

Prato Reaction of $M_3N@I_h-C_{80}$ ($M = Sc, Lu, Y, Gd$) with Reversible Isomerization

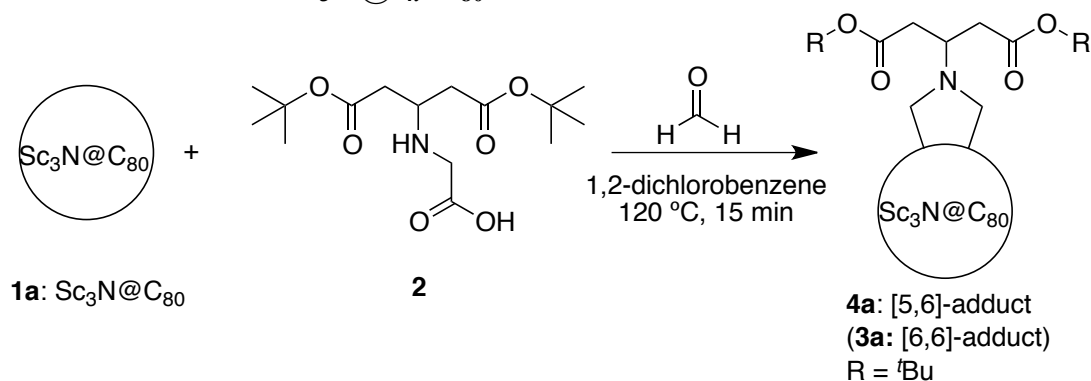
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Supporting Information

General. NMR spectra were recorded on Bruker 400 spectrometer, or Bruker 600 spectrometer equipped with a CryoProbe (Bruker BioSpin GmbH, Rheinstetten, Germany). MALDI-MS spectra were recorded in a positive mode on a Bruker MALDI-TOF (Bruker Daltonics GmbH, Bremen, Germany) and HR-MS on a Bruker maXis ESI (Bruker Daltonics). FT-IR spectra were recorded on PerkinElmer Spectrum One FT-IR Spectrometer with Universal ATR Sampling Accessory (PerkinElmer Inc., Waltham, MA, USA). UV/Vis/NIR were recorded on JASCO V-570 spectrophotometer. HPLC analyses were carried out by JASCO PU-2080 Plus HPLC pump, JASCO MD-2018 Plus detector, and ChromNAV Chromatography Data System (JASCO Co., Tokyo, JPN) using Buckyprep or PBB columns (analytical and semi-preparative) from Nakalai Tesque (Kyoto, JPN). All the solvents used are HPLC grade and were purchased from Acros Organic (Thermo Fischer Scientific, Inc., Geel, Belgium). All the reagents were purchased from corresponding suppliers and purified as described when needed. Column chromatography were performed on SilicaFlash® F60 (230 – 400 mesh) (SiliCycle Inc., Quebec City, CAN). All $M_3N@C_{80}$ were purchased from Luna Innovations (Roanoke, VA, USA). Electrochemical measurements were performed on EG&G potentiostat model 263A (Princeton Applied Research, AMTEC Inc., Berwyn, PA, USA), equipped with a glassy carbon from eDAQ as a working electrode ($\varnothing = 1.0$ mm), a platinum wire as a counter electrode ($\varnothing = 0.1$ mm) and a silver wire as a reference electrode ($\varnothing = 0.3$ mm). All the electrochemical measurement were recorded in *o*-dichlorobenzene (distilled over CaH_2) in the presence of 0.05 M Bu_4NPF_6 as an electrolyte. DPV measurement conditions: scan rate 20 mV/sec, pulse amplitude 50 mV, pulse width 50 mV, CV conditions scan rate 100 mV/sec.

Prato reaction of $Sc_3N@I_h-C_{80}$



Starting material purification: Purification of $Sc_3N@I_h-C_{80}$: $Sc_3N@C_{80}$ was carried out since the purchased material included D_{5h} impurity. The procedure reported by Echegoyen and co-workers¹ using Magic Blue was applied. The purity was checked by HPLC analysis (Figure S1). Purification was not necessary for other $M_3N@C_{80}$ materials used in this study.

¹ *J. Am. Chem. Soc.* **2005**, *127*, 10885.

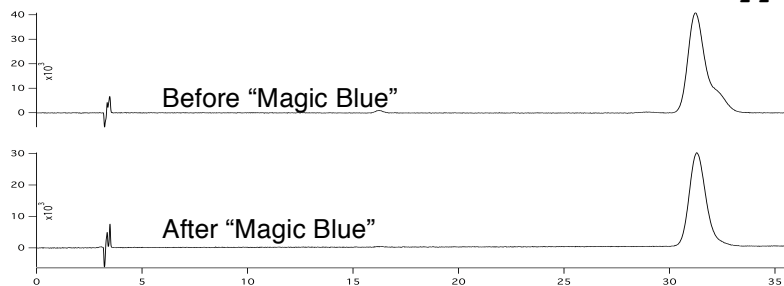


Figure S1. HPLC diagram of $\text{Sc}_3\text{N}@\text{C}_{80}$ purchased (a) and after purification (b). Column: Buckyprep (Nakalai Tesque, \varnothing 4.6 x 250 mm), toluene, 1 mL/min, 390 nm.

4a ([5,6]-adduct of $\text{Sc}_3\text{N}@\text{I}_h\text{-C}_{80}$). (**1a**, 1.9 mg, 1.71 μmol , 1 eq, purified), **2** (4.7 mg, 14.8 μmol , 8.6 eq.), and paraformaldehyde (2.3 mg, 77 μmol , 45 eq.) were mixed in *o*-DCB (11.3 mL) and were treated under sonication for 10 min. The nitrogen gas was bubbled through the mixed solution for 10 min to remove oxygen. The reaction was carried out at 120°C for 15 min and was monitored by HPLC analysis (Buckyprep column (\varnothing 4.6 x 250 mm, toluene, 1 mL/min, 390 nm, Figure S2). After cooling to the room temperature, the mixture was purified by column chromatography (SiO_2 45 g, F2.3 x 7 cm) using toluene as an eluent. After the starting material ($\text{Sc}_3\text{N}@\text{I}_h\text{-C}_{80}$) was eluted, the monoadduct **4a** fraction was concentrated to dryness, and then dissolved in 4 mL of toluene and injected for semi-preparative HPLC (PBB column, Nakalai Tesque, \varnothing 4.6 x 250 mm, toluene, 1 mL/min, 390 nm) for the further purification. The solvent was removed and dried for 24 h under vacuum to provide **4a** (0.8 mg, 0.58 μmol , isolated yield 34%); IR (Neat) $\nu_{\text{max}}(\text{cm}^{-1})$: 1722 (s), 1451 (m), 1364 (s), 1255 (w), 1212 (w), 1133 (s), 1032 (w), 948 (w), 842 (m), 792 (m), 774 (w), 726 (w), 693 (w), 637 (w), 604 (s), 581 (m); ^1H -NMR (300 MHz, $\text{CS}_2\text{-CDCl}_3$ 1:2) 1.56 (s, $\text{C}(\text{CH}_3)_3$, 18H), 2.58 (dd, $J = 6.75$ Hz, $J = 15$ Hz, $\text{CH-CHH-CO}_2^t\text{Bu}$, 2H), 2.71 (dd, $J = 6.75$ Hz, $J = 15$ Hz, $\text{CH-CHH-CO}_2^t\text{Bu}$, 2H), 3.07 (d, $J = 9.0$ Hz, C-CHH-N , 2H), 3.94 (m, $J = 6.75$ Hz, $(\text{CH}_2)_2\text{-CH-N}$, 1H), 4.03 (d, $J = 9.0$ Hz, C-CHH-N , 2H). ^{13}C (100 MHz, $\text{CS}_2\text{-CDCl}_3$ 1:2) 28.27 (s, $\text{C}(\text{CH}_3)_3$, 37.99 ($\text{CH-CH}_2\text{-CO}_2^t\text{Bu}$), 53.84 ($(\text{CH}_2)_2\text{-CH-N}$), 64.88 ($\text{C-CH}_2\text{-N}$), 80.84 ($\text{C}(\text{CH}_3)_3$), 170.53 ($\text{CH}_2\text{-CO}_2^t\text{Bu}$), fullerene core: 57.25 ($\text{C-CH}_2\text{-N}$), 114.76 (2C, adjacent to sp^3), 115.34 (2C, adjacent to sp^3), 129.28 (2C), 130.55 (2C), 130.80 (2C), 131.83 (2C), 133.30 (2C), 133.68 (2C), 134.88 (1C), 135.15 (2C), 136.37 (2C), 136.86 (2C), 137.27 (2C), 138.00 (1C), 138.28 (2C), 138.56 (2C), 138.71 (2C), 139.12 (2C), 139.40 (2C), 139.45 (2C), 140.05 (1C), 140.37 (1C), 140.41 (2C), 140.70 (2C), 141.00 (2C), 141.76 (1C), 142.24 (2C), 143.19 (2C), 143.82 (2C), 144.11 (1C), 144.20 (2C), 144.32 (2C), 144.95 (2C), 145.57 (2C), 147.68 (2C), 148.45 (2C), 149.16 (2C), 149.67 (2C), 150.50 (2C), 154.25 (1C), 155.03 (2C), 156.26 (1C), 158.71 (2C); LR-MS (MALDI $^+$, matrix: 9-nitroanthracene) m/z : 1110 ($[\text{Sc}_3\text{N}@\text{C}_{80} + \text{H}]^+$), 1395 ($[\text{M} + \text{H}]^+$); HRMS (MALDI $^+$) m/z calcd. for $\text{C}_{95}\text{H}_{28}\text{N}_2\text{O}_4\text{Sc}_3$: 1395.0727, found: 1395.0729 $[\text{M} + \text{H}]^+$.

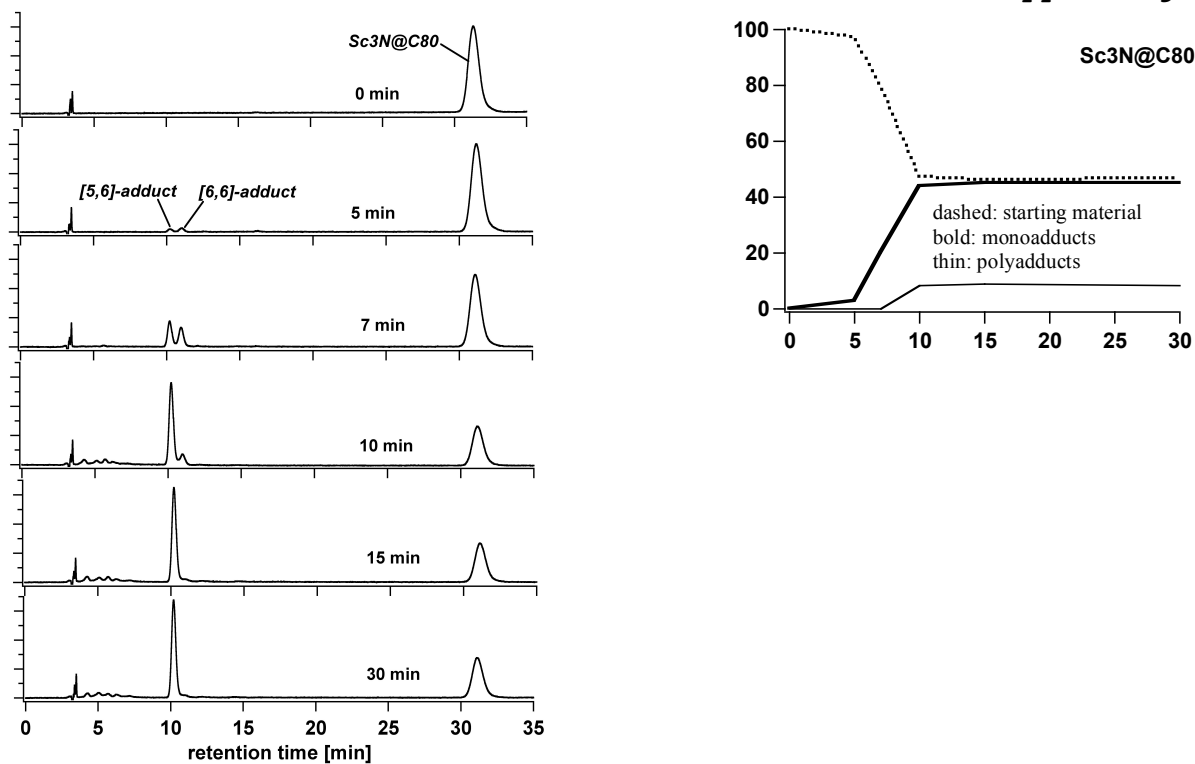


Figure S2. Reaction monitor by HPLC analysis.

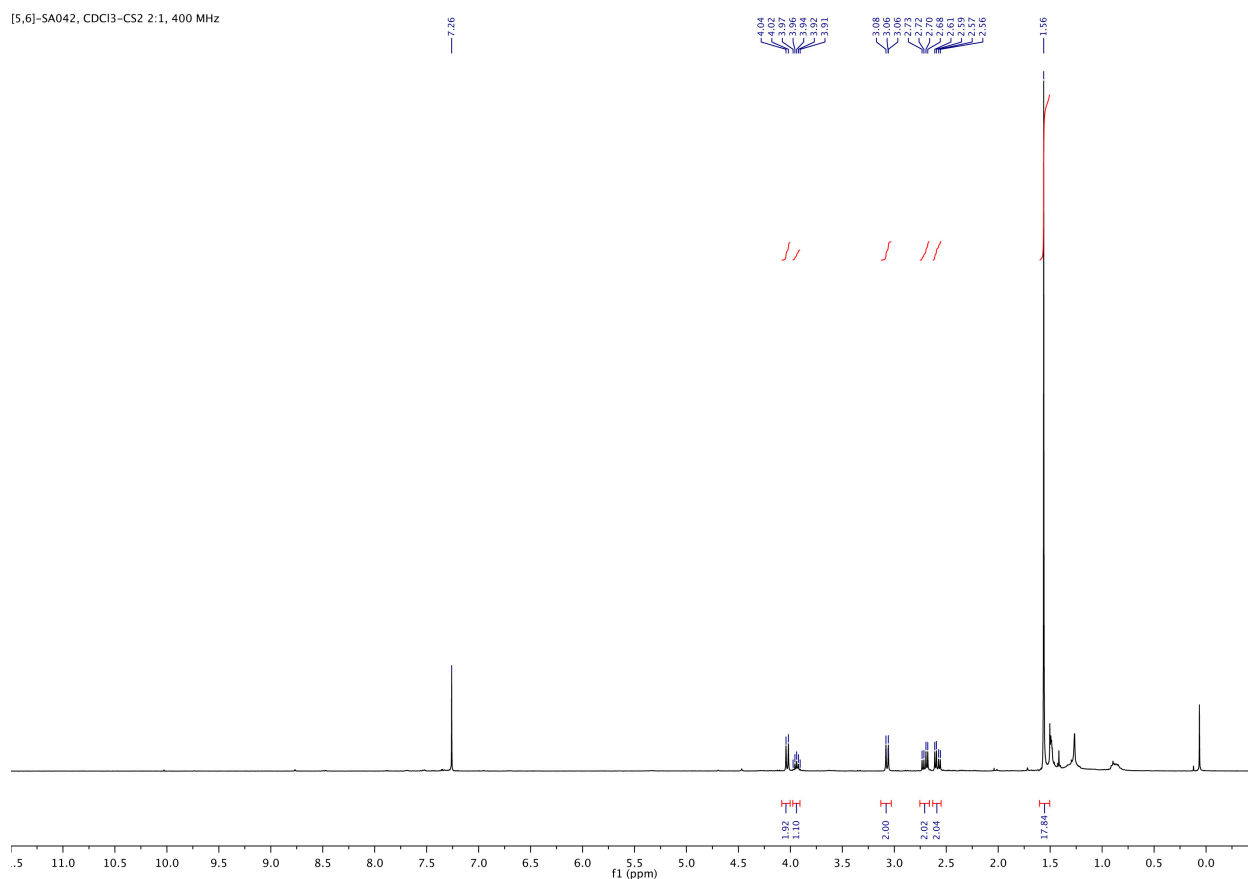


Figure S3. ¹H-NMR spectra of [5,6]-adduct of Sc₃N@C₈₀ (**4a**) (in CHCl₃-CS₂ (2:1), 400 MHz).

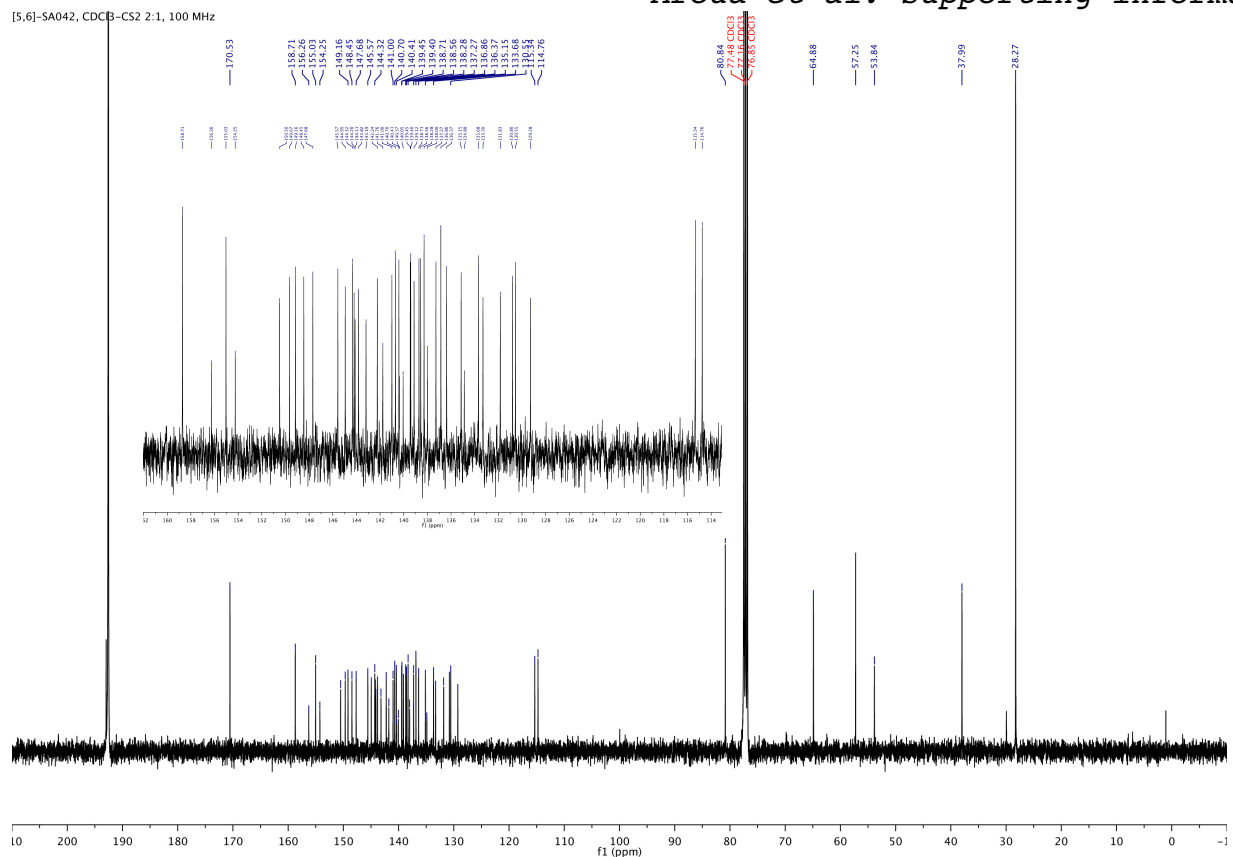


Figure S4. ^{13}C -NMR spectra of [5,6]-adduct of $\text{Sc}_3\text{N}@\text{C}_{80}$ (**4a**) (in $\text{CHCl}_3\text{-CS}_2$ (2:1), 100 MHz).

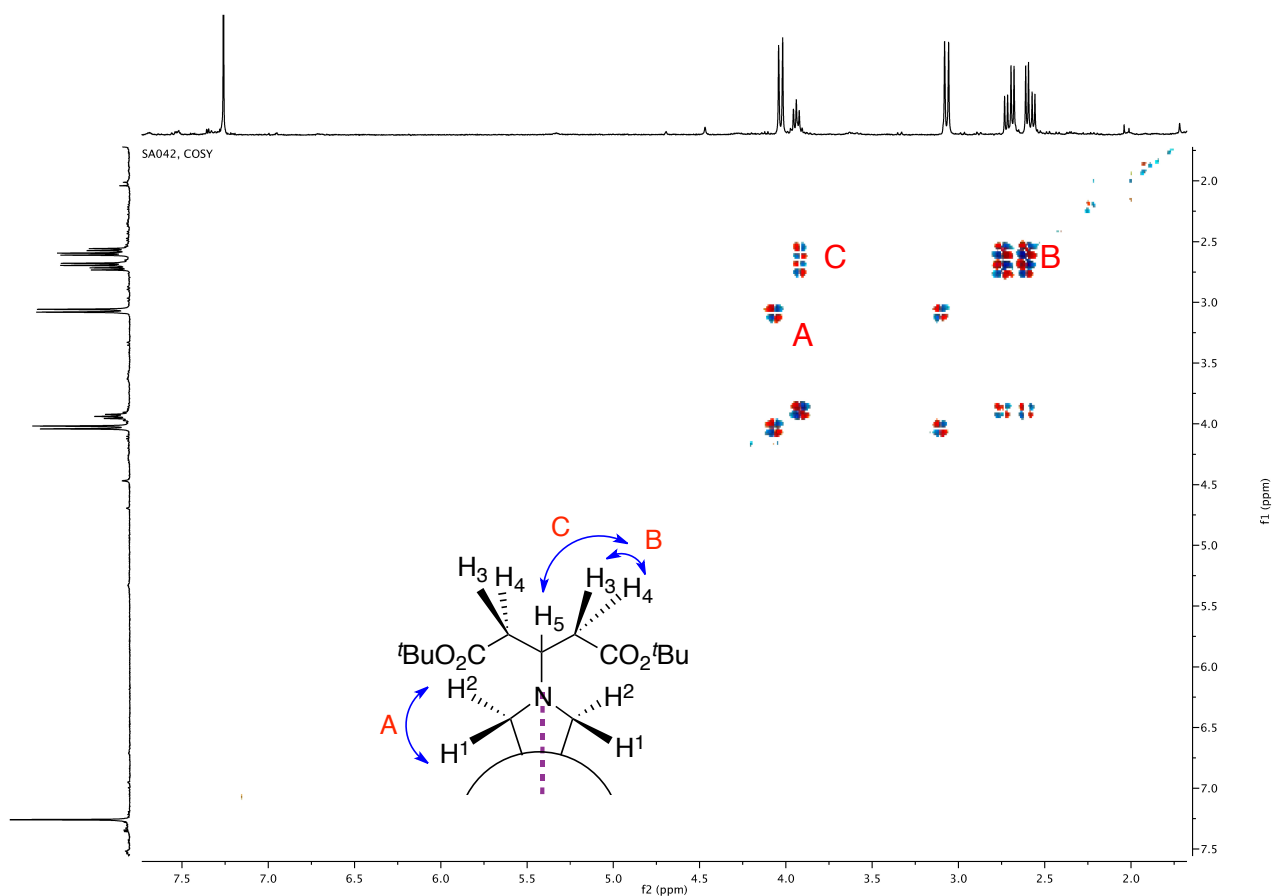


Figure S5. DQF COSY-NMR spectra of [5,6]-adduct of $\text{Sc}_3\text{N}@\text{C}_{80}$ (**4a**) (in $\text{CHCl}_3\text{-CS}_2$ (2:1)).

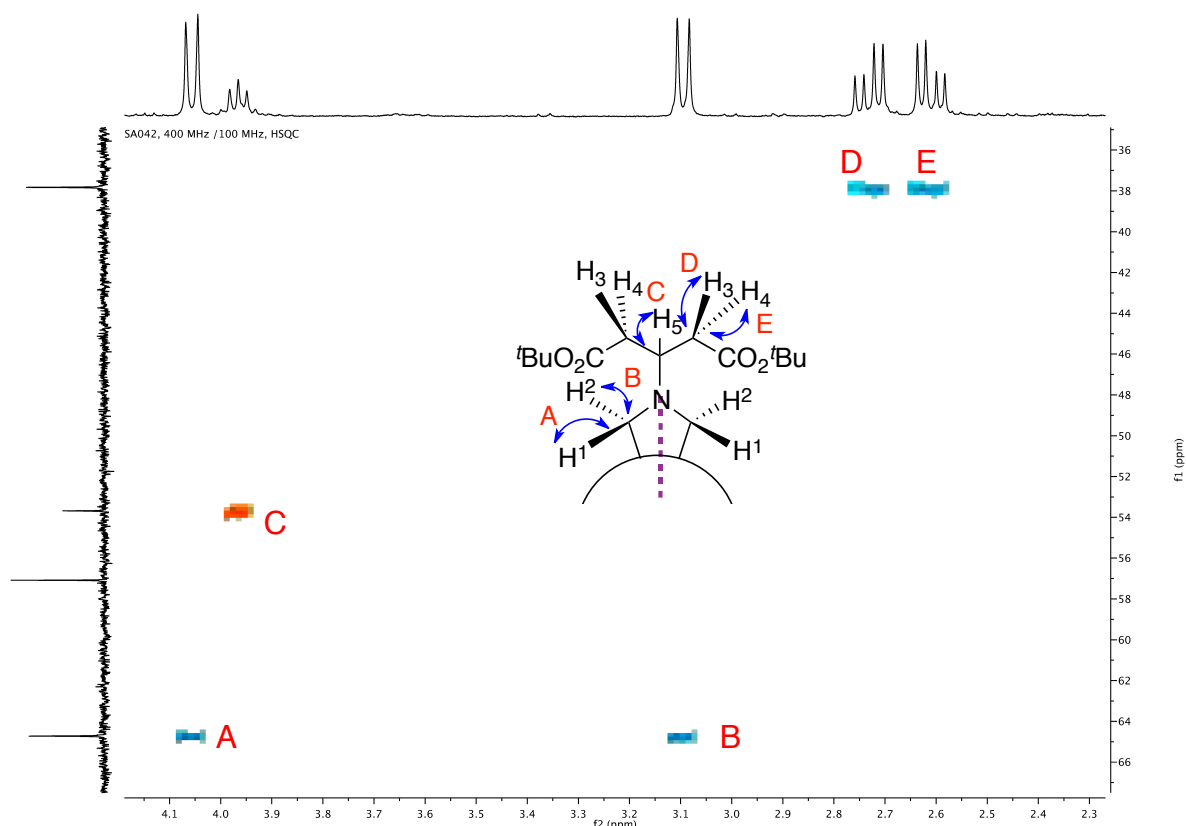


Figure S6. HSQC-NMR spectra of [5,6]-adduct of $\text{Sc}_3\text{N}@C_{80}$ (**4a**) (in $\text{CHCl}_3\text{-CS}_2$ (2:1), 400/100 MHz).

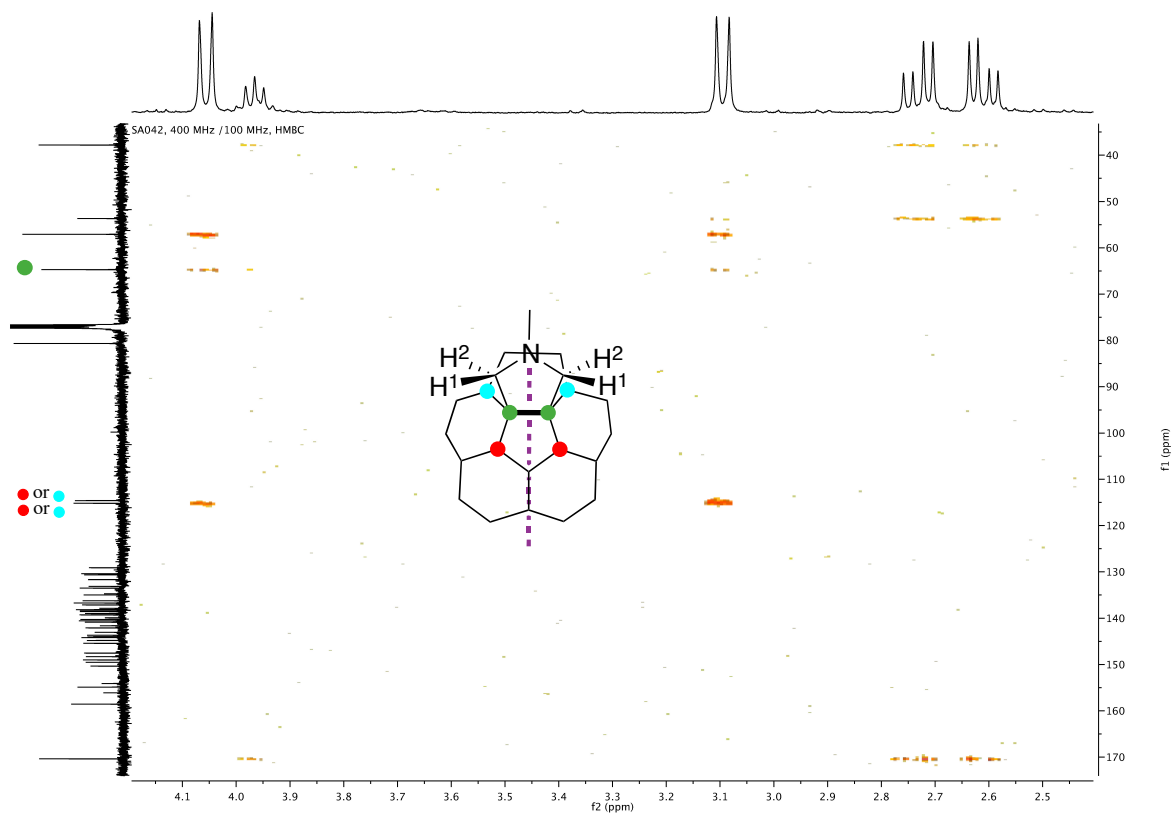


Figure S7. HMBC-NMR spectra of [5,6]-adduct of $\text{Sc}_3\text{N}@C_{80}$ (**4a**) (in $\text{CHCl}_3\text{-CS}_2$ (2:1), 400/100 MHz).

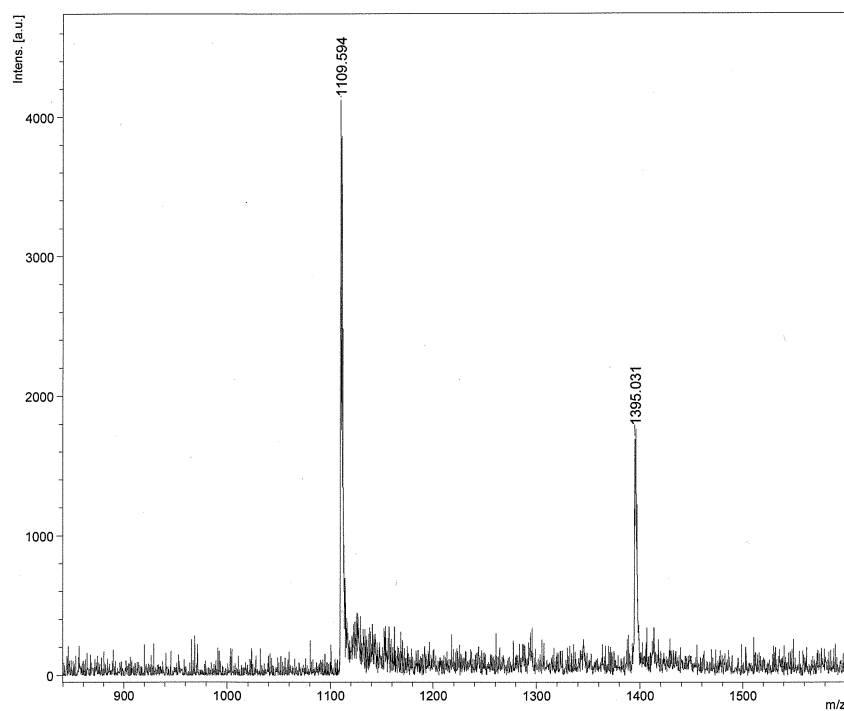


Figure S8. MALDI-TOF MS of compound **4a** (Matrix 9-nitroanthracene).

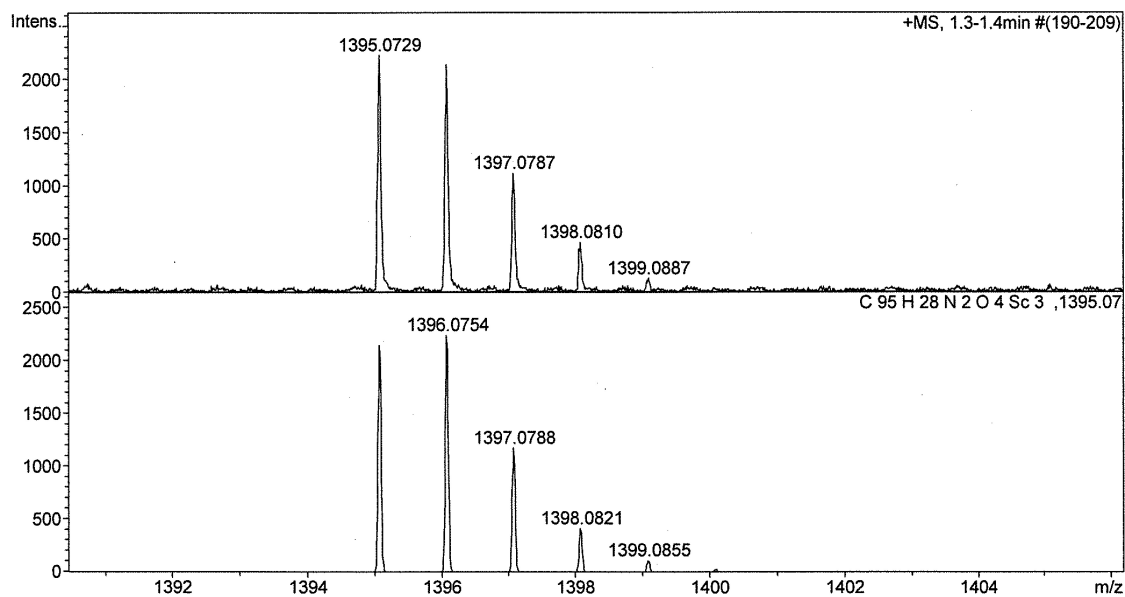


Figure S9. HR-MS (ESI+) of compound **4a**.

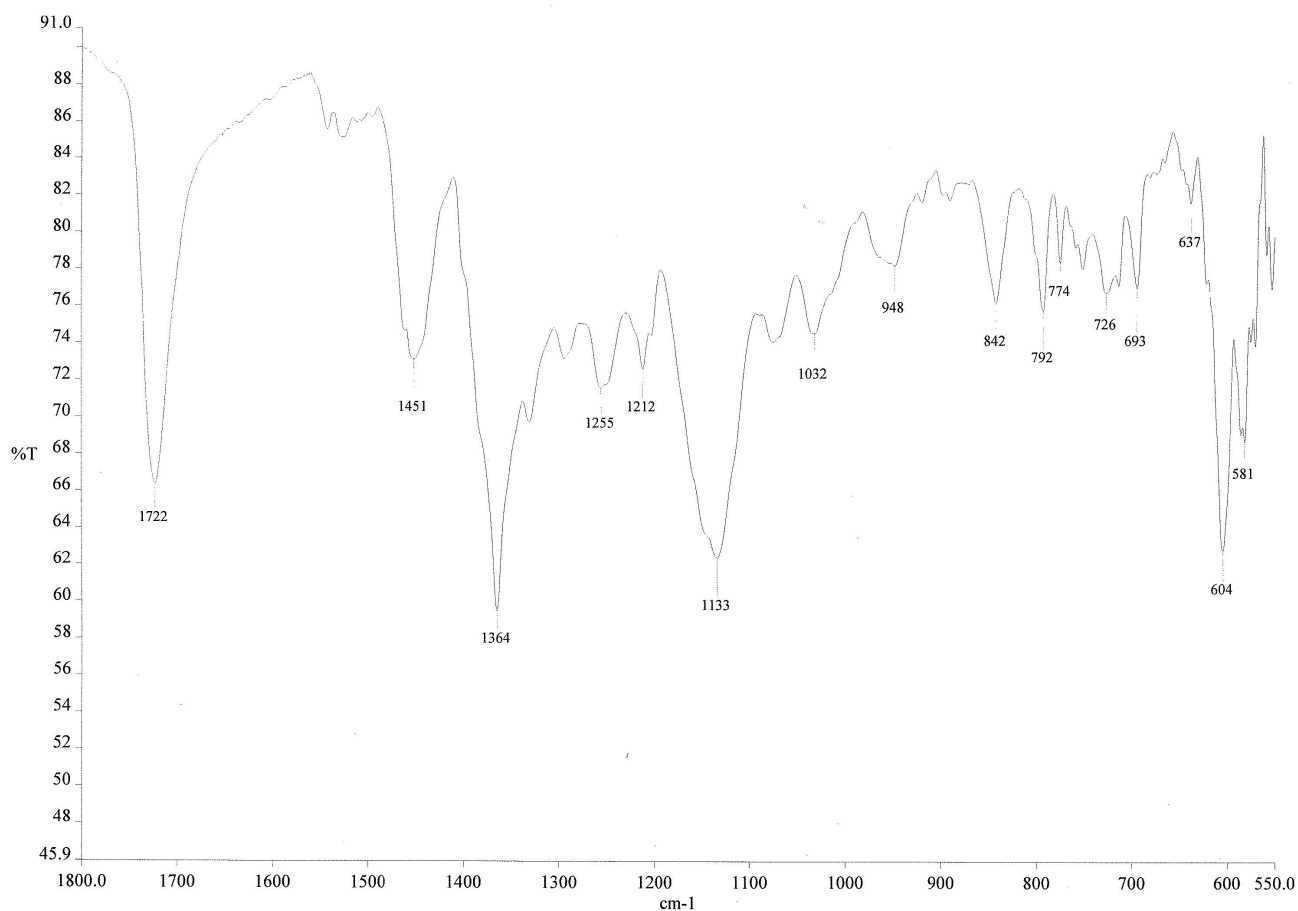


Figure S10. FT-IR of 4a.

