Supporting Information

for

Building N-hydroxyphthalimide Organocatalytic Sites into Covalent Organic Framework for Metal-free and Selective Oxidation of Silanes

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Contents

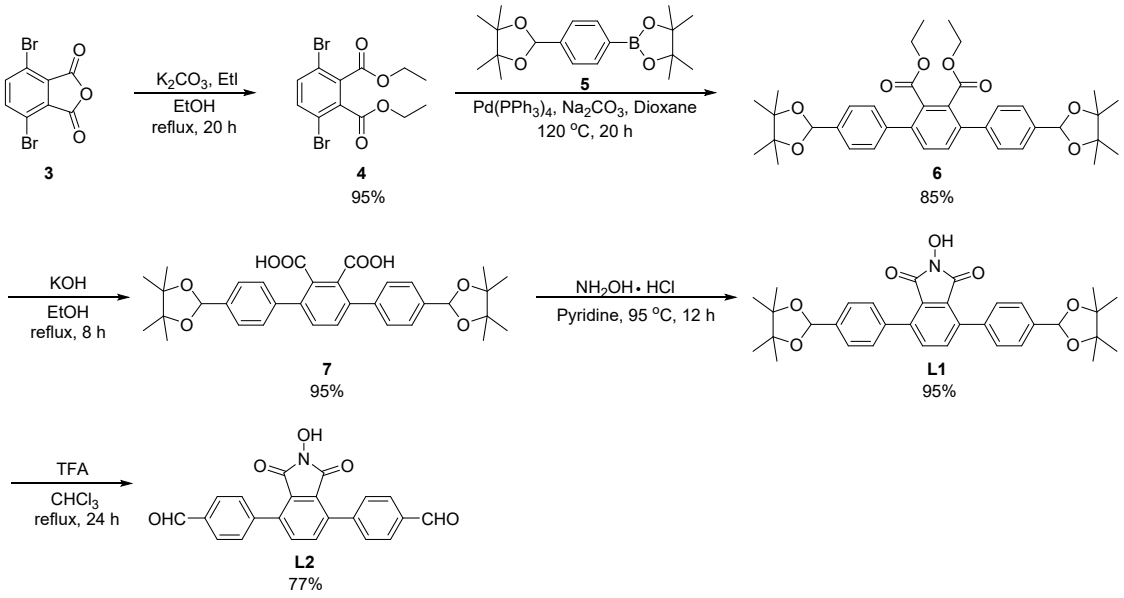
1. General remarks

Nuclear magnetic resonance (NMR) data were obtained by Bruker ARX400 and ARX600 spectrometer (400 MHz/600 MHz). The samples were dissolved in DMSO-d_6 (0.6 mL) or $CDCl_3$ (0.6 mL) to conduct the NMR measurements. Powder X–ray diffraction (PXRD) patterns were collected on a Bruker D8 Advance diffractometer at 40 mA, 40 kV on Cu *K*α (λ = 1.5418 Å) at room temperature with 2° min^{-1} at the range of 2–40°. Scanning electron microscopy (SEM) images were performed on a Hitachi S−4800 (Japan) instrument and transmission electron microscopy (TEM) images were conducted on JEOL JEM−2100F (Japan) instrument. The possible structures and Pawley refinement for the COF were carried out on Accelrys Material Studio 2019 software package. The simulated PXRD patterns were determined by the Reflex module. Pawley refinement of the experimental PXRD of the COF was conducted to optimize the lattice parameters iteratively until the R_{wp} value converges. Thermal gravimetric analysis (TGA) was performed on a differential thermal analyzer (TA, Q500) by heating the samples from 20 °C to 600 °C with a heating rate of 10 °C min^{-1} in N_2 atmosphere (60 mL min^{-1}). Fourier-Transform Infrared (FT–IR) spectroscopy was recorded using a BRUKER ALPHA spectrophotometer in 4000−400 cm^{-1} region. Gas adsorption measurements were conducted using the gas adsorption equipment TRISTAR 3020. The synthesized COF samples were washed with *N, N*-dimethylformamide (DMF) and soaked in anhydrous Ethanol (EtOH) and Tetrahydrofuran (THF) to remove the guests from the channels, respectively. Finally the upper solution was replaced with fresh CH_3CN once a day for 3 days and the COF

solids were collected and dried under vacuum at 70 °C for 12 h prior to the gas sorption analysis. The catalytic performance tests were carried out on Ruicheng Ts100 oscillator with constant temperatures and oscillation frequencies. The reaction products of aerobic oxidation were analyzed by gas chromatography mass spectrometry (GC–MS, SHIMADZU GCMS−QP2010 SE W) using SH–Rxi–5Sil MS column. Electron Paramagnetic Resonance (EPR) was conducted on Bruker A300 spectrometer set with the following experimental parameters: frequency, 9.853203 GHz; power, 15.68 mW; modulation amplitude, 0.1 G; modulation frequency, 100 kHz; sweep time, 46.08 s; center field, 3507 G; sweep width, 30 G.

2. Ligand syntheses

Reagents and solvents used in the syntheses and measurements were purchased from reagents companies, unless otherwise specified, were used without further purification. Compounds **3** and **5** were synthesized according to the literature reports with slight modifications.[1–3] The NMR shifts of the solvents involved are as follows. $CDCl_3$ (^1H (δ) = 7.26 and ^{13}C (δ) = 77.16). DMSO-d_6 (^1H (δ) = 2.50 and ^{13}C (δ) = 39.52). And the multiplicities are simplified as singlet (s), doublet (d), triplet (t), and multiplet (m).



Scheme S1 Synthetic scheme of **L1** and **L2**.

Synthesis of compound 4. To a round-bottom flask was added a mixture of compound **3** (2.0 g, 6.54 mmol), K_2CO_3 (2.72 g, 19.62 mmol) and ethanol (30.0 mL). Then EtI (2.4 mL, 30.0 mmol) was added dropwise into the mixture, and the reaction mixture was refluxed for 20 h. After the reaction was complete, the reaction mixture was extracted with CH_2Cl_2 and washed with water. The organic layer was dried over anhydrous $MgSO_4$ and filtered. The solution was evaporated in vacuo to give the product **4** as white solid (2.36 g, 95% yield).^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (s, 2H), 4.31 (q, 4H), 1.31 (t, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.2, 135.7, 135.5, 119.3, 62.6, 14.0. HRMS (ESI–TOF): *m/z* calculated for $C_{12}H_{12}O_4Br_2$ $[M+Na]^+$: 400.8995, found: 400.8987.

Synthesis of compound 6. The as-synthesized **4** (150.0 mg, 0.39 mmol), **5** (302.0 mg, 0.91 mmol) and Na_2CO_3 (171.6 mg, 1.56 mmol) were added to a mixture of dioxane (20.0 mL) and water (1.0 mL). After bubbling the mixture with nitrogen for 30 min,

$Pd(PPh_3)_4$ (23.0 mg, 0.02 mmol) was added and the resulting solution was refluxed at 120 °C for 20 h under nitrogen atmosphere. After the reaction was complete, the reaction mixture was extracted with ethyl acetate and washed with water. The organic layer was dried over anhydrous $MgSO_4$ and filtered. The resulting solution was evaporated in vacuo to give the crude product. By silica gel column chromatography using petroleum ether/ethyl acetate (6 : 1) as eluent the pure product was obtained as white solid (205 mg, 85% yield).^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, 4H), 7.37 (s, 2H), 7.28 (d, 4H), 5.95 (s, 2H), 3.96 (q, 4H), 1.25 (s, 12H), 1.19 (s, 12H), 0.87 (t, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.3, 140.1, 139.6, 139.5, 132.3, 131.5, 128.3, 126.2, 99.6, 82.8, 61.5, 24.3, 22.2, 13.6. HRMS (ESI–TOF): *m/z* calculated for $C_{38}H_{46}O_8$ $[M+Na]^+$: 653.3085, found: 653.3081.

Synthesis of compound 7. To an aluminium cap sealable tube was added a mixture of **6** (100.0 mg, 0.16 mmol), KOH (622.6 mg, 11.0 mmol), water (1.0 mL) and ethanol (10.0 mL), and then the tube was sealed and subjected to a microwave reactor. After implementation of microwave radiation at 100 °C for 8 h, the reaction was allowed to room temperature. The volatiles were removed from the reaction mixture by rotary evaporation. After water (100 mL) was added to the resulting solid, the aqueous solution was acidified to pH 1–2 with 2 M HCl solution. The white precipitate formed was collected by centrifugation, washed twice with water, and dried at 55 °C in vacuum for 12 h. The pure product was obtained as white solid (82 mg, 95% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.13 (s, 2H), 7.51 (d, 6H), 7.42 (d, 4H), 5.94 (s, 2H), 1.28 (s, 12H), 1.23 (s, 12H). ^{13}C NMR (151 MHz, DMSO-d_6) δ

169.6, 140.3, 139.4, 138.3, 133.0, 131.4, 128.4, 126.9, 99.3, 82.8, 24.6, 22.3. HRMS (ESI–TOF): *m/z* calculated for $C_{34}H_{38}O_8$ $[M+Na]^+$: 597.2459, found: 597.2463.

Synthesis of compound L1. Compound **7** (130 mg, 0.23 mmol) and hydroxylamine hydrochloride (17.3 mg, 0.25 mmol) were added to a solution of pyridine (6.0 mL) and subsequently heated at 95 °C for 12 h. After the solution was cooled to ambient temperature, the pyridine was removed under reduced pressure. Water (10.0 mL) was added to the resulting solid. And then the aqueous solution was acidified to pH 1–2 with 2 M HCl. The yellow precipitate was collected by centrifugation, washed twice with water, and dried at 55 °C in vacuo for 5 h. The pure product was obtained as white solid (123 mg, 95% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (t, 6H), 7.52 (d, 4H), 6.03 (s, 2H), 1.34 (s, 12H), 1.29 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.3, 140.3, 139.8, 136.4, 136.3, 129.5, 126.2, 125.5, 99.7, 83.0, 24.4, 22.3. HRMS (ESI–TOF): *m/z* calculated for $C_{34}H_{37}NO_7$ $[M+Na]^+$: 594.2462, found: 594.2459.

Synthesis of compound L2. To a round-bottom flask containing **L1** (200 mg, 0.35 mmol) in chloroform (20 mL) was slowly added trifluoroacetic acid (TFA, 0.53 mL, 7.13 mmol) at 0 °C. And then the resulting solution was refluxed for 24 h under a nitrogen atmosphere. The yellow precipitate was collected by centrifugation, and washed twice with water, and dried at 55 °C in vacuo for 5 h. The pure product was obtained as yellow solid (100 mg, 77% yield). ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.82 (s, 1H), 10.11 (s, 2H), 8.02 (d, 4H), 7.85 (d, 6H).^{13}C NMR (151 MHz, DMSO-d_6) δ 193.0, 163.0, 141.8, 137.9, 135.9, 130.4, 129.1, 126.0. HRMS (ESI–TOF): *m/z* calculated for $C_{22}H_{13}NO_5$ $[M+H]^+$: 372.0866, found: 372.0872.

Solubility Test of L1 and L2.

