Supplementary Information (SI) for Green Chemistry.

Supporting Information

Solvent-less mechanochemical asymmetric reactions in a ball mill utilizing polymer-supported Hayashi-Jørgensen catalyst: effect of polymer backbone and flexibility on its catalytic performance

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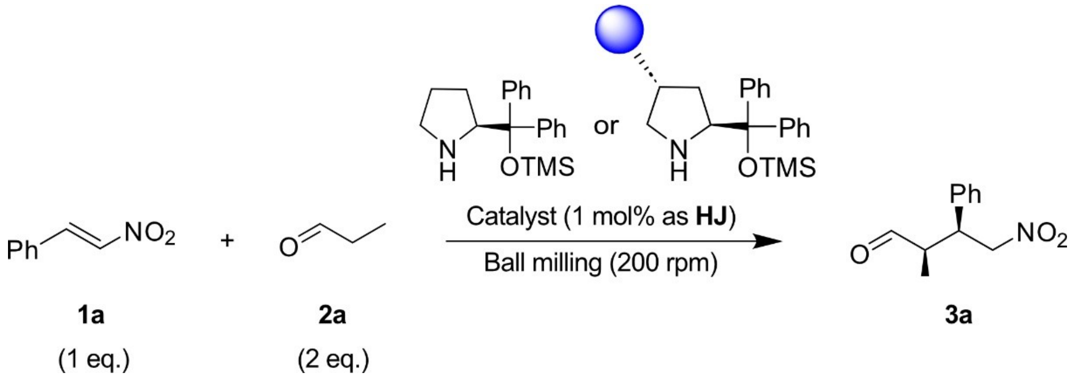
1. Materials and methods

Materials were obtained from commercial suppliers unless otherwise noted. Styrene (**S**) (>99.0% GC purity, stabilized with 4-*tert*-butylcatechol, Tokyo Chemical Industry Co., Ltd., Tokyo, Japan), 4-*tert*-butylstyrene (**^{t}BuS**) (>90.0% GC purity, stabilized with 4-*tert*-butylcatechol, Tokyo Chemical Industry Co., Ltd.) and methyl methacrylate (**MMA**) (>98.0% GC purity, FUJIFILM Wako Pure Chemical Co., Osaka, Japan) were purified using a short alumina column. 2,2′-Azo-bis(isobutyronitrile) (AIBN) (98.0% absorptiometry purity, FUJIFILM Wako Pure Chemical Co.) was purified by recrystallization from MeOH. (E)-β-Nitrostyrene (>92% NMR purity, FUJIFILM Wako Pure Chemical Co.) and propionaldehyde (>98.0% GC purity, Tokyo Chemical Industry Co., Ltd.) were used as substrates for the asymmetric Michael addition reaction. (*R*)-(+)-α,α-Diphenyl-2-pyrrolidinemethanol trimethylsilyl ether (>98.0% GC purity, Tokyo Chemical Industry Co., Ltd.) was used as unsupported HJ catalyst (**HJ**). The **HJ monomer** and styrene monomer with ethylene glycol moiety (**EGS**) were synthesized according to the previous reports.

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a JEOL ECZ400S spectroscopy, operating at 400 MHz. Chemical shift values for the ^{1}H NMR spectra were referenced to Me_4Si. High-performance liquid chromatography (HPLC) analyses were performed on a JASCO LC-2000Plus system equipped with a JASCO DG-980-50 degasser, a JASCO PU-980 pump, a Kanto Chemical Mightysil RP-18 GP 250-4.6 column (Kanto Chemical Co., Tokyo, Japan), a JASCO UV-2077Plus UV detector, and a JASCO CO-2065Plus column oven (JASCO Co., Tokyo, Japan). Acetonitrile/water (58 : 42 v/v) containing trifluoroacetic acid (0.1 vol%) was employed as a mobile phase in the HPLC measurements (40°C, 1.0 mL min^{-1}). HPLC analyses for enantiomeric excess (ee) were performed on a JASCO LC-2000Plus system equipped with a JASCO DG-980-50 degasser, a JASCO PU-986 pump, a CHIRALPAK OD-H 250-4.6 column (Daicel Co., Osaka, Japan), a JASCO MD-4010 photo diode array detector, and a JASCO CO-2060Plus column oven (JASCO Co.). 2-Propanol/hexane (9.1 : 90.1 v/v) was employed as a mobile phase in the HPLC measurements (25°C, 1.0 mL min^{-1}). Size exclusion chromatography (SEC) was performed on an HLC-8320 GPC Eco-SEC equipped with a TSKgel Super AW guard column and TSKgel Super AW (4000 and 2500) columns (Tosoh Co., Tokyo, Japan). DMF with LiBr (10 mM) was employed as a mobile phase in the SEC measurements (40°C, 0.5 mL min^{-1}). The SEC system was calibrated with a polymethylmethacrylate standard (Shoko Science Co., Ltd., Yokohama, Japan). All the samples for SEC analysis were previously filtered through a 0.45 μm PTFE filter (Kanto Chemical Co.).

DSC measurements were performed using a Hitachi High Tech Science X-DSC7000 (Hitachi High-Tech Analysis Co., Tokyo, Japan). Scans were performed under a N_2 atmosphere using a heating rate of 10°C min^{-1} over a temperature range appropriate for each sample. The glass transition temperature (T_g) was determined from the DSC curves in second heating step. The mechanochemical reactions were performed using a planetary ball mill (Pulverisette 7 Premium Line, Fritsch Japan Co., Ltd., Kanagawa, Japan). Milling jars (inner volume = 20 mL) and balls (Φ = 10 mm) were composed of ZrO_2. All the ball millings were performed in 15 min revolution + 5 min stop cycles, where the reaction time was denoted as the summation of the revolution time. The temperature of the milling jar after the reaction was measured using a HIKMICRO thermal camera E03 (Hangzhou Microimage Software Co., Ltd., Hangzhou, China). Field emission-scanning electron microscopy (FE-SEM) analysis was performed on a Hitachi SU8000 microscopy equipped with energy dispersive X-ray spectroscopy (EDX) detector (Hitachi High-Tech Co.).

Solvent-less Michael addition using ball milling



(E)-β-Nitrostyrene (**1a**) (268.5 mg, 1.80 mmol, 1.0 eq.), HJ catalyst (1 mol%), and four balls were added to a jar. Then, propionaldehyde (**2a**) (260 μL, 3.60 mmol, 2.0 eq.) was added, and the jar was sealed and milled with a ball mill (15 – 240 min). After the reaction, the jar was opened, and the mixture was dissolved in acetonitrile (5 mL) and recovered. The crude product was purified by normal-phase flash column chromatography (hexane/EtOAc = 94:6 to 50:50).

^{1}H NMR (400 MHz, chloroform-*d*): δ 9.72 (d, *J* = 1.4 Hz, *syn* isomer, 0.93H), 9.55 (d, *J* = 1.8 Hz, *anti* isomer, 0.07H), 7.43-7.16 (m, 6H), 4.83-4.66 (m, 2H), 3.82 (td, *J* = 9.1, 5.5 Hz, 1H), 2.82-2.74 (m, 1H), 1.22 (d, *J* = 7.3 Hz, *anti* isomer, 0.22H), 1.02-0.96 (m, *syn* isomer, 2.86H).

Chiral HPLC analysis: Retention time = 15.7 (minor *syn* isomer), 20.0 (minor *anti* isomer), 21.5 (major *syn* isomer), 24.3 min (major *anti* isomer).

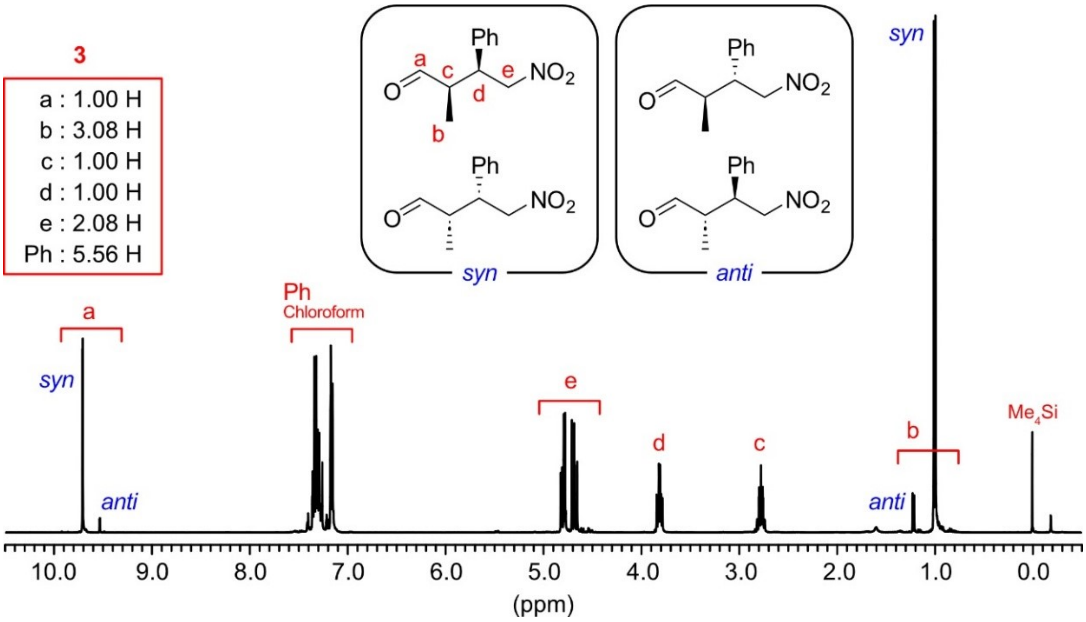


Fig. S1. ^{1}H NMR spectrum of **3** (400 MHz, chloroform-*d*).

