Supporting Information for:

Integration of Phosphine Ligand and Ionic Liquid Both in Structure and Property: An Efficient and Economical Catalytic System for Homogeneous-Catalyst Recycling

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1 Experimental Procedure

1.1 General procedure for recycling of Rh-2a catalyst in Rh-2a/1-octene/MeOH-HCBS hydroformylation system

Under an argon atmosphere, a 60 mL autoclave was loaded with $Rh(acac)(CO)_2$ (1.0 mg, 3.88×10^{-3} mmol), 20 equivalents of **2a** (110 mg, 7.76×10^{-2} mmol) and MeOH (3 mL). Subsequently, 5×10^3 equivalents of 1-octene (3 mL, 19.4 mmol) and the internal standard were added, and the reaction temperature and syngas pressure were raised to 100 °C and 5.0 MPa, respectively, with an intense stirring. After 1 h, the reaction was terminated by placing the autoclave in an ice bath. Upon releasing the syngas and after a GC analysis, the methanol was removed *in vacuo* and *n*-heptane (4.5 mL) was added to extract the aldehydes. The upper organic phase was removed, then the fresh 1-octene and methanol were replenished to the IL phase for next run. (Note: 1.0 μL of N, N, N', N'-tetramethylguanidine was added in runs 1, 6 and 9)

1.2 General procedure for recycling of Rh-3a catalyst in Rh-3a/1-octene/EtOH-HCBS hydroformylation system

Under an argon atmosphere, a 60 mL autoclave was loaded with $Rh(acac)(CO)_2$ (1.0 mg, 3.88×10^{-3} mmol), 20 equivalents of **3a** (105 mg, 7.76×10^{-2} mmol) and EtOH (5 mL). Subsequently, 5×10^3 equivalents of 1-octene (3 mL, 19.4 mmol) and the internal standard were added, and the reaction temperature and syngas pressure were raised to 100 °C and 5.0 MPa, respectively, with an intense stirring. After 6 h, the reaction was terminated by placing the autoclave in an ice bath. Upon releasing the syngas and after a GC analysis, the ethanol was removed *in vacuo* and *n*-heptane (4.5 mL) was added to extract the aldehydes. The upper organic phase was removed, then the fresh 1-octene and ethanol were replenished to the IL phase for next run. (Note: 1.0 μL of N, N, N', N'-tetramethylguanidine was added in cycles 2, 4 and 6)

1.3 General procedure for recycling of Rh-2b catalyst in Rh-2b/1-octene/MeOH-HCBS hydrogenation system

Under an argon atmosphere, a 60 mL autoclave was loaded with $RhCl_3\cdot3H_2O$ (1.0 mg, 3.8×10^{-3} mmol), 20 equivalents of **2b** (228 mg, 7.6×10^{-2} mmol) and MeOH. Subsequently, 1×10^3 equivalents of 1-octene (0.6 mL, 3.8 mmol) and the internal standard were added, and the reaction temperature and H_2 pressure were raised to 80 °C and 6.0 MPa, respectively, with an intense stirring. After 5 h, the reaction was terminated by placing the autoclave in an ice bath. Upon releasing the gas and after a GC analysis, the methanol and products were removed *in vacuo*, then the fresh 1-octene and methanol were replenished to the IL phase for next run.

2 NMR Spectra

2.1 ^{1}H NMR spectrum of **2a**

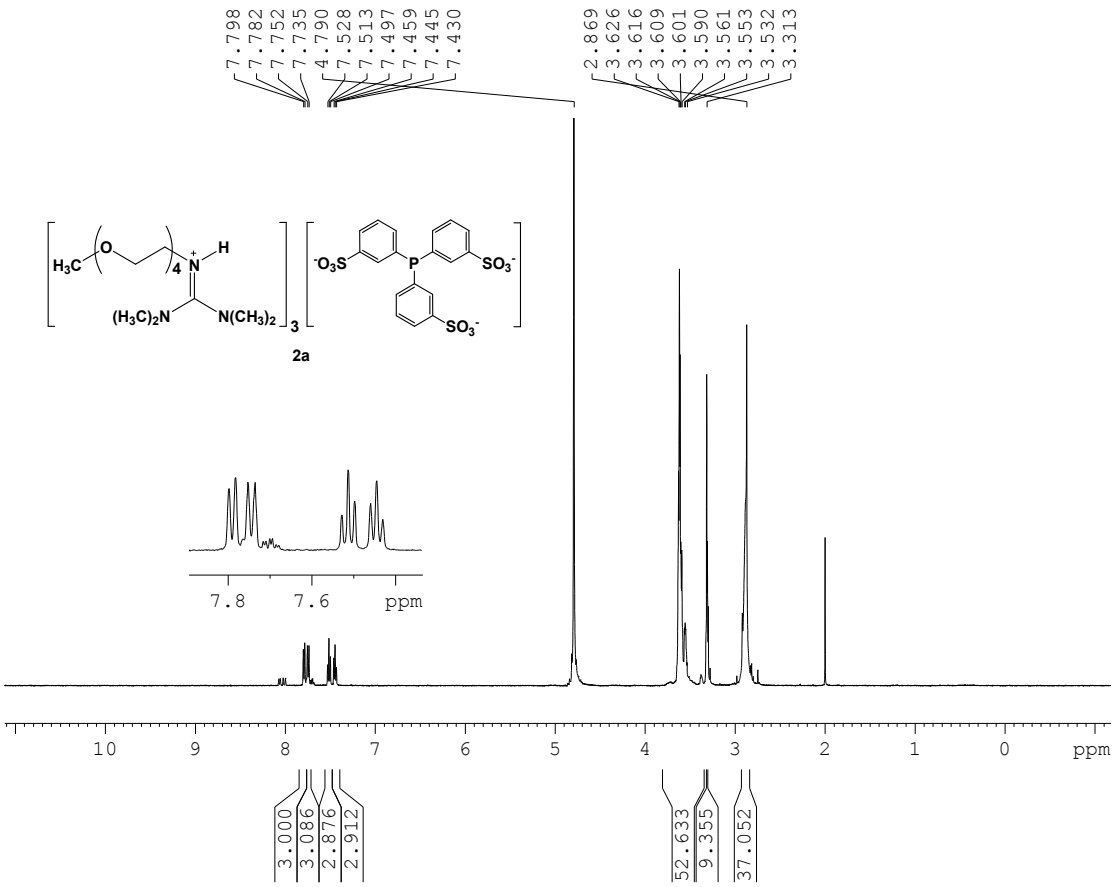


Figure S1. ^{1}H NMR spectrum of **2a** (500.0 MHz, D_2O)

2.2 ^{13}C NMR spectrum of **2a**

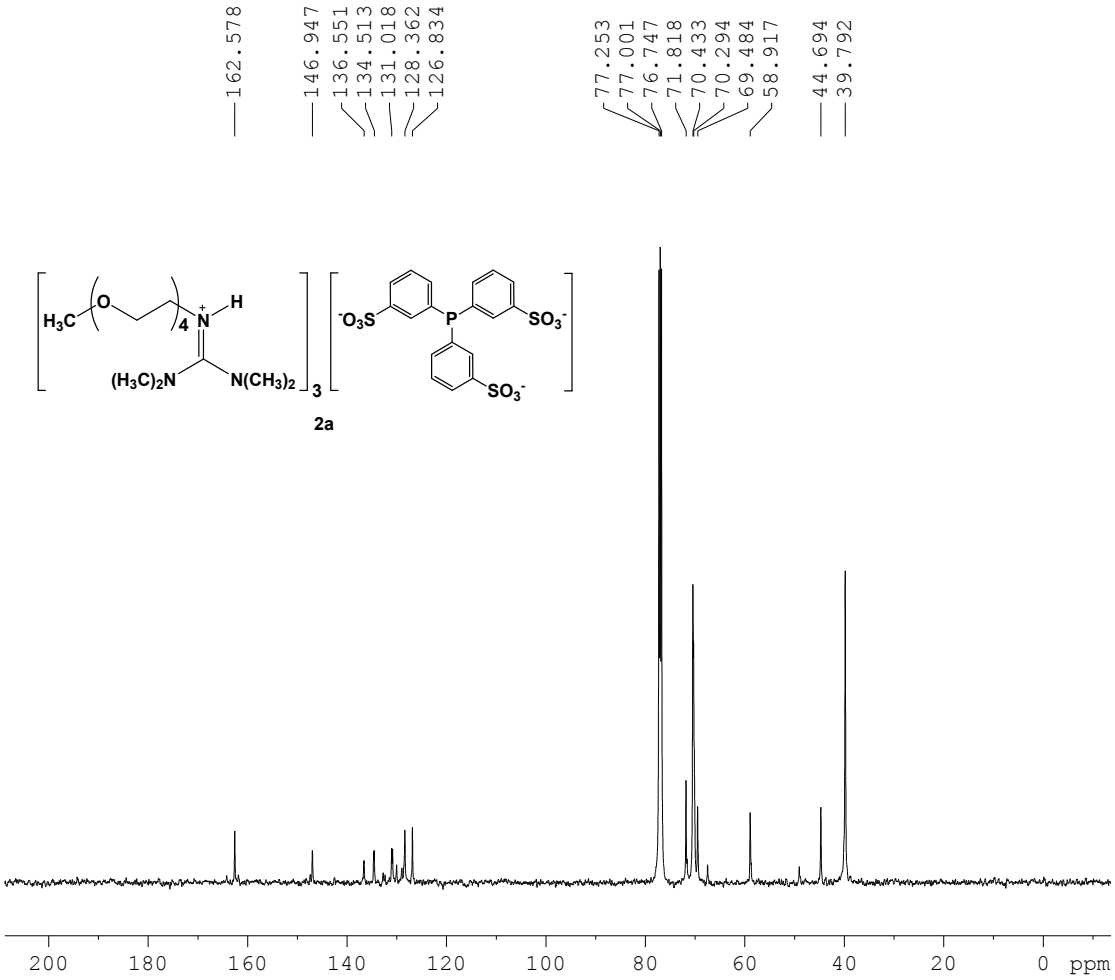
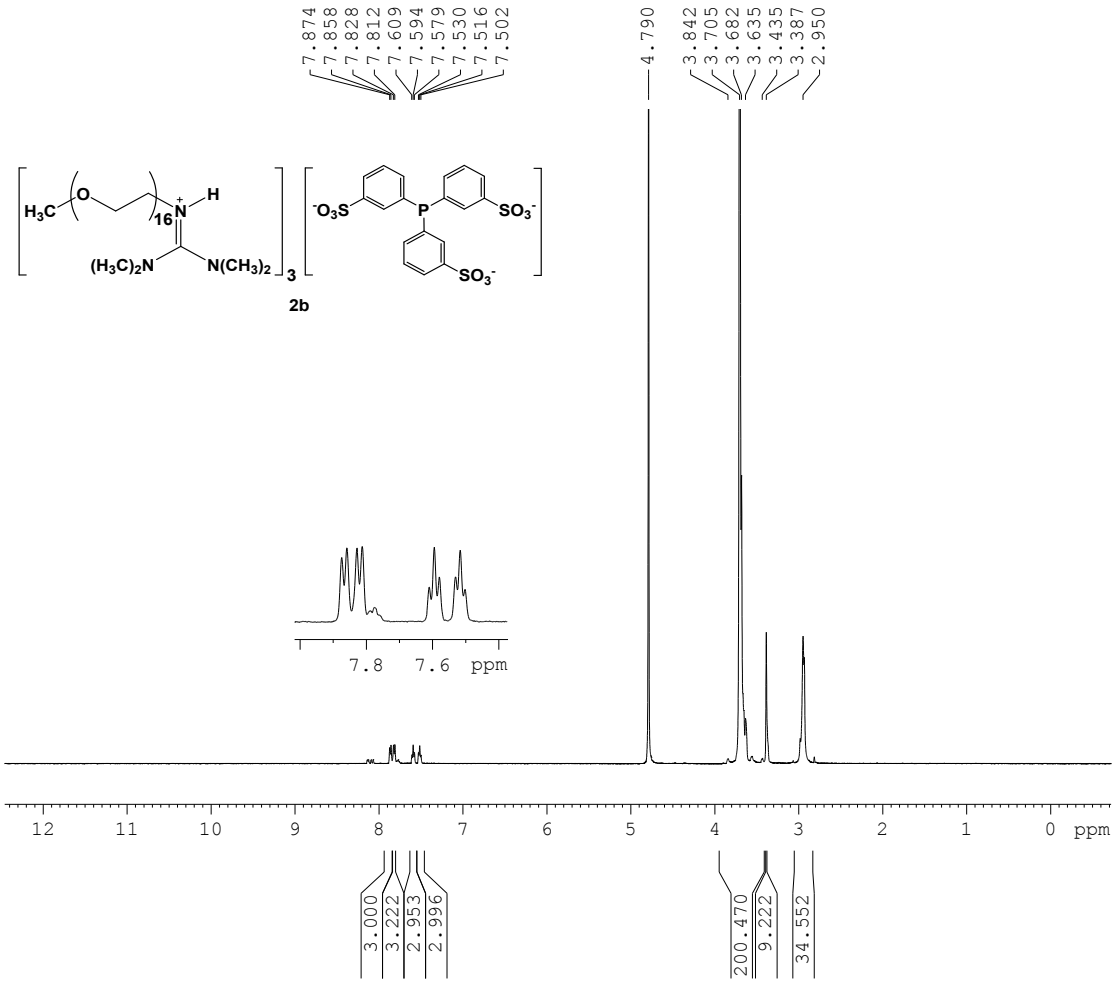


Figure S2. ^{13}C NMR spectrum of **2a** (125.7 MHz, $CDCl_3$)

2.3 ^{31}P NMR spectrum of **2a**

Figure S3. ^{31}P NMR spectrum of **2a** (202.4 MHz, D_2O)

2.4 ^{1}H NMR spectrum of **2b**



2b

Figure S4. ^{1}H NMR spectrum of **2b** (500.0 MHz, D_2O)

2.5 ^{13}C NMR spectrum of **2b**

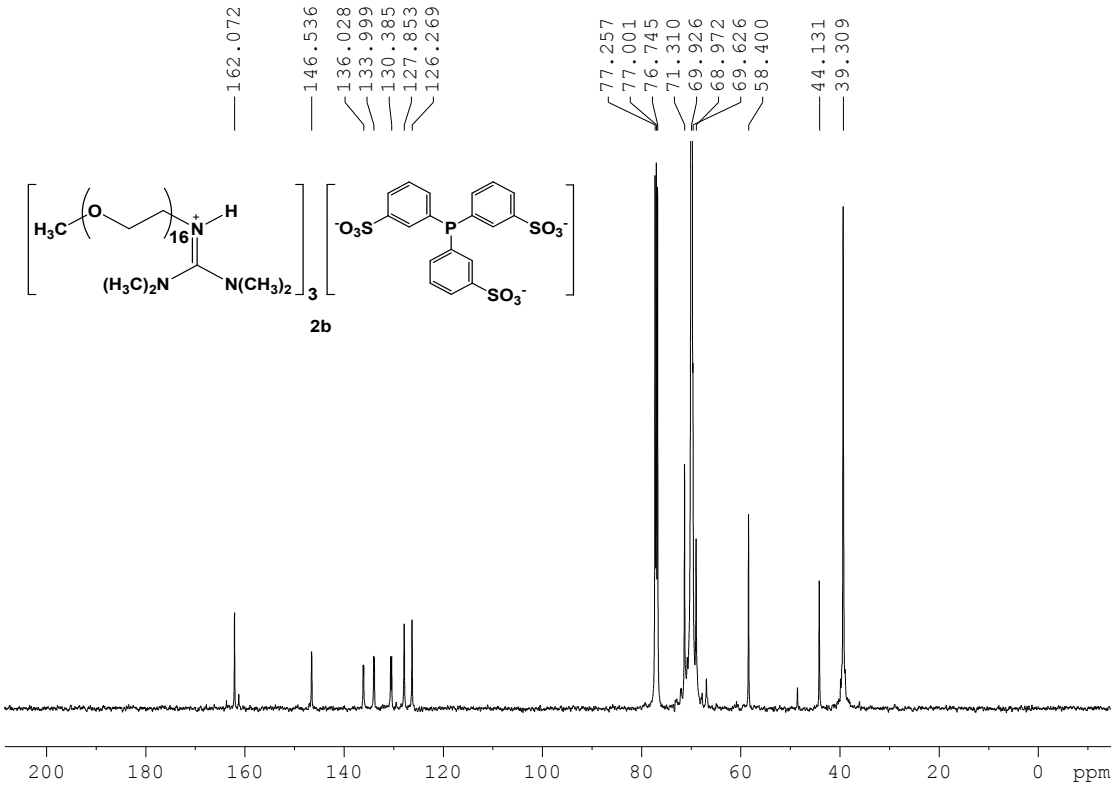


Figure S5. ^{13}C NMR spectrum of **2b** (125.7 MHz, $CDCl_3$)

2.6 ^{31}P NMR spectrum of **2b**

Figure S6. ^{31}P NMR spectrum of **2b** (202.4 MHz, D_2O)

