Supplementary Information

“A new family of fullerene tethers – [60]Pyrrolidino-*N*-oxides”

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Experimentals section

Materials

mCPBA (77% purity) and ^{15}N glycine used as received. Fullerene molecule **1a**¹ and molecule **1b**² were prepared according to literature procedures. Other reagents and solvents were purchased reagent grade and used without further purification. Mass spectra were taken at an accelerating voltage of 60-90 eV, and compounds were dissolved in methanol unless otherwise noted. Unless stated, NMR spectra were recorded at room temperature in CDCl_3 (^1H at 200 MHz and 400 MHz, and ^{13}C at 50 MHz). A relaxation time of 16 seconds was used for ^{13}C NMR spectra. Heteronuclear ^1H - ^{15}N HMBC correlation spectrum was recorded with 2048 data points in t2 and 256 increments in t1. The number of scans accumulated was 32. Sweep widths for ^1H and ^{15}N dimensions were 3004 Hz and 26315 Hz, respectively. Evolution time was 50 ms and $J(\text{NH})$ constant was fixed to 92 Hz. The spectrum was calibrated with CH_3NO_2 in DMSO as external standard. Chemical shifts were reported in ppm. ^1H and ^{13}C spectra were referenced to TMS or residual solvent protons. HPLC experiments were carried out using a semi-preparative 5 μm silica 100 Å column. Toluene: iPrOH 80:20 was used as the mobile phase. Flow rate gradient 0-1 mL/min (0-3 min), followed by a constant flow rate of 1 mL/min (3-57 min). TGA experiments were performed at 10°C/min under nitrogen.

Abbreviations

Symbols and abbreviations for amino acids and peptides are in accord with the recommendations of the IUPAC-IUB Commission on Nomenclature (*J. Biol. Chem.* **1972**, 247, 977).

General Procedure for 1,3-dipolar cycloaddition

A toluene solution (200 mL) of C_{60} (200.0 mg, 0.28 mmol) and the appropriate aldehyde (0.28 mmol) and amino acid (0.28 mmol) was heated to reflux for 3 hours. After cooling to room temperature, the

product was purified by column chromatography (toluene or toluene / ethyl acetate 7:3). The brown solids **1a-c**, **2a-c** and **3a-b** were dissolved in CH₂Cl₂ and precipitated by addition of CH₃OH or Et₂O. This precipitation procedure was repeated another two times.

Compound 1a¹

C₆₉H₁₈N₂O₂ (MW 906.89), 30.7% yield (78.8 mg, 0.086 mmol). m/z (CHCl₃/ MeOH 1:1) 907 M⁺. λ_{max} nm (CH₂Cl₂) 255, 322, 430, 703. ¹H NMR: δ 4.47 (s, 4H, pyrrolidine), 3.71-3.65 (m, 2H, CH₂), 3.29-3.23 (m, 2H, CH₂), 1.51 (bs, 9H, CH₃). ¹³C NMR: δ 154.73, 146.19, 146.01, 145.94, 145.37, 145.23, 144.49, 143.05, 142.58, 142.14, 142.01, 141.83, 140.11, 136.15, 70.66, 67.75, 54.20, 28.54. IR-DRIFT (KBr): 2980, 2790, 1705, 1510, 1120, 770, 525.

Compound 1c

C₆₇H₁₅NO (MW 849.84), yield 30.4% (72.3 mg, 0.085 mmol). λ_{max} nm (CH₂Cl₂ / CH₃OH 8:2) 256, 323, 431, 702. m/z (CHCl₃/ MeOH 1:1) 850 M⁺. ¹H NMR: δ 4.42 (s, 4H, pyrrolidine), 3.81-3.79 (m, 2H), 3.15-3.08 (t, 2H), 2.04-2.01 (m, 2H), 1.77-1.72 (m, 4H). IR-DRIFT (KBr): 3425, 2929, 2858, 2779, 1471, 1432, 1353, 1197, 1125, 786.

Compound 2a (reference compound)

λ_{max} nm (CH₂Cl₂) 256, 327, 431, 701. ¹H NMR (CDCl₃): δ 4.81 (s, 4H, pyrrolidino), 3.01 (s, 3H, CH₃).

