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Highly enantioselective Michael addition of acetone to nitroolefins catalyzed by chiral bifunctional primary amine-thiourea catalysts with acetic acid

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ABSTRACT

Highly enantioselective Michael reaction of acetone with a variety of nitroolefins catalyzed by *N*-[(1*R*,2*R*)-2-aminocyclohexyl]-*N*′-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-thiourea (**1b**) together with acetic acid is described. The Michael addition products were obtained in high yields (76–94%) and up to 96% ee.

1. Introduction

Asymmetric Michael addition to nitroalkenes has been developed as a powerful tool in organic synthesis, and the optically active nitroalkane Michael adducts are versatile building blocks for the agricultural and pharmaceutical compounds.[1] Over the past years the asymmetric organocatalysis has received growing attentions.[2] Various efficient chiral organocatalysts have been developed for the enantioselective Michael addition of aldehydes,[3] ketones[4,5] and, 1,3-dicarbonyl compounds[6,7] to nitroalkenes. However, few organocatalysts have demonstrated excellent enantioselective for the Michael addition of acetone to nitroolefins.[5] Thus, the use of acetone as donor still remains challenge for the asymmetric nitro-Michael addition.

Recently, Ma and co-workers[8] reported the chiral bifunctional primary amine-thiourea catalysts (**1a**, **1b**) based on saccharides, which were highly enantioselective (up to 98% ee) for the Michael addition of aromatic ketones to nitroolefins, but less enantioselective (only 65% ee) for the nitro-Michael reaction using acetone as donor. We found that the reactivity and the enantioselectivity were improved when acid additives were used as co-catalysts. Herein we report the Michael reaction of acetone and β-nitrostyrenes catalyzed by chiral bifunctional primary amine-thiourea catalysts in the presence of acetic acid (Scheme 1).

2. Results and discussion

Initially, the catalytic asymmetric Michael reaction of acetone with β-nitro-4-nitrostyrene was carried out with 15 mol % of **1a** at room temperature in CH_2Cl_2. As indicated in Table 1, the Michael reaction proceeded very slowly, and the adduct was obtained in 50% yield with 84% ee (entry 1). Surprisingly, the addition of 15 mol % of AcOH significantly improved the reactivity and slightly increased the enantioselectivity (entry 2). Different from the recent reports[5b–d] on primary amine catalysts for this reaction, we found the use of water as an additive was inefficient in this catalytic system (entry 3 vs 2). In addition, the chemical yield and enantioselectivity were affected by the reactant concentration, and 0.125 M was optimal (entry 4).

Since the reactivity and enantioselectivity mainly depended on the nature of the thiourea functional group and the chiral diamine scaffold, we screened various saccharide-based catalysts, including D-glucose, D-galactose, and D-mannose. The results indicated that their catalytic activities varied significantly, which could be resulted from the match or mismatch between the chiral diamine and the appended sugars (Table 2). The (*R*,*R*)-configuration of 1,2-diaminocyclohexane or 1,2-diphenylethane-1,2-diamine matched the D-sugars, thus the catalysts possessing (*R*,*R*)-configuration scaffold were more active than their corresponding diastereoisomers, and the absolute configuration of the product was resulted from the chiral diamine scaffold. For example, the reaction using catalyst **1d** was completed in 24 h to give 91% yield and 87% ee (*S* configuration), while catalyst **1c** only gave the product in 23% yield and 85% ee (*R* configuration) even after 48 h (entry 3 vs 4). For comparison the cyclohexane-derived thiourea **1i**[9] was examined, and the Michael adduct was obtained in 65% yield and 86% ee. Obviously, the catalysts **1b** and **1h** derived from commercially available D-glucose were the best catalysts in term of reactivity and enantioselectivity (entries 2 and 8). Thus the catalyst **1b** was selected for further studies.

To obtain even higher yield and enantioselectivity, various acids were employed as additives and the results are summarized in Table 3. Among the screened acids, AcOH and HCO_2H afforded

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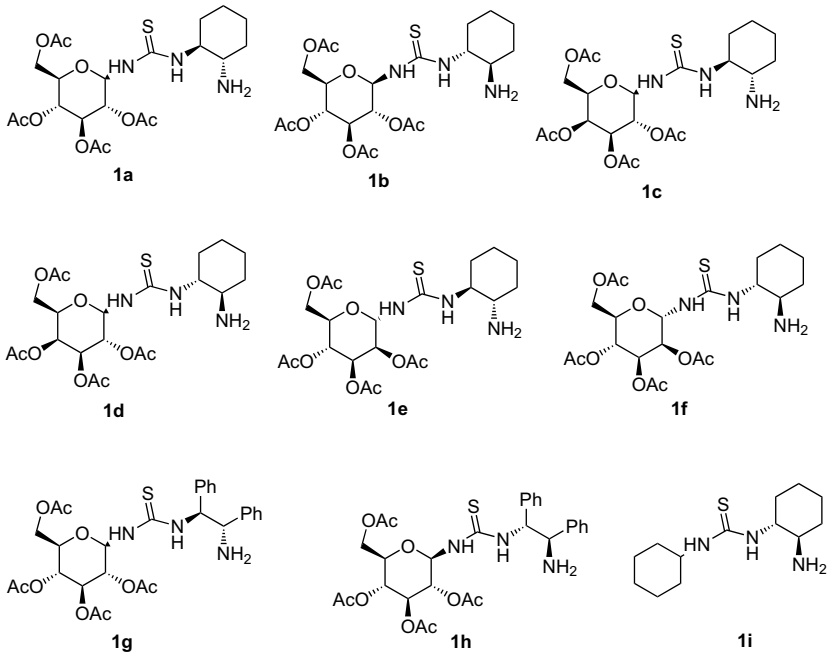


