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Supporting Information

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Supporting Information

for

[Ru(phgly)$_2$(binap)]–Li$_2$CO$_3$: A Highly Active, Robust, and Enantioselective Catalyst for Cyanosilylation of Aldehydes

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CONTENTS

(A) General Remarks

Gas chromatographic (GC) analysis was conducted on a Shimadzu GC-17A or GC-2010 instrument using helium carrier gas (72.0 kPa). NMR spectra were obtained on a JEOL JNM-EX270 or JNM-A400 spectrometer. Carbon multiplicity was assigned by DEPT experiments. IR spectra were recorded on a JASCO FT/IR-4100 spectrophotometer. Optical rotations were taken on a JASCO DIP-360 polarimeter. Silica-gel column chromatography was performed with Silica Gel 60N (63–210 μm; Kanto Chemical Co. Inc). Preparative thin layer chromatography (TLC) was carried out with PLC plates (20 x 20 cm, silica gel 60F$_{254}$, 1.0 mm; Merck Ltd). Mass-spectrometry measurements were carried out at the Center for Instrumental Analysis, Hokkaido University.

(B) Preparation of [Ru{(*S*)-phgly}$_2${(*S*)-binap}] [(*S*,*S*,*S*)-3]

A dry, 100-mL Schlenk tube [Note 1] connected to a supply of argon [Note 2] was equipped with a Teflon-coated magnetic stirring bar and a glass stopper. The vessel was charged with $[RuCl_2(benzene)]_2$ (258 mg, 0.52 mmol) [Note 3] and (*S*)-BINAP (661 mg, 1.06 mmol) [Note 4], and then was evacuated and filled with argon. *N*,*N*-Dimethylformamide (DMF) (15 mL) [Note 5] was introduced with a syringe under a stream of argon. The reddish brown suspension was stirred at 100 ºC for 10 min and the resulting clear reddish brown solution including a BINAP–Ru(II) complex was cooled to 25 °C.[1]

Another dry, 50-mL Schlenk tube was charged with sodium (*S*)-phenylglycinate (533 mg, 3.08 mmol) [Note 6] and CH_3OH (30 mL) [Note 7], and the solution was degassed by three freeze-thaw cycles. It was transferred into the DMF solution of the BINAP–Ru(II) complex described above by a syringe under a stream of argon, and the obtained light red solution was stirred at 25 ºC for 12 h. Water (50 mL) was added to the solution with vigorous stirring, precipitating a yellowish orange solid. After filtration, the collected solid was dissolved in CH_2Cl_2 (40 mL). The solution was washed with three 50-mL-portions of water, and dried over $MgSO_4$. After filtration through a celite pad, the solution was concentrated under reduced pressure (0.4 mmHg) to give a yellowish orange solid. The crude product was purified by preparative TLC (silica gel, eluent; ethyl acetate, R_f = 0.45–0.61, extraction with a mixture of CH_2Cl_2 and CH_3OH (10:1)). The obtained yellow solid was reprecipitated with a mixture of CH_2Cl_2 (10 mL) and pentane (100 mL) followed by filtration and drying under the reduced pressure to afford (*S*,*S*,*S*)-**3** as a light yellow powder (787 mg, 74% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.45 (brs, 2H, N*H*H), 3.23 (brs, 2H, NH*H*), 3.63 (t, 2H, *J* = 8.3 Hz, 2PhC*H*), 6.24 (d, 2H, *J* = 9.3 Hz, aromatic H), 6.50 (m, 6H, aromatic H), 6.71 (m, 6H, aromatic H), 7.07–7.67 (m, 24H, aromatic H), 8.06 ppm (m, 4H, aromatic H); ^{31}P NMR (161.7 MHz, $CDCl_3$): δ = 52.3 ppm (s); ESI-MS: *m/z* calcd for $C_{60}H_{48}N_2O_4P_2Ru$: 1024.21494 ($[M]^+$); found: 1024.21231.

Notes

[1] All apparatuses were dried in a 55 ºC oven before use.

[2] Argon of 99.99% purity was used.

[3] $[RuCl_2(benzene)]_2$ was obtained from Aldrich Co.

[4] (*S*)-BINAP was available from Kanto Chemical Co.

[5] Anhydrous DMF (99.5% purity) was purchased from Kanto Chemical Co., and was degassed by three freeze-thaw cycles before use.

[6] (*S*)-Phenylglycine was available from Acros Co. Its sodium salt was prepared by mixing with equimolar amounts of NaOH in an aqueous solution.

[7] Anhydrous CH_3OH (99.9% purity) was purchased from Kanto Chemical Co.

(C) General Procedure of Asymmetric Cyanosilylation (S/C = 10,000)

Cyanosilylation of benzaldehyde (**1a**) was described as the typical reaction procedure. *Caution: $(CH_3)_3SiCN$ must be used in a well-ventilated hood due to its high toxicity.*

A 40-mL Schlenk flask equipped with a Teflon-coated magnetic stirring bar was filled with argon.[Note 1] $(CH_3)_3SiCN$ (1.19 g, 12.0 mmol) [Note 2] and 0.10 M aqueous solution of Li_2CO_3 (10 μL, 1.0 μmol) [Note 3] were placed in the flask, and the mixture was stirred for 20 min at 25 °C. To the pale yellow solution were added $(C_2H_5)_2O$ (10 mL) [Note 4] and a 20 mM-THF solution [Note 4] of (*S*,*S*,*S*)-**3** (50 μL, 1.0 μmol), and the mixture was stirred for 30 min. The resulting yellow solution was cooled down to –78 °C. Then **1a** (1.05 g, 9.9 mmol) was charged into the flask, and the mixture was stirred for 12 h. After the solvent and the volatile compounds were evaporated under reduced pressure at ambient temperature, the residue was purified by a short-path distillation to give (*R*)-2-phenyl-2-trimethylsilyloxyacetonitrile [(*R*)-**2a**] (1.99 g, 98% yield, 97% *ee*) as a colorless oil. Bp 68 °C / 0.08 mmHg; $[\alpha]_D^{23} = +28.4$ ($c = 1.12$, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.23$ (s, 9H, $Si(CH_3)_3$), 5.50 (s, 1H, CHCN), 7.37–7.50 ppm (m, 5H, aromatic H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -0.3$, 63.9, 119.2, 126.3, 128.9, 129.3, 136.2 ppm; HRMS (EI): *m*/*z* calcd for $C_{11}H_{15}NOSi$: 205.0923 ($[M]^+$); found: 205.0931. The *ee* of **2a** was determined by GC analysis: column, CP-Chirasil-Dex (0.32 mm i.d. x 25 m, df = 0.25 μm, Varian); column temp, 110 °C; injection temp, 220 °C; retention time (t_R) of (*R*)-**2a**, 14.7 min (98.4%); t_R of (*S*)-**2a**, 14.3 min (1.6%).

Notes

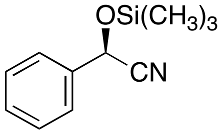
[1] Argon of 99.99% purity was used.

[2] $(CH_3)_3SiCN$ purchased from Wako Pure Chemical Industries, Ltd. was purified by distillation before use.

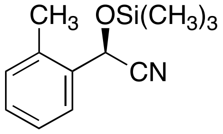
[3] Li_2CO_3 was available from Aldrich Co., Ltd.

[4] Anhydrous $(C_2H_5)_2O$ (99.5% purity) and THF (99.5% purity) were purchased from Kanto Chemical Co.

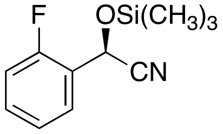
(D) Analytical Data of Asymmetric Cyanosilylation Products



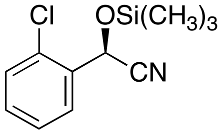
(*R*)-2-Phenyl-2-trimethylsilyloxyacetonitrile [(*R*)-2a]. See Part C.



