Supplementary Information for

Construction of perylene supramolecular assemblies with enhanced singlet oxygen generation for heteroatom photooxidation

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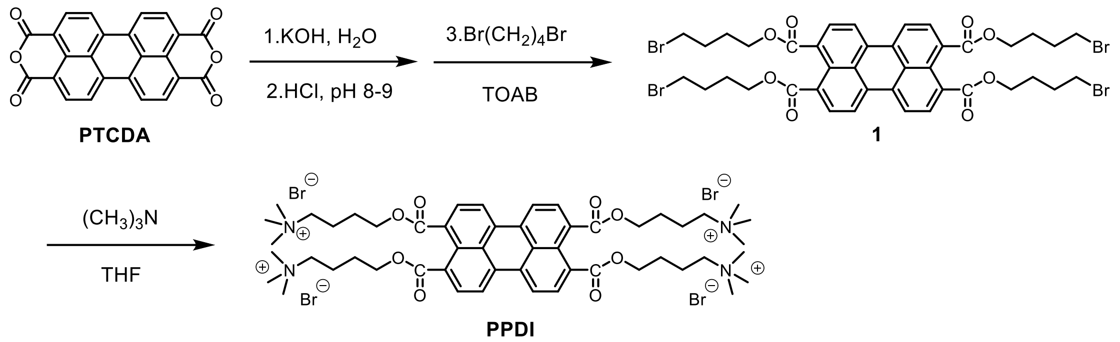
1. Materials and instruments.

Unless otherwise stated, all chemicals were purchased from commercial suppliers (Bide Pharmatech Ltd., Sigma Aldrich, TCI, Heowns Biochem) and used without further purification. ^{1}H NMR spectra were recorded on a Bruker Avance 400 spectrometer (400 MHz) at 298 K, and the chemical shifts (δ) were expressed in ppm, and J values were given in Hz. Chemical shifts were calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$: 7.26 ppm ^{1}H NMR). Multiplicities were presented as: s (singlet); d (doublet); t (triplet); and m (multiplet). UV-vis absorption spectra were characterized by a Shimadzu UV-2450 spectrophotometer. Fluorescence emission spectra were obtained by fluorescence spectrophotometer F-380A. DLS and Zeta potential tests were constructed on Malvern Zeta sizer Nano ZS90. The time-resolved fluorescence decay curve was obtained by the FLS 920 Steady-State/Transient Fluorescence Spectrometer. The photocatalytic reaction was performed on WATTCAS Parallel Photocatalytic Reactor (WP-TEC-HSL) with 10W COB LED.

2. Synthesis of PPDI



Scheme S1. Two step synthetic route of PPDI.

Synthesis of compound PPDI ((((4,9-bis((4-(trimethylammonio)butoxy)carbonyl)perylene-3,10-dicarbonyl)bis(oxy))bis(butane-4,1-diyl)) bis(dimethyl-l4-azanediyl))dimethylium:

Step 1: Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) (784 mg, 2.0 mmol), KOH (1.0 g, 17.7 mmol), and 30 mL deionized water were added into a 100 mL flask and stirred at 70°C for 30 min. The solution was filtered and its pH value was adjusted to 8–9 with 1 M HCl. Subsequently, tetraoctylammonium bromide (TOAB) (400 mg, 0.7 mmol) was added. The mixture was stirred vigorously for 15 min, and 1,4-dibromobutane (4.3 g, 20.0 mmol) was added. The solution was refluxed with vigorous stirring for 2 h. The aqueous solution became clear and colorless, and on top of it a layer of red oil formed. Next, CH_2Cl_2 (30 mL) was added to the reaction mixture. The organic phase was washed three times with 15% aqueous NaCl (30 mL) and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of CH_2Cl_2/petroleum ether (2:1) as eluent. After drying under vacuum, compound 1 (1.05 g, 55.2%) was obtained as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 8.0 Hz, 4H), 8.06 (d, J = 7.9 Hz, 4H), 4.38 (t, J = 6.2 Hz, 8H), 3.51 (t, J = 6.4 Hz, 8H), 2.11 – 2.02 (m, 8H), 1.98 (td, J = 6.4, 2.7 Hz, 8H). The spectral data obtained were identical with those reported in literature.[1]

Step 2: Compound 1 (484 mg, 0.5 mmol) was dissolved in THF (50 mL) in a 100 mL flask. An excess amount of trimethylamine (5 mL, 30% aqueous solution) was added. The solution was refluxed for 3 days. During this period, water was added at several intervals (total of 15 mL). The organic solvent was evaporated under reduced pressure, and the aqueous solution was washed with CH_2Cl_2 (30 mL) three times. After solvent evaporation and drying under vacuum, PPDI (0.43 g, 72%) was obtained as a red solid.^{1}H NMR (400 MHz, DMSO-d_6) δ 8.75 (d, J = 8.2 Hz, 4H), 8.14 (d, J = 7.9 Hz, 4H), 4.33 (t, J = 6.3 Hz, 8H), 3.17 (s, 8H), 3.09 (s, 36H), 1.86 (t, J = 8.5 Hz, 8H), 1.77 (q, J = 7.2, 6.8 Hz, 8H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.17, 133.10, 131.14, 130.34, 128.53, 128.44, 123.16, 65.21, 64.98, 59.97, 52.65, 25.45, 19.55.The spectral data obtained were identical with those reported in the literature.[1]

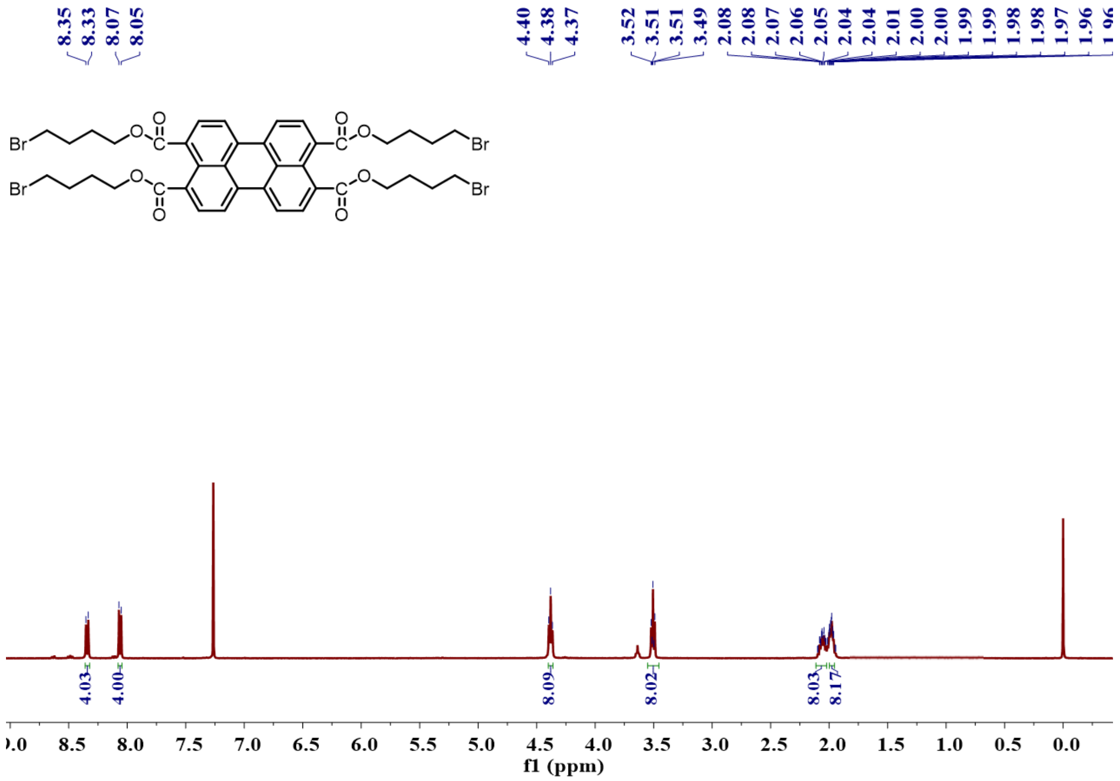


Fig. S1. ^{1}H NMR spectra of **1** in $CDCl_3$.

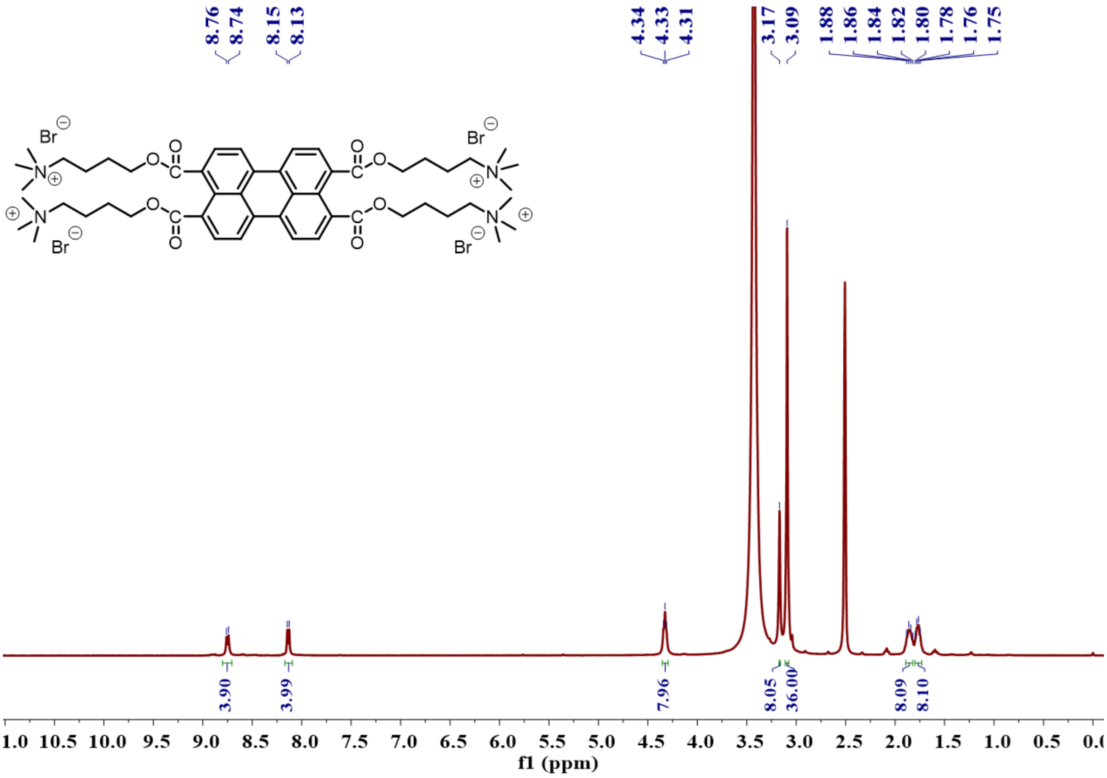


Fig. S2. ^{1}H NMR spectra of **PPDI** in DMSO-d_6.

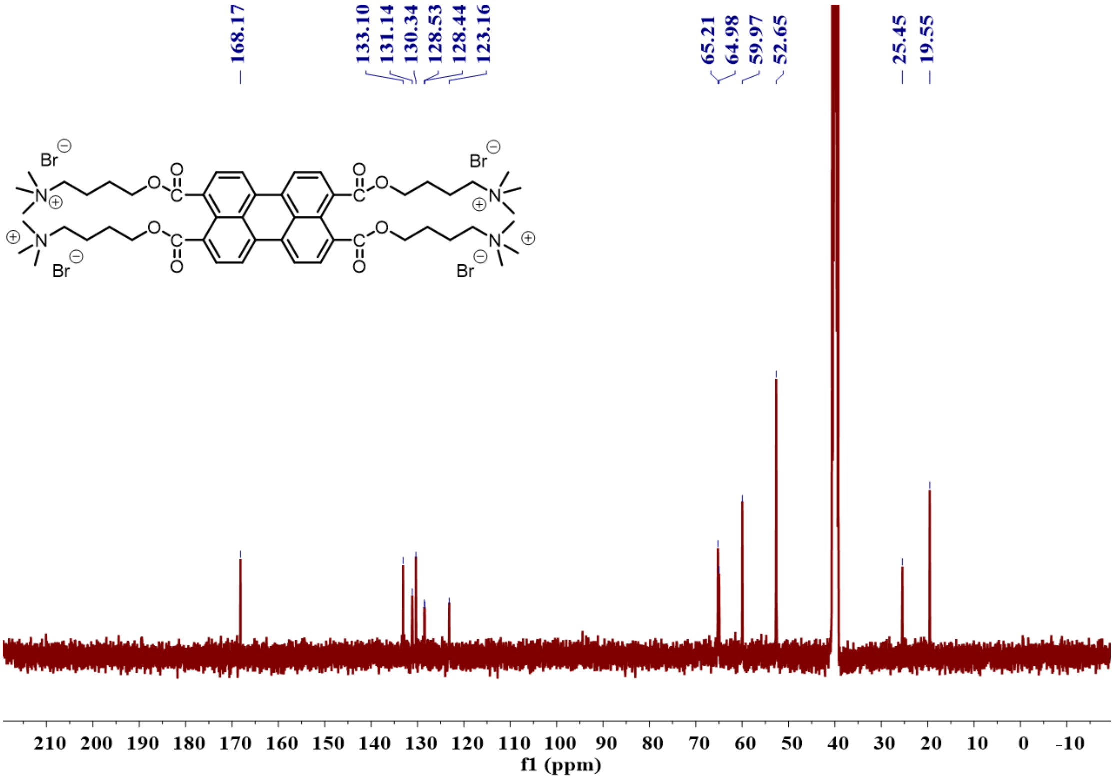


Fig. S3. ^{13}C NMR spectra of **PPDI** in DMSO-d_6.

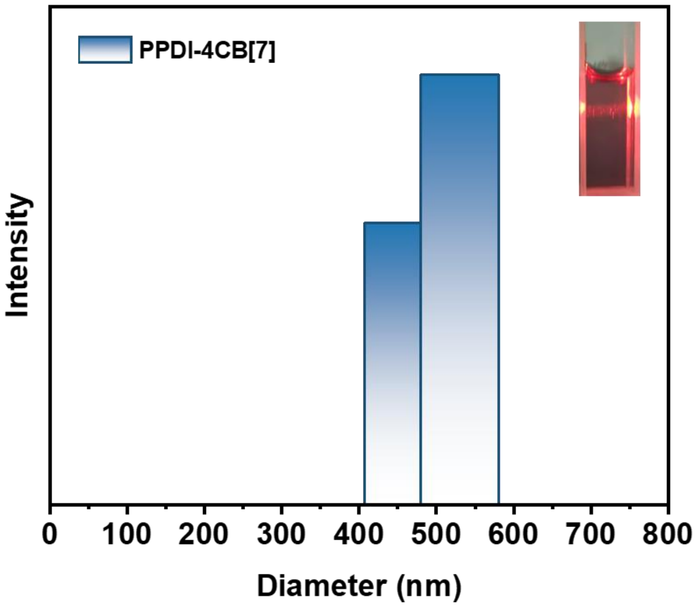


Fig. S4. DLS of PPDI-4CB[7].

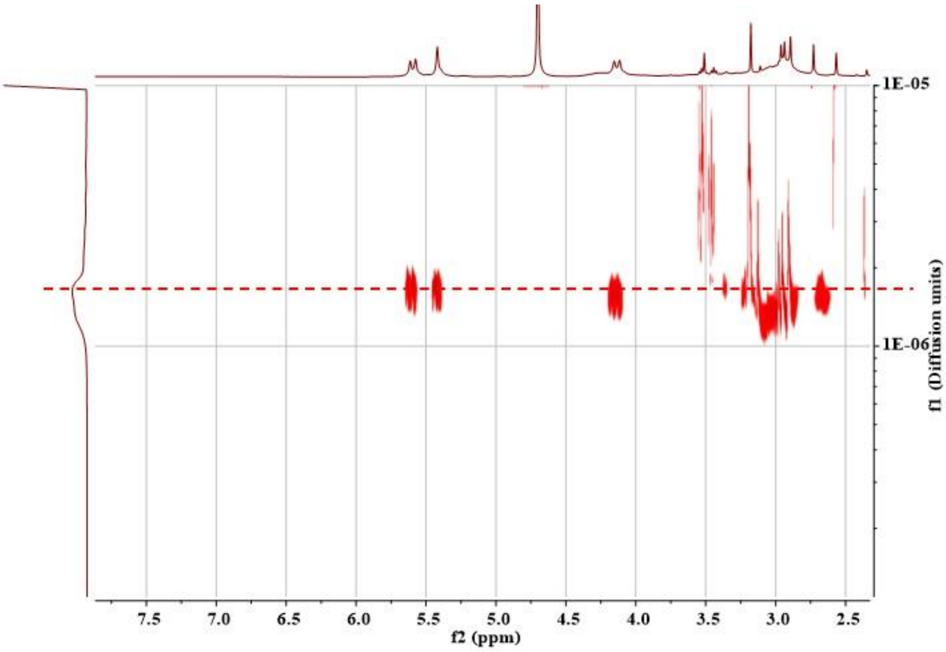


Fig. S5. DOSY NMR spectra (400 MHz) of the mixture of PPDI and CB[7] (1:4) in D_2O.

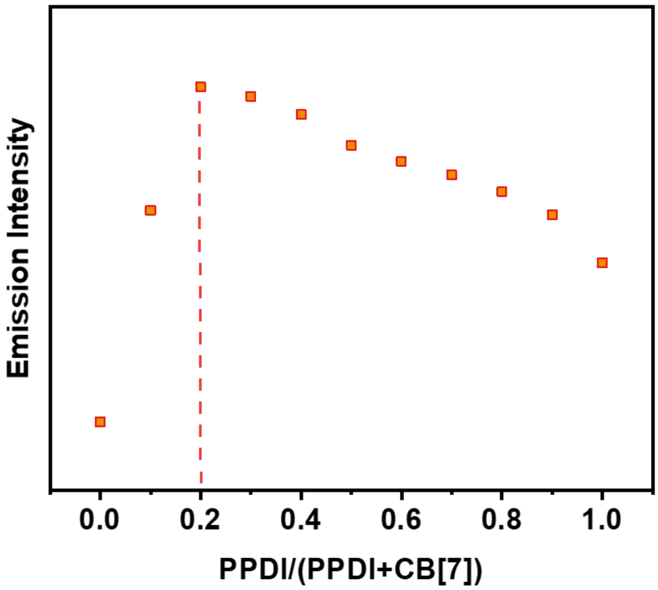


Fig. S6. Job's plot for the complexation between PPDI and CB[7] with the total concentration of PPDI and CB[7] fixed at 2.0×10^{-5} M.

Detection of Overall ROS

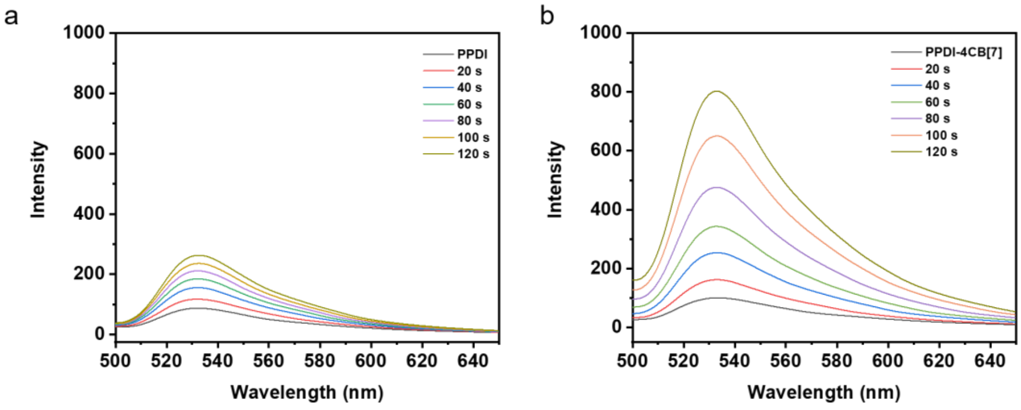


Fig. S7. The fluorescence spectra of DCFH (20 μM) after irradiation (450-455 nm, 10 W) for different time in the presence of (a) PPDI and (b) PPDI-4CB[7]. [PPDI] = 2.0 × 10^{-5} M.

Procedure for $^1O_2$ Quantum Yield Measurement.

The $^1O_2$ quantum yield was measured using Rose Bengal (RB) as the reference photosensitizer and calculated using the following Equation 1:

$$\Phi_{probe}=\Phi_{RB}\times(K_{probe}A_{RB}/\ K_{RB}A_{probe})\ \text{(Equation 1)}$$

where K_{probe} and K_{RB} are the decomposition rate constants of ABDA in the presence of the probe and RB, respectively. Φ_{RB} is the $^1O_2$ quantum yield of RB (Φ_{RB} = 0.75 in water). A_{probe} and A_{RB} represent the integration area of absorption bands ranging from 450 to 455 nm of the probe and RB, respectively. The ABDA (1.5×10^{-7} mol) in 3 mL of the probe solution was exposed to Blue light irradiation (450-455 nm) with a power density of 10W. The natural logarithm of the absorbance ratio (A_0/A) of ABDA at 378 nm was plotted against irradiation time and the slope is regarded as the decomposition rate.

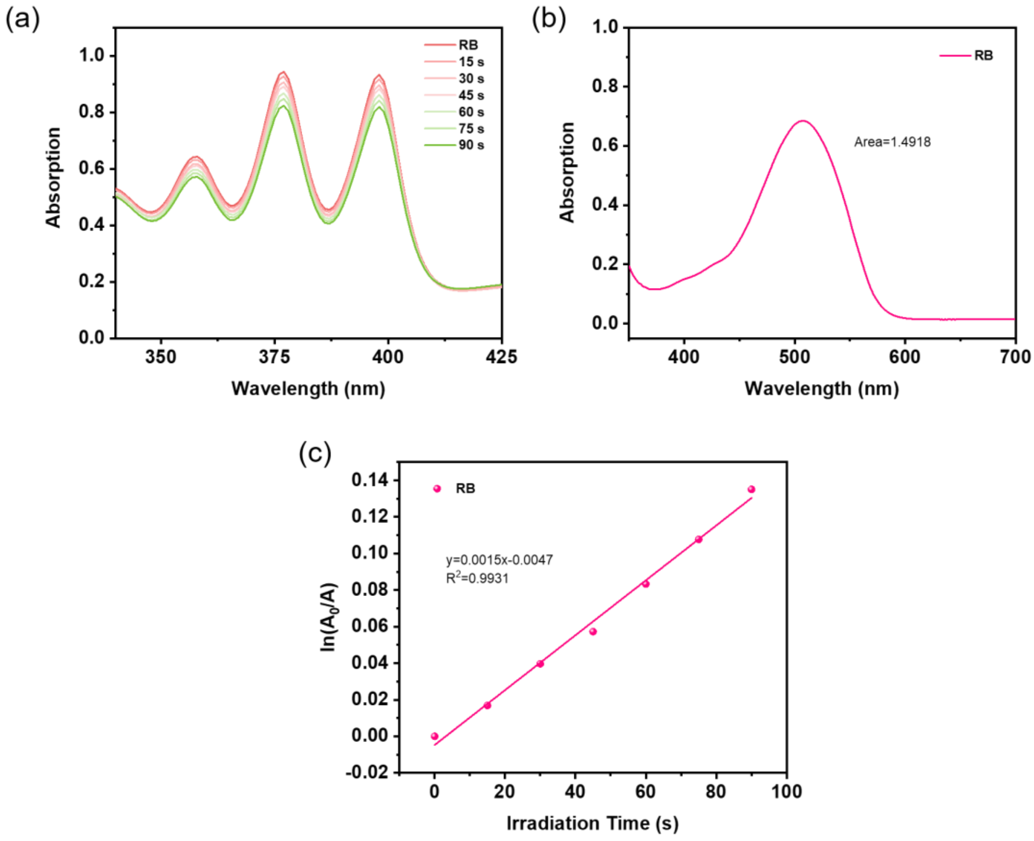


Fig. S8. (a) The absorption spectra of ABDA after irradiation (450-455 nm, 10 W) for different time in the presence of RB; (b) The UV-vis absorption spectra of RB in the aqueous solution; (c) The decomposition rates of ABDA in the presence of RB.