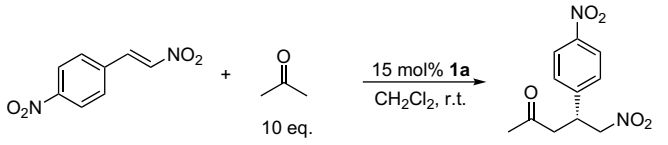
Scheme 1. Various primary amine-thiourea catalysts.

the best results (entries 1 and 2), and $CH_3CH_2CO_2H$, $PhCO_2H$, and $PhCH_2CO_2H$ also provided good yields and enantioselectivities. However, stronger acids such as 3-nitrobenzonic acid, *p*-toluenesulfonic acid and trifluoromethanesulfonic acid etc. reduced the reactivity (entries 6–10, Table 3). The results indicated that the proper acidity of the acid additives was critical for this reaction. Thus AcOH was selected as the additive for further investigation.

Other aspects of this reaction such as solvents, acetone amount, and catalyst loading were investigated. The results indicated that the solvents had a significant effect on the rate and enantioselectivity of this reaction (Table 4, entries 1–9). For example, polar solvents resulted in a significant decrease in both chemical yield (11–21% yield) and enantioselectivity (58–72% ee) (entries 1–4), since these solvents probably inhibit hydrogen-bonding interaction between β-nitrostyrene and the thiourea moiety of **1b**. In contrast, the reaction carried out in nonpolar or low polar solvents such as toluene, benzene, CH_2Cl_2, $CHCl_3$, and ether gave higher yield (88–95%) and enantioselectivity (79–90% ee) (entries 5–9). Further investigation revealed that catalyst loading and the amount of acetone could be decreased to 5 mol% and 5 equiv to the nitroolefin, respectively (entries 9–14). The adduct was obtained in 94% yield and 90% ee at a slight expense of reaction time (entry 13). These results prompted us to select the reaction conditions using CH_2Cl_2 as solvent, 5 equiv acetone at room temperature in the presence of 5 mol% of **1b** to probe the scope of the nitroolefins.

Under the optimized reaction conditions, various β-nitrostyrenes were tested with acetone as donor. As shown in Table 5, the reactions proceeded smoothly to generate chiral Michael adducts in good yields (76–94%) and high to excellent

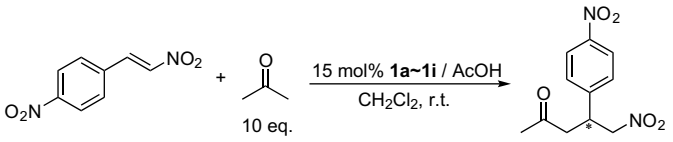
Table 1
Primary optimizations of the reaction condition catalyzed by **1a**[a]



Entry	Additive	Time (h)	Yield[b] (%)	ee[c] (%)
1	None	72	50	84
2	15 mol% AcOH	48	92	87
3	15 mol% AcOH 200 mol% H_2O	60	84	87
4[d]	15 mol% AcOH	48	92	87
5[e]	15 mol% AcOH	48	95	83

[a] Conditions: to the solution of 15 mol% **1a** in 3 mL CH_2Cl_2 (0.08 M), was added 0.25 mmol β-nitro-4-nitrostyrene and 2.5 mmol acetone, the reaction mixture was stirred at room temperature.
[b] Isolated yield after silica gel column chromatography.
[c] The ee values were determined by HPLC using chiralpak AD-H column.
[d] 2 mL CH_2Cl_2 (0.125 M).
[e] 1 mL CH_2Cl_2 (0.25 M).

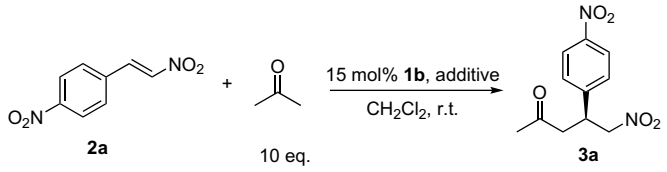
Table 2
Catalyst screening in the Michael reaction[a]



Entry	Catalyst	Time (h)	Yield[b] (%)	ee[c] (%)	Config.
1	**1a**	48	92	87	*R*
2	**1b**	20	94	90	*S*
3	**1c**	48	23	85	*R*
4	**1d**	24	91	87	*S*
5	**1e**	48	73	84	*R*
6	**1f**	20	88	85	*S*
7	**1g**	60	80	91	*R*
8	**1h**	60	92	90	*S*
9	**1i**	15	65	86	*S*

[a] Conditions: to the solution of 15 mol% catalyst in 2 mL CH_2Cl_2 (containing 15 mol% AcOH) was added 0.25 mmol β-nitro-4-nitrostyrene and 2.5 mmol acetone, the reaction mixture was stirred at room temperature.
[b] Isolated yield after silica gel column chromatography.
[c] The ee values were determined by HPLC using chiralpak AD-H column.