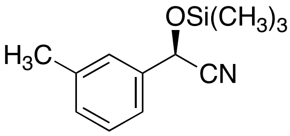
(*R*)-2-(2-Methylphenyl)-2-trimethylsilyloxyacetonitrile [(*R*)-2b]. 99% (isolated yield). Bp 75 ºC / 0.08 mmHg (bulb-to-bulb); $[\alpha]_D^{23}$ = +24.7 (*c* = 1.00, $CHCl_3$), 96% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.20 (s, 9H, $Si(CH_3)_3$), 2.44 (s, 3H, $CH_3C_6H_4$), 5.57 (s, 1H, CHCN), 7.20–7.30 (m, 3H, aromatic H), 7.52 ppm (d, *J* = 6.8 Hz, 1H, aromatic H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.3, 18.8, 62.0, 118.8, 126.4, 127.0, 129.4, 131.1, 134.1, 135.6 ppm; HRMS (EI): *m*/*z* calcd for $C_{12}H_{17}NOSi$: 219.1080 ($[M]^+$); found: 219.1065; GC: column, CP-Chirasil-Dex; column temp, 140 °C; injection temp, 220 °C; t_R of (*R*)-**2b**, 19.5 min (98.0%); t_R of (*S*)-**2b**, 18.9 min (2.0%).



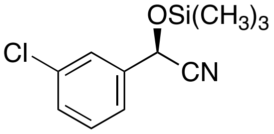
(*R*)-2-(2-Fluorophenyl)-2-trimethylsilyloxyacetonitrile [(*R*)-2c]. 97% (isolated yield). Bp 63 ºC / 0.08 mmHg (bulb-to-bulb); $[\alpha]_D^{22}$ = +24.6 (*c* = 1.00, $CHCl_3$), 96% *ee*; ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.24 (s, 9H, $Si(CH_3)_3$), 5.76 (s, 1H, CHCN), 7.10 (m, 1H, aromatic H), 7.23 (m, 1H, aromatic H), 7.40 (m, 1H, aromatic H), 7.65 ppm (m, 1H, aromatic H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = –0.5, 57.6 (d, $^3J_{C\text{-}F}$ = 5.0 Hz), 115.6 (d, $^2J_{C\text{-}F}$ = 20.7 Hz), 118.3, 123.8 (d, $^2J_{C\text{-}F}$ = 13.2 Hz), 124.7 (d, $^3J_{C\text{-}F}$ = 3.3 Hz), 128.4 (d, $^4J_{C\text{-}F}$ = 2.5 Hz), 131.3 (d, $^3J_{C\text{-}F}$ = 8.3 Hz), 159.4 ppm (d, $^1J_{C\text{-}F}$ = 248.9 Hz); HRMS (EI): *m*/*z* calcd for $C_{11}H_{14}FNOSi$: 223.0829 ($[M]^+$); found: 223.0846; GC: column, CP-Chirasil-Dex; column temp, 110 °C; injection temp, 220 °C; t_R of (*R*)-**2c**, 11.5 min (97.9%); t_R of (*S*)-**2c**, 11.1 min (2.1%).



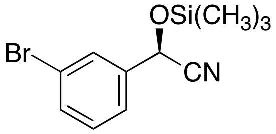
(*R*)-2-(2-Chlorophenyl)-2-trimethylsilyloxyacetonitrile [(*R*)-2d]. 97% (isolated yield). Bp 71 ºC / 0.06 mmHg (bulb-to-bulb); $[\alpha]_D^{22}$ = +6.9 (*c* = 1.00, $CHCl_3$), 94% *ee*; ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.26 (s, 9H, $Si(CH_3)_3$), 5.80 (s, 1H, CHCN), 7.34–7.40 (m, 3H, aromatic H), 7.73 ppm (dd, 1H, *J* = 2.4 and 7.3 Hz, aromatic H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = –0.3, 60.7, 118.3, 127.5, 128.3, 129.7, 130.6, 132.0, 133.9 ppm; HRMS (EI): *m*/*z* calcd for $C_{11}H_{14}ClNOSi$: 239.0533 ($[M]^+$); found: 239.0543; GC: column, CP-Chirasil-Dex; column temp, 110 °C; injection temp, 220 °C; t_R of (*R*)-**2d**, 25.3 min (97.2%); t_R of (*S*)-**2d**, 24.5 min (2.8%).



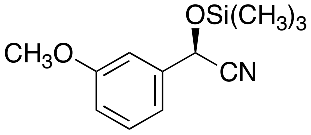
(*R*)-2-(3-Methylphenyl)-2-trimethylsilyloxyacetonitrile [(*R*)-2e]. 99% (isolated yield). Bp 85 ºC / 0.10 mmHg (bulb-to-bulb); $[\alpha]_D^{23}$ = +30.1 (*c* = 1.00, $CHCl_3$), 97% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.24 (s, 9H, $Si(CH_3)_3$), 2.39 (s, 3H, $CH_3C_6H_4$), 5.46 (s, 1H, CHCN), 7.19–7.33 ppm (m, 4H, aromatic H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.3, 21.3, 63.6, 119.2, 123.4, 127.0, 128.8, 130.1, 136.1, 138.8 ppm; HRMS (EI): *m*/*z* calcd for $C_{12}H_{17}NOSi$: 219.1080 ($[M]^+$); found: 219.1087; GC: column, InertCap CHIRAMIX (0.25 mm i.d. x 30 m, df = 0.25 μm, GL science); column temp, 150 °C; injection temp, 220 °C; t_R of (*R*)-**2e**, 23.3 min (98.3%); t_R of (*S*)-**2e**, 24.0 min (1.7%).



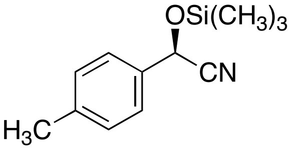
(*R*)-2-(3-Chlorophenyl)-2-trimethylsilyloxyacetonitrile [(*R*)-2f]. 98% (isolated yield). Bp 84 ºC / 0.10 mmHg (bulb-to-bulb); $[\alpha]_D^{24}$ = +25.3 (*c* = 1.00, $CHCl_3$), 98% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.25 (s, 9H, $Si(CH_3)_3$), 5.47 (s, 1H, CHCN), 7.35–7.38 (m, 3H, aromatic H), 7.47 ppm (d, 1H, *J* = 1.5 Hz, aromatic H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.3, 62.9, 118.7, 124.3, 126.5, 129.5, 130.2, 134.9, 138.1 ppm; HRMS (EI): *m*/*z* calcd for $C_{11}H_{14}ClNOSi$: 239.0533 ($[M]^+$); found: 239.0547; GC: column, Chiraldex γ-TA (0.25 mm i.d. x 30 m, df = 0.25 μm, Superco); column temp, 130 °C; injection temp, 220 °C; t_R of (*R*)-**2f**, 23.4 min (98.9%); t_R of (*S*)-**2f**, 24.6 min (1.1%).



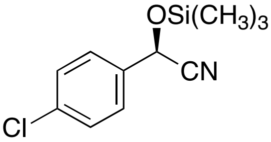
(*R*)-2-(3-Bromophenyl)-2-trimethylsilyloxyacetonitrile [(*R*)-2g]. 98% (isolated yield). Bp 85 ºC / 0.05 mmHg (bulb-to-bulb); $[\alpha]_D^{24}$ = +20.2 (*c* = 1.00, $CHCl_3$), 98% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.26 (s, 9H, $Si(CH_3)_3$), 5.46 (s, 1H, CHCN), 7.29 (t, 1H, *J* = 7.8 Hz, aromatic H), 7.40 (d, 1H, *J* = 7.8 Hz, aromatic H), 7.53 (d, 1H, *J* = 7.8 Hz, aromatic H), 7.62 ppm (s, 1H, aromatic H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.3, 62.8, 118.6, 122.9, 124.8, 129.3, 130.5, 132.5, 138.3 ppm; HRMS (EI): *m*/*z* calcd for $C_{11}H_{14}BrNOSi$: 283.0028 ($[M]^+$); found: 283.0022; GC: column, Chiraldex γ-TA; column temp, 135 °C; injection temp, 220 °C; t_R of (*R*)-**2g**, 29.8 min (98.8%); t_R of (*S*)-**2g**, 30.9 min (1.2%).



