

# **Modular Synthesis of Propargylamine Modified Cyclodextrins by a Gold(III)-catalyzed Three Component Coupling Reaction**

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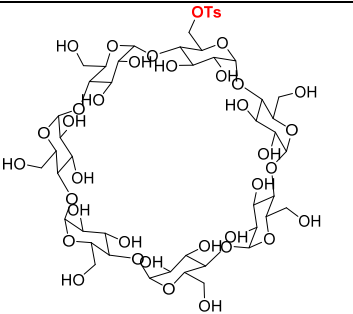
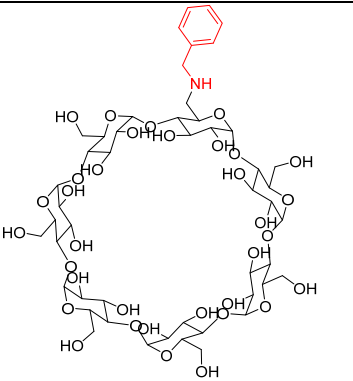
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## **Supporting Information**

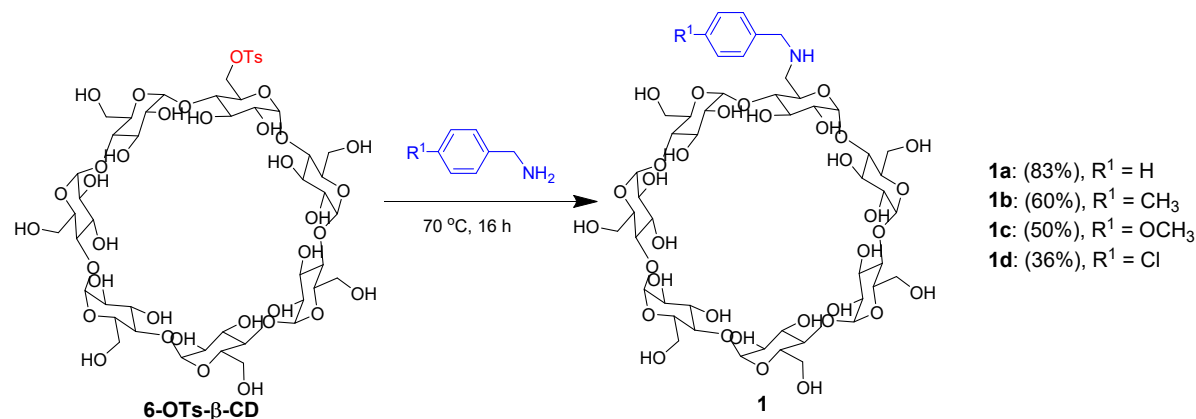
## Literature references of modified $\beta$ -cyclodextrins

 <p>6-OTs-<math>\beta</math>-CD</p>	<p>H.-S. Byun, N. Zhong, R. Bittman, <i>Org. Synth.</i> <b>2000</b>, 77, 225-230.</p>
 <p><b>1a</b></p>	<p>C. Wang, F. Chen, X.-W. He, S.-Z. Kang, C.-C. You, Y. Liu. <i>Analyst.</i> <b>2001</b>, 126, 1716-1720.</p>

## General Method:

Chemicals were purchased from commercial sources and were used without further purification. 1-(*p*-Toluenesulfonyl)imidazole and 6-*O*-*p*-toluenesulfonyl- $\beta$ -cyclodextrin (6-OTs- $\beta$ -CD) were synthesized by following the literature procedure (*Org. Synth.* **2000**, 77, 225-230).  $^1\text{H}$ ,  $^{13}\text{C}$  and 2D NMR spectra were performed at 600 MHz and 150 MHz on Bruker DPX-600 spectrometer. Chemical shifts (ppm) were referenced to residual solvent or TMS signals and coupling constants are given in Hz. Data for  $^1\text{H}$  NMR were recorded as follows: chemical shift ( $\delta$ , ppm), multiplicity (s, singlet; brs, broad singlet; d, doublet; dd, double doublet; t, triplet; td, triple doublet; tt, triple triplet; q, quartet; qd, quadruple doublet, m, multiplet), coupling constant (Hz), integration. Data for  $^{13}\text{C}$  NMR are reported in terms of chemical shift ( $\delta$ , ppm). Low resolution and high resolution mass spectra were measured on LCQ Advantage Mass, Waters 7890A and Waters Q-TOF 2TM spectrometer. Infrared spectroscopy was conducted using Nicolet 380 FT-IR.

## General Procedure for Synthesis of Mono-(6-benzylamino-6-deoxy)- $\beta$ -cyclodextrin 1

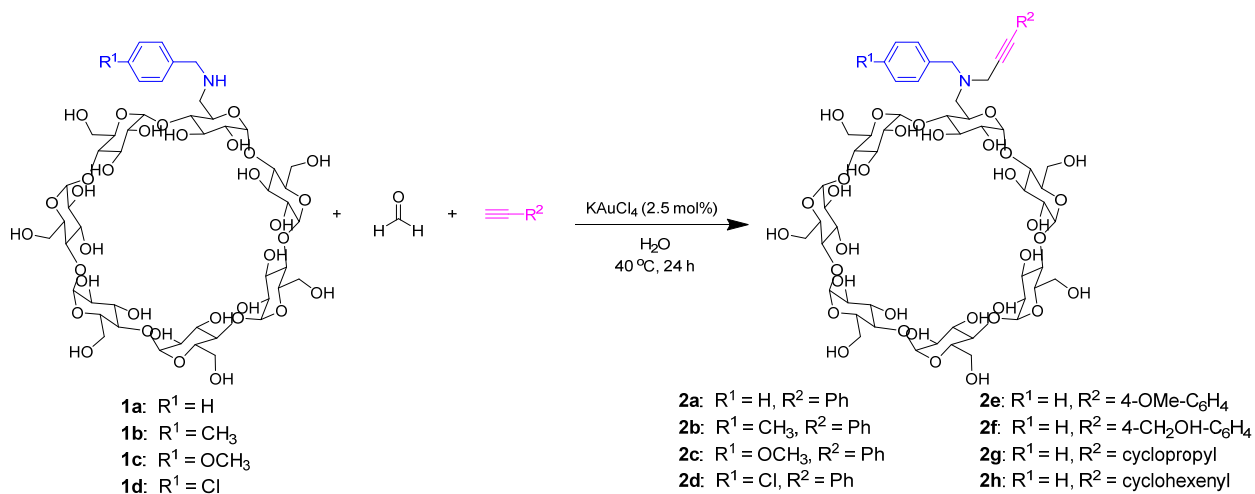


**Scheme S1.** Synthesis of mono-(6-benzylamino-6-deoxy)- $\beta$ -cyclodextrin **1**

6-*O*-*p*-Toluenesulfonyl- $\beta$ -cyclodextrin (3.0 g, 2.33 mmol) was heated in benzyl amine (20 mL) at 70 °C with stirring overnight. The resulting solution was added dropwise into excess acetone (150 mL). The resulting suspension was filtered to collect yellow solid. The yellow solid was then dissolved in water and heated up until all solid was dissolved. The solution was standed for overnight to allow precipitation of solid. The suspension was filtered to collect white solid. The

white solid was dried to constant weight under reduced pressure to give the corresponding mono-(6-benzylamino-6-deoxy)- $\beta$ -cyclodextrins **1a-1d** with moderate to good yield (36-83%).

### General Procedure for Synthesis of Mono-(6-(benzylpropargyl)amino-6-deoxy)- $\beta$ -cyclodextrin **2**



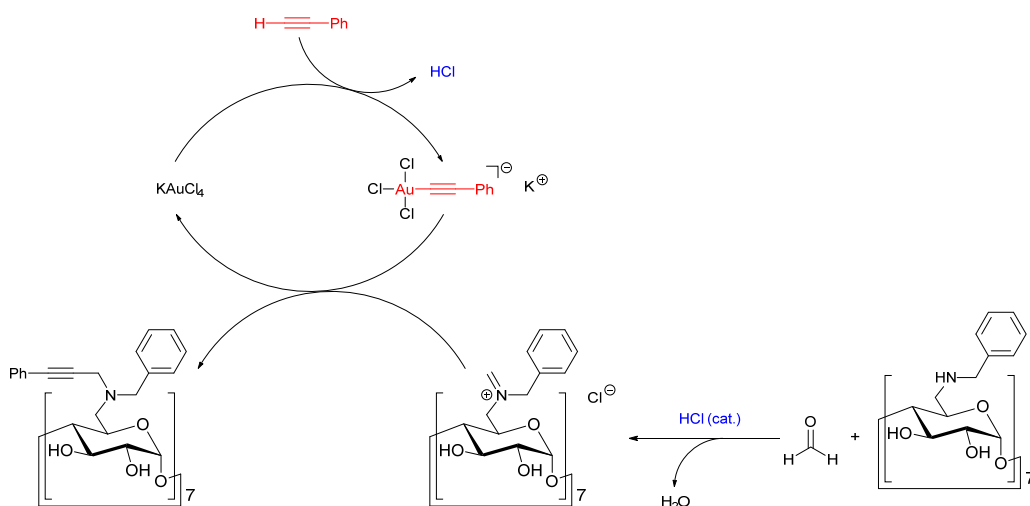
### Scheme S2. Synthesis of mono-(6-(benzylpropargyl)amino-6-deoxy)- $\beta$ -cyclodextrin **2**

Mono-(6-benzylamino-6-deoxy)- $\beta$ -cyclodextrin **1** (1.0 *equiv.*), formaldehyde (10.0 *equiv.*), alkyne (10.0 *equiv.*) and potassium gold(III) chloride KAuCl<sub>4</sub> (2.5 mol%) were heated in water (10 mL) at 40 °C for 24 h. The resulting suspension was filtered to collect the solid. The solid was then dissolved in water and heated at 80 °C for 20 min. The insoluble solid was removed by filtration. The solution was allowed to stand in air and precipitate for few days. The suspension was filtered to collect the white solid. The white solid was dried to constant weight under reduced pressure to give the corresponding mono-(6-benzylpropargylamino-6-deoxy)- $\beta$ -cyclodextrin **2a-2h** with moderate to good yield (26-67%).

**Table S1** Attempt of gold(III) catalyzed three component coupling reaction of primary amine modified  $\beta$ -cyclodextrin, phenylacetylene and various aldehydes.<sup>[a]</sup>

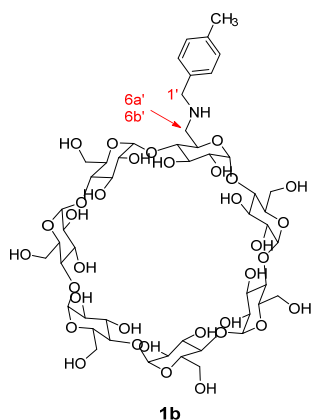
Entry	R	Catalyst	Solvent	Yield of <b>2aa</b> (%) <sup>[b]</sup>
1	H	KAuCl <sub>4</sub>	H <sub>2</sub> O	0
2	Ph	KAuCl <sub>4</sub>	H <sub>2</sub> O	0
3	4-OMeC <sub>6</sub> H <sub>4</sub>	KAuCl <sub>4</sub>	H <sub>2</sub> O	0
4	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	KAuCl <sub>4</sub>	H <sub>2</sub> O	0
5	PhCH <sub>2</sub> CH <sub>2</sub>	KAuCl <sub>4</sub>	H <sub>2</sub> O	0
6	CH <sub>3</sub>	KAuCl <sub>4</sub>	H <sub>2</sub> O	0
7	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	KAuCl <sub>4</sub>	H <sub>2</sub> O	0
8	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	KAuCl <sub>4</sub>	H <sub>2</sub> O	0

[a] Reaction conditions: **1aa** (0.1 mmol), aldehyde (1.0 mmol), phenylacetylene (1.0 mmol), 40 °C, 24 h. [b] Detected by ESI-MS and TLC analysis.