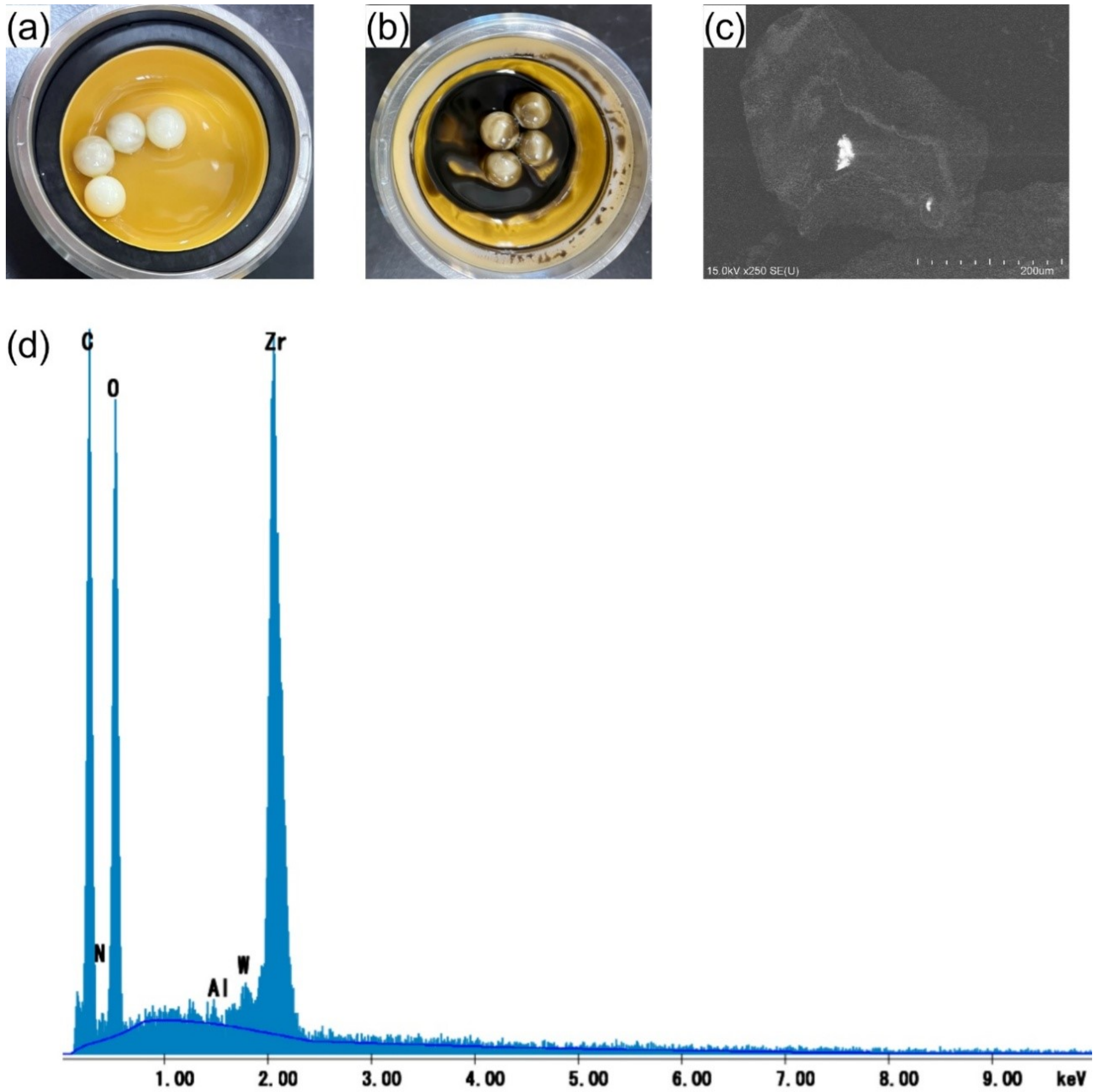


Fig. S2. The reaction mixture after ball milling for 4 h at (a) 200 and (b) 400 rpm. (c) FE-SEM image of the black powder isolated from the reaction mixture. (d) EDX spectrum of the black powder.

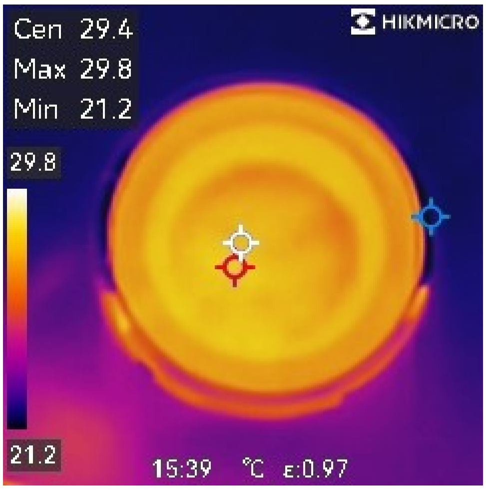


Fig. S3. Thermographic image of the reaction mixture after ball milling for 4 h, which was taken immediately after opening the jar. This suggested that temperature of the reaction mixture was around 30°C.

3. In situ observation of the reaction mixture

In situ powder X-ray diffraction (PXRD) was conducted at BL13XU of SPring-8.[1] A Retsch Ball Mill apparatus MM400 (Retsch GmbH, Germany) was originally customized by Kasai, Nishibori, and coworkers.[2] The apparatus enabled the X-ray beam to pass through a sample in a milling jar. The flat panel detector (FPD), Varex Imaging XRD1611 with a pixel size of 100 μm was used for measurements with the sample-to-detector distance of 353 mm. Milling jar was 3D-printed from polycarbonate (PC) resin and designed to give inner volume of 4.98 mL. Two balls composed of $ZrO2$ (F = 10 mm) were used. The ball milling was operated at 15 Hz. The wavelength of incident X-ray was 0.50 Å calibrated using the $CeO2$ standard sample. In situ PXRD data were collected with an exposure time of 2 s.

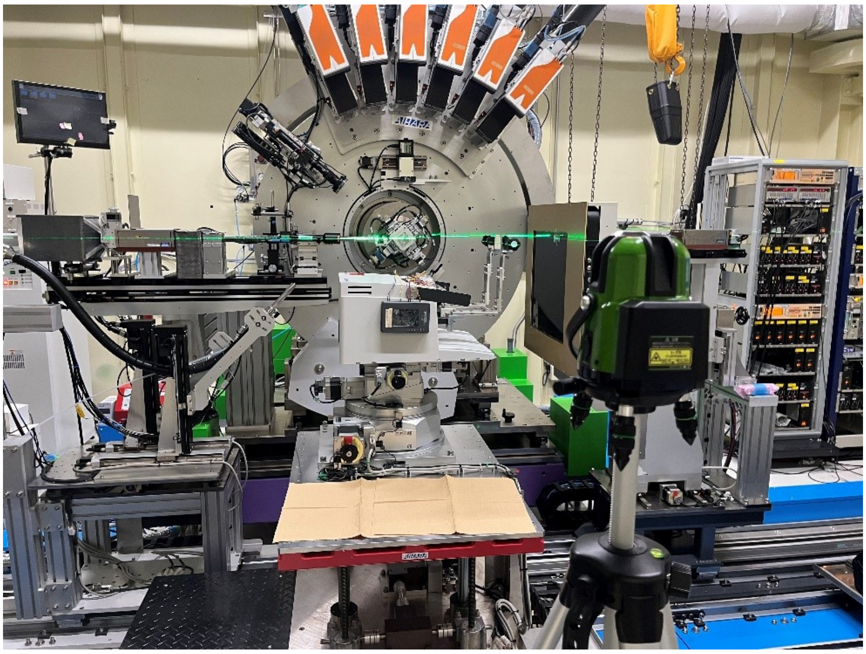
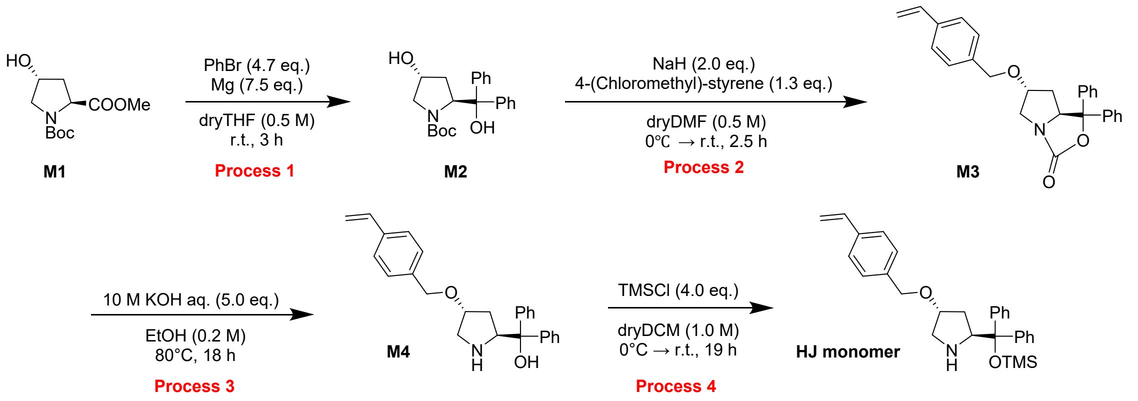
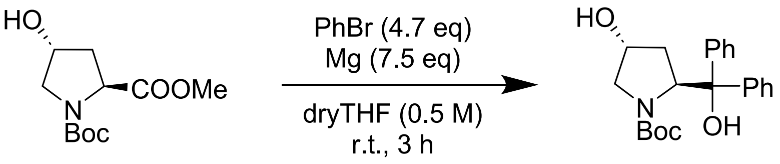


Fig. S4. Overview of the in situ PXRD measurement system.

