Electronic Supplementary Information for

Tetraphenylethylene-based photoresponse supramolecular organic framework and its metallization for photocatalytic redox reactions

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1. Experimental section

Materials

Unless specifically mentioned, all chemicals are commercially available and were used as received.

Characterization

^{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 spectra were obtained on a Shimadzu UV-1601PC spectrophotometer in a quartz cell (light path 10 mm) at 298 K. Steady-state fluorescence measurements were carried out using a Hitachi 4500 spectrophotometer. Dynamic light scattering (DLS) and zeta potential are measured on Malvern Zetasizer Nano ZS90. Transmission electron microscopy (TEM) images were obtained on a JEM 2100 operating at 120 kV. Samples for TEM measurements were prepared by dropping the mixture aqueous solution on carbon-coated copper grid (300 mesh) and drying by slow evaporation. Inductively coupled plasma-mass spectrometry (ICP-MS) data were obtained with an Agilent 7800x ICP-MS and analyzed using ICP-MS Mass Hunter. The photocatalytic reaction was performed on WATTCAS Parallel Photocatalytic Reactor (WP-TEC-HSL) with 10W COB LED.

Detection of $^1O_2$ production in solution

Compound 9,10-anthracenediyl-bis(methylene)-dimalonic acid (ABDA) was used as an indicator for detection of $^1O_2$ in solution (Fig. S6). 50 μM of photocatalyst was dissolved in 3.0 mL solution containing 250 μM of ABDA. The mixture was then placed in a cuvette and irradiated with a UV LEDs (365-367 nm). The absorption change of the sample at 378 nm was recorded by the UV-Vis absorption spectrophotometer.

Detection of $O_2^{\bullet-}$ production in solution

N,*N*,*N'*,*N'*-tetramethyl-phenylenediamine (TMPD) was used as the scavenger monitors $O_2^{\bullet-}$. The 5 mM TMPD solution in DMSO was added to the aqueous solution to form a 0.25 mM solution. 50 μM NA-TPE, 50 μM MV-DPY and 50 μM MVDPY-NATPE-CB[8] were added into TMPD solution respectively for $O_2^{\bullet-}$ generation measurement. The mixture was then placed in a cuvette and irradiated with UV LEDs (365-367 nm). The generation of $O_2^{\bullet-}$ was detected by monitoring the absorption at 612 nm through UV-vis absorption spectra.

General procedure for the aerobic oxidation reaction of N-phenyltetrahydroiso-quinoline

N-phenyltetrahydroisoquinoline (0.1 mmol, 20.9 mg) was added in the newly produced solution of MVDPY-NATPE-CB[8] (1.0 mol%, 3.0 mL, [NA-TPE] = 3.33×10^{-4} M, [MV-DPY] = 6.67×10^{-4} M, CB[8] = 1.33×10^{-3} M). The reaction was irradiated with UV LEDs (10 W, 365 nm-367 nm) at room temperature under the ambient air condition for 24 h. Then the mixture was extracted with dichloromethane, and the combined organic layer was dried with anhydrous Na_2SO_4. Then the organic solvent was removed in vacuo and purified by flash column chromatography with petroleum ether/ethyl acetate to afford the products.

General procedure for the aerobic oxidation reaction of 1,2-diphenylhydrazine

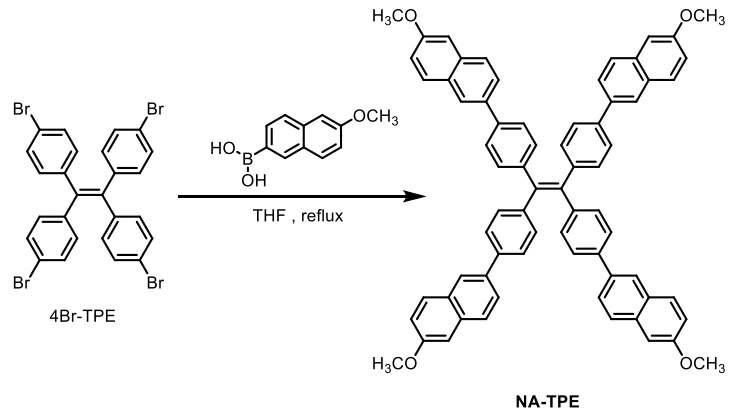
1,2-Diphenylhydrazine (0.2 mmol, 36.4 mg) was added in the newly produced solution of MVDPY-NATPE-CB[8] (1.0 mol%, 3.0 mL, [NA-TPE] = 3.33×10^{-4} M,

[MV-DPY] = 6.67 × 10^{-4} M, [CB[8]] = 1.33 × 10^{-3} M). The reaction was irradiated with UV LEDs (10 W, 365 nm-367 nm) at room temperature under the ambient air condition for 24 h. Then the mixture was extracted with dichloromethane, and the combined organic layer was dried with anhydrous Na_2SO_4. Then the organic solvent was removed in vacuo and purified by flash column chromatography with petroleum ether/ethyl acetate to afford the products.

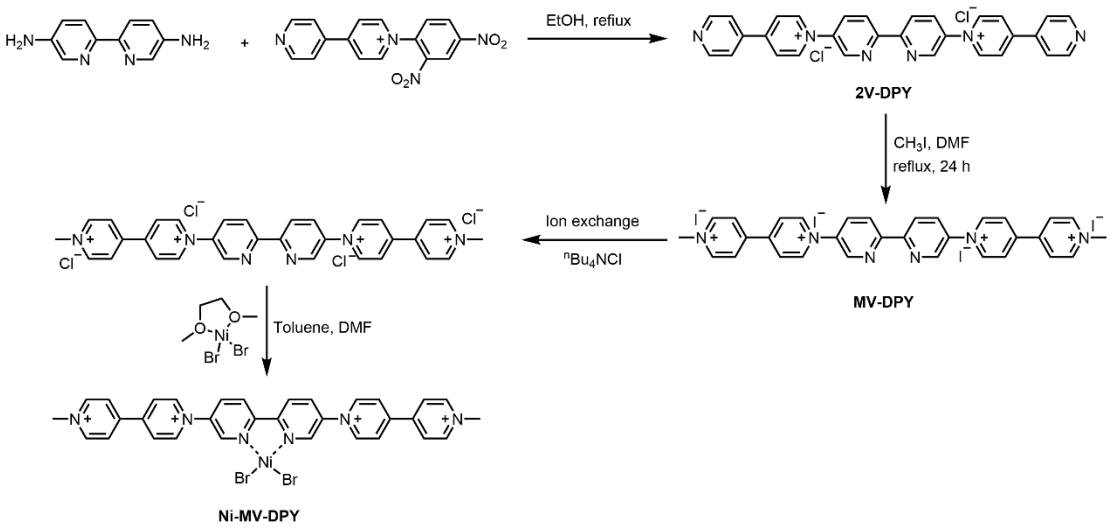
General procedure for the photocatalytic cross coupling reaction of p-toluenesulphenol and 4'-bromoacetophenone

4'-Bromoacetophenone (0.2 mmol, 39.8 mg), p-toluenesulphenol (0.2 mmol, 49.8 mg) was added in the newly produced solution of Ni- MVDPY-NATPE-CB[8] (1.0 mol%, 3.0 mL, [NA-TPE] = 3.33 × 10^{-4} M, [Ni-MV-DPY] = 6.67 × 10^{-4} M, [CB[8]] = 1.33 × 10^{-3} M). The reaction was irradiated with UV LEDs (10 W, 365 nm-367 nm) at room temperature under the ambient air condition for 24 h. Then the mixture was extracted with dichloromethane, and the combined organic layer was dried with anhydrous Na_2SO_4. Then the organic solvent was removed in vacuo and purified by flash column chromatography with petroleum ether/ethyl acetate to afford the products.

Synthesis of NA-TPE and Ni-MV-DPY



Scheme S1 Synthetic route of NA-TPE.



Scheme S2 Synthetic route of MV-DPY and Ni-MV-DPY.

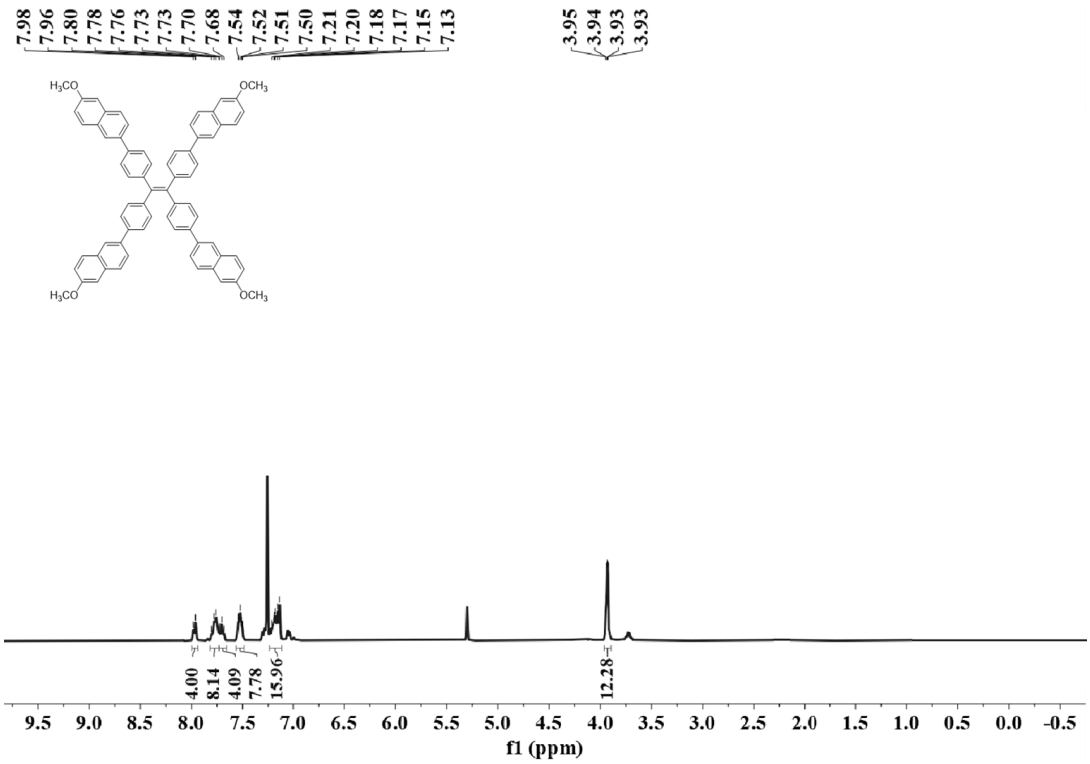


Fig. S1 ^{1}H NMR spectrum of compound NA-TPE in $CDCl_3$.

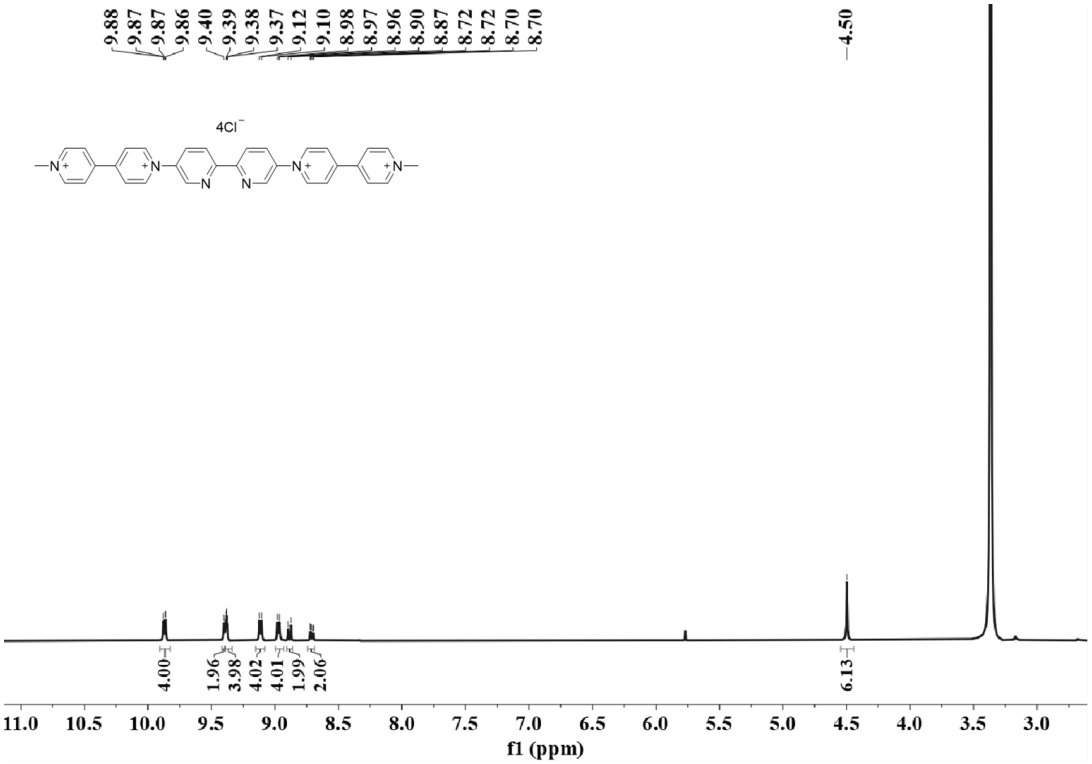


Fig. S2 ^{1}H NMR spectrum of compound MV-DPY in DMSO-d_6.

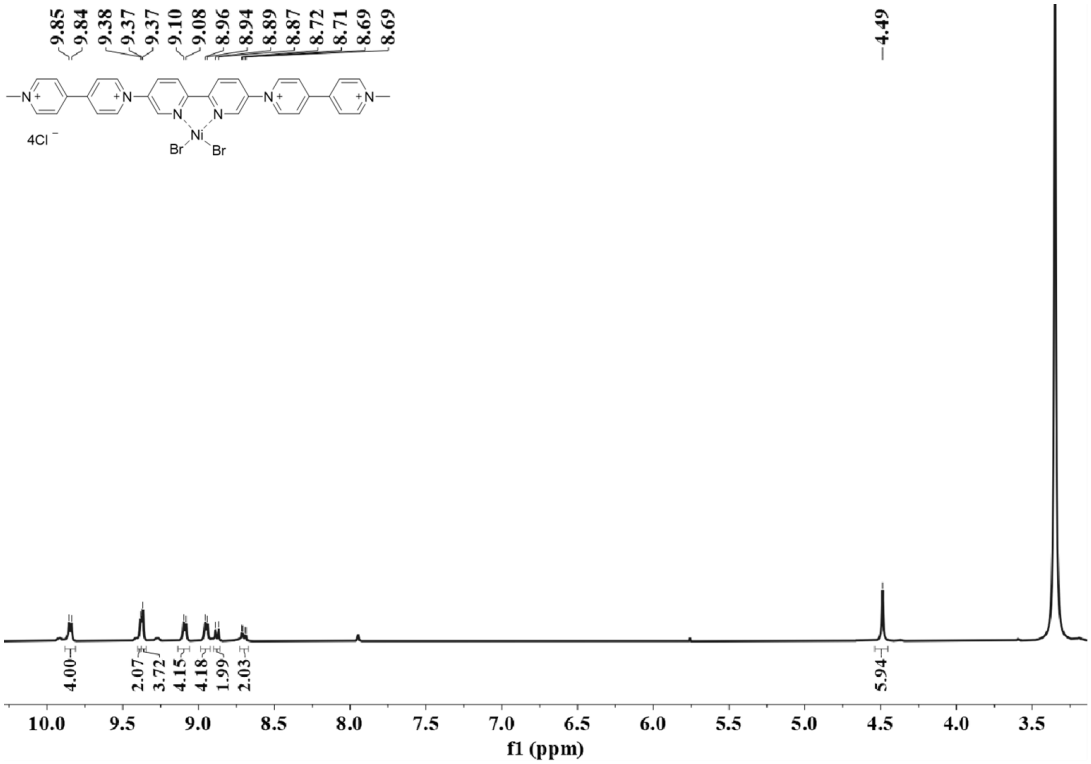


Fig. S3 ^{1}H NMR spectrum of compound Ni-MV-DPY in DMSO-d_6.

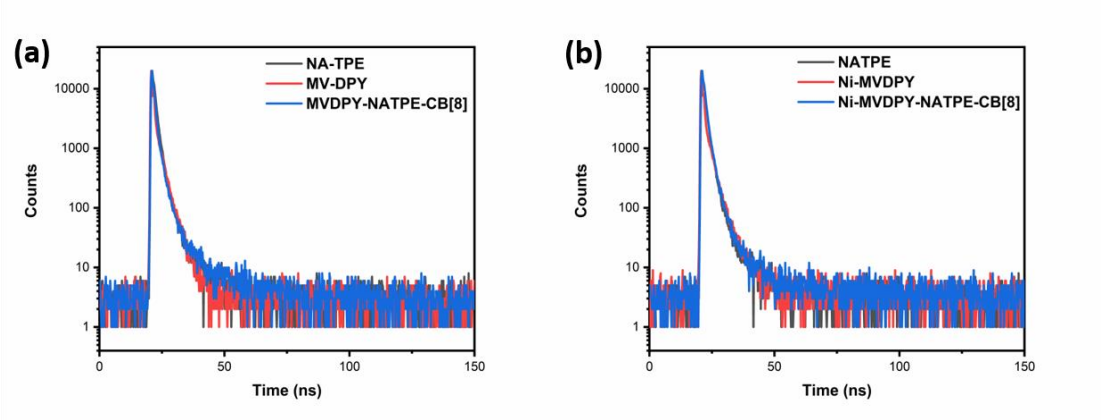


Fig. S4 Time-resolved fluorescence decay curves of (a) NA-TPE, MV-DPY, and MVDPY-NATPE-CB[8] and (b) NA-TPE, Ni-MV-DPY, and Ni-MVDPY-NATPE-CB[8].

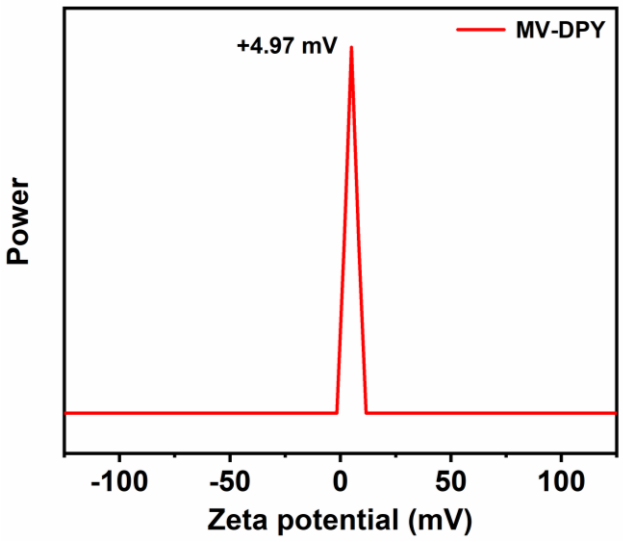


Fig. S5 Zeta potential of MV-DPY (2.0 $\times 10^{-5}$ M).

