

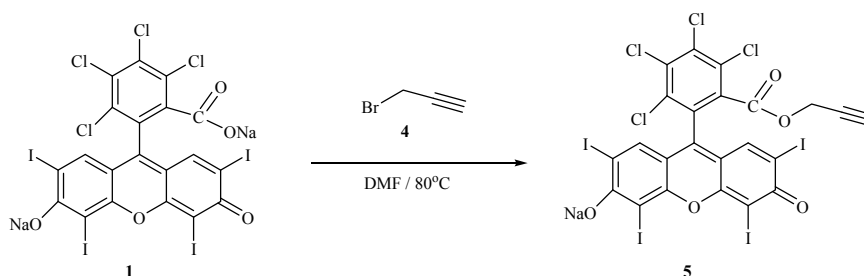
Supporting Information

Synthesis and Use of Imidazolium Bound Rose Bengal Derivatives for Singlet Oxygen Generation

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To a stirred solution of Rose Bengale (3.5 g, 3.5 mmol) in DMF (150 mL) was added propargyl bromide **4** (1.12 g, 9.4 mmol). The resulting mixture was stirred at 80 °C for 3 hs. The DMF was distilled off under vacuo and the residue stirred in diethyl ether overnight. After filtration and thorough washing with diethyl ether, the residue was stirred with water for 6 h and filtered, to afford a deep purple powder which was dried under vacuum and purified by column chromatography on silica (MeOH/CH₂Cl₂, 5/95) to afford compound **5** (3.2 g, 89%). *R_f* = 0.11 (MeOH/CH₂Cl₂ 1:9) ¹H NMR (DMSO-d₆, 400 MHz) δ : 7.47 (2H, s, H-6,10); 4.64 (2H, d, J = 2.5 Hz, CH₂-22); 2.98 (1H, t, J = 2.4 Hz, H-24).

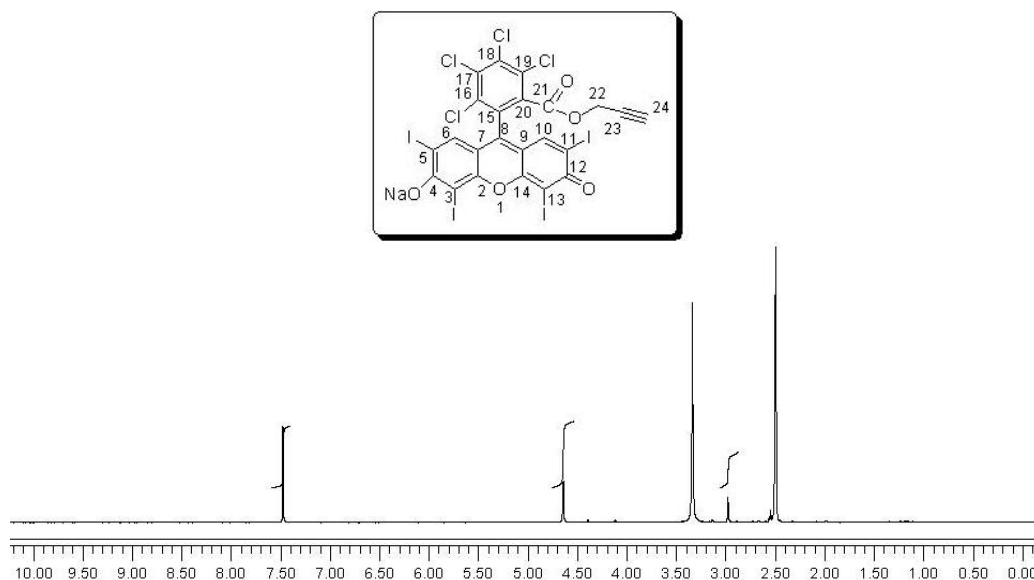
¹³C NMR (DMSO-d₆, 400 MHz) δ: 171.62 (C-4,12); 162.29 (C=O); 156.98 (C-2,14); 138.93; 135.21; 134.35; 132.64; 131.87; 130.12; 128.79 (C-20, 15, 16, 17, 18, 19, 8); 135.96 (CH-6,10); 110.46 (C-7,9); 97.23 (C-3,13); 77.30 (CH-24); 76.24 (C-5,11); 53.43 (CH₂-22).

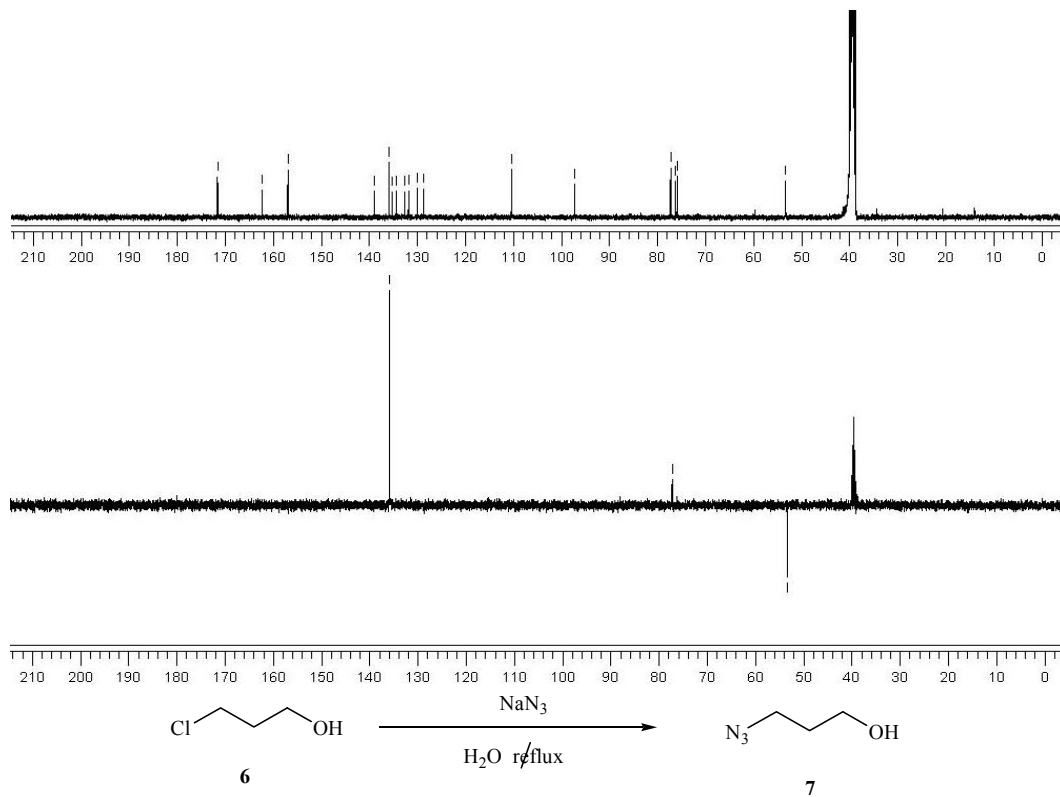
IR-(CDCl₃, ν(cm⁻¹)): 2348 ; 2301 ; 2100 ; 1740 (C=O ester); 1613; 1541; 1455; 1339; 1236; 1011.

