Supporting Information

Catalytic Addition of Terminal Alkynes to Carbodiimides by Half-Sandwich Rare Earth Metal Complexes

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Experimental Section

General Methods. All reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an MBRAUN glovebox. The argon was purified by being passed through a Dryclean column (4Å molecular sieves, Nikka Seiko Co.) and a Gasclean GC-XR column (Nikka Seiko Co.). The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an $\text{O}_2/\text{H}_2\text{O}$ Combi-Analyzer (MBRAUN) to ensure both were always below 1 ppm. IR spectra were obtained on a Shimadzu IRPrestige-21 spectrophotometer using Nujol mulls between KBr disks. HRMS were recorded on a JEOL JMS-700 instrument operated in EF-FAB⁺ mode. Samples for NMR spectroscopic measurements were prepared in the glovebox by use of J. Young valve NMR tubes (Wilmad 528-JY). ^1H and ^{13}C NMR spectra were recorded on a JEOL-AL400 spectrometer (FT, 400 MHz for ^1H ; 100 MHz for ^{13}C) or a JNM-AL300 spectrometer (FT, 300 MHz for ^1H ; 75 MHz for ^{13}C). Solvents were distilled from sodium/benzophenone ketyl, degassed by the freeze-pump-thaw method (three times), and dried over fresh Na chips in the glovebox. $\{\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{NPh})\}\text{Y}(\text{CH}_2\text{SiMe}_3)(\text{THF})_2$ **1a**, $\{\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^i\text{Bu})\}\text{Y}(\text{CH}_2\text{SiMe}_3)(\text{THF})_2$ **1b**, $\{\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{NPh})\}\text{Yb}(\text{CH}_2\text{SiMe}_3)(\text{THF})_2$ **1c** and $\{\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{NC}_6\text{H}_2\text{Me}_3-2,4,6)\}\text{Lu}(\text{CH}_2\text{SiMe}_3)(\text{THF})$ **1d** were synthesized according to literature (Nishiura, M.; Hou, Z.; Wakatsuki, Y.; Yamaki, T.; Miyamoto, T. *J. Am. Chem. Soc.* **2003**, *125*, 1184).

Synthesis of complex $[\{\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{NPh})\}\text{Y}(\mu\text{-C}\equiv\text{CPh})(\text{THF})]_2$ (2**).**

(i) NMR Tube Reaction. In the glovebox, a J. Young valve NMR tube was charged with **1a** (59 mg, 0.1 mmol), toluene- d_8 (0.45 mL), phenylacetylene (10 mg, 0.1 mmol). The reaction was immediately monitored by ^1H NMR spectroscopy and 1,3,5-trimethylbenzene used as an internal standard. The corresponding phenylacetylide complex **2** was formed in almost quantitative NMR yield.

(ii) Preparative Scale Reaction. In the glovebox, a toluene solution (3 mL) of phenylacetylene (51 mg, 0.497 mmol) was added to a toluene solution (2 mL) of **1a** (293 mg, 0.497 mmol) in a flask. After 1 minute, the solvent was removed under reduced pressure. Then the residue was extracted with toluene/hexane (1/1) and filtered to give a clean solution. After removing the solvent under vacuum, the residue was recrystallized in toluene/hexane to provide light yellow solid **2** (254 mg, 0.239 mmol, 96% yield). IR (Nujol, cm^{-1}): $\nu = 2027, 1585, 1481, 1454, 1377, 1283, 1248, 1179, 1013, 920, 831, 800, 756, 691$. ^1H NMR (400 MHz, C_6D_6): δ 0.71 (s, 12H, SiCH_3), 1.18 (br, 8H, $\beta\text{-CH}_2$, THF), 2.22 (s, 12H, C_5Me_4), 2.31 (s, 12H, C_5Me_4), 3.90 (br, 8H, $\alpha\text{-CH}_2$, THF), 6.79 (t, $J = 7.2$ Hz, 2H, C_6H_5), 6.88-6.95 (m, 6H, C_6H_5), 6.99 (d, $J = 8.0$ Hz, 4H, C_6H_5), 7.19 (d, $J = 8.0$ Hz, 4H, C_6H_5), 7.28-7.31 (m, 4H, C_6H_5); ^{13}C NMR (100 MHz, C_6D_6): δ 4.7, 12.7, 14.9, 25.5, 72.4, 107.4, 115.5, 120.7, 123.2, 124.9, 127.9, 128.3, 128.5, 129.3, 129.4, 132.9, 138.7 (t, $J_{\text{Y-C}} = 22.5$ Hz), 156.7.