2.7 ^{1}H NMR spectrum of **2c**

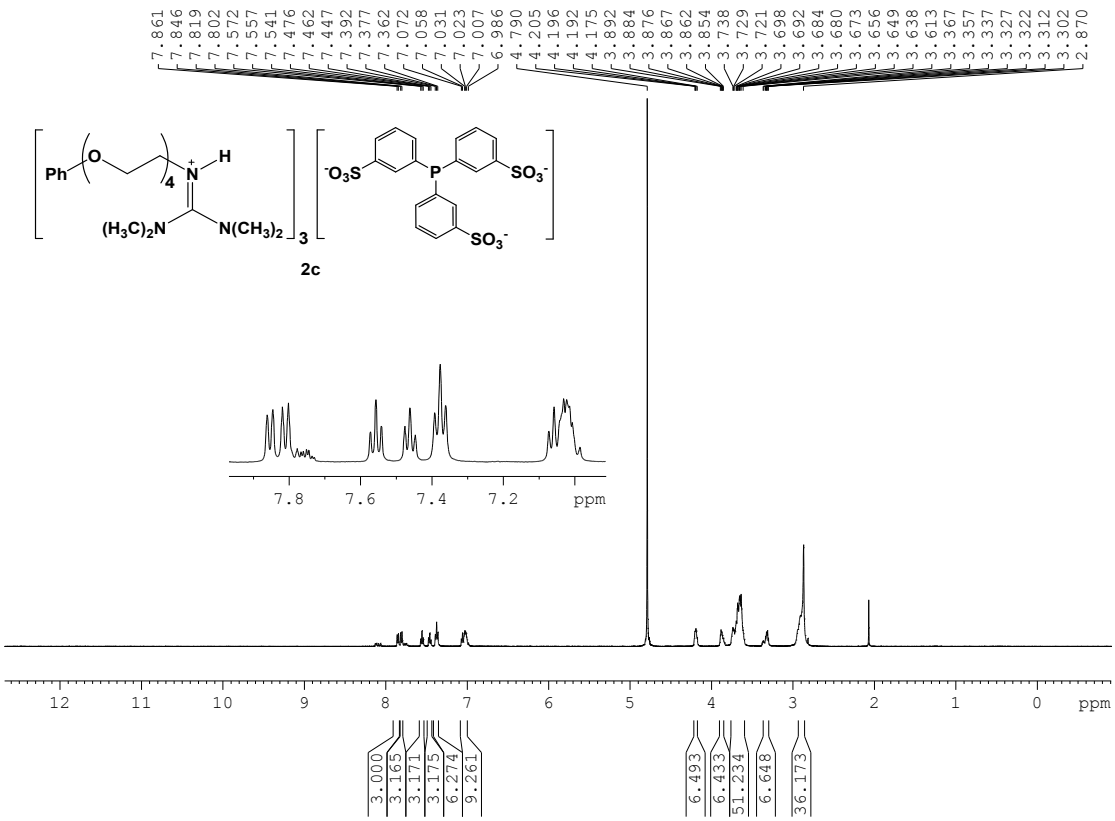


Figure S7. ^{1}H NMR spectrum of **2c** (500.0 MHz, D_2O)

2.8 ^{13}C NMR spectrum of **2c**

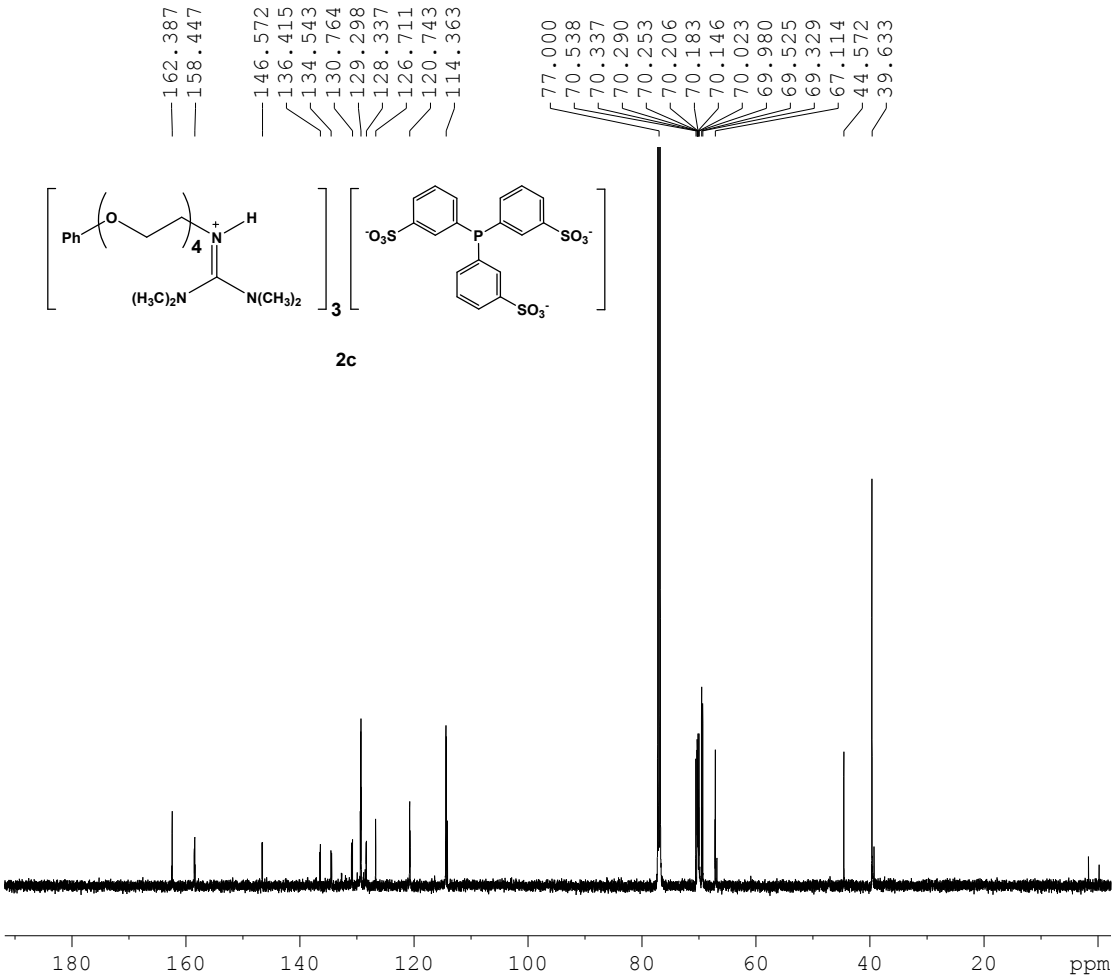


Figure S8. ^{13}C NMR spectrum of **2c** (150.9 MHz, $CDCl_3$)

2.9 ^{31}P NMR spectrum of **2c**

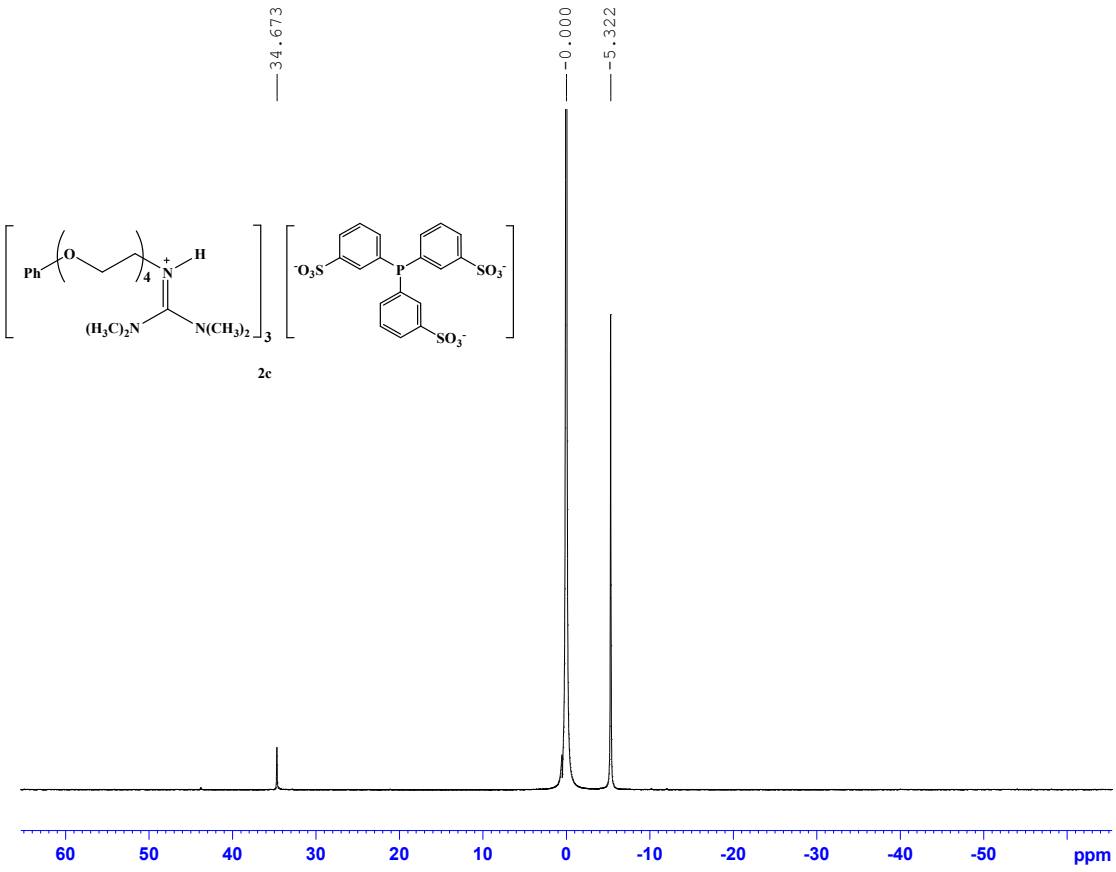


Figure S9. ^{31}P NMR spectrum of **2c** (202.4 MHz, D_2O)

2.10 ^{1}H NMR spectrum of **2d**

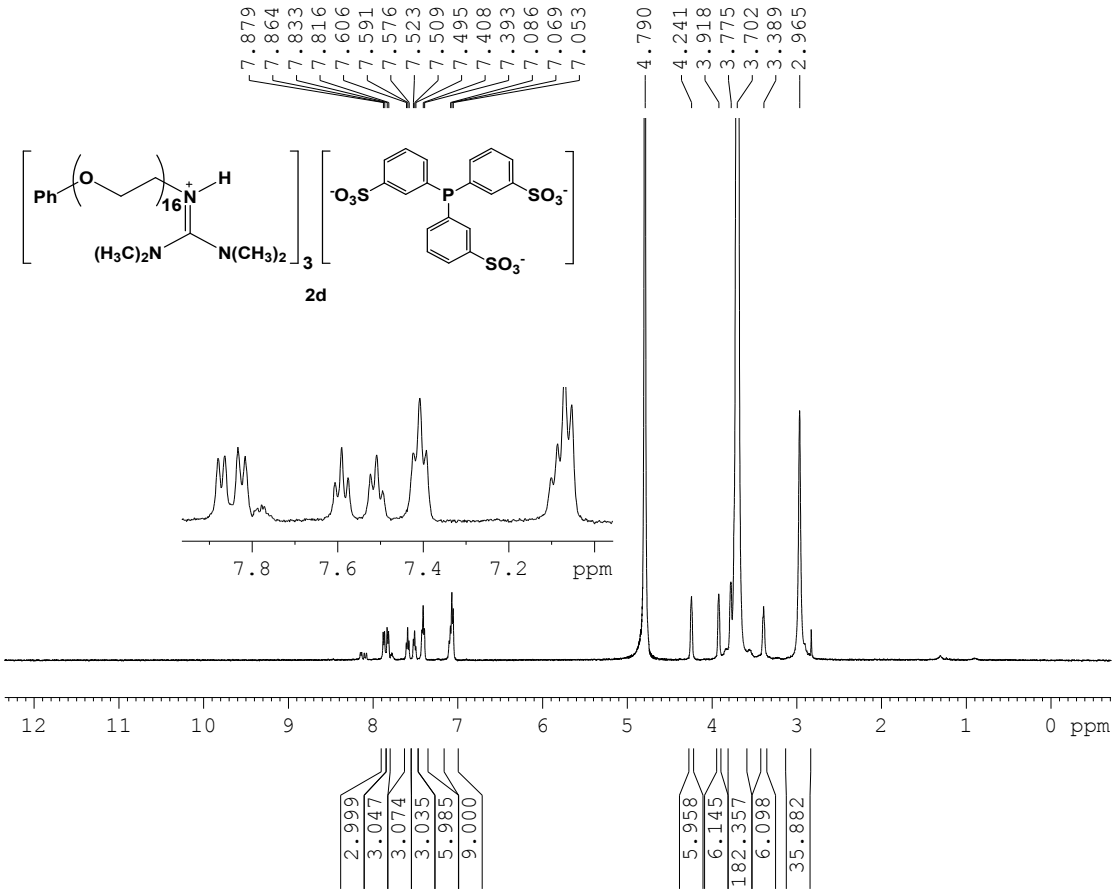


Figure S10. ^{1}H NMR spectrum of **2d** (500.0 MHz, D_2O)

2.11 ^{13}C NMR spectrum of **2d**

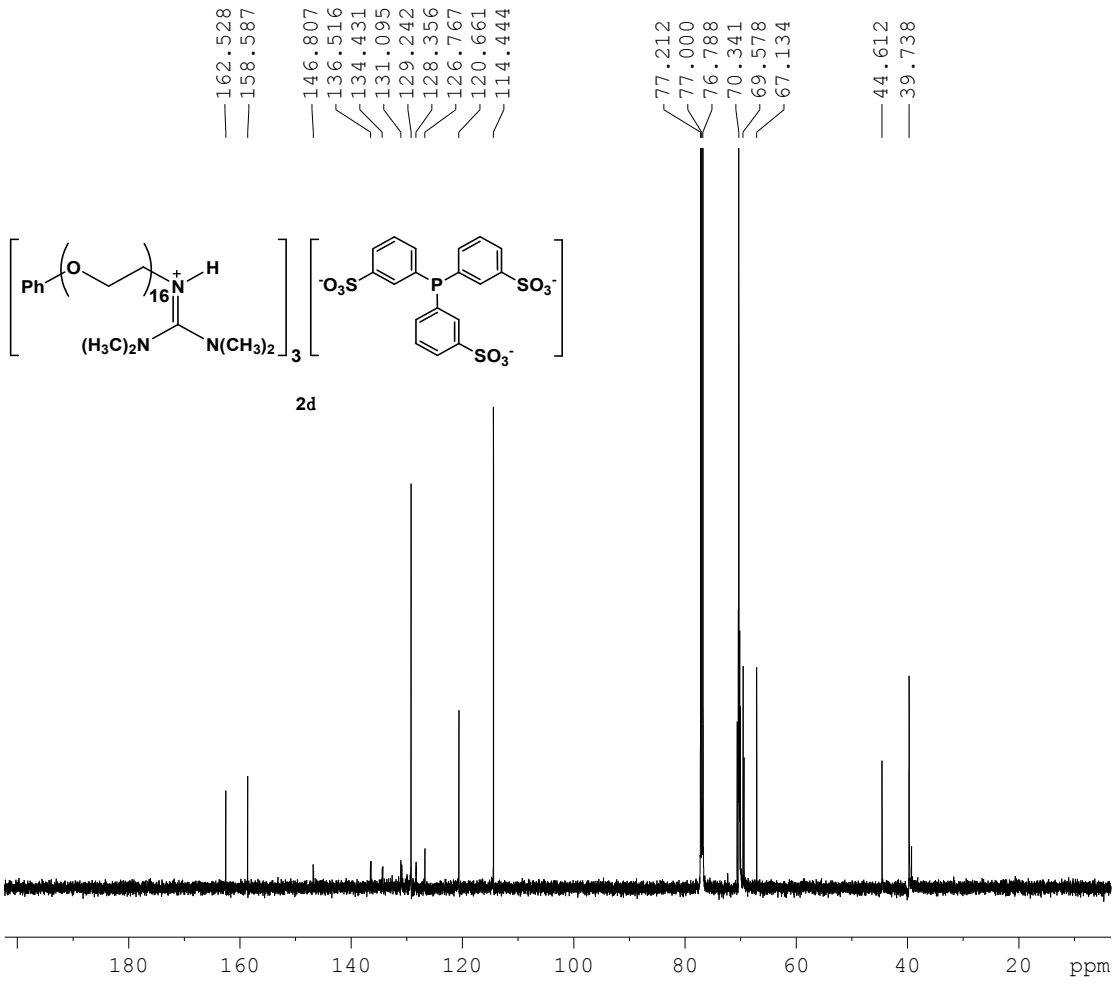


Figure S11. ^{13}C NMR spectrum of **2d** (150.9 MHz, $CDCl_3$)

