Electronic Supplementary Material (ESI) for RSC Advances.

Synthesis, Optical, Electrochemical Properties and Anticancer Activity of (S)-BINOL Cored, Triazole Bridged, Dendrimers Decorated with Rhodamine B Surface Group

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Supporting Information

Content

Experimental Section

General procedure for Cu (I)-catalyzed 'Click' reaction (Procedure A)

A mixture of the azide and the alkyne in the presence of $CuSO_4.5H_2O$ (5 mol%) and sodium ascarbate (10 mol%) in a mixture of THF–H_2O (1:1) was stirred for 12 h at room temperature and after the completion of the reaction, solvent was evaporated. The residue thus obtained after evaporation of the solvent was dissolved in $CHCl_3$ (150 mL) and washed with NH_4Cl solution (50 mL) and brine solution (50 mL) and dried over Na_2SO_4 and then concentrated to give a residue, which was purified by column chromatography (SiO_2), using the eluent specified under each compound.

General procedure for the conversion of chloride/bromide to azide (Procedure B)

To the dendritic chloride/bromide (1.0 mmol, 1.0 equiv.) dissolved in a mixture of acetone/water (4 : 1, 60 mL) was added NaN_3 (1.5 mmol, 1.5 equiv.) and the reaction mixture was heated to 60 ^oC for 6 h. The reaction mixture was then cooled to room temperature. The solvent was evaporated and the reaction mixture was diluted with water (100 mL), and extracted with EtOAc (2 ×100 mL). The combined organic layer was washed with saturated NaCl (100 mL), dried over Na_2SO_4 and then solvent was evaporated to give the corresponding azido compound.

Zeroth generation dendrimer 1

Following the general procedure A 1.0 equiv. of the bispropargyloxy (S) -BINOL **12** (0.8g, 0.20 mmol) was reacted with 2.1 equiv. of the dendritic azide **6** (0.30g, 0.62 mmol,) to give the

zeroth generation dendrimer **1** as brown solid, after purification from silica gel column with $CHCl_3$-MeOH as eluent (19.5:0.5). Yield : 87%. M.P : 112–114 ^oC. ^1H NMR : (300 MHz, $CDCl_3$): δ_H 1.14 (t, 24H, *J* = 7.2Hz); 3.32 (q, 16H, *J* = 6.3Hz); 3.59 (t, 4H, *J* = 7.5Hz), 4.16 (t, 4H, *J* = 7.2Hz), 5.21 (s, 4H); 6.19 (d, 3H, *J* = 8.7Hz); 6.29-6.6. 34 (m, 5H); 6.38 (s, 4H); 6.49 (d, 1H, *J*= 6.9Hz); 7.06-7.09 (m, 2H); 7.11-7.15 (m, 3H); 7.18-7.21 (m, 2H); 7.38-7.41 (m, 2H); 7.46-7.49 (m, 6H); 7.73 (d, 2H, *J* = 7.8Hz); 7.81 (d, 2H, *J* = 8.4Hz); 7.9 (s, 2H). ^{13}C NMR :(75 MHz, $CDCl_3$): δ_C 12.5, 44.3, 46.2, 47.8, 61.8, 65.1, 97.8, 104.7, 108.2, 114.0, 122.9, 123.9, 128.2, 128.4, 130.5, 132.8, 139.2, 148.9, 153.3, 153.4, 159.7, 168.3. Elemental Analysis. calcd for $C_{86}H_{86}N_{12}O_6$: C, 74.65 ; H, 6.26; N, 12.15%. Found: C, 73.38; H, 6.06; N, 11.91%.

First generation dendrimer 2

Following the general procedure A 1.0 equiv. of the bispropargyloxy (S)-BINOL **12** (0.100g, 0.27 mmol) was reacted with 2.1 equiv. of the dendritic azide **9** (0.73g, 0.58 mmol) to give the first generation dendrimer **2** as dark red solid, after purification from silica gel column with $CHCl_3$-MeOH as eluent (19:1). Yield: 86%. M.P: 122–123 ^oC. ^1H NMR : (300 MHz, $CDCl_3$): δ_H 1.12 (s, 48H); 3.30 (s, 32H); 3.87 (t, 8H, *J* = 7.5Hz), 4.27 (t, 8H, *J* = 7.2Hz), 5.10 (s, 8H); 5.26 (s, 4H); 5.38 (s, 4H); 6.18 (s, 9H); 6.23 (d, 9H, *J* =7.8Hz); 6.38 (s, 9H); 6.50 (s, 2H); 6.62 (d, 3H, *J* = 8.1Hz); 6.79-6.91 (s, 2H); 7.06 (d, 6H, *J* = 3Hz); 7.20 (d, 2H, *J* = 5.4Hz); 7.43 (s, 2H); 7.53 (s, 9H); 7.61-7.71 (m, 3H); 7.86 (s, 3H); 8.02 (s, 5H). ^{13}C NMR : (75 MHz, $CDCl_3$): δ_C 12.5, 44.3, 46.2, 48.8, 59.0, 60.2, 61.8, 65.1, 97.9, 98.2, 104.7, 108.3, 114.0, 122.9, 123.4, 123.9, 125.2, 126.3, 128.2, 128.4, 129.4, 130.5, 132.8, 133.08, 139.2, 148.9, 153.3, 153.4, 159.7, 168.3. Elemental Analysis. calcd for $C_{172}H_{176}N_{30}O_{14}$: C, 71.55 ; H, 6.14; N, 14.55%. Found: C, 70.44; H, 6.01; N, 14.38%.

