Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION

A Fluorescent bistable [2]rotaxane molecular switch on SiO_2 nanoparticles

Zhan-Qi Cao, Qi Miao, Qi Zhang, Hong Li, Da-Hui Qu* and He Tian

Experimental Section

General Methods

^1H NMR and ^{13}C NMR spectra were measured on a Brüker AV-400 spectrometer. The electronic spray ionization (ESI) mass spectra were acquired on an LCT Premier XE mass spectrometer. UV−Vis absorption spectra and fluorescence spectra were recorded on a Varian Cary 100 spectrometer and a Varian Cary Eclipse (1 cm quartz cells), respectively. SEM images were recorded on a JSM-6360LV apparatus. Confocal fluorescence micrographs were measured on a NIKON A1R confocal laser scanning microscope.

Materials

Chemicals were used as received from Acros, Aldrich, Fluka, or Merck. All solvents were reagent grade and were dried and distilled prior to use according to standard procedures. The molecular structures were confirmed using ^1H NMR, ^{13}C NMR spectroscopies and High Resolution ESI mass spectrometry. Ferrocene-containing DB24C8 crown ether **3**, the alkyne **4** and compound **9** were synthesized according to previous reports.[1,2,3]

Synthesis

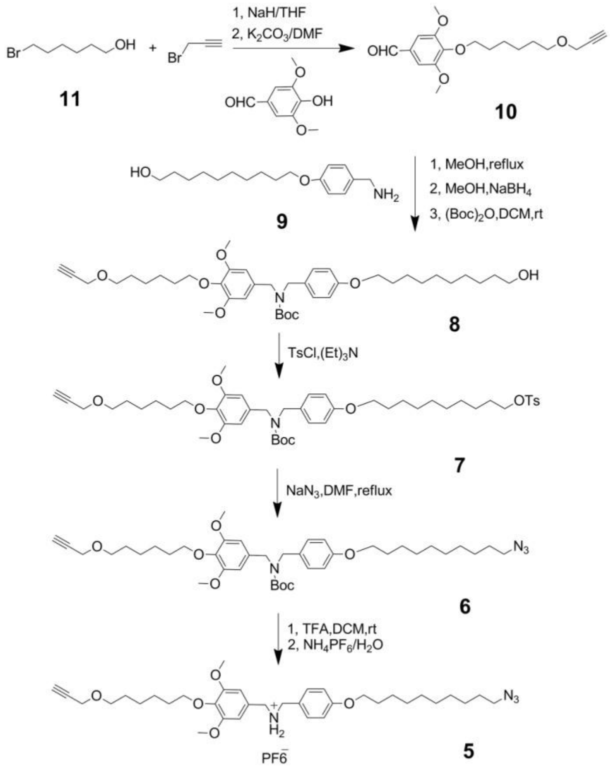


Figure S1. Syntheses of compound **5**.

Compound **10**: A mixture of compound **11** (0.7 g, 3.87 mmol) and 3-bromopropyne (2.27 g, 19.08 mol) in dry THF (20 mL) was added solid NaH (280 mg, 11.67 mmol). The resulting suspension was stirred at room temperature for 24 h, then the reaction mixture was diluted with water (50 mL) and extracted with CH_2Cl_2 (3×25 mL). The organic layer was washed with water (3×50 mL), dried over Na_2SO_4 and evaporated in vacuo to give a brown liquid. The brown liquid was then dissolved in dry DMF (25 mL), then added 3,5-dimethoxy-4-hydroxybenzaldehyde (1.0 g, 5.49 mmol) and K_2CO_3 (1.26 g, 9.12 mmol) and the mixture was stirred overnight under Ar atmosphere at 80 ^{o}C. The mixture was poured into 100 mL water and extracted with ethyl acetate (3×50 mL). The organic layer was washed with brine (3×100 mL), dried over Na_2SO_4 and evaporated in vacuo to give a dark brown liquid, and purification was performed by column chromatography (SiO_2, CH_2Cl_2/MeOH = 50/1) to yield product **10** as a brown liquid (0.52 g, 42.0 %). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 9.83 (s, 1H), 7.09 (s, 2H), 4.10 (d, *J* = 2.0 Hz, 2H), 4.04 (t, *J* = 6.4 Hz, 2H), 3.88 (s, 6H), 3.49 (t, *J* = 6.4 Hz, 2H), 2.43-2.37 (m, 1H), 1.77-1.70 (m, 2H), 1.63-1.56 (m, 2H), 1.50-1.36 (m,4H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 190.1, 152.9, 142.0, 130.6, 105.7, 79.0, 73.2, 72.5, 69.1, 57.0, 55.2, 29.0, 28.5, 24.8, 24.6. HRMS (ESI) (m/z): $[M+Na]^+$ calcd for $C_{18}H_{24}O_5Na$, 343.1521; found, 343.1517.

Compound **8**: A mixture of compound **10** (0.69 g, 2.15 mmol) and compound **9** (0.72g, 2.58 mmol) in dry MeOH (50 mL) was refluxed overnight under argon atmosphere. After being cooled to room temperature, the reaction mixture was added $NaBH_4$ (0.41 g, 10.77 mmol) in portion under ice bath. After the mixture was stirred for 10 h, the solution was poured into water (100 mL) and extracted by CH_2Cl_2 (3 × 50 mL). The organic layer was dried over anhydrous sodium sulfate, and then concentrated to give the free amine compound. The mixture was then dissolved in dry CH_2Cl_2 (10 mL), then added Boc_2O (4.6 g, 21.08 mmol) and the mixture was stirred overnight. The solvent was removed under vacuum, the crude product was purified via column chromatography (SiO_2, CH_2Cl_2/MeOH = 100/1) to give compound **8** (1.10 g, 74.7%) as a white solid.^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.21-7.05 (m, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.41 (s, 1H), 6.35 (s, 1H), 4.36-4.23 (m, 4H), 4.13 (d, *J* = 2.0 Hz, 2H), 3.93 (t, *J* = 6.4 Hz, 4H), 3.78 (s, 6H), 3.63 (t, *J* = 6.4 Hz, 2H), 3.52 (t, *J* = 6.4 Hz, 2H), 2.41 (t, *J* = 2.4 Hz, 1H), 1.79-1.73 (m, 4H), 1.67-1.54 (m, 5H), 1.49-1.41 (m, 15H), 1.39-1.21 (m, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 158.4, 156.0, 153.4, 136.3, 129.8, 129.4, 128.8, 114.5, 105.0, 104.4, 80.0, 74.2, 73.3, 70.2, 68.0, 62.8, 58.0, 56.1, 32.7, 30.0, 29.5, 29.4, 29.3, 28.5, 26.0, 25.9, 25.8, 25.7. HRMS (ESI) (m/z): $[M+Na]^+$ calcd for $C_{40}H_{61}NO_8Na$, 706.4295; found, 706.4289.

Compound **7**: The compound **8** (0.294 g, 0.43 mmol) and TsCl (0.16 g, 0.84 mmol) were dissolved in dry CH_2Cl_2 (10 mL), then added Et_3N (0.22 g, 2.17 mmol). The mixture was stirred at room temperature for overnight and then evaporated in vacuo to give a crude product, which was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH = 100/1) to yield product **7** (0.207 g, 57.5 %). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.20-7.05 (m, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.41 (s, 1H), 6.35 (s, 1H), 4.40-4.20 (m, 4H), 4.12 (d, *J* = 2.4 Hz, 2H), 4.01 (t, *J* = 6.4 Hz, 2H), 3.96-3.88 (m, 4H), 3.78 (s, 6H), 3.51 (t, *J* = 6.8 Hz, 2H), 2.44 (s, 3H), 2.41 (t, *J* = 2.4 Hz, 1H), 1.80-1.72 (m, 4H), 1.66-1.59 (m, 4H), 1.49 (s, 9H), 1.47-1.37 (m, 6H), 1.32-1.21 (m, 10H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 158.4, 156.0, 153.5, 144.6, 133.2, 129.8, 129.4, 128.8, 127.9, 114.5, 105.0, 104.4, 80.0, 74.1, 73.3, 70.7, 70.2, 68.0, 58.0, 56.1, 30.0, 29.5, 29.4, 29.3, 28.9, 28.8, 28.5, 26.0, 25.9, 25.7, 25.3, 21.6. HRMS (ESI) (m/z): $[M+Na]^+$ calcd for $C_{40}H_{67}NO_{10}SNa$, 860.4383; found, 860.4391.

Compound **6**: In a 25 mL flask, compound **7** (0.398 g, 0.47 mmol) and NaN_3 (0.15 g, 2.31 mmol) were mixed in dry DMF (10 mL), and the mixture was stirred overnight under Ar atmosphere at 80 ^oC. The mixture was poured into 50 mL water and extracted with ethyl acetate (3×25 mL). The organic layer was washed with brine (3×50 mL), dried over Na_2SO_4 and evaporated in vacuo to give a crude product, and purification was performed by column chromatography (SiO_2, CH_2Cl_2/MeOH = 100/1). Compound **6** (0.16 g, 47 %) was obtained as a brown solid. ^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.20-7.05 (m, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.41 (s, 1H), 6.35 (s, 1H), 4.36-4.20 (m, 4H), 4.13 (d, *J* = 2.0 Hz, 2H), 3.93 (t, *J* = 6.8 Hz, 4H), 3.79 (s, 6H), 3.52 (t, *J* = 6.8 Hz, 2H), 3.25 (t, *J* = 6.8 Hz, 2H), 2.41 (t, *J* = 2.4 Hz, 1H), 1.83-1.70 (m, 4H), 1.69-1.60 (m, 5H), 1.53-1.40 (m, 16H), 1.35-1.28 (m, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 171.1, 158.4, 156.0, 153.5, 129.8, 129.4, 128.8, 114.4, 105.1, 104.4, 80.0, 74.1, 73.3, 70.2, 68.0, 60.4, 60.0, 56.0, 51.5, 49.1, 49.0, 30.0, 29.7, 29.5, 29.4, 29.3, 29.1, 28.8, 28.5, 26.7, 26.0, 25.9, 25.7, 21.0, 14.2. HRMS (ESI) (m/z): $[M+ H]^+$ calcd for $C_{40}H_{61}N_4O_7$, 709.4540; found, 709.4537.

