Supporting Information for:

Integration of A Phosphine Ligand into An Ionic Liquid: A Highly Effective Biphasic System for The Rh-Catalyzed Hydroformylation of 1-Octene

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1 Experimental Procedure

1.1 Synthesis of $[CH_3(EO)_4TMG]_3[P(C_6H_4SO_3)_3]$ (**2a**)

2a was synthesized by an ion exchange reaction between TPPTS and **1a** as described for **2d**, and obtained as a yellow viscous liquid; yield: 86%. **^{1}H NMR** (500.0 MHz, D_2O): δ = 7.79 (d, 3H, P-Ph-*H*), 7.74 (d, 3H, P-Ph-*H*), 7.51 (t, 3H, P-Ph-*H*), 7.45 (t, 3H, P-Ph-*H*), 3.63-3.53 (m, 53H, OCH_2CH_2), 3.31 (s, 9H, OCH_3), 2.87 (s, 36H, 6×N(CH_3)$_2$); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ = 162.58, 146.95, 136.55, 134.51, 131.02, 128.36, 126.83, 71.82, 70.43, 70.29, 69.48, 58.92, 44.69, 39.79; **^{31}P NMR** (202.4 MHz, D_2O): δ = -5.33; **HRMS** (Q-Tof MS, ES+): *m*/*z* = 262.2122, calcd. for $C_{12}H_{28}O_3N_3$ ($[CH_3(OCH_2CH_2)_3TMG]^+$): 262.2125; *m*/*z* = 306.2382, calcd. for $C_{14}H_{32}O_4N_3$ ($[CH_3(OCH_2CH_2)_4TMG]^+$): 306.2387; *m*/*z* = 350.2642, calcd. for $C_{16}H_{36}O_5N_3$ ($[CH_3(OCH_2CH_2)_5TMG]^+$): 350.2649; *m*/*z* = 394.2903, calcd. for $C_{18}H_{40}O_6N_3$ ($[CH_3(OCH_2CH_2)_6TMG]^+$): 394.2912; **HRMS** (Q-Tof MS, ES−): *m*/*z* = 166.3133 (*z* = 3), calcd. for $C_{18}H_{12}O_9PS_3$: 166.3133; *m*/*z* = 249.9729 (*z* = 2), calcd. for $C_{18}H_{13}O_9PS_3$: 249.9735.

1.2 Synthesis of $[CH_3(EO)_{16}TMG]_3[P(C_6H_4SO_3)_3]$ (**2b**)

2b was synthesized by an ion exchange reaction between TPPTS and **1b** as described for **2d**, and obtained as a yellow viscous liquid at room temperature. As the temperature fell below 10 °C, **2b** solidified gradually; yield: 90%. **^{1}H NMR** (500.0 MHz, D_2O): δ = 7.87 (d, 3H, P-Ph-*H*), 7.82 (d, 3H, P-Ph-*H*), 7.59 (t, 3H, P-Ph-*H*), 7.52 (t, 3H, P-Ph-*H*), 3.84-3.44 (m, 200H, OCH_2CH_2), 3.39 (s, 9H, OCH_3), 2.95 (s, 36H, 6×N(CH_3)$_2$); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ = 162.07, 146.54, 136.03, 134.00, 130.39, 127.85, 126.27, 71.31, 69.93, 69.63, 68.97, 58.40, 44.13, 39.31; **^{31}P NMR** (202.4 MHz, D_2O): δ = -5.11; **HRMS** (Q-Tof MS, ES+): *m*/*z* = 746.4994, calcd. for $C_{34}H_{72}O_{14}N_3$ ($[CH_3(OCH_2CH_2)_{14}\ TMG]^+$): 746.5009; *m*/*z* = 790.5256, calcd. for $C_{36}H_{76}O_{15}N_3$ ($[CH_3(OCH_2CH_2)_{15}TMG]^+$): 790.5271; *m*/*z* = 834.5518, calcd. for $C_{38}H_{80}O_{16}N_3$ ($[CH_3(OCH_2CH_2)_{16}TMG]^+$): 834.5533; *m*/*z* = 878.5779, calcd. for $C_{40}H_{84}O_{17}N_3$ ($[CH_3(OCH_2CH_2)_{17}TMG]^+$): 878.5795; *m*/*z* = 922.6041, calcd. for $C_{42}H_{88}O_{18}\ N_3$ ($[CH_3(OCH_2CH_2)_{18}TMG]^+$): 922.6057; **HRMS** (Q-Tof MS, ES-): *m*/*z* = 166.3132 (*z* = 3), calcd. for $C_{18}H_{12}O_9PS_3$: 166.3133; *m*/*z* = 249.9730 (*z* = 2), calcd. for $C_{18}H_{13}O_9PS_3$: 249.9735.

1.3 Synthesis of $[Ph(EO)_4TMG]_3[P(C_6H_4SO_3)_3]$ (**2c**)

2c was synthesized by an ion exchange reaction between TPPTS and **1c** as described for **2d**, and obtained as a yellow viscous liquid; yield: 90%. **^{1}H NMR** (500.0 MHz, D_2O): δ = 7.85 (d, 3H, P-Ph-*H*), 7.81 (d, 3H, P-Ph-*H*), 7.56 (t, 3H, P-Ph-*H*), 7.46 (t, 3H, P-Ph-*H*), 7.38 (t, 6H, O-Ph-*H*), 7.03 (m, 9H, O-Ph-*H*), 4.20-3.30 (m, 70H, OCH_2CH_2), 2.87 (s, 36H, 6×N(CH_3)$_2$); **^{13}C NMR** (150.9 MHz, $CDCl_3$): δ = 162.39, 158.45, 146.62, 136.41, 134.54, 130.76, 129.30, 128.34, 126.71, 120.74, 114.36, 70.54–69.98, 69.52, 69.33, 67.11, 44.57, 39.63; **^{31}P NMR** (202.4 MHz, D_2O): δ = -5.32; **HRMS** (Q-Tof MS, ES+): *m*/*z* = 324.2274, calcd. for $C_{17}H_{30}O_3N_3$ ($[Ph(OCH_2CH_2)_3TMG]^+$): 324.2282; *m*/*z* = 368. 2535, calcd. for $C_{19}H_{34}O_4N_3$ ($[Ph(OCH_2CH_2)_4TMG]^+$): 368.2544; *m*/*z* = 412.2795, calcd. for $C_{21}H_{38}O_5N_3$ ($[Ph(OCH_2CH_2)_5TMG]^+$): 412.2806; *m*/*z* = 456.3054, calcd. for $C_{23}H_{42}O_6N_3$ ($[Ph(OCH_2CH_2)_6TMG]^+$): 456. 3068; *m*/*z* = 500.3312, calcd. for $C_{25}H_{46}O_7N_3$ ($[Ph(OCH_2CH_2)_7TMG]^+$): 500.3330; **HRMS** (Q-Tof MS, ES-): *m*/*z* = 166.3133 (*z* = 3), calcd. for $C_{18}H_{12}O_9PS_3$: 166.3133; *m*/*z* = 249.9729 (*z* = 2), calcd. for $C_{18}H_{13}O_9\,PS_3$: 249.9735.

2 NMR Spectra

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

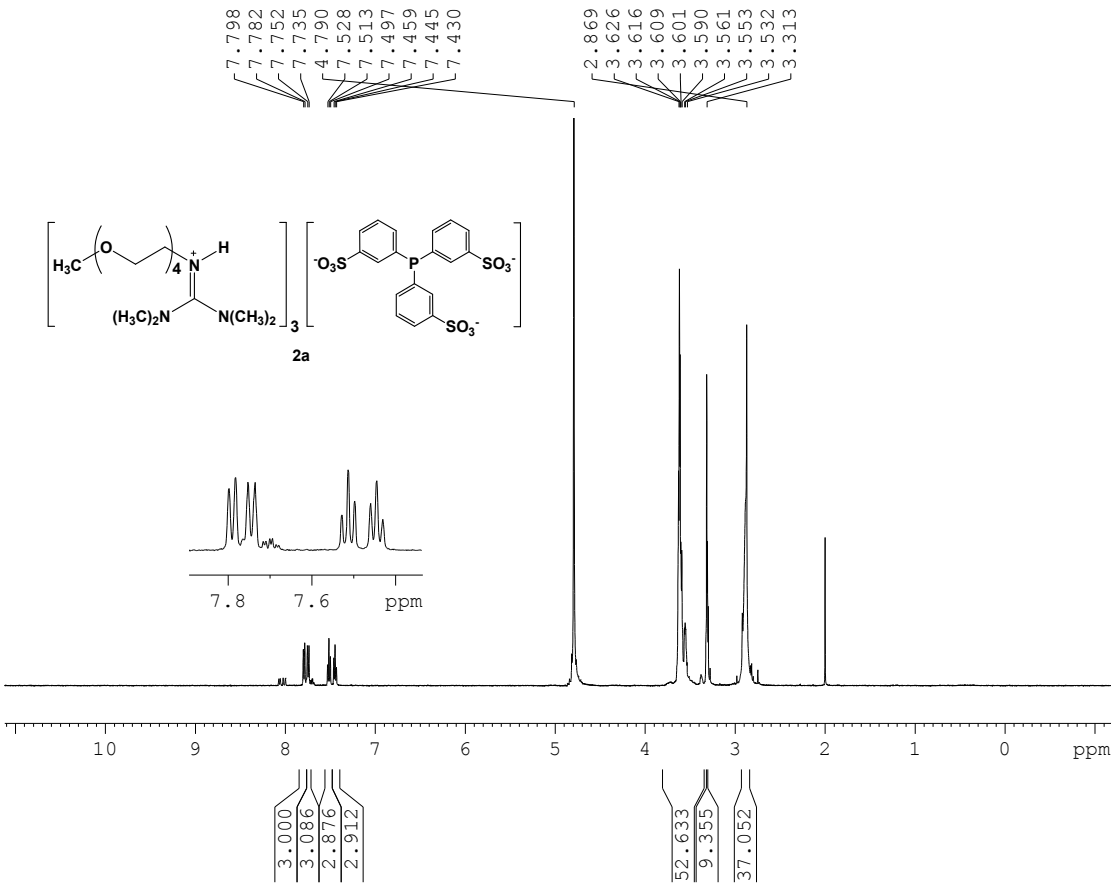


Figure S1. ^{1}H NMR spectrum of **2a** (500.0 MHz, D_2O)