Table 3
Various acids as additive in the Michael reaction[a]

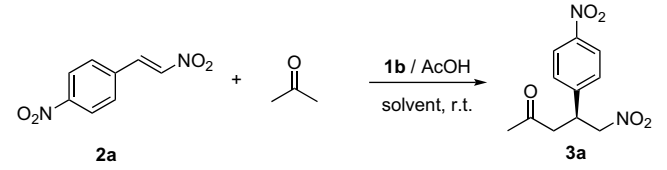


Entry	Additive	pK_a	Time (h)	Yield[b] (%)	ee[c] (%)
1	HCO_2H	3.75	20	94	90
2	AcOH	4.76	20	94	90
3	$CH_3CH_2CO_2H$	4.87	20	90	91
4	$PhCO_2H$	4.20	24	89	90
5	$PhCH_2CO_2H$	4.28	24	89	89
6	3-NO_2PhCO_2H	3.47	24	47	90
7	p-TsOH	−6.62	48	NR[d]	nd[e]
8	TfOH	0.23	48	Trace	nd[e]
9	D-Tartaric acid	2.98	72	19	90
10	L-Tartaric acid	2.98	72	17	91

[a] Conditions: to the solution of 15 mol % **1b** and acid in 2 mL CH_2Cl_2 was added 0.25 mmol β-nitro-4-nitrostyrene and 2.5 mmol acetone, the mixture was stirred at room temperature.
[b] Isolated yield after silica gel column chromatography.
[c] The ee values were determined by HPLC using chiralpak AD-H column.
[d] No reaction.
[e] Not determined.

enantioselectivity (88–96% ee). The absolute configurations of the Michael reaction products were determined by comparing the optical rotation values with those reported in the literatures. Regardless of the nature of substituted group on the aromatic ring, in every case, good chemical yields and high enantioselectivity were achieved. However, the β-nitro-3-nitrostyrene provided a slightly reduced enantioselectivity. When a heterocyclic nitroolefin was used as substrate, a decrease was observed in the yield, while the enantioselectivity was retained (entry 14).

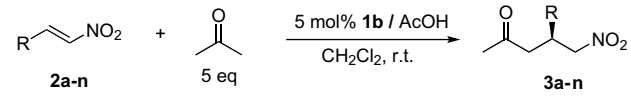
Table 4
The effect of solvents, acetone amount and catalyst loading on Michael reaction[a]



Entry	Solvent	Acetone (equiv)	Catalyst (mol %)	Time (h)	Yield[b] (%)	ee[c] (%)
1	THF	10	15	48	21	62
2	Acetone	10[d]	15	48	37	58
3	CH_3CN	10	15	48	10	69
4	CH_3OH	10	15	48	11	72
5	Toluene	10	15	24	94	84
6	Benzene	10	15	24	94	85
7	Ether	10	15	20	88	79
8	$CHCl_3$	10	15	20	95	87
9	CH_2Cl_2	10	15	20	94	90
10	CH_2Cl_2	5	15	24	95	91
11	CH_2Cl_2	2	15	36	93	91
12	CH_2Cl_2	5	10	30	95	90
13	CH_2Cl_2	5	5	36	94	90
14	CH_2Cl_2	5	2	72	50	90

[a] Conditions: to the solution of 15 mol % **1b** in 2 mL solvent (containing 15 mol % AcOH) was added 0.25 mmol β-nitro-4-nitrostyrene and acetone, the mixture was stirred at room temperature.
[b] Isolated yield after silica gel column chromatography.
[c] The ee values were determined by HPLC using chiralpak AD-H column.
[d] Acetone was used as solvent.

Table 5
Michael reaction of acetone with various β-nitrostyrenes[a]



Entry	Substrate	Time (h)	Yield[b] (%)	ee[c] (%)	Config.[d]
1	4-$NO_2C_6H_4$	20	94 (**3a**)	90	+
2	2-$NO_2C_6H_4$	60	92 (**3b**)	92	−
3	3-$NO_2C_6H_4$	30	90 (**3c**)	88	+
4	4-CNC_6H_4	60	92 (**3d**)	91	+
5	4-FC_6H_4	36	92 (**3e**)	93	+
6	4-ClC_6H_4	36	92 (**3f**)	95	+
7	2-ClC_6H_4	36	93 (**3g**)	93	+
8	4-BrC_6H_4	36	91 (**3h**)	93	*S* (+)
9	4-$CF_3C_6H_4$	96	76 (**3i**)	91	−
10	2,4-$Cl_2C_6H_3$	60	91 (**3j**)	91	+
11	Ph	60	91 (**3k**)	92	*S* (+)
12	4-$CH_3C_6H_4$	60	92 (**3l**)	93	*S* (+)
13	4-$CH_3OC_6H_4$	60	91 (**3m**)	93	*S* (−)
14	2-Furyl	15	80 (**3n**)	96	*S* (+)

[a] Conditions: to the solution of 5 mol % **1b** in 2 mL CH_2Cl_2 (containing 5 mol % AcOH) was added 0.25 mmol β-nitro-4-nitrostyrene and 1.25 mmol acetone, the mixture was stirred at room temperature.
[b] Isolated yield after silica gel column chromatography.
[c] The ee values were determined by HPLC using chiralpak AD-H or AS-H column.
[d] The absolute configuration was assigned by comparison the optical rotation values with those reported in the literatures.

3. Conclusion

In conclusion, we have developed a highly enantioselective Michael reaction of acetone with nitroolefins catalyzed by saccharide-derived primary amine-thioureas. The match between the chiral diamine and the appended sugars was important for the reactivity and enantioselectivity. And the suitable acidic additives promoted the reaction. In the presence of 5 mol % *N*-[(1*R*,2*R*)-2-aminocyclohexyl]-*N*′-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-thiourea (**1b**) together with acetic acid, the nitro-Michael adducts were obtained in excellent enantioselectivity (88–96% ee) and good to excellent yields (76–94%).

