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Electronic supplementary information

Squaramide-Decorated Covalent Organic Framework as a New Platform for Biomimetic Hydrogen-Bonding Organocatalysis

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General Methods. All reagents were purchased from commercial sources and used without further treatments. The solid phase ^{13}C-NMR spectra were obtained on a Varian 300 MHz Solid State Infinityplus 300 NMR spectrometer. ^{1}H NMR and ^{13}C NMR spectra was recorded on Bruker AV400 instruments at 400 MHz. Chemical shifts were reported in parts per million (ppm) down field from internal tetramethylsilane. Thermogravimetric analysis (TGA) was carried out on a Delta Series TA-SDTQ600 analyzer in nitrogen atmosphere from room temperature to 800℃ (10℃ min^{-1}) using aluminum crucibles. Powder X-ray diffraction measurements were recorded on a D/Max-2500 X-ray diffractometer using Cu-Kα radiation by depositing powder on glass substrate, from 2θ = 2° up to 40° with 1° increment. The Brunauer-Emmett-Teller (BET) surface areas were screened by nitrogen adsorption and desorption at 77 K using ASAP-2020. Pore size distributions and pore volumes were derived from the adsorption branches of the isotherms using the density functional theory (DFT) pore model for pillared clay with cylindrical pore geometry. Fourier transform infrared spectra (FTIR) spectra was recorded on a Nicolet iS 50 ATR-FTIR instument. A Hitachi SU3500 SEM

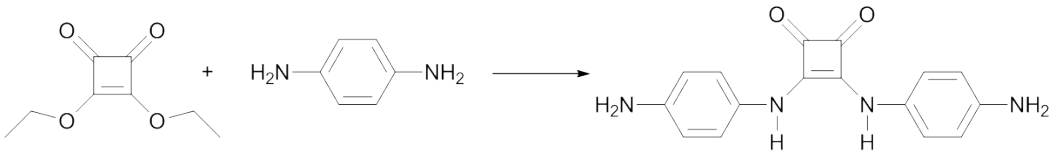
instrument was used for acquiring images using a 30 kV energy source under vacuum. Samples were transferred to conductive carbon tape on a sample holder disk, and coated by Au-sputter for 1.5min.

Refinements of PXRD pattern were done using Reflex module of Material studio. ref：Accelrys, Material Studio Release Notes, Release 4.2, Accelrys Software, San Diego 2006.

Single crystals of monmer **1** was collected at 120 K, on an Oxford SuperNova diffractometer equipped with graphite monochromated Mo-Ka radiation (λ = 0.71073 Å). The crystal data files of monomer **1** was deposited into the Cambridge Crystallographic Data Centre (CCDC) and assigned number 1839497.

Scheme S1. Synthetic scheme of monomer 1.

Synthesis of the 3,4-bis((4-aminophenyl)amino)cyclobut-3-ene-1,2-dione (1)



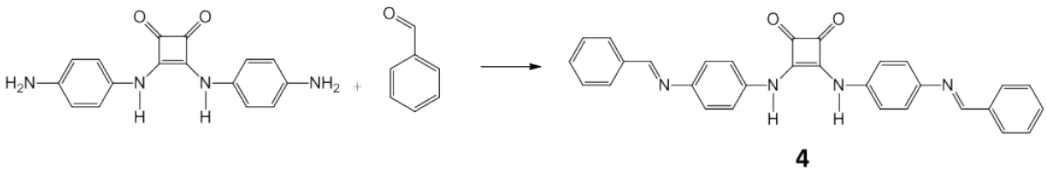
1

3,4-diethoxycyclobut-3-ene-1,2-dione (1.25 g, 7.35 mmol), benzene-1,4-diamine (1.59 g, 14.70 mmol) and EtN_3 (10.24 mL) were dissolved in 50 mL EtOH. The mixture was stirred at room temperature for 24 h. After that, the resulting precipitate was collected by filtration and washed with EtOH then Et_2O to yield the product as a beige/yellow

solid.[1] ^{1}H NMR (400 MHz, DMSO) δ 9.44 (s, 2H), 7.15 (s, 4H), 6.59 (s, 4H), 5.64 – 4.64 (m, 4H). ^{13}C NMR (101 MHz, DMSO) δ 181.21, 164.93, 145.58, 128.38, 120.47, 114.81. ESI-MS: Calcd for $C_{16}H_{14}N_4O_2$ [M]+, 294.31, found 295.1.

Scheme S2. Synthetic scheme of molecular analogue 4.

Synthesis of the model compound 3,4-bis((4-((E)-benzylideneamino)phenyl)amino)cyclobut-3-ene-1,2-dione (4)



In a 25 mL round bottom flask, 3,4-bis((4-aminophenyl)amino)cyclobut-3-ene-1,2 -dione (**1**) (58.9 mg, 0.2 mmol) was dissolved in 9.0 mL MeOH/DMF (v/v = 5:4). Then benzaldehyde (130.5 mg, 0.8 mmol) was added. The resulting mixture was transferred to an oil bath preheated to 90 °C and stirred vigorously for 24 h. After that, the resulting precipitate was collected by filtration and washed with MeOH then CH_2Cl_2 to yield the product as a off-white solid. ^{1}H NMR (400 MHz, DMSO) δ 10.00 (s, 2H), 8.67 (s, 2H), 7.95 (s, 4H), 7.54 (s, 10H), 7.38 (s, 4H). ^{13}C NMR (101 MHz, DMSO) δ 182.15, 165.83, 160.00, 147.07, 136.62, 129.05, 122.76, 119.80.

Synthesis of the COF-SQ

The synthesis of **COF-SQ** was carried out by utilizing the protocol with a mixture of

3,4-bis((4-aminophenyl)amino)cyclobut-3-ene-1,2-dione (**1**) (44.2 mg, 0.15 mmol) and 1,3,5-Triformylbenzene (**2**) (16.2 mg, 0.10 mmol) in the present of 6 M acetic acid (0.5 mL) using mesitylene (1.5 mL) and 1,4-dioxane (1.5 mL) as solvent. This mixture was sonicated for 10-15 minutes in order to get a homogenous dispersion. The tube was then flash frozen at 77 K (liquid N_2 bath) and degassed by three freeze-pump-thaw cycles. The tube was sealed off and then heated at 120 °C for 3 days. After the reaction, the **COF-SQ** powders were filtered out, and washed with THF and acetone using Soxhlet extraction for 24 h, respectively. Then it was dried under vacuum at 120 °C for 10 hours to give brown powder.

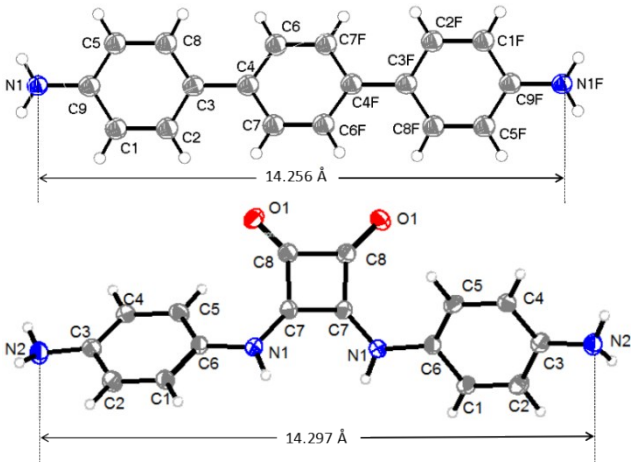


Fig. S1 Molecular structures of **1** and **3**.

Table S1 Crystal data of monomer **1**

	1
Empirical formula	$C_{16}H_{14}N_4O_2$
CCDC number	1839497
FW	294.31
T (K)	120
Space group	*C2/c*
Crystal system	monoclinic
a (Å)	13.7783 (13)
b (Å)	9.7768 (7)
c (Å)	10.5658 (8)
α (deg)	90
β (deg)	110.828 (10)
γ (deg)	90
V (Å)^3	1330.3 (2)
Z	4
ρ_{calc} *(g/ cm^3)*	1.347
μ */ mm^{-1}*	0.101
index ranges	-16≦h≦16 -11≦k≦8 -12≦l≦11
reflns collected	2386
Independent (R_{int})	1174 (0.0394)
GoF on F^2	0.847
*R*1, *ωR*2 [*I*>2σ (*I*)]	0.0523, 0.1255
*R*1, *ωR*2 (all data)	0.0775, 0.1551
largest diff. peak/hole (e/Å^{-3})	0.24/-0.22
Completeness	99.7%

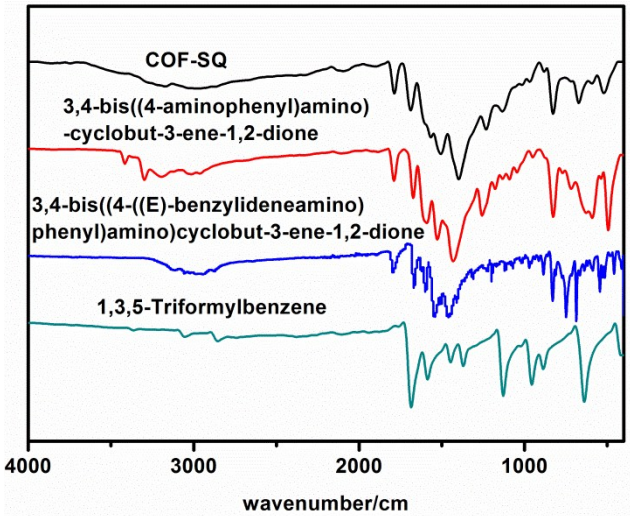


Fig. S2 FT-IR spectra of **COF-SQ**, 3,4-bis((4-aminophenyl)amino)cyclobut -3-ene-1,2-dione (**1**), 3,4-bis((4-((E)-benzylideneamino)phenyl)amino)cyclobut-3-ene -1,2-dione (**4**) and benzene-1,3,5-tricarbaldehyde (**2**).

