

Triblock and pentablock copolymerizations of ϵ -caprolactone with L-lactide catalyzed by N-heterocyclic carbene

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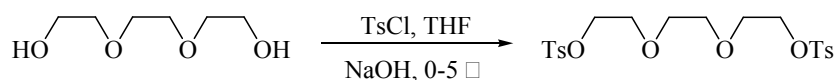
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Supporting Information (SI)

Supporting Information of general procedure for catalyst preparation:

Synthesis of triethylene glycol ditosylate

To a 1000 mL round bottomed flask, equipped with a stirrer bar, was added triethylene glycol (42.08 g, 160 mmol) and THF (160 mL). The flask was cooled to 0~5 °C, in an ice bath, and the sodium hydroxide (32.00 g, 800 mmol) dissolved in water (160 mL) was added. Then a solution of p-toluene sulfonyl chloride (99.00 g, 520 mmol) in THF (120 mL) was added dropwise via a constant pressure funnel. Stirring was continued for 2 h at 0~5 °C. Upon completion of the reaction, the mixture was poured into ice-water and the white precipitate was obtained. Recrystallization from methanol gave the title product as colorless crystals.¹



Synthesis of 2, 3-benzo-1, 4, 7, 10-tetraoxacyclododecane (Benzo-12-crown-4)

Pyrocatechol (11.00 g, 100 mmol) was added to a stirred suspension of LiOH (12.60 g, 300 mmol) and NaOH (4.00 g, 100 mmol) in THF (400 mL) at 65 °C. Then the mixture was refluxed for 1 h under N₂. To the mixture was added triethylene glycol ditosylate (45.80 g, 100 mmol) in THF (200 mL) over 2 h, and stirring was continued for 72 h at 65 °C. The solvent was evaporated, the resultant mixture was diluted with water (100 mL) and the aqueous phase was extracted with dichloromethane (3×100 mL). The combined organic phases were dried over anhydrous MgSO₄ and concentrated under reduced pressure. The residue was extracted with boiling n-heptane. After cooling, the pure product was isolated as colorless crystals.² C₁₂H₁₆O₄ ¹H NMR (600 MHz, CDCl₃, 25 °C) shown in fig. S1, δ ppm: 3.80-3.87 (t, 8H), 4.18 (d, 4H), 6.97 (s, 4H).

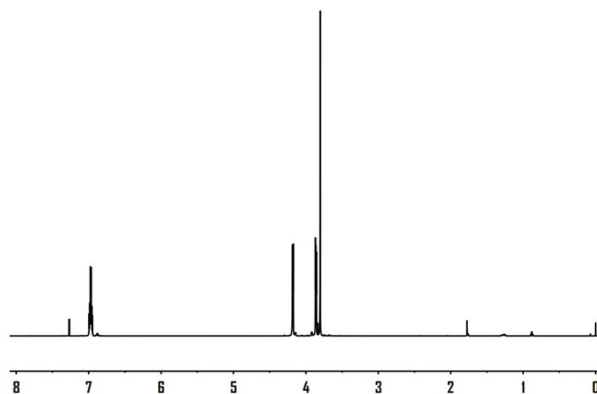
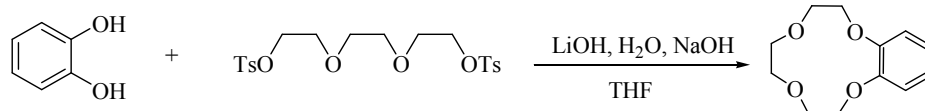
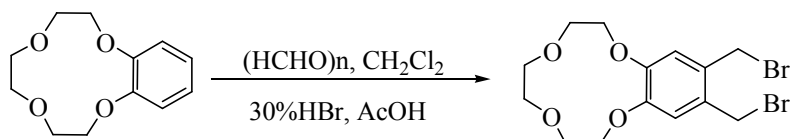


Fig. S1 The ¹H NMR spectrum of benzo-12-crown-4

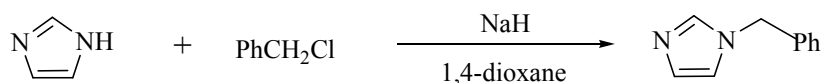
Synthesis of 4,5-dibromomethyl benzo-12-crown-4

A mixture of benzo-12-crown-4 (1.00 g, 4.46 mmol), paraformaldehyde (0.30 g, 10.00 mmol) and HBr/AcOH (30%) (9.16 ml) in dichloromethane (20 mL) was stirred at refluxing temperature under nitrogen atmosphere and TLC tracking. After reaction of 24 h, the reaction mixture was poured into ice-water (100 mL) and neutralized with a saturated solution of K_2CO_3 until the pH = 7. The solution was then extracted with dichloromethane (3×20 mL), and the combined organic phases were dried ($MgSO_4$). The solvent was removed in vacuo to afford the title product.