4. Experimental

4.1. General

Acetone was dried from anhydrous K_2CO_3. CH_2Cl_2, $CHCl_3$, and CH_3CN were distilled from CaH_2. THF, Benzene, Toluene, and Ether were distilled from sodium–benzophenone. CH_3OH was distilled from Magnesium–iodine. NMR spectra were recorded with a Bruker spectrometer at 500 or 400 (^{1}H NMR), 125 (^{13}C NMR) MHz in $CDCl_3$ or DMSO-d_6 solution and chemical shifts were reported in parts per million (δ) relative to the internal standard Me_4Si (0 ppm) and solvent signals (central peak at 77.70 ppm for $CDCl_3$). IR spectra were recorded on a Nicolet Magna-IR 550 spectrometer. Mass spectra were recorded on a Micromass LCT spectrometer with EI or ESI resource. HPLC analysis was performed on a Waters 510 instrument with a 2487 detector using a Daicel Chiralpak AS-H or Chiralpak AD-H column. β-Nitrostyrenes[12] and glycosyl isothiocyanates[13] were prepared according to the literature.

4.2. Preparation of catalysts

To a solution of 0.75 mmol of chiral diamine in 1 mL CH_2Cl_2 was added 195 mg (0.5 mmol) saccharide-derived isothiocyanate at 0 °C. After the reaction mixture was stirred for 0.5 h (monitored by TLC), the solvent was removed and the residue was purified by

column chromatography on silica gel (10:1 EA: MeOH, 0.5% Et_3N) to afford the pure desired product.

*4.2.1. N-[(1S,2S)-2-Aminocyclohexyl]-N′-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-thiourea (**1a**)*[8]

White solid; 47% yield; mp 87–89 °C; $[\alpha]_D^{20}$ −47.6 (*c* 0.57, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 6.10 (br, 1H), 5.49 (br, 1H), 5.36–5.31 (m, 1H), 5.10–5.03 (m, 2H), 4.31 (d, *J*=12.4 Hz, 1H), 4.14–4.11 (m, 2H), 4.86 (d, *J*=9.6 Hz, 1H), 2.94 (br, 1H), 2.53 (br, 1H), 2.08 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 2.08–2.02 (m, 2H), 1.92 (br, 2H), 1.74 (br, 2H), 1.28–1.24 (m, 4H).

*4.2.2. N-[(1R,2R)-2-Aminocyclohexyl]-N′-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-thiourea (**1b**)* [8]

White solid; 45% yield; mp 150 °C (decomp.); $[\alpha]_D^{20}$ +47.0 (*c* 0.51, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 6.15 (br, 1H), 5.83 (br, 1H), 5.34 (t, *J*=9.5 Hz, 1H), 5.10–5.03 (m, 2H), 4.33 (dd, *J*=4.6, 12.5 Hz, 1H), 4.14–4.10 (m, 2H), 3.87–3.84 (m, 1H), 3.20 (br, 1H), 2.54–2.53 (m, 1H), 2.10 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 2.05–2.01 (m, 2H), 1.92 (m, 2H), 1.73 (br, 2H), 1.28–1.25 (m, 4H).

*4.2.3. N-[(1S,2S)-2-Aminocyclohexyl]-N′-(2,3,4,6-tetra-O-acetyl-β-D-galactosyl)-thiourea (**1c**)*

White solid; 51% yield; mp 82–84 °C; $[\alpha]_D^{20}$ −13.3 (*c* 0.75, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 6.21 (br, 1H), 5.51–5.49 (m, 1H), 5.44 (br, 1H), 5.22–5.14 (m, 2H), 4.19–4.04 (m, 4H), 2.97 (br, 1H), 2.56–2.51 (m, 1H), 2.14 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 1.99 (s, 3H), 2.06–1.99 (m, 2H), 1.93–1.88 (m, 2H), 1.74 (br, 2H), 1.32–1.23 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.8, 171.5, 171.1, 170.8, 170.4, 85.0, 72.9, 71.7, 69.2, 67.9, 61.8, 61.0, 58.0, 35.7, 32.9, 25.4, 21.6, 21.4, 21.3, 21.2, 14.8; IR (film, cm^{-1}): ν 3362, 2936, 2861, 1748, 1548, 1372, 1232, 1054; HRMS (ESI): calcd for $C_{21}H_{34}N_3O_9S$ [M+H]: 504.2016, found 504.2020.

*4.2.4. N-[(1R,2R)-2-Aminocyclohexyl]-N′-(2,3,4,6-tetra-O-acetyl-β-D-galactosyl)-thiourea (**1d**)*

White solid; 51% yield; mp 91–93 °C; $[\alpha]_D^{20}$ +65.5 (*c* 0.58, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 6.11 (br, 1H), 5.80 (br, 1H), 5.45 (s, 1H), 5.21–5.19 (m, 2H), 4.19–4.04 (m, 4H), 3.20 (br, 1H), 2.56–2.52 (m, 1H), 2.16 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 1.99 (s, 3H), 2.07–1.99 (m, 2H), 1.95–1.91 (m, 2H), 1.74 (br, 2H), 1.28–1.18 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 172.8, 172.6, 172.1, 171.8, 171.4, 85.5, 74.1, 73.0, 70.4, 69.0, 62.9, 62.1, 57.4, 36.5, 33.8, 26.3, 22.6, 22.4, 22.4, 22.2, 15.9; IR (film, cm^{-1}): ν 3442, 2937, 1749, 1546, 1371, 1232, 1055; HRMS (ESI): calcd for $C_{21}H_{34}N_3O_9S$ [M+H]: 504.2016, found 504.2031.