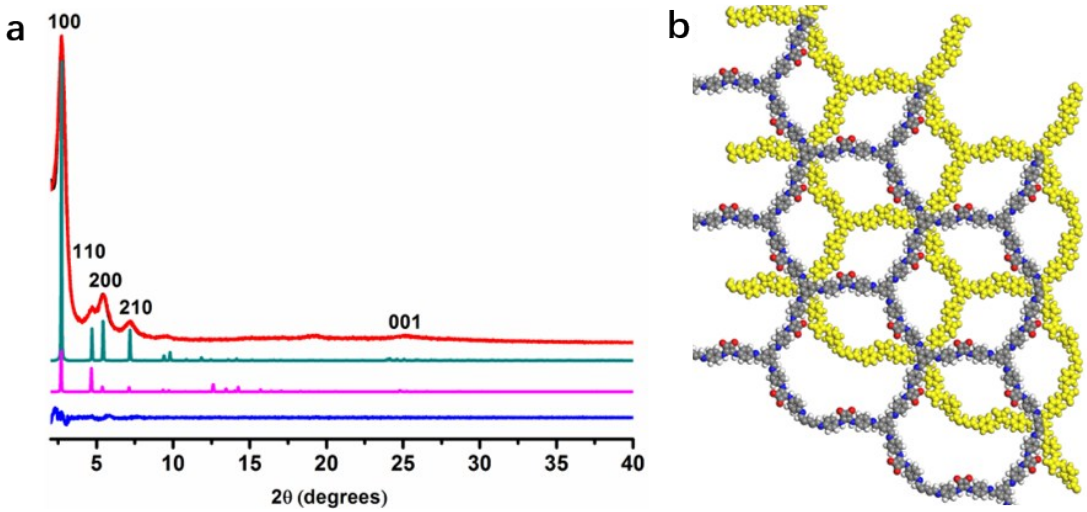


Fig. S3 *Left*: Comparison AA and AB packing PXRD patterns for **COF-SQ**: experimental (red) as well as calculated from the eclipsed (green) and staggered (pink) stacking models. *Right*: Proposed structure of **COF-SQ.**

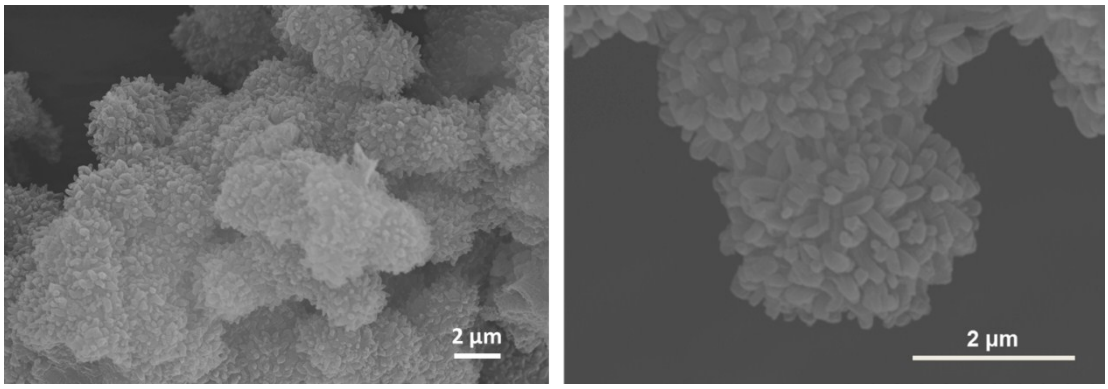


Fig. S4 Scanning electron microscopy (SEM) of **COF-SQ.**

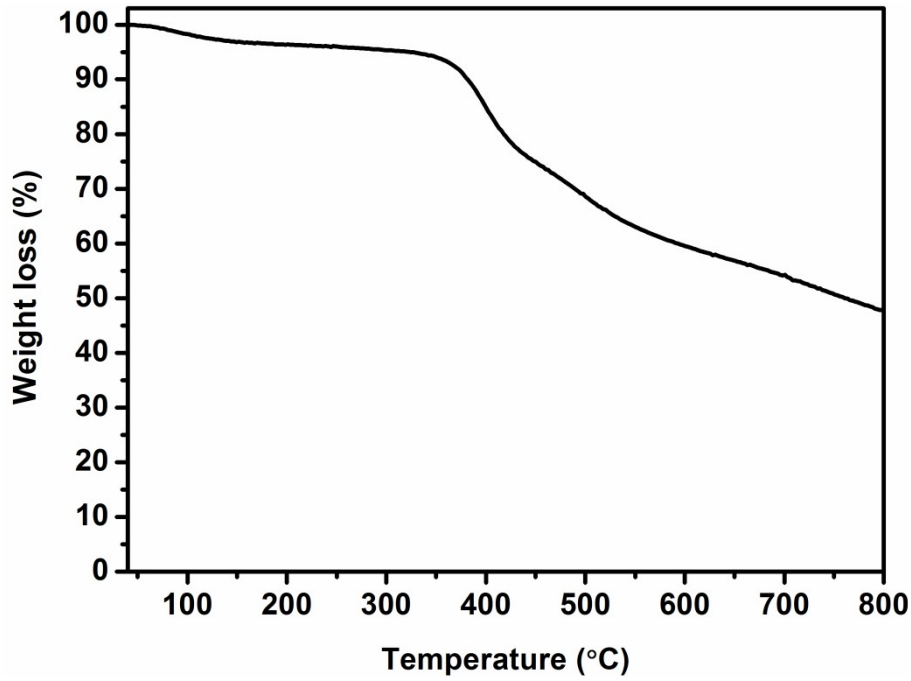


Fig. S5 TGA trace of **COF-SQ.**

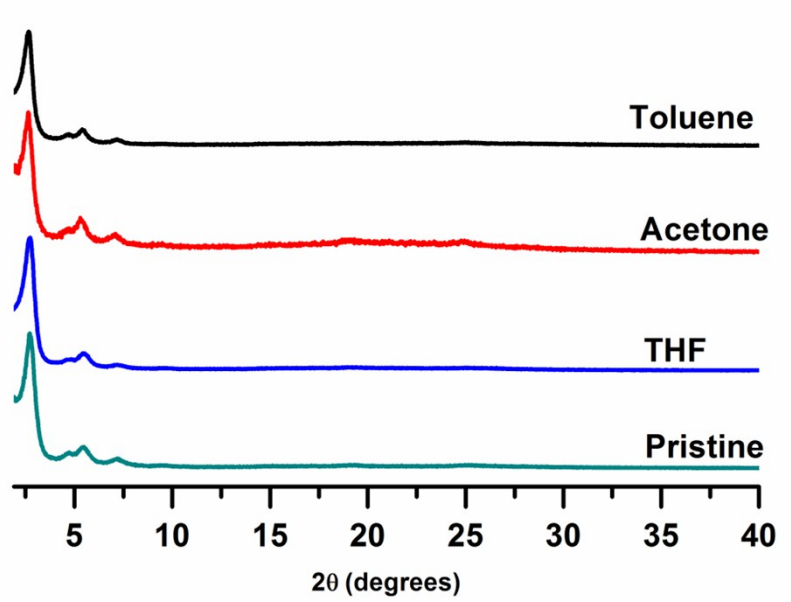


Fig. S6 For the stability tests, 10.0 mg of the COF sample was placed in a 10.0 mL scintillation vial with 5.0 mL of the treatment solution. After 24 hours, the solvent was decanted and the material was transferred to a Soxhlet extractor and washed with THF for 12 h. Then the material was dried under vacuum at 120 °C for 10 hours.

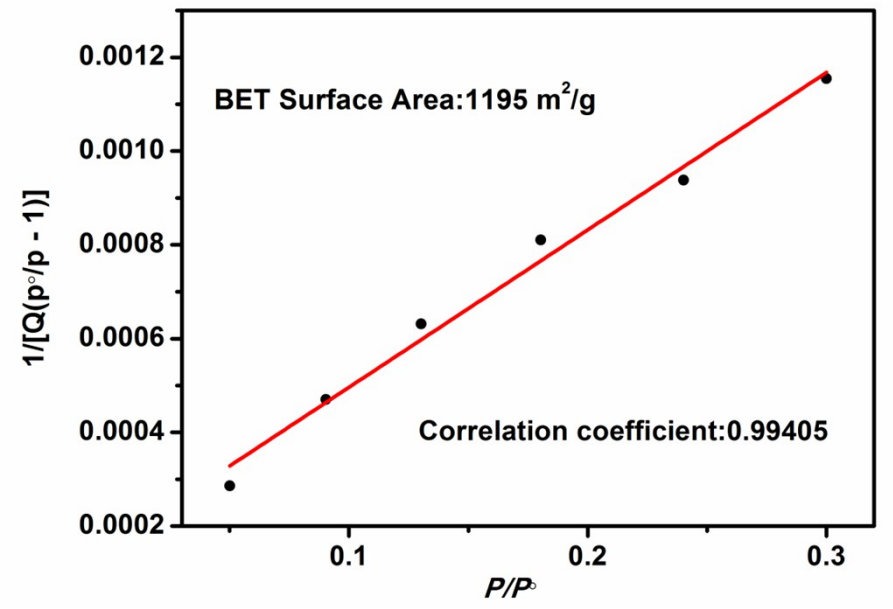


Fig. S7 Multiple point BET plot of **COF-SQ** giving a specific surface area of 1195

m^2/g.

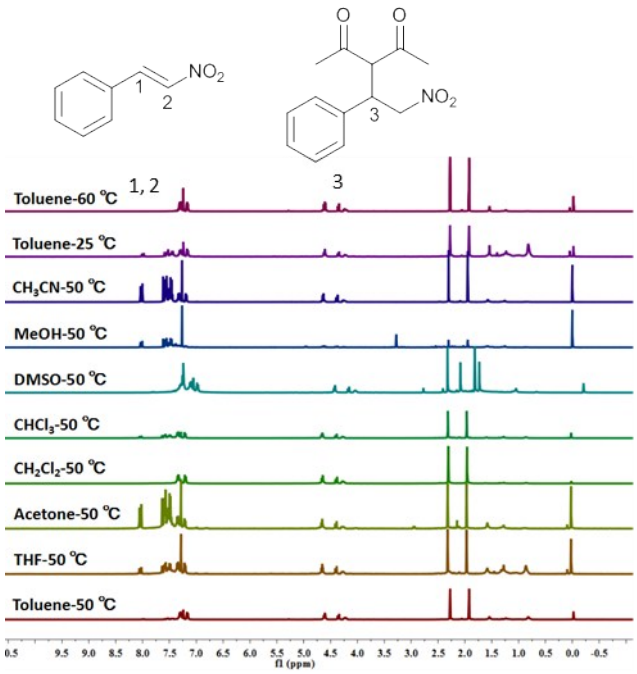


Fig. S8 ^{1}H NMR spectrum (400 MHz) monitoring the reaction between acetylacetone and *β*-nitrostyrene in toluene, CH_3CN, MeOH, DMSO, $CHCl_3$, CH_2Cl_2, acetone and THF solvents. The reaction was carried out using 10 mol% of **COF-SQ** catalyst in 1.0 mL of solvent for 24 h at the temperature indicated in the figure.

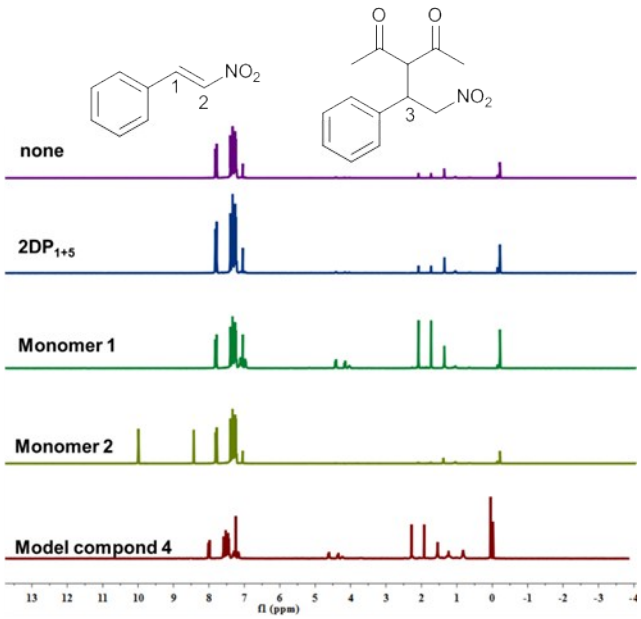


Fig. S9 ^{1}H NMR spectrum (400 MHz) monitored the reaction between acetylacetone and *β*-nitrostyrene with no catalyst, **2DP$_{1+5}$**, monomer **1**, monomer **2** and model compound **4** at 50 ºC for 24 h (10 mol% loading of catalyst).

