Chiral Sulfoxides as Neutral Coordinate-Organocatalysts in Asymmetric Allylation of *N*-Acylhydrazones Using Allylic Trichlorosilanes

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Supporting Information

General Methods. Melting points are uncorrected. IR spectra were recorded on a Jasco FT/IR-610 infrared spectrometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA300, JNM-LA400 or JNM-LA500 spectrometer in CDCl_3 unless otherwise noted. Tetramethylsilane (TMS) served as internal standard ($\delta = 0$) for ^1H NMR, and CDCl_3 was used as internal standard ($\delta = 77.0$) for ^{13}C NMR. Column chromatography was conducted on Silica gel 60 (Merck) and preparative thin-layer chromatography (PTLC) was carried out using Wakogel B-5F. Dichloromethane was distilled from P_2O_5 , and then from CaH_2 and stored over MS 4A. All other solvents were purified based on standard procedures.

Chemicals. Hydrazones **1a-j** were prepared according to our reported procedure.¹ Allyltrichlorosilane (**2**), 2-methyl-2-butene, and diisopropylethylamine were purchased from Tokyo Kasei Kogyo Co., LTD, and were used after distillation. (*E*)-² and (*Z*)-crotyltrichlorosilane (**4**),³ chiral sulfoxides **6a**⁴, **6b-c**⁵, and **6d-f**⁶ were prepared according to the reported procedures. Dimethyl sulfoxide (DMSO) was distilled from CaH_2 and stored over MS 4A. All other chemicals were purified based on standard procedures.

General Experimental Procedures

(1) Survey of neutral coordinate-organocatalysts (NCOs) for allylation of *N*-benzoylhydrazone derived from 3-phenylpropanal (1a**):** To a solution of *N*-benzoylhydrazone **1a** (75.7 mg, 0.3 mmol) and an achiral or racemic NCO (0.2-10 equiv. relative to **1a**) in dichloromethane (2 mL) was added dropwise allyltrichlorosilane (**2**) (65 μ L, 0.45 mmol) at -78 $^{\circ}$ C. After stirred at -78 $^{\circ}$ C for the indicated time, the reaction was quenched by adding saturated aqueous NaHCO_3 at -78 $^{\circ}$ C. After warmed to room temperature and addition of brine, the mixture was extracted with dichloromethane (three times). The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was purified by preparative TLC to afford **3a**. The results were summarized in Table S-1.

Table S-1. Survey of NCOs in Allylation of *N*-Benzoylhydrazone **1a**

entry	NCO (equiv.)	yield of 3a /%
1	– (–)	9
2	DMF (1.0)	47
3	NMP (1.0)	49
4	$\text{Me}_2\text{NCONMe}_2$ (1.0)	38
5	Pyridine <i>N</i> -oxide (1.0)	36
6	Pyridine <i>N</i> -oxide (0.2)	30
7	HMPA (1.0)	64
8	HMPA (0.2)	16
9	$\text{Ph}_3\text{P=O}$ (1.0)	70
10	DMSO (1.0)	65
11	Tetramethylene sulfone (1.0)	9
12	Diphenyl sulfoxide (1.0)	40
13	Dibenzyl sulfoxide (1.0)	73
14	Tetramethylene sulfoxide (1.0)	57
15	$(\pm)$ -Methyl phenyl sulfoxide (1.0)	57
16	DMSO (0.2)	24
17	DMSO (2.0)	85
18	DMSO (3.0)	99
19	DMSO (5.0)	86
20	DMSO (10.0)	33

(2) Allylation/crotylation of *N*-benzoylhydrazones using DMSO: To a solution of *N*-benzoylhydrazone **1** (0.3 mmol) and DMSO (64 μ L, 0.9 mmol) in dichloromethane (2 mL) was added dropwise allyltrimethylsilane (**2**) (65 μ L, 0.45 mmol) or crotyltrimethylsilane (**4**) (0.45 mmol) at -78 $^{\circ}$ C. After stirred at -78 $^{\circ}$ C for the indicated time, the reaction was quenched by adding saturated aqueous NaHCO_3 at -78 $^{\circ}$ C. The same work-up and purification procedures as those mentioned above afforded allylation or crotylation product **3**. For crotylation of **1a**, diisopropylamine (0.1 equiv.) was added before introducing crotyltrimethylsilane. The results were summarized in Table S-2.

