

# A facile one-step synthesis of star-shaped alkynyl carbonates from CO<sub>2</sub>

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## Supporting Information

### Experimental Section

**General Methods.** CO<sub>2</sub> gas was generated from dry ice and introduced into a Schlenk tube containing the reactants by cannula. A balloon was then attached to the tube to collect the gas and maintain a 1 atm pressure (Figure S1). All reagents and analytical grade solvents were used as received. Propargyl alcohol and *N,N*-dimethylacetamide (DMA) were obtained from Alfa Aesar. Benzyl bromide, 1,3,5-tris(bromomethyl)benzene, hexakis(bromomethyl)benzene, 4-(chloromethyl)benzyl alcohol, bases (K<sub>2</sub>CO<sub>3</sub> and Cs<sub>2</sub>CO<sub>3</sub>) and TBAB were obtained from Sigma-Aldrich.



**Figure S1.** Experimental setup.

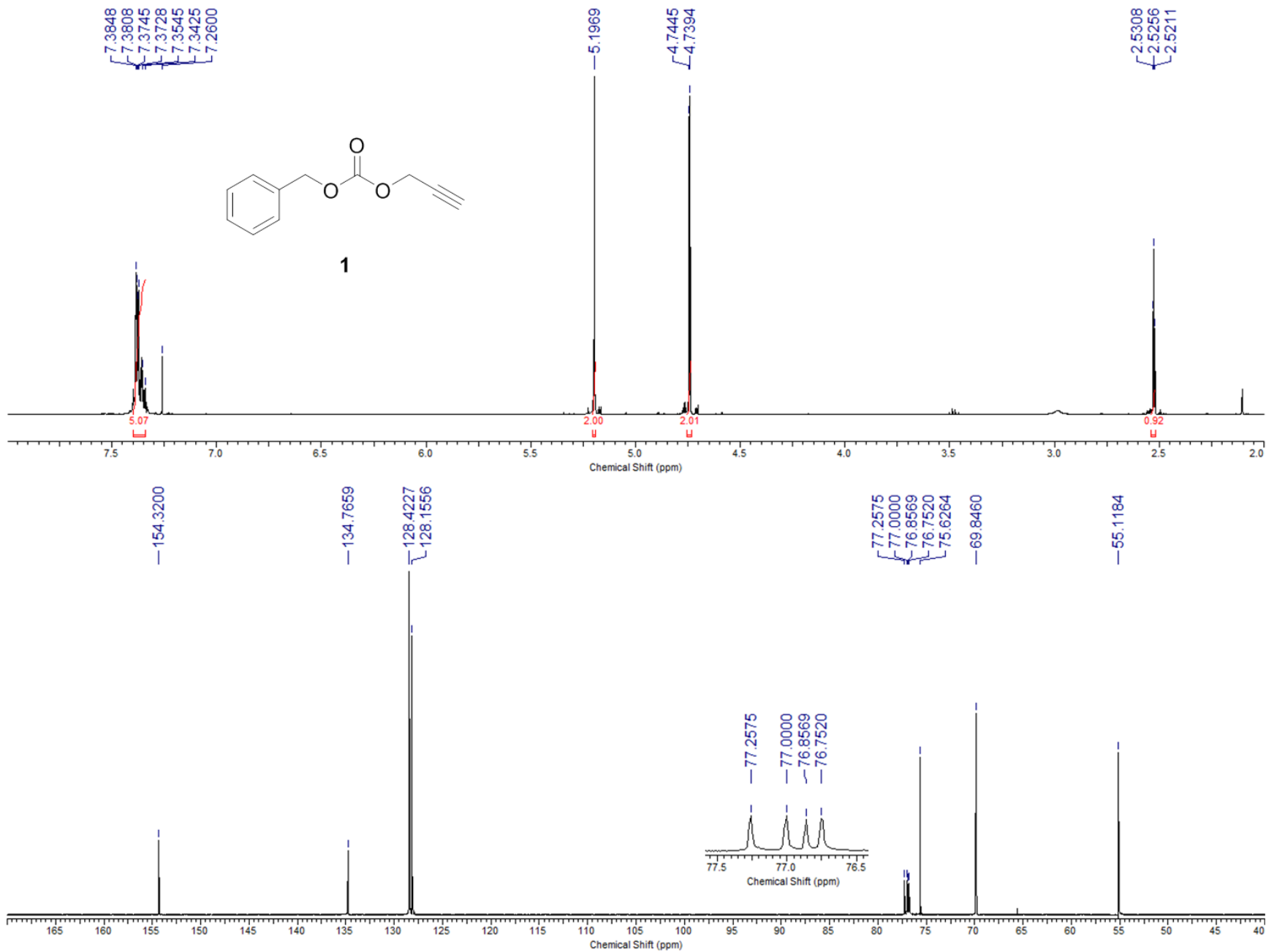
**Physical Measurements.**  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were recorded on a JEOL Resonance 500 MHz spectrometer. The chemical shifts of  $^1\text{H-NMR}$  were measured relative to  $\text{SiMe}_4$  ( $^1\text{H}$ ). A Finnigan LCQ spectrometer was used to record electrospray ionization mass spectra. A Perkin Elmer FT-IR spectrum 200 spectrometer was used to record infrared spectra. A Bruker Autoflex III TOF/TOF mass spectrometer was used for MALDI-TOF measurements. Elemental analyses were conducted in the microanalysis laboratory at the Department of Chemistry in the National University of Singapore.

