

## Supporting Information

# Photocatalytic Regio- and Stereo-Selective [2+2] Cycloaddition of Styrene Derivatives Using a Heterogeneous Organic Photocatalyst

*Run Li, Beatriz Chiyin Ma, Wei Huang, Lei Wang, Di Wang, Hao Lu, Katharina Landfester and Kai. A. I. Zhang\**

*Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany*

*kai.zhang@mpip-mainz.mpg.de*

## Table of contents

I. General information

II. Synthesis of B-BT

III. General procedure for photocatalytic [2+2] cycloaddition reaction using B-BT

IV. Compound characterization

V. Physical characterizations such as BET surface area, CV, EPR, TGA and UPS measurements

VI.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of products

## I. General information:

*trans*-Anethole, *a*-asarone, *trans*-isoeugenol and *trans*-isomethyleugenol were purchased from commercial sources and used without further purification. Other styrene derivatives were purified by elution through neutral aluminium oxide (50-200 um) and anhydrous  $\text{CaCl}_2$  (w/w, 95/5). Chemicals and solvents purchased from commercial sources were used as received unless otherwise noted. The reactions conversions were monitored by GC-MS. Column flash chromatography was conducted with silica 60 (0.063-0.2 mm). Reaction yield refer to pure compound after being purified with column.

## Methods

UV-Vis absorption and FTIR spectra were recorded on a Perkin Elmer Lambda 100 spectrophotometer and Varian 1000 FT-IR spectrometer at ambient temperature, respectively. Electron paramagnetic resonance (EPR) spectrum was performed on a Magnettech Miniscope MS200 spectrometer with spin trapping EPR at DMPO (0.1 M), catalyst (1 mg/ml) and anethole (0.1 M) in nitromethane. Another spin trapping EPR for PBN trapping experiment was conducted at PBN (0.1 M), catalyst (1 mg/ml) and anethole (0.1 M) in nitromethane on a Bruker EMX-plua spectrometer (Bruker B-VT 2000). The related simulation for the EPR spectrum was according to the condition: g factor was 2.00604. Frequency of measurement was 9.313456 (GHz) and  $B_c$  (magnetic center field) is 3317 (G). Cyclic voltammetry measurement was recorded on a Metrohm Autolab PGSTAT204 potentiostat/galvanostat in a three-electrode-cell system: glassy carbon electrode as the working electrode,  $\text{Hg}/\text{HgCl}_2$  electrode as the reference electrode, platinum wire as the counter electrode, and  $\text{Bu}_4\text{NPF}_6$  (0.1 M acetonitrile) as supporting electrolyte with a scan rate of 100 mV  $\text{s}^{-1}$  in the range of -2 eV to 2 eV. The morphology was recorded by a scanning electron microscope (SEM) (LEO Gemini 1530, Germany) with an in lens SE detector and a transmission electron microscope (TEM) (JEOL JEM-1400). Thermogravimetric analysis (TGA) was conducted in a nitrogen atmosphere with temperature increasing from room temperature to 1000 °C at a rate of 10 K/min. GC-MS measurement was conducted on Shimadzu GC-2010 plus gas chromatography and QP2010 ultra mass spectrometer with fused silica column (122-5532, DB-5MS) and flame ionization detector.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for all compounds were measured using Bruker AVANCE 300 MR (at 300 MHz) and are referenced to 0.00 ppm and 0.0 ppm for  $\text{SiMe}_4$ . Surface areas and pore size distributions were carried out by nitrogen adsorption and desorption at 77.3 K by Autosorb 1 (Quantachrome Instruments). Data were obtained using QuadraWin software from Quantachrome Instruments. Pore size distributions and pore volumes were calculated from the adsorption branches of the isotherms using Quenched Solid Density Functional Theory (QSDFT,  $\text{N}_2$ , evaluating carbon adsorbent with slit pores). B-BT was degassed at 80 °C for 24 h under vacuum before analysis. The BET surface area was obtained based on data points received from  $0 < \text{P}/\text{P}_0 < 0.25$  with the nonlinear density functional theory (NLDFT) equilibrium model being employed as the BET model fitting.

## II. Synthesis of B-BT

The conjugated microporous polymer B-BT was prepared by palladium catalyzed Sonogashira-Hagihara cross coupling reactions. Typically, 4,7-dibromobenzo[c][1,2,5]thiadiazole (117.6 mg, 0.4 mmol), 1,3,5-triethylbenzene (60.1 mg, 0.4 mmol), tetrakis(triphenylphosphine)palladium(0) (7 mg, 0.006 mmol), cooper(I) iodide (1.4 mg, 0.007 mmol) were dissolved in dry DMF (20 ml). Then, 0.8 ml trimethylamine was added following by degassing with N<sub>2</sub> for 30 min. After degassing process, the reactive mixture was heated at 80 °C for 72 h. The obtained precipitate was washed with chloroform, water and acetone for three times and then extracted in a Soxhlet extractor with acetone and THF for 48 h each, respectively. Finally, a yellow solid product was collected after dry in vacuum oven at 60 °C for 24 h.

## III. General procedure of the photocatalytic [2+2] cycloaddition reaction using B-BT.

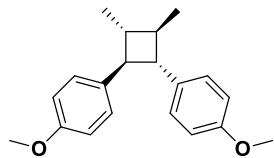
### General procedure A: homo [2+2] cycloaddition

In a 40 ml vial was charged with 0.24 mmol alkene-1 (*trans*-Anethole, *a*-Asarone, *trans*-Isoeugenol and *trans*-Isomethyleugenol), B-BT (2.4 mg) and CH<sub>3</sub>NO<sub>2</sub> (2.4 ml). Then the vial was placed under air condition in front of a blue LED lamp (460nm, 1.2 W/cm<sup>2</sup>). The conversion of alkene-1 was determined by GC-MS measurement. Upon consumption of alkene-1, the mixture was poured into a separatory funnel containing the mixture of Et<sub>2</sub>O and water (v/v, 1/1). The organic layers was separated and extracted with Et<sub>2</sub>O (30 ml). A crude product was obtained after drying over anhydrous MgSO<sub>4</sub> and concentrating with rotary evaporator. Finally, the cycloaddition products could be obtained after purification with flash-column chromatography.