**Scheme S3.** Proposed reaction mechanism

## Characterization Data of Mono-(6-benzylamino-6-deoxy)- $\beta$ -cyclodextrin **1** and Mono-(6-benzylpropargylamino-6-deoxy)- $\beta$ -cyclodextrin **2**



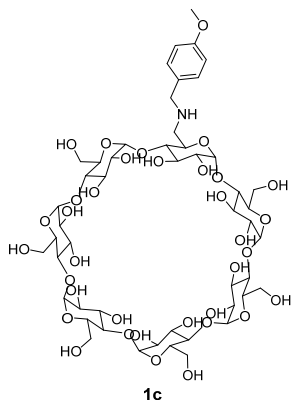
White solid; 60% yield;

**$^1\text{H NMR}$**  (600 MHz,  $d^6$ -DMSO):  $\delta$  7.19 (d,  $J = 7.8$  Hz, 2H, Ar-H), 7.10 (d,  $J = 7.9$  Hz, 2H, Ar-H), 5.87 – 5.67 (m, 15H, OH-2, OH-3, NH), 4.83-4.83 (m, 7H, H-1), 4.63 – 4.46 (m, 6H, OH-6), 3.77 – 3.26 (m, 42H, H-2, H-3, H-4, H-5, H-6a, H-6b, H-1'), 2.90 (d,  $J = 11.7$  Hz, 1H, H-6a'), 2.72 (dd,  $J = 12.2, 6.8$  Hz, 1H, H-6b'), 2.28 (s, 3H,  $\text{CH}_3$ );

**$^{13}\text{C NMR}$**  (150 MHz,  $d^6$ -DMSO):  $\delta$  138.4, 135.8, 129.1, 128.2, 102.8, 102.4, 102.3, 102.2, 84.2, 82.00, 81.96, 81.93, 81.8, 73.5 – 72.5, 71.0, 60.3 – 60.2, 53.3, 49.5, 21.2;

**IR** ( $\text{cm}^{-1}$ , KBr): 3414, 2927, 1653, 1636, 1560, 1541, 1502, 1458, 1419, 1374, 1157, 1079, 1031, 948, 756, 706, 582;

**MS** (ESI):  $m/z$  1238.5 ( $[\text{M}+\text{H}]^+$ ); **HRMS** (ESI): Calcd. For  $\text{C}_{50}\text{H}_{80}\text{NO}_{35}^+$  1238.4483, found 1238.4552.



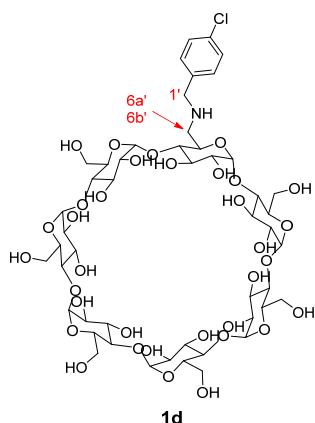
White solid; 50% yield;

**<sup>1</sup>H NMR** (600 MHz, d<sup>6</sup>-DMSO):  $\delta$  7.22 (d,  $J$  = 8.1 Hz, 2H, Ar-H), 6.86 (d,  $J$  = 8.2 Hz, 2H, Ar-H), 5.84-5.71 (m, 15H, OH-2, OH-3, NH), 4.84 (s, 7H, H-1), 4.54 (m, 6H, OH-6), 3.73 (s, 3H, OMe), 3.72 – 3.26 (m, 42H, H-2, H-3, H-4, H-5, H-6a, H-6b, H-1'), 2.90 (d,  $J$  = 11.4 Hz, 1H, H-6a'), 2.72 (s, 1H, H-6b');

**<sup>13</sup>C NMR** (150 MHz, d<sup>6</sup>-DMSO):  $\delta$  158.4, 133.4, 129.4, 113.9, 102.8, 102.4, 102.34, 102.29, 84.2, 82.0, 81.9, 81.83, 81.82, 73.5 – 72.5, 71.0, 60.4 – 60.2, 55.5, 52.9, 49.3;

**IR** (cm<sup>-1</sup>, KBr): 3366, 2929, 1637, 1514, 1420, 1368, 1302, 1247, 1156, 1079, 1031, 947, 757, 707, 582;

**MS** (ESI):  $m/z$  1254.4 ([M+H]<sup>+</sup>); **HRMS** (ESI): Calcd. For C<sub>50</sub>H<sub>80</sub>NO<sub>35</sub><sup>+</sup> 1254.4433, found 1254.4523.



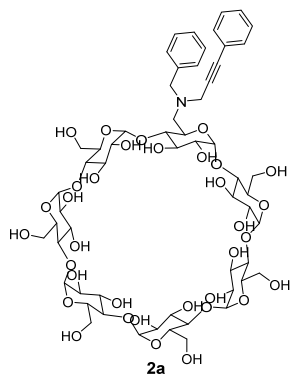
White solid; 36% yield;

**<sup>1</sup>H NMR** (600 MHz, d<sup>6</sup>-DMSO):  $\delta$  7.35 (s, 4H, Ar-H), (5.85 (d,  $J$  = 6.5 Hz, 1H), 5.81 – 5.68 (m, 13H), OH-2, OH-3), 4.92 – 4.74 (m, 7H, H-1), 4.62 – 4.39 (m, 6H, OH-6), 3.83 – 3.20 (m, 42H, H-2, H-3, H-4, H-5, H-6a, H-6b, H-1'), 2.90 (d,  $J$  = 11.4 Hz, 1H, H-6a'), 2.73 (dd,  $J$  = 11.8, 6.7 Hz, 1H, H-6b');

**<sup>13</sup>C NMR** (150 MHz, d<sup>6</sup>-DMSO):  $\delta$  140.6, 131.4, 130.0, 128.4, 102.8, 102.43, 102.40, 102.38, 102.3, 84.2, 82.02, 81.97, 81.93, 81.85, 73.5 – 72.5, 71.0, 60.4 – 60.2, 52.6, 49.3;

**IR** (cm<sup>-1</sup>, KBr): 3373, 2928, 1637, 1492, 1410, 1368, 1300, 1244, 1205, 1156, 1079, 1031, 947, 858, 757, 706, 581, 531;

**MS** (ESI):  $m/z$  1258.4 ([M+H]<sup>+</sup>); **HRMS** (ESI): Calcd. For C<sub>49</sub>H<sub>77</sub>ClNO<sub>34</sub><sup>+</sup> 1258.3937, found 1258.4048.



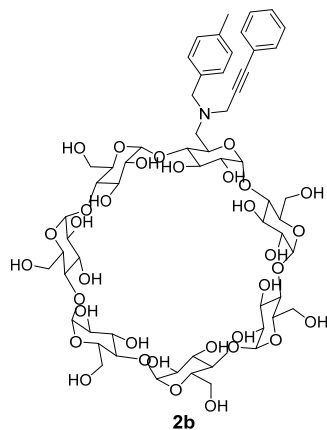
White solid; 50% yield;

**<sup>1</sup>H NMR** (600 MHz, d<sup>6</sup>-DMSO):  $\delta$  7.47 (dd,  $J = 6.5, 2.8$  Hz, 2H, Ar-H), 7.43 – 7.38 (m, 3H, Ar-H), 7.34 (dt,  $J = 15.1, 7.4$  Hz, 4H, Ar-H), 7.24 (t,  $J = 7.0$  Hz, 1H, Ar-H), 5.98 (d,  $J = 6.4$  Hz, 1H, OH-2 or OH-3), 5.83-5.72 (m, 13H, OH-2, OH-3), 4.96 (d,  $J = 3.1$  Hz, 1H, H-1), 4.86 – 4.84 (m, 6H, H-1), 4.53 – 4.48 (m, 6H, OH-6), 3.93 – 3.24 (m, 44H, H-2, H-3, H-4, H-5, H-6a, H-6b, H-1', H-2'), 3.04 – 2.85 (m, 2H, H-6a', H-6b');

**<sup>13</sup>C NMR** (150 MHz, d<sup>6</sup>-DMSO):  $\delta$  139.5, 131.9, 129.1, 128.73, 128.70, 127.4, 123.2, 102.8, 102.6, 102.5, 102.4, 102.1, 86.1, 85.4, 84.2, 82.1, 81.94, 81.88, 81.8, 81.6, 73.7 – 72.5, 60.4 – 60.2, 58.6, 54.3, 43.5;

**IR** (cm<sup>-1</sup>, KBr): 3384, 2927, 1637, 1491, 1419, 1369, 1156, 1079, 1029, 947, 862, 757, 701, 581, 528;

**MS** (ESI):  $m/z$  1338.5 ([M+H]<sup>+</sup>); **HRMS** (ESI): Calcd. For C<sub>58</sub>H<sub>84</sub>NO<sub>34</sub><sup>+</sup> 1338.4796, found 1338.4874.



White solid; 51% yield;

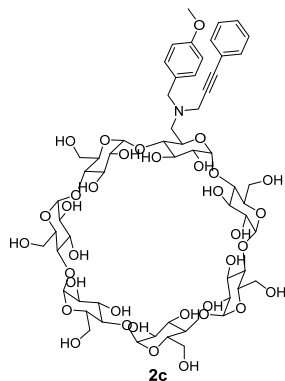


**<sup>1</sup>H NMR** (600 MHz, d<sup>6</sup>-DMSO):  $\delta$  7.49-7.46 (m, 2H, Ar-H), 7.39 (d,  $J = 3.8$  Hz, 3H, Ar-H), 7.23 (d,  $J = 7.5$  Hz, 2H, Ar-H), 7.13 (d,  $J = 7.5$  Hz, 2H, Ar-H), 5.99 – 5.64 (m, 14H, OH-2, OH-3), 4.94-4.84 (m, 7H, H-1), 4.52 (s, 6H, OH-6), 3.87 (s, 44H, H-2, H-3, H-4, H-5, H-6a, H-6b, H-1', H-2'), 2.91 (dd,  $J = 39.3, 10.7$  Hz, 2H, H-6a', H-6b'), 2.30 (s, 3H, CH<sub>3</sub>);

**<sup>13</sup>C NMR** (150 MHz, d<sup>6</sup>-DMSO):  $\delta$  136.4, 131.9, 129.2, 128.7, 128.5, 126.0, 123.2, 102.7, 102.6, 102.45, 102.42, 102.38, 102.0, 86.2, 85.3, 84.1, 82.1, 81.94, 81.85, 81.8, 81.5, 73.7– 72.4, 60.4 – 60.2, 58.6, 54.3, 43.7, 21.3;

**IR** (cm<sup>-1</sup>, KBr): 3374, 2927, 1637, 1514, 1491, 1414, 1368, 1244, 1156, 1079, 1030, 946, 860, 758, 693, 581, 527;

**MS** (ESI):  $m/z$  1352.7 ([M+H]<sup>+</sup>); **HRMS** (ESI): Calcd. For C<sub>59</sub>H<sub>86</sub>NO<sub>35</sub><sup>+</sup> 1352.4953, found 1352.5014.



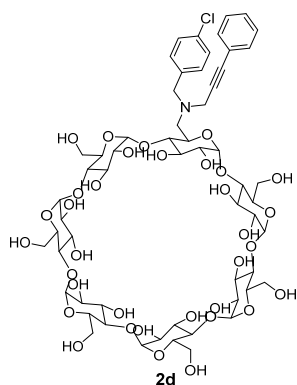
White solid; 42% yield;

**<sup>1</sup>H NMR** (600 MHz, d<sup>6</sup>-DMSO):  $\delta$  7.49 – 7.35 (m, 5H, Ar-H), 7.25 (d,  $J = 8.1$  Hz, 2H, Ar-H), 6.89 (d,  $J = 8.2$  Hz, 2H, Ar-H), 5.97 (d,  $J = 5.7$  Hz, 1H, OH-2 or OH-3), 5.87 – 5.73 (m, 13H, OH-2, OH-3), 4.96 – 4.81 (m, 7H, H-1), 4.58 (m, 6H, OH-6), 3.74 (s, 3H, OMe), 3.71 – 3.31 (m, 44H, H-2, H-3, H-4, H-5, H-6a, H-6b, H-1', H-2'), 2.98 – 2.86 (m, 2H, H-6a', H-6b');

**<sup>13</sup>C NMR** (150 MHz, d<sup>6</sup>-DMSO):  $\delta$  158.8, 131.9, 131.1, 130.5, 129.1, 128.7, 123.2, 114.0, 102.7, 102.5, 102.42, 102.37, 102.1, 86.2, 85.4, 84.0, 82.3, 82.0, 81.9, 81.8, 81.6, 73.6 – 72.4, 60.4 – 60.2, 58.0, 55.5, 55.3, 54.2, 43.1;

**IR** (cm<sup>-1</sup>, KBr): 3393, 2928, 1636, 1513, 1491, 1419, 1369, 1302, 1248, 1156, 1079, 1029, 946, 758, 693, 581, 528;

**MS** (ESI):  $m/z$  1368.5 ([M+H]<sup>+</sup>); **HRMS** (ESI): Calcd. For C<sub>59</sub>H<sub>86</sub>NO<sub>35</sub><sup>+</sup> 1368.4902, found 1368.4970.



