

SUPPORTING INFORMATION

The Effects of Counterion Composition on the Rheological and Conductive Properties of Mono- and Diphosphonium Ionic Liquids

Reimi Yonekura[†] and Mark W. Grinstaff^{*‡}

[†]Department of Mechanical Engineering, Boston University, Boston, Massachusetts 02215, United States

[‡]Departments of Chemistry and Biomedical Engineering, Boston University, Boston, Massachusetts 02215, United States

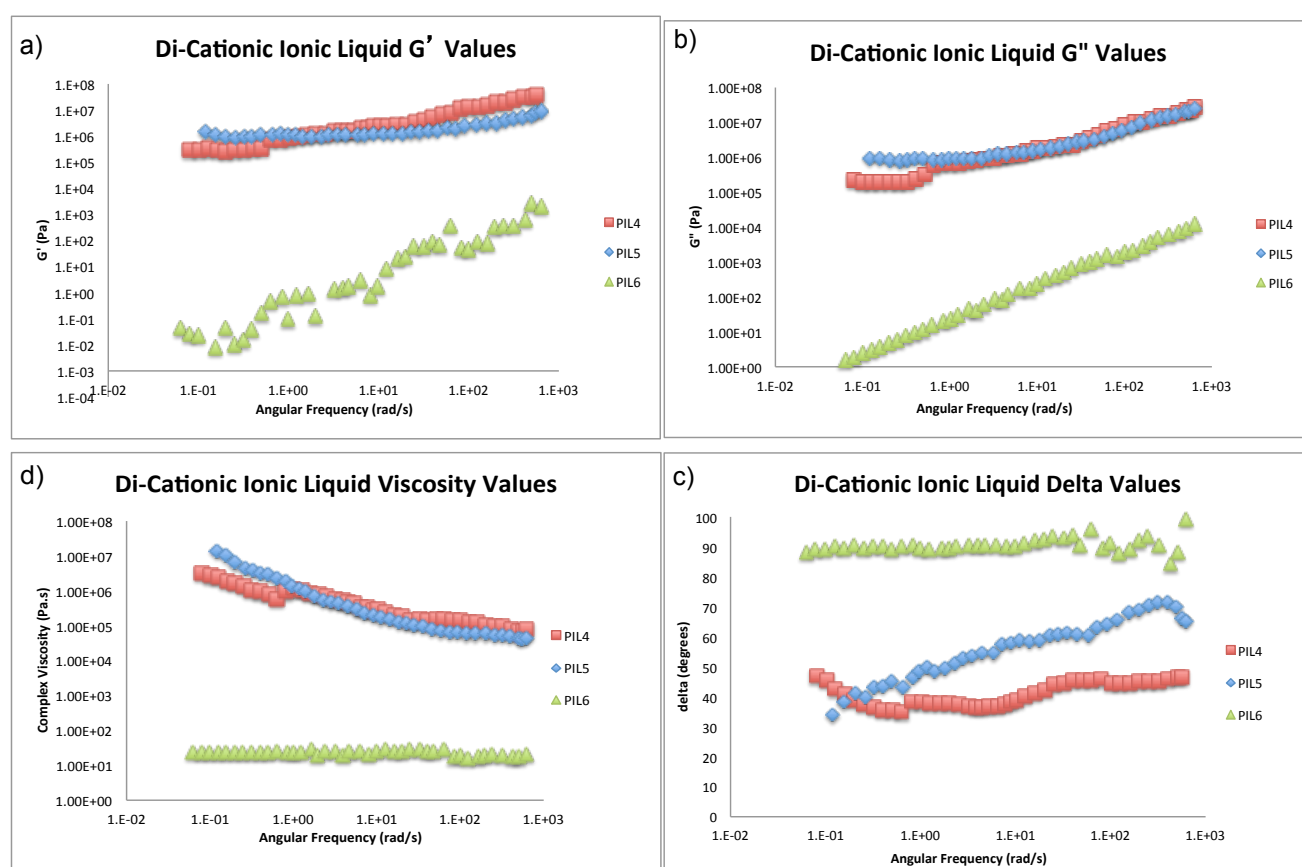


Figure SI1. Frequency sweep of dicationic chloride ILs (clock-wise from top left: (a) G' (storage modulus), (b) G'' (loss modulus), (c) δ (phase angle), and (d) η^* (complex viscosity)) [Due to the large difference in the physical properties of the octyl dicationic ILs from the butyl and hexyl analogs, the same geometry could not be used as the corrected values for the storage modulus, G' , in particular, were overcompensated and lack physical meaning. A same large flat geometry was used for the monocationic ILs that have similar modulus values to the dicationic octyl IL.]