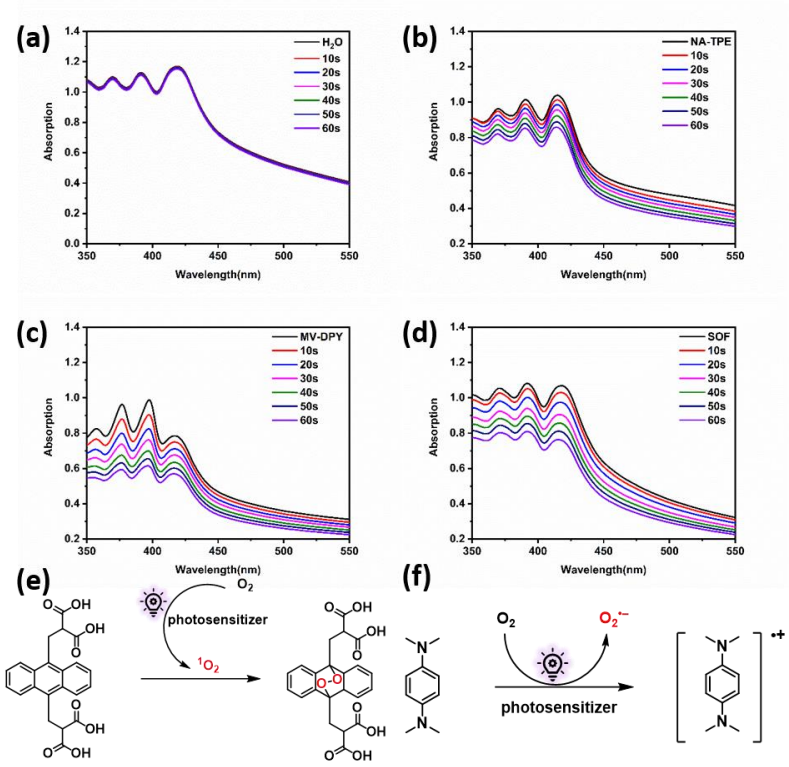


Fig. S6 UV-vis absorption spectra of (a) ABDA + H_2O, (b) ABDA + NA-TPE (5.0 × 10^{-5}M, 1.0 × 10^{-5} M), (c) ABDA + MV-DPY (5.0 × 10^{-5} M, 2.0 × 10^{-5} M) and (d) ABDA + SOF (5.0 × 10^{-5} M, 1.0 × 10^{-5} M) after irradiated by UV LEDs for different times; The reaction mechanism of (e) ABDA with $^1O_2$ and (f) TMPD with $O_2^{\bullet-}$.

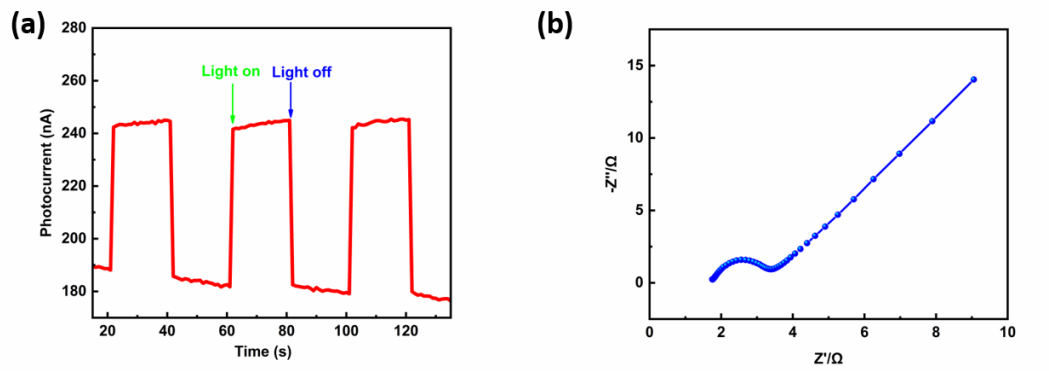


Fig. S7 (a) The transient photocurrent response and (b) The electrochemical impedance spectra of MVDPY-NATPE-CB[8].

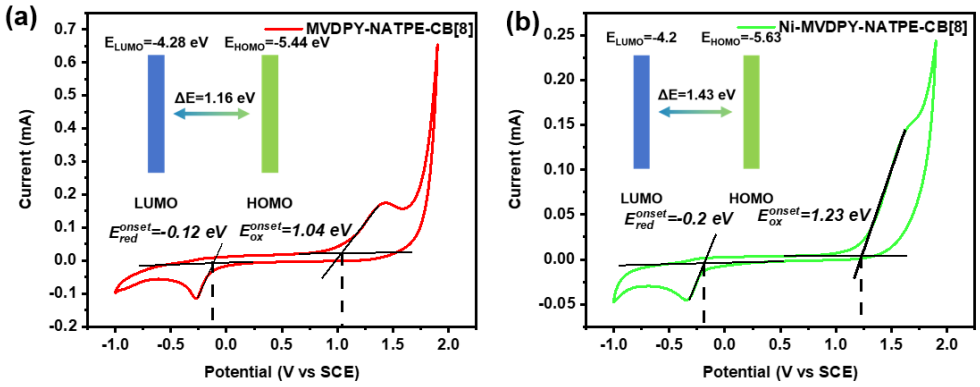


Fig. S8 Cyclic voltammograms of (a) MVDPY-NATPE-CB[8] and (b) Ni-MVDPY-NATPE-CB[8].

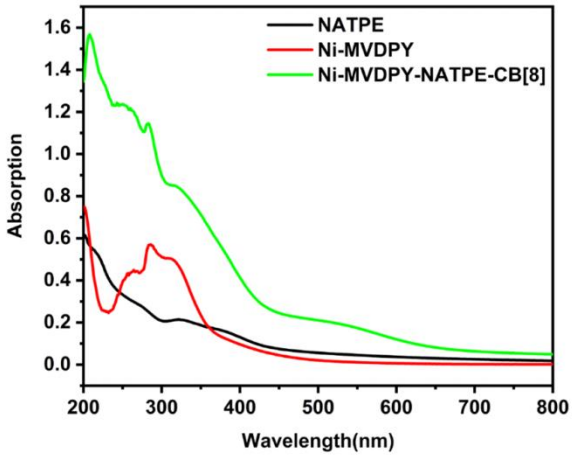
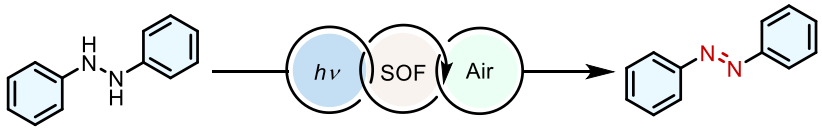


Fig. S9 UV-vis absorption spectra of MV-DPY (2.0×10^{-5} M), Ni-MV-DPY (2.0×10^{-5} M) and Ni-MV-DPY-NATPE-CB[8] (2.0×10^{-5} M) in the aqueous solution.

Table S1. Optimization of the aerobic oxidation reaction of 1,2-diphenylhydrazine conditions.[a,b]

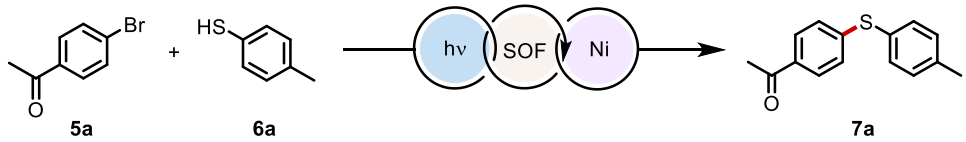


3a 4a

Entry	Variation from standard conditions	Yield[b](%)
1	None	86
2	NA-TPE	No reaction
3	MV-DPY	33
4	0.5 mol% SOF	54
5	2.0 mol% SOF	88
6	18 h	64
7	32 h	87
8	No light	No reaction

[a]Reaction conditions: 1,2-diphenylhydrazine (0.2 mmol, 36.4 mg), DMVPY-NATPE-CB[8] as photocatalyst, UV LEDs (365-367 nm), room temperature, 24 h; [b]Isolated yield.

Table S2. Optimization of the cross coupling reaction of p-toluenesulphenol and 4'-bromoacetophenone conditions.[c,d]



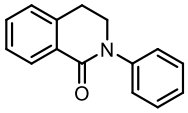
5a 6a 7a

Entry	Variation from standard conditions	Yield[b](%)
1	None	80
2	NA-TPE	No reaction
3	MV-DPY	25
4	0.5 mol% SOF-Ni	51
5	2.0 mol% SOF-Ni	82
6	18 h	56
7	32 h	81
8	No light	No reaction

[c]Satandard conditions: **1a** (0.20 mmol,39.8 mg), **2a** (0.40 mmol, 24.9 mg), pyridine (0.2 mmol, 15.8 mg), 1.0 mol% Ni-DMVPY-NATPE-CB[8] as photocatalyst, UV LEDs (365-367 nm), room temperature, 24 h; [d]Isolated yield.

^{1}H NMR and ^{13}C NMR data of 2a-2f, 4a-4i, and 7a-7f

2a. 2-phenyl-3,4-dihydroisoquinolin-1(2H)-one



83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 7.7 Hz, 1H), 7.46 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.24 (q, J = 8.3 Hz, 6H), 3.97 (t, J = 6.4 Hz, 2H), 3.14 (t, J = 6.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.25, 143.11, 138.32, 132.07, 129.73, 128.96, 128.78, 127.24, 126.97, 126.29, 125.34, 49.44, 28.65.

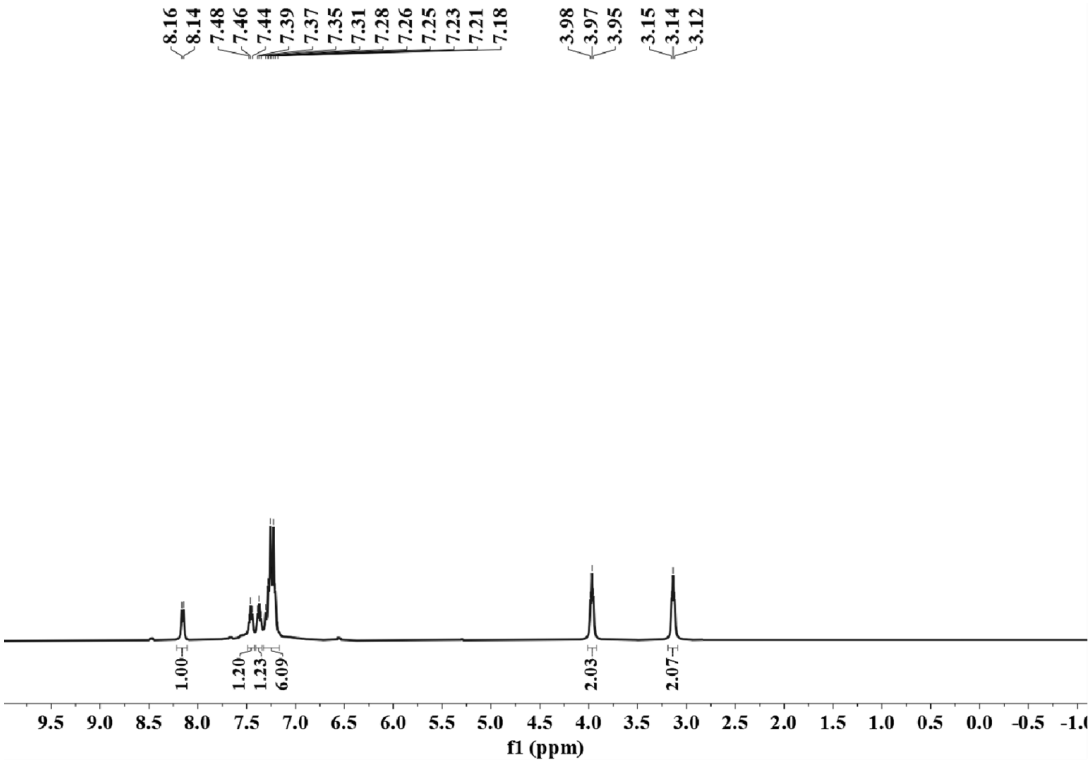


Fig. S10 ^{1}H NMR spectra of 2-phenyl-3,4-dihydroisoquinolin-1(2H)-one in $CDCl_3$.

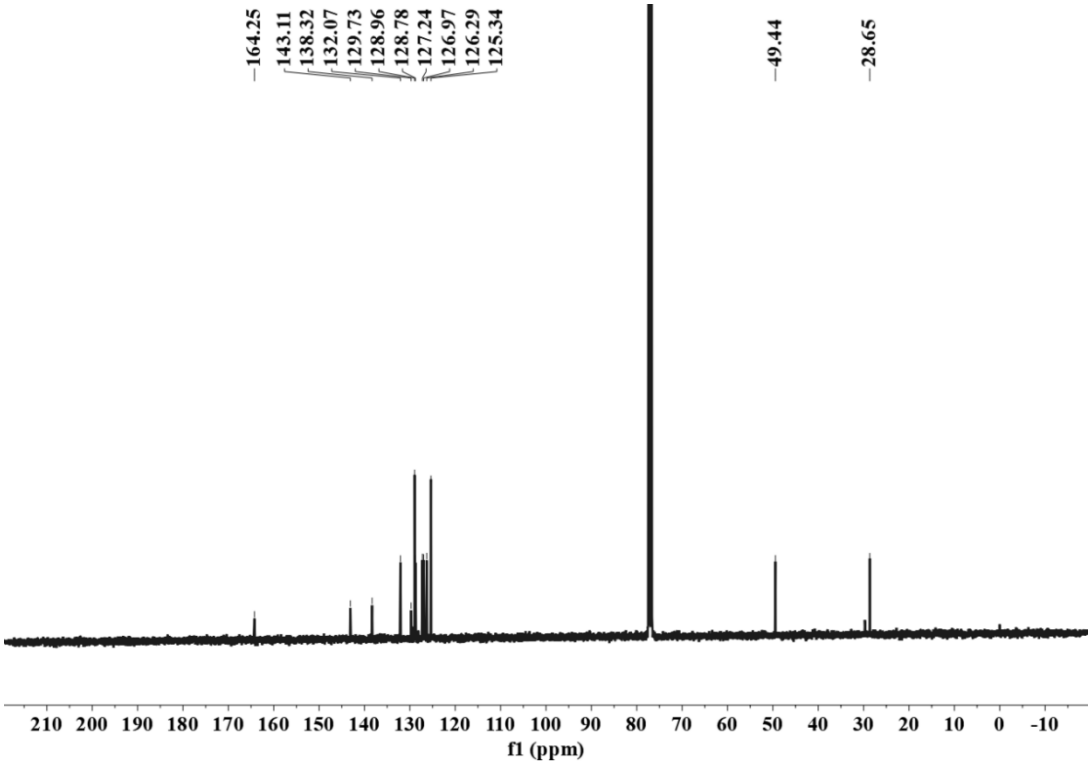
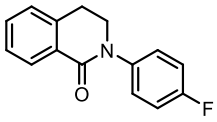


Fig. S11 ^{13}C NMR spectra of 2-phenyl-3,4-dihydroisoquinolin-1(2H)-one in $CDCl_3$.

2b. 2-(4-fluorophenyl)-3,4-dihydroisoquinolin-1(2H)-one



86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, J = 7.7, 1.5 Hz, 1H), 7.48 (td, J = 7.5, 1.5 Hz, 1H), 7.42 - 7.32 (m, 3H), 7.25 (d, J = 8.2 Hz, 1H), 7.14 - 7.07 (m, 2H), 3.97 (dd, J = 7.0, 6.0 Hz, 2H), 3.16 (t, J = 6.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.40, 139.07, 138.26, 132.19, 129.49, 128.75, 127.29, 127.16, 127.07, 127.03, 115.89, 115.67, 49.58, 28.60.

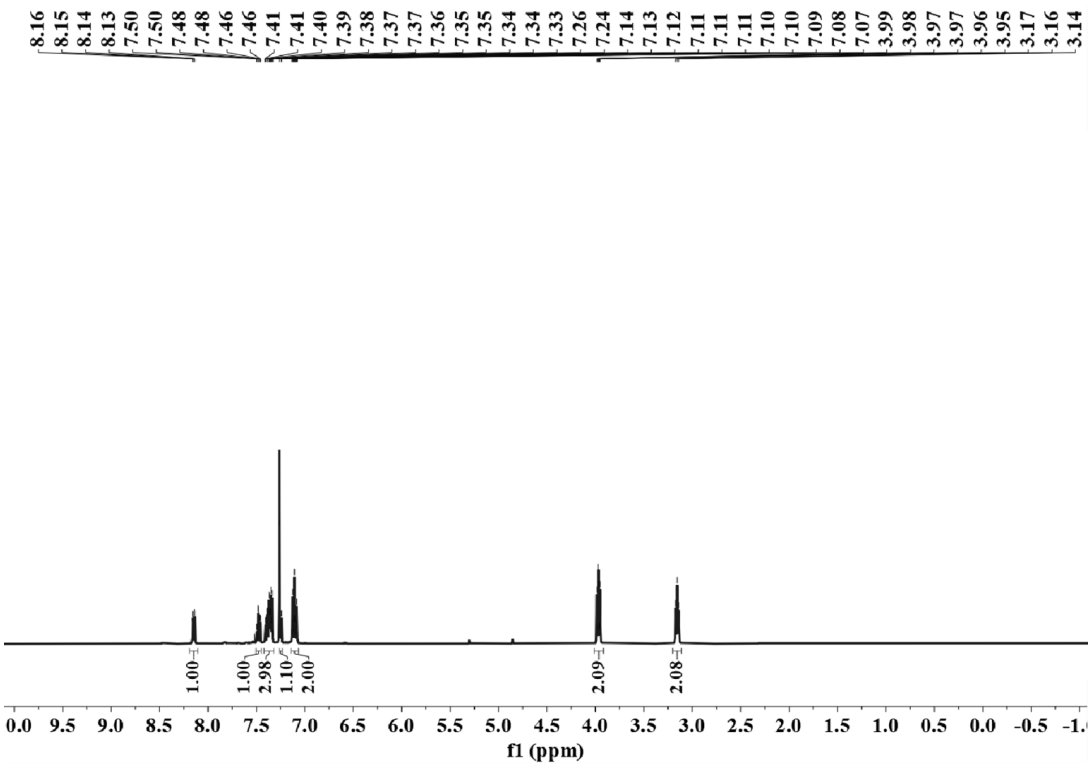


Fig. S12 ^{1}H NMR spectra of 2-(4-fluorophenyl)-3,4-dihydroisoquinolin-1(2H)-one in $CDCl_3$.

