Cyanosilylation of Aromatic Aldehydes by Cationic Ruthenium(II) Complexes of Benzimidazole-Derived O-Functionalized N-Heterocyclic Carbenes at Ambient Temperature under Solvent-Free Conditions

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ABSTRACT: A series of ruthenium complexes, namely, \( \{1-(N-R_1-2-acetamido)-3-(R_2)-benzimidazol-2-ylidene\}Ru(p-cymene)-Cl\]Cl, where \( R_1 = 2,6-(i-Pr)_2C_6H_4, R_2 = i-Pr (1c); R_1 = 2,6-(i-Pr)_2C_6H_4, R_2 = Et (2c); R_1 = 2,4,6-(CH_3)_3C_6H_2, R_2 = Et (3c) \), of benzimidazole-derived N/O-functionalized N-heterocyclic carbene ligands successfully carried out the cyanosilylation reaction of aromatic aldehydes and heteroaryl aldehydes with trimethylsilyl cyanide, providing good to excellent yields (ca. 60–95%) at room temperature under solvent-free condition. The ruthenium (1–3\( c \)) complexes were synthesized from the silver (1–3\( b \)) analogues in ca. 67–80% yields. The silver (1–3\( b \)) complexes exhibited an argentophilic \( d^{10} \cdots d^{10} \) interaction in its dinuclear macrometallacyclic motif, as observed by a short Ag····Ag contact of 3.1894(3) Å in single-crystal X-ray diffraction studies for a representative silver complex \( 1b \) and also in photoluminescence studies that showed characteristic emission band(s) at ca. 534–536 nm in the CHCl\(_3\) solution and at ca. 482–487 and 530–533 nm in the solid state.

INTRODUCTION

The cyanosilylation reaction is an important C–C bond-forming reaction that provides access to a variety of fine and specialty chemicals, including a wide range of multifunctionalized building blocks like \( \alpha \)-hydroxy acids, \( \beta \)-amino alcohols, and also the biologically active compounds.\(^1\) The reaction proceeds with the protection of a resulting alcohol functional moiety through the benzimidazole-derived N/O-functionalized N-heterocyclic carbene ligands, namely, 1-(\( N-R_1-2-acetamido \))-3-(\( R_2 \))-benzimidazol-2-ylidene \( \{R_1 = 2,6-(i-Pr)_2C_6H_4, R_2 = i-Pr (1c); R_1 = 2,6-(i-Pr)_2C_6H_4, R_2 = Et (2c); R_1 = 2,4,6-(CH_3)_3C_6H_2, R_2 = Et (3c) \} \) of benzimidazole-derived N/O-functionalized N-heterocyclic carbene ligands successfully carried out the cyanosilylation reaction of aromatic aldehydes and heteroaryl aldehydes with trimethylsilyl cyanide, providing good to excellent yields (ca. 60–95%) at room temperature under solvent-free conditions. The ruthenium (1–3\( c \)) complexes were prepared by following a transmetallation route from the silver (1–3\( b \)) analogues in ca. 67–80% yields. The silver (1–3\( b \)) complexes exhibited an argentophilic \( d^{10} \cdots d^{10} \) interaction in its dinuclear macrometallacyclic motif, as observed by a short Ag····Ag contact of 3.1894(3) Å in single-crystal X-ray diffraction studies for a representative silver complex \( 1b \) and also in photoluminescence studies that showed characteristic emission band(s) at ca. 534–536 nm in the CHCl\(_3\) solution and at ca. 482–487 and 530–533 nm in the solid state.

RESULTS AND DISCUSSION

Benzimidazole-derived N-heterocyclic ligands, namely, 1-(\( N-R_1-2-acetamido \))-3-(\( R_2 \))-benzimidazol-2-ylidene \( \{R_1 = 2,6-(i-Pr)_2C_6H_4, R_2 = i-Pr (1a); R_1 = 2,6-(i-Pr)_2C_6H_4, R_2 = Et (2a); R_1 = 2,4,6-(CH_3)_3C_6H_2, R_2 = Et (3a) \} \), were constructed by...
incorporation of N/O-functionalized side arms on the benzimidazole fragments. Specifically, the reaction of 2-chloro-N-R1-acetamide \[R_1 = 2,6-(i-Pr)_2C_6H_3, 2,4,6-(CH_3)_3C_6H_2\] with N-1-R2-benzimidazole \(R_2 = i-Pr, Et\) gave 1-(N-R1-2-acetamido)-3-(R2)-benzimidazolium chloride salts \(\text{1a} \rightarrow \text{3a}\) in ca. 71−79% yields. Subsequently, the reaction of the benzimidazolium chloride salts \(\text{1−3}\) with Ag2O in CH2Cl2 under the exclusion of light at ambient temperature resulted in the formation of corresponding Ag−NHC complexes \(\text{1−3}\) in ca. 88−95% yields. Quite expectedly, the characteristic Ag−Ccarbene resonances of the silver complexes \(\text{1−3}\) appeared highly downfield shift at ca. \(\delta 183.3−189.1\) ppm in the \(^{13}\)C\{1H\} NMR spectrum.

The molecular structure of a representative \(2b\) complex (Table 2 and Figure 2) has been determined by single-crystal X-ray diffraction studies that confirmed the dimeric macro metallacyclic nature of the silver complex of the type \(\{1-(N-R_1-2-acetamido)-3-(R_2)-benzimidazol-2-ylidine\}_2Ag\) \([R_1 = Et; R_2 = 2,6-(i-Pr)_2C_6H_3]\), similar to that observed earlier for the related silver analogues.\(^{49−51}\) The geometry around each of the two silver atoms was nearly linear \(\angle C(1)−Ag(1)−N(3)i = 168.61(8)°\) with the metal atom bound to amido−N at one end and to Ccarbene atom at the other end. The Ag−Ccarbene bond distance of 2.073(2) Å was slightly shorter than the sum of the individual covalent radii of C and Ag (2.18 Å)\(^{52}\) but compared well to that of the related analogues, namely, \(1-(R_3)-3-\{N-(2,6-di-(i)-propylphenylacetamido)-imidazol-2-ylidine\}_2Ag\) \([R_3 = i-Pr [2.066(8) Å], t-Bu [2.032(4) Å]\).\(^{49}\) Similarly, the Ag−Namido distance of 2.0898(18) Å too was observed to be shorter than the sum of the individual covalent radii of N and Ag (2.16 Å)\(^{52}\) and also comparable to that of the related complexes, \(1-(R_3)-3-\{N-(2,6-di-(i)-propylphenylacetamido)-imi-
The Ag--Ag distance of 3.1894(3) Å and the corresponding emissions at 534 nm in CHCl₃ and at 486 and 530 nm in the solid state at room temperature for the structurally characterized representative silver complex 2b compare well with the related structurally characterized dinuclear silver complexes, namely, 1-(R,R)-3-[N-(2,6-di-i-propylphenylacetamido)-imidazol-2-ylidine]₂Ag₂ [Rᵢ = i-Pr (emission at 647 nm in CHCl₃ and 635 nm in solid state at room temperature for a Ag--Ag distance of 3.550 Å), t-Bu (emission at 630 nm in CHCl₃ and 632 nm in solid state at room temperature for a Ag--Ag distance of 3.771 Å)], and other related complexes.⁵⁹,⁶⁴