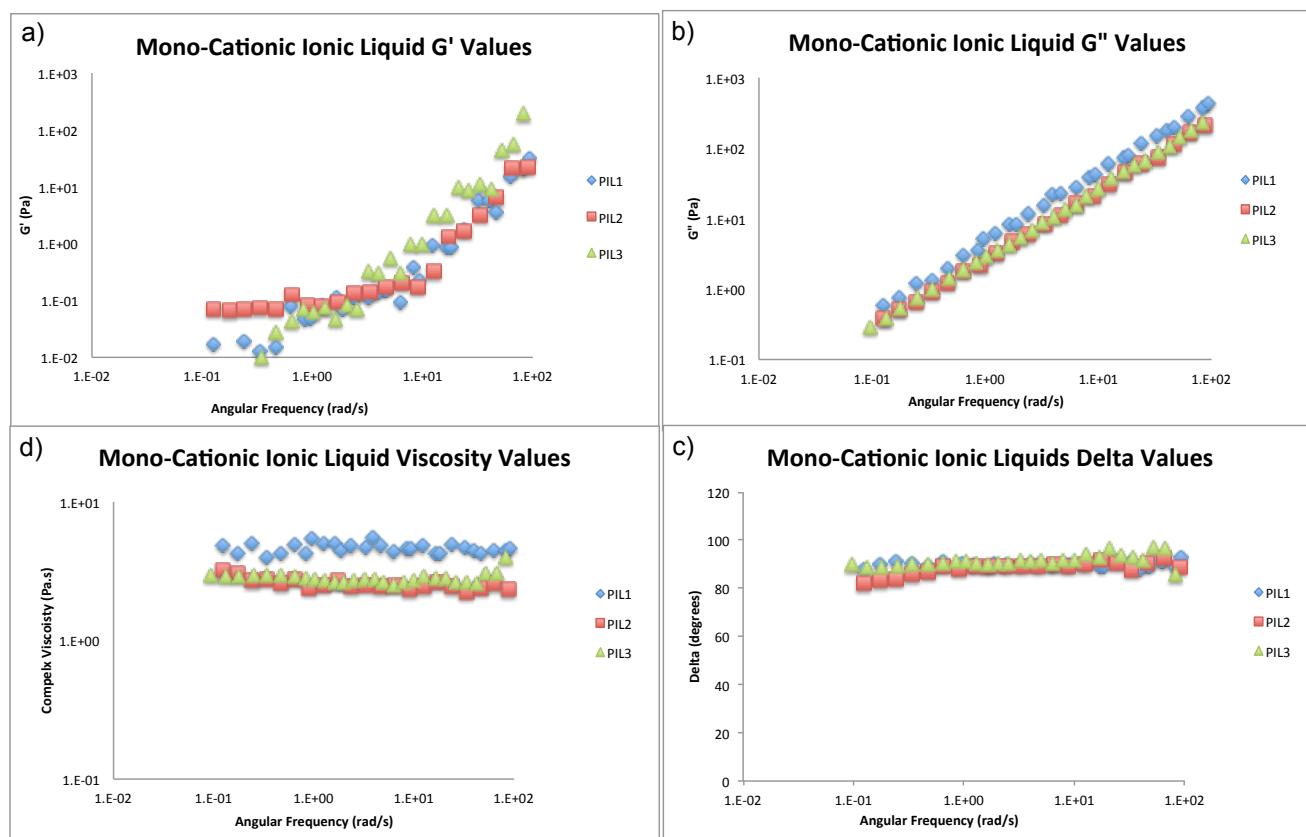


Figure SI2. Frequency sweep of monocationic chloride ILs (clock-wise from top left: (a) G' (storage modulus), (b) G'' (loss modulus), (c) delta (δ), and (d) η^* (complex viscosity))