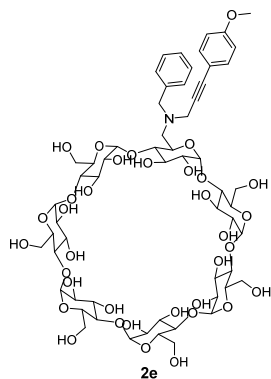
White solid; 49% yield;

**<sup>1</sup>H NMR** (600 MHz, *d*<sup>6</sup>-DMSO):  $\delta$  7.51 – 7.43 (m, 2H, Ar-H), 7.43 – 7.33 (m, 7H, Ar-H), 5.97 (d,  $J$  = 6.4 Hz, 1H, OH-2 or OH-3), 5.85 – 5.71 (m, 13H, OH-2, OH-3), 4.93 (d,  $J$  = 3.1 Hz, 1H, H-1), 4.86-4.83 (m, 6H, H-1), 4.56-4.46 (m, 6H, OH-6), 3.90 – 3.26 (m, 44H, H-2, H-3, H-4, H-5, H-6a, H-6b, H-1', H-2'), 3.03 – 2.82 (m, 2H, H-6a', H-6b');

**<sup>13</sup>C NMR** (150 MHz, *d*<sup>6</sup>-DMSO):  $\delta$  138.5, 131.9, 131.1, 129.1, 128.8, 128.6, 126.0, 123.1, 102.8, 102.54, 102.47, 102.41, 102.39, 102.1, 86.0, 85.4, 84.2, 82.1, 82.0, 81.84, 81.80, 81.7, 73.6 – 72.4, 60.4 – 60.2, 58.1, 54.2, 43.7;

**IR** (cm<sup>-1</sup>, KBr): 3373, 2928, 1637, 1491, 1410, 1368, 1336, 1245, 1156, 1079, 1029, 946, 860, 758, 694, 582, 528;

**MS** (ESI):  $m/z$  1372.4 ([M+H]<sup>+</sup>); **HRMS** (ESI): Calcd. For C<sub>58</sub>H<sub>82</sub>ClNO<sub>34</sub><sup>+</sup> 1372.4407, found 1372.4488.



White solid; 50% yield;

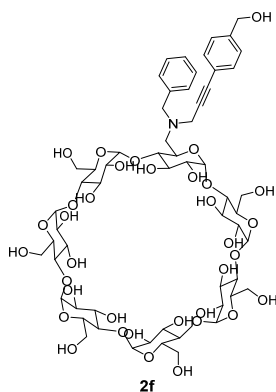
**<sup>1</sup>H NMR** (600 MHz, *d*<sup>6</sup>-DMSO):  $\delta$  7.41 (d,  $J$  = 8.7 Hz, 2H, Ar-H), 7.35-7.31 (m, 4H, Ar-H), 7.23 (t,  $J$  = 6.7 Hz, 1H, Ar-H), 6.94 (d,  $J$  = 8.8 Hz, 2H, Ar-H), 5.98 (d,  $J$  = 6.5 Hz, 1H, OH-2 or OH-3), 5.85 – 5.70 (m, 13H, OH-2, OH-3), 4.96 (d,  $J$  = 3.1 Hz, 1H, H-1), 4.85 (dd,  $J$  = 7.8, 3.4

Hz, 6H, H-1), 4.56 – 4.47 (m, 6H, OH-6,), 3.88 – 3.25 (m, 47H, H-2, H-3, H-4, H-5, H-6a, H-6b, H-1', H-2', OMe), 2.91 (dt,  $J = 14.4, 9.6$  Hz, 2H, H-6a', H-6b');

$^{13}\text{C}$  NMR (150 MHz,  $d^6$ -DMSO):  $\delta$  159.8, 139.8, 133.6, 129.3, 128.9, 127.5, 115.4, 114.9, 103.0, 102.8, 102.7, 102.6, 102.3, 85.6, 84.4, 84.3, 82.3, 82.2, 82.14, 82.07, 82.0, 81.8, 73.9 – 72.7, 60.6 – 60.4, 58.6, 55.9, 54.3, 43.6;

IR ( $\text{cm}^{-1}$ , KBr): 3373, 2928, 1637, 1607, 1510, 1413, 1368, 1338, 1293, 1249, 1156, 1079, 1029, 946, 834, 755, 704, 580, 533;

MS (ESI):  $m/z$  1368.5 ( $[\text{M}+\text{H}]^+$ ); HRMS (ESI): Calcd. For  $\text{C}_{59}\text{H}_{86}\text{NO}_{35}^+$  1368.4902, found 1368.4943.



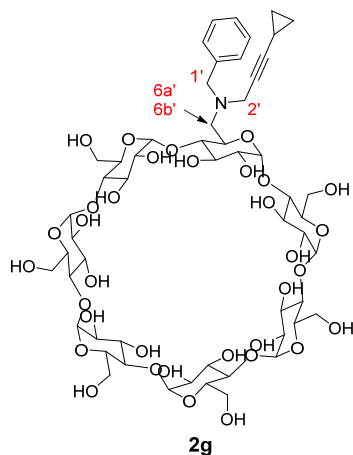
White solid; 67% yield;

$^1\text{H}$  NMR (600 MHz,  $d^6$ -DMSO):  $\delta$  7.43 (d,  $J = 8.1$  Hz, 2H, Ar-H), 7.37 – 7.30 (m, 6H, Ar-H), 7.24 (t,  $J = 6.7$  Hz, 1H, Ar-H), 5.98 (d,  $J = 6.4$  Hz, 1H, OH-2 or OH-3), 5.86 – 5.68 (m, 13H, OH-2, OH-3), 5.29 (t,  $J = 5.8$  Hz, 1H,  $\text{PhCH}_2\text{OH}$ ), 4.96 (d,  $J = 3.0$  Hz, 1H, H-1), 4.92 – 4.78 (m, 6H, H-1), 4.55 – 4.48 (m, 8H, OH-6,  $\text{PhCH}_2\text{OH}$ ), 3.90 – 3.27 (m, 44H, H-2, H-3, H-4, H-5, H-6a, H-6b, H-1', H-2'), 2.93 (dt,  $J = 14.5, 9.5$  Hz, 2H, H-6a', H-6b');

$^{13}\text{C}$  NMR (150 MHz,  $d^6$ -DMSO):  $\delta$  143.5, 139.8, 132.0, 129.3, 128.9, 127.6, 127.2, 121.6, 103.0, 102.8, 102.7, 102.6, 102.3, 85.8, 85.6, 84.3, 82.3, 82.2, 82.1, 82.0, 81.8, 73.9 – 72.7, 63.2, 60.6 – 60.4, 58.6, 54.2, 43.6;

IR ( $\text{cm}^{-1}$ , KBr): 3373, 2927, 1636, 1508, 1413, 1368, 1246, 1205, 1156, 1079, 1029, 946, 848, 754, 703, 581, 530;

MS (ESI):  $m/z$  1368.5 ( $[\text{M}+\text{H}]^+$ ); HRMS (ESI): Calcd. For  $\text{C}_{59}\text{H}_{86}\text{NO}_{35}^+$  1368.4902, found 1368.4938.



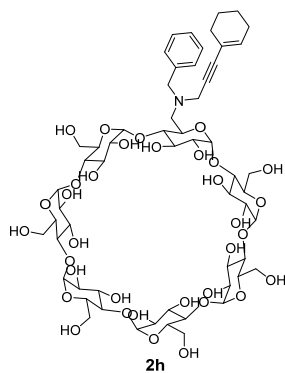
White solid; 52% yield;

**<sup>1</sup>H NMR** (600 MHz, *d*<sup>6</sup>-DMSO):  $\delta$  7.33 – 7.24 (m, 4H, Ar-H), 7.21 (t, *J* = 7.0 Hz, 1H, Ar-H), 5.99 (t, *J* = 5.8 Hz, 1H, OH-2 or OH-3), 5.83 – 5.68 (m, 13H, OH-2, OH-3), 4.93 (d, *J* = 3.3 Hz, 1H, H-1), 4.84 (dd, *J* = 13.8, 3.6 Hz, 6H, H-1), 4.58 – 4.44 (m, 6H, OH-6), 3.82 – 3.28 (m, 43H, H-2, H-3, H-4, H-5, H-6a, H-6b, H-1', H-2'), 3.15 (d, *J* = 17.0 Hz, 1H, H-2'), 2.83 (d, *J* = 13.2 Hz, 1H, H-6a'), 2.76 (dd, *J* = 13.9, 5.9 Hz, 1H, H-6b'), 1.37 – 1.27 (m, 1H), 0.83 – 0.69 (m, 2H), 0.63 – 0.55 (m, 2H);

**<sup>13</sup>C NMR** (150 MHz, *d*<sup>6</sup>-DMSO):  $\delta$  139.6, 129.0, 128.6, 127.2, 102.8, 102.6, 102.5, 102.43, 102.36, 102.0, 88.9, 84.2, 82.1, 82.0, 81.9, 81.6, 81.5, 73.7 – 72.2, 70.8, 60.4 – 60.2, 57.9, 55.4, 42.9, 31.2, 8.64, 8.61;

**IR** (cm<sup>-1</sup>, KBr): 3374, 2929, 1636, 1409, 1369, 1331, 1250, 1203, 1156, 1032, 947, 863, 754, 701, 581, 531;

**MS** (ESI): *m/z* 1302.5 ([M+H]<sup>+</sup>); **HRMS** (ESI): Calcd. For C<sub>55</sub>H<sub>83</sub>NO<sub>34</sub><sup>+</sup> 1302.4796, found 1302.4858.



White solid; 26% yield;

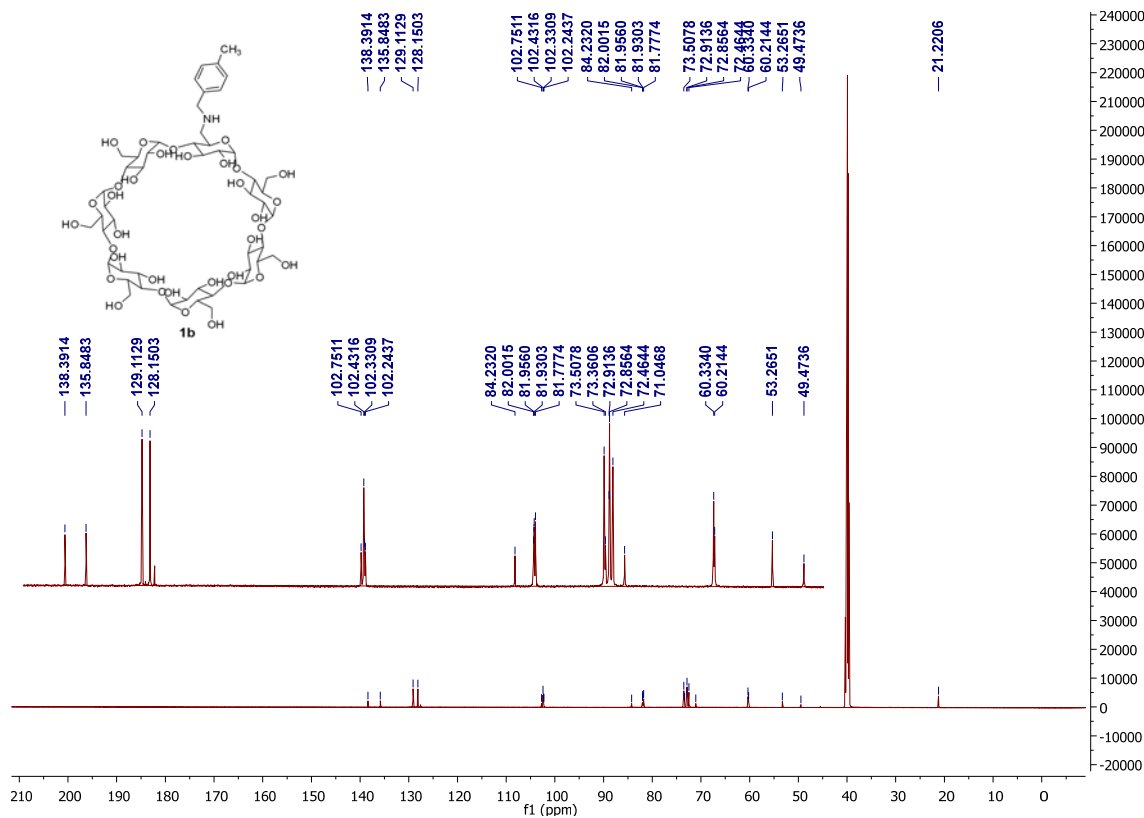
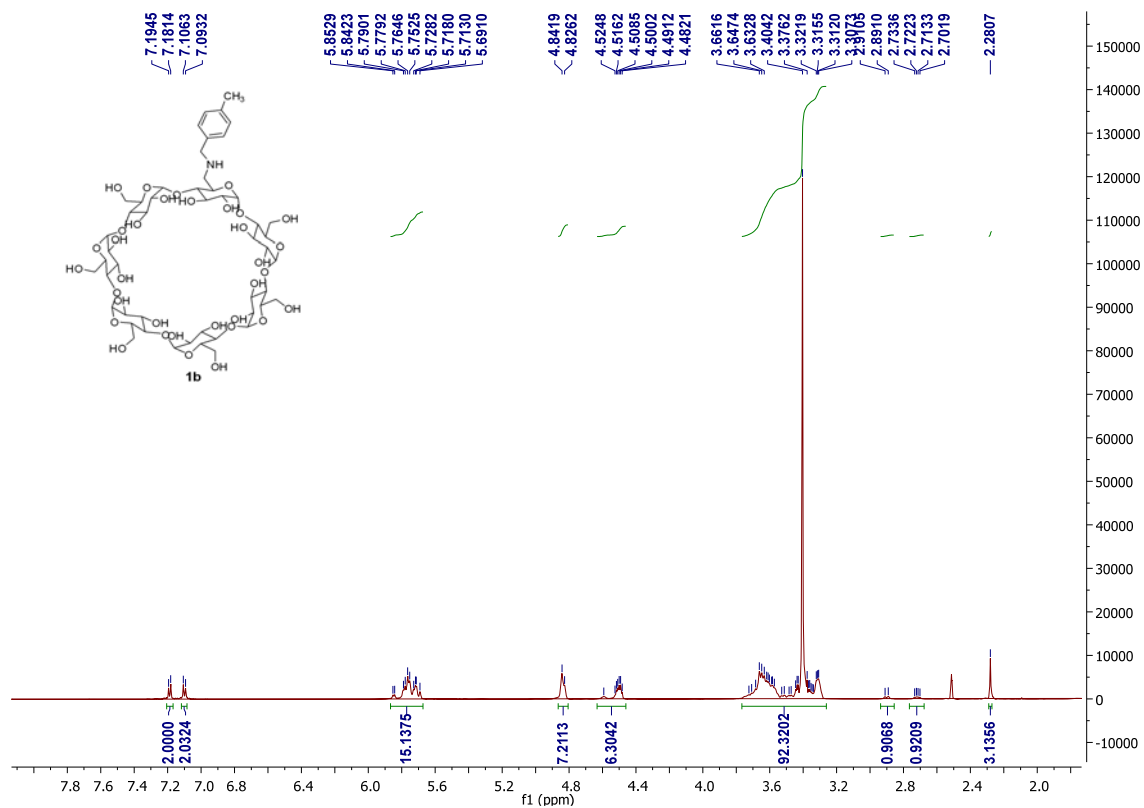
**<sup>1</sup>H NMR** (600 MHz, d<sup>6</sup>-DMSO):  $\delta$  7.31 (d,  $J = 4.3$  Hz, 4H, Ar-H), 7.26 – 7.20 (m, 1H, Ar-H), 6.04 (s, 1H, vinyl **CH**), 6.00 (d,  $J = 6.3$  Hz, 1H, OH-2 or OH-3), 5.83-5.70 (m, 13H, OH-2, OH-3), 4.93 – 4.80 (m, 7H, H-1), 4.57 – 4.46 (m, 6H, OH-6), 3.73 – 3.29 (m, 44H, H-2, H-3, H-4, H-5, H-6a, H-6b, H-1', H-2'), 2.92 (d,  $J = 13.4$  Hz, 1H, H-6a'), 2.78 (dd,  $J = 13.6, 6.3$  Hz, 1H, H-6b'), 2.09 (d,  $J = 10.9$  Hz, 4H, allyl **CH<sub>2</sub>**), 1.58 (ddd,  $J = 10.9, 9.0, 5.4$  Hz, 4H, **-CH<sub>2</sub>CH<sub>2</sub>-**);

