Supplementary data:

Fulleropyrrolidines Derived from Dioxa- and Trioxaalkyl-tethered Diglycines

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Content:

1. General experimental details and procedures

General: IR spectra were recorded with a *Perkin-Elmer FTIR 1725X* spectrophotometer. UV spectra were recorded with a *GBC-Cintra 40* UV-vis spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded with *Varian Gemini 200* (^{1}H at 200 MHz, ^{13}C at 50 MHz) and *Bruker Avance* spectrometers (^{1}H at 500 MHz, ^{13}C at 125 MHz). Chemical shifts are measured in ppm, *J* in Hz. Sample was dissolved in the indicated solvent system, and TMS was used as an internal reference. The high-resolution MS spectra were obtained with an *Agilent Technologies 6210* TOF LC-MS spectrometer. Dry-column flash chromatography (DCFC) was carried out with Merck silica gel 60 (15-40μm). Thin layer chromatography (TLC) was carried out on precoated silica gel 60 F254 plates.

HPTLC. All substances were chromatographed on HPTLC silica gel 60 aluminium sheets (Merck, 4.0 × 6.0 cm) as a stationary phase. Samples were applied by CAMAG Linomat 5 "linomat5_130827" S/N 130827 (1.00.12) device. Spots were detected by CAMAG TLC Scanner 3 „Scanner3_131003" S/N 131003 (1.14.26), at 340 nm. Software application winCATS Planar Chromatography Manager SN 1311W038, V1.4.2 was used for data processing. In addition, UV spectra of the spots were obtained by scanning from 200-700 nm.
System toluene/ethyl-acetate 7:3 was used for HPTLC of bisadducts **7-9**, while toluene/ethyl-acetate 1:1 was used for adducts **10-14** as a mobile phase.

Morphology investigations: Investigations of sample morphology were carried out with SEM, using a *JEOL JSM-840A* instrument, at an acceleration voltage of 30 kV. The samples for investigation of morphology of self-organized stuctures of **7-14** were prepared by dissolving in differente solvents (ODCB, PhMe, $CHCl_3$, PhMe/*i*-PrOH (1:1, v/v), PhMe/dioxane (1:1, v/v) at room temperature. A drop of 0.5 mM solution of fullerene derivative was deposited on the surface of a glass substrate (10x10 mm) and left during 24 h to slowly evaporate in a glass Petri dish (diameter 10 cm) under PhMe atmosphere at room temperature (the exceptions were made in case of ODCB solutions, in which 2-3 days were necessary for total evaporation of the solvent). The investigated samples were gold sputtered in a JFC 1100 ion sputter device and then subjected to SEM observations.

Electrochemical Measurements: The electrochemical behavior of C_{60} bis-adducts was investigated using 1mM solutions of bisadducts **7-13** and **15-19** and difullerene **14** in dry and degased mixture ODCB/DMF 2:1, and in DCM (only bisadducts **7-13**), both containing 0.1 M TBAP as a supporting electrolyte. In order to remove oxigen from the electrolyte, the system was bubbled with argon prior to each experiment and argon atmosphere above the liquid surface was maintained during the scans. The electrochemical mesurements were carried out on *CH1760b Electrochemical workstation potentiostat (CH Instruments, Austin, TX)* using conventional three-electrode cell (5 mL) equipped with GCE (glassy carbon electrode), as a working, Ag/Ag^+ (a silver wire in contact with 0.01 M $AgNO_3$ and 0.10 M TBAP in acetonitrile) , as a reference and the platinum wire as a auxiliary electrodes, calibrated with a ferrocene/ferrocenyl couple (Fc/Fc^+) as an internal standard. All experiments were performed at room temperature in the potential range of -2.5 to 0.5 V vs Ag/Ag^+ (i.e. -3.0 to 0.0 V vs Fc/Fc^+), at sweep rates between 0.01 and 1 V/s. All half-wave reduction potentials are presented in V vs Fc/Fc^+ (measured $E_{1/2}$ of Fc/Fc^+: 0.552 and 0.674 V vs Ag/Ag^+in DCM and ODCB/DMF 2:1, respectively).

Antioxidant Activity in vitro: The antioxidant capacity was determined according to a published procedure with minor changes. *Preparation of liposomal gel of fullerene C_{60} and fullerene derivatives **7-14*** [1]. Liposomes were composed of tested compounds and soybean lecithin in 1:4 mass ratio. Measured fullerene or fullerene bisadduct (0.1-1 mg) and fourfold mass of lecithin are solubilized in minimal volume of PhMe under the ultrasound for 1 minute. Solvent was evaporated and film of lipid-fullerene complex carefully diluted on vortex with deionized water to the concentration of the fullerenic component of 0.02 mg/mL. The final concentration of the pure compound of 0.002 mg/mL was obtained prior to use mixing the solution with water in 1:9 ratio.

[1] M. B. Lens, E. De Marni, R. Gullo,U. Citernesi and R. Crippa, WO 043074 A1, 2007.

FOX reagent preparation[2]. Working FOX reagent was preared by adding 10 mL of Reagent 2 (98 mg of $(NH_4)_2Fe(SO_4)_2x6H_2O$ (FAS) in 100 mL of 250mM H_2SO_4) to 900 mL of Reagent 1 (95 mg of xylenol orange sodium salt (XO) and 880 mg of 2,6-di-t-butyl-4-methylphenol (BHT) in 900 mL of MeOH) giving the final concentrations of 250 μM FAS, 125 μM of XO, 25 mM H_2SO_4, and 4 mM BHT. The reagent was consumed within 24 h. The apsorbance was measured at 560 nm by UV-vis spectrophotometer *GBC-Cintra 40* with 90% MeOH as a zero probe.

The applicability of the method in used range of peroxide concentration was confirmed by preparing standard calibration curve using increasing concentrations of peroxide (TBHP or H_2O_2; 0-200 μM) incubated with FOX reagent at room temperature for 30 min. Absorbances measured at 560 nm at the different concentrations confirmed linear correlation.

Sample preparation. The fullerenesomes and vitamin C solutions (0.02 mg/mL) were diluted by nine-fold volume of water to gain 0.002 mg/mL concentration prior to use (0.050 mL : 0.450 mL of water). The same volume of 200 μM peroxide (obtained by diluting 0.050 mL of 2 mM peroxide with 0.450 mL of water) was added to the sample and vortexed for 1 min. After 10 min of incubation at room temperature, to an aliquot of 0.050 mL of the sample 0.950 mL of FOX reagent was added. Absorbance at 560 nm was determined for each sample after 80 min. of incubation at room temperature.

Standard probe preparation. The standard probe of peroxides were prepared by mixing the same volume of 200 μM peroxide (obtained by diluting 0.050 mL of 2 mM peroxide with 0.450 mL of water) and water. To a 0.050mL of mixture 0.950 mL of FOX reagent was added. The absorbance of the standard probe, determined after 80 min., reffers to the starting (maximum) concentration of the peroxide, prior to incubation. Difference of absorbances of the standard probe (As) and sample (A) is proportional to the quantity of the consumed peroxide by the sample compound.

Blank probe preparation. The blank probe contained 0.950 mL of FOX reagent and 0.050 mL of water. Apsorbance of the blank probe measured at 560 nm (A_0) reffers to the color of the reagent itself in the absence of the peroxide, and all absorbances of the samples and standards are diminished by the value of A_0 for the calculations of the peroxide concentration.

All experiments were performed in triplicates, and the average values were taken.

Antioxidative capacities were calculated according to formula (1):

$$\Delta\ (\%) = 100\times(A-A_s)/(A_s-A_0), \qquad (1)$$

where A_0, As and A are apsorbance values determined at the same conditions for blank probe, standard peroxide solution and probe, respectively.

The antioxidant activities relative to the equimolar concentration of vitamin C were calculated using the equation (2):

$$AOA_{mol}\ \text{vs vit C} = (\Delta/\Delta_{vit\ C})/(M/M_{vit\ C}) \qquad (2)$$

where Δ and Δvit C represent the direct antioxidant capacity of the tested compound and vitamin C, respectivelly and M and $M_{vit\ C}$ their molecular weights.

The antioxidant activities relative to the equimolar concentration of the fullerene C_{60} were calculated using the equation (3):

$$AOA_{mol}\ \text{vs } C_{60} = (\Delta/\Delta_{C60})/(M/M_{C60}) \qquad (3)$$

where Δ and ΔC_{60} represent the direct antioxidant capacity of the tested compound and the C_{60}, respectivelly and M and M_{C60} their molecular weights.

[2] S. Gao, M. Miller, X. Q. Han, EP 1593685 A1, 2005.

2. Synthesis of the compounds 3-6[3]

Dibenzyl-*N,N′*-(3,6-dioxaoctane-1,8-diyl)diglycinate (3). To an ice-cooled solution of diamine **1** (4.06 g, 4.00 mL, 0.027 mol, 1 mol equiv) and TEA (5.53 g, 7.80 mL, 0.055 mol, 2 mol equiv) in DCM (160 mL), solution of BBA (12.6 g, 8.60 mL, 0.055 mol, 2 mol equiv) in DCM (80 mL), was added dropwise, during 5h. After additional stirring for 24h, mixture was washed with H_2O (3 x100 mL) and then with brine (2 x100 mL), and dried over anh. Na_2SO_4. The solvent was removed in vacuo and the remaining material was purified on a SiO_2 column by dry-flash chromatography. Dibenzyl-*N,N′*-(3,6-dioxaoctane-1,8-diyl)diglycinate (**3**) was isolated as a colourless oil (4.94 g, 41%) using EtOAc/MeOH 9:1 as an eluent. IR (ATR): $\tilde{\nu}$/cm^{-1} 3379, 3031, 2872, 1745, 1665, 1456, 1353, 1198, 1117, 1023, 746, 702. NMR: δH (500 MHz, $CDCl_3$, Me_4Si): 7.34 (5H, *s*, CH^{Ar}); 5.15 (2H, *s*, CH_2^{Bn}); 3.61 (2H, *s*, CH_2^4); 3.61 (2H, *t*, *J*=5.0 Hz, CH_2^2); 3.51 (2H, *s*, CH_2^{Gly}); 3.31 (1H, *br s*, N*H*); 2.83 ppm (2H, *t*, *J*=5.0 Hz, CH_2^1). δC (125 MHz, $CDCl_3$, Me_4Si): 171.88 (C=O); 135.49 (C_q^{Ar}); 128.49; 128.28; and 128.25 (CH^{Ar}); 70.22 and 70.04 ($CH_2^{2,4}$); 66.48 (CH_2^{Bn}); 50.62 (CH_2^{Gly}); 48.63 ppm (CH_2^1). HR-MS: *m/z* calc. for $[C_{24}H_{33}N_2O_6+H]^+$: 445.23331, measured 445.23183; calc. for $[C_{24}H_{32}N_2O_6+Na]^+$: 467.21526, measured 467.21342.

Dibenzyl-*N,N′*-(4,7,10-trioxatridecane-1,13-diyl)diglycinate (4) To an ice-cooled solution of diamine **7** (4.02 g; 4.00 mL; 0.018 mol; 1 mol equiv) and TEA (3.68 g; 5.04 mL; 0.036 mol; 2 mol equiv) in DCM (112 mL), solution of BBA (8.34 g; 5.72 ml; 0.036 mol; 2 mol equiv) in DCM (56 mL), was added dropwise, during 6h. After additional stirring for 20h, mixture was washed with H_2O (3 x100 mL) and then with brine (2 x100 mL), and dried over anh. Na_2SO_4. The solvent was removed in vacuo and the remaining material was purified on a SiO_2 column by dry-flash chromatography. Dibenzyl-*N,N′*-(4,7,10-trioxatridecane-1,13-diyl)diglycinate (**4**) was isolated as a colourless oil (1.54 g, 33%) using EtOAc/MeOH 4:1 as an eluent. IR (ATR): $\tilde{\nu}$/cm^{-1} 3340, 3063, 3033, 2941, 2868, 1742, 1458, 1350, 1212, 1184, 1150, 968, 750, 701. NMR: δH (200 MHz, $CDCl_3$, Me_4Si) 7.35 (*s*, 5H, CH^{Ar}); 5.16 (*s*, 2H, CH_2^{Bn}); 3.68-3.48 (*m*, 6H, $CH_2^{3,5,6}$); 3.44 (*s*, 2H, CH_2^{Gly}); 2.69 (*t*, *J*=6.6 Hz, 2H, CH_2^1); 1.86 (*s*, 1H, NH); 1.77 ppm (*quint*, *J*=6.6 Hz, 2H, CH_2^2). δC (50 MHz, $CDCl_3$, Me_4Si) 172.33 (C=O), 135.59 (C_q^{Ar}), 128.53; 128.29 (CH^{Ar}), 70.50; 70.10 ($CH_2^{5,6}$), 69.52 (CH_2^3), 66.38 (CH_2^{Bn}), 50.91 (CH_2^{Gly}), 46.81 (CH_2^1), 29.86 ppm (CH_2^2). HR-MS: *m/z* calc. for $[C_{28}H_{42}N_2O_7+2H]^{2+}$: 259.14905, measured 259.14980; calc. for $[C_{28}H_{40}N_2O_7+Na]^+$: 539.27277, measured 539.27333; calc. for $[C_{28}H_{41}N_2O_7+H]^+$: 517.29083, measured 517.29112.

***N,N′*-(3,6-dioxaoctane-1,8-diyl)diglycine (5).** To a solution of dibenzyl ester **3** (1.61 g; 3.622 mmol, MeOH 100 mL) 5% Pd/C was added (161 mg) and suspension was bubbled with argon. Mixture was hydrogenated at 40 psi for 20 h. After filtering the catalyst and evaporating the solvent, crude diacid **5** was isolated as colorless oil (940 mg; 98%). It was characterized spectroscopicaly and used for cycloaddition reaction without further purification. IR (ATR): $\tilde{\nu}$/cm^{-1} 3093, 2955, 2890, 1626, 1573, 1462, 1417, 1371, 1310, 1242, 1211, 1118, 1085, 868, 600, 563. NMR: δH (500 MHz, CD_3OD, Me_4Si) 3.82 (*t*, *J*=5.0 Hz, 2H, CH_2^2); 3.73 (*s*, 2H, CH_2^4); 3.61 (*s*, 2H, CH_2^{Gly}); 3.29 (*t*, *J*=5.0 Hz, 2H, CH_2^1) ppm. δC (125 MHz, CD_3OD, Me_4Si) 171.54 (C=O); 71.13 (CH_2^4); 66.95 (CH_2^2); 50.43 (CH_2^{Gly}); 48.16 (CH_2^1) ppm. HR-MS: *m/z* calc. for $[C_{10}H_{21}N_2O_6+H]^+$: 265.13941, measured 265.13866; calc.for $[C_{10}H_{20}N_2O_6+Na]^+$: 287.12136, measured 287.11965.

***N,N′*-(4,7,10-trioxatridecane-1,13-diyl)diglycine (6).** To a solution of dibenzyl ester **4** (840 mg; 1.626 mmol , MeOH 100 mL) 5% Pd/C was added (85 mg) and suspension was bubbled with argon. Mixture was hydrogenated at 40 psi for 20 h. After filtering the catalyst and evaporating the solvent, crude diacid **6** was isolated as a colorless oil (530 mg; 97 %). IR (ATR): $\tilde{\nu}$/cm^{-1} 3315, 3064, 2926, 2874, 1740, 1620, 1600, 1454, 1395, 1324, 1243, 1208, 1134, 733, 697. NMR: δH (500 MHz, CD_3OD, Me_4Si) 3.69-3.61 (*m*, 6H,$CH_2^{3,5,6}$); 3.52 (*s*, 2H, CH_2^{Gly}); 3.18 (*t*, *J*=5.0 Hz, 2H, CH_2^1); 1.98 ppm (*quint*, *J*=6.0, 2H, CH_2^2). δC (125 MHz, CD_3OD, Me_4Si) 171.28 (C=O); 71.50 ($CH_2^{5,6}$); 70.73 (CH_2^3); 50.98 (CH_2^{Gly}); 48.32 (CH_2^1); 27.23 ppm (CH_2^2). HR-MS: *m/z* calc. for $[C_{14}H_{30}N_2O_7+2H]^{2+}$: 169.10210, measured 169.10168; calc. for $[C_{14}H_{29}N_2O_7+H]^+$: 337.19693, measured 337.19538; calc. for $[C_{14}H_{28}N_2O_7+Na]^+$: 359.17887, measured 359.17724.

[3] T. Kop , M. Bjelaković and D. Milić, *Tetrahedron*, 2015, **71**, 4801-4809.

3. Synthesis of the fulleropyrrolidines 7-14[3]

Bisadducts 7-9. A suspension of C_{60} (545 mg; 0.757 mmol; 1 mol equiv), diglycine **5** (200 mg; 0.757 mmol; 1 mol equiv) and HCHO (230 mg; 7.570 mmol; 10 mol equiv) in ODCB (150 mL) was maintained at 160°C during 4 h. The obtained reaction mixture was cooled to room temperature, mixed with the same volume of hexane, deposited directly on the top of the SiO_2 column (to remove solvent without further heating) and separated by dry-flash column chromatography. Elution with toluene yielded unreacted C_{60} (220 mg; 40.4%). Bisadducts (187.7 mg; 27.0 %) were eluted by listed eluents: bisadduct **7** (*cis*-1, 17.3 mg; 2.5%) was eluted with PhMe/EtOAc 7:3, bisadduct **8** (*cis*-2; 124.6 mg; 17.9%) with PhMe/EtOAc 6:4 and bisadduct **9** (*cis*-3; 45.8 mg; 6.6 %) with PhMe/EtOAc 1:1. All products were purified by precipitation with MeOH from highly concentrated CS_2/DCM solutions.

Bisadduct 7 (*cis*-1): R_f=0.52 (PhMe/EtOAc 1:1); UV/Vis: λ_{max}(PhMe)/nm 330 (ε/ $mol^{-1}dm^3cm^{-1}$ 30000), 402 (7000), 427 (6000), 622 (210), 654 (200), 684 (160), 722 (160). IR (ATR) $\tilde{\nu}/cm^{-1}$ 2923, 2851, 2785, 2334, 2024, 1505, 1453, 1427, 1334, 1304, 1203, 1150, 1115, 964, 757. NMR: δH (500 MHz, $CDCl_3$, Me_4Si) 4.80 (*d*, *J*=10.0 Hz, 2H, CH^{pyrr}); 4.47 (*d*, *J*=8.5 Hz 2H, CH^{pyrr}); 4.01 (*d*, *J*=8.0 Hz, 2H, CH^{pyrr}); 4.00-3.92 (*m*, 4H, $CH_2^{2,7}$), 3.88-3.82 (*m*, 2H, $CH_2^{4,5}$); 3.82-3.76 (*m*, 2H, $CH_2^{4',5'}$); 3.52 (*d*, *J*=10.0 Hz, 2H, CH^{pyrr}); 3.38 (*ddd*, *J*=3.0; 7.0; 13.5 Hz; 2H, $CH^{1,8}$); 3.11 (*ddd*, *J*=3.0; 5.5; 14.0 Hz; 2H, $CH^{1',8'}$) ppm. δC (125 MHz, $CDCl_3$, Me_4Si) 151.96 (2C); 151.15 (2C); 150.58 (2C); 148.79 (2C); 147.87 (2C); 147. 08 (2C); 146.82 (2C); 146.20 (2C); 145.96 (2C); 145.92 (1C); 145.37 (2C); 145.18 (2C); 144.89 (2C); 144.84 (2C); 144.42 (2C); 144.11(2C); 143.88 (2C); 143.79 (2C); 143.59 (2C); 142.87 (2C); 142.55 (1C); 142.30 (2C); 142.24 (1C); 142.17 (2C); 141.82 (2C); 141.58 (2C); 140.61 (2C); 137.85 (1C); 135.08 (2C); 134.89 (2C); 69.46 ($C^{4,5}$); 68.63 ($C^{2,7}$); 67.59 (2*sp3*-C^{full}); 66.42 ($2CH^{pyrr}$); 66.16 (2*sp3*-C^{full}); 66.06 ($2CH^{pyrr}$); 52.91 ppm ($C^{1,8}$). HR-MS: *m/z* calc. for $[C_{70}H_{20}N_2O_2+H]^+$: 921.15975, measured 921.15538.

Bisadduct 8 (*cis*-2): R_f=0.43 (PhMe/EtOAc 1:1); UV/Vis: λ_{max} (PhMe)/nm 310 (ε/ $mol^{-1}dm^3cm^{-1}$ 40000); 374 (4900); 448 (4800); 487 (3000); 572 (910); 647 (430); 680 (280). IR(ATR): $\tilde{\nu}/cm^{-1}$ 2930, 2880, 2852, 2808, 2771, 1509, 1457, 1425, 1347, 1314, 1179, 1129, 1110, 1081, 973, 733, 526. NMR: δH (500 MHz, $CDCl_3$, Me_4Si) 5.34 (*dd*, *J*=10.0; 2.0 Hz, 2H, CH^{pyrr}), 4.27 (*dd*, *J*=9.0; 2.0 Hz, 2H, CH^{pyrr}); 4.02 (*ddd*, *J*=2.5; 8.0; 9.5 Hz; 2H, $CH^{2,7}$); 3.90-3.80 (*m*, 6H, $CH_2^{2',7',4,5}$); 3.64 (*d*, *J*=9.0 Hz; 2H, CH^{pyrr}); 3.52 (*ddd*, *J*=2.5; 5.5; 13.0 Hz; 2H, $CH^{1,8}$); 3.32 (*d*, *J*=10.0 Hz, 2H, CH^{pyrr}); 2.83 ppm (*ddd*, *J*=2.0, 8.0; 13.0 Hz; 2H, $CH^{1',8'}$). δC (125 MHz, $CDCl_3$, Me_4Si) 159.83 (2C); 155.61 (2C); 149.12 (2C); 148.80 (1C); 148.72 (1C); 148.56 (1C); 147.49 (2C); 147.18 (2C); 147.04 (2C); 146.72 (2C); 146.58 (2C); 146.23 (2C); 146.18 (2C); 146.00 (2C); 145.74 (2C); 145.37 (2C); 145.18 (2C); 145.08 (2C); 144.60 (2C); 144.57 (2C); 144.26 (2C); 143.94 (2C); 143.81 (2C); 143.01 (2C); 141.51 (2C); 140.71 (2C); 139.05 (2C); 133.53 (2C); 132.89 (2C); 129.49 (1C); 71.88 ($C^{2,7}$); 70.38 ($C^{4,5}$); 68.50 ($2CH^{pyrr}$); 68.48 ($2CH^{pyrr}$); 67.78 (2*sp3*-C^{full}); 67.74 (2*sp3*-C^{full}); 52.55 ppm ($C^{1,8}$). HR-MS: *m/z* calc. for $[C_{70}H_{20}N_2O_2+H]^+$: 921.15975; measured 921.16010.

Bisadduct 9 (*cis*-3): R_f=0.17 (PhMe/EtOAc 1:1); R_f=0.48 (PhMe/MeOH 4:1); UV/Vis: λ_{max} (PhMe)/nm 300 (ε/ $mol^{-1}dm^3cm^{-1}$ 47000); 331 (31000); 391 (11000); 431 (2900); 467 (2000); 548 (800); 657 (360); 732 (280). IR (ATR): $\tilde{\nu}/cm^{-1}$ 2916, 2859, 2772, 1676, 1451, 1427, 1341, 1305, 1274, 1112, 965, 759, 521. NMR: δH (500 MHz, $CDCl_3$, Me_4Si) 4.68 (*dd*, *J*=9.5; 2.0 Hz, 2H, CH^{pyrr}); 4.47 (*dd*, *J*=9.0; *J*=2.0 Hz, 2H, CH^{pyrr}); 4.08 (*d*, *J*=9.0 Hz, 2H, CH^{pyrr}); 3.93-3.90 (*m*, 2H, $CH^{4,5}$); 3.90-3.83 (*m*, 4H, $CH_2^{2,7}$); 3.83-3.78 (*m*, 2H, $CH^{4',5'}$); 3.71 (*ddd*, 12.5; 9.5; 5.0 Hz; 2H, $CH^{1,8}$); 3.49 (*d*, *J*=9.5 Hz, 2H, CH^{pyrr}); 2.85 ppm (*dt*, *J*=12.5; 4.0 Hz, 2H, $CH^{1',8'}$). δC (125 MHz, $CDCl_3$, Me_4Si) 153.95 (2C); 149.64 (2C); 149.05 (2C); 148.55 (2C); 148.23 (2C); 148.22 (2C); 147.77 (2C); 146.90 (2C); 146.59 (2C); 146.23 (2C); 146.05 (2C); 145.93 (2C); 145.70 (2C); 145.66 (2C); 145.10 (2C); 144.91 (2C); 144.71 (2C); 142.16 (2C); 142.12 (4C); 142.06 (2C); 141.70 (2C); 139.74 (2C); 138.21 (2C); 137.07 (2C); 135.36 (2C); 134.64 (2C); 130.26 (2C); 70.87 ($C^{4,5}$); 70.36 (2*sp3*-C^{full}); 69.41 ($C^{2,7}$); 69.09 ($2CH_2^{pyrr}$); 66.44 (2*sp3*-C^{full}); 65.72 ($2CH_2^{pyrr}$); 52.28 ppm ($C^{1,8}$). HR-MS: *m/z* calc. for $[C_{70}H_{20}N_2O_2+H]^+$: 921.15975, measured 921.15997.

Compounds 10-14. A suspension of diacid **6** (255 mg; 0.757 mmol; 1 mol equiv), C_{60} (545 mg; 0.757 mmol; 1 mol equiv) and HCHO (230 mg; 7.57 mmol; 10 mol equiv) in ODCB (150 ml) was maintained at 160°C during 4 h. The obtained reaction mixture was cooled to room temperature, mixed with the same volume of hexane, deposited directly on the top of the SiO_2 column (to remove solvent without further heating) and separated by dry-flash column chromatography (DFC). DFC yielded: C_{60} (300 mg; 54.5%; eluent: toluene) difullerene **14** (20.5 mg; 3.2%; eluent: PhMe/EtOAc 8:2) and bisadducts (total yield 194.6 mg; 24.8 %): bisadduct **10** (*cis*-1; 18.9 mg; 2.5%), eluted with PhMe/EtOAc 7:3, bisadduct **13** (*eq*; 24.7 mg; 3.3%), eluted with PhMe/EtOAc 6:4, bisadduct **12** (*cis*-3, 60.5 mg; 7.0 %), eluted with PhMe/EtOAc 1:1 and bisadduct **11** (*cis*-2; 90.5 mg; 12.0 %) eluted also with PhMe/EtOAc 1:1. All products were purified by precipitation with MeOH from highly concentrated DCM solutions.

Bisadduct 10 (*cis*-1): R_f=0.46 (PhMe/EtOAc 1:1). UV/Vis: λ_{max}(PhMe)/nm 328 (ε/ $mol^{-1}dm^3cm^{-1}$ 32000); 406 (7000); 430 (5900); 623 (200); 651 (170); 676 (140); 710 (140). IR (ATR): $\tilde{\nu}$/cm^{-1} 2944, 2870, 2810, 1466, 1426, 1355, 1169, 1124, 735. NMR: δH (500 MHz, $CDCl_3$, Me_4Si) 4.28 (*d*, *J*=9.5 Hz, 2H, CH^{pyrr}); 4.26 (*d*, *J*=8.5 Hz, 2H, CH^{pyrr}); 4.04 (*d*, *J*=8.5 Hz, 2H, CH^{pyrr}); 3.98 (*ddd*, *J*=5.0; 8.0; 10.0 Hz; 2H, $CH^{3,11}$); 3.86-3.76 (*m*, 10H, $CH^{3',11'}$, 4CH_2-O); 3.66 (*d*, *J*=9.5 Hz, 2H, CH^{pyrr}); 3.23 (*ddd*, *J*= 7.0; 8.0; 11.5 Hz; 2H, $CH^{1,13}$); 2.98 (*ddd*, *J*=5.5; 8.5; 12.0 Hz; 2H, $CH^{1',13'}$); 2.23-2.07 ppm (*m*, 4H, $CH_2^{2,12}$). δC (125 MHz, $CDCl_3$, Me_4Si) 151.90 (2C); 151.06 (2C); 150.19 (2C); 148.93 (2C); 148.05 (2C); 147. 24 (2C); 146.99 (2C); 146.34 (2C); 146.09 (2C); 145.91 (1C); 145.43 (2C); 145.34 (2C); 145.00 (4C); 144.57 (2C); 144.22 (2C); 144.04 (2C); 143.96 (2C); 143.72 (2C); 143.00 (2C); 142.69 (1C); 142.43 (2C); 142.34 (1C); 142.30 (2C); 141.91 (2C); 141.56 (2C); 140.77 (2C); 137.94 (1C); 135.24 (2C); 135.06 (2C), 70.91 (C-O); 70.22 (C-O); 69.34 ($C^{3,11}$); 68.46 ($2CH_2^{pyrr}$); 68.10 (2*sp3*-C^{full}); 66.59 ($2CH_2^{pyrr}$); 65.73 (2*sp3*-C^{full}); 52.47 ($C^{1,13}$); 28.87 ppm ($C^{2,12}$). HR-MS: *m/z* calc. for $[C_{74}H_{29}N_2O_3+H]^+$: 993.21727, measured 993.21561.

Bisadduct 11 (*cis*-2): R_f=0.16 (PhMe/EtOAc 1:1); R_f=0.46 (PhMe/MeOH 4:1). UV/Vis: λ_{max}(PhMe)/nm 310 (ε/$mol^{-1}dm^3cm^{-1}$ 43000); 375 (5300); 448 (5100); 483 (3000); 578 (900); 643 (420); 679 (280). IR(ATR): $\tilde{\nu}$/cm^{-1} 2879, 2775, 1452, 1345, 1244, 1120, 1093, 914, 724, 526. NMR: δH (500 MHz, $CDCl_3$, Me_4Si) 4.01 (*d*, *J*=9.0 Hz; 2H, CH^{pyrr}); 3.96 (*d*, *J*=9.0 Hz; 2H, CH^{pyrr}); 3.93 (*d*, *J*=9.5 Hz; 2H, CH^{pyrr}); 3.83-3.75 (*m*, 4H, $CH_2^{3,11}$); 3.81 (*d*, *J*=9.5 Hz; 2H, CH^{pyrr}); 3.81-3.70 (*m*, 4H, 2CH_2-O); 3.72-3.67 (*m*, 4H, 2CH_2-O) 3.16 (*dt*, *J*=12.0; 7.0 Hz; 2H, $CH^{1,13}$); 2.90 (*dt*, *J*=12.0; 6.0 Hz; 2H, $CH^{1',13'}$); 2.07 ppm (*quint*, *J*=5.5 Hz; 4H, $CH_2^{2,12}$). δC (125 MHz, $CDCl_3$, Me_4Si) 159.01 (2C); 156.41 (2C); 149.27 (2C); 148.86 (1C); 148.78 (1C); 148.27 (1C), 147.93 (2C); 147.64 (2C); 147.51 (2C); 147.05 (2C); 146.89 (2C); 146.46 (2C); 146.11 (2C), 145.71 (2C); 145.70 (2C); 145.65 (2C); 145.34 (2C); 145.15 (2C); 144.83 (2C); 144.57 (2C); 144.43 (2C); 144.18 (2C); 144.01 (2C); 142.98 (2C); 141.63 (2C); 140.94 (2C); 138.86 (2C); 133.79 (2C); 133.05 (2C); 129.18 (1C); 70.69 (C-O); 70.58 (C-O); 68.76 ($C^{3,11}$); 68.22 ($2CH^{pyrr}$); 67.43 ($2CH^{pyrr}$); 67.35 (2*sp3*-C^{full}); 67.07 (2*sp3*-C^{full}); 50.96 ($C^{1,13}$); 28.69 ppm ($C^{2,12}$). HR-MS: *m/z* calc. for $[C_{74}H_{29}N_2O_3+H]^+$: 993.21727, measured 993.21682.

Bisadduct 12 (*cis*-3): R_f=0.34 (PhMe/EtOAc 1:1). UV/Vis: λ_{max}(PhMe)/nm 299 (ε/ $mol^{-1}dm^3cm^{-1}$ 49000); 330 (34000); 398 (9600), 435 (3900); 464 (2600); 551 (1400); 640 (470); 729 (320). IR(ATR): $\tilde{\nu}$/cm^{-1} 2944, 2864, 2801, 2778, 1455, 1343, 1120, 767, 526. NMR: δH (500 MHz, $CDCl_3$, Me_4Si) 4.36 (*dd*, *J*=9.0; 1.5 Hz; 2H, CH^{pyrr}); 4.28 (*dd*, *J*=9.5; 1.5 Hz, 2H, CH^{pyrr}); 3.90-3.84 (*m*, 2H, $CH^{3,11}$); 3.85-3.75 (*m*, 8H, 4CH_2-O); 3.78 (*d*, *J*=9.0 Hz, 2H, CH^{pyrr}); 3.70 (*dt*, *J*=10.0; 5.5 Hz; 2H, $CH^{3',11'}$); 3.61 (*d*, *J*=9.5 Hz, 2H, CH^{pyrr}); 3.25 (*dt*, *J*=12.0; 7.0 Hz; 2H, $CH^{1,13}$); 2.81 (*dt*, *J*=12.0; 6.0 Hz; 2H, $CH^{1',13'}$); 2.11-1.99 ppm (*m*, 4H, $CH_2^{2,12}$). δC (125 MHz, $CDCl_3$, Me_4Si) 153.49(2C); 149.79(2C); 149.09(2C); 148.61(2C); 148.29(2C); 148.08(2C); 147.78(2C); 147.03(2C); 146.26(2C); 146.15(2C); 146.12(2C); 145.98(2C); 145.76(2C); 145.62(2C); 145.18(2C); 144.98(2C); 144.85(2C); 142.16 (4C); 142.13 (2C); 142.07 (2C); 141.65(2C); 139.79(2C); 138.37(2C); 137.11 (2C); 135.10(2C); 134.05(2C); 130.49(2C); 71.09 (C-O); 70.58 (C-O); 69.69 (2*sp3*-C^{full}); 69.11 ($2CH_2^{pyrr}$); 68.29 ($C^{3,11}$); 67.33 ($2CH_2^{pyrr}$); 65.66 (2*sp3*-C^{full}); 50.06 ($C^{1,13}$); 28.40 ppm ($C^{2,12}$). HR-MS: *m/z* calc. for $[C_{74}H_{29}N_2O_3+H]^+$: 993.21727; measured 993.21515.

Bisadduct 13 (*eq*): R_f=0.36 (PhMe/EtOAc 1:1); UV/Vis: λ_{max}(PhMe)/nm 319 (ε/ $mol^{-1}dm^3cm^{-1}$ 42000); 399 (6700); 423 (6100); 456 (5900); 553 (1300); 584 (980); 627 (410); 710 (100). IR(ATR): $\tilde{\nu}$/cm^{-1} 3048, 2947, 2870, 2804, 1677, 1474, 1345, 1235, 1175, 1126, 771, 738, 529. NMR: δH (500 MHz, $CDCl_3$, Me_4Si) 4.42 (*dd*, *J*=9.0; 1.0 Hz, 2H, CH^{pyrr-2}); 4.11 (*s*, 2H, CH_2^{pyrr-1}); 4.04 (*s*, 2H, CH_2^{pyrr-1}); 3.80 (*dd*, *J*=9.0; 1.0 Hz, 2H, CH^{pyrr-2}); 3.81-3.77 (*m*, 2H, CH_2^3); 3.78 (*t*, *J*=6.0; 2H, CH_2^{11}); 3.68 (*dd*, *J*=7.0;

6.5 Hz; 2H, CH_2-O); 3.64-3.61 (*m*, 2H, CH_2-O); 3.53 (*dd*, *J*=7.5; 6.0, 2H, CH_2-O); 3.51-3.48 (*m*, 2H, CH_2-O); 3.10 (*t*, *J*=6.0 Hz; 2H, CH_2^{13}); 3.08 (*t*, *J*=6.0 Hz; 2H, CH_2^{1}); 2.04 (*quint*, *J*=6.0 Hz; 2H, CH_2^{12}), 1.98 (*quint*, *J*=6.0 Hz; 2H, CH_2^{2}) ppm. δC (125 MHz, $CDCl_3$, Me_4Si) 159.39 (2C); 154.59 (2C); 153.72 (2C); 152.72 (2C); 149.67 (1C); 148.84 (2C); 148.10 (2C); 147.71 (1C); 147.54 (2C); 147.44 (2C); 147.37 (2C); 147.17 (2C); 146.02 (2C); 145.77 (2C); 145.15 (2C); 145.03 (2C); 144.69 (2C); 144.62 (2C); 144.40 (2C); 143.54 (2C); 143.33 (2C); 142.30 (2C); 141.59 (2C); 141.42 (2C); 141.26 (2C); 140.89 (2C); 138.96 (2C); 136.73 (2C); 135.54 (2C), 70.75 (2*sp3*-$C^{full(pyrr-2)}$), 70.54 (C-O),70.32 (*sp3*-$C^{full(pyrr-1)}$), 70.27 (C-O), 69.98 (*sp3*-$C^{full(pyrr-1)}$), 69.83 (C-O), 69.63 (C-O), 68.97 (C^3), 68.56 (C^{11}), 68.24 (CH_2^{pyrr-1}); 67.27 ($2CH_2^{pyrr-2}$); 66.70 (CH_2^{pyrr-1}); 50.75 (C^{13}); 50.22 (C^1); 29.22 (C^{12}); 28.47 ppm (C^2). HR-MS: *m/z*: calc. for $[C_{74}H_{29}N_2O_3+H]^+$: 993.21727, measured 993.21577.

