Catalytic Asymmetric Cyanosilylation of Ketones by a Chiral Amino Acid Salt

Xiaohua Liu, Bo Qin, Xin Zhou, Bin He, and Xiaoming Feng*

Key Laboratory of Green Chemistry & Technology (Sichuan University), Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, P. R. China

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General. ^1H NMR spectra were recorded on a Varian Unity INOVA 400 (400 MHz) or on Bruker instruments (600, 300 MHz). Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl_3 , $\delta=7.26$). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz), integration, and assignment. ^{13}C NMR data were collected on a Varian Unity INOVA 400 (100 MHz) or on Bruker instruments (150, 75 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard (CDCl_3 , $\delta=77.0$). ^{29}Si NMR spectra were recorded on Bruker instruments (300 MHz). Elemental analyses were performed on a Carlo-1160 apparatus. Enantiomer ratios were determined by chiral GC analysis on Varian Chirasil DEX CB or by chiral HPLC analysis on Daicel Chiralcel OD/OJ in comparison with the authentic racemates. Optical rotation data were recorded on Perkin-Elmer Polarimeter-341. All ketones, TMSCN and amino acids were purchased from Acros, Aldrich and Fluka. Solvents were purified by usual methods.

Catalyst Preparation.

Organic Salts Preparation: Organic salts were prepared by adding 1 equiv of alkali metal hydroxide to the organic acid in methanol at 0 °C and stirring at 25 °C for 1-3 h. After the solvent was evaporated, the salts were dried at 25 °C in vacuo. The salts thus obtained were used without further purification.

***L*-phenylglycine sodium salt.** Anal Calcd for $C_8H_8NNaO_2 \cdot \frac{1}{2}H_2O$: C, 52.26; N, 7.61; H, 4.38. Found: C, 52.05; N, 7.58; H, 4.40.

Preparation of optically active cyanohydrin trimethylsilyl ethers 3

Method A: (footnote a in Table 1) To a mixture of ketone (0.5 mmol) and organic salt **2** (0.15 mmol) in 0.5 mL of solvent was added trimethylsilyl cyanide (1.2 equiv) and 0.5 mL solvent at -20 °C. The reaction was monitored by TLC. After the reaction, organic salts precipitated and was filtrated from the reaction mixture and the residues were purified by flash chromatography to give the pure product with ethyl ether/petroleum ether (1/100, V/V) as the eluent.

Method B: (footnote b in Table 1) To a solution of *L*-phenylglycine sodium salt in 0.5 mL of solvent was added trimethylsilyl cyanide (1.2 equiv) at -20 °C, and the mixture was stirred at 30 °C for 1.0 h. And then ketone (0.5 mmol) in 0.5 mL THF was dropwise added to the solution under the reaction condition indicated in Table 2 and monitored by TLC. After warming to room temperature, *L*-phenylglycine sodium salt was filtrated from the reaction mixture and the residues concentrated and put on a silica gel column to give the pure product with ethyl ether/petroleum ether (1/100, V/V) as the eluent.

Method C: (footnote c in Table 1) *L*-Phenylglycine (22.7 mg, 0.15 mmol) was stirred with NaOH (6.0 mg, 0.15 mmol) in dry THF (0.3 mL) at 25 °C for 0.5 h under N₂ atmosphere. To the resulted catalyst, TMSCN and THF (0.2 mL) was added at -20 °C. After stirring for 1.0 h at 30 °C, ketone in THF was dropwise added. Then the reaction mixture was stirred under the reaction condition indicated in Table 2 of the communication and monitored by TLC. After warming to room temperature, *L*-phenylglycine sodium salt was filtrated from the reaction mixture and the residues concentrated and put on a silica gel column to give the pure product with ethyl ether/petroleum ether (1/100, V/V) as the eluent.