2.12 ^{31}P NMR spectrum of **2d**

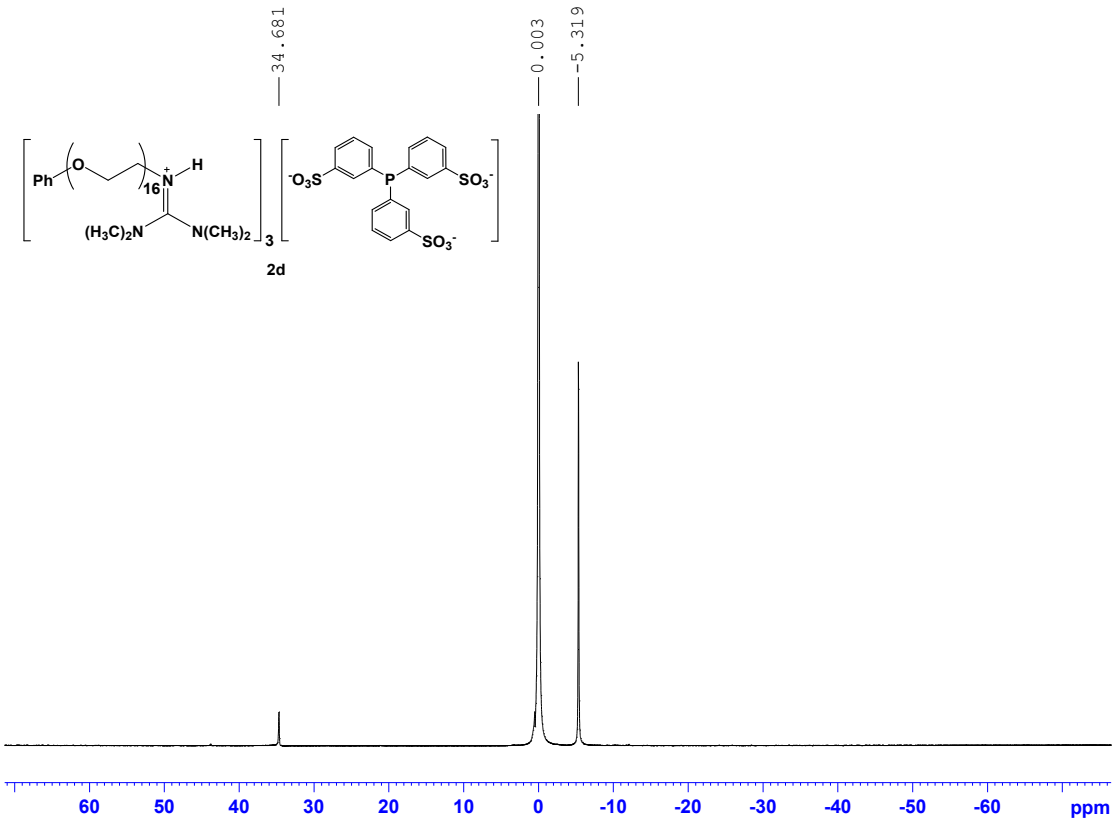


Figure S12. ^{31}P NMR spectrum of **2d** (202.4 MHz, D_2O)

2.13 ^{1}H NMR spectrum of **3a**

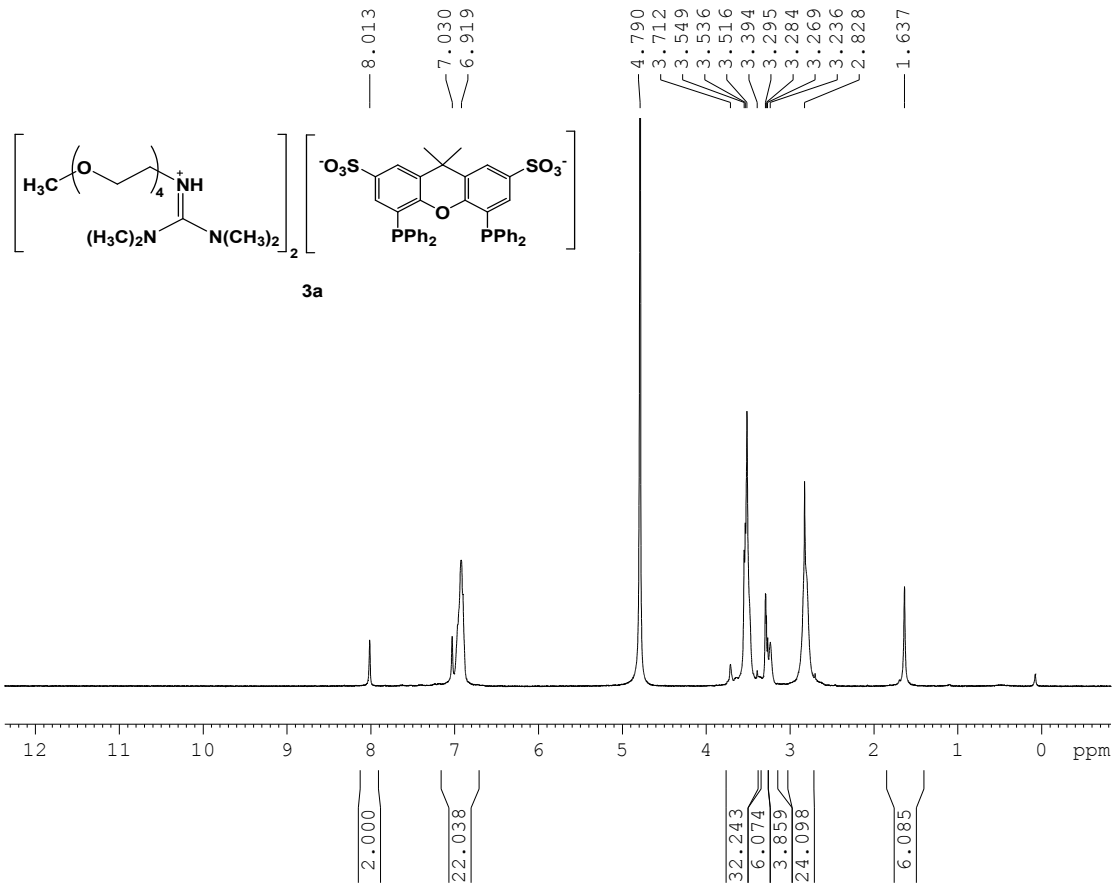


Figure S13. ^{1}H NMR spectrum of **3a** (500.0 MHz, D_2O)

2.14 ^{13}C NMR spectrum of **3a**

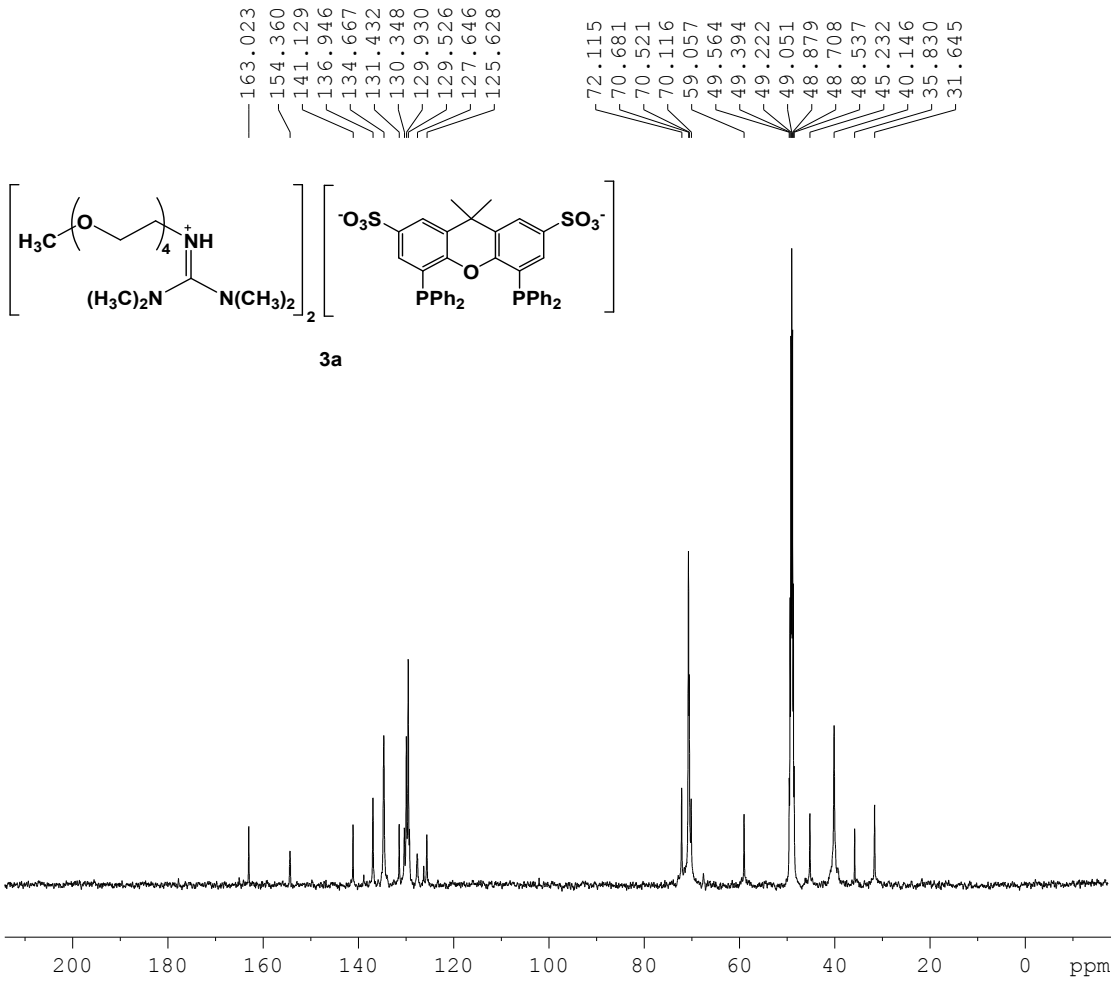
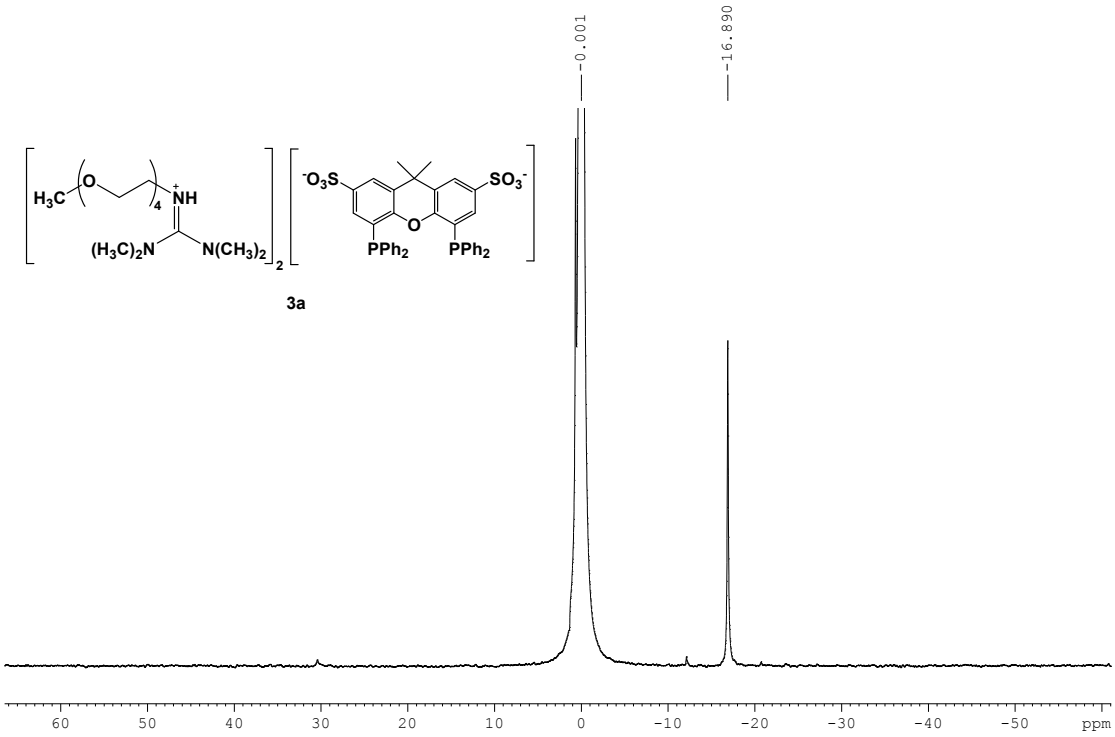


Figure S14. ^{13}C NMR spectrum of **3a** (125.7 MHz, CD_3OD)

2.15 ^{31}P NMR spectrum of **3a**



3a

Figure S15. ^{31}P NMR spectrum of **3a** (202.4 MHz, D_2O)

2.16 ^{1}H NMR spectrum of **3b**

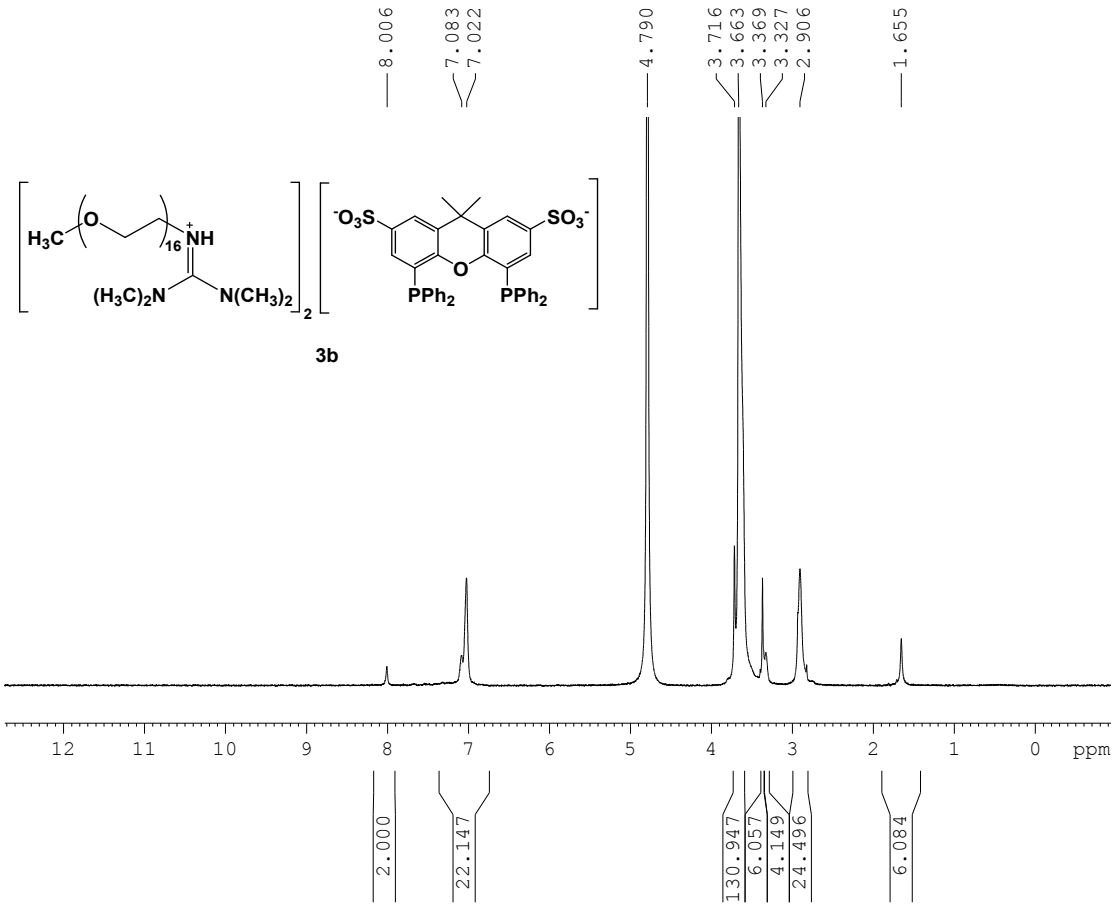


Figure S16. ^{1}H NMR spectrum of **3b** (500.0 MHz, D_2O)

2.17 ^{13}C NMR spectrum of **3b**

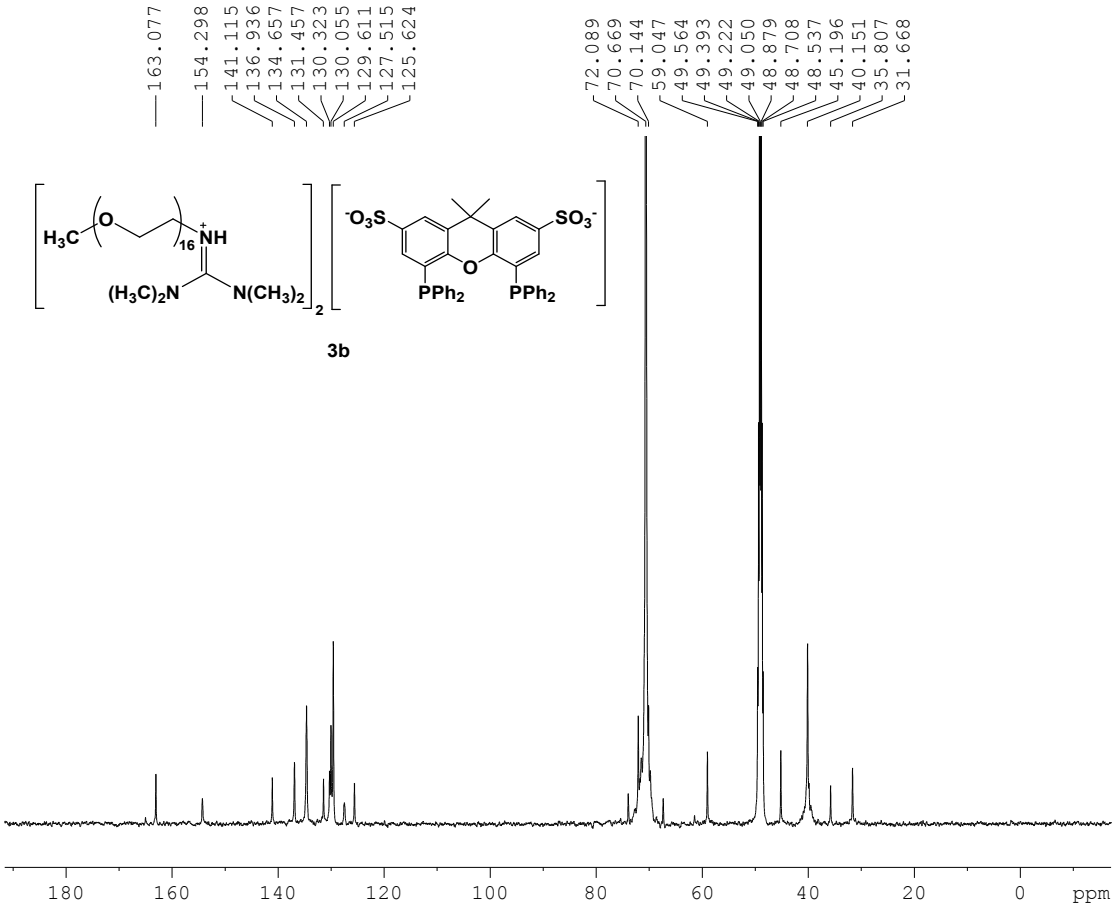


Figure S17. ^{13}C NMR spectrum of **3b** (125.7 MHz, CD_3OD)