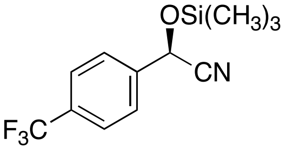
(*R*)-2-(3-Methoxyphenyl)-2-trimethylsilyloxyacetonitrile [(*R*)-2h]. 97% (isolated yield). Bp 87 ºC / 0.08 mmHg (bulb-to-bulb); $[\alpha]_D^{24}$ = +25.3 (*c* = 1.00, $CHCl_3$), 95% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.23 (s, 9H, $Si(CH_3)_3$), 3.83 (s, 3H, CH_3O), 5.46 (s, 1H, CHCN), 6.91–7.04 (m, 3H, aromatic H), 7.32 ppm (t, 1H, *J* = 7.9 Hz, aromatic H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.3, 55.3, 63.5, 111.8, 114.9, 118.5, 119.1, 130.0, 137.7, 160.0 ppm; HRMS (EI): *m*/*z* calcd for $C_{12}H_{17}NO_2Si$: 235.1029 ($[M]^+$); found: 235.1017; GC: column, InertCap CHIRAMIX; column temp, 140 °C; injection temp, 220 °C; t_R of (*R*)-**2h**, 61.1 min (97.5%); t_R of (*S*)-**2h**, 62.4 min (2.5%).



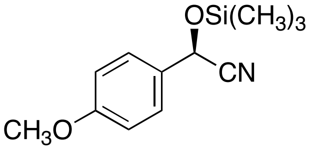
(*R*)-2-(4-Methylphenyl)-2-trimethylsilyloxyacetonitrile [(*R*)-2i]. 95% (isolated yield). Bp 69 ºC / 0.10 mmHg (bulb-to-bulb); $[\alpha]_D^{24}$ = +29.9 (*c* = 1.00, $CHCl_3$), 97% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.22 (s, 9H, $Si(CH_3)_3$), 2.37 (s, 3H, $CH_3C_6H_4$), 5.45 (s, 1H, CHCN), 7.22 (d, 2H, *J* = 8.3 Hz, aromatic H), 7.35 ppm (d, 2H, *J* = 8.3 Hz, aromatic H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.3, 21.2, 63.5, 119.3, 126.4, 129.6, 133.4, 139.3 ppm; HRMS (EI): *m*/*z* calcd for $C_{12}H_{17}NOSi$: 219.1080 ($[M]^+$); found: 219.1069; GC: column, Chiraldex γ-TA; column temp, 120 °C; injection temp, 220 °C; t_R of (*R*)-**2i**, 26.4 min (98.3%); t_R of (*S*)-**2i**, 27.5 min (1.7%).



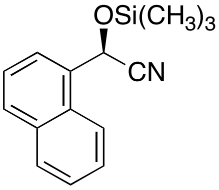
(*R*)-2-(4-chlorophenyl)-2-trimethylsilyloxyacetonitrile [(*R*)-2j]. 96% (isolated yield). Bp 83 ºC / 0.15 mmHg (bulb-to-bulb); $[\alpha]_D^{23}$ = +20.3 (*c* = 1.00, $CHCl_3$), 97% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.24 (s, 9H, $Si(CH_3)_3$), 5.47 (s, 1H, CHCN), 7.40 ppm (s, 4H, aromatic H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.3, 62.9, 118.8, 127.6, 129.1, 134.8, 135.3 ppm; HRMS (EI): *m*/*z* calcd for $C_{11}H_{14}ClNOSi$: 239.0533 ($[M]^+$); found: 239.0528; GC: column, Chiraldex γ-TA; column temp, 135 °C; injection temp, 220 °C; t_R of (*R*)-**2j**, 24.5 min (98.4%); t_R of (*S*)-**2j**, 25.6 min (1.6%).



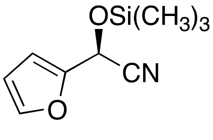
(*R*)-2-(4-Trifluoromethylphenyl)-2-trimethylsilyloxyacetonitrile [(*R*)-2k]. 98% (isolated yield). Bp 67 ºC / 0.15 mmHg (bulb-to-bulb); $[\alpha]_D^{23}$ = +19.6 (*c* = 1.00, $CHCl_3$), 94% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.27 (s, 9H, $Si(CH_3)_3$), 5.55 (s, 1H, CHCN), 7.61 (d, 2H, *J* = 8.6 Hz, aromatic H), 7.70 ppm (d, 2H, *J* = 8.6 Hz, aromatic H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.4, 63.0, 118.5, 123.7 (q, $^1J_{C\text{-}F}$ = 272.5 Hz), 126.0 (q, $J_{C\text{-}F}$ = 4.1 Hz), 126.6, 131.6 (q, $^2J_{C\text{-}F}$ = 32.3 Hz), 140.1 ppm; HRMS (EI): *m*/*z* calcd for $C_{12}H_{14}F_3NOSi$: 273.0797 ($[M]^+$); found: 273.0788; GC: column, CP-Chirasil-Dex; column temp, 130 °C; injection temp, 220 °C; t_R of (*R*)-**2k**, 6.7 min (97.2%); t_R of (*S*)-**2k**, 7.0 min (2.8%).



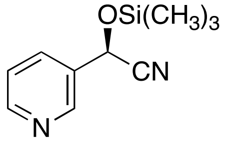
(*R*)-2-(4-Methoxyphenyl)-2-trimethylsilyloxyacetonitrile [(*R*)-2l]. 99% (isolated yield). Bp 96 ºC / 0.10 mmHg (bulb-to-bulb); $[\alpha]_D^{23}$ = +19.9 (*c* = 1.00, $CHCl_3$), 96% *ee*; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.21 (s, 9H, $Si(CH_3)_3$), 3.82 (s, 3H, CH_3O), 5.43 (s, 1H, CHCN), 6.93 (d, 2H, *J* = 8.9 Hz, aromatic H), 7.39 ppm (d, 2H, *J* = 8.9 Hz, aromatic H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.2, 55.3, 63.3, 114.3, 119.3, 127.9, 128.5, 160.3 ppm; HRMS (EI): *m*/*z* calcd for $C_{12}H_{17}NO_2Si$: 235.1029 ($[M]^+$); found: 235.1014; GC: column, Chiraldex γ-TA; column temp, 140 °C; injection temp, 220 °C; t_R of (*R*)-**2l**, 25.5 min (97.8%); t_R of (*S*)-**2l**, 26.6 min (2.2%).



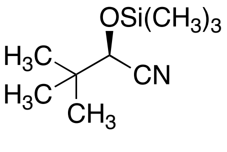
(*R*)-2-(Naphth-1-yl)-2-trimethylsilyloxyacetonitrile [(*R*)-2m]. 97% (isolated yield). Bp 116 ºC / 0.15 mmHg (bulb-to-bulb); $[\alpha]_D^{22}$ = +31.9 (*c* = 1.50, $CHCl_3$), 95% *ee*; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.20 (s, 9H, $Si(CH_3)_3$), 6.05 (s, 1H, CHCN), 7.47–7.64 (m, 3H, aromatic H), 7.71 (d, 1H, *J* = 6.8 Hz, aromatic H), 7.91 (m, 2H, aromatic H), 8.17 ppm (d, 1H, *J* = 8.8 Hz, aromatic H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.2, 62.7, 119.1, 123.1, 125.1, 125.4, 126.3, 127.0, 128.9, 129.9, 130.4, 131.3, 133.9 ppm; HRMS (EI): *m*/*z* calcd for $C_{15}H_{17}NOSi$: 255.1079 ($[M]^+$); found: 255.1073. GC: column, CP-Chirasil-Dex; column temp, 160 °C; injection temp, 220 °C; t_R of (*R*)-**2m**, 19.9 min (97.4%); t_R of (*S*)-**2n**, 3.2 min (2.6%).



