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Supplementary Information

Fullerene bisadduct regioisomers containing an asymmetric diamide tether

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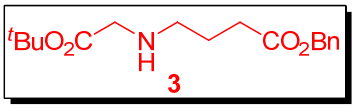
Content

Experimental section

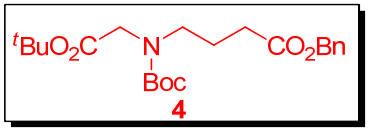
General: Flash column chromatography (FCC) and dry-column flash chromatography (DCFC) were carried out with Merck silica gel 0.04–0.063 mm and 0.015-0.04 mm, respectively. Thin layer chromatography (TLC) was carried out on precoated silica gel 60 F_{254} plates. Melting points were determined on a Digital melting point WRS-1B apparatus and are uncorrected. 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. The sample was dissolved in the indicated solvent system, and TMS was used as an internal reference. The homonuclear 2D (DQF-COSY) and the heteronuclear 2D ^{1}H-^{13}C spectra (HSQC, HMBC) were recorded with the usual settings. The NMR spectra of all carbamates (**4**−**7**, **11** and **12)** are consistent with the expected structure but are complicated (splitting of some signals) by the presence of carbamate rotamers. The high-resolution mass spectra were obtained with an *Agilent Technologies 6210* TOF LC-MS spectrometer. SEM: Investigations of sample morphology were carried out with SEM, using a JEOL JSM-840A instrument, at an acceleration voltage of 30 kV. A drop of 1 mM solution of sample in $CHCl_3$ and ODCB was deposited on the surface of glass substrate and left for 24 h to slowly evaporate in a glass petri dish (diameter 10 cm) under a PhMe atmosphere at room temperature. The investigated samples were gold sputtered in a JFC 1100 ion sputterer and then subjected to SEM observations. The solvents used for the SEM experiments (HPLC grade) were stored over 3 Å molecular sieves and degassed under vacuum prior use.

Synthesis of compounds 2-14.

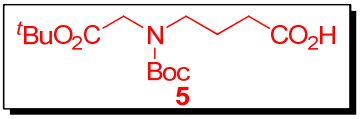
Compound 2. A suspension of γ-aminobutanoic acid (GABA) **1** (3.50 g, 0.034 mol), benzyl alcohol (7.30 g, 7 mL, 0.068 mmol) and *p*-toluenesulfonic acid monohydrate (PTSA) (7.10 g, 0.037 mol) in PhMe (200 mL) was heated to reflux for 5 h with azeotropic removal of water. The reaction mixture was concentrated to a one third of the volume and the product precipitated by addition of Et_2O (100 mL). The precipitate was filtered, dissolved in CH_3OH (60 mL) and again precipitated by addition of Et_2O (100 ml), giving after filtration and drying the benzyl ester **2** (12.30 g, 99%) as white crystals. M.p. 106.2-106.7 ºC (Et_2O); IR(ATR): 3100, 3039, 2942, 1732, 1642, 1532, 1188, 1125 cm^{-1}; ^{1}H NMR (200 MHz, CD_3OD): δ=7.71 (d, *J*=8.0 Hz, 2H, H^{PTSA}), 7.37-7.30 (m, 5H, HC^{Ar}), 7.20 (d, *J*=8.4 Hz, 2H, H^{PTSA}), 5.11 (s, 2H, H_2C^{Bn}), 2.95 (t, *J*=7.5 Hz, 2H, $H_2C(4)^{GABA}$), 2.47 (t, *J*=7.3 Hz, 2H, $H_2C(2)^{GABA}$), 2.33 (s, 3H, H_3C^{PTSA}), 1.92 (quint, *J*=7.4 Hz, 2H, $H_2C(3)^{GABA}$) ppm; ^{13}C NMR (50 MHz, CD_3OD): δ=173.83 (CO_2Bn), 143.35, 141.82, 137.43, 129.91, 129.59, 129.30, 126.91 (C^{Ar}), 67.44 (CH_2^{Bn}), 40.00 ($CH_2(4)^{GABA}$), 31.59 ($CH_2(2)^{GABA}$), 23.65 ($CH_2(3)^{GABA}$), 21.30 (CH_3^{PTSA}) ppm; MS(ESI): Calcd for $C_{11}H_{16}NO_2$ $(M+H)^+$: 194.1181, found: 194.1167.



Compound 3. A solution of the PTSA salt **2** (0.567 g, 1.6 mmol) in CH_2Cl_2 (15 mL) was washed with a saturated aqueous $NaHCO_3$ solution (3 × 15 mL) and dried over anh. Na_2SO_4. The solvent was evaporated leaving the corresponding free amine, which was used in the next step. To a stirred, ice bath cooled solution of the free amine of **2** (0.253 g, 1.3 mmol) and Et_3N (263 mg, 0.5 mL)) in dry CH_2Cl_2 (10 mL) a solution of *tert*-butyl bromoacetate (TBBA) (255 mg, 0.21 mL, 1.3 mmol) in dry CH_2Cl_2 (5 mL) was added dropwise for 1 h. The reaction mixture was stirred with cooling for an additional 4 h. The solvent was evaporated and the remaining crude product was chromatographed on a SiO_2 column by DCFC. Elution with PhMe/EtOAc (1/1) mixture gave the product **3** (143 mg, 30%) as yellow oil. IR(ATR): 3340, 2979, 2938, 1743, 1695, 1238, 1167 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ=7.32-7.15 (m, 5H, HC^{Ar}), 5.11 (s, 2H, H_2C^{Bn}), 3.26 (s, 2H, H_2C-CO_2tBu), 2.62 (t, *J*=7 Hz, 2H, $H_2C(4)^{GABA}$), 2.43 (t, *J*=7.3 Hz, 2H, $H_2C(2)^{GABA}$), 1.82 (quint, *J*=7.0 Hz, 2H, $H_3C(3)^{GABA}$), 1.46 (s, 9H, H_3C^{tBu}) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ=173.30 (CO_2Bn), 171.71 (CO_2tBu), 135.99, 128.98, 127.47, 126.89 (C^{Ar}), 81.10 (C^{tBu}), 66.09 (CH_2^{Bn}), 51.47 (CH_2CO_2tBu), 48.52 ($CH_2(4)^{GABA}$), 31.90 ($CH_2(2)^{GABA}$), 28.00 (CH_3^{tBu}), 25.15 ($CH_2(3)^{GABA}$) ppm; MS(ESI): Calcd for $C_{17}H_{26}NO_4$ $(M+H)^+$: 308,1856, found: 308,1861.

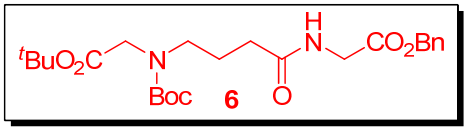


Compound 4. To a stirred, ice bath cooled solution of compound **3** (0.73 g, 2.4 mmol) in $CHCl_3$ (15 mL) a solution of di(*tert*-butyl)dicarbonate (Boc_2O, 1.05 g, 4.8 mmol) in $CHCl_3$ (10 mL) was added dropwise. After additional stirring for 24 h, the mixture was washed with brine and dried over anh. Na_2SO_4. The solvent was removed in *vacuo* and the remaining material was purified on a SiO_2 column by DCFC. Elution with PhMe/EtOAc (8/2) gave *N*-Boc protected compound **4** as yellow oil (0.76 g, 78%). IR(ATR): 2977, 2934, 1742, 1701, 1458, 1367, 1247, 1153 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, compound exists as a 40:60 mixture of rotamers): *δ*=7.35 (s, 5H, HC^{Ar}), 5.12 (s, 2H, H_2C^{Bn}), 3.81 and 3.72 (two s, 2H, H_2C-CO_2tBu), 3.32 and 3.28 (two t, *J*=6.8 Hz, 2H, $H_2C(4)^{GABA}$), 2.41 and 2.40 (two t, *J*=7.6 Hz, 2H, $H_2C(2)^{GABA}$), 1.86 (quint, *J*=7.3 Hz, 2H, $H_2C(3)^{GABA}$), 1.45 and 1.43 (two s, 18H, H_3C^{tBu}) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): *δ*=173.13, 172.97 (CO_2Bn), 169.17 (CO_2tBu), 155.64, 155.39 (CO^{Boc}), 135.98, 128.53, 128.19 (C^{Ar}), 81.37, 80.08 and 79.94 (C^{tBu}), 66.17 (CH_2^{Bn}), 50.29 and 49.67 (CH_2-CO_2tBu), 47.65 ($CH_2(4)^{GABA}$), 31.32 ($CH_2(2)^{GABA}$), 28.15, 28.04 and 27.94 (CH_3^{tBu}), 23.68, 23.46 ($CH_2(3)^{GABA}$) ppm; MS(ESI): Calcd for $C_{22}H_{33}NNaO_6$ $(M+Na)^+$: 430.2200, found 430.2183.

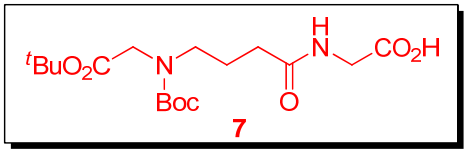


Compound 5. To a solution of benzyl ester **4** (1.23 g, 3.0 mmol) in MeOH (100 mL) 5% Pd/C (123 mg) was added and suspension was bubbled with argon. Mixture was hydrogenated at 40 psi at room temperature for 1 h. After filtering the catalyst and evaporating the solvent, crude acid **5** was isolated as colorless oil (0.95 g; 99%). IR(ATR):

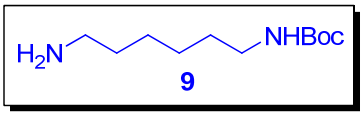
3188, 2979, 2936, 1744, 1707, 1476, 1370, 1251, 1158 cm^{-1}; ^1H NMR (500 MHz, CD_3OD): δ=3.83 and 3.82 (two s, 2H, H_2C-CO_2tBu), 3.34-3.29 (m, 2H, $H_2C(4)^{GABA}$), 2.34 and 2.33 (two t, J=7.5 Hz, 2H, $H_2C(2)^{GABA}$), 1.80 (m, 2H, $H_2C(3)^{GABA}$), 1.48, 1.47, 1.46, 1.43 (4s, 18H, H_3C^{tBu}) ppm; ^{13}C NMR (125 MHz, CD_3OD): δ=177.19, 177.03 (COOH), 171.11, 170.99 (CO_2tBu), 157.73, 157.49 (CO^{Boc}), 82.88, 82.79, 81.81, 81.60 (C^{tBu}), 51.40, 50.98, 50.00 (CH_2-CO_2tBu, $CH_2(4)^{GABA}$), 32.20, 31.96 ($CH_2(2)^{GABA}$), 28.77, 28.71, 28.50, 28.46 (CH_3^{tBu}), 24.87, 24.76 ($CH_2(3)^{GABA}$) ppm; MS(ESI): Calcd for $C_{15}H_{27}NNaO_6$ $(M+Na)^+$: 340,1731, found: 340,1714; Calcd for $C_{15}H_{27}KNO_6$ $(M+K)^+$: 356,1470, found: 356,1456.



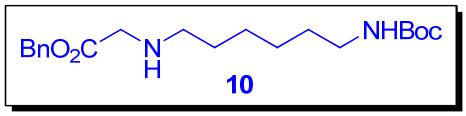
Compound 6. To a solution of acid **5** (55 mg, 0.17 mmol, 1 equiv.), DCC (70.2 mg, 0.34 mmol, 2 equiv.), and DMAP (2.1 mg, 0.017 mmol, 0.1 equiv.) and Et_3N (17.2 mg, 0.02 mL) in dry CH_2Cl_2 (2 mL), a solution of glycine benzyl ester (GlyOBn, 28.1 mg, 0.17 mmol, 1 equiv.) in CH_2Cl_2 (1 mL) was added dropwise under an atmosphere of argon. The reaction mixture was stirred for 48 h. The solvent was evaporated to dryness and the reaction mixture was purified by FCC on SiO_2. Elution with PhMe/EtOAc 7:3 gave the amide **6** (40 mg, 50%) as colorless oil. IR(ATR): 3332, 2977, 2936, 1747, 1697, 1459, 1368, 1249, 1176 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$, compound exists as a 75:25 mixture of rotamers): δ=7.43-7.05 (m, 5H, HC^{Ar}), 7.03 and 6.22 (2 br s, NH), 5.17 (s, 2H, H_2C^{Bn}), 4.07 (d, J=5,8 Hz, 2H, H_2C-CO_2Bn), 3.82 and 3.73 (two s, 2H, H_2C-CO_2tBu), 3.34 (t, J=6,2 Hz, 2H, $H_2C(4)^{GABA}$), 2.30 (t, J=7,0 Hz, 2H, $H_2C(2)^{GABA}$), 1.90-1.72 (m, 2H, $H_2C(3)^{GABA}$), 1.46 and 1.44 (two s, 18H, CH_3^{tBu}) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ=173.43 (CO^{GABA}), 169.88 and 169.22 (CO_2Bn, CO_2tBu), 156.11 (CO^{Boc}), 135.34, 129.00, 128.58, 128.34, 125.27 (C^{Ar}), 81.48, 80.26 (C^{tBu}), 66.97 (CH_2^{Bn}), 50.34 (CH_2-CO_2tBu), 47.34 ($CH_2(4)^{GABA}$), 41.37 (CH_2-CO_2Bn), 33.14 ($CH_2(2)^{GABA}$), 28.21 and 27.99 (CH_3^{tBu}), 24.60 ($CH_2(3)^{GABA}$) ppm; MS(ESI): Calcd for $C_{24}H_{37}N_2O_7$ $(M+H)^+$: 465.2595, found 465.2575.



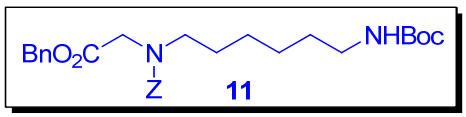
Compound 7. To a solution of benzyl ester **6** (340 mg, 0.73 mmol) in MeOH (100 mL) 5% Pd/C (34 mg) was added and suspension was bubbled with argon. Mixture was hydrogenated (40 psi) at room temperature for 1 h. After filtering the catalyst and evaporating the solvent, crude acid **7** (272 mg, 99 %) was isolated as colorless oil. IR(ATR): 3395, 2979, 2935, 2488, 1740, 1681, 1475, 1370, 1251, 1159 cm^{-1}; ^1H NMR (200 MHz, CD_3OD, compound exists as a 48:52 mixture of rotamers): δ=3.89 and 3.84 (two s, 4H, H_2C-CO_2tBu, H_2C-CO_2H), 3.30 (m, 2H, $H_2C(4)^{GABA}$), 2.28 (t, J=7,3 Hz, 2H, $H_2C(2)^{GABA}$), 1.83 (m, 2H, $H_2C(3)^{GABA}$), 1.47 and 1.43 (two s, 18H, CH_3^{tBu}) ppm; ^{13}C NMR (50 MHz, CD_3OD): δ=176.05, 175.91 (CO_2H), 173.16 (CO^{GABA}), 171.10 (CO_2tBu), 157.63, 157.46 (CO^{Boc}), 82.72 and 81.54 (C^{tBu}), 51.29, 51.02, 50.28 and 47.72 (CH_2-CO_2tBu, $CH_2(4)^{GABA}$), 41.83 (CH_2-CO_2H), 34.73 and 33.82 ($CH_2(2)^{GABA}$), 28.57and 28.33 (CH_3^{tBu}), 26.71, 26.02, 25.62, 25.35 ($CH_2(3)^{GABA}$) ppm; MS(ESI): Calcd for $C_{17}H_{31}N_2O_7$ $(M+H)^+$: 375.2126, found 375.2129.



Compound 9. Solution of Boc_2O (0.5 M; 1.83 g; 8.6 mmol) in $CHCl_3$ (17 mL) was added dropwise to a stirred ice-cooled 0.25 M solution of 1,6-hexanediamine **8** (5.00 g; 43.0 mmol) in $CHCl_3$ (172 mL), for 6 h. Stirring was continued at room temperature for the next 18 h. Suspension was filtered over a sintered funnel and the solvent was evaporated under vacuum. The residual mixture was redissolved in EtOAc (50 mL), washed with a saturated aqueous NaCl solution (4×15 mL), and dried over anh. Na_2SO_4. Solvent was removed under vacuum, yielding **9** as colorless oil (1.48 g, 80%). Further purification was not necessary. (If it is necessary, product may be purified by DCFC on silica-gel, with solvent mixtures EtOAc/MeOH/NH_3 (80:20:3→80:20:10) as eluents). IR(ATR): 3363, 2931, 1700, 1176, 871 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ=4.97 (s, 1H, NH-Boc), 3.10 (q, J=6.2 Hz, 2H, H_2C-NHBoc), 2.68 (t, J=6.2 Hz, 2H, H_2C-NH_2), 1.44 (s, 9H, H_3C^{Boc}), 1.52 (s, 2H, NH_2), 1.51-1.25 (m, 8H, H_2C^{2-5}) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ=155.9 (CO^{Boc}), 78.5 (C^{Boc}), 41.8 (CH_2-NH_2), 40.2 (CH_2-NHBoc), 33.3, 29.8 ($2CH_2$), 28.1 (CH_3^{Boc}), 26.3, 26.2 ($2CH_2$) ppm; ESI-TOF-MS: *m/z*: Calculated for $C_{11}H_{25}N_2O_2$: 217.1910 $[M+H]^+$; found 217.1912.

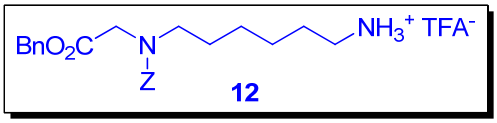


Compound 10. Solution of BBA (0.844 g; 0.582 mL; 3.70 mmol; 1 equiv.) in dry CH_2Cl_2 (6.75 mL) was added dropwise into a stirred solution of amine **9** (1.00 g, 4.63 mmol; 1.25 equiv.) and Et_3N (0.374 g; 0.515 mL; 3.70 mmol; 1 equiv.) in dry CH_2Cl_2 (19.2 mL), at 0 °C. The addition of BBA solution was completed after 1 h. The reaction mixture was then stirred at room temperature for 24 h, washed with H_2O (3×15 mL) and saturated aqueous NaCl (2×15 mL), and dried over anh. $NaSO_4$. After filtering and evaporation of the solvent, the reaction mixture was purified by DCFC on SiO_2. Elution with EtOAc gave compound **10** as pale yellow oil (0.813 g; 60%). IR(ATR): 3346, 2974, 2932, 2858, 1741, 1711, 1524, 1457, 1366, 1251, 1175, 967, 751, 700 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 7.36 (s, 5H, HC^{Ar}), 5.17 (s, 2H, H_2C^{Bn}), 4.55 (s, 1H, NH-Boc), 3.45 (s, 2H, H_2C-CO_2Bn), 3.10 (q, J=6.2 Hz, 2H, H_2C-NHBoc), 2.59 (t, J=6.7 Hz, 2H, H_2C-NH-GlyOBn), 1.70 (s, 1H, NH-GlyOBn), 1.44 (s, 9H, H_3C^{Boc}), 1.57-1.26 (m, 8H, H_2C^{2-5}) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 172.5 (CO_2Bn), 156.0 (CO^{Boc}), 135.6 (C^{Ar}), 128.6; 128.4 (CH^{Ar}), 79.0 (C^{Boc}), 66.5 (CH_2^{Bn}), 50.9 (CH_2-CO_2Bn), 49.4 (CH_2-NHGlyOBn), 40.5 (CH_2-NHBoc), 29.9 ($2CH_2$), 28.4 (CH_3^{Boc}), 26.8, 26.6 ($2CH_2$) ppm; ESI-TOF-MS: *m/z*: calculated for $C_{20}H_{33}N_2O_4$: 365.2435 $[M+H]^+$, found 365.2428.



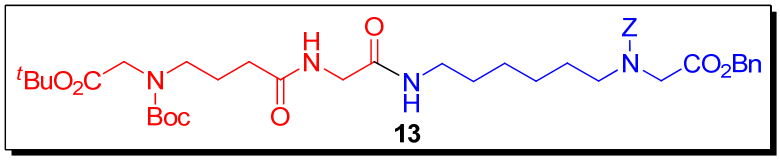
Compound 11. Solution of benzyl chloroformate (ZCl, 439 mg, 433 µL, 2.56 mmol, 1.1 equiv.) in dry CH_2Cl_2 (39 mL) was added dropwise in solution of compound **10** (850 mg; 2.33 mmol; 1 equiv.) and Et_3N (704 mg, 970 µL, 6.99 mmol, 3 equiv.) in dry CH_2Cl_2 (116 mL), at 0 °C for 2 h. Reaction mixture was stirred for additional 2 h at room temperature, and purified by DCFC on SiO_2. Elution with mixtures of solvents PhMe/EtOAc (9:1→1:1) afforded pure product **11** as yellow oil (0.99 g, 83%). IR(ATR): 3373, 2975, 2936, 2836, 1745, 1712, 1520, 1457, 1390, 1366,

1252, 1176, 999, 743, 700 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$, compound exists as a mixture of rotamers): δ=7.38-7.13 (m, 10H, HC^{Ar}), 5.18, 5.16 (2s, 2H, H_2C^{Bn}), 5.09, 5.08 (2s, 2H, H_2C^{Z}), 4.58 (br s, 1H, NHBoc), 4.06, 3.98 (2s, 2H, H_2C-CO_2Bn), 3.32 (q, J=7.0 Hz, 2H, H_2C-N(Z)GlyOBn), 3.08 (q, J=6.0 Hz, 2H, H_2C-NHBoc), 1.44 (s, 9H, CH_3^{Boc}), 1.27, 1.22 (2br s, 8H, H_2C^{2-5}) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ=169.6 (CO_2Bn), 156.5 (CO^{Z}), 155.9 (CO^{Boc}); 155.7 (CO^{Z}), 136.5 ($C^{Ar(Z)}$), 135.3 ($C^{Ar(Bn)}$), 128.5, 128.34, 128.29, 128.1, 127.85, 127.82, 127.6 (CH^{Ar}), 78.8 (C^{Boc}), 67.3, 67.1 (CH_2^{Z}), 66.73, 66.68 (CH_2^{Bn}), 49.0, 48.8, 48.1 (CH_2-CO_2Bn, CH_2-N(Z)GlyOBn), 40.4 (CH_2-NHBoc), 29.8, 29.0 ($2CH_2$), 28.4 (CH_3^{Boc}), 28.1, 27.7, 26.5, 26.4 ($2CH_2$) ppm. ESI-TOF-MS: *m/z*: calculated for $C_{28}H_{38}N_2O_6Na$: 521.2622 $[M+Na]^+$; found 521.2620.



12

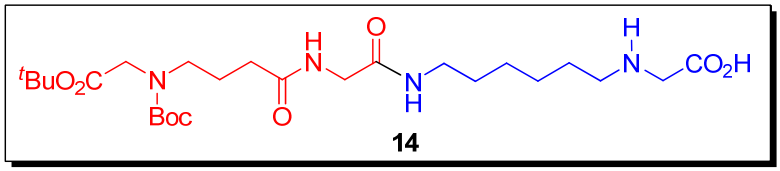
Compound 12. To the solution of compound **11** (500 mg; 1.00 mmol) in CH_2Cl_2 (1 mL) TFA (1 mL) was added, and reaction mixture was stirred overnight at room temperature. Solvent and TFA were removed from the mixture by successive co-evaporations with PhMe (5×5 mL, at least). TFA salt **12** remained as colorless oil (510 mg, 100%). IR(ATR): 3067, 2942, 2872, 1694, 1622, 1596, 1533, 1496, 1436, 1190, 1140, 948, 838, 799, 723 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$, compound exists as a mixture of rotamers): δ=7.63 (br s, 3H, NH_3^+), 7.40-7.15 (m, 8H, HC^{Ar}), 6.93 (br s, 2H, HC^{Ar}), 5.14, 5.13, 5.08, 5.03 (4s, 4H, $H_2C^{Bn,Z}$), 4.01, 3.96, 3.91 (3s, 2H, H_2C-CO_2Bn), 3.30 (br s, 2H, H_2C-N(Z)GlyOBn), 2.84 (br s, 2H, H_2C-NHBoc), 1.68-1.40 (m, 4H), 1.40-1.12 (m, 4H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ=169.6 (CO_2Bn), 161.6 (q, $^2J_{C,F}$ =40 Hz, CO^{TFA}), 157.2, 157.7, 156.4 (CO^{Z}), 136.2 (C^{Z}), 135.2 (C^{Bn}), 128.6, 128.5, 128.3, 128.1, 127.8, 127.5, 127.1 (C^{Ar}), 116.0 (q, $^1J_{C,F}$=290 Hz, CF_3), 67.6 (CH_2^{Z}), 67.0 (CH_2^{Bn}), 49.2, 48.9 (CH_2-CO_2Bn), 48.3, 48.2 (CH_2N(Z)GlyOBn), 39.7, 39.6 (CH_2-NH_3^+), 27.9, 27.3, 26.9, 25.8, 25.1 (CH_2^{2-5}) ppm; ESI-TOF-MS: *m/z*: calculated for $C_{23}H_{31}N_2O_4$: 399.2278 $[M - CF_3COO^-]^+$; found 399.2266.



13

Compound 13. To an ice bath cooled solution of TFA salt **12** (77.3 mg, 0.15 mmol, 1 equiv.), Et_3N (30.3 mg, 0.05 mL, 0.3 mmol, 1 equiv.) in CH_2Cl_2 (1 mL), acid **7** (56.3 mg, 0.15 mmol, 1 equiv.) and DMAP (1.8 mg, 0.015 mmol) were added. A solution of DCC (61.9 mg, 0.3 mmol, 2 equiv.) in DCM (1 mL) was added to the reaction mixture (2 h) and stirred for 24 h. The solvent was evaporated in vacuo and the residue chromatographed by DCFC on SiO_2 column using EtOAc/MeOH 50:1 to obtain amide **13** (65 mg, 57%) as yellow oil. IR(ATR): 3350, 2976, 2935, 2861, 1747, 1698, 1542, 1460, 1248, 1172 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$, compound exists as a mixture of rotamers): δ=7.40-7.20 (m, 10H, HC^{Ar}), 6.88 (m, 1H, HN), 6.64 (m, 1H, HN), 5.18, 5.16, 5.10, 5.08 (4s, 4H, H_2C^{Bn}, H_2C^{Z}), 4.10-3.70 (m, 6H, H_2C^{Gly}), 3.31 (m, 4H, $H_2C(1, 6^{hexyl})$), 3.20 (t, J=6.2 Hz, 2H, $H_2C(4)^{GABA}$), 2.32 (t, J=7.0, 2H, $H_2C(2)^{GABA}$), 1.82 (m, 2H, $H_2C(3)^{GABA}$), 1.47 and 1.43 (two s, 18H, CH_3^{tBu}) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ=173.36 (CO^{GABA}), 169.27, 169.14 (CO^{Gly}), 156.56, 156.19, 155.93 (NCO_2Bn, NCO_2^tBu), 136.56, 136.48, 135.35, 128.59, 128.43, 128.27, 127.95 (C^{Ar}), 81.58 and 80.36 (C^{tBu}), 67.40, 67.29 and 66.87 (CH_2^{Bn}), 50.24, 49.12, 48.89, 48.59, 48.18, 47.13 (CH_2^{GlyOBn}, $CH_2^{GlyO^tBu}$, $CH_2(4)^{GABA}$, CH_2N(Z)GlyOBn), 43.51 (CH_2^{Gly}), 39.29, 39.12 (CH_2),

32.78 ($CH_2(2)^{GABA}$), 29.33, 29.22 (CH_2), 28.18, 28.02 ($CH_3{}^{tBu}$), 27.70, 26.47, 26.25, 25.98 (CH_2), 24.22 ($CH_2(3)^{GABA}$) ppm; MS(ESI): Calcd for $C_{40}H_{59}N_4O_{10}$ $(M+H)^+$: 755.4226, found 755.4220.



14

12. **Compound 14.** To a solution of benzyl ester **13** (165 mg, 0.22 mmol) in MeOH (100 mL) 5% Pd/C (16.5 mg) was added and suspension was bubbled with argon. Mixture was hydrogenated at 40 psi for 24 h. After filtering the catalyst and evaporating the solvent, crude acid **14** (115.1 mg, 99%) was isolated as colorless oil.

IR(ATR): 3378, 3054, 2979, 2936, 2862, 2497, 1743, 1650, 1462, 1369, 1266, 1156 cm^{-1}; ^1H NMR (500 MHz, CD_3OD, compound exists as a mixture of rotamers): δ=3.88/3.85 (minor) and 3.83/3.80 (major) (four s, 4H, $H_2C^{GlyOtBu}$, $H_2C^{Gly(amide)}$), 3.48 (s, 2H, H_2C^{GlyOH}), 3.33-3.28 (m, 2H, $H_2C(6)^{hexyl}$), 3.23/3.20 (two t, J=7.5 Hz, 2H, $H_2C(1)^{hexyl}$)), 2.99 (br t, J=7.5 Hz, 2H, $H_2C(4)^{GABA}$), 2.32/2.30 (m, 2H, $H_2C(2)^{GABA}$), 1.81 (m, 2H, $H_2C(3)^{GABA}$), 1.48/1.44 (major) and 1.47/1.46 (minor) (four s, 18H, $CH_3{}^{tBu}$) ppm; ^{13}C NMR (50 MHz, CD_3OD): δ=176.06 (COOH), 172.02, 171.73, 171.14, 171.02, 170.94 (CO), 157.69 (CO^{Boc}), 82.86, 82.78, 81.75, 81.60 (C^{tBu}), 51.16, 51.03, 50.80, 48.69, 48.46 ($CH_2{}^{GlyOtBu}$, $CH_2{}^{GlyOH}$), 43.94, 43.67 ($CH_2{}^{Gly}$), 40.24, 40.19 (CH_2NHGlyOH), 33.99, 33.38 ($CH_2(1)^{hexyl}$), 33.38 ($CH_2(2)^{GABA}$), 30.25 ($CH_2(2)^{GABA}$), 28.81/28.48 (minor) and 28.77/28.53 (major) ($CH_3{}^{tBu}$), 27.33, 27.25, 27.21 ($CH_2{}^{hexyl}$), 25.68, 24.95 ($CH_2(3)^{GABA}$) ppm; MS(ESI): Calcd for $C_{25}H_{47}N_4O_8$ $(M+H)^+$: 531.3388, $(M+Na)^+$: 553.3208; found: 531.3374, 553.3188.

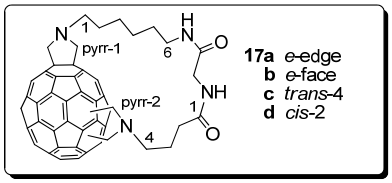
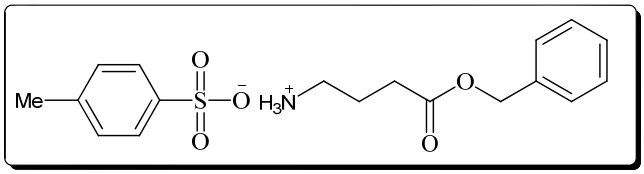


Table S1. ^{1}H /^{13}C NMR chemical shifts (δ (ppm)) of bisadducts **17.**

	17a (*e*-edge)	**17b** (*e*-face)	**17c** (*trans*-4)	**17d** (*cis*-2)
HC(pyrr-1)	4.05s/65.02	4.33d; 3.71d/66.92	4.60d; 3.84d/68.5	4.23d; 3.58d/66.52
	4.04s/68.46		4.58d; 3.57d/66.69	3.95d; 3.73d/67.77
sp^{3}C(full)	69.44; 69.90	70.22	69.80; 69.41;	67.14; 66.95;
			69.24; 69.17	66.74; 66.68
H_2C(1)	2.92/53.95	2.91/52.21	3.04-2.98/54.00	2.98;2.75/53.81
H_2C(2)	1.76/24.47	1.69/25.95	1.91-1.72/27.06	1.88;1.71/26.85
H_2C(3)	1.76/27.08	1.69/27.56	1.91-1.74/26.24	1.76;1.52/25.21
H_2C(4)	1.46/25.11	1.42/26.22	1.61-1.50/25.47	1.47/25.39
H_2C(5)	1.59/28.11	1.55/29.62	1.61-1.50/29.35	1.65/28.15
H_2C(6)	3.21/38.27	3.20/39.85	3.33;3.22/39.23	3.42;3.06/39.36
NH-hexyl	5.61	5.65	5.60	6.00
CO-Gly	167.74	168.59	168.19	168.72
H_2C-Gly	3.90/42.51	3.83/42.76	3.87; 3.68/43.13	4.11;3.76/43.30
NH-Gly	6.85	7.20	6.86	6.93
CO-GABA	172.84	173.77	172.96	173.72
H_2C(2)-GABA	2.60/33.17	2.65/33.54	2.61-2.46/34.75	2.62;2.47/33.86
H_2C(3)-GABA	2.09/23.36	2.13/23.82	2.89; 2.06/22.80	2.10/24.28
H_2C(4)-GABA	2.90/51.13	3.12/50.77	3.08; 2.96/51.93	3.04;2.94/52.02
HC(pyrr-2)	4.29d; 3.65d/67.10	4.04s/67.53; 65.37	4.60d; 3.85d/67.62	4.36d; 3.87d/67.98
			4.44d; 3.70d/67.07	3.96d; 3.72d/65.88
sp^{3}C(full)	69.57	69.44; 69.73		