Synthesis of complex $\{\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{NPh})\}\text{Y}(\text{THF})\{\text{t-BuNC}(\text{C}\equiv\text{CPh})\text{Nt-Bu}\}$ (3**):** In the glovebox, a THF solution (3 mL) of phenylacetylene (42 mg, 0.412 mmol) was added to a THF solution (2 mL) of **1a** (243 mg, 0.412 mmol) in a Schlenk tube. Then 1,3-di-*tert*-butylcarbodiimide (64 mg, 0.412 mmol) was added to the above reaction mixture. The Schlenk tube was taken outside and the mixture was stirred at 80 °C for 0.5 h. After the solvent was removed under reduced pressure, the residue was extracted with hexane and filtered to give a clean solution. The solution volume was reduced under vacuum to precipitate **3** as light yellow crystalline powder (266 mg, 0.387 mmol, 94% yield). Single crystals of **3**·1.5THF suitable for X-ray analysis were grown in THF/hexane at -30 °C overnight. IR (Nujol, cm^{-1}): $\nu = 2205, 1585, 1491, 1452, 1425, 1379, 1287, 1200, 1074, 926, 760$. ^1H NMR (300 MHz, C_6D_6): δ 0.98 (s, 6H, SiCH_3), 1.26 (br, 4H, $\beta\text{-CH}_2$, THF), 1.57 (s, 18H, *t*-Bu), 2.21 (s, 6H, C_5Me_4), 2.42 (s, 6H, C_5Me_4), 3.61 (br, 4H, $\alpha\text{-CH}_2$, THF), 6.71 (t, $J = 7.2$ Hz, 1H, C_6H_5), 6.83 (d, $J = 7.5$ Hz, 2H, C_6H_5), 6.97-6.99 (m, 3H, C_6H_5), 7.16-7.22 (m, 2H, C_6H_5), 7.44-7.47 (m, 2H, C_6H_5); ^1H NMR (400 MHz, THF- d_8): δ 0.59 (s, 6H, SiCH_3), 1.40 (s, 18H, *t*-Bu), 2.06 (s, 6H, C_5Me_4), 2.20 (s, 6H, C_5Me_4), 6.31 (t, $J = 7.2$ Hz, 1H, C_6H_5), 6.48 (d, $J = 7.6$ Hz, 2H, C_6H_5), 6.85 (t, $J = 8.0$ Hz, 2H, C_6H_5), 7.36-7.38 (m, 3H, C_6H_5), 7.48-7.51 (m, 2H, C_6H_5); ^{13}C NMR (100 MHz, THF- d_8): δ 5.3, 12.9, 15.5, 26.6, 32.0, 53.4, 68.4, 85.3, 100.8, 108.8, 115.3, 120.9, 123.0, 124.3, 126.7 (d, $J_{\text{Y-C}} = 1.7$ Hz), 129.0, 129.6, 130.5, 131.6, 156.9, 159.4 (d, $J_{\text{Y-C}} = 1.7$ Hz).

NMR tube reaction of the amidinate **3 with phenylacetylene:** A mixture of **3** (79 mg, 0.1 mmol) and phenylacetylene (10 mg, 0.1 mmol) in toluene- d_8 was added to an NMR tube in a glovebox. The reaction was monitored by ^1H NMR spectroscopy. No change was observed at room temperature for a long time. Then the reaction was heated to 80 °C. After 1 h, the ^1H NMR shift for terminal hydrogen of phenylacetylene completely disappeared and $\text{t-BuN}=\text{C}(\text{CPh})\text{NHt-Bu}$ (**4b**) and **2** were formed almost quantitatively.

¹H NMR spectra of the mixture of **3** and phenylacetylene

¹H NMR spectra for the reaction of **3** with phenylacetylene at 80 °C for 1 h. ¹H NMR shift of terminal hydrogen for phenylacetylene completely disappeared.

Typical Procedures for Catalytic Cross-Coupling of Carbodiimides with Terminal Alkynes:

(i) NMR Tube Reaction by Use of Complex 1a as a Catalyst. In the glovebox, a J. Young valve NMR tube was charged with **1a** (6 mg, 0.01 mmol), THF- d_8 (0.45 mL), phenylacetylene (36 mg, 0.35 mmol), 1,3-diisopropylcarbodiimide (43 mg, 0.34 mmol). The tube was taken outside and heated to 80 °C in an oil bath. Formation of **4a** and disappearance of phenylacetylene were easily monitored by ^1H NMR. The conversion of phenylacetylene was determined by ^1H NMR using 1,3,5-trimethylbenzene as an internal standard. The reaction was completed in 1 h. No other coupling products were observed.

(ii) Preparative Scale Reaction by Use of Complex 1a as a Catalyst. In the glovebox, a THF solution (3 mL) of phenylacetylene (210 mg, 2.07 mmol) was added to a THF solution (2 mL) of **1a** (36 mg, 0.06 mmol) in a Schlenk tube. Then 1,3-diisopropylcarbodiimide (255 mg, 2.01 mmol) was added to the above reaction mixture. The Schlenk tube was taken outside and the mixture was stirred at 80 °C for 1 h. After the solvent was removed under reduced pressure, the residue was extracted with hexane and filtered to give a clean solution. After removing the solvent under vacuum, the residue was recrystallized in hexane to provide a colorless solid **4a**.

It should be noted that this type of amidine, which contains a conjugated C–C triple bond, is very sensitive to moisture, and must be stored under a moisture-free atmosphere. Upon exposure to the air, **4a** was hydrolyzed to the amide compound $\text{PhC}\equiv\text{CCONH}^i\text{Pr}$ (**4a'**).