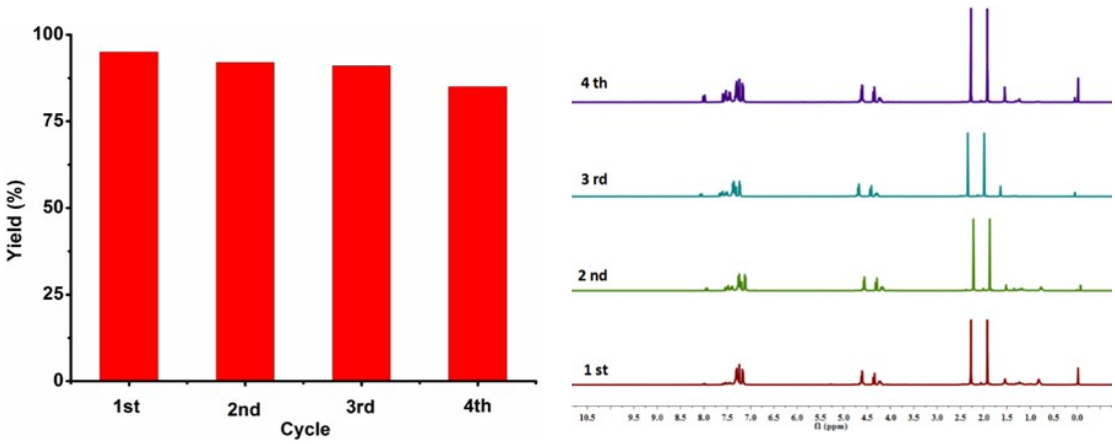


Fig. S10 *Left*: ^{1}H NMR spectrum (400 MHz) of catalyst recycling performed with 10 mol% of **COF-SQ** in toluene at 50 ºC for 24 h. *Right*: Graphical depiction of the reaction yield for each run.

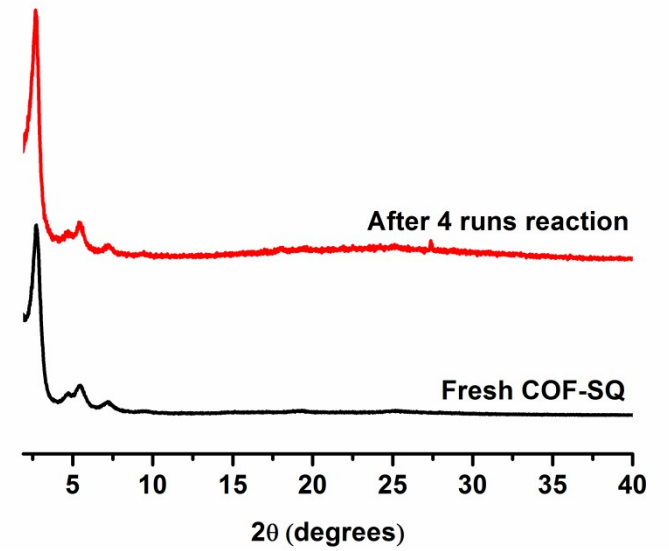


Fig. S11 PXRD patterns experimental **COF-SQ** before catalysis (black), and experimental **COF-SQ** catalyst after 4 reaction cycles (red).

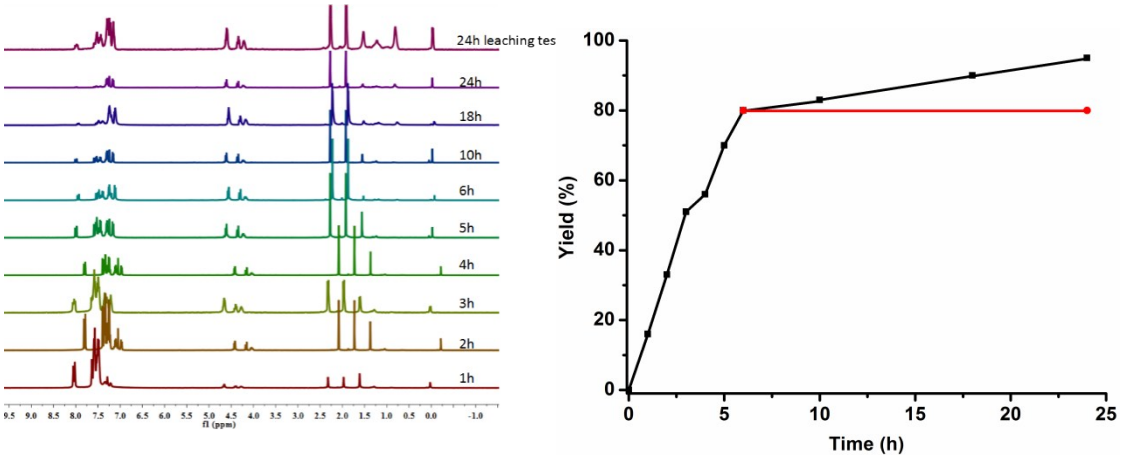


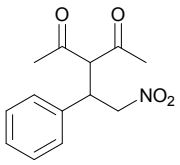
Fig. S12 *Left*: ^{1}H NMR spectrum (400 MHz) of the reaction between acetylacetone and *β*-nitrostyrene from 1 h to 24 h using 10 mol% of **COF-SQ** catalyst at 50 ºC. *Right*: Graphical depiction of the reaction conversion at each time point (black line). A test was performed with the same catalysis procedure where the reaction progress was measured after 6h, and then the COF was removed using a PTFE microfilter. The reaction progress was again measured after another 18 h, which showed no progression

of the reaction (red line, and top ^{1}H NMR spectrum at left).

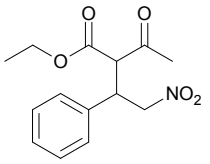
General Procedure for Catalysis Experiments.

Acetylacetone (10.0 mg, 0.15 mmol), β-nitrostyrene (15.0 mg, 0.1 mmol), and 10 mol% COF catalyst were added to 1.0 mL of dry toluene in a 8.0 mL glass vial. The reaction mixture was incubated at 50 ºC for 24 h. After cooling down, the COF was filtered off and the solution was evaporated under vacuum to remove the solvent and 500 μL $CDCl_3$ was used to dissolve the product for ^{1}H NMR analysis.[2]

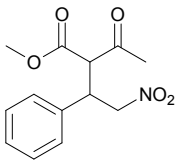
The reaction was monitored by ^{1}H NMR spectroscopy via the integration of α-vinyl and β-vinyl proton of β-nitrostyrene (δ 8.02 - 8.07 ppm) and the resulting aliphatic proton of the product 3-(2-nitro-1-phenylethyl)pentane-2,4-dione (δ 4.15 - 4.58 ppm). To test recyclability, the supernatant was separated from the catalyst by centrifugation. The solid catalysts were soaked in the THF and acetone for 24 h. After soaking, the solids were centrifuged and dried in air. The dried COFs were directly used for the next run of Michael addition catalysis.



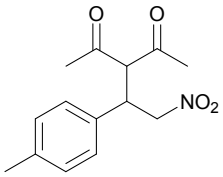
3-**(2-nitro-1-phenylethyl)pentane-2,4-dione (3aa).** Flash column chromatography (3:1 hexanes : EtOAc) afforded **3aa** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 3H), 7.13 (s, 2H), 4.56 (s, 2H), 4.31 (d, J = 10.8 Hz, 1H), 4.19 (s, 1H), 2.21 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.77, 201.04, 136.02, 129.34, 128.55, 127.96, 78.18, 77.38, 77.07, 76.75, 70.67, 42.80, 30.46, 29.61.



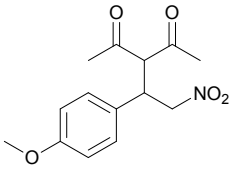
ethyl 2-acetyl-4-nitro-3-phenylbutanoate (3ab). Flash column chromatography (3:1 hexanes : EtOAc) afforded **3ab** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 3H), 7.23 (s, 2H), 4.91 – 4.72 (m, 2H), 4.33 – 4.17 (m, 2H), 4.17 – 4.02 (m, 1H), 3.98 (t, J = 10.7 Hz, 1H), 2.32 (s, 1H), 2.07 (s, 1H), 1.29 (s, 2H), 1.02 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.20, 200.38, 167.54, 166.88, 136.41 (d, J = 5.9 Hz), 129.18, 128.96, 128.35 (d, J = 8.5 Hz), 127.96 (d, J = 7.8 Hz), 77.86 (d, J = 9.9 Hz), 77.39, 77.07, 76.75, 62.24, 61.99, 61.68, 42.56, 42.31, 30.33, 30.13, 14.00, 13.69.



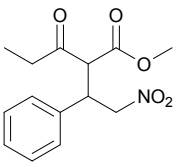
methyl 2-acetyl-4-nitro-3-phenylbutanoate (3ac). Flash column chromatography (3:1 hexanes : EtOAc) afforded **3ac** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 3H), 7.22 (d, J = 7.4 Hz, 2H), 4.91 – 4.72 (m, 2H), 4.34 – 4.18 (m, 1H), 4.11 (dd, J = 33.3, 9.7 Hz, 1H), 3.78 (s, 1H), 3.53 (s, 1H), 2.30 (s, 1H), 2.06 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.19, 200.34, 168.04, 167.41, 136.35 (d, J = 15.3 Hz), 129.12 (d, J = 17.8 Hz), 128.38 (d, J = 10.6 Hz), 127.88 (d, J = 4.2 Hz), 77.96 – 77.40 (m), 77.09, 76.77, 61.81, 61.41, 53.02, 52.82, 42.61, 42.31, 30.37 (d, J = 12.8 Hz).



4-(2-nitro-1-(p-tolyl)ethyl)pentane-2,4-dione (3ba). Flash column chromatography (3:1 hexanes : EtOAc) afforded **3ba** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (dd, J = 25.2, 8.1 Hz, 4H), 4.67 – 4.57 (m, 2H), 4.37 (d, J = 10.9 Hz, 1H), 4.26 – 4.18 (m, 1H), 2.31 (d, J = 5.4 Hz, 6H), 1.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.93, 201.16, 138.38, 132.81, 130.02, 127.79, 78.38, 77.37, 77.06, 76.74, 70.83, 42.46, 30.44, 29.48, 21.08.

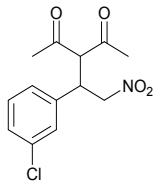


3-(1-(4-methoxyphenyl)-2-nitroethyl)pentane-2,4-dione (3ca). Flash column chromatography (3:1 hexanes : EtOAc) afforded **3ca** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 8.6 Hz, 2H), 6.99 (d, J = 8.6 Hz, 2H), 4.74 (d, J = 6.4 Hz, 2H), 4.48 (d, J = 10.9 Hz, 1H), 4.39 – 4.30 (m, 1H), 3.92 (s, 3H), 2.43 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.89, 201.21, 159.51, 129.09, 114.68, 78.45, 77.38, 77.07, 76.75, 70.89, 55.23, 42.13, 30.39, 29.50.

