Supplemental Material for

(1R, 2R)-(+)-(1, 2)-DPEN bonded sulfonic acid resin: a trifunctional heterogeneous catalyst for asymmetric Michael additions of acetone to nitroolefins

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General Methods. ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance 400 spectrometer, and tetramethylsilane was used as a reference. ^1H NMR spectroscopic data are represented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet, br = broad), integration, coupling constants in Hertz (Hz). ^{13}C NMR spectroscopic data are reported in ppm. High-resolution mass spectra were measured with a Bruker Daltonics micrOTOF-Q II instrument (ESI). HPLC analysis was measured using ChiralPak AS-H column.

The functional groups of the catalyst were characterized by infrared spectroscopy (Nicolet AVATAR 370 FTIR spectrometer). The surface morphologies of the sulfonyl chloride resin and catalyst **2** were observed by a scanning electronic microscope (SEM; S4800; Hitachi, Japan). N_2 adsorption and desorption experiments were performed in liquid nitrogen using a NOVA 2000e analyzer (Quantachrome, US). The total surface area (S_{BET}) was calculated from the linear part of the Brunauer-Emmer-Teller (BET). The micro pore volume (V_{micro}) and the external surface area (S_{EXT}) were estimated by the t-plot. The pore-size distributions were obtained using the method of Barret-Joyner-Halenda (BJH).

Materials: (1R, 2R)-(+)-(1, 2)-DPEN was purchased from Jiangsu Lianyuangang chiral chemical Co., Ltd. Sulfonyl chloride resin was obtained from Tianjin Nankai Hecheng Science & Technology Co., Ltd. (2.1 mmol/g sulfonyl chloride group). All the other chemicals in the present study were reagent grade and purchased from

commercial suppliers without further purification unless otherwise noted.

General preparation for β -nitroolefins

(E)-(2-nitrovinyl)benzene (4a)^[1, 2]: A round bottom flask was charged with methanol (50 mL), nitromethane (6.1 g, 100 mmol) and benzaldehyde (10.6 g, 100mmol). The flask which fitted with a mechanical stirrer and a thermometer was packed in ice-salt baths. A solution of sodium hydroxide was prepared by dissolving 4.2 g (105 mmol) of sodium hydroxide in adequate water and cooled. It was then diluted to 50 mL with ice water, and poured into the above mixture. The reaction mixture was stirred at room temperature for 6h, and then was adjusted to PH = 7 with HCl (aq, 1M). The resulting aqueous solution was extracted with EtOAc (3×20mL). The organic extracts were combined, dried over Na₂SO₄ and filtered. The filtrate was concentrated and a brown solid was obtained. The crude solid was purified by recrystallization with ethanol.

The β -nitroolefins (**4b-4g**) were prepared by the same method and were all known compounds with spectroscopic data identical to those reported in the literature.^[2, 3] All of β -nitroolefins were determined by comparison with the known ¹H NMR.

¹H NMR (400 MHz, CDCl₃) δ : 7.35–7.57 (m, 5H), 7.60 (d, J = 13.5 Hz 1H), 8.00 (d, J=13.5 Hz, 1H).

¹H NMR (400 MHz, CDCl₃) δ : 3.87 (s, 3H), 6.97 (d, J=8.5 Hz, 2H), 7.50 (d, J=13.7 Hz, 2H), 7.55 (d, J=9.0 Hz, 1H), 7.98 (d, J=13.7 Hz, 1H).

^1H NMR (400 MHz, CDCl_3) δ : 2.43 (s, 3H), 7.27–7.47 (m, 4H), 7.57 (d, J = 13.5Hz, 1H), 7.99 (d, J =13.5 Hz, 1H).

^1H NMR (400 MHz, CDCl_3) δ : 7.32–7.42 (m, 4H), 7.58 (d, J =13.7 Hz, 1H), 7.95 (d, J =13.7 Hz, 1H).

^1H NMR (400 MHz, CDCl_3) δ : 7.37–7.46 (m, 2H), 7.53 (dd, J_1 =8.0 Hz, J_2 =1.0 Hz, 1H), 7.62 (dd, J_1 =7 Hz, J_2 =1.7 Hz, 1H), 7.63 (d, J =13.7 Hz, 1H), 8.44 (d, J =13.7 Hz, 1H).

^1H NMR (400 MHz, CDCl_3) δ : 8.32 (d J =8.6, 2H), 8.03 (d, J =13.7, 1H), 7.74 (d, J =8.6 Hz, 2H), 7.63 (d, J =13.7 Hz 1H).

