Fig. S4 ^{1}H NMR spectra of TPCI in DMSO-d_6.

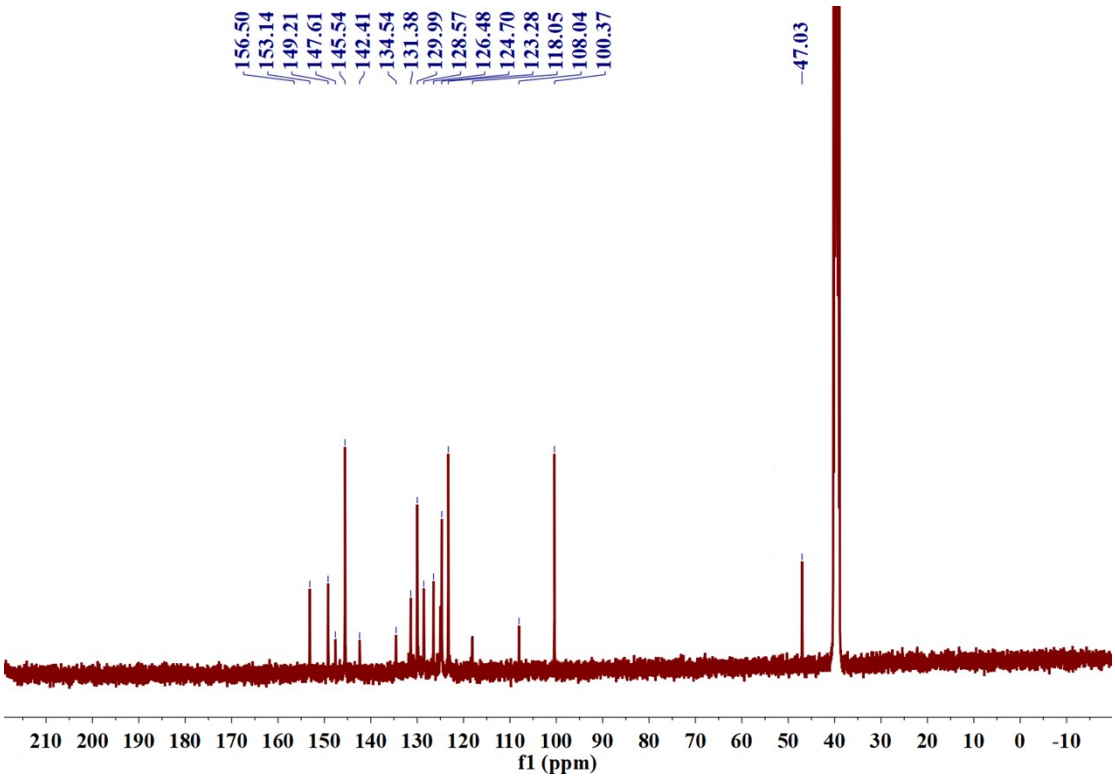


Fig. S5 ^{13}C NMR spectrum of TPCI in DMSO-d_6.

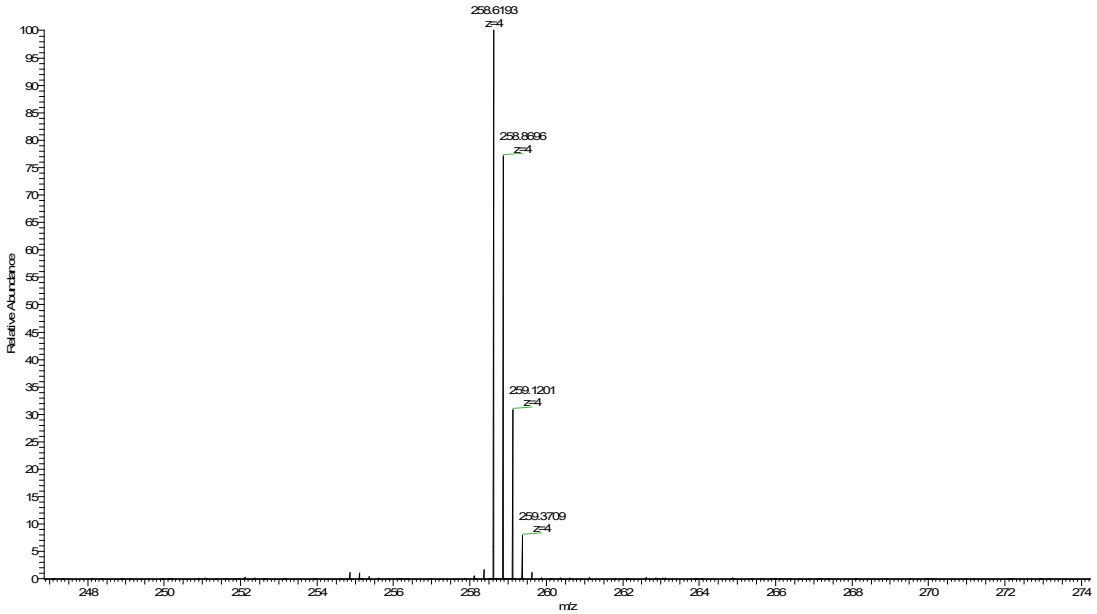


Fig. S6 HR-ESI-MS spectrum of TPCI.

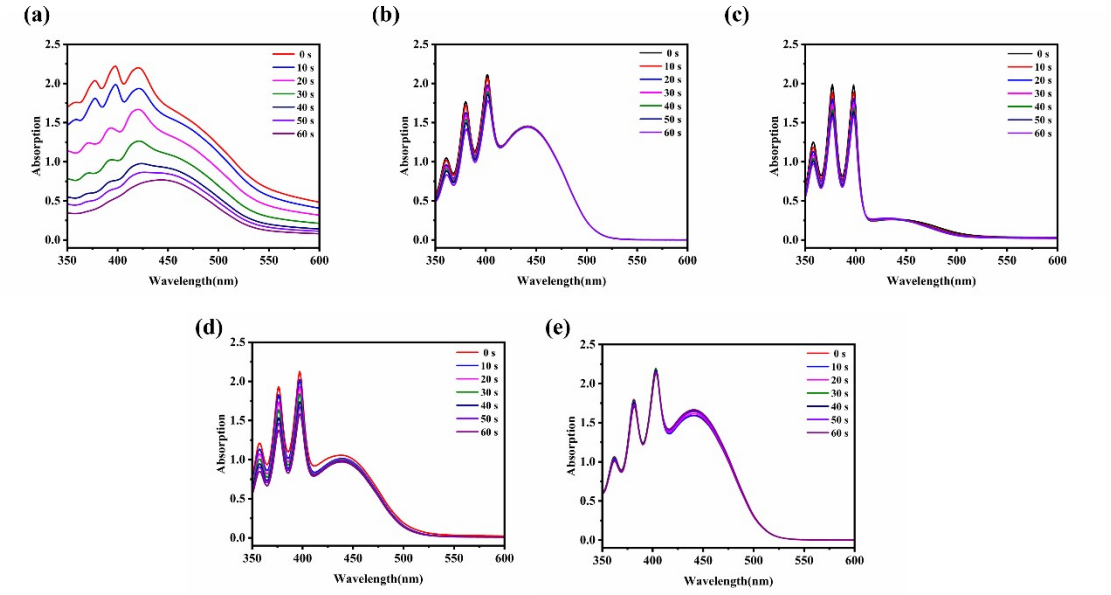
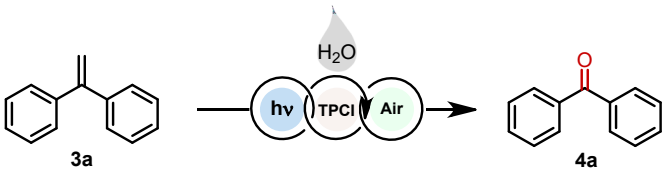


Fig. S7 The absorption spectra of ABDA (1.6×10^{-4} M) after irradiation (blue LEDs) for different times in the presence of TPCI (2.0×10^{-5} M) in water (a); DMF (b); THF (c); MeCN (d); DMSO (e).

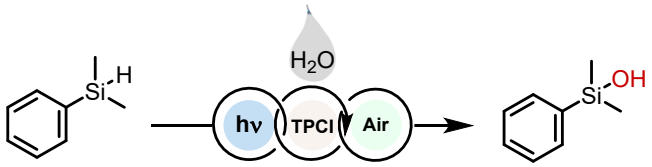
Table S1 Control experiment of photocatalytic oxidation of 1,1-diphenylethylene by oxidative bond breaking reaction.



Entry	Deviation from standard conditions[a]	Yield[b][%]
1	None	95
2	DMF instead of H_2O	47
3	THF instead of H_2O	52
4	MeCN instead of H_2O	56
5	DMSO instead of H_2O	32
6	12 h instead of 24 h	43
7	18 h instead of 24 h	61
8	30 h instead of 24 h	95
9	PC (0.5 mol%)	49
10	PC (1.5 mol%)	96
11	390 - 400 nm LEDs	91
12	400 - 410 nm LEDs	87
13	410 - 420 nm LEDs	89
14	420 - 430 nm LEDs	90
15	430 - 440 nm LEDs	92
16	440 - 450 nm LEDs	94
17	450 - 455 nm LEDs	91
18	Without O_2	NR
19	Without PC	NR
20	Without Light	NR

[a]Standard conditions: 3a (0.2 mmol), PC (1.0 mol%), in H_2O (3.0 mL) were irradiated with blue LEDs (465 - 475 nm) for 24 h at room temperature; [b] Isolated yield; NR = no reaction; PC: TPCI.

Table S2 Control experiment of photocatalytic oxidation of dimethyl(phenyl)silane by oxidative reaction.



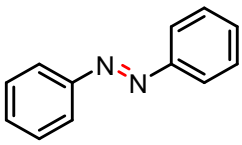
5a **6a**

Entry	Deviation from standard conditions[a]	Yield[b][%]
1	None	92
2	DMF instead of H_2O	35
3	THF instead of H_2O	48
4	MeCN instead of H_2O	57
5	DMSO instead of H_2O	27
6	12 h instead of 24 h	58
7	18 h instead of 24 h	71
8	30 h instead of 24 h	94
9	PC (0.5 mol%)	58
10	PC (1.5 mol%)	96
11	390 - 400 nm LEDs	86
12	400 - 410 nm LEDs	88
13	410 - 420 nm LEDs	89
14	420 - 430 nm LEDs	84
15	430 - 440 nm LEDs	90
16	440 - 450 nm LEDs	88
17	450 - 455 nm LEDs	92
18	Without O_2	NR
19	Without PC	NR
20	Without Light	NR

[a]Standard conditions: 5a (0.2 mmol), PC (1.0 mol%), in H_2O (3.0 mL) were irradiated with blue LEDs (465-475 nm) for 24 h at room temperature; [b] Isolated yield; NR = no reaction; PC: TPCI.

^{1}H NMR and ^{13}C NMR data of 2a-2i

2a. 1,2-diphenyldiazene



Orange solid, 94% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.90 (m, 4H), 7.55 – 7.46 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 131.0, 129.1, 122.8.
The spectral data obtained were identical with those reported in literature.[3]

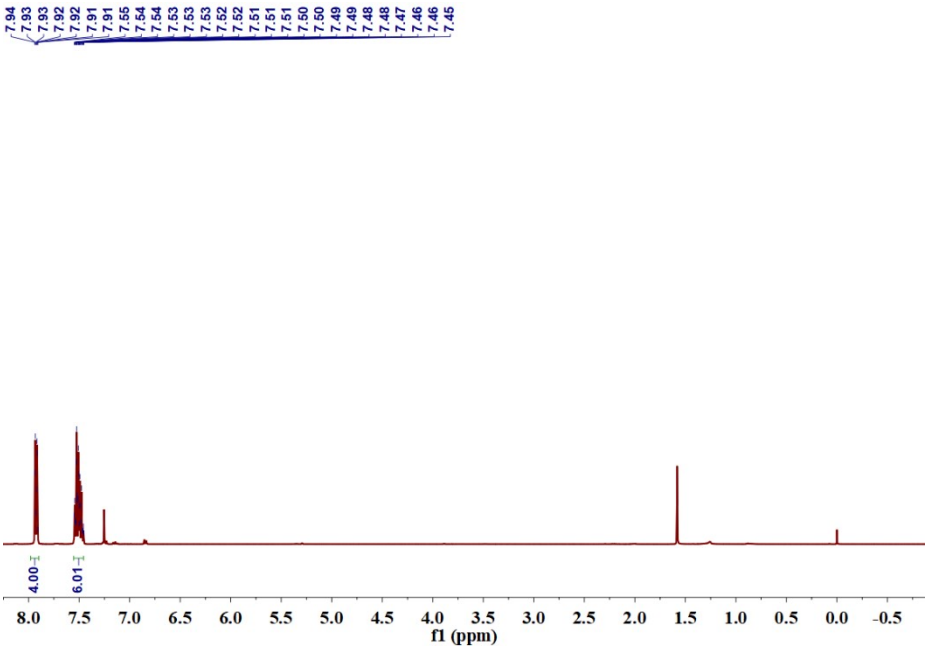


Fig. S8. ^{1}H NMR spectra of 2a in $CDCl_3$.