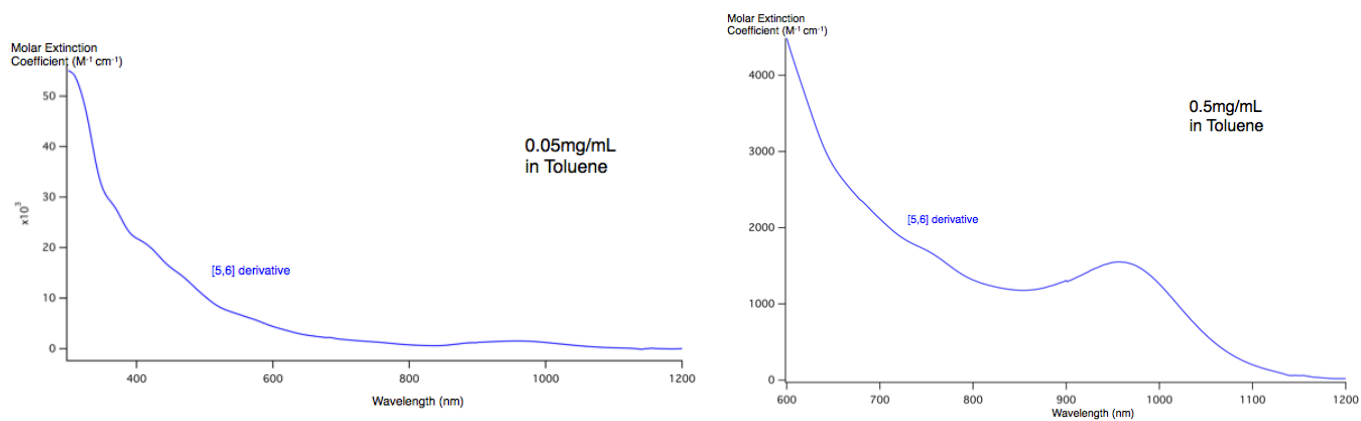


Figure S11. UV-Vis spectra of [5,6]-fulleropyrrolidine Sc₃N@C₈₀ 4a in toluene.

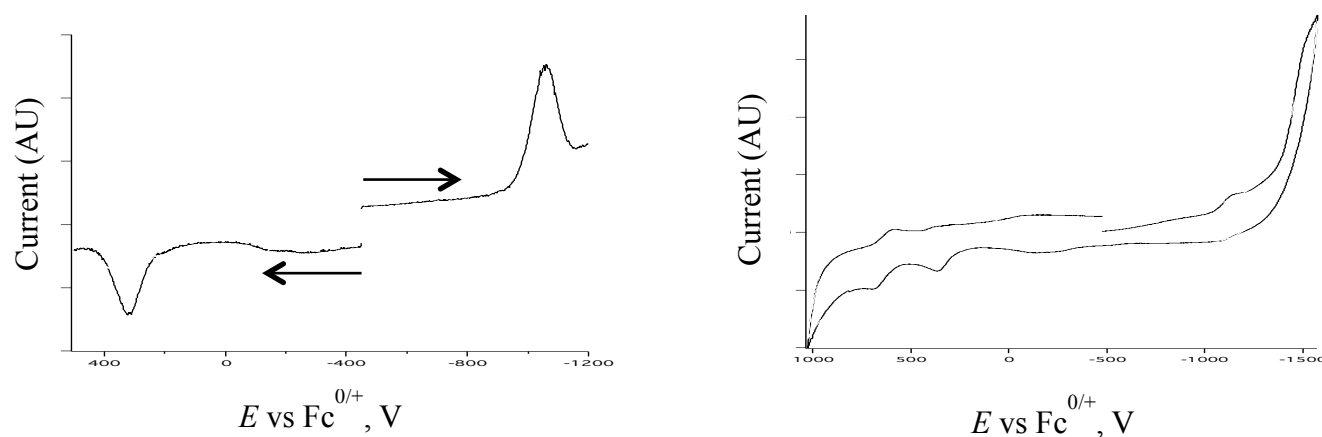
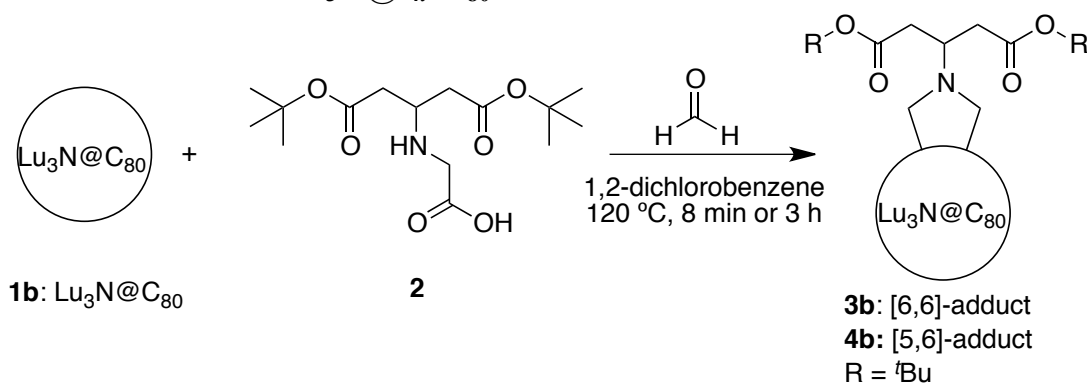


Figure S12. DPV of compound **4a** (left image); CV of compound **4a** (right image).

Prato reaction of $\text{Lu}_3\text{N}@I_h\text{-C}_{80}$



3b ([6,6]-adduct of $\text{Lu}_3\text{N}@I_h\text{-C}_{80}$). $\text{Lu}_3\text{N}@I_h\text{-C}_{80}$ (**1b**, 5.0 mg, 3.33 μmol , 1 eq.), **2** (9.1 mg, 28.7 μmol 8.6 eq.), and paraformaldehyde (4.5 mg, 150 μmol , 45 eq.) were mixed with in *o*-DCB (22 mL) and were treated under sonication for 10 min. The nitrogen gas was bubbled through the mixed solution for 10 min to remove oxygen. The reaction was carried out at 120°C for 8 min. After cooling to the room temperature, the mixture was purified by column chromatography (SiO_2 45 g, \varnothing 2.3 x 7 cm) using toluene as an eluent. After the starting material ($\text{Lu}_3\text{N}@I_h\text{-C}_{80}$) was eluted, the monoadduct was concentrated to dryness, and then dissolved in 4 mL of toluene and further purified by a semi-preparative HPLC (Buckyprep, Nakalai Tesque, \varnothing 10 x 250 mm, toluene, 1mL/min, 390 nm). The solvent was removed and dried for 24 h under vacuum to provide **3b** (3.0 mg, 1.68 μmol , isolated yield 50%). **3b:** IR (Neat) $\nu_{\text{max}}(\text{cm}^{-1})$: 1722 (s), 1450 (m), 1364 (s), 1293 (w), 1209 (w), 1139 (s), 1033 (w), 953 (w), 841 (m), 785 (w), 727 (w), 680 (s), 570 (w); ^1H -NMR (400 MHz, $\text{CS}_2\text{-CDCl}_3$ (99.98%) 1:2) 1.51 (s, $\text{C}(\text{CH}_3)_3$, 18H), 2.60 (dd, $J = 6.75$ Hz, $J = 15$ Hz, $\text{CH-CHH-CO}_2^t\text{Bu}$, 2H), 2.72 (dd, $J = 6.75$ Hz, $J = 15$ Hz, $\text{CH-CHH-CO}_2^t\text{Bu}$, 2H), 3.92 (m, $J = 6.75$ Hz, $(\text{CH}_2)_2\text{-CH-N}$, 1H), 3.99 (s, $\text{C-CH}_2^1\text{-N}$, 2H), 4.00 (s, $\text{C-CH}_2^2\text{-N}$, 2H). ^{13}C (150 MHz, $\text{CS}_2\text{-CDCl}_3$ 1:2) 28.25 (s, $\text{C}(\text{CH}_3)_3$, 38.19 ($\text{CH-CH}_2\text{-CO}_2^t\text{Bu}$), 53.76 ($(\text{CH}_2)_2\text{-CH-N}$), 58.28 ($\text{C-CH}_2\text{-N}$), 64.89 ($\text{C-CH}_2\text{-N}$), 81.13 ($\text{C}(\text{CH}_3)_3$), 170.37 ($\text{CH}_2\text{-CO}_2^t\text{Bu}$), fullerene core: 53.89 ($\text{C-CH}_2\text{-N}$), 67.84 ($\text{C-CH}_2\text{-N}$), 113.09 (2C, adjacent to sp^3), 130.54 (1C), 134.21 (2C), 134.63 (1C), 135.80 (1C), 136.23 (2C), 136.28 (2C), 136.47 (2C), 136.59 (2C), 137.12 (2C), 137.21 (2C), 138.00 (2C), 138.36 (2C), 138.70 (2C), 139.01 (2C, adjacent to sp^3), 140.32 (2C), 140.53 (2C), 140.70 (1C), 141.11 (2C), 141.34 (2C), 141.75 (1C), 141.77 (2C), 141.85 (2C), 142.09 (2 + 2C overlap), 142.30 (2C), 142.47 (2C), 142.84 (2C), 142.95 (2C), 143.17 (2C), 144.35 (2C), 144.24 (1C), 144.43 (2C), 144.68 (2C), 144.73 (2C), 145.49 (2C), 145.77 (2C), 145.89 (2C), 147.33 (2C), 148.00 (2C), 148.98 (2C), 151.26 (2C); MS (MALDI⁺, matrix: 9-nitroanthracene) m/z : 1500 ($\text{Lu}_3\text{N}@C_{80} + \text{H}^+$), 1786 ($[\text{M} + \text{H}]^+$).

4b ([5,6]-adduct of $\text{Lu}_3\text{N}@I_h\text{-C}_{80}$). $\text{Lu}_3\text{N}@I_h\text{-C}_{80}$ (**1b**, 5.0 mg, 3.33 μmol , 1 eq.), **2** (9.1 mg, 28.7 μmol 8.6 eq.), and paraformaldehyde (4.5 mg, 150 μmol , 45 eq.) were mixed with in *o*-DCB (22 mL) and were treated under sonication for 10 min. The nitrogen gas was bubbled through the mixed solution for 10 min to remove oxygen. The reaction was carried out at 120°C for 3h and was monitored by HPLC analysis (Buckyprep, Nakalai Tesque, \varnothing 4.6 x 250 mm, toluene, 1mL/mL, 390 nm, Figure S10). After cooling to the room temperature, the mixture was purified by column chromatography (SiO_2 45 g, \varnothing 2.3 x 7 cm) using toluene as an eluent. After the starting material ($\text{Lu}_3\text{N}@I_h\text{-C}_{80}$) was eluted, the monoadduct was concentrated to dryness, and then dissolved in 4 mL of toluene and further purified by a semi-preparative HPLC (PBB column, Nakalai Tesque, \varnothing 4.6 x 250 mm, toluene, 1mL/min, 390 nm). The solvent was removed and dried for 24 h under vacuum to provide **4b** (2.3 mg 1.29 μmol , isolated yield 39%). **4b**: IR (Neat) $\nu_{\text{max}}(\text{cm}^{-1})$: 1722 (s), 1434 (m), 1363 (s), , 1324 (w), 1202 (w), 1138 (s), 1031 (w), 902 (m), 840 (m), 798 (m), 727 (s), 682 (m), 648 (w), 619 (w), 600 (w), 585 (w), 569 (w); $^1\text{H-NMR}$ (400 MHz, $\text{CS}_2\text{-CDCl}_3$ (99.98%) 1:2 1.56 (s, $\text{C}(\text{CH}_3)_3$, 18H), 2.60 (dd, $J = 6.75 \text{ Hz}$, $J = 15 \text{ Hz}$, $\text{CH-CHH-CO}_2^t\text{Bu}$, 2H), 2.72 (dd, $J = 6.75 \text{ Hz}$, $J = 15 \text{ Hz}$, $\text{CH-CHH-CO}_2^t\text{Bu}$, 2H), 3.01 (d, $J = 9.0 \text{ Hz}$, C-CHH-N , 2H), 3.94 (m, $J = 6.75 \text{ Hz}$, $(\text{CH}_2)_2\text{-CH-N}$, 1H), 4.01 (d, $J = 9.0 \text{ Hz}$, C-CHH-N , 2H). ^{13}C (150 MHz, $\text{CS}_2\text{-CDCl}_3$ 1:2) 28.27 (s, $\text{C}(\text{CH}_3)_3$, 37.99 ($\text{CH-CH}_2\text{-CO}_2^t\text{Bu}$), 54.15 ($(\text{CH}_2)_2\text{-CH-N}$), 65.11 ($\text{C-CH}_2\text{-N}$), 80.92 ($\text{C}(\text{CH}_3)_3$), 170.53 ($\text{CH}_2\text{-CO}_2^t\text{Bu}$), fullerene core: 58.18 ($\text{C-CH}_2\text{-N}$), 111.52 (2C, adjacent to sp^3), 114.01 (2C, adjacent to sp^3), 129.57 (2C), 132.68 (1C), 134.08 (2C), 134.57 (2C), 134.65 (2C), 135.03 (2C), 135.60 (2C), 135.79 (2C), 137.02 (2C), 137.51 (2C), 137.59 (2C), 137.61 (2C), 138.12 (1C), 138.51 (2 + 2 C overlap), 138.83 (2C), 140.28 (2C), 140.49 (2C), 140.64 (1C), 141.12 (2C), 141.19 (2C), 141.23 (2C), 141.78 (2C), 141.84 (2C), 142.04 (2C), 143.02 (2C), 144.41 (2C), 144.41 (2C), 144.62 (1C), 144.67 (1C), 144.76 (2C), 145.01 (2C), 146.64 (2C), 146.80 (2C), 148.16 (2C), 148.46 (2 + 2 C overlap), 152.40 (1C), 153.54 (2C), 155.87 (1C), 157.23 (1C), 157.67 (2C); MS (MALDI+, matrix: 9-nitroanthracene) m/z : 1500 ($\text{Lu}_3\text{N}@C_{80} + \text{H}^+$), 1786 ($[\text{M} + \text{H}]^+$).

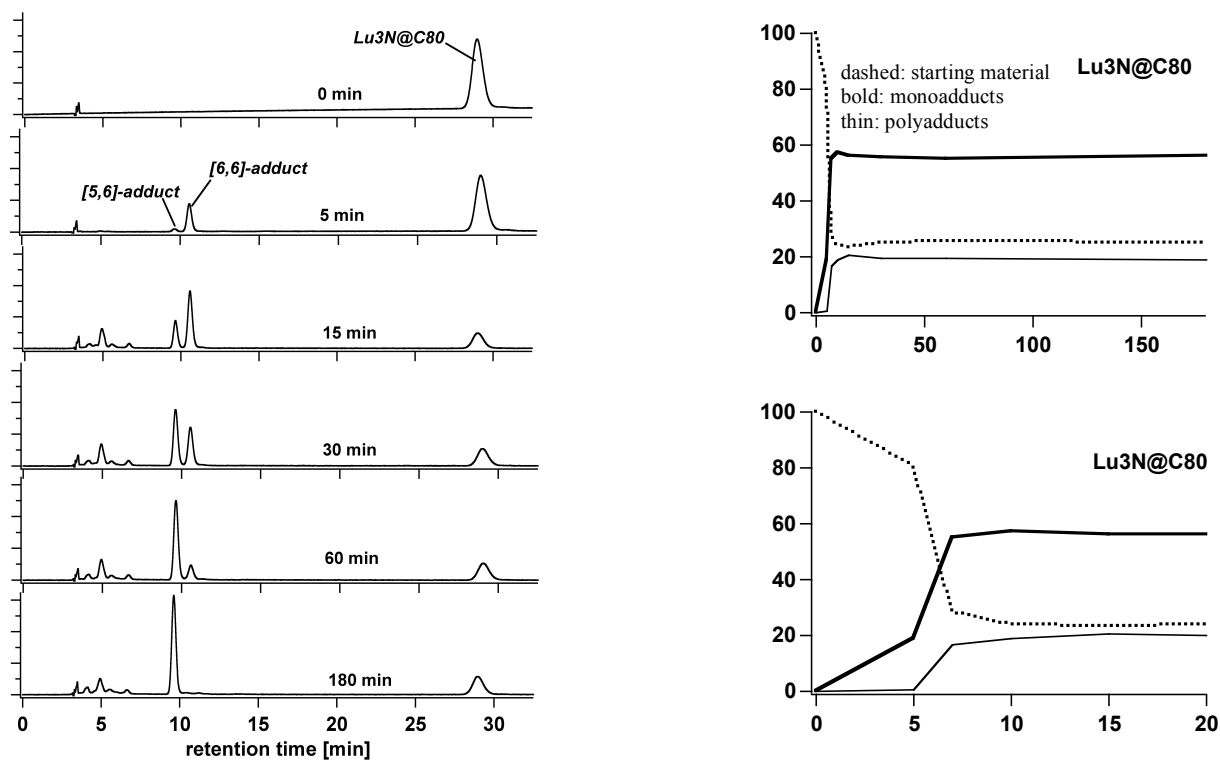
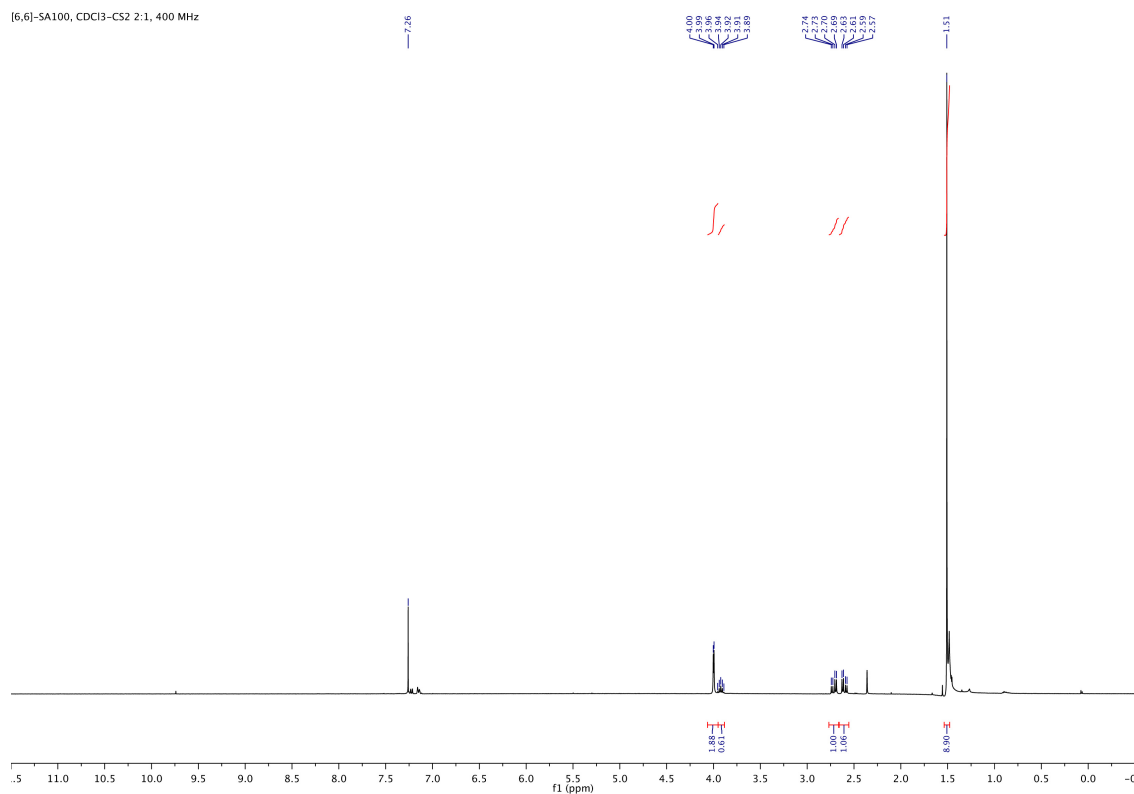


Figure S13. Reaction monitor by HPLC analysis.

Figure S14. ¹H-NMR spectra of [6,6]-adduct of Lu₃N@C₈₀ (3b) (in CHCl₃-CS₂ (2:1), 400 MHz)

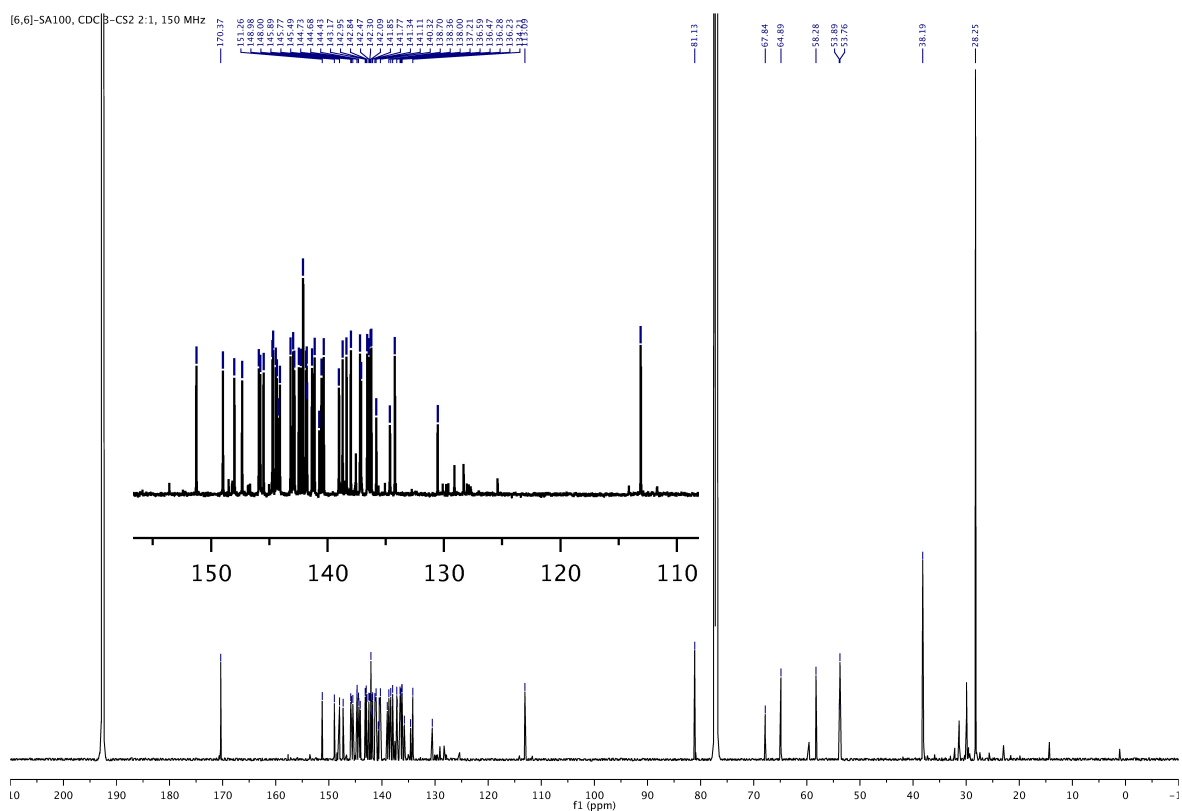


Figure S15. ^{13}C -NMR spectra of [6,6]-adduct of $\text{Lu}_3\text{N}@C_{80}$ (**3b**) (in $\text{CHCl}_3\text{-CS}_2$ (2:1), 150 MHz, contains traces of toluene)

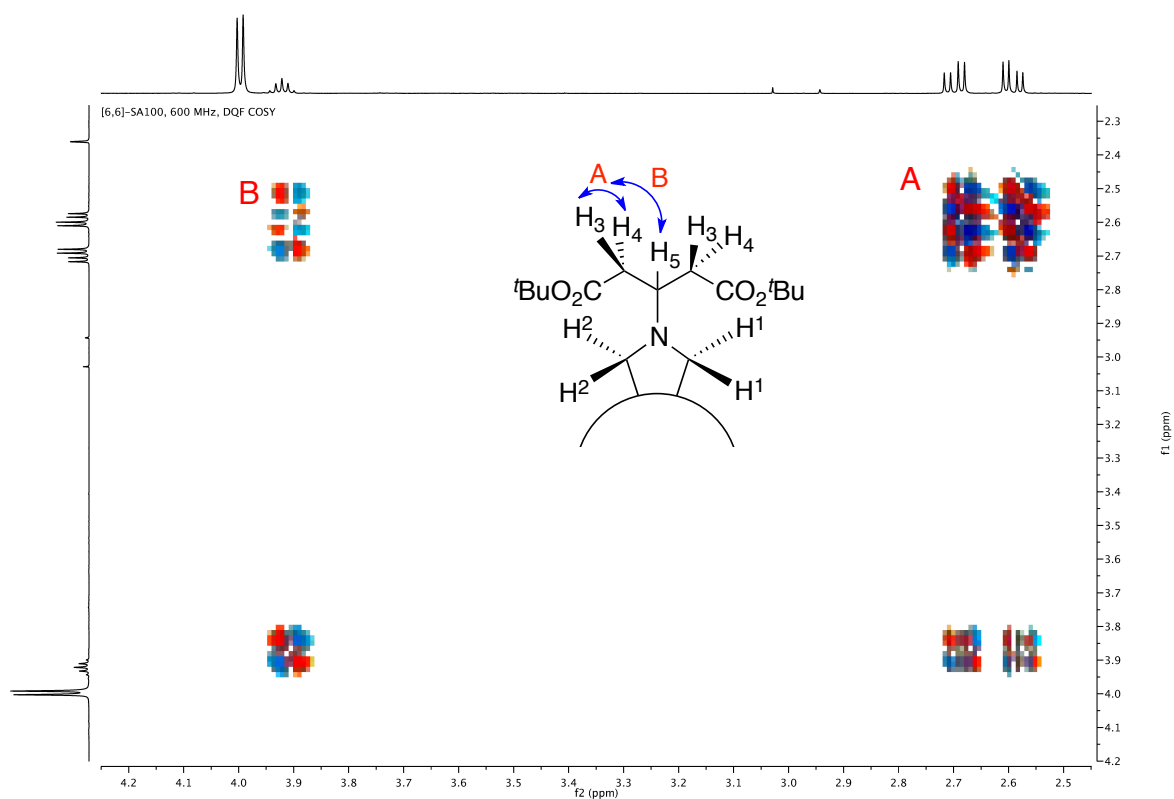


Figure S16. DQF COSY-NMR spectra of [6,6]-adduct of $\text{Lu}_3\text{N}@C_{80}$ (**3b**) (in $\text{CHCl}_3\text{-CS}_2$ (2:1), 600 MHz).

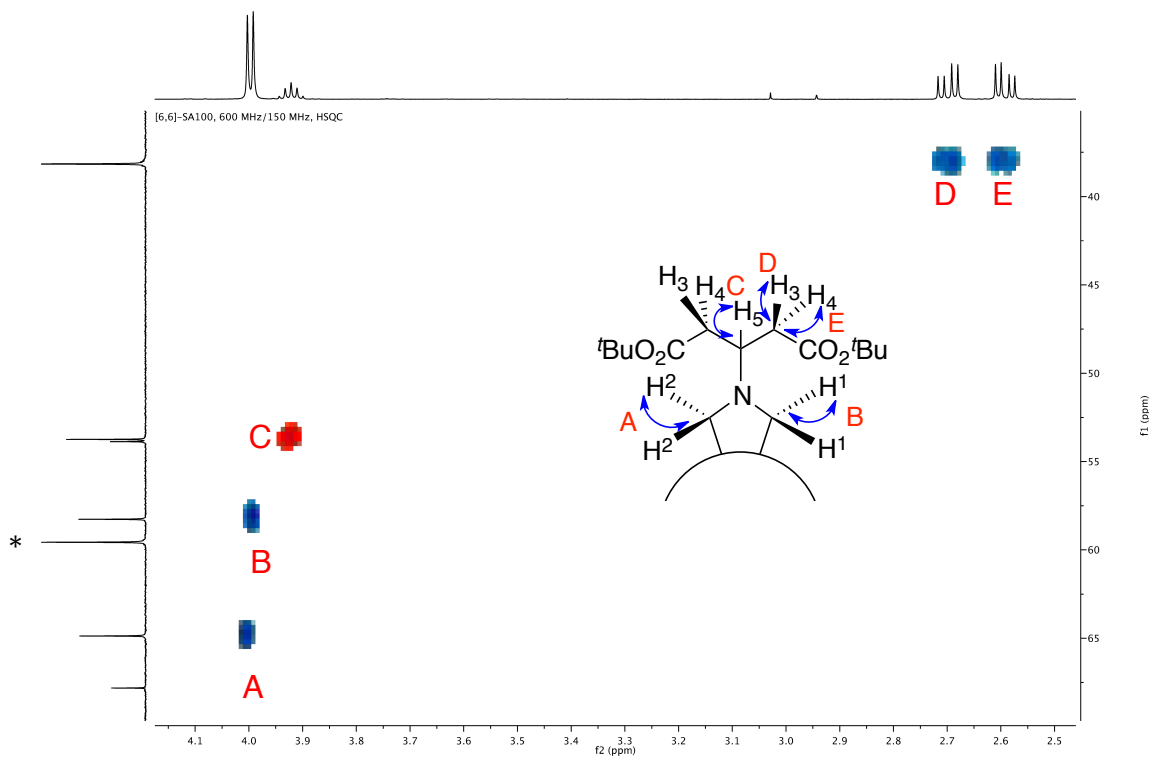


Figure S17. HSQC-NMR spectra of [6,6]-adduct of $\text{Lu}_3\text{N}@\text{C}_{80}$ (**3b**) (in $\text{CHCl}_3\text{-CS}_2$ (2:1), 600/150 MHz). Asterisk denotes an impurity.

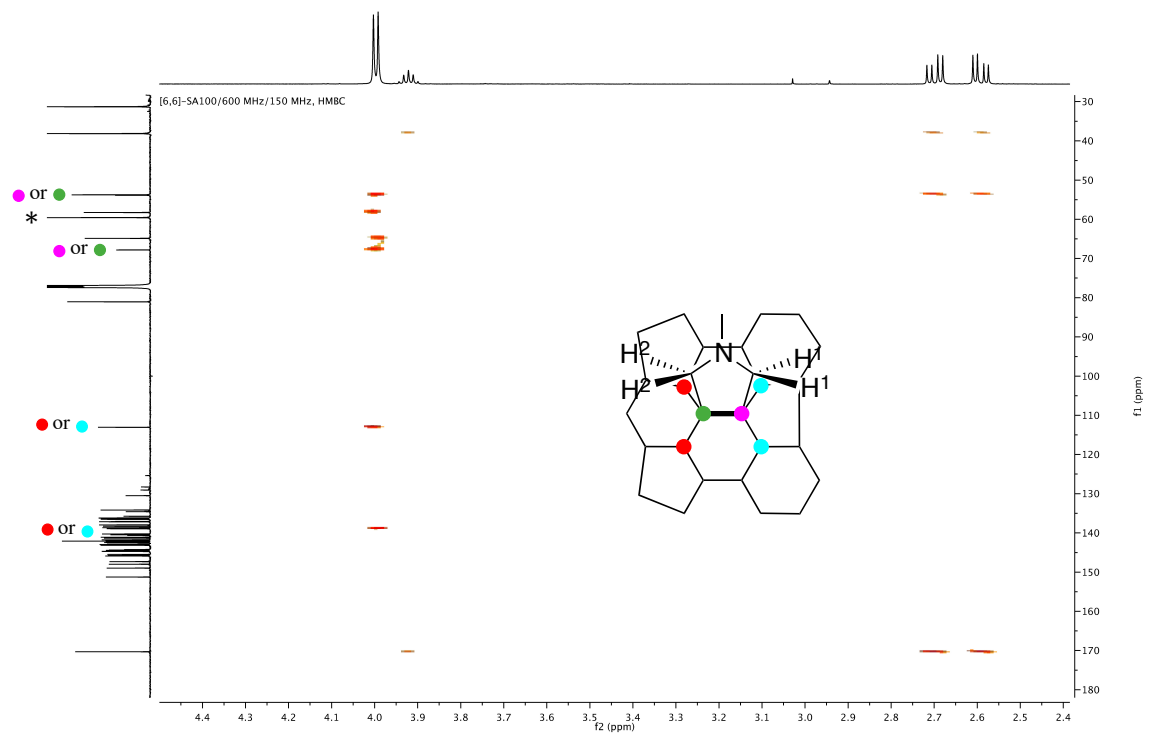


Figure S18. HMBC-NMR spectra of [6,6]-adduct of $\text{Lu}_3\text{N}@\text{C}_{80}$ (**3b**) (in $\text{CHCl}_3\text{-CS}_2$ (2:1), 600/150 MHz). Asterisk denotes an impurity.

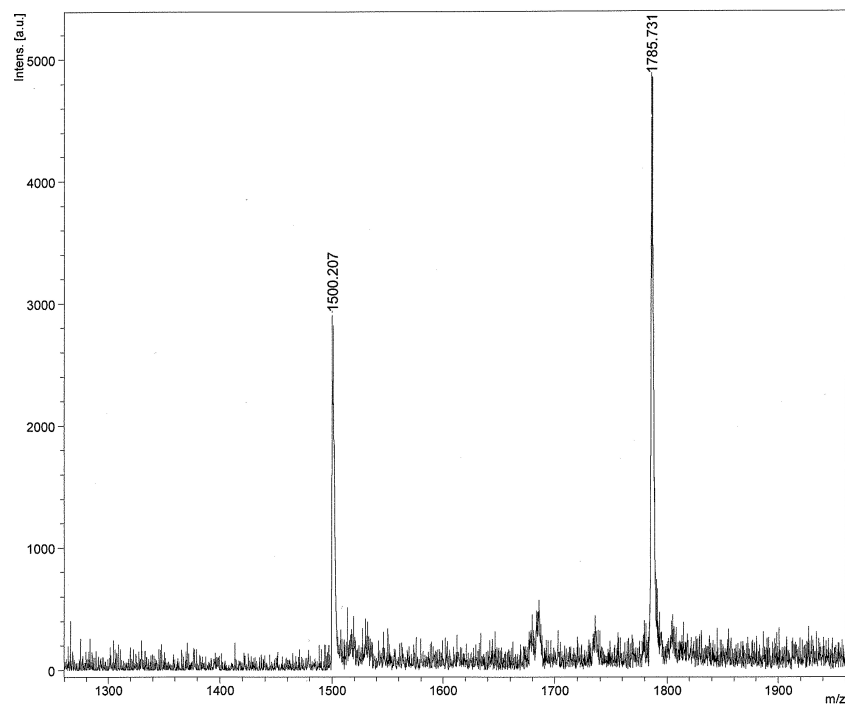


Figure S19. MALDI-TOF MS of compound **3b** (Matrix 9-nitroanthracene).

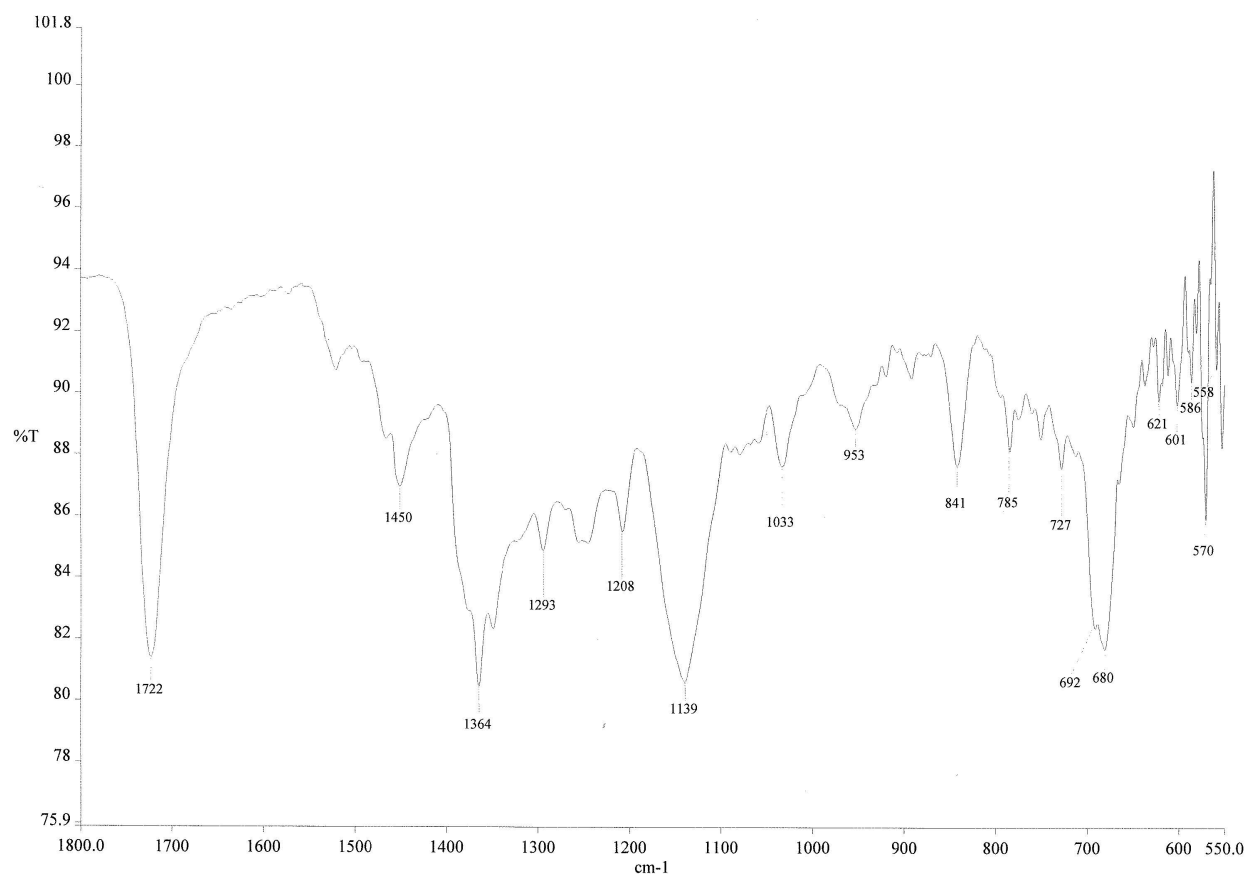


Figure S20. FT-IR of compound **3b**.