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

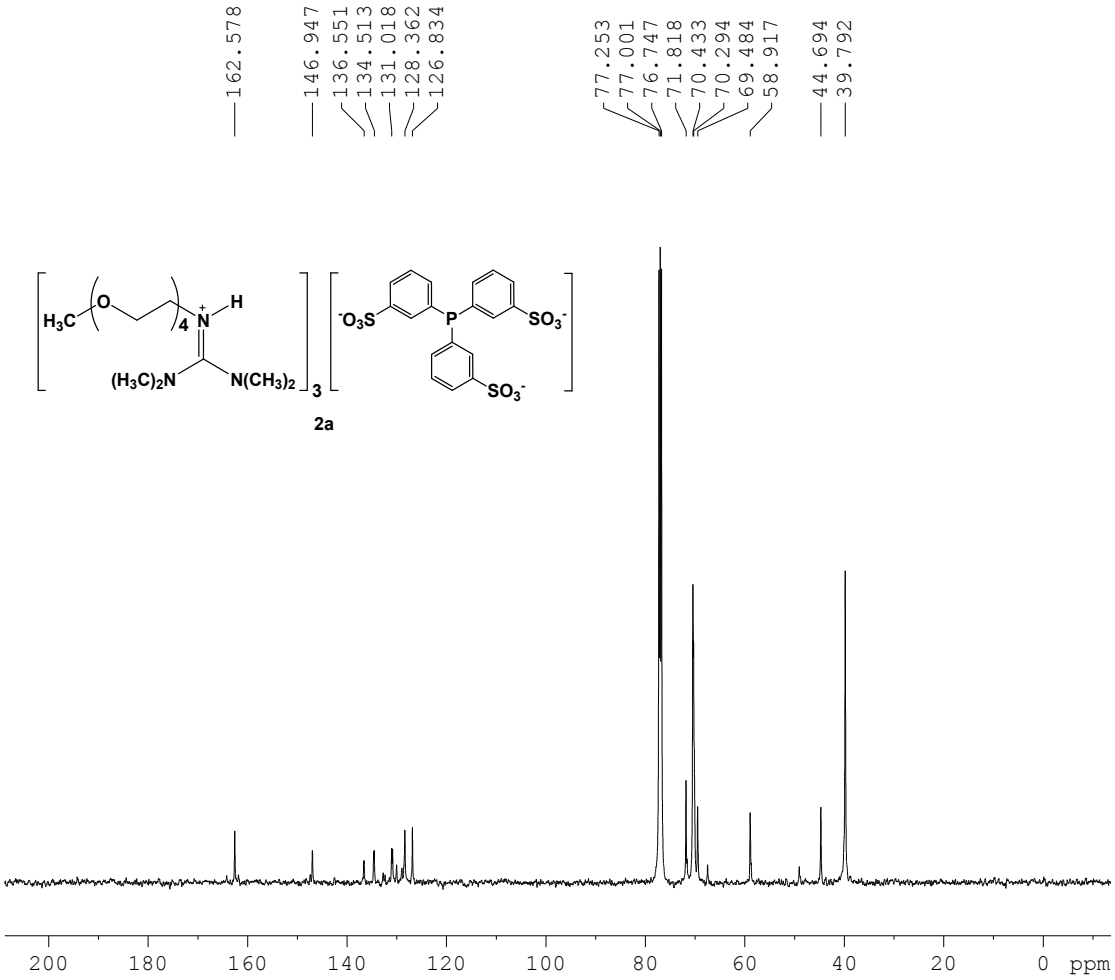
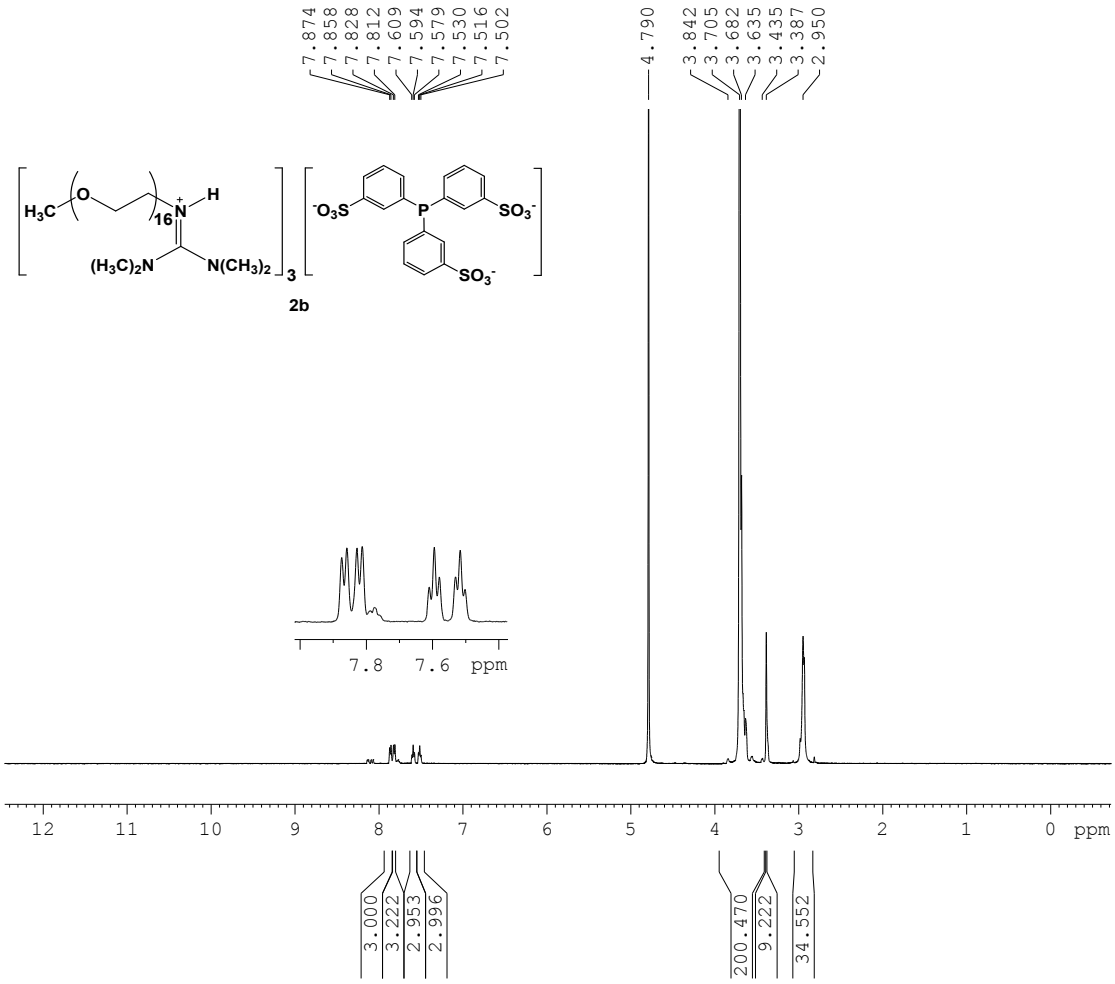


Figure S2. ^{13}C NMR spectrum of **2a** (125.7 MHz, $CDCl_3$)