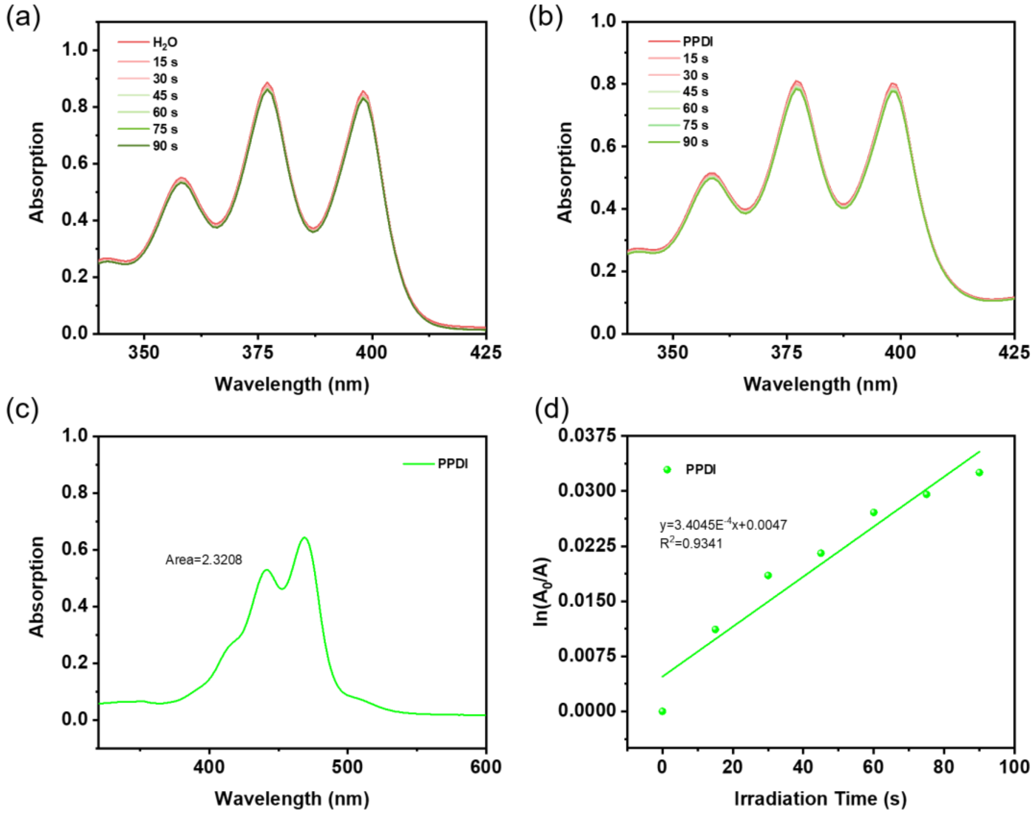


Fig. S9. (a)The absorption spectra of ABDA after irradiation (450-455 nm, 10 W) for different time in the presence of (a) Control: ABDA without any additive; (b) PPDI; (c) The UV-vis absorption spectra of PPDI in the aqueous solution; (d) The decomposition rates of ABDA in the presence of PPDI. [PPDI] = 2.0 × 10^{-5} M.

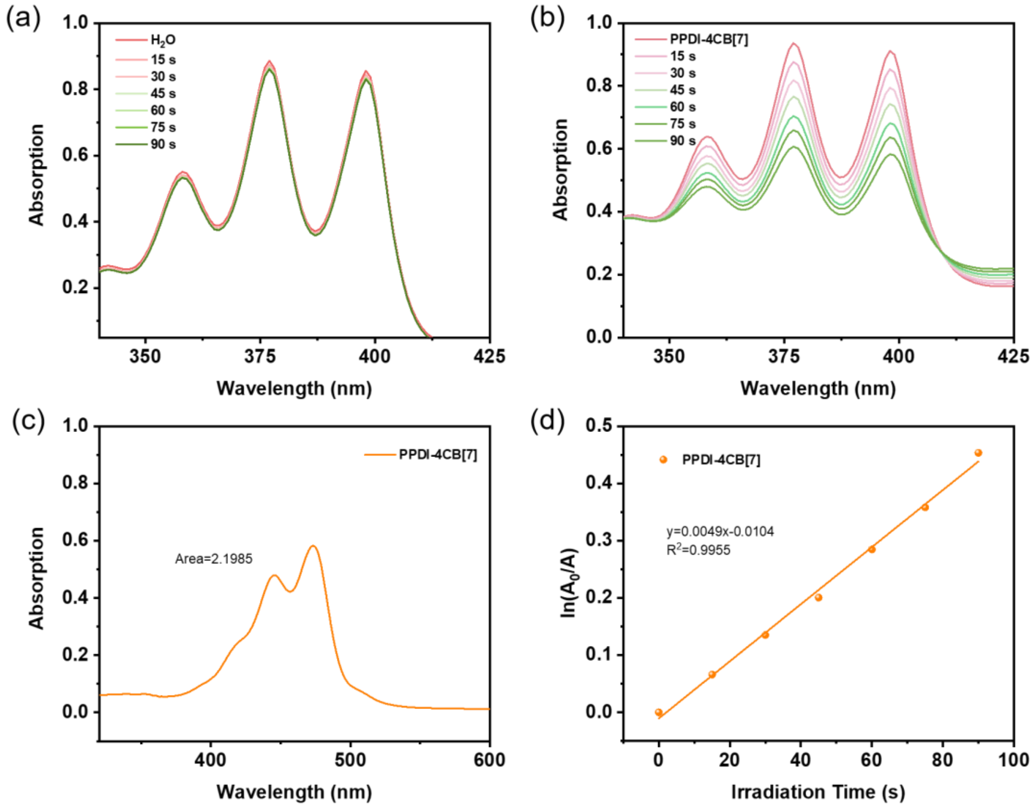


Fig. S10. (a)The absorption spectra of ABDA after irradiation (450-455 nm, 10 W) for different time in the presence of (a) Control: ABDA without any additive; (b) PPDI-4CB[7]; (c) The UV-vis absorption spectra of PPDI-4CB[7] in the aqueous solution; (d) The decomposition rates of ABDA in the presence of PPDI-4CB[7]. [PPDI] = 2.0×10^{-5} M, [CB[7]] = 8.0×10^{-5} M.

General procedure for photooxidation reactions of thioanisole and its derivatives.

Thioanisole (28 μL, 0.2 mmol) was dissolved in freshly prepared PPDI-4CB[7] aqueous solution (Catalyst total amount: 2 mL, [PPDI]=1.0 × 10^{-3} mol/L, [CB[7]]=4.0 × 10^{-3} mol/L). The mixture was subsequently irradiated with Blue LEDs (10 W, $\lambda = 455$ nm) for 8 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 organic solution was concentrated in a vacuum and purified by rapid column chromatography to obtain the corresponding products.

General procedure for photooxidation reactions of phenylsilane and its derivatives.

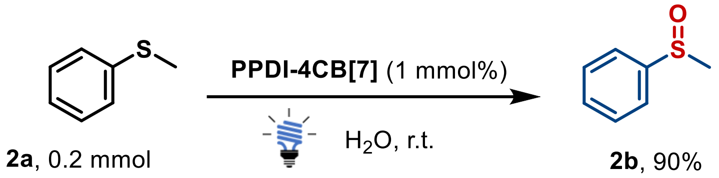
Phenylsilane (25 uL, 0.2 mmol) was dissolved in freshly prepared PPDI-4CB[7] aqueous solution (Catalyst total amount: 2 mL, [PPDI]=1.0 × 10^{-3} mol/L, [CB[7]]=4.0 × 10^{-3} mol/L). The mixture was subsequently irradiated with Blue LEDs (10 W, $\lambda = 455$ nm) for 12 h at room temperature. Afterward, the organic product was extracted with ethyl acetate, and the mixed organic layer was dried with anhydrous Na_2SO_4 the organic solution was concentrated in a vacuum and purified by rapid column chromatography to obtain the corresponding products.

General procedure for photooxidation reactions of triphenylphosphine and its derivatives.

Triphenylphosphine (52.5 mg, 0.2 mmol) was dissolved in freshly prepared PPDI-4CB[7] aqueous solution (Catalyst total amount: 2 mL, [PPDI]=3.0×10^{-3} mol/L, [CB[7]]=1.2×10^{-2} mol/L). The mixture was subsequently irradiated with Blue LEDs (10 W, $\lambda = 455$ nm) for 36 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 organic solution was concentrated in a vacuum and purified by rapid column chromatography to obtain the corresponding products.

Optimization of reaction conditions.

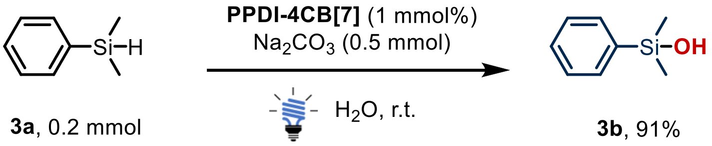
Table S1. PPDI-4CB[7] as photocatalysts for photooxidation of thioanisole under different conditions. [a,b]



Entry	Variation from standard conditions	Yield[b] (%)
1	none	90
2	PPDI instead of PPDI-4CB[7]	32
3	PPDI-4CB[7] (0.5 mmol%)	45
4	PPDI-4CB[7] (1.5 mmol%)	92
5	4 h instead of 8 h	53
6	12 h instead of 8 h	91
7	390-395 nm	36
8	470-475 nm	47
9	no PPDI-4CB[7]	0
10	no Light	0

[a] Reaction conditions: Thioanisole (28 μL, 0.2 mmol), PPDI and PPDI-4CB[7] aqueous soiution (1 mmol%, 2 mL), Blue LEDs (10 W, λ = 450-455 nm), room temperature (r.t.), 8 h. [b] Isolated yield.

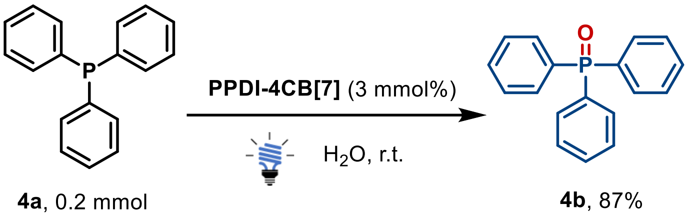
Table S2. PPDI-4CB[7] as photocatalysts for photooxidation of phenylsilane under different conditions. [a,b]



Entry	Variation from standard conditions	Yield[b] (%)
1	none	91
2	PPDI instead of PPDI-4CB[7]	trace
3	PPDI-4CB[7] (0.5 mmol%)	53
4	PPDI-4CB[7] (1.5 mmol%)	92
5	8 h instead of 12 h	48
6	16 h instead of 12 h	90
7	Na_2CO_3(0.2 mmol)	33
8	Na_2CO_3(0.8 mmol)	90
9	390-395 nm	42
10	470-475 nm	49
11	no PPDI-4CB[7]	0
12	no Light	0

[a]Reaction conditions: Phenylsilane (25 μL, 0.2 mmol), Na_2CO_3(0.5 mmol); PPDI and PPDI-4CB[7] aqueous soiution (1 mmol%, 2 mL), Blue LEDs (10 W, λ = 450-455 nm), room temperature (r.t.), 12 h. [b]Isolated yield.

Table S3. PPDI-4CB[7] as photocatalysts for photooxidation of triphenylphosphine under different conditions. [a,b]



Entry	Variation from standard conditions	Yield[b] (%)
1	none	87
2	PPDI instead of PPDI-4CB[7]	20
3	PPDI-4CB[7] (1 mmol%)	32
4	PPDI-4CB[7] (5 mmol%)	90
5	24 h instead of 36 h	48
6	48 h instead of 36 h	90
7	390-395 nm	36
8	470-475 nm	43
9	no PPDI-4CB[7]	0
10	no Light	0

[a]Reaction conditions: Triphenylphosphine (52.5 mg, 0.2 mmol), PPDI and PPDI-4CB[7] aqueous soiution (3 mmol%, 2 mL), Blue LEDs (10 W, λ = 450-455 nm), room temperature (r.t.), 36 h. [b]Isolated yield.

Fluorescence quenching experiment

The quenching experiments were conducted under an oxygen atmosphere. Using a microsyringe, substrates 2a, 3a, and 4a at different concentrations (0, 1, 2, 3, 4, 5 mM) were titrated into 3 mL of an aqueous solution of PPDI-4CB[7]. Specifically, in a well-sealed reaction vessel, the oxygen gas was first introduced to displace the ambient air to ensure a pure oxygen environment. Then, with precise operation of the microsyringe, incremental amounts of the substrates were added to the PPDI-4CB[7] solution. After each addition, the solution was gently stirred to ensure uniform mixing. Subsequently, the fluorescence emission spectra of the resulting solutions were recorded. The procedures carried out under a nitrogen atmosphere are identical to those described above.

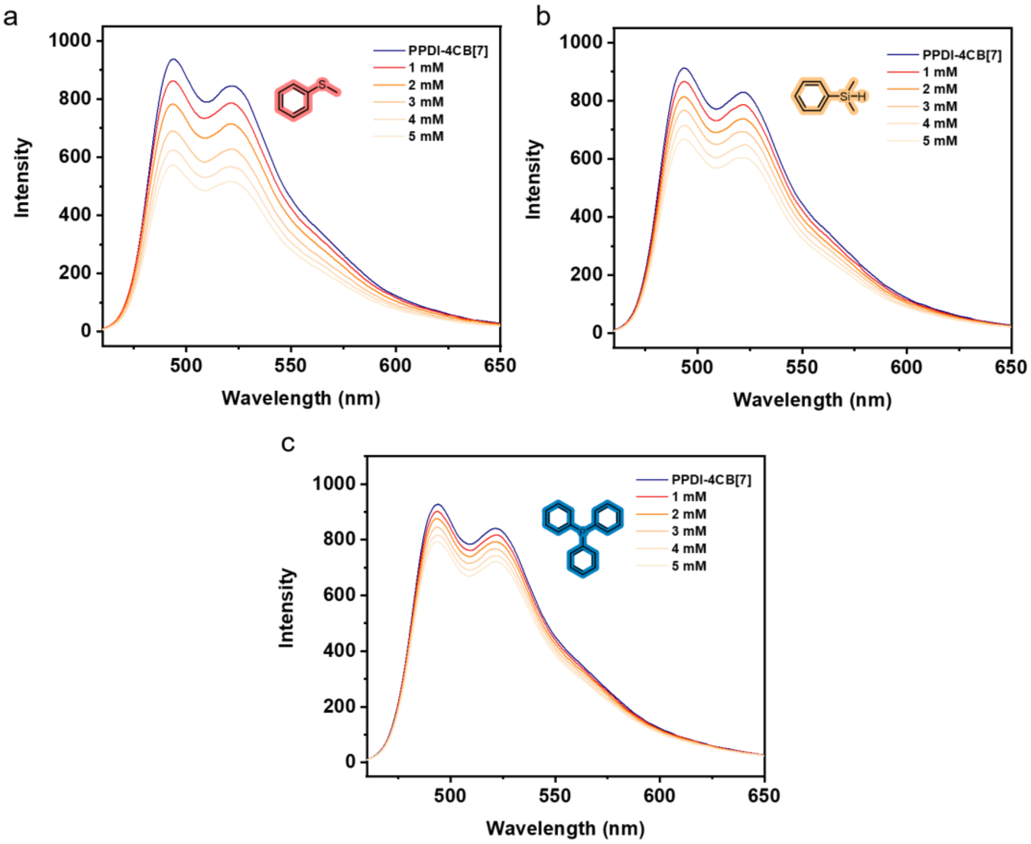


Fig. S11. Stern-Volmer quenching studies of PPPDI-4CB[7] in an Oxygen (O_2) Atmosphere with (a) thioanisole, (b) phenylsilane, and (c) triphenylphosphine used as quenchers. [PPDI]=5.0 × 10^{-5} mol/L.

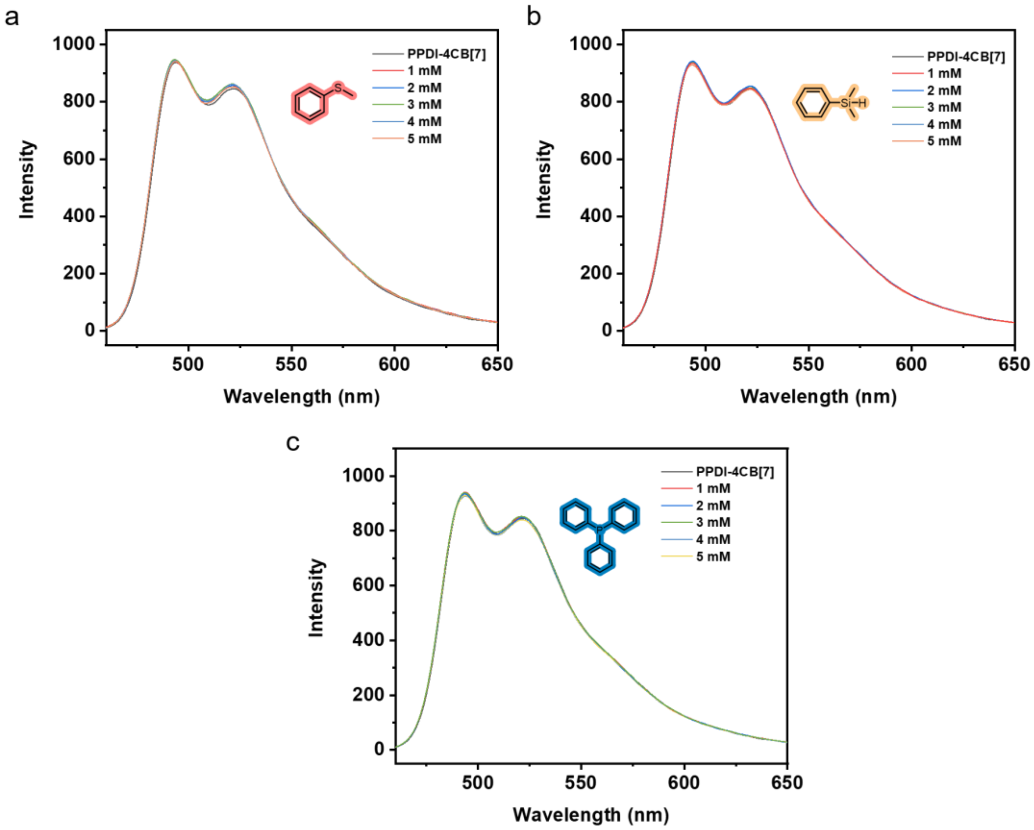
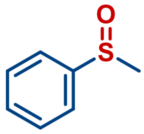


Fig. S12. Stern-Volmer quenching studies of PPPDI-4CB[7] in the nitrogen (N_2) atmosphere by using (a) thioanisole, (b) phenylsilane, and (c) triphenylphosphine as quenchers. [PPDI]=5.0 × 10^{-5} mol/L.

^{1}H NMR data of 2b-2p

2b. (methylsulfinyl)benzene



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=20:1) to give 2b as a colorless oil. (25.2mg, 90% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, J = 8.0, 1.6 Hz, 2H), 7.57 – 7.49 (m, 3H), 2.74 (s, 3H).[2]

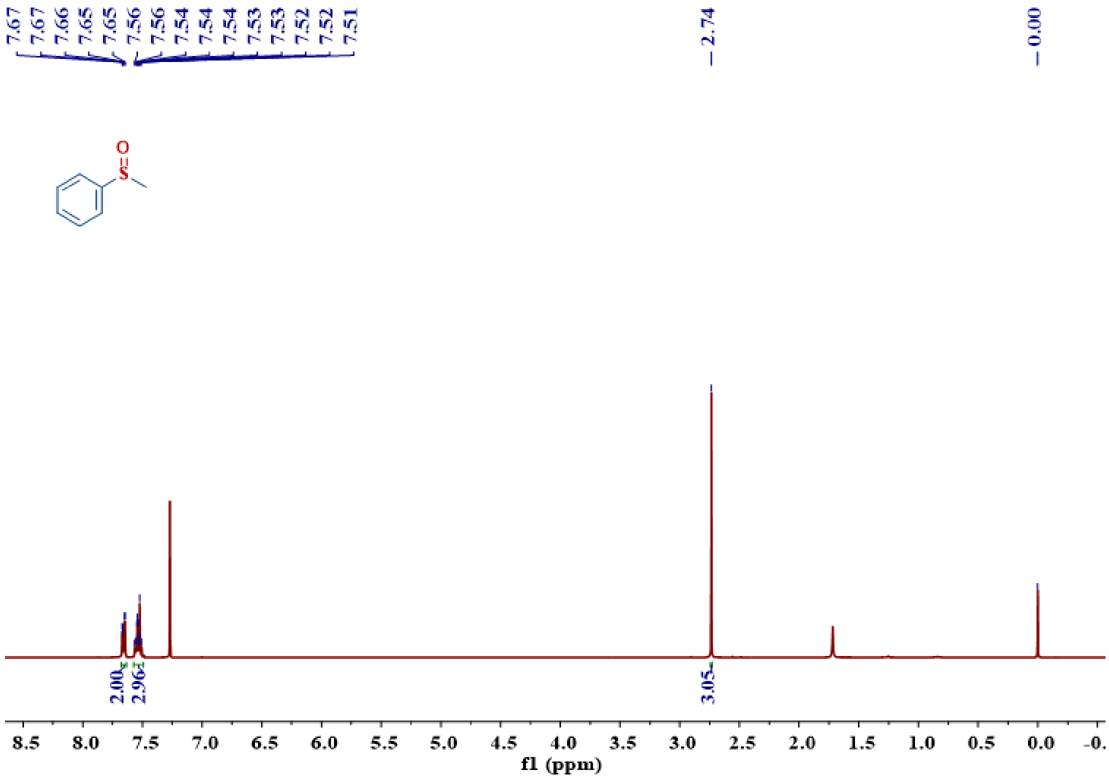
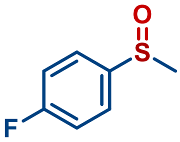


Fig. S13. ^{1}H NMR spectra of (methylsulfinyl)benzene in $CDCl_3$.

