Syntheses, Characterization and Application of Tridentate Phenoxyimino-phenoxy Aluminum Complexes for the Coupling of Epoxide with CO_2: from Binary System to Single Component Catalyst

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Experimental Section

2-Aminophenol (99%), 4-tertbutylphenol, aqueous dimethylamine solution (40 wt.%), iodomethane, 3,5-ditertbutylsalicyaldehyde (98%), anhydrous $MgCl_2$, paraformaldehyde and diethyl aluminium chloride (1 mol/L, in hexane) are commercially available and used as received. Propylene oxide, 1,2-butylene oxide, epichlorohydrin, styrene oxide and triethylamine were distilled over CaH_2 before use. THF, hexane and acetonitrile were pre-dried over 4Å molecular sieves before distillation over sodium with benzophenone as the indicator under an argon atmosphere and stored over freshly cut sodium in a glovebox. CO_2 (99.999% purity) was purchased from Shenyang Hongsheng Gas Limited Corporation, China. Ethanol and formic acid were used as received without further handling.

General procedures: All reactions sensitive to air and moisture were carried out in a glovebox filled with dry argon. 5-tertbutylsalicylaldehyde, 3-(N,N-dimethylaminomethyl)-5-tertbutylsalicylaldehyde, 2-hydroxy-3-(N,N-dimethyl)aminomethyl-aniline were synthesized according to the literature methods[1-3]. Proligands $\mathbf{H_2L^1}$-$\mathbf{H_2L^3}$ were synthesized by the equimolar reaction of the corresponding functional salicylaldehyde with functional aminophenol and structurally identified by ^{1}H NMR and ^{13}C NMR. Elemental analyses were performed at DUT Chemistry Analysis & Research Centre, Dalian University of Technology. The aluminium complexes **1-3** were prepared by equimolar reaction of the proligands with $AlEt_2Cl$ in the glovebox. The structures of the complexes **1-3** are characterized by ^{1}H NMR, ^{13}C NMR and MS. The cycloaddition of epoxide with CO_2 was carried in a stainless steel autoclave equipped with a magnetic stirring bar. The reaction mixture was analyzed by the ^{1}H NMR spectra with $CDCl_3$ as a solvent. The ^{1}H and ^{13}C NMR spectra were recorded using AVANCE III 500 MHz spectrometer. Mass spectra of the complexes **1-3** were obtained in the electrospray positive mode (ESI+) on LTQ Orbitrap XL spectrometer, samples were diluted in methanol or ethanol, at DUT Chemistry Analysis & Research Centre.

The typical procedure for the cycloaddition of PO with CO_2 by the complex **1** under elevated pressure. The complex **1** and cocatalyst were dissolved in PO in a Schlenk tube. Then the solution was transferred via syringe into the pre-dried autoclave under CO_2 atmosphere. The autoclave was pressurized with CO_2 and heated. After the designated time the autoclave was cooled in an ice bath. The excess of the CO_2 was vented out. The conversion of PO was determined by GC analysis and ^{1}H NMR of the reaction mixture and yield was calculated based on isolated propylene carbonate. The results showed that the GC result was consistent with that by weight analysis of the PC.

The typical procedure for the cycloaddition of PO with CO_2 by the complex **2** under elevated pressure. Complex **2** was first placed in the pre-dried autoclave. After the internal atmosphere of the autoclave was displaced by CO_2 for three times, PO was injected followed by charging CO_2 to 2 MPa. Then the autoclave was heated for the designated time. The analysis was the same as the above method.

The typical procedure for the cycloaddition of CO_2 with CPO by the complex **2** at atmospheric CO_2 pressure. Complex **2** was placed in a 10 mL round bottom flask in a glovebox. The flask was taken out, equipped with a balloon. The flask was vacuumed, recharged with CO_2. After the injection of the prescribed amount of CPO, the flask was heated and maintained at 100 ºC. The samples were taken out periodically and analysed by GC to determine the conversion of CPO.

