Polymer–Micelle Incarcerated Scandium as a Novel Polymer-Supported Catalyst for High-Throughput Organic Synthesis

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Supporting Information

General. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA300, JNM-LA400, or ECX-400 spectrometer in CDCl_3 unless otherwise stored. Tetramethylsilane (TMS) was used as internal standard ($\delta = 0$) for ^1H NMR spectroscopy, and CDCl_3 was used as internal standard ($\delta = 77.0$) for ^{13}C NMR spectroscopy. IR spectra were measured on a JASCO FT/IR-610 spectrometer. FAB-MS were measured with a JEOL JMS-MS700V. Commercially available chemicals and dry solvents (THF, CH_2Cl_2 , CH_3CN , toluene, CHCl_3), purchased from Aldrich, Kanto Chemical, Tokyo Chemical Industry and Wako Pure Chemical Industry, were purified according to standard procedures as required before use. Column chromatography was conducted on Silica gel 60 (Merck) and preparative thin-layer chromatography (PTLC) was carried out using Wakogel B-5F. The weight- and number-average molecular weights (M_w and M_n , respectively) and polydispersity indices (M_w/M_n) of the linear copolymers were measured by gel permeation chromatography (GPC) at 40 °C using Shimadzu GPC system (system controller (SCL-10A VP), column oven (CTP-10A VP), liquid chromatography (LC-10AD VP), degasser (DCV-12A), and refractive index detector (RID-10A)) equipped with a guard column (Shimadzu GPC-800P) and three mixed columns (Shimadzu GPC-8025 (exclusion limit = 2×10^4), GPC-803 (exclusion limit = 7×10^4), and GPC-804 (exclusion limit = 4×10^5)). GPC was performed using THF as an eluent at a flow rate of 1 mL/min. Linear polystyrene standards were used for calibration. XRF and ICP analyses were performed using Shimadzu EDX-800 and Shimadzu ICPS-7510, respectively. Transmission electron microscopic (TEM) images were obtained using a JEOL JEM-1010 Electron Microscope operated at 80 kV. The details of TEM specimens were described below. The structures of known compounds were confirmed by comparison with data shown in literature.

XRF analysis. The recovered crude compounds after the reaction were dissolved in THF and diluted to 5 mL with THF. The THF solution was used for XRF analysis to determine the Sc leaching. The solutions were recovered to isolate the desired compound after the analysis.

ICP analysis. The recovered crude compounds after the reaction were dissolved in CH₃CN (1 mL). The CH₃CN solution was diluted to 10 mL with CH₃CN and 5 mL of the solution was used for ICP analysis to determine the Sc leaching. The half of the solution was concentrated under reduced pressure, and the recovered crude compounds were treated to determine the yield of the desired compound. Corrected yield means double the isolated yield.

Preparation of copolymer 1. Styrene (8.33 g, 80.0 mmol), 2-[(2-phenylallyloxy)methyl]oxirane¹ (1.90 g, 9.99 mmol), tetraethyleneglycol mono-2-phenyl-2-propenyl ether² (3.10 g, 9.99 mmol), and AIBN (84.0 mg, 0.511 mmol) were mixed in CHCl₃ (12 mL). The mixture was stirred for 48 h at reflux and then cooled to room temperature. The resulting polymer solution was poured slowly onto MeOH. The resulting white precipitated polymer was collected by filtration and washed with MeOH several times. The collected polymer was purified by repeated reprecipitation from the THF solution into MeOH and dried under reduced pressure to give copolymer **1** (9.00 g, 68% yield). The molar ratio of the components was determined by ¹H NMR analysis (x/y/z = 90/6/4). M_w : 35 019, M_n : 14 524, M_w/M_n = 2.41.

Preparation of PI Sc(OTf)₃. Copolymer **1** (2.00 g) was dissolved in toluene (40 mL) at room temperature, and to this solution was added Sc(OTf)₃ (200 mg, 0.406 mmol). The mixture was stirred for 20 min at this temperature. Hexane (160 mL) was slowly added to the mixture at room temperature. Coacervates were found to envelope Sc(OTf)₃ in the media. The resulting catalyst capsules were collected by filtration after additional stirring for 30 min at room temperature and washed with hexane several times, then dried under reduced pressure. Next, the collected capsules were left at 120 °C for 2 h under solvent-free conditions to cross-link the polymer chain. Finally, the cross-linked catalyst was washed with toluene and CH₂Cl₂ several times, and dried at room temperature under reduced pressure to give PI Sc(OTf)₃ (2.08 g, 0.191 mmol/g of Sc(OTf)₃ was loaded). The Sc leaching in all filtrates and washings

was measured by XRF analysis to determine the catalyst loading.