^1H NMR (400 MHz, CDCl_3) δ : 7.61–7.65 (m, 1 H), 7.68–7.74 (m, 1 H), 7.75–7.8 (m, 1 H), 8.22 (dd, J_1 = 8.13 Hz, J_2 =1.3 Hz, 1 H), 8.53 (d, J = 13.5 Hz, 1 H).

General preparation for the raceme

Acetone (0.1 mol), β -nitroolefins (4a-4g, 0.1 mol) and DL-proline (2mmol) were dissolved in methanol (20 mL). The reaction mixture was stirred vigorously at refluxing temperature until TLC showed the β -nitroolefins disappeared. The mixture was concentrated and the residue was then purified by column chromatography on silica gel (200 –300 mesh).

NMR and HRMS data for catalysts and Michael addition products

White powder (yield: 65%). ^1H NMR (400 MHz, CDCl_3) δ : 2.33 (s, 3H), 4.14 (d, J =5.2 Hz, 1H), 4.39 (d, J =5.2 Hz, 1H), 6.98 (d, J =8.2 Hz, 2H), 7.09–7.25 (m, 10H), 7.32 (d, J =8.2 Hz, 2H).

^{13}C NMR (125 MHz, CDCl_3): δ (ppm) =142.5, 141.5, 139.3, 137.2, 129.1, 128.3, 128.2, 127.4, 127.3, 127.0, 126.8, 126.6, 63.5, 60.6, 21.4.

HRMS (ESI Positive): calc. for $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2\text{S}$, $[\text{M}+\text{H}]^+$ 367.1480, found 367.1476.

White powder (yield: 60%). ^1H NMR (400 MHz, CDCl_3) δ : 4.02 (d, J =9.1 Hz, 1H), 4.38 (d, J =9.1 Hz, 1H), 6.56 (d, J =8.7 Hz, 2H), 6.78–7.15 (m, 10H), 7.34 (d, J =8.7 Hz, 1H).

^{13}C NMR (125 MHz, CDCl_3): δ (ppm) =160.1, 141.5, 139.2, 131.2, 129.1, 129.0, 128.4, 128.2, 127.4, 127.0, 126.8, 126.5, 63.4, 60.5.

HRMS (ESI Positive): calc. for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_3\text{S}$, $[\text{M}+\text{H}]^+$ 369.1284, found 369.1286.

White powder (yield: 62%). ^1H NMR (400 MHz, CDCl_3) δ : 7.36–7.22 (m, 10H), 4.56 (d, J =5.0, 1H), 4.29 (d, J =5.0, 1H), 2.25 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3): δ (ppm) =141.8, 139.6, 128.7, 128.6, 127.9, 127.8, 126.8, 126.6, 63.3, 60.1, 40.6.

HRMS (ESI Positive): calc. for $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$, $[\text{M}+\text{H}]^+$ 291.1167, found 291.1167.

White powder (yield: 55%). ^1H NMR (400 MHz, CDCl_3) δ : 7.23–7.39 (m, 10H), 4.70 (d, $J=4.7\text{Hz}$, 1H), 4.34 (d, $J=4.7\text{Hz}$, 1H), 2.82 (d, $J=14.9$, 1H), 2.29–2.34 (m, 2H), 2.17–2.22 (m, 1H), 2.01–2.03 (m, 1H), 1.91–1.95 (m, 1H), 1.86 (d, $J=18.5\text{Hz}$, 1H), 1.65–1.70 (m, 1H), 1.32–1.37 (m, 1H), 0.90 (s, 3H), 0.69 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3): δ (ppm) = 215.3, 141.2, 140.0, 128.5, 127.8, 127.6, 127.1, 63.8, 60.1, 58.5, 50.5, 48.0, 45.9, 42.6, 26.9, 25.4, 19.8, 19.5.

HRMS (ESI Positive): calc. for $\text{C}_{24}\text{H}_{30}\text{N}_2\text{O}_3\text{S}$, $[\text{M}+\text{H}]^+$ 427.2072, found 427.2069.

^1H NMR (400 MHz, CDCl_3) δ : 7.20–7.35 (m, 5H), 4.69 (dd, $J_1=12.5\text{ Hz}$, $J_2=6.5\text{ Hz}$, 1H), 4.60 (dd, $J_1=12.5\text{ Hz}$, $J_2=8.0\text{ Hz}$, 1H), 3.97–4.03 (m, 1H), 2.92 (d, $J=5\text{ Hz}$, 2H), 2.12 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3): δ (ppm) = 205.4, 138.8, 129.1, 127.9, 127.4, 79.5, 46.1, 39.0, 30.4.