1,13-Bis(*N*-fulleropyrrolidino)-4,7,10-trioxatridecane (14): R_f=0.73 (PhMe/EtOAc 1:1); UV/Vis: λ_{max}(PhMe)/nm 330 (ε/ $mol^{-1}dm^3cm^{-1}$ 39000); 431 (3800); 546 (2100); 610 (1300); 698 (560). IR(KBr): $\tilde{\nu}/cm^{-1}$ 2854, 2771, 1731, 1638, 1456, 1423, 1340, 1301, 1232, 1108, 1039, 877, 766, 730, 524. NMR: δH (500 MHz, $CDCl_3$+CS_2, Me_4Si) 4.41 (*s*, 8H, CH_2^{pyrr}); 3.86 (*t*, *J*=6.5 Hz, 4H, $CH_2^{3,11}$); 3.77 (*br s,* 8H, 4CH_2-O); 3.21 (*t*, *J*=7.0 Hz, 4H, $CH_2^{1,13}$); 2.23 ppm (*quint*, *J*=6.5 Hz; 4H, $CH_2^{2,12}$). δC (125 MHz, $CDCl_3$+CS_2, Me_4Si): 154.91 (8C); 147.18 (4C); 146.14 (8C); 145.95 (16C); 145.57 (4C); 145.33 (8C); 145.18 (8C); 144.46 (8C); 143.01 (4C); 142.54 (8C); 142.14 (8C); 141.97 (8C); 141.79 (8C); 140.08 (8C); 136.15 (8C); 70.80 (2C-O); 70.58 (4*sp3*-C^{full}); 70.50 (2C-O); 69.31 ($C^{3,11}$); 67.89 (4CH_2^{pyrr}); 51.64 ($C^{1,13}$); 29.12 ppm ($C^{2,12}$). HR-MS: *m/z* calc. for $[C_{134}H_{29}N_2O_3+H]^+$: 1713.21727, measured 1713.25252.

4. Table S1. Visible region absorption bands 400–800 nm of bisadduct isomers.

Regioizomer	λ_1/ε	λ_2/ε	λ_3/ε	λ_4/ε	λ_5/ε
7 *cis*-1	402 /7000	427 /6000	654 /200	684 /160	722 /160
10 *cis*-1	406 /7000	430 /5900	651 /170	676 /140	710 /140
8 *cis*-2	448 /4800	487 /3000	572 /910	647 /430	680 /280
11 *cis*-2	448 /5100	483 /3000	578 /900	643 /420	679 /280
9 *cis*-3	431 /2900	467 /2000	548 /800	657 /360	732 /280
12 *cis*-3	435 /3900	464 /2600	551 /1400	640 /470	729 /320
13 *eq*	423 /6100	456 /5900	553 /1300	627 /410	710 /100

5. Table S2 ^{13}C NMR chemical shifts of the fullerene moiety of the bridged bisadducts.

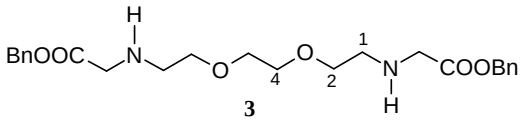
cis-1		*cis*-2		*cis*-3		*eq*
$-C_6O_2-$	$-C_{10}O_3-$	$-C_6O_2-$	$-C_{10}O_3-$	$-C_6O_2-$	$-C_{10}O_3-$	$-C_{10}O_3-$
151.96	151.90	159.83	159.01	153.95	153.49	159.39
151.15	151.06	155.61	156.41	149.64	149.79	154.59
150.58	150.19	149.12	149.27	149.05	149.09	153.72
148.79	148.93	148.80*	148.86*	148.55	148.61	152.72
147.87	148.05	148.72*	148.78*	148.23	148.29	149.67*
147.08	147.24	148.56*	148.27*	148.22	148.08	148.84
146.82	146.99	147.49	147.93	147.77	147.78	148.10
146.20	146.34	147.18	147.64	146.90	147.03	147.71*
145.96	146.09	147.04	147.51	146.59	146.26	147.54
145.92*	145.91*	146.72	147.05	146.23	146.15	147.44
145.37	145.43	146.58	146.89	146.05	146.12	147.37
145.18	145.34	146.23	146.46	145.93	145.98	147.17
144.89	145.00**	146.18	146.11	145.70	145.76	146.02
144.84		146.00	145.71	145.66	145.62	145.77
144.42	144.57	145.74	145.70	145.10	145.18	145.15
144.11	144.22	145.37	145.65	144.91	144.98	145.03
143.88	144.04	145.18	145.34	144.71	144.85	144.69
143.79	143.96	145.08	145.15	142.16	142.16**	144.62
143.59	143.72	144.60	144.83	142.12**		144.40
142.87	143.00	144.57	144.57		142.13	143.54
142.55*	142.69*	144.26	144.43	142.06	142.07	143.33
142.30	142.43	143.94	144.18	141.70	141.65	142.30
142.24*	142.34*	143.81	144.01	139.74	139.79	141.59
142.17	142.30	143.01	142.98	138.21	138.37	141.42
141.82	141.91	141.51	141.63	137.07	137.11	141.26
141.58	141.56	140.71	140.94	135.36	135.10	140.89
140.61	140.77	139.05	138.86	134.64	134.05	138.96
137.85*	137.94*	133.53	133.79	130.26	130.49	136.73
135.08	135.24	132.89	133.05			135.54
134.89	135.06	129.49*	129.18*			

* Carbon peaks of relative intensity 1.
** Carbon peaks of relative intensity 4 (the others of relative intensity 2).

6. Table S3 ^{1}H NMR and ^{13}C NMR chemical shifts of the non-fullerene moiety of the bridged bisadducts.

	δ(sp^3-C^{full})	δ(CH_2^{pyrr})	δ (CH_2^{tether})
cis-1 **(7)**	67.59 66.16	4.80d(10.0); 3.52d(10.0); 66.06 4.47d(8.5); 4.01d(8.0); 66.42	CH_2(1,8) - 3.11ddd(3.0; 5.5; 14.0); 3.38ddd(3.0; 7.0; 13.5); 52.91 CH_2(2,7) – 4.00-3.92m; 68.63 CH_2(4,5) - 3.88-3.82m; 3.82-3.76m; 69.46
cis-2 **(8)**	67.78 67.74	5.34dd(10.0; 2.0); 3.32d(10.0); 68.48 4.27dd(9.0; 2.0); 3.64d(9.0); 68.50	CH_2(1,8) - 2.83ddd(2.0; 8.0; 13.0); 3.52ddd(2.5; 5.5; 13.0); 52.55 CH_2(2,7) - 4.02ddd(2.5; 8.0; 9.5); 3.80-3.90m; 71.88 CH_2(4,5) - 3.80-3.90m; 70.38
cis-3 **(9)**	70.36 66.44	4.68dd(9.5; 2.0); 3.49d(9.5); 65.72; 4.47dd(9.0; 2.0); 4.08d(9.0); 69.09	CH_2(1,8) - 2.85dt(12.5; 4.0); 3.71ddd(12.5; 9.5; 5.0); 52.28 CH_2(2,7) - 3.83-3.90m; 69.41 CH_2(4,5) - 3.93-3.90m; 3.78-3.83m; 70.87
cis-1 **(10)**	68.10 65.73	4.28d(9.5); 3.66d(9.5); 68.46; 4.26d(8.5); 4.04d(8.5); 66.59	CH_2(1,13) - 3.23ddd(7.0; 8.0; 11.5); 2.98ddd(5.5; 8.5; 12.0); 52.47 CH_2(2,12) - 2.07-2.23m; 28.87 CH_2(3,11) - 3.98ddd(5.0; 8.0; 10.0); 3.76-3.86m; 69.34 CH_2-O - 3.76-3.86m; 70.91 CH_2-O - 3.76-3.86m; 70.22
cis-2 **(11)**	67.35 67.07	4.01d(9.0); 3.96d(9.0); 67.43; 3.93d(9.5); 3.81d(9.5); 68.22	CH_2(1,13) - 2.90dt(12.0; 6.0); 3.16dt(12.0; 7.0); 50.96 CH_2(2,12) - 2.07quint(5.5); 28.69 CH_2(3,11) - 3.75-3.83m; 68.76 CH_2-O - 3.70-3.81m ; 70.58 CH_2-O - 3.67-3.72m ; 70.69
cis-3 **(12)**	69.69 65.66	4.36dd(9.0; 1.5); 3.78d(9.0); 67.33 4.28dd(9.5; 1.5); 3.61d(9.5); 69.11	CH_2(1,13) - 2.81dt(12.0; 6.0); 3.25dt(12.0; 7.0); 50.06 CH_2(2,12) – 1.99-2.11m; 28.40 CH_2(3,11) - 3.84-3.90m; 3.70dt(10; 5.5); 68.29 CH_2-O - 3.77-3.85m; 70.58 CH_2-O - 3.75-3.81m; 71.09
eq **(13)**	70.75(2C) 70.32(1C) 69.98(1C)	4.42dd(9.0; 1.0); 3.80dd(9.0; 1.0); 67.27 4.11s; 68.24; 4.04s; 66.70	CH_2(1) - 3.08t(6.0),50.22; CH_2(13)- 3.10t (6.0), 50.75 CH_2(2) - 1.98quint(6.0), 28.47; CH_2(12) -2.04quint (6.0), 29.22 CH_2(3) - 3.81-3.77m; 68.97; CH_2(11) – 3.78t(6.0), 68.56 CH_2-O - 3.64-3.61m; 70.54; CH_2-O - 3.51-3.48m; 70.27 CH_2-O - 3.53dd(7.5; 6.0); 69.83;CH_2-O - 3.68dd(7.0; 6.5); 69.63
Bis-C_{60} **(14)**	70.58	4.41s; 67.89	CH_2(1,13) - 3.21t(7.0); 51.64 CH_2(2,12) - 2.23quint(6.5); 29.12 CH_2(3,11) - 3.86t(6.5); 69.31 CH_2-O - 3.77br s; 70.80, 70.50
δ range	65-71	3.30-5.40 65-69	Dioxa-C10: CH_2(1) → 52.28-52.91 CH_2(2) → 68.63-71.88 CH_2(4) → 69.46-70.71 Trioxa-C13: CH_2(1) → 50.06-52.47 CH_2(2) → 28.40-29.22 CH_2(3) → 68.29-69.34 CH_2(5,6) → 69-71

7. Figures S1-S51 NMR and **HR-M spectra** of compounds **3-14**



3

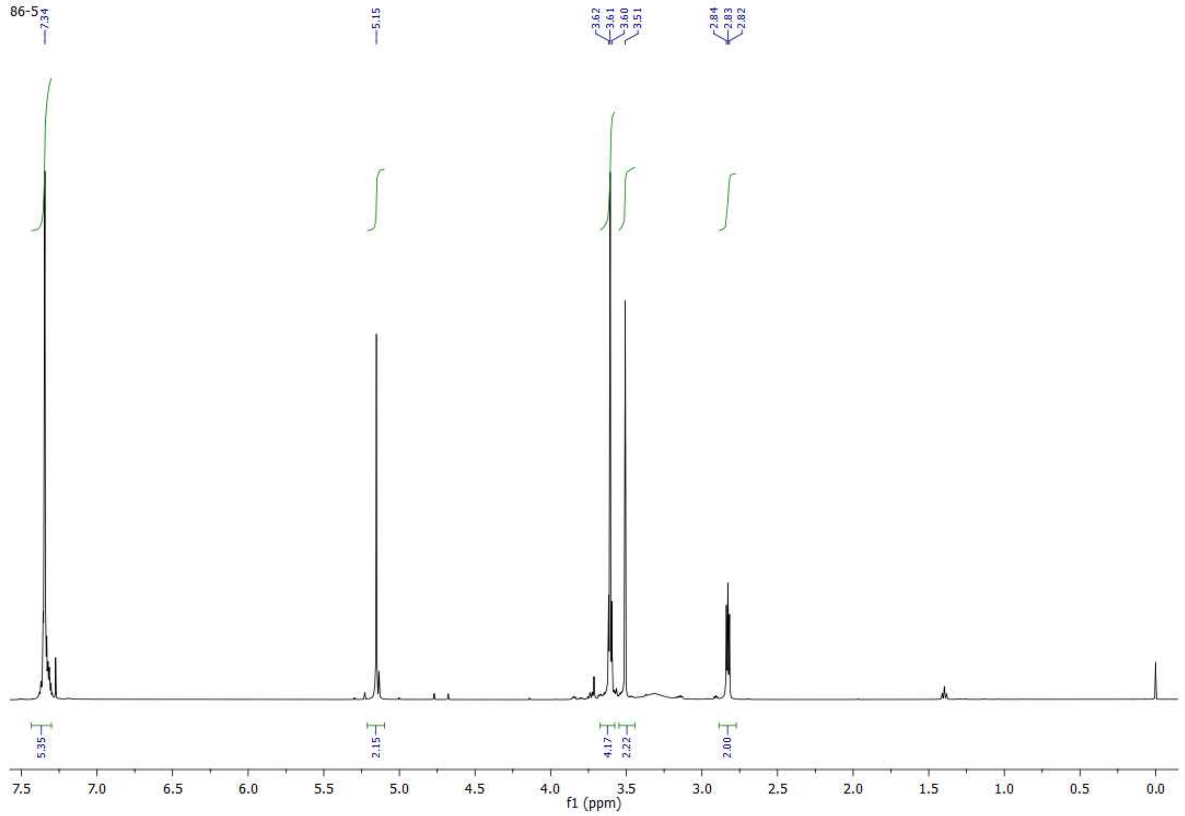


Fig.S1 [1]H NMR spectrum of compound **3**

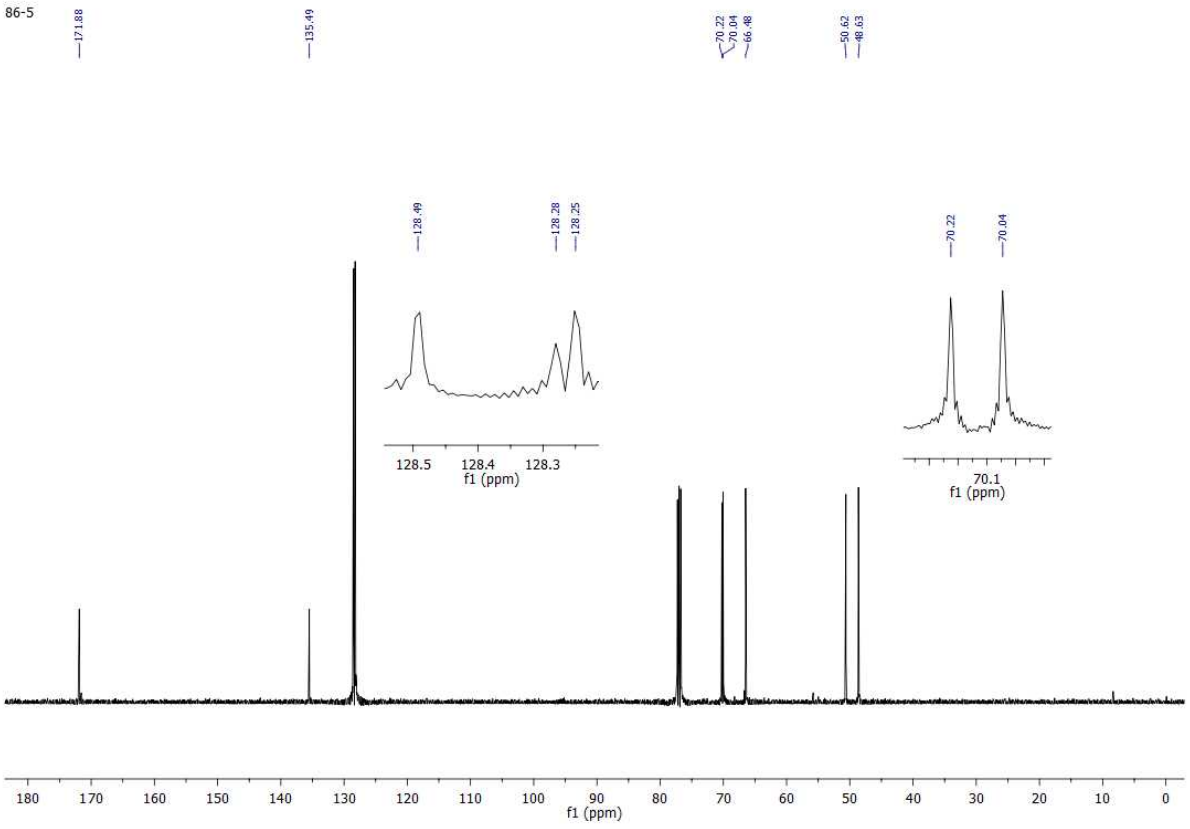
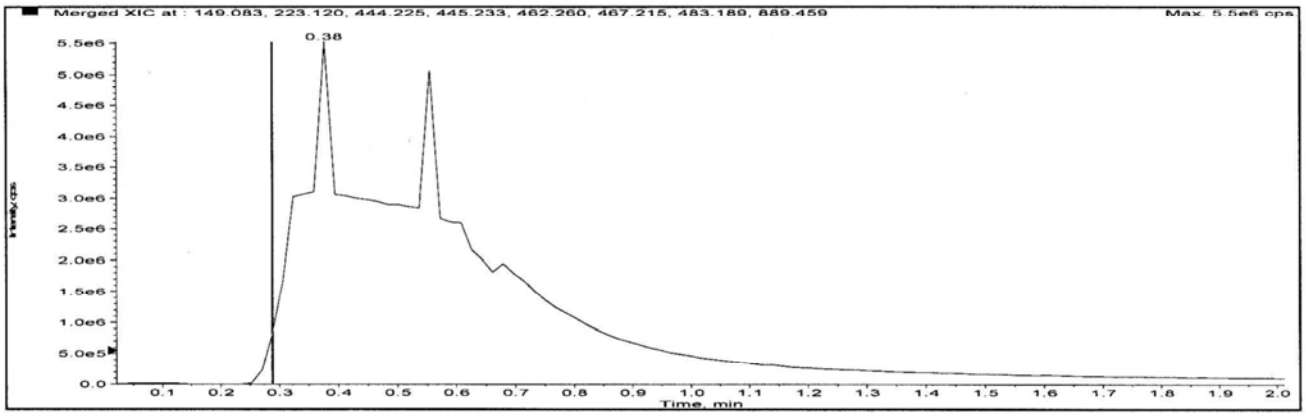


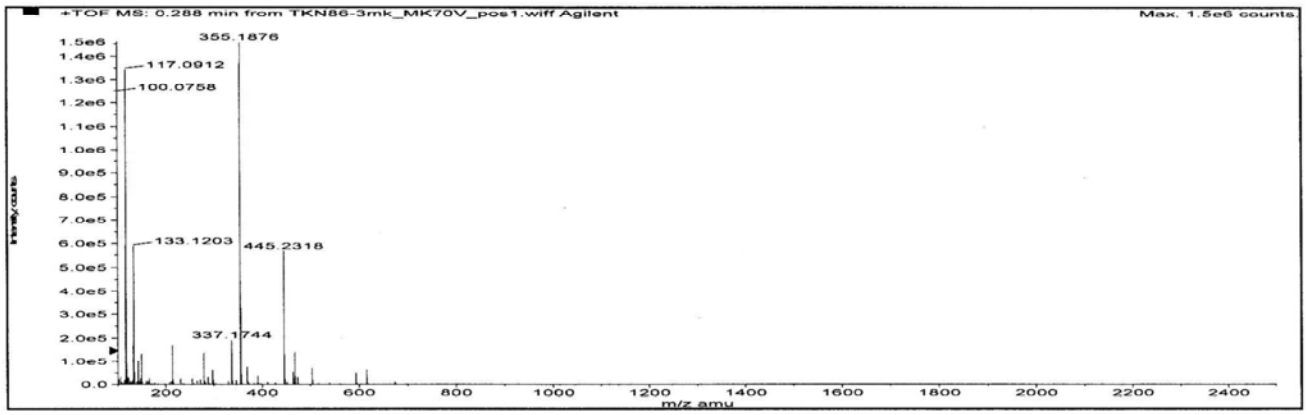
Fig.S2 [13]C NMR spectrum of compound **3**

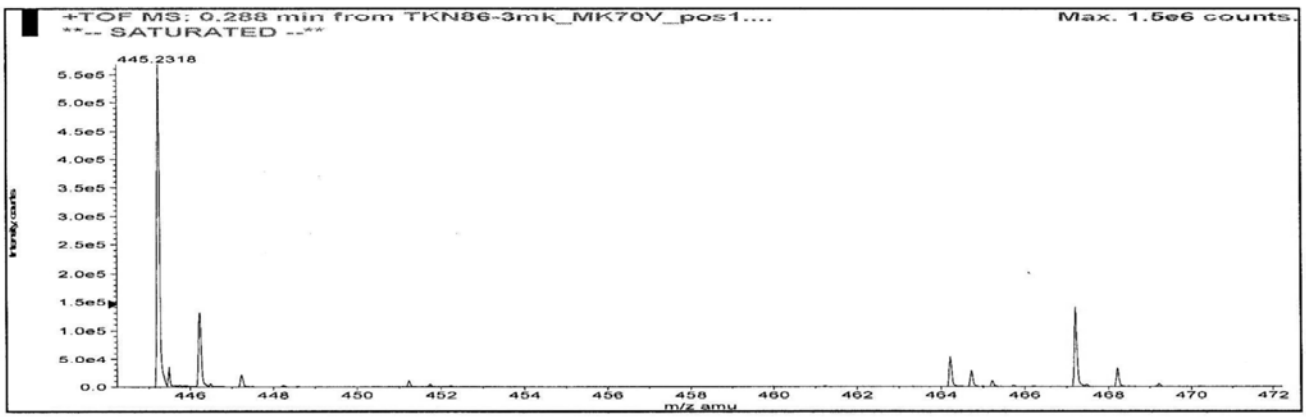
Sample Name: **TKN86-3** Sample Location: **P1-B7** Sample Id: Operator: **Milka**
Data File Name: **D:\PE Sciex Data\Projects\D_Milic\Data\TKN86-3mk_MK70V_pos1.wiff** Acq Time: **April 09 2012, 04:27:03 PM**
Method: **D:\TOF_Data\damethods\Night_Seq_Comp_ident1.anm\efc.xml**

One or more scans have failed IRM. Review the data file for details.



Merged XIC, Period# : 1 Experiment# : 1

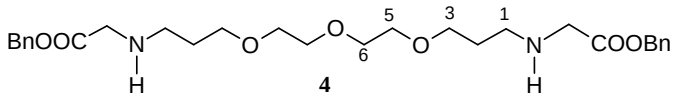




Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C24H32N2O6	--	444.22604	0.38	2.79088 E7	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+H]+	569759.42	445.23331	445.23183	-1.48025	-3.32	--
[M+Na]+	139967.85	467.21526	467.21342	-1.84058	-3.94	--

Fig. S3 HR-MS spectrum of compound **3**



4

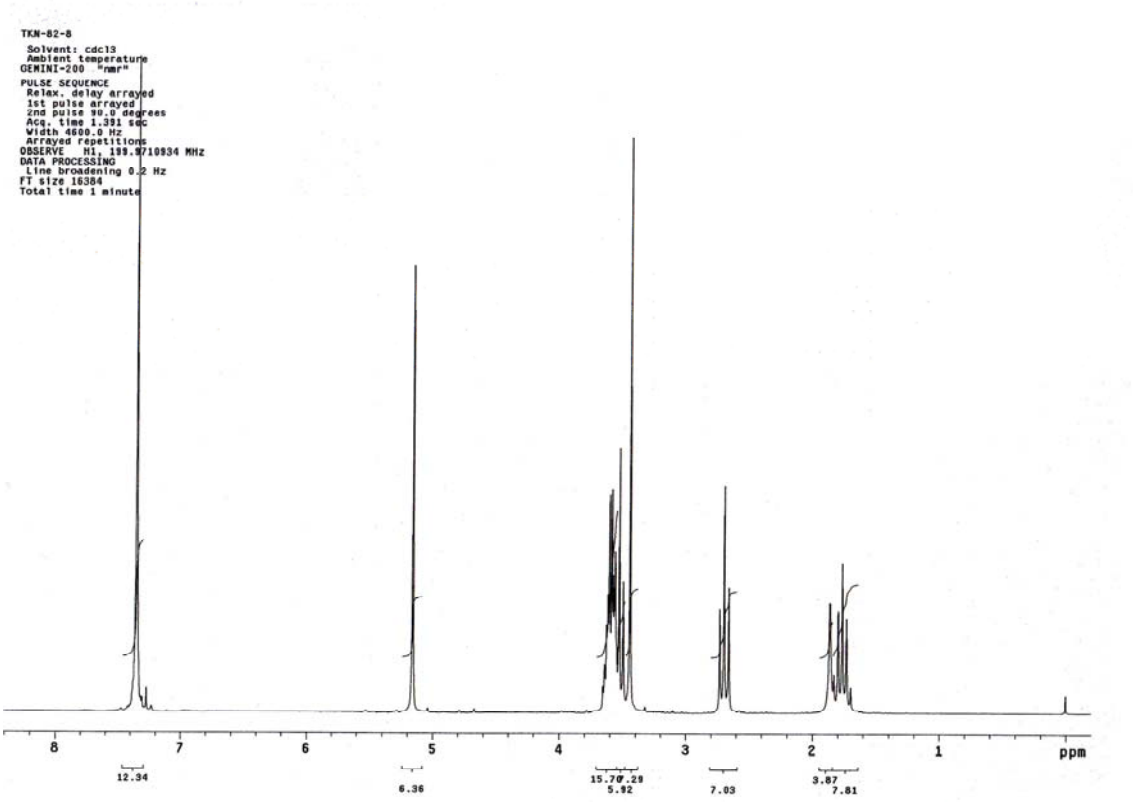


Fig.S4 ^{1}H NMR spectrum of compound **4**

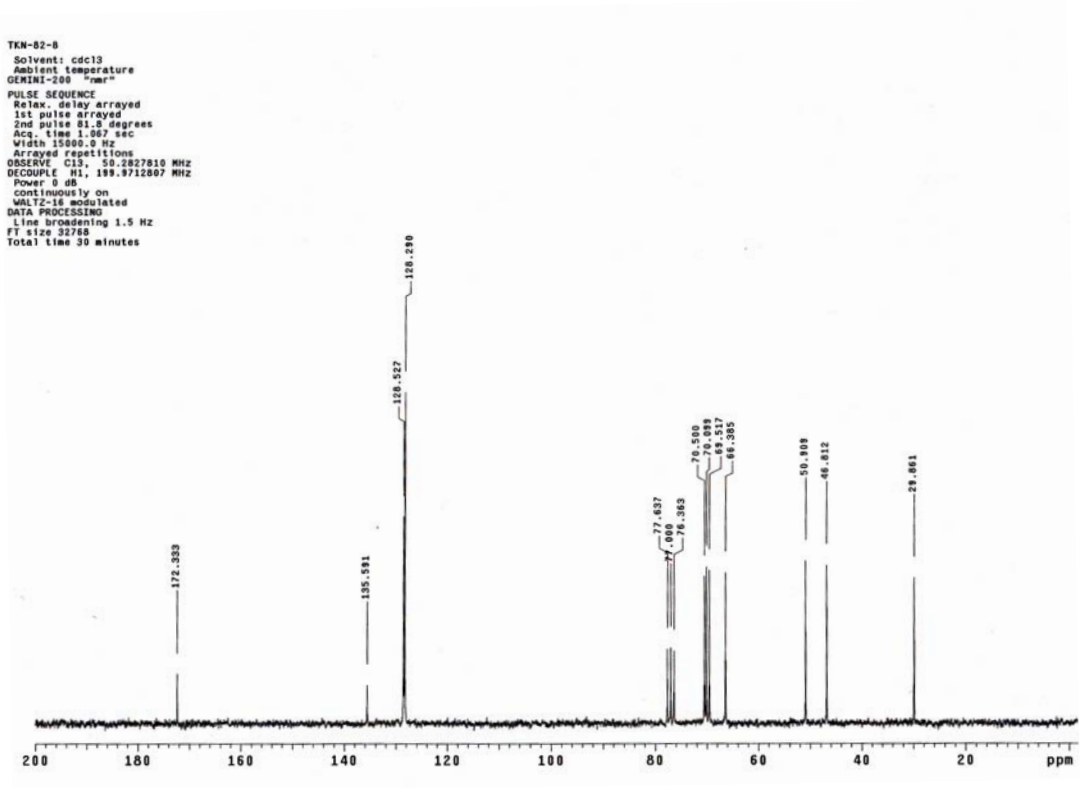
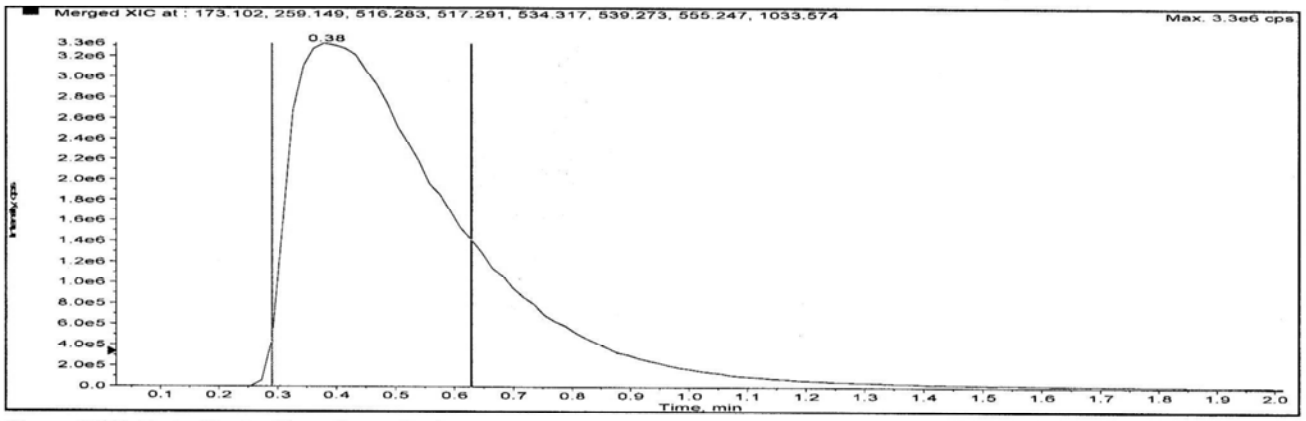


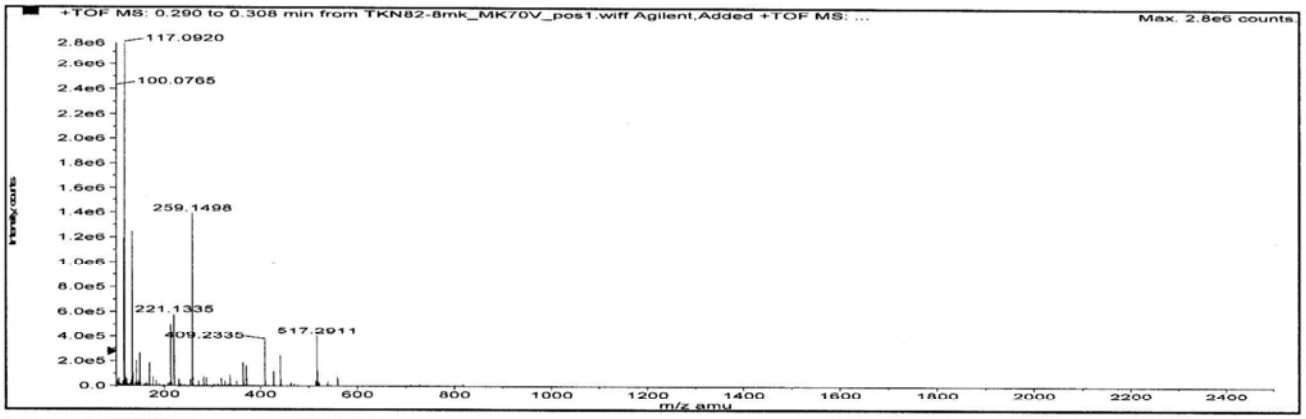
Fig.S5 ^{13}C NMR spectrum of compound **4**

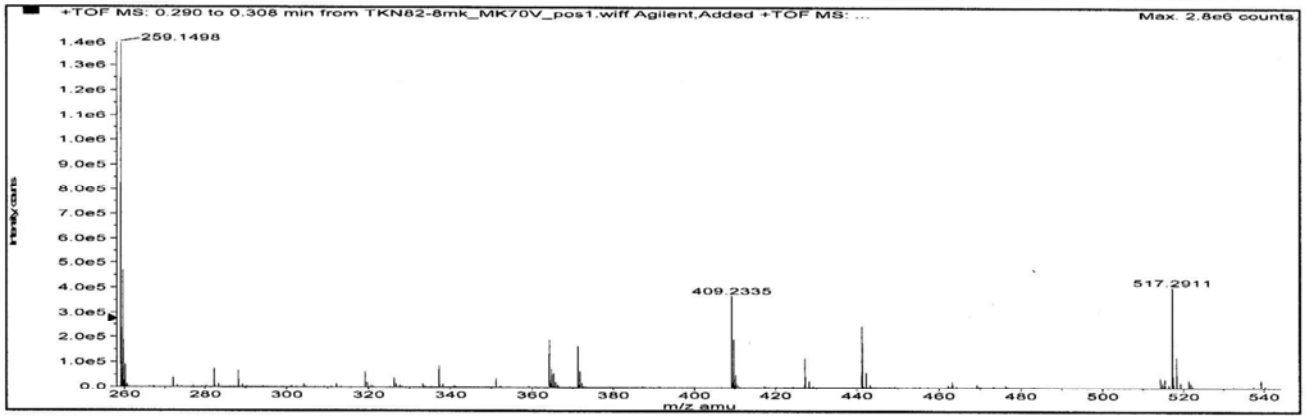
Sample Name: **TKN82-8** Sample Location: **P1-B5** Sample Id: Operator: **Milka**
Data File Name: **D:\PE Sciex Data\Projects\D_Milic\Data\TKN82-8mk_MK70V_pos1.wiff** Acq Time: **April 09 2012, 04:20:20 PM**
Method: **D:\TOF_Data\damethods\Night_Seq_Comp_ident1.anm\efc.xml**

One or more scans have failed IRM. Review the data file for details.



