Supporting Information

A Highly Stable but Highly Reactive Zinc Catalyst for Transesterification Supported by Bis(Imidazole) Ligand

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1. General

All reactions were carried out using heat gun dried glassware under a positive pressure of dry argon unless otherwise noted. The test tubes were fitted with a 3-way glass stopcock and catalytic reactions were run under argon atmosphere. Air- and moisture-sensitive liquids were transferred via a syringe and a stainless-steel needle. Reactions were magnetically stirred and monitored by thin layer chromatography using Merck Silica Gel 60 F254 plates. All work-up and purification procedures were carried out with reagent-grade solvents under ambient atmosphere. Flash chromatography was

performed using silica gel 60N (spherical neutral, particle size 40–50μm) purchased from Kanto Chemical Co. Ltd.

2. Instrumentation

NMR was recorded on 400 MHz Varian Unity instruments and 500 MHz Bruker Advanced III. Chemical shifts for proton are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CDCl_3$: δ 7.26 ppm). For ^{13}C NMR, chemical shifts were reported in the scale relative to NMR solvent ($CDCl_3$: 77.0 ppm) as an internal reference. NMR data are reported as follows: chemical shifts, multiplicity (s: singlet, d: doublet, dd: doublet of doublets, t: triplet, q: quartet, sep: septet, m: multiplet, br: broad signal), coupling constant (Hz), and integration. Infrared (IR) spectra were recorded on with Shimadzu FTIR-8400. High-resolution mass spectroscopy (HRMS) was obtained with Waters ACQUITY UPLC®–LCT-Premier™ XE system and Bruker MicrOTOF II. Optical rotation was measured with JASCO DIP-370 polarimeter. Chiral HPLC analysis was performed with DAICEL CHIRALPAK AD-3 column series.

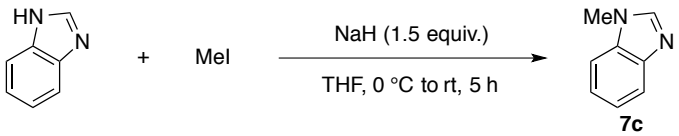
3. Materials

THF and diisopropyl ether were distilled from sodium/benzophenone ketyl prior to use. For the reaction with methyl acrylate derivatives, freshly distilled diisopropyl ether should be used to prevent peroxide formation. Toluene, xylene, chlorobenzene, dimethylcarbonate, ethylacetate, methylbenzoate were distilled from calcium hydride. Benzylalcohol and cyclohexanol were distilled from MS4A. DME, DMF and dichrolomethane were dried over MS4A. All other commercially available reagents were used as received. $Zn(OCOCF_3)_2$ and $Zn_4(OCOCF_3)_6O$ were prepared as the previous report.

4. Ligand Syntheses and Characterization

Synthesis and Characterization of Ligands

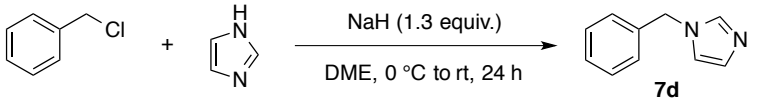
1-Methylbenzimidazole (7c)[2]; CAS Registry Number 1632-83-3



To a solution of benzimidazole (591 mg, 5.00 mmol) in THF (10 mL) was added NaH (60% in mineral oil, 309 mg, 7.7 mmol) in portion-wise at 0 °C over a period of 50 min. Iodomethane (0.342 mL, 5.49 mmol)

was then added to the reaction mixture in one portion at the same temperature. After stirring for 5 hours at room temperature, it was quenched by 1 M HCl solution. The resultant mixture was extracted with CH_2Cl_2 and collected organic extract was washed with saturated $NaHCO_3$ solution and brine. The organic layer was dried over Na_2SO_4 and filtered then purified by flash column chromatography (CH_2Cl_2/MeOH = 50/1 to 20/1) to give the desired product **7c** as a white solid. (92% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.86 (s, 1H, NC*H*N), 7.81 (d, *J* = 6.8 Hz, 1H, *Ar*), 7.39 (d, *J* = 6.8 Hz, 1H, *Ar*), 7.34–2.67 (m, 2H, *Ar*), 3.84 (s, 3H, C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 143.8, 143.5, 134.6, 122.9, 122.1, 120.3, 109.3, 31.0.

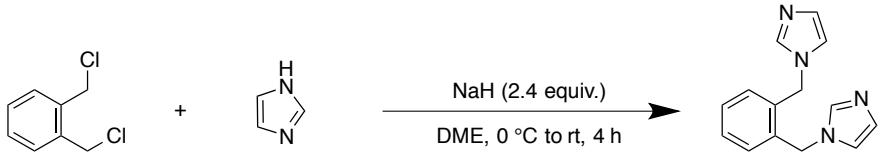
1-Benzylimidazole (7d)[3]; CAS Registry Number 4238-71-5



7d

To a solution of imidazole (409 mg, 6.00 mmol) in DME (10 mL) was added NaH (60% in mineral oil, 309 mg, 7.7 mmol) in portion-wise at 0 °C over a period of 45 min. Benzyl chloride (0.560 mL, 4.87 mmol) was then added to the reaction mixture in one portion at the same temperature. The reaction mixture was then stirred at room temperature for 24 hours. The resultant mixture was diluted with 20% NaOH solution and extracted with EtOAc, and washed with brine. The organic layer was dried over Na_2SO_4 and filtered and purified by flash column chromatography (CH_2Cl_2/MeOH = 30/1) to give the desired product **7d** as a white solid. (79% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.54 (s, 1H, NC*H*N), 7.37–7.32 (m, 3H, *Ar*), 7.15 (d, *J* = 7.6 Hz, 2H, *Ar*), 7.09 (s, 1H, NCHC*H*NCH$_2$), 6.90 (s, 1H, NC*H*CHNCH$_2$), 5.12 (s, 2H, C*H*$_2$); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 137.5, 136.2, 129.9, 129.0, 128.3, 127.3, 119.3, 50.8.

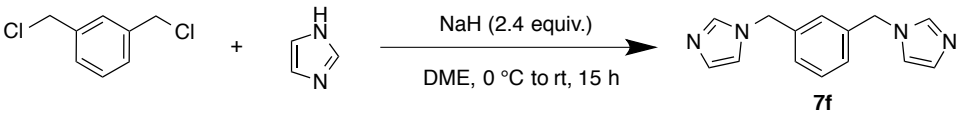
1,2-Bis((1*H*-imidazol-1-yl)methyl)benzene (7e); CAS Registry Number 42032-51-9



7e

This compound was obtained according to the same procedure as that the synthesis of **7d** using dichloro-*o*-xylene. (CH_2Cl_2/MeOH = 20/1, white solid, 78% yield); ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) 7.44 (s, 2H, NC*H*N), 7.38 (dd, *J* = 9.0, 2.5 Hz, 2H, *Ar*), 7.12 (s, 2H, CH$_2$NCHC*H*), 7.09 (dd, *J* = 9.0, 2.0 Hz, 2H, *Ar*), 6.79 (s, 2H, CH$_2$NC*H*CH), 5.03 (s, 4H, NC*H*$_2$); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 137.3, 133.7, 130.1, 129.4, 119.2, 48.1.

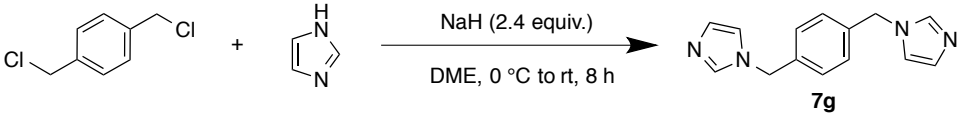
1,3-Bis((1*H*-imidazol-1-yl)methyl)benzene (7f); CAS Registry Number 69506-92-9



7f

This compound was obtained according to the same procedure as that the synthesis of **7d** using dichloro-*m*-xylene. (CH_2Cl_2/MeOH = 20/1, white solid, 98% yield); ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 7.53 (s, 2H, NC*H*N), 7.35 (t, *J* = 2.5 Hz, 1H, *Ar*), 7.10 (s, 2H, *Ar*), 7.09 (s, 2H, CH_2NCHC*H*), 6.92 (s, 1H, *Ar*), 6.88 (s, 2H, CH_2NC*H*CH), 5.10 (s, 4H, NCH_2); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 137.4, 137.2, 130.0, 129.7, 127.1, 125.9, 119.21, 50.4.

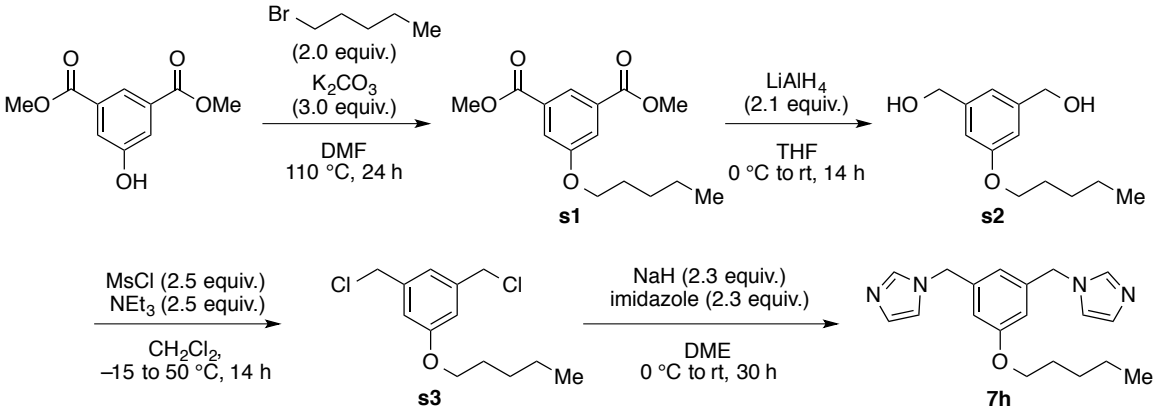
1,4-Bis((1*H*-imidazol-1-yl)methyl)benzene (7g); CAS Registry Number 56643-83-5



7g

This compound was obtained according to the same procedure as that the synthesis of **7d** using dichloro-*p*-xylene. (CH_2Cl_2/MeOH = 20/1, white solid, 51% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.53 (s, 2H, NC*H*N), 7.14 (s, 4H, *Ar*), 7.09 (s, 2H, CH_2NCHC*H*), 6.88 (s, 2H, CH_2NC*H*CH), 5.11 (s, 4H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 137.4, 136.4, 130.0, 127.9, 119.2, 50.3.

1,1'-((5-(Pentyloxy)-1,3-phenylene)bis(methylene))bis(1*H*-imidazole) (7h)



s1 **s2** **s3** **7h**

dimethyl 5-(pentyloxy)isophthalate (s1)[4]; CAS Registry Number 94112-26-2; To a mixture of dimethyl 5-hydroxyisophthalate (4.20 g, 20.0 mmol) and K_2CO_3 (8.30 g, 60.1 mmol) in DMF (40 mL) was added 1-bromo pentane (5.00 mL, 40.4 mmol) then the solution was heated to 110 °C and stirred for 24 hours. After being cooled to room temperature, the solid was filtrated off and the filtrate was concentrated

under reduced pressure. The residue was dissolved in CH_2Cl_2 and washed with 1 M HCl solution and brine successively. The organic layer was dried over Na_2SO_4 and filtered. After removal of volatile, the crude mixture was purified by flash column chromatography (Hexane/EtOAc = 50/1 to 30/1) to give the desired product **s1** as colorless oil. (85% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 8.26 (s, 1H, *Ar*), 7.74 (s, 2H, *Ar*), 4.04 (t, *J* = 6.4 Hz, 2H, OCH_2), 3.94 (s, 6H, OCH_3), 1.81 (tt, *J* = 7.5, 6.5 Hz, 2H, OCH_2CH_2), 1.48-1.1.39 (m, 4H, $OCH_2CH_2CH_2CH_2$), 0.94 (t, *J* = 7.0 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 166.2, 159.3, 131.7, 122.8, 119.9, 68.6, 52.4, 28.8, 28.1, 22.4, 14.1.

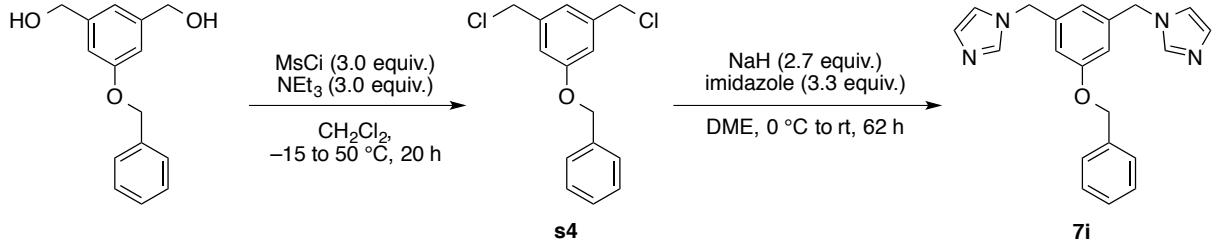
(5-(pentyloxy)-1,3-phenylene)dimethanol (s2)[5]; To a solution of dimethyl 5-(pentyloxy)isophthalate (4.07 g, 14.5 mmol) in THF (20 mL) was added a solution of $LiAlH_4$ (1.17 g, 30.8 mmol) in THF (30 mL) in portion-wise at 0 °C and the solution was warmed to room temperature and stirred for 14 hours. The reaction mixture was quenched with 1M HCl solution. The resultant mixture was extracted with ethyl acetate and collected organic extract was washed with saturated $NaHCO_3$ solution and brine. The organic layer was dried over Na_2SO_4 and filtered then purified by flash column chromatography (CH_2Cl_2/MeOH = 30/1 to 20/1) to give the desired product **s2** as a white solid. (92% yield); IR (KBr) 3287, 3171, 2940, 2870, 1604, 1458, 1034, 702 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 6.92 (s, 1H, *Ar*), 6.84 (s, 2H, *Ar*), 4.66 (d, *J* = 6.0 Hz, 4H, CH_2OH), 3.97 (t, *J* = 6.4 Hz, 2H, OCH_2), 1.78 (tt, *J* = 7.5, 6.5 Hz, 2H,OCH_2CH_2), 1.70 (t, *J* = 6.0 Hz, 2H, O*H*), 1.48-1.34 (m, 4H, $OCH_2CH_2CH_2CH_2$), 0.93 (t, *J* = 6.8 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 159.7 (*C*O), 142.7 (*C*CH_2OH), 117.3 (CH_2CCCCH_2), 112.2 (OC*C*H), 68.1 (O*C*H_2CH_2), 65.2 (*C*H_2OH), 29.0 (OCH_2CH_2), 28.2 ($OCH_2CH_2CH_2$), 22.4 (*C*H_2CH_3), 14.0 (*C*H_3); HRMS (EI) *m/z* calcd. for $C_{13}H_{19}O_3$ 223.1334 found 223.1334.

