Supporting Information

Bisbenzothieno[*b*]-fused BODIPYs in panchromatic photoinitiating for the free radical and cationic photopolymerization and application in 3D printing

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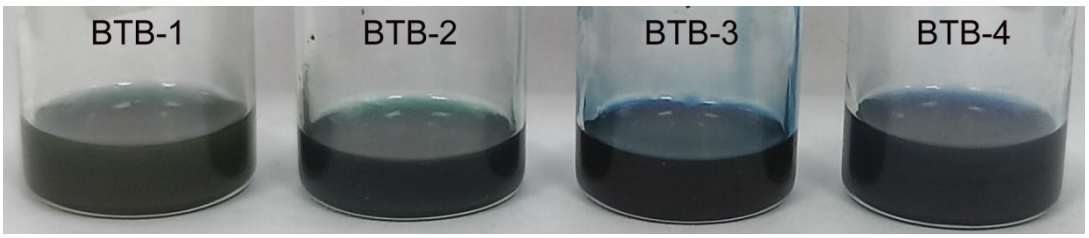


Figure S1. *In-situ* photographs of the TMPTA resin in the presence of different BODIPY/Iod/EDB (0.1 wt%/2 wt%/2 wt%) photoinitiating systems, respectively.

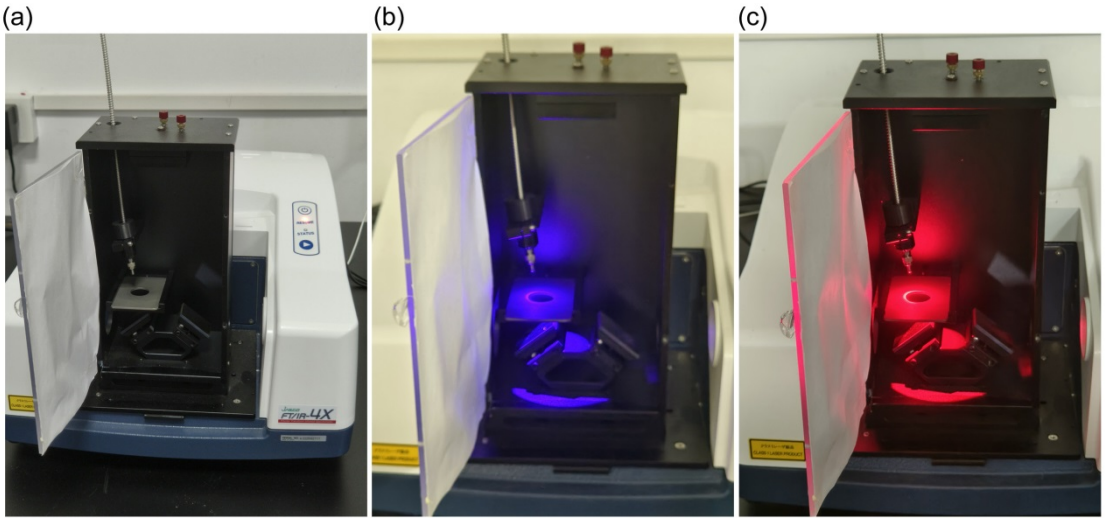


Figure S2. *In-situ* photographs of the experimental set-up for the photopolymerization procedure: (a) RT-FTIR instrument; (b) LED@405 nm and (c) LED@660 nm visible LEDs irradiation used, respectively.

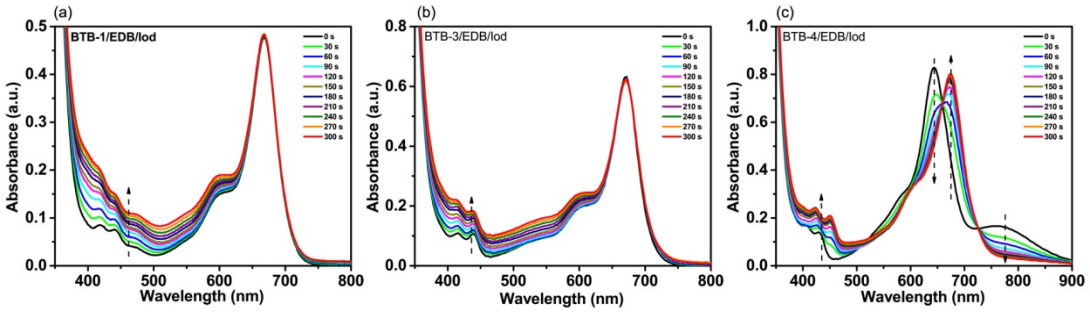


Figure S3. Photolysis results of (a) BTB−1, (b) BTB−3 and (c) BTB−4 (1.5×10^{-5} M) in dichloromethane in the presence of Iod/EDB couple (1×10^{-2} M/1×10^{-2} M) under exposure to the LED@405 nm irradiation for 5 minutes, respectively.

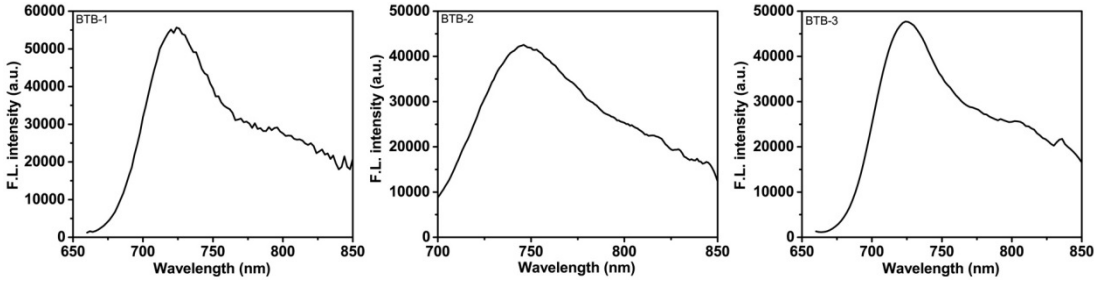


Figure S4. Fluorescence properties of the BODIPY dyes (BTB–1~BTB–3) in the solvent of dichloromethane ($3x10^{-5}$ M), respectively.