4. Synthesis of HJ monomer[3,4]



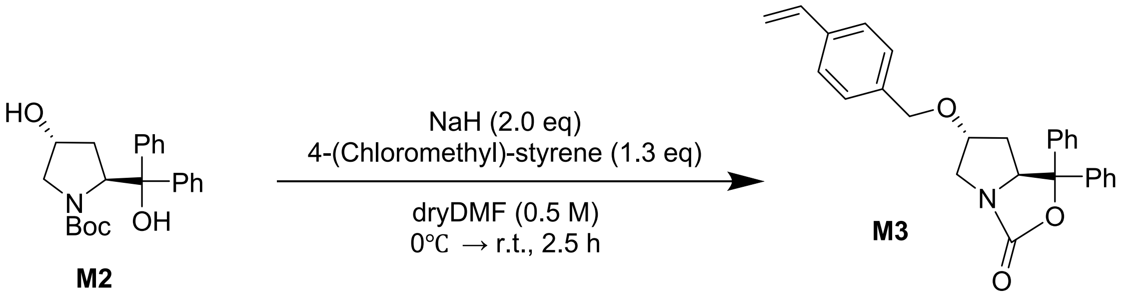
Process 1



M1 **M2**

A 500 mL two-neck round-bottom flask was equipped with a magnetic stirring bar and dried with a heat gun under evacuation for 5 min. The flask was evacuated and backfilled with Ar three times. Mg (22.6 g, 929.7 mmol, 7.5 eq), I_2 (few particles), and dryTHF (51 mL) were added to the flask. Bromobenzene (60.4 mL, 574.1 mmol, 4.7 eq) in dryTHF (90 mL) was added dropwise using a dropping funnel. After completion of the addition, the reaction mixture was cooled in an ice-water bath. A solution of **M1** (29.9 g, 122.0 mmol, 1.0 eq.) in dryTHF (104 mL) was added dropwise to the reaction mixture and continuously stirring overnight. After confirming the completion of the reaction by TLC, the reaction was quenched with HCl aq (1 M, 50 mL). The aqueous layer was extracted with EtOAc four times. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The **M2** crude mixture was used in the next reaction without further purification.

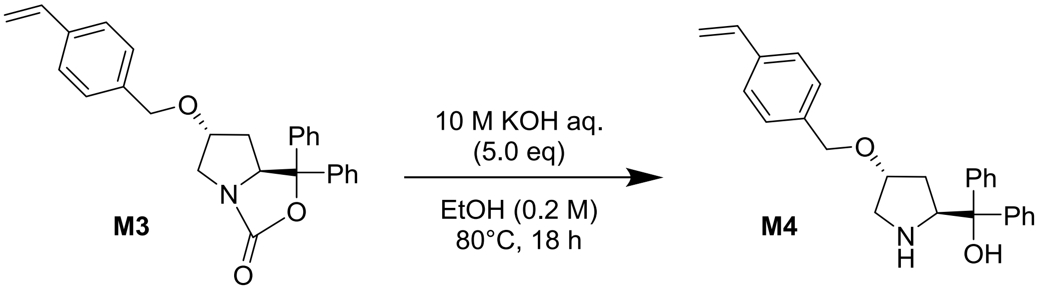
Process 2



A 1-L two-neck round-bottom flask was equipped with a magnetic stirring bar and dried with a heat gun under evacuation for 5 min. The flask was evacuated and backfilled with Ar three times. The flask was charged with NaH (4.89 g, 122.2 mmol, 1.0 eq), dispersed in dryDMF (40 mL) and cooled in an ice-water bath. A solution of **M2** (crude mixture, 122.0 mmol, 1.0 eq) in dryDMF (135 mL) was added dropwise, followed by the addition of 1-(chloromethyl)styrene (17.2 mL, 122.0 mmol, 1.0 eq) in dryDMF (70 mL). The reaction mixture was continuously stirred overnight. After confirming the completion of the reaction by TLC, the reaction was quenched with HCl aq. (1 M, 20 mL) in an ice-water bath. The aqueous layer was extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude mixture was purified by normal-phase flash column chromatography (hexane/EtOAc = 85:15 to 40:60) to give a target compound **M3** as yellow solid (31.4 g, 63% yield in 2 steps).

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.52-7.23 (m, 15H), 6.69 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.75-5.71 (m, 1H), 5.23 (d, *J* = 11.4 Hz, 1H), 4.85 (q, *J* = 5.3 Hz, 1H), 4.42 (s, 2H), 4.13 (t, *J* = 5.7 Hz, 1H), 3.30 (dd, *J* = 12.8, 1.4 Hz, 1H), 1.88 (dd, *J* = 13.3, 5.0 Hz, 1H), 1.27-1.13 (m, 2H).

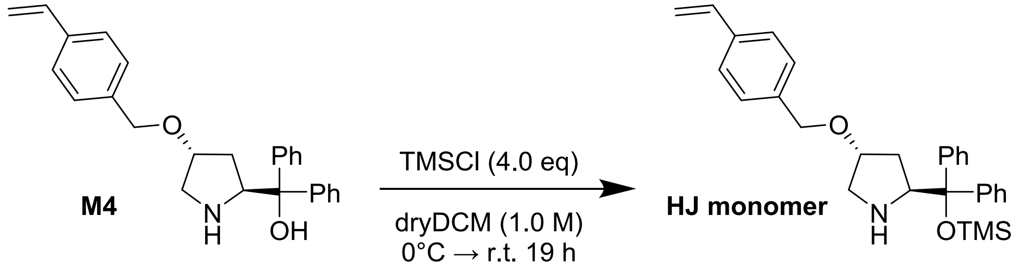
Process 3



A 1-L two-neck round-bottom flask was charged with a solution of **M3** (31.9 g, 76.3 mmol, 1.0 eq) in EtOH (382 mL). A solution of KOH (20.9 g, 381.5 mmol, 5.0 eq) in water (38.2 mL) was added to the reaction mixture. The reaction mixture was heated in an oil bath at 80°C and continuously stirred overnight. After confirming the completion of the reaction by TLC, the reaction mixture was cooled to room temperature, and HCl aq. (1 M, 300 mL) was added to quench the reaction. EtOH was removed under reduced pressure, and the aqueous layer was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude mixture was purified by recrystallization from EtOH to give a target compound **M4** as a white and powdered crystal (19.6 g, 42% yield).

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.57-7.12 (m, 14H), 6.69 (dd, *J* = 17.6, 10.7 Hz, 1H), 5.72 (d, *J* = 17.8 Hz, 1H), 5.22 (d, *J* = 11.0 Hz, 1H), 4.54 (dd, *J* = 9.6, 6.4 Hz, 1H), 4.39 (dd, *J* = 14.0, 12.1 Hz, 2H), 4.01 (t, *J* = 2.1 Hz, 1H), 3.13-3.05 (m, 2H), 1.80-1.62 (m, 2H)

Process 4



A 12.5-mL glass vial was charged with a solution of **M4** (1.77 g, 4.6 mmol, 1.0 eq) and imidazole (1.25 g, 18.4 mmol, 4.0 eq) in dryDCM (4.6 mL). The reaction mixture was cooled in an ice-water bath followed by addition of chlorotrimethylsilane (TMSCl) (2.3 mL, 18.4 mmol, 4.0 eq) dropwise. After removing the ice-water bath, the reaction mixture was continuously stirred for 19 h. After confirming the completion of the reaction by TLC, the reaction was quenched with phosphate buffer aq. (pH 7.0, ca. 6 mL) in the ice-water bath. The aqueous layer was extracted with EtOAc three times. The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude mixture was purified by normal-phase flash column chromatography (hexane/EtOAc = 63:37) to give a target compound **HJ monomer** as a yellow and oily material (2.05 g, 97% yield).