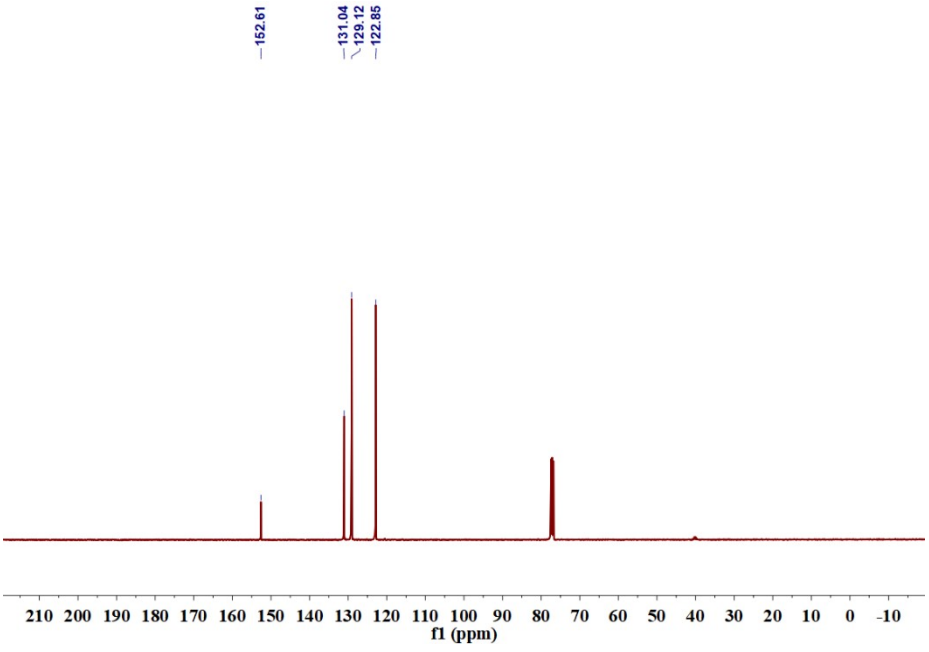
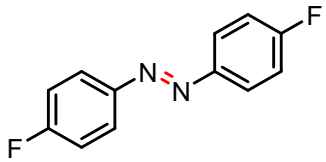


Fig. S9. ^{13}C NMR spectra of 2a in $CDCl_3$.

2b. 1,2-bis(4-fluorophenyl)diazene



Orange solid, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.89 (m, 4H), 7.20 (dd, J = 9.0, 8.2 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 163.1, 149.0, 148.9, 124.9, 124.8, 116.2, 116.0.

The spectral data obtained were identical with those reported in literature.[3]

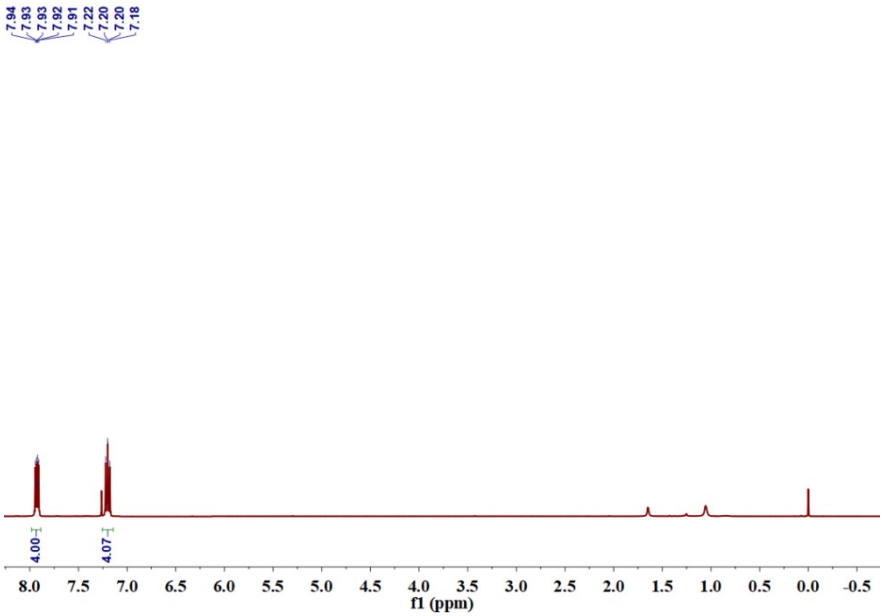


Fig. S10. ^{1}H NMR spectra of 2b in $CDCl_3$.

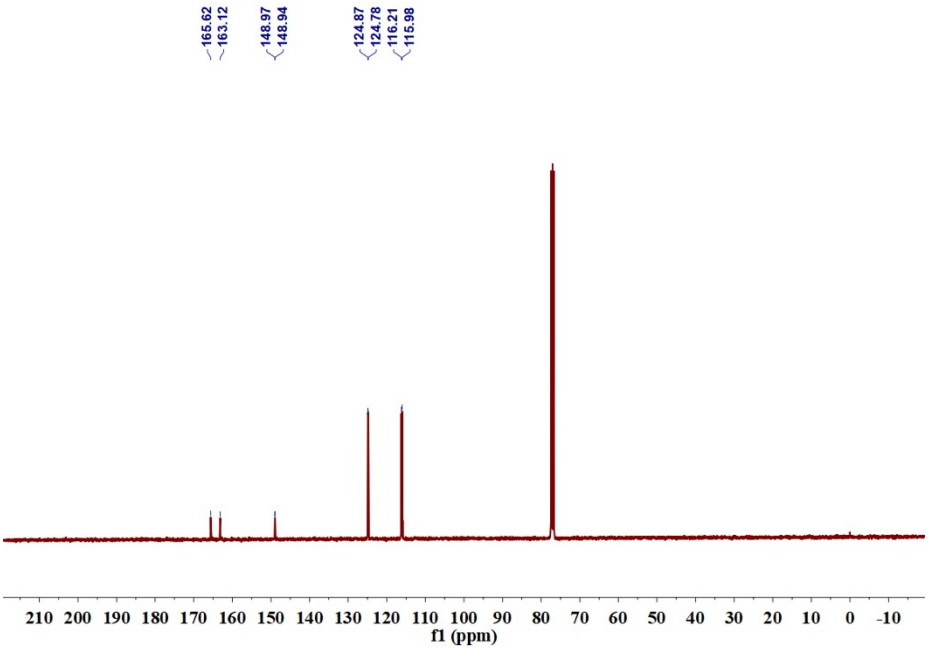
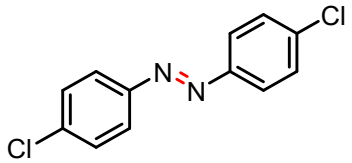


Fig. S11. ^{13}C NMR spectra of 2b in $CDCl_3$.

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



Orange solid, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.83 (m, 4H), 7.53 – 7.46 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 137.2, 129.4, 124.2.
The spectral data obtained were identical with those reported in literature.[3]

Fig. S12. ^{1}H NMR spectra of 2c in $CDCl_3$.

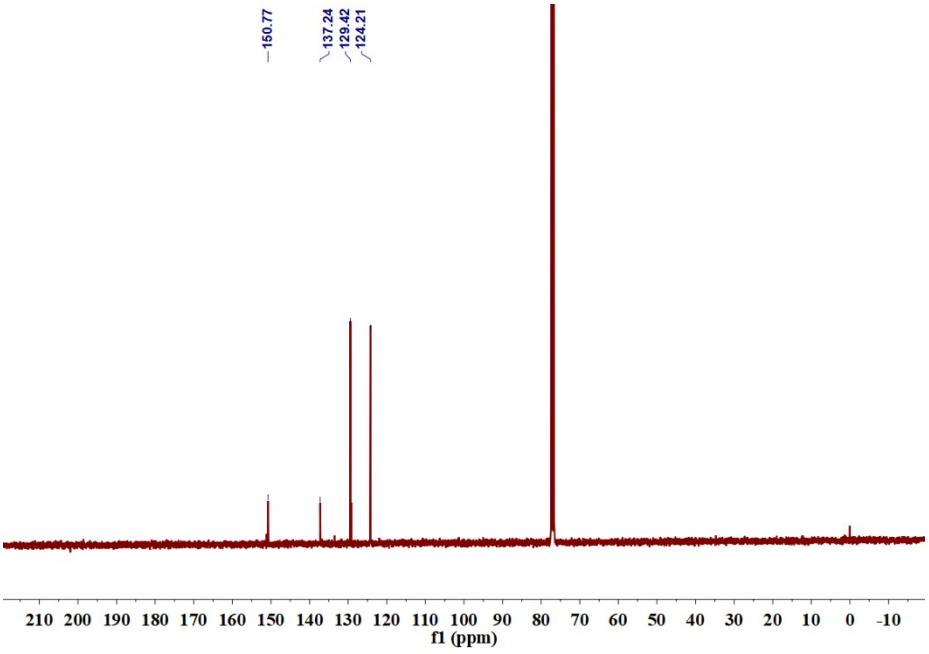
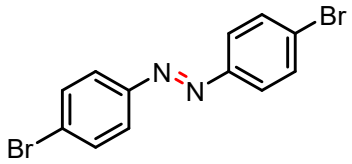


Fig. S13. ^{13}C NMR spectra of 2c in $CDCl_3$.

2d. 1,2-bis(4-bromophenyl)diazene



Orange solid, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.78 (m, 4H), 7.68 – 7.63 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.1, 132.4, 125.8, 124.4.
The spectral data obtained were identical with those reported in literature.[4]

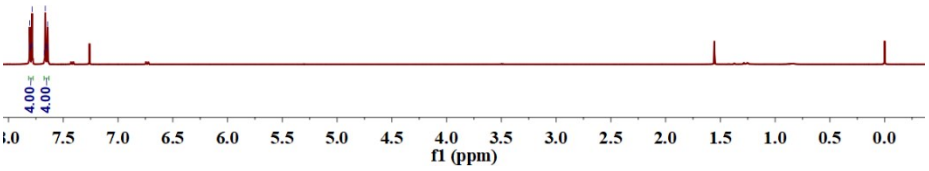


Fig. S14. ^{1}H NMR spectra of 2d in $CDCl_3$.

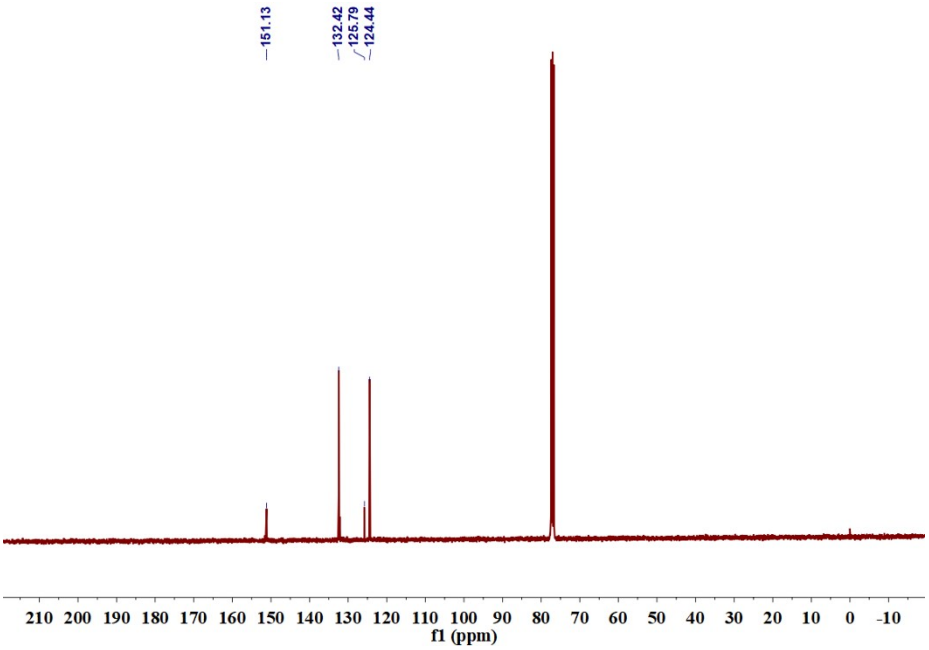
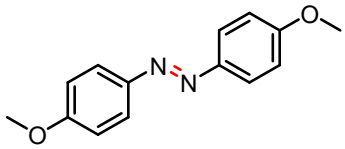


Fig. S15. ^{13}C NMR spectra of 2d in $CDCl_3$.

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



Orange solid, 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.85 (m, 4H), 7.01 (d, *J* = 9.0 Hz, 4H), 3.89 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6, 147.0, 124.4, 114.2, 55.6.

The spectral data obtained were identical with those reported in literature.[3]

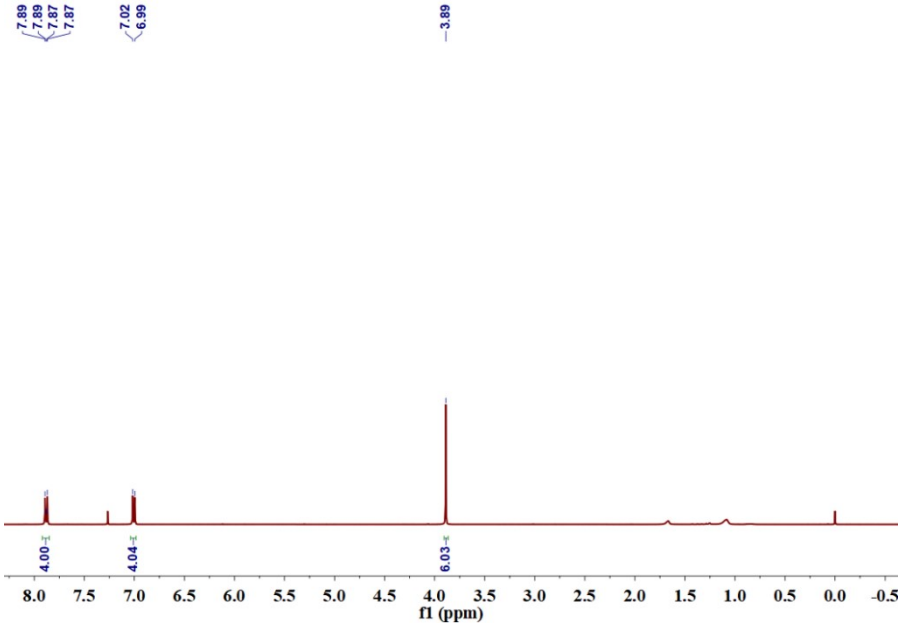


Fig. S16. ^{1}H NMR spectra of 2e in $CDCl_3$.

