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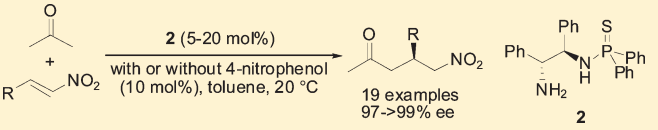
A Recyclable Organocatalyst for Asymmetric Michael Addition of Acetone to Nitroolefins

Aidang Lu, Tao Liu, Ronghua Wu, Youming Wang,* Guiping Wu, Zhenghong Zhou,* Jianxin Fang, and Chuchi Tang

State Key Laboratory of Elemento-Organic Chemistry, Institute of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, P. R. China

Supporting Information

ABSTRACT: Based on different chiral diamine skeletons, a series of bifunctional primary amine-thiophosphoramides were synthesized and screened as the catalysts for the asymmetric Michael addition of acetone to both aromatic and aliphatic nitroolefins. Under the catalysis of a thiophosphoramide derived from 1,2-diphenylethane-1,2-diamine, the corresponding adducts were obtained in high yields (up to >99%) with excellent enantioselectivities (97−99% ee) under mild reaction conditions. Moreover, the catalyst could be recovered via simple phase separation and reused at least five times without any loss of both catalytic activity and stereocontrol.



INTRODUCTION

Michael addition of ketone to nitroolefins represents a convenient access to γ-nitroketones, which are valuable building blocks in organic synthesis.[1] Since the proline-catalyzed direct nitro-Michael addition emerged,[2] much effort has been devoted to the development of more selective and efficient catalytic systems for this synthetically useful transformation. In sharp contrast to the high enantioslectivities obtained with the organocatalyzed Michael addition of cyclic ketones, especially cyclohexanones, to nitroalkenes,[3] acetone is still one of the most problematic substrates for the nitro-Michael addition. To our knowledge, only limited cases have been reported with enantiomeric excesses of over 90% for the Michael products of acetone.[4] Employing chiral primary amine-thiourea catalysts Jacobsen[4a] and Tsogoeva[4b,c] have independently developed the highly enantioselective conjugate addition of acetone to aromatic nitroolefins, affording the conjugated addition products with the highest ee value of 99% and 92%, respectively. Feng described an amine organocatalyst based on bispidine for this transformation and achieved an enantioselecitivity of 96% ee.[4d] Zhao developed a self-assembled organocatalyst based on ionic interactions between L-phenylglycine and cinchonoid thiourea that could mediate the asymmetric nitro-Michael addition of acetone with enantioselectivities up to 98% ee.[4e] In addition, chiral primary amine-thiourea bearing a glycosyl scaffold,[4f] *N*-diphenylphosphinyl-*trans*-1,2-diphenylethane-1,2-diamine,[4g] and Noyori's Ts-DPEN ligand[4h] have also been describe as effective catalysts for the asymmetric Michael addition of acetone to nitroolefin, giving high levels of enantioselectivity. Despite these recent advances, there are still some drawbacks associated with these previously reported procedures, such as the substrate limitation to aromatic nitroolefin, need of an acidic co-catalyst, and in some cases, unsatisfactory selectivity. Therefore, the development of highly efficient alternative catalysts for the asymmetric Michael addition of acetone to both aromatic and aliphatic nitroolefins is highly desirable. Recently, we have demonstrated that functionalized thiophosphoramides can function as a novel type of hydrogen bond donor catalyst in asymmetric nitro-Michael addition.[5] Among them, primary amine-thiophosphoramide catalyst **1** could promote the asymmetric Michael addition of acetone to nitroolefin, providing the conjugate addition product with high levels of enantioselectivity (Scheme 1).[5b] Herein we report our further results on a highly efficient and recyclable thiophosphoramide catalyst for the Michael addition of acetone to both aromatic and aliphatic nitroolefins.

RESULTS AND DISCUSSION

Designed primary amine-thiophosphoramides **2**−**5** bearing different chiral diamine skeletons were readily synthesized via the condensation of the corresponding diamine with thiophosphoryl chloride in the presence of triethylamine in acceptable yields. Thiophosphoramide **6** was prepared through the reaction of the monolithium salt of (*R*)-1,1′-binaphthyl-2,2′-diamine with diphenylphosphinothioic chloride (Scheme 2).

With these catalysts in hand, screening of their catalytic efficacy and enantioselectivity was carried out with the model reaction between β-nitrostyrene (**7a**) and acetone (Table 1). Results, listed in Table 1, clearly indicated that their catalytic activity and enantioselectivity are highly dependent on their chiral diamine skeleton. Moreover, the substituents on the phosphorus atom also have considerable influence on both catalytic activity and enantioselectivity. In the absence of acid co-catalyst, only moderate conversion of **7a** with ee value of 89% was achieved when thiophosphoramide **1** derived from (1*R*,2*R*)-cyclohexane-1,

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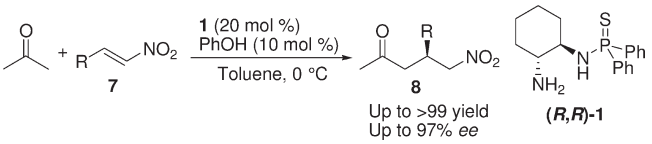
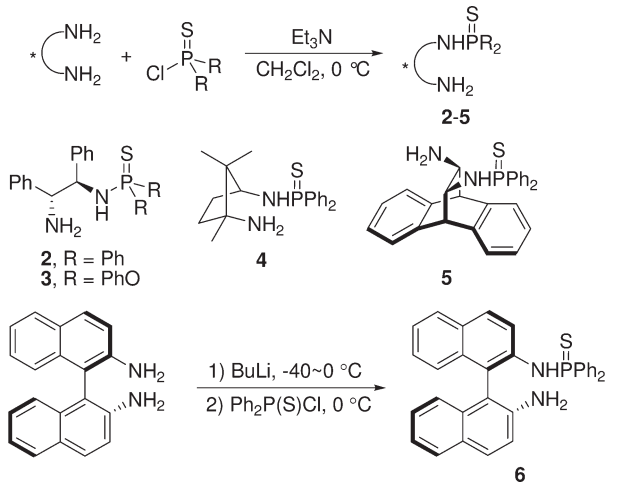
Scheme 1. (*R*,*R*)-1 Catalyzed Asymmetric Michael Addition of Acetone to *β*-Nitrostyrene



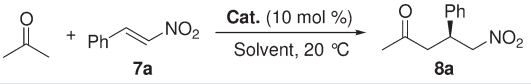
Scheme 2. Preparation of Primary Amine-thiophosphoramide Catalyst 2−6



2-diamine was employed as the catalyst (Table 1, entry 1). The use of diphenylphosphinothioamide **2** bearing (*R*,*R*)-1,2-diphenylethane-1,2-diamine skeleton resulted in a full conversion of nitrostyrene **7a** with high enantioselectivity of 98% ee (Table 1, entry 3). In contast, catalyst *O*,*O*-diphenyl thiophosphoramide **3** with the same chiral diamine skeleton as that of catalyst **2** afforded the desired conjugate addition product in only 51% yield with slightly lower enantioselectivity of 95% ee in prolonged reaction time (Table 1, entry 8). Under identical conditions, thiophosphoramide catalysts **4**−**6** prepared from (+)-*cis*-1,2,2-trimethylcyclopentane-1,3-diamine, (*R*,*R*)-11,12-diamino-9,10-dihydro-9,10-ethanonanthracene, and (*R*)-1,1′-binaphthyl-2,2′-diamine were completely inactive in the model reaction and failed to afford product **8a**. Addition of 10 mol % of 4-nitrophenol as acid co-catalyst significantly accelerated the reaction in comparison with that without the co-catalyst (Table 1, entry 2 vs entry 1, entry 11 vs entry 3, and entry 15 vs entry 14). However, even with the aid of the acidic co-catalyst thiophosphoramides **1**, **3**, **5** were not active enough to ensure a full conversion of **7a** over 66 h (Table 1, entries 2, 15, and 19), and catalysts **4** and **6** were still not active at all (Table 1, entries 17 and 21). In general, the same high level of enantioselectivity was achieved consistently with or without the acidic co-catalyst.