Compound **5**: TFA (0.1 mL, 1.32 mmol) was added to a solution of compound **6** (47 mg, 0.07 mmol) in dichloromethane (5 mL) and the mixture was stirred for 10 h. A saturated aqueous solution of NH_4PF_6 (5 mL) was added to the reaction mixture for 4 h. The organic layer was separated and evaporated under reduced pressure to get the yellow solid, which was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH = 100:1) to afford product **5** (46 mg, 91.9 %) as a brown solid. ^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.39 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.58 (s, 2H), 4.18 (s, 2H), 4.09 (d, *J* = 2.0 Hz, 2H), 4.06 (s, 2H), 3.91 (t, *J* = 6.4 Hz, 2H), 3.80-3.69 (m, 8H), 3.47 (t, *J* = 6.8 Hz, 2H), 3.24 (t, *J* = 6.8 Hz, 2H), 2.41 (t, *J* = 2.0 Hz, 1H), 1.81-1.70 (m, 2H), 1.62-1.52 (m, 4H), 1.48-1.4 (m, 4H), 1.40-1.26 (m, 16H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 160.5, 153.5, 137.0, 131.5, 125.1, 121.3, 115.3, 106.8, 80.0, 74.2, 73.3, 70.1, 68.1, 58.0, 56.1, 51.8, 51.5, 31.9, 31.4, 29.7, 29.4, 29.2, 29.1, 28.8, 26.7, 26.0, 25.8, 25.4, 22.7, 14.1. HRMS (ESI) (m/z): $[M – PF_6]^+$ calcd for $C_{35}H_{53}N_4O_8$, 609.4016; found, 609.4011.

Compound **2-H**: A mixture of crown ether **3** (74 mg, 0.079 mmol) and compound **5** (30 mg, 0.039 mmol) in dry CH_2Cl_2 (5 mL) was stirred at room temperature for 30 minutes. Then compound **4** (64 mg, 0.200 mmol) and $[Cu(CH_3CN)_4]PF_6$ (16 mg, 0.043 mmol) were added to the solution, and the mixture was stirred for 72 h under Ar atmosphere. After removal of the solvent, the residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH = 100/1) to give compound **2-H**

(45 mg, 56.4%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.60 (d, *J* = 7.2 Hz, 1H), 8.54 (d, *J* = 8.0 Hz, 1H), 8.42 (d, *J* = 8.4 Hz, 1H), 7.71 (t, *J* = 8.0 Hz, 1H), 7.61 (s, 1H), 7.53-7.44 (m, 2H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.94-6.90 (m, 2H), 6.82-6.77 (m, 2H), 6.65 (d, *J* = 8.4 Hz, 2H), 6.56 (s, 2H), 5.49 (s, 2H), 5.16 (s, 4H), 4.82-4.77 (m, 4H), 4.58-4.51 (m, 2H), 4.47-4.40 (m, 2H), 4.40-4.37 (m, 4H), 4.26 (t, *J* = 7.2 Hz, 2H), 4.20-4.14 (m, 4H), 4.13-4.08 (m, 6H), 4.07 (s, 10H), 4.01 (t, *J* = 4.4 Hz, 4H), 3.88-3.75 (m, 12H), 3.57 (s, 6H), 3.54-3.44 (m, 10H), 3.26 (t, *J* = 4.4 Hz, 4H), 2.42 (t, *J* = 2.4 Hz, 1H), 2.06-1.97 (m, 2H), 1.87-1.80 (m, 2H), 1.76-1.65 (m, 6H), 1.48-1.36 (m, 10H), 1.34-1.30 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 171.6, 159.8, 153.5, 147.3, 137.5, 130.8, 130.1, 127.3, 122.9, 122.1, 114.5, 113.1, 112.4, 105.9, 80.3, 74.3, 73.4, 71.6, 70.9, 70.6, 70.2, 70.0, 69.7, 68.3, 68.0, 66.9, 65.5, 58.1, 56.0, 53.4, 52.2, 30.0, 29.9, 29.5, 29.3, 29.1, 25.9, 25.7. HRMS (ESI) (m/z): $[M - PF_6]^+$ calcd for $C_{102}H_{121}N_6O_{20}Fe_2$, 1862.7368; found, 1862.7367

Compound **1-H**: A solution of **2-H** (200 mg, 0.010 mmol) in CH_3I (5.0 mL) and $CHCl_3$ (1.0 mL) was stirred at 40 °C for 3 d. The reaction mixture was cooled to room temperature, and CH_3I was evaporated off in vacuo. The residue was dissolved in MeOH (10 mL), followed by the addition of 5.0 mL saturated NH_4PF_6 solution. After the mixture was stirred for overnight, the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layer was evaporated, and the residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH = 100/1) to give **1-H** (200mg, 92.6%) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 8.54 (d, *J* = 7.2 Hz, 1H), 8.48 (d, *J* = 8.4 Hz, 1H), 8.42 (d, *J* = 8.0 Hz, 1H), 8.35 (s, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.55-7.46 (m, 2H), 7.23-7.13 (m, 3H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 4.0 Hz, 2H), 6.84-6.77 (m, 2H),6.67 (d, *J* = 8.4 Hz, 2H), 6.54 (s, 2H), 5.50 (s, 2H), 5.15 (s, 4H), 4.84-4.74 (m, 4H), 4.60-4.50 (m, 5H), 4.49-4.41 (m, 4H), 4.40-4.36 (m, 4H), 4.21-4.14 (m, 4H), 4.14-4.09 (m, 6H), 4.07 (s, 10H), 4.02-3.97 (m, 4H), 3.88-3.72 (m, 12H), 3.56 (s, 6H), 3.54-3.38 (m, 10H), 3.29-3.22 (m, 4H), 2.42 (t, *J* = 2.4 Hz, 1H), 2.00-1.94 (m, 2H), 1.76-1.66 (m, 6H), 1.65-1.58 (m, 10H), 1.44-1.37 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 170.5, 160.1, 162.5, 158.8, 155.6, 152.4, 146.3, 146.2, 138.9, 136.4, 132.4, 130.9, 130.3, 129.7, 129.1, 129.0, 126.4, 124.9, 121.8, 121.1, 121.0, 114.5, 114.0, 113.6, 112.0, 111.4, 104.9, 79.0, 73.2, 72.3, 70.5, 69.8, 69.5, 69.2, 69.0, 68.7, 67.2, 66.9, 65.8, 64.5, 57.0, 55.0, 53.2, 52.4, 51.4, 51.2, 37.5, 30.9, 30.7, 29.0, 28.7, 28.5, 28.3, 28.1, 27.9, 27.8, 27.6, 24.9, 24.7, 24.6, 21.7, 13.1. HRMS (ESI) (m/z): $[M - PF_6]^+$ calcd for

$C_{103}H_{124}N_6O_{20}Fe_2PF_6$, 2022.7245; found, 2022.7230. $[M - 2PF_6]^{2+}$ calcd for $C_{103}H_{124}N_6O_{20}Fe_2/2$, 938.8802; found, 938.8929.

Experimental procedures for surface modification

5-azidopentyltriethoxysilane monolayer on SiO_2 nanoparticles surface

Firstly, SiO_2 nanoparticles were obtained according to the literature.[4] In a 50 mL flask, 1.0 g SiO_2 nanoparticles and 1.0 g 5-azidopentyltriethoxysilane[5] were mixed in dry toluene (25 mL) and the mixture was refluxed under Ar atmosphere for 24 h. The mixture was centrifuged, washed with toluene and ethanol many times, then dried under vacuum environment. The azide-functionalized SiO_2 nanoparticles was obtained as a white solid.

Attaching 1-H to azide-functionalized SiO_2 nanoparticles surface

Compound **1-H** was grafted to the azide-functionalized SiO_2 nanoparticles at room temperature by ultraphonic dispersing the azide-functionalized SiO_2 nanoparticles into CH_2Cl_2 solution of **1-H** (1 mM) containing $[Cu(CH_3CN)_4]PF_6$ (1 mM) as catalyst. The mixture was centrifuged, washed with CH_2Cl_2 (3 times) and ethanol (3 times) to ensure **1-H** molecules physical adsorbed on the SiO_2 surface were eliminated completely, then dried under vacuum environment. The **1-H @SiO_2** nanoparticles was obtained as a yellow solid.

The solid powder of 1-H@SiO_2 nanoparticles after addition excess DBU.

The **1-H@SiO_2** nanoparticles were ultraphonic dispersed into the CH_2Cl_2 solution, then excess DBU was added. The mixture was stirred overnight and centrifuged, then washed with CH_2Cl_2 and ethanol many times and dried under vacuum environment. A faint yellow solid powder was obtained.

The photophysical properties of [2]rotaxane 1-H and 1-H@SiO_2

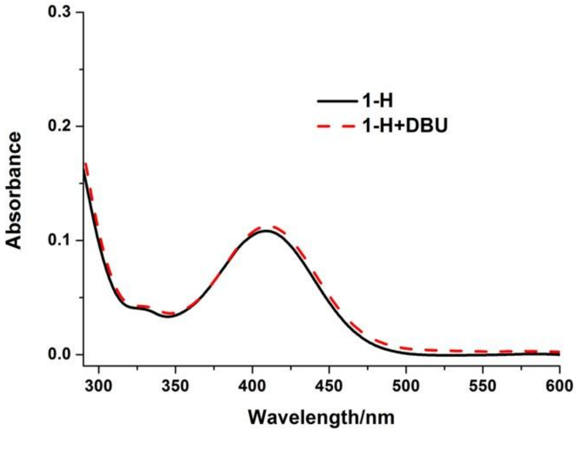


Figure S2. The UV/Vis absorption spectra of a CH_2Cl_2 solution of [2]rotaxane **1-H** (1×10^{-5} M) and the mixture obtained after adding excess DBU to the solution of [2]rotaxane **1-H.**

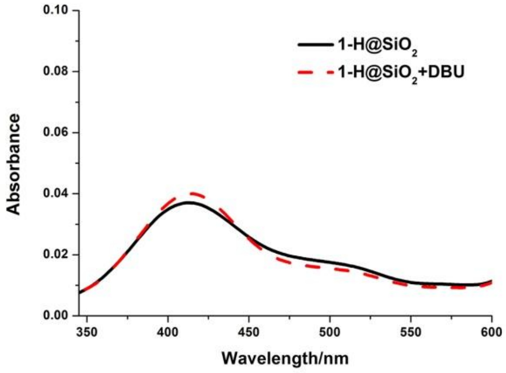


Figure S3. The UV/Vis absorption spectra of a CH_2Cl_2 solution of **1-H@SiO$_2$** (0.5 mg/ml) and the mixture obtained after adding excess DBU to the solution of **1-H@SiO$_2$**.