Preparation of PMI Sc(OTf)₃. Copolymer **1** (2.00 g) was dissolved in THF–cyclohexane (1 : 3, 140 mL) at room temperature, and to this solution was slowly added a THF–cyclohexane (1 : 3, 20 mL) solution of Sc(OTf)₃ (200 mg, 0.406 mmol). After stirring for 30 min at room temperature, hexane (160 mL) was slowly added and then the mixture was stirred for 1 h at room temperature. The precipitated catalyst capsules were collected by filtration and washed with hexane several times, and dried under reduced pressure. Next, the collected capsules were left at 120 °C for 2 h under solvent-free conditions to cross-link the polymer chain. Finally, the cross-linked catalyst was washed with toluene and CH₂Cl₂ several times, and dried at room temperature under reduced pressure to give PMI Sc(OTf)₃ (2.01 g, 0.185 mmol/g of Sc(OTf)₃ was loaded).

Preparation of TEM specimens in microencapsulation of Sc(OTf)₃ using toluene as a solvent. Copolymer **1** (100 mg) was dissolved in toluene (2 mL) at room temperature, and to this solution was added Sc(OTf)₃ (10 mg, 0.020 mmol). The mixture was stirred for 20 min at this temperature. The resulting solution of 100 µL was diluted to 4 mL with toluene and the diluted solution was dropped on carbon-coated Cu grids. The specimens without staining were allowed to dry in air.

Preparation of TEM specimens in microcapsulation of Sc(OTf)₃ using THF–cyclohexane as a solvent. Copolymer **1** (100 mg) was dissolved in THF–cyclohexane (1 : 3, 7 mL) at room temperature, and to this solution was slowly added a THF–cyclohexane (1 : 3, 1 mL) solution of Sc(OTf)₃ (10 mg, 0.020 mmol). The mixture was stirred for 30 min at this temperature. The resulting solution of 100 µL was diluted to 1 mL with THF–cyclohexane (1 : 3) and the diluted solution was dropped on carbon-coated Cu grids. The specimens without staining were allowed to dry in air.

A typical procedure for Mukaiyama aldol reaction. To a suspension of PMI Sc(OTf)₃ (135 mg, 0.025 mmol, 5 mol%) in CH₂Cl₂ (3.0 mL) were added a solution of benzaldehyde (53 mg, 0.50 mmol) in CH₂Cl₂ (1.0 mL) and a solution of the ketene silyl acetal derived from methyl isobutyrate (113 mg, 0.65 mmol) in CH₂Cl₂ (1.0 mL) at 0 °C under Ar. The mixture was stirred for 10 min at the same temperature and stirred for 3 h at room temperature. After filtration and washing (CH₂Cl₂, hexane), the filtrate was concentrated

under reduced pressure. The divided crude compounds (see: ICP analysis section) were treated with 1N HCl/THF (1/10) at room temperature to hydrolyze the silyl ether. After usual work up, the crude compounds were purified by PTLC to give methyl 3-hydroxy-2,2-dimethyl-3-phenylpropionate (48 mg, 46% (corrected yield; 92%)). PMI Sc(OTf)₃ was recovered quantitatively (> 97%) and reused, the 2nd run; 96%, the 3rd run; 94%. In the 2nd and 3rd run, all recovered crude compounds after the reaction were treated to determine the yield of the desired compound.

Table 5. Substrate Scope for Mukaiyama Aldol Reaction

(1.3 equiv)

entry	cat.	R ¹	R ²	R ³	Y	yield (%)	entry	cat.	R ¹	R ²	R ³	Y	yield (%)
1	PI	4-Me-Ph	Me	Me	OMe	90	8	PI	Ph	H	Me	SEt	80 ^b
2	PI	2-Me-Ph	Me	Me	OMe	93	9	PI	Ph	H	H	SEt	83
3	PI	4-Cl-Ph	Me	Me	OMe	93	10	PI	Ph	Me	H	Ph	70 ^c
4	PI	PhCH ₂ CH ₂	Me	Me	OMe	70	11	PMI	Ph	Me	H	Ph	78 ^d
5	PI	2-Furyl	Me	Me	OMe	75	12	Sc(OTf) ₃	Ph	Me	H	Ph	50 ^e
6	PMI	2-Furyl	Me	Me	OMe	85	13 ^a	PMI	Ph	Me	H	Ph	74 ^f
7	PI	2-Thienyl	Me	Me	OMe	93	14 ^a	MC Sc(OTf) ₃	Ph	Me	H	Ph	57 ^g

^a Reaction condition; catalyst (5 mol%) in CH₃CN at rt for 3 h. ^bSyn/anti = 35/65. ^cSyn/anti = 58/42. ^dSyn/anti = 60/40. ^eSyn/anti = 56/44. ^fSyn/anti = 50/50. ^gSyn/anti = 47/53.

Methyl 3-hydroxy-2,2-dimethyl-3-phenylpropionate:³

White powder; ¹H NMR (CDCl₃) δ = 1.10 (s, 3H), 1.14 (s, 3H), 3.03 (br s, 1H), 3.70 (s, 3H), 4.88 (s, 1H), 7.22–7.33 (m, 5H); ¹³C NMR (CDCl₃) δ = 19.0, 22.9, 47.7, 52.0, 78.6, 127, 6, 127.7, 139.9, 178.1.