Method D: (footnote d in Table 1) To a solution of *L*-phenylglycine sodium salt **2f** $\cdot \frac{1}{2}H_2O$ in 0.5 mL of THF was added trimethylsilyl cyanide (1.5 equiv) at -20 °C, and the mixture was stirred at 30 °C for 1.0 h. And then ketone (0.5 mmol) was charged sequentially at -45 °C and stirred for 15 min. ⁱPrOH (0.25 mmol) and 0.5 mL THF were then added via syringe. The reaction stirred at -45 °C for certain time and monitored by TLC. After warming to room temperature, *L*-phenylglycine sodium salt was filtrated from the reaction mixture and the residues concentrated and put on a silica gel column to give the pure product with ethyl ether/petroleum ether (1/100, V/V) as the eluent.

Note: 0.3 equiv methanol could also be added at the initial stage before TMSCN was syringed in Method D and the same results could be obtained. The tolerance of the catalyst enhanced greatly by this method. It may due to the optimal capacity of protonic impurity in the catalyst is within the range of 0.5-1.0 equiv of the catalyst **2f**, and the methanol could play the same role as water at the first stage of the reaction.

Optimization Studies.

Solvent effects were studied with the results summarized in Table 1. THF was the most favorable solvent for enantioselectivity.

Table I Effects of solvent on the asymmetric addition of TMSCN to acetophenone.^a

solvent	Loading (mol %)	Yield(%) ^b	Ee(%) ^c
Et ₂ O	30	45	44
CH ₂ Cl ₂	30	51	36
CHCl ₃	30	84	29
Toluene	30	64	31
Benzene	30	70	26
Acetonitrile	30	52	20
1,4 -Dioxane	30	71	34
<i>t</i> -BuOMe	30	55	26
THF	30	50	54

^a The reactions were carried out on a 0.5 mmol scale with 30 mol % catalyst **2f** and 1.2 eq TMSCN at -20 °C by **Method A** mentioned above. ^b Isolated yield. ^c Determined by chiral GC analysis on Chiasil DEX CB.

Table II. Effects of catalyst loading on the asymmetric addition of TMSCN to acetophenone.^a

Catalyst loading (mol %)	concentration (M)	Yield(%) ^b	Ee(%) ^c
5	0.5	31	0
10	0.5	60	0
10	1.5	65	11
20	0.5	66	38
20	1.0	68	56
20	1.5	72	61
20	2.0	72	61
25	0.5	73	60
30	0.2	24	11
30	0.4	42	79
30	0.5	60	81
30	1.0	52	82

35	0.5	46	83
40	0.5	21	83
50	0.5	18	82

^a The reactions were carried out with catalyst **2f** and 1.2 eq TMSCN in THF at -20 °C by **Method C** mentioned above. ^b Isolated yield. ^c Determined by chiral GC analysis on Chiasil DEX CB.

The effects of catalyst loading were systematically studied. The results, described in Table 2, indicated that the enantioselectivity and yield were influenced by the amount of the chiral amino acid salt. The best result was obtained when 30 mol % catalyst loading was used. Lowering the catalyst loading to less than 10 mol % led to dramatic drops in ee value with racemic products and the reaction solution appeared a semitransparent state nor a heterogeneous state. On increasing of the catalyst loading from 30 to 50 mol %, the yield was sharply decreased for the water contained in the catalyst reacted with TMSCN and delayed the addition of TMSCN to acetophenone and a small amount of undetermined by-product was formed under this reaction condition.

In order to survey the role of the amino group of catalyst **2f**, modified amino acid salts were used as catalysts for cyanosilylation of acetophenone. From Table 4, we can see that any modification of the primary amine lower the ee values of the products.

Table III. Structural effect of the catalysts on the asymmetric cyanosilylation of acetophenone^a

Entry	catalyst	Time(h)	yield (%)	ee (%)
1		68	40	2
2		68	59	2
3		68	34	5
4		64	80	12

^a The reactions were carried out on a 0.5 mmol scale with 30 mol % catalyst loading and 1.2 eq TMSCN at -20 °C by **Method A** mentioned above. ^b isolated yield. ^c determined by chiral GC analysis on Chiasil DEX CB.