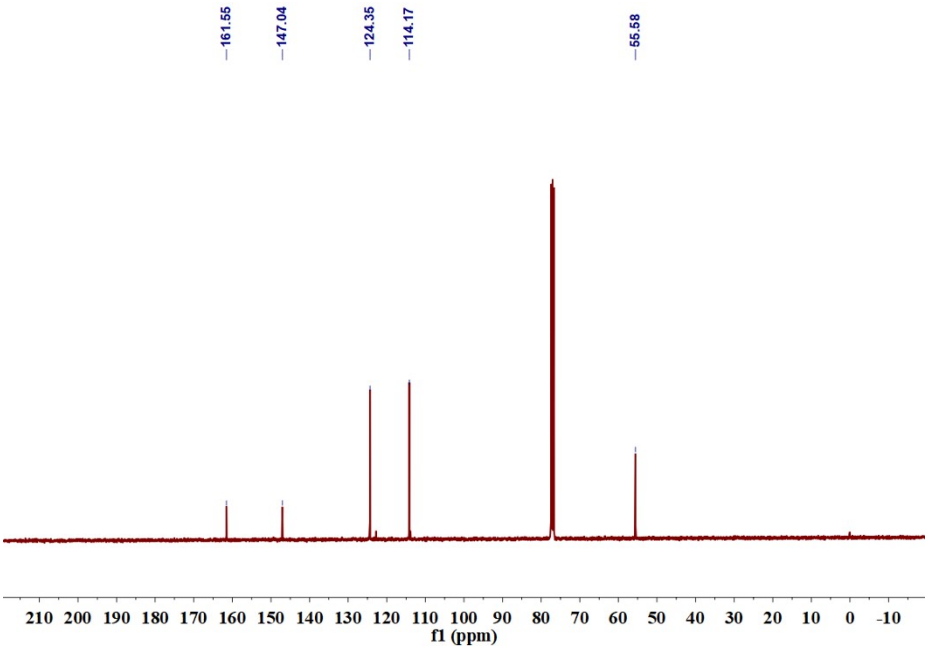
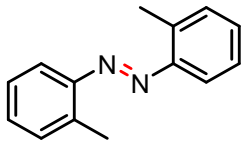


Fig. S17. ^{13}C NMR spectra of 2e in $CDCl_3$.

2f. 1,2-di-o-tolyldiazene



Red solid, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.58 (m, 2H), 7.38 – 7.31 (m, 4H), 7.25 (ddd, *J* = 10.3, 5.5, 2.3 Hz, 2H), 2.74 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1, 131.3, 130.7, 126.4, 115.8, 17.7.

The spectral data obtained were identical with those reported in literature.[5]

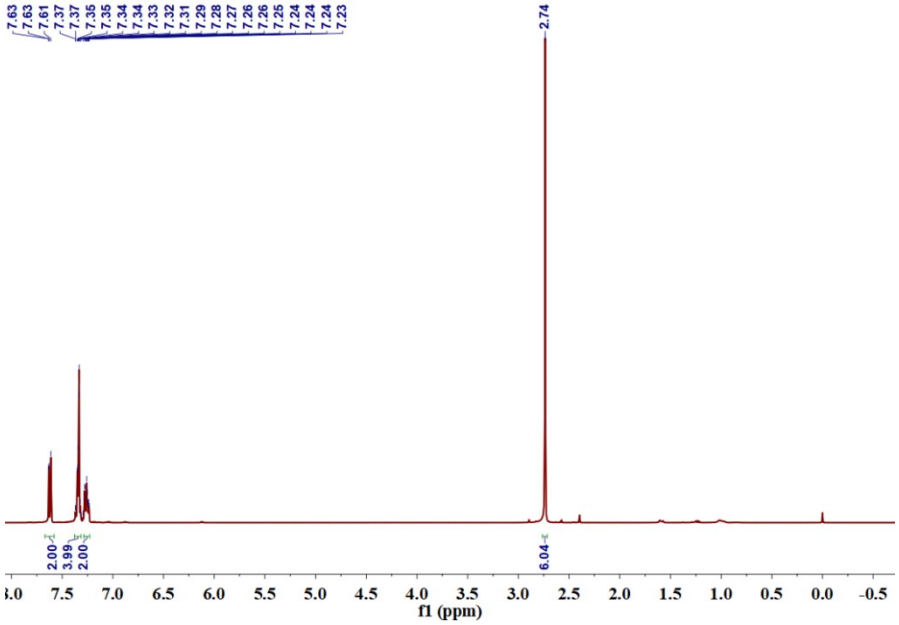


Fig. S18. ^{1}H NMR spectra of 2f in $CDCl_3$.

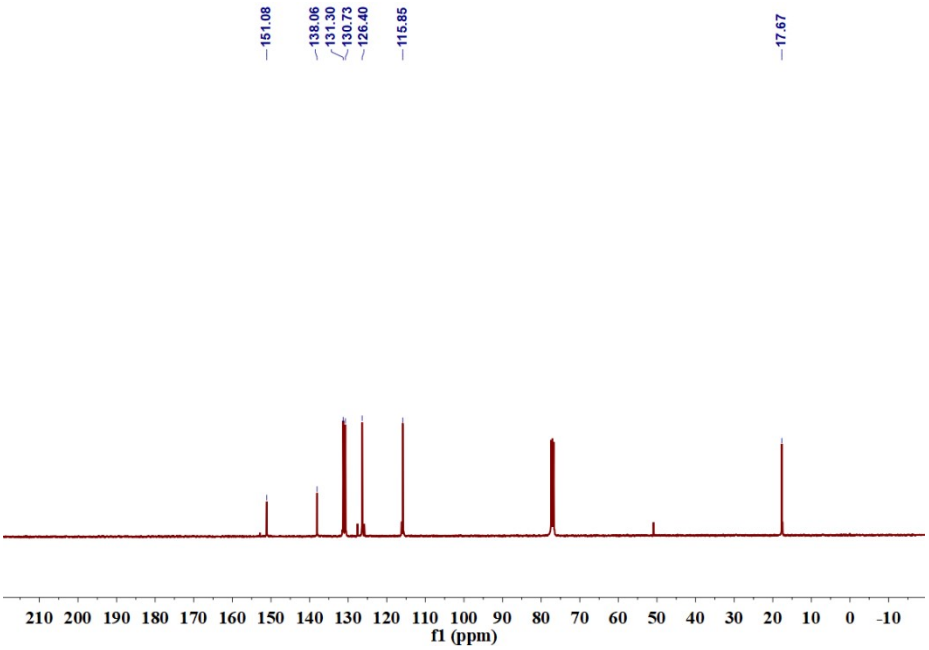
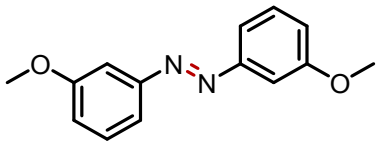


Fig. S19. ^{13}C NMR spectra of 2f in $CDCl_3$.

2g. 1-(3-methoxyphenyl)-2-(4-methoxyphenyl)diazene



Orange solid, 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 2H), 7.47 – 7.39 (m, 4H), 7.04 (ddd, *J* = 8.2, 2.7, 1.0 Hz, 2H), 3.89 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 153.8, 129.8, 117.9, 117.2, 105.7, 55.5.

The spectral data obtained were identical with those reported in literature.[3]

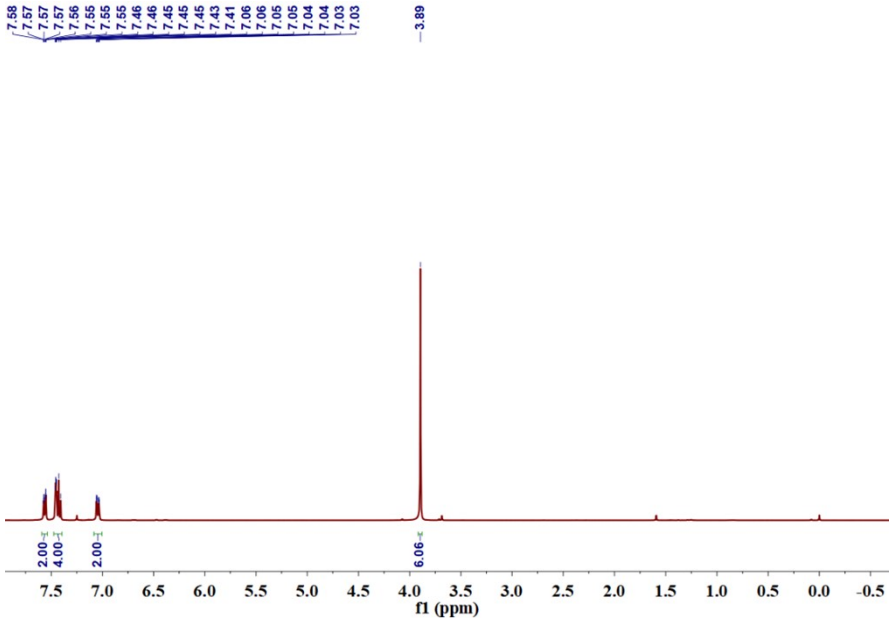


Fig. S20. ^{1}H NMR spectra of 2g in $CDCl_3$.

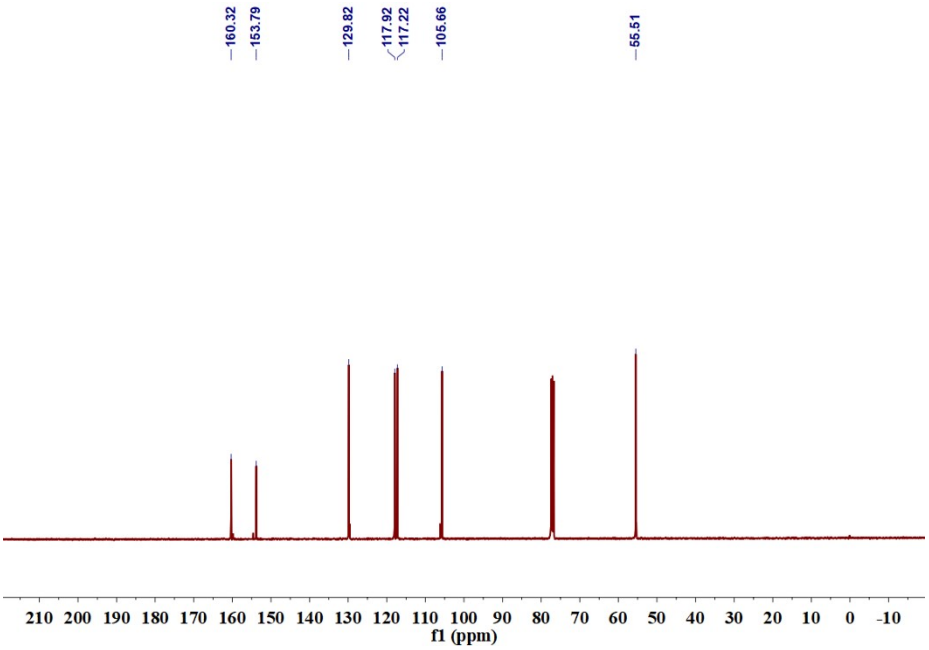
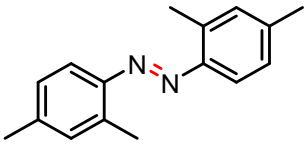


Fig. S21. ^{13}C NMR spectra of 2g in $CDCl_3$.