The results summarized in Table 1 demonstrate that phosphoramide catalyst **2** bearing the (*R*,*R*)-1,2-diphenylethane-1,2-diamine skeleton was highly efficient for the Michael addition of acetone to nitroolefin **7a**. The corresponding adduct **8a** could be attained quantitatively with a high enantioselectivity of 98% ee at the catalyst loading of 10 mol % in toluene at room temperature without an acidic co-catalyst (Table 1, entry 3). The reaction proceeded well even at 5 mol % catalyst loading, with slight improvement in the

Table 1. Catalyst Screening[a]



entry	catalyst	solvent	time	yield (%)[b]	ee (%)[c]
1	**1**	toluene	132 h	47	89
2	**1**[d]	toluene	66 h	45	90
3	**2**	toluene	36 h	>99	98
4	**2**	CH_3CN	42 h	50	93
5	**2**	THF	42 h	10	ND[e]
6	**2**	MeOH	42 h	tr	
7	**2**	hexane	22 h	94	96
8	**2**	CH_2Cl_2	42 h	81	95
9	**2**	neat	42 h	71	93
10	**2**[f]	toluene	72 h	>99	99
11	**2**[d]	toluene	12 h	>99	98
12	**2**[d,f]	toluene	31 h	>99	99
13	**2**[d,g]	toluene	7 d	93	98
14	**3**	toluene	108 h	51	95
15	**3**[d]	toluene	66 h	57	95
16	**4**	toluene	6 d	NR[h]	
17	**4**[d]	toluene	66 h	NR[h]	
18	**5**	toluene	6 d	NR[h]	
19	**5**[d]	toluene	66 h	17	ND[e]
20	**6**	toluene	6 d	NR[h]	
21	**6**[d]	toluene	66 h	NR[h]	

[a] All reactions were carried out using acetone (0.9 mmol, 3 equiv) and **7a** (0.3 mmol) in the presence of catalyst (10 mol %) in toluene (0.5 mL) at 20 °C. [b] Yield of the isolated product after chromatography on silica gel. tr = trace. [c] Determined by chiral HPLC analysis. [d] 10 mol % of 4-nitrophenol was added as co-catalyst. [e] ND = not determined. [f] In the presence of 5 mol % of catalyst **2**. [g] In the presence of 2 mol % of catalyst 2. [h] NR = no reaction occurred.

observed ee only at the expense of reaction time (Table 1, entry 10). Solvent evaluation revealed that toluene was the best solvent for the reaction, and no better results were obtained in other solvents (Table 1, entries 3−9). It was gratifying that the catalyst loading could be successfully reduced to 5 mol % without any detrimental effect on the reaction when 10 mol % of 4-nitrophenol was added as an acidic co-catalyst (Table 1, entry 12).[6] Although the enantioselectivity remained unaltered, further reducing the catalyst loading to 2 mol % resulted in a very sluggish reaction (Table 1, entry 13).

On the basis of the optimized conditions for nitroolefin **7a**, a variety of nitroolefins were further examined either under condition A (10 mol % of **2** alone as the catalyst, in toluene, at 20 °C) or condition B (5 mol % of **2** in combination with 10 mol % 4-nitrophenol as the catalyst, in toluene, at 20 °C), and the results are collected in Table 2.

As shown in Table 2, the reaction has a broad substrate scope with respect to the nitroolefins. Under either condition A or condition B, a wide range of electron-rich and electron-deficient aromatic nitroalkenes underwent the Michael addition reaction of acetone with comparable high yields and enantioselectivities (Table 2, entries 1−6, 8−14; 98−99% ee). It is more significant that the less reactive nitroethylenes bearing a linear alkyl, branched alkyl, and alkenyl substituent at the *β*-position also proved to be suitable substrates when 20 mol % of catalyst **2** was employed. The corresponding reactions ran smoothly, affording the desired products in excellent yields with slightly eroded

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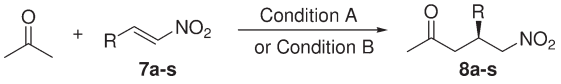
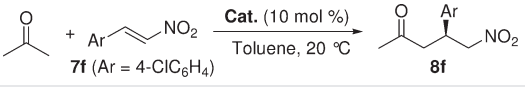
Table 2. Substrate Scope of 2 Catalyzed Asymmetric Michael Addition of Acetone to Nitroolefins[a]



		condition A			condition B		
entry	R	time (h)	yield (%)[b]	ee (%)[c]	time (h)	yield (%)[b]	ee (%)[c]
1	Ph (**a**)	36	>99	98	31	>99	99
2	2-$MeOC_6H_4$ (**b**)	59	99	99	49	92	98
3	4-$MeOC_6H_4$ (**c**)	36	94	99	60	99	98
4	3,4-$OCH_2OC_6H_3$ (**d**)	36	90	98	60	86	99
5	2-ClC_6H_4 (**e**)	21	>99	99	41	>99	>99
6	4-ClC_6H_4 (**f**)	24	>99	98	36	90	98
7	4-ClC_6H_4 (**f**)[d]	26	95	>99			
8	2-BrC_6H_4 (**g**)	24	99	99	40	97	>99
9	2-$CF_3C_6H_4$ (**h**)	36	91	>99	60	90	>99
10	2-$NO_2C_6H_4$ (**i**)	21	95	>99	75	67	99
11	4-$NO_2C_6H_4$ (**j**)	16	>99	>99	22	>99	99
12	1-naphthyl (**k**)	20	>99	99	48	94	98
13	2-furyl (**l**)	21	98	98	49	93	98
14	2-thienyl (**m**)	36	>99	98	60	87	98
15	(*E*)-styryl (**n**)[e]	48	90	98			
16	$BnCH_2$ (**o**)[e]	108	>99	97			
17	Et (**p**)[e]	72	85	97[g]			
18	^{i}Bu (**q**)[e]	72	95	98[g]			
19	^{i}Bu (**q**)[e,f]	96	93	98[g]			
20	Pr (**r**)[e]	67	86	97[g]			
21	Cy (**s**)[e]	72	75	98[g]			

[a] All reactions were carried out on 0.3 mmol scale. [b] Yield of the isolated product after chromatography on silica gel. [c] Determined by chiral HPLC analysis. [d] The reaction was performed on a 40 mmol scale. [e] In the presence of 20 mol % of catalyst **2**. [f] The reaction was conducted on a 30 mmol scale. [g] Determined by chiral GC analysis.