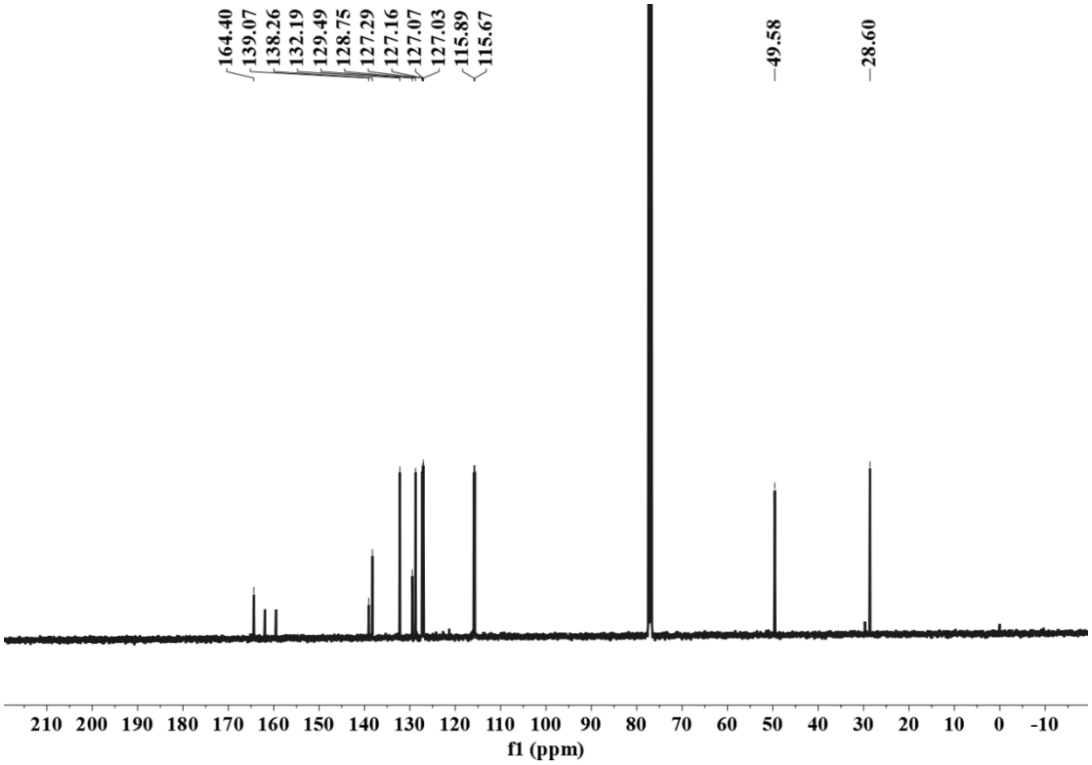
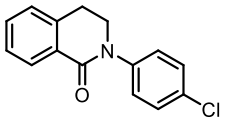


Fig. S13 ^{13}C NMR spectra of 2-(4-fluorophenyl)-3,4-dihydroisoquinolin-1(2H)-one in $CDCl_3$.

2c. 2-(4-chlorophenyl)-3,4-dihydroisoquinolin-1(2H)-one



84% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, J = 7.8, 1.5 Hz, 1H), 7.41 (td, J = 7.5, 1.5 Hz, 1H), 7.29 (dddd, J = 15.6, 8.9, 6.4, 3.2 Hz, 5H), 7.20 - 7.16 (m, 1H), 3.90 (t, J = 6.5 Hz, 2H), 3.08 (t, J = 6.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.19, 140.50, 137.19, 131.22, 130.52, 128.36, 127.95, 127.73, 126.26, 125.99, 125.50, 48.27, 27.50.

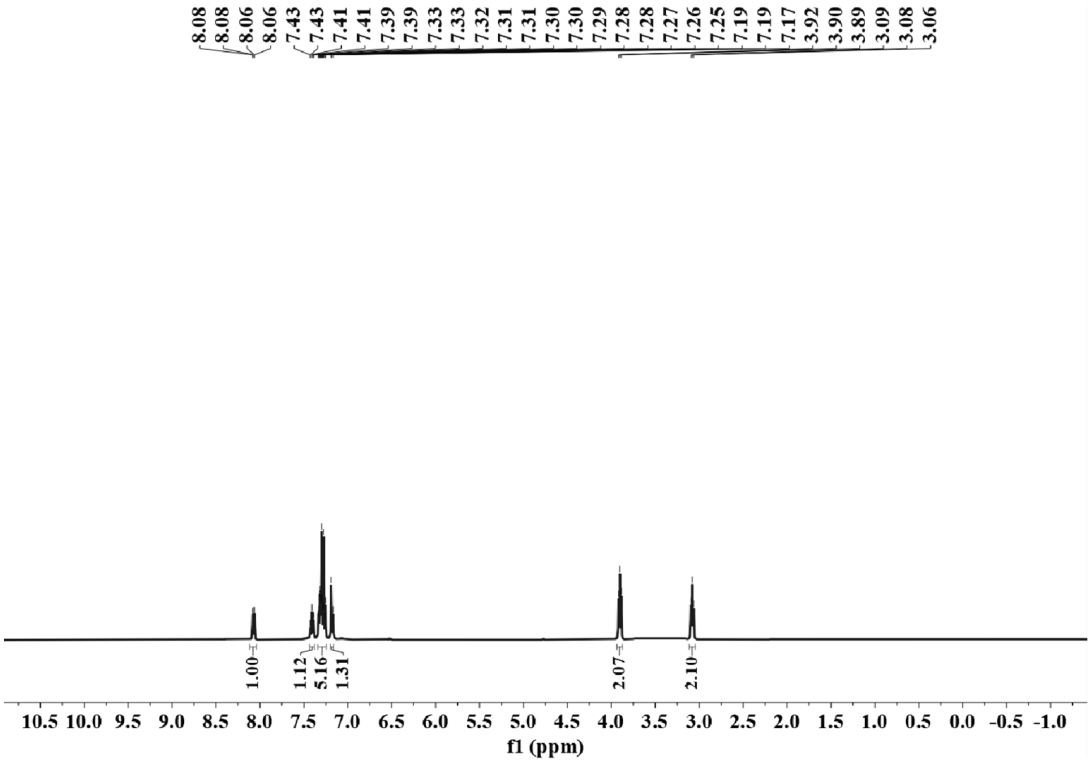


Fig. S14 ^{1}H NMR spectra of 2-(4-chlorophenyl)-3,4-dihydroisoquinolin-1(2H)-one in $CDCl_3$.

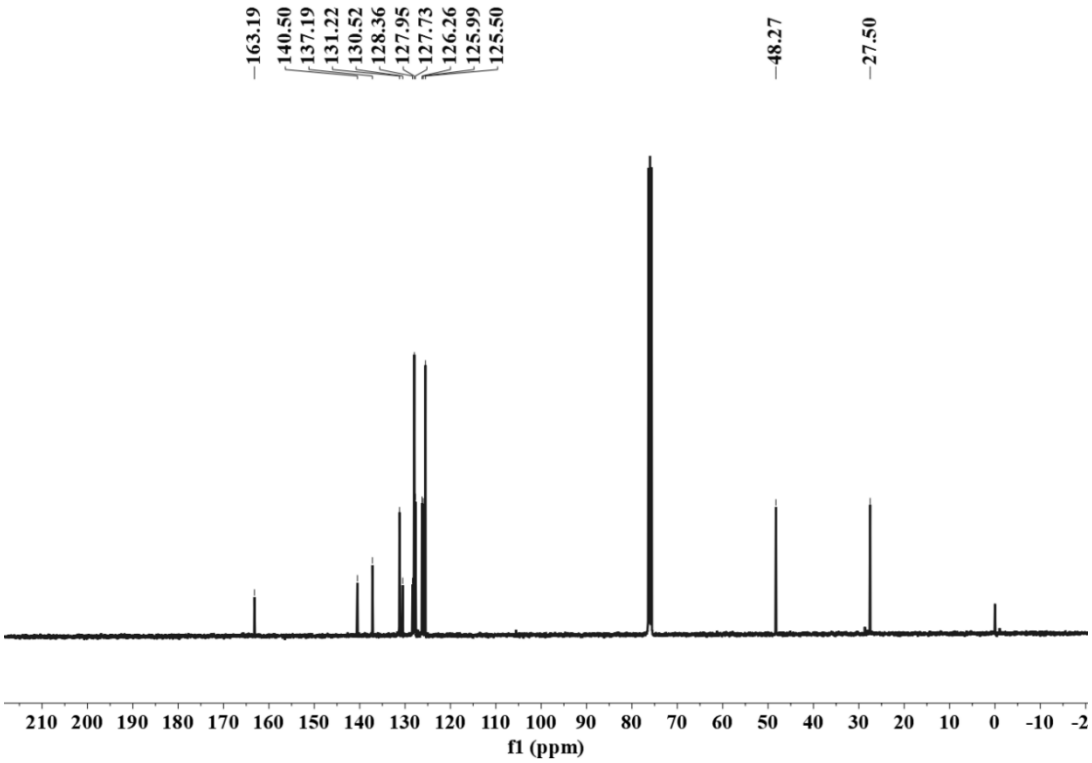
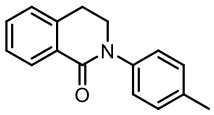


Fig. S15 ^{13}C NMR spectra of 2-(4-chlorophenyl)-3,4-dihydroisoquinolin-1(2H)-one in $CDCl_3$.

2d. 2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline



80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, J = 7.8, 1.5 Hz, 1H), 7.46 (td, J = 7.5, 1.5 Hz, 1H), 7.37 (td, J = 7.6, 1.3 Hz, 1H), 7.29 (d, J = 10.7 Hz, 1H), 7.26 - 7.18 (m, 4H), 3.99 - 3.93 (m, 2H), 3.13 (t, J = 6.5 Hz, 2H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.57, 138.31, 136.10, 131.97, 129.80, 129.58, 128.74, 127.19, 126.94, 125.23, 49.53, 28.66, 21.09.

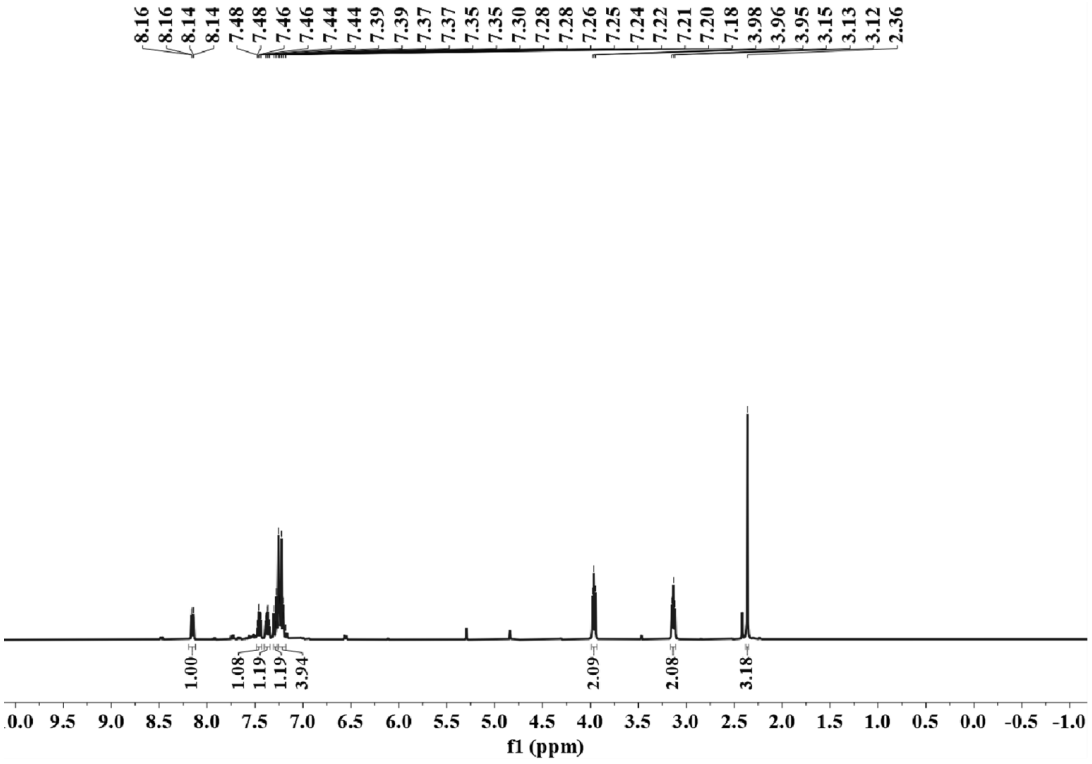


Fig. S16 ^{1}H NMR spectra of 2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline in $CDCl_3$.

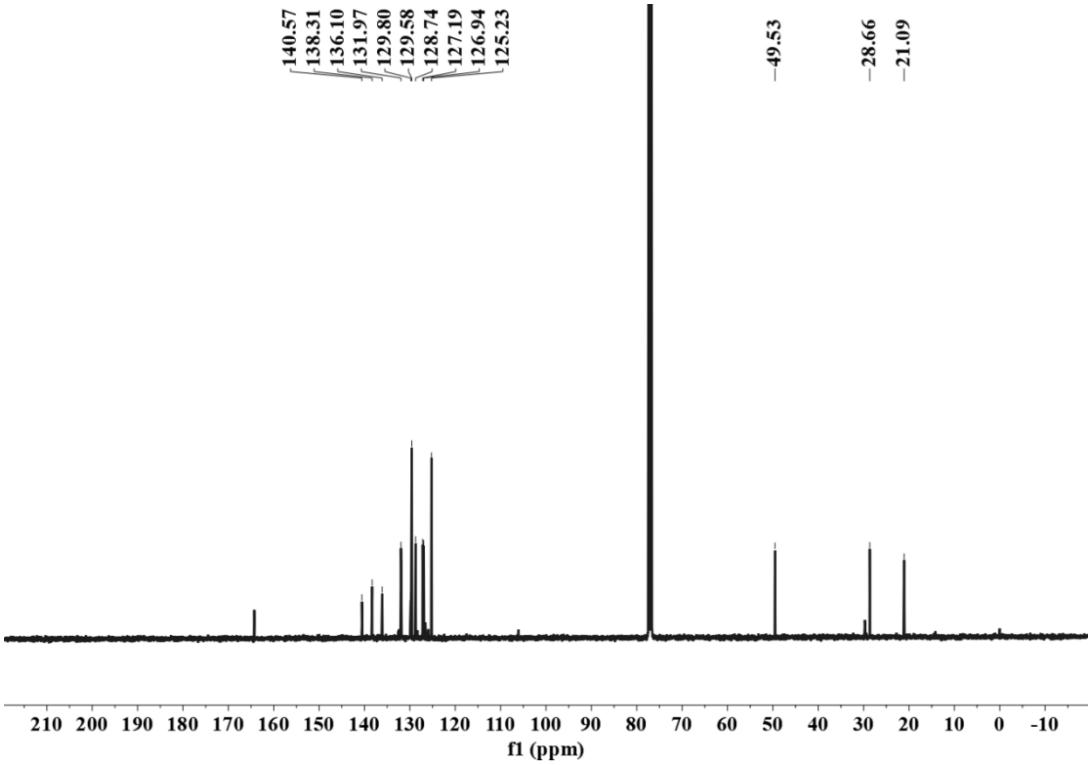
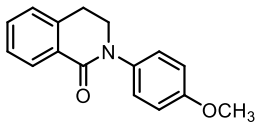


Fig. S17 ^{13}C NMR spectra of 2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline in $CDCl_3$.

2e. 2-(4-methoxyphenyl)-3,4-dihydroisoquinolin-1(2H)-one



76% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, J = 7.7, 1.4 Hz, 1H), 7.46 (td, J = 7.5, 1.5 Hz, 1H), 7.37 (td, J = 7.5, 1.5 Hz, 1H), 7.32 - 7.27 (m, 2H), 7.26 - 7.21 (m, 1H), 6.97 - 6.91 (m, 2H), 3.95 (dd, J = 7.0, 6.0 Hz, 2H), 3.83 (s, 3H), 3.14 (t, J = 6.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.44, 157.82, 138.30, 136.10, 131.96, 129.76, 128.71, 127.19, 126.95, 126.69, 114.26, 55.59, 55.53, 49.73, 28.66.

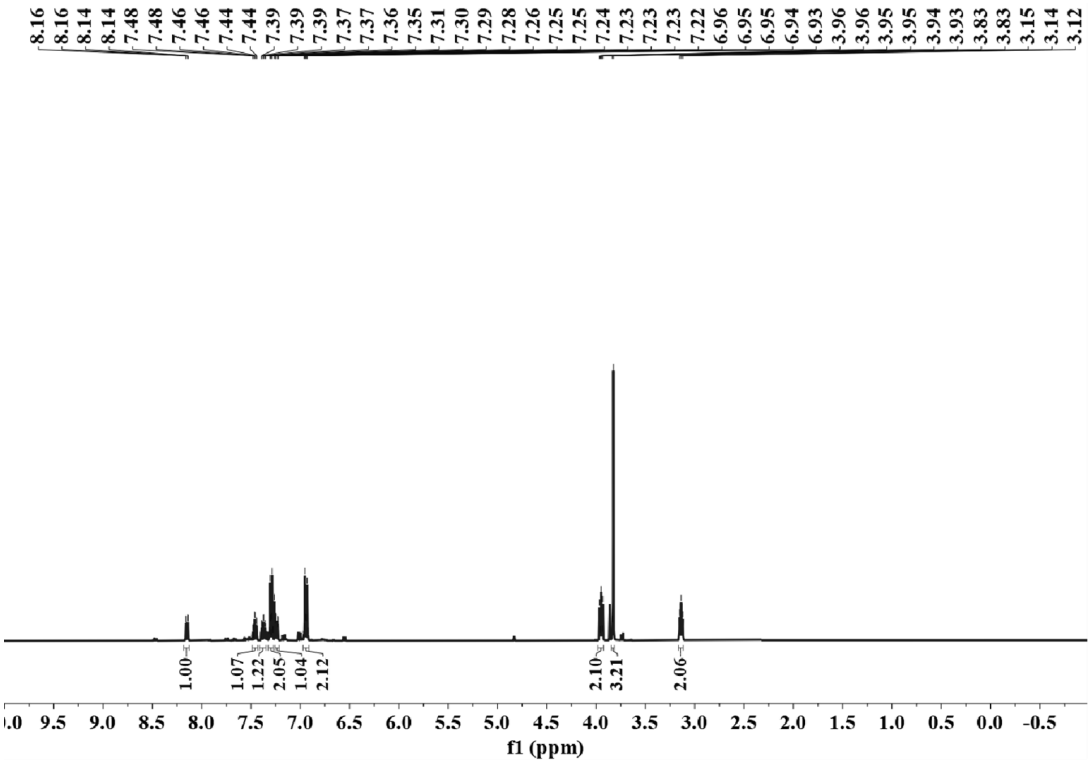


Fig. S18 ^{1}H NMR spectra of 2-(4-methoxyphenyl)-3,4-dihydroisoquinolin-1(2H)-one in $CDCl_3$.

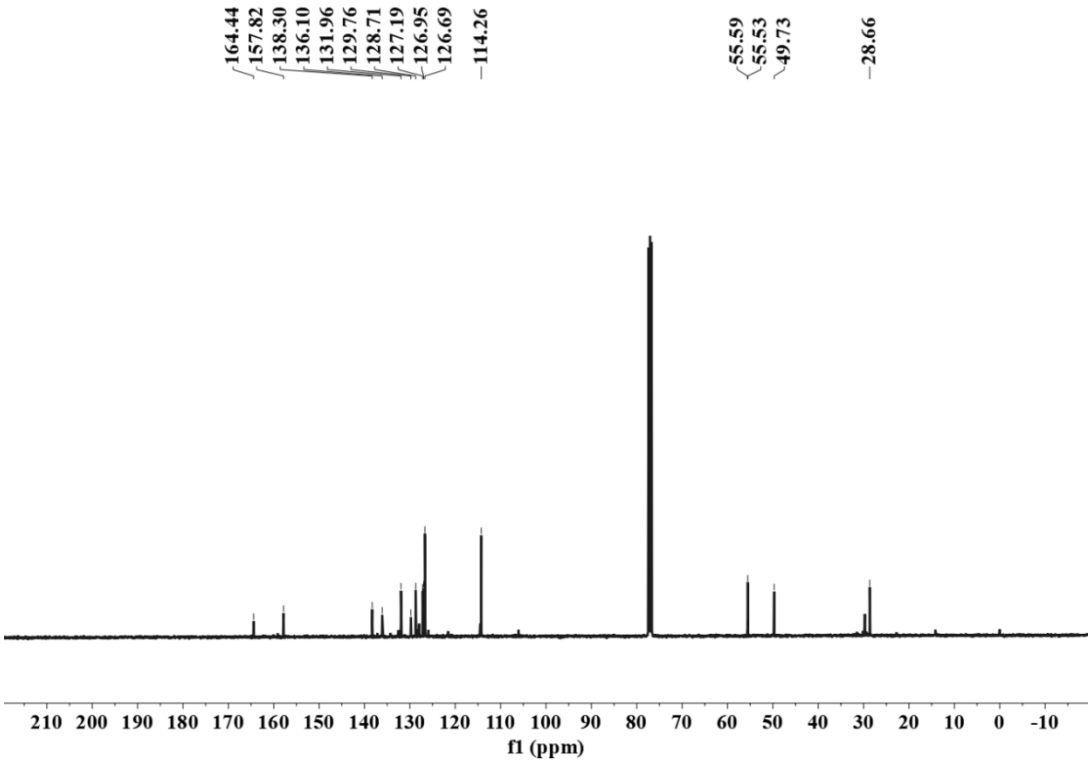
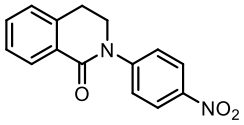


Fig. S19 ^{13}C NMR spectra of 2-(4-methoxyphenyl)-3,4-dihydroisoquinolin-1(2H)-one in $CDCl_3$.