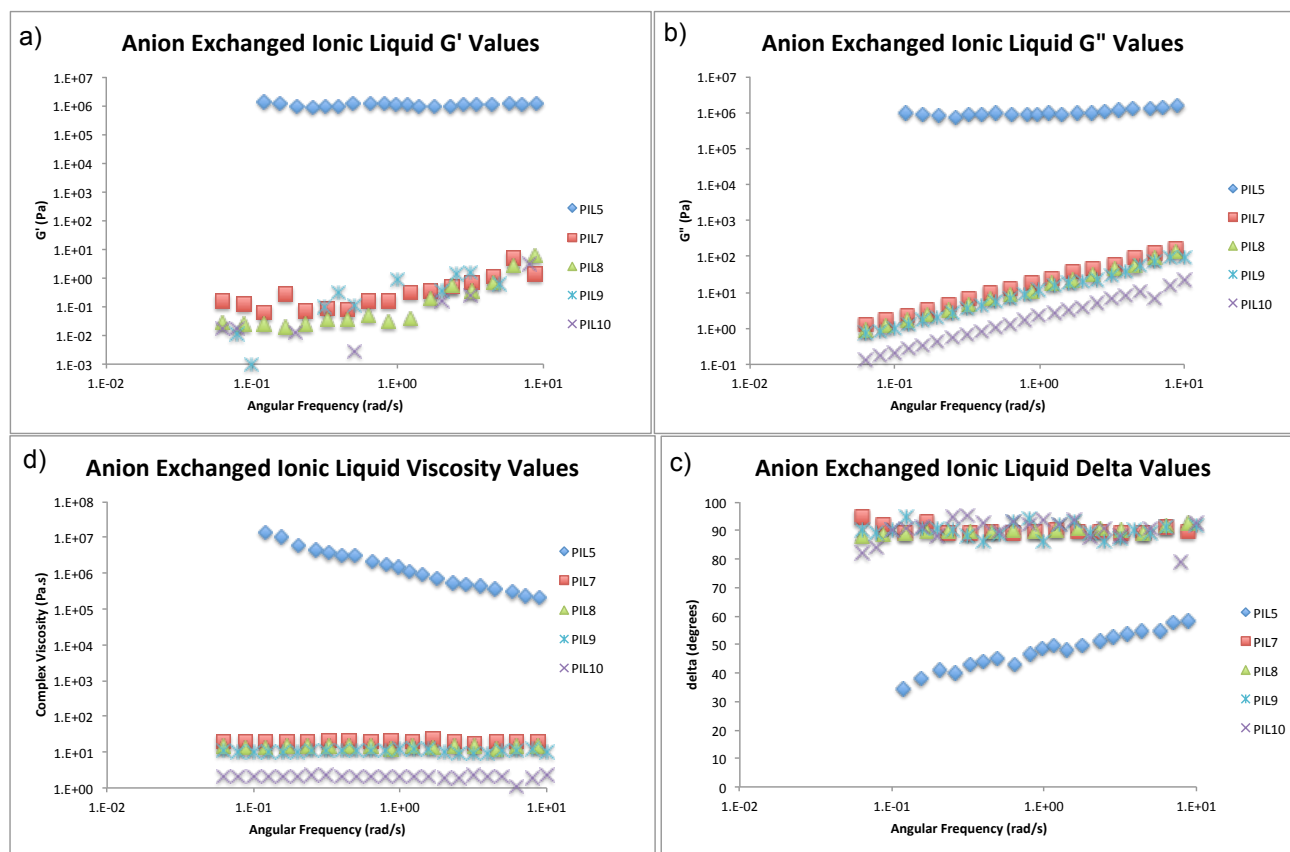


Figure S13. Frequency sweep of dicationic hexyl anion exchanged ILs (clock-wise from top left: (a) G' (storage modulus), (b) G'' (loss modulus), (c) δ (δ), and (d) η^* (complex viscosity))