Merged XIC, Period# : 1 Experiment# : 1

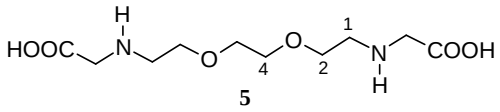




Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C28H40N2O7	--	516.28355	0.38	6.32908 E7	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+2H]2+	1428936.78	259.14905	259.14980	0.75157	2.90	--
[M+H]+	430308.58	517.29083	517.29112	0.28791	0.56	--
[M+Na]+	33890.98	539.27277	539.27333	0.55252	1.02	--

Fig. S6 HR-MS spectrum of compound **4**



5

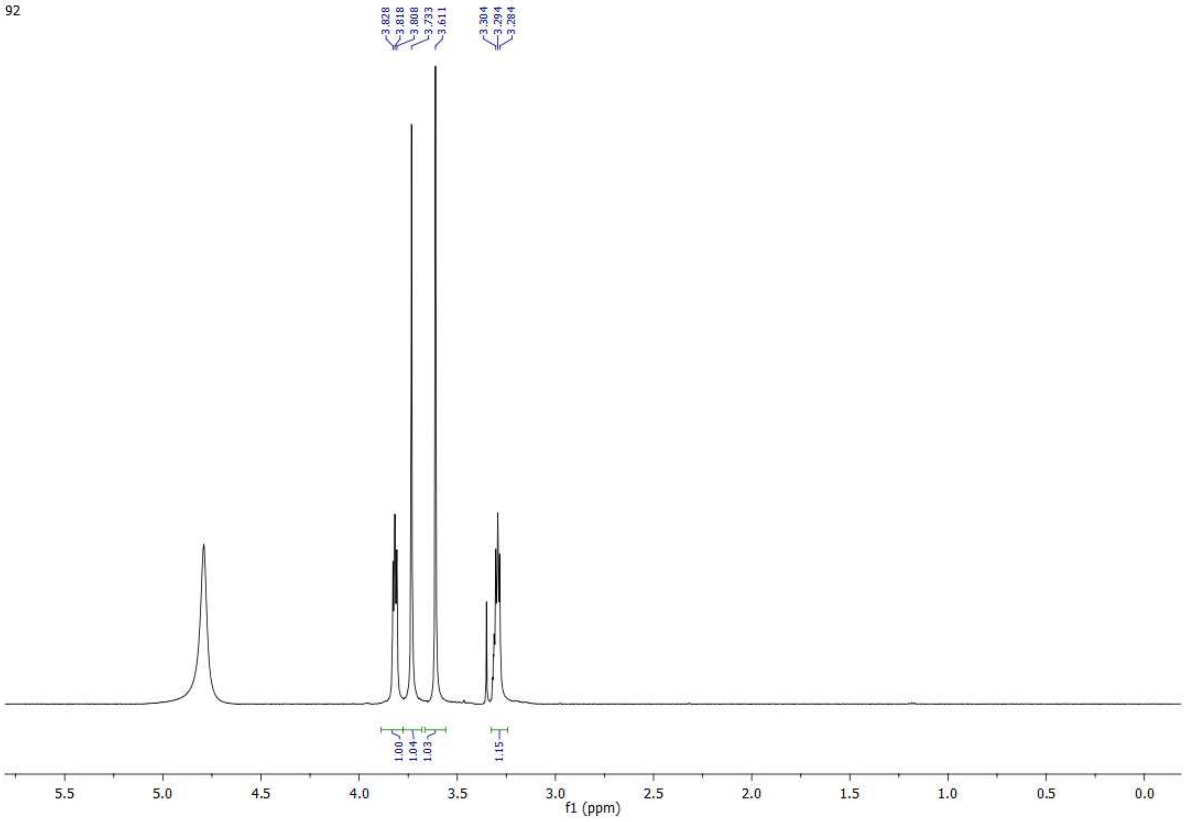


Fig.S7 ^{1}H NMR spectrum of compound **5**

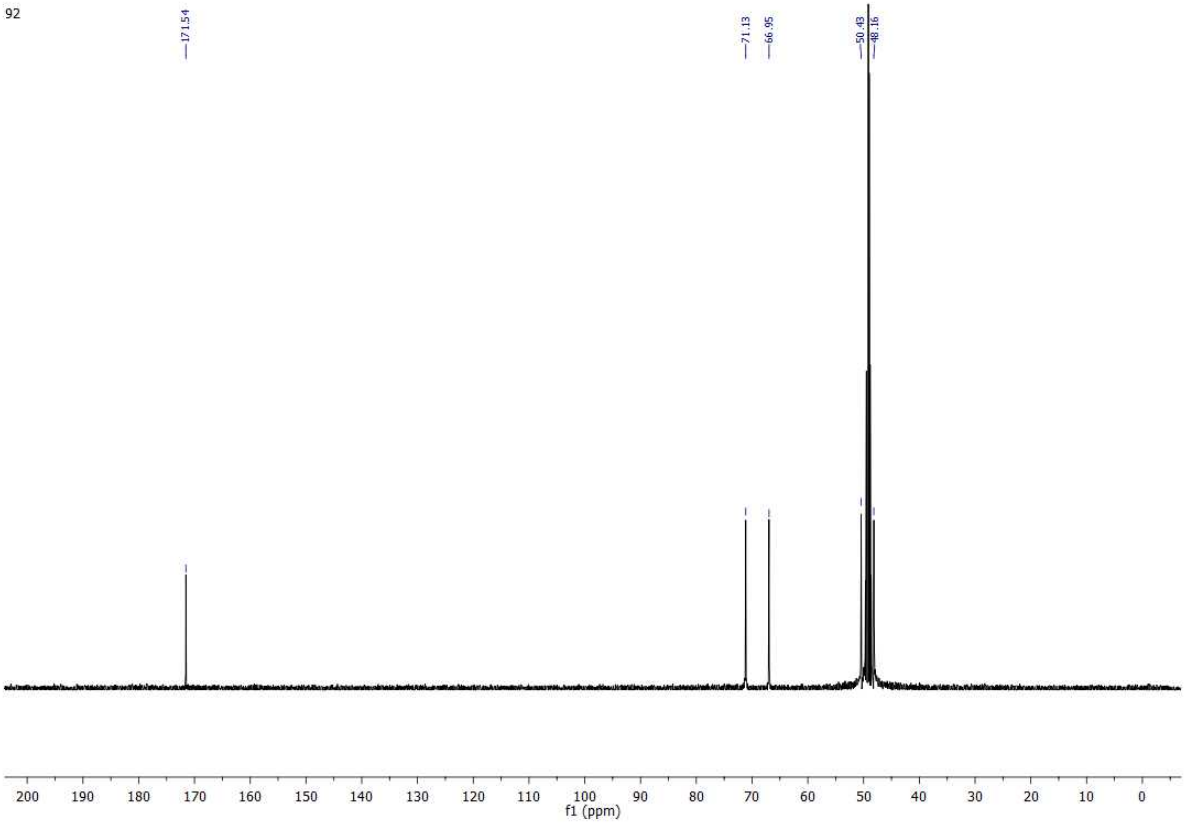
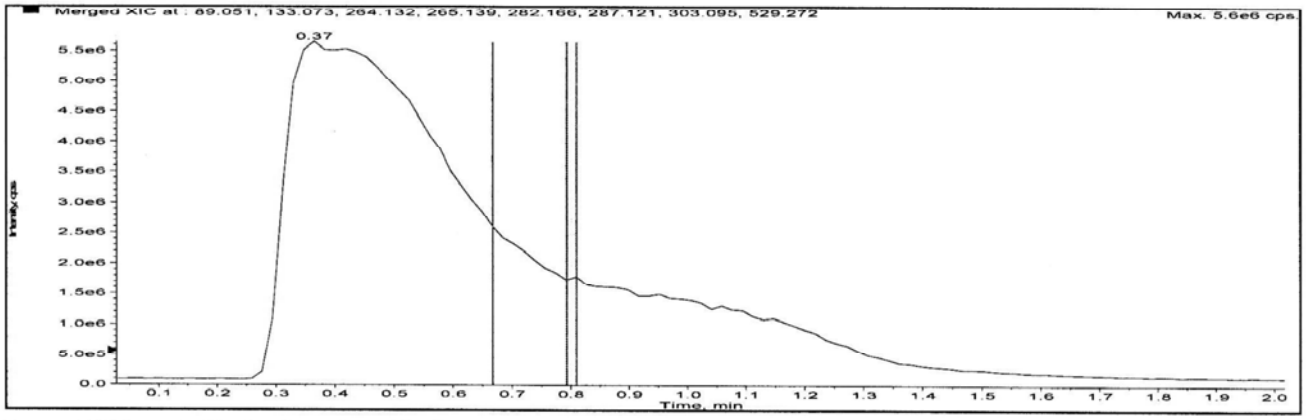


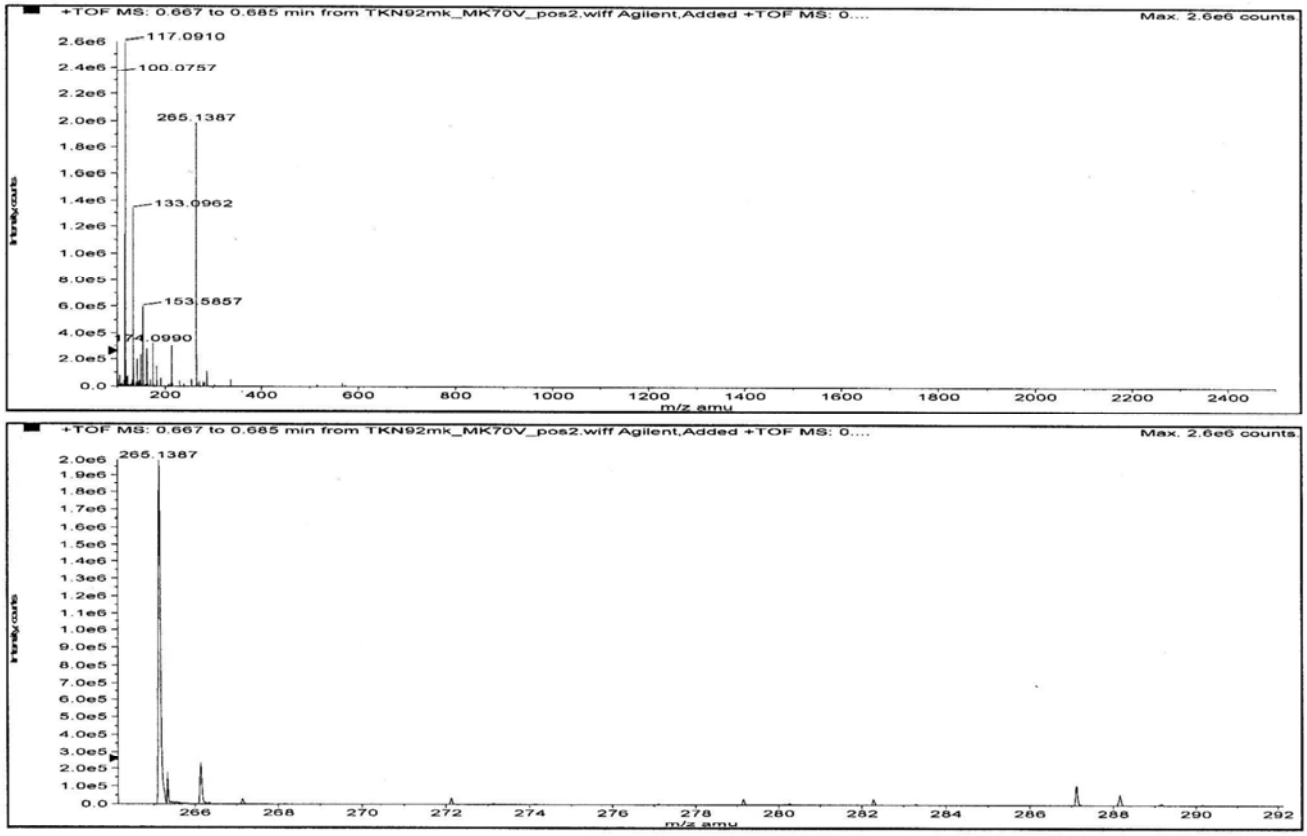
Fig.S8 ^{13}C NMR spectrum of compound **5**

Sample Name: **TKN92** Sample Location: **P1-B9** Sample Id: Operator: **Milka**
Data File Name: **D:\PE Sciex Data\Projects\D_Milic\Data\TKN92mk_MK70V_pos2.wiff** Acq Time: **April 09 2012, 04:49:56 PM**
Method: **D:\TOF_Data\damethods\Night_Seq_Comp_ident1.anm\efc.xml**

One or more scans have failed IRM. Review the data file for details.



Merged XIC, Period# : 1 Experiment# : 1



Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C10H20N2O6	--	264.13214	0.37	1.46081 E8	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+H]+	2082262.46	265.13941	265.13866	-0.75030	-2.83	--
[M+Na]+	114103.32	287.12136	287.11965	-1.70249	-5.93	--

Fig. S9 HR-MS spectrum of compound **5**

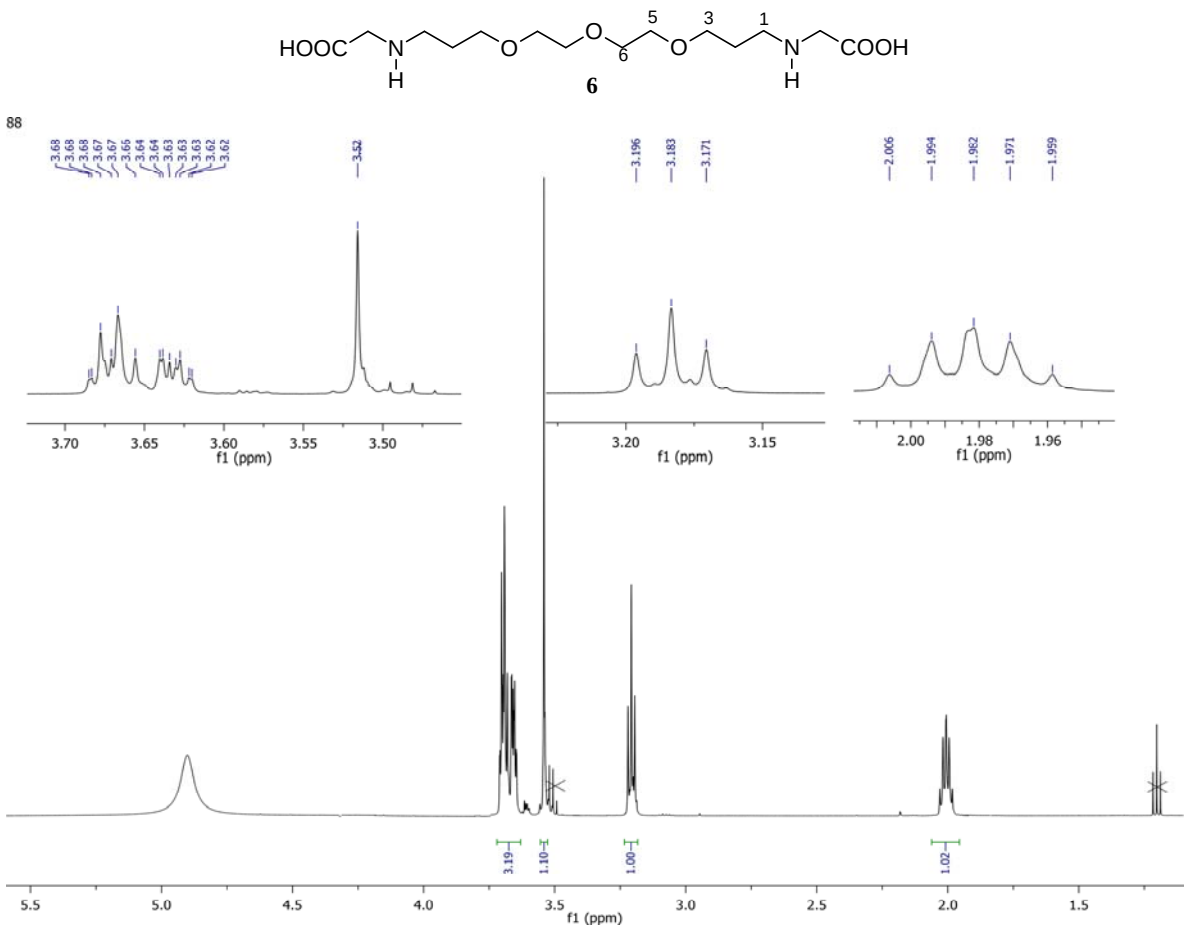


Fig.S10 [1]H NMR spectrum of compound **6**

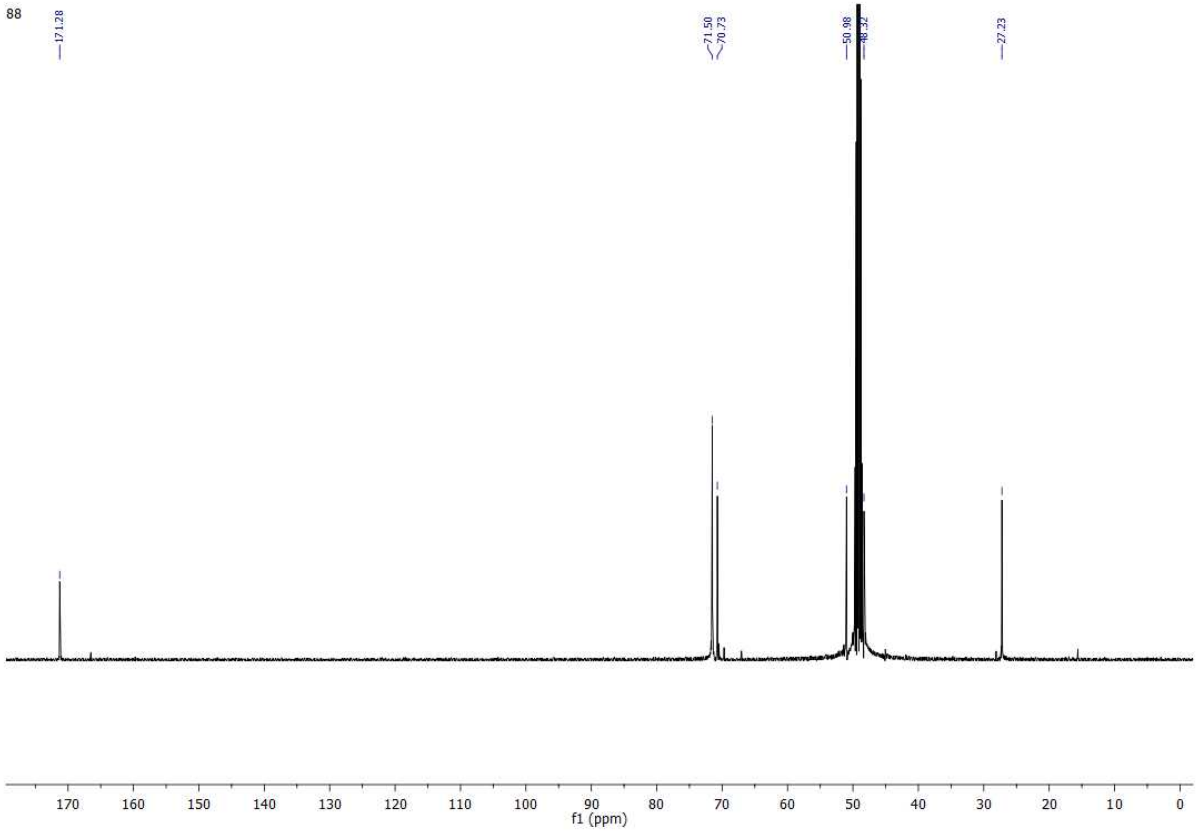
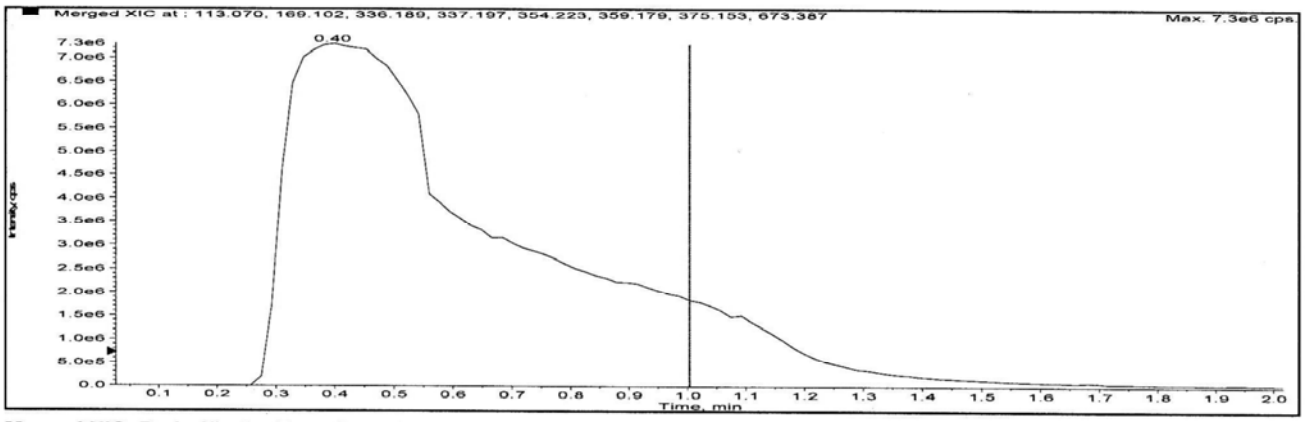


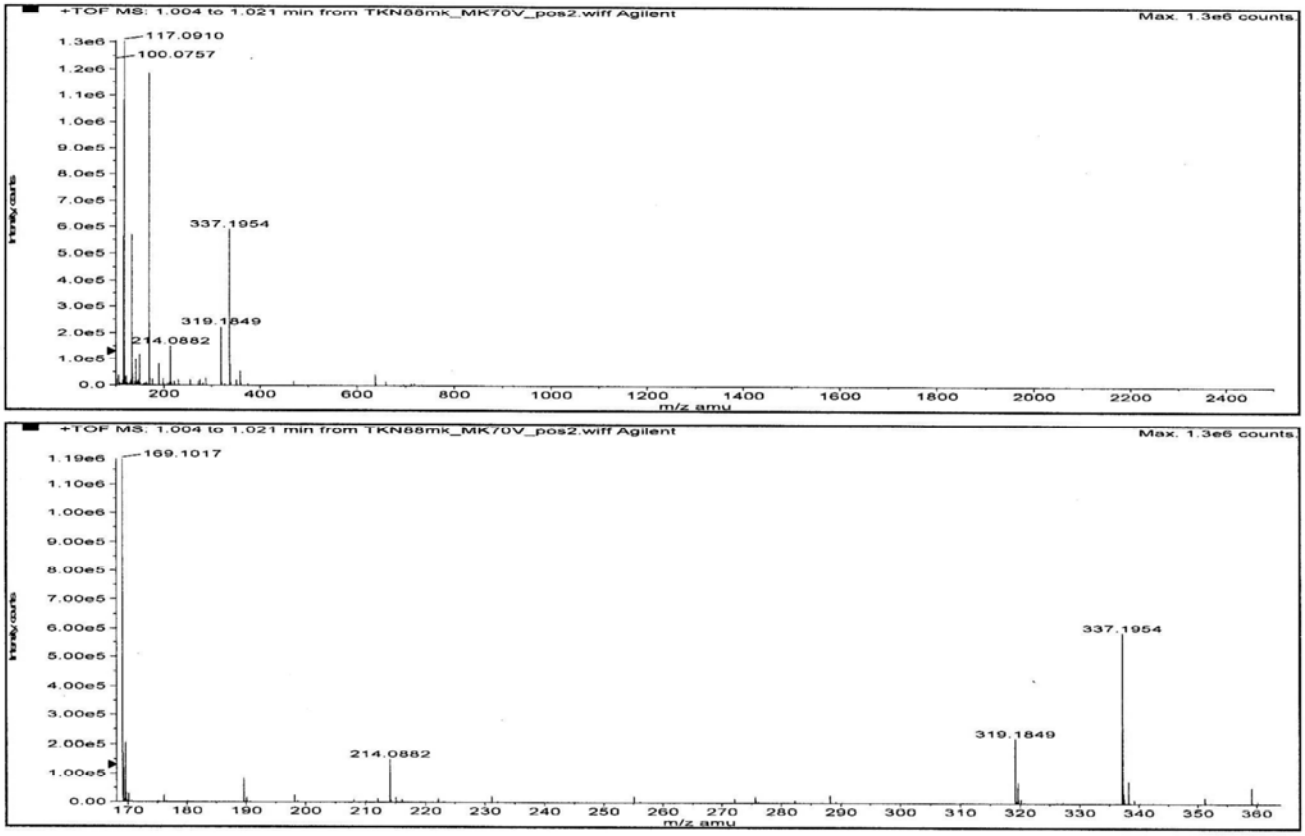
Fig.S11 [13]C NMR spectrum of compound **6**

Sample Name: **TKN88** Sample Location: **P1-B8** Sample Id: Operator: **Milka**
Data File Name: **D:\PE Sciex Data\Projects\D_Milic\Data\TKN88mk_MK70V_pos2.wiff** Acq Time: **April 09 2012, 04:46:42 PM**
Method: **D:\TOF_Data\damethods\Night_Seq_Comp_ident1.anm\efc.xml**

One or more scans have failed IRM. Review the data file for details.



Merged XIC, Period# : 1 Experiment# : 1



Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C14H28N2O7	--	336.18965	0.40	1.91919 E8	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+2H]2+	1245594.51	169.10210	169.10168	-0.42034	-2.49	--
[M+H]+	591544.29	337.19693	337.19538	-1.54941	-4.59	--
[M+Na]+	57682.29	359.17887	359.17724	-1.63500	-4.55	--

Fig S12 HR-MS spectrum of compound **6**

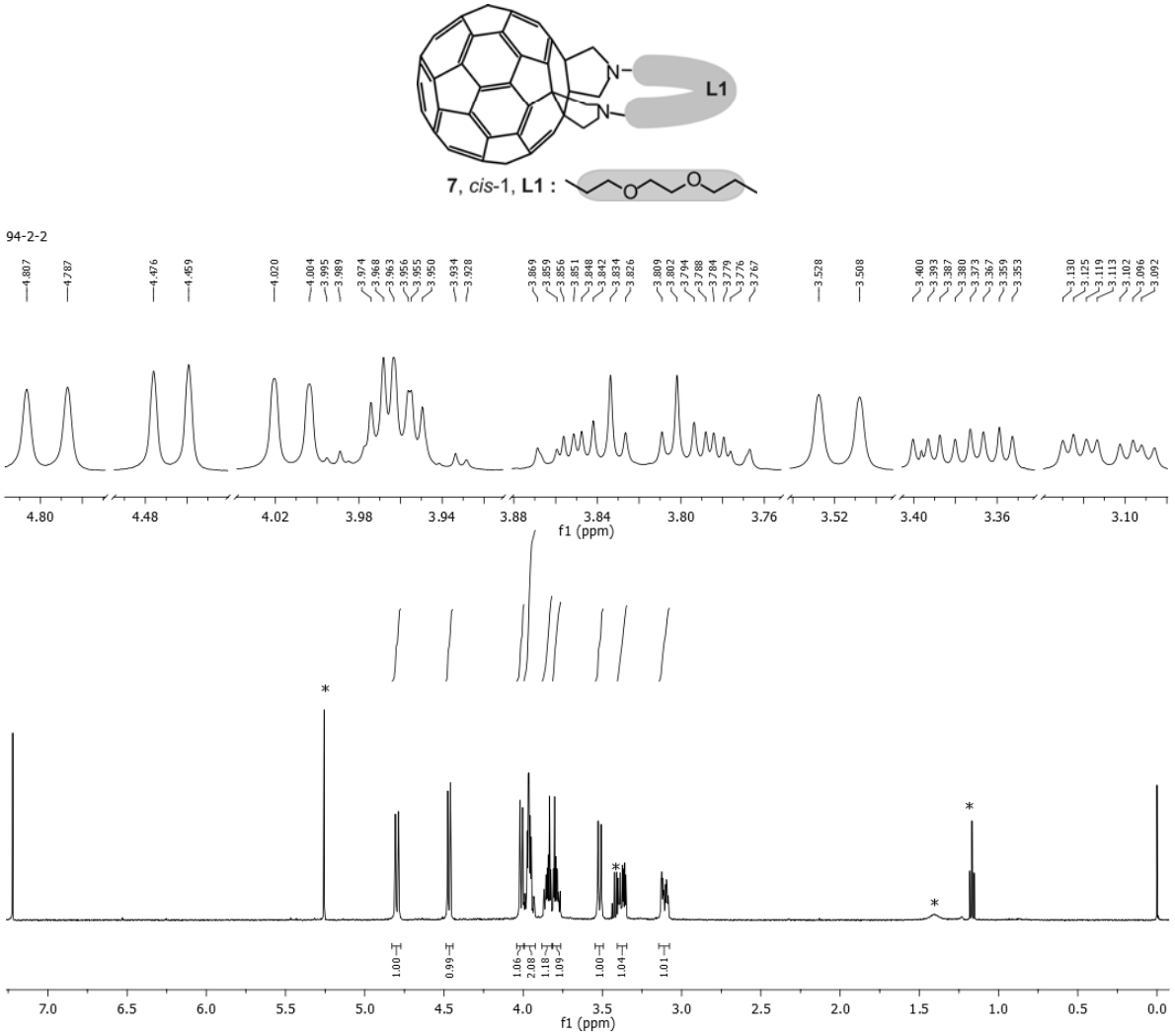


Fig.S13 ^{1}H NMR spectrum of compound **7**

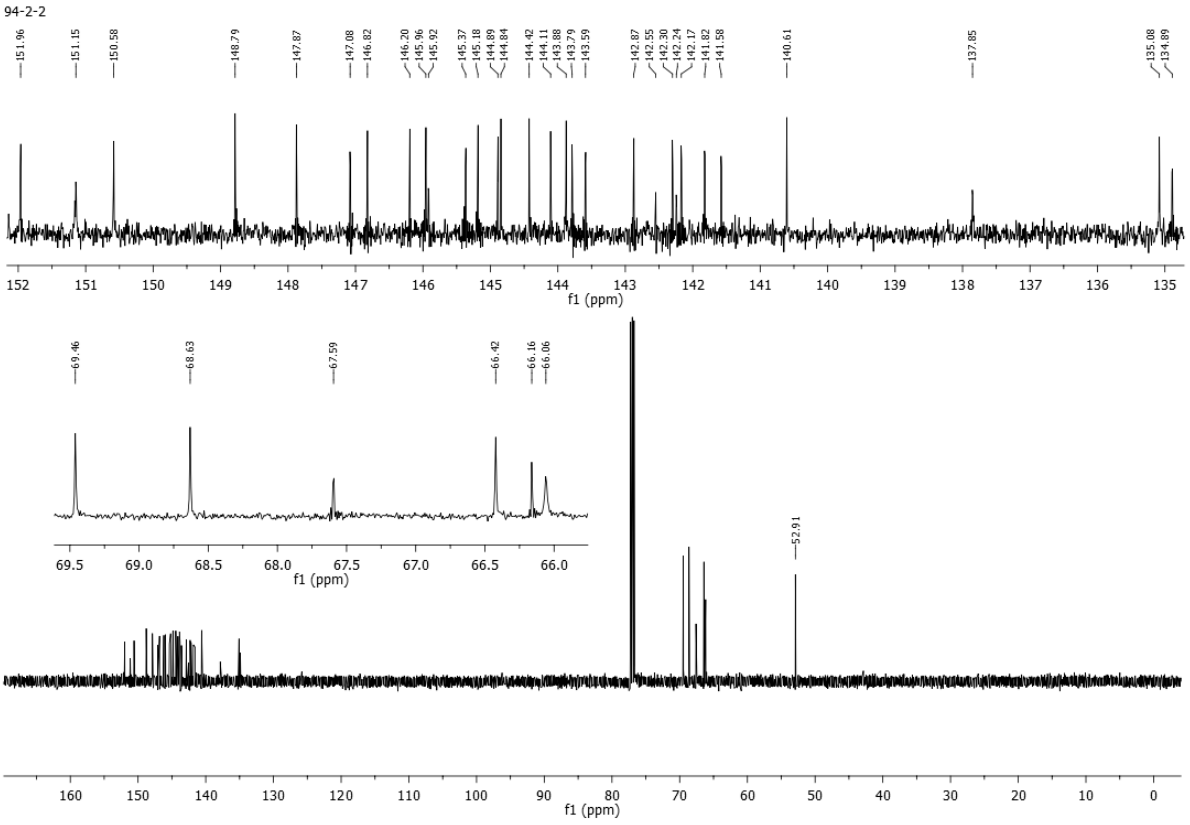


Fig.S14 ^{13}C NMR spectrum of compound **7**

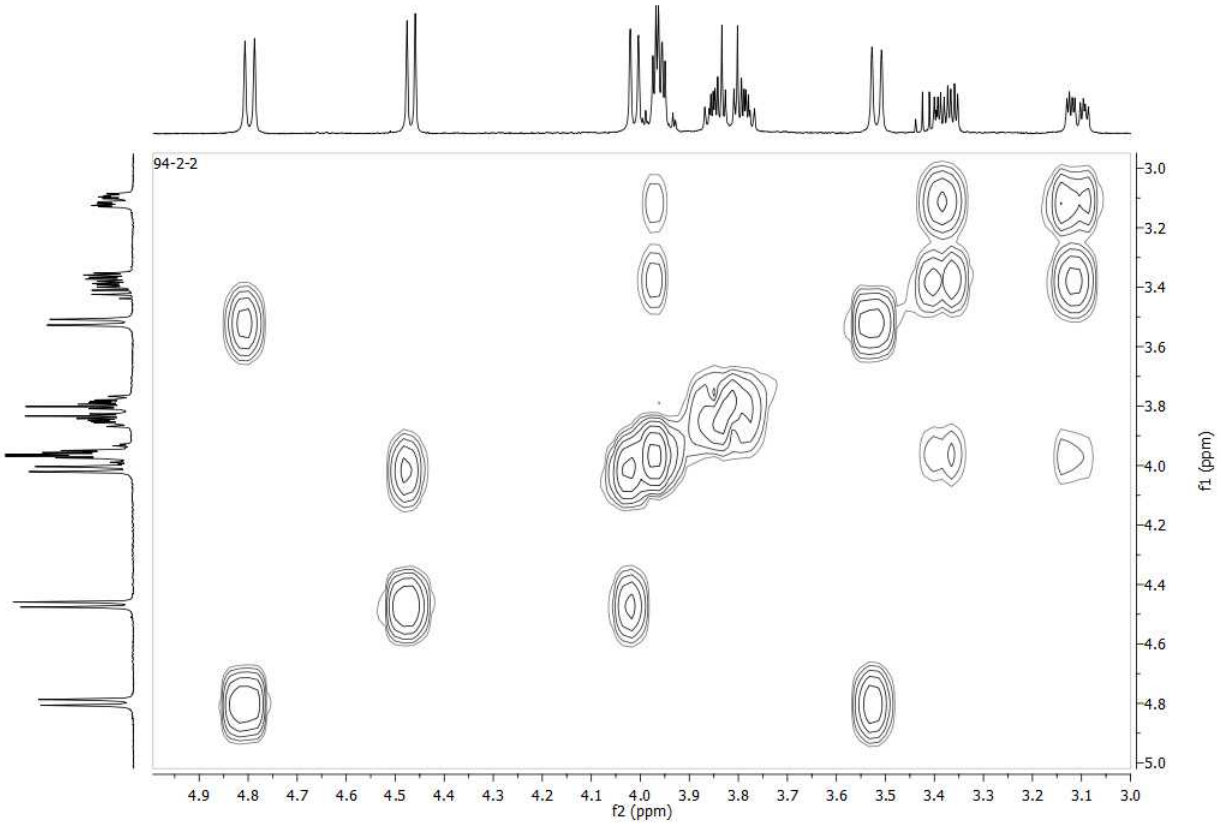


Fig S15 COSY spectrum of compound **7**

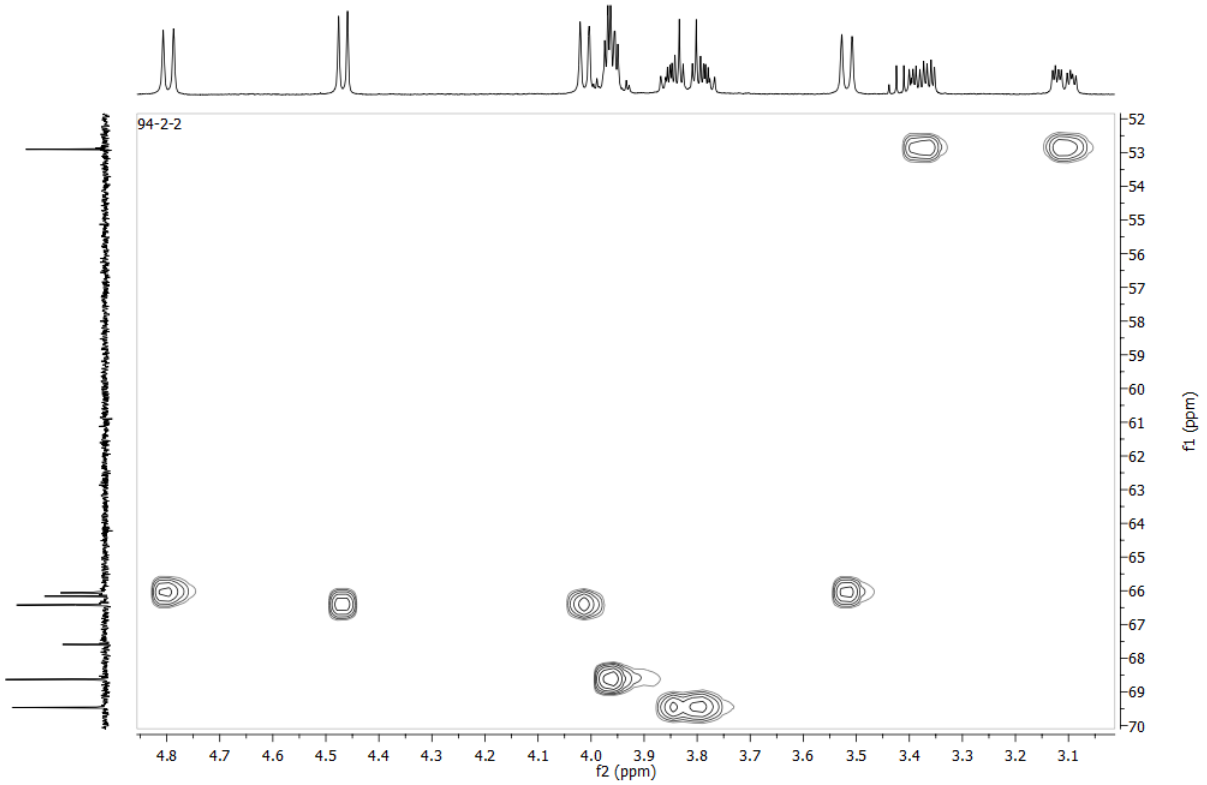
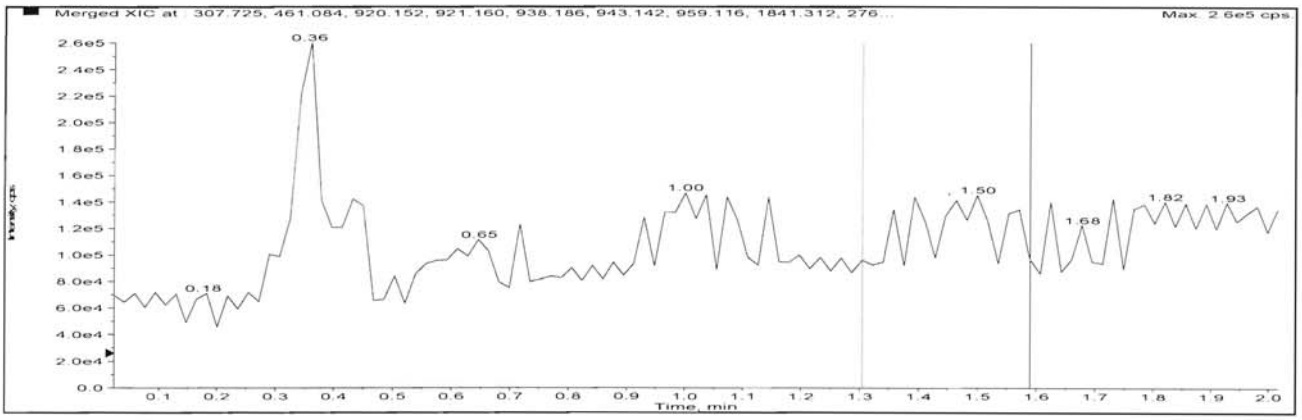
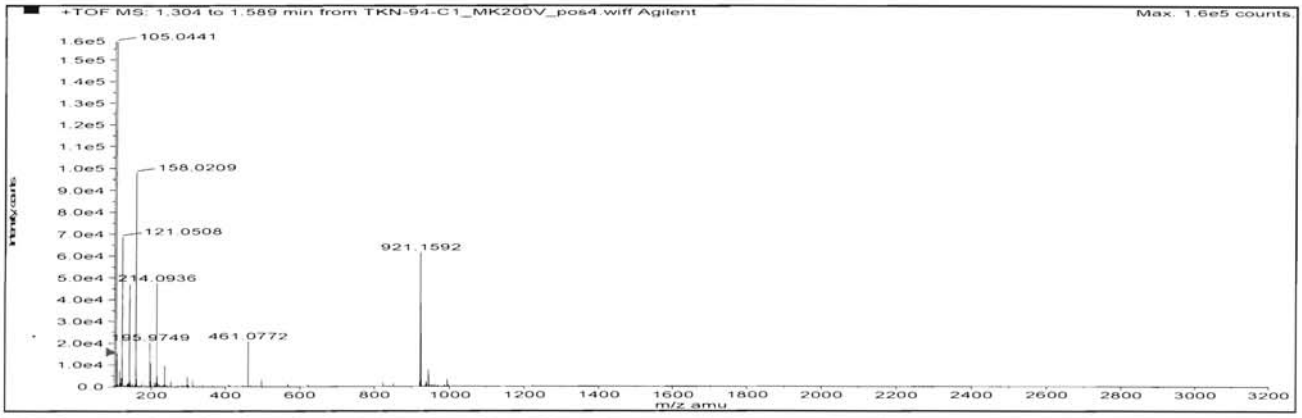