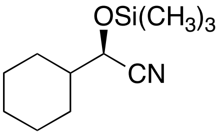
(*R*)-2-(Fur-2-yl)-2-trimethylsilyloxyacetonitrile [(*R*)-2n]. 97% (isolated yield). Bp 59 ºC / 0.15 mmHg (bulb-to-bulb); $[\alpha]_D^{24}$ = +22.3 (*c* = 1.00, $CHCl_3$), 93% *ee*; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.20 (s, 9H, $Si(CH_3)_3$), 5.54 (s, 1H, CHCN), 6.41 (dd, 1H, *J* = 2.0 and 3.4 Hz, aromatic H), 6.54 (d, 1H, *J* = 3.4 Hz, aromatic H), 7.46 ppm (d, 1H, *J* = 2.0 Hz, aromatic H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.4, 57.4, 109.7, 110.8, 117.1, 143.9, 148.2 ppm; HRMS (EI): *m*/*z* calcd for $C_9H_{13}NO_2Si$: 195.0716 ($[M]^+$); found: 195.0722; GC: column, CP-Chirasil-Dex; column temp, 130 °C; injection temp, 220 °C; t_R of (*R*)-**2n**, 3.4 min (96.3%); t_R of (*S*)-**2n**, 3.2 min (3.7%).



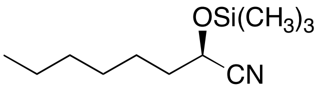
(*R*)-2-(Pyridin-3-yl)-2-trimethylsilyloxyacetonitrile [(*R*)-2o]. 99% (GC yield); 93% *ee*; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.26 (s, 9H, $Si(CH_3)_3$), 5.55 (s, 1H, CHCN), 7.38 (dd, 1H, *J* = 4.9 and 7.8 Hz, aromatic H), 7.84 (d, 1H, *J* = 7.8 Hz, aromatic H), 8.66 ppm (dd, 1H, *J* = 1.5 and 4.9 Hz, aromatic H), 8.70 (d, 1H, *J* = 1.5 Hz, aromatic H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.4, 61.6, 118.3, 123.7, 132.2, 134.0, 147.8, 150.7 ppm; HRMS (EI): *m*/*z* calcd for $C_{10}H_{14}N_2OSi$: 206.0875 ($[M]^+$); found: 206.0878; GC: column, Chiraldex γ-TA; column temp, 130 °C; injection temp, 220 °C; t_R of (*R*)-**2o**, 19.5 min (96.3%); t_R of (*S*)-**2o**, 20.8 min (3.7%). The corresponding cyanohydrin was obtained as the isolated product in the yield of 91%.



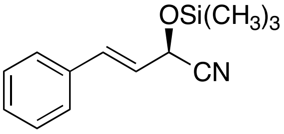
(*R*)-3,3-dimethyl-2-trimethylsilyloxybutanenitrile [(*R*)-2p]. 92% (isolated yield). Bp 90 ºC / 45 mmHg (bulb-to-bulb); $[\alpha]_D^{24}$ = +68.5 (*c* = 1.00, $CHCl_3$), 95% *ee*; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.21 (s, 9H, $Si(CH_3)_3$), 1.01 (s, 9H, $C(CH_3)_3$), 3.99 ppm (s, 1H, CHCN); ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.5, 24.9, 35.8, 70.8, 119.3 ppm; HRMS (EI): *m*/*z* calcd for $C_9H_{19}NOSi$: 185.1236 ($[M]^+$); found: 185.1239; GC: column, CP-Chirasil-Dex; column temp, 70 °C; injection temp, 220 °C; t_R of (*R*)-**2p**, 8.7 min (97.7%); t_R of (*S*)-**2p**, 9.3 min (2.3%).



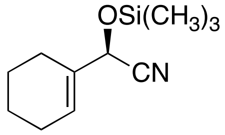
(*R*)-2-Cyclohexyl-2-trimethylsilyloxyacetonitrile [(*R*)-2q]. 97% (isolated yield). Bp 65 ºC / 0.17 mmHg (bulb-to-bulb); $[\alpha]_D^{25}$ = +44.6 (*c* = 1.00, $CHCl_3$), 88% *ee*; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.20 (s, 9H, $Si(CH_3)_3$), 1.03–1.28 (m, 5H, *cyclo*-C_6H_{11}), 1.64–1.89 (m, 6H, *cyclo*-C_6H_{11}), 4.14 ppm (d, 1H, *J* = 6.4 Hz, CHCN); ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.5, 25.5, 26.0, 27.9, 28.1, 42.9, 66.5, 119.4 ppm; HRMS (EI): *m*/*z* calcd for $C_{11}H_{21}NOSi$: 211.1392 ($[M]^+$); found: 211.1388; GC: column, Chiraldex γ-TA; column temp, 110 °C; injection temp, 220 °C; t_R of (*R*)-**2q**, 17.2 min (93.8%); t_R of (*S*)-**2q**, 18.3 min (6.2%).



(*R*)-2-Trimethylsilyloxyoctanenitrile [(*R*)-2r]. 98% (isolated yield). Bp 58 ºC / 0.15 mmHg (bulb-to-bulb); $[\alpha]_D^{23}$ = +34.1 (*c* = 1.00, $CHCl_3$), 70% *ee*; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.21 (s, 9H, $Si(CH_3)_3$), 0.89 (t, 3H, *J* = 6.8 Hz, CH_3CH_2), 1.30–1.55 (m, 8H, $(CH_2)_4$), 1.75–1.81 (m, 2H, CH_2CH), 4.38 ppm (t, 1H, *J* = 6.6 Hz, CHCN); ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.4, 14.0, 22.5, 24.5, 28.6, 31.5, 36.2, 61.5, 120.1 ppm; HRMS (EI): *m*/*z* calcd for $C_{11}H_{23}NOSi$: 213.1549 ($[M]^+$); found: 213.1535; GC: column, CP-Chirasil-Dex; column temp, 100 °C; injection temp, 220 °C; t_R of (*R*)-**2r**, 15.5 min (84.9%); t_R of (*S*)-**2r**, 16.5 min (15.1%).



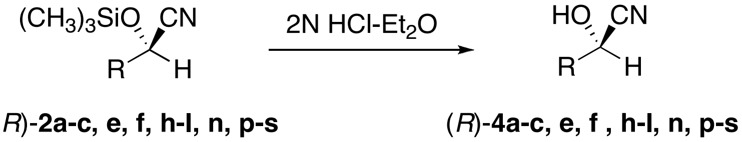
(*R*)-(*E*)-4-phenyl-2-trimethylsilyloxy-3-butenenitrile [(*R*)-2s]. 93% (isolated yield). Bp 87 ºC / 0.08 mmHg (bulb-to-bulb); $[\alpha]_D^{23}$ = +4.3 (*c* = 1.00, $CHCl_3$), 91% *ee*; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.26 (s, 9H, $Si(CH_3)_3$), 5.12 (dd, 1H, *J* = 1.5 and 5.9 Hz, CHCN), 6.19 (dd, 1H, *J* = 5.9 and 15.6 Hz, $C_6H_5CH{=}C\mathit{H}$), 6.81 (dd, 1H, *J* = 1.5 and 15.6 Hz, $C_6H_5C\mathit{H}{=}CH$), 7.31–7.42 ppm (m, 5H, aromatic H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.1, 62.2, 118.4, 123.5, 126.9, 128.7, 128.8, 133.9, 135.0 ppm; HRMS (EI): *m*/*z* calcd for $C_{13}H_{17}NOSi$: 231.1079 ($[M]^+$); found: 231.1074; GC: column, CP-Chirasil-Dex; column temp, 140 °C; injection temp, 220 °C; t_R of (*R*)-**2s**, 17.3 min (95.3%); t_R of (*S*)-**2s**, 18.2 min (4.7%).