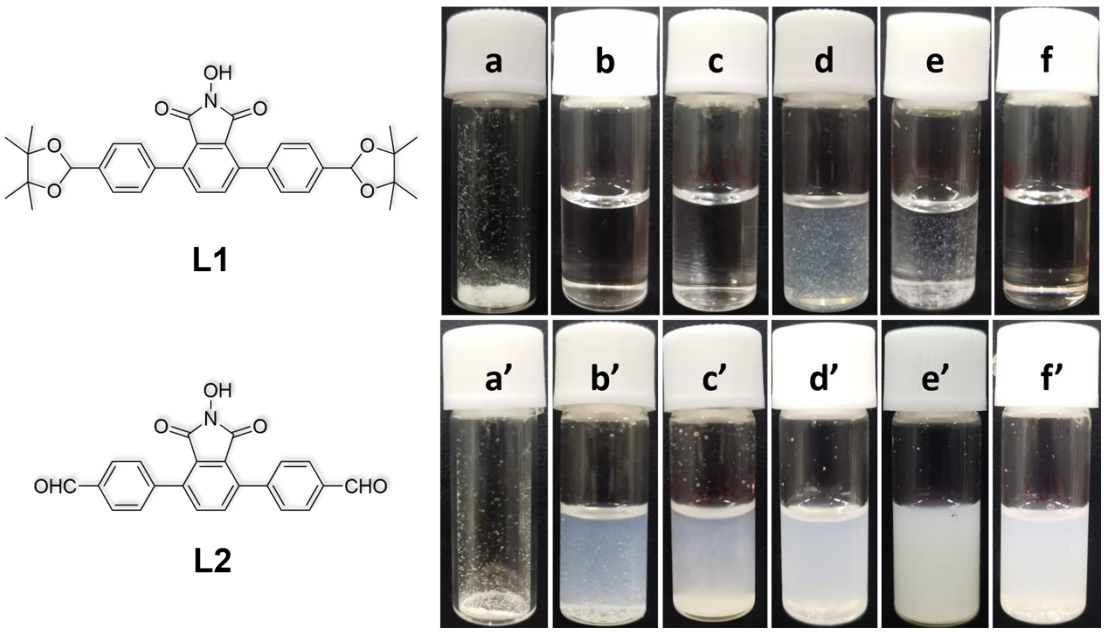
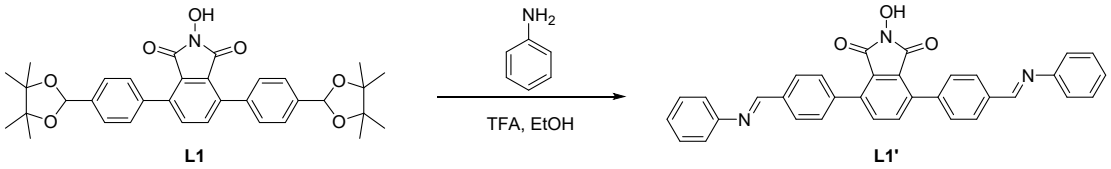


Fig. S1 Comparison of the solubility of monomer **L1** (upper) and the corresponding **L2** (bottom) in different solvents. From left to right: solid sample (a or a'), 1, 4-dioxane (b or b'), acetonitrile (c or c'), 1, 2-dichlorobenzene (d or d'), *n*-Butanol (e or e'), a mixture of 1, 2-dichlorobenzene and *n*-Butanol in 1 : 1 volume ratio (f or f').

3. Model reaction

A mixture of **L1** (11 mg, 0.02 mmol), aniline (7 μL, 0.08 mmol), TFA (74 μL, 1 mmol), and EtOH (2 mL) was heated at 80 °C for 24 h under nitrogen. Upon cooling, the reaction mixture was filtered directly and the solid was washed with EtOH and water, and then dried in vacuo to afford **L1′** as green solid (6.5 mg, 65% yield). ^{1}H NMR (600 MHz, DMSO) δ 10.78 (s, 1H), 8.73 (s, 2H), 8.05 (d, 4H), 7.85 (s, 2H), 7.78 (d, 4H), 7.45 (t, 4H), 7.33 (d, 4H), 7.28 (t, 2H). The ^{13}C NMR spectrum is not available because of the poor solubility of **L1′** in common deuterated solvents.



Scheme S2 Synthetic scheme of the model compound **L1′**.

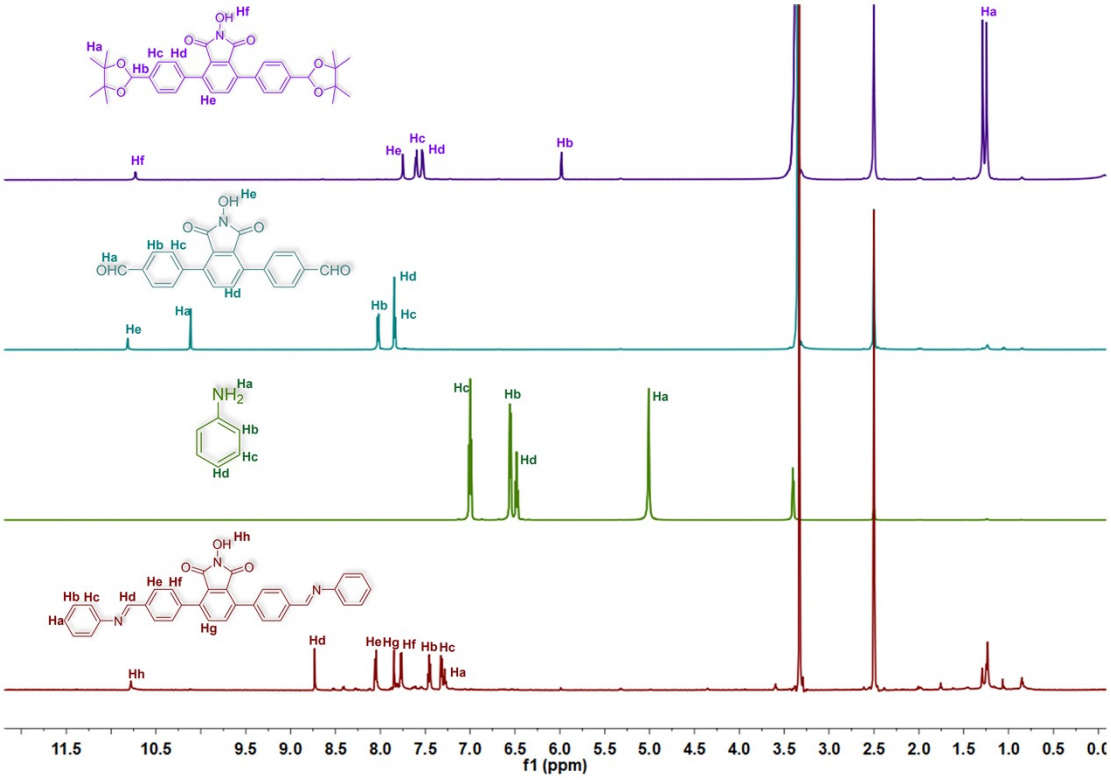


Fig. S2 ^{1}H NMR spectra of the reactants and model compound **L1′**.

4. Synthesis of COF-NHPI

Screening the optimal condition for synthesis of COF-NHPI.

Monomer **L1** (17 mg, 0.03 mmol) and 2,4,6-tris(4-aminophenyl)-1,3,5-triazine (TAPT, 7 mg, 0.02 mmol) were charged into a glass ampoule (volume ca. 10 mL, length 18 cm). To the ampoule was added a mixture of 1,2-dichlorobenzene (o-DCB,

x mL), *n*-butanol (*n*-BuOH, y mL, x + y = 1.0 mL), and trifluoroacetic acid (TFA, 3.0 M, 0.025 mL). The ampoule was flash frozen in a liquid nitrogen bath and evacuated for 3 min using a Schlenk line, and sealed by flame, reducing the total length by *ca.* 10 cm. Upon warming to room temperature, the ampoule was placed in an oven and heated to 80 °C, keeping undisturbed for 3 days. The obtained solid was transferred into a vial and washed with DMF (3 × 5 mL) and EtOH (3 × 5 mL). Subsequently the solid was stirred in CH_3CN for 12 h, and then carefully separated by decantation. The wet solid was immediately examined by PXRD.

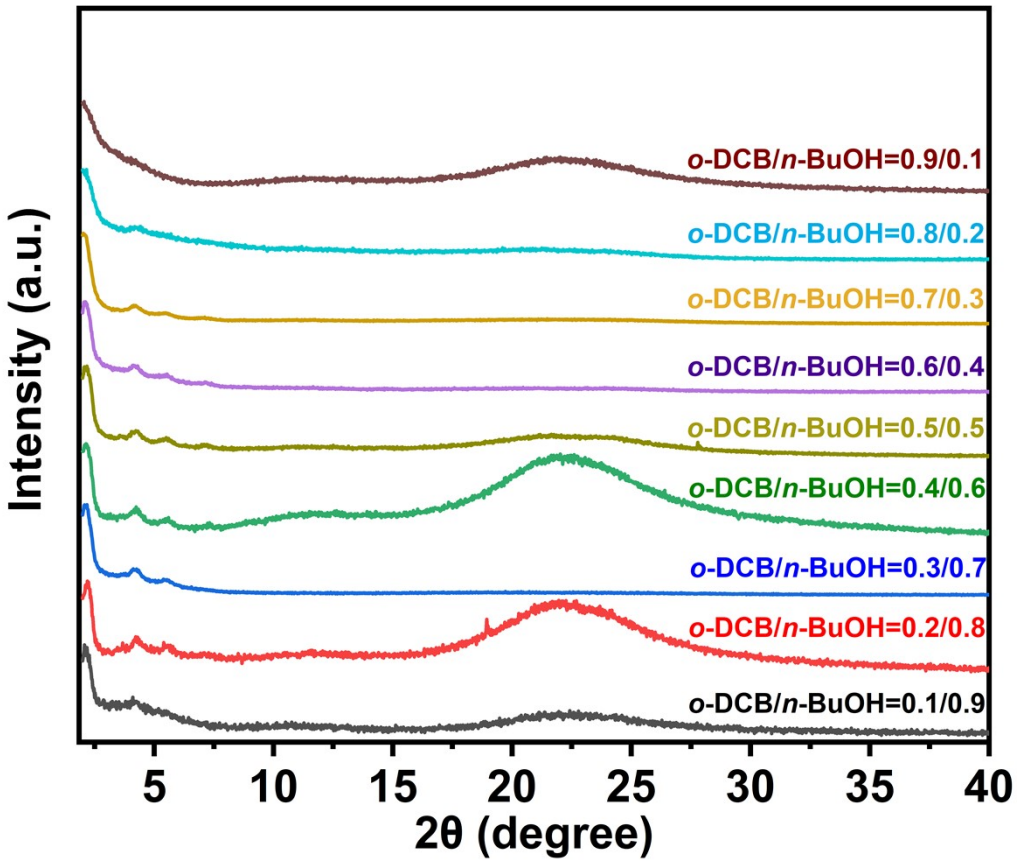


Fig. S3 PXRD profiles of the wet solid synthesized under different conditions.

Synthesis of COF-NHPI under the optimal condition and the workup procedure.

Monomer **L1** (17 mg, 0.03 mmol) and 2,4,6-tris(4-aminophenyl)-1,3,5-triazine

(TAPT, 7 mg, 0.02 mmol) were charged into a glass ampoule (volume *ca.* 10 mL, length 18 cm). To the ampoule was added a mixture of 1,2-dichlorobenzene (*o*-DCB, 0.3 mL), *n*-butanol (*n*-BuOH, 0.7 mL), and trifluoroacetic acid (TFA, 3.0 M, 0.025 mL). The ampoule was flash frozen in a liquid nitrogen bath and evacuated for 3 min using a Schlenk line, and sealed by flame, reducing the total length by *ca.* 10 cm. Upon warming to room temperature, the ampoule was placed in an oven and heated to 80 °C, keeping undisturbed for 3 days. The obtained solid was transferred into a vial and washed with DMF (3 × 5 mL) and EtOH (3 × 5 mL). Subsequently the solid was stirred in CH_3CN for 12 h, and then carefully separated by decantation. Finally the collected solid was dried at 70 °C in vacuo for 12 h to yield **COF-NHPI** as yellow powder.

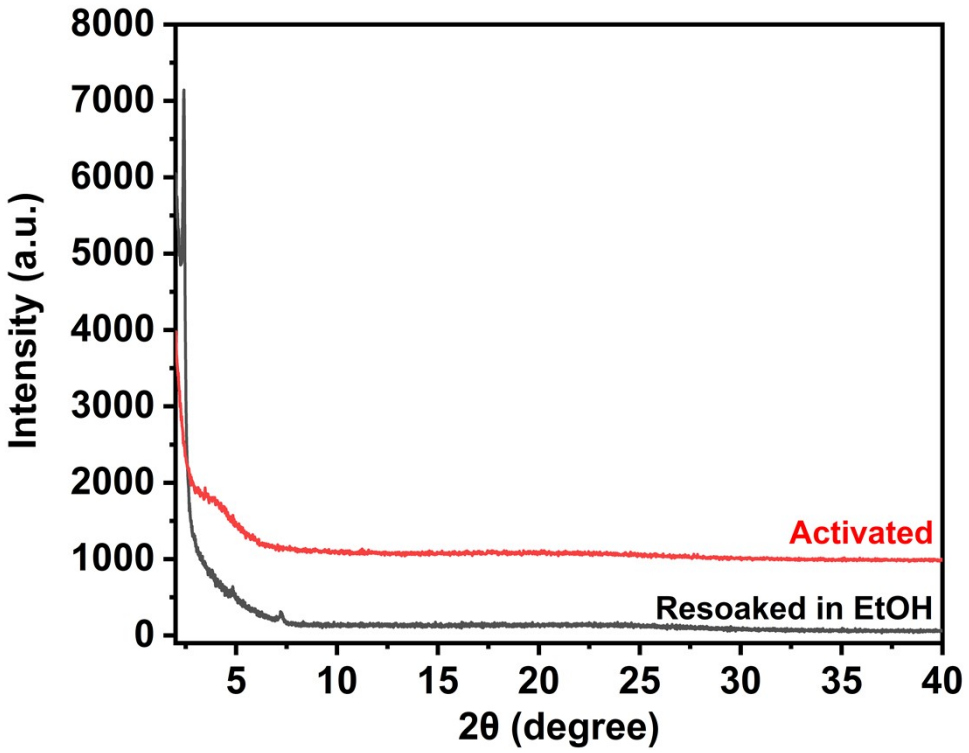


Fig. S4 PXRD profiles of the obtained **COF-NHPI** activated for BET measurement

and resoaked in EtOH after BET measurement. The intense peak at small angle in the PXRD profile after resoaked in EtOH indicated that the **COF-NHPI** can restore its high crystallinity from the activated amorphous state by EtOH solvent.

