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Supplementary Information

Rationally designed conjugated microporous polymers for efficient

photocatalytic chemical transformations of isocyanides

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Experimental Section

1. materials

1,3,5-Tribromobenzene, (trimethylsilyl)acetylene, 4-aminophenylboronic acid pinacol ester, 3aminophenylboronic acid pinacol ester, 2,5-dibromothiophene, 1,3,5-tribromobenzene, amines were purchased from Beijing Inno Chem Science & Technology Co., Ltd. Copper sulfate pentahydrate (CuSO₄·5H₂O), sodium ascorbate, sodium acetate (NaOAc), 2,2,6,6tetramethylpiperidinooxy (TEMPO), ethyl acetate (EtOAc), tetrahydrofuran (THF), dichloromethane (CH2Cl2), acetonitrile (CH3CN), N,N-dimethylformamide (DMF), 1,4-dioxane, methanol (CH₃OH), isopropyl alcohol (*i*-PrOH) and dimethyl sulfoxide (DMSO) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Ethynyltrimethylsilane, [1,1'bis(diphenylphosphino)ferrocene]dichloropalladium(II) (PdCl₂(dppf)), and tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) were purchased from TCI. These chemicals were used as received without further purification.

2. Instrumentions

Fourier transform infrared (FT-IR) spectra were recorded on an IR-spectrum one (Perkin Elmer) spectrometer. NMR spectra were recorded on Varian Unity Inova 400 spectrometer (¹H at 400 MHz and ¹³C at 100 MHz). ¹³C cross-polarization magic-angle spinning (CP/MAS) NMR spectra were obtained on Varian Infinity-plus 300 spectrosmeter. Thermogravimetric analysis (TGA) were carried out in a N₂ atmosphere with a heating rate of 20 °C/min on a Diamond TG/DTA thermal analyzer (Perkin Elmer). Powder X-ray diffraction (PXRD) measurements were taken with a Bruker D8 advance with Cu K α radiation at a scan rate of 10°/min. Scanning electron microscopy (SEM) images were conducted on a JEOL JSM-6510 electron microscope. Transmission electron microscope (TEM) images were taken with Tecnai G2 F20. The nitrogen sorption isotherms were measured at 77 K on a Micromeritics ASAP 2460 instrument. Surface areas were calculated from the adsorption data from $0.05 \le P/P_0 \le 0.30$ by using Brunauer-Emmett-Teller (BET) methods. The pore size distribution curves were obtained from the adsorption branches by using Barrett-Joyner-Halenda (BJH) method. UV-vis diffuse reflectance spectra were recorded on a Lambda 900 spectrophotometer (Perkin-Elmer). The photoluminescence (PL) spectra of the polymer powders were carried out at room temperature using a Hitachi 4600 spectrofluorimeter (Hitachi). Timeresolved PL spectra were measured in the solid state on an Edinburgh FLS980 spectrometer.

Theoretical calculations were carried out with the Gaussian 16 suite of programs. The geometries were fully optimized in vacuum with DFT B3LYP method and 6-311+G(d) basis set. Frontier molecular orbital maps are generated with GaussView software based on the fchk file of geometry optimization.

3. Electrochemical measurements

Cyclic voltammetry (CV) experiments were performed using a CH Instruments Model 760E electrochemical work station (CH Instruments Inc.). The three-electrode-cell system consisted of a glassy carbon working electrode, a platinum wire counter electrode and a saturated calomel electrode (SCE) reference electrode. The samples were prepared by first mixing ground polymer or substrates with 5 wt% Nafion to give a homogeneous suspension, then a 10 μ L drop was placed on top of a glassy carbon working electrode and let the solvent evaporate in a vacuum chamber for 60 min. The measurement was carried out in a Bu₄NPF₆ solution (0.1 M in acetonitrile) as supporting electrolyte (pH 3.87) with a scan rate of 0.1 V s⁻¹ in the range of -1.7 V to 0.5 V. The Mott-Schottky measurement was carried out in 0.1 M Na₂SO₄ aqueous solution at frequencies of 800 Hz, 1000 Hz and 1500 Hz. The transient photocurrent response was also measured in the above-mentioned three-electrode system. The samples were used as the working electrode, while a platinum wire as the counter electrode and Ag/AgCl (saturating KCl) as the reference electrode, respectively. Bias potentials applied on the working electrode were 0.5 V. The working electrode obtained from the polymer and 5 wt% Nafion was immersed in Na₂SO₄ aqueous solution (0.1 M).

4. Synthesis of building blocks

4.1. Synthesis of Az



Az-1 and Az were synthesized according to the published procedure.¹

a) Synthesis of Az-1

4-Aminophenylboronic acid pinacol ester (2.41 g, 11.00 mmol), potassium carbonate (1.52 g, 11.00 mmol), and tetrakis(triphenylphosphine)palladium (0.25 g, 0.22 mmol) were first placed in a 250 mL three-necked flask. The flask was evacuated with an oil pump for 5 minutes and equilibrated with nitrogen. Then, 60 mL of a mixture of 1,4-dioxane and water (3:1, v/v) was added to the flask, followed by the addition of the 2,5-dibromothiophene (1.07 g, 4.42 mmol). The mixture was heated

at 110 °C for 5 h under a nitrogen atmosphere, until the starting materials were completely consumed as detected by TLC. The solution was cooled to room temperature and extracted with dichloromethane (40 mL × 3). The combined organic layers were washed with brine, dried over MgSO₄, concentrated and purified on a silica gel column (petroleum ether/dichloromethane 8:1, v/v) to give **Az-1** as a light yellow powder (1.10 g, 93%). ¹H NMR (400 MHz, CDCl₃) δ 7.45-7.39 (m, 4H), 7.08 (s, 2H), 6.72-6.66 (m, 4H), 3.73 (s, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 145.78, 136.44, 126.73, 122.01, 115.33, 114.10.