Finally, the ruthenium complexes (1−3)c were obtained from silver complexes (1−3)b in ca. 67−80% yields by reaction with [RuCl₂(η-cymene)]₂ at room temperature. The ¹H NMR spectra of the (1−3)c complexes showed the amido−NH resonance at δ ca. 12.18−12.50 ppm, whereas the ¹³C{¹H} NMR spectra showed the characteristic Ru−C(carbene) resonance at δ ca. 187.6−189.1 ppm. Unlike the case of the benzimidazolium chloride salts (1−3)a and the silver (1−3)b complexes, for which the methylene (CH₂) resonances appeared as singlets at δ 5.96−6.05 and 5.28−5.36 ppm, respectively, the same for the ruthenium (1−3)c complexes appeared as diastereotopic doublets at δ 5.31 and 5.32 ppm (1c), δ 5.40 and 5.41 ppm (2c), and δ 5.18 and 5.02 ppm (3c), exhibiting two-bond (IH−IH) geminal coupling constants of 14−15 Hz in the ¹H NMR spectra. The IR spectra of the (1−3)c complexes showed the amido−CO stretching frequency at ca. 1624−1627 cm⁻¹, which is significantly at a lower energy with regard to the amido−CO stretching frequency of the free ligands, 1, a (1679 cm⁻¹), 2a (1679 cm⁻¹), and 3a (1690 cm⁻¹), and has been ascribed to the coordination of amido−O atom to the ruthenium center in the (1−3)c complexes, as observed earlier.⁵⁵

The molecular structures of all of the three (1−3)c complexes (Table 2 and Figures 5−7) have been determined by single-crystal X-ray diffraction studies, which showed these complexes exhibiting a conventional "piano stool" structure with the ruthenium center being bound to η²-p-cymene, η²-amido-functionalized N-heterocyclic carbene ligand and chloride atoms. The Ru−C(carbene) bond distances in 1c [2.0556(15) Å], 2c [2.0383(3) Å], and 3c [2.0410(18) Å] were slightly shorter than the sum of individual covalent radii of Ru and C atoms (2.19 Å) but compared well with other reported analogues, namely, [(1-(N-benzylacetamido)-3-(R,R)-imidazol-2-ylidine)Ru(p-cymene)Cl]Cl [Rᵢ = Me [2.0172(19) Å], i-Pr [2.033(5) Å], and CH₃Ph [2.0193(3) Å]⁵⁶ and [(1-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-(mesityl-imidazol-2-ylidine)Ru(p-cymene)Cl]PF₆ [2.0383(3) Å].⁵⁷ Likewise, the Ru−Cl bond distances in 1c [2.4041(4) Å], 2c [2.3907(8) Å], and 3c [2.4005(5) Å] were in agreement with the related complexes [(1-(N-benzylacetamido)-3-(R,R)-imidazol-2-ylidine)Ru(p-cymene)Cl]Cl [Rᵢ = Me [2.4256(14) Å], i-Pr [2.4325(8) Å], and CH₃Ph [2.4404(7) Å]]⁵⁶ and [(1-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-(mesityl-imidazol-2-ylidine)Ru(p-cymene)Cl]PF₆ [2.420(1) Å],⁵⁷ and the Ru−Oₐmid complex bond distances in 1c [2.1563(11) Å], 2c [2.148(2) Å], and 3c [2.1276(13) Å] with a related complex [(1-(N-benzylacetamido)-3-(pyridin-2-ylmethyl-imidazol-2-yliden)-Ru(CH₃CN)₃(PPh₃)](PF₆)₂ [2.143(4) Å].⁵⁷

Quite significantly, the ruthenium (1−3)c complexes carried out the cyanosilylation of ary aldehydes (eq 1) and heteroaryl aldehydes (eq 2) at room temperature under solvent-free conditions (Tables 3 and 4). Specifically, catalyst optimization

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**Table 1. Absorption and Emission Data for Compounds 1a, 1b, 2a, 2b, 3a, and 3b**

| Compounds | λₑmax. (nm) | λₑmax. (nm) in solution | λₑmax. (nm) in solid state |
|-----------|-------------|-------------------------|--------------------------|
| 1a        | 271 (4207)  | 302, 359                | 353                      |
| 1b        | 276 (8850)  | 302, 361, 535           | 388, 487, 533            |
| 2a        | 270 (3840)  | 360                     | 358                      |
| 2b        | 276 (10520) | 360, 534                | 386, 482, 530            |
| 3a        | 271 (4187)  | 354                     | 361                      |
| 3b        | 277 (9168)  | 316, 536                | 386, 487, 532            |

*Excited at 270 nm and the spectrum recorded in CHCl₃ at room temperature. *Excited at 270 nm and the spectrum recorded in solid state.
studies conducted on a representative pair of substrates, namely, benzaldehyde and trimethylsilyl cyanide (TMSCN), showed a maximum yield of 87% for the 1c complex after 6 h of reaction time at 2 mol % of catalyst loading. The control experiment, when performed with [Ru(p-cymene)Cl]2 at the identical 2 mol % of the ruthenium loading, produced the corresponding product 2-phenyl-2-(trimethylsilyloxy)-acetonitrile (4) in 30% yield under analogous reaction conditions and thereby upheld the amplification observed in the product yields (ca. 77–87%) in case of the (1−3)c complexes. The Hg drop experiment performed for the (1−3)c complexes showed nearly equal yields both in the presence and absence of Hg, thus indicating the homogeneous nature of catalysis. Substrate scope studies were subsequently performed for the ruthenium (1−3)c complexes for a variety of aryl aldehydes and heteroaryl aldehydes, namely, picolinaldehyde,
Table 2. X-ray Crystallographic Data of Ruthenium (1–3)c Complexes and Silver 2b Complex

|                  | 1c          | 2c          | 3c          | 2b          |
|------------------|-------------|-------------|-------------|-------------|
| lattice          | triclinic   | triclinic   | triclinic   | monoclinic  |
| empirical formula| C_{12}H_{16}Cl_{2}N_{4}Ru-CH_{3}CN | C_{12}H_{16}Cl_{2}N_{4}Ru-CH_{3}CN | C_{12}H_{16}Cl_{2}N_{4}Ru-CH_{3}CN | C_{12}H_{16}Ag_{4}N_{6}O_{2} |
| formula weight   | 724.75      | 789.04      | 803.65      | 940.70      |
| crystal size (mm³)| 0.139 × 0.132 × 0.186 | 0.245 × 0.115 × 0.089 | 0.203 × 0.093 × 0.083 | 0.396 × 0.296 × 0.230 |
| space group      | PT          | PT          | PT          | P2₁/n       |
| a (Å)            | 11.620(3)   | 11.04197(15)| 9.098(2)    | 9.8105(3)   |
| b (Å)            | 13.330(7)   | 13.336(3)   | 11.737(9)   | 15.9779(3)  |
| c (Å)            | 13.892(5)   | 13.4517(3)  | 14.695(6)   | 14.0138(4)  |
| α (deg)          | 62.692(3)   | 69.6572(18) | 109.236(19)| 90          |
| β (deg)          | 85.611(2)   | 83.3894(13)| 99.6774(18)| 106.163(3)  |
| γ (deg)          | 70.196(3)   | 82.6029(13)| 107.5084(18)| 90         |
| V (Å³)           | 1789.82(11)| 1836.58(6) | 1469.48(5)  | 2109.86(9)  |
| Z                | 2           | 2           | 2           | 2           |
| temperature (K)  | 293(2)      | 293(2)      | 293(2)      | 150(2)      |
| radiation (Å, Å) | 0.71073     | 0.71073     | 0.71073     | 0.71073     |
| µ (calcd) (g cm⁻³) | 1.345    | 1.427      | 1.459      | 1.481      |
| absorption coefficient (mm⁻¹) | 0.620 | 0.821 | 0.747 | 0.973 |
| θ range (deg)    | 2.245–24.999 | 2.596–24.999 | 2.323–24.993 | 2.601–24.998 |
| reflections collected | 45 279  | 27 452 | 15 201 | 12 562 |
| data/restraints/parameters | 6266/0/407 | 6219/18/405 | 5141/0/353 | 3631/0/258 |
| independent reflections [Rint] | 6266 [0.0396] | 6219 [0.0493] | 5141 [0.0377] | 3631 [0.0263] |
| completeness to θ = 25.000 | 99.5% | 96.2% | 99.3% | 97.6% |
| final R indices (I > 2σ) | R1 = 0.0222, wR2 = 0.0526 | R1 = 0.0418, wR2 = 0.1010 | R1 = 0.0248, wR2 = 0.0600 | R1 = 0.0272, wR2 = 0.0715 |
| R indices (all data) | R1 = 0.0243, wR2 = 0.0534 | R1 = 0.0459, wR2 = 0.1035 | R1 = 0.0293, wR2 = 0.0617 | R1 = 0.0287, wR2 = 0.0723 |
| GOF              | 1.045       | 1.037       | 1.044       | 1.056       |
| largest diff. peak and hole (eÅ⁻³) | 0.314 and −0.499 | 1.778 and −1.552 | 0.447 and −0.649 | 1.127 and −0.295 |