(E)-N,N'-diisopropyl-3-phenylpropiolamidine (4a): colorless solid, isolated yield, 98%. IR (Nujol, cm^{-1}): ν = 3439 (N–H), 2218 ($\text{C}\equiv\text{C}$), 1609 ($\text{C}=\text{N}$). ^1H NMR (400 MHz, CDCl_3): δ 1.15–1.19 (m, 12H, CH_3), 3.90–3.95 (m, 1H, NCH), 4.00–4.08 (m, 2H, NHCH_2 , NH), 7.33–7.38 (m, 3H, C_6H_5), 7.48–7.51 (m, 2H, C_6H_5); ^{13}C NMR (100 MHz, CDCl_3): δ 23.1, 24.7, 43.1, 52.3, 79.2, 91.5, 121.3, 128.2, 129.1, 131.7, 141.0. ^1H NMR (400 MHz, C_6D_6): δ 1.00 (d, J = 6.0 Hz, 6H, $\text{NCH}(\text{CH}_3)_2$), 1.40 (d, J = 6.0 Hz, 6H, $\text{NHCH}(\text{CH}_3)_2$), 3.79 (s, 1H, NH), 4.22–4.29 (m, 2H, CH), 6.96–6.98 (m, 3H), 7.38–7.40 (m, 2H); ^{13}C NMR (100 MHz, C_6D_6): δ 22.8, 25.6, 42.8, 53.3, 80.9, 90.3, 122.2, 128.7, 129.3, 132.1, 140.0. HRMS Calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{15}\text{H}_{21}\text{N}_2$ 229.1705, Found 229.1720.

A comparison experiment--an attempt to prepare the amidine 4a by use of a lithium reagent (cf. Fujita, H.; Endo, R.; Aoyama, A.; Ichii, T. *Bull. Chem. Soc. Jpn.* **1972**, 45, 1846): Under an atmosphere of nitrogen, to a THF solution (5 mL) of phenylacetylene (204 mg, 2.00 mmol) was added *n*-BuLi (2 mmol) at –30 °C in a Schlenk tube and the reaction mixture was allowed to warm to room temperature and then stirred for 1 h. 1,3-Diisopropylcarbodiimide (252 mg, 2.00 mmol) was added to the above reaction mixture. After stirring for 1 h, the reaction mixture was quenched with ice water or saturated NH_4Cl solution and immediately extracted with hexane (10×3). The combined organic layers were dried over MgSO_4 , filtered, and concentrated in vacuum to give the amide $\text{PhC}\equiv\text{CCONH}^i\text{Pr}$ (**4a'**) as a colorless solid. Isolated yield, 92%. IR (Nujol, cm^{-1}): ν = 3363 (N–H), 2225 ($\text{C}\equiv\text{C}$), 1587 ($\text{C}=\text{O}$). ^1H NMR (300 MHz, CDCl_3): δ 1.01 (d, J = 6.6 Hz, 6H, CH_3), 3.79–3.86 (m, 1H, CH), 3.93 (br, 1H, NH), 7.20 (br, 3H, C_6H_5), 7.31–7.35 (m, 2H, C_6H_5); ^{13}C NMR (75 MHz, CDCl_3): δ 23.8, 47.7, 79.3, 91.6, 121.4, 128.4, 129.2, 131.9, 141.2. HRMS Calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{12}\text{H}_{14}\text{NO}$ 188.1075, Found 188.1070. These data showed unambiguously the structure of the amide compound $\text{PhC}\equiv\text{CCONH}^i\text{Pr}$ (**4a'**). No reaction was observed between phenylacetylene and the in-situ generated lithium amidinate species.

(E)-N,N'-di-tert-butyl-3-phenylpropiolamidine (4b): light orange solid, isolated yield, 94%. IR (Nujol, cm^{-1}): ν = 3437 (N–H), 2210 ($\text{C}\equiv\text{C}$), 1620 ($\text{C}=\text{N}$). ^1H NMR (300 MHz, C_6D_6): δ 1.28 (s, 9H, $\text{NC}(\text{CH}_3)_3$), 1.51 (s, 9H, $\text{NHC}(\text{CH}_3)_3$), 3.89 (s, 1H, NH), 6.91–6.94 (m, 3H, C_6H_5), 7.29–7.32 (m, 2H, C_6H_5); ^{13}C NMR (75 MHz, C_6D_6): δ 29.0, 31.1, 51.7, 53.3, 84.1, 89.1, 122.3, 128.8, 129.3, 131.6, 137.4. HRMS Calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{17}\text{H}_{25}\text{N}_2$ 257.2018, Found 257.2028.

(E)-N,N'-dicyclohexyl-3-phenylpropiolamidine (4c): colorless solid, isolated yield, 95%. IR (Nujol, cm^{-1}): ν = 3439 (N–H), 2218 ($\text{C}\equiv\text{C}$), 1611 ($\text{C}=\text{N}$). ^1H NMR (300 MHz, C_6D_6): δ 0.89–2.07 (m, 20H, Cy), 3.91–4.06 (m, 3H, NH and CH), 6.94–6.96 (m, 3H, C_6H_5), 7.41–7.44 (m, 2H, C_6H_5); ^{13}C NMR (100 MHz, C_6D_6): δ 25.5, 25.7, 26.4, 26.7, 33.5, 36.0, 49.9, 61.5, 81.2, 90.4, 122.2, 128.7, 129.3, 132.2, 140.1. HRMS Calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{21}\text{H}_{29}\text{N}_2$ 309.2331, Found 309.2303.