Table 3. Catalyst Recovery and Reuse in Michael Addition of Acetone to Nitroolefin 7f Using 10 mol % of Catalyst 2[a]



run	time (h)	yield (%)[b]	ee (%)[c]
1	17	83	>99
2	24	110	>99
3	24	83	>99
4	36	115	>99
5	72	96	>99

[a] All reactions were performed on a 30 mmol scale in 50 mL of toluene. [b] Yield of the product precipitated from the reaction mixture, average yield 97.4%. [c] Determined by chiral HPLC analysis.

enantioselectivities (Table 2, entries, 97−98% ee). To demonstrate the potential of this method for preparative purposes, the reaction is also carried out in gram scale giving the isolated product with unaltered enantioselectivity. For example, the reactions of aromatic nitroolefin **7f** and aliphatic nitroalkene **7q** on 40 and 30 mmol scale resulted in the formation of conjugated addition product **8f** and **8q** with enantiomeric excess of >99% and 98%, respectively (Table 2, entries 7 and 19).

To further reduce the amount of catalyst, the possibility of recovery and reuse of catalyst **2** was investigated by performing the Michael addition of acetone to 4-chloro-substituted *trans*-β-nitrostryene (**7f**) on a 30 mmol scale. Gratifying, catalyst **2** could be easily recovered via simple phase separation and reused at least five times without any loss of efficacy and stereocontrol, giving almost quantitative yields (average 97.4%, because of the accumulation of the unprecipitated product in the mother liquor, yields of >100% was observed in some cases) and excellent enantioselectivities (>99% ee) (Table 3). The product **8f** was separated at the end after each run by precipitation from the reaction mixture with the addition of 60 mL of hexane. The mother liquor containing catalyst **2** was evaporated under reduced pressure to remove hexane and then reused directly in the subsequent nitro-Michael addition.

The asymmetric addition of other methyl ketones to nitrostyrene **7a** also ran smoothly in the presence of 20 mol % of thiophosphoramide **2** to provide the desired adducts in high yield with both high regioselectivities and enantioselectivities (Scheme 3). For example, methyl ethyl ketone and methyl hydroxymethyl ketone underwent reaction with nitrostyrene **7a** with excellent regioselectivity, favoring branched products **9a,b** over their chromatographically separable regioisomer. Moreover, both **9a** and **9b** were generated with high enantioselectivities (98% ee) albeit with moderate diastereoselectivities (77/23 and 74/26 dr, respectively). More sterically demanding methyl isobutyl ketone afforded linear product (**9c**) exclusively in excellent chemical yield (93%) with high degree of enantioselectivity (96% ee).

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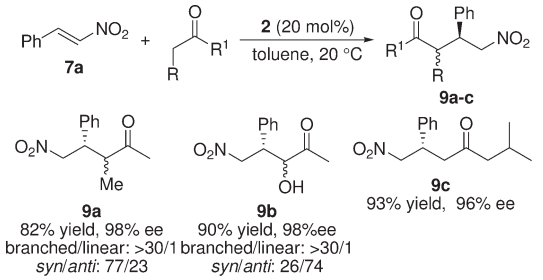
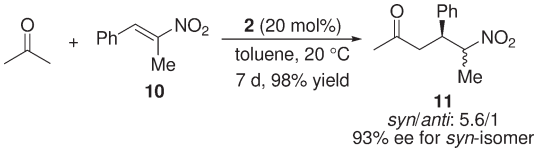
Scheme 3. Asymmetric Michael Addition of Other Ketones Catalyzed by 2



Scheme 4. Asymmetric Michael Addition to (*E*)-α-Methyl *β*-Nitrostyrene Catalyzed by 2



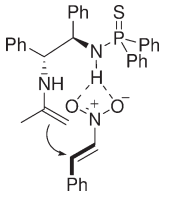


Figure 1. Possible transition state.

The reaction of less reactive *trans*-*β*-methyl-*β*-nitrostyrene (**10**), an interesting acceptor, since two contiguous tertiary stereocenters will be created in the Michael reaction, can afford the desired product **11** in good yield at the expense of reaction time. Compound **11** was obtained almost quantitatively as a pair of separable diastereomers with an *syn*/*anti* selectivity of 5.6/1, and the ee value of the *syn*-isomer was 93% (Scheme 4).

The relative configurations of the major diastereomer were assigned by comparison of ^{1}H and/or ^{13}C NMR of the products with the known compounds. The absolute configuration of the major isomer was established by comparison to the literature value of optical rotation.

Similar to our previous report,[5b] thiophosphoramide **2** is believed to function as a bifunctional catalyst. The primary amine first reacts with a carbonyl compound to form an enamine with or without the aid of acidic co-catalyst. Subsequently, the acidic hydrogen orientates the nitro group via hydrogen-bonding interaction so that the enamine will nucleophilic attack the nitroolefin from the *si* face to give the desired highly enantioselective conjugate addition product.

CONCLUSION

The chiral diamine skeleton was found to be crucial to both the catalytic activity and chiral induction ability of the primary amine-thiophosphoramide catalyst for the asymmetric Michael addition of problematic acetone to nitroolefins. Both the catalytic efficacy and enantioselectivity were significantly improved with thiophosphoramide catalyst **2** bearing the 1,2-diphenylethane-1,2-diamine skeleton relative to other thiophosphoramides catalyst derived from different chiral diamines. The reaction tolerated a broad substrate scope; not only aromatic but also aliphatic nitroolefins could be converted into the corresponding adducts in high yields with excellent enantioselectivities (97−99% ee). Moreover, catalyst **2** can be easily recovered via simple phase separation and reused at least five times without any lost of catalytic activity and stereocontrol.

EXPERIMENTAL SECTION

All reagents and solvents were commercial grade and purified prior to use when necessary. NMR spectra were acquired on a 400 MHz instrumental. Chemical shifts are measured relative to residual solvent peaks as an internal standard set to δ 7.26 and δ 77.0 ($CDCl_3$). Enantiomeric excesses were determined on a HPLC instrument (chiral column; mobile phase hexane/*i*-PrOH). Column chromatography was performed on silica gel (100−200 mesh).

Preparation of Thiophosphoramides 2−5. To a stirred solution of chiral diamine (11 mmol) and triethylamine (1.11 g, 11 mmol) in dry CH_2Cl_2 (15 mL) was added dropwise a solution of thiophosphoryl chloride (10 mmol) in dry CH_2Cl_2 (50 mL) at 0 °C over a period of 2 h. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The resulting mixture was washed with water, and the separated organic phase was dried over anhydrous magnesium sulfate. After removal of solvent the crude product was purified through column chromatography on silica gel (100−200 mesh, petroleum ether/ethyl acetate = 6:1−3:1) to afford the desired thiophosphoramides **2**−**5**.

Data for 2. White solid, 3.64 g, 85% yield, mp 112−113 °C, $[\alpha]_D^{20}$ −23.4 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.56 (br. s, 2 H), 4.10−4.13 (m, 1 H), 4.23 (d, *J* = 5.6 Hz, 1 H), 4.45−4.51 (m, 1 H), 7.05−7.15 (m, 5 H), 7.17−7.21 (m, 2 H), 7.23−7.39 (m, 9 H), 7.58−7.63 (m, 4 H). ^{31}P NMR ($CDCl_3$, 161.7 MHz): δ 59.12. ^{13}C NMR ($CDCl_3$, 100.6 MHz): 61.3 (d, *J* = 7.4 Hz), 61.8, 131.0, 131.1, 131.2, 131.3, 131.7, 131.8, 133.6, 133.9, 134.6, 134.9, 141.0, 142.5. HRMS (ESI) *m*/*z* calcd for $C_{26}H_{25}N_2PS$ $[M + H]^+$: 429.1549, found 429.1545.

