

Supporting Information For

**Porous cross-linked polymer TTEB@Ir-catalyzed the selective
synthesis of acylhydrazone and benzenesulfonylhydrazone
derivatives †**

Yan Chen,^a Kai Zhang,^a Haiyan Zhu,^a Xiao-Feng Xia,^a Dawei Wang,^{*a} Zheng-Chao
Duan,^{* b}

^a*Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical
and Material Engineering, Jiangnan University, Wuxi 214122, China. E-mail:
wangdw@jiangnan.edu.cn*

^b*School of Chemical and Environmental Engineering, Hubei Minzu University, Enshi 445000,
China.*

Contents

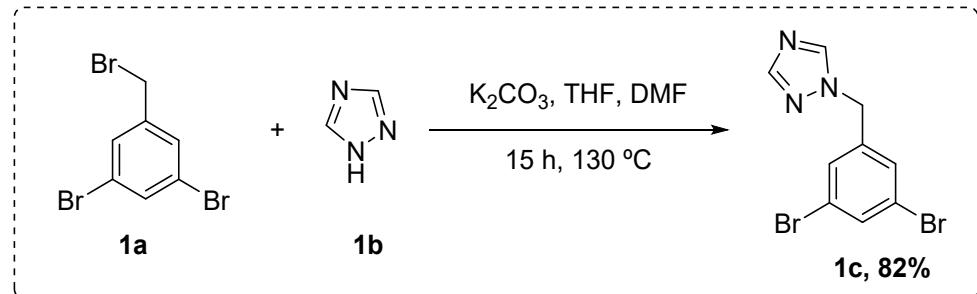
1. General methods and materials.....	S2
2. Synthesis of TTEB@Ir.....	S2-S6
3. Characterization of TTEB@Ir	S6
4. General procedure for all the reactions.....	S6-S7
5. Hammett plot equation.....	S7-S8
6. Analytical data of the obtained compounds.....	S8-S15
7. References.....	S15

1. General methods and materials

All the reactions dealing with air and/or moisture-sensitive reactions were carried out under an atmosphere of nitrogen using oven/flame-dried glassware and standard syringe/septa techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on Varian 400 or 101 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or CDCl_3 (δ 7.26 ppm) for ^1H NMR and CDCl_3 (δ 77.0 ppm) for ^{13}C NMR. Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250 μ) and visualized by fluorescence and by charring after treatment with potassium permanganate stain. HRMS were recorded on LTQ-FTUHRA spectrometer. TEM was recorded on a transmission electron microscope (JEM-2100, JEOL, Japan), operating at 200 kV. SEM image and EDS spectra was performed on a HITACHI S-4800 field-emission scanning electron microscope. XPS data were recorded with electron energy analyzer (ESCALAB 250Xi, Thermo Fisher Co, USA).

2. Synthesis of TTEB@Ir

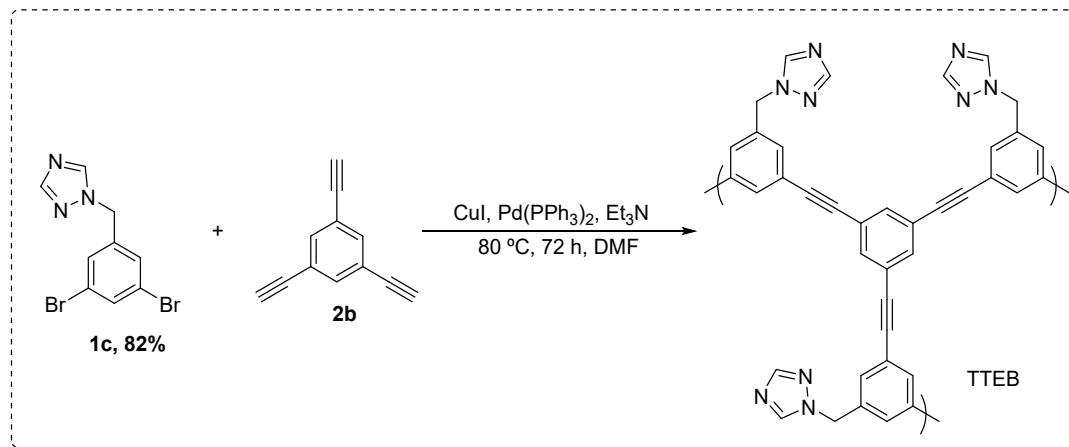
2.1 Procedure for synthesis of 1-(3,5-dibromobenzyl)-1*H*-1,2,4-triazole



The synthesis of 1-(3,5-dibromobenzyl)-1*H*-1,2,4-triazole ^[1] (**1c**) was conducted in accordance with the procedures outlined in the literature. In a nitrogen environment, anhydrous potassium

carbonate was added to 30 mL of THF and stirred at a temperature of 100 °C for a period of 5 minutes. Thereafter, 1,2,4-triazole (2.01 g, 29.0 mmol) was added and stirred at a temperature of 100 °C for 1 h. Finally, 1,3-dibromo-5-bromomethylbenzene (2.46 g, 7.5 mmol) dissolved in *N,N*-dimethylformamide was added slowly. Subsequently, the mixture was stirred at reflux for 15 hours. At the conclusion of the reaction, the mixture was cooled to room temperature and then quenched by the addition of ice water. The reaction was extracted three times with ether, and the collected organic phase was washed with water each time. The resulting aqueous phase was then dried with anhydrous magnesium sulfate and concentrated under reduced pressure to remove the solvent, thereby obtaining the crude product. Purification of the crude product was achieved by silica gel column chromatography, resulting in the isolation of a white solid, which was identified as the target product 1-(3,5-dibromobenzyl)-1,2,4-triazole (**1c**, 82%).