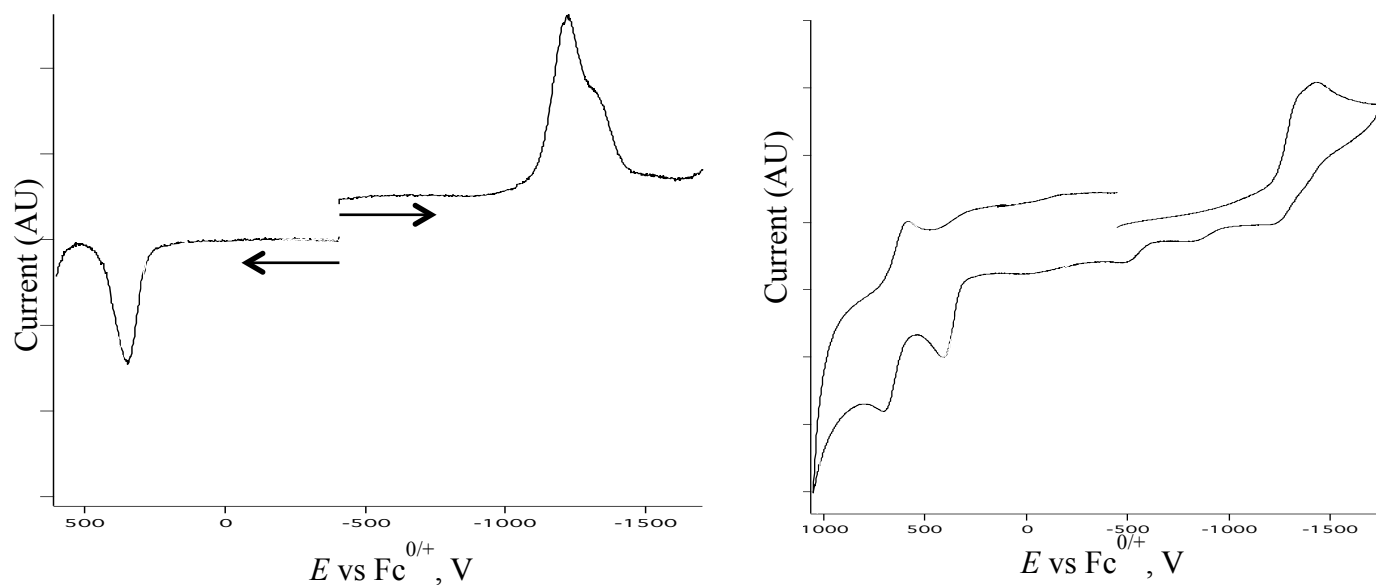


Figure S21. DPV of compound **3b** (left image); CV of compound **3b** (right image).

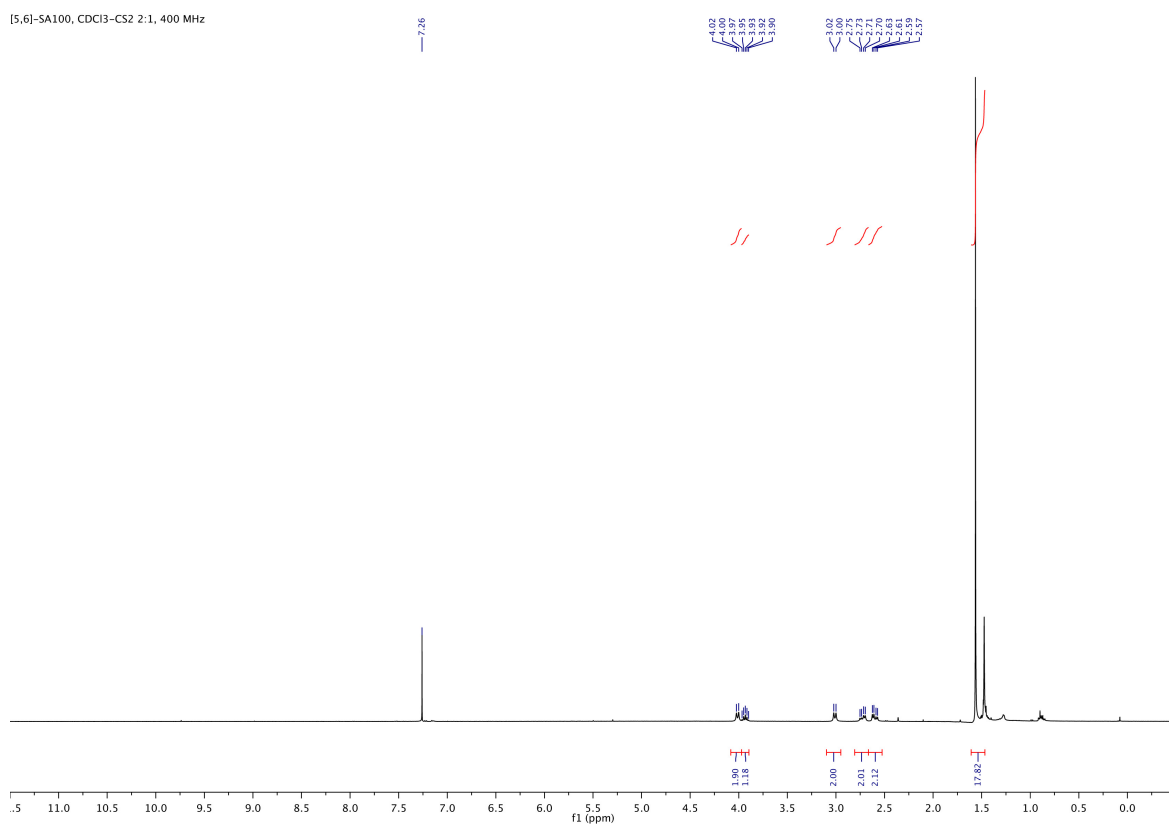


Figure S22. ^1H -NMR spectra of [5,6]-adduct of $\text{Lu}_3\text{N}@C_{80}$ (**4b**) (in $\text{CHCl}_3\text{-CS}_2$ (2:1), 400 MHz).

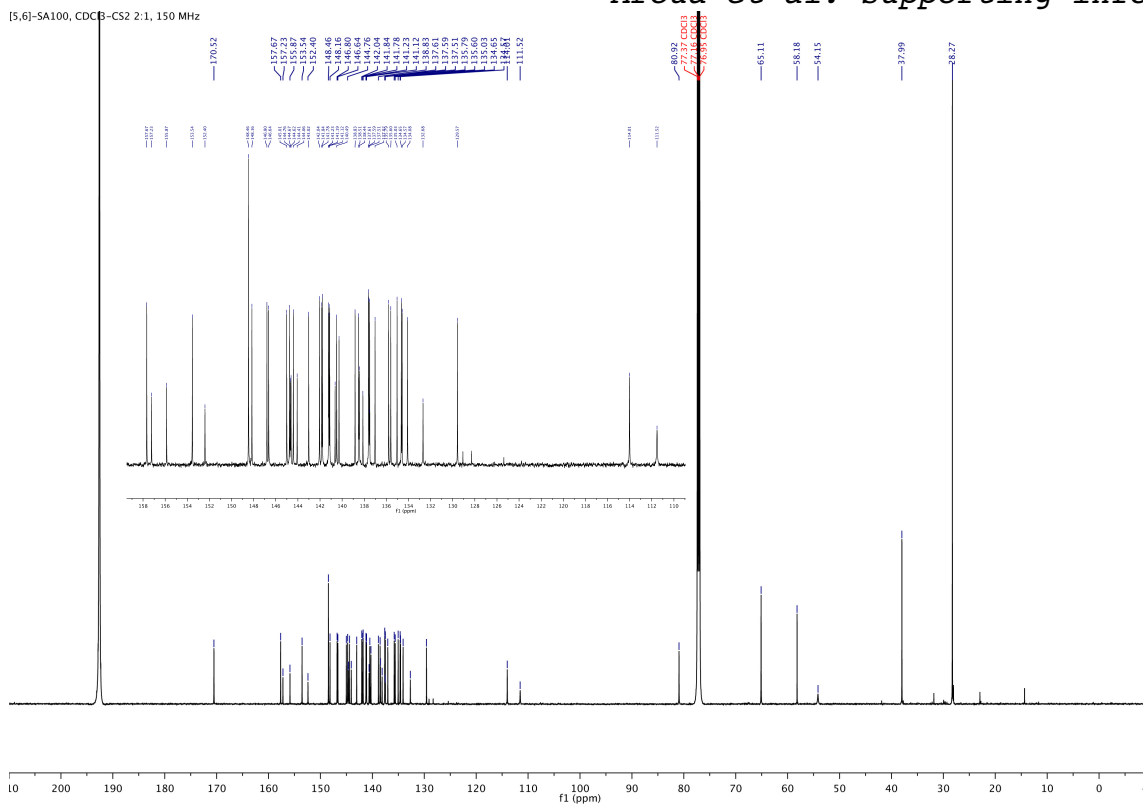


Figure S23. ^{13}C -NMR spectra of [5,6]-adduct of $\text{Lu}_3\text{N}@\text{C}_{80}$ (**4b**) (in $\text{CHCl}_3\text{-CS}_2$ (2:1), 150 MHz, contains traces of toluene).

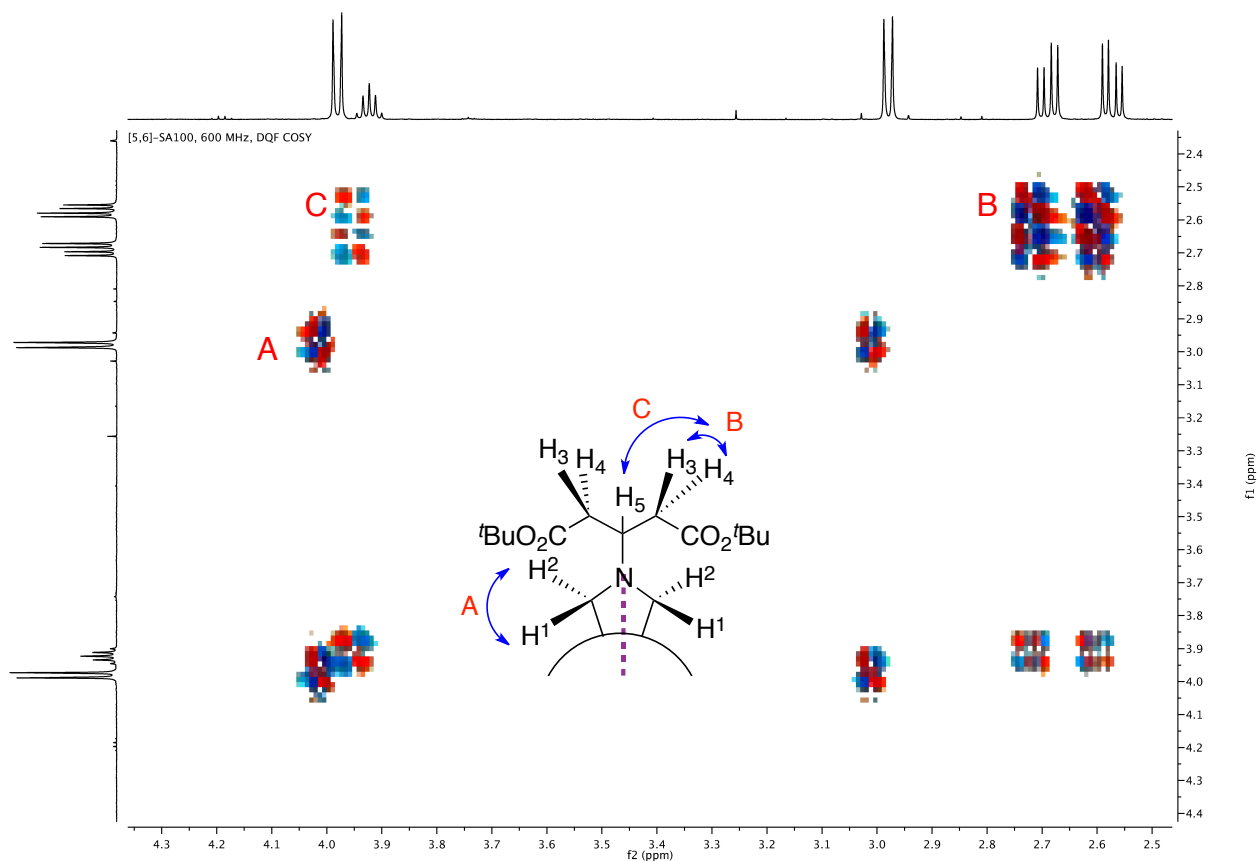


Figure S24. DQF COSY-NMR spectra of [5,6]-adduct of $\text{Lu}_3\text{N}@\text{C}_{80}$ (**4b**) (in $\text{CHCl}_3\text{-CS}_2$ (2:1), 600 MHz).

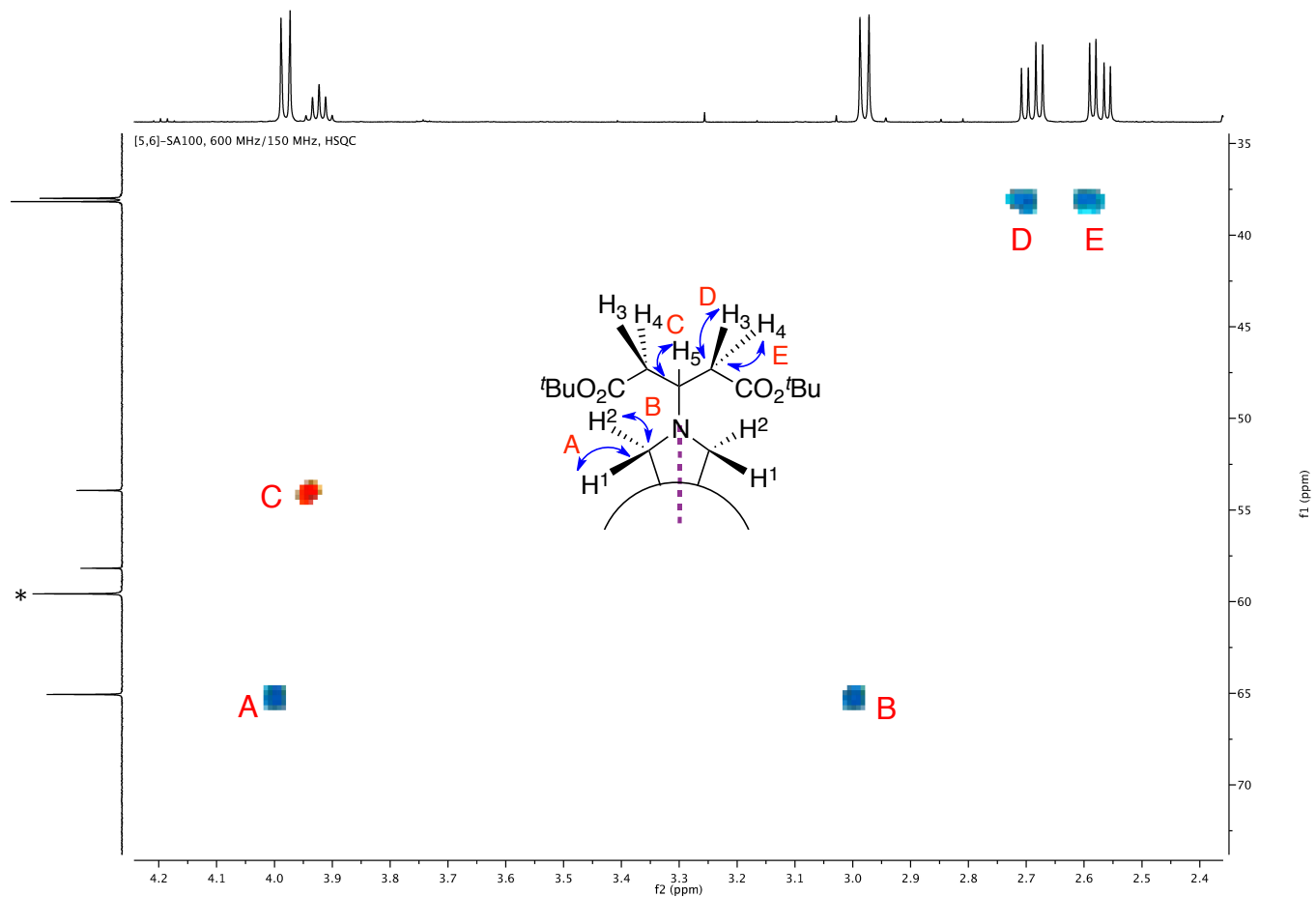


Figure S25. HSQC-NMR spectra of [5,6]-adduct of $\text{Lu}_3\text{N}@\text{C}_{80}$ (**4b**) (in $\text{CHCl}_3\text{-CS}_2$ (2:1), 600/150 MHz). Asterisk denotes an impurity.

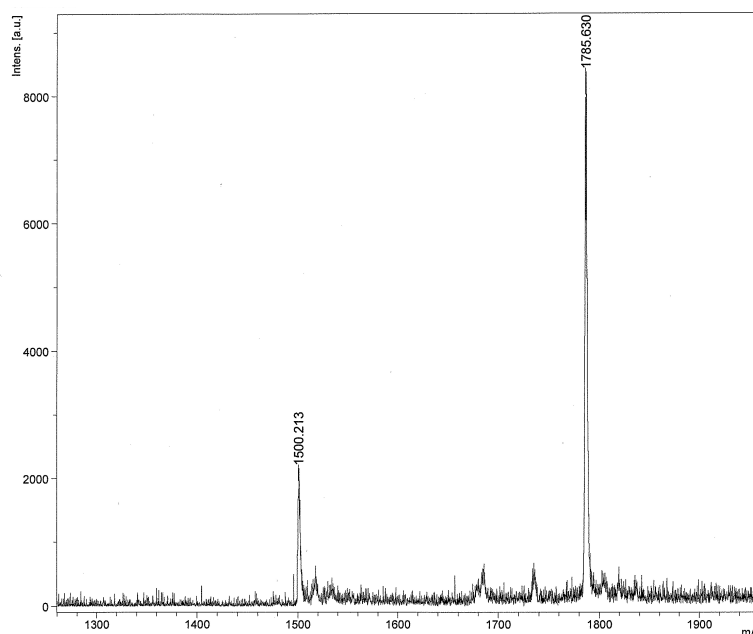


Figure S26. MALDI-TOF MS of compound **4b** (Matrix 9-nitroanthracene).

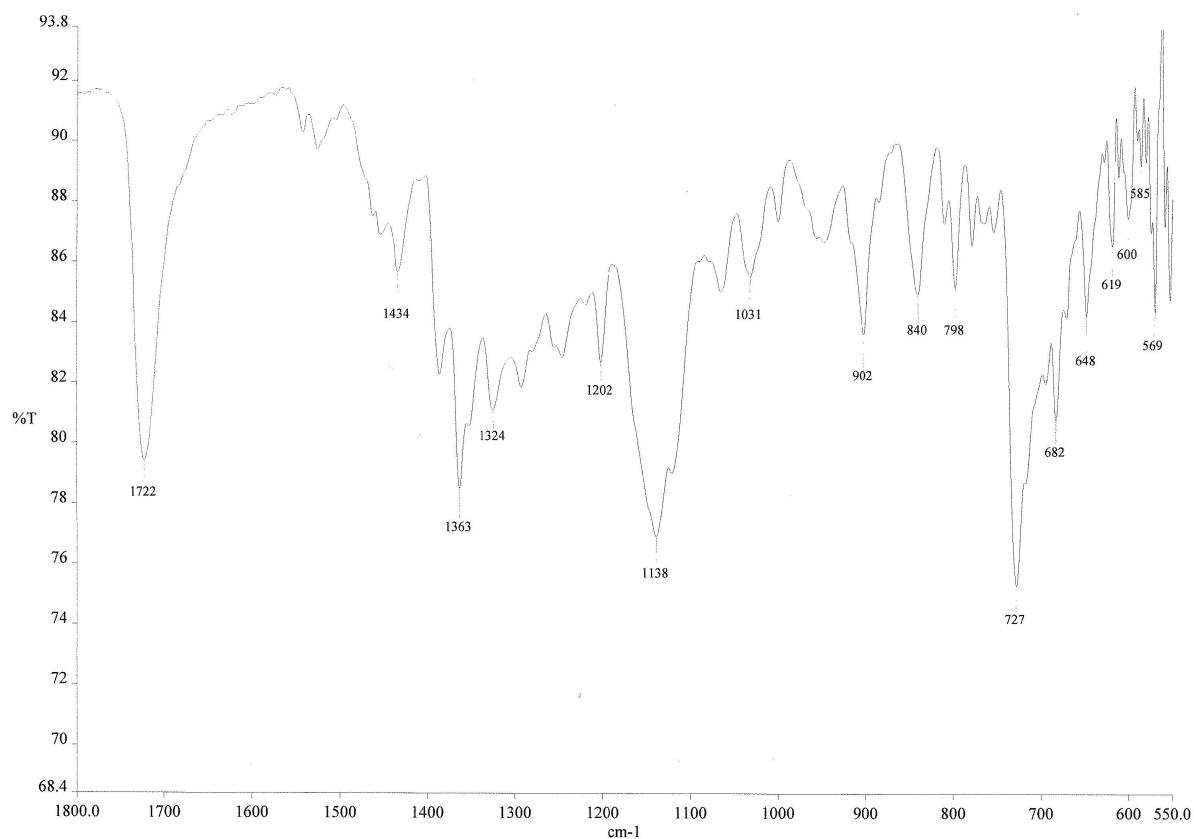


Figure S27. FT-IR of compound **4b**.

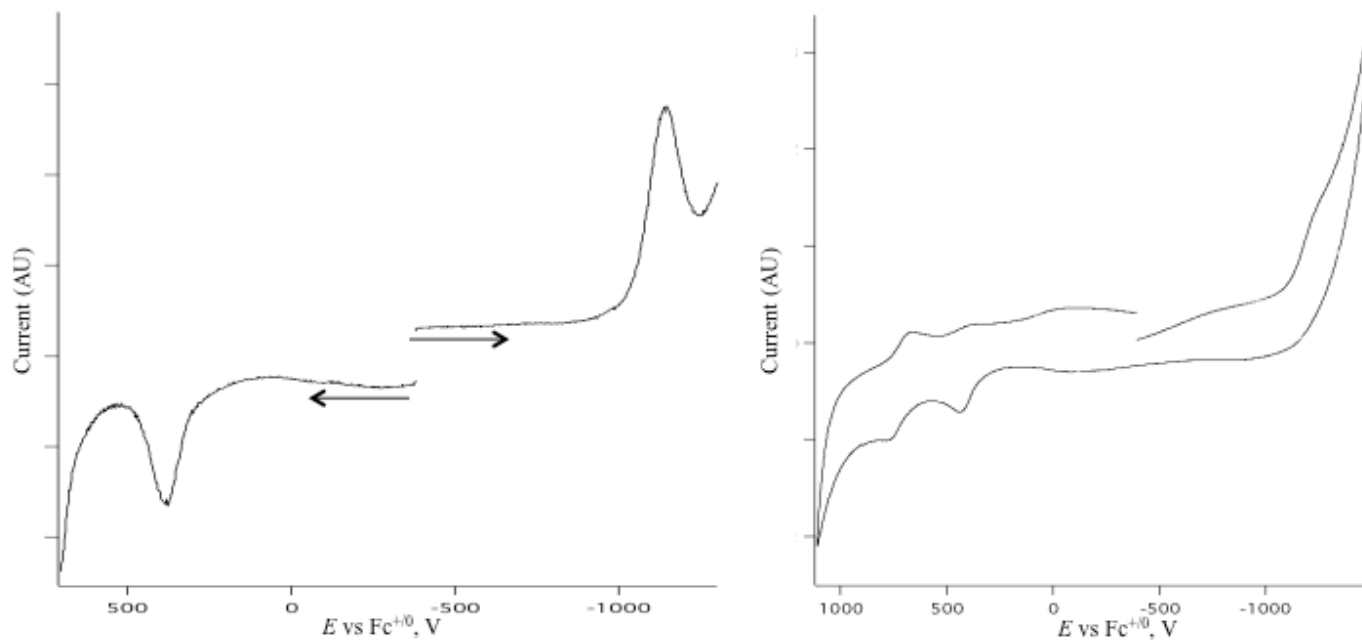


Figure S28. DPV of compound **4b** (left image); CV of compound **4b** (right image).

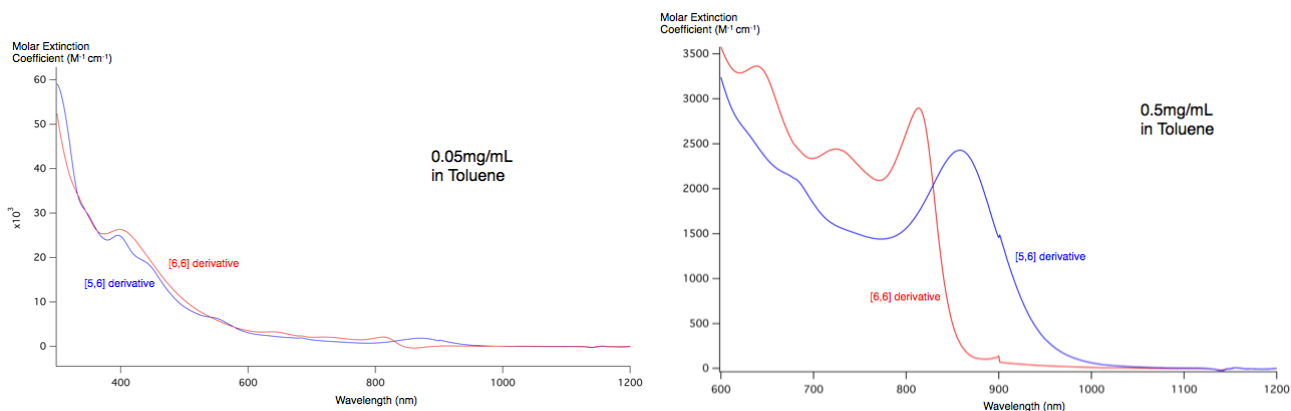
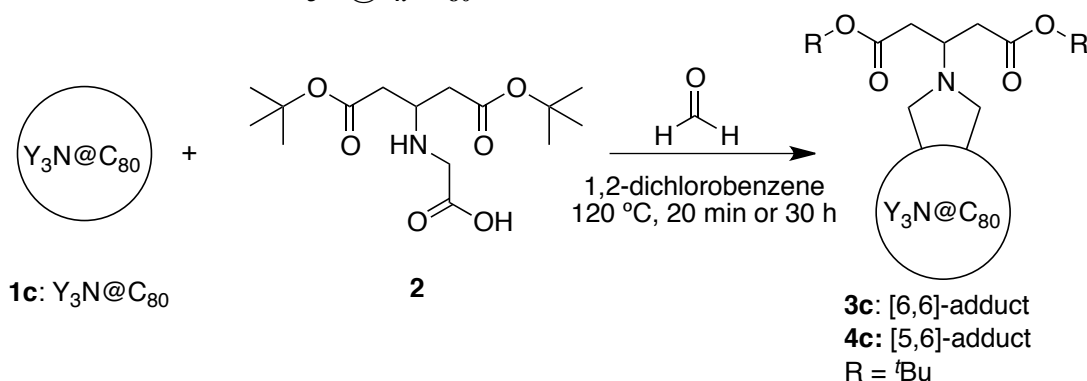


Figure S29. UV-Vis spectra of [6,6]- and [5,6]-fulleropyrrolidine $\text{Lu}_3\text{N}@\text{C}_{80}$ **3b** and **4b** in toluene.

Prato reaction of $\text{Y}_3\text{N}@\text{I}_h\text{-C}_{80}$



3c ([6,6]-adduct of $\text{Y}_3\text{N}@\text{I}_h\text{-C}_{80}$). $\text{Y}_3\text{N}@\text{I}_h\text{-C}_{80}$ (**1c**, 4.2 mg, 3.38 μmol , 1 eq.), **2** (9.2 mg, 29.0 μmol , 8.6 eq.), paraformaldehyde (4.6 mg, 153 μmol , 45 eq.) were mixed in *o*-DCB (22 mL) and were treated under sonication for 10 min. The nitrogen gas was bubbled through the mixed solution for 10 min to remove oxygen. The reaction was carried out at 120°C for 20 min. After cooling to the room temperature, the mixture was purified by column chromatography (SiO_2 45 g, \varnothing 2.3 x 7 cm) using toluene as an eluent. After the starting material ($\text{Y}_3\text{N}@\text{I}_h\text{-C}_{80}$) was eluted, the fraction of monoadduct was concentrated to dryness, and then dissolved in 4 mL of toluene and further purified by a semi-preparative HPLC (Buckyprep, Nakalai Tesque, \varnothing 10 x 250 mm, toluene, 5 mL/min, detection wavelength: 390 nm). The solvent was removed and dried for 24 h under vacuum to provide **3c** (1.9 mg, 1.24 μmol , isolated yield 37%). **3c:** IR (Neat) $\nu_{\text{max}}(\text{cm}^{-1})$: 1718 (s), 1520 (w), 1450 (m), 1363 (s), 1292 (m), 1249 (m), 1205(m), 1137 (s), 1029 (m), 949 (m), 901 (m), 840 (m), 787 (w), 726 (m), 693 (s), 648 (w); ^1H -NMR (400 MHz, $\text{CS}_2\text{-CDCl}_3$ (99.98%) 1:2) 1.51 (s, $\text{C}(\text{CH}_3)_3$, 18H), 2.62 (dd, $J = 6.75$ Hz, $J = 15$ Hz, $\text{CH-CHH-CO}_2^t\text{Bu}$, 2H), 2.74 (dd, $J = 6.75$ Hz, $J = 15$ Hz, $\text{CH-CHH-CO}_2^t\text{Bu}$, 2H), 3.96 (s, $\text{C-CH}_2^1\text{-N}$, 2H), 3.96 (m, $J = 6.75$ Hz, $(\text{CH}_2)_2\text{-CH-N}$, 1H), 4.09 (s, $\text{C-CH}_2^2\text{-N}$, 2H). ^{13}C (150 MHz, $\text{CS}_2\text{-CDCl}_3$ 1:2) 28.22 (s, $\text{C}(\text{CH}_3)_3$, 38.14 ($\text{CH-CH}_2\text{-CO}_2^t\text{Bu}$), 53.95 ($(\text{CH}_2)_2\text{-CH-N}$), 58.66 ($\text{C-CH}_2\text{-N}$), 64.60 ($\text{C-CH}_2\text{-N}$), 81.08 ($\text{C}(\text{CH}_3)_3$), 170.51 ($\text{CH}_2\text{-CO}_2^t\text{Bu}$), fullerene core: 57.67 ($\text{C-CH}_2\text{-N}$), 67.96 ($\text{C-CH}_2\text{-N}$), 115.23 (2C, adjacent to sp^3), 128.46 (1C), 132.47 (2C), 135.02 (1C), 136.05 (2C), 136.41 (2C), 136.62 (2C), 137.87 (2C), 137.99 (2C), 138.00 (2C), 138.82 (1C), 138.95 (2C, adjacent to sp^3), 139.08 (2C), 139.45 (2C), 139.83 (2C), 140.18 (2C), 140.60 (2 + 2 C overlap), 140.84 (2 + 1 C overlap), 141.04 (2C), 141.14 (2C), 141.36 (2C), 142.08 (2C), 142.15 (2C), 142.46 (1C), 142.52 (1C), 142.86 (2C), 143.08 (2C), 143.17 (2C), 143.26 (2C), 143.97 (2C), 145.64 (2C), 145.72 (2C), 146.83 (2C), 147.92 (2C), 148.14 (2C), 148.35 (2C), 148.61 (2C), 149.02 (2C), 149.18 (2C), 150.26 (2C); MS (MALDI⁺, matrix: 9-nitroanthracene) m/z : 1242 ($\text{Y}_3\text{N}@\text{C}_{80} + \text{H}$)⁺, 1527 ($[\text{M} + \text{H}]^+$).

4c ([5,6]-adduct of $Y_3N@I_h-C_{80}$). $Y_3N@I_h-C_{80}$ (**1c**, 4.2 mg, 3.38 μ mol, 1 eq.), **2** (9.2 mg, 29.0 μ mol, 8.6 eq.), paraformaldehyde (4.6 mg, 153 μ mol, 45 eq.) were mixed in *o*-DCB (22 mL) and were treated under sonication for 10 min. The nitrogen gas was bubbled through the mixed solution for 10 min to remove oxygen. The reaction was carried out at 120°C for 30 hours and was monitored by HPLC analysis (Buckyprep, Nakalai Tesque, \varnothing 4.6 x 250 mm, toluene, 1mL/mL, 390 nm, Figure S22). After cooling to the room temperature, the mixture was purified by column chromatography (SiO_2 45 g, \varnothing 2.3 x 7 cm) using toluene as an eluent. After the starting material ($Y_3N@I_h-C_{80}$) was eluted, the fraction of monoadduct was concentrated to dryness, and then dissolved in 4 mL of toluene and further purified by a semi-preparative HPLC (Buckyprep, Nakalai Tesque, \varnothing 10 x 250 mm, toluene, 5 mL/min, detection wavelength: 390 nm). The solvent was removed and dried for 24 h under vacuum to provide **4c** (1.3 mg, 0.85 μ mol, isolated yield 25%). **4c**: IR (Neat) $\nu_{max}(cm^{-1})$: 1722 (s), 1454 (w), 1428 (m), 1386 (m), 1364 (m), 1310 (m), 1199 (m), 1139 (s), 1031 (m), 953 (m), 840 (m), 800 (m), 701 (s), 650 (w), 621 (w). 1H -NMR (400 MHz, CS_2 - $CDCl_3$ (99.98%) 1:2) 1.56 (s, $C(CH_3)_3$, 18H), 2.60 (dd, $J = 6.75$ Hz, $J = 15$ Hz, $CH-CHH-CO_2^tBu$, 2H), 2.73 (dd, $J = 6.75$ Hz, $J = 15$ Hz, $CH-CHH-CO_2^tBu$, 2H), 3.01 (d, $J = 9.0$ Hz, $C-CHH-N$, 2H), 3.94 (m, $J = 6.75$ Hz, $(CH_2)_2-CH-N$, 1H), 4.01 (d, $J = 9.0$ Hz, $C-CHH-N$, 2H). ^{13}C (150 MHz, CS_2 - $CDCl_3$ 1:2) 28.28 (s, $C(CH_3)_3$, 37.98 ($CH-CH_2-CO_2^tBu$), 54.24 ($(CH_2)_2-CH-N$), 65.08 ($C-CH_2-N$), 80.99 ($C(CH_3)_3$), 170.51 ($CH_2-CO_2^tBu$), fullerene core: 59.30 ($C-CH_2-N$), 110.58 (2C, adjacent to sp^3), 114.35 (2C, adjacent to sp^3), 131.86 (1C), 133.14 (2C), 135.44 (2C), 135.75 (2C), 136.22 (2C), 136.70 (1C), 137.16 (2C), 138.16 (2C), 138.19 (2C), 138.33 (2C), 138.35 (2C), 138.38 (2C), 139.00 (2C), 139.34 (2C), 139.44 (2C), 139.56 (2C), 140.12 (1C), 140.55 (2 + 2 C overlap), 140.85 (2C), 141.29 (2C), 141.37 (2C), 141.60 (2C), 143.39 (2C), 144.14 (2C), 144.18 (2C), 144.65 (2C), 145.33 (2C), 146.08 (2C), 146.29 (2C), 146.45 (2C), 147.43 (1C), 147.49 (1C), 147.51 (2C), 147.68 (2C), 148.01 (2C), 152.34 (2C), 152.82 (1C), 155.03 (1C), 156.20 (1C), 156.96 (2C); MS (MALDI+, matrix: 9-nitroanthracene) m/z : 1242 ($Y_3N@C_{80} + H^+$), 1527 ($[M + H]^+$).

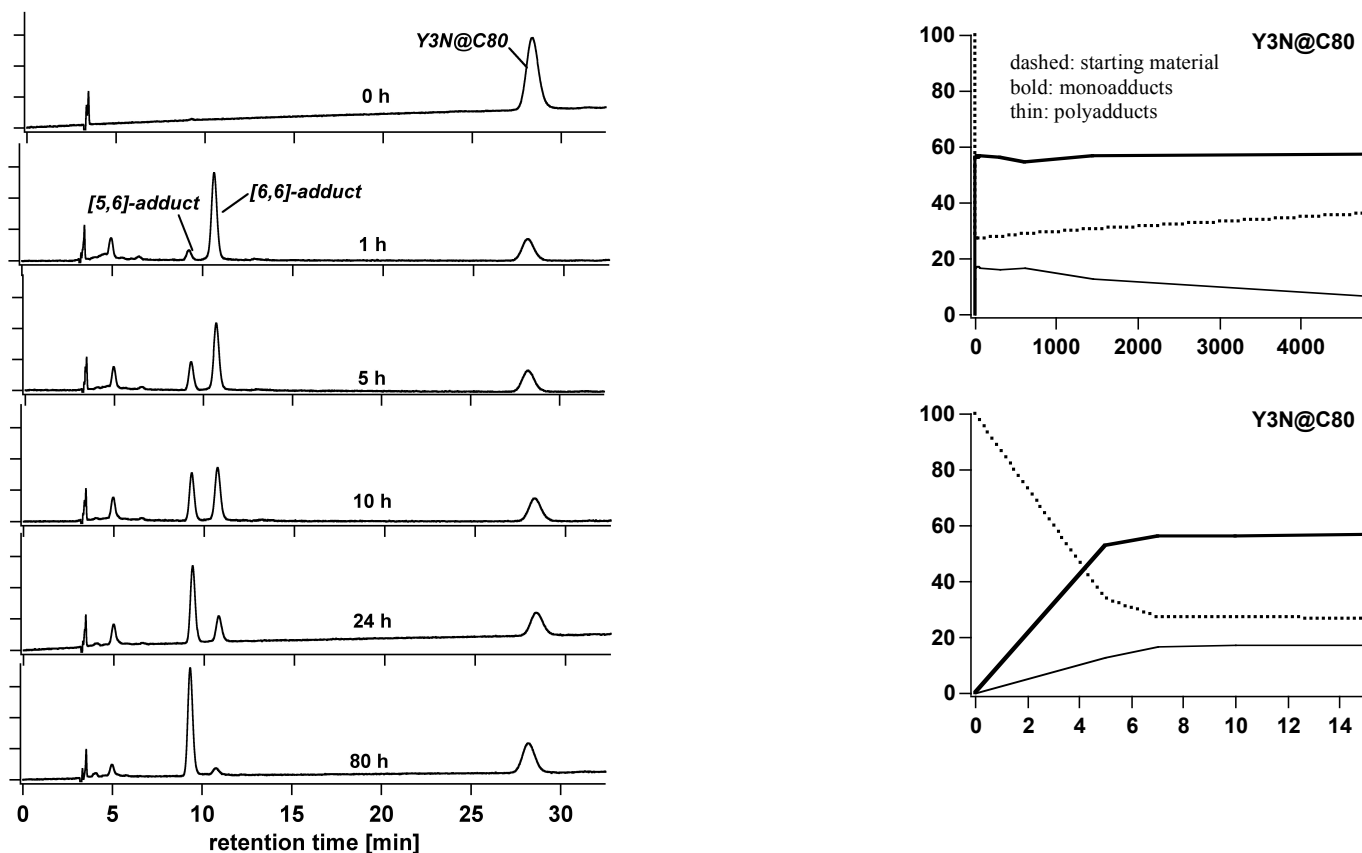


Figure S30. Reaction monitor by HPLC analysis.