2h. 1,2-bis(2,4-dimethylphenyl)diazene



Orange solid, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.2 Hz, 2H), 7.16 – 7.11 (m, 2H), 7.05 (dd, J = 8.2, 1.9 Hz, 2H), 2.69 (s, 6H), 2.37 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 140.8, 137.9, 131.8, 127.1, 115.7, 21.4, 17.6.
The spectral data obtained were identical with those reported in literature.[6]

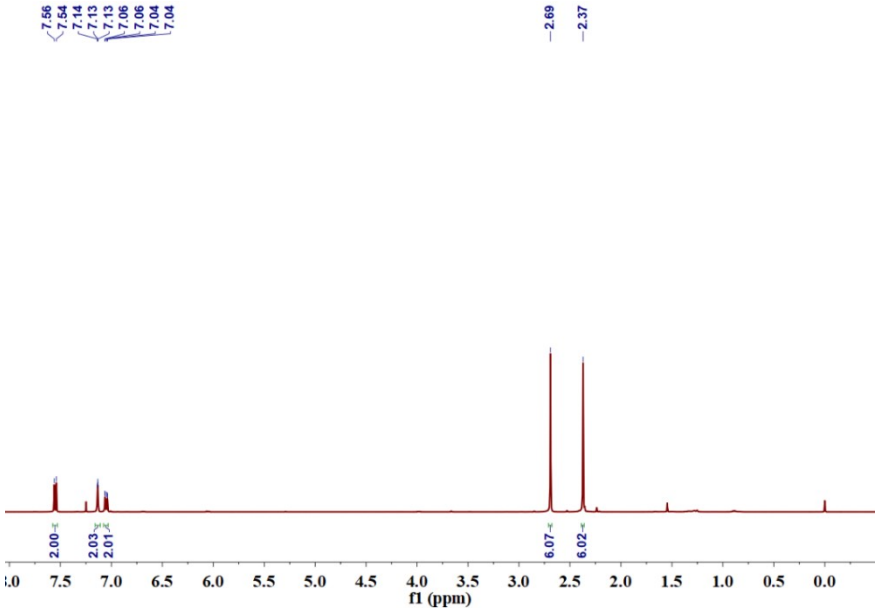


Fig. S22. ^{1}H NMR spectra of 2h in $CDCl_3$.

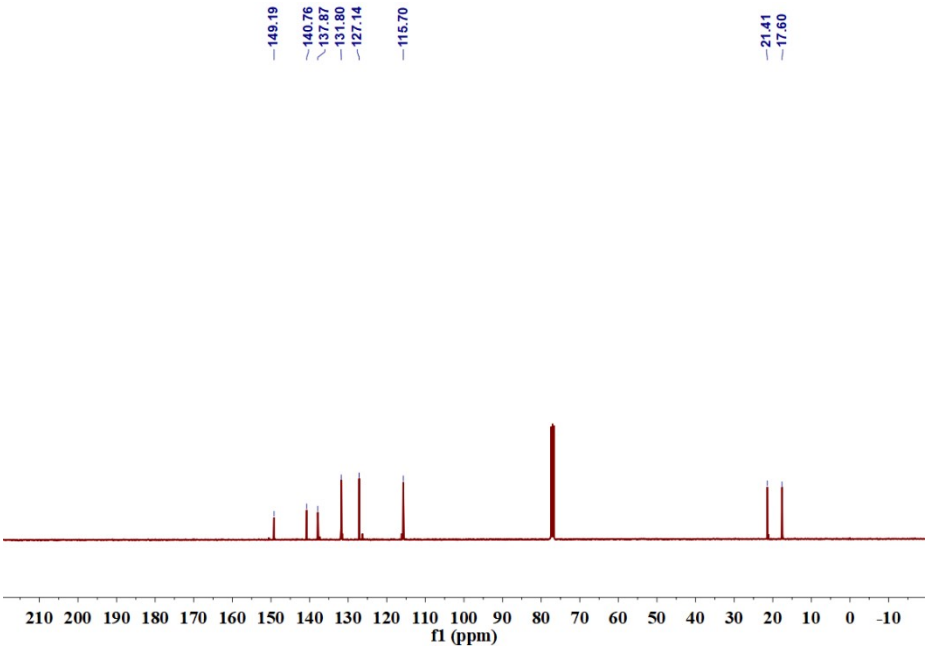
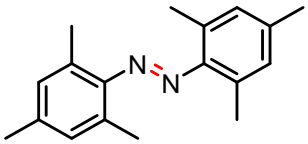


Fig. S23. ^{13}C NMR spectra of 2h in $CDCl_3$.

2i. 1,2-dimesityldiazene



Red solid, 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 4H), 2.41 (s, 12H), 2.34 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1, 138.4, 131.7, 130.1, 21.1, 20.1.
The spectral data obtained were identical with those reported in literature.[3]

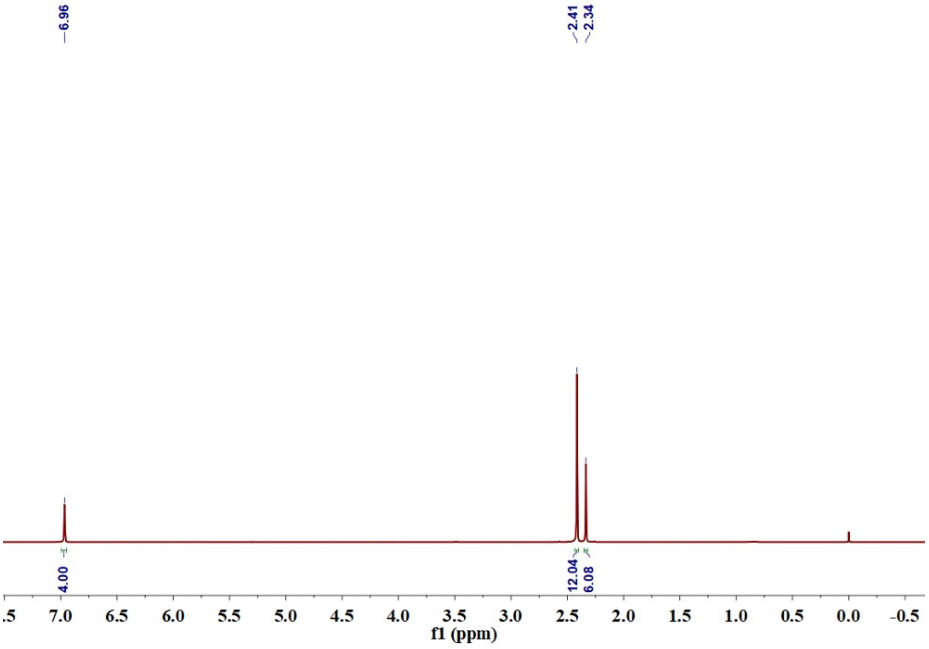


Fig. S24. ^{1}H NMR spectra of 2i in $CDCl_3$.

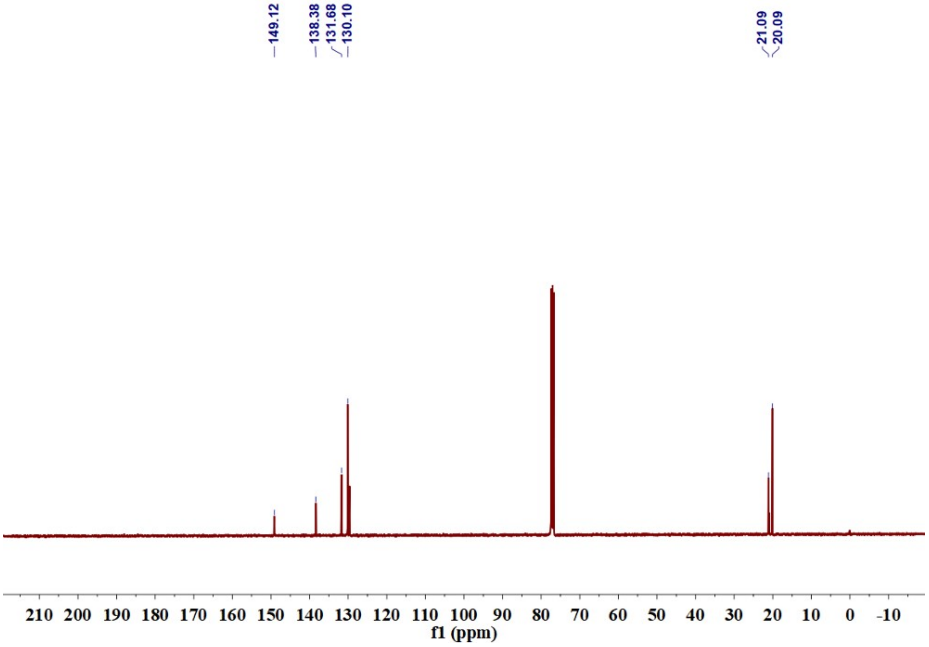
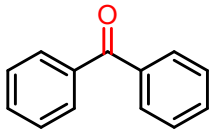


Fig. S25. ^{13}C NMR spectra of 2i in $CDCl_3$.

^{1}H NMR data of 4a-4o

4a. benzophenone



White solid, 95% yield;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 4H), 7.62 – 7.56 (m, 2H), 7.48 (t, J = 7.6 Hz, 4H).

The spectral data obtained were identical with those reported in literature.[7]

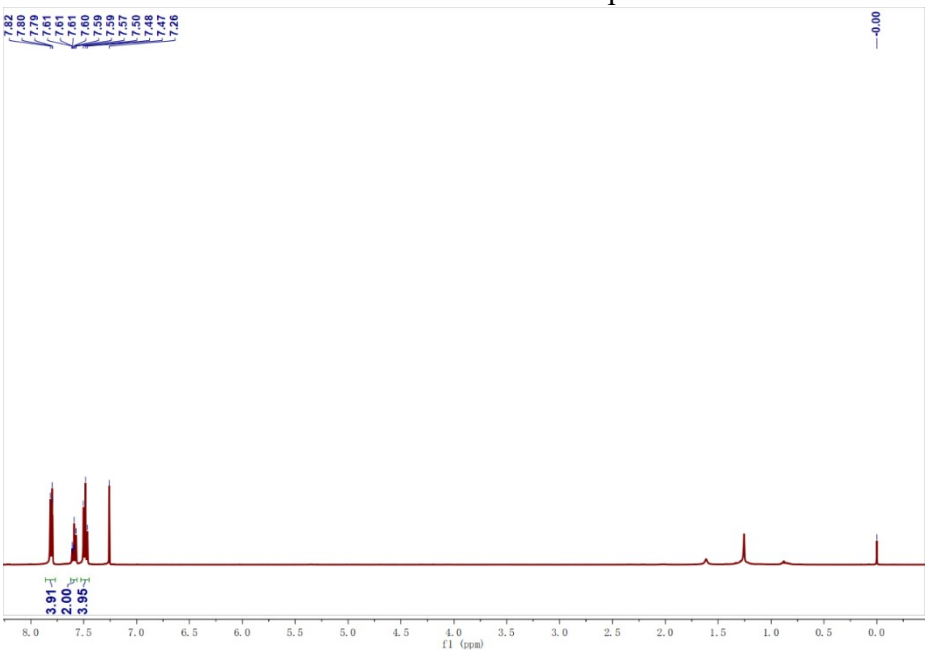
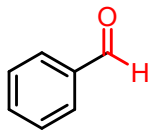


Fig. S26. ^{1}H NMR spectra of 4a in $CDCl_3$.

4b, 4m, and 4n benzaldehyde



Colorless oil, 74% yield for **4b**, 68% yield for **4m**, and 65% yield for **4n** (Note: The yield was obtained based on 0.4 mmol product); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.92 – 7.86 (m, 2H), 7.68 – 7.61 (m, 1H), 7.57 – 7.50 (m, 2H).

The spectral data obtained were identical with those reported in literature.[7]

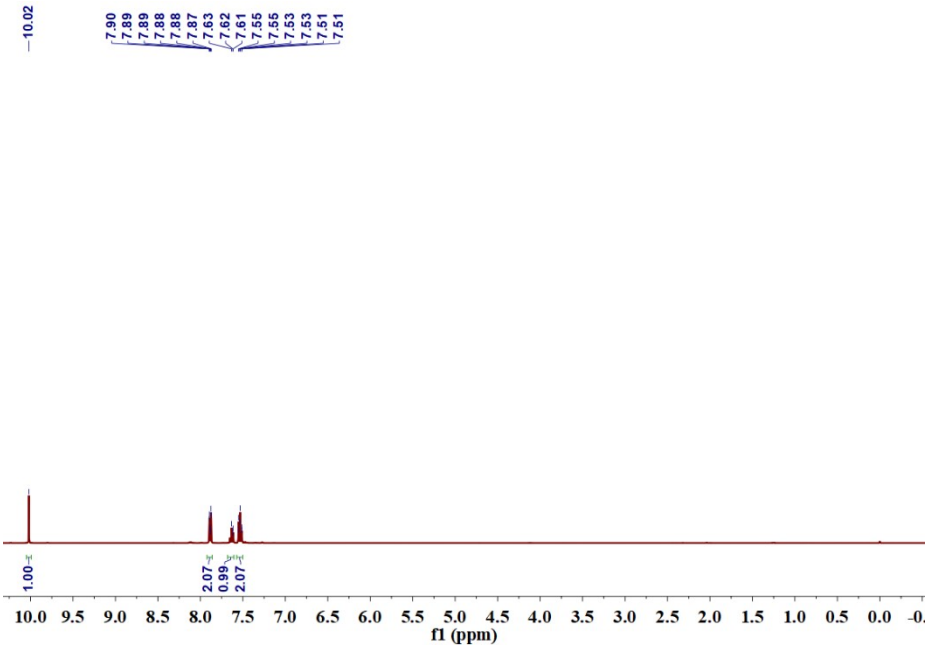
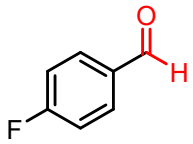


Fig. S27. ^{1}H NMR spectra of 4b, 4m, and 4n in $CDCl_3$.

4c. 4-fluorobenzaldehyde



Colorless oil, 77% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.94 – 7.87 (m, 2H), 7.20 (t, J = 8.5 Hz, 2H).