UV (MeOH, λ(nm)): 563; 283; 273; 206.

MS (EI⁺)[m/z,(%)]: 1034.49 ([M + 1]⁺, 15); 1032.50 ([C₂₃H₆Cl₄I₄NaO₅]⁺, 13); 1012.50 ([C₂₃H₇Cl₄I₄O₅]⁺, 100); 1010.52 ([C₂₃H₆Cl₄I₄O₅]⁺, 87); 370.84 (12).

EI-HRMS: calcd for C₂₃H₅Cl₄I₄NaO₅ (m/z) [M⁺] 1033.7025, found 1033.5074.



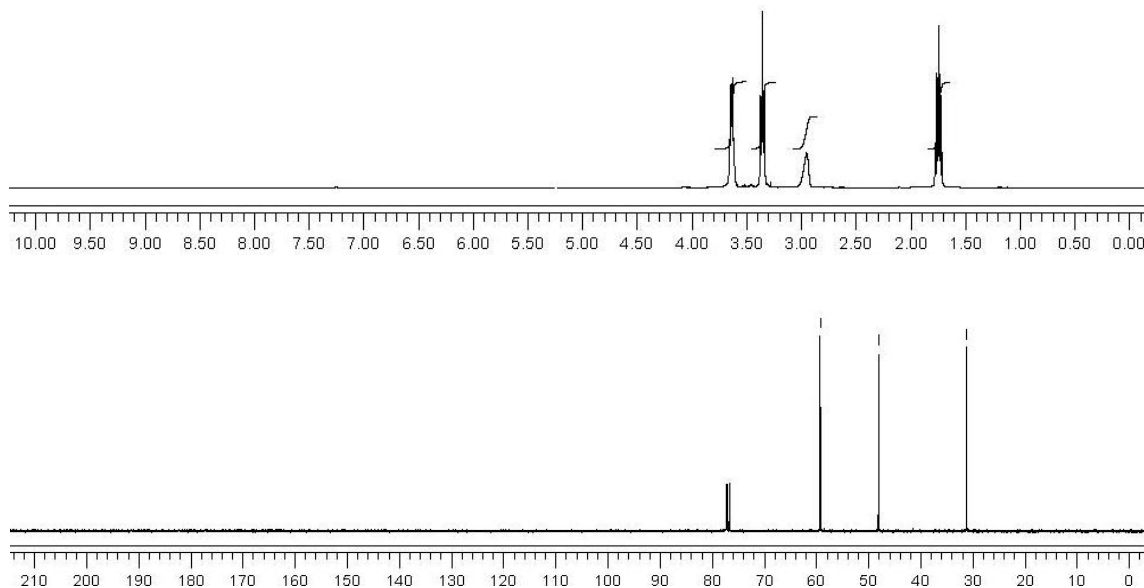
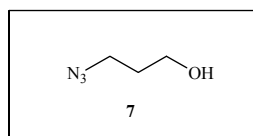


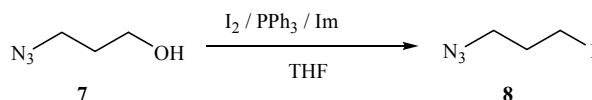
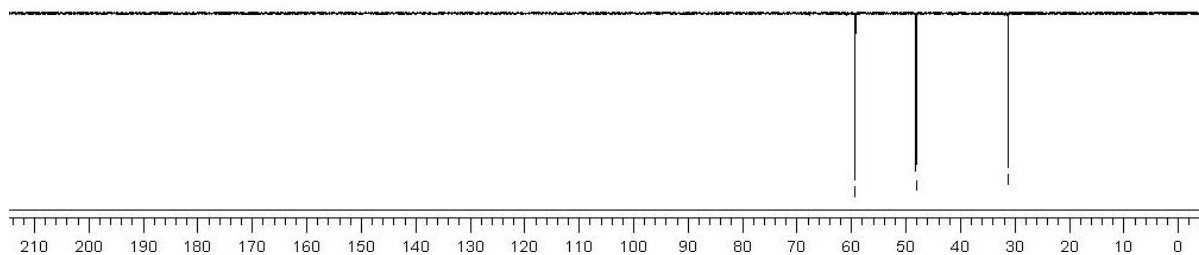
To a solution of NaN_3 (5.82 g, 89.6 mmol) in H_2O (70 mL) was added portionwise **6** (3.00 mL, 44.8 mmol). The mixture was refluxed for 16h then allowed to reach room temperature and extracted with CH_2Cl_2 (80 mL x 3). The combined organic layers were dried over Na_2SO_4 , filtered and the solvent rotatory evaporated to afford azide **7** as a colourless liquid (2.37 g, 98%). $R_f = 0.46$ (EtOAc/hexane 3:7)

$^1\text{H-NMR}$ (CDCl_3 , δ): 3.63 (2H, q, $J = 5.07$, H-1); 3.35 (2H, t, $J = 6.66$, H-3); 2.95 (1H, s, OH); 1.74 (2H, m, H-2).