### General procedure B: heterogeneous unsymmetrical [2+2] cycloaddition

In a 40 ml vial was charged with 0.24 mmol alkene-1 (*trans*-Anethole, *a*-Asarone, *trans*-Isoeugenol and *trans*-Isomethyleugenol), 1.2 mmol alkene-2 (other styrene derivatives), B-BT (2.4 mg) and CH<sub>3</sub>NO<sub>2</sub> (2.4 ml). Then the vial was placed under air condition in front of a blue LED lamp (460nm, 1.2 W/cm<sup>2</sup>). The conversion of alkene-1 was determined by GC-MS measurement. Upon consumption of alkene-1, the mixture was poured into a separatory funnel containing the mixture of Et<sub>2</sub>O and water (v/v, 1/1). The organic layers was separated and extracted with Et<sub>2</sub>O (30 ml). A crude product was obtained after drying over anhydrous MgSO<sub>4</sub> and concentrating with rotary evaporator. Finally, the cycloaddition products could be obtained after purification with flash-column chromatography.

#### IV. Compound Characterization



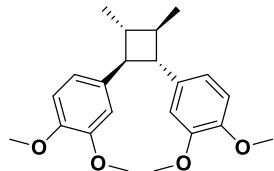
##### **4,4'-(1S,2S,3R,4R)-3,4-dimethylcyclobutane-1,2-diyl)bis(methoxybenzene):**

According to the general procedure A, a 40 ml vial with a magnetic stir bar was charged with *trans*-anethole (35.6 mg, 0.24 mmol), B-BT (2.4 mg) and  $\text{CH}_3\text{NO}_2$  (2.4 ml). After the reaction was completed, the mixture was performed as the workup protocol and purified by chromatography on silica with hexane/ethyl acetate (15/1) as the elution to afford the pure cycloadduct as clear oil.

$R_f$  (hexane/ethyl acetate 15/1): 0.12

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.07 (AA' of AA'BB',  $J$  = 9 Hz, 4H), 6.76 (BB' of AA'BB',  $J$  = 9 Hz, 4H), 3.69 (s, 6H), 2.74 (inverted d, 2H), 1.76 (m, 2H), 1.11 (d,  $J$  = 6 Hz, 6H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  157.95, 135.94, 127.74, 113.71, 55.26, 52.50, 43.24, 18.90.



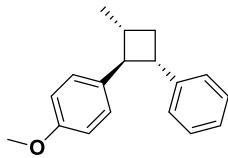
##### **4,4'-(1S,2S,3R,4R)-3,4-dimethylcyclobutane-1,2-diyl)bis(1,2-dimethoxybenzene):**

According to the general procedure A, a 40 ml vial with a magnetic stir bar was charged with *trans*-isomethyleugenol (40.7  $\mu\text{l}$ , 0.24 mmol), B-BT (2.4 mg) and  $\text{CH}_3\text{NO}_2$  (2.4 ml). After the reaction was completed, the mixture was performed as the workup protocol and purified by chromatography on silica with hexane/ethyl acetate (3/1) as the elution to afford the pure cycloadduct as clear oil.

$R_f$  (hexane/ethyl acetate): 0.41

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  6.83 (d,  $J$  = 3 Hz, 2H), 6.79 (d,  $J$  = 1.5 Hz, 2H), 6.72 (m, 2H), 3.86 (s, 6H), 3.85 (s, 6H), 2.82 (d,  $J$  = 9 Hz, 2H), 1.87 (m, 2H), 1.22 (d,  $J$  = 6 Hz, 6H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  148.82, 147.43, 136.47, 118.56, 111.23, 110.26, 55.93, 55.83, 53.01, 42.93, 18.89.

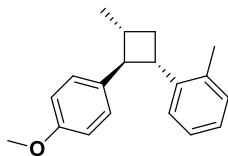


**1-methoxy-4-((1S,2R,4S)-2-methyl-4-phenylcyclobutyl)benzene:** According to the general procedure B, a 40 ml vial with a magnetic stir bar was charged with *trans*-anethole (35.6 mg, 0.24 mmol), styrene (138  $\mu$ l, 1.2 mmol), B-BT (2.4 mg) and  $\text{CH}_3\text{NO}_2$  (2.4 ml). After the reaction was completed, the mixture was performed as the workup protocol and purified by chromatography on silica with hexane/dichloromethane (6/1) as the elution to afford the pure cycloadduct as clear oil.

$R_f$  (hexane/dichloromethane 6/1): 0.26

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.33 (m, 2H), 7.22 (m, 5H), 6.93 (BB' of AA'BB',  $J$  = 9 Hz 2H), 3.84 (s, 3H), 3.44 (q,  $J$  = 12 Hz, 1H), 3.01 (t,  $J$  = 9 Hz, 1H), 2.56 (dt,  $J$  = 9 Hz, 15 Hz, 1H), 2.39 (m, 1H), 1.75 (q,  $J$  = 9 Hz, 1H), 1.26 (d,  $J$  = 6 Hz 3H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  158.10, 144.69, 135.87, 128.27, 127.82, 126.66, 125.95, 113.79, 55.58, 55.28, 44.14, 35.55, 33.97, 20.52.

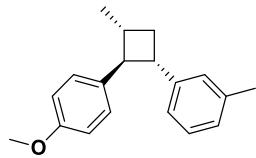


**1-((1S,2S,3R)-2-(4-methoxyphenyl)-3-methylcyclobutyl)-2-methylbenzene:** According to the general procedure A, a 40 ml vial with a magnetic stir bar was charged with *trans*-anethole (35.6 mg, 0.24 mmol), 2-methylstyrene (154.8  $\mu$ l, 1.2 mmol), B-BT (2.4 mg) and  $\text{CH}_3\text{NO}_2$  (2.4 ml). After the reaction was completed, the mixture was performed as the workup protocol and purified by chromatography on silica with hexane/dichloromethane (6/1) as the elution to afford the pure cycloadduct as clear oil.

$R_f$  (hexane/dichloromethane 6/1): 0.31

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.22 (d,  $J$  = 9 Hz, 1H), 7.11 (AA' of AA'BB',  $J$  = 9 Hz, 2H), 7.06 (m, 1H), 6.99 (m, 2H), 6.75 (BB' of AA'BB',  $J$  = 9 Hz, 2H), 3.66 (s, 3H), 3.44 (q,  $J$  = 12 Hz, 1H), 3.03 (t,  $J$  = 12 Hz, 1H), 2.51 (q,  $J$  = 12 Hz, 1H), 2.24 (m, 1H), 2.09 (s, 3H), 1.47 (q,  $J$  = 12 Hz, 1H), 1.11 (d,  $J$  = 6 Hz, 3H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  158.14, 142.39, 136.12, 136.02, 130.06, 127.85, 125.98, 125.91, 125.82, 113.82, 55.30, 53.44, 41.81, 35.77, 34.79, 20.71, 19.93.