2c. 1-fluoro-4-(methylsulfinyl)benzene



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=20:1) to give 2c as a colorless oil. (29.1 mg, 92% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 2H), 7.14 – 7.08 (m, 2H), 2.60 (s, 3H). [2]

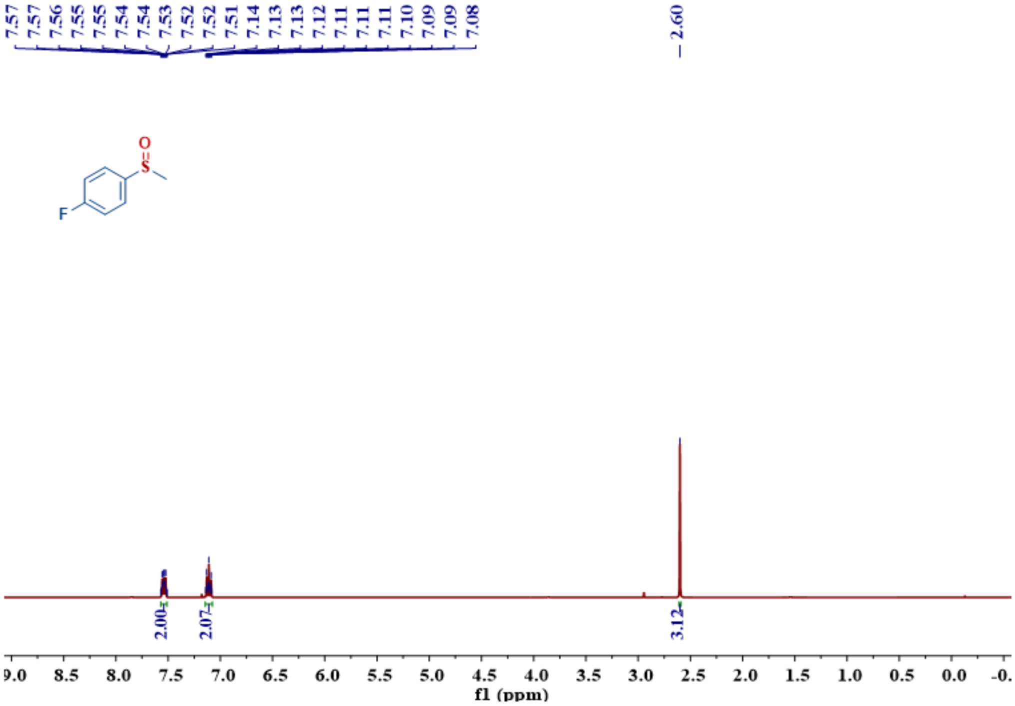
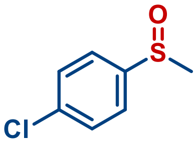


Fig. S14. ^{1}H NMR spectra of Methyl 1-fluoro-4-(methylsulfinyl)benzene in $CDCl_3$.

2d. 1-chloro-4-(methylsulfinyl)benzene



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=20:1) to give 2d as a colorless oil. (31.8 mg, 91% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.54 – 7.50 (m, 2H), 7.45 – 7.41 (m, 2H), 2.65 (s, 3H). [2]

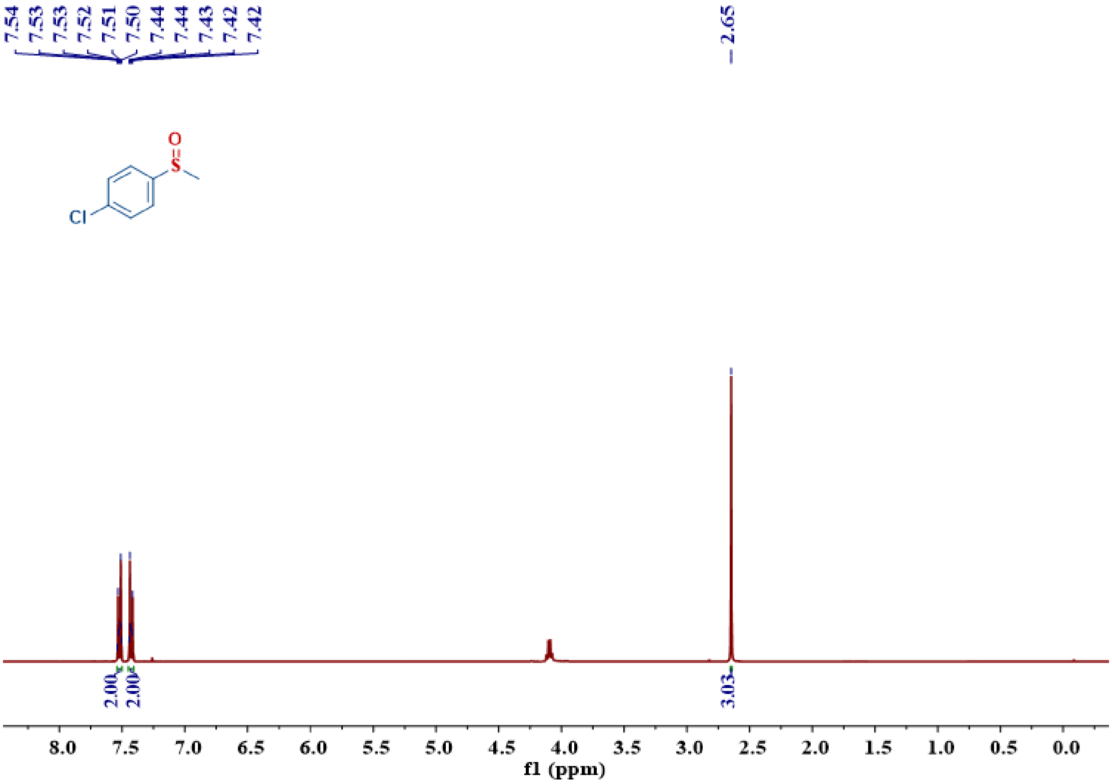
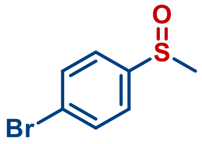


Fig. S15. ^{1}H NMR spectra of 1-chloro-4-(methylsulfinyl)benzene in CDCl$_3$.

2e. 1-bromo-4-(methylsulfinyl)benzene



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=20:1) to give 2e as orange clear liquid. (39.4 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 2H), 7.46 – 7.42 (m, 2H), 2.63 (s, 3H). [2]

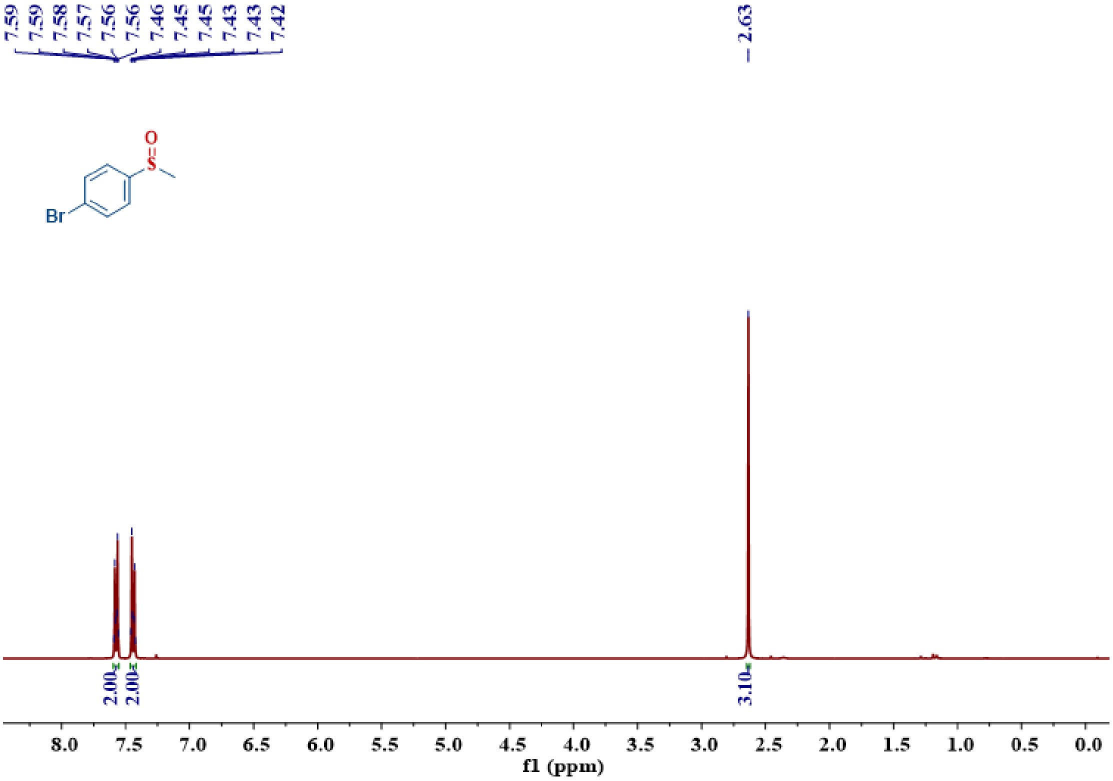
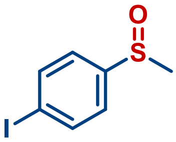


Fig. S16. ^{1}H NMR spectra of 1-bromo-4-(methylsulfinyl)benzene in $CDCl_3$.

2f. 1-iodo-4-(methylsulfinyl)benzene



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=20:1) to give 2f as a colorless oil. (46.6 mg, 89% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.84 – 7.77 (m, 2H), 7.35 – 7.30 (m, 2H), 2.67 – 2.65 (m, 3H). [2]

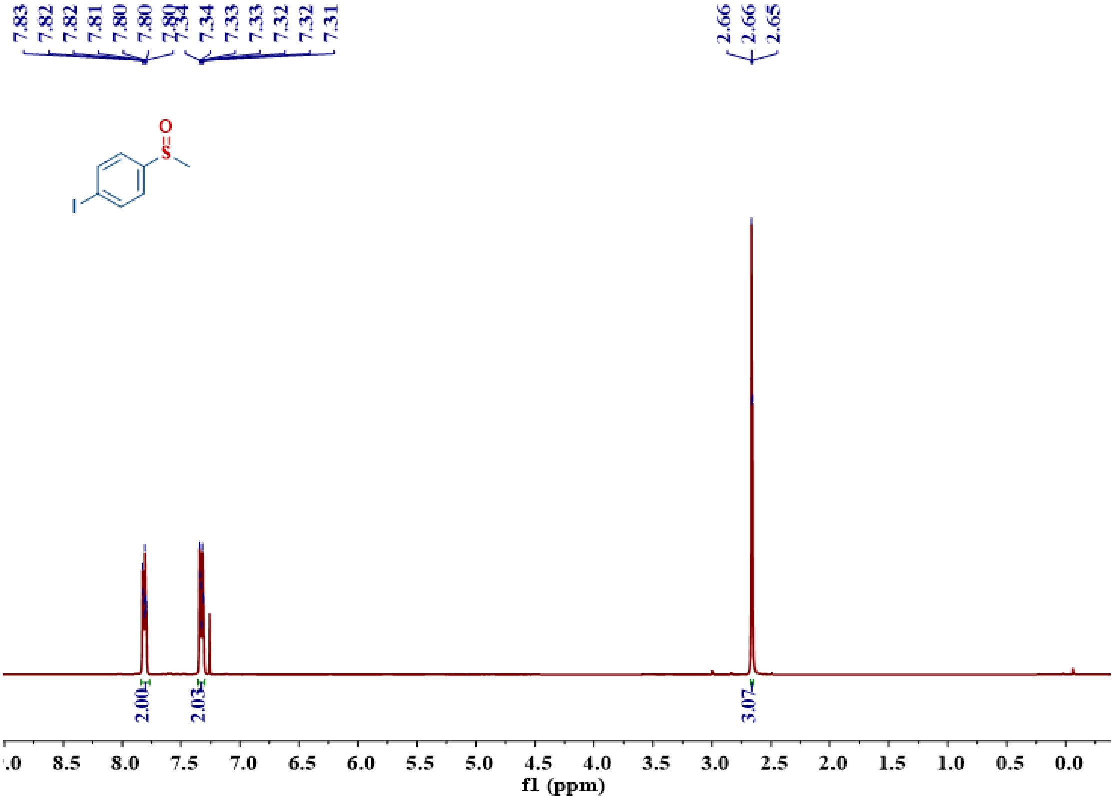
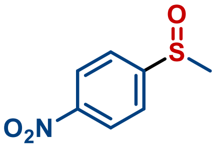


Fig. S17. ^{1}H NMR spectra of 1-iodo-4-(methylsulfinyl)benzene in CDCl$_3$.

2g. 1-(methylsulfinyl)-4-nitrobenzene



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=20:1) to give 2g as a colorless oil. (33.6 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 – 8.35 (m, 2H), 7.85 – 7.80 (m, 2H), 2.78 (s, 3H).[3]

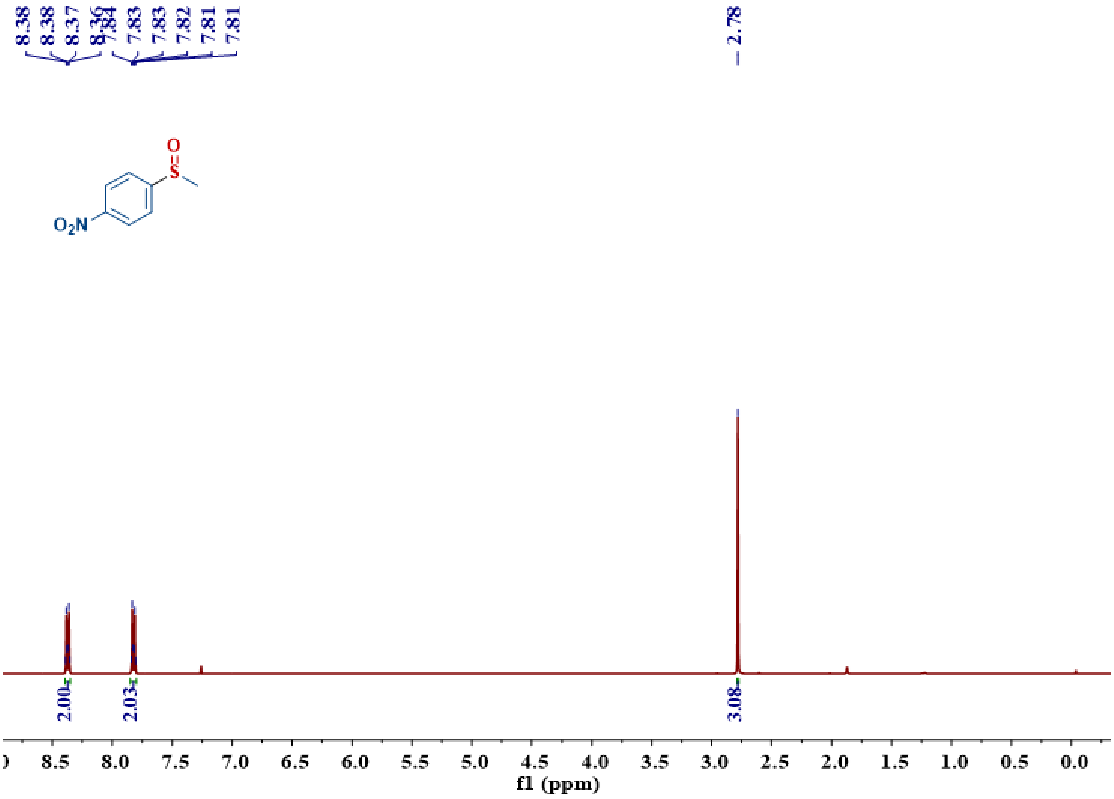
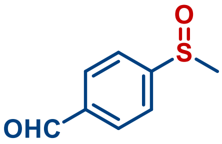


Fig. S18. ^{1}H NMR spectra of 1-(methylsulfinyl)-4-nitrobenzene in $CDCl_3$.

2h. 4-(methylsulfinyl)benzaldehyde



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=20:1) to give 2h as a colorless oil. (29.6 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 8.02 – 7.99 (m, 2H), 7.80 – 7.77 (m, 2H), 2.75 (s, 3H). [2]

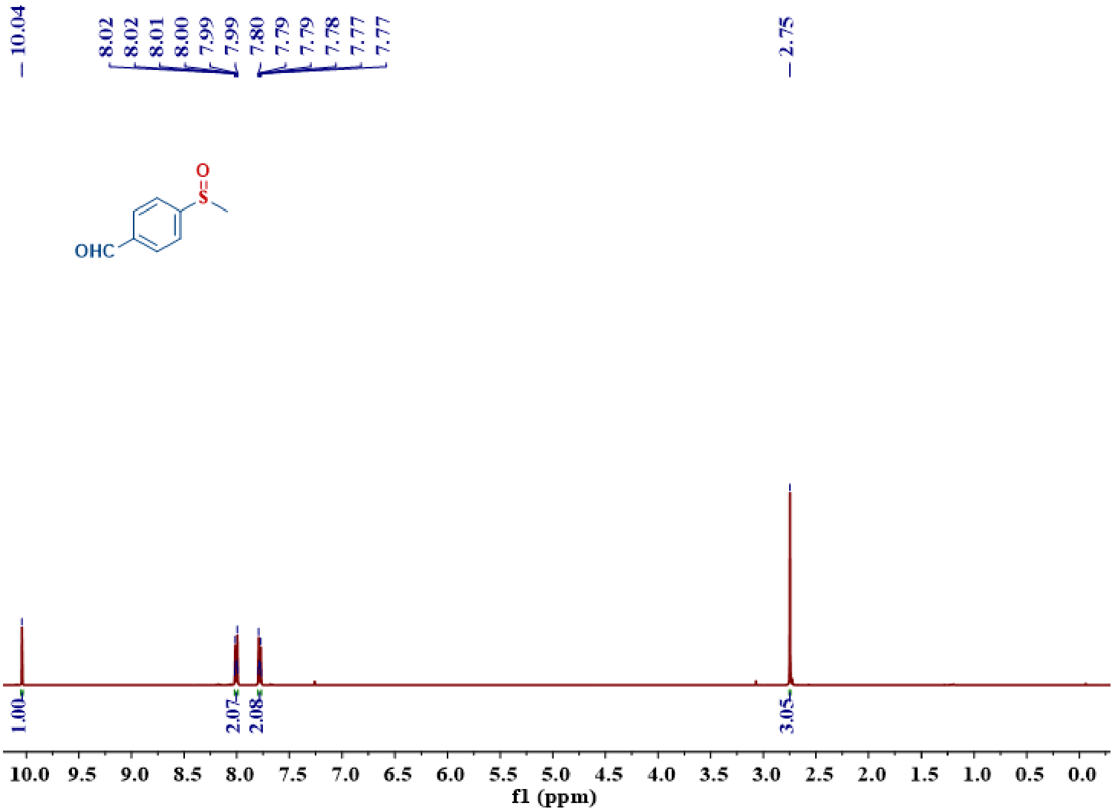
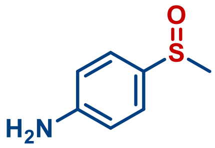


Fig. S19. ^{1}H NMR spectra of 4-(methylsulfinyl)benzaldehyde in $CDCl_3$.

2i 4-(methylsulfinyl)aniline



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=20:1) to give 2i as a colorless oil. (25.1 mg, 81% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.46 – 7.41 (m, 2H), 6.77 – 6.72 (m, 2H), 2.67 (s, 3H). [3]

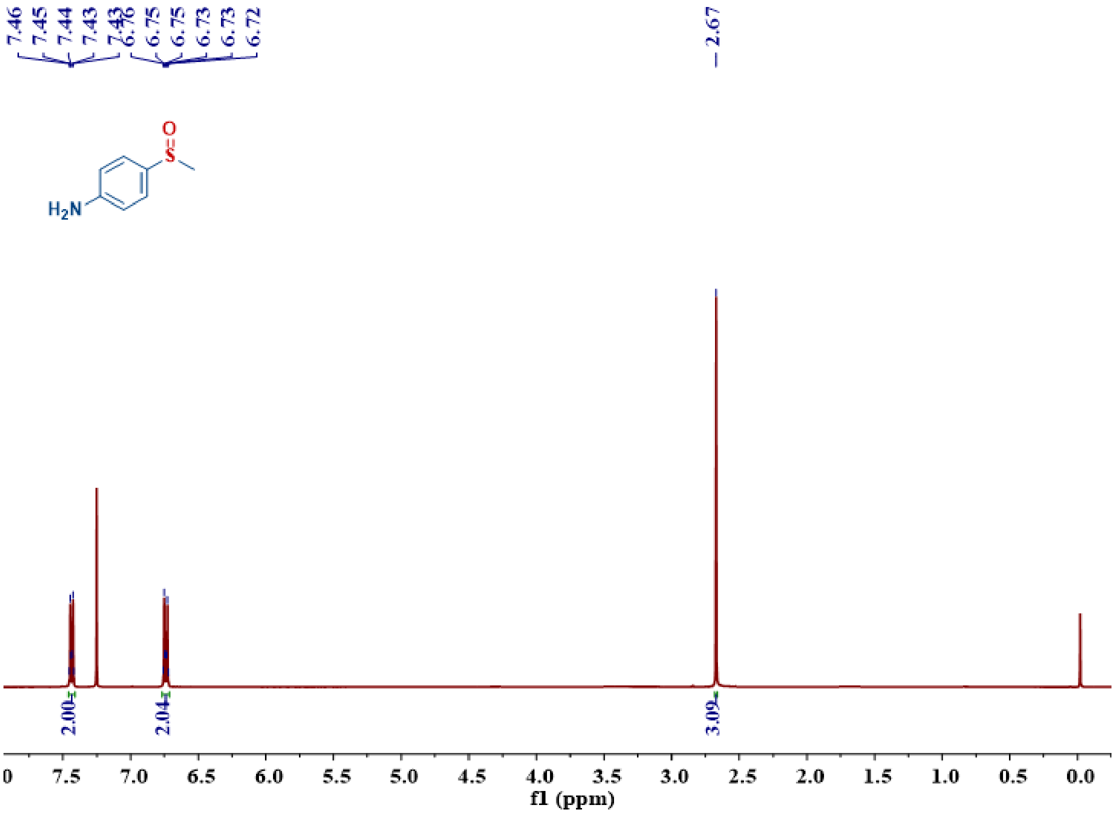
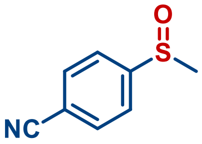


Fig. S20. ^{1}H NMR spectra of 4-(methylsulfinyl)aniline in CDCl$_3$.

