

Supplementary Material

Click-based conjugated microporous polymers as efficient heterogeneous photocatalysts for aerobic organic transformations

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Experimental Section

1. materials

2,3,4,5-Tetrabromothiophene, 2-bromothiophene, 3,5-dibromoaniline, 1-bromo-4-iodobenzene, 4-fluoronitrobenzene, carbazole, 4-bromotriphenylamine, diphenylamine, ethyl isocyanoacetate, tertbutyl isocyanide, tosylmethyl isocyanide and thiols were purchased from Beijing Inno Chem Science & Technology Co., Ltd. Copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), sodium ascorbate, sodium acetate (NaOAc), 2,2,6,6-tetramethylpiperidinoxy (TEMPO), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), triethylamine (Et_3N), diisopropylethylamine (*i*-PrEt₂N), tetramethylethylenediamine (TMEDA), tetrahydrofuran (THF), ethyl acetate (EtOAc), dichloromethane (CH_2Cl_2), acetonitrile (CH_3CN), N,N-dimethylformamide (DMF), chloroform (CHCl_3), 1,4-dioxane, methanol (CH_3OH), and dimethyl sulfoxide (DMSO) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Ethynyltrimethylsilane, tetrakis(triphenylphosphine)palladium(0) ($\text{Pd}(\text{PPh}_3)_4$), and [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) ($\text{PdCl}_2(\text{dppf})_2$) were purchased from TCI. These chemicals were used as received without further purification.

2. Sample characterizations

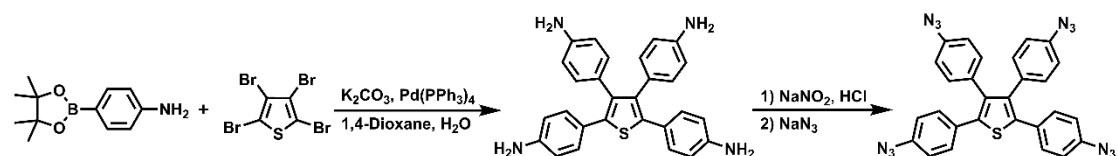
Fourier transform infrared (FT-IR) spectra were recorded on an IR-spectrum one (Perkin Elmer) spectrometer. NMR spectra were recorded on Varian Unity Inova 400 spectrometer (¹H at 400 MHz and ¹³C at 100 MHz). ¹³C cross-polarization magic-angle spinning (CP/MAS) NMR spectra were obtained on Varian Infinity-plus 300 spectrometer. 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 $0.05 < P/P_0 < 0.30$ 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).

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 SCE reference electrode. The samples were prepared by first mixing ground polymer with 5 wt% Nafion to give a homogeneous suspension, then a 10 μL 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 Bu_4NPF_6 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 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 Na_2SO_4 aqueous solution (0.1 M).

4. Synthesis of building blocks

4.1. Synthesis of 2,3,4,5-tetrakis(4-azidophenyl)thiophene



a) Synthesis of 2,3,4,5-tetrakis(4-aminophenyl)thiophene

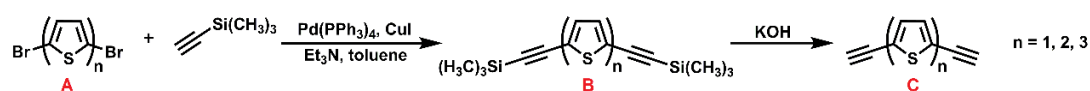
4-Aminophenylboronic acid pinacol ester (2.19 g, 10 mmol), potassium carbonate (1.38 g, 10 mmol), and tetrakis(triphenylphosphine)palladium (0.23 g, 0.2 mmol) were first placed in a 250 mL three-necked flask. The flask was evacuated with an oil pump for 5 minutes and equilibrated with nitrogen. Then, 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 2,3,4,5-tetrabromothiophene (0.77 g, 2.27 mmol). The mixture was heated at 110°C for 12 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 ($50 \text{ mL} \times 3$). The combined organic layers were washed with brine, dried over MgSO_4 , concentrated and purified on a silica gel column (DCM/EtOAc 5:1, v/v) to give 2,3,4,5-tetrakis(4-aminophenyl)thiophene as a light yellow solid (0.74 g, 73%). $^1\text{H NMR}$ (400 MHz,

DMSO-*d*₆) δ 6.82 (d, J = 8.5 Hz, 4H), 6.55 (d, J = 8.4 Hz, 4H), 6.38 (d, J = 8.6 Hz, 4H), 6.31 (d, J = 8.4 Hz, 4H), 5.04 (s, 8H); ¹³C NMR (101 MHz, DMSO-*d*₆) δ 148.09, 147.08, 138.66, 135.94, 131.48, 129.70, 125.05, 122.46, 113.99, 113.96.

b) Synthesis of 2,3,4,5-tetrakis(4-azidophenyl)thiophene

In a round-bottom flask equipped with a magnetic stirring bar, 2,3,4,5-tetrakis(4-aminophenyl)thiophene (0.70 g, 1.56 mmol) was suspended in HCl (6 N, 3 mL) cooled in an ice bath. Then 10 mL of aqueous solution of NaNO₂ (0.22 g, 3.18 mmol) was added dropwise. The reaction mixture was stirred for 0.5 h and 10 mL of aqueous solution of NaN₃ (0.46 g, 7.04 mmol) was added dropwise. After addition, the mixture was allowed to stir for another 12 h at room temperature. Then the mixture was extracted with ethyl acetate (15 mL \times 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/EtOAc 5:1, v/v) to afford 2,3,4,5-tetrakis(4-azidophenyl)thiophene as a dark brown solid (0.78 g, 91%). ¹H NMR (400 MHz, CDCl₃) δ 7.19 (d, J = 8.6 Hz, 4H), 6.96-6.88 (m, 8H), 6.83 (d, J = 8.6 Hz, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 139.32, 138.80, 138.42, 137.98, 132.74, 132.14, 130.55, 130.52, 119.18, 118.91. HRMS (m/z): calcd for C₂₈H₁₇N₁₂S 553.1420 [M + H]⁺, found 553.1418.

4.2. Synthesis of diacetylenes C



To a stirred solution of dibromides **A** (4.0 mmol), tetrakis(triphenylphosphine) palladium (232 mg, 0.2 mmol) and CuI (40 mg, 0.2 mmol) in dry triethylamine (10 mL) and toluene (10 mL) was added (trimethylsilyl)acetylene (864 mg, 8.8 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 **B**. Then **B** was suspended in tetrahydrofuran (10 mL) and methanol (10 mL), and an aqueous KOH solution (2 M, 10 mL) was added dropwise. The mixture was stirred at room temperature for 3 h and extracted with dichloromethane (30 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/DCM 5:1, v/v) to afford diacetylenes C.

2,5-Diethynylthiophene (806 mg, 68%): green liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.13 (s, 2H), 3.37 (s, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 132.76, 123.67, 82.34, 76.32.

5,5'-Diethynyl-2,2'-bithiophene (608 mg, 71%): green solid. ^1H NMR (400 MHz, CDCl_3) δ 7.17 (d, $J = 3.8$ Hz, 2H), 7.03 (d, $J = 3.8$ Hz, 2H), 3.42 (s, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 138.22, 134.09, 124.03, 121.56, 82.79, 76.77.

5,5''-Diethynyl-2,2':5',2''-terthiophene (370 mg, 70%): green solid. ^1H NMR (400 MHz, CDCl_3) δ 7.18 (d, $J = 3.8$ Hz, 2H), 7.08 (s, 2H), 7.02 (d, $J = 3.8$ Hz, 2H), 3.42 (s, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 138.55, 136.00, 134.06, 125.11, 123.45, 120.98, 82.61, 76.77.

4.3. Synthesis of Ta-Ths

4.1. Synthesis of Ta-Th-4

To a stirred solution of 2,3,4,5-tetrakis(4-azidophenyl)thiophene (276 mg, 0.5 mmol), and 2,5-diethynylthiophene (132 mg, 1.0 mmol) in DMF (60 mL) were added $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (50 mg, 0.2 mmol) and sodium ascorbate (40 mg, 0.2 mmol). Afterward, the mixture was heated to 100 °C for 48 h. The resultant precipitate was collected by filtration, rinsed with DMF (2×30 mL) and methanol (2×30 mL), and then dispersed in saturated EDTA-2Na solution (30 mL) at room temperature for 12 h. The suspension was filtered and the residue was washed with excess H_2O , CH_3OH , THF and CH_2Cl_2 . Further purification of the sample was performed by Soxhlet extraction with THF and CH_2Cl_2 successively for 24 h each time. The powder was then dried in vacuum at 100 °C overnight to give Ta-Th-4 as a yellow powder (367 mg, 90 %).

4.2. Synthesis of Ta-Th-5

Ta-Th-5 was synthesized with a similar procedure to Ta-Th-4 using 2,3,4,5-tetrakis(4-azidophenyl)thiophene (276 mg, 0.5 mmol) and 5,5'-diethynyl-2,2'-bithiophene (214 mg, 1.0 mmol) as comonomers. The polymer was obtained as a yellowish brown powder (446 mg, 91 %).

4.3. Synthesis of Ta-Th-6

Ta-Th-6 was synthesized with a similar procedure to Ta-Th-4 using 2,3,4,5-tetrakis(4-azidophenyl)thiophene (414 mg, 0.75 mmol) and 5,5''-diethynyl-2,2':5',2''-terthiophene (445 mg, 1.5 mmol) as comonomers. The polymer was obtained as a brown powder (816 mg, 95 %).

4.4. Synthesis of substrates

Isocyanides and N-Substituted tetrahydroisoquinolines were synthesized according to the published procedures [1,2].