b) Synthesis of Az

In a round-bottom flask equipped with a magnetic stirring bar, **Az-1** (1.04 g, 3.91 mmol) was suspended in HCl (6 N, 5 mL) cooled in an ice bath. Then 10 mL of aqueous solution of NaNO₂ (0.55 g, 7.96 mmol) was added dropwise. The reaction mixture was stirred for 0.5 h and 25 mL of aqueous solution of NaN₃ (1.14 g, 17.59 mmol) was added dropwise. After addition, the mixture was allowed to stir for another 16 h at room temperature. Then the mixture was extracted with ethyl acetate (40 mL × 3). The combined organic extracts were washed with brine and dried over MgSO₄. The volatiles were removed under vacuum to give crude product, which was purified by column chromatography on silica gel (petroleum ether) to afford **Az** as a reddish brown solid (1.05 g, 85%). ¹H NMR (400 MHz, CDCl₃) δ 7.64-7.56 (m, 4H), 7.24 (s, 2H), 7.08-7.02 (m, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 142.61, 139.18, 131.10, 126.95, 124.01, 119.56.

4.2. Synthesis of o-Az



a) Synthesis of o-Az-1

Following a similar synthetic procedure to **Az-1** except 3-aminophenylboronic acid pinacol ester (2.41 g, 11.00 mmol) was used instead of 4-aminophenylboronic acid pinacol ester, the product was obtained as a white powder (1.08 g, 92%). ¹H NMR (400 MHz, CDCl₃) δ 7.24 (s, 2H), 7.17 (t, J = 7.8 Hz, 2H), 7.05 (d, J = 7.8 Hz, 2H), 6.96 (t, J = 1.8 Hz, 2H), 6.64 (dd, $J_1 = 7.8$, $J_2 = 1.8$ Hz, 2H), 3.75 (s, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 146.80, 143.57, 135.35, 129.86, 123.83, 116.25, 114.41, 112.19.

b) Synthesis of o-Az

Following a similar synthetic procedure to Az except o-Az-1 (1.08 g, 4.05 mmol) was used

instead of **Az-1**, the product was obtained as a white solid (1.16 g, 90%). ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.27 (m, 2H), 7.21 (s, 2H), 7.17-7.14 (m, 2H), 6.88 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 142.98, 140.78, 135.79, 130.35, 124.76, 122.29, 118.09, 116.10. HRMS (m/z): calcd for C₁₆H₁₁N₆S 319.0766 [M + H]⁺, found 319.0761.

4.3. Synthesis of m-Az



a) Synthesis of m-Az-1

4-Aminophenylboronic acid pinacol ester (1.31 g, 6.00 mmol), potassium carbonate (0.83 g, 6.00 mmol), and tetrakis(triphenylphosphine)palladium (0.12 g, 0.10 mmol) were first placed in a 250 mL three-necked flask. The flask was evacuated with an oil pump for 5 minutes and equilibrated with nitrogen. Then, 80 mL of a mixture of 1,4-dioxane and water (3:1, v/v) was added to the flask, followed by the addition of the 2,5-dibromothiophene (5.76 g, 24.00 mmol). The mixture was heated at 110 °C for 3 h under a nitrogen atmosphere. The solution was cooled to room temperature and extracted with dichloromethane (40 mL × 3). The combined organic layers were washed with brine, dried over MgSO₄, concentrated and purified on a silica gel column (petroleum ether/dichloromethane 4:1, v/v) to give **m-Az-1** as a yellow powder (1.25 g, 82%). ¹H NMR (400 MHz, CDCl₃) δ 7.35-7.28 (m, 2H), 6.97 (d, *J* = 3.8 Hz, 1H), 6.88 (d, *J* = 3.8 Hz, 1H), 6.70-6.64 (m, 2H), 3.76 (s, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 146.56, 146.40, 130.67, 126.92, 124.34, 121.36, 115.31, 109.28.

b) Synthesis of m-Az-2

3-Aminophenylboronic acid pinacol ester (1.34 g, 6.13 mmol), potassium carbonate (0.85 g, 6.15 mmol), and tetrakis(triphenylphosphine)palladium (0.25 g, 0.22 mmol) were first placed in a 250 mL three-necked flask. The flask was evacuated with an oil pump for 5 minutes and equilibrated with nitrogen. Then, 40 mL of a mixture of 1,4-dioxane and water (3:1, v/v) was added to the flask, followed by the addition of **m-Az-1** (1.20 g, 4.72 mmol). The mixture was heated at 110 °C for 3 h under a nitrogen atmosphere. The solution was cooled to room temperature and extracted with dichloromethane (40 mL \times 3). The combined organic layers were washed with brine, dried over