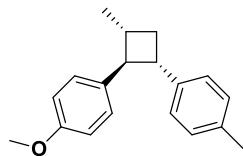


**1-((1S,2S,3R)-2-(4-methoxyphenyl)-3-methylcyclobutyl)-3-methylbenzene:** According to the general procedure B, a 40 ml vial with a magnetic stir bar was charged with *trans*-anethole (35.6 mg, 0.24 mmol), 3-methylstyrene (157.6  $\mu$ l, 1.2 mmol), B-BT (2.4 mg) and  $\text{CH}_3\text{NO}_2$  (2.4 ml). After the reaction was completed, the mixture was performed as the workup protocol and purified by chromatography on silica with hexane/dichloromethane (10/1) as the elution to afford the pure cycloadduct as clear oil.

$R_f$  (hexane/dichloromethane 10/1): 0.21

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.24 (m, 3H), 7.09 (m, 3H), 6.94 (BB' of AA'BB',  $J$  = 9 Hz, 2H), 3.86 (s, 3H), 3.45 (q,  $J$  = 9 Hz, 1H), 3.03 (t,  $J$  = 9 Hz, 1H), 2.60 (dt,  $J$  = 12, 6 Hz, 1H), 2.42 (m, 1H), 2.39 (s, 3H), 1.78 (q,  $J$  = 9 Hz, 1H), 1.28 (d,  $J$  = 6 Hz, 3H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  158.08, 144.66, 137.80, 135.99, 128.20, 127.82, 127.43, 126.75, 123.77, 113.78, 55.44, 55.28, 44.08, 35.55, 34.14, 21.54, 20.56.

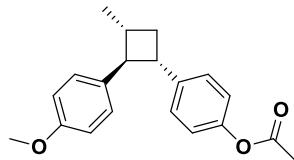


**1-methoxy-4-((1S,2R,4S)-2-methyl-4-(p-tolyl)cyclobutyl)benzene:** According to the general procedure B, a 40 ml vial with a magnetic stir bar was charged with *trans*-anethole (35.6 mg, 0.24 mmol), 4-methylstyrene (157.6  $\mu$ l, 1.2 mmol), B-BT (2.4 mg) and  $\text{CH}_3\text{NO}_2$  (2.4 ml). After the reaction was completed, the mixture was performed as the workup protocol and purified by chromatography on silica with hexane/dichloromethane (6/1) as the elution to afford the pure cycloadduct as clear oil.

$R_f$  (hexane/dichloromethane 6/1): 0.35

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.09 (AA' of AA'BB',  $J$  = 9 Hz, 2H), 7.00 (s, 4H), 6.77 (BB' of AA'BB',  $J$  = 9 Hz, 2H), 3.70 (s, 3H), 3.27 (q,  $J$  = 9 Hz, 1H), 2.84 (t,  $J$  = 9 Hz, 1H), 2.42 (q,  $J$  = 9 Hz, 1H), 2.25 (m, 1H), 2.22 (s, 3H), 1.60 (q,  $J$  = 9 Hz, 1H), 1.11 (d,  $J$  = 6 Hz, 3H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  158.04, 141.67, 135.98, 135.40, 128.94, 127.78, 126.56, 113.75, 55.63, 55.27, 35.42, 34.13, 21.04, 20.54.

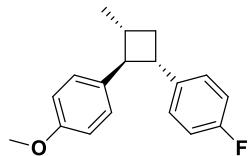


**4-((1S,2S,3R)-2-(4-methoxyphenyl)-3-methylcyclobutyl)phenyl acetate:** According to the general procedure B, a 40 ml vial with a magnetic stir bar was charged with *trans*-anethole (35.6 mg, 0.24 mmol), 4-vinylphenyl acetate (183.6 ul, 1.2 mmol), B-BT (2.4 mg) and CH<sub>3</sub>NO<sub>2</sub> (2.4 ml). After the reaction was completed, the mixture was performed as the workup protocol and purified by chromatography on silica with hexane/diethyl ether (5/1) as the elution to afford the pure cycloadduct as clear oil.

R<sub>f</sub> (hexane/diethyl ether 5/1): 0.40

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.23 (AA' of AA'BB', J = 6 Hz, 2H), 7.20 (AA' of AA'BB', J = 6 Hz, 2H), 7.01 (BB' of AA'BB', J = 9 Hz, 2H), 6.89 (BB' of AA'BB', J = 9 Hz, 2H), 3.83 (s, 3H), 3.42 (td, J = 12, 6 Hz, 1H), 2.96 (t, J = 9 Hz, 1H), 2.54 (q, J = 9 Hz, 1H), 2.37 (m, 1H), 2.32 (s, 3H), 1.71 (q, J = 9 Hz, 1H), 1.21 (d, J = 9 Hz, 3H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 300 MHz): δ 169.73, 158.14, 148.79, 142.28, 135.60, 127.82, 127.57, 121.24, 113.82, 55.67, 55.27, 43.57, 35.59, 34.00, 21.15, 20.49.

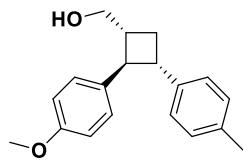


**1-fluoro-4-((1S,2S,3R)-2-(4-methoxyphenyl)-3-methylcyclobutyl)benzene:** According to the general procedure B, a 40 ml vial with a magnetic stir bar was charged with *trans*-anethole (35.6 mg, 0.24 mmol), 1-fluoro-4-vinylbenzene (143 ul, 1.2 mmol), B-BT (2.4 mg) and CH<sub>3</sub>NO<sub>2</sub> (2.4 ml). After the reaction was completed, the mixture was performed as the workup protocol and purified by chromatography on silica with hexane/dichloromethane (8/1) as the elution to afford the pure cycloadduct as clear oil.