(E)-N,N'-di-tert-butyl-3-*p*-tolylpropiolamidine (4d): light yellow crystals, isolated yield, 94%. IR (Nujol, cm^{-1}): ν = 3437 (N–H), 2210 ($\text{C}\equiv\text{C}$), 1620 ($\text{C}=\text{N}$). ^1H NMR (400 MHz, C_6D_6): δ 1.36 (s, 9H, $\text{NC}(\text{CH}_3)_3$), 1.61 (s, 9H, $\text{NHC}(\text{CH}_3)_3$), 1.98 (s, 3H, *p*-Me C_6H_4), 3.96 (s, 1H, NH), 6.80 (d, J = 8.4 Hz, 2H, *m*- C_6H_4), 7.34 (d, J = 8.4 Hz, 2H, *o*- C_6H_4); ^{13}C NMR (100 MHz, C_6D_6): δ 21.5, 29.2, 31.3, 51.9, 53.5, 83.8, 89.5, 119.4, 129.6, 131.6, 137.6, 139.5. HRMS Calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{18}\text{H}_{27}\text{N}_2$ 271.2174, Found 271.2180.

(E)-N,N'-dicyclohexyl-3-(4-(trifluoromethyl)phenyl)propiolamidine (4e): light yellow solid, isolated yield,

96%. IR (Nujol, cm^{-1}): $\nu = 3439$ (N–H), 2220 ($\text{C}\equiv\text{C}$), 1611 ($\text{C}=\text{N}$). ^1H NMR (300 MHz, C_6D_6): δ 0.91–2.01 (m, 20H, Cy), 3.84–4.00 (m, 3H, NH and CH), 7.12 (d, $J = 8.7$ Hz, 2H, *o*- C_6H_4), 7.17 (d, $J = 8.7$ Hz, 2H, *m*- C_6H_4); ^{13}C NMR (75 MHz, C_6D_6): δ 25.2, 25.4, 26.2, 26.4, 33.2, 35.8, 49.8, 61.4, 82.9, 88.4, 124.4 (q, $J_{\text{C-F}} = 270.1$ Hz), 125.6 (q, $J_{\text{C-CCF}} = 3.8$ Hz), 127.9, 130.8 (q, $J_{\text{C-CF}} = 32.8$ Hz), 132.3, 139.4. HRMS Calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{22}\text{H}_{28}\text{F}_3\text{N}_2$ 377.2205, Found 377.2223.

(E)-N,N'-diisopropyl-3-(4-methoxyphenyl)popiolamidine (4f): light yellow solid, isolated yield, 96%. IR (Nujol, cm^{-1}): $\nu = 3439$ (N–H), 2214 ($\text{C}\equiv\text{C}$), 1614 ($\text{C}=\text{N}$). ^1H NMR (400 MHz, C_6D_6): δ 1.02 (d, $J = 6.8$ Hz, 6H, $\text{NCH}(\text{CH}_3)_2$), 1.42 (d, $J = 6.0$ Hz, 6H, $\text{NHCH}(\text{CH}_3)_2$), 3.19 (s, 3H, Me), 3.84 (s, 1H, NH), 4.25–4.31 (m, 2H, CH), 6.59 (d, $J = 8.8$ Hz, 2H, *m*- C_6H_4), 7.37 (d, $J = 8.8$ Hz, 2H, *o*- C_6H_4); ^{13}C NMR (100 MHz, C_6D_6): δ 22.9, 25.7, 42.7, 53.2, 54.9, 79.9, 90.7, 114.1, 114.5, 133.8, 140.4, 160.7. HRMS Calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{16}\text{H}_{23}\text{N}_2\text{O}$ 259.1810, Found 259.1831.

(E)-N,N'-di-tert-butyl-3-(4-chlorophenyl)popiolamidine (4g): light yellow crystals, isolated yield, 95%. IR (Nujol, cm^{-1}): $\nu = 3437$ (N–H), 2214 ($\text{C}\equiv\text{C}$), 1618 ($\text{C}=\text{N}$). ^1H NMR (400 MHz, C_6D_6): δ 1.36 (s, 9H, $\text{NC}(\text{CH}_3)_3$), 1.59 (s, 9H, $\text{NHC}(\text{CH}_3)_3$), 3.89 (s, 1H, NH), 6.86 (d, $J = 8.8$ Hz, 2H, *m*- C_6H_4), 7.02 (d, $J = 8.8$ Hz, 2H, *o*- C_6H_4); ^{13}C NMR (100 MHz, C_6D_6): δ 29.1, 31.2, 52.0, 53.5, 84.9, 87.9, 120.6, 129.1, 132.8, 135.5, 137.0. HRMS Calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{17}\text{H}_{24}\text{ClN}_2$ 291.1628, Found 291.1638.