2.18 ^{31}P NMR spectrum of **3b**

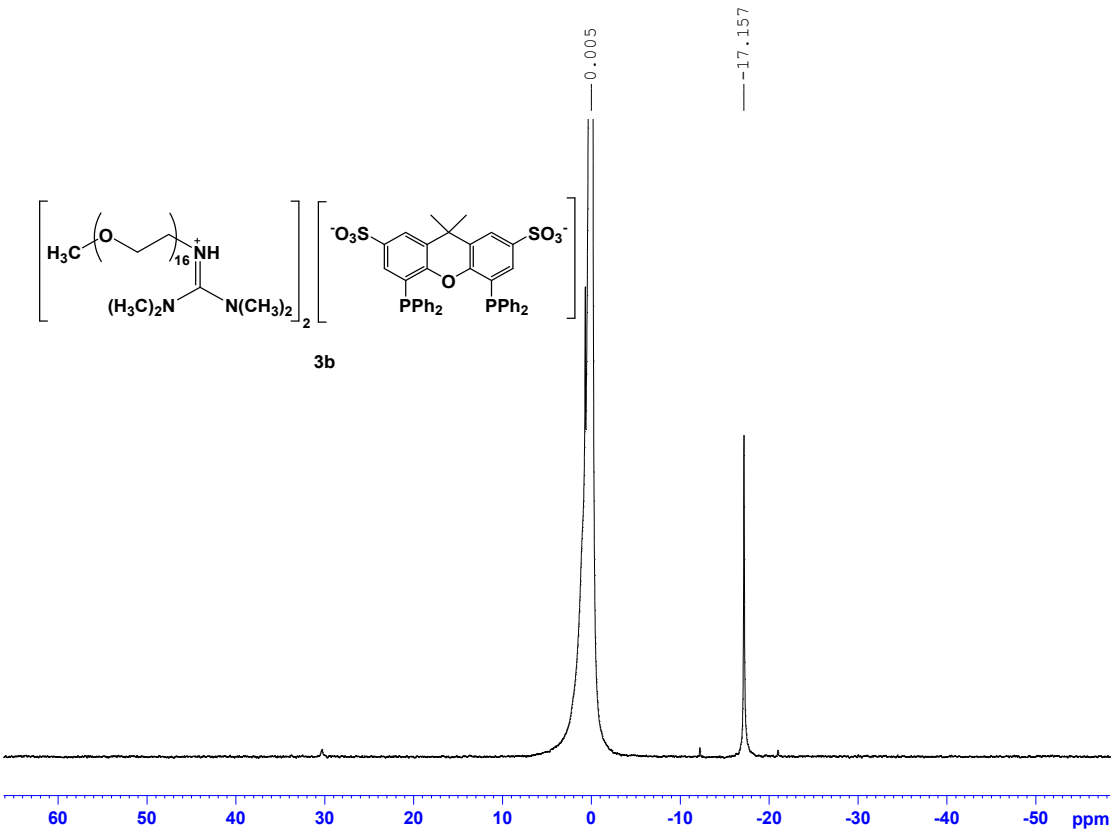


Figure S18. ^{31}P NMR spectrum of **3b** (202.4 MHz, D_2O)

2.19 ^{1}H NMR spectrum of **3c**

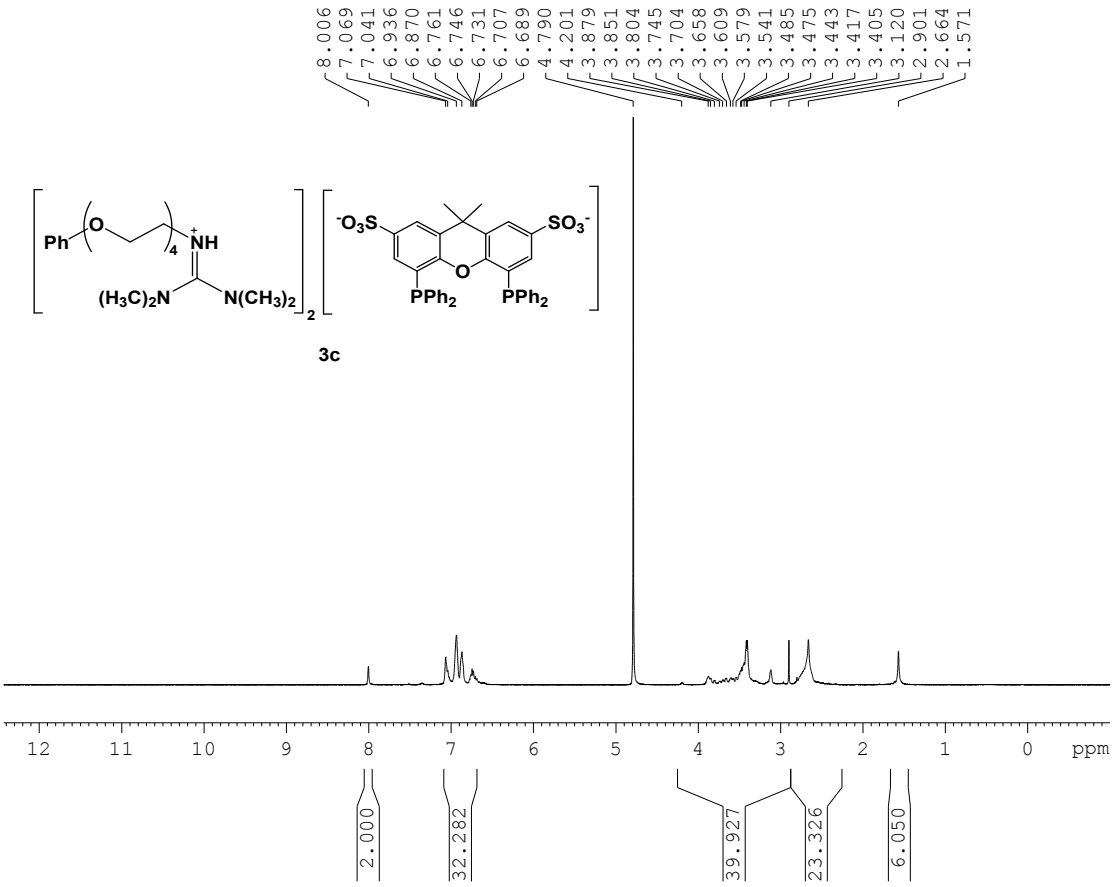


Figure S19. ^{1}H NMR spectrum of **3c** (500.0 MHz, D_2O)

2.20 ^{13}C NMR spectrum of **3c**

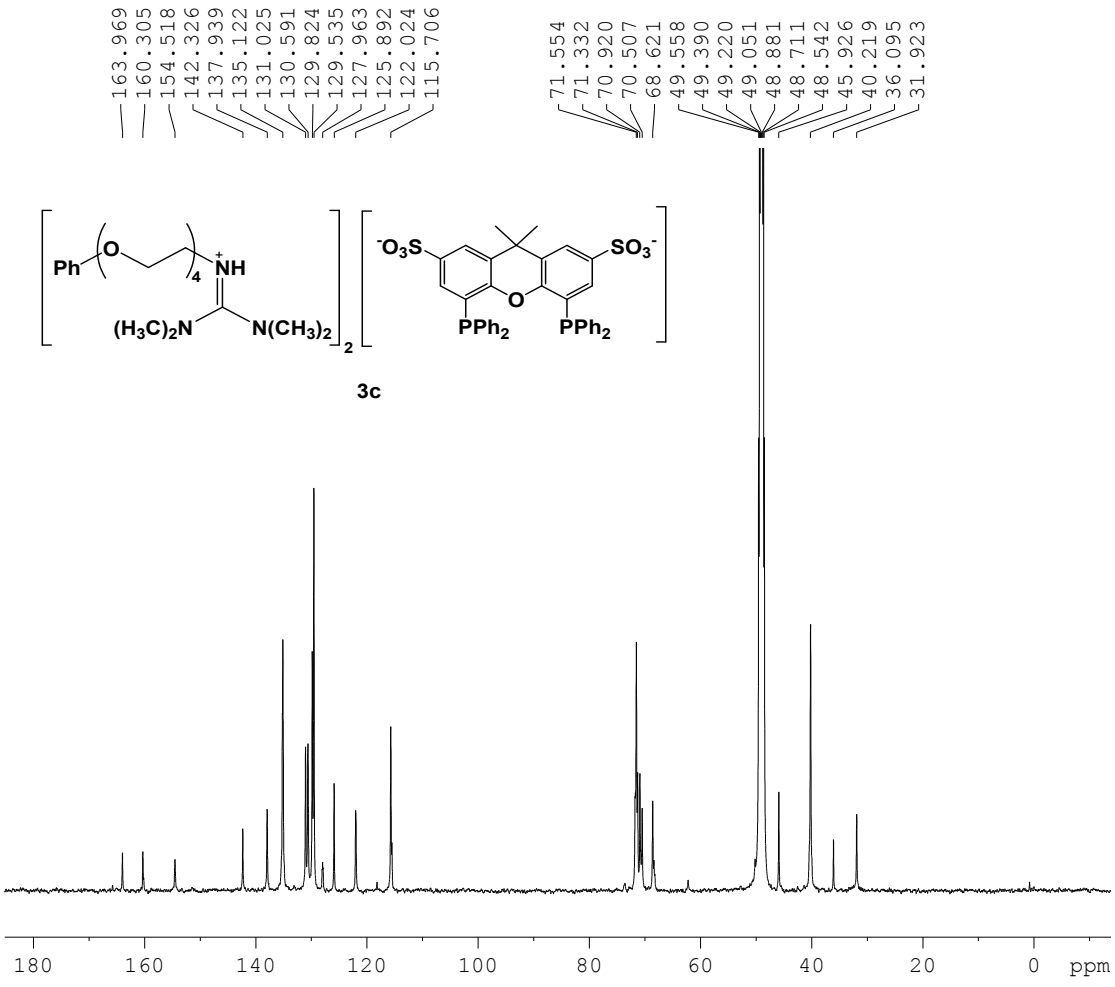
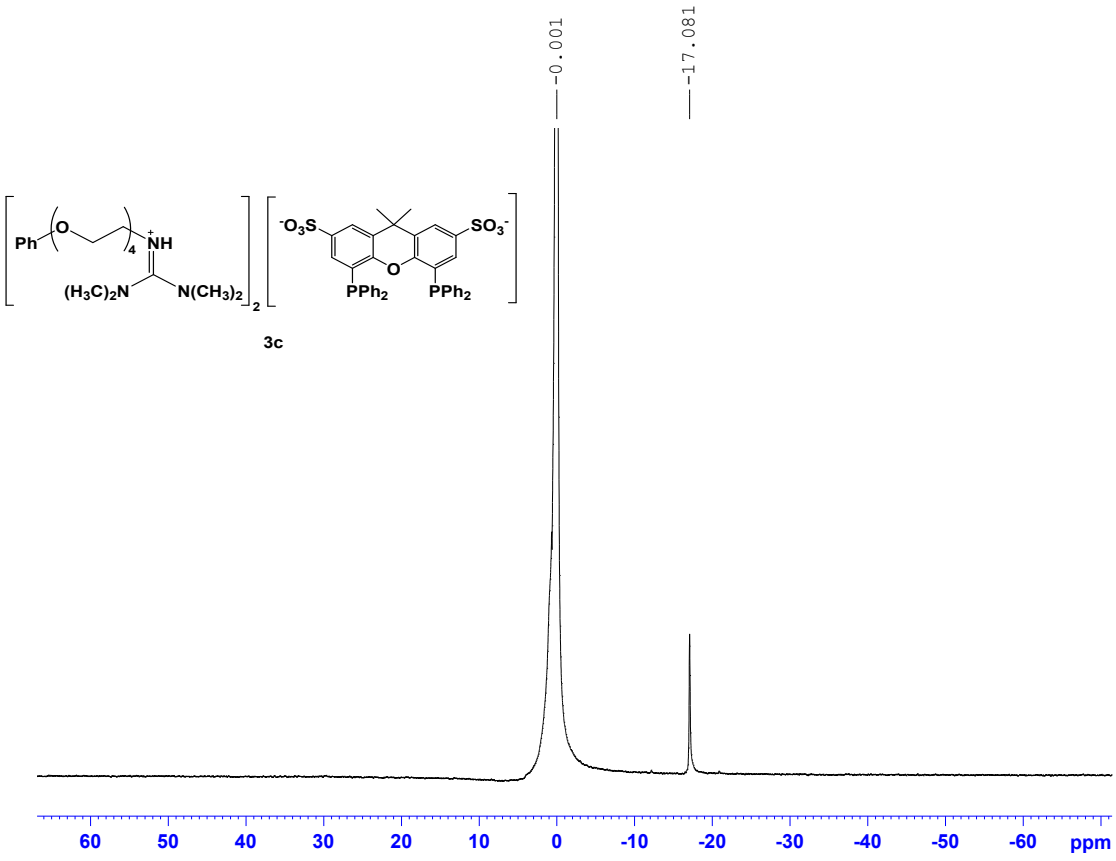


Figure S20. ^{13}C NMR spectrum of **3c** (125.7MHz, CD_3OD)

2.21 ^{31}P NMR spectrum of **3c**



3c

Figure S21. ^{31}P NMR spectrum of **3c** (202.4 MHz, D_2O)

2.22 ^{1}H NMR spectrum of **3d**

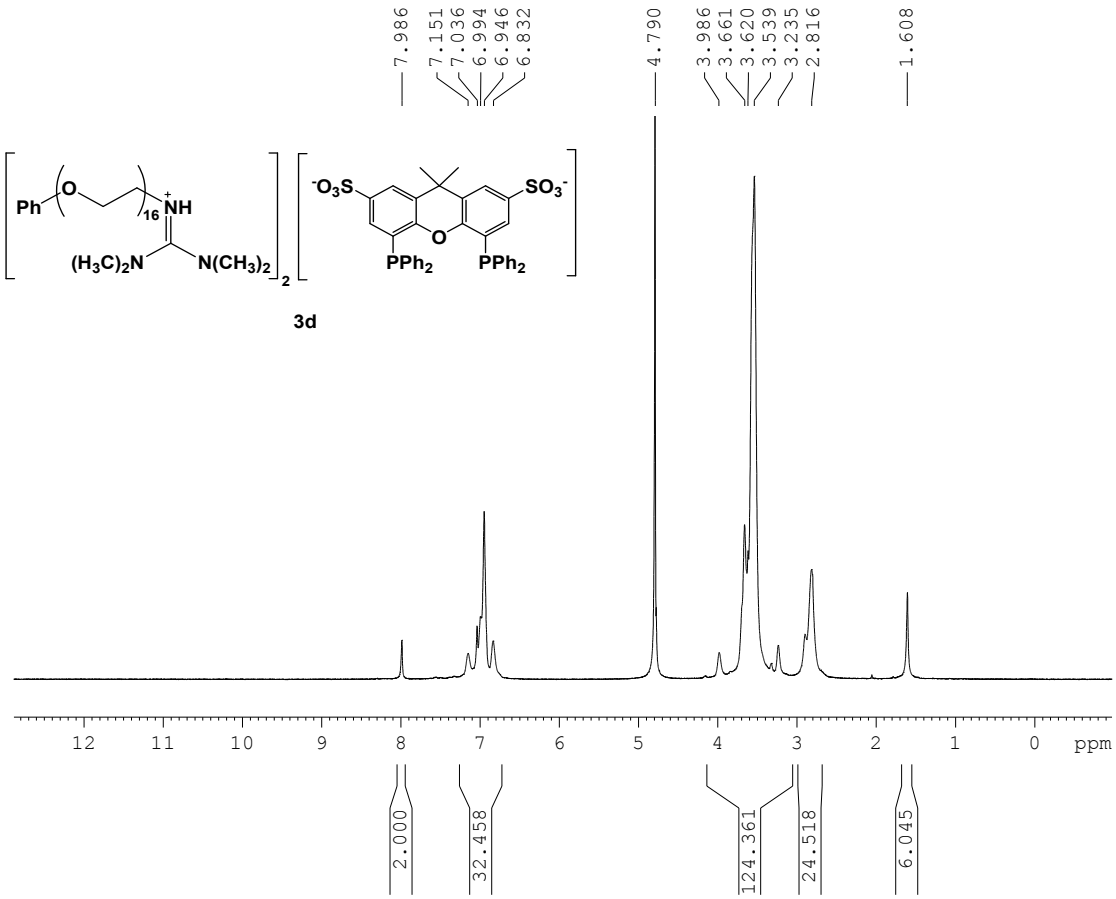


Figure S22. ^{1}H NMR spectrum of **3d** (500.0 MHz, D_2O)