Synthesis of Proligand H_2L^1: 3,5-ditertbutylsalicyaldehyde (2.34 g, 10 mmol) and 2-aminophenol (1.09g, 10 mmol) were dissolved in methanol (60 mL). after addition of drops of HCOOH the mixture was stirred for 8 h at room temperature. The desired product **H_2L^1** was isolated as yellow solids in 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.68 (s, 2H, O**H**) , 8.72 (s, 1H, C**H**=N), 7.51 (s, 1H, Ar-**H**), .22 (s, 1H, Ar-**H**), 7.16 (s, 1H, Ar-**H**), 7.03 (s, 1H, Ar-**H**), 6.97 (s, 1H, Ar-**H**), 5.87 (s, 1H, Ar-**H**), 1.49 (s, 9H, *t*-Bu), 1.35 (s, 9H, *t*-Bu). Anal. Calcd for $C_{21}H_{27}NO_2$ (%): C, 77.50; H, 8.36; N, 4.30. Found: C, 77.47; H, 8.34; C, 4.28.

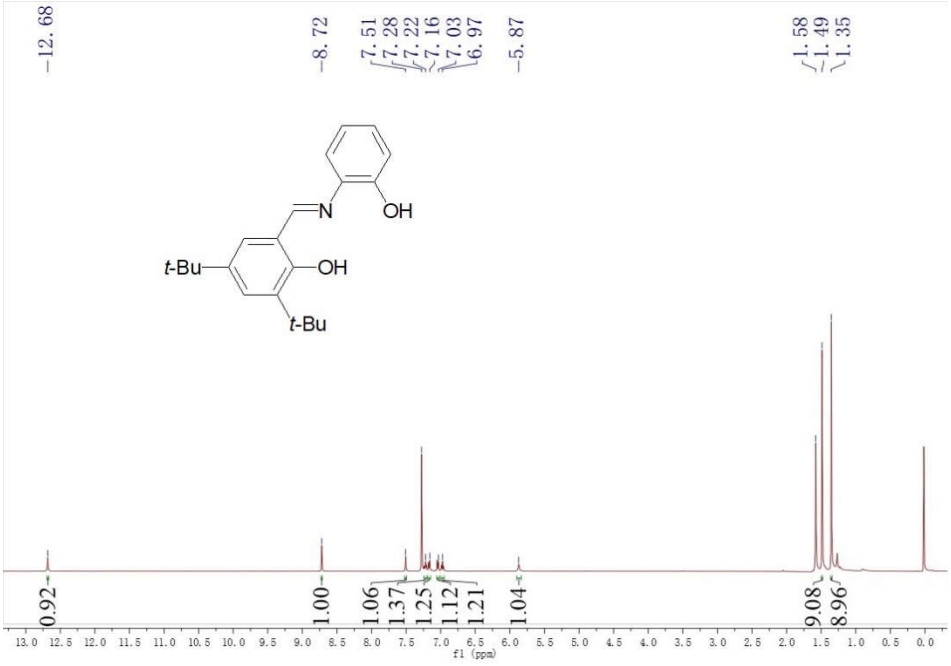


Figure S1. ^{1}H NMR spectrum of proligand H_2L^1 in $CDCl_3$

Synthesis of proligand H_2L^2: 3-(N,N-dimethylaminomethyl)-5-tertbutylsalicylaldehyde (2.35 g, 10 mmol) and 2-aminophenol (1.09 g, 10 mmol) were dissolved in 50 mL MeOH. After addition of several drops of HCOOH, the mixture was stirred for 24 h at room temperature. After removal of MeOH by rotary evaporation, the resulting mixture was washed by n-hexane for 5 times to give $\mathbf{H_2L^2}$ as orange solids in 72% yield. ^{1}H NMR (500 MHz, DMSO): δ 9.00 (s, 1H, C**H**=N) , 7.57 (s, 1H, Ar-**H**), 7.48 (s, 1H, Ar-**H**), 7.38 (d, 1H, Ar-**H,** J = 7.5Hz), 7.14 (t, 1H, Ar-**H**, J = 7.5 Hz), 6.98 (d, 1H, Ar-**H**, J = 7.5 Hz), 6.89 (t, 1H, Ar-**H**, J = 7.5 Hz), 3.62 (s, 2**H**, Ar-C**H**$_2$-NMe$_2$), 2.30 (s, 6H, N(C**H**$_3$)$_2$), 1.31 (s, 9H, *t*-Bu). ^{13}C NMR (126 MHz, DMSO) δ 161.96, 158.61, 151.62, 140.50, 134.95, 132.07, 128.48, 128.43, 123.61, 120.02, 119.78, 118.84, 117.01, 56.51, 44.62, 34.24, 31.68. Anal. Calcd for $C_{20}H_{26}N_2O_2$ (%): C, 73.59; H, 8.03; N, 8.58. Found: C, 73.57; H, 8.00; N, 8.55.