MgSO₄, concentrated and purified on a silica gel column (petroleum ether/dichloromethane 8:1, v/v) to give **m-Az-2** as a yellow powder (1.11 g, 88%). ¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, *J* = 8.5 Hz, 2H), 7.23-7.09 (m, 3H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.94 (s, 1H), 6.70 (d, *J* = 8.5 Hz, 2H), 6.63-6.55 (m, 1H), 3.74 (s, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 146.77, 146.04, 144.09, 141.96, 135.55, 129.81, 126.87, 125.13, 123.81, 122.03, 116.11, 115.32, 114.12, 112.05.

c) Synthesis of m-Az

Following a similar synthetic procedure to Az except m-Az-2 (1.10 g, 4.14 mmol) was used instead of Az-1, the product was obtained as a brown solid (1.20 g, 91%). ¹H NMR (400 MHz, CDCl₃) δ 7.65-7.58 (m, 2H), 7.42-7.36 (m, 2H), 7.30 (d, *J* = 3.7 Hz, 1H), 7.25-7.22 (m, 2H), 7.10-7.02 (m, 2H), 7.00-6.94 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 143.33, 142.24, 140.75, 139.31, 135.89, 130.97, 130.32, 127.01, 124.78, 123.98, 122.20, 119.58, 117.94, 116.01. HRMS (m/z): calcd for C₁₆H₁₁N₆S 319.0766 [M + H]⁺, found 319.0760.

4.4. Synthesis of 1,3,5-triethynylbenzene



To stirred solution of 1,3,5-Tribromobenzene (3.15)10.00 а g, mmol), tetrakis(triphenylphosphine) palladium (0.58 g, 0.50 mmol) and CuI (0.10 g, 0.50 mmol) in dry triethylamine (25 mL) and toluene (25 mL) was added (trimethylsilyl)acetylene (3.24 g, 33.00 mmol). The mixture was heated at 70 °C for 10 h under a nitrogen atmosphere. After cooling to room temperature, the reaction mixture was filtered and the filtrate was concentrated under reduced pressure to give crude 1. Then 1 was suspended in tetrahydrofuran (25 mL) and methanol (25 mL), and an aqueous KOH solution (2 M, 20 mL) was added dropwise. The mixture was stirred at room temperature for 3 h and extracted with dichloromethane (50 mL \times 3). The combined organic layers were washed with brine and dried over anhydrous MgSO4. The volatiles were removed under vacuum to give the crude product, which was purified by column chromatography on silica gel (petroleum ether) to obtain 1,3,5-triethynylbenzene as a white solid (1.40 g, 93%). ¹H NMR (400 MHz, CDCl₃) & 7.57 (s, 3H), 3.11 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) & 135.68, 122.92, 81.66, 78.77.

5. Synthesis of substrates

The isocyanides were synthesized according to the published procedures.^{2,3}

6. Reaction setup

20 mL glass tubes are placed at the hole of photo reactive plant. Two parallel LED lamps (total 24 W) are place perpendicularly to the sidewall of glass tubes (at approximately 1 cm away from the light source), so that the reactions vials can be equally exposed to the LEDs (about 6W was distributed to each hole). A clip fan at one end of the plant had been kept working during the reaction, offsetting the heat generated from the LED light and to stabilize reaction temperature for reproducible results.



Fig. S0 (a) The white light device for photocatalysis. (b) The emission spectrum of the white LED light. (b) The blue light device for photocatalysis. (d) The emission spectrum of the blue LED light.

References

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Fig. S1 TGA curves of Ta-Ths.



Fig. S2 PXRD curves of Ta-Ths.



Fig. S3 SEM images of (a) Ta-Th-7, (b) Ta-Th-8, and (c) Ta-Th-9, and TEM images of (d) Ta-Th-7, (e) Ta-Th-8, and (f) Ta-Th-9.



Fig. S4 N_2 adsorption-desorption isotherms for (a) Ta-Th-7, (c) Ta-Th-8 and (e) Ta-Th-9, and pore size distributions for (b) Ta-Th-7, (d) Ta-Th-8, and (f) Ta-Th-9.



Fig. S5 IR spectra for (a) Ta-Th-7, (b) Ta-Th-8, (c) Ta-Th-9 and respective monomers.



Fig. S6 XPS survey spectra of Ta-Ths.



Fig. S7 N 1s spectra of Ta-Ths.



Fig. S8 Optical band gaps calculated by Tauc-plot method.



Fig. S9 Cyclic voltammograms of (a) Ta-Th-7, (b) Ta-Th-8 and (c) Ta-Th-9.



Fig. S10 Mott-Schottky plots of (a) Ta-Th-7, (b) Ta-Th-8 and (c) Ta-Th-9.

Polymer	$E_{g}^{a}(eV)$	LUMO (V vs. SCE)		HOMOd (Virg SCE)
		CV^b	Mott-Schottky ^c	HOMO" (V VS. SCE)
Ta-Th-7	2.63	-0.96	-0.99	1.67
Ta-Th-8	2.87	-0.98	-1.01	1.89
Ta-Th-9	2.99	-1.01	-1.03	1.98

Table S1 Summary of the photoelectric properties of Ta-Ths.

^{*a*} Optical band gap derived from the absorption spectra. ^{*b*} Determined by the cyclic voltammograms. ^{*c*} Determined by the Mott-Schottky plots. ^{*d*} Calculated from the equation HOMO = $LUMO_{CV} + E_g$.