1,3-bis(chloromethyl)-5-(pentyloxy)benzene (s3); To a solution of (5-(pentyloxy)-1,3-phenylene)dimethanol (3.05 g, 13.6 mmol) and TEA (4.70 mL, 33.7 mmol) in CH_2Cl_2 (24 mL) was added methanesulfornyl chloride (2.60 mL, 33.6 mmol) in a drop-wise at –15 °C. After stirring 40 min at –15 °C, the ice/salt bath was removed and stirring was continued for 14 hours at 50 °C. The reaction mixture was washed with 1 M HCl solution, saturated $NaHCO_3$ solution and brine successively. The organic layer was dried over Na_2SO_4 and filtered then purified by flash column chromatography (Hexane/EtOAc = 30/1) to give the desired product **s3** as a pale yellow oil. (72% yield); IR (KBr) 2940, 2338, 1579, 1458, 1335, 1173, 1057, 718 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 6.97 (s, 1H, *Ar*), 6.88 (s, 2H, *Ar*), 4.54 (s, 4H, CH_2Cl), 3.97 (t, *J* = 6.4 Hz, 2H, OCH_2), 1.79 (tt, *J* = 7.5, 6.4 Hz, 2H, OCH_2CH_2), 1.47–1.36 (m, 4H, $OCH_2CH_2CH_2CH_2$), 0.94 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 159.7 (*C*O), 139.3 (*C*CH_2Cl), 120.6

($CH_2CCHCCH_2$), 114.7 (OC*C*H), 68.2 (O*C*H_2), 45.9 (*C*H_2Cl), 28.9 (OCH$_2$*C*H_2), 28.2 (OCH$_2$CH$_2$*C*H_2), 22.4 (*C*H_2CH$_3$), 14.0 (*C*H_3); HRMS (EI) *m/z* calcd. for $C_{13}H_{19}Cl_2O$ 261.0813 found 261.0812.

1,1'-((5-(Pentyloxy)-1,3-phenylene)bis(methylene))bis(1*H*-imidazole) (7h); This compound was obtained according to the same procedure as that the synthesis of **7d**. (CH_2Cl_2/MeOH = 20/1, white solid, 91% yield); IR (KBr) 3109, 2939, 2870, 1605, 1505, 1451, 1057, 741 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 7.53 (s, 2H, NC*H*N), 7.10 (s, 2H, CH$_2$NCHC*H*), 6.88 (s, 2H, CH$_2$NC*H*CH), 6.58 (s, 2H, *Ar*), 6.50 (s, 1H, *Ar*), 5.04 (s, 4H, NC*H*$_2$), 3.84 (t, *J* = 6.5 Hz, 2H, OC*H*$_2$), 1.73 (tt, *J* = 7.5, 6.5 Hz, 2H, OCH$_2$C*H*$_2$), 1.41–1.35 (m, 4H, C*H*$_2$C*H*$_2$CH$_3$), 0.92 (t, *J* = 7.0 Hz, 3H, C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 160.3 (*C*O), 138.6 (CH$_2$*C*), 137.5 (N*C*N), 130.0 (CH$_2$NCH*C*H), 119.3 (CH$_2$N*C*HCH), 117.8 (CH$_2$*C*CHCCH$_2$), 113.0 (OC*C*H), 68.2 (O*C*H$_2$), 50.5 (N*C*H$_2$), 28.8 (OCH$_2$*C*H$_2$), 28.1 (OCH$_2$CH$_2$*C*H$_2$), 22.4 (*C*H$_2$CH$_3$), 14.0 (*C*H$_3$); HRMS (EI) *m/z* calcd. for $C_{19}H_{25}N_4O$ 325.2028 found 325.2029.

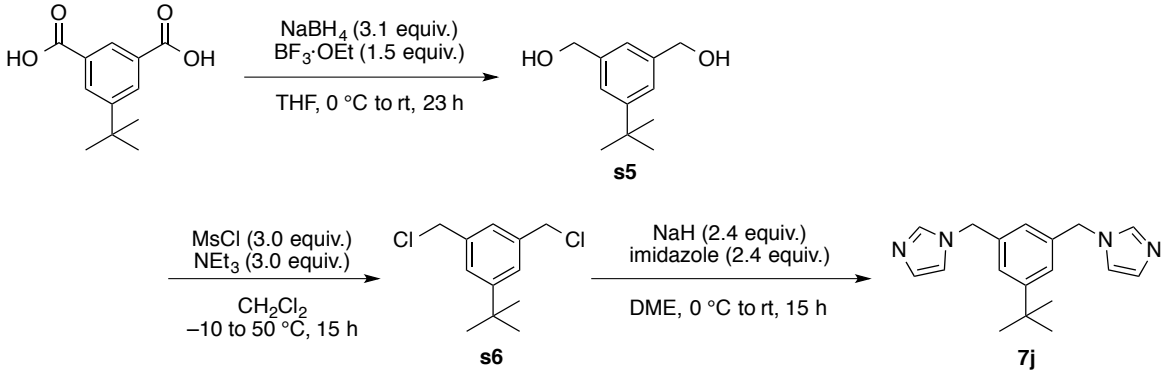
1,1'-((5-(Benzyloxy)-1,3-phenylene)bis(methylene))bis(1*H*-imidazole) (7i)



1-(benzyloxy)-3,5-bis(chloromethyl)benzene (s4); CAS Registry Number 1027755-92-5; This compound was obtained according to the same procedure as that the synthesis of **s3**. (Hexane/EtOAc = 20/1, white solid, 84% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.43–7.37 (m, 5H, *Ar*), 7.01 (s, 1H, *Ar*), 6.97 (s, 2H, *Ar*), 5.08 (s, 2H, OC*H*$_2$), 4.54 (s, 4H, ClC*H*$_2$); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 159.3, 139.4, 136.5, 128.7, 128.2, 127.6, 121.1, 115.0, 70.2, 45.8.

1,1'-((5-(Benzyloxy)-1,3-phenylene)bis(methylene))bis(1*H*-imidazole) (7i); CAS Registry Number 885317-83-9; This compound was obtained according to the same procedure as that the synthesis of **7d**. (CH_2Cl_2/MeOH = 20/1, white solid, 74% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.51 (s, 2H, NC*H*N), 7.35 (m, 5H, *Ar*), 7.10 (s, 2H, CH$_2$NCHC*H*), 6.86 (s, 2H, CH$_2$NC*H*CH), 6.65 (s, 2H, *Ar*), 6.52 (s, 1H, CH$_2$CC*H*CCH$_2$), 5.04 (s, 4H, NC*H*$_2$), 4.96 (s, 2H, OC*H*$_2$); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 159.7, 138.7, 137.4, 136.1, 130.0, 128.7, 128.2, 127.5, 119.2, 118.1, 113.4, 70.1, 50.4.

1,1'-((5-(*tert*-Butyl)-1,3-phenylene)bis(methylene))bis(1*H*-imidazole) (7j)

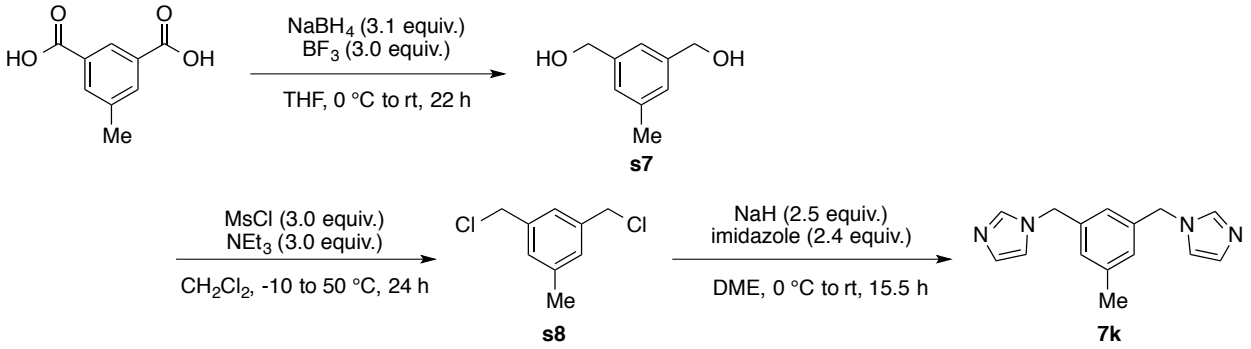


(5-(*tert*-butyl)-1,3-phenylene)dimethanol (s5)[6]; CAS Registry Number 22157-91-1; To a mixture of 5-tert-butylisophthalic acid (6.67 g, 30.0 mmol) and $NaBH_4$ (3.46 g, 91.5 mmol) in THF (100 mL) was added boron trifluoride-ethyl ether complex (11.8 mL, 44.9 mmol) in portion-wise at 0 °C. After stirring for 23 hours at room temperature, it was quenched by H_2O. The resultant mixture was extracted with EtOAc and collected organic extract was washed with 1M HCl solution, saturated $NaHCO_3$ solution and brine. The organic layer was dried over Na_2SO_4 and filtered then purified by flash column chromatography (CH_2Cl_2/MeOH = 30/1 to 20/1) to give the desired product **s5** as a white solid (95% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.33 (s, 2H, *Ar*), 7.20 (s, 1H, *Ar*), 4.70 (s, 4H, CH_2), 1.33 (s, 9H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 152.0, 140.9, 123.4, 122.9, 65.5, 34.8, 31.4.

1-(*tert*-butyl)-3,5-bis(chloromethyl)benzene (s6); CAS Registry Number 116584-83-9; This compound was obtained according to the same procedure as that the synthesis of **s3**. (Hexane/EtOAc = 30/1, white solid, 84% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.35 (s, 2H, *Ar*), 7.25 (s, 1H, *Ar*), 4.58 (s, 4H, CH_2), 1.33 (s, 9H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 152.5, 137.7, 126.0, 125.8, 46.3, 34.8, 31.3.

1,1'-((5-(*tert*-Butyl)-1,3-phenylene)bis(methylene))bis(1*H*-imidazole) (7j); CAS Registry Number 222405-68-7; This compound was obtained according to the same procedure as that the synthesis of **7d**. (CH_2Cl_2/MeOH = 20/1, white solid, 91% yield); ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 7.52 (s, 2H, NC*H*N), 7.10 (d, *J* = 6.4 Hz, 2H, *Ar*), 7.10 (d, *J* = 6.4 Hz, 2H, CH_2NCHC*H*), 6.88 (s, 2H, CH_2NC*H*CH), 6.70 (s, 1H, *Ar*), 5.08 (s, 4H, CH_2), 1.26 (s, 9H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 153.2, 137.4, 136.9, 130.0, 124.2, 123.2, 119.2, 50.7, 34.8, 31.2.

1,1'-((5-methyl-1,3-phenylene)bis(methylene))bis(1*H*-imidazole) (7k)

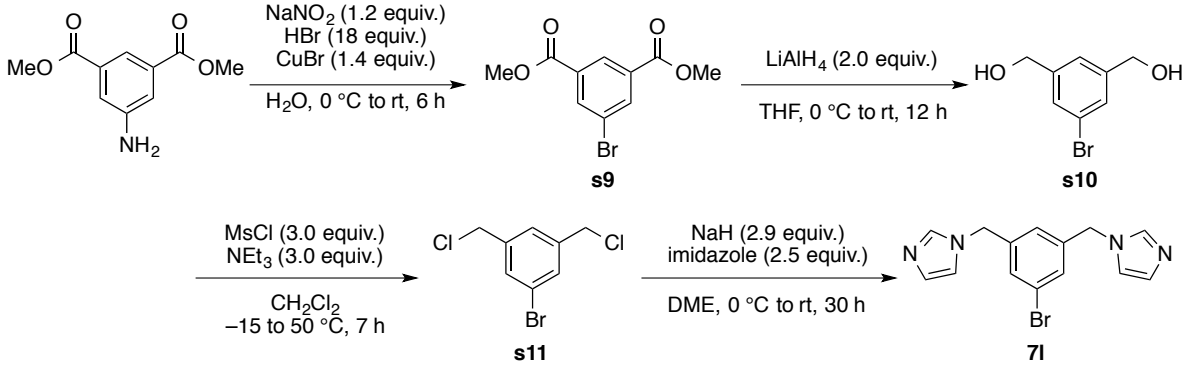


(5-methyl-1,3-phenylene)dimethanol (s7); CAS Registry Number 27711-63-3; This compound was obtained according to the same procedure as that the synthesis of **s5**. (CH_2Cl_2/MeOH = 20/1, pale yellow oil, 57% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.11 (s, 1H, *Ar*), 7.05 (s, 2H, *Ar*), 4.61 (s, 4H, C*H*$_2$); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 141.2, 138.7, 127.1, 122.7, 65.3, 21.3.

1,3-bis(chloromethyl)-5-methylbenzene (s8); CAS Registry Number 79539-14-3; This compound was obtained according to the same procedure as that the synthesis of **s3**. (Hexane/EtOAc = 100/1, white solid, 57% yield); ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 7.21 (s, 1H, *Ar*), 7.16 (s, 2H, *Ar*), 4.55 (s, 4H, C*H*$_2$); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 139.2, 138.0, 129.4, 125.8, 45.9, 21.2.