^{1}H NMR (400 MHz,Chloroform-*d*): δ 7.48-7.17 (m, 14H), 6.68 (dd, *J* = 17.8, 11.0 Hz, 1H), 5.71 (dd, *J* = 17.4, 0.9 Hz, 1H), 5.21 (dd, *J* = 11.0, 0.9 Hz, 1H), 4.38-4.33 (m, 3H), 3.79-3.77 (m, 1H), 2.99-2.79 (m, 2H), 1.71-1.68 (m, 2H), -0.11 (s, 9H)

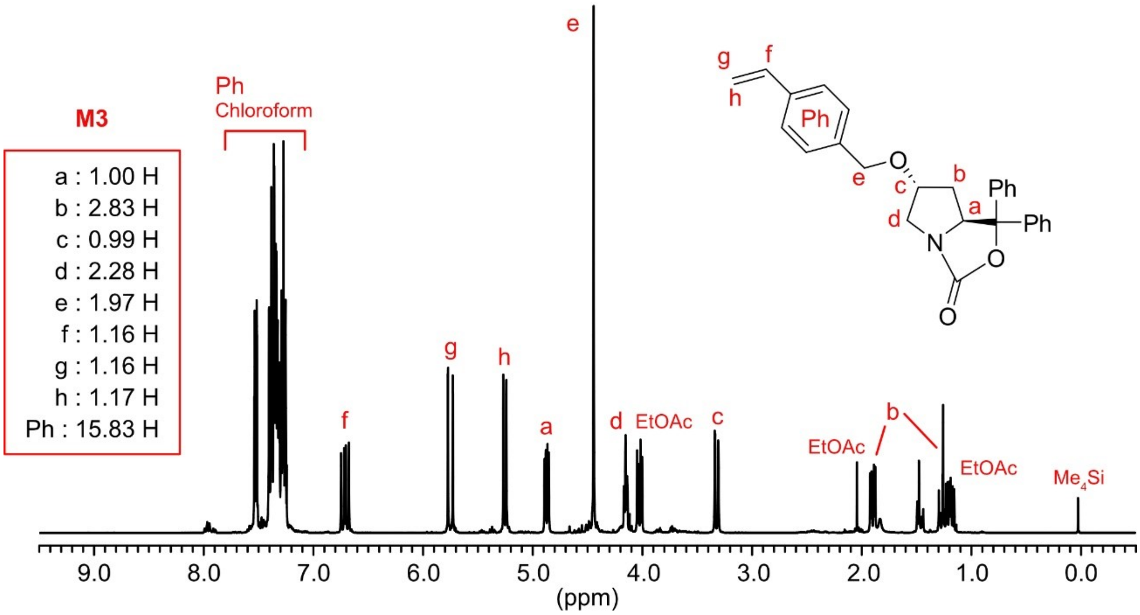


Fig. S5. ^{1}H NMR spectrum of **M3** (400 MHz, chloroform-*d*).

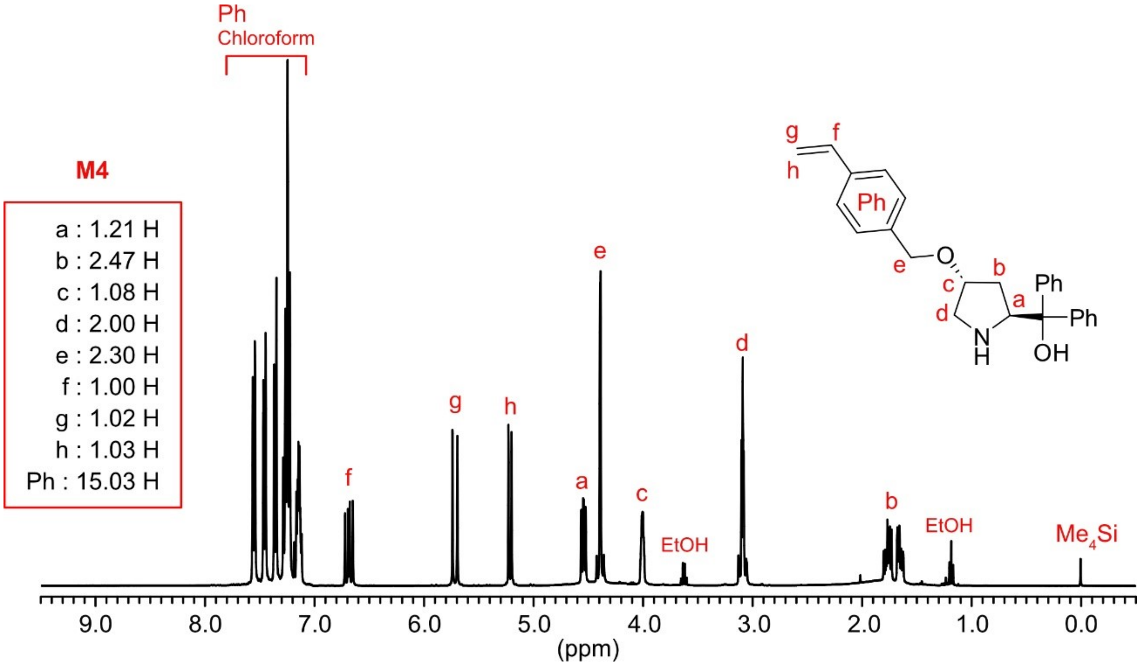


Fig. S6. ^{1}H NMR spectrum of **M4** (400 MHz, chloroform-*d*).

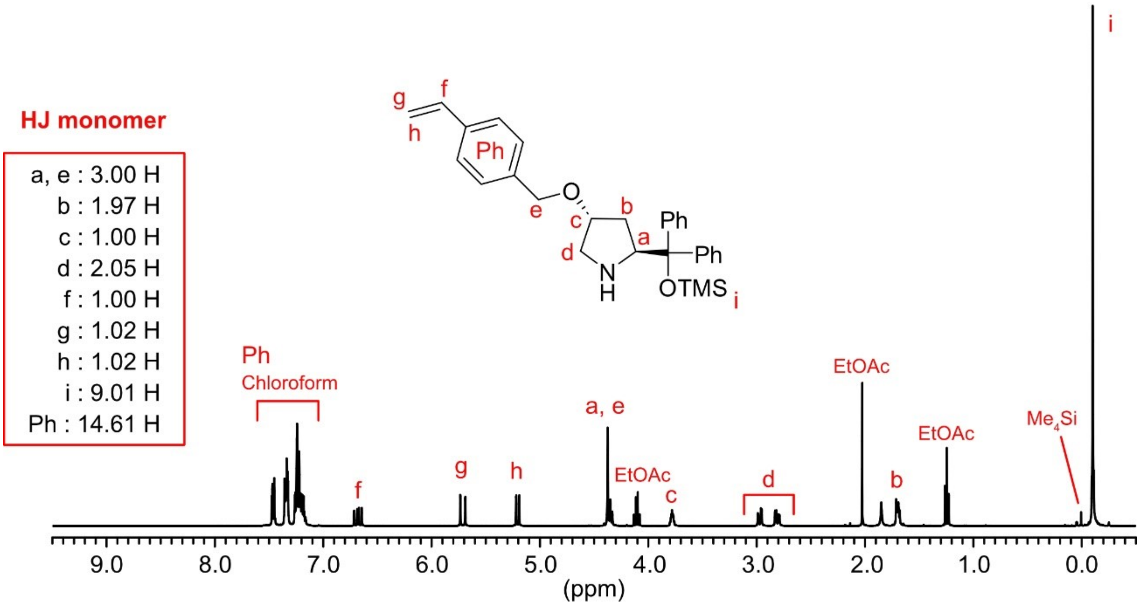
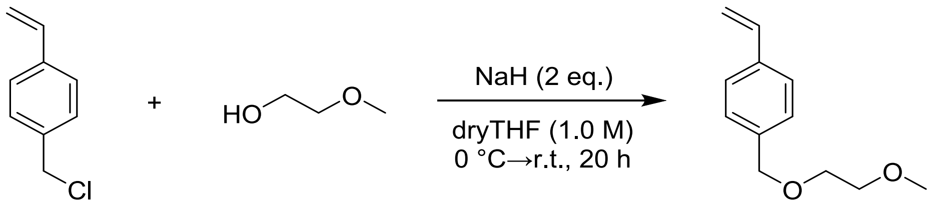


Fig. S7. ^{1}H NMR spectrum of **HJ monomer** (400 MHz, chloroform-*d*).

5. Synthesis of EGS[5]



EGS

A 200-mL two-neck round-bottom flask was charged with NaH (2.62 g, 65.6 mmol, 2 eq.) and dryTHF (5 mL) and stirred. The flask was transferred to an ice bath, and a solution of 2-methoxyethanol (5140.0 mL, 4986.1 mg, 65.5 mmol, 2 eq.) diluted with dryTHF (18 mL) was added dropwise over 15 min. Similarly, a solution of 4-(chloromethyl)styrene (4.63 mL, 5.00 g, 32.8 mmol, 1 eq.) diluted with dryTHF (10 mL) was added dropwise over 10 min, and the mixture was allowed to warm to room temperature and stirred for 20 h. The reaction was quenched by adding 1 M HCl aq. (30 mL). The organic phase was extracted twice with diethyl ether and washed once with sat. NaCl aq. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by normal-phase flash column chromatography (hexane/EtOAc = 94:6 to 58:42) to give the target compound as a yellow oil (5.15 g, 82% yield).

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.40-7.26 (m, 4H), 6.71 (dd, *J* = 17.6, 10.7 Hz, 1H), 5.74 (d, *J* = 17.8 Hz, 1H), 5.23 (d, *J* = 11.0 Hz, 1H), 4.56 (s, 2H), 3.62-3.55 (m, 4H), 3.39 (s, 3H).

