Tether-directed Selective Synthesis of Fulleropyrrolidine Bisadducts

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¹H NMR, ¹³C NMR, 2D NMR, MALDI-MS data and/or selected spectra for compounds 1-19:

¹H NMR (400 MHz acetone-d₆/CS₂ 1:2) of bisadduct **6**: δ 2.44 (s, 6H), 4.12 (d, 2H), 4.53 (s, 2H), 4.87 (d, 2H), 5.11 (d, 2H), 5.20 (d, 2H), 6.79 (d, 4H), 7.25 (s, 4H), 7.30 (d, 4H); ¹³C NMR (100 MHz acetone-d₆/CS₂ 1:2) of bisadduct **6**: δ 40.2, 67.5, 69.1, 70.4, 75.3, 84.5, 115.6, 127.4 (4C), 129.0, 137.4, 137.5 (2C), 137.6, 140.2, 141.2, 141.8, 141.9, 142.1, 143.2, 144.3, 144.8, 145.1, 145.7, 145.8, 145.9, 146.0 (2C), 148.2, 148.8, 148.9, 149.0, 149.5, 149.6, 150.3, 153.8, 156.0, 157.9, 158.2 (2C); MALDI-MS: m/z 1121.1 (MH⁺).

¹H NMR (400 MHz acetone-d₆/CS₂ 1:2) of bisadduct **7**: δ 2.38 (s, 3H), 2.40 (s, 3H), 3.78 (d, 1H), 3.80 (d, 1H), 4.36 (s, 1H), 4.39 (s, 1H), 4.40 (d, 1H), 4.48 (d, 1H), 4.56 (d, 1H), 5.10 (d, 1H), 5.29 (d, 1H), 5.40 (d, 1H), 6.95 (d, 2H), 7.09 (m, 2H), 7.15 (m, 2H), 7.36 (d, 2H), 7.42 (d, 2H), 7.60 (d, 2H); ¹³C NMR (100 MHz acetone-d₆/CS₂ 1:2) of bisadduct **7**: δ 39.7, 40.4, 68.7, 68.8, 69.1, 69.9 (2C), 75.1, 75.8, 76.4, 83.1, 83.2, 115.3, 120.8, 126.1, 129.0, 129.6, 129.7, 129.8, 130.8, 131.6, 132.1, 135.6, 135.9, 136.6, 137.1, 138.6 (2C), 139.8 (2C), 140.1, 140.2, 140.9, 141.4, 141.7, 141.8, 142.0, 142.1, 142.2, 142.3, 142.8, 143.0, 143.1, 143.7, 143.9, 144.2, 144.4, 145.0, 145.1, 145.2 (2C), 145.3, 145.4, 145.7, 145.8 (2C), 145.9, 146.3, 146.5, 147.0, 147.1, 147.6, 147.7, 147.8, 148.0, 148.1 (2C), 148.2, 148.4, 148.7, 148.8, 149.3, 149.5, 150.4, 151.1, 151.7, 153.3, 153.4, 153.8 (2C), 154.6, 158.8 (2C), 159.0 (3C), 160.0, 160.8; MALDI-MS: m/z 1120.7 (M⁺).

¹H NMR (400 MHz acetone-d₆/CS₂ 1:2) of bisadduct **8**: δ 2.44 (s, 3H), 2.72 (s, 3H), 3.90 (d, 1H), 4.01 (d, 1H), 4.49 (s, 1H), 4.50 (d, 1H), 4.53 (s, 1H), 4.69 (d, 1H), 4.83 (d, 1H), 5.18 (s, 2H), 5.78 (d, 1H), 6.75 (d, 2H), 7.06 (d, 2H), 7.10 (m, 1H), 7.28 (m, 1H), 7.42 (m, 2H), 7.54 (m, 1H), 7.59 (m, 2H), 7.81 (m, 1H); ¹³C NMR (100 MHz acetone-d₆/CS₂ 1:2) of bisadduct **8**: δ 40.3, 40.7, 65.9, 67.9, 69.1, 69.4, 69.9, 70.0, 76.6, 76.7, 81.4, 82.5, 112.0, 115.3, 118.1, 129.2, 129.6, 130.4, 130.6, 131.3, 132.8 (2C), 133.5 (2C), 134.1 (2C), 135.6, 136.4, 136.6, 137.7, 138.2 (2C), 139.3, 140.9, 141.4, 141.8, 142.1, 142.2, 142.6, 142.9 (2C), 143.1, 143.2, 143.3, 143.9, 144.2, 144.3, 144.8,