1,1'-((5-methyl-1,3-phenylene)bis(methylene))bis(1*H*-imidazole) (7k); CAS Registry Number 314288-91-0; This compound was obtained according to the same procedure as that the synthesis of **7d**. (CH_2Cl_2/MeOH = 30/1 to 10/1, white solid, 78% yield); ^{1}H NMR (400 MHz, d_6-DMSO, 30 °C) δ 7.69 (s, 2H, NC*H*N), 7.12 (s, 2H, *Ar*), 6.98 (s, 2H, CH_2NCHC*H*), 6.96 (s, 2H, CH_2NC*H*CH), 6.88 (s, 1H, *Ar*), 5.11 (s, 4H, C*H*$_2$); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 139.8, 137.4, 137.1, 129.9, 127.8, 123.2, 119.3, 50.5, 21.3.

1,1'-((5-Bromo-1,3-phenylene)bis(methylene))bis(1*H*-imidazole) (7l)



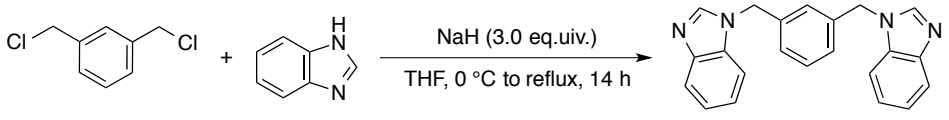
dimethyl 5-bromoisophthalate (s9)[7]; CAS Registry Number 51760-21-5; To a solution of dimethyl 5-amino-1,3-benzenedicarboxylate (2.10 g, 10.0 mmol) in 15% hydrobromic acid (40 mL) was added a solution of sodium nitrite (0.830 g, 12.0 mmol) in H_2O (4.8 mL) in portion-wise at 0 °C. The solution of diazonium bromide was added to a solution of CuBr (2.01 g, 14.0 mmol) in 15% hydrobromic acid (20 mL) under stirring and the temperature was kept under 0 °C. After the addition was completed, it is kept on stirring under room temperature for 6 hours. The reaction mixture was quenched with H_2O. The resultant mixture was extracted with EtOAc and collected organic extract was washed with 1M HCl solution, saturated $NaHCO_3$ solution and brine. The organic layer was dried over Na_2SO_4 and filtered then purified by flush column chromatography (Hexane/EtOAc = 10/1 to 4/1) to give the desired product **s9** as a white solid. (83% yield); ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 8.61 (s, 1H, *Ar*), 8.35 (s, 2H, *Ar*), 3.96 (s, 6H, OC*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 165.0, 136.6, 132.3, 129.3, 122.6, 52.7.

(5-bromo-1,3-phenylene)dimethanol (s10); CAS Registry Number 51760-22-6; This compound was obtained according to the same procedure as that the synthesis of **s2**. (CH_2Cl_2/MeOH = 20/1, white solid, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.45 (s, 2H, *Ar*), 7.29 (s, 1H, *Ar*), 4.69 (s, 4H, C*H*$_2$); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 143.3, 129.0, 123.7, 122.8, 64.4.

1-bromo-3,5-bis(chloromethyl)benzene (s11); CAS Registry Number 108835-03-6; This compound was obtained according to the same procedure as that the synthesis of **s3**. (Hexane/EtOAc = 40/1, white solid, 90% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.50 (s, 2H, *Ar*), 7.34 (s, 1H, *Ar*), 4.53 (s, 4H, C*H*$_2$); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 140.0, 131.5, 127.3, 122.8, 44.8.

1,1'-((5-Bromo-1,3-phenylene)bis(methylene))bis(1*H*-imidazole) (7l); CAS Registry Number 691884-18-1; This compound was obtained according to the same procedure as that the synthesis of **7d**. (CH_2Cl_2/MeOH = 20/1, white solid, 84% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.53 (s, 2H, NC*H*N), 7.23 (s, 2H, CH_2NCHC*H*), 7.12 (s, 2H, CH_2NC*H*CH), 6.87 (s, 2H, *Ar*), 6.80 (s, 1H, *Ar*), 5.07 (s, 4H, C*H*$_2$); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 139.4, 137.4, 130.3, 130.0, 124.3, 123.8, 119.2, 49.8.

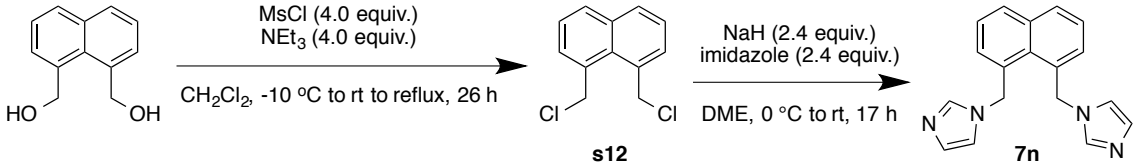
1,3-Bis(benzimidazol-1ylmethyl)benzene (7m) CAS Registry Number 188600-95-5



7m

This compound was obtained according to the same procedure as that the synthesis of **7d**. (CH_2Cl_2/MeOH = 20/1, white solid, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.92 (s, 2H, NC*H*N), 7.83 (d, 2H), 7.3-7.2 (m, 7H), 7.11(d, 2H), 7.01 (s, 1H), 5.31 (s, 4H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 144.0, 143.1, 136.6, 133.8, 129.9, 127.0, 125.6, 123.2, 122.4, 120.6, 109.9, 48.5.

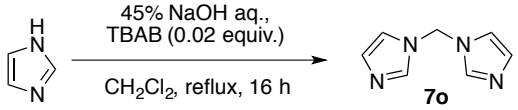
1,8-bis((1*H*-imidazol-1-yl)methyl)naphthalene (7n)



1,8-bis(chloromethyl)naphthalene (s12): CAS Registry Number 50585-29-0; This compound was obtained according to the same procedure as that the synthesis of **s3**. (Hexane/EtOAc = 20/1, white solid, 74% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.92 (d, *J* = 8.4 Hz, 2H, *Ar*), 7.63 (d, *J* = 7.2 Hz, 2H, *Ar*), 7.50 (t, *J* = 7.6 Hz, 2H, *Ar*), 5.33 (s, 4H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 136.1, 132.9, 132.8, 131.9, 129.5, 125.6, 48.4.

1,8-bis((1*H*-imidazol-1-yl)methyl)naphthalene (7n); This compound was obtained according to the same procedure as that the synthesis of **7d**. (CH_2Cl_2/MeOH = 20/1, white solid, 92% yield); IR (KBr) 3102, 2970, 2831, 2724, 2484, 2330, 1512, 1227, 1072, 826, 779 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 8.00 (d, *J* = 8.0 Hz, 2H, *Ar*), 7.51 (t, *J* = 7.6 Hz, 2H, *Ar*), 7.29 (m, 4H, *Ar*), 7.13 (s, 2H, CH_2NCHC*H*), 6.81 (s, 2H, CH_2NC*H*CH), 5.38 (s, 4H, NCH_2); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 136.8 (N*C*N), 136.1 (*Ar*), 131.7 (*Ar*), 131.6 (*Ar*), 130.6 (*Ar*), 130.3 (CH_2NCH*C*H), 129.8 (*Ar*), 125.8 (*Ar*), 118.8 (CH_2N*C*HCH), 51.5 (*C*H_2); HRMS (EI) *m/z* calcd. for $C_{18}H_{17}N_4$ 289.1453 found 289.1453.

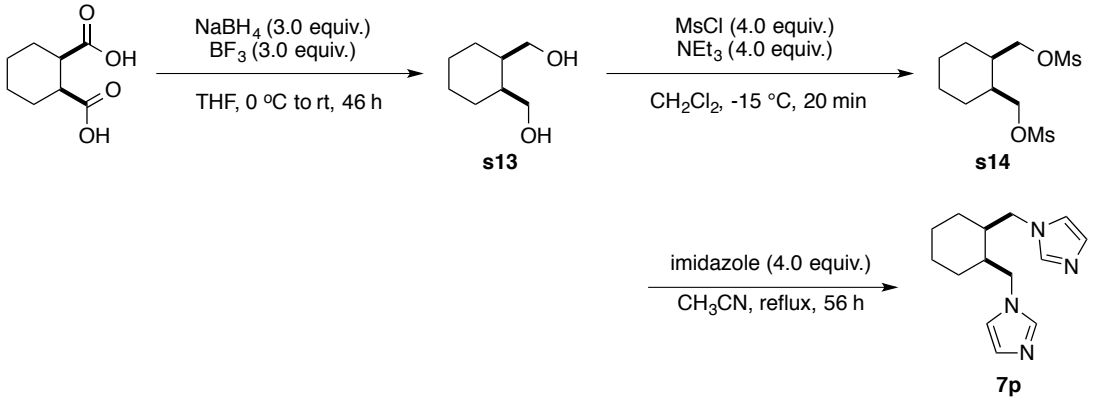
di(1*H*-imidazol-1-yl)methane (7o)[8]; CAS Registry Number 84661-56-3



A mixture of imidazole (1.36 g, 20.0 mmol) and tetrabuthylammoniumbromide (0.129 g, 0.400 mmol) in CH_2Cl_2 (30 mL) and 45% NaOH solution (11mL) was stirred under reflux condition. After 16 hours, volatile was removed under reduced pressure, then the residue was purified by flash column chromatography (CH_2Cl_2/MeOH = 10/1 to 4/1) to give the desired product **7o** as a white solid. (82% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.79 (s, 2H, NC*H*N), 7.09 (s, 2H, CH_2NCHC*H*), 6.97 (s, 2H, CH_2NC*H*CH), 6.20 (s, 2H,

C*H*$_2$); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 136.6, 131.2, 118.1, 56.3.

(1*R*,2*S*)-1,2-bis((1*H*-imidazol-1-yl)methyl)cyclohexane (7p)



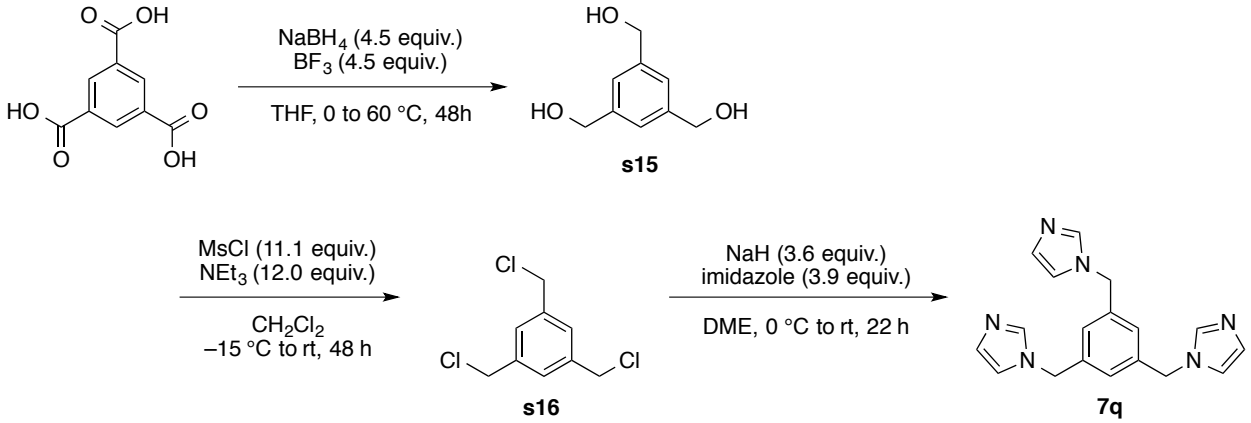
(1*R*,2*S*)-cyclohexane-1,2-diyldimethanol (s13): CAS Registry Number 3971-29-7; This compound was obtained according to the same procedure as that the synthesis of **s5**. (Hexane/EtOAc = 1/2, white solid, 84% yield); ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 3.80-3.58 (m, 4H, C*H*$_2$OH), 2.46 (s, 2H, O*H*), 1.97-1.37 (m, 8H, *Cyclohexane*); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 64.6, 39.9, 27.3, 24.1.

(1*R*,2*S*)-cyclohexane-1,2-diylbis(methylene) dimethanesulfonate (s14): CAS Registry Number 412321-68-7; To a mixture of (1*R*,2*S*)-cyclohexane-1,2-diyldimethanol **s13** (2.31 g, 16.0 mmol) and TEA (9.00 mL, 64.6 mmol) in CH_2Cl_2 (25 mL) was added methanesulfornyl chloride (4.95 mL, 64.0 mmol) in a drop-wise at –15 °C. After stirring for 20 min at –15 °C, it was quenched by 1M HCl solution. The biphasic mixture was extracted with CH_2Cl_2 and collected organic extract was washed with saturated $NaHCO_3$ solution and brine. The organic layer was dried over Na_2SO_4 and filtered then purified by flush column chromatography (Hexane/EtOAc = 2/1) to give the desired product **s14** as a white solid. (76% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 29 °C) δ 4.29-4.17 (m, 4H, C*H*$_2$OMs), 3.04 (s, 6H, C*H*$_3$), 2.2 (m, 2H, C*H*CH_2OMs), 1.57–1.45 (m, 8H, *cyclohexyl*); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 69.8, 37.4, 36.6, 25.9, 23.0.

(1*R*,2*S*)-1,2-bis((1*H*-imidazol-1-yl)methyl)cyclohexane (7p) : CAS Registry Number 1629801-82-6; A mixture of imidazole (2.72 g, 40.0 mmol) and (1*R*,2*S*)-cyclohexane-1,2-diylbis(methylene) dimethanesulfonate **s14** (3.00 g, 10.0 mmol) in CH_3CN (30 mL) was refluxed. After 56 hours, reaction mixture was cooled to room temperature and diluted with EtOAc and washed with 20% NaOH solution and brine successively. The organic layer was dried over Na_2SO_4 and filtered then purified by flush column chromatography (silica gel, CH_2Cl_2/MeOH = 20/1) to give the desired product **7p** as a white solid.