Compound **2**



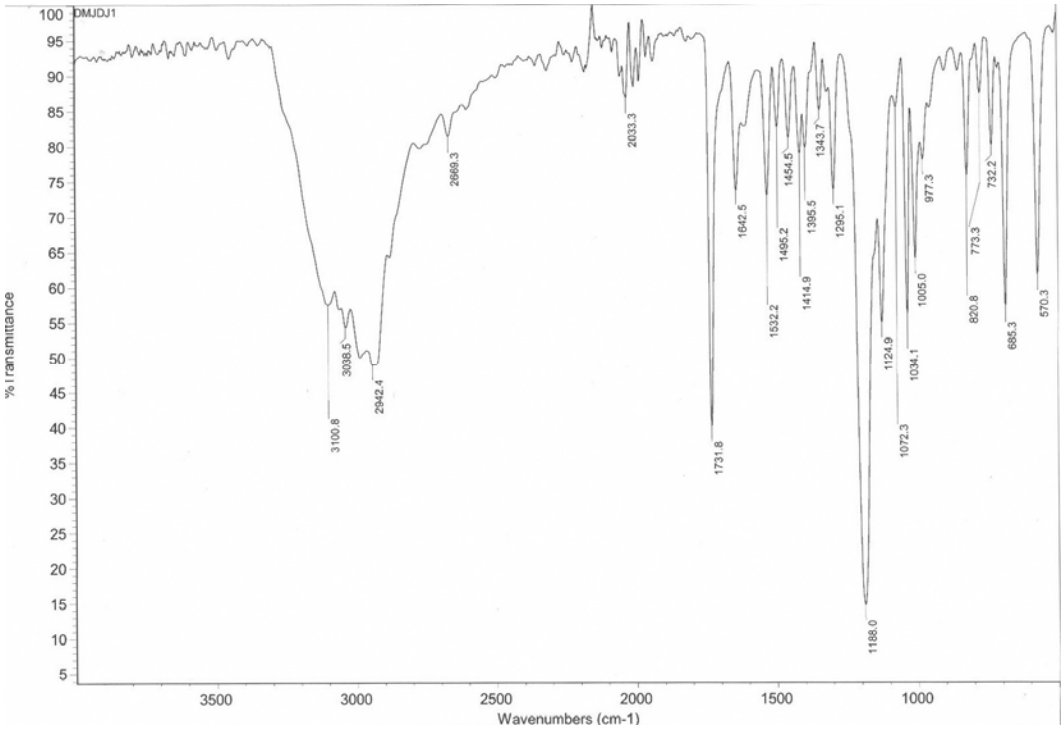


Figure S1. IR spectrum of **2**

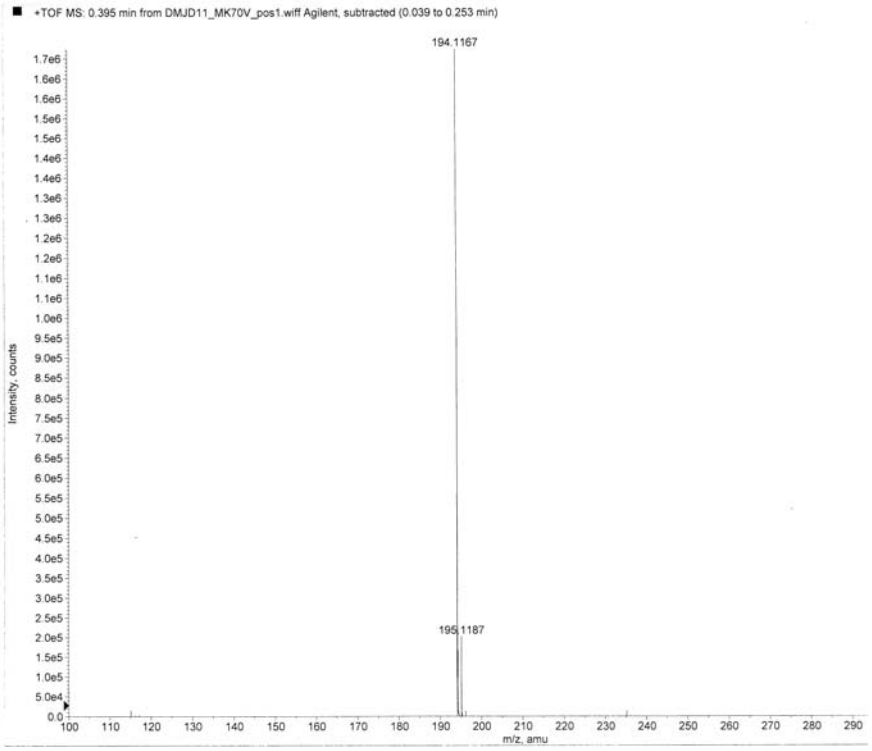


Figure S2. Mass spectum of **2**

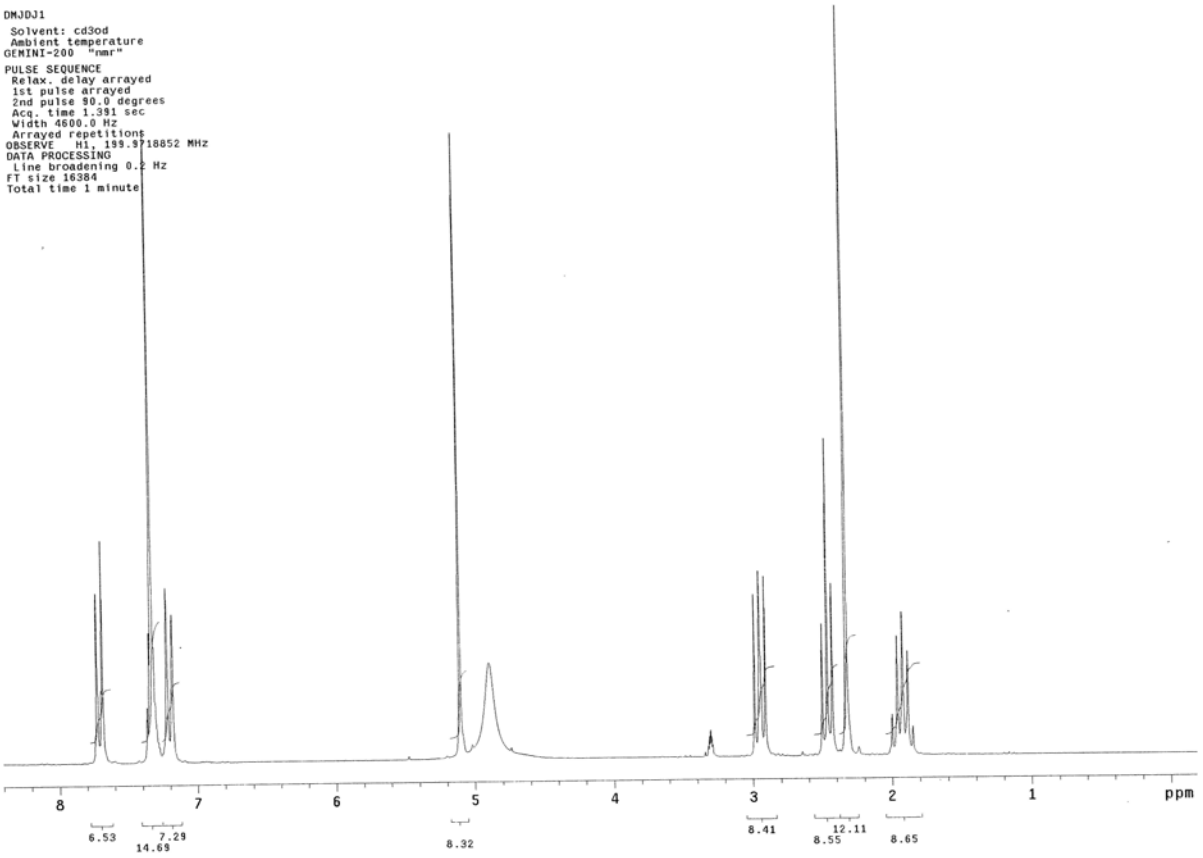


Figure S3. ^{1}H NMR spectrum of **2**

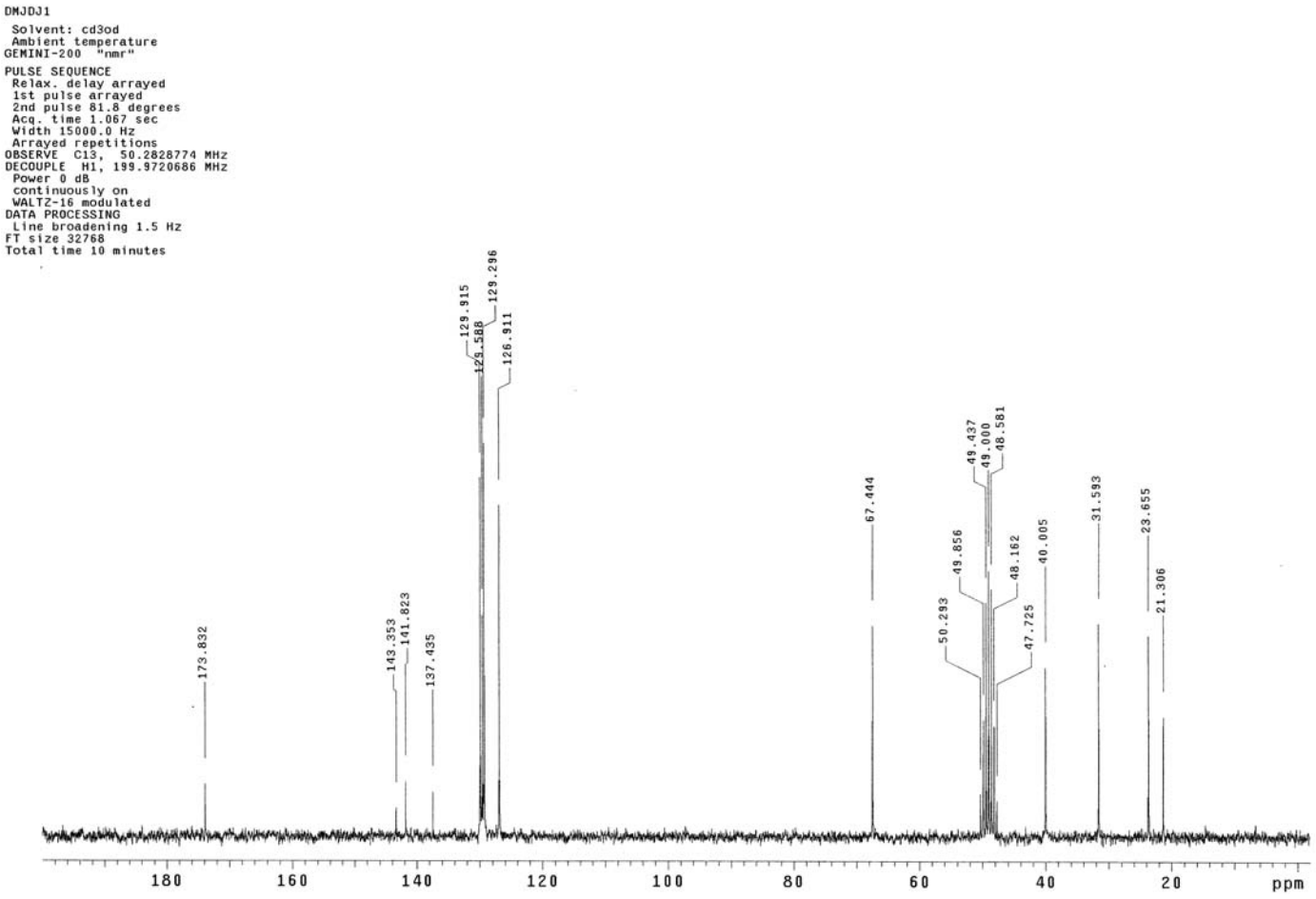
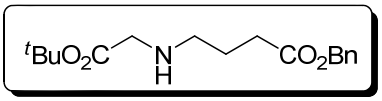


Figure S4. ^{13}C NMR spectrum of **2**

Compound **3**



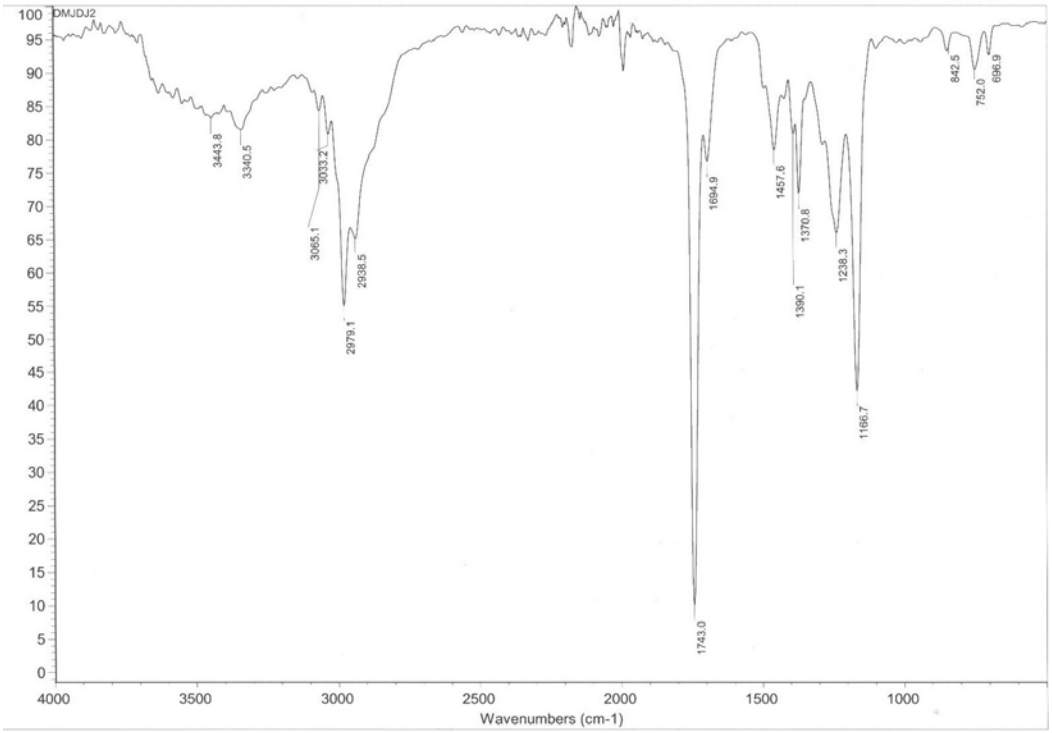
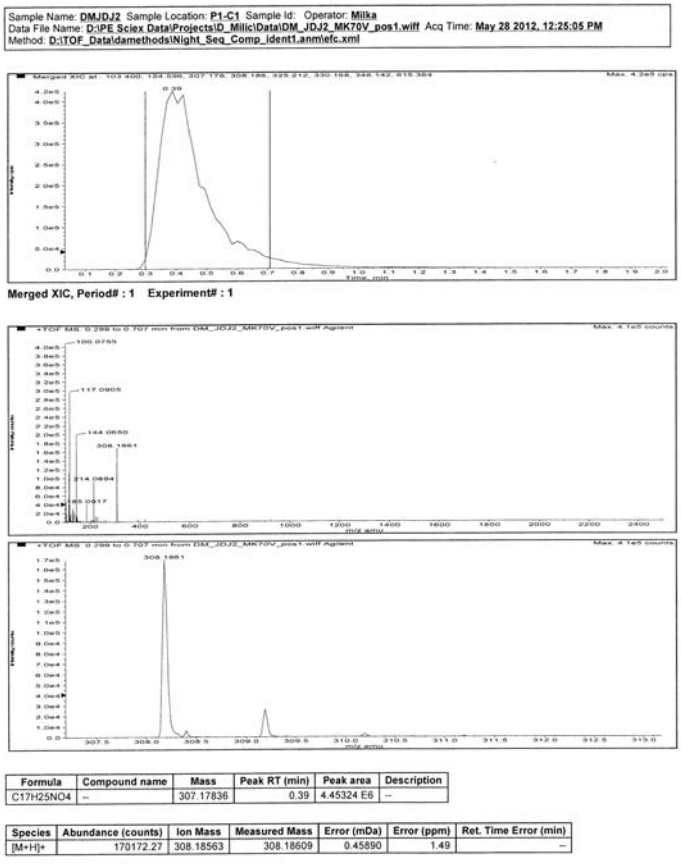


Figure S5. IR spectrum of **3**



Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C17H25NO4	--	307.17836	0.39	4.45324 E6	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+H]+	170172.27	308.18563	308.18609	0.45890	1.49	--

Figure S6. Mass spectrum of **3**

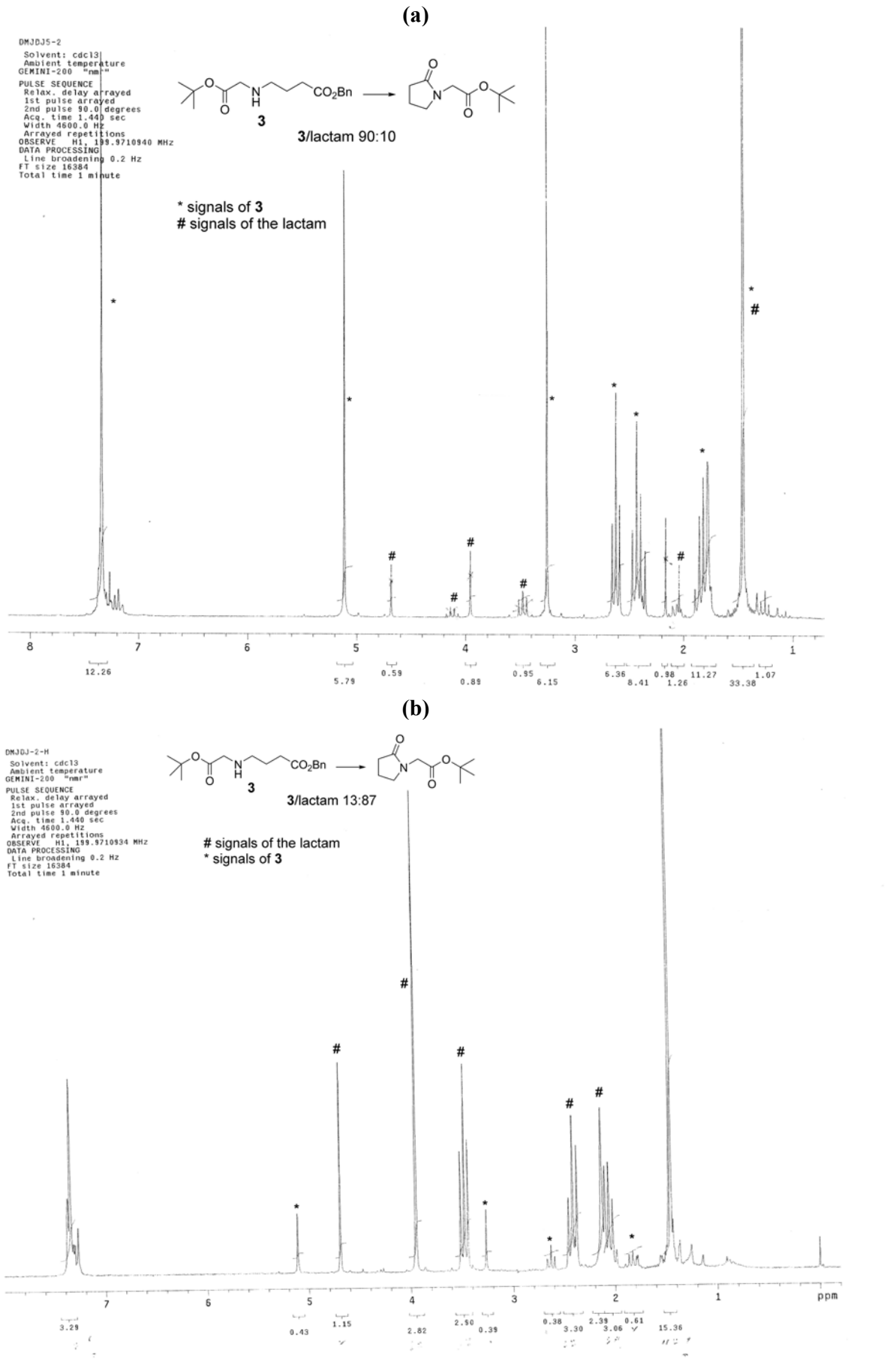


Figure S7. ^{1}H NMR spectra of **3** immediately after isolation (a) and lactam formed upon standing (b)

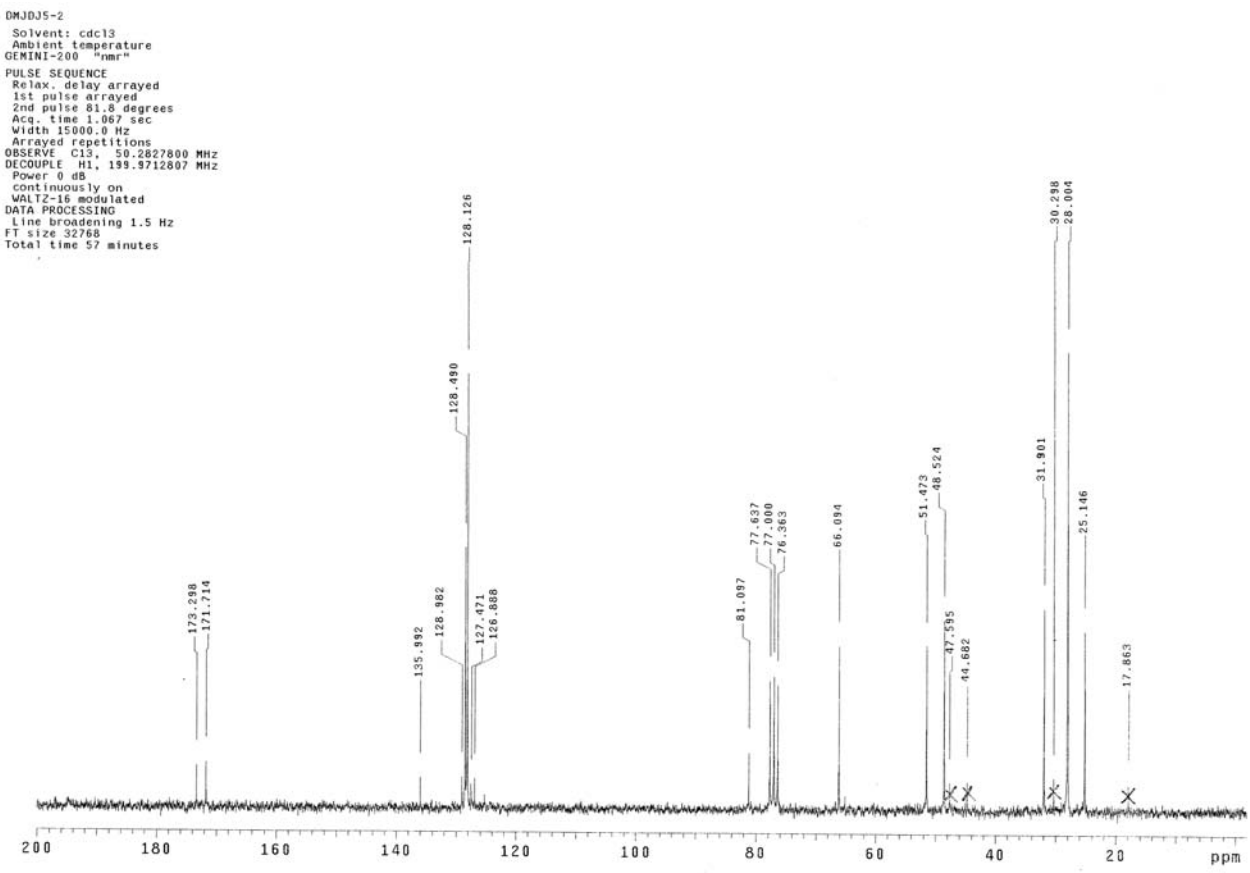
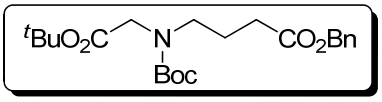


Figure S8. ^{13}C NMR spectrum of **3**

Compound **4**



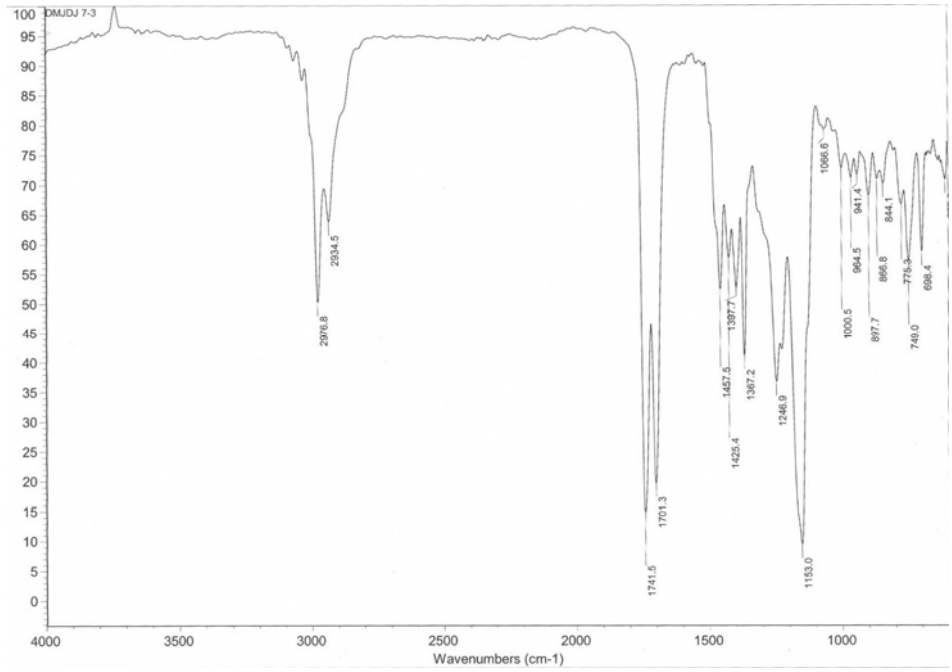


Figure S9. IR spectrum of **4**

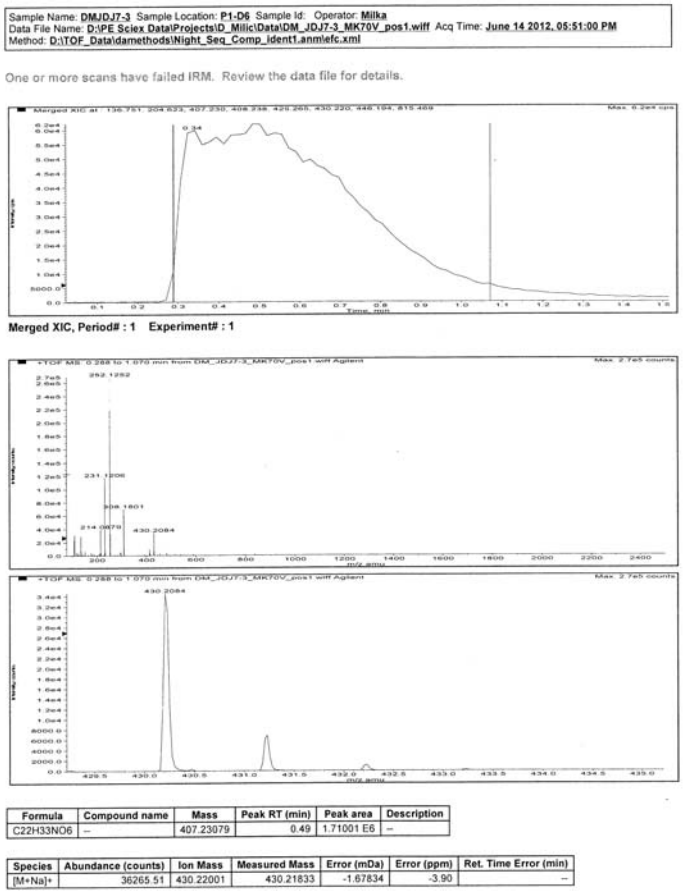


Figure S10. Mass spectrum of **4**

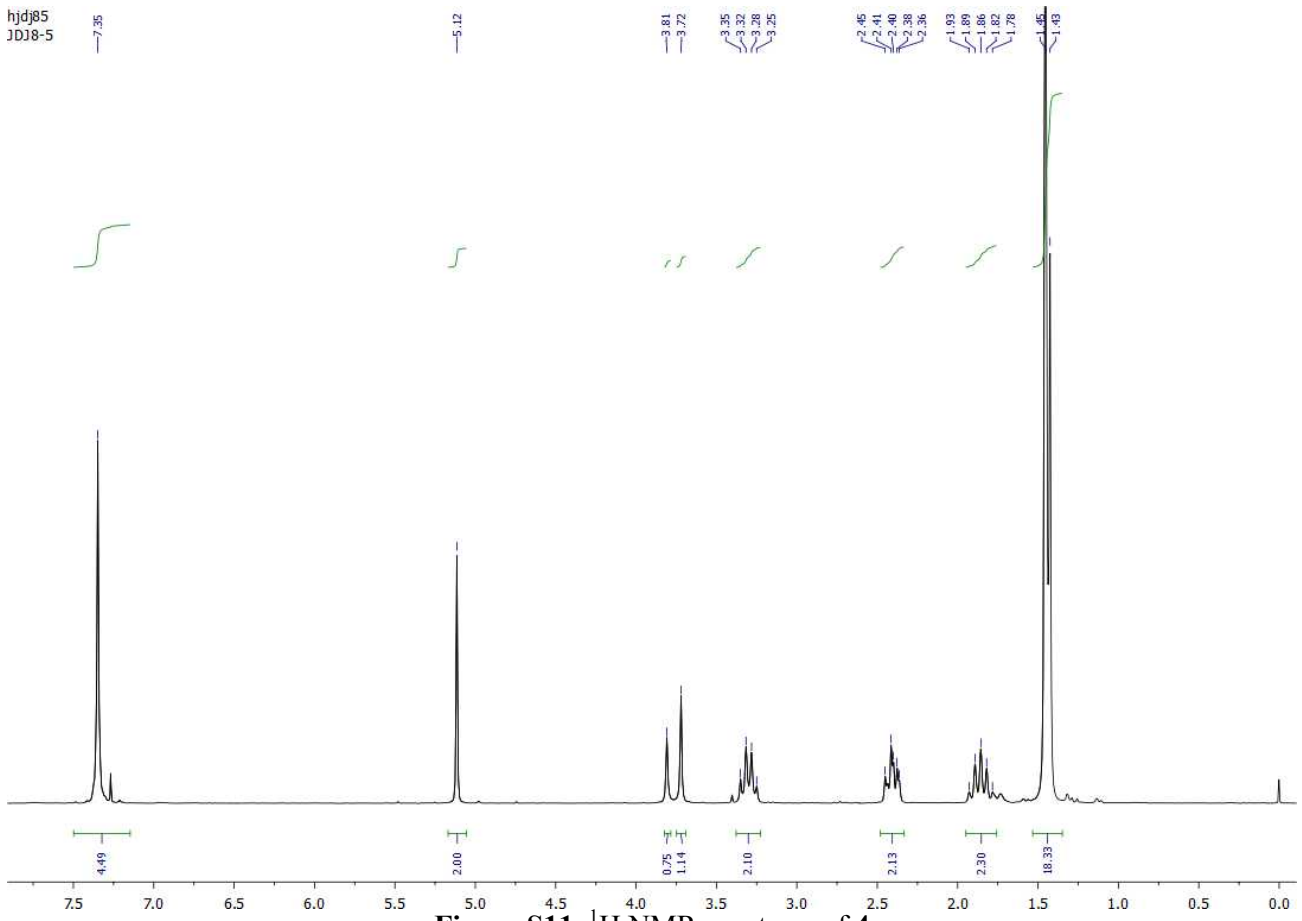


Figure S11. ^{1}H NMR spectrum of **4**

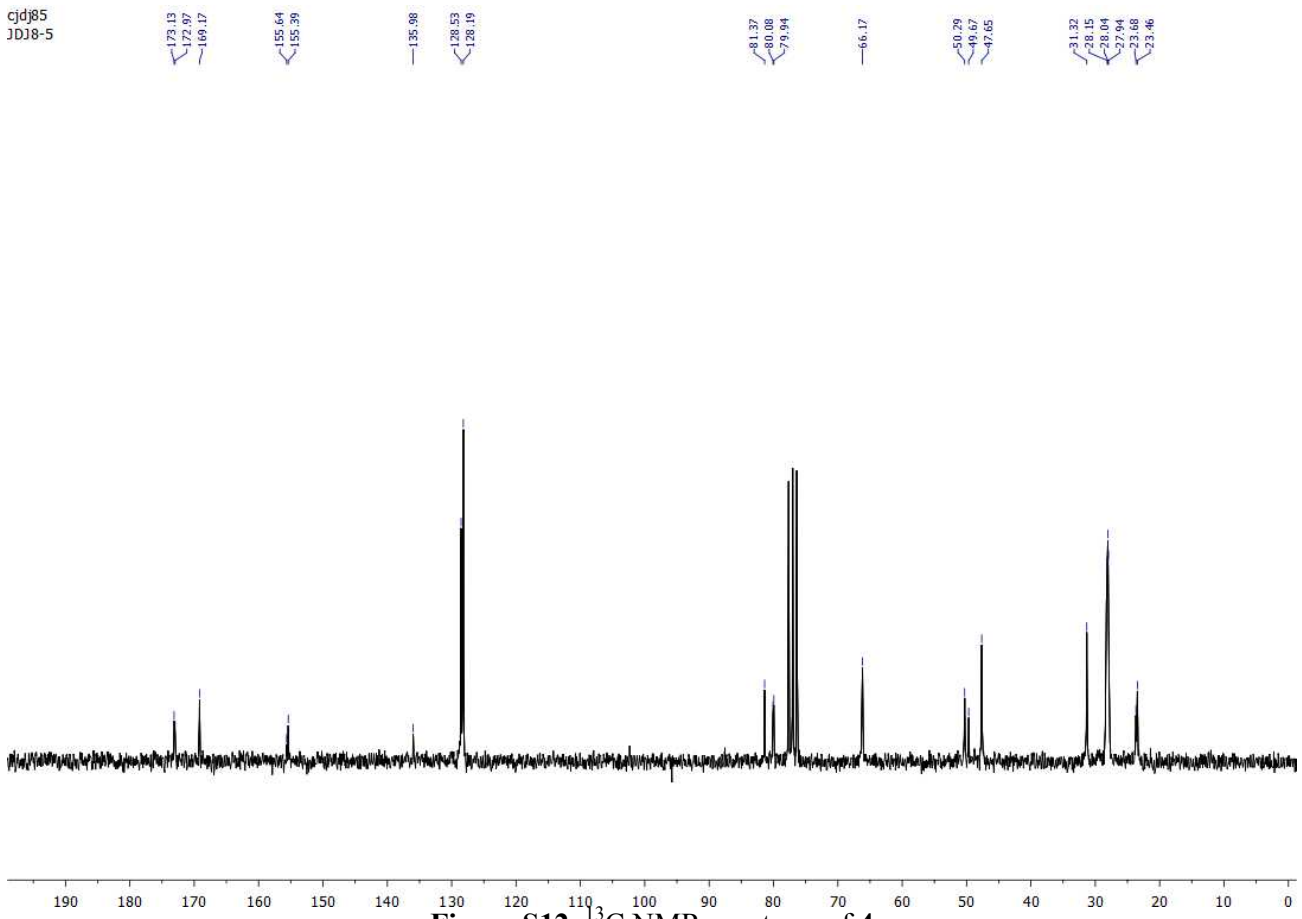
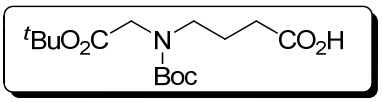


Figure S12. ^{13}C NMR spectrum of **4**

Compound **5**



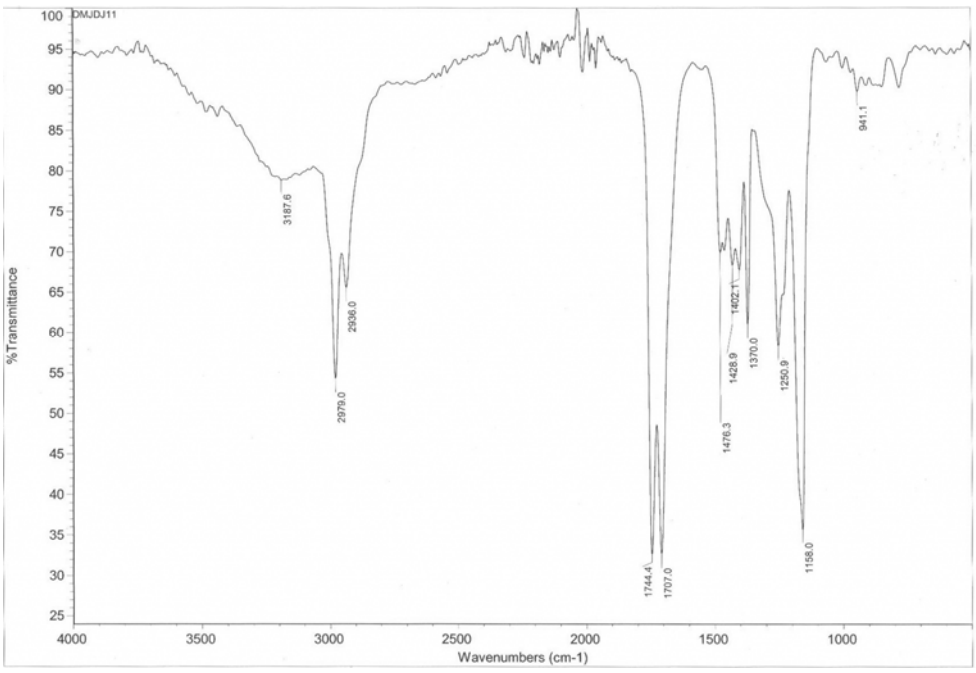
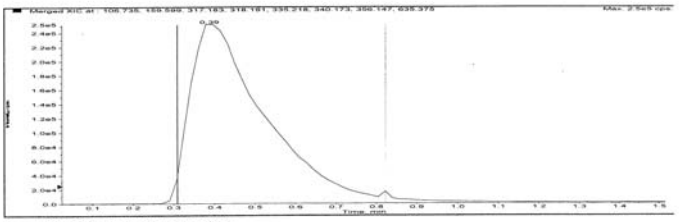


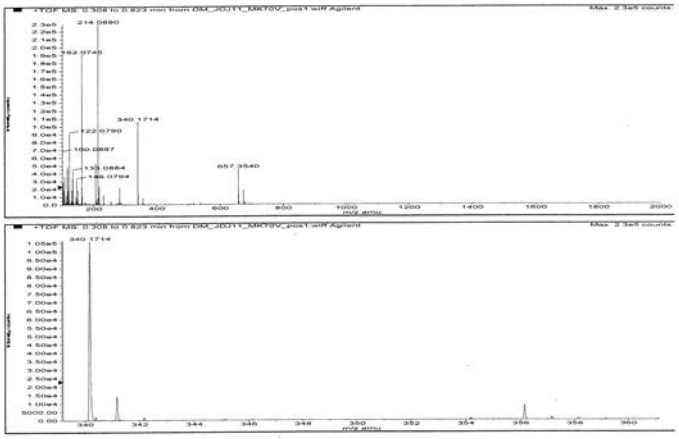
Figure S13. IR spectrum of **5**

Sample Name: **DMJDJ11** Sample Location: **P1-D9** Sample Id: Operator: **Milka**
Data File Name: **D:\PE Sciex Data\Projects\D_Milic\Data\DM_JDJ11_MK70V_pos1.wiff** Acq Time: **July 18 2012, 05:48:37 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
C15H27NO6	--	317.18384	0.39	3.22727 E6	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+Na]+	108890.97	340.17306	340.17135	-1.70813	-5.02	--
[M+K]+	9102.20	356.14700	356.14565	-1.34170	-3.77	--

Figure S14. Mass spectrum of **5**

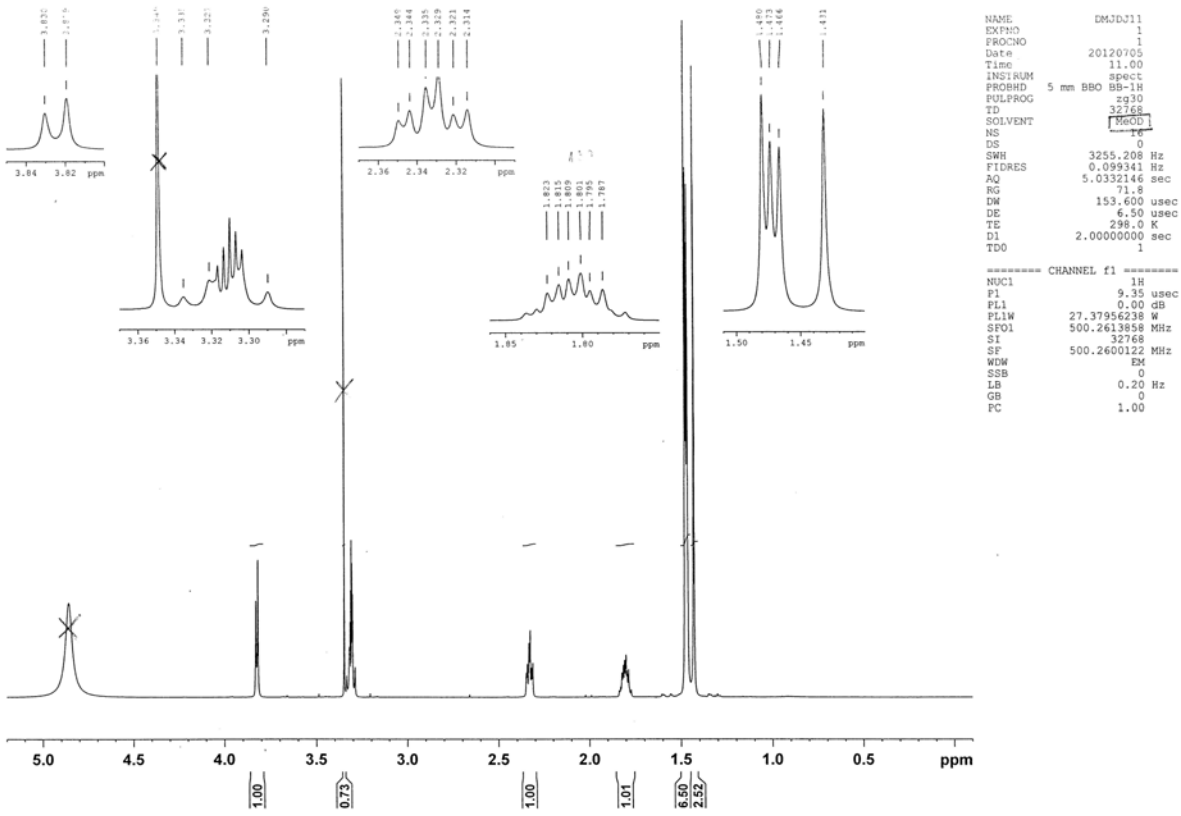


Figure S15. ^{1}H NMR spectrum of **5**

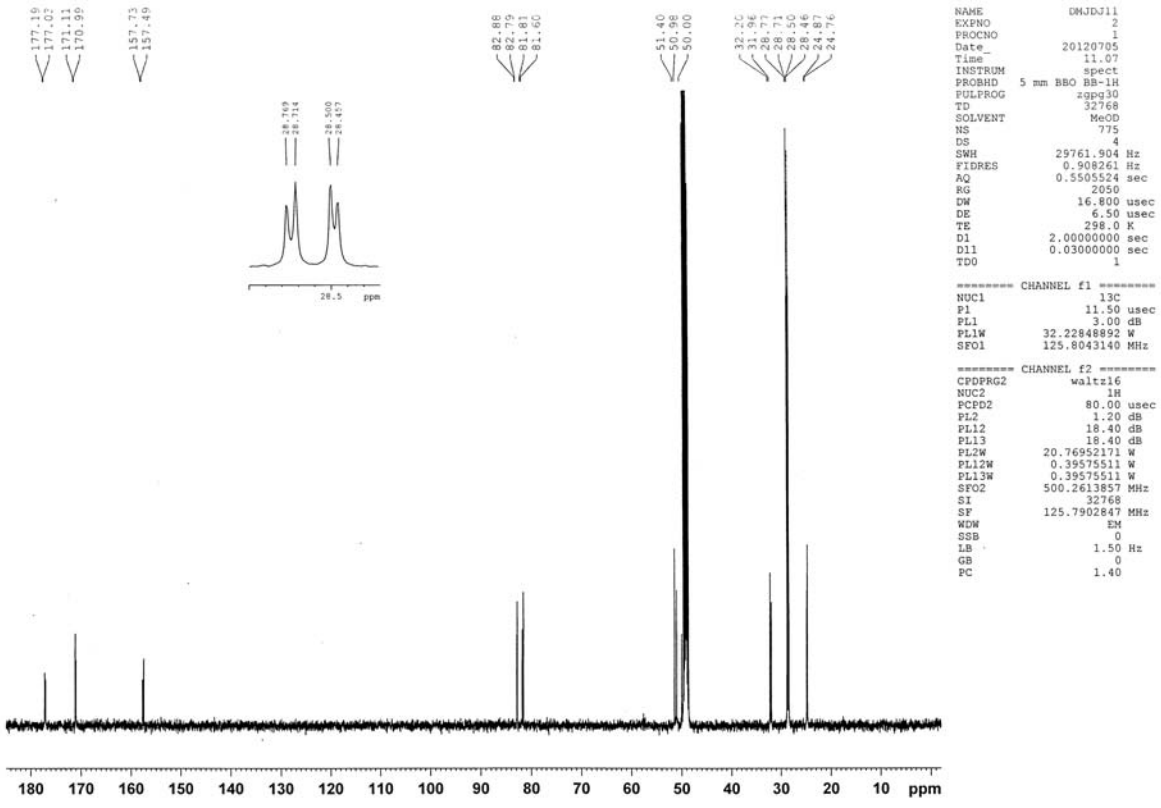
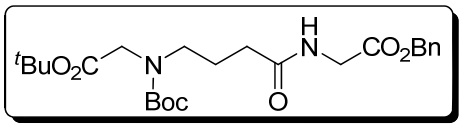