145.2, 145.3, 145.4 (2C), 145.5, 145.6, 145.8, 145.9, 146.0, 146.2, 146.6, 146.7, 146.8, 147.6, 147.8, 147.9, 148.1, 148.2, 148.3, 148.4, 148.6, 148.7 (2C), 148.9, 149.1, 149.6, 149.8, 150.6, 151.4, 152.4, 153.2, 154.2, 154.3, 154.8, 159.5 (2C), 159.7, 160.0 (2C), 161.1; MALDI-MS: m/z 1119.8 (M^+).

^1H NMR (400 MHz acetone- d_6 /CS $_2$ 1:2) of bisadduct **9**: δ 2.71 (s, 3H), 4.15 (d, 2H), 4.59 (s, 2H), 4.72 (d, 2H), 4.80 (d, 2H), 4.84 (d, 2H), 6.59 (d, 2H), 6.61 (d, 2H), 7.00 (m, 2H), 7.09 (m, 2H), 7.19 (m, 2H), 7.38-7.43 (m, 2H); ^{13}C NMR (100 MHz acetone- d_6 /CS $_2$ 1:2) of bisadduct **9**: δ 40.5, 68.4, 69.6, 70.4, 77.3, 82.8, 113.5, 116.1, 126.3, 129.2, 129.8, 129.9, 130.0 (2C), 131.4, 132.2, 136.3, 137.1, 137.9, 140.2, 142.1, 142.2, 142.3, 142.4, 143.1, 144.3, 144.7, 145.0, 145.6, 145.9, 146.0, 146.1, 148.3, 149.0, 149.2, 149.4, 149.9, 150.0, 150.8, 154.9, 155.8, 158.3, 158.5, 159.8 (2C); MALDI-MS: m/z 1120.4 (M^+).

^1H NMR (400 MHz acetone- d_6 /CS $_2$ 1:2) of bisadduct **10**: δ 2.73 (s, 3H), 2.79 (s, 3H), 3.91 (d, 1H), 4.29 (d, 1H), 4.30 (s, 1H), 4.50 (d, 1H), 4.62 (d, 1H), 4.75 (s, 1H), 4.88 (d, 1H), 4.90 (d, 1H), 5.04 (d, 1H), 5.10 (d, 1H), 6.62 (d, 1H), 6.81 (d, 1H), 7.01 (m, 1H), 7.09 (m, 1H), 7.21-7.30 (m, 5H), 7.40 (d, 1H), 7.49 (d, 1H), 7.62 (d, 1H); ^{13}C NMR (100 MHz acetone- d_6 /CS $_2$ 1:2) of bisadduct **10**: δ 40.2, 40.7, 68.3, 69.0, 69.2, 70.8, 71.3, 71.9, 77.1, 78.2, 81.1, 84.8, 115.4, 116.8, 126.4, 128.3 (2C), 128.7 (2C), 129.3, 130.0 (2C), 130.1, 130.7, 130.8, 130.9, 131.8, 135.0, 135.1, 133.9, 137.8, 138.3, 138.5 (2C), 139.2, 140.1, 141.4, 141.6, 142.0, 142.1, 142.3, 142.5, 142.9, 143.0, 143.7, 144.3, 144.5, 144.6, 144.7, 144.8, 144.9, 145.4, 145.5, 145.7, 145.8, 145.9, 146.0 (3C), 146.1 (3C), 146.3, 147.2, 148.7, 148.8, 148.9, 149.0, 149.2, 149.4, 149.6, 149.7, 149.9, 150.1, 150.2, 150.3, 154.4, 154.9, 155.4, 155.8, 157.7, 157.8, 158.5, 158.7, 160.1 (2C), 162.1 (2C); MALDI-MS: m/z 1120.3 (M^+).

