The Synthesis and Characterisation of Mono- and Bis-methano[60]fulleryl Amino Acid Derivatives and their Reductive Ring-Opening Retro-Bingel Reactions

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(a)

(b)

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(a)

(b)

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(a)

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(a) **(b)**

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Synthesis of Addends

l-Menthyl *N*-(diphenylmethyldiene)glycinate (**5**) and its precursors were synthesised according to literature procedures.^{S1}

Synthesis of glycinate **6**.

Ethoxycarbonylmethyl N-(*tert*-butoxycarbonyl)glycinate. Potassium carbonate (1.58 g, 114 mmol) was added to a stirred solution of *N*-*tert*-butoxycarbonylglycine (1.00 g, 5.71 mmol) and ethyl bromoacetate (0.95 g, 5.71 mmol) in DMF (15 mL) at RT and the mixture was stirred overnight. The reaction mixture was diluted with diethyl ether (50 mL) and the resultant precipitate was removed by gravity filtration. The filtrate was washed with saturated ammonium chloride solution (2 x 20 mL), followed by brine (20 mL). The organic layer was dried (MgSO_4), and concentrated *in vacuo* to afford the titled compound as a bright yellow oil (0.85 g, 57%). ^1H NMR (CDCl_3 ,

400 MHz): δ 1.29 (t, 3H, J 8 Hz), 1.45 (s, 9H), 4.04 (d, 2H, J 4 Hz), 4.23 (q, 2H, J 8 Hz), 4.67 (s, 2H), 5.11 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 169.9, 167.3, 155.1, 80.4, 70.0, 61.6, 42.6, 28.6, 14.0. MS(CI): m/z 262 ($M+1$).

Ethoxycarbonylmethyl glycine. trifluoroacetate salt. Ethoxycarbonylmethyl *N*-(tert-butoxycarbonyl)glycinate (0.85 g, 3.25 mmol) was added to neat TFA (5.0 mL) and the reaction mixture was stirred for 1 h and then concentrated *in vacuo*. The reaction mixture was redissolved in distilled water (10 mL) and washed several times with diethyl ether (10 mL). The aqueous layer was retained and freeze-dried overnight to yield ethoxycarbonylmethyl glycine. trifluoroacetate salt (0.49 g, 55%) as a colorless oil. ^1H NMR (D_2O , 300 MHz): δ 1.32 (t, 3H, J 8 Hz), 4.67 (s, 2H), 3.91 (s, 2H). MS(CI): m/z 162 (RNH_3^+).

Ethoxycarbonylmethyl N-(diphenylmethylidene)glycinate (6). To a suspension of ethoxycarbonylmethylglycine. trifluoroacetate salt (0.83 g, 3.01 mmol) in DCM/MeCN (20 mL/10 mL) was added benzophenone imine (0.55 g, 3.01 mmol) and the reaction mixture was stirred vigorously for 24 h before being filtered and concentrated *in vacuo*. The yellow oil was then redissolved in diethyl ether (20 mL) and washed with brine (2 x 10 mL). The organic layer was dried (MgSO_4) and concentrated *in vacuo* to yield **6** as a white amorphous solid (0.53 g, 54%). ^1H NMR (CDCl_3 , 400 MHz): δ 1.30 (t, 3H, J 5.7 Hz), 4.15 (s, 2H), 4.25 (q, 2H, J 5.7 Hz), 4.69 (s, 2H), 7.34 (d, 2H, J 7.2 Hz), 7.59 (t, 4H, J 7.2 Hz), 7.71 (d, 4H, J 7.2 Hz). ^{13}C NMR (CDCl_3 , 100 MHz): δ 173.2, 137.5, 132.4, 130.0, 128.2, 61.5, 60.5, 60.1, 14.1. MS(CI): m/z 326 ($M+1$).

N-(*tert*-butoxycarbonyl)glycine 1,2-phenylenebis(methylene) ester (**26**). To a solution of 1,2-benzenedimethanol (1.50 g, 10.9 mmol), *N*-*tert*-butoxycarbonyl glycine (3.81 g, 21.7 mmol) and DMAP (0.27 g, 2.18 mmol) in THF (20 mL) was added DCC (4.7 g, 22.9 mmol). The mixture was stirred overnight and then filtered, and the filtrate concentrated *in vacuo*. The crude product was redissolved in DCM (100 mL) and washed with 0.1M HCl (20 mL), 0.1M sodium carbonate solution (20 mL) and brine (20 mL). The organic layer was dried, and concentrated *in vacuo*. Flash column chromatography (silica gel), eluting with DCM/MeOH (98/2) provided **26** (3.84 g, 78%) as a pale yellow oil. ¹H NMR (CDCl₃, 300 MHz): δ 1.44 (s, 18H), 3.93 (bd, 4H, *J* 6.0 Hz), 5.19 (bs, 2H), 5.26 (s, 4H), 7.38 (m, 4H). ¹³C NMR (CDCl₃, 75 MHz): δ 170.2, 156.1, 132.2, 128.9, 127.3, 79.7, 64.7, 42.1, 28.1. MS(CI): *m/z* 453 (*M*+1).