**<sup>13</sup>C NMR** (150 MHz, d<sup>6</sup>-DMSO):  $\delta$  139.7, 134.3, 129.3, 128.8, 127.5, 120.8, 103.0, 102.8, 102.7, 102.6, 102.3, 87.3, 84.7, 83.4, 82.3, 82.1, 81.9, 81.7, 74.0 – 72.4, 60.6 – 60.4, 59.1, 55.6, 55.3, 43.9, 29.8, 25.7, 22.6, 21.8;

**IR** (cm<sup>-1</sup>, KBr): 3382, 2927, 1637, 1419, 1369, 1243, 1156, 1079, 1029, 946, 847, 755, 704, 581, 531;

**MS** (ESI):  $m/z$  1342.5([M+H]<sup>+</sup>); **HRMS** (ESI): Calcd. For C<sub>58</sub>H<sub>88</sub>NO<sub>34</sub><sup>+</sup> 1342.5109, found 1342.5128.

$^1\text{H}$  NMR (600 MHz,  $d^6$ -DMSO) and  $^{13}\text{C}$  NMR (150 MHz,  $d^6$ -DMSO) spectra of **1b**

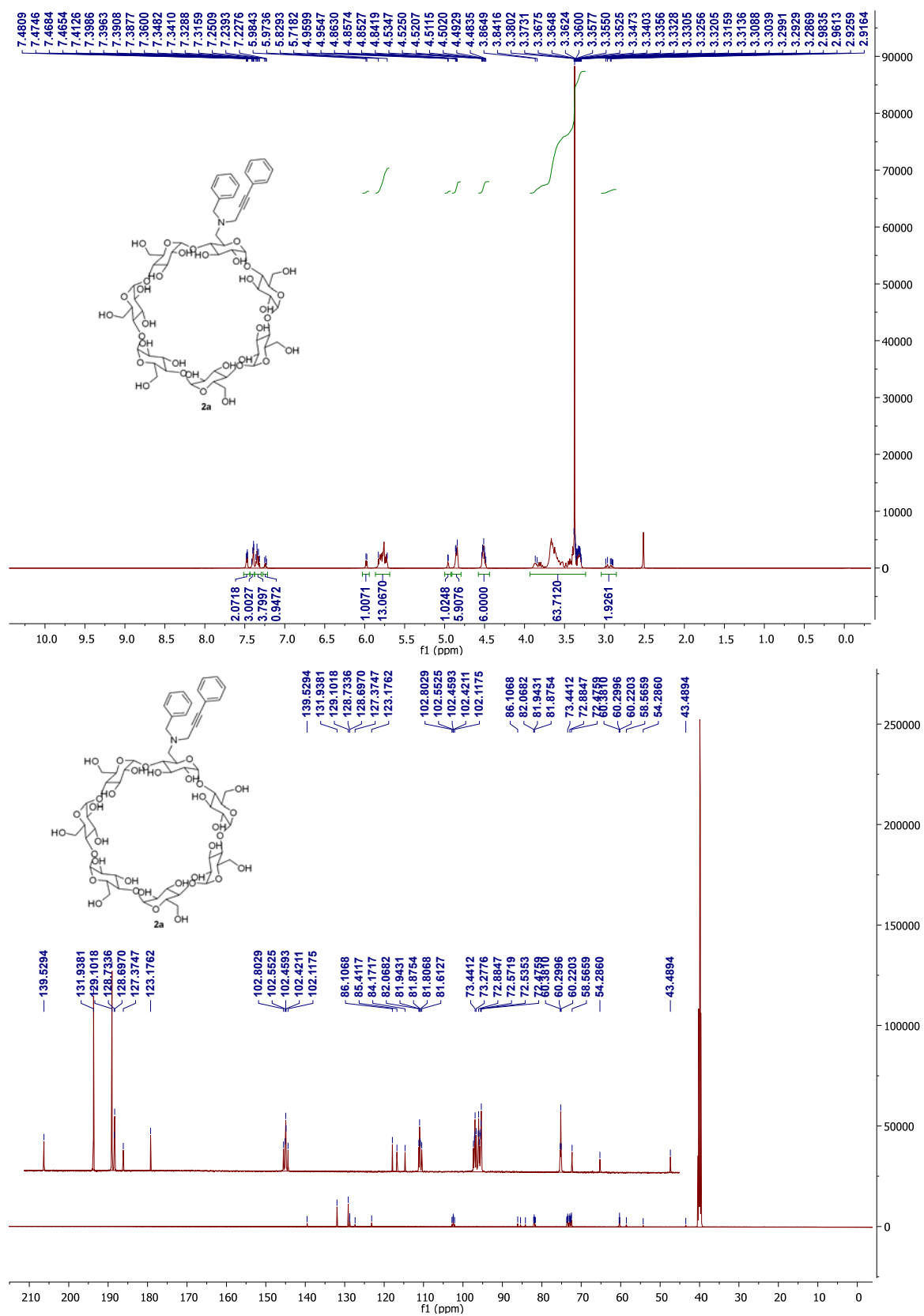




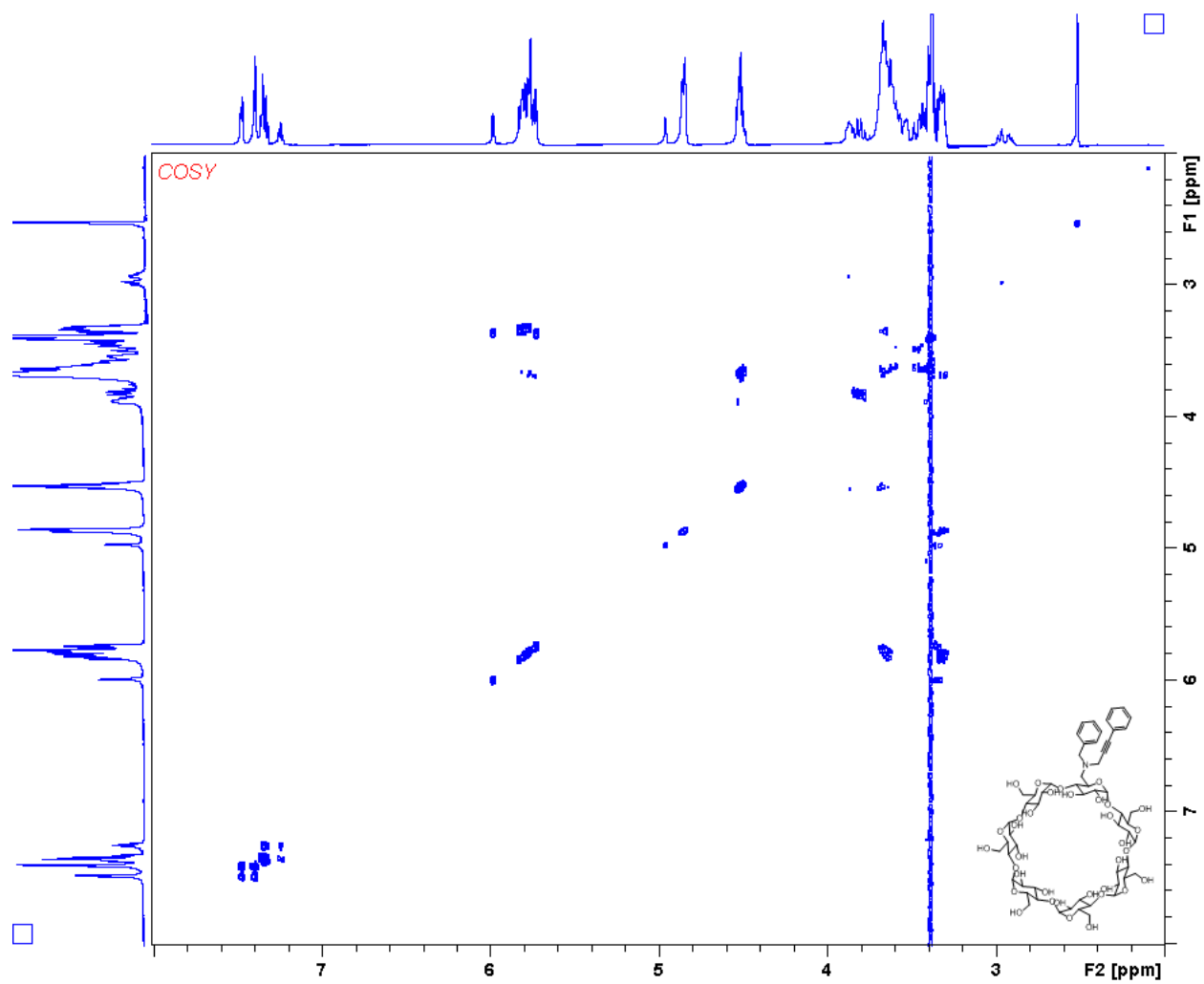




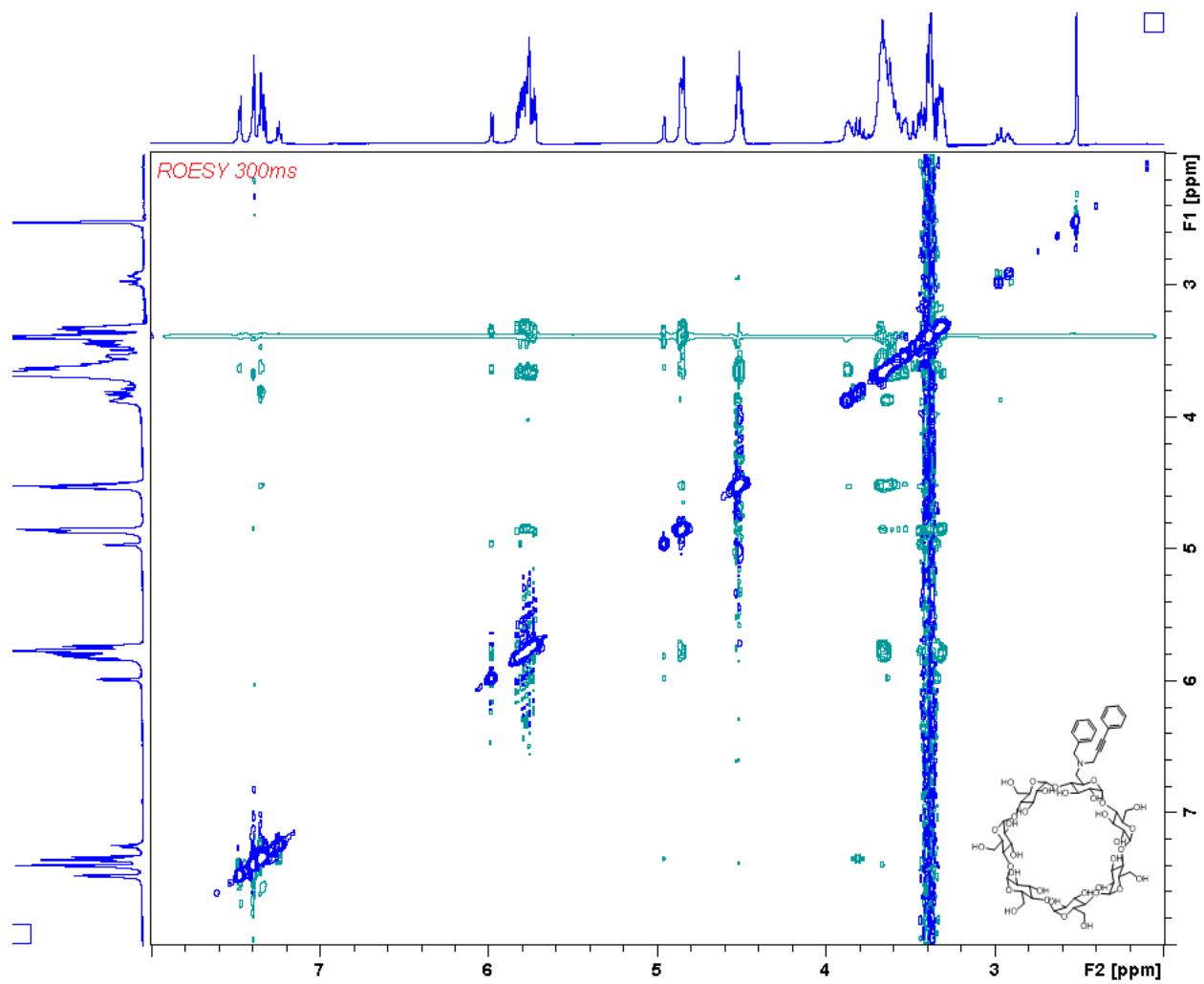
$^1\text{H}$  NMR (600 MHz,  $d^6$ -DMSO) and  $^{13}\text{C}$  NMR (150 MHz,  $d^6$ -DMSO) spectra of **2a**