^1H NMR (400 MHz acetone- d_6 /CS $_2$ 1:2) of bisadduct **11**: δ 2.52 (s, 6H), 4.10 (d, 2H), 4.50 (s, 2H), 4.79 (d, 2H), 4.99 (s, 4H), 6.56 (d, 4H), 7.02 (m, 2H), 7.11 (m, 2H), 7.19-7.23 (m, 3H), 7.32 (s, 1H); MALDI-MS: m/z 1121.2 (M^+). ^1H NMR (400 MHz acetone- d_6 /CS $_2$ 1:2) of bisadduct **12**: δ 2.35 (s, 3H), 2.41 (s, 3H), 3.78 (d, 1H), 3.81 (d, 1H), 4.30 (s, 1H), 4.34 (s, 1H), 4.42 (d, 1H), 4.51 (d, 1H), 4.75 (d, 1H), 4.92 (d, 1H),

5.14 (d, 1H), 5.35 (d, 1H), 6.62 (d, 2H), 6.82 (m, 2H), 6.94 (m, 2H), 7.20 (s, 1H), 7.36-7.42 (m, 3H), 7.80 (s, 2H); MALDI-MS: m/z 1121.1 (MH^+). 1H NMR (400 MHz acetone- d_6 /CS $_2$ 1:2) of bisadduct **13**: δ 2.35 (s, 3H), 2.41 (s, 3H), 3.89 (d, 1H), 4.24 (d, 1H), 4.29 (s, 1H), 4.65 (s, 1H), 4.70 (d, 1H), 4.86 (d, 1H), 4.90 (d, 1H), 4.98 (d, 1H), 5.00 (s, 1H), 5.06 (d, 1H), 6.59 (m, 2H), 6.80 (m, 2H), 6.91 (s, 1H), 7.14 (m, 2H), 7.28-7.35 (m, 3H), 7.84 (m, 2H); MALDI-MS: m/z 1120.8 (M^+).

1H NMR (400 MHz, CS $_2$ /acetone- d_6) of **14**: δ 2.83 (s, 3H), 2.92 (s, 3H), 4.06 (d, 1H), 4.30 (d, 1H), 4.70 (s, 1H), 4.82 (d, 1H), 5.09 (s, 1H), 5.15 (d, 1H), 5.20 (d, 1H), 5.26 (m, 3H), 6.52 (d, 1H), 6.67 (d, 1H), 6.97-7.06 (m, 6H), 7.12 (d, 1H), 7.18-7.24 (m, 4H), 7.48 (d, 1H), 7.64 (d, 1H), 8.05 (d, 1H); ^{13}C NMR (100 MHz, CS $_2$ /acetone- d_6) of **14**: δ 40.2, 40.4, 67.7, 67.9, 68.2, 68.3, 70.5 (2C), 76.7, 77.2, 82.7, 82.9, 126.1, 126.8, 16.9, 127.3, 128.2, 128.9, 129.6, 129.7, 130.2, 130.3, 130.6, 130.7, 131.2, 133.8, 134.5, 134.8, 134.9, 136.8 (2C), 136.9, 138.9 (2C), 139.1, 139.2 (2C), 140.2, 140.3, 140.8, 141.3, 141.8, 141.9 (2C), 142.0, 142.1, 142.3, 142.8, 142.9, 143.0, 143.2, 143.4, 143.6, 144.0, 144.1, 144.3, 144.5, 144.6, 144.7, 145.1, 145.3, 145.7, 145.8, 145.9, 146.0, 146.1, 146.2, 146.3, 146.5, 146.6, 146.7, 146.9 (2C), 147.0, 147.2, 147.5, 147.6, 147.8, 148.5, 148.7, 149.0, 150.1, 151.9, 152.4, 152.8, 152.9, 154.2, 155.1, 157.8 (2C), 158.2 (2C), 158.4, 158.5, MALDI-MS: m/z 1120.1 (M^+). 1H NMR (400 MHz, CS $_2$ /acetone- d_6) of **15**: δ 2.81 (s, 3H), 2.96 (s, 3H), 4.30 (d, 1H), 4.40 (d, 1H), 4.79 (d, 1H), 4.83 (s, 1H), 4.90 (d, 1H), 5.00 (s, 1H), 5.10-5.18 (m, 3H), 5.32 (d, 1H), 6.25 (d, 1H), 6.70 (d, 1H), 6.80-6.91 (m, 4H), 6.94-7.03 (m, 4H), 7.35 (d, 1H), 7.40 (d, 1H), 7.52 (d, 1H), 7.59 (d, 1H), 7.64 (d, 1H), 7.84 (d, 1H); MALDI-MS: m/z 1120.1 (M^+).