*4.2.5. N-[(1S,2S)-2-Aminocyclohexyl]-N′-(2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl)-thiourea (**1e**)*

White solid; 64% yield; mp 84–85 °C; $[\alpha]_D^{20}$ −5.0 (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz): δ 7.02 (br, 1H), 6.13–6.02 (m, 1H), 5.29–5.24 (m, 3H), 4.40–4.22 (m, 1H), 4.20–4.01 (m, 2H), 3.95 (br, 1H), 3.20 (br, 1H), 2.61 (br, 1H), 2.17 (s, 3H), 2.11 (s, 3H), 2.07(s, 3H), 2.01(s, 3H), 2.11–2.01 (m, 4H), 1.71 (br, 2H), 1.29–1.25 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 186.5, 171.5, 171.2, 170.6, 170.1, 82.3, 70.5, 69.6, 66.7, 63.7, 63.0, 61.1, 56.9, 35.7, 33.0, 25.3, 21.7, 21.5, 21.4, 21.3, 14.8; IR (film, cm^{-1}): ν 3357, 2935, 1748, 1548, 1371, 1231, 1055, 800; HRMS (ESI): calcd for $C_{21}H_{34}N_3O_9S$ [M+H]: 504.2016, found 504.2025.

*4.2.6. N-[(1R,2R)-2-Aminocyclohexyl]-N′-(2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl)-thiourea (**1f**)*

White solid; 68% yield; mp 82–83 °C; $[\alpha]_D^{20}$ +42.5 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.32 (br, 1H), 6.23–5.70 (m, 1H), 5.31–5.27 (m, 3H), 4.33–4.29 (m, 1H), 4.19 (d, *J*=11.0 Hz, 1H), 4.13–4.01 (m, 1H), 3.94–3.79 (m, 1H), 3.14 (br, 1H), 2.59 (br, 2H), 2.30–2.20 (m 1H), 2.16 (s, 3H), 2.09 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 2.09–2.02 (m, 2H), 1.74 (br, 2H), 1.27–1.23 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 172.8, 172.5, 171.9, 171.6, 171.2, 82.5, 71.2, 70.8, 70.4, 64.2, 63.8, 62.1, 57.0, 37.9, 33.8, 26.3, 22.7, 22.5, 22.4, 22.3, 15.8; IR (film, cm^{-1}): ν 3359, 2934, 2854, 1747, 1547, 1371, 1231, 1055, 800; HRMS (ESI): calcd for $C_{21}H_{34}N_3O_9S$ [M+H]: 504.2016, found 504.2028.

*4.2.7. N-[(1S,2S)-2-Amino-1,2-diphenylethyl]-N′-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-thiourea (**1g**)*

White solid; 63% yield; mp 178 °C (decomp.); $[\alpha]_D^{20}$ −11.5 (*c* 1.0, $CHCl_3$);. ^1H NMR (DMSO-d_6, 500 MHz): δ 8.45 (br, 1H), 8.37 (d, *J*=8.7 Hz, 1H), 7.35–7.30 (m, 4H), 7.26–7.18 (m, 5H), 7.11 (br, 1H), 5.72 (t, *J*=9.2 Hz, 1H), 5.52 (d, *J*=2.8 Hz, 1H), 5.30 (t, *J*=9.6 Hz, 1H), 4.91 (t, *J*=9.6 Hz, 1H), 4.84 (t, *J*=9.4 Hz, 1H), 4.29 (d, *J*=2.8 Hz, 1H), 4.17–4.14 (m, 1H), 3.91–3.88 (m, 2H), 1.97 (s, 3H), 1.96 (s, 3H), 1.94 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 183.3, 17.0, 169.5, 169.3, 169.2, 143.0, 141.1, 128.1, 127.7, 127.0, 126.9, 126.8, 81.4, 72.7, 72.0, 70.5, 67.9, 63.0, 61.6, 59.8, 59.4, 20.5, 20.4, 20.3; IR (film, cm^{-1}): ν 3308, 1748, 1547, 1370, 1233, 1041; HRMS (ESI): calcd for $C_{29}H_{35}N_3O_9SNa$ [M+Na]: 624.1992, found 624.2007.

*4.2.8. N-[(1R,2R)-2-Amino-1,2-diphenylethyl]-N′-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-thiourea (**1h**)*

White solid; 59% yield; mp 176 °C (decomp.); $[\alpha]_D^{20}$ +19.7 (*c* 0.76, $CHCl_3$); ^1H NMR (DMSO-d_6, 400 MHz): δ 8.50 (d, *J*=9.2 Hz, 1H), 8.49 (br, 1H), 7.44–7.42 (m, 2H), 7.31–7.18 (m, 8H), 5.77–5.72 (m, 1H), 5.37 (d, *J*=2.4 Hz, 1H), 5.29 (t, *J*=9.6 Hz, 1H), 4.91 (t, *J*=9.6 Hz, 1H), 4.83 (t, *J*=9.6 Hz, 1H), 4.30 (d, *J*=3.6 Hz, 1H), 4.18–4.14 (m, 1H), 4.05–3.91 (m, 2H), 1.98 (s, 3H), 1.96 (s, 3H), 1.93 (s, 3H), 1.87 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 183.1, 169.9, 169.4, 169.3, 169.2, 142.9, 141.6, 128.0, 127.9, 127.0, 126.9, 126.6, 126.4, 81.7, 72.5, 72.1, 71.0, 67.9, 63.3, 61.6, 59.7, 59.2, 20.5, 20.4, 20.3, 20.2; IR (film, cm^{-1}): ν 3364, 3119, 3066, 2954, 2865, 1747, 1724, 1576, 1524, 1378, 1232, 1040, 910, 783, 704, 601; HRMS (EI): calcd for $C_{29}H_{35}N_3O_9S$ [M]: 601.2094, found 601.2094.