5. General procedure for the photocatalytic Ugi multicomponent reaction

A glass tube was charged with substrate N,N-dimethylaniline (0.4 mmol), aryl isocyanide (0.2 mmol), H₂O (2.0 mmol), photocatalyst (10 mg), and THF (3 mL). The resulting mixture was irradiated with blue LED light (18 W, 460-465 nm, 6000-7000 K) at room temperature and O₂ atmosphere with an O₂ balloon. After reaction, the catalyst was isolated by centrifugation and thoroughly washed with THF and CH₂Cl₂. The combined organic phases were evaporated under reduced pressure, and the residue was purified by silica gel column chromatography to give the desired product. For reuse studies, the isolated catalyst was dried in vacuum before being reused in further reactions under the same conditions.

6. General procedure for the photocatalytic α -oxidation of N-substituted tetrahydroisoquinolines

A glass tube was charged with substrate N-substituted tetrahydroisoquinoline (0.2 mmol), Ta-Th-6 (10 mg), DBN (0.4 mmol) and DMSO (3 mL). The resulting mixture was irradiated with blue LED light (18 W, 460-465 nm, 6000-7000 K) at room temperature and O₂ atmosphere with an O₂ balloon. After reaction, the catalyst was isolated by centrifugation and thoroughly washed with THF and CH₂Cl₂. The combined organic phases were evaporated under reduced pressure, and the residue was purified by silica gel column chromatography to give the desired product. For reuse studies, the isolated catalyst was dried in vacuum before being reused in further reactions under the same conditions.

References

- [1] W. Bao, M. He, J. Wang, X. Peng, M. Sung, Z. Tang, S. Jiang, Z. Cao and W. He, *J. Org. Chem.*, 2019, **84**, 6065-6071.
- [2] P. Gao, X. Weng, Z. Wang, C. Zheng, B. Sun, Z. Chen, S. You, T. Mei, *Angew. Chem. Int. Ed.*, 2020, **132**, 15366-15371.

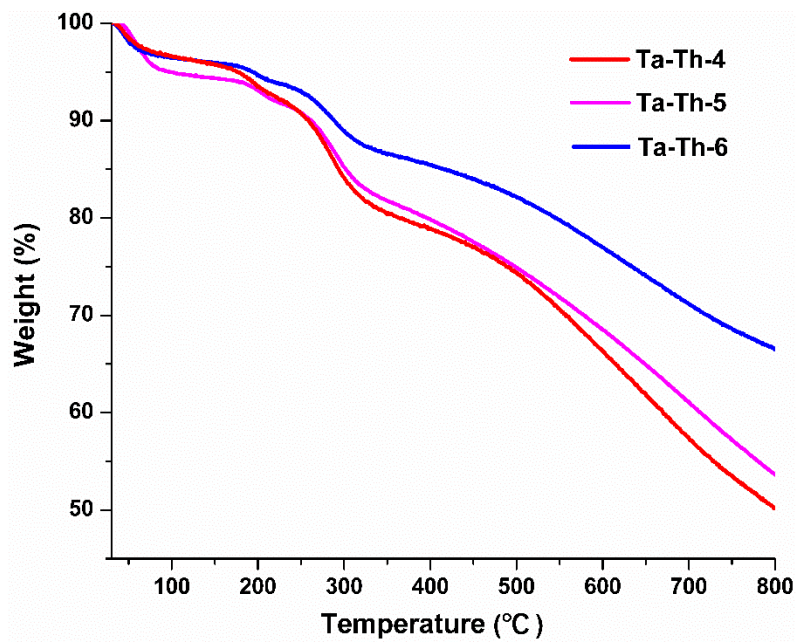


Fig. S1 TGA curves of Ta-Ths.

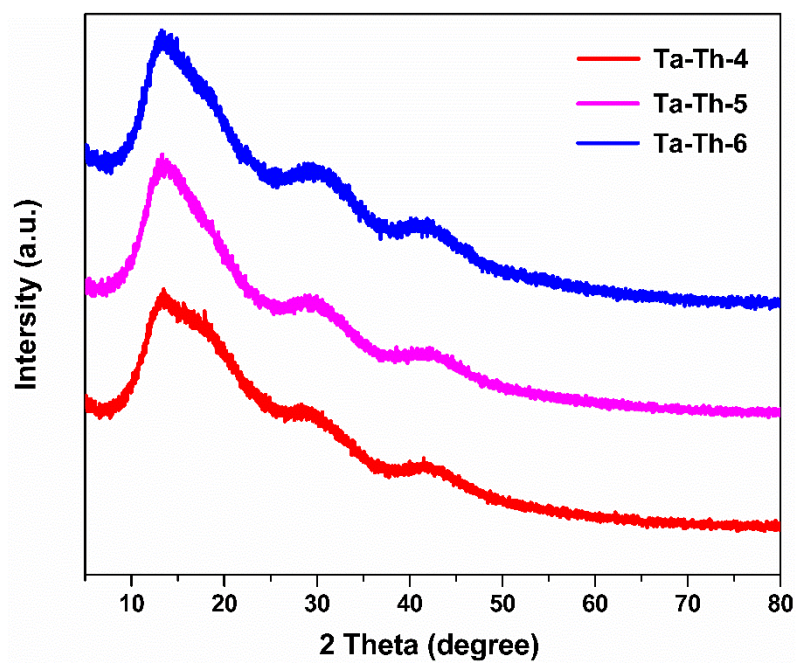


Fig. S2 PXRD curves of Ta-Ths.

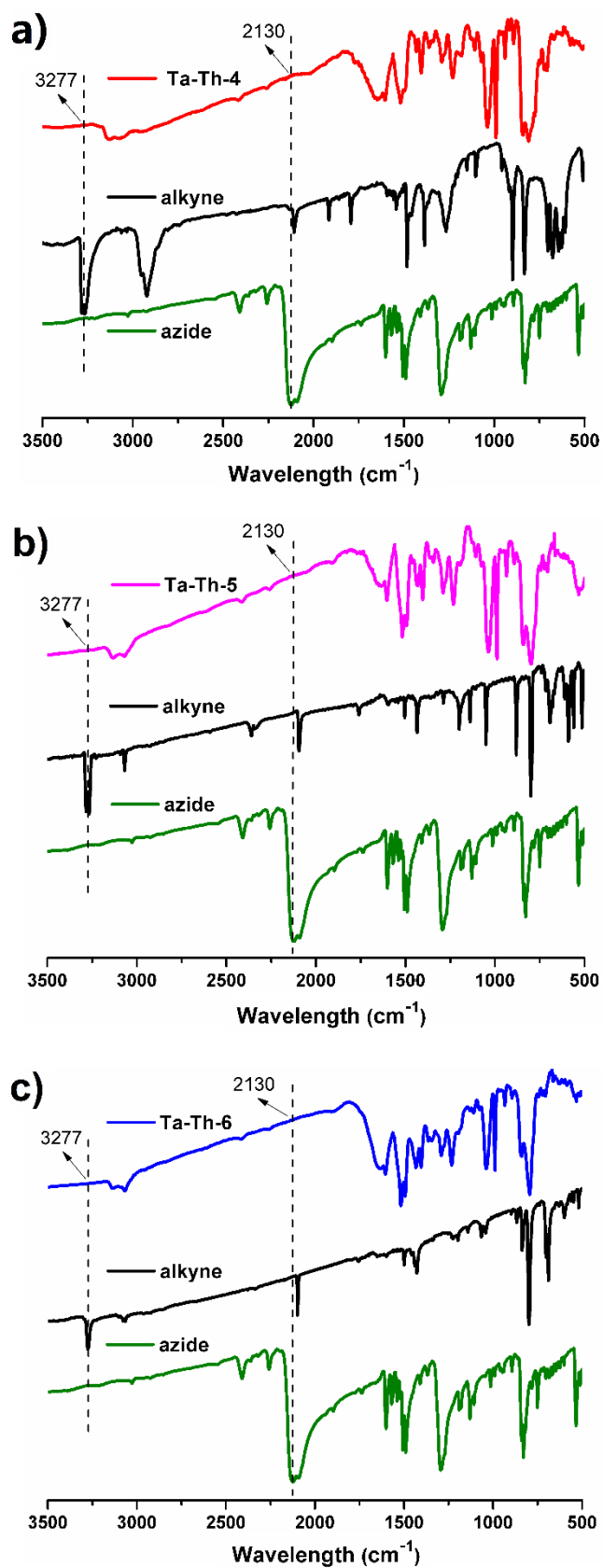


Fig. S3 IR spectra for (a) Ta-Th-4, (b) Ta-Th-5, (c) Ta-Th-6 and respective monomers.

