

Supporting Information

Bottom-up Construction of a Supramolecular Catalyst for Highly Active and Selective Intramolecular Alkyne Carboxylation

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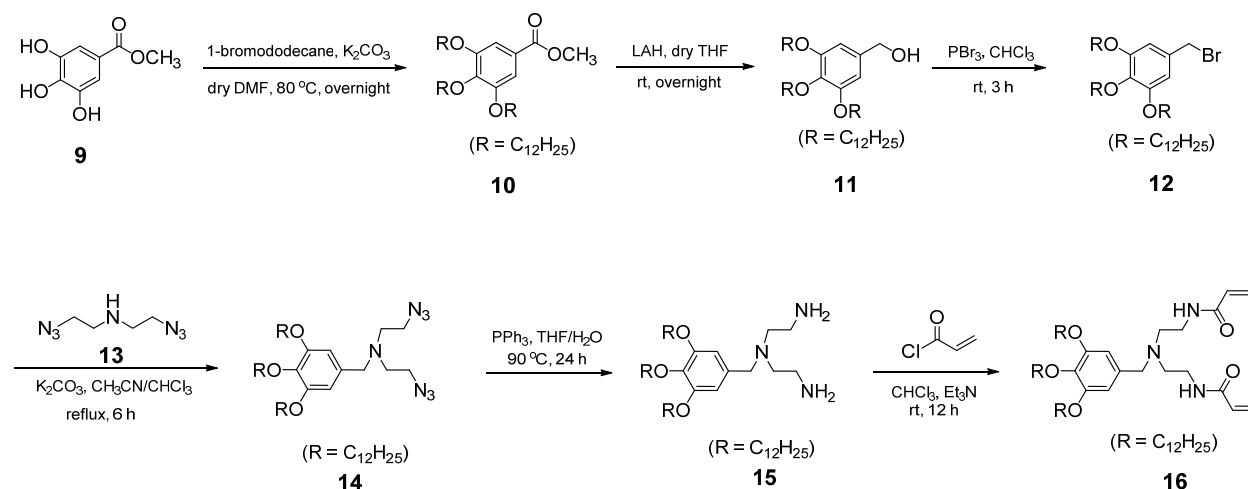
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General

All reagents and solvents were of ACS certified grade or higher and were used as received from commercial suppliers. Routine ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-400 and Bruker DRX-400 spectrometer. ESI-MS was performed on a FINNIGAN TSQ700 mass spectrometer. Dynamic light scattering (DLS) was performed on a PD2000DLS^{PLUS} dynamic light scattering detector. Fluorescence spectra were recorded at ambient temperature on a Varian Cary Eclipse fluorescence spectrophotometer. UV-vis spectra were recorded at ambient temperature on a Cary 50 Bio UV-visible spectrophotometer.

Synthesis



Scheme 1S. Synthesis of compound **16**

Methyl 3,4,5-tris(dodecyloxy)benzoate (10).¹ Potassium carbonate (23.8 g, 172.20 mmol) was added to a solution of methyl 3,4,5-trihydroxybenzoate (**9**) (5.10 g, 27.54 mmol) in DMF (150 mL) at room temperature. After the mixture was stirred at 60 °C for 2 h, 1-bromododecane (21.3 mL, 88.0 mmol) was added slowly. The reaction mixture was stirred overnight at 80 °C, cooled to room temperature, and poured over 750 mL of icy water. The crude product was collected by suction filtration and purified by crystallization from acetone to give a yellow solid (20.0 g, quantitative). ^1H NMR (400 MHz, CDCl₃, δ): 7.24 (s, 2 H), 3.99 (t, 6 H), 3.88 (s, 3 H), 1.82-1.25

¹ Percec, V.; Peterca, M.; Tsuda, Y.; Rosen, B. M.; Uchida, S.; Imam, M. R.; Ungar, G.; Heiney, P. A. *Chem.–Eur. J.* **2009**, *15*, 8994–9004.

(m, 60 H), 0.86 (t, 9 H).