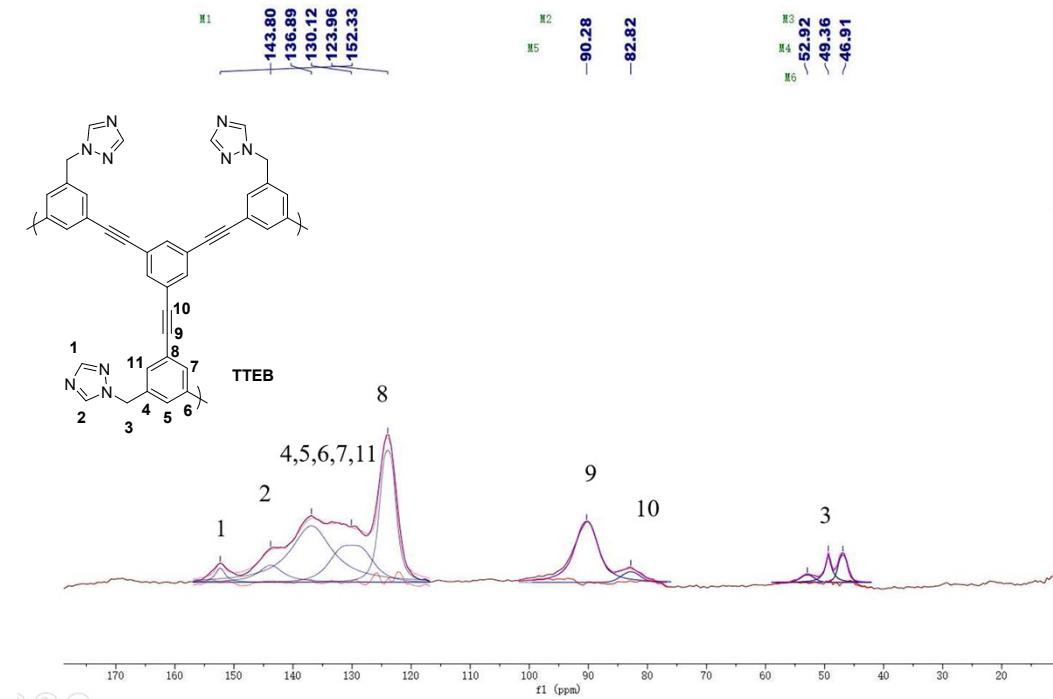
2.3 Procedure for synthesis of TTEB



In a nitrogen atmosphere, the following reagents were added: 1-(3,5-dibromobenzyl)-1,2,4-triazole (354 mg, 1.5 mmol), 1,3,5-triethynylbenzene (150 mg, 1.0 mmol), bis(triphenylphosphine)-palladium dichloride (20 mg), cuprous iodide (30 mg), *N,N*-dimethylformamide (50 mL), *N,N*-dimethylformamide (50 mL) and triethylamine (50 mL). The reaction mixture was stirred at 80 °C

for 24 hours. Following this, the reaction mixture was allowed to cool to room temperature. The solid was then filtered under reduced pressure. The filtrate was subsequently washed with dichloromethane and methanol. The crude product was subjected to a 48-hour methanol solution wash and then extracted via Soxhlet. The residue was dried in a vacuum oven at 60 °C for 12 hour to afford the product **TTEB** [2]. The structure of the solid was validated by solid-state NMR, which demonstrated that the major peaks of the solid could be attributed to the expected chemical composition.

Table.S1. Solid state NMR spectra for TTEB



The presence of these structural features was corroborated by FTIR, ≡C-H bond stretching vibration at 3286 cm⁻¹, C≡C bond stretching vibration at 2185 cm⁻¹, ≡C-H bond bending vibration at 650 cm⁻¹. The C=N bond strong stretching vibration at 1586 cm⁻¹ The asymmetric stretching vibration of C-N-C is observed at 1273, 1269 cm⁻¹, while the symmetric stretching vibration of C-N-C is seen at 1135, 1143 cm⁻¹. The peaks of the C-N-C bond are split due to the conjugation of the benzene ring with the C=N bond.

Table.S2. Comparison of infrared spectra of TTEB

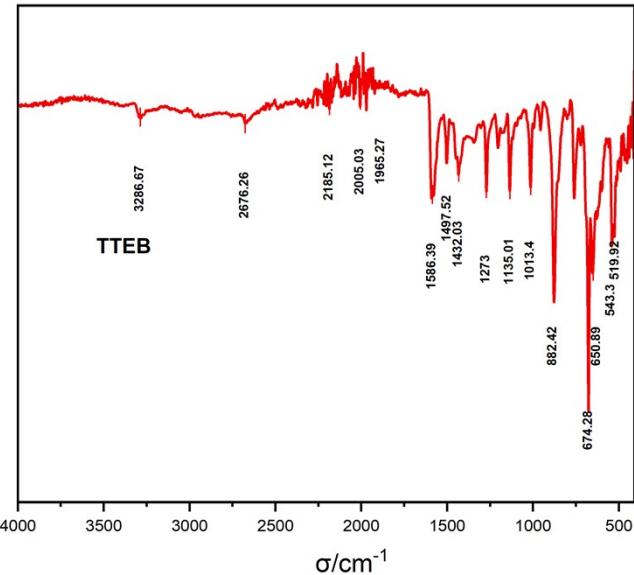
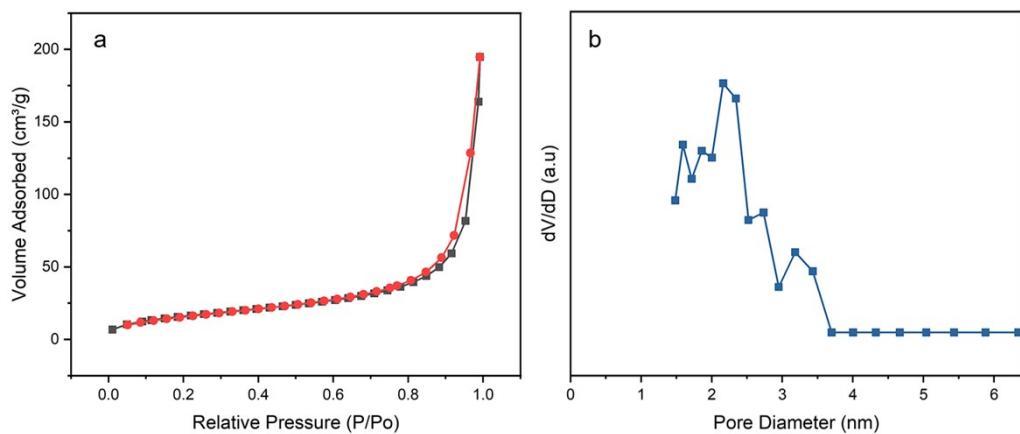