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**

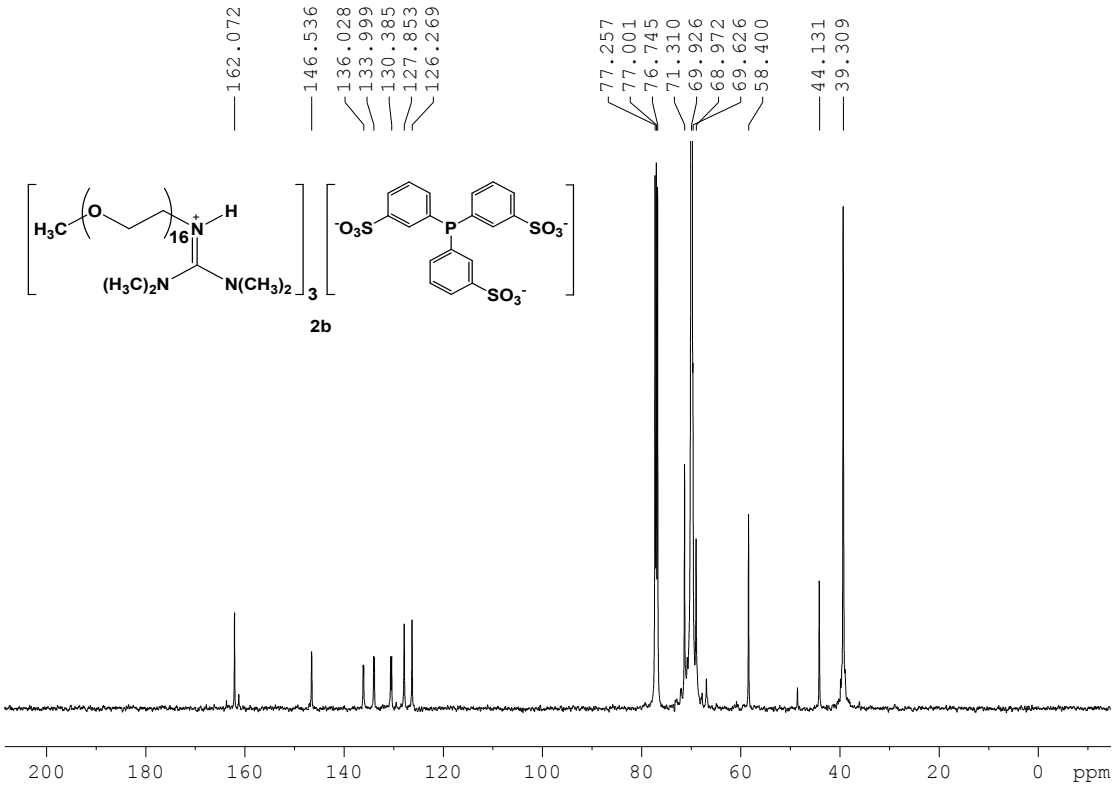


Figure S5. ^{13}C NMR spectrum of **2b** (125.7 MHz, $CDCl_3$)

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**

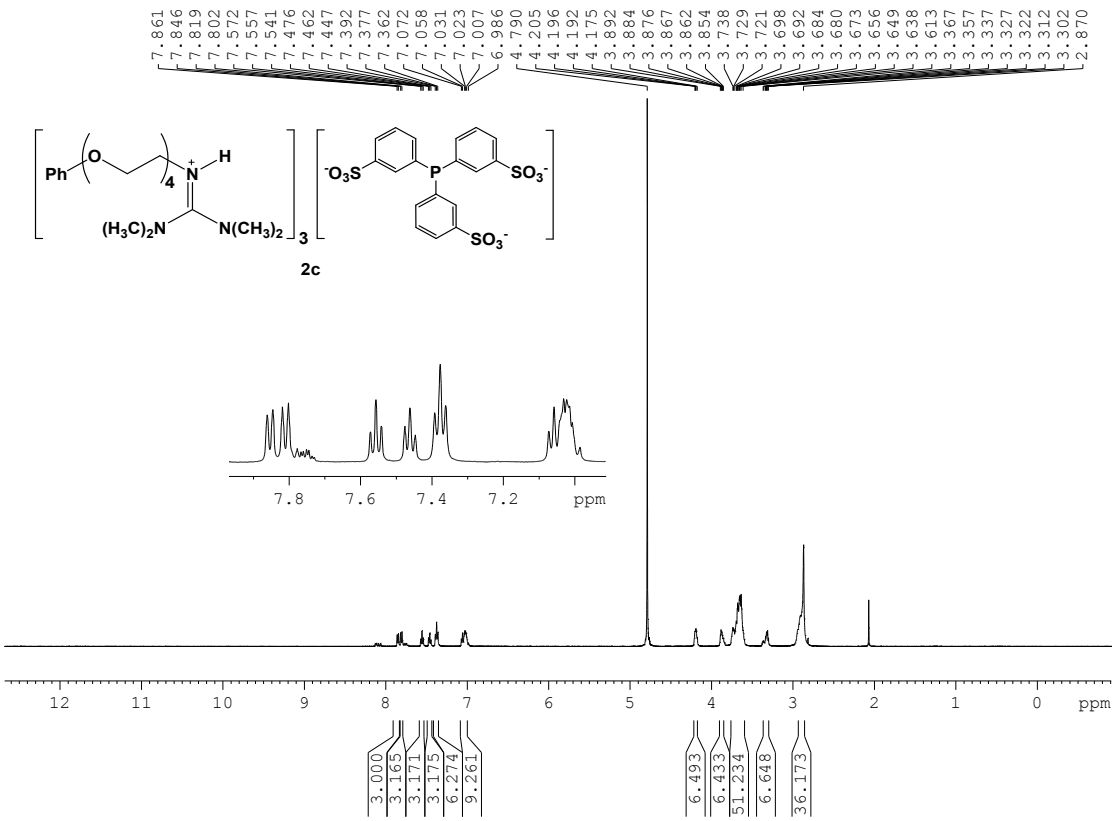


Figure S7. ^{1}H NMR spectrum of **2c** (500.0 MHz, D_2O)

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

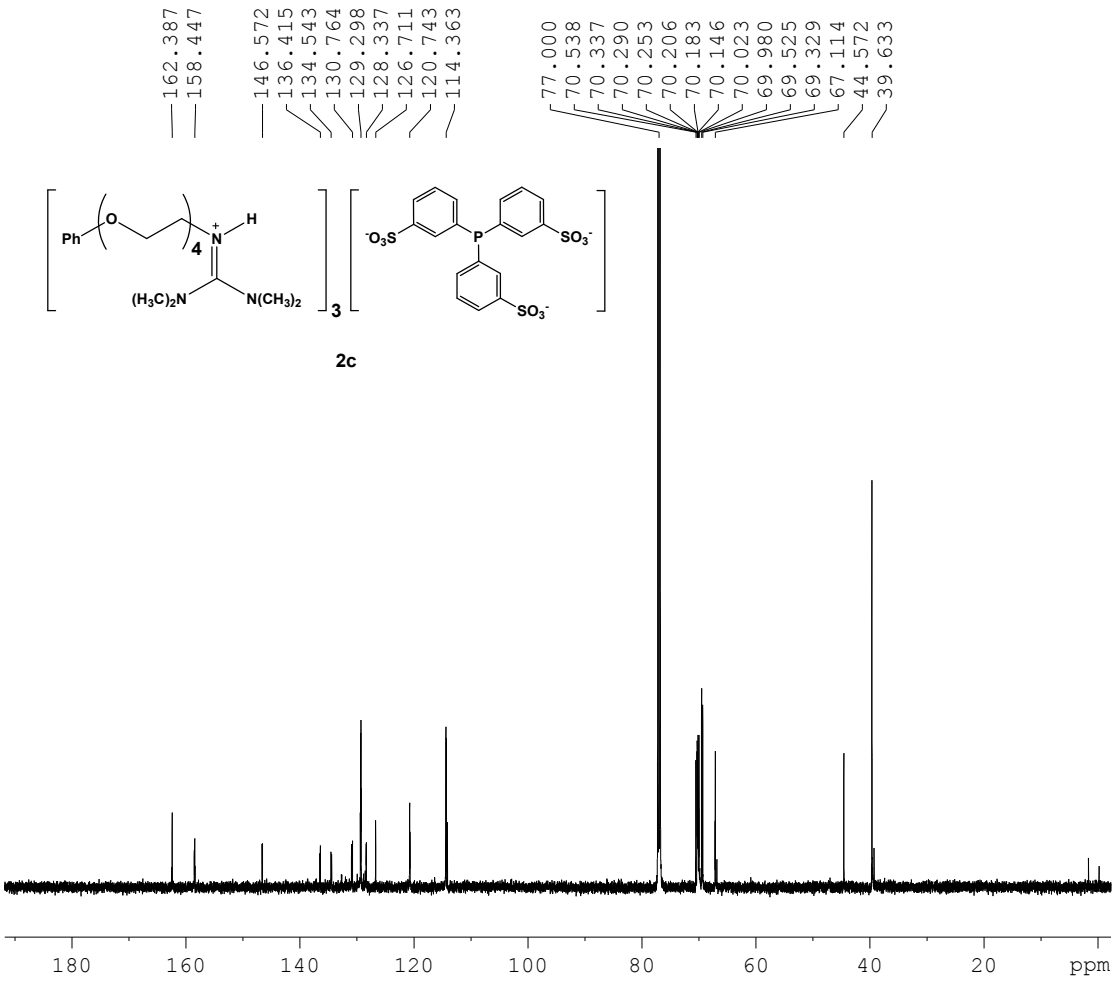


Figure S8. ^{13}C NMR spectrum of **2c** (150.9 MHz, $CDCl_3$)