2f. 2-(p-nitrobenzene)-1,2,3,4-tetrahydroisoquinoline



87% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8.6 Hz, 1H), 8.17 (d, J = 7.8 Hz, 1H), 7.61 (d, J = 8.7 Hz, 1H), 7.51 (d, J = 7.5 Hz, 1H), 7.42 (t, J = 7.8 Hz, 1H), 7.28 (d, J = 11.6 Hz, 1H), 4.09 (t, J = 6.4 Hz, 1H), 3.20 (t, J = 6.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.22, 148.66, 144.74, 138.22, 132.83, 129.07, 128.94, 127.55, 127.16, 124.80, 124.30, 48.99, 29.73.

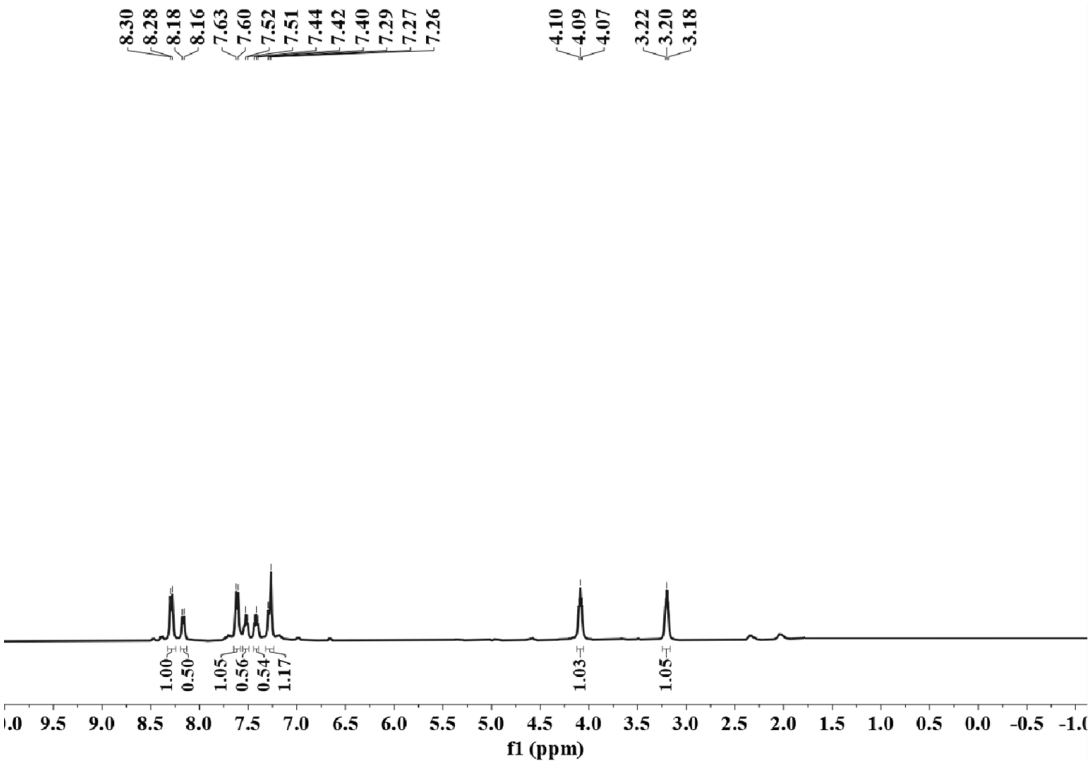


Fig. S20 ^{1}H NMR spectra of 2-(p-nitrobenzene) -1,2,3,4-tetrahydroisoquinoline in $CDCl_3$.

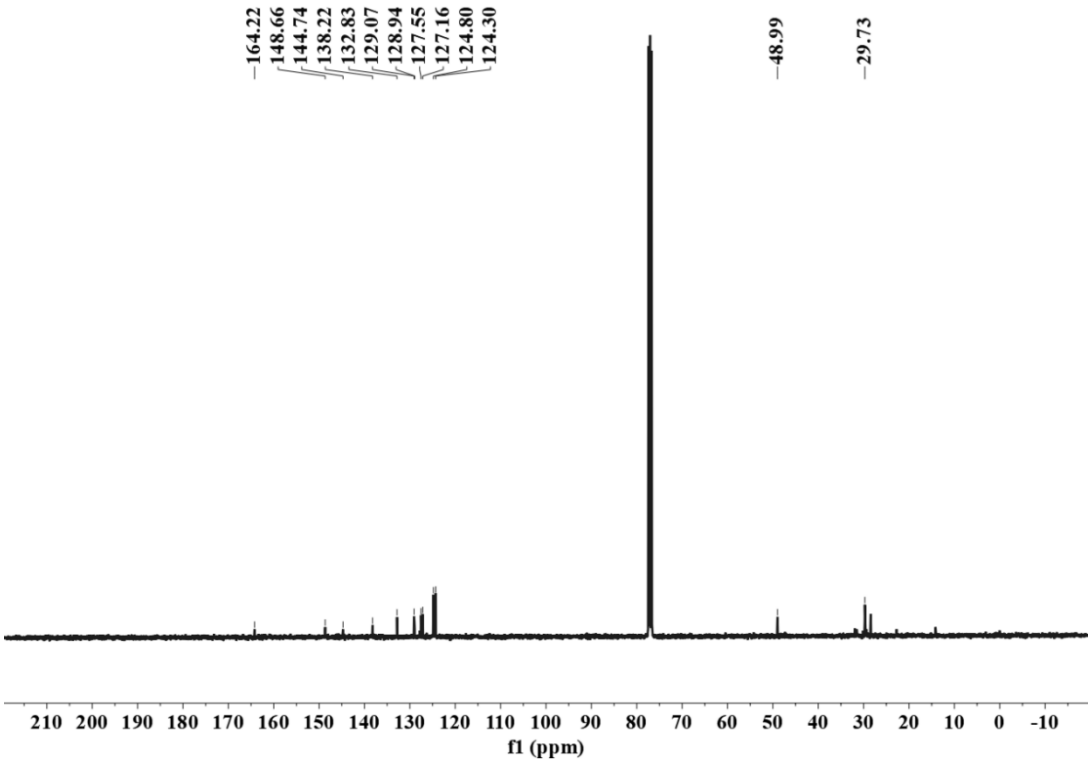
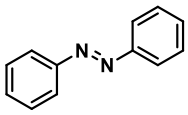


Fig. S21 ^{13}C NMR spectra of 2-(p-nitrobenzene)-1,2,3,4-tetrahydroisoquinoline in $CDCl_3$.

4a. 1,2-diphenylhydrazine



86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 -7.89 (m, 4H), 7.56 - 7.44 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.61, 131.04, 129.12, 122.85.

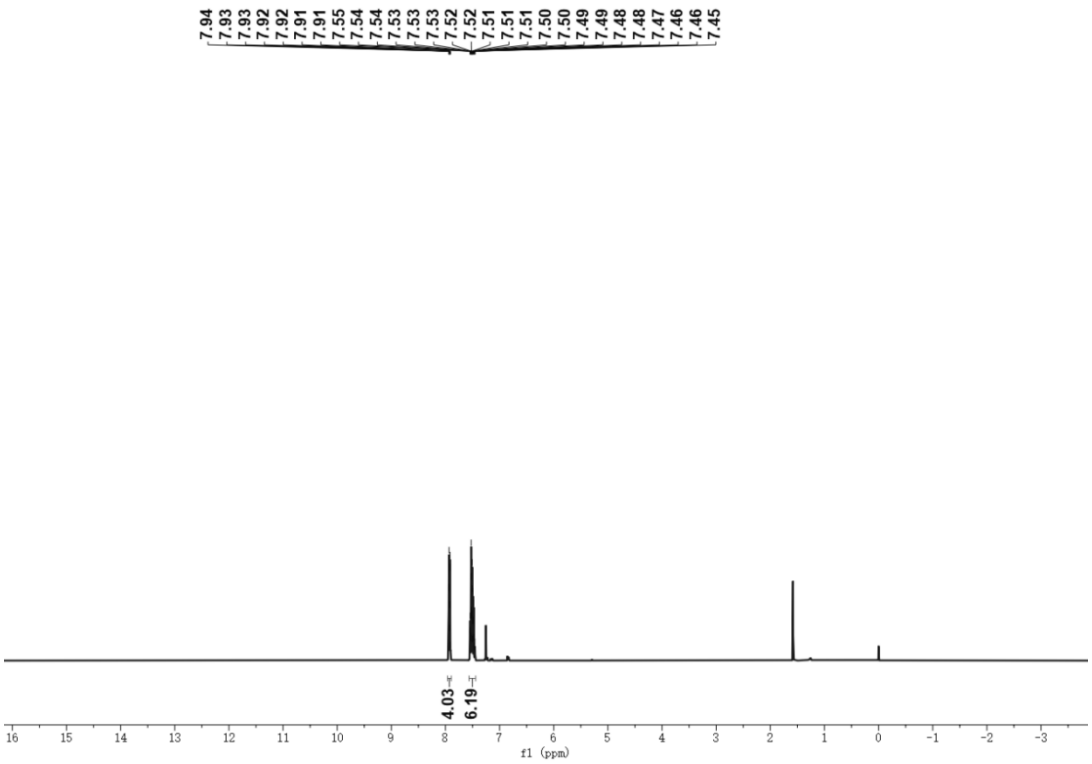


Fig. S22 ^{1}H NMR spectra of 1,2-diphenylhydrazine in $CDCl_3$.

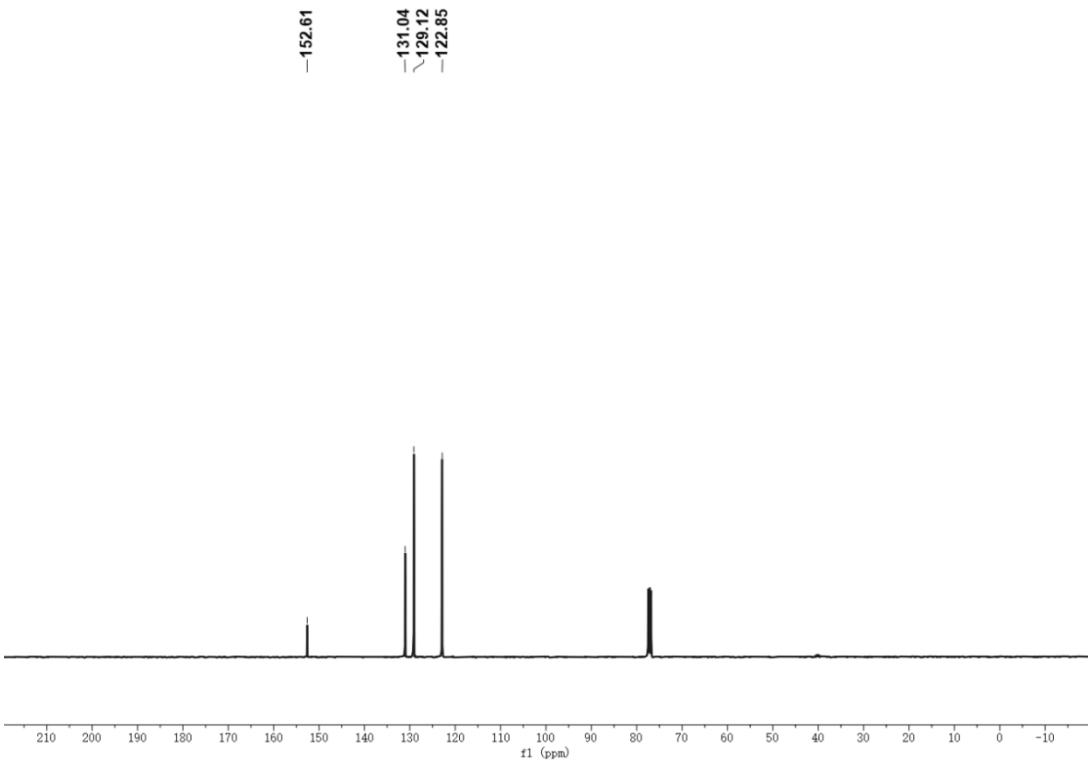
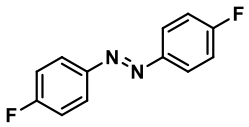


Fig. S23 ^{13}C NMR spectra of 1,2-diphenylhydrazine in $CDCl_3$.

4b. 4,4'-difluoroazobenzene



93% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 - 7.86 (m, 4H), 7.25 - 7.15 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.62, 163.12, 148.97, 148.94, 124.87, 124.78, 116.21, 115.98.

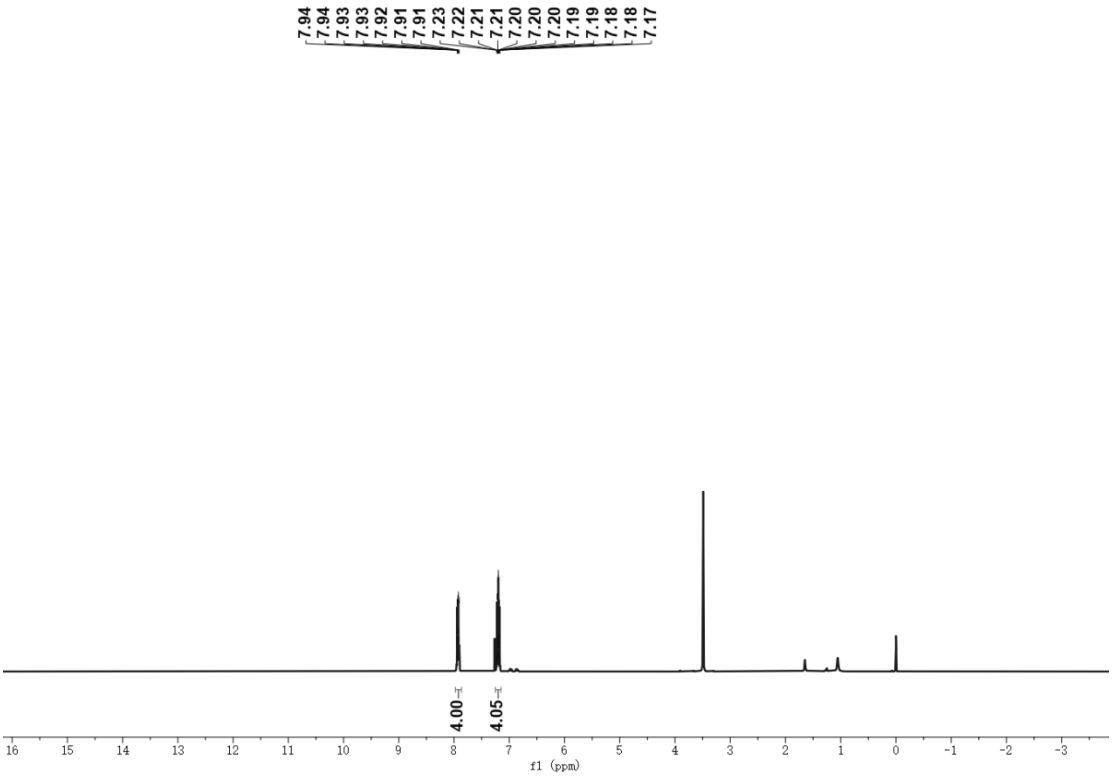


Fig. S24 ^{1}H NMR spectra of 4'4-difluoroazobenzene in $CDCl_3$.

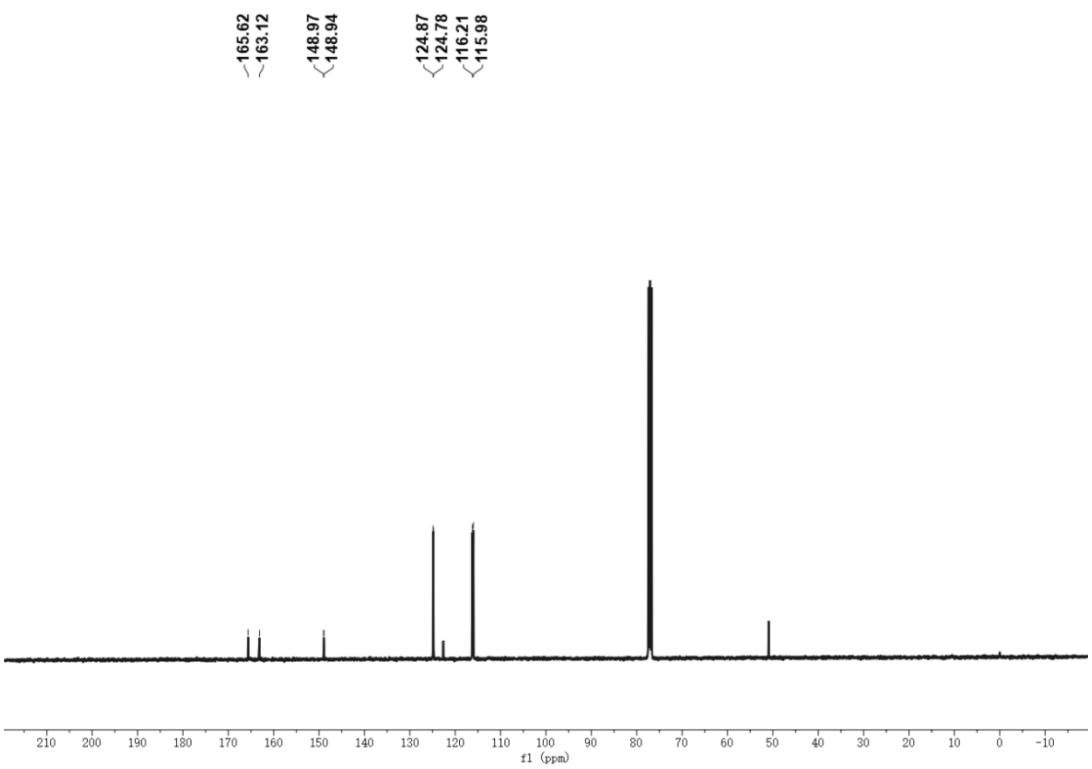
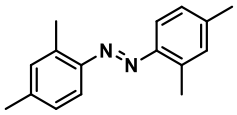


Fig. S25 ^{13}C NMR spectra of 4'4-difluoroazobenzene in $CDCl_3$

4c. 2,2',4,4'-tetramethylazobenzene



78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.2 Hz, 2H), 7.13 (d, J = 1.9 Hz, 2H), 7.05 (dd, J = 8.3, 2.0 Hz, 2H), 2.69 (s, 6H), 2.37 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.19, 140.76, 137.87, 131.80, 127.14, 115.70, 21.41, 17.60.