$^{13}\text{C-NMR}$ (CDCl_3 , δ): 59.30 (CH₂-1); 48.14 (CH₂-3); 31.22 (CH₂-2).

MS (EI^+) (m/z , %): 86.06 ($[\text{C}_3\text{H}_6\text{ON}_2]^+$, 100).

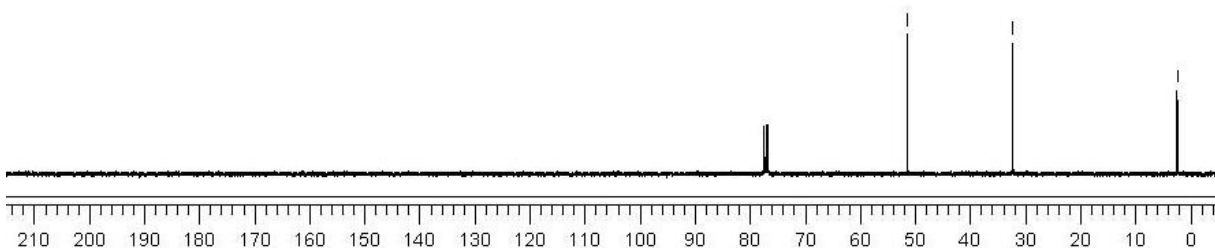
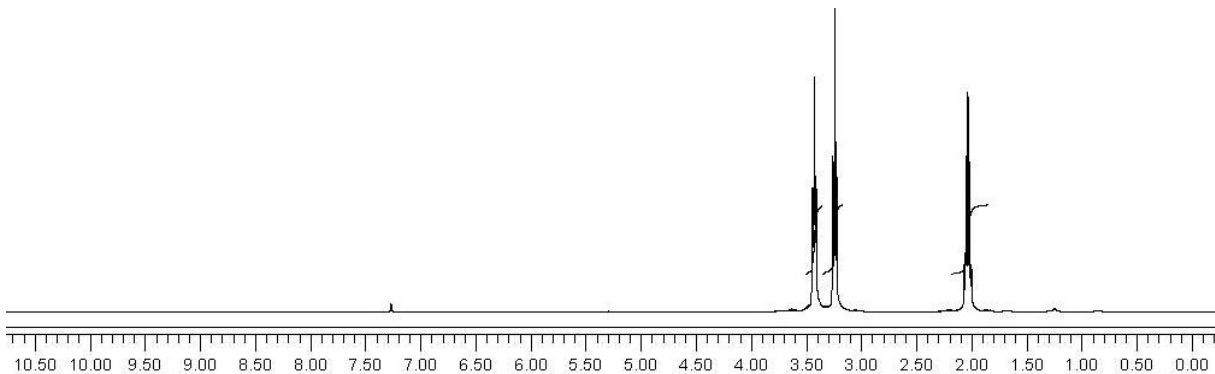
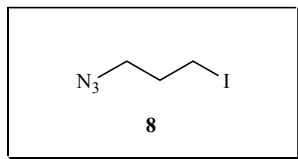


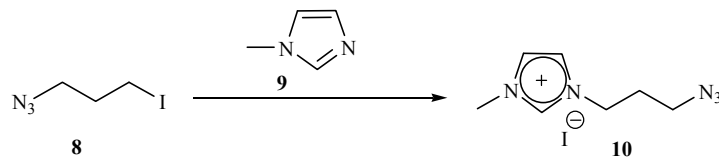
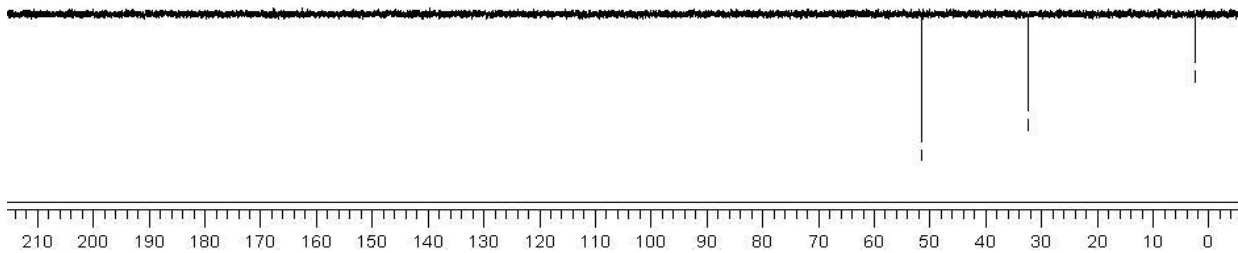


To a vigorously stirred solution of azide **7** (8.14 g, 80.6 mmol) in THF (150 mL) and under argon atmosphere were added PPh₃ (25.36 g, 96.36 mmol) and imidazole (16.46 g, 241.8 mmol). The mixture was stirred until total dissolution of the reagents, then cooled to -20 °C, before adding portionwise I₂ (26.59 g, 104.78 mmol) dissolved in THF (50 mL). The reaction mixture was stirred at -20 °C for 10 mn, then allowed to reach room temperature for 30 mn. The reaction mixture was spurred into ice-water and an saturated aqueous solution of NaHCO₃ (100mL) was added. A precipitate was formed, which was filtered and the filtrate extracted with ether (3 x 120 mL). The combined organic layers were dried over Na₂SO₄, filtered and the solvent rotatory evaporated to afford a residue which was purified by column chromatography on silica (hexane/EtOAc, 7/3) to afford compound **8** (13.4 g, 99%) as a yellow oil. *R*_f = 0.78 (hexane/EtOAc, 7/3).