Second generation dendrimer 3

Following the general procedure A 1.0 equiv. of the bispropargyloxy (S)-BINOL **12** (0.17g, 0.46 mmol, 1.0 equiv.) was reacted with 2.1 equiv. of the dendritic azide **11** (1.26g, 0.98 mmol) to give the second generation dendrimer **3** as dark red solid, after purification from silica gel column with $CHCl_3$-MeOH as eluent (19:1)**.** Yield: 78%. M.P: 131–132 ^{o}C. ^{1}H NMR : (300 MHz, $CDCl_3$): δ_H 1.14 (s, 96H); 3.31 (s, 64H); 3.81 (t, 16H, J = 7.5Hz); 4.60 (t, 16H, J = 7.2Hz), 5.01 (s, 4H); 5.26 (s, 24H); 5.37 (s, 12H); 6.25 (s, 16H); 6.35-6.38 (m, 19H); 6.71 (s, 10H); 6.91 (s, 12H); 7.08 – 7.14 (m, 8H); 7.44 (s, 12H); 7.51-7.54 (m, 22H); 7.57-7.87(m, 16H); 7.97 (m, 10H). ^{13}C NMR : (75 MHz, $CDCl_3$): δ_C 12.6, 44.3, 47.4, 53.8, 62.5, 64.1, 65.1, 97.9, 98.2, 104.8, 108.2, 109.0, 120.7, 122.4, 122.9, 123.9, 125.3, 126.3, 128.0, 128.2, 128.4, 128.5, 129.5, 130.4, 132.8, 133.0, 133.8, 144.2, 148.9, 153.2, 153.5, 153.7, 153.9, 168.6. Elemental Analysis. calcd for $C_{345}H_{357}N_{65}O_{30}$: C, 70.30; H, 6.11 ; N, 15.45%. Found: C, 69.89; H, 6.01; N, 15.01%.

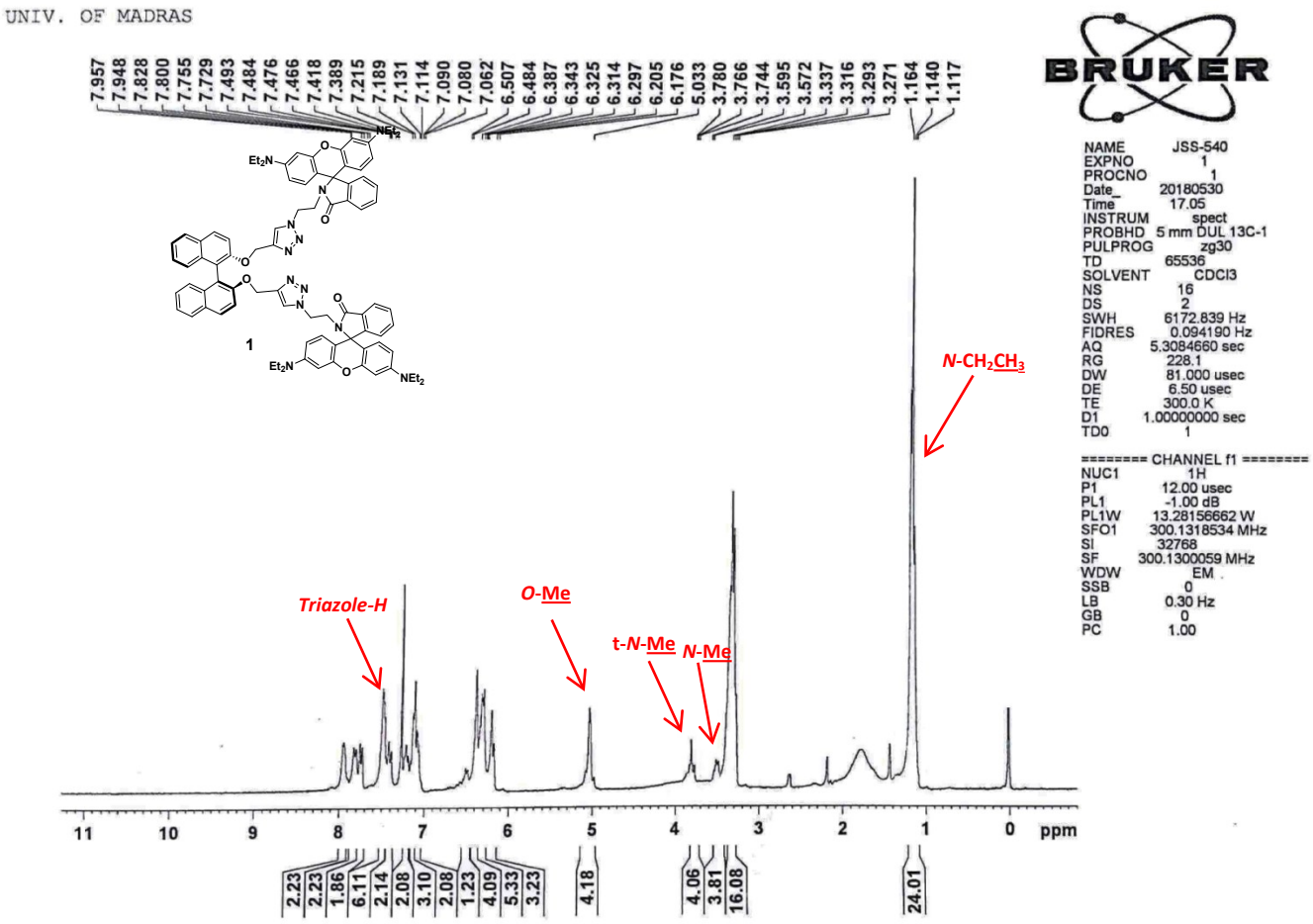
Second generation chloro dendron 10

Using general procedure A the dendritic chloride **10** was obtained as pink solid from the 3,5-bispropargyloxy benzyl chloride **7** (0.250 g, 1.07 mmol) and the rhodamine azide **6** (1.14 g, 2.24 mmol) after purification from silica gel column with $CHCl_3$: MeOH as eluent (19:1). Yield: 86%. ^{1}H NMR : (300 MHz, $CDCl_3$): δ_H 1.15 (t, 48H, J = 6.6Hz); 3.30-3.32 (q, 32H, J = 6.6Hz); 3.59 (t, 8H, J = 7.5Hz), 4.16 (t, 8H, J = 7.2Hz); 4.68 (s, 2H); 5.03 (s, 12H); 5.40 (s, 4H); 6.25 (s, 11H); 6.37 (d, 12H, 8.2Hz); 6.45-6.49 (m, 10H); 7.08 (m, 4H); 7.44 (s, 8H); 7.58 (s, 6H); 7.87 (s, 4H). ^{13}C NMR: (75 MHz, $CDCl_3$): δ_C 12.5, 41.9, 42.0, 44.3, 64.8, 69.3, 98.3, 105.8,