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

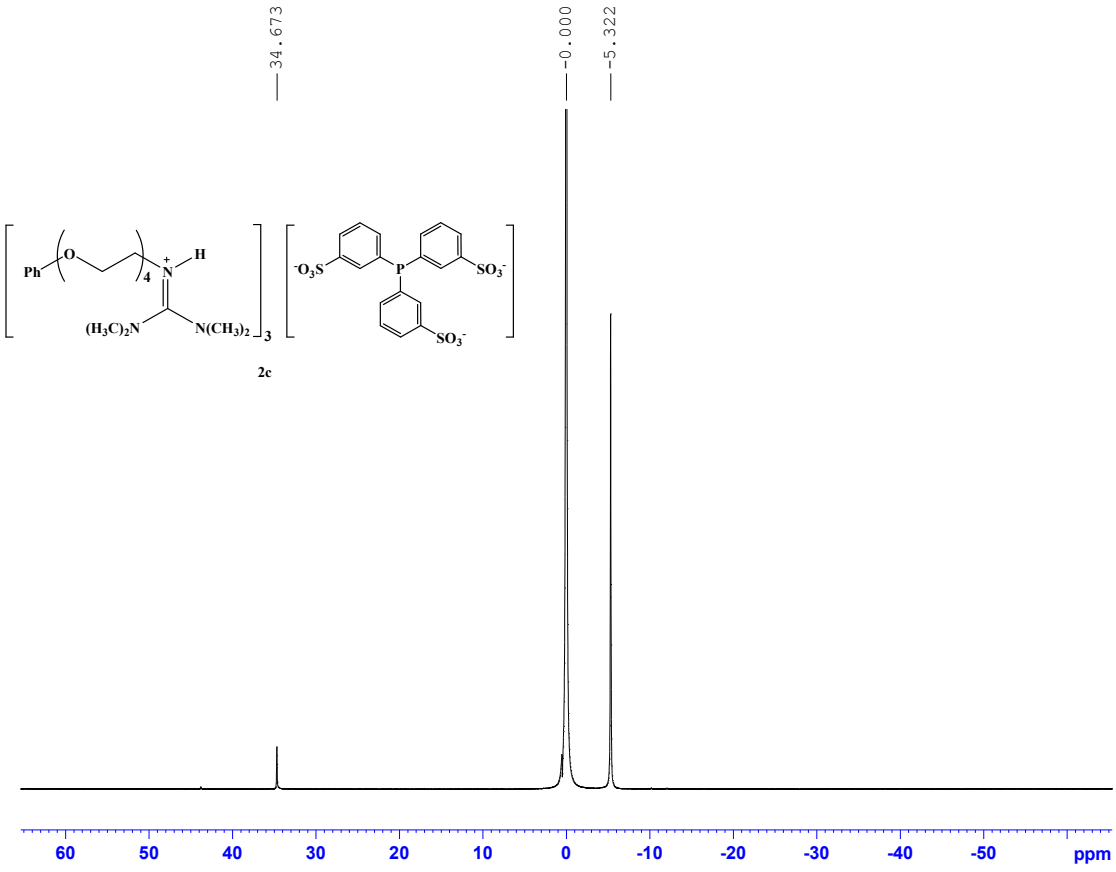


Figure S9. ^{31}P NMR spectrum of **2c** (202.4 MHz, D_2O)

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

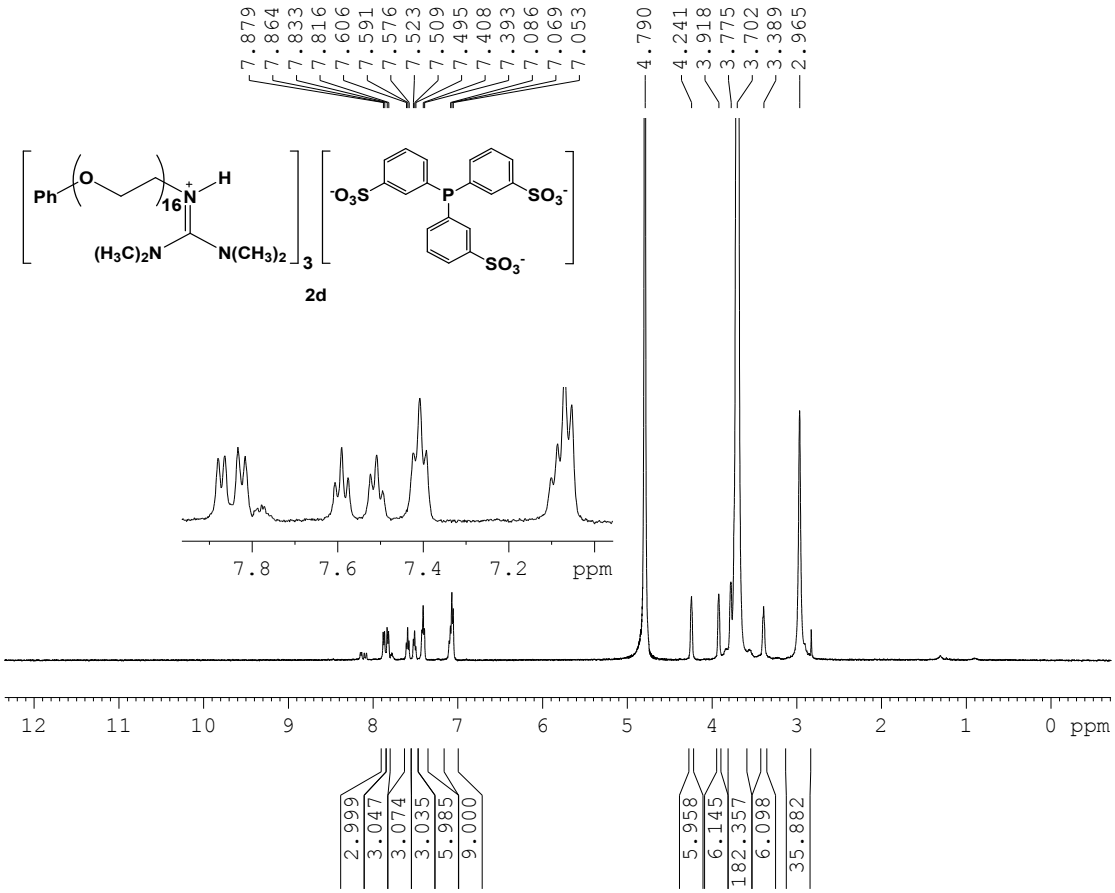


Figure S10. ^{1}H NMR spectrum of **2d** (500.0 MHz, D_2O)

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

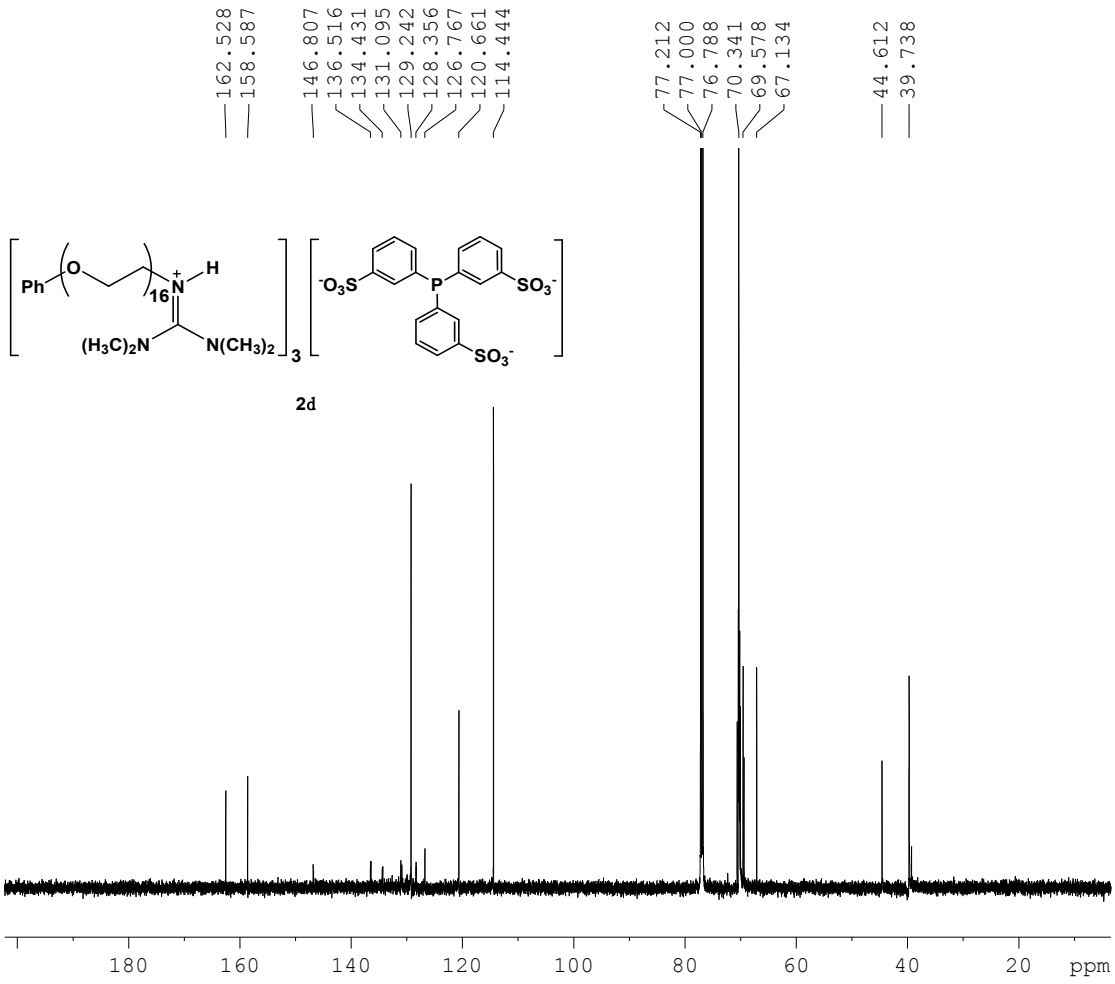


Figure S11. ^{13}C NMR spectrum of **2d** (150.9 MHz, $CDCl_3$)