3,4,5-Tris(dodecyloxy)benzyl alcohol (11).¹ A solution of methyl 3,4,5-tris(dodecyloxy)-benzoate (**10**) (16.3 g, 23.6 mmol) in dry THF (125 mL) was added dropwise to a stirred suspension of LiAlH₄ (1.50 g, 38.7 mmol) in dry THF (40 mL) at 0 °C. The reaction mixture was stirred overnight at room temperature and was quenched carefully by methanol (10 mL) and water (10 mL). The solid formed was removed by filtration and the filtrate was concentrated *in vacuo*. The residue was dissolved in CHCl₃ (250 mL). The resulting solution was washed with water (2 × 100 mL), brine (2 × 100 mL), dried over anhydrous MgSO₄, and concentrated *in vacuo* to give a white powder (11.0 g, 71%). ¹H NMR (400 MHz, CDCl₃, δ): 6.56 (s, 2H), 4.59 (s, 2H), 4.02-3.88 (m, 6H), 1.86-1.26 (m, 60H), 0.88 (t, 9H).

3,4,5-Tris(dodecyloxy)benzyl bromide (12).¹ A solution of PBr₃ (0.50 mL, 5.3 mmol) in CHCl₃ (5 mL) was slowly added to a stirred solution of 3,4,5-tris(dodecyloxy)benzyl alcohol (1.80 g, 2.67 mmol) in CHCl₃ (30 mL) at 0 °C. The reaction mixture was stirred at room temperature for 3 h and slowly poured into water (20 mL). The product was extracted with CHCl₃ (2 × 30 mL). The combined organic phase was washed with brine (2 × 20 mL), dried over anhydrous MgSO₄, and concentrated *in vacuo* to give a white solid (1.70 g, 89%). ¹H NMR (400 MHz, CDCl₃, δ): 6.57 (s, 2H), 4.43 (s, 2H), 3.98-3.94 (m, 6H), 1.8-1.26 (m, 60H), 0.88 (t, 9H).

Compound (14). Bis-(2-azidoethyl)amine² (34 mg, 0.22 mmol) was dissolved in solution of compound **12** (80.0 mg, 0.11 mmol) and K₂CO₃ (46.0 mg, 0.33 mmol) in CHCl₃ (2 mL) and CH₃CN (3 mL). The reaction mixture was stirred at 80 °C for 6 h. The solid was removed by filtration and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography over silica gel using CH₂Cl₂ as the eluent to give a yellow oil (81.0 mg, 92%). ¹H NMR (400 MHz, CDCl₃, δ): 6.56 (s, 2H), 3.97-3.92 (dd, *J* = 13.6 Hz and 6.4 Hz, 6H), 3.59 (s, 2H), 3.28 (t, *J* = 6.0 Hz, 4H), 2.75 (t, *J* = 6.4 Hz, 4H), 1.82-1.72 (m, 6H), 1.46-1.26 (m, 54H), 0.88 (t, *J* = 6.8 Hz, 9H). ¹³C NMR (100 MHz, CDCl₃, δ): 153.17, 137.28, 133.64, 106.71, 73.38, 69.07, 59.76, 49.44, 31.98, 31.96, 30.38, 29.80, 29.77, 29.74, 29.73, 29.70, 29.68, 29.66, 29.48, 29.47, 29.43, 29.41, 26.18, 26.14, 22.73, 14.14.; ESI-MS (*m/z*): [M+H]⁺ calcd for C₄₇H₈₈N₇O₃, 798.6949; found 798.6944.

Compound (15). Ph₃P (197.0 mg, 0.75 mmol) was dissolved in solution of compound **14** (100.0 mg, 0.125 mmol) in THF (10 mL) and H₂O (1 mL). The reaction mixture was stirred at 80 °C for

² Gao, Y.; Chen, L.; Zhang, Z.; Gu, W.; Li, Y. *Biomacromolecules* **2010**, *11*, 3102-3111.