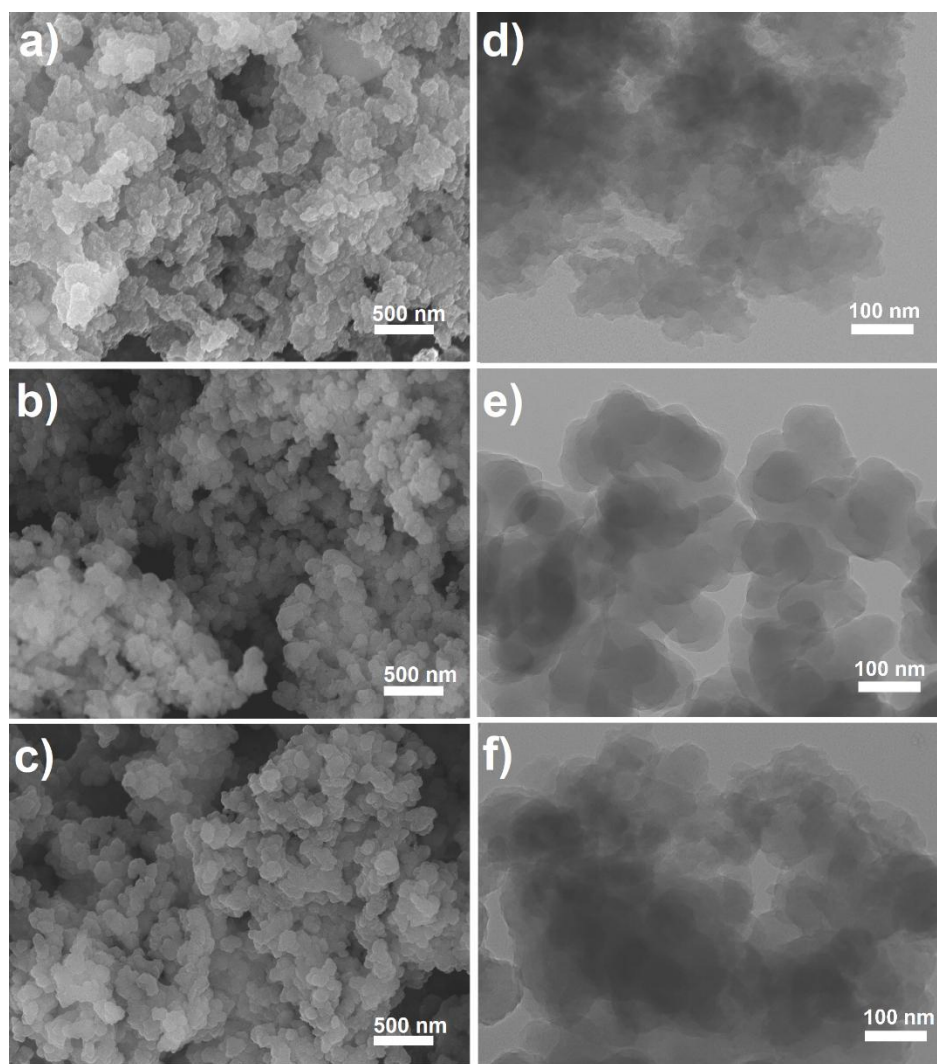


Fig. S4 SEM images of (a) Ta-Th-4, (b) Ta-Th-5, and (c) Ta-Th-6, and TEM images of (d) Ta-Th-4, (e) Ta-Th-5, and (f) Ta-Th-6.

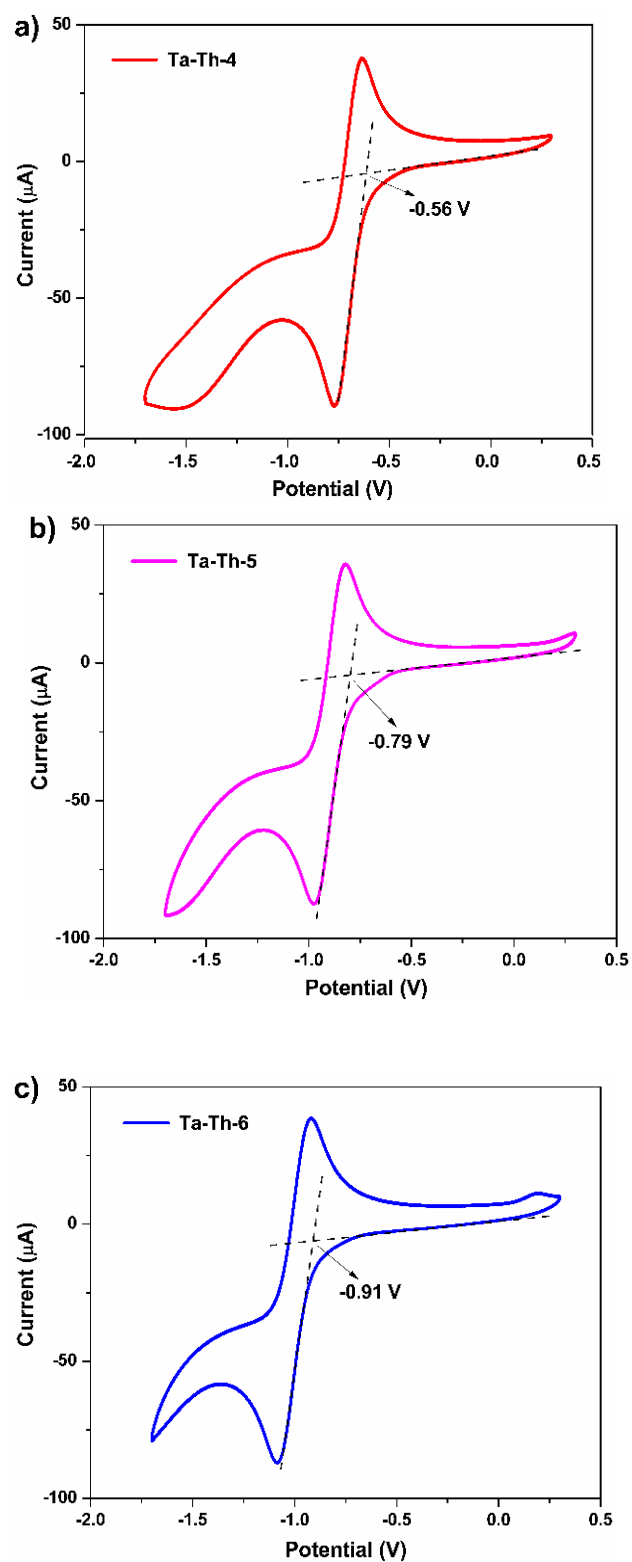
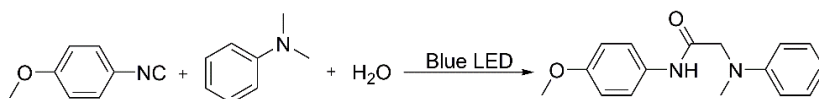
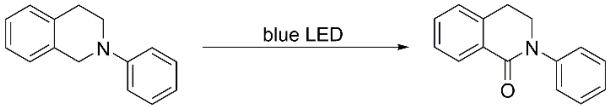


Fig. S5 Cyclic voltammograms of (a) Ta-Th-4, (b) Ta-Th-5 and (c) Ta-Th-6.

Table S1 Multicomponent Ugi reaction under various conditions^a

Entry	Catalyst	Atmosphere	Additive	Yield ^b (%)
1	Ta-Th-6	Dark	-	0
2	No catalyst	O ₂	-	0
3	Ta-Th-6	N ₂	-	0
4 ^c	Ta-Th-6	O ₂	CuCl ₂	16
5 ^d	Ta-Th-6	O ₂	KI	21
6 ^e	Ta-Th-6	O ₂	Benzoquinone	12
7 ^f	Ta-Th-6	O ₂	NaN ₃	70

^a Reaction condition: Reaction conditions: 4-methoxyphenylisocyanide (0.2 mmol), N,N-dimethylaniline (0.4 mmol), H₂O (2.0 mmol), Ta-Th-6 (10 mg), THF (3 mL), O₂ balloon, blue LED (18 W), room temperature, 12 h. ^b Isolated yield. ^c CuCl₂ as an electron scavenger. ^d Benzoquinone as a superoxide scavenger. ^e KI as a hole scavenger. ^f NaN₃ as a singlet oxygen scavenger.

Table S2 α -oxidation of N-phenyltetrahydroisoquinoline under various conditions^a

The reaction scheme shows the α -oxidation of N-phenyltetrahydroisoquinoline (a bicyclic amine with a phenyl group on the nitrogen) to N-phenyl-2-oxotetrahydroisoquinoline (the corresponding imino-ketone) under blue LED light.

Entry	Catalyst	Atmosphere	Additive	Yield ^b (%)
1	Ta-Th-6	Dark	-	0
2	No catalyst	O ₂	-	0
3	Ta-Th-6	N ₂	-	0
4 ^c	Ta-Th-6	O ₂	-	23
5 ^d	Ta-Th-6	O ₂	CuCl ₂	Trace
6 ^e	Ta-Th-6	O ₂	KI	24
7 ^f	Ta-Th-6	O ₂	Benzoquinone	13
8 ^g	Ta-Th-6	O ₂	NaN ₃	87

^a Reaction conditions: N-phenyltetrahydroisoquinoline (0.2 mmol), Ta-Th-6 (10 mg), base (0.4 mmol), solvent (3 mL), O₂ balloon, blue LED (18 W), room temperature, 12 h. ^b Isolated yield. ^c No base was used. ^d CuCl₂ as an electron scavenger. ^e KI as a hole scavenger. ^f Benzoquinone as a superoxide scavenger. ^g NaN₃ as a singlet oxygen scavenger.

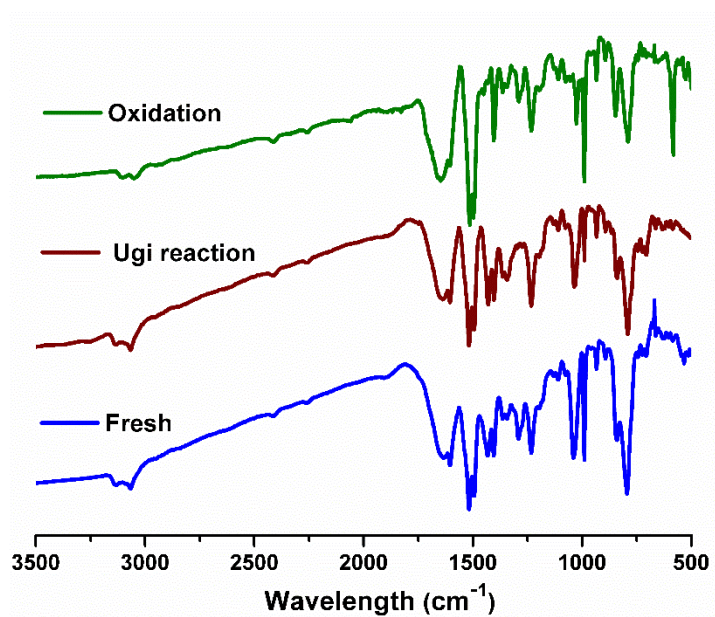


Fig. S6 FT-IR spectra of fresh and 5th recycled Ta-Th-6.