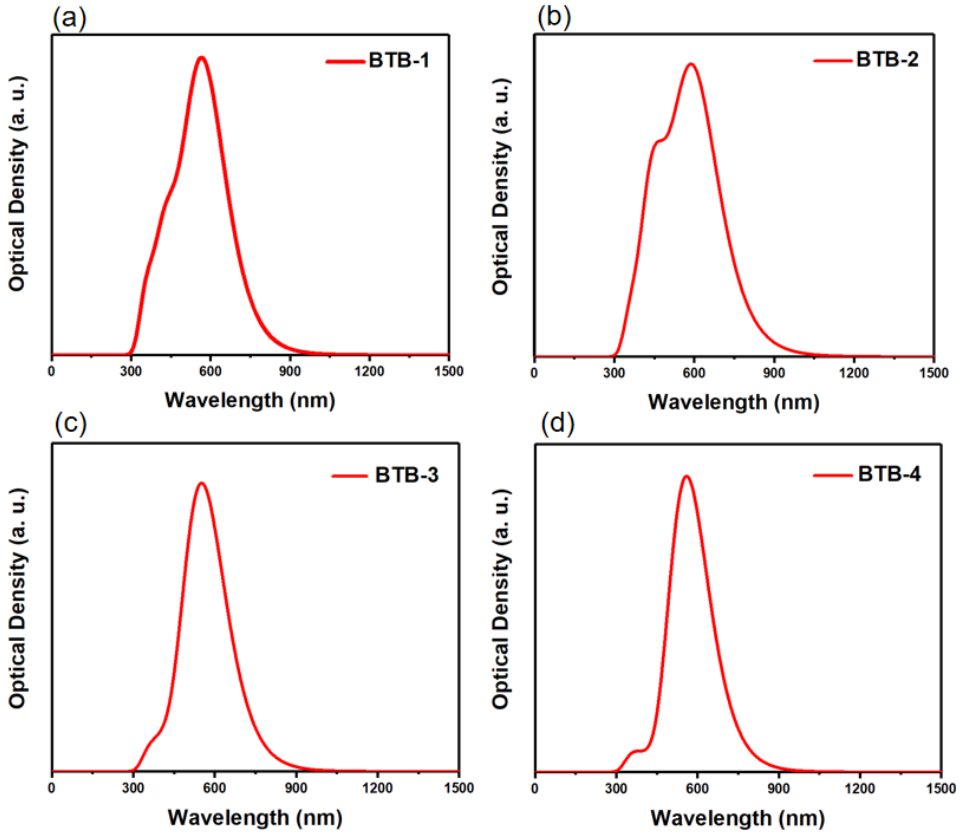


Figure S5. Simulated absorption spectra of the four investigated dyes (a) BTB–1; (b) BTB–2; (c) BTB–3; (d) BTB–4 optimized at the B3LYP/6-31G* level of theory, respectively.

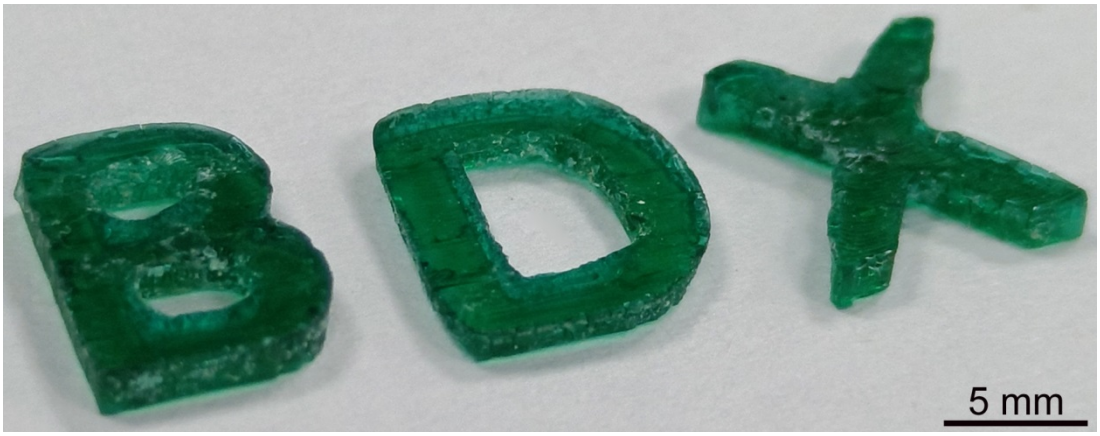


Figure S6. *In-situ* optical photograph of the fabricated three-dimensional patterns printed from TMPTA/EPOX (50 wt%/50 wt%) mixture in the presence of BTB–2/Iod/EDB (0.1 wt%/2 wt%/2 wt%) three-component PIS, the scale bar is 5 mm.

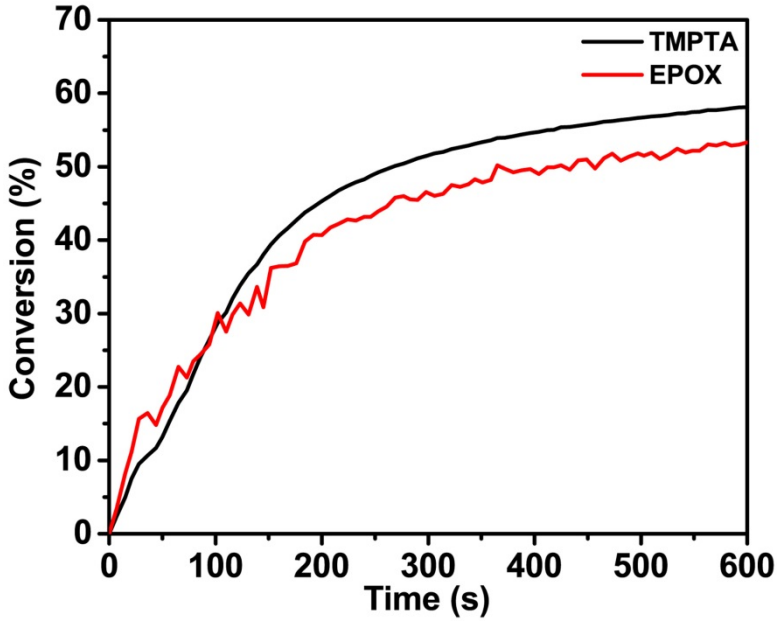
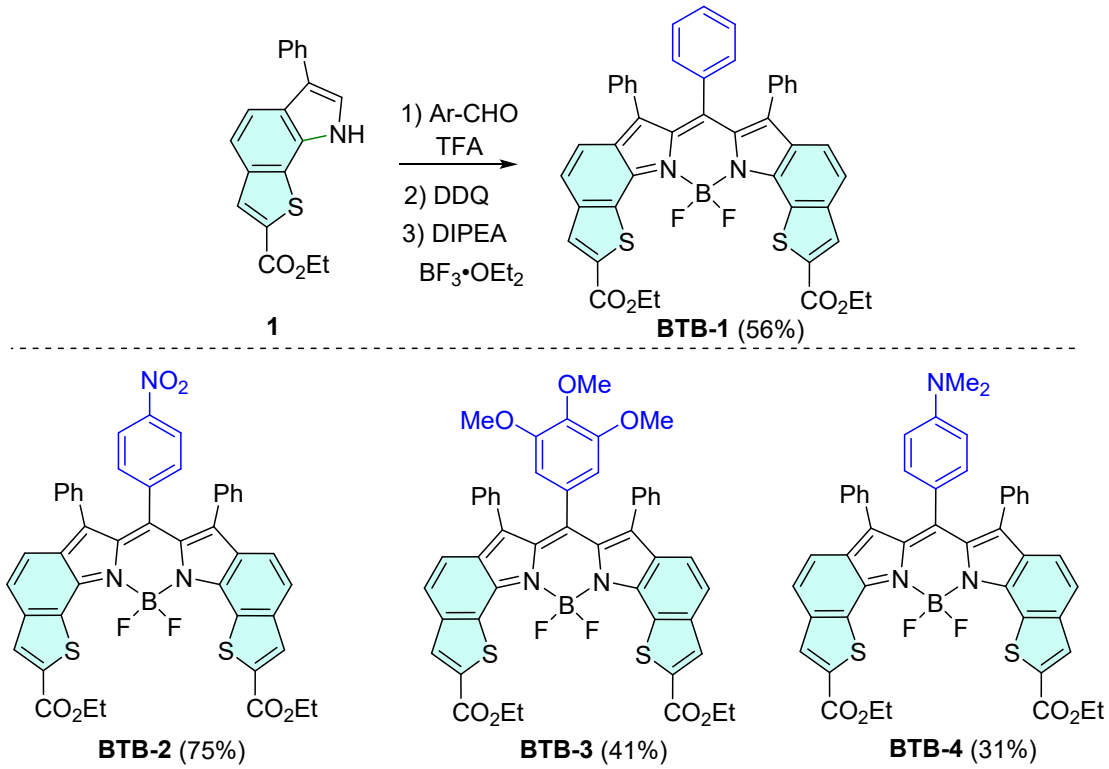