Table.S3. (a) N_2 sorption isotherms of TTEB, (d) pore size distribution of TTEB.



The results showed that TTEB@Ir exhibits a specific surface area of $59.88 \text{ m}^2/\text{g}$, with the pore size distribution predominantly centered at 2.1 nm. As illustrated in Figure (a), the TTEB@Ir exhibits a sharp N_2 uptake at low relative pressure, indicating the presence of micropores within the polymer framework. Moreover, the characteristic H2 hysteresis loop further confirms the existence of porous structures in the material.

2.4. Procedure for synthesis of TTEB@Ir

In a 25 mL Schlenk tube, 1.0 g of TTEB, 821 mg of $[\text{Cp}^*\text{IrCl}_2]$, and 10 mL of dry MeOH were added under N_2 atmosphere. Subsequently, the resulting mixture was stirred at 70°C for 24 h. After

cooling to room temperature, centrifugation, washing with water three times, and drying at 80 °C, the dark brown solid was obtained, which was denoted as **TTEB@Ir**. Tested to a load of 1.53 wt.%.

Table S4. ICP data for TTEB@Ir.

Sample number	Sample mass m ₀ (g)	Constant volume V ₀ (mL)	Test element	Test Solution Element Concentration C ₀ (mg/L)	Dilution factor f	Sample Elemental Composition of Elimination Solution/Original Sample Solution C ₁ (mg/L)	Sample Elemental Composition C _x (mg/kg)	Sample Elemental Content w(%)
1	0.0435	10	Ir	0.46	100	44.82	15341.32	1.53

3. Characterization of TTEB@Ir

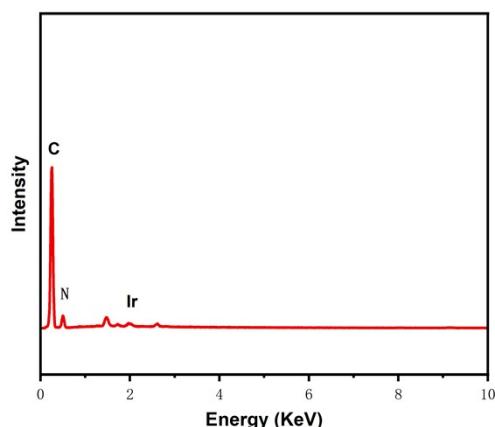


Figure S1. EDS pattern of TTEB@Ir.

Table S5. Quantitative elemental composition of C, N, Ir, from the TTEB@Ir XPS data.

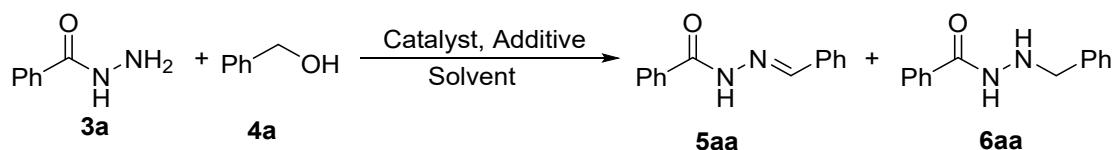
Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Atomic %
C1s	297.98	284.52	279.18	73641.68	1.81	158056.28	2215.93	87.23
Ir4f	71.98	62.18	56.18	8310.24	1.48	33079.85	29.16	1.15
N1s	409.98	399.93	392.18	9540.5	3.26	32683.58	295.36	11.63

4. General procedure for all the reactions

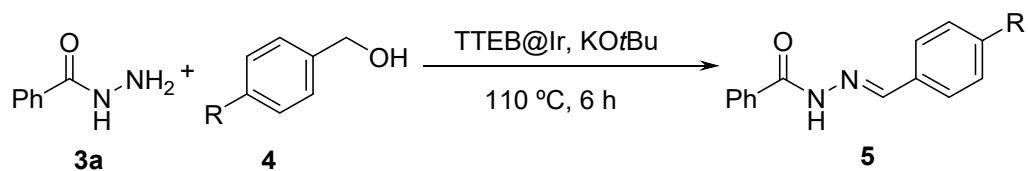
A reaction mixture was prepared by combining benzohydrazide (**3a**) (1.0 mmol), benzyl alcohol (**4a**) (1.0 mmol), **TTEB@Ir** (10 mg), and KO₂Bu (0.5 mmol) within a toluene reaction tube. Subsequently, the reaction tube was carefully positioned in an oil bath set to a temperature of 110 °C, where it was allowed to react for a duration of 6 h. After completion of the reaction, the mixture

was cooled to room temperature for further processing, the reaction mixture was added water and extracted with ethyl acetate three times. The organic phases were dried over anhydrous MgSO_4 and concentrated by removing the solvent under vacuum to give a crude product. The crude product was purified by column chromatography, eluting with petroleum ether/ethyl acetate to afford the desired product **5aa**.