2.23 ^{13}C NMR spectrum of **3d**

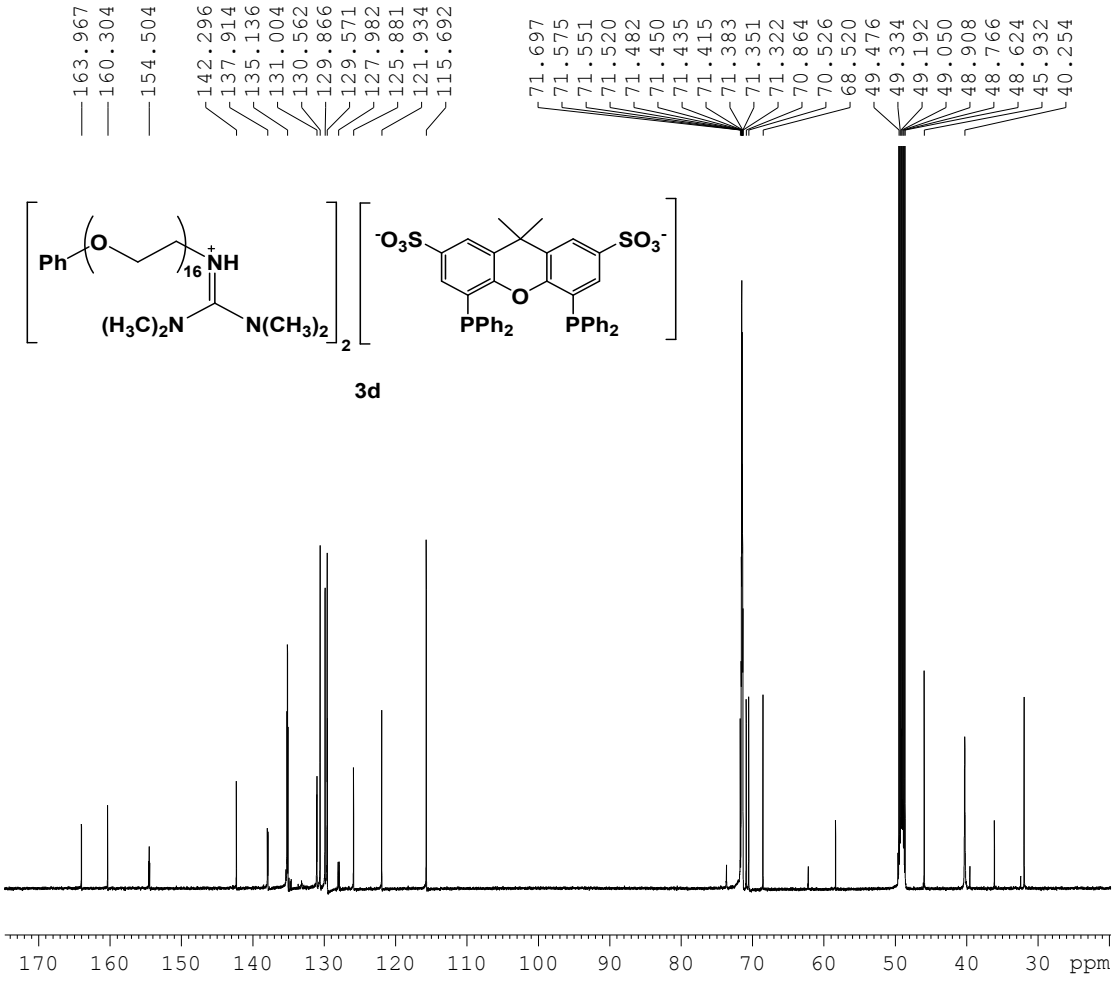


Figure S23. ^{13}C NMR spectrum of **3d** (150.9 MHz, CD_3OD)

2.24 ^{31}P NMR spectrum of **3d**

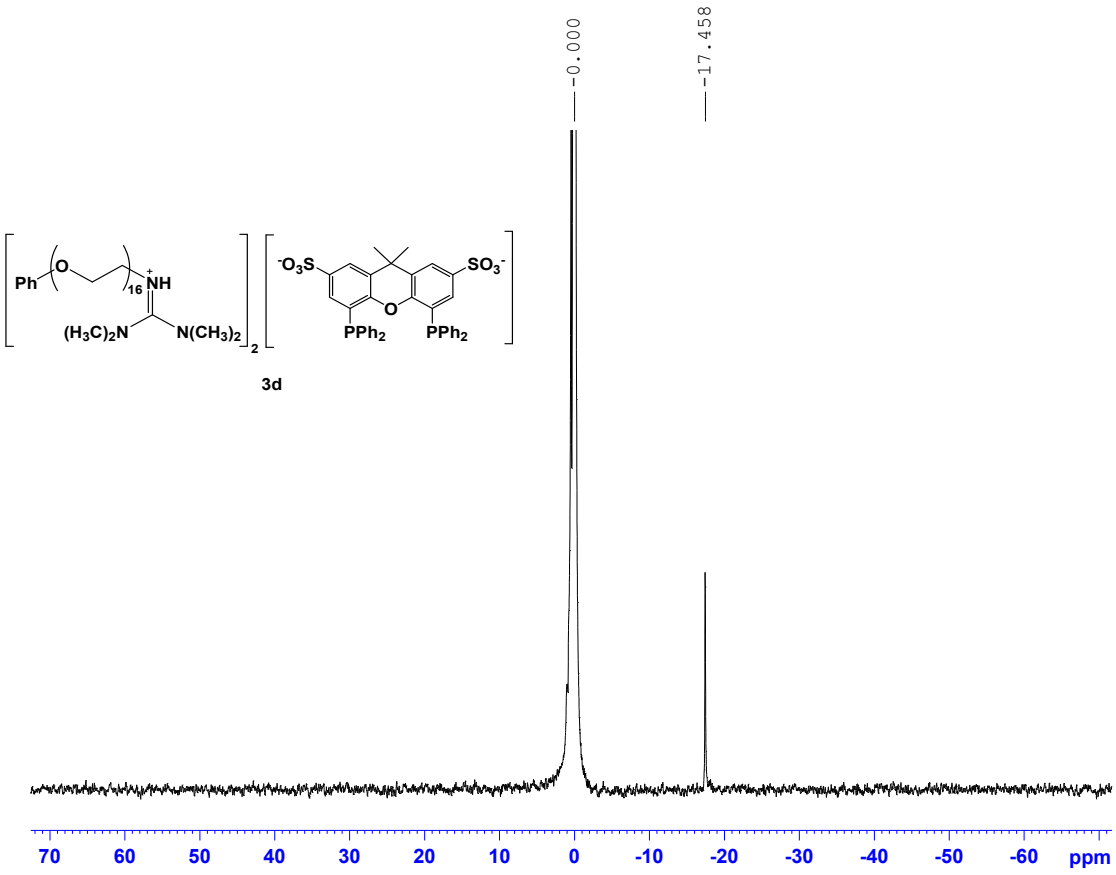


Figure S24. ^{31}P NMR spectrum of **3d** (202.4 MHz, D_2O)