Fig. S11 EPR spectra of (a) Ta-Th-7, (b) Ta-Th-8, and (c) Ta-Th-9 taken in darkness and under light irradiation.



Fig. S12 Structure models for DFT calculations.



Fig. S13 HOMO diagrams of structure models.



Fig. S14 Yield as a function of time in the insertion reaction between 4-methoxyphenyl isocyanide and pyrrolidine.



Fig. S15 The absorption spectra (380-800 nm) of Ta-Th-7 in various solvents.

SH + EtO_2C NC blue LED S N CO ₂ Et					
		6а			
Entry	Catalyst	Solvent	$\operatorname{Yield}^{b}(\%)$		
1	Ta-Th-7	THF	58		
2	Ta-Th-7	DCM	61		
3	Ta-Th-7	MeCN	63		
4	Ta-Th-7	1,4-dioxane	50		
5	Ta-Th-7	DMSO	36		
6	Ta-Th-7	DMF	43		
7	Ta-Th-7	EtOAc	84		
8	Ta-Th-7	H ₂ O	Trace		
13 ^c	Ta-Th-7	EtOAc	61		
14^d	Ta-Th-7	EtOAc	57		
15	Ta-Th-8	EtOAc	54		
16	Ta-Th-9	EtOAc	36		

Table S2 Screening of solvents and photocatalysts in the reaction of thiol and isocyanides^a

^{*a*} Reaction conditions: **3a** (0.2 mmol), **4a** (0.5 mmol), Ta-Th-7 (15 mg), H₂O (0.1 mL), solvent (3 mL), O₂ balloon, blue LED (6 W), room temperature, 2.5 h. ^{*b*} Isolated yield. ^{*c*} Under air atmosphere. ^{*d*} Under white LED irradiation.



Fig. S16 Plausible reaction mechanism for the photosynthesis of thiocarbamates.



Fig. S17 FT-IR spectra of fresh and recycled Ta-Th-7.



Fig. S18 SEM images of (a) fresh Ta-Th-7, (b) 5th recycled Ta-Th-7 in the photosynthesis of 3a, and (c) 5th recycled Ta-Th-7 in the photosynthesis of **6a**.

Products characterization



3a

Prepared according to general catalytic procedure and obtained as a yellow solid. ¹H NMR (400 MHz, CDCl₃): δ 7.77 (s, 1H), 7.00-6.91 (m, 2H), 6.85-6.77 (m, 2H), 3.76 (s, 3H), 3.57-3.47 (m, 4H), 1.98-1.87 (m, 4H). ¹³C NMR (101 MHz, CDCl₃): δ 155.79, 150.20, 144.44, 121.83, 114.45, 55.62, 55.60, 25.13. HRMS

(ESI): $m/z [M + H]^+$ calcd. for $C_{12}H_{17}N_2O$: 205.1341, found: 205.1340.



Prepared according to general catalytic procedure and obtained as a yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.46 (s, 1H), 6.94-6.86 (m, 2H), 6.84-6.77 (m, 2H), 3.77 (s, 3H), 3.64-3.23 (m, 4H), 1.72-1.54 (m, 6H). ¹³C

NMR (101 MHz, CDCl₃): δ 155.48, 152.49, 145.35, 121.68, 114.32, 55.53, 55.52, 29.73, 24.74. HRMS (ESI): m/z [M + H]⁺ calcd. for C₁₃H₁₉N₂O: 219.1497, found: 219.1495.



Prepared according to general catalytic procedure and obtained as a reddish brown solid. ¹H NMR (400 MHz, CDCl₃): δ 7.42 (s, 1H), 6.92-6.86 (m, 2H), 6.83-6.77 (m, 2H), 4.10 (t, J = 7.6 Hz, 4H), 3.77 (s, 3H), 2.44-2.35 (m, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 154.76, 152.88, 139.91, 116.46, 114.84, 55.75, 55.73, 19.74. HRMS (ESI): $m/z [M + H]^+$ calcd. for $C_{11}H_{15}N_2O$: 191.1184, found: 191.1181.



Prepared according to general catalytic procedure and obtained as a yellow solid. ¹H NMR (400 MHz, CDCl₃): δ 7.54 (s, 1H), 6.94-6.86 (m, 2H), 6.86-6.77 (m, 2H), 3.78 (s, 3H), 3.64-3.53 (m, 2H), 3.45-3.30 (m,

2H), 1.93-1.62 (m, 8H). ¹³C NMR (101 MHz, CDCl₃): δ 155.37, 153.24, 144.61, 121.82, 114.31, 55.55, 51.21, 30.82, 26.70. HRMS (ESI): $m/z [M + H]^+$ calcd. for $C_{14}H_{21}N_2O$: 233.1654, found: 233.1651.



Prepared according to general catalytic procedure and obtained as a yellow solid. ¹H NMR (400 MHz, CDCl₃): δ 7.49 (s, 1H), 6.93-6.87 (m, 2H), 6.85-6.79 (m, 2H), 3.78 (s, 3H), 3.76-3.71 (m, 4H), 3.61-3.36 (m, 4H). ¹³C NMR (101 MHz, CDCl₃): δ 155.84, 152.08, 144.72, 121.70, 114.38, 66.71, 55.53, 46.82. HRMS (ESI): $m/z [M + H]^+$ calcd. for C₁₂H₁₇N₂O₂: 221.1290, found: 221.1285.