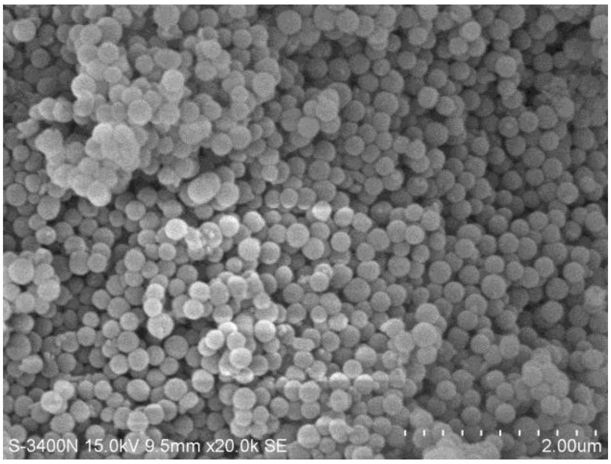


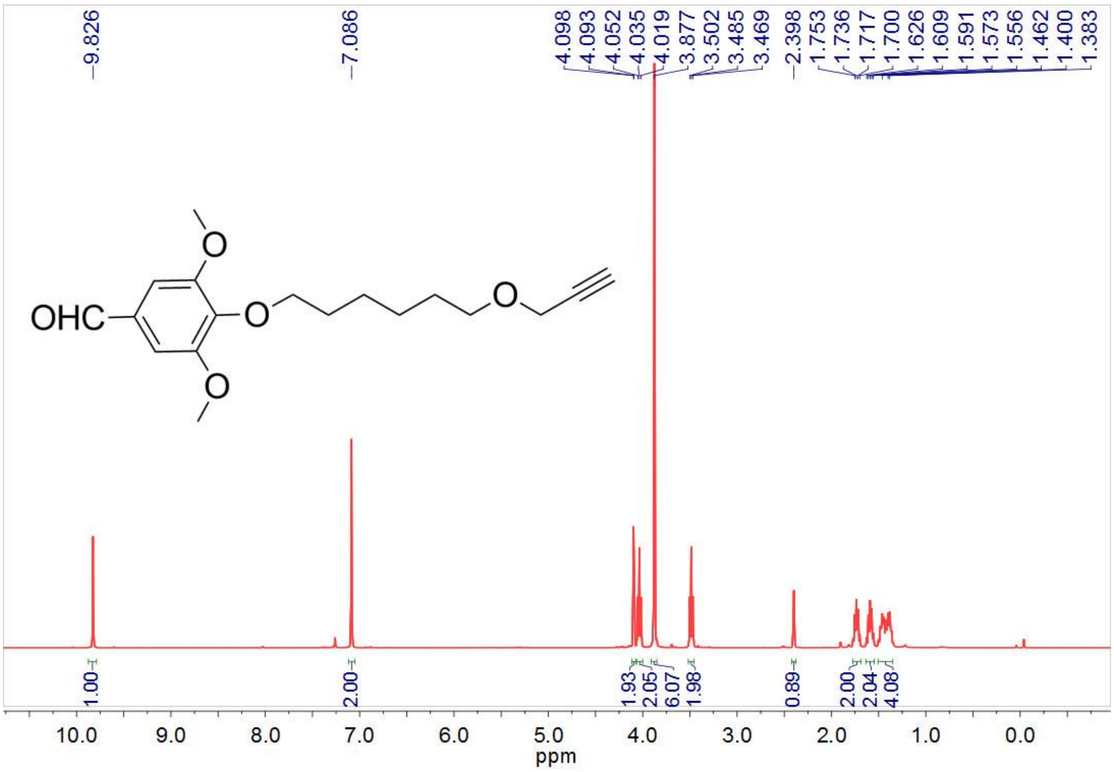
Figure S4. SEM images of solid **1-H@SiO$_2$**

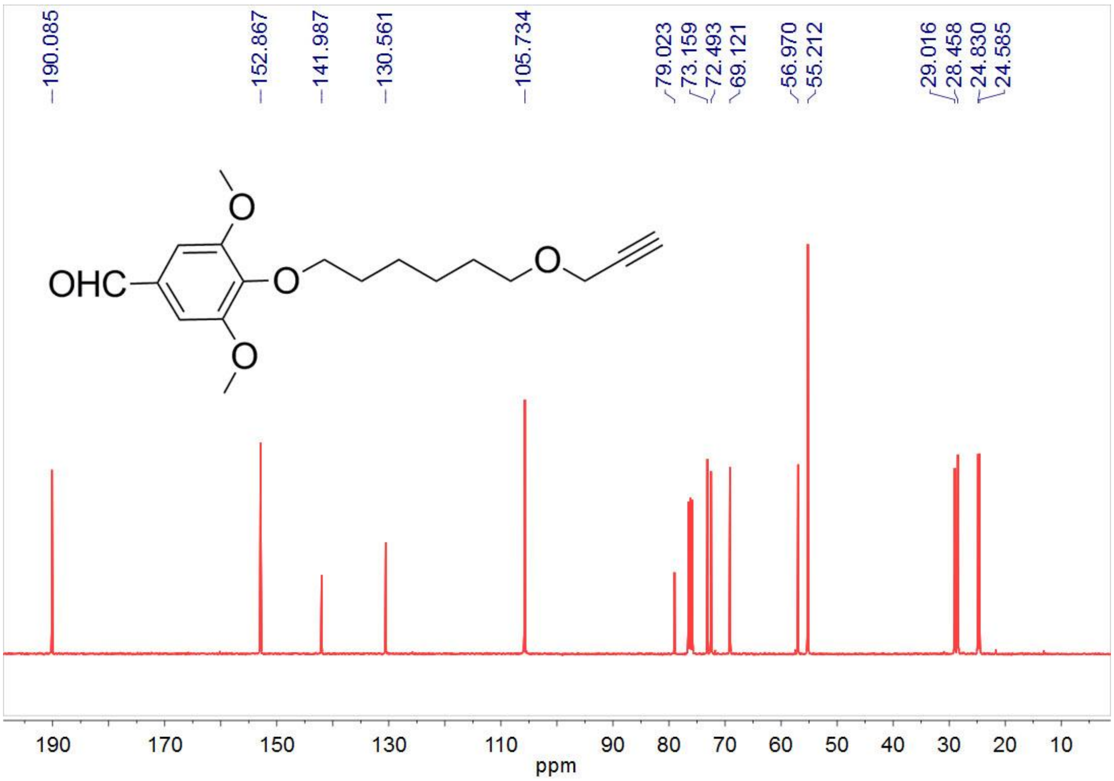
Reference:

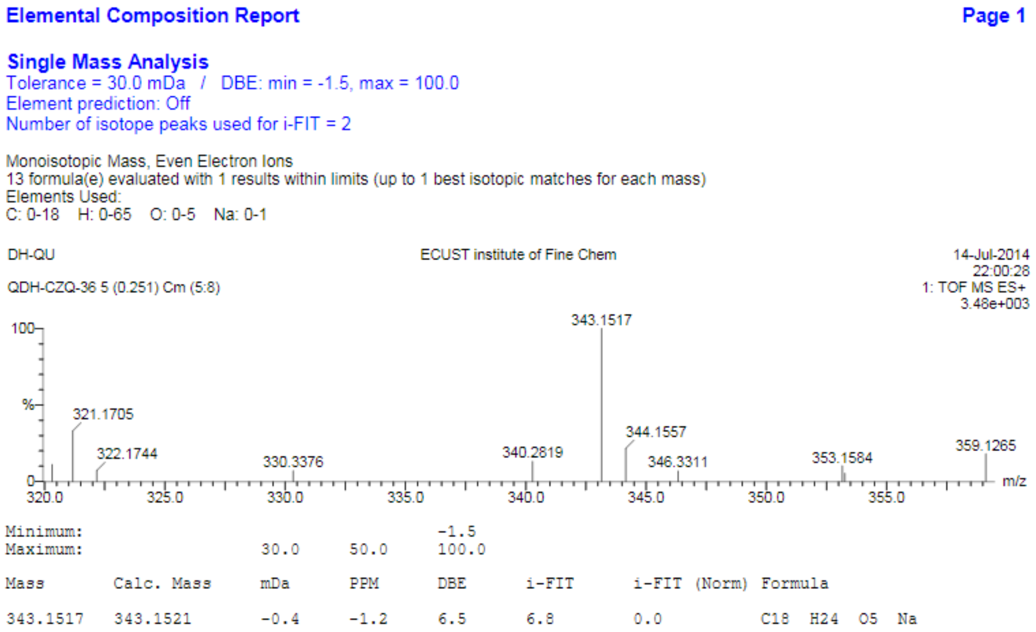
1. H. Zhang, J. Hu and D. H. Qu, *Org. Lett.*, 2012, **14**, 2334.
2. M. Berchel, J. P. Haelters, H. C. Gourvès, L. Deschamps, P. Midoux, P. Lehn, P. A. Jaffrès, *Eur J. Org. Chem.*, 2011, **31**, 6294.
3. Y. Jiang, J. B. Guo, C. F. Chen, *Chem. Commun.*, 2010, **46**, 5536.
4. Y. Chen, H.-R. Chen, Y. Sun, Y.-Y. Zheng, D.-P. Zeng, F.-Q. Li, S.-J. Zhang, X. Wang, K. Zhang, M. Ma, Q.-J. He, L.-L. Zhang and J.-L Shi, *Angew. Chem.*, 2011, **123**, 12717.
5. A. T. Dickschat, F. Behrends, M. Bühner, J.-J Ren, M. Weiß, H. Eckert and A. Studer, *Chem. Eur. J.*, 2012, **18**, 16689.

^{1}H NMR, ^{13}C NMR and Mass spectra

Compound 10







Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
13 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-18 H: 0-65 O: 0-5 Na: 0-1

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ECUST institute of Fine Chem
14-Jul-2014
22:00:28
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1: TOF MS ES+
3.48e+003

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Minimum:                                    -1.5
Maximum:                    30.0     50.0    100.0

Mass        Calc. Mass      mDa      PPM      DBE       i-FIT      i-FIT (Norm) Formula