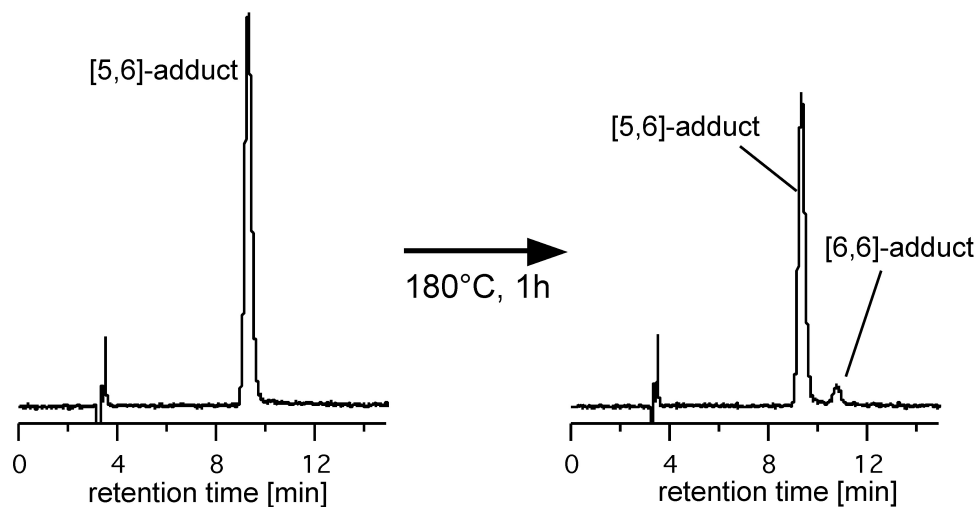


Figure S31. Partial isomerization of **4c** to **3c** upon heating at 180°C for 1h (Buckyprep, toluene, 1 mL/min).

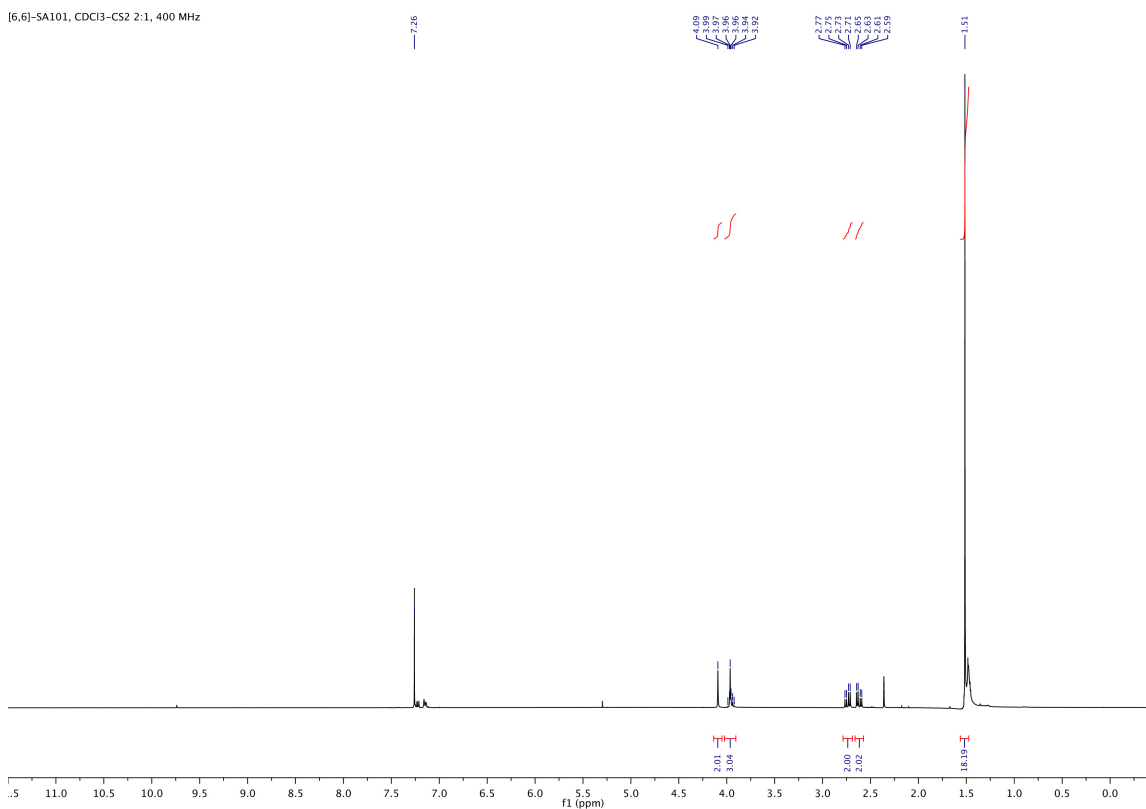


Figure S32. ^1H -NMR spectra of [6,6]-adduct of $\text{Y}_3\text{N}@C_{80}$ (**3c**) (in $\text{CHCl}_3\text{-CS}_2$ (2:1), 400 MHz)

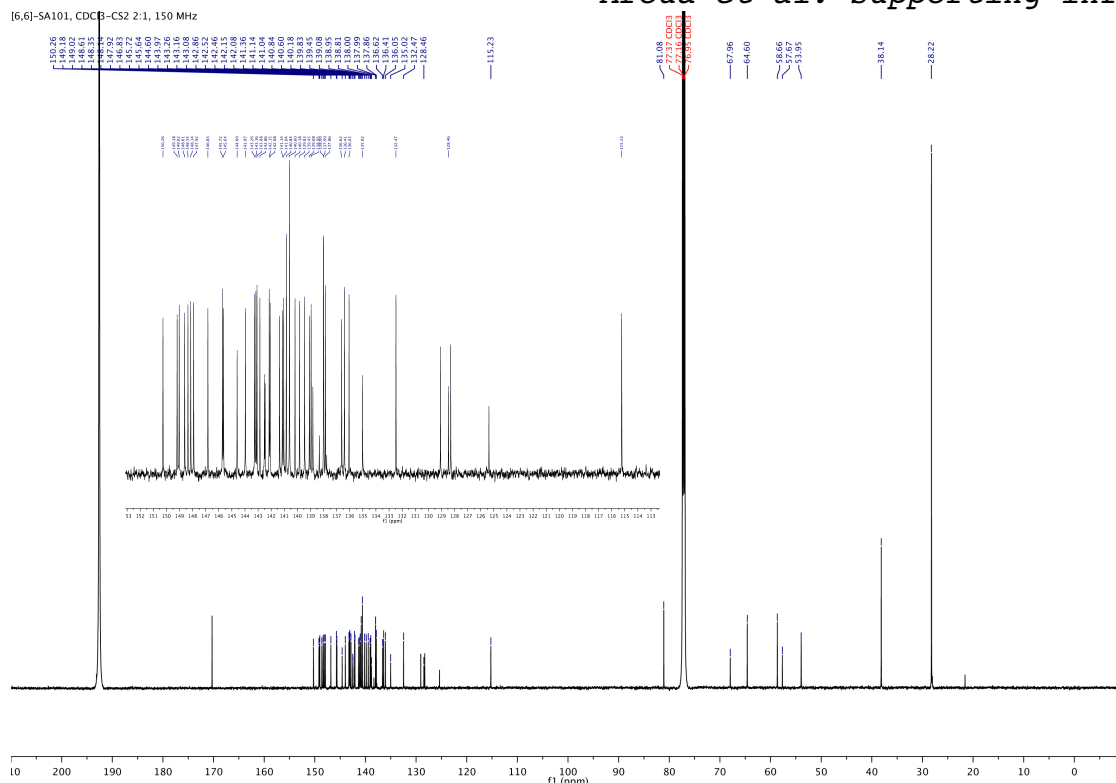


Figure S33. ^{13}C -NMR spectra of [6,6]-adduct of $\text{Y}_3\text{N}@\text{C}_{80}$ (**3c**) (in $\text{CHCl}_3\text{-CS}_2$ (2:1), 150 MHz, contains traces of toluene)

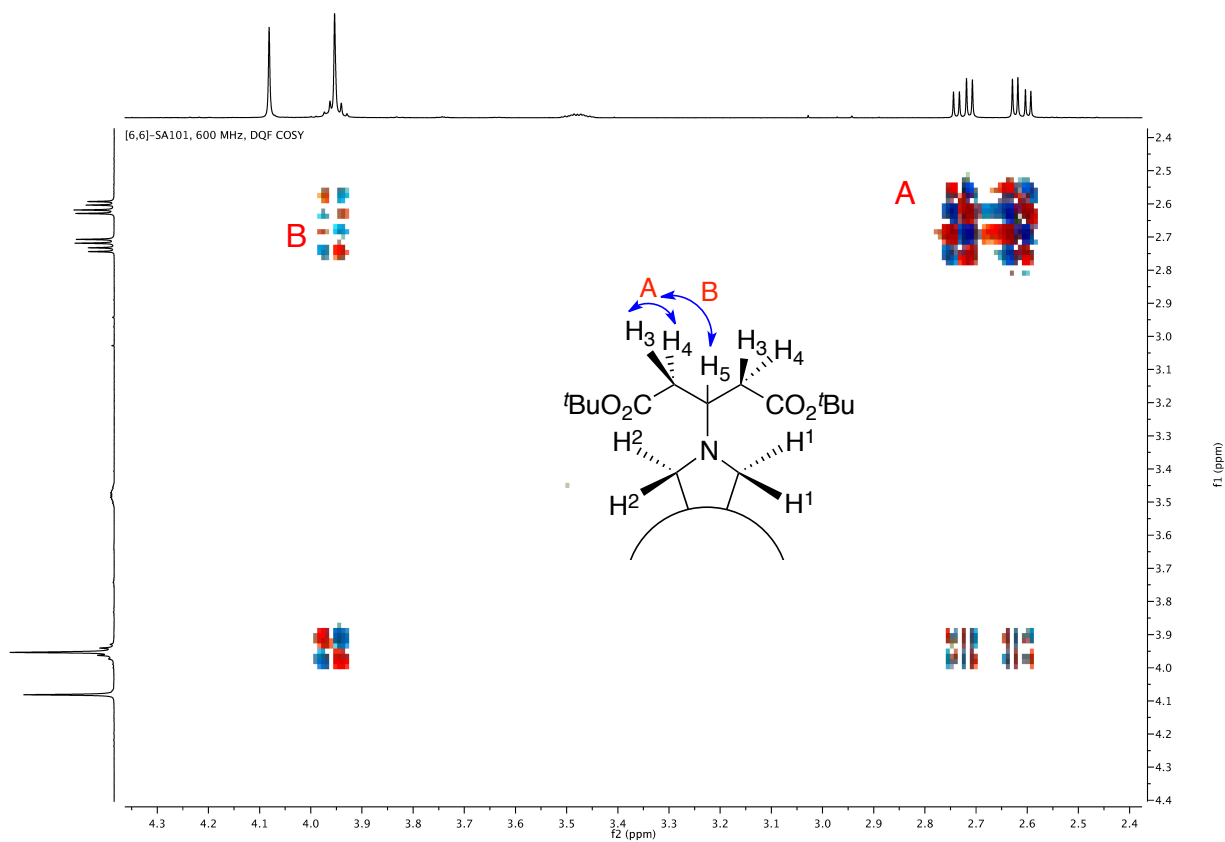


Figure S34. DQF COSY-NMR spectra of [6,6]-adduct of $\text{Y}_3\text{N}@\text{C}_{80}$ (**3c**) (in $\text{CHCl}_3\text{-CS}_2$ (2:1), 600 MHz).

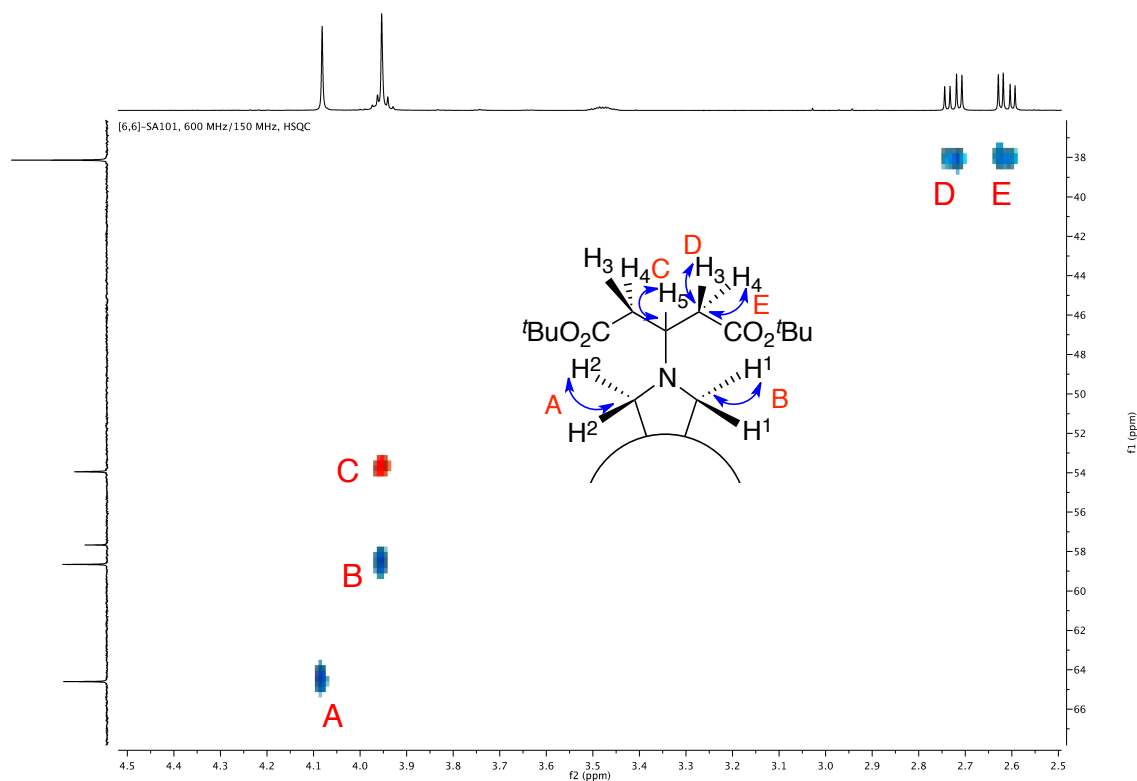


Figure S35. HSQC-NMR spectra of [6,6]-adduct of $Y_3N@C_{80}$ (**3c**) (in $CHCl_3$ - CS_2 (2:1), 600 MHz/150 MHz).

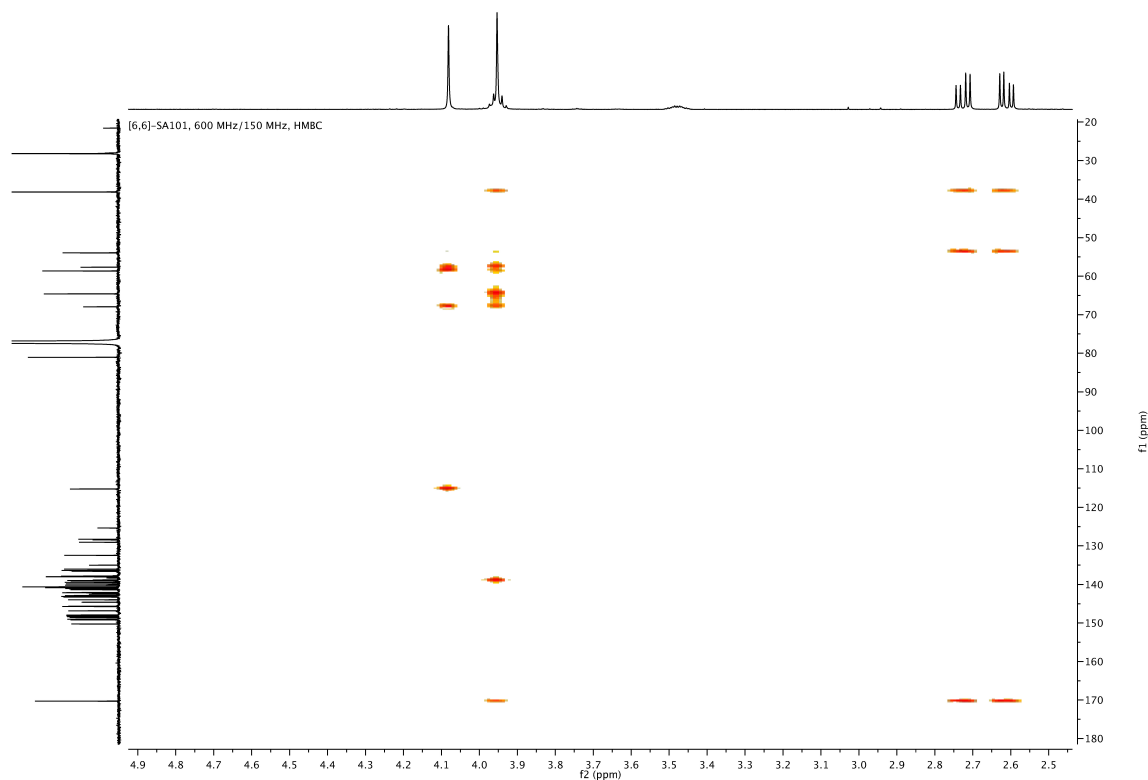


Figure S36. HMBC-NMR spectra of [6,6]-adduct of $Y_3N@C_{80}$ (**3c**) (in $CHCl_3$ - CS_2 (2:1), 600 MHz/150 MHz).

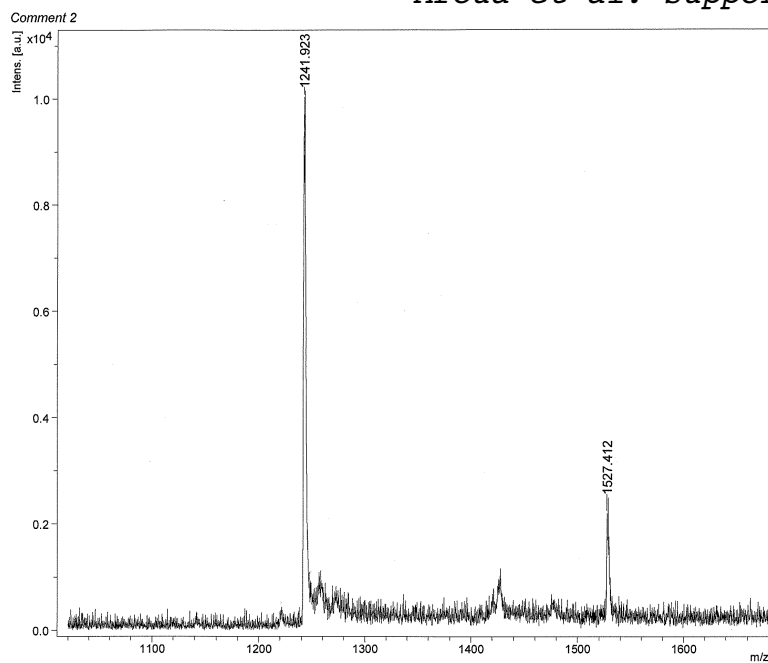


Figure S37. MALDI-TOF MS of compound **3c** (Matrix 9-nitroanthracene).

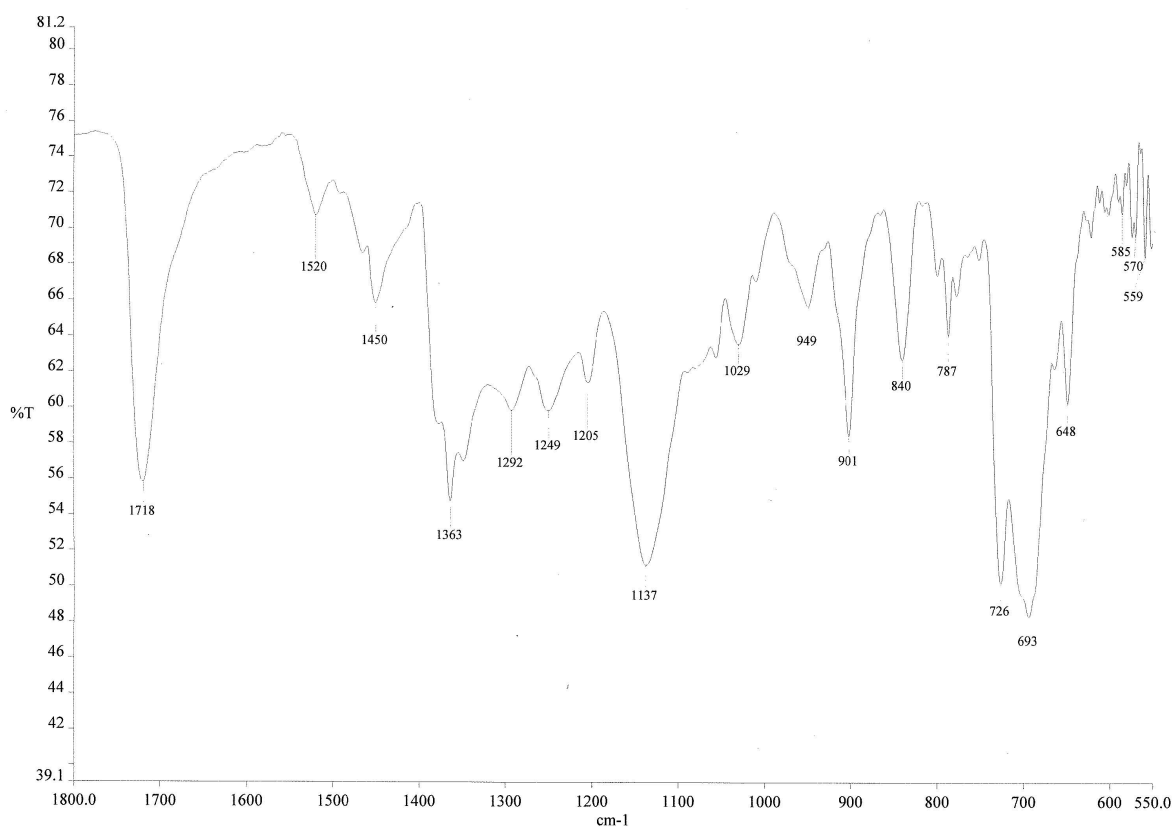


Figure S38. FT-IR of compound **3c**.

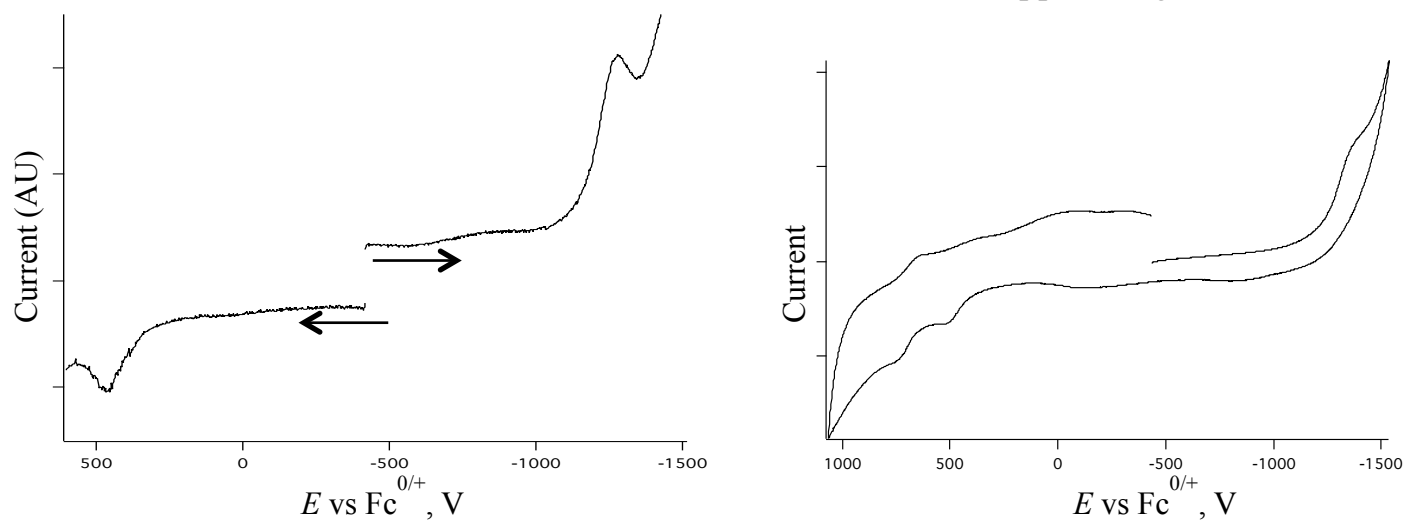


Figure S39. DPV of compound **3c** (left image); CV of compound **3c** (right image).

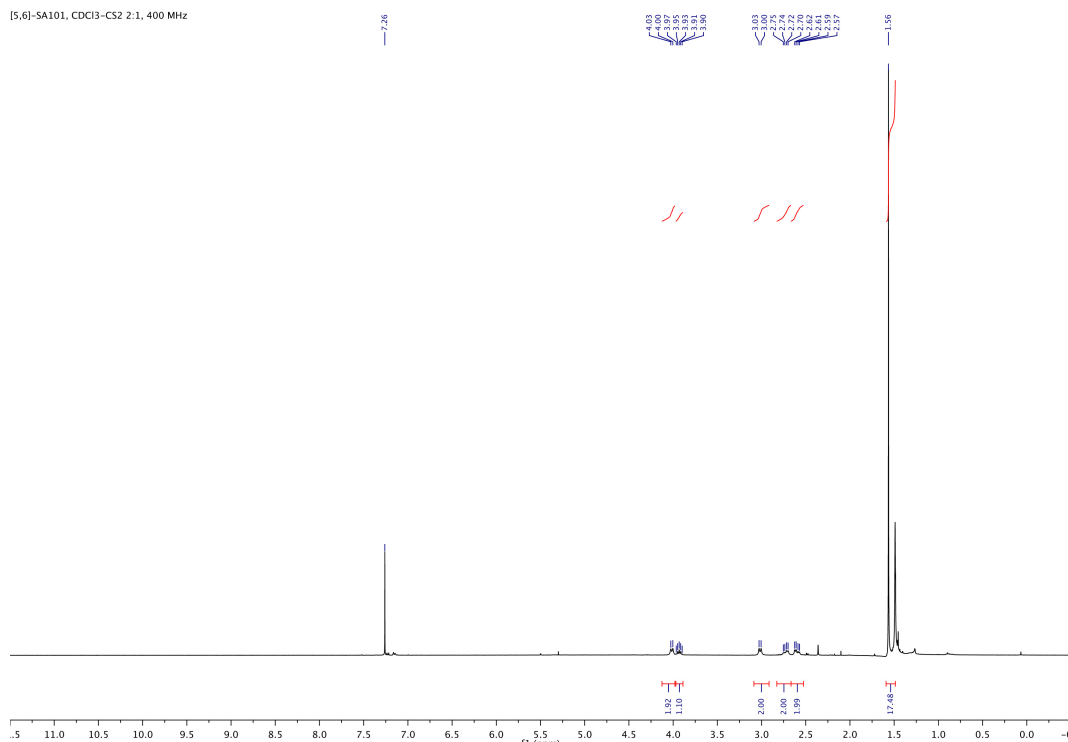


Figure S40. 1H -NMR spectra of [5,6]-adduct of $Y_3N@C_{80}$ (**4c**) (in $CHCl_3$ - CS_2 (2:1), 400 MHz)

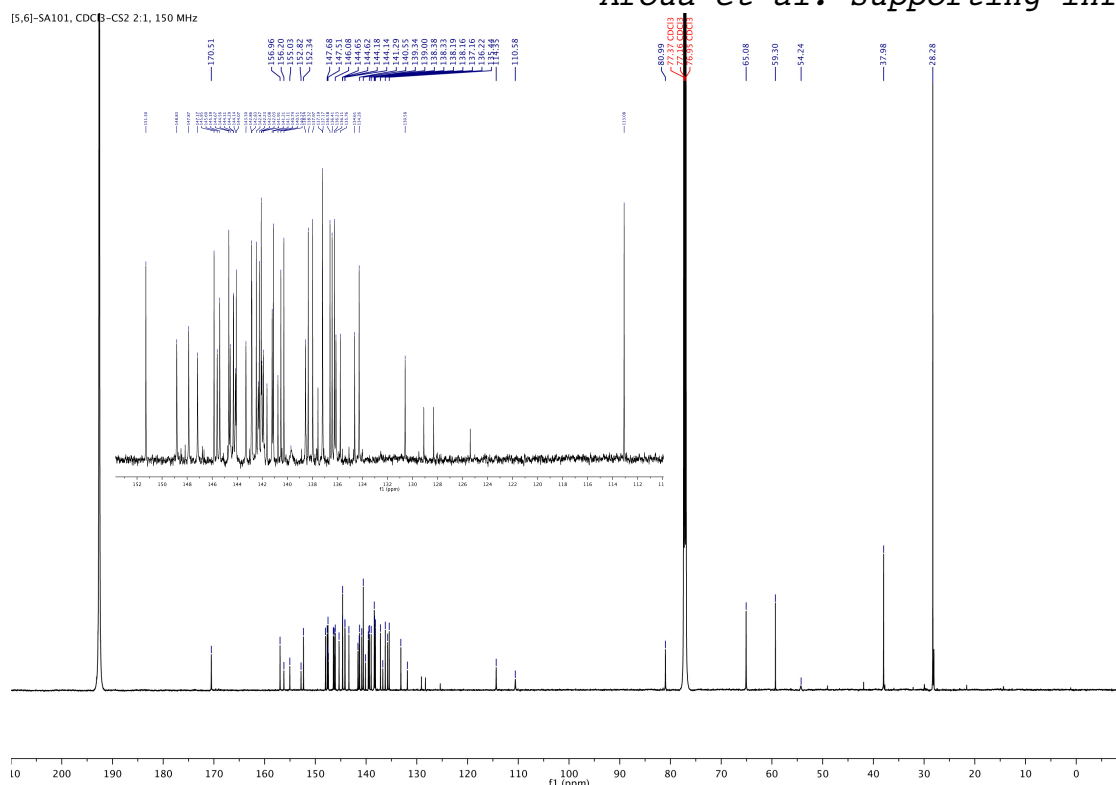


Figure S41. ¹³C-NMR spectra of [5,6]-adduct of Y₃N@C₈₀ (**4c**) (in CHCl₃-CS₂ (2:1), 150 MHz, contains traces of toluene)

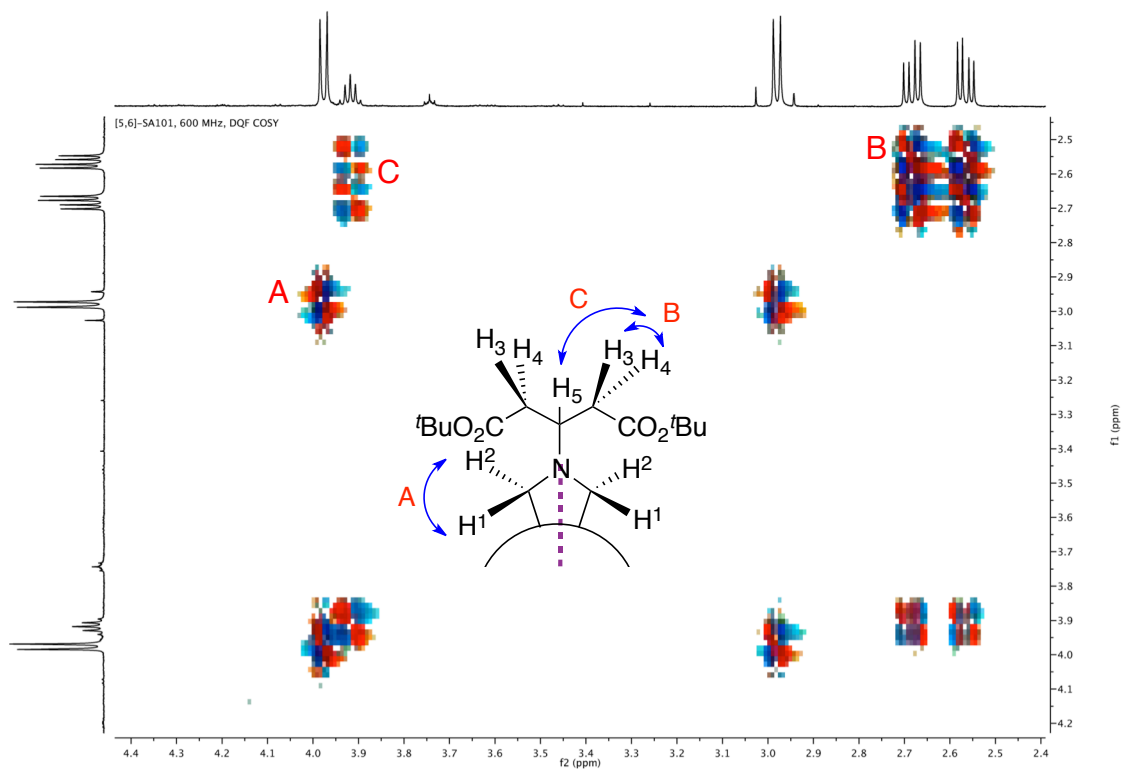


Figure S42. DQF COSY-NMR spectra of [5,6]-adduct of Y₃N@C₈₀ (**4c**) (in CHCl₃-CS₂ (2:1), 600 MHz).

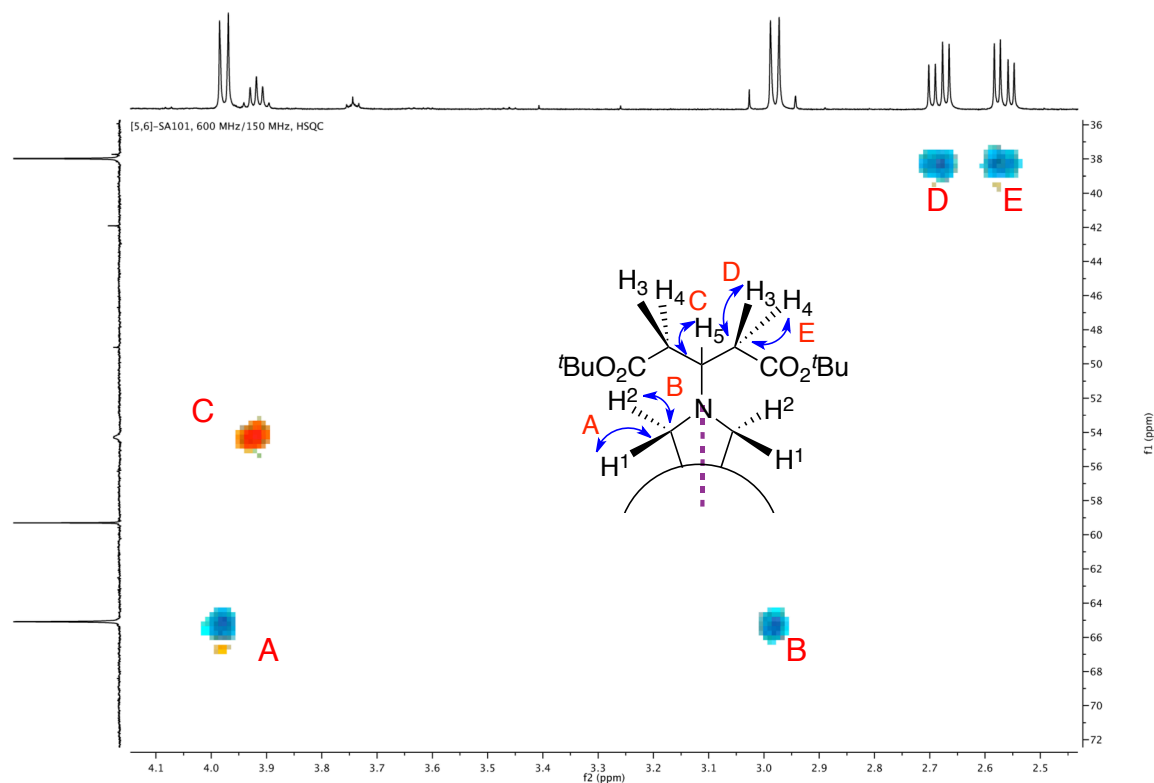


Figure S43. HSQC-NMR spectra of [5,6]-adduct of $Y_3N@C_{80}$ (**4c**) (in $CHCl_3$ - CS_2 (2:1), 600 MHz/150 MHz).

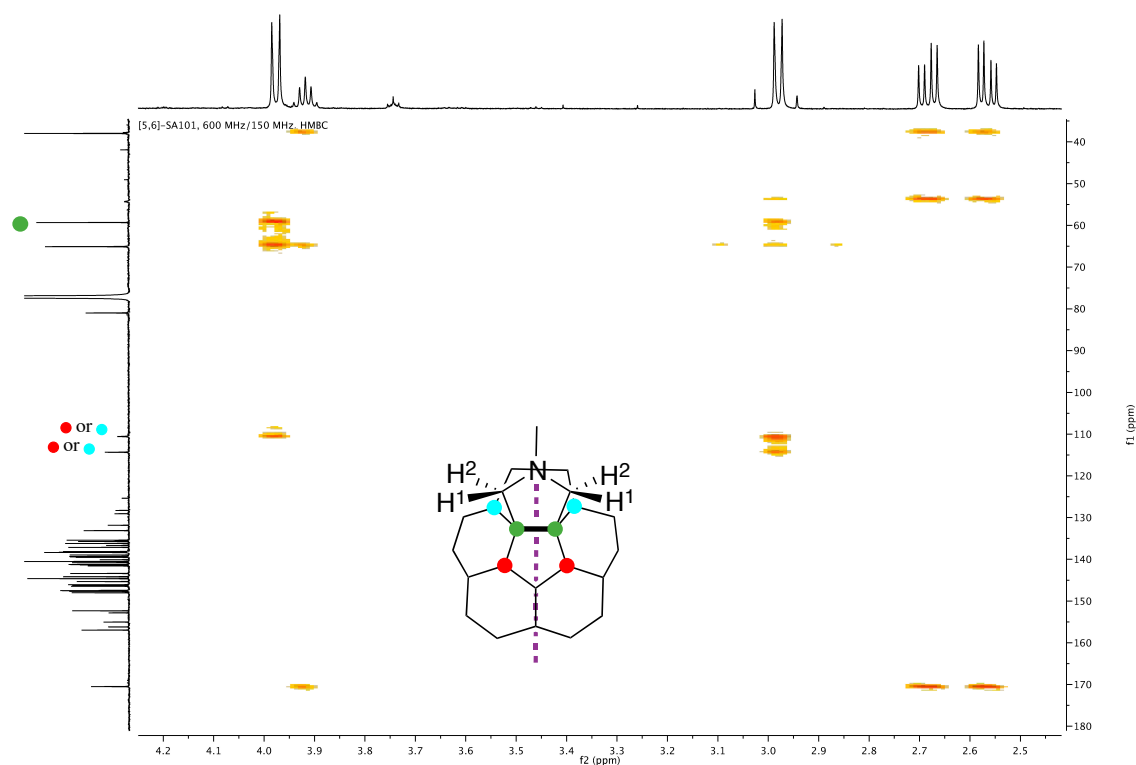


Figure S44. HMBC-NMR spectra of [5,6]-adduct of $Y_3N@C_{80}$ (**4c**) (in $CHCl_3$ - CS_2 (2:1), 600 MHz/150 MHz).