Prepared according to general catalytic procedure and obtained as a yellow solid. ¹H NMR (400 MHz, CDCl₃): δ 7.55 (s, 1H), 7.35-7.30 (m, 2H), 7.24-7.19 (m, 3H), 7.01-6.91 (m, 2H), 6.88-6.79 (m, 2H), 3.78 (s, 3H), 3.48-3.36 (m, 1H), 3.20-2.99 (m, 2H), 2.88-2.61 (m, 2H), 1.98-1.89 (m, 2H), 1.81-1.67

(m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 155.81, 152.18, 145.33, 128.85, 128.63, 126.79, 126.55, 121.73, 114.40, 55.54, 42.84, 41.48, 29.73. HRMS (ESI): m/z [M + H]⁺ calcd. for C₁₉H₂₃N₂O: 295.1810, found: 295.1807.

Prepared according to general catalytic procedure and obtained as a yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.48 (s, 1H), 6.93-6.86 (m, 2H), 6.85-6.77 (m, 2H), 3.77 (s, 3H), 3.00 (s, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 3a 155.51, 153.18, 145.47, 121.76, 114.33, 55.54, 55.53. HRMS (ESI): m/z [M + H]⁺ calcd. for C₁₀H₁₅N₂O: 179.1184, found: 179.1182.



Prepared according to general catalytic procedure and obtained as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.57 (s, 1H), 7.17-7.01 (m, 2H), 6.87-6.80 (m, 2H), 7.01-6.91 (m, 2H), 6.88-6.79 (m, 2H), 3.78 (s, 3h 3H), 3.74-3.25 (m, 4H), 1.26 (t, J = 7.2 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 156.41, 151.58, 144.85, 121.80, 114.49, 55.57, 53.40, 14.29. HRMS (ESI): m/z [M + H]⁺ calcd. for C₁₂H₁₉N₂O: 207.1497, found: 207.1494.



Prepared according to general catalytic procedure and obtained as a pale yellow solid. ¹H NMR (400 MHz, CDCl₃): δ 7.71 (s, 1H), 7.47-7.29 (m, 5H), 7.00-6.90 (m, 2H), 6.88-6.80 (m, 2H), 4.42 (s, 2H), 3.79

(s, 3H), 2.93 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 155.63, 153.19, 145.29, 137.17, 130.52, 128.55, 128.47, 121.85, 114.37, 55.56, 54.46, 29.74. HRMS (ESI): m/z [M + H]⁺ calcd. for C₁₆H₁₉N₂O: 255.1497, found: 255.1492.



3j

Prepared according to general catalytic procedure and obtained as a yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.76 (s, 1H), 7.09-7.03 (m, 2H), 6.91-6.86 (m, 2H), 3.51 (t, *J* = 6.5 Hz, 4H), 2.29 (s, 3H), 1.98-1.92 (m, 4H). ¹³C NMR (101 MHz, CDCl₃): δ 150.39, 149.90, 131.61, 129.60, 121.00, 48.77,

25.06, 20.79. HRMS (ESI): $m/z [M + H]^+$ calcd. for $C_{12}H_{17}N_2$: 189.1392, found: 189.1390.



Prepared according to general catalytic procedure and obtained as a yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.77 (s, 1H), 6.66 (s, 1H), 6.62 (s, 2H), 3.55-3.41 (m, 4H), 2.28 (s, 6H), 2.00-1.86 (m, 4H). ¹³C NMR (101 MHz, CDCl₃): δ 152.29, 150.34, 138.47, 124.15, 119.09, 48.94, 25.07, 21.38.

HRMS (ESI): $m/z [M + H]^+$ calcd. for $C_{13}H_{19}N_2$: 203.1548, found: 203.1546.



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Prepared according to general catalytic procedure and obtained as a yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.40 (s, 1H), 6.99 (d, *J* = 7.4 Hz, 2H), 6.82 (t, *J* = 7.4 Hz, 1H), 3.58-3.42 (m, 4H), 2.15 (s, 6H), 2.02-1.92 (m, 4H). ¹³C NMR (101 MHz, CDCl₃): δ 152.48, 150.47, 129.90, 127.74, 121.98,

49.09, 25.13, 18.76. HRMS (ESI): m/z [M + H]⁺ calcd. for C₁₃H₁₉N₂: 203.1548, found: 203.1545.



Prepared according to general catalytic procedure and obtained as a yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.73 (s, 1H), 6.73 (d, *J* = 8.5 Hz, 1H), 6.59 (d, *J* = 2.4 Hz, 1H), 6.44 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.4 Hz, 1H), 3.83 (s,

3H), 3.80 (s, 3H), 3.50-3.42 (m, 4H), 1.95-1.84 (m, 4H). ¹³C NMR (101 MHz, CDCl₃): δ 150.21, 149.20, 146.26, 144.80, 111.76, 110.99, 106.12, 56.14, 55.71, 25.02. HRMS (ESI): m/z [M + H]⁺ calcd. for C₁₃H₁₉N₂O₂: 235.1447, found: 235.1446.



