Journal of the Serbian Chemical Society
JSCS@tmf.bg.ac.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. 86 (11) S284–S358 (2021) *Supplementary material*

SUPPLEMENTARY MATERIAL TO

Fulleropyrrolidines with orthogonally flexible substituents – Synthesis and electrochemical properties

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J. Serb. Chem. Soc. 86 (11) (2021) 1023–1037

ANALYTICAL AND SPECTRAL DATA

Monoadduct ***6a***. A suspension of C_{60} (100 mg, 0.139 mmol), amino acid **4a** (38 mg, 0.139 mmol) and 4-methoxybenzaldehyde (94.5 mg, 84.4 μL, 0.694 mmol, 5 mol-equiv.) in PhMe (100 mL) was heated at reflux for 0.5 h. DCFC: PhMe gave unreacted C_{60} (39.9 mg, 40 %); PhMe/EtOAc 9:1 gave monoadduct **6a** (51.5 mg, 35 %). IR (ATR, cm^{-1}): 3446, 3366, 1713, 1513, 1250, 1175; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm): 7.70 (2H, *brs*, $HC(2,6)_{ar}$), 6.94 (2H, *d*, *J* = 8.5 Hz, $HC(3,5)_{ar}$), 5.07 (1H, *d*, *J* = 9.5 Hz, H_2C_{pyrr}), 5.00 (1H, *s*, HC_{pyrr}), 4.55 (1H, brs, NHBoc), 4.10 (1H, *d*, *J* = 9.5 Hz, H_2C_{pyrr}), 3.81 (3H, s, OCH_3), 3.24-3.12 (3H, *m*, HC(1) + $H_2C(6)$), 2.57-2.49 (1H, *m*, HC(1)), 2.01-1.92 (1H, *m*, HC(2)), 1.92-1.82 (1H, *m*, HC(2)), 1.73-1.63 (1H, *m*, HC(3)), 1.63-1.42 (5H, *m*, HC(3), $H_2C(4)$, $H_2C(5)$), 1.46 (9H, *s*, H_3C); ^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm): 159.70 ($C_{ar}(4)$), 156.88, 156.16 (**C**OO^{t}Bu), 154.51, 153.95, 147.46, 147.01, 146.70, 146.55, 146.45, 146.41, 146.36, 146.30, 146.25, 146.09, 145.93, 145.73, 145.71, 145.68, 145.61, 145.47, 145.42, 145.38, 145.36, 145.28, 144.87, 144.80, 144.56, 143.30, 143.14, 142.82, 142.72, 142.70, 142.50, 142.44, 142.27, 142.16, 142.13, 141.97, 141.82, 141.67, 140.31, 140.27, 140.04, 139.67, 136.94, 136.73, 135.91, 135.88, 130.73 ($C_{ar}(2,6)$), 129.45 ($C_{ar}(1)$), 114.11 ($C_{ar}(3,5)$), 82.25 (CH_{pyrr}), 79.23 (C(^{t}Bu)), 77.09 (sp^3-C_{60}), 69.01 (sp^3-C_{60}), 67.01 (H_2C_{pyrr}), 55.36 (OCH_3), 53.06 (C(1)), 40.82 (C(6)), 30.32 (C(5)), 28.62 (CH_3), 28.44 (C(2)), 27.42 (C(3)), 27.04 (C(4)); UV/Vis (CH_2Cl_2, λ_{max} / nm, (ε / $mol^{-1}dm^3cm^{-1}$)): 267 (120630), 308 (48720), 430 nm (4250); HRMS(HESI-Orbitrap) (*m/z*): Calcd. for $C_{80}H_{32}N_2O_3$ +H^+: 1069.2491. Found: 1069.2496.

Monoadduct ***7a***. A suspension of C_{60} (100 mg, 0.139 mmol), amino acid **4a** (38 mg, 0.139 mmol) and decanal (108 mg, 130 μL, 0.694 mmol, 5 mol-equiv) in PhMe (100 mL) was heated at reflux for 0.5 h. DCFC: PhMe gave unreacted C_{60} (39.0 mg, 39 %); PhMe/EtOAc 9:1 gave monoadduct **7a** (53.8 mg, 36 %). IR (ATR / cm^{-1}): 3363, 1713, 1459, 1169; ^{1}H-NMR (500 MHz, $CDCl_3$, δ/ ppm): 4.90 (1H, *d*, *J* = 10.0 Hz, H_2C_{pyrr}), 4.57 (1H, *brs*, NHBoc), 4.13 (1H, *t*, *J* = 4.5 Hz, HC_{pyrr}), 4.12 (1H, *d*, *J* = 10 Hz, H_2C_{pyrr}), 3.56-3.49 (1H, *m*, HC(1)),

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3.20 (2H, *brq*, *J* = 6 Hz, $H_2C(6)$), 2.87-2.80 (1H, *m*, HC(1)), 2.52-2.43 (1H, *m*, HC(1')), 2.43-2.34 (1H, *m*, HC(1')), 2.01-1.79 (4H, *m*, $H_2C(2)$, $H_2C(2')$), 1.72-1.25 (33H, *m*), 1.56 (9H, *s*, CH_3), 0.87 (3H, *t*, *J* = 5 Hz, $H_3C(9')$; ^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm): 156.75, 156.01 (**C**OO^{t}Bu), 155.12, 155.04, 154.98, 153.74, 147.19, 147.17, 146.73, 146.61, 146.34, 146.25, 146.23, 146.14, 146.05, 146.01, 145.96, 145.93, 145.78, 145.69, 145.59, 145.34, 145.27, 145.23, 145.22, 145.17, 144.72, 144.58, 144.40, 143.19, 143.05, 142.66, 142.63, 142.59, 142.25, 142.22, 142.15, 142.11, 142.05, 141.82, 141.75, 141.69, 140.23, 140.17, 139.81, 139.59, 137.09, 136.23, 135.64, 135.47, 79.13 (C(^{t}Bu)), 77.41 (CH_{pyrr}), 76.34 (sp^3-C_{60}), 70.80 (sp^3-C_{60}), 66.88 (H_2C_{pyrr}), 52.46 (C(1)), 40.61 (C(6)), 31.91 (C7'), 31.14 (C(1')), 30.21 (C(5)), 29.53 (C(3')), 29.48 (C(8')), 29.29, 28.66 (C(2)), 28.46 (CH_3(^{t}Bu)), 27.48 (C(2')), 27.41 (C(3)), 26.91 (C(4)), 22.69 (C(8'), 14.14 (C(9'); UV/Vis (CH_2Cl_2, λ_{max} / nm (ε / mol^{-1}dm^{3}cm^{-1})): 256 (31200), 309 (10200), 430 (1300); HRMS(ESI/TOF): (*m/z*) calcd. for $C_{82}H_{44}N_2O_2$+H)$^+$: 1089.3476. Found: 1089.3454.

*Monoadduct **8b***. A suspension of C_{60} (50.5 mg, 0.070 mmol), amino acid **4b** (23.0 mg, 0.070 mmol) and PhCHO (37.1 mg, 35.58 µl, 0.350 mmol) in PhMe (50 mL) was heated at reflux for 4 h. DCFC: PhMe gave unreacted C_{60} (16.7 mg, 33 %) and monoadduct **8b** (19.6 mg, 26 %). IR (ATR, cm^{-1}): 3338, 1710, 1243, 1165; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm): 7.81 (2H, *brs*, $HC(2,6)_{ar}$), 7.41 (2H, *t*, *J* = 7.5 Hz, $HC(3,5)_{ar}$), 7.32 (1H, *tt*, *J* = 7.5 Hz & 1.0 Hz, $HC(4)_{ar}$), 5.10 (1H, *d*, *J* = 9 Hz, H_2C_{pyrr}), 5.06 (1H, *s*, HC_{pyrr}), 4.50 (1H, *brs*, NHBoc), 4.12 (1H, *d*, *J* = 9 Hz, H_2C_{pyrr}), 3.27-3.19 (1H, *m*, HC(1)), 3.12 (2H, brq, *J* = 6.5 Hz, $H_2C(10)$, 2.58-2.52 (1H, *m*, HC(1)), 2.00-1.93 (1H, *m*, HC(2)), 1.91-1.83 (1H, *m*, HC(2)), 1.67-1.60 (1H, *m*, HC(3)), 1.45 (9H, *s*, CH_3), 1.60-1.28 (*m*); ^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm): 156.63, 155.97 (**C**OO^{t}Bu), 154.35, 153.62, 147.29, 146.84, 146.51, 146.29, 146.24, 146.20, 146.18, 146.14, 146.11, 146.08, 145.91, 145.75, 145.57, 145.55, 145.51, 145.47, 145.30, 145.25, 145.21, 145.19, 145.12, 144.71, 144.61, 144.39, 143.14, 142.98, 142.66, 142.54, 142.33, 142.27, 142.12, 142.10, 142.01, 141.92, 141.81, 141.66, 141.49, 140.16, 140.11, 139.82, 139.37, 137.40 (C_{ar}(1)), 136.80, 136.57, 135.81, 135.70, 129.48 (C_{ar}(2,6)), 128.57 (C_{ar}(3,5)), 128.39 (C_{ar}(4)), 82.59 (CH_{pyrr}), 79.00 (C(^{t}Bu)), 77.00 (sp^3-C_{60}), 68.95 (sp^3-C_{60}), 66.89 (H_2C_{pyrr}), 53.12 (C(1)), 40.65 (C(10)), 30.09 (C(9)), (29.66, 29.61, 29.58, 29.33 C(4-7)), 28.44 (CH_3), 28.35 (C(2)), 27.53 (C(3)), 26.85 (C(8)); UV/Vis ($CHCl_3$, λ_{max} / nm (ε / mol^{-1}dm^{3}cm^{-1}): 325 (13129), 431 (3107), 692 (2089). HRMS(ESI/TOF): (*m/z*): calcd for $C_{83}H_{38}N_2O_2$+H)$^+$: 1095.3006. Found: 1095.3002.

*Monoadduct **9b***. A suspension of C_{60} (50.5 mg, 0.070 mmol), amino acid **4b** (23 mg, 0.070 mmol) and 4-methoxybenzaldehyde (47.6 mg, 42.58 µL, 0.350 mmol) in PhMe (50 mL) was heated at reflux for 4 h. DCFC: PhMe gave unreacted C_{60} (17.2 mg, 34 %) and monoadduct **9b** (17.9 mg, 23 %). IR (ATR, cm^{-1}): 3354, 1705, 1246, 1170; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm): 7.72 (2H, brs, $HC(2,6)_{ar}$), 6.94 (2H, *d*, *J* = 8.5 Hz, $HC(3,5)_{ar}$), 5.08 (1H, *d*, *J* = 9.0 Hz, H_2C_{pyrr}), 5.01 (1H, *s*, HC_{pyrr}), 4.50 (1H, *brs*, NHBoc), 4.10 (1H, *d*, *J* = 9.5 Hz, H_2C_{pyrr}), 3.81 (3H, *s*, OCH_3), 3.24-3.17 (1H, *m*, HC(1)), 3.12 (2H, *brq*, *J* = 6 Hz, $H_2C(10)$), 2.56-2.49 (1H, *m*, HC(1)), 2.00-1.92 (1H, *m*, HC(2)), 1.90-1.81 (1H, *m*, HC(2)), 1.45 (9H, *s*, CH_3), 1.69-1.28 (25H, *m*); ^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm): 159.50 (C_{ar}(4)), 156.76, 155.98 (**C**OO^{t}Bu), 154.40, 153.83, 147.29, 146.87, 146.55, 146.40, 146.29, 146.24, 146.20, 146.12, 146.08, 145.92, 145.91, 145.76, 145.58, 145.55, 145.51, 145.44, 145.30, 145.26, 145.21, 145.20, 145.12, 144.71, 144.64, 144.40, 143.15, 142.97, 142.66, 142.56, 142.54, 142.34, 142.29, 142.11, 142.00, 141.96, 141.81, 141.66, 141.51, 140.15, 140.09, 139.88, 139.50, 136.79, 136.58, 135.75, 130.58 (C_{ar}(2,6)), 129.36 (C_{ar}(1)), 113.92 (C_{ar}(3,5)), 82.10 (CH_{pyrr}), 79.01 (C(^{t}Bu)), 77.13 (sp^3-C_{60},from HMBC), 68.87 (sp^3-C_{60}),

66.86 (H_2C_{pyrr}), 55.20 (CH_3O), 53.02 (C(1)), 40.47 (C(10)), 30.10 (C(9)), 29.66, 29.62, 29.59, 29.34 (C(4-7)), 28.45 (CH_3), 28.33 (C(2)), 27.55 (C(3), 26.85 (C(8); UV/Vis (CH_2Cl_2, λ_{max} / nm (ε / $mol^{-1}dm^3cm^{-1}$): 324 (17977), 431 (2112), 702 (168); HTMS (ESI/TOF): *m/z* calcd for $(C_{84}H_{40}N_2O_3+H)^+$ 1125.3112. Found: 1125.3112.

*Monoadduct **10b***. A suspension of C_{60} (50.5 mg, 0.070 mmol), amino acid **4b** (22.9 mg, 0.069 mmol) and 4-nitrobenzaldehyde (52.4 mg, 0.347 mmol, 5 mol-equiv) in PhMe (50 mL) was heated at reflux for 4 h. DCFC: PhMe gave unreacted C_{60} (15.6 mg, 31 %) and monoadduct **10b** (24.2 mg, 30 %). IR (ATR, cm^{-1}): 3452, 1712, 1522, 1245, 1168; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm): 8.29 (2H, *d*, *J* = 9 Hz, $HC(3,5)_{ar}$), 8.03 (2H, brs, $HC(2,6)_{ar}$), 5.18 (1H, *s*, HC_{pyrr}), 5.14 (1H, *d*, *J* = 9.5 Hz, H_2C_{pyrr}), 4.51 (1H, *brs*, NHBoc), 4.17 (1H, *d*, *J* = 9.0 Hz, H_2C_{pyrr}), 3.15-3.03 (3H, *m*, HC(1) & $H_2C(10)$), 2.64-2.56 (m, 1H, HC(1)), 2.03-1.95 (m, 1H, HC(2)), 1.93-1.86 (m, 1H, HC(2)), 1.69-1.62 (1H, *m*, HC(3)), 1.59-1.28 (*m*), 1.45 (9H, *s*, CH_3); ^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm): 156.00 (C_{full} and **C**OO^{t}Bu), 153.79, 152.50 ($C_{ar}(4)$), 152.07, 147.97, 147.38, 147.34, 146.34, 146.25, 146.20, 146.16, 145.99, 145.65, 145.63, 145.57, 145.48, 145.43 ($C(1)_{ar}$), 145.38, 145.30, 145.23, 144.75, 144.54, 144.45, 144.34, 143.21, 143.06, 142.76, 142.64, 142.58, 142.28, 142.24, 142.18, 142.15, 142.08, 142.05, 142.00, 141.96, 141.83, 141.81, 141.72, 141.59, 140.28, 140.00, 139.54, 137.14, 136.29, 136.08, 135.53, 130.21 ($C_{ar}(2,6)$), 123.85 ($C_{ar}(3,5)$), 81.66 (CH_{pyrr}), 79.02 (C(^{t}Bu)), 76.18 (sp^3-C_{60}), 68.95 (sp^3-C_{60}), 66.87 (H_2C_{pyrr}), 53.38 (C(1)), 40.64 (C(10)), 30.10 (C(9)), (29.64, 29.61, 29.57, 29.32, C(4-7), 28.44 (CH_3), 28.33 (C(2)), 27.54 (C(3)), 26.83 (C(8)); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 323 (41002), 431 (4123), 700 nm (296 $mol^{-1}dm^3cm^{-1}$); HRMS (ESI/TOF): *m/z* calcd for $(C_{83}H_{37}N_3O_4+H)^+$: 1140.2857. Found: 1140.2846.

*Monoadduct **11c***.[1] A suspension of C_{60} (285 mg, 0.395 mmol), amino acid **4c** (150 mg, 0.395 mmol) and formaldehyde (59.3 mg, 1.977 mmol, 5 mol-equiv) in PhMe (250 mL) was heated at reflux for 10 min. DCFC: PhMe gave unreacted C_{60} (145 mg, 51 %); PhMe/EtOAc 8:2 gave monoadduct **11c** (112.7 mg, 27 %). IR (ATR, cm^{-1}): 3359, 2927, 2866, 1710, 1515, 1363, 1346, 1248, 1171, 1119; ^{1}H-NMR ($CDCl_3$, 500 MHz, δ / ppm): 5.00 (1H, *brs*, NHBoc), 4.42 (4H, *s*, H_2C_{pyrr}), 3.85 (2H, *t*, *J* = 6.0 Hz, $H_2C(3)$), 3.77-3.73 (4H, *m*, $H_2C(5,6)$), 3.73-3.61 (4H, *m*, $H_2C(8,9)$), 3.57 (2H, *t*, *J* = 6.0 Hz, $H_2C(11)$), 3.28-3.22 (2H, *m*, $H_2C(13)$), 3.20 (2H, *t*, *J* = 7.5 Hz, $H_2C(1)$), 2.24 (2H, *quint*, *J* = 7.0 Hz, $H_2C(2)$), 1.78 (2H, *quint*, *J* = 6.0 Hz, $H_2C(12)$), 1.45 (9H, *s*, H_3C); ^{13}C-NMR (125 MHz, $CDCl_3$, 125 MHz, δ / ppm): 156.20 (**C**OO^{t}Bu), 155.25, 147.47, 146.41, 146.25, 146.23, 145.56 145.45, 144.73, 143.26, 142.79, 142.41, 142.23, 142.05, 140.31, 136.38, 79.11 (**C**(^{t}Bu)), 70.89 (sp^3-C_{60}), 70.88 & 70.82 (C(6,8)), 70.58 & 70.46 (C(5,9)), 69.82 (C(11)), 69.64 (C(3)), 68.13 (H_2C_{pyrr}),51.89 (C(1)), 38.77 (C(13)), 29.83 (C(12)), 29.14 (C(2)), 28.65 (CH_3); UV-Vis (CH_2Cl_2, λ_{max} / nm (ε / $mol^{-1}dm^3cm^{-1}$)): 254 (169400), 429 (5800), 700 (800); HRMS (ESI/TOF): *m/z* calcd for $(C_{77}H_{34}N_2O_5+H)^+$: 1067.2552. Found: 1067.2530.

*Monoadduct **12c***. A suspension of C_{60} (250 mg, 0.346 mmol), amino acid **4c** (131.2 mg, 0.346 mmol) and C_6H_5CHO (183.7 mg, 176 μL, 1.72 mmol) in PhMe (250 mL) was heated at reflux for 4 h. DCFC: PhMe gave unreacted C_{60} (134.9 mg, 54 %); PhMe/EtOAc 85:15 gave monoadduct **12c** (135.6 mg, 34 %). IR (ATR, cm^{-1}): 3455, 3427, 3348, 2920, 2854, 2802, 1709, 1247, 1170, 1120; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm): 7.79 (2H, *brs*, $HC(2,6)_{ar}$), 7.41 (2H, *t*, *J* = 7.5 Hz, $HC(3,5)_{ar}$), 7.32 (1H, *tt*, *J* = 7.5 Hz & 1.5 Hz, $HC(4)_{ar}$), 5.11 (1H, *d*, *J* = 9.5 Hz, H_2C_{pyrr}), 5.08 (1H, *s*, HC_{pyrr}), 4.97 (1H, *brs*, NHBoc), 4.14 (1H, *d*, *J* = 9 Hz, H_2C_{pyrr}), 3.89-3.77 (2H, *m*, $H_2C(3)$), 3.74-3.68 (4H, *m*, $H_2C(5,6)$), 3.68-3.58 (4H, *m*, $H_2C(8,9)$), 3.55 (2H, *t*, *J* = 6 Hz, $H_2C(11)$), 3.36 (1H, *dt*, *J* = 12.0 Hz & 8.0 Hz, HC(1)), 3.27-3.20 (2H, *m*, $H_2C(13)$), 2.68-2.61 (1H, *m*, HC(1)), 2.30-2.15 (2H, *m*, $H_2C(2)$), 1.77 (2H, *quint*,

J = 6 Hz, $H_2C(12)$), 1.45 (9H, *s*, CH_3); ^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm): = 156.53, 156.03 (**C**OO^{t}Bu), 154.19, 153.52, 153.46, 147.30, 146.81, 146.47, 146.30, 146.25, 146.22, 146.15, 146.13, 146.09, 145.93, 145.73, 145.53, 145.48, 145.31, 145.27, 145.22, 145.20, 145.13, 144.71, 144.61, 144.40, 144.38, 143.15, 142.98, 142.68, 142.55, 142.29, 142.27, 142.15, 142.13, 142.10, 142.01, 141.97, 141.91, 141.80, 141.68, 141.51, 140.18, 140.14, 139.83, 139.38, 137.20, 136.74, 136.51, 135.84, 135.72, 129.48 6)), 128.57 128.45)), 82.52 (CH_{pyrr}), 78.92 (C(^{t}Bu)), 76.72 (sp^3-C_{60}, from HMBC), 70.72 & 70.65 (C(6,8)), 70.36 & 70.27 (C(5,9)), 69.65 (C(11)), 69.41 (C(3)), 68.90 (sp^3-C_{60}), 66.82 (H_2C_{pyrr}), 49.79 (C(1)), 38.61 (C(13)), 29.64 (C(12)), 28.48 (CH_3), 28.40 (C(2)); UV/Vis (CH_2Cl_2, λ_{max} / nm, (ε / mol^{-1}dm^{3}cm^{-1})): 324 (38839), 431 (4318), 702 (320); HRMS(ESI/TOF): *m/z* calcd for ($C_{83}H_{38}N_2O_5$ +H)$^+$ 1143.2854. Found: 1143.2857.

Monoadduct ***13c***. A suspension of C_{60} (100 mg, 0.139 mmol), amino acid **4c** (52.5 mg, 0.139 mmol) and 2-methoxybenzaldehyde (47.25 mg, 0.347 mmol, 2.5 equiv) in PhMe (100 mL) was heated at reflux for 10 min. DCFC: PhMe gave unreacted C_{60} (37.6 mg, 38 %); PhMe/EtOAc 80:20 gave monoadduct **13c** (53.7 mg, 33 %). IR (ATR, cm^{-1}): 3361, 3048, 2929, 2868, 1711, 1493, 1247, 1172, 1118; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm): 7.97 (1H, *dd*, *J* = 7.5 Hz & 1.5 Hz, $HC(6)_{ar}$), 7.27 (1H, *td*, *J* = 7.5 Hz & 2.0 Hz, $HC(4)_{ar}$), 7.06 (1H, *t*, *J* = 7.5 Hz, $HC(5)_{ar}$), 6.91 (1H, *d*, *J* = 8.5 Hz, $HC(3)_{ar}$), 5.70 (H, *s*, $1HC_{pyrr}$), 5.09 (1H, *d*, *J* = 9.0 Hz, H_2C_{pyrr}), 4.98 (1H, brs, NHBoc), 4.17 (1H, *d*, *J* = 9 Hz, H_2C_{pyrr}), 3.90-3.84 (1H, *m*, HC(3)), 3.84-3.77 (1H, *m*, HC(3)), 3.75-3.69 (4H, *m*, $H_2C(5,6)$), 3.71 (3H, *s*, OCH_3), 3.69-3.58 (4H, *m*, $H_2C(8,9)$), 3.55 (2H, *t*, *J* = 6 Hz, $H_2C(11)$), 3.37 (1H, *dt*, *J* = 12.0 Hz & 8.0 Hz, HC(1)), 3.24 (2H, *brq*, *J* = 5.5 Hz, $H_2C(13)$), 2.65-2.58 (1H, *m*, HC(1)), 2.31-2.15 (2H, *m*, $H_2C(2)$), 1.77 (2H, *quint*, *J* = 6.5 Hz, $H_2C(12)$), 1.45 (9H, s, CH_3); ^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm): 158.34 ($C_{ar}(2)$), 157.24, 156.19 (**C**OO^{t}Bu), 155.28, 154.47, 154.26, 147.44, 146.93, 146.72, 146.38, 146.35, 146.32, 146.25, 146.20, 146.09, 146.06, 145.85, 145.73, 145.72, 145.69, 145.44, 145.40, 145.37, 145.24, 145.21, 145.16, 144.73, 144.58, 144.52, 143.20, 143.14, 142.78, 142.71, 142.68, 142.48, 142.43, 142.33, 142.24, 142.11, 141.96, 141.86, 141.69, 140.35, 140.28, 139.54, 139.52, 136.69, 136.53, 136.31, 134.67, 130.14 ($C_{ar}(6)$), 129.11 ($C_{ar}(4)$), 125.92 ($C_{ar}(1)$), 121.20 ($C_{ar}(5)$), 111.17 ($C_{ar}(3)$), 79.07 (C(^{t}Bu)), 76.16 (sp^3-C_{60}), 74.45 (CH_{pyrr}), 70.88 and 70.82 (C(6,8)), 70.50 and 70.43 (C(5,9)), 69.81 (C(11)), 69.63 (C(3)), 69.32 (sp^3-C_{60}), 66.85 (H_2C_{pyrr}), 55.33 (OCH_3), 50.00 (C(1)), 38.78 (C(13)), 29.79 (C(12)), 28.64 (CH_3), 28.61 (C(2)); UV/Vis (CH_2Cl_2, λ_{max} / ppm, (ε / mol^{-1} dm^3 cm^{-1})): 256 (104400), 307 (38700), 431 (4700), 704 (900); HRMS (ESI/TOF): *m/z* calcd. for ($C_{84}H_{40}N_2O_6$+Na)$^+$: 1195.2790. Found: 1195.2776.

Monoadduct ***14c***. A suspension of C_{60} (200 mg, 0.277 mmol), amino acid **4c** (105 mg, 0.277 mmol) and 3-methoxybenzaldehyde (187.8 mg, 169 μL, 1.38 mmol) in PhMe (100 mL) was heated at reflux for 20 min. DCFC: PhMe gave unreacted C_{60} (73.8 mg, 37 %); PhMe/EtOAc 80:20 gave monoadduct **14c** (120.1 mg, 37 %). IR (ATR / cm^{-1}): 3366, 3050, 2952, 1711, 1266, 1173, 1122; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm): 7.36 (2H, brs, $HC(2)_{ar}$ &, $HC(6)_{ar}$), 7.31 (1H, *t*, *J* = 8 Hz, $HC(5)_{ar}$), 6.86 (1H, *brd*, *J* = 8 Hz, $HC(4)_{ar}$), 5.10 (1H, *d*, *J* = 9.5 Hz, H_2C_{pyrr}), 5.04 (1H, *s*, HC_{pyrr}), 4.98 (1H, *brs*, NHBoc), 4.13 (1H, *d*, *J* = 9.5 Hz, H_2C_{pyrr}), 3.90-3.83 (1H, *m*, HC(3)), 3.83-3.75 (1H, *m*, HC(3)), 3.81 (3H, *s*, OCH_3), 3.75-3.69 (4H, *m*, $H_2C(5,6)$), 3.69-3.58 (4H, *m*, $H_2C(8,9)$), 3.55 (2H, *t*, *J* = 6 Hz, $H_2C(11)$), 3.38 (1H, *dt*, *J* = 12.0 Hz & 8.5 Hz, HC(1)), 3.24 (2H, *brq*, *J* = 5.5 Hz, $H_2C(13)$), 2.69-2.61 (1H, *m*, HC(1)), 2.32-2.13 (2H, *m*, $H_2C(2)$), 1.77 (2H, *quint*, *J* = 6.5 Hz, $H_2C(12)$), 1.45 (9H, *s*, CH_3); ^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm): 159.94 ($C(3)_{ar}$), 156.60, 156.18 (**C**OO^{t}Bu), 154.36, 153.78, 153.60, 147.46, 147.07, 146.60, 146.46, 146.41, 146.37, 146.31, 146.26, 146.24,

146.09, 145.89, 145.68, 145.48, 145.45, 145.42, 145.39, 145.36, 145.28, 144.86, 144.78, 144.55, 143.31, 143.13, 142.83, 142.72, 142.41, 142.30, 142.27, 142.22, 142.16, 142.07, 141.95, 141.83, 141.70, 140.34, 140.28, 139.96, 139.61, 138.99 (C_{ar}(1)), 136.72, 136.69, 135.96, 135.86, 129.71 (C_{ar}(5)), 122.15 (C_{ar}(6)), 114.94 (C_{ar}(2)), 114.00 (C_{ar}(4), 82.56 (CH_{pyrr}), 79.07 (C(^{t}Bu)), 76.72 (sp^3-C_{60}), 70.86 and 70.80 (C(6,8)), 70.50 and 70.42 (C(5,9)), 69.79 (C(11)), 69.60 (C(3)), 69.04 (sp^3-C_{60}), 66.95 (H_2C_{pyrr}), 55.51 (OCH_3), 50.01 (C(1)), 38.77 (C(13)), 29.80 (C(12)), 28.63 (CH_3), 28.54 (C(2)); UV/Vis (CH_2Cl_2, λ_{max} / nm, (ε / mol^{-1}dm^{3}cm^{-1})): = 256 (173200), 305 (60000), 431 (6900), 702 (1100); HRMS (ESI/TOF): *m/z* calcd for ($C_{84}H_{40}N_2O_6$+Na)$^+$: 1195.2790. Found 1195.2781.

*Monoadduct **15c***. A suspension of C_{60} (97.8 mg, 0.136 mmol), amino acid **4c** (51.4 mg, 0.136 mmol) and 4-methoxybenzaldehyde (92.6 mg, 82.7 μL, 0.680 mmol) in PhMe (100 mL) was heated at reflux for 10 min. DCFC: PhMe gave unreacted C_{60} (25.7 mg, 26 %); PhMe/EtOAc 80:20 gave monoadduct **15c** (54.0 mg, 34 %). IR (ATR, cm^{-1}): 3343, 2923, 2862, 1709, 1299, 1168, 1104; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm): 7.70 (2H, *brs*, $HC(2,6)_{ar}$), 6.93 (2H, *d*, *J* = 9 Hz, $HC(3,5)_{ar}$), 5.08 (1H, *d*, *J* = 9 Hz, H_2C_{pyrr}), 5.02 (1H, *s*, HC_{pyrr}), 4.99 (1H, *brs*, NHBoc), 4.12 (1H, *d*, *J* = 9 Hz, H_2C_{pyrr}), 3.88-3.83 (1H, *m*, HC(3)), 3.80 (3H, *s*, OCH_3), 3.82-3.76 (1H, *m*, HC(3)), 3.73-3.69 (4H, *m*, H_2C(5,6)), 3.69-3.58 (4H, *m*, H_2C(8,9)), 3.55 (2H, *t*, *J* = 6 Hz, H_2C(11)), 3.33 (1H, *dt*, *J* = 12.0 Hz & 8.5 Hz, HC(1)), 3.24 (2H, *brq*, *J* = 5 Hz, H_2C(13)), 2.65-2.58 (1H, *m*, HC(1)), 2.29-2.15 (2H, *m*, H_2C(2)), 1.77 (2H, *quint*, *J* = 6 Hz, H_2C(12)), 1.44 (9H, *s*, CH_3); ^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm): = 159.53 (C_{ar}(4)), 156.64, 156.02 (**C**OO^{t}Bu), 154.22, 153.72, 147.29, 146.82, 146.50, 146.34, 146.24, 146.20, 146.13, 146.11, 146.08, 145.92, 145.73, 145.52, 145.44, 145.32, 145.30, 145.26, 145.19, 145.11, 144.70, 144.62, 144.39, 143.13, 142.97, 142.66, 142.53, 142.29, 142.26, 142.14, 142.10, 141.98, 141.93, 141.79, 141.66, 141.50, 140.15, 140.10, 139.87, 139.50, 136.72, 136.51, 135.77, 135.73, 130.57 (C_{ar}(2,6)), 129.15 (C_{ar}(1)), 113.88 (C_{ar}(3,5)), 82.01 (CH_{pyrr}), 78.90 (C(^{t}Bu)), 76.90 (sp^3-C_{60}), 70.70 and 70.64 (C(6,8)), 70.34 and 70.25 (C(5,9)), 69.62 (C(11)), 69.46 (C(3)), 68.80 (sp^3-C_{60}), 66.77 (H_2C_{pyrr}), 55.19 (OCH_3), 49.68 (C(1)), 38.59 (C(13)), 29.63 (C(12)), 28.47 (CH_3), 28.37 (C(2)); UV/Vis (CH_2Cl_2, λ_{max} / nm (ε / mol^{-1}dm^{3}cm^{-1})): 324 (41735), 431 (4760), 702 (375); HRMS(ESI/TOF): *m/z*: calcd for ($C_{84}H_{40}N_2O_6$ +H]$^+$: 1173.2959. Found: 1173.2971.

*Unsuccessful attempts (a, b) to synthesize 2-(2-nitrophenyl)fulleropyrrolidine monoadduct **16c***. (a - according to the general procedure, SI-Fig. S-1) - A suspension of C_{60} (100 mg, 0.138 mmol, 1 mol-equiv), amino acid **4c** (52.5 mg, 0.138 mmol, 1 mol-equiv) and 2-nitrobenzaldehyde (104.8 mg, 0.694 mmol, 5 mol-equiv) in PhMe (100 mL) was heated at reflux for 1.5 h. DCFC: PhMe gave unreacted C_{60} (35.0 mg, 35 %); PhMe/EtOAc 75:25 gave monoadduct **11c** (17.8 mg, 11 %).

(b - according to the procedure for the synthesis of 2-(2-nitrophenyl)fulleropyrrolidine derivative reported by Chinese authors, molar ratio of C_{60}/2-nitrobenzaldehyde/amino acid are 1:1:2, at 100 °C, SI-Fig' S-1)[2] - A suspension of C_{60} (10.7 mg, 0.0148 mmol, 1 mol-equiv), amino acid **4c** (10.8 mg, 0.0286 mmol, 2 mol-equiv) and 2-nitrobenzaldehyde (2.2 mg, 0.0145 mmol, 1 mol-equiv) in PhMe (100 mL) was heated at 100 °C for 24 h. DCFC: PhMe gave unreacted C_{60} (5.4 mg, 50 %); PhMe/EtOAc 75:25 gave monoadduct **11c** (4.75 mg, 28 %). In both cases (a, b), the expected 2-(2-nitrophenyl)fulleropyrrolidine was not obtained.

*Monoadduct **17c***. A suspension of C_{60} (100 mg, 0.138 mmol), amino acid **4c** (52.5 mg, 0.138 mmol) and 3-nitrobenzaldehyde (104.8 mg, 0.694 mmol) in PhMe (100 mL) was heated at reflux for 10 min. DCFC: PhMe gave unreacted C_{60} (35.0 mg, 35 %); PhMe/EtOAc 85:15 gave monoadduct **17c** (48 mg, 29 %). IR (ATR / cm^{-1}): 3360, 3063, 2926, 2867, 1709, 1530,

1348, 1248, 1171, 1121; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm): 8.67 (1H, *brs*, $HC(2)_{ar}$), 8.21 (2H, *brdd*, J = 8.5 Hz & 2.0 Hz, $HC(4,6)_{ar}$), 7.62 (1H, *t*, J = 7.5 Hz, $HC(5)_{ar}$), 5.20 (1H, *s*, HC_{pyrr}), 5.14 (d, J = 9.5 Hz, 1H, H_2C_{pyrr}), 4.96 (br s, 1H, NHBoc), 4.19 (d, J = 9.5 Hz, 1H, H_2C_{pyrr}), 3.84 (t, J = 6.5 Hz, 2H, $H_2C(3)$), 3.75-3.67 (m, 4H, $H_2C(5,6)$), 3.67-3.57 (m, 4H, $H_2C(8,9)$), 3.54 (t, J = 6 Hz, 2H, $H_2C(11)$), 3.29 (dt, J = 12.0, 8.0 Hz,1H, HC(1)), 3.24 (br q, J = 6.0 Hz, 2H, $H_2C(13)$), 2.72-2.66 (1H, *m*, HC(1)), 2.31-2.16 (2H, *m*, $H_2C(2)$), 1.77 (2H, *quint*, J = 6.0 Hz, $H_2C(12)$), 1.44 (9H, *s*, H_3C); ^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm): 156.16, 156.11 (**C**OO^{t}Bu), 153.75, 152.58, 152.08, 148.57 $(C(3)_{ar}$, from HMBC), 147.52, 147.48, 146.47, 146.39, 146.36, 146.31, 146.23, 146.13, 145.79, 145.72, 145.62, 145.56, 145.53, 145.46, 145.37, 144.89, 144.63, 144.60, 144.48, 143.32, 143.19, 142.89, 142.78, 142.70, 142.40, 142.33, 142.29, 142.22, 142.20, 142.16, 141.96, 141.93, 140.44, 140.42, 140.26, 140.04 $(C(1)_{ar}$, 139.62, 137.35, 136.44, 136.26, 135.74, 135.56 $(C(6)_{ar})$, 129.79 $(C(5)_{ar})$, 124.34 $(C(2)_{ar})$, 123.77 $(C(4)_{ar})$, 81.63 (CH_{pyrr}), 79.06 (C(^{t}Bu)), 76.29 (sp^3-C_{60})), 70.82 & 70.75 (C(6,8)), 70.51 & 70.38 (C(5,9)), 69.73 (C(11)), 69.18 (C(3)), 68.93 (sp^3-C_{60}), 66.86 (H_2C_{pyrr}), 50.09 (C(1)), 38.72 (C(13)), 29.81 (C(12)), 28.62 (CH_3), 28.45 (C(2)); UV/Vis (CH_2Cl_2, λ_{max} / nm (ε / mol^{-1}dm^{3}cm^{-1})): 256 (156900), 311 (51800), 431 (5500), 702 (800); HRMS (ESI/TOF): *m/z* calcd for $(C_{83}H_{37}N_3O_7$+Na)$^+$: 1210.2535. Found: 1210.2506.