(*R*)-2-(Cyclohexen-1-yl)-2-trimethylsilyloxyacetonitrile [(*R*)-2t]. 92% (isolated yield). Bp 56 °C / 0.17 mmHg (bulb-to-bulb); $[\alpha]_D^{24}$ = +15.5 (*c* = 1.00, $CHCl_3$), 93% *ee*; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.21 (s, 9H, $Si(CH_3)_3$), 1.58–1.71 (m, 4H, $CH_2(CH_2)_2CH_2$), 2.08–2.10 (m, 4H, $CH_2C{=}CHCH_2$), 4.76 (s, 1H, CHCN), 5.94 ppm (m, 1H, C=CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.3, 21.8, 22.1, 23.8, 24.9, 66.1, 118.8, 127.3, 133.3 ppm; HRMS (EI): *m*/*z* calcd for $C_{11}H_{19}NOSi$: 209.1236 ($[M]^+$); found: 209.1231; GC: column, Chiraldex γ-TA; column temp, 110 °C; injection temp, 220 °C; t_R of (*R*)-**2t**, 23.7 min (96.5%); t_R of (*S*)-**2t**, 24.5 min (3.5%).

(E) Determination of the Absolute Configuration of Products

The absolute configuration of products **2a–c**, **e**, **f**, **h–l**, **n,** **p–s** were determined by the sign of optical rotation of the corresponding cyanohydrins **4**, which were obtained by treatment of **2** with 2N HCl in $(C_2H_5)_2O$.



(*R*)-2-Hydroxy-2-phenylacetonitrile [(*R*)-4a]. $[\alpha]_D^{25}$ +45.4 (*c* = 1.40, $CHCl_3$) [lit.[2] $[\alpha]_D^{24}$ +36.8 (*c* = 2.00, $CHCl_3$) for *R* enantiomer in 85% *ee*]; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.68 (d, 1H, *J* = 6.9 Hz, OH), 5.56 (d, 1H, *J* = 6.9 Hz, CHCN), 7.45–7.48 (m, 3H, aromatic H), 7.54–7.88 ppm (m, 2H, aromatic H).

(*R*)-2-Hydroxy-2-(2-methylphenyl)acetonitrile [(*R*)-4b]. $[\alpha]_D^{26}$ +48.2 (*c* = 0.50, $CHCl_3$) [lit.[3] $[\alpha]_D^{26}$ +21.3 (*c* = 1.00, $CHCl_3$) for *R* enantiomer in 51% *ee*]; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 3H, CH_3), 3.19 (d, 1H, *J* = 6.4 Hz, OH), 5.62 (d, 1H, *J* = 6.4 Hz, CHCN), 7.21–7.34 (m, 3H, aromatic H), 7.62 ppm (d, 1H, *J* = 7.3 Hz, aromatic H).

(*R*)-2-Hydroxy-2-(2-fluorophenyl)acetonitrile [(*R*)-4c]. $[\alpha]_D^{27}$ +26.4 (*c* = 1.00, $CHCl_3$) [lit.[4] $[\alpha]_D^{20}$ +21.9 (*c* = 3.60, $CHCl_3$) for *R* enantiomer in 84% *ee*]; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.76 (d, 1H, *J* = 6.8 Hz, OH), 5.80 (d, 1H, *J* = 6.8 Hz, CHCN), 7.16 (ddd, 1H, *J* = 1.0, 8.3, and 9.3 Hz, aromatic H), 7.26 (dt, 1H, *J* = 1.0 and 6.3 Hz, aromatic H), 7.42–7.48 (m, 1H, aromatic H), 7.61–7.65 ppm (m, 1H, aromatic H).

(*R*)-2-Hydroxy-2-(3-methylphenyl)acetonitrile [(*R*)-4e]. $[\alpha]_D^{27}$ +43.4 (*c* = 1.50, $CHCl_3$) [lit.[3] $[\alpha]_D$ +41.2 (*c* = 3.30, $CHCl_3$) for *R* enantiomer in 91% *ee*]; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3H, CH_3), 3.05 (d, 1H, *J* = 6.8 Hz, OH), 5.48 (d, 1H, *J* = 6.8 Hz, CHCN), 7.23 (m, 1H, aromatic H), 7.30–7.34 ppm (m, 3H, aromatic H).

(*R*)-2-Hydroxy-2-(3-chlorophenyl)acetonitrile [(*R*)-4f]. $[\alpha]_D^{27}$ +42.3 (*c* = 0.90, $CHCl_3$) [lit.[3] $[\alpha]_D$ +32.0 (*c* = 1.30, $CHCl_3$) for *R* enantiomer in 57% *ee*]; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.89 (d, 1H, *J* = 6.8 Hz, OH), 5.53 (d, 1H, *J* = 6.8 Hz, CHCN), 7.39–7.41 (m, 3H, aromatic H), 7.55 ppm (brs, 1H, aromatic H).

(*R*)-2-Hydroxy-2-(3-methoxyphenyl)acetonitrile [(*R*)-4h]. $[\alpha]_D^{26}$ +38.1 (*c* = 1.40, $CHCl_3$) [lit.[3] $[\alpha]_D$ +36.9 (*c* = 1.60, $CHCl_3$) for *R* enantiomer in 90% *ee*]; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.88 (d, 1H, *J* = 6.8 Hz, OH), 3.83 (s, 1H, CH_3O), 5.51 (d, 1H, *J* = 6.8 Hz, CHCN), 6.96 (dd, 1H, *J* = 2.4 and 8.3 Hz, aromatic H), 7.06 (brs, 1H, aromatic H), 7.10 (d, 1H, *J* = 7.8 Hz, aromatic H), 7.36 ppm (t, 1H, *J* = 7.8 Hz, aromatic H).

(*R*)-2-Hydroxy-2-(4-methylphenyl)acetonitrile [(*R*)-4i]. $[\alpha]_D^{26}$ +46.5 (*c* = 1.40, $CHCl_3$) [lit.[3] $[\alpha]_D$ +47.4 (*c* = 1.60, $CHCl_3$) for *R* enantiomer in 92% *ee*]; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.38 (s, 1H, CH_3), 3.12 (d, 1H, *J* = 6.8 Hz, OH), 5.46 (d, 1H, *J* = 6.8 Hz, CHCN), 7.23 (d, 1H, *J* = 8.0 Hz, aromatic H), 7.39 ppm (d, 1H, *J* = 8.0 Hz, aromatic H).

(*R*)-2-Hydroxy-2-(4-chlorophenyl)acetonitrile [(*R*)-4j]. $[\alpha]_D^{27}$ +39.7 (*c* = 0.70, $CHCl_3$) [lit.[3] $[\alpha]_D$ +27.2 (*c* = 1.50, $CHCl_3$) for *R* enantiomer in 66% *ee*]; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.76 (d, 1H, *J* = 6.8 Hz, OH), 5.54 (d, 1H, *J* = 6.8 Hz, CHCN), 7.42–7.49 ppm (m, 4H, aromatic H).

(*R*)-2-Hydroxy-2-(4-trifluoromethylphenyl)acetonitrile [(*R*)-4k]. $[\alpha]_D^{26}$ +25.0 (*c* = 1.00, $CHCl_3$) [lit.[3] $[\alpha]_D$ +19.0 (*c* = 1.80, $CHCl_3$) for *R* enantiomer in 80% *ee*]; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.14 (d, 1H, *J* = 6.8 Hz, OH), 5.64 (d, 1H, *J* = 6.8 Hz, CHCN), 7.66 (d, 1H, *J* = 8.8 Hz, aromatic H), 7.72 ppm (d, 1H, *J* = 8.8 Hz, aromatic H).