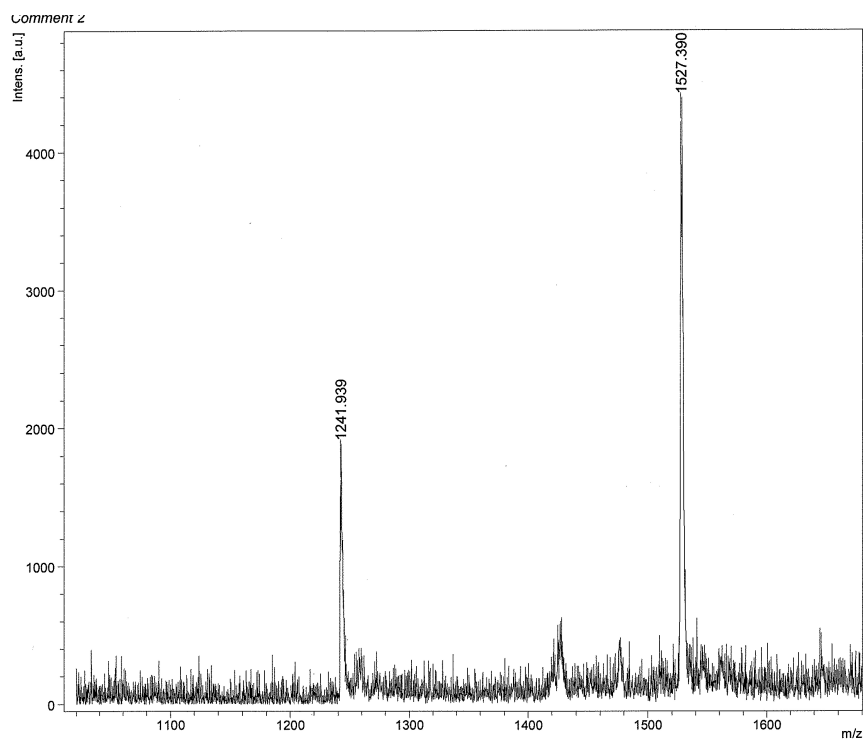


Figure S45. MALDI-TOF MS of compound **4c** (Matrix 9-nitroanthracene).

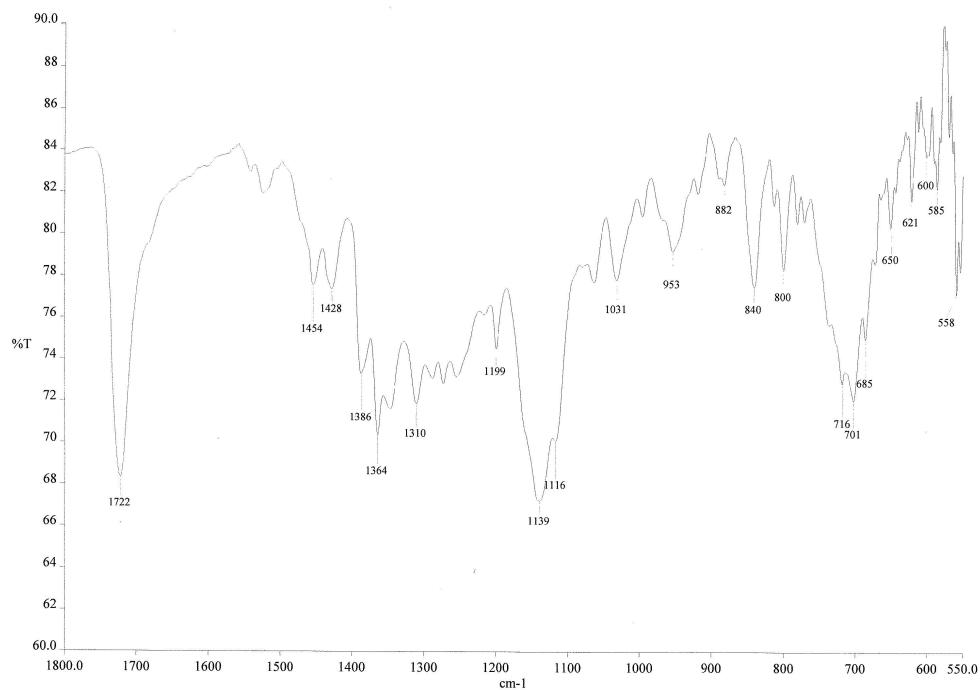


Figure S46. FT-IR of compound **4c**.

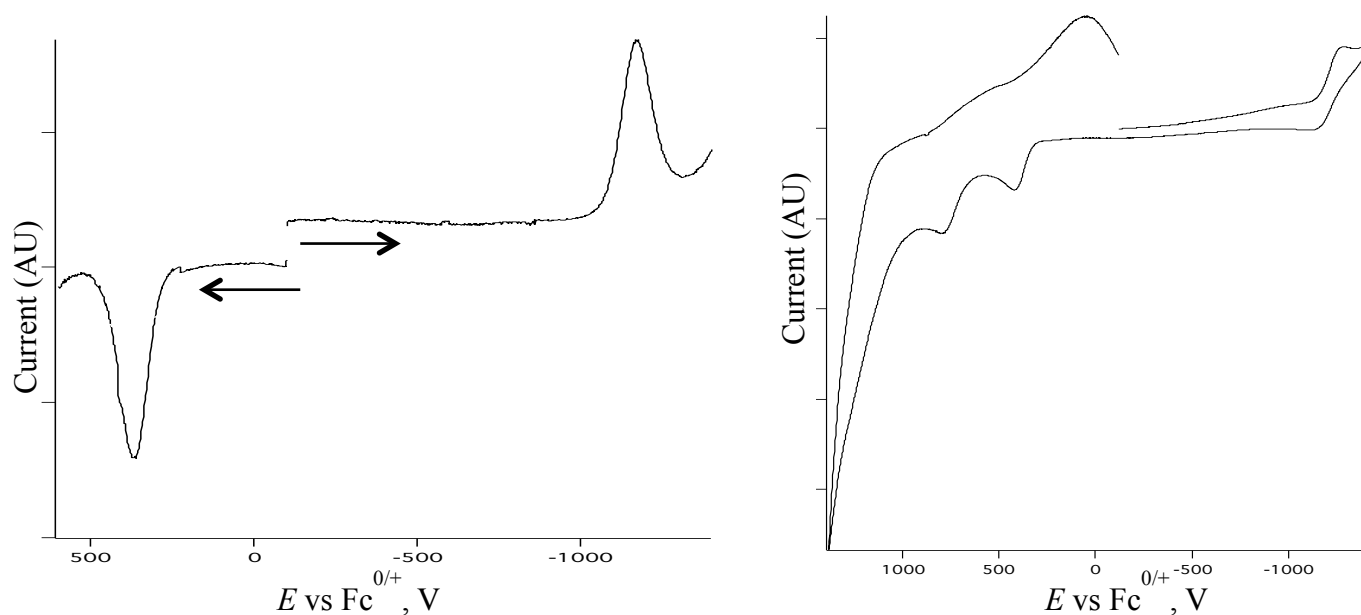


Figure S47. DPV of compound **4c** (left image); CV of compound **4c** (right image).

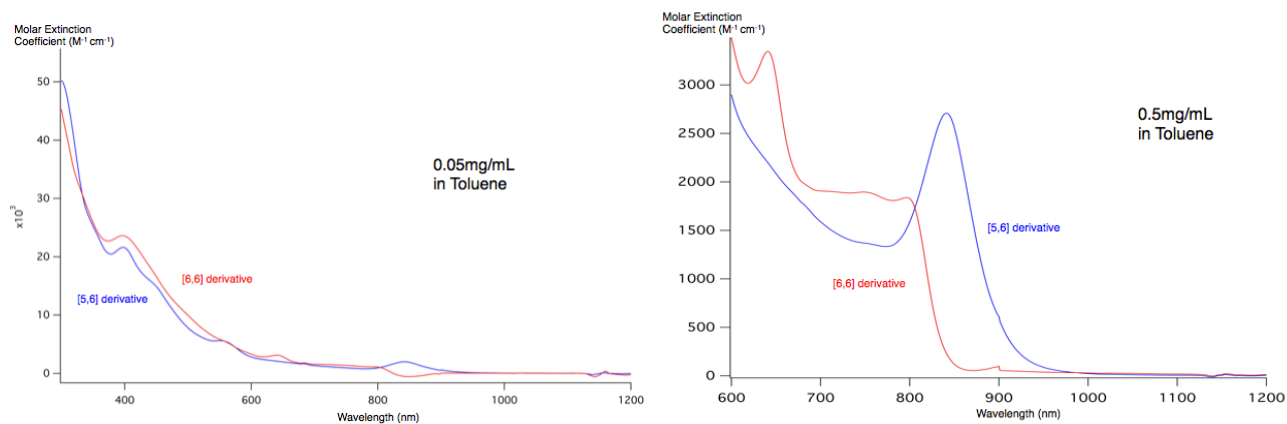
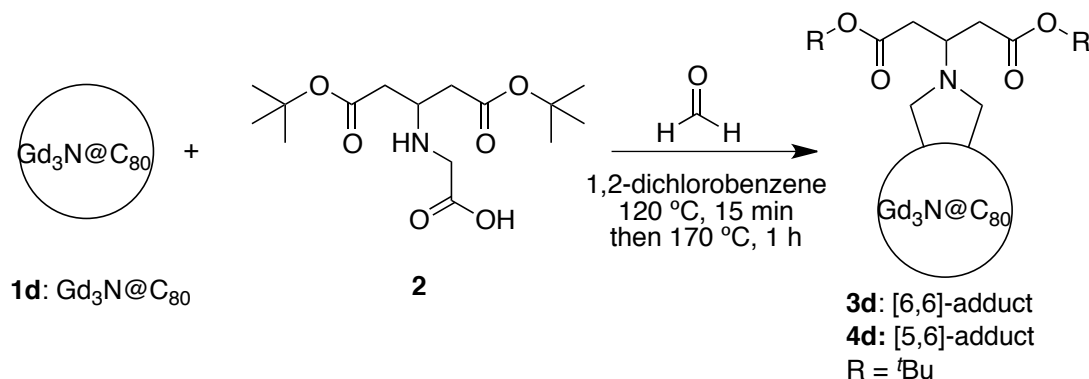


Figure S48. UV-Vis spectra of [6,6]- and [5,6]-fulleropyrrolidine $\text{Y}_3\text{N}@C_{80}$ **3c** and **4c** in toluene.

Prato reaction of $\text{Gd}_3\text{N}@I_h\text{-C}_{80}$ 

3d ([6,6]-adduct of $\text{Gd}_3\text{N}@I_h\text{-C}_{80}$). and **4d ([5,6]-adduct of $\text{Gd}_3\text{N}@I_h\text{-C}_{80}$).** $\text{Gd}_3\text{N}@I_h\text{-C}_{80}$ (**1d**, 17.4 mg, 12.0 μmol , 1 eq.), **2** (32.25 mg, 101.6 μmol , 8.5 eq.), paraformaldehyde (15.7 mg, 523 μmol , 44 eq.) were mixed in *o*-DCB (80 mL) and were treated under sonication for 10 min. The nitrogen gas was bubbled through the mixed solution for 10 min to remove oxygen. The reaction was carried out at 120°C for 15 min then at 170°C for 1 h. After cooling to the room temperature, the mixture was purified by column chromatography (SiO_2 45 g, \varnothing 2.3 x 7 cm) using toluene as an eluent. After the starting material ($\text{Gd}_3\text{N}@I_h\text{-C}_{80}$) was eluted, the fraction of both monoadducts (**3d** and **4d**) was concentrated to dryness, and then dissolved in 4 mL of toluene and further purified by a semi-preparative HPLC (Buckyprep, Nakalai Tesque, \varnothing 10 x 250 mm, toluene, 5 mL/min, detection wavelength: 390 nm). The solvent was removed and dried for 24 h under vacuum to provide **3d** (2.1 mg, 1.21 μmol , isolated yield 10%) and **4d** (2.9 mg, 1.67 μmol , isolated yield 14%); **3d**: IR (Neat) $\nu_{\text{max}}(\text{cm}^{-1})$: 1722 (s), 1450 (m), 1364 (s), 1250 (m), 1137 (s), 841 (m), 728 (m), 677 (s), 664 (s), 570 (w); MS (MALDI+, matrix: 9-nitroanthracene) m/z : 1733 (M^+); **4d**: IR (Neat) $\nu_{\text{max}}(\text{cm}^{-1})$: 1723 (s), 1514 (w), 1453 (m), 1385 (m), 1363 (s), 1137 (s), 1030 (m), 948 (m), 890 (w), 841 (m), 796 (m), 728 (m), 682 (m), 664 (m), 570 (w); MS (MALDI+, matrix: 9-nitroanthracene) m/z : 1734 ($[\text{M}+\text{H}]^+$).

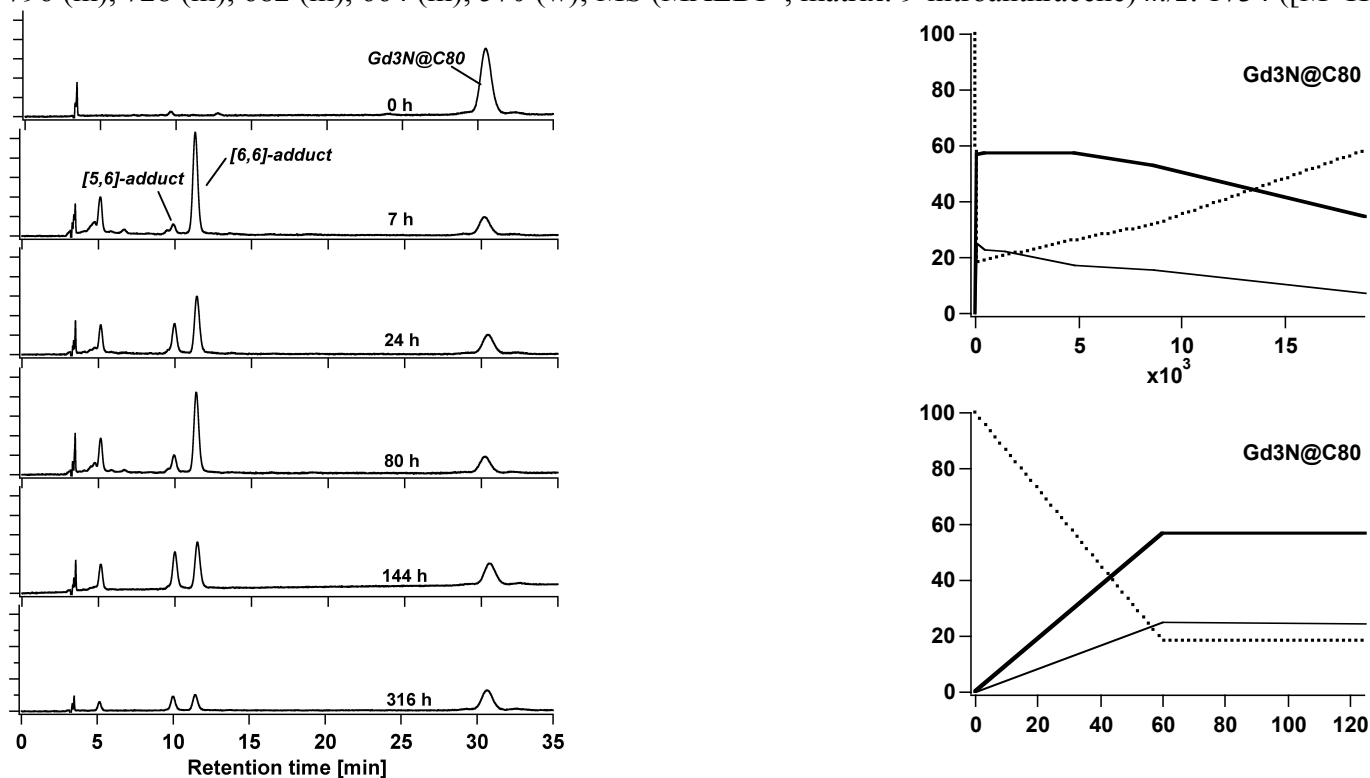


Figure S49. Reaction monitor by HPLC analysis.

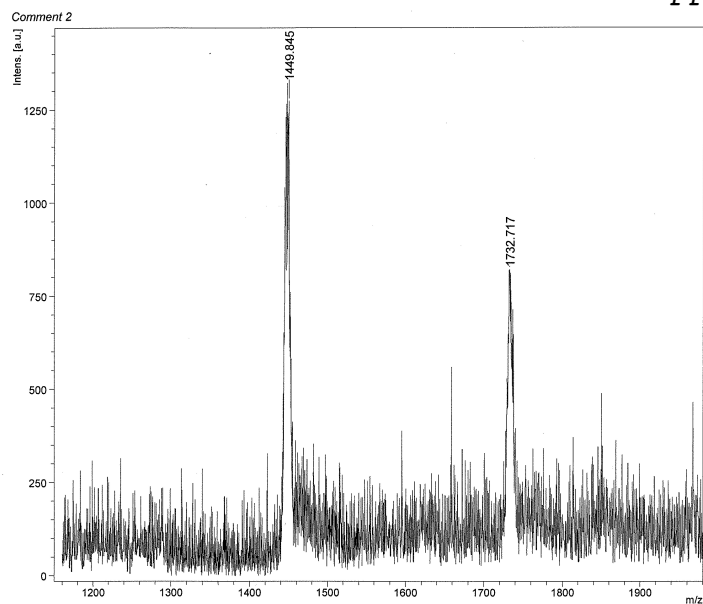


Figure S50. MALDI-TOF MS of compound **3d** (Matrix 9-nitroanthracene).

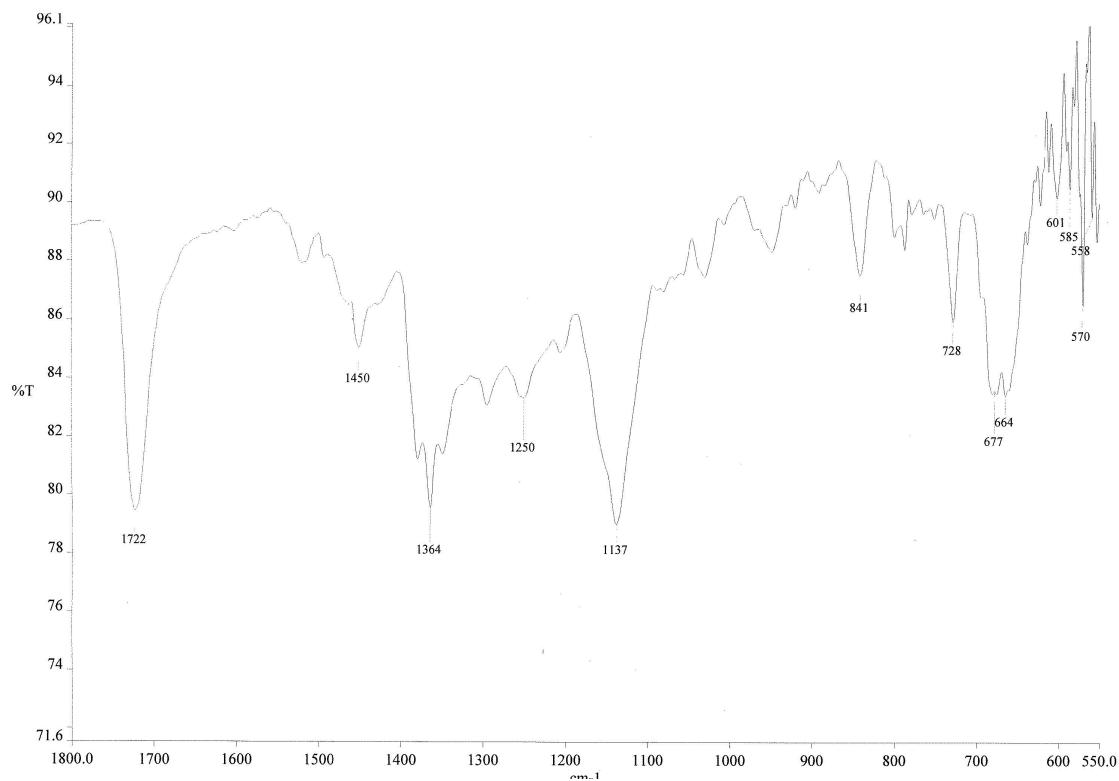


Figure S51. FT-IR of compound **3d**.

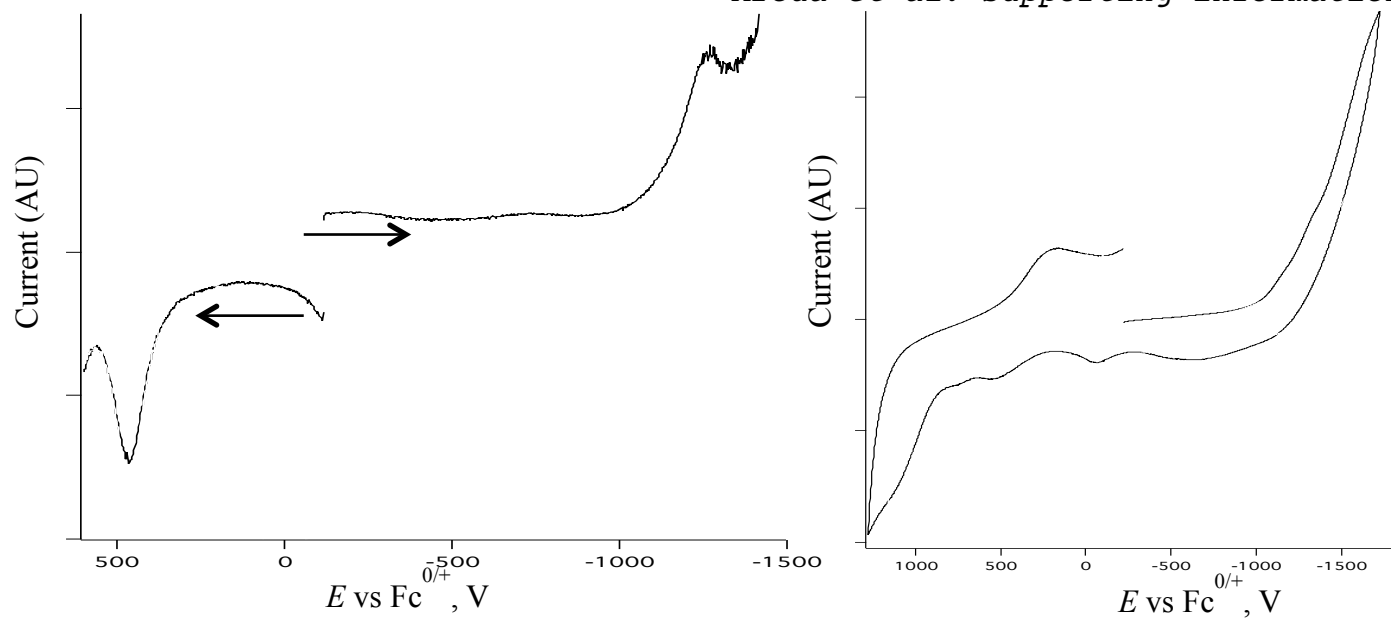


Figure S52. DPV of compound **3d** (left image); CV of compound **3d** (right image).

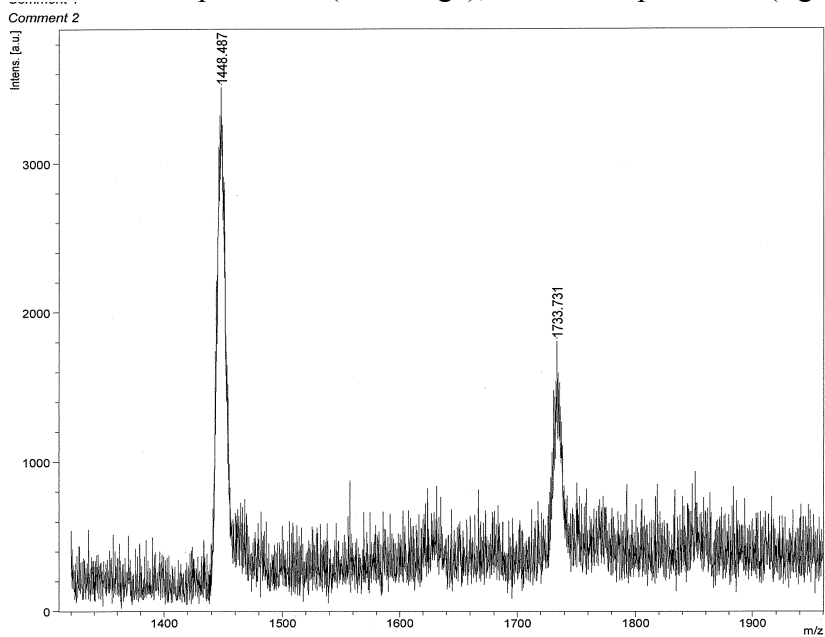


Figure S53. MALDI-TOF MS of compound **4d** (Matrix 9-nitroanthracene).

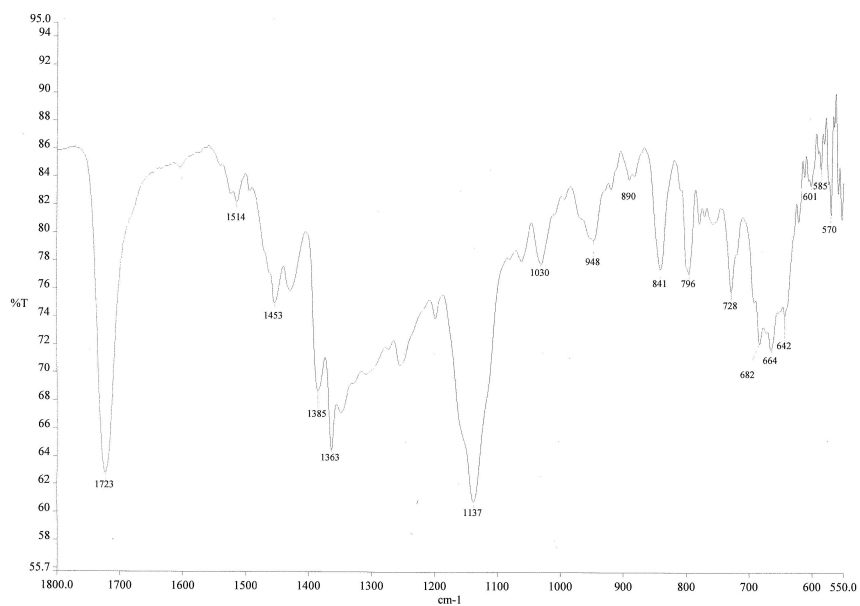


Figure S54. FT-IR of compound **4d**.

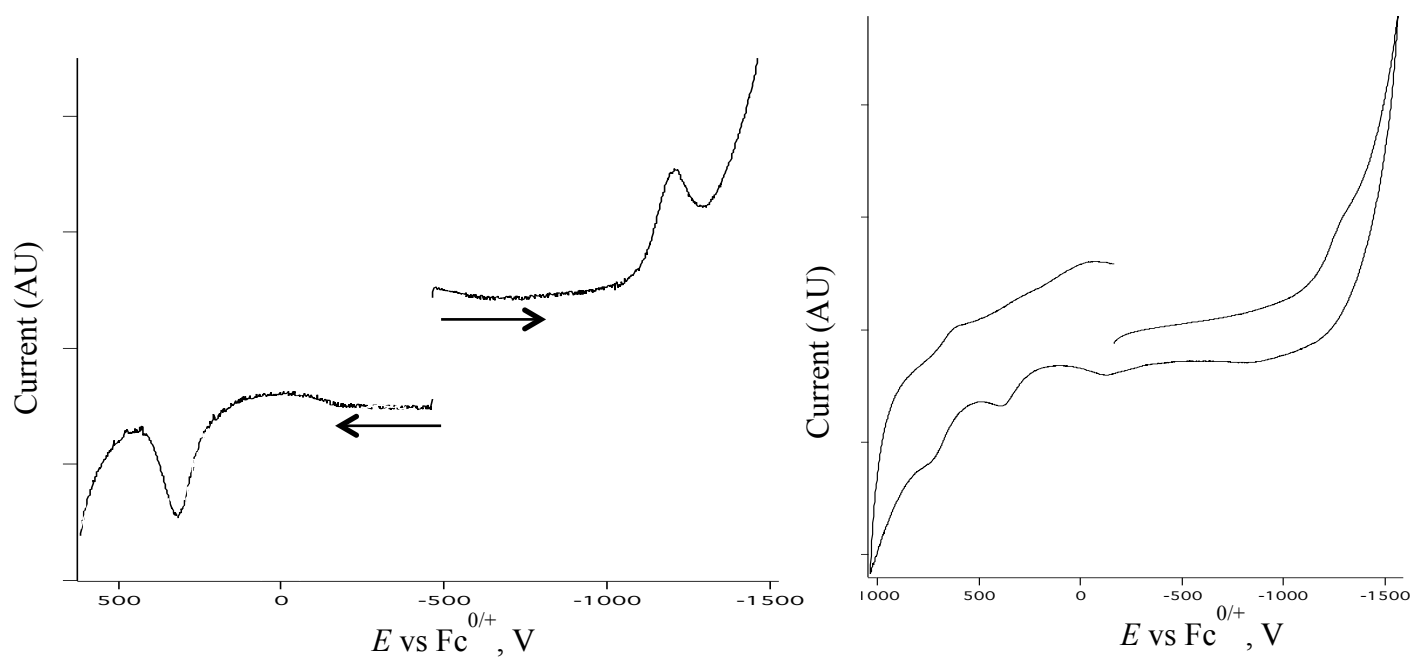


Figure S55. DPV of compound **4d** (left image); CV of compound **4d** (right image).

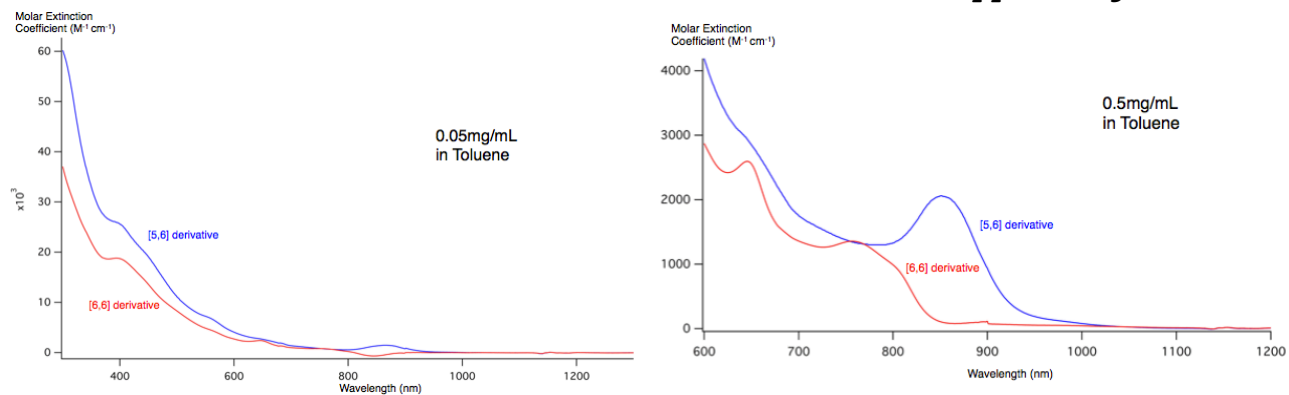
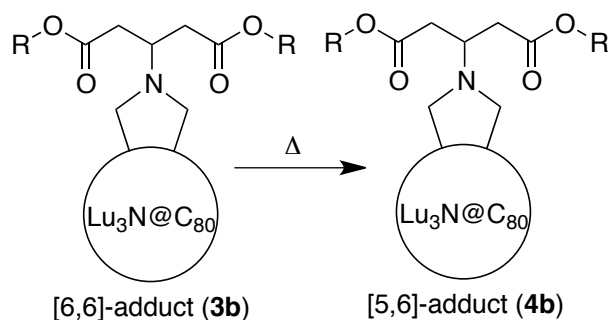


Figure S56. UV-Vis spectra of [5,6]- and [6,6]-fulleropyrrolidine Gd₃N@C₈₀ **3d** and **4d** in toluene.

Eyring Plot experiment (determination of energy barrier)

$$\ln \frac{k_1}{T} = -\frac{\Delta H^\ddagger}{R} \cdot \frac{1}{T} + \ln \frac{k_B}{h} + \frac{\Delta S^\ddagger}{R}$$

Thermal isomerization of the adducts of $\text{Lu}_3\text{N}@I_h\text{-C}_{80}$ 

3b ([6,6]-adduct of $\text{Lu}_3\text{N}@C_{80}$, purified by HPLC, solution of 0.05 mg/mL) was heated at 100, 110, 120, 130, or 140 °C to see the generation of **4b**. Aliquot (10 μL) of the reaction mixture was taken after certain time and subjected to HPLC analysis. The peak areas of **4b** (RT at 9.55 min) and **3b** (RT at 10.50 min) were compared depending on the reaction time

(1) 100°C

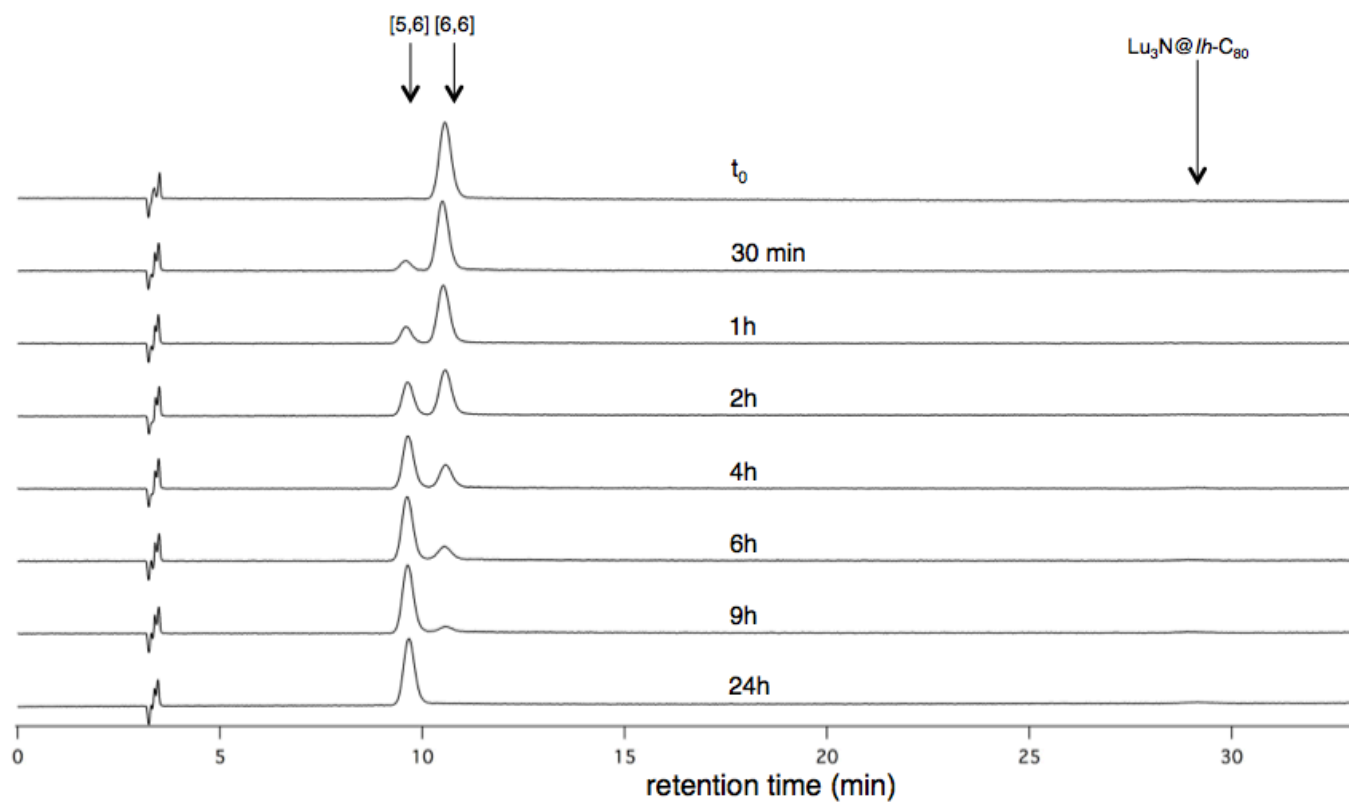


Figure S57.

Table S1.

time (h)	HPLC ratio (390 nm)	HPLC ratio (390 nm)
	[5,6]	[6,6]
0	0	100
0.5	11	89
1	20.5	79.5
2	39	61
4	65	35
6	77	23
9	91.5	8.5
24	100	0

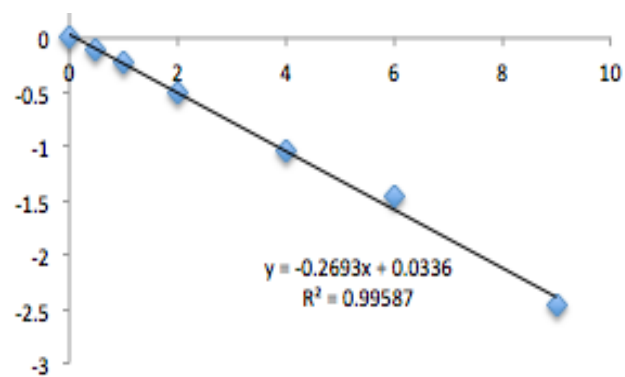


Figure S58.