24 h. After THF was removed by rotary evaporation, the mixture was extracted with CHCl₃ (3 × 10 mL). The combined organic phase was washed with 0.1 M NaOH (3 × 5 mL), dried over anhydrous MgSO₄, and concentrated by rotary evaporation. The residue was purified by column chromatography over silica gel using CH₂Cl₂/MeOH/Et₃N = 6:1:0.1 (v/v/v) as the eluent to give a yellow oil (58 mg, 62%). ¹H NMR (400 MHz, CDCl₃): 6.50 (s, 2H), 3.96-3.91 (dd, *J* = 12.8 Hz and 6.4 Hz, 6H), 3.50 (s, 2H), 2.76 (t, *J* = 6.0 Hz, 4H), 2.52 (t, *J* = 6.0 Hz, 4H), 1.82-1.72 (m, 6H), 1.46-1.26 (m, 54H), 0.88 (t, *J* = 6.8 Hz, 9H). ¹³C NMR (100 MHz, CDCl₃, δ): 152.94, 137.12, 134.74, 107.03, 73.35, 69.10, 59.52, 57.48, 39.85, 31.90, 31.89, 30.32, 29.72, 29.70, 29.67, 29.66, 29.62, 29.60, 29.44, 29.42, 29.35, 29.33, 26.11, 26.11, 22.65, 14.07. ESI-MS (*m/z*): [M+H]⁺ calcd for C₄₇H₉₂N₃O₃, 746.7139; found 746.7144.

Compound (16). Acryloyl chloride (41.2 μL, 0.52 mmol) was added dropwise to in solution of compound **15** (180 mg, 0.24 mmol) and triethylamine (0.2 mL, 1.44 mmol) in CHCl₃ (10 mL). The reaction mixture was stirred at room temperature for 12 h and slowly poured into water (5 mL). The product was extracted with CHCl₃ (3 × 5 mL). The combined organic phase was washed with brine (3 × 5 mL), dried over anhydrous MgSO₄. After CHCl₃ was removed by rotary evaporation, the residue was purified by column chromatography over silica gel using CH₂Cl₂/MeOH = 10:1 (v/v) as the eluent to give a white powder (168 mg, 82%). The compound was acidified with HBr in CHCl₃/CH₃OH to give compound **2**, which was used without further purification. ¹H NMR (400 MHz, CDCl₃, δ): 6.39 (s, 2H), 6.29-6.15(m, 4H), 5.59-5.57(dd, *J* = 7.6 Hz and 1.2 Hz, 2H), 3.92-3.85(m, 6H), 3.42-3.38(m, 6H), 2.6 (t, *J* = 5.4 Hz, 4H), 1.78-1.71 (m, 6H), 1.48-1.26 (m, 54H), 0.88 (t, *J* = 6.8 Hz, 9H). ¹³C NMR (100 MHz, CDCl₃, δ): 166.07, 152.94, 137.04, 134.36, 130.99, 126.04, 107.38, 73.40, 69.05, 58.74, 53.42, 37.33, 31.93, 31.91, 30.34, 29.76, 29.74, 29.71, 29.69, 29.66, 29.64, 29.48, 29.45, 29.38, 29.36, 26.14, 22.68, 14.11. ESI-MS (*m/z*): [M+H]⁺ calcd for C₅₃H₉₅N₃O₅, 854.7350; found 854.7343.

Preparation of ICRM(2). Preparation of ICRMs, detailed characterization of the materials, and the template synthesis of Au@ICRM have been reported previously.³ Compound **2** (18.7 mg, 0.02 mmol) was dissolved in 0.5 ml of heptane, to which water (1.8 μL, 0.1 mmol) was added. The mixture was ultrasonicated at room temperature until the water droplet dissolved in the mixture and the solution became completely clear. After addition of 2-hydroxy-1-(4-(2-hydroxyethoxy)phenyl)-2-methylpropan-1-one (0.224 mg, 1 × 1 μmol), the mixture was

³ (a) Zhang, S.; Zhao, Y. *ACS Nano* **2011**, 5, 2637-2646. (b) Zhang, S.; Zhao, Y. *Langmuir* **2012**, 28, 3606-3613.

irradiated in a Rayonet photoreactor for 2 h until alkenic protons in **2** were consumed. The organic solvents were removed by rotary evaporation and the residue was washed by cold methanol and dried under vacuum to give a yellowish power (13.2 mg).