HRMS (ESI Positive): calc. for $\text{C}_{11}\text{H}_{13}\text{NO}_3$, $[\text{M}+\text{H}]^+$ 208.0974, found 208.0964.

The enantiomeric excess was determined by chiral HPLC with a Chiralpack AS-H column at 213nm (n-hexane:2-propanol = 85:15), 1.0 mL/min; $t_r=22.6\text{ min}$ (minor), 29.4 min (major).

^1H NMR (400 MHz, CDCl_3) δ : 7.13 (d, $J = 9.4\text{ Hz}$, 2H), 6.84 (d, $J = 9.4\text{ Hz}$, 2H), 4.65 (dd $J_1=12.2\text{ Hz}$, $J_2=6.9\text{ Hz}$, 1H), 4.55 (dd, $J_1=12.2\text{ Hz}$, $J_2=7.8\text{ Hz}$, 1H), 3.94–3.98 (m, 1H), 3.77 (s, 3H), 2.88 (d, $J=7.1\text{ Hz}$, 2H), 2.10 (s, 3H)

^{13}C NMR (125 MHz, CDCl_3): δ (ppm) = 205.5, 159.1, 130.7, 128.4, 114.4, 79.7, 55.2,

48.3, 38.4, 30.4.

HRMS (ESI Positive): calc. for $C_{12}H_{15}NO_4$, $[M+H]^+$ 238.1079, found 238.1080.

The enantiomeric excess was determined by chiral HPLC with a Chiralpack AS-H column at 213nm (n-hexane:2-propanol =8:2), 1.4 mL/min; t_r =16.9 min (minor), 36.6 min (major).

1H NMR (400 MHz, $CDCl_3$) δ : 2.13 (s, 3H), 2.33 (s, 3H), 2.91 (d, J =7.2Hz, 2H), 3.99 (m, 1H), 4.59 (dd, J = 8.0, 12.0 Hz, 1H), 4.68 (dd, J =6.8, 12 Hz, 1H), 7.11–7.16 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) =205.7, 137.9, 136.0, 130.0, 127.5, 79.9, 46.4, 39.0, 30.7, 21.3.

HRMS (ESI Positive): calc. for $C_{12}H_{15}NO_3$, $[M+Na]^+$ 244.095, found 244.0972.

The enantiomeric excess was determined by chiral HPLC with a Chiralpack AS-H column at 213nm (n-hexane:2-propanol =85:15), 1.0 mL/min; t_r =13.8 min (minor), 19.4 min (major).

1H NMR (400 MHz, $CDCl_3$) δ : 7.30 (d, J =8.5 Hz, 2H), 7.15 (d, J =8.5 Hz, 2H), 4.68 (dd, J_1 =12.4 Hz, J_2 =6.7 Hz, 1H), 4.57 (dd, J_1 =12.4 Hz, J_2 =7.9 Hz, 1H), 3.97–4.03 (m, 1H), 2.89 (d, J =7.0 Hz, 2H), 2.13 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) =205.2, 137.6, 134.0, 130.2, 129.1, 79.4, 46.2, 38.6, 30.6.

HRMS (ESI Positive): calc. for $C_{11}H_{12}ClNO_3$, $[M+Na]^+$ 264.0403, found 264.0415.

The enantiomeric excess was determined by chiral HPLC with a Chiralpack AS-H column at 213nm (n-hexane:2-propanol =85:15), 1.0 mL/min; t_r =19.2 min (minor), 29.0 min (major).

^1H NMR (400 MHz, CDCl_3) δ : 7.39–7.41 (m, 1H), 7.19–7.25 (m, 3H), 4.76 (m, 2H), 4.46 (m, 1H), 2.93–3.09 (m, 2H), 2.16 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3): δ (ppm) = 205.2, 135.9, 133.6, 130.3, 129.0, 128.3, 127.3, 77.4, 44.4, 35.7, 30.1.

HRMS (ESI Positive): calc. for $\text{C}_{11}\text{H}_{12}\text{ClNO}_3$, $[\text{M}+\text{Na}]^+$ 264.0403, found 264.0412.

The enantiomeric excess was determined by chiral HPLC with a Chiralpack AS-H column at 213nm (n-hexane:2-propanol =9:1), 1.0 mL/min; t_r =18.8 min (minor), 21.8 min (major).