2j 4-(methylsulfinyl)benzonitrile



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=20:1) to give 2j as a colorless oil. (28.4 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.77 (m, 2H), 7.76 – 7.71 (m, 2H), 2.73 (s, 3H). [2]

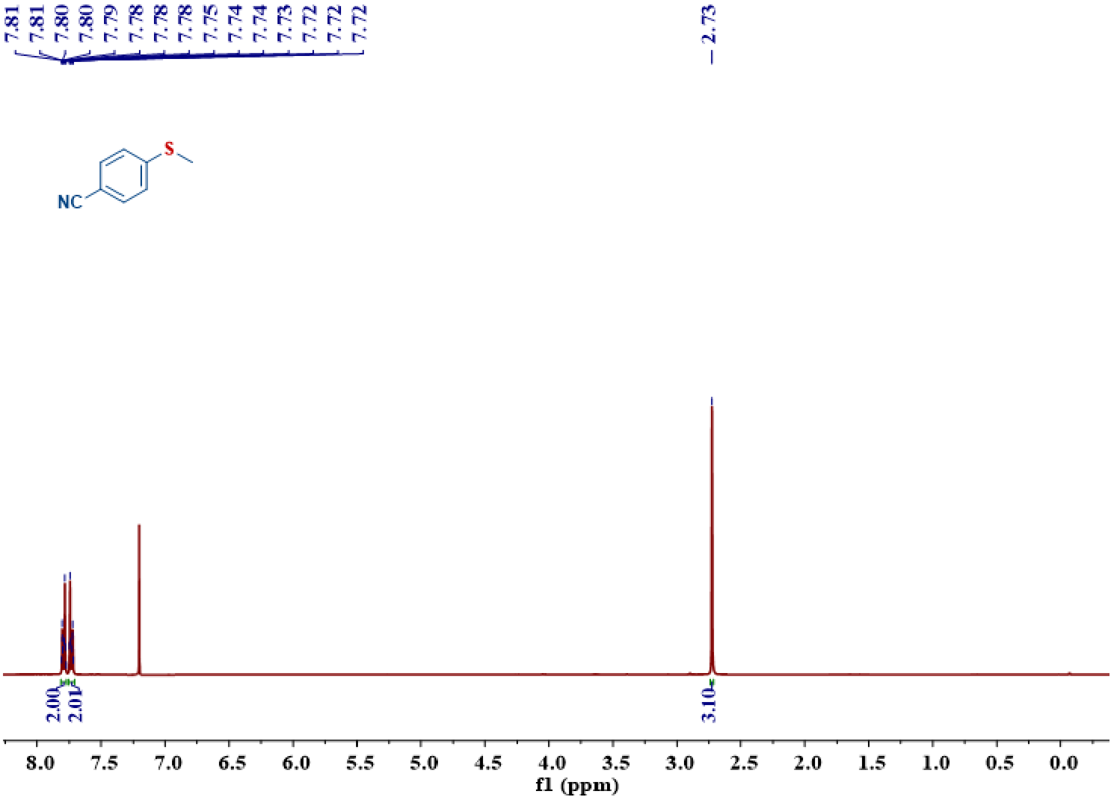
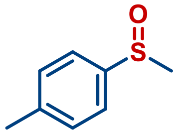


Fig. S21. ^{1}H NMR spectra of 4-(methylsulfinyl)benzonitrile in $CDCl_3$.

2k. 1-methyl-4-(methylsulfinyl)benzene



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=20:1) to give 2k as a colorless oil. (24.6 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.34 – 7.30 (m, 2H), 2.69 (s, 3H), 2.40 (s, 3H). [3]

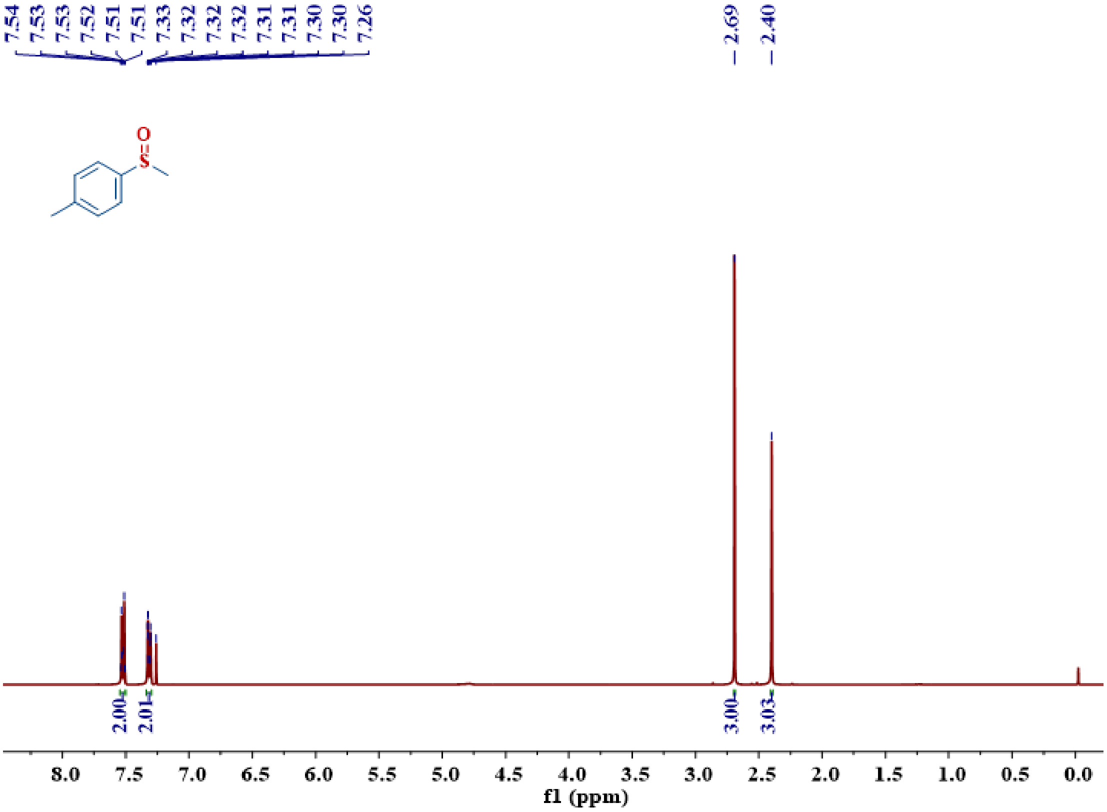
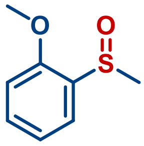


Fig. S22. ^{1}H NMR spectra of 1-methyl-4-(methylsulfinyl)benzene in $CDCl_3$.

2l. 1-methoxy-2-(methylsulfinyl)benzene



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=20:1) to give 2l as a colorless oil. (27.7 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.43 (ddd, *J* = 8.2, 7.4, 1.7 Hz, 1H), 7.17 (td, *J* = 7.6, 1.0 Hz, 1H), 6.90 (dd, *J* = 8.1, 1.0 Hz, 1H), 3.87 (s, 3H), 2.75 (s, 3H). [3]

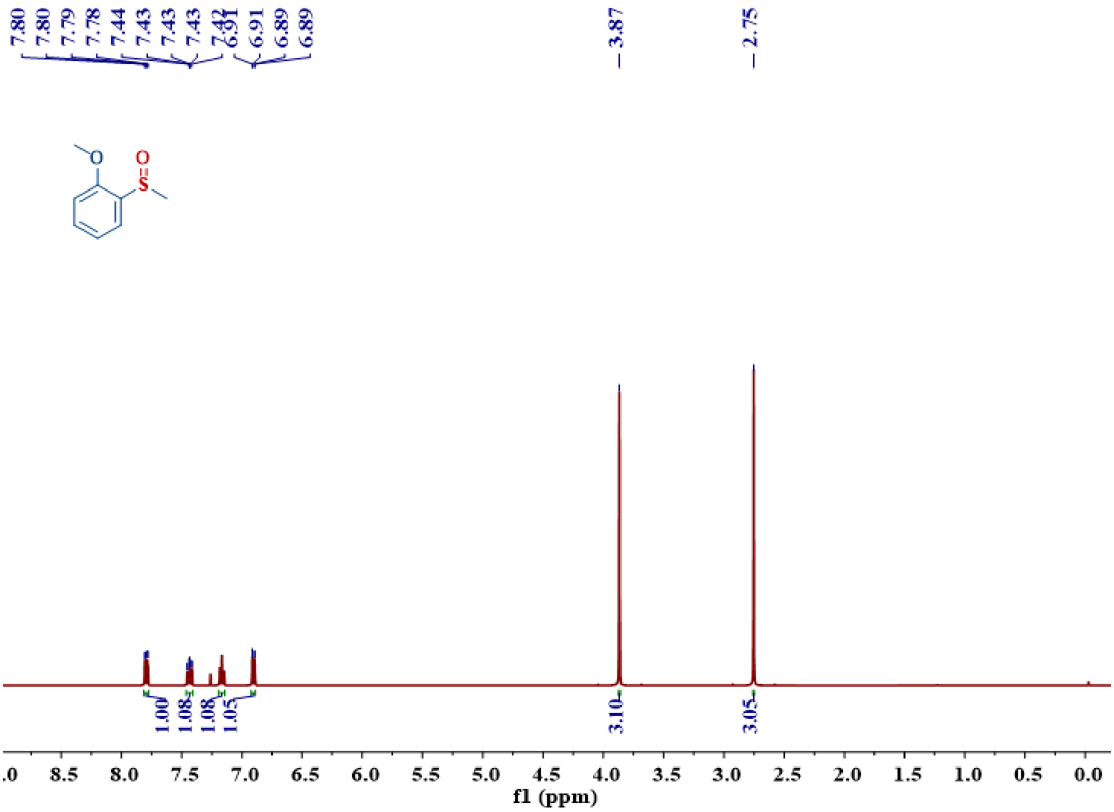
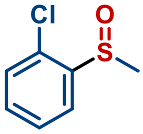


Fig. S23. ^{1}H NMR spectra of 1-methoxy-2-(methylsulfinyl)benzene in $CDCl_3$.

2m.1-chloro-2-(methylsulfinyl)benzene



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=20:1) to give 2m as a colorless oil. (31.4 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.46 (td, *J* = 7.5, 1.3 Hz, 1H), 7.41 – 7.28 (m, 2H), 2.76 – 2.74 (m, 3H). [2]

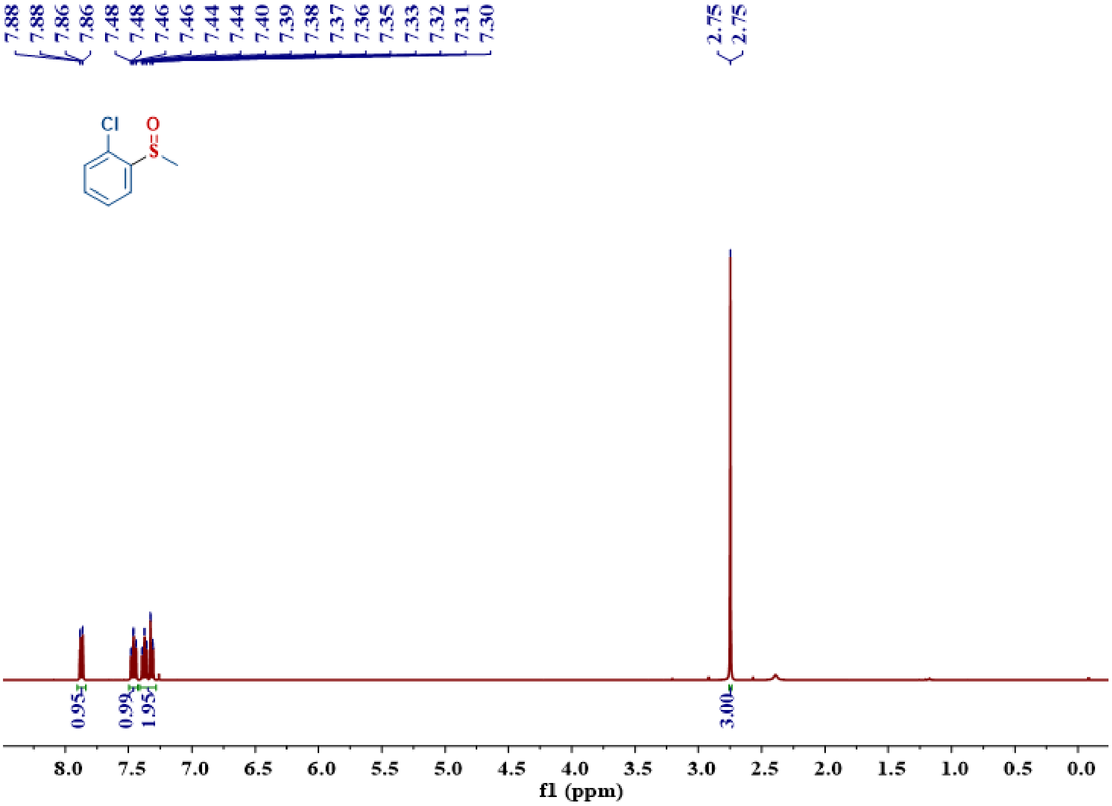
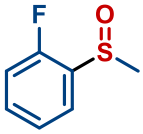


Fig. S24. ^{1}H NMR spectra of 1-chloro-2-(methylsulfinyl)benzene in $CDCl_3$.

2n. 1-fluoro-2-(methylsulfinyl)benzene



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=20:1) to give 2n as a colorless oil. (29.1 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.34 (ddd, *J* = 8.0, 7.3, 1.7 Hz, 1H), 2.78(s,3H).[2]

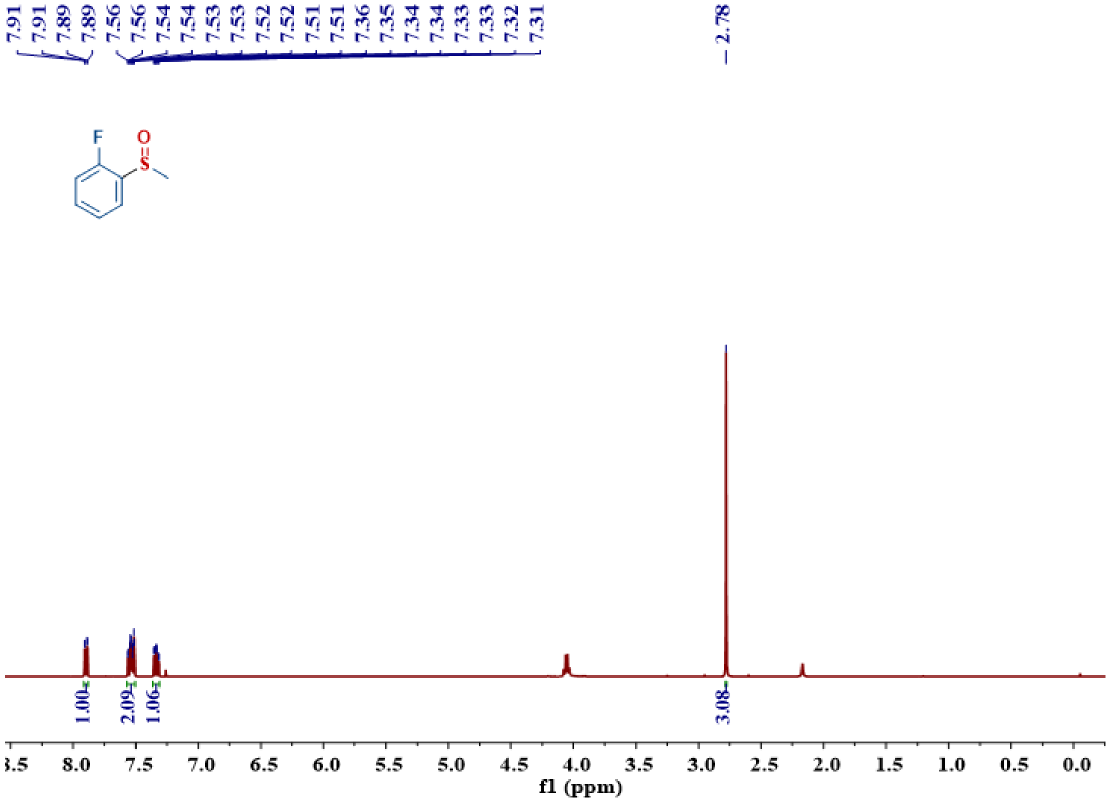
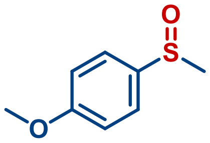


Fig. S25. ^{1}H NMR spectra of 1-fluoro-2-(methylsulfinyl)benzene in $CDCl_3$.

2o. 1-methoxy-4-(methylsulfinyl)benzene



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=20:1) to give 2o as a colorless oil. (28.5 mg, 83% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.61 – 7.56 (m, 2H), 7.05 – 7.00 (m, 2H), 3.84 (s, 3H), 2.69 (s, 3H). [2]

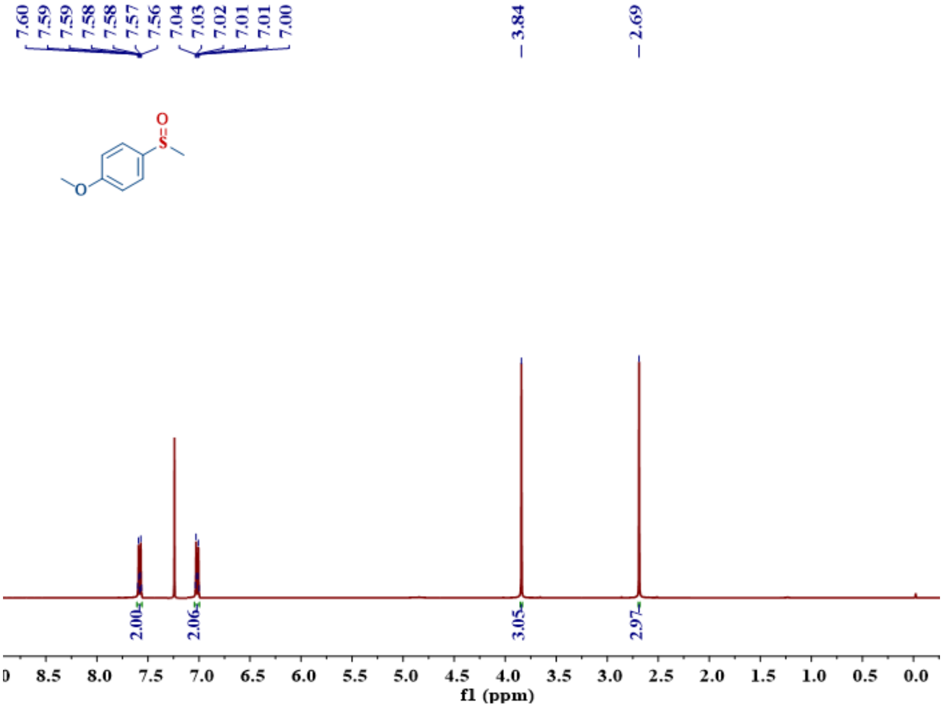
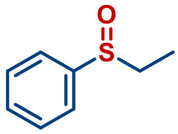


Fig. S26. ^{1}H NMR spectra of 1-methoxy-4-(methylsulfinyl)benzene in CDCl$_3$.

2p. (ethylsulfinyl)benzene



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=20:1) to give 2p as a colorless oil. (23.1 mg, 75% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.61 – 7.57 (m, 2H), 7.53 – 7.47 (m, 3H), 2.89 (dq, J = 13.3, 7.4 Hz, 1H), 2.76 (dq, J = 13.3, 7.4 Hz, 1H), 1.18 (t, J = 7.4 Hz, 3H). [3]

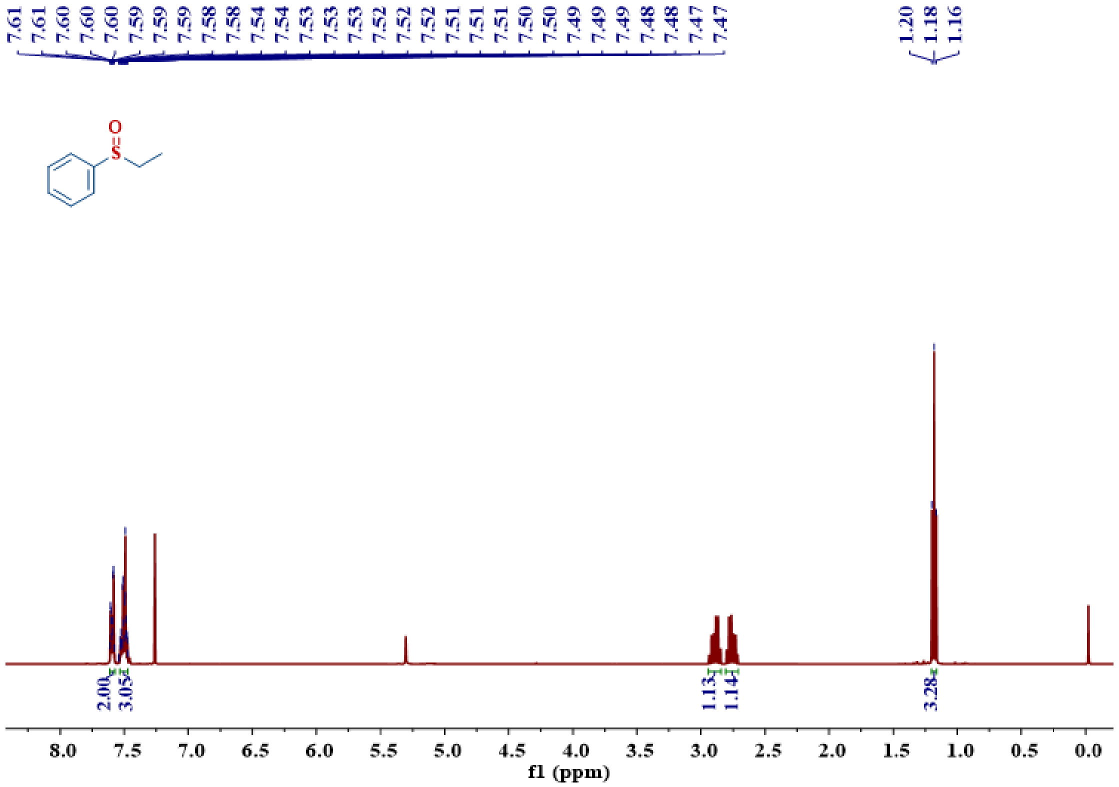
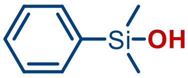


Fig. S27. ^{1}H NMR spectra of (ethylsulfinyl)benzene in CDCl$_3$.

^{1}H NMR data of 3b-3m

3b. dimethyl(phenyl)silanol



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=10:1) to give 3b as a colorless oil. (27.7 mg, 91% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.52 – 7.46 (m, 2H), 7.34 – 7.26 (m, 3H), 0.27 (s, 6H).[4]

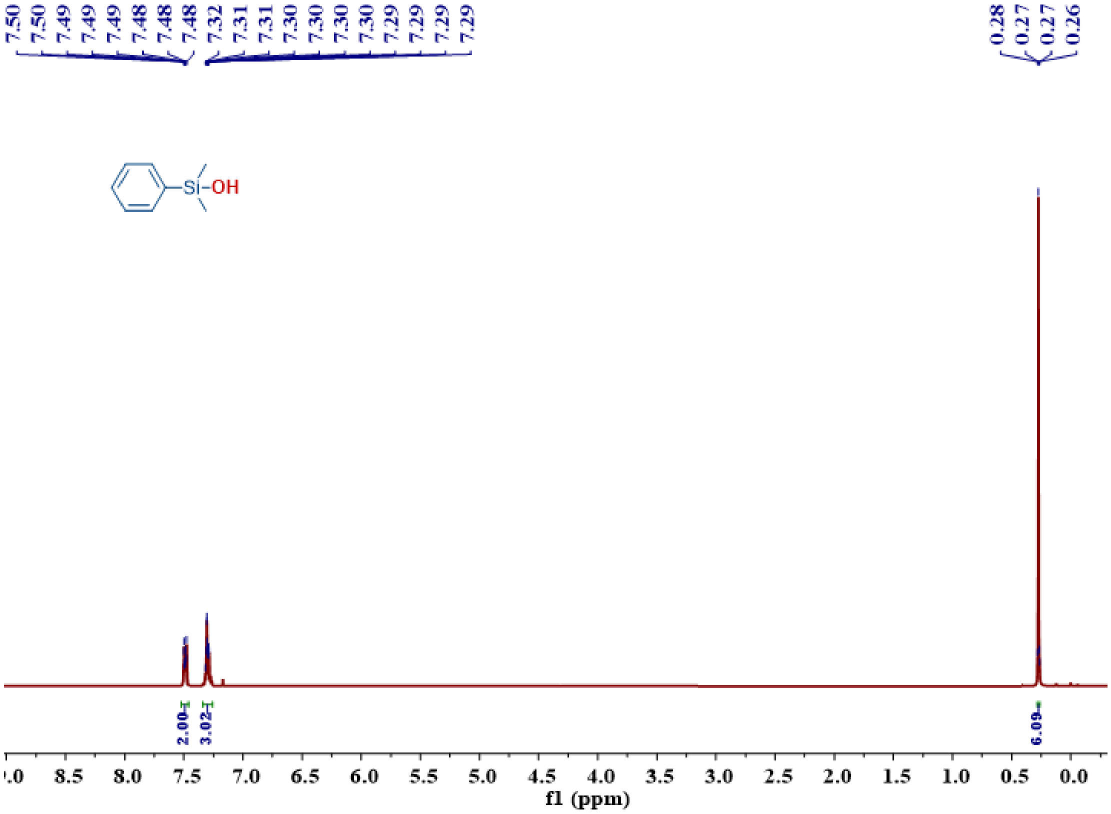
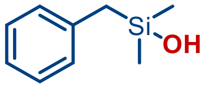


Fig. S28. ^{1}H NMR spectra of dimethyl(phenyl)silanol in CDCl$_3$.