3 HRMS Spectra

3.1 Mass spectrum (ES+) of **2a**

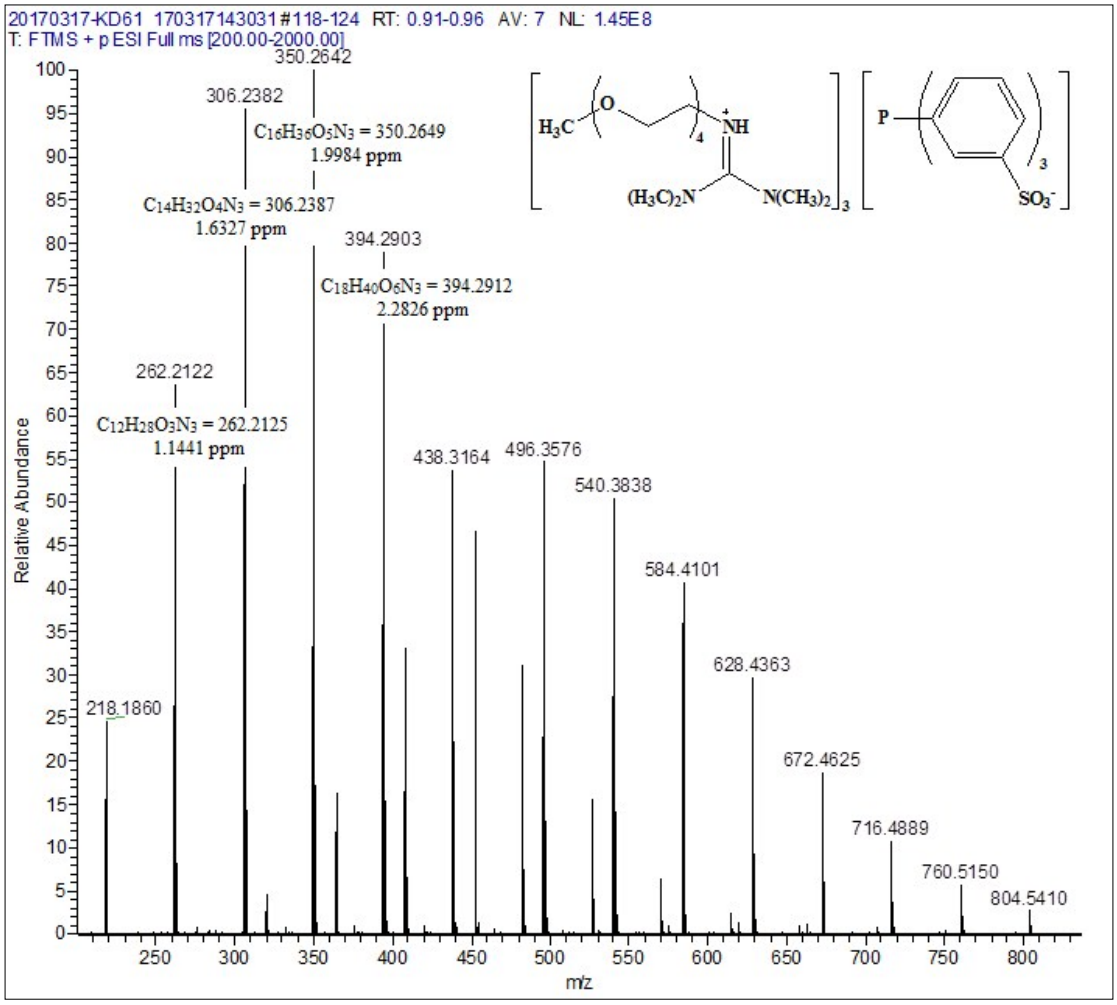


Figure S25. Mass spectrum (ES+) of **2a**

3.2 Mass spectrum (ES-) of **2a**

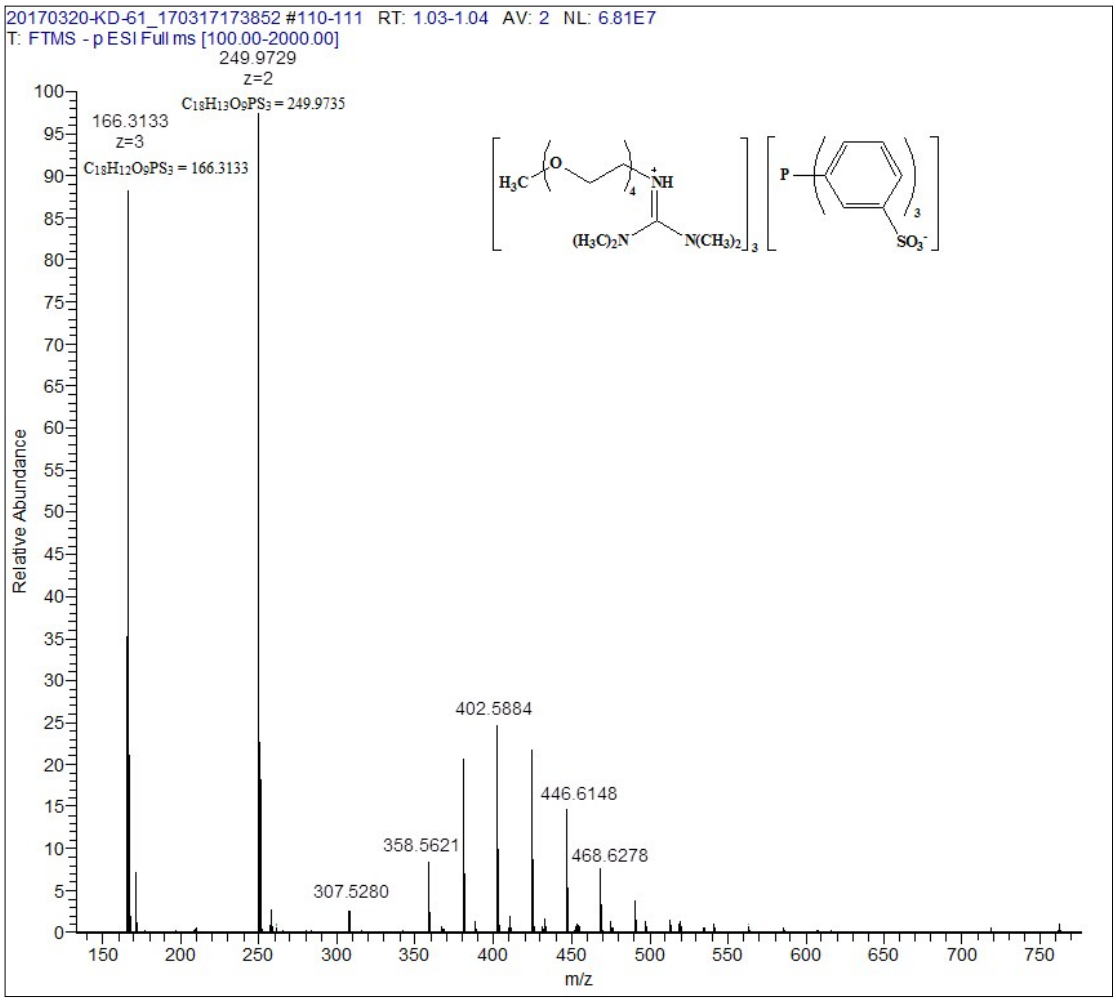


Figure S26. Mass spectrum (ES-) of **2a**

3.3 Mass spectrum (ES+) of **2b**

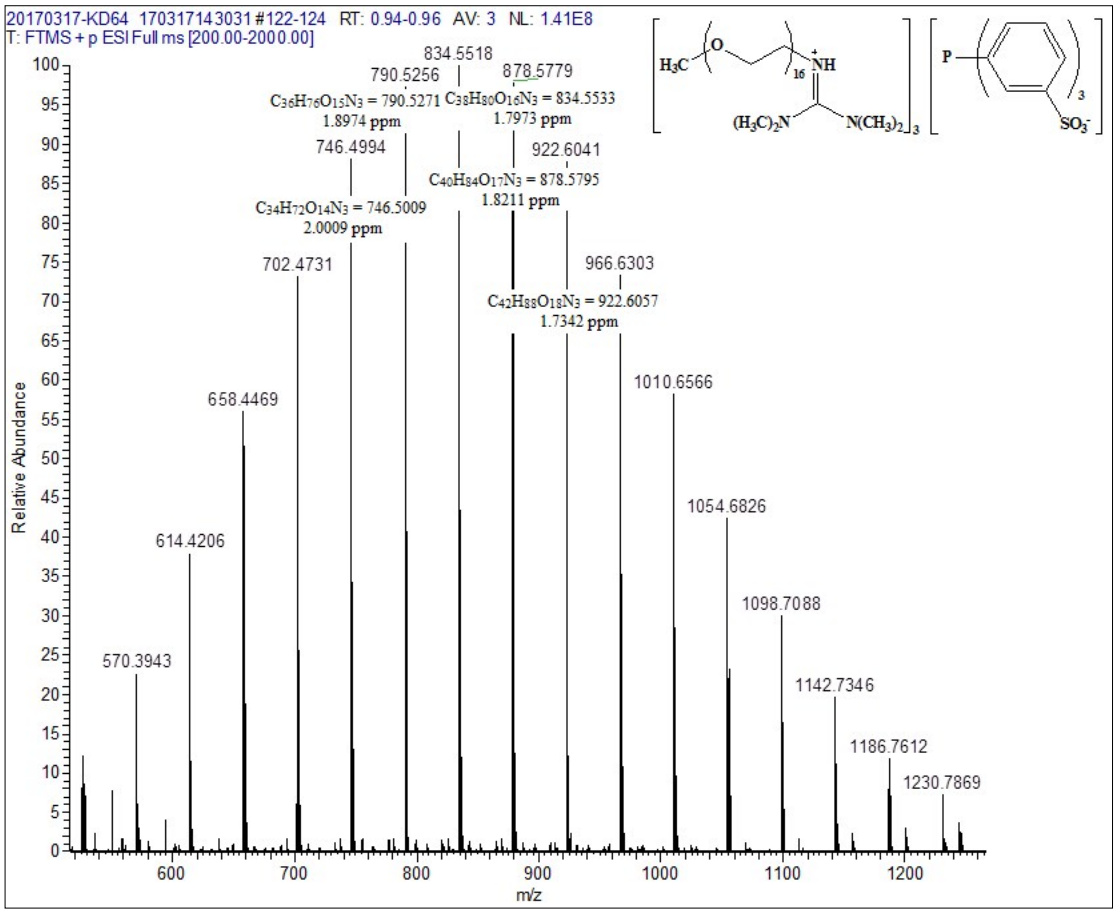


Figure S27. Mass spectrum (ES+) of **2b**

3.4 Mass spectrum (ES-) of **2b**

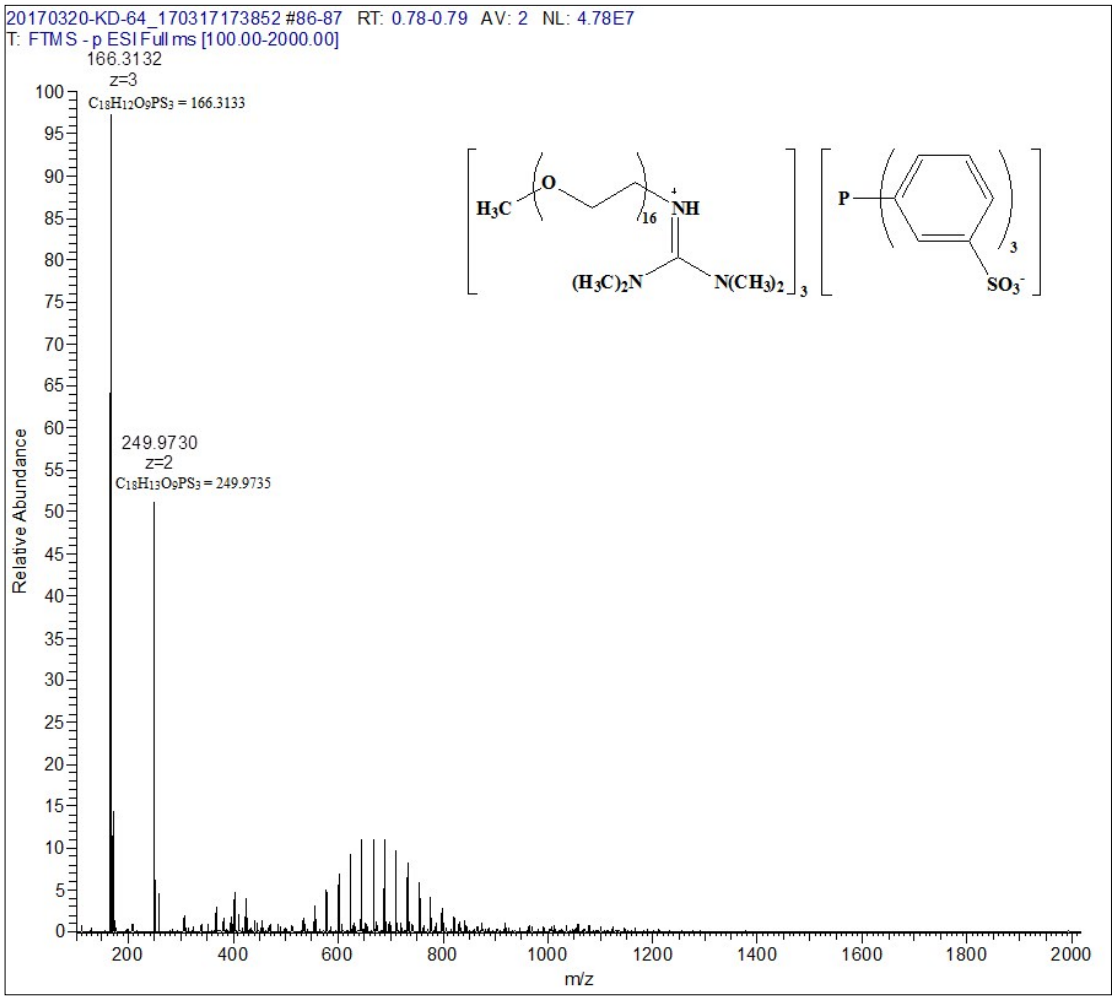


Figure S28. Mass spectrum (ES-) of **2b**

3.5 Mass spectrum (ES+) of **2c**

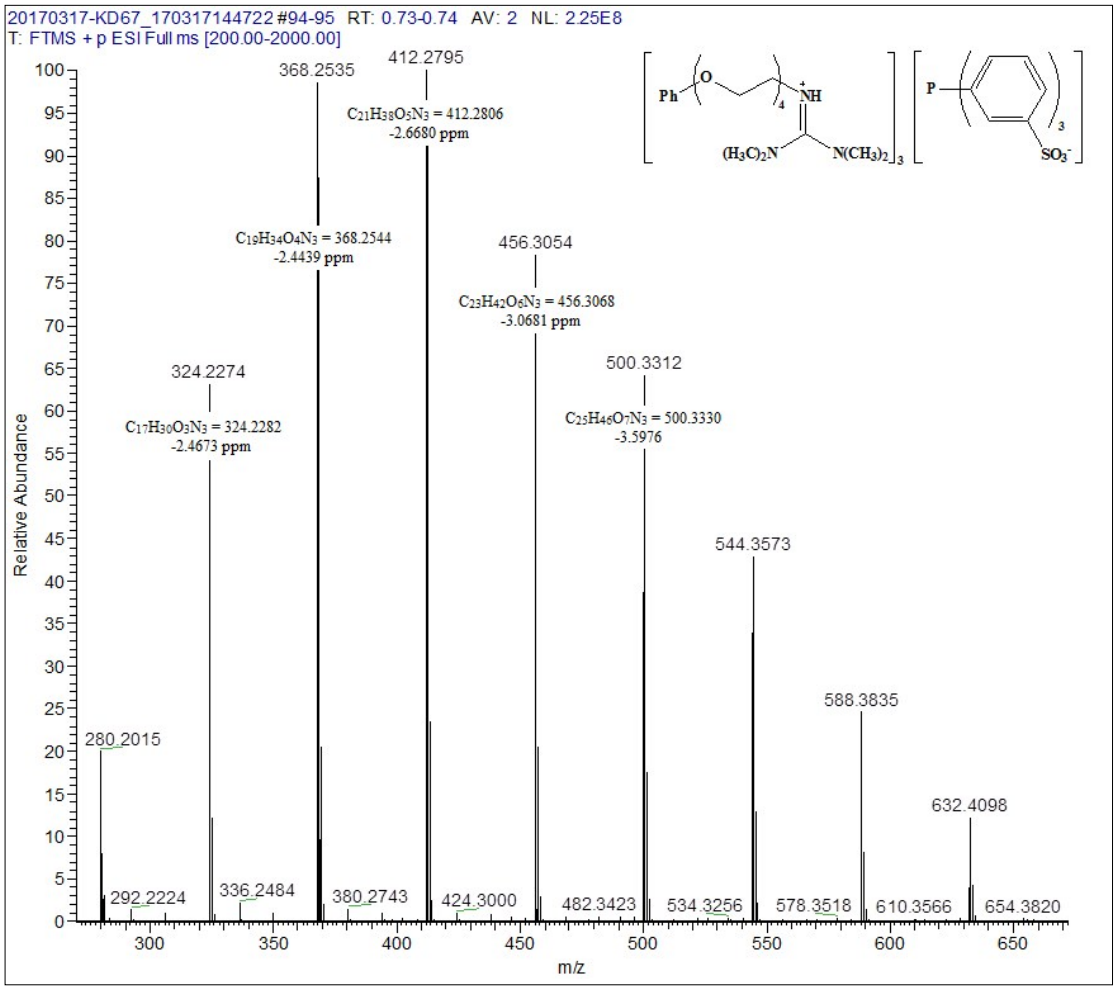


Figure S29. Mass spectrum (ES+) of **2c**

3.6 Mass spectrum (ES-) of **2c**

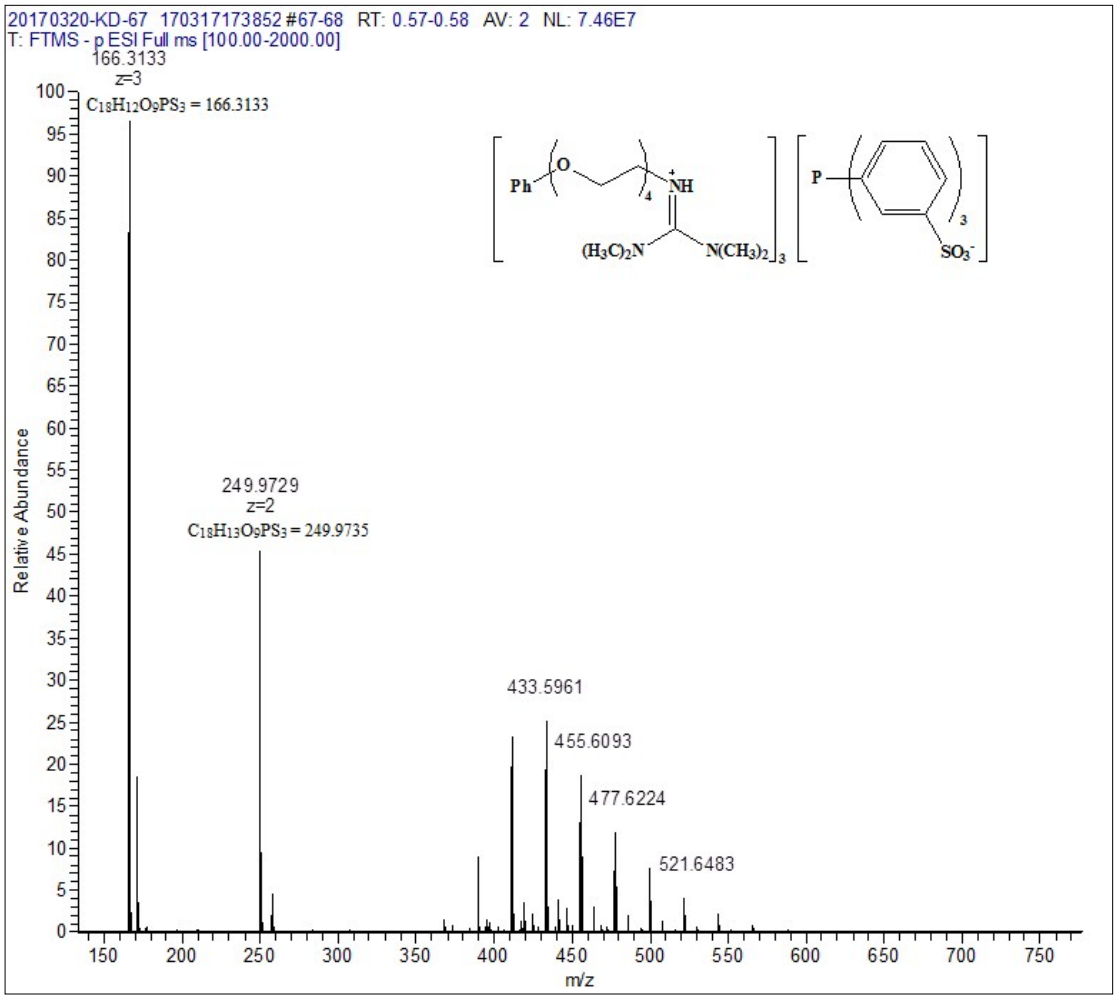


Figure S30. Mass spectrum (ES-) of **2c**

3.7 Mass spectrum (ES+) of **2d**

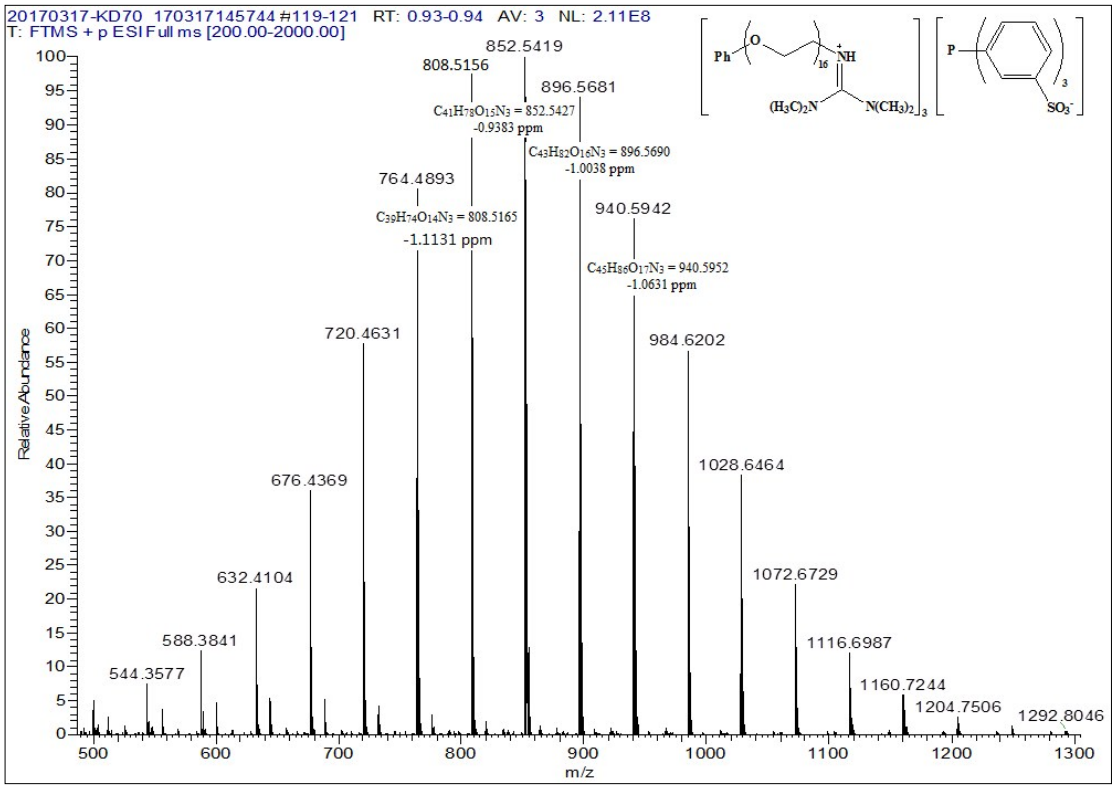