Data for 3. White solid, 3.45 g, 75% yield, mp 110−112 °C, $[\alpha]_D^{20}$ −9.5 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.52 (br. s, 2 H), 4.36 (br. s, 1 H), 4.81 (dt, *J* = 3.2 and 9.2 Hz, 1 H), 5.17 (dd, *J* = 9.2 and 16.4 Hz, 1 H), 6.74 (d, *J* = 8.4 Hz, 2 H), 6.78 (d, *J* = 8.0 Hz, 2 H), 7.06−7.19 (m, 6 H), 7.28−7.44 (m, 10 H). ^{31}P NMR ($CDCl_3$, 161.7 MHz): δ 62.73. ^{13}C NMR ($CDCl_3$, 100.6 MHz): 60.7 (d, *J* = 8.7 Hz), 62.6, 120.7, 120.8, 120.9, 121.0, 124.6, 124.7, 126.9, 127.3, 127.6, 128.3, 128.5, 129.1, 129.2, 141.3, 141.9, 150.9, 151.0. HRMS (ESI) *m*/*z* calcd for $C_{26}H_{25}N_2PO_2S$ $[M + H]^+$: 461.1447, found 461.1444.

Data for 4. Brown solid, 3.30 g, 92% yield, mp 97−100 °C, $[\alpha]_D^{20}$ +57.6 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.77 (s, 3 H, CH_3), 1.04 (s, 3 H, CH_3), 1.05 (s, 3 H, CH_3), 1.12 (br. s, 2 H, NH_2), 1.53−1.60 (m, 1 H), 1.65−1.72 (m, 1 H), 1.92−2.00 (m, 1 H), 2.09−2.18 (m, 1 H), 3.26−3.34 (m, 1 H), 4.89 (t, *J* = 9.6, 10.4 Hz, 1 H), 7.39−7.43 (m, 6 H), 7.93−8.01 (m, 4 H). ^{31}P NMR ($CDCl_3$, 161.7 MHz): δ 55.06. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 17.7, 24.3, 26.4, 31.1, 38.0, 47.4 (d, *J* = 6.8 Hz), 61.7, 61.9, 128.0 (d, *J* = 5.9 Hz), 128.2 (d, *J* = 5.7 Hz), 131.4 (d, *J* = 10.9 Hz), 131.6 (d, *J* = 10.9 Hz), 135.1 (d, *J* = 90.5 Hz), 136.1 (d, *J* = 88.3 Hz). HRMS (ESI) *m*/*z* calcd for $C_{20}H_{27}N_2PS$ $[M + H]^+$: 359.1705, found 359.1704.

Data for 5. Pale yellow solid, 2.40 g, 53% yield, mp 84−86 °C, $[\alpha]_D^{20}$ −48.0 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.48 (br. s, 2 H), 3.01−3.08 (m, 2 H), 4.13 (d, *J* = 2.4 Hz, 1 H), 4.37 (d, *J* = 2.4 Hz, 1 H), 7.10−7.16 (m, 4 H), 7.22−7.24 (m, 1 H), 7.30−7.32 (m, 2 H),

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7.37−7.50 (m, 7 H), 7.92−8.02 (m, 4 H). ^{31}P NMR ($CDCl_3$, 161.7 MHz): δ 58.08. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 51.2 (d, J = 5.8 Hz), 51.8, 61.6 (d, J = 4.7 Hz), 62.3, 124.3, 124.4, 126.0, 126.1, 126.4, 126.5, 126.7, 128.4, 128.5, 128.6, 131.5, 131.6, 131.8, 133.5, 133.7, 134.6, 134.7, 138.3, 139.0, 140.6, 142.3. HRMS (ESI) m/z calcd for $C_{28}H_{25}N_2PS$ $[M + H]^+$: 453.1549, found 453.1547.

Preparation of Thiophosphinamide 6. To a stirred solution of (*R*)-1,1′-binaphthyl-2,2′-diamine (0.57 g, 2 mmol) in dry THF (5 mL) was added dropwise a solution of BuLi in THF (0.8 mL, 2 mmol, 2.5 M) at −40 °C. After being stirred for 1 h the resulting mixture was allowed to warm to 0 °C. Then a solution of diphenylphosphinothioic chloride (0.51 g, 2 mmol) in dry THF (5 mL) was added dropwise. After addition the reaction mixture was allowed to warm to room temperature and stirred for 2 h. The reaction was quenched with slowly addition of saturated aqueous $NaHCO_3$ and extracted twice with methylene chloride (15 mL). The combined organic phase was dried over anhydrous magnesium sulfate. After removal of solvent the crude product was purified through column chromatography on silica gel (100−200 mesh, petroleum ether/ethyl acetate = 6:1) to afford the desired thiophosphinamide **6** as a yellow solid: 0.40 g, 40% yield, mp 101−103 °C, $[\alpha]_D^{20}$ −26.1 (c 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.55 (br. s, 2 H), 5.14 (d, J = 7.6 Hz, 1 H), 7.11−7.16 (m, 2 H), 7.23−7.46 (m, 11 H), 7.55−7.64 (m, 3 H), 7.74−7.84 (m, 6 H). ^{31}P NMR ($CDCl_3$, 161.7 MHz): δ 52.29. ^{13}C NMR ($CDCl_3$, 100.6 MHz): 110.6, 118.2, 119.2, 119.3, 119.7, 119.8, 122.6, 124.0, 124.1, 124.8, 126.9, 127.2, 128.3, 128.5, 128.6, 128.9, 129.9, 130.2, 130.8, 130.9, 131.6, 131.7, 131.8, 133.0, 133.3, 133.7, 133.8, 134.4, 134.8, 137.3, 143.0. HRMS (ESI) m/z calcd for $C_{32}H_{25}N_2PS$ $[M + H]^+$: 501.1549, found 501.1541.

General Procedure for 2 Catalyzed Asymmetric Michael Addition to Nitroolefins. Condition A: A mixture of the catalyst **2** (12.9 mg, 0.03 mmol) and acetone (52 mg, 0.9 mmol, 3 equiv) in toluene (0.5 mL) was stirred at 20 °C to form a clear solution. Then, to the resulting solution was added nitroolefin (0.3 mmol) at the same temperature. After the reaction was complete (monitored by TLC), the mixture was purified by column chromatography on silica gel (100−200 mesh, PE/EtOAc = 5:1) to afford the desired product. The enantiomeric excess of the pure product was determined by chiral HPLC analysis.

Condition B: A mixture the catalyst **2** (6.4 mg, 0.015 mmol), 4-nitrophenol (4.2 mg. 0.03 mmol) and acetone (52 mg, 0.9 mmol, 3 equiv) in toluene (0.5 mL) was stirred at 20 °C to form a clear solution. Then, to the resulting solution was added nitroolefin (0.3 mmol) at the same temperature. After the reaction is complete (monitored by TLC), the mixture was purified by column chromatography on silica gel (100−200 mesh, PE/EtOAc = 5:1) to afford the desired product. The enantiomeric excess of the pure product was determined by chiral HPLC analysis.