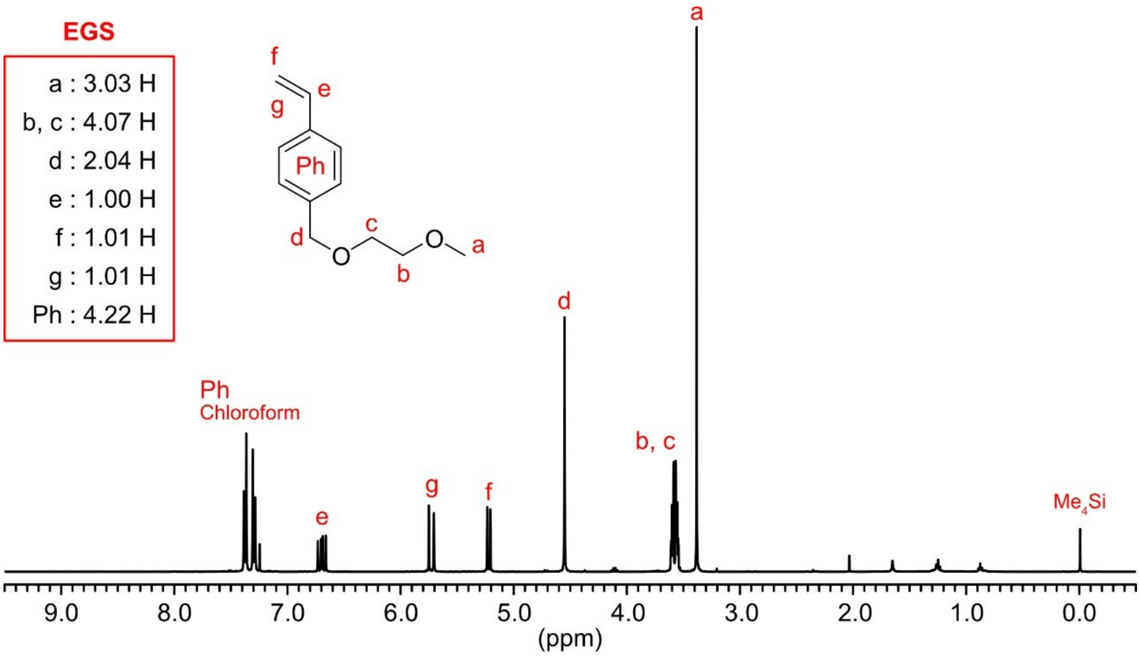
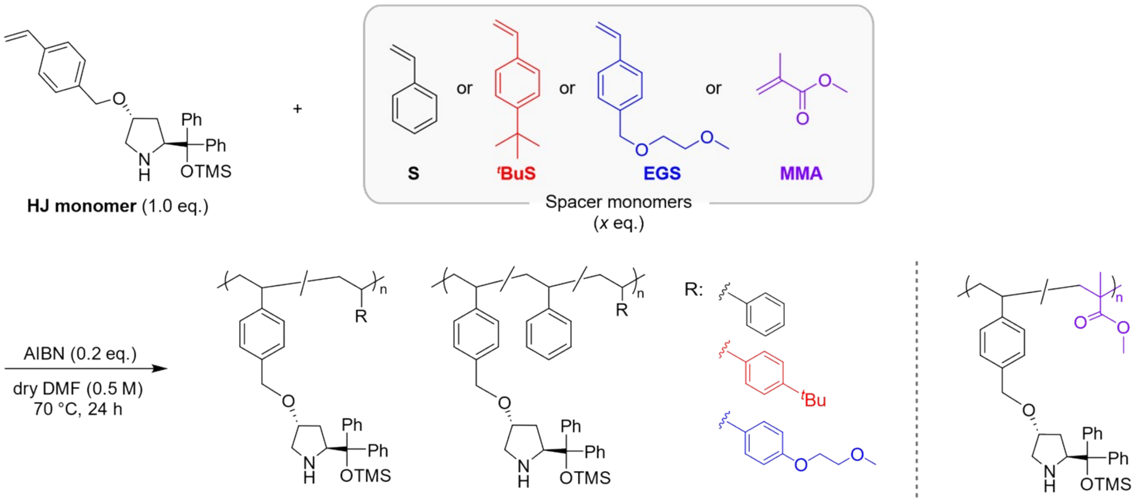


Fig. S8. ^{1}H NMR spectrum of **EGS** (400 MHz, chloroform-*d*).

6. Preparation of polymer-supported HJ



HJ monomer (1.0 eq.), spacer monomers (**S**, **^{t}BuS**, **EGS** or **MMA**, *x* eq.), and AIBN (0.2 eq.) were dissolved in dryDMF (0.5 M with respect to **HJ monomer**, **Table S1**). The prepared solution was degassed by freeze-thaw cycle (3 cycles) or N_2 bubbling (30 min) and placed in an incubator (70°C) for 24 h. The crude mixtures were purified by either reprecipitation in methanol or dialysis in acetone (M.W.C.O. = 1 kDa). After drying in vacuo overnight, the polymer was obtained as white or yellowish powder. ^{1}H NMR spectroscopy, SEC, and DSC measurements were performed to determine the HJ catalyst loading, molecular weight, and T_g, respectively.

Table S1. Yields and material properties of polymer-supported **HJ**

Polymer	Spacer monomers (*x* eq.)	Yield [%]	**[HJ]** [mmol g^{-1}][a]	M_w [g mol^{-1}][b]	T_g [°C][c]
pHJ-S	**S** (9.0 eq.)	63	0.55	25,200	97.4
pHJ-^{t}BuS	**^{t}BuS** (9.0 eq.)	60	0.39	8,900	137.1
pHJ-EGS	**EGS** (4.0 eq.)	60	0.26	38,300	22.8
pHJ-S-^{t}BuS	**S** (4.5 eq.), **^{t}BuS** (4.5 eq.)	69	0.49	23,000	108.9
pHJ-S-EGS	**S** (2.0 eq.), **EGS** (2.0 eq.)	28	0.62	23,800	57.9
pHJ-MMA	**MMA** (9.0 eq.)	60	1.21	32,500	103.3

[a] Determined from ^{1}H NMR spectra. [b] Determined by SEC. [c] Determined by DSC.

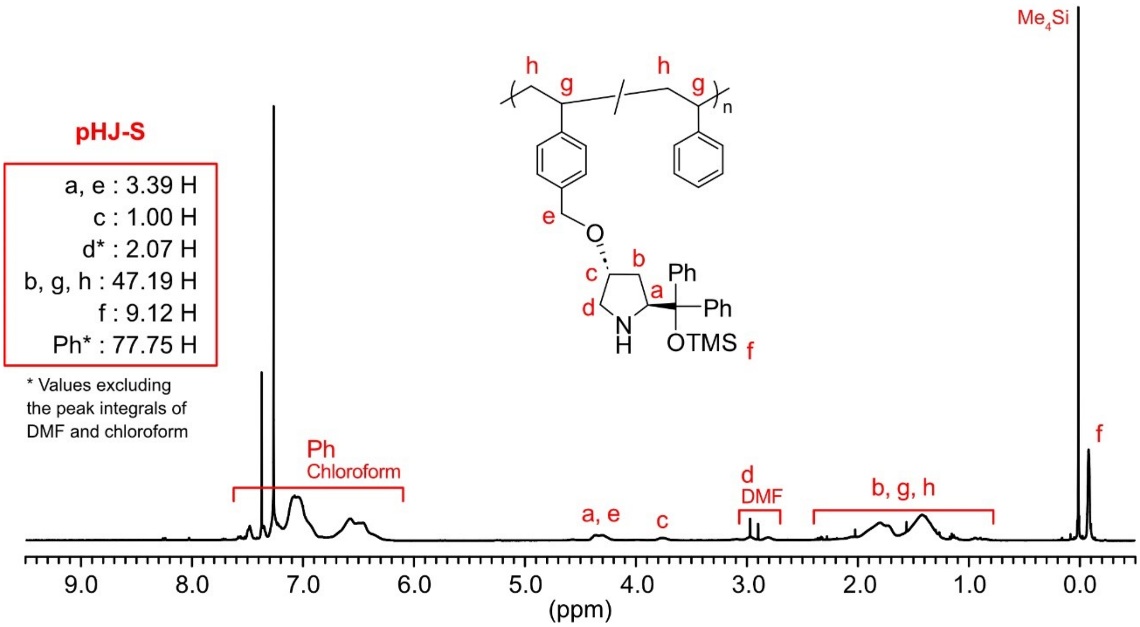


Fig. S9. ^{1}H NMR spectrum of **pHJ-S** (400 MHz, chloroform-*d*).