Figure S16. ^{13}C NMR spectrum of **5**

Compound **6**



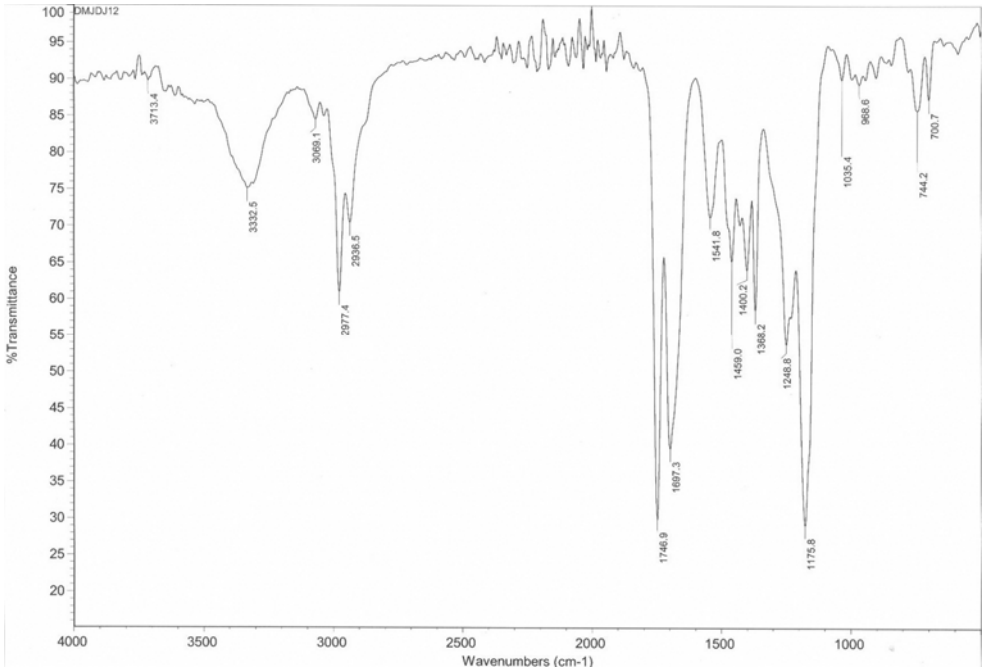
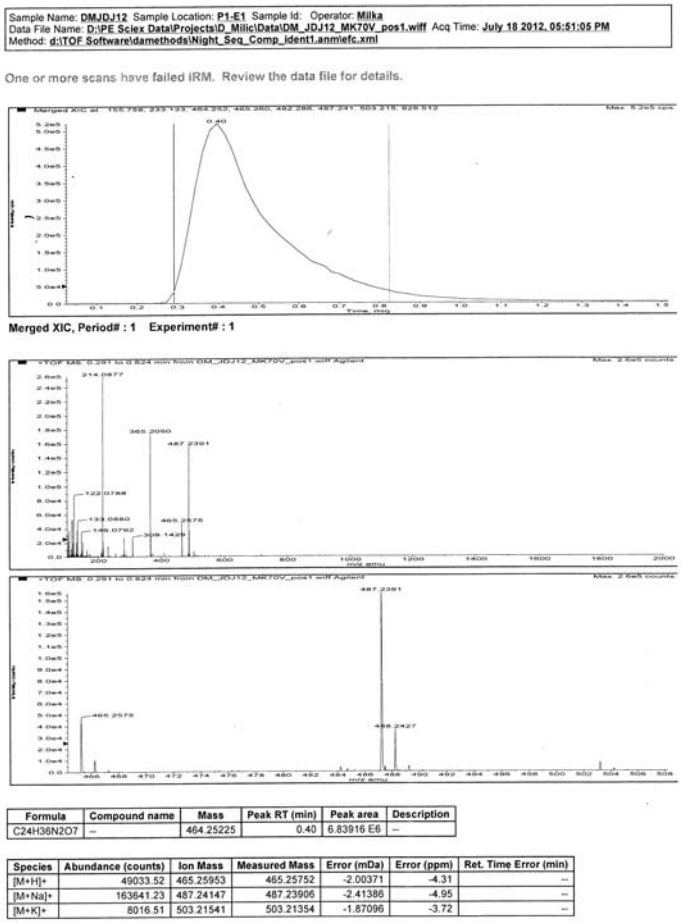


Figure S17. IR spectrum of **6**



Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C24H36N2O7	--	464.25225	0.40	6.83916 E6	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+H]+	49033.52	465.25953	465.25752	-2.00371	-4.31	--
[M+Na]+	163641.23	487.24147	487.23906	-2.41386	-4.95	--
[M+K]+	8016.51	503.21541	503.21354	-1.87096	-3.72	--

Figure S18. Mass spectrum of **6**

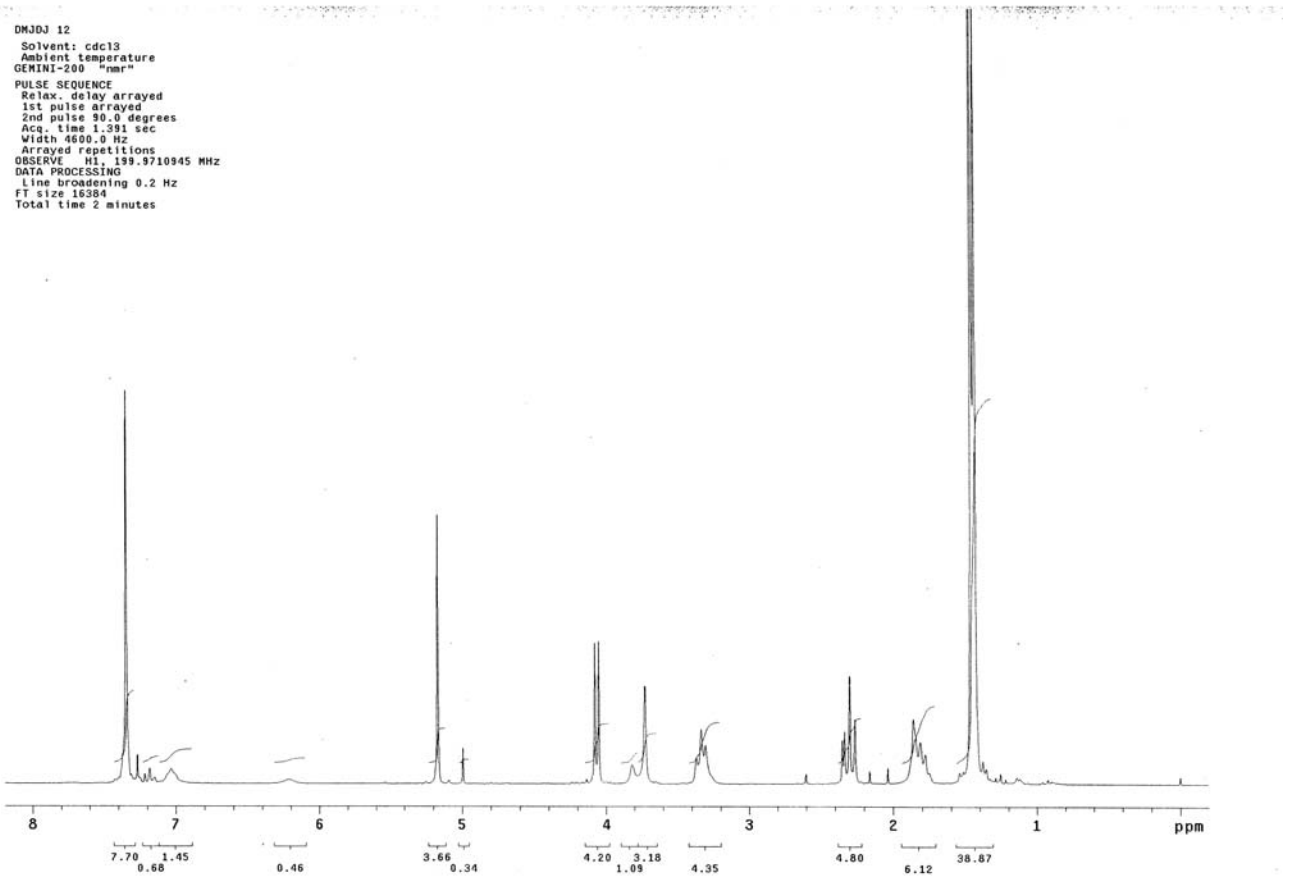


Figure S19. ^{1}H NMR spectrum of **6**

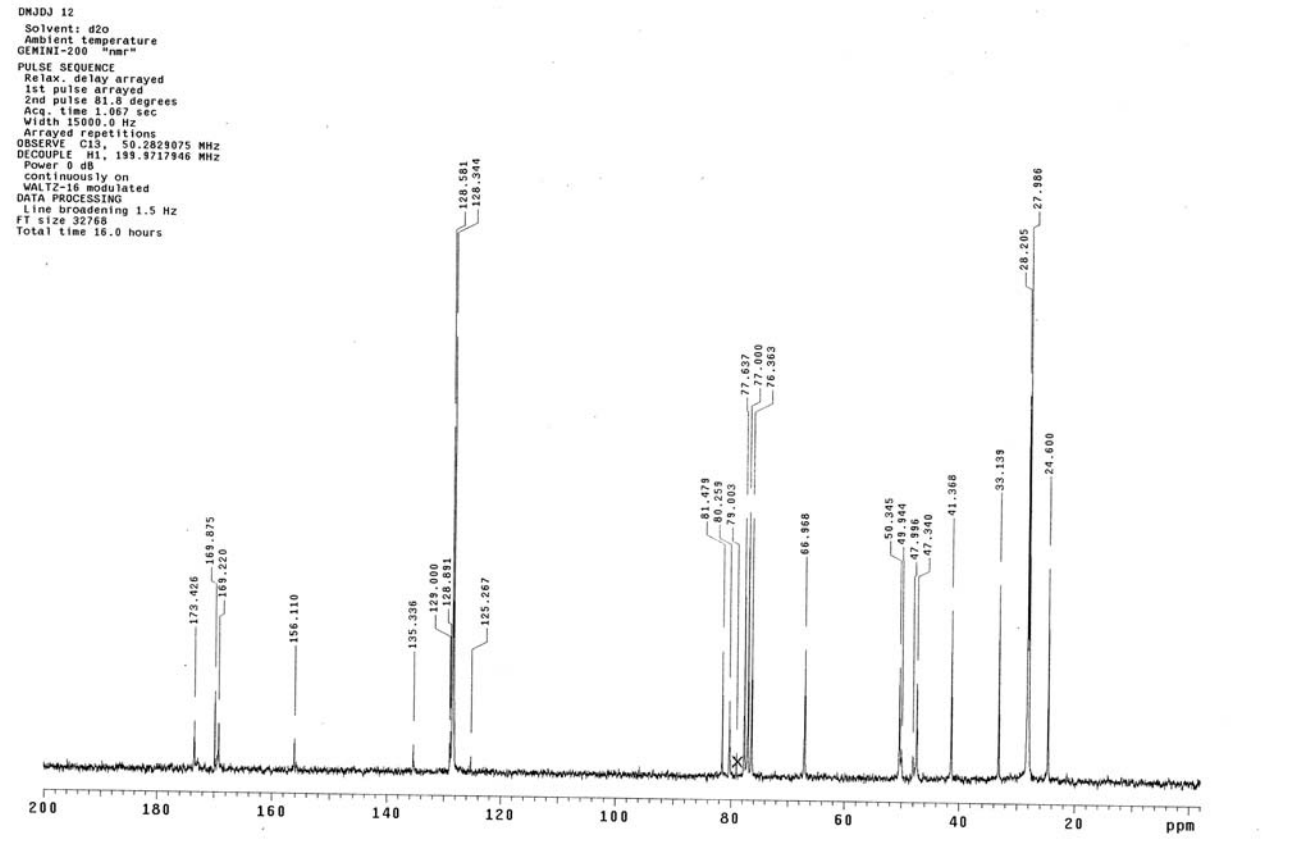
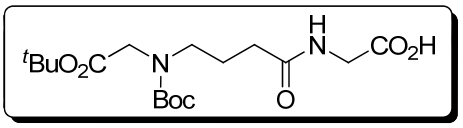


Figure S20. ^{13}C NMR spectrum of **6**

Compound **7**



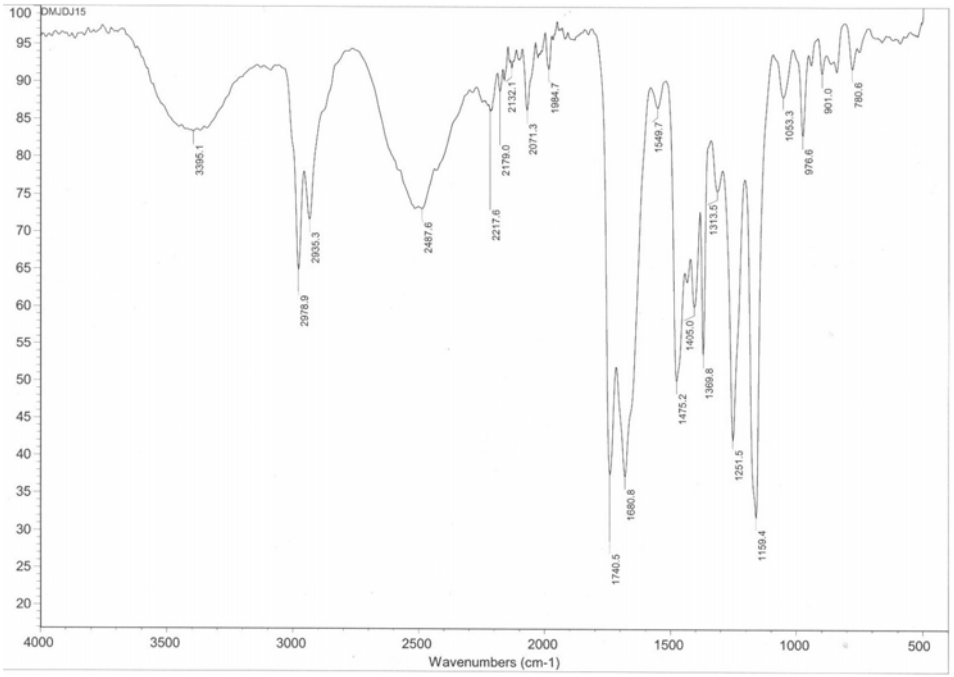
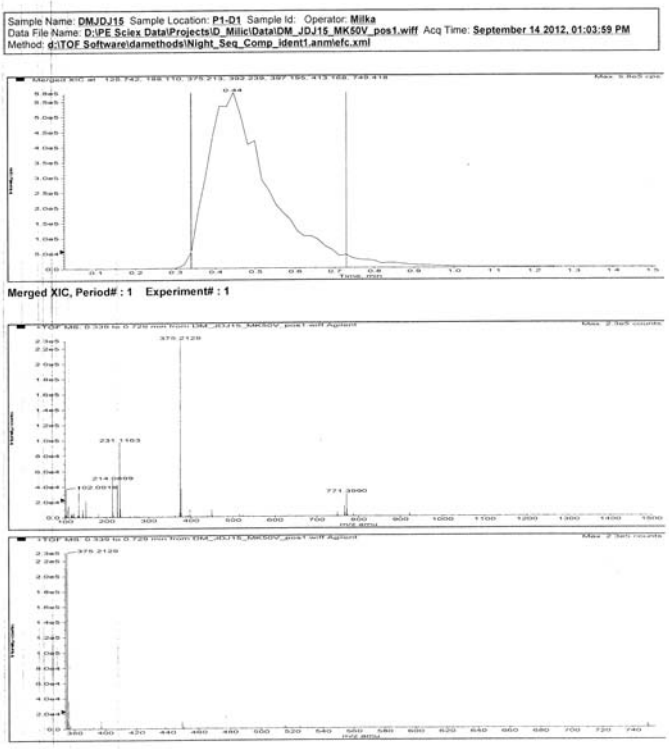


Figure S21. IR spectrum of **7**



Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C17H30N2O7	--	374.20530	0.44	6.23063 E6	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+H]+	23478.19	375.21258	375.21286	0.28071	0.75	--
[M+Na]+	9778.88	397.19452	397.19472	0.20134	0.51	--
[2M+H]+	5852.61	749.41788	749.41769	-0.19409	-0.26	--

Figure S22. Mass spectrum of **7**

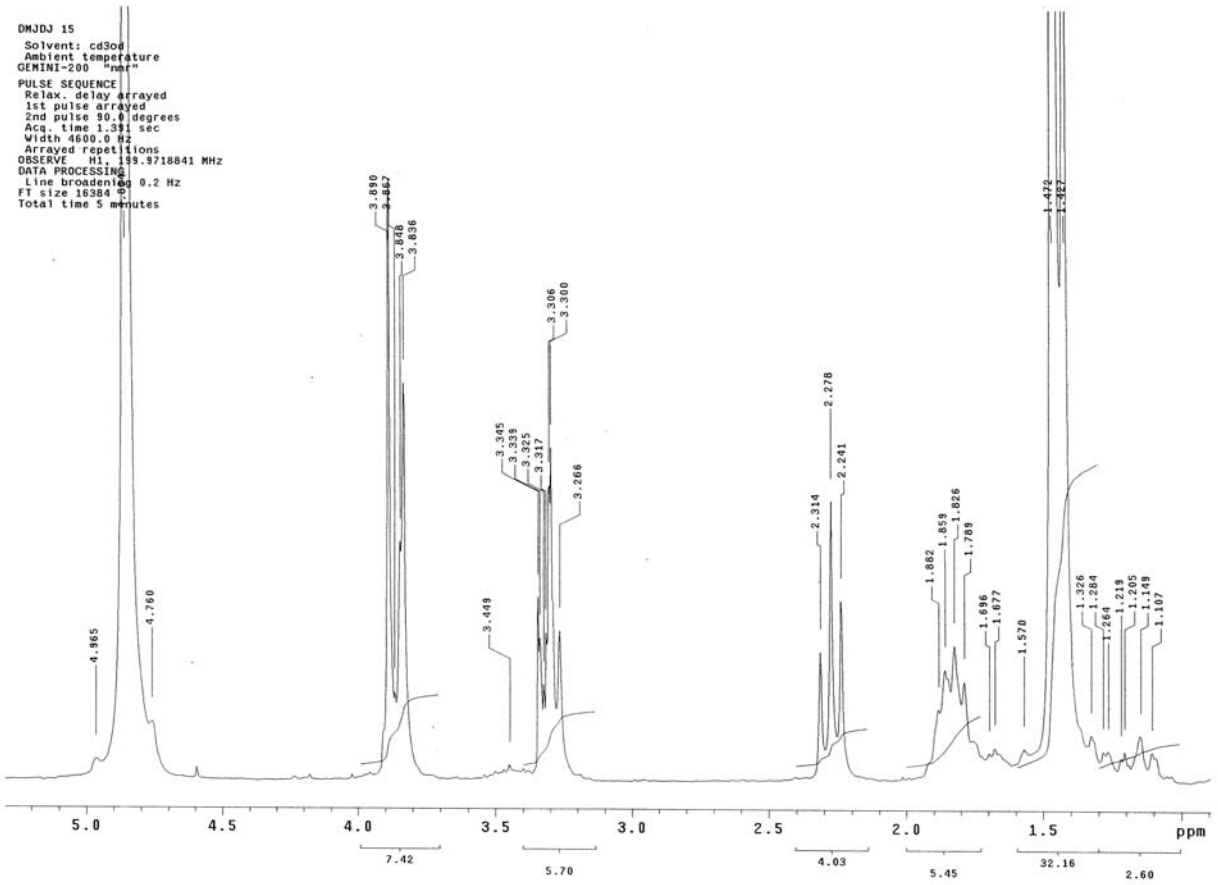


Figure S23. ^{1}H NMR spectrum of **7**

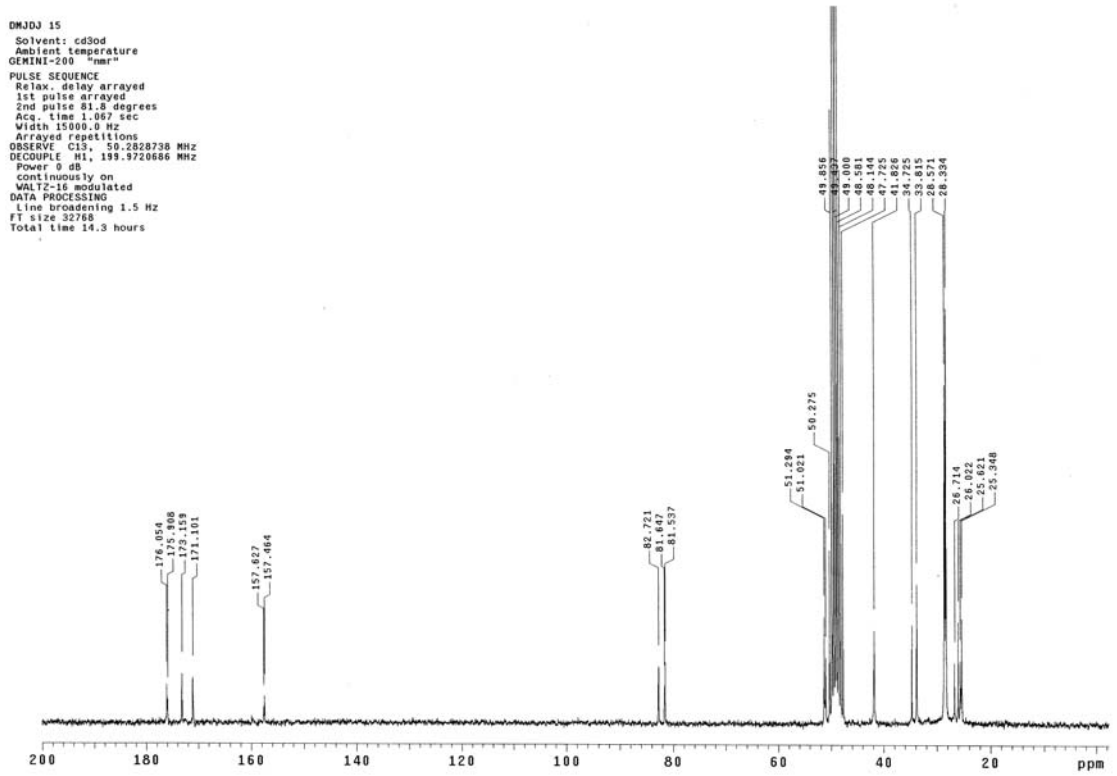
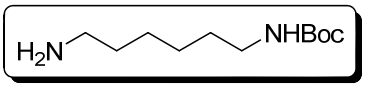


Figure S24. ^{13}C NMR spectrum of **7**

Compound **9**



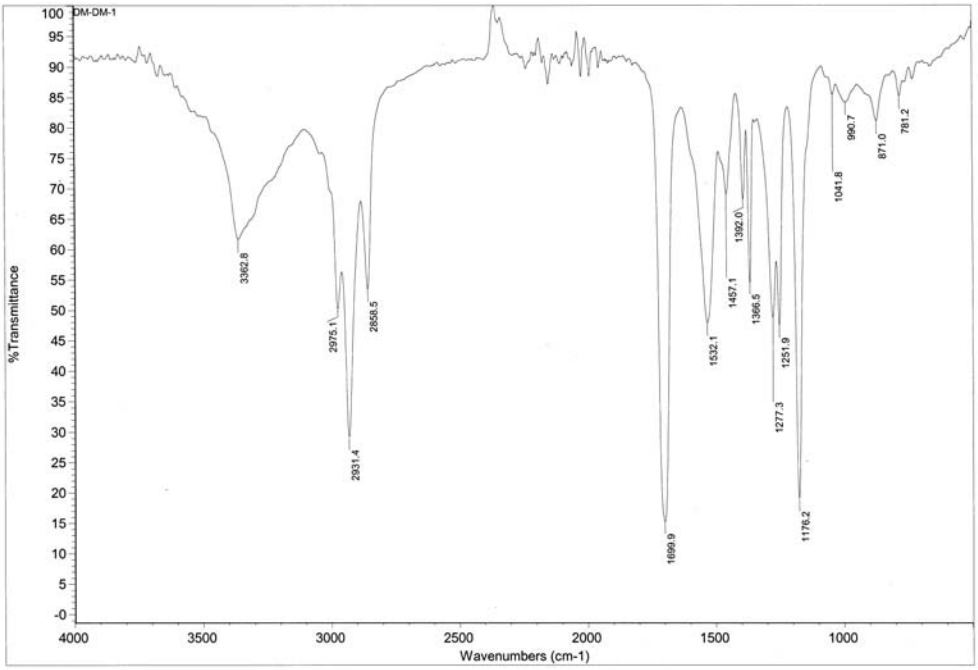
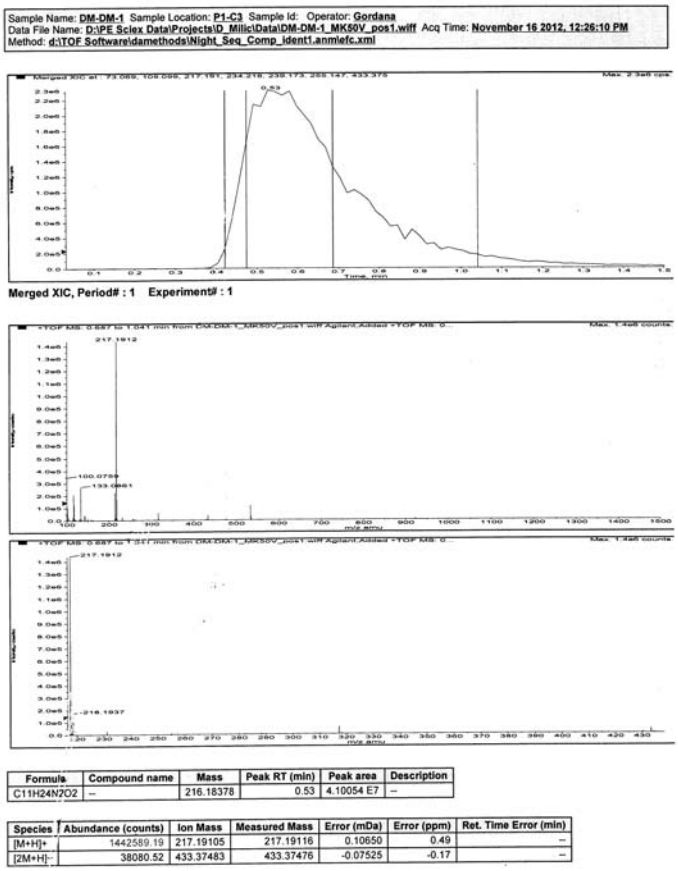


Figure S25. IR spectrum of **9**



Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C11H24N2O2	--	216.18378	0.53	4.10054 E7	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+H]+	1442589.19	217.19105	217.19116	0.10650	0.49	--
[2M+H]+	38080.52	433.37483	433.37476	-0.07525	-0.17	--

Figure S26. Mass spectrum of **9**

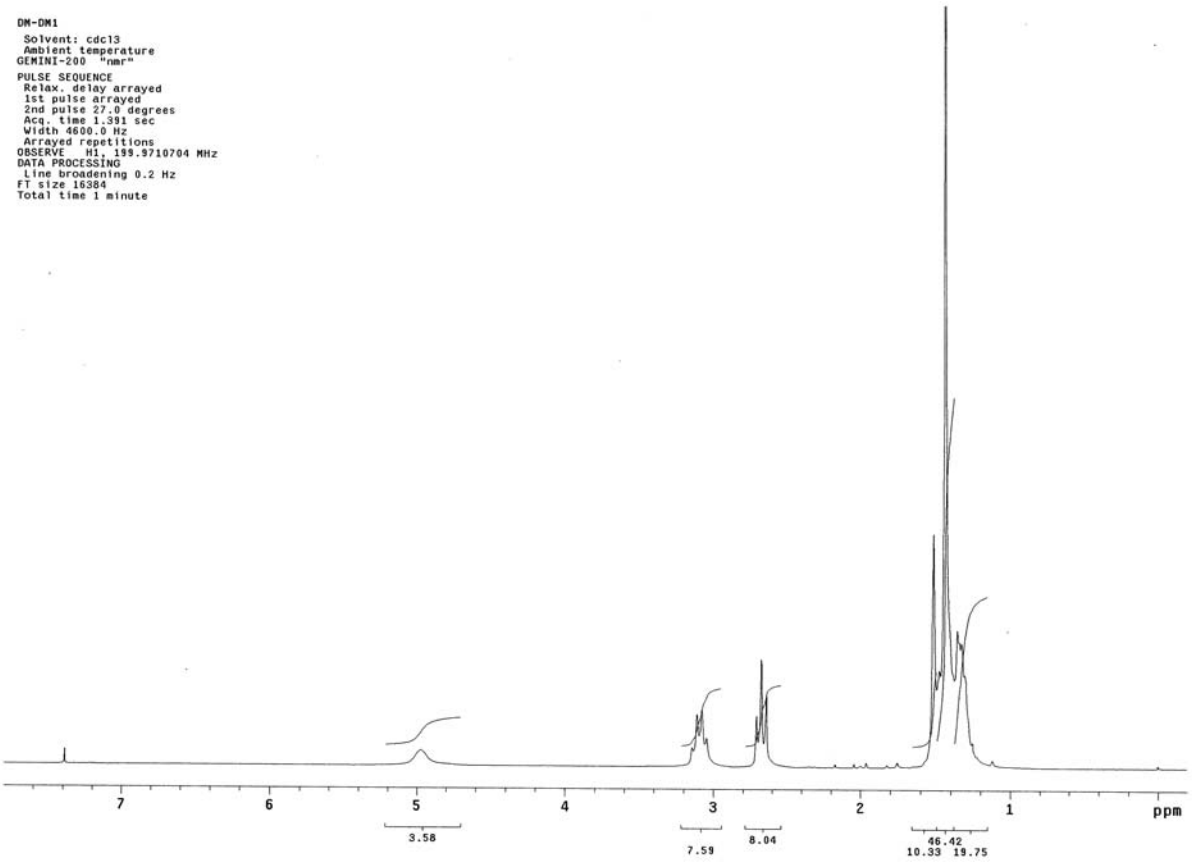


Figure S27. ^{1}H NMR spectrum of **9**

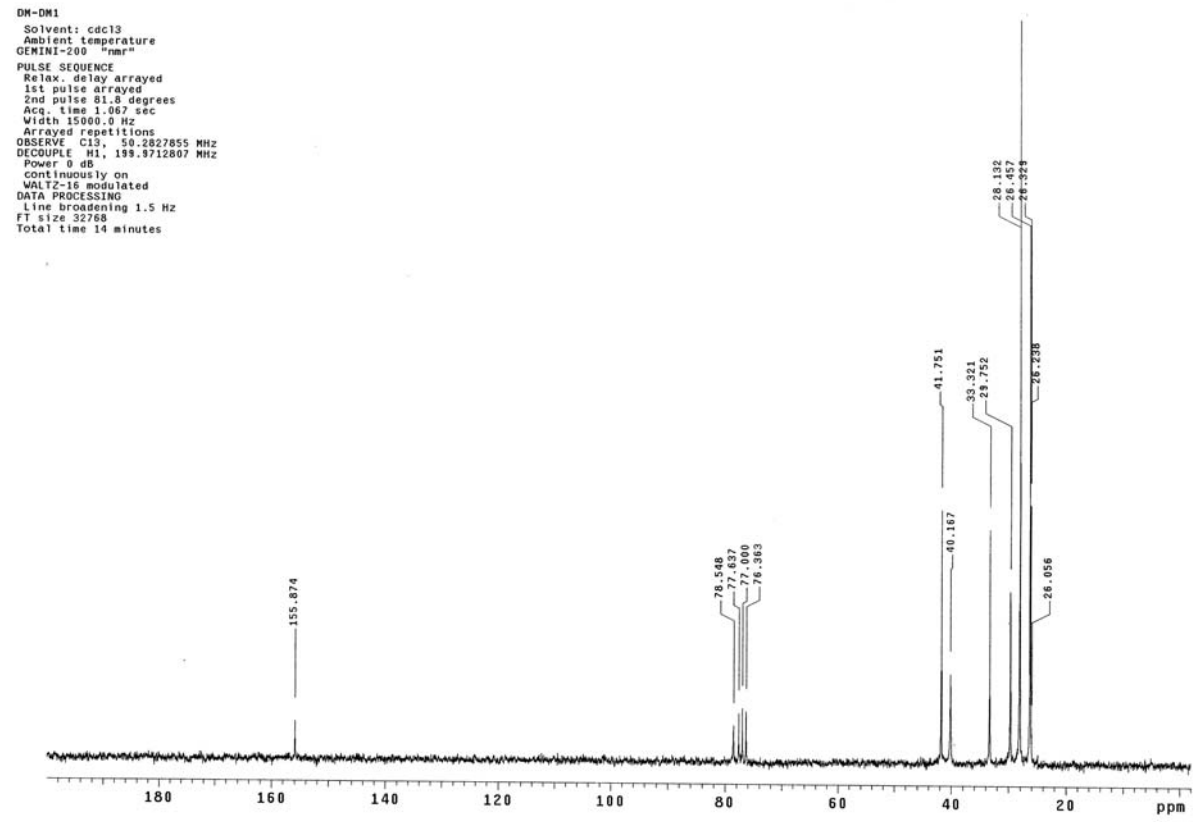
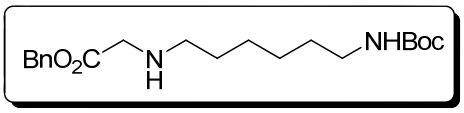