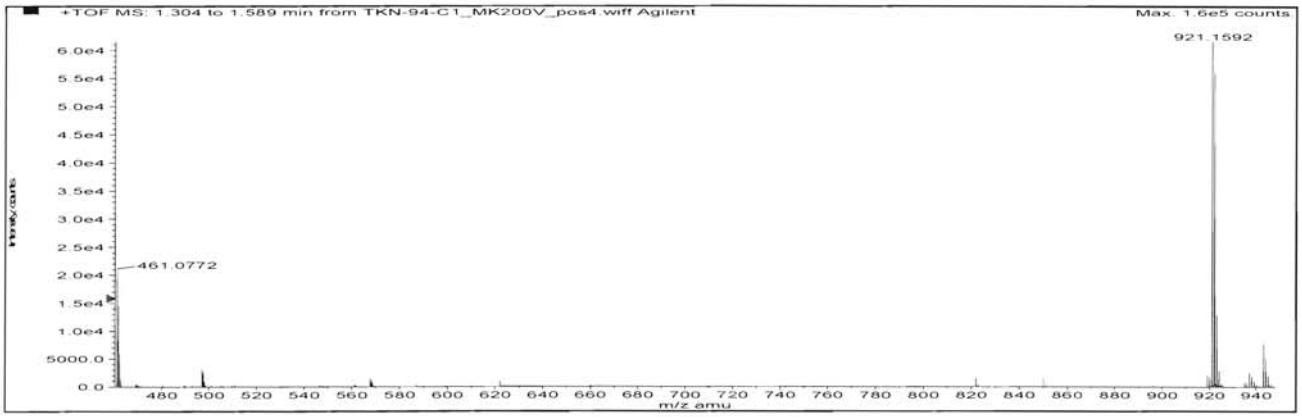
Fig S16 HSQC spectrum of compound **7**

Sample Name: **TKN-94-C1** Sample Location: **P1-C1** Sample Id: Operator: **Milka**
Data File Name: **D:\PE Sciex Data\Projects\D_Milic\Data\TKN-94-C1_MK200V_pos4.wiff** Acq Time: **July 28 2015, 10:54:37 AM**
Method: **d:\TOF_Data\damethods\Night_Seq_Comp_ident1.anm\efc.xml**



Merged XIC, Period# : 1 Experiment# : 1





Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C70H20N2O2	--	920.15248	1.50	5.70343 E5	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+2H]2+	21142.04	461.08352	461.08192	-1.59089	-3.45	--
M+	1640.21	920.15193	920.14423	-7.70308	-8.37	--
[M+H]+	61804.07	921.15975	921.15538	-4.36965	-4.74	--
[M+NH4]+	1902.36	938.18630	938.15406	-32.23965	-34.36	--
[M+Na]+	7683.76	943.14170	943.13855	-3.14719	-3.34	--

Fig. S17 HR-MS spectrum of compound **7**

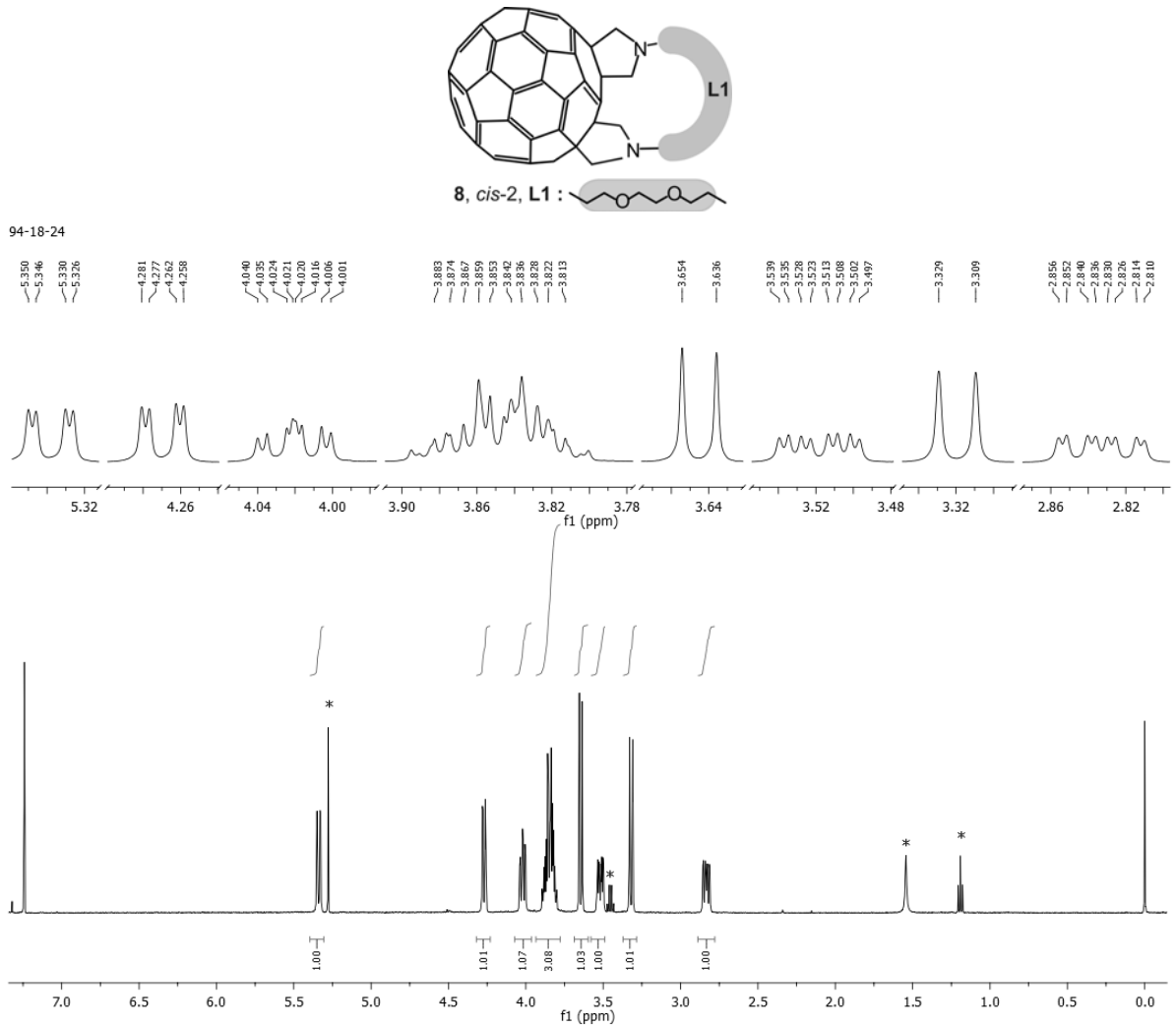


Fig.S18 ^{1}H NMR spectrum of compound **8**

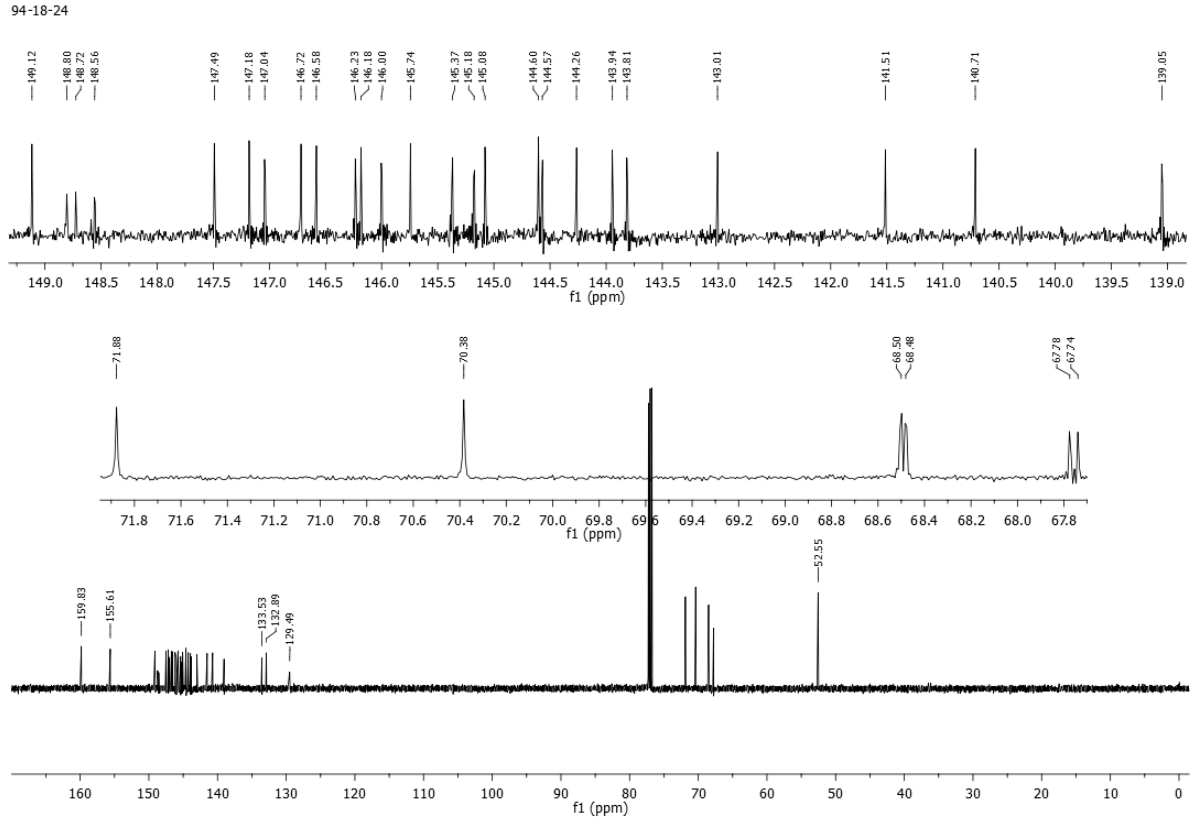


Fig.S19 ^{13}C NMR spectrum of compound **8**

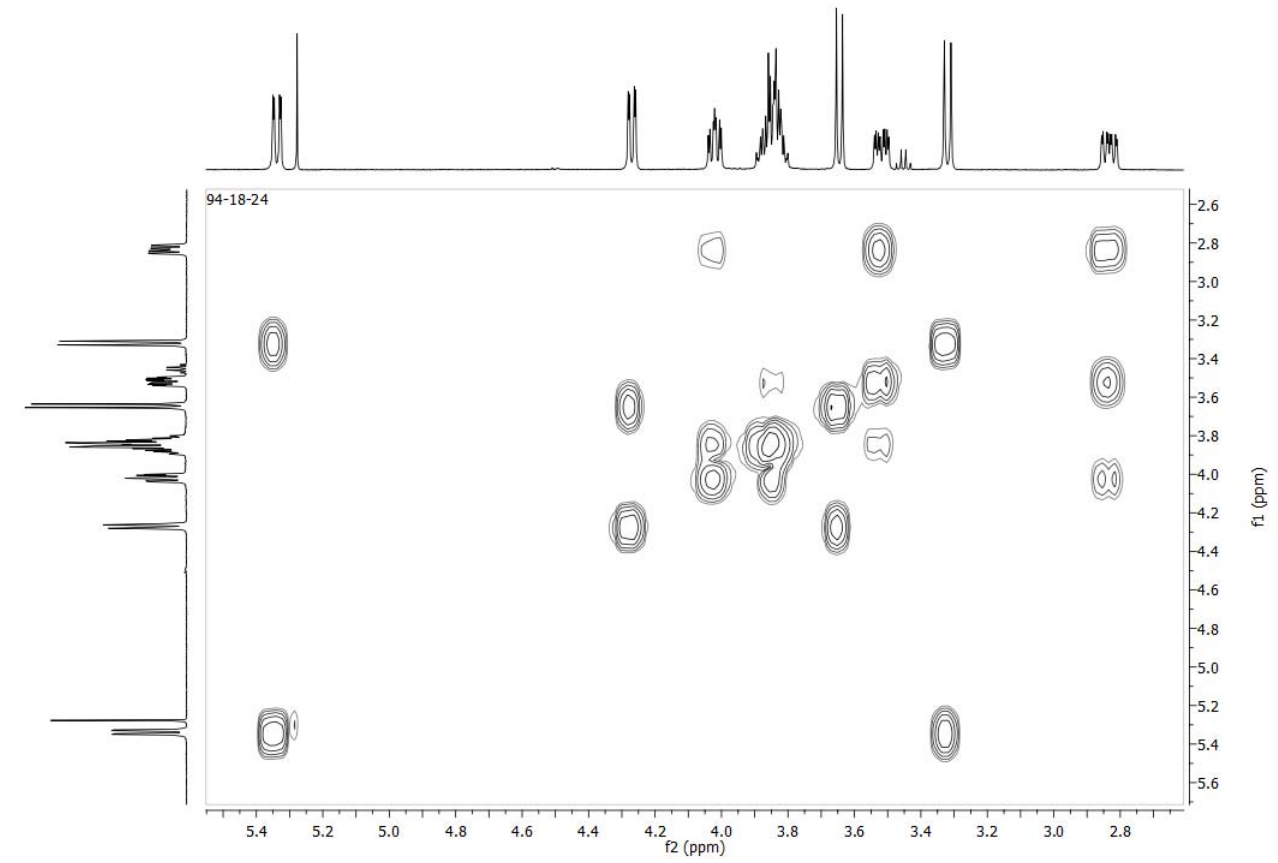


Fig. S20 COSY spectrum of compound **8**

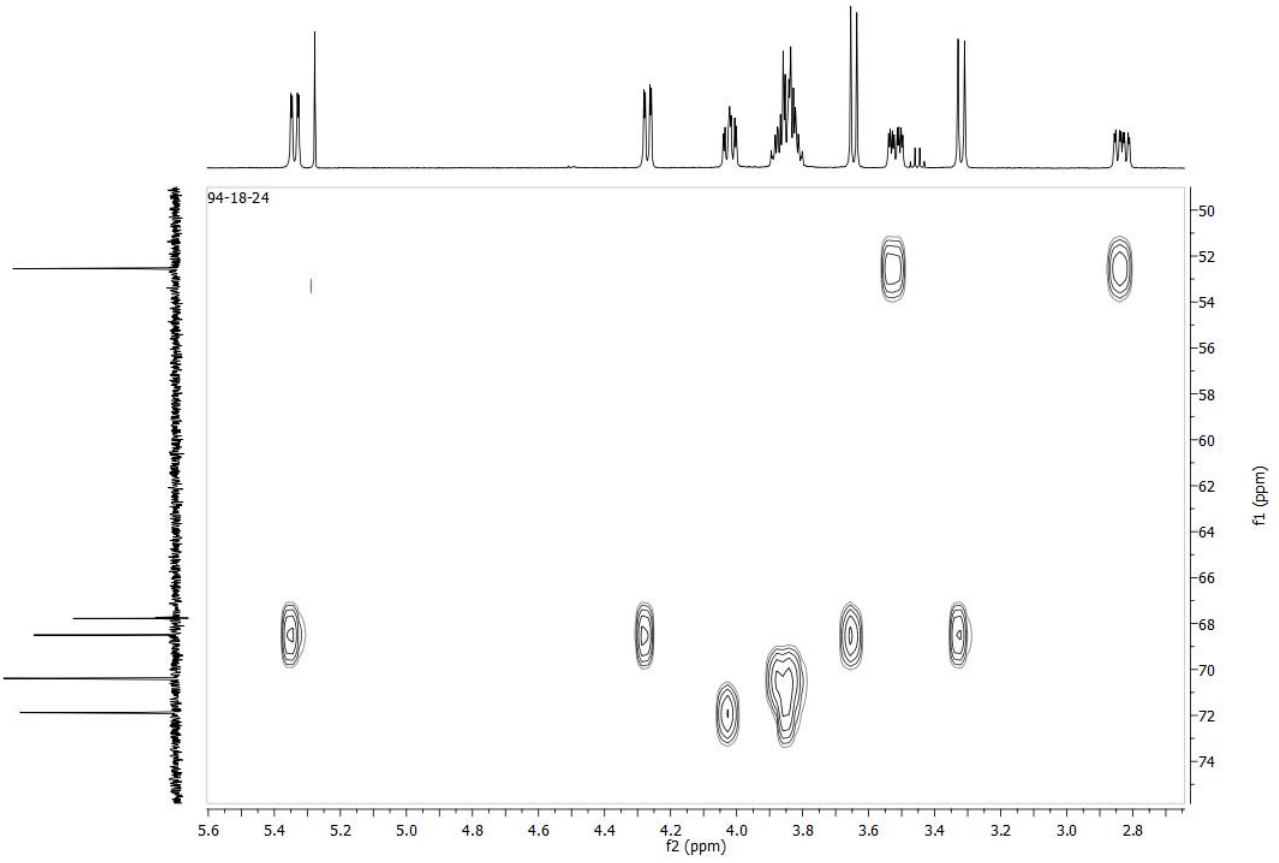
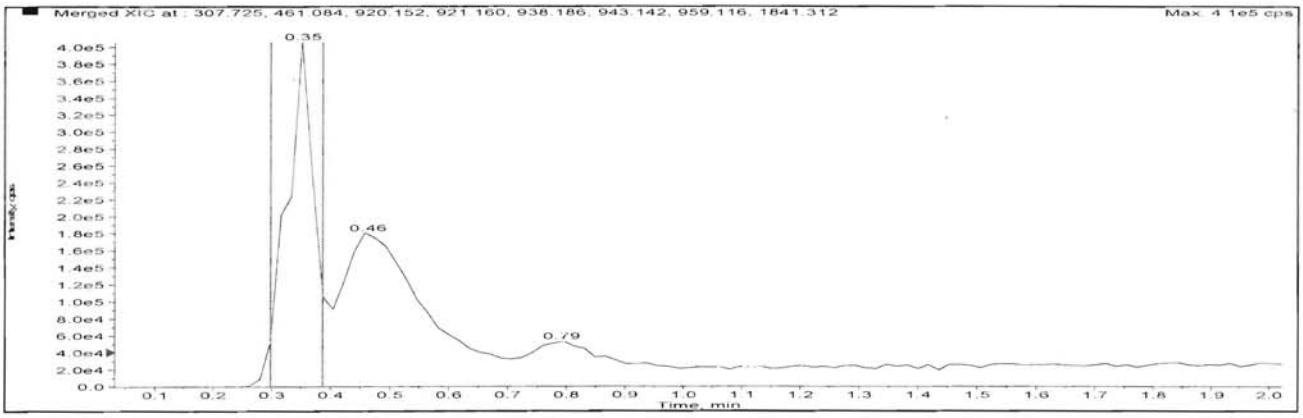


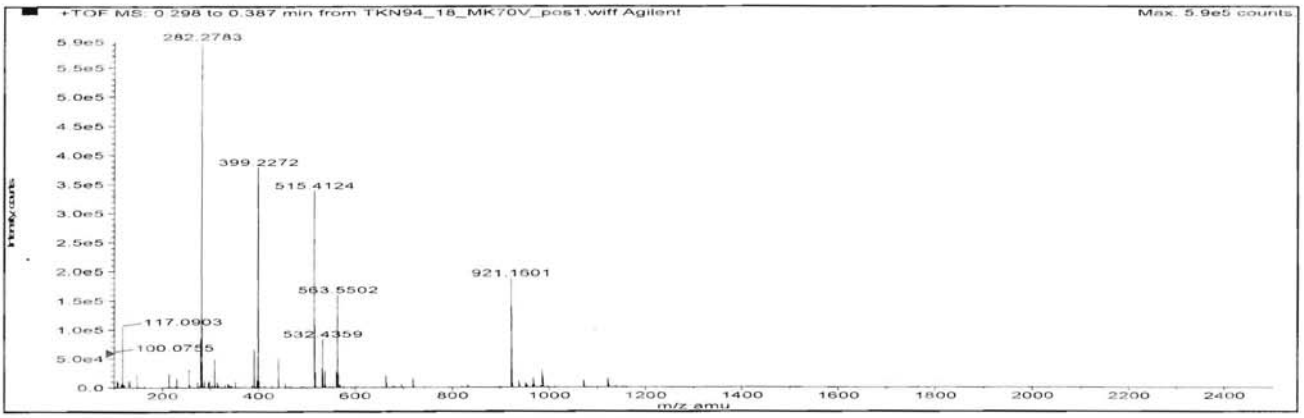
Fig. S21 HSQC spectrum of compound **8**

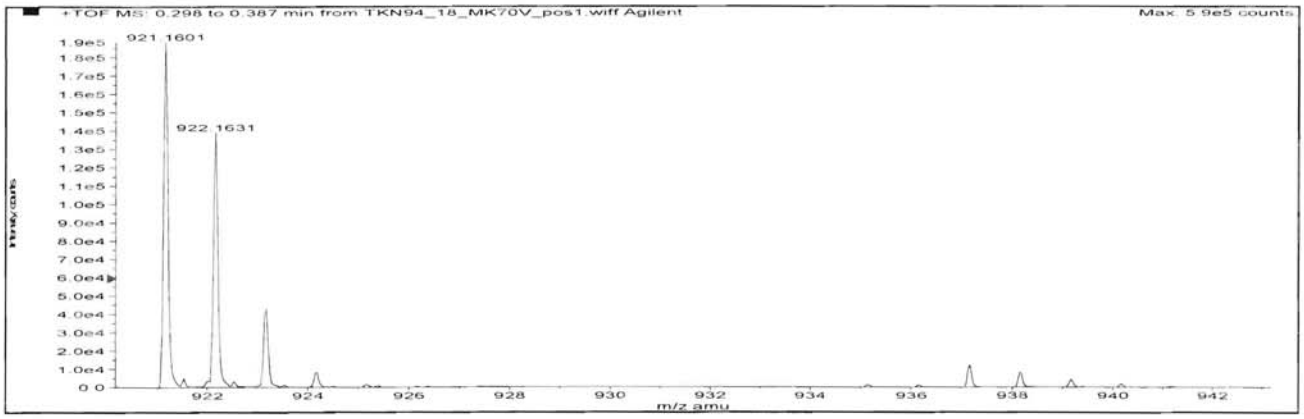
Sample Name: **TKN94-18** Sample Location: **P1-C3** Sample Id: Operator: **Milka**
Data File Name: **D:\PE Sciex Data\Projects\D_Milic\Data\TKN94_18_MK70V_pos1.wiff** Acq Time: **April 27 2012, 11:11:04 AM**
Method: **D:\TOF_Data\damethods\Night_Seq_Comp_ident1.anm\efc.xml**

One or more scans have failed IRM. Review the data file for details.



Merged XIC, Period# : 1 Experiment# : 1





Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C70H20N2O2	--	920.15248	0.35	1.00097 E6	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+H]+	188342.12	921.15975	921.16010	0.34509	0.37	--
[M+NH4]+	8444.71	938.18630	938.15891	-27.39731	-29.20	--

Fig. S22 HR-MS spectrum of compound **8**

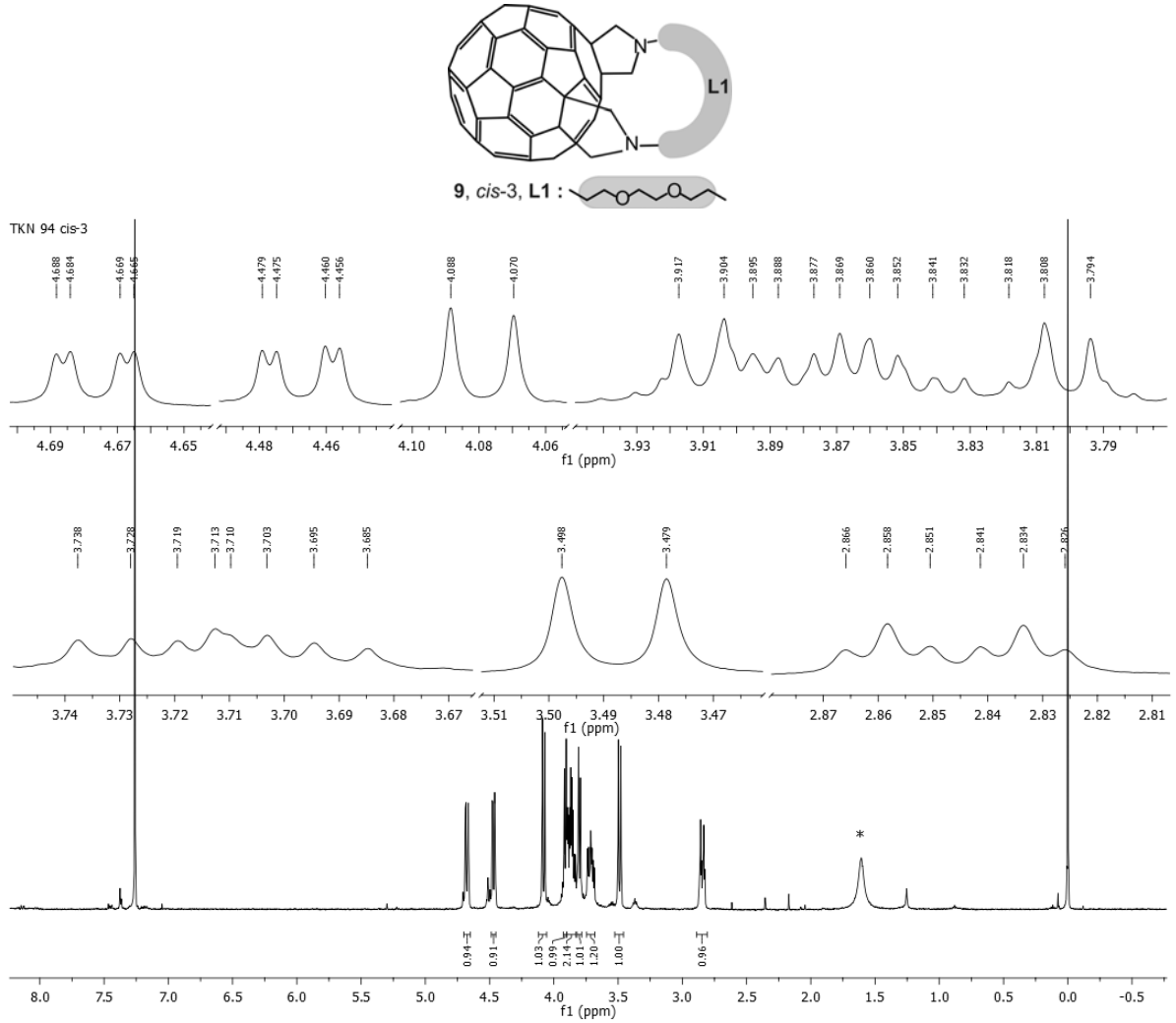


Fig.S23 ^{1}H NMR spectrum of compound **9**

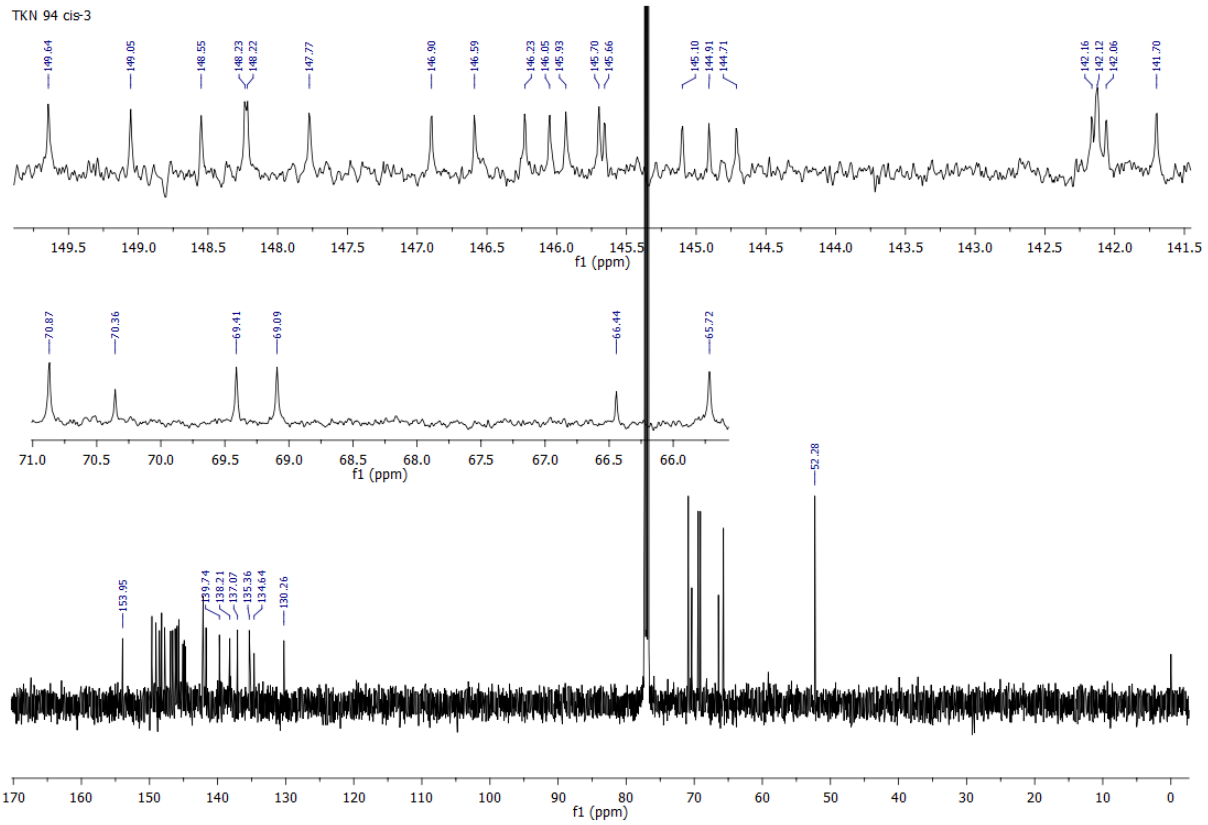


Fig.S24 ^{13}C NMR spectrum of compound **9**

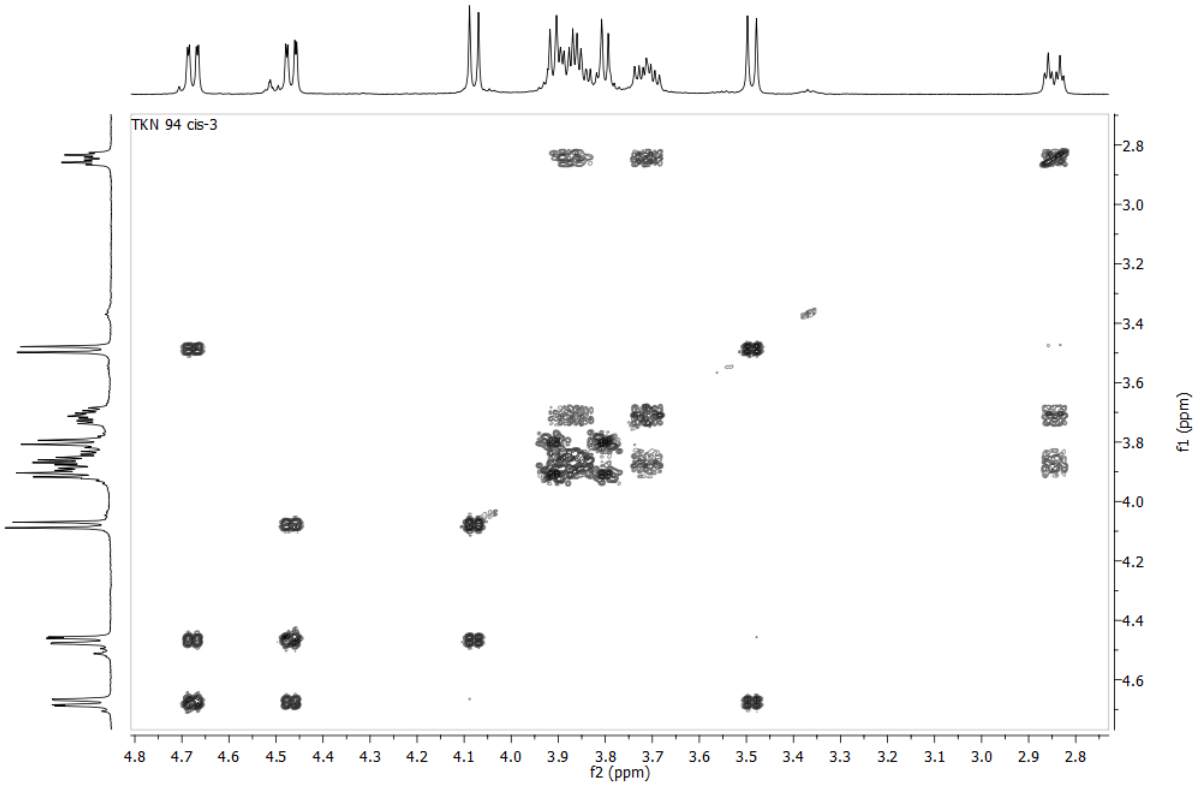


Fig. S25 COSY spectrum of compound **9**

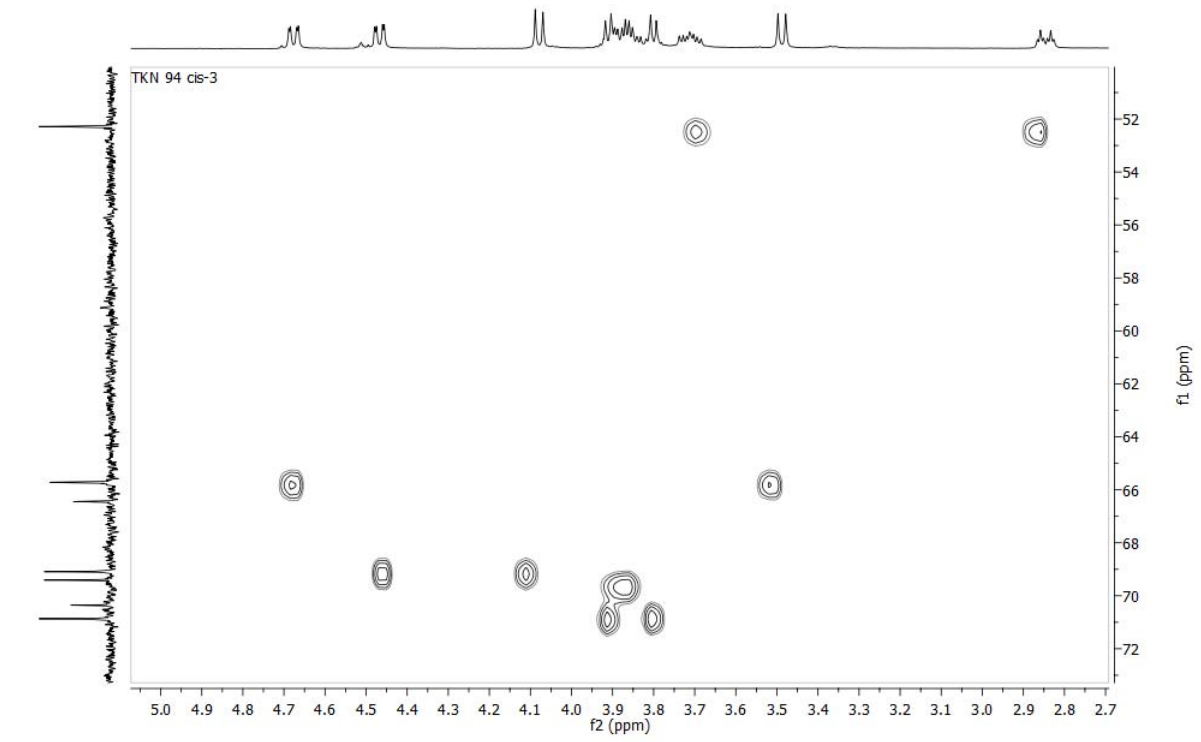
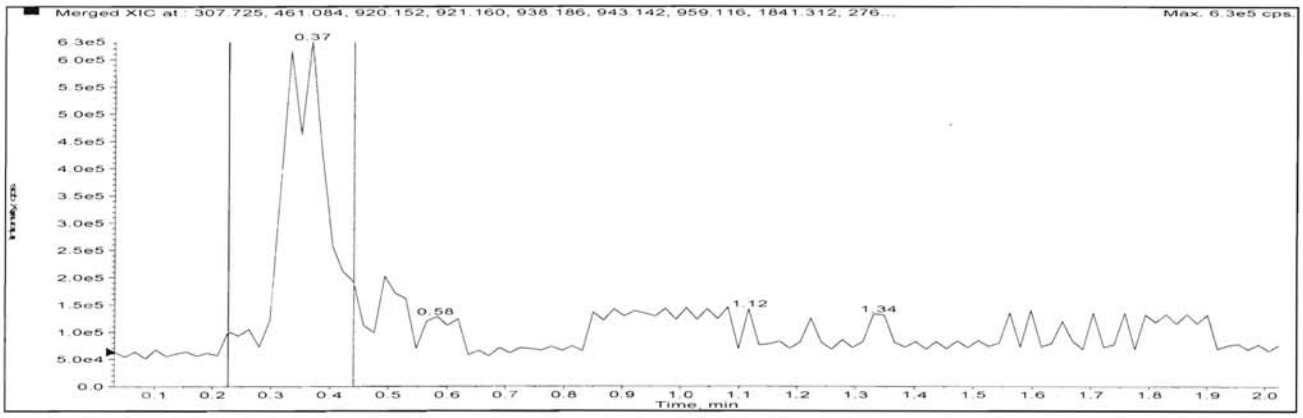


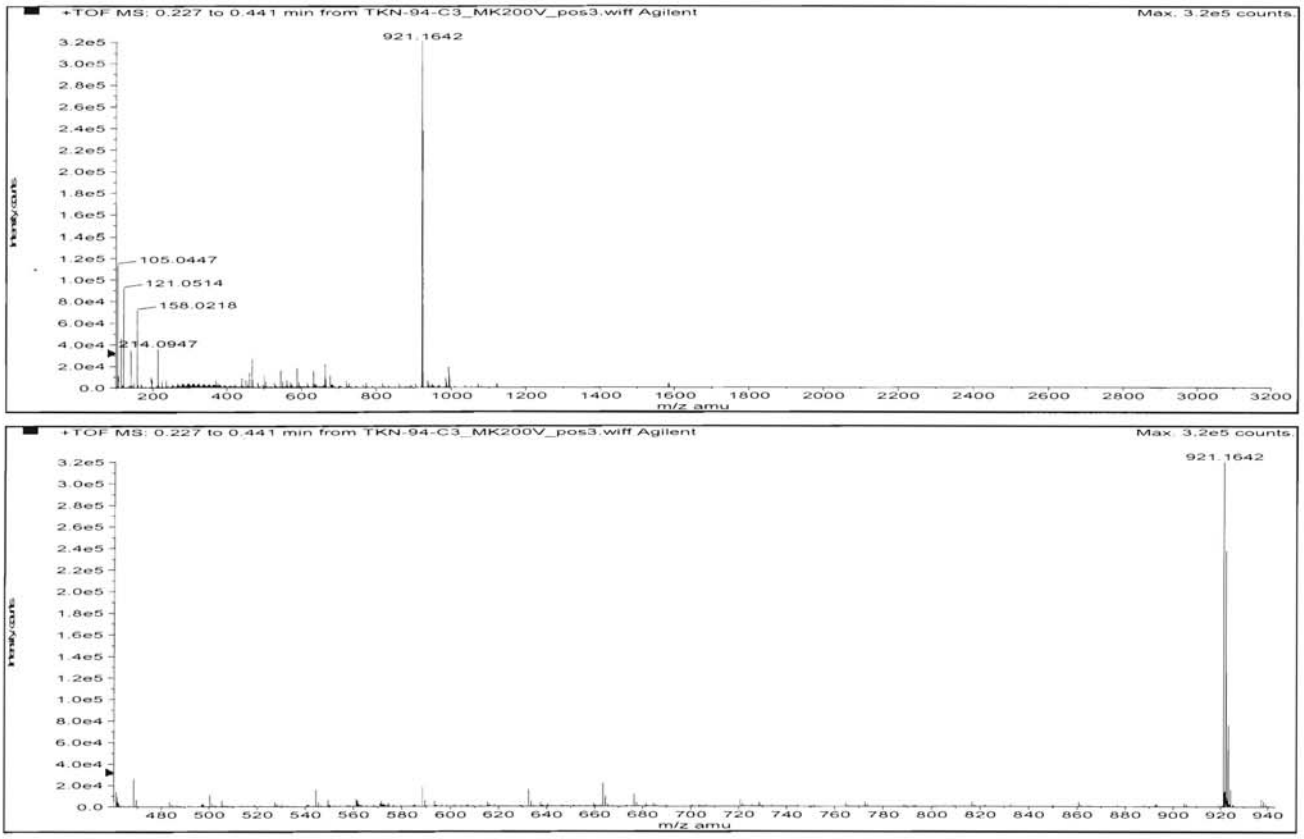
Fig. S26 HSQC spectrum of compound **9**

Sample Name: **TKN-94-C3** Sample Location: **P1-C2** Sample Id: Operator: **Milka**
Data File Name: **D:\PE Sciex Data\Projects\D_Milic\Data\TKN-94-C3_MK200V_pos3.wiff** Acq Time: **July 28 2015, 10:49:42 AM**
Method: **d:\TOF_Data\damethods\Night_Seq_Comp_ident1.anm\efc.xml**

One or more scans have failed IRM. Review the data file for details.