Compound 2b

C₇₂H₂₅N (MW 903.98), yield 30.0% (75.5 mg, 0.084 mmol). Eluent (toluene / cyclohexane 1:1). m/z (THF) 904 M⁺. λ_{max} nm (CH₂Cl₂) 257, 325, 431, 703. ¹H NMR (200Mhz, CDCl₃): δ 4.81 (d, 1H, pyrrolidine, J= 9.23 Hz), 4.15 (d, 1H, pyrrolidine, J= 9.26 Hz), 3.89 (t, 1H, pyrrolidine), 2.98 (s, 3H), 1.90 (m, 2H, -CH₂R), 1.25 (s, 14H), 0.87(m, 3H,-RCH₃). IR-DRIFT (KBr): 2924, 2854, 2776, 1440, 1475, 1350, 1187.

Compound 2c

C₆₉H₁₁N (MW 853.83), yield 34.6% (83.2mg, 0.097 mmol). Eluent (toluene / cyclohexane 1:1). m/z (THF) 854 M⁺. $\lambda_{\max}$ nm (CH₂Cl₂) 256, 325, 431, 701. ¹H NMR (200Mhz, CDCl₃): δ 7.82-7.79 (m, 2H, aromatic), 7.47 – 7.34 (m, 3H, aromatic), 5.02 (d, 1H, pyrrolidine, *J* = 9.46 Hz), 4.94 (s, 1H, pyrrolidine), 4.27 (d, 1H, pyrrolidine, *J* = 9.46 Hz), 2.81 (s, 3H, CH₃). IR-DRIFT (KBr): 2952, 2781, 1440, 1338, 1191, 913, 741.

Compound 3a

C₇₅H₂₃NO₃ (MW 985.99), yield 30.7% (85.1 mg, 0.086 mmol). m/z (CHCl₃/ MeOH 1:1) 986 M⁺. $\lambda_{\max}$ nm (CH₂Cl₂) 255, 322, 430, 703. IR-DRIFT (KBr): 2965, 2888, 2797, 1594, 1473, 1313, 1122, 773, 537. ¹H NMR: δ 7.83-7.79 (d, 2H, aromatic), 7.45-7.32 (m, 3H, aromatic), 5.23 (d, 1H, pyrrolidine, *J*= 9.72 Hz), 5.17 (s, 1H, pyrrolidine), 4.31 (d, 1H, pyrrolidine, *J*= 9.65 Hz), 4.07-3.95 (m, 2H), 3.80-3.71 (m, 8H), 3.60-3.55 (m, 2H), 3.37 (s, 3H, CH₃). ¹³C NMR: δ 153.47, 147.24, 146.75, 146.60, 146.45, 146.27, 146.22, 146.09, 145.86, 145.24, 143.10, 142.49, 142.22, 137.13, 129.48, 128.60, 82.44, 72.03, 70.80, 70.70, 70.65, 70.52, 69.27, 67.74, 59.11, 52.10.

Compound 3b

C₇₄H₂₁N₃O₂ (MW 983.98), yield 32.1% (88.6 mg, 0.090 mmol). Eluent (toluene / EtOAc 7:3). $\lambda_{\max}$ nm (CH₂Cl₂) 255, 322, 430, 703. m/z (CHCl₃/ MeOH 1:1) 984 M⁺. ¹H NMR: δ 9.02 (s, 1H, pyridine), 8.63-8.61 (d, 1H, pyridine), 8.19-8.15 (d, 1H, pyridine), 7.42-7.36 (m, 1H pyridine), 5.19 (s, 1H, pyrrolidino), 4.22 (d, 2H, pyrrolidino, *J*= 9.38 Hz), 3.36-3.23 (m, 2H), 2.79-2.73 (m, 2H), 1.51 (s, 9H, CH₃). ¹³C NMR: δ 155.97, 152.36, 150.60, 150.14, 147.29, 146.25, 146.17, 145.58, 145.34, 142.16, 142.11, 140.20, 136.83, 136.28, 135.97, 135.54, 132.73, 123.68, 79.85, 68.82, 66.73, 52.95, 28.12. IR-DRIFT (KBr): 2988, 2860, 1714, 1531, 1435, 1372, 1181, 727.