(E)-3-(4-bromophenyl)-N,N'-diisopropylpopiolamidine (4h): light yellow solid, isolated yield, 93%. IR (Nujol, cm^{-1}): $\nu = 3339$ (N–H), 2218 ($\text{C}\equiv\text{C}$), 1614 ($\text{C}=\text{N}$). ^1H NMR (400 MHz, C_6D_6): δ 0.99 (d, $J = 6.4$ Hz, 6H, $\text{NCH}(\text{CH}_3)_2$), 1.39 (d, $J = 6.4$ Hz, 6H, $\text{NHCH}(\text{CH}_3)_2$), 3.72 (s, 1H, NH), 4.16–4.25 (m, 2H, CH), 6.96 (d, $J = 8.4$ Hz, 2H, *m*- C_6H_4), 7.06 (d, $J = 8.4$ Hz, 2H, *o*- C_6H_4); ^{13}C NMR (100 MHz, C_6D_6): δ 22.8, 25.6, 42.8, 53.3, 81.8, 89.1, 120.8, 123.8, 132.0, 133.4, 139.7. HRMS Calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{15}\text{H}_{20}^{79}\text{BrN}_2$ 307.0810, Found 307.0794.

(E)-3-(2-chlorophenyl)-N,N'-diisopropylpopiolamidine (4i): light red crystals, isolated yield, 97%. IR (Nujol, cm^{-1}): $\nu = 3439$ (N–H), 2222 ($\text{C}\equiv\text{C}$), 1614 ($\text{C}=\text{N}$). ^1H NMR (400 MHz, C_6D_6): δ 0.98 (d, $J = 6.8$ Hz, 6H, $\text{NCH}(\text{CH}_3)_2$), 1.42 (d, $J = 6.4$ Hz, 6H, $\text{NHCH}(\text{CH}_3)_2$), 3.84 (s, 1H, NH), 4.20–4.28 (m, 1H, NCH), 4.31–4.37 (m, 1H, NHCH), 6.65–6.68 (m, 2H, C_6H_4), 7.02–7.04 (m, 1H, C_6H_4), 7.23–7.26 (m, 1H, C_6H_4); ^{13}C NMR (100 MHz, C_6D_6): δ 22.8, 25.6, 42.9, 53.3, 85.7, 86.9, 122.2, 126.6, 129.6, 130.3, 133.8, 136.5, 139.7. HRMS Calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{15}\text{H}_{20}\text{ClN}_2$ 263.1315, Found 263.1316.

(E)-3-(2-bromophenyl)-N,N'-diisopropylpropiolamidine (4j): light red solid, isolated yield, 94%. IR (Nujol, cm^{-1}): $\nu = 3439$ (N–H), 2220 ($\text{C}\equiv\text{C}$), 1614 ($\text{C}=\text{N}$). ^1H NMR (400 MHz, C_6D_6): δ 1.00 (d, $J = 5.6$ Hz, 6H, $\text{NCH}(\text{CH}_3)_2$), 1.42 (d, $J = 5.2$ Hz, 6H, $\text{NHCH}(\text{CH}_3)_2$), 3.86 (s, 1H, NH), 4.23–4.26 (m, 1H, NCH), 4.34–4.37 (m, 1H, NHCH), 6.56–6.61 (m, 1H, C_6H_4), 6.69–6.73 (m, 1H, C_6H_4), 7.22–7.25 (m, 2H, C_6H_4); ^{13}C NMR (100 MHz, C_6D_6): δ 22.9, 25.7, 42.9, 53.3, 85.0, 88.6, 124.4, 126.0, 127.2, 130.4, 132.8, 133.9, 139.7. HRMS Calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{15}\text{H}_{20}^{79}\text{BrN}_2$ 307.0810, Found 307.0809.

(E)-N,N'-diisopropyl-3-o-tolylpropiolamidine (4k): colorless crystals, isolated yield, 97%. IR (Nujol, cm^{-1}): $\nu = 3439$ (N–H), 2214 ($\text{C}\equiv\text{C}$), 1614 ($\text{C}=\text{N}$). ^1H NMR (400 MHz, C_6D_6): δ 1.01 (d, $J = 6.8$ Hz, 6H, $\text{NCH}(\text{CH}_3)_2$), 1.40 (d, $J = 6.4$ Hz, 6H, $\text{NHCH}(\text{CH}_3)_2$), 2.34 (s, 3H, Me), 3.87 (s, 1H, NH), 4.22–4.27 (m, 2H, CH), 6.88–6.93 (m, 2H, C_6H_4), 6.97–7.01 (m, 1H, C_6H_4), 7.43–7.44 (m, 1H, C_6H_4); ^{13}C NMR (100 MHz, C_6D_6): δ 21.0, 22.9, 25.6, 42.9, 53.3, 84.6, 89.4, 122.0, 126.0, 129.4, 129.9, 132.6, 140.3, 140.8. HRMS Calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{16}\text{H}_{23}\text{N}_2$ 243.1861, Found 243.1881.

(E)-N,N'-diisopropyl-3-m-tolylpropiolamidine (4l): colorless crystals, isolated yield, 97%. IR (Nujol, cm^{-1}): $\nu = 3439$ (N–H), 2218 ($\text{C}\equiv\text{C}$), 1614 ($\text{C}=\text{N}$). ^1H NMR (400 MHz, C_6D_6): δ 1.00 (d, $J = 6.8$ Hz, 6H, $\text{NCH}(\text{CH}_3)_2$), 1.42 (d, $J = 6.4$ Hz, 6H, $\text{NHCH}(\text{CH}_3)_2$), 1.96 (s, 3H, Me), 3.80 (s, 1H, NH), 4.24–4.33 (m, 2H, CH), 6.83–6.95 (m, 2H, C_6H_4), 7.27 (br, 1H, C_6H_4), 7.30 (s, 1H, C_6H_4); ^{13}C NMR (100 MHz, C_6D_6): δ 21.2, 22.9, 25.6, 42.8, 53.3, 80.6, 90.6, 122.0, 128.7, 129.3, 130.2, 132.8, 138.4, 140.1. HRMS Calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{16}\text{H}_{23}\text{N}_2$ 243.1861, Found 243.1860.