**Benzyl prop-2-yn-1-yl carbonate (1).** Propargyl alcohol (0.30 mL, 5.08 mmol), potassium carbonate (0.70 mg, 5.06 mmol) and TBAB (0.41 mg, 1.26 mmol) were added to a solution containing 5 mL of DMA. Carbon dioxide was introduced and the reaction mixture stirred for 1 h. Benzyl bromide (0.15 mL, 1.26 mmol) was then added into the reaction mixture and stirred for 18 hours. The reaction was then worked up first by centrifugation to separate the solid and obtain a clear solution. The latter was diluted with water (100 mL) and extracted with ether (10 mL x 3). The combined organic ether phases were washed with 10 mL water, and removal of ether by rotary evaporator afforded **1** as a yellow liquid. Yield = 185 mg, 77%.  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.32–7.42 (m, 5H), 5.20 (s, 2H), 4.74 (sd,  $J = 2.6$  Hz, 2H), 2.53 (st,  $J = 2.4$  Hz, 1H);  $^{13}\text{C-NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 154.3, 134.8, 128.4, 128.2, 76.9, 69.8, 55.1; IR (NaCl)  $\nu$  1758  $\text{cm}^{-1}$  (C=O), 1240  $\text{cm}^{-1}$  (C-O). Elemental Analysis, calcd. for  $\text{C}_{11}\text{H}_{10}\text{O}_3$  (190.20): C 69.46%, H 5.30%, O 25.24%; Found: C 68.66% %, H 5.36%, O 25.98%.