N-(*tert*-butoxycarbonyl)glycine 1,3-phenylenebis(methylene) ester (**27**). The title compound was prepared from 1,3-benzenedimethanol (3.50 g, 25.4 mmol), *N*-*tert*-butoxycarbonyl glycine (8.87 g, 50.6 mmol), DMAP (0.92 g, 7.56 mmol) and DCC (10.9 g, 52.9 mmol) in THF (20 mL) using an analogous procedure to that described above for the synthesis of **26** to yield **27** (8.10 g, 71%) as a white solid. ¹H NMR (CDCl₃, 300 MHz): δ 1.44 (s, 18H), 3.94 (bd, 4H, *J* 4.2 Hz), 5.09 (bs, 2H), 5.16 (s, 4H), 7.32 (m, 4H). ¹³C NMR (CDCl₃, 75 MHz): δ 170.2, 156.1, 132.2, 128.8, 127.1, 127.3, 79.7, 64.5, 42.2, 28.1. MS(CI): *m/z* 453 (*M*+1).

N-(*tert*-butoxycarbonyl)glycine 1,4-phenylenebis(methylene) ester (**28**). The title compound was prepared from 1,4-benzenedimethanol (5.00 g, 36.0 mmol), *N*-*tert*-butoxycarbonyl glycine (12.60 g, 71.9 mmol), DMAP (0.88 g, 7.19 mmol) and DCC (15.59 g, 75.5 mmol) in THF (20 mL) using an analogous procedure to that described

above for the synthesis of **26** to yield **28** (14.29 g, 87%) as a white solid. ^1H NMR (CDCl_3 , 400 MHz): δ 1.42 (s, 18H), 3.91 (bd, 4H, J 5.2 Hz), 5.12 (bs, 2H), 5.14 (s, 4H), 7.33 (s, 4H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 170.2, 156.1, 132.3, 127.3, 79.7, 64.5, 42.2, 28.1. MS (CI): m/z 453 ($M+1$).

Glycine 1,2-phenylenebis(methylene) ester. bistrifluoroacetate salt (29). The title compound was prepared from **28** (3.84 g, 8.49 mmol) using an analogous procedure to that described above for the synthesis of ethoxycarbonylmethyl glycine. trifluoroacetate salt to yield **29** (3.61 g, 89%) as a colorless oil. ^1H NMR (D_2O , 300 MHz): δ 3.68 (s, 4H), 5.23 (s, 4H), 7.31 (m, 4H). MS (CI): m/z 253 (RNH_3^+).

Glycine 1,3-phenylenebis(methylene) ester. bistrifluoroacetate salt (30). The title compound was prepared from **27** (8.10 g, 17.9 mmol) using an analogous procedure to that described above for the synthesis of **29** to yield **30** (7.35 g, 86%) as a colorless oil. ^1H NMR (D_2O , 400 MHz): δ 3.81 (s, 4H), 5.18 (s, 4H), 7.31 (m, 4H). MS (CI): m/z 253 (RNH_3^+).

Glycine 1,4-phenylenebis(methylene) ester.bistrifluoroacetate salt (31). The title compound was prepared from **28** (14.29 g, 31.6 mmol) using the analogous procedure described above for the synthesis of ethoxycarbonylmethyl glycine.trifluoroacetate salt to yield **31** (13.59 g, 90%) as a colourless oil. ^1H NMR (D_2O , 400 MHz): δ 3.81 (s, 4H), 5.21 (s, 4H), 7.31 (s, 4H). MS(CI): m/z 253 ($M+1$).

N-(Diphenylmethylene)glycine 1,2-phenylenebis(methylene) ester (32). The title compound was prepared from **29** (3.83 g, 8.01 mmol) using an analogous procedure to that described above for the synthesis of **6** to yield **32** (3.90 g, 89%) as a viscous

yellow oil. ^1H NMR (CDCl_3 , 300 MHz): δ 4.22 (s, 4H), 5.27 (s, 4H), 7.13 (m, 8H), 7.35 (m, 4H), 7.39 (m, 4H), 7.42 (m, 4H), 7.64 (dd, 4H, J 8.4, 1.6 Hz). ^{13}C NMR (CDCl_3 , 100 MHz): δ 172.1, 170.3, 139.2, 134.4, 129.9, 128.8, 128.7, 128.1, 127.6, 64.1, 55.6. HRMS(CI) calculated for $\text{C}_{38}\text{H}_{32}\text{N}_2\text{O}_4+\text{H}^+$ requires 581.2440, found 581.2427 ($M+1$).