*Monoadduct **18c***. A suspension of C_{60} (101 mg, 0.140 mmol), amino acid **4c** (53.1 mg, 0.140 mmol) and 4-nitrobenzaldehyde (110 mg, 0.728 mmol) in PhMe (100 mL) was heated at reflux for 15 min. DCFC: PhMe gave unreacted C_{60} (35.0 mg, 35 %); PhMe/EtOAc 80:20 gave monoadduct **18c** (73.8 mg, 44 %). IR (ATR / cm^{-1}): 3341, 2925, 2865, 1703, 1520, 1343, 1249, 1168, 1103; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm): 8.29 (2H, *d*, J = 9.0 Hz, $HC(3,5)_{ar}$), 8.03 (2H, *brs*, $HC(2,6)_{ar}$), 5.20 (1H, *s*, HC_{pyrr}), 5.14 (1H, *d*, J = 9.5 Hz, H_2C_{pyrr}), 4.96 (1H, *brs*, NHBoc), 4.18 (1H, *d*, J = 9.5 Hz, H_2C_{pyrr}), 3.88-3.80 (2H, *m*, $H_2C(3)$), 3.75-3.69 (4H, *m*, $H_2C(5,6)$), 3.69-3.58 (4H, *m*, $H_2C(8,9)$), 3.55 (2H, *t*, J = 6 Hz, $H_2C(11)$), 3.30 (1H, *dt*, 8.5 Hz, J = 12.0, HC(1)), 3.24 (2H, *brq*, J = 5.5 Hz, $H_2C(13)$), 2.71-2.64 (1H, *m*, HC(1)), 2.29-2.17 (2H, *m*, $H_2C(2)$), 1.77 (2H, *quint*, J = 6 Hz, $H_2C(12)$), 1.44 (9H, *s*, H_3C); ^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm): 156.01, 155.90 (**C**OO^{t}Bu), 153.63, 152.36, 151.99, 147.96 $(C_{ar}(4))$, 147.37, 147.34, 146.33, 146.22, 146.18, 145.99, 145.63, 145.57, 145.40, 145.34, 145.32, 145.23, 145.00 $(C(1)_{ar})$, 144.73, 144.52, 144.44, 144.33, 143.20, 143.05, 142.76, 142.64, 142.58, 142.23, 142.17, 142.14, 142.08, 142.04, 141.98, 141.94, 141.82, 141.78, 141.72, 141.59, 140.29, 139.99, 139.53, 137.07, 136.23, 136.10, 135.56, 130.24 $(C_{ar}(2,6))$, 123.82 $(C_{ar}(3,5))$, 81.55 (CH_{pyrr}), 78.91 (C(^{t}Bu)), 76.13 (sp^3-C_{60})), 70.72 & 70.65 (C(6,8)), 70.37 & 70.25 (C(5,9)), 69.59 (C(11)), 68.96 (C(3)), 68.89 (sp^3-C_{60}), 66.74 (H_2C_{pyrr}), 49.88 (C(1)), 38.56 (C(13)), 29.66 (C(12)), 28.47 (CH_3), 28.30 (C(2)); UV/Vis (CH_2Cl_2, λ_{max} / nm (ε mol^{-1} dm^3 cm^{-1})): = 323 (37996), 421 (3443), 700 nm (356); HRMS(ESI/TOF): *m/z* calcd for $(C_{83}H_{37}N_3O_7$ +H)$^+$: 1188.2704. Found: 1188.2689.

*Difullerene diamide **19a***. a) Starting from the protected amine derivative **5a** (20.0 mg, 0.021 mmol), the TFA salt (20.0 mg) was obtained; b) TFA salt (20.0 mg), pyridine (160 μL), DMAP (7.9 mg, 0.065 mmol), isophthaloyl chloride (8.45 mg, 0.042 mmol) in dry CH_2Cl_2 (4 mL) and ODCB (5 mL) were used. Due to extreme insolubility of the reaction product, elution with mixtures of different solvents was carried out. FCC: Elution with PhMe/$CHCl_3$/ODCB/MeOH 5:5:0.5:0.5 gave diamide **19a** (2.0 mg, 10 %). FTIR (ATR, cm^{-1}): 3344, 2926, 1651, 1540, 1431, 1159; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm): 8.21 (1H, *s*, $H_{ar}C(2)$), 7.91 (2H, *dd*, J = 9.2, 1.5 Hz, $H_{ar}C(4,6)$), 7.53 (1H, *t*, J = 7.5 Hz, $H_{ar}C(5)$, 6.30 (2H, brs, NHCO), 4.41 (8H, *s*, H_2C_{pyrr}), 3.56 (4H, *q*, J = 7.0 Hz, $H_2C(6)$), 3.10 (4H, *t*, J = 7.5 Hz,

$H_2C(1)$), 1.97 (4H, *quint*, *J* = 7.0 Hz,), 1.77 (*4H*, quint, *J* = 7.0 Hz), 1.73-1.67 (4H, *m*), 1.65-1.58 (4H, *m*).

Difullerene diamide ***20a***, a) Starting from the protected amine derivative **7a** (20.0 mg, 0.018 mmol), TFA salt (20.0 mg) was obtained; b) TFA salt (20.0 mg, 0.028 mmol), pyridine (1 mL), DMAP (6.6 mg, 0.054 mmol), isophthaloyl chloride (1.83 mg, 0.009 mmol) in dry CH_2Cl_2 (20 mL) were used. Due to extreme insolubility of the reaction product, elution with mixtures of different solvents was carried out. FCC: Elution with PhMe/$CHCl_3$/MeOH 5:5:0.024 gave diamide **20a** (8.5 mg, 44 %). FTIR (ATR / cm^{-1}): 3300, 2921, 1652, 1525, 1459, 1182; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm): 8.22 (1H, *s*, $HC(2)_{ar}$), 7.92 (2H, *dd*, *J* = 9.2 & 2.0 Hz, $HC(4,6)_{ar}$), 7.53 (1H, *t*, *J* = 8.0 Hz, $HC(5)_{ar}$), 6.30 (2H, *brt*, *J* = 5.5 Hz, NHCO), 4.91 (2H, *d*, *J* = 10.0 Hz, H_2C_{pyrr}), 4.13 (2H, *t*, *J* = 5.0 Hz, HC_{pyrr}), 4.12 (2H, *d*, *J* = 10.0 Hz, H_2C_{pyrr}), 3.60-3.51 (4H, *q* at 3.56 ppm, *J* = 7.0 Hz, $H_2C(6)$ overlapped with *m* (2H), HC(1)), 2.90-2.82 (2H, *m*, HC(1)), 2.53-2.43 (2H, *m*, HC(1')), 2.43-2.33 (2H, *m*, HC(1')), 2.03-1.90 (4H, *m*, $H_2C(2)$), 1.90-1.82 (4H, *m*, $H_2C(2')$), 1.78 (4H, *quint*, *J* = 7.0 Hz, $H_2C(5)$), 1.74-1.64 (4H, *m*, $H_2C(3)$), 1.64-1.57 (4H, *m*, $H_2C(4)$), 1.46 (4H, *quint*, *J* = 7.0 Hz, $H_2C(3')$), 1.35 (4H, *brquint*, *J* = 7.5 Hz, $H_2C(4')$), 1.32-1.19 (16H, *m*, $H_2C(5'-8')$), 0.87 (6H, *t*, *J* = 7.0 Hz, $H_3C(9')$). ^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm): 166.56 (CO), 156.75, 155.09, 155.01, 153.75, 147.20, 147.18, 146.74, 146.61, 146.35, 146.26, 146.24, 146.15, 146.07, 146.02, 145.98, 145.94, 145.77, 145.71, 145.60, 145.36, 145.34, 145.28, 145.26, 145.24, 145.21, 145.18, 144.71, 144.59, 144.42, 143.19, 143.07, 142.68, 142.65, 142.61, 142.27, 142.24, 142.23, 142.17, 142.15, 142.12, 142.05, 142.04, 141.82, 141.75, 141.71, 137.08, 136.22, 135.65, 135.50, 135.09 ($C_{ar}(1,3)$), 129.70 ($C(4,6)_{ar}$), 129.00 ($C(5)_{ar}$), 125.33 ($C(2)_{ar}$), 77.34 (CH_{pyrr}, from HSQC), 76.39 (sp^3-C_{60}), 70.79 (sp^3-C_{60}), 66.85 (H_2C_{pyrr}), 52.38 (C(1)), 40.25 (C(6)), 31.92 (C(7')), 31.14 (C(1'), 30.22 (C(3'), 29.72 (C(5)), 29.55 (C(4')), 29.50, 29.30, 28.60 (C(2)), 27.53 (C(2'), 27.38 C(3)), 27.04 (C(4)), 22.70 (C(8')), 14.16 (C(9')). UV/Vis (CH_2Cl_2, λ_{max}/ nm, (ε / $mol^{-1}dm^3cm^{-1}$)): 256 (31200), 309 (10200), 431 (1300).

Difullerene diamide ***21a***. a) Starting from the protected amine derivative **7a** (124 mg, 0.114 mmol), TFA salt (126 mg) was obtained; b) TFA salt (126 mg), pyridine (3 mL), DMAP (40 mg, 0.327 mmol), fumaryl chloride (8.72 mg, 6.2 µL, 0.057 mmol) in dry CH_2Cl_2 (30 mL) were used. FCC: Elution with PhMe/$CHCl_3$/MeOH 4:4:0.2 and subsequent precipitation gave diamide **21a** (17.9 mg, 15 %). IR (ATR, cm^{-1}): 3430, 3305, 2924, 2854, 1730, 1643, 1461; ^{1}H-NMR (500 MHz, $CDCl_3$/CS_2/CD_3OH), δ / ppm: 7.98 (1H, *brt*, *J* = 5.5 Hz, NHCO), 6.82 (1H, *s*, HC=), 4.90 (1H, *d*, *J* = 10 Hz, H_2C_{pyrr}), 4.13 (1H, *t*, *J* = 5.0 Hz, HC_{pyrr}; overlapped at 4.12, with 1H, *d*, *J* = 10.0 Hz, H_2C_{pyrr}), 3.57-3.48 (1H, *m*, HC(1)), 3.38 (2H, *brq*, *J* = 6.5 Hz, $H_2C(6)$), 2.88-2.80 (1H, *m*, HC(1)), 2.53-2.43 (1H, *m*, HC(1')), 2.43-2.32 (1H, *m*, HC(1')), 2.00-1.89 (2H, *m*, $H_2C(2)$), 1.89-1.80 (2H, *m*, $H_2C(2')$), 1.75-1.65 (2H, *m*, $H_2C(5)$), 1.65-1.60 (2H, *m*, $H_2C(3)$), 1.60-1.51 (2H, *m*, $H_2C(4)$), 1.46 (2H, *quin*t, *J* = 7.5 Hz, $H_2C(3')$), 1.39-1.32 (2H, *m*, $H_2C(4')$), 1.32-1.18 (8H, *m*, $H_2C(5'+6'+7'+8')$), 0.87 (3H, *t*, *J* = 7.5 Hz, $H_3C(9')$); ^{13}C-NMR (125 MHz, $CDCl_3$/CS_2/CD_3OH, δ / ppm): = 165.07 (C=O), 156.44, 154.80, 154.73, 153.43, 146.99, 146.97, 146.50, 146.38, 146.11, 146.07, 146.05, 145.95, 145.87, 145.82, 145.77, 145.75, 145.57, 145.46, 145.38, 145.18, 145.08, 145.04, 144.97, 144.52, 144.39, 144.23, 144.21, 143.00, 142.87, 142.48, 142.45, 142.41, 142.06, 142.02, 141.97, 141.92, 141.89, 141.86, 141.63, 141.57, 141.52, 140.06, 140.01, 139.65, 139.42, 136.92, 136.06, 135.47, 135.29, 132.41 (CH=)), 77.20 (CH_{pyrr}), 76.13 (sp^3-C_{60}), 70.51 (sp^3-C_{60}), 66.69 (H_2C_{pyrr}), 52.39 (C(1)), 39.81 (C(6)), 31.81 (C(7')), 30.99 (C(1')), 30.12 (C(3'), 29.46 (C(4')), 29.40 (C(5')), 29.20 and 29.13 (C(5), C(6')), 28.54 (C(2)), 27.43 (C(2')), 27.37

(C(3)), 26.97 (C(4)), 22.62 (C(8')), 14.00 (C(9')); UV/Vis (CH_2Cl_2, λ_{max} nm / (ε / mol^{-1}dm^{3}cm^{-1})): 256 (51700), 319 (16800), 431 (1600).

*Difullerene diamide **22c**.* a) Starting from the protected amine derivative **11c** (112.7 mg, 0.106 mmol), TFA salt was obtained; b) TFA salt, pyridine (3.3 mL), DMAP (38.1 mg, 0.312 mmol), fumaryl chloride (7.97 mg, 5.63 μL, 0.052 mmol) in dry CH_2Cl_2 (60 mL) were used. FCC: Elution with $CHCl_3$/MeOH 100:1 and subsequent precipitation gave diamide **22c** (24.5 mg, 23 %). IR (ATR, cm^{-1}): 3370, 2921, 2855, 1732, 1640, 1541, 1370, 1336, 1093; ^{1}H-NMR ($CDCl_3$, 500 MHz, δ / ppm): 6.99 (2H, *brs*, NHCO), 6.91 (2H, *s*, HC=CH), 4.41 (8H, *s*, H_2C_{pyrr}), 3.84 (4H, *brt*, *J* = 6.5 Hz, $H_2C(3)$), 3.81-3.76 (8H, *m*, $H_2C(5,6)$), 3.75-3.60 (12H, *m*, $H_2C(8,9,11)$), 3.56-3.48 (4H, *m*, $H_2C(13)$), 3.17 (4H, *t*, *J* = 7.0 Hz, $H_2C(1)$), 2.21 (4H, *quint*, *J* = 7.0 Hz, $H_2C(2)$), 1.90-1.80 (4H, *m*, $H_2C(12)$); ^{13}C-NMR ($CDCl_3$, 125 MHz, δ / ppm): 164.43 (CO), 155.25, 147.46, 146.40, 146.26, 146.22, 145.86 145.56, 145.45, 144.73, 143.26, 142.79, 142.41, 142.23, 142.04, 140.31, 136.39, 133.27 (CH=), 70.87 (sp^3-C_{60}), 70.81 and 70.68 (C(6,8)), 70.58 & 70.46 (C(5,9)), 70.21 (C(11)), 69.59 (C(3)), 68.11 (H_2C_{pyrr}),51.91 (C(1)), 38.82 (C(13)), 29.12 (C(2)), 28.71 (C(12)); UV-Vis (CH_2Cl_2, λ_{max} / nm (ε / mol^{-1}dm^{3}cm^{-1})): 256 (134100), 322 (42600), 431 (6600), 702 (1500); HRMS (ESI/TOF): *m/z* calcd for $(C_{148}H_{52}N_4O_8+H)^+$: 2013.3869. Found: 2013.3870.

*Difullerene diamide **23c**.* a) Starting from the protected amine derivative **12c** (135.6 mg, 0.119 mmol), TFA salt was obtained; b) TFA salt, pyridine (3.84 mL), DMAP (43.4 mg, 0.355 mmol), fumaryl chloride (9.06 mg, 6.4 μL, 0.059 mmol) in dry CH_2Cl_2 (80 mL) were used. FCC: Elution with $CHCl_3$/MeOH 100:1.2 and subsequent precipitation gave diamide **23c** (39.3 mg, 31 %). IR (ATR, cm^{-1}): 3291, 3077, 3003, 2925, 2868, 1634, 1550, 1461, 1246, 1116; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm): = 7.79 (4H, *brs*, $HC(2,6)_{ar}$), 7.40 (4H, *t*, *J* = 7.5 Hz, $HC(3,5)_{ar}$), 7.32 (2H, *t*, *J* = 7.5, $HC(4)_{ar}$), 6.90 (2H, *t*, *J* = 5.5, NH), 6.87 (2H, *s*, HC=), 5.10 (2H, *d*, *J* = 9.5 Hz, H_2C_{pyrr}), 5.07 (2H, *s*, HC_{pyrr}), 4.13 (2H, *d*, *J* = 9.5 Hz, H_2C_{pyrr}), 3.89-3.75 (4H, *m*, $H_2C(3)$), 3.75 (8H, *s*, $H_2C(5,6)$), 3.70-3.65 (8H, *m*, $H_2C(8,9)$), 3.60 (4H, *t*, *J* = 6 Hz, $H_2C(11)$), 3.53-3.46 (4H, *m*, $H_2C(13)$), 3.34 (2H, *dt*, *J* = 12.0 Hz & 8.5 Hz, HC(1)), 2.67-2.60 (2H, *m*, HC(1)), 2.28-2.12 (4H, *m*, $H_2C(2)$), 1.82 (4H, *quint*, *J* = 5.5 Hz, $H_2C(12)$); ^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm): 164.38 (CO), 156.70, 153.65, 153.62, 147.47, 146.46, 146.38, 146.29, 146.09, 145.91, 145.65, 145.48, 145.44, 145.37, 145.30, 144.57, 144.55, 143.15, 142.72, 142.44, 142.32, 142.26, 142.18, 142.14, 141.97, 141.84, 140.34, 140.30, 139.99, 139.54, 139.39, 138.88, 137.39 ($C_{ar}(1)$), 136.91, 136.68, 136.01, 135.89, 133.24 (HC=), 129.65 ($C_{ar}(2,6)$), 128.75 ($C_{ar}(3,5)$), 128.62 (*p*-$C_{ar}(4)$), 82.67 (CH_{pyrr}), 76.86 (sp^3-C_{60}, from HMBC), 70.81, 70.70, 70.57 and 70.46 (C(5,6,8,9)), 70.26 (C(11)), 69.57 (C(3)), 69.06 (sp^3-C_{60}), 66.98 (H_2C_{pyrr}), 49.96 (C(1)), 38.85 (C(13)), 28.68 (C(12)), 28.55 (C(2)); UV/Vis (CH_2Cl_2, λ_{max} / nm (ε / mol^{-1}dm^{3}cm^{-1})): =256 (124500), 307 (41900), 431 (5200), 702 (900); HRMS (ESI/TOF): *m/z* calcd for $(C_{160}H_{60}N_4O_8+Na)^+$: 2187.4314. Found: 2187.4258.

*Difullerene diamide **24c**.* a) Starting from the protected amine derivative **13c** (120 mg, 0.102 mmol), TFA salt was obtained; b) TFA salt, pyridine (3.2 mL), DMAP (36.9 mg, 0.302 mmol), fumaryl chloride (7.72 mg, 5.46 μL, 0.050 mmol) in dry CH_2Cl_2 (32 mL) were used. FCC: Elution with $CHCl_3$/MeOH 100:0.25 and subsequent precipitation gave diamide **24c** (20 mg, 18 %). IR (ATR, cm^{-1}): 3286, 3071, 3003, 2920, 2863, 2803, 1631, 1549, 1456, 1428, 1333, 1178, 1118, 979; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm): 7.96 (2H, *brd*, *J* = 7.5 Hz, $HC(6)_{ar}$), 7.26 (2H, *brt*, *J* = 7.0 Hz, $HC(4)_{ar}$), 7.06 (2H, *t*, *J* = 7.5 Hz, $HC(5)_{ar}$), 6.92 (2H, *brd*, *J* = 7.0 Hz, $HC(3)_{ar}$), 6.88 (2H, *s*, CH=), 6.87 (1H, *brs*, NHCO), 5.69 (2H, *s*, HC_{pyrr}), 5.08 (2H, *d*, *J* = 9.5 Hz, H_2C_{pyrr}), 4.15 (2H, *d*, *J* = 9.0 Hz, H_2C_{pyrr}), 3.89-3.74 (4H, *m*, $H_2C(3)$), 3.70 (6H, *s*, OCH_3), 3.78-3.72 (8H, *m*, $H_2C(5,6)$), 3.70-3.53 (8H, *m*, $H_2C(8,9)$), 3.60 (4H, *brt*

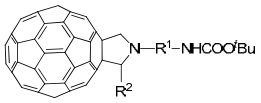
(overlapped with *m*), *J* = 5.0 Hz , $H_2C(11)$), 3.54-3.43 (4H, *m*, $H_2C(13)$), 3.39-3.31 (2H, *m*, H-C(1)), 2.64-2.56 (2H, *m*, H-C(1)), 2.28-2.12 (4H, *m*, $H_2C(2)$), 1.87-1.77 (4H, *m*, $H_2C(12)$); ^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm): 164.40 (C=O), 158.34 $(C(2)_{ar})$, 157.24, 155.28, 154.47, 154.25, 147.43, 146.95, 146.72, 146.38, 146.36, 146.31, 146.25, 146.20, 146.09, 146.05, 145.74, 145.69, 145.43, 145.39, 145.36, 145.23, 145.21, 145.16, 144.73, 144.58, 144.5, 143.19, 143.14, 142.77, 142.70, 142.68, 142.47, 142.44, 142.32, 142.24, 142.23, 142.12, 141.97, 141.86, 141.69, 140.34, 140.28, 139.54, 139.51, 136.70, 136.54, 136.32, 134.69, 133.22 (CH=), 130.13 $(C(6)_{ar})$, 129.12 $(C(4)_{ar})$, 125.93 $(C(1)_{ar})$, 121.22 $(C(5)_{ar})$, 111.19 ($C(3_{ar})$, 76.16 (sp^3-C_{60}), 74.45 (CH_{pyrr}), 70.82, 70.71, 70.44 and 70.27 (C(5,6,8,9)), 70.55 (C(11)), 69.61 (C(3)), 69.32 (sp^3-C_{60}), 66.84 (H_2C_{pyrr}), 55.34 (OCH_3), 50.03 (C(1)), 38.77 (C(13)), 28.72 (C(12)), 28.60 (C(2)); UV/Vis (CH_2Cl_2, λ_{max} / nm (ε / $mol^{-1}dm^3cm^{-1}$)): 254 (204500), 431 (8000), 702 (600); HRMS (ESI/TOF): *m/z* calcd for $(C_{162}H_{64}N_4O_{10}+Na)^+$: 2247.4526. Found: 2247.4523.

Difullerene diamide ***25c***. a) Starting from the protected amine derivative **14c** (120 mg, 0.102 mmol), TFA salt was obtained; b) TFA salt, pyridine (3.2 mL), DMAP (36.9 mg, 0.302 mmol), fumaryl chloride (7.72 mg, 5.46 μL, 0.050 mmol) in dry CH_2Cl_2 (32 mL) were used. FCC: Elution with $CHCl_3$/MeOH 100:0.25 and subsequent precipitation gave diamide **25c** (20.6 mg, 18 %). IR (ATR, cm^{-1}): 3366, 2952, 1711, 1603, 1512, 1458, 1363, 1173, 1122, 1045; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm): 7.36 (4H, *brs*, $HC(2,6)_{ar}$), 7.31 (2H, *t*, *J* = 7.5 Hz, $HC(5)_{ar}$), 6.92 (1H, *brs*, NHCO), 6.88 (2H, *s*, CH=), 6.85 (2H, *brd*, *J* = 8.5 Hz, $HC(4)_{ar}$), 5.08 (2H, *d*, *J* = 9.5 Hz, H_2C_{pyrr}), 5.03 (2H, s, HC_{pyrr}), 4.16 (2H, *d*, *J* = 9.5 Hz, H_2C_{pyrr}), 3.90-3.72 (4H, *m*, $H_2C(3)$), 3.80 (3H, *s*, OCH_3), 3.78-3.72 (8H, *m*, $H_2C(5,6)$), 3.70-3.53 (8H, *m*, $H_2C(8,9)$), 3.60 (4H, *brt* (overlapped with *m*), *J* = 4.5 Hz , $H_2C(11)$), 3.53-3.43 (4H, *m*, $H_2C(13)$), 3.38-3.31 (2H, *m*, H-C(1)), 2.68-2.59 (2H, *m*, H-C(1)), 2.28-2.08 (4H, *m*, $H_2C(2)$), 1.87-1.75 (4H, *m*, $H_2C(12)$); ^{13}C-NMR (125 MHz, $CDCl_3$, δ /ppm): 164.38 (C=O), 159.90 $(C(3)_{ar})$, 156.60, 154.36, 153.79, 153.60, 147.46, 147.07, 146.62, 146.46, 146.41, 146.37, 146.31, 146.26, 146.24, 146.09, 145.91, 145.69, 145.48, 145.45, 145.42, 145.39, 145.36, 145.29, 144.87, 144.78, 144.55, 143.31, 143.14, 142.84, 142.72, 142.43, 142.41, 142.29, 142.27, 142.22, 142.17, 142.15, 142.08, 141.95, 141.83, 141.70, 140.34, 140.28, 139.96 $(C(1)_{ar})$, 139.61, 139.01, 136.74, 136.71, 135.98, 135.88, 133.24 (CH=), 129.73 $(C(5)_{ar})$, 121.90 $(C(6)_{ar})$, 115.37 ($C(2)_{ar}$, from HMBC), 114.03 $(C(4)_{ar})$, 82.54 (CH_{pyrr}), 76.72 (sp^3-C_{60}), 70.80, 70.69, 70.42 and 70.26 (C(5,6,8,9)), 70.55 (C(11)), 69.60 (C(3)), 69.05 (sp^3-C_{60}), 66.94 (H_2C_{pyrr}), 55.54 (OCH_3), 50.06 (C(1)), 38.77 (C(13)), 28.71 (C(12)), 28.54 (C(2)); UV/Vis (CH_2Cl_2, λ_{max} / nm (ε / $mol^{-1}dm^3cm^{-1}$)): 254 (101900), 431 (3900), 702 (200); HRMS (ESI/TOF): *m/z* calcd for $(C_{162}H_{64}N_4O_{10}+Na)^+$: 2247.4526. Found: 2247.4572.

Difullerene diamide ***26c***. a) Starting from the protected amine derivative **15c** (64.2 mg, 0.055 mmol), TFA salt (74.7 mg) was obtained; b) TFA salt (74.7 mg, 0.063 mmol), pyridine (2 mL), DMAP (23.1 mg, 0.189 mmol), fumaryl chloride (4.81 mg, 3.4 μL, 0.031 mmol) in dry CH_2Cl_2 (30 mL) were used. FCC: Elution with PhMe/$CHCl_3$/MeOH 2:6:0.2 and subsequent precipitation gave diamide **26c** (8.9 mg, 15 %). IR (ATR, cm^{-1}): 3309, 3078, 2954, 2923, 2868, 1724, 1649, 1341, 1099; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 7.69 (2H, brs, $HC(2,6)_{ar}$), 6.93 (2H, *d*, *J* = 8.5 Hz, $HC(3,5)_{ar}$), 6.90 (1H, brs, NHCO), 6.88 (1H, *s*, CH=), 5.07 (1H, *d*, *J* = 9 Hz, H_2C_{pyrr}), 5.01 (1H, *s*, HC_{pyrr}), 4.10 (1H, *d*, *J* = 9 Hz, H_2C_{pyrr}), 3.88-3.81 (2H, *m*, $H_2C(3)$), 3.80 (3H, *s*, OCH_3), 3.78-3.72 (4H, *m*, $H_2C(5,6)$), 3.70-3.57 (4H, *m*, $H_2C(8,9)$), 3.61 2H, (t (overlapped with *m*), *J* = 5.5 Hz , $H_2C(11)$), 3.49 (2H, *quint*, *J* = 5 Hz, $H_2C(13)$), 3.34-3.27 (1H, *m*, H-C(1)), 2.64-2.57 (1H, *m*, H-C(1)), 2.26-2.11 (2H, *m*, $H_2C(2)$), 1.82 (2H, *quint*, *J* = 6 Hz, $H_2C(12)$); ^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm): 164.22 (C=O),

159.53 (*p*-C_{ar}), 156.65, 154.24, 153.73, 153.68, 147.30, 146.83, 146.53, 146.35, 146.29, 146.25, 146.21, 146.14, 146.12, 146.09, 145.92, 145.75, 145.54, 145.45, 145.31, 145.26, 145.21, 145.12, 144.71, 144.63, 144.40, 143.14, 142.98, 142.67, 142.54, 142.32, 142.28, 142.11, 142.00, 141.80, 141.67, 141.51, 140.15, 140.11, 139.88, 139.51, 136.74, 136.53, 135.78, 135.75, 133.08 (CH=), 130.58 (C_{ar}(2,6), 129.18 (C_{ar}(1)), 113.94 (C_{ar}(3,5)), 82.00 (CH_{pyrr}), 76.90 (sp^3-C_{60}, from HMBC), 70.65, 70.54, 70.41, 70.27 (C(5, 6, 8, 9)), 70.09 (C(11)), 69.46 (C(3)), 68.81 (sp^3-C_{60}), 66.77 (H_2C_{pyrr}), 55.21 (OCH_3), 49.73 (C(1)), 38.62 (C(13)), 28.55 (C(12)), 28.37 (C(2)); UV/Vis (CH_2Cl_2, λ_{max} / nm (ε / $mol^{-1}dm^3cm^{-1}$)): 318 (30630), 327 (29350), 431 (4020); HRMS (ESI/TOF): *m/z* calcd for $(C_{162}H_{64}N_4O_{10}+Na)^+$: 2247.4526. Found: 2247.4492.

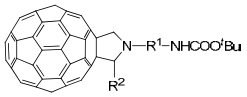
TABLE S-I. ^{1}H- and ^{13}C-NMR chemical shifts of characteristic signals of fullerene monoadducts **6**–**10**



^{1}H/^{13}C		**6a**	**7a**	**8b**	**9b**	**10b**
		Chemical shifts, ppm				
	R^1	$(CH_2)_6$[1]			$(CH_2)_{10}$[1]	
	R^2	4-MeO-C_6H_4	C_9H_{19}[2]	C_6H_5	4-MeO-C_6H_4	4-NO_2-C_6H_4
HC(2)$_{pyrr}$		5.00s, 82.25	4.13t, 77.41	5.06s, 82.59	5.01s, 82.10	5.18s, 81.66
H_2C(5)$_{pyrr}$	**pyrr.**	5.07d/4.10d 67.01	4.90d/4.12d 66.88	5.10d/4.12d 66.89	5.08d/4.10d 66.86	5.14d/4.17d 66.87
H_2C(1)		3.24-3.12m 2.57-2.49m 53.06	3.56-3.49m 2.87-2.80m 52.46	3.27-3.19m 2.58-2.52m 53.12	3.24-3.17m 2.56-2.49m 53.02	3.15-3.03m 2.64-2.56m 53.38
H_2C(6)		3.24-3.12m 40.82	3.20brq, 40.61	-	-	-
H_2C(10)	**R^1**			3.20br q, 40.65	3.12br q, 40.47	3.15-3.03m, 40.64
NH		4.55br s	4.57br s	4.50br s	4.50br s	4.51br s
CO		156.16	156.01	155.97	155.98	156.00
^{t}Bu		1.46s 28.62 79.23	1.56s 28.46 79.13	1.45s 28.44 79.00	1.45s 28.45 79.01	1.45s 28.44 79.02
H_2C(1')		-	2.52-2.43m 2.43-2.34m 31.14	-	-	-
H_3C(9')		-	0.87t, 14.14	-	-	-
C_{ar}(1)		-	-	137.40	129.36	145.43
HC$_{ar}$(2,6)	**R^2**	7.70br s 130.73	-	7.81br s 129.48	7.72br s 130.58	8.03br s 130.21
HC$_{ar}$(3,5)		6.94d 114.11	-	7.41t 128.57	6.94d 113.92	8.29d 123.85
HC$_{ar}$(4)		- 159.70	-	7.32tt 128.39	- 159.50	- 145.43
MeO		3.81s 55.36	-	-	3.81s 55.20	-

[1]C atoms of R^1 substituent (hexamethylene and decamethylene) are numbered starting from the *N*-pyrrolidine ring; [2]C atoms of the nonyl-group, presented as C', are numbered starting from the pyrrolidine C(2) atom

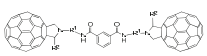
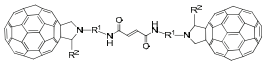
TABLE S-II. ^{1}H- and ^{13}C-NMR chemical shifts of characteristic signals of the fullerene monoadducts **11c-18c**



^{1}H/^{13}C		**11c**	**12c**	**13c**	**14c**	**15c**	**17c**	**18c**
		Chemical shifts, ppm						
	R[1]	$(CH_2)_3O(CH_2)_2O(CH_2)_2O(CH_2)_3$						
	R[2]	H	C_6H_5	2-MeO-C_6H_4	3-MeO-C_6H_4	4-MeO-C_6H_4	3-NO_2-C_6H_4	4-NO_2-C_6H_4
$HC(2)_{pyrr}$	**pyr r.**	4.42s	5.08s 82.52	5.70s 74.45	5.04s 82.56	5.02s 82.01	5.20s 81.63	5.20s 81.55
$H_2C(5)_{pyrr}$			5.11d/4.14d 66.82	5.09d/4.17d 66.85	5.10d/4.13d 66.95	5.08d/4.12d 66.77	5.14d/4.19d 66.86	5.14d/4.18d 66.74
$H_2C(1)$		3.20t 51.89	3.36dt 2.68-2.61m 49.79	3.37dt 2.65-2.58m 50.00	3.38dt 2.69-2.61m 50.01	3.33dt 2.65-2.58m 49.68	3.29dt 2.72-2.66 50.09	3.30dt 2.71-2.64m 49.88
$H_2C(13)$		3.28-3.22m 38.77	3.27-3.20m 38.61	3.24br q 38.78	3.24br q 38.77	3.24br q 38.59	3.24br q 38.72	3.24br q 38.56
H_2C-O (6C-O)	**R[1]**	3.88-3.53 68-71	3.90-3.50 69-71	3.75-3.53 70-71	3.90-3.50 69-71	3.90-3.50 69-71	3.90-3.50 68-71	3.90-3.50 68-71
NH		5.00br s	4.97br s	4.98br s	4.98br s	4.99br s	4.96br s	4.96br s
CO		156.20	156.03	156.19	156.18	156.02	156.11	155.90
^{t}Bu		1.45 28.65	1.45s 28.48 78.92	1.45s 28.64 79.07	1.45s 28.63 79.07	1.44s 28.47 78.90	1.44s 28.62 79.06	1.44s 28.47 78.91
$C_{ar}(1)$		-	137.20	125.92	138.99	129.15	140.04	145.00
$HC_{ar}(2)$		-	7.79br s 129.48	- 158.34	7.36 br s 114.94	7.70br s 130.57	8.67br s 124.34	8.03br s 130.24
$HC_{ar}(3)$		-	7.41t 128.57	6.91d 111.17	- 159.94	6.93d 113.88	- 148.57	8.29d 123.82
$HC_{ar}(4)$	**R[2]**	-	7.32tt 128.45	7.27td 129.11	6.86br d 114.00	- 159.53	8.21br dd 123.77	- 145.00
$HC_{ar}(5)$		-		7.06t 121.20	7.31t 129.71		7.62t 129.79	
$HC_{ar}(6)$		-		7.97dd 130.14	7.36br s 122.15		8.21br dd 135.56	
MeO		-	-	3.71 55.33	3.81s 55.51	3.80s 55.19	-	-

C atoms of R^1 substituent (4,7,10-trioxatridecamethylene) are numbered starting from the *N*-pyrrolidine ring.

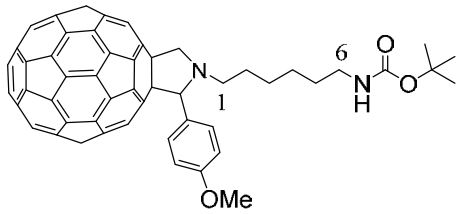
TABLE S-III. ^{1}H- and ^{13}C-NMR chemical shifts of characteristic signals of difullerene diamides **19-26**

$^{1}H/^{13}C$		**19a***	**20a**	**21a**	**22c**	**23c**	**24c**	**25c**	**26c**
		Chemical shifts, ppm							
	R^1	$(CH_2)_6$	$(CH_2)_6$		$(CH_2)_3O(CH_2)_2O(CH_2)_2O(CH_2)_3$				
	R^2	H	C_9H_{19}	C_9H_{19}	H	C_6H_5	2-MeO-$-C_6H_4$	3-MeO-$-C_6H_4$	4-MeO-$-C_6H_4$
$HC(2)_{pyrr}$	**pyrr.**	4.41s -	4.13t 77.34	4.13t 77.20	4.41s 68.11	5.07s 82.67	5.69s 74.45	5.03s 82.54	5.01s 82.00
$H_2C(5)_{pyrr}$			4.91d/4.12d 66.85	4.90d/4.13d 66.69		5.10d/4.13d 66.98	5.08d/4.15d 66.84	5.08d/4.16d 66.94	5.07d/4.10d 66.77
$H_2C(1)$		3.10t -	2.90-2.82m 52.38	3.57-3.48m 2.88-2.80m 52.39	3.17t 51.91	3.38-3.30m 2.67-2.60m 50.00	3.38-3.31m 2.64-2.56m 50.03	3.38-3.31m 2.68-2.59m 50.06	3.34-3.27m 2.64-2.57m 49.73
$H_2C(6)$		3.56q -	3.60-3.51m 40.25	3.38br q 39.81	-	-	-	-	-
$H_2C(13)$	**R^1**	-	-	-	3.56-3.48m 38.82	3.53-3.46m 38.81	3.54-3.43m 38.77	3.53-3.43m 38.77	3.49quint 38.62
H_2C-O (6C)		-	-	-	3.90-3.55 69-71	3.90-3.55 69-71	3.90-3.55 69-71	3.90-3.55 69-71	3.90-3.55m 69-71
NH		6.30br s-	6.30br t	7.98br t	6.99br s	6.90br t	6.87br s	6.92br s	6.90br s
CO			166.56	165.07	164.43		164.40	164.38	164.22
$H_2C(1')$		- - -	2.53-2.43m 2.43-2.33m 31.14	2.53-2.43m 2.43-2.32m 30.99	-	-	-	-	-
$H_3C(9')$		- -	0.87t 14.16	0.87t 14.00	-	-	-	-	-
$C_{ar}(1)$		-	-	-	-	137.39	125.93	139.96	129.18
$HC_{ar}(2)$		-	-	-	-	7.79br s 129.65	- 158.34	7.36br s 115.37	7.69br s 130.58
$HC_{ar}(3)$	**R^2**	-	-	-	-	7.40t 128.75	6.92br d 111.19	- 159.90	6.93d 113.94
$HC_{ar}(4)$		-	-	-	-	7.32t 128.62	7.26br d 129.12	6.85br d 113.89	- 159.53
$HC_{ar}(5)$		-	-	-	-		7.06t 121.22	7.31t 129.73	
$HC_{ar}(6)$		-	-	-	-		7.96br d 130.13	7.36brs 121.90	
MeO		-	-	-	-		3.70s 55.34	3.80s 55.54	3.80s 55.21
HC=CH	**fumaryl or iso-phthaloyl uuus**	-	-	6.82s 132.41	6.91 133.27	6.87s 133.24	6.88 133.22	6.88s 133.24	6.88s 133.08
$C_{ar}(1,3)$		-	- /135.1	-			-	-	-
$HC_{ar}(2)$		8.21s	8.22s/125.3	-			-	-	-
$HC_{ar}(4,6)$		7.91dd	7.92dd/129.7	-			-	-	-
$HC_{ar}(5)$		7.53t	7.53t/129.0	-			-	-	-

* Only the ^{1}H NMR spectrum was recorded due to its low solubility.
C atoms of R^1 substituent ($(CH_2)_6$and 4,7,10-trioxatridecamethylene) are numbered starting from the *N*-pyrrolidine ring.
C atoms of C_9H_{19}-group, presented as C', are numbered starting from the pyrrolidine C(2) atom.

2-Methoxyphenyl-substituted fulleropyrrolidine derivative ***6a***



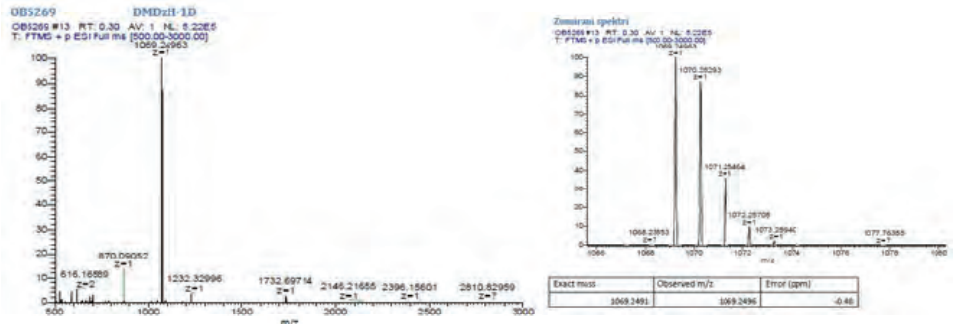


Fig. S-1. Mass spectrum of **6a**.