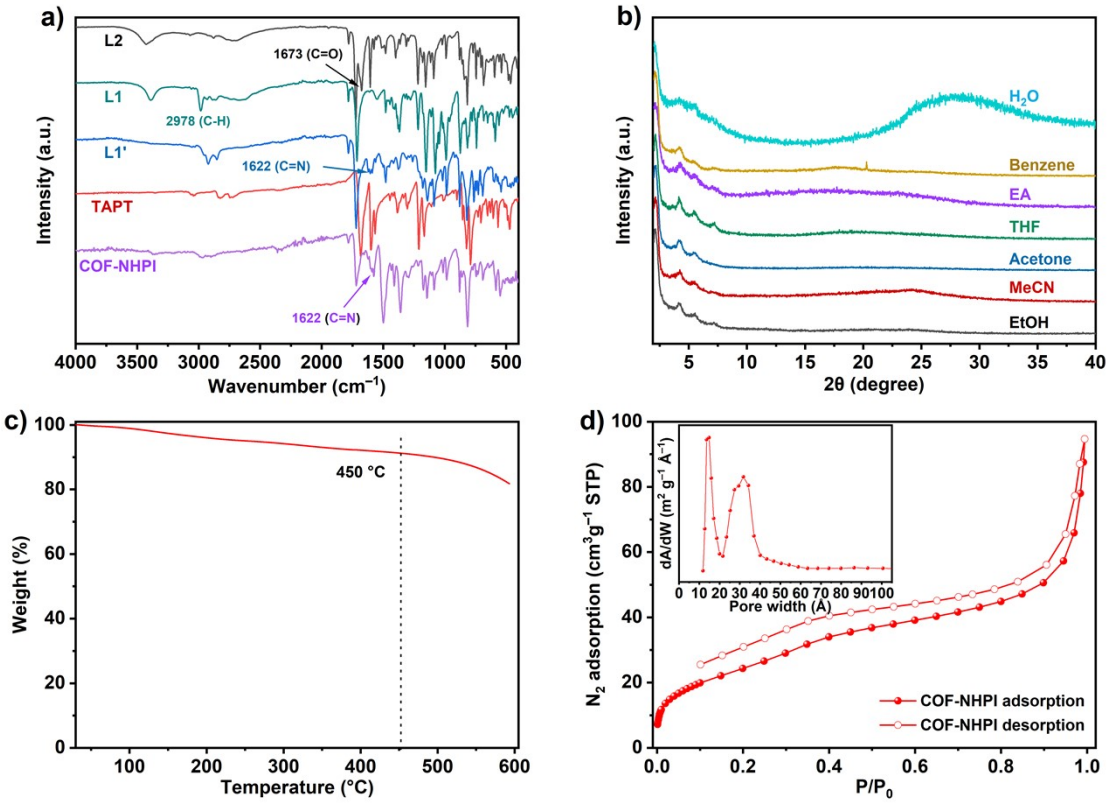


Fig. S5 (a) FT–IR spectra of **L2** (black), **L1** (green), **L1′** (blue), **TAPT** (red) and **COF-NHPI** (purple). (b) PXRD profiles after treating with different solvents. (c) TGA curve of the activated **COF-NHPI** under N_2 atmosphere. (d) N_2 sorption isotherms at 77 K on the activated **COF-NHPI** (Inset: pore size distribution). The Brunauer–Emmett–Teller (BET) surface area was calculated to be 73 $m^2\ g^{-1}$ with the pore volume of 0.14 $cm^3\ g^{-1}$. The pore size distribution peaks at *ca.* 15 and 32 Å are smaller than the simulated value of 54 Å, indicating the existence of some amount of AB-stacking frameworks.[4]

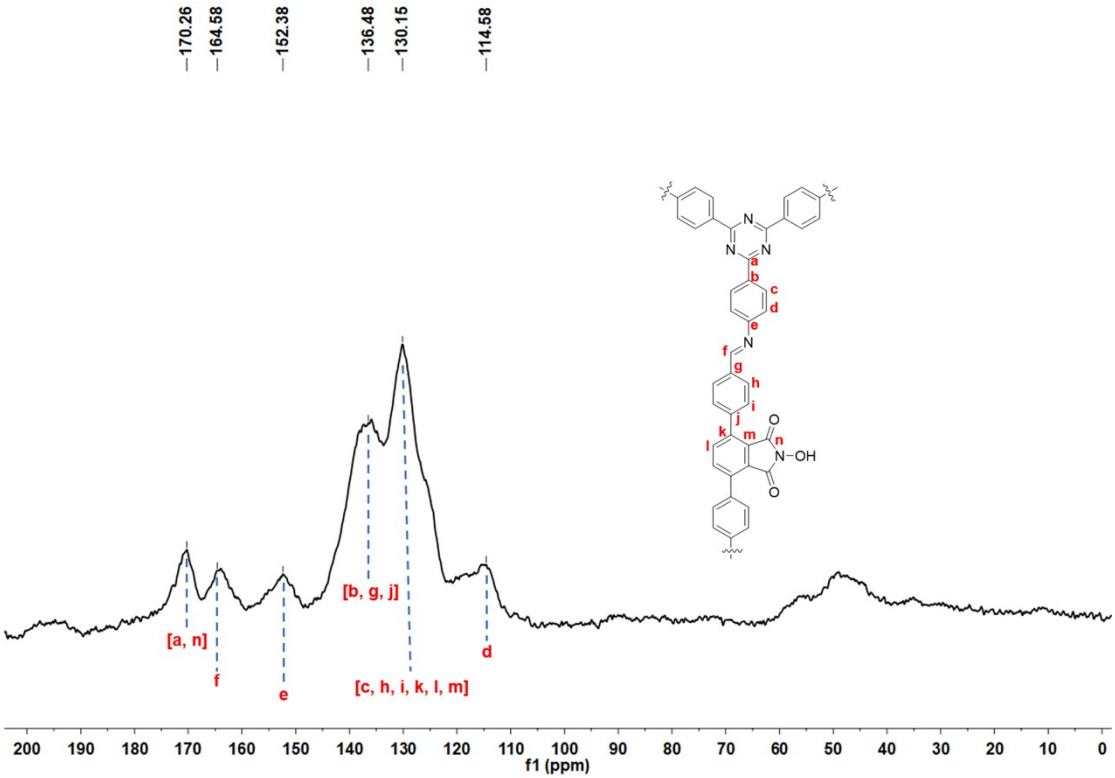


Fig. S6 Solid-state ^{13}C CP/MAS NMR spectrum of **COF-NHPI**.

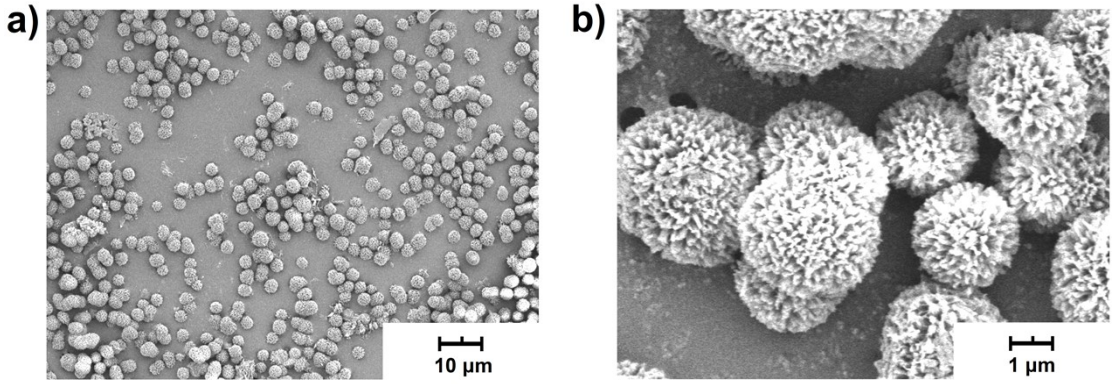


Fig. S7 SEM images of **COF-NHPI**.

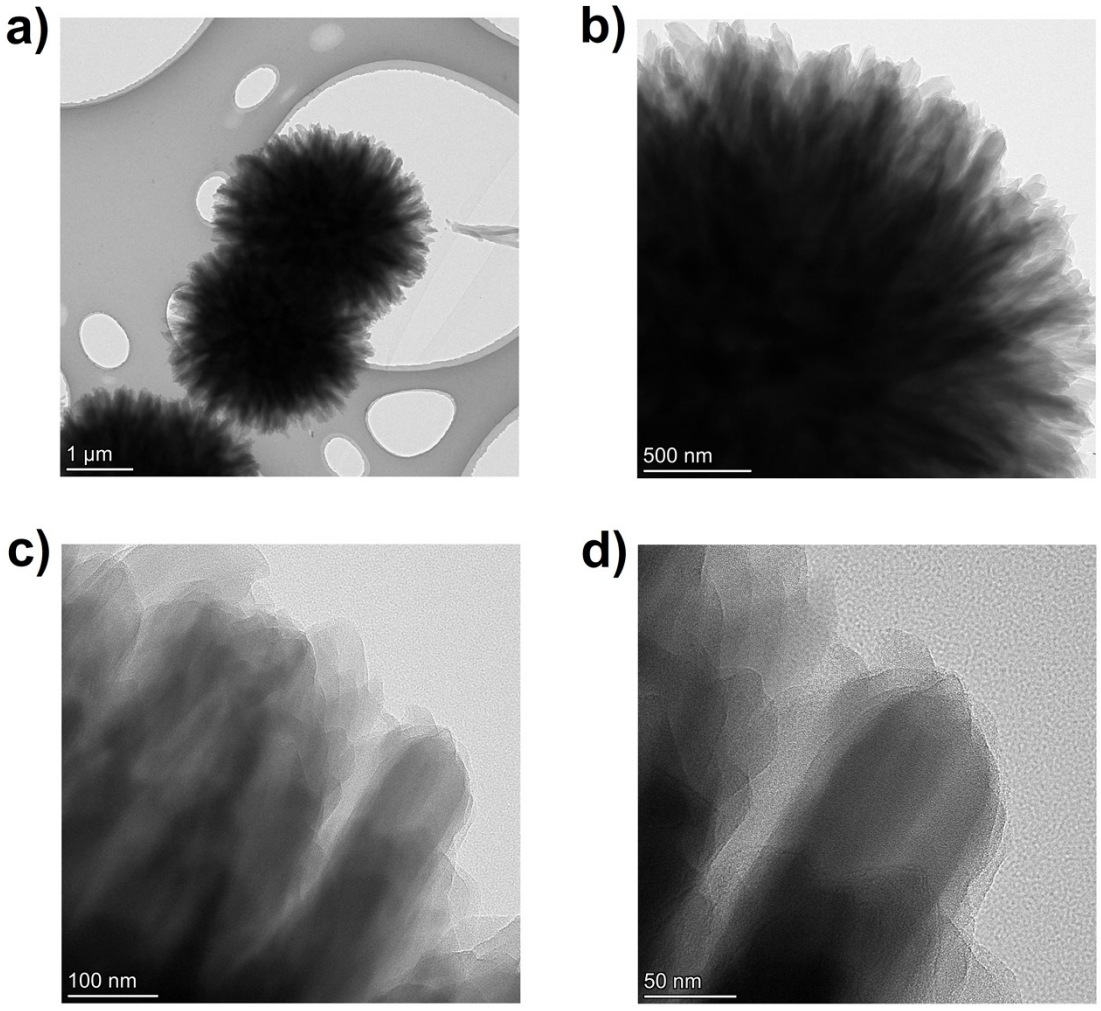


Fig. S8 TEM images of **COF-NHPI**.