Figure S28. ^{13}C NMR spectrum of **9**

Compound **10**



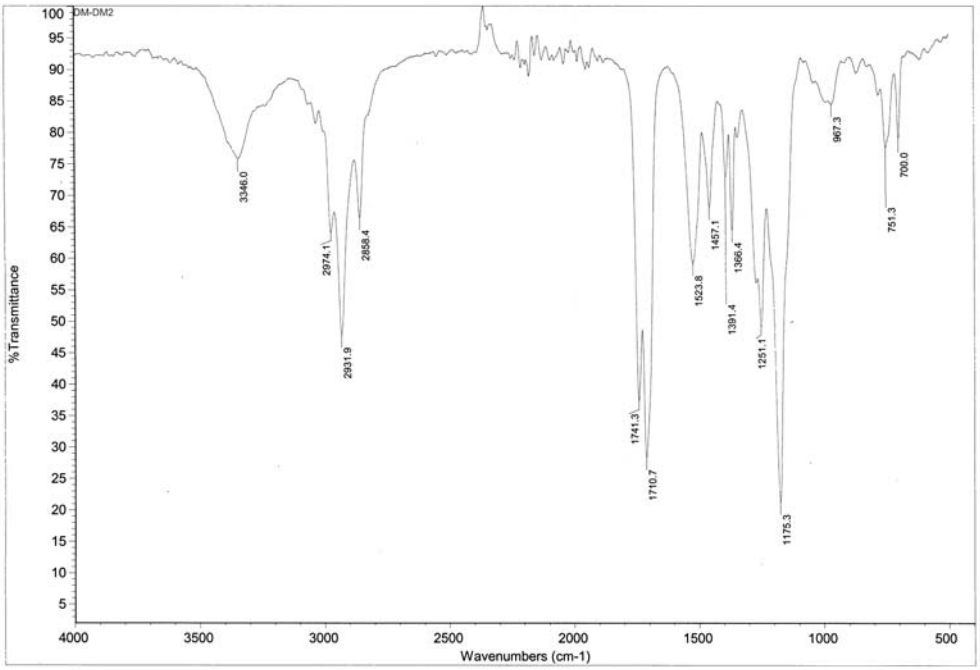


Figure S29. IR spectrum of **10**

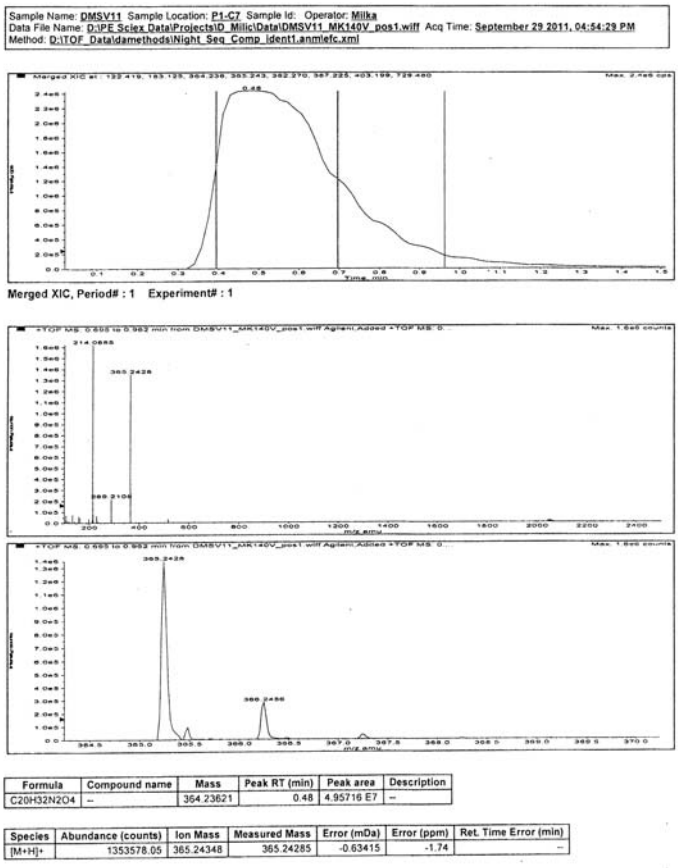


Figure S30. Mass spectrum of **10**

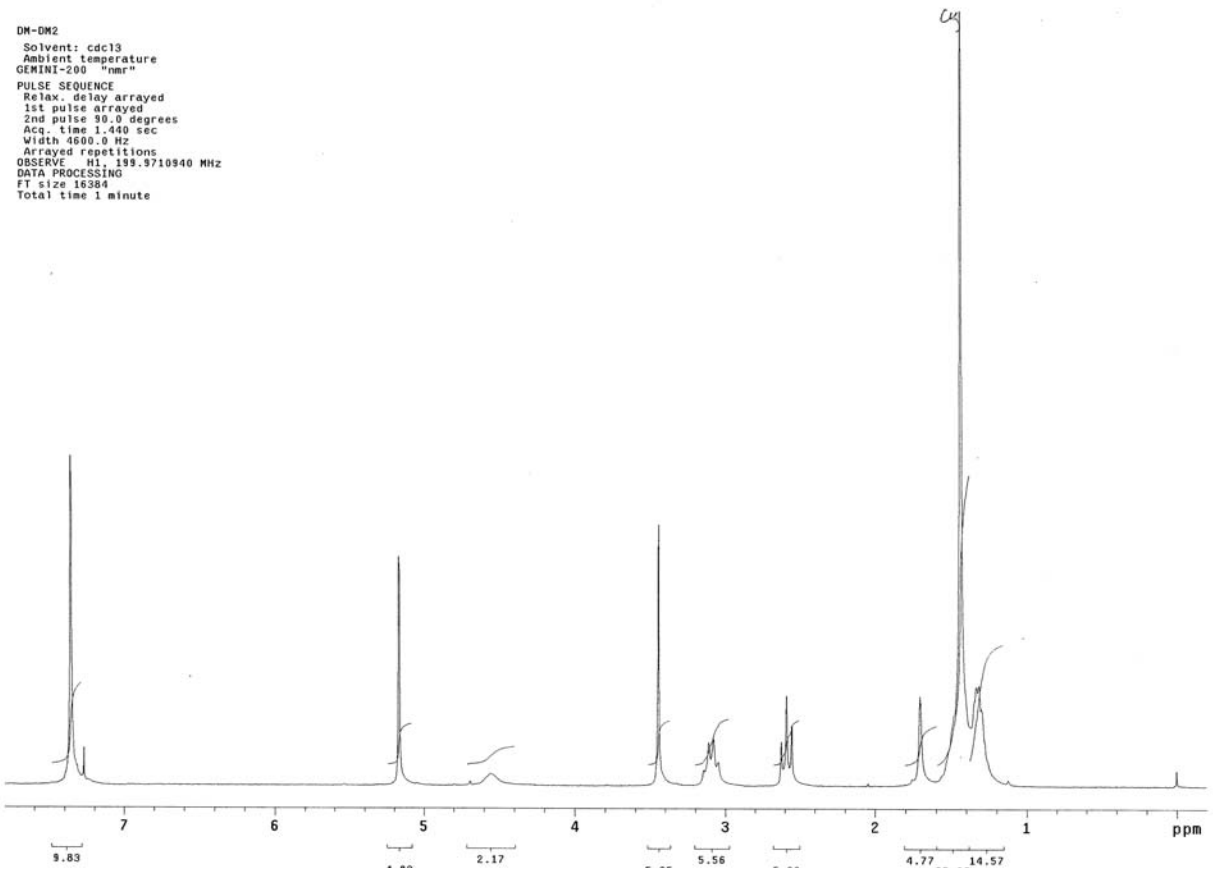


Figure S31. ^{1}H NMR spectrum of **10**

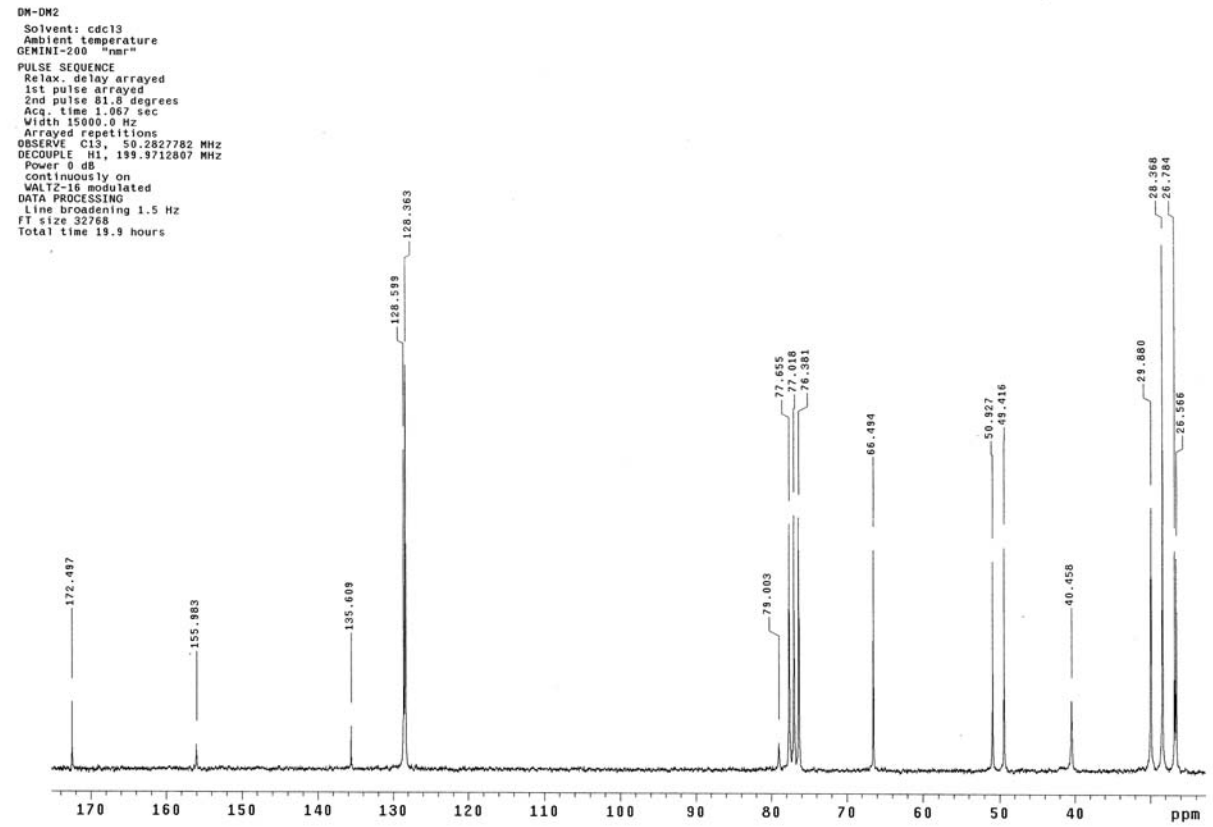
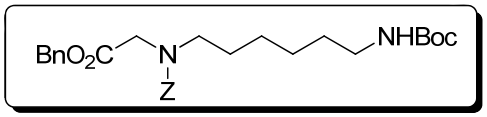


Figure S32. ^{13}C NMR spectrum of **10**

Compound **11**



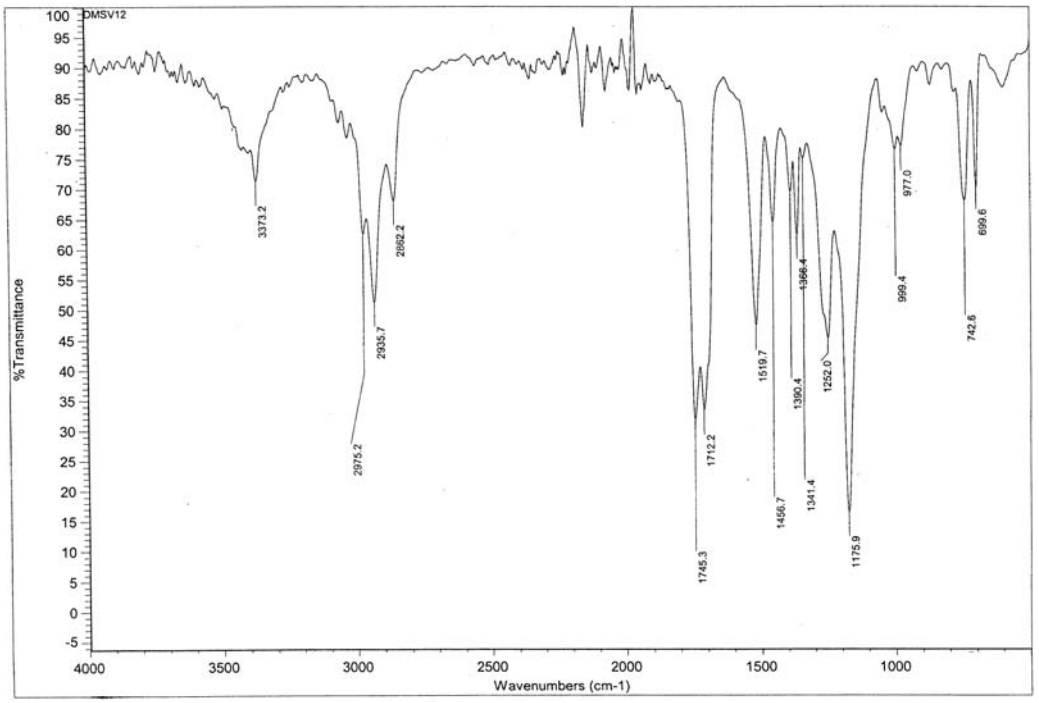


Figure S33. IR spectrum of **11**

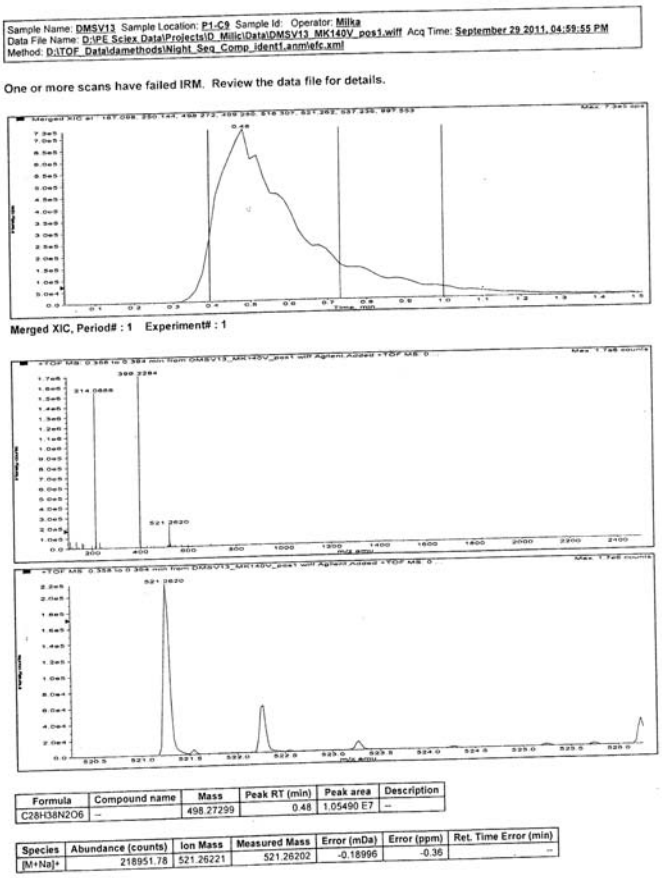


Figure S34. Mass spectrum of **11**

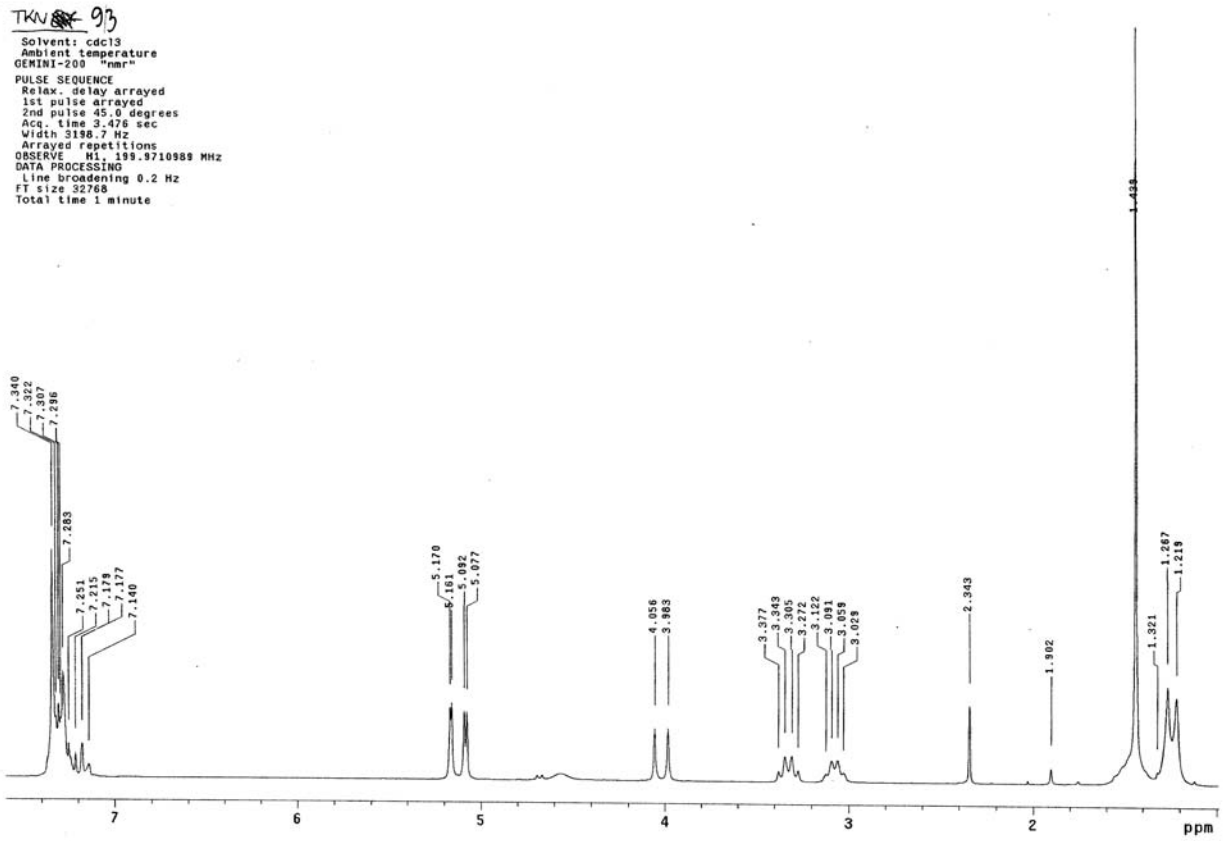


Figure S35. ^{1}H NMR spectrum of **11**

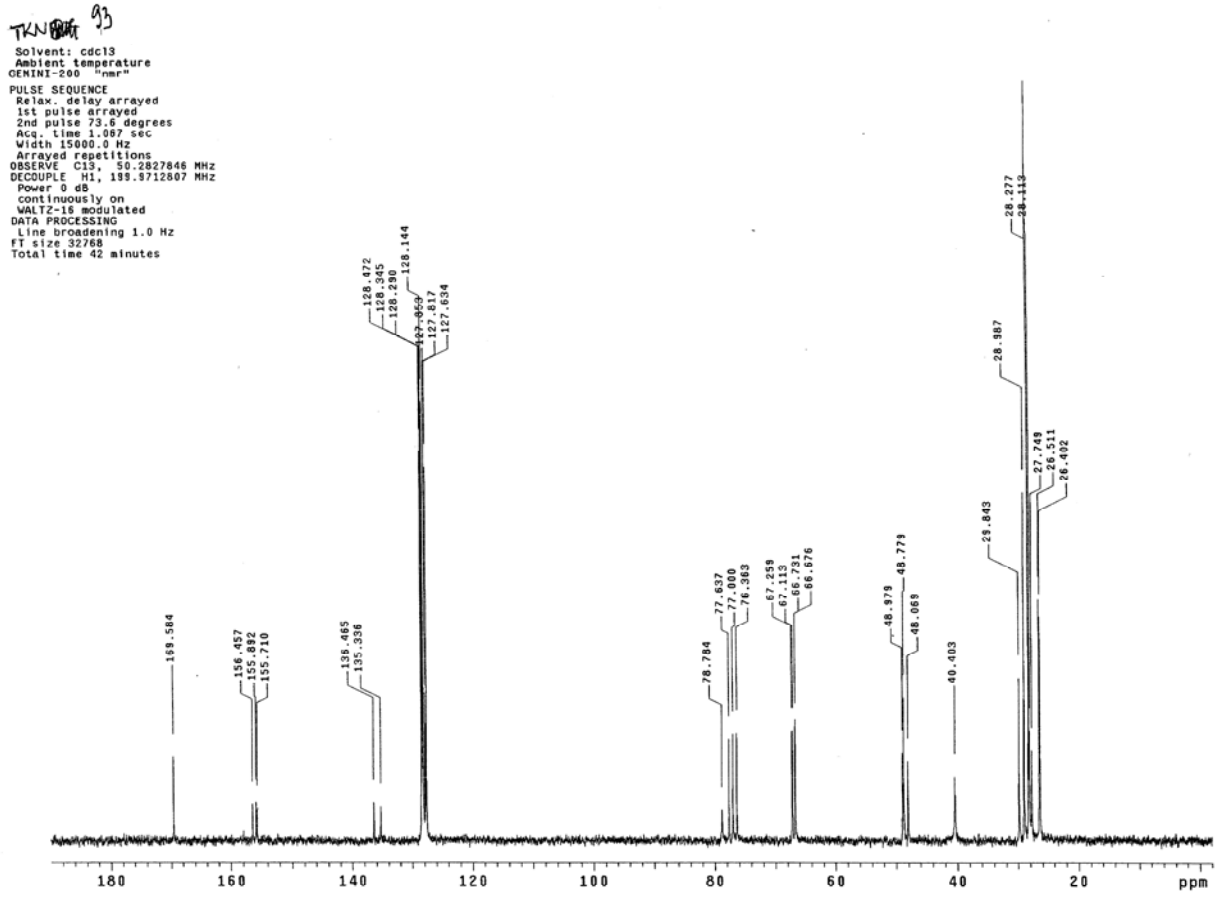
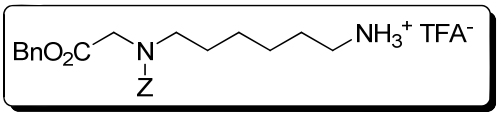


Figure S36. ^{13}C NMR spectrum of **11**

Compound **12**



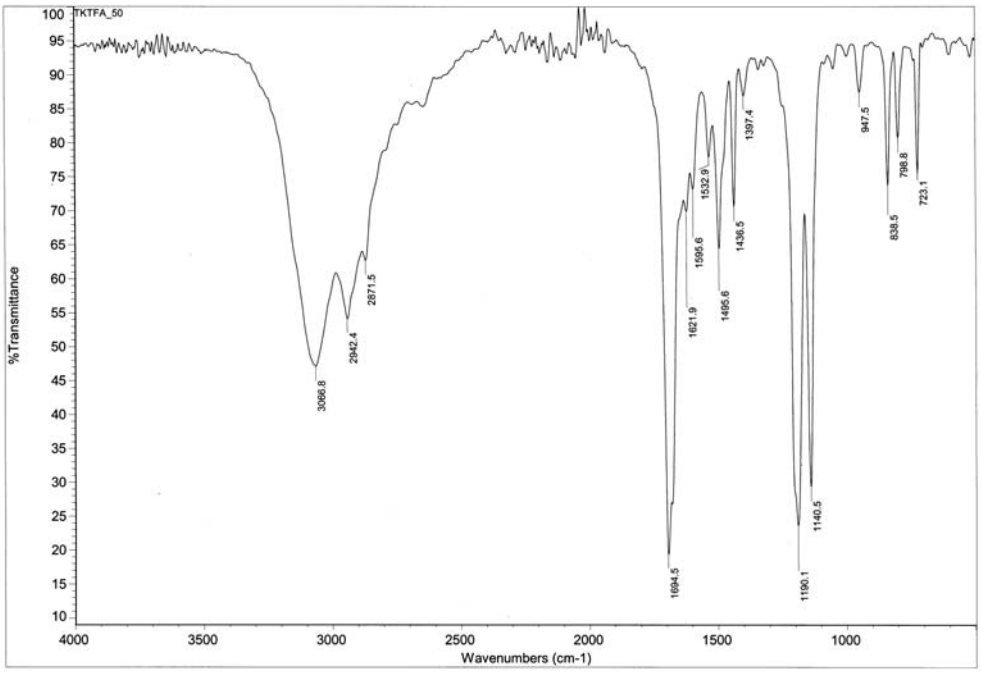
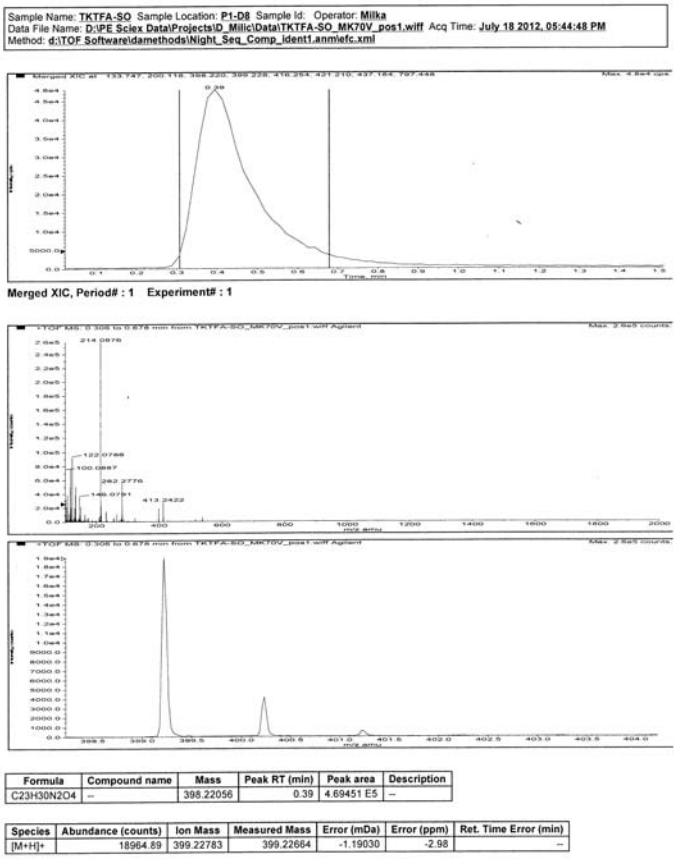


Figure S37. IR spectrum of **12**



Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C23H30N2O4	--	398.22056	0.39	4.69451 E5	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+H]+	18964.89	399.22783	399.22664	-1.19030	-2.98	--

Figure S38. Mass spectrum of **12**

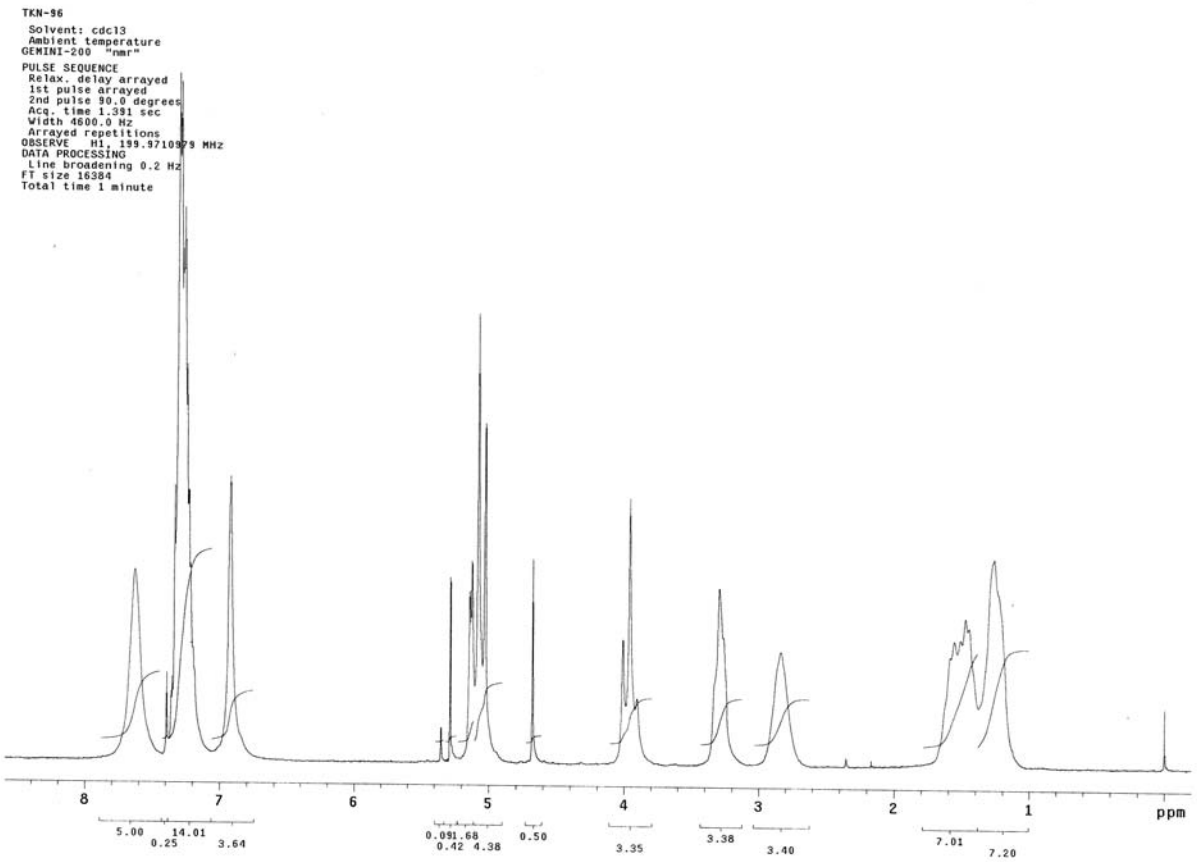


Figure S39. ^{1}H NMR spectrum of **12**

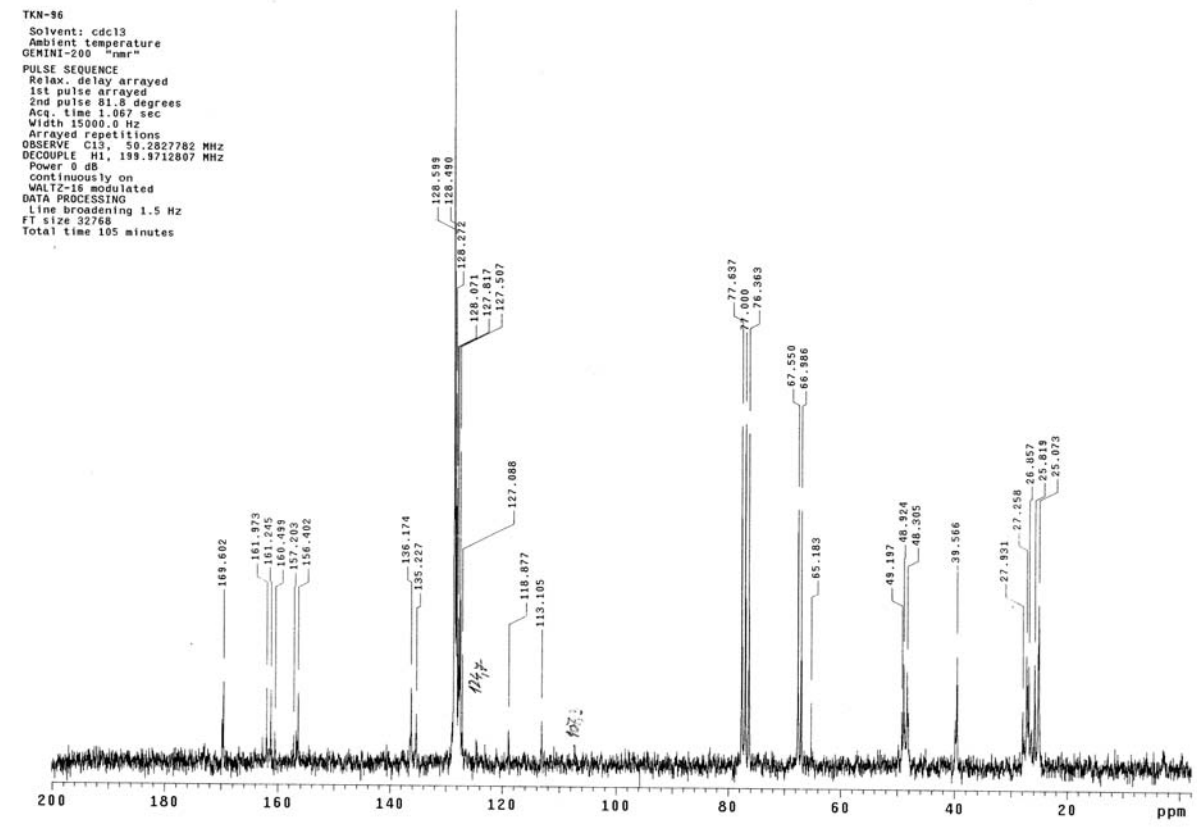
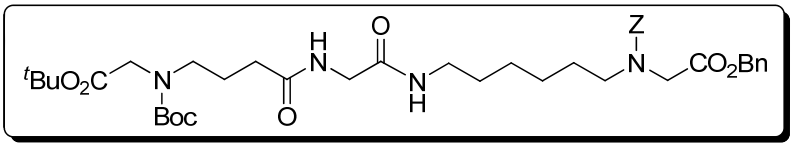


Figure S40. ^{13}C NMR spectrum of **12**

Compound **13**



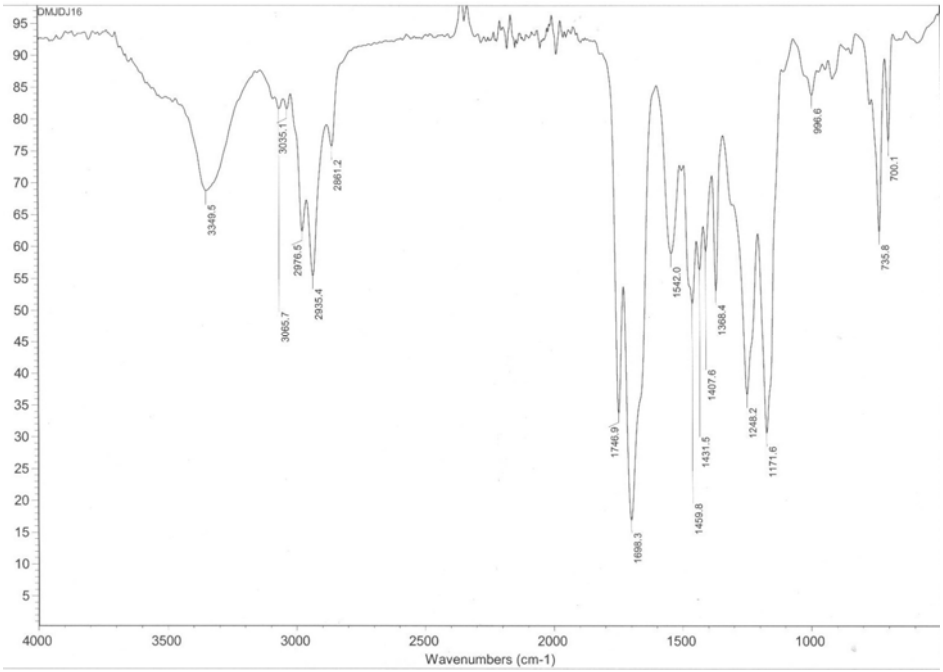
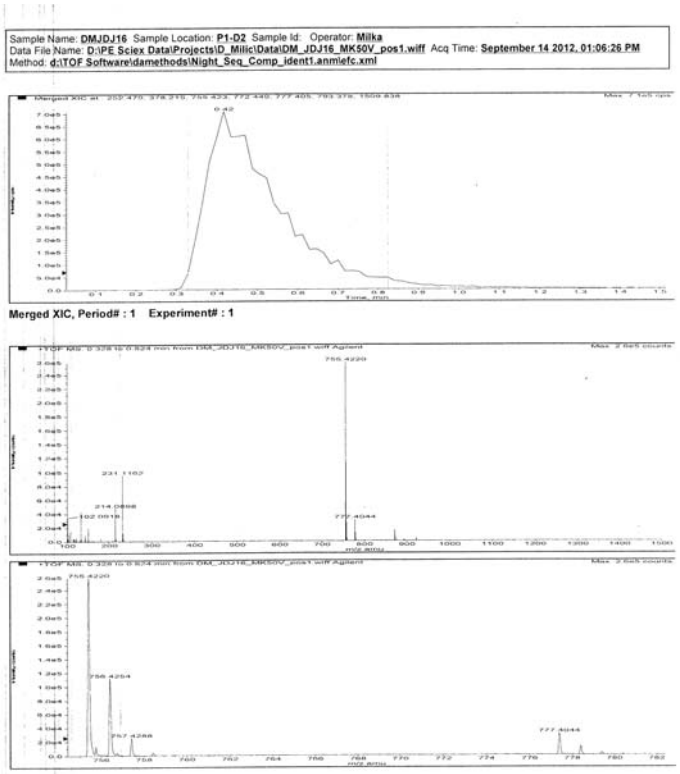


Figure S41. IR spectrum of **13**



Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C40H58N4O10	--	754.41529	0.42	8.62217 E6	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+H]+	2643.48 E1	755.42257	755.42195	-0.61824	-0.82	--
[M+Na]+	31774.43	777.40452	777.40439	-0.12395	-0.16	--