Figure 5. ORTEP of 1c ellipsoids are at 50% probability level. All hydrogen atoms (except H3) and co-crystallized CH₃CN have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)–C(1) 2.0356(15), Ru(1)–O(1) 2.1565(11), Ru(1)–Cl(1) 2.4041(4), O(1)–C(12) 1.2551(19), N(3)–C(12) 1.325(2), N(3)–H(3) 0.8600, N(2)–C(1) 1.356(2), N(2)–C(11) 1.4555(19), N(1)–C(1) 1.360(2), C(11)–C(12) 1.510(2), C(1)–Ru(1)–O(1) 85.12(5), C(1)–Ru(1)–Cl(1) 84.06(4), O(1)–Ru(1)–Cl(1) 83.28(3), C(12)–O(1)–Ru(1) 124.67(11), C(12)–N(3)–H(3) 116.7, C(1)–N(2)–C(11) 123.77(13), N(2)–C(1)–N(1) 106.20(13), N(2)–C(1)–C(12) 109.90(12), O(1)–C(12)–C(11) 121.09(13), O(1)–C(12)–N(3) 123.67(14), N(3)–C(12)–C(11) 115.24(13), N(2)–C(1)–Ru(1) 121.49(11), N(1)–C(1)–Ru(1) 131.87(11).

furfural, and thiophene-2-aldehyde substrates, which gave good to excellent product yields. Interestingly, the 1c complex, containing sterically demanding i-Pr group, gave better yields than the other two catalysts 2c and 3c.

It is important to compare the catalytic activity of the ruthenium (1–3)c complexes with the others reported in the literature. In the absence of any report on the use of a ruthenium N-heterocyclic complex in the cyanosilylation
reaction, the comparison is thus made with the structurally characterized examples of the transition-metal complexes of other ligands (Table 5). For example, for the cyanosilylation of benzaldehyde with TMSCN, a ruthenium complex, namely, [Ru(phgly)₂(binap)/Li₂CO₃ (phgly = phenylglycinate, binap = 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl), exhibited 98% of the product yield at −78 °C after 12 h of reaction time. Both of these ruthenium complexes thus exhibited superior activities to our ruthenium (1−3)c complexes that exhibited ca. 77−87% yields at room temperature after 6 h of reaction time at a higher 2 mol % of catalyst loadings. However, a vanadyl salen complex 7 displayed 94% of the product yield at −20 °C after 24 h of reaction time at a 5 mol % of catalyst loading. Another iron complex, [(Cp)₂Fe]PF₆, showed 94% of product yield at room temperature after 10 h of reaction time at a 2.5 mol % of catalyst loading under solvent-free condition.

■ CONCLUSIONS

In summary, a series of three new N/O-functionalized benzimidazole-2-ylidene-based cationic ruthenium (1−3)c complexes have been synthesized by employing the transmetallation route from their corresponding silver (1−3)b complexes in good yields. The silver (1−3)b complexes exhibited argentophilic d₁₀···d₁₀ interaction as observed by the emission band(s) at ca. 534−536 nm in the CHCl₃ solution and at ca. 482−487 and 530−533 nm in the solid state and also from the structural characterization of a representative silver complex 2b, which showed a short Ag···Ag contact of 3.1894(3) Å in its dimeric macrometallacyclic structure. Structural characterization of the ruthenium (1−3)c complexes revealed the chelation of the N-heterocyclic carbene ligand to the metal center through an Oamido sidearm moiety and a carbene moiety. Significantly enough, the ruthenium (1−3)c complexes efficiently carried out the cyanosilylation of various aryl aldehydes and heteroaryl aldehydes at room temperature under solvent-free condition in good to excellent yields. Out of the three complexes, the ruthenium 1c complex, containing sterically demanding i-Pr group, exhibited superior activity.

General equation for the cyanosilylation reaction of aryl aldehyde substrates catalyzed by ruthenium (1−3)c complexes

Figure 7. ORTEP of 3c ellipsoids are at 50% probability level. All hydrogen atoms (except H₃) and co-crystalized H₂O have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−C(1) 2.0410(18), Ru(1)−O(1) 2.1276(13), Ru(1)−Cl(1) 2.4005(5), O(1)−C(11) 1.252(2), N(2)−C(1) 1.357(2), N(2)−C(10) 1.455(2), N(3)−C(11) 1.316(2), N(3)−H(3) 0.8600, N(1)−C(1) 1.354(2), C(10)−C(11) 1.510(3), C(1)−Ru(1)−O(1) 84.84(6), C(1)−Ru(1)−Cl(1) 85.87(5), O(1)−Ru(1)−Cl(1) 83.62(4), C(11)−O(1)−Ru(1) 125.03(12), C(1)−N(2)−C(10) 124.38(15), C(11)−N(3)−C(12) 126.19(16), C(11)−N(3)−H(3) 116.9, N(2)−C(10)−C(11) 111.33(16), N(1)−C(1)−N(2) 105.89(15), N(2)−C(1)−Ru(1) 121.97(14), N(1)−C(1)−Ru(1) 132.14(14), O(1)−C(11)−N(3) 122.65(17), O(1)−C(11)−C(10) 121.85(17), N(3)−C(11)−C(10) 115.46(16).
General equation for the cyanosilylation reaction of heteroaryl aldehyde substrates catalyzed by ruthenium (1−3)c complexes

Table 3. Solvent-Free Cyanosilylation Reaction of Benzaldehyde and TMSCN Substrates Catalyzed by the Ruthenium (1−3)c Complexes

| S. No. | catalyst | time (hours) | yield (a) | yield (a) with Hg (%) |
|--------|----------|--------------|-----------|----------------------|
| 1      | (1e)     | 6            | 87        | 86                   |
| 2      | (2e)     | 6            | 81        | 80                   |
| 3      | (3e)     | 6            | 77        | 72                   |
| 4      | [Ru(p-cymene)Cl2] | 6            | 30        | –                    |

(a) Reaction condition: benzaldehyde (0.106 g, 1.00 mmol), TMSCN (0.297 g, 3.00 mmol), with 2 mol % of catalyst, except entry 4 (1 mol %). Reaction time: 6 h, room temperature (a) isolated yields.