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

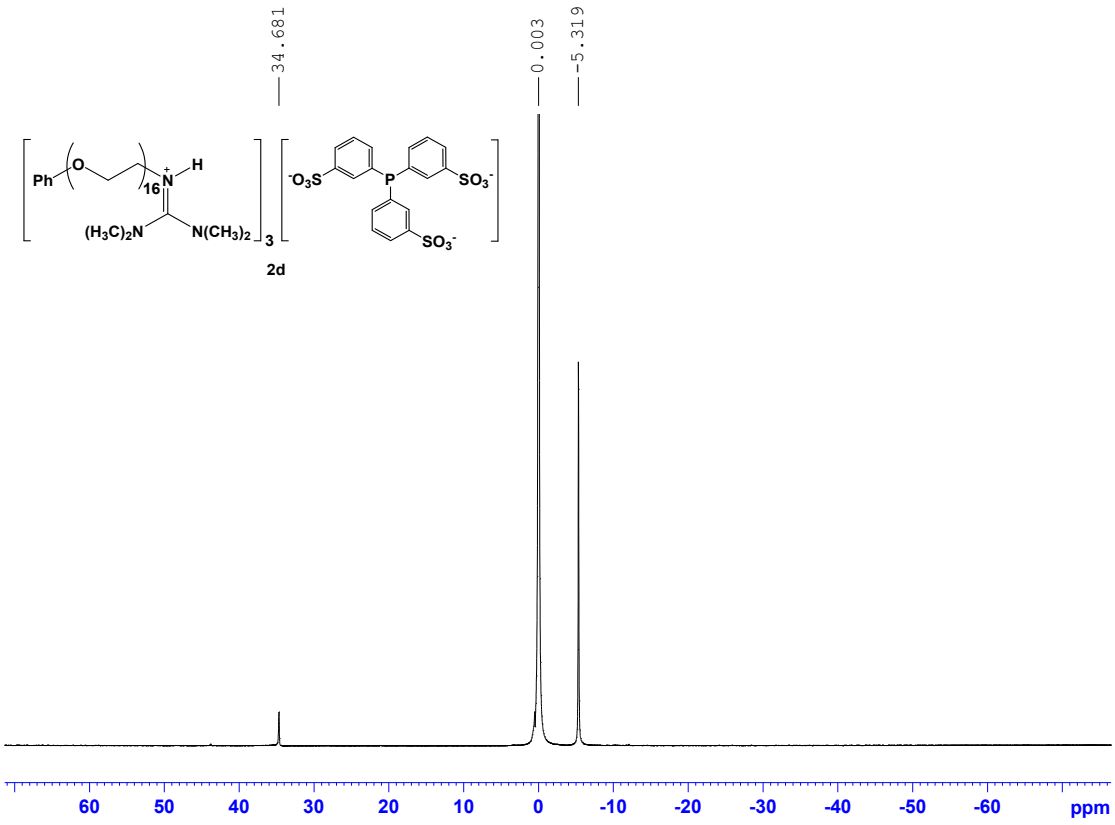


Figure S12. ^{31}P NMR spectrum of **2d** (202.4 MHz, D_2O)