Table IV. Effects of additive and experiment procedure on the asymmetric addition of TMSCN to acetophenone^a

Entry	catalyst	procedure	TMSCN (eq.)	additive	temp (°C)	yield (%)	ee (%)
1	2f	a	1.2	--	-20	58	5.2

2	2f · $\frac{1}{2}$ H ₂ O	a	1.2	--	-20	50	51
3	L-phenglycine + NaOH	a	1.2	--	-20	70	54
4	L-phenglycine + NaOH	c	1.2	--	-20	68	80
5	L-phenglycine + NaOH	b	1.2	--	-45	55	53
6	L-phenglycine + NaOH	c	1.2	--	-45	64	94
7	L-phenglycine + NaOH	c	1.5	--	-45	84	92
8	2f · $\frac{1}{2}$ H ₂ O	d	2.0	H ₂ O (0.5 eq.)	-20	97	64
9	2f · $\frac{1}{2}$ H ₂ O	d	1.5	CH ₃ OH (0.5 eq.)	-45	85	93
10	2f · $\frac{1}{2}$ H ₂ O	d	1.5	ⁱ PrOH (0.5 eq.)	-45	96	94
11	2f · $\frac{1}{2}$ H ₂ O	e	1.5	ⁱ PrOH (0.5 eq.)	-45	95	94

^a Procedure a: the reactions were carried out by **Method A** mentioned above ; Procedure b: *L*-Phenylglycine (22.7 mg, 0.15 mmol) was stirred with NaOH (6.0 mg, 0.15 mmol) in dry THF (0.3 mL) at 25 °C for 0.5 h under N₂ atmosphere. To the resulted catalyst, acetophenone (0.5 mmol) and THF (0.2 mL) was added at -20 °C and stirred at 30 °C for an hour, and then added TMSCN (1.2 eq) and 0.5 mL THF at -45 °C; Procedure c: the reactions were carried out by **Method C** mentioned above; Procedure d: the reaction was carried out by **Method D** and ⁱPrOH was replace by the corresponding additives; Procedure e: To a solution of *L*-phenylglycine sodium salt and 0.3 equiv CH₃OH in 0.5 mL of THF was added trimethylsilyl cyanide (1.5 equiv) at -20 °C, and the mixture was stirred at 30 °C for 1.0 h. And then ketone (0.5 mmol) was charged sequentially at -45 °C and stirred for 15 min. ⁱPrOH (0.25 mmol) and 0.5 mL THF were then added via syringe. The reaction stirred at -45 °C for certain time and monitored by TLC. ^b isolated yield; ^c determined by chiral GC analysis on Chiasil DEX CB

One key feature associated with the use of *L*-phenylglycine sodium salt was the experimental procedure (Table 5). When the catalyst was stirred with TMSCN in THF for 1h at 30 °C before acetophenone was added, the enantioselectivity was greatly improved from 54% to 80% ee at -20 °C and up to 94% ee at a lower reaction temperature (-45 °C). A little moisture was crucial to retain enantioselectivity, and any attempt to remove water contained in the catalyst gave bad result (Table IV, entries 1-3). However, introduction of alcohol increased catalytic activity and led to product formation in 96% yield and 94% ee (entries 7,9-10) .

Preparation of racemic samples for GC and HPLC analysis.

To 30 mol% K₂CO₃ , ketone and 1.2 TMSCN were dropwise added and stirred at room temperature for 24 h. Then K₂CO₃ was filtrated form the reaction mixture and the residues was put on a silica gel column to give the pure product with ethyl ether/petroleum ether (1/100, V/V) as the eluent.

Physical Data of the Cyanohydrin TMS Ethers Reported in the communication.