Compound 13

C₆₉H₁₉NO₃ (MW 909.89) 8.0% (20.3mg, 0.022 mmol). Eluent (toluene / EtOAc 7:3). m/z (CHCl₃/ MeOH 1:1) 910 M⁺. ¹H NMR: δ 4.52 (s, 4H, pyrrolidine), 4.07-4.05 (m, 2H), 3.86-3.84 (m, 2H), 3.79-

3.77 (m, 2H), 3.73-3.71 (m, 2H), 3.58-3.56 (m, 2H), 3.37 (m, 5H). ^{13}C NMR: δ 155.08, 147.26, 146.20, 146.03, 145.67, 145.37, 145.26, 144.53, 143.08, 142.59, 142.21, 142.04, 141.86, 140.11, 136.20, 72.01, 70.86-70.50 (multiplet), 68.47-68.45 (doublet), 59.08, 54.20-54.17 (doublet). IR-DRIFT (KBr): 2895, 2797, 1696, 1470, 1118, 860, 770, 571.

General Procedure B - Oxidation of compounds 1a-c, 2a-c, 3a-b & 13

To a solution of compounds **1a-c**, **2a-c**, **3a-b** & **13** (0.0497 mmol in 100 mL CHCl_3) was added, dropwise, mCPBA (1 equivalent, 0.0497 mmol, in 25 mL CHCl_3) over a period of one hour. Progress was monitored by TLC. The solution was stirred for a further 30 minutes and then filtered through a short column of SiO_2 , first washing with toluene to remove organic compounds and then with eluent solution to take the product mixture. Concentration on a rotavap to a small amount of liquid (3 ml approx.) and flash chromatography on SiO_2 (toluene / EtOH or CHCl_3 / EtOH mixtures as eluent) gave the product (**4a-c**, **5a-c**, **6a-b** & **14**) as a brown solid.

Compound 4a

$\text{C}_{69}\text{H}_{18}\text{N}_2\text{O}_3$ (MW 922.89), yield 32.8% (15.5 mg, 0.016 mmol). Eluent ($\text{CHCl}_3/\text{EtOH}$ 9:1). λ_{max} nm (CH_2Cl_2) 255, 322, 430, 703. m/z ($\text{CHCl}_3/\text{CH}_3\text{OH}$ 1:1) 924 M^+ . Purity was checked on HPLC, estimated at 97%. ^1H NMR (CDCl_3): δ 5.42-5.22 (AB quartet, 4H, $J = 10.27$ Hz, pyrrolidino Hs), 4.15 (bs, 4H, $-\text{CH}_2\text{CH}_2$), 1.50 (s, 9H, *tert*-butylcarbonyl). ^{13}C NMR (CDCl_3 / CD_3OD 8:2): δ 153.92, 151.51, 147.11, 146.05, 145.59, 145.72, 145.59, 145.44, 145.08, 145.00, 144.68, 144.47, 144.06, 142.39, 141.81, 141.61, 141.46, 141.24, 139.75, 137.78, 135.34, 79.89, 68.86, 35.63, 28.12. IR-DRIFT: (KBr) cm^{-1} 2973, 1710, 1518, 1373, 1288, 1266, 1174, 767, 545.

Compound 4b

$C_{69}H_{19}NO_4$ (MW 925.89), yield 37.3% (22.0 mg, 0.024 mmol, 37.3 % yield). Eluent (toluene/EtOAc/EtOH 4:4:1). IR-DRIFT: (KBr) cm^{-1} 2916, 2845, 1700, 1653, 1521, 1457, 11446, 1116, 542. m/z ($CHCl_3$ / MeOH 1:1) 927 MH^+ . λ_{max} nm (CH_2Cl_2) 255, 322, 430, 703. λ_{max} nm (CH_2Cl_2 / CH_3OH 8:2) 255, 309, 430, 701. 1H NMR (400Mhz, $CDCl_3$): δ 5.46-5.27 (AB quartet, 4H, J = 10.66 Hz, pyrrolidine), 4.51 (m, 2H), 4.18 (m, 2H), 3.88 (m, 2H), 3.77 (m, 2H), 3.69 (m, 2H), 3.54 (m, 2H), 3.35 (s, 3H). ^{13}C NMR: δ 154.51, 152.23, 147.33, 146.26, 146.20, 146.14, 145.93, 145.88, 145.80, 145.33, 145.27, 145.18, 145.04, 144.76, 144.23, 142.57, 142.28, 142.19, 142.06, 141.99, 141.65, 141.34, 139.89, 138.52, 135.37, 78.58, 71.95, 70.48, 69.48, 68.35, 65.85, 64.64, 59.08.