^1H NMR (400 MHz, CDCl_3) δ : 2.16 (s, 3H), 2.96 (dd, J = 6.9, 1.9Hz 2H), 4.12–4.17(m, 1H), 4.65 (dd, J =8.2, 12.8 Hz, 1H), 4.75 (dd, J =6.3, 12.8Hz, 1H), 7.42–7.44 (m, 2H), 8.19–8.22 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3): δ (ppm) =204.4, 147.5, 146.3, 128.6, 124.2, 78.6, 45.7, 38.6, 30.3.

HRMS (ESI Positive): calc. for $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_5$, $[\text{M}+\text{Na}]^+$ 275.0644, found 275.0636.

The enantiomeric excess was determined by chiral HPLC with a Chiralpack AS-H column at 213nm (n-hexane:2-propanol =8:2) 1.2 mL/min; t_r =58.6 min (minor), 70.1 min (major).

^1H NMR (400 MHz, CDCl_3) δ : 7.87–7.84 (m, 1H), 7.61–7.57 (m, 1H), 7.55–7.37 (m, 2H), 4.86–4.79 (m, 2H), 4.55–4.46 (m, 1H), 3.03(d, J = 6.80Hz, 2H), 2.14(s, 3H).

^{13}C NMR (125 MHz, CDCl_3): δ (ppm) =203.8, 148.8, 132.5, 132.3, 127.7, 127.5, 124.2, 76.9, 44.2, 32.9, 29.1.

HRMS (ESI Positive): calc. for C₁₁H₁₂N₂O₅, [M+Na]⁺ 275.0644, found 275.0643.

The enantiomeric excess was determined by chiral HPLC with a Chiralpack AS-H column at 213nm (n-hexane:2-propanol =8:2) 1.0 mL/min; t_r=28.8 min (minor), 34.5 min (major).

HPLC spectra for Michael addition adducts

分析结果表					
峰号	峰名	保留时间	峰高	峰面积	含量
1		23.450	464932.750	38209388.000	50.5978
2		29.668	209334.703	37306456.000	49.4022
总计			674267.453	75515844.000	100.0000

分析结果表					
峰号	峰名	保留时间	峰高	峰面积	含量
1		9.013	191323.734	4393928.500	19.4978
2		22.612	251601.203	16715846.000	74.1756
3		29.410	15981.467	1425736.500	6.3266
总计			458906.404	22535511.000	100.0000

分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		18.698	463841.844	37910728.000	50.8975
2		40.965	108496.742	36573796.000	49.1025
总计			572338.586	74484524.000	100.0000

分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		12.523	56019.973	1932710.250	9.1161
2		16.860	268681.438	18234492.000	86.0075
3		36.628	8240.915	1033855.500	4.8764
总计			332942.325	21201057.750	100.0000

分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		15.807	882294.688	48527684.000	51.1867
2		22.890	264463.063	46277504.000	48.8133
总计			1146757.750	94805188.000	100.0000

分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		6.960	122151.266	2244357.000	11.3609
2		13.770	391372.188	16911146.000	85.6036
3		19.410	15173.574	599675.125	3.0355
总计			528697.027	19755178.125	100.0000

分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		24.238	195491.469	15001503.000	51.0970
2		37.387	61620.637	14357365.000	48.9030
总计			257112.105	29358868.000	100.0000

分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		9.428	26363.432	620570.688	2.4361
2		19.153	352963.375	22683800.000	89.0479
3		28.970	19683.234	2169349.250	8.5160
总计			399010.041	25473719.938	100.0000

分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		21.030	504004.250	32163894.000	49.6602
2		24.353	409075.250	32604052.000	50.3398
总计			913079.500	64767946.000	100.0000

分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		8.445	73387.617	1703559.250	8.0383
2		18.825	322003.125	17730082.000	83.6604
3		21.758	32577.848	1759281.625	8.3013
总计			427968.590	21192922.875	100.0000

分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		56.360	43296.281	12473784.000	49.8803
2		66.762	34778.711	12533642.000	50.1197
总计			78074.992	25007426.000	100.0000

分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		22.377	114423.023	7827780.000	24.9962
2		58.600	66558.617	22322318.000	71.2812
3		70.128	5596.226	1165739.875	3.7225
总计			186577.867	31315837.875	100.0000

分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		29.242	471933.156	48796064.000	49.6199
2		35.267	412068.219	49543712.000	50.3801
总计			884001.375	98339776.000	100.0000

分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		19.163	142107.063	7970458.500	20.0896
2		28.778	308386.844	29502550.000	74.3614
3		34.485	23485.854	2201526.250	5.5490
总计			473979.760	39674534.750	100.0000

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