4.3. General procedure for the Michael reaction of acetone and β-nitrostyrene

To a solution of *N*-[(1*R*,2*R*)-2-aminocyclohexyl]-*N*′-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)- thiourea (**1b**) (6.3 mg, 0.0125 mmol) in CH_2Cl_2 [2 mL, containing 0.0125 mmol AcOH] was added acetone (0.076 mL, 1.25 mmol), β-nitrostyrene (0.25 mmol). After the reaction mixture was stirred at room temperature for the appropriate time (monitored by TLC), the solvent was removed and the residue was purified by column chromatography on silica gel to afford the pure desired product. The enantiomeric excesses were determined by HPLC using chiralpak AD-H or AS-H column. The absolute configuration was determined by comparing of optical rotation values with those reported in the literatures.

*4.3.1. (4S)-5-Nitro-4-(4-nitrophenyl)-pentan-2-one (**3a**)*[10]

Yield 94%; $[\alpha]_D^{20}$ +9.8 (*c* 0.56, $CHCl_3$); 90% ee, Chiralpak AD-H, hexane/*i*-PrOH=80/20, UV 254 nm, flow rate 1.0 mL/min, t_R=20.8 min (major), t_R=29.2 min (minor). ^1H NMR ($CDCl_3$, 500 MHz): δ 8.22–8.20 (m, 2H), 7.44–7.42 (m, 2H), 4.75 (dd, *J*=6.3, 12.8 Hz, 1H), 4.65 (dd, *J*=8.2, 12.8 Hz, 1H), 4.17–4.12 (m, 1H), 2.96 (dd, *J*=6.8, 5.7 Hz, 2H), 2.16 (s, 3H).

*4.3.2. (4S)-5-Nitro-4-(2-nitrophenyl)-pentan-2-one (**3b**)*

Yield 92%; $[\alpha]_D^{20}$ −31.0 (*c* 0.39, $CHCl_3$); 92% ee, Chiralpak AD-H, hexane/*i*-PrOH=85/15, UV 254 nm, flow rate 1.0 mL/min, t_R=25.5 min (major), t_R=27.9 min (minor). ^1H NMR ($CDCl_3$, 500 MHz): δ 7.91–7.89 (m, 1H), 7.61–7.57 (m, 1H), 7.47–7.43 (m, 1H), 7.39–7.37 (m, 1H), 4.88–4.81 (m, 2H), 4.54–4.50 (m, 1H), 3. 06–3.04 (m, 2H), 2.17(s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz,): δ 205.5, 150.5, 134.2, 133.9, 129.3, 129.1, 125.7, 78.5, 45.9, 34.4, 30.6; IR (film, cm^{-1}):

ν 2918, 1713, 1614, 1564, 1555, 1537, 1433, 1359, 1167, 956, 856, 787, 751, 710; HRMS (EI) calcd for $C_{11}H_{12}NO_3$ [M−NO_2]: 206.0817, found: 206.0827.

4.3.3. (4S)-5-Nitro-4-(3-nitrophenyl)-pentan-2-one (**3c**)[11]

Yield 90%; $[\alpha]_D^{20}$ +12.2 (*c* 0.37, $CHCl_3$); 88% ee, Chiralpak AD-H, hexane/*i*-PrOH=85/15, UV 254 nm, flow rate 1.0 mL/min, t_R=17.5 min (major), t_R=19.3 min (minor). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.16–8.14 (m, 1H), 8.12–8.11 (m, 1H), 7.63–7.61 (m, 1H), 7.55–7.52 (m, 1H), 4.77 (dd, *J*=6.2, 12.8 Hz, 1H), 4.66 (dd, *J*=8.3, 12.8 Hz, 1H), 4.16 (1H, m), 2.99 (dd, *J*=2.7, 7.0 Hz, 2H), 1.26 (s, 3H).

4.3.4. (4S)-5-Nitro-4-(4-cyanophenyl)-pentan-2-one (**3d**)

Yield 92%; $[\alpha]_D^{20}$ +14.0 (*c* 0.36, $CHCl_3$); 91% ee, Chiralpak AD-H, hexane/*i*-PrOH=85/15, UV 220 nm, flow rate 1.0 mL/min, t_R=22.4 min (major), t_R=28.7 min (minor). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.64 (d, *J*=8.2 Hz, 2H), 7.37 (d, *J*=8.3 Hz, 2H), 4.73 (dd, *J*=6.8, 12.8 Hz, 1H), 4.63 (dd, *J*=8.2, 12.8 Hz, 1H), 4.11–4.05 (m, 1H), 2.94 (dd, *J*=4.5, 6.8 Hz, 2H), 2.15 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz,): δ 204.5, 144.4, 132.8, 128.5, 118.3, 111.9, 78.6, 45.6, 38.9, 30.3; IR (film, cm^{-1}): ν 3640, 3409, 2919, 2229, 1928, 1715, 1609, 1554, 1506, 1422, 1378, 1165, 1019, 831, 566; HRMS (ESI): calcd for $C_{12}H_{12}N_2O_3Na$ [M+Na]: 255.0746, found: 255.0744.