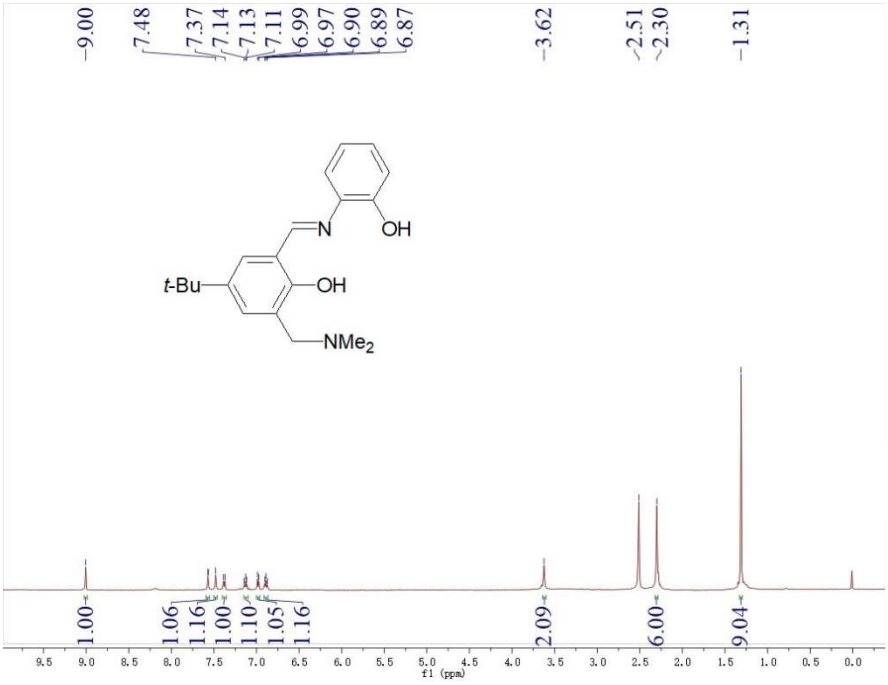


Figure S2. ^{1}H NMR spectrum of proligand H_2L^2 in DMSO-d_6

Proligand H_2L^3: 3-(N,N-dimethylaminomethyl)-5-tertbutylsalicylaldehyde (2.35 g, 10 mmol) and 2-hydroxy-3-(N,N-dimethyl)aminomethyl-aniline (1.66g, 10 mmol)were dissolved in 50 mL MeOH. After addition of several drops of HCOOH, the mixture was stirred for 24 h at room temperature. After removal of MeOH by rotary evaporation, the resulting mixture was washed by n-hexane for 5 times to give $\mathbf{H_2L^2}$ as dark orange solids in 68% yield.^{1}H NMR (500 MHz, DMSO): δ 9.09 (s, 1H, C**H**=N) , 7.58 (s, 1H, Ar-**H**), 7.52 (s, 1H, Ar-**H**), 7.38 (d, 1H, Ar-**H**, J = 7.5 Hz), 7.02 (d, 1H, Ar-**H**, J = 7.5 Hz), 6.84 (t, 1H, Ar-**H**, J = 7.5 Hz), 3.75 (s, 4H, C**H**$_2$-NMe$_2$), 2.39 (s, 6H, NMe$_2$), 2.33 (s, 6H, NMe$_2$), 1.31 (s, 9H, *t*-Bu). ^{13}C NMR (126 MHz, DMSO) δ 163.73, 162.36, 159.40, 152.72, 140.91, 134.59, 132.92, 129.21, 128.22, 124.12, 123.21, 119.65, 119.26, 119.24, 62.09, 56.50, 44.66, 44.63, 34.67, 32.08. Anal. Calcd for $C_{23}H_{33}N_3O_2$ (%): C, 72.03; H, 8.67; N, 10.96. Found: C, 72.00; H, 8.64; N, 10.94.