Benzenesulfonyl hydrazide (1.0 mmol), $\text{KO}t\text{Bu}$ (0.5 eq.), benzyl alcohol derivative (1.0 mmol) and **TTEB@Ir** (15 mg) were added to a 25 mL reaction tube. The mixture is then stirred at 110 °C for 8 hours in the presence of O_2 . When the reaction was complete, the mixture was cooled to room temperature, the reaction tube was removed and cooled, ice water was added, and the reaction was transferred to a separating funnel and extracted three times with ethyl acetate. After drying with anhydrous magnesium sulphate, the solvent was removed by a rotary evaporator to give the crude product, which was then purified by column chromatography on silica gel to give the *N*-alkyl compounds.



5. Hammett plot equation



Experimental procedure: To 25 mL reaction tube was added benzohydrazide (**3a**) (2.0 mmol), benzyl alcohol derivatives (**4**) (1.0 mmol), **TTEB@Ir** (10 mg), $\text{KO}t\text{Bu}$ (0.5 equiv.). Then, the reaction tube was heated at 110 °C for 1 h. After centrifugation and recycle the catalyst, the water

mixture was extracted with ethyl acetate three times. Next, the yield of product **5** was determined by ^1H NMR.

R	OMe	Me	H	Br	NO ₂
Yield	17%	21%	15%	12%	9%

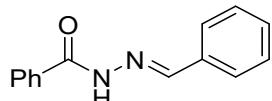
6. Analytical data of the obtained compounds

(1) 1-(3,5-dibromobenzyl)-1*H*-1,2,4-triazole (1c)



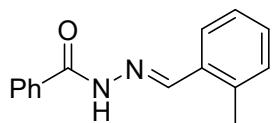
White solid, ^1H NMR (400 MHz, CDCl_3) δ 8.14 (s, 1H), 8.00 (s, 1H), 7.65 (t, $J = 1.7$ Hz, 1H), 7.33 (d, $J = 1.7$ Hz, 2H), 5.29 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 152.62, 143.32, 138.42, 134.37, 129.58, 123.56, 52.04.

(2) (E)-N'-benzylidenebenzohydrazide (5aa)



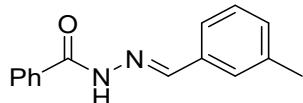
White solid, ^1H NMR (400 MHz, DMSO) δ 11.85 (s, 1H), 8.48 (s, 1H), 7.93 (d, $J = 7.5$ Hz, 2H), 7.77 – 7.71 (m, 2H), 7.60 (t, $J = 7.2$ Hz, 1H), 7.53 (t, $J = 7.4$ Hz, 2H), 7.47 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 163.38, 148.05, 134.58, 133.68, 131.98, 130.31, 129.08, 128.71, 127.85, 127.32.

(3) (E)-N'-(2-methylbenzylidene)benzohydrazide (5ab)



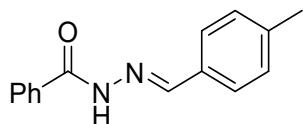
White solid, ^1H NMR (400 MHz, DMSO) δ 11.88 (s, 1H), 8.77 (s, 1H), 7.94 (d, $J = 7.6$ Hz, 2H), 7.64 – 7.46 (m, 4H), 7.34 – 7.21 (m, 3H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 163.47, 146.93, 137.33, 133.92, 132.80, 132.21, 131.33, 130.22, 129.30, 128.04, 126.65, 126.34, 79.11, 19.49.

(4) (E)-N'-(3-methylbenzylidene)benzohydrazide (5ac)



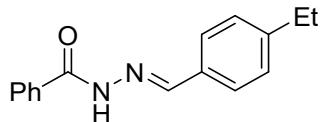
White solid, ^1H NMR (400 MHz, DMSO) δ 12.04 (s, 1H), 8.48 (s, 1H), 7.96 (d, $J = 7.5$ Hz, 2H), 7.62 – 7.44 (m, 6H), 7.39 – 7.23 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 163.63, 148.39, 138.52, 134.86, 133.97, 132.14, 131.21, 129.29, 129.18, 128.90, 128.13, 127.82, 124.97, 79.66, 21.36.

(5) (E)-N'-(4-methylbenzylidene)benzohydrazide (5ad)



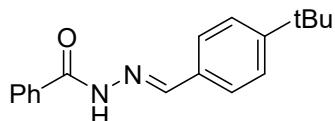
White solid, m.p. 174–176 °C. ^1H NMR (400 MHz, DMSO) δ 11.79 (s, 1H), 8.44 (s, 1H), 7.98 – 7.88 (m, 2H), 7.67 – 7.49 (m, 5H), 7.28 (d, J = 7.7 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 163.54, 148.34, 140.37, 134.01, 132.13, 129.92, 128.92, 128.07, 127.55, 21.50.

(6) (E)-N'-(4-ethylbenzylidene)benzohydrazide (5ae)



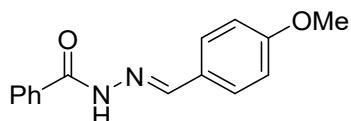
^1H NMR (400 MHz, DMSO) δ 11.81 (s, 1H), 8.47 (s, 1H), 7.94 (d, J = 7.5 Hz, 2H), 7.67 (d, J = 7.8 Hz, 2H), 7.60 (t, J = 7.2 Hz, 1H), 7.53 (t, J = 7.4 Hz, 2H), 7.30 (d, J = 7.8 Hz, 2H), 2.65 (q, J = 7.6 Hz, 2H), 1.20 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 163.57, 148.36, 146.58, 134.01, 132.39, 132.14, 128.92, 128.72, 128.07, 127.64, 28.57, 15.77.