COSY (600 MHz, d<sup>6</sup>-DMSO) spectrum of **2a**

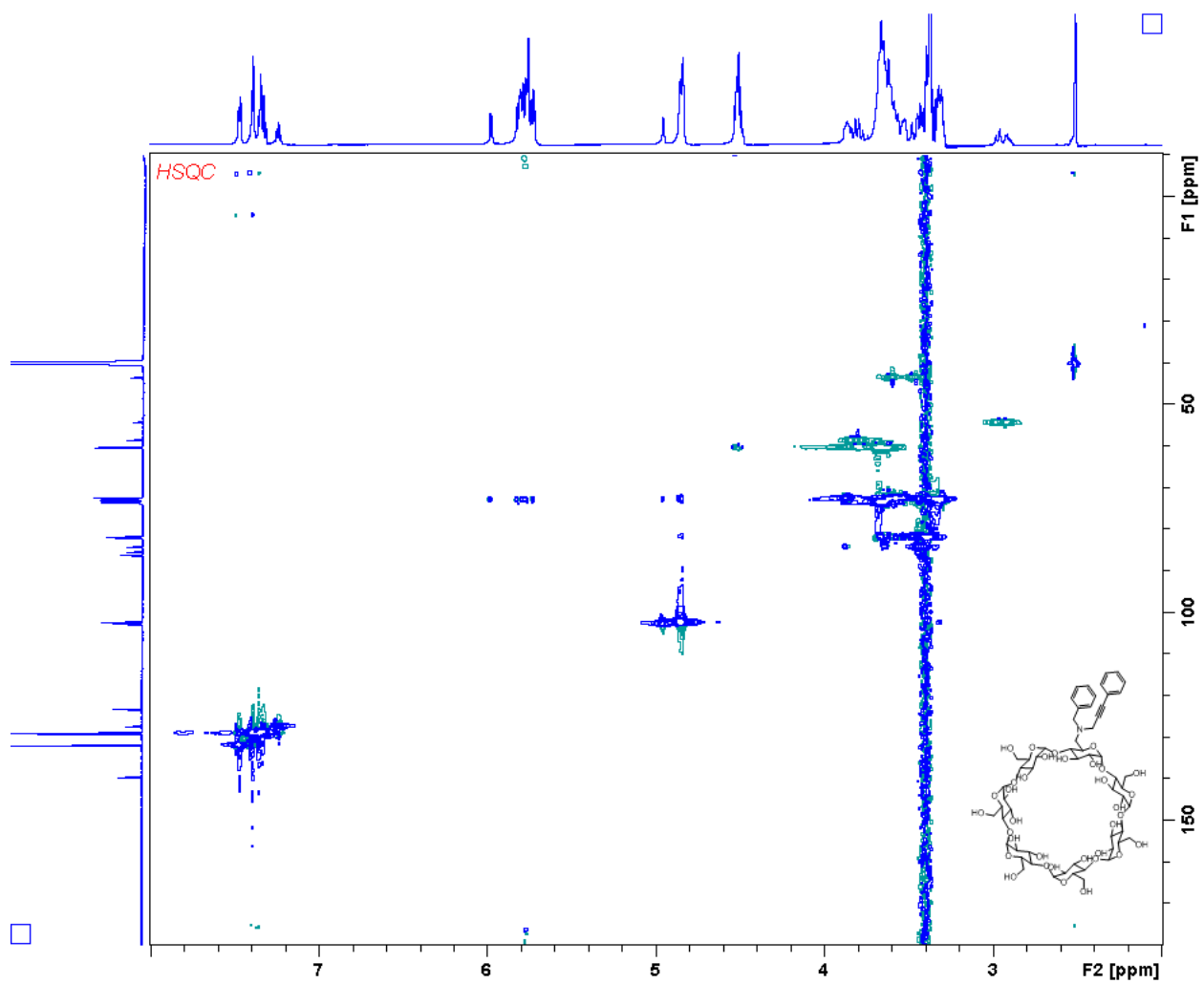


ROESY (600 MHz, d<sup>6</sup>-DMSO) spectrum (300ms) of **2a**

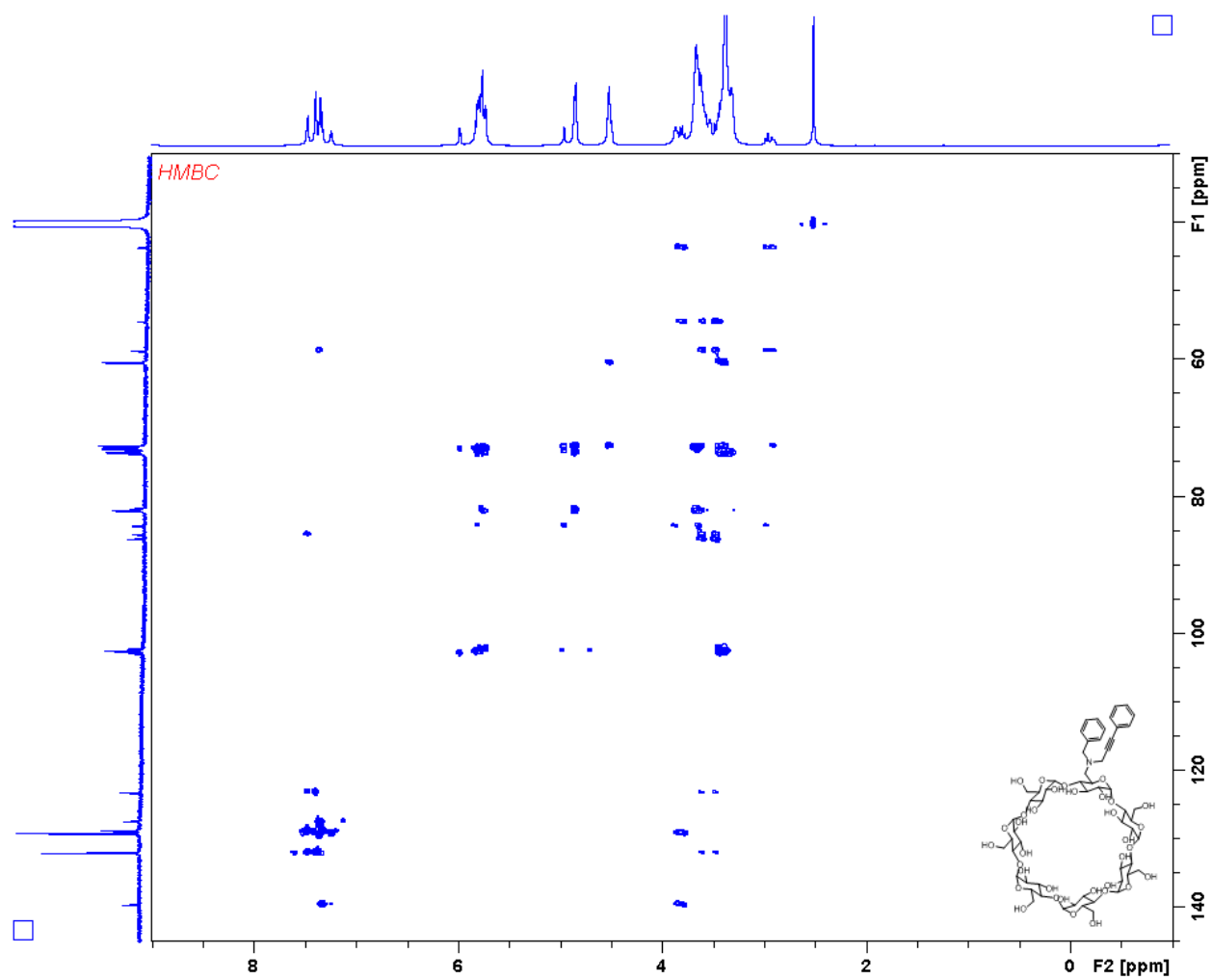




HSQC (600 MHz, d<sup>6</sup>-DMSO) spectrum of **2a**

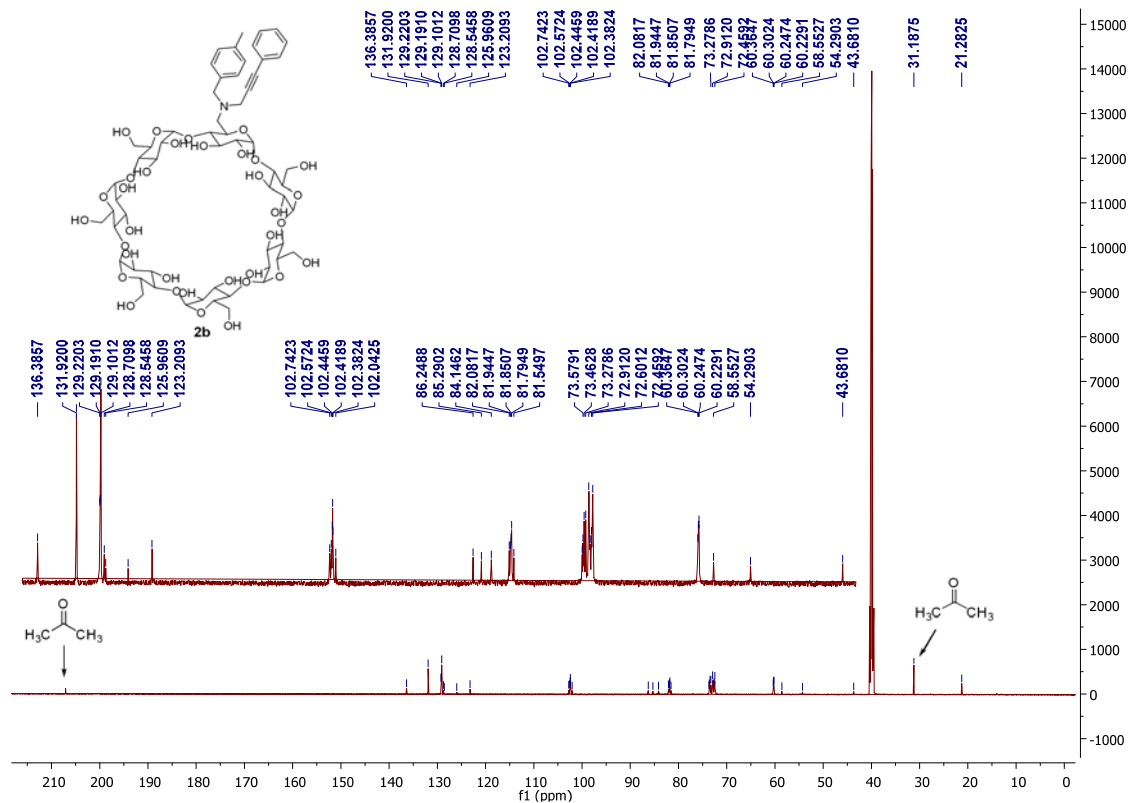