(2) at 110°C

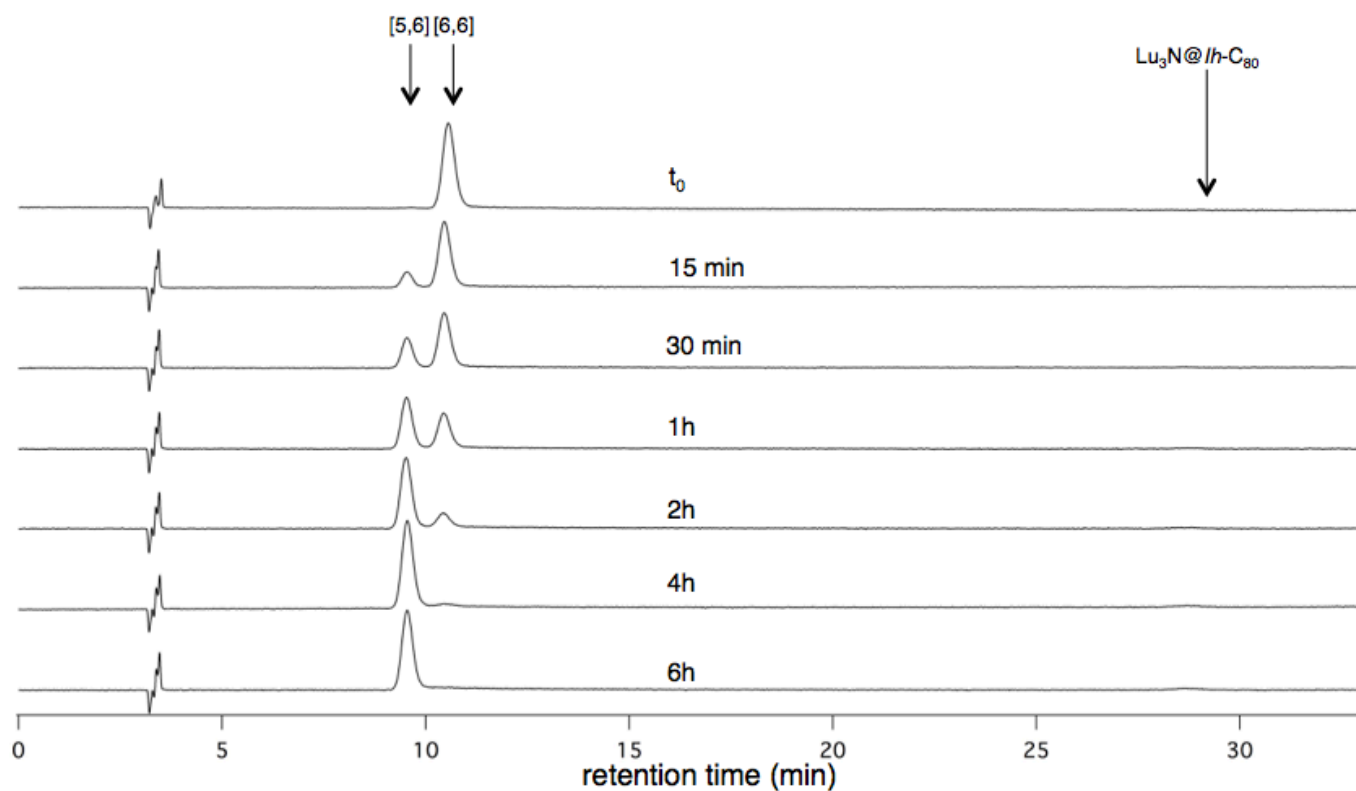


Figure S59.

Table S2.

time (h)	HPLC ratio (390 nm)	HPLC ratio (390 nm)
	[5,6]	[6,6]
0	0	100
0.25	18	82
0.5	33	67
1	55	45
2	78	22
4	93.3	6.5
6	100	0

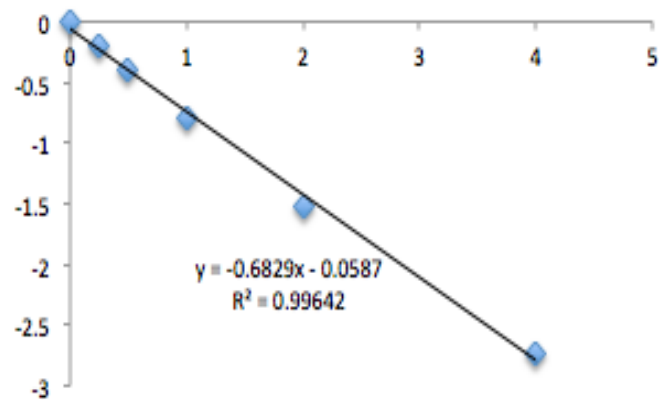


Figure S60.

(3) at 120°C

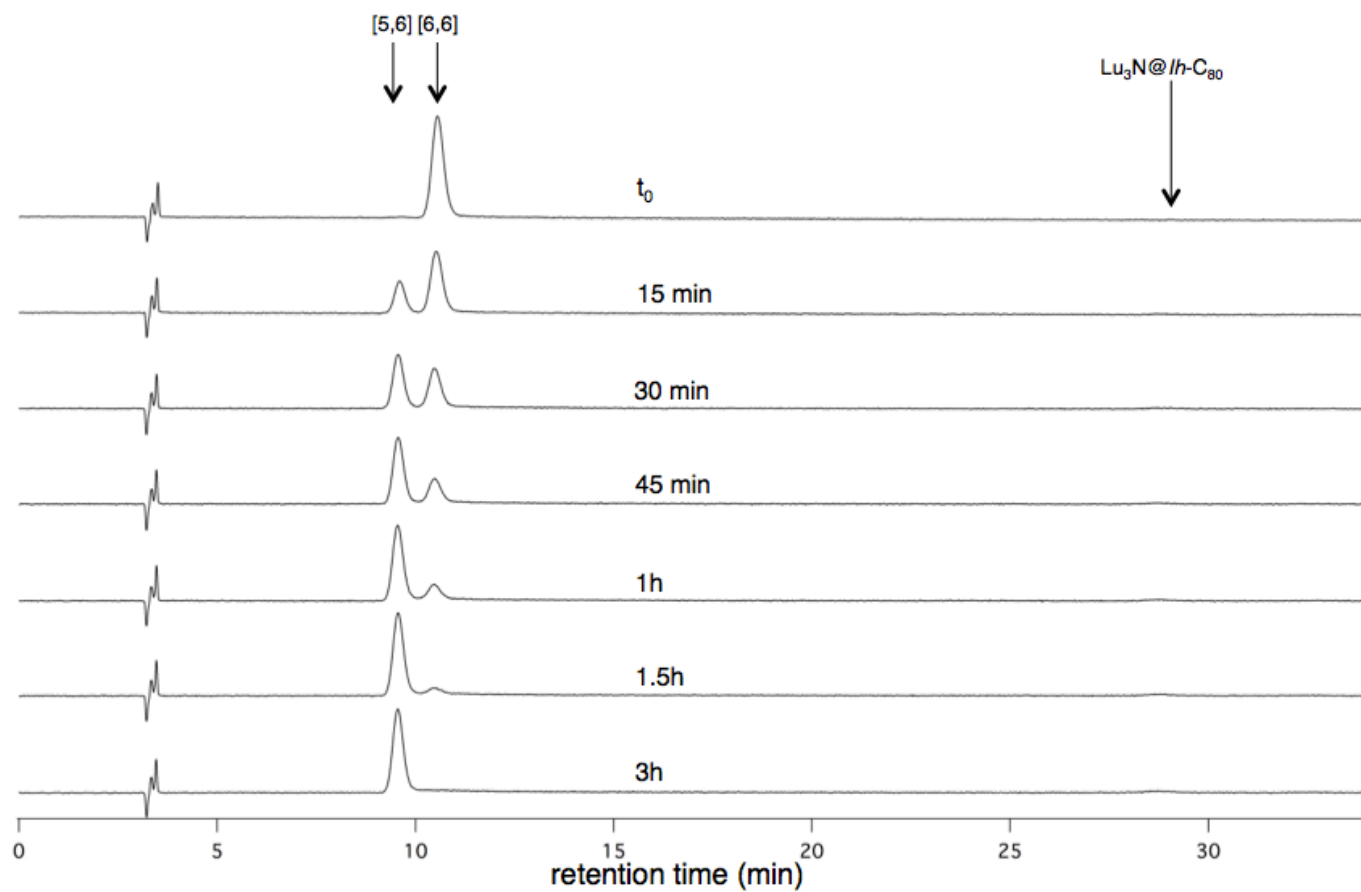


Figure S61.

Table S3.

time (h)	HPLC ratio (390 nm)	
	[5,6]	[6,6]
0	0	100
0.25	31	69
0.5	53.5	46.5
0.75	68.5	31.5
1	77.5	22.5
1.5	86.5	13.5
3	100	0

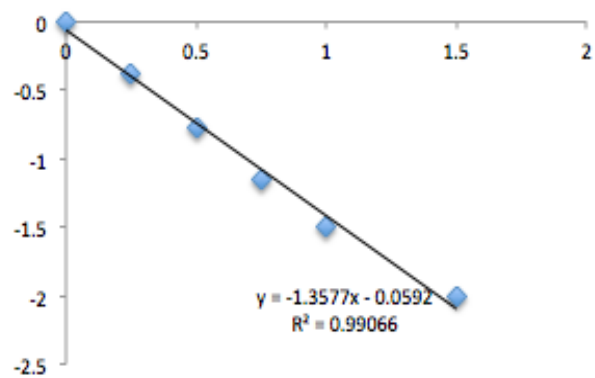


Figure S62.

(3) at 130°C

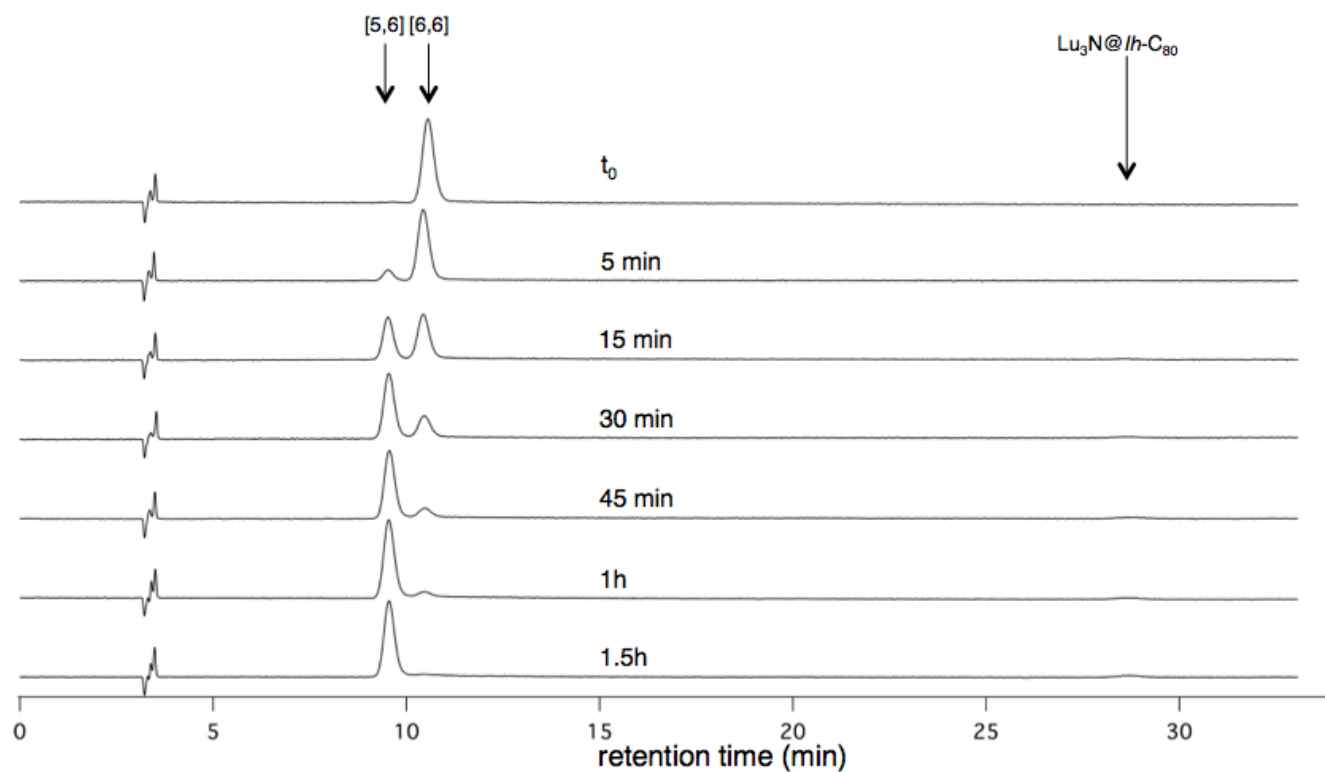


Figure S63.

Table S4.

time (h)	HPLC ratio (390 nm)	HPLC ratio (390 nm)
	[5,6]	[6,6]
0	0	100
0.0833	11	89
0.25	44	56
0.5	70.5	29.5
0.75	84	16
1	89	11
1.5	100	0

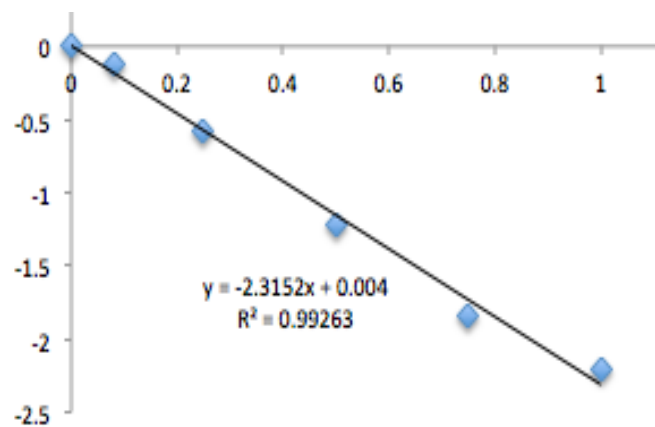


Figure S64.

(4) at 140°C

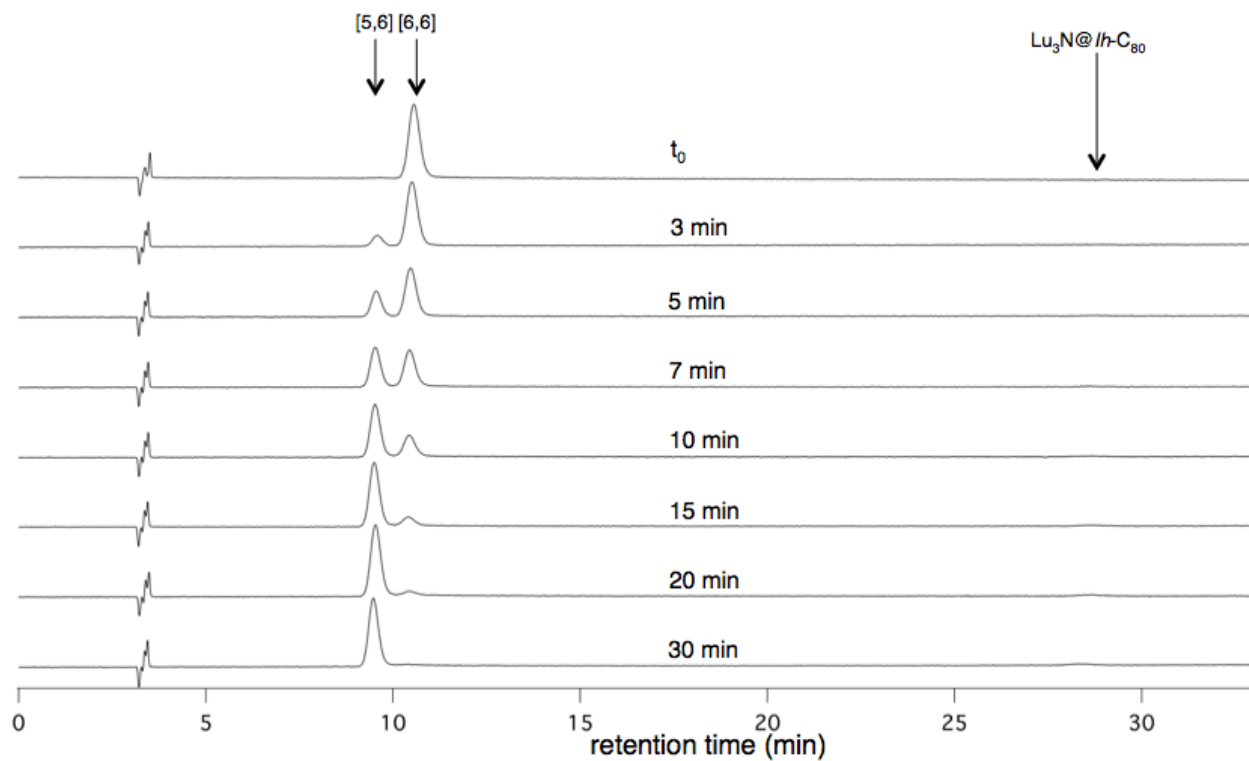


Figure S65.

Table S5.

time (h)	HPLC ratio (390 nm)	HPLC ratio (390 nm)
	[5,6]	[6,6]
0	0	100
0.05	13	87
0.083	32	68
0.117	48	52
0.167	66	34
0.25	83	17
0.33	91.5	8.5
0.5	100	0

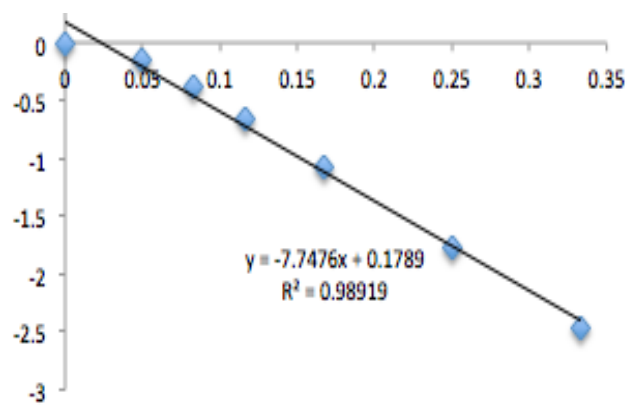
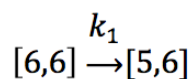


Figure S66.

The isomerization rate is following a first order law.² The rate constant of the reaction was calculated by using the formula below:



$$\ln[6,6] = -k_1 t + \ln[6,6]_0$$

Table S6.

T(°C)	T(°K)	1/T(K ⁻¹)	k ₁ (s ⁻¹)	ln(k ₁ /T)
100	373.15	2.68E-03	7.48E-05	-15.42
110	383.15	2.61E-03	1.90E-04	-14.52
120	393.15	2.54E-03	3.77E-04	-13.86
130	403.15	2.48E-03	6.43E-04	-13.35
140	413.15	2.42E-03	2.15E-03	-12.16

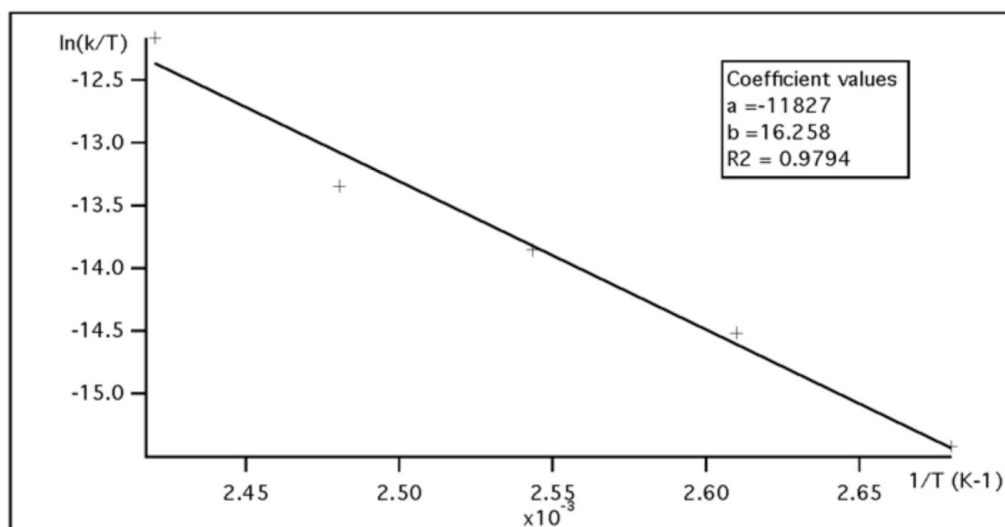
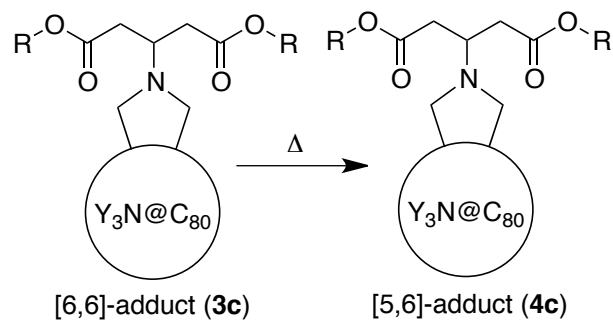


Figure S67.

² *J. Am. Chem. Soc.*, **2006**, 128, 6480.

Thermal isomerization of the adducts of $Y_3N@I_h-C_{80}$ 

3c ([6,6]-adduct of $Y_3N@C_{80}$, purified by HPLC, solution of 0.05 mg/mL) were heated at 110, 120, 130, 140, or 150 °C to see the generation of **4c**. Aliquot (10 μ L) of the reaction mixture was taken after certain time and subjected to HPLC analysis. The peak areas of **4c** (RT at 9.24 min) and **3c** (RT at 10.65 min) were compared depending on the reaction time.

(1) at 110°C

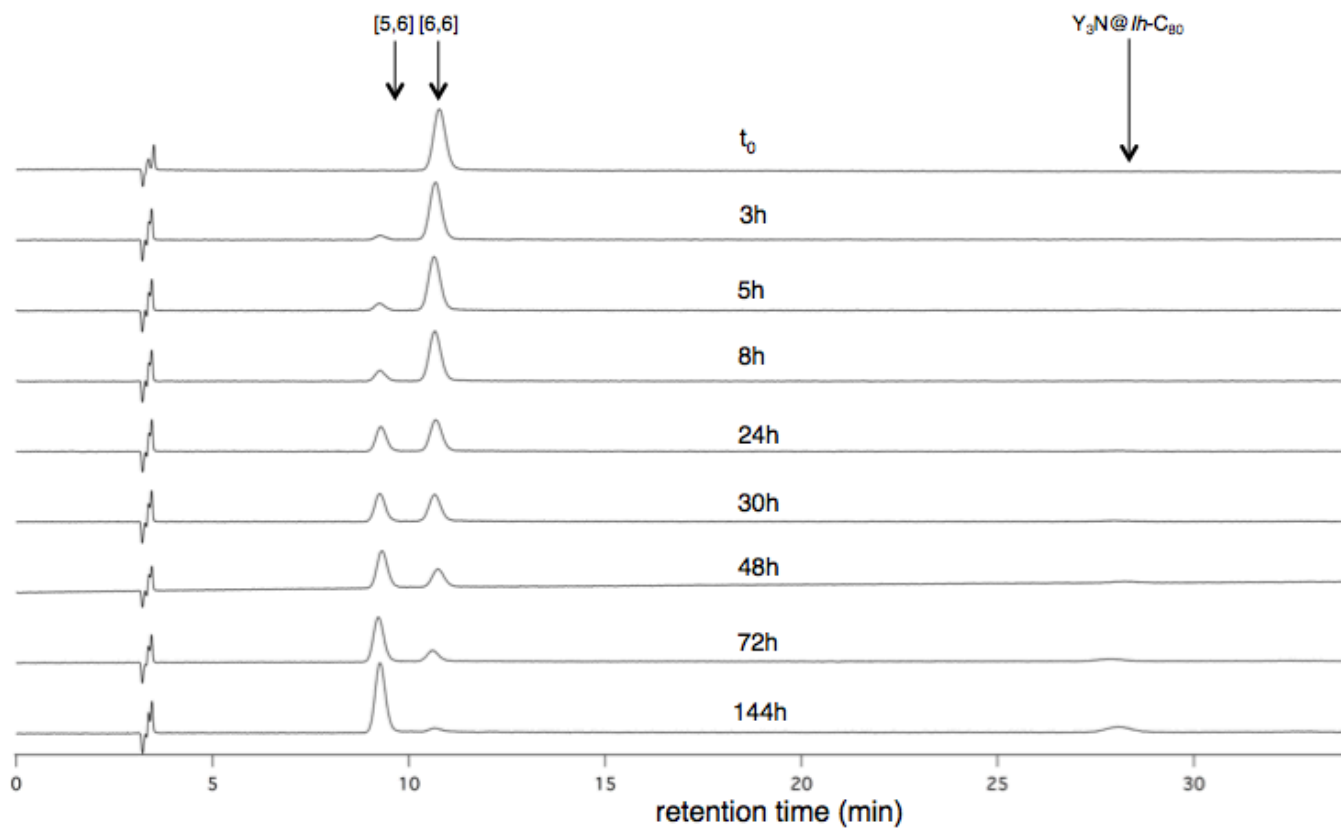


Figure S68.

Table S7.

time (h)	HPLC ratio (390 nm)	HPLC ratio (390 nm)
	[5,6]	[6,6]
0	0	100
3	7.5	92.5
5	11	89
8	16	84
24	41	59
30	48	52
48	64	36
72	77	23
144	90	10

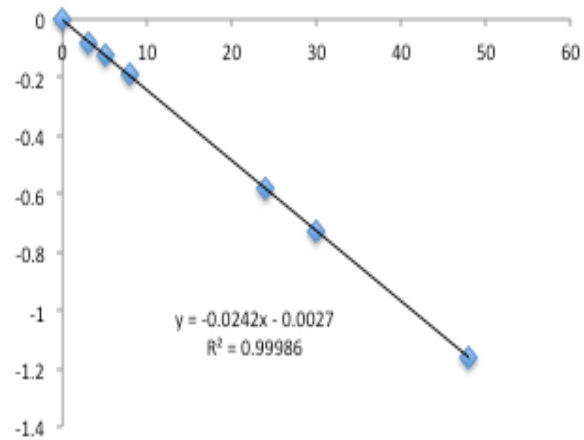


Figure S69.

(2) at 120°C

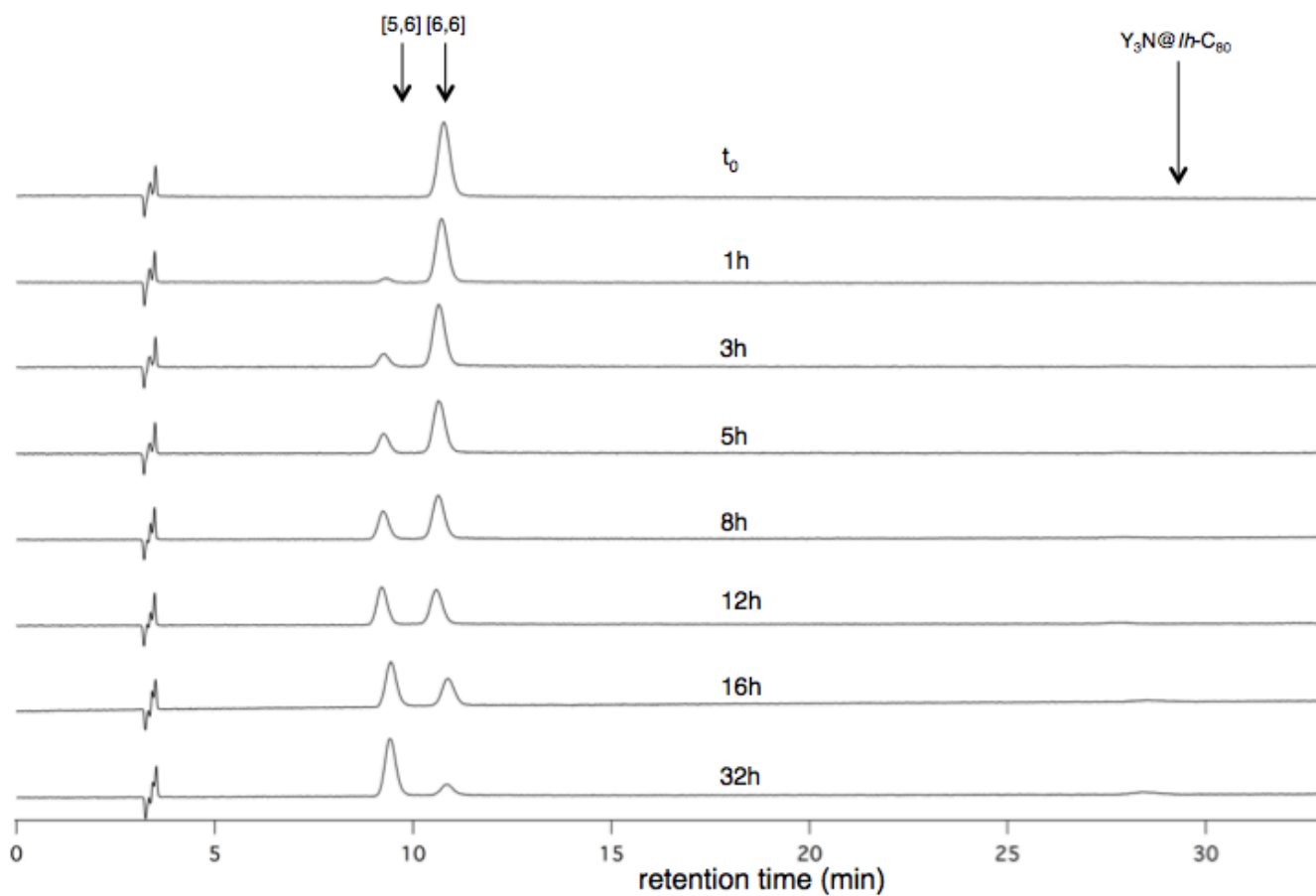


Figure S70.

Table S8.

time (h)	HPLC ratio (390 nm)	HPLC ratio (390 nm)
	[5,6]	[6,6]
0	0	100
1	5.5	94.5
3	16	84
5	25	75
8	36	64
12	48	52
16	62	38
32	81	19

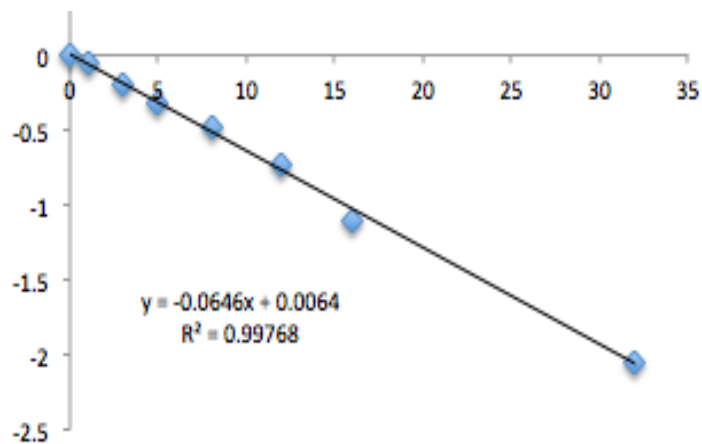


Figure S71

(3) at 130°C

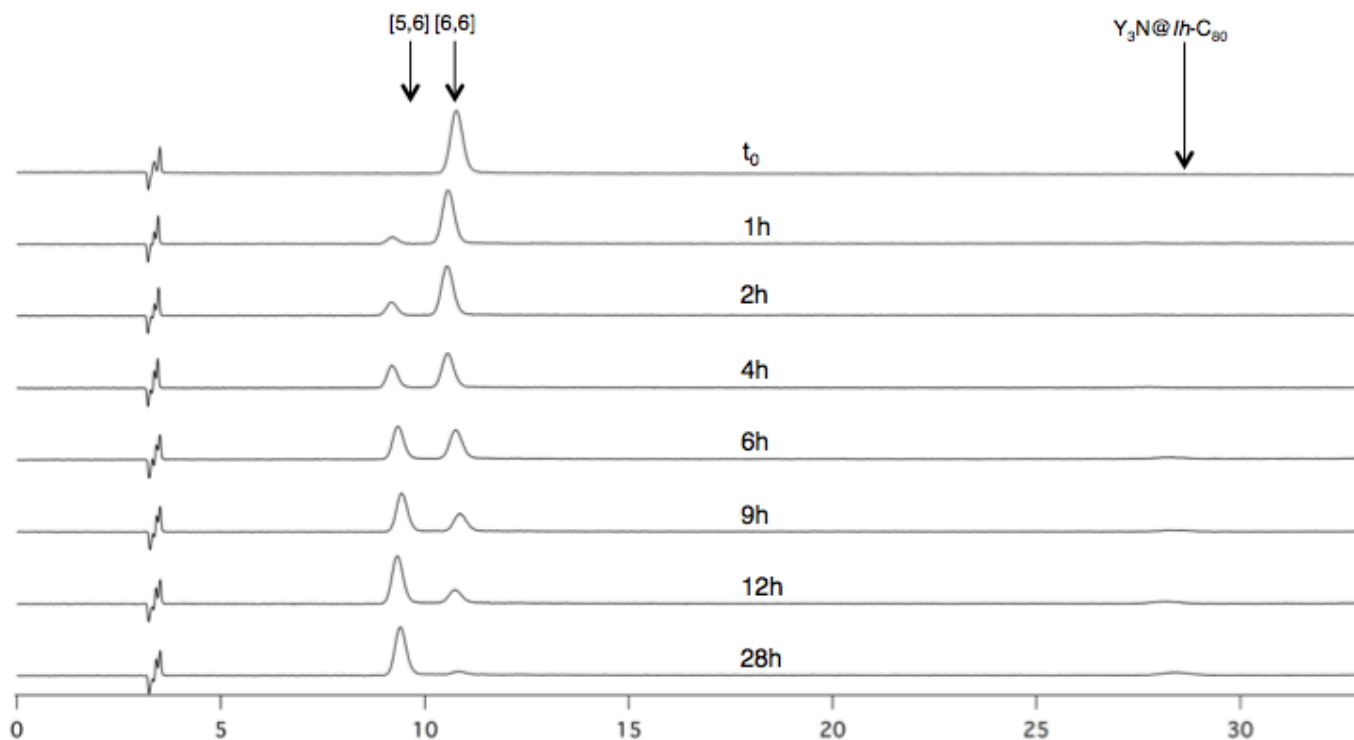


Figure S72.

Table S9

time (h)	HPLC ratio (390 nm)	HPLC ratio (390 nm)
	[5,6]	[6,6]
0	0	100
1	9.5	90.5
2	21	79
4	36.5	63.5
6	49	51
9	64	36
28	90	10

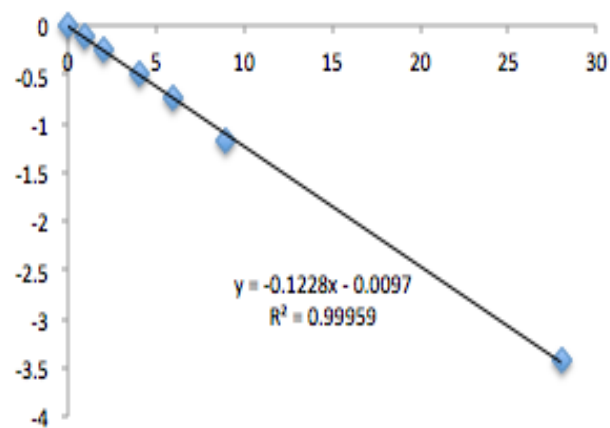


Figure S73.

(4) at 140°C

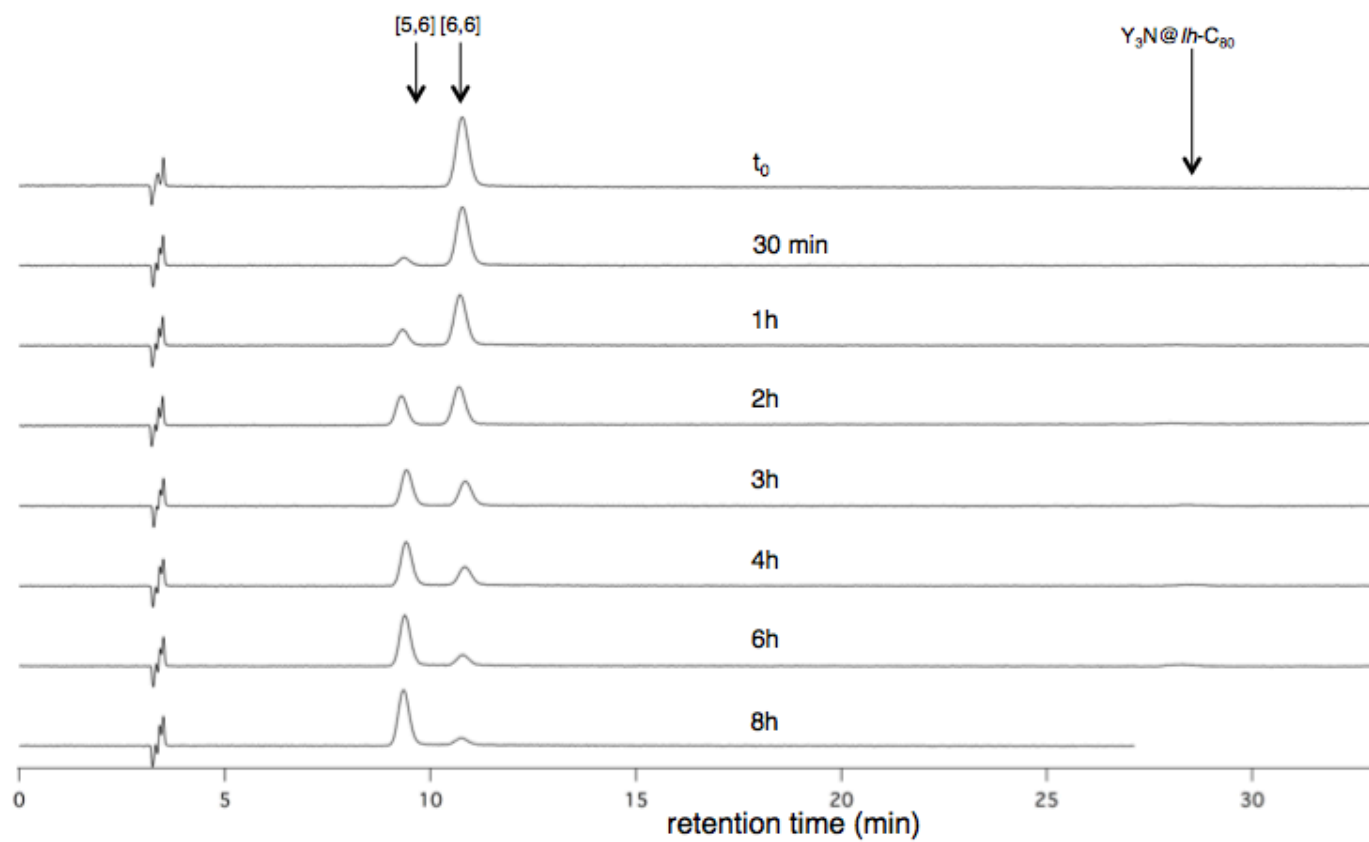


Figure S74.