5. Structural modeling and powder X–ray diffraction analysis

The models of AA-stacking and AB-stacking were defined based on monomer **L1** and **TAPT** *via* –C=N– linkages. The MS Forcite module was used to optimize these models. In contrast with the AB-stacking model, PXRD pattern of the experimental value was in good agreement with that of the simulated AA-stacking model data. The fractional atomic coordinates for the unit cell of **COF-NHPI** are listed in **Table S1**.

Table S1 Atomic coordinates of **COF-NHPI**.

Space group: *P6/mmm* ***a* = 60.0298 Å, *b* = 60.0368 Å, *c* = 9.9983 Å,** **α = 90.0221°, β = 89.8626°, γ = 120.1237°**							
Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C1	0.30762	0.67919	0.32571	**C97**	0.8904	1.42987	0.32132
N2	0.27711	0.66141	0.32837	**C98**	0.87293	1.39964	0.31825
C3	0.26216	0.63081	0.32835	**C99**	0.84214	1.3851	0.31699
N4	0.27971	0.61842	0.32599	**C100**	0.9221	1.44592	0.32087
C5	0.30991	0.63387	0.32331	**C101**	0.93802	1.47552	0.35396
N6	0.32297	0.66417	0.32316	**C102**	0.96885	1.49198	0.35448
C7	0.41079	0.55296	0.30798	**C103**	0.98665	1.48038	0.32173
C8	0.44076	0.56432	0.30106	**C104**	0.97046	1.45106	0.28535
C9	0.45431	0.5473	0.29957	**C105**	0.94013	1.43487	0.2851
C10	0.43913	0.51714	0.30376	**H106**	0.83467	1.44205	0.33244
C11	0.40899	0.50552	0.31358	**H107**	0.88596	1.46621	0.33391
C12	0.39528	0.52268	0.31413	**H108**	0.88261	1.38751	0.32026
C13	0.4542	0.50021	0.30091	**H109**	0.83092	1.36316	0.31331
C14	0.48428	0.5129	0.31968	**N110**	0.77379	1.3577	0.31754
C15	0.4995	0.49714	0.31791	**C111**	0.79538	1.3872	0.32093
C16	0.48626	0.46704	0.29734	**C112**	0.93251	1.40807	0.22906
C17	0.45648	0.45491	0.27524	**C113**	0.98013	1.4335	0.22955
C18	0.44152	0.47041	0.27655	**N114**	0.95693	1.40752	0.19761
H19	0.45363	0.58615	0.2969	**O115**	1.00767	1.44131	0.19748
H20	0.47624	0.55763	0.29473	**O116**	0.90562	1.38682	0.19659
H21	0.39624	0.48381	0.32386	**O117**	0.95792	1.38572	0.13466

H22	0.37337	0.51246	0.32031	**H118**	0.94018	1.37412	0.07515
N23	0.36968	0.56624	0.31515	**C119**	1.01828	1.49819	0.32318
C24	0.39902	0.57279	0.30897	**C120**	1.03172	1.52812	0.33261
C25	0.41357	0.45134	0.2352	**C121**	1.062	1.5463	0.33325
C26	0.43696	0.42714	0.23336	**C122**	1.08149	1.53622	0.32591
N27	0.41114	0.4253	0.21097	**C123**	1.06832	1.50613	0.31875
O28	0.44284	0.40593	0.20526	**C124**	1.03769	1.48774	0.31907
O29	0.39276	0.45781	0.20827	**H125**	1.01913	1.53733	0.33855
O30	0.38769	0.40218	0.16202	**H126**	1.07008	1.56798	0.33952
H31	0.37589	0.40821	0.10367	**H127**	1.08102	1.49703	0.31422
C32	0.5028	0.45159	0.29593	**H128**	1.02961	1.46609	0.31962
C33	0.53287	0.46672	0.28961	**N129**	1.13481	1.55522	0.32527
C34	0.54978	0.45315	0.28669	**C130**	1.11247	1.55723	0.32713
C35	0.53854	0.42321	0.29123	**H131**	0.92696	1.48584	0.37919
C36	0.50829	0.40757	0.29975	**H132**	0.97846	1.51333	0.38014
C37	0.49113	0.42135	0.30308	**H133**	0.78812	1.40148	0.32362
H38	0.54322	0.48865	0.28638	**H134**	1.11765	1.57826	0.33279
H39	0.5716	0.46604	0.28102	**C135**	0.48426	1.03345	0.32544
H40	0.49811	0.38565	0.30449	**C136**	0.47469	1.04934	0.40856
H41	0.46944	0.4086	0.31414	**C137**	0.48977	1.08024	0.41693
N42	0.5566	0.38456	0.29095	**C138**	0.51588	1.09881	0.34202
C43	0.56458	0.41468	0.28733	**C139**	0.52504	1.08306	0.25354
C44	0.60468	0.30624	0.30528	**C140**	0.50973	1.05195	0.24415
N45	0.63433	0.31782	0.30724	**H141**	0.45606	1.0382	0.46812
C46	0.64782	0.30152	0.31024	**H142**	0.48134	1.08945	0.48459

N47	0.62996	0.27139	0.31126	**H143**	0.54379	1.09425	0.1949
C48	0.59968	0.257	0.31003	**H144**	0.51764	1.04278	0.17315
N49	0.58786	0.27557	0.3068	**C145**	0.53589	1.17612	0.32297
H50	0.49596	0.53461	0.33586	**C146**	0.55187	1.20721	0.31494
H51	0.52126	0.50844	0.33287	**C147**	0.58228	1.22395	0.31472
H52	0.41401	0.59417	0.30464	**C148**	0.59494	1.20638	0.31738
H53	0.58021	0.42894	0.27996	**C149**	0.57899	1.17542	0.32543
C54	0.57053	1.36654	0.2963	**H150**	0.51398	1.16621	0.3278
C55	0.60007	1.37577	0.29851	**H151**	0.54052	1.21774	0.31097
C56	0.61079	1.356	0.30209	**H152**	0.61686	1.21632	0.31502
C57	0.59304	1.32561	0.30383	**H153**	0.59041	1.16498	0.3321
C58	0.56368	1.31665	0.30172	**N154**	0.53371	1.129	0.39034
C59	0.55306	1.33626	0.29815	**C155**	0.54862	1.15856	0.3305
H60	0.6145	1.39732	0.29733	**C156**	0.46856	1.00092	0.32405
H61	0.63254	1.36439	0.30353	**C157**	0.47899	0.98334	0.26705
H62	0.54918	1.29511	0.30282	**C158**	0.46378	0.95263	0.26696
H63	0.53129	1.32778	0.29691	**C159**	0.44062	0.98318	0.38553
C64	0.32622	1.61761	0.32325	**C160**	0.42511	0.95187	0.38538
C65	0.35654	1.63049	0.31928	**C161**	0.50634	0.99205	0.215
C66	0.37131	1.61432	0.31702	**N162**	0.50813	0.96834	0.18308
C67	0.35682	1.58398	0.31879	**C163**	0.48276	0.94437	0.21547
C68	0.32672	1.57147	0.32284	**O164**	0.52859	1.01935	0.20973
C69	0.31211	1.58746	0.32483	**O165**	0.47822	0.91728	0.21202
H70	0.36859	1.65241	0.31787	**O166**	0.53176	0.96859	0.13796
H71	0.39326	1.62532	0.31403	**H167**	0.54894	0.98662	0.17205

H72	0.31457	1.54956	0.32443	**C168**	0.43571	0.9346	0.32347
H73	0.29016	1.57636	0.32757	**C169**	0.41932	0.90208	0.32096
C74	1.1664	1.57426	0.32322	**C170**	0.42678	0.88513	0.23157
C75	1.18008	1.60494	0.32338	**C171**	0.41085	0.85415	0.22702
C76	1.21087	1.62372	0.32124	**C172**	0.38541	0.83661	0.30923
C77	1.23077	1.61383	0.31856	**C173**	0.37801	0.85354	0.40006
C78	1.2169	1.58347	0.31832	**C174**	0.3941	0.88464	0.40545
C79	1.18621	1.56475	0.32045	**H175**	0.43067	0.99317	0.43302
H80	1.16746	1.61415	0.32511	**H176**	0.40511	0.94154	0.43266
H81	1.21874	1.64539	0.32149	**H177**	0.44406	0.89546	0.16217
H82	1.22949	1.57424	0.31652	**H178**	0.41788	0.84418	0.15555
H83	1.17837	1.54308	0.32002	**H179**	0.35967	0.84316	0.46254
C84	0.67941	1.31535	0.31419	**H180**	0.38672	0.89469	0.47416
C85	0.69711	1.34551	0.31447	**N181**	0.36489	0.80688	0.26305
C86	0.7278	1.35978	0.31595	**C182**	0.35275	0.7769	0.31409
C87	0.74289	1.34477	0.31688	**C183**	0.36735	0.76111	0.31504
C88	0.72513	1.3147	0.31674	**C184**	0.35301	0.73002	0.32083
C89	0.69458	1.30048	0.31566	**C185**	0.32272	0.71162	0.32509
H90	0.68752	1.35777	0.31362	**C186**	0.3083	0.72745	0.32854
H91	0.73918	1.38173	0.31611	**C187**	0.32258	0.75836	0.32287
H92	0.73469	1.3024	0.31749	**H188**	0.38926	0.77228	0.30728
H93	0.68324	1.27853	0.31563	**H189**	0.36552	0.7207	0.32048
C94	0.82681	1.3999	0.32156	**H190**	0.28636	0.71629	0.33377
C95	0.84437	1.4299	0.32793	**H191**	0.30998	0.76758	0.32141
C96	0.87484	1.44428	0.32858				

6. Catalytic reactions

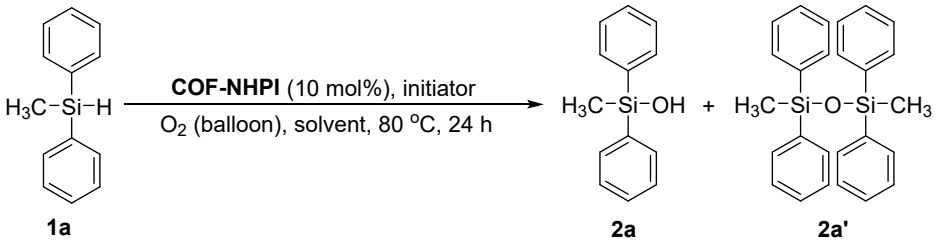
General procedure for oxidation of methyldiphenylsilane under air.

To a 10 mL glass tube was added a mixture of the methyldiphenylsilane (7.50 μmol), catalyst (0.75 μmol of **COF-NHPI** or other catalyst), *tert*-butyl nitrite (7.50 μmol) and 0.5 mL CH_3CN. The glass tube was sealed with rubber stopper and connected to an air balloon through a needle. The glass tube was fixed in a thermoshaker and heated at 80 °C with a shaking speed of 900 rpm for a set time, and the conversions were checked by GC–MS.

General procedure for oxidation of substrates under O_2.

To a 10 mL glass tube was added a mixture of the hydrosilanes (7.50 μmol), catalyst (0.75 μmol of **COF-NHPI** or other catalyst), *tert*-butyl nitrite (7.50 μmol) and 0.5 mL CH_3CN. The glass tube was sealed with rubber stopper and connected to an O_2 balloon through a needle. After gently discharging the air in the glass tube by oxygen bubbling, the reaction mixture was fixed in a thermoshaker and heated at 80 °C with a shaking speed of 900 rpm for a set time, and the conversions were checked by GC–MS.