The spectral data obtained were identical with those reported in literature.[7]

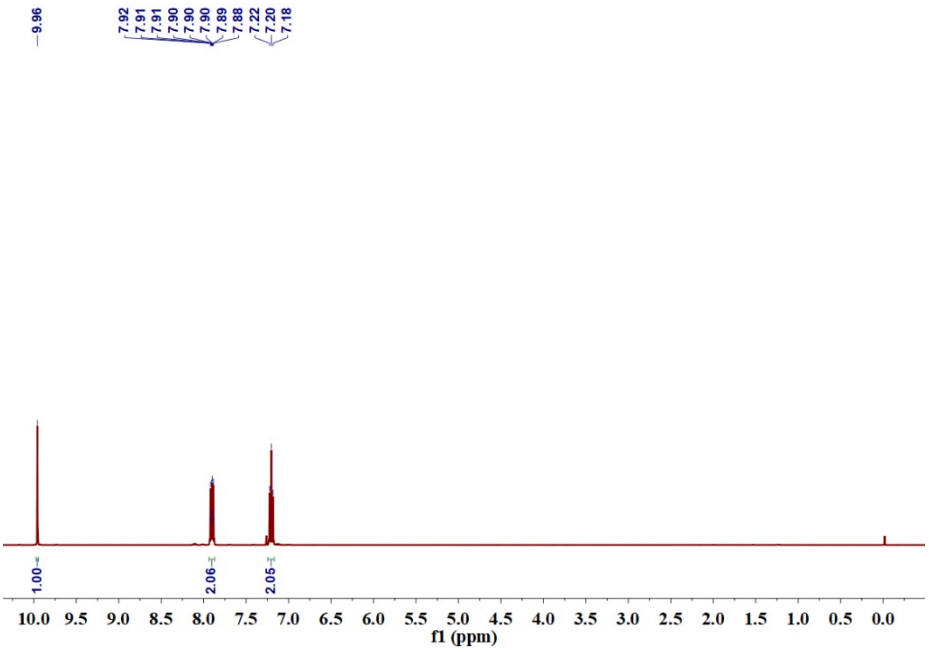
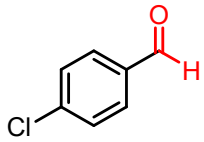


Fig. S28. ^{1}H NMR spectra of 4c in $CDCl_3$.

4d. 4-chlorobenzaldehyde



Colorless oil, 82% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.83 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H).

The spectral data obtained were identical with those reported in literature.[7]

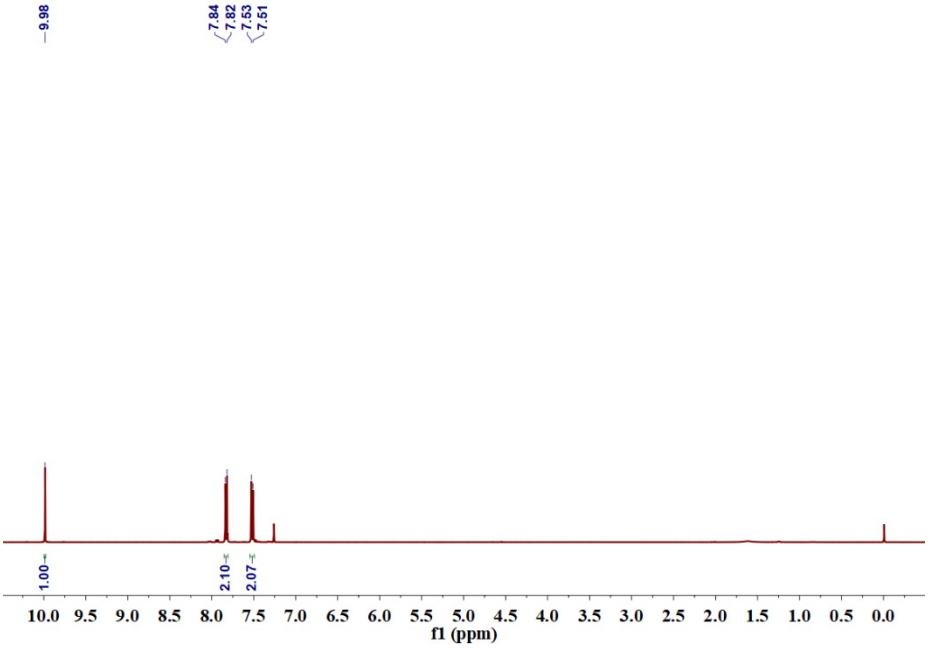
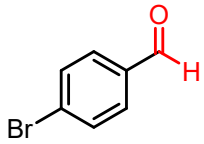


Fig. S29. ^{1}H NMR spectra of 4d in $CDCl_3$.

4e. 4-bromobenzaldehyde



Colorless oil, 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.75 (d, J = 8.5 Hz, 2H), 7.69 (d, J = 8.5 Hz, 2H).

The spectral data obtained were identical with those reported in literature.[7]

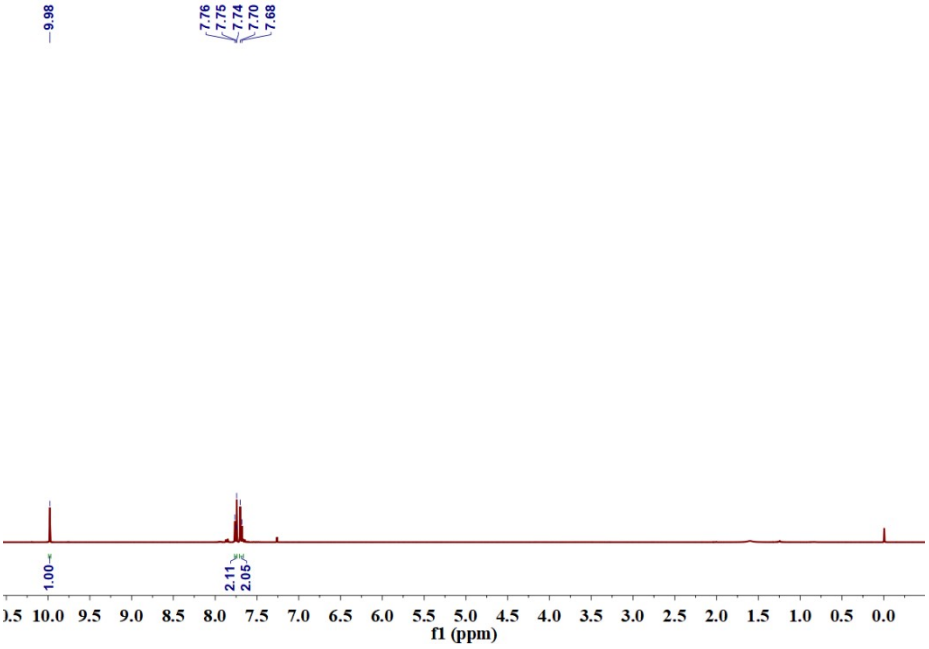
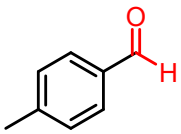


Fig. S30. ^{1}H NMR spectra of 4e in $CDCl_3$.

4f. 4-methylbenzaldehyde



Colorless oil, 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.80 – 7.74 (m, 2H), 7.32 (d, J = 7.9 Hz, 2H), 2.43 (s, 3H).
The spectral data obtained were identical with those reported in literature.[7]

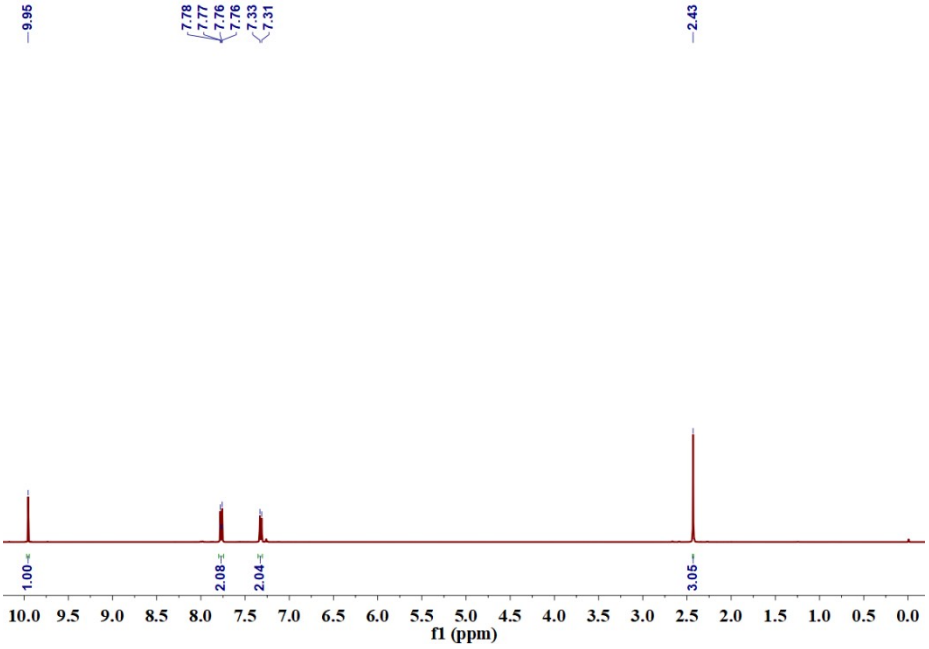
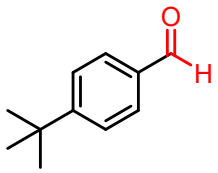


Fig. S31. ^{1}H NMR spectra of 4f in $CDCl_3$.

4g. 4-(tert-butyl)benzaldehyde



Colorless oil, 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.82 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 1.35 (s, 9H).
The spectral data obtained were identical with those reported in literature.[8]

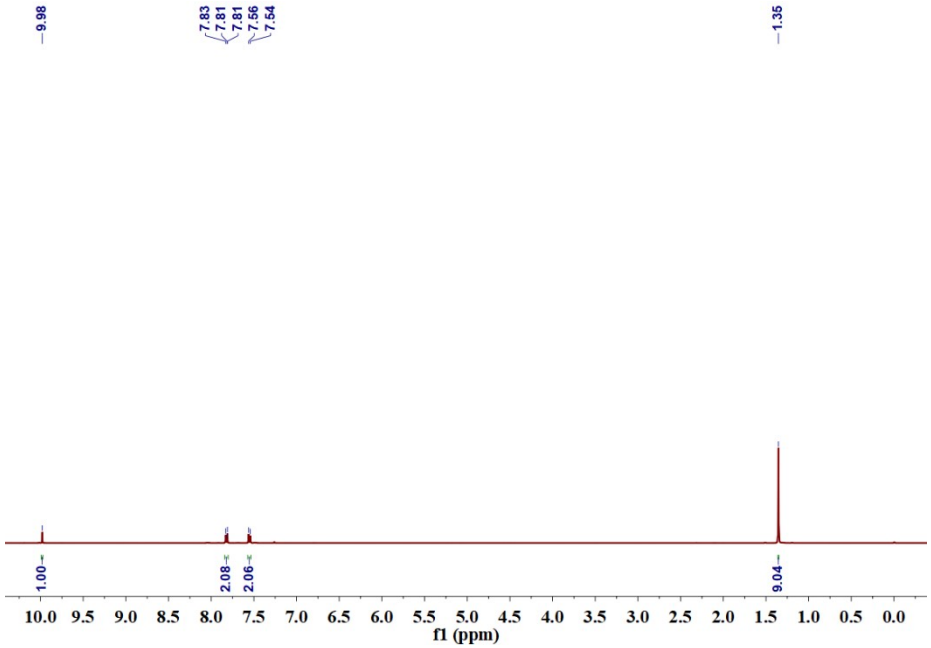
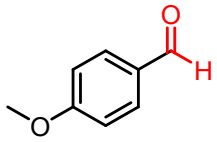


Fig. S32. ^{1}H NMR spectra of 4g in $CDCl_3$.

4h. 4-methoxybenzaldehyde



Colorless oil, 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.87 – 7.82 (m, 2H), 7.01 (d, J = 8.7 Hz, 2H), 3.90 (s, 3H).

The spectral data obtained were identical with those reported in literature.[8]

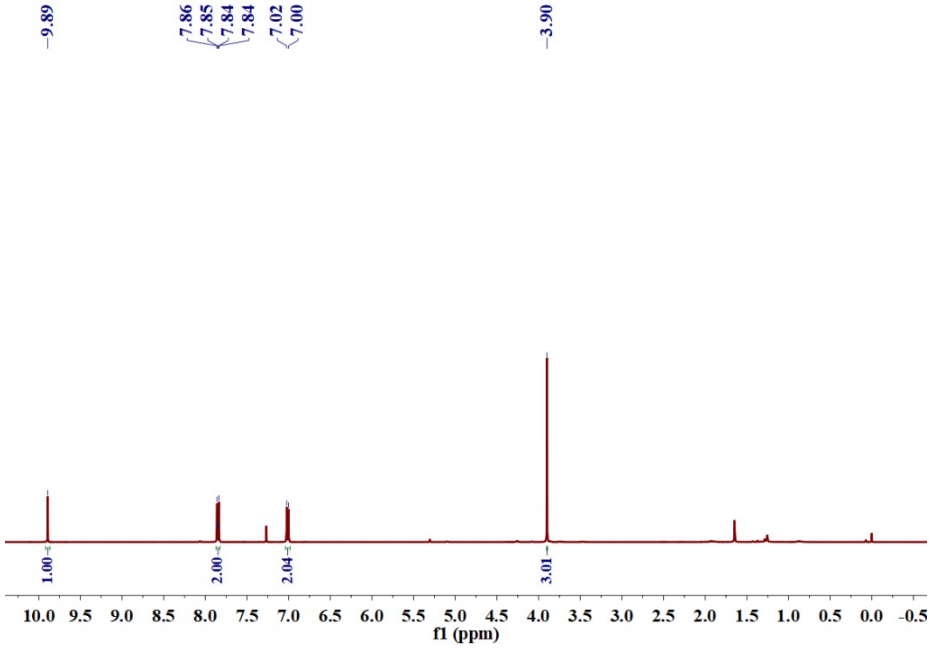
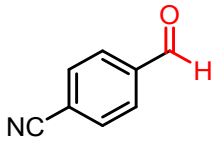


Fig. S33. ^{1}H NMR spectra of 4h in $CDCl_3$.

