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Enantioselective cyanosilylation of ketones catalyzed by Mn(salen)/Ph_3PO

Sung Soo Kim,* Sang Hyuck Lee and Ju Myung Kwak

Department of Chemistry, Inha University, Incheon 402-751, South Korea

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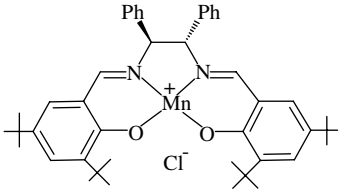
Abstract—TMSCN asymmetrically adds to a variety of ketones by catalysis with **1**/Ph_3PO. This is a double activation where **1** acts as a Lewis acid and Ph_3PO as a Lewis base. Various ketones were subjected to the enantioselective addition to give up to 85% ee.

1. Introduction

Asymmetric addition of trimethylsilyl cyanide (TMSCN) to carbonyl compounds and subsequent hydrolysis produced chiral cyanohydrins that are useful intermediates for the synthesis of numerous pharmaceuticals.[1–3] Such chiral compounds are useful intermediates for the synthesis of pharmaceuticals. The two functional groups (–OH and –CN) can be easily transformed into various homochiral ones including α-hydroxy acids,[4,5] α-hydroxy aldehydes,[6] α-hydroxy ketones,[6] β-hydroxy amines[5,6] and α-amino acid derivatives.[7]

Snapper and Hoveyda have established that a chiral peptide ligand and $Al(O^iPr)_3$ can effectively promote the enantioselective addition of TMSCN to ketones.[8] Belokon and North reported the asymmetric addition of TMSCN to ketones catalyzed by a bimetallic, chiral (salen) titanium complex.[9] Shibasaki has disclosed the first general catalytic enantioselective cyanosilylation of ketones by a novel bifunctional catalyst containing Ti(IV).[10,11] Feng has described the enantioselective cyanosilylation of ketones employing chiral salen-Ti(IV) complex as the Lewis acid and achiral *N*-oxide as the Lewis base.[12,13] Shibasaki has carried out enantioselective cyanosilylation of ketones utilizing the chiral ligand complexed with $Gd(O^iPr)_3$[14] and $Sm(O^iPr)_3$,[15] respectively. Deng has used chiral cinchona alkaloid catalysts for the enantioselective cyanosilylation of ketones.[16,17] Corey has shown that a chiral oxazaborolidinium salt is an excellent catalyst for the cyanosilylation of methyl ketones.[18] Jacobsen has proven that chiral thiourea is a very effective catalyst for the enantioselective cyanosilylation of ketones.[19] Feng has succeeded in the catalytic asymmetric cyanosilylation of ketones with a chiral amino acid salt.[20] The enantioselective cyanosilylation of aldehydes and ketones employing Al(salen)/Ph_3PO was developed by us.[21–23] We also investigated the similar reactions for aldehydes utilizing **1**/Ph_3PO.[24] Herein, we report the cyanosilylation of ketones employing **1**/Ph_3PO as a catalyst.



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2. Results and discussion

The amount of Mn(salen) was compared for the best ee, which indicates that 5 mol % gives a better outcome than 10 mol % (entries 1 and 2). The additive quantity was also varied (entries 2–6) with 50 mol % (entry 5) proving to be the optimal amount. The catalyst amount was further reduced to 1 mol % from 5 mol %, giving rise to negative effects in terms of reaction time, yield and ee (entries 5 and 7). Temperature decreases from rt to 0 °C greatly lengthen the reaction time (45–96 h) with lower yields (entries 5 and 8). CH_2Cl_2 was better solvent than Et_2O, THF and toluene

* Corresponding author. Tel.: +82 32 864 4966; fax: +82 32 867 5604; e-mail: sungsoo@inha.ac.kr

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(entries 9–11). Addition of CF_3CH_2OH, NMO and 4 Å molecular sieves, respectively, to the additive Ph_3PO showed no favourable influence for the ee. The reaction conditions of entry 5 of Table 1 were chosen for enantioselective cyanosilylation of ketones. Numerous ketones have undergone cyanosilylation under these conditions (Table 2). The role of the catalyst during the reaction is shown in Figure 1. Both Mn of Mn(salen) and silicon atom of TMSCN could have bonded to carbonyl oxygen. Ph_3PO may assist CN of TMSCN to make a bond with carbonyl carbon. The possible mechanism and transition state[21–24] involved in this catalytic reaction is given in Figure 1.