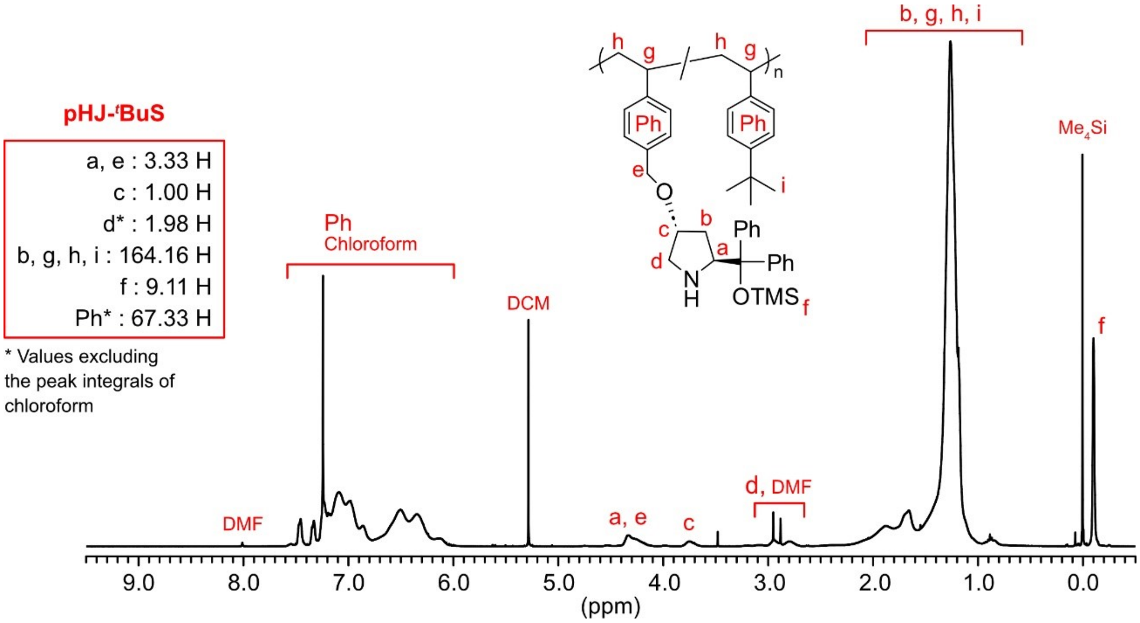


Fig. S10. ^{1}H NMR spectrum of **pHJ-^{t}BuS** (400 MHz, chloroform-*d*).

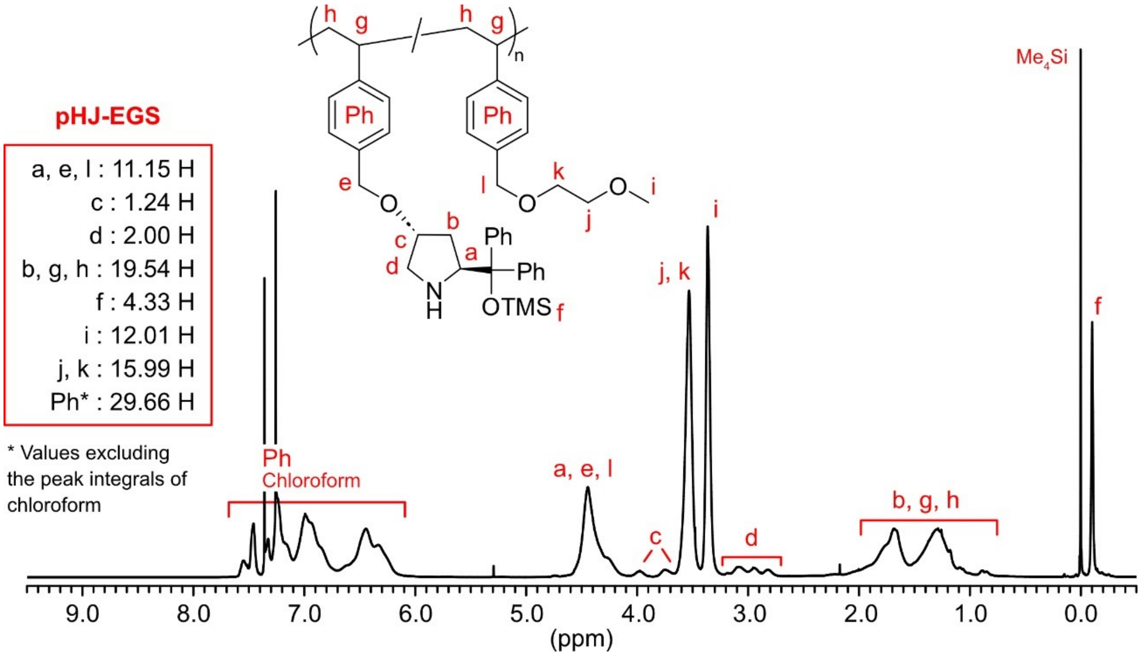


Fig. S11. ^{1}H NMR spectrum of **pHJ-EGS** (400 MHz, chloroform-*d*).

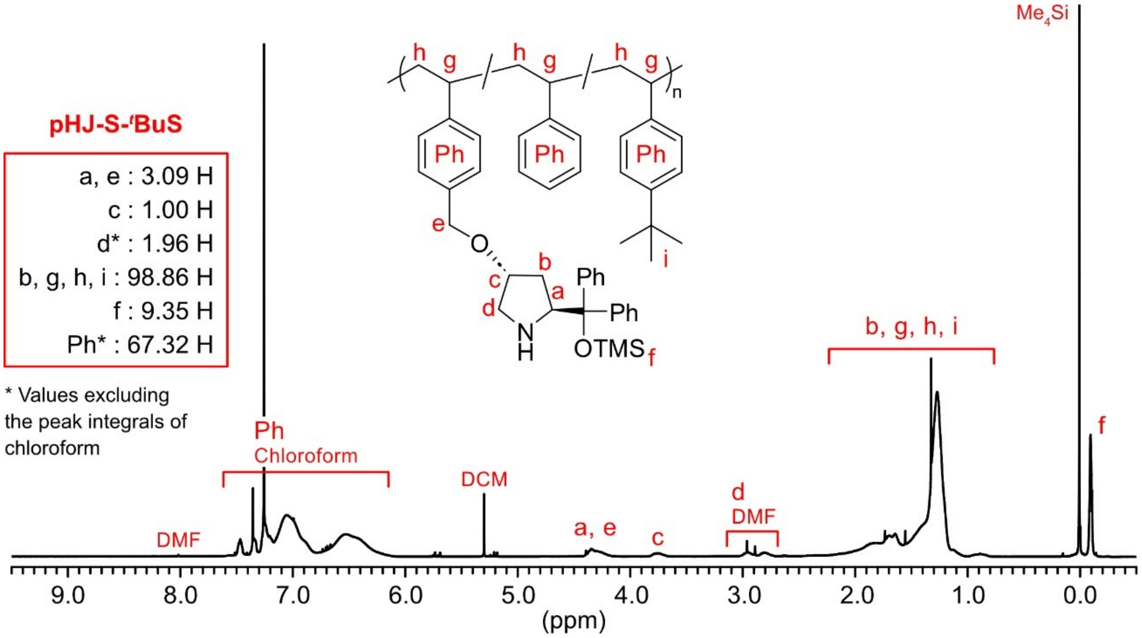


Fig. S12. ^{1}H NMR spectrum of **pHJ-S-^{t}BuS** (400 MHz, chloroform-*d*).

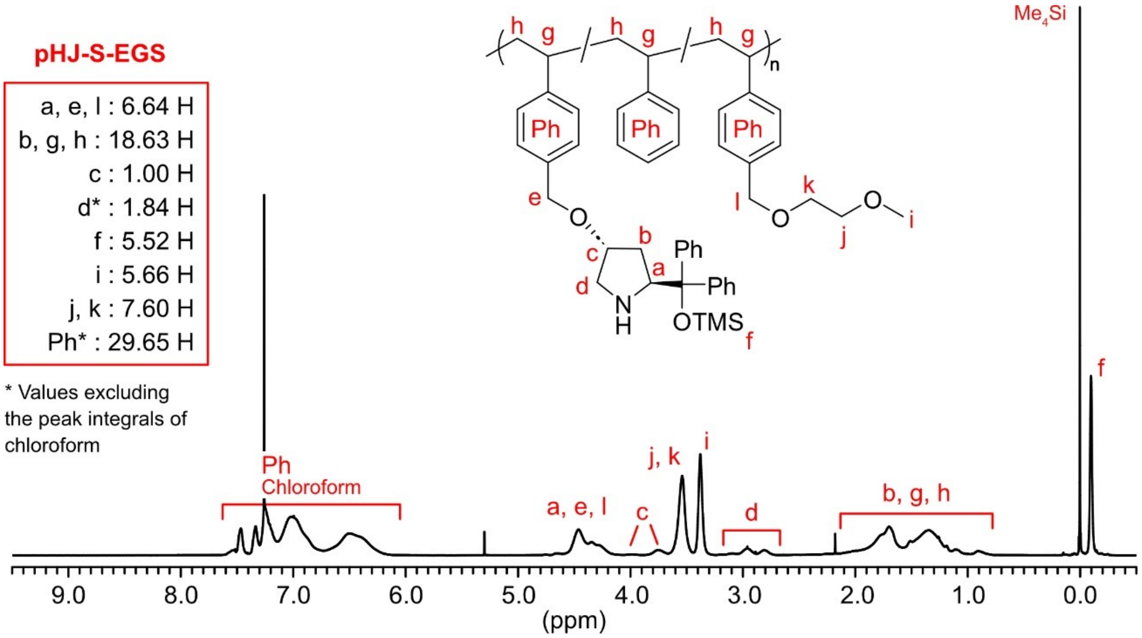


Fig. S13. ^{1}H NMR spectrum of **pHJ-S-EGS** (400 MHz, chloroform-*d*).