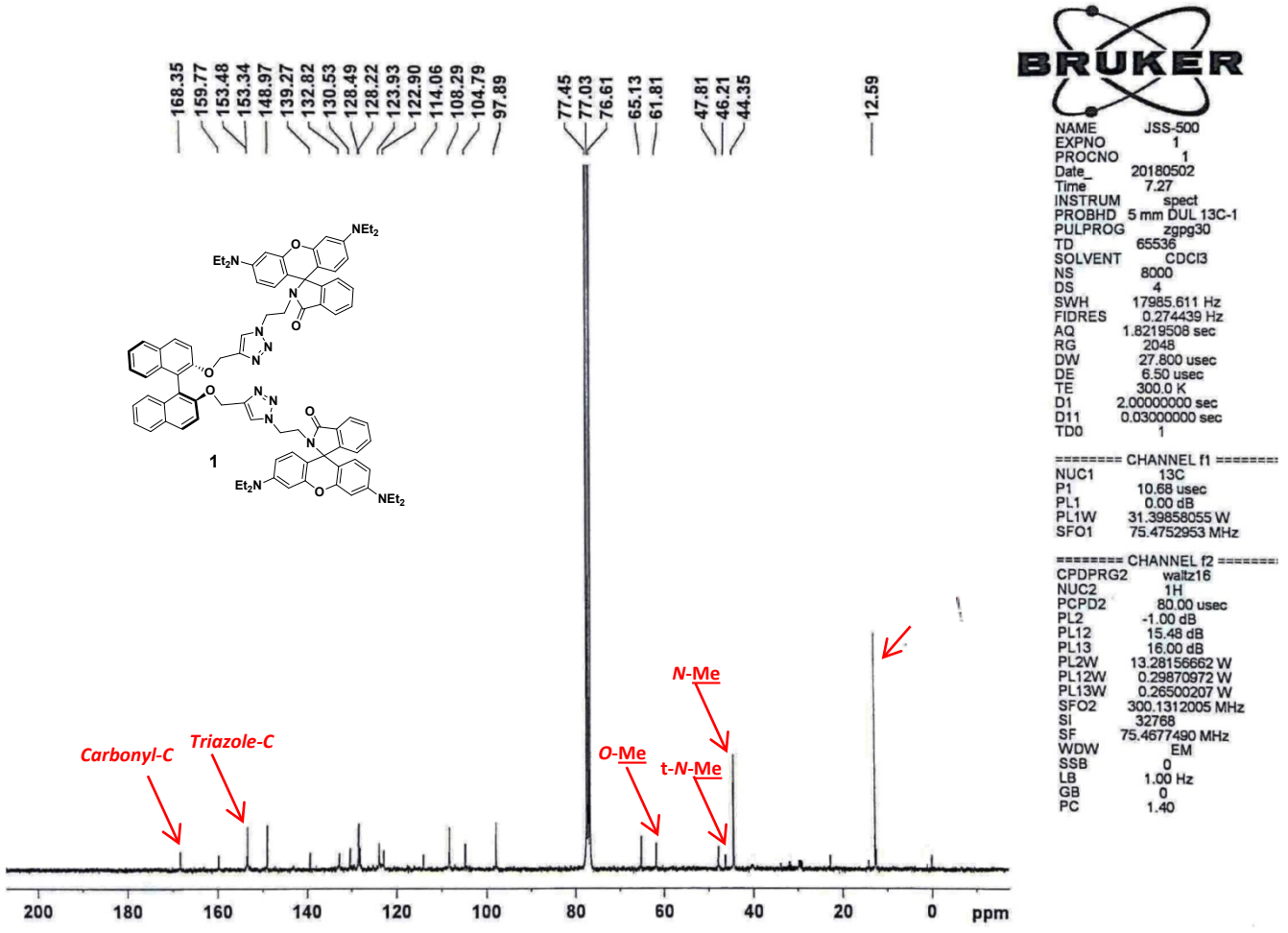
108.5, 122.8, 123.7, 127.9, 128.5, 130.8, 132.4, 149.2, 153.3, 153.5, 167.8, 168.0. Elemental Analysis. calcd for $C_{59}H_{169}ClN_{30}O_{14}$: C, 69.20; H, 6.17; N, 15.23%. Found: C, 68.91; H, 5.89; N, 14.92%.