2-trimethylsilyloxy-2-phenylpropanenitrile (3a)

96% yield, 94% ee. ¹H NMR (300 MHz, CDCl₃) : δ = 0.19 (s, 9H), 1.87 (s, 3H), 7.38-7.58 (m, 5H) ppm. GC analysis (Varian, CP-Chirasil DEX CB, 0.25mm x 25m ,105 °C, 8 psi): *t_r* (major) = 22.0 min, *t_r* (minor) = 21.3 min. [α]_D²⁵ + 22.0

($c = 0.204$ in CH_2Cl_2 , 94% ee). [lit. $[\alpha]_{\text{D}}^{24} -21.9$ ($c = 1.18$ in CH_2Cl_2 , 93% ee)]; Fuerst, D. E.; Jacobsen, E. N. *J. Am. Chem. Soc.* 2005, 127, 8964-8965.

2-trimethylsilyloxy-2-(4'-methoxyphenyl)propanenitrile (3b)

81% yield, 92% ee. ^1H NMR (400 MHz, CDCl_3): $\delta = 0.19$ (s, 9H), 1.87 (s, 3H), 3.85 (s, 3H), 6.93 (m, 2H), 7.49 (m, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 33.41, 55.33, 71.28, 113.89, 121.81, 126.06, 134.04, 159.80$ ppm. GC analysis (Varian, CP-Chirasil DEX CB, 0.25mm x 25m, 105 °C, 8 psi): t_{r} (major) = 86.4 min, t_{r} (minor) = 85.2 min. $[\alpha]_{\text{D}}^{25} + 22.9$ ($c = 0.188$ in CH_2Cl_2 , 92% ee). [lit. $[\alpha]_{\text{D}}^{20} + 22.6$ ($c = 1.09$ in CHCl_3 , 91% ee)]; Deng, H.; Isler, M. P.; Snapper, M. L.; Hoveyda, A. H. *Angew. Chem. Int. Ed.* **2002**, 41, 1009-1021.

2-trimethylsilyloxy-2-(4'-methylphenyl)propanenitrile (3c)

75% yield, 97% ee. ^1H NMR (400 MHz, CDCl_3): $\delta = 0.16$ (s, 9H), 1.84 (s, 3H), 2.36 (s, 3H), 7.21 (m, 2H), 7.43 (m, 2H) ppm. $\text{C}_{13}\text{H}_{19}\text{NOSi}$: C 66.90, H 8.21, N 6.00; found C 66.78, H 8.03, N 6.39. GC analysis (Varian, CP-Chirasil DEX CB, 0.25mm x 25m, 105 °C, 8 psi): t_{r} (major) = 38.4 min, t_{r} (minor) = 37.8 min. $[\alpha]_{\text{D}}^{25} + 24.3$ ($c = 0.192$ in CH_2Cl_2 , 97% ee). [lit. $[\alpha]_{\text{D}}^{25} + 22.1$ ($c = 2.44$ in CH_2Cl_2 , 92% ee)]; Chen, F. X.; Zhou, H.; Liu, X. H.; Qin, B.; Feng, X. M.; Zhang, G. L.; Jiang, Y. Z. *Chem. Eur. J.* **2004**, 10, 4790-4797.

2-trimethylsilyloxy-2(4'-fluorophenyl)propanenitrile (3d)

90% yield, 92% ee. ^1H NMR (400 MHz, CDCl_3) : δ = 0.18 (s, 9H), 1.84 (s, 3H), 7.08 (m, 2H), 7.52 (m, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 1.0, 33.5, 71.0, 115.6 (d, $^2J_{\text{CCF}}$ = 21.9 Hz), 121.4, 126.5 (d, $^3J_{\text{CCCF}}$ = 8.5 Hz), 138.0, 162.2 (d, $^1J_{\text{CF}}$ = 246.4 Hz) ppm. GC analysis (Varian, CP-Chirasil DEX CB, 0.25mm x 25m, 115 °C, 8 psi): t_{r} (major) = 19.1 min, t_{r} (minor) = 18.3 min. $[\alpha]_{\text{D}}^{25}$ +17.8 (c = 0.212 in CH_2Cl_2 , 92% ee). [lit. $[\alpha]_{\text{D}}^{22}$ + 17.6 (c = 2.7 in CH_2Cl_2 , 92% ee)]; Chen, F. X.; Zhou, H.; Liu, X. H.; Qin, B.; Feng, X. M.; Zhang, G. L.; Jiang, Y. Z. *Chem. Eur. J.* **2004**, 10, 4790-4797.

