## Supporting Information

# Preparation of Half- and Post-metallocene Hafnium Complexes with Tetrahydroquinoline and Tetrahydrophenanthroline Frameworks for Olefin Polymerization 

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Figure S1. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra of $\mathbf{1}$.


Figure S2. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra of $\mathbf{2}$.


Figure S3. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra of $\mathbf{3}$.


Figure S4. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra of 4 .


Figure S5. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra of 5 .



Figure S6. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra of 6 .


Figure S7. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra of 9 .


Figure S8. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra of $\mathbf{1 0}$.




Figure S9. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra of $\mathbf{1 1}$.


Figure S10. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra of $\mathbf{1 2}$.




Figure S11. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra of 13 .



Figure S12. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra of $\mathbf{1 4 .}$


Figure S13. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra of $\mathbf{1 5}$.


Figure S14. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra of $\mathbf{1 6}$.




Figure S15. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra recorded on the reaction of $\mathbf{1}$ with $\left[\left(\mathrm{C}_{18} \mathrm{H}_{37}\right)_{2} \mathrm{~N}(\mathrm{H}) \mathrm{Me}\right]^{+}\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{4}\right]^{-}$at 3 h .



Figure S16. ${ }^{1} \mathrm{H}$ NMR spectrum recorded on the reaction of 2 with $\left[\left(\mathrm{C}_{18} \mathrm{H}_{37}\right)_{2} \mathrm{~N}(\mathrm{H}) \mathrm{Me}\right]^{+}\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{~F} 5\right)_{4}\right]^{-}$at 3 h.




Figure S17. ${ }^{1} \mathrm{H}$ NMR spectrum recorded on the reaction of $\mathbf{3}$ with $\left[\left(\mathrm{C}_{18} \mathrm{H}_{37}\right)_{2} \mathrm{~N}(\mathrm{H}) \mathrm{Me}\right]^{+}\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{~F} 5\right)_{4}\right]^{-}$at 5 h.


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Figure S18. ${ }^{1} \mathrm{H}$ NMR spectrum recorded on the reaction of 4 with $\left[\left(\mathrm{C}_{18} \mathrm{H}_{37}\right)_{2} \mathrm{~N}(\mathrm{H}) \mathrm{Me}\right]^{+}\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{~F} 5\right)_{4}\right]^{-}$at 5 h.


Figure S19. ${ }^{1} \mathrm{H}$ NMR spectrum recorded on the reaction of $\mathbf{5}$ with $\left[\left(\mathrm{C}_{18} \mathrm{H}_{37}\right)_{2} \mathrm{~N}(\mathrm{H}) \mathrm{Me}\right]^{+}\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{~F} 5\right)_{4}\right]^{-}$at 3 h.


Figure S20. ${ }^{1} \mathrm{H}$ NMR spectrum recorded on the reaction of $\mathbf{6}$ with $\left[\left(\mathrm{C}_{18} \mathrm{H}_{37}\right)_{2} \mathrm{~N}(\mathrm{H}) \mathrm{Me}\right]^{+}\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{~F} 5\right)_{4}\right]^{-}$at 3 h.


Figure S21. ${ }^{1} \mathrm{H}$ NMR spectrum recorded on the reaction of $\mathbf{1 0}$ with $\left[\left(\mathrm{C}_{18} \mathrm{H}_{37}\right)_{2} \mathrm{~N}(\mathrm{H}) \mathrm{Me}\right]^{+}\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{~F} 5\right) 4\right]^{-}$ at 0.5 h .



Figure S22. ${ }^{1} \mathrm{H}$ NMR spectrum recorded on the reaction of $\mathbf{1 1}$ with $\left[\left(\mathrm{C}_{18} \mathrm{H}_{37}\right)_{2} \mathrm{~N}(\mathrm{H}) \mathrm{Me}\right]^{+}\left[\mathrm{B}(\mathrm{C} 6 \mathrm{~F} 5)_{4}\right]^{-}$ at 0.5 h .


Figure S23. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra recorded on the reaction of $\mathbf{1 2}$ with $\left[\left(\mathrm{C}_{18} \mathrm{H}_{37}\right)_{2} \mathrm{~N}(\mathrm{H}) \mathrm{Me}\right]^{+}\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{4}\right]^{-}$at 0.5 h .


Figure S24. ${ }^{1} \mathrm{H}$ NMR spectrum recorded on the reaction of $\mathbf{1 5}$ with $\left[\left(\mathrm{C}_{18} \mathrm{H}_{37}\right)_{2} \mathrm{~N}(\mathrm{H}) \mathrm{Me}\right]^{+}\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{4}\right]^{-}$ at 1 h ..


Figure S25. ${ }^{1} \mathrm{H}$ NMR spectrum recorded on the reaction of $\mathbf{1 6}$ with $\left[\left(\mathrm{C}_{18} \mathrm{H}_{37}\right)_{2} \mathrm{~N}(\mathrm{H}) \mathrm{Me}\right]^{+}\left[\mathrm{B}(\mathrm{C} 6 \mathrm{~F} 5)_{4}\right]^{-}$ at 1 h .


Figure S26. ${ }^{1} \mathrm{H}$ NMR spectrum recorded on the reaction of $\mathbf{1 6}$ with $\left[\left(\mathrm{C}_{18} \mathrm{H}_{37}\right)_{2} \mathrm{~N}(\mathrm{H}) \mathrm{Me}\right]^{+}\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{4}\right]^{-}$ containing water at 1 h .



Figure S27. ${ }^{1} \mathrm{H}$ NMR spectrum of anhydrous $\left[\left(\mathrm{C}_{18} \mathrm{H}_{37}\right)_{2} \mathrm{~N}(\mathrm{H}) \mathrm{Me}\right]^{+}\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{~F} 5\right) 4\right]^{-}$prepared in this work.


Figure S28. ${ }^{1} \mathrm{H}$ NMR spectrum of $\left[\left(\mathrm{C}_{18} \mathrm{H}_{37}\right)\right)_{2} \mathrm{~N}(\mathrm{H}) \mathrm{Me}^{+}\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{4}\right]^{-}$containing water prepared by the method reported in patent.


Figure S29. ${ }^{1}$ H NMR spectrum of polymer (entry 3 in Table 1).

Figure S30. ${ }^{1} \mathrm{H}$ NMR spectrum of Polymer (entry 5 in Table 1).


Figure S31. DSC Thermograms
$<$ Entry 1 in Table $1>$

$<$ Entry 2 in Table 1>

$<$ Entry 3 in Table 1>

<Entry 4 in Table 1>

$<$ Entry 6 in Table 1>

<Entry 7 in Table 1>

$<$ Entry 8 in Table $1>$

$<$ Entry 9 in Table 1>

$<$ Entry 10 in Table $1>$

<Entry 11 in Table 1>



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