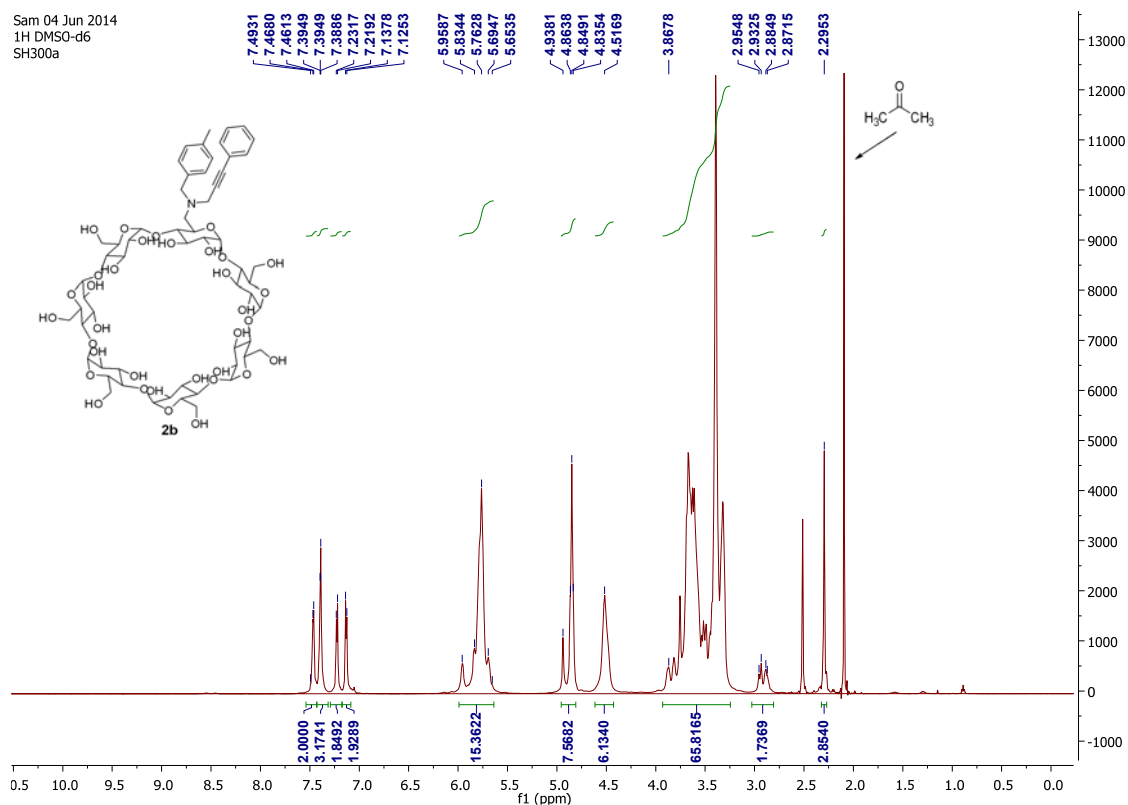


HMBC (600 MHz,  $d^6$ -DMSO) spectrum of **2a**



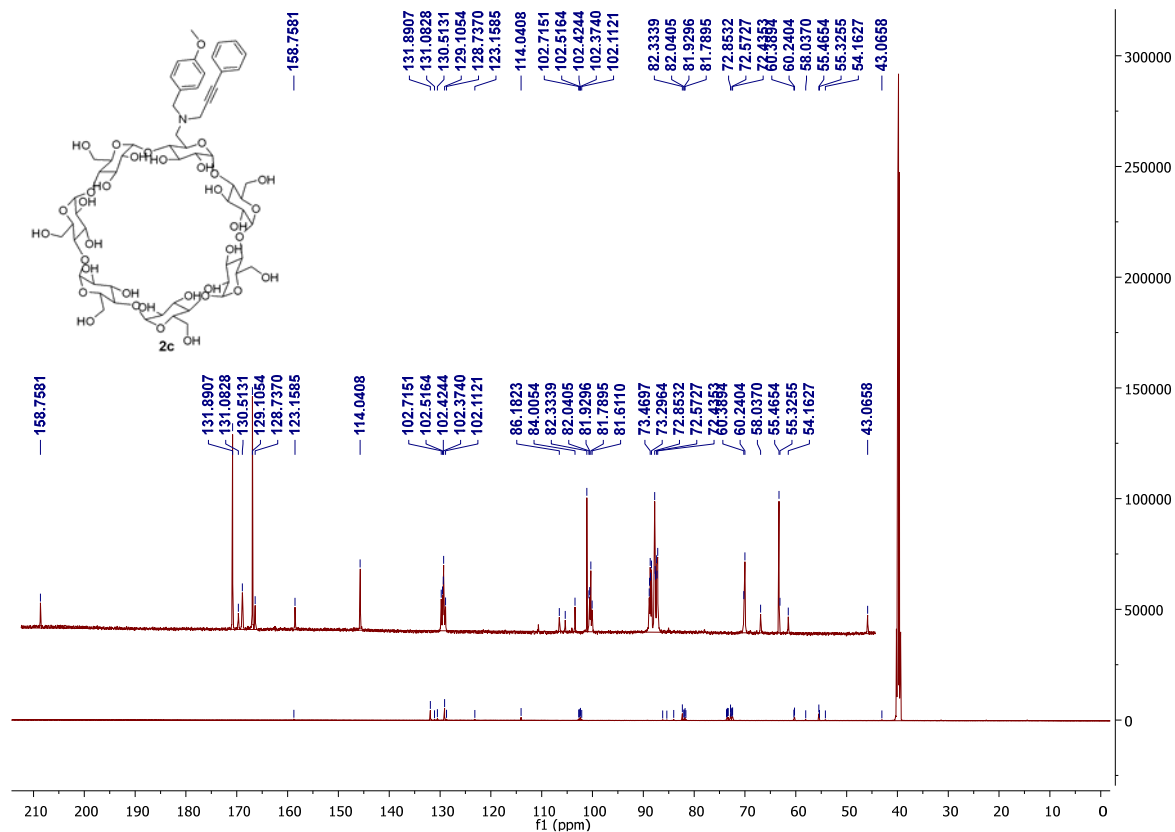
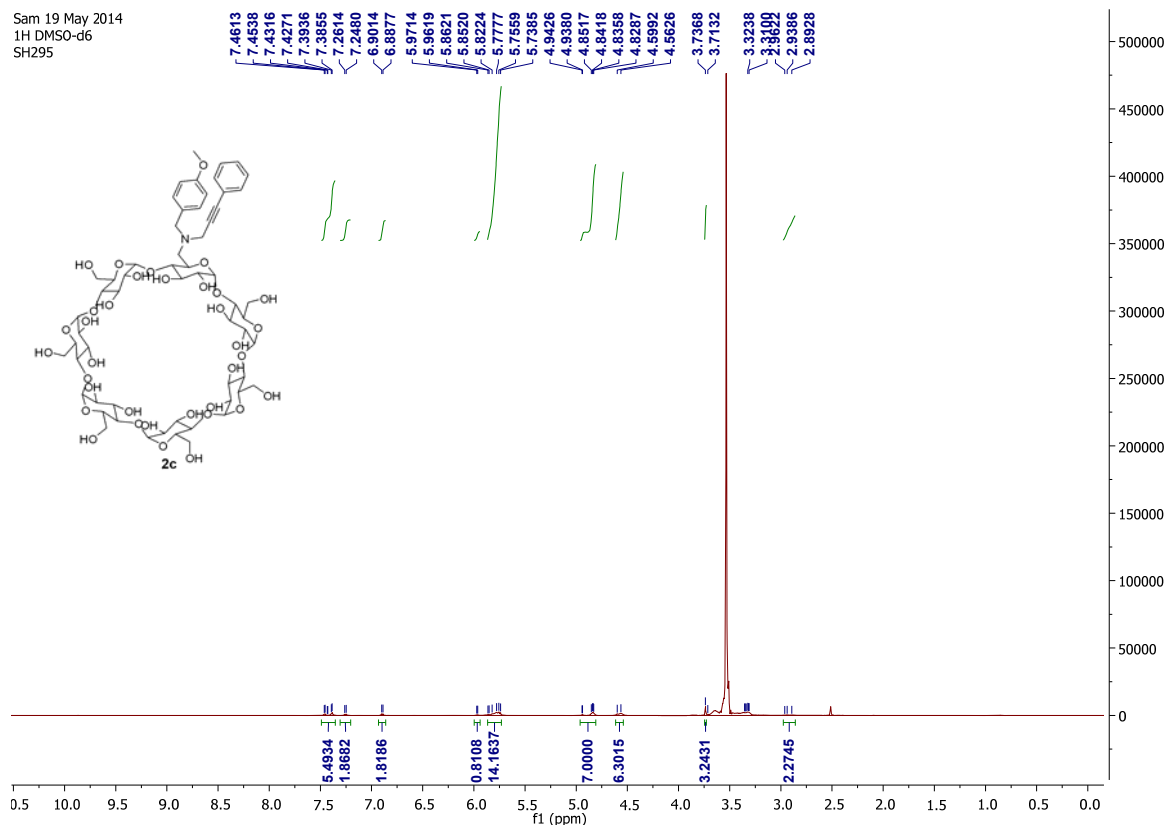
<sup>1</sup>H NMR (600 MHz, d<sup>6</sup>-DMSO) and <sup>13</sup>C NMR (150 MHz, d<sup>6</sup>-DMSO) spectra of **2b**