3 HRMS Spectra

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

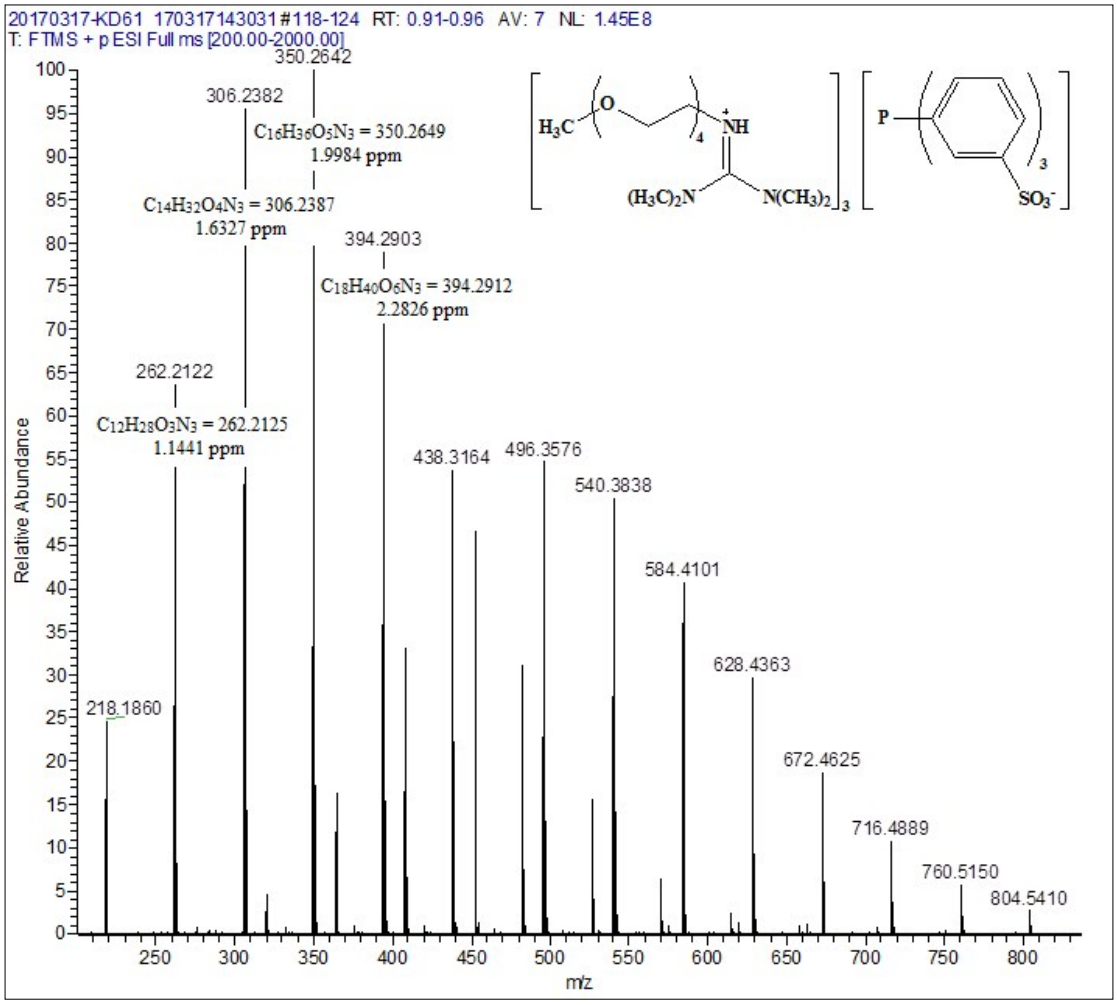


Figure S13. Mass spectrum (ES+) of **2a**

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

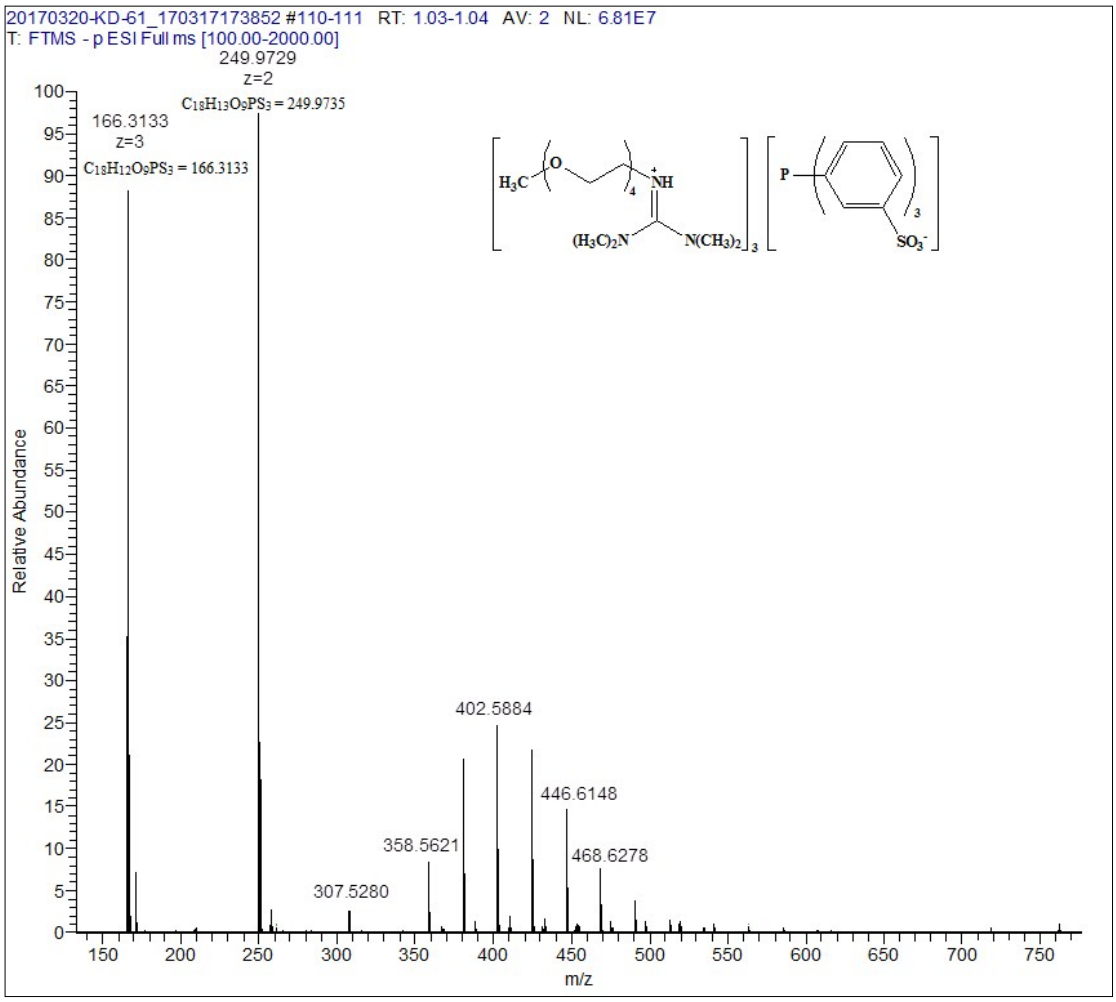


Figure S14. Mass spectrum (ES-) of **2a**

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

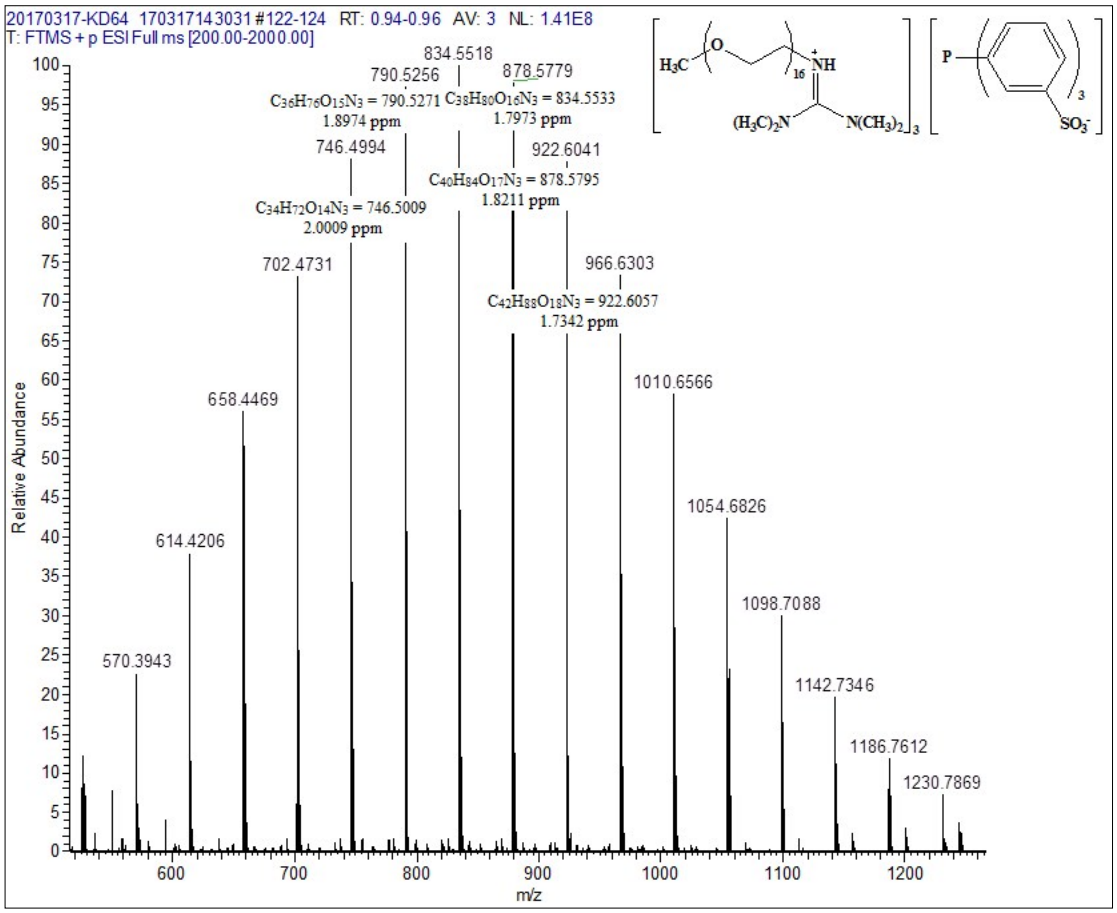


Figure S15. Mass spectrum (ES+) of **2b**

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

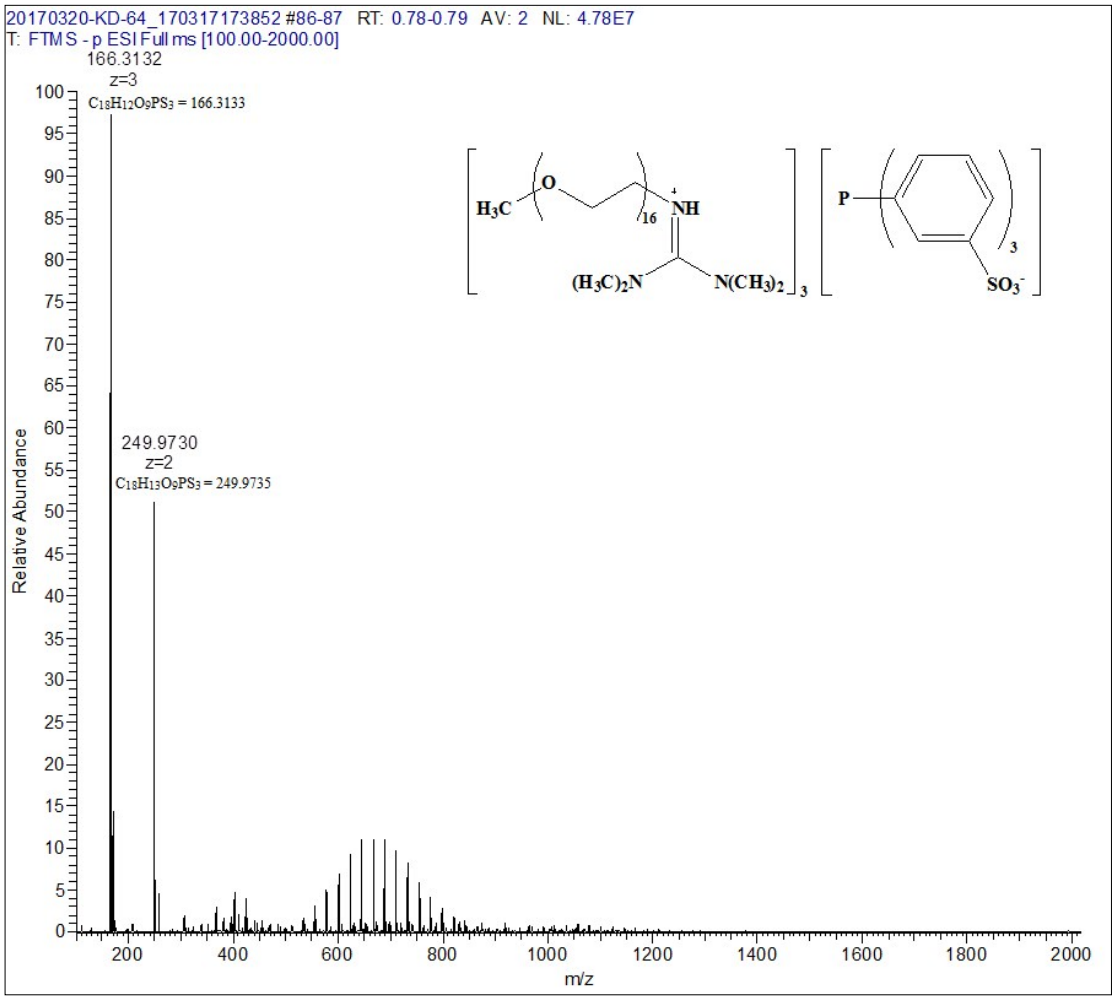