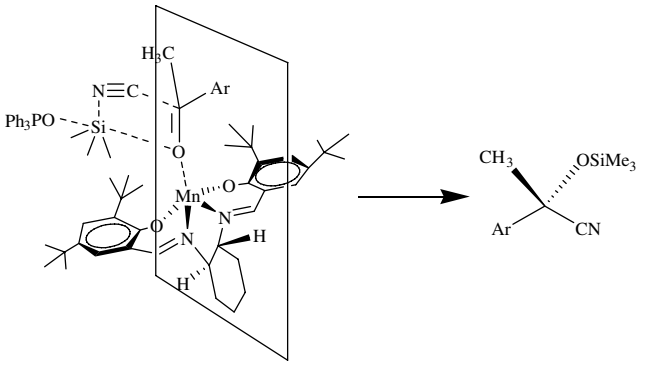


Figure 1. Transition state involved in the enantioselective cyanosilylation of ketones by double-activation catalysis.

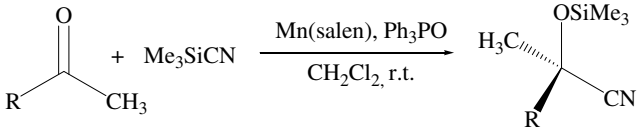
Substituted acetophenones (entries 1–7) show significant variation of reactivities in terms of reaction time and ee. The yields varied from 82% to 93%. Moderately electron-withdrawing groups (entries 2, 3 and 4) reduce the reaction time (from 45 to 20–36 h) and increase the yield. *p*-Bromoacetophenone gave the highest ee of 85% among the present reactions. Weakly electron-attracting substituents (entry 5) increase the reaction time with similar yield and ee (compare entries 1 and 5). Strongly electron-withdrawing

Table 1. Enantioselective cyanosilylations of ketones catalyzed by Mn(salen) under various conditions[a]

Entry	Substrate	Solvent	Mn(salen) (mol %)	$PO(Ph)_3$ (mol %)	Temperature (°C)	Time (h)	% Yield	% ee
1	Acetophenone	CH_2Cl_2	10	10	rt	49	50	41
2		CH_2Cl_2	5	10	rt	45	55	50
3		CH_2Cl_2	5	20	rt	50	71	60
4		CH_2Cl_2	5	40	rt	50	83	62
5		CH_2Cl_2	5	50	rt	45	82	63
6		CH_2Cl_2	5	100	rt	32	83	61
7		CH_2Cl_2	1	50	rt	45	67	48
8		CH_2Cl_2	5	50	0	96	12	61
9		Et_2O	5	50	rt	56	90	50
10		THF	5	50	rt	80	39	21
11		Toluene	5	50	rt	48	38	28

[a] Substrate concentration is 1 M.

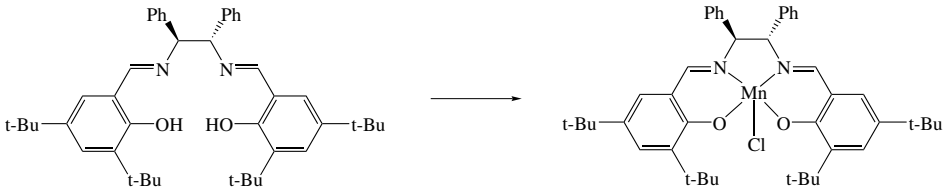
Table 2. Catalytic asymmetric cyanosilylation of ketones with Mn(salen)/Ph_3PO[a]



Entry	Substrate[b]	σ	Time (h)	% Yield	% ee[c]	Config.
1	Acetophenone	0	45	82	63	*R*[d]
2	3-Chloroacetophenone	0.37	20	91	63	*R*[d]
3	4-Chloroacetophenone	0.24	26	90	57	*R*[d]
4	4-Bromoacetophenone	0.26	36	89	85	—
5	4-Fluroacetophenone	0.15	50	82	60	—
6	3-Nitroacetophenone	0.71	10	93	46	—
7	4-Nitroacetophenone	0.81	6	89	50	—
8	4-Methoxyacetophenone	−0.12	45	38	55	—
9	Isobutylrophenone	—	38	75	57	—
10	4-Methoxyphenylacetone	—	7	90	82	—
11	3,4-Dichlorophenylacetone	—	5	95	75	—
12	1-Phenylbutan-2-one	—	32	94	72	—
13	Benzylacetone	—	10	89	60	*R*[d]
14	1-Indanone	—	70	56	58	—