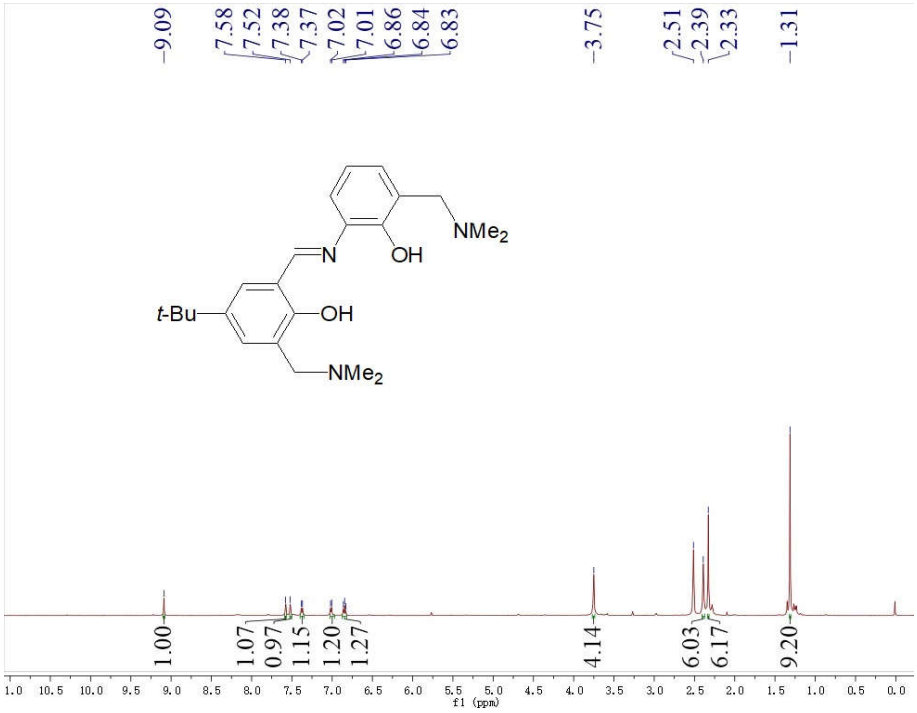


Figure S3. ^{1}H NMR spectrum of proligand H_2L^3 in DMSO-d_6

Syntheses of complexes 1~3.

Typical procedure for the synthesis of complex **1**: H_2L^1 (4 mmol)in 15 mL anhydrous THF was added dropwise to a stirred hexane solution of Et_2AlCl (4.2 mmol) under –30 ºC. The mixture was allowed to warm up to room temperatue and stirred for another 4 h. Ater all the volatiles were removed under reduced pressure, the residues were washed by n-hexane (3×10 mL) to give the desired product and dried in vacuum to constant weight.

Complex 1: ^{1}H NMR ($CDCl_3$, 25 ºC, 500 Hz): δ 8.06 (s, 1H, C**H**=N), 7.31 (d, 1H, ^{4}J = 2.5 Hz, 2H, Ar-**H**), 7.06 (d, ^{4}J = 2.5 Hz, 1H, Ar-**H**), 6.95 (t, ^{3}J = 7.5 Hz, 1H, Ar-**H**), 6.87 (d, ^{3}J = 8 Hz, 1H, Ar-**H**), 6.74 (d, ^{3}J = 8.0 Hz, 1H, Ar-**H**), 6.67 (t, ^{3}J = 7.5, 1H, Ar-**H**), 1.32 (s, 9H, C(C**H**$_3$)$_3$), 0.84 (s, 9H, C(C**H**$_3$)$_3$). ^{13}C NMR (125.77 MHz, $CDCl_3$, 25 ºC): δ 165.2, 157.7, 149.8,141.2, 137.1, 135.9, 128.7, 128.4, 127.2, 120.9, 118.4,118.2, 115.6, 35.1, 34.2, 31.4, 29.4 ppm. ESI MS: $C_{21}H_{25}NO_2Al$, theoretical calculation: 350.1701, found m/z = 350.1566 (weak); $C_{23}H_{33}NO_4Al$, theoretical calculation: 414.2225, found m/z = 414.2219 (very strong).