(7) (E)-N'-(4-(tert-butyl)benzylidene)benzohydrazide (5af)



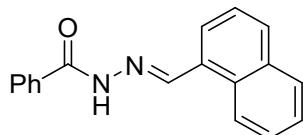
White solid, ^1H NMR (400 MHz, DMSO) δ 11.76 (s, 1H), 8.40 (s, 1H), 7.91 – 7.85 (m, 2H), 7.63 (d, J = 8.2 Hz, 2H), 7.58 – 7.53 (m, 1H), 7.52 – 7.43 (m, 4H), 1.27 (s, 9H). ^{13}C NMR (101 MHz, DMSO) δ 163.61, 153.44, 148.31, 134.04, 132.17, 129.02, 128.14, 127.48, 126.21, 35.15, 31.51.

(8) (E)-N'-(4-methoxybenzylidene)benzohydrazide (5ag)



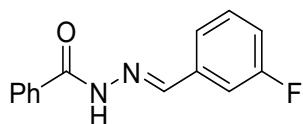
Cream solid, ^1H NMR (400 MHz, DMSO) δ 11.72 (s, 1H), 8.39 (s, 1H), 7.92 – 7.85 (m, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.51 – 7.46 (m, 1H), 7.43 (dd, J = 8.1, 6.4 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 3.70 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 163.62, 161.35, 148.33, 134.11, 132.07, 129.20, 128.88, 128.08, 127.41, 114.77, 55.69.

(9) (E)-N'-(naphthalen-1-ylmethylene)benzohydrazide (5ah)



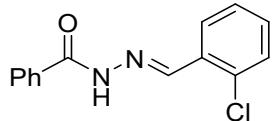
White solid, m.p. 173–174 °C. ^1H NMR (400 MHz, DMSO) δ 11.96 (s, 1H), 9.16 (s, 1H), 8.90 (d, J = 8.5 Hz, 1H), 8.06 – 7.94 (m, 5H), 7.69 (t, J = 7.7 Hz, 1H), 7.65 – 7.53 (m, 5H). ^{13}C NMR (101 MHz, DMSO) δ 163.60, 148.19, 134.05, 133.93, 132.29, 131.04, 130.74, 130.09, 129.28, 129.01, 128.22, 128.11, 127.80, 126.76, 126.04, 124.71.

(10) (E)-N'-(3-fluorobenzylidene)benzohydrazide (5aj)



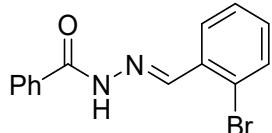
White solid, m.p.202-204 °C ^1H NMR (400 MHz, DMSO) δ 12.00 (s, 1H), 8.52 (s, 1H), 7.97 (d, J = 7.5 Hz, 2H), 7.57 (tt, J = 16.5, 7.7 Hz, 6H), 7.28 (td, J = 8.5, 2.6 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 164.12, 163.78, 161.70, 146.92, 137.47, 133.79, 132.30, 131.38, 131.29, 128.94, 128.15, 123.92, 117.35, 117.13, 113.57, 113.34.

(11) (E)-N'-(2-chlorobenzylidene)benzohydrazide (5ak)



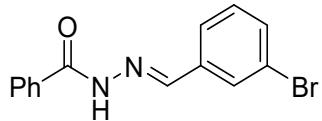
White solid, m.p.188-190 °C ^1H NMR (400 MHz, DMSO) δ 12.08 (s, 1H), 8.89 (s, 1H), 8.05 (t, J = 4.8 Hz, 1H), 7.95 (d, J = 7.5 Hz, 2H), 7.62 (t, J = 7.3 Hz, 1H), 7.55 (dd, J = 8.4, 6.0 Hz, 3H), 7.46 (dd, J = 6.7, 3.3 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 163.65, 144.16, 133.67, 132.40, 132.10, 131.95, 130.40, 128.98, 128.15, 128.10, 127.37.

(12) (E)-N'-(2-bromobenzylidene)benzohydrazide (5al)



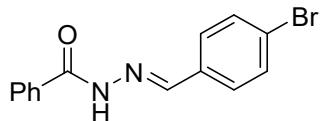
White solid, ^1H NMR (400 MHz, DMSO) δ 8.85 (s, 1H), 8.03 (d, J = 7.8 Hz, 1H), 7.96 (d, J = 7.6 Hz, 2H), 7.73 – 7.67 (m, 1H), 7.62 (t, J = 7.3 Hz, 1H), 7.55 (t, J = 7.4 Hz, 3H), 7.48 – 7.40 (m, 1H), 7.39 – 7.30 (m, 1H). ^{13}C NMR (101 MHz, DMSO) δ 163.68, 146.50, 133.64, 133.60, 132.40, 132.20, 128.97, 128.58, 128.16, 127.76, 124.04.

(13) (E)-N'-(3-bromobenzylidene)benzohydrazide (5am)



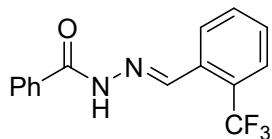
White solid, m.p.156-158 °C ^1H NMR (400 MHz, DMSO) δ 12.04 (s, 1H), 8.48 (s, 1H), 7.97 (d, J = 7.9 Hz, 3H), 7.78 (d, J = 7.7 Hz, 1H), 7.66 (dd, J = 12.9, 7.4 Hz, 2H), 7.58 (t, J = 7.5 Hz, 2H), 7.48 (t, J = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 163.76, 146.45, 137.31, 133.72, 133.05, 132.35, 131.49, 129.58, 128.97, 128.14, 126.72, 122.65.

