## Supporting information

## Branched phosphazenium salts as effective, versatile cocatalysts for epoxide/ $\mathrm{CO}_{2}$ coupling

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Figure S1. Examples of phosphazene bases with different P number and topologies (linear, branched and cyclic)





Figure S2. ${ }^{1} \mathrm{H}$ NMR spectrum of the crude PCHC obtained (Table 1, entry 2 ).


Figure S3. ${ }^{1} \mathrm{H}$ NMR spectrum of the crude PCHC obtained (Table 1, entry 6).


Figure S4. SEC chromatograms of selected samples from Table 1.


Figure S5. DSC thermograms of selected sample from Table 1


Figure S6. SEC chromatograms of selected samples from Table 2


Figure S7. DSC thermograms of selected sample from Table 2


Figure S8. DSC curves of selected samples from Table 3

Entry 17 Table 3


Figure S9. ${ }^{1} \mathrm{H}$ NMR spectrum of crude polypropylene carbonate from $\mathrm{PPZCI} / 1 \mathrm{~d}$ (entry 17 in Table 3)


Figure S10. ${ }^{1} \mathrm{H}$ NMR spectrum of crude polypropylene carbonate from $\mathrm{PPZN}_{3} / \mathbf{1 d}$ (entry 19 in Table 3)


Figure S11. SEC chromatograms of selected samples from Table 3


Figure S12. SEC chromatograms of selected entries in Table 4


Figure S13. DSC curves of selected entries from Table 4


Figure S14. ${ }^{1} \mathrm{H}$ NMR spectrum of crude polypropylene carbonate from $\mathrm{PPZN}_{3} / \mathbf{2 a}$ (entry $\mathbf{2 1}$ in Table 4)

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Entry 22 Table 4
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Figure S15. ${ }^{1} \mathrm{H}$ NMR spectrum of crude polypropylene carbonate from $\mathrm{PPZN}_{3} / \mathbf{2 a}$ (entry $\mathbf{2 2}$ in Table 4)

Entry 26 Table 4


Figure S16. ${ }^{1} \mathrm{H}$ NMR spectrum of crude polypropylene carbonate from $\mathrm{PPZCI} / \mathbf{2 b}$ (entry 26 in Table 4)

gure S17. ${ }^{1} \mathrm{H}$ NMR spectrum of crude polypropylene carbonate from $\mathrm{PPZN}_{3} / \mathbf{2 b}$ (entry 27 in Table 4)


Scheme S1. General reaction mechanism to yield either polycarbonate or cyclic carbonate.
Table S1. Connolly Molecular Surface Area for the cocatalysts used in this work.

| Cocatalyst | Molecular <br> Area $\left(\AA^{2}\right)$ |
| :--- | :--- |
| PPNCl | 360.0 |
| PPNN $_{3}$ | 370.3 |
| PPZCl | 465.3 |
| PPZN | 450.5 |
| TPPCl | 254.4 |
| UHFFA | 268.5 |

Calculated with ChemDraw 3D by Chemoffice 20.0.