2-trimethylsilyloxy-2(4'-chlorophenyl)propanenitrile (3e)

83% yield, 90% ee. ^1H NMR (400 MHz, CDCl_3) : δ = 0.19 (s, 9H), 1.83 (s, 3H), 7.38 (m, 2H), 7.48 (m, 2H) ppm. $\text{C}_{12}\text{ClH}_{16}\text{NOSi}$: C 56.79, H 6.35, N 5.52; found C 56.82, H 6.41, N 5.93. GC analysis (Varian, CP-Chirasil DEX CB, 0.25mm x 25m, 110 °C, 8 psi): t_{r} (major) = 53.6 min, t_{r} (minor) = 51.5 min. $[\alpha]_{\text{D}}^{25}$ +18.1 (c = 0.240 in CH_2Cl_2 , 90% ee). [lit. $[\alpha]_{\text{D}}^{25}$ +18.2 (c = 2.06 in CH_2Cl_2 , 90% ee)]; Chen, F. X.; Zhou, H.; Liu, X. H.; Qin, B.; Feng, X. M.; Zhang, G. L.; Jiang, Y. Z. *Chem. Eur. J.* **2004**, 10, 4790-4797.

2-trimethylsilyloxy-2(3'-chlorophenyl)propanenitrile (3f)

80% yield, 96% ee. ^1H NMR (300 MHz, CDCl_3): δ = 0.22 (s, 9H), 1.86 (s, 3H), 7.34-7.55 (m, 4H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 1.0, 33.4, 70.9, 121.0, 122.7, 124.8, 128.8, 129.9, 134.6, 144.0 ppm. $\text{C}_{12}\text{ClH}_{16}\text{NOSi}$: C 56.79, H 6.35, N 5.52; found C 56.61, H 6.39, N 5.90. GC analysis (Varian, CP-Chirasil DEX CB, 0.25mm x 25m, 105 °C, 8 psi): t_{r} (major) = 49.9 min, t_{r} (minor) = 49.0 min. $[\alpha]_{\text{D}}^{25}$ + 25.0 (c = 0.244 in CH_2Cl_2 , 96% ee). [lit. $[\alpha]_{\text{D}}^{26}$ +19.6 (c = 2.88 in CH_2Cl_2 , 90% ee)]; Chen, F. X.; Zhou, H.; Liu, X. H.; Qin, B.; Feng, X. M.; Zhang, G. L.; Jiang, Y. Z. *Chem. Eur. J.*

2-trimethylsilyloxy-2(2'-fluorophenyl)propanenitrile (3g)

77% yield, 90% ee. ^1H NMR (400 MHz, CDCl_3) : δ = 0.26 (s, 9H), 1.94 (s, 3H), 7.07-7.12 (m, 1H), 7.16-7.20 (m, 1H), 7.33-7.38 (m, 1H), 7.56-7.60 (m, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 1.0, 30.8, 68.4, 116.5, 120.6, 124.2, 126.7, 130.6, 159.4 ppm. GC analysis (Varian, CP-Chirasil DEX CB, 0.25mm x 25m, 105 °C, 8 psi): t_r (major) = 25.6 min, t_r (minor) = 25.0 min. $[\alpha]_D^{25} + 14.8$ (c = 0.196 in CH_2Cl_2 , 90% ee). [lit. $[\alpha]_D^{26} - 12.7$ (c = 1.18 in CHCl_3 , 76% ee)]; Chen, F. X.; Qin, B.; Feng, X. M.; Zhang, G. L.; Jiang, Y. Z. *Tetrahedron* **2004**, 60, 10449-10460.