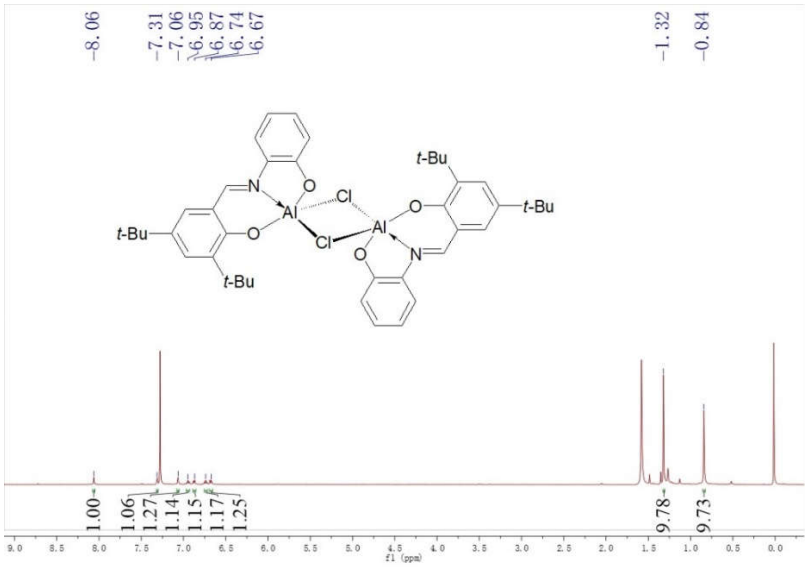


Figure S4. ^{1}H NMR spectrum of the complex **1** in $CDCl_3$.

Complex 2: ^{1}H NMR (500 MHz, DMSO): δ 9.11 (s, 1H, C**H**=N), 9.01 (s, 1H, C**H**=N), 7.74 (d, 1H, Ar-**H**), 7.70 (d, 1H, Ar-**H**), 7.6 (b, 2H, Ar-**H**), 7.56 (s, 1H, Ar-**H**), 7.51 (s, 2H, Ar-**H**), 7.27 (d, 1H, Ar-**H**), 7.14 (m, 1H, Ar-**H**), 6.66 (b, 2H, Ar-**H**), 6.57 (t, 1H, Ar-**H**), 3.41 (s, 4**H**, Ar-C**H**$_2$-NMe$_2$), 2.51 (s, 12H, NMe$_2$), 1.32 (s, 18H, *t*-Bu), 1.30. ^{13}C NMR (126 MHz, DMSO) δ 165.93, 162.51, 161.65, 138.05, 133.42, 132.55, 132.19, 130.31, 130.11, 129.67, 119.85, 117.89, 115.41, 67.50, 42.46, 34.18, 31.68. ESI MS: $C_{22}H_{30}AlN_2O_3$, theoretical calculation: 397.2072, found: m/z = 397.1085; $C_{42}H_{54}Al_2ClN_4O_5$, theoretical calculation: 783.3414, found: m/z = 783.3226.

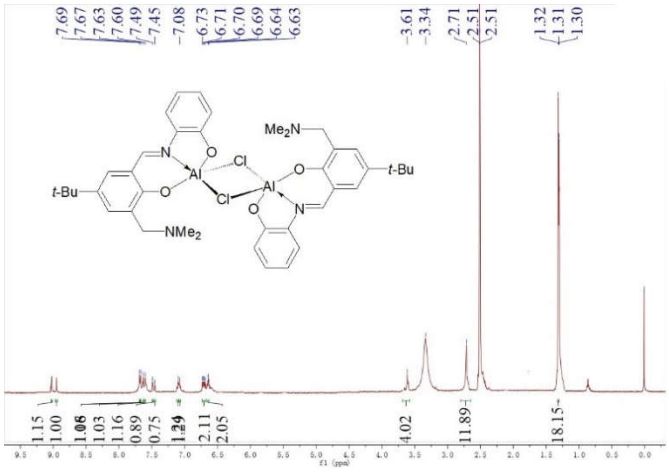


Figure S5. ^{1}H NMR spectrum of the complex **2** in DMSO-d$_6$

Complex 3: ^{1}H NMR (500 MHz, DMSO): δ 9.11 (s, 1H, C**H**=N), 9.01 (s, 1H, C**H**=N), 7.74 (d, 2H, Ar-**H**, *J* = 7.5 Hz), 7.60 (s, 2H, Ar-**H**, *J* = 7.5 Hz), 7.51 (s, sH, Ar-**H**), 7.27 (s, 1H, Ar-**H**), 7.14 (d, 2H, Ar-**H**, *J* = 7.5 Hz), 6.57 (t, 2H, Ar-**H**, *J* = 7.5 Hz), 3.82 (m, 8H, C**H**$_2$-NMe$_2$), 2.29 (s, 12H, NMe$_2$), 2.19 (s, 12H, NMe$_2$), 1.28 (s, 18, *t*-Bu). ^{13}C NMR (126 MHz, DMSO) δ 166.01, 162.92, 156.79, 132.14, 119.67, 119.66, 67.50, 55.09, 42.89, 42.86, 41.93, 41.72, 34.10, 34.02, 31.70, 31.69. ESI MS: $C_{25}H_{39}AlN_3O_4$,

theoretical calculation: 472.2756, found: m/z = 472.4619; $C_{46}H_{62}Al_2ClN_6O_4$: theoretical calculation: 851.4152, found: m/z = 851.4619.