Figure S7. Photopolymerization profiles of the composite: (black line) 50 wt% TMPTA (C=C bond conversion versus irradiation time) and (red line) 50 wt% EPOX (epoxy function versus irradiation time) in thin films (thickness≈25 μm) in the presence of BTB–2/Iod/EDB (0.1 wt%/2 wt%/2 wt%) three-component PIS under irradiation of LED@405 nm, respectively. Irradiation starts at t=10 s.

Synthesis information

All reagents and solvents were purchased from Aldrich or Aladdin and used as received, the purification was unnecessary unless otherwise specified. The reaction progress was monitored by TLC based on 0.20 mm silica gel plates with a UV indicator. Flash column chromatography was also performed with silica gel. NMR spectra were recorded on a 500/600 MHz NMR spectrometer in $CDCl_3$ with chemical shifts (δ) reported in ppm relative to tetramethylsilane (TMS, δ = 0 ppm) for ^1H, and $CDCl_3$ (δ = 77.16) NMR as the external standard. HRMS was obtained by employing TOF (ESI) in positive mode. The general synthetic routes were listed as following:



Synthetic procedure for BTBs 1-4: Following the reported procedure, to the mixture of compound 1 (321 mg, 1.0 mmol) and aromatic aldehyde (0.5 mmol, 0.5 equivalent) in anhydrous dichloromethane (10 mL) was added trifluoroacetic acid (TFA, 0.05 mL), and the reaction mixture was stirred at room temperature under N_2 atmosphere for 6-12 h. Upon the completion of the reaction, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 136 mg, 0.6 mmol) was added and the mixture was refluxed for under N_2 atmosphere for 2 h. N,N-Diisopropylethylamine (DIPEA, 1.0 mL, 5.7 mmol) and boron trifluoride diethyl ether (1.0 mL, 8.0 mmol) were then added and the reaction mixture was further stirred at room temperature for 4-12 h. Then, water (3 × 200 mL) was poured into the reaction mixture. Dichloromethane (3 × 100 mL) phase was separated and dried with anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by silica gel chromatography (V_{hexane} : V_{DCM} = 1 : 1 or DCM) to afford the desired BTBs.

BTB–1 was prepared following the same procedure in prior literature[1] utilizing compound 1 (321 mg, 1.0 mmol) and benzaldehyde (53 mg, 0.5 mmol), resulting in

BTB-1 by column chromatography on silica gel (eluent: dichloromethane/petroleum ether) as dark brown solid in 56% yield (218 mg, 0.56 mmol). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (s, 2H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.99 – 6.94 (m, 2H), 6.94 – 6.90 (m, 4H), 6.84 – 6.80 (m, 2H), 6.77 (d, *J* = 7.0 Hz, 4H), 6.64 (t, *J* = 7.6 Hz, 1H), 6.43 (t, *J* = 7.6 Hz, 2H), 4.49 (q, *J* = 7.2 Hz, 4H), 1.50 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.7, 145.3, 143.9, 143.6, 142.4, 138.9, 136.7, 133.5, 132.5, 132.0, 131.6, 130.8, 129.9, 129.4, 129.0, 127.6, 127.0, 126.8, 121.4, 120.4, 61.8, 14.6. HRMS (ESI): calcd for $C_{45}H_{31}BFN_2O_4S_2$ $[M\text{-}F]^+$ m/z 757.1797; found *m/z* 757.1798.

BTB–2 was prepared following the same procedure in prior literature[1] utilizing compound 1 (321 mg, 1.0 mmol) and *p*-nitrobenzaldehyde (76 mg, 0.5 mmol), resulting in BTB-2 by column chromatography on silica gel (eluent: dichloromethane/petroleum ether) as dark blue solid in 75% yield (308 mg, 0.75 mmol). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (s, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.00 – 6.94 (m, 4H), 6.93 – 6.85 (m, 6H), 6.72 (d, *J* = 7.4 Hz, 4H), 4.50 (q, *J* = 7.1 Hz, 4H), 1.51 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.4, 147.5, 145.9, 145.7, 143.9, 143.2, 139.5, 137.6, 136.2, 132.9, 132.4, 131.4, 129.9, 128.6, 127.7, 127.7, 127.4, 121.7, 121.4, 120.1, 61.8, 14.4. HRMS (ESI): calcd for $C_{45}H_{30}BFN_3O_6S_2$ $[M\text{-}F]^+$ m/z 802.1648; found *m/z* 802.1652.

BTB–3 was prepared following the same procedure in prior literature[1] utilizing compound 1 (321 mg, 1.0 mmol) and 3,4,5-trimethoxy benzaldehyde (99 mg, 0.5 mmol), resulting in BTB-3 by column chromatography on silica gel (eluent: dichloromethane/petroleum ether) as dark blue solid in 41% yield (178 mg, 0.41 mmol). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (s, 2H), 7.34 (d, *J* = 8.9 Hz, 2H), 7.11 – 7.00 (m, 8H), 6.93 – 6.89 (m, 4H), 6.15 (s, 2H), 4.49 (q, *J* = 7.1 Hz, 4H), 3.60 (s, 3H), 3.54 (s, 6H), 1.49 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.5, 161.6, 151.8, 145.3, 143.5, 143.4, 138.8, 137.8, 136.5, 133.7, 132.2, 131.5, 129.5, 128.8, 127.4, 127.3, 126.7, 121.4, 120.1, 109.6, 61.7, 59.9, 55.7, 14.4. HRMS (ESI): calcd for $C_{48}H_{37}BFN_2O_7S_2$ $[M\text{-}F]^+$ m/z 847.2114; found *m/z* 847.2121.