N-(Diphenylmethylene)glycine 1,3-phenylenebis(methylene) ester (**33**). The title compound was prepared from **30** (15.80 g, 33.1 mmol) using an analogous procedure to that described above for the synthesis of **6** to yield **33** (14.59 g, 76%) as a white amorphous solid. ^1H NMR (CDCl_3 , 400 MHz): δ 4.17 (s, 4H), 5.09 (s, 4H), 7.13 (m, 8H), 7.35 (m, 4H), 7.39 (m, 4H), 7.42 (m, 4H), 7.64 (dd, 4H, J 8.4, 1.6 Hz). ^{13}C NMR (CDCl_3 , 100 MHz): δ 171.9, 170.3, 139.0, 137.4, 135.9, 132.3, 130.4, 129.9, 128.6, 128.1, 66.1, 55.4. HRMS (CI) calculated for $\text{C}_{38}\text{H}_{32}\text{N}_2\text{O}_4+\text{H}^+$ requires 581.2440, found 581.2398 ($M+1$).

N-(Diphenylmethylene)glycine 1,4-phenylenebis(methylene) ester (**34**). The title compound was prepared from **31** (8.60 g, 17.9 mmol) using an analogous procedure to that described above for the synthesis of **6** to yield **34** as a white amorphous solid (7.57 g, 73%). ^1H NMR (CDCl_3 , 400 MHz): δ 4.17 (s, 4H), 5.09 (s, 4H), 7.13 (m, 8H), 7.35 (m, 4H), 7.39 (m, 4H), 7.42 (m, 4H), 7.64 (dd, 4H, J 8.4, 1.6 Hz). ^{13}C NMR (CDCl_3 , 100 MHz): δ 171.9, 170.3, 137.4, 132.3, 129.9, 128.6, 128.1, 127.9, 66.0, 55.5. HRMS (CI) calculated for $\text{C}_{38}\text{H}_{32}\text{N}_2\text{O}_4+\text{H}^+$ requires 581.2440, found 581.2440 ($M+1$).

N-(tert-butoxycarbonyl)glycine 1,3-naphthylenebis(methylene) ester (**42**). The title compound was prepared from 1,3-naphthalenedimethanol,^{S2} (0.12 g, 0.64 mmol), *N*-

tert-butoxycarbonylglycine (0.22 g, 1.28 mmol), DMAP (0.02 g, 0.128 mmol) and DCC (0.02 g, 0.128 mmol) in THF (10 mL) using an analogous procedure to that described above for the synthesis of **26** to yield **42** (0.26 g, 82%) as a pale yellow oil. ^1H NMR (CDCl_3 , 300 MHz): δ 1.43 (s, 9H), 1.44 (s, 9H), 3.96 (d, 2H, J 6.3 Hz), 3.99 (d, 2H, J 6.9 Hz), 5.08 (bs, 2H), 5.34 (s), 5.64 (s), 7.56 (m, 3H), 7.84 (s, 1H), 7.88 (dd, 1H, J 7.2, 2.4 Hz), 7.97 (d, 1H, J 7.2 Hz). ^{13}C NMR (CDCl_3 , 75 MHz): δ 170.2, 155.7, 133.3, 132.0, 131.4, 131.0, 128.7, 127.1, 127.0, 126.3, 123.1, 79.7, 66.5, 64.7, 42.2, 42.1, 28.1. MS (CI): m/z 503 ($M+1$).

Glycine 1,3-naphthylenebis(methylene) ester.bistrifluoroacetate salt (43). The title compound was prepared from **42** (0.26 g, 0.52 mmol) using an analogous procedure to that described above for the synthesis of **29** to yield **43** as a pale yellow oil (0.19 g, 70%). ^1H NMR (D_2O , 300 MHz): δ 3.84 (s, 2H), 3.89 (s, 2H), 5.36 (s, 2H), 5.67 (s, 2H), 7.57 (m, 3H), 7.91 (d, 1H, J 1.8 Hz), 7.94 (bs, 1H), 8.01 (d, 1H, J 8.1 Hz). MS (CI): m/z 303 (RNH_3^+).

N-(Diphenylmethylene)glycine 1,3-naphthylenebis(methylene) ester (44). The title compound was prepared from **43** (0.19 g, 0.36 mmol) using an analogous procedure to that described above for the synthesis of **6** to yield **44** (0.12 g, 51%) as a viscous yellow oil. ^1H NMR (CDCl_3 , 300 MHz): δ 4.25 (s, 2H), 4.28 (s, 2H), 5.32 (s, 2H), 5.62 (s, 2H), 7.11 (m, 4H), 7.15 (m, 4H), 7.34 (m, 2H), 7.40 (m, 4H), 7.50 (m, 4H), 7.57 (t, 2H, J 6.8 Hz), 7.64 (t, 2H, J 8.0 Hz), 7.80 (d, 4H, J 8.0 Hz). ^{13}C NMR (CDCl_3 , 75 MHz): δ 172.0, 170.4, 139.2, 137.5, 135.8, 133.5, 132.3, 131.8, 131.2, 130.5, 130.0, 128.8, 128.3, 128.0, 127.5, 126.9, 126.4, 123.6, 66.4, 64.6, 55.6. HRMS (CI) calculated for $\text{C}_{42}\text{H}_{34}\text{N}_2\text{O}_4+\text{H}^+$ requires 631.25968, found 631.25933 ($M+1$).