[a] 5 mol % of **1** and 50 mol % of Ph_3PO were used for the cyanosilylations.
[b] Substrate concentration is 1 M.
[c] Determined by HPLC.[8,10,11,14,22]
[d] The reported specific reactions indicate positive values with (*R*)-configuration. Present specific rotations also carry a positive value.[8,10,11,14,22,25]

substituents (entries 6 and 7) greatly reduce the reaction time with comparable yield but relatively low ee (46% and 50%). Strongly electron-donating group (entry 8) gives rise to poor yield and ee. Isopropyl phenyl ketones (entry 9) produce somewhat low yield and ee. 1-(4-Methoxyphenyl)propan-2-one and 1-(3,4-dichlorophenyl)propan-2-one (entries 10 and 11) reacted quite fast (7 h and 5 h) with comparatively high yield and ee (82% and 75%). 4-Phenylbutan-2-one (entry 13) reacts much faster than 1-phenylbutan-2-one (entry 12), but the latter shows a higher yield and ee. 2,3-Dihydroinden-1-one reacts very slowly to give a low yield (entry 14). Al(III) appears to have effective bonding with chiral peptide[8] and chiral salen[21–23] for the formation of catalytic site. Ti(salen) complexes[9,12,13] are also used for the catalytic enantioselective cyanosilylation of ketones. Here Mn site forms partial bond with carbonyl oxygen for the enantioselective cyanosilylations of ketones. Accordingly, the addition of TMSCN to ketones occurs on the plane depicted in Figure 1.

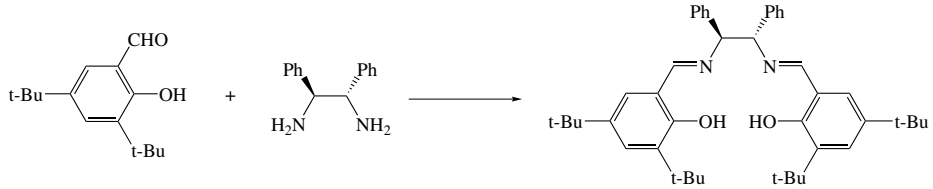


3. Conclusion

An effective double-activation process for cyanosilylation of ketones has been developed utilizing chiral Mn(salen)/Ph_3PO as catalyst and additive. Moderately electron-withdrawing substituents give rise to a relatively better outcome. The electronic nature of the substituent has no consistent effect on ee or yield. The presence of a methylene group between benzene ring and carbonyl gives good ee and yield. The mechanism of cyanosilylation is depicted. We are continuing to explore for other optimal catalysts for the enantioselective reactions.

4. Experimental

4.1. Synthesis of (*S*,*S*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-diphenylethylenediamine



(*S*,*S*)-1,2-Diphenylethylenediamine (0.25 g, 1.18 mmol) and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (0.55 g, 2.35 mmol) were refluxed in absolute ethanol (10 mL) for 3 h. A small amount of water was added to the reaction mixture, then it was allowed cool to 2 °C and kept at that temperature for 2 h. The product was collected by suction filtration to afford a yellow powder, yield 0.53 g (70%) mp 197–198 °C. IR (KBr): 3087, 3062, 3030, 2958, 2909, 2869, 1626, 1598, 1469, 1454, 1442, 1362, 1250, 1174, 876, 776, 700 cm^{-1}. ^1H NMR: δ 1.22 (18H, s, *t*-Bu), 1.42 (18H, s, *t*-Bu), 4.72 (2H, s, CH–N), 6.98 (2H, d, $J = 2.4$ Hz, Ar–H), 7.18 (10H, s, Ph), 7.31 (2H, d, $J = 2.4$ Hz, Ar–H), 8.40 (2H, s, CH=N), 13.59 (2H, s, OH). ^{13}C NMR: δ 29.4, 31.4, 34.0, 34.9, 80.0, 117.7, 126.2, 127.0, 127.3, 127.9, 128.1, 136.2, 139.7, 139.9, 157.8, 167.1. HRMS (EI) *m*/*z*: calcd for $C_{44}H_{56}N_2O_2$ 644.4342, found 644.4329.