Compound 4c

$C_{67}H_{15}NO_2$ (MW 865.84), yield 31.9% (16.30 mg, 0.019 mmol). Eluent ($CHCl_3$ /IPA 9:1). λ_{max} nm (CH_2Cl_2 / CH_3OH 8:2) 254, 311, 430, 700. m/z ($CHCl_3$ / MeOH 1:1) 866 MH^+ . 1H NMR ($CDCl_3$ / CD_3OD): δ 5.43-5.26 (AB quartet, 4H, J = 11.07 Hz), 4.05-4.0 (t, 2H), 3.64-3.58 (t, 2H), 2.28-2.23 (bm, 2H), 1.12-1.05 (t, 2H). IR-DRIFT: (KBr) cm^{-1} 3290, 2915, 2846, 1657, 1518, 1469, 1189, 1082, 786, 548.

Compound 5a

$C_{63}H_7NO$ (MW 793.74), yield 39.3% (15.5 mg, 0.019 mmol). Eluent (toluene / EtOH 8:2). m/z ($CHCl_3$ / MeOH 2:1) 794 M^+ . λ_{max} nm (CH_2Cl_2) 254, 311, 429, 698. 1H NMR: δ 5.34 (s, 4H, pyrrolidine) δ 4.02 (s, 3H, CH_3); 1H NMR ($CDCl_3$ / CD_3OD 8:2): δ 5.48-5.27 (AB quartet, 4H, J = 10.66 Hz, pyrrolidine), 3.95 (s, 3H, CH_3). ^{13}C NMR: ($CDCl_3$ / CD_3OD 8:2): δ 153.66, 151.36, 146.06, 145.88, 145.70, 145.05, 142.37, 141.85, 141.78, 139.70, 137.87, 135.31, 78.02, 69.44, 55.70.

Compound 5b

$C_{72}H_{25}NO$ (MW 919.98), yield 34.1% (15.6 mg, 0.017 mmol). Eluent (toluene / IPA 9:1). m/z (THF / MeOH 2:1) 920 M^+ . λ_{max} nm (CH_2Cl_2) 256, 308, 431, 698. λ_{max} nm (CH_2Cl_2 / CH_3OH 8:2) 255, 309, 430, 700. 1H NMR ($CDCl_3$): δ 5.47-5.35 (AB quartet, 2H, J = 10.88 Hz), 5.00 (m, 1H), 3.85 (s, 3H),

2.95-2.79 (m, 2H), 1.25 (bs, 14H), 0.90-0.83 (m, 3H, CH₃). ¹³C NMR (CDCl₃ / CD₃OD 8:2): δ 154.94, 151.95, 151.52, 151.02, 147.15, 146.10, 145.88, 145.76, 145.55, 145.09, 145.00, 144.59, 144.15, 144.10, 142.46, 141.90, 141.08, 139.88, 139.15, 138.86, 137.87, 135.40, 84.94, 74.06, 67.88, 54.28, 31.64, 29.64, 29.19, 29.00, 28.24, 27.09, 22.44, 13.82. IR-DRIFT: (KBr) cm⁻¹ 2954, 1662, 1584, 1514, 1386, 745, 557.

Compound 5c

C₆₉H₁₁NO (MW 869.83), yield 20.6% (8.9 mg, 0.010 mmol). Eluent (toluene / IPA 9:1). λ_{max} nm (CH₂Cl₂) 255, 311, 431, 701. ¹H NMR: δ 7.57-7.45 (m, 5H, phenyl), 6.30 (s, 1H, pyrrolidine), 5.68-5.22 (AB quartet, 2H, *J* = 10.74 Hz), 4.01 (s, 1H, CH₃). ¹³C NMR: δ 153.93, 151.44, 147.31, 146.43, 146.28, 146.21, 145.87, 145.76, 145.60, 145.33, 145.27, 145.19, 144.86, 144.83, 144.54, 144.15, 142.64, 142.04, 141.79, 141.20, 140.24, 140.13, 139.82, 139.37, 139.08, 138.92, 135.22, 134.98, 134.24, 132.18, 131.10, 129.97, 128.30, 127.88, 89.86, 74.97, 68.38.