(E)-3-(4-fluoro-3-methylphenyl)-N,N'-diisopropylpropiolamidine (4m): colorless crystals, isolated yield, 95%. IR (Nujol, cm^{-1}): $\nu = 3439$ (N–H), 2214 ($\text{C}\equiv\text{C}$), 1616 ($\text{C}=\text{N}$). ^1H NMR (400 MHz, C_6D_6): δ 1.02 (d, $J = 6.4$ Hz, 6H, $\text{NCH}(\text{CH}_3)_2$), 1.42 (d, $J = 6.4$ Hz, 6H, $\text{NHCH}(\text{CH}_3)_2$), 1.87 (s, 3H, Me), 3.80 (s, 1H, NH), 4.23–4.28 (m, 2H, CH), 6.59–6.63 (m, 1H, C_6H_3), 7.05–7.10 (m, 2H, C_6H_3); ^{13}C NMR (100 MHz, C_6D_6): δ 14.3 (d, $J_{\text{C-CCF}} = 3.3$ Hz), 22.9, 25.6, 42.8, 53.3, 80.3, 89.6, 115.7 (d, $J_{\text{C-CF}} = 23.9$ Hz), 117.8 (d, $J_{\text{C-CCCF}} = 3.3$ Hz), 125.8 (d, $J_{\text{C-CF}} = 18.2$ Hz), 131.6 (d, $J_{\text{C-CCF}} = 8.2$ Hz), 135.4 (d, $J_{\text{C-CCF}} = 5.8$ Hz), 140.0, 161.9 (d, $J_{\text{C-F}} = 250.5$ Hz). HRMS Calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{16}\text{H}_{22}\text{FN}_2$ 261.1767, Found 261.1787.

(E)-N,N'-diisopropyl-3-(pyridin-3-yl)propiolamidine (4n): yellow crystals, isolated yield, 98%. IR (Nujol, cm^{-1}): $\nu = 3242$ (N–H), 2216 ($\text{C}\equiv\text{C}$), 1595 ($\text{C}=\text{N}$). ^1H NMR (400 MHz, C_6D_6): δ 1.02 (d, $J = 6.4$ Hz, 6H, $\text{NCH}(\text{CH}_3)_2$), 1.38 (d, $J = 6.4$ Hz, 6H, $\text{NHCH}(\text{CH}_3)_2$), 4.03 (s, 1H, NH), 4.12–4.19 (m, 1H, NCH), 4.20–4.28 (m, 1H, NHCH), 6.50–6.53 (m, 1H, 3-Py), 7.22–7.25 (m, 1H, 3-Py), 8.32–8.33 (m, 1H, 3-Py), 8.80 (s, 1H, 3-Py); ^{13}C NMR (100 MHz, C_6D_6): δ 22.8, 25.6, 42.8, 53.3, 83.6, 87.0, 118.9, 123.0, 138.3, 139.5, 149.7, 152.7. HRMS Calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{14}\text{H}_{20}\text{N}_3$ 230.1657, Found 230.1662.

(E)-N,N'-dicyclohexyl-3-(pyridin-2-yl)propiolamidine (4o): light red solid, isolated yield, 98%. IR (Nujol, cm^{-1}): $\nu = 3269$ (N–H), 2227 ($\text{C}\equiv\text{C}$), 1600 ($\text{C}=\text{N}$). ^1H NMR (400 MHz, C_6D_6): δ 0.87–2.04 (m, 20H, Cy), 3.95–4.02 (m, 3H, NH and CH), 6.50–6.54 (m, 1H, 2-Py), 6.85–6.90 (m, 1H, 2-Py), 7.13–7.16 (m, 1H, 2-Py), 8.36–8.38 (m, 1H, 2-Py); ^{13}C NMR (100 MHz, C_6D_6): δ 25.4, 25.5, 26.3, 26.6, 33.2, 35.9, 49.8, 61.4, 79.8, 89.5, 123.2, 127.6, 135.6, 139.4, 142.8, 150.5. HRMS Calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{20}\text{H}_{28}\text{N}_3$ 310.2283, Found 310.2249.

(E)-N,N'-diisopropyloct-2-ynamidinium (4p): colorless oil, isolated yield, 70%. IR (Nujol, cm^{-1}): $\nu = 3438$ (N–H), 2217 ($\text{C}\equiv\text{C}$), 1613 ($\text{C}=\text{N}$). ^1H NMR (300 MHz, C_6D_6): δ 0.74 (t, $J = 7.2$ Hz, 3H, CH_3), 0.91 (d, $J = 6.6$ Hz, 6H, $\text{NCH}(\text{CH}_3)_2$), 1.03–1.24 (m, 4H, CH_2), 1.30 (d, $J = 6.3$ Hz, 6H, $\text{NHCH}(\text{CH}_3)_2$), 1.30–1.36 (m, 2H, CH_2), 1.98 (t, $J = 7.2$ Hz, 2H, CH_2), 3.67 (br, 1H, NH), 4.03–4.16 (m, 2H, CH); ^{13}C NMR (75 MHz, C_6D_6): δ 14.0, 18.9, 22.7, 25.4, 26.6, 28.3, 31.2, 42.5, 52.9, 73.0, 91.7, 140.5. HRMS Calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{14}\text{H}_{27}\text{N}_2$ 223.2174, Found 223.2178.