(*R*)-2-Hydroxy-2-(4-methoxyphenyl)acetonitrile [(*R*)-4l]. $[\alpha]_D^{26}$ +40.7 (*c* = 0.90, $CHCl_3$) [lit.[3] $[\alpha]_D$ +36.3 (*c* = 1.00, $CHCl_3$) for *R* enantiomer in 83% *ee*]; ^1H NMR (400

MHz, $CDCl_3$): δ = 2.71 (d, 1H, *J* = 6.8 Hz, OH), 3.83 (s, 3H, CH_3O), 5.48 (d, 1H, *J* = 6.8 Hz, CHCN), 6.93–6.97 (m, 2H, aromatic H), 7.44–7.47 ppm (m, 2H, aromatic H).

(*R*)-2-Hydroxy-2-(2-furyl)acetonitrile [(*R*)-4n]. $[\alpha]_D^{25}$ +42.2 (*c* = 1.10, $CHCl_3$) [lit.[3] $[\alpha]_D$ +14.0 (*c* = 1.90, $CHCl_3$) for *R* enantiomer in 79% *ee*]; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.77 (d, 1H, *J* = 8.0 Hz, OH), 5.54 (d, 1H, *J* = 8.0 Hz, CHCN), 6.41 (dd, 1H, *J* = 2.0 and 3.4 Hz, aromatic H), 6.58 (d, 1H, *J* = 3.4 Hz, aromatic H), 7.48 ppm (brs, 1H, aromatic H).

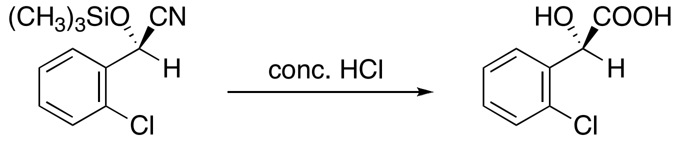
(*R*)-2-Hydroxy-3,3-dimethylbutanenitrile [(*R*)-4p]. $[\alpha]_D^{26}$ +21.5 (*c* = 0.70, $CHCl_3$) [lit.[2] $[\alpha]_D^{24}$ +14.5 (*c* = 1.00, $CHCl_3$) for *R* enantiomer in 70% *ee*]; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.08 (s, 9H, $C(CH_3)_3$), 2.91 (d, 1H, *J* = 6.3 Hz, OH), 4.13 ppm (d, 1H, *J* = 6.3 Hz, CHCN).

(*R*)-2-Cyclohexyl-2-hydroxyacetonitrile [(*R*)-4q]. $[\alpha]_D^{26}$ +8.5 (*c* = 1.30, $CHCl_3$) [lit.[2] $[\alpha]_D^{24}$ +6.1 (*c* = 3.80, $CHCl_3$) for *R* enantiomer in 65% *ee*]; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.05–1.33 (m, 5H, *cyclo*-C_6H_{11}), 1.68–1.91 (m, 6H, *cyclo*-C_6H_{11}), 2.89 (d, 1H, *J* = 6.3 Hz, OH), 4.26 ppm (t, 1H, *J* = 6.3 Hz, CHCN).

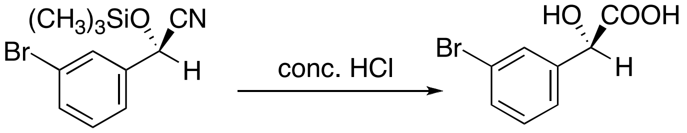
(*R*)-2-Hydroxyoctanenitrile [(*R*)-4r]. $[\alpha]_D^{26}$ +9.7 (*c* = 0.70, $CHCl_3$) [lit.[5] $[\alpha]_D^{26}$ +9.1 (*c* = 2.80, $CHCl_3$) for *R* enantiomer in 66% *ee*]; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, 3H, *J* = 6.8 Hz, CH_3CH_2), 1.28–1.39 (m, 6H, $(CH_2)_3$), 1.47–1.54 (m, 2H, CH_2), 1.83–1.88 (m, 2H, CH_2CH), 2.31 (d, 1H, *J* = 6.3 Hz, OH). 4.48 ppm (q, 1H, *J* = 6.8 Hz, CHCN).

(*R*)-2-Hydroxy-4-phenyl-3-butenenitrile [(*R*)-4s]. $[\alpha]_D^{25}$ +26.6 (*c* = 1.10, $CHCl_3$) [lit.[3] $[\alpha]_D^{24}$ +19.2 (*c* = 1.90, $CHCl_3$) for *R* enantiomer in 72% *ee*]; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.54 (d, 1H, *J* = 7.3 Hz, OH), 5.17 (ddd, 1H, *J* = 1.5, 5.9 and 7.3 Hz, CHCN), 6.27 (dd, 1H, *J* = 5.9 and 15.6 Hz, $C_6H_5CH{=}CH$), 6.93 (dd, 1H, *J* = 1.0 and 15.6 Hz, $C_6H_5CH{=}CH$), 7.31–7.44 ppm (m, 5H, aromatic H).

The absolute configuration of **2d** and **2g** were determined by the sign of rotation after conversion to the corresponding mandelic acids **5d** and **5g** according to the procedure described in the literature.[6]



(*R*)-**2d** (*R*)-**6d**

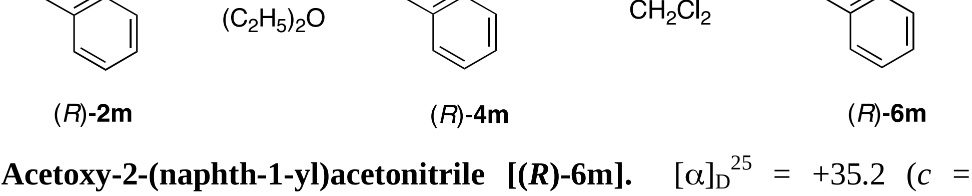


(*R*)-**2g** (*R*)-**6g**

(*R*)-2-(2-Chlorophenyl)-2-hydroxyacetic acid [(*R*)-5d]. $[\alpha]_D^{22}$ –153 (*c* = 0.60, C_2H_5OH) [lit.[7] $[\alpha]_D^{20}$ –138 (*c* = 0.50, C_2H_5OH) for *R* enantiomer in 96% *ee*]; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.37 (brs, 1H, CHO*H*), 5.34 (s, 1H, CHCN), 7.30–7.38 (m, 2H, aromatic H), 7.44 (dd, 1H, *J* = 2.0 and 7.7 Hz, aromatic H), 7.51 (dd, 1H, *J* = 2.0 and 7.2 Hz, aromatic H), 12.7 ppm (brs, 1H, COOH); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 69.6, 127.5, 128.9, 129.4, 129.6, 132.4, 138.2, 173.3 ppm.

(*R*)-2-(3-Bromophenyl)-2-hydroxyacetic acid [(*R*)-5g]. $[\alpha]_D^{24}$ –86.8 (*c* = 0.50, C_2H_5OH) [lit.[7] $[\alpha]_D^{20}$ –84.8 (*c* = 0.50, C_2H_5OH) for *R* enantiomer in 98% *ee*]; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.35 (brs, 1H, CHO*H*), 5.06 (s, 1H, CHCN), 7.33 (t, 2H, *J* = 7.8 Hz, aromatic H), 7.41 (d, 1H, *J* = 7.8 Hz, aromatic H), 7.57 (d, 1H, *J* = 8.3 Hz, aromatic H), 7.70 (brs, 1H, aromatic H), 12.6 ppm (brs, 1H, COOH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 71.8, 121.6, 125.9, 129.4, 130.6, 130.7, 143.1, 173.7 ppm.