4i. 4-formylbenzonitrile



Colorless oil, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 1H), 8.02 – 7.98 (m, 2H), 7.85 (d, J = 8.3 Hz, 2H).

The spectral data obtained were identical with those reported in literature.[9]

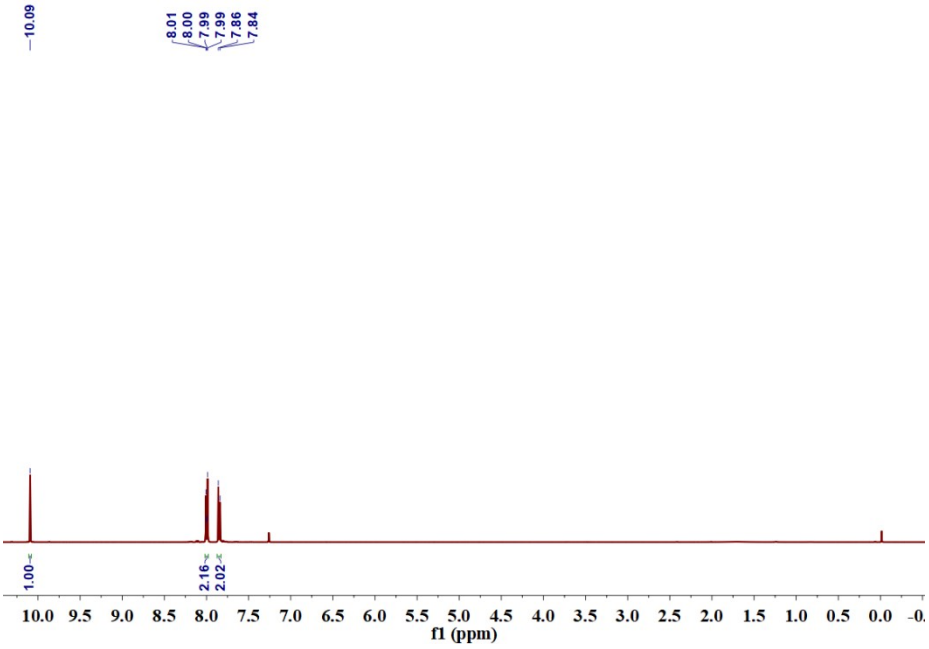
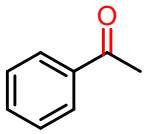


Fig. S34. ^{1}H NMR spectra of 4i in $CDCl_3$.

4j. acetophenone



Colorless oil, 94% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.92 (m, 2H), 7.60 – 7.54 (m, 1H), 7.47 (dd, J = 8.4, 7.0 Hz, 2H), 2.61 (s, 3H).
The spectral data obtained were identical with those reported in literature.[7]

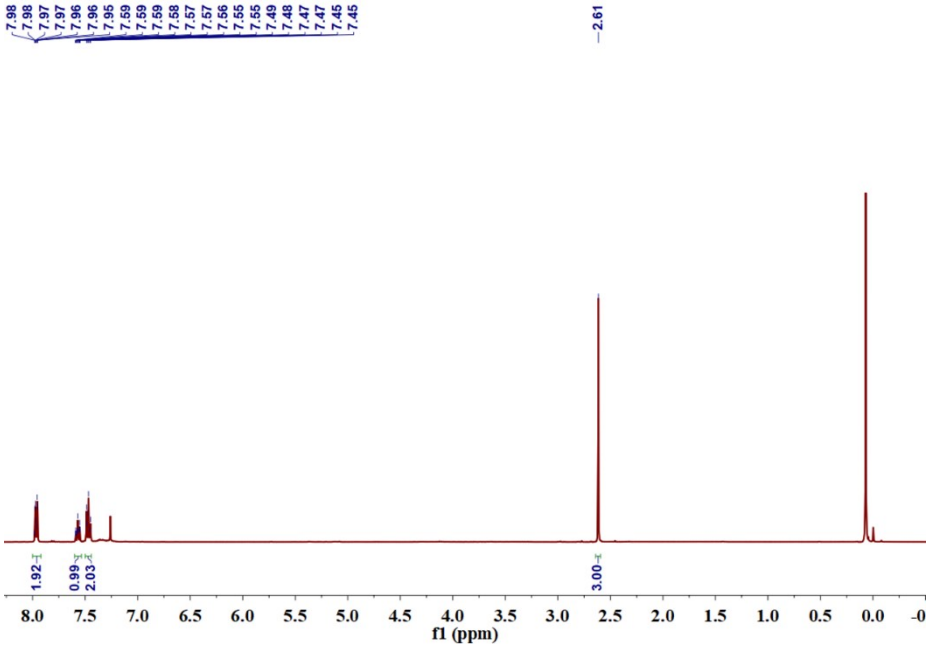
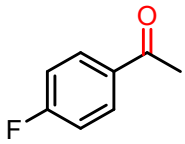


Fig. S35 ^{1}H NMR spectra of 4j in $CDCl_3$.

4k. 1-(4-fluorophenyl)ethan-1-one



Colorless oil, 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.82 (m, 2H), 7.44 – 7.36 (m, 2H), 2.56 (s, 3H).

The spectral data obtained were identical with those reported in literature.[7]

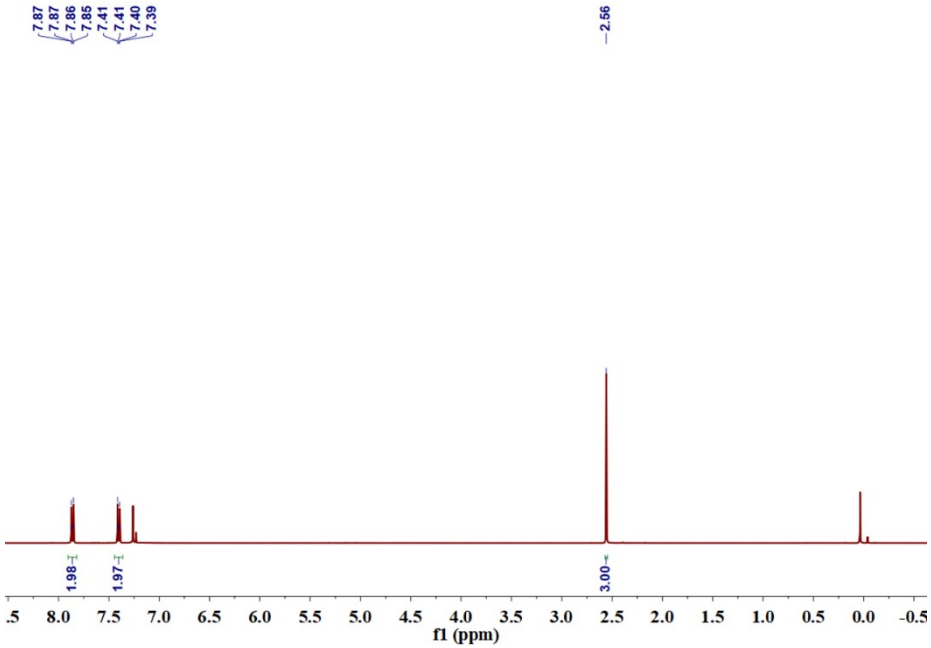
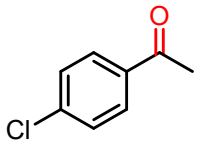


Fig. S36. ^{1}H NMR spectra of 4k in $CDCl_3$.

4l. 1-(4-chlorophenyl)ethan-1-one



Colorless oil, 93% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.92 (m, 2H), 7.19 – 7.07 (m, 2H), 2.59 (s, 3H).

The spectral data obtained were identical with those reported in literature.[7]

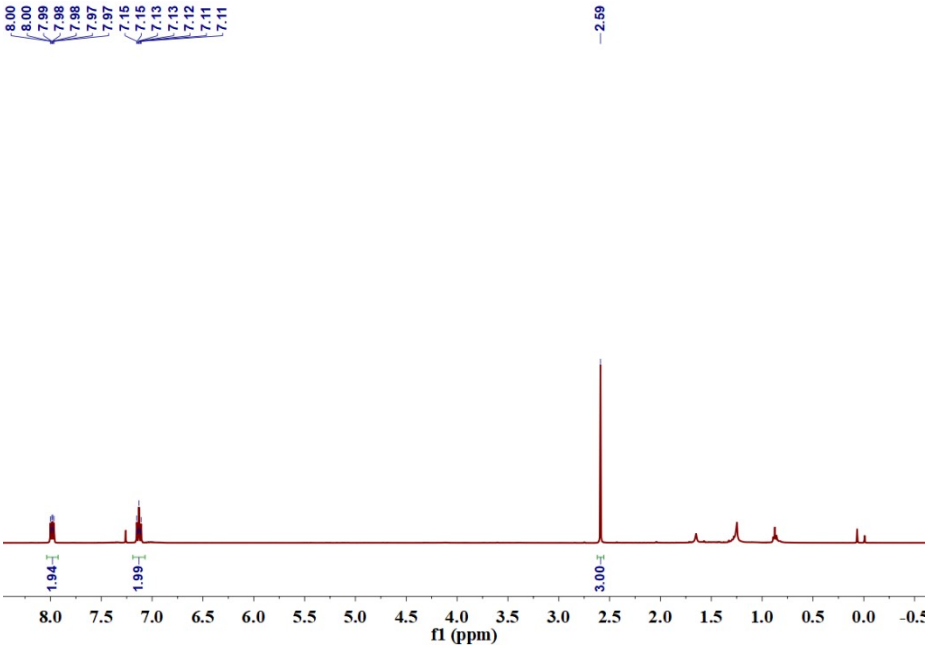
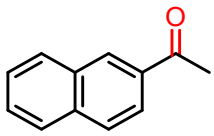


Fig. S37. ^{1}H NMR spectra of 4l in $CDCl_3$.

4o. 1-(naphthalen-2-yl)ethan-1-one



White solid, 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 – 8.45 (m, 1H), 8.04 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.89 (dd, *J* = 8.4, 6.3 Hz, 2H), 7.59 (dddd, *J* = 19.6, 8.2, 6.9, 1.4 Hz, 2H), 2.74 (s, 3H).
The spectral data obtained were identical with those reported in literature.[10]

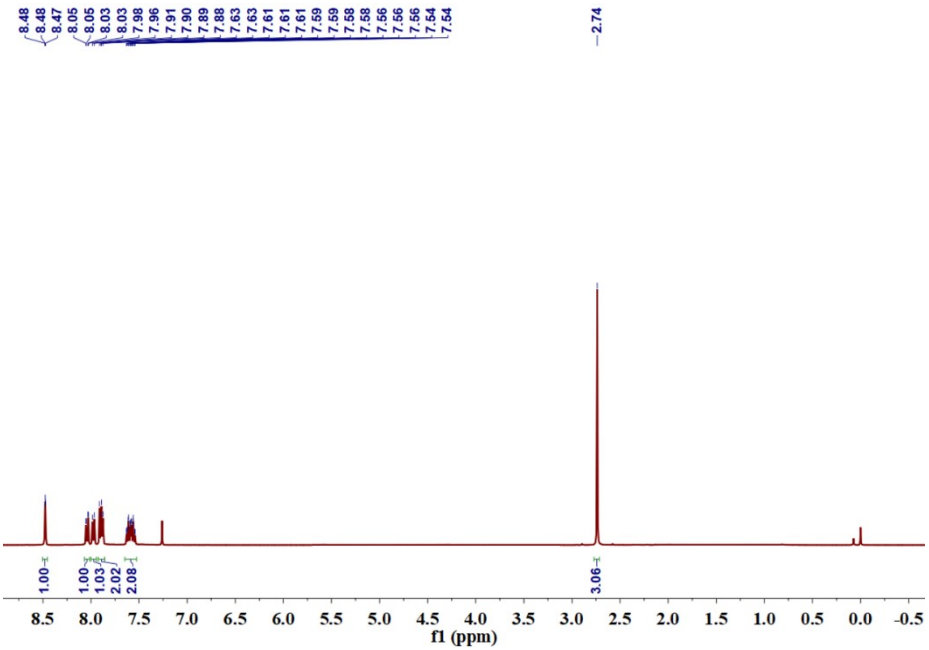
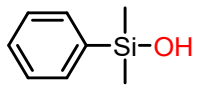


Fig. S38. ^{1}H NMR spectra of 4o in $CDCl_3$.

^{1}H NMR and ^{13}C NMR data of 6a-6f.