Figure S42. Mass spectrum of **13**

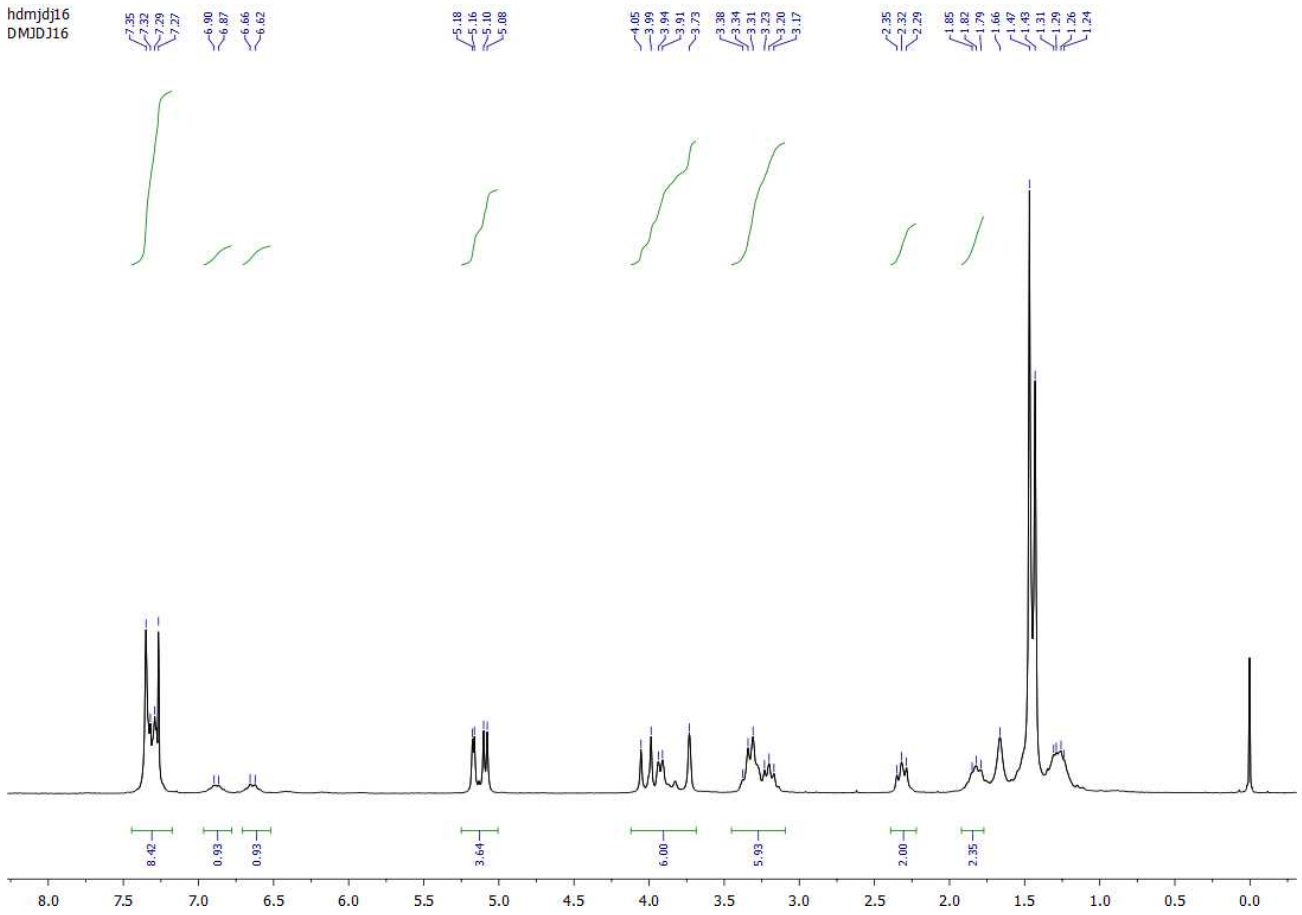


Figure S43. ^{1}H NMR spectrum of **13**

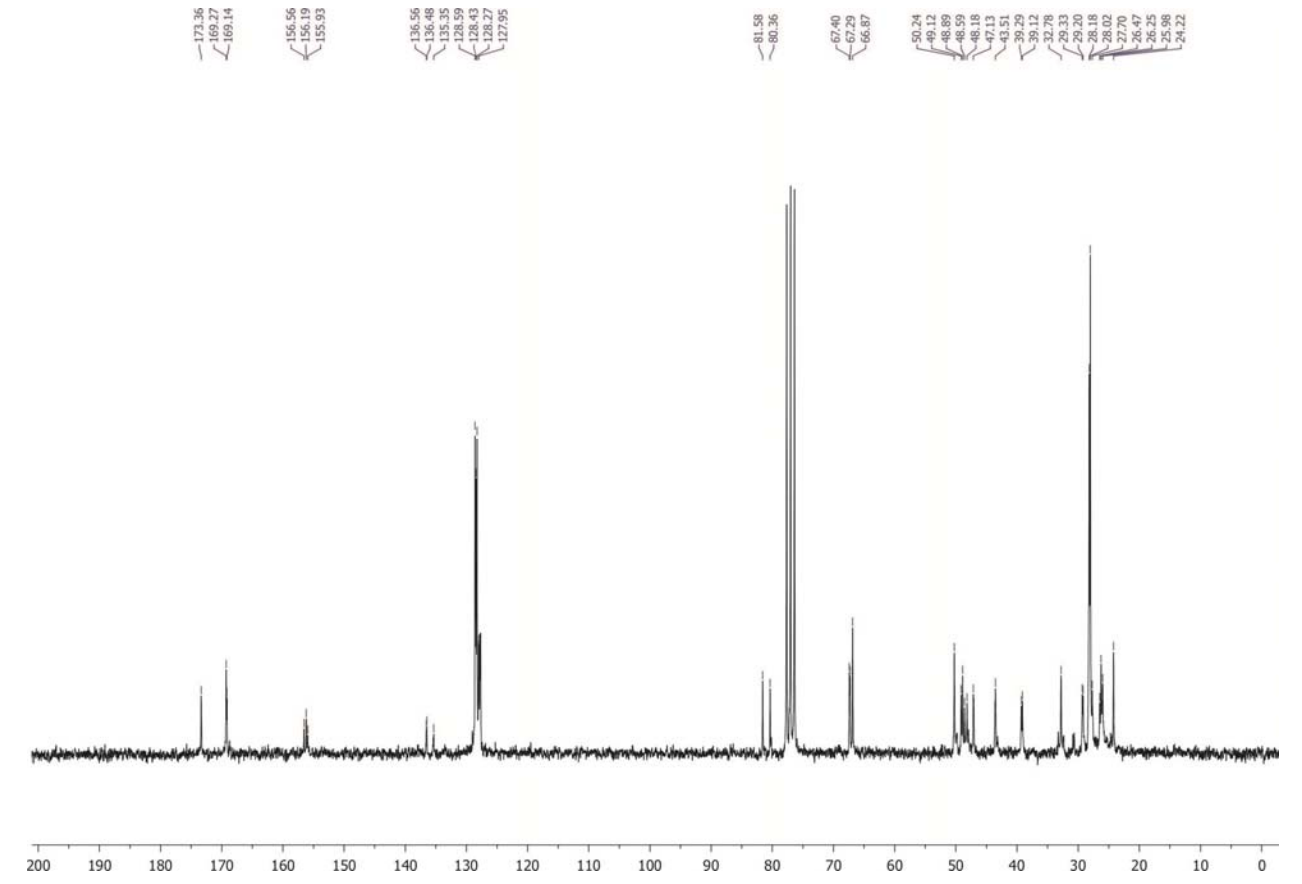
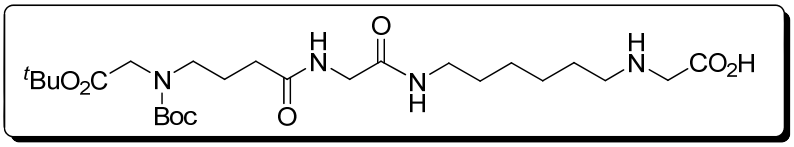


Figure S44. ^{13}C NMR spectrum of **13**

Compound **14**



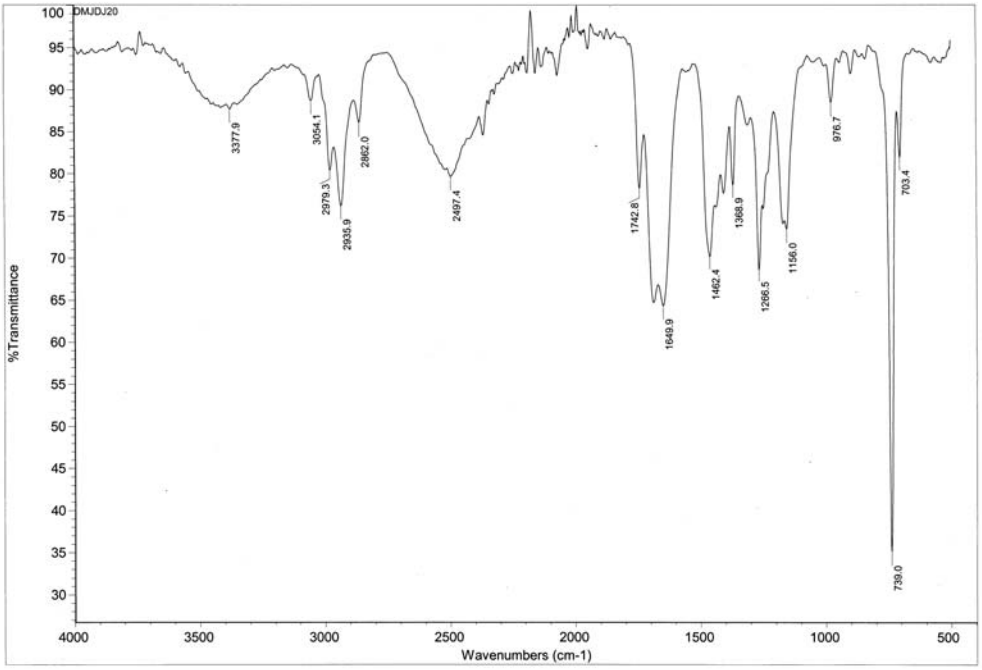
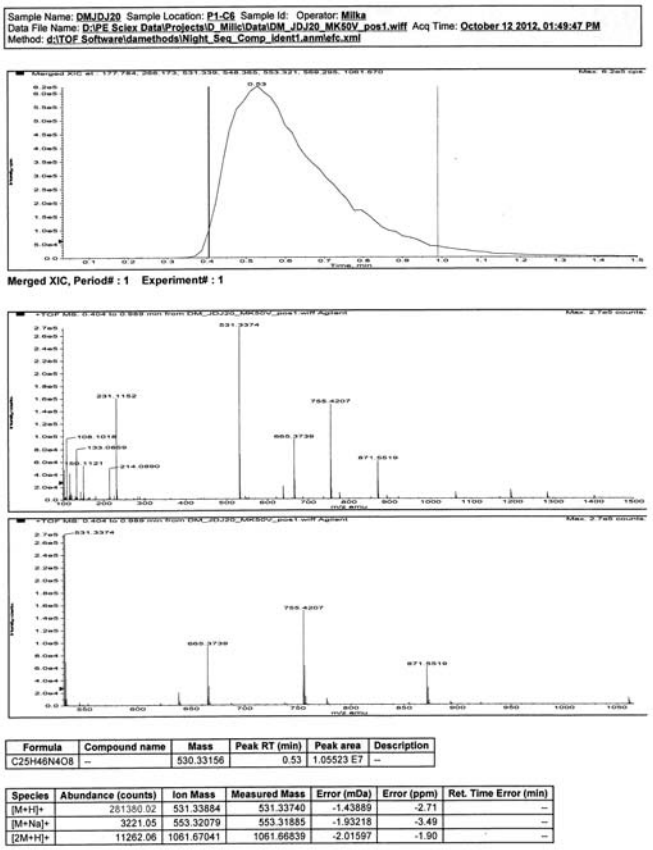


Figure S45. IR spectrum of **14**



Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C25H46N4O8	--	530.33156	0.53	1.05523 E7	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+H]+	281360.02	531.33884	531.33740	-1.43889	-2.71	--
[M+Na]+	3221.05	553.32079	553.31885	-1.93218	-3.49	--
[2M+H]+	11262.06	1061.67041	1061.66839	-2.01597	-1.90	--

Figure S46. Mass spectrum of **14**

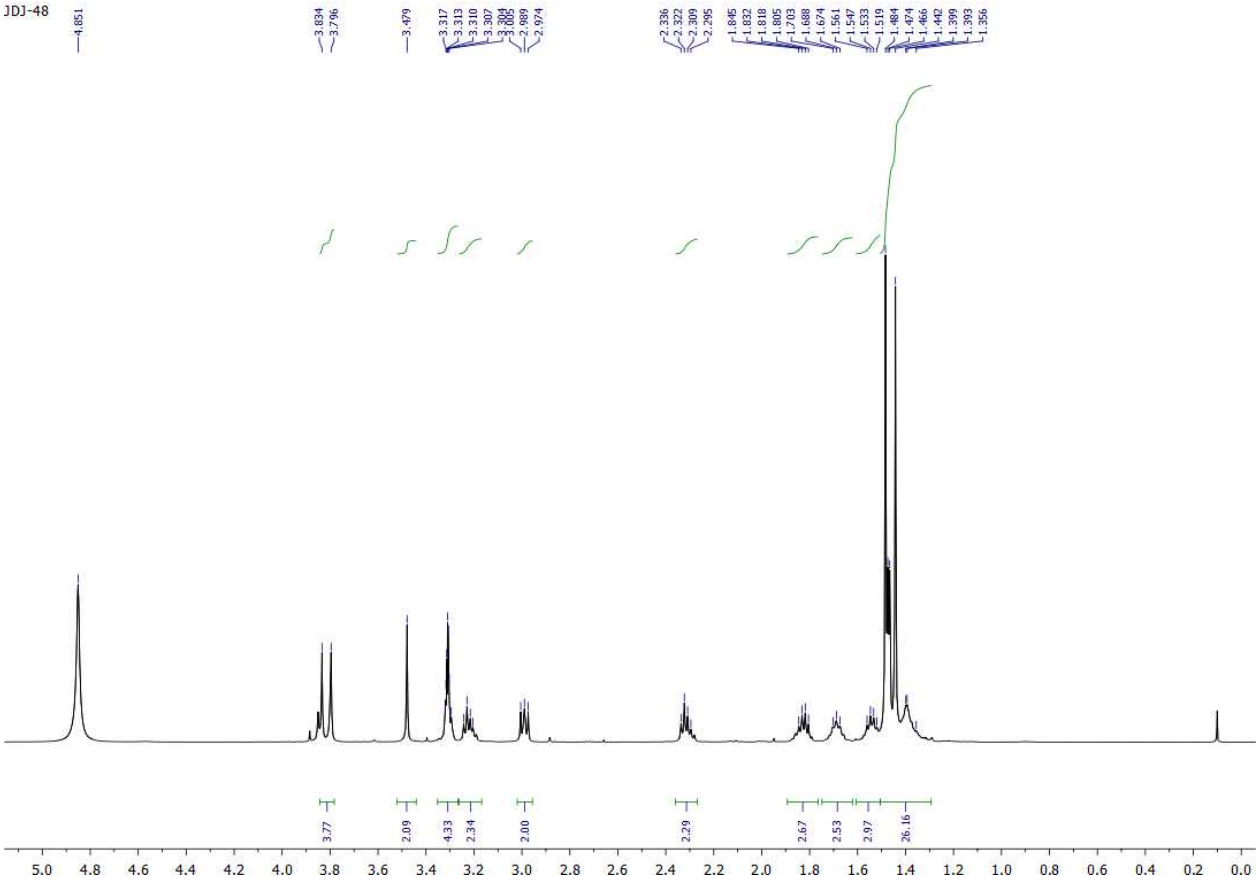


Figure S47. ^{1}H NMR spectrum of **14**

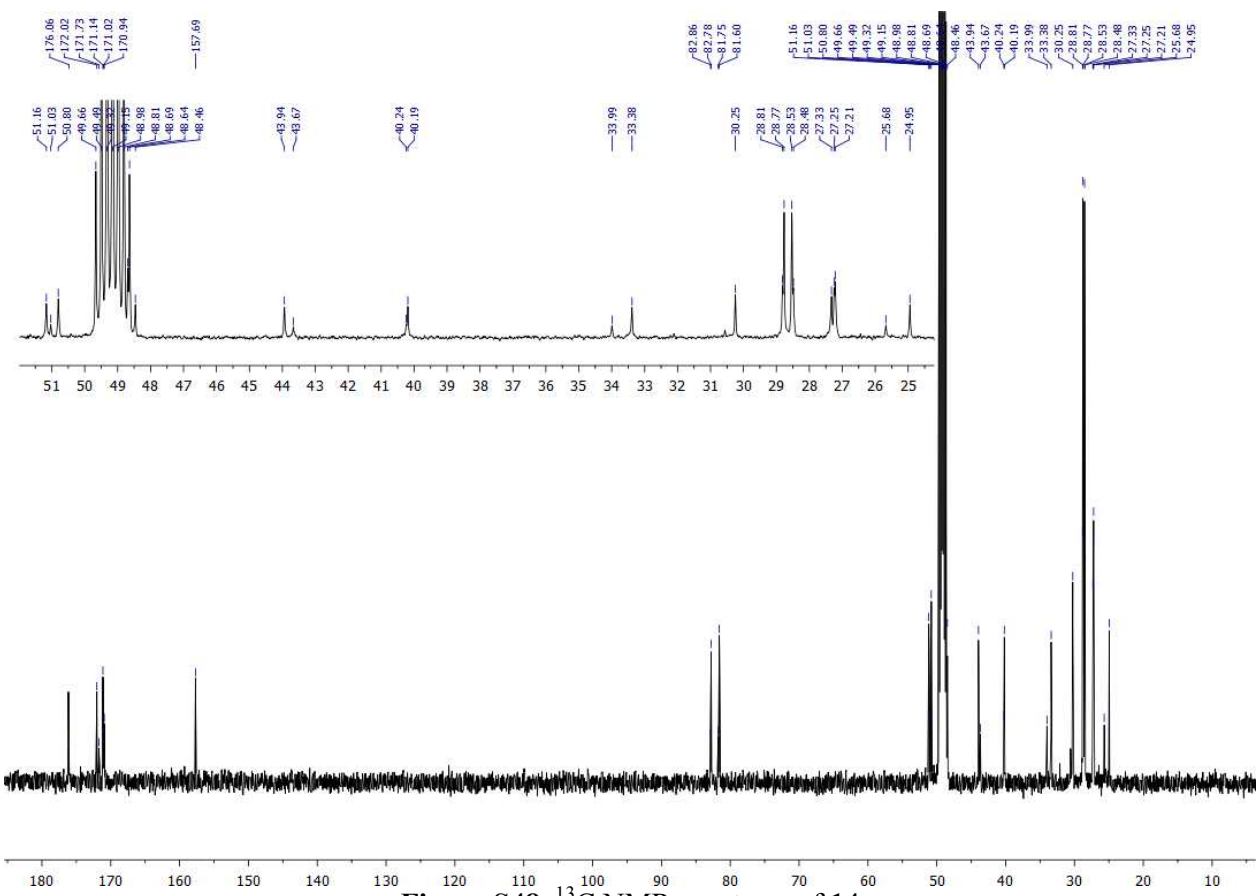
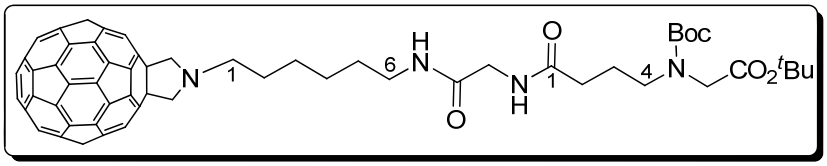


Figure S48. ^{13}C NMR spectrum of **14**

Compound **15**



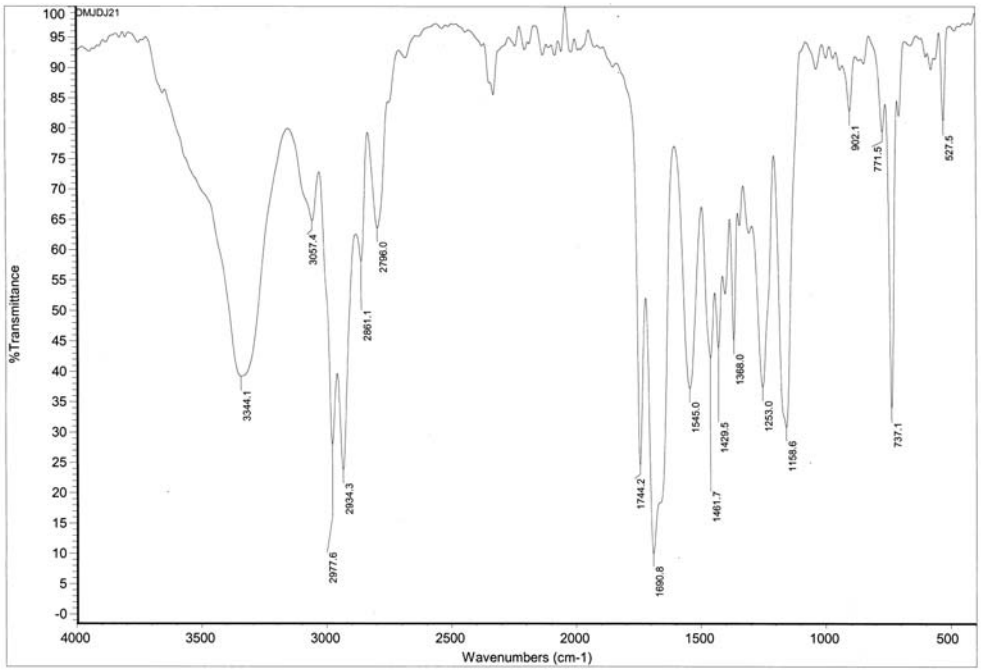


Figure S49. IR spectrum of **15**

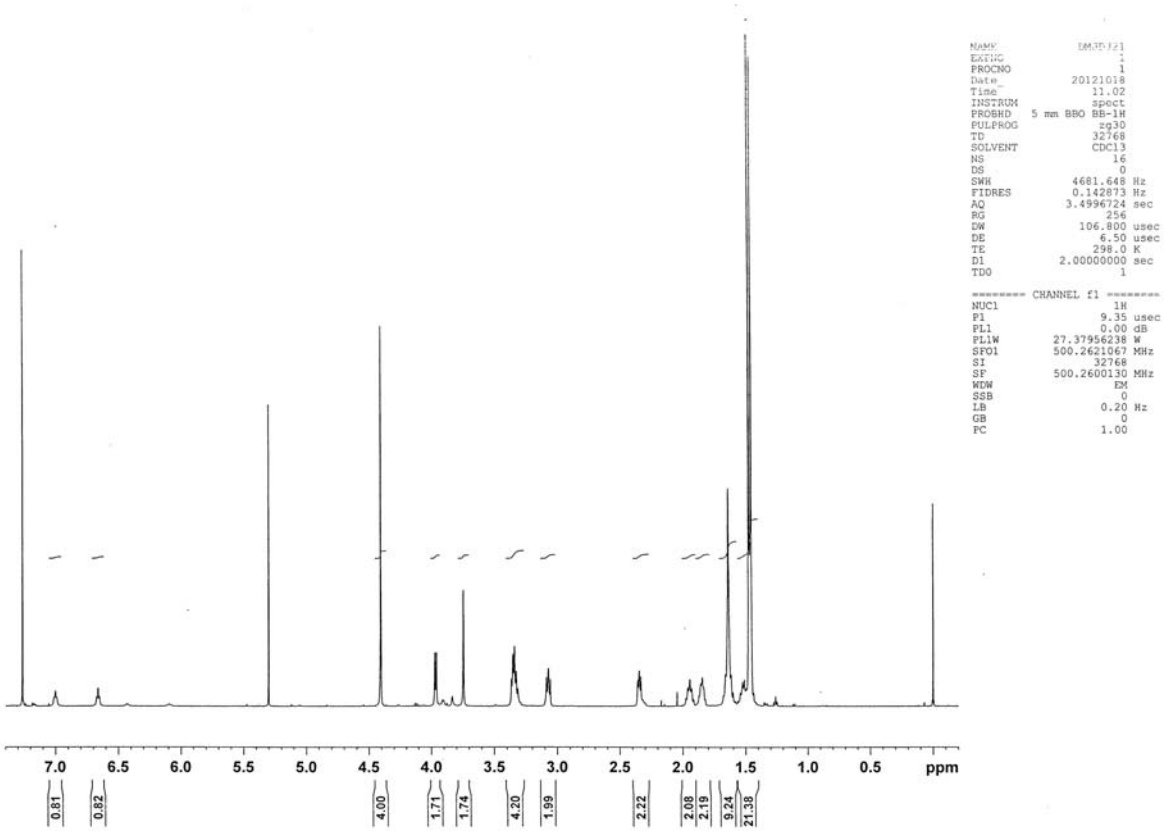


Figure S50. ^{1}H NMR spectrum of **15**

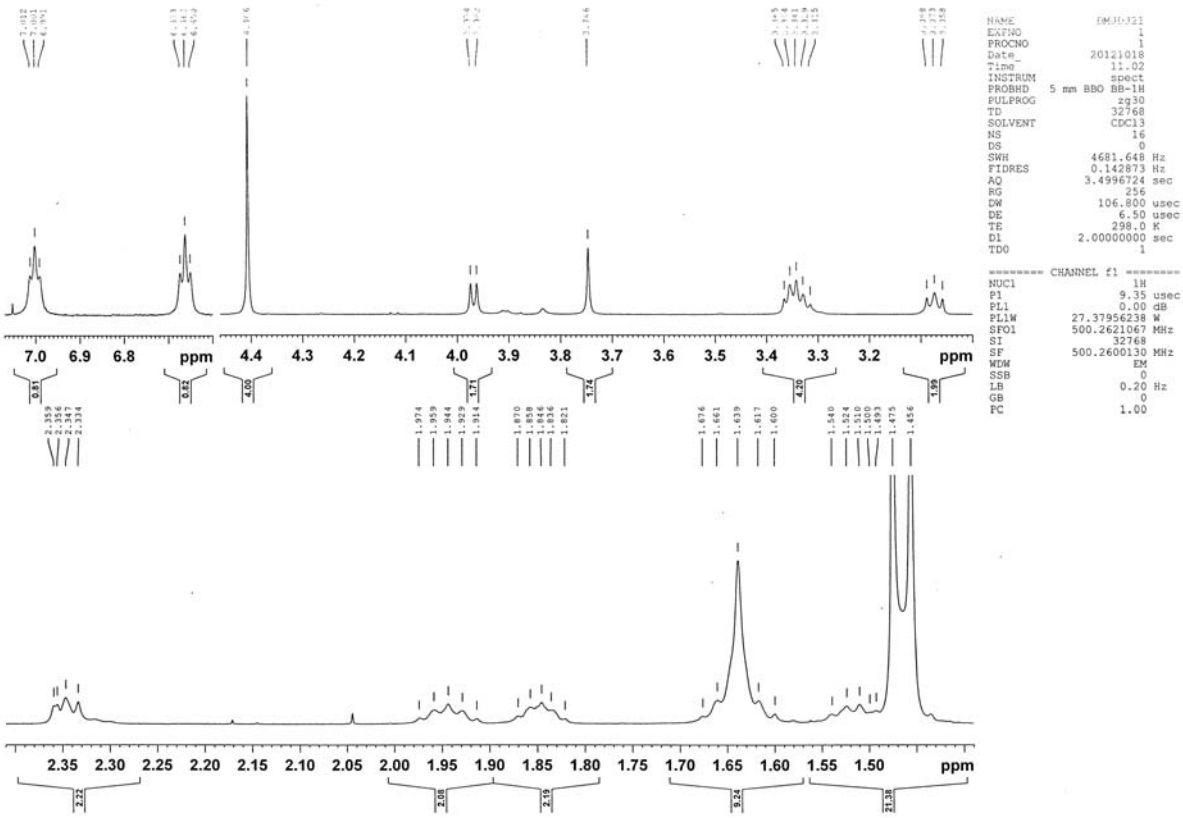


Figure S51. Expanded parts of ^{1}H NMR spectrum of **15**

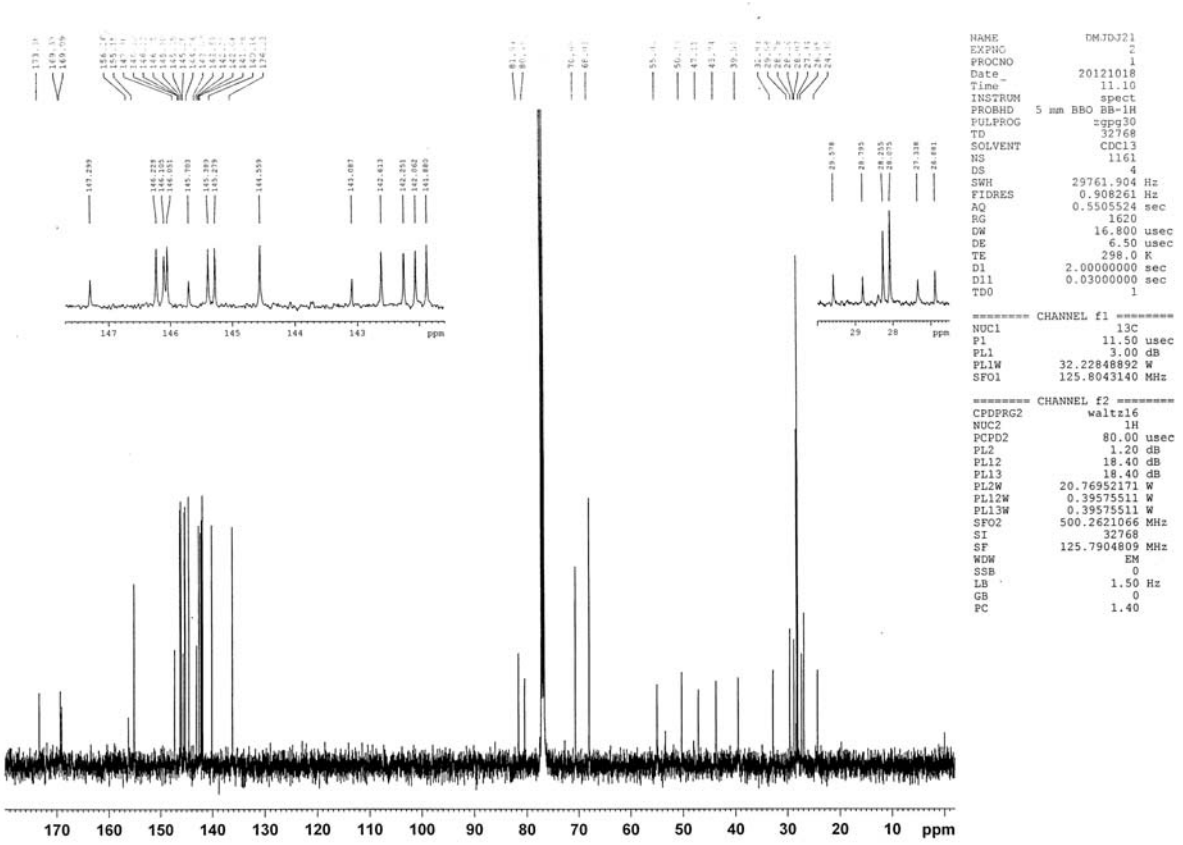


Figure S52. ^{13}C NMR spectrum of **15**

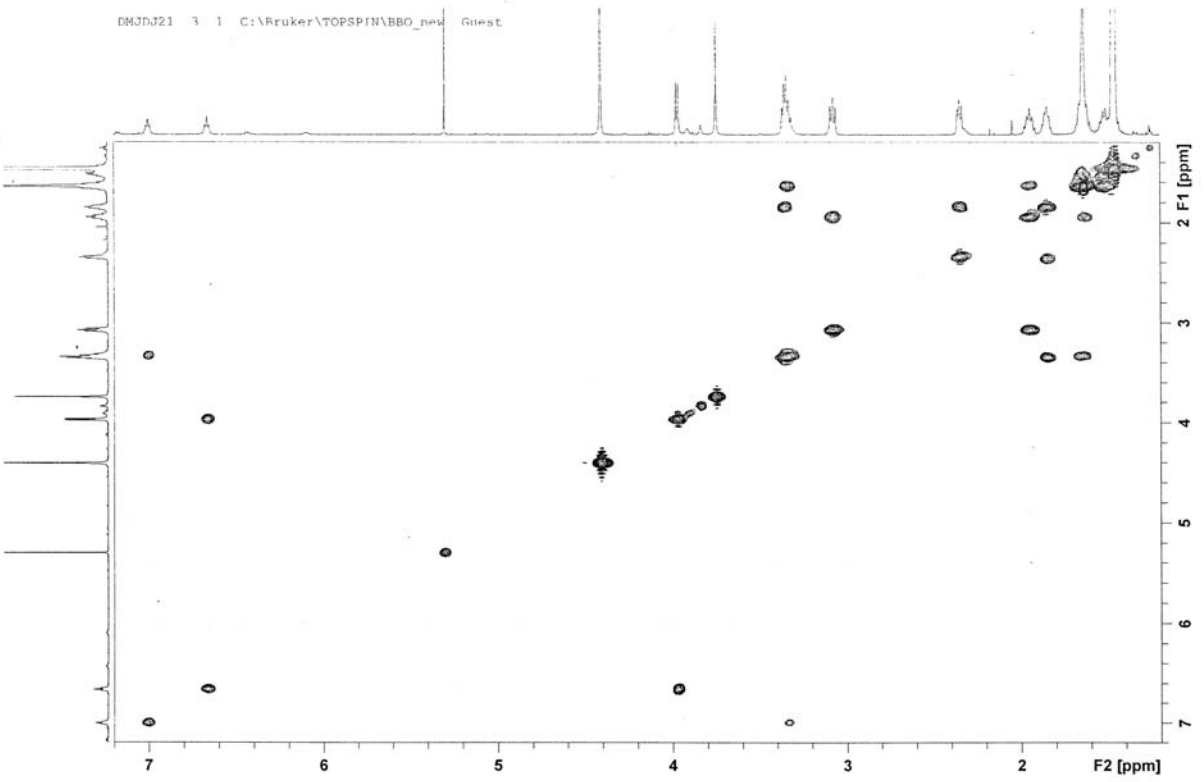


Figure S53. COSY spectrum of **15**

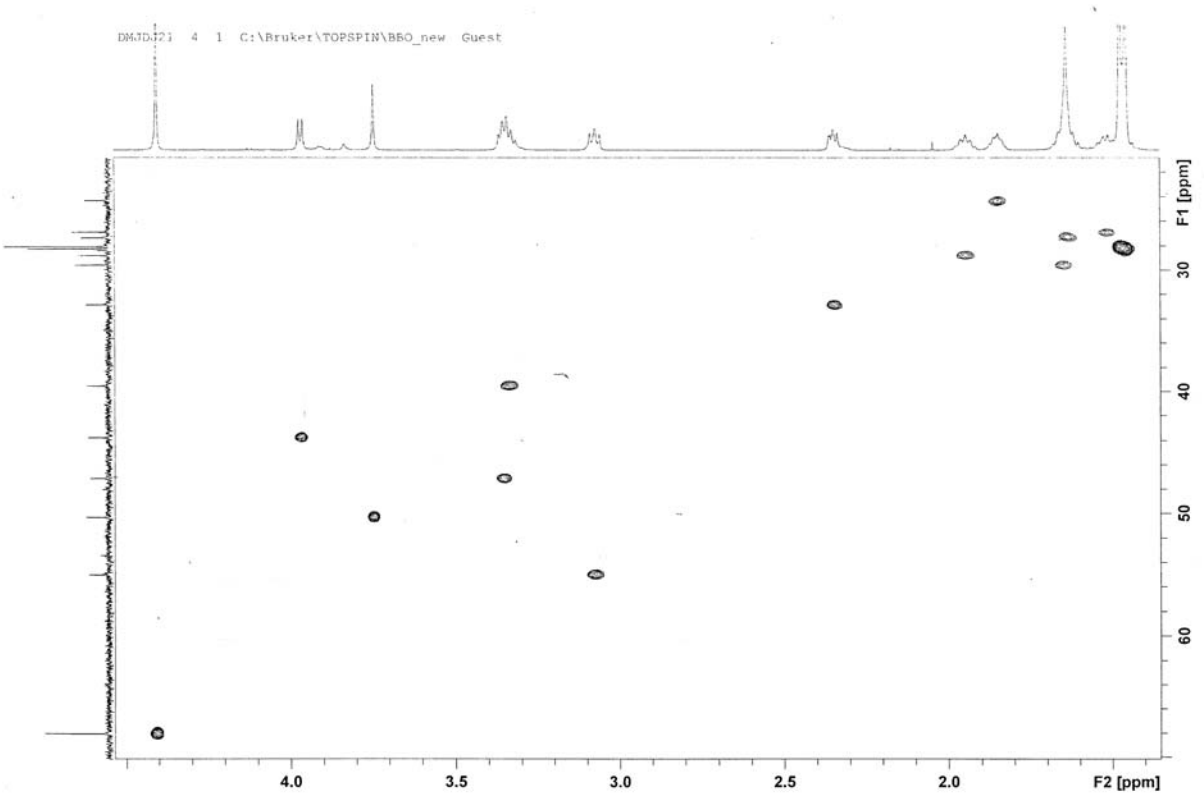


Figure S54. HSQC spectrum of **15**

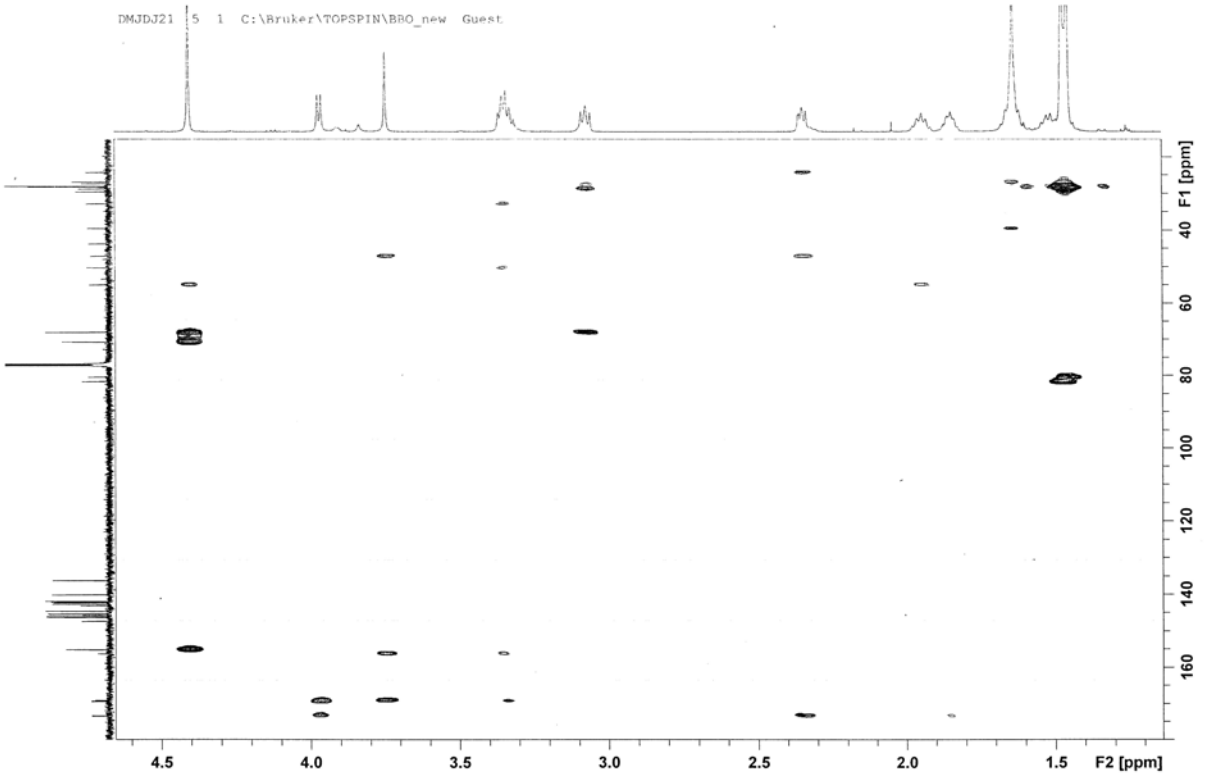
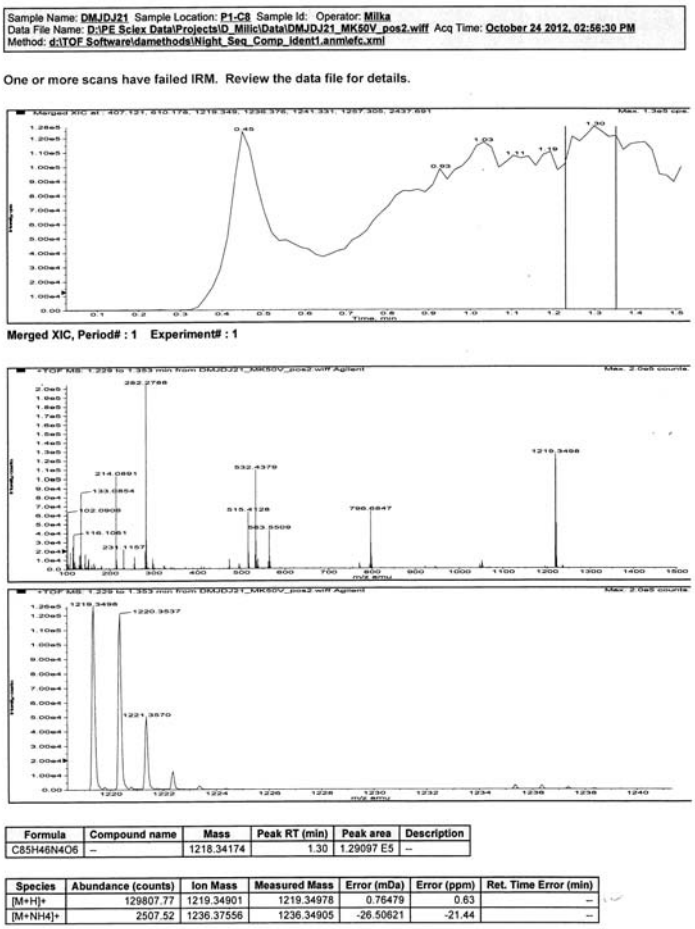