*(S)-5-Nitro-4-phenylpentan-2-one (**8a**)*[4a]. White solid, 62 mg, >99% yield for condition A, 62 mg, >99% yield for condition B, mp 110−112 °C, $[\alpha]_D^{20}$ +4.3 (c 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.12 (s, 3 H), 2.92 (d, J = 7.2 Hz, 2 H), 4.06 (quintet, J = 7.2 Hz, 1 H), 4.59 (dd, J = 7.6 and 12.4 Hz, 1 H), 4.69 (dd, J = 6.8 and 12.4 Hz, 1 H), 7.21−7.30 (m, 2 H), 7.31−7.35 (m, 3 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 30.4, 39.0, 46.1, 79.4, 127.4, 127.9, 129.0, 138.8, 205.3. HPLC analysis (Chiralpak AD-H column, hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, wavelength = 220 nm): t_R = 10.15 (major) and 10.89 min (minor), 98% ee (condition A); t_R = 9.90 (major) and 10.63 min (minor), 99% ee (condition B).

*(S)-4-(2-Methoxyphenyl)-5-nitropentan-2-one (**8b**)*[7]. Pale yellow oil, 70 mg, 99% yield for condition A, 65 mg, 92% yield for condition B, $[\alpha]_D^{20}$ +23.4 (c 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.12 (s, 3 H), 2.95 (dd, J = 6.4 and 18.0 Hz, 1 H), 3.02 (dd, J = 7.6 and 18.0 Hz, 1 H), 3.85 (s, 3 H), 4.21 (quintet, J = 6.8 Hz, 1 H), 4.68−4.76 (m, 2 H), 6.89 (t, J = 8.4 Hz, 2 H), 7.13 (dd, J = 1.6 and 7.6 Hz, 1 H), 7.24 (dt, J = 1.6 and 7.6 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 30.1, 35.2, 44.4, 55.25, 77.7, 110.9, 120.8, 126.3, 128.9, 129.2, 157.0, 206.1. HPLC analysis (Chiralpak AS-H column, hexane/2-propanol = 85:15, flow rate = 1.0 mL/min, wavelength = 210 nm): t_R = 17.50 (major) and 19.98 min (minor), 99% ee (condition A); t_R = 17.42 (major) and 19.93 min (minor), 98% ee (condition B).

*(S)-4-(4-Methoxyphenyl)-5-nitropentan-2-one (**8c**)*[4a,d,7]. White solid, 67 mg, 94% yield for condition A, 70 mg, 99% yield for condition B, mp 84−86 °C, $[\alpha]_D^{20}$ −2.3 (c 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.10 (s, 3 H), 2.88 (d, J = 6.8 Hz, 2 H), 3.77 (s, 3 H), 3.95 (quintet, J = 6.8 Hz, 1 H), 4.55 (dd, J = 7.6 and 12.0 Hz, 1 H), 4.65 (dd, J = 7.2 and 12.4 Hz, 1 H), 6.85 (d, J = 8.8 Hz, 2 H), 7.13 (d, J = 8.8 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 30.4, 38.4, 46.2, 55.2, 79.7, 114.4, 128.4, 130.6, 159.1, 205.5. HPLC analysis (Chiralpak AD-H column, hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, wavelength = 210 nm): t_R = 14.19 (major) and 15.77 min (minor), 99% ee (condition A); t_R = 14.08 (major) and 15.72 min (minor), 98% ee (condition B).

*(S)-4-(Benzo[d][1,3]dioxol-5-yl)-5-nitropentan-2-one (**8d**)*[7]. Pale brown solid, 68 mg, 90% yield for condition A, 65 mg, 86% yield for condition B, mp 62−63 °C, $[\alpha]_D^{20}$ −2.8 (c 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.11 (s, 3 H), 2.85 (d, J = 7.2 Hz, 2 H), 3.91 (quintet, J = 7.2 Hz, 1 H), 4.53 (dd, J = 8.0 and 12.4 Hz, 1 H), 4.63 (dd, J = 6.8 and 12.4 Hz, 1 H), 5.92 (s, 2 H), 6.65−6.68 (m, 2 H), 6.73 (d, J = 7.6 Hz). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 30.3, 38.8, 46.2, 79.6, 101.2, 107.6, 108.6, 120.7, 132.4, 147.1 148.1, 205.3. HPLC analysis (Chiralpak AD-H column, hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, wavelength = 210 nm): t_R = 18.83 (major) and 20.59 min (minor), 98% ee (condition A); t_R = 18.57 (major) and 20.44 min (minor), 99% ee (condition B).

*(S)-4-(2-Chlorophenyl)-5-nitropentan-2-one (**8e**)*[4h]. White solid, 72 mg, >99% yield for condition A, 72 mg, >99% yield for condition B, mp 57−59 °C, $[\alpha]_D^{20}$ +18.8 (c 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.14 (s, 3 H), 2.94 (dd, J = 6.0 and 18.4 Hz, 1 H), 3.03 (dd, J = 8.0 and 18.0 Hz, 1 H), 4.41−4.49 (m, 1 H), 4.64−4.74 (m, 2 H), 7.18−7.23 (m, 3 H), 7.36−7.39 (m, 1 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 30.1, 35.6, 44.4, 77.2, 127.3, 128.2, 128.9, 130.3, 133.6, 135.9, 205.3. HPLC analysis (Chiralpak AD-H column, hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, wavelength = 210 nm): t_R = 14.29 (major) and 16.78 min (minor), 99% ee (condition A); t_R = 14.14 (major) and 16.46 min (minor), >99% ee (condition B).

*(S)-4-(4-Chlorophenyl)-5-nitropentan-2-one (**8f**)*[4e]. White solid, 72 mg, >99% yield for condition A, 65 mg, 90% yield for condition B, mp 89−91 °C, $[\alpha]_D^{20}$ +5.5 (c 1.1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.12 (s, 3 H), 2.88 (d, J = 7.2 Hz, 2 H), 3.98 (quintet, J = 7.2 Hz, 1 H), 4.56 (dd, J = 7.2 and 12.4 Hz, 1 H), 4.67 (dd, J = 6.4 and 12.4 Hz, 1 H), 7.16 (d, J = 8.4 Hz, 2 H), 7.30 (d, J = 8.4 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 30.3, 38.4, 45.9, 79.1, 128.8, 129.2, 133.7, 137.3, 205.0. HPLC analysis (Chiralpak AD-H column, hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, wavelength = 210 nm): t_R = 12.21 (major) and 14.06 min (minor), 98% ee (condition A); t_R = 12.28 (major) and 14.12 min (minor), 98% ee (condition B).

*(S)-4-(2-Bromophenyl)-5-nitropentan-2-one (**8g**)*[4e]. Pale yellow oil, 85 mg, 99% yield for condition A, 83 mg, 97% yield for condition B, $[\alpha]_D^{20}$ +14.9 (c 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.18 (s, 3 H), 2.96 (dd, J = 6.0 and 18.0 Hz, 1 H), 3.05 (dd, J = 8.0 and 18.0 Hz, 1 H), 4.44−4.52 (m, 1 H), 4.68−4.77 (m, 2 H), 7.14−7.22 (m, 2 H), 7.28−7.32 (m, 1 H), 7.61 (dd, J = 1.2 and 8.0 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 30.1, 37.8, 44.7, 77.4, 124.3, 128.0, 129.2, 129.4, 133.7, 137.5, 205.2. HPLC analysis (Chiralpak AS-H column, hexane/2-propanol = 85:15, flow rate = 1.0 mL/min, wavelength = 210 nm): t_R = 18.99 (major) and 23.15 min (minor), 99% ee (condition A); t_R = 19.02 (major) and 23.21 min (minor), >99% ee (condition B).