BTB–4 was prepared following the same procedure in prior literature[1] utilizing compound 1 (321 mg, 1.0 mmol) and 4-dimethylaminobenzaldehyde (75 mg, 0.5 mmol), resulting in BTB-4 by column chromatography on silica gel (eluent: dichloromethane/petroleum ether) as dark blue solid in 31% yield (127 mg, 0.31 mmol). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (s, 2H), 7.35 (d, *J* = 8.8 Hz, 2H), 7.16 (d, *J* = 8.9 Hz, 2H), 6.98 (t, *J* = 7.4 Hz, 4H), 6.90 (t, *J* = 7.5 Hz, 2H), 6.85 (d, *J* = 7.4 Hz, 4H), 6.68 (d, *J* = 8.3 Hz, 2H), 5.70 (d, *J* = 8.1 Hz, 2H), 4.49 (q, *J* = 7.1 Hz, 4H), 2.74 (s, 6H), 1.50 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.8, 145.0, 142.6, 142.4, 137.8, 136.1, 134.3, 134.1, 131.7, 131.4, 130.0, 129.1, 127.6, 126.3, 120.8, 119.9, 118.7, 117.4, 116.2, 110.8, 61.6, 40.0, 14.5. HRMS (ESI): calcd for $C_{47}H_{36}BFN_3O_4S_2$ $[M\text{-}F]^+$ m/z 800.2219; found *m/z* 800.2229.

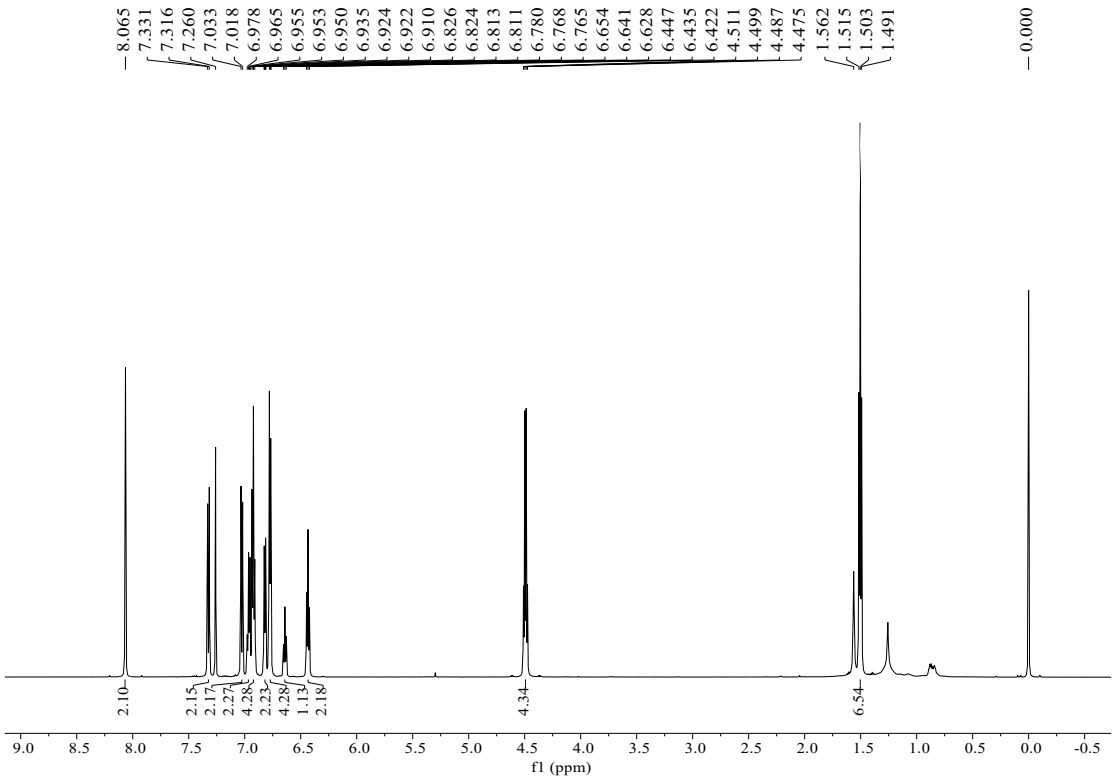


Figure S8. ^{1}H NMR (600 MHz) spectrum of BTB−1 in $CDCl_3$.

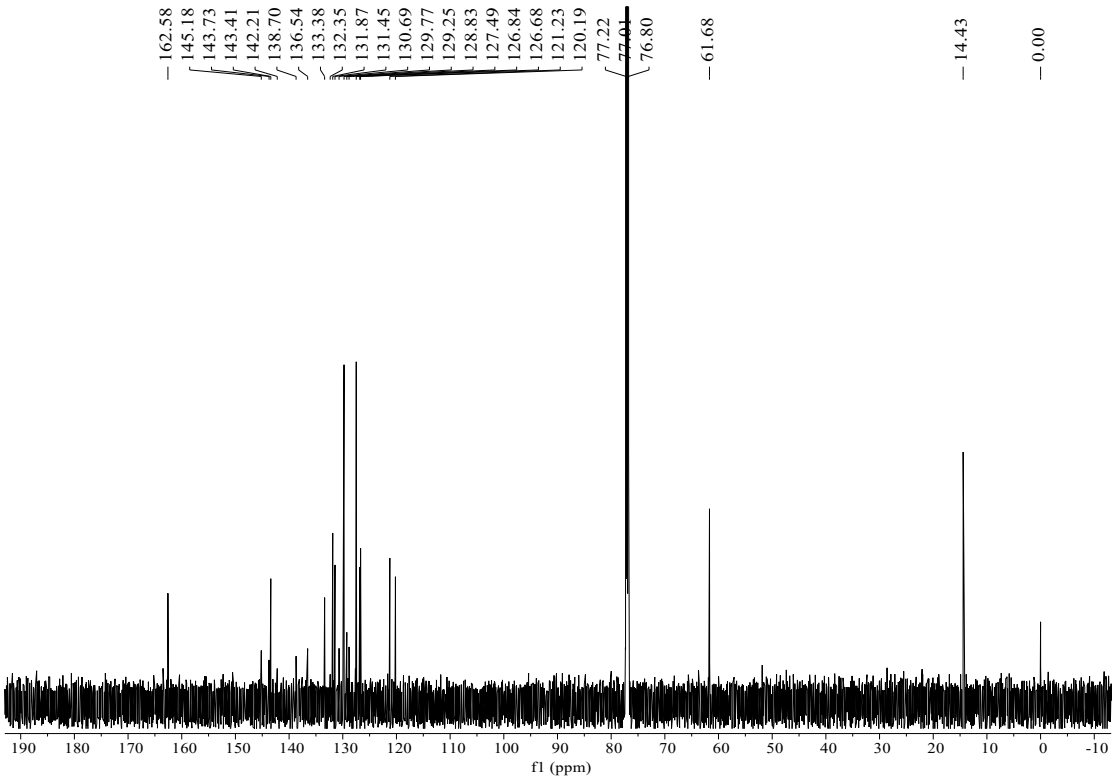


Figure S9. ^{13}C NMR (151 MHz) spectrum of BTB−1 in $CDCl_3$.