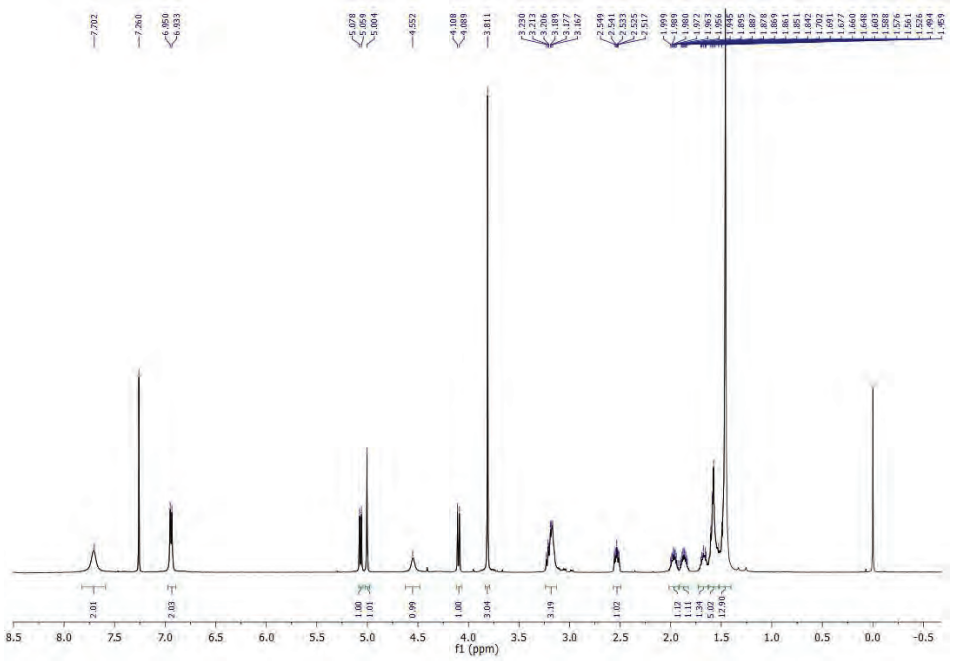


Fig. S-2. ^{1}H-NMR spectrum of **6a**.

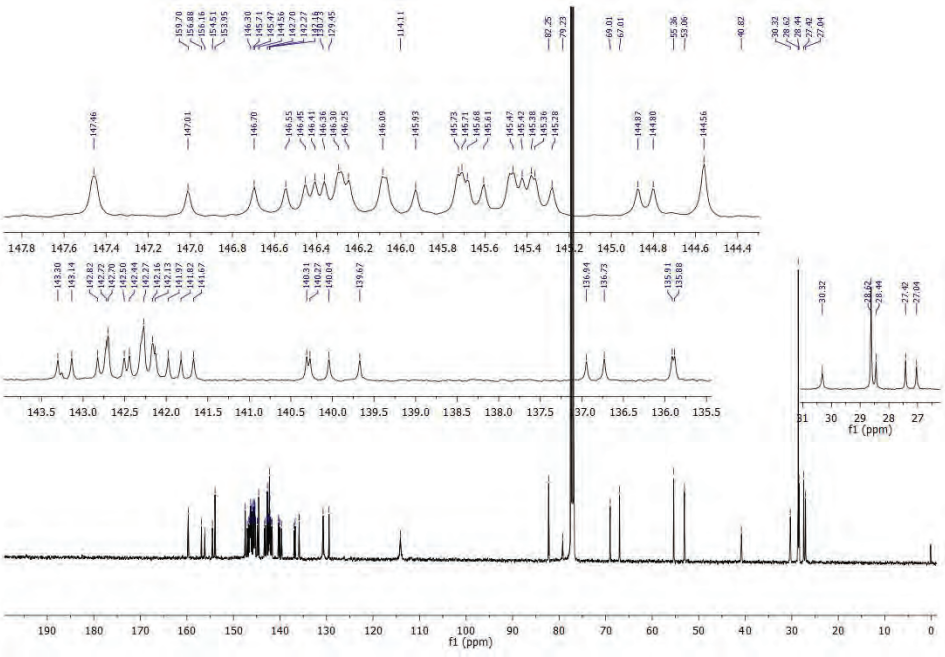


Fig. S-3. ^{13}C-NMR spectrum of **6a**.

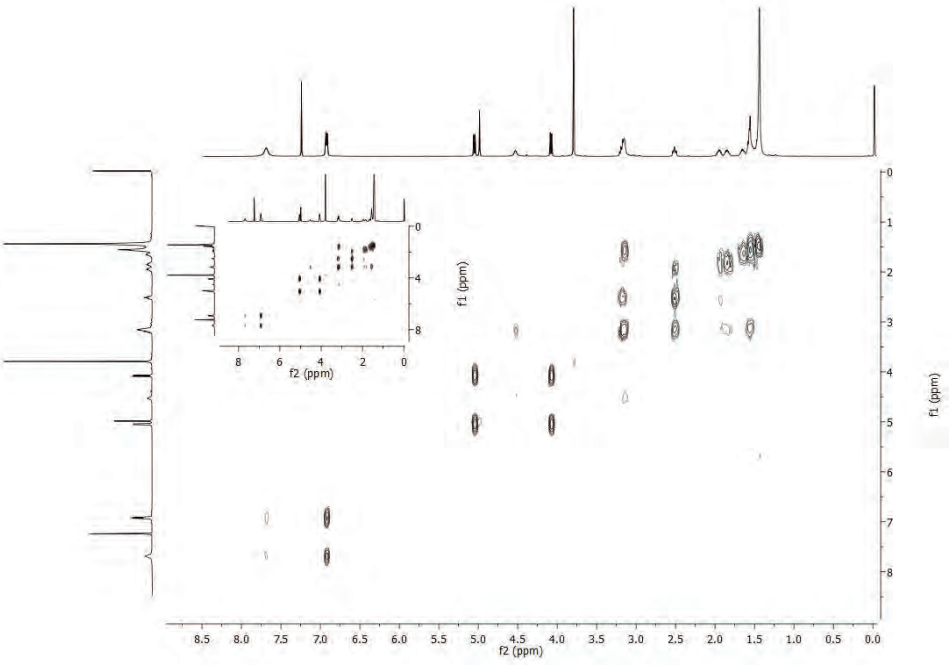


Fig. S-4. COSY spectrum of **6a**.

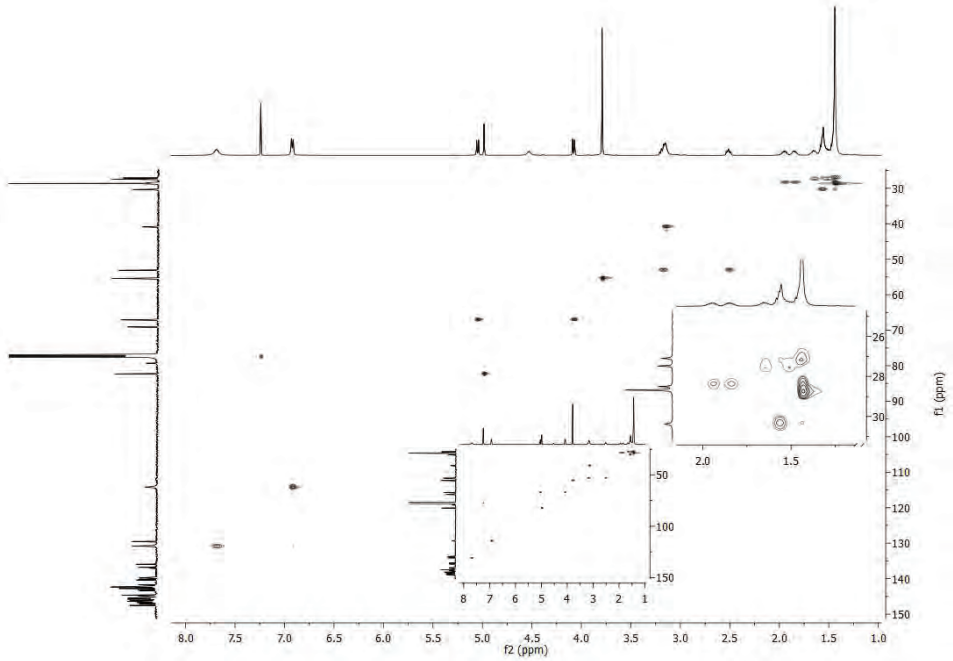


Fig. S-5. HSQC spectrum of **6a**.

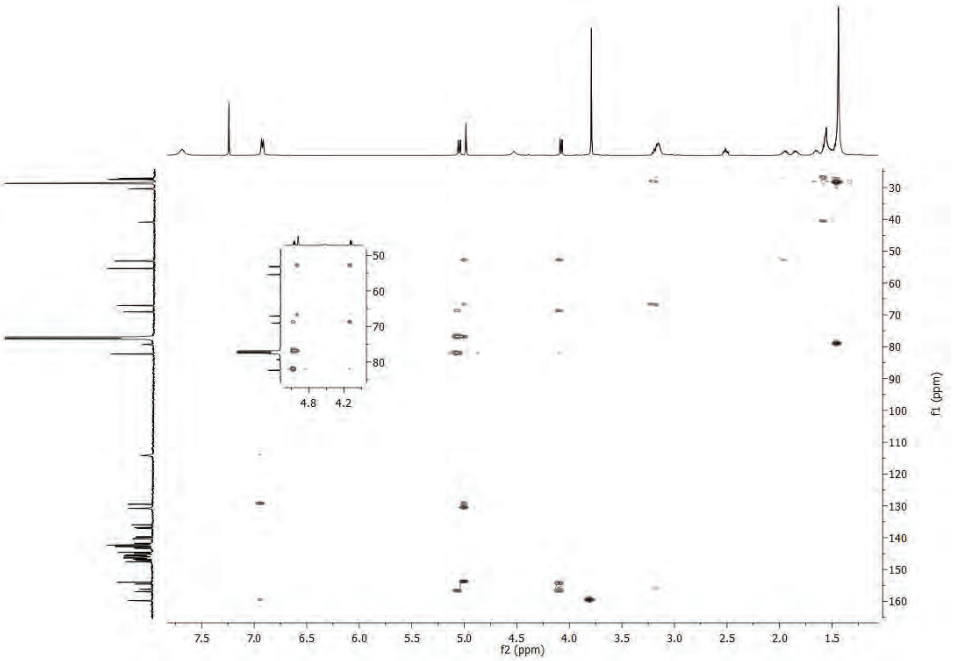
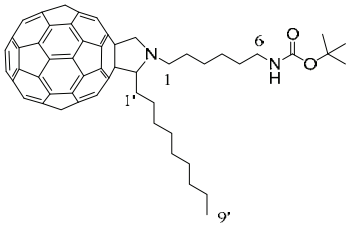
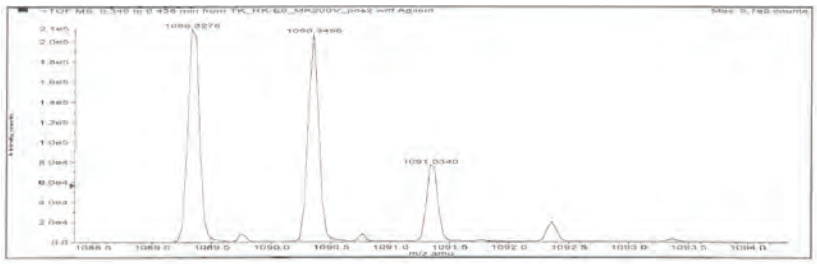


Fig. S-6. HMBC spectrum of **6a**.

Nonyl-substituted fulleropyrrolidine derivative ***7a***





Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C82H44N2O2	–	1088.34028	0.38	1.39537 E6	–

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
(M+H)+	225149.68	1089.34756	1089.34545	-2.10045	-1.94	–

Fig. S-7. Mass spectrum of **7a**.

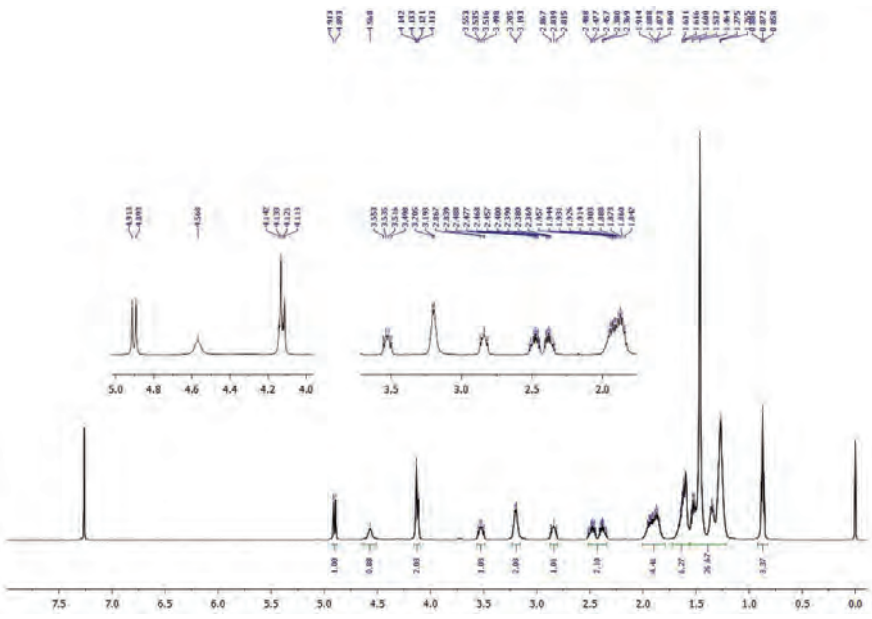


Fig. S-8. ^{1}H-NMR spectrum of **7a**.

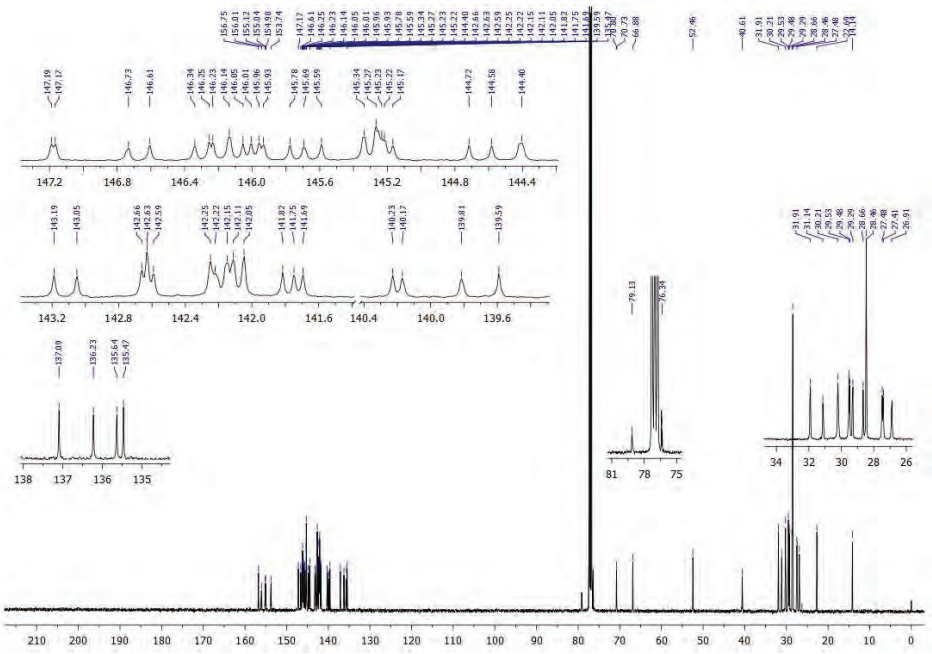


Fig. S-9. ^{13}C-NMR spectrum of **7a**.

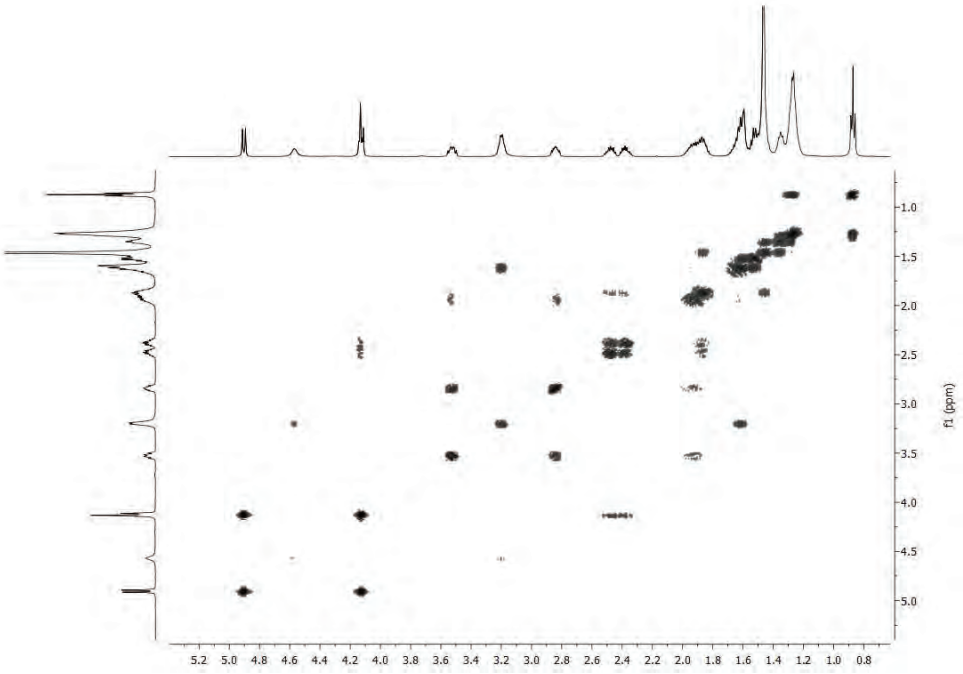


Fig. S-10. COSY spectrum of **7a**.

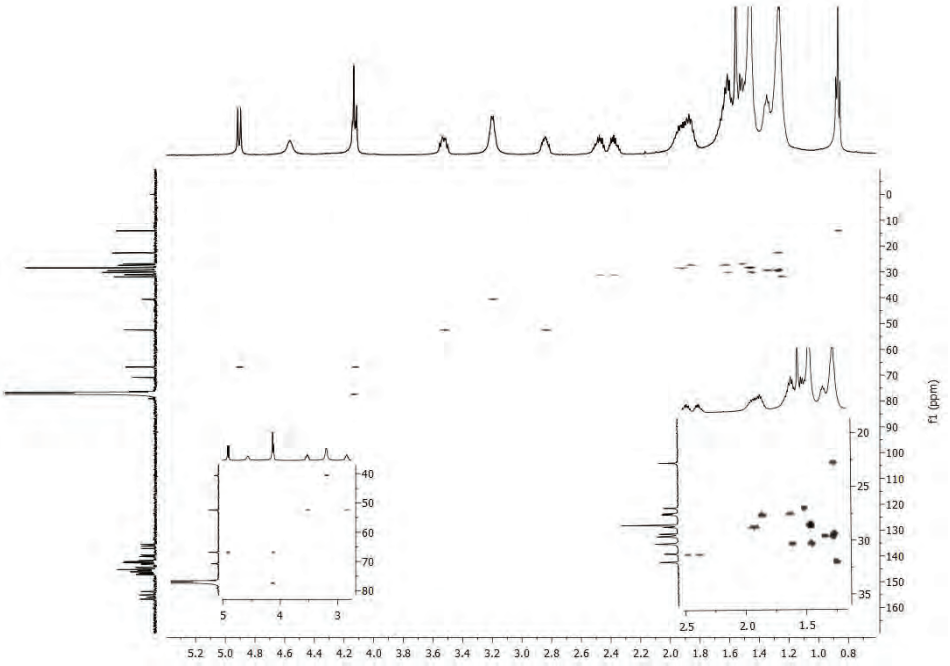


Fig. S-11. HSQC spectrum of **7a**.

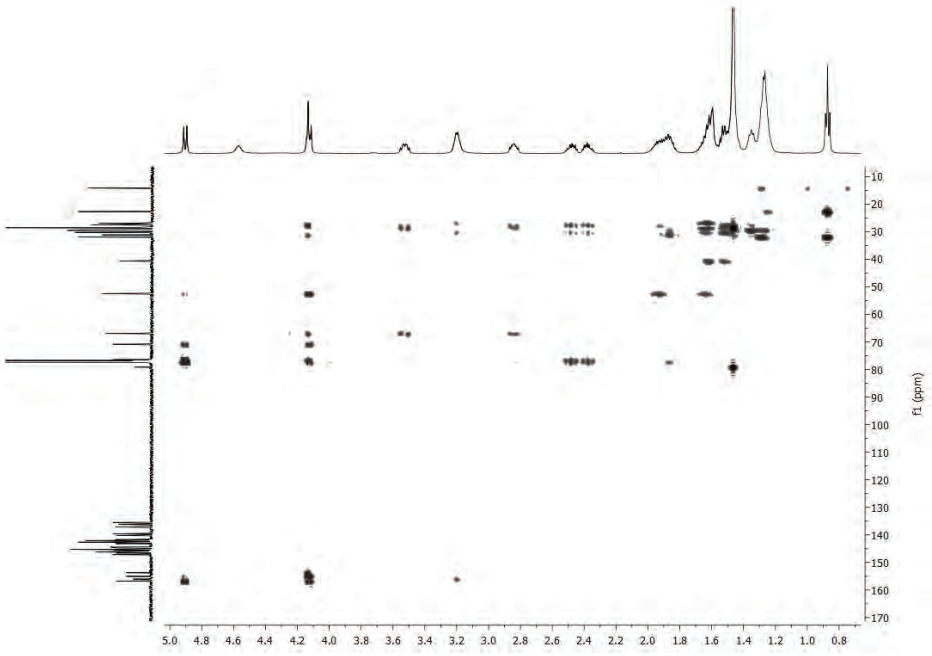
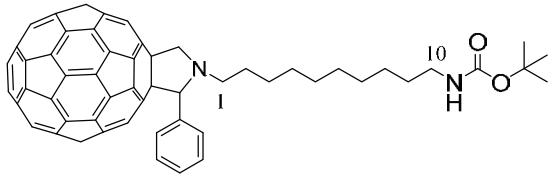
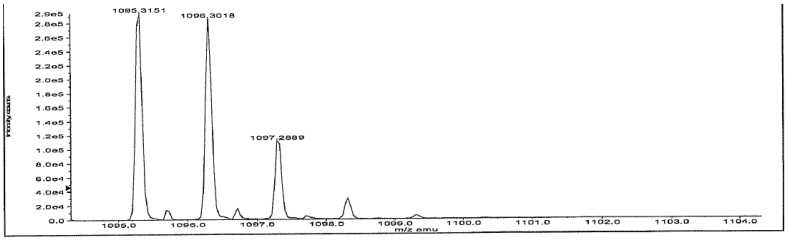


Fig. S-12. HMBC spectrum of **7a**.

Phenyl-substituted fulleropyrolidine derivative ***8b***





Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C83H38N2O2	–	1094.29333	0.38	2.45318 E6	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+H]+	306739.07	1095.30060	1095.30025	-0.35594	-0.32	

Fig. S-13. Mass spectrum of **8b**.

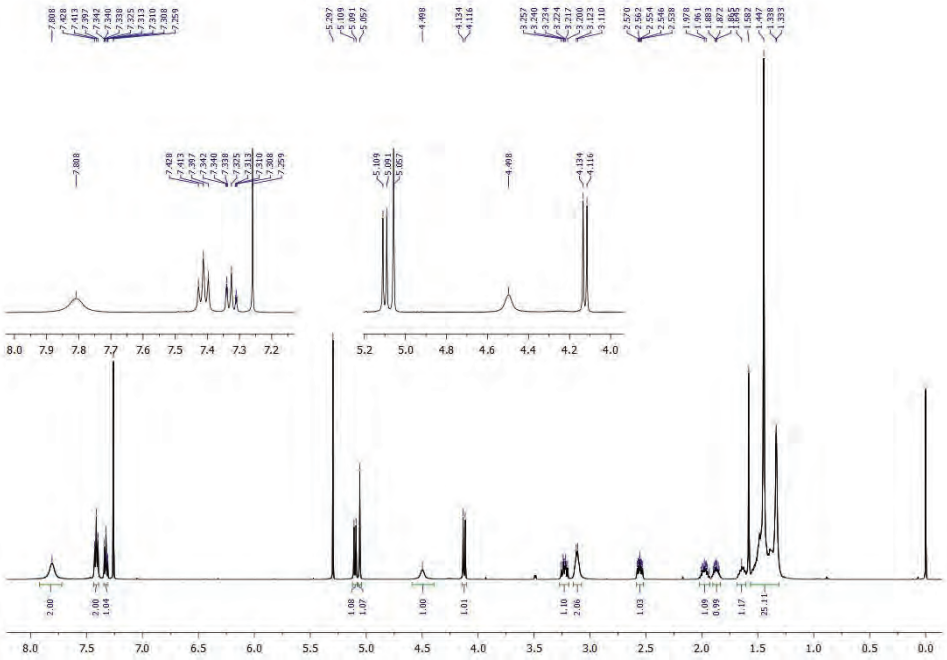


Fig. S-14. ^{1}H-NMR spectrum of **8b**.

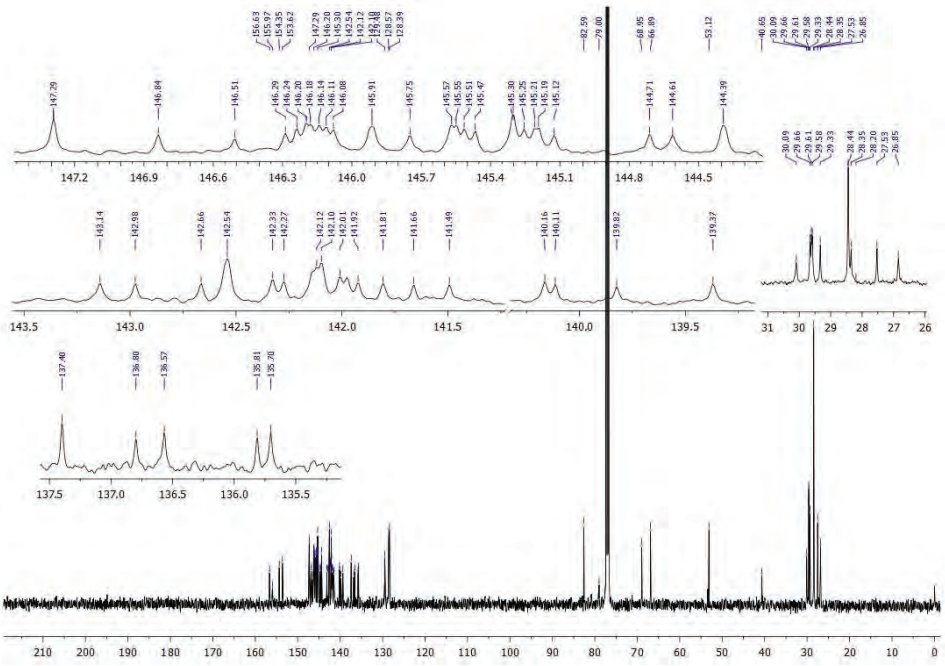


Fig. S-15. ^{13}C-NMR spectrum of **8b**.

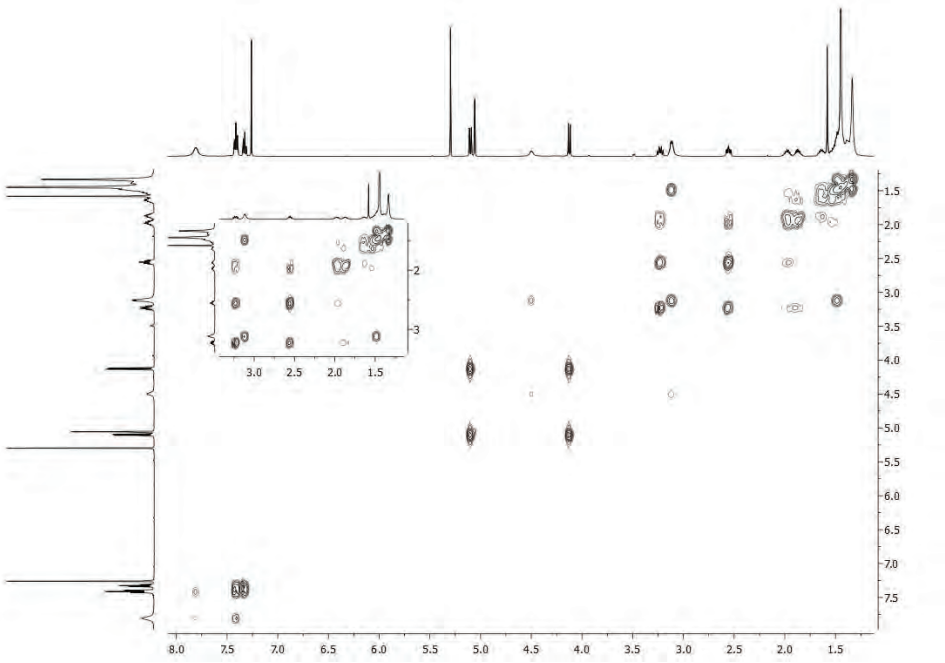


Fig. S-16. COSY spectrum of **8b**.

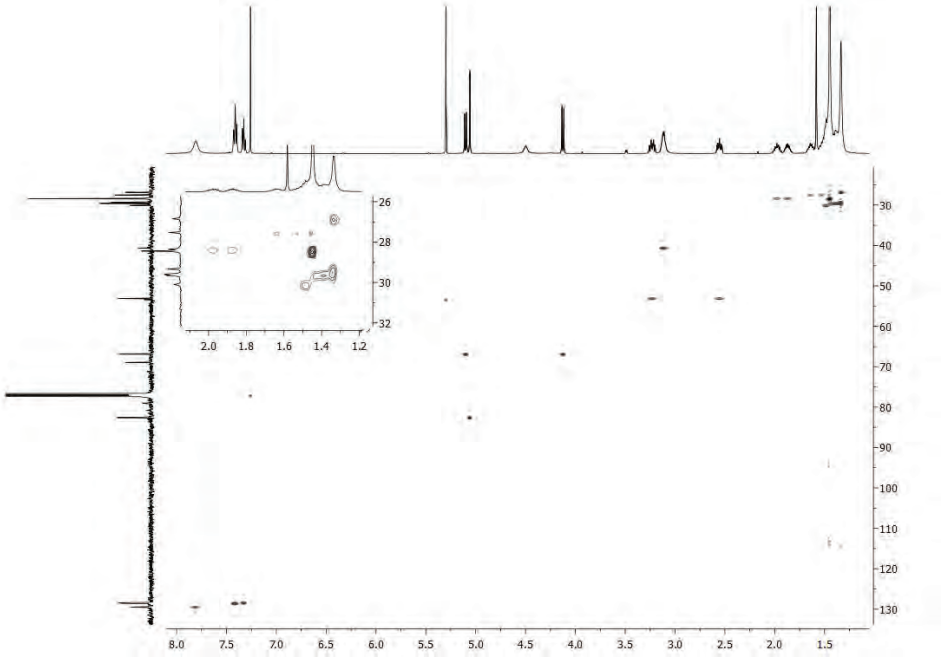


Fig. S-17. HSQC spectrum of **8b**.

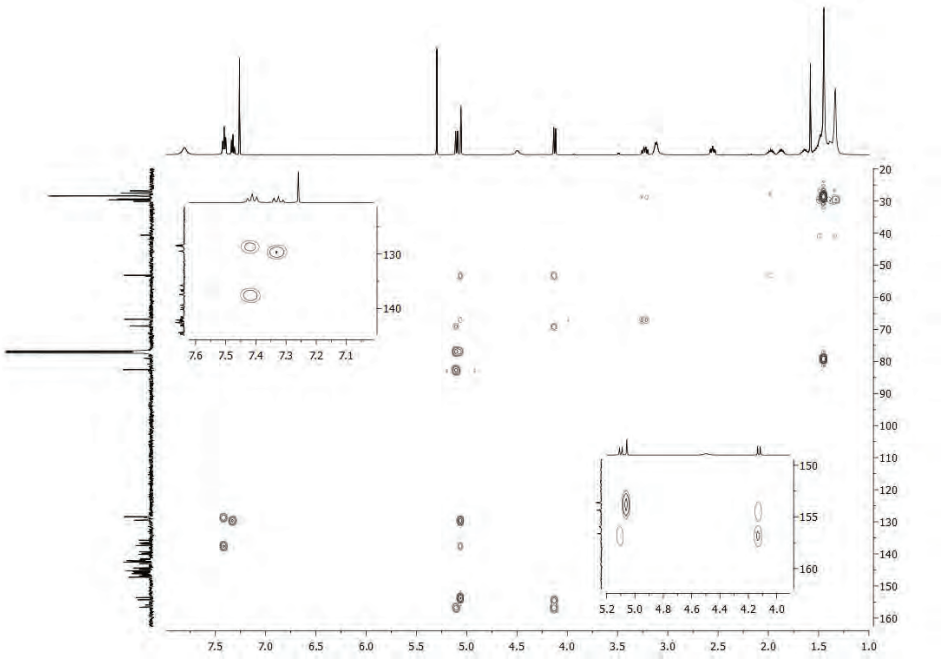
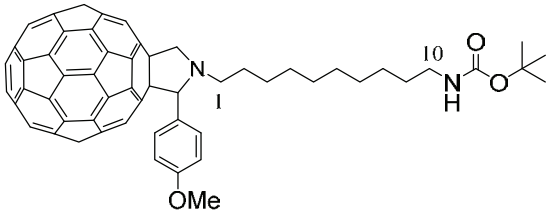
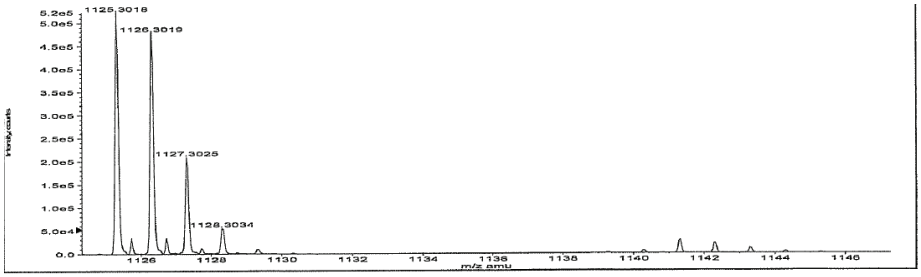


Fig. S-18. HMBC spectrum of **8b**.

4-Methoxyphenyl-substituted fulleropyrolidine derivative ***9b***





Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C84H40N2O3	--	1124.30389	0.38	4.77221 E6	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+H]+	529296.69	1125.31117	1125.31122	0.05235	0.05	--

Fig. S-19. Mass spectrum of **9b**.

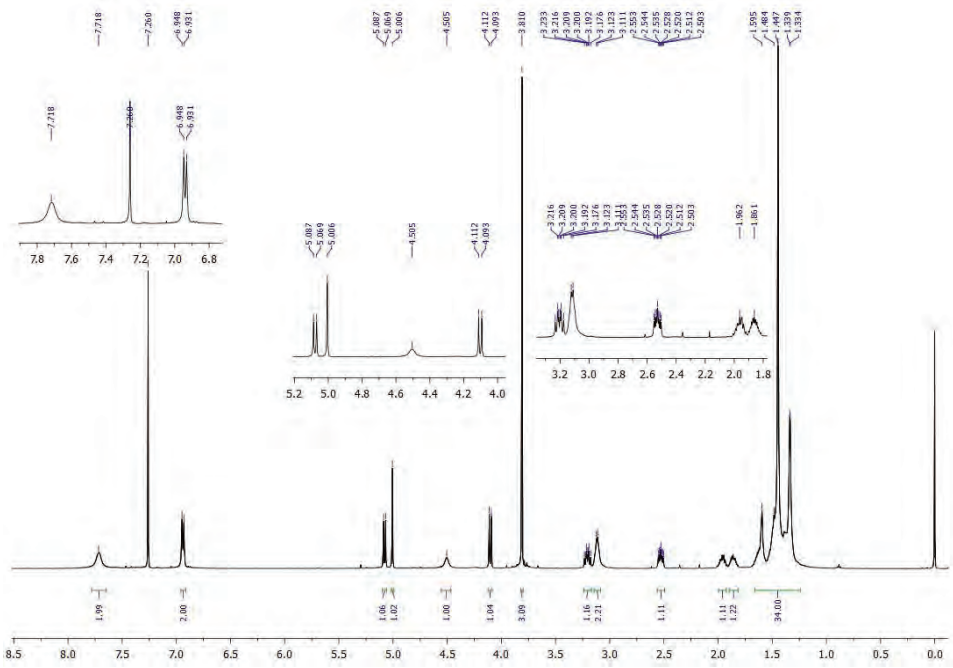


Fig. S-20. ^{1}H-NMR spectrum of **9b**.

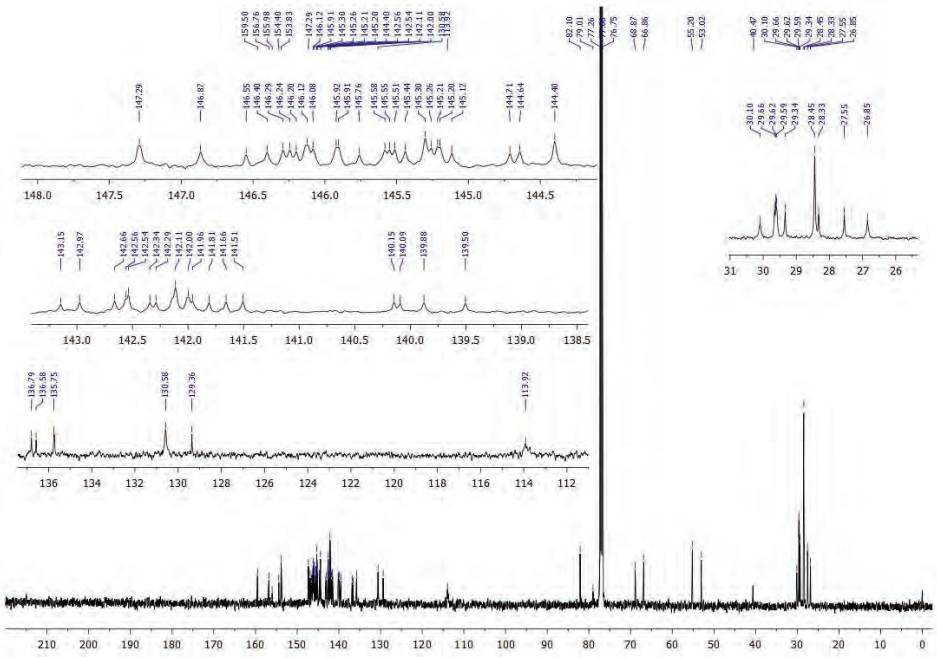


Fig. S-21. ^{13}C-NMR spectrum of **9b**.