Bingel Reactions

Ethyl 61-diphenylmethylenediamino-1,2-methano[60]fullerene-61-carboxylate (8).

The title compound was prepared from DBU (0.85 mL, 5.62 mmol), [60]fullerene (1.00 g, 1.38 mmol), carbon tetrabromide (0.50 g, 1.51 mmol) and **4** (0.41 g, 1.53 mmol) in chlorobenzene (900 mL) using an analogous procedure to that described above for the synthesis of **7** to yield **8** as black crystals (0.99 g, 72%). UV-vis (DCM): 430 (18000), 610 (1800), 690 (800) nm. ¹H NMR (CDCl₃, 400MHz): δ 1.54 (t, 3H, *J* 6.8 Hz), 4.62 (q, 2H, *J* 6.8 Hz), 7.40 (t, 2H, *J* 8.0 Hz), 7.50 (t, 4H, *J* 8.0 Hz), 8.07 (d, 4H, *J* 8.0 Hz). ¹³C NMR (CDCl₃, 75MHz): δ 159.2, 157.4, 150.2, 145.5, 144.5, 144.0, 143.9, 143.3, 142.9, 142.8, 142.4 (2 x C), 142.1, 141.8 (2 x C), 141.1, 139.9, 139.7 (2 x C), 139.3 (2 x C), 138.8 (2 x C), 138.3, 136.7, 136.1, 133.7, 131.6, 126.9, 125.3, 92.9, 79.8, 60.0, 11.3. MALDI-TOF (-ve ion mode, 9-nitroanthracene): *m/z* 985 (*M*⁻), 720 (C₆₀⁻).

l-Menthyl 60-diphenylmethylenediamino-1,2-methano[60]fullerene-60-carboxylate (9).

The title compound was prepared from DBU (0.11 mL, 0.76 mmol), [60]fullerene (0.25 g, 0.35 mmol), carbon tetrabromide (0.13 g, 0.38 mmol) and **5** (0.16 g, 0.42 mmol) in chlorobenzene (200 mL) using an analogous procedure to that described above for the synthesis of **7** to yield **9** (0.12 g, 31%) as a brown amorphous solid. UV-vis (DCM): 410 (sh, 5000), 440 (3000) nm. ¹H NMR (CDCl₃, 300 MHz): δ 0.83 (d, 3H, *J* 6.9 Hz), 0.92 (d, 3H, *J* 6.9 Hz), 0.98 (d, 3H, *J* 6.9 Hz), 1.25 (m, 3H), 1.59 (m, 2H), 1.78 (bd, 1H, *J* 12.3 Hz), 2.01 (pd, 1H, 6.9, 2.4 Hz), 2.24 (bd, 1H, *J* 11.7 Hz), 5.10 (td, 1H, *J* 11.1, 4.5), 7.36 (m, 6H), 7.47 (t, 2H *J* 7.8 Hz), 8.03 (d, 2H, *J* 7.8 Hz). ¹³C NMR (CDCl₃, 100 MHz): δ 161.7, 160.6, 153.0, 152.9, 148.5, 148.3, 147.3, 146.9, 146.8, 146.7, 146.1, 145.7, 145.6, 145.2, 145.0, 144.9, 144.6, 143.9,

142.8, 142.5, 142.2, 141.6, 141.57, 141.2, 141.1, 140.9, 140.8, 139.5, 139.0, 138.9, 136.4, 136.3, 134.6, 134.2, 129.5, 128.1, 128.1, 128.0, 95.8, 82.7, 82.6, 77.3, 46.8, 40.6, 34.2, 31.5, 26.7, 23.9, 22.0, 20.5, 16.6. MALDI-TOF (-ve ion mode, 9-nitroanthracene): m/z 1096 (M^-), 720 (C_{60}^-).

Ethoxycarbonylmethyl 61-diphenylmethylideneamino-1,2-methano[60]fullerene-61-carboxylate (10). The title compound was prepared from DBU (0.09 mL, 0.58 mmol), [60]fullerene (0.20 g, 0.28 mmol), carbon tetrabromide (0.10 g, 0.31 mmol) and **6** (0.10 g, 0.31 mmol) in chlorobenzene (120 mL) using an analogous procedure to that described above for the synthesis of **7** to yield **10** as a brown amorphous solid (0.13 g, 46%). UV-vis (DCM): 430 (18000), 610 (1800), 690 (800) nm. 1H NMR ($CDCl_3$, 300 MHz): δ 1.34 (t, 3H, J 8 Hz), 4.23 (q, 2H, J 8.0 Hz), 4.78 (s, 2H), 7.40 (t, 2H, J 8.0 Hz), 7.50 (t, 4H, J 8.0 Hz), 8.12 (d, 4H, J 8.0 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 165.8, 161.2, 159.2, 152.9, 148.1, 147.5, 146.9, 146.8, 146.2, 145.8, 145.6, 145.3, 145.2, 144.9, 144.7, 144.04, 144.0, 142.8, 142.6, 142.5, 142.2, 141.7, 141.6, 141.5, 141.1, 140.6, 139.6, 139.0, 136.6, 134.5, 129.6, 128.3, 128.2, 95.9, 82.7, 62.0, 61.6, 14.0. MALDI-MS (-ve ion mode, 9-nitroanthracene): m/z 1043 (M^-), 720 (C_{60}^-).