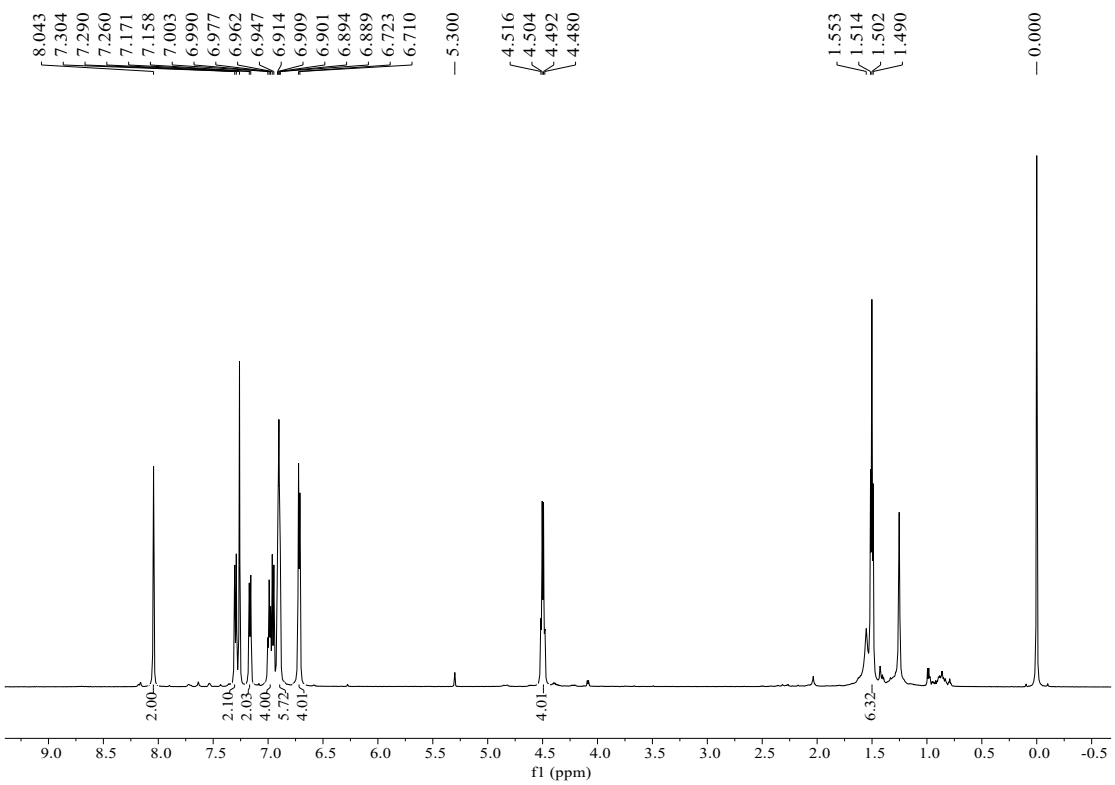


Figure S10. ^{1}H NMR (600 MHz) spectrum of BTB−2 in $CDCl_3$.

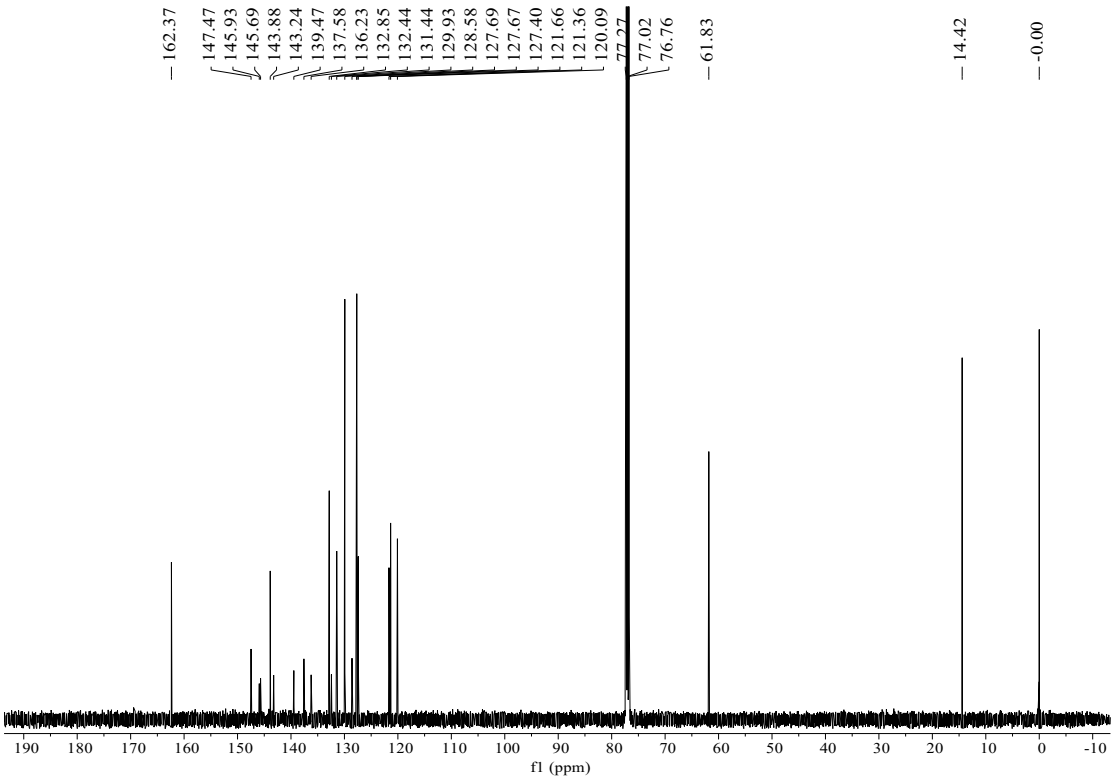


Figure S11. ^{13}C NMR (151 MHz) spectrum of BTB−2 in $CDCl_3$.