4.2. Synthesis of [(*S*,*S*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-diphenylethylenediamine]chloromanganese(III)

Solid $Mn(OAc)_2{\cdot}4H_2O$ (0.40 g, 1.63 mmol) was added to a solution of (*S*,*S*)-*N*,*N*′-bis(3,5-di-*tert*-butyl-salicylidene)-1,2-diphenylethylenediamine (0.51 g, 0.79 mmol) in absolute ethanol (10 mL), and the dark brown mixture was refluxed for 2 h under air. Solid LiCl (0.11 g, 2.60 mmol) was then added and the mixture was refluxed for an additional 2 h and then stirred at 70 °C overnight. The reaction mixture was cooled, and then water was added resulting in the precipitation of a brown powder, which was collected by suction filtration. The powder was redissolved in CH_2Cl_2 and extracted with water and brine. The organic phase was dried over anhydrous Na_2SO_4, and the solvent evaporated to afford a brown powder, yield 0.54 g (93%), mp > 300 °C. IR (KBr): 3063, 3027, 2956, 2904, 2867, 1610, 1534, 1455, 1429, 1317, 1252, 1174, 857, 700, 579 cm^{-1}. MS(FAB) *m*/*z* 697.6 (M−Cl)+. Anal. Calcd for $C_{44}H_{54}ClMnN_2O_2{\cdot}1/2H_2O$: C, 71.19; H, 7.47; N, 3.77. Found: C, 71.36; H, 7.47; N, 3.66.

4.3. Silylcyanation of the ketones catalyzed by Mn(salen) and Ph_3PO

To a stirred CH_2Cl_2 solution of Mn(salen) (5 mol %) and $POPh_3$ (50 mol %) was added a ketone (1mmol) and stirred for 30 min at rt TMSCN (1.5 mmol) was added to the reaction mixture using a syringe pump and the mixture reacted at the same temperature for 5–50 h. The solvent was then evaporated. The crude product was further purified by flash chromatography (hexane/ethyl acetate = 9:1) to give cyanohydrin in more than 75% yield. The sample was identified by ^1H, ^{13}C NMR, HRMS and ee % was determined by chiral HPLC column (DAICEL CHIRALCEL OJ-H, DAICEL CHIRALCEL OD and DAICEL CHIRALCEL OB-H). ^1H and ^{13}C NMR were taken utilizing Varian Jemini 2000 (200 MHz) or Varian Unity Inova 400 (400 MHz) NMR spectrometer. Hewlett–Packard 5890A Gas Chromatograph/Jeol JMS-DX303 Mass Spectrometer was used for HRMS data. Analytical high performance liquid chromatography (HPLC) was performed on Gilson 305 series HPLC using the indicated chiral column. All data were in accordance with literature values. Absolute configurations were determined by optical rotations.[26]

4.3.1. 2-Trimethylsilyloxy-2-phenylpropanenitrile. ^1H NMR ($CDCl_3$) δ 0.19 (s, 9H), 1.87 (s, 3H), 7.38–7.58 (m, 5H, aromatic H); ^{13}C NMR ($CDCl_3$) δ 1.03, 33.5, 71.6, 121.6, 128.6, 142.0; $[\alpha]_D^{24} = +10.4$ (*c* 1.14, $CHCl_3$, 63% ee) {lit. $[\alpha]_D^{20} = +21.9$ (*c* 1.18, $CHCl_3$, for the (*R*)-enantiomer with 93% ee)} HRMS(M+) calcd for $C_{12}H_{17}NOSi$: 219.1079; found: 219.1082 HPLC (DAICEL CHIRALCEL OB-H, ^{i}PrOH/hexane = 0.5/99.5, flow = 0.25 mL/min) 19.6 and 20.7 min.

4.3.2. 2-Trimethylsilyloxy-2-(3-chlorophenyl)propanenitrile. ^1H NMR ($CDCl_3$) δ 0.22 (s, 9H), 1.86 (s, 3H), 7.34–7.55 (m, 4H aromatic H); ^{13}C NMR ($CDCl_3$) δ 1.0, 33.4, 70.9, 121.0, 122.7, 124.8, 128.8, 129.9, 134.6, 144.0; $[\alpha]_D^{24} = +11.2$ (*c* 1.3, $CHCl_3$, 63% ee) {lit. $[\alpha]_D^{26} = +7.1$ (*c* 0.34, $CHCl_3$, for the (*R*)-enantiomer with 33% ee)} HRMS(M+) calcd for $C_{12}H_{16}ClNOSi$: 253.0690; found: 253.0692 HPLC (DAICEL CHIRALCEL OB-H, *i*PrOH/hexane = 0.25/99.75, flow = 0.25 mL/min) 29.8 and 32.8 min.