Compound 6a

C₇₅H₂₃NO₅ (MW 1017.99), yield 12.3 mg. Eluent (toluene/EtOAc/EtOH 7:3:2). *m/z* (CHCl₃ / CH₃OH 1:1) 1018 M+ 1034 M+16 1050 M+32. ¹H NMR could not be resolved owing to the presence of broad indistinct peaks. This is a consequence of the product being a mixture and having restricted bond rotation. HPLC shows a multitude of peaks. No further characterization was carried out.

Compound 6b

C₇₄H₂₁N₃O₄ (MW 1015.98), yield 11.6 mg. Eluent (toluene / EtOH 95:5). *m/z* (CDCl₃ / CH₃OH 1:1) 1016 M+ 1032 M+16. ¹H NMR could not be resolved owing to the presence of broad peaks. This is a consequence of the product being a mixture and having restricted bond rotation. HPLC showed a multitude of peaks. No further characterization was carried out.

Compound 7 Boc-[¹⁵N]Gly-OH). Errore. Il segnalibro non è definito.

To an aqueous solution of H-[¹⁵N]Gly-OH (1.045 g, 13.9 mmol) and NaOH (834 mg, 21 mmol, 100 mL of 1:1 H₂O/dioxane) a solution of Boc₂O (4.55 mg, 21 mmol, 25 mL of dioxane) was added dropwise, over a period of 30 mins. The solution was stirred for a further 24 hrs at room temperature and then the dioxane was evaporated. The remaining aqueous solution was washed with Et₂O (2×50 mL) and the organic phase is extracted with a saturated solution of NaHCO₃ (2×50 mL). The aqueous phases were acidified with 1N KHSO₄ solid and extracted with AcOEt (3×100 mL). After drying over Na₂SO₄, filtration and evaporation a white solid (2.33 g, 13 mmol) was isolated of **7** in 95% yield.

¹H NMR: δ 5.11 (br s, 1H), 3.76-3.67 (m, 2H), 1.44 (s, 9H). ¹³C NMR: δ 172.42, 79.12, 41.34, 27.27.

Compound 8 Boc-[¹⁵N]Gly-OBzl). Errore. Il segnalibro non è definito.

To a solution of Boc-[¹⁵N]Gly-OH (2.28 mg, 12.9 mmol, 100 mL of CH₃CN) and DBU (1.823 mL, 12.9 mmol) at 0 °C, benzylbromide (1.537 mL, 12.9 mmol) was added dropwise over a period of 1 h. The reaction was stirred for 65 h at room temperature, then CH₃CN was evaporated and the crude mixture dissolved in CH₂Cl₂. The organic phase was extracted with 1N KHSO₄ (2×50mL) and saturated NaHCO₃ (2×50mL), then dried over Na₂SO₄, filtered and evaporated to give **8** as a transparent oil (2.63 g, 9.9 mmol) in 76% yield.

¹H NMR: δ 7.36-7.24 (m, 5H), 5.15 (s, 2H), 3.88 (d, 2H, *J* = 5.59 Hz), 1.43 (s, 9H). ¹³C NMR: δ 170.89, 155.77, 141.05, 128.61, 128.49, 128.37, 127.51, 126.95, 80.04, 67.05, 42.29, 28.30.

Compound 9 HCl×H-[¹⁵N]Gly-OBzl). Errore. Il segnalibro non è definito.

Boc-[¹⁵N]Gly-OBzl (2.58 g, 9.7 mmol) was dissolved in a solution of 4N HCl in dioxane (17 mL) and stirred for 2 h at room temperature. The solvent was evaporated and the crude mixture was precipitated in Et₂O to give **9** as a white solid (1.965 mg, 9.7 mmol) in quantitative yield.

^1H NMR: δ 7.36-7.24 (m, 5H), 5.15 (s, 2H), 3.93 (d, 2H, $J = 5.61$ Hz). ^{13}C NMR: δ 170.89, 155.77, 141.05, 128.61, 128.49, 128.37, 127.51, 126.95, 80.01, 67.10, 42.35.