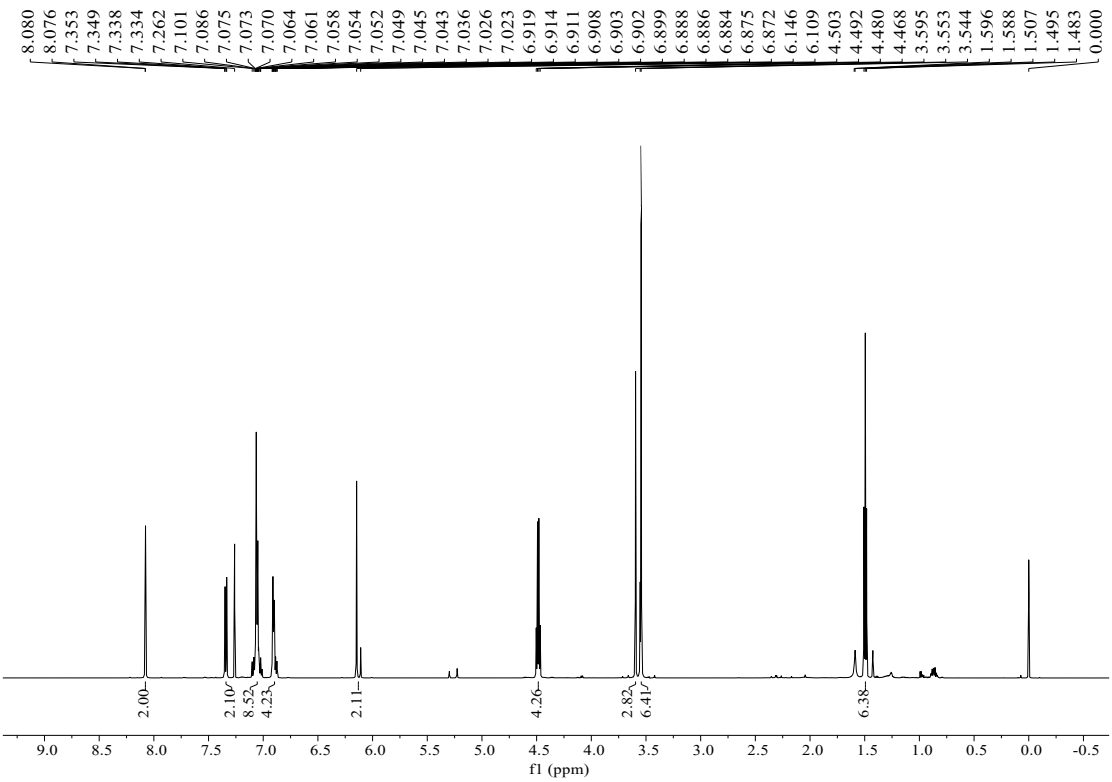


Figure S12. ^{1}H NMR (600 MHz) spectrum of BTB−3 in $CDCl_3$.

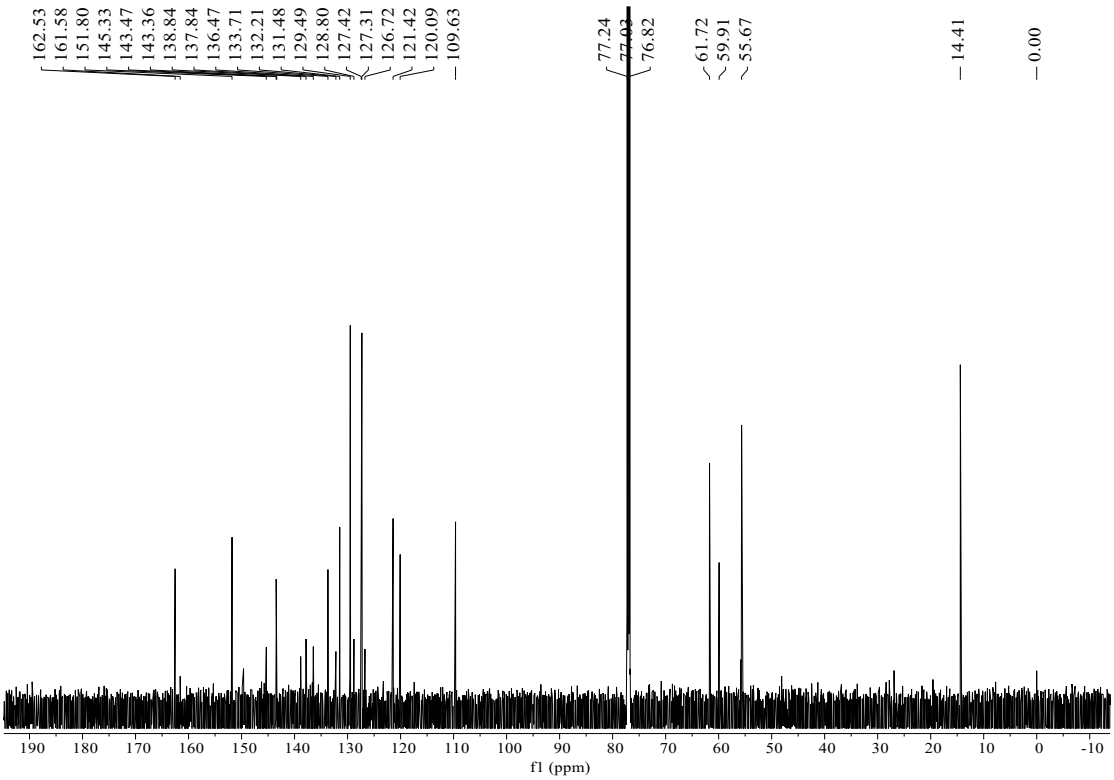


Figure S13. ^{13}C NMR (151 MHz) spectrum of BTB−3 in $CDCl_3$.

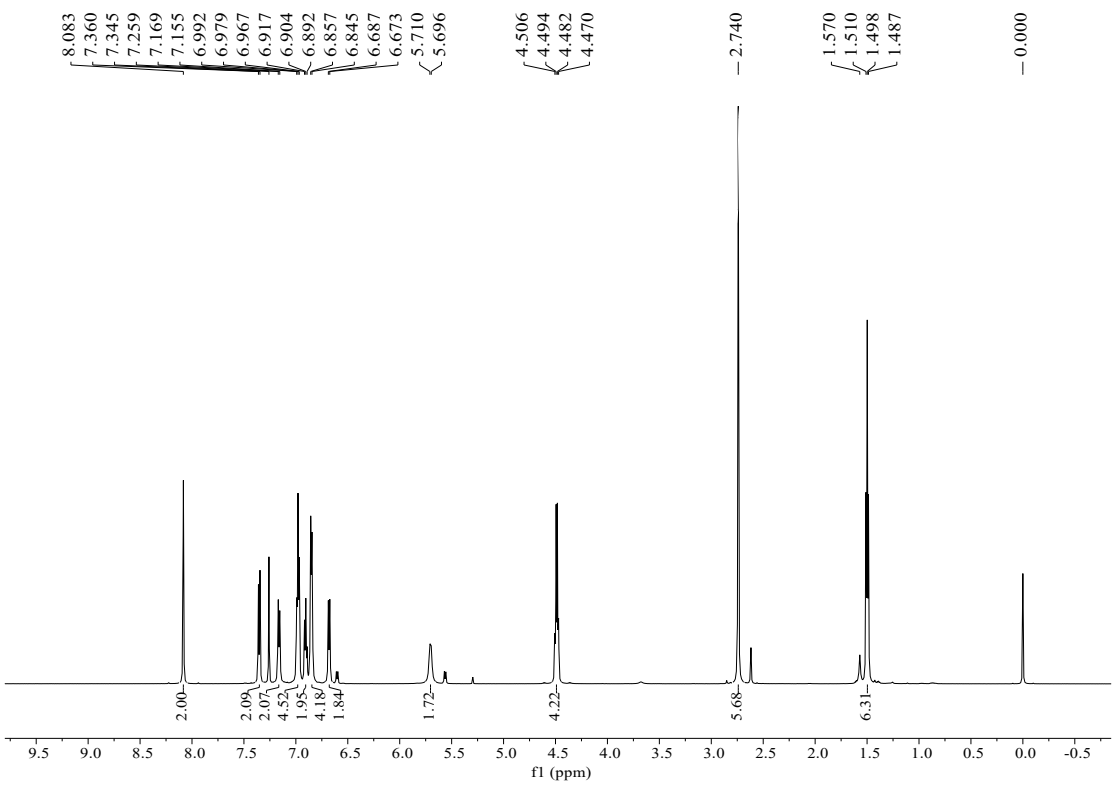


Figure S14. ^{1}H NMR (600 MHz) spectrum of BTB–4 in $CDCl_3$.