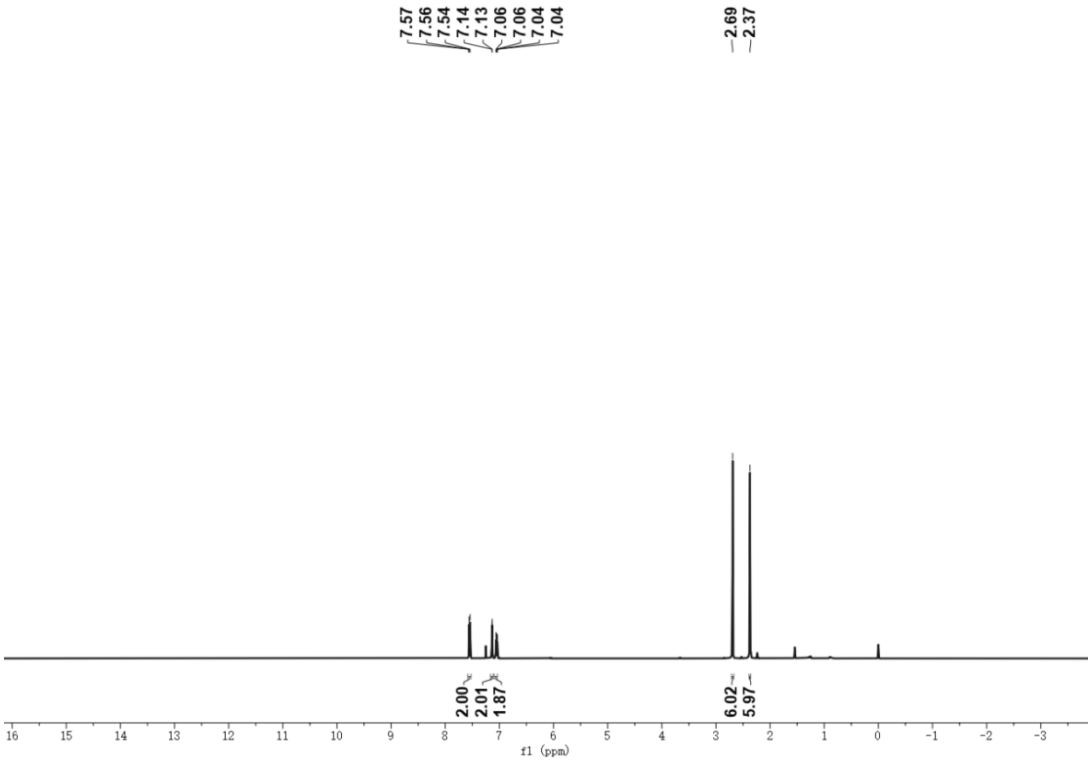


Fig. S26 ^{1}H NMR spectra of 2,2',4,4' -tetramethylazobenzene in $CDCl_3$.

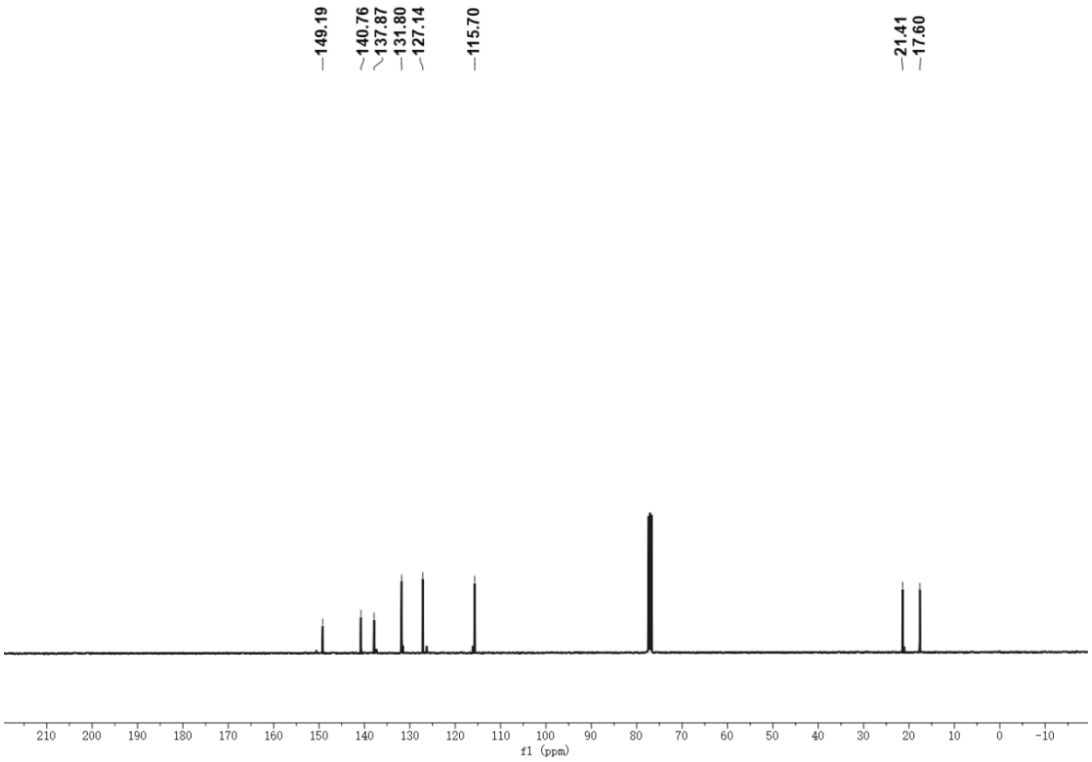
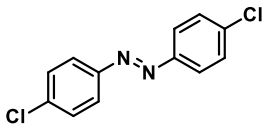


Fig. S27 ^{13}C NMR spectra of 2,2',4,4' -tetramethylazobenzene in $CDCl_3$.

4d. 4,4'-dichloroazobenzene



92% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 - 7.84 (m, 4H), 7.51 - 7.47 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.77, 137.24, 129.42, 124.21.

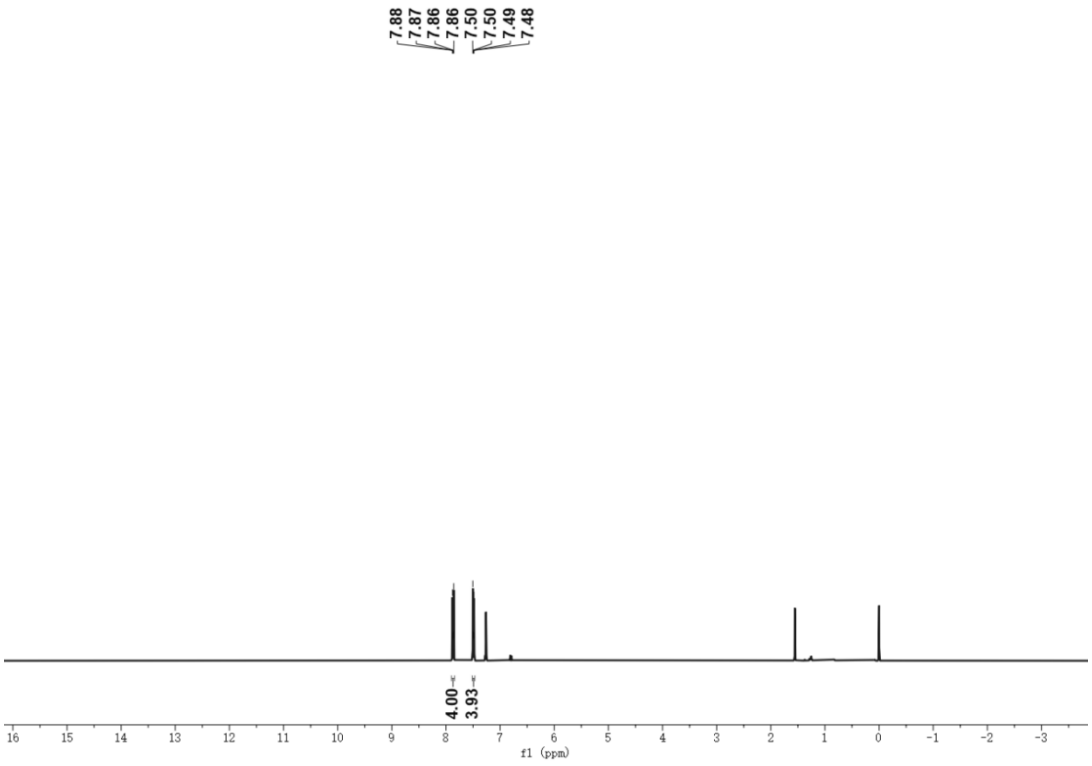


Fig. S28 ^{1}H NMR spectra of 4,4'-dichloroazobenzene in $CDCl_3$.

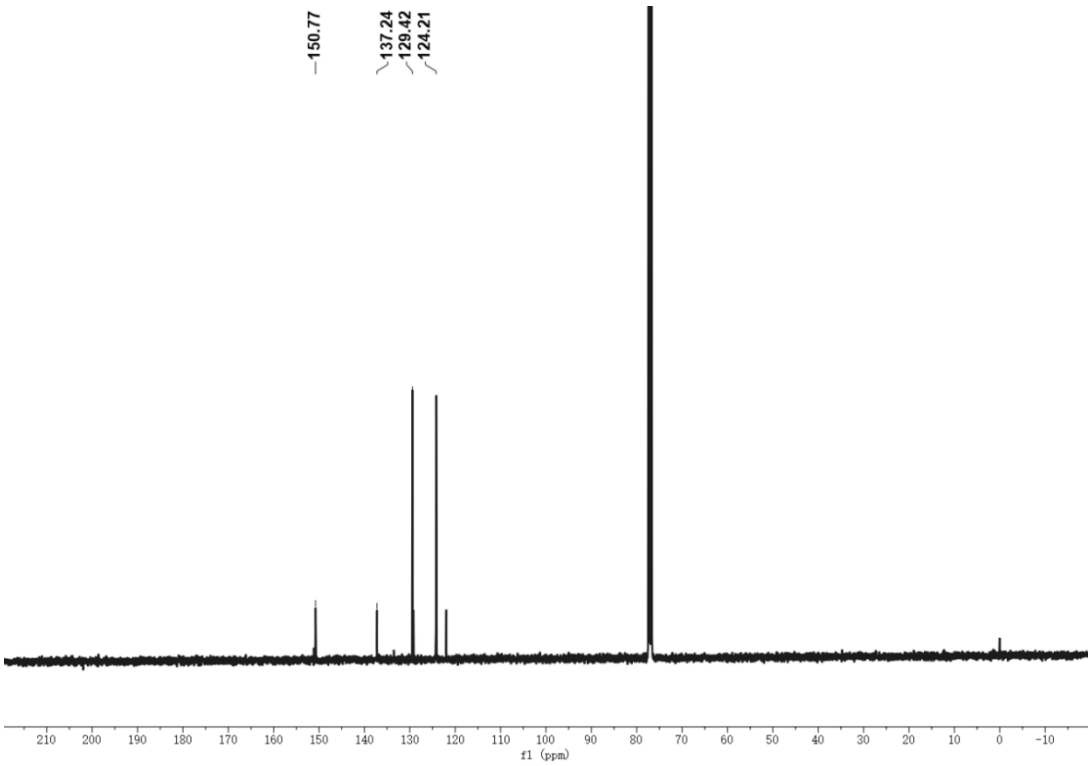
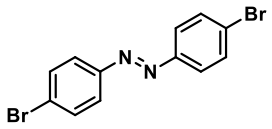


Fig. S29 ^{13}C NMR spectra of 4,4'-dichloroazobenzene in $CDCl_3$.

4e. 4,4'-dibromoazo benzene



89% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 - 7.78 (m, 4H), 7.67 - 7.63 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.13, 132.42, 125.79, 124.44.

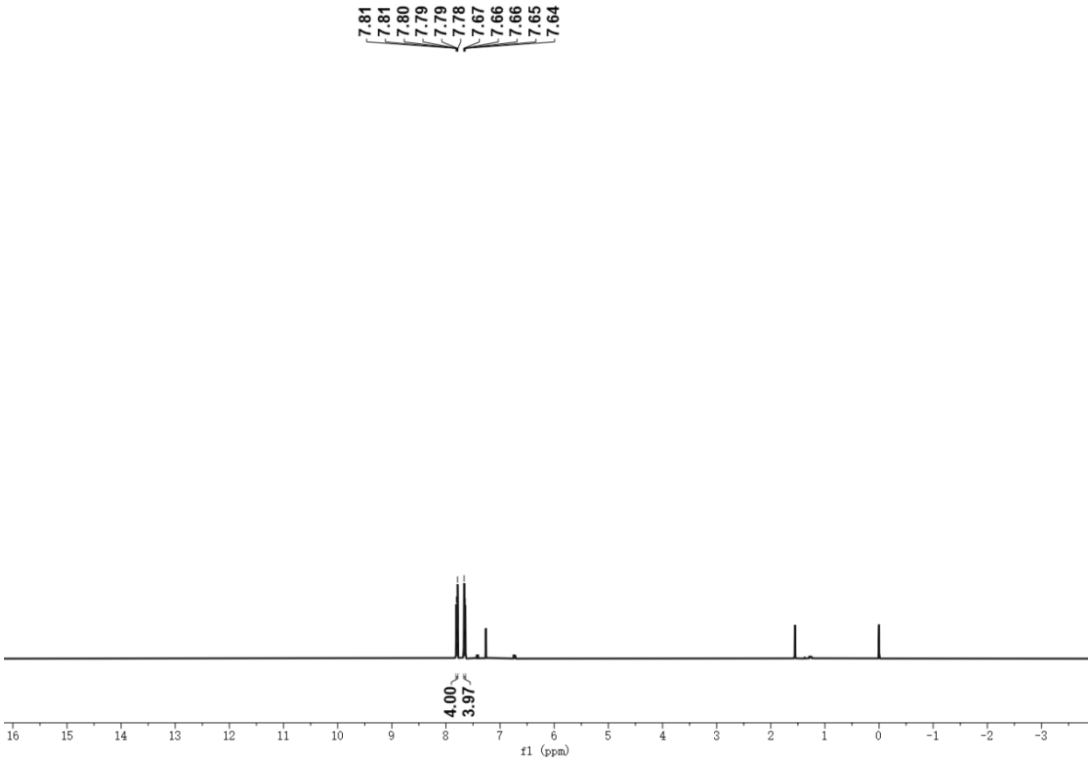


Fig. S30 ^{1}H NMR spectra of 4,4'-dibromoazo benzene in $CDCl_3$.

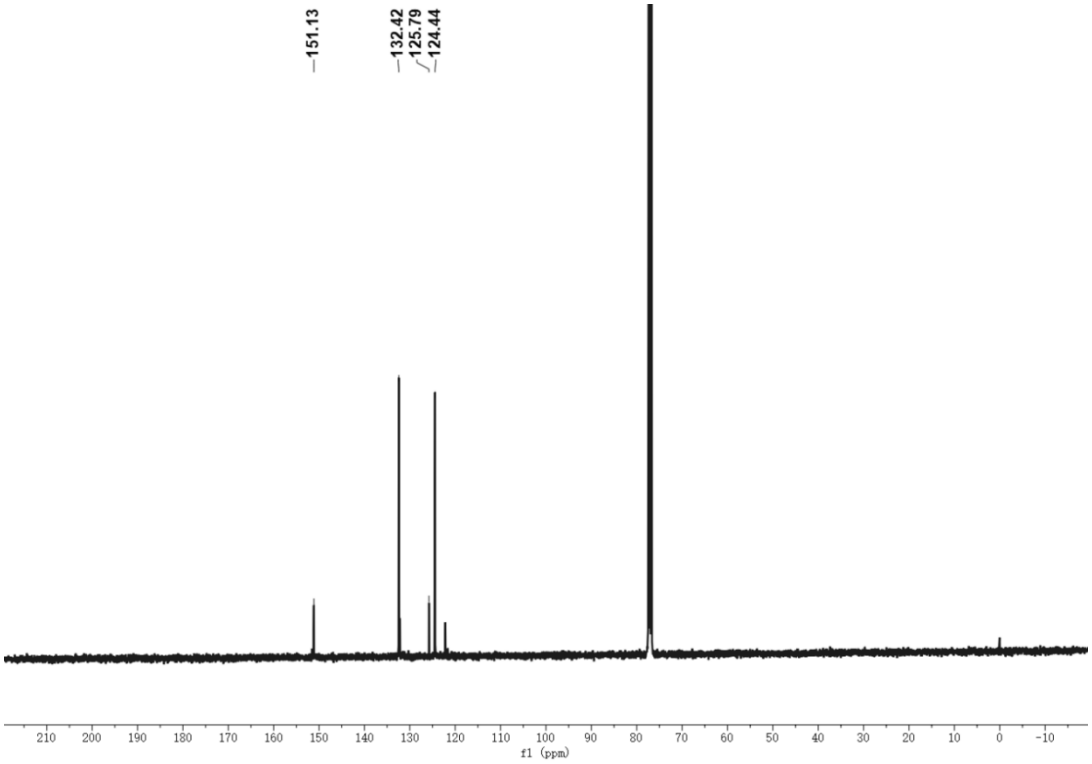
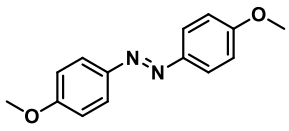


Fig. S31 ^{13}C NMR spectra of 4,4'-dibromoazo benzene in $CDCl_3$.

4f. 4,4'-diethoxyazobenzene



86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 - 7.84 (m, 4H), 7.04 - 6.99 (m, 4H), 3.89 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.55, 147.04, 124.35, 114.17, 55.58.

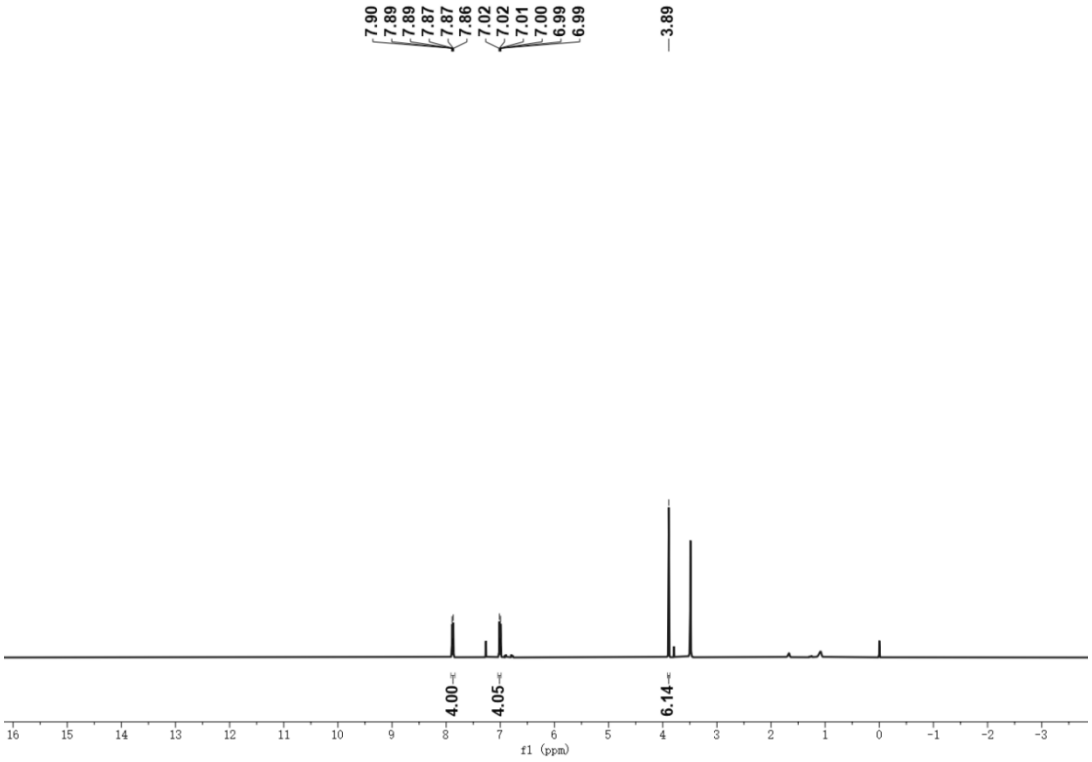


Fig. S32 ^{1}H NMR spectra of 4,4'-diethoxyazobenzene in $CDCl_3$.