Methyl 3-Hydroxy-2,2-dimethyl-3-(4-methylphenyl)propionate (entry 1):³

White powder; ¹H NMR (CDCl₃) δ = 1.09 (s, 3H), 1.13 (s, 3H), 2.33 (s, 3H), 2.97 (br s, 1H), 3.71 (s, 3H), 4.85 (s, 3H), 7.10–7.19 (m, 4H); ¹³C NMR (CDCl₃) δ = 19.0, 21.1, 23.0, 47.7, 52.0, 78.5, 127.5, 128.4, 137.0, 137.3, 178.2.

Methyl 3-hydroxy-2,2-dimethyl-3-(2-methylphenyl)propionate (entry 2):

Colorless oil; ¹H NMR (CDCl₃) δ = 1.12 (s, 3H), 1.20 (s, 3H), 2.37 (s, 3H), 2.96 (br s, 1H), 3.74 (s, 3H), 5.25 (s, 1H), 7.10–7.22 (m, 3H), 7.42 (dd, *J* = 8.0 and 2.0 Hz, 1H); ¹³C NMR (CDCl₃) δ = 18.8, 20.2, 23.2, 48.5, 52.1, 73.5, 125.6, 127.4, 127.5, 130.3, 135.9, 138.4, 178.5; IR (naet) 3498, 2952, 1725 cm⁻¹; HRMS (FAB) Exact mass calcd for C₁₃H₁₉O₃ [M+H]⁺, 223.1334. Found 223.1326.

Methyl 3-hydroxy-2,2-dimethyl-3-(4-chlorophenyl)propionate (entry 3):³

White powder; ¹H NMR (CDCl₃) δ = 1.08 (s, 3H), 1.12 (s, 3H), 3.22 (br s, 1H), 3.71 (s, 3H), 4.85 (s, 3H), 7.21–7.25 (m, 2H), 7.27–7.30 (m, 2H); ¹³C NMR (CDCl₃) δ = 19.0, 22.8, 47.6, 52.1, 77.9, 127.9, 128.9, 133.4, 138.4, 178.0.

Methyl 3-hydroxy-2,2-dimethyl-5-phenylpentanoate (entry 4):³

Colorless oil; ¹H NMR (CDCl₃) δ = 1.16 (s, 3H), 1.18 (s, 3H), 1.55–1.67 (m, 1H), 1.70–1.81 (m, 1H), 2.56 (br s, 1H), 2.59–2.70 (m, 1H), 2.90–3.00 (m, 1H), 3.60–3.65 (m, 1H), 3.67 (s, 3H), 7.15–7.30 (m, 5H); ¹³C NMR (CDCl₃) δ = 20.3, 22.3, 32.8, 33.6, 47.1, 51.9, 76.0, 125.8, 128.3, 128.4, 142.1, 178.4.

Methyl 3-(2-furyl)-3-hydroxy-2,2-dimethylpropionate (entry 5):⁴

Colorless oil; ¹H NMR (CDCl₃) δ = 1.20 (s, 6H), 3.19 (br s, 1H), 3.72 (s, 3H), 4.79 (s, 1H), 6.23–6.27 (m, 1H), 6.31–6.34 (m, 1H), 7.33–7.36 (m, 1H); ¹³C NMR (CDCl₃) δ = 20.1, 22.7, 47.1, 52.1, 73.3, 107.7, 110.0, 141.7, 153.9, 177.6.

Methyl 3-hydroxy-2,2-dimethyl-3-(2-thienyl)propionate (entry 7):

White powder; mp 45–46 °C; ¹H NMR (CDCl₃) δ = 1.20 (s, 3H), 1.23 (s, 3H), 3.17 (br s, 1H), 3.73 (s, 3H), 5.10 (s, 1H), 6.93–6.98 (m, 2H), 7.23–7.27 (m, 1H); ¹³C NMR (CDCl₃) δ = 19.9, 22.7, 47.7, 52.1, 75.6, 124.8, 125.6, 126.2, 143.6, 177.9; IR (neat) 3475, 2982, 1722 cm⁻¹; HRMS (FAB) Exact mass calcd for C₁₀H₁₃O₂S [M–H₂O]⁺, 197.0636. Found 197.0640.

S-Ethyl 3-hydroxy-2-methyl-3-phenylpropanedioate (entry 8):⁵

Colorless oil; (*syn/anti* = 35/65): ¹H NMR (CDCl₃) δ = 0.92 (d, *J* = 7.2 Hz, 1.95H), 1.16 (d, *J* = 6.8 Hz, 1.05H), 1.19 (t, *J* = 7.2 Hz, 1.05H), 1.24 (t, *J* = 7.2 Hz, 1.95H), 2.79–3.02 (m, 4H), 4.79 (d, *J* = 8.0 Hz, 0.65H), 5.07 (d, *J* = 3.6 Hz, 0.35H), 7.23–7.40 (m, 5H); ¹³C NMR (CDCl₃) δ = 11.4, 14.5, 15.3, 23.1, 23.2, 54.9, 55.4, 73.7, 76.5, 126.0, 126.6, 127.4, 128.0, 128.1, 128.4, 141.2, 141.6, 203.6, 203.9.