Second generation azido dendron 11

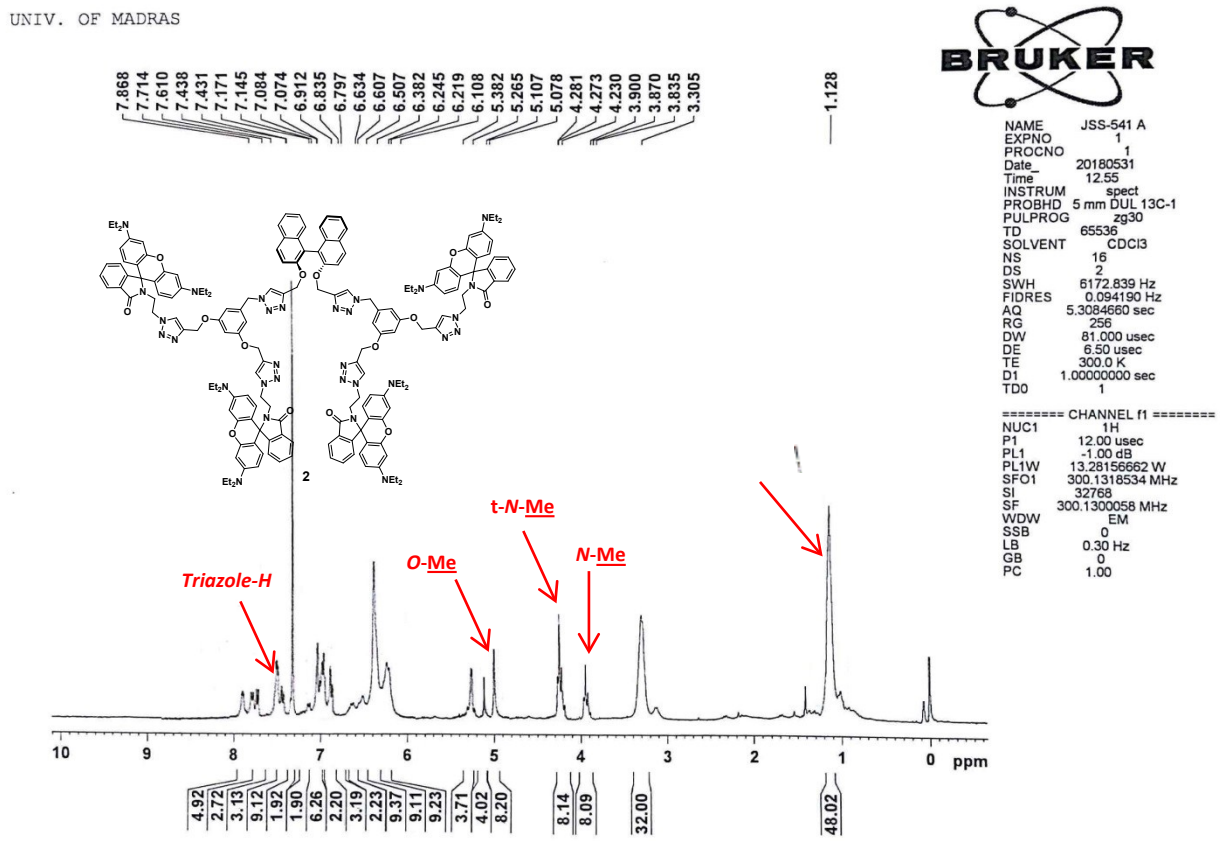
Using the general procedure B, the dendritic azide **11** was obtained as pink solid from the dendritic chloride **10** (1.02 g, 0.40 mmol) and sodium azide (0.06 g, 1.20 mmol) after purification from silica gel column with $CHCl_3$ as eluent. Yield : 92%. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.14 (t, 48H, J = 6.0 Hz); 3.30-3.31 (q, 32H, J = 6.3Hz); 3.57 (s, 2H); 3.59 (t, 8H, J = 7.5Hz), 4.16 (t, 8H, J = 7.2Hz), 5.03 (s, 12H); 5.13 (s, 4H); 6.23 (d, 10H, J = 8.4Hz); 6.36 (d, 12H, 7.8Hz); 6.46 (s, 3H); 6.53 (s, 8H); 7.07 (s, 4H); 7.44 (s, 8H); 7.57(s, 6H); 7.87 (s, 4H). ^{13}C NMR: (75 MHz, $CDCl_3$): δ_C 12.6, 40.1, 44.3, 47.8, 61.8, 65.2, 97.8, 104.7, 108.3, 114.0, 122.9, 123.9, 128.2, 128.4, 130.4, 132.8, 139.2, 148.9, 153.3, 153.4, 159.8, 168.4.



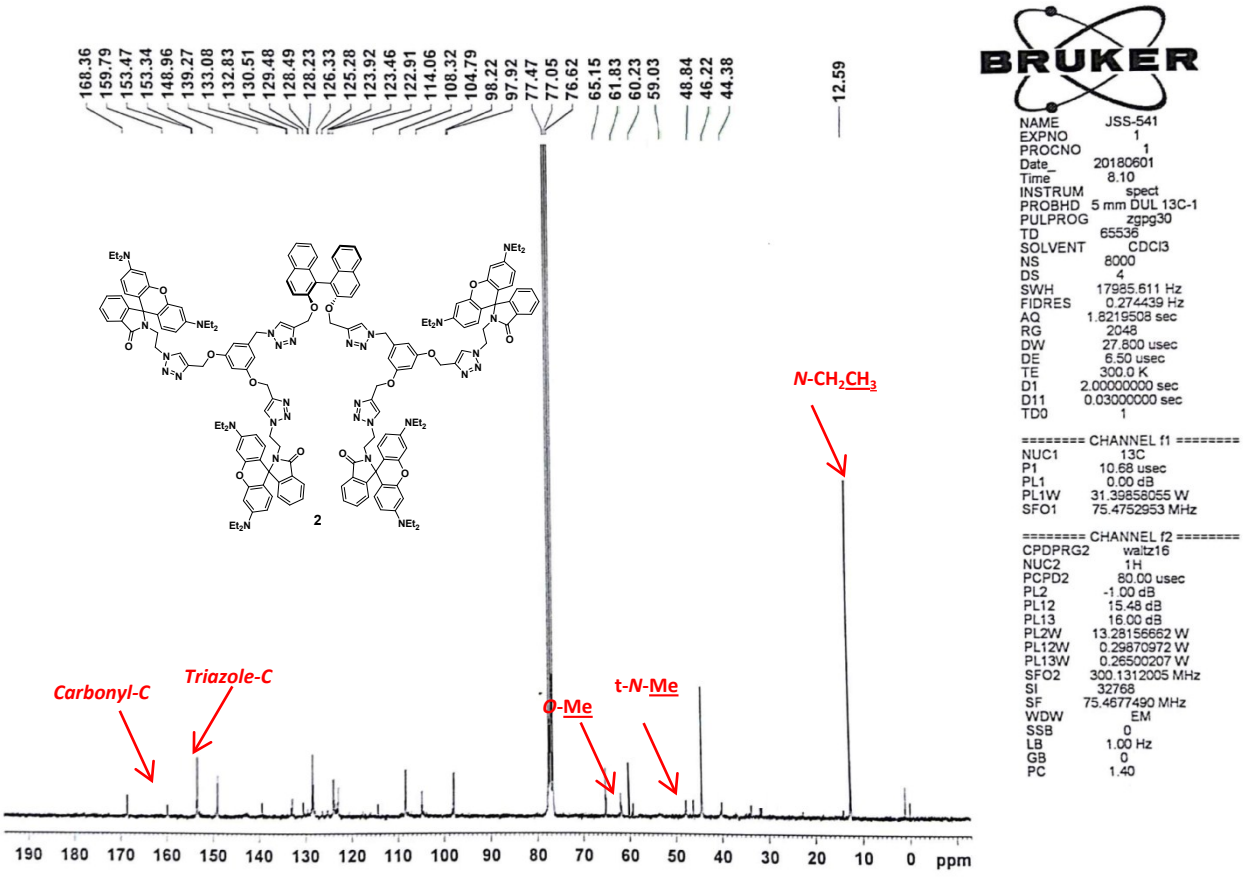
^{1}H NMR Spectrum (300MHz, $CDCl_3$) of dendrimer 1