*(S)-5-Nitro-4-(2-(trifluoromethyl)phenyl)pentan-2-one (**8h**)*[8]. Colorless oil, 75 mg, 91% yield for condition A, 74 mg, 90% yield for

condition B, $[\alpha]_D^{20}$ +12.8 (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ 2.14 (s, 3 H), 2.90 (dd, J = 5.2 and 18.0 Hz, 1 H), 2.99 (dd, *J* = 8.4 and 18.0 Hz, 1 H), 4.41 (quintet, *J* = 6.8 Hz, 1 H), 4.72 (dd, *J* = 2.8 and 6.8 Hz, 2 H), 7.35−7.40 (m, 2 H), 7.53 (t, *J* = 7.6 Hz, 1 H), 7.68 (d, *J* = 8.0 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 29.9, 34.2, 46.1, 78.2, 122.7, 125.5, 126.7 (q, *J* = 5.7 Hz), 127.5, 127.8, 132.4, 137.7, 204.9. HPLC analysis (Chiralpak AD-H column, hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, wavelength = 210 nm): t_R = 7.99 (major) and 8.67 min (minor), >99% ee (condition A); t_R = 8.17 (major) and 8.88 min (minor), >99% ee (condition B).

(S)-5-Nitro-4-(2-nitrophenyl)pentan-2-one (**8i**)[4e,7]. Yellow oil, 72 mg, 95% yield for condition A, 51 mg, 67% yield for condition B, $[\alpha]_D^{20}$ −32.2 (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ 2.13 (s, 3 H), 3.03 (d, *J* = 6.8 Hz, 2 H), 4.51 (quintet, *J* = 6.8 Hz, 1 H), 4.80 (dd, J = 4.0 and 6.8 Hz, 2 H), 7.38 (d, *J* = 8.0 Hz, 1 H), 7.42 (t, *J* = 7.2 Hz, 1 H), 7.57 (t, *J* = 7.6 Hz, 1 H), 7.85 (dd, *J* = 0.8 and 8.0 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 30.00, 33.71, 45.24, 78.84, 125.12, 128.41, 128.65, 133.25, 133.45, 149.80, 204.77. HPLC analysis (Chiralpak AD-H column, hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, wavelength = 210 nm): t_R = 22.61 (major) and 25.04 min (minor), >99% ee (condition A); t_R = 21.80 (major) and 24.20 min (minor), 99% ee (condition B).

(S)-5-Nitro-4-(4-nitrophenyl)pentan-2-one (**8j**)[4h,7]. Pale yellow solid, 75 mg, >99% yield for condition A, 75 mg, >99% yield for condition B, mp 50−51 °C, $[\alpha]_D^{20}$ +4.8 (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ 2.14 (s, 3 H), 2.95 (dd, *J* = 2.4 and 7.2 Hz, 2 H), 4.13 (quintet, *J* = 7.2 Hz, 1 H), 4.63 (dd, *J* = 8.4 and 12.8 Hz, 1 H), 4.74 (dd, *J* = 8.4 and 12.8 Hz, 1 H), 7.42 (d, *J* = 8.8 Hz, 2 H), 8.17 (d, *J* = 8.8 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 30.2, 38.5, 45.6, 78.5, 124.1, 128.5, 146.4, 147.4, 204.4. HPLC analysis (Chiralpak AD-H column, hexane/2-propanol = 80:20, flow rate = 1.0 mL/min, wavelength = 210 nm): t_R = 17.68 (major) and 24.11 min (minor), >99% ee (condition A); t_R = 16.95 (major) and 23.27 min (minor), 99% ee (condition B).

(S)-4-(Naphthalen-1-yl)-5-nitropentan-2-one (**8k**)[4d,h]. Colorless oil, 77 mg, >99% yield for condition A, 73 mg, 94% yield for condition B, $[\alpha]_D^{20}$ +17.6 (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ 2.14 (s, 3 H), 3.08−3.12 (m, 2 H), 4.79−4.80 (m, 2 H), 4.95 (quintet, *J* = 6.8 Hz, 1 H), 7.33 (d, *J* = 7.2 Hz, 1 H), 7.43 (t, *J* = 7.2 Hz, 1 H), 7.53 (t, *J* = 7.2 Hz, 1 H), 7.61 (dt, *J* = 1.2 and 6.8 Hz, 1 H), 7.79 (d, *J* = 8.0 Hz, 1 H), 7.89 (d, *J* = 8.4 Hz, 1 H), 8.17 (d, *J* = 8.4 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 30.9, 33.4, 46.0, 78.8, 122.3, 123.6, 125.2, 126.1, 126.9, 128.5, 129.3, 130.9, 134.1, 134.7, 205.5. HPLC analysis (Chiralpak AD-H column, hexane/2-propanol = 80:20, flow rate = 1.0 mL/min, wavelength = 210 nm): t_R = 18.09 (major) and 21.89 min (minor), 99% ee (condition A); t_R = 18.13 (major) and 22.02 min (minor), 98% ee (condition B)

(R)-4-(Furan-2-yl)-5-nitropentan-2-one (**8l**)[4a,7]. Brown solid, 58 mg, 98% yield for condition A, 55 mg, 93% yield for condition B, mp 48−49 °C, $[\alpha]_D^{20}$ +5.7 (*c* 0.5, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ 2.15 (s, 3 H), 2.88 (dd, *J* = 7.2 and 18.0 Hz, 1 H), 2.96 (dd, *J* = 6.4 and 18.0 Hz, 1 H), 4.08 (quintet, *J* = 6.8 Hz, 1 H), 4.64−4.67 (m, 2 H), 6.12 (d, *J* = 3.2 Hz, 1 H), 6.27 (dd, *J* = 2.0 and 3.2 Hz, 1 H), 7.32 (d, *J* = 1.2 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 30.1, 32.8, 43.4, 107.0, 110.4, 142.2, 151.6, 205.1. HPLC analysis (Chiralpak AD-H column, hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, wavelength = 210 nm): t_R = 9.73 (major) and 11.08 min (minor), 98% ee (condition A); t_R = 9.55 (major) and 10.86 min (minor), 98% ee (condition B).

(R)-5-Nitro-4-(thiophen-2-yl)pentan-2-one (**8m**)[4c]. Brown solid, 64 mg, >99% yield for condition A, 56 mg, 87% yield for condition B, mp 37−38 °C, $[\alpha]_D^{20}$ −21.7 (*c* 1.0, $CHCl_3$), 95% *ee*. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.16 (s, 3 H), 2.97 (d, *J* = 6.8 Hz, 2 H), 4.32 (quintet, *J* = 6.8 Hz, 1 H), 4.61 (dd, *J* = 7.6 and 12.4 Hz, 1 H), 4.71 (dd, *J* = 6.4 and 12.4 Hz, 1 H), 6.86−6.95 (m, 2 H), 7.20 (dd, *J* = 1.2 and 5.2 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 30.3, 34.5, 46.8, 79.7, 124.7, 125.5, 127.1, 141.5, 205.0. HPLC analysis (Chiralpak AD-H column, hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, wavelength = 210 nm): t_R = 11.54 (major) and 12.96 min (minor), 98% ee (condition A); t_R = 11.31 (major) and 12.73 min (minor), 98% ee (condition B).