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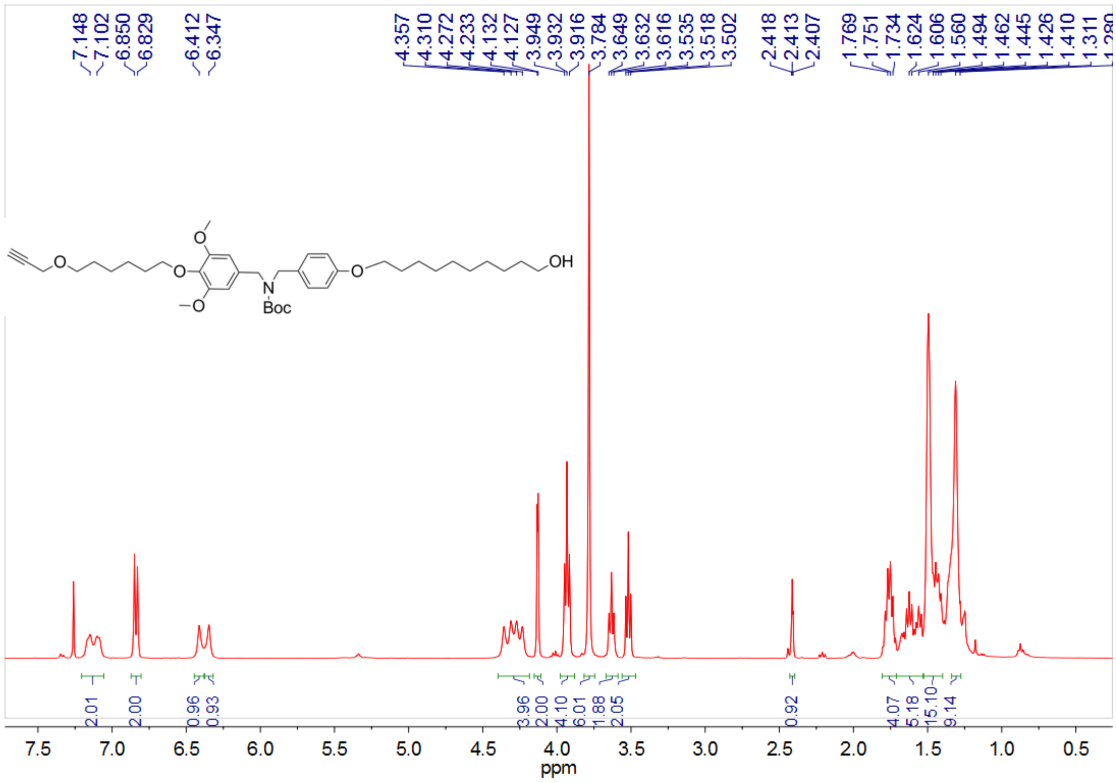
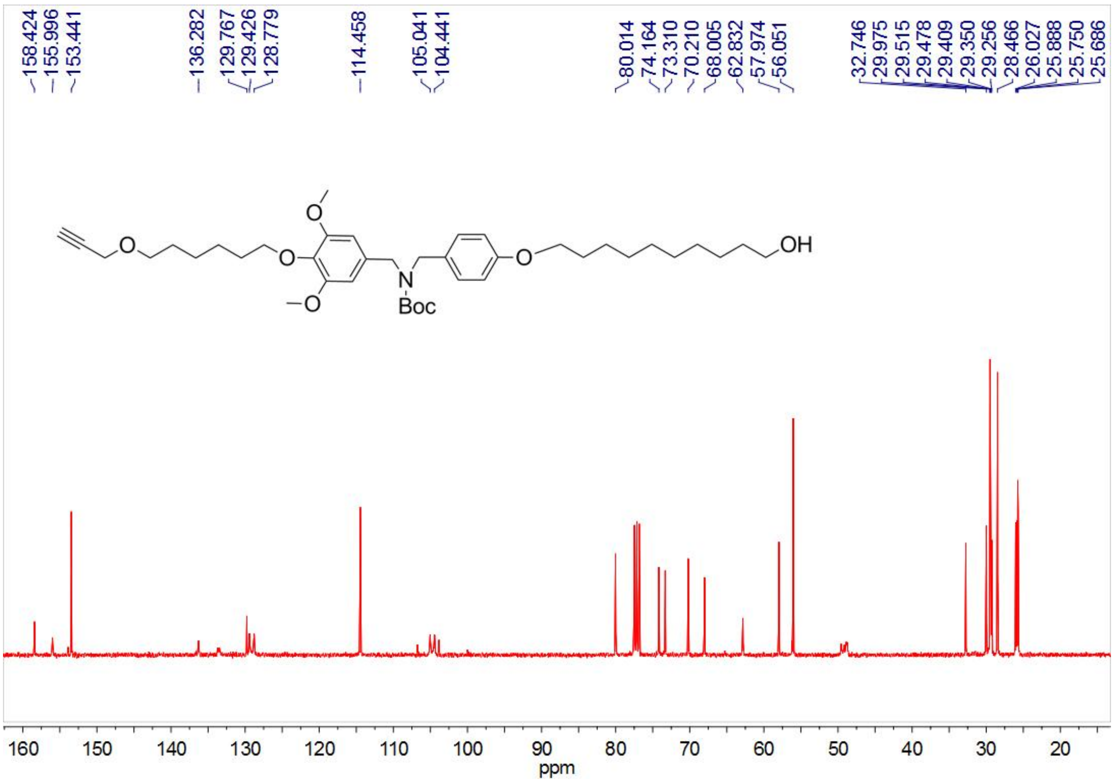
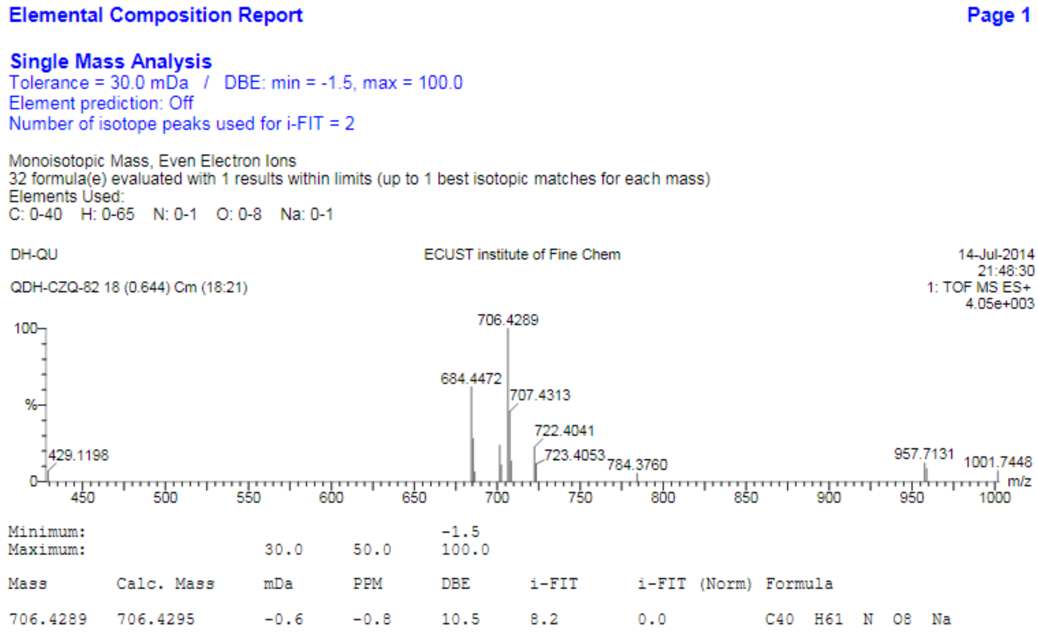
Compound 8







Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
32 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-40 H: 0-65 N: 0-1 O: 0-8 Na: 0-1

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21:48:30
QDH-CZQ-82 18 (0.644) Cm (18:21) 1: TOF MS ES+
4.05e+003

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Minimum:                                    -1.5
Maximum:                30.0      50.0      100.0

Mass        Calc. Mass  mDa       PPM       DBE        i-FIT       i-FIT (Norm) Formula

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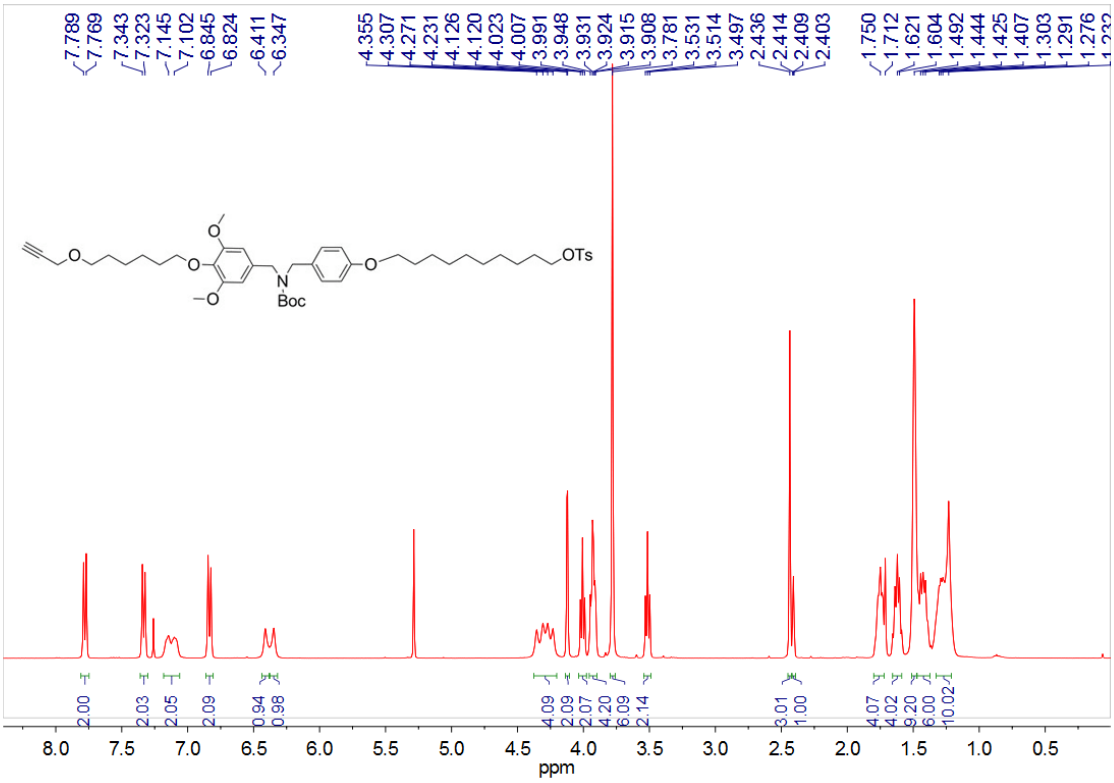
Compound 7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7.323
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6.824
6.411
6.347
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4.307
4.271
4.231
4.126
4.120
4.023
4.007
3.991
3.948
3.931
3.924
3.915
3.908
3.781
3.531
3.514
3.497
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1.291
1.276
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O
O
N
Boc
O
OTs
2.00
2.03
2.05
2.09
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0.98
4.09
2.09
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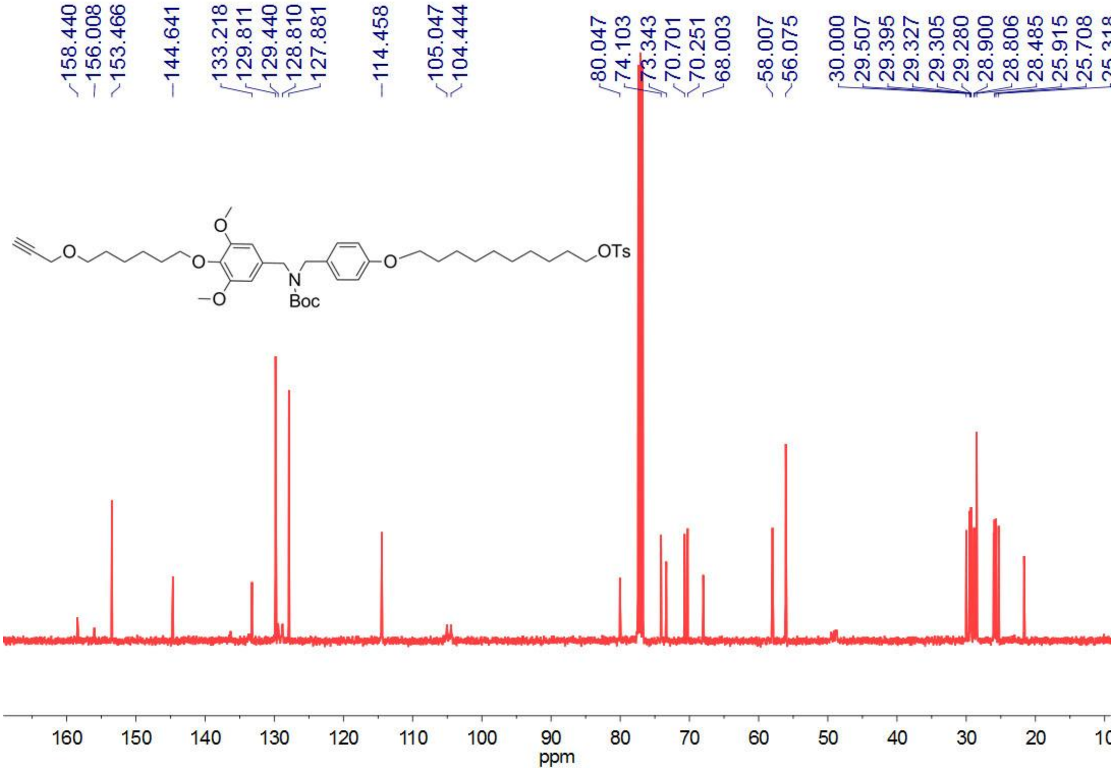
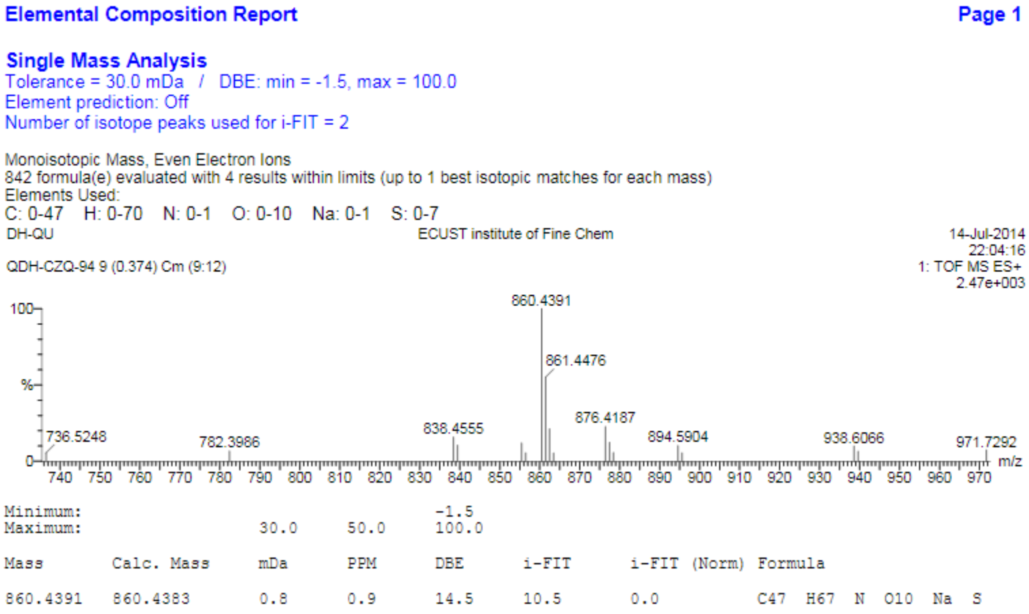
4.20
6.09
2.14
3.01
1.00
4.07
4.02
9.20
6.00
10.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