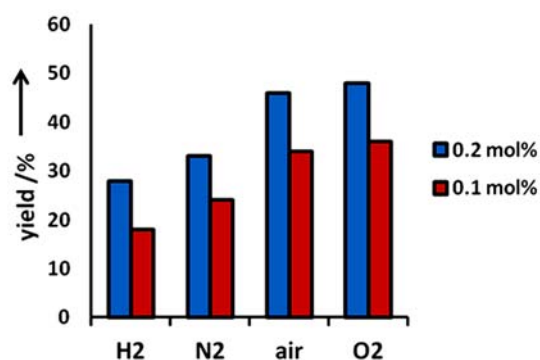


Figure S1. Yields of intramolecular cyclization of 4-pentynoic acid catalyzed by Au@ICRM(2) with 10% aurate loading and $W_0 = 5$ under different atmosphere at room temperature for 1 h.

Emission and Excitation Spectra of Au@ICRMs

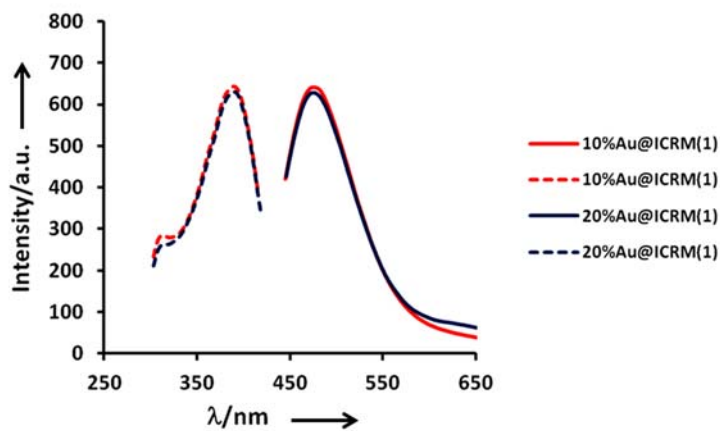


Figure S2. Emission (solid lines) and excitation (dashed lines) spectra of Au@ICRM(1) in chloroform with different aurate loading. $W_0 = [\text{H}_2\text{O}]/[\text{surfactant}] = 5$. [Cross-linked **1** in the ICRM] = 3.0 mM.

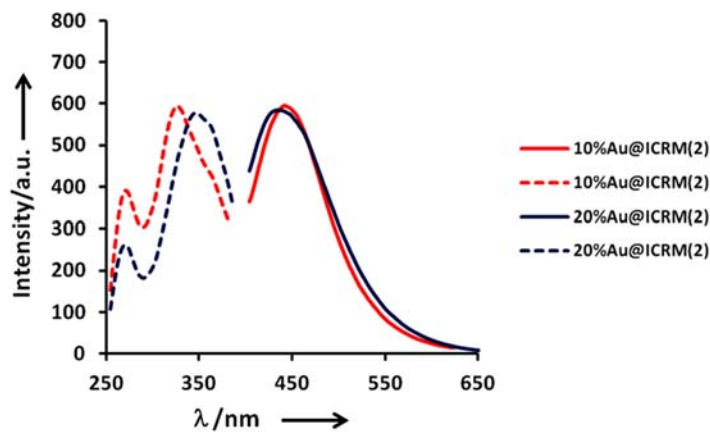


Figure S3. Emission (solid lines) and excitation (dashed lines) spectra of Au@ICRM(2) in chloroform with different aurate loading. $W_0 = [\text{H}_2\text{O}]/[\text{surfactant}] = 5$. [Cross-linked **2** in the ICRM] = 3.0 mM.

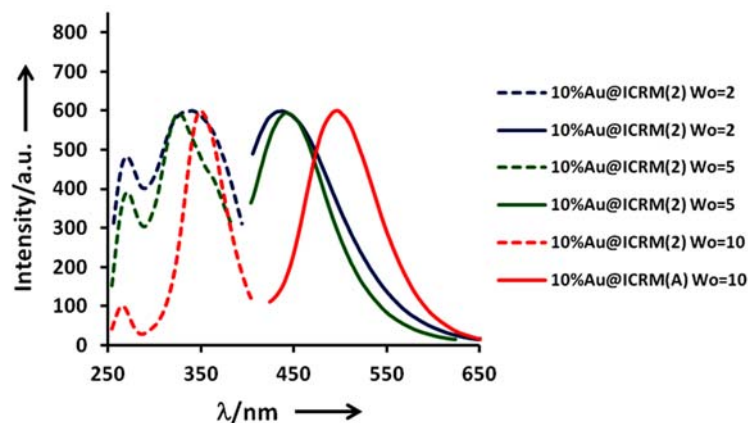


Figure S4. Emission (solid lines) and excitation (dashed lines) spectra of Au@ICRM(2) in chloroform with different W_0 . [Cross-linked **2** in the ICRM] = 3.0 mM. Aurate loading = $[\text{HAuCl}_4]/[\text{surfactant}] = 10\%$.