endo,endo-(p-Phenylenedimethyl)61,62-bis-(N-diphenylmethylideneamino)-1,2:33,50-bis(methano)[60]fullerene-61,62-dicarboxylate (37) and *endo,endo-(p-Phenylenedimethyl)61,62-bis-(N-diphenylmethylideneamino)-1,2:34,35-bis(methano)[60]fullerene-61,62-dicarboxylate (38)*. The title compound was prepared from DBU (0.45 mL, 3.01 mmol), [60]fullerene (0.43 g, 0.60 mmol), carbon tetrabromide (0.54 g, 1.42 mmol) and **34** (0.47 g, 0.81 mmol) in chlorobenzene (200 mL) using an analogous procedure to that described above for the synthesis of **35/36**

to yield **37** (0.29 g, 37%) and **38** (0.08 g, 10%) as brown amorphous solids. **37**: UV-vis (DCM): 330 (15000), 430 (sh, 180), 620 (210), 690 (80) nm. ^1H NMR (CDCl_3 , 400 MHz): δ 5.21 (d, 2H, J 11.6 Hz), 5.58 (d, 2H, J 11.6 Hz), 7.16 (d, 2H J 4.4 Hz), 7.39 (d, 2H, J 4.4 Hz), 7.51 (m, 8H), 7.62 (t, 4H, J 7.2 Hz), 8.16 (d, 4H, J 7.2 Hz), 8.21 (d, 4H, J 7.2 Hz). ^{13}C NMR (CDCl_3 , 100 MHz): too insoluble to obtain adequate spectrum. MALDI-TOF (-ve ion mode, 9-nitroanthracene): m/z 1296 (M^-), 720 (C_{60}^-). **38**: UV-vis (DCM): 320 (19000), 640 (210), 695 (180) nm. ^1H NMR (CDCl_3 , 400 MHz): δ 5.17 (d, 2H J 14.4 Hz), 5.72 (d, 2H, J 14.4 Hz), 7.29 (m, 4H), 7.40 (m, 4H), 7.46 (t, 4H, J 10.0 Hz, 1.6 Hz), 7.55 (t, 4H, J 9.6 Hz), 7.92 (d, 4H, J 9.6 Hz), 8.02 (d, 4H, J 9.6 Hz). ^{13}C NMR (CDCl_3 , 100 MHz): δ 67.9, 86.8, 83.0, 96.7, 128.1, 128.2, 128.4, 129.6, 129.7, 134.2, 135.6, 136.2, 137.3, 138.4, 139.8, 140.7, 141.2, 141.5, 143.9, 144.1, 145.5, 145.8, 145.9, 146.8, 146.9, 147.4, 147.6, 148.89, 150.3, 151.0, 160.7, 161.3. MALDI-TOF (-ve ion mode, 9-nitroanthracene): m/z 1296 (M^-), 720 (C_{60}^-).

endo,endo-(1',3'-Naphthylenedimethyl)-61,62-bi-(*N*-diphenylmethylideneamino)-1,2:34,35-bis(methano)[60]fullerene-61,62-dicarboxylate (**45**) and *endo,endo*-(1,3-naphthylenedimethyl)-61,62-bis-(*N*-diphenylmethylideneamino)-1,2:16,17-bis(methano)[60]fullerene-61,62-dicarboxylate (**46**). The title compound was prepared from DBU (0.18 mL, 1.17 mmol), [60]fullerene (0.20 g, 0.28 mmol), carbon tetrabromide (0.18 g, 0.56 mmol) and **44** (0.19 g, 0.31 mmol) in chlorobenzene (200 mL) using an analogous procedure to that described above for the synthesis of **35/36** to yield **45** (0.034 g, 9%) and **46** (0.019 g, 5%) as brown amorphous solids. **45**: UV-vis (DCM): 440 (170000), 470 (sh, 150000), 630 (3000), 690 (2300) nm. ^1H NMR (400 MHz, CDCl_3): δ 5.05 (d, 1H, J 11.2 Hz), 5.24 (d, 1H, J 11.6 Hz), 6.04 (d, 1H, J