(14) (E)-N'-(4-bromobenzylidene)benzohydrazide (5an)



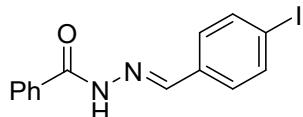
White solid, m.p.189-190 °C ^1H NMR (400 MHz, DMSO) δ 11.92 (s, 1H), 8.43 (s, 1H), 7.92 (d, J = 7.5 Hz, 2H), 7.71 – 7.45 (m, 7H). ^{13}C NMR (101 MHz, DMSO) δ 163.80, 147.10, 134.10, 132.28, 130.05, 129.41, 128.94, 128.14, 127.59, 123.81.

(15) (E)-N'-(2-(trifluoromethyl)benzylidene)benzohydrazide (5ao)



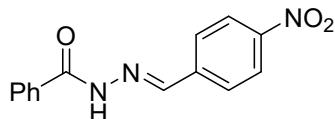
White solid, ^1H NMR (400 MHz, DMSO) δ 12.22 (s, 1H), 8.90 (s, 1H), 8.28 (d, J = 7.9 Hz, 1H), 7.99 (d, J = 7.6 Hz, 2H), 7.86 – 7.74 (m, 2H), 7.69 – 7.60 (m, 2H), 7.57 (t, J = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 163.81, 143.26, 133.56, 133.25, 132.73, 132.44, 130.50, 128.95, 128.18, 127.46, 127.35, 127.15, 126.38, 126.32, 126.01, 123.29.

(16) (E)-N'-(4-iodobenzylidene)benzohydrazide (5ap)



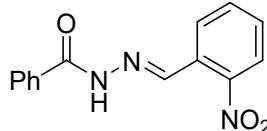
White solid, ^1H NMR (400 MHz, DMSO) δ 11.88 (s, 1H), 8.37 (s, 1H), 7.91 – 7.85 (m, 2H), 7.80 (d, J = 8.0 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.49 (dt, J = 7.3, 3.3 Hz, 4H). ^{13}C NMR (101 MHz, DMSO) δ 163.72, 147.30, 138.24, 134.46, 133.87, 132.38, 129.45, 129.05, 128.19, 97.41.

(17) (E)-N'-(4-nitrobenzylidene)benzohydrazide (5aq)



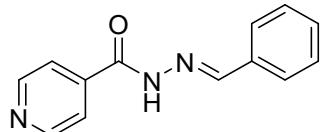
Yellow solid, m.p. 235-237 °C ^1H NMR (400 MHz, DMSO) δ 12.12 (s, 1H), 8.51 (s, 1H), 8.25 (d, J = 8.3 Hz, 2H), 7.92 (dd, J = 16.3, 7.9 Hz, 4H), 7.61 – 7.44 (m, 3H). ^{13}C NMR (101 MHz, DMSO) δ 164.06, 148.38, 145.85, 141.16, 133.55, 132.61, 129.11, 128.55, 128.28, 124.61.

(18) (E)-N'-(2-nitrobenzylidene)benzohydrazide (5ar)



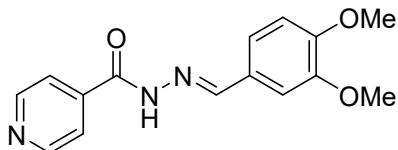
Yellow solid, m.p. 222-224 °C ^1H NMR (400 MHz, DMSO) δ 12.20 (s, 1H), 8.86 (s, 1H), 8.17 – 8.01 (m, 2H), 7.92 (d, J = 7.5 Hz, 2H), 7.78 (t, J = 7.6 Hz, 1H), 7.68 – 7.46 (m, 4H). ^{13}C NMR (101 MHz, DMSO) δ 163.86, 148.79, 143.47, 134.29, 133.52, 132.58, 131.23, 129.28, 129.07, 128.48, 128.29, 125.23.

(19) (E)-N'-benzylideneisonicotinohydrazide (5os)



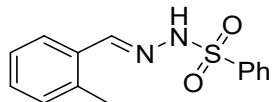
White solid, m.p. 192-193 °C ^1H NMR (400 MHz, DMSO) δ 12.08 (s, 1H), 8.84 – 8.78 (m, 2H), 8.50 (s, 1H), 7.87 – 7.83 (m, 2H), 7.79 – 7.75 (m, 2H), 7.48 (dd, J = 5.2, 2.0 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 162.11, 150.81, 149.54, 140.96, 134.52, 130.85, 129.35, 127.75, 122.00.

(20) (E)-N'-(3,4-dimethoxybenzylidene)isonicotinohydrazide (5ot)



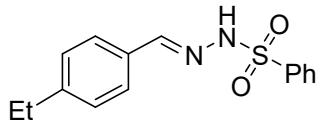
White solid, m.p. 186-188 °C. ^1H NMR (400 MHz, DMSO) δ 11.97 (s, 1H), 8.82 – 8.77 (m, 2H), 8.40 (s, 1H), 7.85 – 7.79 (m, 2H), 7.37 (d, J = 1.9 Hz, 1H), 7.24 (dd, J = 8.3, 1.9 Hz, 1H), 7.05 (d, J = 8.3 Hz, 1H), 3.83 (d, J = 4.4 Hz, 6H). ^{13}C NMR (101 MHz, DMSO) δ 161.90, 151.51, 150.78, 149.73, 149.60, 141.12, 127.20, 122.64, 121.97, 112.02, 108.89, 56.08, 55.97.