Table S2 Catalytic oxidation of methyldiphenylsilane under different reaction conditions.[a]

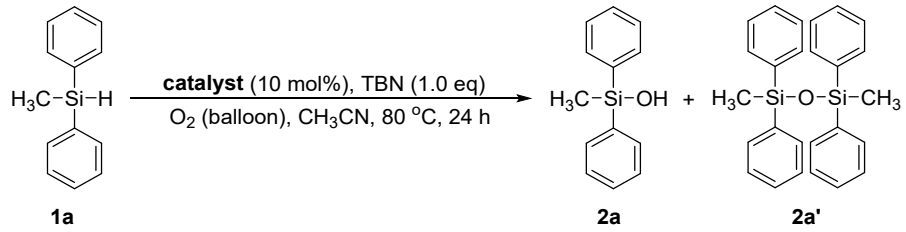


1a **2a** **2a'**

Entry	Initiator	Solvent	Conversion (%)[b]	Selectivity to **2a** (%)[b]
1	/	CH_3CN	Trace	Trace
2[c]	$Co(NO_3)_2{\cdot}6H_2O$	CH_3CN	46	100
3[c]	$Fe(NO_3)_3{\cdot}9H_2O$	CH_3CN	96	96
4[c]	$Cu(NO_3)_2{\cdot}2.5H_2O$	CH_3CN	100	0
5[c]	$Cu(OAc)_2$	CH_3CN	100	Trace
6[c]	TBN	CH_3CN	7	100
7[d]	TBN	CH_3CN	52	100
8	TBN	CH_3CN	100	100
9	TBN	THF	Trace	Trace
10	TBN	DCE	8	100
11	TBN	DMSO	87	81
12	TBN	DMF	20	100
13	TBN	EA	14	100
14	TBN	EtOH	Trace	Trace

[a] Reaction condition: 0.5 mL solvent, 0.0075 mmol methyldiphenylsilane, **COF-NHPI** (10 mol%), TBN (1.0 eq). (TBN: *tert*-butyl nitrite). [b] GC–MS analysis. [c] Reaction condition: 0.5 mL solvent, 0.0075 mmol methyldiphenylsilane, **COF-NHPI** (10 mol%), Initiator (0.3 eq). [d] Reaction condition: 0.5 mL solvent, 0.0075 mmol methyldiphenylsilane, **COF-NHPI** (10 mol%), Initiator (0.5 eq). EA: ethyl acetate. DCE: 1,2-dichloroethane.

Table S3 Catalytic oxidation of **1a** with different catalysts and atmospheres. [a]



1a **2a** **2a'**

Entry	Atmosphere	Catalyst	Conversion (%)[b]	Selectivity to **2a** (%)[b]
1	Argon	**COF-NHPI**	14	100
2	Air	**COF-NHPI**	48	100
3	O_2	**COF-NHPI**	100	100
4[c]	O_2	/	25	46
5[c]	O_2	**L1**	100	100
6[d]	O_2	**L1′**	67	100

[a] Reaction condition: 0.5 mL CH_3CN, 0.0075 mmol methyldiphenylsilane, catalyst (10 mol%), TBN (1.0 eq). [b] GC–MS analysis. [c] In the absence of catalyst.

Procedure for verification of the ordered porosity to affect the catalysis.

Monomer **L1** (17 mg, 0.03 mmol) and TAPT (7 mg, 0.02 mmol) were charged into a glass ampoule (volume *ca.* 10 mL, length 18 cm). To the ampoule was added a mixture of 1,4-dioxane (0.7 mL), EtOH (0.3 mL), and trifluoroacetic acid (TFA, 3.0 M, 0.050 mL). The ampoule was flash frozen in a liquid nitrogen bath and evacuated for 3 min using a Schlenk line, and sealed by flame, reducing the total length by *ca.* 10 cm. Upon warming to room temperature, the ampoule was placed in an oven and heated to 80 °C, keeping undisturbed for 3 days. The obtained solid was transferred into a vial, washed with DMF (3 × 5 mL) and EtOH (3 × 5 mL) and finally dried in vacuo to yield **Polymer-NHPI** which was used for the catalysis under the same

condition.

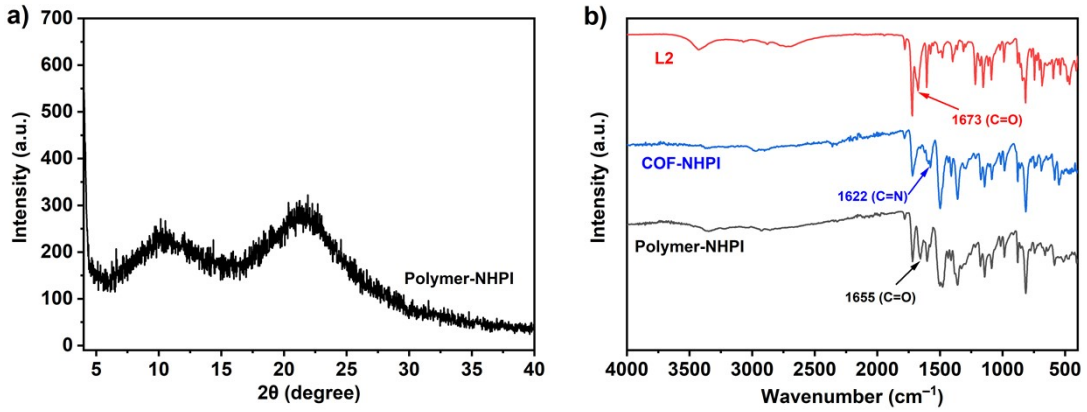
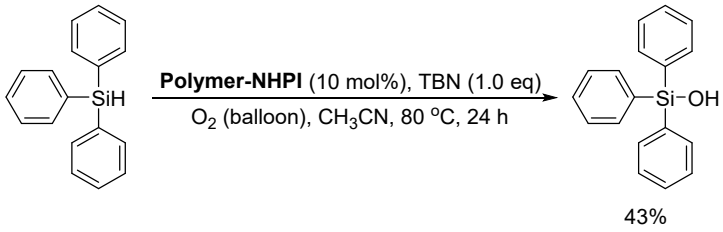


Fig. S9 a) PXRD pattern of the **Polymer-NHPI** and b) FT–IR spectra of the **L2**, **COF-NHPI** and **Polymer-NHPI.**



Scheme S3 Catalytic oxidation of the triphenylsilane under the same condition using **Polymer-NHPI** as catalyst.

Procedure for verification of the heterogeneous characteristic.

To a 10 mL glass tube was added a mixture of methyldiphenylsilane (7.50 μmol), 0.75 μmol of **COF-NHPI**, TBN (7.50 μmol) and 1.0 mL CH_3CN. The glass tube was sealed with rubber stopper and connected to an O_2 balloon through a long needle. After gently degassing with oxygen gas, the glass tube was fixed in a thermoshaker and heated at 80 °C with a shaking speed of 900 rpm for 4 h, and the reaction was monitored by GC–MS analysis. The hot reaction mixture was filtered to remove the

solid catalyst and the filtrate was collected in another glass tube. The glass tube was sealed with rubber stopper and connected to an O_2 balloon through a long needle. After gently degassing with oxygen gas, the glass tube was fixed in a thermoshaker again and heated at 80 °C with a shaking speed of 900 rpm for another 20 h. During this period, the conversions were monitored by GC–MS analysis.

Procedure for verification of the recyclability.

To a 10 mL glass tube was added a mixture of **1f** (37.50 μmol), **COF-NHPI** (3.75 μmol), TBN (37.50 μmol) and 2.0 mL CH_3CN. After gently degassing with oxygen gas, the glass tube was fixed in a thermoshaker and heated at 80 °C with a shaking speed of 900 rpm for 8 h, and the conversion was monitored by GC–MS analysis. The catalyst was separated by centrifugation, washed with CH_3CN (3 × 5 mL), and directly used for the next catalytic cycle under the same reaction condition.

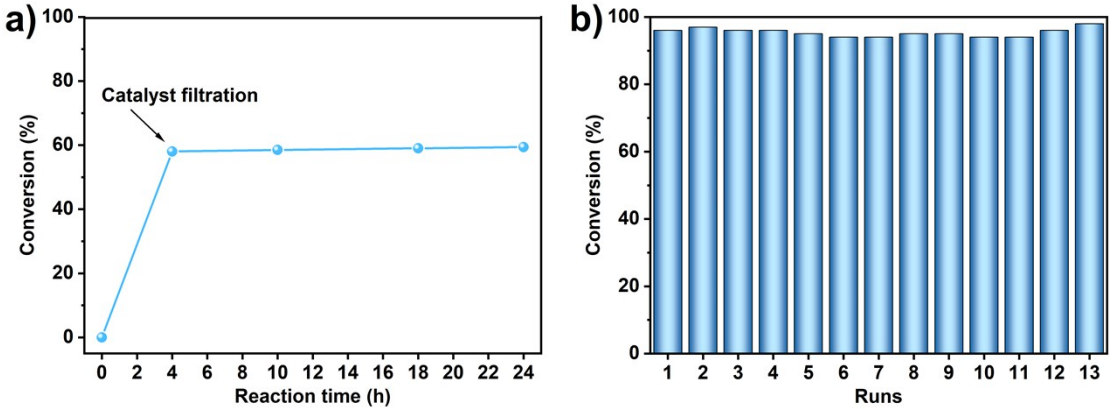


Fig. S10 (a) Plot of conversion *vs.* reaction time of the **1a** oxidation catalyzed by **COF-NHPI**. (b) Recyclability of this heterogeneous catalytic system using **1f** as substrate.

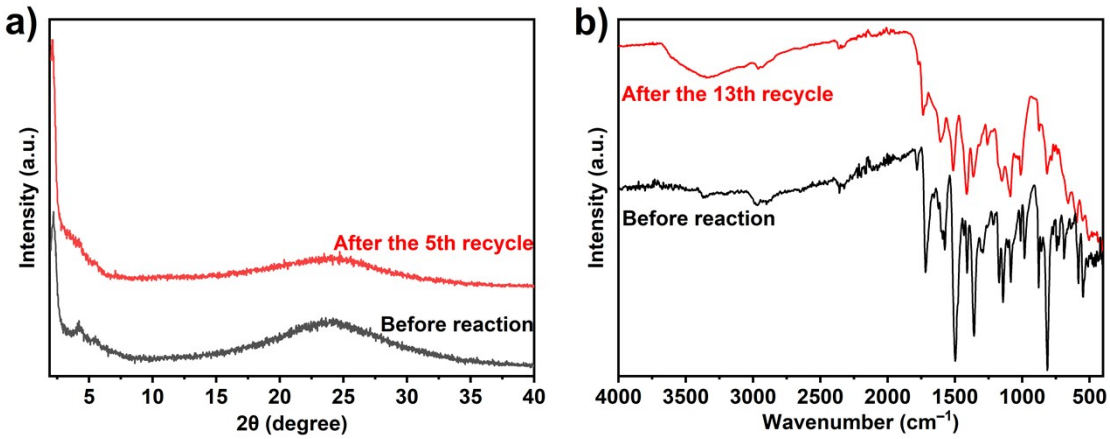


Fig. S11 (a) PXRD patterns and (b) FT−IR spectra of the **COF-NHPI** before and after the catalytic reactions.

General procedure for verifying the involvement of radicals in this catalytic oxidation system.

To a 10 mL glass tube was added a mixture of methyldiphenylsilane (7.50 μmol), 2,6-di-*tert*-butyl-4-methylphenol (BHT, 7.50 μmol), **COF-NHPI** (0.75 μmol), TBN (7.50 μmol) and 0.5 mL CH_3CN. The glass tube was sealed with rubber stopper and connected to an O_2 balloon through a long needle. The glass tube was fixed in a thermoshaker and heated at 80 °C with a shaking speed of 900 rpm for 24 h, and a conversion of 4% was obtained by GC−MS analysis.

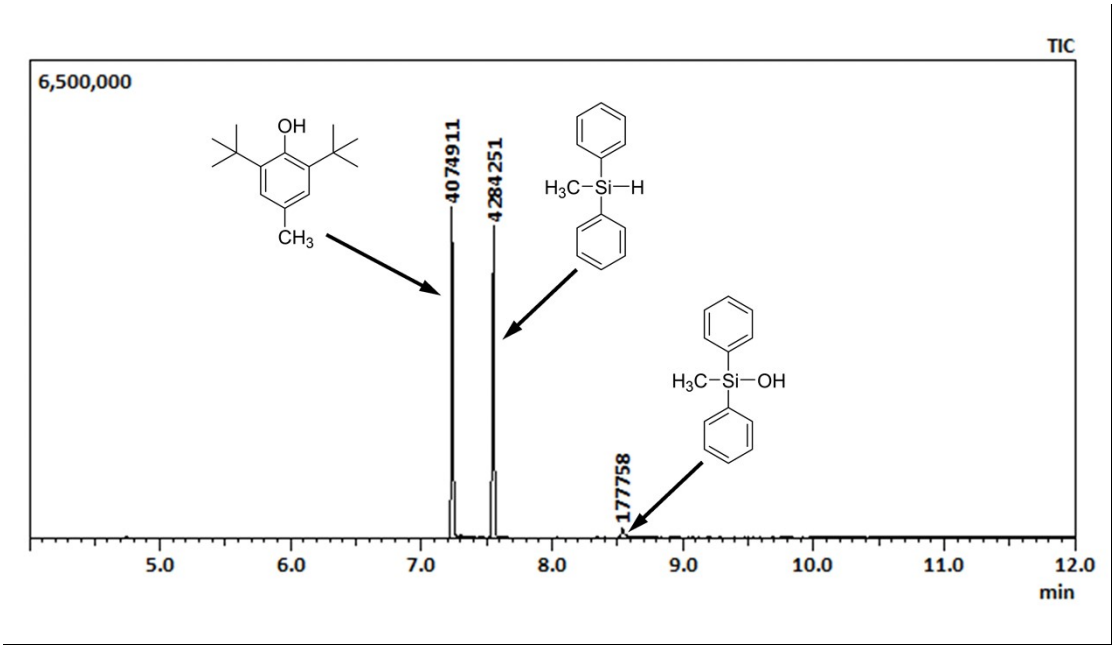


Fig. S12 GC−MS analysis report of the reaction with radical scavenger BHT.