2-trimethylsilyloxy- (1'-thiophene)-1-carbonitrile (3h)

58% yield, 92% ee (84% yield, 86% ee) . ^1H NMR (300 MHz, CDCl_3) : δ = 0.20 (s, 9H), 2.00 (s, 3H), 7.00 (m, 1H), 7.21-7.34 (m, 2H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 0.78, 33.40, 68.24, 120.82, 124.70, 125.97, 126.61, 146.27 ppm. $\text{C}_{10}\text{H}_{15}\text{NOSSi}$: C 53.29, H 6.71, N 6.21; found C 53.48, H 6.94, N 6.43. GC analysis (Varian, CP-Chirasil DEX CB, 0.25mm x 25m, 110 °C, 8 psi): t_r (major) = 22.7 min, t_r (minor) = 21.8 min. $[\alpha]_D^{25} + 51.1$ (c = 0.188 in CH_2Cl_2 , 92% ee), $[\alpha]_D^{25} + 49.2$ (c = 0.248 in CH_2Cl_2 , 86% ee). [lit. $[\alpha]_D^{22} - 57.6$ (c = 1.0 in CHCl_3 , 97% ee)]; Fuerst, D. E.; Jacobsen, E. N. *J. Am. Chem. Soc.* 2005, 127, 8964-8965.

2-trimethylsilyloxy- 2-methyl-4-phenyl-3-butenenitrile (3i)

96% yield, 97% ee. ^1H NMR (300 MHz, CDCl_3) : δ = 0.27 (s, 9H), 1.77 (s, 3H), 6.15 (d, J = 15.9 Hz, 1H), 6.91 (d, J = 15.9 Hz, 1H), 7.331-7.45 (m, 5H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 1.3, 30.8, 69.9, 120.6, 126.8, 128.5, 128.7, 129.5, 130.9, 135.1 ppm. HPLC (Chiralcel OD, *i* PrOH/*n*-hexane, 1:99, flow: 1.0 $\text{mL}\cdot\text{min}^{-1}$). t_r (major) = 5.0 min, t_r (minor) = 4.2 min. $[\alpha]_{\text{D}}^{25}$ +63.2 (c = 0.200 in CH_2Cl_2 , 97% ee). [lit. $[\alpha]_{\text{D}}^{25}$ -61.9 (c = 1.0 in CHCl_3 , 96% ee)]; Fuerst, D. E.; Jacobsen, E. N. *J. Am. Chem. Soc.* 2005, 127, 8964-8965.

2-trimethylsilyloxy-2(2'-naphthyl)propanenitrile (3j)

90% yield, 96% ee. ^1H NMR (300 MHz, CDCl_3) : δ = 0.22 (s, 9H), 1.97 (s, 3H), 7.54-7.66 (m, 3H), 7.90-7.93 (m, 3H), 8.07 (d, J = 1.8 Hz, 1H) ppm. HPLC (Chiralcel OJ, *i* PrOH/*n*-hexane, 0.5:99.5, flow: 0.5 $\text{mL}\cdot\text{min}^{-1}$): t_r (major) = 10.3 min, t_r (minor) = 14.7 min. $[\alpha]_{\text{D}}^{25}$ +14.4 (c = 0.194 in CH_2Cl_2 , 96% ee). [lit. $[\alpha]_{\text{D}}^{20}$ -14.2 (c = 1.0 in CHCl_3 , 97% ee)]; Fuerst, D. E.; Jacobsen, E. N. *J. Am. Chem. Soc.* 2005, 127, 8964-8965.