Figure S16. Mass spectrum (ES-) of **2b**

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

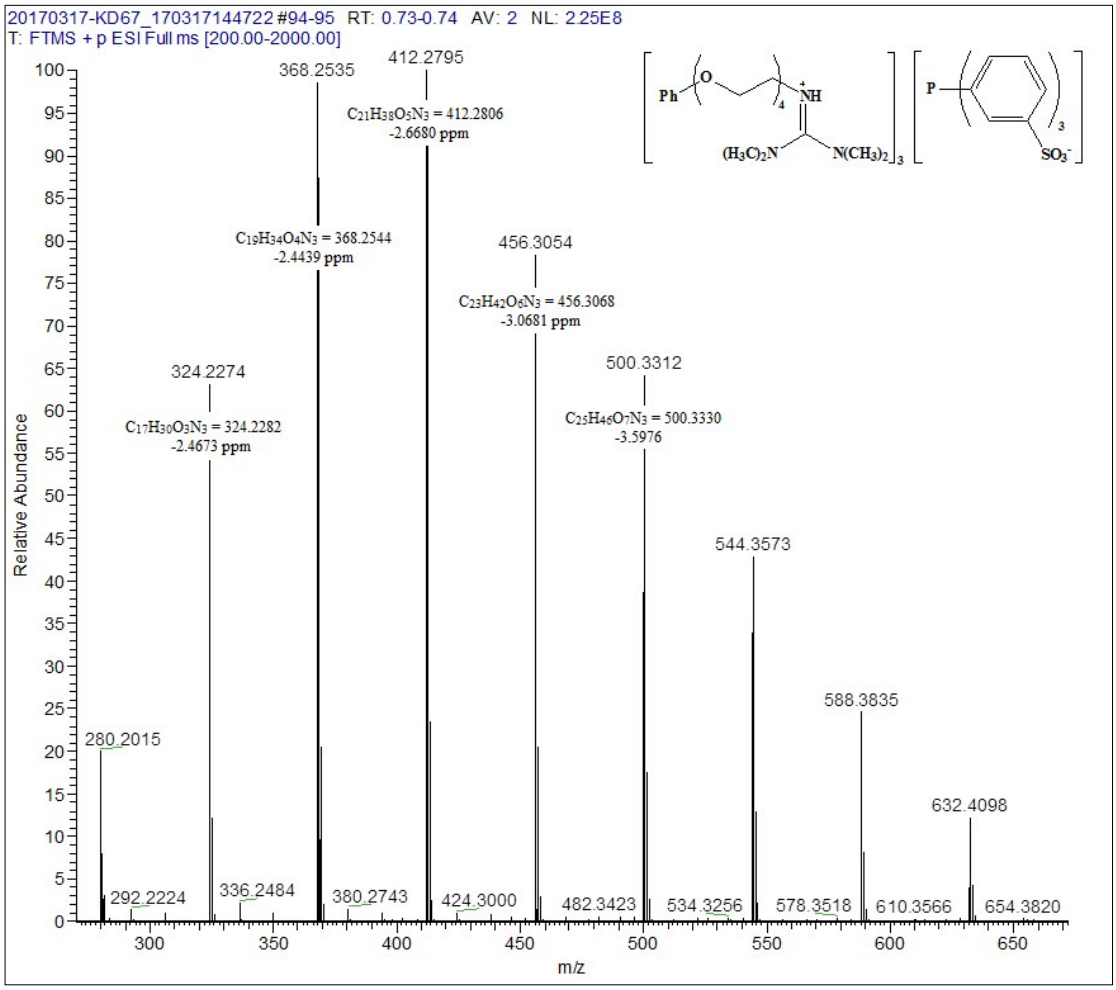


Figure S17. Mass spectrum (ES+) of **2c**

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

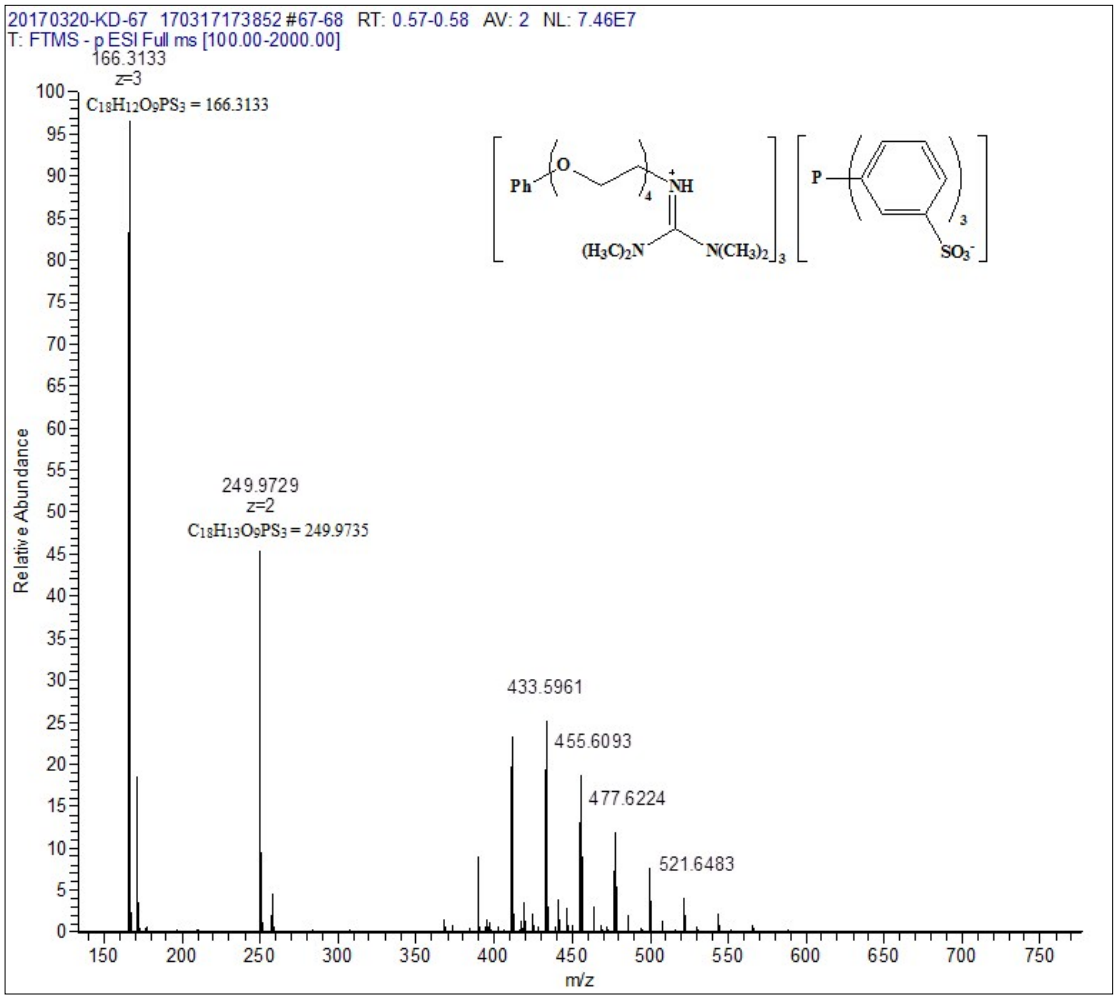


Figure S18. Mass spectrum (ES-) of **2c**

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

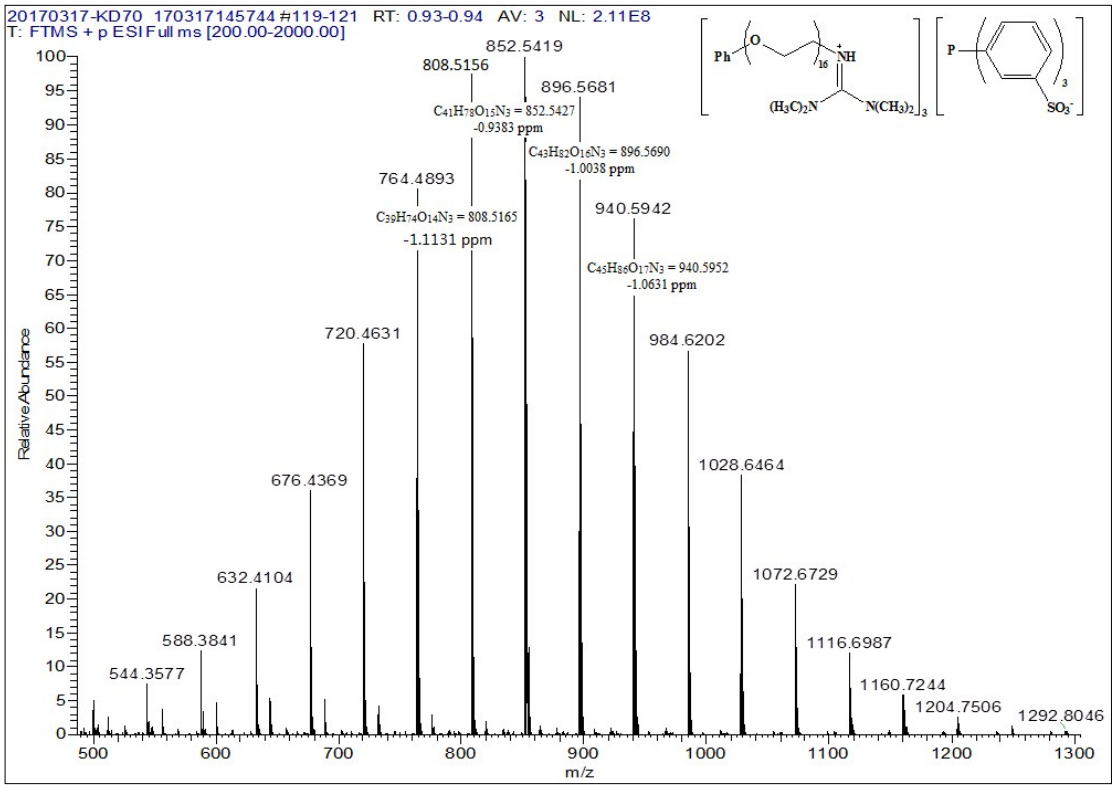


Figure S19. Mass spectrum (ES+) of **2d**

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

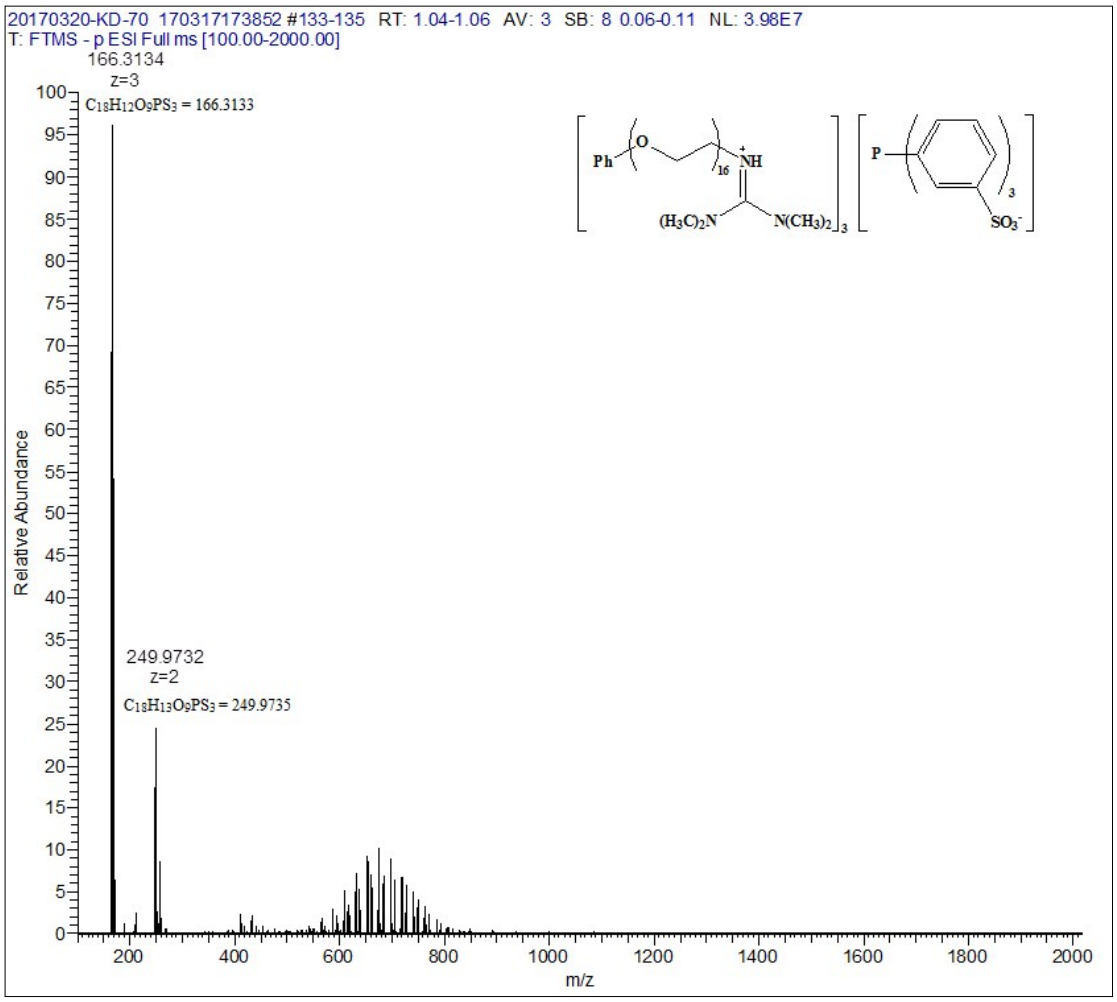