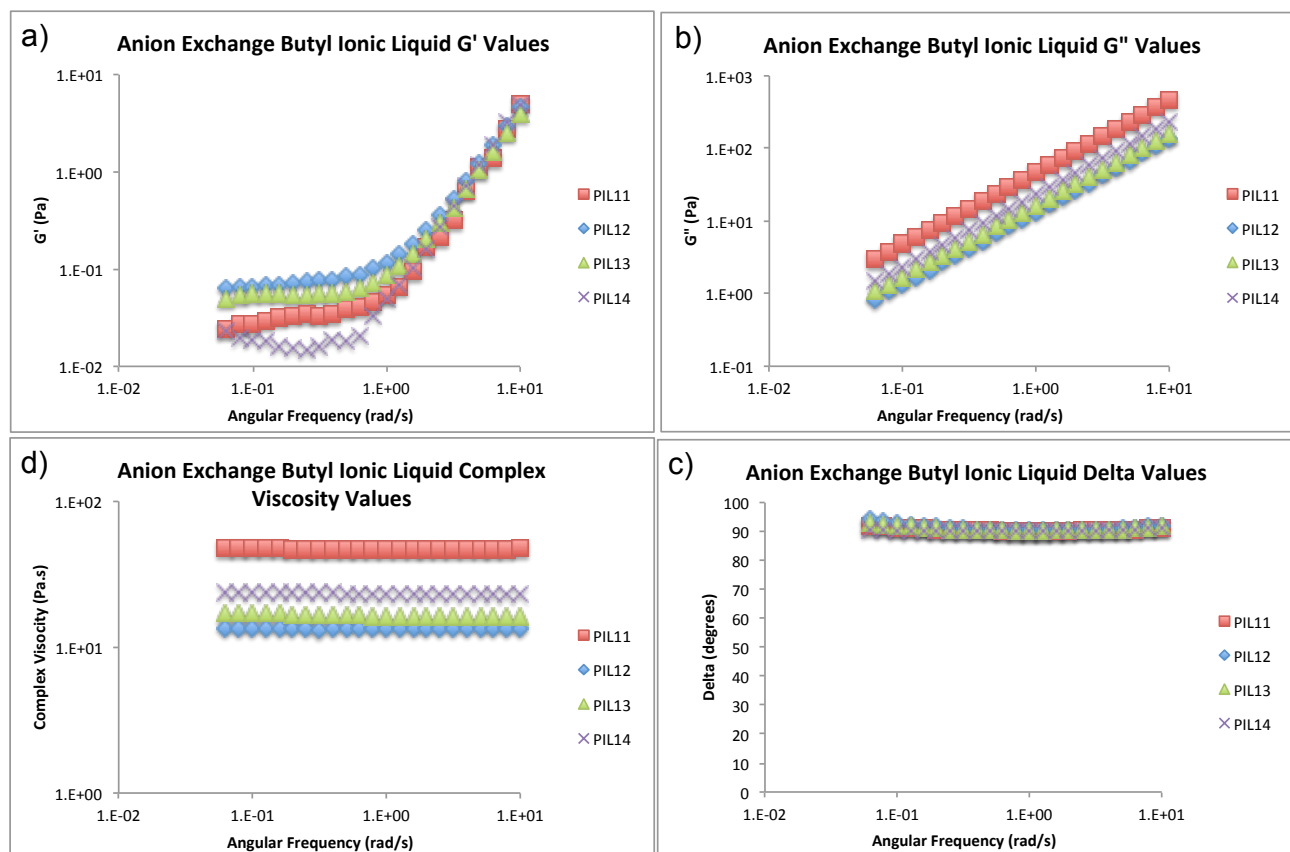


Figure SI4. Frequency sweep of dicationic butyl anion exchanged ILs (clock-wise from top left: (a) G' (storage modulus), (b) G'' (loss modulus), (c) δ (δ), and (d) η^* (complex viscosity))