6a. dimethyl(phenyl)silanol



White solid, 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 2H), 7.34 – 7.26 (m, 3H), 0.27 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 132.1, 128.4, 126.8. The spectral data obtained were identical with those reported in literature.[11]

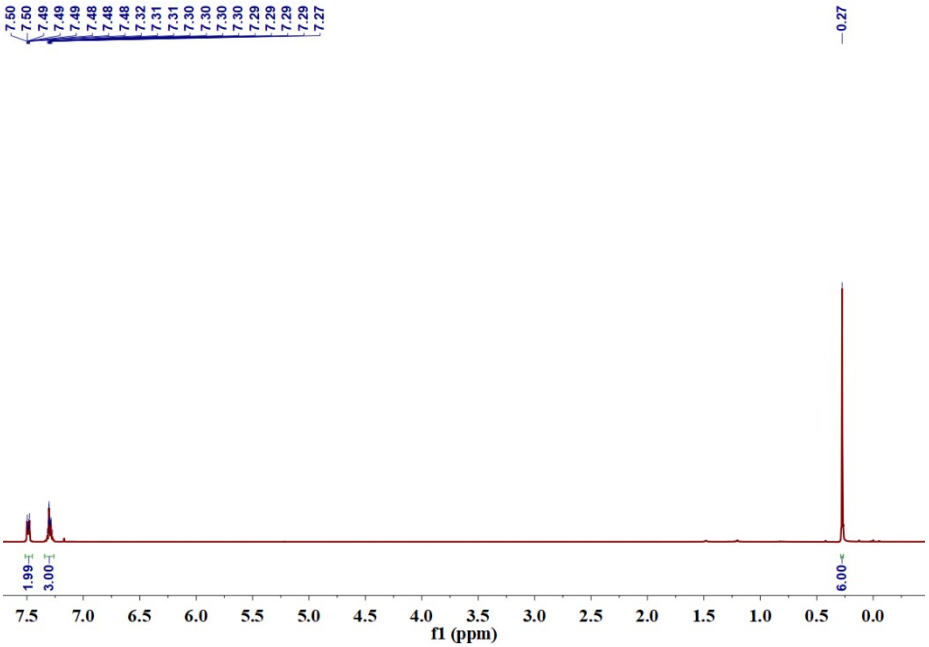


Fig. S39. ^{1}H NMR spectra of 6a in $CDCl_3$.

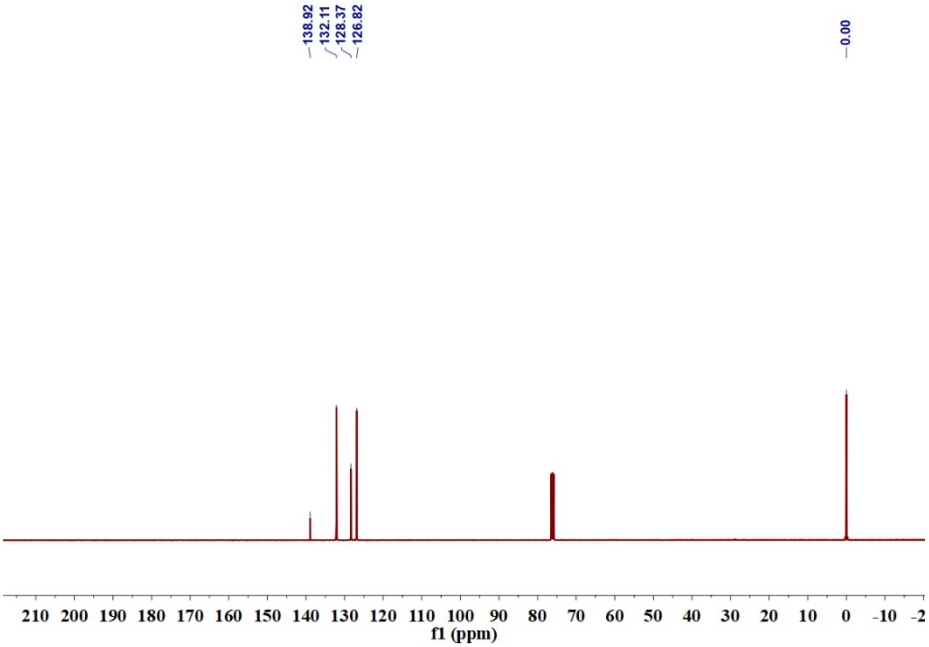
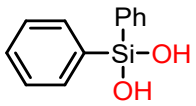


Fig. S40. ^{13}C NMR spectra of 6a in $CDCl_3$.

6b. diphenylsilanediol



White solid, 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (ddt, J = 11.4, 6.6, 1.4 Hz, 4H), 7.44 – 7.30 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.0, 134.3, 130.3, 130.3, 128.0, 127.9.

The spectral data obtained were identical with those reported in literature.[11]

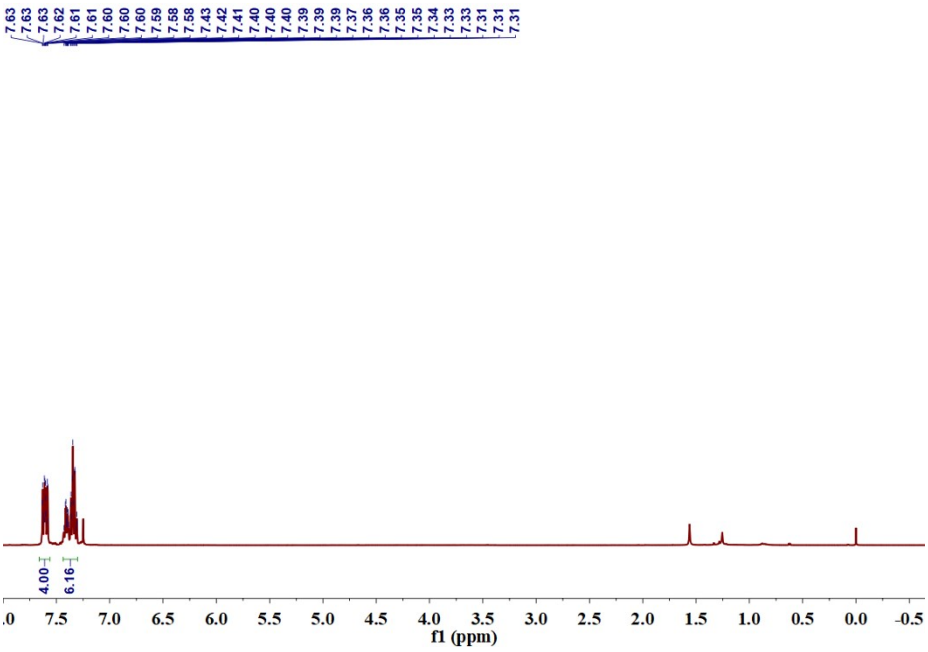


Fig. S41. ^{1}H NMR spectra of 6b in $CDCl_3$.

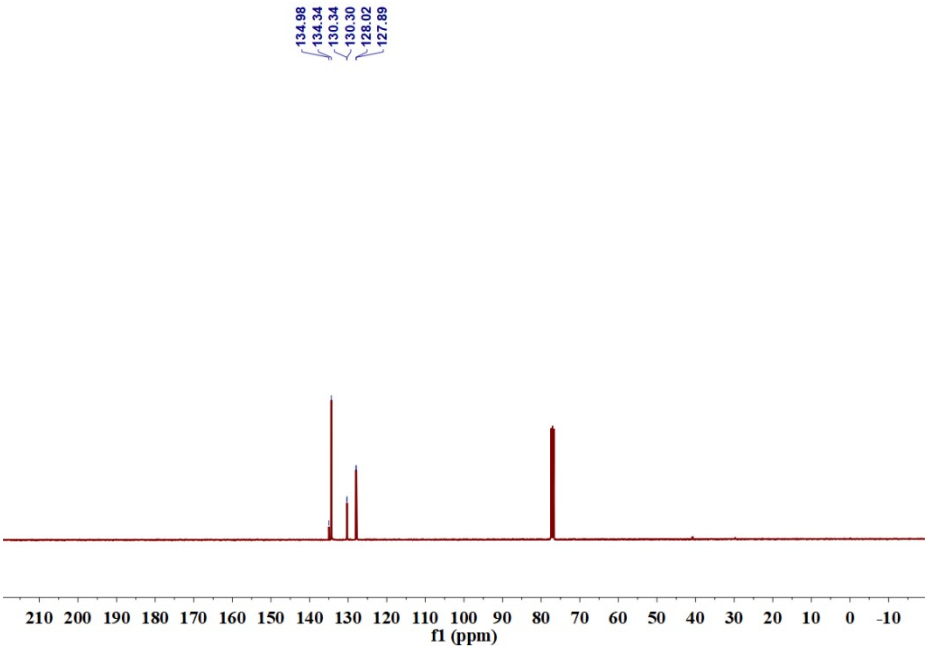
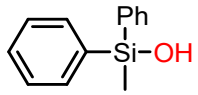


Fig. S42. ^{13}C NMR spectra of 6b in $CDCl_3$.

6c. methyldiphenylsilanol



White solid, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 4H), 7.42 – 7.30 (m, 6H), 0.62 (d, J = 3.9 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 135.4, 134.9, 129.6, 128.0, -4.9.

The spectral data obtained were identical with those reported in literature.[12]

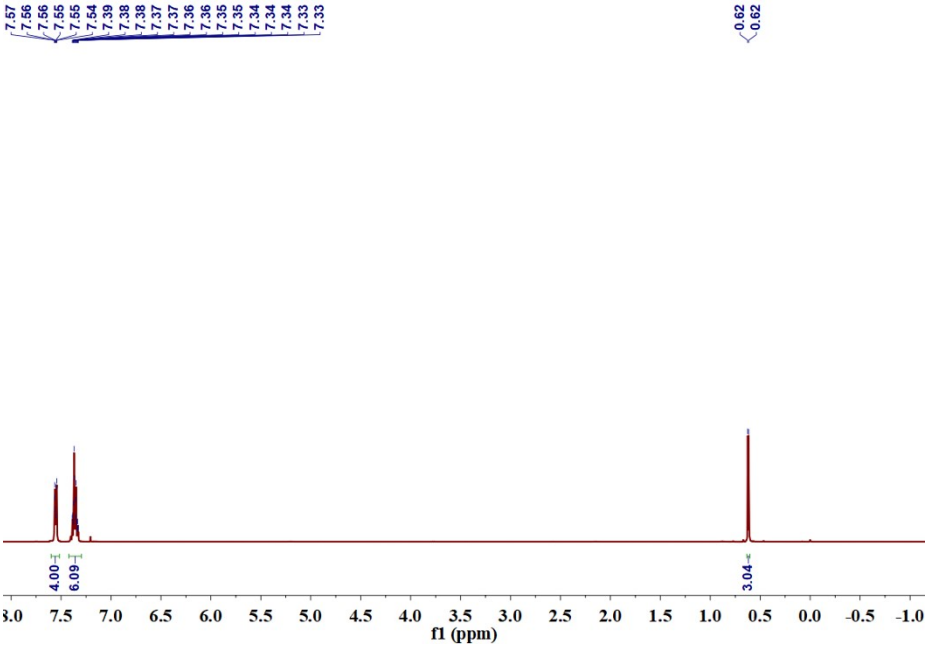


Fig. S43. ^{1}H NMR spectra of 6c in $CDCl_3$.

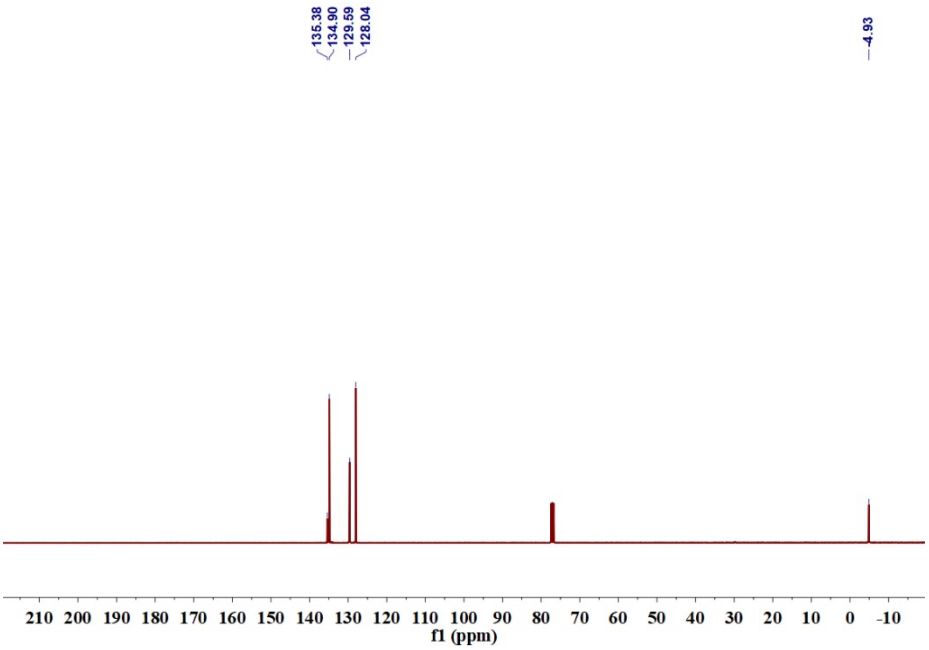
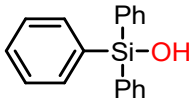


Fig. S44. ^{13}C NMR spectra of 6c in $CDCl_3$.

6d. triphenylsilanol



White solid, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.1 Hz, 6H), 7.41 (d, J = 7.1 Hz, 3H), 7.36 (t, J = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.4, 135.1, 130.1, 127.9.