158.440
156.008
153.466
144.641
133.218
129.811
129.440
128.810
127.881
114.458
105.047
104.444
80.047
74.103
73.343
70.701
70.251
68.003
58.007
56.075
30.000
29.507
29.395
29.327
29.305
29.280
28.900
28.806
28.485
25.915
25.708
O
O
O
N
Boc
O
OTs
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

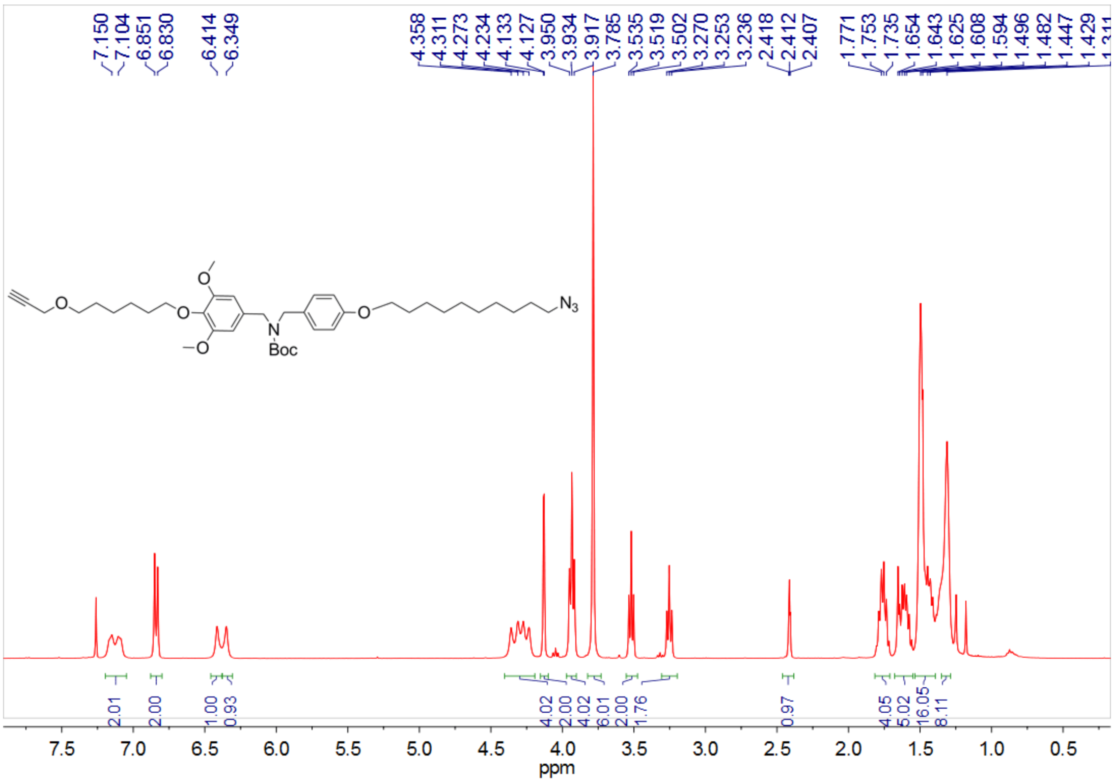
Monoisotopic Mass, Even Electron Ions
842 formula(e) evaluated with 4 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-47 H: 0-70 N: 0-1 O: 0-10 Na: 0-1 S: 0-7

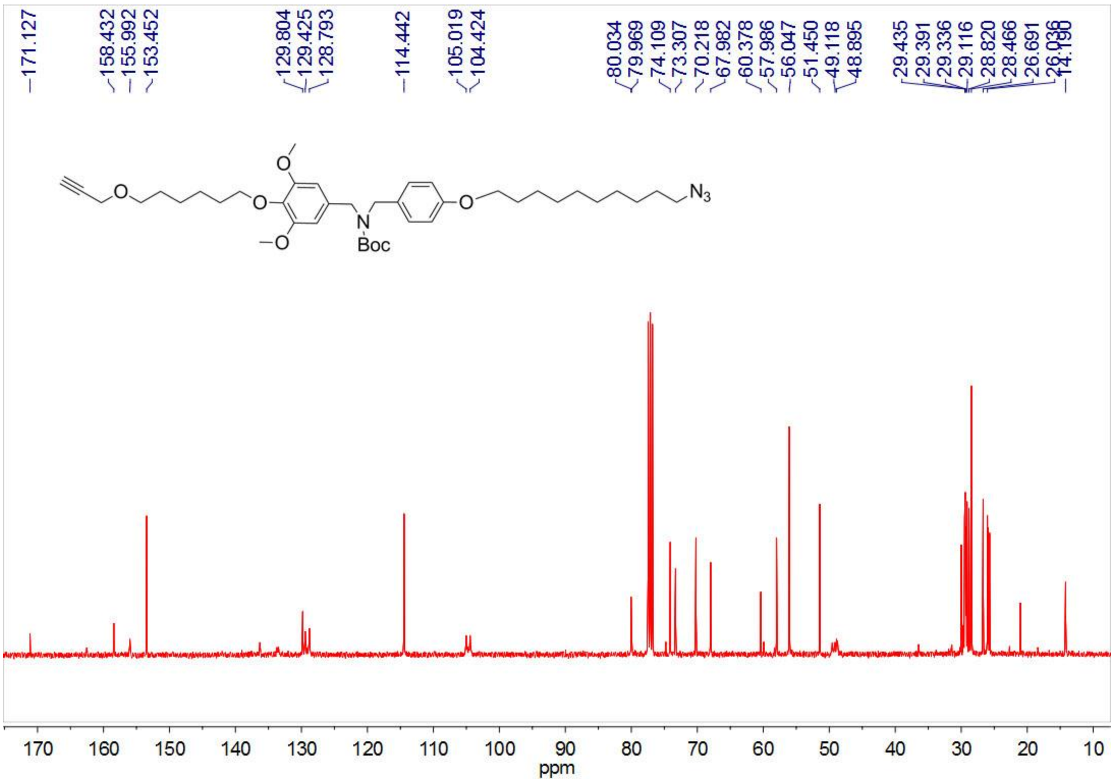
DH-QU ECUST institute of Fine Chem 14-Jul-2014
22:04:16