¹H-NMR (CDCl₃, δ): 3.42 (2H, t, J = 6.34Hz, H-3); 3.24 (2H, t, J = 6.64Hz, H-1); 2.03 (2H, m, H-2)

¹³C-NMR (CDCl₃, δ): 51.48 (CH₂-3); 32.34 (CH₂-2); 2.49 (CH₂-1)





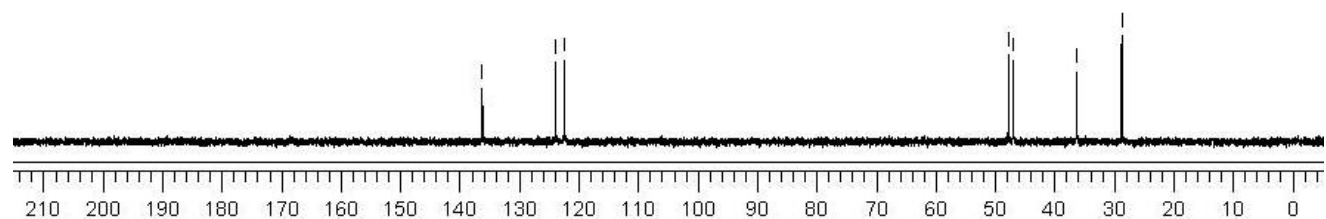
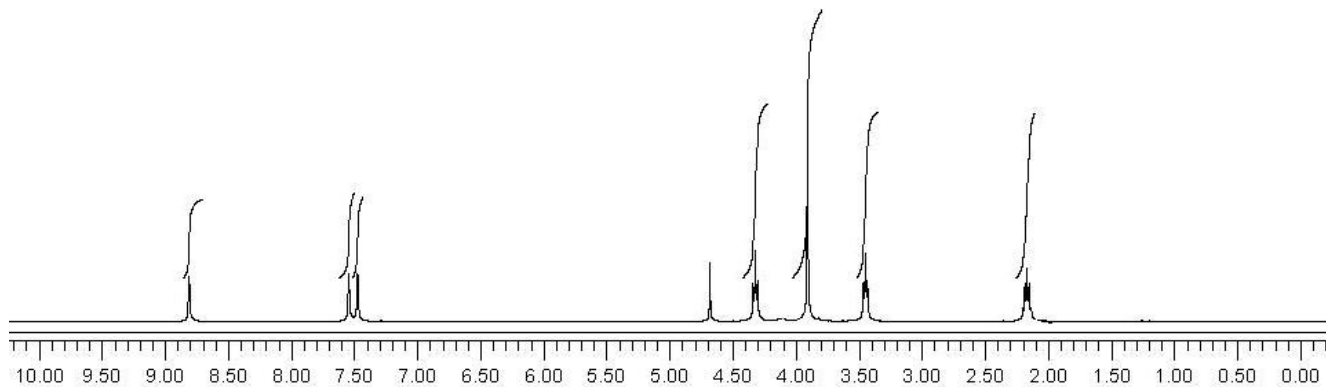
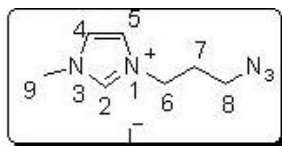
To iodide **8** (3.31 g, 16.82 mmol) was added methylimidazole **9** (1.47 mL, 18.5 mmol) and the mixture stirred at room temperature for 48h. The resulting yellow and viscous oil was washed with EtOAc AcOEt (5 x 25 mL) to yield ionic liquid **10** (4.37 g; 95 %).

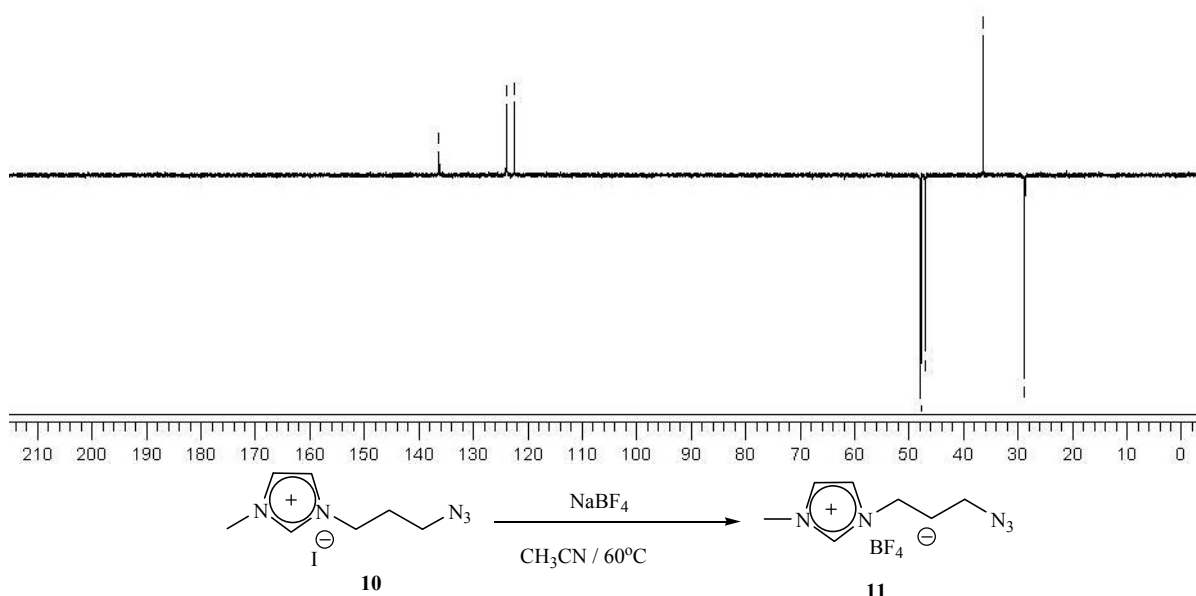
¹H-NMR (D₂O, δ): 8.69 (1H, s, H-2); 7.42 (1H, s, H-4); 7.35 (1H, s, H-5); 4.21 (2H, t, J = 6.9 Hz, H-6); 3.80 (3H, s, H-9); 3.33 (2H, t, J = 6.9, H-8); 2.06 (2H, q, J = 6.7 Hz, H-7).