Figure S20. Mass spectrum (ES-) of **2d**

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

4.1 ^{31}P NMR spectrum of fresh catalyst

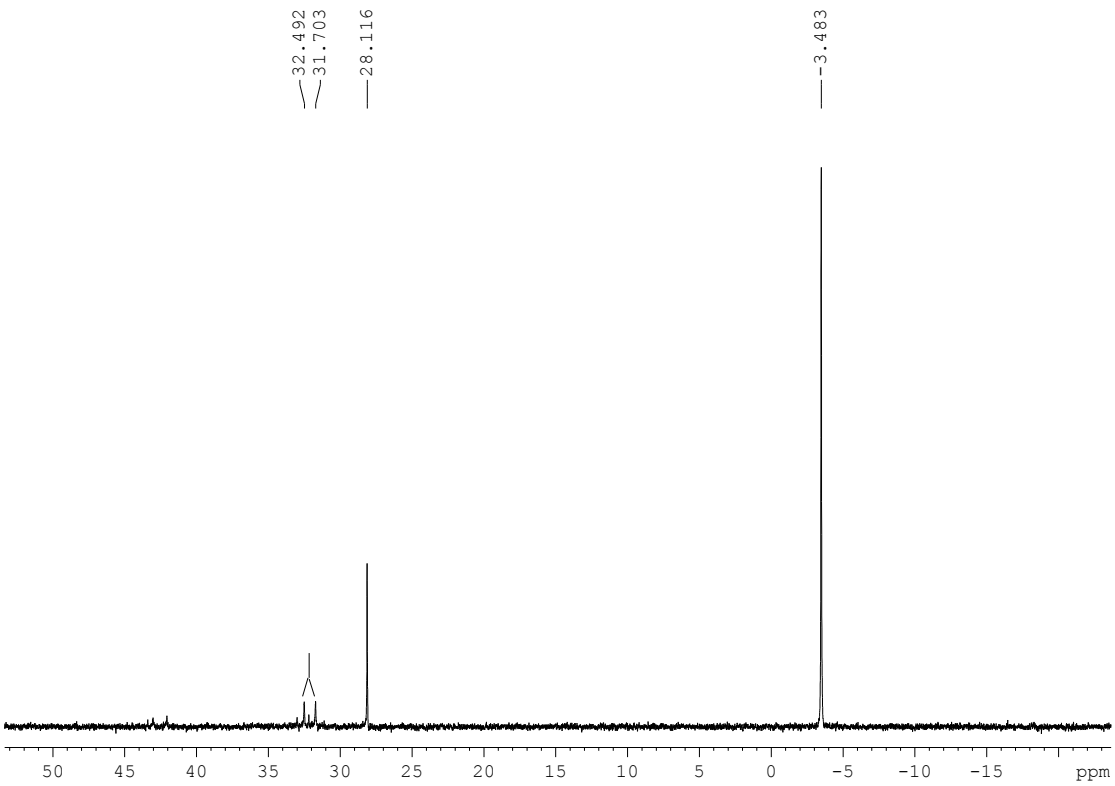


Figure S21. ^{31}P NMR spectrum of freshly prepared Rh-**2d** catalyst **(**161.9 MHz, $CDCl_3$, 85% phosphoric acid as the internal standard)

4.2 ^{31}P NMR spectrum of spent catalyst

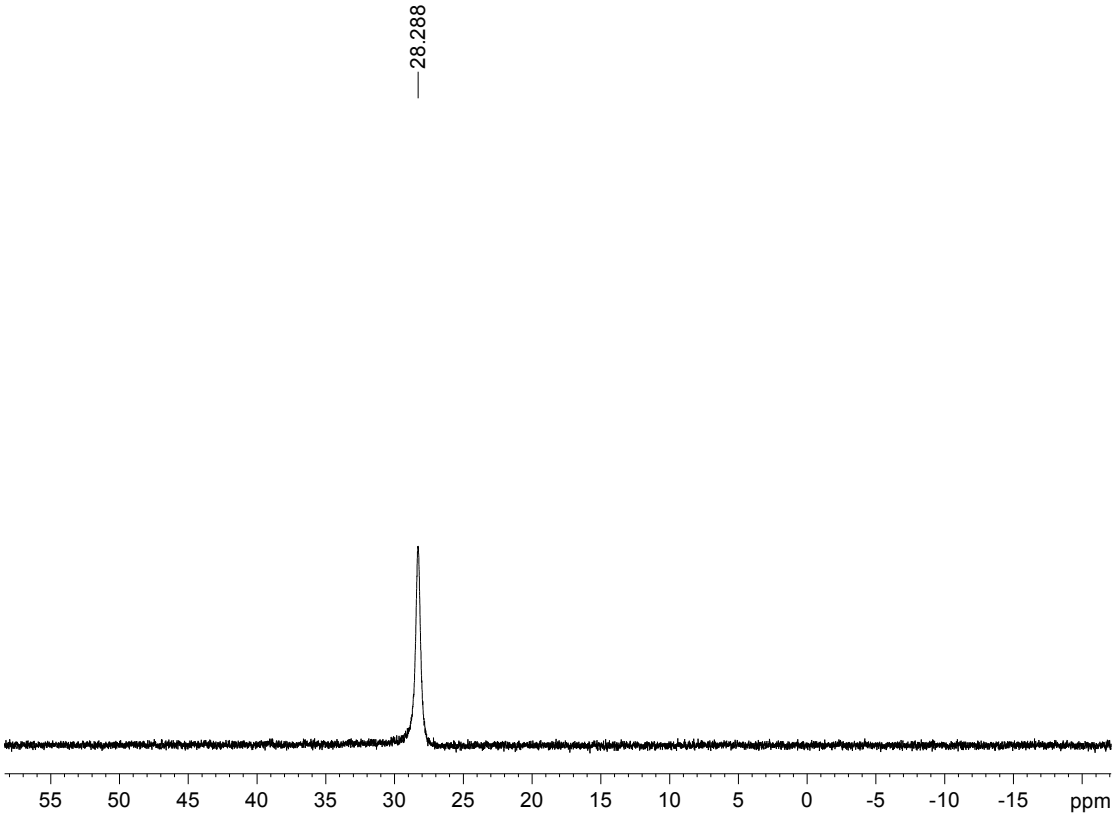


Figure S22. ^{31}P NMR spectrum of reused Rh-**2d** catalyst after the eleventh cycle (161.9 MHz, $CDCl_3$, 85% phosphoric acid as the internal standard)