EXPERIMENTAL SECTION

General Procedures. All of the experiments were performed using a glovebox and Schlenk techniques. Solvents were purified and degassed by standard procedures. 1-i-Propylbenzimidazole, 58 1-ethylbenzimidazole, 58 2-chloro-N-mesitylacetamide, 59 [Ru(p-cymene)Cl2]2, 60 and 2-chloro-N-(2,6-di-i-propylphenyl)acetamide 59 were synthesized according to the procedures reported in the literature. 1H NMR spectra and 13C[1H] NMR spectra were recorded on Bruker 400 and 500 MHz NMR spectrometers, respectively. The multiplicities of the 1H NMR peaks are assigned as singlet (s), doublet (d),
triplet (t), quartet (q) broad (br), triplet of triplets (tt), doublet of doublets (dd), multiplet (m), and septet (sept). A PerkinElmer Spectrum One FT-IR spectrometer was used for recording IR spectra. Mass spectrometry analysis was performed using Micromass Q-Tof and a Bruker Maxis Impact spectrometer. Elemental analysis data were obtained from the Elemental Analyzer Thermo Quest FLASH 1112 SERIES. The electronic spectra of compounds 1a, 1b, 2a, 2b, and 3a, 3b were recorded in CH$_3$Cl using a Varian Cary UV 100 spectrophotometer. Emission spectra of compounds 1a, 1b, 2a, 2b, and 3a, 3b were recorded in both CH$_3$Cl solution and solid state using a Varian Cary Eclipse spectrophotometer. Single-crystal X-ray diffraction study of compounds (1–3)c and 2b was conducted on a Rigaku Hg 724+ diffractometer, and crystal data collection and refinement parameters are summarized in Table 2. The structures were solved using direct methods and standard difference map techniques and were refined by full-matrix least-squares procedures on F$^2$ with SHELXTL (version 6.10).

| S.No | aryl aldehydes | product  | time (hrs) | (1e) yield$^a$ | (2e) yield$^a$ | (3e) yield$^a$ |
|------|----------------|----------|------------|---------------|---------------|---------------|
| 1    | C$_6$H$_5$CHO  | OTMS     | 6          | 87            | 81            | 77            |
| 2    | (4) C$_6$H$_5$CHO | OTMS     | 6          | 80            | 75            | 66            |
| 3    | (5) C$_6$H$_5$CHO | OTMS     | 6          | 77            | 66            | 69            |
| 4    | (6) MeO C$_6$H$_5$CHO | OTMS   | 6          | 76            | 74            | 73            |
| 5    | (7) MeO C$_6$H$_5$CHO | OTMS   | 6          | 81            | 76            | 75            |
| 6    | (8) MeO C$_6$H$_5$CHO | OTMS   | 6          | 77            | 67            | 60            |
| 7    | (9) MeO C$_6$H$_5$CHO | OTMS   | 6          | 95            | 94            | 92            |
| 8    | (10) N$_2$CHO   | OTMS     | 6          | 95            | 95            | 90            |
| 9    | (11) O$_2$CHO   | OTMS     | 6          | 75            | 72            | 75            |
| 10   | (12) S$_2$CHO   | OTMS     | 6          | 85            | 91            | 85            |

$^a$Reaction condition: Aryl aldehydes and heteroaryl aldehydes (1.00 mmol), TMSCN (0.297 g, 3.00 mmol), with 2 mol % of catalyst. Reaction time: 6 h, room temperature (a) isolated yield.
For the catalysis runs, gas chromatography–mass spectrometry (GC–MS) analyses were done using Agilent Technologies 7890A GC systems with 5975C inert XL EI/CI MSD Triple-Axis detector and the chiral GC resolutions were done using Agilent Technologies 7890A GC systems with CP-Chirasil-Dex CB chiral column.

Synthesis of 1-(N-(2,6-Di-i-propylphenyl)-2-acetamido)-3-(i-propyl)-benzimidazolium Chloride (1a). To a stirred solution of 1-i-propylbenzimidazole (1.00 g, 6.24 mmol) in CH₃CN (ca. 50 mL), 2-chloro-N-(2,6-di-i-propylphenyl)-acetamide (1.64 g, 6.48 mmol) was added and the reaction mixture was refluxed overnight. After the completion of reaction, all of the volatiles were removed in vacuo and the crude mass was washed repeatedly with petroleum ether to get the product 1a as a white solid (2.03 g, 79%). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ ppm, 11.10 (s, 1H, CH₂CON), 10.80 (s, 1H, NCH(CH₃)₂), 8.16 (d, 1H, J_H-H = 8 Hz, C₇H₅N₂), 7.71–7.69 (m, 1H, C₇H₅N₂), 7.63–7.61 (m, 2H, C₆H₃), 7.19 (t, 1H, J_H-H = 8 Hz, 2,6-{(CH₃)₂CH}₂C₆H₃), 7.06 (d, 2H, J_H-H = 8 Hz, 2,6-{(CH₃)₂CH}₂C₆H₃), 5.96 (br, 2H, CH₂CONH), 4.88 (sept, 1H, J_H-H = 7 Hz, NCH(CH₃)₂), 2.96 (sept, 2H, J_H-H = 6 Hz, 2,6-{(CH₃)₂CH}₂C₆H₃), 1.80 (d, 3H, J_H-H = 7 Hz, NCH(CH₃)₂), 1.79 (d, 3H, J_H-H = 7 Hz, NCH(CH₃)₂), 1.00 (d, 12H, J_H-H = 7 Hz, 2,6-{(CH₃)₂CH}₂C₆H₃). ¹³C NMR (CDCl₃, 100 MHz, 25 °C): 164.3 (CH₂CON), 145.8 (NCH(CH₃)₂), 141.6 (2,6-{(CH₃)₂CH}₂C₆H₃), 132.1 (C-H₃N₂), 131.2 (2,6-{(CH₃)₂CH}₂C₆H₃), 130.3 (C-H₃N₂), 128.0 (C-H₃N₂), 127.1 (2,6-{(CH₃)₂CH}₂C₆H₃), 123.1 (2,6-{(CH₃)₂CH}₂C₆H₃, 114.7 (C-H₃N₂), 112.9 (C-H₃N₂), 51.6