(21) (E)-N'-(2-methylbenzylidene)benzenesulfonohydrazide (7aa)



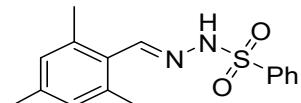
White solid, ^1H NMR (400 MHz, CHLOROFORM-*D*) δ 8.27 – 8.16 (m, 1H), 8.06 – 7.92 (m, 3H), 7.67 – 7.43 (m, 4H), 7.29 – 7.01 (m, 3H), 2.36 (t, J = 4.0 Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 147.36, 138.28, 137.28, 133.48, 131.21, 131.04, 130.30, 129.19, 128.07, 127.51, 126.27, 19.98.

(22) (E)-N'-(4-ethylbenzylidene)benzenesulfonohydrazide (7ba)



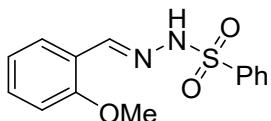
White solid, ^1H NMR (400 MHz, DMSO) δ 11.43 (s, 1H), 7.88 – 7.83 (m, 3H), 7.62 – 7.53 (m, 4H), 7.45 – 7.41 (m, 2H), 7.17 (d, J = 8.0 Hz, 2H), 2.53 (q, J = 7.6 Hz, 2H), 1.09 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 147.84, 146.73, 139.56, 133.57, 131.72, 129.77, 128.76, 128.20, 127.71, 127.39, 126.02, 28.58, 15.89.

(23) (E)-N'-(2,4,6-trimethylbenzylidene)benzenesulfonohydrazide (7ca)



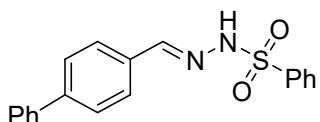
White solid, m.p. 140-141 °C. ^1H NMR (400 MHz, DMSO) δ 11.57 (s, 1H), 7.89 (s, 1H), 7.49 – 7.41 (m, 2H), 7.38 – 7.26 (m, 3H), 6.98 (s, 2H), 2.62 (s, 6H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 145.80, 142.81, 139.76, 134.38, 133.90, 132.16, 130.43, 129.33, 127.01, 23.07, 20.81.

(24) (E)-N'-(2-methoxybenzylidene)benzenesulfonohydrazide (7da)



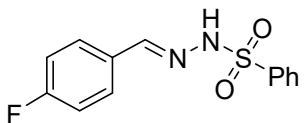
White solid, m.p. 176-177 °C. ^1H NMR (400 MHz, DMSO) δ 11.47 (s, 1H), 8.22 (s, 1H), 7.89 – 7.85 (m, 2H), 7.58 (td, J = 5.4, 2.8 Hz, 4H), 7.31 (ddd, J = 8.9, 7.3, 1.8 Hz, 1H), 6.97 (dd, J = 8.5, 1.0 Hz, 1H), 6.90 (t, J = 7.5 Hz, 1H), 3.73 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 157.96, 143.33, 139.57, 133.57, 132.35, 129.81, 127.68, 125.82, 122.06, 121.35, 112.46, 56.20.

(25) (E)-N'-([1,1'-biphenyl]-4-ylmethylene)benzenesulfonohydrazide (7ea)



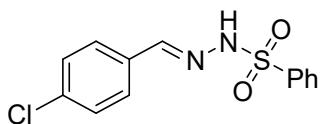
White solid, ^1H NMR (400 MHz, DMSO) δ 11.57 (s, 1H), 7.97 – 7.76 (m, 3H), 7.70 – 7.48 (m, 9H), 7.47 – 7.24 (m, 3H). ^{13}C NMR (101 MHz, DMSO) δ 147.33, 142.16, 139.79, 139.56, 133.64, 133.25, 129.83, 129.69, 128.45, 127.92, 127.73, 127.57, 127.21.

(26) (E)-N'-(4-fluorobenzylidene)benzenesulfonohydrazide (7fa)



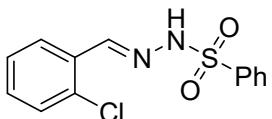
White solid, ^1H NMR (400 MHz, DMSO) δ 11.52 (s, 1H), 7.89 (s, 1H), 7.88 – 7.83 (m, 2H), 7.65 – 7.54 (m, 5H), 7.18 (t, J = 8.9 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 164.85, 162.39, 146.66, 139.51, 133.63, 130.78, 130.75, 129.81, 129.56, 129.48, 128.21, 127.72, 126.03, 116.52, 116.30.

(27) (E)-N'-(4-chlorobenzylidene)benzenesulfonohydrazide (7ga)



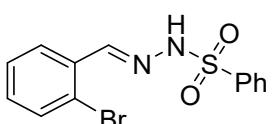
White solid, ^1H NMR (400 MHz, DMSO) δ 11.80 (s, 1H), 8.04 (q, J = 3.2 Hz, 3H), 7.71 – 7.58 (m, 5H), 7.45 (d, J = 8.3 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 146.35, 139.55, 135.13, 133.46, 132.99, 129.65, 129.25, 128.80, 127.68.

(28) (E)-N'-(2-chlorobenzylidene)benzenesulfonohydrazide (7ha)



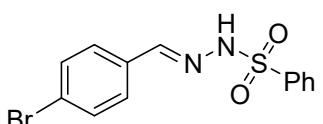
White solid, ^1H NMR (400 MHz, DMSO) δ 11.93 (s, 1H), 8.34 (s, 1H), 8.02 – 7.96 (m, 2H), 7.81 (dd, J = 7.3, 2.2 Hz, 1H), 7.71 – 7.64 (m, 3H), 7.48 – 7.44 (m, 1H), 7.40 (qd, J = 6.9, 1.9 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 143.35, 139.43, 133.61, 133.38, 131.94, 131.26, 130.29, 129.77, 128.01, 127.64, 127.05.