Figure S55. HMBC spectrum of **15**

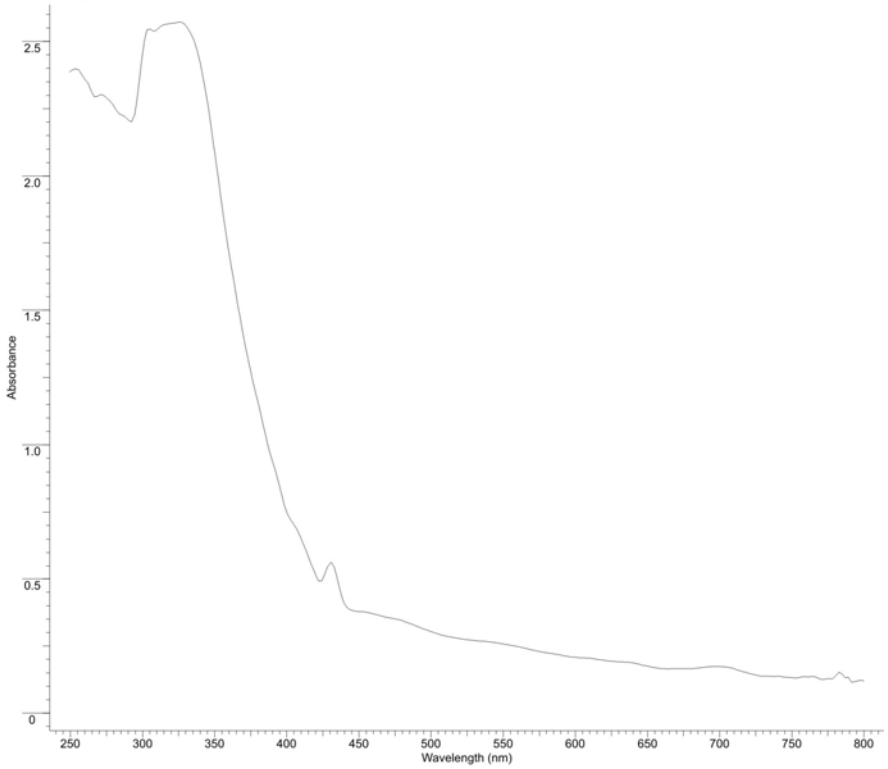


Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C85H46N4O6	--	1218.34174	1.30	1.29097 E5	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+H]+	129807.77	1219.34901	1219.34978	0.76479	0.63	--
[M+NH4]+	2507.52	1236.37556	1236.34905	-26.50621	-21.44	--

Figure S56. Mass spectrum of **15**

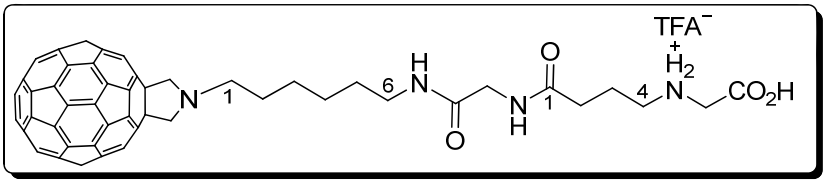
Comment	monoaduct CH2Cl2	***File Name***	C:\USERS\USER\DESKTOP\TANJA KOP UV\09 06 2016 JDJ UV\DMJDJ21.UVD		
Date Stamp	06/09/16 10:28:17	***Date***	09 Jun 2016 10:28:18	***Technique***	UV-Visible
Spectral Region	UV-Vis-NIR	***X Axis***	Wavelength (nanometers)		
Y Axis	Absorbance	***Spectrum Range***	249.2000 - 800.0000	***Points Count***	256
Data Spacing	2.1600				



No	nm	A	Intensity
1	253.52	2.398	VS
2	305.36	2.545	VS
3	326.96	2.572	VS
4	430.64	0.564	W
5	698.48	0.174	VW
6	782.72	0.152	VW

Figure S57. UV spectrum of **15**

Compound **16**



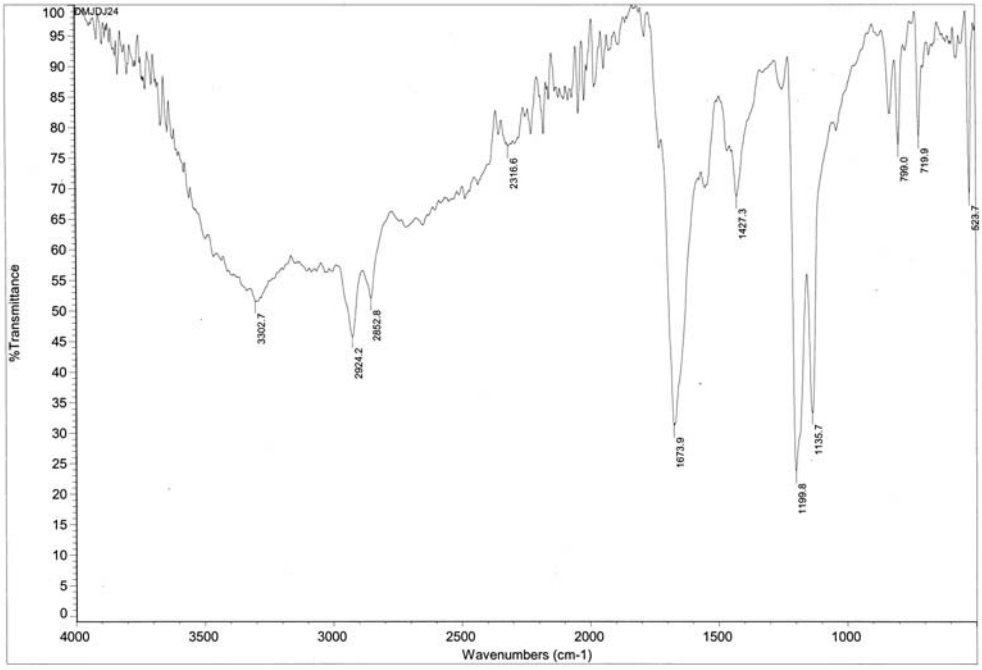
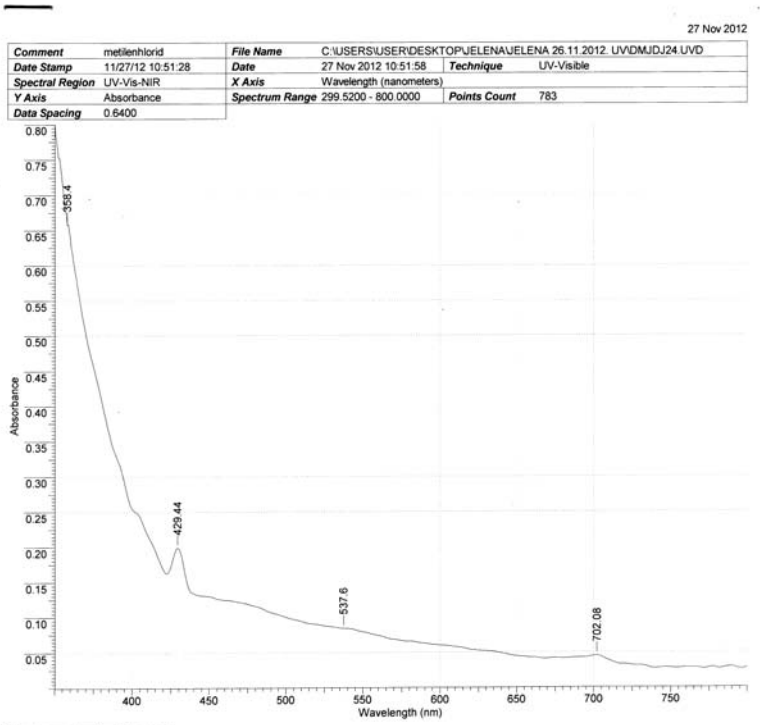


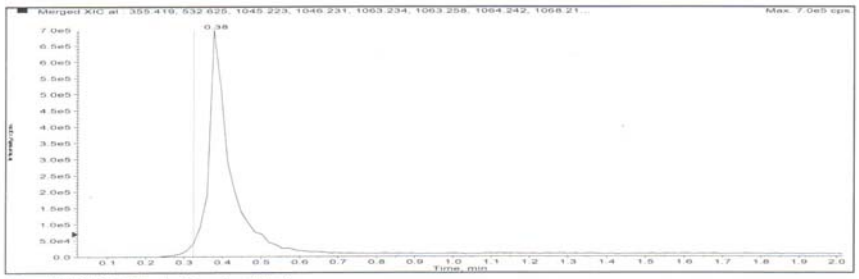
Figure S58. IR spectrum of **16**



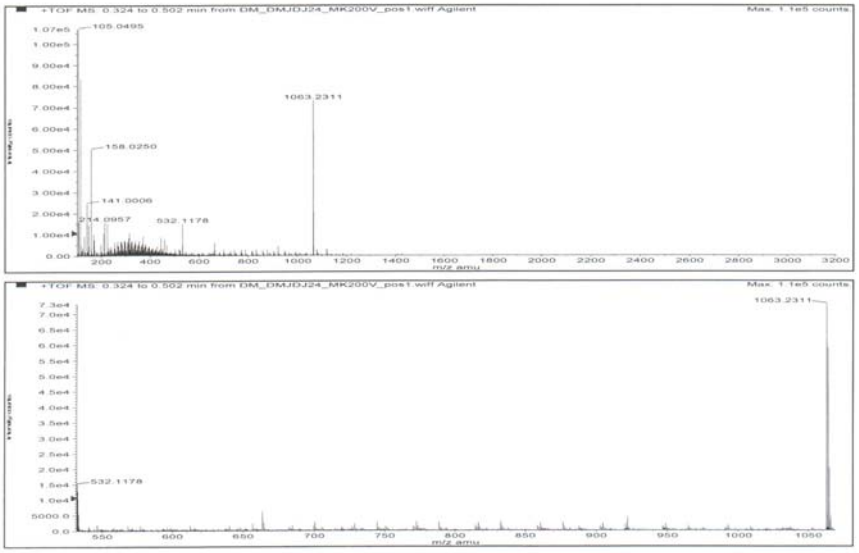
No	nm	A	Intensity
1	358.40	0.658	M
2	429.44	0.199	VW
3	537.60	0.084	VW
4	702.08	0.045	VW

Figure S59. UV spectrum of **16**

Sample Name: **DMJDJ24** Sample Location: **P1-C1** Sample Id: Operator: **Milka**
Data File Name: **D:\PE Sciex Data\Projects\D_Milic\Data\DM_DMJDJ24_MK200V_pos1.wiff** Acq Time: **June 10 2016, 11:48:14 AM**
Method: **d:\TOF_Data\damethods\Night_Seq_Comp_ident1.anm\efc.xml**



Merged XIC, Period# : 1 Experiment# : 1



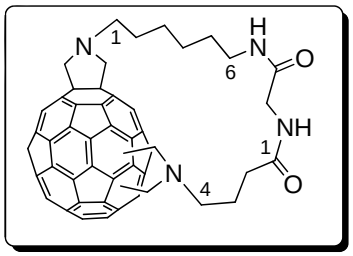
Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C76H31N4O4	--	1063.23453	0.38	2.73438 E6	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+2H]2+	12898.30	532.62454	532.62195	-2.58682	-4.86	--
M+	73132.64	1063.23398	1063.23246	-1.52685	-1.44	--
[M+H]+	59268.06	1064.24181	1064.23578	-6.02974	-5.67	--

OK! MJ

Figure S60. Mass spectrum of **16**

Spectra of bisadducts **17a-d**



Bisadduct **17a** (*e*-edge)

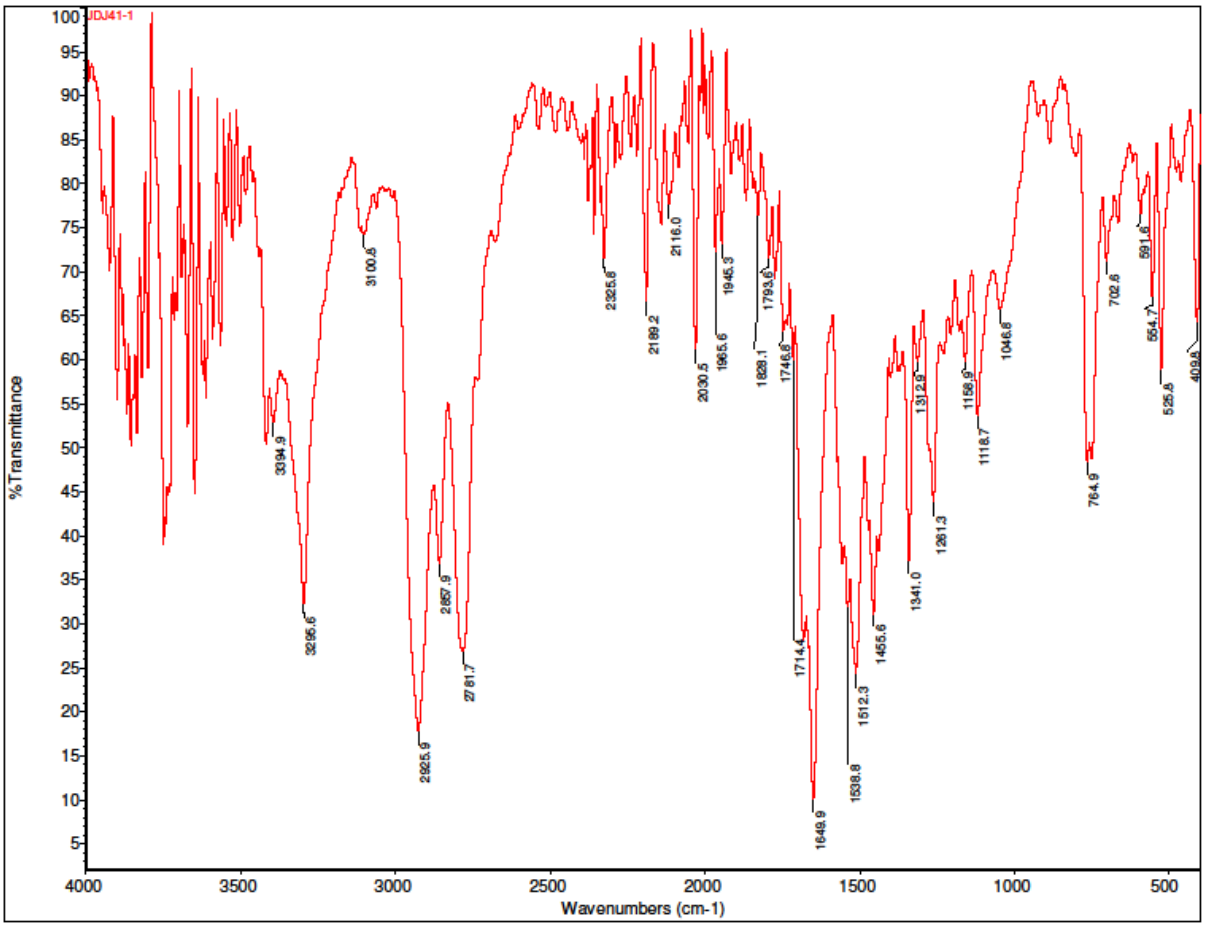


Figure S61. IR spectrum of **17a**

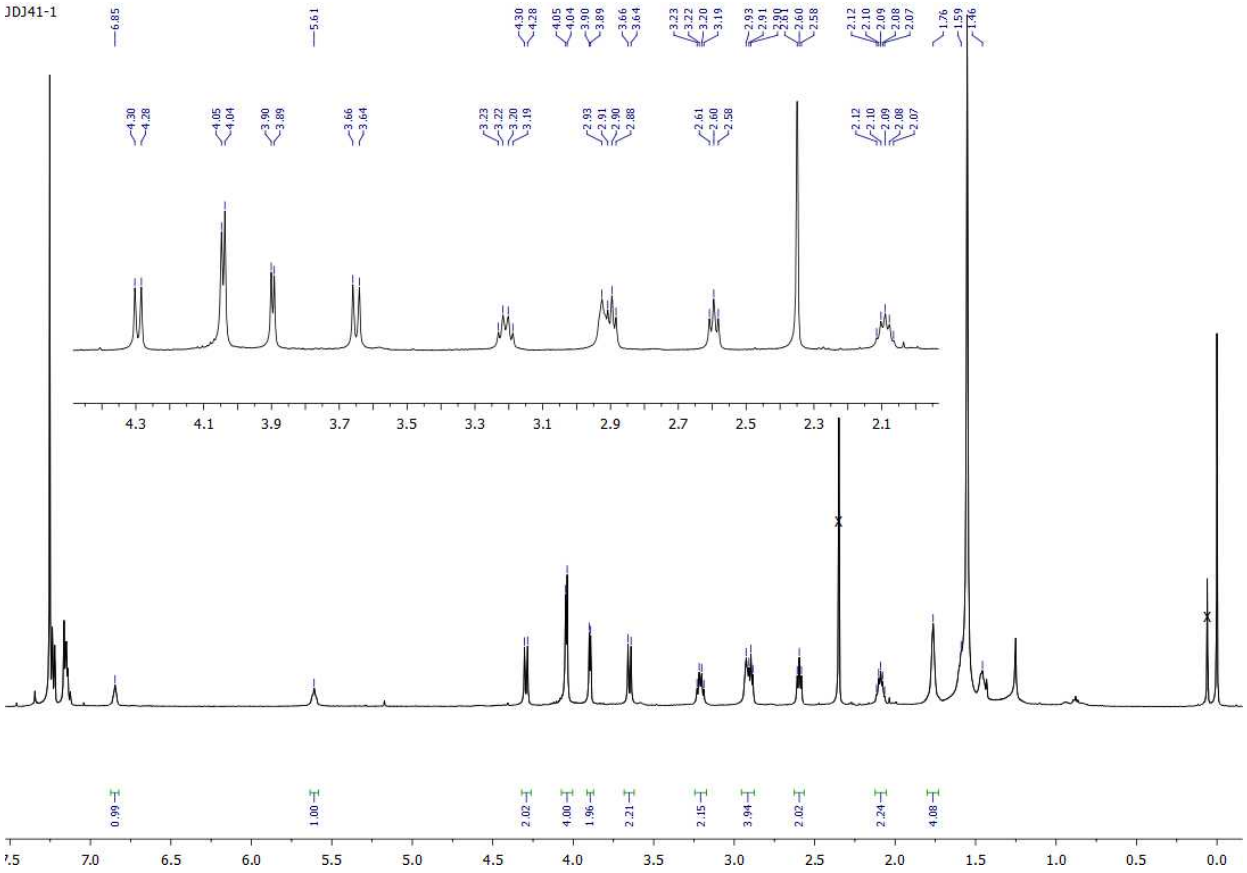


Figure S62. ^{1}H NMR spectrum of **17a**

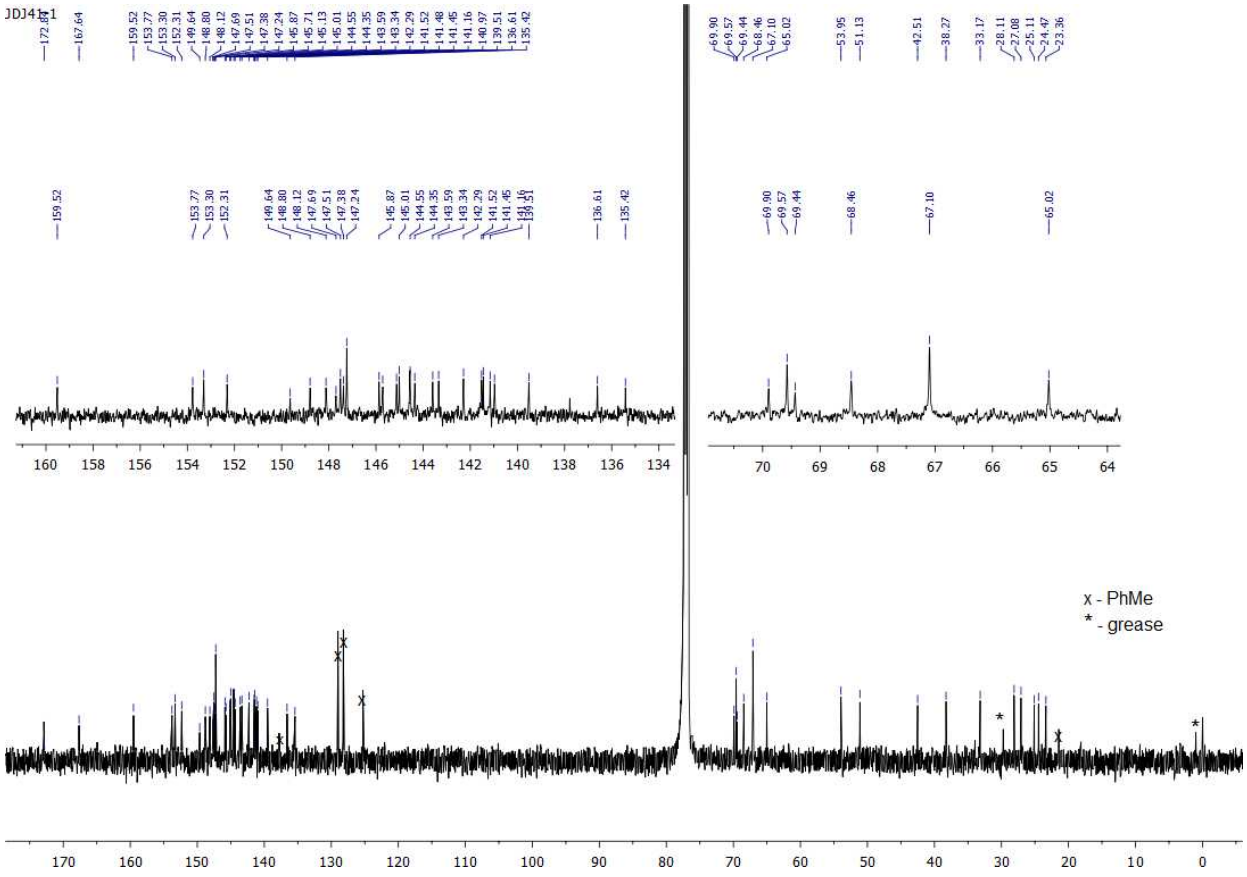


Figure S63. ^{13}C NMR spectrum of **17a**

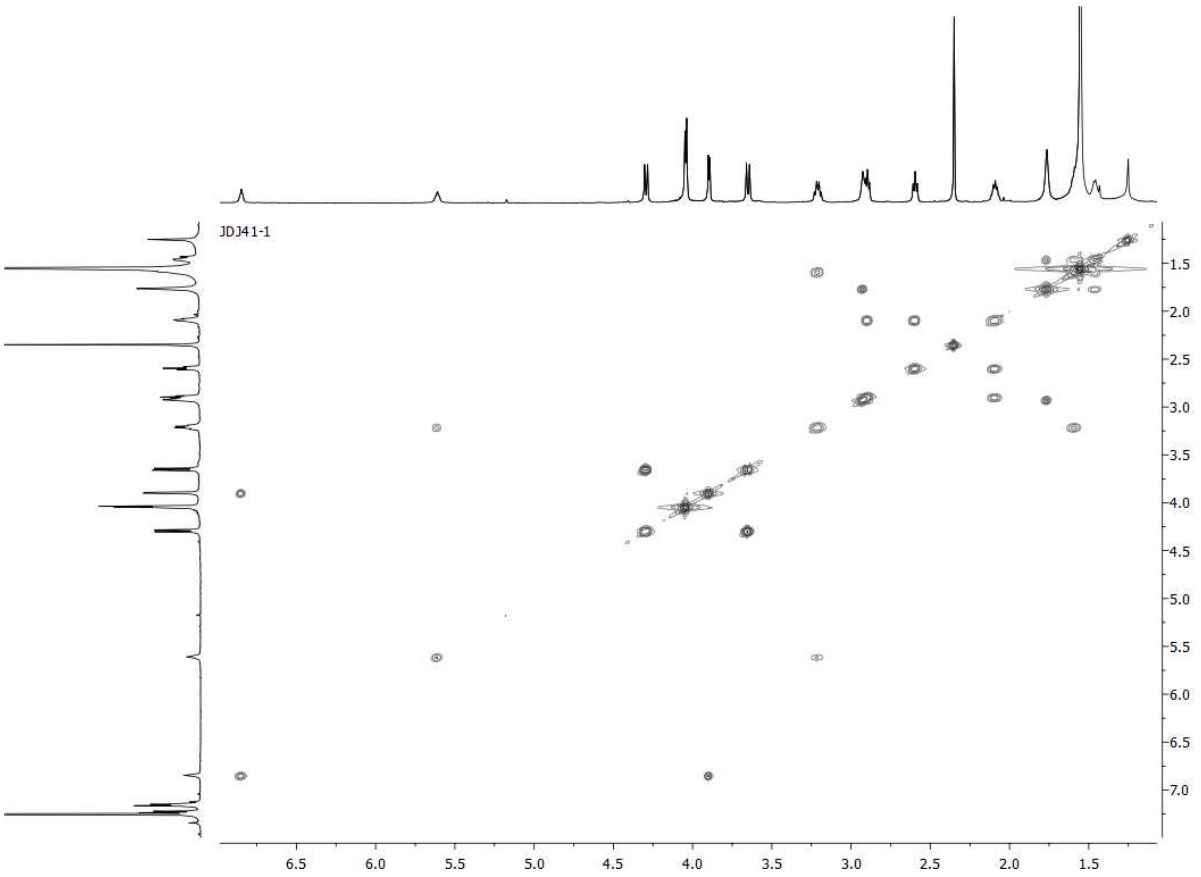


Figure S64. COSY spectrum of **17a**

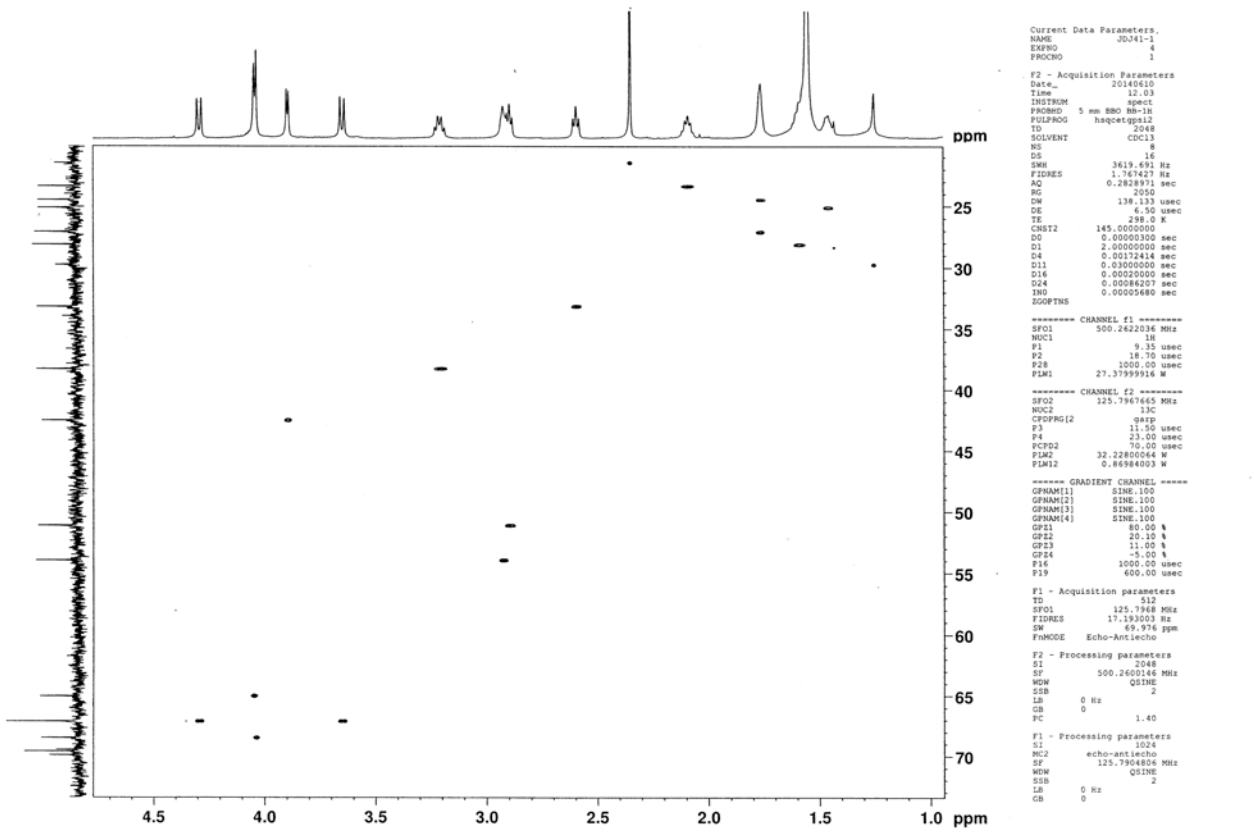


Figure S65. HSQC spectrum of **17a**

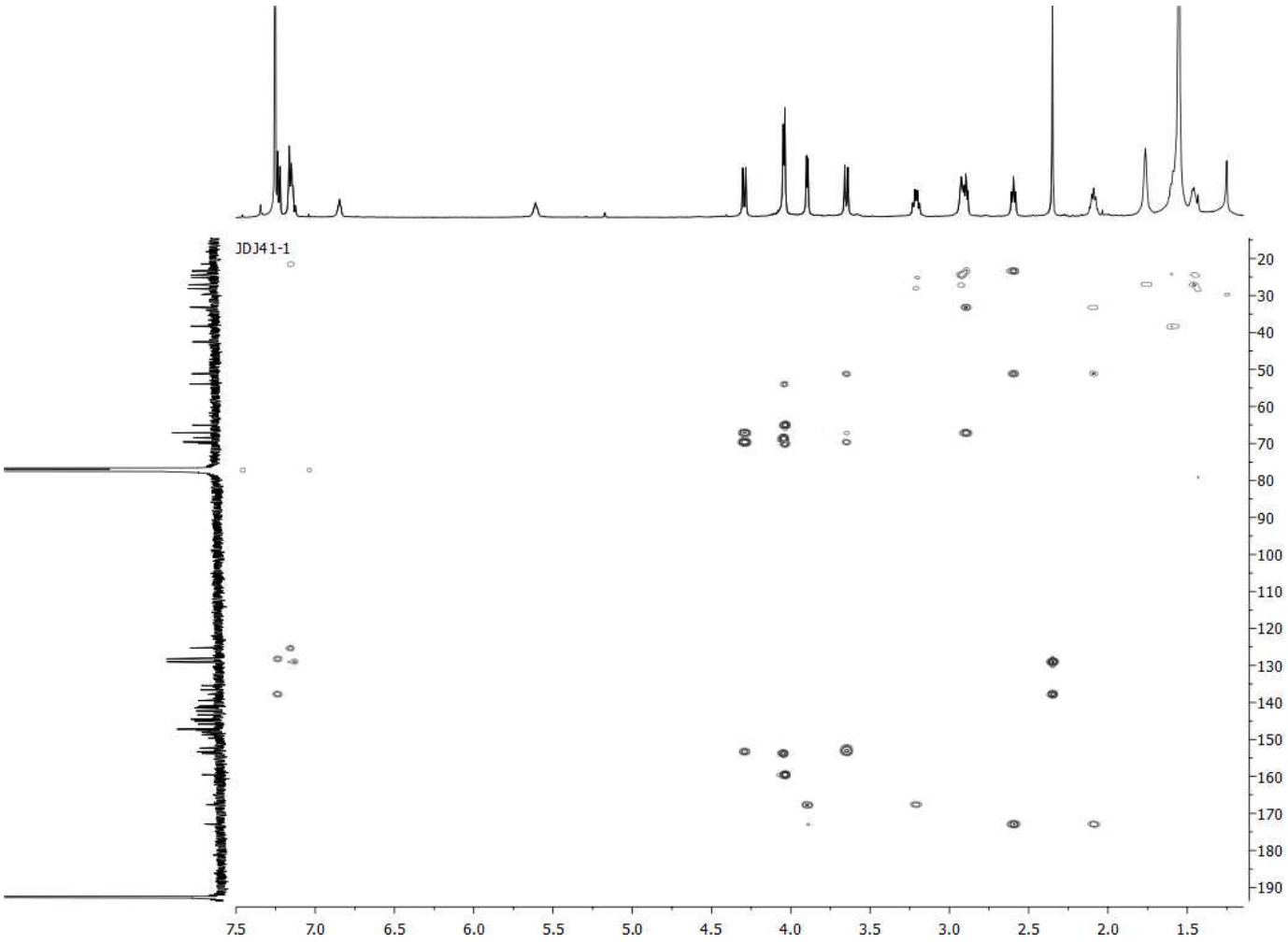
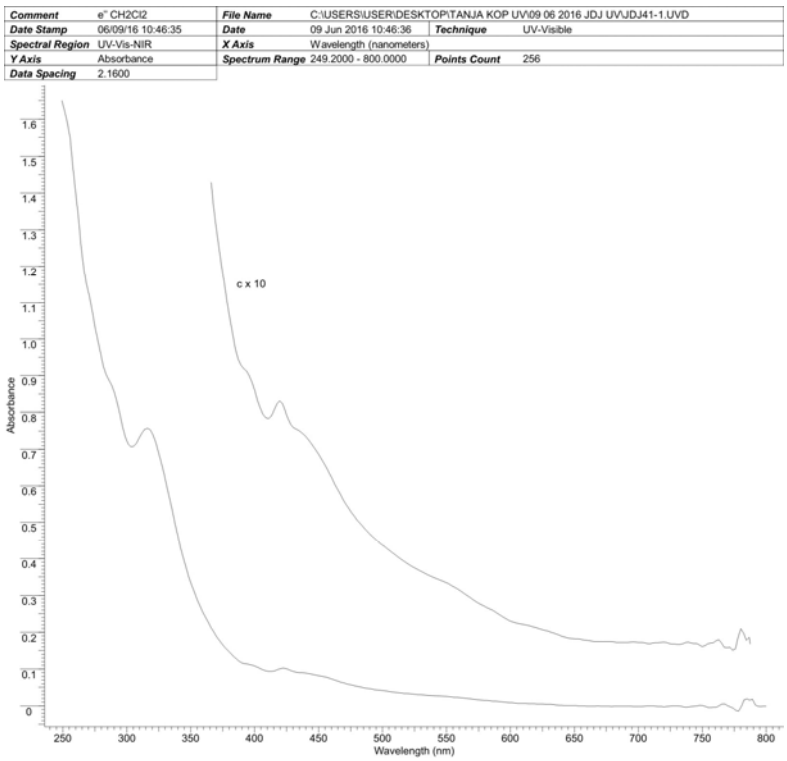


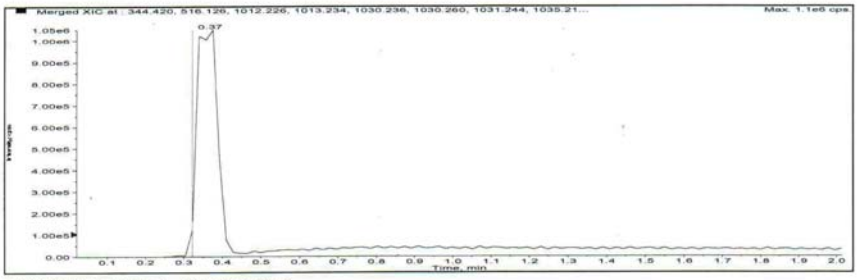
Figure S66. HMBC spectrum of **17a**



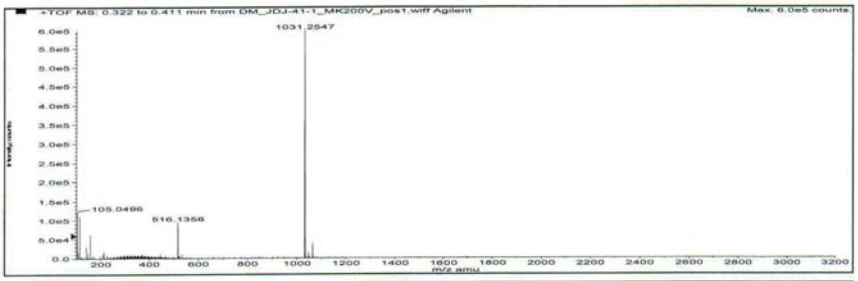
No	nm	A	Intensity
1	316.16	0.757	M
2	422.00	0.102	VW

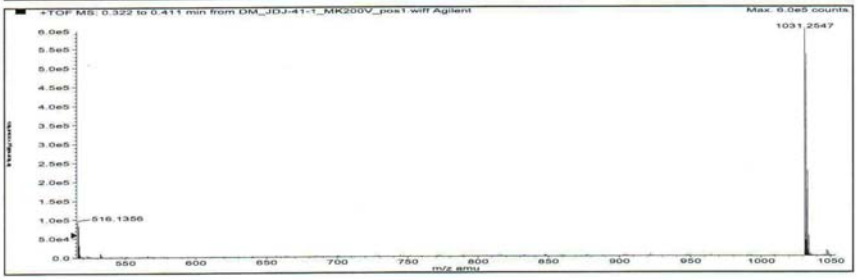
Figure S67. UV spectrum of **17a**

Sample Name: JDJ-41-1 Sample Location: P1-C2 Sample Id: Operator: Milka
Data File Name: D:\PE Sciex Data\Projects\D_Milic\Data\DM_JDJ-41-1_MK200V_pos1.wiff Acq Time: June 10 2016, 11:51:15 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
C76H30N4O2	--	1030.23688	0.37	3.93582 E6	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+2H]2+	98587.96	516.12571	516.12654	0.82170	1.59	--
[M+H]+	603602.35	1031.24415	1031.24815	3.99396	3.87	--
[M+Na-H2O]+	9449.31	1035.21553	1035.25899	43.46227	41.98	--
[M+NH4]+	12037.32	1048.27070	1048.24460	-26.09770	-24.90	--

Figure S68. Mass spectrum of **17a**

Bisadduct **17b** (*e*-face)