Compound 10 Nos- ^{15}N Gly-OBzl

To a solution of $\text{HCl} \times \text{H}-[^{15}\text{N}]\text{Gly-OBzl}$ (1.695 g, 9.7 mmol) and DIEA (3.376 mL, 21.3 mmol) in distilled CH_2Cl_2 (50 mL), a solution of nosyl chloride (2.362 g, 10.7 mmol, 20 mL of distilled CH_2Cl_2) was added dropwise over a period of 1 h. The solution was stirred for 16 h at room temperature and then concentrated under vacuum. The crude mixture dissolved in AcOEt. The organic phase was washed with 1N KHSO_4 (2 $\times$ 50mL), H_2O (2 $\times$ 50mL), saturated NaHCO_3 (2 $\times$ 50mL) and H_2O (2 $\times$ 50mL), then dried over Na_2SO_4 , filtered and evaporated to give **10** as a yellow solid (3.30 g, 9.4 mmol) in 97% yield.

^1H NMR: δ 8.06-8.01 (m, 1H), 7.89-7.84 (m, 1H), 7.72-7.61 (m, 2H), 7.37-7.31 (m, 3H), 7.25-7.20 (m, 2H), 6.07 (t, 1H, $J=5.60$ Hz), 5.01 (s, 2H), 4.06 (d, 2H). ^{13}C NMR: δ 168.41, 133.95, 133.62, 132.84, 128.73, 128.67, 128.48, 125.69, 67.55, 45.04.

Compound 11 (Nos-(MeOTEG)- ^{15}N Gly-OBzl)

To a solution of triethylene glycol monomethyl ether (840 μL , 5.13 mmol), Nos- ^{15}N Gly-OBzl (600 mg, 1.71 mmol) and TPP-PS resin (830 mg, 2.5 mmol) in distilled CH_2Cl_2 (10 mL) was added, dropwise, a solution of DEAD (395 μL , 2.5 mmol, 5 mL distilled CH_2Cl_2) over a period of 30 minutes. The solution was stirred for a further 2 hours at r.t. then the resin was filtered and washed with CH_2Cl_2 . The organic phase was extracted with KOH 1M (50 mL) and the aqueous phase re-extracted with ethyl acetate (50 mL) and then the two organic phases evaporated. The crude mixture was purified using

flash chromatography on SiO₂ (CH₂Cl₂ / acetone 5%) giving **11** as a yellow oil, 385 mg, 0.77 mmol, 45% yield.

m/z 520 (Na⁺ complex) 537 (K⁺ complex); ¹H NMR: δ 8.03-7.98 (m, 1H), 7.66-7.50 (m, 3H), 7.36-7.23 (m, 5H), 5.04 (s, 2H), 4.40 (s, 2H), 3.67-3.44 (m, 12H), 3.32 (s, 3H). ¹³C NMR: δ 168.95, 147.88, 135.15, 133.53, 133.28, 131.72, 130.74, 128.56, 128.43, 128.37, 124.13, 71.86, 70.57, 70.49, 67.04, 59.98, 49.77, 48.23.

Compound 12 (H-(MeOTEG)[¹⁵N]Gly-OH)

A solution of Nos-(MeOTEG)[¹⁵N]Gly-OBzl (240 mg, 0.49 mmol), 2-mercaptoethanol (70 μL, 1.00 mmol) and LiOH (48 mg, 2.00 mmol) in DMF (5 mL) was stirred at r.t. for 1 hour. The solution was evaporated and the crude mixture extracted with CH₂Cl₂ (2x25mL) and H₂O (25mL). The aqueous phase was lyophilised to give **12** as a yellow solid, 100 mg, 0.43 mmol, 85% yield.

¹H NMR: δ 3.80-3.50 (m, 12H), 3.37 (s, 3H), 3.29-3.20 (m, 2H). ¹³C NMR: 71.81, 70.33, 58.97.

Compound 14

C₆₉H₁₉NO₄ (MW 925.89), yield 29.1% (3.0 mg, 0.0032 mmol) - from 10.0 mg of **13**. Eluent (toluene/EtOAc/EtOH 4:4:1). IR-DRIFT: (KBr) cm⁻¹ 2916, 2845, 1700, 1653, 1521, 1457, 11446, 1116, 542. m/z (CHCl₃/ MeOH 1:1) 927 MH⁺. λ_{max} nm (CHCl₃) 255, 322, 430, 703. λ_{max} nm (CHCl₃ / CH₃OH 8:2) 255, 309, 430, 701. ¹H NMR (500Mhz, CDCl₃): δ 5.34-5.32, pyrrolidine of molecule **14**), 4.52 (bs, CH₂ of **14** and pyrrolidine of **13**), 4.07-4.06 (m), 3.92-3.90 (m), 3.86-3.84 (m), 3.80-3.76 (m), 3.74-3.69 (m), 3.58-3.54 (m), 3.38 (s, CH₃ of **13**) 3.34 (s, CH₃ of **14**). See text for the ¹⁵N-¹H correlation spectrum.