X-ray Crystallographic Studies.

Crystals for X-ray analyses were obtained as described in the preparations. The crystals were manipulated in the glovebox under a microscope and were sealed in thin-walled glass capillaries. Data collections were performed at -110 °C on a Bruker CCD APEX diffractometer with a CCD area detector, using graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71069$ Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. These structures were solved by use of SHELXTL program. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data, processing parameters, and structural data of **3**, **4g** and **4i** are given below.

STable 1. Crystal data and structure refinement for **3**·1.5THF

Identification code	3	
Empirical formula	C ₄₄ H ₆₆ N ₃ O _{2.5} Si Y	
Formula weight	794.00	
Temperature	173(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 42.83(2) Å	α = 90°.
	b = 9.935(5) Å	β = 99.994(10)°.
	c = 20.393(12) Å	γ = 90°.
Volume	8546(8) Å ³	
Z	8	
Density (calculated)	1.234 Mg/m ³	
Absorption coefficient	1.432 mm ⁻¹	
F(000)	3392	
Crystal size	0.65 x 0.35 x 0.15 mm ³	
Theta range for data collection	1.93 to 25.14°	
Index ranges	-50 ≤ h ≤ 50, -10 ≤ k ≤ 11, -24 ≤ l ≤ 17	
Reflections collected	19974	
Independent reflections	7493 [R(int) = 0.0525]	
Completeness to theta = 25.14°	98.0 %	
Absorption correction	Empirical	
Max. and min. transmission	0.86 and 0.50	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7493 / 0 / 439	
Goodness-of-fit on F ²	1.003	
Final R indices [I > 2σ(I)]	R1 = 0.0576, wR2 = 0.1670	
R indices (all data)	R1 = 0.0987, wR2 = 0.1820	
Largest diff. peak and hole	0.946 and -1.019 e.Å ⁻³	

STable 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 3·1.5THF. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Y(1)	922(1)	2374(1)	936(1)	34(1)
Si(1)	788(1)	1031(2)	2277(1)	42(1)
N(1)	1052(1)	3353(5)	-55(2)	39(1)
N(2)	1314(1)	1522(5)	381(2)	41(1)
N(3)	1099(1)	1843(5)	2028(2)	37(1)
O(1)	1027(1)	4609(4)	1363(2)	48(1)
O(2)	0	6209(15)	2500	184(5)
O(3)	2025(2)	6052(9)	738(4)	183(3)
C(1)	1269(1)	2430(6)	-102(3)	37(1)
C(2)	1448(2)	2405(6)	-643(3)	45(2)
C(3)	1613(2)	2363(6)	-1051(3)	45(2)
C(4)	1818(1)	2294(6)	-1530(3)	43(2)
C(5)	2003(2)	3390(7)	-1635(4)	62(2)
C(6)	2202(2)	3305(10)	-2093(4)	77(2)
C(7)	2214(2)	2120(11)	-2446(4)	81(3)
C(8)	2041(2)	1054(9)	-2328(4)	68(2)
C(9)	1844(2)	1135(7)	-1886(3)	56(2)
C(10)	1549(2)	388(6)	425(3)	47(2)
C(11)	1459(2)	-574(7)	-168(4)	76(2)
C(12)	1885(2)	878(8)	482(4)	67(2)
C(13)	1517(2)	-396(7)	1051(3)	60(2)
C(14)	946(1)	4391(6)	-567(3)	42(2)
C(15)	791(2)	3727(7)	-1222(3)	61(2)
C(16)	1214(2)	5329(7)	-684(3)	55(2)
C(17)	696(2)	5244(7)	-315(3)	54(2)
C(18)	516(1)	1039(6)	1459(3)	40(2)
C(19)	566(1)	190(6)	910(3)	42(2)
C(20)	437(2)	825(7)	317(3)	48(2)
C(21)	296(2)	2037(7)	464(3)	49(2)
C(22)	342(1)	2171(6)	1162(3)	44(2)
C(23)	698(2)	-1228(6)	967(3)	56(2)
C(24)	413(2)	241(8)	-383(3)	71(2)
C(25)	77(2)	2886(8)	-24(4)	75(2)
C(26)	202(2)	3299(7)	1498(4)	63(2)
C(27)	609(2)	1891(8)	2940(4)	65(2)
C(28)	905(2)	-668(7)	2632(3)	58(2)
C(29)	1386(2)	2174(6)	2408(3)	38(1)
C(30)	1450(2)	2169(6)	3103(3)	43(2)
C(31)	1737(2)	2554(6)	3460(3)	53(2)
C(32)	1979(2)	2937(7)	3145(4)	57(2)
C(33)	1924(2)	2965(7)	2460(4)	59(2)
C(34)	1640(1)	2584(6)	2109(3)	46(2)
C(35)	946(2)	5126(7)	1973(3)	56(2)
C(36)	1235(2)	5720(7)	2347(3)	65(2)
C(37)	1429(2)	6093(7)	1824(3)	64(2)
C(38)	1268(2)	5506(7)	1204(3)	59(2)
C(39)	95(2)	7069(8)	2004(4)	75(2)
C(40)	-4(2)	8417(8)	2137(4)	79(2)
C(41)	2106(3)	4655(13)	796(7)	179(5)
C(42)	2350(4)	4398(16)	435(7)	191(6)
C(43)	2409(3)	5690(14)	212(6)	186(5)
C(44)	2271(3)	6608(14)	653(7)	178(5)