1H NMR (400 MHz CDCl $_3$) of **17**: δ 2.76 (s, 3H), 4.22 (d, 1H), 4.84 (s, 1H), 4.92 (d, 1H), 5.11 (s, 2H), 5.23 (s, 2H), 6.93 (d, 2H), 6.99 (d, 2H), 7.32 (m, 2H), 7.43 (m, 2H), 7.65 (m, 2H), 7.75 (d, 2H), 9.81 (s, 1H); ^{13}C NMR (100 MHz CDCl $_3$) of **17**: δ 40.2, 68.2, 68.3, 68.9, 70.0, 83.1 (2C), 116.0, 128.7 (2C), 128.9, 129.4, 129.6, 130.3, 130.6, 132.0 (2C), 134.4, 134.8, 135.8, 135.9, 136.6, 136.9, 139.6, 140.0, 140.2, 140.3, 141.6, 141.8, 141.9, 142.0 (2C), 142.1 (2C), 142.2 (2C), 142.3, 142.6 (2C), 142.7, 142.8, 143.1, 143.2, 144.4, 144.5, 144.7, 144.8, 145.2 (2C), 145.3 (2C), 145.4, 145.5 (2C), 145.6 (2C), 145.7, 145.8, 146.0 (2C), 146.1, 146.2, 146.3 (2C), 146.4 (3C), 146.5,

146.8, 147.3 (2C), 153.2, 153.4, 154.1, 156.2, 158.6, 163.4, 189.8; MALDI-MS: m/z 1066.1 (M^+).

^1H NMR (400 MHz CDCl_3) of **18**: δ 2.80 (s, 3H), 4.25 (d, 1H), 4.90 (s, 1H), 5.00 (d, 1H), 5.05 (s, 2H), 5.18 (s, 2H), 6.95 (d, 2H), 7.05 (d, 2H), 7.10 (m, 1H), 7.34 (m, 3H), 7.49 (s, 1H), 7.66 (m, 1H), 7.72 (d, 2H), 9.79 (s, 1H); ^{13}C NMR (100 MHz CDCl_3) of **18**: δ 39.9, 69.1, 69.7, 69.9, 70.1, 77.6, 83.2, 115.5, 125.5, 126.8, 127.1, 127.3, 128.4, 128.9, 129.1, 129.3, 130.6, 131.8 (2C), 136.0, 136.1, 136.7, 136.8 (2C), 137.0, 137.7 (2C), 139.6, 140.1, 140.2, 140.3, 141.7, 141.8, 141.9, 142.1, 142.2, 142.3 (2C), 142.4 (2C), 142.5 (2C), 142.7 (3C), 142.8, 143.1, 143.3, 144.5, 144.6, 144.8, 144.9, 145.2, 145.3 (2C), 145.4 (2C), 145.5, 145.6, 145.7 (2C), 145.8, 145.9, 146.1 (2C), 146.2 (2C), 146.3 (2C), 146.4 (2C), 146.6, 146.8, 147.0, 147.4 (2C), 153.9, 154.3, 156.7, 159.0, 163.7, 189.2; MALDI-MS: m/z 1066.2 (M^+).