4.3.3. 2-Trimethylsilyloxy-2-(4-chlorophenyl)propanenitrile. ^1H NMR ($CDCl_3$) δ 0.21 (s, 9H), 1.83 (s, 3H), 7.38 (m, 2H), 7.49 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 1.05, 33.53, 71.06, 121.25, 126.07, 128.83, 134.60, 140.71; $[\alpha]_D^{24} = +12.4$ (*c* 1.68, $CHCl_3$, 57% ee) {lit. $[\alpha]_D^{20} = +29.5$ (*c* 1.04, $CHCl_3$, for the (*R*)-enantiomer with 92% ee)} HRMS(M+) calcd for $C_{12}H_{16}ClNOSi$: 253.0690; found: 253.0687 HPLC (DAICEL CHIRALCEL OJ-H, *i*PrOH/hexane = 0.25/99.75, flow = 0.25 mL/min) 19.6 and 20.9 min.

4.3.4. 2-Trimethylsilyloxy-2-(4-bromophenyl)propanenitrile. ^1H NMR ($CDCl_3$) δ 0.19 (s, 9H), 1.83 (s, 3H), 7.40–7.4 (m, 2H), 7.51–7.55 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 1.0, 33.4, 71.0, 121.1, 122.7, 126.3, 131.7, 141.2; $[\alpha]_D^{22} = +20.7$ (*c* 1.65, $CHCl_3$, 85% ee) HRMS(M+) calcd for $C_{12}H_{16}BrNOSi$: 297.0185; found: 297.0181 HPLC (DAICEL CHIRALCEL OB-H, ^{i}PrOH/hexane = 0.5/99.5, flow = 0.25 mL/min) 17.0 and 18.4 min.

4.3.5. 2-Trimethylsilyloxy-2-(4-fluorophenyl)propanenitrile. ^1H NMR ($CDCl_3$) δ 0.18 (s, 9H), 1.84 (s, 3H), 7.08 (m, 2H), 7.52 (m, 2H) ^{13}C NMR ($CDCl_3$) δ 1.0, 33.5, 71.0, 115.6, 121.4, 126.5, 138.0, 162.2 $[\alpha]_D^{22} = +15.3$ (*c* 1.4, $CHCl_3$, 60% ee) HPLC (DAICEL CHIRALCEL OB-H, ^{i}PrOH/hexen = 1/99, flow = 0.25 mL/min) 16.4 and 17.8 min.

4.3.6. 2-Trimethylsilyloxy-2-(3′-nitrophenyl)propanenitrile. ^1H NMR ($CDCl_3$) δ 0.22 (s, 9H), 1.86 (s, 3H), 7.34–7.55 (m, 4H aromatic H); HRMS(M+) calcd for $C_{12}H_{16}N_2O_3Si$: 264.0930; found: 264.0935 HPLC (DAICEL CHIRALCEL OJ-H, ^{i}PrOH/hexane = 0.5/99.5, flow = 1 mL/min) 32.6 and 34.4 min.

4.3.7. 2-Trimethylsilyloxy-2-(4′-nitrophenyl)propanenitrile. ^1H NMR ($CDCl_3$) δ 0.26 (s, 9H), 1.89 (s, 3H), 7.75 (d, 2H), 8.30 (d, 2H) ^{13}C NMR ($CDCl_3$) δ 1.0, 33.5, 71.0, 115.6, 121.4, 126.5, 138.0, 162.2 $[\alpha]_D^{22} = +8.1$ (*c* 1.62, $CHCl_3$, 50% ee) HRMS(M+) calcd for $C_{12}H_{16}N_2O_3Si$: 264.0930; found: 264.0933 HPLC (DAICEL CHIRALCEL OJ-H, ^{i}PrOH/hexane = 1/99, flow = 0.25 mL/min) 51.38 and 54.61 min.

4.3.8. 2-Trimethylsilyloxy-2-(4-methoxylphenyl)propanenitrile. ^1H NMR ($CDCl_3$) δ 0.1 (s, 9H), 1.73 (s, 1H), 2.71–2.93 (m, 2H), 3.75 (s, 3H), 6.76–7.23 (m, 4H); $[\alpha]_D^{20} = +18.2$ (*c* 1.5, $CHCl_3$, 82% ee) HRMS(M+) calcd for $C_{14}H_{21}NO_2Si$: 263.1342; found: 263.1345 HPLC (DAICEL CHIRALCEL OJ-H, ^{i}PrOH/hexane = 0.25/99.75, flow = 0.5 mL/min) 28.5 and 29.9 min.