(21% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 29 °C) δ 7.45 (s, 2H, NC*H*N), 7.09 (s, 2H, CH_2NCHC*H*), 6.86 (s, 2H, CH_2NC*H*CH), 3.95 (d, *J* = 7.6 Hz, 4H, NCH_2), 2.11 (m, 2H, CH2CH_2CH), 1.65 (m, 2H, CH2CH_2CH), 1.47–1.33 (m, 6H, CH_2CH$_2$C*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 137.3, 129.9, 118.8, 46.9, 39.1, 26.0, 22.8.

1,3,5-Tris(imidazol-1-ylmethyl)benzene (7q)

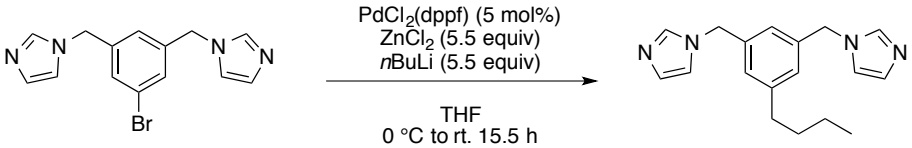


benzene-1,3,5-triyltrimethanol (s15); CAS Registry Number 4464-18-0; This compound was obtained according to the same procedure as that the synthesis of **s5**. (CH_2Cl_2/MeOH = 10/1 to 5/1, white solid, 60% yield); ^{1}H NMR (400 MHz, d_6-DMSO, 29 °C) δ 7.11 (s, 3H, *Ar*), 4.55 (s, 6H, CH_2); ^{13}C NMR (125 MHz, d_6-DMSO, 27 °C) δ 142.1, 122.9, 63.0.

1,3,5-tris(chloromethyl)benzene (s16); CAS Registry Number 17299-97-7; This compound was obtained according to the same procedure as that the synthesis of **s3**. (Hexane/EtOAc = 15/1, white solid, 41% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 29 °C) δ 7.38 (s, 3H, *Ar*), 4.58 (s, 6H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 138.7, 128.6, 45.4.

1,3,5-Tris(imidazol-1-ylmethyl)benzene (7q); CAS Registry Number 147951-02-8; This compound was obtained according to the same procedure as that the synthesis of **7d**. (CH_2Cl_2/MeOH = 5/1, white solid, 92% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 29 °C) δ 7.60 (s, 3H, NC*H*N), 7.12 (s, 3H, CH_2NCHC*H*), 6.85 (m, 6H, *Ar,* CH_2NC*H*CH) 5.08 (s, 6H, NCH_2); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 138.5, 137.3, 130.3, 125.6, 119.2, 50.1.

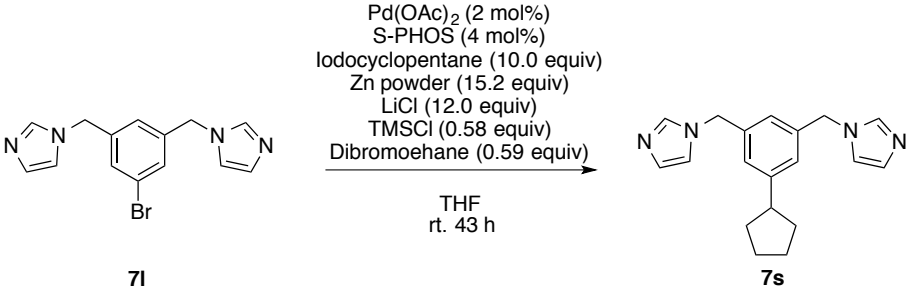
1,1'-((5-butyl-1,3-phenylene)bis(methylene))bis(1*H*-imidazole) (7r)



7l **7r**

Under an inert atmosphere of argon, ^{n}BuLi in hexane (3.5 mL, 5.5 mmol) and pre-dried $ZnCl_2$ (0.751 g, 5.51 mmol) were mixed at 0 ˚C and stirred over 15 min at room temperature. To a solution of 1,1'-((5-Bromo-1,3-phenylene)bis(methylene))bis(1*H*-imidazole) **7l** (0.318 g, 1.00 mmol) and $PdCl_2$(dppf) (42.4 mg, 0.0519 mmol) in THF (3 ml) was added pre-mixed zinc-lithium solution in one portion at the room temperature. The reaction mixture was then stirred at the same temperature for 15.5 hours. The reaction mixture was quenched by 1.0 M HCl aq and precipitation was removed by Celite filtration. The resultant biphasic filtrate was separated and organic layer was extracted with 1.0 M HCl aq. The collected aqueous layer was basified with 10% NaOH aq, and the aqueous layer was back-extracted with EtOAc. The organic layer was dried over Na_2SO_4 and filtered then purified by flash column chromatography (CH_2Cl/MeOH = 20/1) to give the desired product **7r** as a slightly brown solid. (41% yield); IR (KBr) 3109, 2949, 2926, 1605,1506, 1431, 1287, 1219, 1076, 1034, 9-7, 750, 664 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ7.52 (s, 2H, *Ar*), 7.10 (s, 2H, *Ar*), 6.90-6.88 (m, 4H, *Ar*), 6.73 (s, 1H, *Ar*), 5.06 (s, 4H, Ar*C*H_2N), 2.54 (t, 2H, J = 7.0, Ar*C*H_2CH$_2$), 1.55-1.40 (m, 2H, ArCH$_2$CH_2), 1.35-1.26 (m, 2H, ArCH$_2$CH$_2$CH_2), 0.90 (t, 3H, J = 7.5, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ144.9 (*C*CH$_2$CH$_2$), 137.4 (*C*CH$_2$N), 137.1 (N*C*N), 130.0 (CH$_2$NCH*C*H), 127.2 (NCH$_2$C*C*HCCH$_2$CH$_2$), 123.3 (NCH$_2$C*C*HCCH$_2$N), 119.2 (N*C*HCH), 50.5 (N*C*H$_2$), 35.4 (Ar*C*H$_2$CH$_2$), 33.5 (ArCH$_2$*C*H$_2$), 22.3 (*C*H$_2$CH$_3$), 13.9 (*C*H$_3$); HRMS (EI) *m/z* calcd. for $C_{18}H_{23}N_4$ 295.1923 found 295.1925.

1,1'-((5-cyclopentyl-1,3-phenylene)bis(methylene))bis(1*H*-imidazole) (7s)

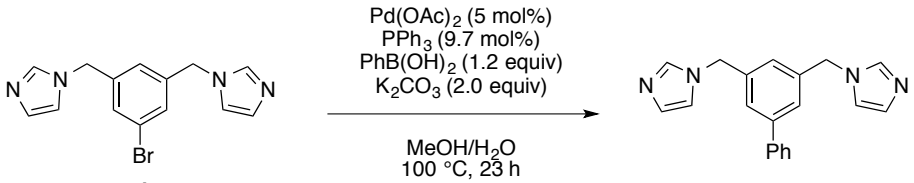


7l **7s**

Lithium chloride (0.508 g, 12.0 mmol) and zinc powder (0.992 g, 15.2 mmol) were dried by heating at 250 ˚C under 2 torr for 2 h. Under an inert atmosphere of argon, To a mixture of pre-dried lithium chloride and zinc powder was added THF (6 mL), TMSCl (50.0 µL, (0.580 mmol), 1,2-dibromoethane (50.0 µL, 0.586 mmol) and cyclopentyl iodide (1.15 mL, 9.97 mmol) at room temperature then the solution

was stirred at 50 ˚C for 23 h. To a solution of aryl bromide **7l** (0.317 g, 1.00 mmol), $Pd(OAc)_2$ (4.5 mg, 0.020 mmol) and S-PHOS (16.4 mg, 0.0399 mmol) in THF (3 mL) was added pre-mixed zinc-lithium solution slowly at the room temperature. The reaction mixture was then stirred at the same temperature for 43 hours. The reaction mixture was quenched by 1.0 M HCl aq and precipitation was removed by celite filtration. The resultant biphasic filtrate was separated and organic layer was extracted with 1.0 M HCl aq. The collected aqueous layer was basified with 10% NaOH aq, and precipitation was removed by celite filtration then the aqueous layer was back-extracted with EtOAc. The organic layer was dried over Na_2SO_4 and filtered then purified by flash column chromatography (CH_2Cl/MeOH = 20/1) to give the desired product **7s** as a slightly brown solid. (39% yield); IR (KBr) 3077, 2949, 1603, 1506, 1441, 1393, 1236, 1111, 1071, 1028, 910, 826, 733, 669 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, 27 °C) δ7.53 (s, 2H, *Ar*), 7.10 (s, 2H, *Ar*), 6.95 (s, 2H, *Ar*), 6.88 (s, 2H, *Ar*) , 6.72 (s, 1H, *Ar*), 5.06 (s, 4H, Ar*C*H_2N), 2.92 (m, 1H, Ar*C*H), 2.05-1.99 (m, 2H, cyclopentyl), 1.80-1.76 (m, 2H, cyclopentyl), 1.69-1.64 (m, 2H, cyclopentyl), 1.50-1.44 (m, 2H, cyclopentyl) ; ^{13}C-NMR (125 MHz, $CDCl_3$, 27 °C) δ148.7 (*C*CH), 137.4 (*C*CH_2), 137.1 (N*C*HN), 130.0 (CH_2NCH*C*H), 125.9 (C*C*HC), 123.4 (CH_2*C*CHCCH_2), 119.3(CH_2N*C*HCH), 50.6 (N*C*H_2), 45.7 (C*C*H), 34.6 (CCH*C*H_2), 25.4 (CCHCH_2*C*H_2); HRMS (EI) *m/z* calcd. for $C_{19}H_{23}N_4$ 307.1923 found 307.1923.

3,5-bis((1*H*-imidazol-1-yl)methyl)-1,1'-biphenyl (7t)

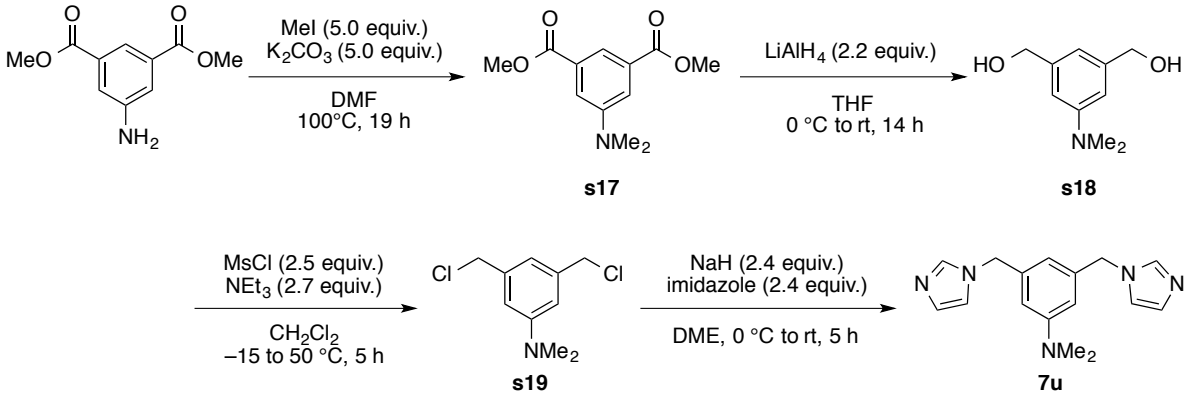


7l **7t**

Under inert atmosphere of argon, a solution of aryl bromide **7l** (0.316 g, 1.00 mmol), phenylboronic acid (0.146 g, 1.20 mmol), $Pd(OAc)_2$ (11.2 mg, 0.0499 mmol), triphenylphosphine (25.4 mg, 0.0968 mmol) and potassium carbonate (0.272 g, 1.97 mmol) in mixed solvent (MeOH/H_2O = 10/1, 2.2 ml) was refluxed for 23 h. The resultant mixture was filtrated and extracted with EtOAc. The organic layer was dried over Na_2SO_4 and filtered and purified by flash column chromatography (CH_2Cl_2/MeOH = 10/1) to give the desired product **7t** as a white solid. (76% yield); IR (KBr) 3125, 3096, 3042, 1674, 1601, 1578, 1508, 1462, 1389, 1356, 1286, 1236, 1186, 1109, 1076, 1030, 909, 860, 833, 770, 745, 696, 665 cm^{-1}; ^1H-NMR (500 MHz, $CDCl_3$, 27 °C) δ7.57 (s, 2H, *Ar*), 7.47-7.41 (m, 4H, *Ar*), 7.38-7.35 (m, 1H, *Ar*), 7.29 (s, 2H, *Ar*), 7.12 (s, 2H, *Ar*), 6.92 (s, 2H, *Ar*), 6.89 (s, 1H, *Ar*), 5.16 (s, 4H, CH_2); ^{13}C-NMR (125 MHz, $CDCl_3$, 27 °C) δ143.1 (*C*Ph), 139.6 (*Ph*), 137.9 (CH_2*C*), 137.5 (N*C*N), 130.2 (*C*H_2NCH*C*H), 129.0 (*Ph*), 128.1 (*Ph*), 127.1 (*Ph*), 125.8 (PhC*C*H), 124.6 (*Ph*), 119.3 (*C*H_2N*C*HCH), 50.5 (*C*H_2); HRMS (EI) *m/z* calcd. for $C_{20}H_{18}N_4$ 315.1610 found

315.1610.

3,5-bis((1*H*-imidazol-1-yl)methyl)-*N*,*N*-dimethylaniline (7u)



dimethyl 5-(dimethylamino)isophthalate (s17); CAS Registry Number 2718-64-1; To a solution of dimethyl 5-aminoisophthalate (1.68 g, 8.03 mmol) and potassium carbonate (5.53 g, 40.0 mmol) in DMF (16 mL) was added methyl iodide (2.50 mL, 40.2 mmol) at room temperature. The solution was stirred at 100 ˚C for 19 h. The resultant mixture was filtrated and purified by flash column chromatography (Hexane/EtOAc = 5/1) to give the desired product **s17** as a white solid. (85% yield); ^{1}H-NMR (500 MHz, $CDCl_3$, 27 °C) δ8.00 (s, 1H, *Ar*), 7.55 (s, 2H, *Ar*), 3.93 (s, 6H, COOCH_3), 3.04 (s, 6H, NCH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 167.1, 150.4, 131.1, 118.3, 117.0, 52.2, 40.5.

