Supporting Information

Efficient Synthesis of Open-Cage Fullerene Derivatives Having 16-Membered-Ring Orifices

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A) Experimental Procedures

General Considerations. All reactions were performed under argon atmosphere. ^1H NMR and ^{13}C NMR spectra were recorded on 500 MHz (125 MHz for ^{13}C) and 300 MHz (75 MHz for ^{13}C) spectrometers, in CDCl_3 or $\text{CDCl}_3/\text{CS}_2$ solutions. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS), by using the residual solvent peak as internal standard. FT-IR spectra were recorded on a fourier transform infrared spectrometer, as KBr pellets. UV-VIS spectra were performed on a UV/Visible spectrometer. Negative-ion MALDI spectra were recorded for all the new compounds using DCTB as the matrix. TLC was carried out on SiO_2 (silica gel F₂₅₄). Flash column chromatography was carried out on SiO_2 (silica gel 60, SDS, 230-400 mesh ASTM). Evaporation of the solvents was accomplished with a rotary evaporator or by high vacuum distillation.

B) Characterization Data of Compounds 10b-d, 11a-d, 13a and 13b.

Data for 10b. IR (KBr): ν (cm⁻¹) 3376, 3051, 2919, 1687, 1628, 1583, 1537, 1477, 1429, 1237, 1065, 997, 906, 867, 822, 747, 726, 542, 505; UV-vis (CHCl₃): λ_{max} (nm) 253, 257, 328, 441, 537; MS (MALDI): m/z 1221 (M⁺); ¹H NMR (500 MHz, CDCl₃/CS₂): δ 13.59 (s, 1H), 8.66 (m, 1H), 7.93 (m, 1H), 7.80-7.70 (m, 4H), 7.60 (m, 4H), 7.37 (m, 1H), 7.19 (m, 3H), 7.08 (m, 3H), 6.98 (m, 1H), 5.46 (d, J = 20 Hz, 1H), 4.83 (d, J = 20 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃/CS₂): δ 184.22, 167.45, 153.56, 152.17, 150.97, 149.95, 149.82, 149.68, 149.58, 149.43, 149.13, 148.83, 148.78, 148.58, 148.39, 148.18, 148.16, 148.05, 147.77, 147.57, 147.53, 147.43, 146.99, 146.93, 146.50, 145.81, 145.74, 145.62, 144.84, 144.23, 144.04, 143.55, 143.40, 143.30, 142.75, 142.73, 142.04, 141.97, 141.78, 141.11, 140.59, 139.64, 138.50, 138.39, 138.28, 138.01, 137.85, 137.76, 137.48, 137.13, 136.74, 136.70, 136.66, 136.12, 135.97, 133.75, 133.13, 132.53, 131.90, 131.26, 130.34, 130.15, 129.19, 128.94, 128.81, 128.32, 127.75, 127.45, 127.35, 127.27, 123.60, 123.47, 118.25, 117.57, 76.20, 53.20, 44.37 (one carbonyl carbon could not be detected due to low solubility or overlapping with CS₂ peak).

Data for 10c. IR (KBr): ν (cm⁻¹) 3370, 3054, 2915, 2830, 1677, 1627, 1581, 1531, 1510, 1480, 1461, 1427, 1408, 1243, 1162, 1064, 1032, 998, 827, 695, 539, 506; UV-vis (CHCl₃): λ_{max} (nm) 257, 331, 449, 551; MS (MALDI): m/z 1172 (M⁺); ¹H NMR (500 MHz, CDCl₃/CS₂): δ 13.78 (s, 1H), 8.64 (m, 1H), 7.93 (m, 1H), 7.83 (m, 1H), 7.72 (m, 3H), 7.66 (m, 2H), 7.36 (m, 1H), 7.17 (m, 3H), 7.02 (m, 6H), 5.47 (d, J = 20 Hz, 1H), 4.81 (d, J = 20 Hz, 1H), 3.90 (s, 3H); ¹³C NMR (75 MHz, CDCl₃/CS₂): δ 193.16, 183.17, 166.60, 162.89, 157.33, 153.04, 151.55, 150.33, 149.40, 149.15, 149.05, 148.97, 148.71, 148.36, 148.23, 148.03, 147.75, 147.59, 147.47, 147.41, 147.28, 147.04, 146.97, 146.83, 146.37, 146.22, 145.95, 145.24, 145.12, 145.00,