Merged XIC, Period# : 1 Experiment# : 1



Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C70H20N2O2	--	920.15248	0.37	2.86071 E6	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+2H]2+	14217.34	461.08352	461.08479	1.27093	2.76	--
[M+H]+	321713.99	921.15975	921.15997	0.22049	0.24	--
[M+NH4]+	5088.87	938.18630	938.16024	-26.06655	-27.78	--

Fig. S27 HR-MS spectrum of compound **9**

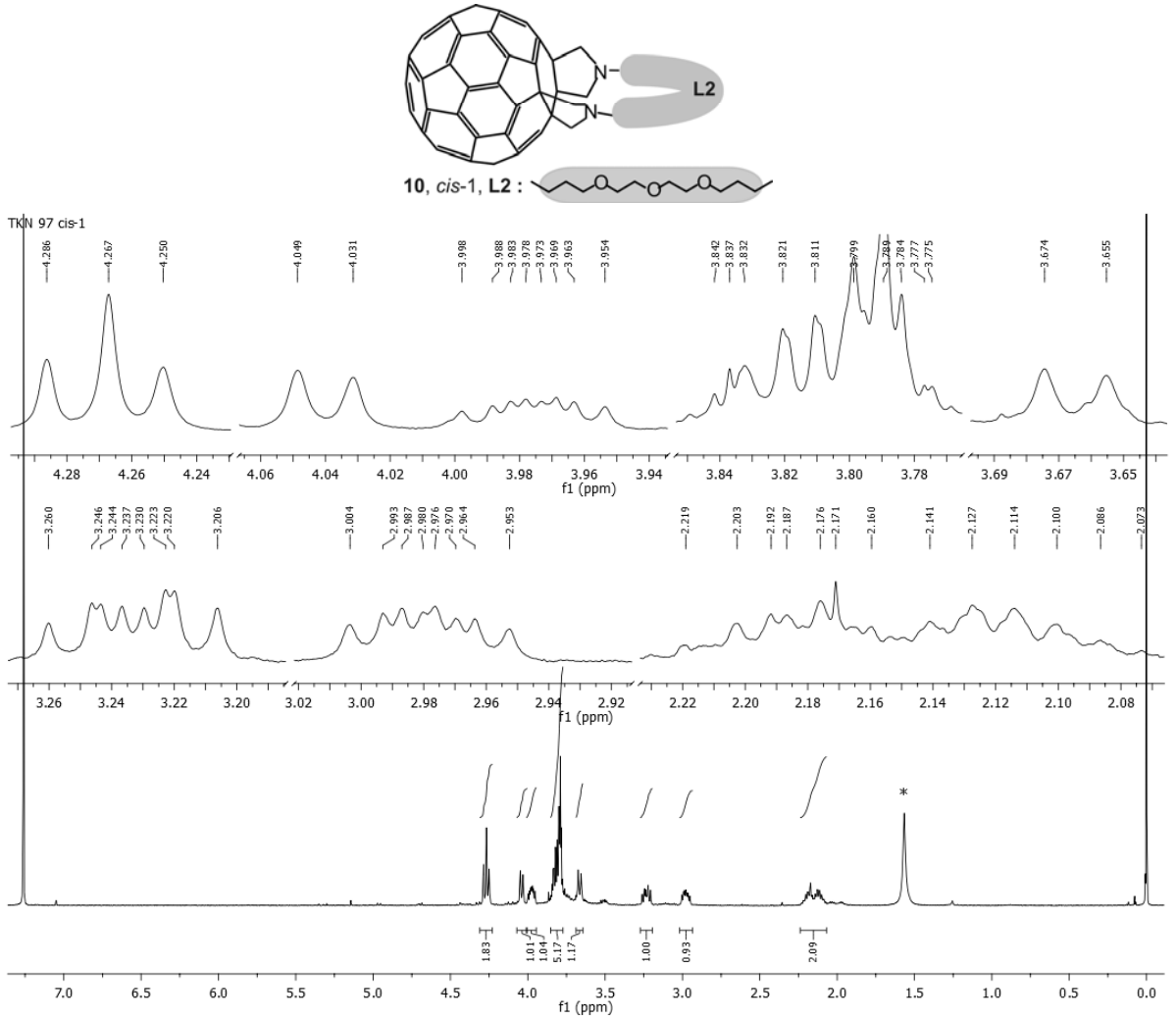


Fig.S28 ^{1}H NMR spectrum of compound **10**

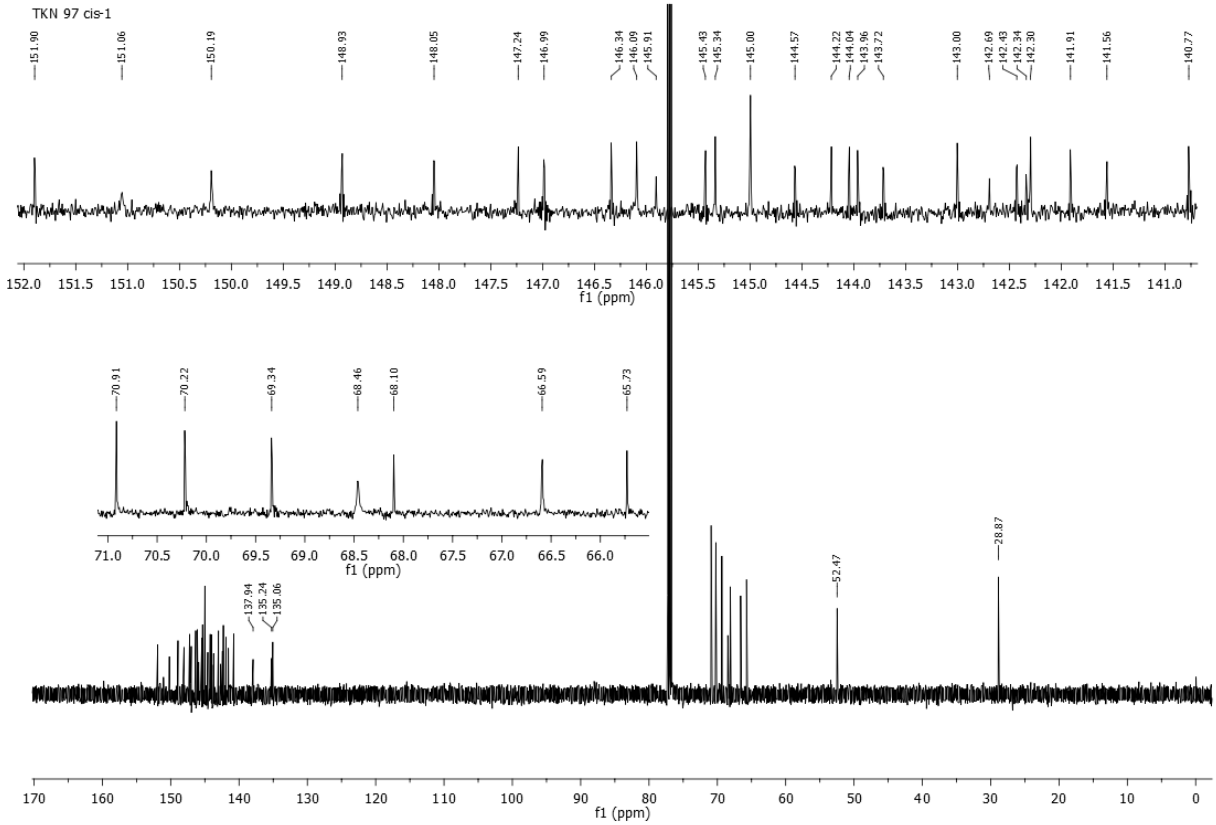


Fig.S29 ^{13}C NMR spectrum of compound **10**

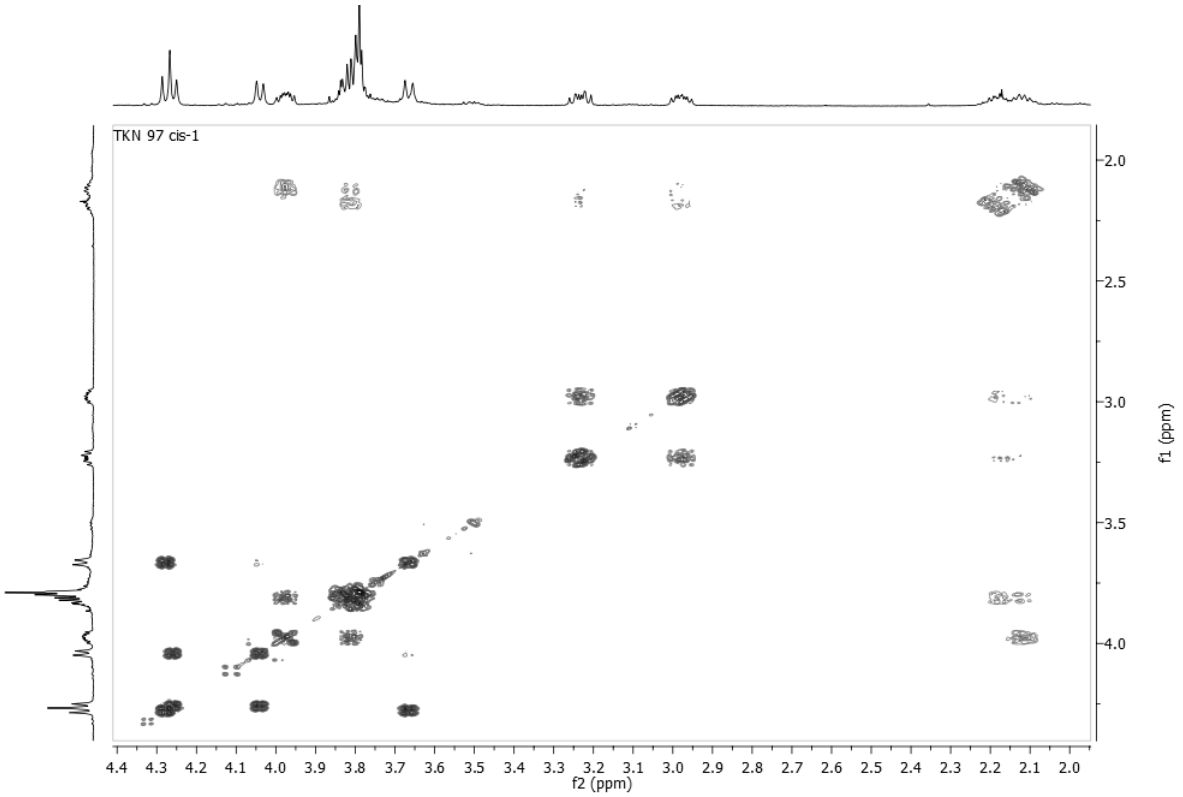


Fig. S30 COSY spectrum of compound **10**

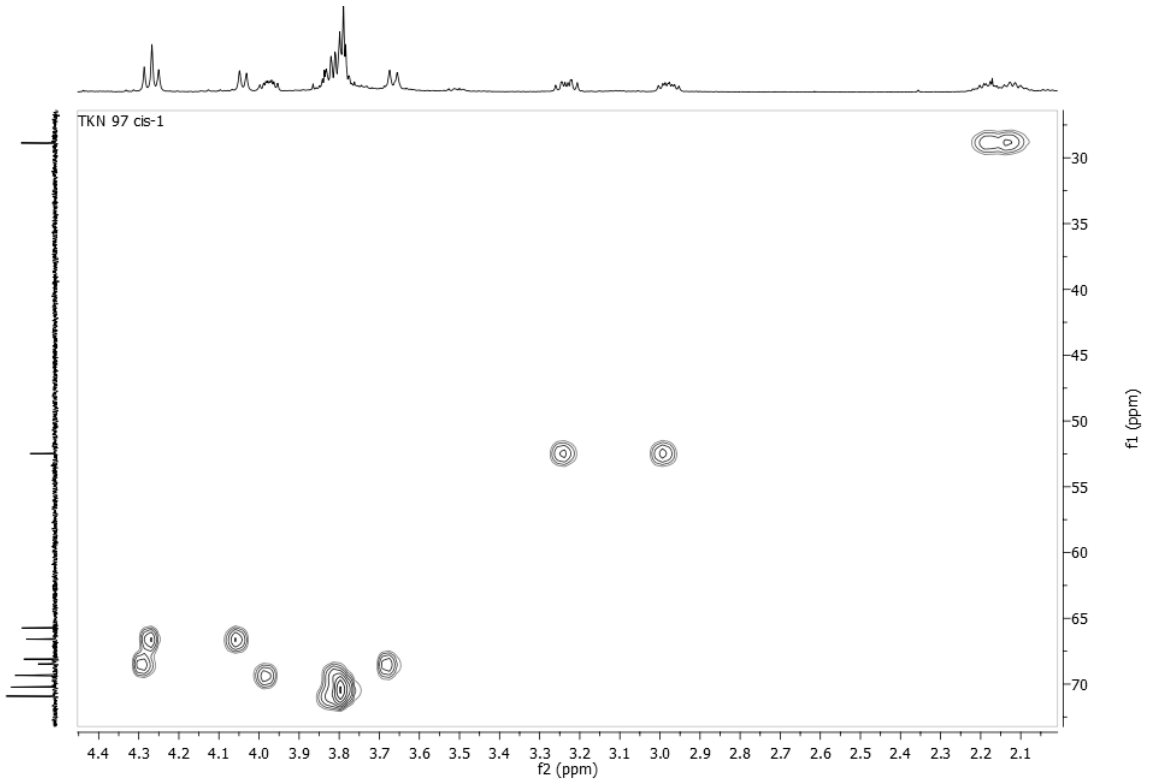
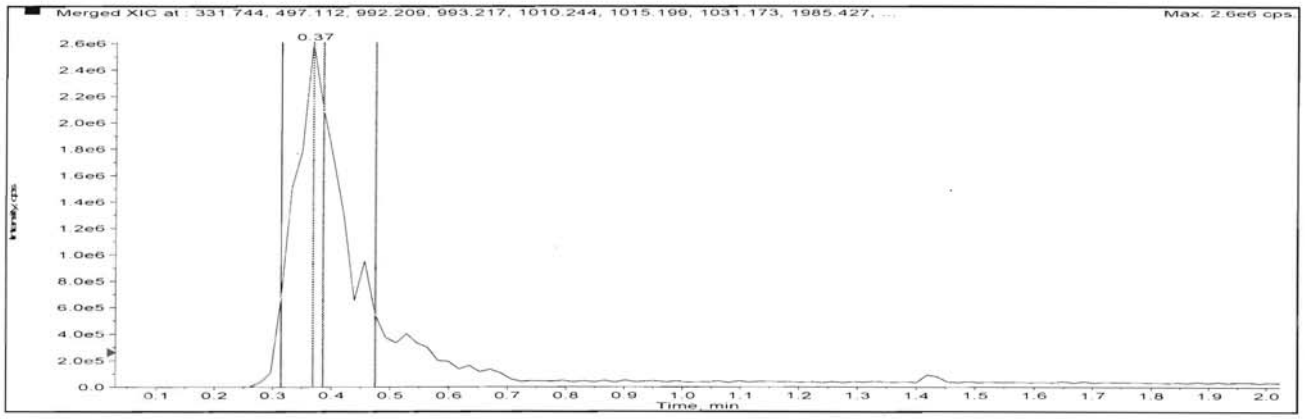
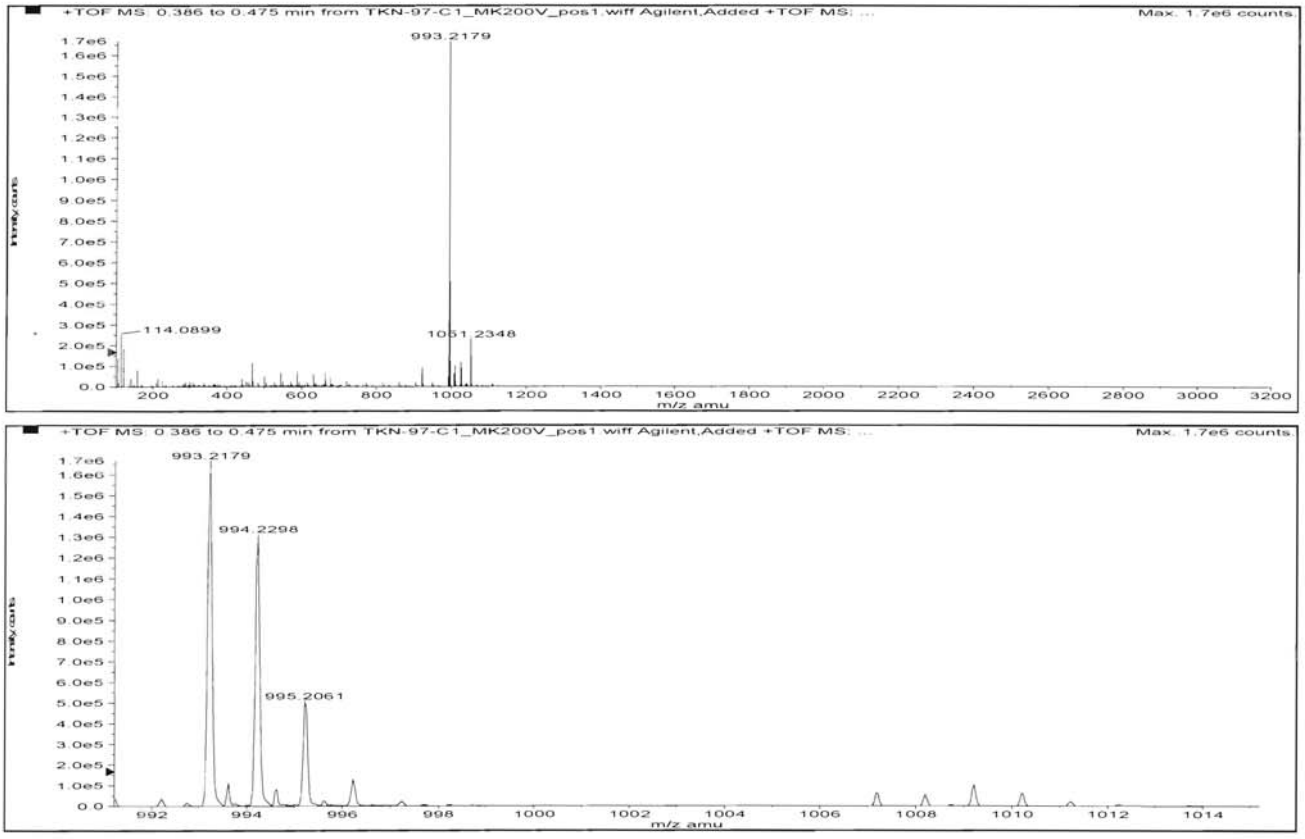


Fig. S31 HSQC spectrum of compound **10**

Sample Name: **TKN-97-C1** Sample Location: **P1-C3** Sample Id: Operator: **Milka**
Data File Name: **D:\PE Sciex Data\Projects\D_Milic\Data\TKN-97-C1_MK200V_pos1.wiff** Acq Time: **July 28 2015, 10:19:53 AM**
Method: **d:\TOF_Data\damethods\Night_Seq_Comp_ident1.anm\efc.xml**



Merged XIC, Period# : 1 Experiment# : 1



Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C74H28N2O3	--	992.20999	0.37	1.34865 E7	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
M+	36030.60	992.20944	992.20436	-5.08845	-5.13	--
[M+H]+	1671238.55	993.21727	993.21561	-1.66295	-1.67	--
[M+NH4]+	63146.49	1010.24382	1010.21360	-30.22208	-29.92	--

Fig. S32 HR-MS spectrum of compound **10**

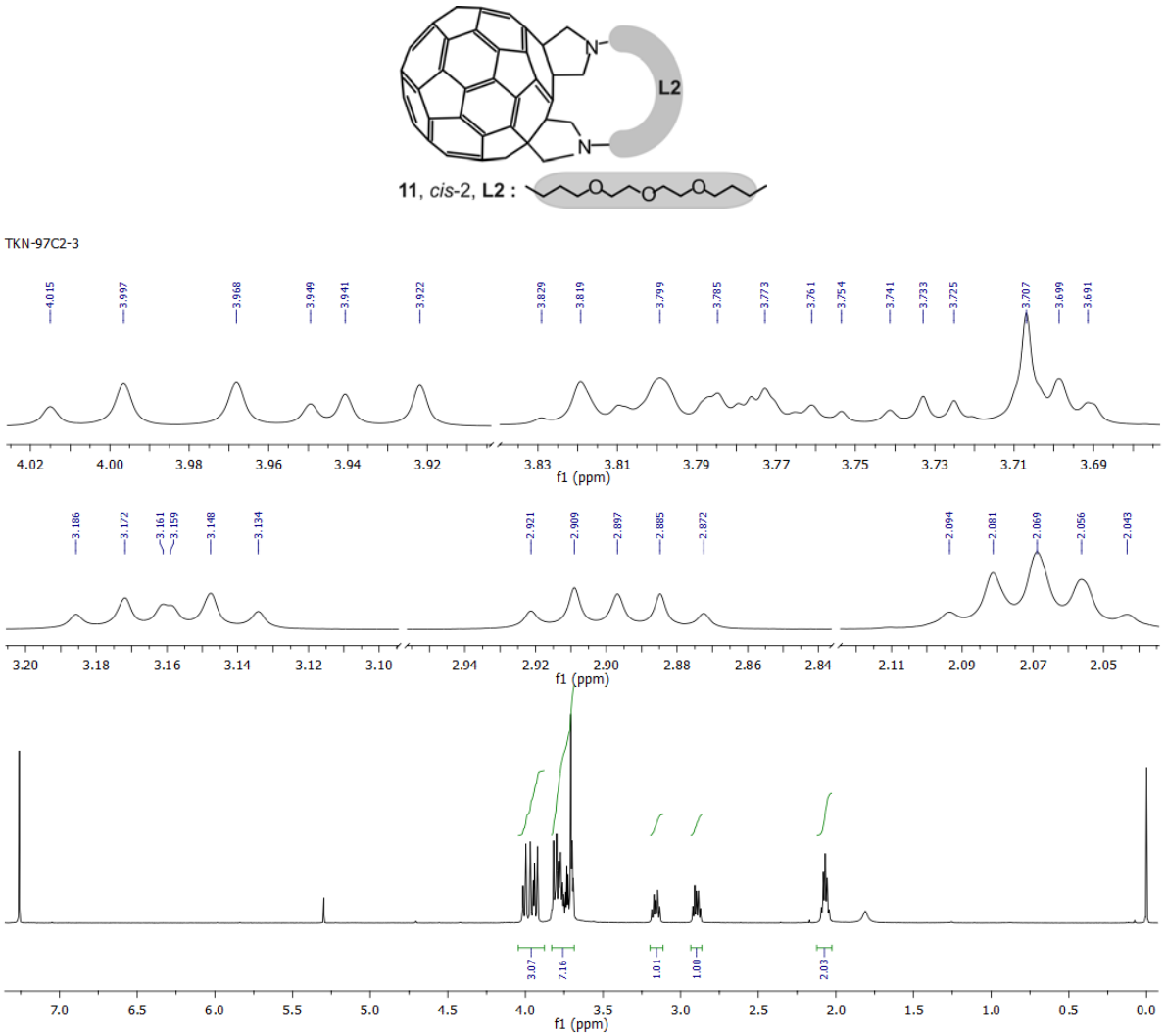


Fig.S33 ^{1}H NMR spectrum of compound **11**

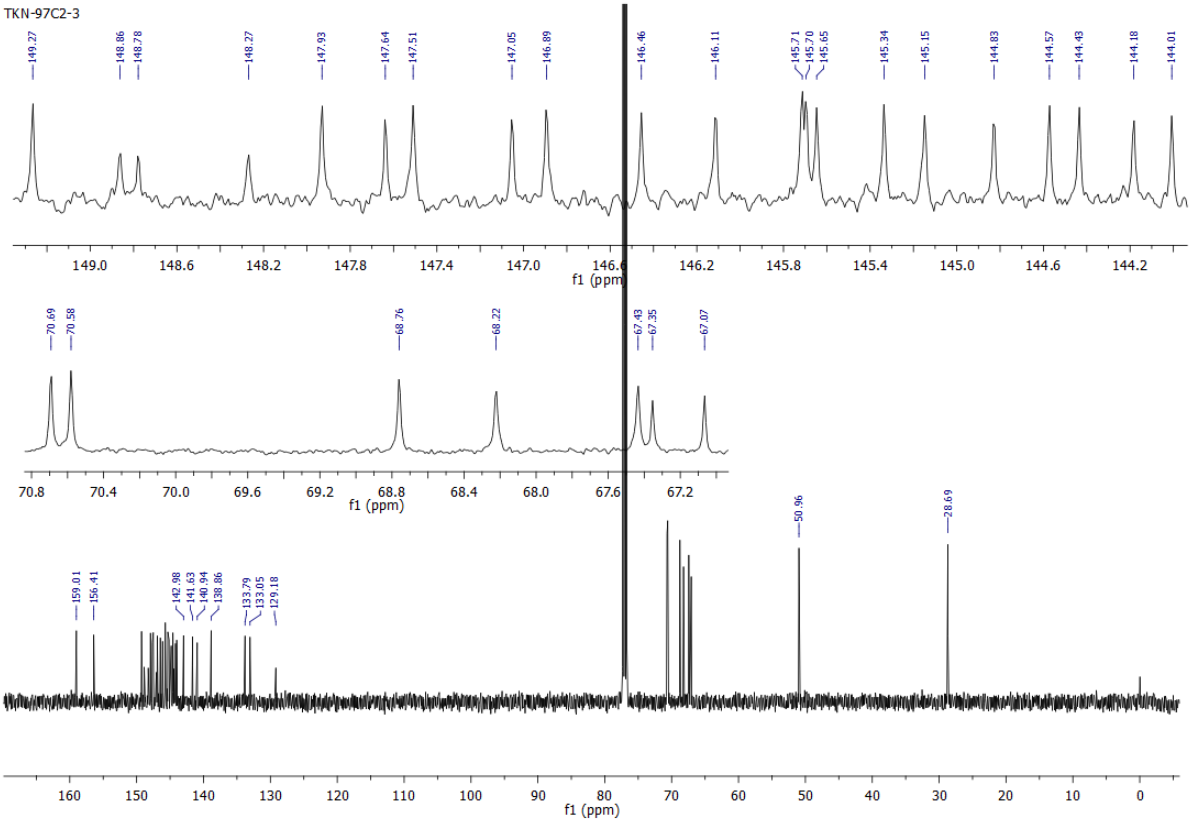


Fig.S34 ^{13}C NMR spectrum of compound **11**

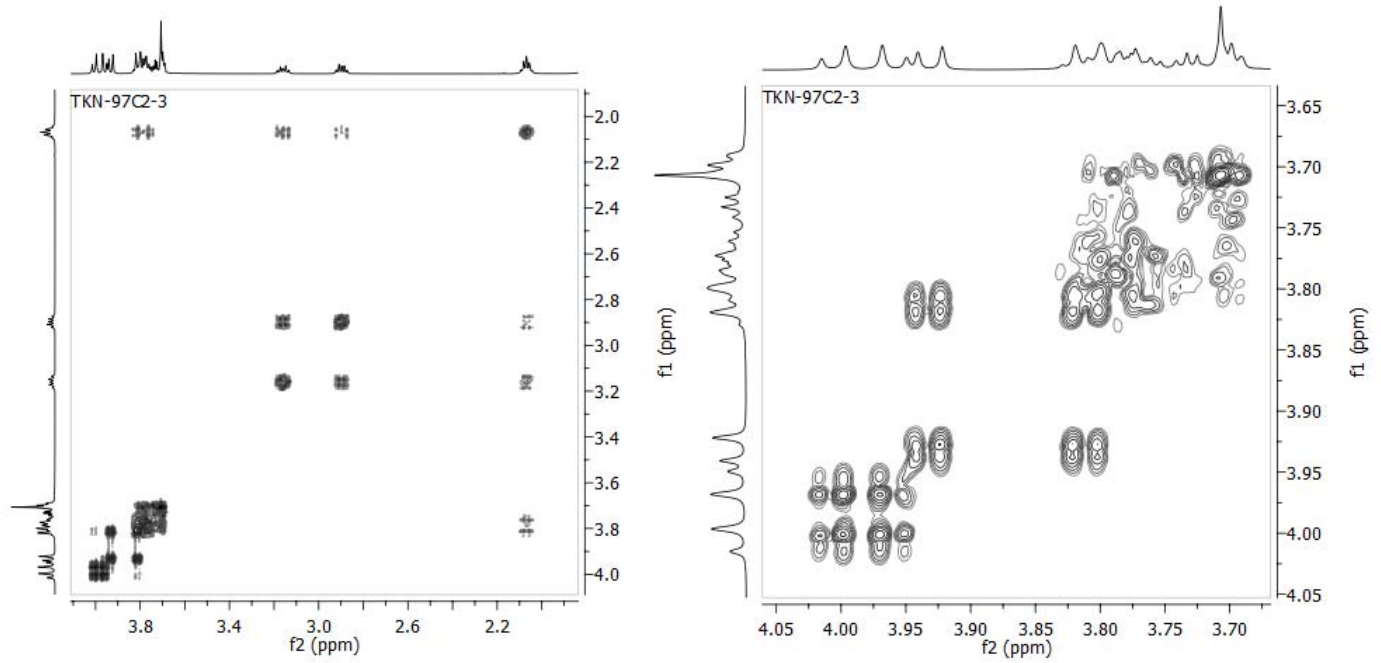


Fig. S35 COSY spectrum of compound **11**

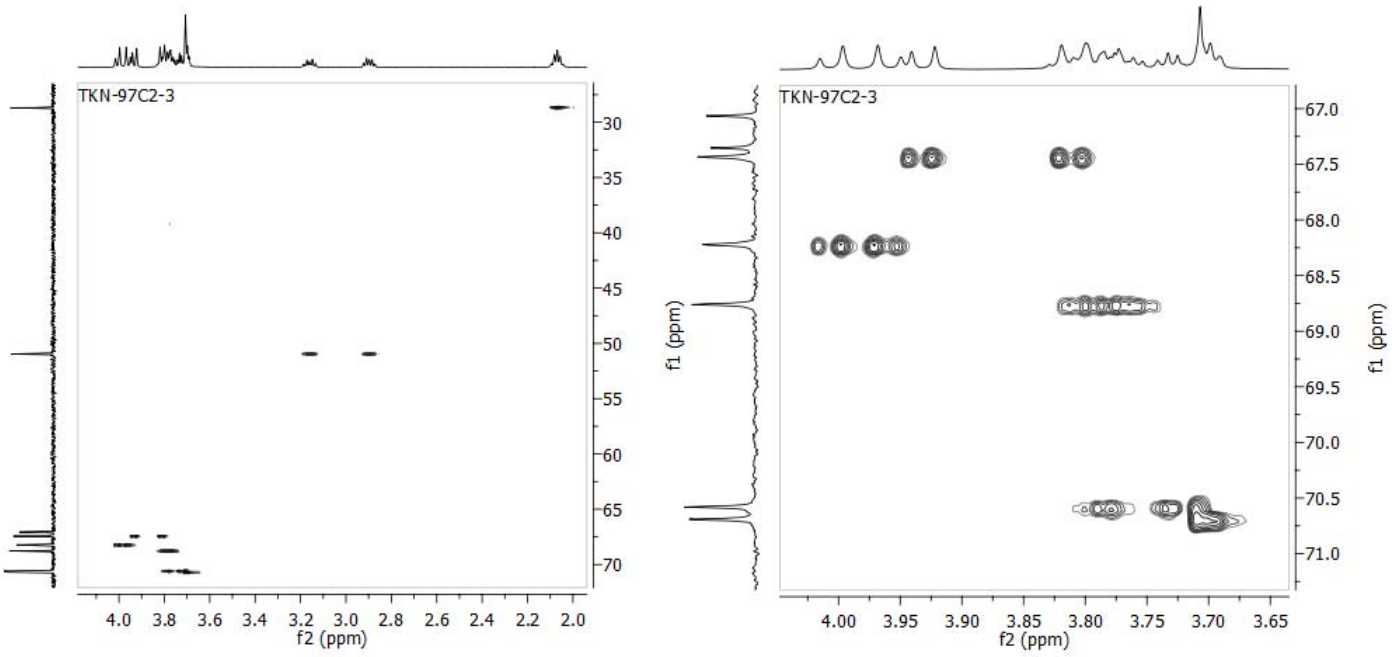
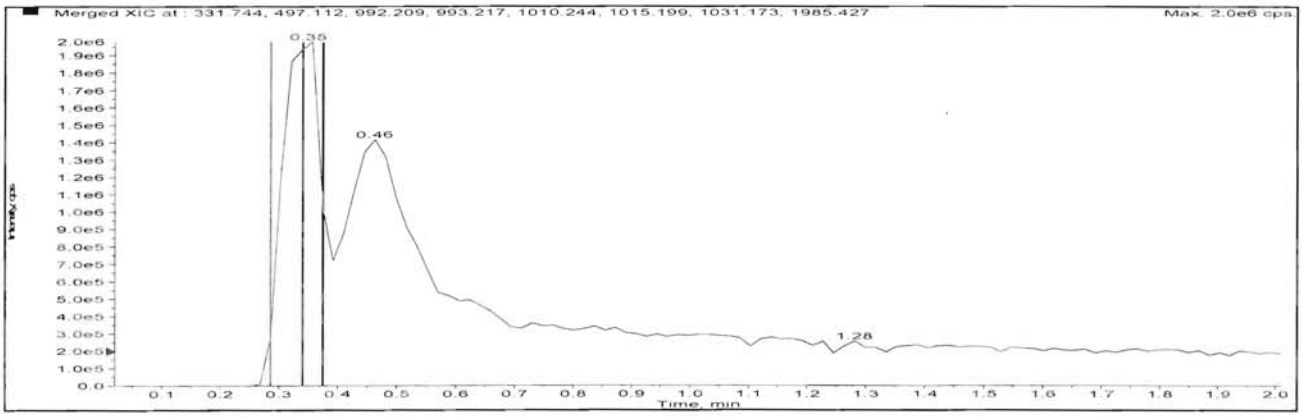


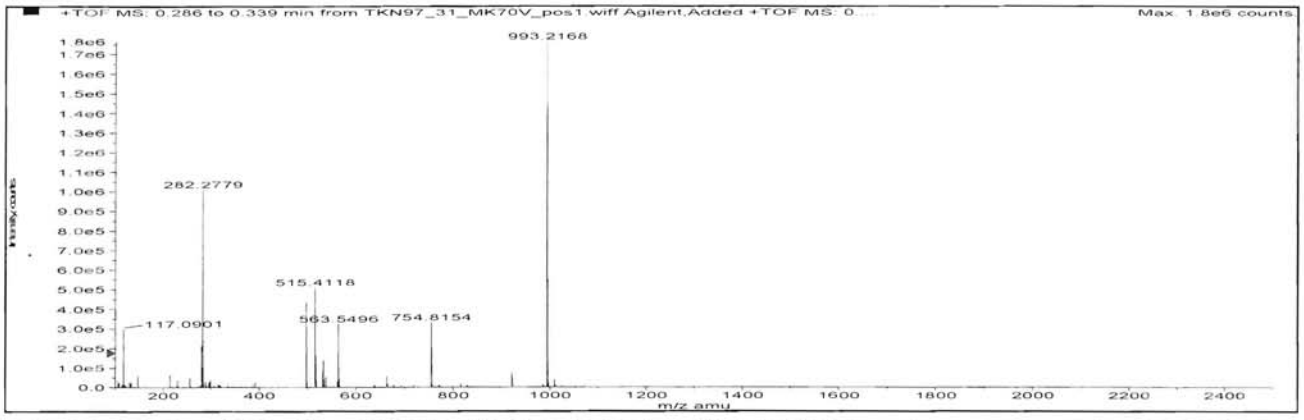
Fig. S36 HSQC spectrum of compound **11**

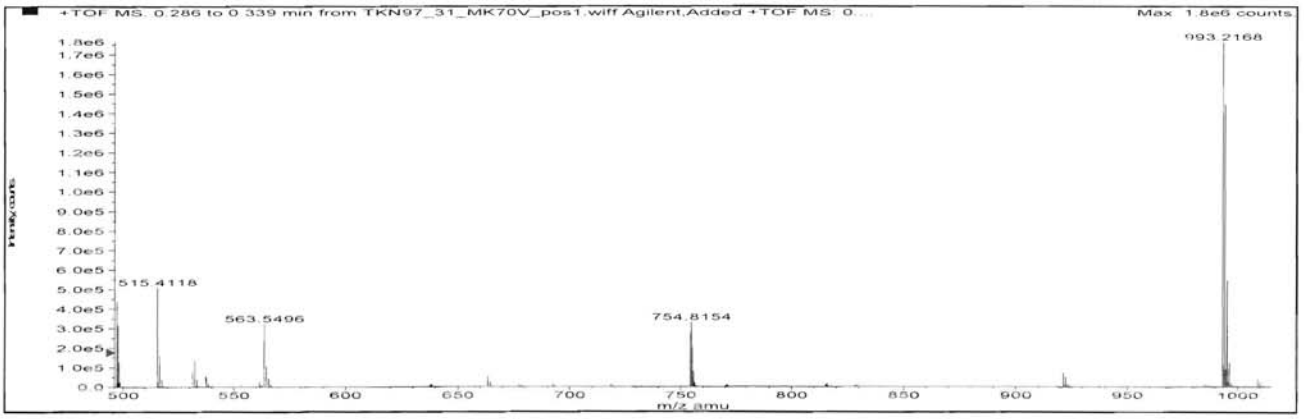
Sample Name: **TKN97-31** Sample Location: **P1-C4** Sample Id: Operator: **Milka**
Data File Name: **D:\PE Sciex Data\Projects\D_Milic\Data\TKN97_31_MK70V_pos1.wiff** Acq Time: **April 27 2012, 11:14:17 AM**
Method: **D:\TOF_Data\damethods\Night_Seq_Comp_ident1.anm\efc.xml**

One or more scans have failed IRM. Review the data file for details.