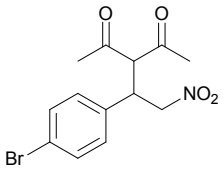


methyl 2-(2-nitro-1-phenylethyl)-3-oxopentanoate (3ad). Flash column chromatography (3:1 hexanes : EtOAc) afforded **3ad** as a white solid. ^{1}H NMR (400

MHz, $CDCl_3$) δ 7.46 – 7.03 (m, 5H), 4.96 – 4.66 (m, 2H), 4.24 (dt, J = 10.0, 4.5 Hz, 1H), 4.09 (dd, J = 42.7, 9.6 Hz, 1H), 3.65 (d, J = 92.2 Hz, 3H), 2.74 – 2.02 (m, 2H), 1.26 (s, 2H), 1.06 (t, J = 7.2 Hz, 1H), 0.83 (t, J = 7.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.19, 203.19, 168.08, 167.57, 136.52, 136.31, 129.11 (d, J = 11.8 Hz), 128.35 (d, J = 7.2 Hz), 127.85 (d, J = 12.7 Hz), 77.86 – 77.26 (m), 77.04, 76.73, 60.90, 60.64, 52.97, 42.76, 42.45, 37.14, 36.82, 29.72, 7.36 (d, J = 19.2 Hz).



4-(1-(3-chlorophenyl)-2-nitroethyl)pentane-2,4-dione (3da). Flash column chromatography (3:1 hexanes : EtOAc) afforded **3da** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, J = 7.1, 2.1 Hz, 1H), 7.25 (dd, J = 6.7, 3.1 Hz, 2H), 7.19 – 7.12 (m, 1H), 4.84 (dd, J = 12.2, 6.7 Hz, 1H), 4.78 – 4.71 (m, 1H), 4.66 (dd, J = 12.2, 3.9 Hz, 1H), 4.60 (d, J = 9.9 Hz, 1H), 2.29 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.92, 200.87, 133.78, 133.42, 130.68, 129.74, 127.68, 77.36, 77.04, 76.72, 76.20, 69.00, 38.84, 30.91, 29.71, 28.46.



3-(1-(4-bromophenyl)-2-nitroethyl)pentane-2,4-dione (3ea). Flash column chromatography (3:1 hexanes : EtOAc) afforded **3ea** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 4.68 – 4.53 (m, 2H), 4.33 (d, J = 10.7 Hz, 1H), 4.27 – 4.17 (m, 1H), 2.30 (s, 3H), 1.98 (s, 3H). ^{13}C NMR

(101 MHz, $CDCl_3$) δ 201.40, 200.59, 135.09, 132.53, 129.65, 122.68, 77.85, 77.38, 77.06, 76.74, 70.44, 42.20, 30.48, 29.73.

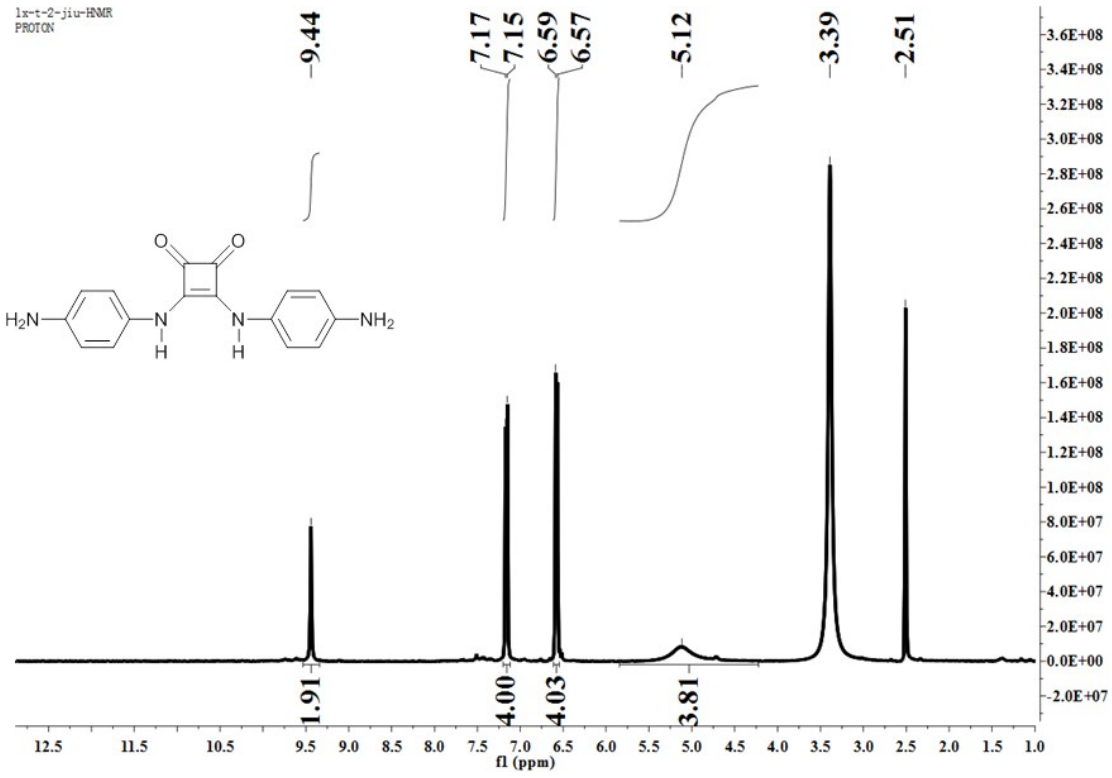


Fig. S13 ^{1}H NMR spectrum (400 MHz) of monomer **1**.

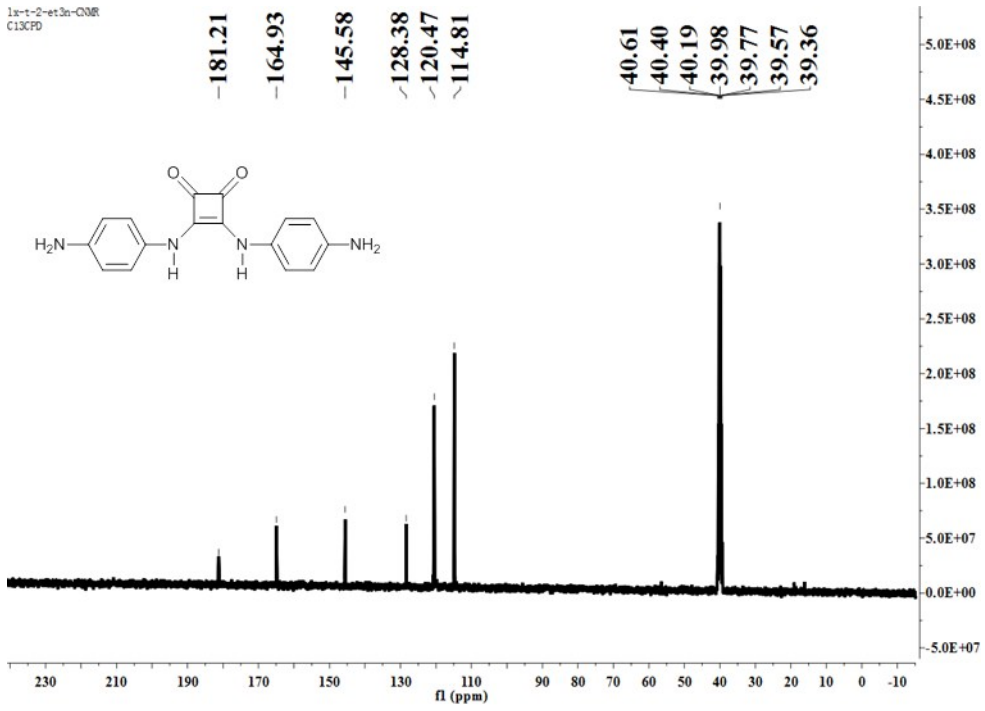


Fig. S14 ^{13}**C** NMR spectrum (101 MHz) of monomer **1**.

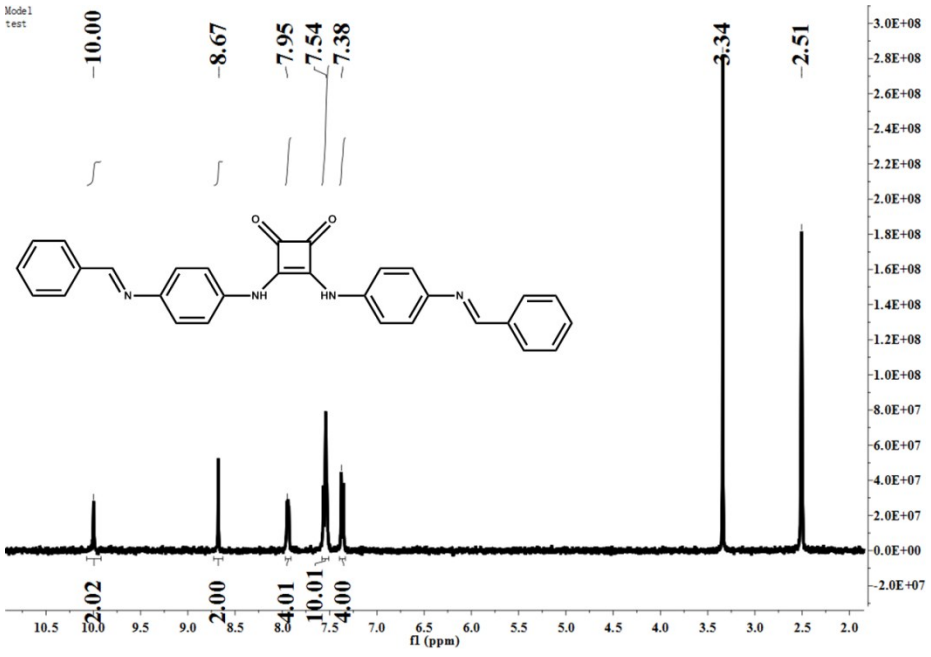


Fig. S15 ^{1}H NMR spectrum (400 MHz) of model compound **4**.