The absolute configuration of product **2m** was determined after conversion to the corresponding acetate **6m** by the following procedures: a) Deprotection of the silyl group by treatment with 2N HCl in $(C_2H_5)_2O$, b) acetylation of the hydroxy group with acetic anhydride and pyridine in CH_2Cl_2.

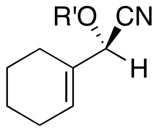


(*R*)-**2m** (*R*)-**4m** (*R*)-**6m**

(*R*)-2-Acetoxy-2-(naphth-1-yl)acetonitrile [(*R*)-6m]. $[\alpha]_D^{25}$ = +35.2 (*c* = 1.10,

$CHCl_3$) [lit.[8] $[\alpha]_D^{25}$ –25.6 (c = 1.00, $CHCl_3$) for *S* enantiomer in 70% *ee*]; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.21 (s, 3H, $COCH_3$), 7.04 (s, 1H, CHCN), 7.51–7.66 (m, 3H, aromatic H), 7.82 (d, 1H, *J* = 7.0 Hz, aromatic H), 7.94 (d, 1H, *J* = 7.8 Hz, aromatic H), 7.98 (d, 1H, *J* = 8.4 Hz, aromatic H), 8.03 ppm (d, 1H, *J* = 8.3 Hz, aromatic H); GC: column, CP-Chirasil-Dex; column temp, 160 °C; injection temp, 220 °C; t_R of (*R*)-**6m**, 19.9 min; t_R of (*S*)-**6m**, 20.6 min.

The absolute configuration of **2t** was estimated by ^1H-NMR analysis after conversion to the (*R*)- and (*S*)-2-methoxy-2-phenyl-2-(trifluoromethyl)acetic acid (MTPA) esters **7t** according to the procedure described in the literature.[9] The values of Δδ (δ_R-δ_S) listed in Figure S1 were all plus for two allylic and a vinylic protons. Thus, the absolute configuration of **2t** was determined to be *R*.



7t

R' = (*R* or *S*)-MTPA

Δδ ($\delta_R - \delta_S$)
CH_2 (allylic): +0.03, +0.02
CH (vinylic) : +0.05

Figure S1. Determination of the absolute configuration

(F) Asymmetric Cyanosilylation of Benzaldehyde (1a) with an S/C of 100,000 [Note 1]

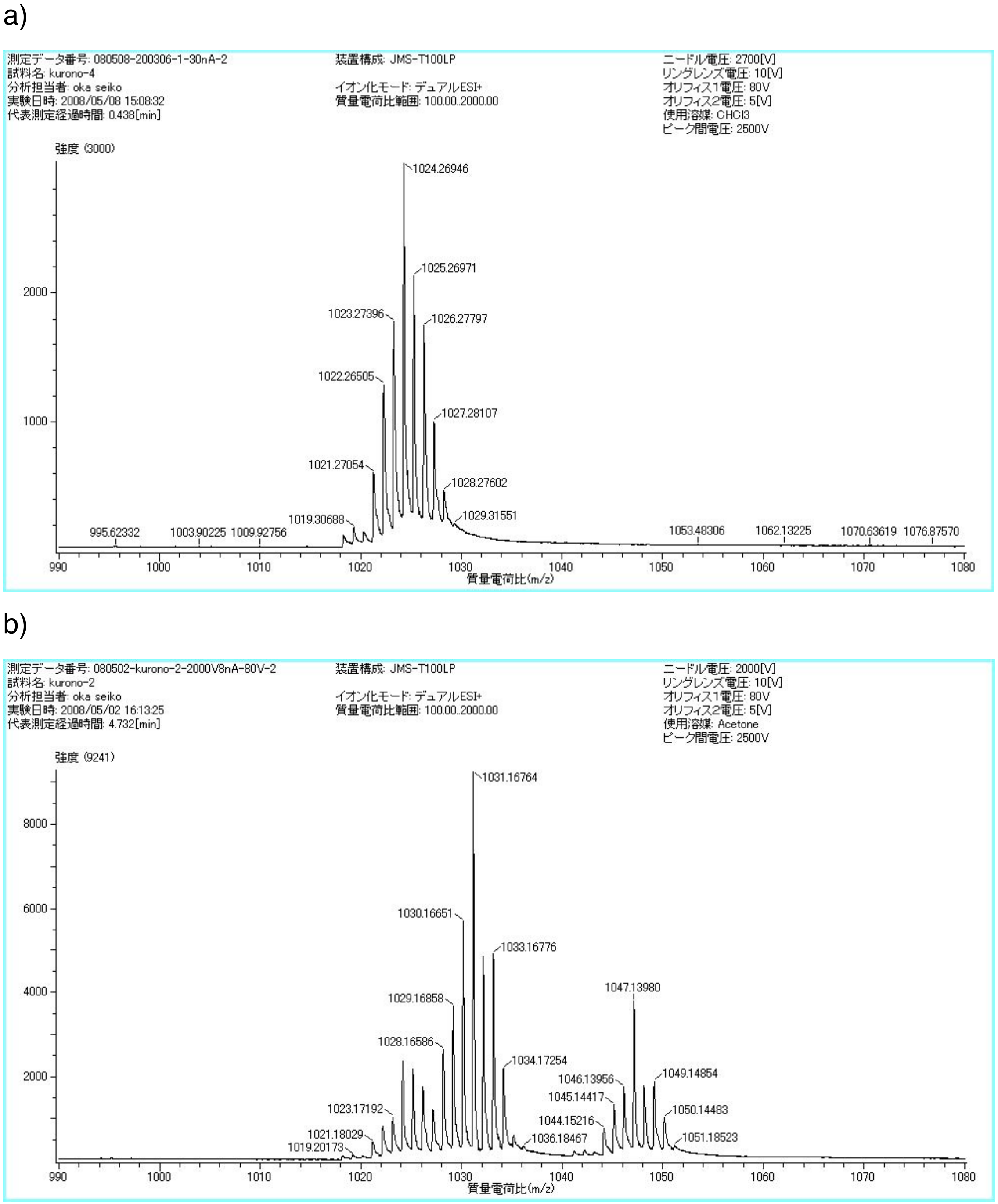
A 100-mL Schlenk flask equipped with a Teflon-coated magnetic stirring bar was filled with argon. $(CH_3)_3SiCN$ (6.20 g, 62.5 mmol) and 0.05 M aqueous solution of Li_2CO_3 (10 μL, 0.5 μmol) were placed in the flask, and the mixture was stirred for 20 min at 25 °C. To the pale yellow solution was added a 20 mM-THF solution of (*S*,*S*,*S*)-**3** (25 μL, 0.5 μmol), and the mixture was stirred for 30 min. The resulting solution was diluted with $(C_2H_5)_2O$ (50 mL) and cooled down to –40 °C. Then **1a** (5.38 g, 50.7 mmol) was charged into the flask, and the mixture was stirred for 24 h. After the solvent and the volatile compounds were evaporated under reduced pressure at ambient temperature, the residue was purified by a short-path distillation to give (*R*)-**2a** (9.74 g, 94% yield, 90% *ee*).[Note 2]

Notes

[1] See Notes in Part C.

[2] For analytical data of (*R*)-**2a** see Part C.