4.3.5. (4S)-5-Nitro-4-(4-fluorophenyl)-pentan-2-one (**3e**)

Yield 92%; $[\alpha]_D^{20}$ +8.7 (*c* 0.35, $CHCl_3$); 93% ee, Chiralpak AD-H, hexane/*i*-PrOH=85/15, UV 220 nm, flow rate 1.0 mL/min, t_R=13.1 min (major), t_R=14.8 min (minor). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.21–7.19 (m, 2H), 7.04–7.00 (m, 2H), 4.68 (dd, *J*=6.6, 12.4 Hz, 1H), 4.57 (dd, *J*=7.9, 12.4 Hz, 1H), 4.03–3.98 (m, 1H), 2.90 (dd, *J*=1.6, 6.9 Hz, 2H), 2.13 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz,): δ 205.5, 162.2, 134.6, 129.1, 116.0, 79.4, 46.2, 38.4, 30.4; IR (film, cm^{-1}): ν 2957, 1898, 1715, 1609, 1549, 1511, 1438, 1410, 1379, 1366, 1323, 1231, 1162, 1097, 950, 858, 828, 736, 716, 554; HRMS (EI): calcd for $C_{11}H_{12}FO$ [M−NO_2]: 178.0794, found: 178.0809.

4.3.6. (4S)-5-Nitro-4-(4-chlorophenyl)-pentan-2-one (**3f**)

Yield 92%; $[\alpha]_D^{20}$ +9.5 (*c* 0.48, $CHCl_3$); 95% ee, Chiralpak AD-H, hexane/*i*-PrOH=85/15, UV 220 nm, flow rate 1.0 mL/min, t_R=13.4 min (major), t_R=15.6 min (minor). ^{1}H NMR ($CDCl_3$, 500 MHz,): δ 7.32–7.29 (m, 2H), 7.18–7.15 (m, 2H), 4.68 (dd, *J*=6.6, 12.5 Hz, 1H,), 4.57 (dd, *J*=7.9, 12.5 Hz, 1H), 4.01–3.98 (m, 1H), 2.90 (dd, *J*=7.1, 2.4 Hz, 2H), 2.13 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 205.0, 137.4, 133.8, 129.3, 128.8, 79.2, 45.9, 38.4, 30.4. IR (film, cm^{-1}): ν 3413, 1716, 1554, 1492, 1406, 1384, 1364, 1166, 1108, 1016, 818, 545; HRMS (ESI): calcd for $C_{11}H_{12}ClNO_3Na$ [M+Na]: 264.0403, found: 264.0392.

4.3.7. (4S)-5-Nitro-4-(2-chlorophenyl)-pentan-2-one (**3g**)

Yield 93%; $[\alpha]_D^{20}$ +17.6 (*c* 0.37, $CHCl_3$); 93% ee, Chiralpak AS-H, hexane/*i*-PrOH=90/10, UV 220 nm, flow rate 1.0 mL/min, t_R=20.2 min (major), t_R=23.6 min (minor). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38–7.36 (m, 1H), 7.21–7.19 (m, 3H), 4.74–4.72 (m, 2H), 4.49–4.44 (m, 1H), 3.05–2.91 (m, 2H), 2.13 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.0, 136.6, 134.2, 130.9, 129.6, 128.9, 128.0, 78.0, 45.1, 36.2, 30.7; IR (film, cm^{-1}): ν 3066, 2919, 1714, 1555, 1478, 1434, 1378, 1165, 1038, 759; HRMS (ESI): calcd for $C_{11}H_{12}NO_3ClNa$ [M+Na]: 264.0403, found 264.0399.

4.3.8. (4S)-5-Nitro-4-(4-bromophenyl)-pentan-2-one (**3h**)[5b]

Yield 91%; $[\alpha]_D^{20}$ −8.1 (*c* 0.43, $CHCl_3$); 93% ee, Chiralpak AD-H, hexane/*i*-PrOH=85/15, UV 220 nm, flow rate 1.0 mL/min, t_R=13.8 min (major), t_R=16.1 min (minor).^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.47–7.43 (m, 2H), 7.12–7.09 (m, 2H), 4.68 (dd, *J*=6.6, 12.5 Hz, 1H), 4.57 (dd, *J*=8.0, 12.5 Hz, 1H), 4.11–3.95 (m, 1H), 2.89 (dd, *J*=1.9, 7.0 Hz, 2H), 2.13 (s, 3H).

4.3.9. (4S)-5-Nitro-4-(4-trifluoromethylphenyl)-pentan-2-one (**3i**)

Yield 76%; $[\alpha]_D^{20}$ −13.1 (*c* 0.30, $CHCl_3$); 91% ee, Chiralpak AD-H, hexane/*i*-PrOH=85/15, UV 220 nm, flow rate 1.0 mL/min, t_R=8.6 min (major), t_R=9.9 min (minor). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.60 (d, *J*=8.1 Hz, 2H), 7.36 (d, *J*=8.0 Hz, 2H), 4.73 (dd, *J*=6.5, 12.6 Hz, 1H), 4.62 (dd, *J*=8.1, 12.6 Hz, 1H), 4.12–4.06 (m, 1H), 2.94 (dd, *J*=1.0, 7.0 Hz, 2H), 2.14 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 203.8, 142.0, 126.9, 125.1, 125.0, 77.9, 44.8, 37.7, 29.3; IR (film, cm^{-1}): ν 2921, 1715, 1620, 1555, 1424, 1378, 1327, 1166, 1118, 1070, 1017, 842; HRMS (ESI): calcd for $C_{12}H_{12}F_3NO_3Na$ [M+Na]: 298.0667, found: 298.0654.