(S,E)-4-(Nitromethyl)-6-phenyl-5-hexen-2-one (**8n**)[9]. White solid, 63 mg, 90% yield, mp 111−113 °C, $[\alpha]_D^{20}$ −7.0 (*c* 1.0, $CHCl_3$), 97.5% ee. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.19 (s, 3 H), 2.75 (d, *J* = 6.8 Hz, 2 H), 3.48−3.57 (m, 1 H), 4.52 (dd, *J* = 7.2 and 12.0 Hz, 1 H), 4.59 (dd, *J* = 6.4 and 12.0 Hz, 1 H), 6.08 (dd, *J* = 8.8 and 16.0 Hz, 1 H), 6.53 (d, *J* = 16.0 Hz, 1 H), 7.24−7.34 (m, 5 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 30.5, 37.0, 44.9, 78.6, 126.2, 126.4, 128.0, 128.6, 133.4, 136.1, 205.5. HPLC analysis (Chiralpak AS-H column, hexane/2-propanol = 85:15, flow rate = 1.0 mL/min, wavelength = 210 nm): t_R = 24.96 (major) and 30.40 min (minor).

(R)-4-(Nitromethyl)-6-phenylhexan-2-one (**8o**)[9]. Yellow oil, 70 mg, >99% yield, $[\alpha]_D^{20}$ +6.6 (*c* 1.0 $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ 1.70−1.76 (m, 2 H), 2.16 (s, 3 H), 2.59−2.73 (m, 5 H), 4.48−4.51 (m, 2 H), 7.16−7.22 (m, 3 H), 7.28−7.31 (m, 2 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 30.4, 32.6, 32.9, 33.1, 44.5, 78.02 126.2, 128.2, 128.6, 140.7, 206.5. HPLC analysis (Chiralpak AS-H column, hexane/2-propanol = 85:15, flow rate = 1.0 mL/min, wavelength = 210 nm): t_R = 13.67 (major) and 15.70 min (minor), 97% ee.

(R)-4-(Nitromethyl)hexan-2-one (**8p**)[9]. Yellow oil, 41 mg, 85% yield, $[\alpha]_D^{20}$ −8.3 (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ 0.95 (t, *J* = 7.2 Hz, 3 H), 1.40−1.47 (m, 2 H), 2.17 (s, 3 H), 2.52−2.62 (m, 3 H), 4.44 (d, *J* = 4.8 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 11.0, 24.34 30.4, 34.5, 44.2, 78.0, 206.6. GC analysis (BETA DEX 120 column, from 40 to 200 °C at a rate of 1 °C/min): t_R = 65.54 (minor) and 65.72 min (major), 97% ee.

(R)-6-Methyl-4-(nitromethyl)heptan-2-one (**8q**)[4a]. Yellow oil, 53 mg, 95% yield, $[\alpha]_D^{20}$ −8.8 (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ 0.87 (d, *J* = 6.8 Hz, 3 H), 0.90 (d, *J* = 6.8 Hz, 3 H), 1.15−1.24 (m, 2 H), 1.56−1.66 (m, 1 H), 2.15 (s, 3 H), 2.47−2.71 (m, 3 H), 4.42 (d, *J* = 5.6 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 22.3, 22.4, 25.0, 30.4, 30.8, 40.5, 44.7, 78.5, 206.7. GC analysis (Chiralsil-DEX CB column, from 40 to 160 °C at a rate of 1 °C/min): t_R = 62.02 (minor) and 62.18 min (major), 98% ee.

(R)-4-(Nitromethyl)heptan-2-one (**8r**)[4a]. Pale yellow oil, 45 mg, 86% yield, $[\alpha]_D^{20}$ −14.1 (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ 0.92 (t, *J* = 6.8 Hz, 3 H), 1.33−1.37 (m, 4 H), 2.17 (s, 3 H), 2.52−2.63 (m, 3 H), 4.44 (d, *J* = 5.6 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 13.9, 19.8, 30.5, 32.8, 33.6, 44.6, 78.4, 206.7. GC analysis (Chiralsil-DEX CB column, from 40 to 160 °C at a rate of 1 °C/min): t_R = 82.28 (minor) and 82.80 min (major), 97% ee.

(S)-4-Cyclohexyl-5-nitropentan-2-one (**8s**). Colorless oil, 48 mg, 75% yield, $[\alpha]_D^{20}$ −12.1 (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ 0.89−0.99 (m, 2 H), 1.08−1.26 (m, 3 H), 1.36−1.44 (m, 1 H), 1.64−1.76 (m, 5 H), 2.16 (s, 3 H), 2.48−2.64 (m, 3 H), 4.42 (d, *J* = 6.0 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 26.2, 29.7, 30.0, 30.3, 38.1, 38.7, 42.2, 76.9, 206.7. HRMS (ESI) *m*/*z* calcd for $C_{11}H_{19}NO_3$ $[M+Na]^+$: 236.1257, found 236.1264. GC analysis (Chiralsil-DEX CB column, from 40 to 160 °C at a rate of 1 °C/min): t_R = 59.99 (minor) and 60.72 min (major), 98% ee.

(4S)-3-Methyl-5-nitro-4-phenylpentan-2-one (**9a**)[3j]. Colorless oil, 54 mg, 82% yield, $[\alpha]_D^{20}$ −6.5 (*c* 1.0, $CHCl_3$), *syn*/*anti*: 77/23, 98% ee for *syn*-isomer and 71% ee for *anti*-isomer. ^1H NMR ($CDCl_3$, 400 MHz): δ 0.98 (d, *J* = 7.2 Hz, 2.38 H, *syn*-isomer), 1.21 (d, *J* = 6.8 Hz, 0.71 H, *anti*-isomer), 1.94 (s, 0.66 H, *anti*-isomer), 2.23 (s, 2.20 H, *syn*-isomer), 2.94−3.02 (m, 1 H), 3.65−3.81 (m, 1 H), 4.60−4.81 (m, 2 H), 7.15−7.20 (m, 2 H), 7.27−7.35 (m, 3 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 14.2 (*anti*-isomer), 15.9 (*syn*-isomer) 29.2 (*syn*-isomer), 29.4 (*anti*-isomer), 45.7 (*anti*-isomer), 45.8 (*syn*-isomer), 49.1 (*syn*-isomer), 49.8 (*anti*-isomer), 77.6 (*anti*-isomer), 78.4 (*syn*-isomer), 127.8 (*anti*-isomer), 127.9 (*syn*-isomer), 128.9 (*anti*-isomer), 129.0 (*syn*-isomer),

137.4 (*syn*-isomer), 137.9 (*anti*-isomer), 209.8 (*anti*-isomer), 210.7 (*syn*-isomer). HPLC analysis (Chiralpak AD-H column, hexane/2-propanol = 95:5, flow rate = 1.0 mL/min, wavelength = 220 nm): t_R = 14.28 (minor, *syn*-isomer), 17.40 (major, *syn*-isomer), 22.91 (major, *anti*-isomer) and 25.36 min (minor, *anti*-isomer).