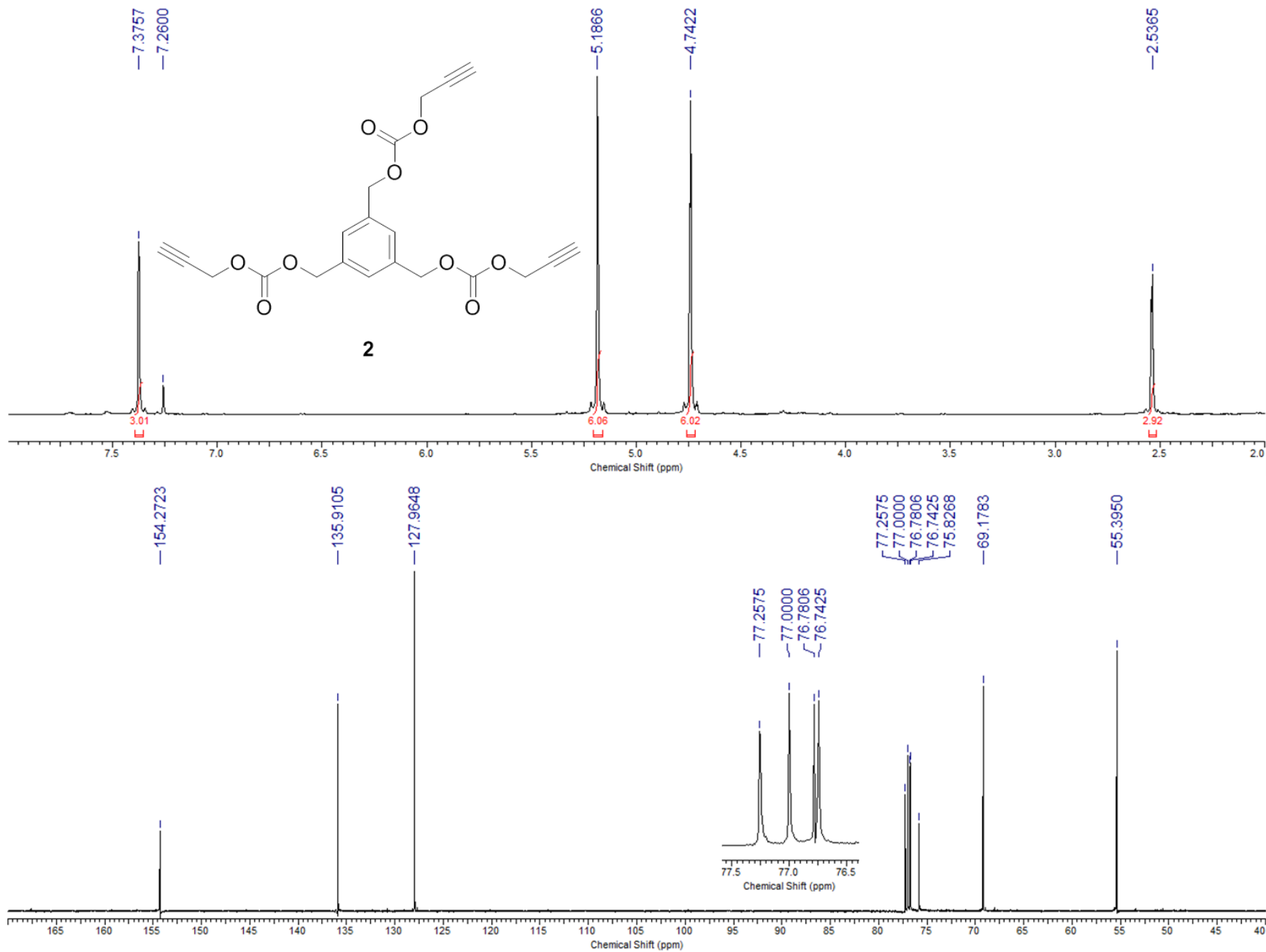
**Benzene-1,3,5-triyltris(methylene) tri(prop-2-yn-1-yl) tricarboxylate (2).** Propargyl alcohol (0.20 mL, 3.43 mmol), potassium carbonate (465 mg, 3.36 mmol) and TBAB (271 mg, 0.84 mmol) were added to a solution containing 3 mL of DMA. Carbon dioxide was introduced and the reaction mixture was further stirred for 1 h. 1,3,5-tris(bromomethyl) benzene (100 mg, 0.28 mmol) dissolved in 2 mL of DMA was then added into the reaction mixture and stirring was maintained for 48 h. The reaction mixture was then worked up first by centrifugation to separate the solid and obtain a clear solution. The latter was diluted with 100 mL water and extracted with ether (10 mL x 3). The combined organic ether phases were washed with water (10 mL), and removal of ether by rotary evaporator afforded a crude product. It was then purified via column chromatography on a pipette using dichloromethane (DCM) as an eluent to obtain **2**, a white

solid. Yield: 82.4 mg, 71%.  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.37 (s, 3H), 5.19 (s, 6H), 4.74 (s, 6H), 2.54 (s, 3H);  $^{13}\text{C-NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 154.3, 135.9, 128.0, 76.8, 69.2, 55.4; IR (KBr)  $\nu$  1750  $\text{cm}^{-1}$  (C=O) and 1261  $\text{cm}^{-1}$  (C-O); ESI-MS:  $m/z$  413.2 [M-H] $^-$ . Elemental Analysis, calcd. for  $\text{C}_{21}\text{H}_{18}\text{O}_9$  (414.37): C 60.87%, H 4.38%, O 34.75%; Found: C 60.82%, H 4.58%, O 34.60.