Table S10.

time (h)	HPLC ratio (390 nm) [5,6]	HPLC ratio (390 nm) [6,6]
0	0	100
0.5	10	90
1	22	78
2	40	60
3	55	45
6	77	23
8	83	17

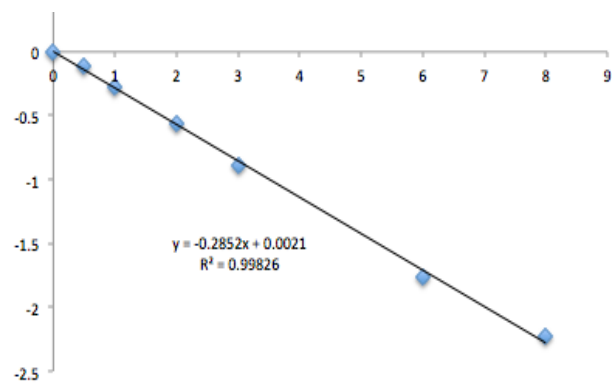


Figure S75.

(5) at 150°C

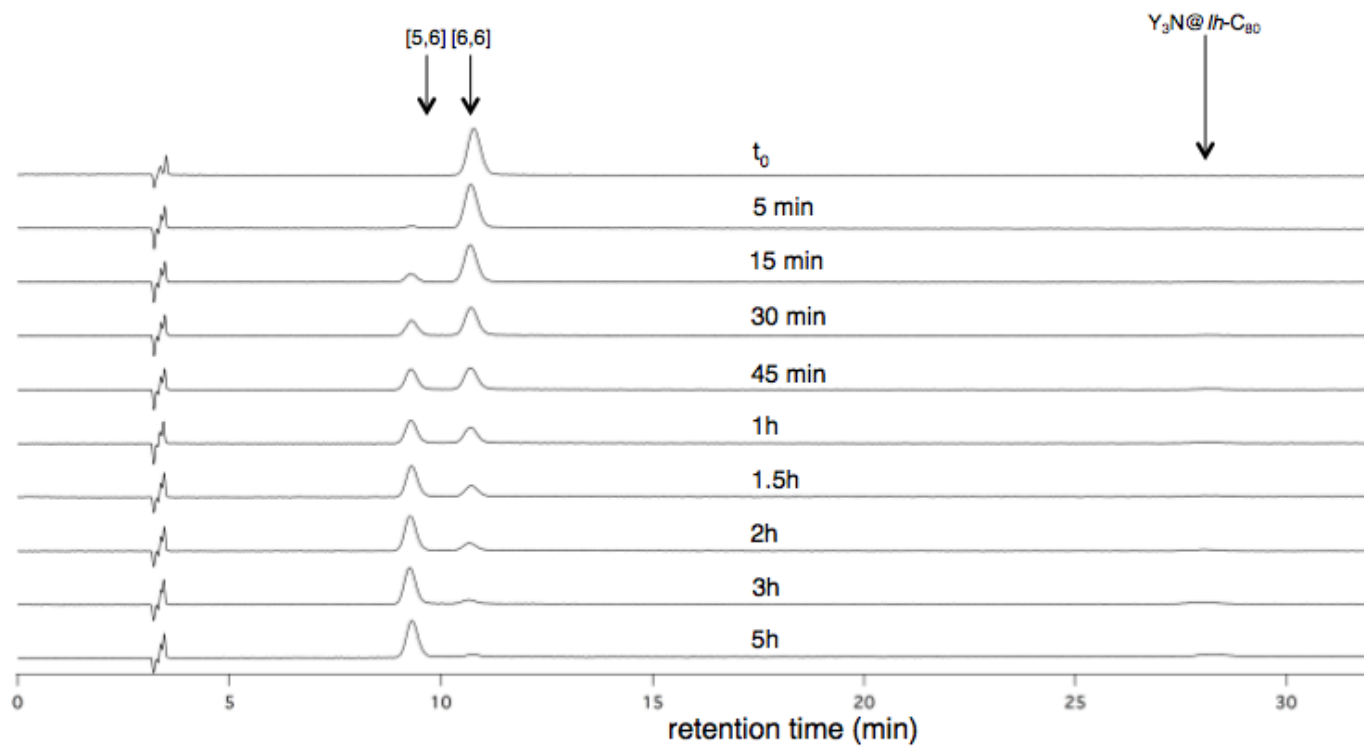


Figure S76.

Table S11.

time (h)	HPLC ratio (390 nm)	HPLC ratio (390 nm)
	[5,6]	[6,6]
0	0	100
0.083	5	95
0.25	17.5	82.5
0.5	33	67
0.75	45.5	54.5
1	54	46
1.5	70	30
5	92	8

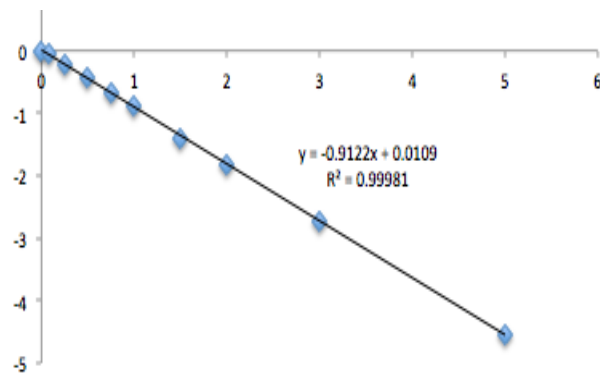
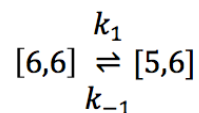


Figure S77.

The isomerization rate is following a first order equilibrium law. The rate constant of the reaction was calculated by using the formula below:



$$K = \frac{k_1}{k_{-1}} = \frac{93}{7} = 13.3$$

$$\ln \frac{[6,6]_t - [6,6]_{eq}}{[6,6]_0 - [6,6]_{eq}} = -(k_1 + k_{-1})t$$

Table S12.

T(°C)	T(°K)	1/T(K ⁻¹)	k ₁ (s ⁻¹)	k ₋₁ (s ⁻¹)	ln(k ₁ /T)	ln(k ₋₁ /T)
110	383.15	2.61E-03	6.25E-06	4.70E-07	-17.93	-20.52
120	393.15	2.54E-03	1.67E-05	1.25E-06	-16.97	-19.56
130	403.15	2.48E-03	3.17E-05	2.39E-06	-16.36	-18.95
140	413.15	2.42E-03	7.37E-05	5.54E-06	-15.54	-18.13
150	423.15	2.36E-03	2.36E-04	1.77E-05	-14.40	-16.99

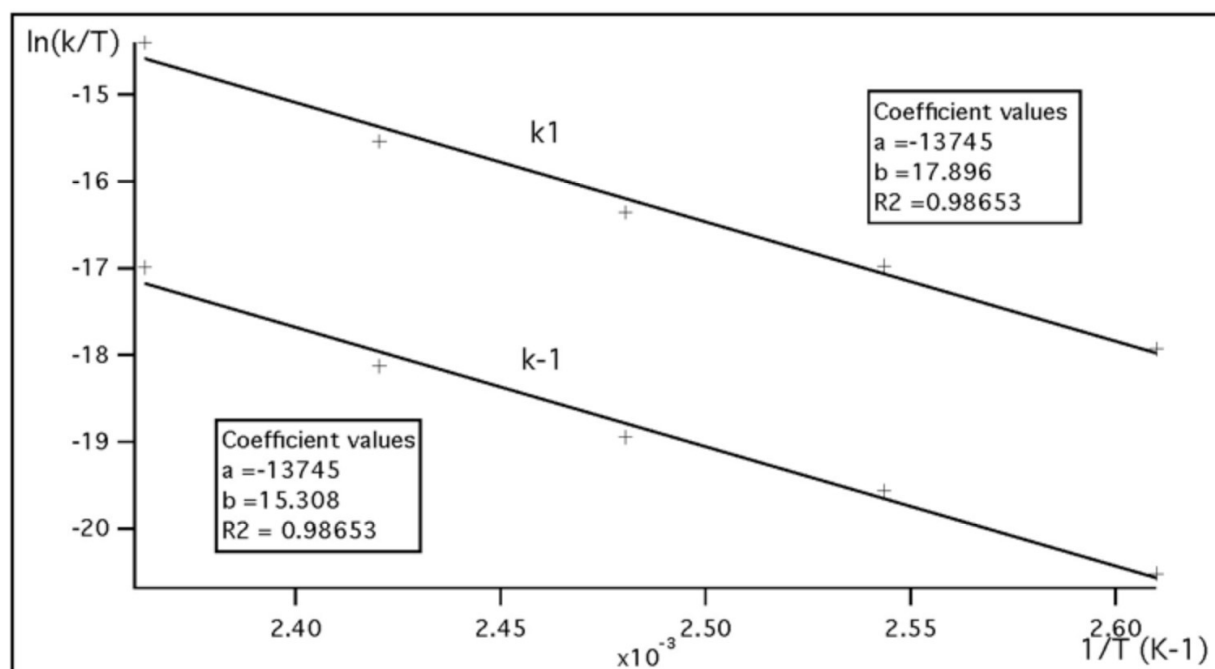
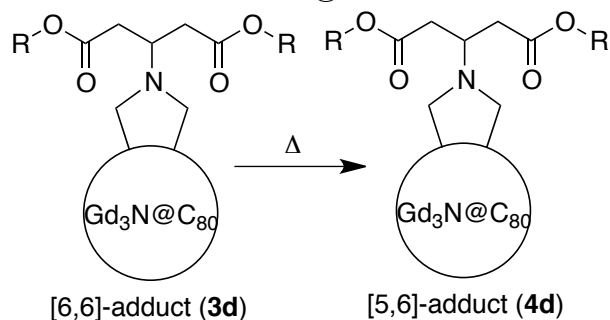


Figure S78.

Thermal isomerization of the adducts of $\text{Gd}_3\text{N}@I_h\text{-C}_{80}$

Isomerization of $\text{Gd}_3\text{N}@I_h\text{-C}_{80}$ derivatives from **4d** to **3d**



[6,6]-**3d** ([6,6]-adduct of $\text{Gd}_3\text{N}@C_{80}$, purified by HPLC, solution of 0.05 mg/mL) and heated at 140, 150, 160, 170, 180 °C to see the generation of **4d**. Aliquot (10 μL) of the reaction mixture was taken after certain time and subjected to HPLC analysis. The peak areas of **4d** (RT at 9.81 min) and **3d** (RT at 11.23 min) were compared depending on the reaction time.

(1) at 140°C

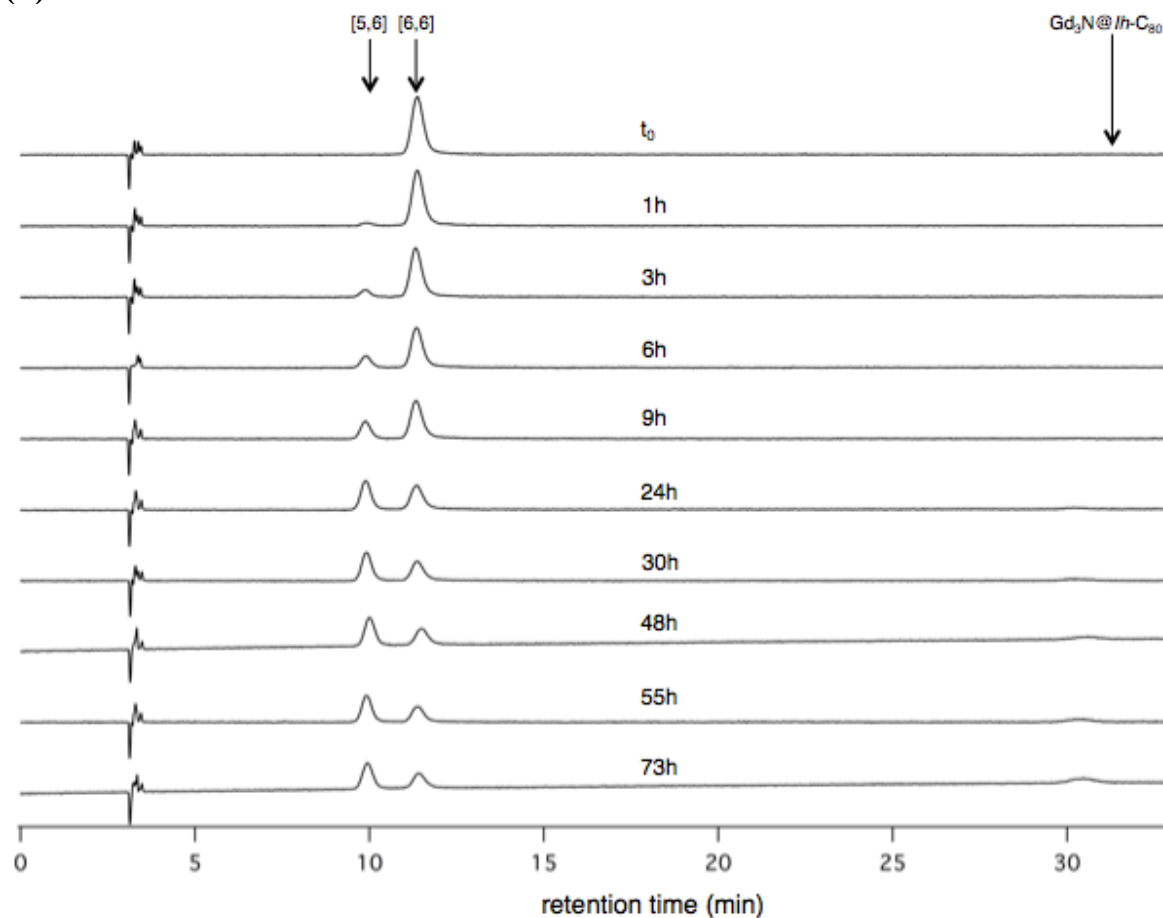


Figure S79.

Table S13.

time (h)	HPLC ratio (390 nm)		normalized ratio	
	[5,6]	[6,6]	[5,6]	[6,6]
0	0	100	0.0	100.0
1	4	96	2.6	97.4
3	11.5	88.5	7.7	92.3
6	19	81	13.1	86.9
9	27.5	72.5	19.7	80.3
24	48.5	51.5	37.8	62.2
30	54.5	45.5	43.6	56.4
48	58	42	47.1	52.9
55	58	42	47.1	52.9
73	60	40	49.2	50.8

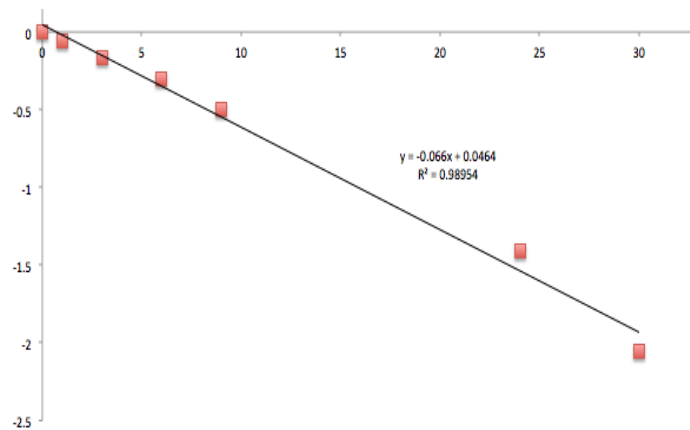


Figure S80.

(2) 150°C

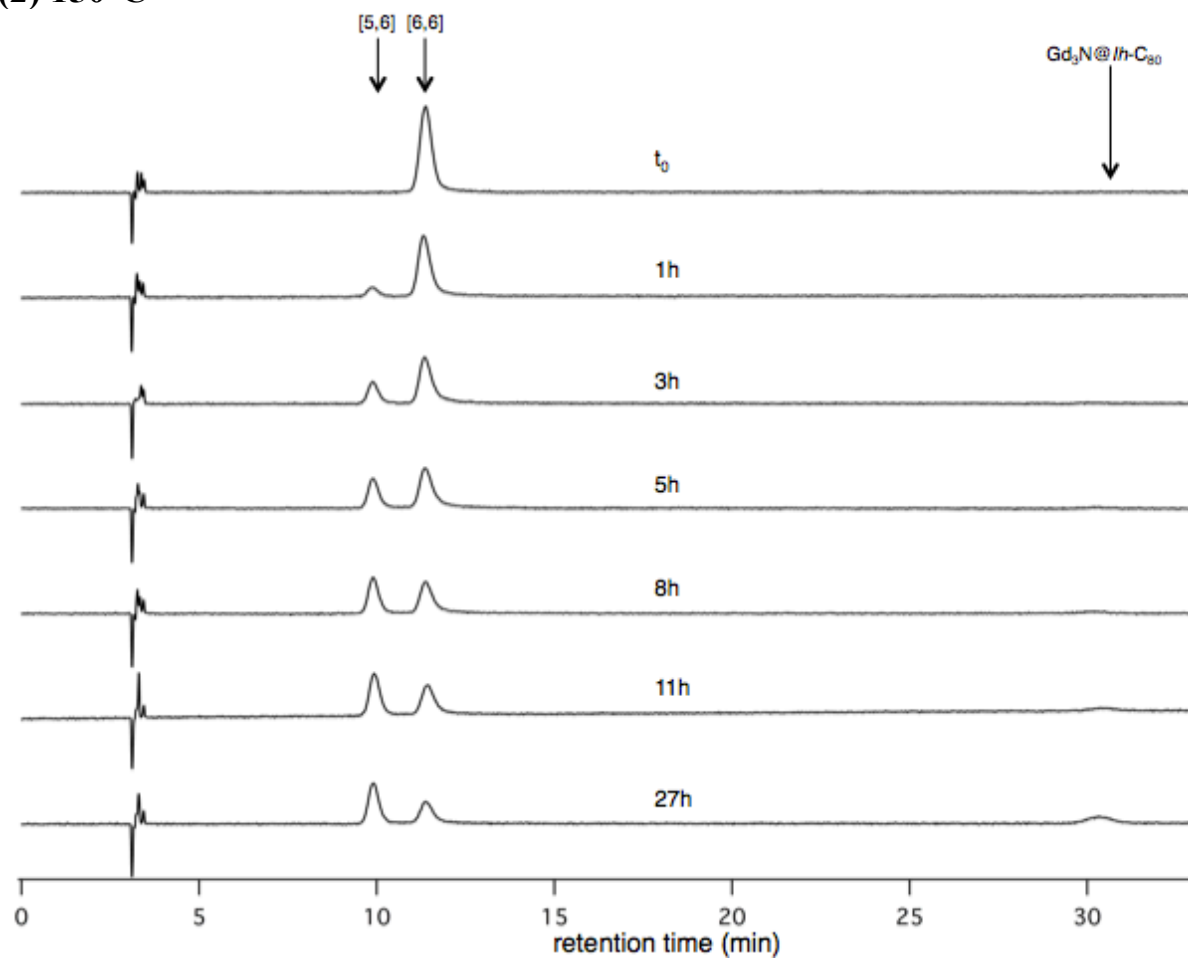


Figure S81.

Table S14.

time (h)	HPLC ratio (390 nm)		normalized ratio	
	[5,6]	[6,6]	[5,6]	[6,6]
0	0	100	0.0	100.0
1	11.5	88.5	7.7	92.3
3	28	72	20.1	79.9
5	36	64	26.6	73.4
8	46.5	53.5	35.9	64.1
11	53	47	42.1	57.9
27	60	40	49.2	50.8

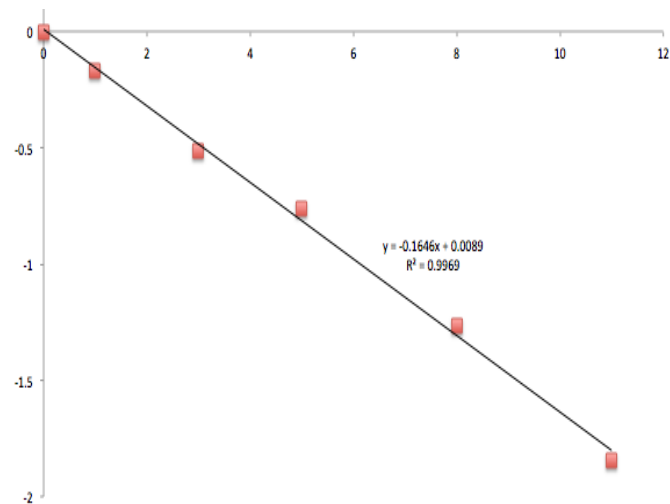


Figure S82.

(3) 160°C

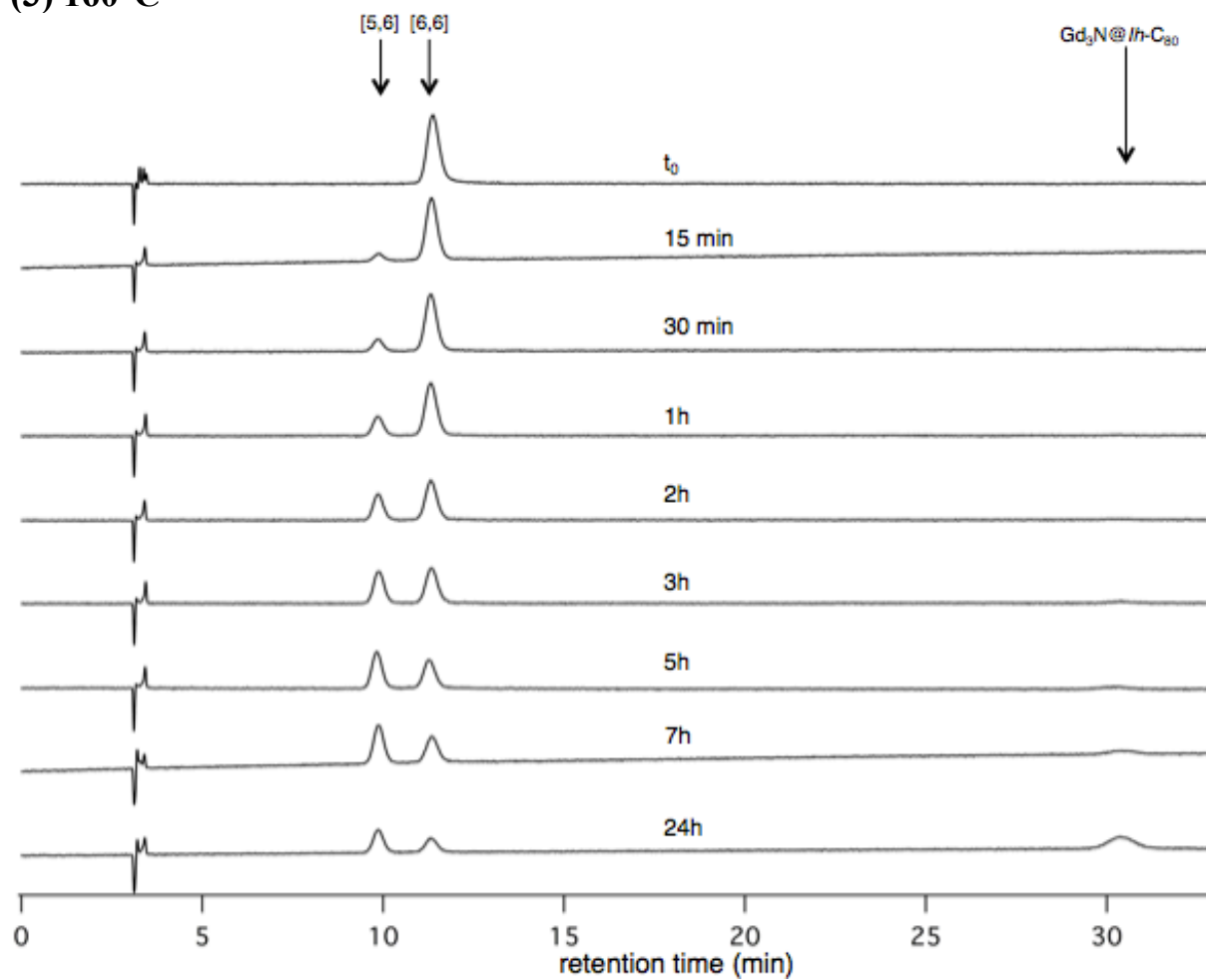


Figure S83.

Table S15.

time (h)	HPLC ratio (390 nm)		normalized ratio	
	[5,6]	[6,6]	[5,6]	[6,6]
0	0	100	0.0	100.0
0.25	9.5	90.5	6.3	93.7
0.5	16	84	10.9	89.1
1	24.5	75.5	17.3	82.7
2	35.5	64.5	26.2	73.8
3	43.5	56.5	33.2	66.8
5	51	49	40.2	59.8
7	55	45	44.1	55.9
10.5	57	43	46.1	53.9

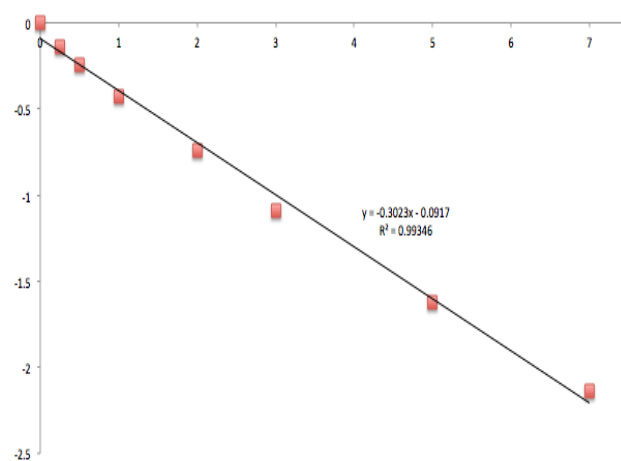


Figure S84.

(4) at 170°C

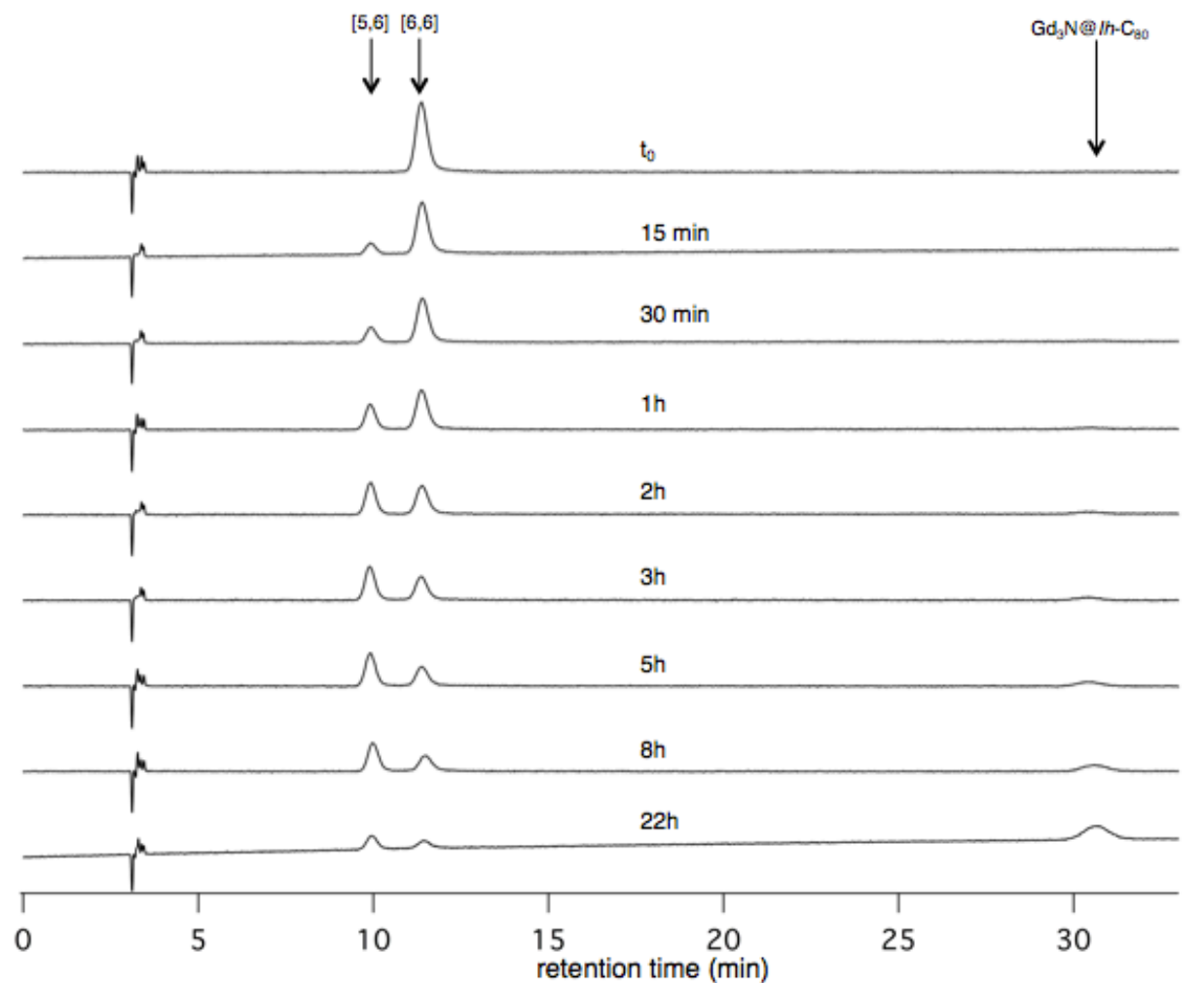


Figure S85.

Table S16.

time (h)	HPLC ratio (390 nm)		normalized ratio	
	[5,6]	[6,6]	[5,6]	[6,6]
0	0	100	0.0	100.0
0.25	15	85	10.2	89.8
0.5	22.5	77.5	15.8	84.2
1	35	65	25.8	74.2
2	48	52	37.3	62.7
3	53	47	42.1	57.9
5	59	41	48.1	51.9
8	59	41	48.1	51.9

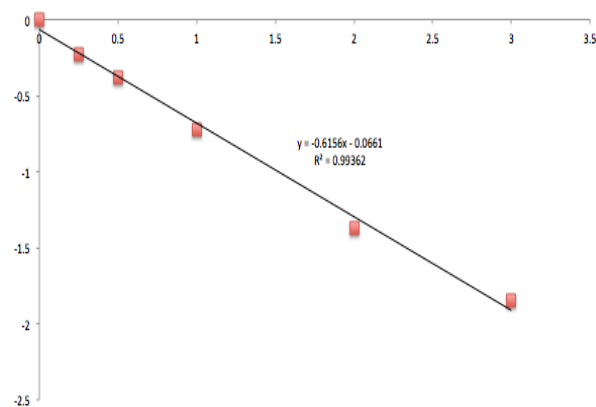


Figure S86.

(5) at 180°C

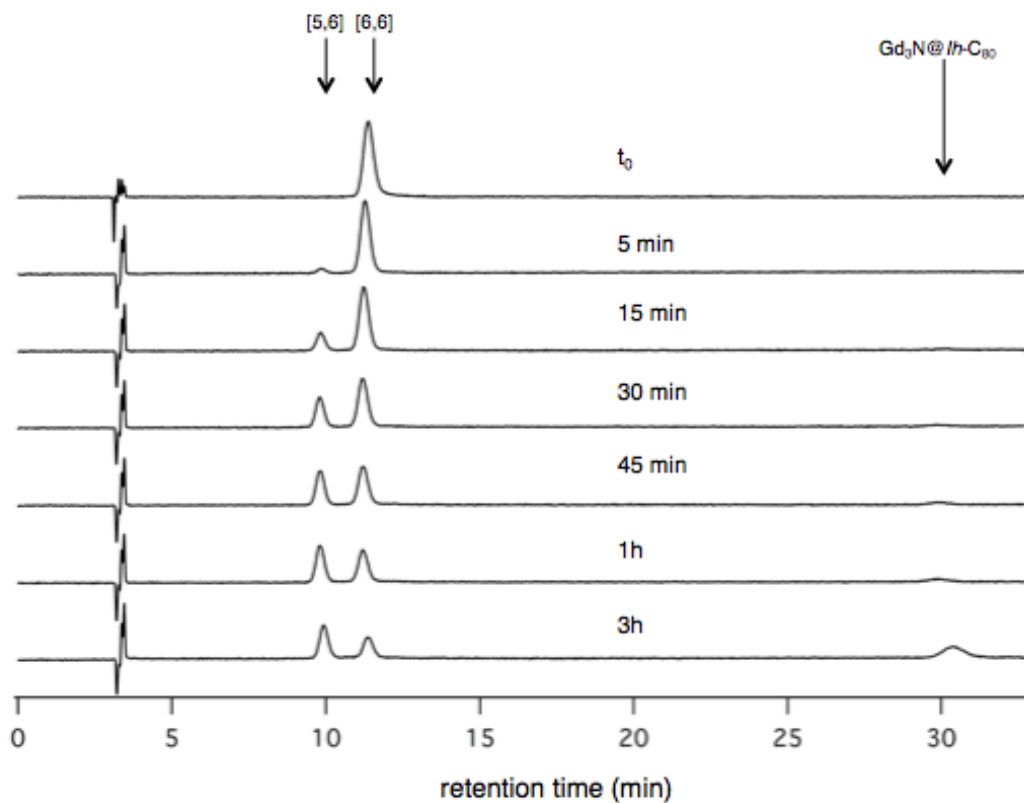


Figure S87.

Table S17.

time (h)	HPLC ratio (390 nm)		normalized ratio	
	[5,6]	[6,6]	[5,6]	[6,6]
0	0	100	0	100
0.083	5.5	94.5	3.5	96.5
0.25	20.5	79.5	14.5	85.5
0.5	34.5	65.5	25.5	74.5
0.75	43	57	32.5	67.5
1	50.5	49.5	39.5	60.5
3	57	43	46	54

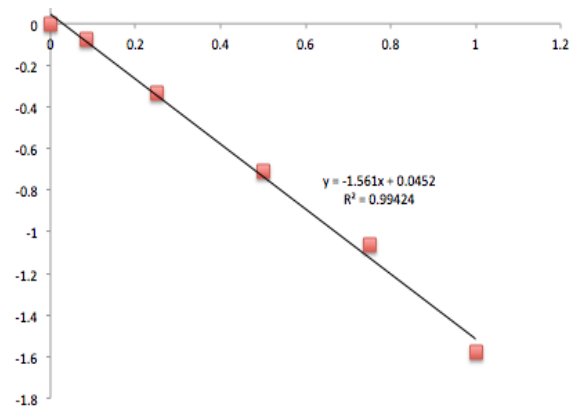
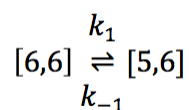


Figure S88.

The isomerization rate is following a first order equilibrium law. The rate constant of the reaction was calculated by using the formula below:



$$K = \frac{k_1}{k_{-1}} = \frac{50}{50} = 1$$

$$\ln \frac{[6,6]_t - [6,6]_{eq}}{[6,6]_0 - [6,6]_{eq}} = -(k_1 + k_{-1})t$$

Table S18.

T(°C)	T(°K)	1/T(K ⁻¹)	k ₁ (s ⁻¹)	k ₋₁ (s ⁻¹)	ln(k ₁ /T)	ln(k ₋₁ /T)
140	413.15	2.42E-03	9.17E-06	9.17E-06	-17.62	-17.62
150	423.15	2.36E-03	2.29E-05	2.29E-05	-16.73	-16.73
160	433.15	2.31E-03	4.19E-05	4.19E-05	-16.15	-16.15
170	443.15	2.26E-03	1.12E-04	1.12E-04	-15.20	-15.20
180	453.15	2.21E-03	2.17E-04	2.17E-04	-14.55	-14.55

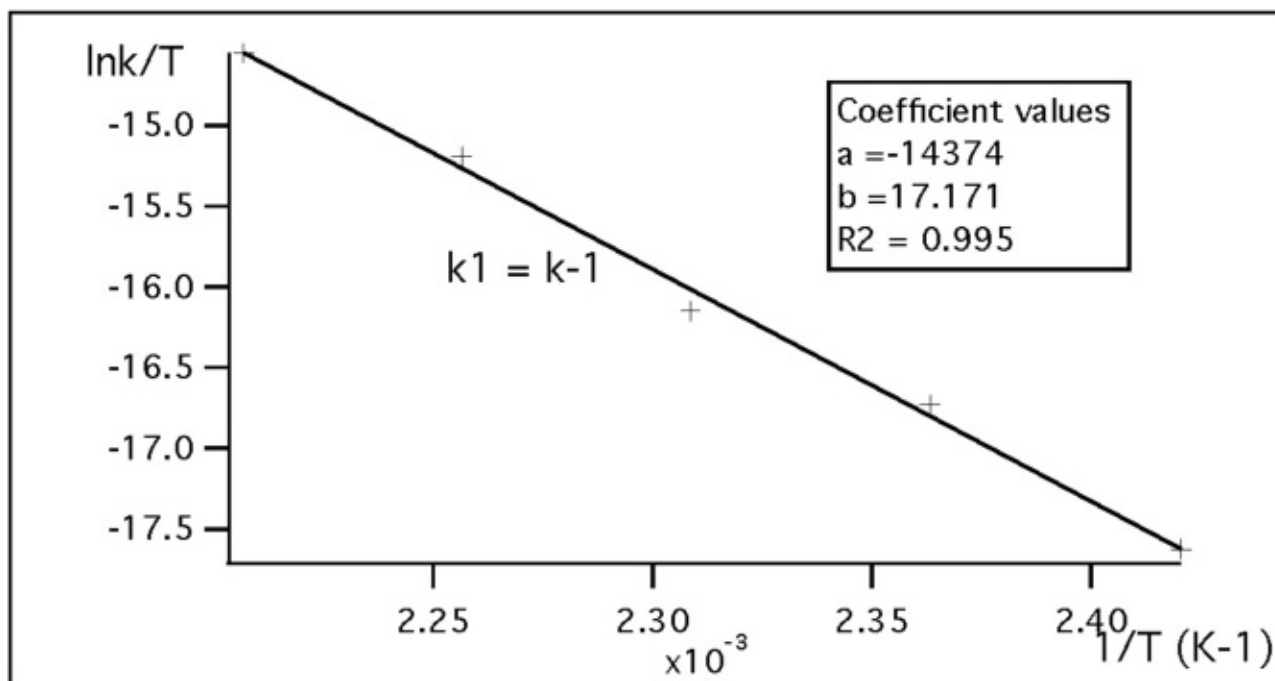
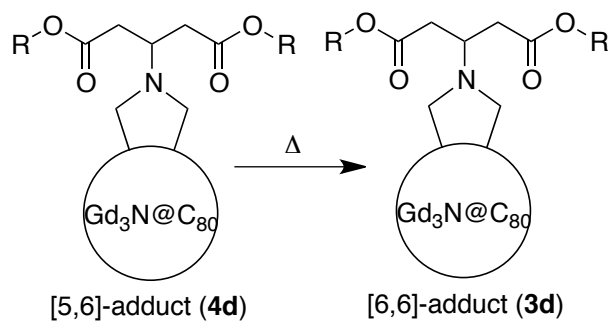


Figure S89.