*(4S)-3-Hydroxy-5-nitro-4-phenylpentan-2-one (**9b**)*[10]. White solid, 60 mg, 90% yield, mp 35−36 °C, $[\alpha]_D^{20}$ +6.9 (*c* 0.87, $CHCl_3$), *anti*/*syn*: 74/26, 98% ee for *anti*-isomer and 88% ee for *syn*-isomer. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.99 (s, 2.27 H, *anti*-isomer), 2.10 (s, 0.80 H, *syn*-isomer), 3.69 (br. s, 1 H, OH), 3.73−3.78 (m, 1 H), 4.31 (d, *J* = 5.2 Hz, 0.74 H, *anti*-isomer), 4.45 (d, *J* = 2.8 Hz, 0.26 H, *syn*-isomer), 4.58 (dd, *J* = 8.4 and 13.6 Hz, 0.81 H, *anti*-isomer), 4.66 (dd, *J* = 7.2 and 13.6 Hz, 0.31 H, *syn*-isomer), 4.75 (dd, *J* = 6.4 and 13.6 Hz, 0.79 H, *anti*-isomer), 4.95 (dd, *J* = 8.0 and 13.6 Hz, 0.29 H, *syn*-isomer), 7.16−7.25 (m, 2 H), 7.28−7.31 (m, 3 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 25.8 (*syn*-isomer), 26.7 (*anti*-isomer) 46.0 (*syn*-isomer), 47.1 (*anti*-isomer), 77.2 (*syn*-isomer), 77.3 (*anti*-isomer), 78.9, 128.3 (*anti*-isomer), 128.7 (*syn*-isomer), 128.8 (*anti*-isomer), 128.9 (*syn*-isomer), 129.2 (*syn*-isomer), 129.6 (*anti*-isomer), 134.0 (*syn*-isomer), 137.4 (*anti*-isomer), 206.6 (*syn*-isomer), 208.3 (*anti*-isomer). HPLC analysis (Chiralpak AD-H column, hexane/2-propanol = 95:5, flow rate = 1.0 mL/min, wavelength = 220 nm): t_R = 41.13 (minor, *syn*-isomer), 45.26 (major, *syn*-isomer) 63.04 (major, *anti*-isomer) and 77.72 min (minor, *anti*-isomer).

*(S)-6-Methyl-1-nitro-2-phenylheptan-4-one (**9c**)*[4a]. Yellow oil, 70 mg, 93% yield, $[\alpha]_D^{20}$ +3.1 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.83 (d, *J* = 6.8 Hz, 6 H), 2.01−2.11 (m, 1 H), 2.16−2.27 (m, 2 H), 2.79−2.90 (m, 2 H), 4.01 (quintet, *J* = 7.2 Hz, 1 H), 4.58 (dd, *J* = 8.0 and 12.4 Hz, 1 H), 4.68 (dd, *J* = 6.8 and 12.4 Hz, 1 H), 7.19−7.24 (m, 3 H), 7.29−7.32 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75.0 MHz): 22.3, 22.4, 24.4, 39.0, 45.7, 52.2, 79.4, 127.3, 127.7, 128.9, 138.9, 207.4. HPLC analysis (Chiralpak AS-H column, hexane/2-propanol = 98:2, flow rate = 0.7 mL/min, wavelength = 210 nm): t_R = 14.00 (minor) and 17.06 min (major), 96% ee.

*(S)-5-Nitro-4-phenylhexan-2-one (**11**)*[11,12]. Yellowish-green oil, 65 mg, 98% yield, $[\alpha]_D^{20}$ +6.4 (*c* 1.0, $CHCl_3$) (diastereomer mixture), +10.0 (*c* 1.0, $CHCl_3$) (*syn*-isomer), 85/15 dr, 93% ee for *syn*-isomer. ^{1}H NMR ($CDCl_3$, 400 MHz): diastereomer mixture, δ 1.31 (d, *J* = 6.4 Hz, 2.52 H, *syn*-isomer), 1.48 (d, *J* = 6.4 Hz, 0.45 H, *anti*-isomer), 2.01 (s, 2.36 H, *syn*-isomer), 2.11 (s, 0.42 H, *anti*-isomer), 2.73 (dd, *J* = 4.4 and 17.2 Hz, 0.84 H, *syn*-isomer), 2.89 (dd, *J* = 7.6 and 17.6 Hz, 0.16 H, *anti*-isomer), 2.97 (dd, *J* = 9.6 and 17.2 Hz, 0.84 H, *syn*-isomer), 3.04 (dd, *J* = 6.8 and 17.6 Hz, 0.15 H, *anti*-isomer), 3.68−3.75 (m, 1 H), 4.72−4.80 (m, 0.84 H, *syn*-isomer), 4.84−4.91 (m, 0.16 H, *anti*-isomer), 7.13−7.20 (m, 2 H), 7.26−7.34 (m, 3 H); *syn*-isomer, 1.31 (d *J* = 6.4 Hz, 3 H), 2.01 (s, 3 H), 2.73 (dd, *J* = 3.2 and 16.8 Hz, 1 H), 2.97 (dd, *J* = 9.6 and 16.8 Hz, 1 H), 3.71 (dt, *J* = 2.8 and 8.0 Hz, 1 H), 4.72−4.80 (m, 1 H), 7.19 (d, *J* = 7.6 Hz, 2 H), 7.26−7.30 (m, 3 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): diastereomer mixture, 16.7 (*anti*-isomer), 17.7 (*syn*-isomer), 30.4 (*syn*-isomer), 30.5 (*anti*-isomer), 44.5 (*anti*-isomer), 44.7 (*anti*-isomer), 45.3 (*syn*-isomer), 46.2 (*syn*-isomer), 85.8 (*anti*-isomer), 87.1 (*syn*-isomer), 127.8 (*syn*-isomer), 127.9 (*anti*-isomer), 128.10 (*anti*-isomer), 128.15 (*syn*-isomer), 128.7 (*anti*-isomer), 129.0 (*syn*-isomer), 137.8 (*anti*-isomer), 138.2 (*syn*-isomer), 204.4 (*anti*-isomer), 204.9 (*syn*-isomer); *syn*-isomer, 17.7, 30.4, 45.3, 46.2, 87.1, 127.8, 128.1, 129.0, 138.2, 204.8. GC analysis (Chiralsil-DEX CB column, from 40 to 160 °C at a rate of 1 °C/min): t_R = 75.90 (major, *syn*-isomer), 76.44 (minor, *syn*-isomer), 78.14 (minor, *anti*-isomer) and 78.70 min (major, *anti*-isomer).

Recovery and Reuse of Catalyst 2. A mixture the catalyst **2** (12.9 mg, 0.03 mmol) and acetone (523 mg, 90 mmol, 3 equiv) in toluene (50 mL) was stirred at 20 °C to form a clear solution. Then, to the resulting solution was added nitroolefin **7f** (5.51 g, 30 mmol) at the same temperature. After the reaction was complete (monitored by TLC), 60 mL of hexane was added, and the whole mixture was allowed to cool to 0 °C to precipitate the conjugate addition product **8f**. After removal of **8f** through filtration, the mother liquor was evaporated under reduced pressure to remove hexane, and the resulting mixture was used for subsequent reaction.

■ ASSOCIATED CONTENT

Supporting Information. Copies of NMR spectra and HPLC analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: z.h.zhou@nankai.edu.cn; youmingwang@eyou.com.

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