(5-(dimethylamino)-1,3-phenylene)dimethanol (s18); CAS Registry Number 56296-23-2; This compound was obtained according to the same procedure as that the synthesis of **s2**. (EtOAc/Hexane = 2/1, white solid, 74% yield); ^{1}H-NMR (500 MHz, $CDCl_3$, 27 °C) δ6.68 (s, 1H, *Ar*), 6.65 (s, 2H, *Ar*), 4.60 (s, 4H, CH_2), 2.95 (s, 6H, NCH_3), 2.13 (br, 2H, O*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 151.2, 142.2, 113.7, 110.4, 65.8, 40.7.

3,5-bis(chloromethyl)-*N*,*N*-dimethylaniline (s19); This compound was obtained according to the same procedure as that the synthesis of **s3**. (Hexane/EtOAc = 20/1, white solid, 20% yield); IR (KBr) 3379, 2816, 1610, 1498, 1368, 1258, 706, 669 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$, 27 °C) δ6.75 (s, 1H, *Ar*), 6.67 (s, 2H, *Ar*), 4.54 (s, 4H, CH_2), 2.98 (s, 6H, NCH_3); ^{13}C-NMR (125 MHz, $CDCl_3$, 27 °C) δ151.0 (N*C*CH), 138.8 (*C*CH_2Cl), 116.6 (*Ar*), 112.4 (*Ar*), 46.6 (*C*H_2Cl), 40.5 (N*C*H_3); HRMS (EI) *m/z* calcd. for $C_{10}H_{13}Cl_2NNa$ 240.0323 found 240.0321.

3,5-bis((1*H*-imidazol-1-yl)methyl)-*N*,*N*-dimethylaniline (7u); This compound was obtained according to

the same procedure as that the synthesis of **7d**. (CH_2Cl_2/MeOH = 10/1, white solid, 97% yield); IR (KBr) 3100, 1501, 1229, 1103, 1034, 976, 909, cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$, 27 °C) δ7.53 (s, 2H, *Ar*), 7.08 (s, 2H, *Ar*), 6.89 (s, 2H, *Ar*), 6.36 (s, 2H, *Ar*), 6.27 (s, 1H, *Ar*), 5.02 (s, 4H, C*H*$_2$), 2.89 (s, 6H, NC*H*$_3$); ^{13}C-NMR (125 MHz, $CDCl_3$, 27 °C) δ151.3 (N*C*), 138.0 (*C*CH$_2$N), 137.5 (N*C*N), 129.8 (CH_2NCH*C*H), 119.3 (CH_2N*C*HCH), 113.7 (*Ar*), 110.4 (*Ar*), 51.0 (*C*H$_2$N), 40.3 (N*C*H$_3$); HRMS (ESI) *m/z* calcd. for $C_{16}H_{20}N_5$ 282.1719 found 282.1716.

5. General Procedure and Characterization of the Products

General Procedure for the Synthesis of Zinc Complex (Scheme 1 and 2.)

An oven–dried schlenk flask equipped with a magnetic stirring bar and reflux condenser was charged with zinc salt (1.0 eq.) and ligand **7** (1.0 or 2.0 eq.). To the flask was added THF (0.25 M) via syringe. The reaction mixture was then refluxed at 90 °C (oil bath temperature) under an argon atmosphere for 1 hour. After being cooled to room temperature, the resulting precipitates of zinc complex **8** was filtrated and washed with *n*-hexane, then dried under reduced pressure to give white solid.

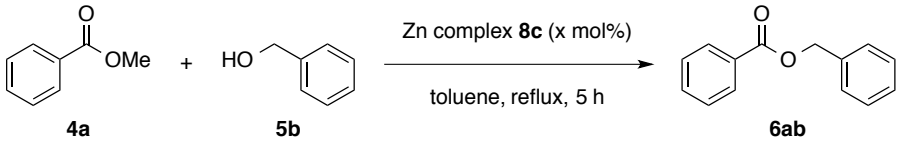
General Procedure for the Transesterification (Table 1.)

An oven–dried schlenk flask equipped with a magnetic stirring bar and reflux condenser was charged with zinc salt **1** (2.5 mol% zinc) and ligand (5.0 mol%). To the flask was added PhCl (1.7 mL) via syringe. To the catalyst solution was added ester **4a** (1.0 mmol) and alcohol **5a** (1.2 mmol) at room temperature. The reaction mixture was then refluxed at 150 ˚C (oil bath temperature) for 5 hours under an argon atmosphere. After being cooled to room temperature, the resulting crude reaction mixture was submitted to GC analysis to determine the chemical yield with nonadecane as an internal standard.

General Procedure for the Transesterification (Table 2. Entries 1-5)

An oven–dried schlenk flask equipped with a magnetic stirring bar and reflux condenser was charged with zinc complex **8c** (5.0 mol% zinc). To the flask was added PhCl (2.0 mL) via syringe. To the catalyst solution was added ester **4** (1.0 mmol) and alcohol **5** (1.2 mmol) at room temperature. The reaction mixture was then refluxed at 150 ˚C (oil bath temperature) under air atmosphere. After consumption of starting material was confirmed by TLC analysis, the resulting crude reaction mixture was purified by flash column chromatography to obtain desired product.

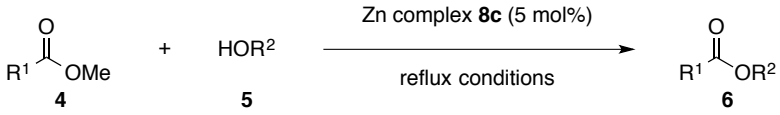
The catalyst loading could be reduced to 1 mol% with the same efficiency as 5 mol% (standard conditions). When 0.1 mol% catalyst was used, high yield of **6ab** was observed with prolonged reaction time (18 h).



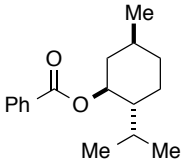
4a **5b** **6ab**

x (mol%)	yield (%)
5	97
1	91
0.5	78
0.1	23
0.1 (18 h)	87

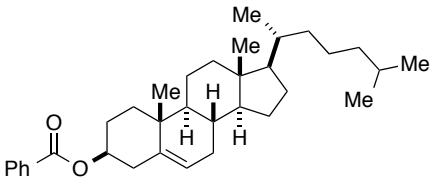
When toluene (refluxed at 130 °C oil bath temperature) was used as solvent instead of chlorobenzene (refluxed at 150 ˚C oil bath temperature), zinc complex **8c** provided product **6ac** in >99% yield after 74 h (in chlorobenzene; 10 h, 94% yield). In general, complex **8c** showed low solubility in toluene. However in the presence of alcohol, such as benzyl alcohol and cyclohexanol, complex **8c** and zinc alkoxide species were soluble under toluene-reflux conditions and reaction proceeded with a decreased reaction rate.



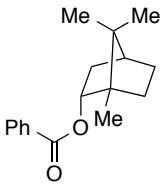
4 **5** **6**



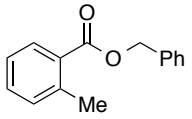
6ac
toluene, > 99% yield, 74 h
PhCl, 94% yield, 10 h



6ad
toluene, 98% yield, 48 h
PhCl, 99% yield, 8 h



6ae
toluene, 85% yield, 96 h
PhCl, 97% yield, 8 h



6bb
toluene, > 99% yield, 46 h
PhCl, 90% yield, 9 h

General Procedure for the Transesterification (Table 2. Entries 6-12)

An oven–dried schlenk flask equipped with a magnetic stirring bar and reflux condenser was charged with zinc salt **1** (5.0 mol% zinc) and ligand **7h** (10 mol%). To the flask was added solvent (2.0 mL) via syringe. To the catalyst solution was added ester **4** (1.0 mmol) and alcohol **5** (1.2 mmol) at room temperature. The reaction mixture was then refluxed under an argon atmosphere. (Oil bath temperatures of each solvent are listed as following: xylene = 160 ˚C, HCOOEt = 70 ˚C, toluene = 130 ˚C and $^{i}Pr_2O$ = 80 ˚C). After consumption of starting material was confirmed by TLC analysis, the resulting crude reaction mixture was purified by flash column chromatography to obtain desired product.

General Procedure for the Transesterification using Dimethylcarbonate (Table 3. Entries 1-7)

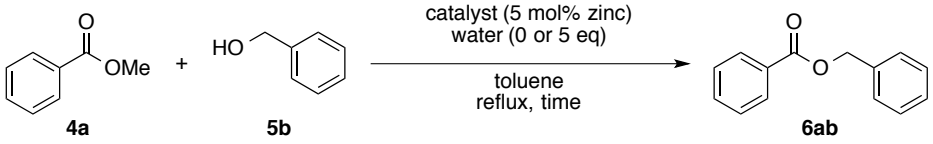
An oven–dried schlenk flask equipped with a magnetic stirring bar and reflux condenser was charged with zinc complex **8c** (5.0 mol% zinc). To the flask was added dimethylcarbonate **9a** (2.0 mL) via syringe. To the catalyst solution was added alcohol **5** or diol **11** (1.0 mmol) at room temperature. The reaction mixture was then refluxed at 110 ˚C (oil bath temperature) under air atmosphere. After consumption of starting material was confirmed by TLC analysis, the resulting crude reaction mixture was purified by flash column chromatography to obtain desired product.

General Procedure for the Synthesis of Oxazolidinone (Table 3. Entries 8 and 9)

An oven–dried schlenk flask equipped with a magnetic stirring bar and reflux condenser was charged with zinc complex **8c** (5.0 mol% zinc). To the flask was added toluene (2.0 mL) via syringe. To the catalyst solution was added β-amino alcohol **13** (1.0 mmol) and diethylcarbonate **9b** (1.1 mmol) at room temperature. The reaction mixture was then refluxed at 120 ˚C (oil bath temperature) under an argon atmosphere. After consumption of starting material was confirmed by TLC analysis, the resulting crude reaction mixture was purified by flash column chromatography to obtain desired product.

Detailed Procedure of Transesterification in the Presence of Water (Scheme 3.)

An oven–dried schlenk flask equipped with a magnetic stirring bar and reflux condenser was charged with the zinc cluster **1** or complex **8c** (5.0 mol% zinc). To the flask was added toluene (0.5 M) and water (0 or 5.0 mmol) via syringe. To the catalyst solution was added ester **4a** (1.0 mmol) and alcohol **5b** (1.2 mmol) at room temperature. The reaction mixture was then refluxed at 130 ˚C (oil bath temperature) under an argon atmosphere. The conversion was calculated by NMR analysis 5 times (30 min, 1 hour, 2.5 hours, 5 hours and 21 hours).



4a **5b** **6ab**

$Zn_4(OCOCF_3)_6O$ (**1**)

time [h]	0.50	1.0	2.5	5.0	21
conversion [%]	10	23	48	71	98

$Zn_4(OCOCF_3)_6O$ (**1**) + water (5 eq)

time [h]	0.50	1.0	2.5	5.0	21
conversion [%]	6	13	24	31	43

Zn complex **8c**

time [h]	0.50	1.0	2.5	5.0	21
conversion [%]	15	37	90	100	100

Zn complex **8c** + water (5 eq)

time [h]	0.50	1.0	2.5	5.0	21
conversion [%]	10	28	60	80	100

Detailed Procedure of Reuse and Recovery Experiment (Scheme 4.)

An oven–dried schlenk flask equipped with a magnetic stirring bar and reflux condenser was charged with complex **8c** (5.0 mol% zinc). To the flask was added toluene (0.5 M) via syringe. To the catalyst solution was added ester **4a** (1.0 eq.) and alcohol **5b** (1.2 eq.) at room temperature. The reaction mixture was then refluxed at 130 ˚C (oil bath temperature) for 5 hours under an air atmosphere. After being cooled to room temperature, the resulting crude reaction mixture was distilled under reduced pressure. The residue was washed with *n*-hexane. The combined reaction solvent was submitted to GC analysis to determine the chemical yield with nonadecane as an internal standard. To the residue precipitate was added a solution of ester **4a** (1.0 eq.) and alcohol **5b** (1.2 eq.) in toluene (0.50 M) at room temperature, which was refluxed at 130 ˚C (oil bath temperature) for 5 hours. This operation was repeated.

Detailed Procedure of Reuse and Recovery Experiment using Simple Deposition and Decantation Techniques.

An oven–dried schlenk flask equipped with a magnetic stirring bar and reflux condenser was charged with complex **8c** (5.0 mol% zinc). To the flask was added toluene (0.50 M) via syringe. To the catalyst solution was added ester **4a** (1.0 eq.) and alcohol **5b** (1.2 eq.) at room temperature. The reaction mixture was then refluxed at 130 ˚C (oil bath temperature) for 5 hours under an air atmosphere. After being cooled to room temperature. To the crude mixture was added *n*-hexane and white precipitates (zinc

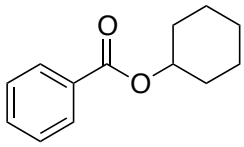
catalyst) was formed. The suspended reaction mixture was filtered and washed with *n*-hexane to give zinc catalyst as white solid. The yield of **6ab** was determined by GC analysis of filtrate.

General Procedure for the Transesterification (Table S1.)

All reactions were carried out according to the same procedure as the general procedure for the transesterification (Table 1) using (-)-menthol (**5c**) as a model substrate instead of alcohol **5b**. For GC analysis, pentadecane was used as an internal standard to determine the chemical yield.