Table S-2. DMSO-promoted Allylation of *N*-Acylhydrazones

Reaction scheme: $\text{R}^1\text{-N}=\text{N}-\text{NHCOAr}$ (**1**) + $\text{R}^2\text{-CH=CH-Si(CH}_3\text{)}_3$ (**2** or **4**) $\xrightarrow[\text{-78 } ^{\circ}\text{C}]{\text{DMSO (3 equiv.)}, \text{CH}_2\text{Cl}_2}$ $\text{R}^1\text{-CH(R}^2\text{)-CH=CH-Si(CH}_3\text{)}_3$ ($\pm$ -**3** or $\pm$ -**5**)

entry	1 (R^1 , Ar)	2 or 4	time/h	3 (%yield, selectivity)
1	1a ($\text{Ph}(\text{CH}_2)_2$, Ph)	2	6	3a (99)
2	1b (Me, Ph)	2	15	3b (78)
3	1c (<i>n</i> - C_7H_{15} , Ph)	2	1	3c (86)
4	1d (<i>i</i> -Pr, Ph)	2	6	3d (89)
5	1e (<i>c</i> -Hex, Ph)	2	6	3e (88)
6	1f (<i>p</i> - MeOC_6H_4 , Ph)	2	6	3f (70)
7	1g (<i>p</i> - ClC_6H_4 , Ph)	2	6	3g (33)
8	1h ($\text{PhC}\equiv\text{C}$, Ph)	2	8	3h (93)
9	1i (Ph, <i>p</i> - MeOC_6H_4)	2	6	3i (87)
10	1j (<i>p</i> - MeC_6H_4 , Ph)	2	6	3j (72)
11 ^a	1a	(<i>E</i>)- 4 ^b	6	5a (71, 98% <i>syn</i>) ^d
12 ^a	1a	(<i>Z</i>)- 4 ^c	6	5a (69, >99% <i>anti</i>) ^d

^a*i*-Pr₂EtN (0.1 equiv.) was added. ^b98% *E*. ^c>99% *Z*. ^dNo α -adduct was obtained.

(3) Enantioselective allylation/crotylation of *N*-benzoylhydrazones:

Method A: To a solution of *N*-benzoylhydrazone **1** (0.3 mmol), chiral sulfoxide **6** (0.9 mmol), and 2-methyl-2-butene (16 μ L, 0.15 mmol) in dichloromethane (2 mL) was added dropwise allyltrimethylsilane (**2**) (65 μ L, 0.45 mmol) at -78 $^{\circ}$ C. After stirred at -78 $^{\circ}$ C for the indicated time, the reaction was quenched by adding saturated aqueous NaHCO_3 or triethylamine (0.2 mL, 1.5 mmol) in anhydrous methanol (1 mL)

at $-78\text{ }^{\circ}\text{C}$. After warmed to room temperature and addition of brine, the mixture was extracted with dichloromethane (three times). The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was purified by preparative TLC (dichloromethane/hexane/ethyl acetate = 3/1/1) to afford the adduct. Sulfoxide **6** was recovered in $>90\%$ with $>97\%$ ee. For the reactions at a higher concentration (0.3 M), a half amount of dichloromethane (total 1 mL) was used.

Method B: To a solution of chiral sulfoxide **6** (0.9 mmol) and 2-methyl-2-butene (0.15 mmol, 16 μL) in dichloromethane (0.8 mL) was added dropwise allyltrichlorosilane (**2**) (65 μL , 0.45 mmol) or crotyltrichlorosilane (**4**) (0.45 mmol) at $-78\text{ }^{\circ}\text{C}$. After stirred for 15 min, *N*-benzoylhydrazone **1** (0.3 mmol) in dichloromethane (1.2 mL) was added to the solution over a period of 30 min. After stirred at $-78\text{ }^{\circ}\text{C}$ for the indicated time, the same work-up and purification procedures as Method A afforded allylation or crotylation product **3**. Sulfoxide **6** was recovered in $>90\%$ with $>97\%$ ee. For the reactions at a higher concentration (0.3 M), a half amount of dichloromethane (total 1 mL) was used. For crotylation of **1a**, a solution of **1a** in dichloromethane was added to the sulfoxide/allyltrichlorosilane solution over a period of 1.5 h, and then the mixture was stirred for 4 h.

The results were summarized in Tables 1-3 in the text.

Physical Data and Analytical Conditions of Allylation/Crotylation Products

(*R*)-*N'*-(1-Phenethylbut-3-enyl)benzohydrazide (3a**):** $[\alpha]_{\text{D}}^{21} -3.0$ (c 0.815, CHCl_3 , 88% ee (*R*)); ^1H NMR, ^{13}C NMR, and IR data (see ref. 1); HPLC (CHIRALCEL OD-H, 0.46 cm $\varnothing$ $\times$ 25 cmL, hexane/2-propanol = 19/1, flow rate 1.0 mL/min, UV detection at 254 nm) $t_{\text{R}} = 21.5$ min (*R*), $t_{\text{R}} = 26.3$ min (*S*).