UV-vis Absorption spectra of Au@ICRMs

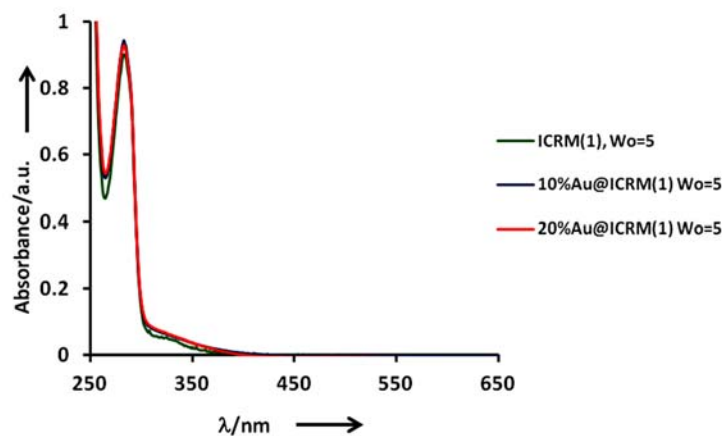


Figure S5. Absorption spectra of Au@ICRM(1) in chloroform with 10 and 20% aurate loading. [Cross-linked **1**] = 0.2 mM. $W_0 = [\text{H}_2\text{O}]/[\text{surfactant}] = 5$.

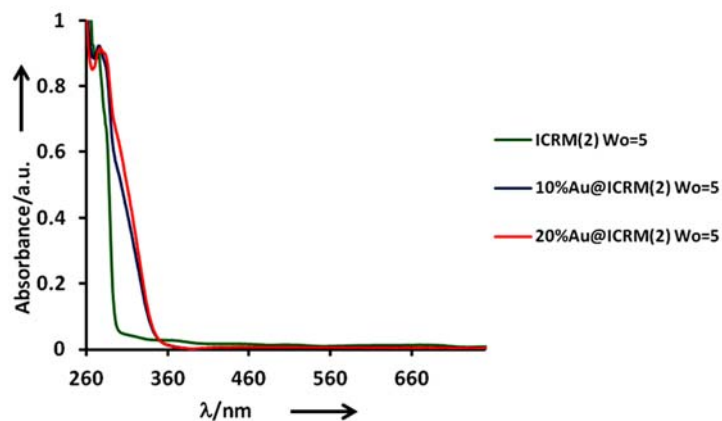


Figure S6. Absorption spectra of Au@ICRM(2) in chloroform with 10 and 20% aurate loading. [Cross-linked **2**] = 0.2 mM. $W_0 = [\text{H}_2\text{O}]/[\text{surfactant}] = 5$.

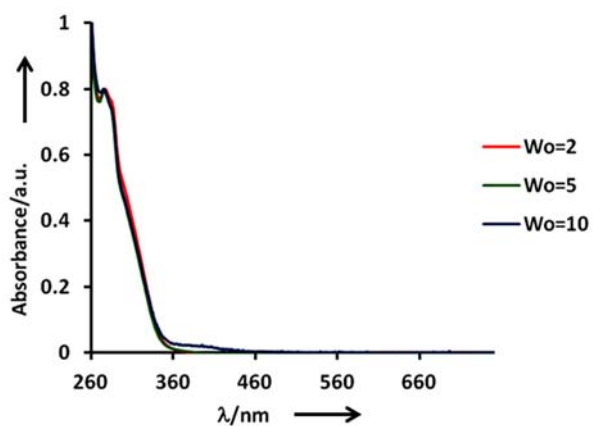


Figure S7. Absorption spectra of Au@ICRM(2) in chloroform with 10% aurate loading. $W_0 = [\text{H}_2\text{O}]/[\text{surfactant}] = 5$. [Cross-linked **2**] = 0.2 mM. $W_0 = [\text{H}_2\text{O}]/[\text{surfactant}] = 2, 5, \text{ and } 10$.