Prepared according to general catalytic procedure and obtained as a brown yellow solid. ¹H NMR (400 MHz, CDCl₃): δ 7.70 (s, 1H), 6.68 (d, J = 8.2 Hz, 1H), 6.52 (d, J = 2.1 Hz, 1H), 6.39 (dd, $J_1 = 8.2$ Hz, $J_2 = 2.1$

Hz, 1H), 5.88 (s, 2H), 3.53-3.41 (m, 4H), 1.97-1.86 (m, 4H). ¹³C NMR (101 MHz, CDCl₃): δ 150.28, 147.94, 147.44, 143.06, 113.16, 108.24, 102.62, 100.83, 48.64, 25.04. HRMS (ESI): m/z [M + H]⁺ calcd. for $C_{12}H_{15}N_2O_2$: 219.1134, found: 219.1131.



Prepared according to general catalytic procedure and obtained as a yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.72 (s, 1H), 7.10-6.97 (m, 3H), 6.80-6.72 (m, 1H), 3.62-3.45 (m, 4H), 2.40 (s, 3H), 1.99-1.90 (m, 4H). ¹³C NMR (101 MHz, CDCl₃): δ 149.69, 149.29, 132.75, 124.90, 123.72, 122.88,

118.06, 55.68, 25.11, 14.46. HRMS (ESI): m/z [M + H]⁺ calcd. for C₁₂H₁₇N₂S: 221.1112, found: 221.1108.



3p

Prepared according to general catalytic procedure and obtained as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.69 (s, 1H), 7.20-7.11 (m, 2H), 6.90-6.82 (m, 2H), 3.51-3.40 (m, 4H), 1.99-1.81 (m, 4H). ¹³C NMR (101 MHz, CDCl₃): δ 151.03, 150.55, 128.89, 127.28, 122.37, 48.84, 25.15. HRMS (ESI): m/z [M + H]⁺ calcd. for C₁₁H₁₄ClN₂: 209.0846, found: 209.0843.

3q

Prepared according to general catalytic procedure and obtained as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.73 (s, 1H), 7.37-7.29 (m, 2H), 6.87-6.79 (m, 2H), 3.55-3.44 (m, 4H), 2.03-1.89 (m, 4H). ¹³C NMR (101 MHz, CDCl₃): δ 151.39, 150.59, 131.89, 122.88, 121.44, 48.93, 25.21. HRMS (ESI): m/z [M + H]⁺ calcd. for C₁₁H₁₄BrN₂: 253.0340, found: 253.0336.



3r

Prepared according to general catalytic procedure and obtained as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.72 (s, 1H), 7.51 (d, *J* = 8.5 Hz, 2H), 6.72 (d, *J* = 8.3 Hz, 2H), 3.56-3.43 (m, 4H), 1.98-1.90 (m, 4H). ¹³C NMR

 $(101 \text{ MHz}, \text{CDCl}_3)$: δ 152.08, 150.55, 137.86, 123.48, 85.41, 49.02, 25.19. HRMS (ESI): m/z [M + H]⁺ calcd. for C₁₁H₁₄IN₂: 301.0202, found: 301.0200.



Prepared according to general catalytic procedure and obtained as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.79 (s, 1H), 7.52-7.44 (m, 2H), 7.01-6.92 (m, 2H), 3.58-3.47 (m, 4H), 2.01-1.91 (m, 4H). ¹³C NMR (101

MHz, CDCl₃): δ 156.48, 150.90, 133.27, 121.73, 119.98, 49.11, 45.58, 25.18, 24.74. HRMS (ESI): m/z [M + H]⁺ calcd. for C₁₂H₁₄N₃: 200.1188, found: 200.1182.



Prepared according to general catalytic procedure and obtained as a colorless oil. ¹H NMR (400 MHz, DMSO-d6): δ 8.08 (s, 1H), 7.76-7.66 (m, 2H), 7.13-7.05 (m, 2H), 3.60-3.49 (m, 2H), 3.41-3.35 (m, 2H), 3.13 (s, 3H), 1.94-1.79 (m, 4H). ¹³C NMR (101 MHz, DMSO-d6): δ 157.58,

 $152.27, 133.17, 128.65, 121.43, 48.90, 45.69, 44.53, 25.19, 24.67. \ HRMS \ (ESI): \ m/z \ [M+H]^+ \ calcd.$ for $C_{12}H_{17}N_2O_2S: 253.1011, \ found: 253.1006.$



Prepared according to general catalytic procedure and obtained as a yellow solid. ¹H NMR (400 MHz, CDCl₃): δ 7.84 (s ,1H), 7.66-7.56 (m, 2H), 7.55-7.47 (m, 2H), 7.46-7.37 (m, 2H), 7.33-7.26 (m, 1H), 7.12-6.99 (m,

2H), 3.64-3.44 (m, 4H), 2.05-1.86 (m, 4H). ¹³C NMR (101 MHz, CDCl₃): δ 151.66, 150.46, 141.17, 135.17, 128.69, 127.71, 126.70, 126.56, 121.53, 48.99, 25.10. HRMS (ESI): m/z [M + H]⁺ calcd. for C₁₇H₁₉N₂: 251.1548, found: 251.1545.