11.2 Hz), 6.43 (d, 1H, J 11.6 Hz), 7.25 (m, 17H), 7.35 (t, 1H, J 7.2 Hz), 7.42 (td, 1H, J 7.2, 1.2 Hz), 7.52 (t, 1H, J 7.2 Hz), 7.55 (td, 1H, J 7.2, 1.2 Hz), 7.79 (d, 1H, J 1.0 Hz), 7.85 (d, 1H, J 7.2 Hz), 7.86 (d, 1H, J 7.2 Hz), 7.99 (d, 1H, J 7.2 Hz), 8.00 (d, 1H, J 7.2 Hz). ^{13}C NMR (75 MHz, CDCl_3): δ 161.8, 160.8, 160.6, 160.5, 151.2, 150.8, 150.7, 149.8, 149.6, 148.9, 148.5, 148.4, 147.34, 147.3, 146.8, 146.7, 146.62, 146.6, 146.4, 146.2, 145.8, 145.7, 145.66, 145.6, 145.5, 145.2, 145.1, 144.7, 144.6, 144.3, 143.6, 143.5, 142.3, 141.9, 141.97, 141.5, 141.3, 141.24, 141.22, 141.1, 141.0, 140.9, 140.88, 140.85, 140.8, 140.6, 139.62, 139.58, 138.6, 137.49, 137.45, 137.2, 136.5, 136.4, 133.8, 133.6, 133.5, 133.2, 131.5, 131.48, 130.9, 130.7, 129.6, 129.5, 129.4, 129.3, 129.1, 128.3, 128.2, 128.1, 128.0, 127.9, 126.9, 123.3, 97.2, 96.7, 81.9, 81.7, 81.5, 81.3, 67.9, 65.1. MALDI-TOF (-ve ion mode, 9-nitroanthracene): m/z 1346 (M^-), 720 (C_{60}^-). **46**: UV-vis (DCM): 440 (sh, 130000), 460 (80000), 490 (sh, 60000), 630 (1000), 690 (4000) nm. ^1H NMR (400 MHz, CDCl_3): δ 5.23 (d, 1H, J 15.6 Hz), 5.40 (d, 1H, J 15.2 Hz), 5.87 (d, 1H, J 15.6 Hz), 6.16 (d, 1H, J 15.2 Hz), 7.09 (d, 1H, J 2.0 Hz), 7.37 (tt, 1H, J 9.2, 2.0 Hz), 7.51 (m, 17H), 7.62 (tt, 1H, J 10.8, 2.0 Hz), 7.77 (d, 1H, J 10.4 Hz), 7.90 (td, 1H, J 10.8, 1.3 Hz), 8.03 (d, 1H, J 10.0 Hz), 8.14 (d, 1H, J 10.0 Hz), 8.22 (d, 1H, J 10.0 Hz), 8.27 (d, 1H, J 10.0 Hz). ^{13}C NMR (75 MHz, CDCl_3): δ 161.4, 161.2, 161.1, 160.8, 154.2, 153.8, 153.7, 153.5, 151.1, 150.8, 148.97, 148.96, 148.94, 148.8, 148.77, 148.6, 148.3, 147.9, 147.8, 147.6, 147.5, 147.3, 147.27, 147.2, 146.9, 145.0, 144.9, 144.8, 144.7, 144.5, 144.4, 144.3, 144.2, 144.1, 144.02, 144.0, 143.7, 143.4, 143.1, 142.9, 141.8, 141.76, 141.4, 141.3, 141.1, 141.0, 140.9, 140.7, 140.5, 139.2, 138.72, 138.7, 138.2, 135.2, 135.0, 134.8, 134.1, 134.05, 133.4, 132.7, 131.6, 130.3, 130.1, 130.0, 129.92, 129.9, 129.7, 129.6, 129.2, 128.6, 128.5, 128.3, 128.2, 127.9, 126.9, 123.4, 96.6, 95.9, 82.4, 81.94, 81.9, 81.8, 68.5, 66.6. MALDI-TOF (-ve ion mode, 9-nitroanthracene): m/z 1346 (M^-), 720 (C_{60}^-).

Transesterification Reactions

Diethyl *endo,endo-61,62-bis-(N-diphenylmethyldeneamino)-1,2:34,35-bis(methano)[60]fullerene-61,62-dicarboxylate (40)*. The title compound was prepared from potassium carbonate (0.21 g, 1.53 mmol) and **35** (0.17 g, 0.13 mmol) or **38** (0.02 g, 0.02 mmol) in THF : EtOH (2 : 1, 100 mL) using an analogous procedure to that described above for the synthesis of **39** to yield **40** (0.082 g, 51% from **35**; 0.008 g, 42% from **38**) as a brown amorphous solid. UV-vis (DCM): 440 (1100), 470 (sh, 650), 690 (470) nm. ¹H NMR (400 MHz, CDCl₃): δ 1.41 (t, 6H, *J* 6.8 Hz), 4.48 (q, 4H, *J* 6.8 Hz), 7.29 (t, 4H, *J* 7.2 Hz), 7.38 (t, 4H, *J* 8.0 Hz), 7.46 (t, 4H, *J* 7.2 Hz), 7.56 (t, 4H, *J* 8.0 Hz), 7.90 (dd, 2H, *J* 7.2 Hz, 1.2 Hz), 8.06 (dd, 2H, *J* 7.6 Hz, 1.2 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 162.2, 160.5, 151.4, 151.0 (2 x C), 150.1, 148.8, 148.7 (2 x C), 147.8, 147.6, 147.2, 146.8 (2 x C), 146.7, 146.6, 146.4, 145.9, 145.8, 145.75, 145.7, 143.9, 142.3, 142.0 (2 x C), 141.9, 141.6, 141.4, 140.8, 140.7, 140.1, 139.0, 136.8, 136.6, 134.0, 131.4, 129.8, 129.6, 128.4, 128.2, 128.1, 96.6, 82.0, 81.5, 63.0, 14.2. MALDI-TOF (-ve ion mode, 9-nitroanthracene): *m/z* 1250 (*M*), 720 (*C*₆₀⁻).