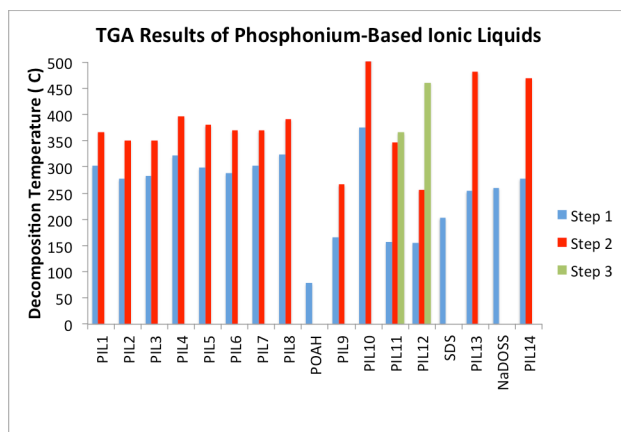


Figure SI5. Decomposition temperatures (T_d) trend from TGA results for phosphonium ionic liquids and a selection of starting materials (perfluorooctanoic acid POAH, sodium dodecyl sulfate SDS, and sodium dioctyl sulfosuccinate NaDOSS.)

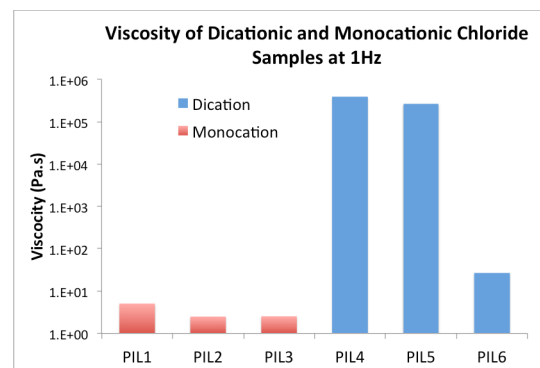


Figure SI6. Comparison of viscosity values of monocationic and dicationic chloride samples at 1 Hz.

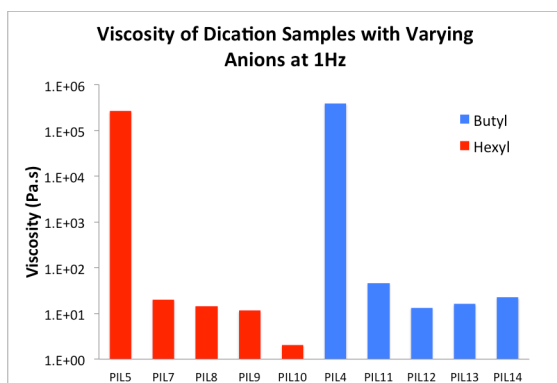


Figure SI7. Viscosity values for dicationic hexyl samples (Cl^- , PF_6^- , SbF_6^- , POA^- , and NTf_2^-) (red bars) and dicationic butyl samples (Cl^- , OA^- , POA^- , DS^- , and DOSS^-) (blue bars).

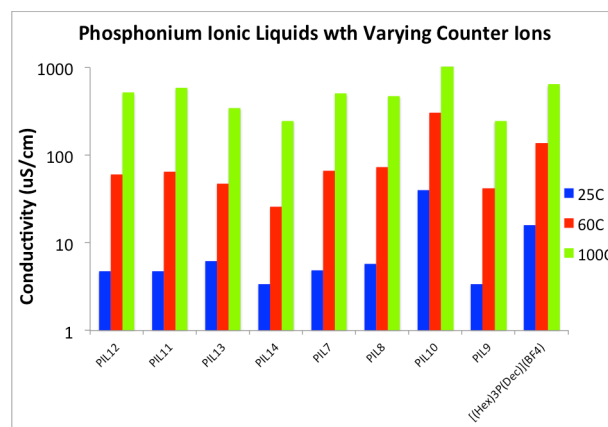


Figure SI8. Conductivity values of the phosphonium ionic liquids samples with non-chloride counterions.