R<sub>f</sub> (hexane/dichloromethane 8/1): 0.35

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.19 (m, 4H), 7.00 (t, J = 6 Hz, 3H), 6.92 (BB' of AA'BB', J = 9 Hz, 2H), 3.84 (s, 3H), 3.38 (q, J = 9 Hz, 1H), 2.93 (t, J = 9 Hz, 1H), 2.57 (q, J = 9 Hz, 1H), 2.38 (m, 1H), 1.72 (q, J = 9 Hz, 1H), 1.24 (d, J = 6 Hz, 3H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 300 MHz): δ 162.62 (<sup>1</sup>J<sub>CF</sub> = 969 Hz), 158.17, 140.30 (<sup>1</sup>J<sub>CF</sub> = 12 Hz), 135.54, 128.04 (<sup>3</sup>J<sub>CF</sub> = 30 Hz), 127.78, 115.09 (<sup>2</sup>J<sub>CF</sub> = 84 Hz), 113.84, 55.93, 55.26, 43.57, 35.45, 34.11, 20.46.

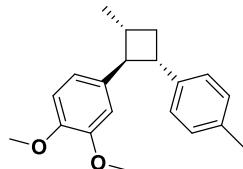


**((1R,2R,3S)-2-(4-methoxyphenyl)-3-(p-tolyl)cyclobutyl)methanol:** According to the general procedure B, a 40 ml vial with a magnetic stir bar was charged with (*E*)-3-(4-methoxyphenyl)prop-2-en-1-ol (39.4 mg, 0.24 mmol), 4-methylstyrene (157.6  $\mu$ l, 1.2 mmol), B-BT (2.4 mg) and  $\text{CH}_3\text{NO}_2$  (2.4 ml). After the reaction was completed, the mixture was performed as the workup protocol and purified by chromatography on silica with hexane/ethyl acetate (8/1) as the elution to afford the pure cycloadduct as clear oil.

$R_f$  (hexane/ethyl acetate 8/1): 0.10

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.11 (AA',  $J$  = 9 Hz, 2H), 7.01 (m, 4H), 6.76 (BB',  $J$  = 9 Hz, 2H), 3.68 (s, 3H), 3.66 (m, 1H), 3.62 (m, 1H), 3.32 (td,  $J$  = 9, 6 Hz, 1H), 3.12 (t,  $J$  = 9 Hz, 1H), 2.46 (m, 1H), 2.36 (m, 1H), 2.22 (s, 3H), 1.81 (q,  $J$  = 9 Hz, 1H), 1.61 (br s, 1H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  158.14, 141.25, 135.66, 135.51, 129.02, 127.94, 126.57, 113.85, 66.03, 55.28, 50.21, 43.97, 41.61, 28.66, 21.06.

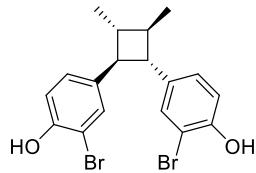


**1,2-dimethoxy-4-((1S,2R,4S)-2-methyl-4-(p-tolyl)cyclobutyl)benzene:** According to the general procedure B, a 40 ml vial with a magnetic stir bar was charged with (*E*)-1,2-dimethoxy-4-(prop-1-en-1-yl)benzene (40.7  $\mu$ l, 0.24 mmol), 4-methylstyrene (157.6  $\mu$ l, 1.2 mmol), B-BT (2.4 mg) and  $\text{CH}_3\text{NO}_2$  (2.4 ml). After the reaction was completed, the mixture was performed as the workup protocol and purified by chromatography on silica with hexane/dichloromethane (1/1) as the elution to afford the pure cycloadduct as clear oil.

$R_f$  (hexane/dichloromethane 1/1): 0.31

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.01 (m, 4H), 6.72 (m, 2H), 6.67 (m, 1H), 3.77 (s, 6H), 3.26 (q,  $J$  = 9 Hz, 1H), 2.82 (t,  $J$  = 9 Hz, 1H), 2.43 (dt,  $J$  = 3, 9 Hz, 1H), 2.27 (m, 1H), 2.23 (s, 3H), 1.62 (q,  $J$  = 9 Hz, 1H), 1.12 (d,  $J$  = 6 Hz, 3H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  148.86, 147.49, 141.59, 136.55, 135.43, 128.93, 126.52, 118.67, 111.24, 110.24, 56.15, 55.94, 55.84, 43.82, 35.40, 33.88, 21.01, 20.55.



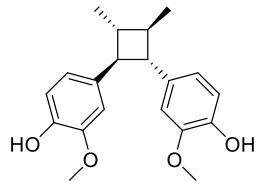
**4,4'-(1R,2R,3S,4S)-3,4-dimethylcyclobutane-1,2-diyl)bis(2-bromophenol):**

The compound was obtained via two steps methods, including bromination process and demethylation procedure, which was similar to previous reports.<sup>1-2</sup> Typically, a 40 ml vial with a magnetic stir bar was charged with anethole dimer (94 mg, 0.3193 mmol) and acetic acid (2 ml), and was cooled at 0 °C. Then, Br<sub>2</sub> (42  $\mu$ l, 2.5 equiv.) was added dropwise and the reactive solution was keep stirring at room temperature for another 30 min. After that, the reaction was quenched with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, extracted with dichloromethane for 3 times, washed with brine, water, dried over MgSO<sub>4</sub>, and concentrated *in vacuo*. The crude product was used for next step without further purification. More precisely, after dried in over for overnight, the crude mixture was added with anhydrous DCM (14 ml) at 0 °C. Then, a solution of BBr<sub>3</sub> (6.4 ml, 1 M in DCM) was added dropwise and the reaction was kept at 0 °C for 2 h. Finally, the reactive solution was stirred at room temperature for 24 h. After the reaction finished, the mixture was cooled to 0 °C, and quenched with water, then extracted with DCM, wash with brine, water, dried over MgSO<sub>4</sub>, and concentrated *in vacuo*. After purified by chromatography on silica with hexane/acetone (8/1) as the elution, a pure product of light red oil (101 mg) was obtained with the yield of 75 % over two steps.

$R_f$  (hexane/acetone 8/1): 0.21

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  7.23 (d, J = 2 Hz, 2H), 6.98 (dd, J = 3, 9 Hz, 2H), 6.88 (d, J = 9 Hz, 2H), 5.33 (bs, 2H), 2.66 (dd, J = 3, 6 Hz, 2H), 1.78 (m, 2H), 1.12 (d, J = 6 Hz, 6H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  150.64, 137.01, 129.95, 127.64, 115.93, 110.20, 52.28, 43.23, 18.68.