Diethyl *endo,endo-61,62-bis-(N-diphenylmethyldeneamino)-1,2:16,17-bis(methano)[60]fullerene-61,62-dicarboxylate (47)*. The title compound was prepared from potassium carbonate (0.21 g, 1.53 mmol) and **46** (0.17 g, 0.13 mmol) in THF : EtOH (2 : 1) (100 mL) using an analogous procedure to that described above for the synthesis of **40** to yield **47** (0.078 g, 48%) as a brown amorphous solid. UV-vis (DCM): 320 (19000), 430 (sh, 1700), 450 (sh, 1400), 640 (280), 695 (190) nm. ¹H NMR (CDCl₃, 400 MHz): δ 1.42 (t, 6H, *J* 8.0 Hz), 4.48 (q, 4H, *J* 8.0 Hz), 7.36 (t, 4H, *J* 8.0 Hz), 7.49 (m, 4H), 7.63 (t, 4H, *J* 8.0 Hz), 8.09 (d, 4H, *J* 8.0 Hz), 8.25 (d, 4H, *J*

8.0 Hz). ^{13}C NMR (CDCl_3 , 100 MHz): δ 167.8, 162.2, 160.5, 154.2, 153.6, 151.4, 148.7, 148.7, 148.6, 148.57, 148.0, 147.9, 147.8, 147.4, 145.6, 145.3, 145.1, 144.9, 144.5, 144.2, 143.9, 143.88, 143.4, 142.4, 141.9, 141.5, 141.1, 140.8, 140.5, 139.3, 138.5, 136.3, 135.0, 131.0, 130.1, 129.9, 128.8, 128.5, 128.3, 95.9, 82.4, 81.9, 68.1, 62.4, 17.1. MALDI-TOF (-ve ion mode, 9-nitroanthracene): m/z 1250 (M^-), 720 (C_{60}^-).

Reductive Ring-Openings

l-Menthyl 1,2-dihydro- α -diphenylmethylamino-[60]fullerylacetate (**13**). The title compound was prepared from boron trifluoride-diethyl etherate (0.013 g, 91 μmol), **9** (0.050 g, 51 μmol) and sodium cyanoborohydride (0.016 g, 254 μmol) using an analogous procedure to that described above for the synthesis of **12** to yield **13** as a 1:1 diastereomeric mixture (0.022 g, 40%). UV-vis (DCM): 410 (sh, 5000), 440 (3000) nm. ^1H NMR (C_6D_6 , CS_2 (60:40), 300 MHz): δ 0.73 (d, 3H, J 6.8 Hz), 0.83 (d, 3H, J 7.2 Hz), 0.90 (d, 3H, J 6.3 Hz), 0.94 (d, 3H, J 6.3 Hz), 1.03 (d, 3H, J 7.2 Hz), 1.09 (d, 3H, J 7.2 Hz), 1.35 (m, 3H), 1.76 (m, 3H), 1.82 (td, 1H, J 6.3, 2.4 Hz), 2.12 (bd, 2H), 2.17 (td, 1H, J 6.3, 2.4 Hz), 2.38 (m, 2H), 3.68 (bd, 2H), 4.95 (td, 1H, J 11.2, 4.4 Hz), 4.99 (s, 1H), 5.11 (td, 1H, J 11.2, 4.4 Hz), 5.27 (s, 1H), 5.31 (s, 1H), 6.96 (s, 1H), 6.98 (s, 1H), 7.36 (m, 4H), 7.46 (m, 3H), 7.63 (d, 1H, J 8.4 Hz), 7.65 (d, 1H, J 8.0 Hz), 7.77 (d, 1H, J 8.0 Hz). ^{13}C NMR (C_6D_6 , CS_2 (60:40), 75 MHz): δ 171.0, 154.4, 153.7, 153.1, 152.4, 147.7, 147.5, 147.4, 146.9, 146.7, 146.6, 146.59, 146.5, 146.4, 146.1, 146.0, 145.9, 146.8, 146.76, 145.7, 146.6, 145.0, 144.8, 144.7, 143.7, 143.5, 142.7, 142.69, 142.6, 142.4, 142.0, 141.9, 141.8, 141.7, 140.7, 139.8, 139.6, 137.3, 136.9, 136.64, 136.6, 129.2, 129.1, 128.6, 127.9, 127.7, 82.8, 77.3, 76.9, 68.2, 58.8, 46.8, 40.6, 34.2, 31.5, 26.7, 23.9, 22.0, 20.5, 16.6. MALDI-TOF (-ve ion mode, 9-nitroanthracene): m/z 720 (C_{60}^-).