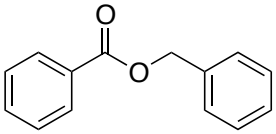
Characterization of Esters

cyclohexyl benzoate (6aa); CAS Registry Number 2412-73-9



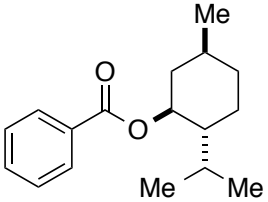
Purified by flash column chromatography (Hexane/EtOAc = 80/1, colorless oil); ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 8.05 (dd, *J* = 8.0, 1.5 Hz, 2H, *Ar*), 7.54 (tt, *J* = 8.0, 1.5 Hz, 1H, *Ar*), 7.43 (dt, *J* = 8.0, 1.5 Hz, 2H, *Ar*), 5.03 (m, 1H, OC*H*), 1.97–1.93 (m, 2H, OCHCH_2), 1.83–1.76 (m, 2H, OCHCH_2CH_2), 1.63–1.27 (m, 6H, *cyclohexyl*); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 166.0, 132.7, 131.0, 129.5, 128.3, 73.0, 31.6, 25.5, 23.7.

benzyl benzoate (6ab); CAS Registry Number 120-51-4



Purified by flash column chromatography (Hexane/EtOAc = 80/1, colorless oil); ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 8.08 (m, 2H, *Ar*), 7.56 (m, 1H, *Ar*), 7.46-7.32 (m, 7H, *Ar*), 5.37 (s, 2H, OCH_2); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 166.4, 136.1, 133.0, 130.2, 129.7, 128.6, 128.4, 128.3, 128.2, 66.7.

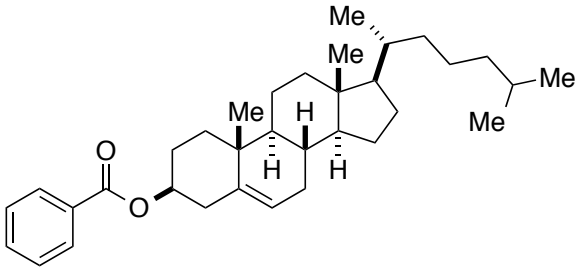
(1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl benzoate (6ac); CAS Registry Number 58641-29-5



Purified by flash column chromatography (Hexane/EtOAc = 100/1, colorless oil); ^{1}H NMR (500 MHz,

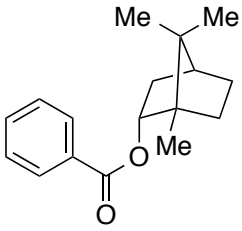
$CDCl_3$, 27 °C) δ 8.04 (d, *J* = 8.0 Hz, 2H, *Ar*), 7.55 (dd, *J* = 7.5 Hz, 1H, *Ar*), 7.44 (dd, *J* = 7.5 Hz, 2H, *Ar*), 4.94 (dt, *J* = 10.75, 10.5 Hz, 1H, OC*H*), 2.13 (m, 1H), 1,97 (m, 1H), 1,74 (m, 2H), 1.56 (m, 2H), 1.13 (m, 2H), 0.92 (m, 7H), 0.80 (d, *J* = 7.0 Hz, 3H, CHCH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 166.1, 132.7, 130.9, 129.6, 128.3, 74.8, 47.3, 41.0, 34.3, 31.5, 26.5, 23.6, 22.1, 20.8, 16.5.

(3*S*,10*R*,17*R*)-10-methyl-17-(6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl benzoate (6ad); CAS Registry Number 604-32-0



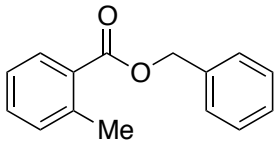
Purified by flash column chromatography (Hexane/EtOAc = 40/1, white solid); ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 7.97 (d, *J* = 7.0 Hz, 2H, *Ar*), 7.47 (t, *J* = 7.0 Hz, 1H, *Ar*), 7.36 (t, *J* = 7.5 Hz, 2H, *Ar*), 5.42 (d, *J* = 4.5 Hz, 1H, CC*H*), 4.86 (m, 1H, OC*H*), 2.46 (d, *J* = 8.0 Hz, 2H, OCHCH_2C), 2.04–0.97 (m, 29H, *cholesterol*), 0.92 (m, 3H), 0.87 (m, 6H, CH(CH_3)$_2$), 0.69 (s, 3H, CCH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 166.0, 139.7, 132.7, 130.9, 129.5, 128.3, 122.8, 74.6, 56.7, 56.2, 50.1, 42.3, 39.8, 39.5, 38.2, 37.0, 36.7, 36.2, 35.8, 32.0, 31.9, 28.2, 28.0, 27.9, 24.3, 23.8, 22.8, 22.6, 21.1, 19.4, 18.7, 11.9.

(1*R*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl benzoate (6ae); CAS Registry Number 26927-90-2



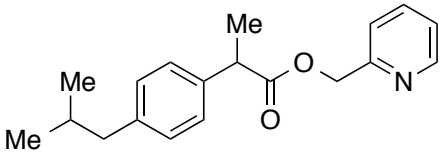
Purified by flash column chromatography (Hexane/EtOAc = 80/1, colorless oil); ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 8.06 (d, *J* = 7.0 Hz, 2H, *Ar*), 7.56 (dd, *J* = 7.25 Hz, 1H, *Ar*), 7.45 (dd, *J* = 7.75 Hz, 2H, *Ar*), 5.12 (dt, *J* = 10.0, 3.0 Hz, 1H, OC*H*), 2.50–2.45 (m, 1H, OCHCH_2), 2.16–2.11 (m, 1H, OCHCH_2), 1.84–1.78 (m, 1H, CHCH_2CH$_2$), 1.74 (t, *J* = 4.5 Hz, 1H, CHCH$_2$CH_2), 1.44–1.41 (m, 1H, C*H*(CH$_3$)$_2$), 1.38 (m, 1H, CHCH_2CH$_2$), 1.13 (dd, *J* = 3.5, 13.5 Hz, 1H, CHCH$_2$CH_2), 0.97 (s, 3H, CCH_3), 0.92 (s, 6H, C(CH_3)$_2$); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 166.8, 132.7, 130.9, 129.5, 128.3, 80.5, 49.1, 47.9, 45.0, 36.9, 28.1, 27.4, 19.7, 18.9, 13.6.

benzyl 2-methylbenzoate (6bb); CAS Registry Number 67157-60-2



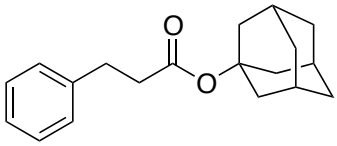
Purified by flash column chromatography (Hexane/EtOAc = 50/1, colorless oil); ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 7.95 (d, *J* = 8.0 Hz, 1H, *Ar*), 7.46-7.22 (m, 8H, *Ar*), 5.34 (s, 2H, CH_2), 2.61 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 167.4, 140.4, 136.2, 132.1, 131.7, 130.7, 129.5, 128.6, 128.2, 125.7, 66.5, 21.8.

pyridin-2-ylmethyl 2-(4-isobutylphenyl)propanoate (6cf); CAS Registry Number 64622-45-3



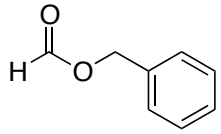
Purified by flash column chromatography (Hexane/EtOAc = 5/1, colorless oil); ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 8.53 (d, *J* = 4.0 Hz, 1H, *Ar*), 7.56 (dt, *J* = 7.5, 1.5 Hz, 1H, *Ar*), 7.24 (d, *J* = 8.0 Hz, 2H, *Ar*), 7.16 (dt, *J* = 7.5, 2.0 Hz, 1H, *Ar*), 7.10 (d, *J* = 8.0 Hz, 2H, *Ar*), 7.04 (d, *J* = 8.0 Hz, 1H, *Ar*), 5.22 (q, *J* = 11.0 Hz, 2H, COOCH_2), 3.82 (q, *J* = 7.0 Hz, 1H, CH_3C*H*), 2.46 (d, *J* = 7.0 Hz, 2H, $(CH_3)_2$CHCH_2), 1.85 (qq, *J* = 6.5 Hz, 1H, $(CH_3)_2$C*H*), 1.54 (d, *J* = 7.0 Hz, 3H, CH_3CH), 0.87 (d, *J* = 6.5 Hz, 6H, $(CH_3)_2$CH); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 174.3, 156.1, 149.3, 140.7, 137.5, 136.6, 129.4, 127.3, 122.6, 121.1, 66.8, 45.1, 45.0, 30.2, 22.4, 18.3.

(3*s*,5*s*,7*s*)-adamantan-1-yl 3-phenylpropanoate (6dg); CAS Registry Number 1629801-90-6



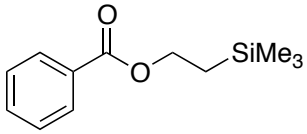
Purified by flash column chromatography (Hexane/EtOAc = 40/1, white solid); ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 7.29–7.19 (m, 5H, *Ar*), 2.90 (t, *J* = 8.0 Hz, 2H, PhCH_2), 2.54 (t, *J* = 8.0 Hz, 2H, CH_2CO), 2.14 (s, 3H, C*H*), 2.07 (d, *J* = 2.5 Hz, 6H, CCH_2), 1.65 (t, 6H, CHCH_2); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 172.0, 140.9, 128.3, 126.1, 80.4, 41.3, 37.2, 36.2, 31.1, 30.8.

benzyl formate (6eb); CAS Registry Number 104-57-4



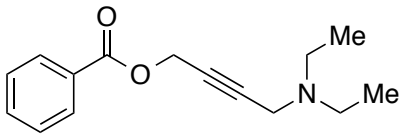
Purified by flash column chromatography (Hexane/EtOAc = 50/1, colorless oil); ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 8.14 (s, 1H, OCO*H*), 7.40-7.33 (m, 5H, *Ar*), 5.21 (s, 2H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 160.8, 135.2, 128.7, 128.5, 128.4, 65.7.

2-(trimethylsilyl)ethyl benzoate (6ah); CAS Registry Number 98760-24-8



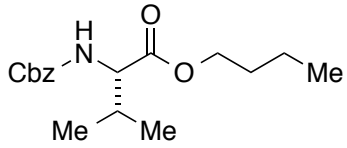
Purified by flash column chromatography (Hexane/EtOAc = 80/1, colorless oil); ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 8.04 (d, *J* = 7.5 Hz, 2H, *Ar*), 7.55 (dd, *J* = 7.25 Hz, 1H, *Ar*), 7.43 (dd, *J* = 7.75 Hz, 2H, *Ar*), 4.44 (t, *J* = 8.5 Hz, 2H, OCH_2), 1.14 (t, *J* = 8.25 Hz, 2H, SiCH_2), 0.09 (s, 9H, Si(CH_3)$_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 166.8, 132.7, 130.7, 129.5, 128.3, 63.2, 17.4, -1.44.

4-(diethylamino)but-2-yn-1-yl benzoate (6ai); CAS Registry Number 6749-55-9



Purified by flash column chromatography (Hexane/EtOAc = 5/1, colorless oil); ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 8.08 (dd, *J* = 8.0, 1.5 Hz, 2H, *Ar*), 7.57 (tt, *J* = 7.5, 1.5 Hz, 1H, *Ar*), 7.45 (t, *J* = 8.0 Hz, 2H, *Ar*), 4.95 (s, 2H, COOCH_2), 3.47 (s, 2H, NCH_2), 2.55 (q, *J* = 7.5 Hz, 4H, NCH_2CH$_3$), 1.07 (t, *J* = 7.5 Hz, 6H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 165.9, 133.2, 129.8, 129.7, 128.4, 82.1, 78.6, 53.0, 47.2, 41.0, 12.6.

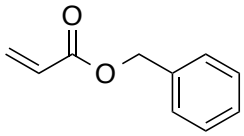
(S)-butyl 2-(((benzyloxy)carbonyl)amino)-3-methylbutanoate (6fj); CAS Registry Number 174872-56-1



Purified by flash column chromatography (Hexane/EtOAc = 10/1, colorless oil); ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 7.37–7.30 (m, 5H, *Ar*), 5.26 (d, *J*=8.5 Hz, 1H, N*H*), 5.11 (s, 2H, BzOCH_2), 4.29 (q, *J* = 4.5 Hz, 1H,

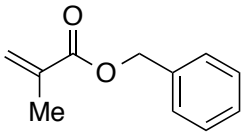
C*H*), 4.16–4.10 (m, 2H, COOCH_2), 2.19–2.13 (m, 1H, $(CH_3)_2$C*H*) 1.65–1.60 (m, 2H, $COOCH_2CH_2$), 1.42–1.35 (m, 2H, CH_3CH_2), 0.98–0.89 (m, 9H, (CH_3)CH, CH_3CH_2); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 172.1, 156.2, 136.3, 128.5, 128.2, 128.1, 67.0, 65.1, 59.0, 31.4, 30.6, 19.1, 19.0, 17.5, 13.6.; HPLC (Chiralcel AD–3, hexane and ^{i}PrOH (90 : 10), detector: 254 nm, flow rate: 1.0 mL / min, t_R = 9.9 min (major), 11.7 min (minor).

benzyl acrylate (6gb); CAS Registry Number 2495-35-4



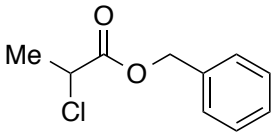
Purified by flash column chromatography (Hexane/EtOAc = 30/1, colorless oil); ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 7.38-7.33 (m, 5H, Ar-*H*), 6.44 (dd, *J* = 1.5, 17.5, 1H, CCH_2), 6.16 (dd, *J* = 10.0, 17.5, 1H, CC*H*), 5.84 (dd, *J* = 1.5, 10.0, 1H, CCH_2), 5.20 (s, 2H, PhCH_2); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 166.0, 135.9, 131.1, 128.6, 128.3, 128.3, 128.2, 66.3.

benzyl methacrylate (6hb); CAS Registry Number 2495-37-6



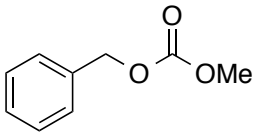
Purified by flash column chromatography (Hexane/EtOAc = 50/1, colorless oil); ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 7.39–7.31 (m, 5H, *Ar*), 6.16 (s, 1H, CCH_2), 5.58 (t, *J* = 1.5 Hz, 1H, CCH_2), 5.20 (s, 2H, CH_2), 1.97 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 167.3, 136.3, 136.1, 128.5, 128.1, 128.0, 125.8, 66.4, 18.4.