Table 5. Comparison of Cyanosilylation of Benzaldehyde with TMSCN in the Presence of Some of the Well-Known Structurally Characterized Catalysts

| S.No. | catalysts | loading (mol %) | solvent | time (hours) | yield |
|-------|-----------|-----------------|---------|--------------|-------|
| 1     | [Image 66x238 to 558x722] | 0.01 | Et₃O | 12 | 98% |
| 2     | [Image 66x238 to 558x722] | 0.01 | Et₃O | 6 | 99% |
| 3     | [Image 66x238 to 558x722] | 5 | CH₃CN | 24 | 94% |
| 4     | [Image 66x238 to 558x722] | 2.5 | – | 10 | 94% |
| 5     | [Image 66x238 to 558x722] | 3 | toluene | 6 | 87% |
| 6     | [Image 66x238 to 558x722] | 2 | – | 6 | 87% (our work) |
| 7     | [Image 66x238 to 558x722] | 2 | – | 6 | 81% (our work) |
| 8     | [Image 66x238 to 558x722] | 2 | – | 6 | 77% (our work) |
To a solution of 1-{N-(2,6-Di-i-propylphenyl)-2-acetamido}-3-(i-propyl)-benzimidazol-2-ylidine)Ag₂ (1b). To a solution of 1-{N-(2,6-di-i-propylphenyl)-2-acetamido}-3-(i-propyl)-benzimidazolium chloride (1a) (1.00 g, 2.41 mmol) in CH₂Cl₂ (ca. 50 mL), Ag₂O (0.583 g, 2.51 mmol) was added and the reaction mixture was stirred at room temperature under dark overnight. After the completion of reaction, the reaction mixture was passed through a pad of celite, the solvent was evaporated, and the obtained solid was dried in vacuo to get the product 1b as a gray solid (1.03 g, 88%).¹ H NMR (CDCl₃, 500 MHz, 25 °C): δ ppm, 8.18 (d, 1H, 3J_H-H = 8 Hz, C-H₅N₂), 7.48 (d, 1H, 3J_H-H = 8 Hz, C-H₅N₂), 7.35–7.33 (t, 2H, 3J_H-H = 5 Hz, C-H₅N₂), 6.99 (s, 3H, 2.6-{(CH₃)₂C₆H₃}C₆H₅), 5.36 (s, 2H, CH₂CON), 4.54 (sept, 1H, 3J_H-H = 7 Hz, NCH₂(CH₃)₂), 2.95 (br, 2H, 2.6-{(CH₃)₂C₆H₃}C₆H₅), 1.38 (d, 6H, 3J_H-H = 7 Hz, NCH₂(CH₃)₂), 0.967 (d, 6H, 3J_H-H = 7 Hz, 2.6-{(CH₃)₂C₆H₃}C₆H₅), 0.829 (br, 6H, 2.6-{(CH₃)₂C₆H₃}C₆H₅).¹³C{¹H} NMR (CDCl₃, 100 MHz, 25 °C): 183.3 (d, J_{Ag-C} = 170 Hz, Ag-NCN of C-H₅N₂), 168.5 (d, J_{C-N} = 10 Hz, CH₂CONHCO), 143.6 (2.6-{(CH₃)₂C₆H₃}C₆H₅), 142.5 (2.6-{(CH₃)₂C₆H₃}C₆H₅), 133.8 (2.6-{(CH₃)₂C₆H₃}C₆H₅), 133.7 (2.6-{(CH₃)₂C₆H₃}C₆H₅), 123.1 (2.6-{(CH₃)₂C₆H₃}C₆H₅), 124.7 (2.6-{(CH₃)₂C₆H₃}C₆H₅), 124.6 (2.6-{(CH₃)₂C₆H₃}C₆H₅), 124.2 (2.6-{(CH₃)₂C₆H₃}C₆H₅), 123.0 (2.6-{(CH₃)₂C₆H₃}C₆H₅), 119.5 (2.6-{(CH₃)₂C₆H₃}C₆H₅), 60.7 (2.6-{(CH₃)₂C₆H₃}C₆H₅), 52.9 (NCH₂(CH₃)₂), 28.1 (2.6-{(CH₃)₂C₆H₃}C₆H₅), 23.9 (2.6-{(CH₃)₂C₆H₃}C₆H₅), 23.7 (2.6-{(CH₃)₂C₆H₃}C₆H₅), 22.6 (NCH₂(CH₃)₂). IR data (cm⁻¹) KBr pellet: 3208 (w), 3057 (w), 2958 (s), 2865 (m), 1694 (m), 1595 (s), 1575 (s), 1475 (s), 1438 (s), 1389 (s), 1256 (m), 1169 (m), 1115 (w), 1088 (m), 1057 (w), 1015 (w), 990 (w), 934 (w), 887 (w), 865 (w), 796 (m), 745 (s), 647 (w), 556 (w). Low-resolution mass spectrometry (LRMS) (ESI): m/z 968.1596 [C₄H₄Ag₂N₂O₂⁺⁺], calcld 968.2876. Anal. calcld for C₄H₄Ag₂N₂O₂: C, 59.51; H, 6.24; N, 8.67; found: C, 59.12; H, 5.97; N, 8.30%.
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room temperature overnight. After completion of the reaction, the reaction mixture was stirred at room temperature under dark overnight. After the completion of reaction, the reaction mixture was passed through a pad of celite, the solvent was vacuum and the crude mass was washed repeatedly with CH2Cl2, 0.192 g, 76%). 1H NMR (CDCl3, 400 MHz, 25 °C): δ ppm, 8.14–8.11 (m, 1H, C=H=N2), 7.42 (d, 1H, JH=N = 9 Hz, C=H=N2), 7.41 (t, 2H, JH=H = 7 Hz, C6H=N2), 7.01 (s, 3H, 2,6-{(CH3)2C6}2C6H3), 5.29 (s, 2H, JH=H = 7 Hz, CH2CONH), 4.07 (q, 2H, JCH3=CH = 7 Hz, NCH2CH2N), 0.967 (br, 12H, 2,6-{(CH3)2C6}2C6H3). 13C{1H} NMR (CDCl3, 100 MHz, 25 °C): 186.3 (Ag–NCN of C=H=N2), 168.4 (CH2CONH), 143.6 (2,6-{(CH3)2C6}2C6H3), 135.0 (C=H=N2), 134.4 (2,6-{(CH3)2C6}2C6H3), 133.3 (C=H=N2), 124.7 (C=H=N2), 124.6 (2,6-{(CH3)2C6}2C6H3), 123.1 (2,6-{(CH3)2C6}2C6H3), 123.0 (2,6-{(CH3)2C6}2C6H3), 112.0 (2,6-{(CH3)2C6}2C6H3), 110.3 (C=H=N2), 109.8 (C=H=N2), 59.8 (CH2CONH), 42.3 (NCH2CH2N), 28.1 (2,6-{(CH3)2C6}2C6H3), 24.0 (2,6-{(CH3)2C6}2C6H3), 23.5 (2,6-{(CH3)2C6}2C6H3), 15.9 (NCH2CH2N). IR data (cm⁻¹) KBr pellet: 3196 (w), 3059 (w), 3030 (w), 2957 (m), 2866 (m), 1688 (w), 1601 (s), 1581 (s), 1478 (m), 1464 (m), 1436 (m), 1380 (m), 1239 (m), 1164 (w), 1085 (w), 1041 (w), 1015 (w), 989 (w), 936 (w), 860 (w), 796 (w), 747 (m), 649 (w), 562 (w), 516 (w). LRMS (ESI): m/z 633.3051 [C46H44AgN3O6Na⁺]⁺, calc 632.2460. Anal. calc. for C46H44AgN3O6Na+: C, 58.73; H, 6.00; N, 8.93; found: C, 58.46; H, 6.05; N, 8.76%.