**4,4'-(1S,2S,3R,4R)-3,4-dimethylcyclobutane-1,2-diyl)bis(1,2-dimethoxybenzene):**

The compound was obtained via BINAM-copper (I) catalyzed Ullmann-type coupling, which was similar to previous reports.<sup>2-3</sup> Typically, a 25 ml schlenk flask was charged with the starting compound (94 mg, 0.22 mmol), Cs<sub>2</sub>CO<sub>3</sub> (287.5 mg, 4 equiv.), CuI (16.8 mg, 0.04 equiv.), and BINAM (25.1 mg, 0.04 equiv.). The schlenk flask was evacuated and back-filled with anhydrous argon for three times. Then sparged MeOH (1.5 ml) was added under the argon bath, and the reaction mixture was stirring at 110 °C for 36 h. Then the mixture was allowed to cool to room temperature and diluted with water. After quenched with 3 M HCl at 0 °C, the mixture was extracted with DCM for 3 times, dried over MgSO<sub>4</sub> and concentrated *in vacuo*. After purified by chromatography on silica with hexane/acetone (6/1) as the elution, a pure product of yellow oil (56 mg) was obtained with the yield of 78 %.

R<sub>f</sub> (hexane/acetone 6/1): 0.07

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 6.76 (d, J = 6 Hz, 2H), 6.67 (dd, J = 3, 6 Hz, 2H), 6.60 (d, J = 3 Hz, 2H), 5.40 (bs, 2H), 3.78 (s, 6H), 2.67 (dd, J = 3, 6 Hz, 2H), 1.76 (m, 2H), 1.11 (d, J = 2.1 Hz, 6H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 300 MHz): δ 146.34, 143.94, 135.81, 119.33, 114.17, 109.41, 55.86, 53.22, 43.00, 18.87.

## V. Photocatalyst characterizations

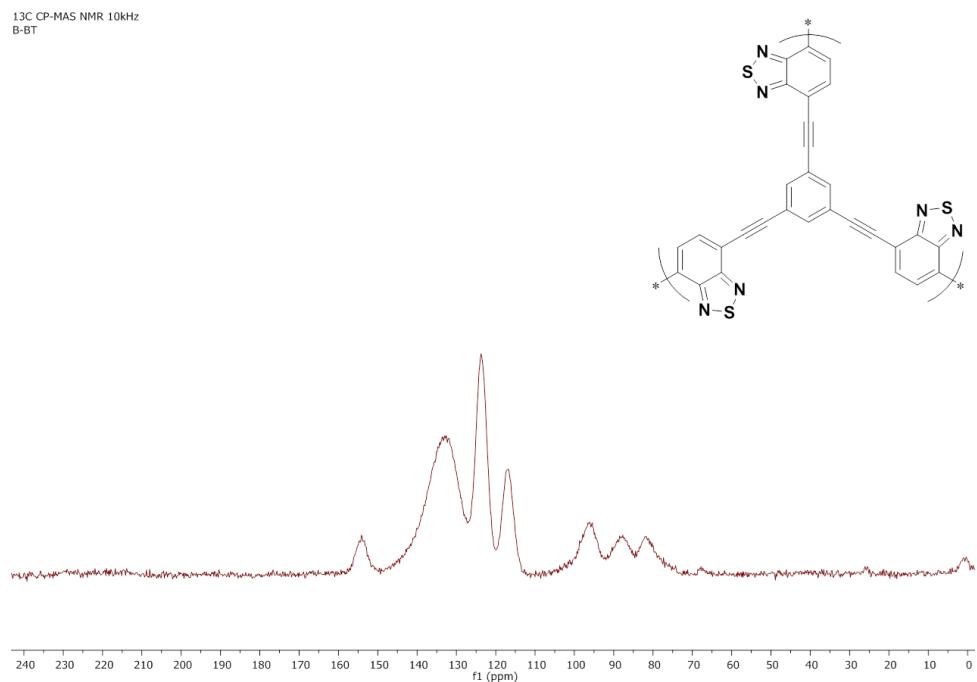


Figure S1. Solid-state <sup>13</sup>C CP-MAS NMR of B-BT.