S-Ethyl 3-hydroxy-3-phenylpropanedioate (entry 9):³

Colorless oil; ¹H NMR (CDCl₃) δ = 1.25 (t, *J* = 7.3 Hz, 3H), 2.86–3.01 (m, 4H including q, *J* = 7.3 Hz, 2H at 2.90), 3.13 (br s, 1H), 5.14–5.19 (m, 1H), 7.25–7.37 (m, 5H); ¹³C NMR (CDCl₃) δ = 14.5, 23.4, 52.5, 70.8, 125.6, 127.8, 128.5, 142.3, 198.9.

3-hydroxy-2-methyl-1,3-diphenyl-1-propanone (entry 10):⁶

Colorless oil; (*syn/anti* = 58/42): ¹H NMR (CDCl₃) δ = 1.04 (d, *J* = 7.2 Hz, 1.26H), 1.18 (d, *J* = 7.2 Hz, 1.74H), 3.38 (br, 1H), 3.70 (qd, *J* = 7.2 and 3.2 Hz, 0.58H), 3.82 (dq, *J* = 8.4 and 7.2 Hz, 0.42H), 4.97 (d, *J* = 8.4 Hz, 0.42H), 5.21 (d, *J* = 3.2 Hz, 0.58H), 7.20–7.60 (m, 8H), 7.91 (d, *J* = 7.2 Hz, 1.16H), 7.96 (d, *J* = 7.6 Hz, 0.84H); ¹³C NMR (CDCl₃) δ = 11.2, 15.6, 47.0, 47.9, 73.1, 76.7, 126.0, 126.7, 127.2, 127.8, 128.2, 128.4, 128.6, 128.7, 133.2, 133.4, 135.6, 136.7, 141.8, 142.2, 204.8, 205.5.

A typical procedure for Mannich-type reaction. To a suspension of PMI Sc(OTf)₃ (136 mg, 0.025 mmol, 10 mol%) in CH₃CN (3.0 mL) were added a solution of *N*-benzylideneaniline (45 mg, 0.25 mmol) in CH₃CN (1.0 mL) and a solution of ketene silyl acetal derived from methyl isobutyrate (65 mg, 0.37 mmol) in CH₃CN (1.0 mL) at 0 °C under Ar. The mixture was stirred for 10 min at the same temperature and stirred for 3 h at room temperature. After filtration and washing (CH₂Cl₂, hexane), the filtrate was concentrated under reduced pressure. The divided crude compounds (see: ICP analysis section) were purified by PTLC to give methyl 2,2-dimethyl-3-phenyl-3-(*N*-phenylamino)propionate (35 mg, 49% (corrected yield; 98%)). PMI Sc(OTf)₃ was recovered quantitatively (> 97%), and reused, the 2nd run; 99%, 3rd run; 97%. In the 2nd and 3rd use, all recovered crude compounds after the reaction were treated to determine the yield of the desired compound.

Table 6. Substrate Scope for Mannich-type Reaction

entry	R ¹	X	R ²	R ³	Y	time (h)	yield (%)
1	Ph	Ph	Me	Me	OMe	3	96 ^{a, b}
2	Ph	Ph	Me	Me	SEt	3	98
3	2-Thienyl	Ph	Me	Me	OMe	4	92
4	2-Thienyl	Ph	Me	Me	SEt	4	97
5	PhCH ₂ CH ₂	NHBz	Me	Me	OMe	24	80
6	EtO ₂ C	NHBz	Me	Me	OMe	24	73
7	Ph	Ph	H	H	Ph	3	80

^a Corrected yield. Half of the crude compound was used for ICP analysis. ^b 2nd use, quant; 3rd use, quant.

Methyl 2,2-dimethyl-3-phenyl-3-(*N*-phenylamino)propionate (entry 1):⁵

Pale brown powder; ¹H NMR (CDCl₃) δ = 1.16 (s, 3H), 1.27 (s, 3H), 3.63 (s, 3H), 4.49 (s, 1H), 4.84 (br s, 1H), 6.45–6.53 (m, 2H), 6.55–6.62 (m, 1H), 7.00–7.06 (m, 2H), 7.18–7.30 (m, 5H);

^{13}C NMR (CDCl_3) δ = 20.7, 24.5, 46.9, 52.0, 64.4, 113.4, 117.3, 127.4, 127.9, 128.2, 129.0, 139.1, 146.8, 177.0.

S-Ethyl 2,2-dimethyl-3-phenyl-3-(N-phenylamino)propanethioate (entry 2):

Gray powder; mp 70–71 °C; ^1H NMR (CDCl_3) δ = 1.17 (t, J = 8.0 Hz, 3H), 1.23 (s, 3H), 1.25 (s, 3H), 2.83 (m, 2H), 4.51 (s, 1H), 4.80 (br s, 1H), 6.45–6.50 (m, 2H), 6.55–6.60 (m, 1H), 7.01–7.04 (m, 2H), 7.20–7.31 (m, 5H); ^{13}C NMR (CDCl_3) δ = 14.4, 19.9, 23.4, 25.1, 53.2, 64.9, 113.3, 117.2, 127.4, 127.9, 128.5, 128.9, 139.0, 146.9, 206.1; IR (neat) 3409, 2972, 1665, 1601 cm^{-1} ; HRMS (FAB) Exact mass calcd for $\text{C}_{19}\text{H}_{24}\text{NOS}$ $[\text{M}+\text{H}]^+$, 314.1579. Found 314.1574.