4.3.10. (4S)-5-Nitro-4-(2,4-dichlorophenyl)-pentan-2-one (**3j**)

Yield 91%; $[\alpha]_D^{20}$ +16.1 (*c* 0.31, $CHCl_3$); 91% ee, Chiralpak AS-H, hexane/*i*-PrOH=90/10, UV 220 nm, flow rate 1.0 mL/min, t_R=17.6 min (major), t_R=21.6 min (minor). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.43 (s, 1H), 7.23 (d, *J*=8.4 Hz, 1H), 7.16 (d, *J*=8.4 Hz, 1H), 4.76–4.72 (m, 2H), 4.43–4.39 (m, 1H), 3.05 (dd, *J*=7.8, 18.2 Hz, 1H), 2.95 (dd, *J*=6.0, 18.2 Hz, 1H), 2.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 205.7, 135.3, 135.1, 134.9, 130.8, 130.0, 128.3, 78.0, 44.9, 36.0, 30.8; IR (film, cm^{-1}): ν 3095, 2919, 1714, 1590, 1555, 1476, 1433, 1378, 1165, 1108, 820; HRMS (EI): calcd for $C_{11}H_{11}Cl_2NO_3$ [M]: 275.0116, found: 275.0118.

4.3.11. (4S)-5-Nitro-4-phenyl-pentan-2-one (**3k**)[5a]

Yield 91%; $[\alpha]_D^{20}$ +4.8 (*c* 0.32, $CHCl_3$), Lit[5a] $[\alpha]_D^{20}$ +2.4 (*c* 1.03, $CHCl_3$); 92% ee, Chiralpak AD-H, hexane/*i*-PrOH=85/15, UV 220 nm, flow rate 1.0 mL/min, t_R=9.6 min (major), t_R=10.3 min (minor). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.35–7.21 (m, 5H), 4.69 (dd, *J*=6.9, 12.3 Hz, 1H), 4.60 (dd, *J*=7.7, 12.3 Hz, 1H), 4.03–3.98 (m, 1H), 3.78(s, 3H), 2.91 (d, *J*=70 Hz, 2H), 2.12 (s, 3H).

4.3.12. (4S)-5-Nitro-4-(4-methylphenyl)-pentan-2-one (**3l**)[5a]

Yield 92%; $[\alpha]_D^{20}$ +3.0 (*c* 0.34, $CHCl_3$), Lit[5a] $[\alpha]_D^{20}$ +5.5 (*c* 1.59, $CHCl_3$); 93% ee, Chiralpak AD-H, hexane/*i*-PrOH=85/15, UV 220 nm, flow rate 1.0 mL/min, t_R=8.6 min (major), t_R=9.9 min (minor). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.14–7.08 (m, 3H), 4.69 (1H, dd, *J*=6.9, 12.3 Hz), 4.60 (1H, dd, *J*=7.7, 12.1 Hz), 4.0–3.93 (1H, m), 2.91 (2H, d, *J*=6.9 Hz), 2.31 (3H, s).

4.3.13. (4S)-5-Nitro-4-(4-methoxylphenyl)-pentan-2-one (**3m**)[5a]

Yield 91%; $[\alpha]_D^{20}$ −6.9 (*c* 0.36, $CHCl_3$), Lit[5a] $[\alpha]_D^{20}$ −1.5 (*c* 1.32, $CHCl_3$); 93% ee, Chiralpak AD-H, hexane/*i*-PrOH=85/15, UV 220 nm, flow rate 1.0 mL/min, t_R=12.6 min (major), t_R=13.9 min (minor). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.15–7.11 (m, 2H), 6.87–6.83 (m, 2H), 4.66 (dd, *J*=6.8, 12.2 Hz, 1H), 4.56 (dd, *J*=7.8, 12.2 Hz, 1H), 3.97–3.95 (m, 1H), 3.78 (s, 3H), 2.89 (d, *J*=7.1 Hz, 2H), 2.12 (s, 3H).

4.3.14. (4S)-5-Nitro-4-(2-furyl)-pentan-2-one (**3n**)[5a]

Yield 80%; $[\alpha]_D^{20}$ +8.9 (*c* 0.39, $CHCl_3$), Lit[5a] $[\alpha]_D^{20}$ +5.7 (*c* 1.32, $CHCl_3$); 96% ee, Chiralpak AD-H, hexane/*i*-PrOH=85/15, UV 220 nm, flow rate 1.0 mL/min, t_R=8.39 min (major), t_R=9.35 min (minor). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.34–7.33 (m, 1H), 6.30–6.29 (m, 1H), 6.15–6.13 (m, 1H), 4.71–4.62 (m, 2H), 4.13–4.08 (m, 1H), 2.99 (dd, *J*=6.4, 18.0 Hz, 1H), 2.90 (dd, *J*=7.4, 18.0 Hz, 1H), 2.18 (s, 3H).

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