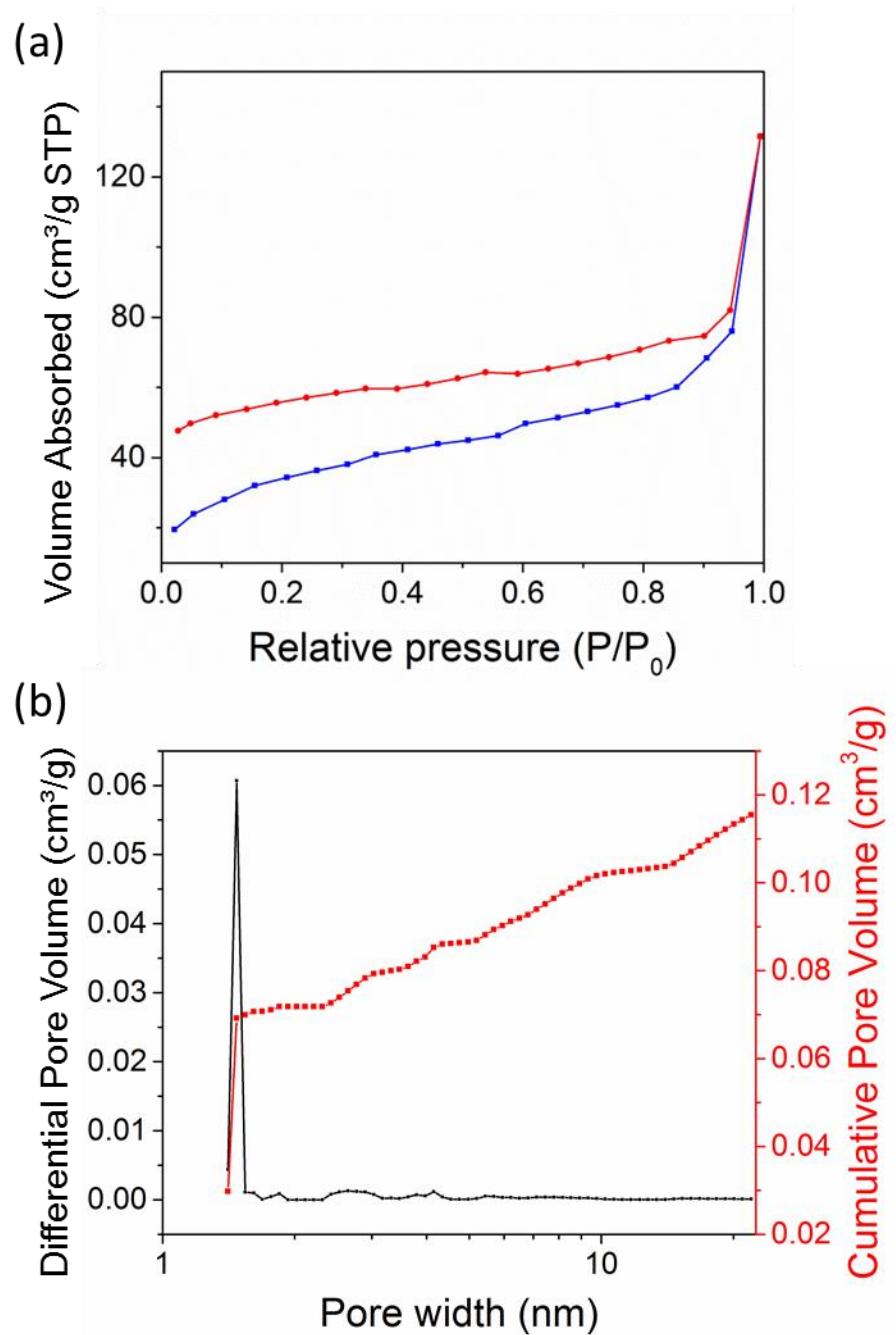


Figure S2. (a) Nitrogen sorption and desorption isotherms, and (b) pore size distributions of B-BT.

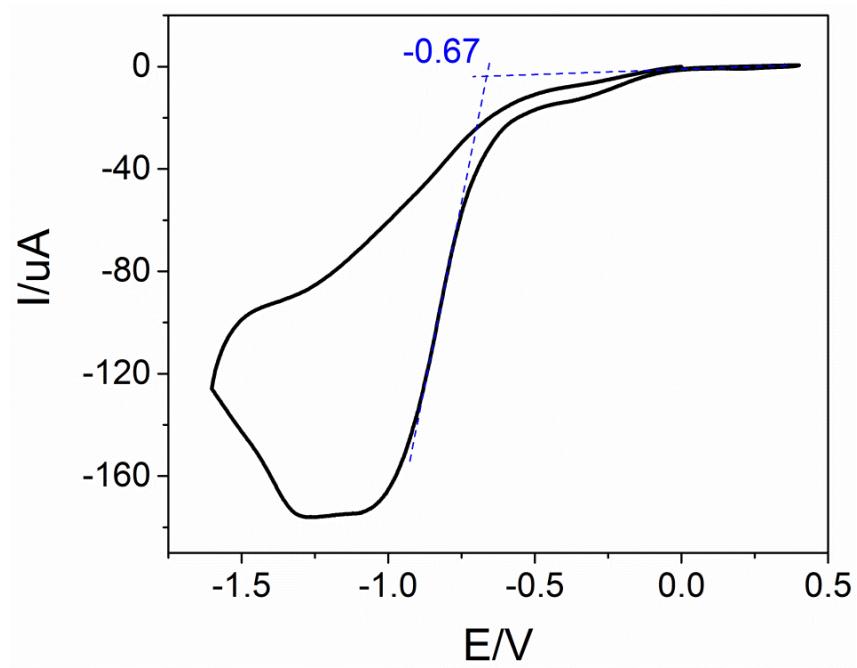


Figure S3. Cyclic voltammetry of B-BT in the reduction cycle.

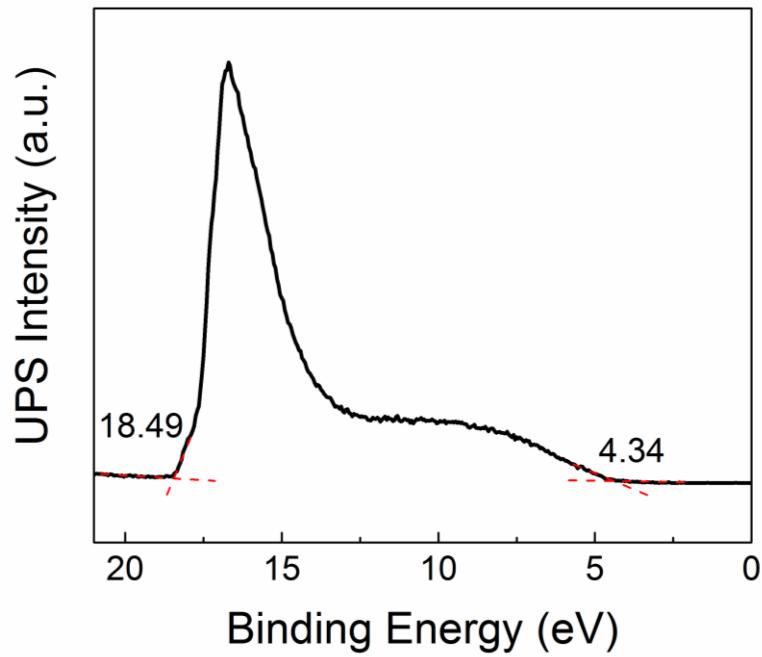


Figure S4. Ultraviolet photoelectron spectroscopy (UPS) of B-BT. The dashed red lines mark the baseline and the tangents of the curve.