¹³C-NMR (D₂O, δ): 136.28 (CH-2); 123.95 (CH-4); 122.49 (CH-5); 47.84 (CH₂-6); 47.04 (CH₂-8); 36.37 (CH₃-9); 28.78 (CH₂-7).

IR-(CDCl₃, ν(cm⁻¹)): 3463; 3081; 2871; 2102; 1569; 1455; 1455; 1265; 1166; 1062; 829; 752; 619.

MS (ESI⁺) (m/z, %): 166.11 (cation, 100)





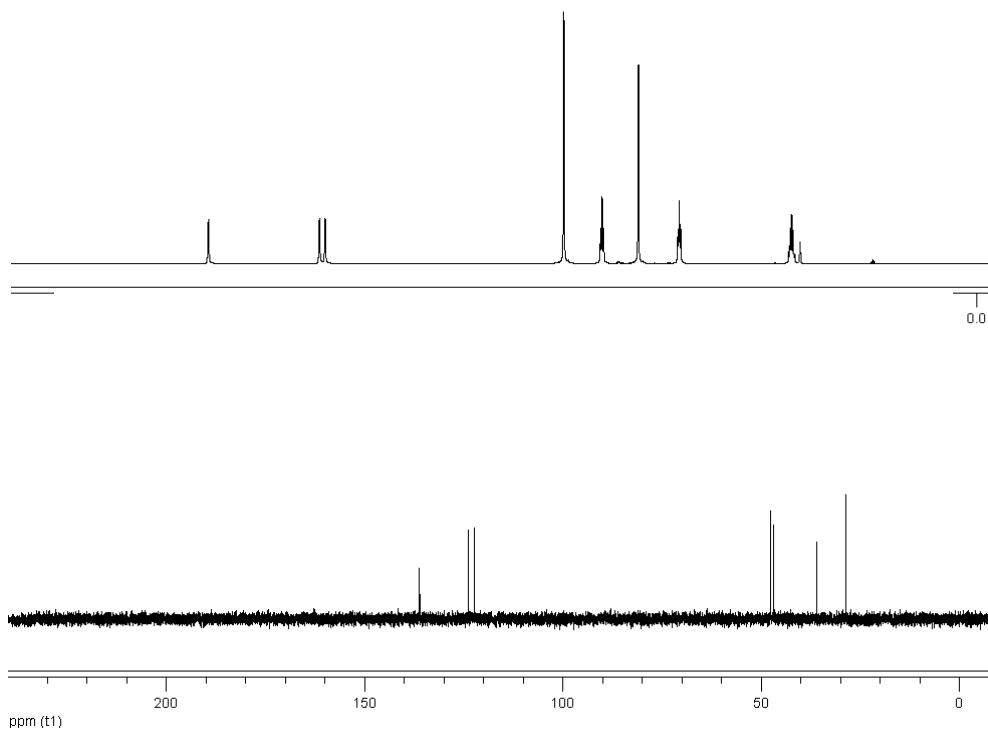
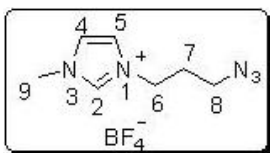
To a solution of **10** (5.23 g, 17.86 mmol) in acetonitrile (40mL) was added NaBF₄ (2.20 g, 19.64 mmol). The mixture was stirred at 60° C for 48 h and the resulting precipitate was filtered off, washed with acetonitrile and the filtrate concentrated under vacuum to afford a yellow viscous oil **11** (4.51 g, 100%).

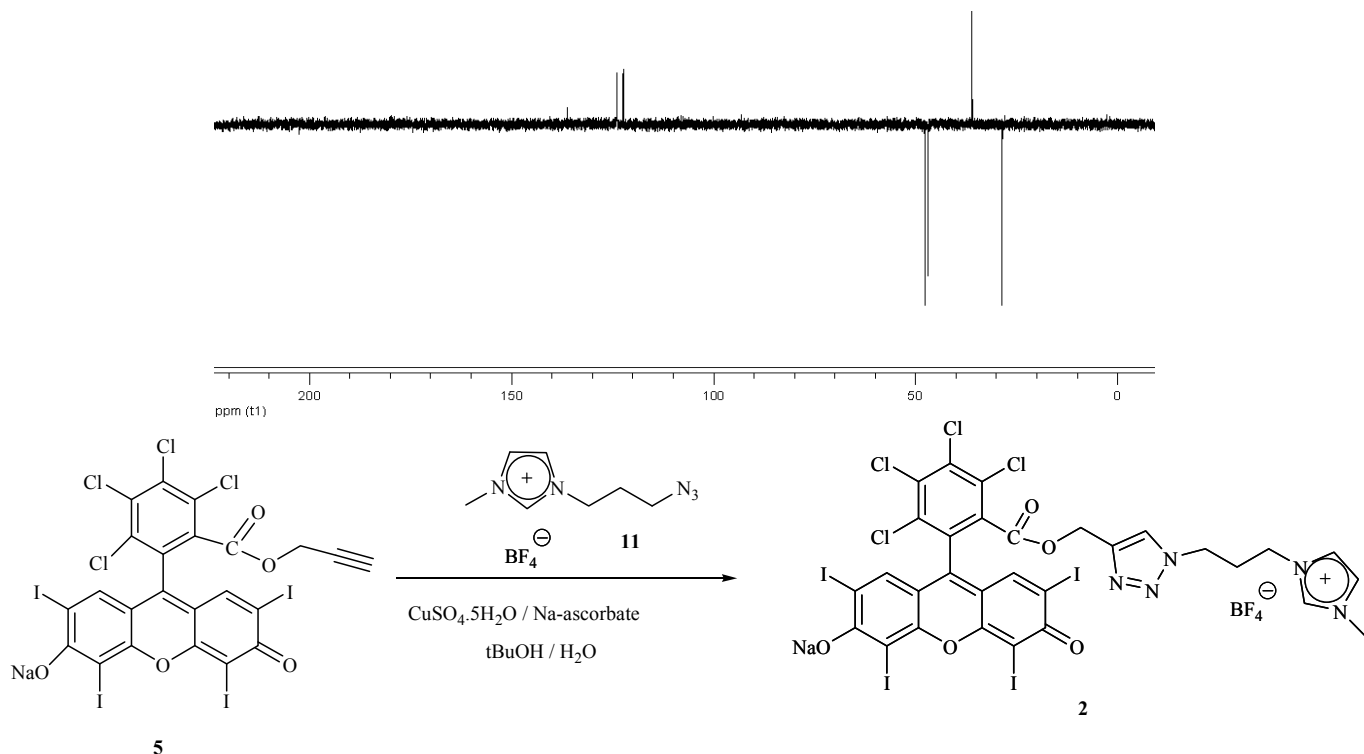
¹H-NMR (D₂O, δ): 8.71 (1H, s, **H**-2); 7.45 (1H, s, **H**-4); 7.39 (1H, s, **H**-5); 4.25 (2H, t, J = 6.9 Hz, **H**-6); 3.83 (3H, s, **H**-9); 3.37 (2H, t, J = 6.4 Hz, **H**-8); 2.10 (2H, q, J = 6.6 Hz, **H**-7).