2-trimethylsilyloxy- 2-methyl-4-phenyl-butanenitrile (3k)

97% yield, 81% ee. ^1H NMR (300 MHz, CDCl_3) : δ = 0.29 (s, 9H), 1.65 (s, 3H), 2.02-2.08 (m, 2H), 2.80-2.91 (M, 2H), 7.22-7.33 (m, 5H) ppm. GC analysis (Varian, CP-Chirasil DEX CB, 0.25mm x 25m, 130 $^{\circ}\text{C}$, 8 psi): t_r (major) = 31.5 min, t_r (minor) = 32.1 min. $[\alpha]_{\text{D}}^{25}$ +12.7 (c = 0.248 in CH_2Cl_2 , 81% ee). [lit. $[\alpha]_{\text{D}}^{25}$ +13.3 (c = 1.15 in CHCl_3 , 81% ee)]; Hamashima, Y.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* 2000, 122, 7412-7413

2-trimethylsilyloxy-2-methyl-3-methylbutanenitrile (3l)

92% yield, 55% ee. ^1H NMR (600 MHz, CDCl_3) : δ = 0.24 (s, 9H), 1.03 (t, J = 6 Hz, 6H), 1.53 (s, 3H), 1.86 (hept, J = 6 Hz, 1H) ppm. GC analysis (Varian, CP-Chirasil DEX CB, 0.25mm x 25m ,65 °C, 8 psi): t_r (major) = 20.8 min, t_r (minor) = 21.5 min. $[\alpha]_D^{25}$ +1.2 (c = 0.170 in CH_2Cl_2 , 55% ee). [lit. $[\alpha]_D^{22}$ -1.1 (c = 1.66 in CH_2Cl_2 , 90% ee)]; Chen, F. X.; Zhou, H.; Liu, X. H.; Qin, B.; Feng, X. M. *Chem. Eur. J.* **2004**, *10*, 4790-4797.

Copy of NMR Spectra of TMSCN and the Catalyst

When a 1:1 mixture of TMSCN and catalyst **2f** in CDCl_3 at 25°C was monitored by ^1H NMR, the development of new CH_3 peak of TMSCN at δ = 0.21 ppm was observed (CH_3 of TMSCN peak at δ = 0.37 ppm). The ^{13}C NMR spectra also changed, with a new CH_3 peak appearing at δ = 1.91 ppm (CH_3 of TMSCN peak at δ = -1.83 ppm). ^{29}Si NMR analysis revealed that another strong TMS singal was found at δ = 0.6 ppm as compared to -17.9 ppm for TMSCN

Current Data Parameters
 DATE 20050406
 EXPNO 1
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20050406
 Time 11:50
 INSTRUM av300
 PROBHD 5 mm QNP 1H/13
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 16
 DS 0
 SWH 5995.204 Hz
 FIDRES 0.182959 Hz
 AQ 2.7329011 sec
 RG 128
 DM 63.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 3.00 usec
 PL1 -2.00 dB
 SF01 300.1320882 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300129 MHz
 WDW EM
 SSB 0
 LB 0.10 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 CY 50.00 cm
 F1 10.000 ppm
 F2 3001.30 Hz
 F2P -0.500 ppm
 F2 -150.06 Hz
 SFOCH 0.52500 ppm/cm
 F2CH 157.56825 Hz/cm

Current Data Parameters

NAME	CO-190-2
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20050406
Time	13.22
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PROBHD	5 mm QNP 1H/13
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
VS	16
DS	0
SWH	5965.204 Hz
FIDRES	0.182959 Hz
AQ	2.7329011 sec
RG	128
DW	63.460 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec

***** CHANNEL f1 *****

MUCL	1H
NUC1	1H
PL1	3.00 usec
PL1	-2.00 dB
SFO1	300.1360882 MHz

F2 - Processing parameters

SI	32768
SF	300.1360128 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00

10 MHz plot parameters

CX	20.00 cm
CY	50.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-0.500 ppm
F2	-150.06 Hz
CPDPRM	0.52500 ppm/cm
ACQ	157.56625 Hz/cm

TMSCl

ppm

127.112

77.424
77.000
76.576

1.897
1.288
-1.841

Current Data Parameters
NAME CO-14-1
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050406
Time 11.52