Synthesis of [(1-N-(2,6-Di-i-propylphenyl)-2-acetamido)-3-(ethyldichloro) (2b) (0.150 g, 0.159 mmol) was taken in CH2CN (ca. 50 mL), to which Ru(p-cymene)Cl2 (0.192 g, 0.314 mmol) was added and the reaction mixture was stirred at room temperature overnight. After completion of the reaction, the reaction mixture was passed through a pad of celite and the filtrate was evaporated. The obtained crude mass was finally purified by column chromatography using silica gel as a stationary phase and eluting with MeOH/CH2Cl2 (5:95 v/v) to get the product 2c as a brown solid (0.170 g, 80%). 1H NMR (CDCl3, 400 MHz, 25 °C): δ ppm, 12.40 (s, 1H, CH2CONH), 8.12 (d, 1H, JH=H = 7 Hz, C=H=N2), 7.48–7.45 (m, 1H, C=H=N2), 7.36 (t, 2H, JH=H = 7 Hz, C=H=N2), 7.33 (t, 1H, JH=H = 5 Hz, 2,6-{(CH3)2C6}2C6H3), 7.08 (d, 2H, JH=H = 8 Hz, 2,6-{(CH3)2C6}2C6H3), 7.48 (d, 1H, JH=H = 7 Hz, (CH3)2C6H3), 5.41 (d, 1H, JH=H = 14 Hz, CH2CONH), 5.40 (d, 1H, JH=H = 14 Hz, CH2CONH), 5.27 (d, 2H, JH=H = 7 Hz, (CH3)2C6H3), 5.25 (sept, 1H, JH=H = 7 Hz, 2,6-{(CH3)2C6}2C6H3), 2.54 (sept, 1H, JH=H = 7 Hz, (CH3)2C6H3), 1.21 (d, 3H, JH=H = 6 Hz, (CH3)2C6H3). IR data (cm⁻¹) KBr pellet: 3445 (s), 3064 (w), 2956 (m), 2923 (m), 2869 (w), 1625 (s), 1466 (w), 1384 (m), 1341 (w), 1278 (w), 1242 (w), 1033 (m), 876 (w), 799 (w), 776 (w), 746 (m), 517 (w). LRMS (ESI): m/z 624.2135 [C45H42AgN3O6Cl⁺], calc 624.2138. Anal. calc. for C46H42AgN3O6Cl: C, 59.19; H, 6.47; N, 6.27; found: C, 58.81; H, 6.13; N, 6.39%.

Synthesis of (1-N-(2,4,6-Trime-thylphenyl)-2-acetamido)-3-(ethyldichloro) (3a). To a stirred solution of 1-ethylbenzimida zole (1.00 g, 6.84 mmol) in CH2CN (ca. 50 mL), 2-chloro-N-mesitylacetamide (1.45 g, 6.84 mmol) was added and the reaction mixture was refluxed overnight. After completion of the reaction, all of the volatiles were removed in vacuo and the crude mass was washed repeatedly with petroleum ether to get the product 3a as a white solid (1.87 g, 76%). 1H NMR (CDCl3, 500 MHz, 25 °C): δ ppm, 10.69 (s, 2H, CH2CONH and NCHN of C=H=N2), 8.08 (d, 1H, JH=H = 7 Hz, C=H=N2), 7.62 (d, 1H, JH=H = 8 Hz, C=H=N2), 7.59 (t, 2H, JH=H = 7 Hz, C=H=N2), 6.71 (s, 2H, 2,4,6-(CH3)2C6H3), 5.99 (s, 2H, CH2CONH), 4.44 (q, 2H, JCH3=CH = 7 Hz, NCH2CH3), 2.16 (s, 3H, 2,4,6-(CH3)2C6H3), 2.08 (s, 6H, 2,4,6-(CH3)2C6H3), 1.63 (t, 3H, JH=H = 7 Hz, NCH2CH3). 13C{1H} NMR (CDCl3, 100 MHz, 25 °C): 163.5 (CH2CONH), 142.8 (NCHN of C=H=N2), 136.5 (2,4,6-(CH3)2C6H3), 135.1 (2,4,6-(CH3)2C6H3), 134.9 (2,4,6-(CH3)2C6H3), 132.0 (C=H=N2), 131.1 (2,4,6-(CH3)2C6H3), 130.7 (C=H=N2), 128.9 (C=H=N2), 128.6 (2,4,6-(CH3)2C6H3), 127.4 (2,4,6-(CH3)2C6H3), 127.1 (C=H=N2), 114.4 (C=H=N2), 114.4 (C=H=N2).
Synthesis of 1-(N-(2,4,6-Trimethylphenyl)-2-acetamido)3-(ethyl)-benzimidazol-2-ylidine)Ag2 (3b). 1-(N-(2,4,6-Trimethylphenyl)-2-acetamido)-3-(ethyl)benzimidazolium chloride (3a) (0.500 g, 1.39 mmol) was dissolved in CH2Cl2 (ca. 50 mL), to which AgO (0.806 g, 3.49 mmol) was added and the reaction mixture was stirred at room temperature under dark overnight. After completion of the reaction, the reaction mixture was passed through a pad of celite, the solvent was evaporated, and the obtained solid was dried in vacuo to get the product 3b as a gray solid (0.565 g, 95%). 1H NMR (CDCl3, 400 MHz, 25 °C): δ ppm, 8.02-7.73 (m, 1H, C7H4N2), 7.41 (d, 1H, JH-H = 7 Hz, C7H4N2), 7.35 (t, 2H, JH-H = 7 Hz, C6H2), 6.68 (s, 2H, 2,4,6-(CH3)3C6H2), 5.28 (s, 2H, CH2CON), 4.23-4.18 (m, 2H, NCH2CH3), 2.14 (s, 3H, 2,4,6-(CH3)3C6H2), 2.00 (s, 6H, 2,4,6-(CH3)3C6H2), 1.54 (t, 3H, JH-H = 7 Hz, NCH2CH3). 13C(td) NMR (CDCl3, 100 MHz, 25 °C): 189.1 (Ag–N(NCN) of C7H4N2), 171.1 (CH2CON), 134.7 (2,4,6-(CH3)3C6H2), 133.4 (2,4,6-(CH3)3C6H2), 126.3 (2,4,6-(CH3)3C6H2), 126.6 (C7H4N2), 122.4 (2,4,6-(CH3)3C6H2), 124.2 (2,4,6-(CH3)3C6H2), 124.0 (CH2CON), 123.7 (C6H2), 111.5 (C7H4N2), 110.8 (C7H4N2), 62.3 (CH2CON), 44.6 (2,4,6-(CH3)3C6H2), 18.6 (2,4,6-(CH3)3C6H2), 16.1 (CH2CH2). IR data (cm−1) KBr pellet: 3446 (m), 3190 (m), 2969 (s), 2919 (s), 2854 (m), 1386 (m), 1302 (w), 1232 (m), 1123 (w), 1041 (s), 960 (m), 846 (m), 808 (s), 746 (s), 719 (s), 655 (s), 619 (w), 572 (w), 555 (m), 496 (s), 474 (w), 445 (m), 426 (s), 400 (m), 355 (s). HRMS (ESI): m/z 856.7491 [C44H41Ag,N2O2]+, calculated 856.6660.

General Procedure of Photoluminescence Studies. Using a Varian Cary Eclipse spectrophotometer, emission spectra of compounds 1a, 1b, 2a, 2b, and 3a, 3b were recorded in CH3CN solution (0.001 M) at 25 °C upon excitation at 270 nm in quartz cuvettes. The solid-state experiment was performed for the respective compounds 1a, 1b, 2a, 2b, and 3a, 3b by mixing with NaCl in the ratio of 1:100 and then grinding the mixture to a powder before recording the emission spectra at 25 °C upon excitation at 270 nm in quartz glass slab.