¹³C-NMR (D₂O, δ): 136.18 (**C**H-2); 123.82 (**C**H-4); 122.34 (**C**H-5); 47.70 (**C**H₂-7); 46.88 (**C**H₂-8); 36.02 (**C**H₃-9); 28.58 (**C**H₂-7).

IR-(CDCl₃, ν(cm⁻¹)): 3463; 3081; 2102; 1569; 1455; 1265; 1166; 1058; 831; 769; 619

MS (ESI⁺) (m/z, %): 166.12 (cation, 100); 167.11 (12); 225.15(2.35).





To a solution of ionic liquid **11** (528.7 mg, 2.09 mmol) in 30 mL of tBuOH/H₂O (2/1) was added compound **5** (2.33 g, 5.95 mmol) a catalytic amount of CuSO₄·5H₂O (5 %), sodium ascorbate (0.42 mL, 0.42 mmol of an 1M solution). The reaction mixture was stirred at room temperature overnight. At the end of the reaction, the solvent was evaporated and the resulting solid was washed with Et₂O (3 x 15 mL), EtOAc (3 x 15 mL), MeOH (3 x 15 mL) then dried under vacuum to afford **2** (2.3 g, 86%) as a rose solid. mp 235-237 °C.

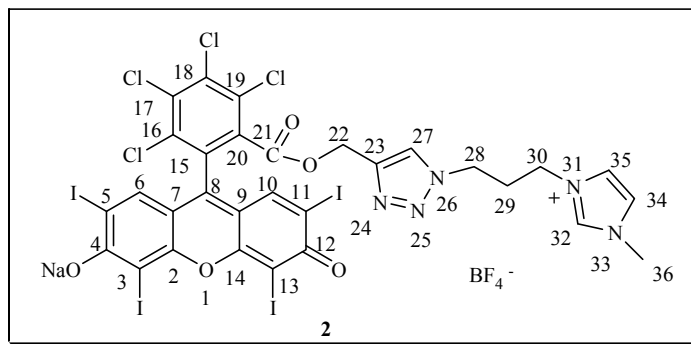
¹H-NMR (DMSO-d₆) δ(ppm): 9.50 (1H, s, **H**-32); 7.90 (1H, t, J=1.75 Hz, **CH**-27); 7.80; 7.79 (2H, s, **H**-34,35); 7.63 (2H, s, **H**-6,10); 4.68 (2H, d, J=2.46 Hz, **H**-22); 4.56 (2H, t, J=7.15 Hz, **H**-30); 4.12 (3H, s, **H**-35); 3.57 (2H, t, J=6.57 Hz, **H**-28); 2.29 (2H, m, **H**-29).