Methyl 2,2-dimethyl-3-(N-phenylamino)-3-(2-thienyl)propionate (entry 3):⁷

Pale brown powder; ^1H NMR (CDCl_3) δ = 1.27 (s, 3H), 1.32 (s, 3H), 3.67 (s, 3H), 4.70 (br s, 1H), 4.82 (s, 1H), 6.50–6.70 (m, 3H), 6.86–6.96 (m, 2H), 7.04–7.16 (m, 3H); ^{13}C NMR (CDCl_3) δ = 21.4, 23.9, 47.3, 52.1, 60.6, 113.6, 117.9, 124.4, 126.0, 126.4, 129.0, 144.0, 146.7, 176.8.

S-Ethyl 2,2-dimethyl-3-(N-phenylamino)-3-(2-thienyl)propanethioate (entry 4):

Pale brown powder; mp 65–66 °C; ^1H NMR (CDCl_3) δ = 1.18 (t, J = 7.6 Hz, 3H), 1.32 (s, 3H), 1.34 (s, 3H), 2.84 (q, J = 7.6 Hz, 2H), 4.67 (br s, 1H), 4.84 (s, 1H), 6.52–6.60 (m, 2H), 6.62–6.68 (m, 1H), 6.88–6.96 (m, 2H), 7.03–7.10 (m, 2H), 7.12–7.16 (m, 1H); ^{13}C NMR (CDCl_3) δ = 14.4, 20.8, 23.4, 24.6, 53.5, 61.2, 113.5, 117.9, 124.5, 126.1, 126.4, 129.0, 144.0, 146.8, 205.9; IR (neat) 3403, 2972, 1664, 1601 cm^{-1} ; HRMS (FAB) Exact mass calcd for $\text{C}_{17}\text{H}_{22}\text{NOS}_2$ $[\text{M}+\text{H}]^+$, 320.1143. Found 320.1153.

Methyl 3-(N'-benzoylhydrazino)-2,2-dimethyl-5-phenylpentanoate (entry 5):⁸

Pale yellow oil; ^1H NMR (CDCl_3) δ = 1.18 (s, 3H), 1.25 (s, 3H), 1.62–1.82 (m, 2H), 2.72–2.82 (m, 1H), 2.98–3.08 (m, 1H), 3.18 (dd, J = 9.6 and 2.4 Hz, 1H), 3.57 (s, 3H), 4.80 (br s, 1H), 7.10–7.27 (m, 5H), 7.35–7.54 (m, 3H), 7.74–7.76 (m, 2H), 7.89 (br s, 1H); ^{13}C NMR (CDCl_3) δ = 20.5, 23.1, 31.1, 33.5, 46.7, 51.9, 66.4, 125.8, 126.7, 128.3, 128.4, 128.6, 131.7, 132.5, 141.8, 166.1, 178.7.

1-Methyl Ethyl 3-(N'-benzoylhydrazino)-2,2-dimethylsuccinate (entry 6):⁹

Colorless powder; ^1H NMR (CDCl_3) δ = 1.25 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H), 1.36 (s, 3H), 3.72 (s, 3H), 3.95 (s, 1H), 4.14–4.28 (m, 2H), 5.35 (br s, 1H), 7.39–7.44 (m, 2H), 7.48–7.53 (m, 1H),

7.74 (d, $J = 7.2$ Hz, 2H), 8.05 (br s, 1H); ^{13}C NMR (CDCl_3) $\delta = 14.0, 21.7, 21.9, 45.6, 52.1, 61.3, 69.3, 126.9, 128.6, 131.8, 132.5, 167.0, 171.2, 176.1$.

1,3-Diphenyl-3-(*N*-phenylamino)propanone (entry 7):⁵

Pale yellow powder; ^1H NMR (CDCl_3) $\delta = 3.44$ (dd, $J = 16.1$ and 7.4 Hz, 1H), 3.52 (dd, $J = 16.1$ and 5.6 Hz, 1H), 4.85 (br s, 1H), 5.00 (dd, $J = 7.4$ and 5.6 Hz, 1H), 6.54 – 6.61 (m, 2H), 6.64 – 6.70 (m, 1H), 7.05 – 7.13 (m, 2H), 7.20 – 7.25 (m, 1H), 7.28 – 7.35 (m, 2H), 7.38 – 7.48 (m, 4H), 7.52 – 7.58 (m, 1H), 7.88 – 7.92 (m, 2H); ^{13}C NMR (CDCl_3) $\delta = 46.2, 55.0, 114.0, 118.0, 126.4, 127.4, 128.2, 128.7, 128.8, 129.1, 133.4, 136.6, 142.7, 146.6, 198.2$.