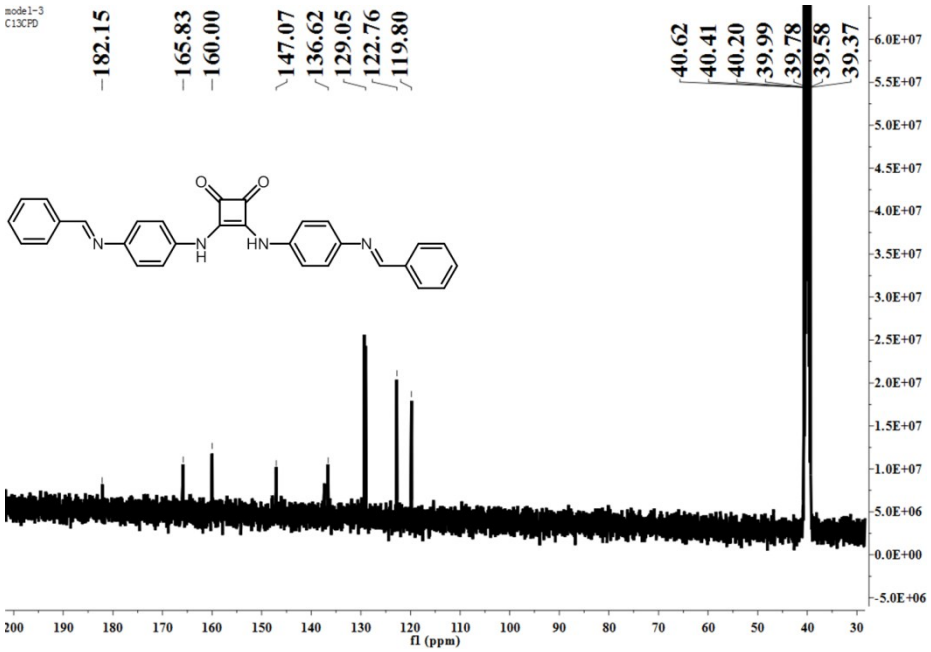


Fig. S16 ^{13}C NMR spectrum (101 MHz) of model compound **4**.

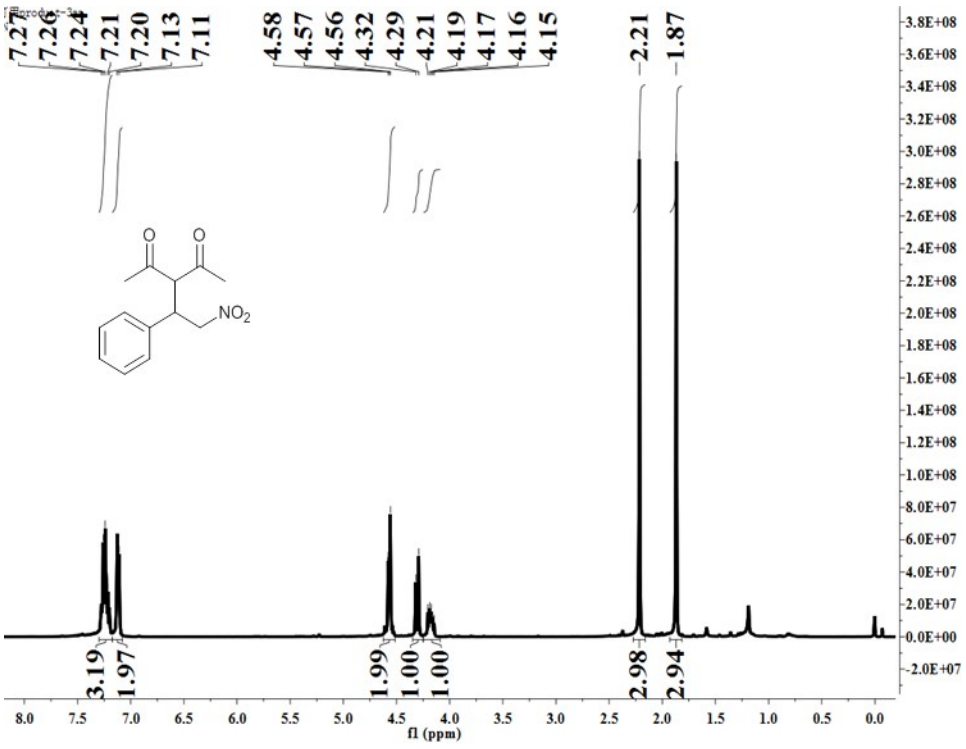


Fig. S17 ^{1}H NMR spectrum (400 MHz) of **3aa**.

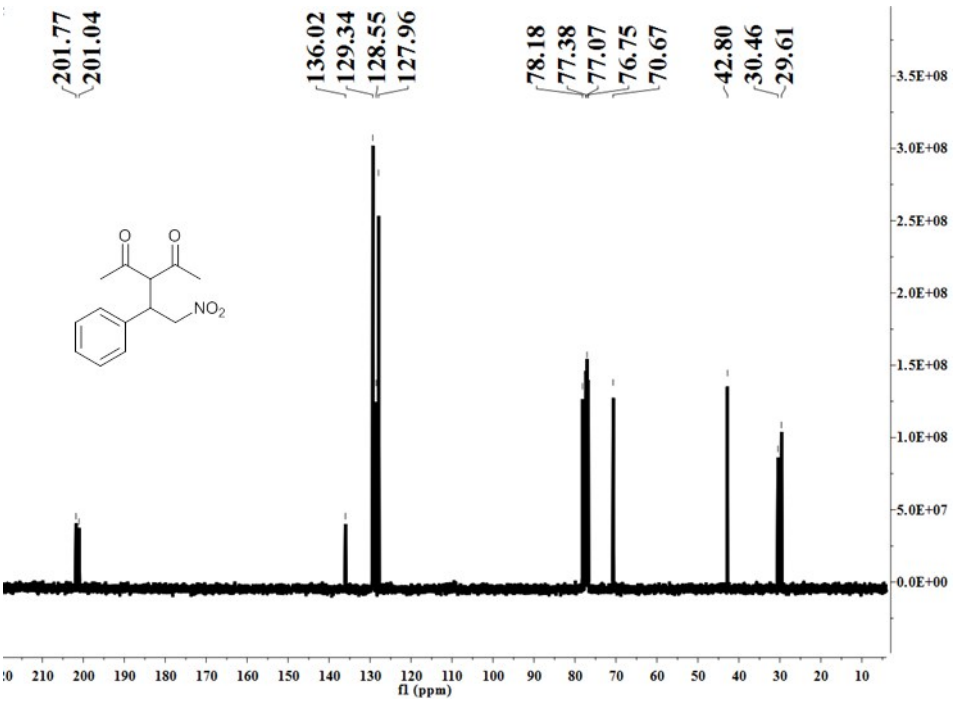


Fig. S18 ^{13}**C** NMR spectrum (101 MHz) **3aa**.

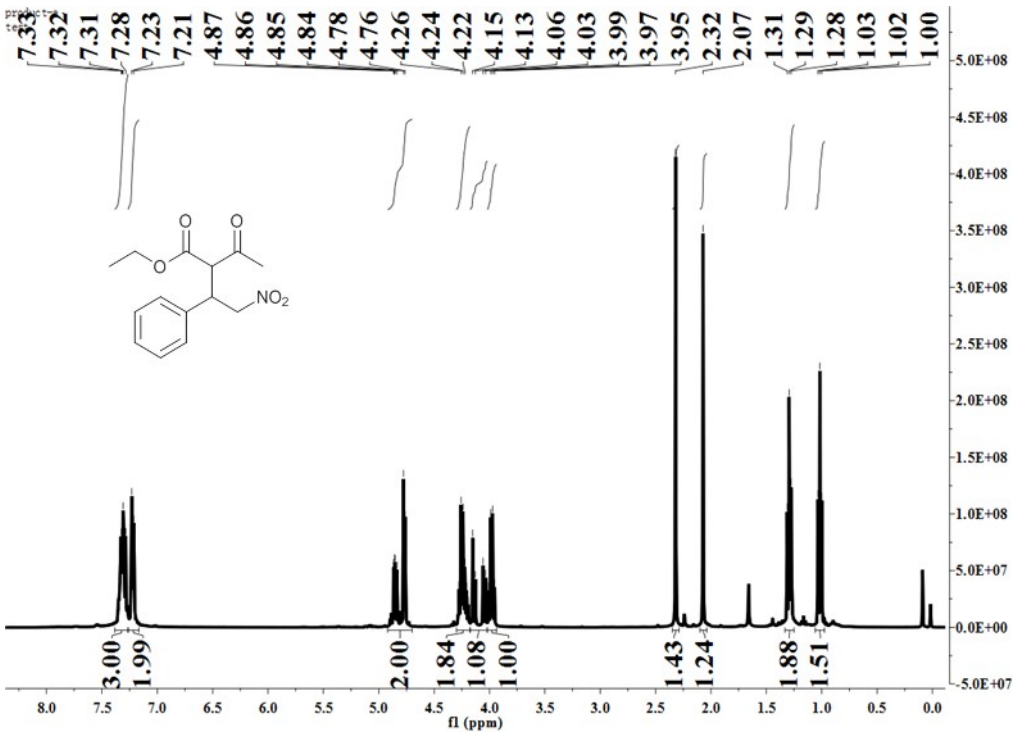


Fig. S19 ^{1}H NMR spectrum (400 MHz) of **3ab**.

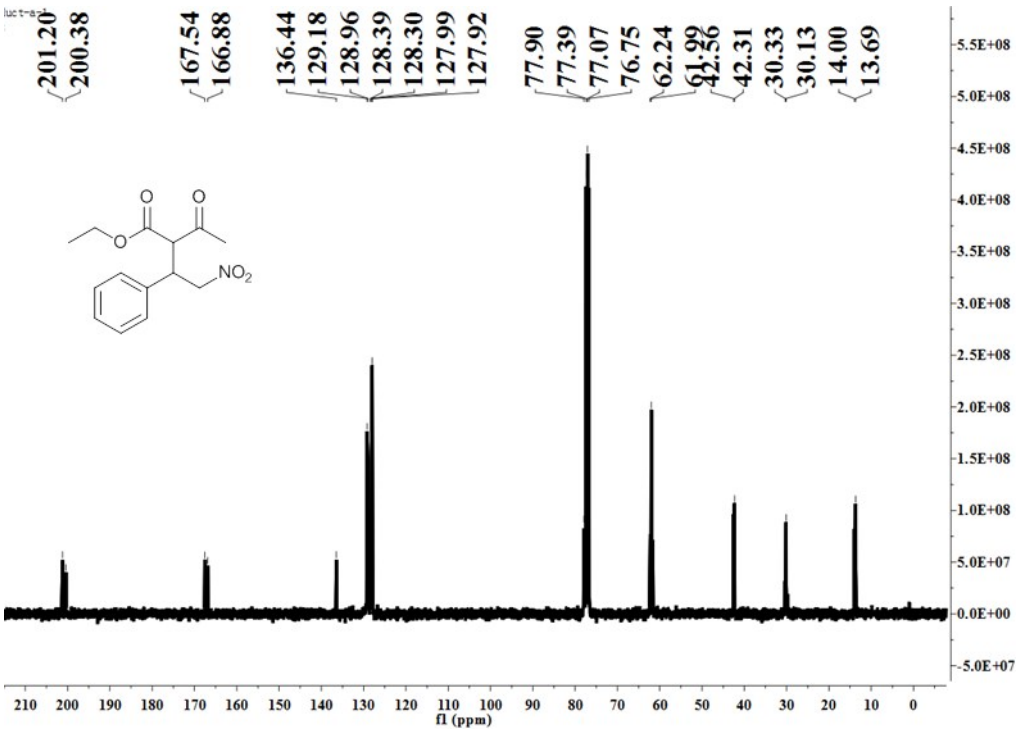


Fig. S20 ^{13}**C** NMR spectrum (101 MHz) **3ab**.