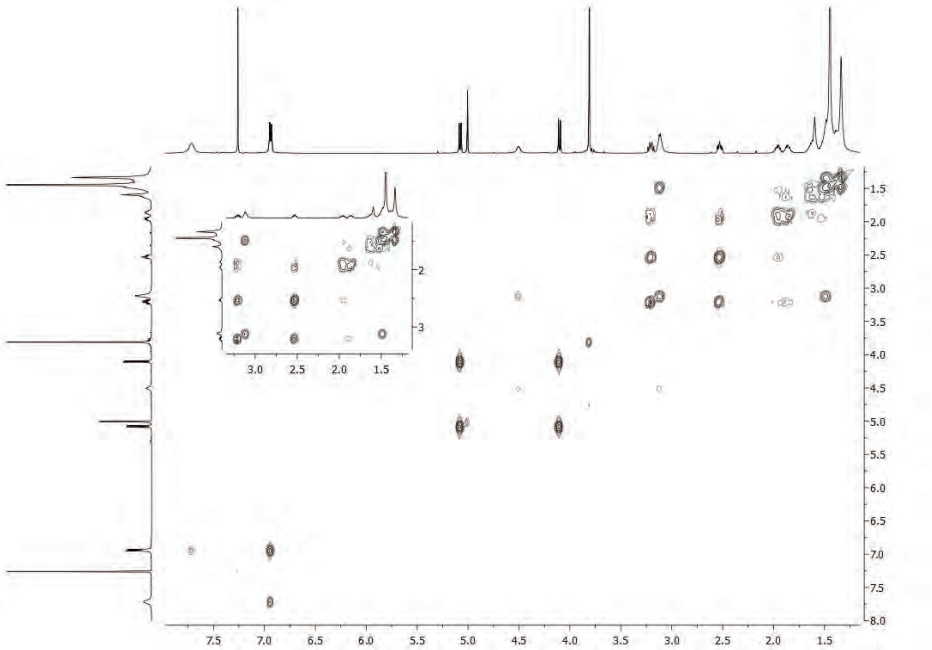


Fig. S-22. COSY spectrum of **9b**.

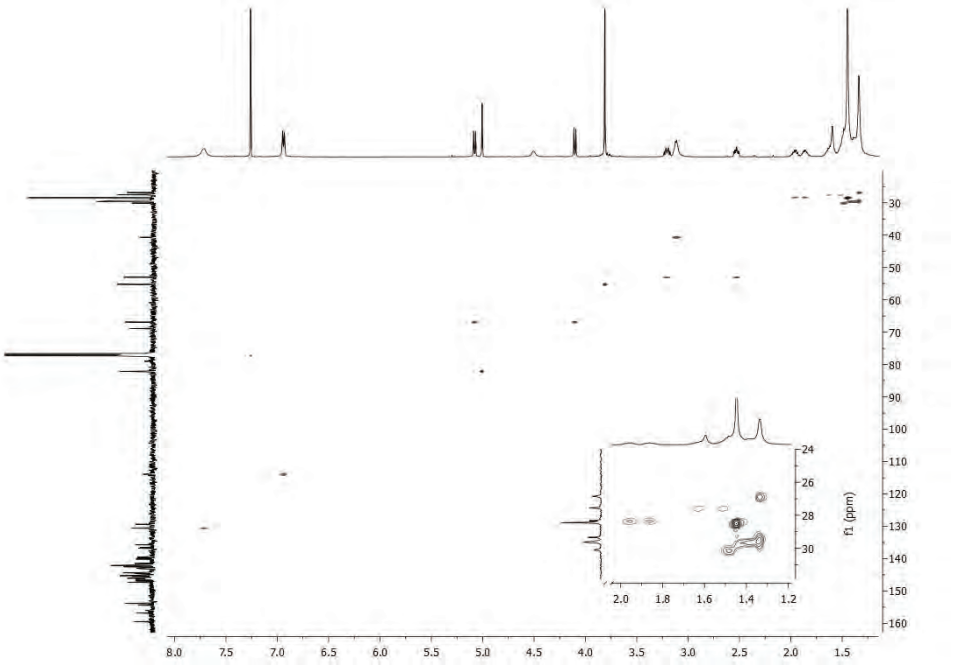


Fig. S-23. HSQC spectrum of **9b**.

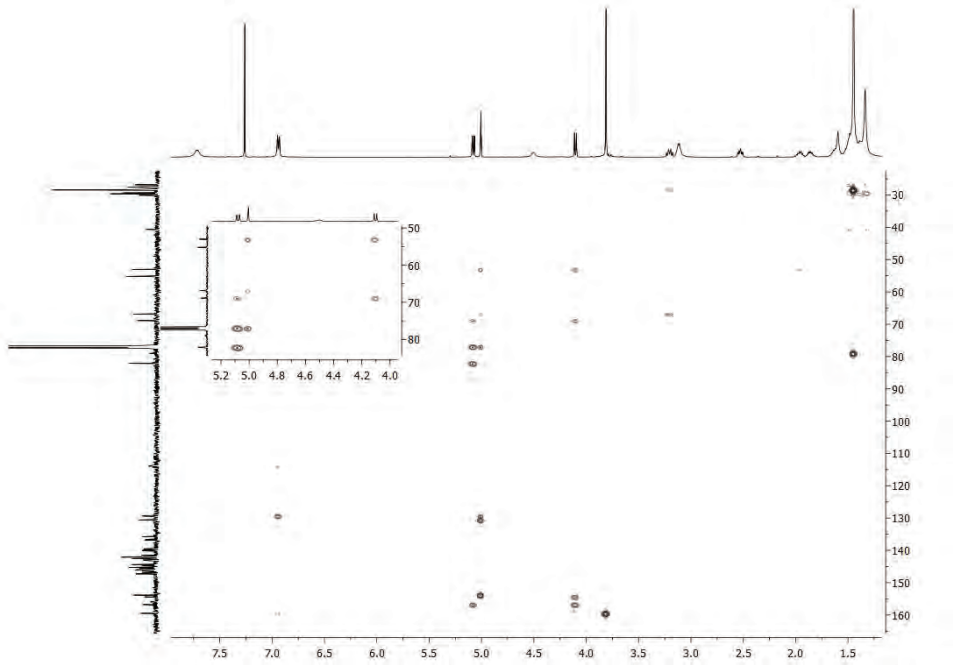
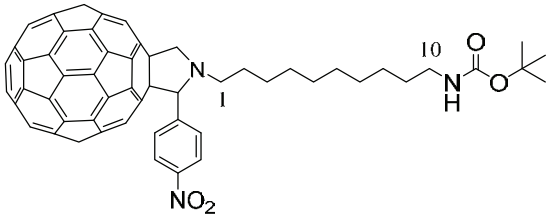
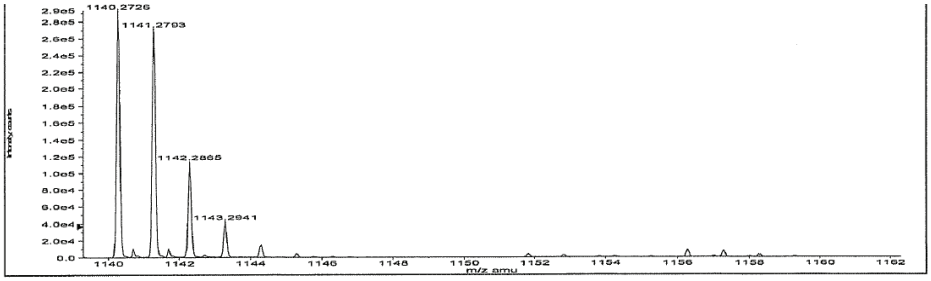


Fig. S-24. HMBC spectrum of **9b**.

4-Nitrophenyl-substituted fulleropyrrolidine derivative ***10b***





Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C83H37N3O4	–	1139.27841	0.37	1.71257 E6	–

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+H]+	299830.20	1140.28568	1140.28465	-1.02968	-0.90	–

Fig. S-25. Mass spectrum of **10b**.

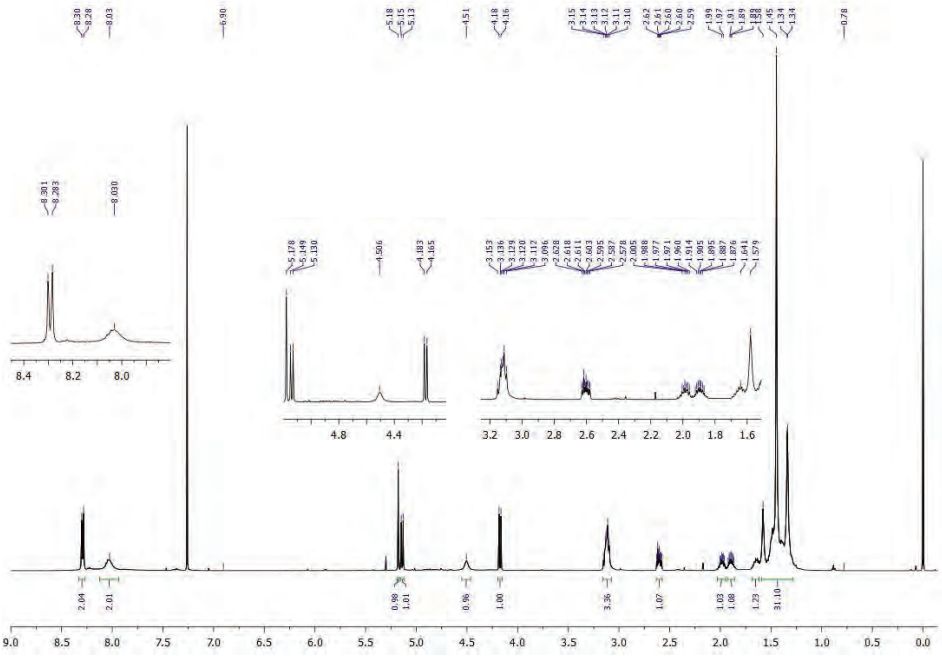


Fig. S-26. ^{1}H-NMR spectrum of **10b**.

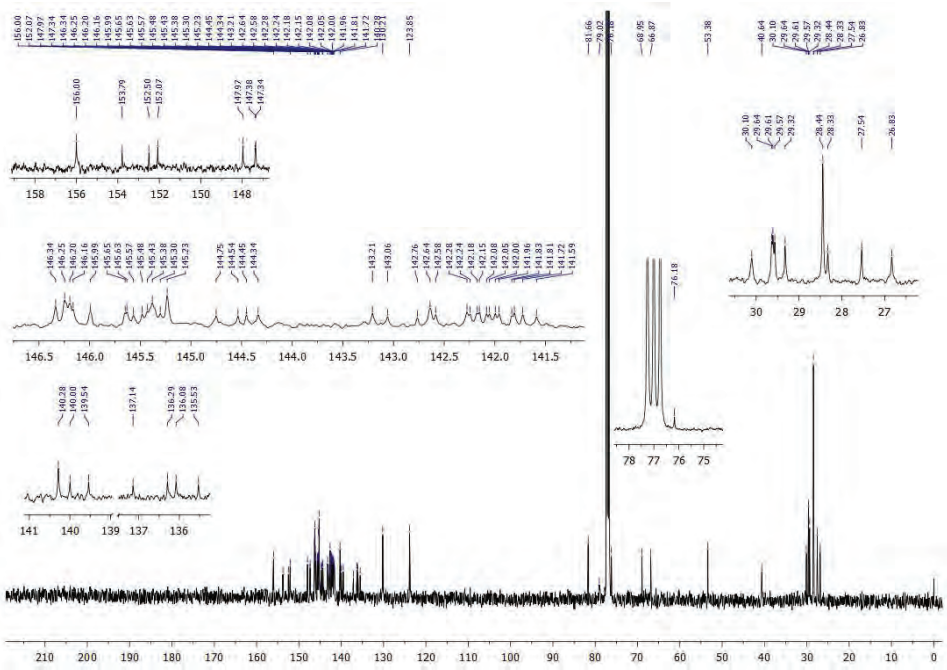


Fig. S-27. ^{13}C-NMR spectrum of **10b**.

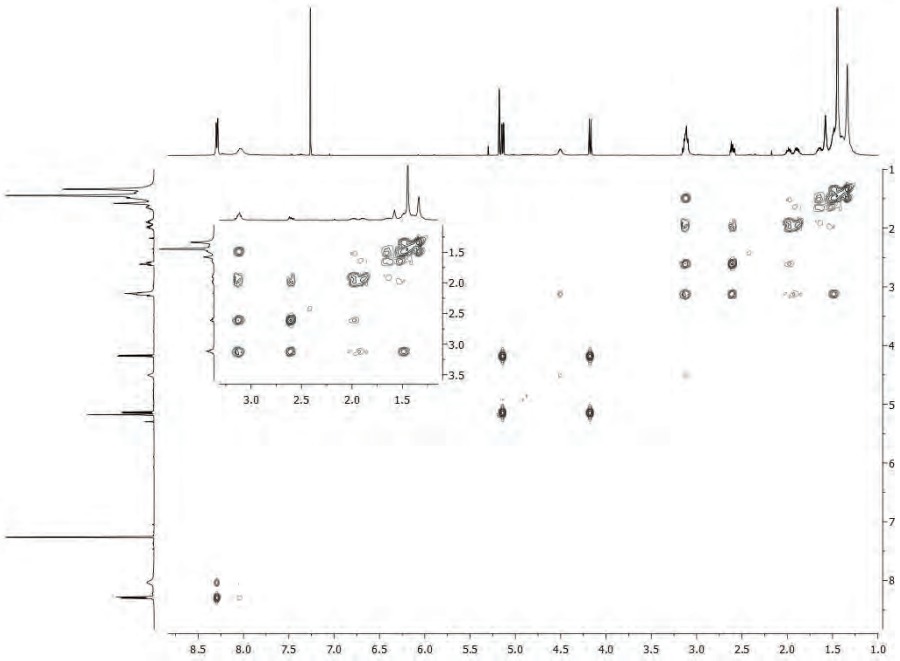


Fig. S-28. COSY spectrum of **10b**.

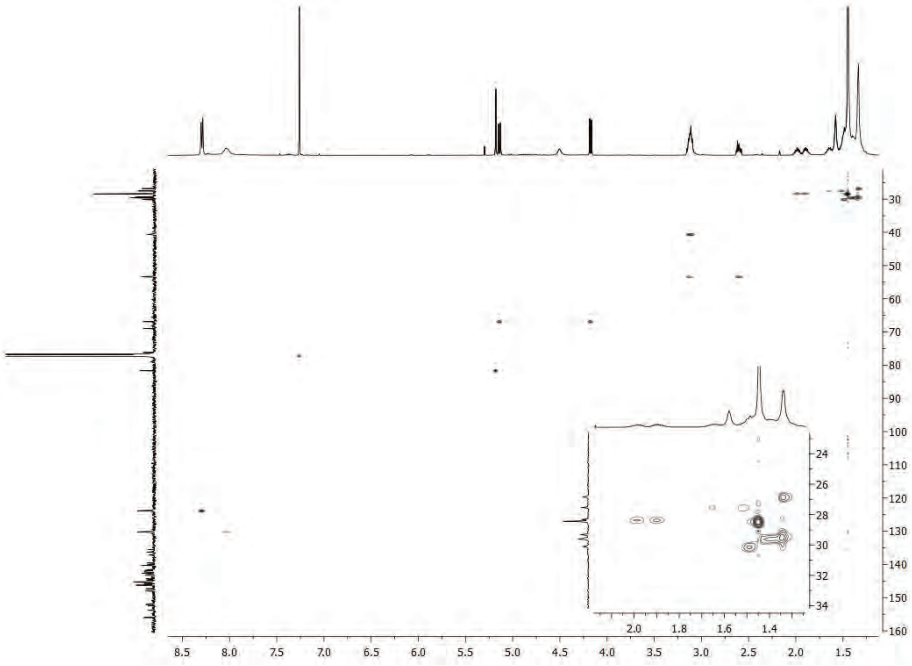


Fig. S-29. HSQC spectrum of **10b**.

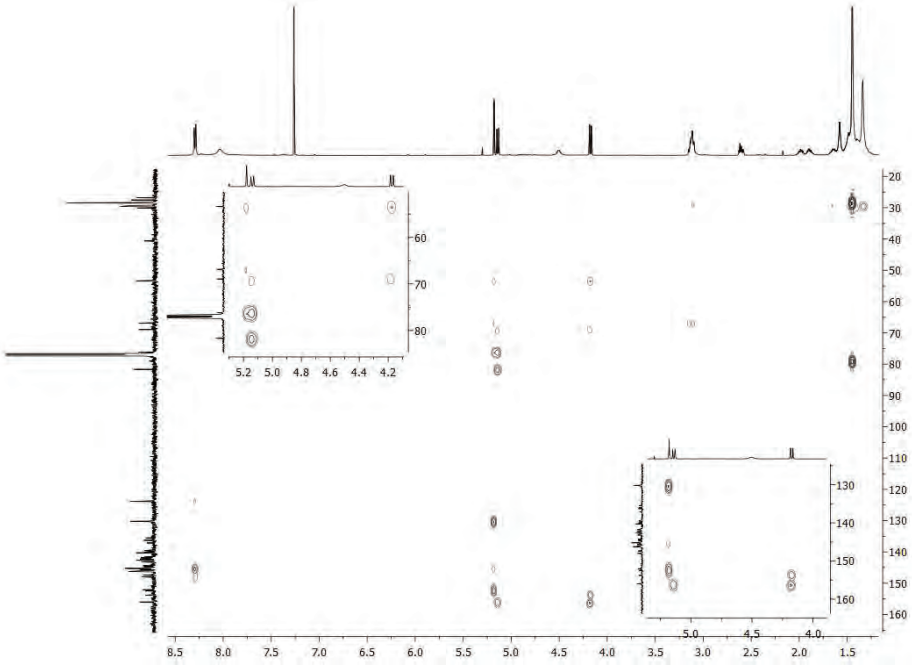
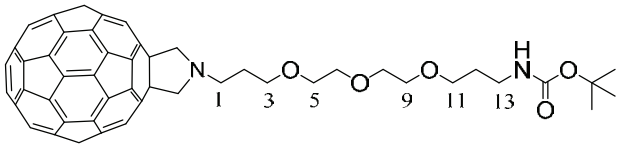


Fig. S-30. HMBC spectrum of **10b**.

Fulleropyrrolidine derivative ***11c***



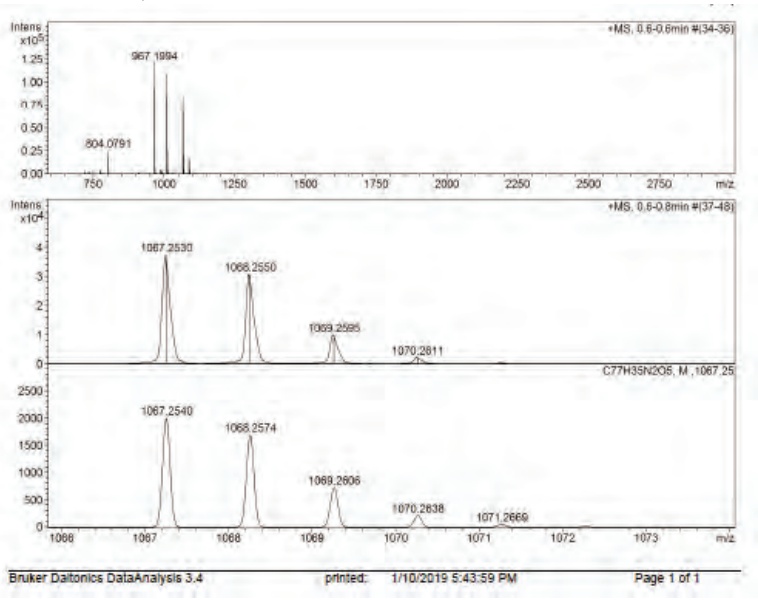


Fig. S-31. Mass spectrum of **11c**.

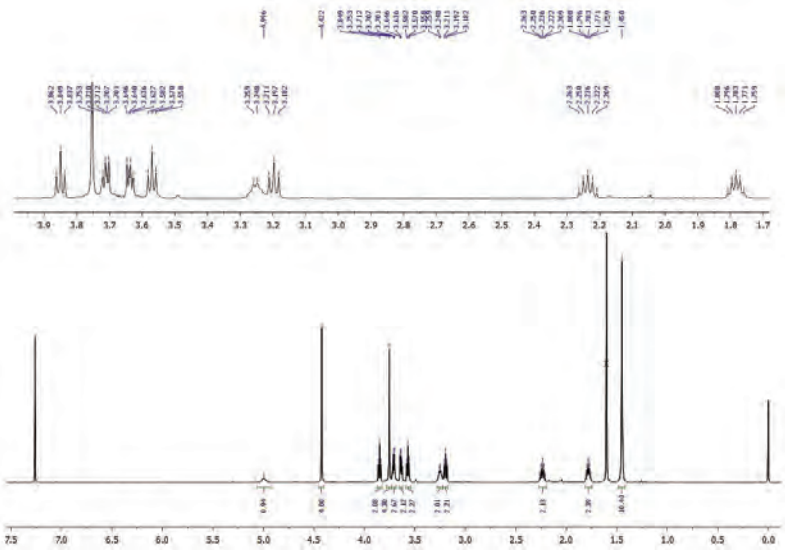


Fig. S-32. ^{1}H-NMR spectrum of **11c**.

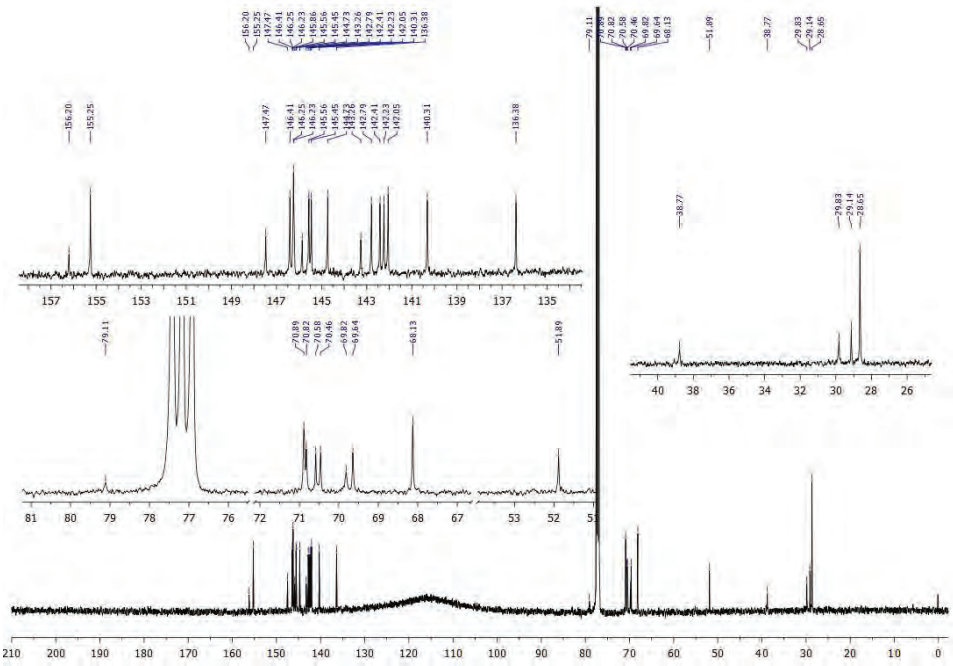


Fig. S-33. ^{13}C-NMR spectrum of **11c**.

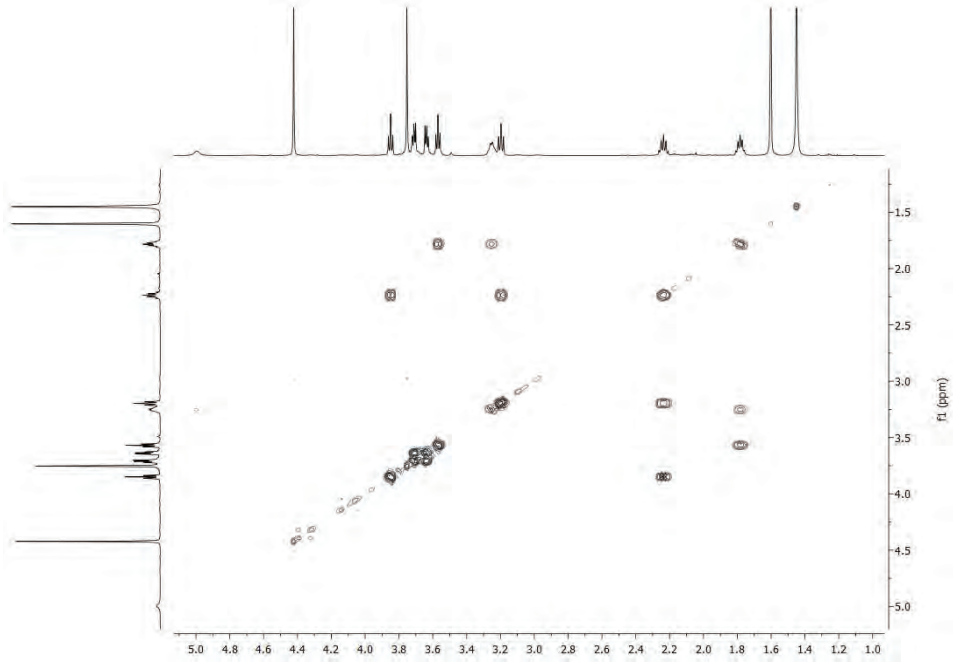


Fig. S-34. COSY spectrum of **11c**.

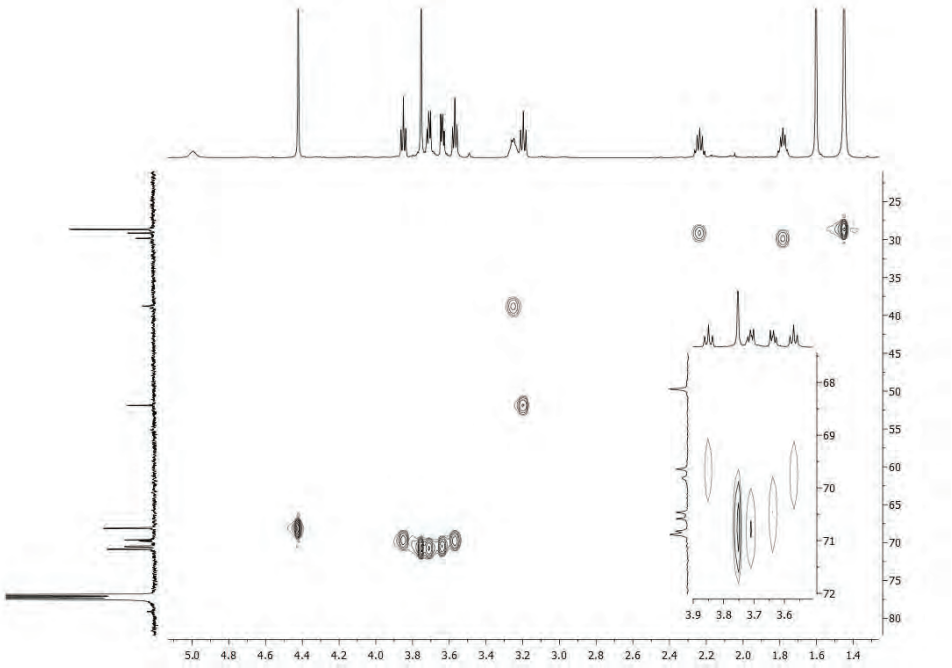


Fig. S-35. HSQC spectrum of **11c**.

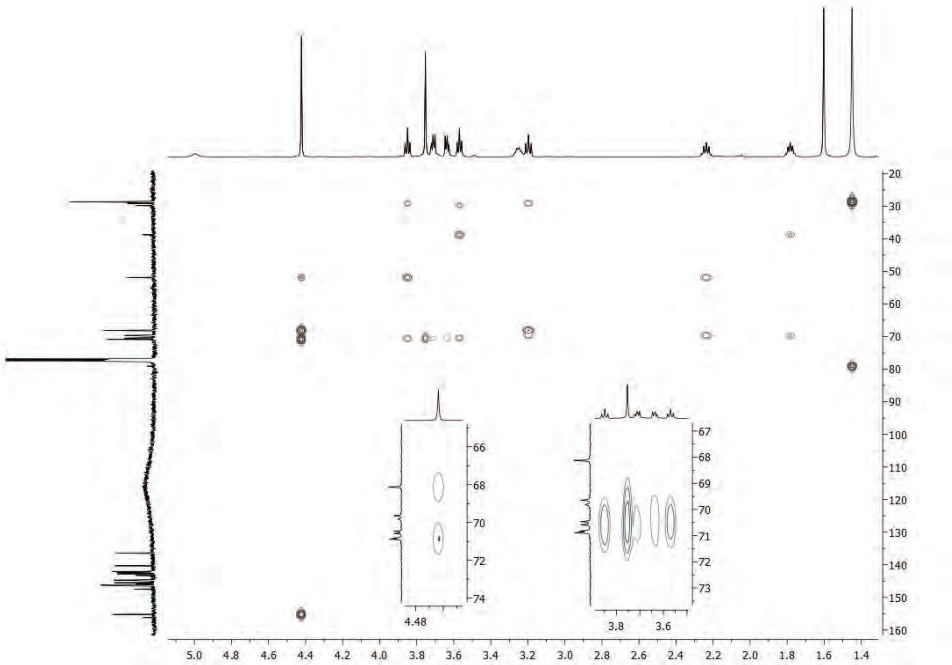
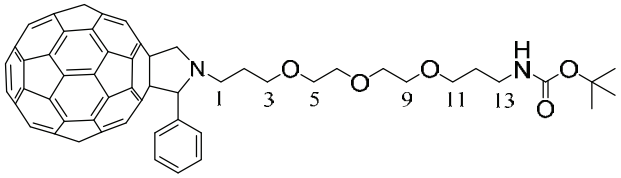
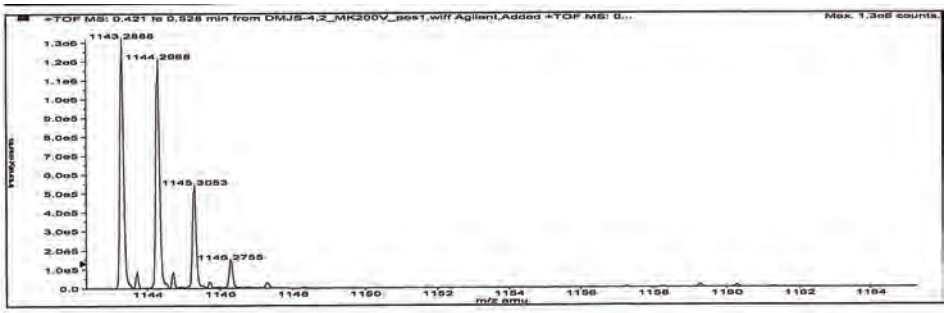


Fig. S-36. HMBC spectrum of **11c**.

Phenyl-substituted fulleropyrrolidine derivative ***12c***





Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C83H38N2O5	–	1142.27807	0.40	8.52645 E6	–

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+H]+	1319795.11	1143.28535	1143.28570	0.34878	0.31	–

Fig. S-37. Mass spectrum of **12c**.

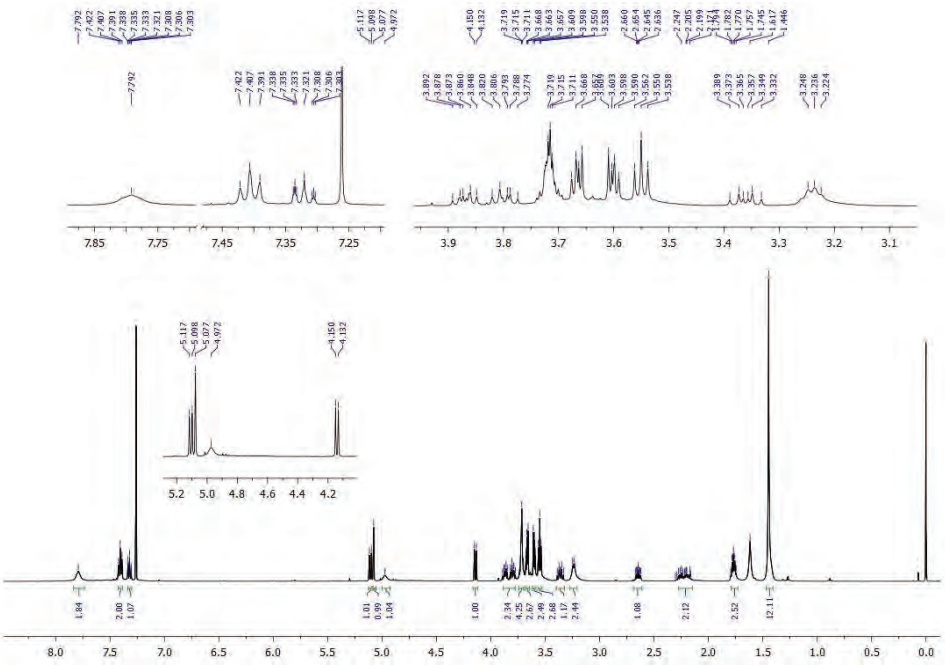


Fig. S-38. ^{1}H-NMR spectrum of **12c**.

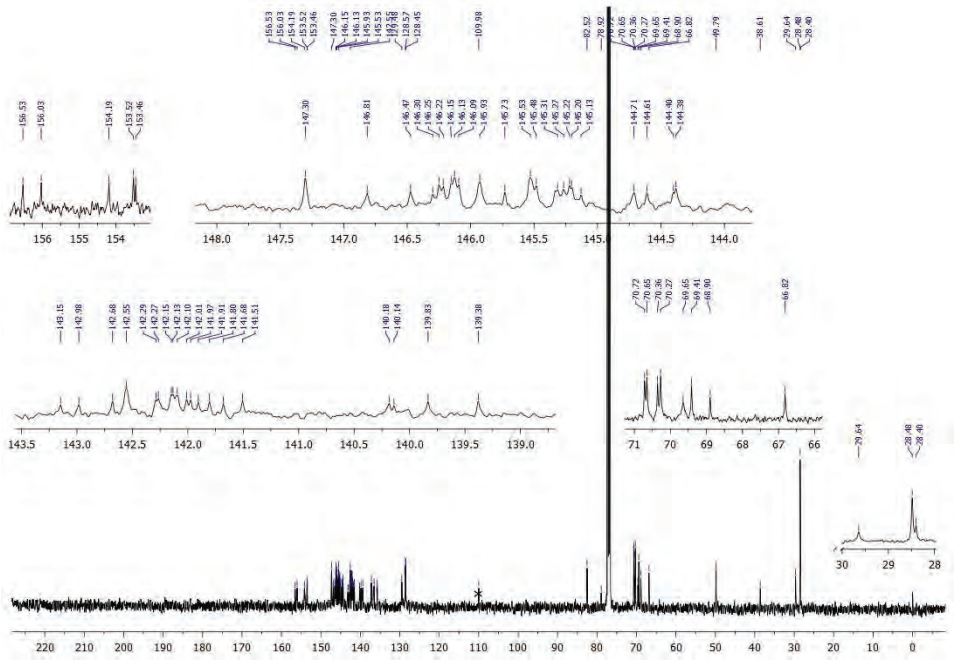


Fig. S-39. ^{13}C-NMR spectrum of **12c**.

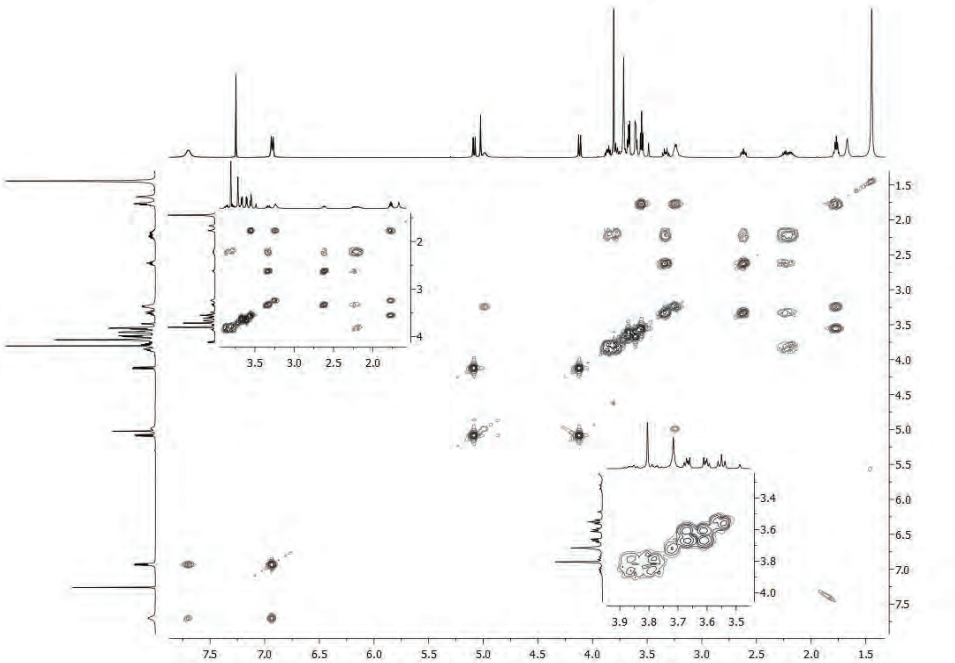


Fig. S-40. COSY spectrum of **12c**.

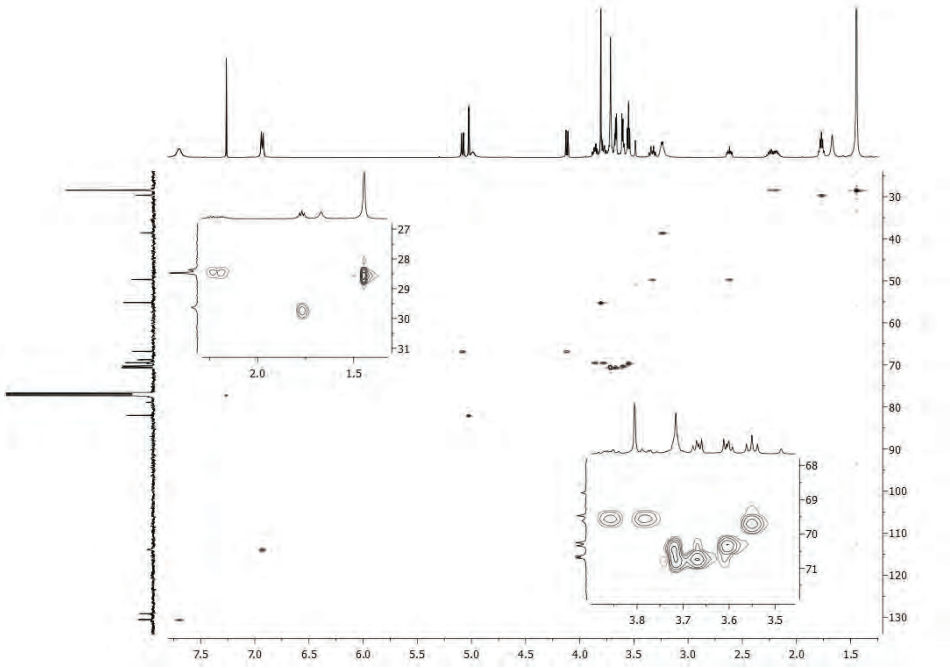


Fig. S-41. HSQC spectrum of **12c**.