(*R*)-*N'*-(1-Methylbut-3-enyl)benzohydrazide (3b**):** Mp 95.5-95.6 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{21} +18.1$ (c 1.000, CHCl_3 , 94% ee); ^1H NMR (300 MHz, CDCl_3) δ 1.02 (d, $J = 6.2$ Hz, 3H), 2.02-2.11 (m, 1H), 2.14-2.23 (m, 2H), 4.99-5.08 (m, 2H), 5.70-5.84 (m, 1H), 7.31-

7.46 (m, 3H), 7.31-7.37 (br, 2H), 7.67-7.70 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 18.5, 39.7, 59.9, 117.3, 126.9, 128.6, 131.8, 132.8, 135.1, 167.3; IR (neat) 3293, 2972, 1637, 1541, 1317, 1093, 989, 916 cm^{-1} ; HR-FABMS calcd for $\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}$ ($\text{M}+\text{H}^+$) 205.1345, found 205.1341; HPLC (CHIRALPAK OJ, 0.46 $\text{cm}\varnothing \times 25 \text{ cmL}$, hexane/2-propanol = 100/1, flow rate 1.5 mL/min, UV detection at 254 nm) $t_R = 17.8 \text{ min}$ (*R*), $t_R = 24.3 \text{ min}$ (*S*).

(*R*)-*N'*-(1-Heptylbut-3-enyl)benzohydrazide (3c): $[\alpha]^{19}_{\text{D}} +22.2$ (c 0.810, CHCl_3 , 91% ee (*R*)); ^1H NMR (400 MHz, CDCl_3) δ 0.80 (t, $J = 7.1 \text{ Hz}$, 3H), 1.13-1.38 (m, 12 H), 2.11-2.26 (m, 2H), 2.95 (apparent t, $J = 5.6 \text{ Hz}$, 1H), 5.04-5.12 (m, 2H), 5.79-5.85 (m, 1H), 7.36-7.69 (m, 7H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.1, 22.6, 25.7, 29.2, 29.8, 31.8, 32.6, 37.6, 59.6, 117.3, 126.8, 128.7, 131.8, 132.8, 135.6, 167.1; IR (neat) 3280, 2927, 1636, 1538, 1464, 1314, 912, 694, 411 cm^{-1} ; HR-FABMS calcd for $\text{C}_{18}\text{H}_{29}\text{N}_2\text{O}$ ($\text{M}+\text{H}^+$) 289.2280, found 289.2268; HPLC (CHIRALCEL OD-H, 0.46 $\text{cm}\varnothing \times 25 \text{ cmL}$, hexane/2-propanol = 60/1, flow rate 1.3 mL/min, UV detection at 254 nm) $t_R = 27.2 \text{ min}$ (*R*), $t_R = 33.3 \text{ min}$ (*S*).

(*R*)-*N'*-(1-Isopropylbut-3-enyl)benzohydrazide (3d): Mp 73.4-73.5 $^{\circ}\text{C}$ (recrystallized from dichloromethane/hexane); $[\alpha]^{19}_{\text{D}} +56.5$ (c 1.00, CHCl_3 , >99% ee (*R*)); ^1H NMR (400 MHz, CDCl_3) δ 0.92 (d, $J = 6.8 \text{ Hz}$, 3H), 0.93 (d, $J = 6.8 \text{ Hz}$, 3H), 1.79-1.88 (m, 1H), 2.02-2.11 (m, 1H), 2.83 (quint, $J = 4.4 \text{ Hz}$, 1H), 5.06-5.16 (m, 2H), 5.89 (dddd, $J = 17.1, 10.1, 8.3, 5.6 \text{ Hz}$, 1H), 7.35-7.39 (m, 2H), 7.42-7.47 (m, 1H), 7.65-7.68 (m, 2H), 7.35-7.47 (br, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 17.6, 18.3, 29.4, 33.9, 64.5, 117.1, 126.8, 128.7, 131.8, 132.9, 136.5, 167.0; IR (KBr) 3241, 2960, 1628, 1466, 1320, 919, 792, 694 cm^{-1} ; Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{N}_2\text{O}$: C, 72.18; H, 8.74; N, 11.97. Found: C, 72.38; H, 8.68; N, 12.06; HPLC (CHIRALPAK AD,

0.46 cm $\varnothing$ $\times$ 25 cmL, hexane/2-propanol = 40/1, flow rate 1.0 mL/min, UV detection at 254 nm) t_R = 32.5 min (*R*), t_R = 38.6 min (*S*).

(*R*)-*N'*-(1-Cyclohexylbut-3-enyl)benzohydrazide (3e): $[\alpha]_D^{22}$ +22.0 (c 0.500, CHCl₃, 84% ee (*R*)); Mp, ¹H NMR, ¹³C NMR, IR data, and elemental analysis (see ref. 1); HPLC (CHIRALPAK AD, 0.46 cm $\varnothing$ $\times$ 25 cmL, hexane/2-propanol = 9/1, flow rate 1.0 mL/min, UV detection at 254 nm) t_R = 9.2 min (*R*), t_R = 22.8 min (*S*).