144.20, 143.43, 142.97, 142.54, 142.48, 142.29, 142.19, 141.43, 141.16, 140.60, 140.10, 138.47, 137.72, 137.65, 137.55, 137.07, 137.02, 136.96, 136.72, 136.10, 135.91, 135.71, 135.59, 134.68, 133.18, 131.07, 130.98, 130.84, 130.69, 129.75, 129.50, 128.41, 128.25, 127.70, 127.07, 126.65, 126.54, 123.01, 122.71, 117.05, 114.95, 55.19, 52.49, 43.56 (one sp^3 quaternary carbon could not be detected due to low solubility or overlapping with CDCl_3 peak).

Data for 10d. IR (KBr): ν (cm^{-1}) 3464, 3052, 2916, 1729, 1687, 1630, 1583, 1528, 1485, 1426, 1246, 1101, 999, 904, 849, 747, 726, 691, 568, 562, 536, 506; UV-vis (CHCl_3): λ_{max} (nm) 256, 328, 436, 547; MS (MALDI): m/z 1218 (M^+); ^1H NMR (500 MHz, CDCl_3): δ 8.70 (m, 1H), 7.97 (m, 1H), 7.84 (m, 3H), 7.76 (m, 1H), 7.45-6.95 (m, 18H), 5.05 (d, $J = 19$ Hz, 1H), 4.97 (d, $J = 19$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 193.36, 181.21, 167.29, 163.65, 154.21, 150.47, 150.17, 149.07, 149.00, 148.85, 148.41, 148.15, 148.05, 147.95, 147.44, 147.36, 147.29, 147.21, 147.03, 146.78, 146.59, 146.32, 145.54, 145.50, 145.10, 144.70, 144.20, 143.76, 143.10, 142.91, 142.38, 142.33, 141.87, 141.40, 140.86, 140.66, 138.32, 137.92, 137.60, 137.53, 137.40, 137.34, 137.24, 136.92, 136.69, 136.61, 136.14, 136.03, 135.56, 135.44, 133.08, 131.69, 131.06, 130.57, 130.32, 130.21, 129.88, 129.53, 129.09, 128.87, 128.81, 128.76, 128.48, 128.28, 128.16, 128.10, 127.45, 127.32, 127.10, 126.89, 126.50, 126.08, 123.38, 123.02, 122.70, 122.46, 122.34, 122.18, 121.74, 120.89, 119.29, 52.61, 40.76 (one sp^3 quaternary carbon could not be detected due to low solubility or overlapping with CDCl_3 peak).

Data for 11a. IR (KBr): ν (cm^{-1}) 3401, 3052, 2915, 2850, 1678, 1630, 1586, 1534, 1476, 1428, 1257, 1180, 1098, 1064, 1027, 1003, 873, 800, 747, 730, 692, 542, 536, 504; UV-vis (CHCl_3): λ_{max} (nm) 256, 326, 434, 540; MS (MALDI): m/z 1142 (M^+); ^1H NMR (500 MHz, CDCl_3): δ 13.94 (s, 1H), 8.60 (m, 1H), 7.93 (m, 2H), 7.86 (m,