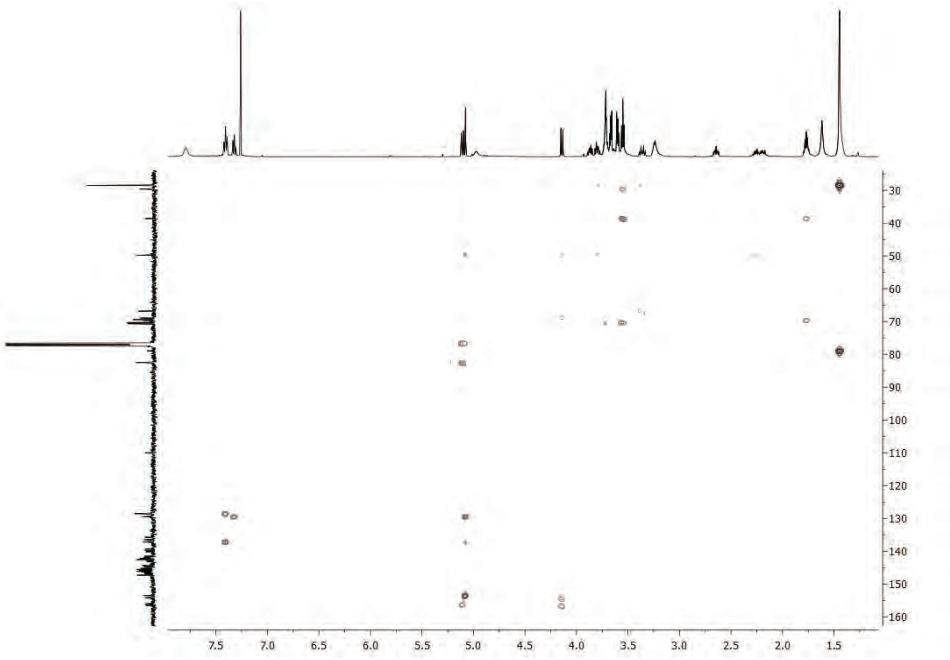


Fig. S-42. HMBC spectrum of **12c**.

*2-Methoxyphenyl-substituted fulleropyrrolidine derivative **13c***

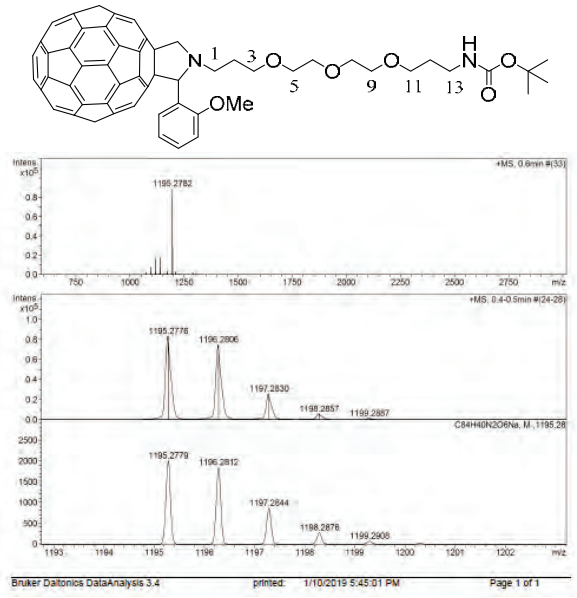


Fig. S-43. Mass spectrum of **13c**.

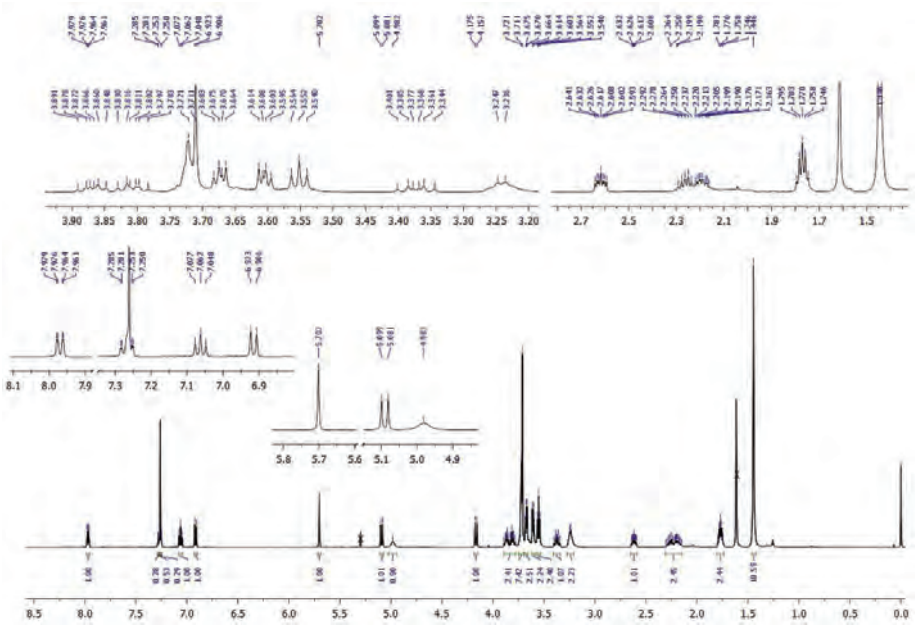


Fig. S-44. ^{1}H-NMR spectrum of **13c**.

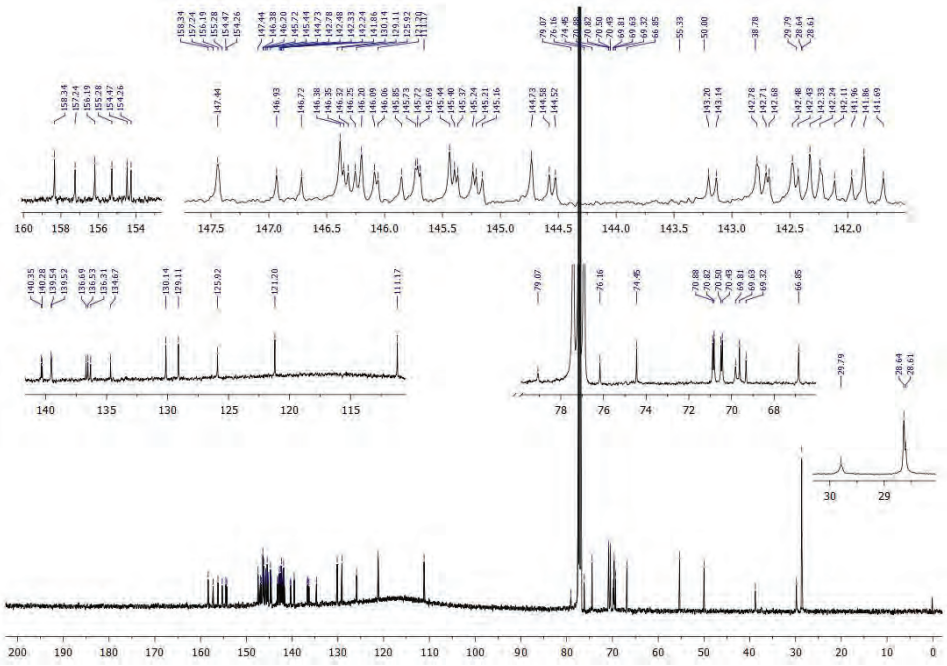


Fig. S-45. ^{13}C-NMR spectrum of **13c**.

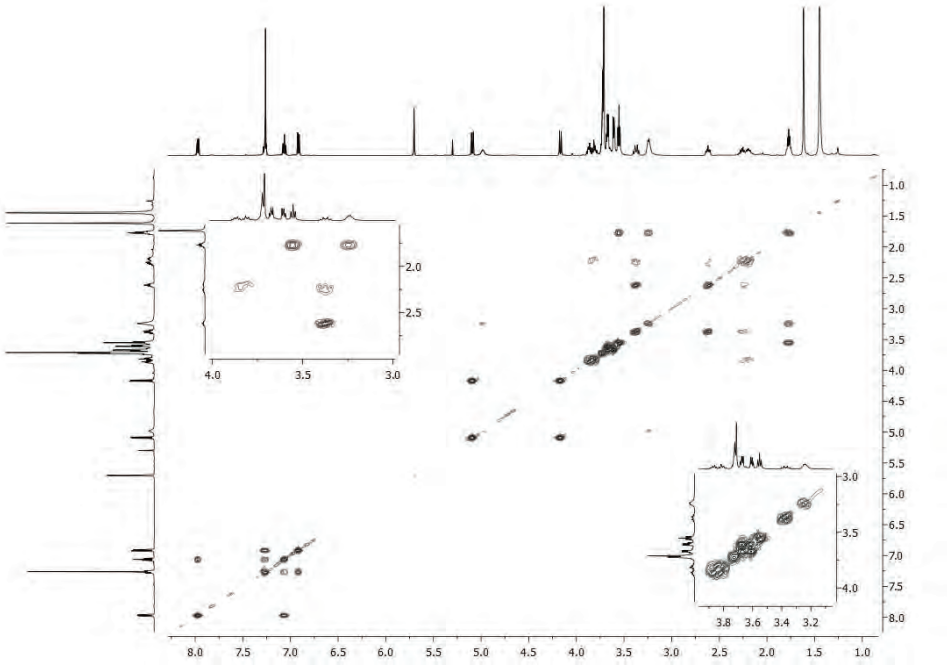


Fig. S-46. COSY spectrum of **13c**.

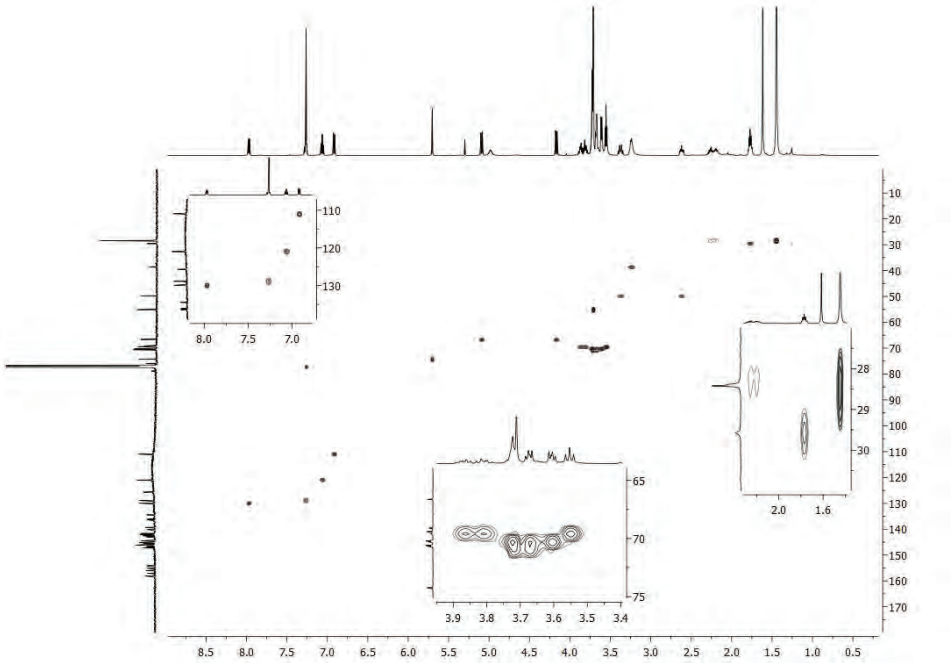


Fig. S-47. HSQC spectrum of **13c**.

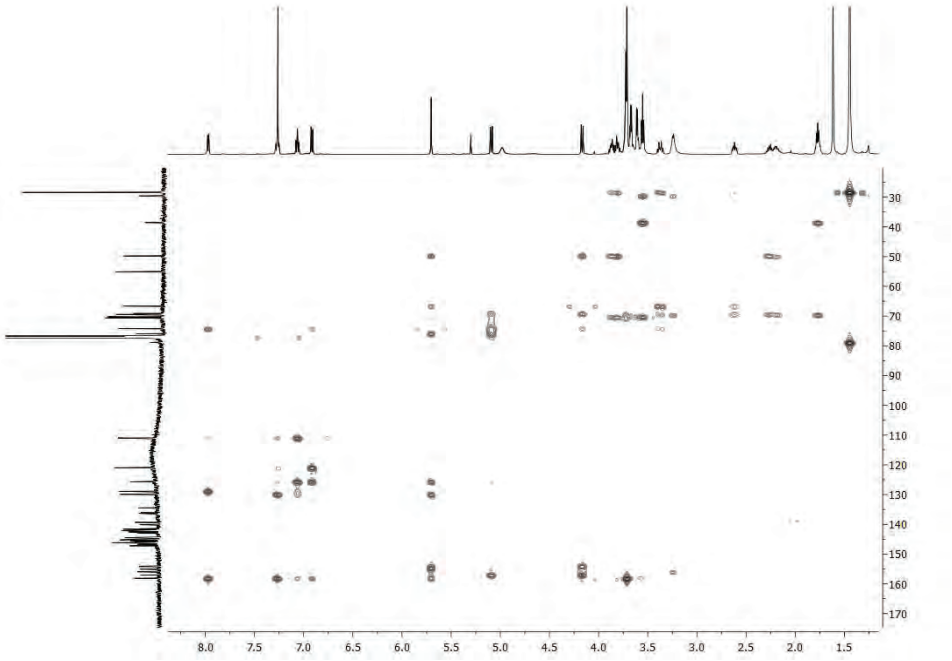


Fig. S-48. HMBC spectrum of **13c**.

3-Methoxyphenyl-substituted fulleropyrrolidine derivative ***14c***

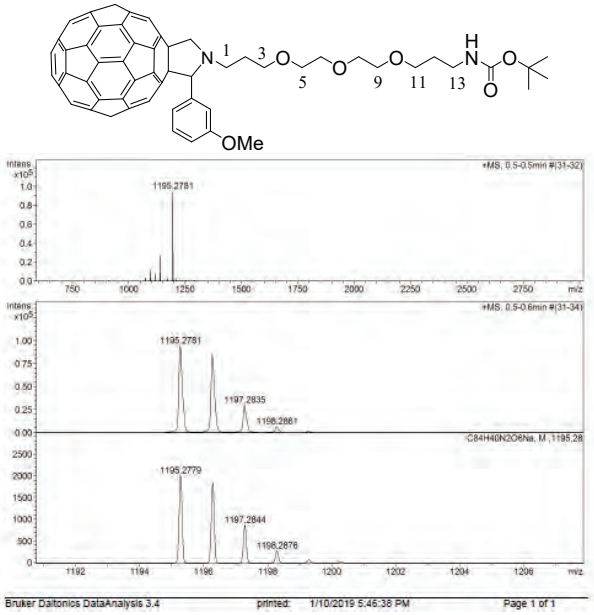


Fig. S-49. Mass spectrum of **14c**.

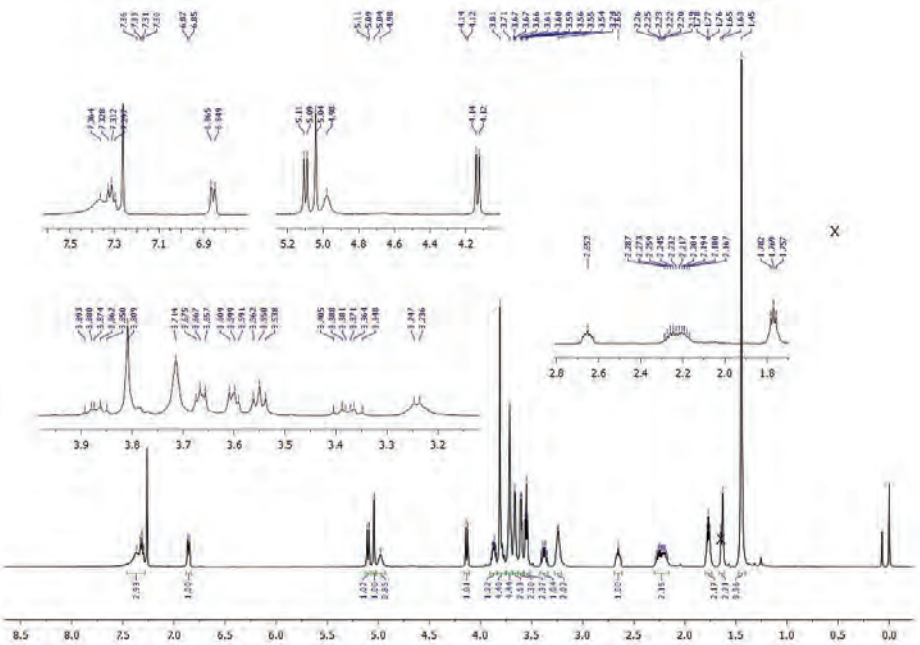


Fig. S-50. ^{1}H-NMR spectrum of **14c**.

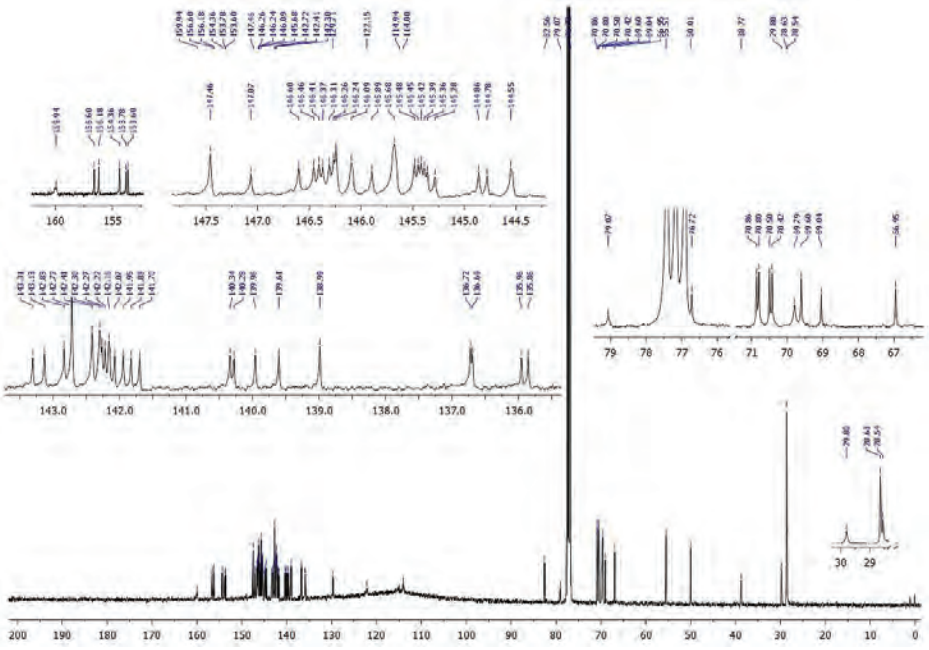


Fig. S-51. ^{13}C-NMR spectrum of **14c**.

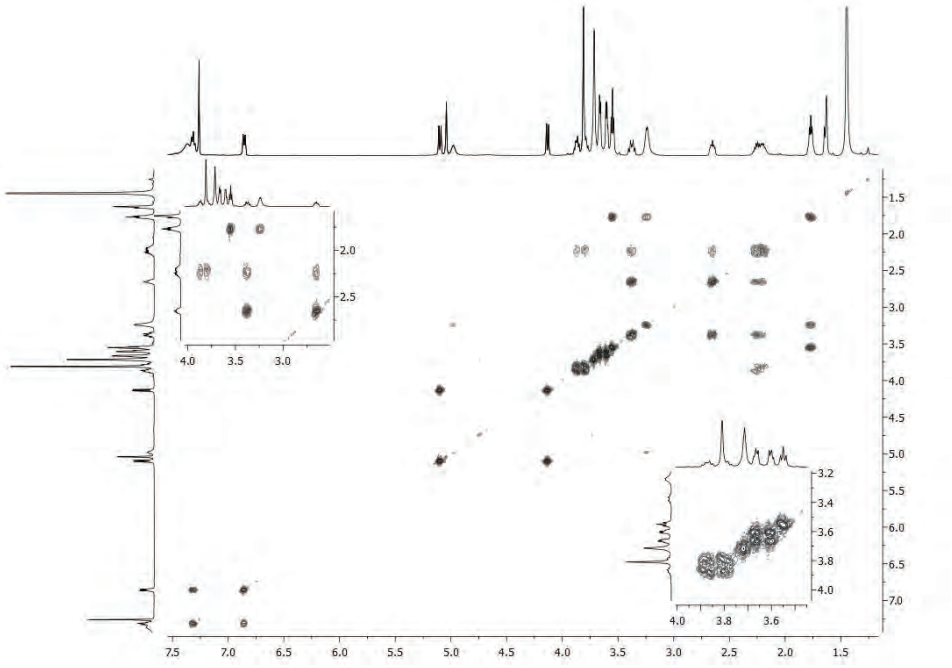


Fig. S-52. COSY spectrum of **14c**.

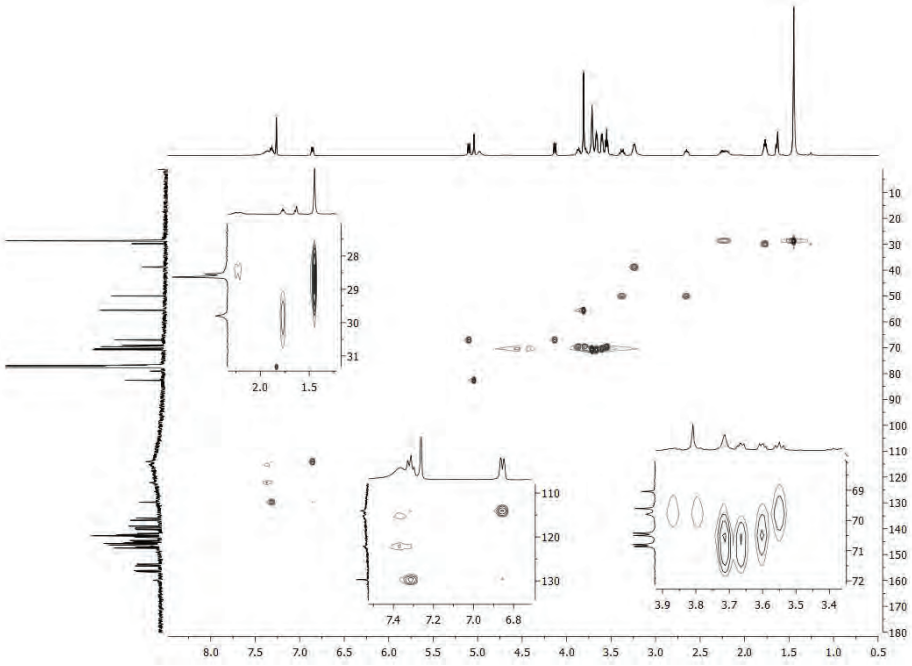


Fig. S-53. HSQC spectrum of **14c**.

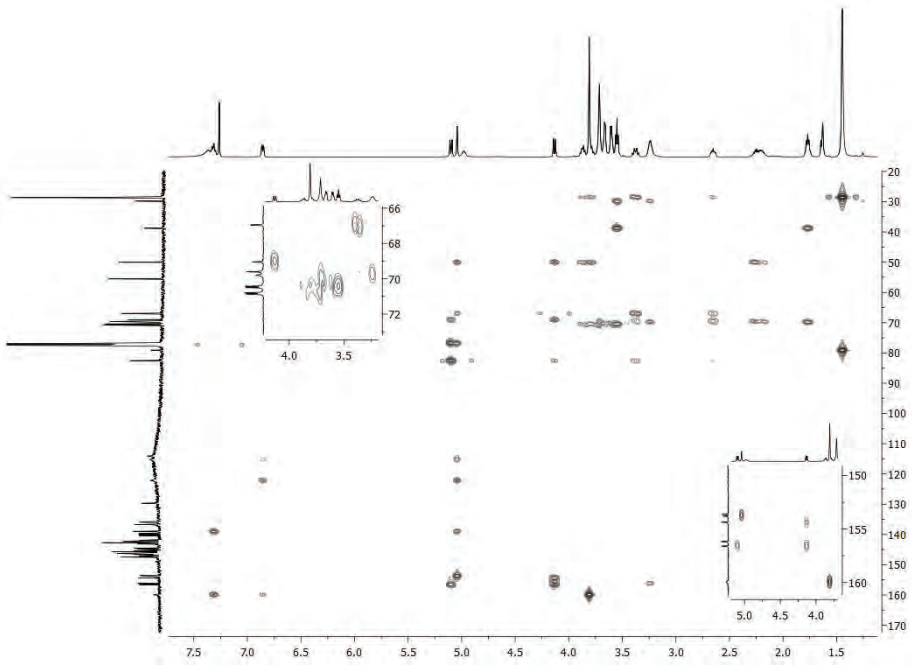
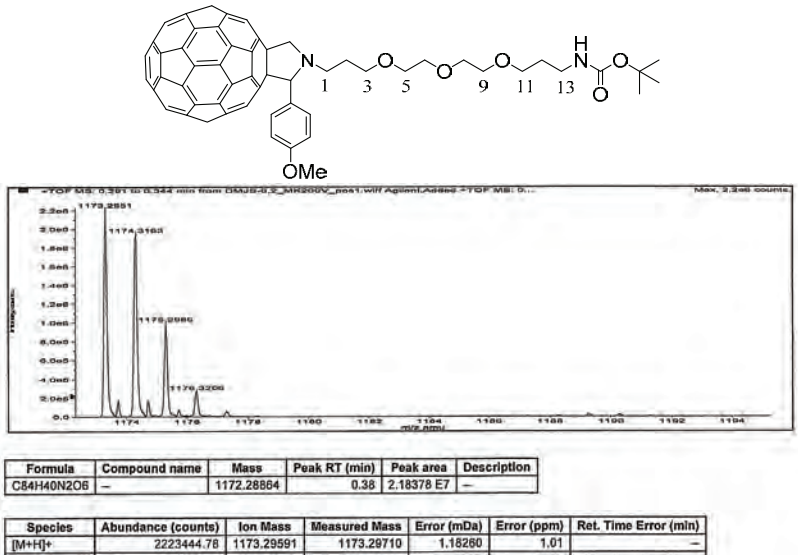


Fig. S-54. HMBC spectrum of **14c**.

4-Methoxyphenyl-substituted fulleropyrrolidine derivative ***15c***



Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C84H40N2O6	–	1172.28864	0.38	2.18378 E7	–

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+H]+	2223444.78	1173.29591	1173.29710	1.18260	1.01	–

Fig. S-55. Mass spectrum of **15c**.

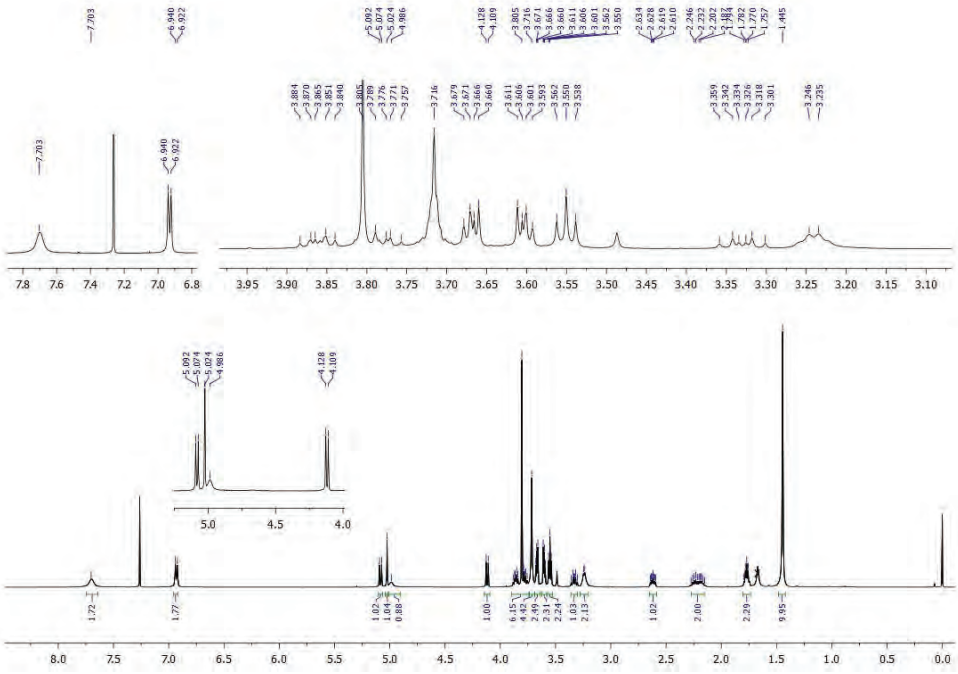


Fig. S-56. ^{1}H-NMR spectrum of **15c**.

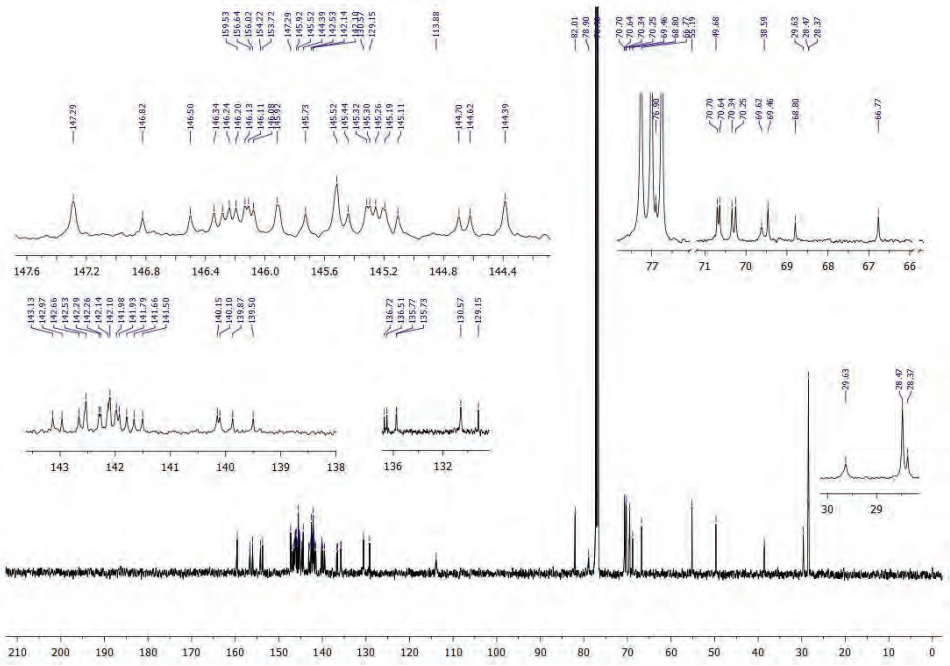


Fig. S-57. ^{13}C-NMR spectrum of **15c**.

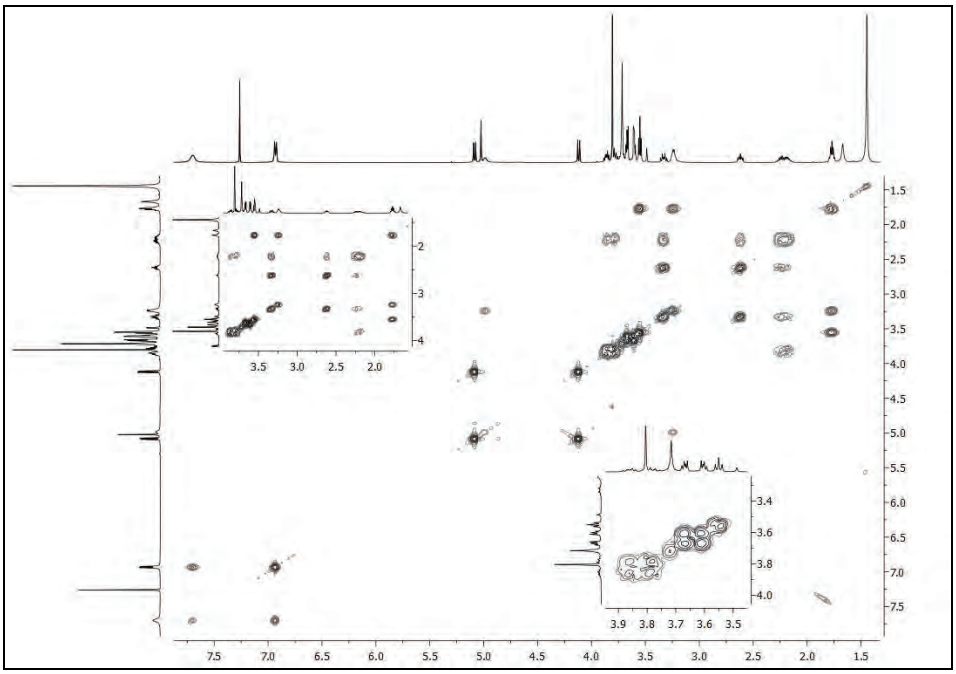


Fig. S-58. COSY spectrum of **15c**.

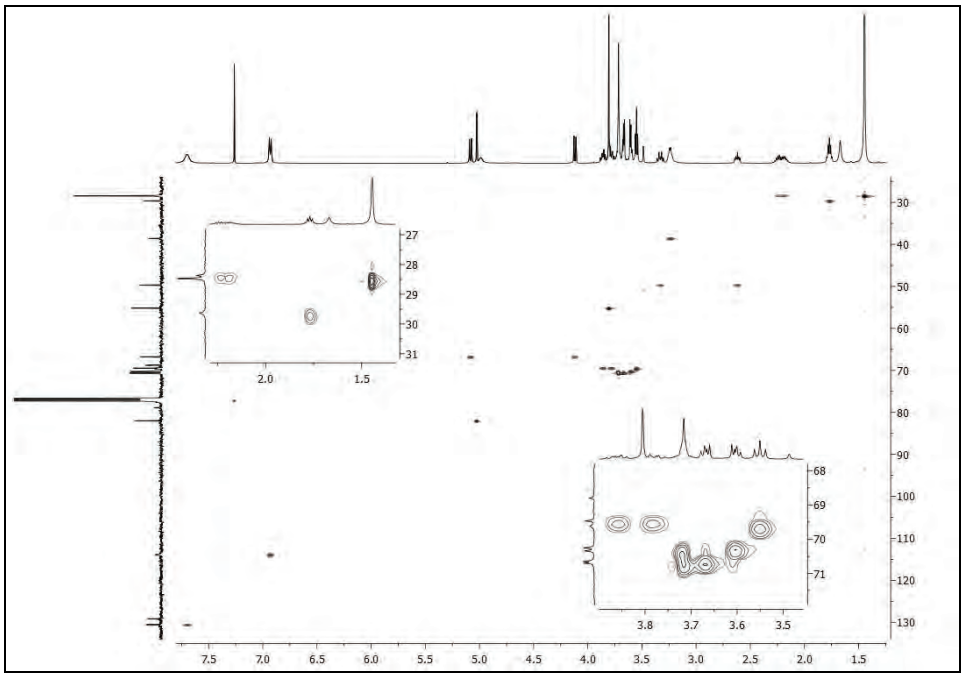


Fig. S-59. HSQC spectrum of **15c**.

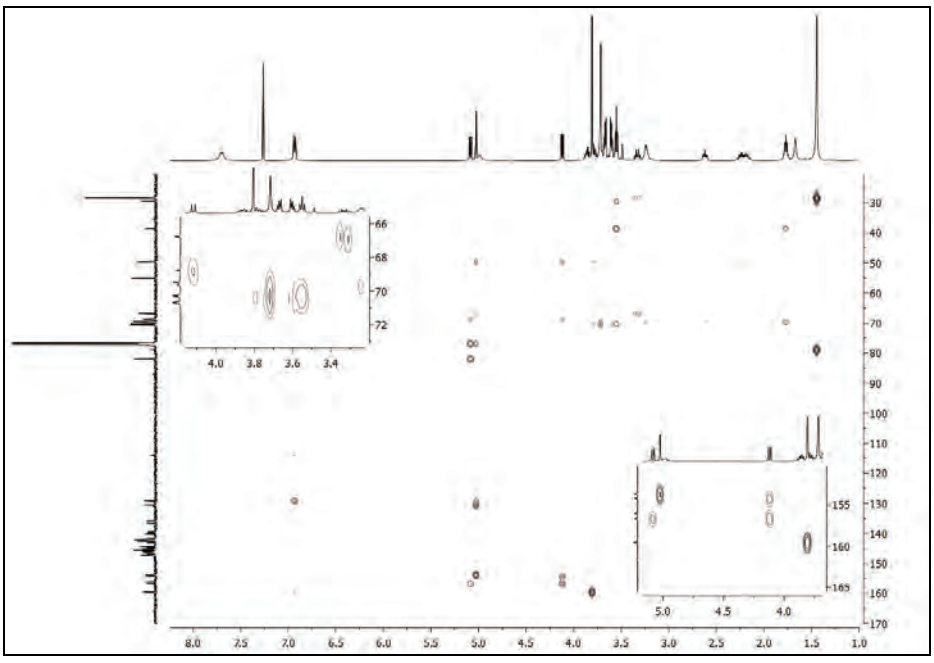


Fig. S-60. HMBC spectrum of **15c**.

Attempts to prepare 2-nitrophenyl-substituted fulleropyrrolidine derivative ***16c*** *(see Experimental part)*

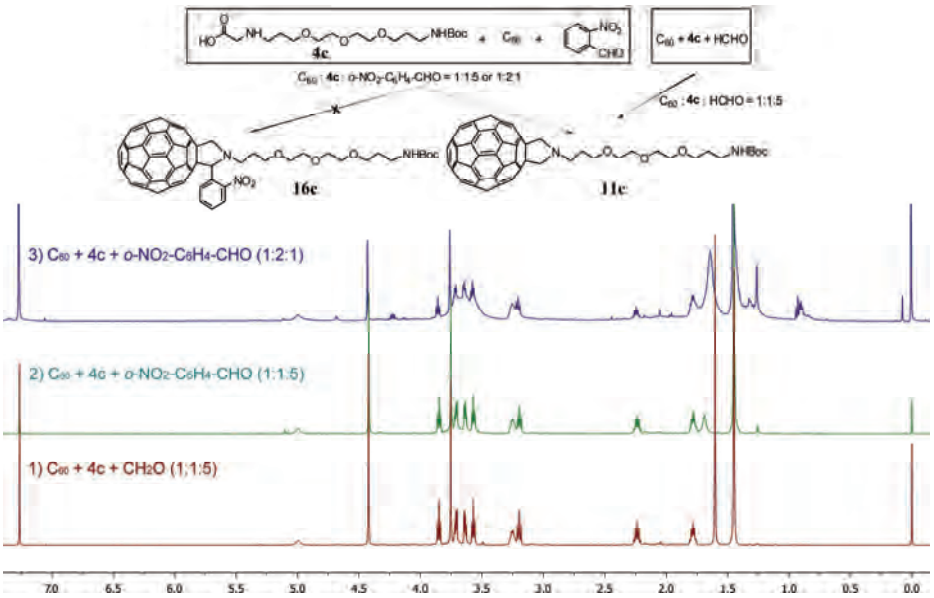


Fig. S-61. Comparison of the ^{1}H-NMR spectra of a same product (**11c**) obtained in the Prato reaction of C_{60} with amino acid **4c** and 2-nitrobenzaldehyde in different relative ratios [2) molar ratio of C_{60}:**4c**:2-nitrobenzaldehyde 1:1:5, reflux; 3) molar ratio of C_{60}:**4c**:2-nitrobenzaldehyde 1:2:1, 100 °C], and with paraformaldehyde [1) molar ratio of C_{60}:**4c**:paraformaldehyde 1:1:5, reflux].