3c. benzyldimethylsilanol



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=10:1) to give 3c as a colorless oil. (28.6 mg, 86% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 8.2, 6.9 Hz, 2H), 7.11 – 7.04 (m, 1H), 7.02 – 6.96 (m, 2H), 2.06 (s, 2H), -0.00 – -0.04 (m, 6H). [4]

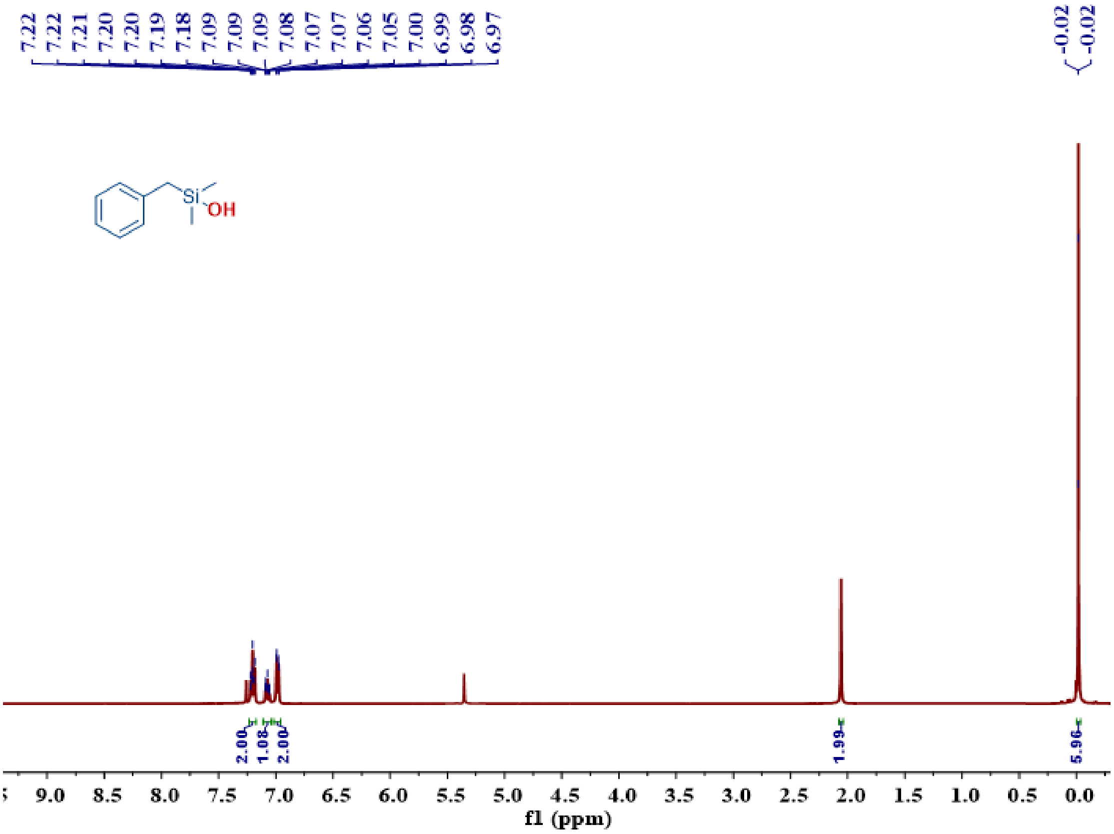
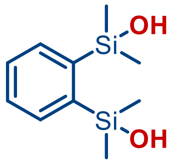


Fig. S29. ^{1}H NMR spectra of benzyldimethylsilanol in $CDCl_3$.

3d. 1,2-phenylenebis(dimethylsilanol)



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=10:1) to give 3d as a colorless oil. (32.5 mg, 72% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.59 (dd, *J* = 5.3, 3.1 Hz, 2H), 7.43 (dd, *J* = 5.4, 3.1 Hz, 2H), 0.38 (s, 12H). [5]

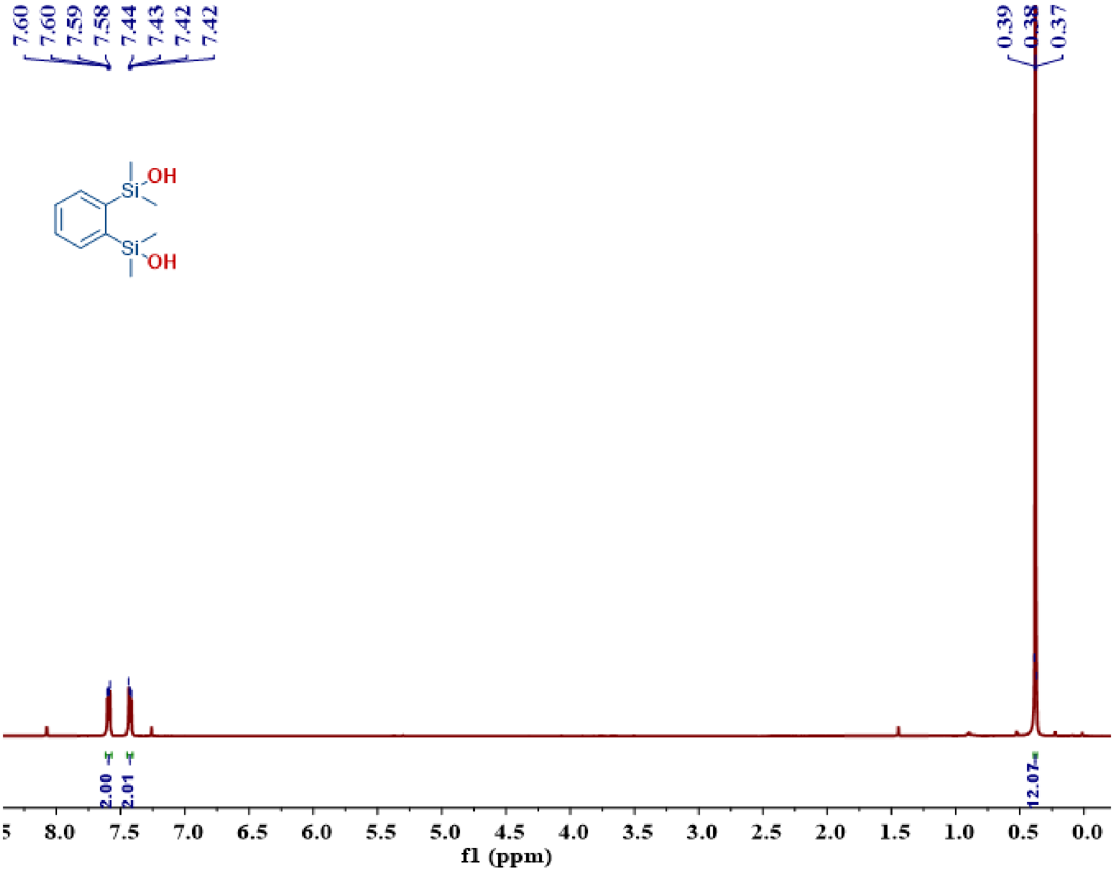
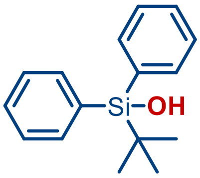


Fig. S30. ^{1}H NMR spectra of 1,2-phenylenebis(dimethylsilanol) in CDCl$_3$.

3e. tert-butyldiphenylsilanol



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=10:1) to give 3e as a colorless oil. (37.7 mg, 74% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.78 – 7.68 (m, 4H), 7.47 – 7.34 (m, 6H), 1.08 (s, 9H). [5]

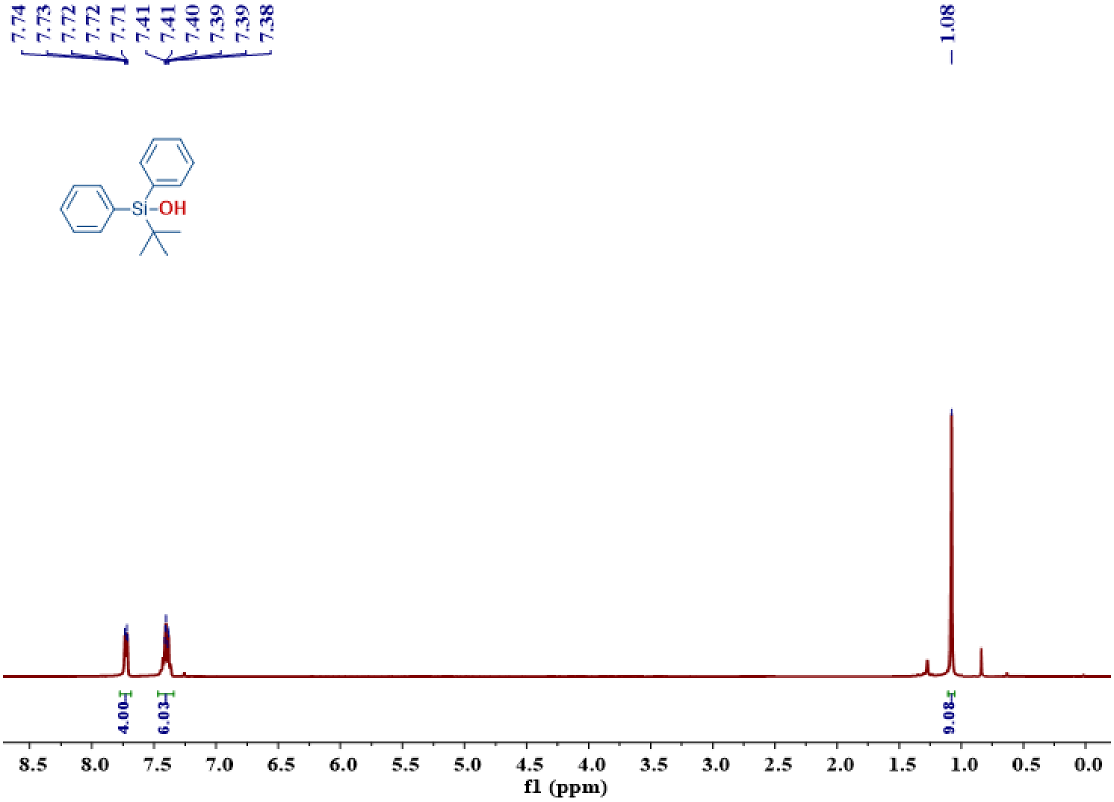
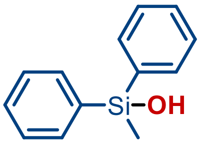


Fig. S31. ^{1}H NMR spectra of tert-butyldiphenylsilanol in CDCl$_3$.

3f. methyldiphenylsilanol



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=10:1) to give 3f as a colorless oil. (37.6 mg, 88% yield).^{1}H NMR (400 MHz, CDCl$_3$) δ 7.55 (dd, J = 7.5, 1.9 Hz, 4H), 7.39 – 7.32 (m, 6H), 0.62 (d, J = 3.8 Hz, 3H). [4]

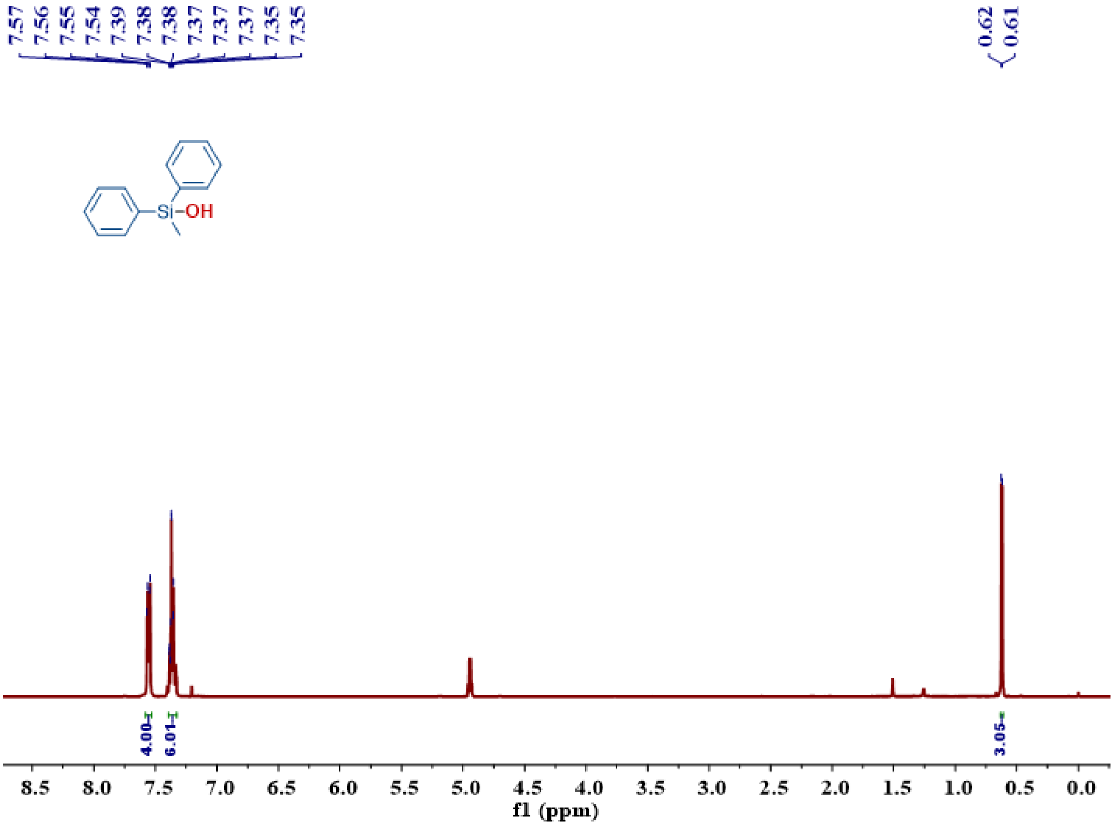
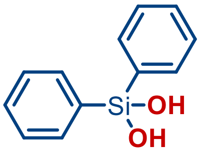


Fig. S32. ^{1}H NMR spectra of methyldiphenylsilanol in CDCl$_3$.

3g. diphenylsilanediol



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=10:1) to give 3g as a colorless oil. (34.6 mg, 80% yield) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.1 Hz, 4H), 7.44 – 7.32 (m, 6H). [4]

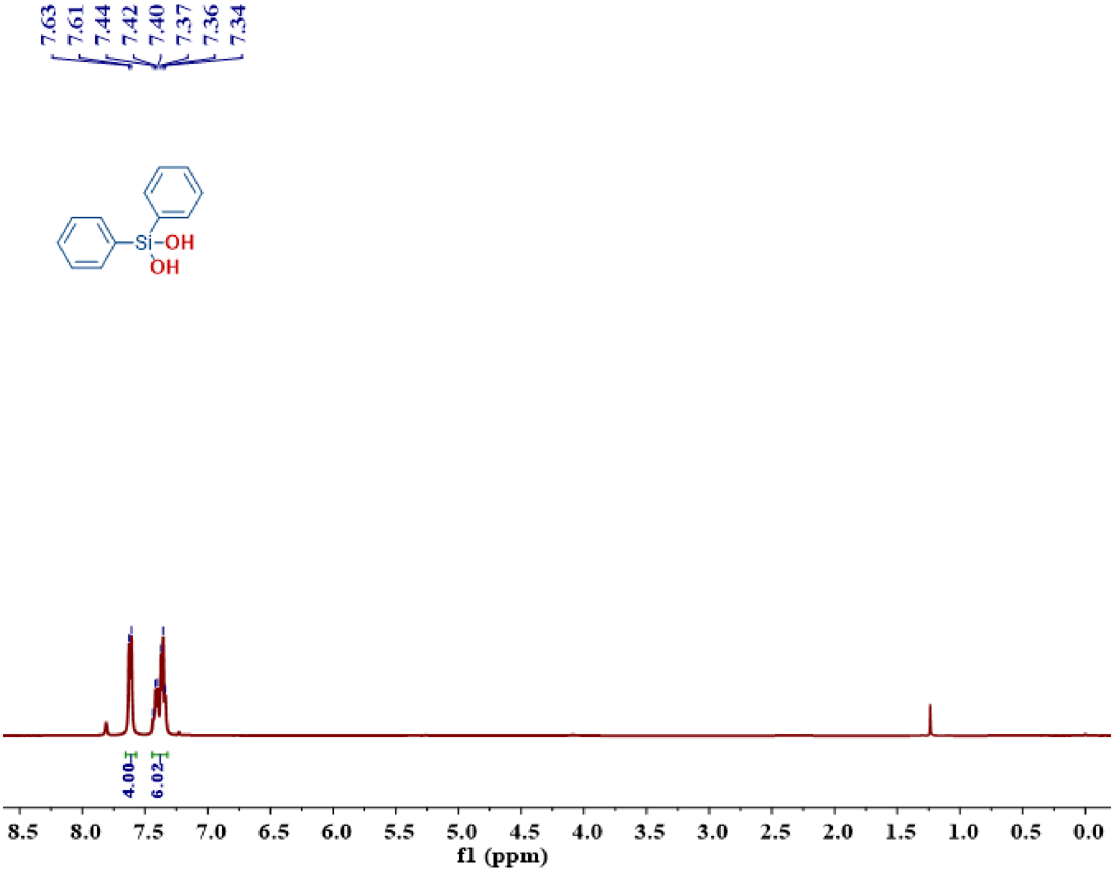
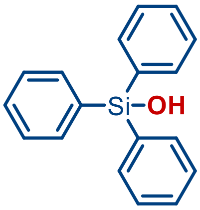


Fig. S33. ^{1}H NMR spectra of diphenylsilanediol in $CDCl_3$.

3h. triphenylsilanol



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=10:1) to give 3h as a colorless oil. (50.6 mg, 92% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.61 (ddt, *J* = 11.4, 6.6, 1.5 Hz, 6H), 7.45 – 7.39 (m, 3H), 7.37 – 7.30 (m, 6H). [4]

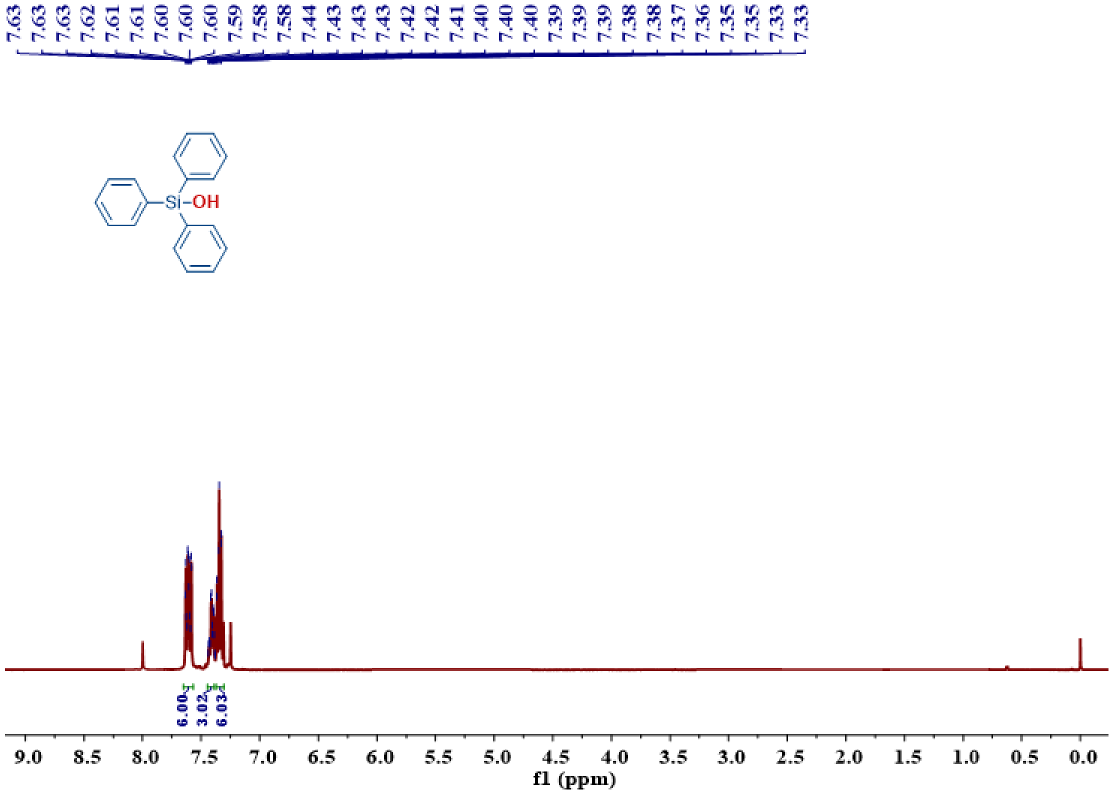
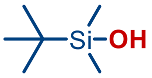


Fig. S34. ^{1}H NMR spectra of triphenylsilanol in CDCl$_3$.