1H), 7.79 (m, 1H), 7.67 (m, 1H), 7.58 (m, 4H), 7.48 (m, 2H), 7.34 (m, 2H), 7.24 (m, 5H), 5.71 (d, $J = 20$ Hz, 1H), 4.88 (d, $J = 20$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 197.24, 186.08, 165.66, 165.54, 155.41, 151.88, 150.92, 150.38, 150.01, 149.73, 149.60, 149.35, 149.27, 148.83, 148.75, 148.69, 148.18, 148.10, 148.05, 148.02, 147.93, 147.83, 147.76, 147.46, 147.43, 146.84, 146.55, 145.78, 145.71, 145.24, 144.38, 144.31, 144.12, 144.07, 144.01, 143.98, 143.52, 143.07, 142.69, 142.65, 141.84, 141.71, 140.79, 140.30, 138.99, 138.88, 138.35, 138.32, 137.59, 137.54, 137.40, 137.21, 136.95, 136.86, 136.39, 136.27, 136.06, 134.93, 133.03, 132.57, 132.49, 132.36, 132.13, 131.70, 131.44, 130.69, 130.35, 130.16, 129.87, 129.37, 129.24, 128.97, 128.87, 127.87, 127.65, 127.53, 126.68, 124.99, 124.39, 122.85, 115.45, 73.38, 61.11, 44.72.

Data for 11b. IR (KBr): ν (cm^{-1}) 3401, 3051, 2914, 1686, 1678, 1630, 1583, 1534, 1426, 1247, 1066, 1002, 820, 800, 746, 730, 691, 548, 501; UV-vis (CHCl_3): λ_{max} (nm) 253, 324, 441, 538; MS (MALDI): m/z 1221 (M^+); ^1H NMR (500 MHz, CDCl_3): δ 13.87 (s, 1H), 8.60 (m, 1H), 7.93 (m, 2H), 7.86 (m, 1H), 7.80 (m, 1H), 7.66 (m, 4H), 7.46 (m, 2H), 7.40-7.17 (m, 6H), 7.12 (m, 1H), 5.65 (d, $J = 20$ Hz, 1H), 4.83 (d, $J = 20$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 197.40, 186.21, 165.58, 165.37, 155.25, 151.79, 150.91, 150.58, 149.98, 149.74, 149.60, 149.39, 149.30, 148.82, 148.73, 148.63, 148.20, 148.13, 148.09, 148.02, 147.81, 147.75, 147.45, 146.85, 146.53, 145.76, 145.69, 145.20, 144.40, 144.33, 144.12, 144.08, 144.00, 143.97, 143.60, 142.66, 142.60, 142.21, 141.85, 141.71, 140.72, 140.19, 139.11, 138.89, 138.31, 137.81, 137.76, 137.60, 137.41, 136.94, 136.59, 136.41, 136.15, 136.03, 134.95, 133.33, 133.02, 132.70, 132.41, 131.79, 131.45, 130.67, 130.14, 129.89, 129.45, 129.23, 128.57, 127.91, 127.78, 127.64, 127.50, 126.63, 124.35, 122.89, 117.37, 116.79, 73.38, 61.06, 44.79.

Data for 11c. IR (KBr): ν (cm⁻¹) 3437, 2919, 2850, 1677, 1627, 1585, 1533, 1510, 1241, 1235, 1161, 1067, 1027, 1003, 873, 823, 746, 730, 692, 549; UV-vis (CHCl₃): λ_{max} (nm) 258, 328, 450; MS (MALDI): m/z 1172 (M⁺); ¹H NMR (500 MHz, CDCl₃): δ 14.09 (s, 1H), 8.60 (m, 1H), 7.94 (m, 2H), 7.87 (m, 1H), 7.80 (m, 1H), 7.65 (m, 1H), 7.56 (m, 2H), 7.38-7.18 (m, 7H), 7.12 (m, 3H), 5.71 (d, J = 20 Hz, 1H), 4.86 (d, J = 20 Hz, 1H), 3.94 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 196.54, 185.32, 165.08, 164.64, 157.16, 154.80, 151.21, 150.29, 149.57, 149.44, 149.08, 148.98, 148.59, 148.28, 148.24, 148.00, 147.55, 147.40, 147.24, 147.18, 147.06, 146.87, 146.24, 145.99, 145.20, 145.10, 144.59, 143.77, 143.60, 143.39, 143.34, 143.26, 142.78, 142.13, 141.24, 141.09, 140.25, 139.72, 138.25, 138.17, 137.70, 136.93, 136.84, 136.70, 136.50, 136.38, 136.15, 135.86, 135.73, 135.48, 134.29, 132.46, 130.86, 130.11, 129.65, 129.21, 128.65, 127.86, 127.19, 126.94, 126.07, 123.75, 122.15, 116.17, 115.18, 72.75, 60.44, 55.54, 43.96.