3-Nitrophenyl-substituted fulleropyrrolidine derivative ***17c***

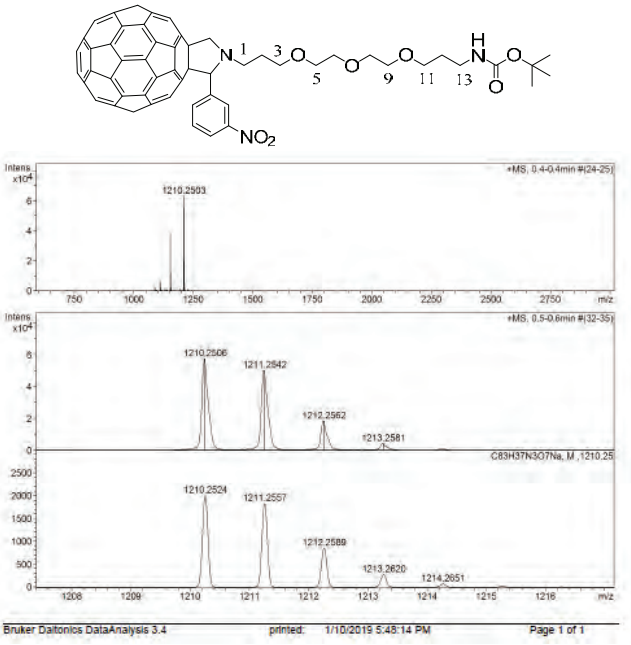


Fig. S-62. Mass spectrum of **17c**.

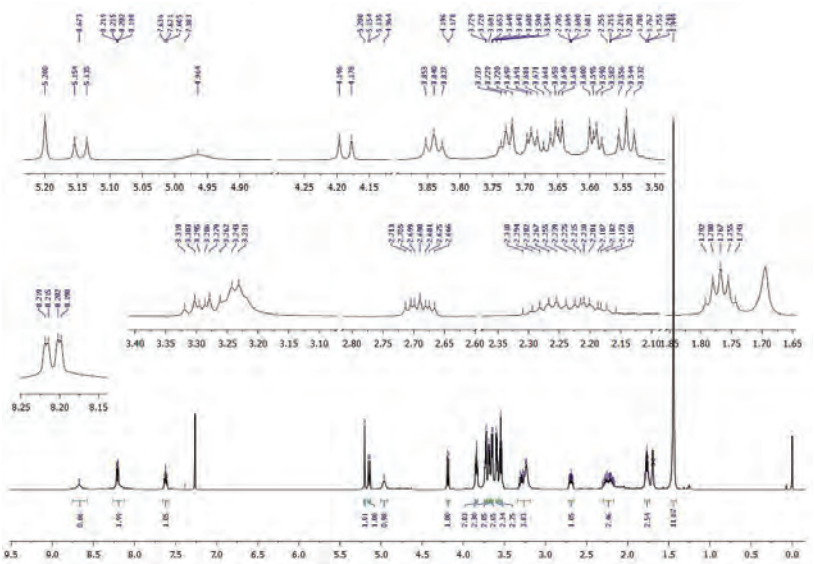


Fig. S-63. ^{1}H-NMR spectrum of **17c**.

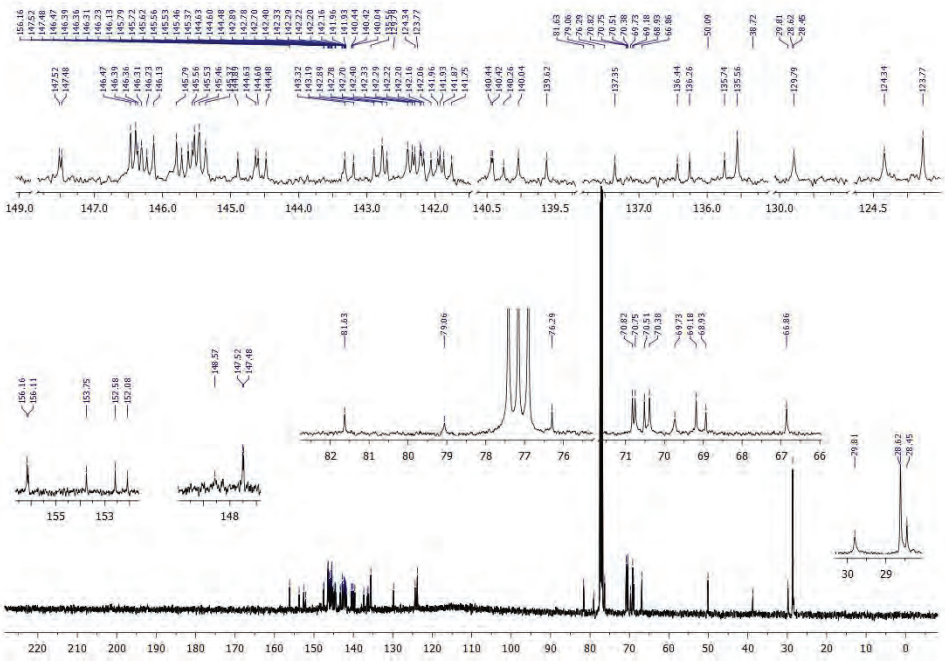


Fig. S-64. ^{13}C-NMR spectrum of **17c**.

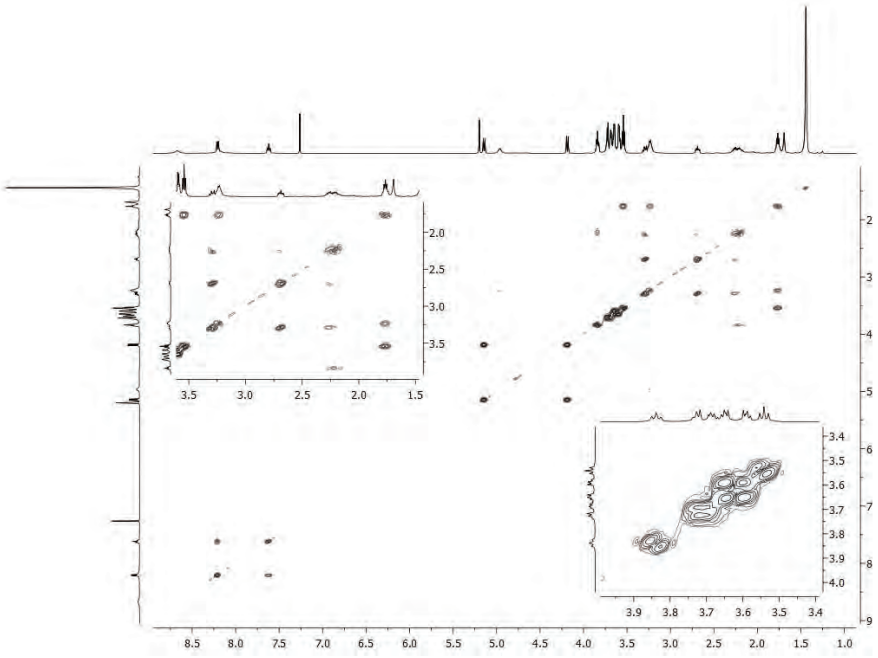


Fig. S-65. COSY spectrum of **17c**.

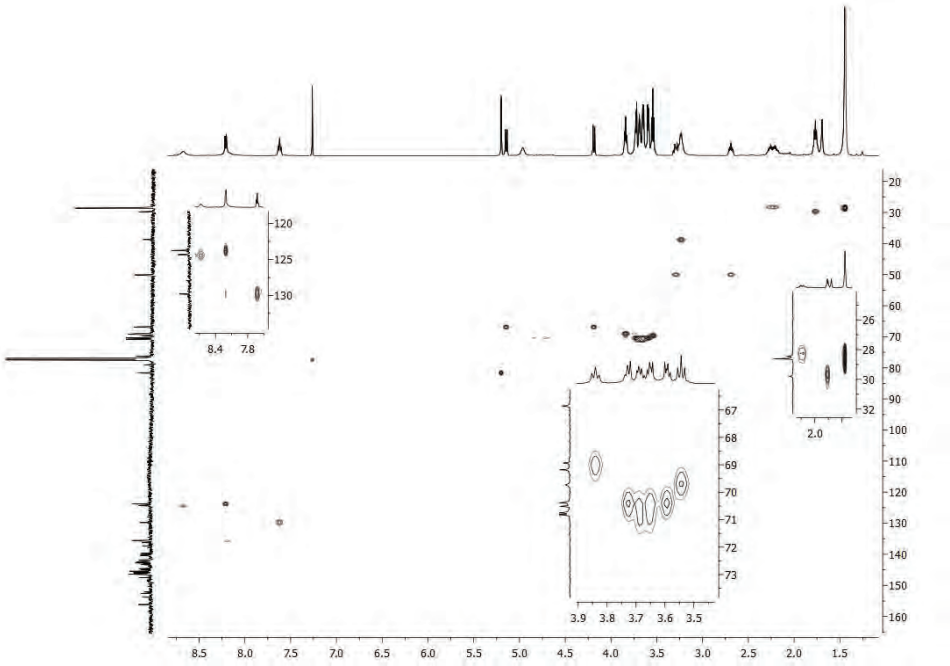


Fig. S-66. HSQC spectrum of **17c**.

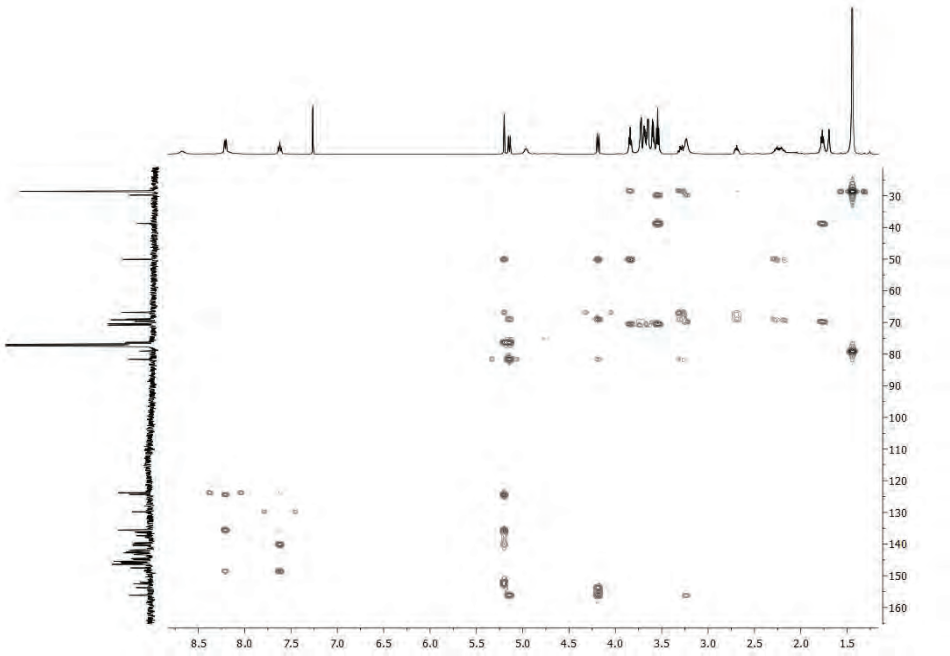


Fig. S-67. HMBC spectrum of **17c**.

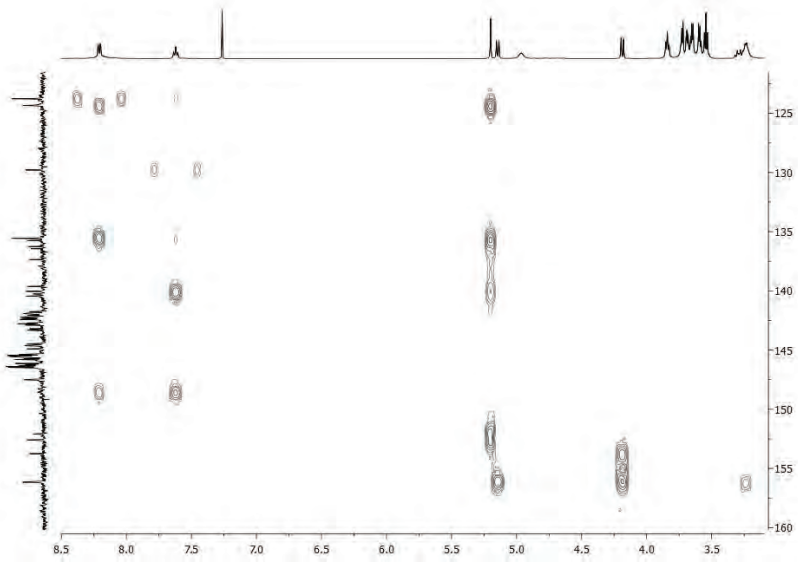


Fig. S-68. Part of the HMBC spectrum of **17c**.

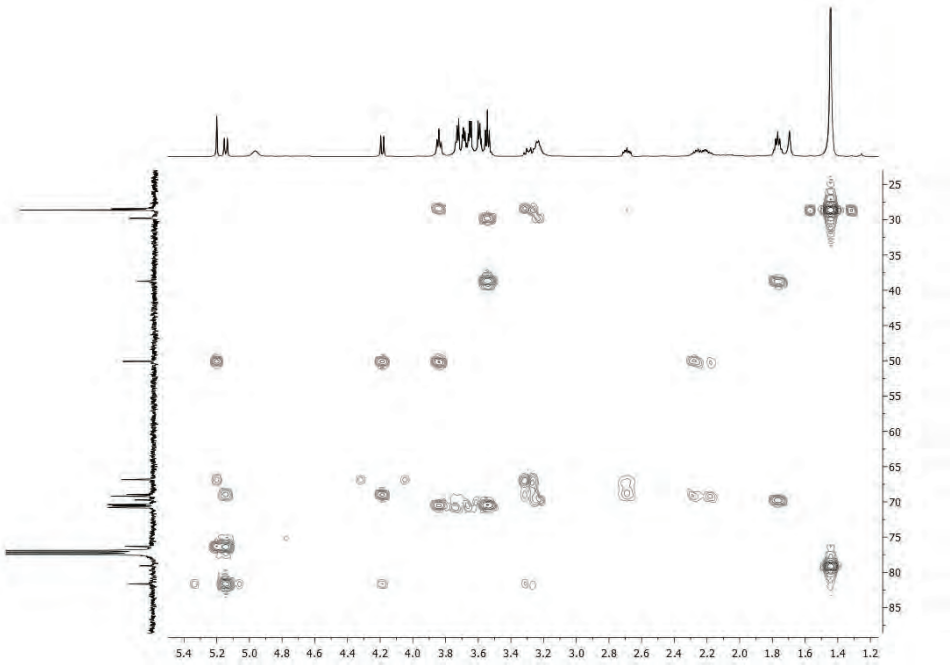
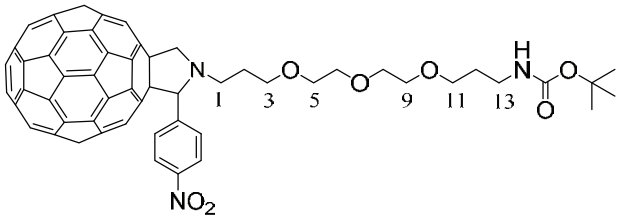
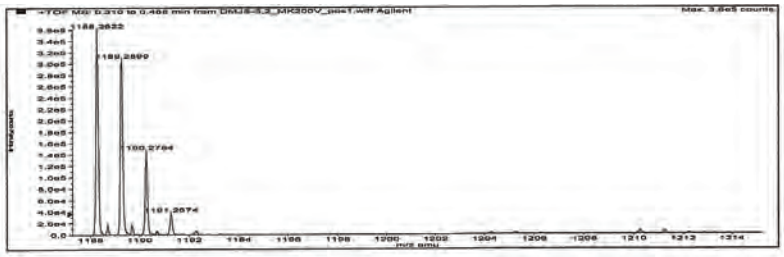


Fig. S-69. Part of the HMBC spectrum of **17c**.

4-Nitrophenyl-substituted fulleropyrrolidine derivative ***18c***





Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C83H37N3O7	–	1187.26315	0.39	4.46294 E6	–

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+H]+	363811.92	1188.27043	1188.26888	-1.54909	-1.30	–

Fig. S-70. Mass spectrum of **18c**

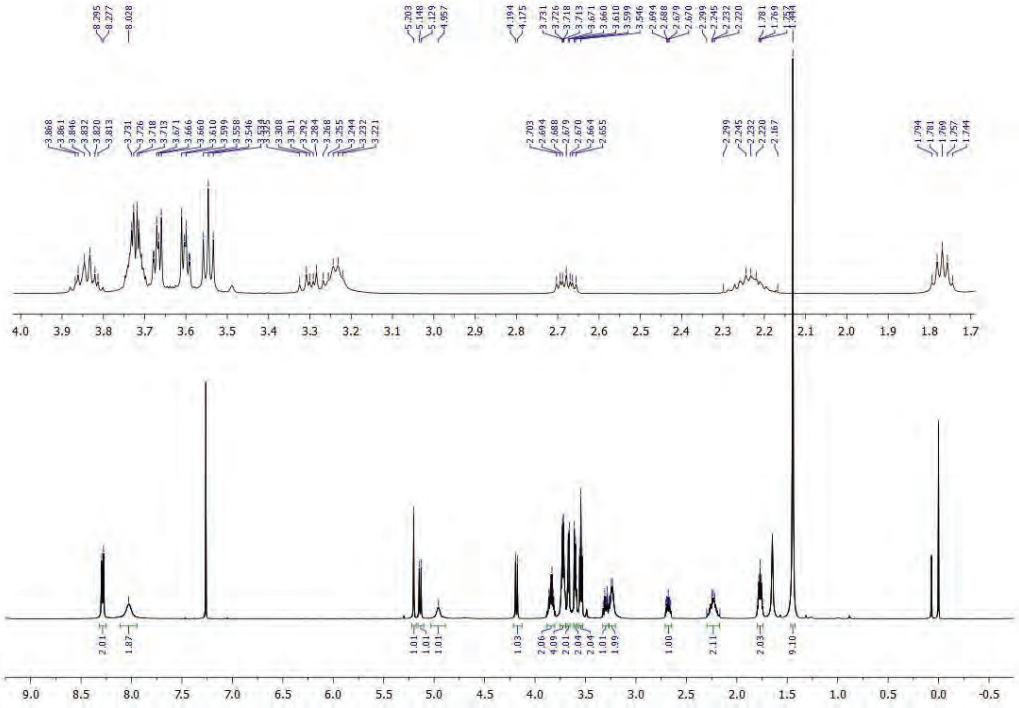


Fig. S-71. ^{1}H-NMR spectrum of **18c**.

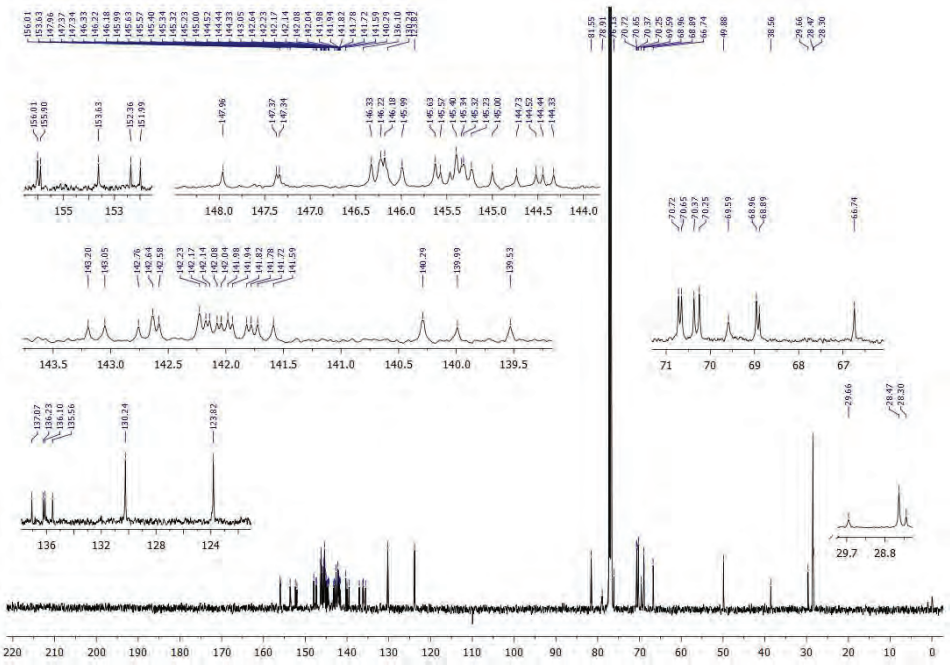


Fig. S-72. ^{13}C-NMR spectrum of **18c**.

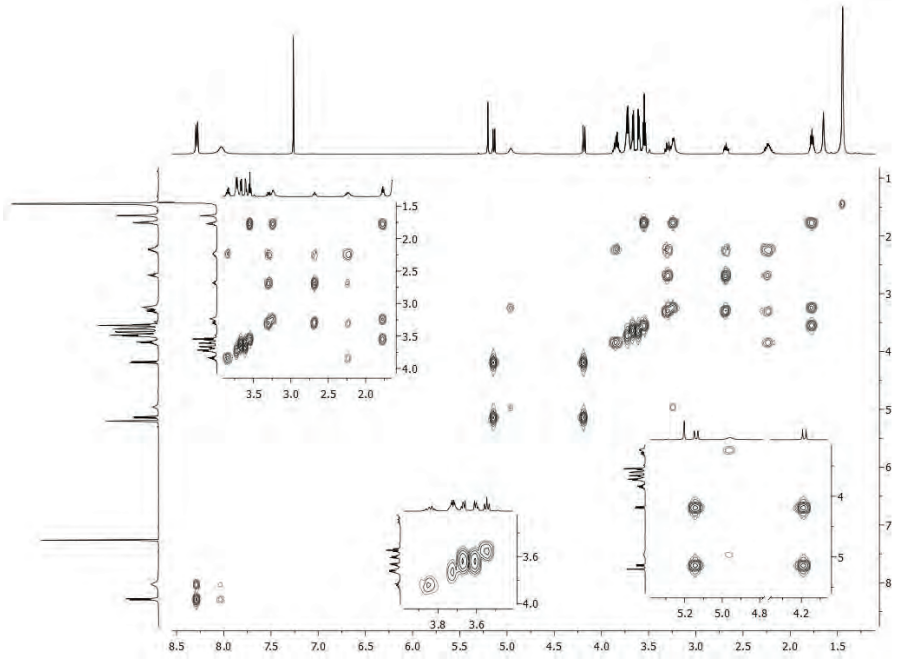


Fig. S-73. COSY spectrum of **18c**.

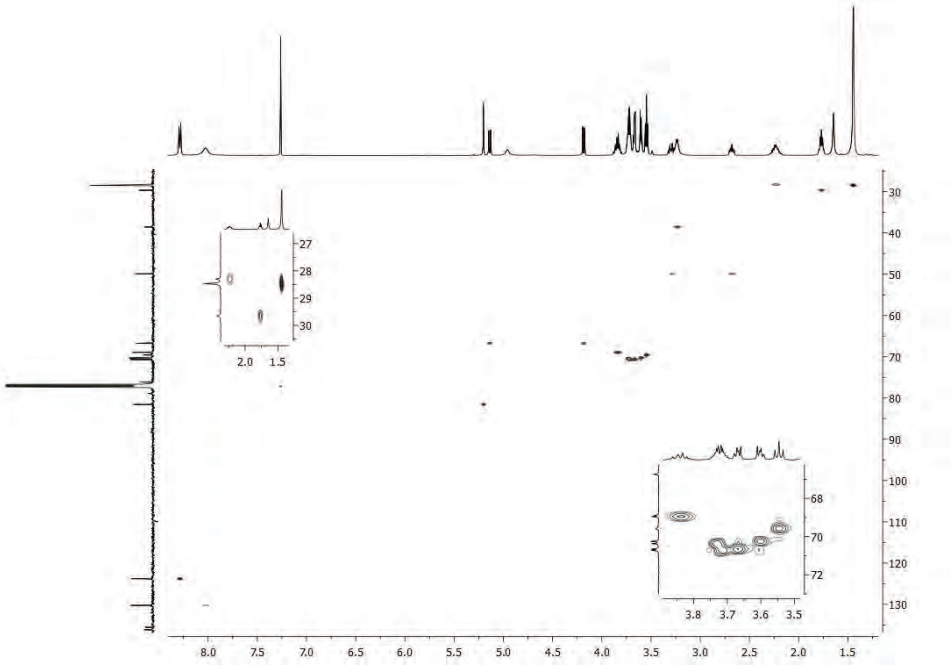


Fig. S-74. HSQC spectrum of **18c**.

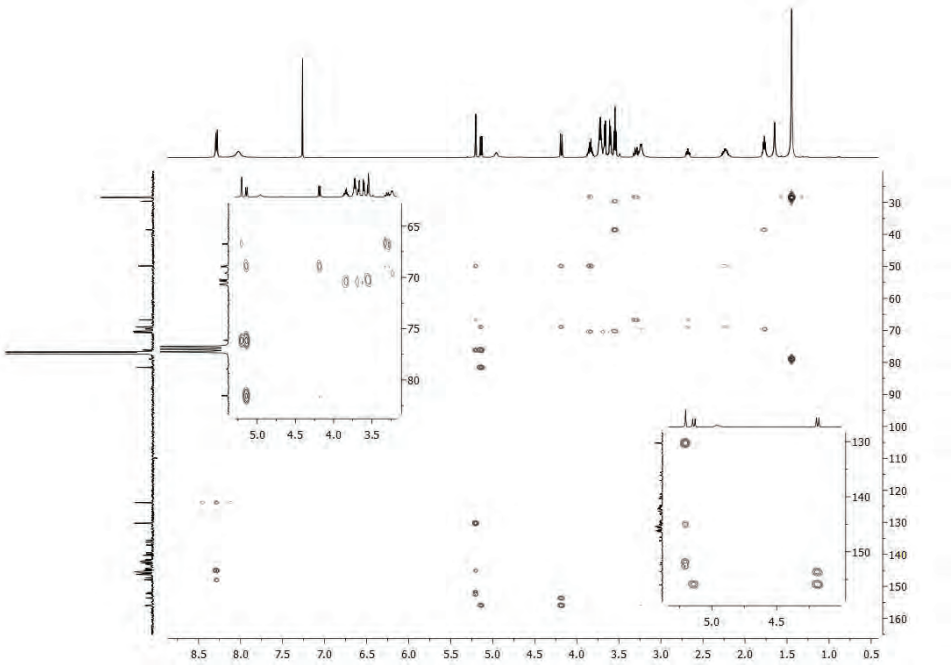


Fig. S-75. HMBC spectrum of **18c**.

Diamide ***19a***

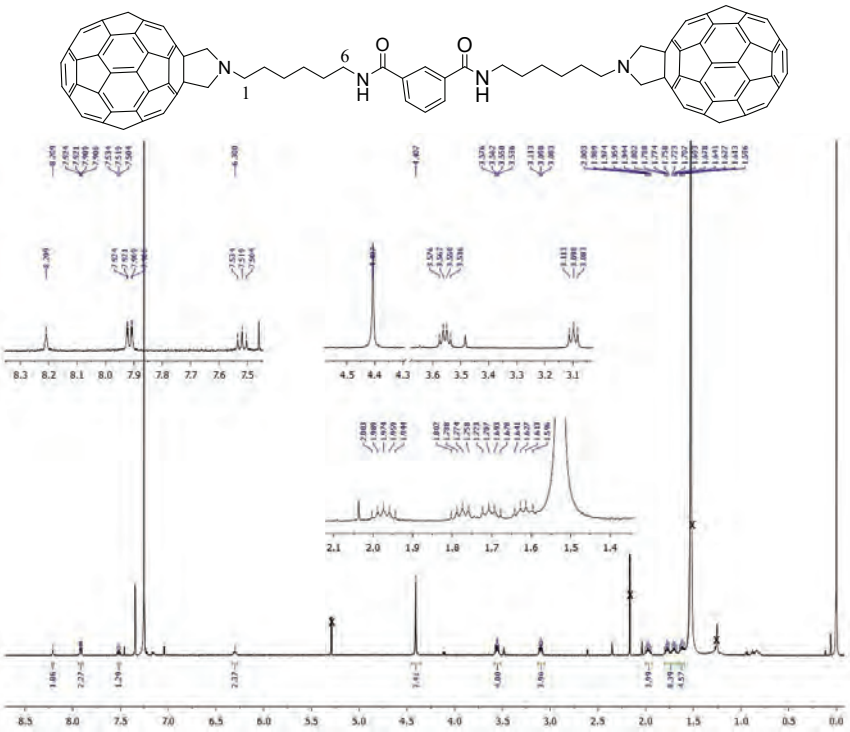


Fig. S-76. ^{1}H-NMR spectrum of **19a**.

*Diamide **20a***

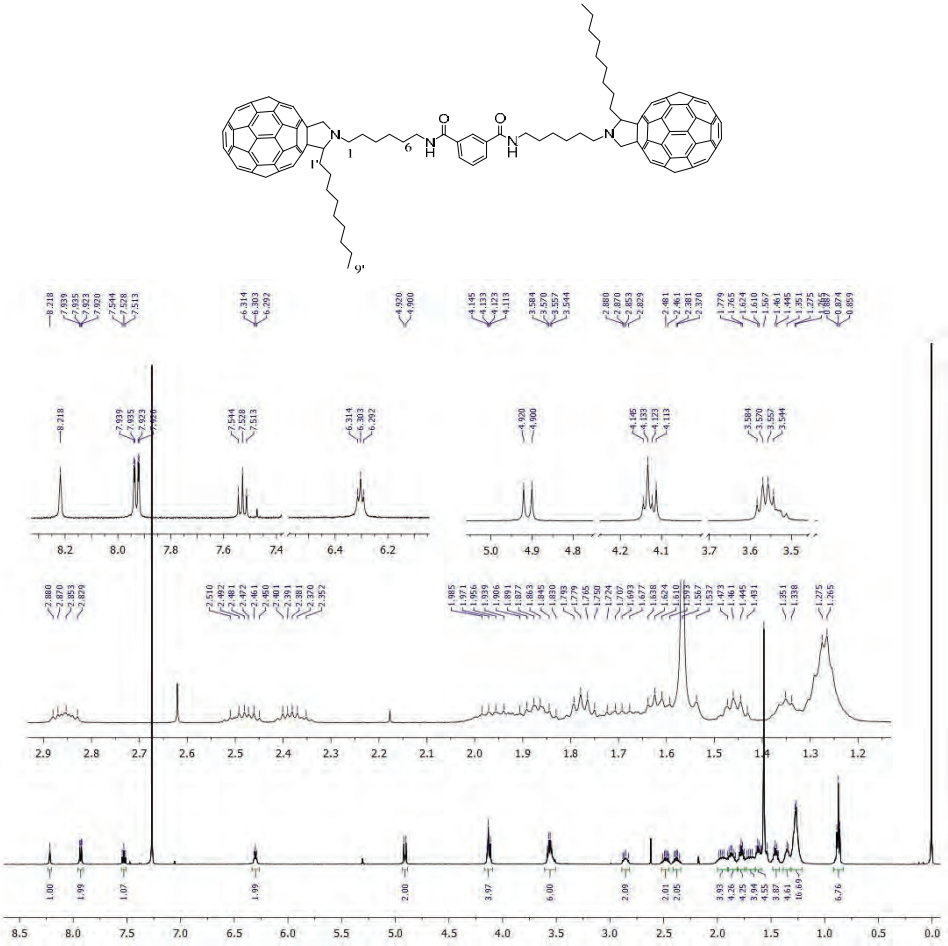


Fig. S-77. ^{1}H-NMR spectrum of **20a**.

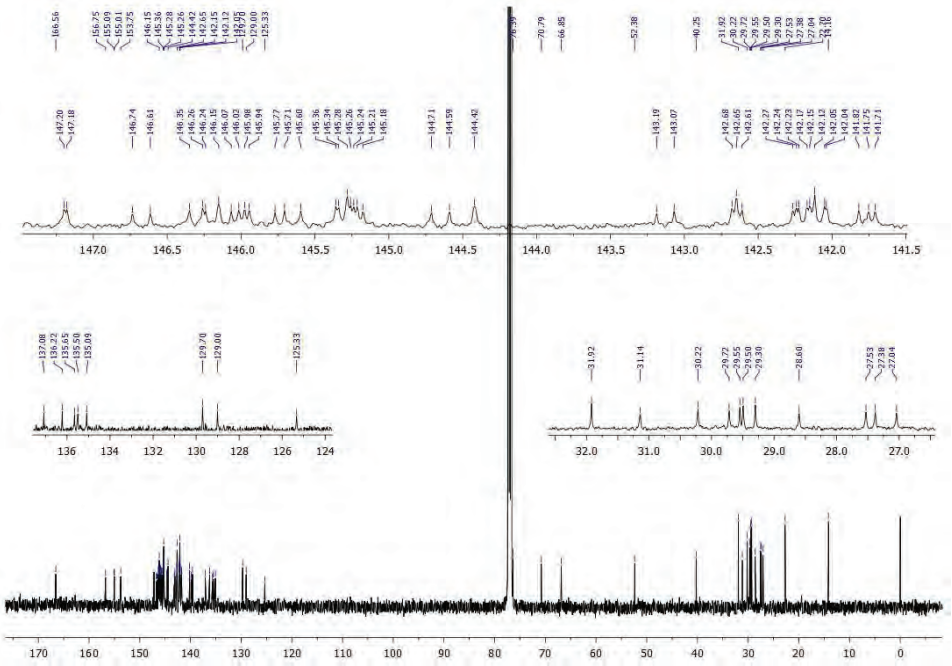


Fig. S-78. ^{13}C-NMR spectrum of **20a**.

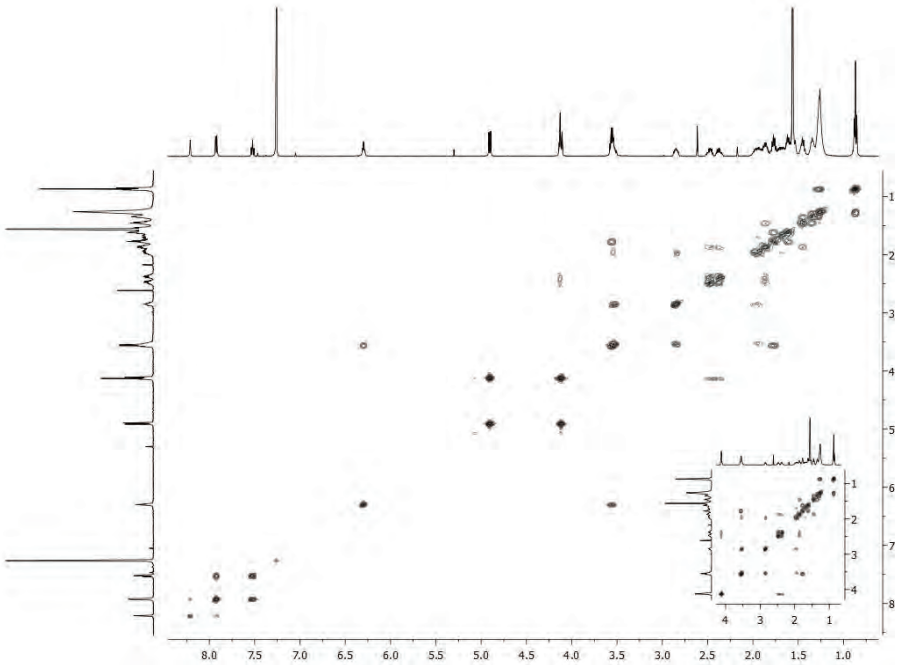


Fig. S-79. COSY spectrum of **20a**.

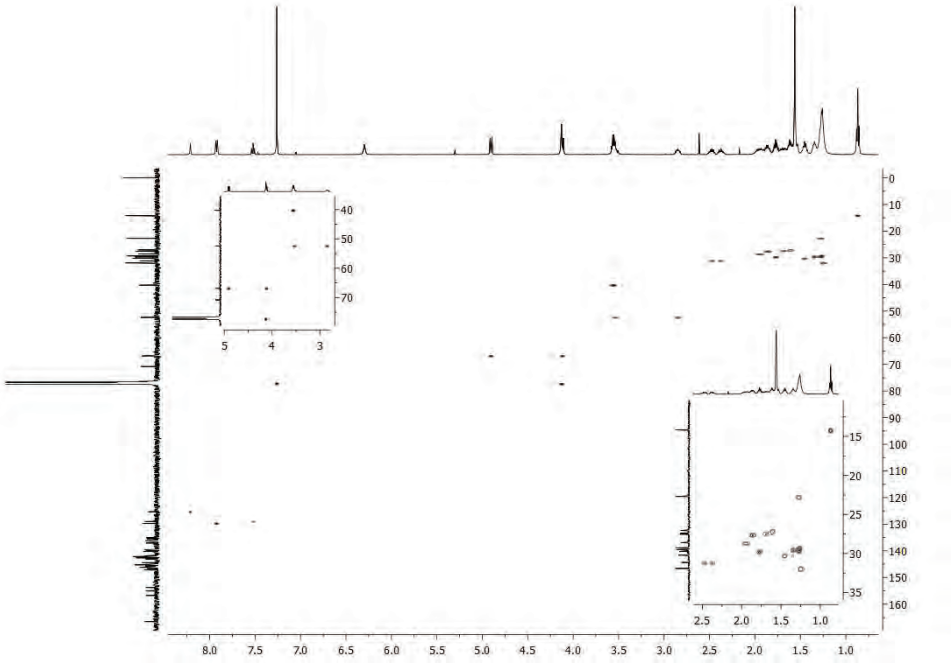


Fig. S-80. HSQC spectrum of **20a**.

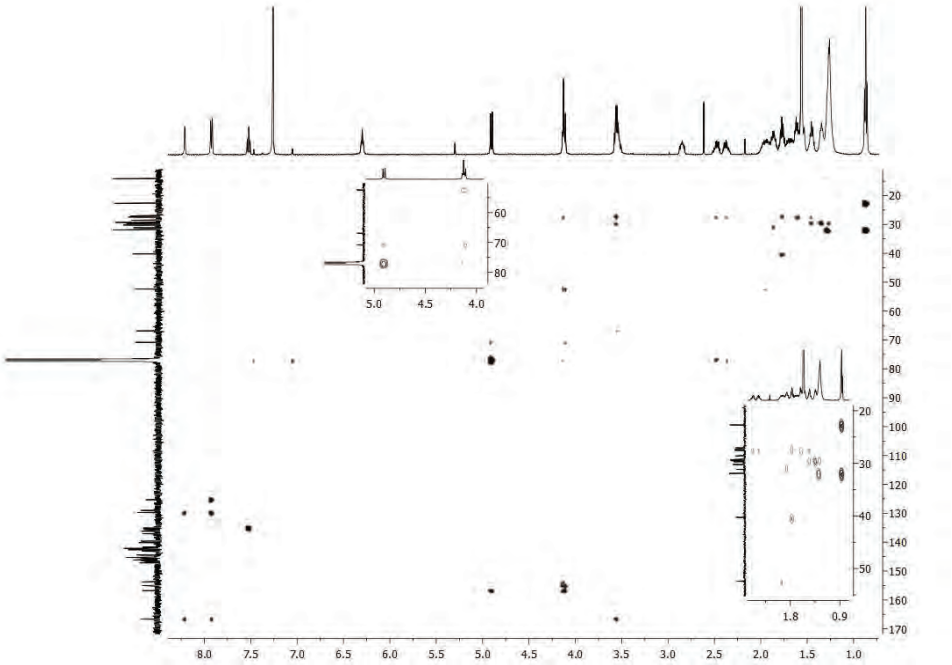


Fig. S-81. HMBC spectrum of **20a**.