Table 2. NMR Spectrums for all ILs presented in the paper**¹H NMR Spectra**

PIL1	δ_H (400 MHz; CDCl ₃ ; Me ₄ Si) 0.88 & 1.0 (12 H, t, Me), 1.26 (12 H, m, CH ₂ -CH ₂), 1.54 (16 H, m, CH ₂ -CH ₂ -P), 2.48 (8 H, m, CH ₂ -P)
PIL2	δ_H (500 MHz; CDCl ₃ ; Me ₄ Si) 0.88 & 0.90 (12 H, t, Me), 1.27-1.33 (24 H, br, CH ₂ -CH ₂), 1.5-1.59 (16 H, br, CH ₂ -CH ₂ -P), 2.48 (8 H, m, CH ₂ -P)
PIL3	δ_H (500 MHz; CDCl ₃ ; Me ₄ Si) 0.8 (12 H, t, Me), 1.21 (36 H, m, CH ₂ -CH ₂), 1.38-1.48 (16 H, br, CH ₂ -CH ₂ -P), 2.4 (8 H, m, CH ₂ -P)
PIL4	δ_H (400 MHz; CDCl ₃ ; Me ₄ Si) 0.95 (18 H, t, Me), 1.3-1.5 (40 H, br, CH ₂ -CH ₂), 2.43-2.54 (16 H, br, H ₂ -P)
PIL5	δ_H (400 MHz; CDCl ₃ ; Me ₄ Si) 0.89 (18 H, t, Me), 1.3-1.5 (64 H, br, CH ₂ -CH ₂), 2.4-2.55 (16 H, br, CH ₂ -P)
PIL6	δ_H (500 MHz; CDCl ₃ ; Me ₄ Si) 0.88 (18 H, t, Me), 1.3-1.5 (88 H, br, CH ₂ -CH ₂), 2.38-2.54 (16 H, br, CH ₂ -P)
PIL7	δ_H (400 MHz; CDCl ₃ ; Me ₄ Si) 0.90 (18 H, t, CH ₃), 1.3-1.56 (64 H, br, CH ₂ -CH ₂), 2.09 (16 H, m, CH ₂ -P)
PIL8	δ_H (400 MHz; CDCl ₃ ; Me ₄ Si) 0.89 (18 H, t, Me), 1.33-1.5 (64 H, br, CH ₂ -CH ₂), 2.1 (16 H, m, CH ₂ -P)
PIL9	δ_H (400 MHz; CDCl ₃ ; Me ₄ Si) 0.89 (18 H, t, Me), 1.1-1.9 (64 H, br, CH ₂ -CH ₂), 2.0-2.8 (16 H, br, CH ₂ -P)
PIL10	δ_H (400 MHz; (CD ₃) ₂ CO; Me ₄ Si) 0.90 (18 H, t, Me), 1.3-1.6 (64 H, br, CH ₂ -CH ₂), 2.0-2.18 (16 H, br, CH ₂ -P)
PIL11	δ_H (400 MHz; CD ₃ OD; Me ₄ Si) 1.01 (24 H, br, Me), 1.38-1.52 (60 H, br, CH ₂ -CH ₂), 2.20 (20 H, br, CH ₂ -P CH ₂ -CO ₂)
PIL12	δ_H (300 MHz; CD ₃ OD; Me ₄ Si) 1.00 (18 H, t, Me), 1.37-1.53 (40 H, br, CH ₂ -CH ₂), 2.22 (16 H, br, CH ₂ -P)
PIL13	δ_H (400 MHz; CD ₃ OD; Me ₄ Si) 0.90 (6 H, t, Me), 1.00 (18 H, t, Me), 1.29-1.63 (80 H, br, CH ₂ -CH ₂), 2.20 (16 H, br, CH ₂ -P), 3.97 (4 H, t, CH ₂ -O)
PIL14	δ_H (400 MHz; CD ₃ OD; Me ₄ Si) 0.90 (24 H, t, Me), 1.00 (18 H, t, Me), 1.31-1.52 (80 H, br, CH ₂ -CH ₂), 2.20 (16 H, br, CH ₂ -P), 3.02 (4 H, m, CO ₂ -CH ₂ -CSH), 4.01-4.07 (10 H, m, CO ₂ -CSH OCH ₂ , O-CH ₂)
[(But) ₃ P(Dec)P(But) ₃](DA) ₂	δ_H (400 MHz; CDCl ₃ ; Me ₄ Si) 0.86 (24 H, t, Me), 1.19-1.59 (76 H, br, CH ₂ -CH ₂), 2.31 (18 H, br, CH ₂ -P)