Prepared according to general catalytic procedure and obtained as a pale yellow solid. ¹H NMR (400 MHz, CDCl₃): δ 7.63-7.49 (m, 3H), 7.40-7.31 (m, 3H), 7.28-7.22 (m, 2H), 7.14-7.05 (m, 1H), 7.01-6.93 (m, 1H), 3.53-3.26 (m, 4H), 1.96-1.79 (m, 4H). ¹³C NMR (101 MHz, CDCl₃): δ 150.47,

140.58, 134.77, 1430.44, 130.25, 128.27, 127.59, 126.24, 122.99, 121.34, 48.93, 25.00. HRMS (ESI): m/z [M + H]⁺ calcd. for C₁₇H₁₉N₂: 251.1548, found: 251.1546.



Prepared according to general catalytic procedure and obtained as a brown solid. ¹H NMR (400 MHz, CDCl₃): δ 7.90 (s, 1H), 7.79-7.68 (m, 3H), 7.42-7.36 (m, 1H), 7.34-7.22 (m, 3H), 3.65-3.48 (m, 4H), 2.03-1.90 (m, 4H). ¹³C NMR (101 MHz, CDCl₃): δ 150.80, 150.21, 134.79,

130.35, 128.68, 127.68, 127.07, 125.98, 123.74, 123.43, 116.06, 49.14, 25.01. HRMS (ESI): m/z [M + H]⁺ calcd. for C₁₅H₁₇N₂: 225.1392, found: 225.1391.



 H
 CO2Et
 Prepared according to general catalytic procedure and obtained as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.44-7.34 (m, 2H), 7.31 (t, J = 7.5 Hz, 1H), 7.24 (d, J = 7.5 Hz, 1H), 5.95 (s, 1H), 4.19 (q, J = 7.2 Hz, 2H),

 4.01 (d, J = 5.1 Hz, 2H), 2.37 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): δ

 169.29, 167.11, 139.57, 136.16, 132.60, 130.83, 129.43, 127.66, 61.71, 42.69, 21.27, 14.12.



6c

Prepared according to general catalytic procedure and obtained as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.58 (d, *J* = 7.6 Hz, 1H), 7.39-7.33 (m, 2H), 7.28-7.21 (m, 1H), 5.85 (s, 1H), 4.18 (q, *J* = 7.2 Hz, H), 2.40 (r, 2H), 1.25 (t, *J* = 7.2 Hz, 2H), ¹3C NMP (101 MHz, CDCl));

2H), 4.00 (d, *J* = 5.2 Hz, 2H), 2.49 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 169.28, 166.70, 143.12, 137.10, 131.20, 130.78, 127.46, 127.13, 61.70, 42.62, 21.09, 14.12.



Prepared according to general catalytic procedure and obtained as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.52-7.44 (m, 2H), 6.96-6.90 (m, 2H), 5.94 (s, 1H), 4.17 (q, J = 7.2 Hz, 2H), 4.00 (d, J = 5.2 Hz, 2H), 3.82 (s, 3H), 1.25 (t, J = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 169.34, 167.81,

161.13, 137.36, 118.59, 115.23, 61.68, 55.42, 42.64, 14.12.

Prepared according to general catalytic procedure and obtained as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.60-7.48 (m, 2H), 7.15-7.07 (m, 2H), 5.93 (s, 1H), 4.21 (q, J = 7.2 Hz, 2H), 4.04 (d, J = 5.1 Hz, 2H), 1.27 6e (t, J = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 169.38, 166.63, 164.96, 162.47, 137.74, 137.66, 123.29, 123.25, 116.76, 116.54, 61.79, 42.77, 14.11.

Prepared according to general catalytic procedure and obtained as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.51-7.45 (m, 2H), 7.40-7.36 (m, 2H), 5.98 (s, 1H), 4.21 (q, J = 7.2 Hz, 2H), 4.04 (d, J = 5.1 6f

Hz, 2H), 1.28 (t, J = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 169.27, 166.06, 136.71, 136.28, 129.66, 126.37, 61.86, 42.80, 14.13.

Prepared according to general catalytic procedure and obtained as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.56-7.50 (m, 2H), 7.44-6g 7.37 (m, 2H), 6.03 (s, 1H), 4.21 (q, J = 7.2 Hz, 2H), 4.03 (d, J = 5.2Hz, 2H), 1.27 (t, J = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 169.28, 165.90, 136.90, 132.59, 127.03, 124.51, 61.85, 42.81, 14.14.

Prepared according to general catalytic procedure and obtained as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.97 (s, 2H), 7.88 (s, 1H), 6.24 (s, 1H), 4.25 (q, J = 7.2 Hz, 2H), 4.10 (d, J = 5.1 Hz, 2H), 1.30 3h (t, J = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 169.16, 163.87, 134.89, 132.75, 132.41, 132.08, 131.74, 131.23, 126.92, 124.21, 123.12, 123.09, 123.05, 123.01, 122.98, 121.49, 118.78, 62.07, 43.00, 14.08. HRMS (m/z): calcd for $C_{13}H_{12}F_6NO_3S$ 376.0442 [M + H]⁺, found 376.0427.



Prepared according to general catalytic procedure and obtained as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 8.12 (s, 1H), 7.92-7.81 (m, 3H), 7.65-7.50 (m, 3H), 5.95 (s, 1H), 4.18 (q, J = 7.2 Hz, 2H), 4.03 (d, J = 5.1 Hz, 2H), 1.24 (t, J = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 169.26, 166.97, 135.64, 133.63, 133.51, 131.67, 129.31, 128.10, 127.85, 127.51, 126.86, 125.22, 61.73, 42.73, 14.10.