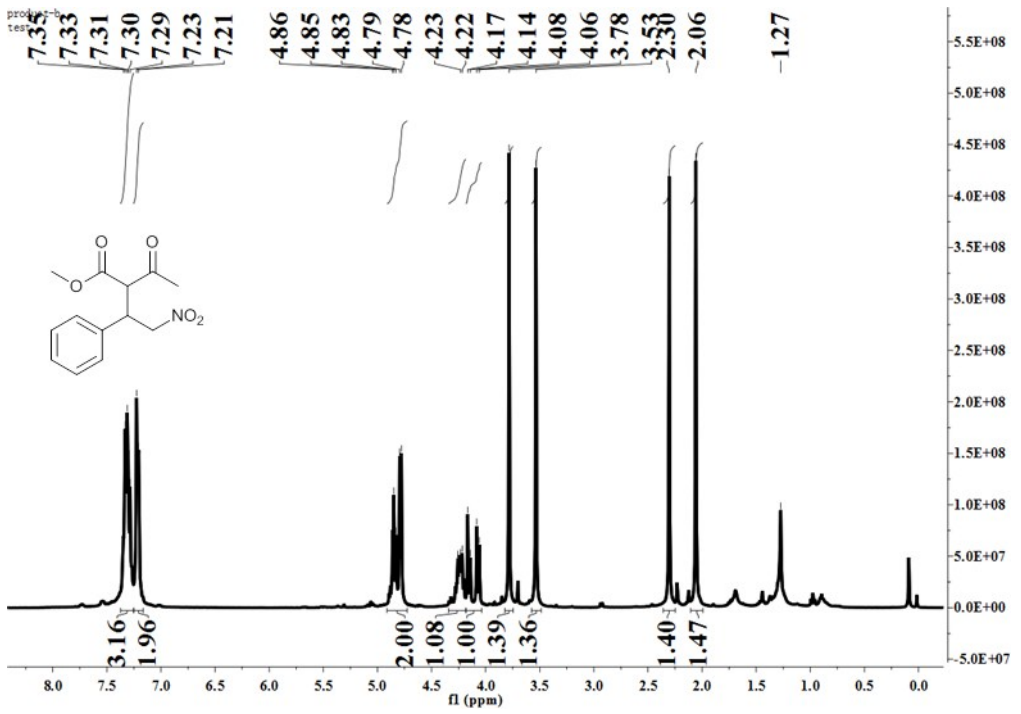


Fig. S21 ^{1}H NMR spectrum (400 MHz) of **3ac.**

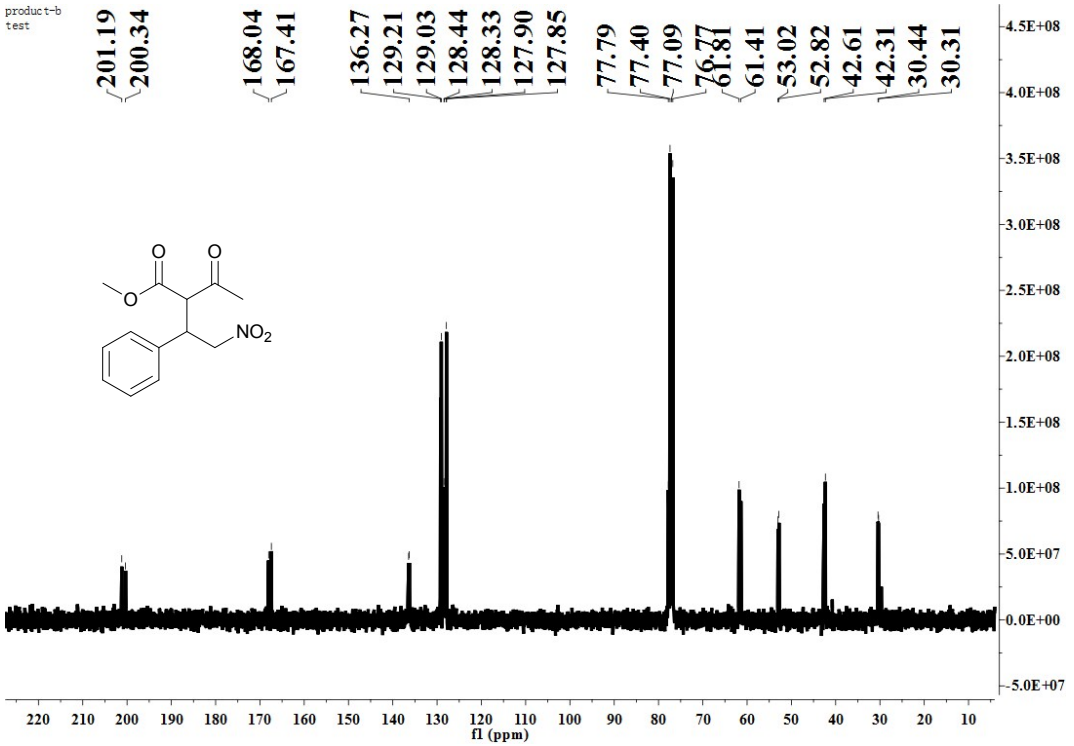


Fig. S22 ^{13}**C** NMR spectrum (101 MHz) **3ac**.

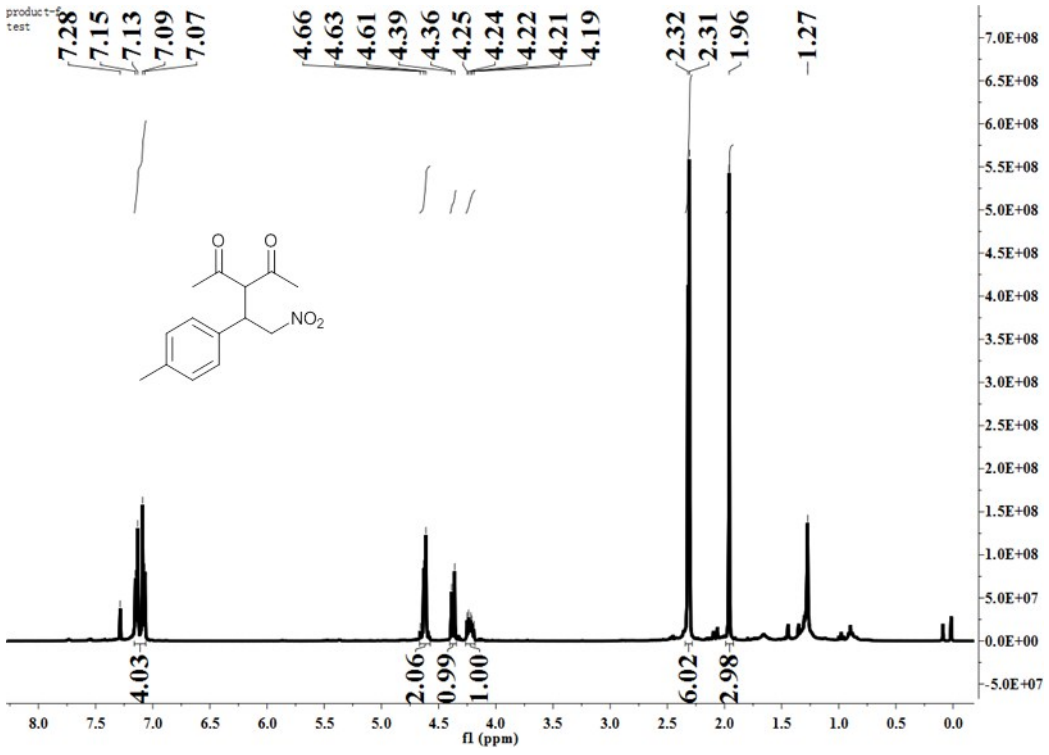


Fig. S23 ^{1}H NMR spectrum (400 MHz) of **3ba.**

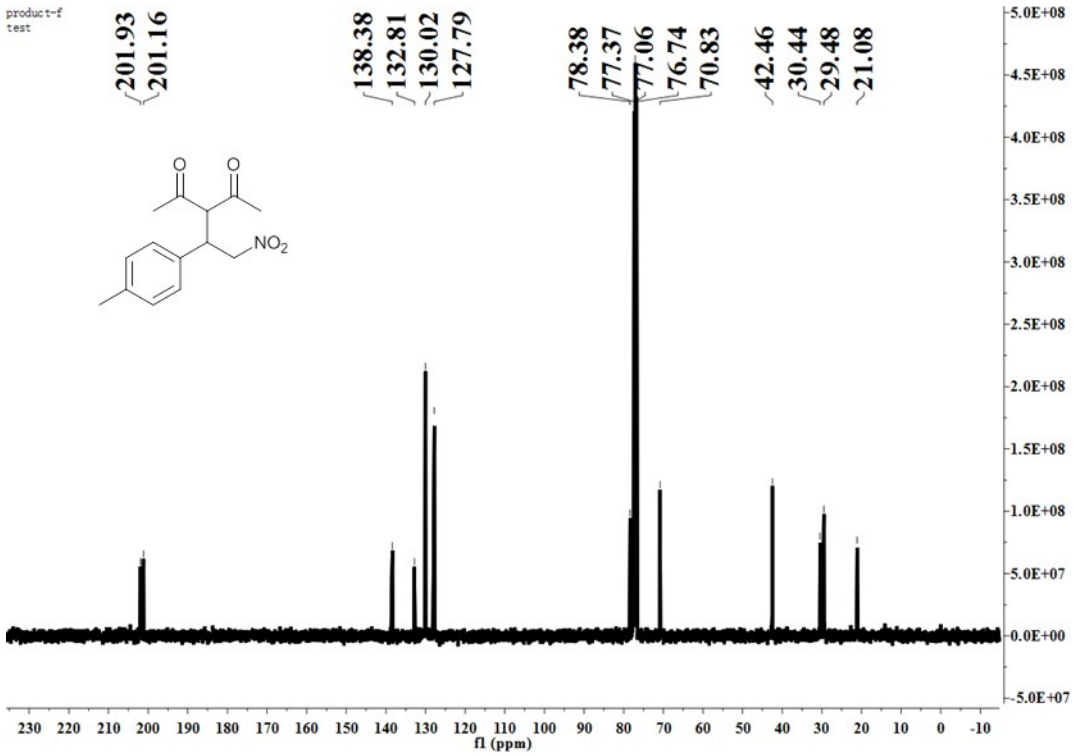


Fig. S24 ^{13}**C** NMR spectrum (101 MHz) **3ba**.