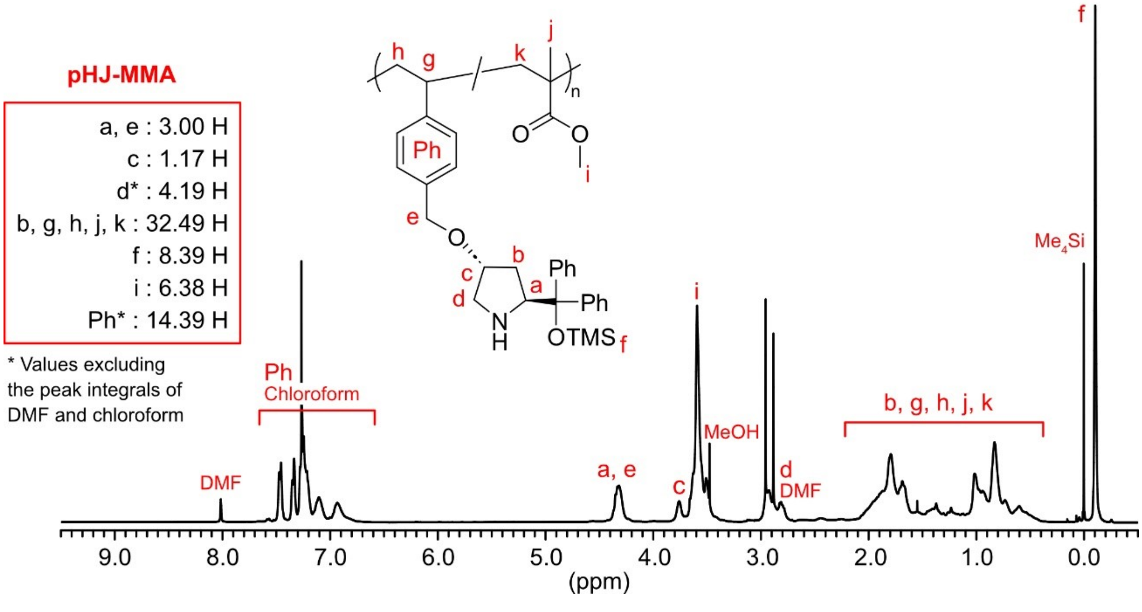


Fig. S14. ^{1}H NMR spectrum of **pHJ-MMA** (400 MHz, chloroform-*d*).

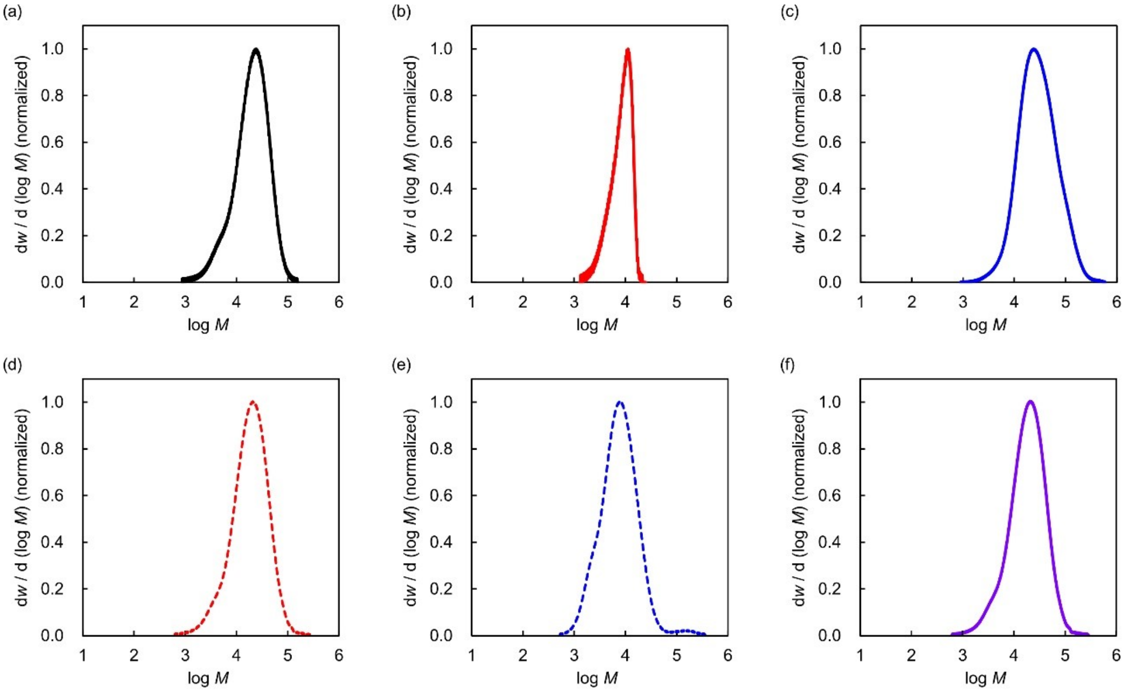


Fig. S15. SEC chromatograms of (a) **pHJ-S**, (b) **pHJ-^{t}BuS**, (c) **pHJ-EGS**, (d) **pHJ-S-^{t}BuS**, (e) **pHJ-S-EGS**, and (f) **pHJ-MMA**. Conditions: eluent = DMF containing LiBr (10 mM) at 0.5 mL min^{-1}.

7. Catalytic activity of polymer-supported HJ with different chemical properties

Table S2. Effect of catalyst loading (**[HJ]**) of **pHJ-S** on catalytic activity.

[HJ] **[mmol g^{-1}]**	**M_w** **[g mol^{-1}]**	**T_g** **[°C]**	**TOF** **[h^{-1}]**[a]	**TON** **[-]**[b]	**d.r.** **(*syn*/*anti*)**[b]
2.2	14,200	69.3	55	>99	82:18–88:12
1.02	24,200	93.1	45	99	88:12–89:11
0.57	25,000	97.4	64	84	75:15–90:10

[a] Determined by yield from 0.25 to 0.5 h. [b] Determined by HPLC.

Table S3. Effect of molecular weight of **pHJ-S** on catalytic activity.

[HJ] **[mmol g^{-1}]**	**M_w** **[g mol^{-1}]**	**T_g** **[°C]**	**TOF** **[h^{-1}]**[a]	**TON** **[-]**[b]	**d.r.** **(syn/anti)**[b]
0.73	15,600	96.2	37	92	86:14–91:9
1.02	24,200	93.1	45	99	88:12–89:11
0.92	34,700	101.0	52	98	88:12–93:7

[a] Determined by yield from 0.25 to 0.5 h. [b] Determined by HPLC.

Table S4. Catalytic activity of PS-supported HJ catalysts.

Catalyst	**T_g** **[°C]**	**TOF** **[h^{-1}]**[a]	**TON** **[-]**[b]	**d.r.** **(syn/anti)**[b]
pHJ-S	97.4	64	84	84:16-90:10
pHJ-EGS	24.6	66	86 ± 9	85:15-92:8
pHJ-S-EGS	57.9	65	>99	87:13-92:8
pHJ-^{t}BuS	137.1	48	76 ± 1	84:16-90:10
pHJ-S-^{t}BuS	108.8	46	92	87:13->99:1

[a] Determined by yield from 0.25 to 0.5 h. [b] Determined by HPLC.

8. Molecular weight of pHJ-S before and after Michael addition using ball milling

After Michael addition reaction using a ball mill, the spent **pHJ-S** was recovered by addition of acetonitrile to the reaction mixture and centrifugation of the resulting suspension. The SEC chromatogram of the spent **pHJ-S** was obtained (Fig. S16, red) and compared with those of **pHJ-S** before ball milling (blue), **1a** (violet), and **3a** (light blue). The peak observed at log M = 2.1 in the SEC chromatogram of the spent **pHJ-S** corresponded to the residual **3a**.

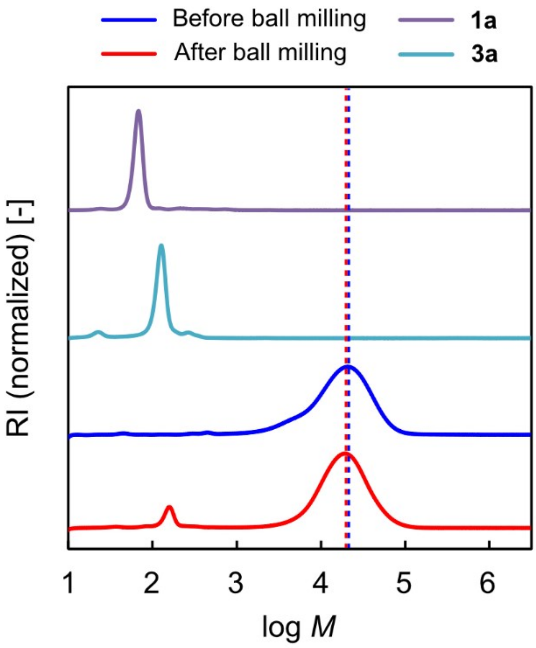


Fig. S16. SEC chromatograms of **1a** (violet), **3a** (light blue), and **pHJ-S** before (blue) and after (red) Michael addition using a ball milling. Conditions: eluent = DMF containing LiBr (10 mM) at 0.5 mL min^{-1}.