Sam 04 Jun 2014  
1H DMSO-d6  
SH300a



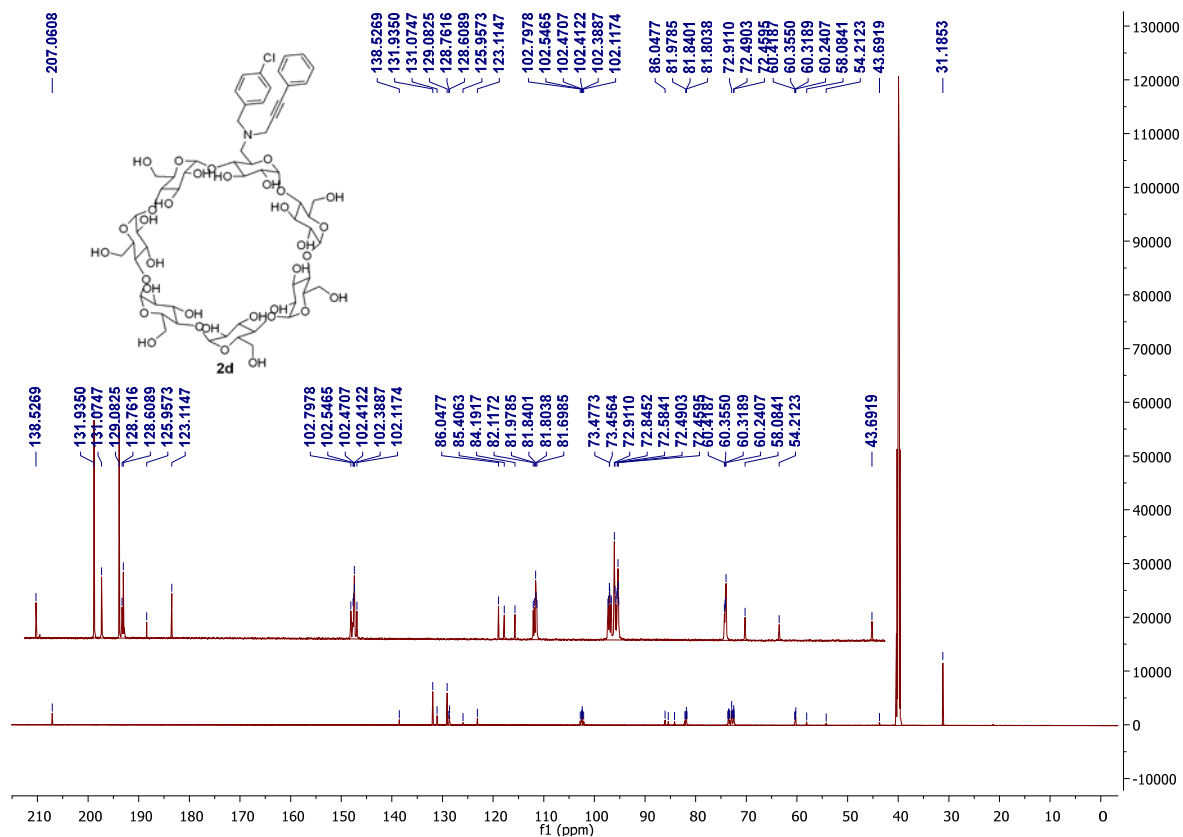
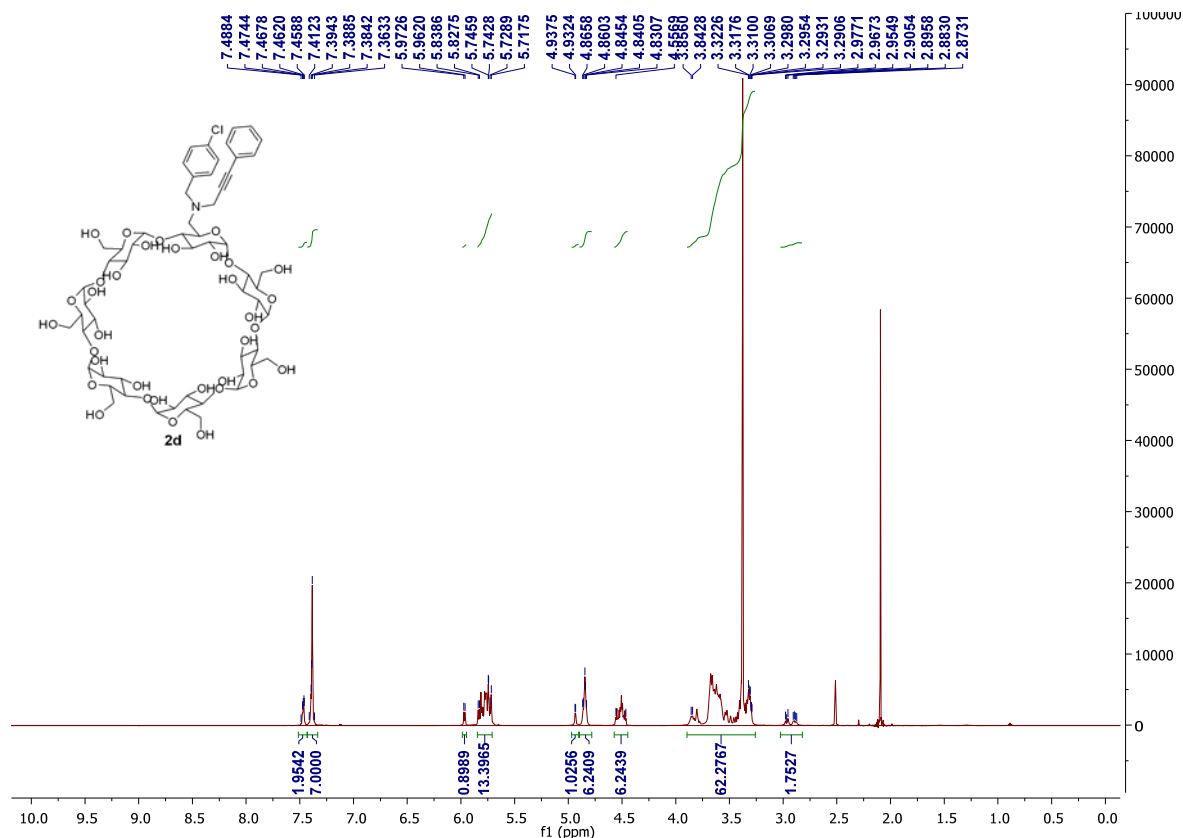
$^1\text{H}$  NMR (600 MHz,  $d^6$ -DMSO) and  $^{13}\text{C}$  NMR (150 MHz,  $d^6$ -DMSO) spectra of **2c**

Sam 19 May 2014  
 $^1\text{H}$  DMSO- $d_6$   
 SH295

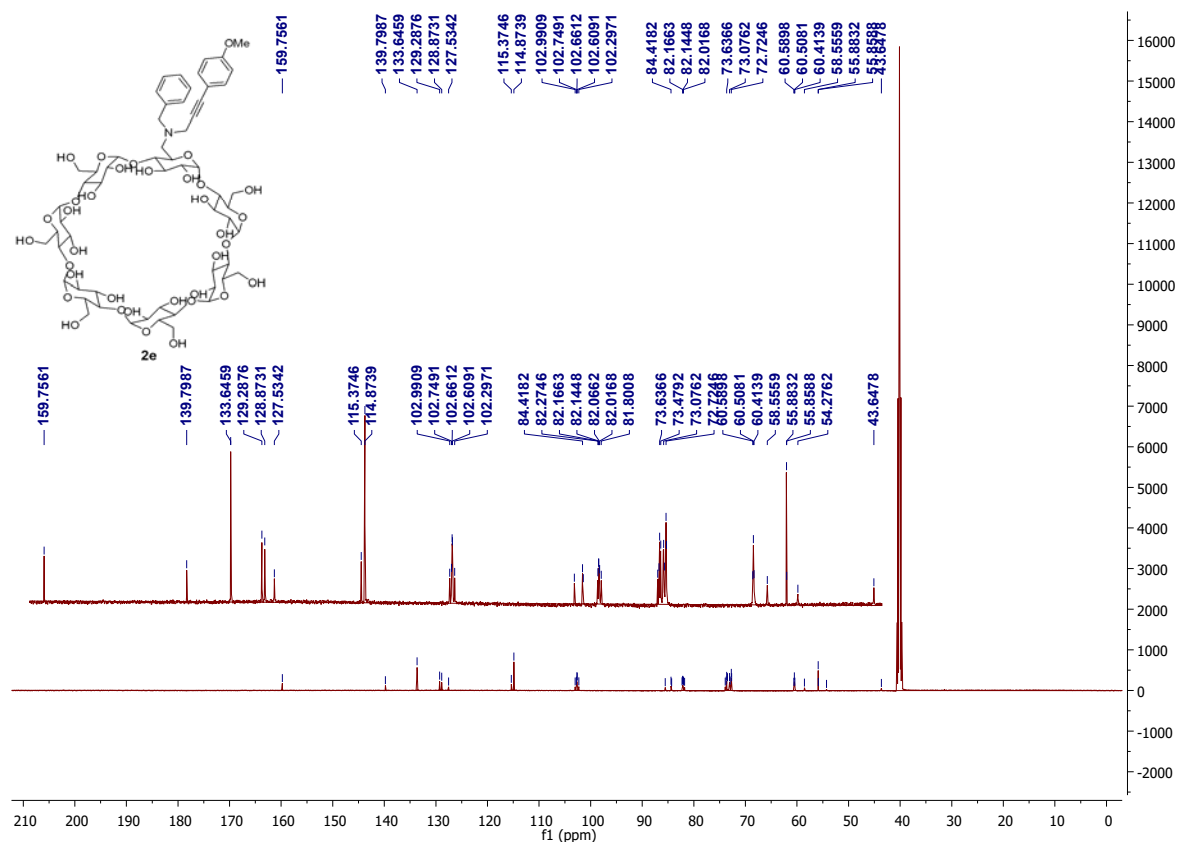
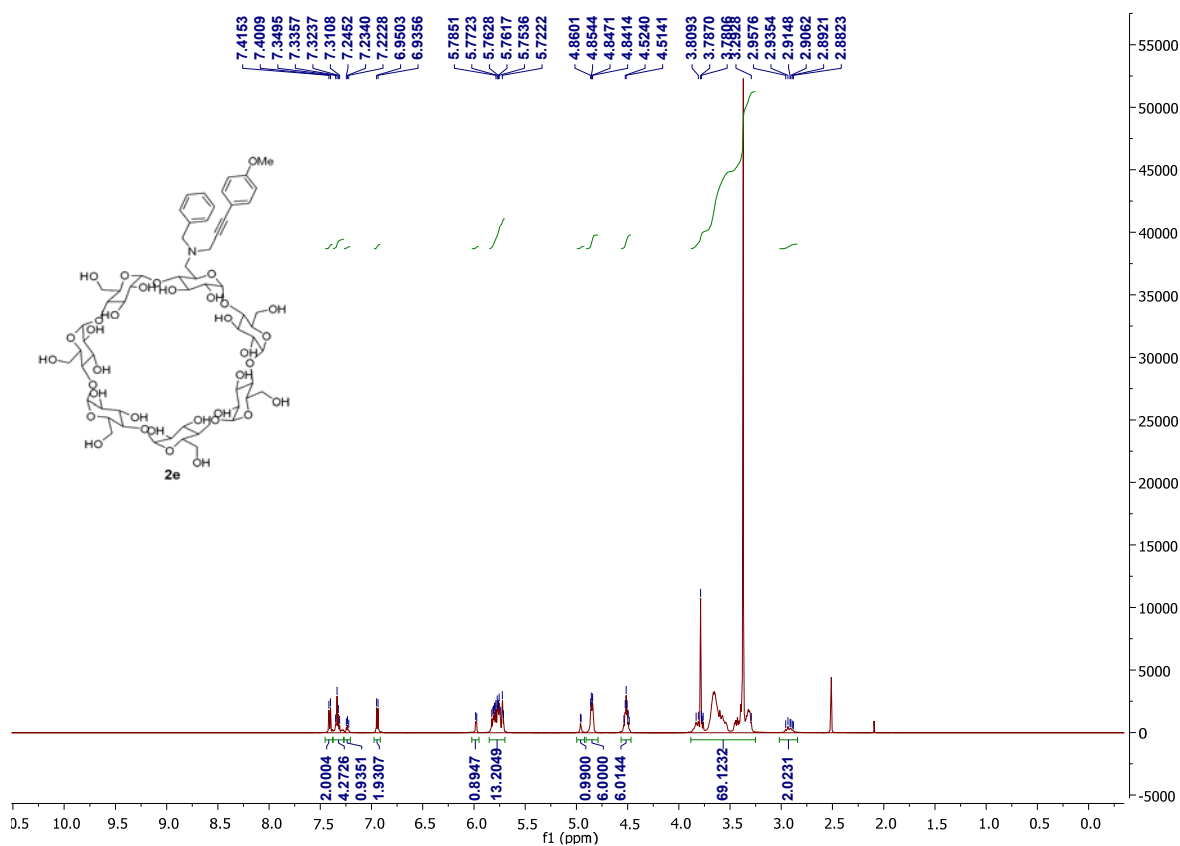