PROBHD 5 mm QNP 1H/13
PULPROG zgpg
NUC1 13C
NUC2 1H
SOLVENT CDCl3
CONC 69536
VS 1436
AQ 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DM 22.050 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00020000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 5.50 usec
PL1 -6.00 dB
SF01 75.477598 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.71 dB
SF02 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677534 MHz
WDW EM
SSB 0
-B 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CY 20.00 cm
CX 15.00 cm
F1P 202.105 ppm
F1 150099.33 Hz
F2P -144.425 ppm
F2 -755.13 Hz
SFOH 10.50630 ppm/cm
-2700 700 kHz

ppm

150

100

50

0

13C NMR

ppm

128.666
127.809
126.776

77.423
77.000
76.576

59.896

1.905
1.305
-0.477
-1.832

===== CHANNEL F1 =====
NUC1 13C
P1 5.50 usec
PL1 -8.00 dB
SFO1 76.475999 MHz

===== CHANNEL F2 =====
NUC2 1H
P2 90.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.71 dB
SFO2 300.131800 MHz

F2 - Processing parameters
SI 32768
SF 75.467593 MHz
WDW EM
SSB 0
GB 0
PC 3.00 Hz
IC 0
TC 1.40

10 MHz plot parameters
CX 20.00 cm
CY 10.00 cm
FZ 500.000 MHz
F1 14093.863 Hz
F2 -10.000 MHz
F3 -755.00 Hz
F4 13.50000 MHz
F5 792.44910 MHz

Current Data Parameters	
NAME	sl.bbl
EXPNO	21
PROCNO	1

F2 - Acquisition Parameters
Date_ 20050408

Time	14.05
INSTRUM	dp x 300
PROBHD	5 mm Dual 13
PULPROG	291930
TD	65536
SOLVENT	CDCl3
NS	1490
DS	2
SMH	11990.407 Hz
FIDRES	0.162959 Hz
AQ	2.7329011 sec
RG	1000
DM	41.700 usec
DE	6.00 usec
TE	300.0 K
D1	10.00000000 sec
111	0.03000000 sec

```
===== CHANNEL f1 =====
NUC1      2951
P1         15.00 usec
PL1        2.00 dB
SF01      59.6261805 MHz
```

CPDRPG2	CHANNEL f2	waltz16
NUC2	1H	
PCPD2	80.00 usec	
PL2	120.00 dB	
PL12	27.00 dB	
SF02	300.1312005 MHz	

F2 - Processing parameters	
SI	32768
SF	59.6277894 MHz
MDM	EM
SSB	0
LB	0.50 Hz
GB	0
PC	1.00

1D NMR plot parameters
CX 20.00 cm
F1P 39.912 ppm
F1 2379.85 Hz
F2P -66.677 ppm
F2 -3975.79 Hz
PPMCH 5.32943 ppm/cm
HZCM 317.78183 Hz/cm

1MSUN2 S129 NMH bd1 probe

Current Data Parameters
 NAME s1.bd1
 EXPNO 21
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20050407

Time 17.33
 INSTRUM dpx300
 PROBHD 5 mm Dual 13
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 4904
 DS 2
 SWH 11990.407 Hz
 FIDRES 0.182959 Hz
 AQ 2.7329011 sec
 RG 1000
 DM 41.700 usec
 DE 6.00 usec
 TE 300.0 K
 D1 10.00000000 sec
 d11 0.0300000 sec

===== CHANNEL f1 =====
 NUC1 29Si
 P1 15.00 usec
 PL1 2.00 dB
 SF01 59.6261805 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 120.00 dB
 PL12 27.00 dB
 SF02 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 59.6277894 MHz
 MDW EM
 SSB 0
 LB 0.50 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 F1P 38.098 ppm
 F1 2271.72 Hz
 F2P -66.878 ppm
 F2 -3987.80 Hz
 PPMCM 5.24883 ppm/cm
 HZCM 312.97607 Hz/cm