^{13}C NMR spectrum (75MHz, $CDCl_3$) of dendrimer 1



^{1}H NMR Spectrum (300MHz, $CDCl_3$) of dendrimer 2



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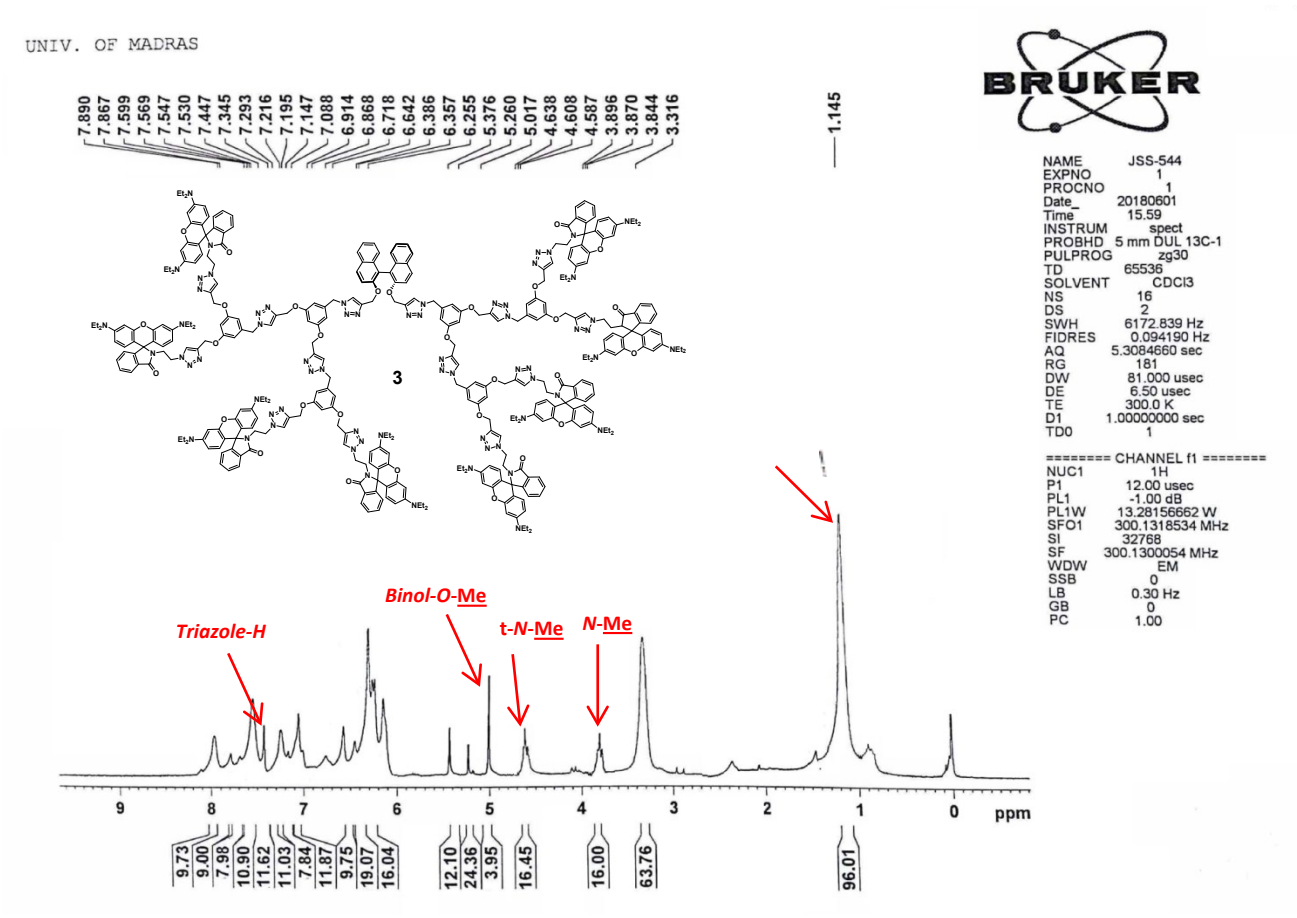
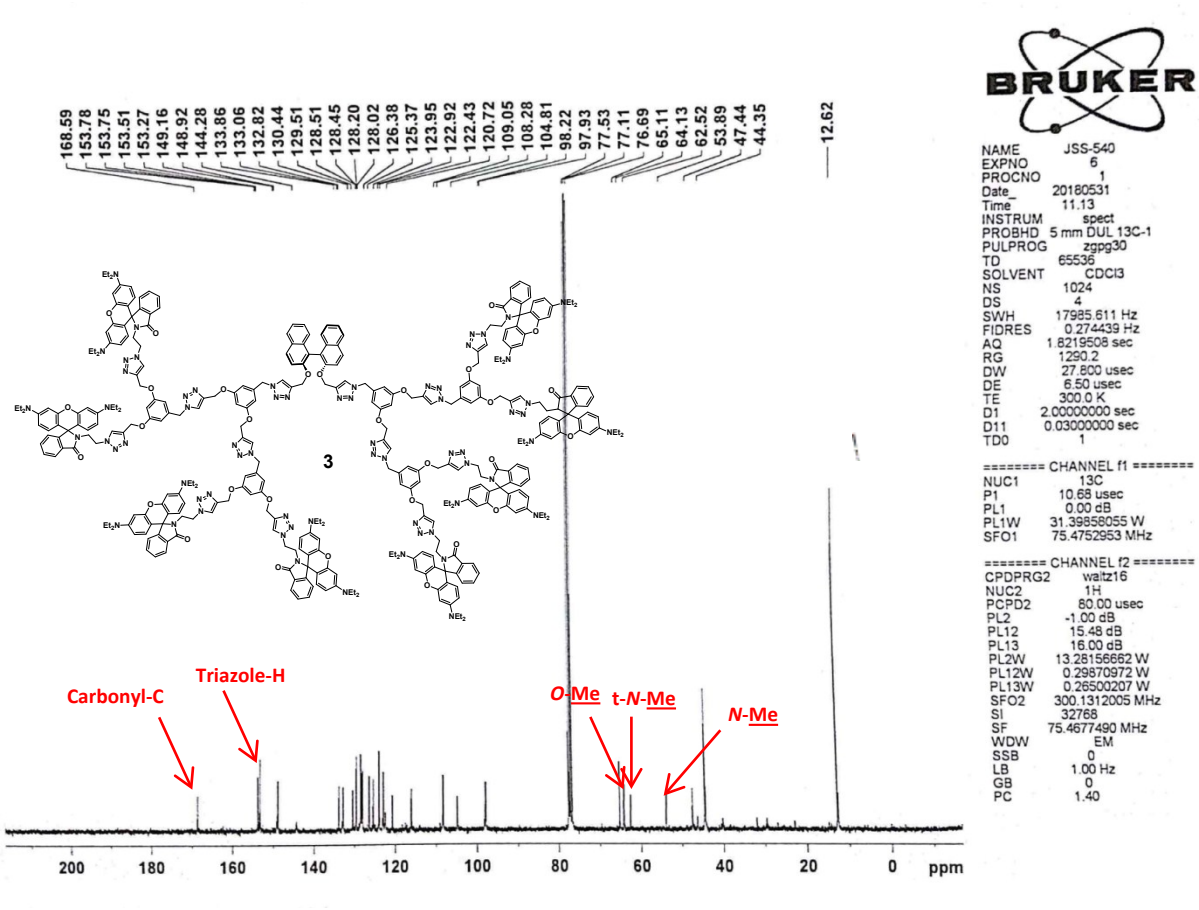
^{13}C NMR spectrum (75MHz, $CDCl_3$) of dendrimer 2