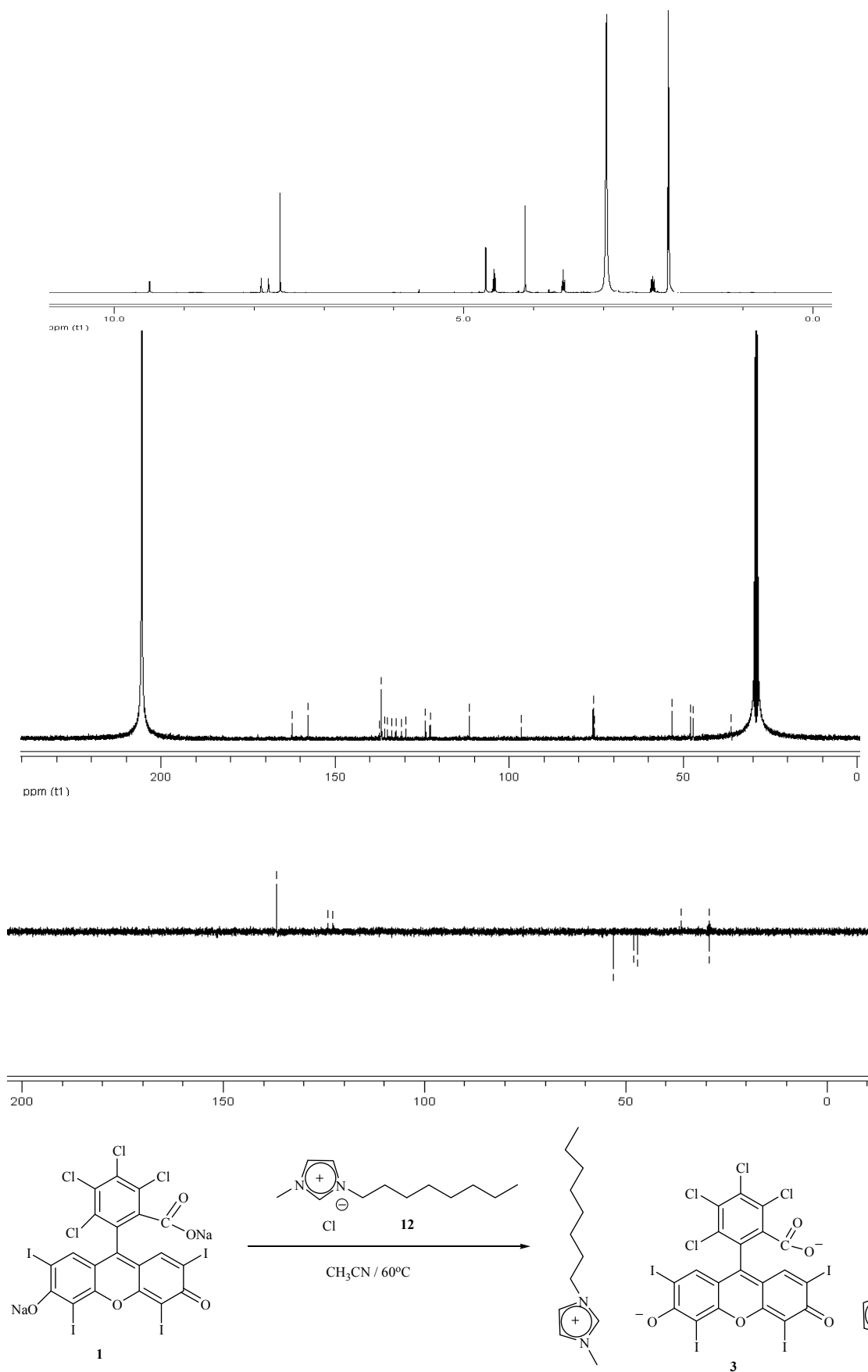
¹³C-NMR (DMSO-d₆) δ(ppm): 174.19 (**C**-4,12); 164.21 (**C**=O); 159.66 (**C**-2,14); 141.29; 137.45; 136.61; 135.47; 134.32; 132.86; 131.47 (**C**-20, 15, 16, 17, 18, 19, 8); 138.39(**CH**-6,10); 125.81 (**CH**- 27); 124.67; 124.45 (**CH**-34,35); 112.82 (**C**-7,9); 98.35 (**C**-3,13); 75.99 (**C**-5,11); 54.89 (**CH**₂-22); 49.73; 48.88 (C-28,30); 37.93 (C-35); 31.52 (CH₂-29)

IR-(CDCl₃, ν(cm⁻¹)): 2360; 2098; 1743 (C=O); 1614; 1546; 1459; 1344; 1247; 1168; 952; 754; 663; 522; 435.

UV (MeOH, λ(nm)): 564; 285; 273; 266; 207.

MS (EI⁺)[m/z,(%)]: X = I: 1175.62([C₃₃H₁₉Cl₄I₄N₃NaO₃]⁺, 100); X = BF₄: 1177.6182 ([M - Na]⁺, 100); 1175.62([C₁₁H₁₀Cl₄I₄N₂₃NaO₄]⁺, 86);