Data for 11d. IR (KBr): ν (cm⁻¹) 3465, 3054, 1730, 1678, 1627, 1586, 1529, 1510, 1485, 1428, 1246, 1205, 1181, 1129, 1097, 1055, 1029, 1008, 999, 872, 747, 731, 695, 567, 556, 541, 509, 489; UV-vis (CHCl₃): λ_{max} (nm) 258, 325, 448; MS (MALDI): m/z 1218 (M⁺); ¹H NMR (500 MHz, CDCl₃/CS₂): δ 8.56 (m, 1H), 7.96 (m, 2H), 7.86 (m, 1H), 7.76 (m, 1H), 7.65 (m, 1H), 7.62-7.20 (m, 17H), 7.17 (m, 1H), 5.05 (d, J = 20 Hz, 1H), 4.98 (d, J = 20 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃/CS₂): δ 195.33, 181.89, 165.29, 164.72, 156.04, 150.16, 150.01, 149.31, 149.11, 148.96, 148.64, 148.47, 148.20, 147.55, 147.48, 147.43, 147.28, 147.02, 146.76, 146.71, 146.32, 145.67, 145.21, 145.14, 144.50, 144.32, 143.79, 143.69, 143.57, 142.88, 142.37, 141.96, 141.38, 140.78, 140.35, 139.54, 138.44, 138.20, 137.75, 136.95, 136.70, 136.56, 136.08, 135.94, 135.67, 134.34, 132.54, 131.92, 130.86, 130.28,

129.72, 129.25, 129.04, 128.24, 128.04, 127.29, 127.08, 126.95, 126.61, 126.51, 124.08, 122.10, 72.66, 60.38, 41.34.

Data for 13a. IR (KBr): ν (cm^{-1}) 3402, 3053, 2915, 2848, 1742, 1692, 1628, 1581, 1489, 1444, 1428, 1270, 748, 694, 539; UV-vis (CHCl_3): λ_{max} (nm) 258, 323; MS (MALDI): m/z 1230 (M^+); ^1H NMR (500 MHz, CDCl_3): δ 8.66 (m, 1H), 8.03 (m, 1H), 7.96 (m, 1H), 7.84 (m, 2H), 7.79 (m, 4H), 7.64 (m, 2H), 7.52 (m, 4H), 7.44 (m, 1H), 7.36 (m, 4H), 7.20-6.95 (m, 4H), 5.15 (d, $J = 20$ Hz, 1H), 5.08 (d, $J = 20$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 193.17, 180.23, 166.37, 165.17, 162.38, 156.52, 154.37, 153.29, 150.15, 149.20, 149.14, 149.10, 148.86, 148.49, 148.27, 148.06, 148.02, 147.70, 147.52, 147.37, 147.24, 147.11, 147.01, 146.66, 146.31, 145.23, 145.05, 144.84, 144.78, 144.20, 144.12, 143.92, 143.81, 143.00, 142.84, 142.02, 141.70, 141.27, 140.90, 140.27, 139.21, 139.14, 137.92, 137.52, 137.44, 137.24, 136.82, 136.63, 136.36, 135.44, 135.41, 135.33, 133.92, 133.18, 132.21, 130.70, 130.07, 129.82, 129.72, 129.56, 128.36, 128.19, 128.04, 126.88, 126.57, 123.67, 122.79, 52.68, 42.91 (one sp^3 quaternary carbon could not be detected due to low solubility or overlapping with CDCl_3 peak).