Procedure to *in-situ* verify the radicals in this catalytic system by EPR spectra.

(i) To a 10 mL glass tube was added **COF-NHPI** (15 mg, 11 μmol), *tert*-butyl nitrite (14 μL, 0.11 mmol) and 0.5 mL CH_3CN. The glass tube was sealed with rubber stopper and connected to an O_2 balloon through a long needle. After gently degassing with oxygen gas, the reaction mixture was transferred into an EPR tube and heated at 80 °C for 1 h. And then the EPR spectrum was recorded.

(ii) To a 10 mL glass tube was added **COF-NHPI** (15 mg, 11 μmol), *tert*-butyl nitrite (14 μL, 0.11 mmol), silane **1e** (18 μL, 0.11 mmol) and 0.5 mL CH_3CN. The glass tube was sealed with rubber stopper and connected to an O_2 balloon through a long needle. After gently degassing with oxygen gas, the reaction mixture was transferred into an EPR tube and heated at 80 °C for 1 h. And then the EPR spectrum was recorded.

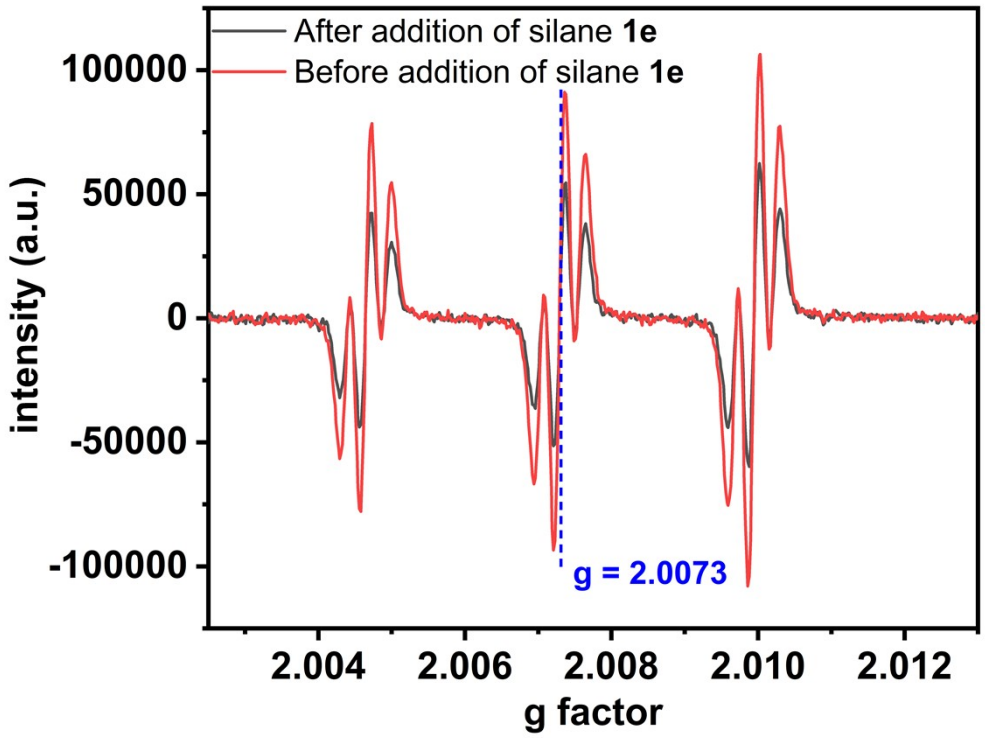


Fig. S13 EPR spectra of the catalytic oxidation system before and after addition of silane **1e**.

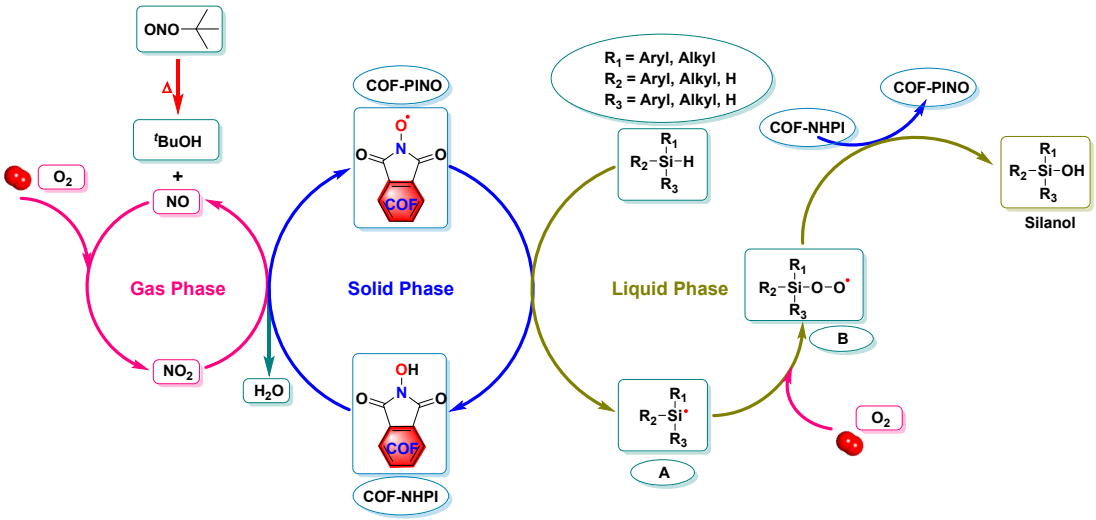


Fig. S14 Proposed mechanism of the oxidation catalyzed by the **COF-NHPI**/TBN/O_2 system.

7. Supplementary figures of NMR spectra

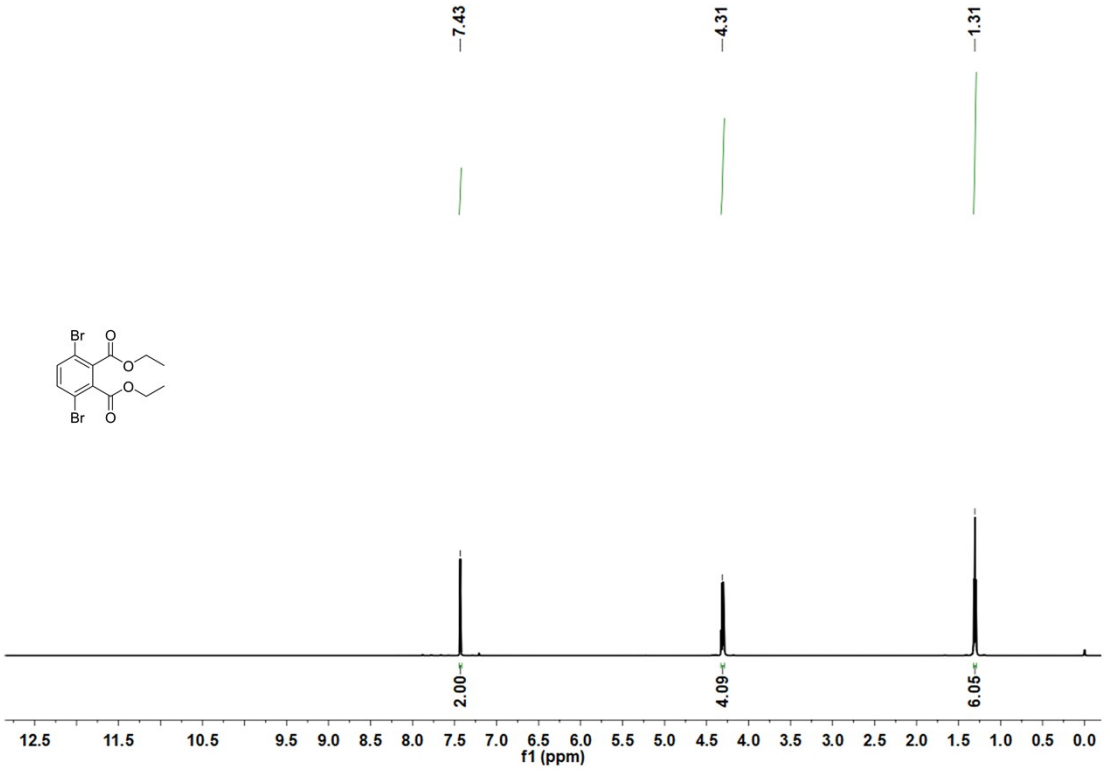


Fig. S15 ^{1}H NMR spectrum of **4** in $CDCl_3$.

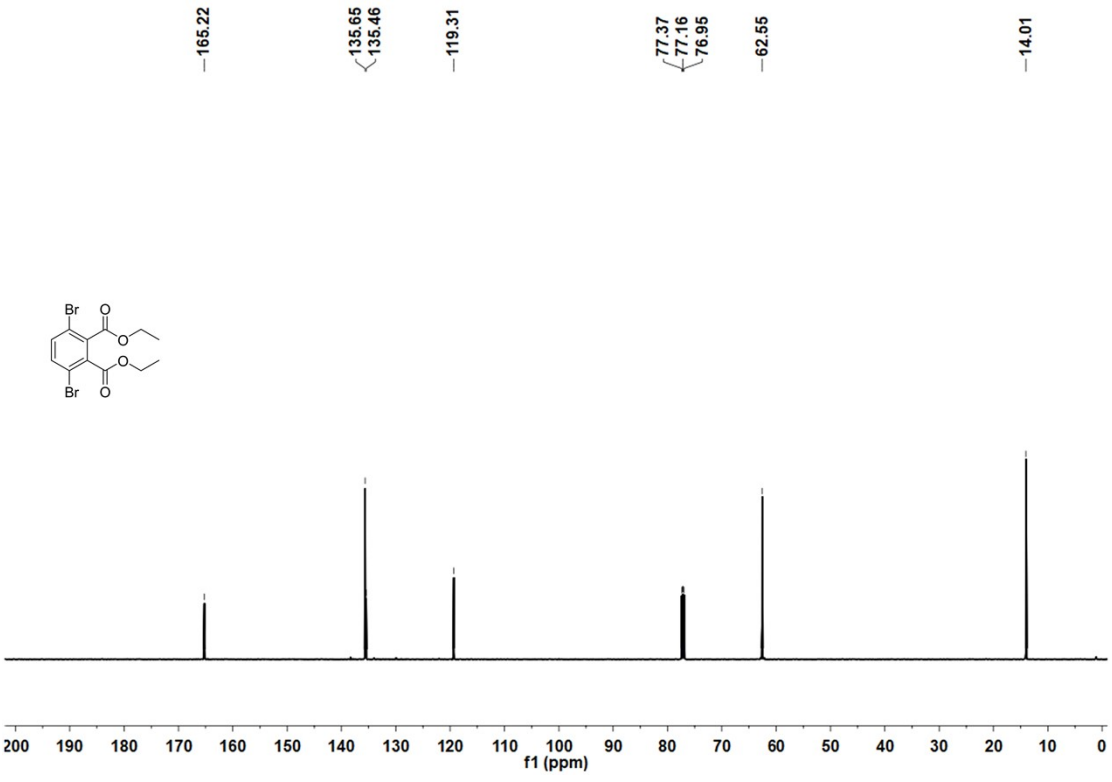


Fig. S16 ^{13}C NMR spectrum of **4** in $CDCl_3$.