^1H NMR (400 MHz CDCl_3) of **19**: δ 2.73 (s, 3H), 4.23 (d, 1H), 4.85 (s, 1H), 4.93 (d, 1H), 5.02 (s, 2H), 5.16 (s, 2H), 6.92 (d, 2H), 7.00 (d, 2H), 7.08 (m, 1H), 7.40 (dd, 4H), 7.50 (dd, 4H), 7.51 (m, 1H), 7.52 (d, 2H), 9.87 (s, 1H); ^{13}C NMR (100 MHz CDCl_3) of **19**: δ 40.3, 69.8, 70.5, 70.8 (2C), 78.4, 83.9, 116.8, 127.5, 128.1 (2C), 128.2 (2C), 129.0 (2C), 129.1 (2C), 129.2, 129.9, 130.1, 131.4 (2C), 132.6 (2C), 136.5, 136.8, 136.9, 137.3, 137.6, 137.9, 140.5, 140.9, 141.1 (2C), 141.2, 141.4, 142.5, 142.7, 142.8, 142.9 (2C), 143.0, 143.1 (2C), 143.2 (2C), 143.3 (2C), 144.0, 144.1, 145.4, 145.6, 145.7, 146.1, 146.2 (3C), 146.3 (2C), 146.5, 146.6 (2C), 146.7, 146.8, 146.9 (2C), 147.0 (2C), 147.1, 147.2 (2C), 147.3, 147.5, 147.6, 147.9, 148.2, 154.8, 155.3, 157.6, 160.0, 164.6, 190.0; MALDI-MS: m/z 1145.1 (M^+).

Figure 1 ^1H NMR (CDCl_3) spectrum of bisaldehyde **2**

Figure 2 ^{13}C NMR (CDCl_3) spectrum of bisaldehyde **2**

Figure 3 ^{13}C NMR ($\text{CS}_2/\text{acetone}$) of fulleropyrrolidine bisadduct **5**
(see extended sp^2 carbon area on next page)

Figure 4 ^{13}C NMR ($\text{CS}_2/\text{acetone}$) of fulleropyrrolidine bisadduct **5**,
extended sp^2 carbon area

Figure 5 ^1H NMR (acetone/ CS_2) spectrum of bisadduct **6**

Figure 6 COSY (acetone/ CS_2) spectrum of bisadduct **6**

Figure 7 ^{13}C NMR ($\text{CS}_2/\text{acetone}$) of fulleropyrrolidine bisadduct **6**

Figure 8 COSY (acetone/CS₂) spectrum of bisadduct **7**

Figure 9 ^1H NMR ($\text{CS}_2/\text{acetone}$) spectrum of bisadduct **10**

Figure 10 COSY NMR ($\text{CS}_2/\text{acetone}$) spectrum of bisadduct **10**

Figure 11 ^1H spectrum ($\text{CS}_2/\text{acetone}$) of bisadduct **15**

Figure 12 COSY spectrum ($\text{CS}_2/\text{acetone}$) of bisadduct **15**

Figure 13 ^1H ($\text{CS}_2/\text{acetone}$) of fulleropyrrolidine monoadduct **16**

Figure 14 ^{13}C NMR ($\text{CS}_2/\text{acetone}$) of fulleropyrrolidine monoadduct **16**

Figure 15 Maldi-tof mass spectrum of bisadduct **12**

Molecular modeling of fulleropyrrolidine bisadducts:

Models for tethered fulleropyrrolidine bisadducts were built using tools in Spartan'04 by Wavefunction[®] (www.wavefunction.com). The structures were initially optimized using molecular mechanic and then refined with semi-empirical AM1 method.

The computation of AM1 heats of formation of all possible bisadduct isomers having the same addition pattern was conducted to assist in establishing the isomeric structures of fulleropyrrolidine bisadducts. The following only shows the optimized structures with relative lower heats of formation. We used *cis* and *trans* to distinguish the stereoisomeric structures.

Figure 16 Modeling of bisadducts derived from *p*-xylene tethered bisaldehydes.

Figure 17 Modeling of bisadducts derived from *o*-xylene tethered bisaldehydes.

Figure 18 Modeling of bisadducts derived from *m*-xylene tethered bisaldehydes.

Figure 19 Modeling of fulleropyrrolidine bisadducts derived from biphenyl tethered bisaldehydes