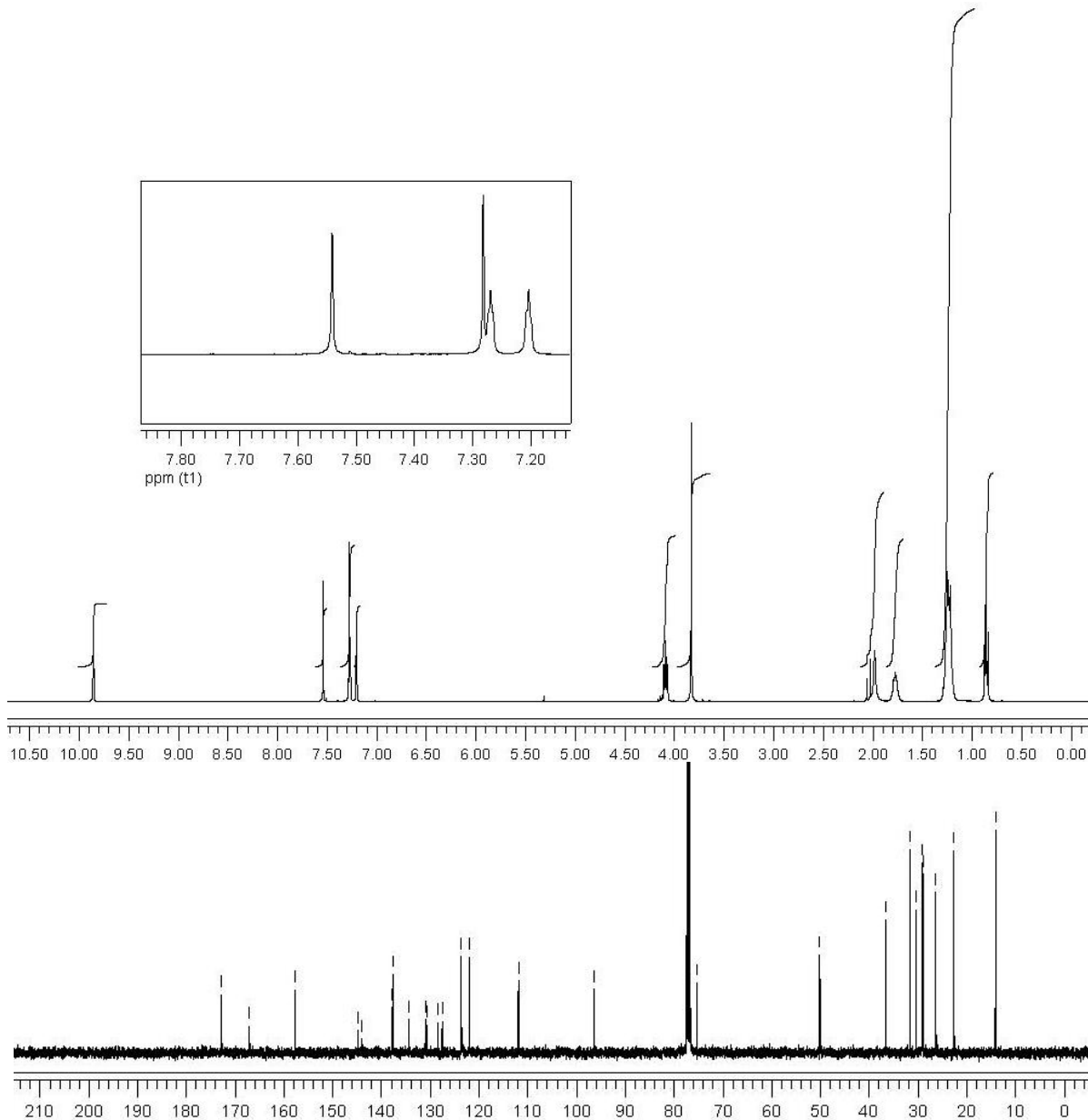
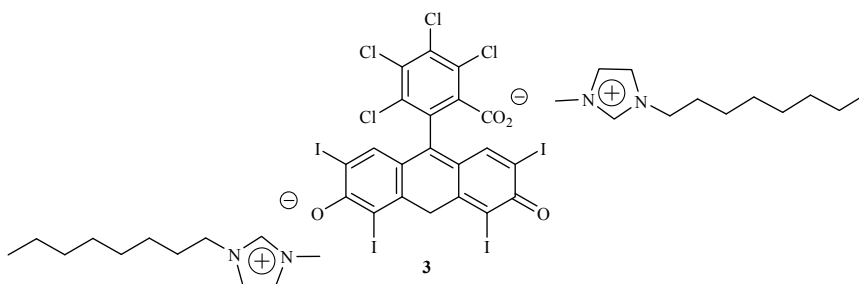
To a stirred solution of [OMIM][Cl] **12** (568 mg, 2.5 mmol) in acetonitrile (15 mL) was added Rose Bengal **1** (1.25 g, 1.23 mmol). The mixture was stirred at 60°C for 24 h then allowed to reach room temperature. The resulting precipitate was filtered,

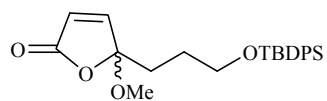
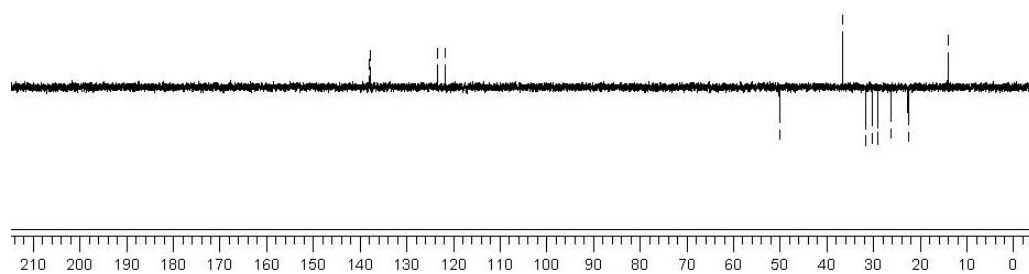
washed with acetonitrile (3 x 20 mL) and the filtrate was concentrated under reduced pressure to afford a deep purple powder which was washed with AcOEt (3 x 20 mL), dried under vacuum to afford **3** (1.14 g, 68%). mp 68-70 °C; IR (CDCl₃) 2923 ; 22852 ; 1614 ; 1545; 1460; 1349; 1225; 1164; 950; 755; 623; 530; 448; 369 cm⁻¹; UV (MeOH, λ(nm)): 555; 518; 318; 211;

¹H-NMR (CDCl₃) δ(ppm): 9.85 (2H, s, **H**-23); 7.54 (2H, s, **H**-6,10); 7.27 (2H, s, **H**-25); 7.20 (2H, s, **H**-26); 4.08 (4H, t, J = 7.51 Hz, **H**-28); 3.83 (6H, s, **H**-36); 1.98 (4H, m, **H**-29); 1.77 (4H, m, **H**-30); 1.29 – 1.22 (8H, m, **H**-31,32,33,34); 0.85 (6H, t, J = 7.09Hz, **H**-35).

¹³C-NMR (CDCl₃) δ(ppm): 172.76 (**C**-4,12); 167.12 (**C**-21); 157.74 (**C**-2,14); 144.80; 144.00; 134.29; 131.02; 130.61; 128.36; 127.56 (**C**-20,15,16,17,18,19,8); 137.79 (**CH**-23); 137.71 (**CH**-6,10); 111.92 (**C**-7,9); 96.44 (**C**-3,13); 75.35 (**C**-5,11); 50.13 (**CH**₂-28); 36.63 (**CH**₃-36); 31.70; 30.34; 29.08; 29.00; 26.33; 22.61 (**CH**₂-29, 30, 31, 32, 33, 34); 14.12 (**CH**₃-35).

MS (ESI) (m/z, %): ESI⁺ 391.28 (cation, 61). ESI⁻ 972.48 (anion, 100); 1166.65 (1cation + anion, 13).





14