General Procedure for Cyanosilylation of Aldehydes Using Ruthenium (1–3) Complexes. Ruthenium (1–3) complexes (0.02 mmol, 2 mol %), aryl aldehyde substrate (1.00 mmol), and TMSCN (3 mmol) were mixed, and the resultant solution was stirred for 6 h at room temperature. All volatiles were then removed in vacuo, and the crude product was purified by column chromatography using neutral Al2O3 as a stationary phase and eluting with petroleum ether/EtOAc (99:1–70:30 v/v) to give the cyano-silylated product (4–13).

Procedure for the Control Experiment Using [Ru(p-cymene)]Cl2. A mixture of [Ru(p-cymene)]Cl2 (0.010 mmol, 1 mol %), benzaldehyde substrate (1.00 mmol), and TMSCN (3 mmol) was stirred for 6 h at room temperature. All volatiles were then removed in vacuo, and the crude product was purified by column chromatography using neutral Al2O3 as a stationary phase and eluting with petroleum ether/EtOAc (99:1–70:30 v/v) to give the desired cyano-silylated product 4 as a colorless liquid (yield: 0.060 g, 30%).

Synthesis of 2-Phenyl-2-(trimethylsilyloxy)acetanitride (4). 2-Phenyl-2-(trimethylsilyloxy)acetanitride (4)

Ruthenium (1–3) complexes (0.020 mmol, 2 mol %), benzaldehyde (1.00 mmol), and TMSCN (3.0 mmol) were
mixed, and the resultant solution was stirred for 6 h at room temperature. All volatiles were then removed in vacuo, and the crude product was purified by column chromatography using neutral Al₂O₃ as a stationary phase and eluting with petroleum ether/EtOAc (99:1 v/v) to give the desired cyanoisylated product 5 as a colorless liquid.

Yields: 0.178 g, 87% (1c); 0.166 g, 81% (2c); 0.157 g, 77% (3c).

¹H NMR (CDCl₃, 500 MHz, 25 °C): δ 7.92–7.54 (m, 1H, C₆H₅), 7.47–7.46 (m, 1H, C₆H₅), 7.44–7.42 (m, 1H, C₆H₅), 7.41–7.39 (m, 1H, C₆H₅), 5.49 (s, 1H, CH₂), 2.33 (s, 9H, O-Si(CH₃)₃). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 25 °C): δ 151.0 (C), 129.5 (C₆H₅), 121.9 (C₆H₅), 112.6 (C₆H₅), 63.9 (CH), −0.06 (O-Si(CH₃)₃). Anal. calcd for C₁₂H_{17}NO₂Si: C, 61.24; H, 7.28; N, 0.06. GC–MS (ESI): m/z = 205 [M]+. GC [CP-Chiral-Dex CB, column temperature = 110 °C (isothermal), injector temperature = 230 °C, detector temperature = 250 °C]: tᵣ = 39.3 min, tᵣ = 38.3 min. 

Synthesis of 2-(4-Methylbenzylidene)-2-((trimethylsilyl)oxy)acetophenone (5).

Ruthenium (1–3)c complexes (0.020 mmol, 2 mol %), 4-methylvanldehyde (1.00 mmol), and TMSCN (3.00 mmol) were mixed, and the resultant solution was stirred for 6 h at room temperature. All volatiles were then removed in vacuo, and the crude product was purified by column chromatography using neutral Al₂O₃ as a stationary phase and eluting with petroleum ether/EtOAc (99:1 v/v) to give the desired cyanoisylated product 5 as a colorless liquid.

Yields: 0.175 g, 80% (1c); 0.164 g, 75% (2c); 0.145 g, 66% (3c).

¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 7.35 (d, 2H, J₉-H = 8 Hz, 4-(CH₃)₂C₆H₄), 7.21 (d, 2H, J₉-H = 8 Hz, 4-(CH₃)₂C₆H₄), 5.46 (s, 1H, CH₂), 2.37 (s, 3H, 4-(CH₃)₂C₆H₄), 0.222 (s, 9H, O-Si(CH₃)₃). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 25 °C): δ 138.6 (CN), 133.6 (4-(CH₃)₂C₆H₄), 129.8 (4-(CH₃)₂C₆H₄), 126.6 (4-(CH₃)₂C₆H₄), 118.5 (4-(CH₃)₂C₆H₄), 63.8 (CH), 21.4 (4-(CH₃)₂C₆H₄), −0.05 (O-Si(CH₃)₃). Anal. calcd for C₁₂H₁₆NO₂Si: C, 68.3; H, 5.2; N, 0.1. GC–MS (ESI): m/z = 219 [M]+. GC [CP-Chiral-Dex CB, column temperature = 95 °C (isothermal), injector temperature = 250 °C, detector temperature = 280 °C]: tᵣ = 118.6 min, tᵣ = 122.0 min. 

Synthesis of 2-(2,5-Dimethoxyphenyl)-2-((trimethylsilyl)oxy)acetophenone (6).

Ruthenium (1–3)c complexes (0.020 mmol, 2 mol %), 4-methoxybenzaldehyde (1.00 mmol), and TMSCN (3.00 mmol) were mixed, and the resultant solution was stirred for 6 h at room temperature. All volatiles were then removed in vacuo, and the crude product was purified by column chromatography using neutral Al₂O₃ as a stationary phase and eluting with petroleum ether/EtOAc (99:1 v/v) to give the desired cyanoisylated product 6 as a colorless liquid.

Yields: 0.180 g, 77% (1c); 0.155 g, 66% (2c); 0.162 g, 69% (3c).

¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 7.32 (t, 1H, J₉-H = 8 Hz, 4-(CH₃)₂C₆H₄), 7.04–7.01 (m, 2H, 3-(CH₃O)C₆H₅), 6.93–6.90 (m, 1H, 3-(CH₃O)C₆H₅), 5.46 (s, 1H, CH₂), 3.83 (s, 3H, 3-(CH₃O)C₆H₅), 0.236 (s, 9H, O-Si(CH₃)₃). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 25 °C): δ 160.2 (CN), 137.9 (3-(CH₃O)C₆H₅), 130.2 (3-(CH₃O)C₆H₅), 119.3 (3-(CH₃O)C₆H₅), 118.7 (3-(CH₃O)C₆H₅), 115.1 (3-(CH₃O)C₆H₅), 112.1 (3-(CH₃O)C₆H₅), 63.7 (CH), 55.5 (3-(CH₃O)C₆H₅), −0.06 (O-Si(CH₃)₃). Anal. calcd for C₁₂H₁₇NO₂Si: C, 61.24; H, 7.28; N, 5.95; found: C, 61.23; H, 6.91; N, 5.80%. GC–MS (ESI): m/z = 235 [M]+. GC [CP-Chiral-Dex CB, column temperature = 100 °C (isothermal), injector temperature = 230 °C, detector temperature = 250 °C]: tᵣ = 259.7 min, tᵣ = 264.7 min. 

Synthesis of 2-(2,5-Dimethoxyphenyl)-2-((trimethylsilyl)oxy)acetophenone (6).
Ruthenium (1–3)c complexes (0.020 mmol, 2 mol %), 2,4,5-trimethoxybenzaldehyde (1.00 mmol), and TMSCN (3.00 mmol) were mixed, and the resultant solution was stirred for 6 h at room temperature. All volatiles were then removed in vacuo, and the crude product was purified by column chromatography using neutral Al2O3 as a stationary phase and eluting with petroleum ether/EtOAc (70:30 v/v) to give the desired cyanosilylated product 10 as a colorless liquid.

Yields: 0.280 g, 95% (1c); 0.271 g, 92% (3c).