(*S*)-*N'*-[1-(4-Methoxyphenyl)but-3-enyl]benzohydrazide (3f): $[\alpha]_D^{20}$ -118.8 (c 0.510, CHCl₃, 77% ee (*S*)); ¹H NMR (300 MHz, CDCl₃) δ 2.26-2.49 (m, 2H), 3.66 (s, 3H), 4.00 (apparent t, J = 7.1 Hz, 1H), 4.74 (brs, 1H), 4.92-5.10 (m, 2H), 5.68 (dddd, J = 17.1, 10.1, 7.9, 6.2 Hz, 1H), 6.74 (apparent d, J = 8.7 Hz, 2H), 7.17 (apparent d, J = 8.7 Hz, 2H), 7.24 (apparent t, J = 7.4 Hz, 2H), 7.34 (apparent t, J = 7.4 Hz, 1H), 7.51 (apparent d, J = 7.4 Hz, 2H), 7.77 (brs, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 40.0, 55.0, 63.2, 113.7, 117.6, 126.8, 128.4, 128.7, 131.6, 132.7, 133.3, 134.5, 158.9, 167.1; IR (neat) 3284, 3067, 3000, 2933, 2836, 1737, 1640, 1513, 1302, 1247, 1177, 1033, 919, 830, 695 cm⁻¹; HR-FABMS calcd for C₁₈H₂₁N₂O₂ (M+H⁺) 297.1603, found 297.1606; HPLC (CHIRALCEL OD-H, 0.46 cm $\varnothing$ $\times$ 25 cmL, hexane/2-propanol = 9/1, flow rate 1.0 mL/min, UV detection at 254 nm) t_R = 12.9 min (*R*), t_R = 16.7 min (*S*).

(*S*)-*N'*-[1-(4-Chlorophenyl)but-3-enyl]benzohydrazide (3g): $[\alpha]_D^{20}$ -136.1 (c 0.535, CHCl₃, 89% ee (*S*)); ¹H NMR (300 MHz, CDCl₃) δ 2.29-2.46 (m, 2H), 4.07 (apparent t, J = 7.4 Hz, 1H), 4.77 (brs, 2H), 5.06-5.09 (m, 2H), 5.63-5.77 (m, 1H), 7.18-7.54 (m, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 40.3, 63.2, 118.2, 126.8, 128.59, 128.64, 129.0, 131.8, 132.6, 133.2, 133.9, 140.1, 167.3; IR (neat) 3283, 3066, 1735, 1638, 1312, 1091, 1014, 921, 824, 694, 516 cm⁻¹; HR-FABMS calcd for

C₁₇H₁₇ClN₂O (M+H⁺) 301.1108, found 301.1106; HPLC (CHIRALPAK AD-H, 0.46 cmø × 25 cmL, hexane/2-propanol = 30/1, flow rate 1.0 mL/min, UV detection at 254 nm) *t_R* = 42.4 min (*R*), *t_R* = 48.0 min (*S*).

(*S*)-*N'*-(1-Phenylethynylbut-3-enyl)benzohydrazide (3h): Mp 103-104 °C; [α]_D²⁷ – 130.1 (c 1.010, CHCl₃, 70% ee (*S*)); ¹H NMR (300 MHz, CDCl₃) δ 2.54 (apparent t, *J* = 6.8 Hz, 2H), 4.18 (t, *J* = 6.4 Hz, 1H), 4.99 (brs, 1H), 5.12-5.29 (m, 2H), 5.97 (ddt, *J* = 17.1, 10.2, 7.0 Hz, 1H), 7.20-7.32 (m, 3H), 7.39-7.44 (m, 4H), 7.49 (apparent tt, *J* = 7.3, 1.7 Hz, 1H), 7.79 (apparent d, *J* = 7.0 Hz, 2H), 8.31 (brs, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 38.1, 52.7, 84.7, 87.9, 118.3, 122.6, 127.0, 128.15, 128.19, 128.56, 131.68, 131.80, 132.6, 133.5, 167.2; IR (KBr) 3290, 3232, 3063, 2997, 2852, 2236, 1637, 1544, 1476, 1323, 911, 754, 689, 651 cm⁻¹; Anal. Calcd for C₁₉H₁₈N₂O: C, 78.59; H, 6.25; N, 9.65. Found: C, 78.37; H, 6.20; N, 9.61; HPLC (CHIRALCEL OD-H, 0.46 cmø × 25 cmL, hexane/2-propanol = 19/1, flow rate 1.0 mL/min, UV detection at 254 nm) *t_R* = 32.2 min (*S*), *t_R* = 38.4 min (*R*).