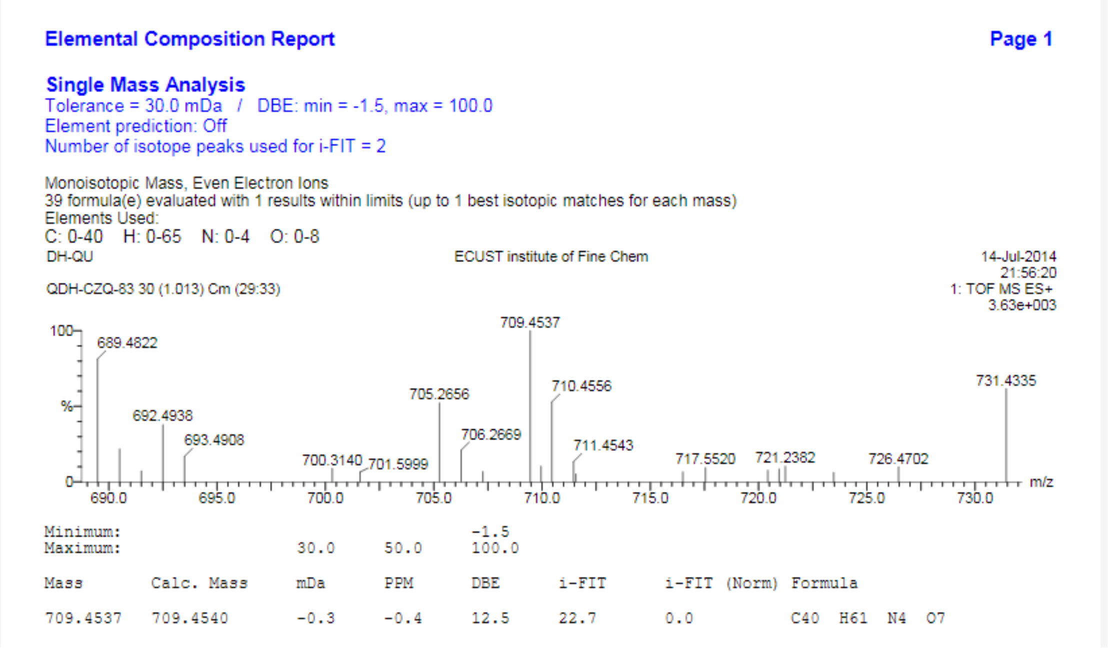
QDH-CZQ-94 9 (0.374) Cm (9:12) 1: TOF MS ES+
2.47e+003

```
Minimum:                                  -1.5
Maximum:                30.0      50.0    100.0

Mass       Calc. Mass   mDa       PPM     DBE      i-FIT      i-FIT (Norm) Formula

860.4391   860.4383     0.8       0.9     14.5     10.5       0.0          C47  H67  N  O10  Na  S
```

Compound 6







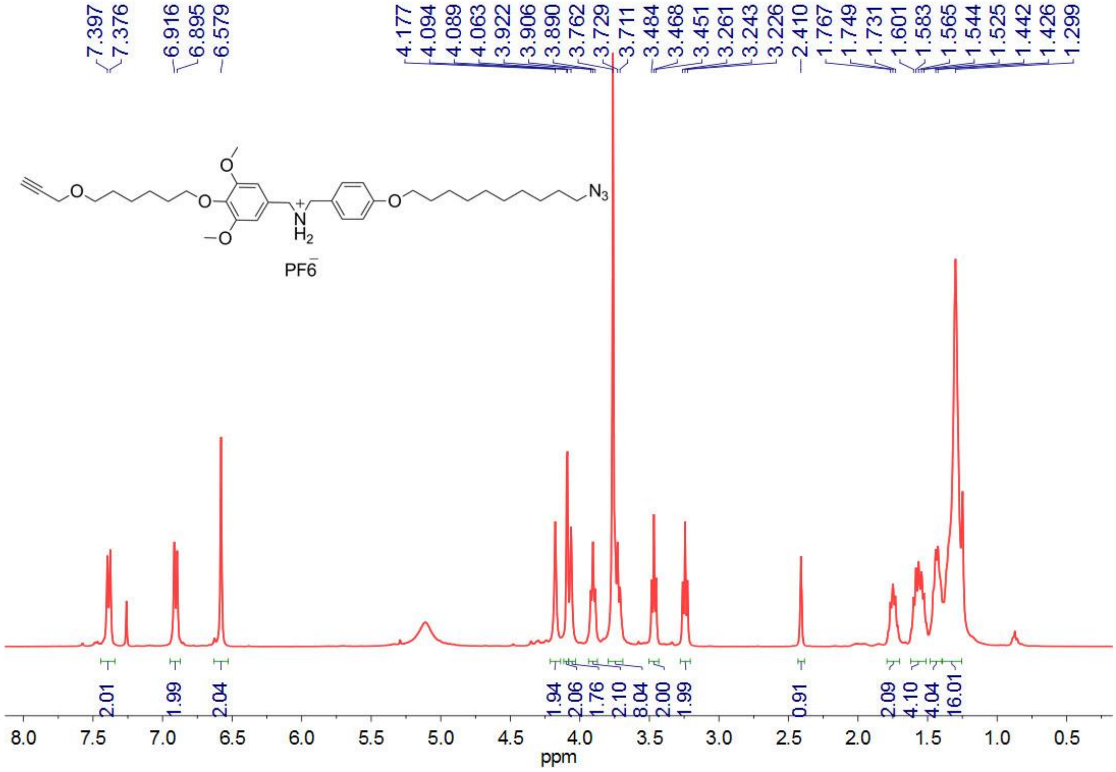
Elemental Composition Report **Page 1**

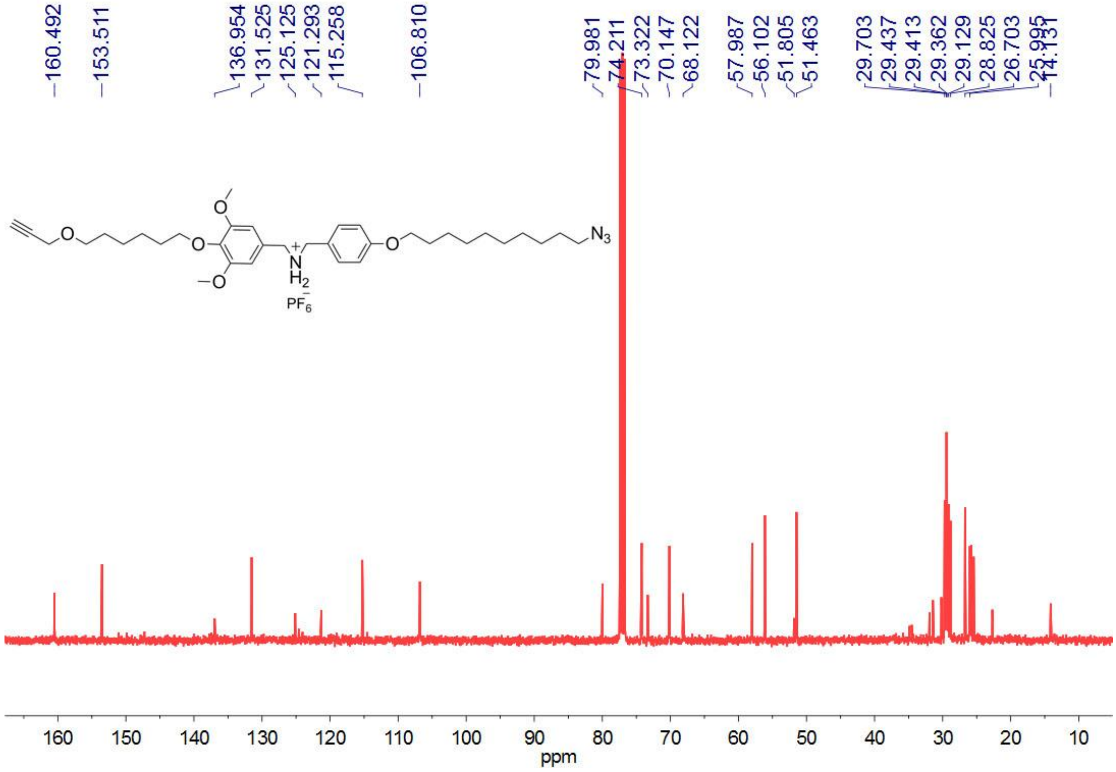
Single Mass Analysis
Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

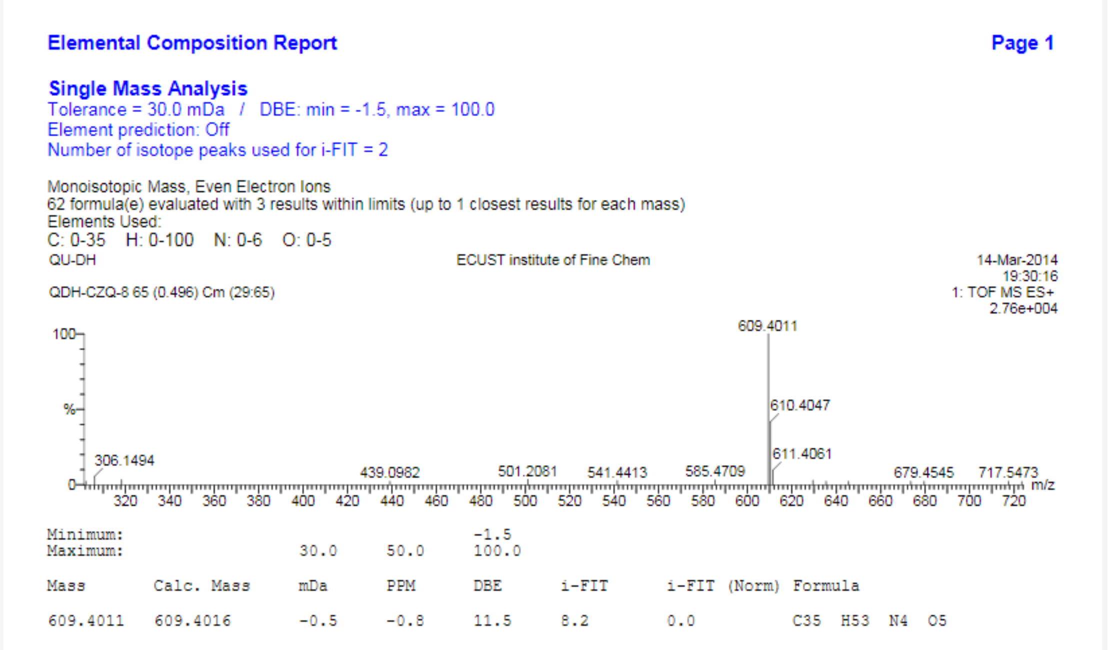
Monoisotopic Mass, Even Electron Ions
39 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-40 H: 0-65 N: 0-4 O: 0-8
DH-QU ECUST institute of Fine Chem 14-Jul-2014
21:56:20
QDH-CZQ-83 30 (1.013) Cm (29:33) 1: TOF MS ES+
3.63e+003

```
Minimum:                                  -1.5
Maximum:              30.0      50.0      100.0

Mass      Calc. Mass     mDa      PPM      DBE       i-FIT      i-FIT (Norm)  Formula

709.4537  709.4540       -0.3     -0.4     12.5      22.7       0.0           C40  H61  N4  O7
```