1H NMR (CDCl3, 500 MHz, 25 °C): δ 7.11 (s, 1H, C6H3), 6.50 (s, 1H, 2,4,5-(CH3O)3C6H2), 5.79 (s, 1H, C6H2), 3.90 (s, 3H, 2,4,5-(CH3O)3C6H2), 3.87 (s, 3H, 2,4,5-(CH3O)3C6H2), 3.85 (s, 3H, 2,4,5-(CH3O)3C6H2), 0.212 (s, 9H, O–Si(CH3)3). Anal. calcd for C14H21NO4Si: C, 56.92; H, 7.17; N, 4.55%. GC–MS (ESI): m/z = 295 [M]+. GC [CP-Chiral-Rex-Dex CB, column temperature = 125 °C (isothermal), inject temperature = 160 °C, detector temperature = 200 °C]; tR = 330.4 min. 

Synthesis of 2-(Pyridin-2-yl)-2-((trimethylsilyl)oxy)acetonitrile (11).

Ruthenium (1–3)c complexes (0.020 mmol, 2 mol %), picolinaldehyde (1.00 mmol), and TMSCN (3.00 mmol) were mixed, and the resultant solution was stirred for 6 h at room temperature. All volatiles were then removed in vacuo, and the crude product was purified by column chromatography using neutral Al2O3 as a stationary phase and eluting with petroleum ether/EtOAc (80:20 v/v) to give the desired cyanosilylated product 11 as a colorless liquid.

Yields: 0.196 g, 95% (1c); 0.185 g, 90% (3c).

1H NMR (CDCl3, 500 MHz, 25 °C): δ 8.59 (s, 1H, C6H4N), 7.79 (t, 1H, C6H4N), 7.59 (d, 1H, C6H4N), 7.31–7.28 (m, 1H, C6H4N), 5.88 (s, 1H, C6H2), 0.258 (s, 9H, O–Si(CH3)3). Anal. calcd for C14H21NO4Si: C, 49.64; H, 7.17; N, 3.29%. GC–MS (ESI): m/z = 206 [M]+. GC [CP-Chiral-Rex-Dex CB, column temperature = 120 °C (isothermal), inject temperature = 160 °C, detector temperature = 200 °C]; tR = 30.5 min.

Synthesis of 2-(Furan-2-yl)-2-((trimethylsilyl)oxy)acetonitrile (12).

Yields: 0.215 g, 81% (1c); 0.201 g, 76% (2c); 0.199 g, 75% (3c).

1H NMR (CDCl3, 500 MHz, 25 °C): δ 7.61 (d, 1H, JH-H = 7 Hz, 3,4-(CH3O)2C6H3), 6.97 (d, 1H, JH-H = 7 Hz, 3,4-(CH3O)2C6H3), 6.87–6.85 (m, 1H, 3,4-(CH3O)3C6H2), 5.42 (s, 1H, C6H2), 3.90 (s, 3H, 3,4-(CH3O)3C6H2), 3.88 (s, 3H, 3,4-(CH3O)3C6H2), 0.212 (s, 9H, O–Si(CH3)3). Anal. calcd for C15H23NO4Si: C, 54.16; H, 6.74; N, 3.98%. GC–MS (ESI): m/z = 265 [M]+. GC [CP-Chiral-Rex-Dex CB, column temperature = 100 °C (isothermal), inject temperature = 230 °C, detector temperature = 250 °C]; tR = 195.4 min, tR = 200.1 min.

Synthesis of 2-(2,4,5-Trimethoxyphenyl)-2-((trimethylsilyl)oxy)acetonitrile (10).
Ruthenium (1–3)c complexes (0.020 mmol, 2 mol %), furan-2-carbaldehyde (1.00 mmol), and TMSCN (3.00 mmol) were mixed, and the resultant solution was stirred for 6 h at room temperature. All volatiles were then removed in vacuo, and the crude product was purified by column chromatography using neutral Al2O3 as a stationary phase and eluting with petroleum ether/EtOAc (90:10 v/v) to give the desired cyanosilylated product 12 as a colorless liquid.

Yields: 0.146 g, 75% (1c); 0.140 g, 72% (2c); 0.146 g, 75% (3c).

1H NMR (CDCl3, 500 MHz, 25 °C): δ 7.46–7.45 (m, 1H, C4H3O), 5.64 (d, 1H, J3–H = 3 Hz, C4H3O), 6.40–6.39 (m, 1H, C4H3O), 5.53 (s, 1H, CH), 0.197 (s, 9H, O–Si(CH3)3). 13C{1H} NMR (CDCl3, 100 MHz, 25 °C): δ 148.5 (CN), 144.1 (C4H3O), 117.3 (C4H3O), 111.0 (C4H3O), 109.3 (C4H3O), 57.7 (CH3), 10.0 (O–Si(CH3)3). Anal. calc. for C9H13NO2Si: C, 48.00; H, 5.89; N, 7.08%. GC–MS (EI): m/z = 211 [M]+. GC [CP-Chirasil-Dex CB, column temperature = 120 °C (isothermal), injector temperature = 160 °C, detector temperature = 200 °C]: tR = 11.4 min, tR = 12.3 min.

Synthesis of 2-(Thiophen-2-yl)-2-[(trimethylsilyloxy)acenonitrile (13).

Ruthenium (1–3)c complexes (0.020 mmol, 2 mol %), thiophene-2-carbaldehyde (1.00 mmol), and TMSCN (3.00 mmol) were mixed, and the resultant solution was stirred for 6 h at room temperature. All volatiles were then removed in vacuo, and the crude product was purified by column chromatography using neutral Al2O3 as a stationary phase and eluting with petroleum ether/EtOAc (90:10 v/v) to give the desired cyanosilylated product 13 as a colorless liquid.

Yields: 0.179 g, 85% (1c); 0.192 g, 91% (2c); 0.179 g, 85% (3c).

1H NMR (CDCl3, 500 MHz, 25 °C): δ 7.36–7.34 (dd, 1H, J3–H = 7 Hz, J4–H = 2 Hz, C4H3S), 7.19 (tt, 1H, J3–H = 5 Hz, J4–H = 1 Hz, C4H3S), 7.01–6.99 (m, 1H, C4H3S), 5.73 (s, 1H, CH), 0.236 (s, 9H, O–Si(CH3)3). 13C{1H} NMR (CDCl3, 100 MHz, 25 °C): δ 139.7 (CN), 127.4 (C4H3S), 127.1 (C4H3S), 126.5 (C4H3S), 118.5 (C4H3S), 59.7 (CH3), −0.11 (O–Si(CH3)3). Anal. calc. for C18H11NO2Si(C4H3O): C, 47.48; H, 4.16; N, 7.83%. GC–MS (EI): m/z = 298 [M]+. GC [CP-Chirasil-Dex CB, column temperature = 120 °C (isothermal), injector temperature = 160 °C, detector temperature = 200 °C]: tR = 25.6 min, tR = 27.4 min.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b02090.

1H NMR, 13C{1H} NMR, IR, HRMS, CHNS, data of the compounds (1–3)a, (1–3)b, and (1–3)c, GC and GC–MS of the catalyst products 4–13; absorbance and emission data of the compounds (1–3)a and (1–3)b (PDF)

X-ray crystallographic data of the ruthenium (1–3)c complexes and silver 2b; CCDC 1524131 (1c), 1536819 (2c), 1524134 (3c), and 1524130 (2b) (CIF)

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Notes

The authors declare no competing financial interest.

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