A typical procedure for Michael reaction. To a suspension of PMI $\text{Sc}(\text{OTf})_3$ (109 mg, 0.020 mmol, 5 mol%) in CH_3CN (4.0 mL) were added a solution of methyl 1-oxoindan-2-carboxylate (76 mg, 0.40 mmol) in CH_3CN (1.0 mL) and methyl vinyl ketone (67 μL , 0.80 mmol) at 0°C under Ar. The mixture was stirred for 10 min at the same temperature and stirred for 4 h at room temperature. After filtration and washing (CH_2Cl_2 , hexane), the filtrate was concentrated under reduced pressure. The divided crude compounds (see: ICP analysis section) were purified by PTLC to give methyl 1-oxo-2-(3-oxo-butyl)indan-2-carboxylate (48 mg, 46% (corrected yield; 92%)). PMI $\text{Sc}(\text{OTf})_3$ was recovered quantitatively ($> 99\%$), and reused, the 2nd run; 94%, 3rd run; 92%. In the 2nd and 3rd use, all recovered crude compounds after the reaction were treated to determine the yield of the desired compound.

Table 7. Michael Reaction Using PMI $\text{Sc}(\text{OTf})_3$ in Other Solvents

entry	solvent	PMI $\text{Sc}(\text{OTf})_3$ (mol%)	time (h)	yield (%)		
				1st	2nd	3rd
1	CH_2Cl_2	10	12	92	92	91
2	toluene	10	4	quant	96	98

Table 8. Substrate Scope for Michael Reaction

donor + acceptor		PMI Sc(OTf) ₃ (5 mol%)		product	
		MeCN, rt			
entry	donor	acceptor	product	time (h)	yield (%)
1				4	94
2				9	92
3				6	96 ^a
4				6	quant ^b
5				6	quant ^c
6				6	81

^a Diastereo ratio = 66/34. ^b Diastereo ratio = 60/40. ^c Diastereo ratio = 55/45.

Methyl 1-oxo-2-(3-oxo-butyl)indan-2-carboxylate (Table 7):¹⁰

White powder; ¹H NMR (CDCl₃) δ = 2.12 (s, 3H), 2.18–2.30 (m, 2H), 2.51 (ddd, *J* = 15.2, 9.6 and 5.6 Hz, 1H), 2.63 (ddd, *J* = 15.2, 10.0 and 6.0 Hz, 1H), 3.05 (d, *J* = 17.6 Hz, 1H), 3.68 (d, *J* = 17.6 Hz, 1H), 3.69 (s, 3H), 7.39–7.44 (m, 1H), 7.46–7.49 (m, 1H), 7.62–7.66 (m, 1H), 7.76–7.79 (m, 1H); ¹³C NMR (CDCl₃) δ = 28.5, 29.9, 37.8, 38.7, 52.7, 59.0, 124.8, 126.4, 127.9, 135.0, 135.5, 152.5, 171.5, 202.2, 207.3.

Ethyl 1-oxo-2-(3-oxo-butyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (Table 8, entry 1):¹¹

Colorless oil; ¹H NMR (CDCl₃) δ = 1.17 (t, *J* = 7.2 Hz, 3H), 2.05–2.28 (m, 3H), 2.15 (s, 3H), 2.50–2.63 (m, 2H), 2.66–2.78 (m, 1H), 2.90–3.10 (m, 2H), 4.15 (d, *J* = 7.2 Hz, 2H), 7.18–7.24 (m, 1H), 7.27–7.35 (m, 1H), 7.43–7.50 (m, 1H), 8.00–8.05 (m, 1H); ¹³C NMR (CDCl₃) δ = 14.0, 25.8, 27.5, 29.9, 31.6, 39.0, 56.5, 61.3, 126.8, 127.8, 128.6, 131.9, 133.5, 142.7, 171.8, 195.5, 207.7.

Ethyl 2-benzoyl-5-oxo-hexanoate (entry 2):¹¹

Colorless oil; ¹H NMR (CDCl₃) δ = 1.17 (t, *J* = 7.2 Hz, 3H), 2.14 (s, 3H), 2.16–2.32 (m, 2H), 2.51–2.68 (m, 2H), 4.10–4.19 (m, 2H), 4.45 (dd, *J* = 6.4 and 6.3 Hz, 1H), 7.45–7.52 (m, 2H),

7.55–7.62 (m, 1H), 8.00–8.05 (m, 2H); ^{13}C NMR (CDCl_3) δ = 13.9, 22.6, 29.9, 40.4, 52.6, 61.3, 128.6, 128.7, 133.5, 135.9, 169.7, 195.2, 207.7.

Methyl 1-oxo-2-(3-oxo-cyclopentyl)indan-2-carboxylate (entry 3):

A mixture of the two diastereomers (dr = 66/34); colorless oil; ^1H NMR (CDCl_3) δ = 1.23–2.62 (m, 6H), 3.15 (d, J = 17.8 Hz, 1H), 3.18–3.30 (m, 1H), 3.70 (s, 1.02H), 3.72 (s, 1.98H), 3.73 (d, J = 17.8 Hz, 1H), 7.39–7.46 (m, 1H), 7.49–7.56 (m, 1H), 7.60–7.70 (m, 1H), 7.74–7.82 (m, 1H); ^{13}C NMR (CDCl_3) δ = 23.9, 25.2, 33.4, 33.8, 38.07, 38.14, 39.3, 40.5, 40.7, 40.8, 52.8, 62.0, 62.4, 124.7, 124.8, 126.2, 126.3, 128.01, 128.04, 135.2, 135.4, 135.7, 152.7, 152.9, 170.6, 170.7, 201.27, 201.33, 216.7, 216.9; IR (neat) 2954, 1743, 1708, 1609 cm^{-1} ; HRMS (FAB) Exact mass calcd for $\text{C}_{16}\text{H}_{17}\text{O}_4$ $[\text{M}+\text{H}]^+$, 273.1127. Found 273.1128.