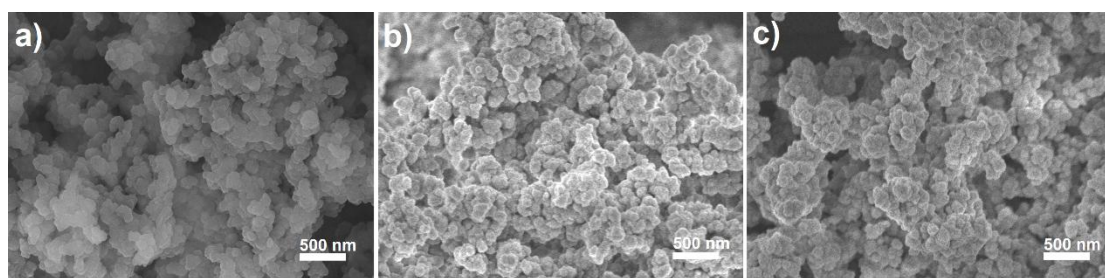
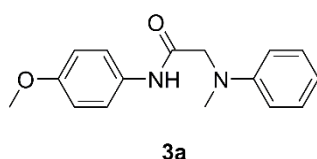
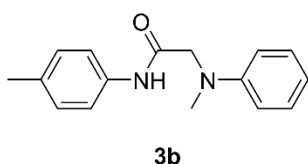


Fig. S7 SEM images of (a) fresh Ta-Th-6, (b) 5th recycled Ta-Th-6 in Ugi reaction, and (c) 5th recycled Ta-Th-6 in oxidation reaction.

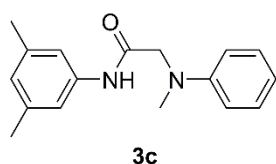
Products characterization



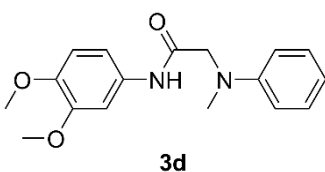
Prepared according to general catalytic procedure and obtained as a white solid. ^1H NMR (400 MHz, CDCl_3): δ 8.35 (s, 1H), 7.45-7.40 (m, 2H), 7.34-7.28 (m, 2H), 6.92-6.81 (m, 5H), 3.94 (s, 2H), 3.78 (s, 3H), 3.08 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 168.56, 156.66, 149.56, 130.41, 129.57, 121.84, 119.31, 114.20, 113.72, 59.93, 55.54, 40.11.



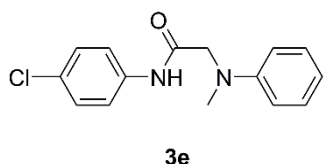
Prepared according to general catalytic procedure and obtained as a white solid. ^1H NMR (400 MHz, CDCl_3): δ 8.36 (s, 1H), 7.43-7.38 (m, 2H), 7.33-7.27 (m, 2H), 7.12 (d, $J = 8.2$ Hz, 2H), 6.89 (t, $J = 7.3$ Hz, 1H), 6.83 (d, $J = 7.9$ Hz, 2H), 3.95 (s, 2H), 3.08 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 168.62, 149.54, 134.69, 134.68, 134.29, 129.54, 120.03, 119.35, 113.74, 60.05, 40.08, 20.94.



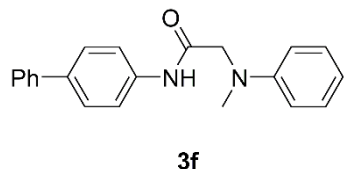
Prepared according to general catalytic procedure and obtained as a white solid. ^1H NMR (400 MHz, CDCl_3): δ 7.93 (s, 1H), 7.36-7.30 (m, 2H), 7.11-7.03 (m, 3H), 6.91-6.86 (m, 3H), 4.06 (s, 2H), 3.15 (s, 3H), 2.18 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 168.96, 149.14, 135.36, 133.28, 129.64, 128.40, 127.58, 119.11, 113.45, 59.06, 40.10, 18.63.



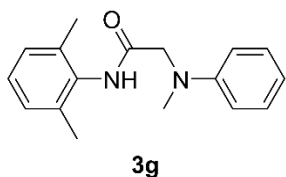
Prepared according to general catalytic procedure and obtained as a white solid. ^1H NMR (400 MHz, CDCl_3): δ 8.37 (s, 1H), 7.34-7.27 (m, 3H), 6.94-6.87 (m, 2H), 6.84 (d, $J = 8.0$ Hz, 2H), 6.78 (d, $J = 8.6$ Hz, 1H), 3.94 (s, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 3.07 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 168.55, 149.58, 149.08, 146.04, 130.89, 129.54, 119.39, 113.77, 111.92, 111.25, 104.75, 60.07, 56.12, 55.99, 40.09.



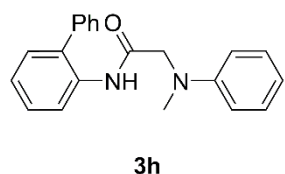
Prepared according to general catalytic procedure and obtained as a white solid. ^1H NMR (400 MHz, CDCl_3): δ 8.45 (s, 1H), 7.50-7.46 (m, 2H), 7.35-7.26 (m, 4H), 6.91 (t, $J = 7.3$ Hz, 1H), 6.83 (d, $J = 8.0$ Hz, 2H), 3.95 (s, 2H), 3.08 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 168.84, 149.45, 135.82, 129.59, 129.58, 129.06, 121.16, 119.61, 113.82, 60.10, 40.20.



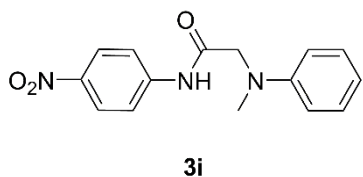
Prepared according to general catalytic procedure and obtained as a white solid. ^1H NMR (400 MHz, CDCl_3): δ 8.51 (s, 1H), 7.64-7.54 (m, 6H), 7.43 (t, $J = 7.6$ Hz, 2H), 7.37-7.30 (m, 3H), 6.92 (t, $J = 7.3$ Hz, 1H), 6.86 (d, $J = 8.0$ Hz, 2H), 3.99 (s, 2H), 3.10 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 168.87, 149.57, 140.52, 137.56, 136.58, 129.63, 128.88, 127.72, 127.26, 126.95, 120.30, 119.55, 113.87, 60.18, 40.20.



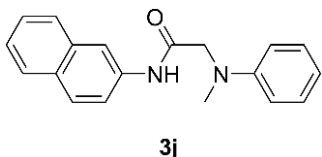
Prepared according to general catalytic procedure and obtained as a white solid. ^1H NMR (400 MHz, CDCl_3): δ 8.34 (s, 1H), 7.33-7.28 (m, 2H), 7.17 (s, 2H), 6.90 (t, $J = 7.3$ Hz, 1H), 6.83 (d, $J = 8.0$ Hz, 2H), 6.77 (s, 1H), 3.94 (s, 2H), 3.08 (s, 3H), 2.29 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 168.69, 149.62, 138.89, 137.15, 129.62, 126.43, 119.45, 117.72, 113.82, 60.21, 40.14, 21.44.



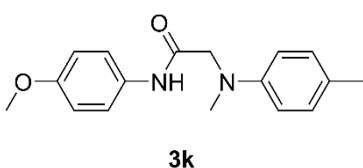
Prepared according to general catalytic procedure and obtained as a white solid. ^1H NMR (400 MHz, CDCl_3): δ 8.74 (s, 1H), 8.55 (d, $J = 8.1$ Hz, 1H), 7.42-7.37 (m, 1H), 7.25-7.04 (m, 9H), 6.85 (t, $J = 7.3$ Hz, 1H), 6.56 (d, $J = 8.1$ Hz, 2H), 3.83 (s, 2H), 2.65 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 168.61, 148.67, 137.53, 134.59, 131.94, 129.83, 129.26, 129.03, 128.79, 128.54, 127.64, 124.12, 119.93, 118.83, 113.15, 59.63, 39.40.



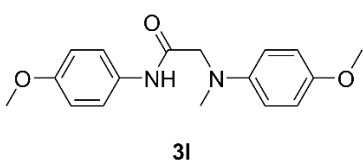
Prepared according to general catalytic procedure and obtained as a white solid. ^1H NMR (400 MHz, CDCl_3): δ 8.79 (s, 1H), 8.22-8.18 (m, 2H), 7.75-7.70 (m, 2H), 7.35-7.29 (m, 2H), 6.93 (t, $J = 7.3$ Hz, 1H), 6.84 (d, $J = 8.0$ Hz, 2H), 3.99 (s, 2H), 3.10 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 169.61, 149.44, 143.91, 143.07, 129.78, 120.12, 119.43, 114.11, 60.38, 40.51.



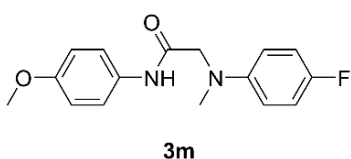
Prepared according to general catalytic procedure and obtained as a white solid. ^1H NMR (400 MHz, CDCl_3): δ 8.61 (s, 1H), 8.23 (s, 1H), 7.83-7.76 (m, 3H), 7.50-7.38 (m, 3H), 7.36-7.30 (m, 2H), 6.95-6.85 (m, 3H), 4.01 (s, 2H), 3.12 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 167.90, 148.50, 133.64, 132.73, 129.74, 128.53, 127.77, 126.63, 126.53, 125.53, 124.11, 118.79, 118.45, 115.72, 112.78, 59.15, 39.12.



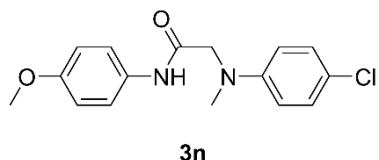
Prepared according to general catalytic procedure and obtained as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 8.41 (s, 1H), 7.45-7.40 (m, 2H), 7.11 (d, $J = 8.4$ Hz, 2H), 6.88-6.83 (m, 2H), 6.77-6.72 (m, 2H), 3.90 (s, 2H), 3.79 (s, 3H), 3.04 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.77, 156.68, 147.57, 130.54, 130.09, 128.87, 121.79, 114.26, 114.08, 60.34, 55.59, 20.40.