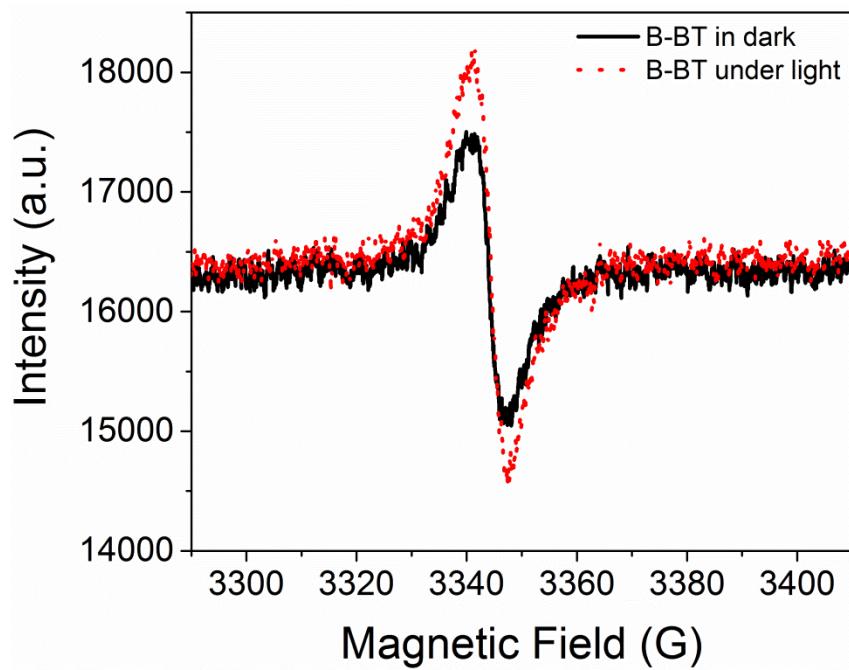


Figure S5. EPR spectra of B-BT taken in dark and after light irradiation for 20 min

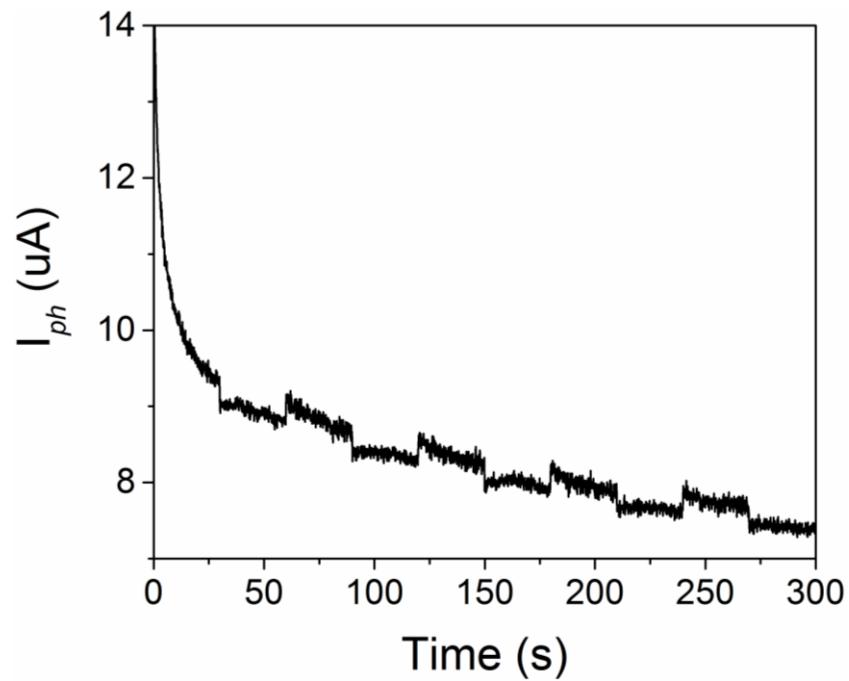


Figure S6. photocurrent responses upon switching the light (blue LED,  $\lambda=460$  nm) on and off.

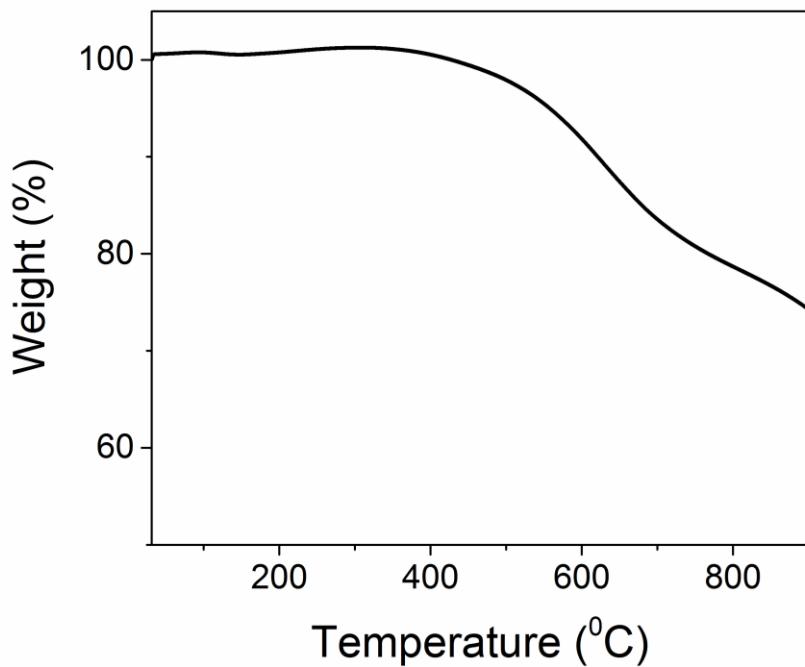


Figure S7. Thermogravimetric analysis of B-BT.

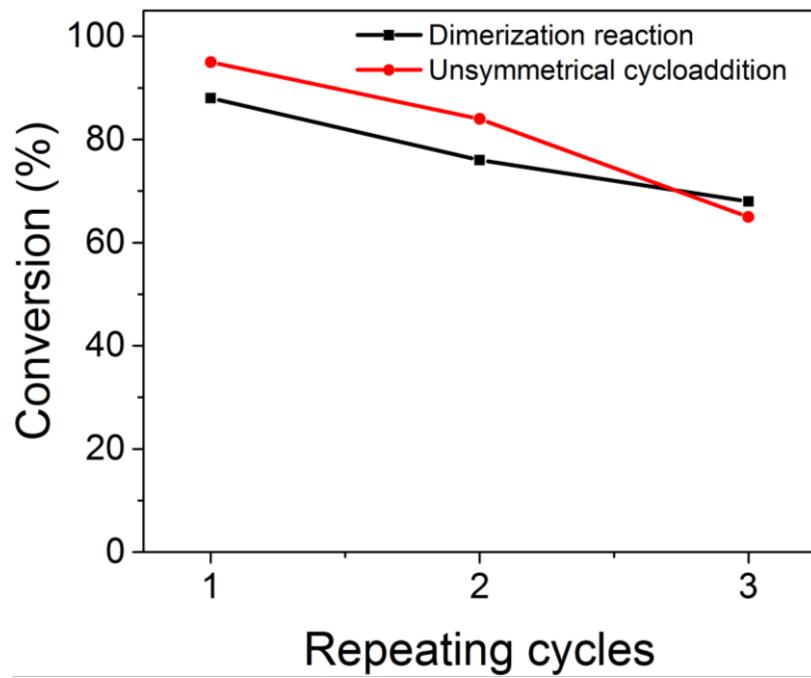


Figure S8. Repeating experiment of dimerization (black) and unsymmetrical cycloaddition (red) for 3 cycles