3i. tert-butyldimethylsilanol



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=10:1) to give 3i as a colorless oil. (18.7 mg, 71% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (d, *J* = 1.0 Hz, 9H), -0.00 (s, 6H).[6]

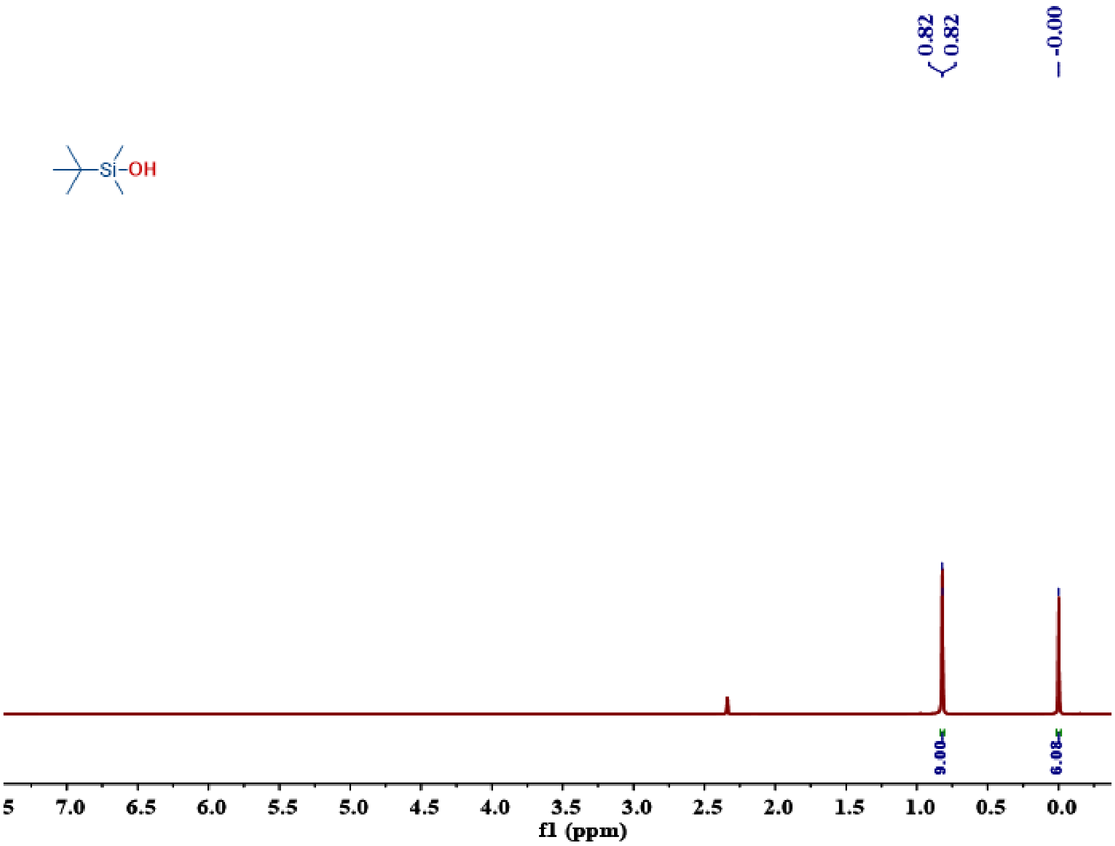


Fig. S35. ^{1}H NMR spectra of tert-butyldimethylsilanol in $CDCl_3$.

3j. 1,4-phenylenebis(dimethylsilanol)

Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=10:1) to give 3j as a colorless oil. (34.8 mg, 77% 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). [4]

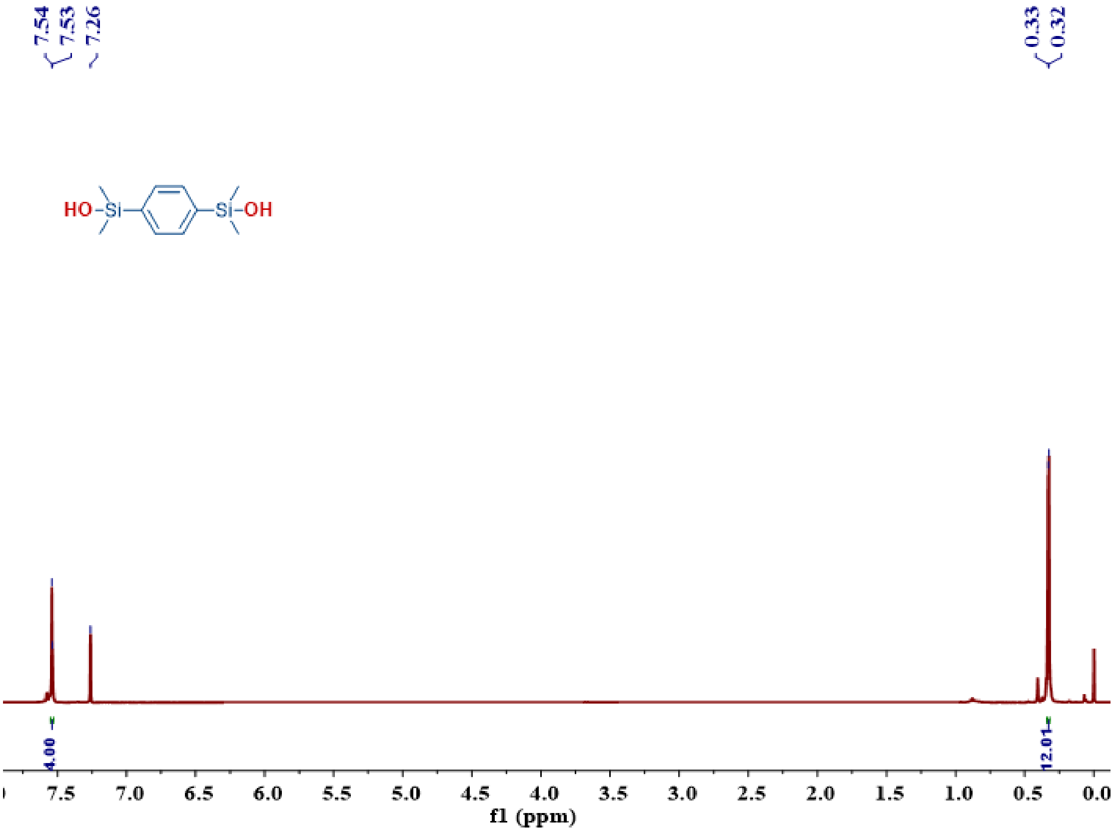
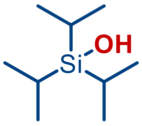


Fig. S36. ^{1}H NMR spectra of 1,4-phenylenebis(dimethylsilanol) in $CDCl_3$.

3k. triisopropylsilanol



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=10:1) to give 3k as a colorless oil. (25.1 mg, 72% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (dd, J = 8.2, 6.9 Hz, 2H), 7.11 – 7.04 (m, 1H), 7.02 – 6.96 (m, 2H), 2.06 (s, 2H), -0.00 – -0.04 (m, 6H). [4]

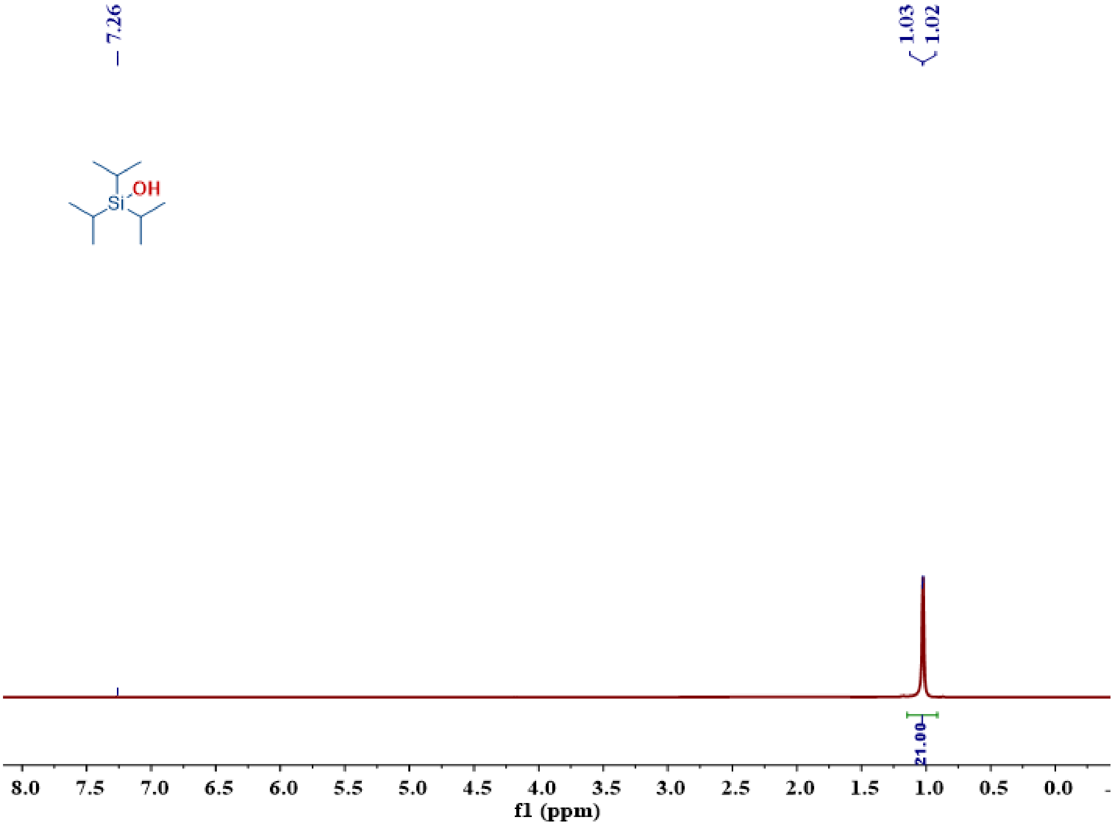
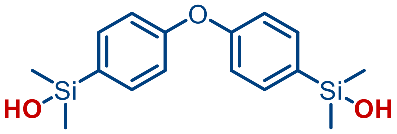


Fig. S37. ^{1}H NMR spectra of triisopropylsilanol in $CDCl_3$.

3l. 4,4'-Bis(dimethylhydroxysilyl)diphenylether



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=10:1) to give 3l as a colorless oil. (47.7 mg, 75% yield).^{1}H NMR (400 MHz, CDCl$_3$) δ 7.55 (d, *J* = 8.4 Hz, 4H), 7.02 (d, *J* = 8.4 Hz, 4H), 0.40 (s, 12H). [5]

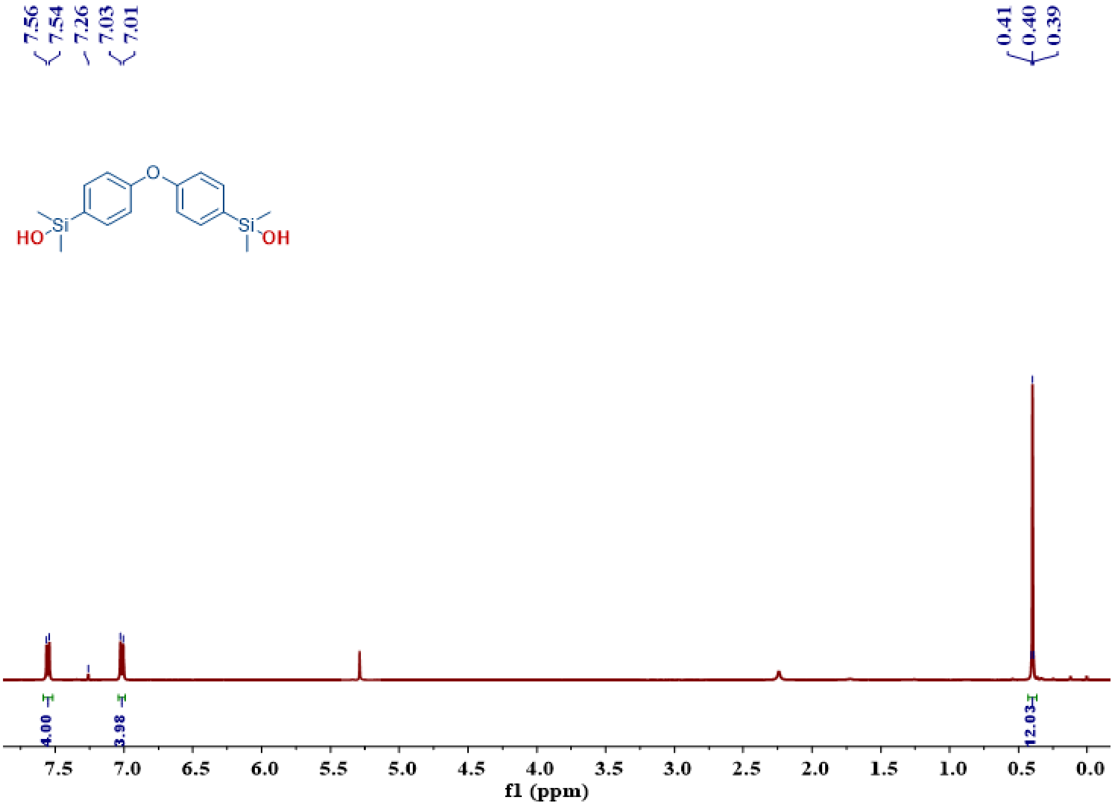
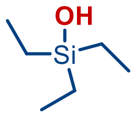


Fig. S38. ^{1}H NMR spectra of 4,4'-Bis(dimethylhydroxysilyl)diphenylether in CDCl$_3$.

3m. triethylsilanol



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=10:1) to give 3m as a colorless oil. (20.6 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, *J* = 8.0 Hz, 9H), 0.56 (q, *J* = 8.0 Hz, 6H). [4]

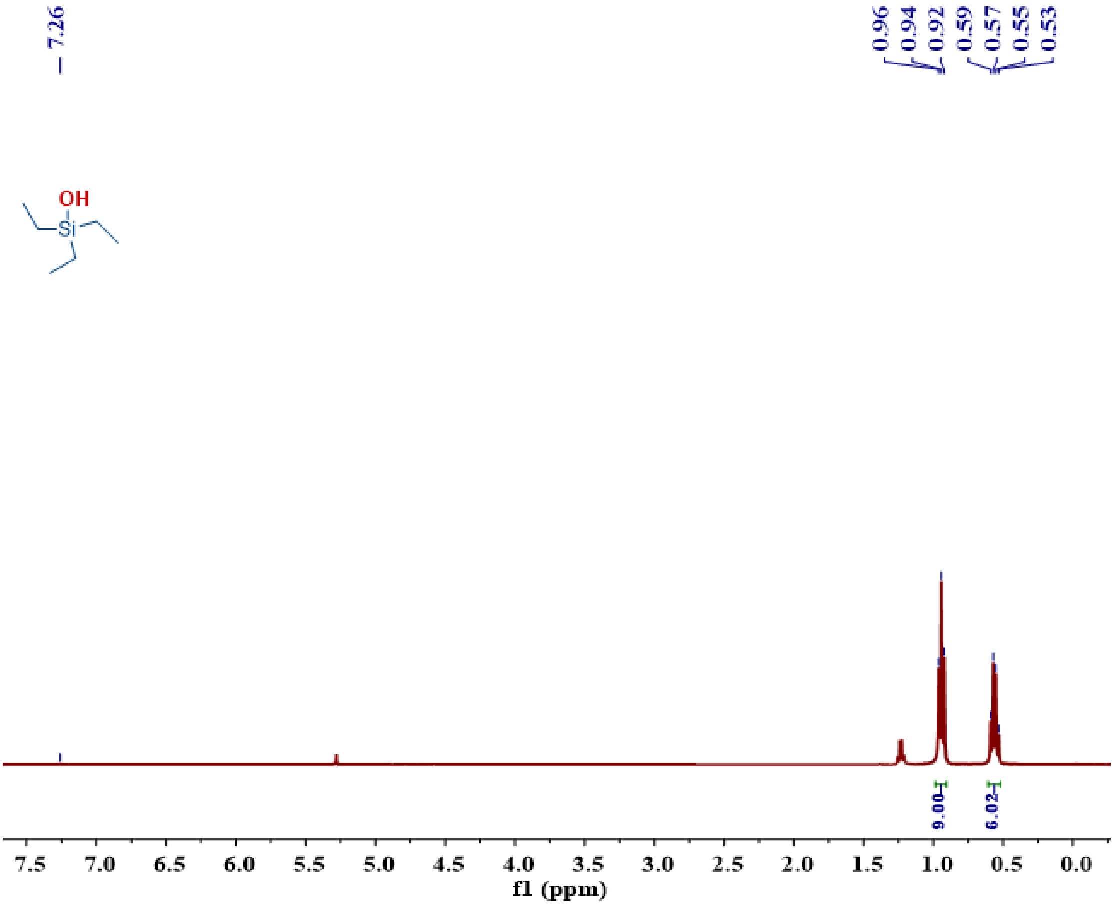
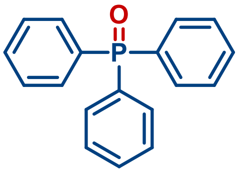


Fig. S39. ^{1}H NMR spectra of triethylsilanol in $CDCl_3$.

^{1}H NMR data of 4b-4p

4b. triphenylphosphine oxide



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=1:1) to give 4b as a colorless oil. (48.3 mg, 87% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.62 (m, 6H), 7.57 – 7.42 (m, 9H).[7]

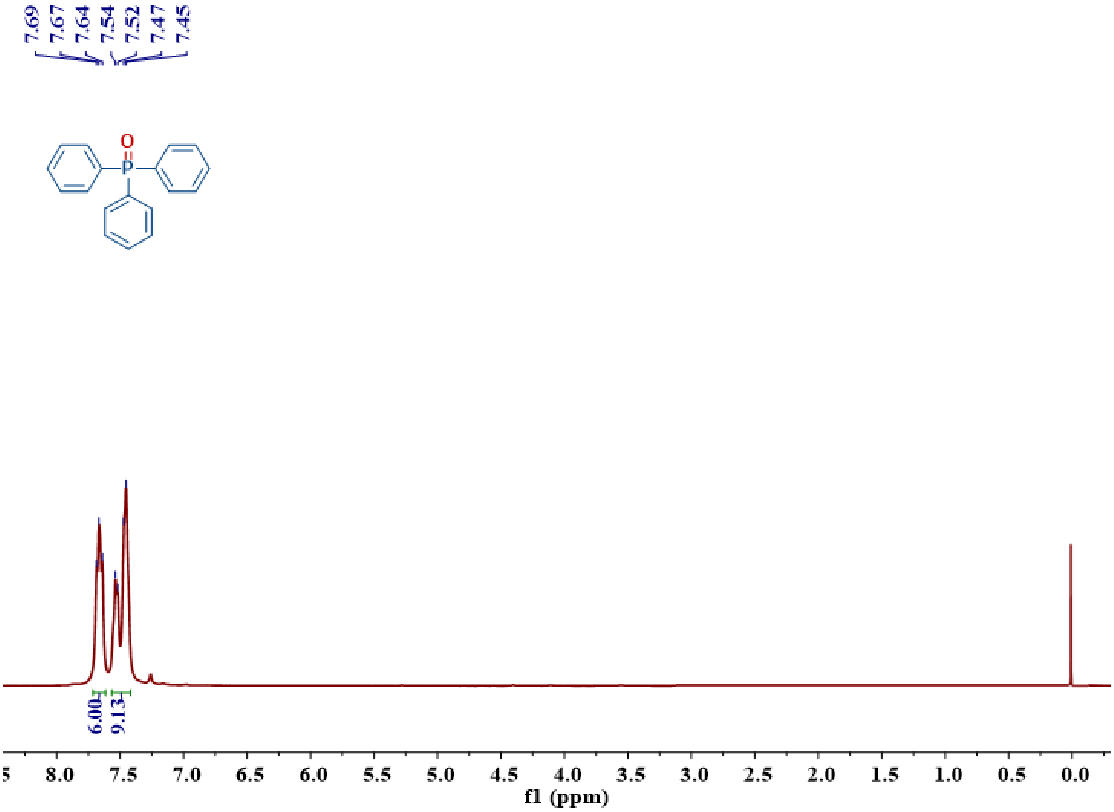
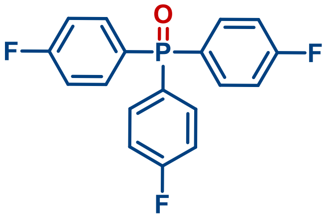


Fig. S40. ^{1}H NMR spectra of triphenylphosphine oxide in $CDCl_3$.

4c. tris(4-fluorophenyl)phosphine oxide



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=1:1) to give 4c as a colorless oil. (60.4 mg, 91% yield).^{1}H NMR (400 MHz, CDCl$_3$ δ 7.63 (ddd, *J* = 11.7, 8.6, 5.6 Hz, 6H), 7.16 (td, *J* = 8.7, 2.2 Hz, 6H). [7]

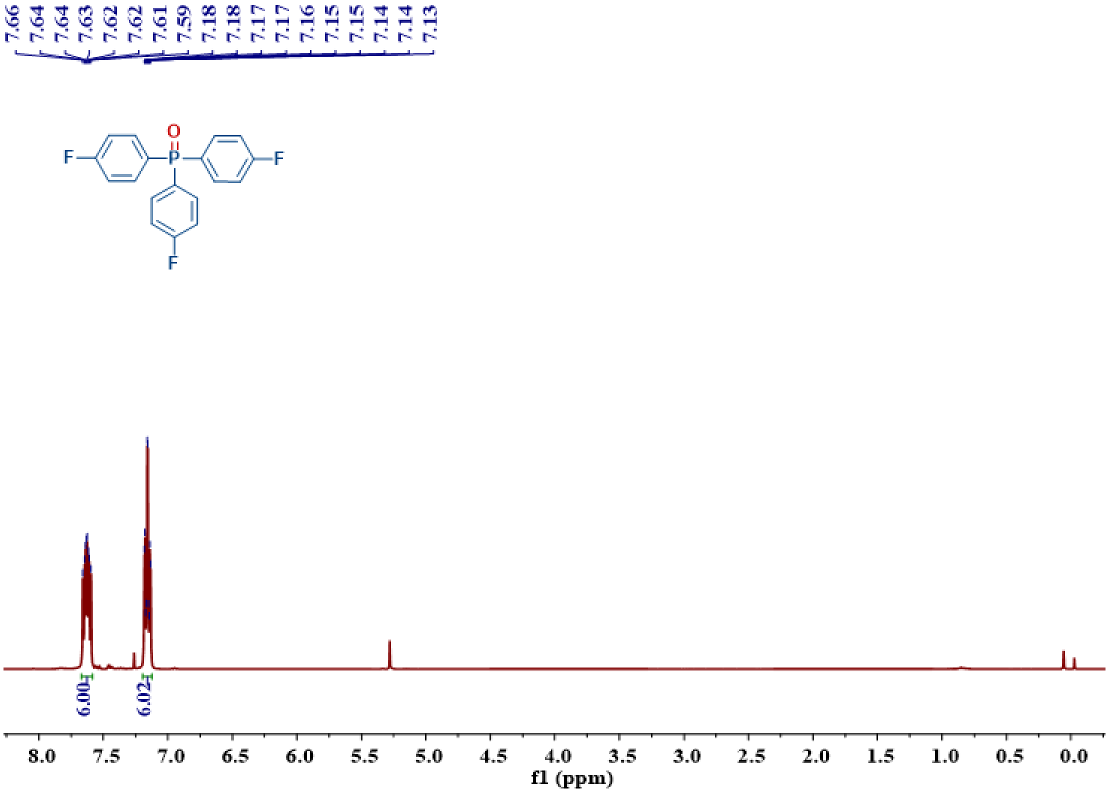
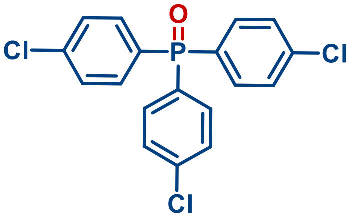


Fig. S41. ^{1}H NMR spectra of tris(4-fluorophenyl)phosphine oxide in CDCl$_3$.

4d. tris(4-chlorophenyl)phosphine oxide



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=1:1) to give 4d as a colorless oil. (68.2 mg, 90% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 6H), 7.47 – 7.43 (m, 6H). [8]

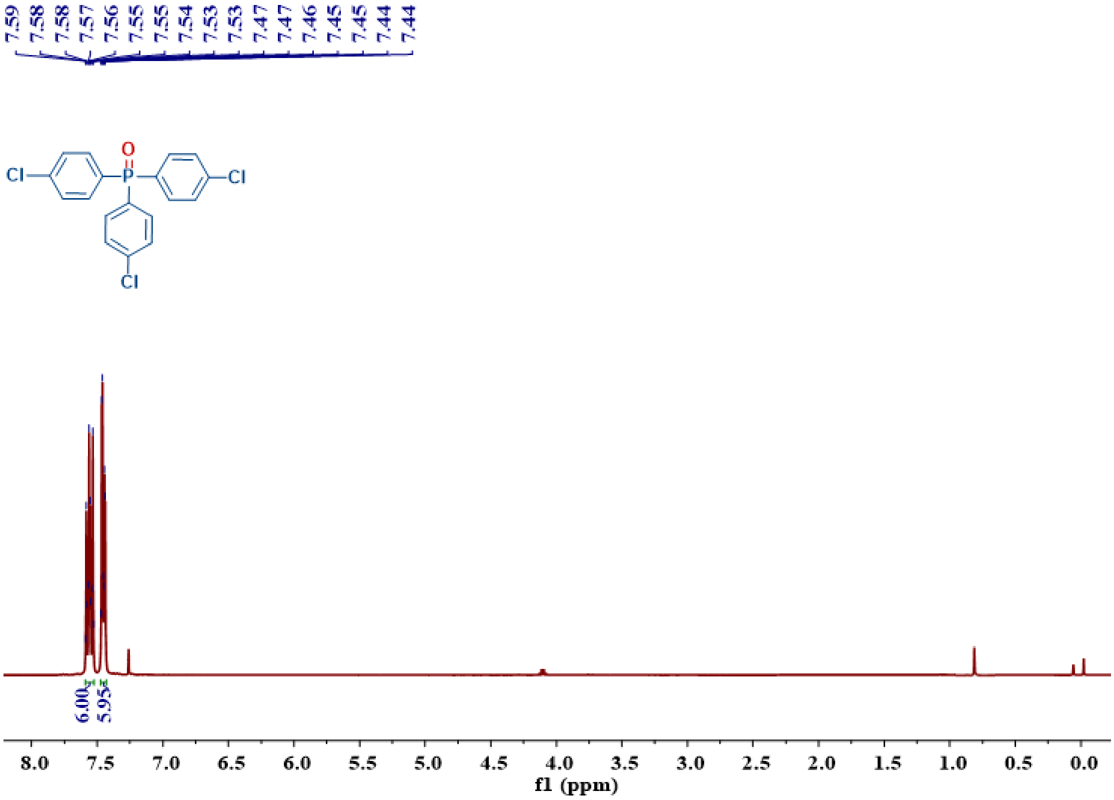
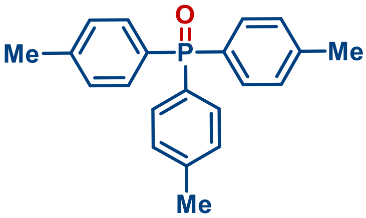


Fig. S42. ^{1}H NMR spectra of tris(4-chlorophenyl)phosphine oxide oxide in $CDCl_3$.

4e. tri-p-tolylphosphine oxide



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=1:1) to give 4e as a colorless oil. (53.7 mg, 84% yield).^{1}H NMR (400 MHz, CDCl$_3$) δ 7.54 (dd, J = 11.8, 8.0 Hz, 6H), 7.25 (dd, J = 8.1, 2.6 Hz, 6H), 2.39 (s, 9H). [7]

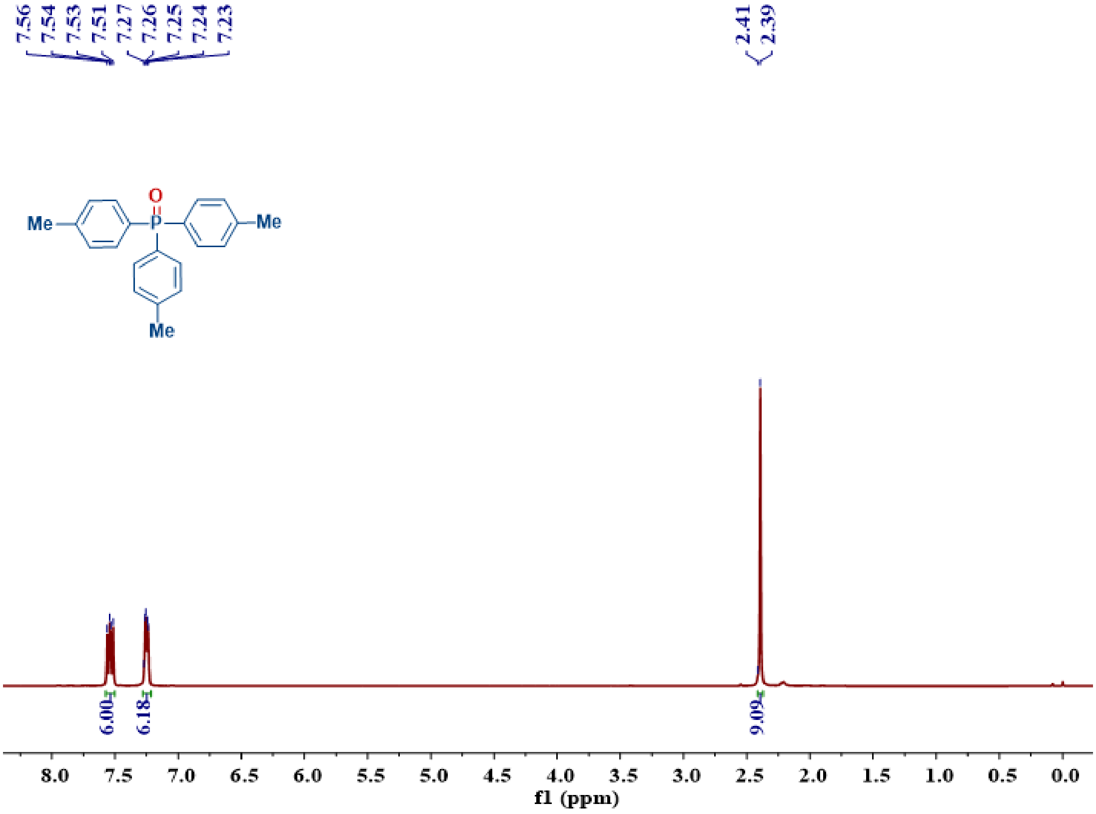
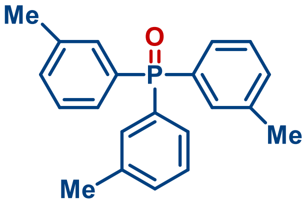


Fig. S43. ^{1}H NMR spectra of tri-p-tolylphosphine oxide in CDCl$_3$.

4f. tri-m-tolylphosphine oxide



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=1:1) to give 4f as a colorless oil. (48.6 mg, 76% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (td, J = 7.5, 6.9, 3.6 Hz, 3H), 7.32 – 7.24 (m, 3H), 7.13 (dd, J = 11.0, 8.2 Hz, 3H), 7.07 (d, J = 8.1 Hz, 3H), 3.79 (d, J = 1.5 Hz, 9H). [7]

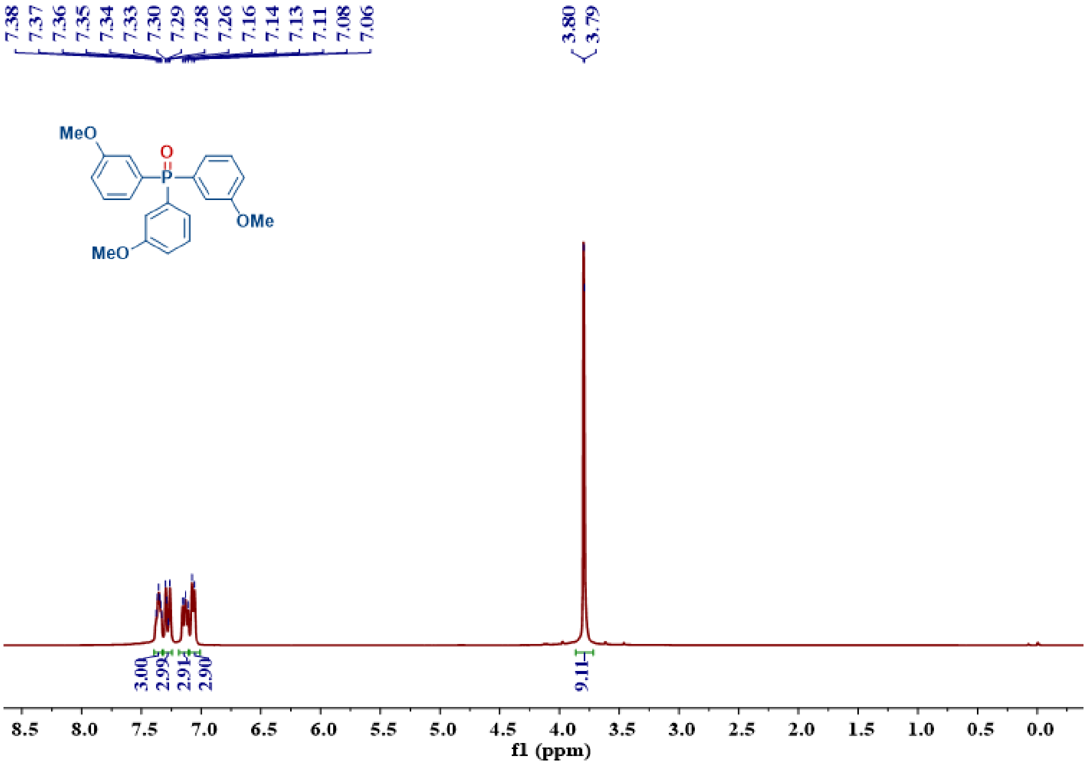
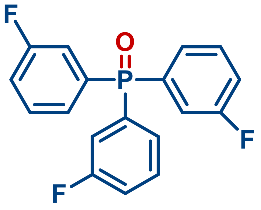


Fig. S44. ^{1}H NMR spectra of tri-m-tolylphosphine oxide in $CDCl_3$.

4g. tris(3-fluorophenyl)phosphine oxide



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=1:1) to give 4g as a colorless oil. (56.4 mg, 85% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 6H), 7.24 – 7.06 (m, 6H). [7]

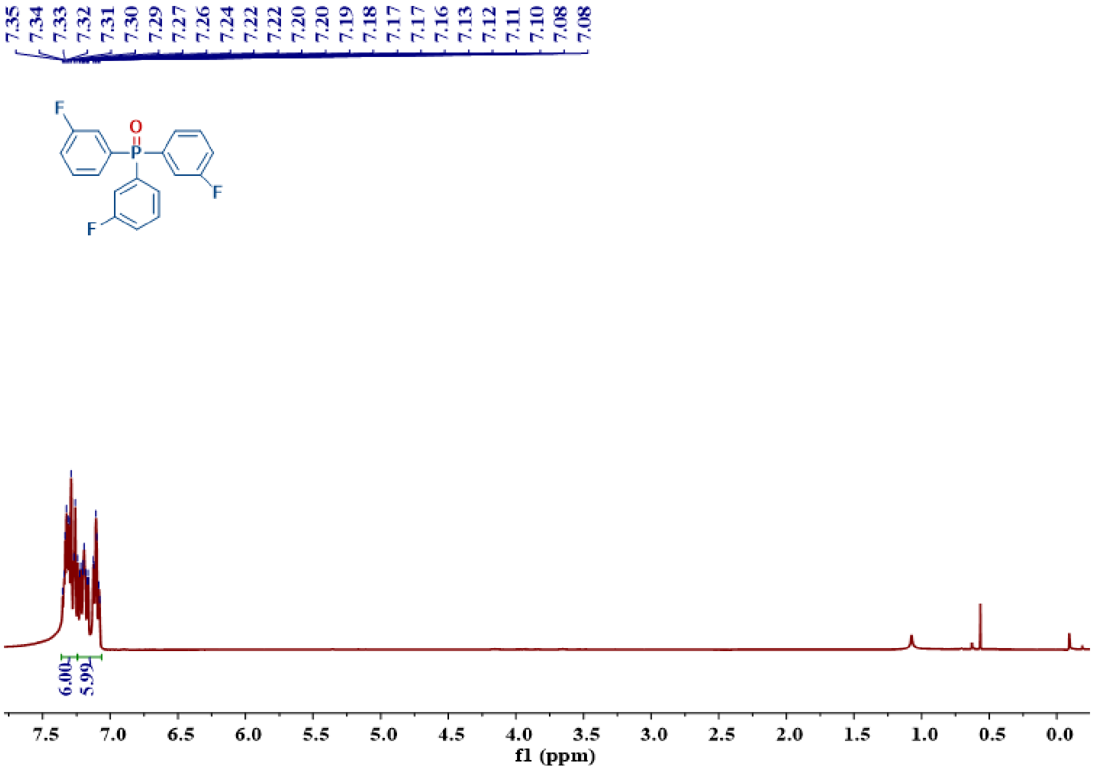
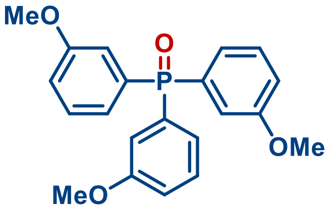


Fig. S45. ^{1}H NMR spectra of tris(3-fluorophenyl)phosphine oxide in $CDCl_3$.

4h. tris(3-methoxyphenyl)phosphine oxide



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=1:1) to give 4j as a colorless oil. (60.4 mg, 72% yield).^{1}H NMR (400 MHz, CDCl$_3$) δ 7.57 (d, J = 12.4 Hz, 3H), 7.39 – 7.34 (m, 3H), 7.33 – 7.28 (m, 6H), 2.35 (s, 9H). [7]

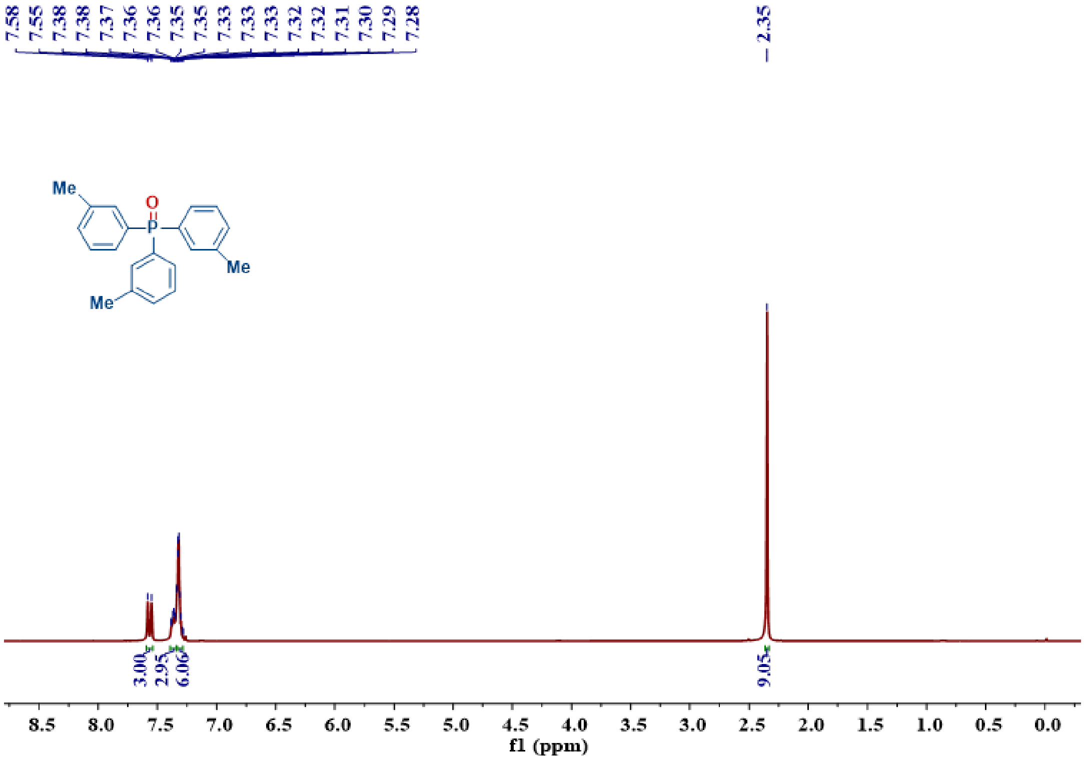
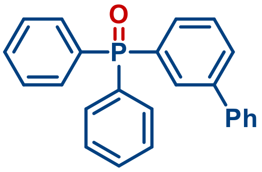


Fig. S46. ^{1}H NMR spectra of tris(3-methoxyphenyl)phosphine oxide in CDCl$_3$.

4i. [1,1'-biphenyl]-3-yldiphenylphosphine oxide



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=1:1) to give 4k as a colorless oil. (59.4 mg, 84% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dt, J = 13.9, 6.8 Hz, 5H), 7.46 – 7.28 (m, 9H), 7.24 – 7.17 (m, 2H), 7.08 – 7.00 (m, 3H). [8]

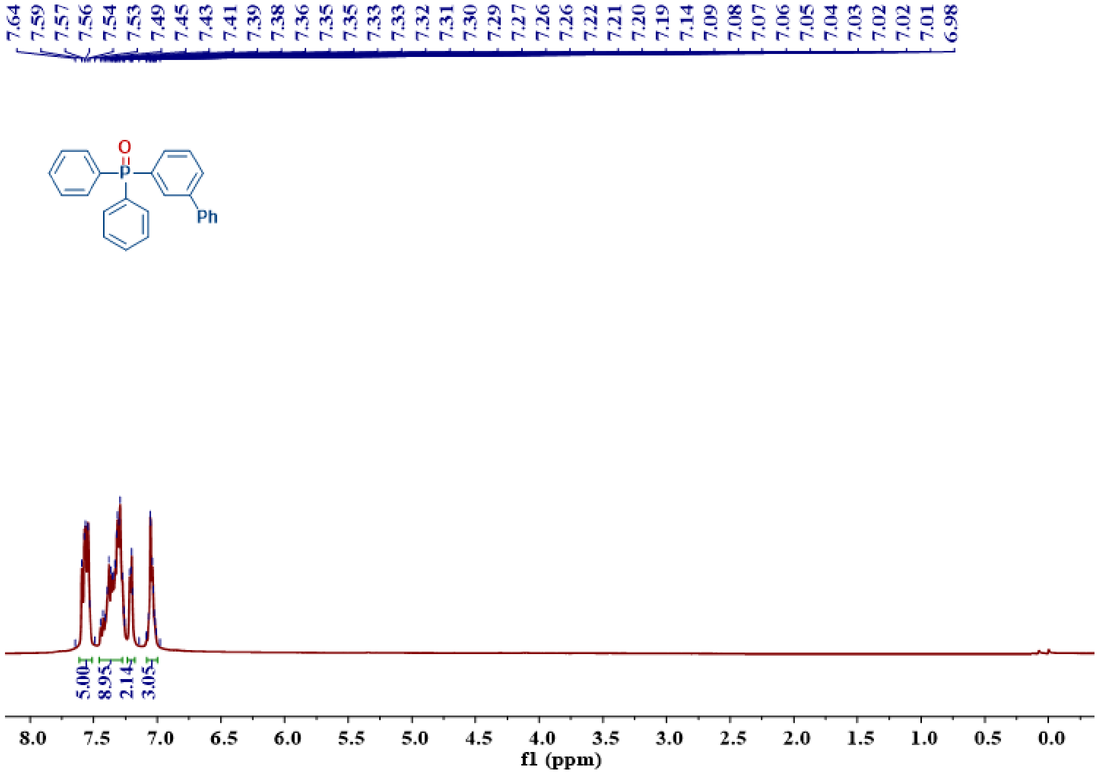
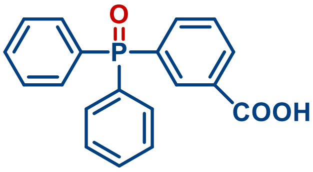


Fig. S47. ^{1}H NMR spectra of [1,1'-biphenyl]-3-yldiphenylphosphine oxide in $CDCl_3$.

4j. 3-(diphenylphosphoryl)benzoic acid



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=1:1) to give 4h as a colorless oil. (56.5 mg, 88% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.40 (s, 6H), 7.21 – 7.09 (m, 6H), 6.90 (dd, J = 14.4, 7.6 Hz, 1H). [7]

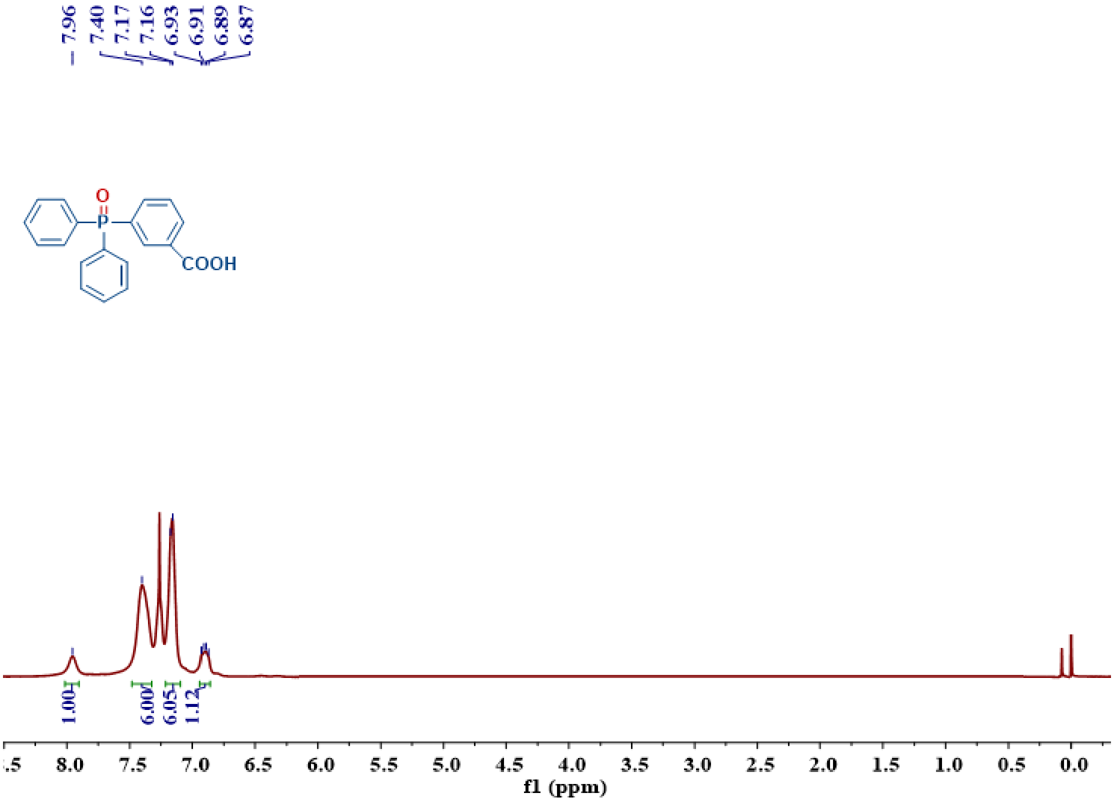
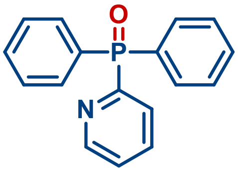


Fig. S48. ^{1}H NMR spectra of 3-(diphenylphosphoryl)benzoic acid in $CDCl_3$.

4k. diphenyl(pyridin-2-yl)phosphine oxide



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=1:1) to give 4i as a colorless oil. (44.6 mg, 80% yield).^{1}H NMR (400 MHz, $CDCl_3$ δ 7.63 (ddd, J = 11.7, 8.6, 5.6 Hz, 6H), 7.16 (td, J = 8.7, 2.2 Hz, 6H). [7]

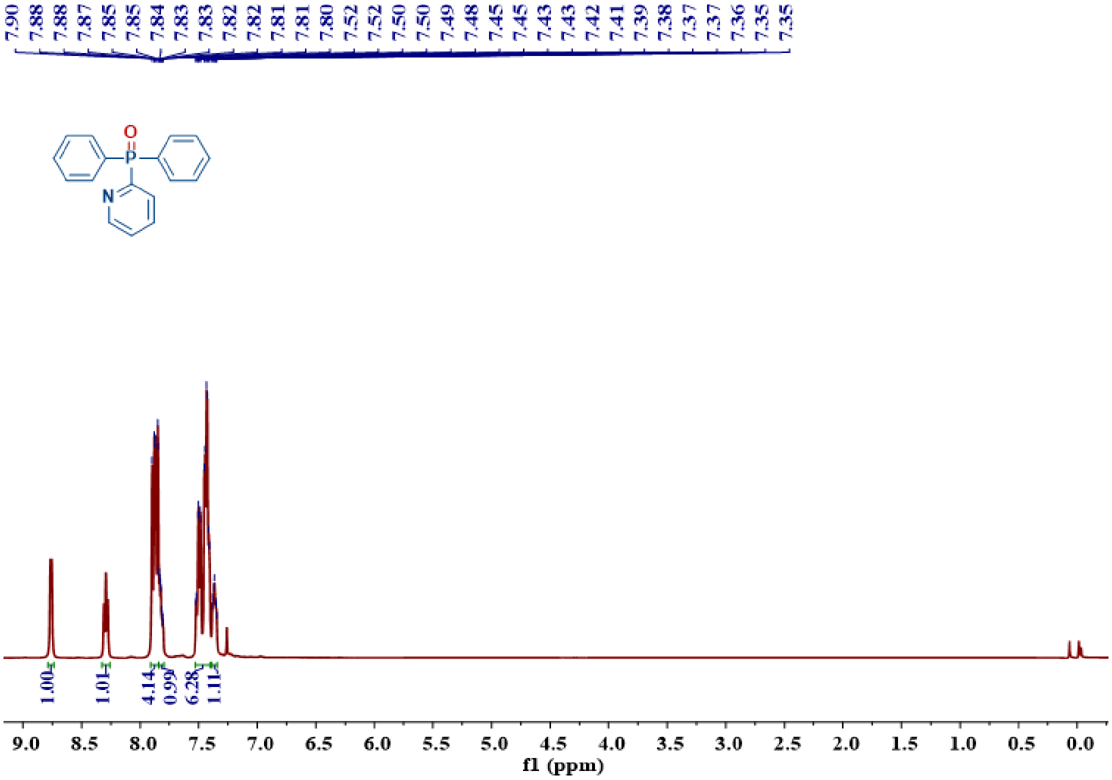
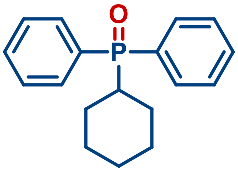


Fig. S49. ^{1}H NMR spectra of diphenyl(pyridin-2-yl)phosphine oxide in $CDCl_3$.

4l. cyclohexyldiphenylphosphine oxide



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=1:1) to give 4l as a colorless oil. (47.1 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (ddt, J = 10.9, 6.3, 1.7 Hz, 4H), 7.52 – 7.43 (m, 6H), 2.24 (tdt, J = 12.4, 6.3, 3.1 Hz, 1H), 1.83 – 1.67 (m, 5H), 1.55 (dq, J = 12.3, 6.5, 5.0 Hz, 2H), 1.31 – 1.21 (m, 3H).[8]

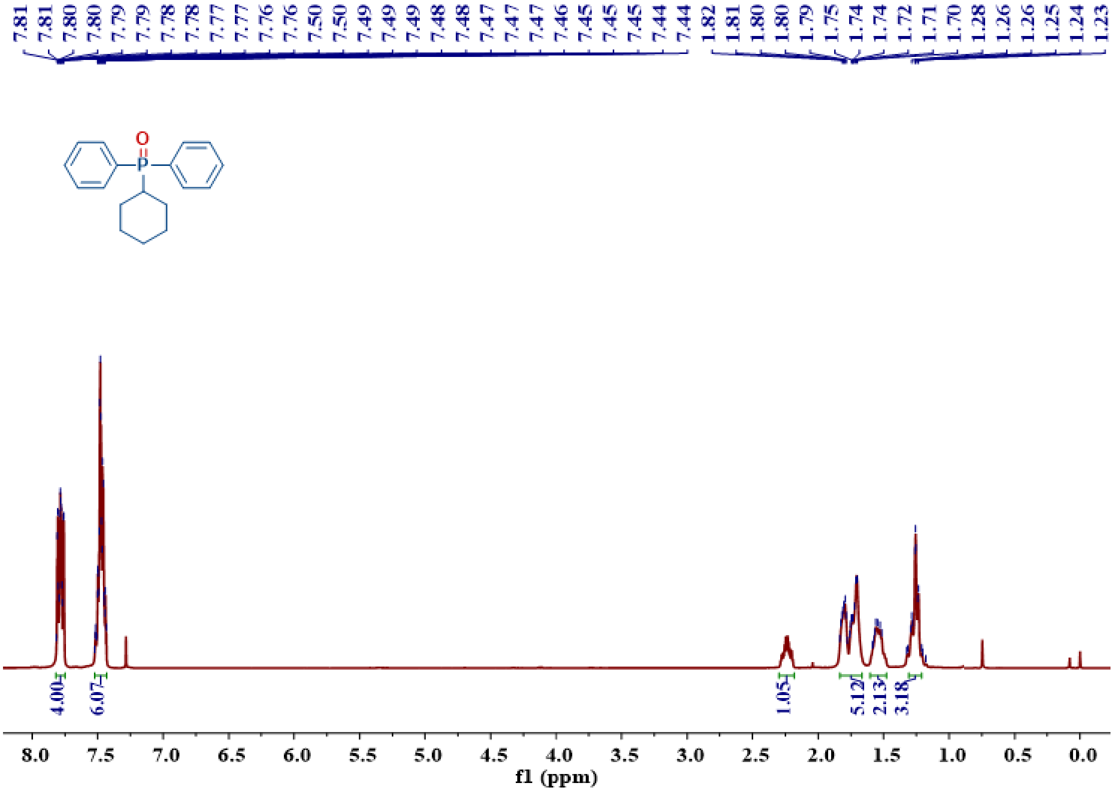
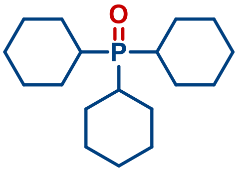


Fig. S50. ^{1}H NMR spectra of cyclohexyldiphenylphosphine oxide in $CDCl_3$.

4m. tricyclohexylphosphine oxide



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=1:1) to give 4m as a colorless oil. (42.1 mg, 76% yield).^{1}H NMR (400 MHz, $CDCl_3$ $CDCl_3$) δ 1.98 – 1.75 (m, 15H), 1.70 (d, J = 5.6 Hz, 3H), 1.47 – 1.15 (m, 15H).[8]

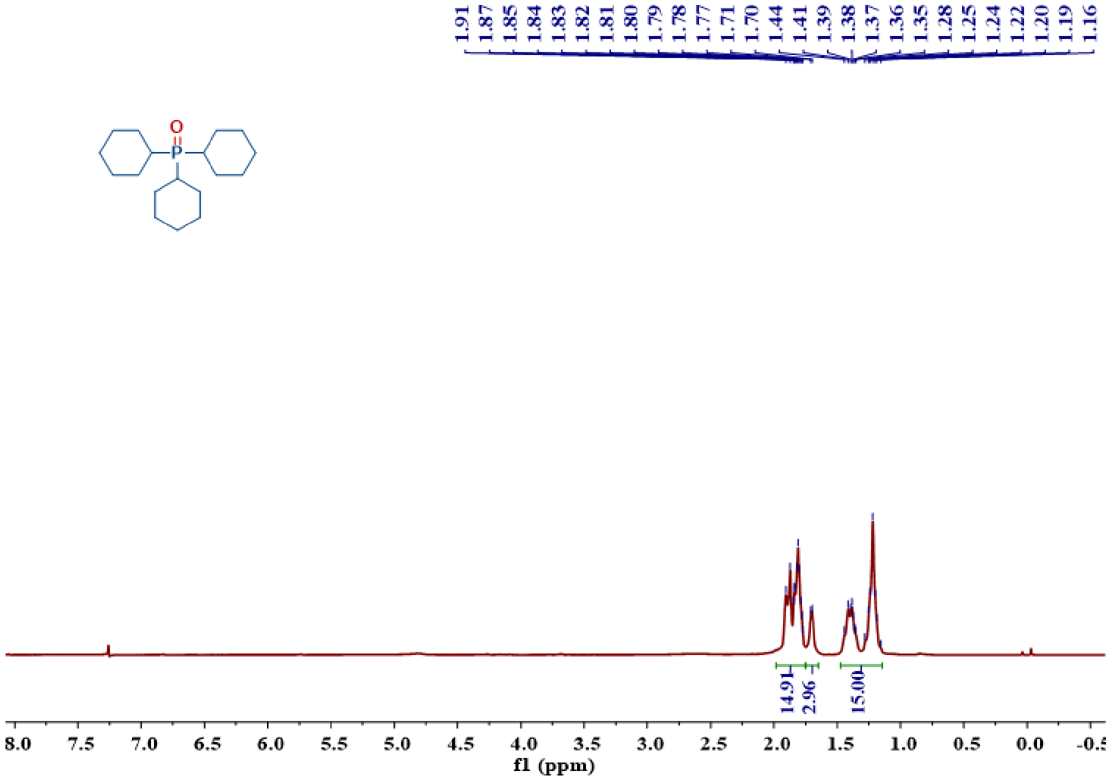
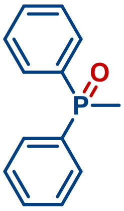


Fig. S51. ^{1}H NMR spectra of tricyclohexylphosphine oxide in $CDCl_3$.

4n. methyldiphenylphosphine oxide



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=1:1) to give 4n as a colorless oil. (35.4 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, J = 12.4, 7.2 Hz, 4H), 7.55 – 7.50 (m, 2H), 7.47 (td, J = 7.9, 2.1 Hz, 4H), 2.03 (d, J = 13.2 Hz, 3H). [9]

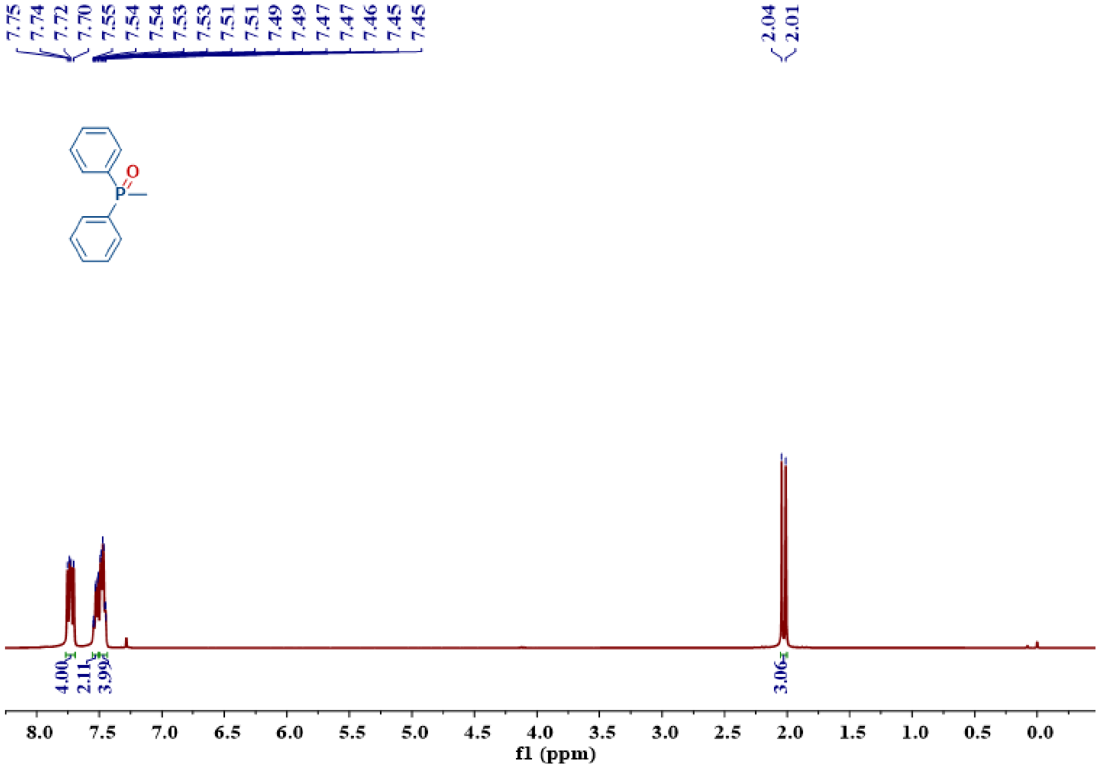
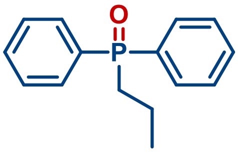


Fig. S52. ^{1}H NMR spectra of methyldiphenylphosphine oxide in $CDCl_3$.

4o. diphenyl(propyl)phosphine oxide



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=1:1) to give 4o as a colorless oil. (38.0 mg, 78% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.78 – 7.71 (m, 4H), 7.53 – 7.44 (m, 6H), 2.29 – 2.22 (m, 2H), 1.72 – 1.61 (m, 2H), 1.03 (td, J = 7.3, 1.2 Hz, 3H). [7]

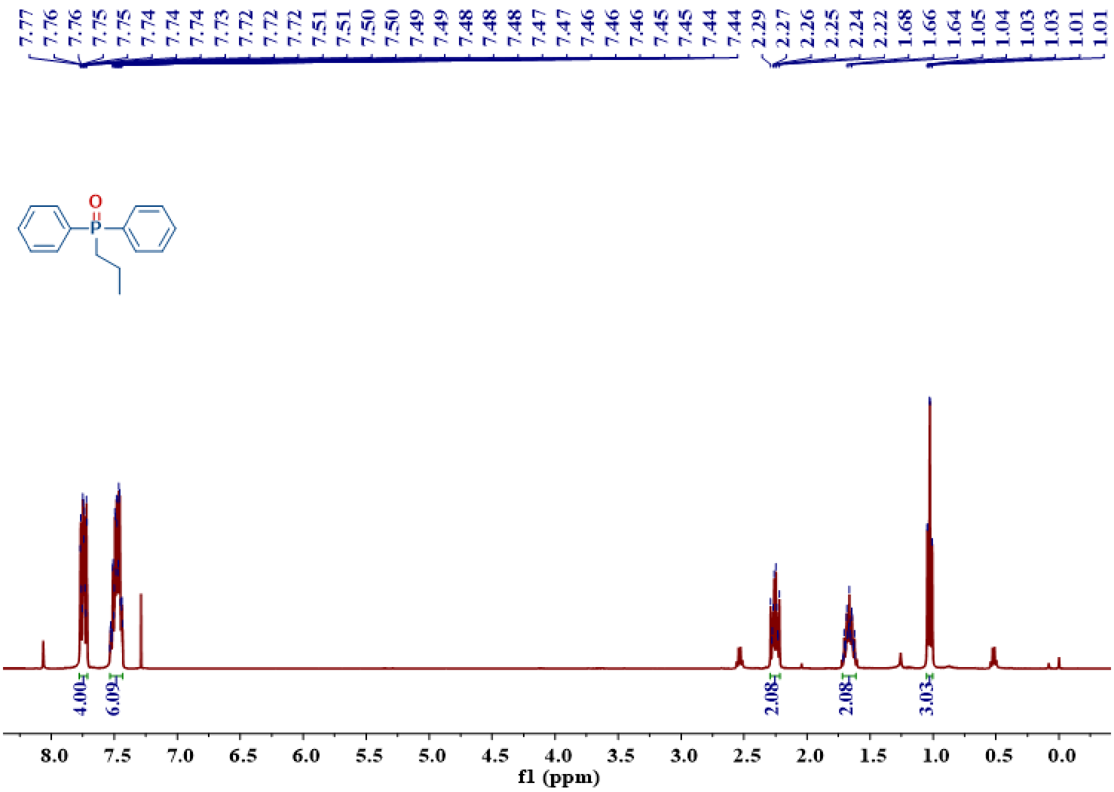
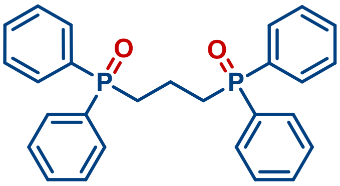


Fig. S53. ^{1}H NMR spectra of diphenyl(propyl)phosphine oxide in CDCl$_3$.

4p. propane-1,3-diylbis(diphenylphosphine oxide)



Following the general procedure, the crude material was purified by rapid column chromatography rapid column chromatography rapid column chromatography (petroleum ether: ethyl acetate=1:1) to give 4p as a colorless oil. (71.0 mg, 80% yield) ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.69 – 7.62 (m, 8H), 7.48 – 7.43 (m, 4H), 7.39 (ddd, J = 8.4, 5.3, 2.1 Hz, 8H), 2.47 (dt, J = 11.0, 7.6 Hz, 4H), 2.03 – 1.91 (m, 2H).[9]

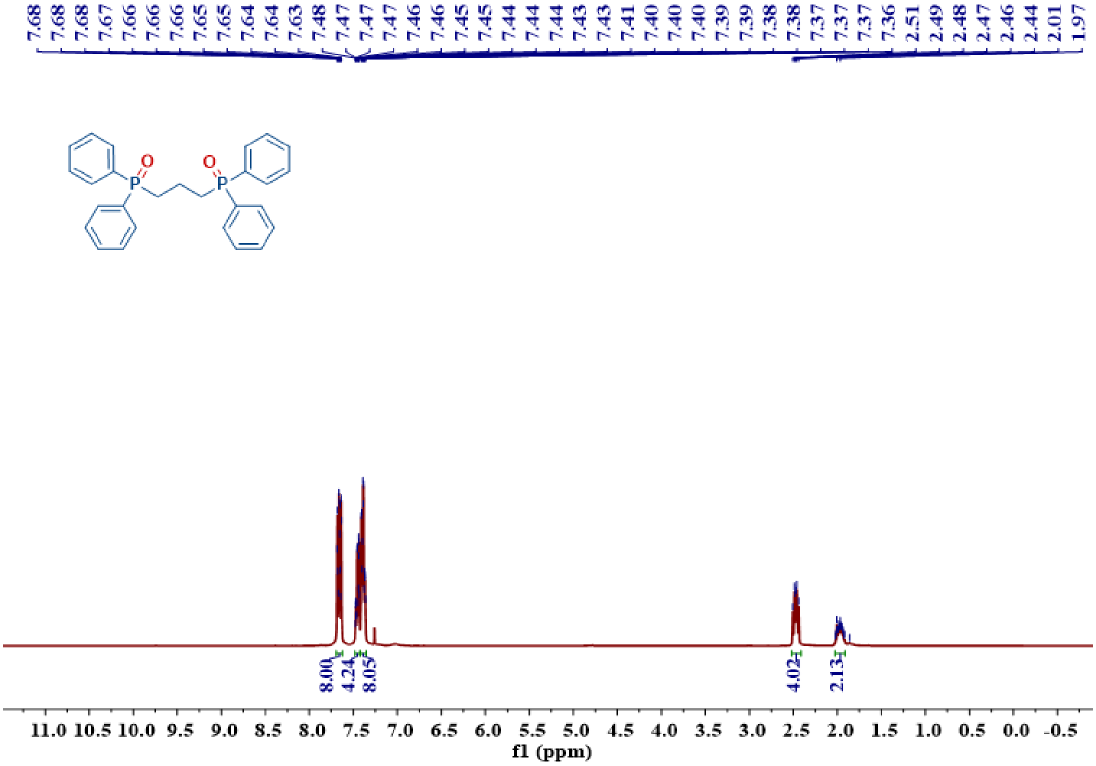


Fig. S54. ^{1}H NMR spectra of t propane-1,3-diylbis(diphenylphosphine oxide) in CDCl$_3$.

5. References

[1]. J. Chen, H. Jiao, W. Li, D. Liao, H. Zhou and C. Yu, Real-Time Fluorescence Turn-On Detection of Alkaline Phosphatase Activity with a Novel Perylene Probe, *Chem. – Asian J.*, 2013, **8**, 276-281.

[2]. M. A. Hoque, T. Jiang, D. L. Poole and S. S. Stahl, Manganese-Mediated Electrochemical Oxidation of Thioethers to Sulfoxides Using Water as the Source of Oxygen Atoms, *J. Am. Chem. Soc.*, 2024, **146**, 21960-21967.

[3]. Q. Song, W. Li, F. Shan, X. Peng, L. Wang, Z. Wang and X.-Q. Yu, Carbonized Polymer Dots-Promoted Photocatalytic Activation of Molecular Oxygen for Efficient and Selective Oxidation of Thioethers to Sulfoxides, *Nano Lett.*, 2024, **24**, 13895-13902.

[4]. H. Li, L. Chen, P. Duan and W. Zhang, Highly Active and Selective Photocatalytic Oxidation of Organosilanes to Silanols, *ACS Sustainable Chem. Eng.*, 2022, **10**, 4642-4649.

[5]. J. Koo, S. H. Kim and S. H. Hong, Hydrogenation of silyl formates: sustainable production of silanol and methanol from hydrosilane and carbon dioxide, *Chem. Commun.*, 2018, **54**, 4995-4998.

[6]. K. Wang, J. Zhou, Y. Jiang, M. Zhang, C. Wang, D. Xue, W. Tang, H. Sun, J. Xiao and C. Li, Selective Manganese-Catalyzed Oxidation of Hydrosilanes to Silanols under Neutral Reaction Conditions, *Angew. Chem. Int. Ed.*, 2019, **58**, 6380-6384.

[7]. H. Song, L. Xu, Y. Tang, L. Wei and Y. Wei, Catalytic Aerobic Photooxidation of Phosphines using Four-coordinated Organoboron Compounds as Photocatalysts, *Synlett*, 2023, **35**, 1698-1702.

[8] D. I. Bugaenko and A. V. Karchava, Electron Donor-Acceptor Complex Initiated Photochemical Phosphorus Arylation with Diaryliodonium Salts toward the Synthesis of Phosphine Oxides, *Adv. Synth. Catal.*, 2023, **365**, 1893-1900.

[9] K. Yin, M. Wei, Z. Wang, W. Luo and L. Li, Tertiary Amine-Mediated Reductions of Phosphine Oxides to Phosphines, *Org. Lett.*, 2023, **25**, 5236-5241.