NB The ¹H NMR spectrum of molecule **14** also contains peaks corresponding to its former molecule **13** owing to degradation that occurred over a period of four days at room temperature.

NMRs and Mass spectra

Figure 1: ^1H NMR of molecule **1c** in CDCl_3

NB insufficient solubility of **1c** to permit ^{13}C NMR analysis.

Figure 2: Mass spectrum of molecule **1c**

Figure 3: ^1H NMR of molecule **2b** in CDCl_3

Figure 4: ^1H NMR of molecule **2c** in CDCl_3

Figure 5: ^1H NMR of **4a** in CDCl_3

Figure 6: ¹³C NMR of **4a** in CDCl₃ / CD₃OD

Figure 7: Mass spectrometry of **4a**

Figure 8: ^1H NMR of molecule **4b** in CDCl_3

Figure 9: ^{13}C NMR of molecule **4b** in CDCl_3

Figure 10: ^1H NMR of molecule **4c** in CDCl_3 / CD_3OD

NB insufficient solubility of **4c** to permit ^{13}C NMR analysis.

Figure 11: Mass spectrum of molecule **4b**

Figure 12: ^1H NMR of molecule **5a** in $\text{CDCl}_3 / \text{CD}_3\text{OD}$

Figure 13: ¹³C NMR of molecule **5a** in CDCl₃ / CD₃OD

Figure 14: Mass spectrum of molecule **5a**

Figure 15: ^1H NMR of **5c** in CDCl_3 / CD_3OD

Figure 16: ^{13}C NMR of **5c** in CDCl_3

Figure 17: Mass spectrum of molecule **5c**

Figure 18: ^1H NMR of molecule **5b** in CDCl_3

Figure 19: ¹³C NMR of molecule **5b** in CDCl₃ / CD₃OD

Figure 20: Mass spectrum of molecule **5b**

Figure 21: ^1H NMR of molecule **7** in CD_3OD

Figure 22: ^{13}C NMR of molecule **7** in CD_3OD

Figure 23: ^1H NMR of molecule **8** in CDCl_3

Figure 24: ^1H NMR of molecule **10** in CDCl_3

Figure 25: ^{13}C NMR of molecule **10** in CDCl_3

Figure 26: ^1H NMR of molecule **11** in CDCl_3

Figure 27: ^{13}C NMR of molecule **11** in CDCl_3

Figure 28: ^1H NMR of molecule **12** in CD_3OD

Figure 29: ¹H NMR of molecule **13** in CDCl₃

Figure 30: ^{13}C NMR of molecule **13** in CDCl_3

Figure 31: Mass spec of molecule **13**

Figure 32: ^1H NMR of molecules **13** and **14** in CDCl_3

HPLC analysis

Figure 33: HPLC of **6a** in toluene / MeOH (8:2) 1mL per min

Thermogravimetric Analyses (TGA)

Figure 34: TGA analysis of molecule **5a**

DSC profiles

Figure 35: DSC analysis of molecule **4c**

Figure 36: DSC analysis of molecule **5b**

Figure 37: DSC analysis using of molecule **5b** using three thermal cycles

Figure 38: DSC analysis of molecule **5c**

Reference

- 1 Kordatos, K., Da Ros, T., Bosi, S., Vazquez, E., Bergamin, M., Cusan, C., Pellarini, F., Tomberli, V., Baiti, B., Pantarotto, D., Georgakilas, V., Spalluto, G., Prato, M. *J. Org. Chem.* **2001**, *66*, 4915-4920.
- 2 a) Kordatos, K., Bosi, S., Da Ros, T., Zambon, A., Lucchini, V., Prato, M., *J. Org. Chem.* **2001**, *66*, 2802-2808. b) Prato, M., Maggini, M., *Acc. Chem. Res.* **1998**, *31*, 519-526.