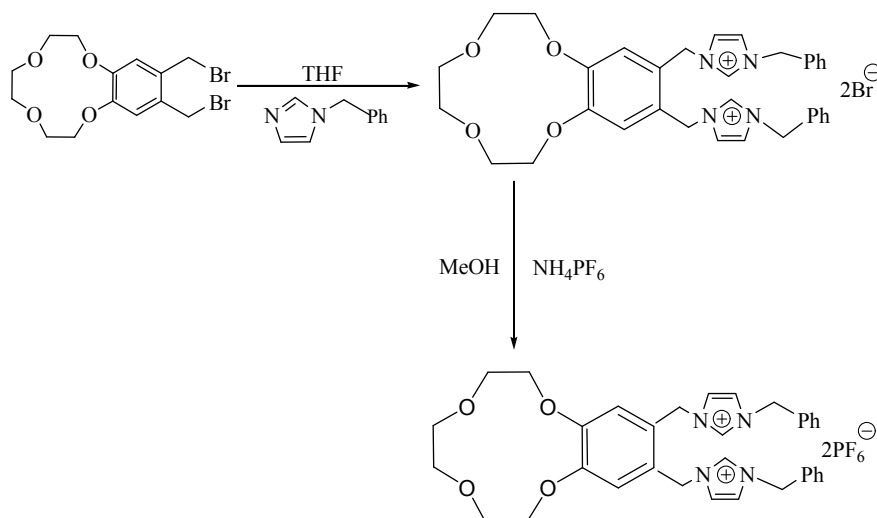
Synthesis of N-benzylimidazole

To a stirring solution of imidazole (12.50 g, 184 mmol) in anhydrous 1,4-dioxane (100 mL) at room temperature was added powdered NaH (4.41 g, 184 mmol) under nitrogen atmosphere. Then the mixture was refluxed for 1 h. The benzyl chloride (23.25 g, 184 mmol) was added dropwise to the mixture. Stirring was continued for 12 h at 90 °C when the addition was completed. The solvent was removed under vacuum and the residue was dissolved in H_2O (60 mL). The resultant mixture was extracted with dichloromethane (3×30 mL) and the organic phase was dried over anhydrous $MgSO_4$. The solvent was removed completely under vacuum to give colorless crystals.



Synthesis of the benzo-12-crown-4 modified imidazole-hexafluorophosphate

A solution of N-benzylimidazole (1.41 g, 8.92 mmol) and 4,5-dibromomethyl benzo-12-crown-4 (1.84 g, 4.46 mmol) in THF (200 mL) was stirred at refluxing temperature under nitrogen atmosphere. The solution was left to stand for 72 h, over which time white solid formed. The mixture was filtered and the equiv of NH_4PF_6 (1.45 g, 4.46 mmol) was then added to the solution of obtained solid in methanol (50 mL). After stirring 2 h, the mixture was poured into ice-water and then the white precipitate was obtained. Recrystallization from dichloromethane and petroleum ether (60-90 °C) gave the product. 1H NMR (600 MHz, DMSO) Shown in fig. S2, δ ppm: 4.02-3.58 (m, 12H), 5.63, 5.40 (dd, 8H), 7.82-7.40 (m, 16H), 9.34 (m, 2H).



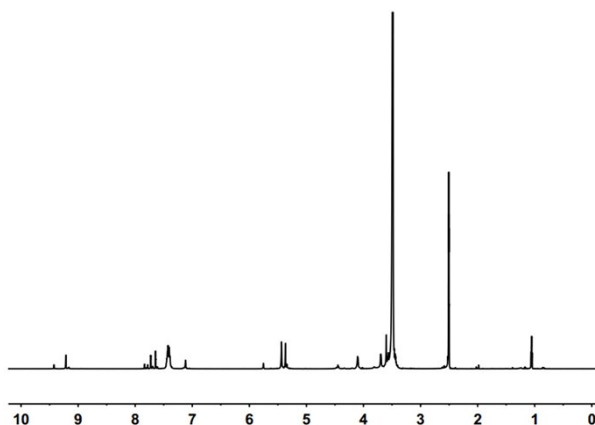
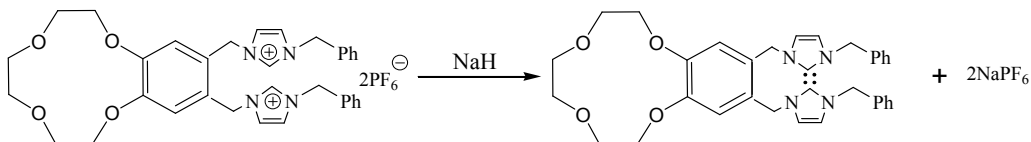


Fig. S2 The ^1H NMR spectrum of benzo-12-crown-4 modified imidazole-hexafluorophosphate

The formation of carbene in situ

To a previously flamed ampoule was added benzo-12-crown-4 modified imidazole-hexafluorophosphate (0.15 g, 1.76 mmol), excess of NaH (0.1 g, 4.17 mmol) and dry THF (4.39 mL). After 2.5 h at room temperature, the mixture was filtered and the scarlet carbene solution was obtained.



Notes and references

- 1 M. Ouchi, Y. Inoue, Y. Liu, S. Nagamune, S. Nakamura, k. Wada and T. Hakushi, *Bull. Chem. Soc. Jpn.* 1990, **63**, 1260-1262.
- 2 Y. Liu, Y. Inoue and T. Hakushi, *Bull. Chem. Soc. Jpn.* 1990, **63**, 3044-3046.