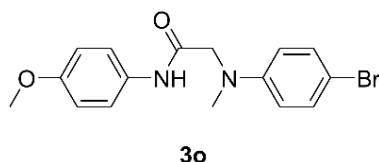
Prepared according to general catalytic procedure and obtained as a white solid. ^1H NMR (400 MHz, CDCl_3): δ 8.79 (s, 1H), 8.22 – 8.18 (m, 2H), 7.75 – 7.70 (m, 2H), 7.32 (dd, $J = 8.7, 7.4$ Hz, 2H), 6.93 (t, $J = 7.3$ Hz, 1H), 6.84 (d, $J = 8.0$ Hz, 2H), 3.99 (s, 2H), 3.10 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 169.61, 149.44, 143.91, 143.07, 129.78, 120.12, 119.43, 114.11, 60.38, 40.51.



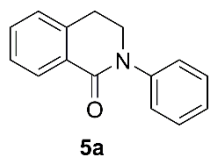
Prepared according to general catalytic procedure and obtained as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 8.36 (s, 1H), 7.48-7.37 (m, 2H), 7.04-6.95 (m, 2H), 6.89-6.83 (m, 2H), 6.80-6.73 (m, 2H), 3.88 (s, 2H), 3.79 (s, 3H), 3.04 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 167.22, 157.06, 155.64, 154.69, 145.11, 129.25, 120.68, 115.04, 114.82, 114.17, 114.09, 113.17, 59.49, 54.47, 39.74.



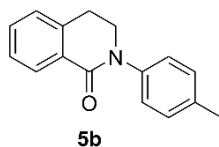
Prepared according to general catalytic procedure and obtained as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 8.21 (s, 1H), 7.43-7.37 (m, 2H), 7.26-7.19 (m, 2H), 6.88-6.82 (m, 2H), 6.75-6.69 (m, 2H), 3.91 (s, 2H), 3.78 (s, 3H), 3.07 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 166.96, 155.69, 146.97, 129.13, 128.29, 120.80, 113.75, 113.16, 58.71, 54.46, 39.28.



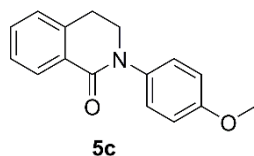
Prepared according to general catalytic procedure and obtained as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 8.15 (s, 1H), 7.43-7.33 (m, 4H), 6.88-6.82 (m, 2H), 6.71-6.65 (m, 2H), 3.92 (s, 2H), 3.78 (s, 3H), 3.07 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 166.88, 155.72, 147.36, 131.22, 129.09, 120.80, 114.19, 113.18, 110.53, 58.65, 54.48, 39.22.



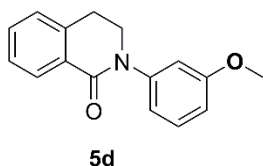
Prepared according to general catalytic procedure and obtained as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 8.16 (dd, $J_1 = 7.7$, $J_2 = 1.1$ Hz, 1H), 7.49-7.44 (m, 1H), 7.43-7.35 (m, 5H), 7.28-7.21 (m, 2H), 3.99 (t, $J = 6.5$ Hz, 2H), 3.14 (t, $J = 6.5$ Hz, 2H); ¹³C NMR (101 MHz, CDCl₃): δ 164.26, 143.15, 138.34, 132.08, 129.75, 128.96, 128.79, 127.24, 126.98, 126.30, 125.37, 49.45, 28.66.



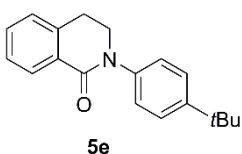
Prepared according to general catalytic procedure and obtained as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 8.12 (dd, $J_1 = 7.7$, $J_2 = 1.5$ Hz, 1H), 7.44-7.38 (m, 1H), 7.35-7.29 (m, 1H), 7.25-7.14 (m, 5H), 3.91 (t, $J = 6.5$ Hz, 2H), 3.08 (t, $J = 6.5$ Hz, 2H), 2.32 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 164.27, 140.60, 138.36, 136.06, 131.97, 129.84, 129.57, 128.72, 127.17, 126.97, 125.24, 49.54, 28.65, 21.09.



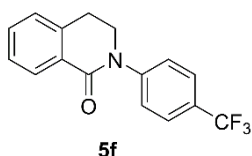
Prepared according to general catalytic procedure and obtained as a yellow solid. ¹H NMR (400 MHz, CDCl₃): δ 8.15 (dd, $J_1 = 7.7$, $J_2 = 1.1$ Hz, 1H), 7.49-7.42 (m, 1H), 7.40-7.34 (m, 1H), 7.32-7.27 (m, 2H), 7.23 (d, $J = 7.5$ Hz, 1H), 6.97-6.91 (m, 2H), 3.94 (t, $J = 6.5$ Hz, 2H), 3.82 (s, 3H), 3.13 (t, $J = 6.5$ Hz, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 164.43, 157.84, 138.33, 136.13, 131.96, 129.79, 128.71, 127.19, 126.97, 126.70, 114.27, 55.54, 49.73, 28.66.



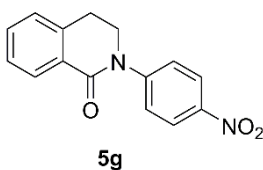
Prepared according to general catalytic procedure and obtained as a white solid. ^1H NMR (400 MHz, CDCl_3): δ 8.16 (dd, $J_1 = 7.7$, $J_2 = 1.1$ Hz, 1H), 7.50-7.43 (m, 1H), 7.40-7.28 (m, 2H), 7.25-7.21 (m, 1H), 6.98-6.94 (m, 2H), 6.84-6.78 (m, 1H), 3.97 (t, $J = 6.5$ Hz, 2H), 3.81 (s, 3H), 3.13 (t, $J = 6.5$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ 164.24, 160.02, 144.32, 138.36, 132.10, 129.74, 129.63, 128.76, 127.22, 127.01, 117.52, 112.19, 111.44, 55.42, 49.52, 28.64.



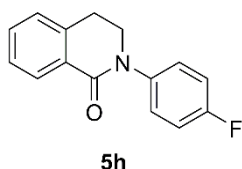
Prepared according to general catalytic procedure and obtained as a white solid. ^1H NMR (400 MHz, CDCl_3): δ 8.16 (dd, $J_1 = 7.7$, $J_2 = 1.1$ Hz, 1H), 7.49-7.29 (m, 6H), 7.25-7.21 (m, 1H), 3.99 (t, $J = 6.5$ Hz, 2H), 3.13 (t, $J = 6.5$ Hz, 2H), 1.33 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ 164.27, 149.12, 140.45, 138.34, 131.98, 129.87, 128.77, 127.20, 126.94, 125.88, 124.76, 49.44, 34.56, 31.39, 28.66.



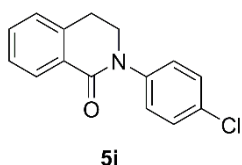
Prepared according to general catalytic procedure and obtained as a white solid. ^1H NMR (400 MHz, CDCl_3): δ 8.16 (dd, $J_1 = 7.7$, $J_2 = 1.1$ Hz, 1H), 7.71-7.63 (m, 2H), 7.57-7.46 (m, 3H), 7.43-7.36 (m, 1H), 7.29-7.23 (m, 1H), 4.03 (t, $J = 6.4$ Hz, 2H), 3.17 (t, $J = 6.4$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ 164.26, 146.10, 138.27, 132.49, 129.27, 128.92, 128.02, 127.69, 127.41, 127.10, 126.03, 126.00, 125.96, 125.92, 125.37, 125.13, 49.12, 28.53.



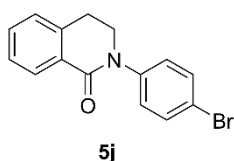
Prepared according to general catalytic procedure and obtained as a yellow solid. ^1H NMR (400 MHz, CDCl_3): δ 8.31-8.24 (m, 2H), 8.16 (dd, $J_1 = 7.7$, $J_2 = 1.1$ Hz, 1H), 7.64-7.59 (m, 2H), 7.45-7.37 (m, 1H), 7.41 (t, $J = 7.4$ Hz, 1H), 7.28 (d, $J = 7.6$ Hz, 1H), 4.08 (t, $J = 6.4$ Hz, 2H), 3.20 (t, $J = 6.4$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ 164.24, 148.68, 144.76, 138.26, 132.84, 129.06, 128.95, 127.55, 127.18, 124.83, 124.29, 49.00, 28.43.



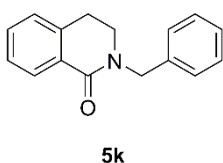
Prepared according to general catalytic procedure and obtained as a white solid. ^1H NMR (400 MHz, CDCl_3): δ 8.15 (dd, $J_1 = 7.7$, $J_2 = 1.1$ Hz, 1H), 7.50-7.45 (m, 1H), 7.41-7.33 (m, 3H), 7.25 (d, $J = 7.6$ Hz, 1H), 7.13-7.06 (m, 2H), 3.96 (t, $J = 6.5$ Hz, 2H), 3.15 (t, $J = 6.5$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ 164.41, 159.52, 139.10, 138.28, 132.19, 129.52, 128.77, 127.30, 127.17, 127.09, 127.04, 115.89, 115.67, 49.59, 28.61.



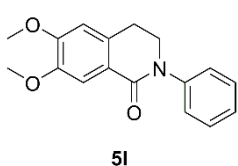
Prepared according to general catalytic procedure and obtained as a white solid. ^1H NMR (400 MHz, CDCl_3): δ 8.14 (dd, $J_1 = 7.7$, $J_2 = 1.1$ Hz, 1H), 7.51-7.44 (m, 1H), 7.41-7.31 (m, 5H), 7.25 (d, $J = 7.5$ Hz, 1H), 3.97 (t, $J = 6.4$ Hz, 2H), 3.14 (t, $J = 6.4$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ 164.24, 141.60, 138.28, 132.28, 131.58, 129.45, 129.01, 128.80, 127.32, 127.06, 126.58, 49.33, 28.56.