benzyl 2-chloropropanoate (6ib); CAS Registry Number 81577-34-6



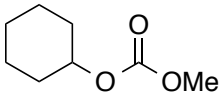
Purified by flash column chromatography (Hexane/EtOAc = 50/1, colorless oil); ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.39-7.31 (m, 5H, *Ar*), 5.21 (s, 2H, CH_2), 4.44 (q, *J* = 7.0 Hz, 1H, C*H*), 1.70 (d, *J* = 7.0 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 169.9, 135.1, 128.7, 128.5, 128.2, 67.6, 52.5, 21.5.

benzyl methyl carbonate (10ab); CAS Registry Number 13326-10-8



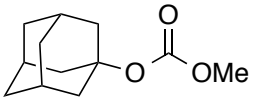
Purified by flash column chromatography (Hexane/EtOAc = 20/1, colorless oil); ^{1}H-NMR (500 MHz, $CDCl_3$, 27 °C) δ 7.40-7.33 (m, 5H, *Ar*), 5.17 (s, 2H, C*H*$_2$), 3.80 (s, 3H, C*H*$_3$); ^{13}C-NMR (125 MHz, $CDCl_3$, 27 °C) δ 155.7, 135.3, 128.6, 128.5, 128.3, 69.7, 54.9.

cyclohexyl methyl carbonate (10aa); CAS Registry Number 25066-36-8



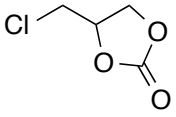
Purified by flash column chromatography (Hexane/EtOAc = 20/1, colorless oil); ^{1}H-NMR (500 MHz, $CDCl_3$, 27 °C) δ 4.64-4.59 (m, 1H, OC*H*), 3.77 (s, 3H, OC*H*$_3$), 1.93-1.90 (m, 2H, cyclohexyl), 1.77-1.73 (m, 2H, cyclohexyl), 1.93-1.32 (m, 6H, cyclohexyl); ^{13}C-NMR (125 MHz, $CDCl_3$, 27 °C) δ 155.3, 60.4, 54.4, 31.5, 25.2, 23.6.

(3*s*,5*s*,7*s*)-adamantan-1-yl methyl carbonate (10ag); CAS Registry Number 37994-86-8



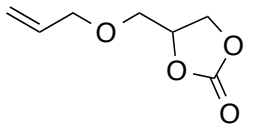
Purified by flash column chromatography (Hexane/EtOAc = 30/1, white solid); ^{1}H-NMR (500 MHz, $CDCl_3$, 27 °C) δ 3.70 (s, 3H, OC*H*$_3$), 2.19 (s, 3H, OCCH$_2$C*H*), 2.11 (s, 6H, OCC*H*$_2$), 1.66 (s, 6H, OCCH$_2$CHC*H*$_2$); ^{13}C-NMR (125 MHz, $CDCl_3$, 27 °C) δ 153.5, 81.8, 53.8, 41.0, 36.0, 30.9.

4-(chloromethyl)-1,3-dioxolan-2-one (12a); CAS Registry Number 2463-45-8



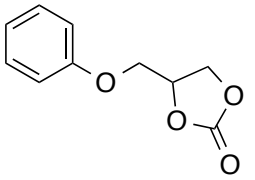
Purified by flash column chromatography (Hexane/EtOAc = 20/1, colorless oil); ^{1}H-NMR (500 MHz, $CDCl_3$, 27 °C) δ 4.98-4.94 (m, 1H, ClCH$_2$C*H*), 4.59 (m, 1H, CHC*H*$_2$OCO), 4.42 (m, 1H, OC*H*$_2$), 3.83-3.72 (m, 2H, ClC*H*$_2$); ^{13}C-NMR (125 MHz, $CDCl_3$, 27 °C) δ 154.0, 74.2, 67.0, 43.5.

4-(allyloxymethyl)-1,3-dioxolan-2-one (12b); CAS Registry Number 826-29-9



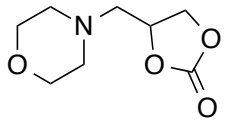
Purified by flash column chromatography (Hexane/EtOAc = 20/1, colorless oil); ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 5.88 (m, 1H, C*H*), 5.27 (m, 2H, CHCH_2), 4.82 (m, 1H, OC*H*), 4.50 (t, 1H, J = 8.5, OC*H*), 4.41 (m, 1H, OC*H*), 4.06 (m, 2H, OCH_2), 3.64 (m, 2H, OCH_2); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 154.9, 133.6, 118.0, 75.0, 72.7, 68.9, 66.3.

4-(phenoxymethyl)-1,3-dioxolan-2-one (12c); CAS Registry Number 4437-83-6



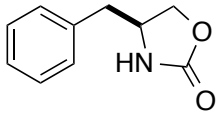
Purified by flash column chromatography (Hexane/EtOAc = 20/1, white solid); ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 7.31 (t, 2H, J = 7.5, Ar-*H*), 7.02 (t, 1H, J = 7.5, Ar-*H*), 6.91 (d, 2H, J = 8.0, Ar-*H*), 5.03 (m, 1H, OC*H*), 4.62 (t, 1H, J = 8.5, OC*H*), 4.55 (t, 1H, J = 8.5, OC*H*), 4.24 (dd, 1H, OC*H*), 4.17 (dd, 1H, OC*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 157.8, 154.7, 129.7, 122.0, 114.6, 74.1, 66.9, 66.2.

4-(morpholinomethyl)-1,3-dioxolan-2-one (12d); CAS Registry Number 103117-98-2



Purified by flash column chromatography (CH_2Cl_2/MeOH = 20/1, pale yellow oil); ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 4.82 (m, 1H, OC*H*), 4.53 (t, 1H, J = 8.0, OC*H*), 4.24 (t, 1H, J = 8.0, OC*H*), 3.70 (t, 4H, J = 4.5, OCH_2), 2.69 (m, 2H), 2.56 (m, 4H, NCH_2); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 154.8, 75.0, 67.8, 66.8, 60.4, 54.5.

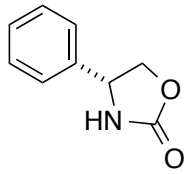
(S)-4-benzyloxazolidinone (14a); CAS Registry Number 90719-32-7



Purified by flash column chromatography (Hexane/EtOAc = 2/1, white solid); ^{1}H NMR (500 MHz, $CDCl_3$,

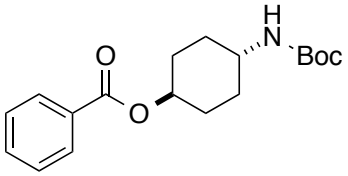
27 °C) δ 7.35-7.17 (m, 5H, Ar-*H*), 5.66 (br, 1H, N*H*), 4.44 (t, 1H), 4.16-4.08 (m, 2H), 2.87 (d, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 159.3, 136.0, 129.0, 129.0, 127.3, 69.6, 53.8, 41.5.; HPLC (Chiralcel OD–3, hexane and ^{i}PrOH (75 : 25), detector: 254 nm, flow rate: 1.0 mL / min, t_S = 12.1 min (major), 13.6 min (minor).

(R)-4-phenyloxazolidinone (14b); CAS Registry Number 90319-52-1



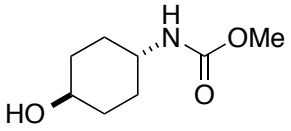
Purified by flash column chromatography (Hexane/EtOAc = 2/1, white solid); ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 7.36 (m, 5H, Ar-*H*), 5.26 (br, 1H, N*H*), 4.96 (t, 1H, J = 8.0, OC*H*), 4.75 (t, 1H, J = 8.0, OC*H*), 4.20 (dd, 1H, NC*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 159.2, 139.3, 129.3, 129.0, 126.1, 72.5, 56.4.; HPLC (Chiralcel OD–3, hexane and ^{i}PrOH (75 : 25), detector: 254 nm, flow rate: 1.0 mL / min, t_R = 12.6 min (major), 14.0 min (minor).

(1*r*,4*r*)-4-((*tert*-butoxycarbonyl)amino)cyclohexyl benzoate (15); CAS Registry Number 1012798-24-1



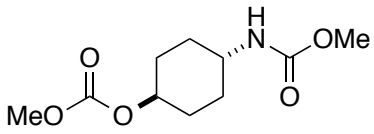
After transesterification reaction according to general procedure with reflux for 4 hours, the solvent was removed under reduced pressure. Triethylamine (0.180 mL, 1.29 mmol) and $(Boc)_2O$ (0.300 mL, 1.31 mmol) were added to crude mixture in CH_2Cl_2 (2.0 mL) at room temperature and reaction mixture was stirred for 30 min. The volatile was removed under reduced pressure and the residue was purified by flash column chromatography (Hexane/AcOEt = 3/1) to give the desired product **15** as a white solid. (93% yield); ^{1}H-NMR (500 MHz, $CDCl_3$, 27 °C) δ 8.02 (d, 2H, *Phenyl*), 7.54 (m, 1H, *Phenyl*), 7.43 (t, 2H, *Phenyl*), 4.94 (m, 1H, OC*H*), 4.48 (br, 1H, CON*H*), 3.53 (br, 1H, NC*H*), 2.11 (m, 4H, *cycloalkyl*), 1.65 (m, 2H, *cycloalkyl*), 1.45 (s, 9H, CH_3), 1.29 (m, 2H, *cycloalkyl*); ^{13}C-NMR (125 MHz, $CDCl_3$, 27 °C) δ 166.0, 155.3, 132.9, 130.6, 129.6, 128.3, 79.3, 48.5, 31.8, 30.0, 28.4, 27.8.

methyl ((1*r*,4*r*)-4-hydroxycyclohexyl)carbamate (s20); CAS Registry Number 1334100-78-5



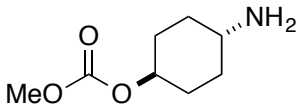
To a solution of trans-4-amino-cyclohexanol (0.116 g, 1.01 mmol) and triethylamine (0.165 mL, 1.19 mmol) in CH_2Cl_2 (2.0 mL) was added methyl chloroformate (100 μL, 1.29 mmol) at the room temperature. The reaction mixture stirred overnight at the same temperature. The precipitation was removed by filtration and resultant was washed by 1 M HCl aq. The organic layer was dried over Na_2SO_4 and filtered then purified by short-pad column chromatography to give a white solid. The solids were crystallized from hexane and AcOEt to yield the product as a white solid. (32% yield); ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 4.47 (br, 1H, N*H*), 3.66-3.49 (m, 4H), 3.48 (br, 1H, NC*H*), 2.04-1.96 (m, 4H), 1.40 (m, 3H), 1.20 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 156.3, 69.8, 52.0, 49.3, 33.9, 31.1.

methyl ((1*r*,4*r*)-4-((methoxycarbonyl)oxy)cyclohexyl)carbamate (s21)



To a solution of methyl ((1*r*,4*r*)-4-hydroxycyclohexyl)carbamate (33.1 mg, 0.191 mmol) and complex **8c** (10.6 mg, 0.0120 mmol) in dimethylcarbonate **9a** (300 μL) was refluxed for 9 hours. The reaction mixture was cooled at the room temperature and purified by short-pad column chromatography to give a white solid. (99% yield); IR (KBr) 3277, 2951, 1744, 1713, 1688, 1557, 1445, 1319, 1267, 1250, 1192, 1051, 1020, 943 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 4.71 (br, 1H, N*H*), 4.55 (m, 1H, OC*H*), 3.77 (s, 3H, OCH_3), 3.65 (s, 3H, NCH_3), 3.51 (br, 1H, NC*H*), 2.05 (m, 4H), 1.54 (m, 2H), 1.27 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 156.3 (*C*ON), 155.2 (*C*OO), 75.7 (O*C*H), 54.6 (O*C*H$_3$), 51.9 (*C*H$_3$OCON), 48.7 (*C*HN), 30.5 (*cyclohexyl*), 29.8 (*cyclohexyl*); HRMS (ESI) *m/z* calcd. for $C_{10}H_{17}NNaO_5$ 254.1004 found 254.0993.

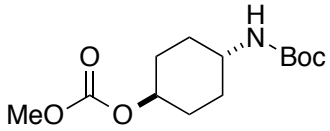
(1*r*,4*r*)-4-aminocyclohexyl methyl carbonate (s22)



Purified by flash column chromatography. (CH_2Cl_2/CH_3OH = 10/1, yellow oil); IR (NaCl) 3360, 2949, 2862, 1732, 1694, 1593, 1445, 1371, 1325, 1267, 1202, 1094, 995, 943, 795, 719 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 4.56 (m, 1H, OC*H*), 3.76 (s, 3H, OCH_3), 2.77 (m, 1H, NC*H*), 2.46 (br, 2H, NH_2), 2.05 (m, 2H),

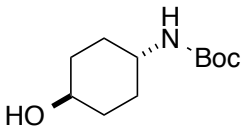
1.92 (m, 2H), 1.49 (m, 2H), 1.25 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 155.2 (O*C*O), 76.4 (O*C*H), 54.5 (O*C*H_3), 49.3 (NH_2*C*H), 33.5 (*cyclohexyl*), 29.9 (*cyclohexyl*); HRMS (ESI) *m/z* calcd. for $C_8H_{16}NO_3$ 174.1130 found 174.1114.