4.3.9. 2-Trimethylsilyloxy-2-phenyl-3-methyl-butanenitrile. ^1H NMR ($CDCl_3$) δ 0.12 (s, 9H), δ 1.03 (q, $J = 7.4$Hz 6H), 1.97 (m, 1H), 7.38 (m, 3H), 7.50 (m, 2H); $[\alpha]_D^{20} = +23.1$ (*c* 2.1, $CHCl_3$, 57% ee) HRMS(M+) calcd for $C_{14}H_{21}NOSi$: 247.1392; found: 247.1395 HPLC (DAICEL CHIRALCEL OD, ^{i}PrOH/hexane = 0.25/99.75, flow = 0.25 mL/min) 19.1 and 21.0 min.

4.3.10. 2-Trimethylsilyloxy-3-(4-methoxyphenyl)-2-methylpropanenitrile. ^1H NMR ($CDCl_3$) δ 0.1 (s, 9H), 1.73 (s, 1H), 2.71–2.93 (m, 2H), 3.75 (s, 3H), 6.76–7.23 (m, 4H); HRMS(M+) calcd for $C_{14}H_{21}NO_2Si$: 263.1342; found: 263.1345 HPLC (DAICEL CHIRALCEL OJ-H, ^{i}PrOH/hexane = 0.25/99.75, flow = 0.5 mL/min) 28.5 and 29.9 min.

4.3.11. 2-Methyl-2-(trimethylsilyloxy)-3-(3,4-dichlorophenyl)-propanenitrile. ^1H NMR ($CDCl_3$) δ 0.15 (s, 9H), 1.59 (s, 3H), 2.93 (m, 2H), 7.11–7.43 (m, 3H); HRMS(M+) calcd for $C_{13}H_{17}Cl_2NOSi$: 301.0456 found: 301.0461 HPLC (DAICEL CHIRALCEL OJ-H, ^{i}PrOH/hexane = 1/99, flow = 0.25 mL/min) 27.1 and 34.3 min.

4.3.12. 2-Trimethylsilyloxy-2-benzyl-butanenitrile. ^1H NMR ($CDCl_3$) δ 0.1 (s, 9H), 1.1 (t, 3H), 1.79 (q, 2H), 2.99 (s, 2H), 7.25–7.36 (m, 5H); HRMS(M+) calcd for $C_{14}H_{21}NOSi$: 247.1392; found: 247.1398; HPLC (DAICEL CHIRALCEL

OB-H, ^{i}PrOH/hexane = 0.25/99.75, flow = 1 mL/min) 20.7 and 21.5 min.

4.3.13. 2-Trimethylsilyloxy-2-methyl-4-phenylbutanenitrile. ^{1}H NMR ($CDCl_3$) δ 0.27 (s, 9H), δ 1.61 (s, 3H), 2.02 (m, 2H), 2.78 (d, 2H) 2.87 (d, 2H), 7.19–7.22 (m, 3H), 7.28–7.3 (m, 2H); $[\alpha]_D^{20} = +9.2$ (*c* 1.8, $CHCl_3$, 60% ee) {lit. $[\alpha]_D^{24} = +13.3$ (*c* 1.15, $CHCl_3$, for the (*R*)-enantiomer with 81% ee)} HRMS(M+) calcd for $C_{14}H_{21}NOSi$: 247.1392; found: 247.1390 HPLC (DAICEL CHIRALCEL OJ-H, *i*PrOH/hexane = 0.25/99.75, flow = 0.25 mL/min) 30.6 and 42.1 min.

4.3.14. 1-(Trimethylsilyloxy)indane-1-carbonitrile. ^{1}H NMR ($CDCl_3$) δ 0.20 (s, 9H), 2.43–2.47 (m, 1H), 2.70–2.74 (m, 1H), 2.97–3.02 (m, 1H), 3.10–3.15 (m, 1H), 7.28 (d, 1H), 7.31 (t, 1H), 7.36 (t, 1H), 7.55 (d, 1H); $[\alpha]_D^{23} = +14.4$ (*c* 1.4, $CHCl_3$, 58% ee) HRMS(M+) calcd for $C_{13}H_{17}NOSi$: 231.1079; found: 231.1082 HPLC (DAICEL CHIRALCEL OD, ^{i}PrOH/hexane = 1/99, flow = 0.25 mL/min) 4.1 and 4.7 min.

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