Compound 5


7.397
7.376
6.916
6.895
6.579
4.177
4.094
4.089
4.063
3.922
3.906
3.890
3.762
3.729
3.711
3.484
3.468
3.451
3.261
3.243
3.226
2.410
1.767
1.749
1.731
1.601
1.583
1.565
1.544
1.525
1.442
1.426
1.299
O
O
O
O
O
N3
+
N
H2
PF6−
2.01
1.99
2.04
1.94
2.06
1.76
2.10
8.04
2.00
1.99
0.91
2.09
4.10
4.04
16.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


160.492
153.511
136.954
131.525
125.125
121.293
115.258
106.810
79.981
74.211
73.322
70.147
68.122
57.987
56.102
51.805
51.463
29.703
29.437
29.413
29.362
29.129
28.825
26.703
25.995
14.131
O
O
O
O
O
N3
+
N
H2
PF6−
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



Elemental Composition Report **Page 1**

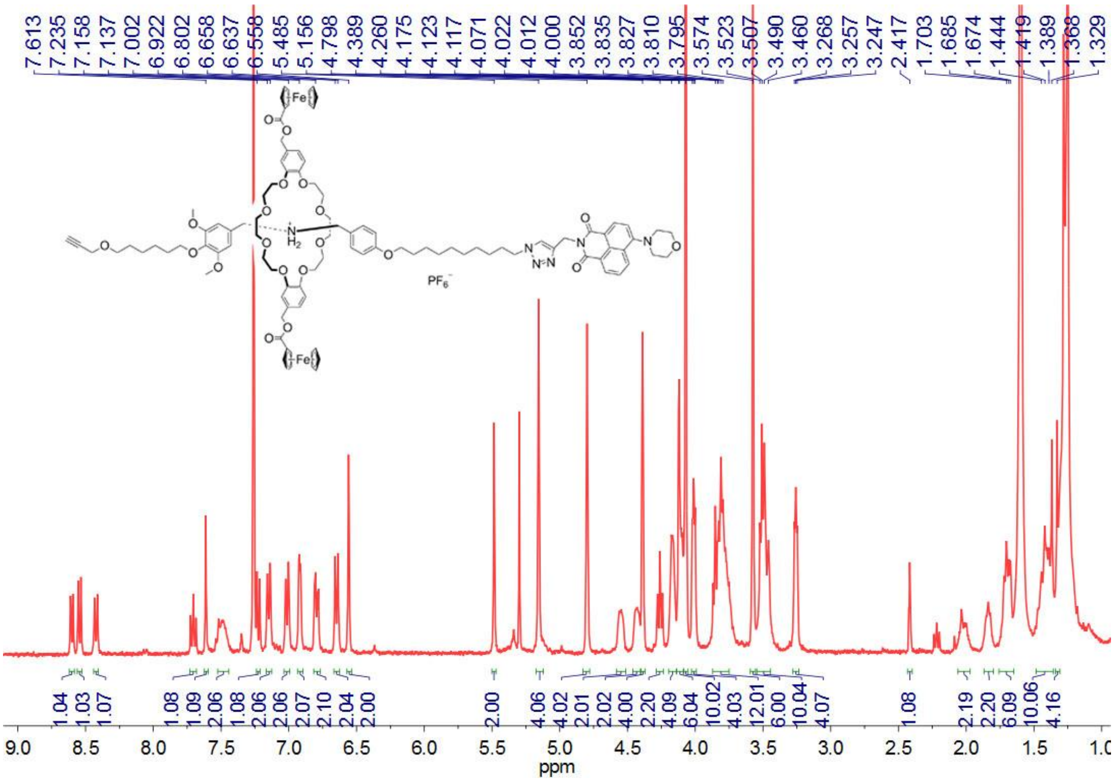
Single Mass Analysis
Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

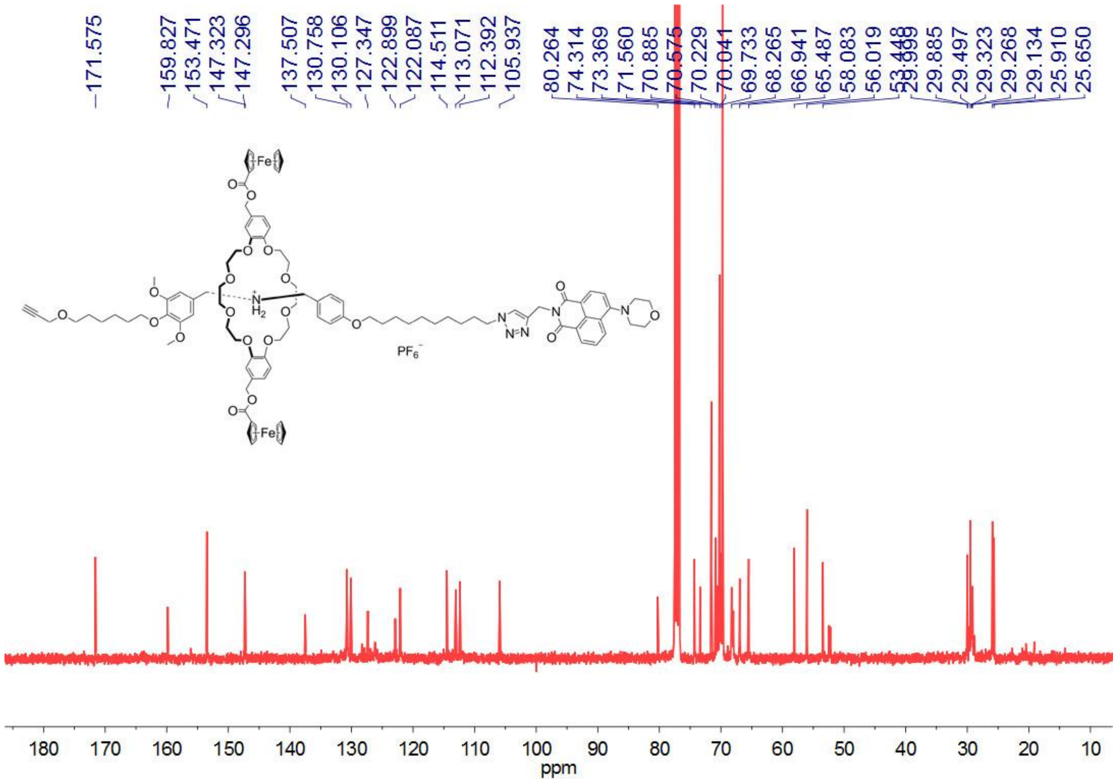
Monoisotopic Mass, Even Electron Ions
62 formula(e) evaluated with 3 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-35 H: 0-100 N: 0-6 O: 0-5

QU-DH ECUST institute of Fine Chem 14-Mar-2014 19:30:16
QDH-CZQ-8 65 (0.496) Cm (29:65) 1: TOF MS ES+ 2.76e+004

```
Minimum:                                  -1.5
Maximum:               30.0      50.0     100.0

Mass       Calc. Mass     mDa      PPM      DBE      i-FIT      i-FIT (Norm) Formula

609.4011   609.4016       -0.5     -0.8     11.5     8.2        0.0          C35  H53  N4  O5
```