Figure 69. IR spectrum of **17b**

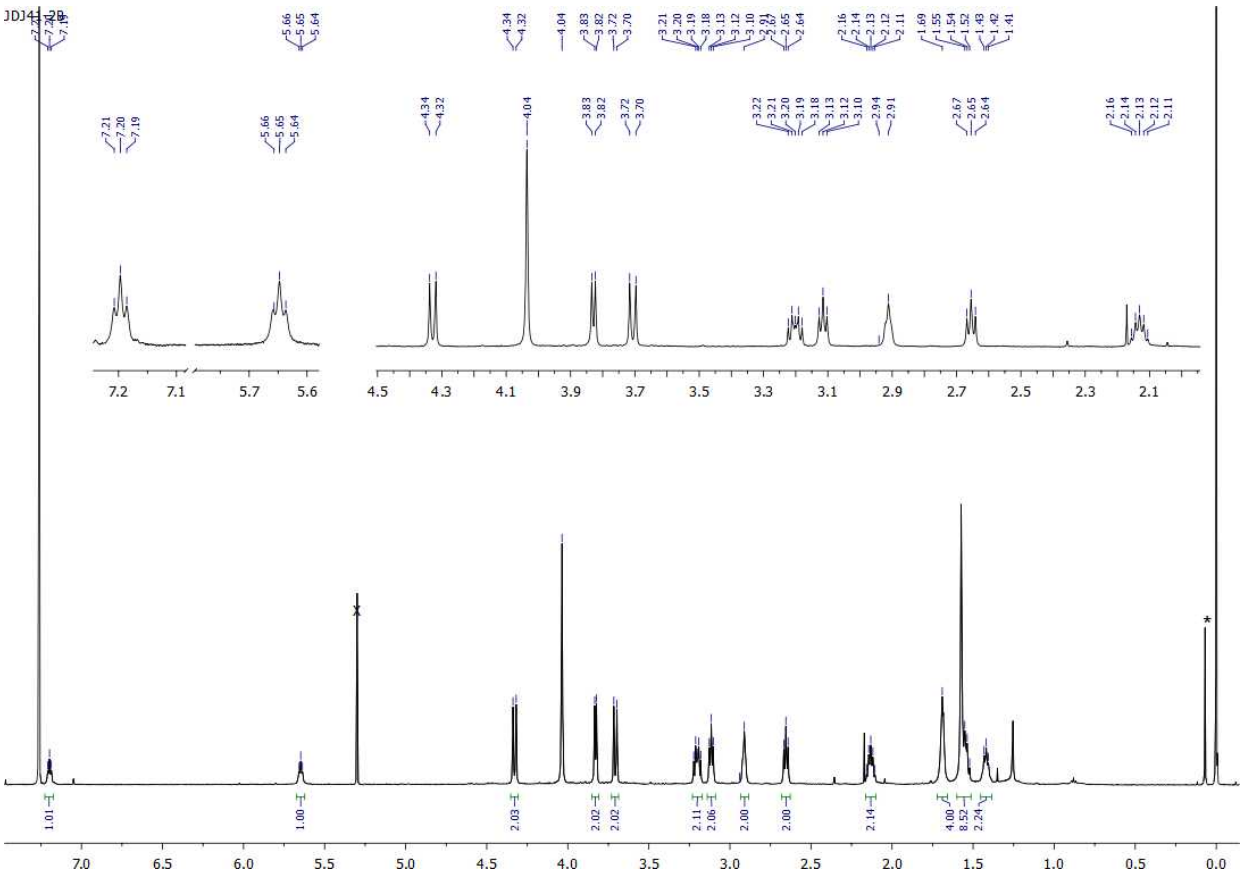


Figure S70. ^{1}H NMR spectrum of **17b**

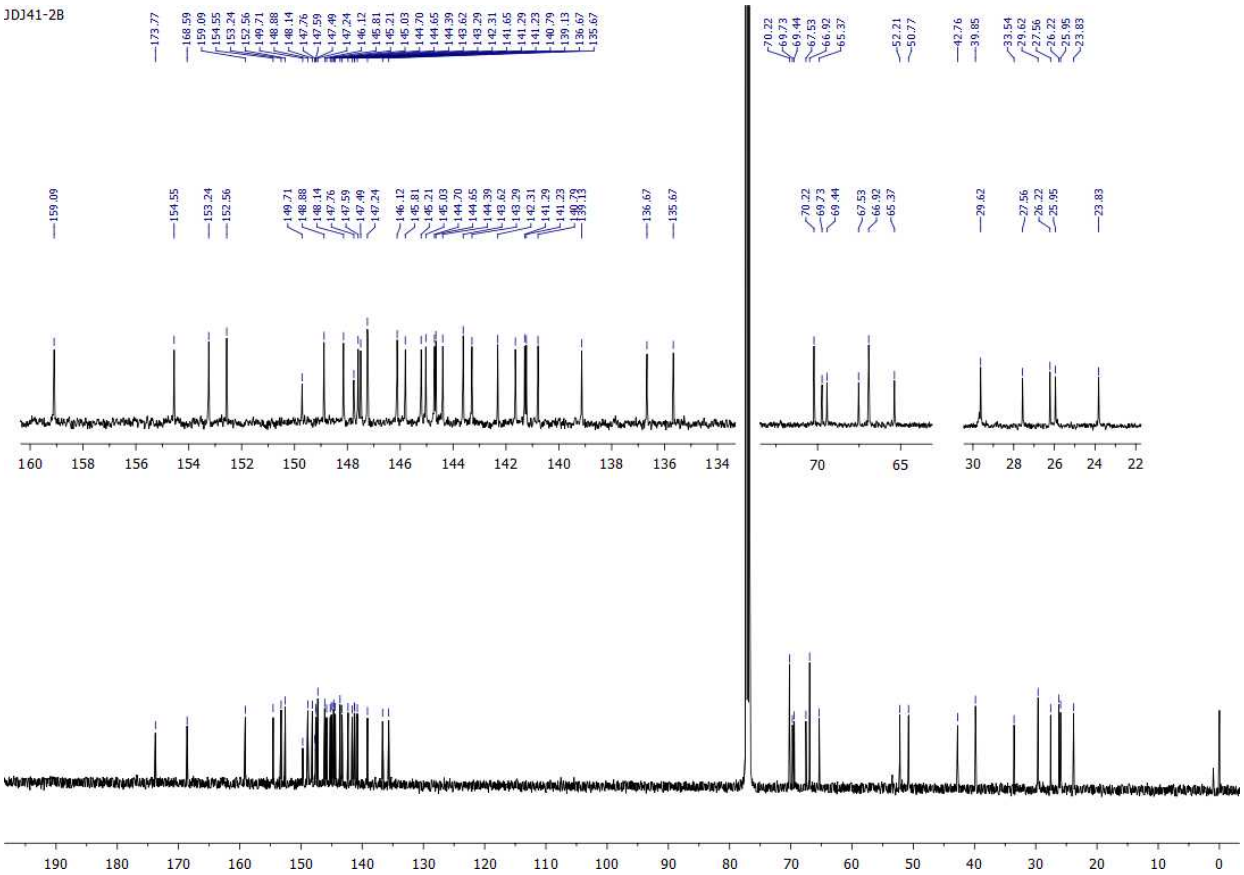


Figure S71. ^{13}C NMR spectrum of **17b**

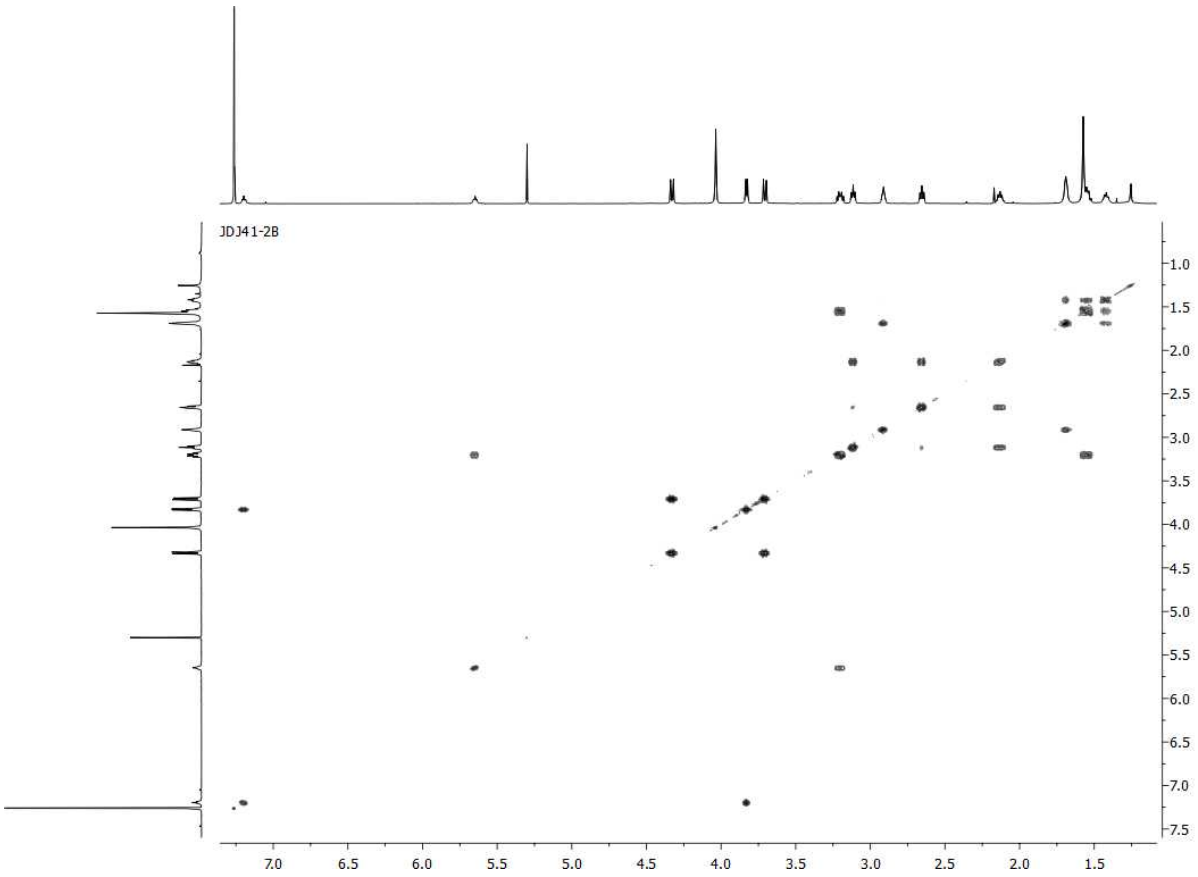


Figure S72. COSY spectrum of **17b**

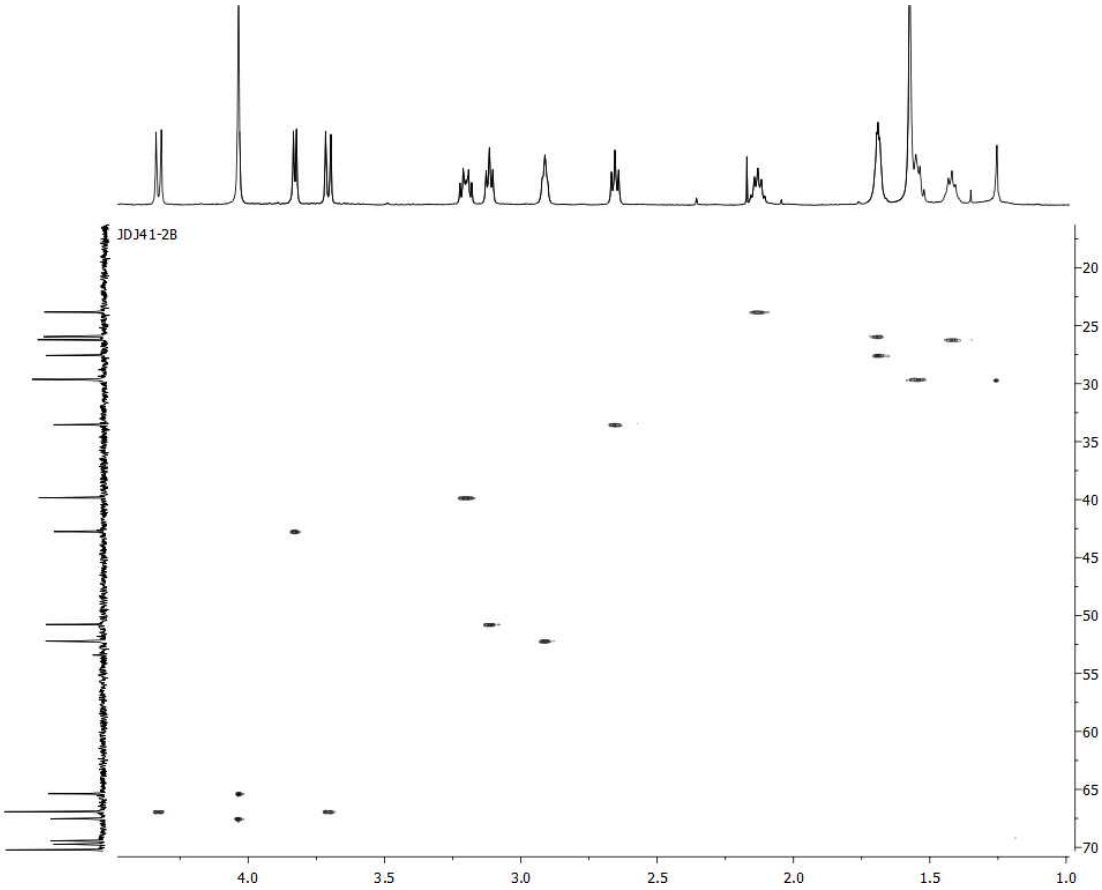


Figure S73. HSQC spectrum of **17b**

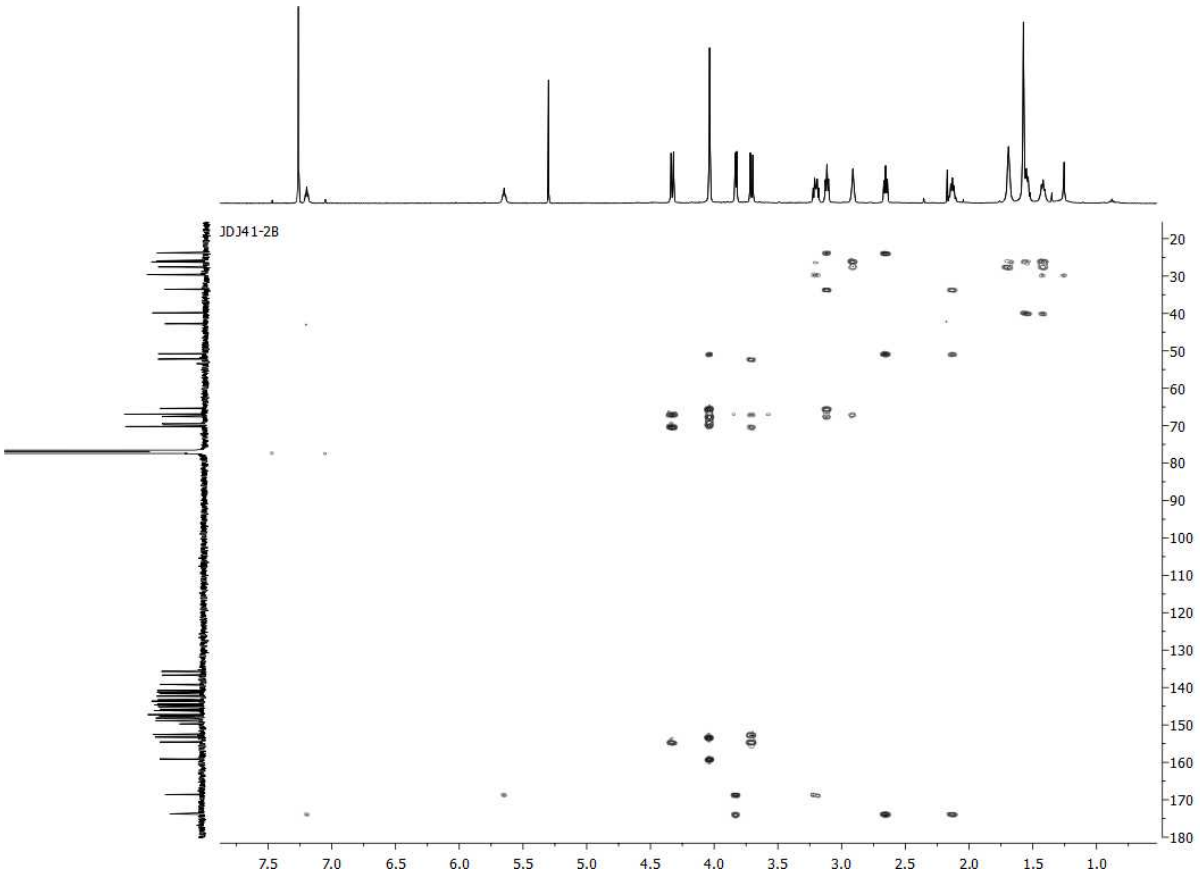


Figure S74. HMBC spectrum of **17b**

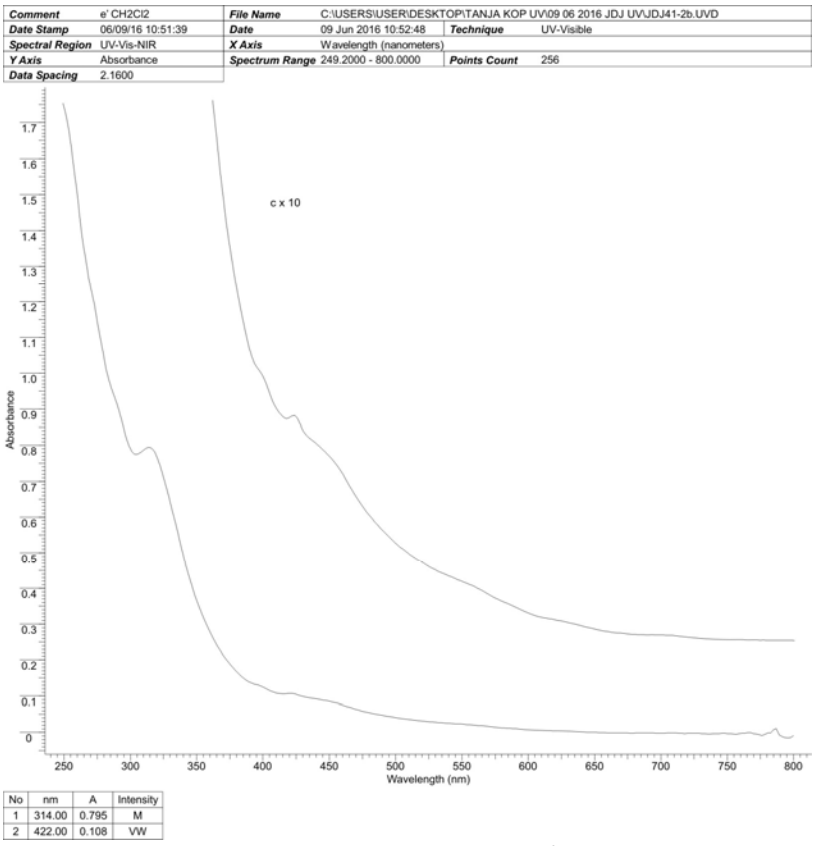
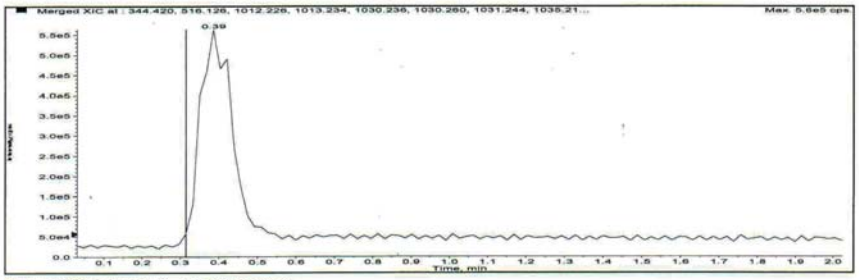
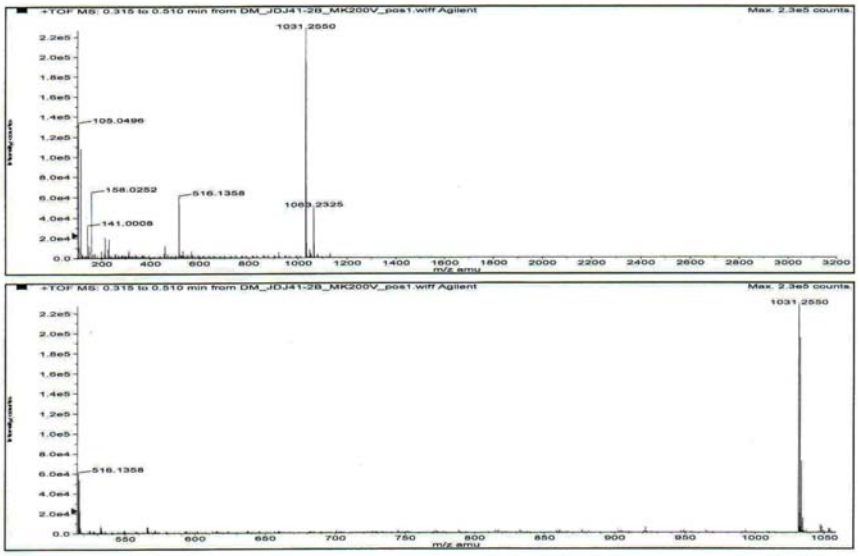


Figure S75. UV spectrum of **17b**



Merged XIC, Period# : 1 Experiment# : 1



Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C76H30N4O2	--	1030.23688	0.39	3.49337 E6	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+2H]2+	63732.54	516.12571	516.12532	-0.39083	-0.76	--
[M+H]+	234146.78	1031.24415	1031.24241	-1.74352	-1.69	--
[M+Na-H2O]+	2667.01	1035.21553	1035.25634	40.81193	39.42	--
[M+NH4]+	6345.58	1048.27070	1048.24251	-28.18822	-26.89	--
[M+Na]+	4606.54	1053.22610	1053.22575	-0.34850	-0.33	--

Figure S76. Mass spectrum of **17b**

Bisadduct **17c** (*trans*-4)