***tert*-butyl ((1*r*,4*r*)-4-((methoxycarbonyl)oxy)cyclohexyl)carbamate (16)**



After transesterification reaction according to general procedure with reflux for 10 hours, the solvent was removed under reduced pressure. Triethylamine (0.180 mL, 1.29 mmol) and $(Boc)_2O$ (0.300 mL, 1.31 mmol) were added to crude mixture in CH_2Cl_2 (2.0 mL) at room temperature and reaction mixture was stirred for 30 min. The volatile was removed under reduced pressure and the residue was purified by flash column chromatography (Hexane/EtOAc =3/1, white solid); IR (KBr) 3395, 2961, 1713, 1518, 1444, 1321, 1283, 1169, 1017, 937 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 4.54 (m, 1H, OC*H*), 4.43 (br, 1H, N*H*), 3.76 (s, 3H, OC*H*$_3$), 3.46 (br, 1H, NC*H*), 2.05 (m, 4H), 1.54 (m, 2H), 1.44 (s, 9H, C*H*$_3$), 1.23 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 155.2 (O*C*O and N*C*O), 79.3 (NCOO*C*), 75.9 (OCOO*C*H), 54.6 (*C*H_3O), 48.4 (*C*HN), 30.6 (*cyclohexyl*), 29.9 (*cyclohexyl*), 28.4 (C*C*H_3); HRMS (ESI) *m/z* calcd. for $C_{13}H_{23}NNaO_5$ 296.1474 found 296.1472.

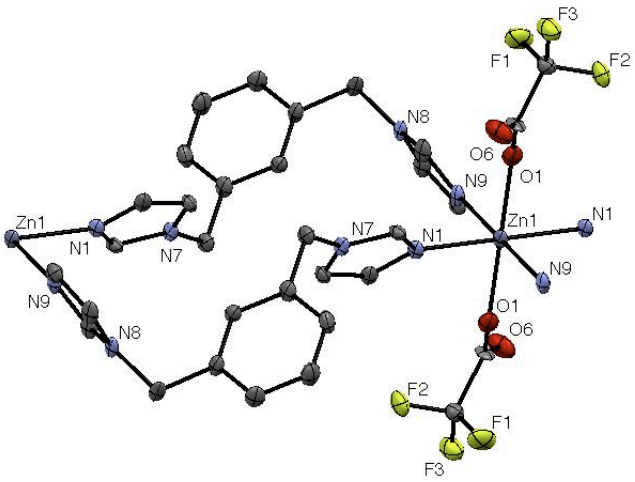
***tert*-butyl ((1*r*,4*r*)-4-hydroxycyclohexyl)carbamate (s23);** CAS Registry Number 111300-06-2



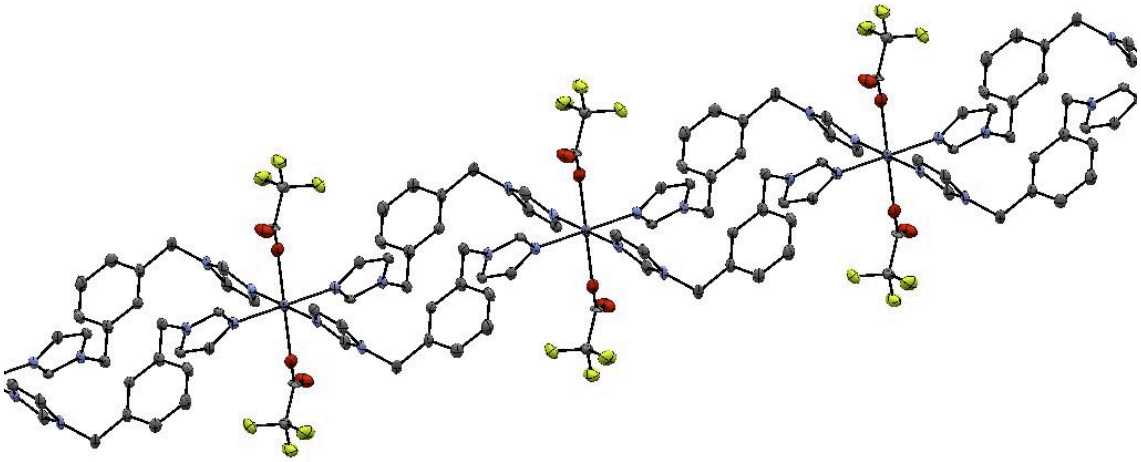
To a solution of trans-4-amino-cyclohexanol (0.344 mg, 2.99 mmol) and triethylamine (500 µL, 3.61 mmol) in CH_2Cl_2 (10 mL) was added $(Boc)_2O$ (830 µL, 3.61 mmol) at room temperature. The reaction mixture was stirred overnight at the same temperature. The precipitation was removed by filtration and resultant was washed by 1 M HCl aq. The organic layer was dried over Na_2SO_4 and filtered then purified by short-pad column chromatography to give a white solid. The solids were crystallized from the mized solvent of hexane and AcOEt to yield the product as a white solid. (73% yield); ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 4.36 (br, 1H, N*H*), 3.60 (m, 1H, OC*H*), 3.43 (br, 1H, NC*H*), 2.02-1.95 (m, 4H), 1.62 (s, 1H, O*H*), 1.44 (s, 9H), 1.34 (m, 2H), 1.16 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 155.2, 79.2, 69.9, 48.8, 34.0, 31.2, 28.4.

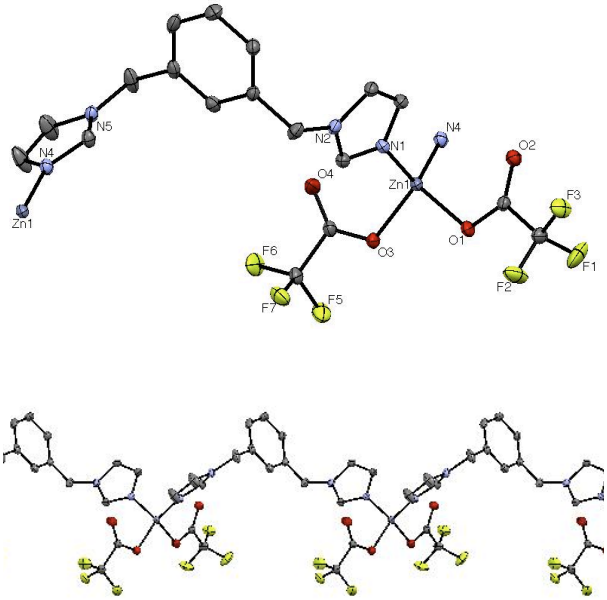
6. X-ray Diffraction Study for Zinc Complex

Suitable crystals were grown by diffusion of diethyl ether into the methanol solution for **8a**, **8b**, **8c**. The crystals were mounted on the CryoLoop with a layer of liquid paraffin and placed in a nitrogen stream at 90 K. All X-ray data were collected on a Bruker AXS APEX II diffractometer with graphite-monochromated MoK radiation (λ = 0.71069 Å). The reflection data were collected using the program $APEX_2$ below 146 K. the molecular structures were solved by direct methods (SIR program). All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included at standard positions (C-H = 0.96 Å, C-C-H = 120 °) and refined isotropically using a rigid model.

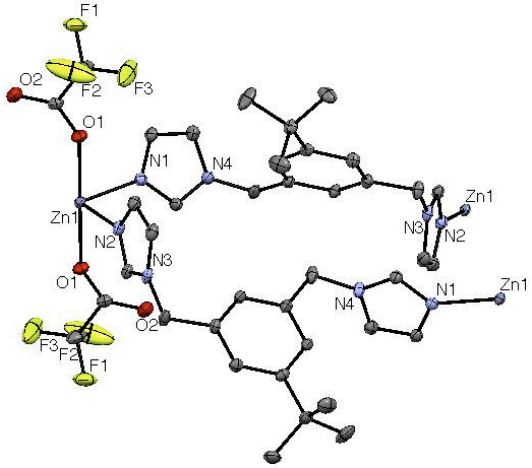


Molecular structure of complex **5a** with thermal ellipsoids at 50% probability. All H-atoms and the solvent molecule (methanol and diethyl ether) were omitted for clarity. Selected bond distances (Å) and angles (degree): Zn1–O1, 2.143(4); Zn1–N1, 2.150(5); Zn1–N9, 2.143(4); O1–Zn1–N1, 87.0(2); O1–Zn1–N9, 92.8(2); O1–Zn1–O1, 180.0(2).

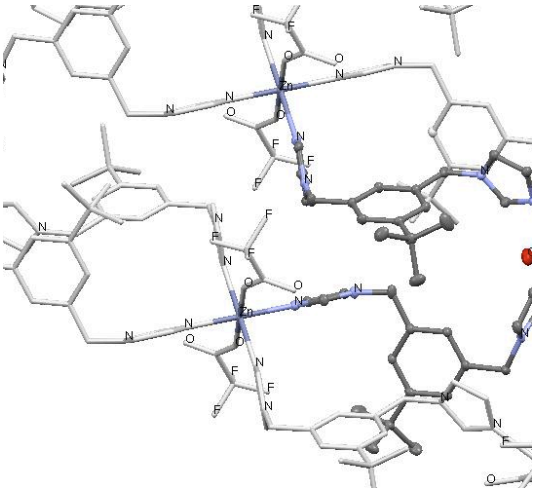




Molecular structure of complex **5b** with thermal ellipsoids at 50% probability. All H-atoms and the solvent molecule (methanol and diethyl ether) were omitted for clarity. Selected bond distances (Å) and angles (degree): Zn1–N1, 1.982(1); Zn1–O1, 1.998(1); N1–Zn1–O1, 105.20(6); N1–Zn1–O3, 110.97(6); N1–Zn1–N4, 113.15(6); O1–Zn1–O3, 95.39(5).



Molecular structure of complex **5c** with thermal ellipsoids at 50% probability. All H-atoms and the solvent molecule (methanol and diethyl ether) were omitted for clarity. Selected bond distances (Å) and angles (degree): Zn1–N1, 2.122(1); Z1–N2, (2.148(1); Zn1–O1, 2.156(1); N1–Zn1–O1, 86.14(5); N2–Zn1–O1, 88.35(5); N1–Zn1–N2, 91.22(5); O1–Zn1–O1, 180.00(5).



Crystal Data and Data Colestion Parameters[a, b]

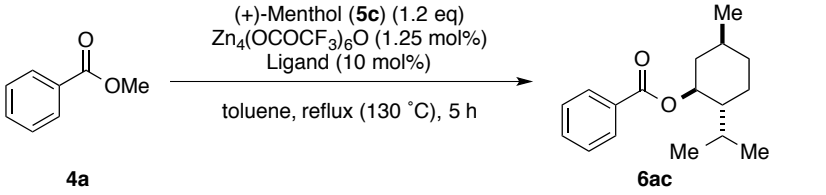
	8a	**8b**	**8c**
empirical formula	$C_{32}H_{28}F_6N_8O_4Zn$	$C_{30}H_{30}F_3N_4O_6Zn$	$C_{40}H_{44}F_6N_8O_4Zn$
formula weight	767.99	664.95	880.20
crystal system	triclinic	triclinic	monoclinic
space group	*P*-1	*P*-1	$P2_1/n$ (No. 14)
a, Å	8.815(4)	9.747(2)	14.5768(12)
b, Å	9.287(5)	11.299(2)	8.9341(7)
c, Å	11.376(6)	11.586(2)	15.9047(13)
α, deg.	82.508(5)	99.020(2)	-
β, deg.	67.980(5)	107.884(2)	103.2940(10)
γ, deg.	67.616(5)	113.050(2)	-
V, Å^3	798.2(7)	1059.9(4)	2015.8(3)
Z	1	1	2
D_{calcd}, g/cm^{-3}	1.598	1.042	1.450
μ [Mo-*K*α], mm^{-1}	0.71069	0.71073	0.71073
T, K	90	90	90
crystal size, mm			
$2\theta_{max}$, deg.	56.6	56.5	57.1
no. of reflections measured	4204	5940	10987
unique data (R_{int})	3332 (0.0390)	4547 (0.0163)	4583 (0.0165)
data / restraints / parameters	3332 / 0 / 246	4547 / 0 / 355	4583 / 0 / 271
*R*1 (*I*>2.0σ(*I*))	0.0864	0.0272	0.0394
w*R*2 (*I*>2.0σ(*I*))	0.2019	0.1001	0.1612
*R*1 (all data)		0.0282	0.0411
w*R*2 (all data)		0.1017	0.1672
GOF on F^2	0.995	0.936	1.549
Δρ, e Å-3	4.450, -5.140	0.447, -0.480	1.222, -1.053

[a] $R1 = (\sum||Fo|-|Fc||)/(\sum|Fo|)$. [b] $wR2 = [\{\sum w(Fo^2-Fc^2)^2\}/\{\sum w(Fo^4)\}]^{1/2}$.

7. Further Ligand Evaluation

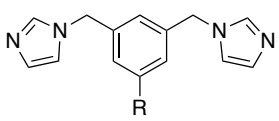
Sterically crowded (+)-menthol **5c** was chosen as a model substrate for further evaluation of ligand activity. Zinc cluster catalyst did not delivered corresponding transesterification product (entry 1). The use of isolated zinc complex **8c** resulted in low conversion due to the low solubility even in toluene-refluxed conditions (entry 2). On the other hand, catalytic activity was gained upon the addition of DMAP (**7a**) providing the product in 54% conversion (entry 3). In entries 4 to 10, in situ prepared zinc complexes were used. Zinc complexes prepared from ligands **7h** and **7r** showed high solubility and superior conversions were observed (entries 4 and 5). Although zinc complex precipitates were observed with the reaction proceeding in use of ligands **7j** and **7s**-**7u**, comparable yields were observed (entries 6 to 9). Zinc complex prepared from ligand **7l** was hardly soluble in toluene-reflux conditions resulting in inferior conversion (entry 10).

Table S1. Ligand Evaluation



4a **6ac**

Entry	Ligand	conversion [%] [a]
1	none	N.D. [b]
2	*t*-Bu complex (**8c**) [c, e]	14
3	DMAP (**7a**) [d]	54
4	R = *O*-*n*-Pen (**7h**)	66
5	R = *n*-Bu (**7r**)	60
6	R = *t*-Bu (**7j**) [e]	66
7	R = *c*-Pen (**7s**) [e]	58
8	R = Phenyl (**7t**) [e]	42
9	R = NMe_2 (**7u**) [e]	38
10	R = Br (**7l**)	14



Ligand

[a] Determined by GC. [b] not detected. [c] 5 mol% on zinc was used as catalyst. [d] 20 mol% of DMAP was used. [e] Zn complex precipitate was obserbed as the reaction progress.

8. **References**

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9. NMR Spectra of New Compounds