³¹P NMR Spectra

PIL1	δ_P (162 MHz; CDCl ₃ ; Me ₄ Si) 32.8 (P ⁺) (36.4)
PIL2	δ_P (162 MHz; CDCl ₃ ; Me ₄ Si) 32.8 (P ⁺)
PIL3	δ_P (162 MHz; CDCl ₃ ; Me ₄ Si) 32.65 (P ⁺) (36.43, 48.65)
PIL4	δ_P (202 MHz; CDCl ₃ ; Me ₄ Si) 32.97 (P ⁺)
PIL5	δ_P (162 MHz; CDCl ₃ ; Me ₄ Si) 32.48 (P ⁺)

PIL6	δ_p (162 MHz; CDCl ₃ ; Me ₄ Si) 32.42(P ⁺) (36.24, 49.24)
PIL7	δ_p (162 MHz; CDCl ₃ ; Me ₄ Si) 31.49 (P ⁺) -125.70, -129.93, -134.19, -138.41, -142.59, -146.81, -151.03 (PF ₆)
PIL8	δ_p (162 MHz; CDCl ₃ ; Me ₄ Si) 32.71(P ⁺)
PIL9	δ_p (162 MHz; CDCl ₃ ; Me ₄ Si) 32.76(P ⁺)
PIL10	δ_p (202 MHz; (CD ₃) ₂ CO; Me ₄ Si) 33.45(P ⁺)
PIL11	δ_p (162 MHz; CD ₃ OD; Me ₄ Si) 33.25 (P ⁺)
PIL12	δ_p (162 MHz; CD ₃ OD; Me ₄ Si) 33.29 (P ⁺), (37.15, 57.57)
PIL13	δ_p (162 MHz; CD ₃ OD; Me ₄ Si) 33.32 (P ⁺), (37.18, 55.48)
PIL14	δ_p (162 MHz; CD ₃ OD; Me ₄ Si) 33.32 (P ⁺)
[(But) ₃ P(Dec)P(But) ₃](DA) ₂	δ_p (162 MHz; CDCl ₃ ; Me ₄ Si) 32.97 (P ⁺)

¹⁹F NMR Spectra

PIL5	δ_F (376 MHz; CDCl ₃ ; Me ₄ Si) N/A (F)
PIL7	δ_F (376 MHz; CDCl ₃ ; Me ₄ Si) -71.03, -73.08 (F)
PIL8	δ_F (376 MHz; CDCl ₃ ; Me ₄ Si) -78.8(F)
PIL9	δ_F (376 MHz; CDCl ₃ ; Me ₄ Si) -81.05, -81.07, -81.09, -81.12, -81.14, -118.71, -118.74, -122.01, -122.37, -122.82, -122.86, -123.09, -126.46, -126.50
PIL10	δ_F (470 MHz; (CD ₃) ₂ CO; Me ₄ Si) -79.64, -79.68.
PIL12	δ_F (282 MHz; CD ₃ OD; Me ₄ Si) -82.38, -120.03, -122.75, -123.12, -123.83, -124.04, -127.39