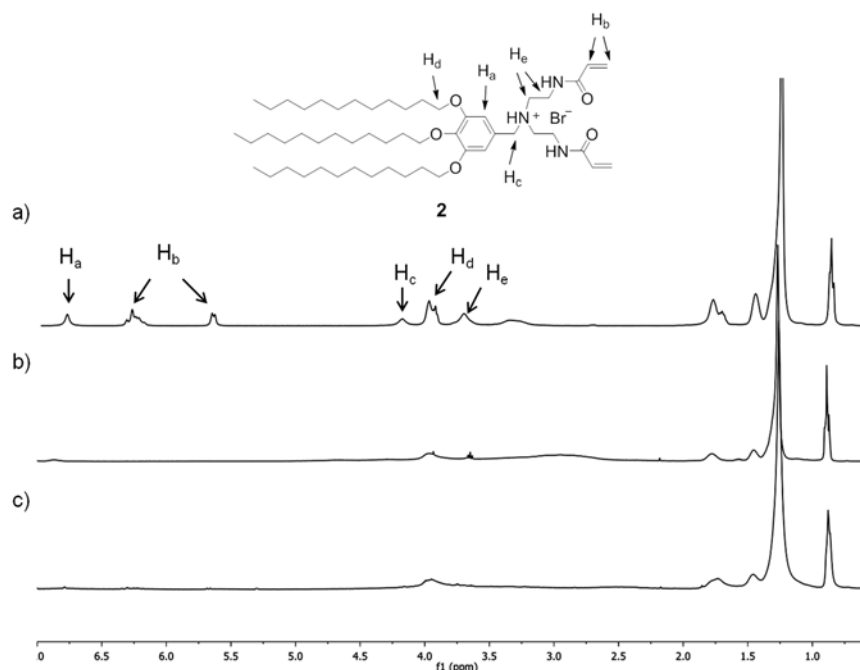


Figure S8. ^1H NMR spectra of compound **2** (a) before irradiation in CDCl_3 , (b) after UV irradiation for 2 h in the reverse-micelle configuration, and (c) after the ICRM was washed with methanol.

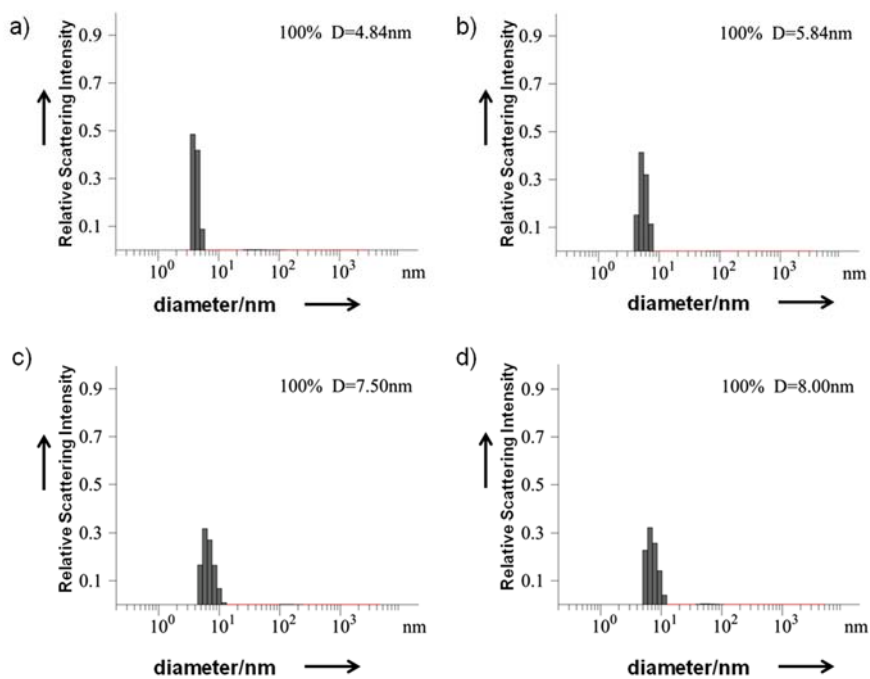


Figure S9. Distribution of the hydrodynamic diameters of ICRM(**2**) in (a) THF, (b) CHCl_3 , (c) heptane, and (d) toluene determined by DLS.