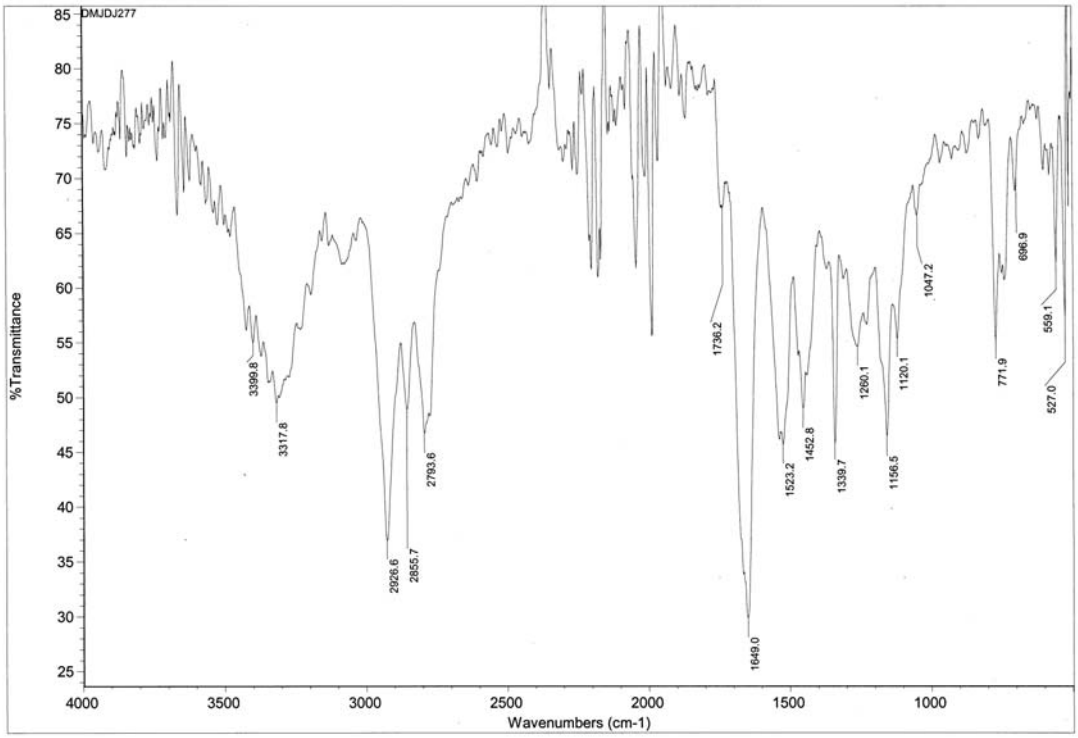


Figure S77. IR spectrum of **17c**

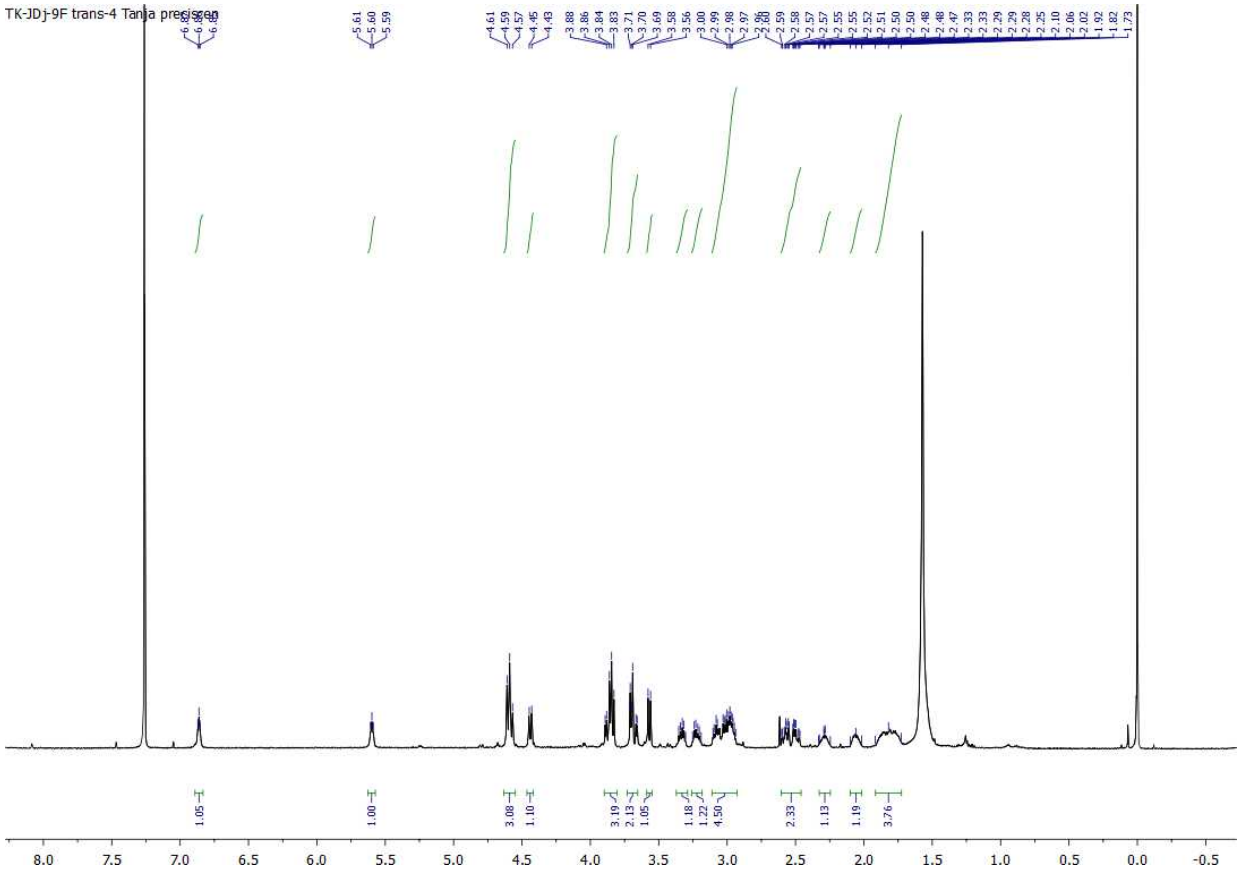


Figure S78. ^{1}H NMR spectrum of **17c**

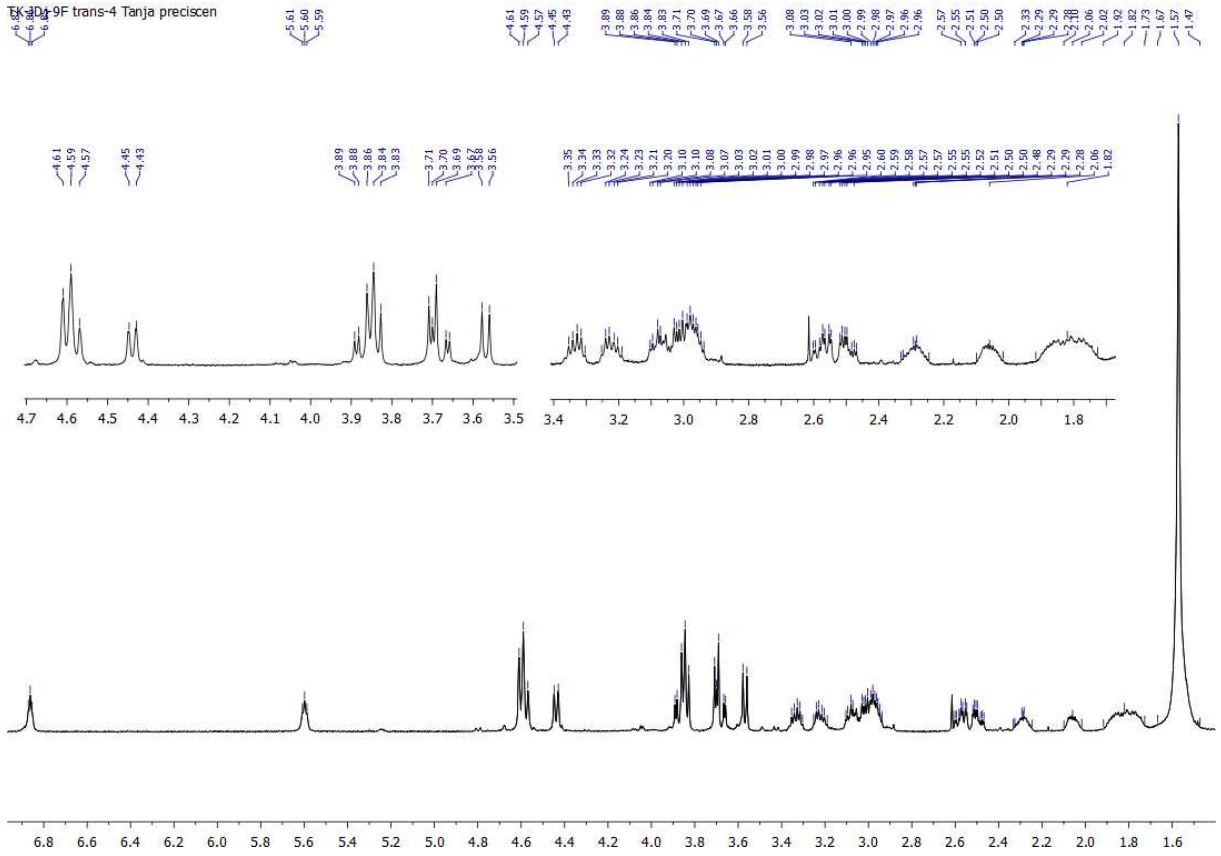


Figure S79. Expanded parts of ^{1}H NMR spectrum of **17c**

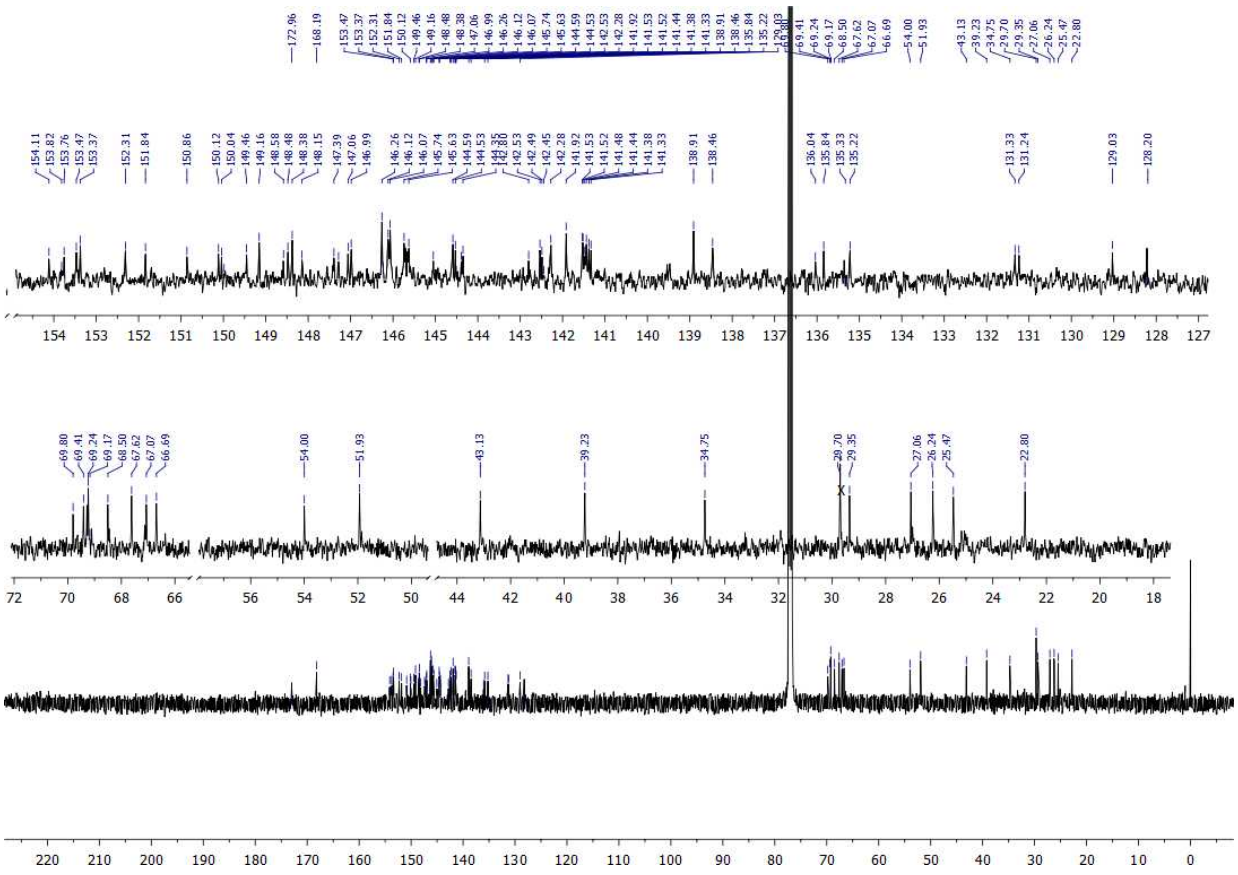


Figure S80. ^{13}C NMR spectrum of **17c**

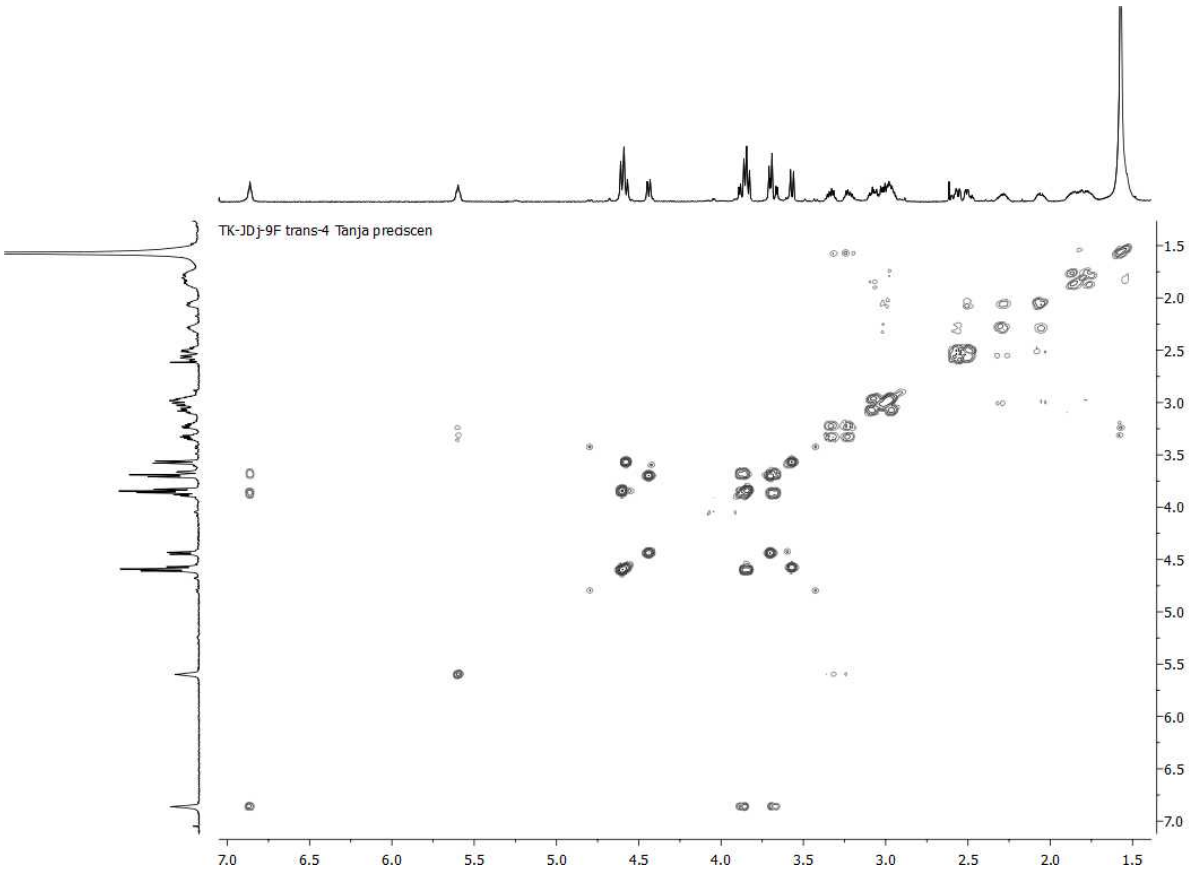


Figure S81. COSY spectrum of **17c**

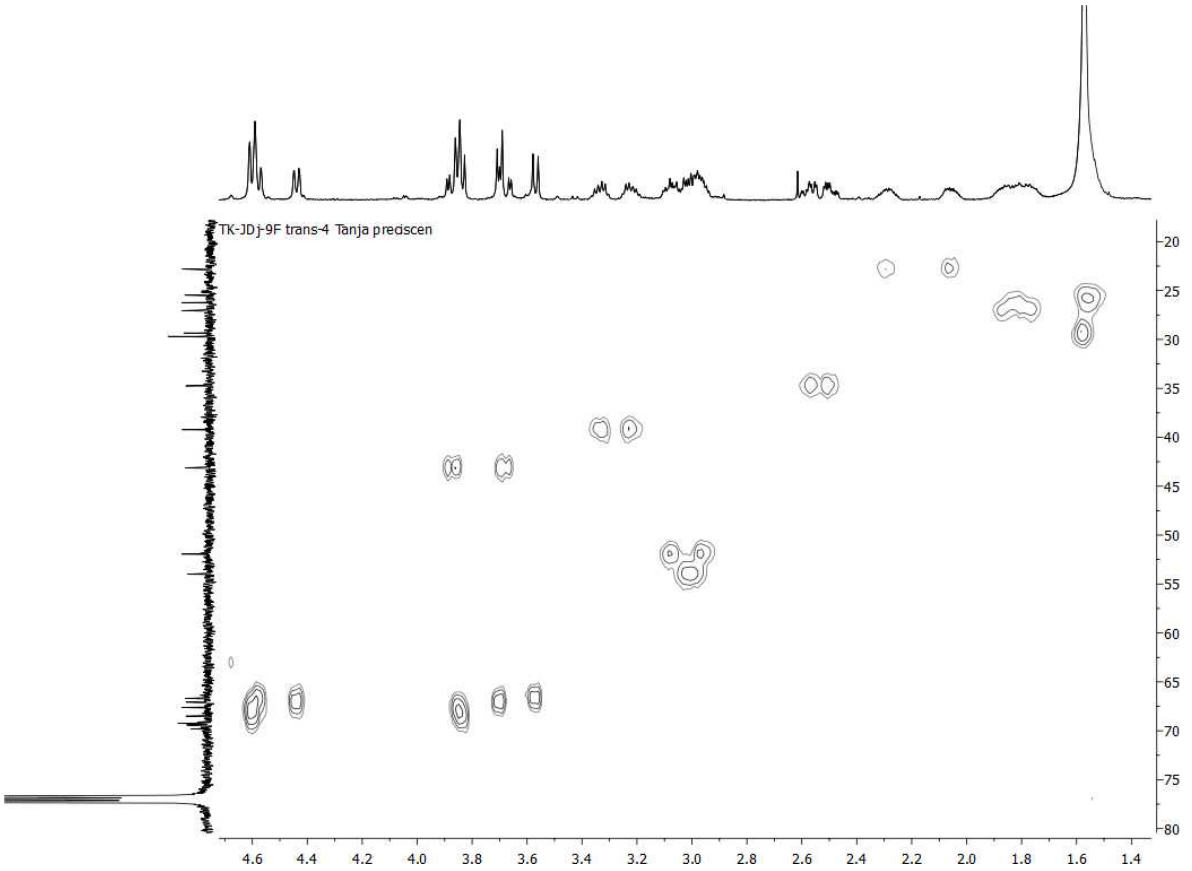


Figure S82. HSQC spectrum of **17c**

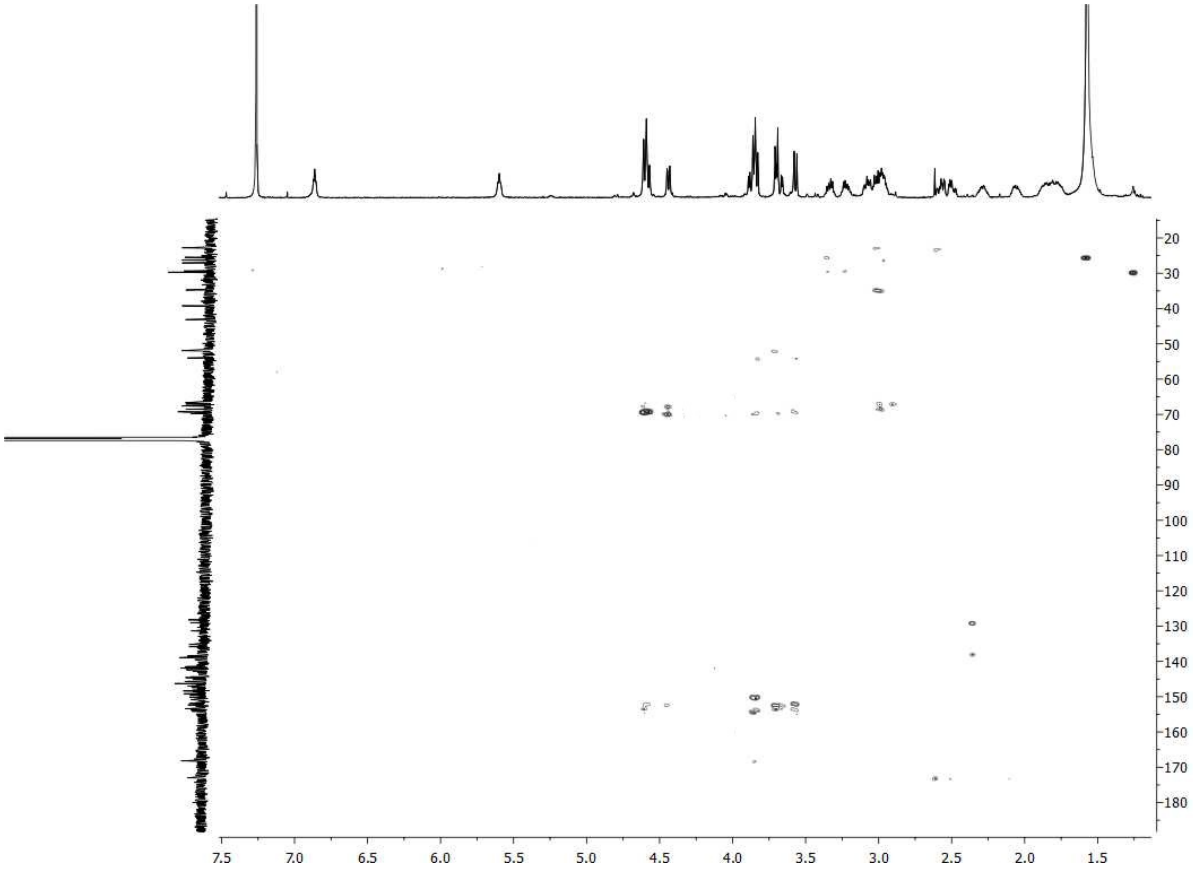


Figure S83. HMBC spectrum of **17c**

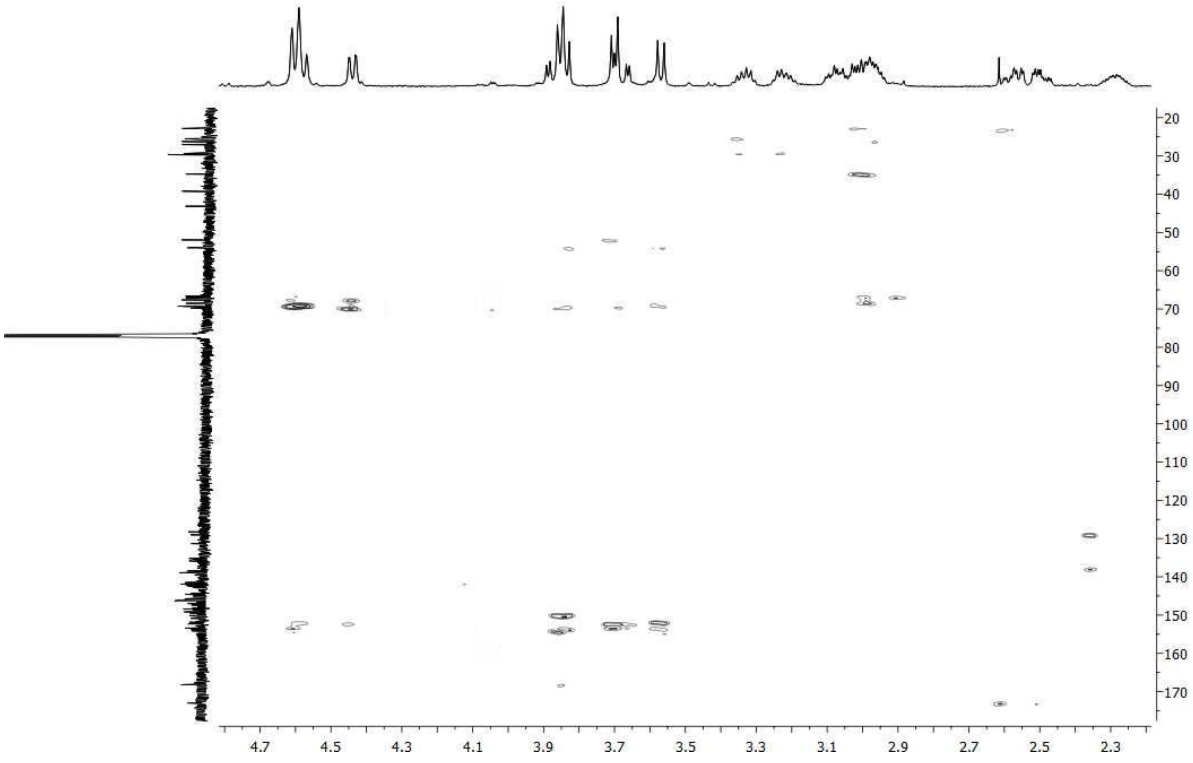
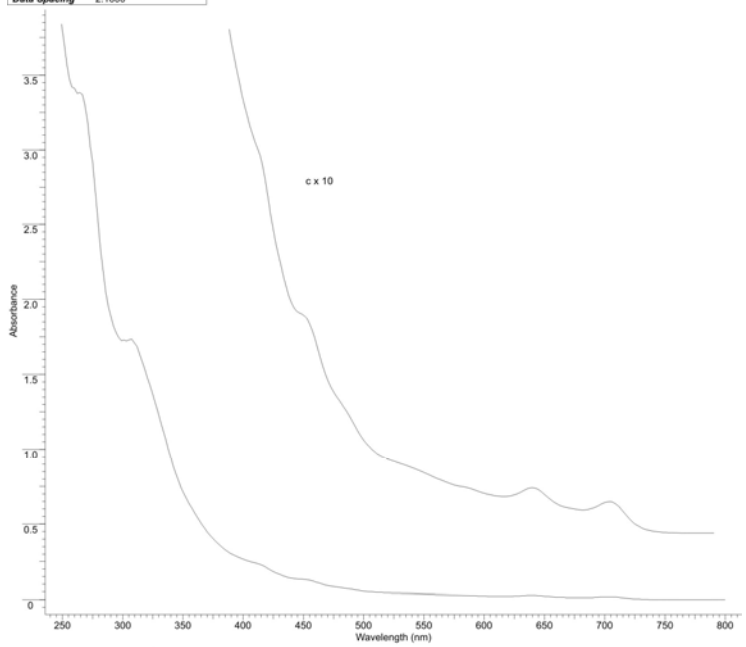


Figure S84. Expanded part of HMBC spectrum of **17c**

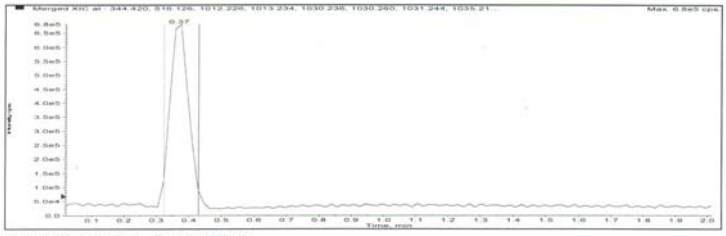
Comment	trans-4 CH2Cl2	**File Name**	C:\USERS\USER\DESKTOP\TANJA KOP UV\09 06 2016 JDJ UV\TKJDJ-9F.UVD		
Date Stamp	06/09/16 11:07:33	**Date**	09 Jun 2016 11:07:34	**Technique**	UV-Visible
Spectral Region	UV-Vis-NIR	**X Axis**	Wavelength (nanometers)		
Y Axis	Absorbance	**Spectrum Range**	249.2000 - 800.0000	**Points Count**	256
Data Spacing	2.1600				



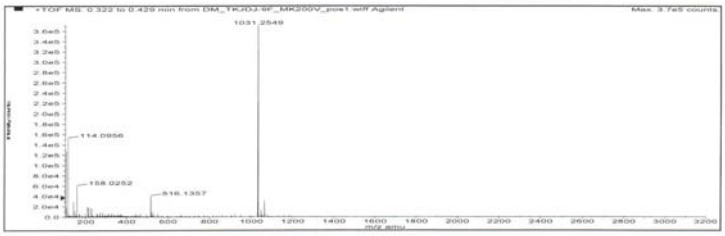
No	nm	A	Intensity
1	264.32	3.384	S
2	307.52	1.734	M
3	638.00	0.028	VW
4	704.96	0.019	VW

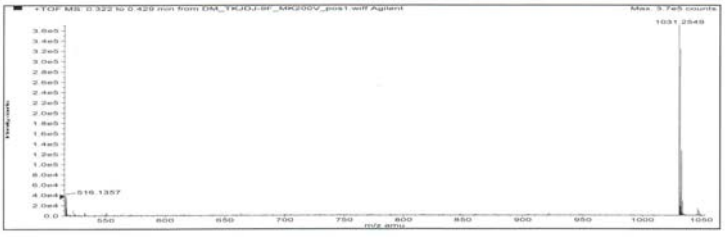
Figure S85. UV spectrum of **17c**

Sample Name: **TKJDJ-9F** Sample Location: **P1-C4** Sample Id: Operator: **Milka**
Data File Name: **D:\PE Sciex Data\Projects\D_Milic\Data\DM_TKJDJ-9F_MK200V_pos1.wiff** Acq Time: **June 10 2016, 11:57:18 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
C76H30N4O2	--	1030.23688	0.37	2.65949 E6	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+2H]2+	42386.31	516.12571	516.12542	-0.29829	-0.58	--
[M+H]+	379816.42	1031.24415	1031.24383	-0.32474	-0.31	--
[M+Na-H2O]+	5002.86	1035.21553	1035.25671	41.17851	39.78	--
[M+NH4]+	10820.60	1048.27070	1048.24211	-28.59627	-27.28	--

Figure S86. Mass spectrum of **17c**

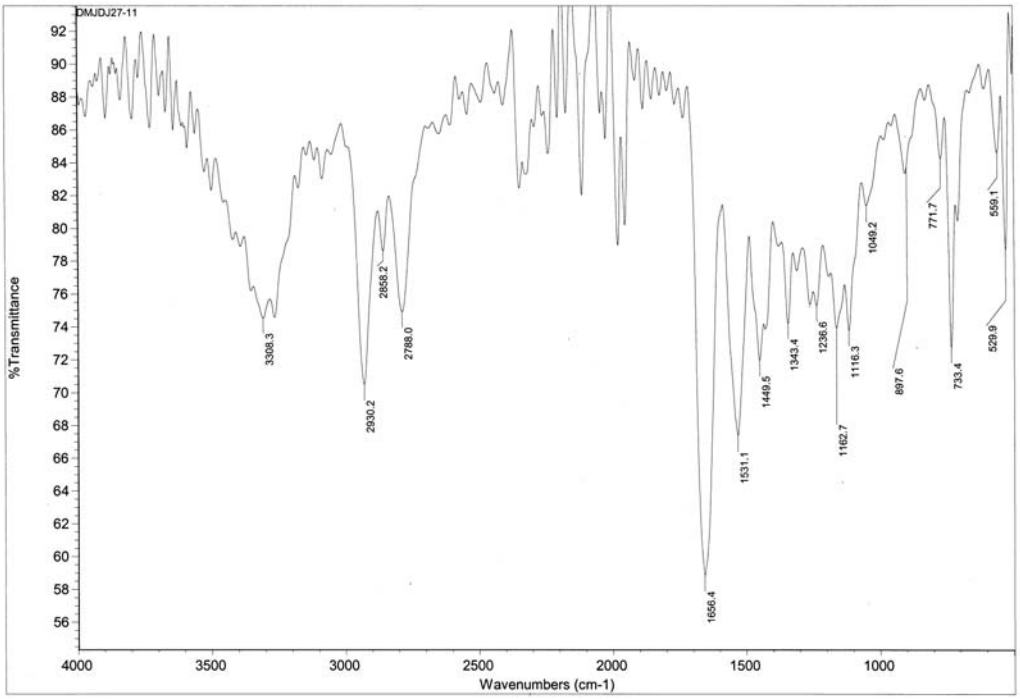


Figure S87. IR spectrum of **17d**

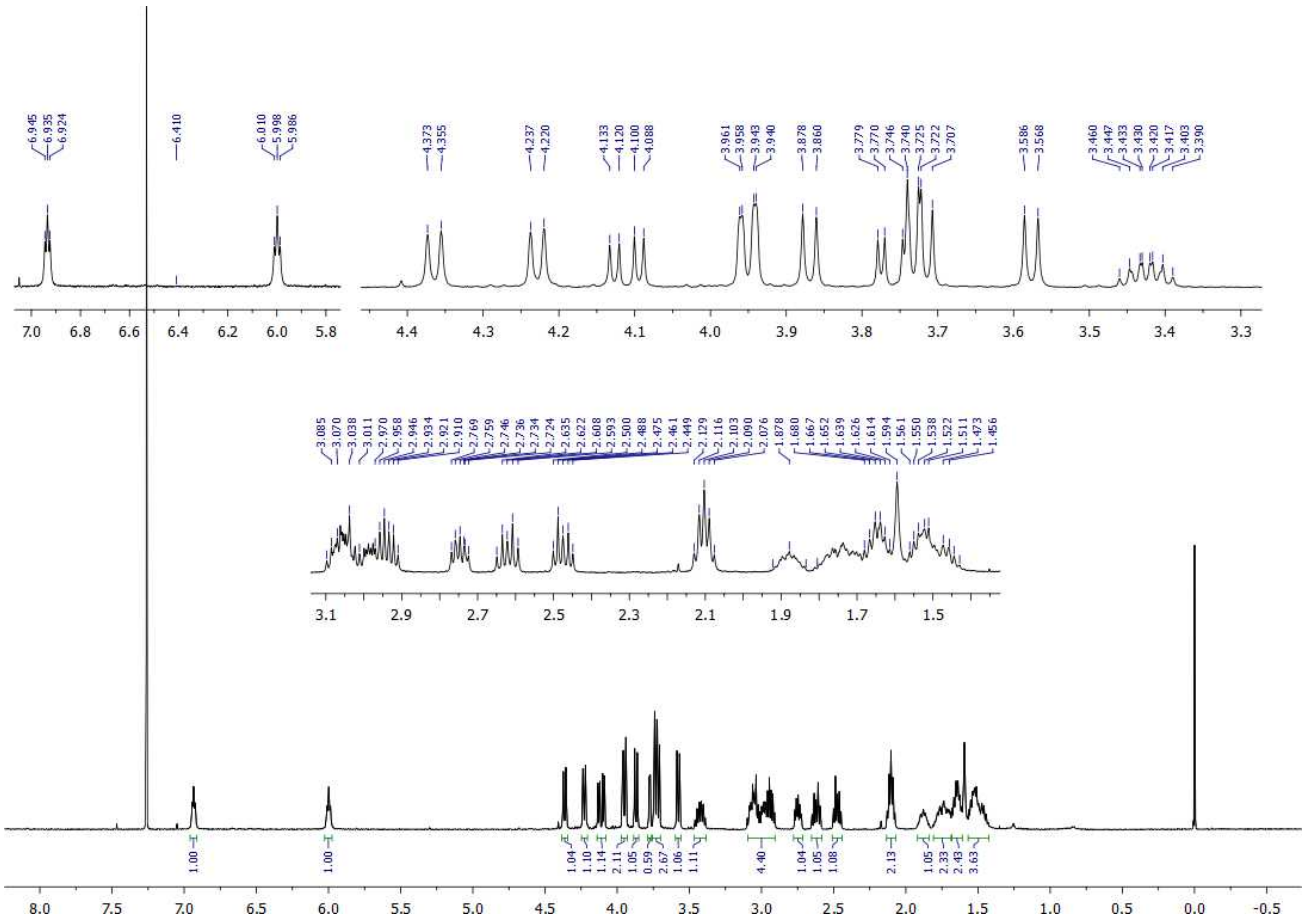


Figure S88. ^{1}H NMR spectrum of **17d**

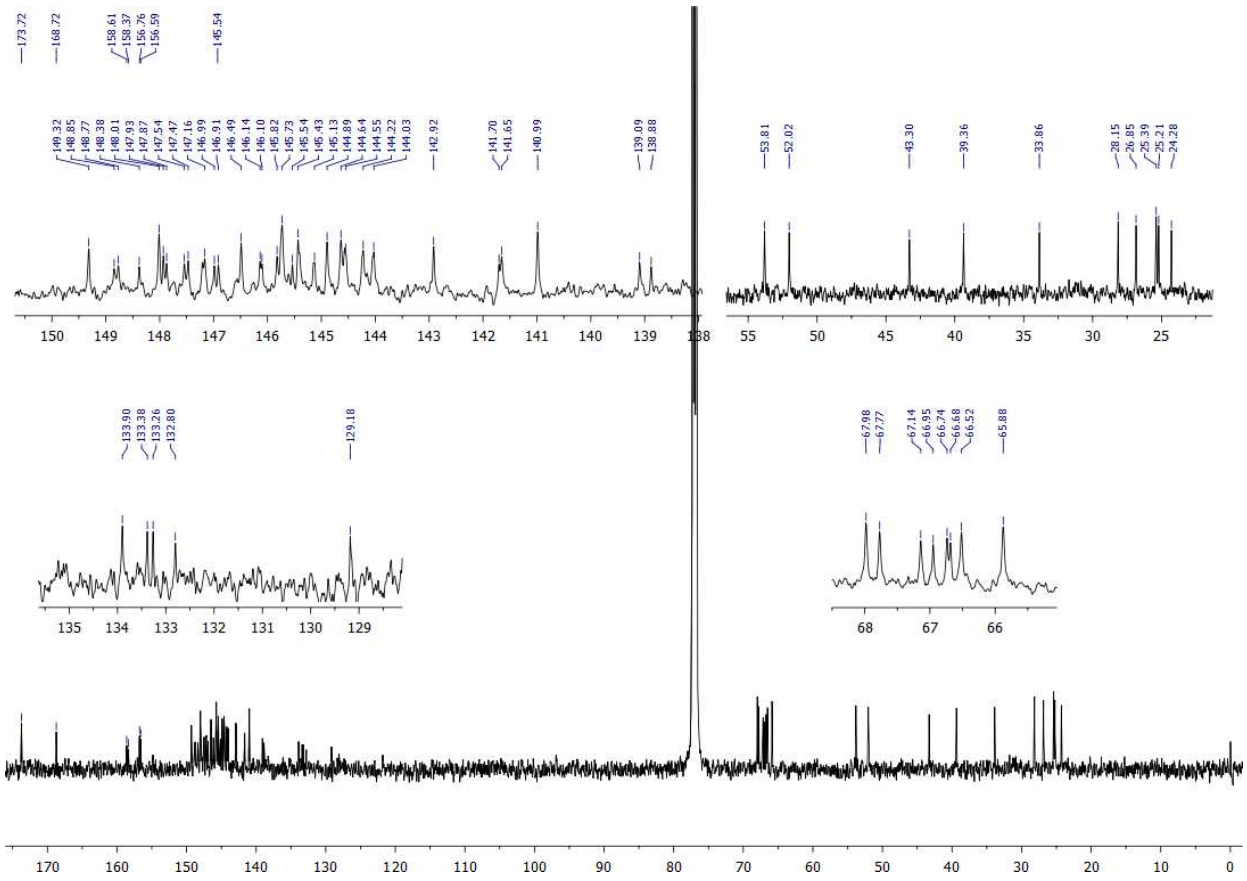


Figure S89. ^{13}C NMR spectrum of **17d**

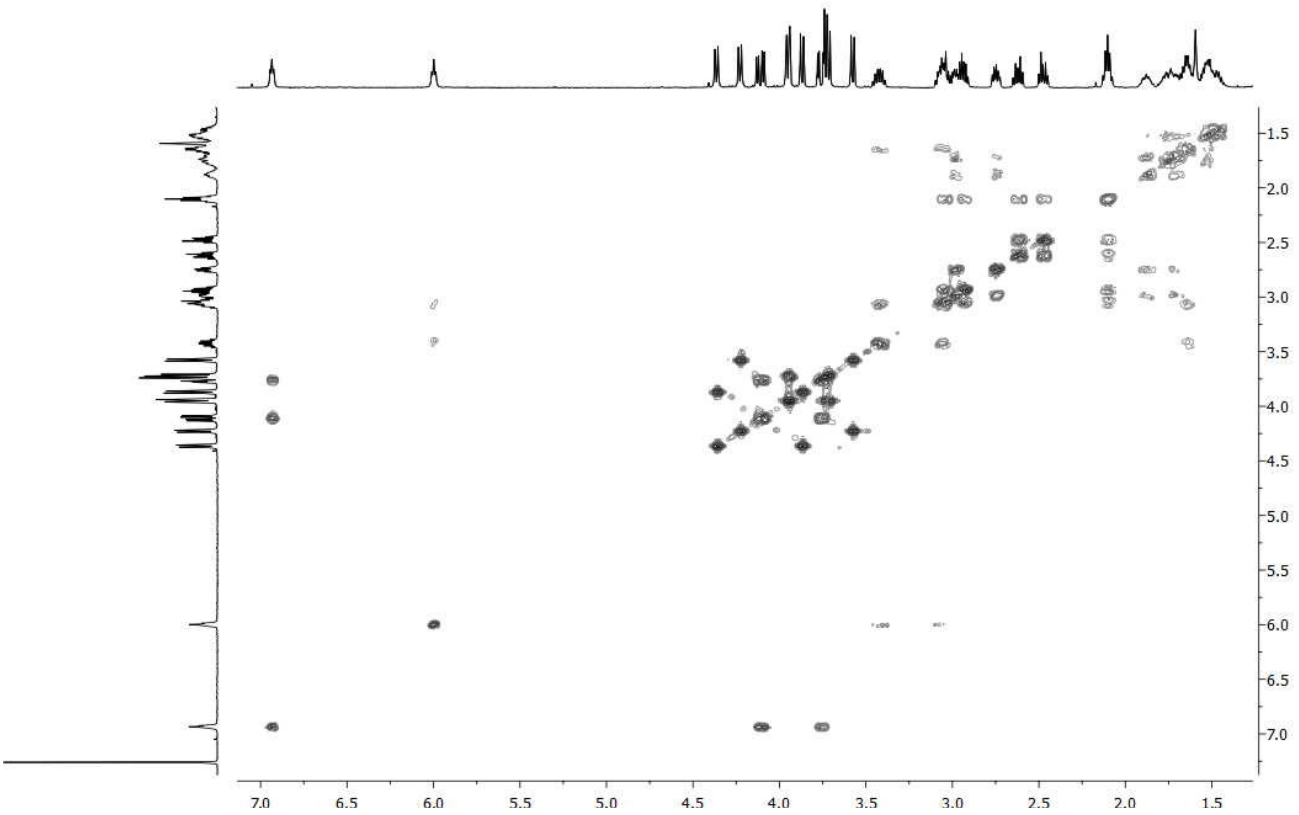


Figure S90. COSY spectrum of **17d**

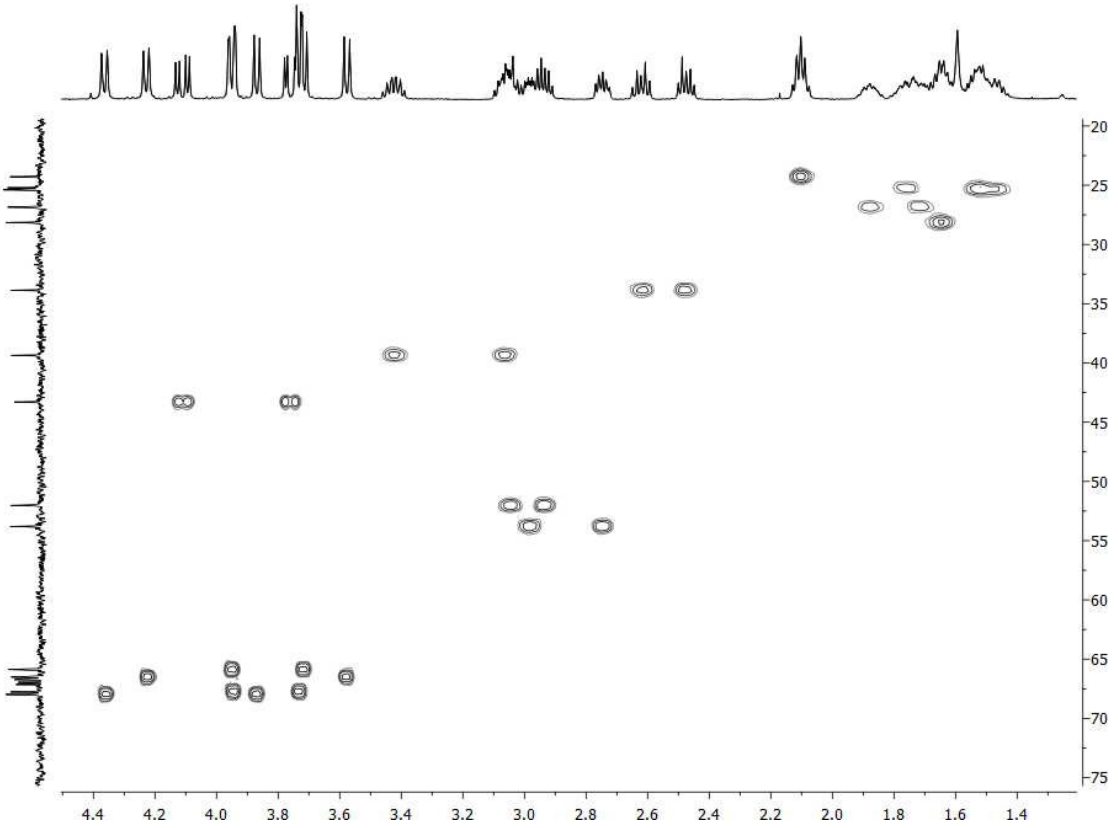


Figure S91. HSQC spectrum of **17d**

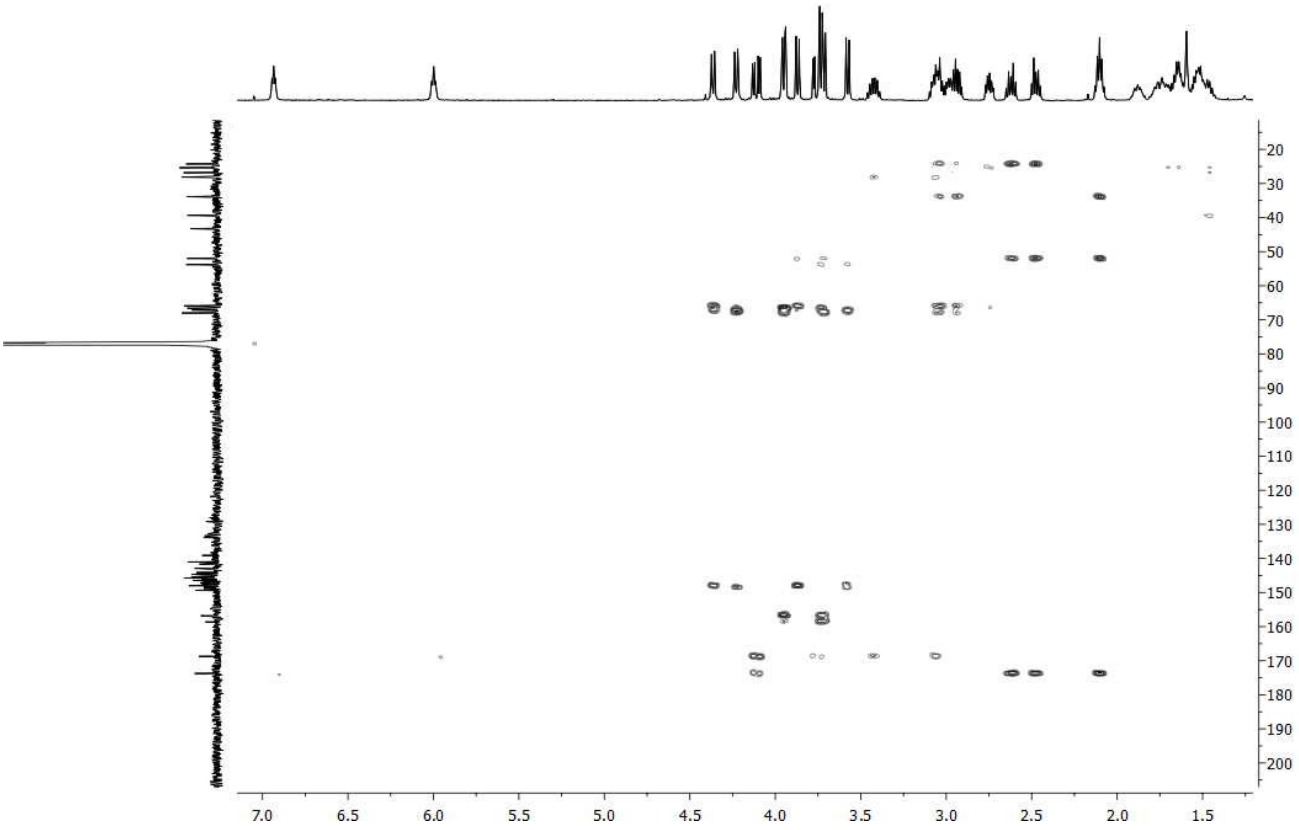
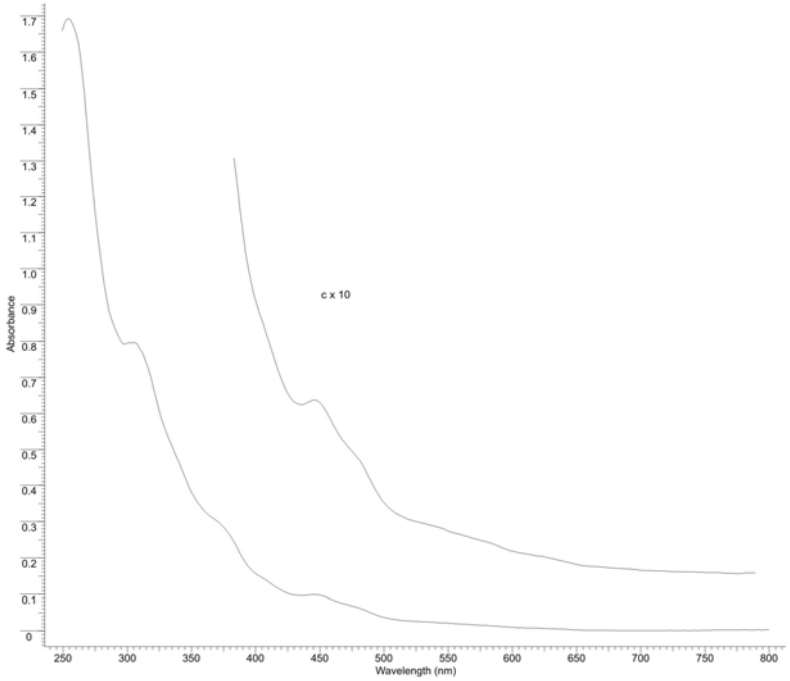


Figure S92. HMBC spectrum of **17d**

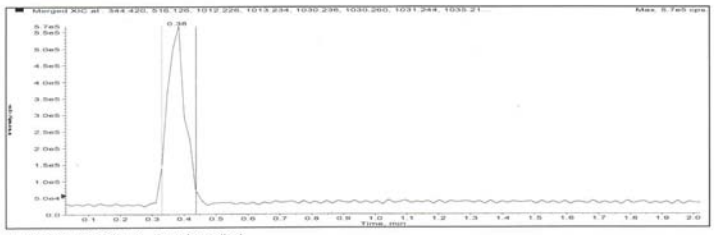
Comment	cis-2 CH2Cl2	**File Name**	C:\USERS\USER\DESKTOP\TANJA KOP UV\09 06 2016 JDJ UV\TKJDJC2.UVD		
Date Stamp	06/09/16 11:12:14	**Date**	09 Jun 2016 11:12:16	**Technique**	UV-Visible
Spectral Region	UV-Vis-NIR	**X Axis**	Wavelength (nanometers)		
Y Axis	Absorbance	**Spectrum Range**	249.2000 - 800.0000	**Points Count**	256
Data Spacing	2.1600				



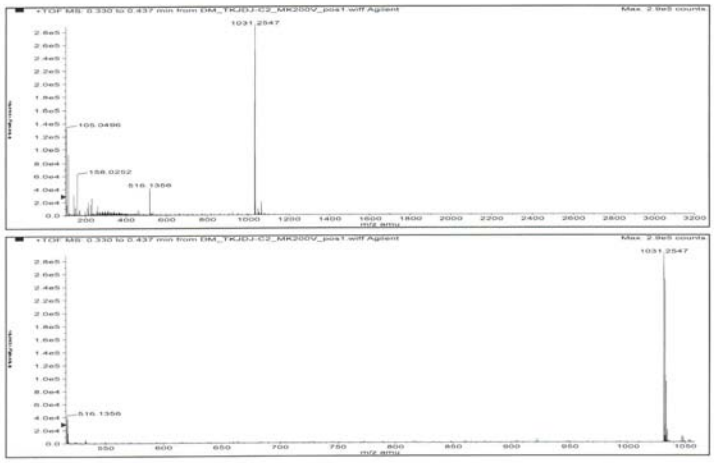
No	nm	A	Intensity
1	305.36	0.798	M
2	445.76	0.099	VW

Figure S93. UV spectrum of **17d**

Sample Name: TKJDJ-C2 Sample Location: P1-C5 Sample Id: Operator: Milka
Data File Name: D:\PE Sciex Data\Projects\D_Milic\Data\DM_TKJDJ-C2_MK200V_pos1.wiff Acq Time: June 10 2016, 12:00:19 PM
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
C76H30N4O2	--	1030.23688	0.38	2.22087 E6	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+2H]2+	43935.87	516.12571	516.12543	-0.28333	-0.55	--
[M+H]+	297041.22	1031.24415	1031.24263	-1.52197	-1.48	--
[M+Na-H2O]+	3454.54	1035.21553	1035.25737	41.83265	40.41	--
[M+NH4]+	8415.79	1048.27070	1048.24313	-27.57179	-26.30	--
[M+Na]+	3724.78	1053.22610	1053.22665	0.55450	0.53	--

Figure S94. Mass spectrum of **17d**