($\pm$)-*N'*-(1-Phenylbut-3-enyl)-4-methoxybenzohydrazide (3i): ¹H NMR (300 MHz, CDCl₃) δ 2.41-2.67 (m, 2H), 3.74 (s, 3H), 4.09 (apparent t, *J* = 7.2 Hz, 1H), 4.11-5.02 (brs, 2H), 5.03-5.14 (m, 2H), 5.70-5.84 (m, 1H), 6.76-6.81 (m, 2H), 7.19-7.33 (m, 5H), 7.46-7.51 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 40.4, 55.4, 63.9, 113.8, 118.0, 125.0, 127.6, 127.7, 128.5, 128.6, 134.5, 141.7, 162.4, 166.8; IR (neat) 3306, 3063, 1631, 1324, 1025, 756 cm⁻¹; HR-FABMS calcd for C₁₈H₂₁N₂O₂ (M+H⁺) 297.1603, found 297.1606.

($\pm$)-*N'*-(1-*p*-Tolylbut-3-enyl)benzohydrazide (3j): Mp 86.7-86.8 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.27 (s, 3H), 2.35-2.49 (m, 2H), 4.06 (apparent t, *J* = 7.3 Hz, 1H), 4.08-5.03 (brs, 2H), 5.04 (dd, *J* = 10.2, 1.0 Hz, 1H), 5.11 (dd, *J* = 17.1, 1.0 Hz, 1H), 5.76 (dddd, *J* = 17.1, 10.1, 7.8, 4.2 Hz, 1H), 7.08 (apparent d, *J* = 8.1 Hz, 2H), 7.20

(apparent d, $J = 7.8$ Hz, 2H), 7.30 (apparent t, $J = 7.6$ Hz, 2H), 7.35-7.41 (m, 1H), 7.52 (apparent d, $J = 7.8$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.1, 40.3, 63.6, 117.9, 126.8, 127.6, 128.6, 129.2, 131.7, 132.8, 134.6, 137.3, 138.5, 167.0; IR (KBr) 3302, 3068, 1627, 1545, 1308, 925, 814, 695 cm^{-1} ; Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}$: C, 76.84; H, 7.30; N, 10.07. Found: C, 77.11; H, 7.19; N, 9.99.

(1*R*,2*R*)-*N'*-(2-Methyl-1-phenethylbut-3-enyl)benzohydrazide (syn-5a): $[\alpha]_{\text{D}}^{21} +26.7$ (c 0.965, CHCl_3 , 99% *syn*, 89% ee (1*R*,2*R*)); ^1H NMR, ^{13}C NMR, IR data, and elemental analysis (see ref. 1); HPLC (CHIRALCEL OD-H, 0.46 cm $\varnothing$ $\times$ 25 cmL, hexane/2-propanol = 19/1, flow rate 1.0 mL/min, UV detection at 254 nm) $t_R = 20.1$ min (1*R*,2*R*), $t_R = 22.8$ min (1*S*,2*S*).

(1*R*,2*S*)-*N'*-(2-Methyl-1-phenethylbut-3-enyl)benzohydrazide (anti-5a): $[\alpha]_{\text{D}}^{25} -9.9$ (c 0.600, CHCl_3 , >99% *anti*, 91% ee (1*R*,2*S*)); ^1H NMR, ^{13}C NMR, IR data, and elemental analysis (see ref. 1); HPLC (CHIRALCEL OD-H, 0.46 cm $\varnothing$ $\times$ 25 cmL, hexane/2-propanol = 19/1, flow rate 1.0 mL/min, UV detection at 254 nm) $t_R = 18.9$ min (1*R*,2*S*), $t_R = 24.7$ min (1*S*,2*R*).

(1*R*,2*R*)-*N'*-(1,2-Dimethylbut-3-enyl)benzohydrazide (syn-5b): $[\alpha]_{\text{D}}^{27} +40.9$ (c 1.15, CHCl_3 , 98% *syn*, 82% ee (1*R*,2*R*)); ^1H NMR (400 MHz, CDCl_3) δ 0.99 (d, $J = 6.3$ Hz, 3H), 1.00 (d, $J = 7.1$ Hz, 3H), 2.13-2.38 (m, 1H), 3.00-3.01 (m, 1H), 5.02-5.08 (m, 2H), 4.98-5.08 (brd, 1H) 5.74-5.89 (m, 1H), 7.34-7.38 (m, 2H), 7.34-7.42 (brd, 1H), 7.42-7.45 (m, 1H), 7.66-7.69 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.9, 15.7, 40.7, 59.5, 115.0, 126.8, 128.7, 131.8, 132.9, 140.3, 167.3; IR (neat) 3285, 2970, 1637, 1577, 1460, 1313, 1074, 914, 694 cm^{-1} ; HR-FABMS calcd for $\text{C}_{13}\text{H}_{18}\text{N}_2\text{O}$ ($\text{M}+\text{H}^+$) 219.1497, found 219.1489; HPLC (CHIRALPAK OJ, 0.46 cm $\varnothing$ $\times$

25 cmL, hexane/2-propanol = 100/1, flow rate 1.5 mL/min, UV detection at 254 nm)
 $t_R = 19.4$ min (1*R*,2*R*), $t_R = 22.9$ min (1*S*,2*S*).