Methyl 1-oxo-2-(1-phenyl-3-oxo-butyl)indan-2-carboxylate (entry 4):

Major: Waxy solid; ^1H NMR (CDCl_3) δ = 2.00 (s, 3H), 2.81 (dd, J = 16.5 and 3.0 Hz, 1H), 3.11 (dd, J = 16.5 and 11.0 Hz, 1H), 3.28 (d, J = 17.4 Hz, 1H), 3.62 (d, J = 17.4 Hz, 1H), 3.63 (s, 3H), 4.35 (dd, J = 11.0 and 3.0 Hz, 1H), 7.18–7.23 (m, 5H), 7.32–7.37 (m, 2H), 7.51–7.56 (m, 1H), 7.73–7.77 (m, 1H); ^{13}C NMR (CDCl_3) δ = 30.1, 35.0, 44.6, 45.3, 52.8, 64.6, 124.4, 126.1, 127.3, 127.7, 128.3, 128.8, 135.4, 136.0, 138.9, 152.8, 170.6, 201.8, 205.8; IR (neat) 2955, 1712, 1605 cm^{-1} ; HRMS (FAB) Exact mass calcd for $\text{C}_{21}\text{H}_{21}\text{O}_4$ $[\text{M}+\text{H}]^+$, 337.1440. Found 337.1439.
Minor: Pale yellow powder; mp 160 $^\circ\text{C}$ (decomp.); ^1H NMR (CDCl_3) δ = 2.06 (s, 3H), 3.12–3.17 (m, 2H), 3.29 (d, J = 17.4 Hz, 1H), 3.72 (s, 3H), 3.73 (d, J = 17.4 Hz, 1H), 4.29 (dd, J = 8.7 and 6.0 Hz, 1H), 7.03–7.27 (m, 5H), 7.32–7.36 (m, 1H), 7.46–7.52 (m, 1H), 7.54–7.58 (m, 1H); ^{13}C NMR (CDCl_3) δ = 29.9, 33.8, 44.2, 45.6, 52.9, 64.8, 124.7, 125.9, 127.3, 127.6, 128.2, 129.3, 134.7, 135.3, 138.2, 152.8, 170.5, 200.7, 206.3; IR (neat) 2933, 1711, 1644 cm^{-1} ; HRMS (FAB) Exact mass calcd for $\text{C}_{21}\text{H}_{21}\text{O}_4$ $[\text{M}+\text{H}]^+$, 337.1440. Found 337.1432.

Methyl 1-oxo-2-(1-methyl-3-oxo-3-phenylpropyl)indan-2-carboxylate (entry 5):

A mixture of the two diastereomers (dr = 55/45); colorless oil; ^1H NMR (CDCl_3) δ = 0.82 (d, J = 6.9 Hz, 1.65H), 0.96 (d, J = 6.9 Hz, 1.35H), 2.69 (dd, J = 15.4 and 11.2 Hz, 0.45H), 2.79 (dd, J = 15.1 and 10.5 Hz, 0.55H), 3.00 (dd, J = 15.1 and 2.3 Hz, 0.55H), 3.20 (d, J = 17.9 Hz, 0.45H), 3.22 (d, J = 17.6 Hz, 0.55H), 3.26–3.45 (m, 1.45H), 3.70 (s, 3H), 3.77 (d, J = 17.9 Hz, 0.45H), 3.78 (d, J = 17.6 Hz, 0.55H), 7.35–7.59 (m, 5H), 7.60–7.68 (m, 1H), 7.72–7.81 (m, 1H), 7.90–7.96 (m, 1H), 7.99–8.05 (m, 1H); ^{13}C NMR (CDCl_3) δ = 14.8, 15.6, 33.0, 33.9, 34.0, 40.9,

42.1, 52.8, 52.9, 64.7, 65.0, 124.5, 124.6, 126.2, 126.3, 127.76, 127.82, 128.2, 128.6, 133.0, 133.1, 135.42, 135.45, 135.6, 135.8, 136.6, 136.7, 153.2, 153.3, 170.8, 198.6, 198.8, 201.6, 202.0; IR (neat) 2958, 1742, 1713, 1606 cm^{-1} ; HRMS (FAB) Exact mass calcd for $\text{C}_{21}\text{H}_{21}\text{O}_4$ $[\text{M}+\text{H}]^+$, 337.1440. Found 337.1439.