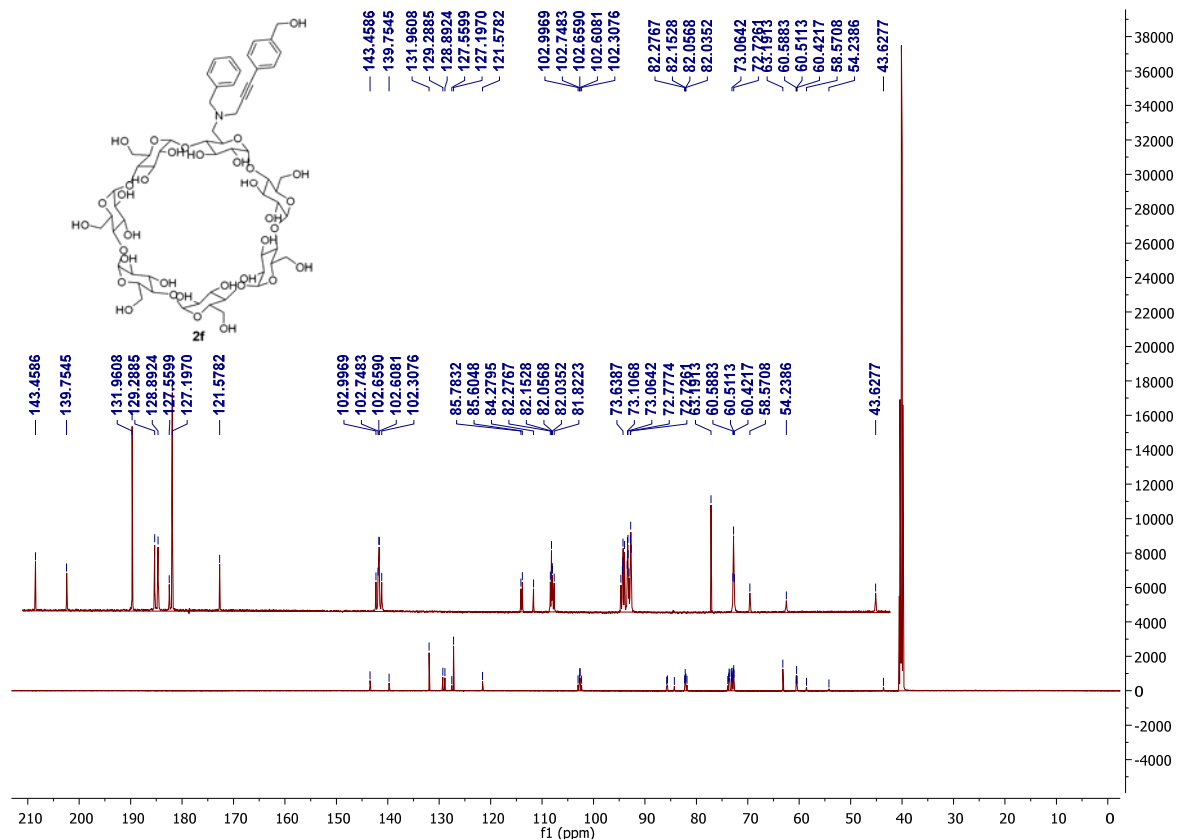
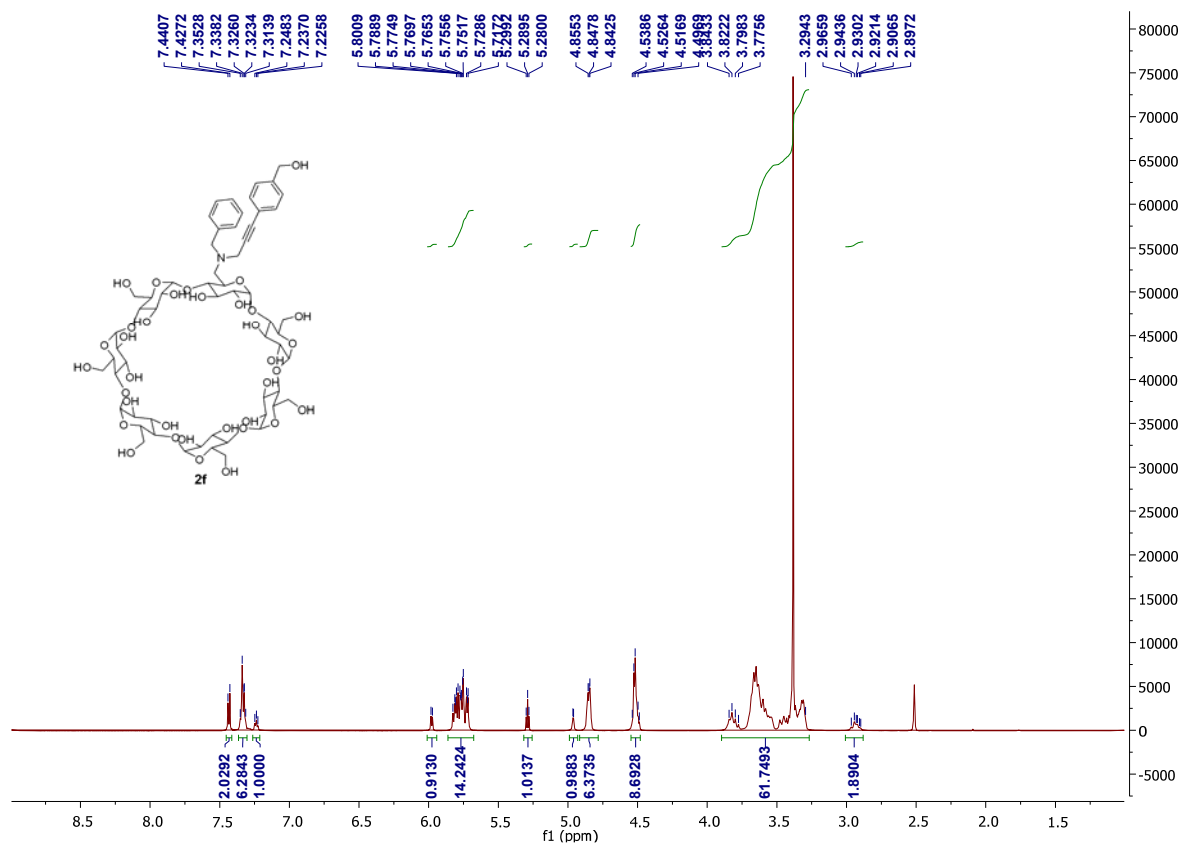
$^1\text{H}$  NMR (600 MHz,  $d^6$ -DMSO) and  $^{13}\text{C}$  NMR (150 MHz,  $d^6$ -DMSO) spectra of **2d**



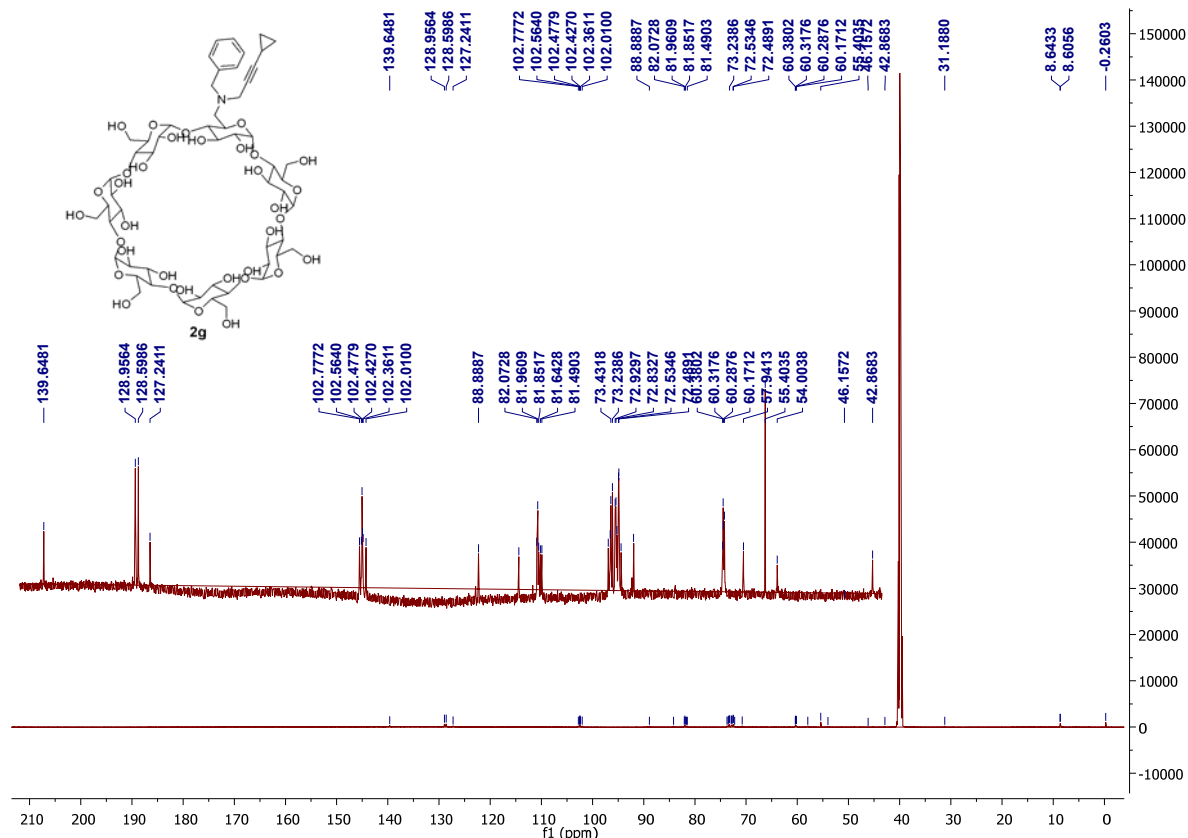
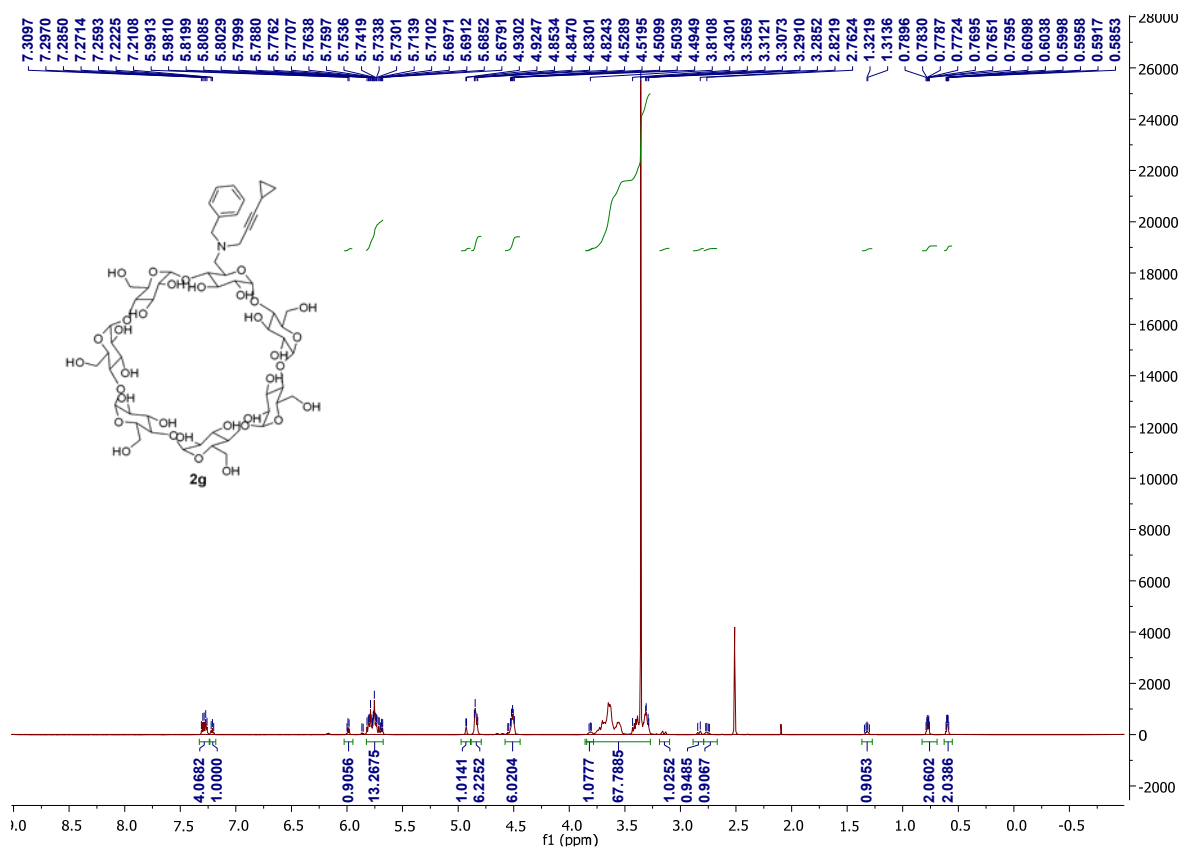
$^1\text{H}$  NMR (600 MHz,  $d_6$ -DMSO) and  $^{13}\text{C}$  NMR (150 MHz,  $d_6$ -DMSO) spectra of **2e**



$^1\text{H}$  NMR (600 MHz,  $d_6$ -DMSO) and  $^{13}\text{C}$  NMR (150 MHz,  $d_6$ -DMSO) spectra of **2f**



$^1\text{H}$  NMR (600 MHz,  $d^6$ -DMSO) and  $^{13}\text{C}$  NMR (150 MHz,  $d^6$ -DMSO) spectra of **2g**



$^1\text{H}$  NMR (600 MHz,  $d_6$ -DMSO) and  $^{13}\text{C}$  NMR (150 MHz,  $d_6$ -DMSO) spectra of **2h**