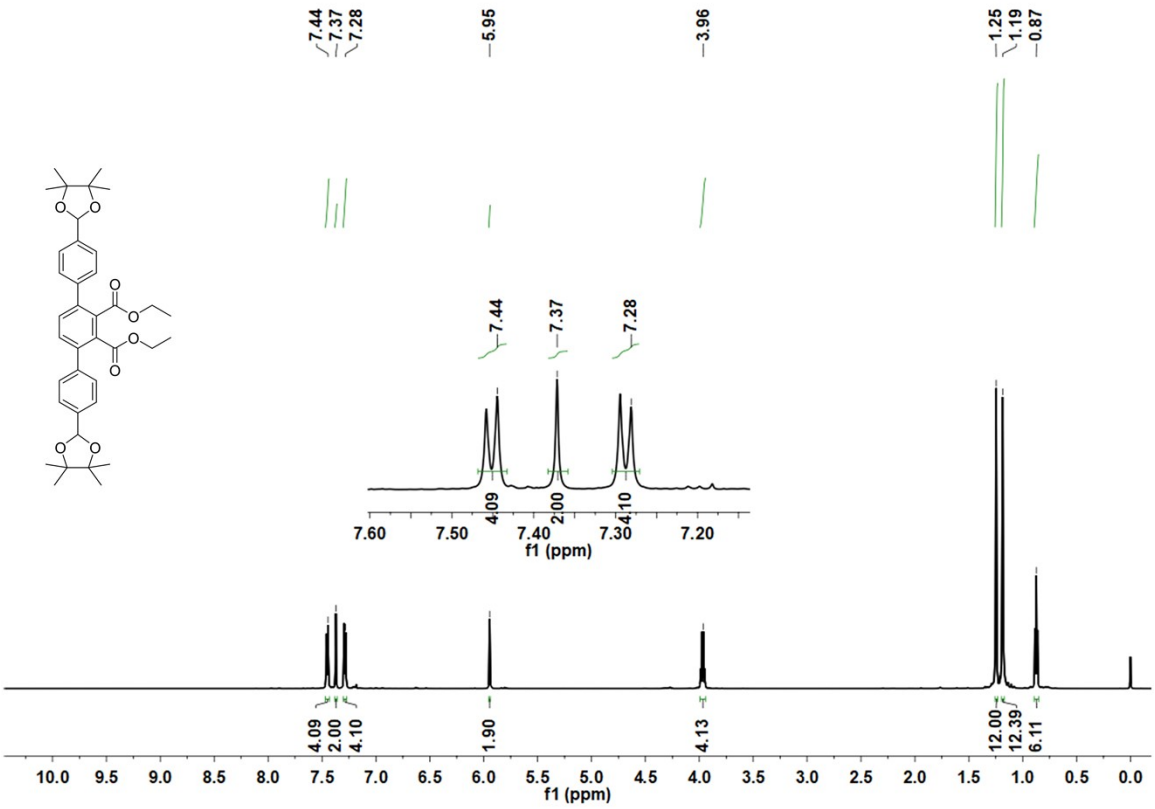


Fig. S17 ^{1}H NMR spectrum of **6** in $CDCl_3$.

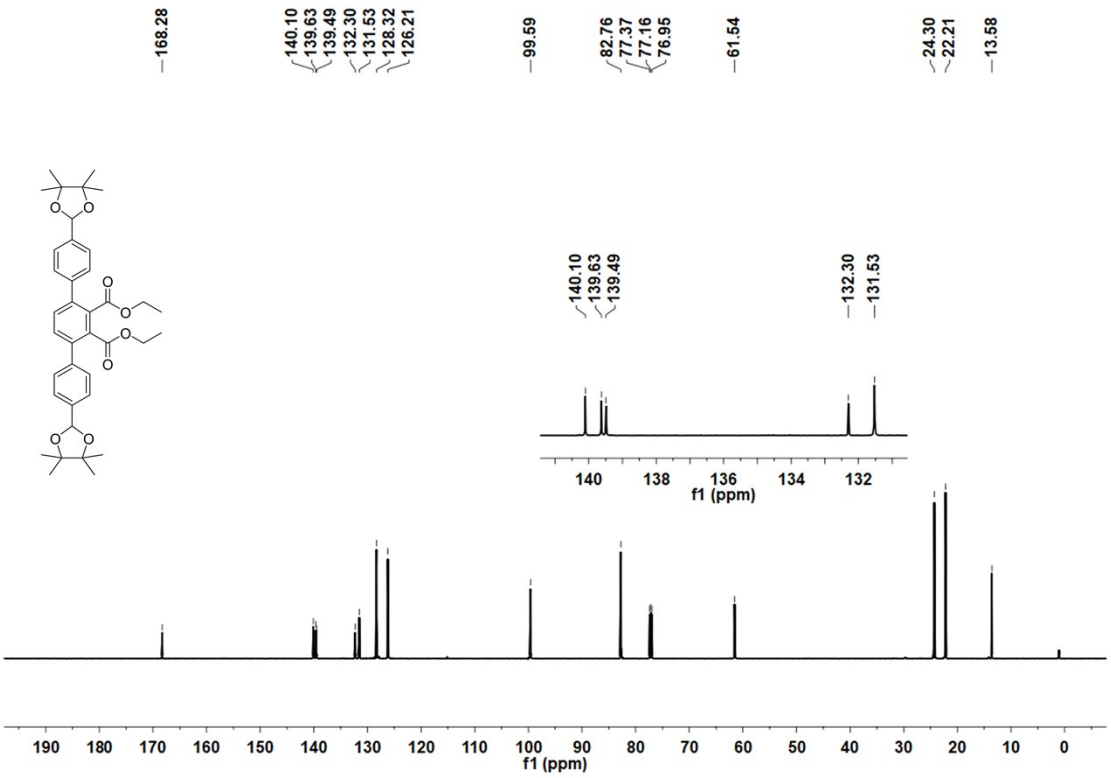


Fig. S18 ^{13}C NMR spectrum of **6** in $CDCl_3$.

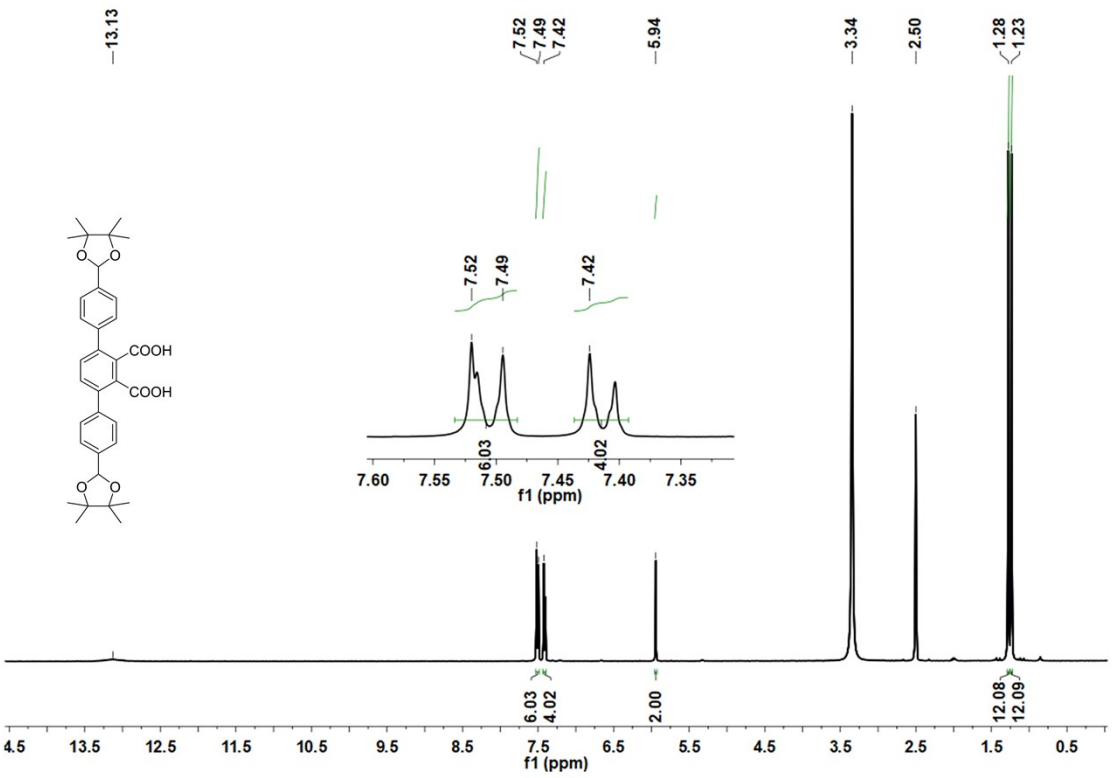


Fig. S19 ^{1}H NMR spectrum of **7** in DMSO-d_6.

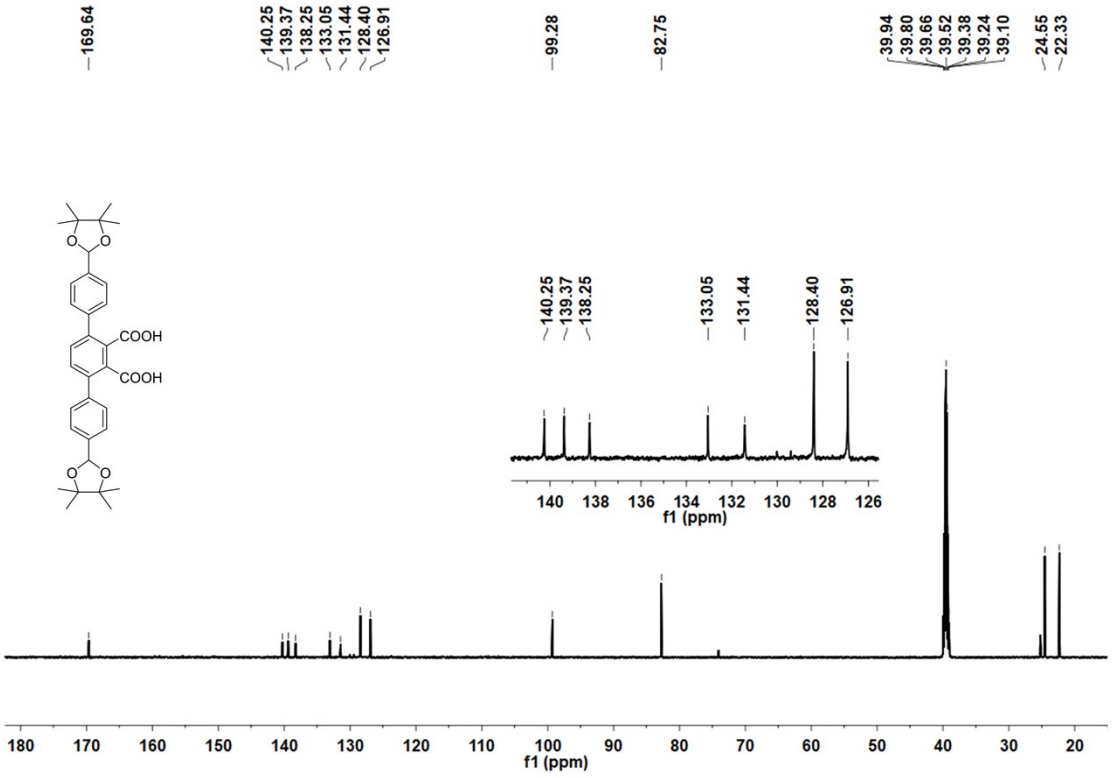


Fig. S20 ^{13}C NMR spectrum of **7** in DMSO-d_6.

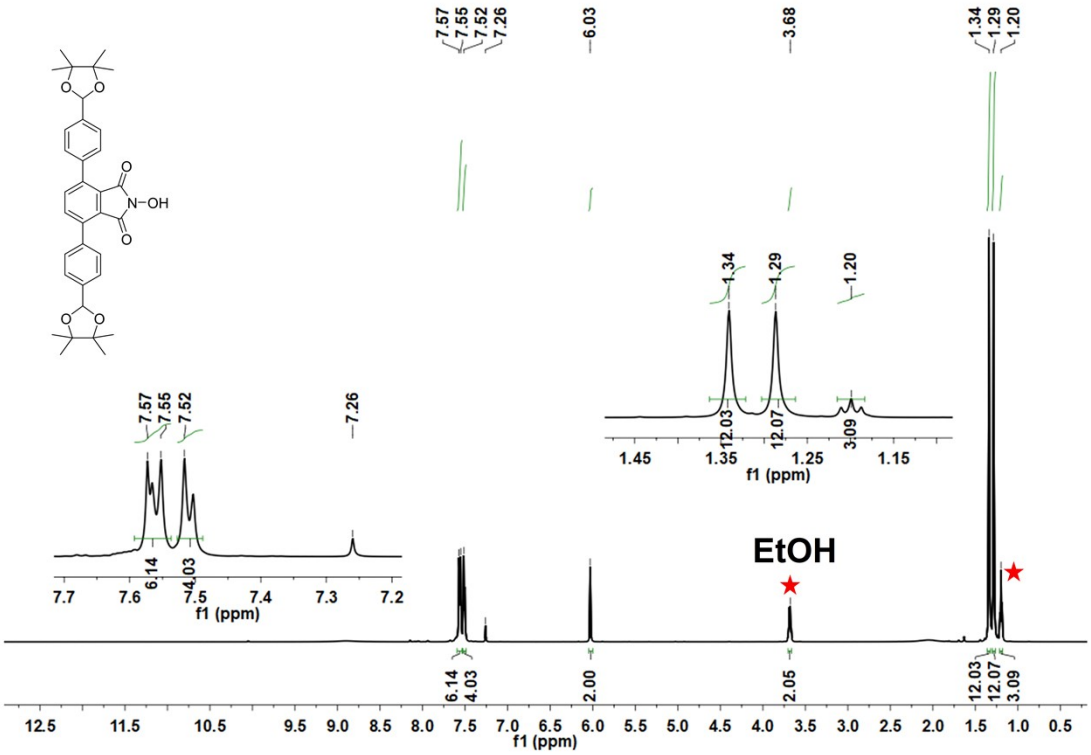


Fig. S21 ^{1}H NMR spectrum of **L1** in $CDCl_3$.