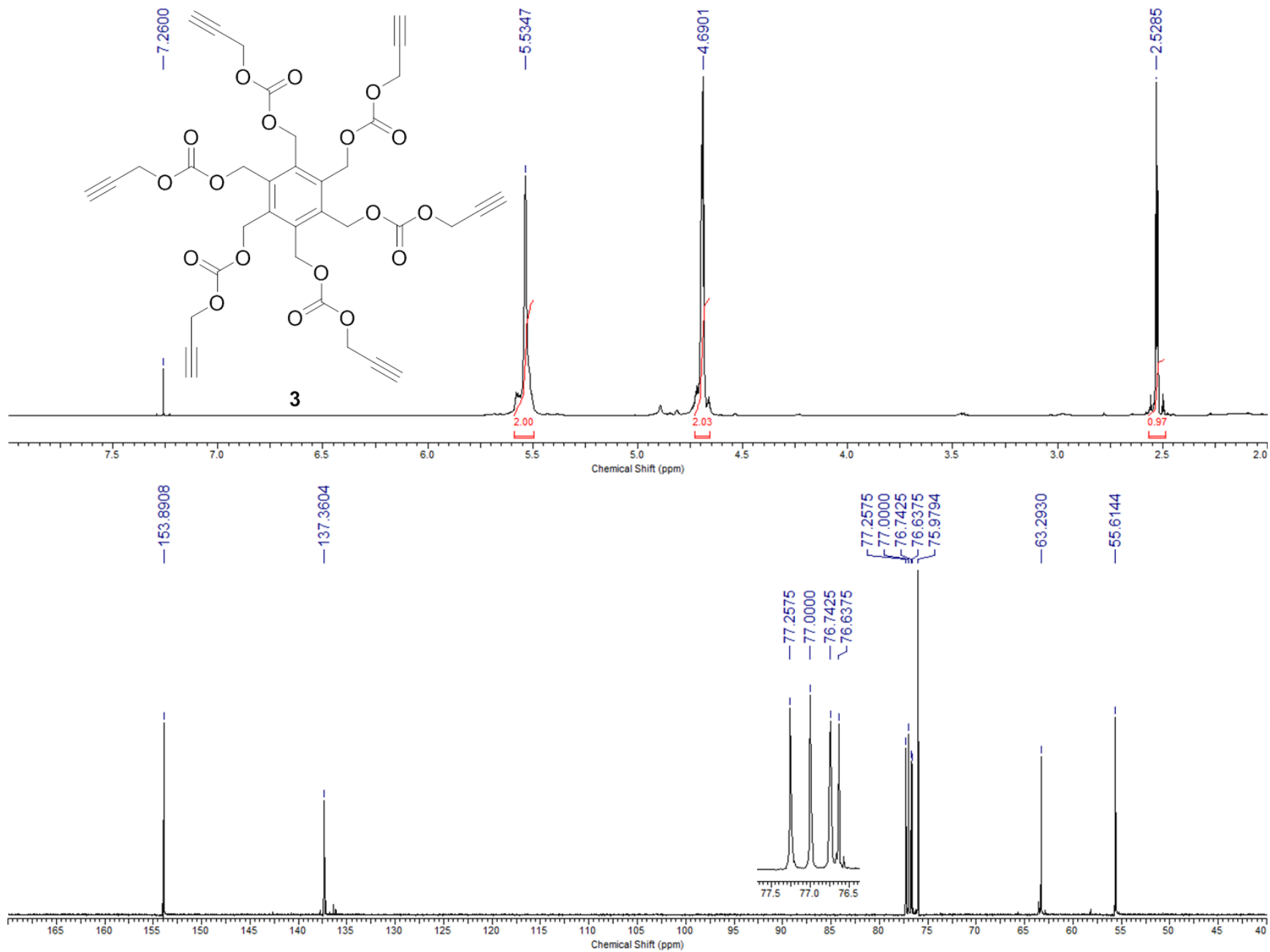
**Benzene-1,2,3-4-5,6-hexaylhexakis(methylene) hexa(prop-2-yn-1-yl) hexacarbonate (3).** Propargyl alcohol (0.22 mL, 3.78 mmol), potassium carbonate (522 mg, 3.78 mmol) and TBAB (304 mg, 0.94 mmol) were added to a solution containing 3 mL of DMA. Carbon dioxide was introduced and the reaction mixture was stirred for 1 h. Hexakis(bromomethyl)benzene (100 mg, 0.16 mmol) was added to 1 mL of DMA and sonicated prior to adding into the reaction mixture. An additional 1 mL of DMA was added to wash any remaining alkyl halide into the Schlenk flask. The reaction mixture was further stirred for 96 h. The work up method used was the same as for **2**. Product **3** is a white solid. Yield: 76.6 mg, 65%.  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 5.53 (s, 12H), 4.69 (s, 12H), 2.53 (s, 6H);  $^{13}\text{C-NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 153.9, 137.4, 76.6, 63.3, 55.6; IR (KBr)  $\nu$  1744  $\text{cm}^{-1}$  (C=O), 1259  $\text{cm}^{-1}$  (C-O); ESI-MS:  $m/z$  748.4 [M-H] $^-$ . Elemental Analysis, calcd. for  $\text{C}_{36}\text{H}_{30}\text{O}_{18}$  (750.62): C 57.61%, H 4.03%, O 38.36%; Found: C 56.79%, H 4.09%, O 39.12%.



**Figure S2.** <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>) of **1**.



**Figure S3.** <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>) of **2**.



**Figure S4.** <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>) of **3**.