*Diamide **21a***

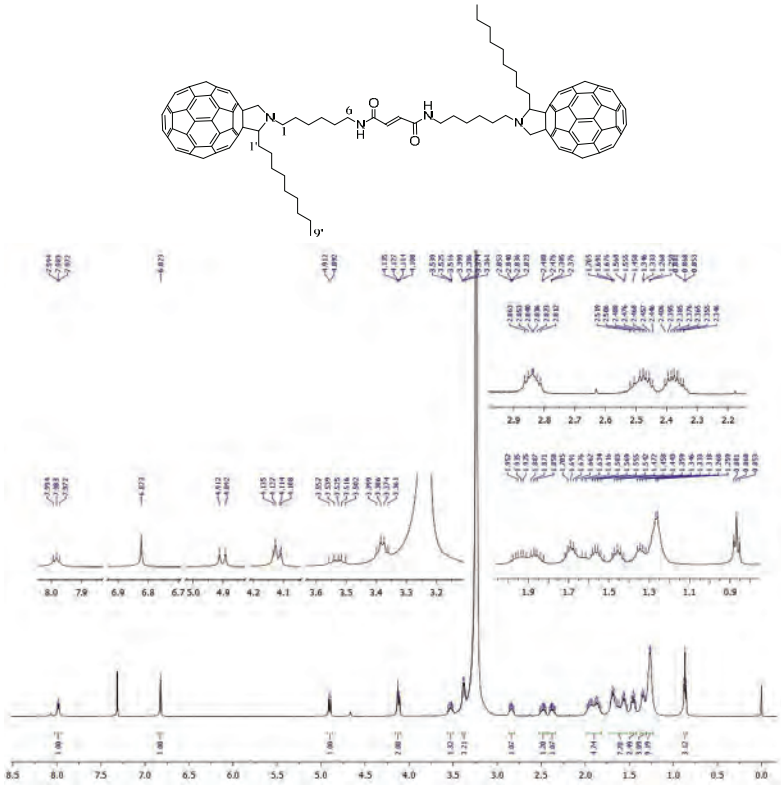


Fig. S-82. ^{1}H-NMR spectrum of **21a**.

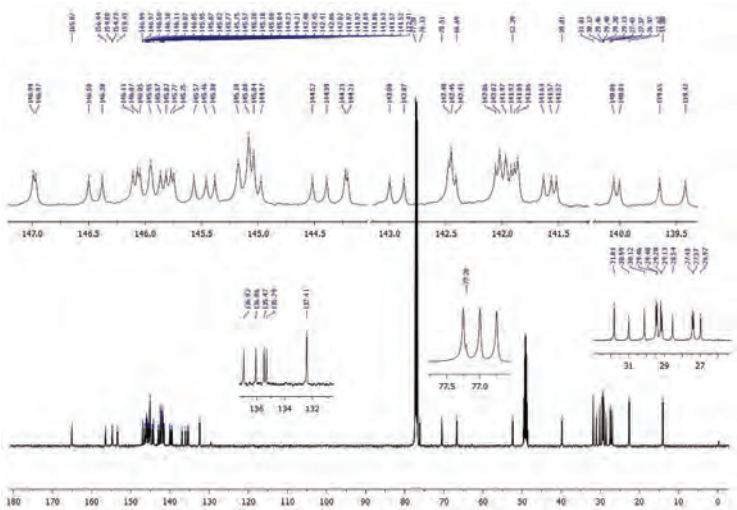


Fig. S-83. ^{13}C-NMR spectrum of **21a**.

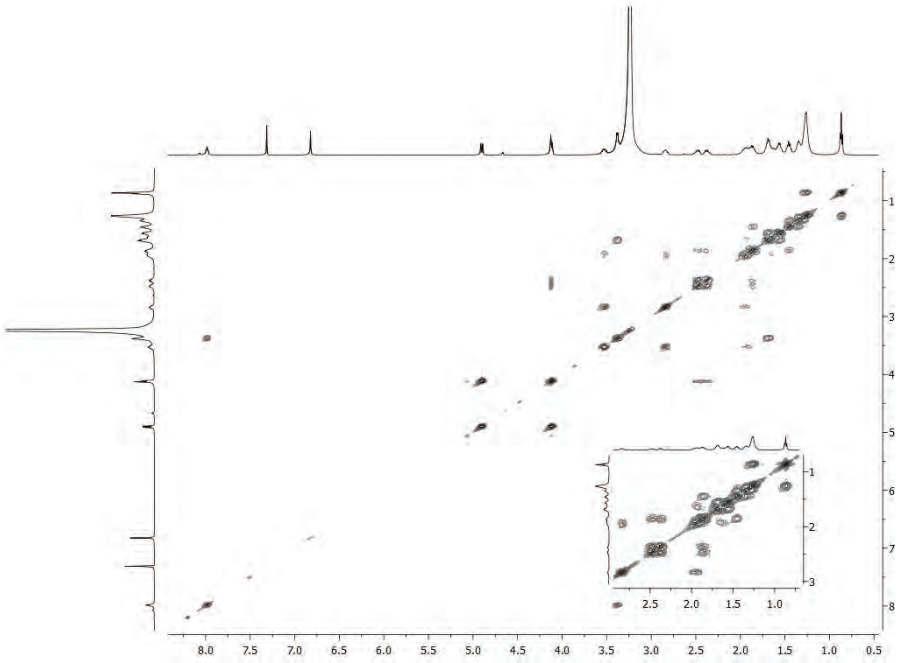


Fig. S-84. COSY spectrum of **21a**.

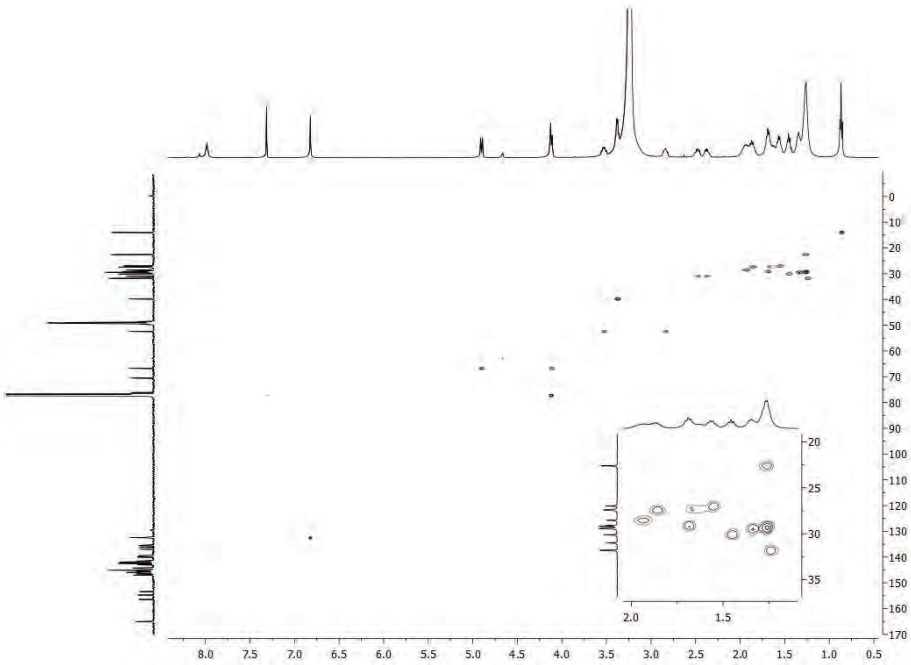


Fig. S-85. HSQC spectrum of **21a**.

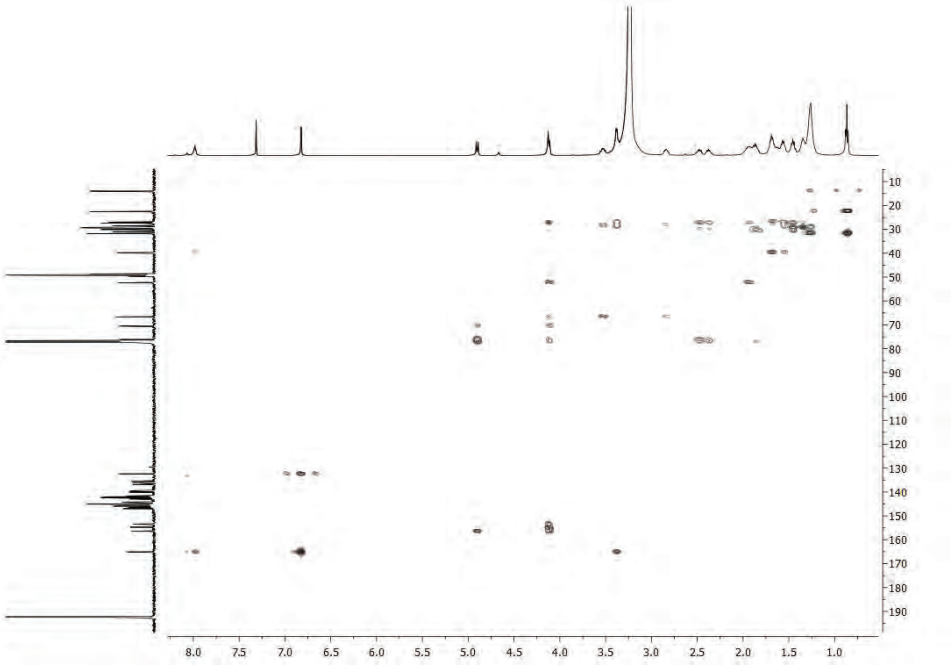


Fig. S-86. HMBC spectrum of **21a**.

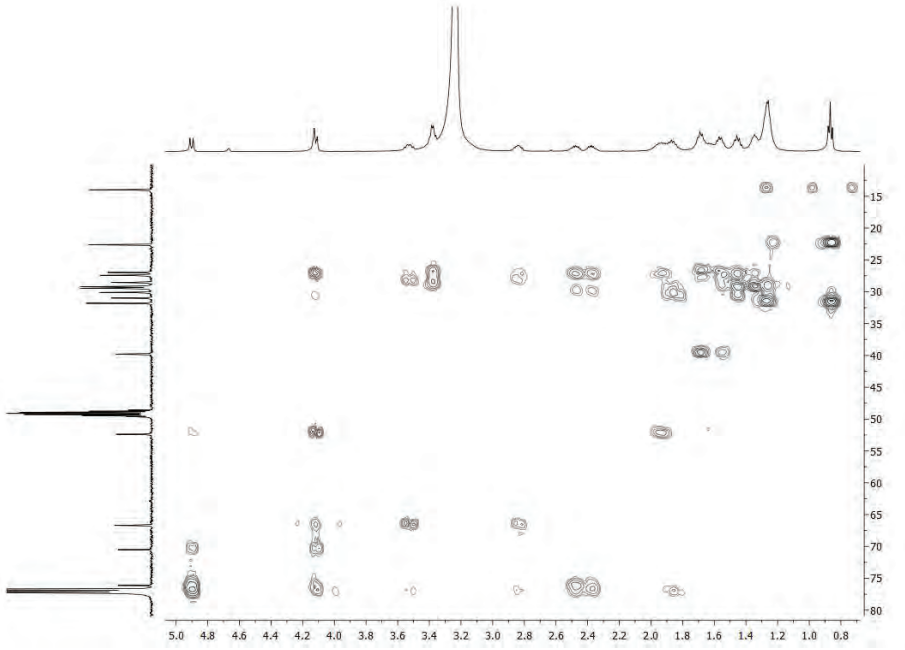
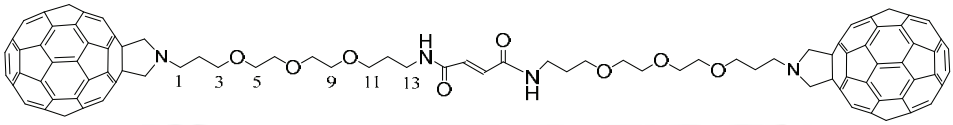


Fig. S-87. Part of the HMBC spectrum of **21a**.

Diamide ***22c***



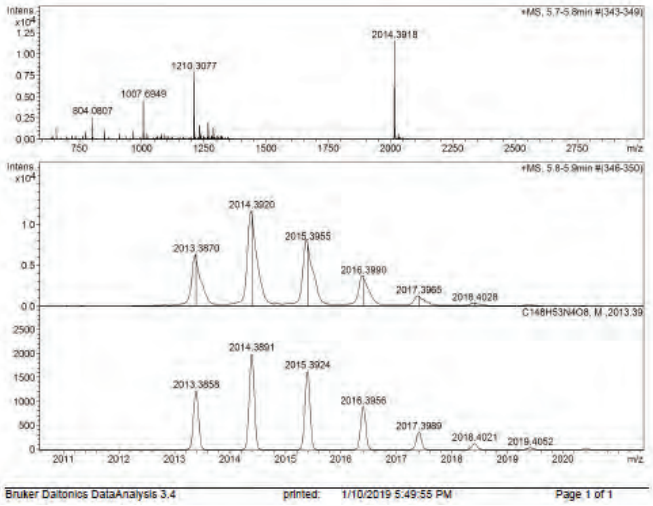


Fig. S-88. Mass spectrum of **22c**.

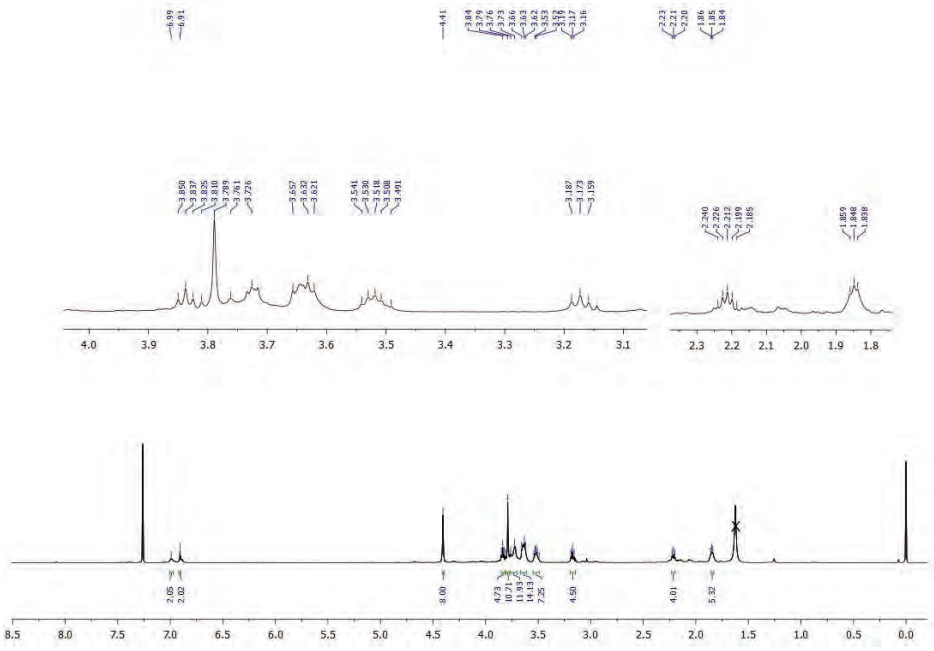


Fig. S-89. ^{1}H-NMR spectrum of **22c**.

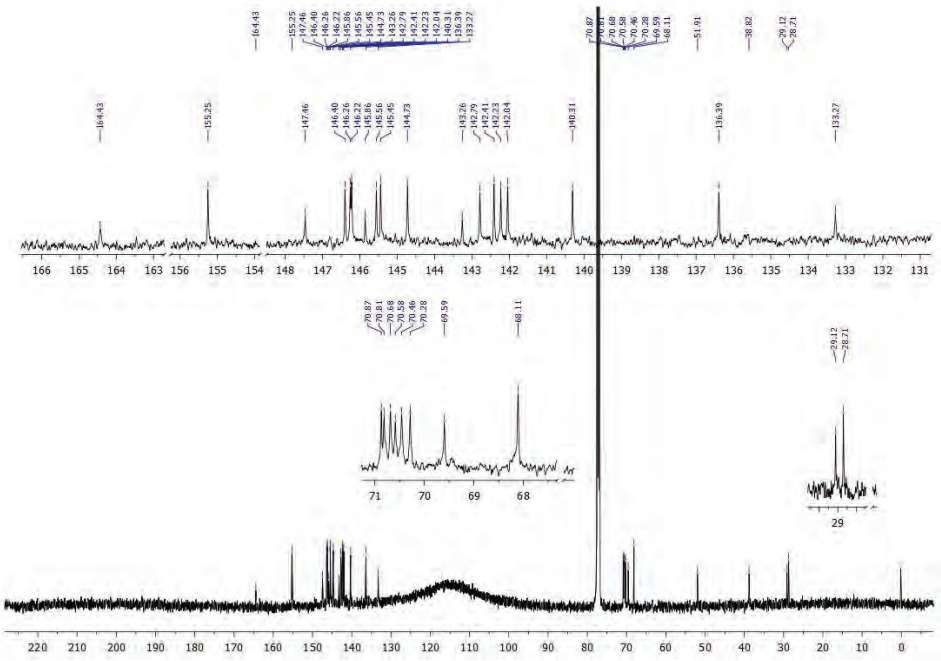


Fig. S-90. ^{13}C-NMR spectrum of **22c**.

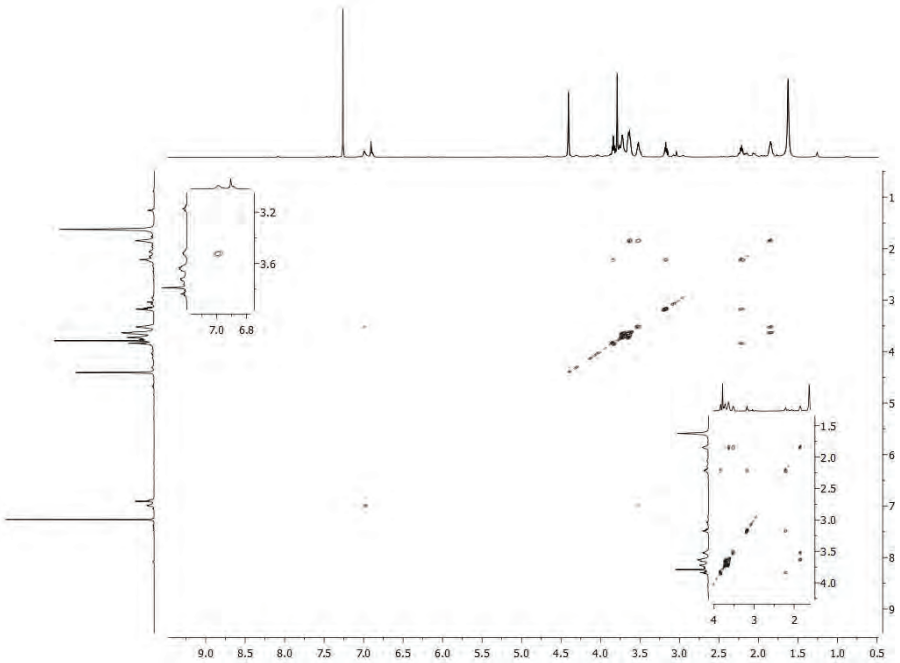


Fig. S-91. COSY spectrum of **22c**.

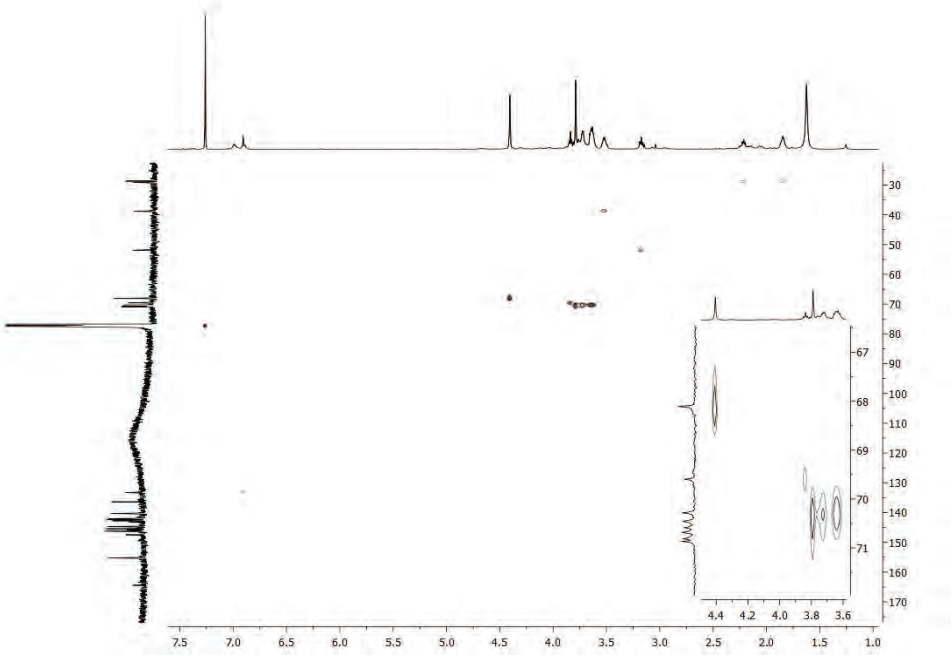


Fig. S-92. HSQC spectrum of **22c**.

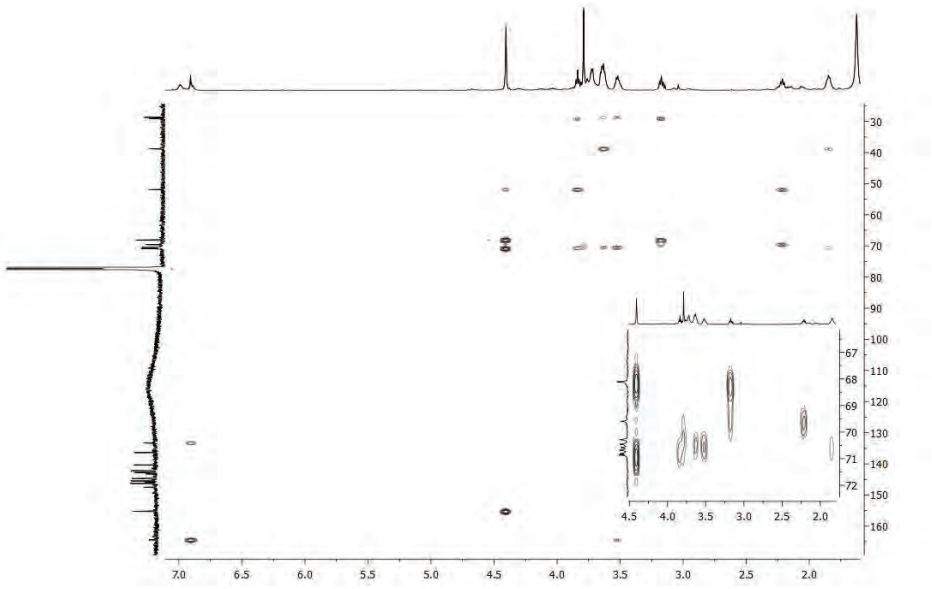


Fig. S-93. HMBC spectrum of **22c**.

Diamide ***23c***

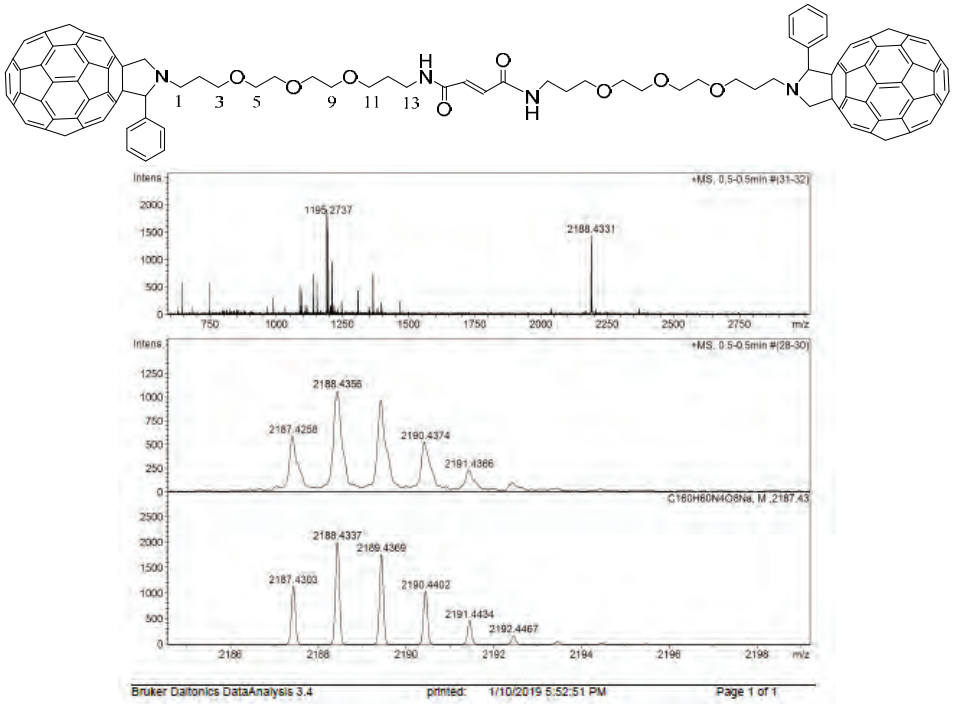


Fig. S-94. Mass spectrum of **23c**.

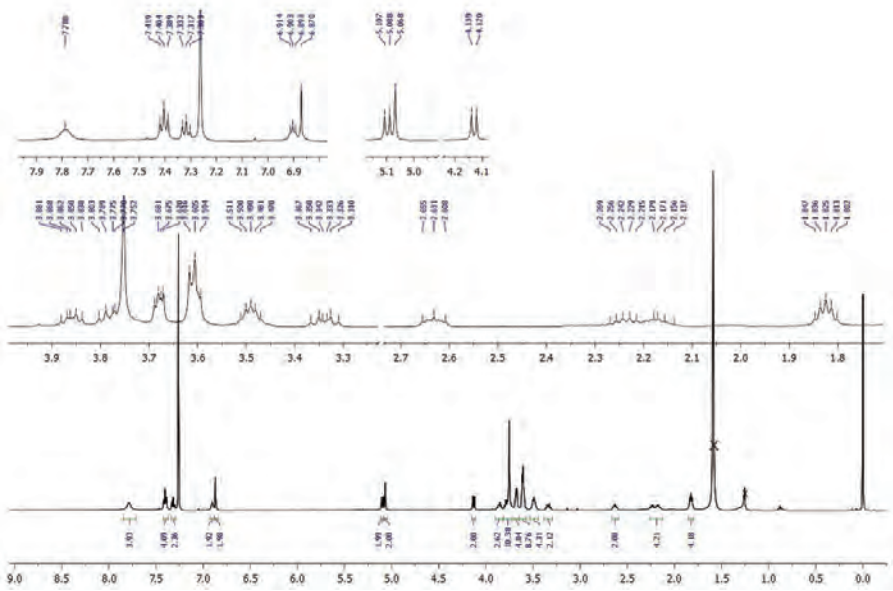


Fig. S-95. ^{1}H-NMR spectrum of **23c**.

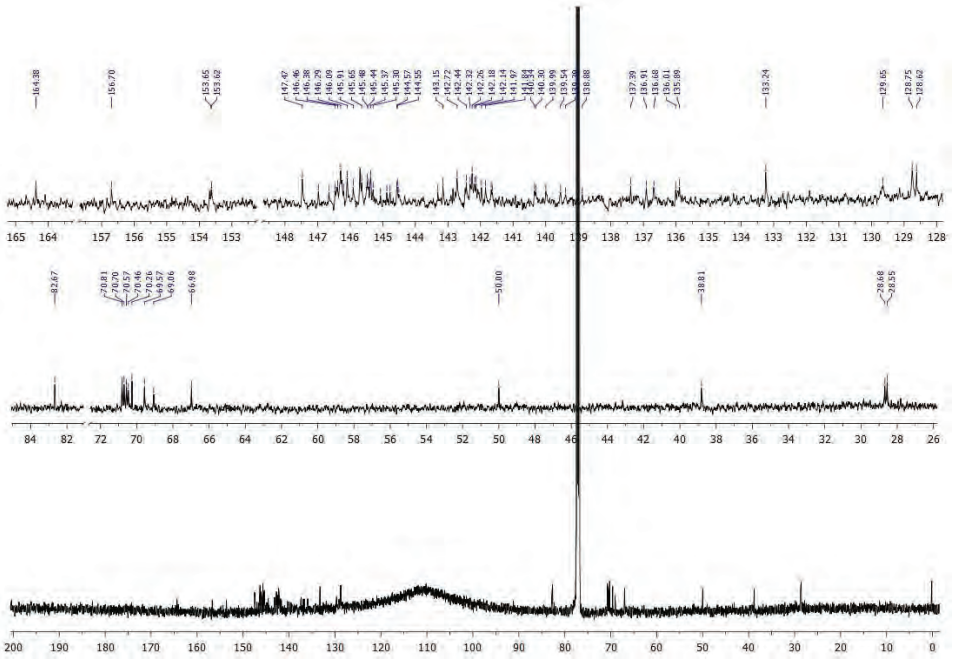


Fig. S-96. ^{13}C-NMR spectrum of **23c**.

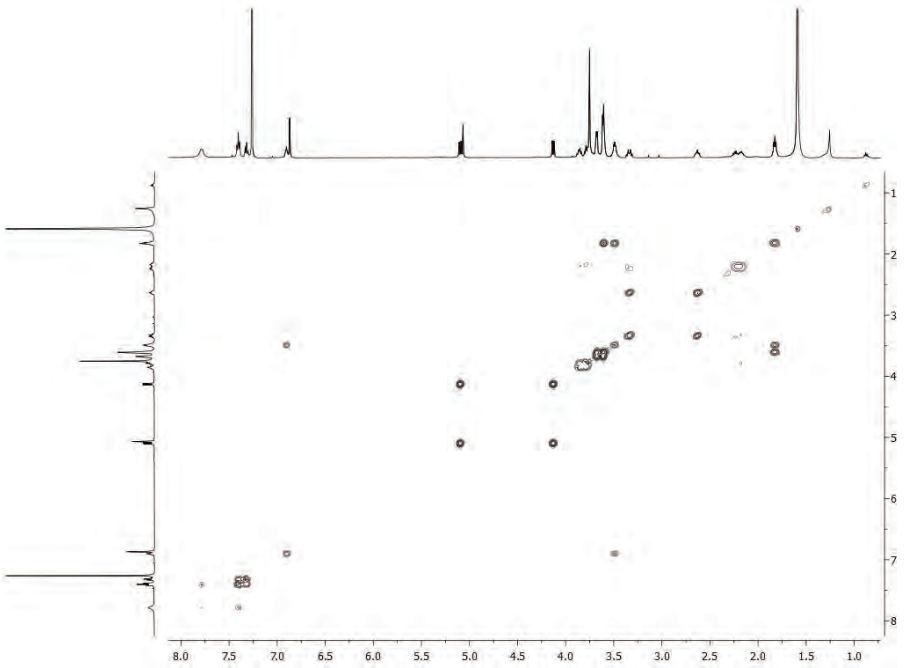


Fig. S-97. COSY spectrum of 23.c

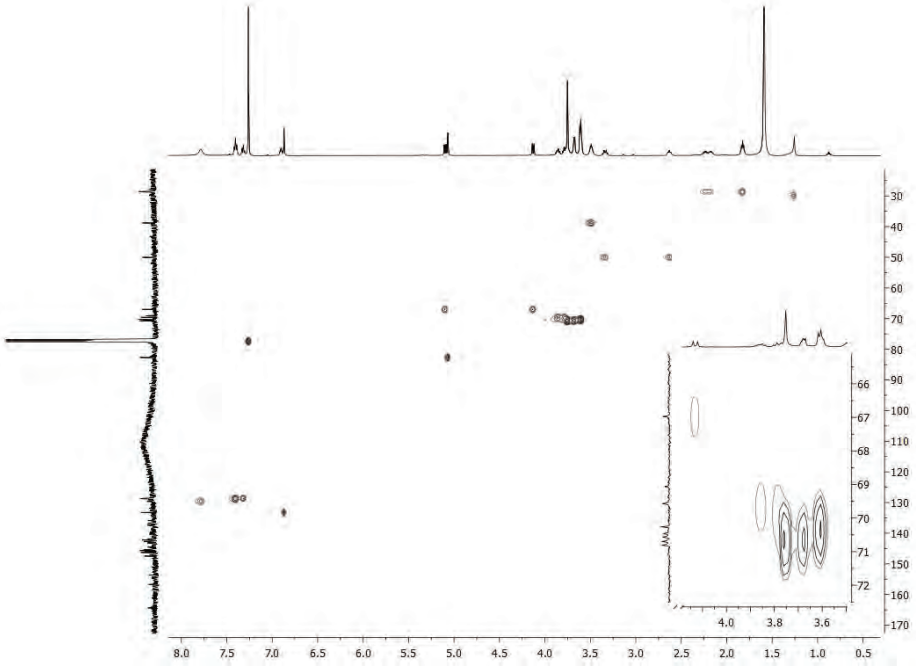


Fig. S-98. HSQC spectrum of **23c**.

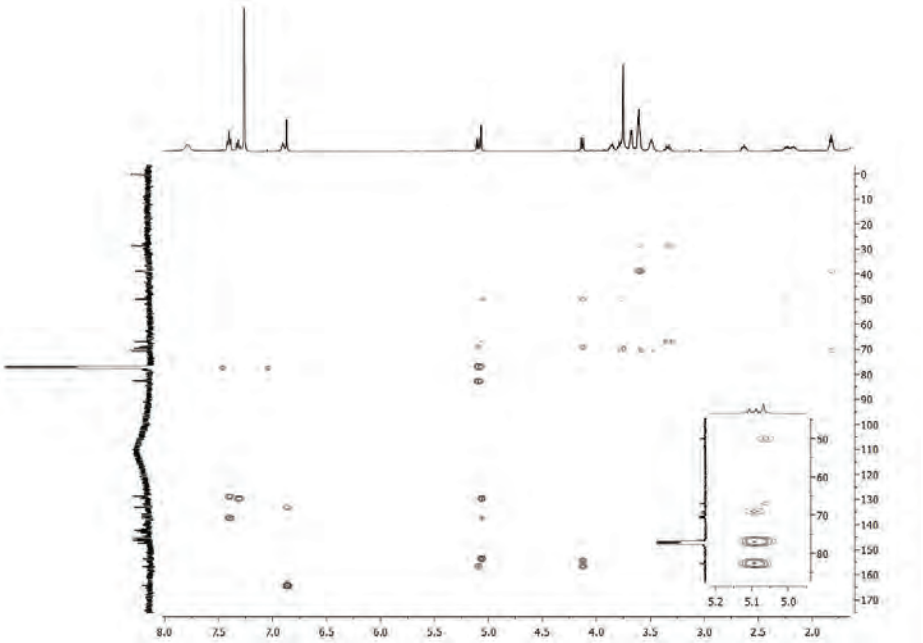


Fig. S-99. HMBC spectrum of **23c**.

*Diamide **24c***

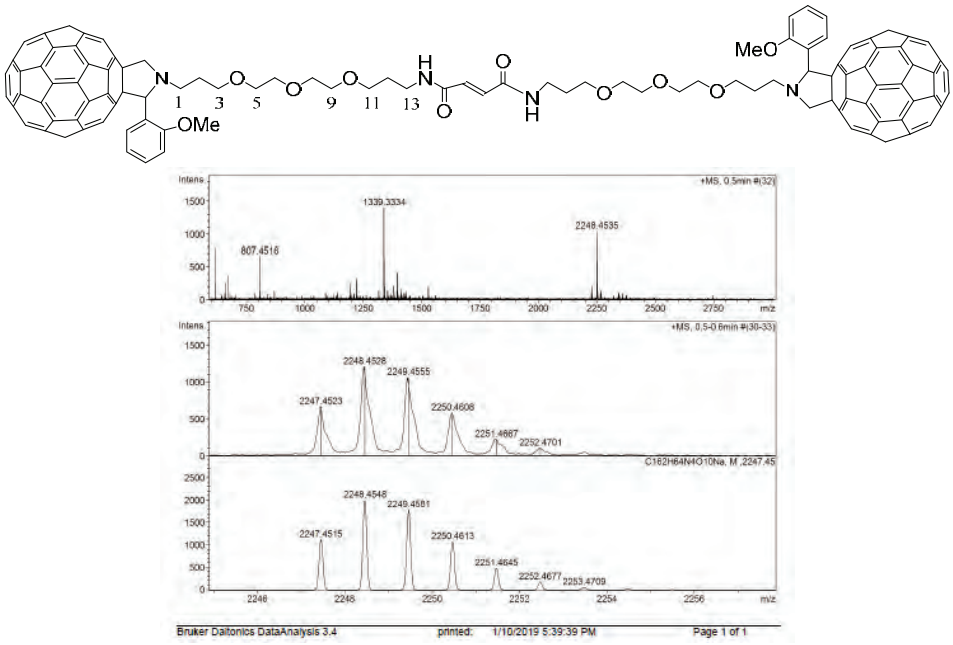


Fig. S-100. Mass spectrum of **24c**.

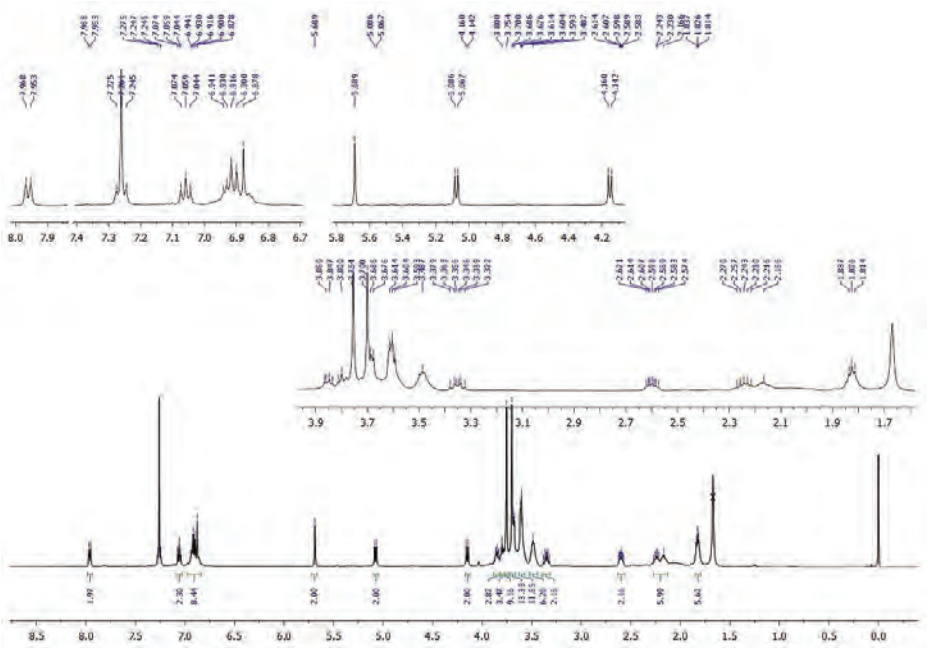


Fig. S-101. ^{1}H-NMR spectrum of **24c**.