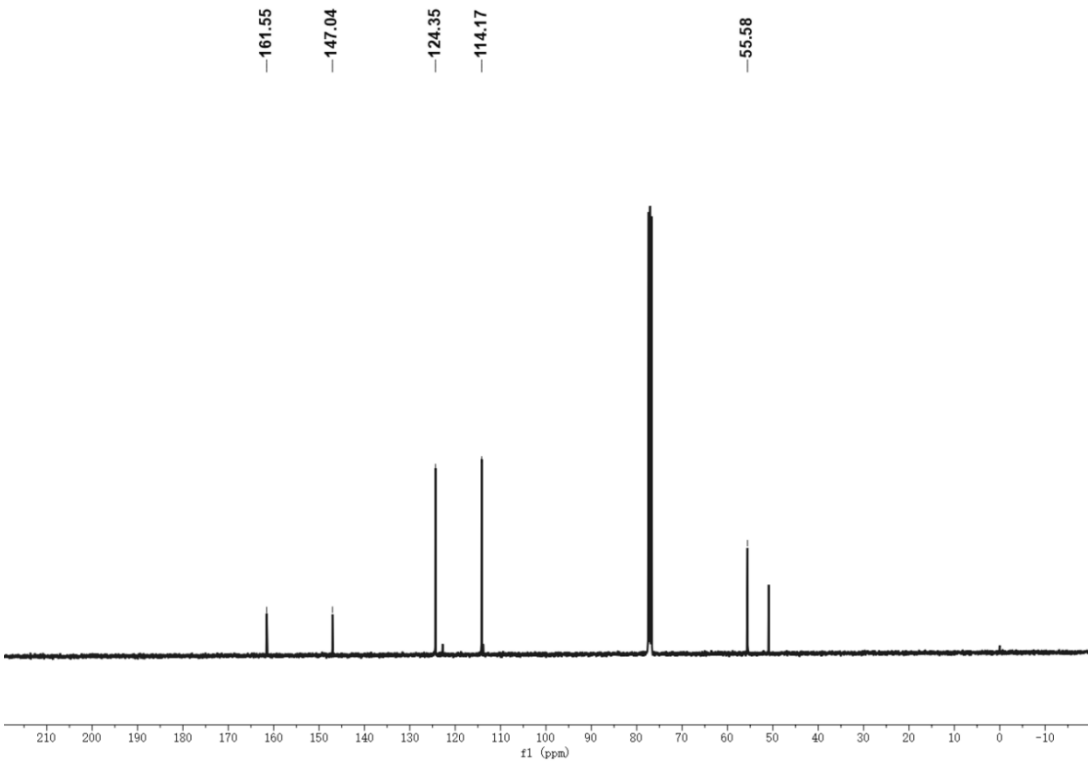
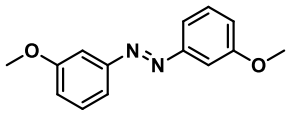


Fig. S33 ^{13}C NMR spectra of 4,4'-diethoxyazobenzene in $CDCl_3$.

4g. 3,3'-dimethoxyazobenzene



83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 - 7.54 (m, 2H), 7.50 - 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 160.32, 153.79, 129.82, 117.92, 117.22, 105.66, 55.51.

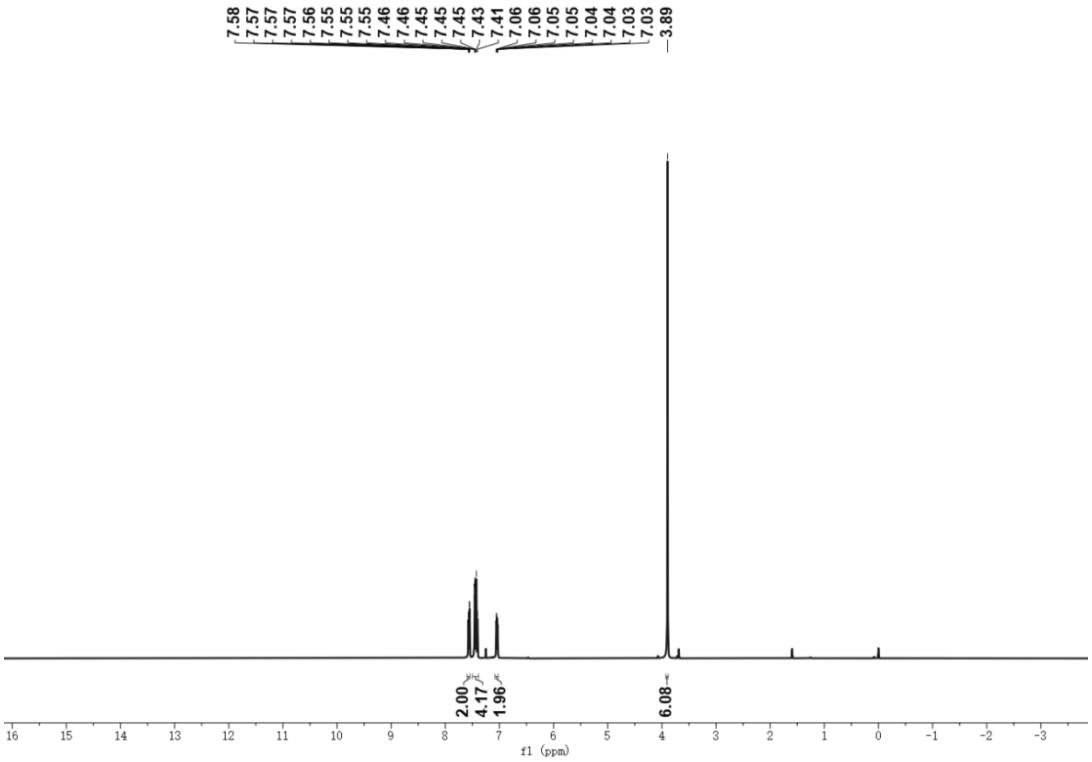


Fig. S34 ^{1}H NMR spectra of 3,3'-dimethoxyazobenzene in $CDCl_3$.

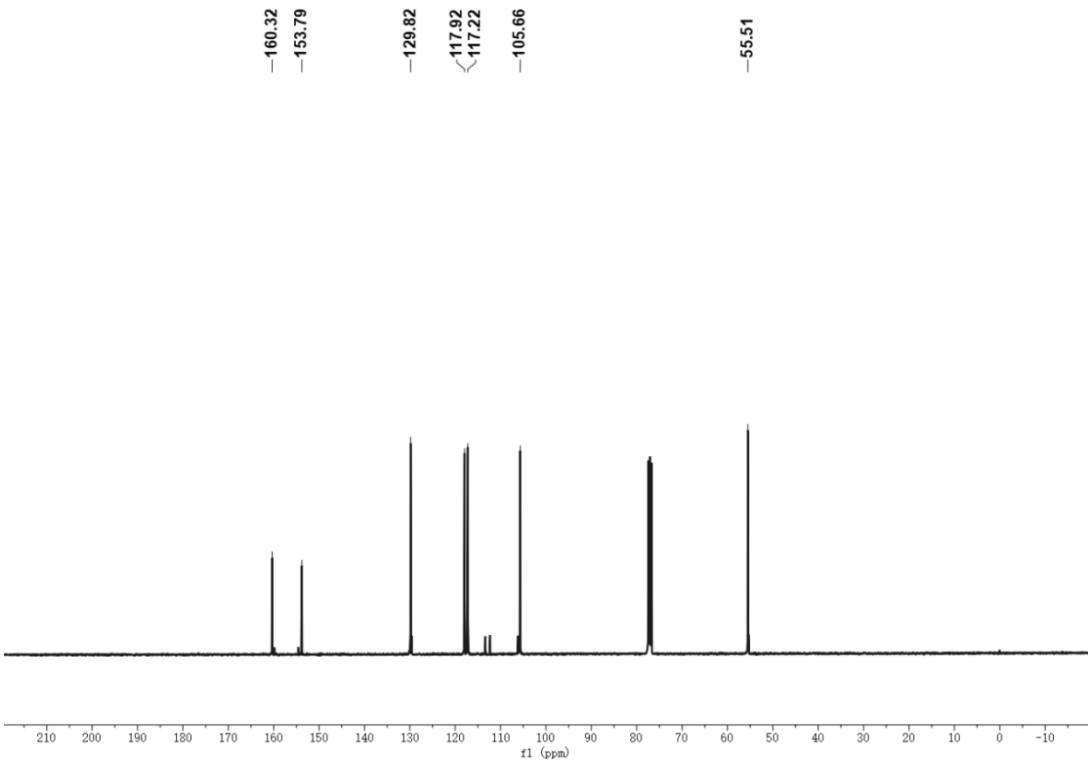
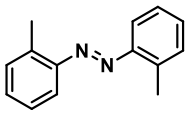


Fig. S35 ^{13}C NMR spectra of 3,3'-dimethoxyazobenzene in $CDCl_3$

4h. 2,2'-dimethylazobenzene



80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 - 7.57 (m, 2H), 7.38 - 7.31 (m, 4H), 7.25 (ddd, J = 10.3, 5.4, 2.3 Hz, 2H), 2.74 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.08, 138.06, 131.30, 130.73, 126.40, 115.85, 17.67.

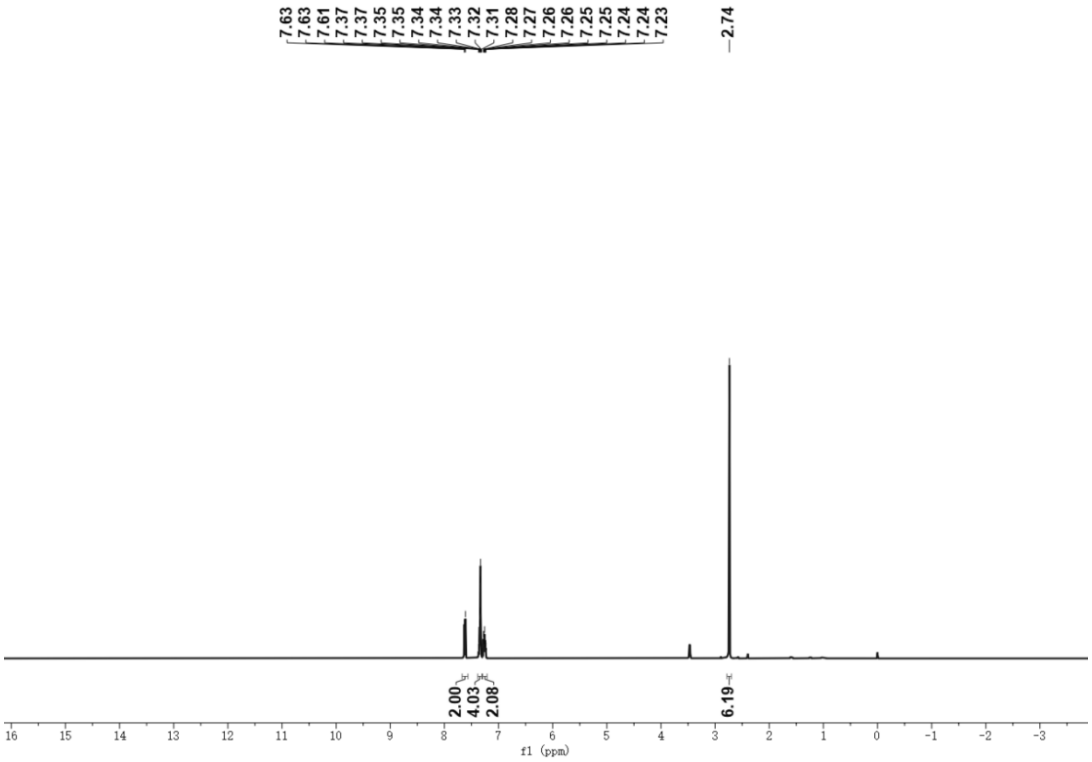


Fig. S36 ^{1}H NMR spectra of 2,2'-dimethylazobenzene in $CDCl_3$.

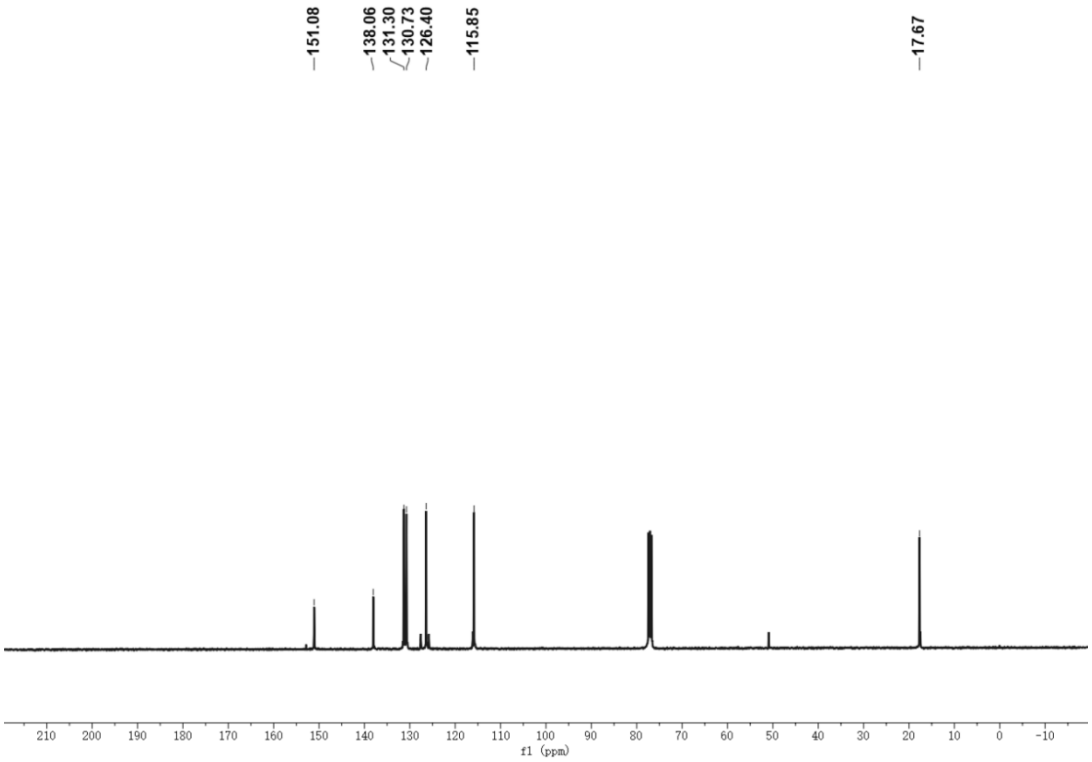
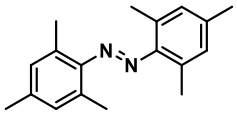


Fig. S37 ^{13}C NMR spectra of 2,2'-dimethylazobenzene in $CDCl_3$.

4i. 2,2',4,4',6,6'-hexamethylmethylazobenzene



77% 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 149.12, 138.38, 131.68, 130.10, 21.09, 20.09.

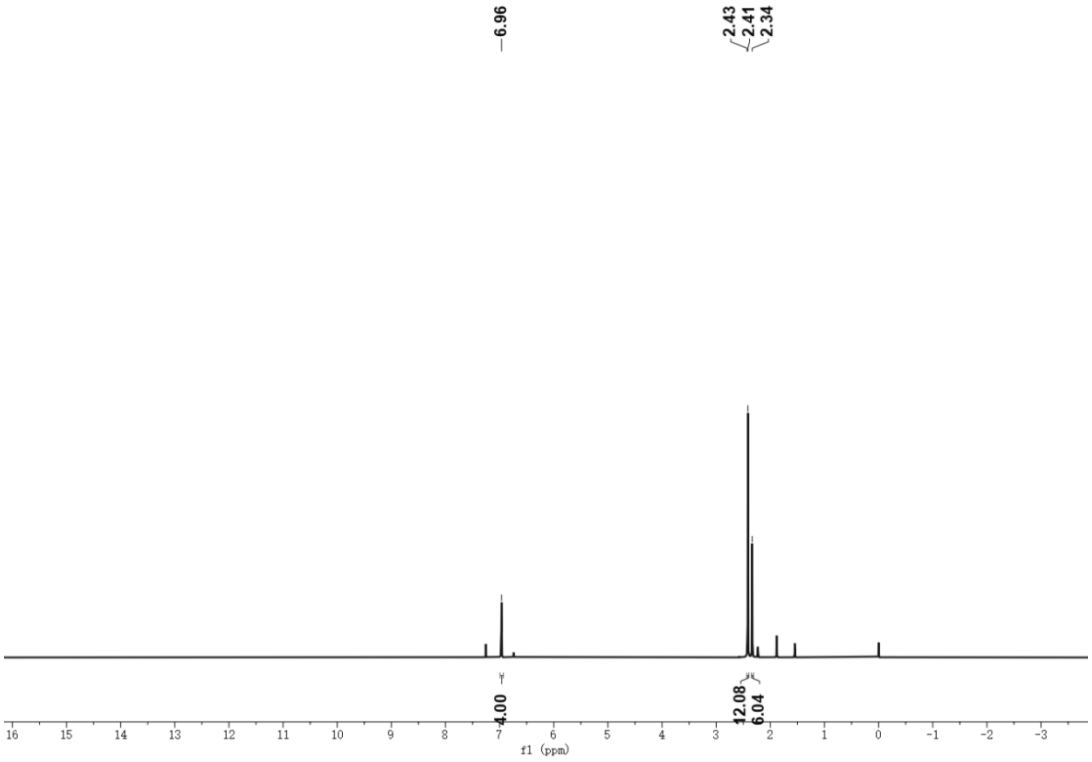


Fig. S38 ^{1}H NMR spectra of 2,2',4,4',6,6'-hexamethylmethylazobenzene in $CDCl_3$.