(G) ESI-MS and ^{1}H-NMR Spectra of Ru Species



a)

測定データ番号: 080508-200306-1-30nA-2
試料名: kurono-4
分析担当者: oka seiko
実験日時: 2008/05/08 15:08:32
代表測定経過時間: 0.438[min]

装置構成: JMS-T100LP
イオン化モード: デュアルESI+
質量電荷比範囲: 100.00..2000.00

ニードル電圧: 2700[V]
リングレンズ電圧: 10[V]
オリフィス1電圧: 80V
オリフィス2電圧: 5[V]
使用溶媒: CHCl3
ピーク間電圧: 2500V

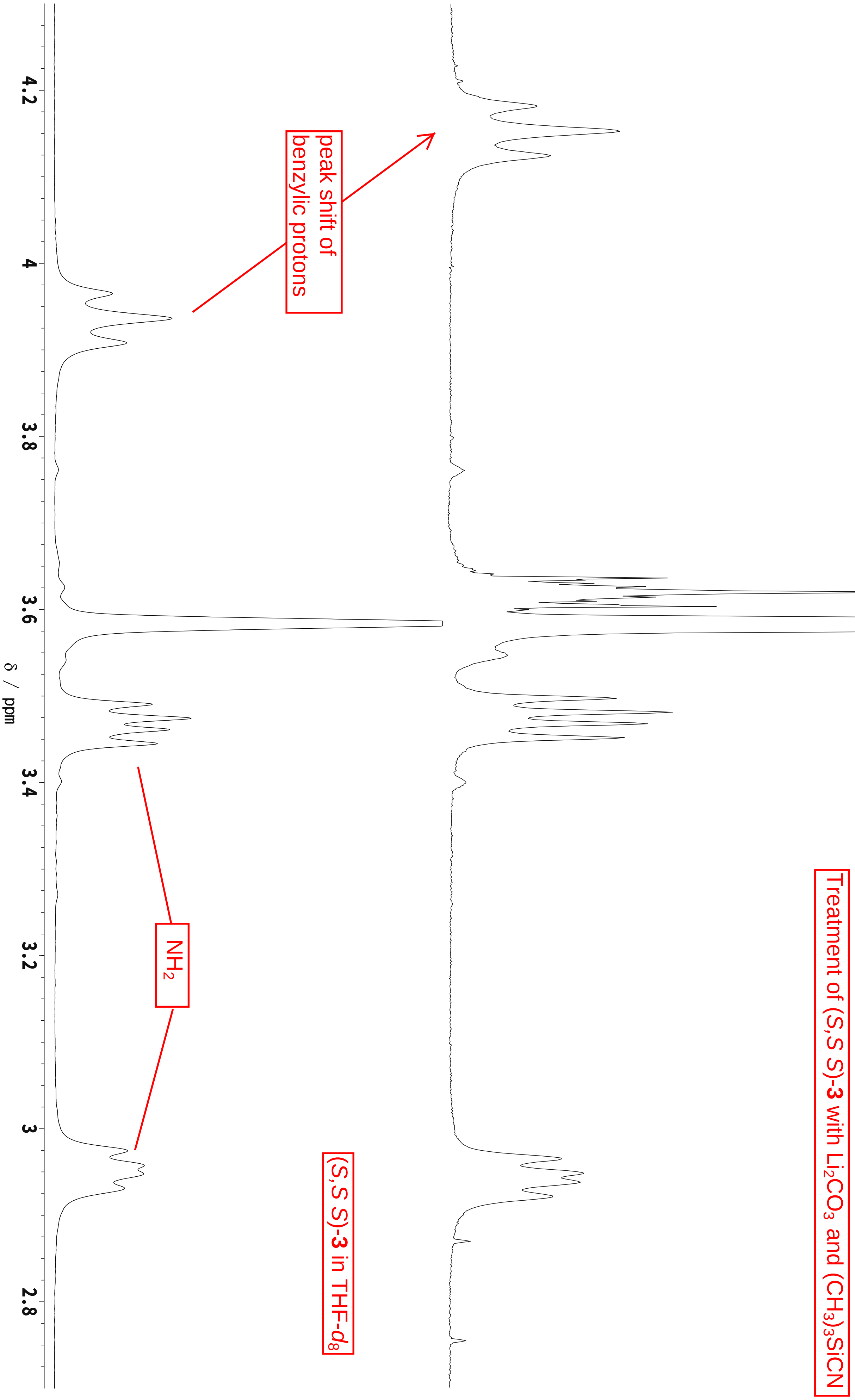
b)

測定データ番号: 080502-kurono-2-2000V8nA-80V-2
試料名: kurono-2
分析担当者: oka seiko
実験日時: 2008/05/02 16:13:25
代表測定経過時間: 4.732[min]

装置構成: JMS-T100LP
イオン化モード: デュアルESI+
質量電荷比範囲: 100.00..2000.00

ニードル電圧: 2000[V]
リングレンズ電圧: 10[V]
オリフィス1電圧: 80V
オリフィス2電圧: 5[V]
使用溶媒: Acetone
ピーク間電圧: 2500V

Figure S2. ESI-MS spectra of a) (*S,S,S*)-**3** and b) mixture of (*S,S,S*)-**3**, Li_2CO_3 (**3**:Li_2CO_3 = 1:1), and excess amount of $(CH_3)_3SiCN$. (*S,S,S*)-**3**: *m/z* = 1024, [(*S,S,S*)-**3**•Li]: *m/z* = 1031.


Treatment of (S,S S)-**3** with Li_2CO_3 and $(CH_3)_3SiCN$
(S,S S)-**3** in THF-d_8
peak shift of benzylic protons
NH_2
4.2
4
3.8
3.6
3.4
3.2
3
2.8
δ / ppm

(H) Experimental Data on Nonlinear Effect and Effect of the Concentration of the Ru Complex (3)

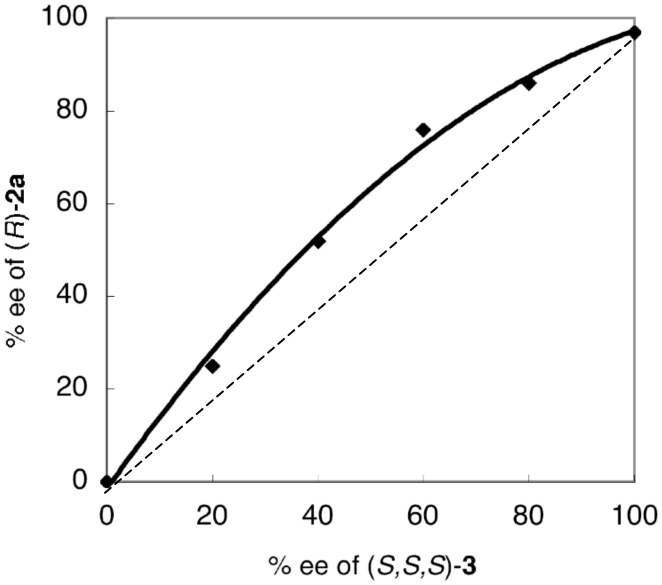
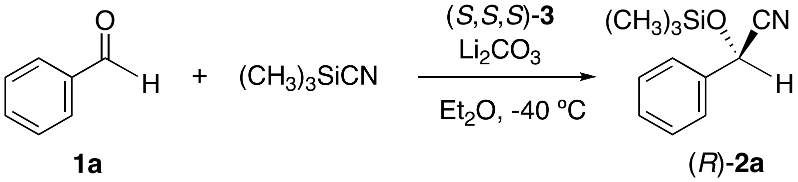


Figure S3. Nonlinear effect between the *ee* of (*S,S,S*)-**3** and the *ee* of (*R*)-**2a**. Weak positive nonlinear effect was observed on the cyanosilylation of **1a** at –78 °C using (*S,S,S*)-**3** with an S/C of 10,000. All reactions proceeded quantitatively.

Table S1. Effect of the concentration of catalyst (*S,S,S*)-**3** on the cyanosilylation of **1a**[a].



Entry	**1a**:**3**:Li_2CO_3	[**3**] [mM][b]	Yield [%][c]	*ee* [%][c]
1	5000:1:1	0.16	>99	82
2	10,000:1:1	0.08	>99	85
3	50,000:1:1	0.016	>99	91
4	100,000:1:1	0.008	>99	90

[a] Reactions were conducted using **1a** (10 mmol) and $(CH_3)_3SiCN$ (12 mmol) in Et_2O (10 mL) under –40 °C for 12 h. [b] Concentration of **3**. [c] Yields and ees were determined by GC analysis.

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