(1*R*,2*S*)-*N'*-(1,2-Dimethylbut-3-enyl)benzohydrazide (*anti*-5b): $[\alpha]_D^{27} -19.1$ (c 0.770, CHCl₃, >99% *anti*, 73% ee (1*R*,2*R*)); ¹H NMR (400 MHz, CDCl₃) δ 0.97 (d, $J = 6.8$ Hz, 3H), 1.00 (d, $J = 6.3$ Hz, 3H), 2.11-2.22 (m, 1H), 2.92 (apparent quint, 1H, $J = 6.6$ Hz), 5.03-5.09 (m, 2H), 5.79 (ddd, $J = 18.3, 10.2, 8.1$ Hz, 1H), 7.35-7.39 (m, 2H), 7.43-7.47 (m, 1H), 7.35-7.47 (br, 2H), 7.66-7.69 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 15.7, 15.8, 42.4, 59.4, 115.3, 126.8, 128.7, 131.8, 132.9, 141.7, 167.2; IR (neat) 3280, 2921, 1636, 1578, 1462, 1109, 913, 693 cm⁻¹; HR-FABMS calcd for C₁₃H₁₈N₂O (M+H⁺) 219.1497, found 219.1489; HPLC (CHIRALPAK OJ, 0.46 cm $\varnothing$ $\times$ 25 cmL, hexane/2-propanol = 100/1, flow rate 1.5 mL/min, UV detection at 254 nm) $t_R = 16.9$ min (1*R*,2*S*), $t_R = 25.1$ min (1*S*,2*R*).

(1*R*,2*R*)-*N'*-(1-Heptyl-2-methylbut-3-enyl)benzohydrazide (*syn*-5c): $[\alpha]_D^{20} +66.8$ (c 0.500, CHCl₃, 95% *syn*, 91% ee (1*R*,2*R*)); ¹H NMR (400 MHz, CDCl₃) δ 0.80 (t, $J = 6.8$ Hz, 3H), 1.00 (d, $J = 6.8$ Hz, 3H), 1.20-1.23 (m, 8H), 1.29-1.43 (m, 4H), 2.39-2.43 (m, 1H), 2.86-2.91 (m, 1H), 5.03-5.09 (m, 2H), 5.94 (ddd, $J = 16.8, 11.0, 6.3$ Hz, 1H), 7.35-7.39 (m, 2H), 7.42-7.47 (m, 1H), 7.65-7.68 (m, 2H), 7.00-7.80 (br, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 14.07, 14.08, 22.6, 26.5, 29.2, 29.7, 29.9, 31.8, 39.0, 64.4, 114.3, 126.8, 128.7, 131.8, 132.9, 141.6, 166.9; IR (neat) 3280, 2927, 1631, 1465, 1314, 911, 694 cm⁻¹; HR-FABMS calcd for C₁₉H₃₁N₂O (M+H⁺) 303.2436, found 303.2439; HPLC (CHIRALPAK AD-H, 0.46 cm $\varnothing$ $\times$ 25 cmL, hexane/2-propanol = 60/1, flow rate 1.0 mL/min, UV detection at 254 nm) $t_R = 24.1$ min (1*R*,2*R*), $t_R = 32.3$ min (1*S*,2*S*).

(1*R*,2*S*)-*N'*-(1-Heptyl-2-methylbut-3-enyl)benzohydrazide (*anti*-5c): $[\alpha]_D^{19} -10.6$

(c 0.505, CHCl₃, >99% *anti*, 86% ee (1*R*,2*S*)); ¹H NMR (400 MHz, CDCl₃) δ 0.81 (t, *J* = 6.6 Hz, 3H), 1.01 (d, *J* = 6.8 Hz, 3H), 1.20-1.29 (m, 8H), 1.33-1.43 (m, 4H), 2.31 (apparent sext, *J* = 6.8 Hz, 1H), 2.76-2.79 (m, 1H), 5.02-5.07 (m, 2H), 5.81 (ddd, *J* = 17.1, 10.5, 7.8 Hz, 1H), 7.35-7.39 (m, 3H), 7.42-7.46 (m, 2H), 7.65-7.67 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 15.7, 22.6, 25.8, 29.2, 29.5, 30.0, 31.8, 40.0, 64.3, 114.9, 126.8, 128.7, 131.7, 133.0, 141.8, 167.0; IR (neat) 3287, 2927, 1632, 1465, 1314, 913, 695, 410 cm⁻¹; HR-FABMS calcd for C₁₉H₃₁N₂O (M+H⁺) 303.2436, found 303.2435; HPLC (CHIRALPAK AD-H, 0.46 cmø × 25 cmL, hexane/2-propanol = 60/1, flow rate 1.0 mL/min, UV detection at 254 nm) *t*_R = 21.6 min (1*R*,2*S*), *t*_R = 28.1 min (1*S*,2*R*).