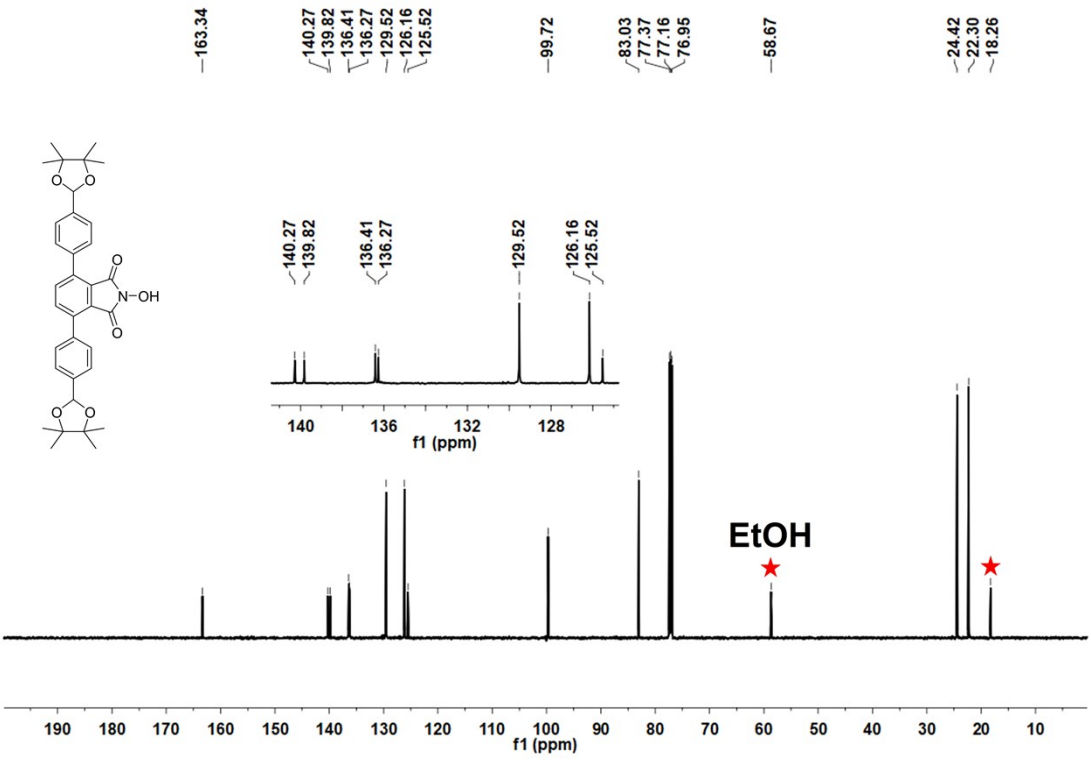


Fig. S22 ^{13}C NMR spectrum of **L1** in $CDCl_3$.

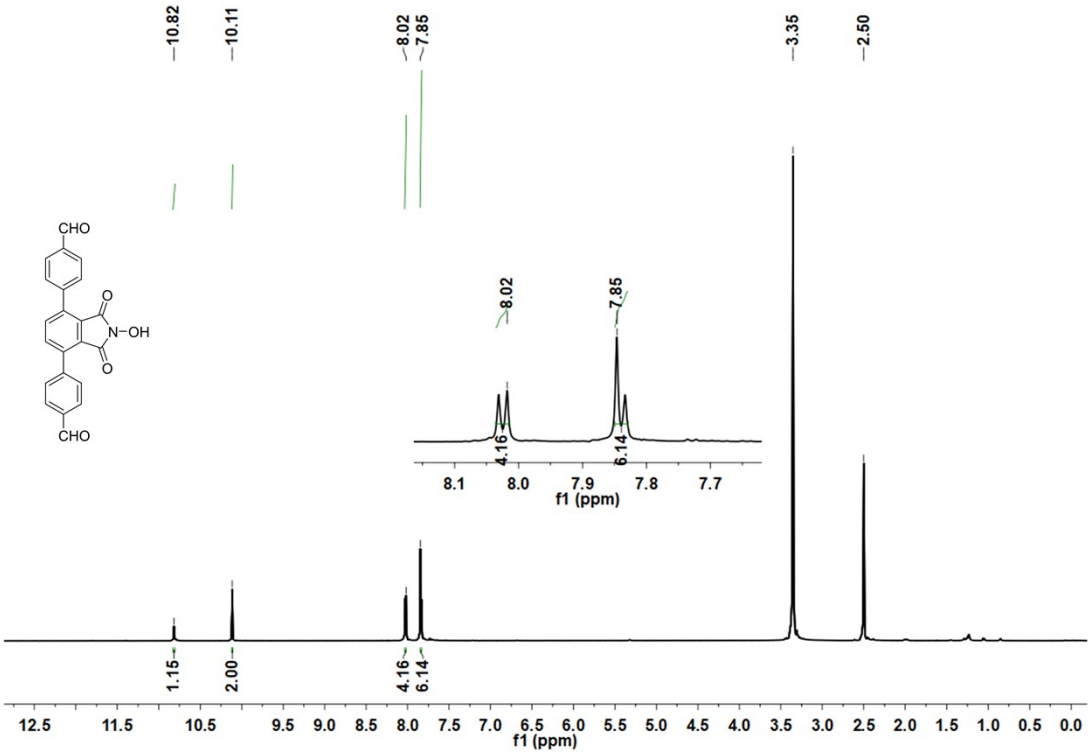


Fig. S23 ^{1}H NMR spectrum of **L2** in DMSO-d_6.

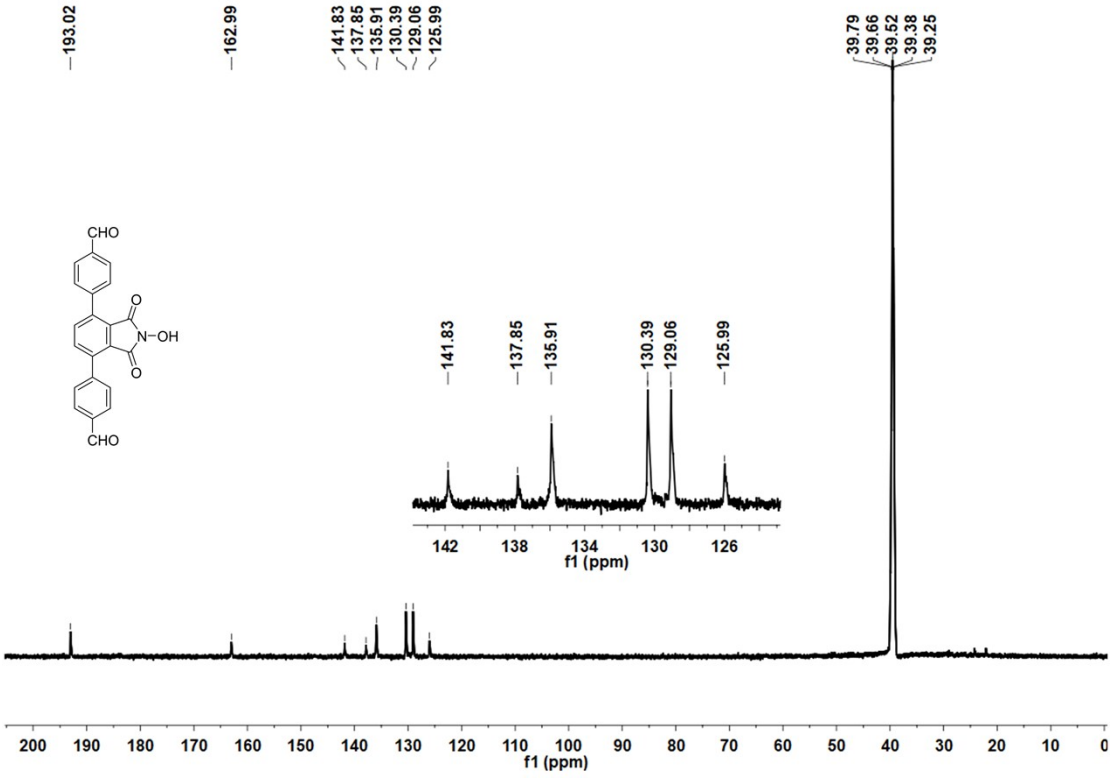


Fig. S24 ^{13}C NMR spectrum of **L2** in DMSO-d_6.

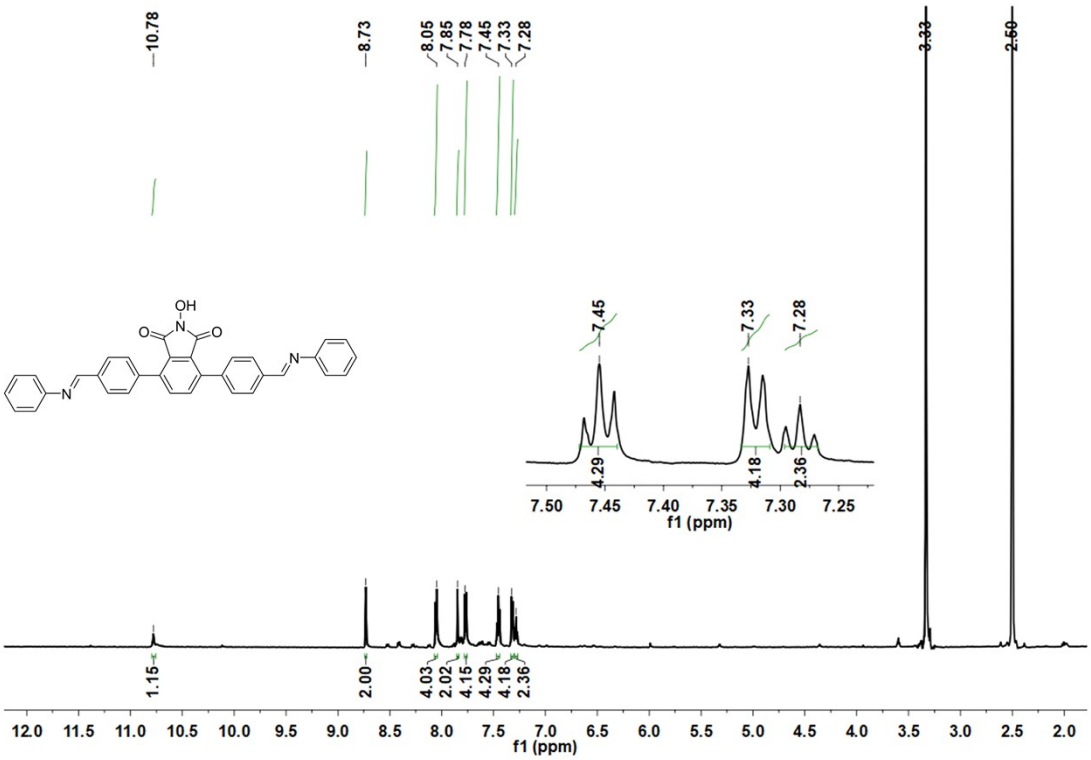


Fig. S25 ^{1}H NMR spectrum of **L1′** in DMSO-d_6.

8. References

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4 Z.-J. Li, S.-Y. Ding, H.-D. Xue, W. Cao and W. Wang, *Chem. Commun.*, 2016, **52**, 7217–7220.