3'[(Diphenylmethylamino)acetoxymethyl]phenyl-1'-methyl)-1,2-dihydro- α -diphenylmethylamino-[60]fullerylacetate (48). The title compound was prepared from boron trifluoride.diethyl etherate (0.104 g, 733 μ mol for **35**; 0.055 g, 385 μ mol for **36**), **35** (0.095 g, 73 μ mol) or **36** (0.050 g, 38 μ mol) and sodium cyanoborohydride (0.046 g, 733 μ mol for **35**; 0.029 g, 462 μ mol) using an analogous procedure to that described above for the synthesis of **12** to yield [60]fullerene (0.006 g, 12% for **35**; 0.004 g, 14% for **36**) and **48** (0.043 g, 42 % from **35**; 0.022 g, 44% from **36**) as a brown amorphous solid. UV-vis (DCM) 330 (sh, 15000), 435 (3000) nm. ^1H NMR (CDCl_3 CS_2 (80:40), 600 MHz): δ 3.37 (s, 2H), 3.66 (dd, 1H, J 12.3, 2.7 Hz), 4.84 (s, 1H), 4.98 (d, 1H, J 12.3 Hz), 5.07 (s, 2H), 5.24 (d, 1H, J 11.9 Hz), 5.28 (d, 1H, J 2.7 Hz), 5.41 (d, 1H J 11.9 Hz), 6.84 (s, 1H), 7.19 (t, 2H, J 7 Hz) 7.38-7.23 (m, 14H), 7.41 (t, 2H, J 7.9 Hz), 7.47 (t, 2H, J 7.6 Hz), 7.64 (d, 2H, J 7.8 Hz), 7.74 (d, 2H, J 7.8 Hz). ^{13}C NMR (CDCl_3 CS_2 (80:40), 600 MHz): δ 172.4, 172.3, 154.0, 153.0, 152.2, 151.1, 147.5, 147.2, 147.1, 146.9, 146.43, 146.42, 146.4, 146.3, 146.25, 146.2, 146.18, 146.16, 145.9, 145.8, 145.7, 145.6, 145.42, 145.4, 145.35 (2 x C), 145.3, 145.2, 144.7, 144.68, 144.4, 144.35, 143.2, 143.13, 143.1, 142.6, 142.58, 142.5, 142.4, 142.2, 142.1, 142.09, 142.06, 142.04, 142.01, 141.72, 141.7, 141.6, 141.5, 141.47, 140.4, 140.37, 139.6, 139.2, 137.3, 136.4, 136.3, 136.1, 135.5, 129.3, 129.12, 129.1, 129.0, 128.9, 128.7, 128.0, 127.7, 127.3, 127.2, 70.4, 67.7, 67.3, 66.6, 66.4, 66.1, 58.9, 49.1. MS (ES): m/z 1327 ($M+23$), 720 (C_{60}).

4'[(Diphenylmethylamino)acetoxymethyl]phenyl-1'-methyl)-1,2-dihydro- α -diphenylmethylamino-[60]fullerylacetate (49). The title compound was prepared from boron trifluoride.diethyl etherate (0.207 g, 1.46 mmol), **37** (0.160 g, 146 μ mol)

and sodium cyanoborohydride (0.092 g, 1.46 mmol) using an analogous procedure to that described above for the synthesis of **12** to yield **49** (0.059 g, 37%) as a brown amorphous solid. UV-vis (DCM) 330 (sh, 15000), 435 (3000) nm. ^1H NMR (CDCl_3 CS_2 (80:40), 600 MHz): δ 3.67 (bd, 1H, J 12.0 Hz), 4.98 (d, 1H, J 12.0 Hz), 5.24 (d, 1H, J 11.9 Hz), 5.28 (bs, 1H), 5.42 (d, 1H, J 11.9 Hz), 6.85 (s, 1H), 7.23 (m, 8H), 7.32 (m, 8H), 7.42 (t, 2H, J 8.0 Hz), 7.47 (t, 2H, J 8.0 Hz), 7.65 (d, 2H, J 7.2 Hz), 7.74 (d, 2H, J 7.2 Hz). ^{13}C NMR (CDCl_3 CS_2 (80:40), 400 MHz): 172.4, 172.3, 154.1, 153.0, 152.2, 151.0, 147.5, 147.2, 147.1, 147.0, 146.42, 146.4, 146.3, 146.27, 146.24, 146.2, 145.9, 145.8, 145.6, 145.5, 145.4, 145.36, 145.3, 145.2, 144.8, 144.7, 144.4, 144.37, 143.6, 143.2, 143.18, 142.7, 142.6, 142.4, 142.3, 142.2, 142.1, 142.08, 142.07, 142.05, 141.73, 141.7, 141.5, 141.49, 141.4, 140.4, 139.6, 139.2, 137.4, 136.38, 136.3, 136.27, 135.2, 129.1, 128.9, 128.5, 128.2, 128.1, 127.7, 127.4, 127.3, 70.4, 67.7, 67.3, 66.6, 66.4, 66.1, 58.9, 49.1.

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