Prepared according to general catalytic procedure and obtained as a white solid. ^1H NMR (400 MHz, CDCl_3): δ 8.14 (dd, $J_1 = 7.7$, $J_2 = 1.1$ Hz, 1H), 7.56-7.44 (m, 3H), 7.42-7.35 (m, 1H), 7.31-7.26 (m, 2H), 7.25 (d, $J = 8.1$ Hz, 1H), 3.97 (t, $J = 6.4$ Hz, 2H), 3.15 (t, $J = 6.4$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ 164.20, 142.10, 138.25, 132.29, 131.98, 129.43, 128.82, 127.34, 127.05, 126.91, 119.48, 49.28, 28.56.

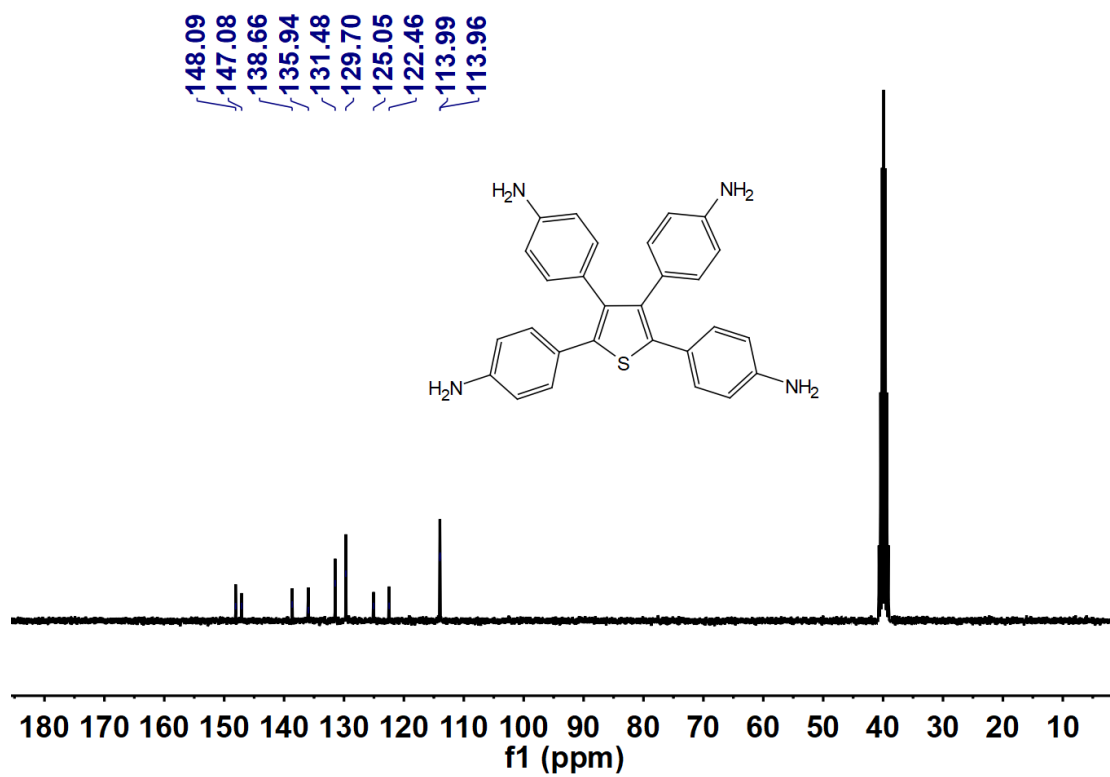
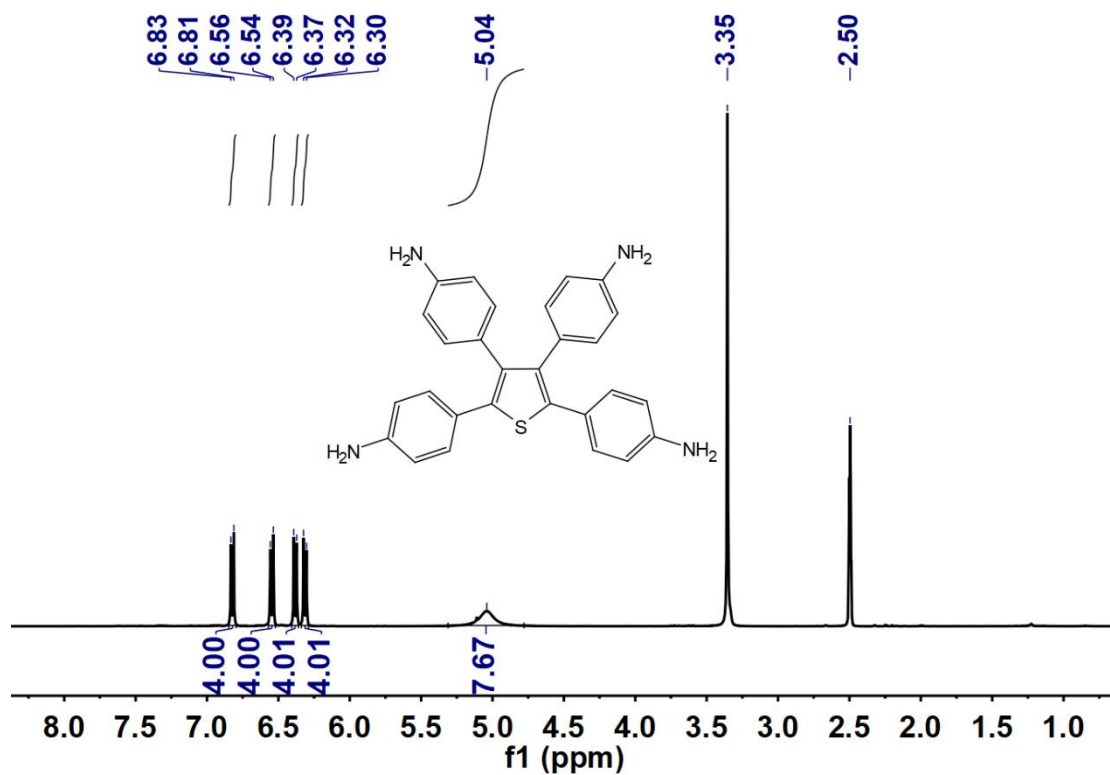


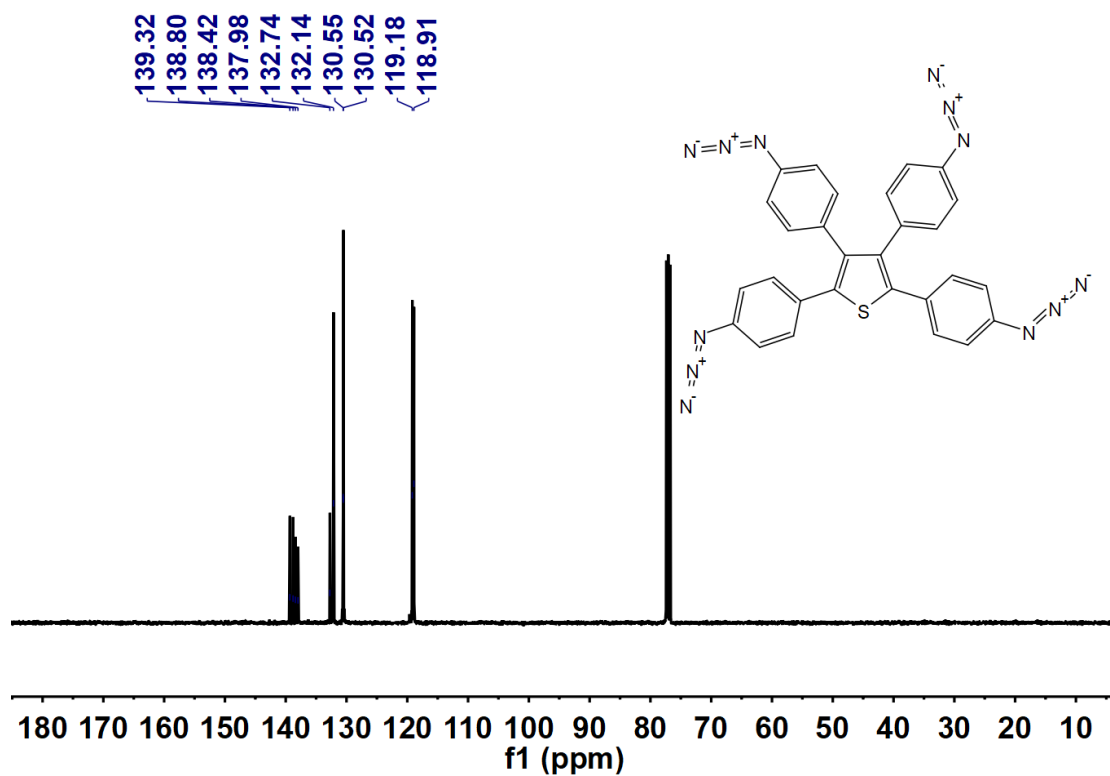
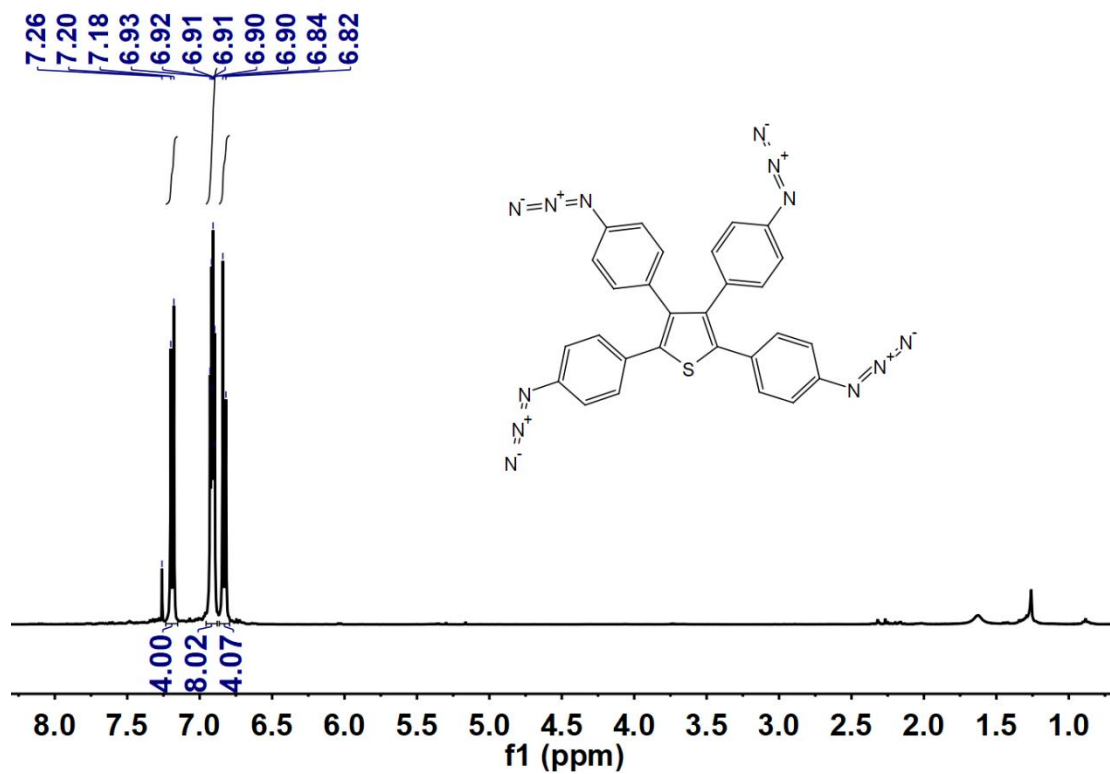
Prepared according to general catalytic procedure and obtained as a yellow solid. ^1H NMR (400 MHz, CDCl_3): δ 8.16 (dd, $J_1 = 7.6$, $J_2 = 1.3$ Hz, 1H), 7.45-7.27 (m, 7H), 7.16 (d, $J = 6.8$ Hz, 1H), 4.80 (s, 2H), 3.49 (t, $J = 6.6$ Hz, 2H), 2.94 (t, $J = 6.6$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ 164.63, 138.10, 137.48, 131.74, 129.41, 128.68, 128.50, 128.09, 127.48, 127.11, 126.94, 50.48, 45.38, 28.12.