^{1}H NMR Spectrum (300MHz, $CDCl_3$) of dendrimer 3



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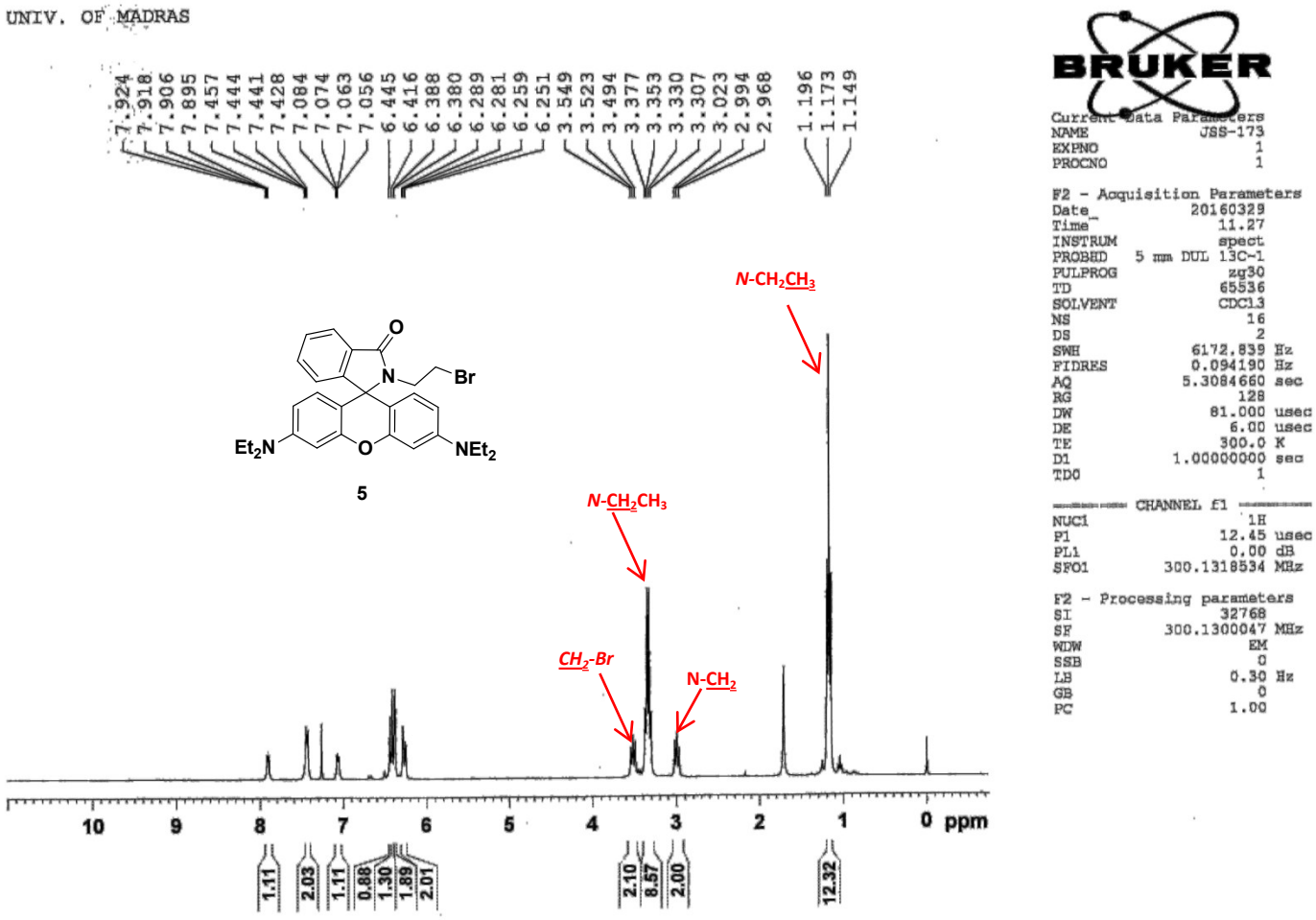
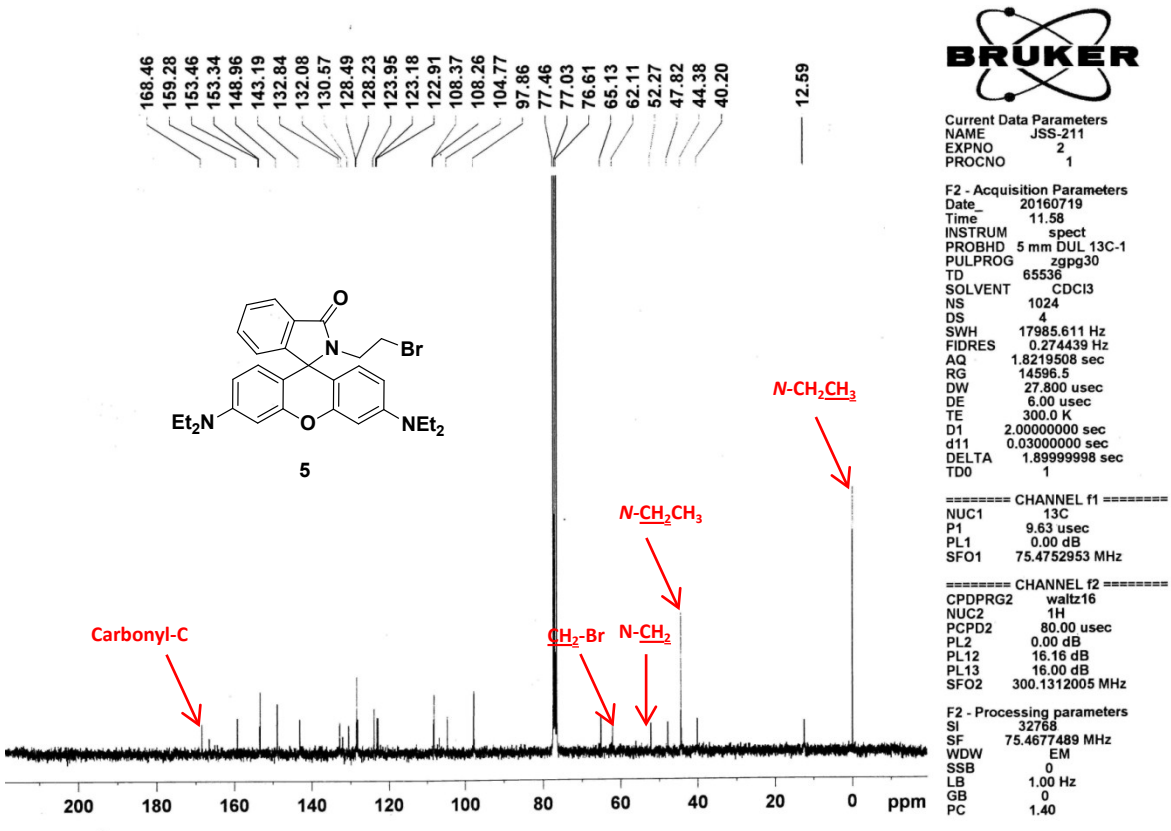
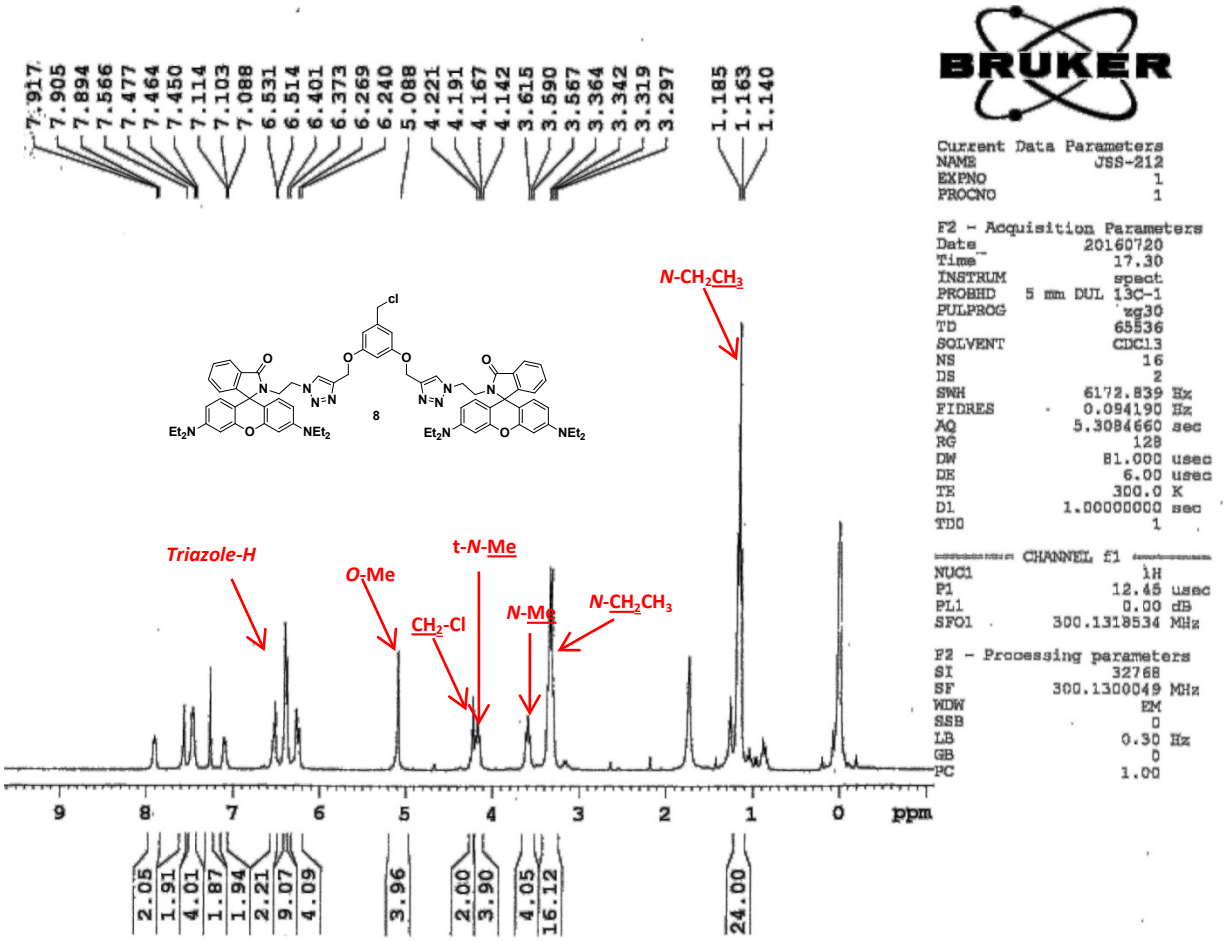