(29) (E)-N'-(2-bromobenzylidene)benzenesulfonohydrazide (7ia)



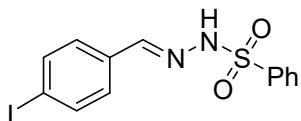
White solid, ^1H NMR (400 MHz, DMSO) δ 11.84 (s, 1H), 8.20 (s, 1H), 7.90 – 7.84 (m, 2H), 7.69 (dd, J = 7.9, 1.8 Hz, 1H), 7.65 – 7.53 (m, 4H), 7.36 – 7.22 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 145.73, 139.41, 133.77, 133.67, 132.78, 132.39, 129.92, 128.69, 127.68, 127.46, 123.76.

(30) (E)-N'-(4-bromobenzylidene)benzenesulfonohydrazide (7ja)



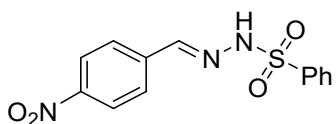
White solid, ^1H NMR (400 MHz, DMSO) δ 11.62 (s, 1H), 7.88 – 7.83 (m, 3H), 7.63 – 7.60 (m, 1H), 7.60 – 7.56 (m, 2H), 7.55 (dt, J = 7.1, 2.1 Hz, 2H), 7.49 – 7.45 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 146.52, 139.48, 133.67, 133.41, 132.35, 129.83, 129.18, 128.21, 127.69, 126.02, 123.93.

(31) (E)-N'-(4-iodobenzylidene)benzenesulfonohydrazide (7ka)



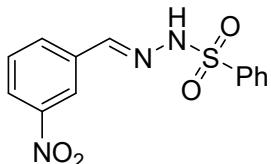
White solid, ^1H NMR (400 MHz, DMSO) δ 11.90 (s, 1H), 8.38 (s, 1H), 7.89 (d, J = 7.6 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H), 7.59 – 7.44 (m, 5H). ^{13}C NMR (101 MHz, DMSO) δ 146.77, 139.47, 138.18, 133.67, 129.83, 129.12, 128.96, 128.19, 127.68, 126.02, 97.52.

(32) (E)-N'-(4-nitrobenzylidene)benzenesulfonohydrazide (7la)



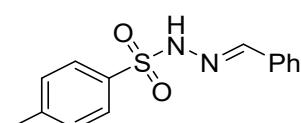
Pale yellow solid ^1H NMR (400 MHz, DMSO) δ 11.98 (s, 1H), 8.21 – 8.14 (m, 2H), 8.00 (s, 1H), 7.88 (dt, J = 6.9, 1.5 Hz, 2H), 7.82 – 7.75 (m, 2H), 7.67 – 7.55 (m, 3H). ^{13}C NMR (101 MHz, DMSO) δ 148.41, 145.12, 140.30, 139.40, 133.81, 129.92, 128.26, 127.68, 124.56.

(33) (E)-N'-(3-nitrobenzylidene)benzenesulfonohydrazide (7ma)



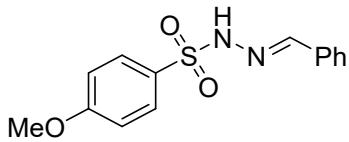
Pale yellow solid, ^1H NMR (400 MHz, DMSO) δ 11.88 (s, 1H), 8.32 (t, J = 2.0 Hz, 1H), 8.17 (ddd, J = 8.3, 2.4, 1.0 Hz, 1H), 8.03 (s, 1H), 7.97 (dt, J = 7.7, 1.4 Hz, 1H), 7.88 – 7.85 (m, 2H), 7.66 – 7.56 (m, 4H). ^{13}C NMR (101 MHz, DMSO) δ 148.67, 145.36, 139.43, 135.94, 133.78, 133.21, 130.96, 129.91, 127.68, 124.91, 121.65.

(34) (E)-N'-benzylidene-4-methylbenzenesulfonohydrazide (7na)



White solid, ^1H NMR (400 MHz, CDCl_3) δ 8.78 (s, 1H), 7.91 – 7.84 (m, 2H), 7.81 – 7.77 (m, 1H), 7.55 – 7.49 (m, 2H), 7.32 – 7.21 (m, 5H), 2.36 (d, J = 2.5 Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM- D) δ 148.22, 144.40, 135.30, 133.36, 130.46, 129.85, 128.70, 128.03, 127.48, 21.69.

(35) (E)-N'-benzylidene-4-methoxybenzenesulfonohydrazide (7oa)



White solid, ^1H NMR (400 MHz, DMSO) δ 11.31 (d, J = 4.1 Hz, 1H), 7.85 (q, J = 7.4 Hz, 3H), 7.59 (dd, J = 12.5, 10.1, 7.2, 3.0 Hz, 3H), 7.50 – 7.39 (m, 2H), 6.95 – 6.81 (m, 2H), 3.73 (d, J = 4.0 Hz,

3H). ^{13}C NMR (101 MHz, DMSO) δ 161.35, 147.80, 139.59, 133.52, 129.74, 128.94, 127.74, 126.74, 114.80, 55.79.

7. References

- [1] L. Wang, N. Liu, B. Dai, *RSC Adv.* **2015**, *5*, 82097-82111.
- [2] L. Xiao, Z. Yang, H. Yang, Z. Lu, R. Zhao, L. Hou, *ACS Appl. Polym. Mater.* **2023**, *5*, 4217-4223.