Merged XIC, Period# : 1 Experiment# : 1





Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C74H28N2O3	--	992.20999	0.35	6.50638 E6	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+2H]2+	437569.35	497.11227	497.11101	-1.26153	-2.54	--
[M+H]+	1770072.97	993.21727	993.21682	-0.44446	-0.45	--
[M+NH4]+	30115.51	1010.24382	1010.21427	-29.55150	-29.25	--

Fig. S37 HR-MS spectrum of compound **11**

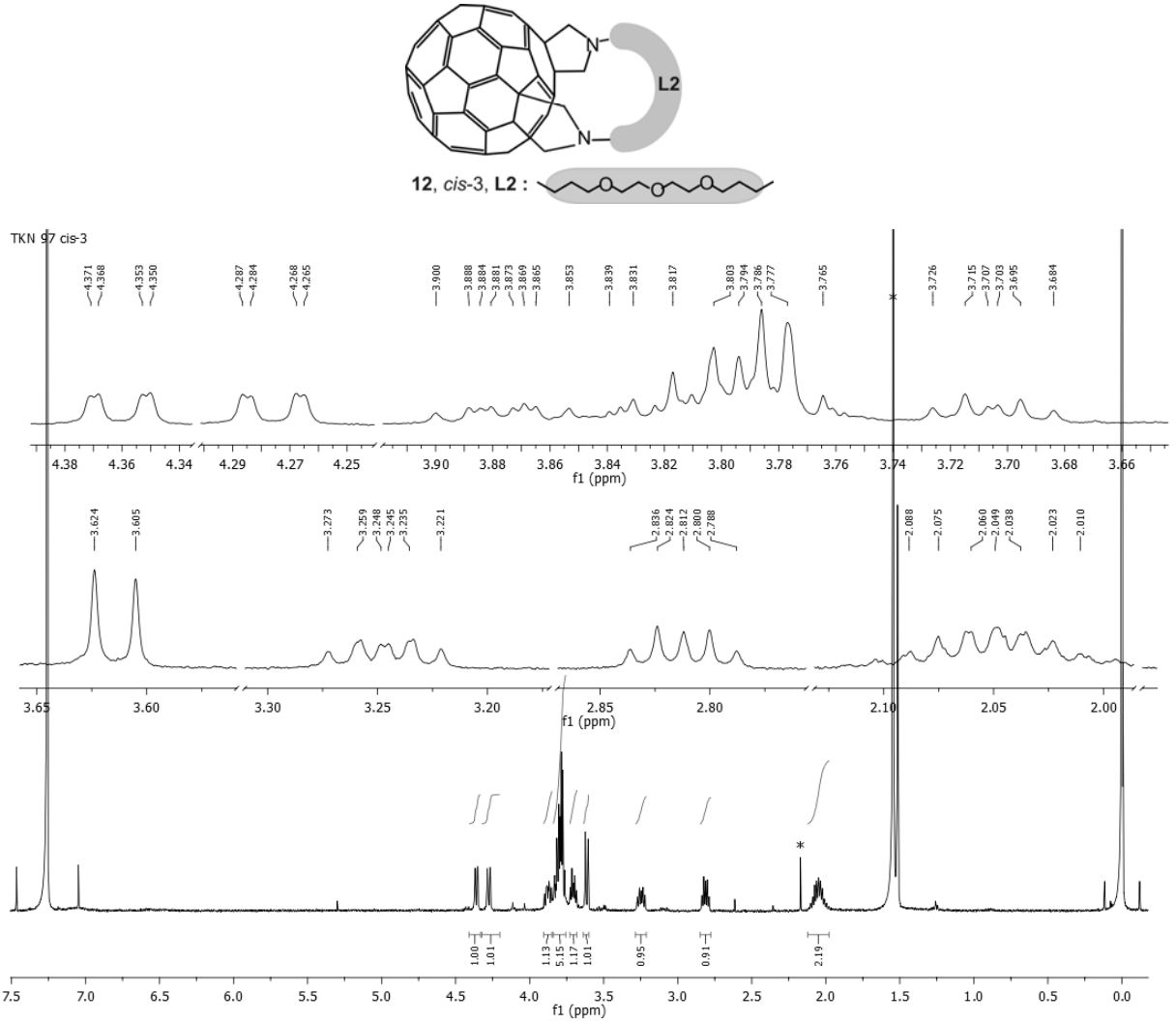


Fig.S38 ^{1}H NMR spectrum of compound **12**

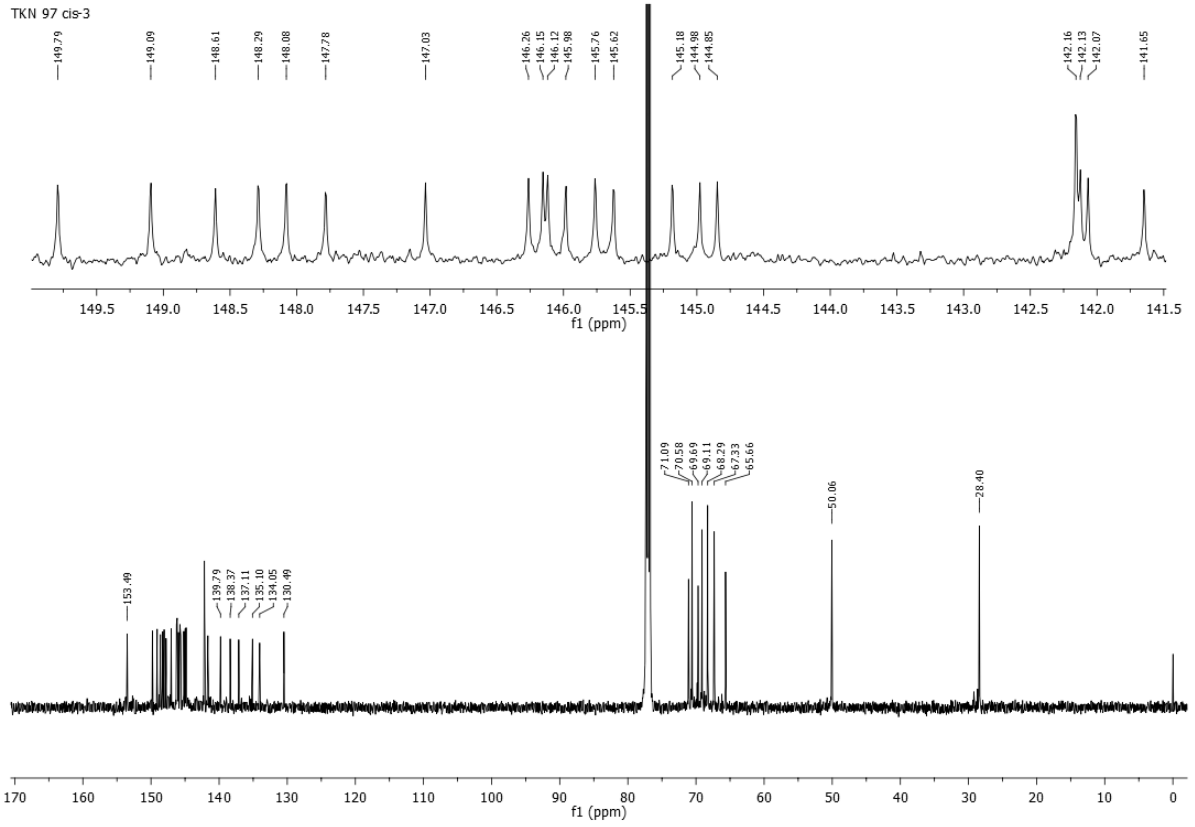


Fig.S39 ^{13}C NMR spectrum of compound **12**

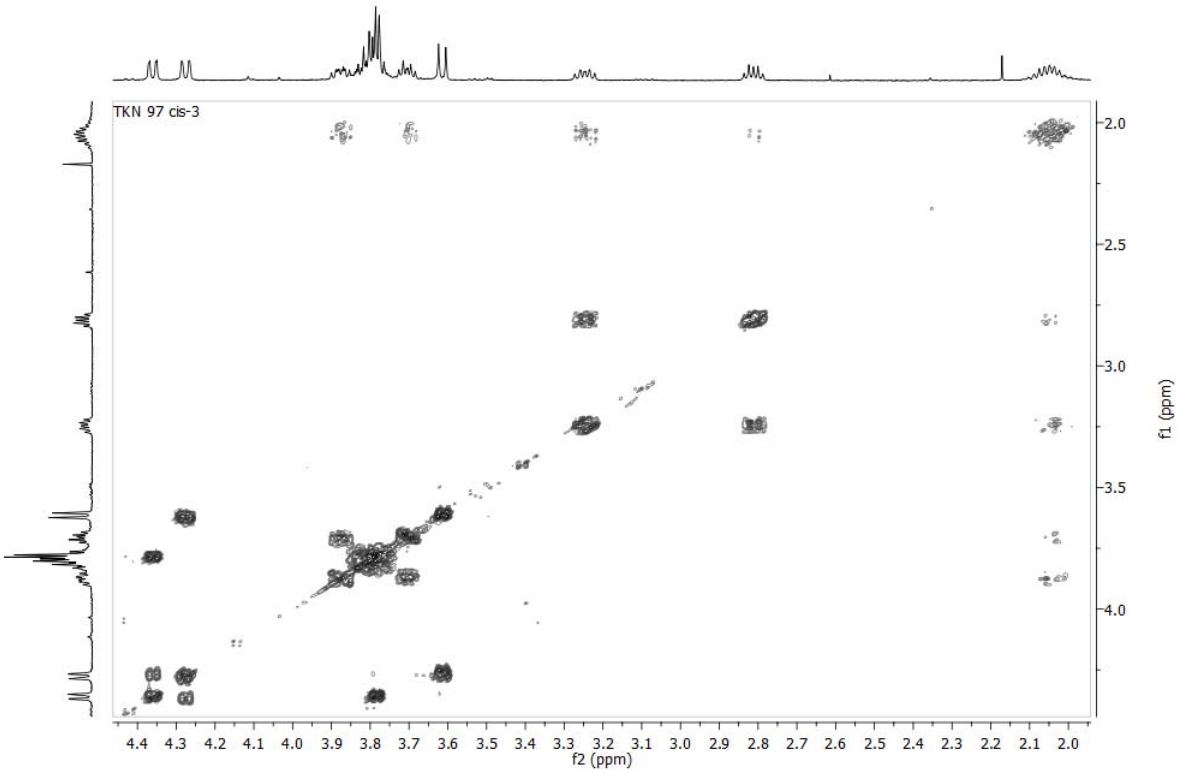


Fig. S40 COSY spectrum of compound **12**

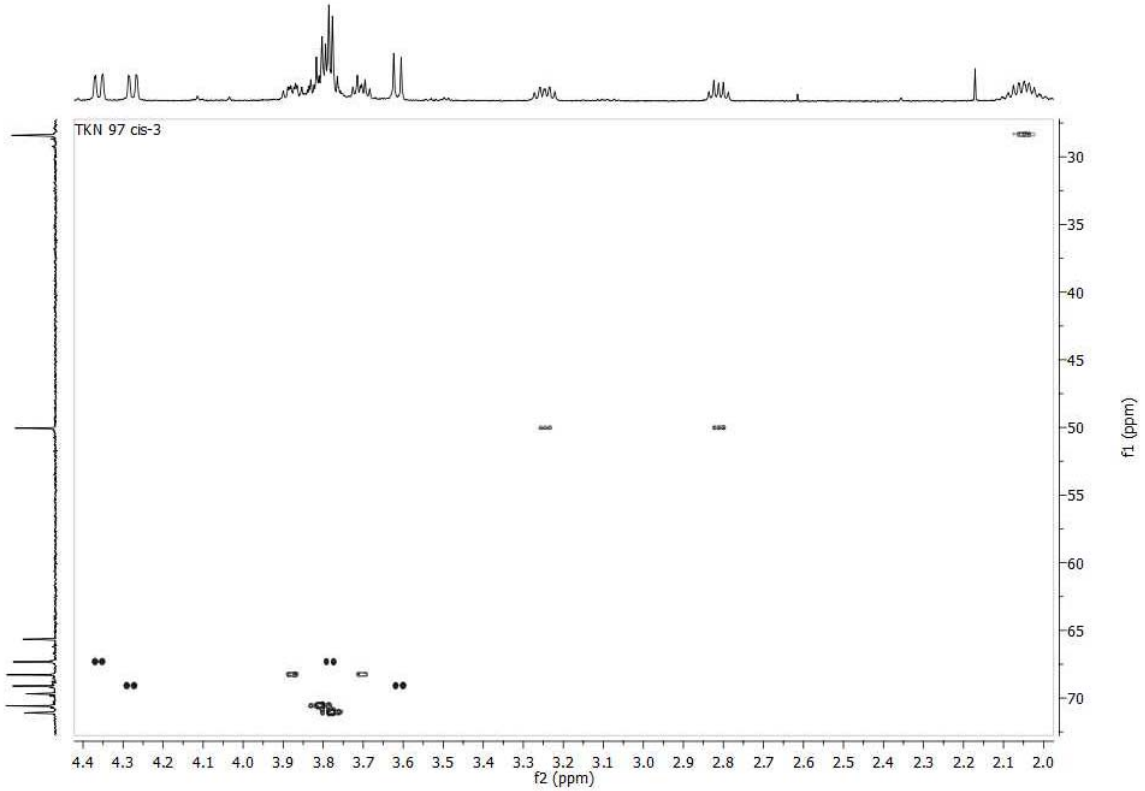
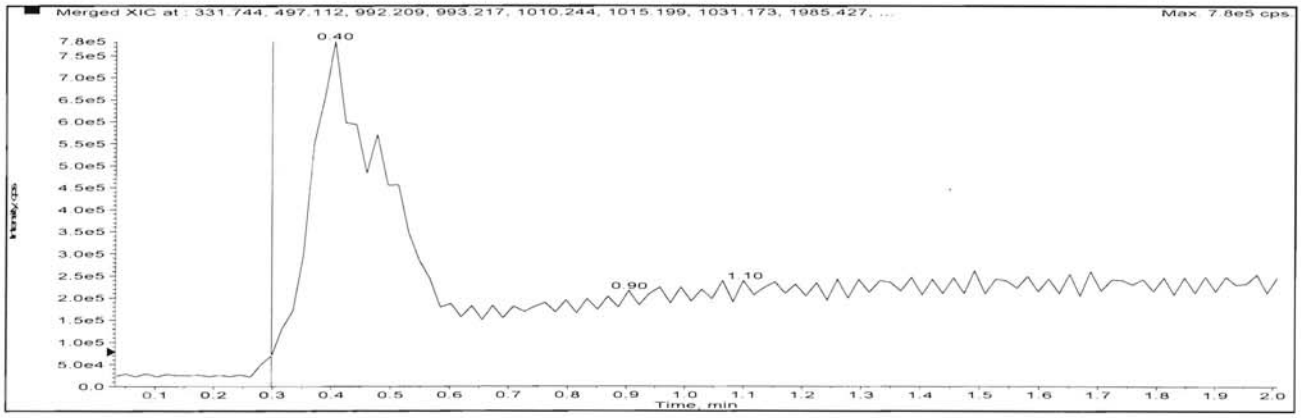
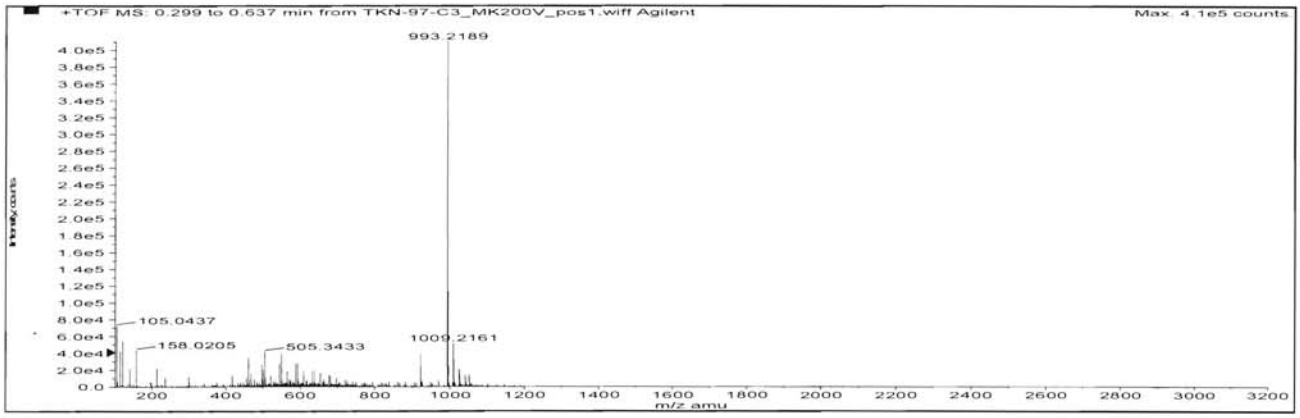


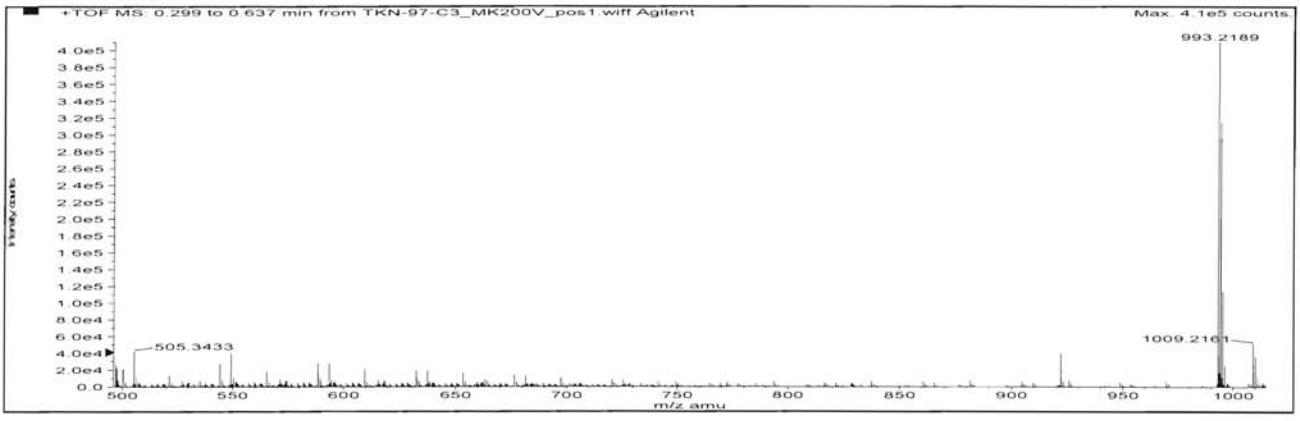
Fig. S41 HSQC spectrum of compound **12**

Sample Name: **TKN-97-C3** Sample Location: **P1-C4** Sample Id: Operator: **Milka**
Data File Name: **D:\PE Sciex Data\Projects\D_Milic\Data\TKN-97-C3_MK200V_pos1.wiff** Acq Time: **July 28 2015, 10:23:04 AM**
Method: **d:\TOF_Data\damethods\Night_Seq_Comp_ident1.anm\efc.xml**



Merged XIC, Period# : 1 Experiment# : 1





Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C74H28N2O3	--	992.20999	0.40	6.01842 E6	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+2H]2+	27465.42	497.11227	497.11162	-0.64813	-1.30	--
[M+H]+	411826.29	993.21727	993.21515	-2.12087	-2.14	--
[M+NH4]+	37755.98	1010.24382	1010.21458	-29.23997	-28.94	--

Fig. S42 HR-MS spectrum of compound **12**

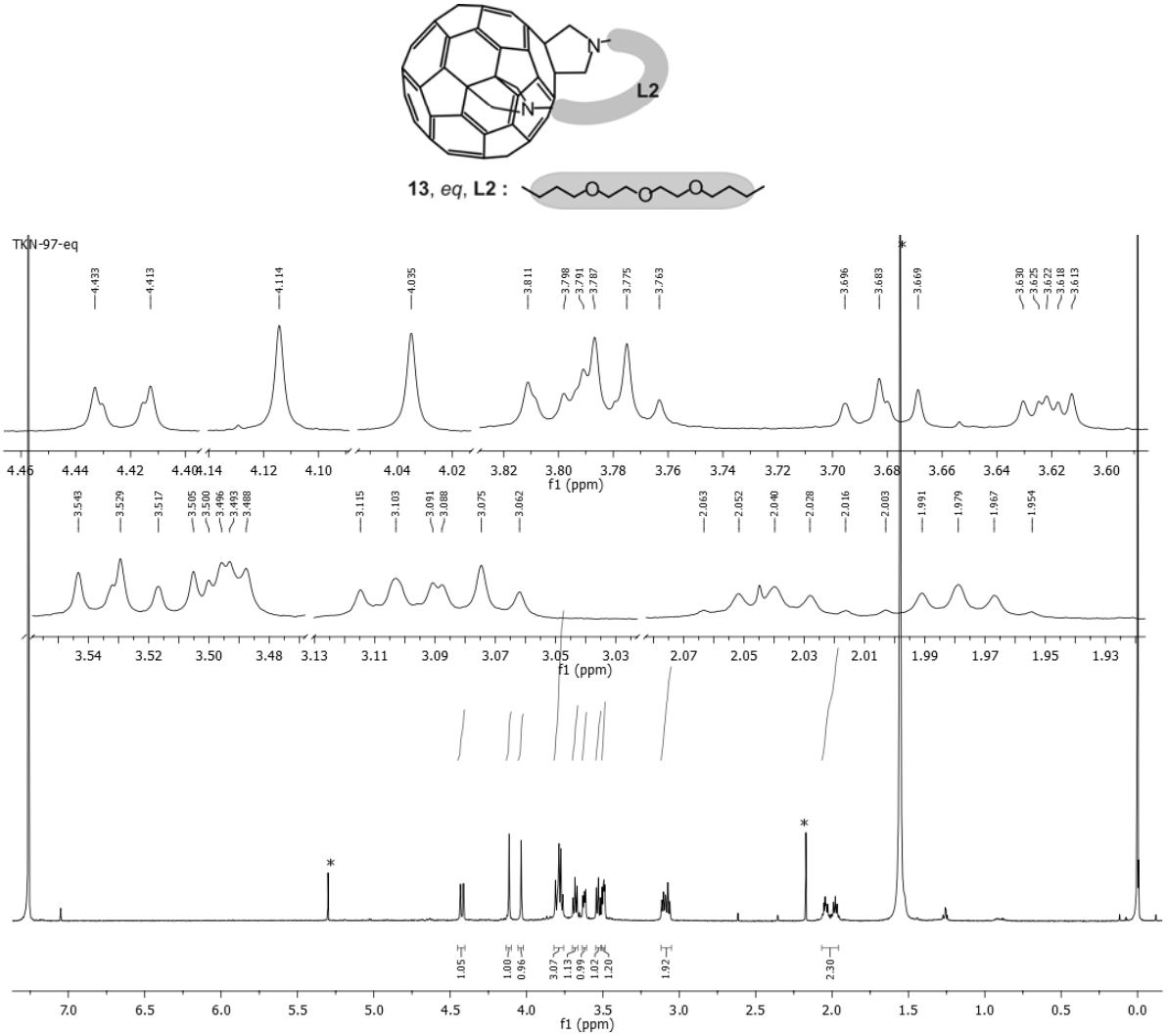


Fig.S43 ^{1}H NMR spectrum of compound **13**

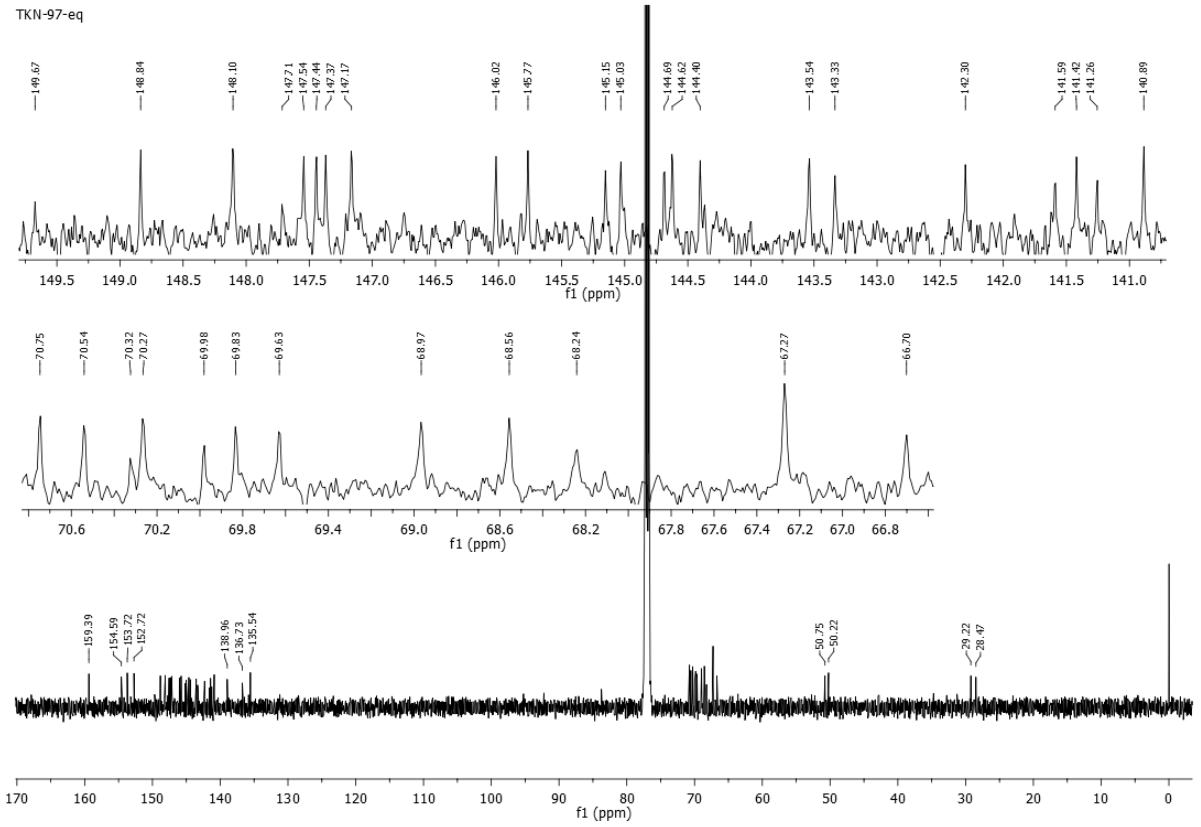


Fig.S44 ^{13}C NMR spectrum of compound **13**

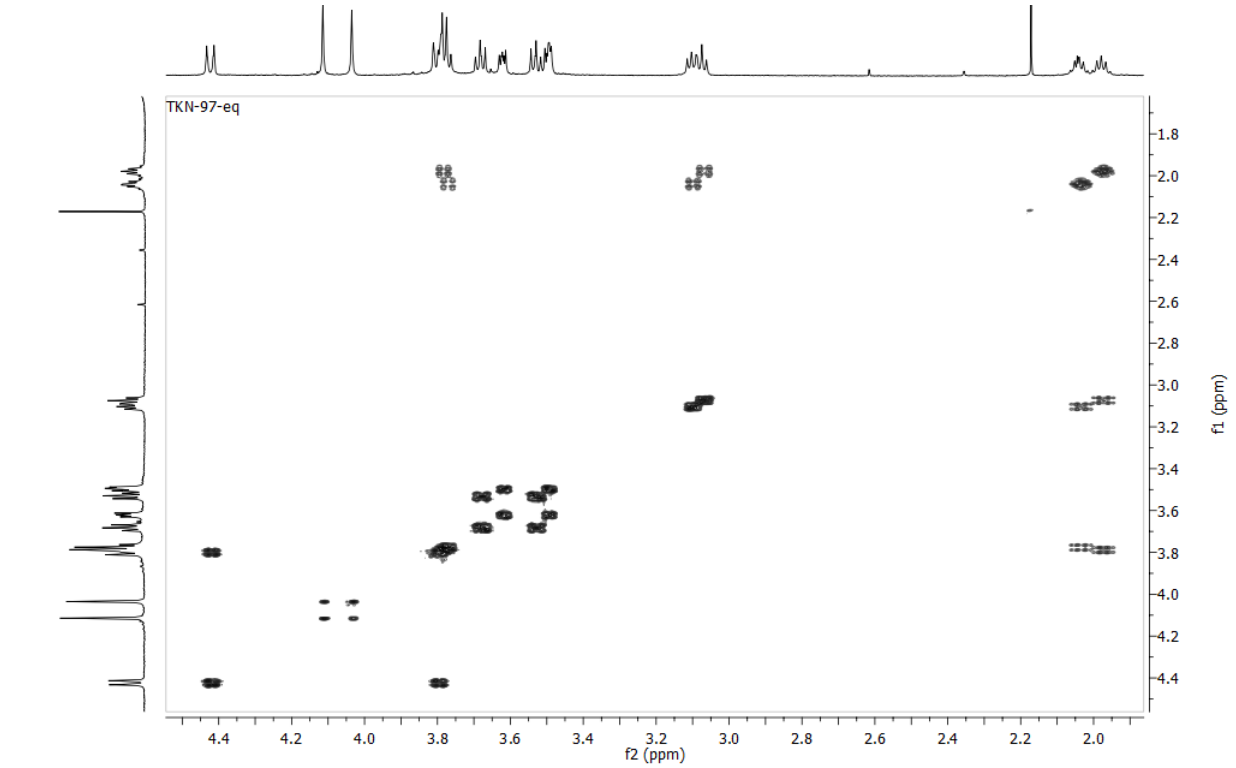


Fig. S44 COSY spectrum of compound **13**

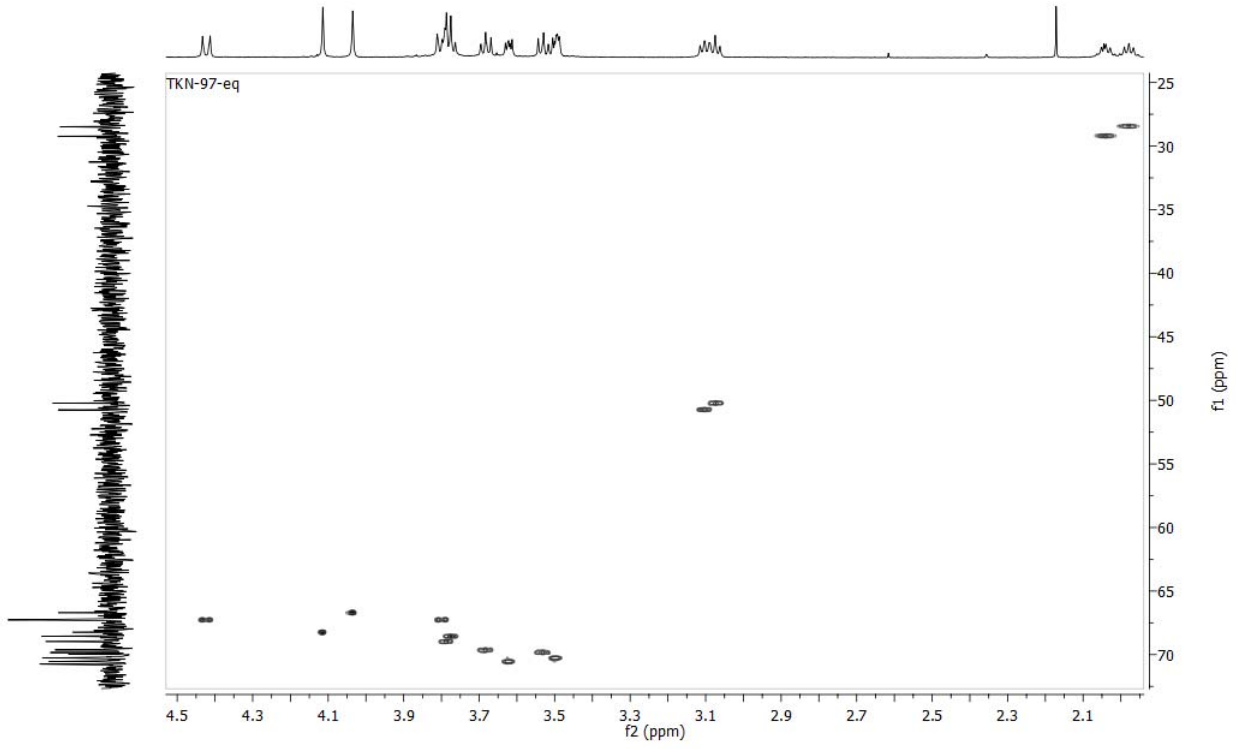
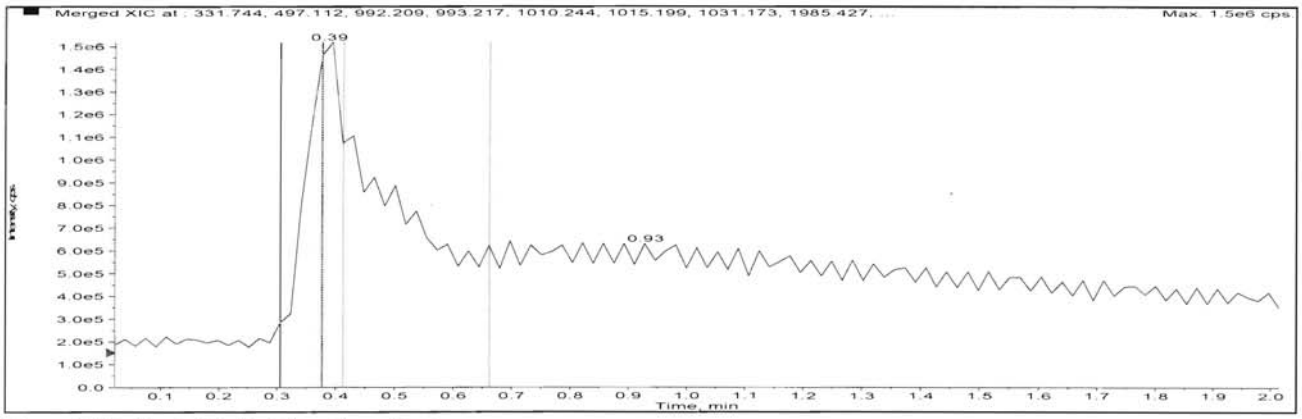
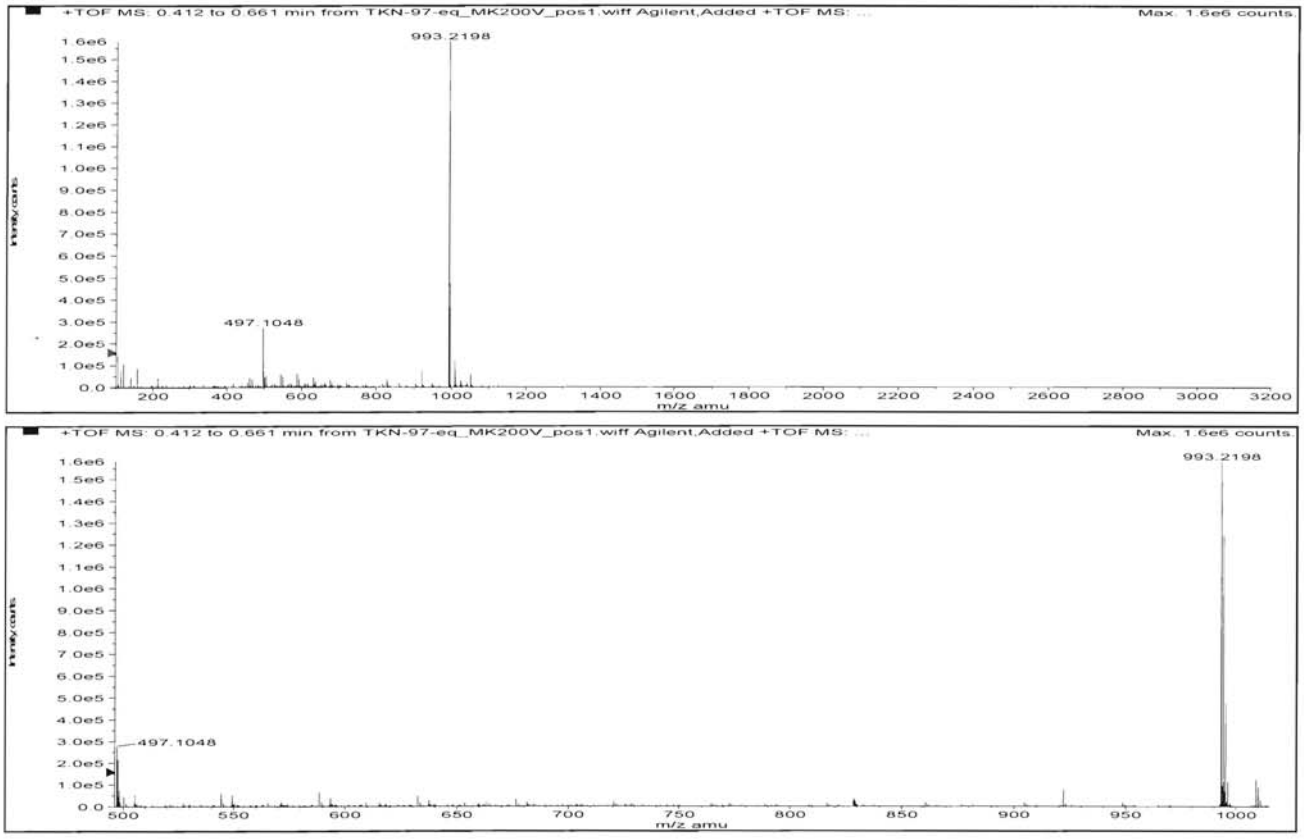