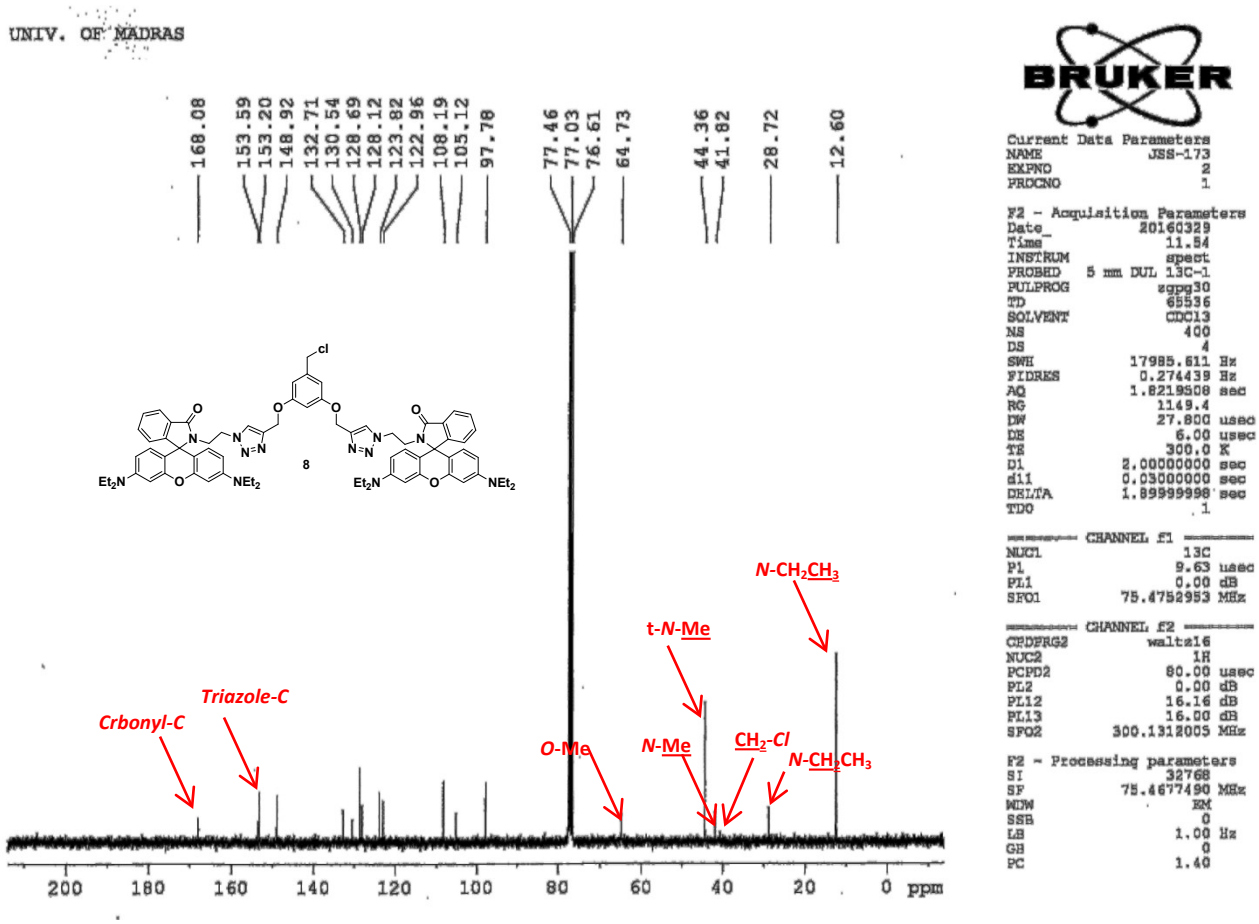
^{1}H NMR Spectrum (300MHz, $CDCl_3$) of rhodamine b bromo dendron 5[19]



^{13}C NMR spectrum (75MHz, $CDCl_3$) of rhodamine b bromo dendron 5[19]



^{1}H NMR Spectrum (300MHz, $CDCl_3$) of rhodamine b chloro dendron 8[19]



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