Data for 13b. IR (KBr): ν (cm^{-1}) 3401, 3053, 2916, 1736, 1678, 1627, 1585, 1490, 1429, 1266, 748, 732, 693, 543, 512; UV-vis (CHCl_3): λ_{max} (nm) 260, 320, 429; MS (MALDI): m/z 1230 (M^+); ^1H NMR (500 MHz, CDCl_3): δ 8.57 (m, 1H), 7.92 (m, 2H), 7.85 (m, 3H), 7.76 (m, 1H), 7.68 (m, 1H), 7.57 (m, 2H), 7.50-7.35 (m, 9H), 7.27-7.10 (m, 5H), 5.40 (d, $J = 20$ Hz, 1H), 5.28 (d, $J = 20$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 196.55, 165.72, 156.80, 155.14, 153.33, 150.76, 150.09, 149.68, 149.64, 149.53, 149.48, 149.11, 148.73, 148.27, 148.24, 148.08, 148.01, 147.86, 147.75, 147.33, 147.12, 146.90, 146.63, 145.41, 145.21, 144.72, 144.66, 144.57, 144.48, 144.40, 144.22, 144.02, 143.85, 142.54, 142.32, 142.02, 141.70, 141.46, 140.28,

139.95, 139.65, 139.00, 138.07, 138.01, 137.67, 137.36, 136.58, 136.44, 135.98, 135.94, 135.42, 134.34, 133.16, 132.66, 131.43, 131.04, 130.79, 130.64, 130.44, 130.01, 129.86, 129.66, 129.09, 128.74, 128.70, 128.45, 127.89, 127.64, 127.60, 127.14, 124.72, 122.85, 73.37, 61.07, 43.68 (one carbonyl carbon could not be detected due to low solubility).

C) NMR, FT-IR and UV-vis Spectra

Compound 10a

1) ^1H NMR (500MHz, $\text{CDCl}_3/\text{CS}_2$)

2) ^{13}C NMR (125MHz, $\text{CDCl}_3/\text{CS}_2$)

3) FT-IR

4) UV-vis (CHCl_3)

Compound 10b

1) ^1H NMR (500MHz, $\text{CDCl}_3/\text{CS}_2$)

2) ^{13}C NMR (125MHz, $\text{CDCl}_3/\text{CS}_2$)

3) FT-IR

4) UV-vis (CHCl_3)

Compound 10c

1) ^1H NMR (500MHz, $\text{CDCl}_3/\text{CS}_2$)

2) ^{13}C NMR (75MHz, $\text{CDCl}_3/\text{CS}_2$)

3) FT-IR

4) UV-vis (CHCl_3)

Compound 10d

1) ^1H NMR (500MHz, CDCl_3)

2) ^{13}C NMR (75MHz, CDCl_3)

3) FT-IR

4) UV-vis (CHCl₃)

Compound 11a

1) ^1H NMR (500MHz, CDCl_3)

2) ^{13}C NMR (125MHz, CDCl_3)

3) FT-IR

4) UV-vis (CHCl_3)

Compound 11b

1) ^1H NMR (500MHz, CDCl_3)

2) ^{13}C NMR (125MHz, CDCl_3)

3) FT-IR

4) UV-vis (CHCl_3)

Compound 11c

1) ^1H NMR (500MHz, CDCl_3)

2) ^{13}C NMR (75 MHz, CDCl_3)

3) FT-IR

4) UV-vis (CHCl_3)

1) ^1H NMR (500MHz, $\text{CDCl}_3/\text{CS}_2$)

3) FT-IR

4) UV-vis (CHCl₃)

Compound 13a

1) ^1H NMR (500MHz, CDCl_3)

2) ^{13}C NMR (75MHz, CDCl_3)

3) FT-IR

4) UV-vis (CHCl₃)

Compound 13b

1) ^1H NMR (500MHz, CDCl_3)

2) ^{13}C NMR (125MHz, CDCl_3)

3) FT-IR

4) UV-vis (CHCl₃)