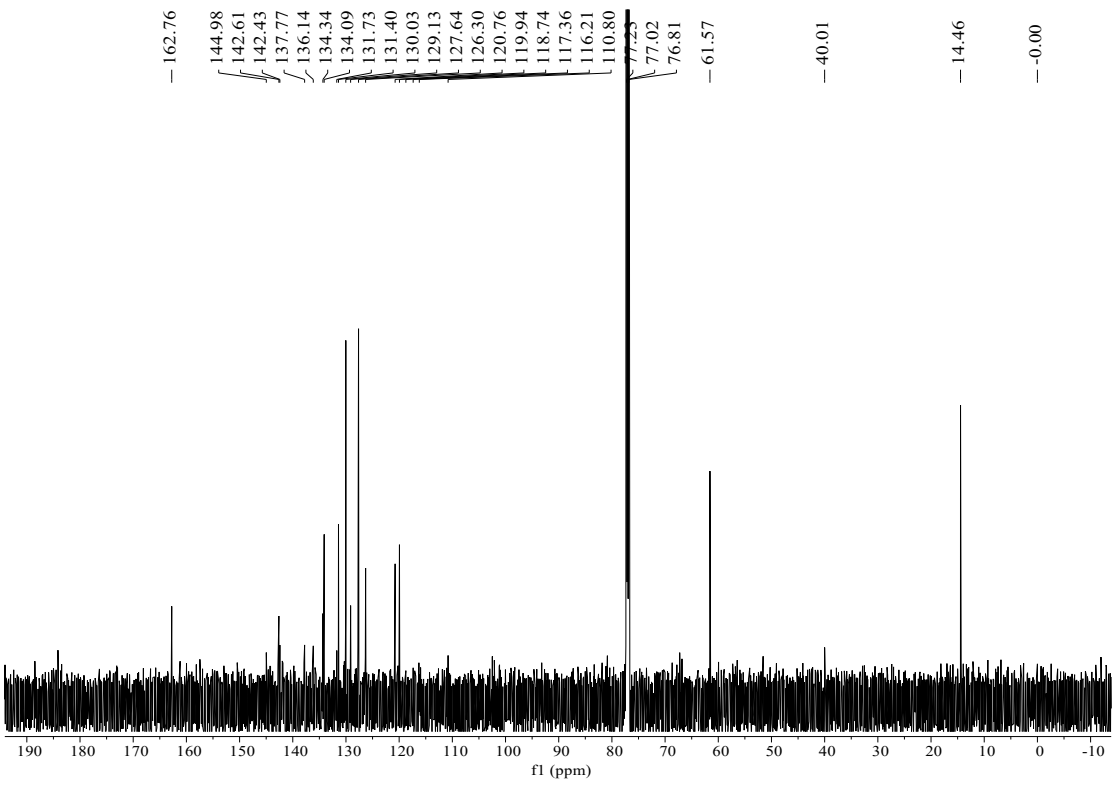


Figure S15. ^{13}C NMR (151 MHz) spectrum of BTB–4 in $CDCl_3$.

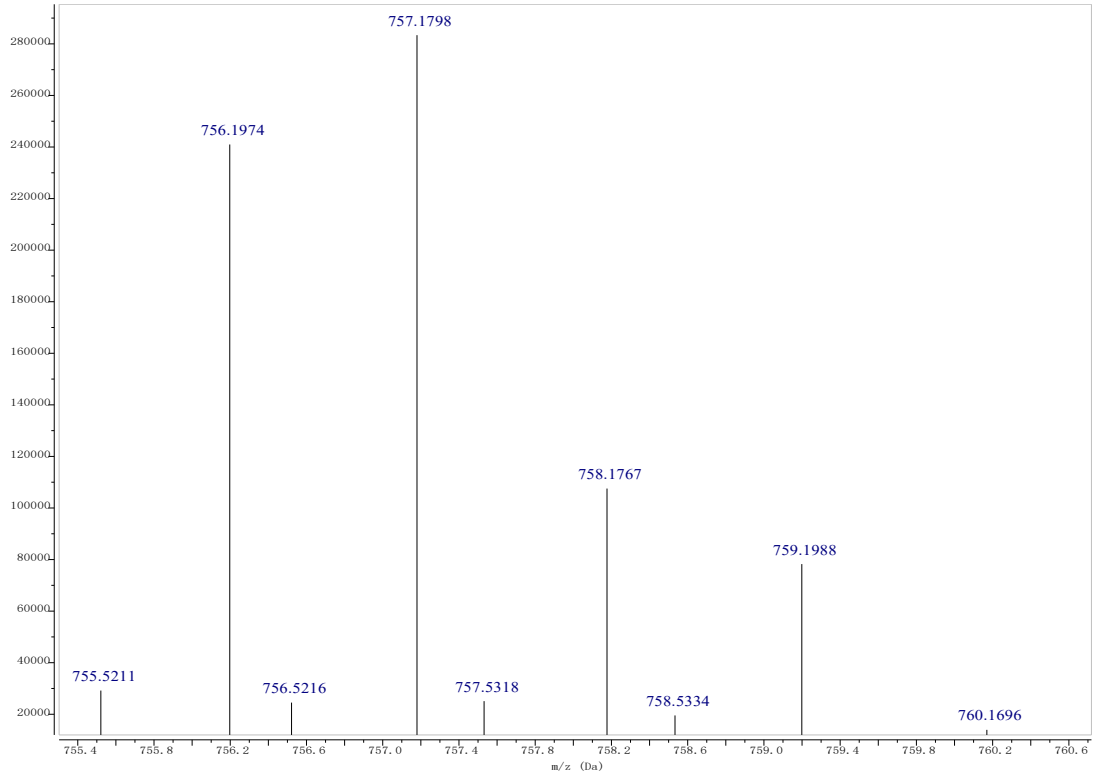


Figure S16. HRMS for BTB−1.