Figure S31. Mass spectrum (ES+) of **2d**

3.8 Mass spectrum (ES-) of **2d**

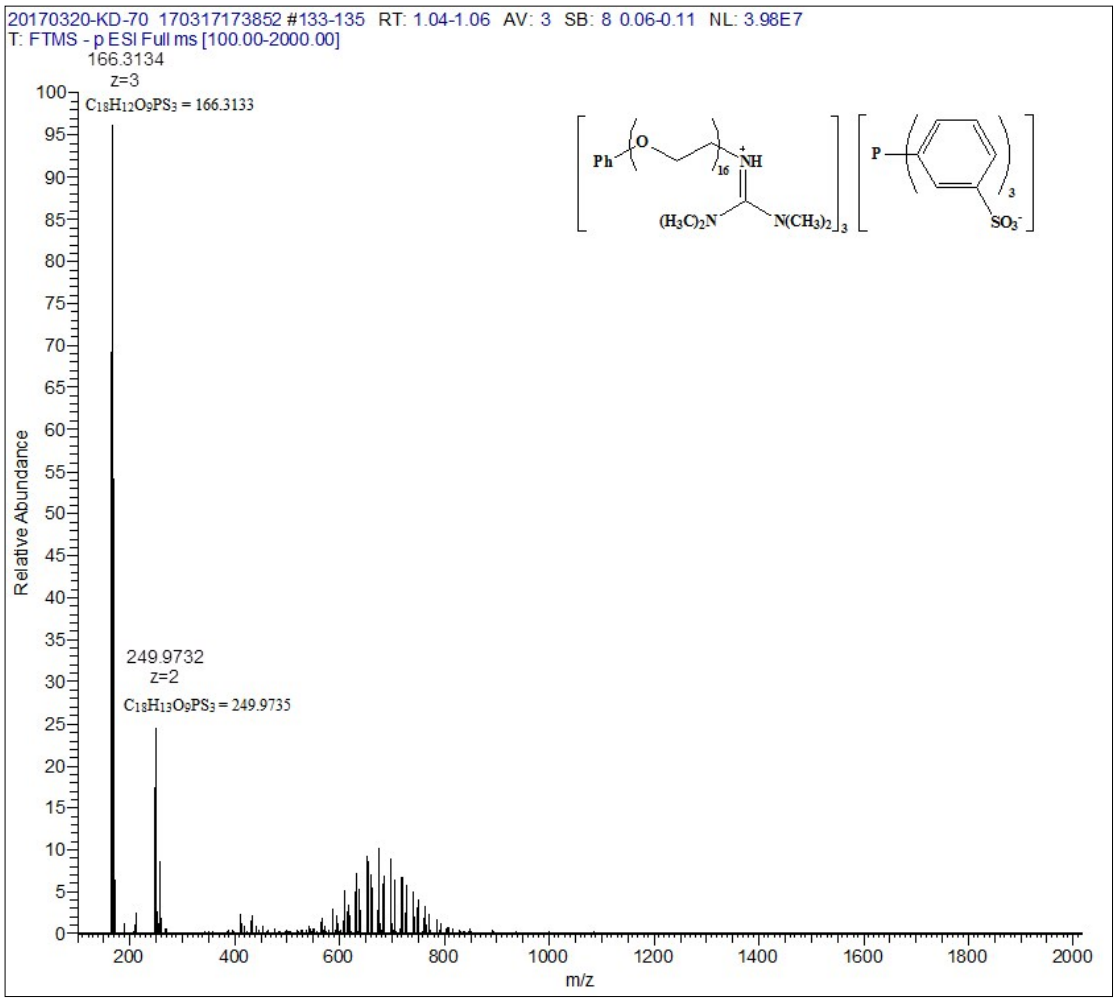


Figure S32. Mass spectrum (ES-) of **2d**

3.9 Mass spectrum (ES+) of **3a**

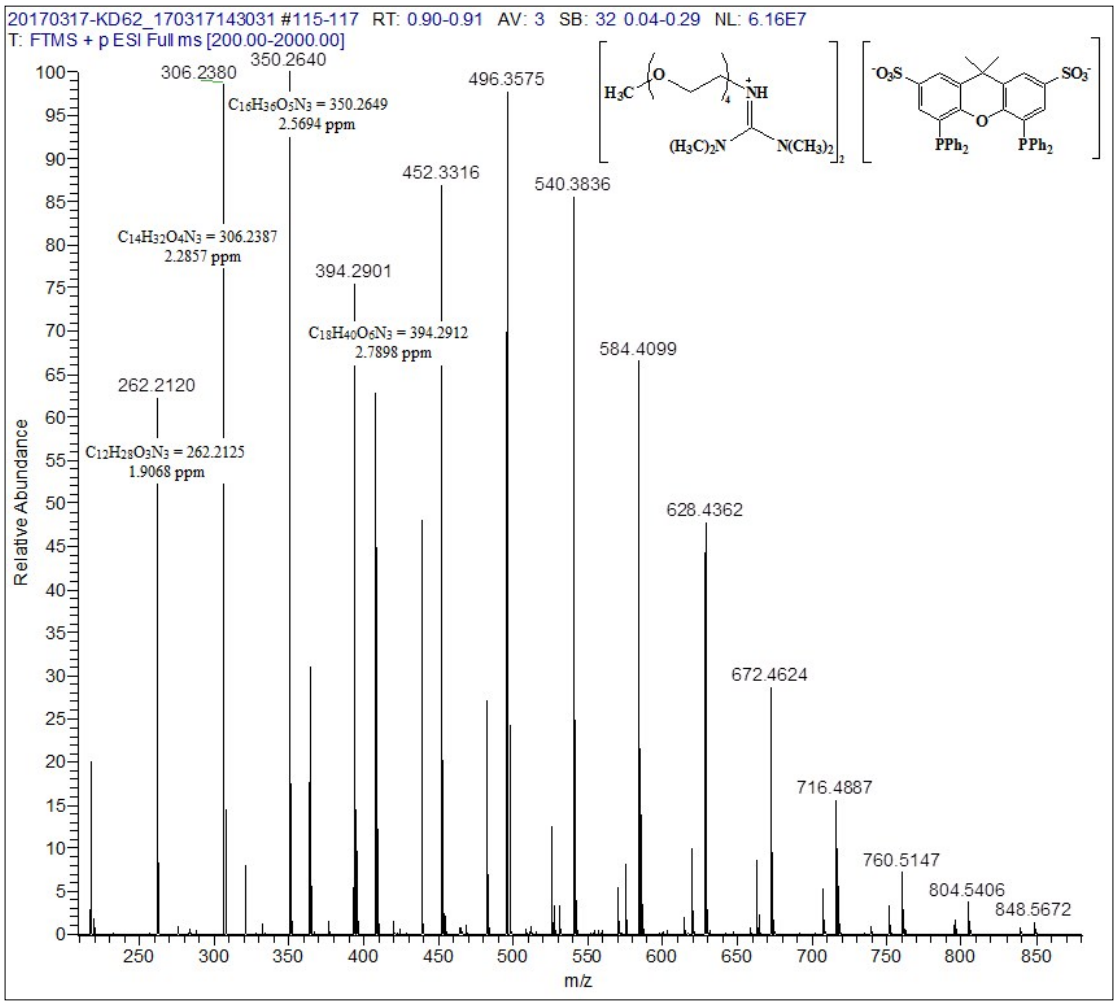


Figure S33. Mass spectrum (ES+) of **3a**

3.10 Mass spectrum (ES-) of **3a**

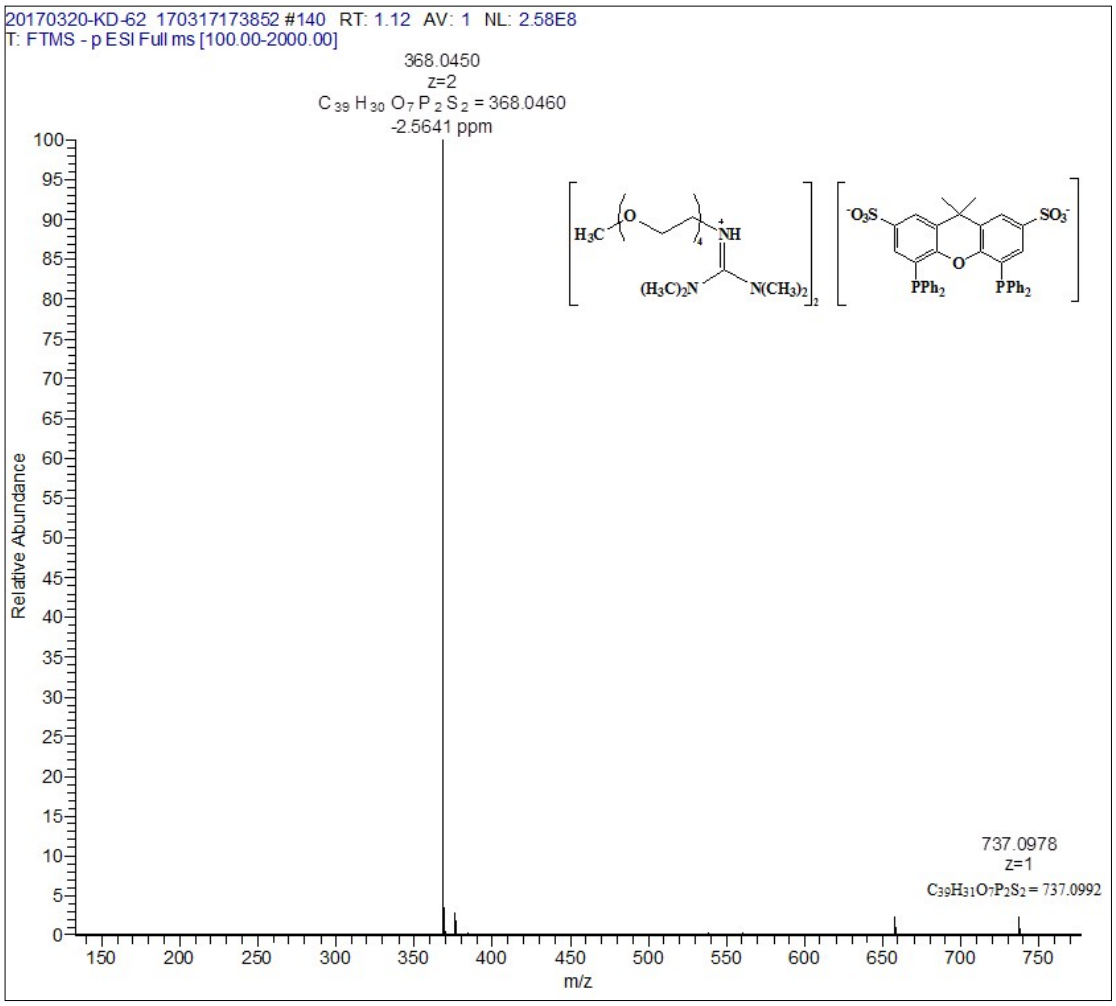


Figure S34. Mass spectrum (ES-) of **3a**

3.11 Mass spectrum (ES+) of **3b**

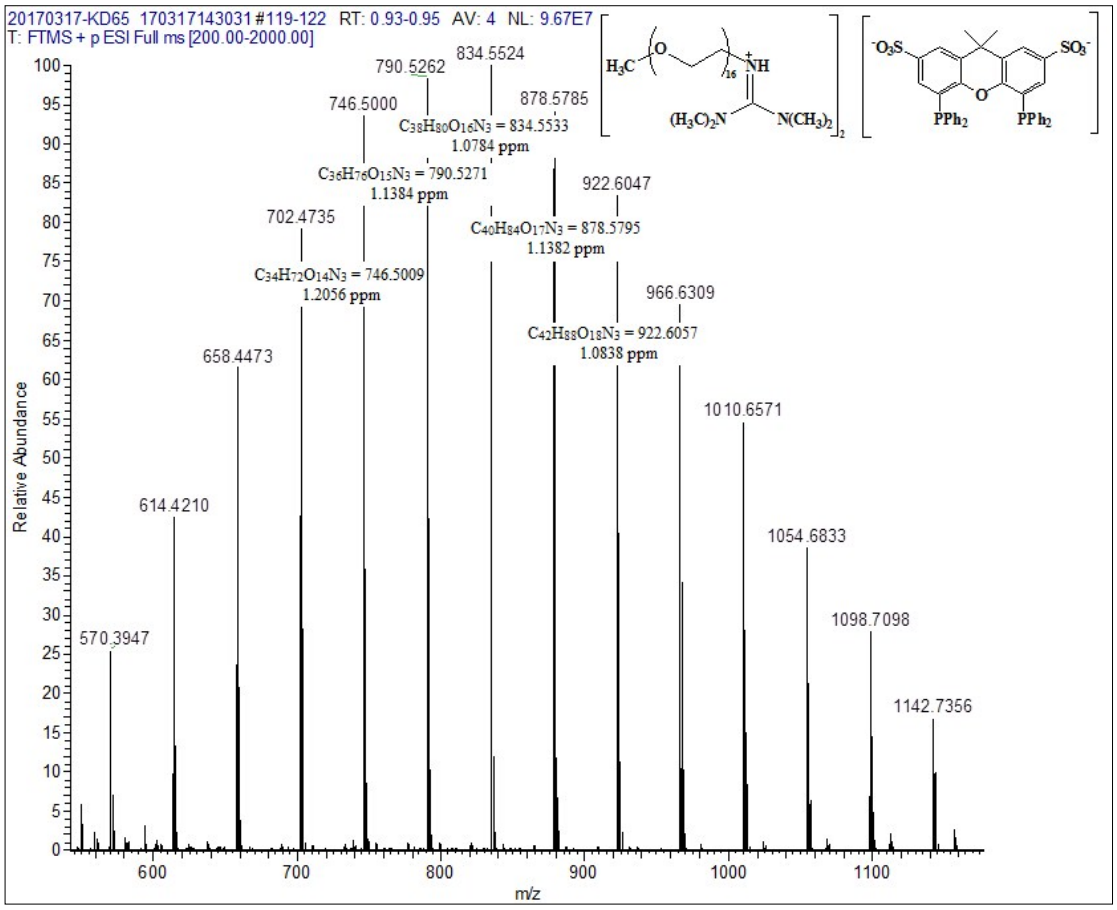


Figure S35. Mass spectrum (ES+) of **3b**

3.12 Mass spectrum (ES-) of **3b**

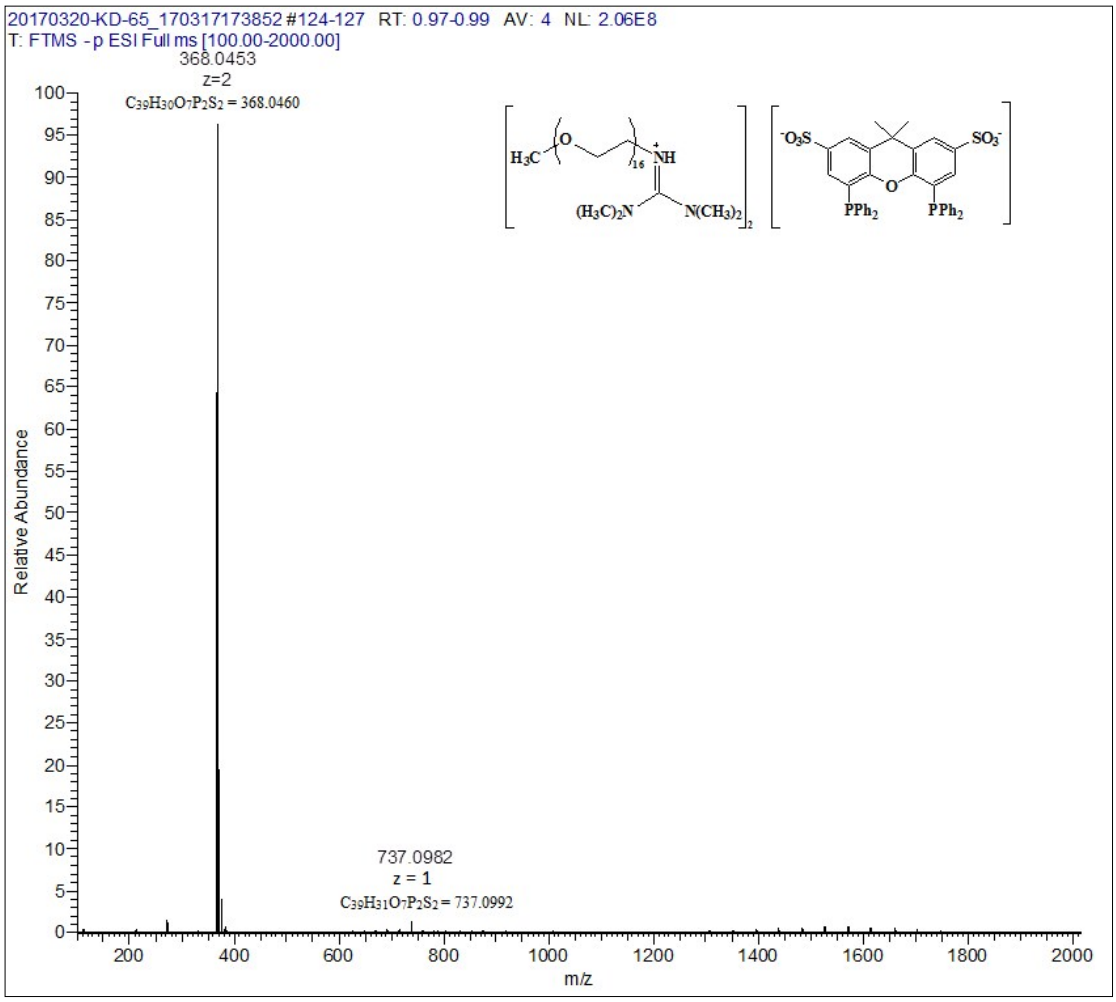


Figure S36. Mass spectrum (ES-) of **3b**

3.13 Mass spectrum (ES+) of **3c**

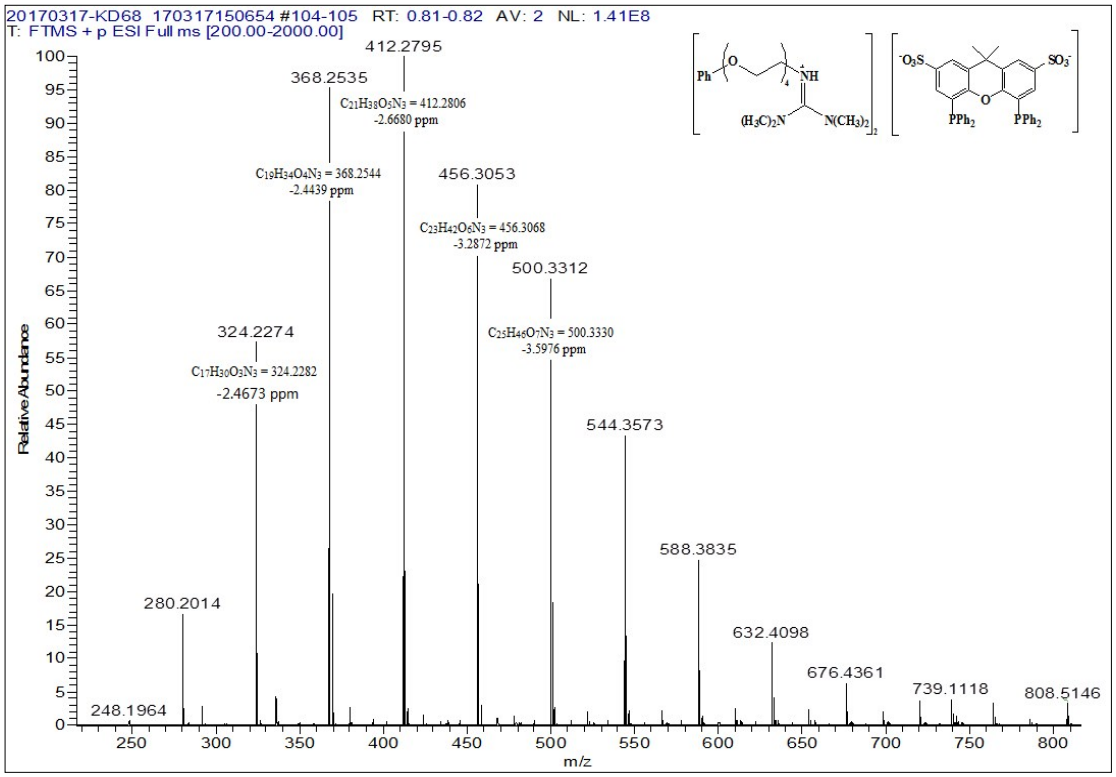


Figure S37. Mass spectrum (ES+) of **3c**

3.14 Mass spectrum (ES-) of **3c**