Prepared according to general catalytic procedure and obtained as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.47-7.39 (m, 2H), 7.24-7.18 (m, 6j 2H), 5.26 (s, 1H), 3.71 (s, 1H), 2.37 (s, 3H), 1.87 (d, J = 9.7 Hz, 2H), 1.66-1.51 (m, 3H), 1.35-1.25 (m, 2H), 1.18-1.02 (m, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 165.49, 139.97, 135.47, 130.28, 125.43, 50.44, 32.86, 25.37, 24.61, 21.35.

6k

Prepared according to general catalytic procedure and obtained as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.41 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 7.9 Hz, 2H), 5.19 (s, 1H), 2.36 (s, 3H), 1.31 (s, 9H). ¹³C NMR (101 MHz, CDCl₃): δ 164.49, 139.67, 135.40, 130.07, 125.58, 53.35, 28.78, 21.27.



Prepared according to general catalytic procedure and obtained as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, *J* = 8.1 Hz, 2H), 7.25-7.21 (m, 4H), 7.16 (s, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 2.38 (s, 3H), 2.28 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 164.81, 140.38, 135.67, 135.10, 134.26, 130.41,

129.58, 124.72, 119.72, 21.40, 20.88.



Prepared according to general catalytic procedure and obtained as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.32-7.26 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 2H),

6.43 (s, 1H), 4.61 (d, J = 6.8 Hz, 2H), 2.45 (s, 3H), 2.36 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 167.03, 145.50, 140.63, 135.33, 133.40, 130.38, 129.94, 128.90, 123.26, 61.17, 21.67, 21.25.



Prepared according to general catalytic procedure and obtained as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.26-7.12 (m, 5H), 5.81 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 4.09 (s, 2H), 3.99 (d, *J* = 4.9 Hz, 2H),

1.20 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 169.51, 167.51, 138.12, 128.96, 128.72, 127.40, 61.89, 42.91, 34.35, 14.25.

HCO2EtPrepared according to general catalytic procedure and obtained as a
colorless oil. ¹H NMR (400 MHz, CDCl3) δ 5.84 (s, 1H), 4.21 (q, J = 7.160Hz, 2H), 4.04 (d, J = 5.1 Hz, 2H), 3.56-3.37 (m, 1H), 2.03-1.91 (m, 2H),1.75-1.65 (m, 2H), 1.61-1.53 (m, 1H), 1.49-1.36 (m, 4H), 1.28 (t, J = 7.1 Hz, 3H), 1.25-1.20 (m, 1H)

1H). ¹³C NMR (101 MHz, CDCl₃): δ 169.67, 168.04, 61.79, 43.87, 42.66, 33.81, 26.12, 25.64, 14.25.



Prepared according to general catalytic procedure and obtained as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 6.00 (s, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 4.05 (d, *J* = 5.0 Hz, 2H), 3.69 (s, 3H), 3.15 (t, *J* = 6.9 Hz,

2H), 2.69 (t, J = 6.9 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 172.27, 169.38, 167.26, 61.78, 51.58, 42.73, 35.11, 25.08, 14.14.

Copies of NMR spectra of building blocks



¹³C NMR spectrum of Az-1





¹³C NMR spectrum of Az



160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 f1 (ppm)

¹³C NMR spectrum of **o-Az-1**



170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 f1 (ppm)

¹³C NMR spectrum of **o-Az-1**



170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 f1 (ppm)

¹³C NMR spectrum of m-Az-1



¹³C NMR spectrum of m-Az-2



¹H NMR spectrum of **m-Az**



170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 f1 (ppm)

¹³C NMR spectrum of **m-Az**

Copies of NMR spectra of products



¹³C NMR spectrum of **3a**






¹³C NMR spectrum of **3c**



¹³C NMR spectrum of **3d**



¹³C NMR spectrum of **3e**



¹³C NMR spectrum of **3f**



¹³C NMR spectrum of **3g**



¹³C NMR spectrum of **3h**



¹³C NMR spectrum of **3i**



¹³C NMR spectrum of **3**j



¹³C NMR spectrum of **3k**



¹³C NMR spectrum of **3**l



¹³C NMR spectrum of **3m**



¹³C NMR spectrum of **3n**



¹³C NMR spectrum of **30**



¹H NMR spectrum of **3p**



¹³C NMR spectrum of **3q**



¹³C NMR spectrum of **3r**



¹H NMR spectrum of **3s**



¹³C NMR spectrum of **3t**



¹³C NMR spectrum of **3u**



¹³C NMR spectrum of **3v**



¹³C NMR spectrum of **3w**







¹³C NMR spectrum of **6b**



¹³C NMR spectrum of **6c**



¹³C NMR spectrum of 6d



¹³C NMR spectrum of **6e**



¹³C NMR spectrum of 6f



¹³C NMR spectrum of **6g**



¹³C NMR spectrum of **6h**



¹³C NMR spectrum of 6i



¹³C NMR spectrum of **6**j



¹³C NMR spectrum of **6k**





¹³C NMR spectrum of **6**l



¹³C NMR spectrum of **6m**



¹³C NMR spectrum of **6n**


¹³C NMR spectrum of **60**



¹³C NMR spectrum of **6p**