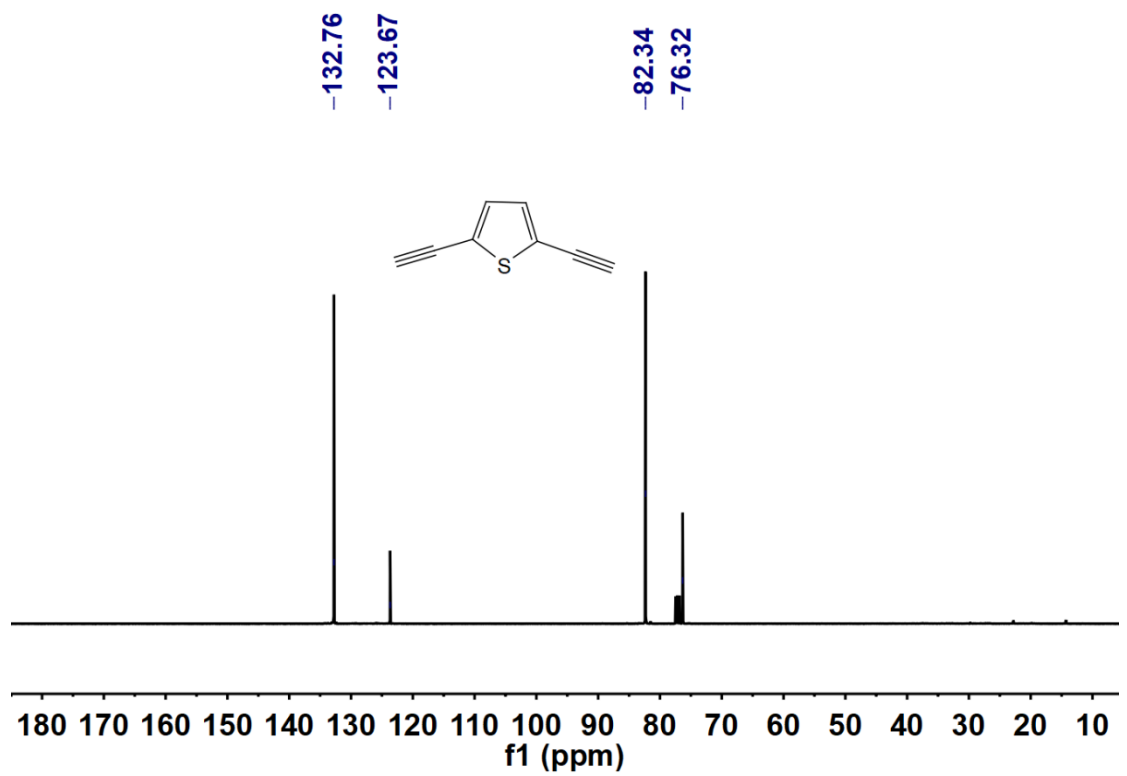
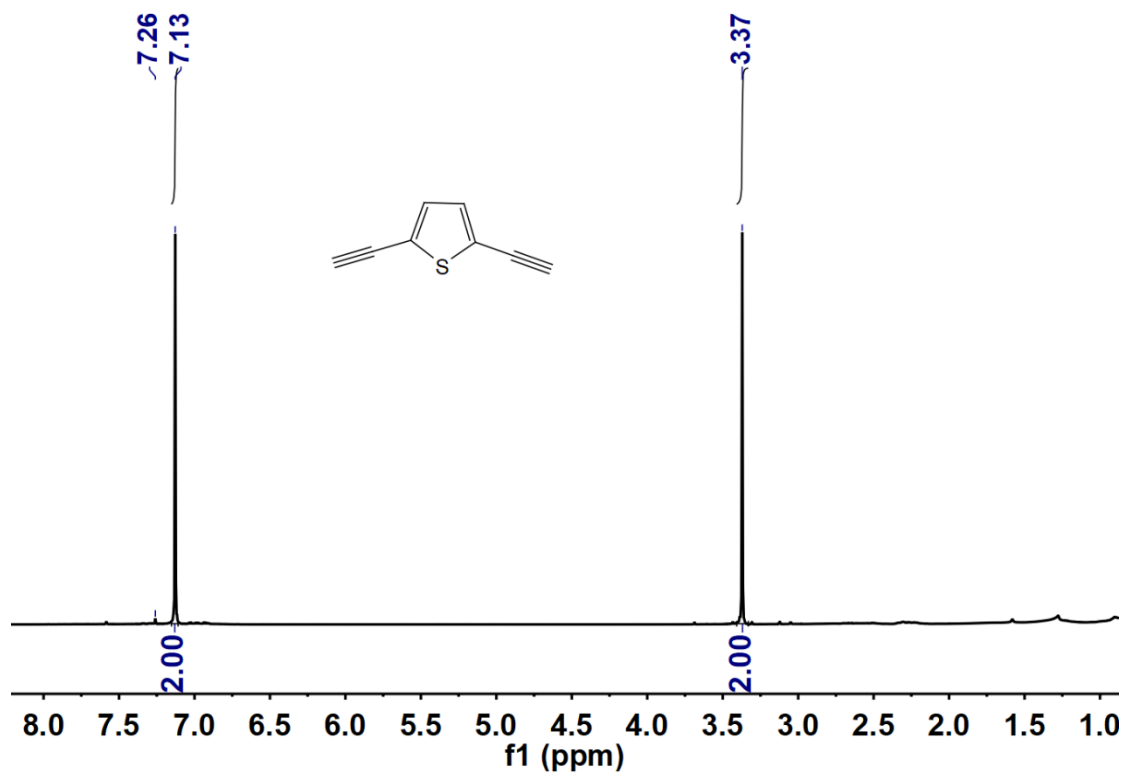