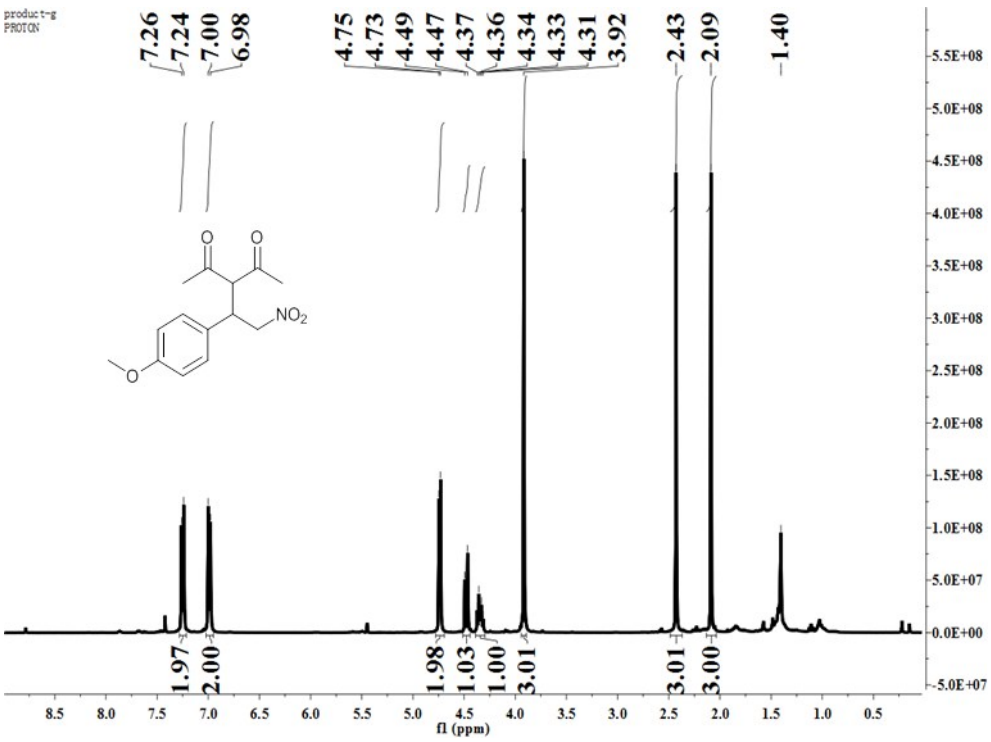


Fig. S25 ^{1}H NMR spectrum (400 MHz) of **3ca.**

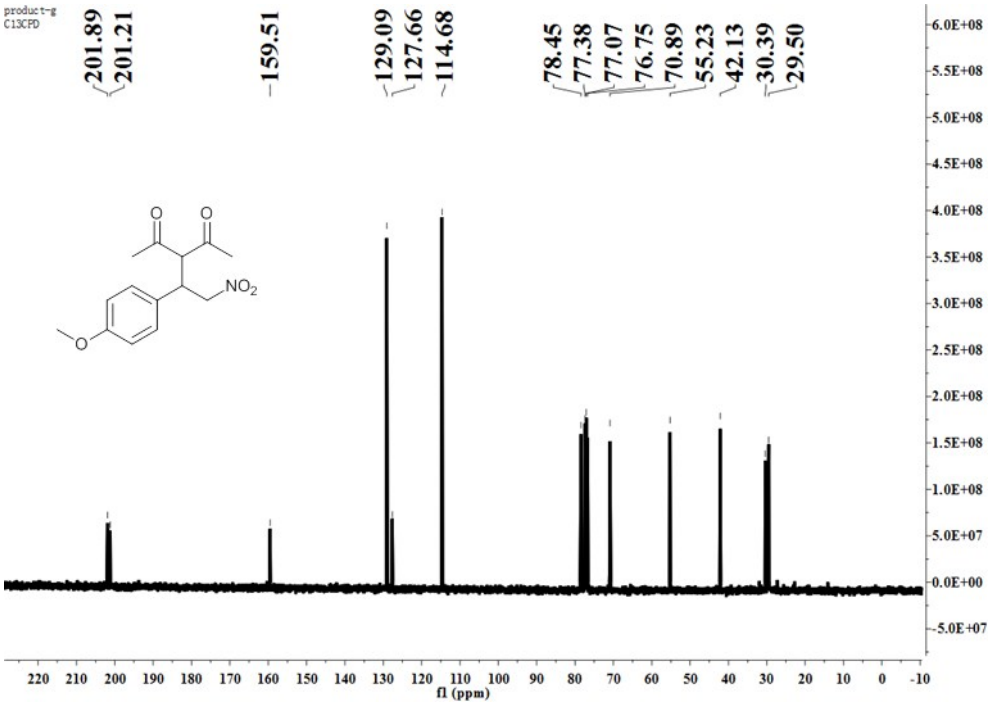


Fig. S26 ^{13}**C** NMR spectrum (101 MHz) **3ca**.

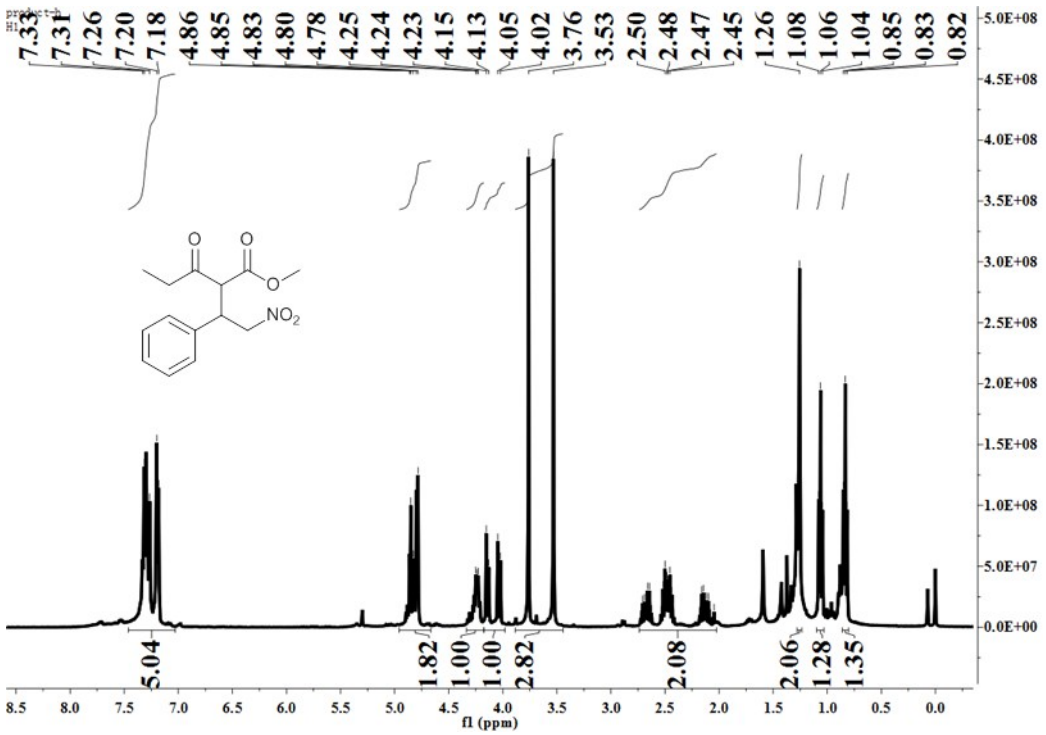


Fig. S27 ^{1}H NMR spectrum (400 MHz) of **3ad.**

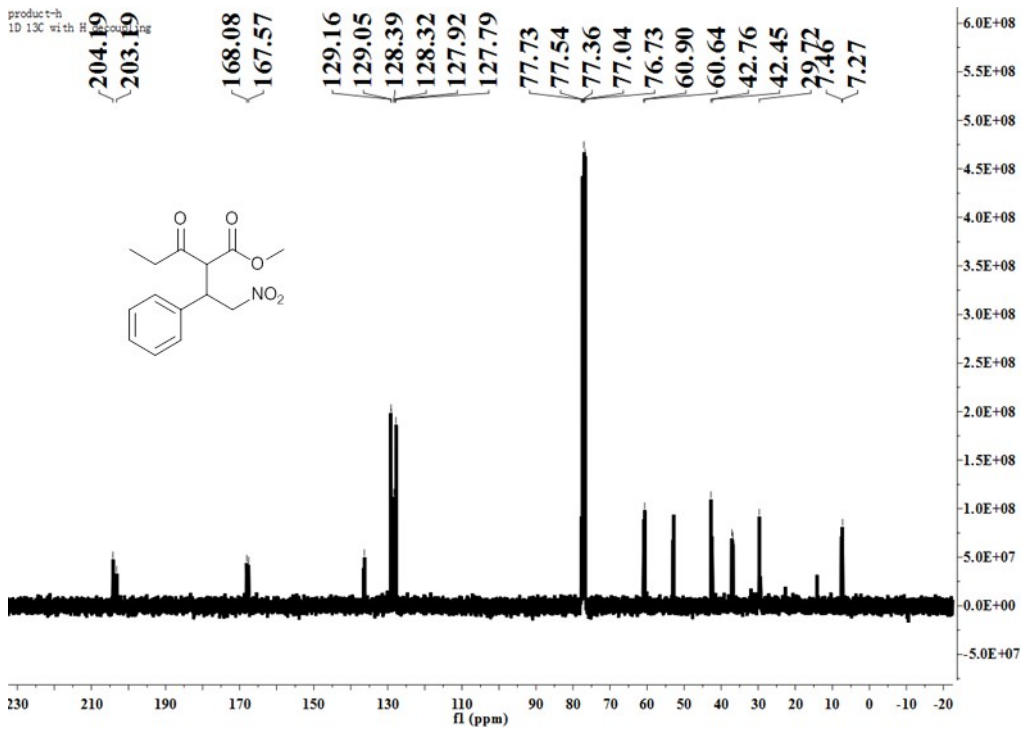


Fig. S28 ^{13}**C** NMR spectrum (101 MHz) **3ad**.