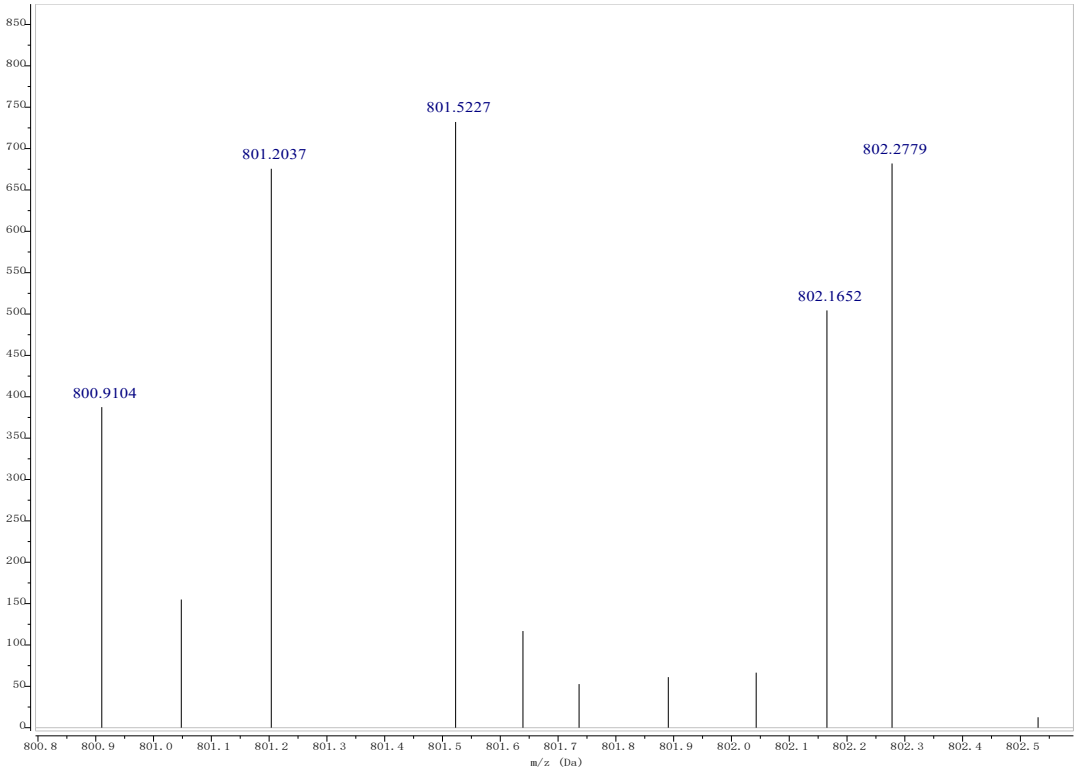


Figure S17. HRMS for BTB−2.

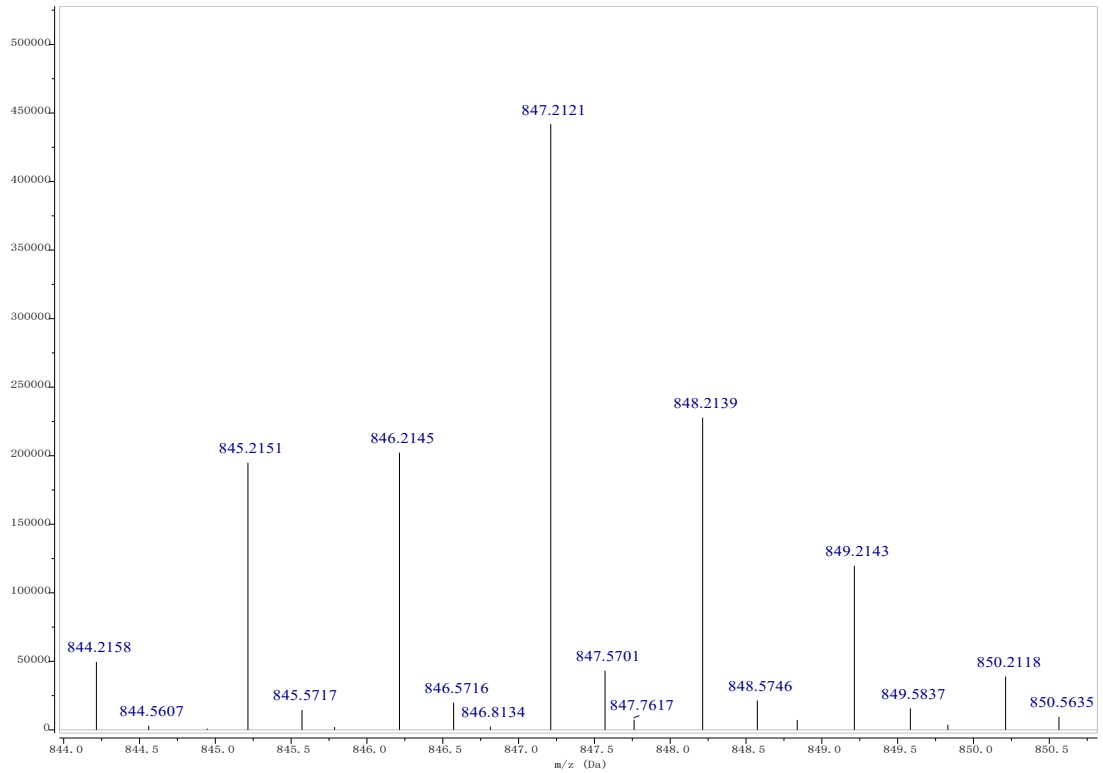


Figure S18. HRMS for BTB–3.

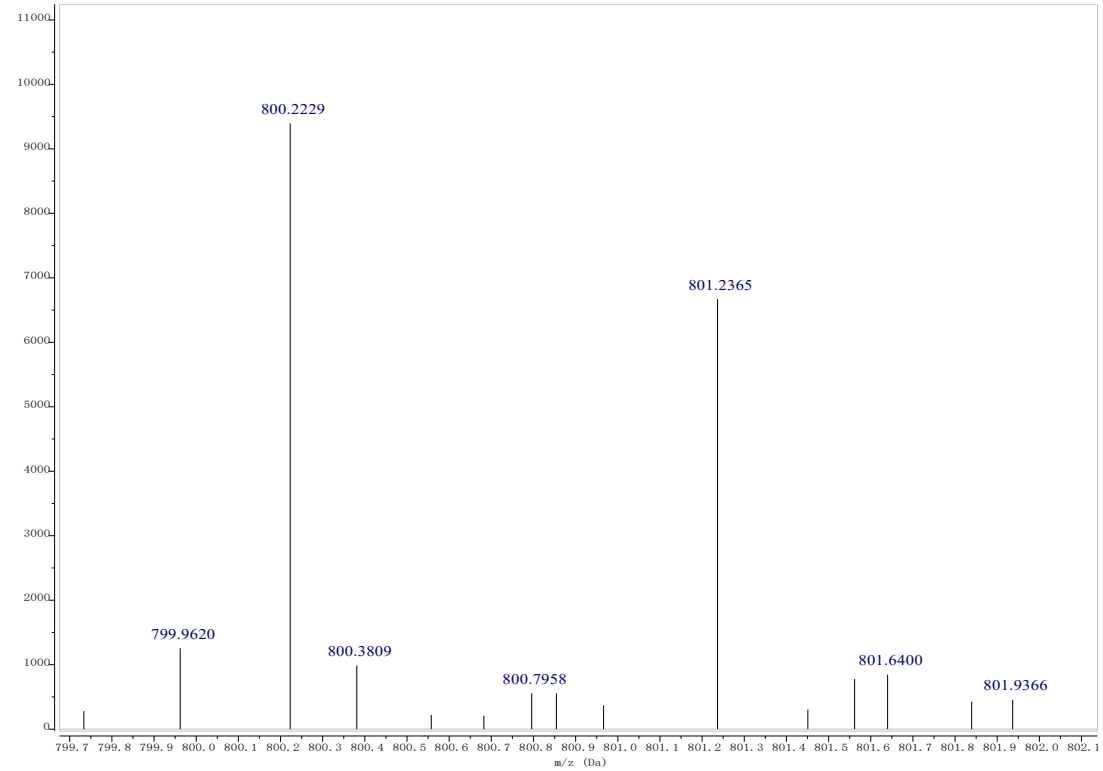


Figure S19. HRMS for BTB–4.

[1] *J. Org. Chem.* 2023, 88, 14368−14376.