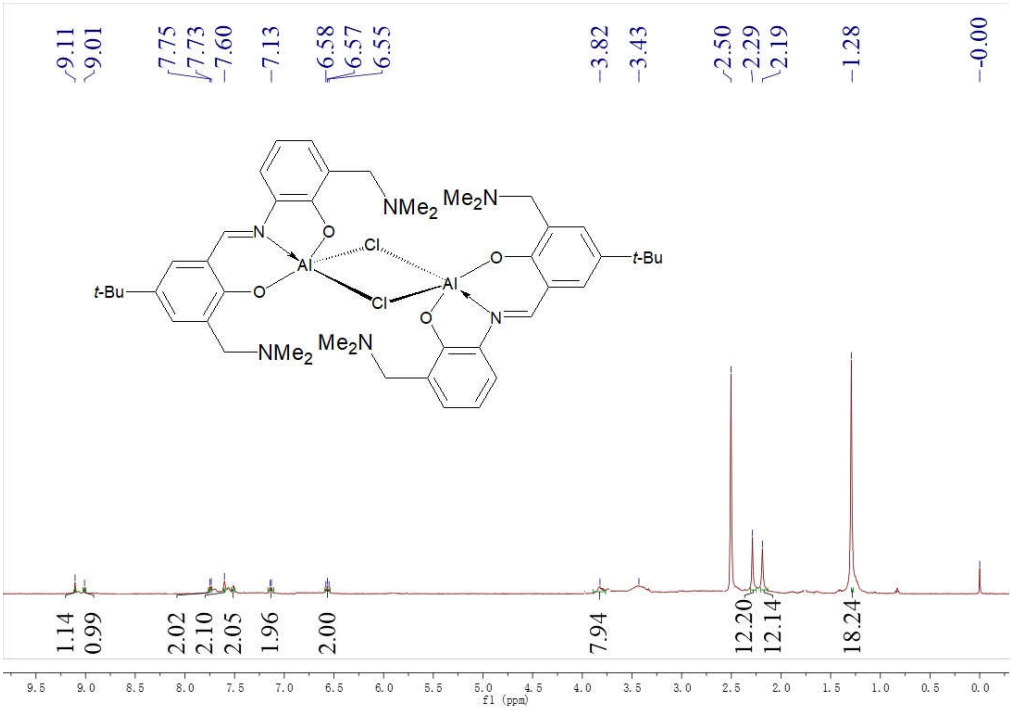
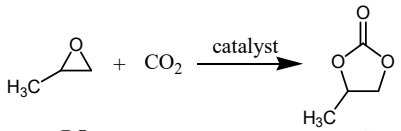


Figure S6. ^{1}H NMR spectrum of the complex **3** in DMSO-d_6

Table S1. Cycloaddition of CO_2 to PO mediated by complex **1** and TBAB [a)]



PO **PC**

entry	[**1**]:[TBAB] (molar ratio)	T (°C)	PO Conv[b)] %	TON[c)]	TOF[d)] (h^{-1})
1	1:2	60	– [e)]	–	–
2	1:4	60	11.3	226	22.6
3	1:10	60	12.0	240	24.0
4	1:20	60	82.7	1654	165.4
5	1:40	60	83.8	1676	167.6
6	1:20	80	85.8	1716	171.6
7	1:40	80	91.2	1824	182.4
8	1:40	100	88.2	1764	176.4

[a)] Conditions: Complex **1** (19.2 mg, 25 μmol), $n_{(1)}/n_{(PO)}$= 1/2000, P_{CO2}: 2 MPa, t = 10 h. [b)] Determined by ^{1}H NMR; [c)] TON = ([PO]/[**1**])×(conversion). [d)] TOF = (TON/reaction time in hours). All selectivity for propylene carbonate > 99%. [e)] not detected.