(1*S*,2*R*)-*N'*-[1-(4-Methoxyphenyl)-2-methylbut-3-enyl]benzohydrazide (*anti*-5f): Mp 87.7-87.8 °C; [α]_D¹⁷ -14.0 (c 0.88, CHCl₃, >99% *anti*, 92% ee (1*S*,2*R*)); ¹H NMR (300 MHz, CDCl₃) δ 0.66 (d, *J* = 6.8 Hz, 3H), 2.28-2.44 (m, 1H), 3.70 (d, 1H, *J* = 9.5 Hz), 3.74 (s, 3H), 4.94-5.13 (br, 1H), 5.16 (dd, 1H, *J* = 10.1, 1.6 Hz), 5.23 (dd, 1H, *J* = 17.2, 1.6 Hz), 5.82-5.94 (m, 1H), 6.81 (brd, 2H, *J* = 8.8 Hz), 6.80-7.21 (br, 1H), 7.17-7.48 (m, 7H); ¹³C NMR (75 MHz, CDCl₃) δ 17.8, 44.1, 55.2, 68.1, 113.8, 116.6, 126.7, 128.6, 129.5, 131.6, 132.6, 132.9, 141.5, 159.1, 166.9; IR (neat) 3292, 2962, 1635, 1469, 1314, 913, 694 cm⁻¹; Anal calcd for C₁₉H₂₂N₂O₂: C, 73.45; H, 7.24; N, 8.94. Found: C, 73.52; H, 7.14; N, 9.03. HPLC (CHIRALPAK AD-H, 0.46 cmø × 25 cmL, hexane/2-propanol = 30/1, flow rate 1.3 mL/min, UV detection at 254 nm) *t*_R = 20.7 min (*R*), *t*_R = 22.7 min (*S*).

HPLC Analytical Conditions for Chiral Sulfoxides:

Methyl *p*-tolyl sulfoxide (6a): HPLC (CHIRALCEL OB, 0.46 cmø × 25 cmL, hexane/2-propanol = 9/1, flow rate 1.5 mL/min, UV detection at 254 nm) *t*_R = 9.2 min (*S*), *t*_R = 20.1 min (*R*).

Ethyl *p*-tolyl sulfoxide (6b): HPLC (CHIRALCEL OB, 0.46 cm $\varnothing$ $\times$ 25 cmL, hexane/2-propanol = 9/1, flow rate 1.5 mL/min, UV detection at 254 nm) t_R = 6.7 min (*S*), t_R = 17.4 min (*R*).

Isopropyl *p*-tolyl sulfoxide (6c): HPLC (CHIRALCEL OB, 0.46 cm $\varnothing$ $\times$ 25 cmL, hexane/2-propanol = 9/1, flow rate 1.0 mL/min, UV detection at 254 nm) t_R = 7.4 min (*S*), t_R = 12.4 min (*R*).

Methyl *o*-tolyl sulfoxide (6d): HPLC (CHIRALCEL OB, 0.46 cm $\varnothing$ $\times$ 25 cmL, hexane/2-propanol = 9/1, flow rate 1.5 mL/min, UV detection at 254 nm) t_R = 10.2 min (*S*), t_R = 25.2 min (*R*).

Methyl *o*-methoxyphenyl sulfoxide (6e): HPLC (CHIRALCEL OB, 0.46 cm $\varnothing$ $\times$ 25 cmL, hexane/2-propanol = 9/1, flow rate 1.5 mL/min, UV detection at 254 nm) t_R = 12.3 min (*S*), t_R = 24.1 min (*R*).

Methyl *p*-methoxyphenyl sulfoxide (6f)⁷: HPLC (CHIRALCEL OD, 0.46 cm $\varnothing$ $\times$ 25 cmL, hexane/2-propanol = 9/1, flow rate 1.0 mL/min, UV detection at 254 nm) t_R = 16.4 min (*S*), t_R = 18.6 min (*R*).

The N-N Bond Cleavage by SmI₂ and Assignment of Absolute Configurations

Determination of the absolute configuration of product 3a as a representative of the aliphatic products:

To a degassed solution of benzohydrazide **3a** (53.5 mg, 0.18 mmol, 43% ee) in methanol (0.4 mL) was added a 0.1 M THF solution of SmI₂ (5.5 mL, 3 equiv.) at rt. After stirred for 15 min, the mixture was concentrated *in vacuo*. The residue was