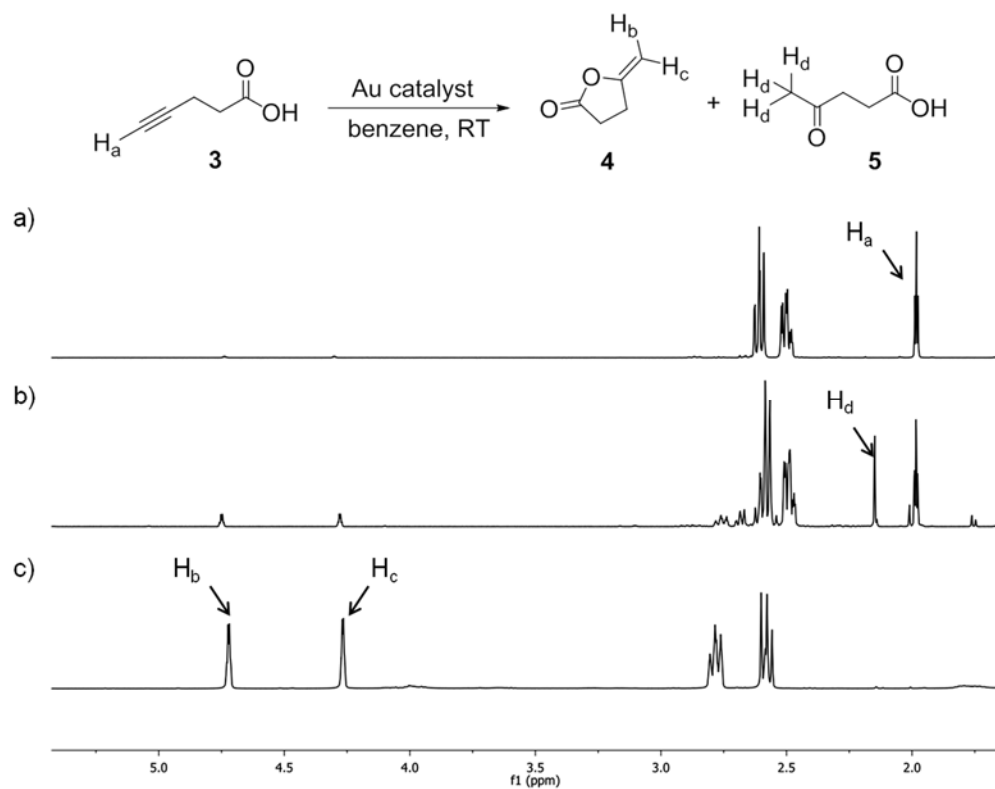
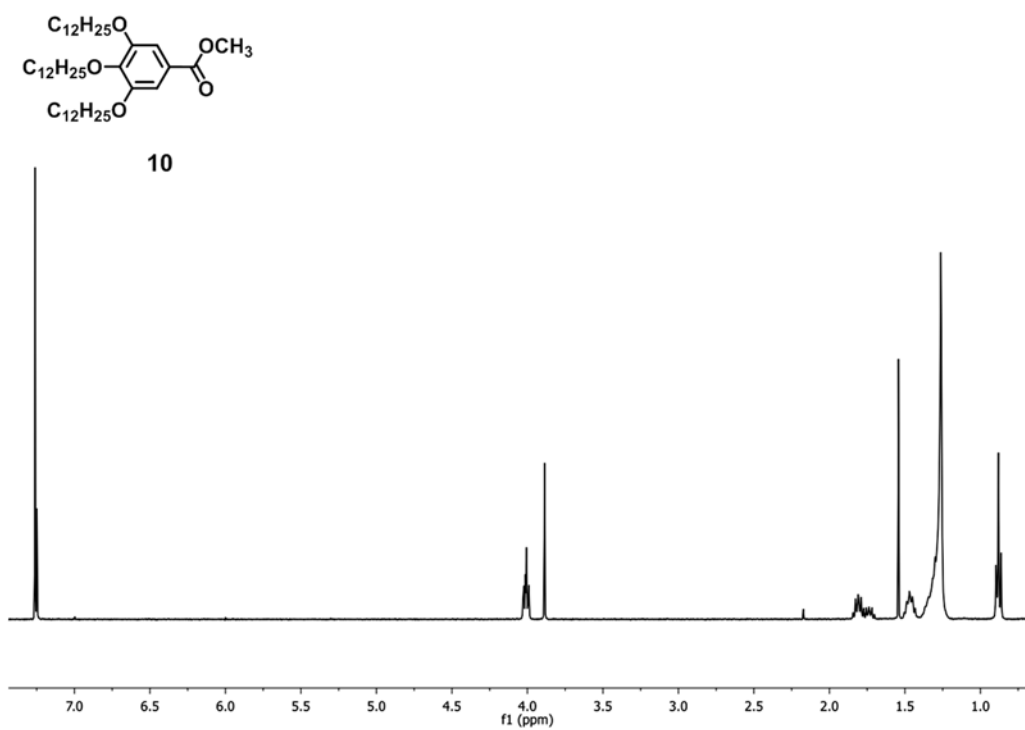
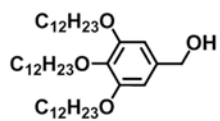