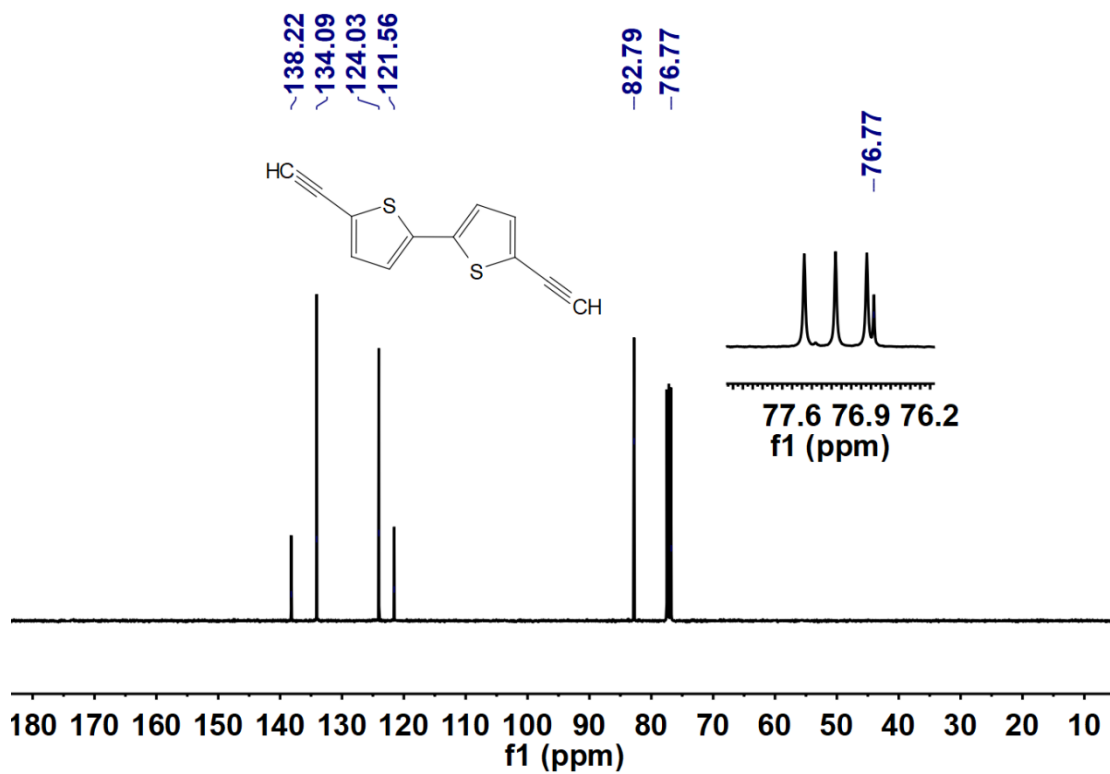
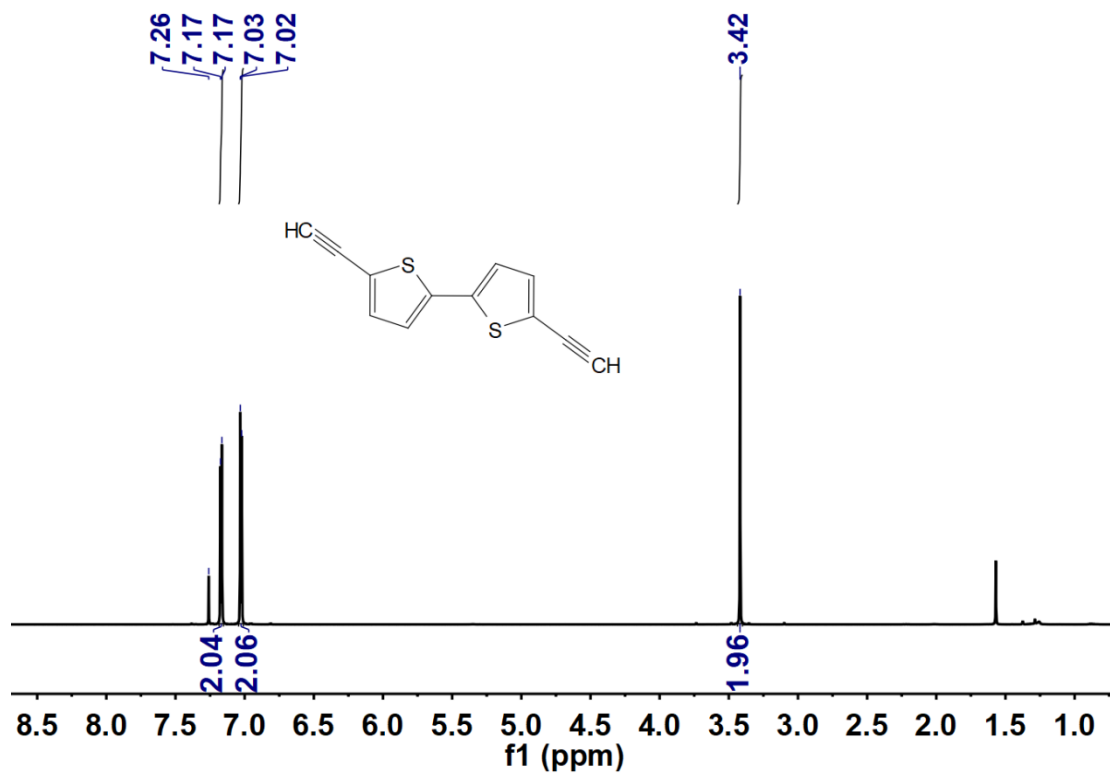
Prepared according to general catalytic procedure and obtained as a yellow solid. ^1H NMR (400 MHz, CDCl_3): δ 7.66 (s, 1H), 7.43-7.35 (m, 4H), 7.26-7.21 (m, 1H), 6.69 (s, 1H), 3.97 (t, $J = 6.5$ Hz, 2H), 3.94 (s, 3H), 3.92 (s, 3H), 3.06 (t, $J = 6.5$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ 164.28, 152.18, 148.13, 143.32, 132.14, 128.88, 126.11, 125.33, 122.21, 110.87, 109.23, 56.11, 49.65, 28.28.

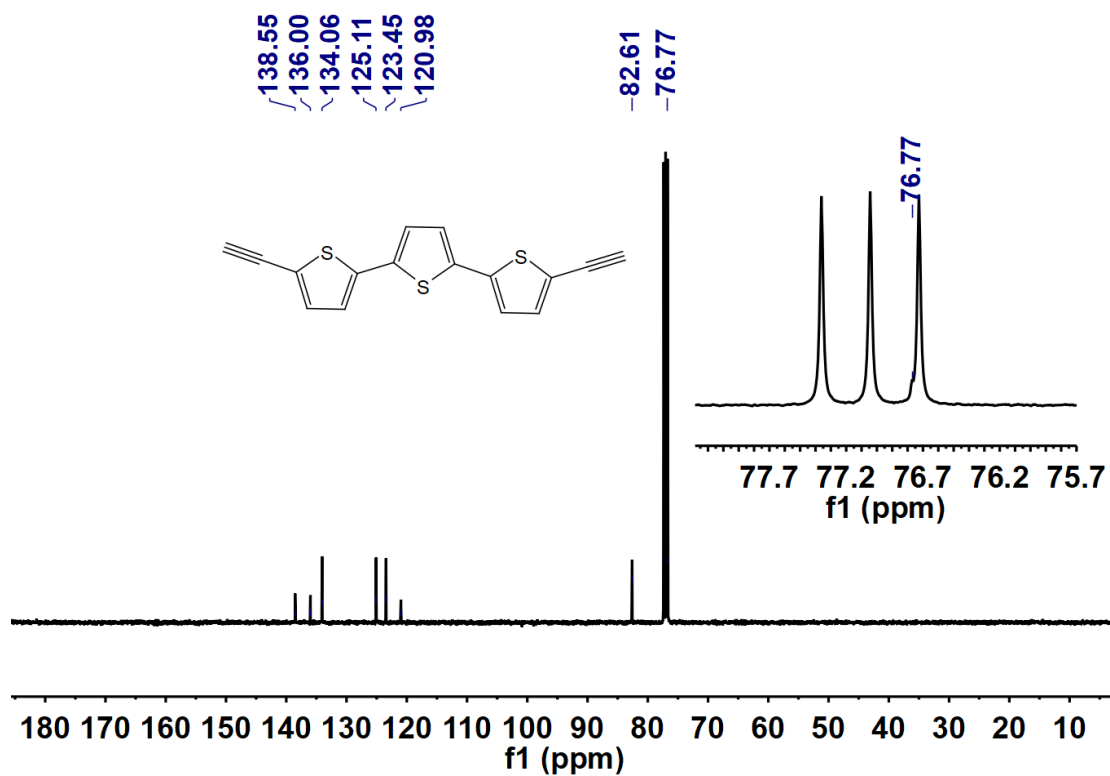
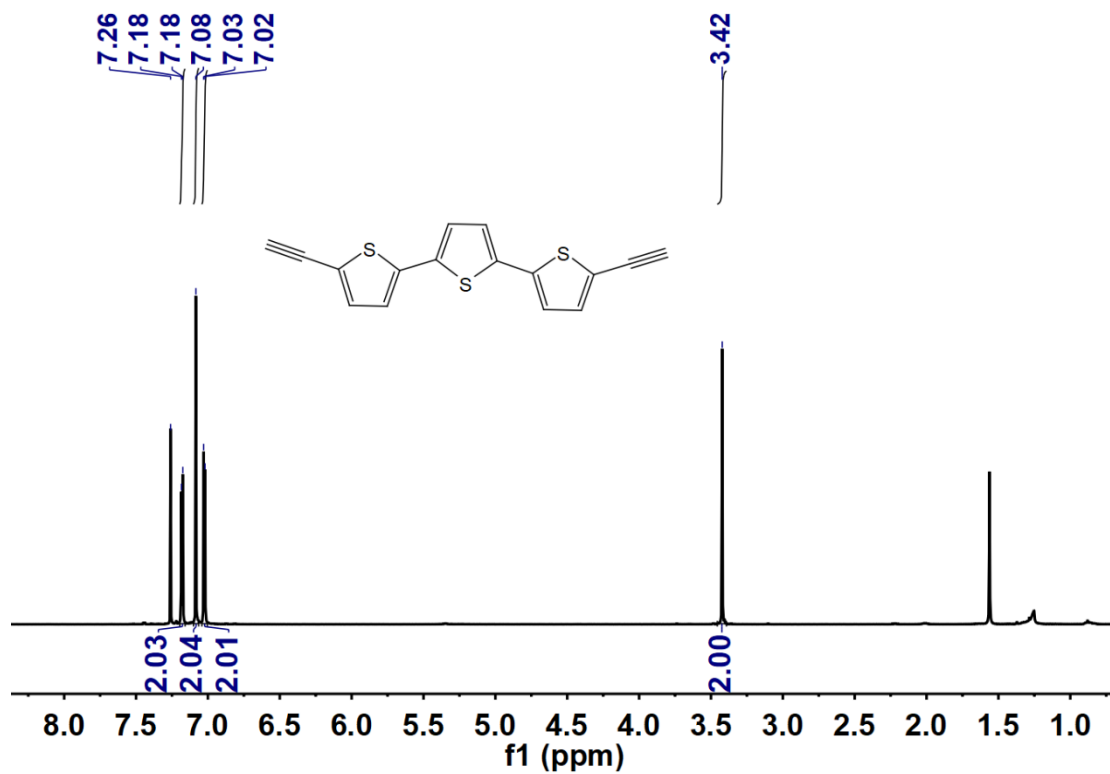
Copies of NMR spectra of building blocks











Copies of NMR spectra of products