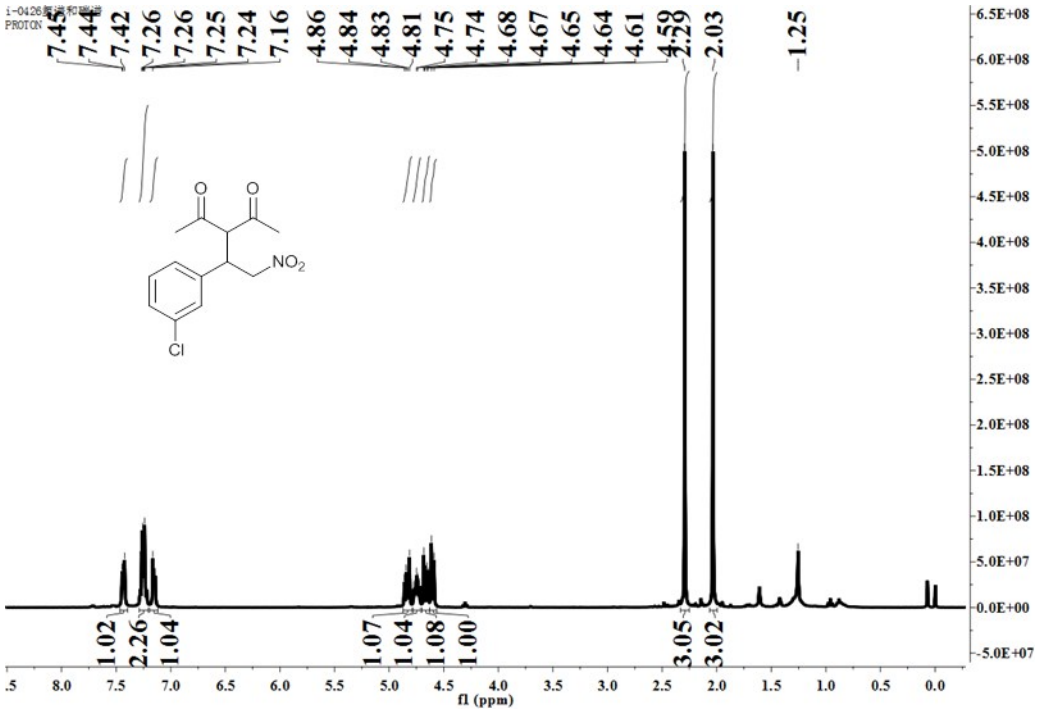


Fig. S29 ^{1}H NMR spectrum (400 MHz) of **3da.**

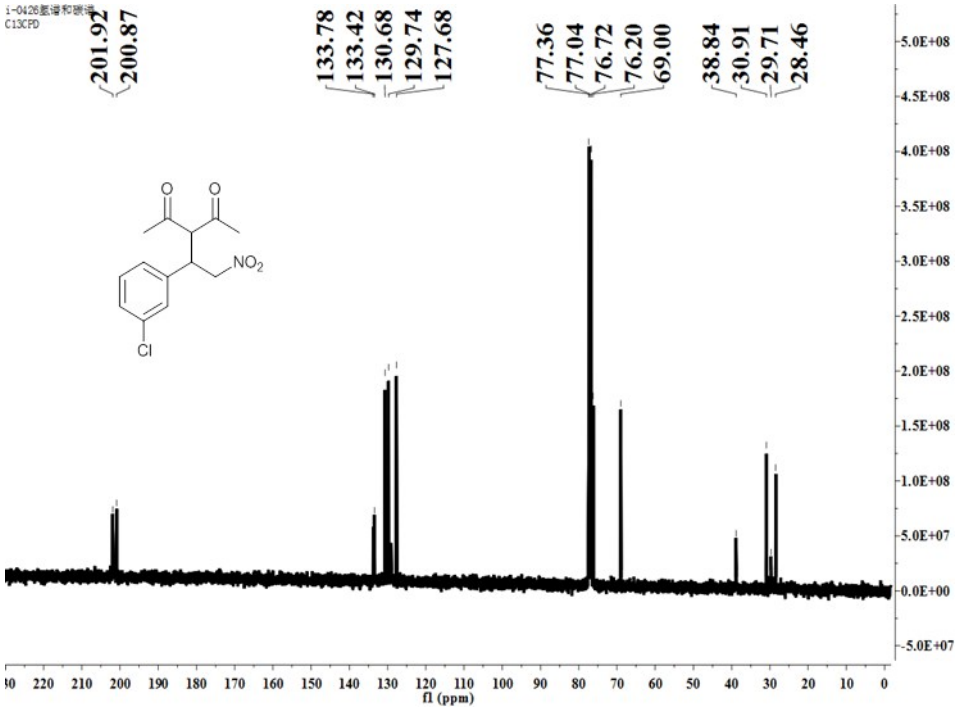


Fig. S30 ^{13}**C** NMR spectrum (101 MHz) **3da**.

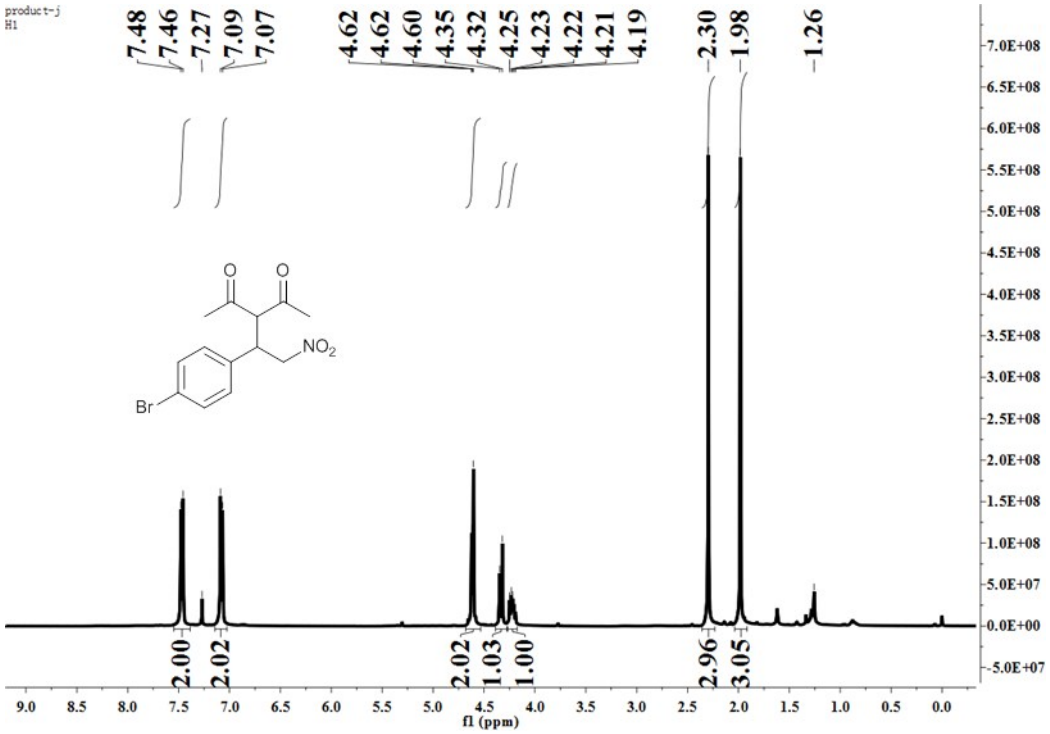


Fig. S31 ^{1}H NMR spectrum (400 MHz) of **3ea.**

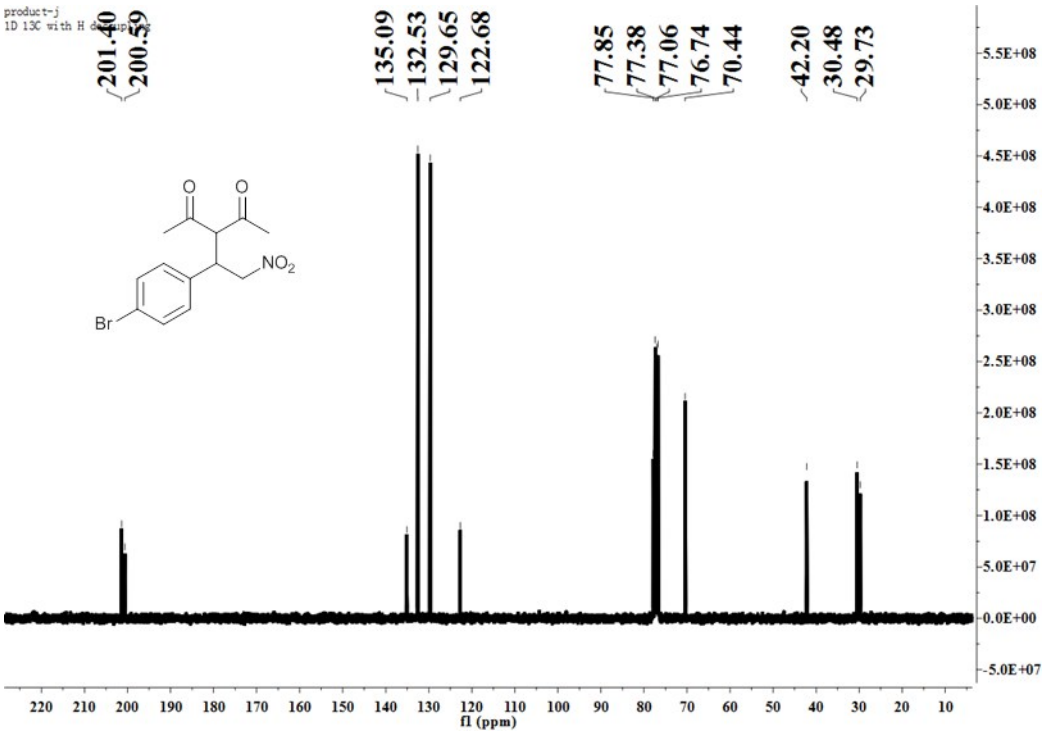


Fig. S32 ^{13}**C** NMR spectrum (101 MHz) **3ea**.

Table S2 Fractional atomic coordinates for the unit cell of **COF-SQ**.

COF-SQ: Space group summetry P3							
a = b = 37.8915 Å, c = 3.5912 Å α = β = 90˚, γ = 120˚							
Atom	x(Å)	y(Å)	z(Å)	Atom	x(Å)	y(Å)	z(Å)
C1	0.30974	0.19596	0.57583	H22	0.37417	0.18111	0.50816
C2	0.35298	0.22014	0.5972	H23	0.15038	0.12702	0.30176
C3	0.35059	0.25657	0.70459	H24	0.17131	0.03411	0.76515
C4	0.30467	0.23112	0.66843	H25	0.24516	0.08189	0.74406
O5	0.27539	0.23697	0.68197	H26	0.51008	0.33041	0.41699
O6	0.37588	0.2919	0.79275	H27	0.50488	0.21744	0.70405
N7	0.28373	0.15548	0.5027	H28	0.43048	0.18318	0.68836
N8	0.3836	0.2116	0.53265	C29	0.04199	0.02829	0.56191
C9	0.24027	0.13241	0.5334	C30	0.01356	0.04155	0.5622
H10	0.29702	0.13755	0.51215	C31	0.08596	0.05844	0.56799
C11	0.21254	0.14474	0.40732	N32	0.11316	0.04741	0.54304
C12	0.17065	0.11688	0.41221	H33	0.02386	0.07415	0.56397
C13	0.15508	0.07716	0.54416	H34	0.09406	0.09098	0.60031
C14	0.18266	0.06503	0.66319	C35	0.64302	0.35196	0.53923
C15	0.22414	0.09214	0.65538	C36	0.62393	0.30941	0.53962
C16	0.42683	0.23667	0.55922	C37	0.57905	0.28406	0.53149
C17	0.45027	0.27906	0.48067	N38	0.55648	0.30057	0.56678
C18	0.49276	0.298	0.48286	H39	0.62406	0.36621	0.53709
C19	0.51346	0.277	0.55892	H40	0.56635	0.25062	0.48803
C20	0.49024	0.23518	0.63749	H41	1.22243	1.17844	0.3839
C21	0.44809	0.21594	0.63305	H42	1.43145	1.29493	0.48194

References

(1) Edwards, S. J.; Valkenier, H.; Busschaert, N.; Gale, P. A.; Davis, A. P. High-Affinity Anion Binding by Steroidal Squaramide Receptors. *Angew. Chemie - Int. Ed.* **2015**, *54* (15), 4592–4596.

(2) Zhang, X.; Zhang, Z.; Boissonnault, J.; Cohen, S. M. Design and Synthesis of Squaramide-Based MOFs as Efficient MOF-Supported Hydrogen-Bonding Organocatalysts. *Chem. Commun.* **2016**, *52* (55), 8585–8588.