4-Acetyl-3-methyl-1-phenylhexane-1,5-dione (entry 6):

Colorless oil; ^1H NMR (CDCl_3) δ = 1.00 (d, J = 6.4 Hz, 3H), 2.20 (s, 3H), 2.23 (s, 3H), 2.80–2.89 (m, 1H), 2.96–3.12 (m, 2H), 3.83 (d, J = 8.7 Hz, 1H), 7.42–7.52 (m, 2H), 7.53–7.60 (m, 1H), 7.88–8.02 (m, 2H); ^{13}C NMR (CDCl_3) δ = 17.7, 29.7, 29.8, 30.2, 42.5, 73.6, 128.0, 128.6, 133.2, 136.8, 198.8, 204.0, 204.3; IR (neat) 2968, 1692, 1597 cm^{-1} ; HRMS (FAB) Exact mass calcd for $\text{C}_{15}\text{H}_{19}\text{O}_3$ $[\text{M}+\text{H}]^+$, 247.1334. Found 247.1330.

Control experiments. PI $\text{Sc}(\text{OTf})_3$ (**2**) was prepared using copolymer **2**, an analogue of copolymer **1**, in which the tetraethyleneglycol moieties were replaced by the isometric alkyl alcohol moieties. PI $\text{Sc}(\text{OTf})_3$ (**2**) was evaluated in the Mukaiyama aldol reaction. It was found that 12.6% of Sc was leached, although a comparable catalytic activity with that of PI $\text{Sc}(\text{OTf})_3$ prepared using copolymer **1** was observed. Moreover, PI $\text{Sc}(\text{OTf})_3$ (**2**) could not be prepared using toluene as a solvent, because coacervation did not occur. These results strongly suggested that the tetramethyleneglycol moieties in copolymer **1** played an important role in the immobilization of $\text{Sc}(\text{OTf})_3$.

Scheme 1. Control Experiments

Preparation of copolymer 2. Styrene (9.08 g, 87.2 mmol), 4-vinylbenzyl glycidyl ether ² (2.07 g, 10.9 mmol), 14-phenylpentadec-14-en-1-ol¹² (3.30 g, 10.9 mmol), and AIBN

(129 mg, 0.785 mmol) were mixed in CHCl_3 (13 mL). The mixture was stirred for 24 h at reflux and then cooled to room temperature. The resulting polymer solution was poured slowly onto MeOH. The resulting white precipitated polymer was collected by filtration and washed with MeOH several times. The collected polymer was purified by repeated reprecipitation from the THF solution into MeOH and dried under reduced pressure to give copolymer **2** (6.95 g, 48% yield). The molar ratio of the components was determined by ^1H NMR analysis ($x/y/z = 79/11/10$). M_w : 23 843, M_n : 18 857, $M_w/M_n = 1.26$.

Preparation of PI $\text{Sc}(\text{OTf})_3$ (2**).** Copolymer **2** (500 mg) was dissolved in CH_2Cl_2 (10 mL) at room temperature, and to this solution was added $\text{Sc}(\text{OTf})_3$ (50 mg, 0.10 mmol). The mixture was stirred for 20 min at this temperature. Hexane (40 mL) was slowly added to the mixture at room temperature. Coacervates were found to envelope $\text{Sc}(\text{OTf})_3$ in the media. The resulting catalyst capsules were collected by filtration after additional stirring for 30 min at room temperature and washed with hexane several times, then dried under reduced pressure. Next, the collected capsules were left at 120 °C for 2 h under solvent-free conditions to cross-link the polymer chain. Finally, the cross-linked catalyst was washed with toluene and CH_2Cl_2 several times, and dried at room temperature under reduced pressure to give PI $\text{Sc}(\text{OTf})_3$ (527 mg, 0.195 mmol/g of $\text{Sc}(\text{OTf})_3$ was loaded).

Scheme 2. Hydroxymethylation with Formaldehyde Water Solution Using PMI $\text{Sc}(\text{OTf})_3$

Hydroxymethylation of the silyl enol ether of propiophenone with a formaldehyde water solution. To a suspension of PMI $\text{Sc}(\text{OTf})_3$ (109 mg, 0.020 mmol, 5 mol%) in CH_3CN (1.85 mL) were added a 37% formaldehyde water solution (150 μL , 201 mmol) and the silyl enol ether of propiophenone (84 mg, 0.41 mmol) at room temperature. The mixture was stirred for 0.5 h at room temperature. After filtration and washing (CH_2Cl_2 , hexane), the filtrate was concentrated under reduced pressure, and the resulting crude compound was purified by PTLCC to give 3-hydroxy-2-methyl-1-phenylpropane-1-one¹⁴ (60 mg, 90%). Colorless oil; ^1H NMR (CDCl_3) $\delta = 1.25$ (d, $J = 6.9$ Hz, 3H), 2.29 (br s, 1H), 3.67 (m, 1H), 3.83 (m, 1H), 3.93 (m, 1H), 7.46–7.61 (m, 3H), 7.95–7.98 (m, 2H); ^{13}C NMR (CDCl_3) $\delta = 14.5$, 42.9, 64.5, 128.4, 128.7, 133.3, 136.1, 204.4. In this reaction, Sc leaching (41%) was observed by XRF analysis.

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