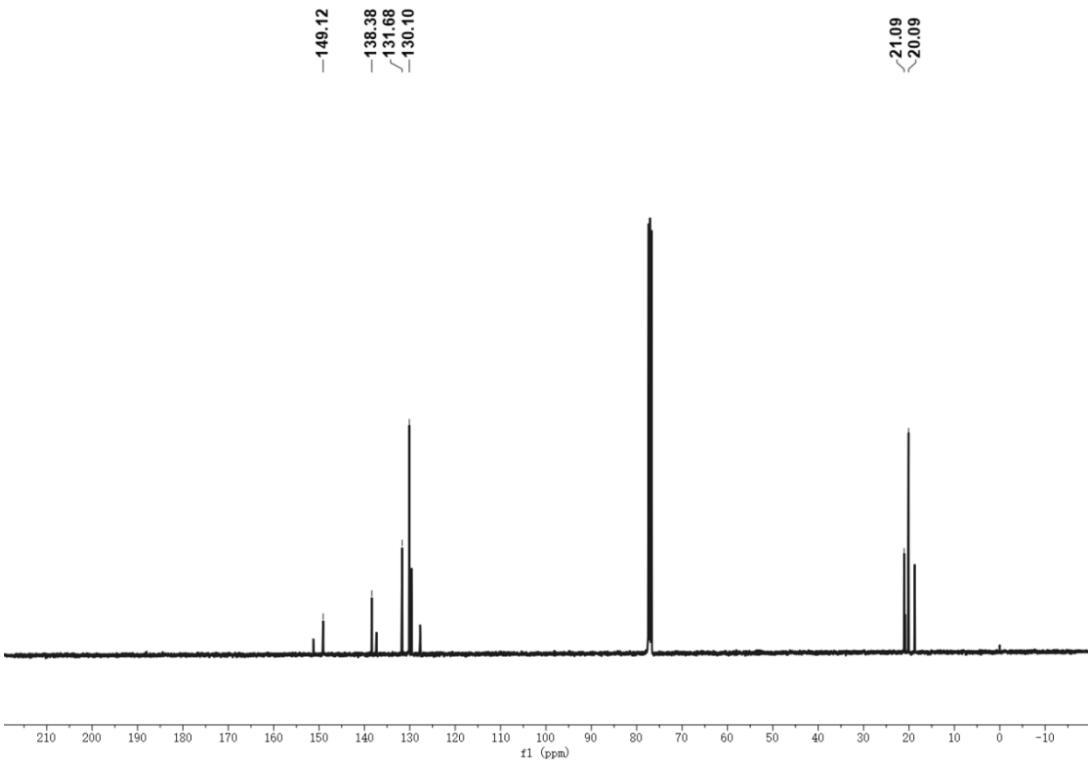
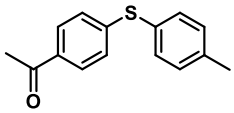


Fig. S39 ^{13}C NMR spectra of 2,2',4,4',6,6'-hexamethylmethylazobenzene in $CDCl_3$

7a. 4-acetyl-4'-methyldiphenyl sulfide



80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 - 7.75 (m, 2H), 7.45- 7.36 (m, 2H), 7.22 (d, J = 7.8 Hz, 2H), 7.18 - 7.10 (m, 2H), 2.53 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.99, 139.39, 134.55, 130.58, 128.86, 127.87, 126.62, 26.50, 21.33.

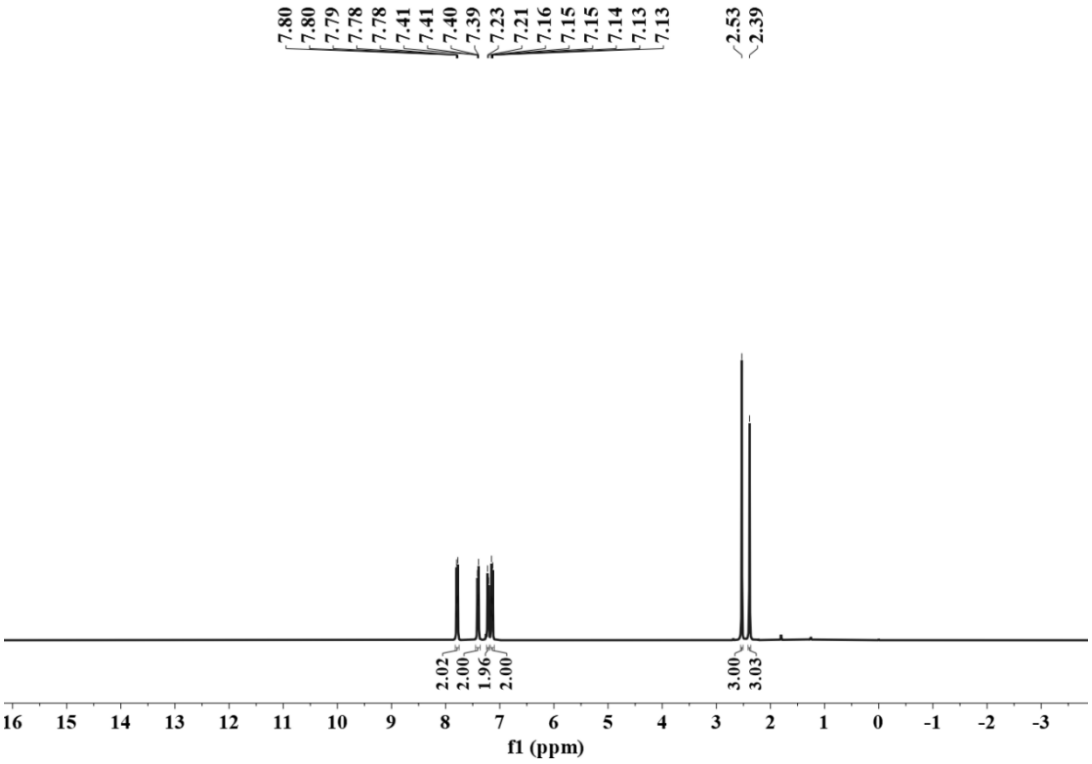


Fig. S40 ^{1}H NMR spectra of 4-acetyl-4'-methyldiphenyl sulfide in $CDCl_3$.

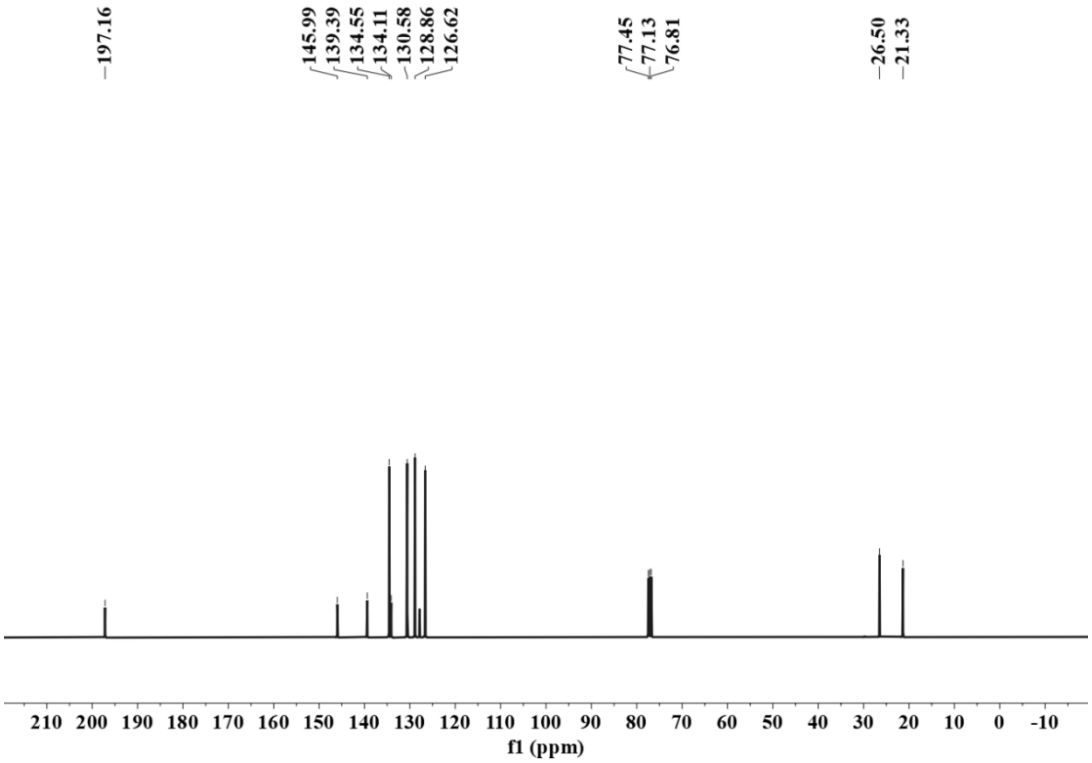
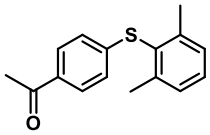


Fig. S41 ^{13}C NMR spectra of 4-acetyl-4'-methyldiphenyl sulfide in $CDCl_3$.

7b. 4-acetyl-2,4 '-methyldiphenyl sulfide



77% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.2 Hz, 2H), 7.30 - 7.24 (m, 1H), 7.21 (d, J = 7.5 Hz, 2H), 6.94 (d, J = 8.2 Hz, 2H), 2.52 (s, 3H), 2.40 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.09, 145.35, 144.00, 133.56, 129.93, 128.99, 128.91, 128.73, 124.77, 26.43, 21.75.

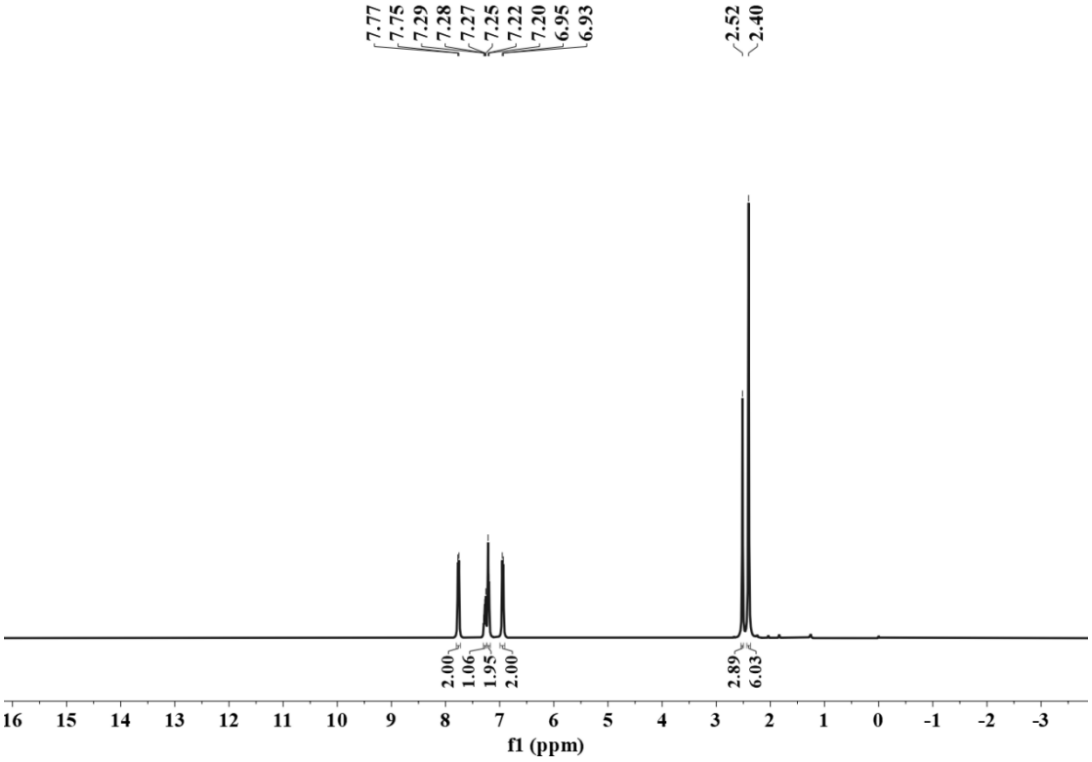


Fig. S42 ^{1}H NMR spectra of 4-acetyl-2, 4'-methyldiphenyl sulfide in $CDCl_3$.

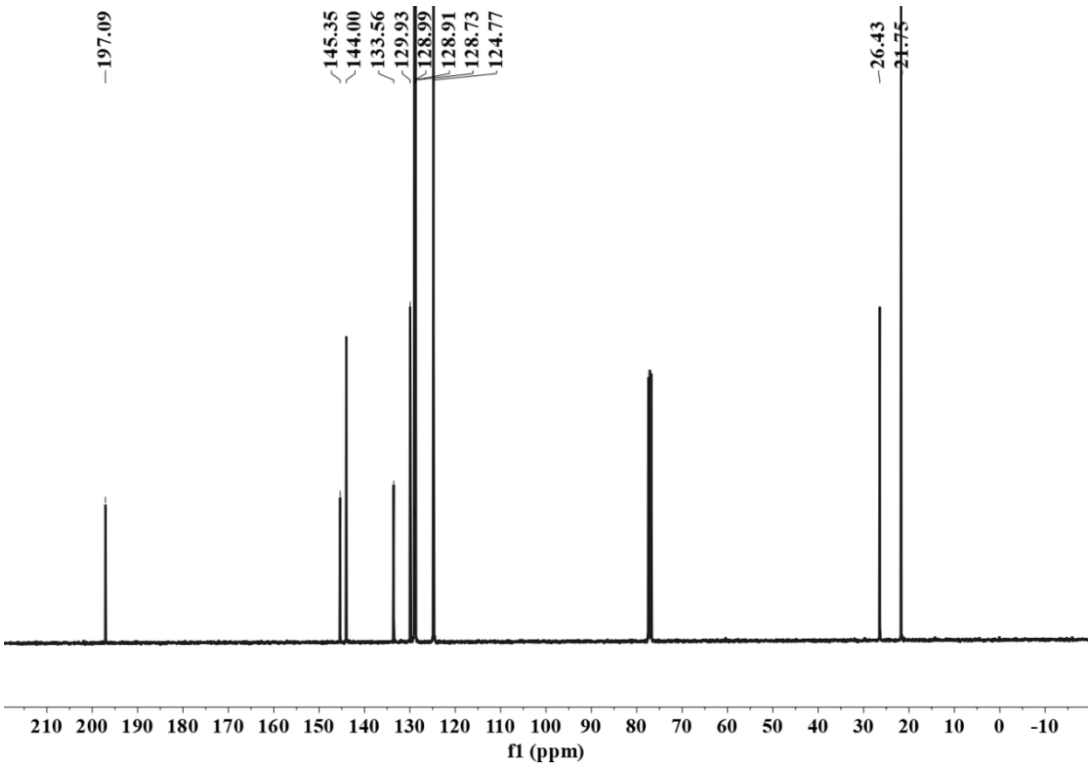
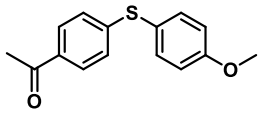


Fig. S43 ^{13}C NMR spectra of 4-acetyl-2, 4'-methyldiphenyl sulfide in $CDCl_3$.

7c. 4-acetyl-4'-methoxydiphenyl sulfide



79% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 - 7.75 (m, 2H), 7.49 - 7.44 (m, 2H), 7.12 - 7.05 (m, 2H), 6.98 - 6.92 (m, 2H), 3.84 (s, 3H), 2.53 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.16, 160.68, 146.93, 136.87, 133.84, 128.82, 125.77, 121.31, 115.39, 55.44, 26.48.

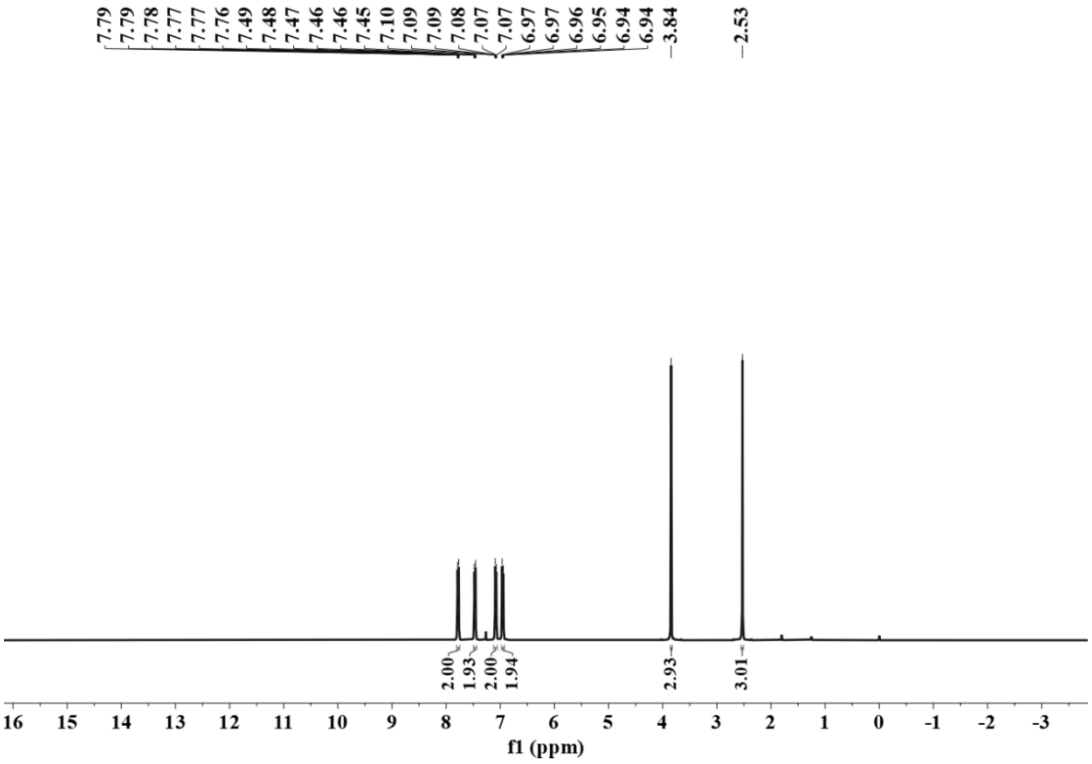


Fig. S44 ^{1}H NMR spectra of 4-acetyl-4'-methoxydiphenyl sulfide in $CDCl_3$.

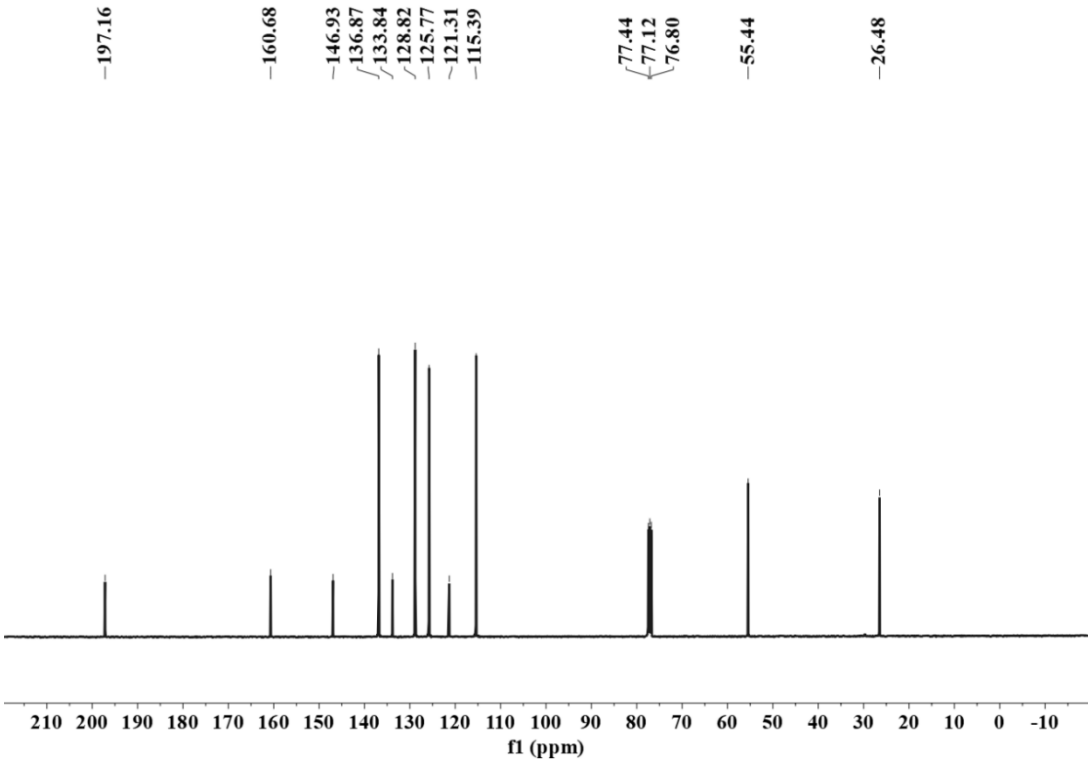
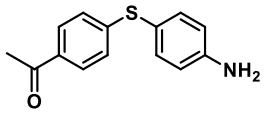


Fig. S45 ^{13}C NMR spectra of 4-acetyl-4'-methoxydiphenyl sulfide in $CDCl_3$.