The spectral data obtained were identical with those reported in literature.[11]

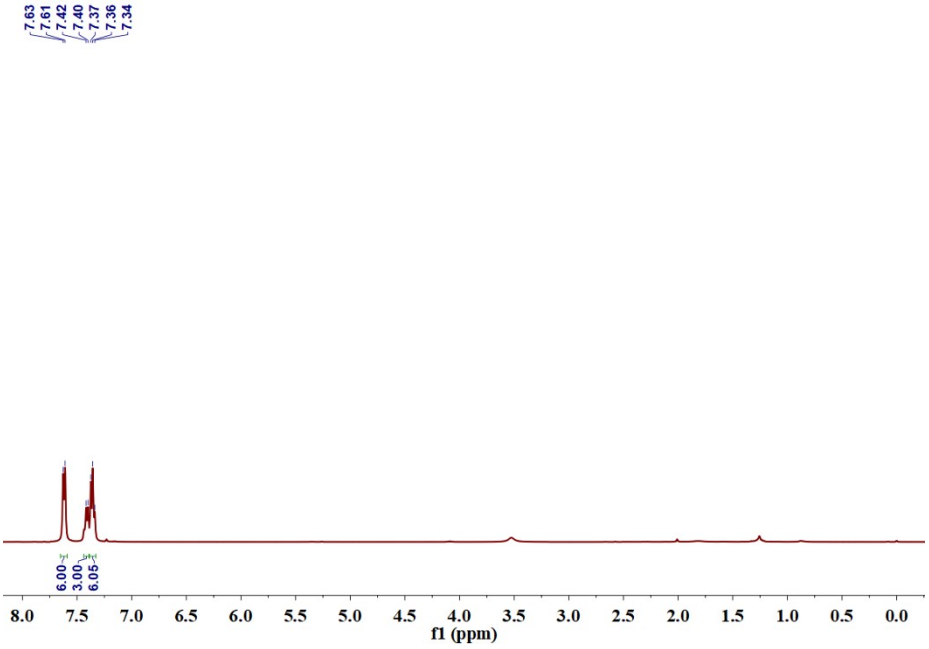


Fig. S45. ^{1}H NMR spectra of 6d in $CDCl_3$.

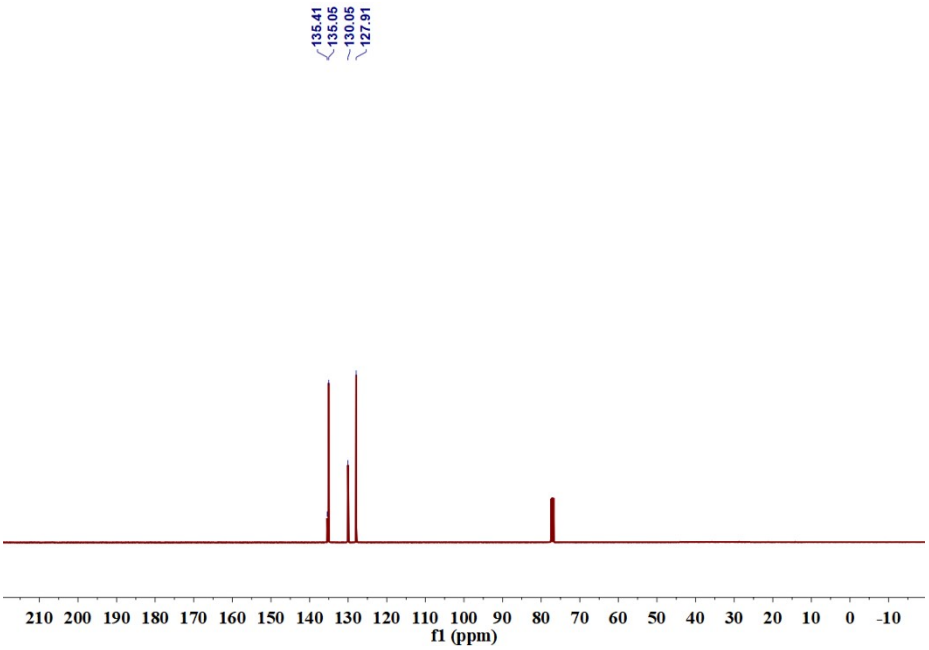
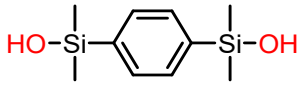


Fig. S46. ^{13}C NMR spectra of 6d in $CDCl_3$.

6e. 1,4-phenylenebis(dimethylsilanol)



White solid, 67% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 2.2 Hz, 4H), 0.33 (d, J = 1.8 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 131.4, 0.1.
The spectral data obtained were identical with those reported in literature.[11]

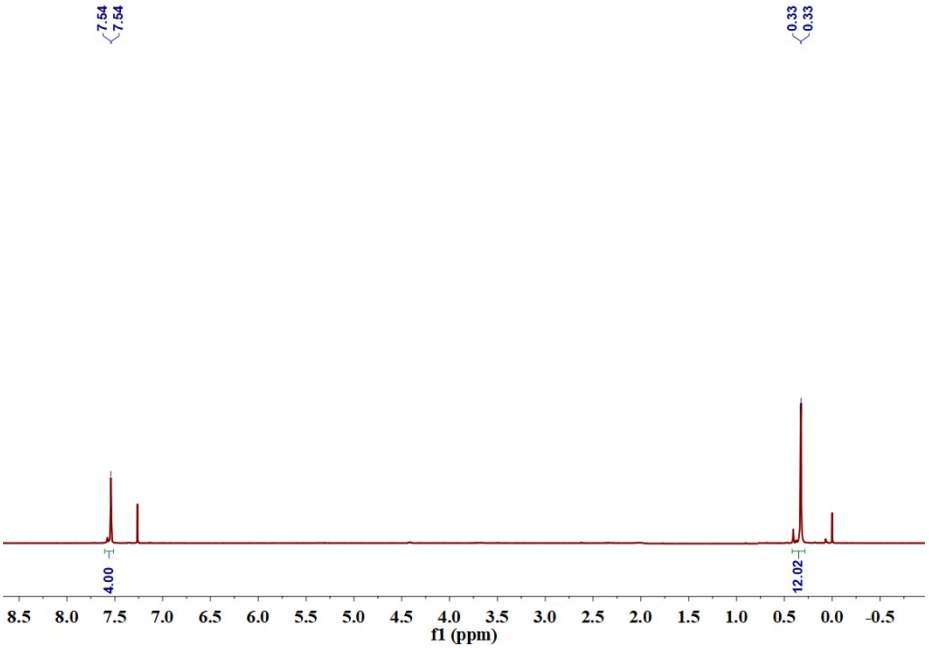


Fig. S47. ^{1}H NMR spectra of 6e in $CDCl_3$.

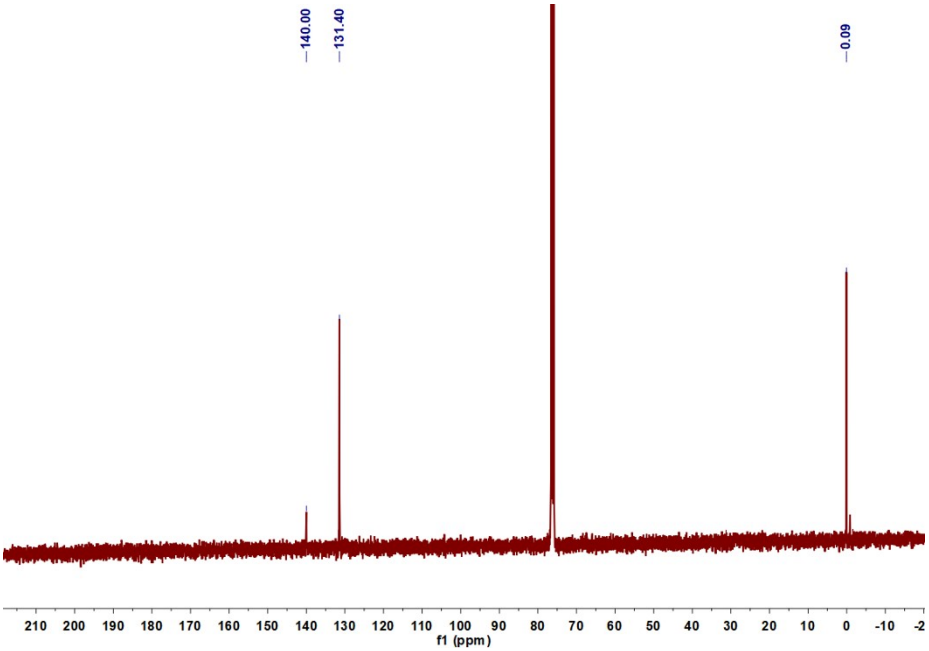
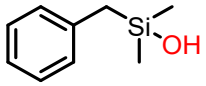


Fig. S48. ^{13}C NMR spectra of 6e in $CDCl_3$.

6f. benzyldimethylsilanol



White solid, 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, J = 8.3, 6.9 Hz, 2H), 7.12 – 7.05 (m, 1H), 7.04 – 6.98 (m, 2H), 2.08 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 129.0, 128.8, 124.7, 29.2, 0.6.
The spectral data obtained were identical with those reported in literature.[13]

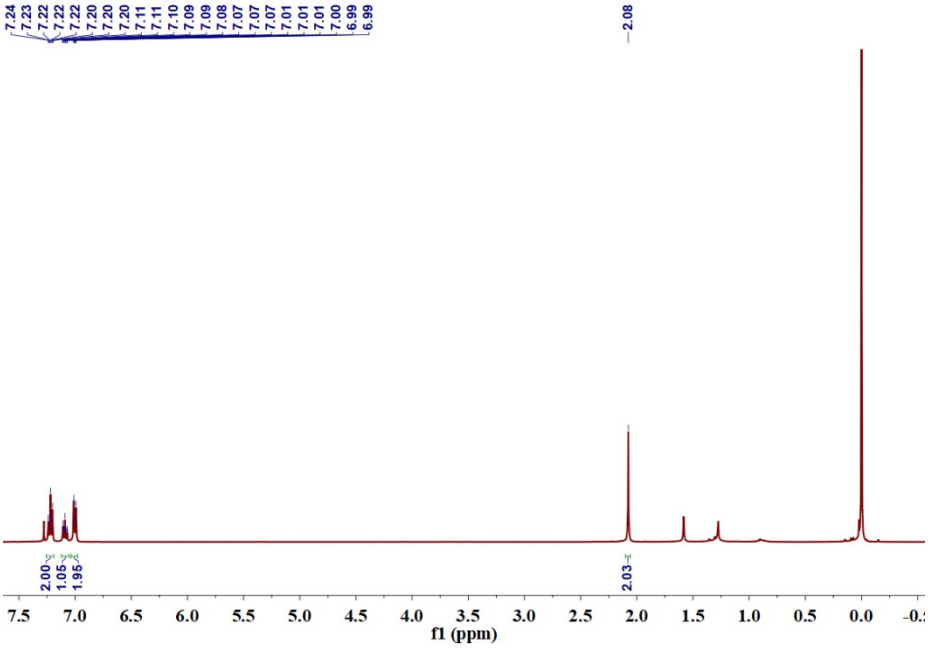


Fig. S49. ^{1}H NMR spectra of 6f in $CDCl_3$.

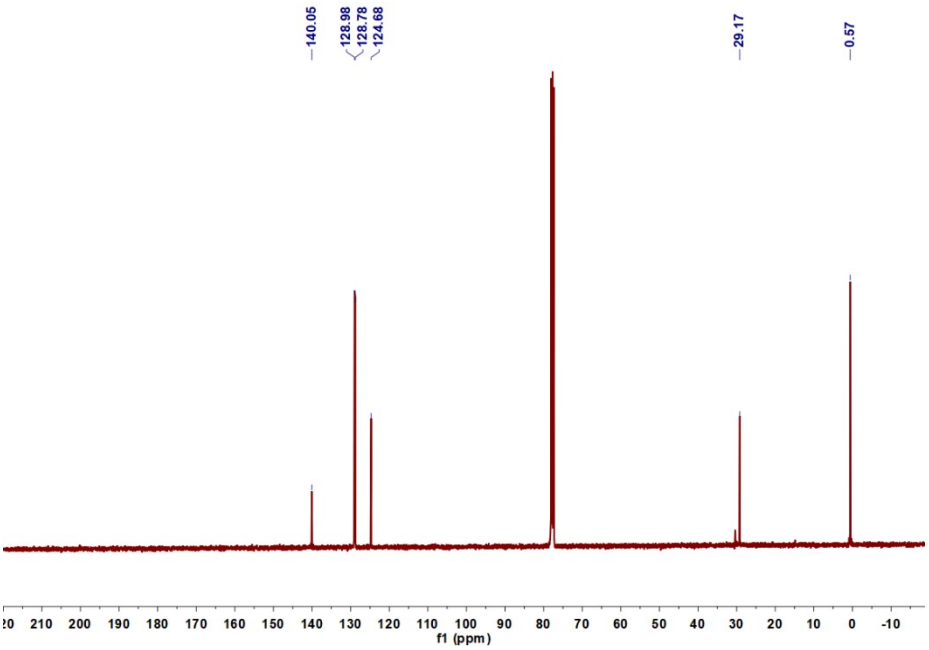


Fig. S50. ^{13}C NMR spectra of 6f in $CDCl_3$.

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