Fig. S45 HSQC spectrum of compound **13**

Sample Name: **TKN-97-eq** Sample Location: **P1-C5** Sample Id: Operator: **Milka**
Data File Name: **D:\PE Sciex Data\Projects\D_Milic\Data\TKN-97-eq_MK200V_pos1.wiff** Acq Time: **July 28 2015, 10:26:12 AM**
Method: **d:\TOF_Data\damethods\Night_Seq_Comp_ident1.anm\efc.xml**



Merged XIC, Period# : 1 Experiment# : 1



Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C74H28N2O3	--	992.20999	0.39	9.92219 E6	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+2H]2+	277699.62	497.11227	497.11116	-1.11351	-2.24	--
[M+H]+	1587182.96	993.21727	993.21577	-1.49781	-1.51	--
[M+NH4]+	92095.94	1010.24382	1010.21498	-28.83545	-28.54	--

Fig. S46 HR-MS spectrum of compound **13**

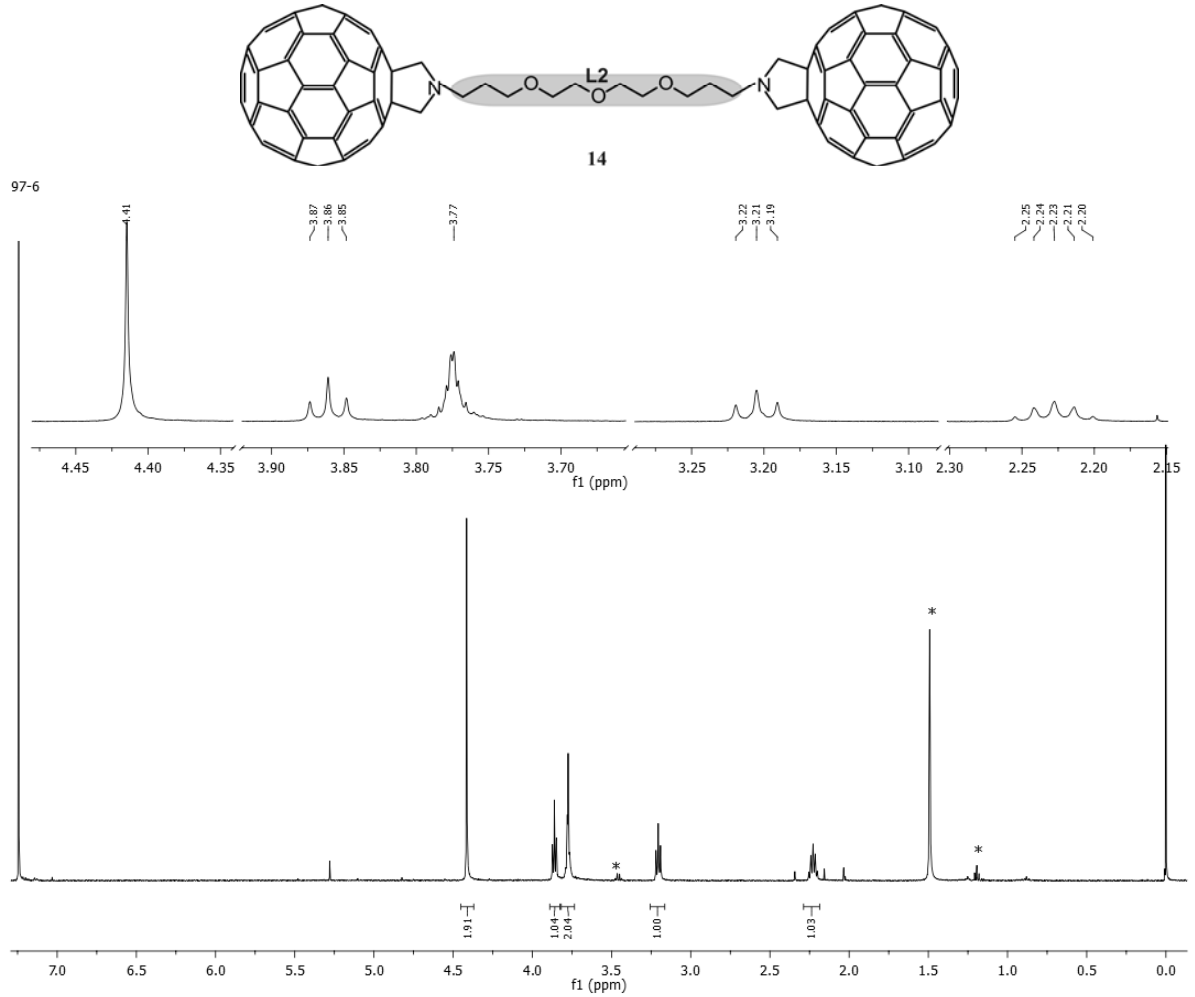


Fig.S47 [1]H NMR spectrum of compound **14**

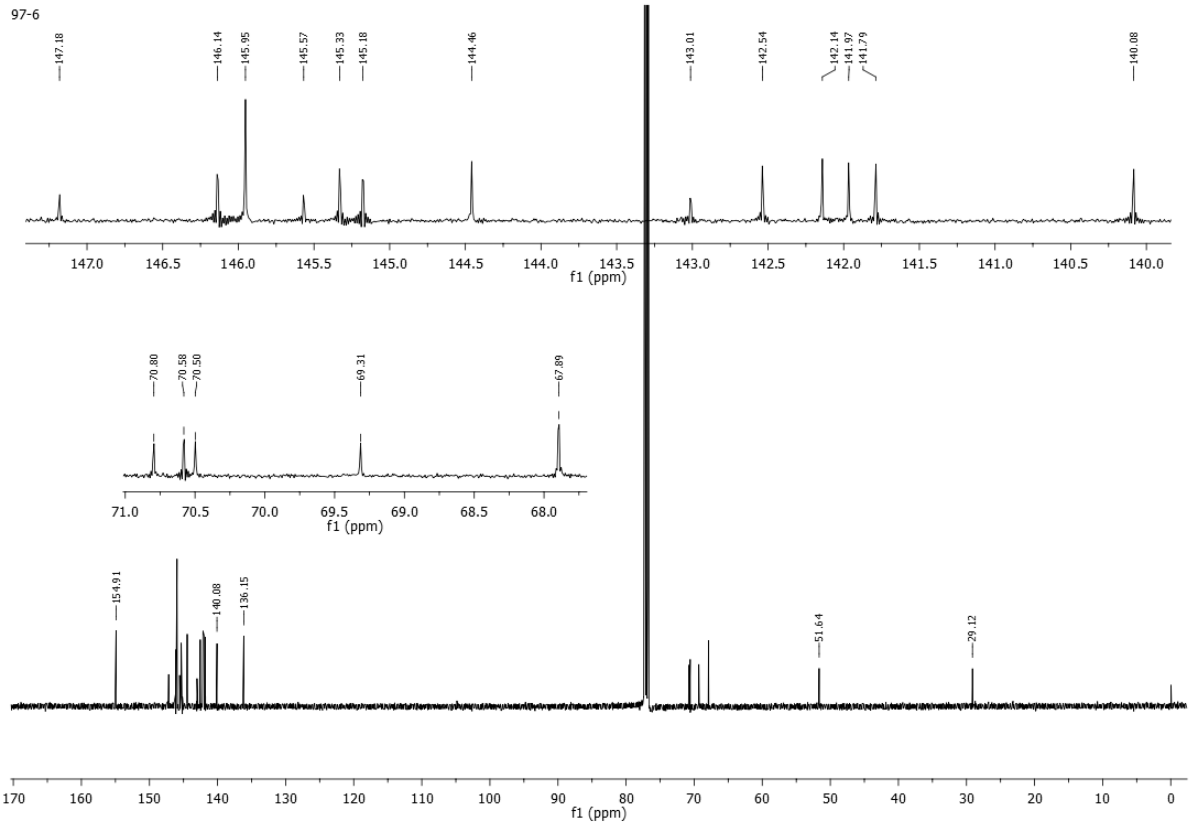


Fig.S48 [13]C NMR spectrum of compound **14**

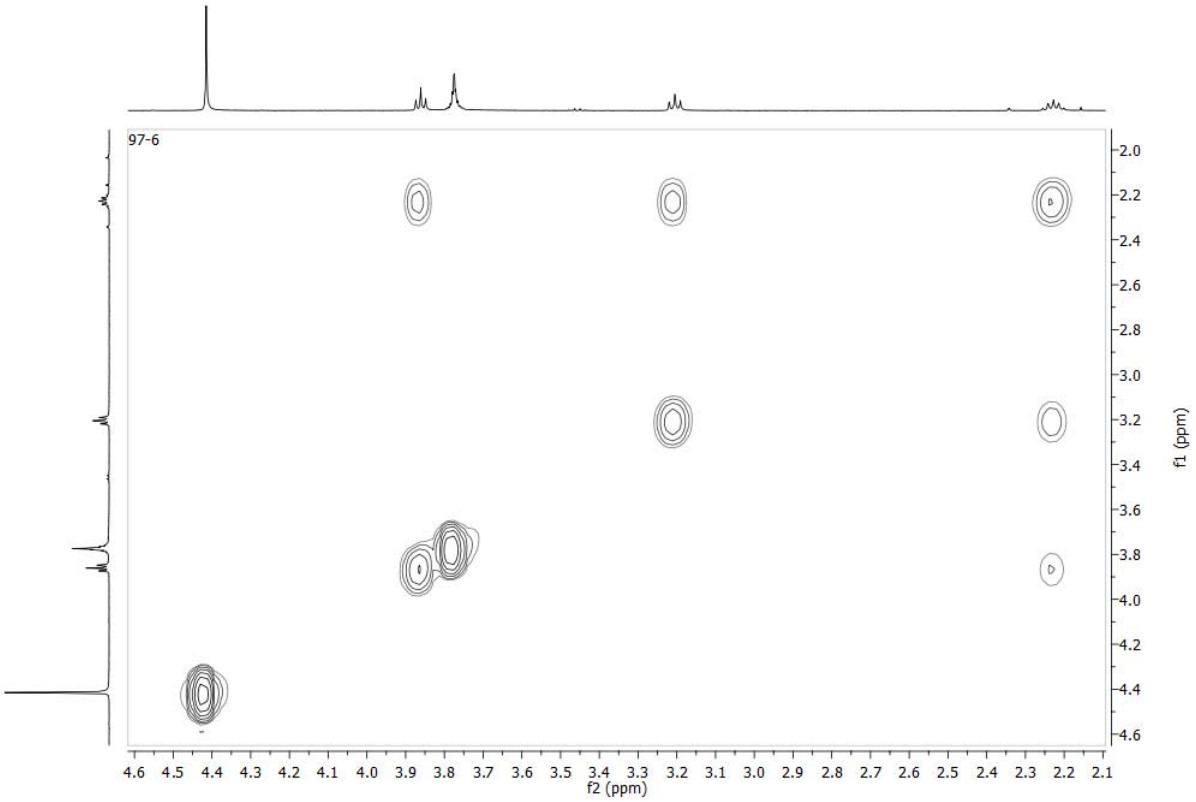


Fig. S49 COSY spectrum of compound **14**

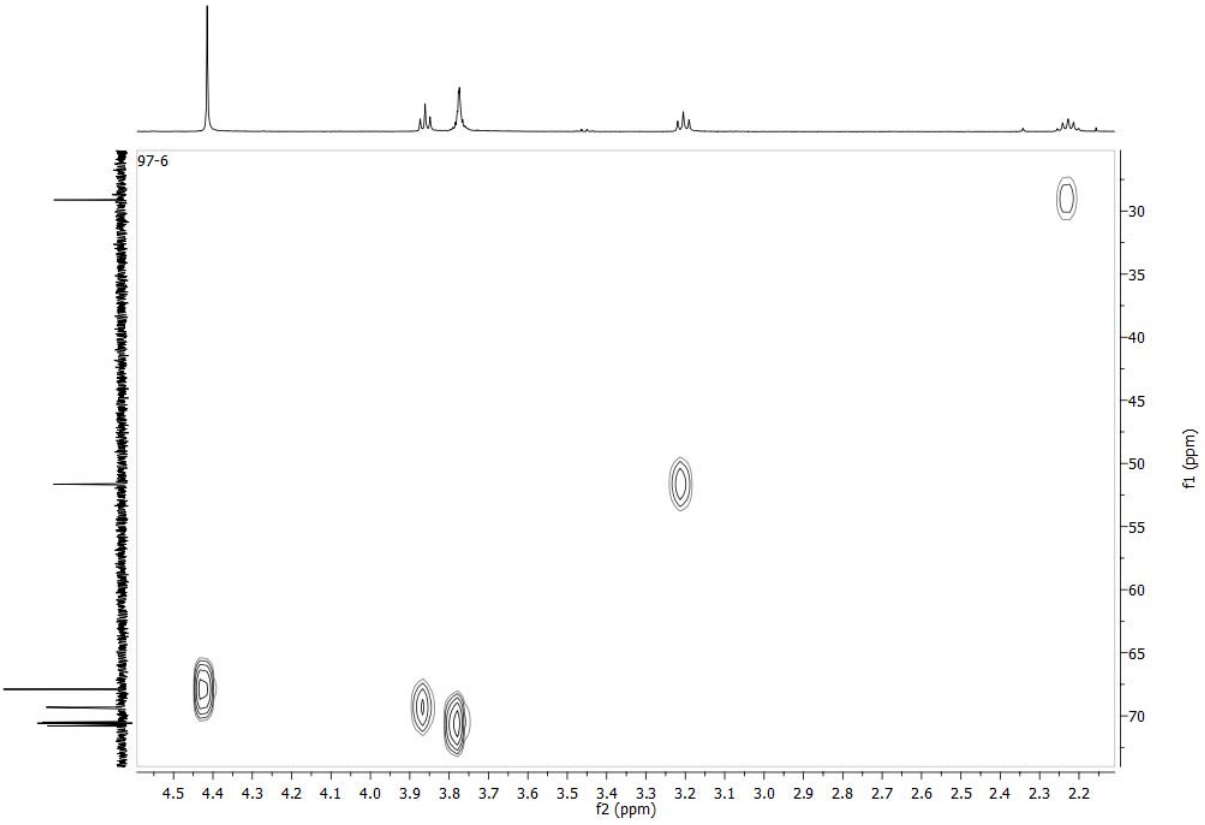
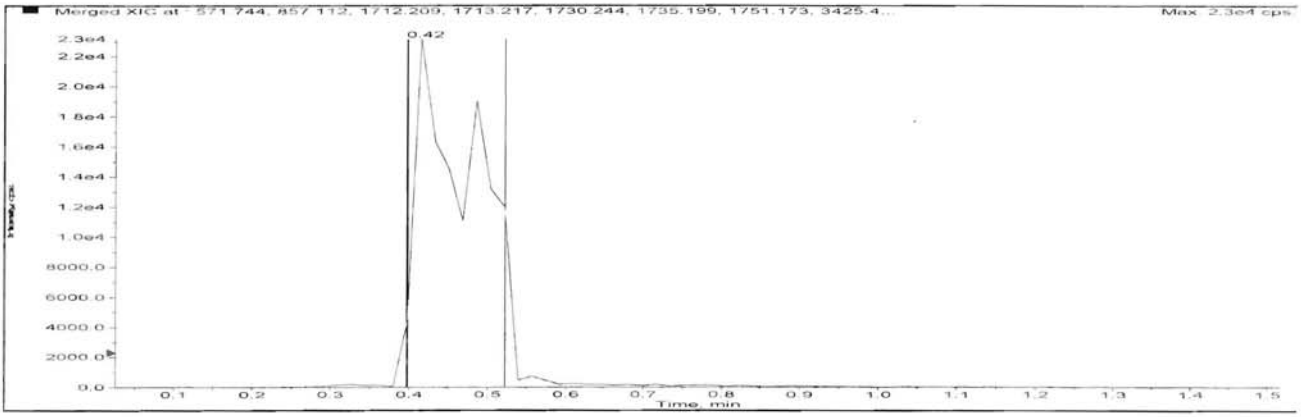


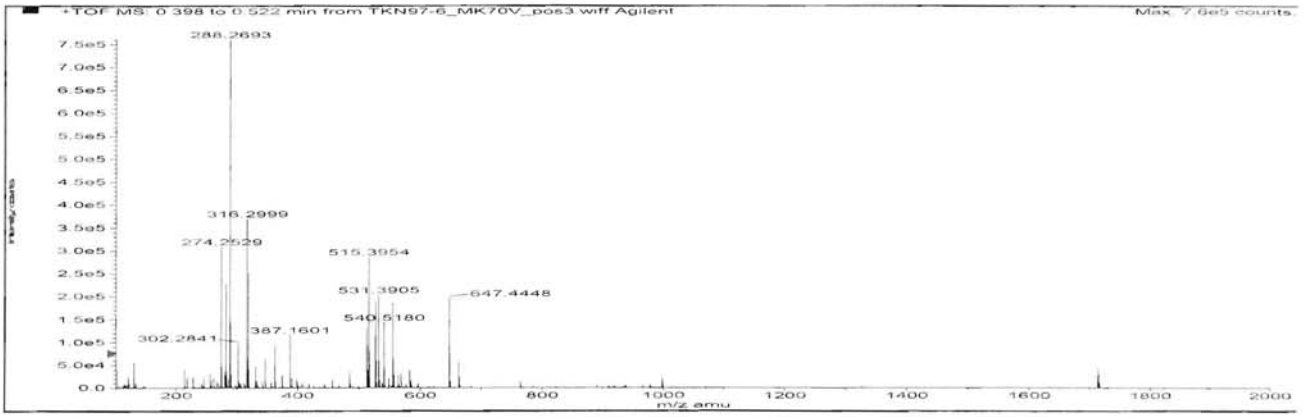
Fig. S50 HSQC spectrum of compound **14**

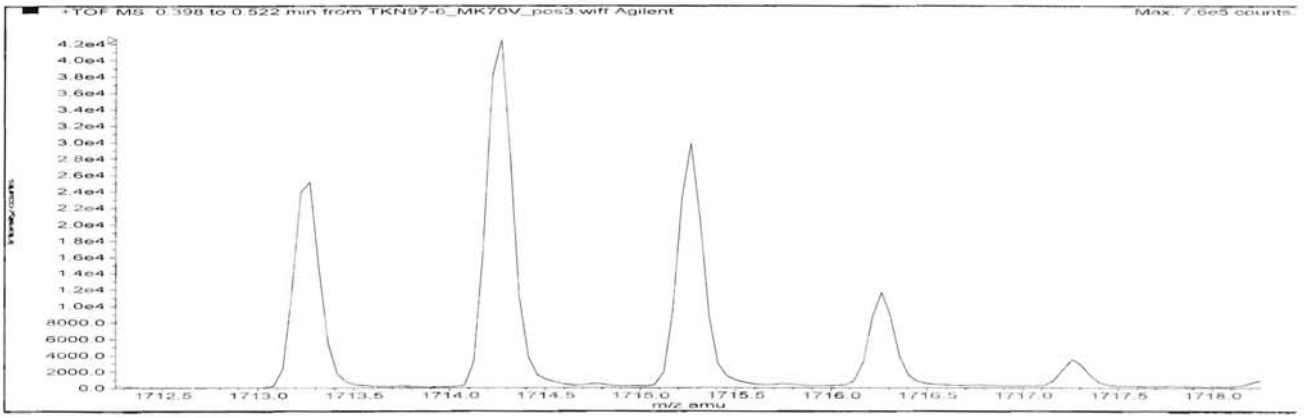
Sample Name: **TKN97-6** Sample Location: **Vial 4** Sample Id: Operator: **Milka**
Data File Name: **D:\PE Sciex Data\Projects\D_Milic\Data\TKN97-6_MK70V_pos3.wiff** Acq Time: **July 19 2012, 02:04:41 PM**
Method: **d:\TOF Software\damethods\Night_Seq_Comp_ident1.anm\efc.xml**

One or more scans have failed IRM. Review the data file for details.



Merged XIC, Period# : 1 Experiment# : 1





Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C134H28N2O3	--	1712.20999	0.42	1.22436 E5	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+H]+	26096.15	1713.21727	1713.25252	35.24829	20.57	--

Fig. S51 HR-MS spectrum of compound **14**

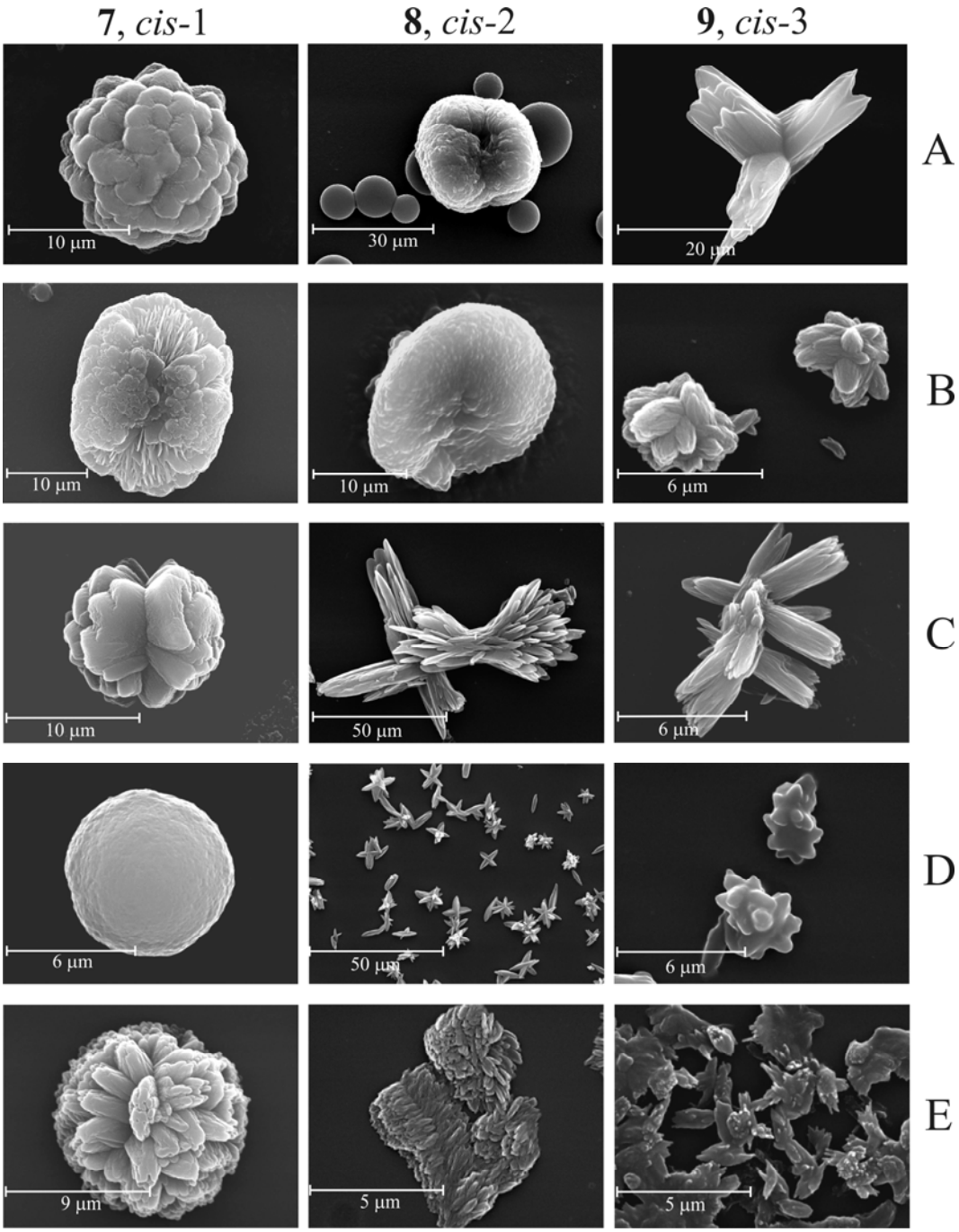


Fig. S52. Representative SEM images of samples prepared from 0.5 mM solution of three regioisomeric bisadducts with the dioxaoctane bridge in **A)** ODCB; **B)** PhMe; **C)** PhMe/iPrOH 1:1; **D)** PhMe/dioksan 1:1 and **E)** $CHCl_3$, on glass substrate at room temperature.

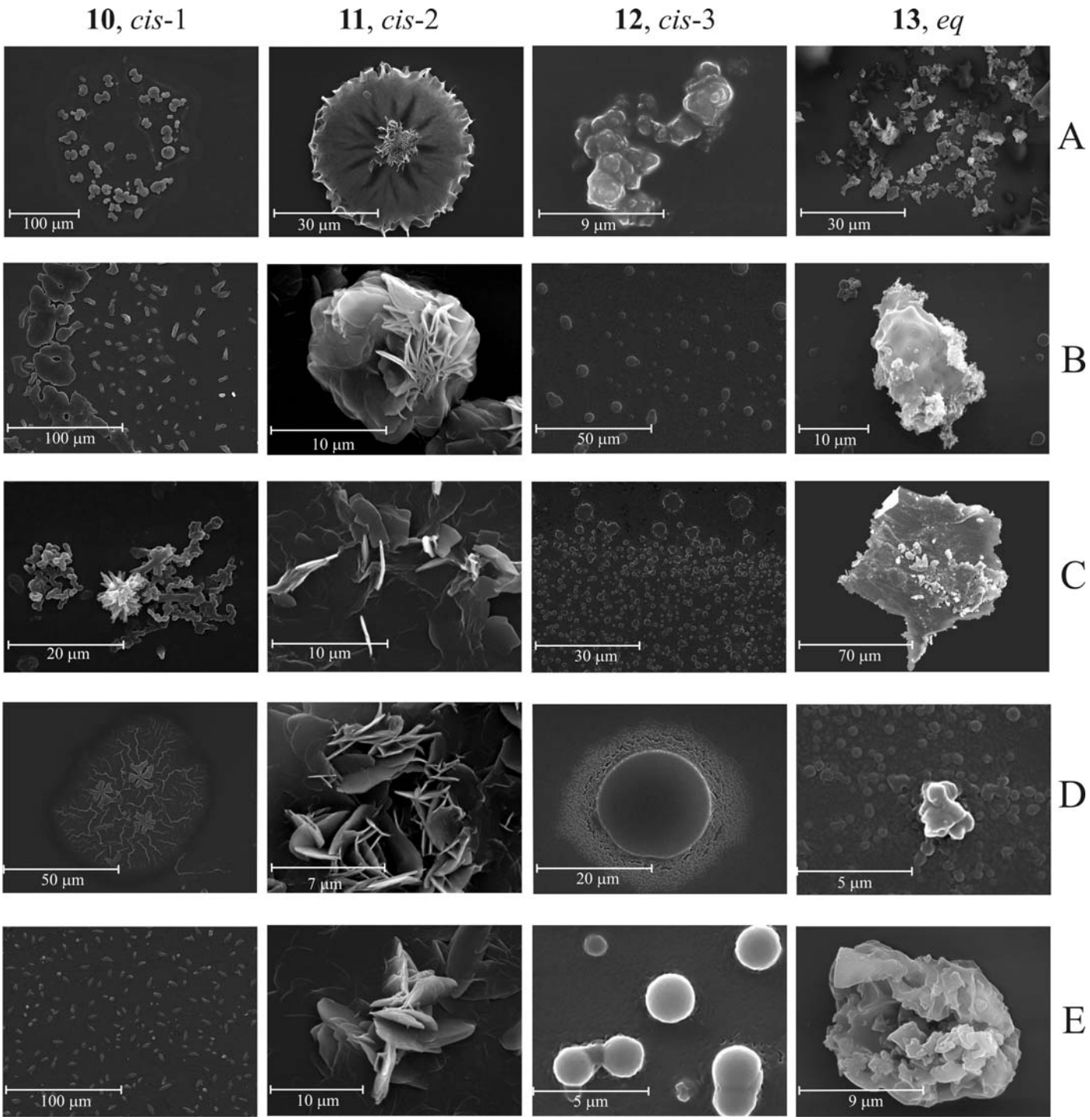


Fig. S53 Representative SEM images of samples prepared from 0.5 mM solutions of regioisomeric bisadducts with the trioxatridecane bridge in **A)** ODCB; **B)** PhMe; **C)** PhMe/*i*-PrOH 1:1; **D)** PhMe/dioxane 1:1, and **E)** $CHCl_3$ on glass substrate at room temperature.

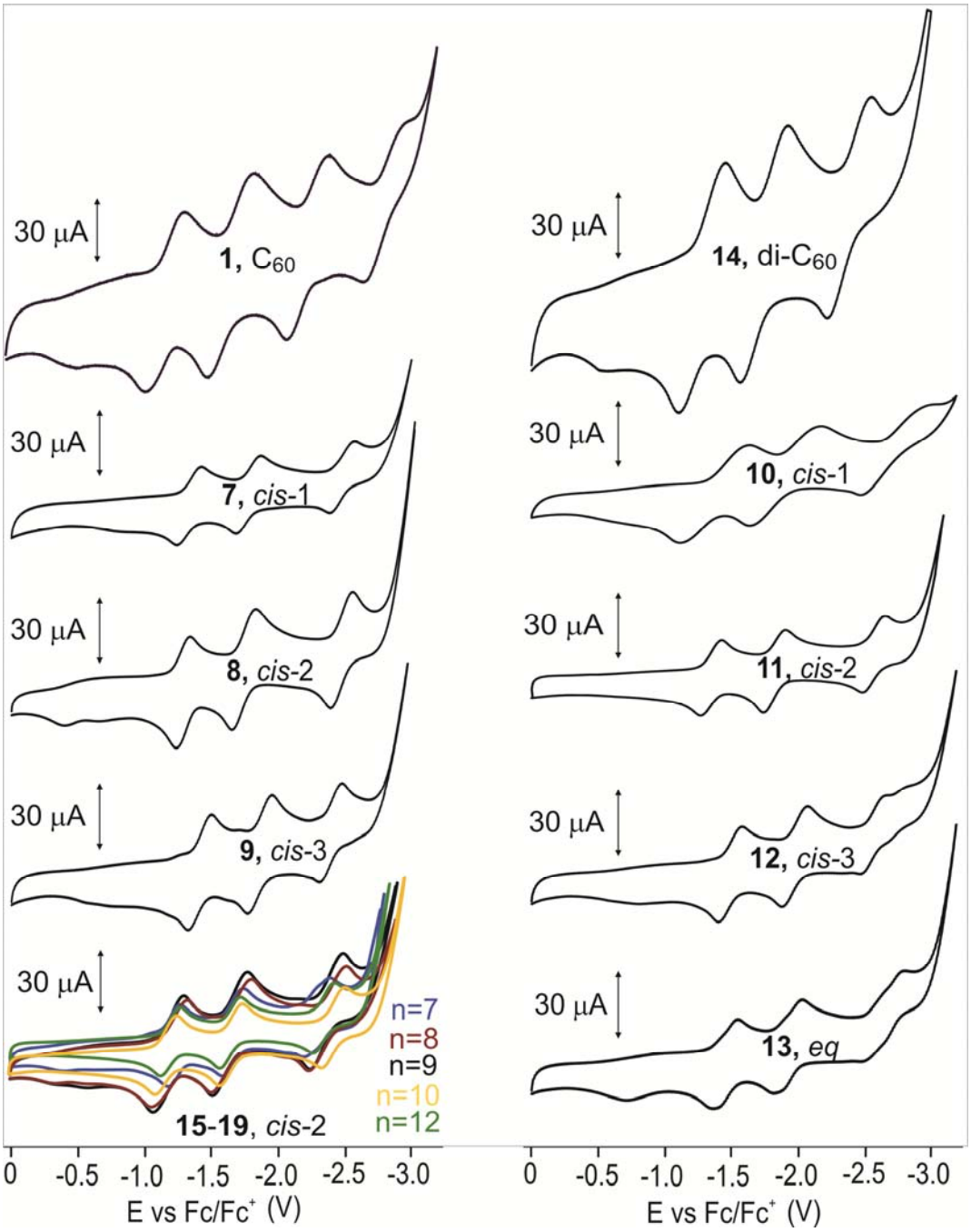


Fig. S54: CVs of compounds **7-19** in ODCB/DMF 2:1, with 0,1 M TBAP as a supporting electrolyte, recorded at the scanning rate of 0.7 V/s, at the room temperature, under the argon atmosphere.