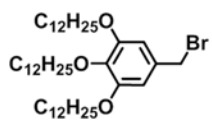
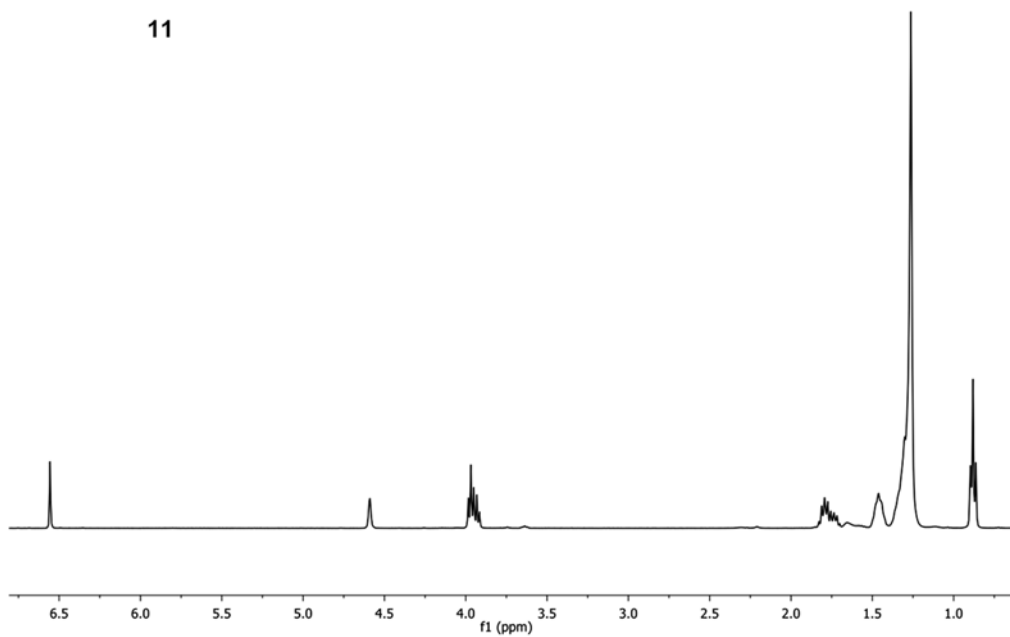
Figure S10. ^1H NMR spectra of (a) 4-pentynoic acid, (b) reaction product of 4-pentynoic acid catalyzed by HAuCl_4 , and (c) reaction product of 4-pentynoic acid catalyzed by $\text{Au@ICRM}(2)$ with 10% aurate loading and $W_0 = 5$. All the reactions were performed with 0.25 mmol of 4-pentynoic acid with 1 mol % gold catalysts in 0.2 mL of benzene- d_6 at room temperature for 3 h.

^1H and ^{13}C NMR spectra of key compounds





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