purified by preparative TLC (hexane/isopropylamine = 10/1) to afford homoallylic amine **7a** (30.0 mg, 94% yield, 41% ee (*R*)). The enantiomeric excess of **7a** was determined by HPLC analysis using CHIRALCEL OD-H column. The absolute configuration of **7a** was assigned by comparison of the retention times in HPLC analysis with that of the authentic sample (*S*)-**7a** which was prepared from (*R*)-1-phenylhex-5-en-3-ol⁸ as follows. To a solution of (*R*)-1-phenylhex-5-en-3-ol (44.6 mg, 0.25 mmol, 67% ee (*R*)) and triethylamine (106 μ L, 3 equiv.) in dichloromethane (2.5 mL) was added methanesulfonyl chloride (29 μ L, 1.5 equiv.) at 0 °C. After stirred for 1 h at 0 °C, brine and diethyl ether were added to the mixture. The organic layer was separated, washed with 10% aqueous citric acid, sat. aqueous NaHCO₃, and brine. After the organic layer was dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*, a mixture of the crude mesylate and sodium azide (165 mg) in DMF (1 mL) was then heated at 100 °C for 3 h. After cooled to rt, diethyl ether and water were added. The organic layer was separated, washed with water (three times) and brine, dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. The crude azide was dissolved in THF (2.5 mL) and treated with lithium aluminum hydride (9.9 mg) at rt. After stirred for 15 min, the reaction was quenched with powdered Na₂SO₄•10H₂O, diluted with dichloromethane, and stirred vigorously. The white precipitates formed were removed by filtration through a Celite pad and washed with dichloromethane. The filtrate was concentrated *in vacuo* and purified by preparative TLC (hexane/isopropylamine = 10/1) to afford (*S*)-**7a** (29.2 mg, 66% yield over three steps, 67% ee (*S*)).

(*R*)-1-Phenethylbut-3-enylamine (7a). $[\alpha]_D^{21} = +2.0$ (c 0.850, CHCl₃, 41% ee (*R*)); ¹H NMR (400 MHz, CDCl₃) δ 1.30 (brs, 2H), 1.61 (dddd, *J* = 13.7, 10.0, 7.8, 5.7 Hz, 1H), 1.75 (dddd, *J* = 13.7, 10.3, 6.4, 4.8 Hz, 1H), 2.02 (apparent dt, *J* = 13.8, 7.8 Hz, 1H), 2.27 (dddt, *J* = 13.8, 6.4, 4.6, 1.4 Hz, 1H), 2.64 (ddd, *J* = 13.6, 10.0, 6.4 Hz, 1H), 2.75 (ddd, *J* = 13.6, 10.3, 5.7 Hz, 1H), 2.81 (apparent tt, *J* = 7.8, 4.8 Hz, 1H), 5.06-5.13 (m, 2H), 5.78 (dddd, *J* = 16.2, 11.2, 7.8, 6.4 Hz, 1H), 7.14-7.22 (m, 3H), 7.24-

7.31 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 32.6, 39.3, 42.6, 50.1, 117.4, 125.7, 128.29, 128.31, 135.6, 142.2 HPLC (CHIRALCEL OD-H, 0.46 cm ϕ $\times$ 25 cmL, hexane/2-propanol/diethylamine = 90/10/0.1, flow rate 1.0 mL/min, UV detection at 254 nm) t_R = 7.1 min (*S*), t_R = 9.6 min (*R*).

Determination of the absolute configuration of product 3f as a representative of the aromatic products:

To a degassed solution of benzohydrazide **3f** (58.7 mg, 0.20 mmol, 71% ee) in methanol (0.4 mL) was added a 0.1 M THF solution of SmI_2 (5.7 mL, 3 equiv.) at rt. After stirred for 15 min, the mixture was concentrated *in vacuo*. The residue was purified by preparative TLC (hexane/isopropylamine = 10/1) to afford homoallylic amine **7f** (35.3 mg, quant., 69% ee (*S*)). The enantiomeric excess of **7f** was determined by HPLC analysis using CHIRALCEL OD-H column. The absolute configuration of **7f** was assigned by comparison of its optical rotation with the reported data⁹.

(*S*)-1-(4-Methoxyphenyl)but-3-enylamine (7f). $[\alpha]_{\text{D}}^{17} = -31.9$ (c 0.905, CHCl_3 , 69% ee (*S*)); ^1H NMR (400 MHz, CDCl_3) δ 1.51 (brs, 2H), 2.33 (apparent dt, J = 13.9, 8.0 Hz, 1H), 2.44 (apparent dt, J = 13.9, 5.8 Hz, 1H), 3.80 (s, 3H), 3.95 (dd, J = 8.1, 5.4 Hz, 1H), 5.16-5.04 (m, 2H), 5.75 (dddd, J = 17.1, 10.0, 7.8, 6.4 Hz, 1H), 6.87 (apparent d, J = 8.7 Hz, 2H), 7.26 (apparent d, J = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 44.2, 54.7, 55.2, 113.7, 117.5, 127.3, 135.6, 138.0, 158.5; HPLC (CHIRALCEL OD-H, 0.46 cm ϕ $\times$ 25 cmL, hexane/2-propanol = 9/1, flow rate 1.0 mL/min, UV detection at 269 nm) t_R = 7.5 min (*R*), t_R = 9.0 min (*S*).

References and Notes

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