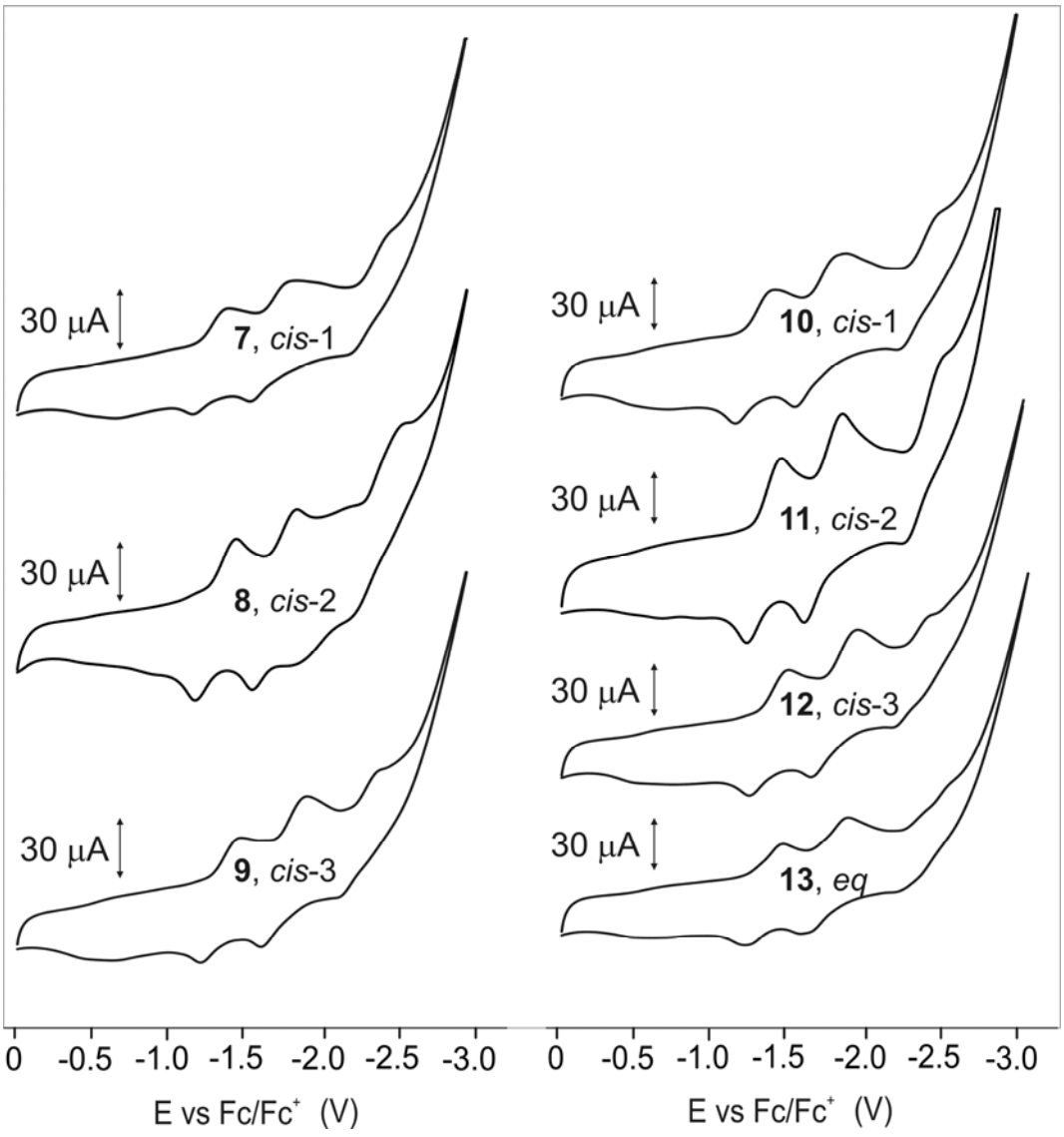
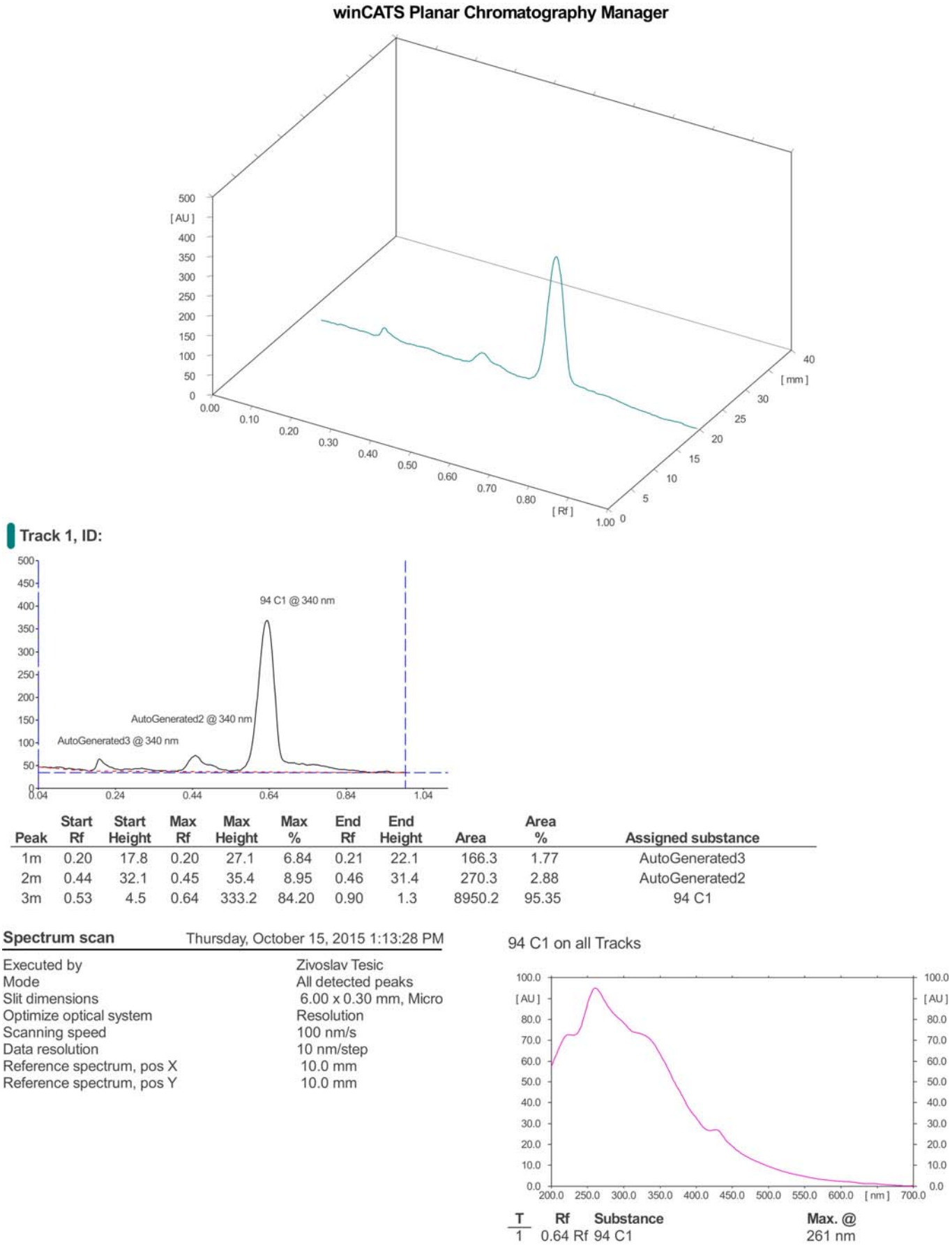


Fig. S55: CVs of compounds **7-13** in DCM, with 0,1 M TBAP as a supporting electrolyte, recorded at the scanning rate of 0.7 V/s, at the room temperature under the argon atmosphere.



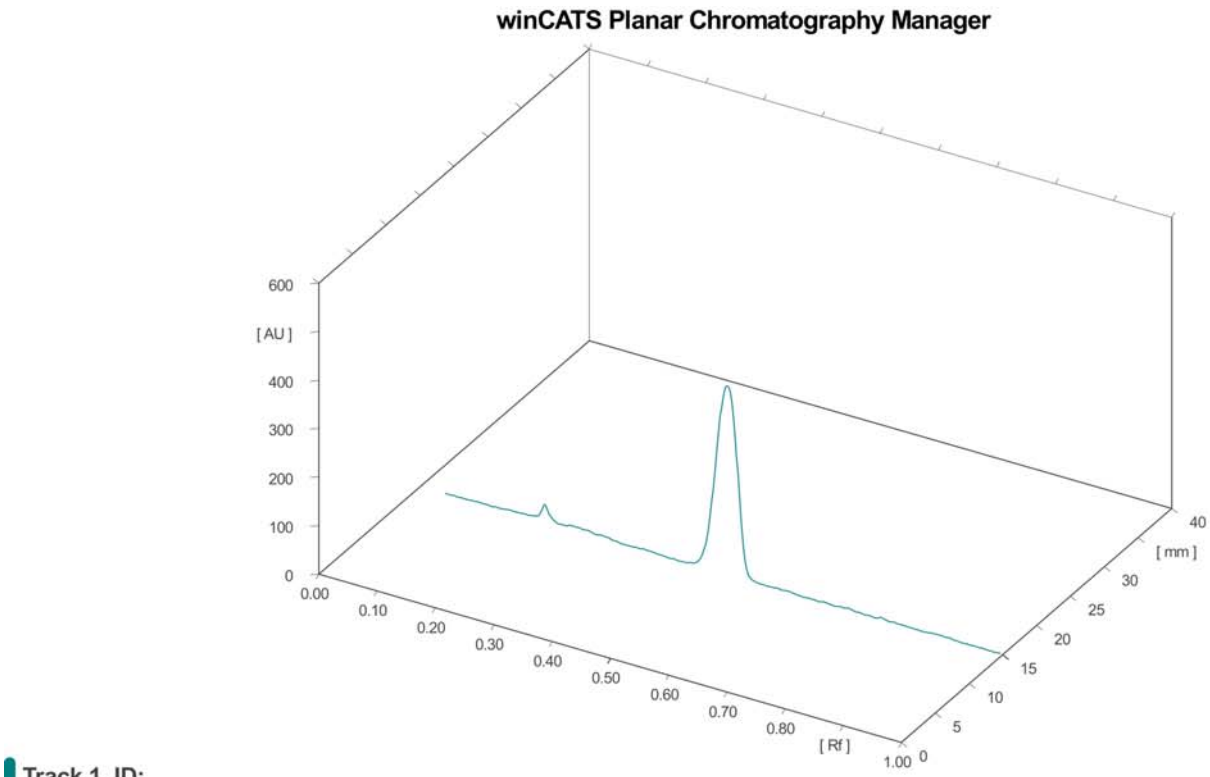
Peak	Start Rf	Start Height	Max Rf	Max Height	Max %	End Rf	End Height	Area	Area %	Assigned substance
1m	0.20	17.8	0.20	27.1	6.84	0.21	22.1	166.3	1.77	AutoGenerated3
2m	0.44	32.1	0.45	35.4	8.95	0.46	31.4	270.3	2.88	AutoGenerated2
3m	0.53	4.5	0.64	333.2	84.20	0.90	1.3	8950.2	95.35	94 C1

Spectrum scan Thursday, October 15, 2015 1:13:28 PM

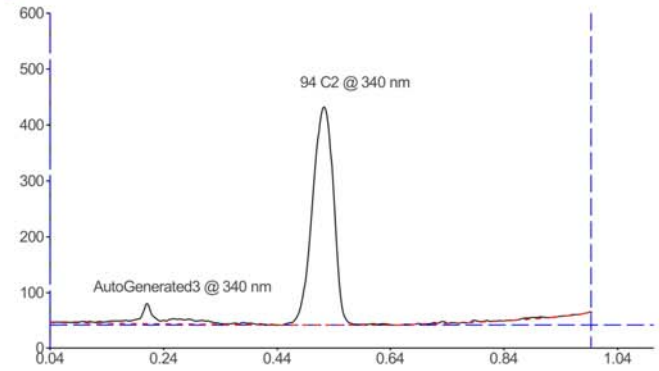
Executed by	Zivoslav Tesic
Mode	All detected peaks
Slit dimensions	6.00 x 0.30 mm, Micro
Optimize optical system	Resolution
Scanning speed	100 nm/s
Data resolution	10 nm/step
Reference spectrum, pos X	10.0 mm
Reference spectrum, pos Y	10.0 mm

T	Rf	Substance	Max. @
1	0.64 Rf	94 C1	261 nm

Fig. S56. HPTLC of bisadduct **7**.



Track 1, ID:

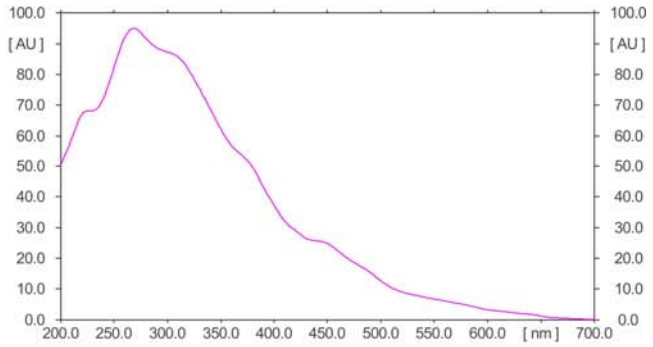


Peak	Start Rf	Start Height	Max Rf	Max Height	Max %	End Rf	End Height	Area	Area %	Assigned substance
1m	0.21	16.6	0.21	36.0	8.44	0.22	15.8	236.2	2.88	AutoGenerated3
2m	0.44	1.5	0.53	390.5	91.56	0.60	1.4	7967.6	97.12	94 C2

Spectrum scan Thursday, October 15, 2015 11:18:15 AM

Executed by	Zivoslav Tesic
Mode	All detected peaks
Slit dimensions	6.00 x 0.30 mm, Micro
Optimize optical system	Resolution
Scanning speed	100 nm/s
Data resolution	10 nm/step
Reference spectrum, pos X	10.0 mm
Reference spectrum, pos Y	10.0 mm

94 C2 on all Tracks



T	Rf	Substance	Max. @
1	0.53 Rf	94 C2	269 nm

Fig. S57. HPTLC of bisadduct **8**.

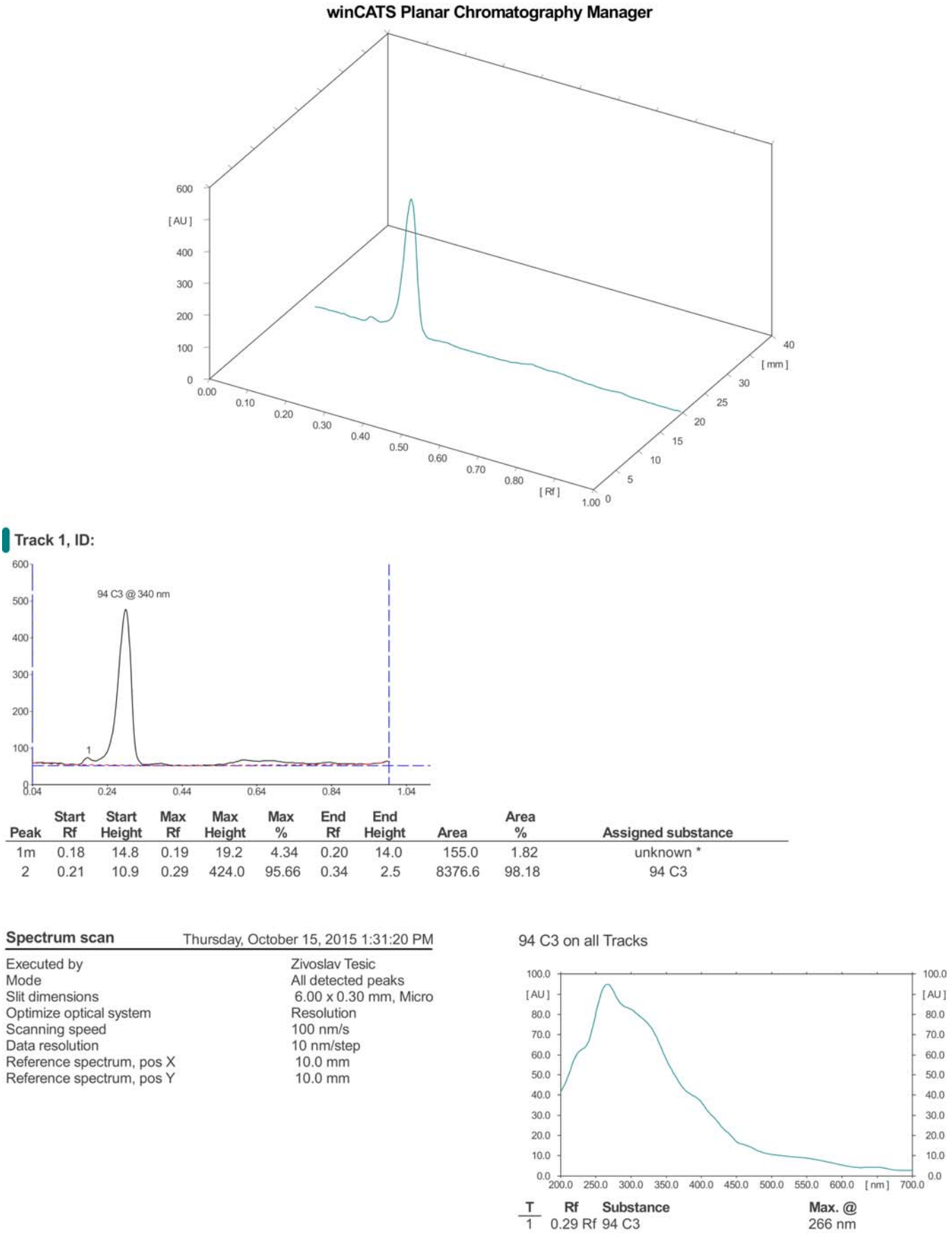


Fig. S58. HPTLC of bisadduct **9**.

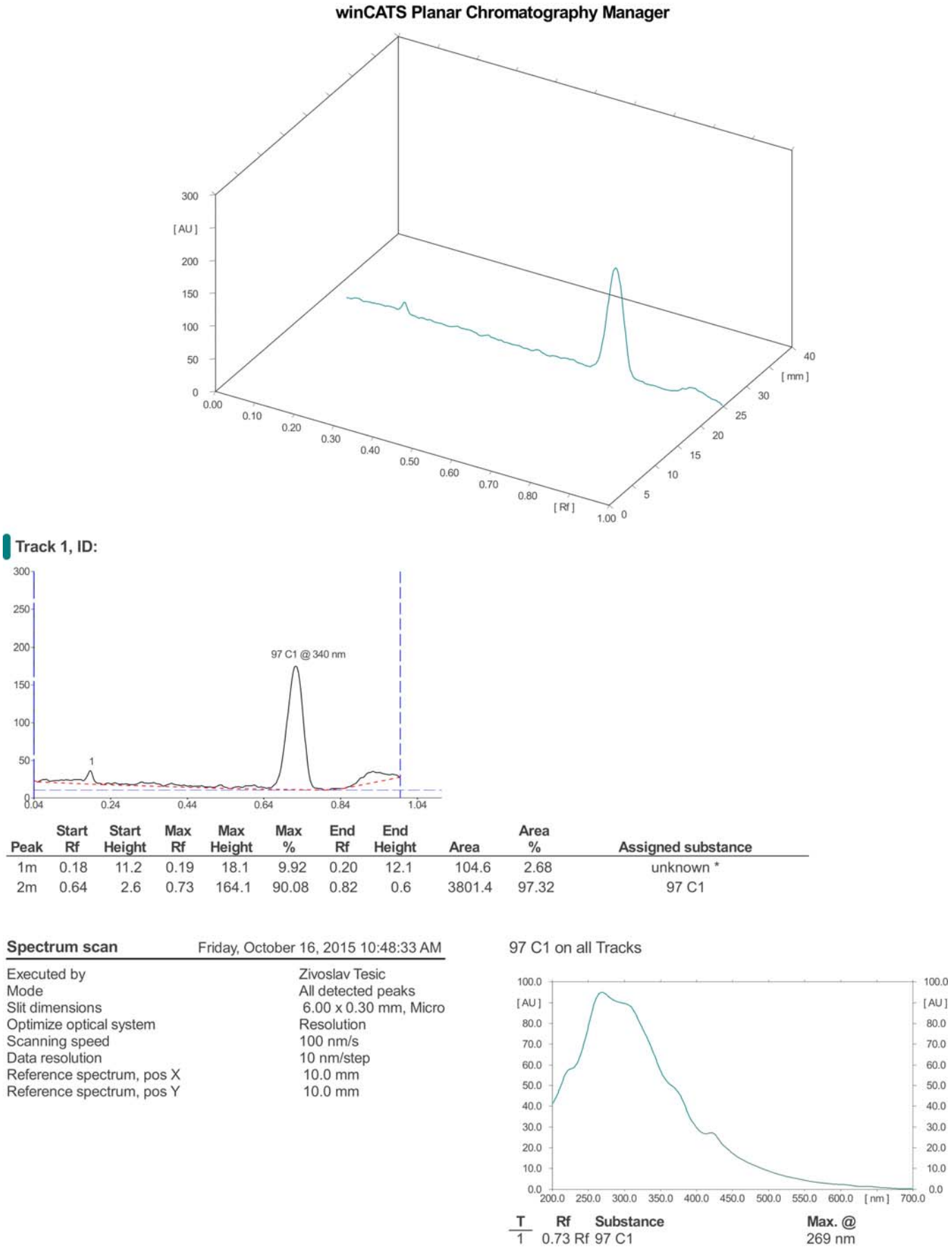
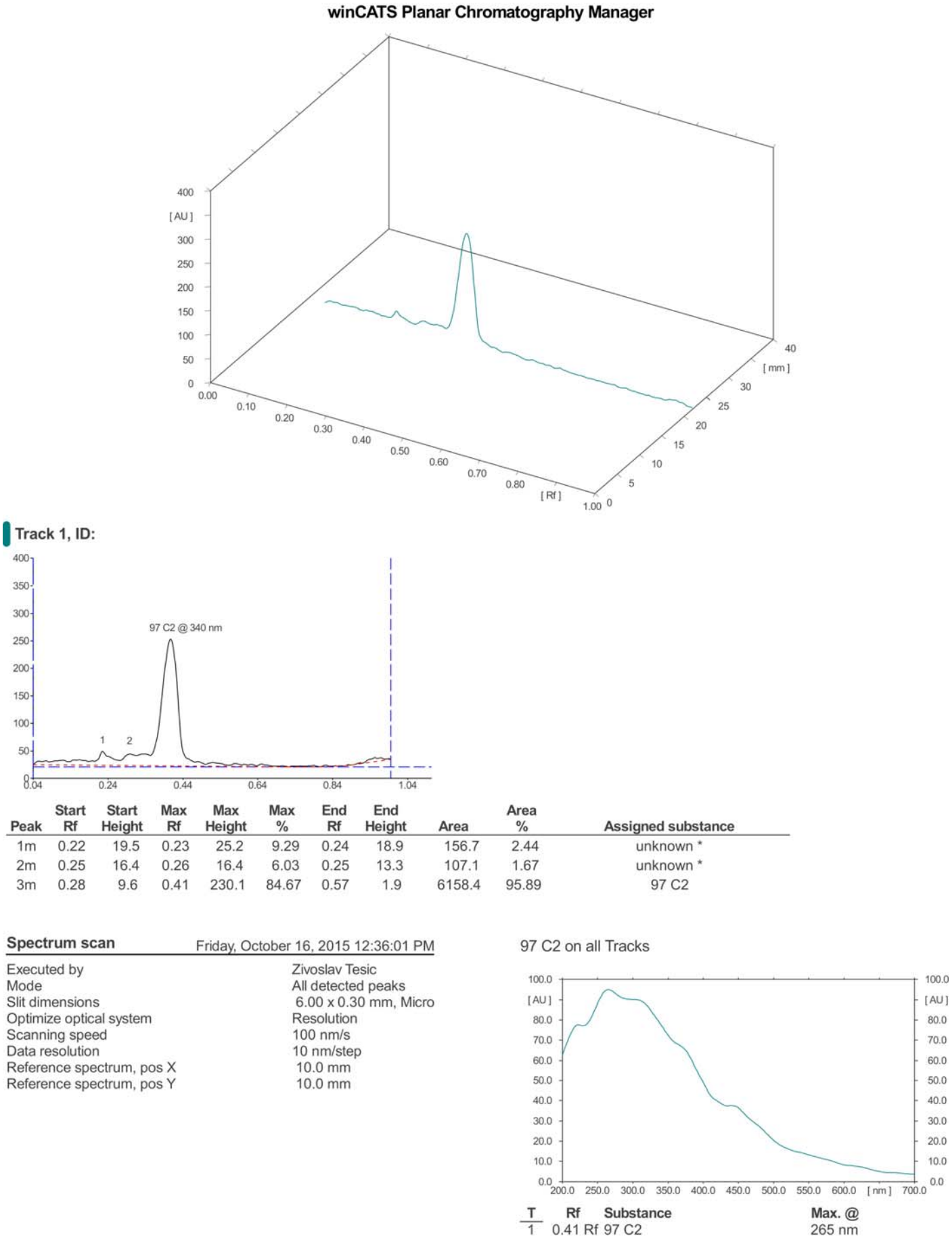


Fig. S59. HPTLC of bisadduct **10**.



Peak	Start Rf	Start Height	Max Rf	Max Height	Max %	End Rf	End Height	Area	Area %	Assigned substance
1m	0.22	19.5	0.23	25.2	9.29	0.24	18.9	156.7	2.44	unknown *
2m	0.25	16.4	0.26	16.4	6.03	0.25	13.3	107.1	1.67	unknown *
3m	0.28	9.6	0.41	230.1	84.67	0.57	1.9	6158.4	95.89	97 C2

Spectrum scan Friday, October 16, 2015 12:36:01 PM

Executed by	Zivoslav Tesic
Mode	All detected peaks
Slit dimensions	6.00 x 0.30 mm, Micro
Optimize optical system	Resolution
Scanning speed	100 nm/s
Data resolution	10 nm/step
Reference spectrum, pos X	10.0 mm
Reference spectrum, pos Y	10.0 mm

Fig. S60. HPTLC of bisadduct **11**.

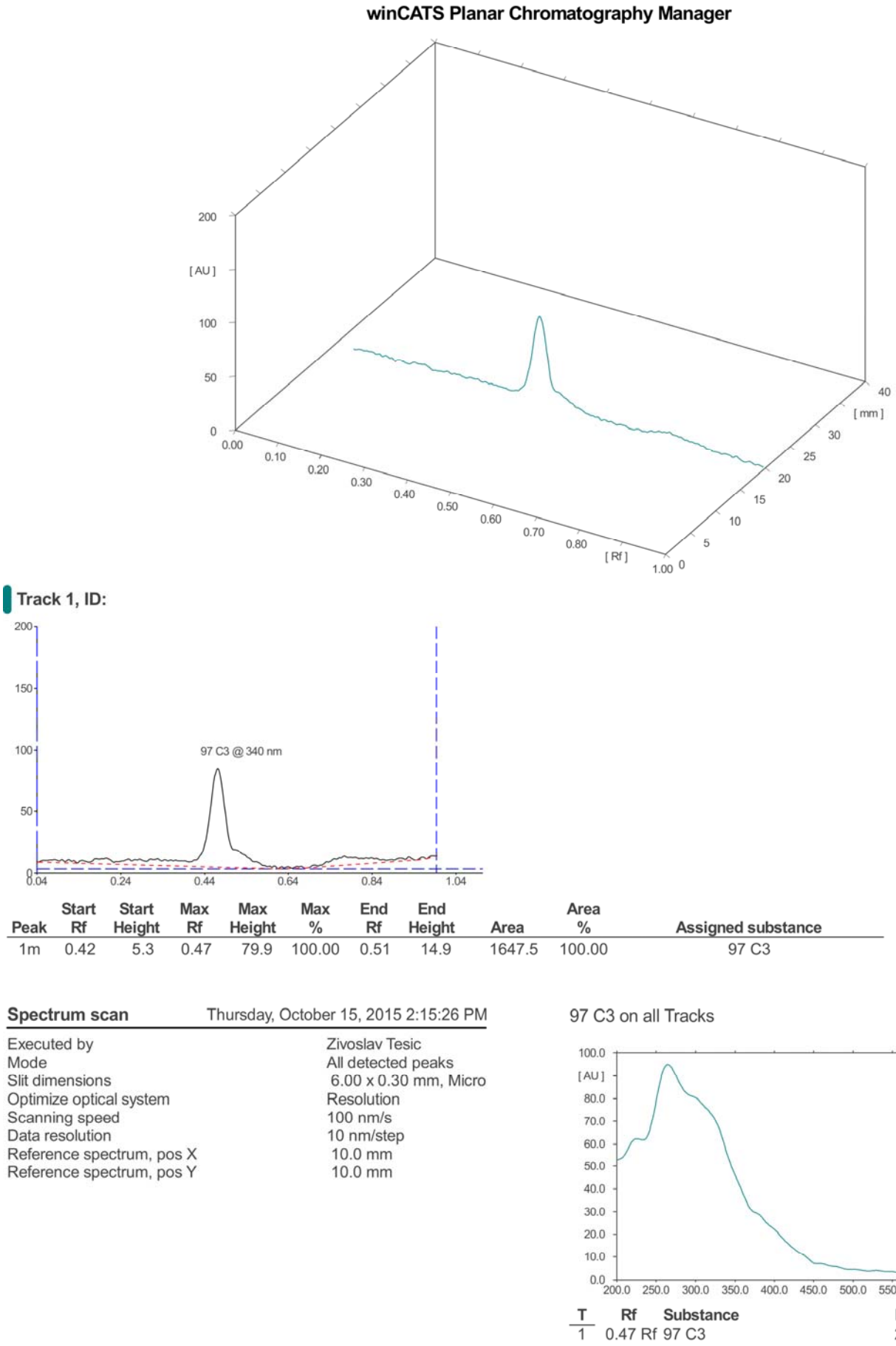
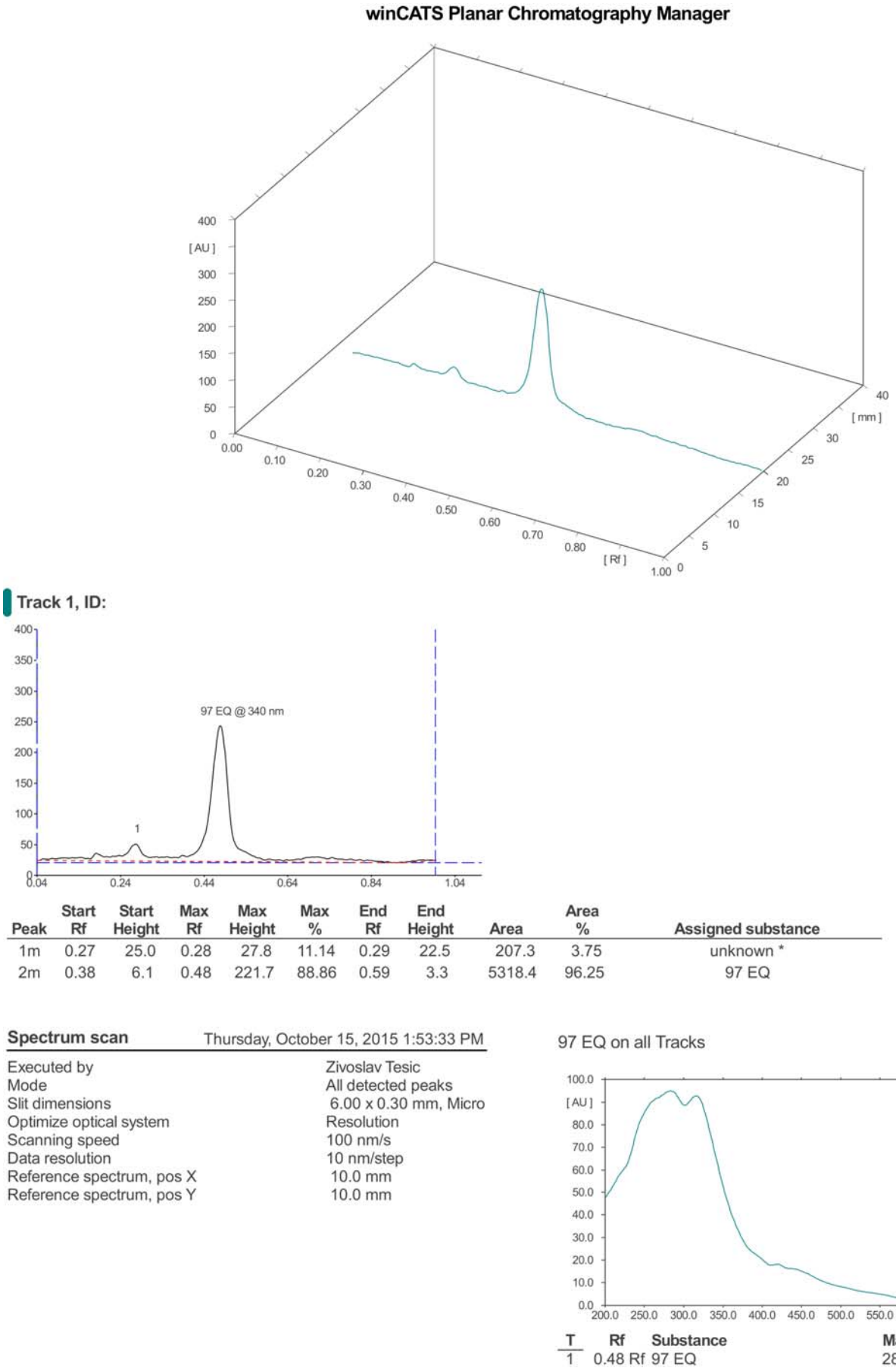


Fig. S61. HPTLC of bisadduct **12**.



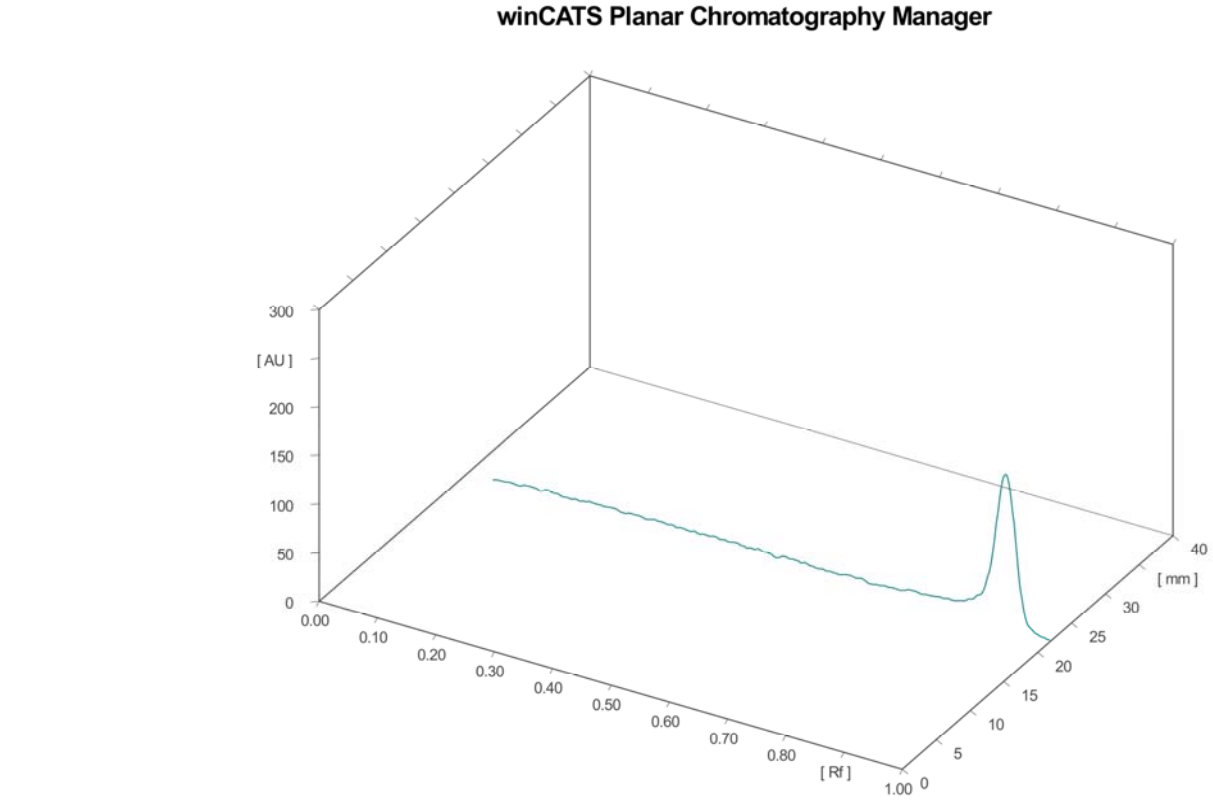
Peak	Start Rf	Start Height	Max Rf	Max Height	Max %	End Rf	End Height	Area	Area %	Assigned substance
1m	0.27	25.0	0.28	27.8	11.14	0.29	22.5	207.3	3.75	unknown *
2m	0.38	6.1	0.48	221.7	88.86	0.59	3.3	5318.4	96.25	97 EQ

Spectrum scan Thursday, October 15, 2015 1:53:33 PM

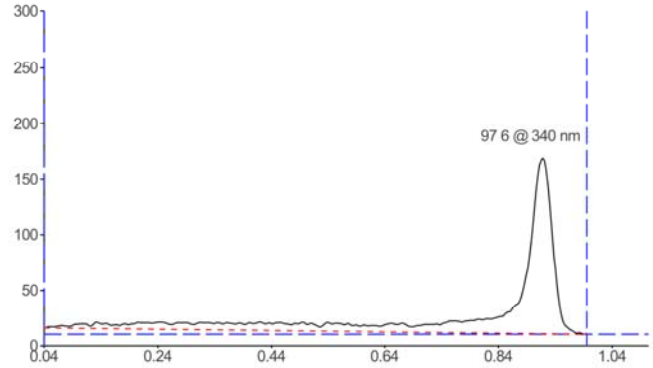
Executed by	Zivoslav Tesic
Mode	All detected peaks
Slit dimensions	6.00 x 0.30 mm, Micro
Optimize optical system	Resolution
Scanning speed	100 nm/s
Data resolution	10 nm/step
Reference spectrum, pos X	10.0 mm
Reference spectrum, pos Y	10.0 mm

T	Rf	Substance	Max. @
1	0.48 Rf	97 EQ	283 nm

Fig. S62. HPTLC of bisadduct **13**.



Track 1, ID:

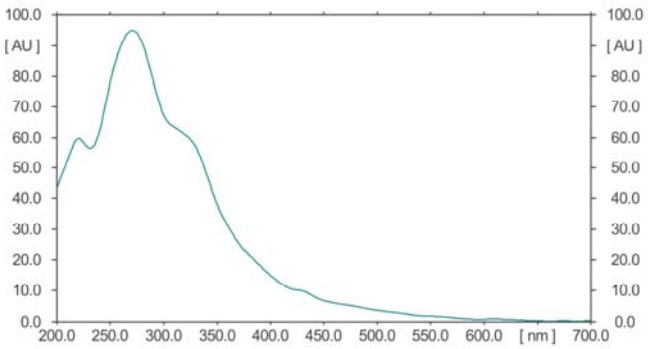


Peak	Start Rf	Start Height	Max Rf	Max Height	Max %	End Rf	End Height	Area	Area %	Assigned substance
1	0.83	12.6	0.92	157.5	100.00	0.98	0.7	3649.4	100.00	97 6

Spectrum scan Friday, October 16, 2015 1:16:29 PM

Executed by	Zivoslav Tesic
Mode	All detected peaks
Slit dimensions	6.00 x 0.30 mm, Micro
Optimize optical system	Resolution
Scanning speed	100 nm/s
Data resolution	10 nm/step
Reference spectrum, pos X	10.0 mm
Reference spectrum, pos Y	10.0 mm

97 6 on all Tracks



T	Rf	Substance	Max. @
1	0.92 Rf	97 6	271 nm

Fig. S63. HPTLC of bisadduct **14**.