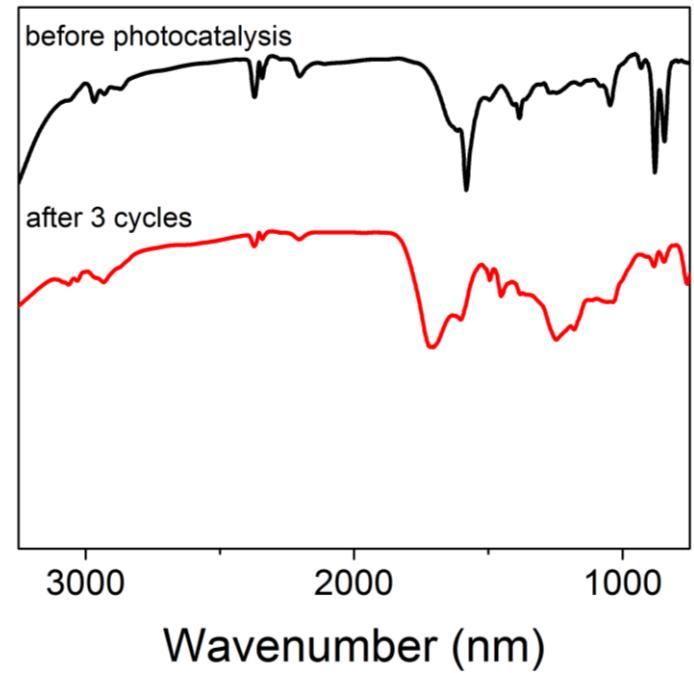


Figure S9. FTIR spectra of B-BT before photocatalysis reaction (black) and after 3 repeating cycles (red)

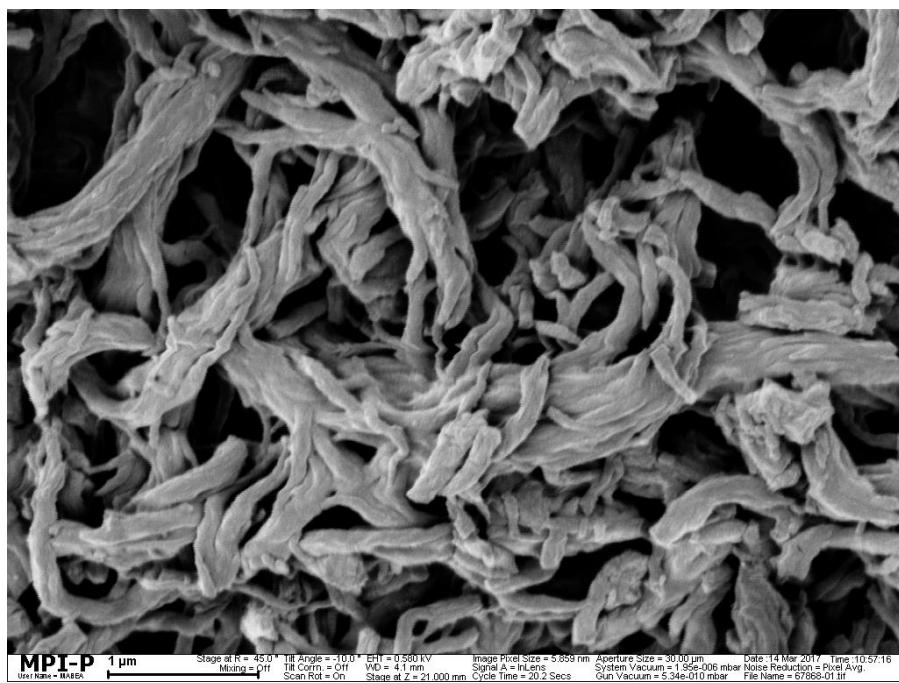


Figure S10. SEM image of B-BT after 3 times repeating experiments

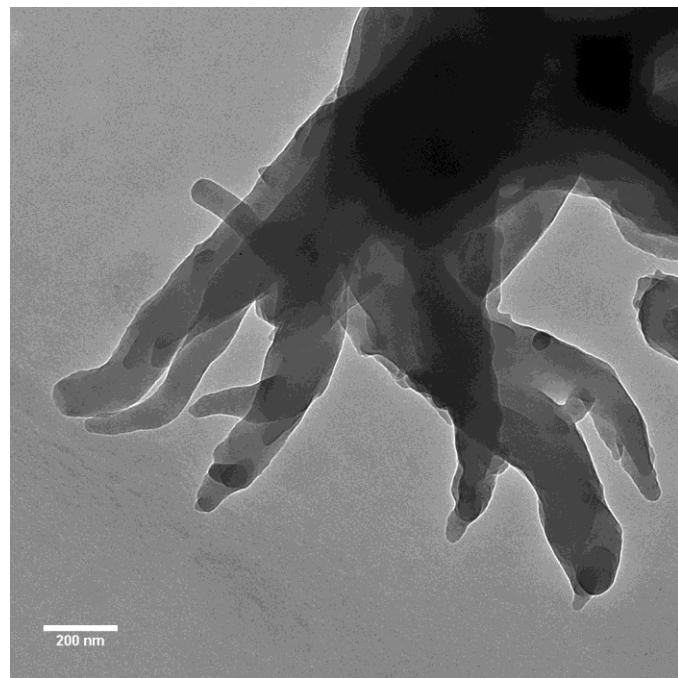


Figure S11. TEM image of B-BT after 3 times repeating experiments

References:

- (1) Tripathi, S.; Chan, M. H.; Chen, C. P.; *Bioorg. Med. Chem. Lett.* **2012**, *22*, 216-221.
- (2) Riener, M.; Nicewicz, D. A.; *Chem. Sci.* **2013**, *4*, 2625-2629.
- (3) Naidu, A. B.; Sekar, D.; *Tetrahedron lett.*, **2008**, *49*, 3147-3151.

VI.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra