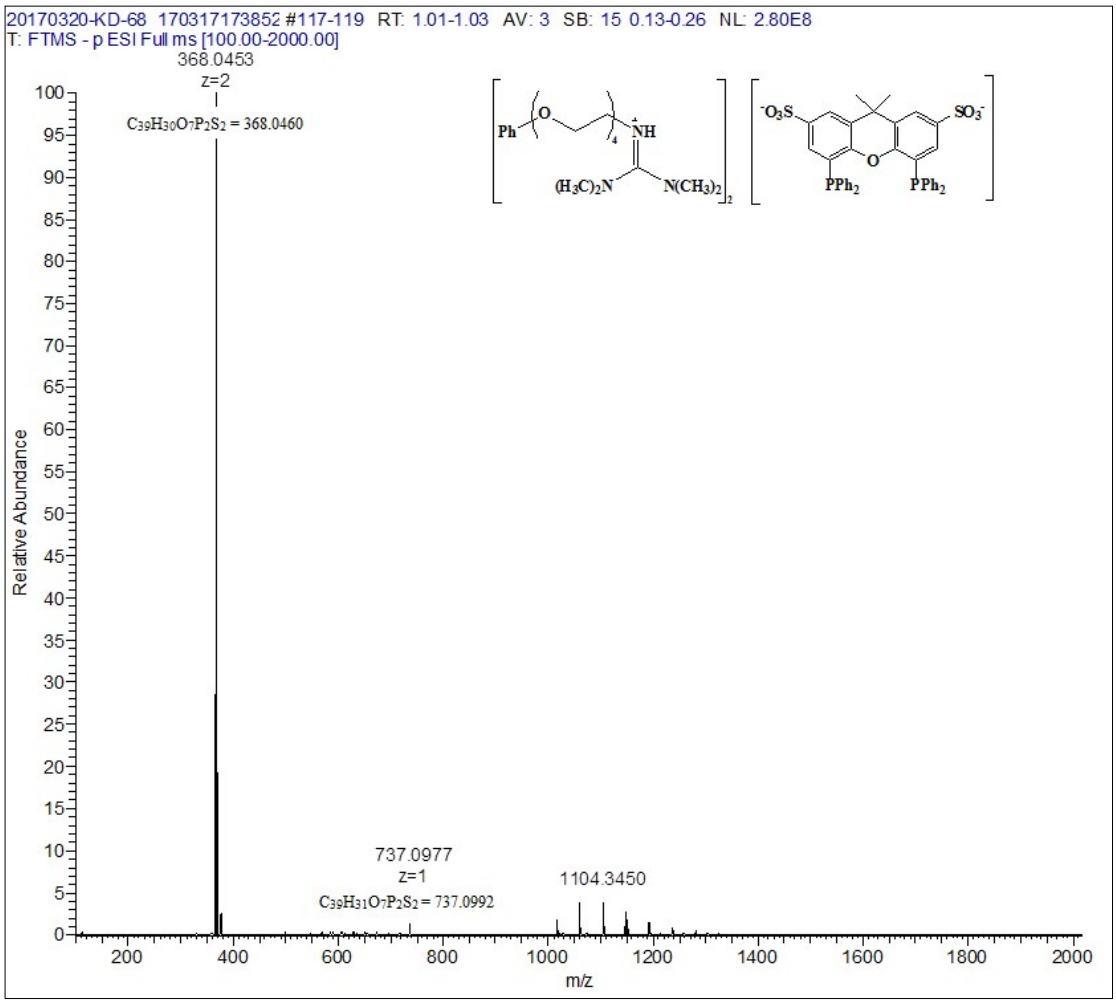


Figure S38. Mass spectrum (ES-) of **3c**

3.15 Mass spectrum (ES+) of **3d**

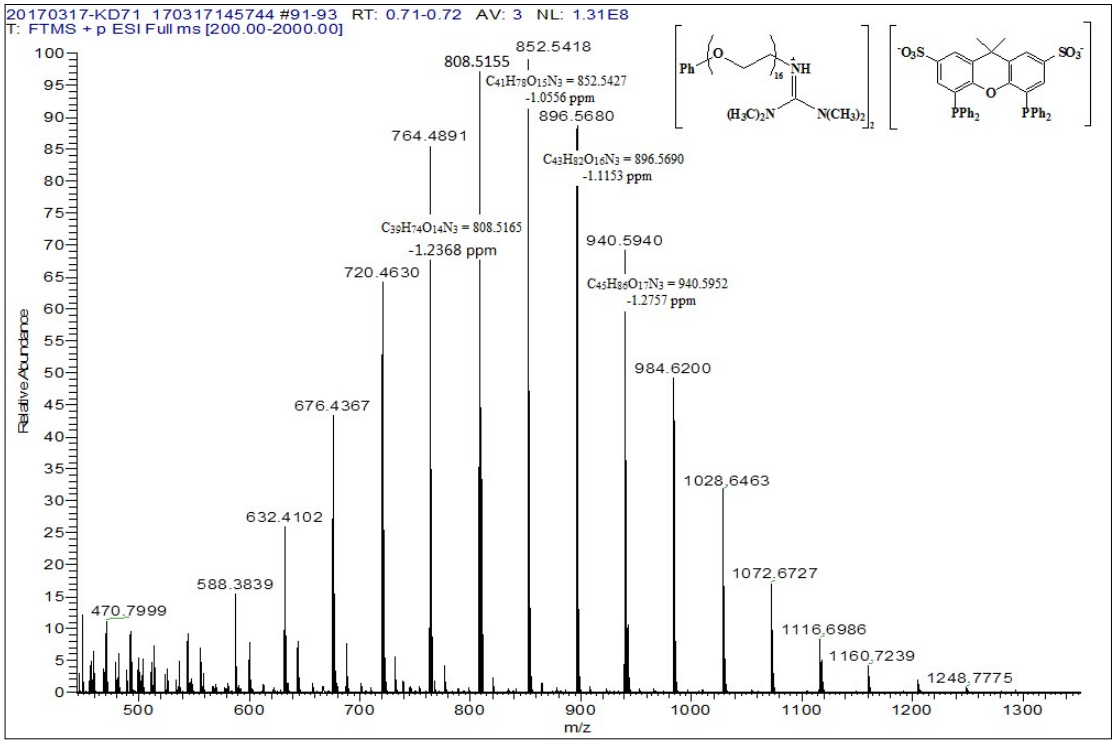


Figure S39. Mass spectrum (ES+) of **3d**

3.16 Mass spectrum (ES-) of **3d**

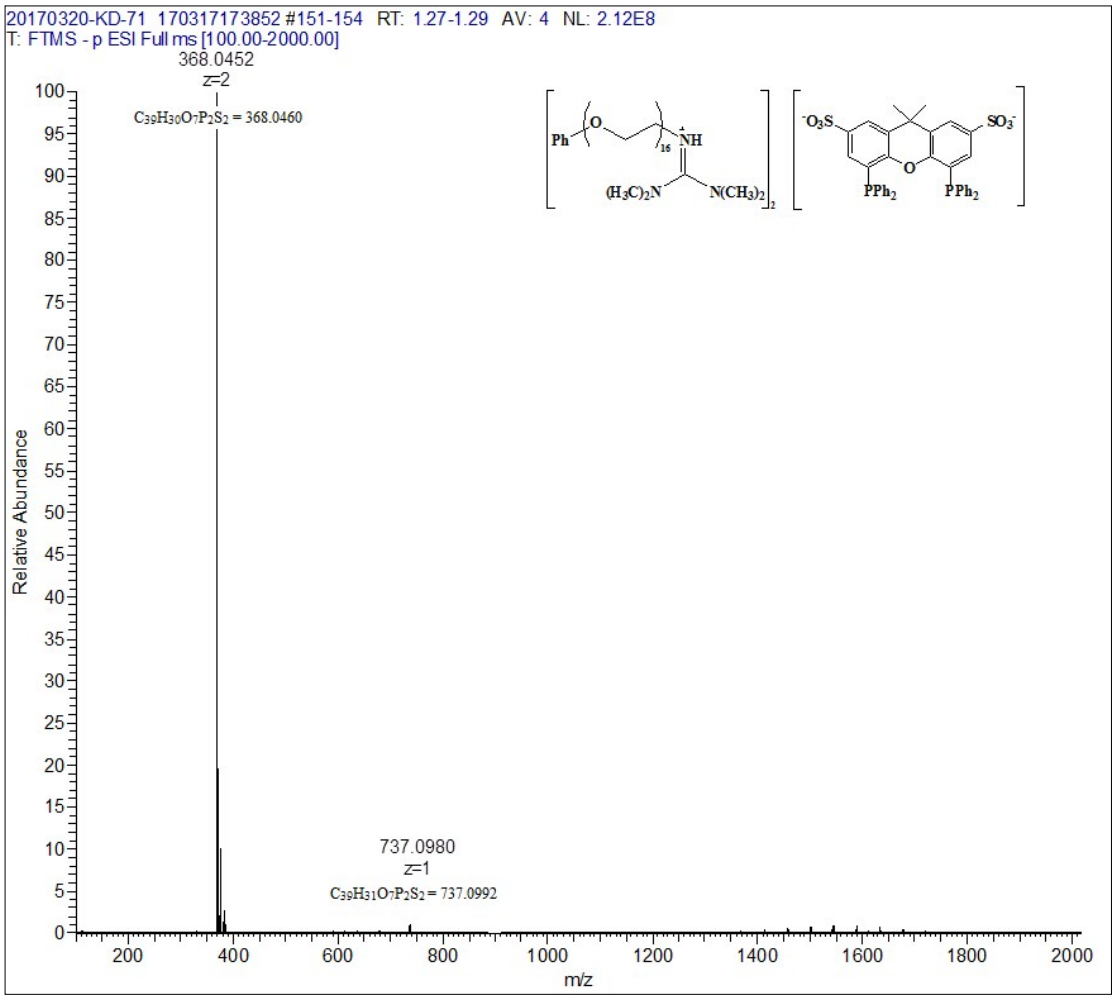


Figure S40. Mass spectrum (ES-) of **3d**

4 ^{31}P NMR Spectra of Fresh and Spent Catalyst

4.1 ^{31}P NMR spectrum of fresh catalyst

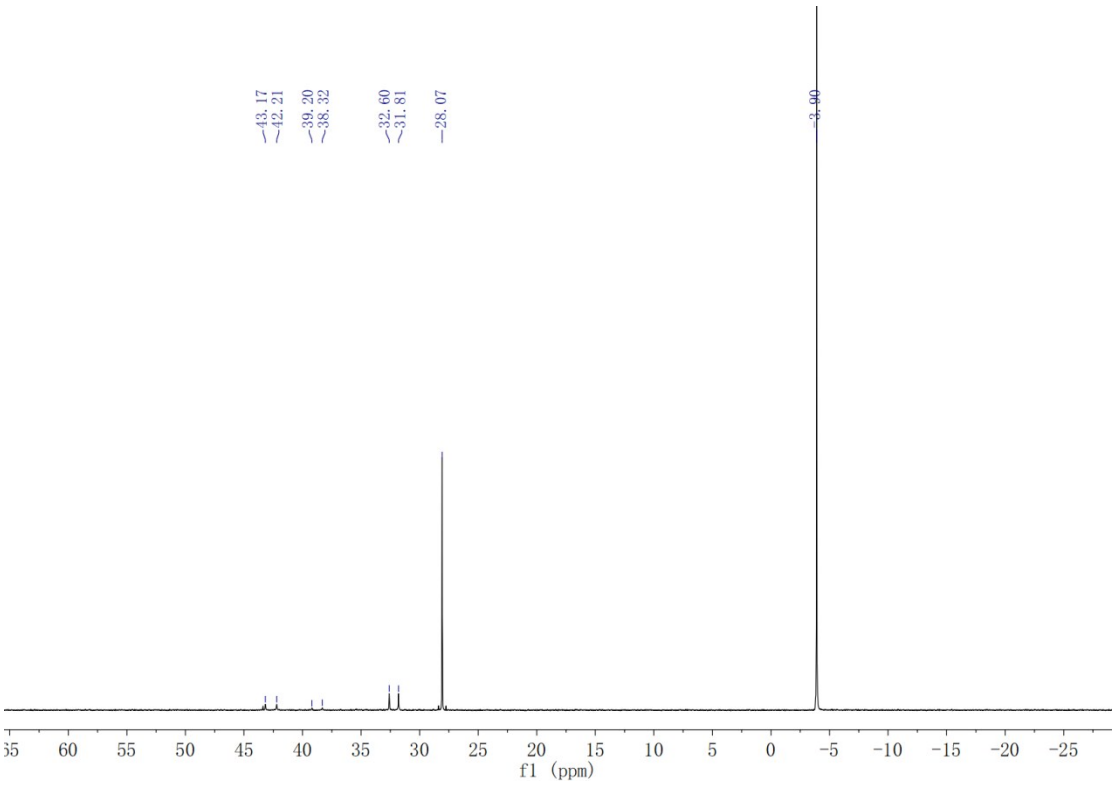


Figure S41. ^{31}P NMR spectrum of fresh Rh-**2a** catalyst **(**161.9 MHz, $CDCl_3$, 85% phosphoric acid as the internal standard**)**

4.2 ^{31}P NMR spectrum of spent catalyst

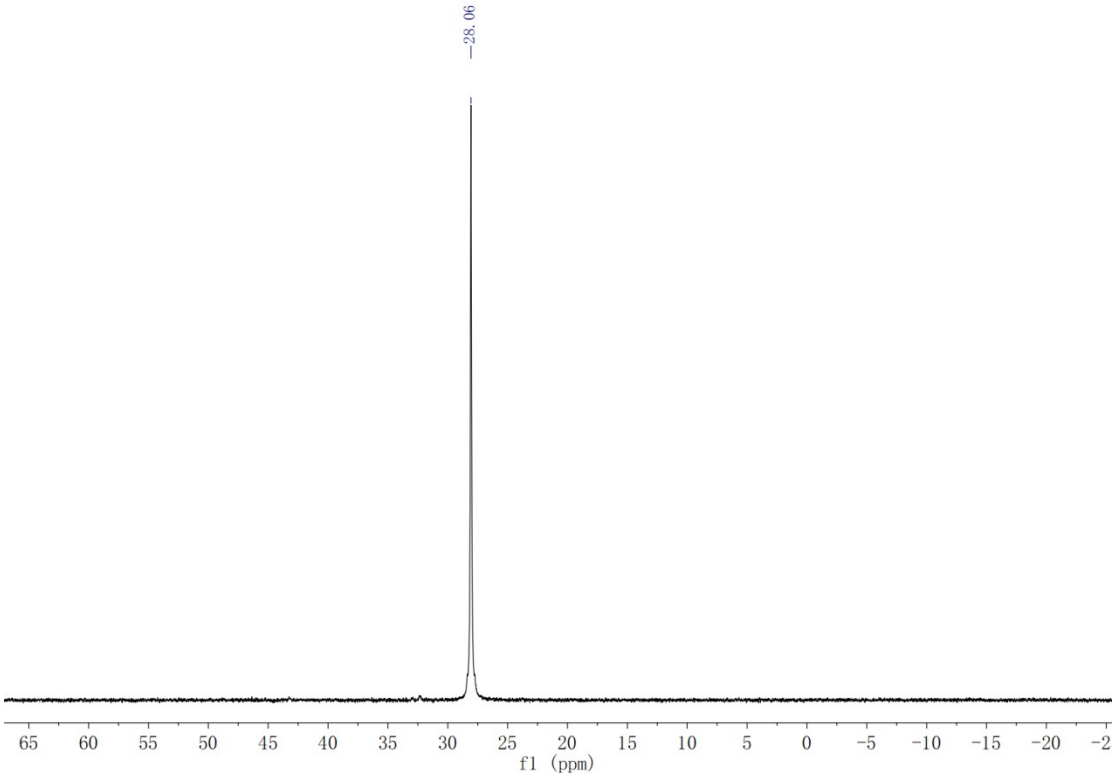


Figure S42. ^{31}P NMR spectrum of spent Rh-**2a** catalyst **(**161.9 MHz, $CDCl_3$, 85% phosphoric acid as the internal standard**)**