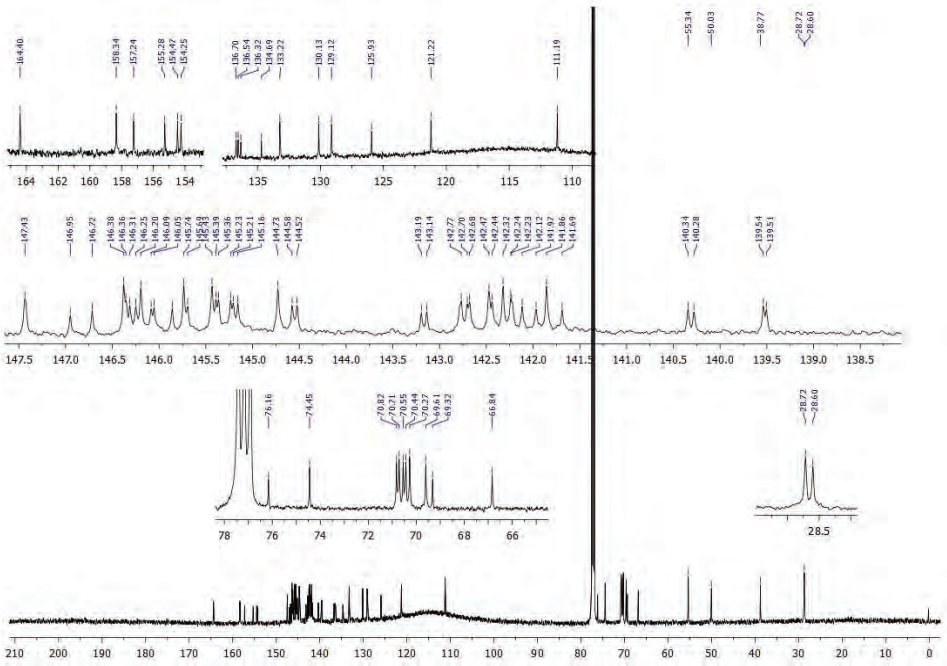


Fig. S-102. ^{13}C-NMR spectrum of **24c**

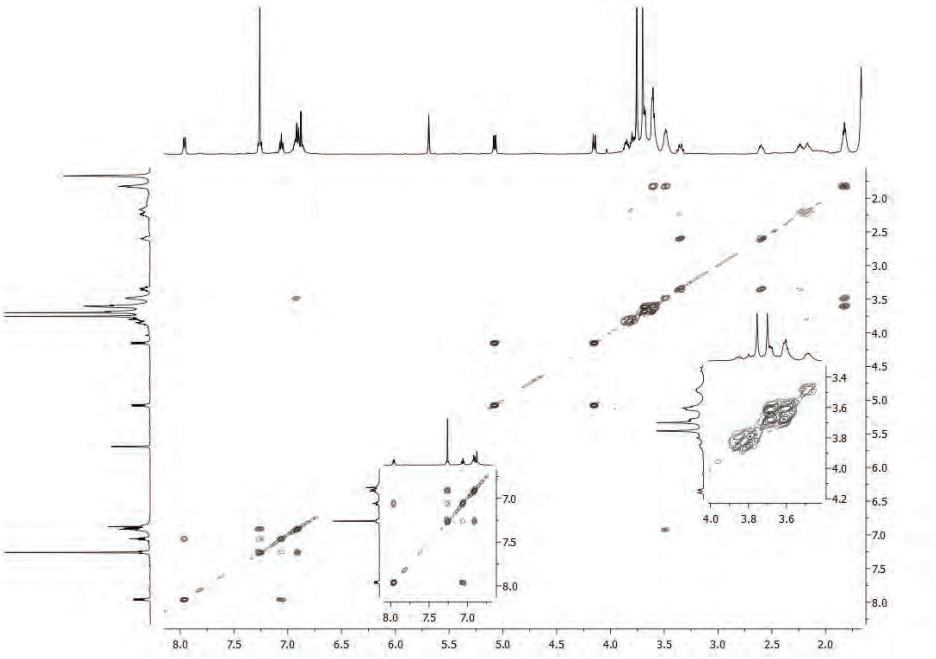


Fig. S-103. COSY spectrum of **24c**.

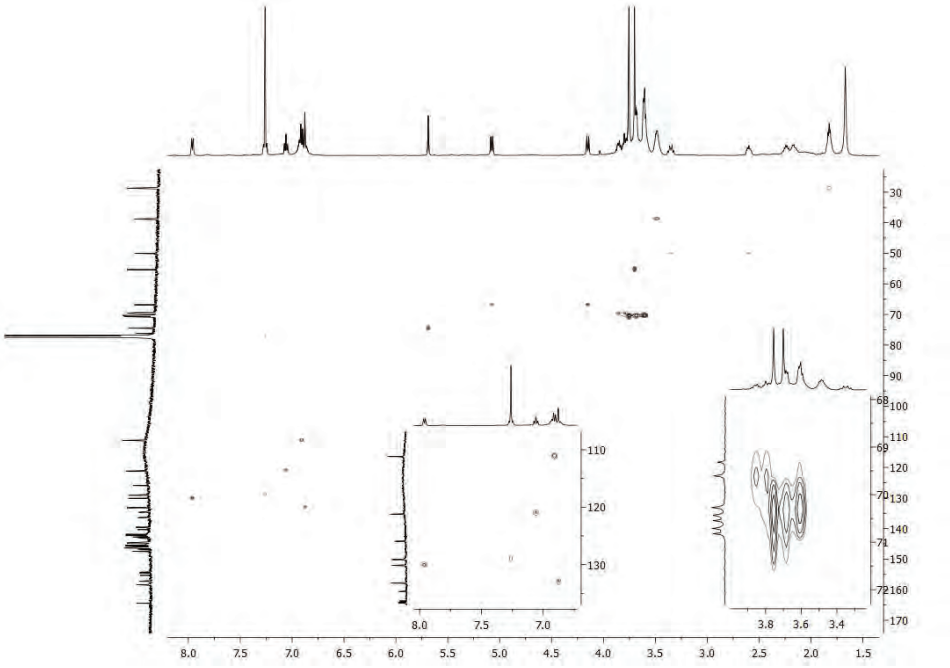


Fig. S-104. HSQC spectrum of **24c**.

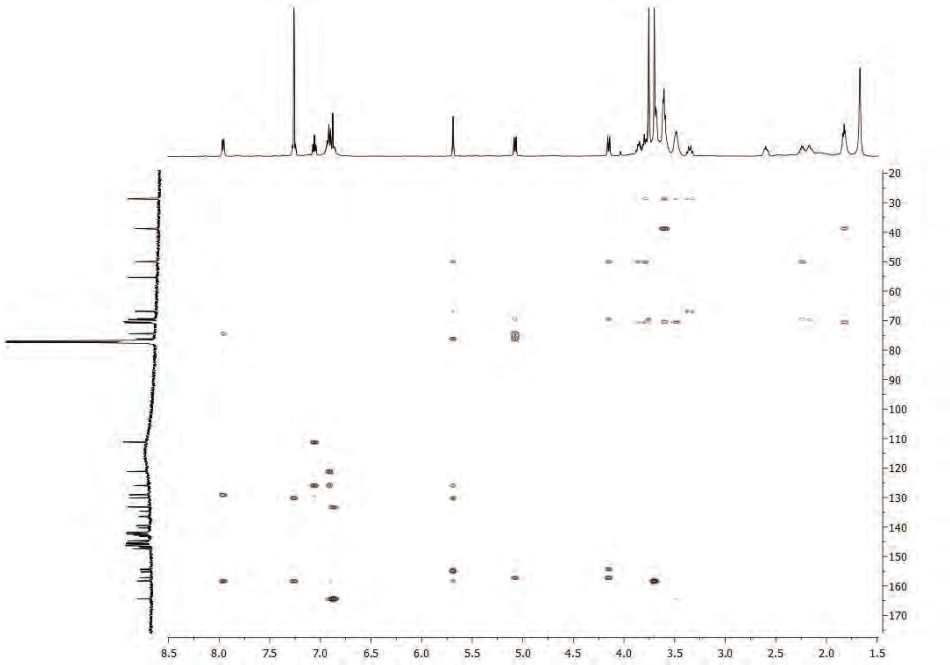
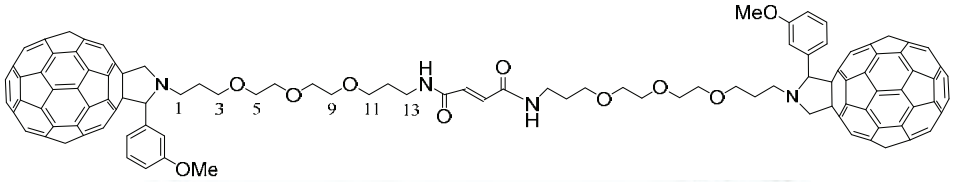


Fig. S-105. HMBC spectrum of **24c**.

Diamide ***25c***



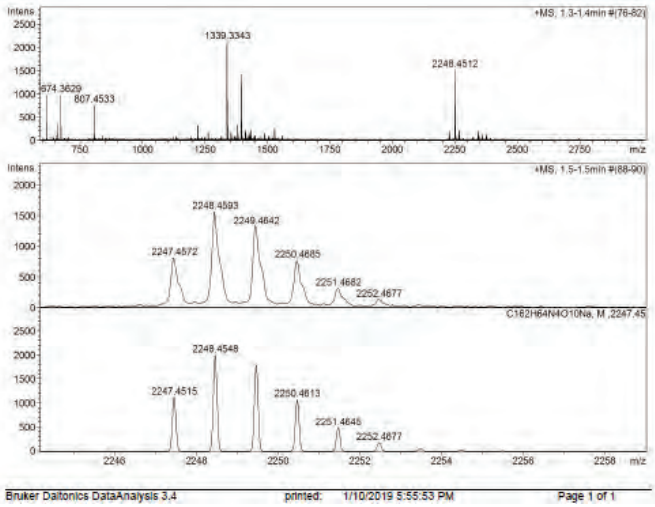


Fig. S-106. Mass spectrum of **25c**.

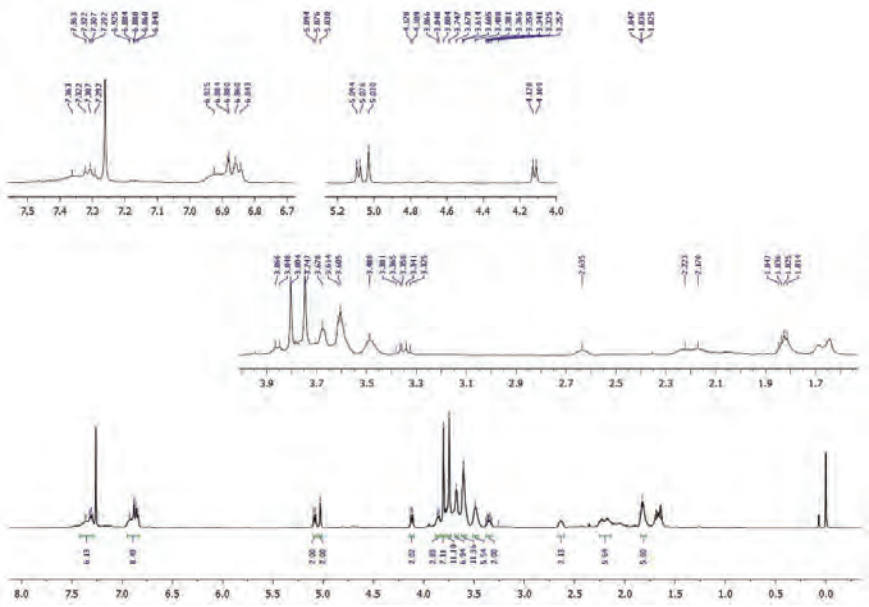


Fig. S-107. ^{1}H-NMR spectrum of **25c**.

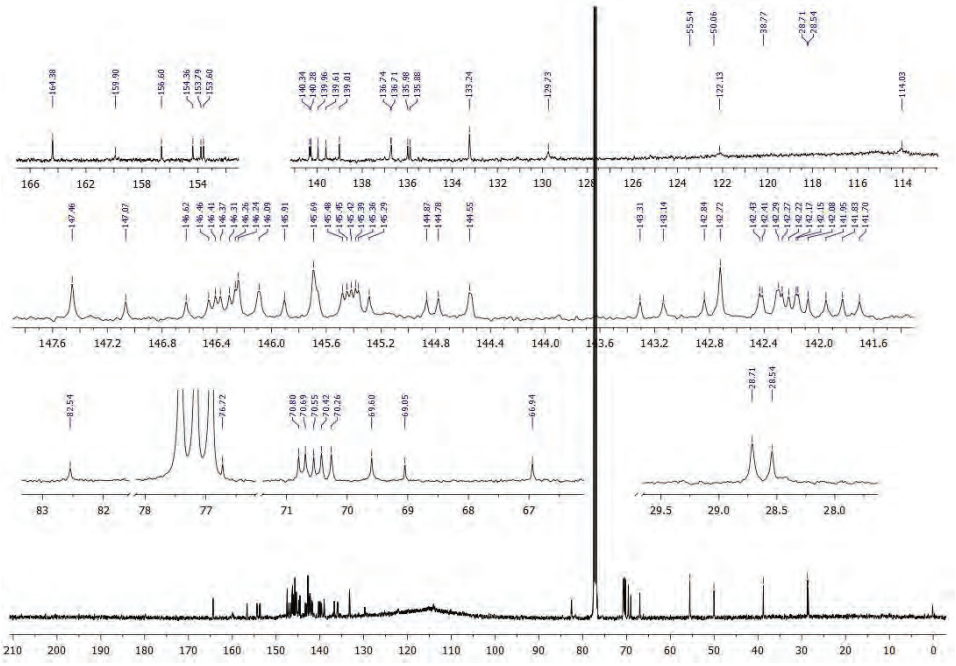


Fig. S-108. ^{13}C-NMR spectrum of **25c**.

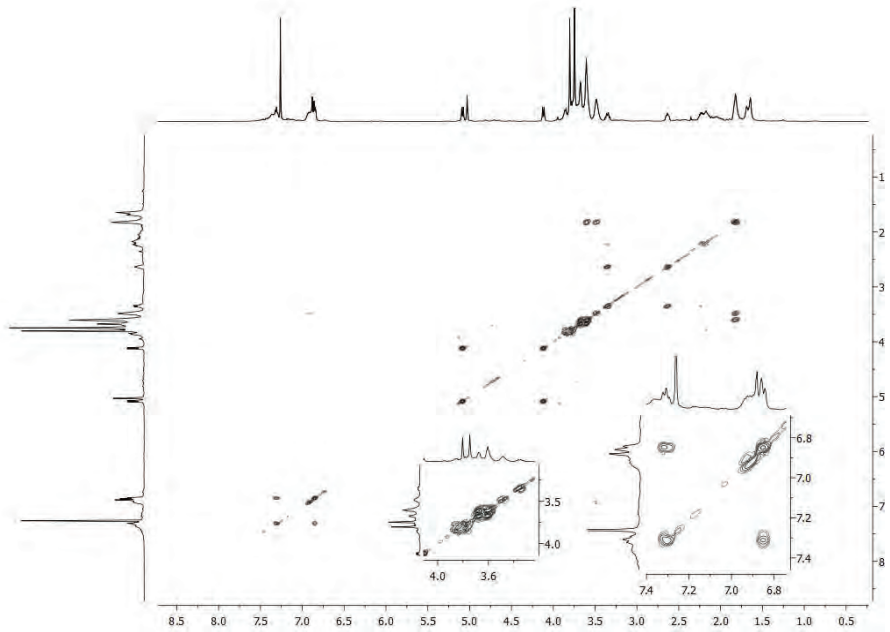


Fig. S-109. COSY spectrum of **25c**.

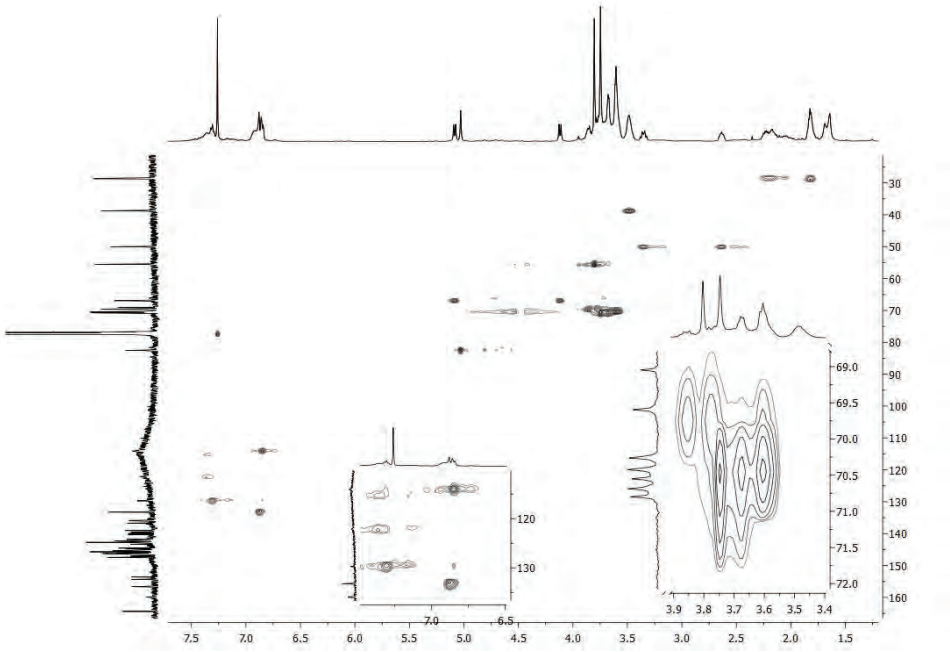


Fig. S-110. HSQC spectrum of **25c**.

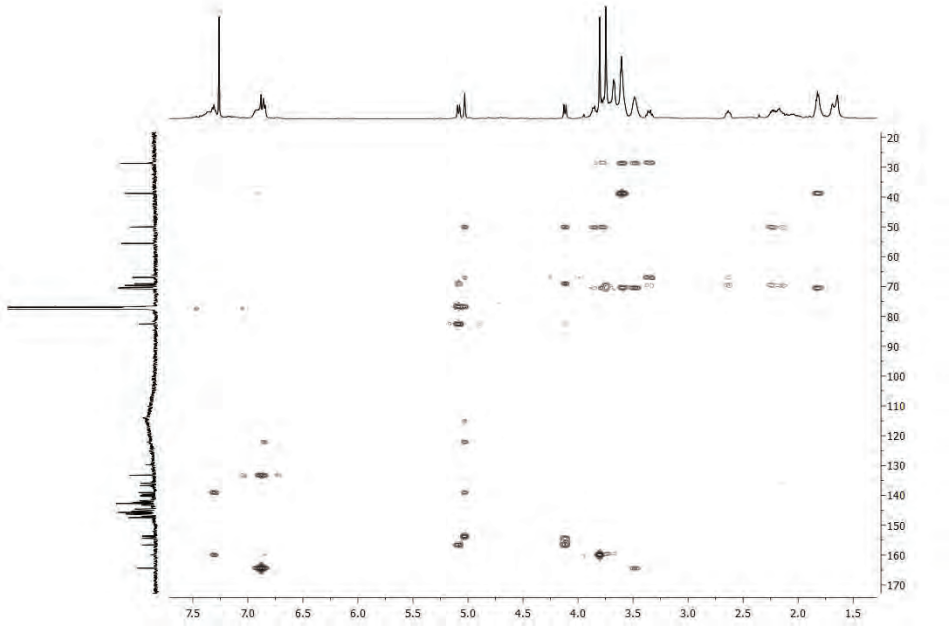


Fig. S-111. HMBC spectrum of **25c**.

Diamide ***26c***

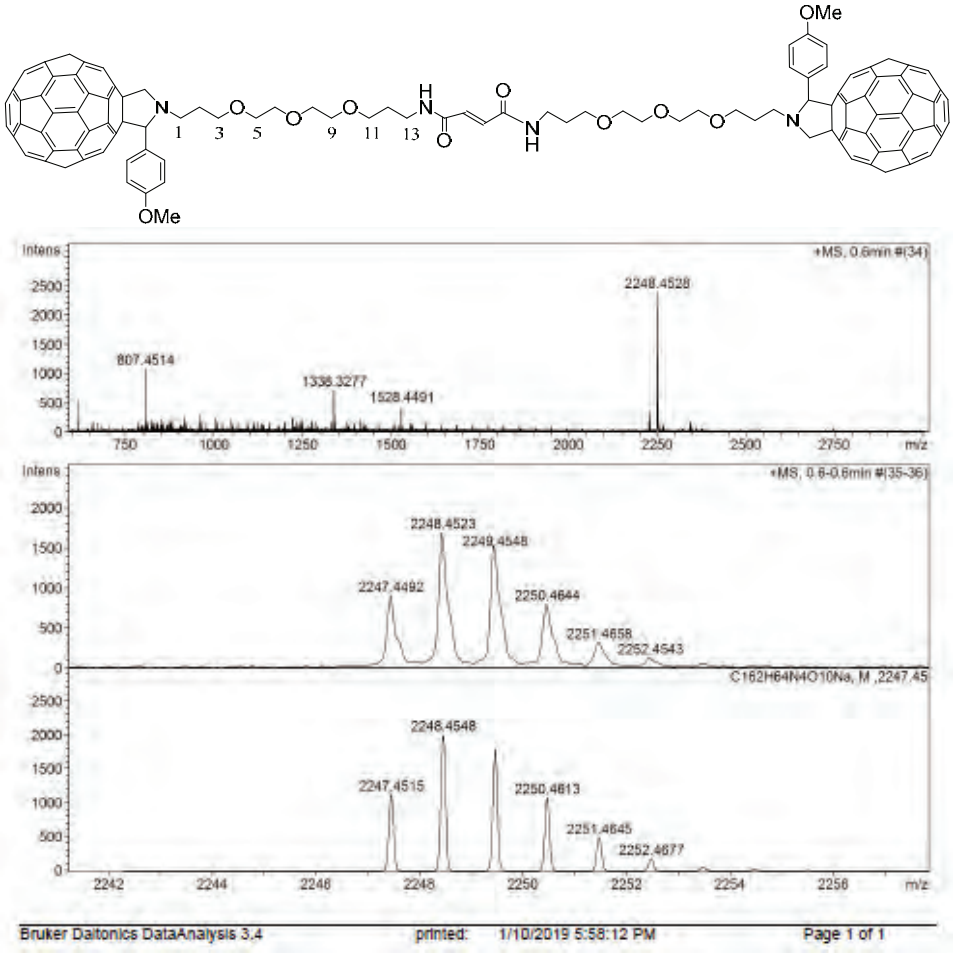


Fig. S-112. Mass spectrum of **26c**.

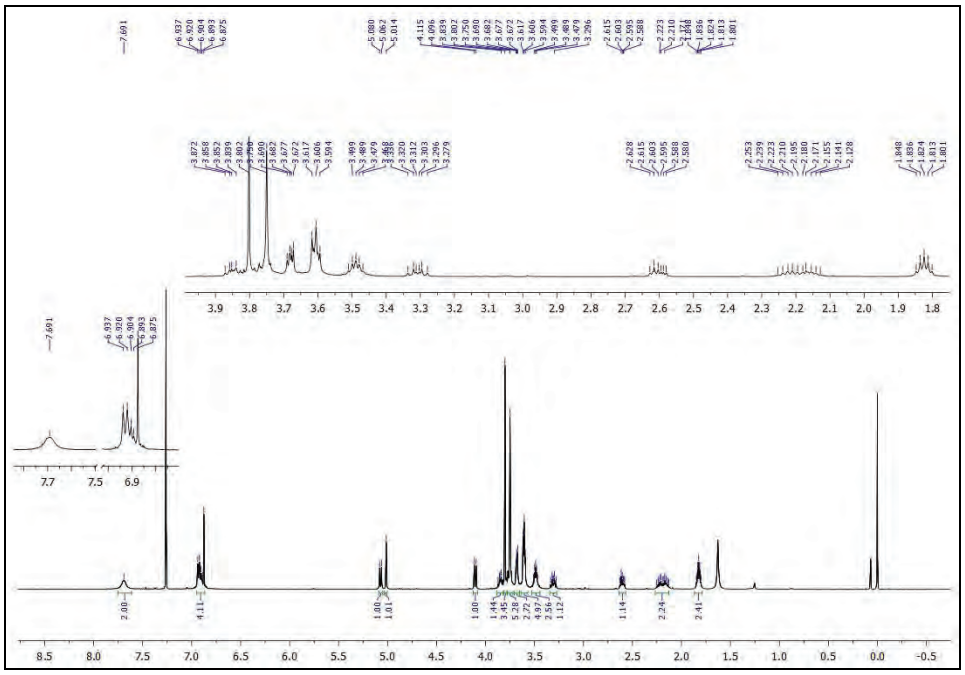


Fig. S-113. ^{1}H-NMR spectrum of **26c**.

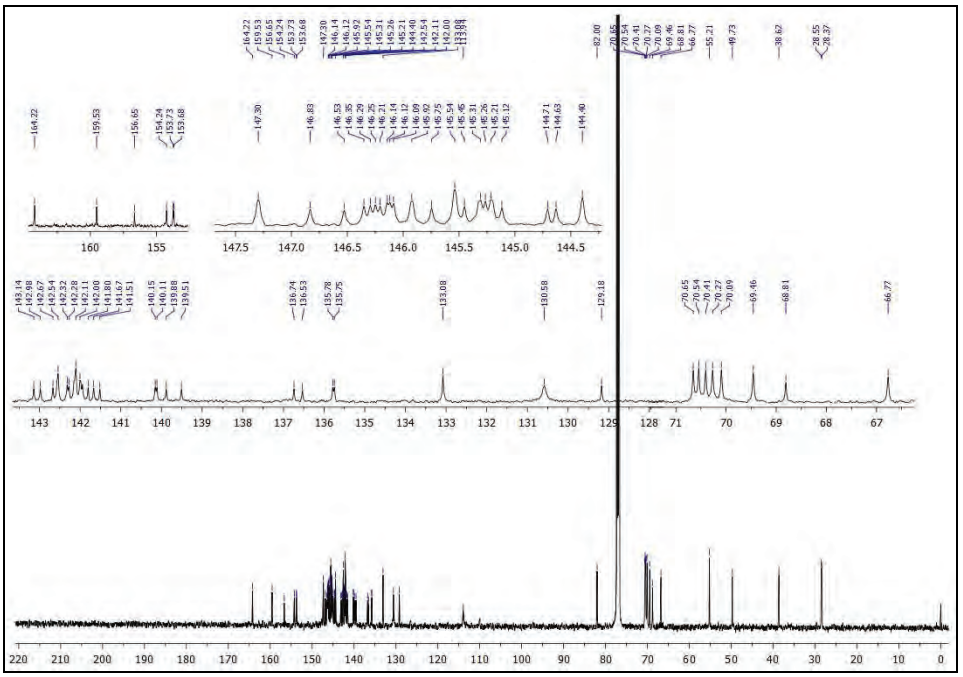


Fig. S-114. ^{13}C-NMR spectrum of **26c**.

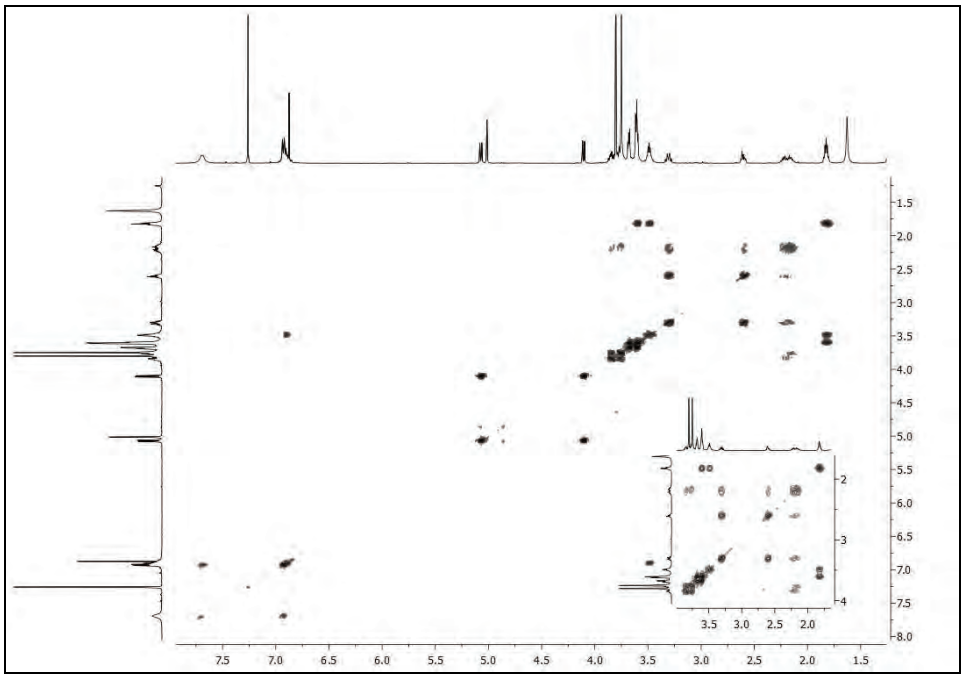


Fig. S-115. COSY spectrum of **26c**.

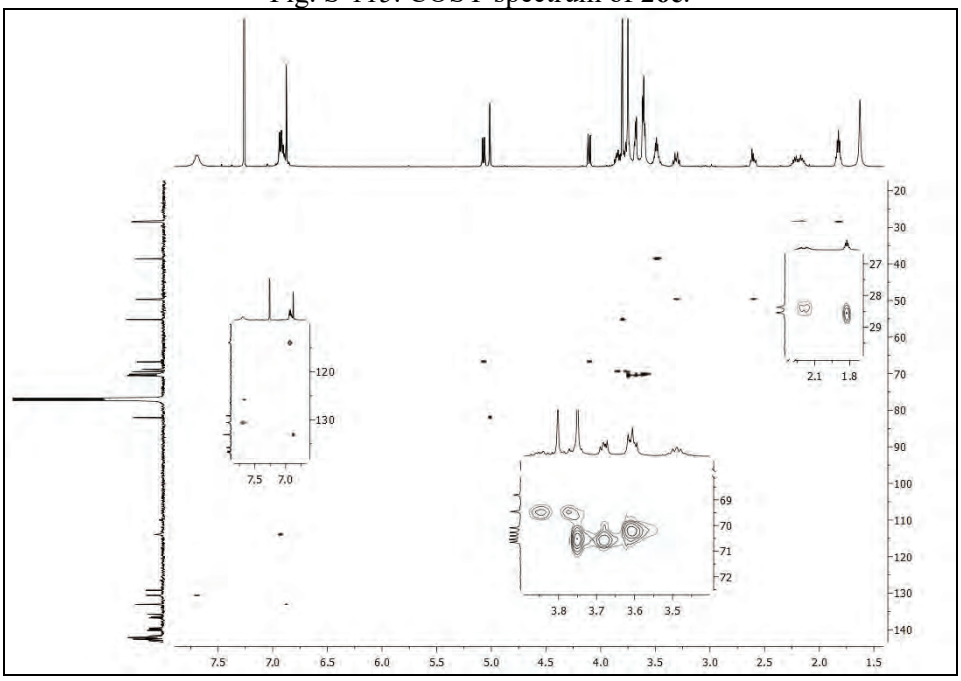


Fig. S-116. HSQC spectrum of **26c**.

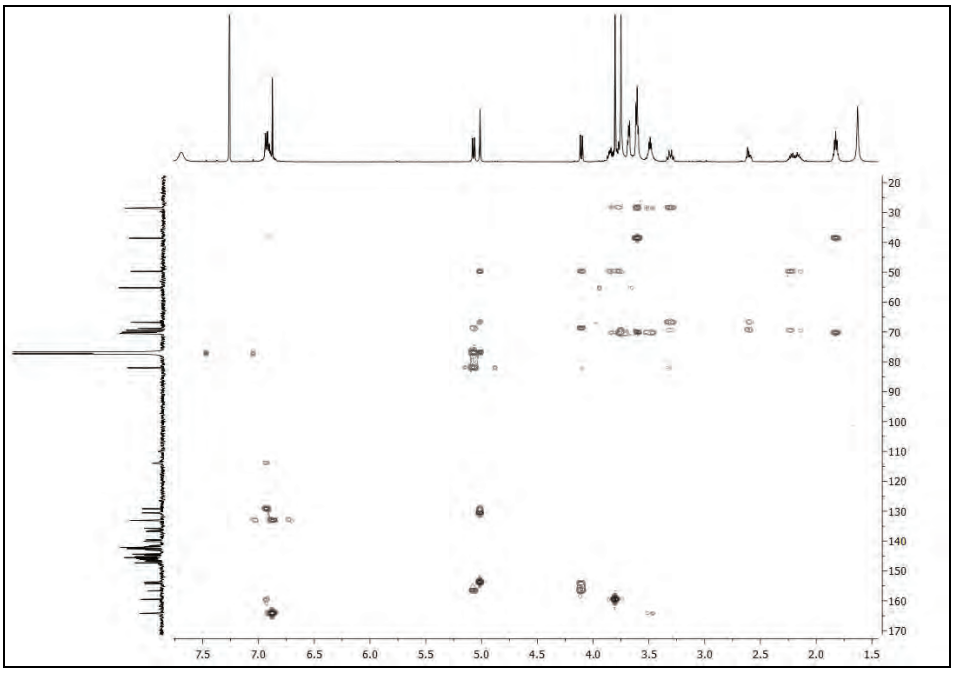


Fig. S-117. HMBC spectrum of **26c**.

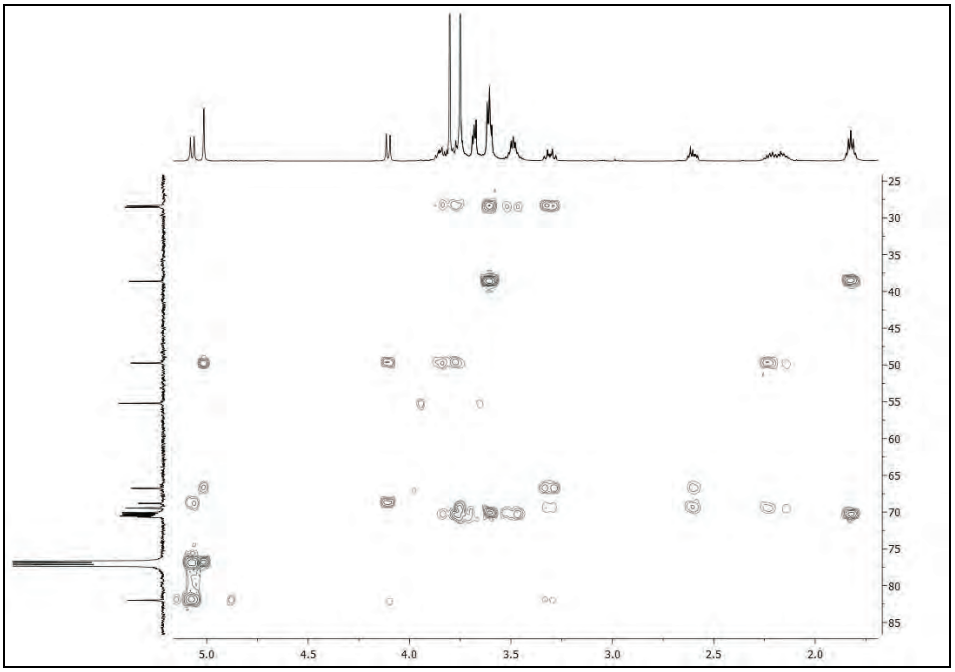


Fig. S-118. Part of the HMBC spectrum of **26c**.

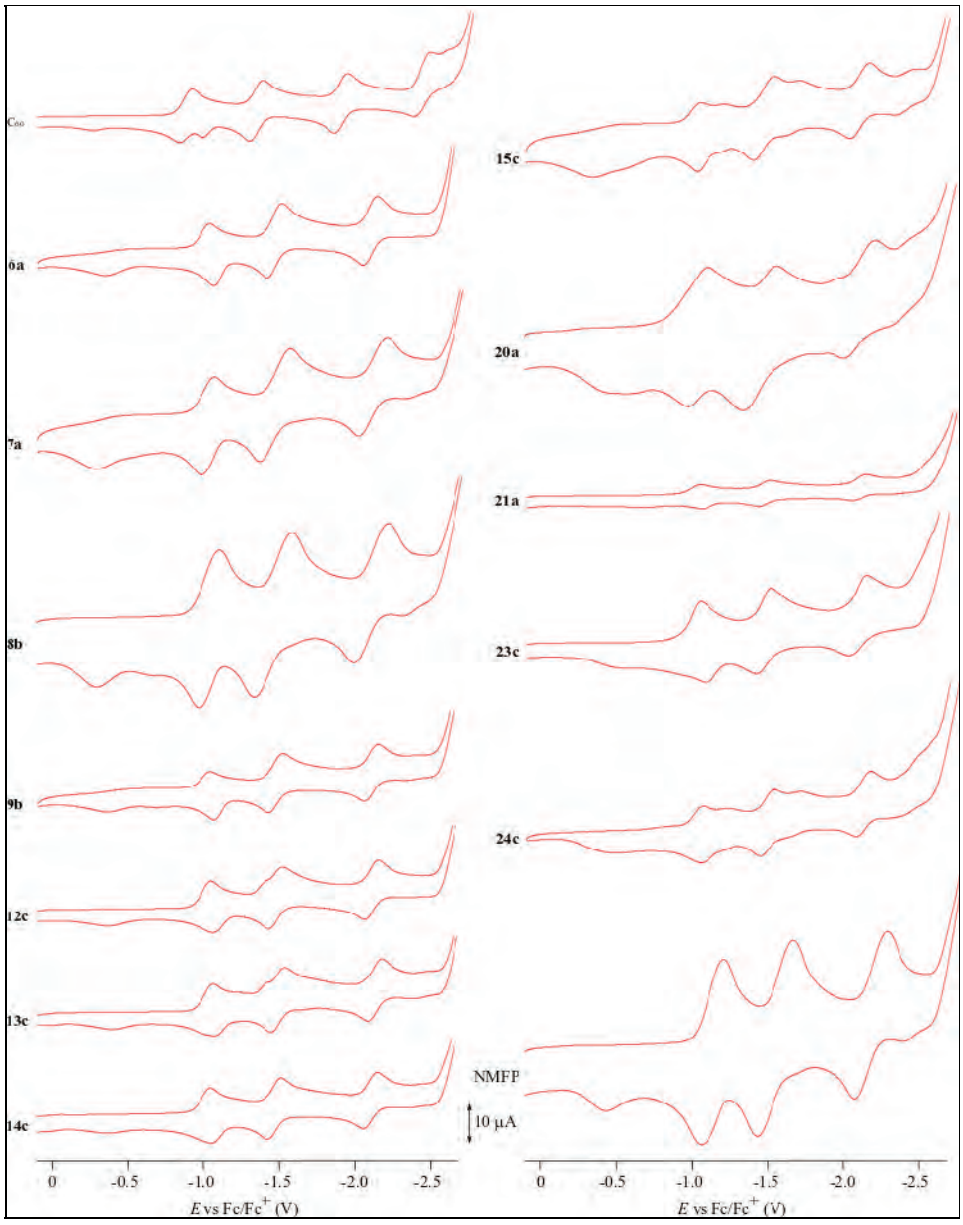


Fig. S-119. CV curves of 1 mM solution in ODCB/DMF mixture (2:1) containing 0.1 M TBAP, recorded with GCE–Ag/Ag$^+$–Pt system at 50 mV.

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