7d. 4-acetyl-4'-aminodiphenyl sulfide



70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 - 7.75 (m, 2H), 7.36 - 7.31 (m, 2H), 7.11 - 7.05 (m, 2H), 6.74 - 6.69 (m, 2H), 3.92 (s, 2H), 2.53 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.29, 147.93, 137.10, 133.57, 128.76, 125.32, 117.58, 116.03, 26.48.

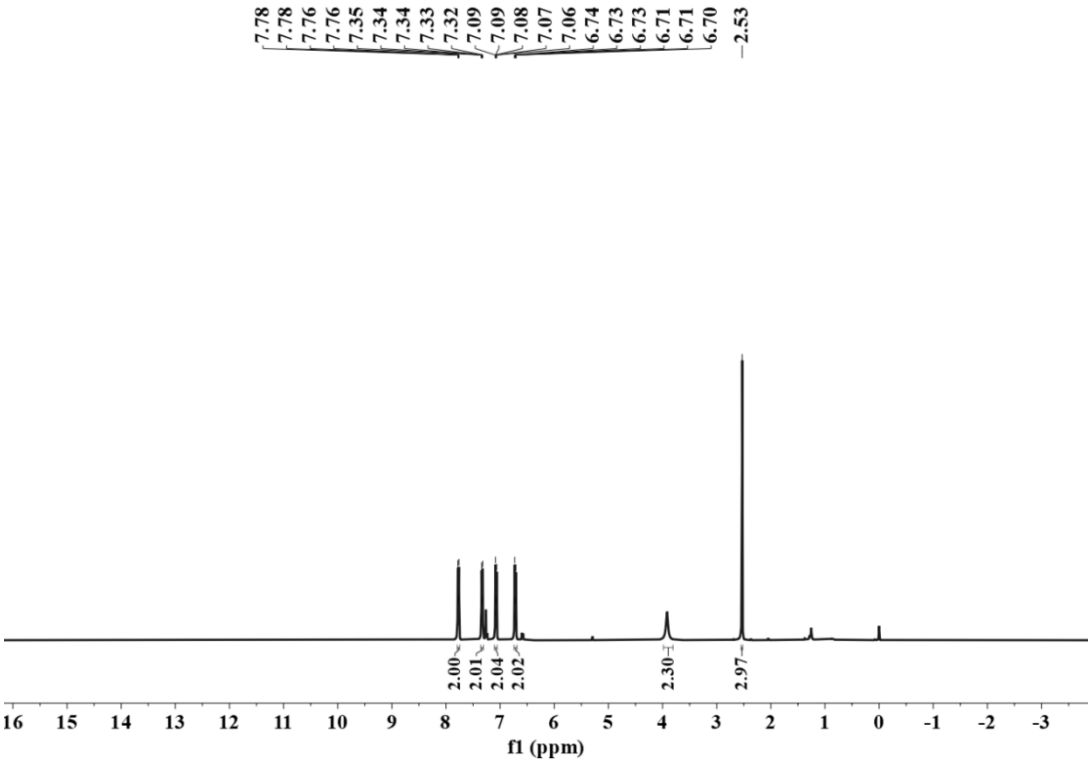


Fig. S46 ^{1}H NMR spectra of 4-acetyl-4'-aminodiphenyl sulfide in $CDCl_3$.

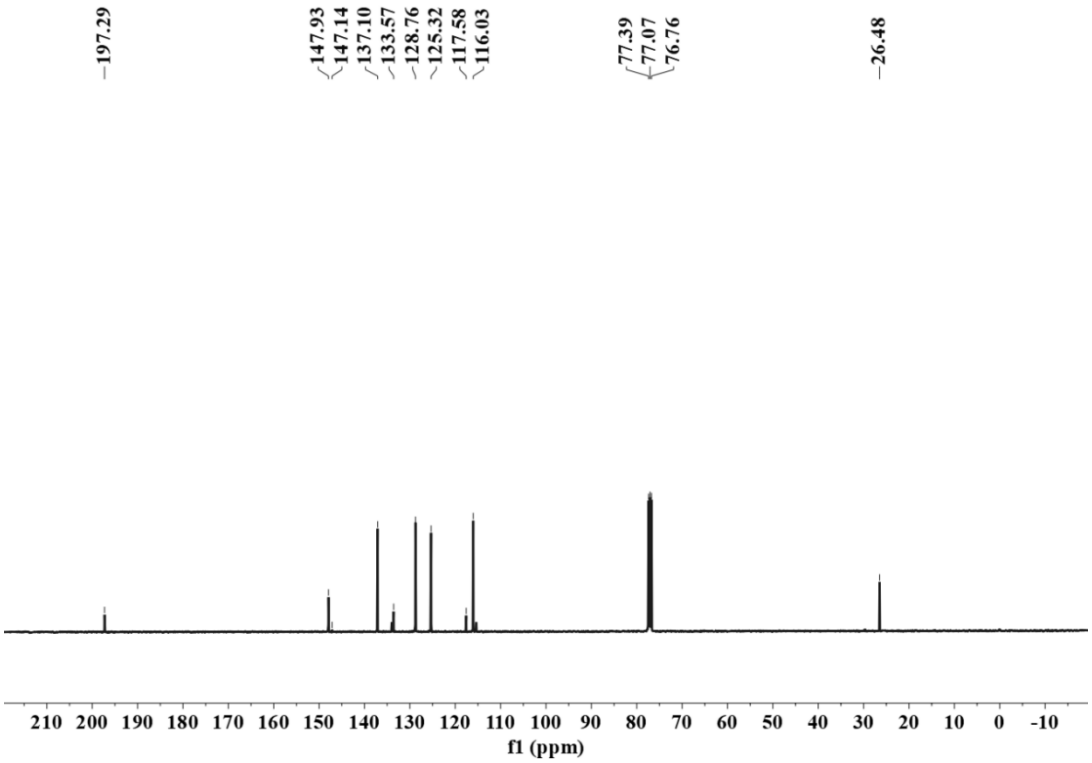
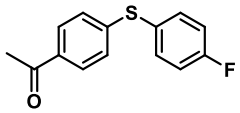


Fig. S47 ^{13}C NMR spectra of 4-acetyl-4'-aminodiphenyl sulfide in $CDCl_3$.

7e. 4-acetyl-4'-fluorodiphenyl sulfide



76% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dq, J = 8.8, 2.2 Hz, 2H), 7.54 - 7.44 (m, 2H), 7.17 - 7.05 (m, 4H), 2.54 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.08, 164.51, 162.03, 145.20, 136.61, 136.52, 134.41, 128.96, 126.78, 117.11, 116.89, 26.50.

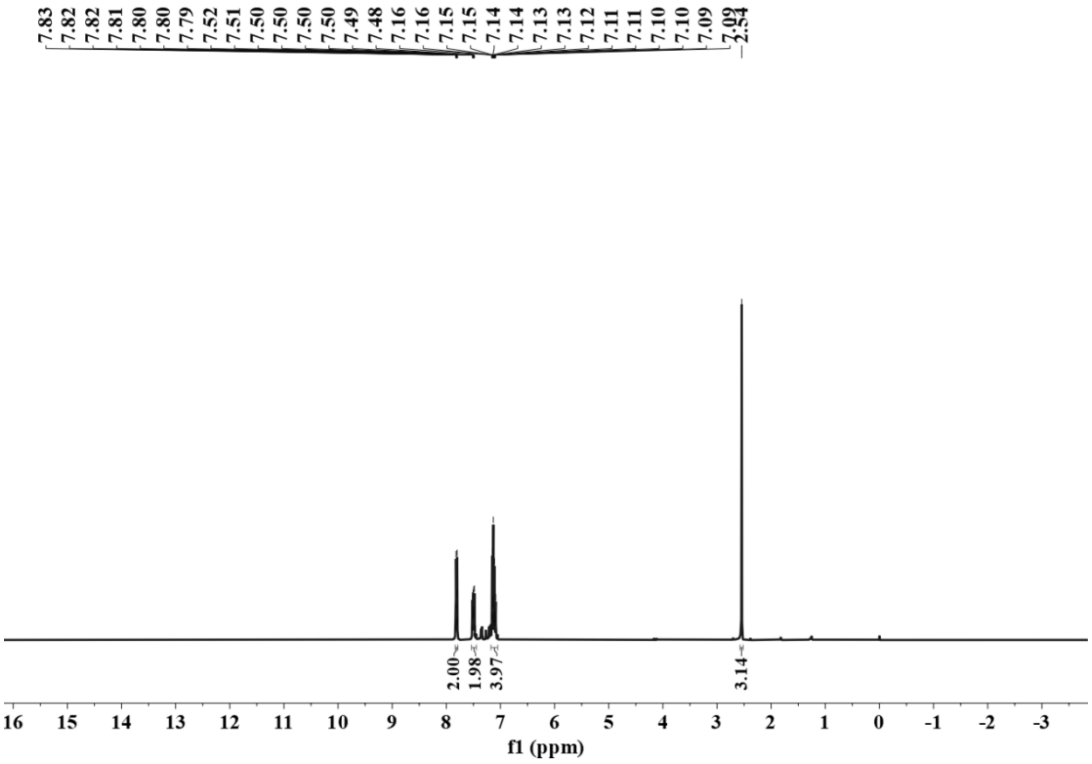


Fig. S48 ^{1}H NMR spectra of 4-acetyl-4'-fluorodiphenyl sulfide in $CDCl_3$.

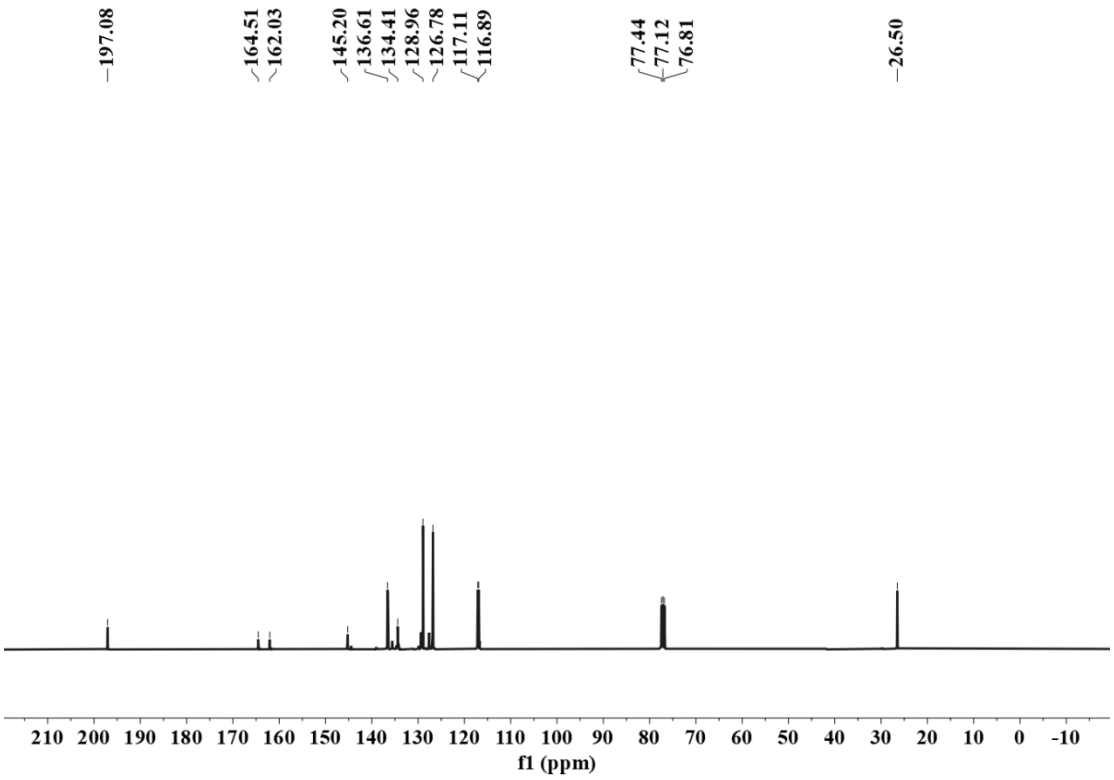
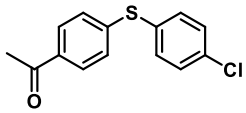


Fig. S49 ^{13}C NMR spectra of 4-acetyl-4'-fluorodiphenyl sulfide in $CDCl_3$.

7f. 4-acetyl-4'-chlorodiphenyl sulfide



78% yield; ^{1}H NMR (400 MHz, CDCl3) δ 7.86 - 7.81 (m, 2H), 7.44 - 7.34 (m, 4H), 7.24 - 7.19 (m, 2H), 2.56 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.11, 144.06, 134.92, 134.79, 130.89, 129.91, 129.03, 127.78, 26.55.

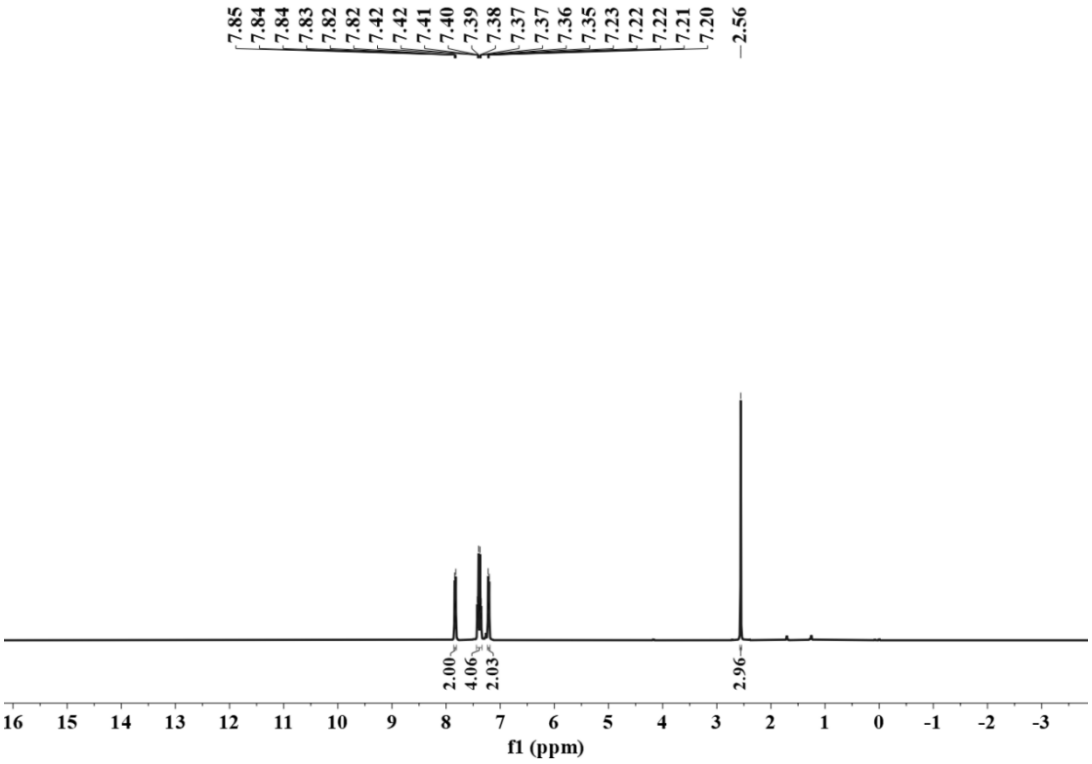


Fig. S50 ^{1}H NMR spectra of 4-acetyl-4'-chlorodiphenyl sulfide in $CDCl_3$.

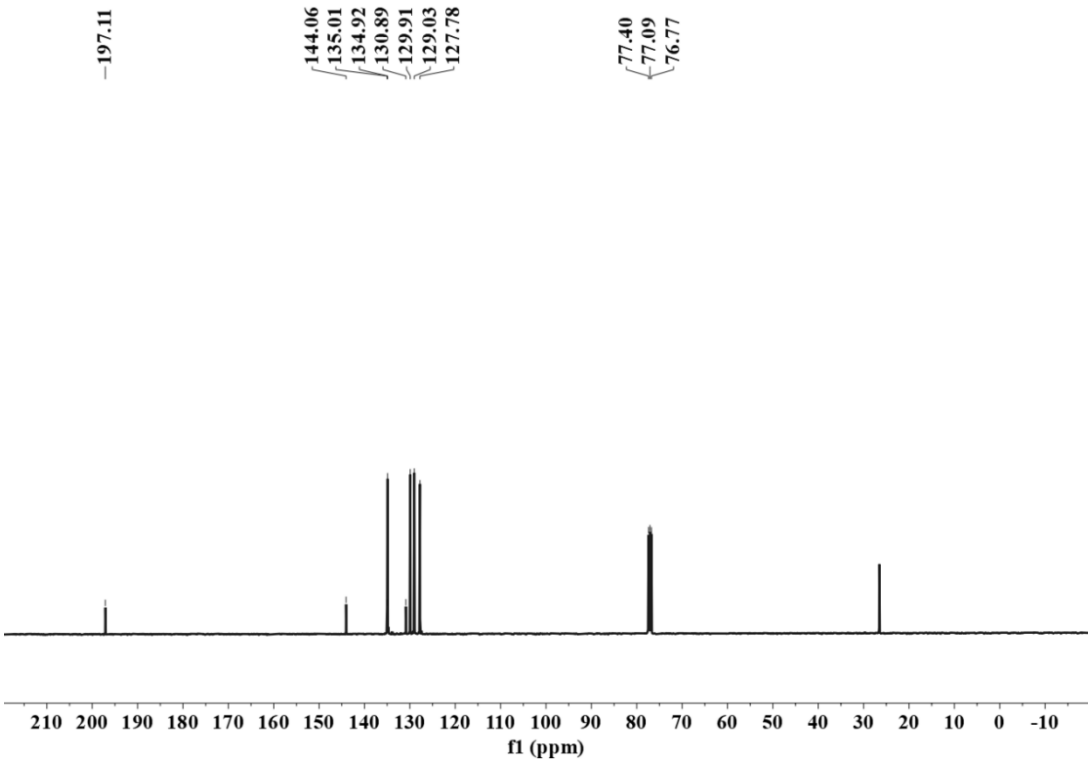


Fig. S51 ^{13}C NMR spectra of 4-acetyl-4'-chlorodiphenyl sulfide in $CDCl_3$.