140 °C

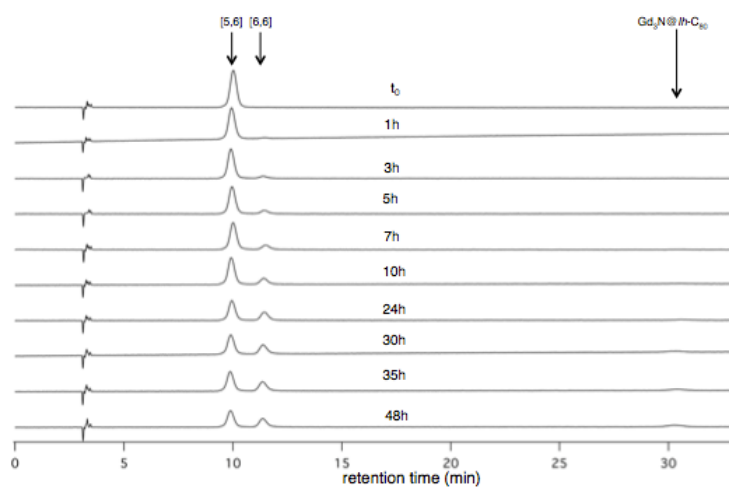


Figure S90.

Table S19.

time (h)	HPLC ratio (390 nm)		normalized ratio	
	[5,6]	[6,6]	[5,6]	[6,6]
0	100	0	100.0	0.0
1	95	5	92.5	7.5
3	90.5	9.5	86.0	14.0
5	86.5	13.5	80.5	19.5
7	82.5	17.5	75.3	24.7
10	78.5	21.5	70.2	29.8
24	67	33	56.7	43.3
30	65.5	34.5	55.1	44.9
35	64.5	35.5	54.0	46.0
48	63	37	52.3	47.7

150 °C

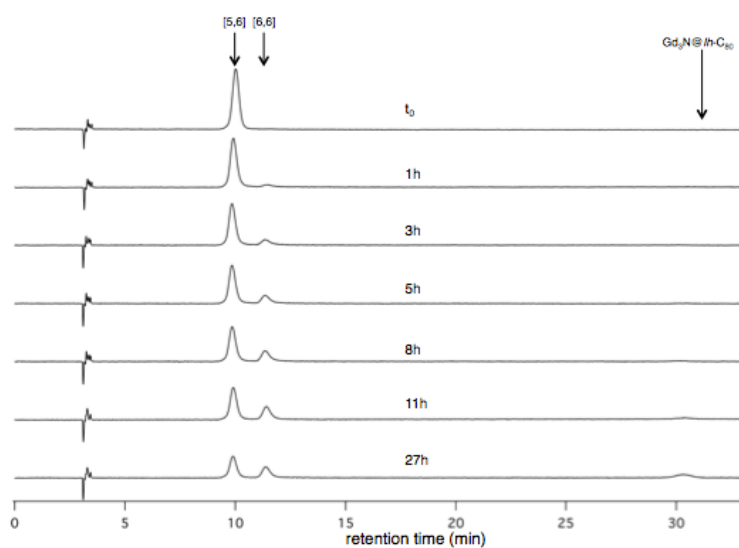


Figure S91.

Table S20.

time (h)	HPLC ratio (390 nm)		normalized ratio	
	[5,6]	[6,6]	[5,6]	[6,6]
0	100	0	100.0	0.0
1	92	8	88.1	11.9
3	84.5	15.5	77.9	22.1
5	78.5	21.5	70.2	29.8
8	73	27	63.6	36.4
11	68.5	31.5	58.4	41.6
27	62.5	37.5	51.8	48.2

160°C

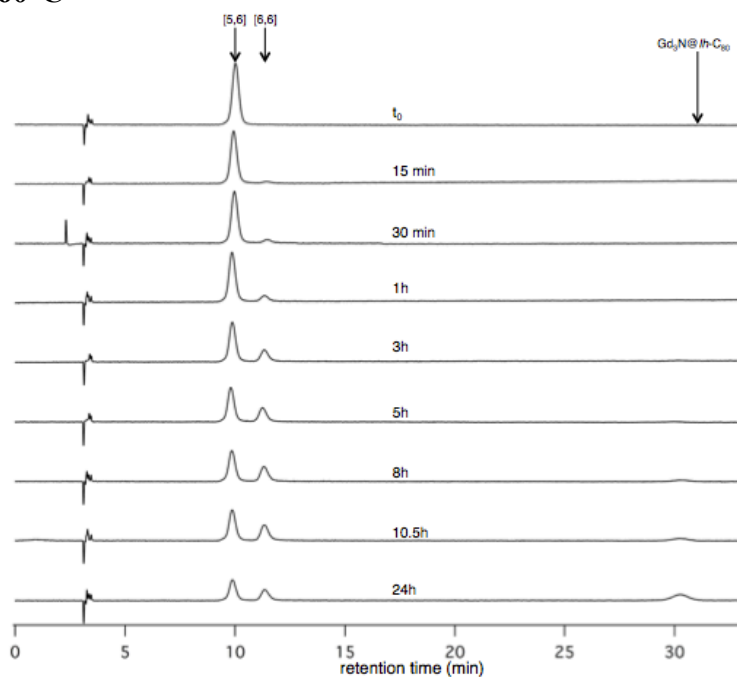


Figure S92.

Table S21.

time (h)	HPLC ratio (390 nm)		normalized ratio	
	[5,6]	[6,6]	[5,6]	[6,6]
0	100	0	100.0	0.0
0.25	92.5	7.5	88.8	11.2
0.5	93	7	89.6	10.4
1	86	14	79.9	20.1
3	74.5	25.5	65.3	34.7
5	67.5	32.5	57.3	42.7
8	63	37	52.3	47.7
10.5	62	38	51.3	48.7
24	61.5	38.5	50.8	49.2

170°C

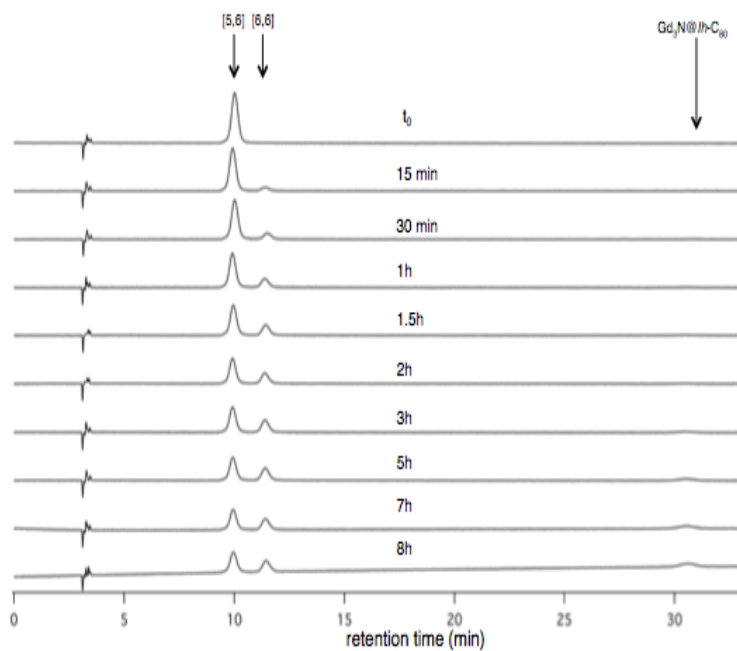


Figure S93.

Table S22.

time (h)	HPLC ratio (390 nm)		normalized ratio	
	[5,6]	[6,6]	[5,6]	[6,6]
0	100	0	100.0	0.0
0.25	89	11	83.9	16.1
0.5	84.5	15.5	77.9	22.1
1	78	22	69.6	30.4
1.5	72	28	62.4	37.6
2	67.5	32.5	57.3	42.7
3	65	35	54.5	45.5
5	63	37	52.3	47.7
8	62	38	51.3	48.7

180°C

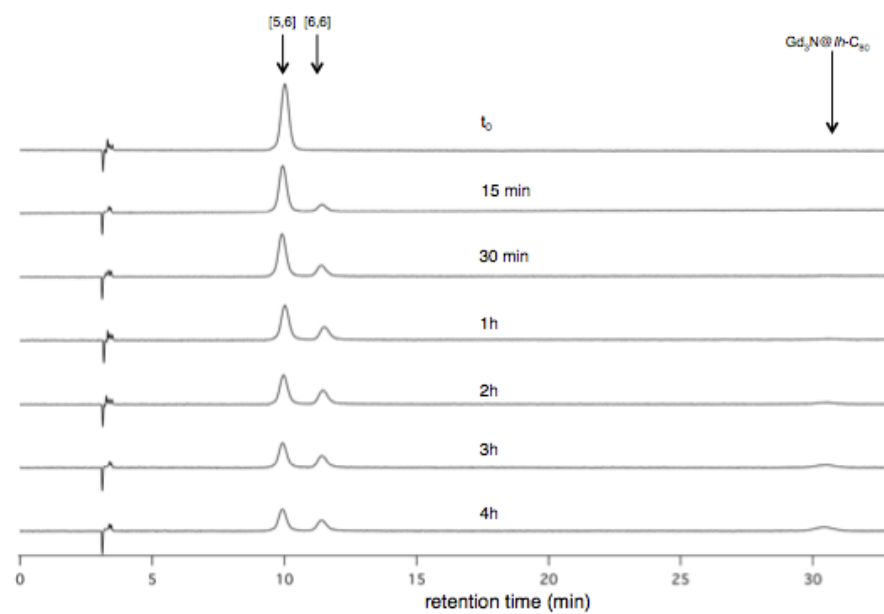
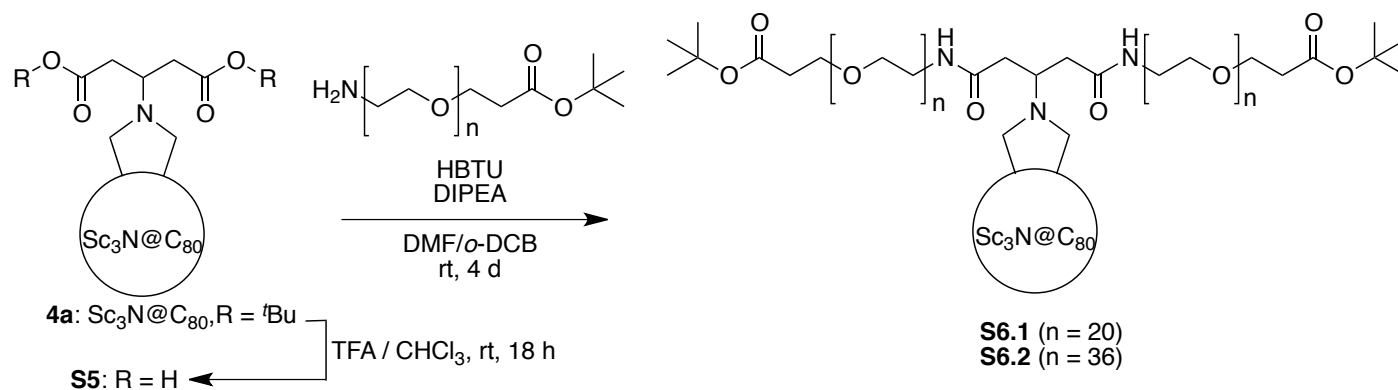


Figure S94.

Table S23.

time (h)	HPLC ratio (390 nm)		normalized ratio	
	[5,6]	[6,6]	[5,6]	[6,6]
0	100	0	100.0	0.0
0.25	82.5	17.5	75.3	24.7
0.5	75.5	24.5	66.5	33.5
1	69	31	58.9	41.1
2	64.5	35.5	54.0	46.0
3	65	35	54.5	45.5
4	63	37	52.3	47.7

Preparation of $M_3N@C_{80}$ -PEG derivatives (M=Sc and Gd)

S5. To a solution of **4a** (29 mg, 20.8 μ mol) in $CHCl_3$ (8 mL) was added trifluoroacetic acid (4 mL). The solution was stirred for 18 hrs at room temperature. The solvents and were removed *in vacuo* and dried under vacuum overnight to obtain a dark powder **S5** (27 mg, 21.0 μ mol, yield = 100%)

S6.1. To a solution of **S5** (6.3 mg, 4.91 μ mol) in distilled DMF - *o*-DCB 1:1 (6.3 mL) was added HBTU (CHEM-IMPEX international, 7.8 mg, 20.6 μ mol), Amino-dPEG₂₀-*t*Bu ester (Quanta Biodesign, 95%, 14.0 mg, 13.6 μ mol), DIPEA (Fluka, distilled, 5.9 mg, 45.6 μ mol). The mixture was stirred for 4 days at room temperature. The solvent was removed *in vacuo* and diluted in a small volume of distilled THF. The crude mixture was subjected to a short SiO_2 plug (SiO_2 : 50 mg, eluent: THF). The elute was concentrated and was followed by precipitation in *n*-hexane (HPLC grade, Acros, 45 mL). The precipitates was dissolved in MeOH and purified by Sephadex LH-20 (10g) and the fractions were collected and dried overnight under vacuum to get a dark sticky solid **S6.1** (13.2 mg, 4.0 μ mol isolated yield 81%). 1H -NMR (600 MHz, $CDCl_3$ (99.98%), 50°C) δ 1.45 (s, $C(CH_3)_3$, 18H), 2.49 (t, 6.6 Hz, $CH_2-CH_2-CO_2NH$, 4H), 2.64 (dd, $J = 6.75$ Hz, $J = 15$ Hz, $CH-CHH-CO_2NH$, 2H), 2.73 (dd, $J = 6.75$ Hz, $J = 15$ Hz, $CH-CHH-CO_2NH$, 2H), 3.18 (d, $J = 9.0$ Hz, $C-CHH-N$, 2H), 3.5-3.8 (CH_2-CH_2-O , 164H), 3.91 (m, $J = 6.75$ Hz, $(CH_2)_2-CH-N$, 1H), 4.03 (d, $J = 9.0$ Hz, $C-CHH-N$, 2H). ^{13}C (150 MHz, $CDCl_3$ (99.98%), RT) 28.25 (s, $C(CH_3)_3$, 36.41 ($CH_2-CH_2-CO_2^tBu$), 38.49 ($CH-CH_2-CO-NH$), 39.44 ($CH_2-CH_2-NH-CO$), 54.43 ($(CH_2)_2-CH-N$), 65.26 ($C-CH_2-N$), 67.04 ($O-CH_2-CH_2-CO_2^tBu$), 69.90-70.90 (CH_2-CH_2-O), 80.66 ($C(CH_3)_3$), 171.05 ($CH_2-CONH-CH_2$), 171.21 ($CH_2-CO_2^tBu$), fullerene core: 57.46 ($C-CH_2-N$), 114.94 (2C), 115.38 (2C), 129.52 (2C), 130.64 (2C), 131.03 (2C), 132.13 (2C), 133.48 (2C), 133.91 (2C), 135.20 (1C), 135.35 (2C), 136.52 (2C), 136.93 (2C), 137.49 (2C), 138.23 (1C), 138.46 (2C), 138.83 (2C), 138.87 (2C), 139.31 (2C), 139.52 (2C), 139.57 (2C), 140.24 (1C), 140.57 (1C), 140.62 (2C), 140.85 (2C), 141.09 (2C), 141.91 (1C), 142.20 (2C), 143.25 (2C), 143.89 (2C), 144.24 (2+1C), 144.44 (2C), 145.00 (2C), 145.61 (2C), 147.74 (2C), 148.49 (2C), 149.26 (2C), 149.77 (2C), 150.61 (2C), 154.33 (1C), 155.06 (2C), 156.25 (1C), 158.76 (2C). MS (MALDI⁺, matrix: DHB) m/z : 3322 ($[M+Na]^+$). **S6.1** was slightly soluble in water.

S6.2. To a solution of **S5** (8.9 mg, 6.93 μ mol) in distilled DMF - *o*-DCB 1:1 (8 mL) was added HBTU (CHEM-IMPEX international, 11.0 mg, 29.0 μ mol), Amino-dPEG₃₆-*t*Bu ester (Quanta Biodesign, 95%), 33.0 mg, 19.06 μ mol), DIPEA (Fluka, distilled, 8.4 mg, 65 μ mol). The mixture was stirred for 4 days at room temperature. The solvent was removed *in vacuo* and diluted in a small volume of distilled THF. The crude mixture was subjected to a short SiO_2 plug (SiO_2 : 50 mg, eluent: THF). The elute was concentrated and was followed by precipitation in *n*-hexane (HPLC grade, Acros, 45 mL). The precipitates was dissolved in MeOH and purified by Sephadex LH-20 (10g) and the fractions were collected and dried overnight under vacuum to get a dark sticky solid **S6.2** (19.8 mg, 4.2 μ mol isolated yield 61%). MS (MALDI⁺, matrix: DHB) m/z : 4731 ($[M+Na]^+$).

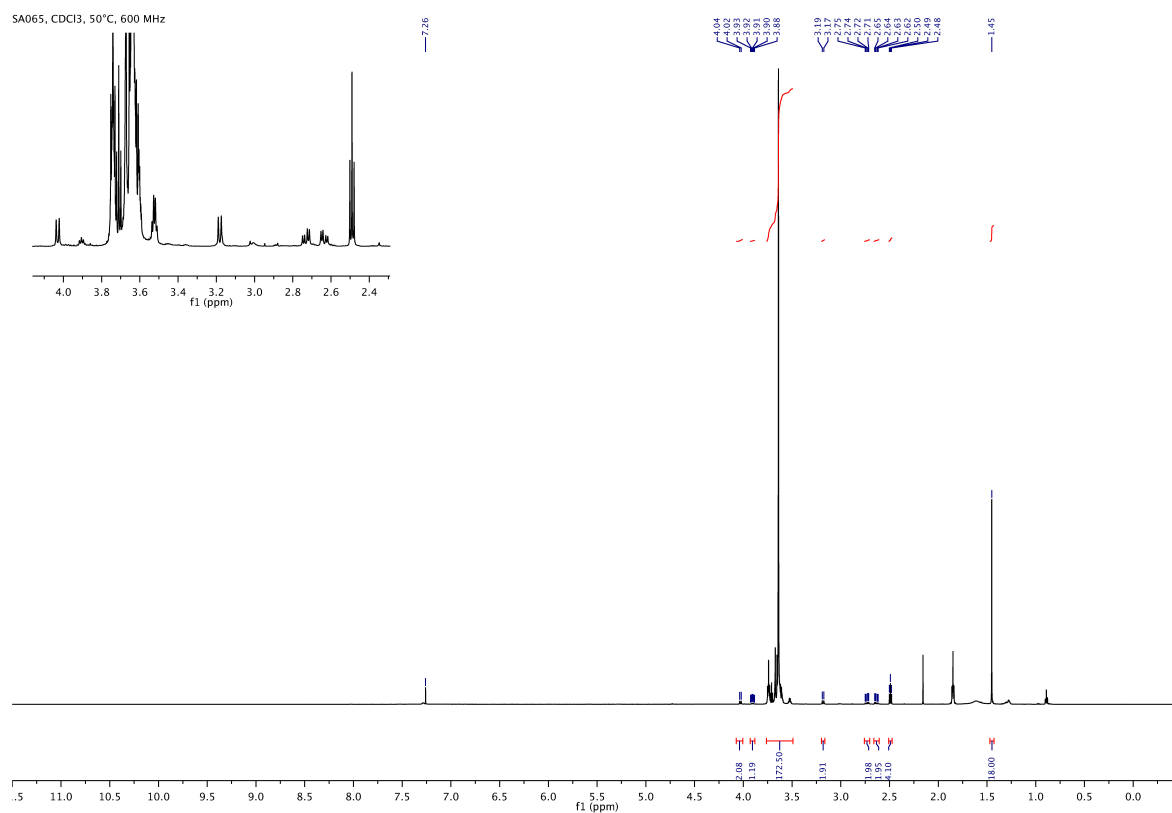


Figure S95. ¹H-NMR spectra of S6.1 (CDCl₃, 600 MHz)

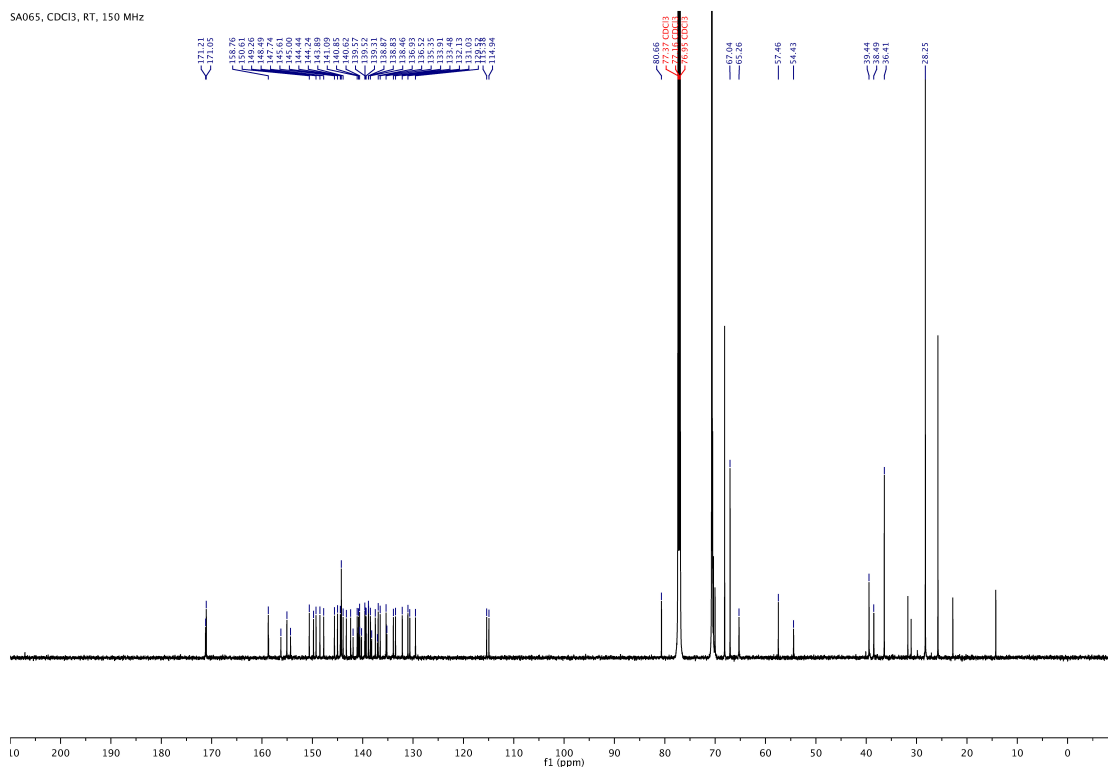


Figure S96. ¹³C-NMR spectra of S6.1 (CDCl₃, 150 MHz)

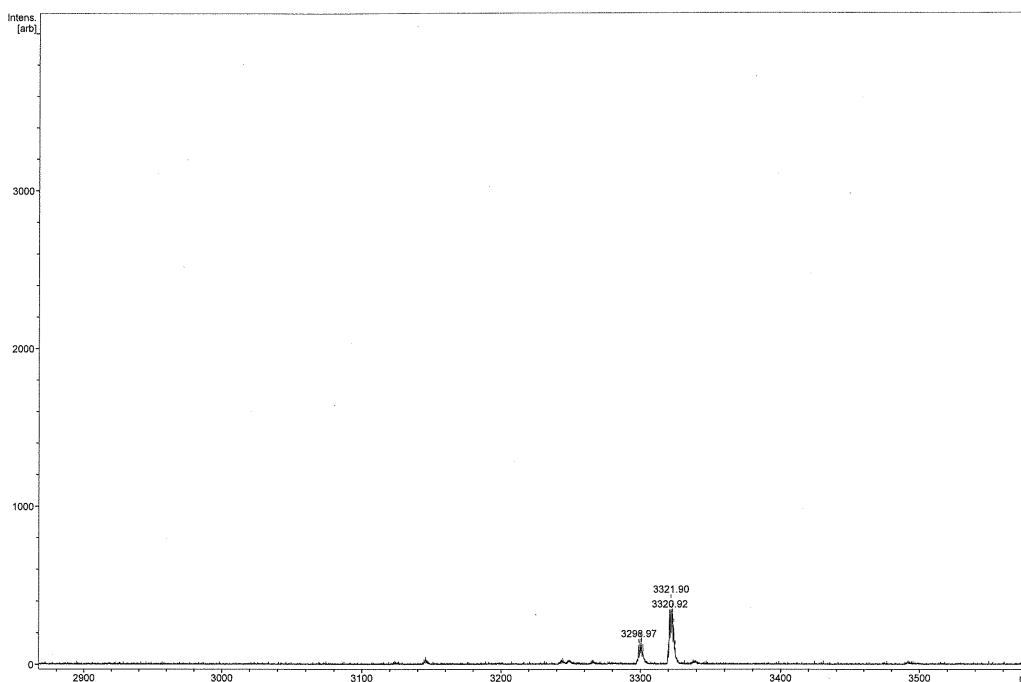


Figure S97. MALDI-TOF MS of compound **S6.1** (Matrix DHB).

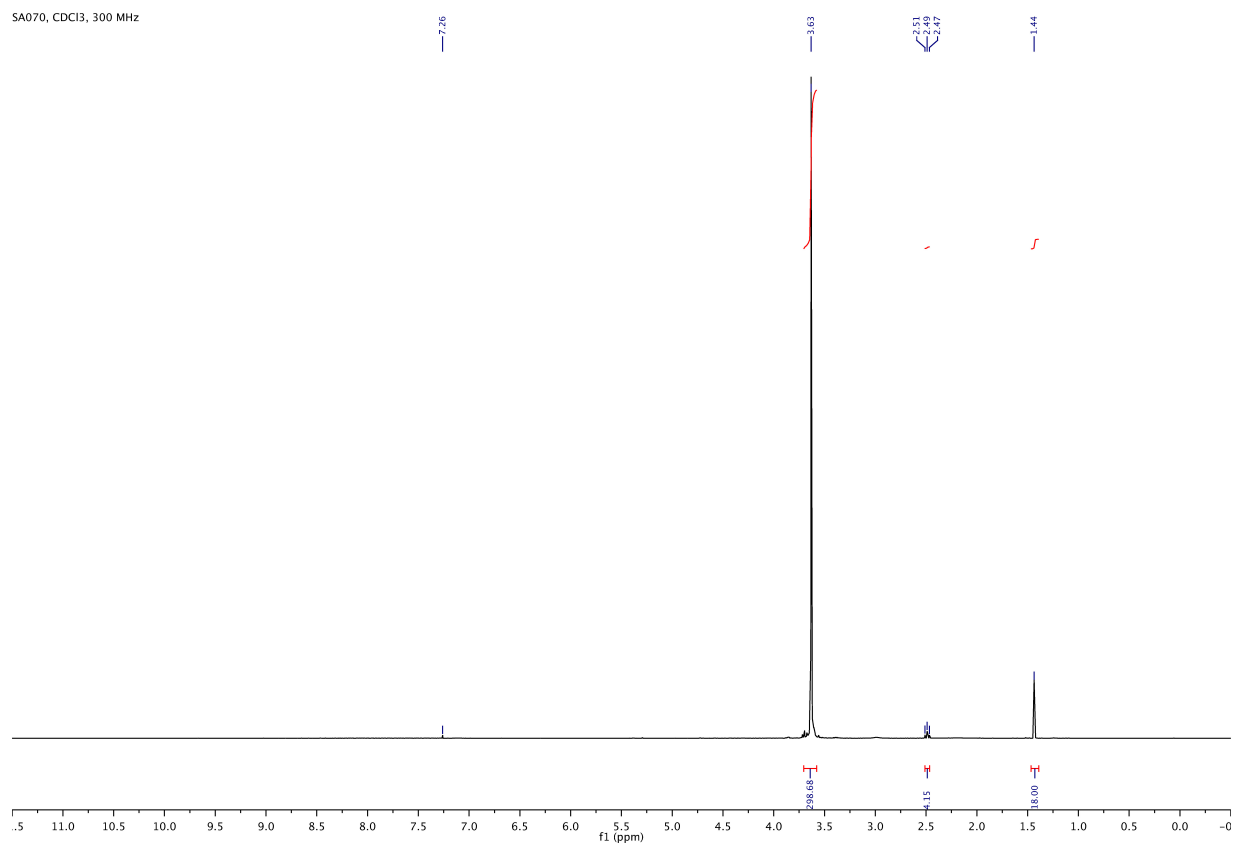


Figure S98. ¹H-NMR spectra of **S6.2** 300 MHz

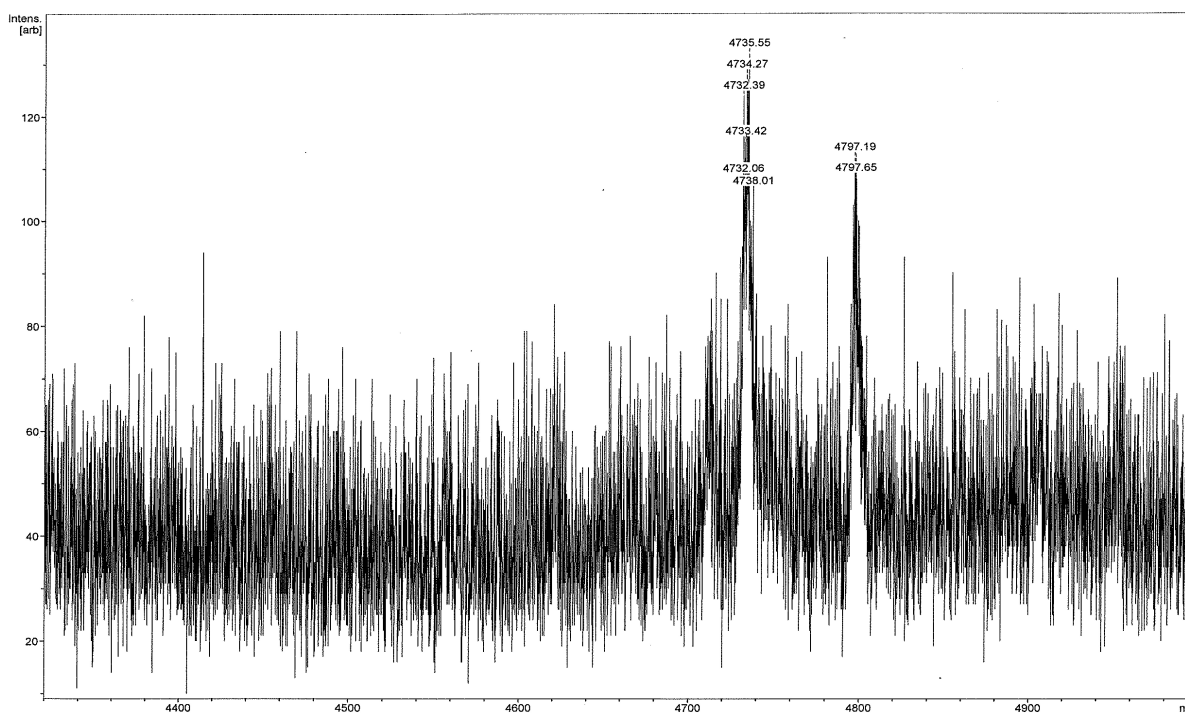
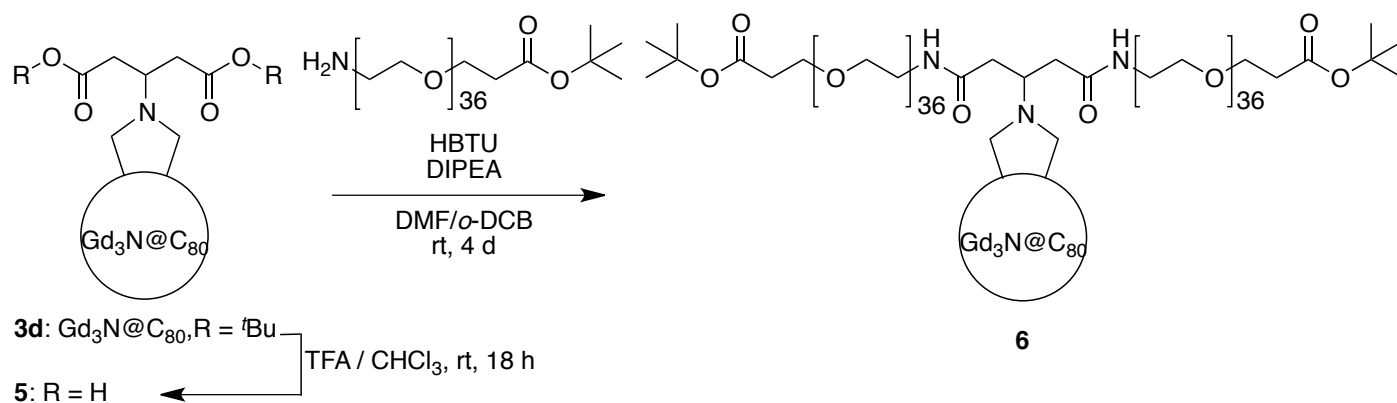


Figure S99. MALDI-TOF MS of compound **S6.2** (Matrix DHB).



5. To a solution of **3d** (11.8 mg, 6.81 μmol) in CHCl_3 (5 mL) was added trifluoroacetic acid (2.5 mL). The solution was stirred for 18 hrs at room temperature. The solvents and were removed *in vacuo* and dried under vacuum overnight to obtain a dark powder **5** (11.0 mg, 6.79 μmol , yield = 100 %).

6. To a solution of **5** (3.3 mg, 2.04 μmol) in distilled DMF - *o*-DCB 1:1 (3.2 mL) was added HBTU (CHEM-IMPEX international, 3.3 mg, 8.7 μmol), Amino-dPEG₃₆-*t*Bu ester (Quanta Biodesign, 95%, 10.0 mg, 5.78 μmol), DIPEA (Fluka, distilled, 2.74 mg, 21.2 μmol). The mixture was stirred for 4 days at room temperature. The solvent was removed *in vacuo* and diluted in small volume of distilled THF. The crude mixture was subjected to a short SiO_2 plug (SiO_2 : 50 mg, eluent: THF. The elute was concentrated and was followed by precipitation in *n*-hexane (HPLC grade, Acros, 45 mL). The precipitates was dissolved in MeOH and purified by Sephadex LH-20 (10g) and the fractions were collected and dried overnight under vacuum to get a dark sticky solid **6** (8.0 mg, 1.58 μmol isolated yield 77%). MS (MALDI⁺, matrix: DHB) m/z : 5069 ($[\text{M}+\text{Na}]^+$).

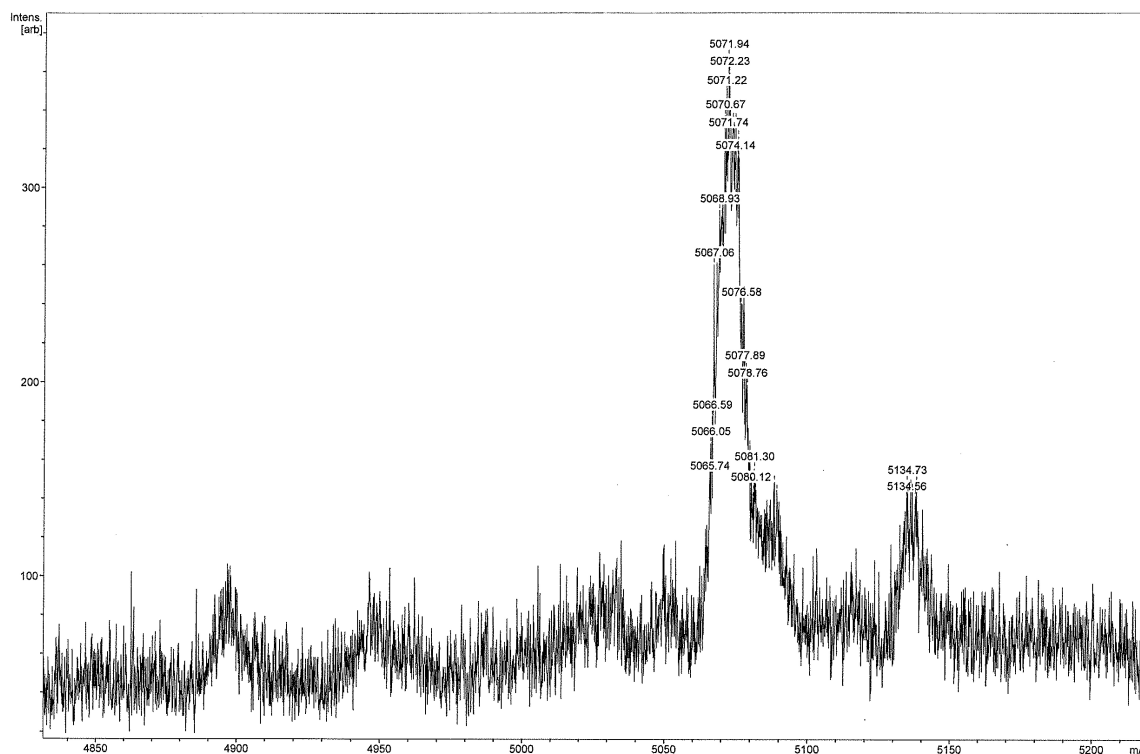


Figure S100. MALDI-TOF MS of compound **6** (Matrix DHB).