¹³C NMR Spectra

PIL1	δ_C (126 MHz; CDCl ₃ ; Me ₄ Si) κ : 13.19, κ' : 13.78, α : 18.64(J=47.8), α' :18.92(J=46.5), β' : 21.58(J=5), δ' : 22.31, 23.52(J=5), 23.66(J=15), 28.64, 28.91, 28.99, 30.5(J=15), 31.5
PIL2	δ_C (126 MHz; CDCl ₃ ; Me ₄ Si) 13.89, 13.96, 19.21(J=47.8), 21.58(J=3.78), 21.61(J=5), 22.3, 22.60, 28.93, 29.2-29.4, 30.38(J=13.8), 30.7(J=15), 31.04, 31.78
PIL3	δ_C (75 MHz; CDCl ₃ ; Me ₄ Si) 13.77, 13.81, 18.9(J=47), 21.6(J=5.3), 22.3, 22.36, 28.64, 28.69, 28.97-29.18, 30.41(J=14.41), 31.41, 31.49
PIL4	δ_C (126 MHz; CDCl ₃ ; Me ₄ Si) κ : 13.31, α : 18.73(J=47.7), α' : 19.1(J=46.5), β' : 21.58(J=5), β : 23.62 (J=5), γ : 23.72(J=15), ϵ' : 28.26, δ' : 28.58, γ' : 30.42(J=15)
PIL5	δ_C (101 MHz; CDCl ₃ ; Me ₄ Si) κ : 13.56, α : 18.78(J=57.8), α' : 18.89(J=57.8), β' : 21.24(J=5), β : 21.42 (J=6.25), δ : 21.00, ϵ' : 27.71, δ' : 28.48, γ : 30.07(J=17.6), θ' : 30.68
PIL6	δ_C (126 MHz; CDCl ₃ ; Me ₄ Si) κ : 13.93, α : 19.0(J=46.5), α' : 19.16(J=46.5), β' : 21.64(J=4), β : 21.76(J=5) δ : 22.46(J=0.02), ϵ' : 28.33, δ' : 28.68, ϵ : 28.83, $\gamma\sim\gamma'$: 30.44-31.41
PIL7	δ_C (101 MHz; CDCl ₃ ; Me ₄ Si) 14.20, 18.71(J=47.28), 18.83(J=47.28), 21.39(J=4), 21.72(J=5), 22.58, 28.39(J=76.43), 29.11-29.39, 30.53(J=14.08), 31.17, 34.03
PIL8	δ_C (126 MHz; CDCl ₃ ; Me ₄ Si) 13.99, 14.04, 19.17(J=47.2), 21.77, 22.50, 28.57(J=76.7), 30.44, 30.56, 31.11
PIL9	δ_C (75 MHz; CDCl ₃ ; Me ₄ Si) 13.86, 19.37, 19.73, 21.98, 22.35, 28.24, 28.74, 30.47, 30.55, 30.66,

	30.72
PIL10	δ_C (75 MHz; $(CD_3)_2CO$; Me_4Si) 13.36, 18.15 (d, $J = 47.7$ Hz), 20.99, 21.05, 22.10, 30.03, 30.39, 30.59, 30.75
PIL11	δ_C (75 MHz; CD_3OD ; Me_4Si) 12.64, 12.66, 13.49, 17.57, 18.20, 18.41, 19.05, 21.14, 21.93, 23.17, 23.55, 23.76, 23.99, 24.40, 24.62, 28.57, 29.28, 29.86, 30.35, 30.59, 31.19, 66.08, 66.38
PIL12	δ_C (75 MHz; CD_3OD ; Me_4Si) 11.69, 12.34, 17.48, 18.16, 21.02, 22.36, 23.02, 23.60, 28.48, 30.33
PIL13	δ_C (75 MHz; $CDCl_3$; Me_4Si) 12.36, 13.09, 17.30, 17.57, 17.94, 18.20, 21.03, 22.95, 23.48, 23.69, 25.57, 28.59, 29.10, 29.35, 30.39, 30.60, 31.69, 67.54
PIL14	δ_C (75 MHz; CD_3OD ; Me_4Si) 10.13, 12.52, 13.26, 17.38, 17.77, 18.08, 20.96, 22.77, 23.14, 23.51, 28.77, 30.13, 33.62, 38.50, 38.81, 47.75, 61.98, 67.22, 104.99, 145.22, 170.65
$[(But)_3P(Dec)P(But)_3](DA)_2$	δ_C (75 MHz; $CDCl_3$; Me_4Si) 13.41, 14.04, 18.39, 18.71, 19.02, 19.34, 21.51, 21.57, 22.59, 23.61, 23.67, 23.77, 23.97, 24.91, 28.20, 28.67, 29.09, 29.24, 29.30, 29.42, 29.53, 30.35, 30.54, 31.80, 34.52

(Central Chain: α' , β' , γ')