9. Analysis of the Michael addition reaction mixture

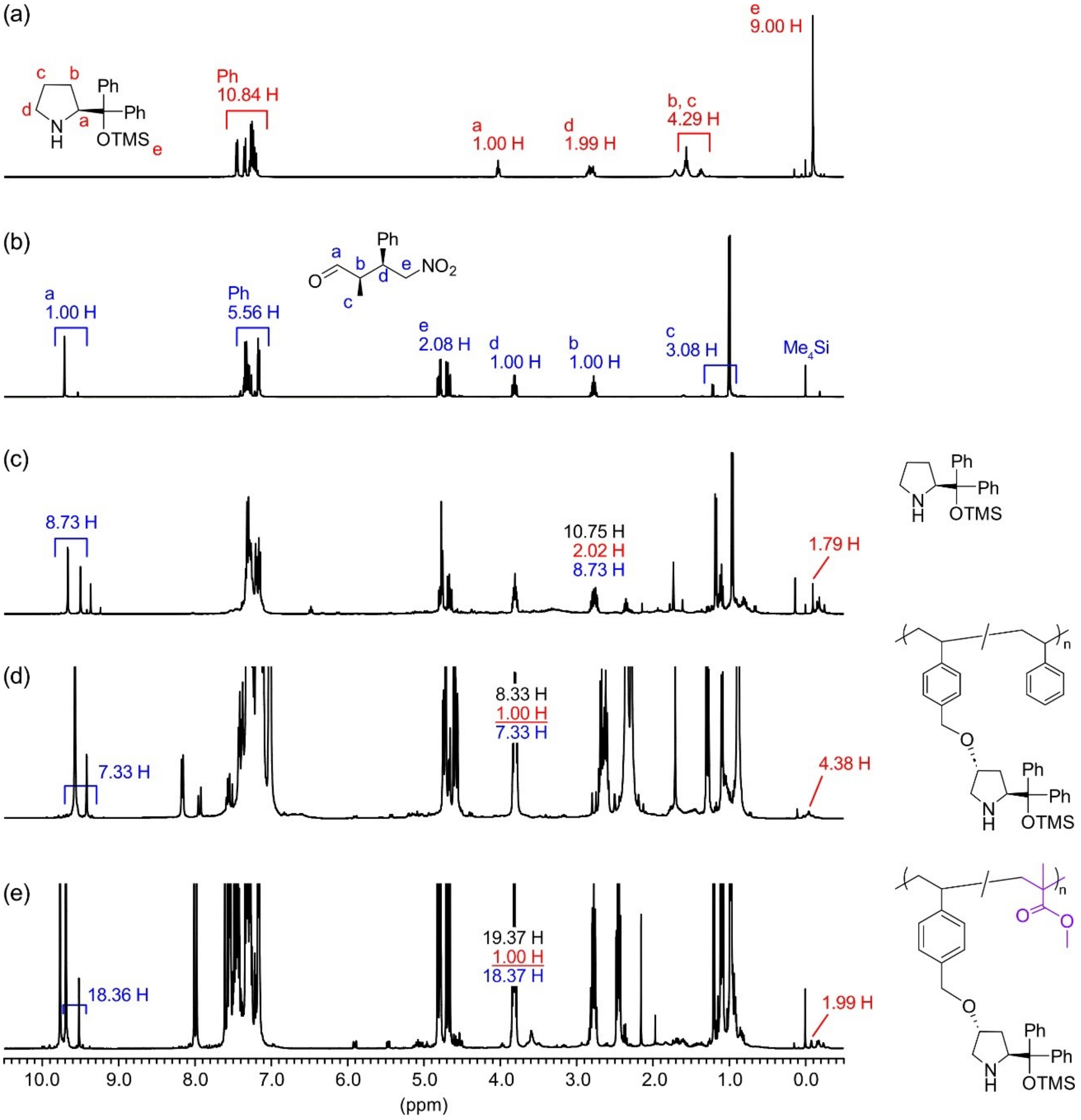


Fig. S17. ^{1}H NMR spectra of (a) **HJ**, (b) **3**, and the reaction mixture with (c) **HJ**, (d) **pHJ-S**, (e) **pHJ-MMA** (reaction time = 4 h). In (c), (d), and (e), the theoretical integrals of the peak originating from the TMS group (approximately –0.1 ppm) is 9. Therefore, the TMS remaining rates were calculated to be 20 (= 1.79/9 × 100), 49 (= 4.38/9 × 100), and 22% (= 1.99/9 × 100) for **HJ**, **pHJ-S**, and **pHJ-MMA**, respectively.

10. State of the polymer-supported HJ before and after the reaction

All the polymer-supported catalysts (white or yellow powders, Fig. S18a) remained as solid after addition of **1a** and **2a** (Fig. S18b). After the reaction, reaction mixture turned into white and paste, where white solid was still observed (Fig. S18c). This suggested that the polymer catalyst powders were grinded into small particles during ball milling, and existed as the solids after completion of the reaction.

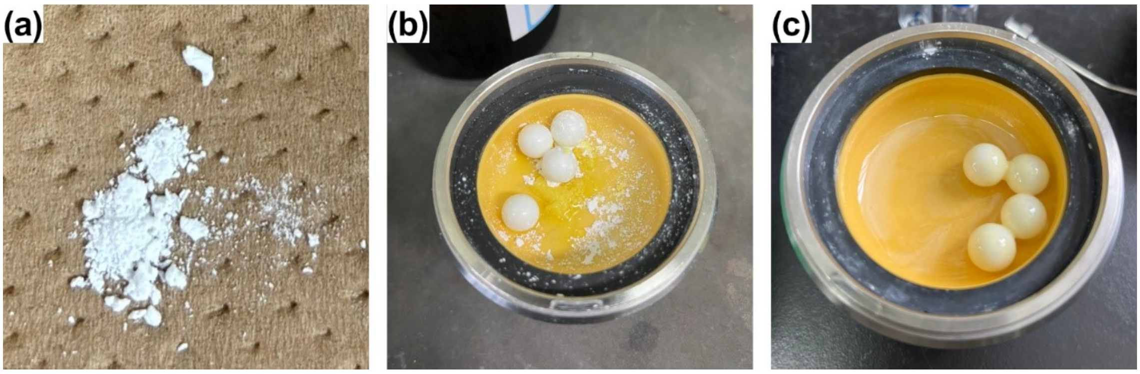
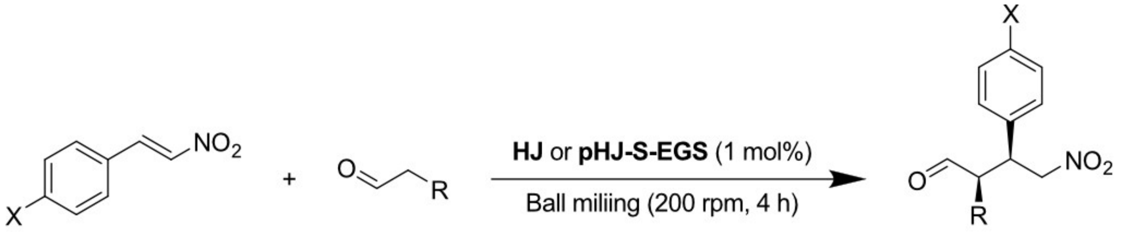


Fig. S18. Photographs of the (a) the **pHJ-S-^{t}BuS**, and the reaction mixture (b) before and (c) after the reaction with a ball mill.

11. Investigation of substrate scope



(1.0 eq.)
1a: X = H
1b: X = Br
1c: X = OMe

(2.0 eq.)
2a: R = Me
2b: R = Et
2c: R = *i*Pr

3a: X = H, R = Me
3b: X = Br, R = Me
3c: X = OMe, R = Me
3d: X = H, R = Et
3e: X = H, R = *i*Pr

A nitrostyrene (**1a**–**c**) (1.80 mmol, 1.0 eq.), **HJ** or **pHJ-S-EGS** (1 mol%), and four balls were added to a jar. Then, an aldehyde (**2a**–**c**) (3.60 mmol, 2.0 eq.) was added, and the jar was sealed and milled with a ball mill (200 rpm, 4 h). After the reaction, the mixture was dissolved in chloroform-*d* (5 mL), followed by the addition of xylene (65.0 μL, 0.54 mmol, 0.3 eq.) as an internal standard. The solution was analyzed using ^{1}H NMR to determine the yield and diastereoselectivity.

Table S5. Solvent-less Michael addition reaction using ball milling with various nitroalkenes and aldehydes.

Product	Catalyst	Yield [%]	*syn*/*anti*
3a	**HJ**	51[a]	94:6[a]
	pHJ-S-EGS	>99[a]	87:13[a]
3b	**HJ**	56[b]	88:12[b]
	pHJ-S-EGS	80[b]	80:20[b]
3c	**HJ**	34[b]	96:4[b]
	pHJ-S-EGS	75[b]	85:15[b]
3d	**pHJ-S-EGS**	17[b]	83:17[b]
3e	**pHJ-S-EGS**	4[b]	83:17[b]

[a] Determined by HPLC. [b] Determined by ^{1}H NMR.

12. Refereneces

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