Table S2. Effect of reaction time on the PO conversion[a)]

entry	t	PO Conv	TON	TOF

	(h)	(%)		(h^{-1})
1	1	10.5	210	210
2	2	23.4	468	234
3	4	39.4	788	197
4	5	42.1	842	168.4
5	6	53.6	1072	178.6
6	8	76.3	1526	190.8
7	10	91.2	1824	182.4

[a)] Conditions: Complex **1** (19.2 mg, 25 μmol), $n_{(1)}/n_{(TBAB)}$ = 1/40, $n_{(1)}/n_{(PO)}$= 1/2000, P_{CO_2}: 2 MPa. Other notes are the same as those in Table S1.

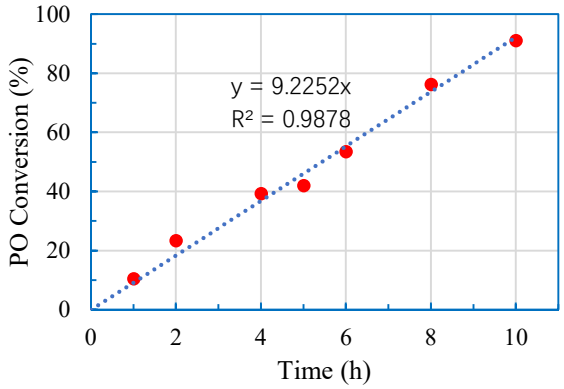


Figure S7. Kinetic study of coupling of PO/CO_2 mediated by **1**/TBAB (1:40 molar ratio), PO conversion *vs* reaction time.

Table S3. Coupling of CO_2/PO catalyzed by **1**/DMAP[a)]

entry	[**1**]:[DMAP] (molar ratio)	T (°C)	PO Conv (%)	TON	TOF (h^{-1})
1	1:2	60	37.2	744	74.4
2	1:4	60	39.7	794	79.4
3	1:10	60	40.7	814	81.4
4	1:20	60	57.2	1144	114.4
5	1:40	60	49.1	982	98.2
6	1:10	80	15.6	312	31.2
7	1:20	80	12.1	242	24.2

[a)] Conditions: Complex **2** (19.2 mg, 25 μmol), $n_{(1)}/n_{(PO)}$ = 1/2000, P_{CO_2}: 2 MPa, t = 10 h. Selectivity for propylene carbonate is higher than 99% in all runs. Other notes are the same as those in Table S1.

Table S4. Coupling of CO_2/PO catalyzed by **1**/1-MeIm.[a)]

entry	[**1**]:[1-MeIm] (molar ratio)	T (°C)	PO Conv (%)	TON	TOF (h^{-1})
1	1:2	60	–	–	–
2	1:4	60	15.2	304	30.4

3	1:10	60	21.3	426	42.6
4	1:20	60	23.5	470	47.0
5	1:2	80	5.3	106	10.6
6	1:4	80	39.1	782	78.2
7	1:10	80	94.6	1892	189.2
8	1:20	80	4.8	96	9.6
9	1:40	80	3.6	72	7.2
10[b)]	1:10	80	22.1	442	88.4
11[c)]	1:10	80	54.8	1096	137

[a)] Conditions: Complex **1** (19.2 mg, 25 μmol), $n_{(1)}/n_{(PO)}$= 1/2000, P_{CO_2}: 2 MPa, t = 10 h unless other condition is stated. All selectivity for propylene carbonate is higher than 99%. b) t = 5 h. c) t = 8 h. Other notes are the same as those in Table S1.

Reference

[1] P. D. Knight, P. N. O'Shaughnessy, I. J. Munslow, B. S. Kimberley, and P. Scott, *J. Organomet. Chem*., **2003**, *683*, 103-113.

[2] M. W. Fennie, E. F. DiMauro, E. M. O'Brien, V. Annamalai, and M. C. Kozlowski, *Tetrahedron*, **2005**, *61*, 6249-6265.

[3] P. Muthumani, Neckmohammed, R. Meera, S. Venkataraman, N. Chidambaranathan, P. Devi, C. A. Suresh Kumar, *Int. J. Pharm. Biomed. Res.*, **2010**, *1*, 78-86.

[4] M. Hong, Y. Kim, H. Kim, H. J. Cho, M.-H. Baik and Y. Kim, *J. Org. Chem.,* **2018**, *83*, 9370-9380.