Compound 2-H

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153.471
147.323
147.296
137.507
130.758
130.106
127.347
122.899
122.087
114.511
113.071
112.392
105.937
80.264
74.314
73.369
71.560
70.885
70.575
70.229
70.041
69.733
68.265
66.941
65.487
58.083
56.019
53.448
29.999
29.885
29.497
29.323
29.268
29.134
25.910
25.650
Fe
O
O
N
H2
PF6-
N
N
N
O
O
N
O
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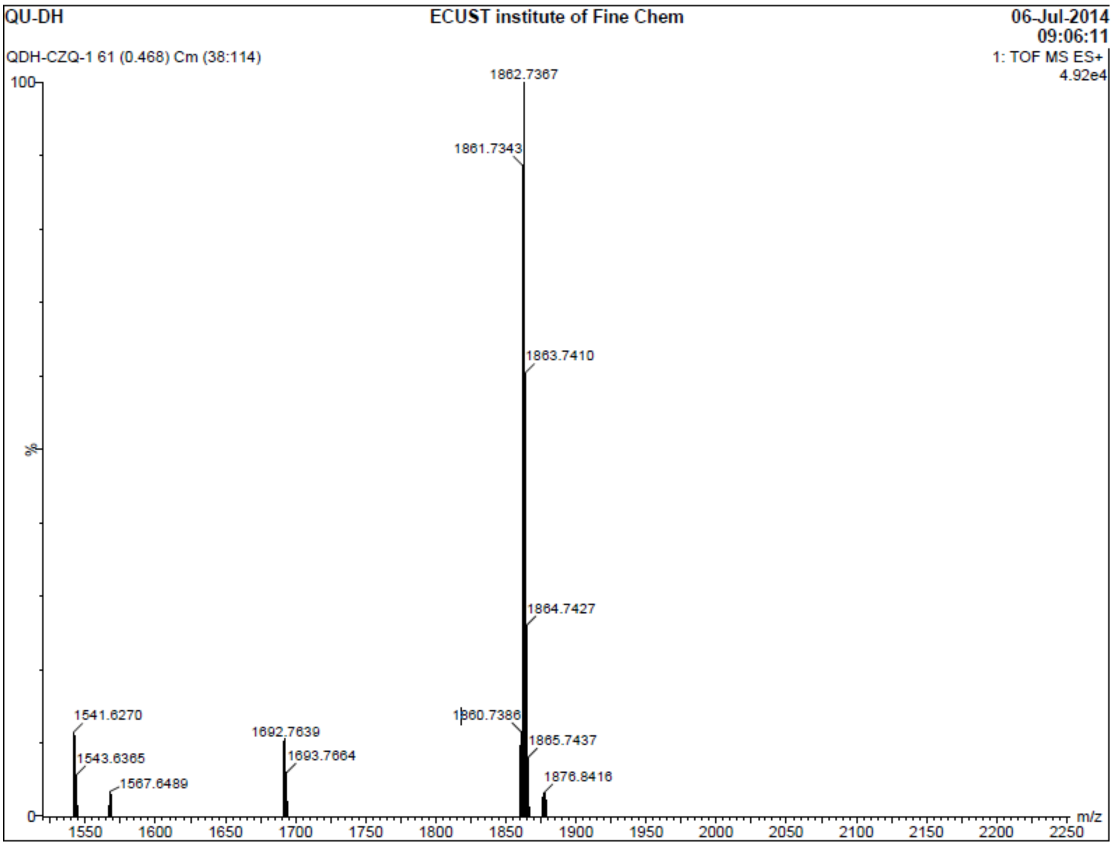
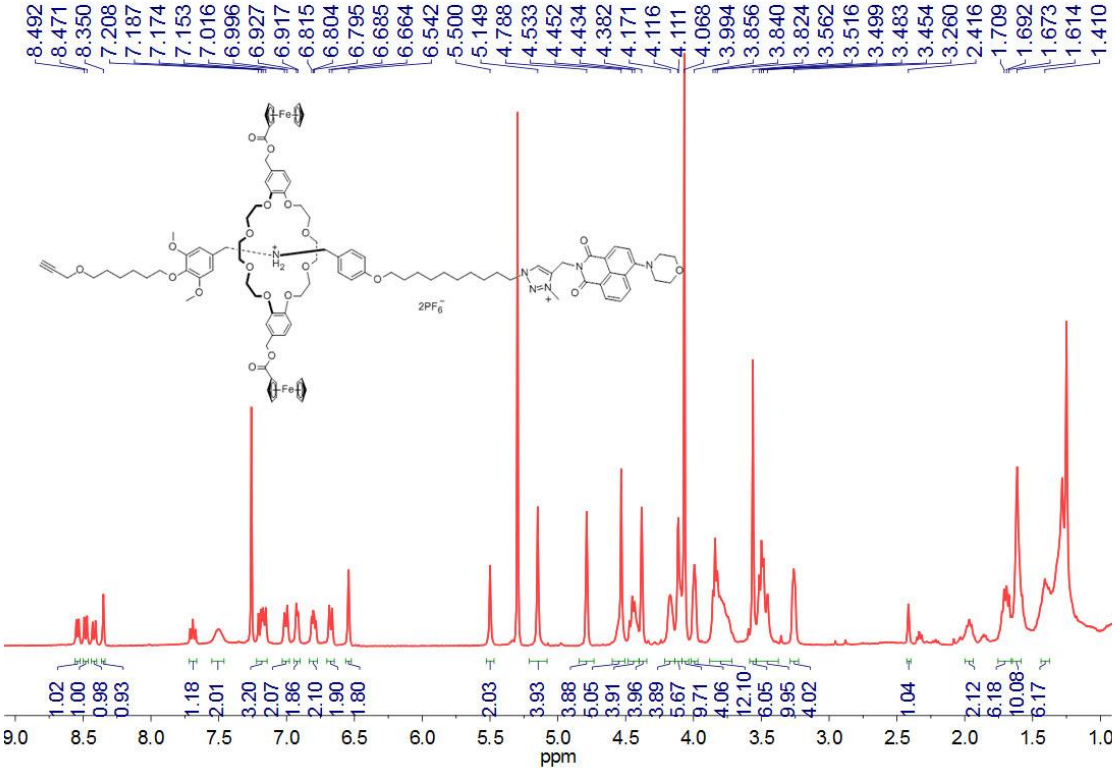
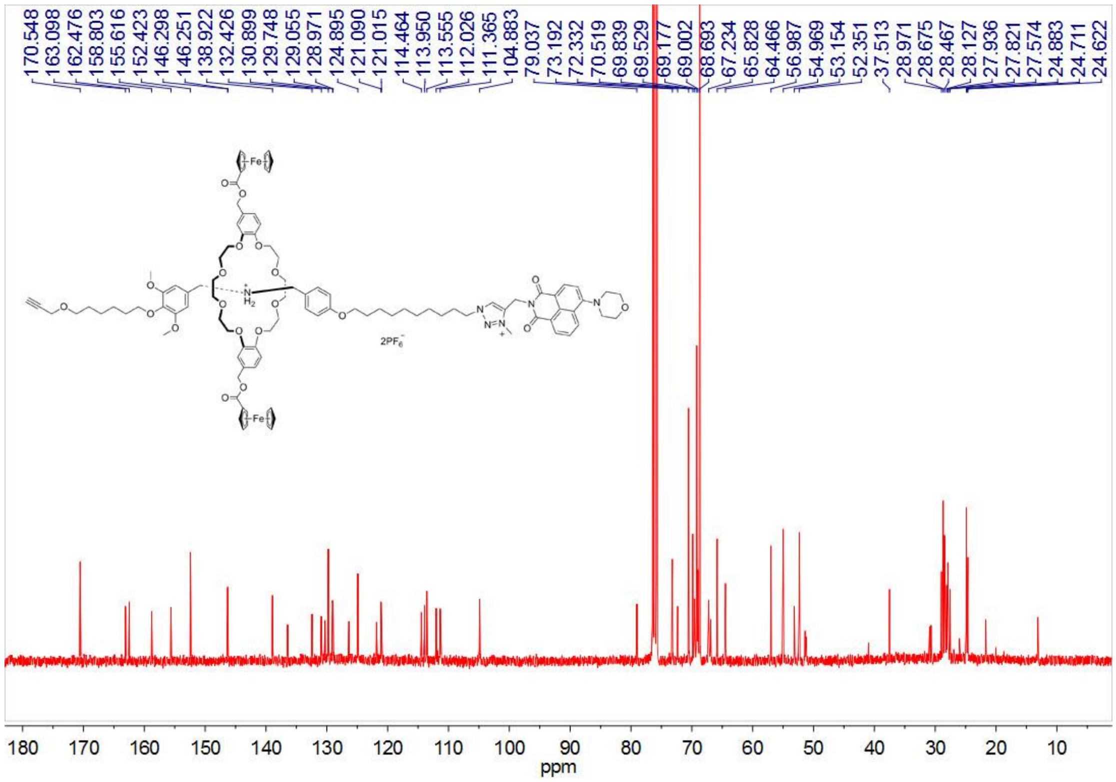
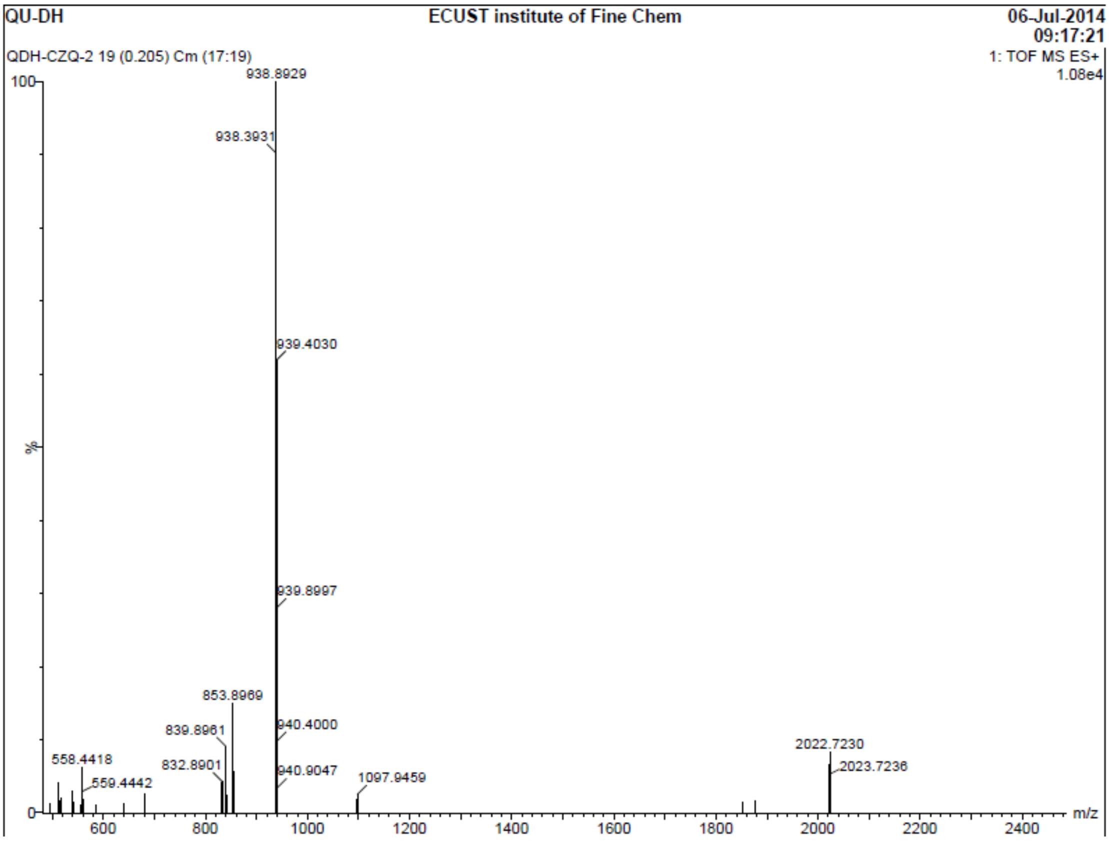
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


QU-DH
ECUST institute of Fine Chem
06-Jul-2014
09:06:11
QDH-CZQ-1 61 (0.468) Cm (38:114)
1: TOF MS ES+
4.92e4
100
%
0
1862.7367
1861.7343
1863.7410
1864.7427
1860.7386
1865.7437
1876.8416
1541.6270
1543.6365
1567.6489
1692.7639
1693.7664
1550
1600
1650
1700
1750
1800
1850
1900
1950
2000
2050
2100
2150
2200
2250
m/z

Compound 1-H


8.492
8.471
8.350
7.208
7.187
7.174
7.153
7.016
6.996
6.927
6.917
6.815
6.804
6.795
6.685
6.664
6.542
5.500
5.149
4.788
4.533
4.452
4.434
4.382
4.371
4.116
4.111
4.068
3.994
3.856
3.840
3.824
3.562
3.516
3.499
3.483
3.454
3.260
2.416
1.709
1.692
1.673
1.614
1.410
Fe
O
N
$\overset{+}{N}H_2$
$2PF_6^-$
+
1.02
1.00
0.98
0.93
1.18
2.01
3.20
2.07
1.86
2.10
1.90
1.80
2.03
3.93
3.88
5.05
3.91
3.96
3.89
5.67
9.71
4.06
12.10
6.05
9.95
4.02
1.04
2.12
6.18
10.08
6.17
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


170.548
163.098
162.476
158.803
155.616
152.423
146.298
146.251
138.922
132.426
130.899
129.748
129.055
128.971
124.895
121.090
121.015
114.464
113.950
113.555
112.026
111.365
104.883
79.037
73.192
72.332
70.519
69.839
69.529
69.177
69.002
68.693
67.234
65.828
64.466
56.987
54.969
53.154
52.351
37.513
28.971
28.675
28.467
28.127
27.936
27.821
27.574
24.883
24.711
24.622
Fe
O
N
$\overset{+}{N}H_2$
$2PF_6^-$
+
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


QU-DH
ECUST institute of Fine Chem
06-Jul-2014
09:17:21
QDH-CZQ-2 19 (0.205) Cm (17:19)
1: TOF MS ES+
1.08e4
100
%
0
938.8929
938.3931
939.4030
939.8997
853.8969
940.4000
839.8961
558.4418
832.8901
940.9047
559.4442
1097.9459
2022.7230
2023.7236
600
800
1000
1200
1400
1600
1800
2000
2200
2400
m/z