H(5)	1993	4180	-1396	75
H(6)	2328	4035	-2166	92
H(7)	2343	2065	-2768	98
H(8)	2058	252	-2555	82
H(9)	1722	390	-1818	67
H(11A)	1239	-819	-208	114
H(11B)	1588	-1368	-97	114
H(11C)	1493	-135	-569	114
H(12A)	1910	1335	79	101
H(12B)	2027	125	551	101
H(12C)	1932	1488	851	101
H(13A)	1577	168	1435	91
H(13B)	1652	-1173	1087	91
H(13C)	1301	-678	1028	91
H(15A)	944	3170	-1386	92
H(15B)	718	4411	-1545	92
H(15C)	616	3185	-1146	92
H(16A)	1314	5707	-267	82
H(16B)	1129	6040	-980	82
H(16C)	1367	4830	-877	82
H(17A)	526	4677	-231	81
H(17B)	615	5904	-645	81
H(17C)	790	5690	89	81
H(23A)	538	-1839	1062	85
H(23B)	878	-1265	1321	85
H(23C)	762	-1479	556	85
H(24A)	568	-457	-380	106
H(24B)	450	939	-685	106
H(24C)	204	-126	-523	106
H(25A)	144	2858	-450	113
H(25B)	83	3799	132	113
H(25C)	-135	2544	-67	113
H(26A)	246	4138	1300	94
H(26B)	292	3306	1963	94
H(26C)	-24	3178	1448	94
H(27A)	731	1685	3369	98
H(27B)	395	1582	2921	98
H(27C)	609	2846	2869	98
H(28A)	1080	-1001	2446	87
H(28B)	729	-1274	2526	87
H(28C)	965	-599	3107	87
H(30)	1292	1893	3333	51
H(31)	1767	2554	3923	63
H(32)	2176	3173	3387	68
H(33)	2084	3250	2236	70
H(34)	1613	2595	1646	55
H(35A)	871	4406	2226	67
H(35B)	781	5801	1877	67
H(36A)	1348	5076	2659	78
H(36B)	1187	6510	2590	78
H(37A)	1442	7063	1783	77
H(37B)	1643	5737	1939	77
H(38A)	1173	6208	904	71
H(38B)	1418	5014	989	71
H(39A)	-5	6784	1563	90
H(39B)	323	7035	2029	90
H(40A)	-217	8600	1900	94

H(40B)	140	9082	2011	94
H(41A)	2175	4422	1260	215
H(41B)	1922	4112	622	215
H(42A)	2535	4026	717	230
H(42B)	2281	3791	66	230
H(43A)	2309	5813	-249	223
H(43B)	2635	5845	249	223
H(44A)	2413	6727	1073	214
H(44B)	2226	7481	445	214

STable3. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3**·1.5THF. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Y(1)	34(1)	38(1)	32(1)	3(1)	13(1)	-1(1)
Si(1)	44(1)	47(1)	38(1)	5(1)	17(1)	-1(1)
N(1)	49(3)	36(3)	33(3)	5(2)	11(2)	2(2)
N(2)	45(3)	41(3)	40(3)	0(2)	19(3)	4(2)
N(3)	36(3)	44(3)	34(3)	-1(2)	13(2)	-1(2)
O(1)	58(3)	39(2)	53(3)	-4(2)	23(2)	-6(2)
C(1)	35(3)	45(3)	34(3)	-2(3)	15(3)	-9(3)
C(2)	47(4)	50(4)	39(3)	5(3)	13(3)	5(3)
C(3)	46(4)	51(4)	42(4)	5(3)	14(3)	6(3)
C(4)	38(3)	57(4)	37(3)	8(3)	13(3)	2(3)
C(5)	65(5)	65(5)	64(5)	6(4)	29(4)	0(4)
C(6)	58(5)	101(7)	79(6)	25(5)	34(5)	-9(5)
C(7)	54(5)	148(9)	49(5)	9(5)	29(4)	24(6)
C(8)	53(5)	102(6)	54(5)	-17(5)	21(4)	11(5)
C(9)	53(4)	61(4)	59(5)	-3(4)	21(4)	0(4)
C(10)	52(4)	48(4)	47(4)	7(3)	22(3)	14(3)
C(11)	112(7)	54(5)	69(5)	-8(4)	37(5)	14(4)
C(12)	55(5)	82(5)	69(5)	21(4)	21(4)	19(4)
C(13)	68(5)	59(4)	57(4)	17(4)	19(4)	19(4)
C(14)	44(4)	47(4)	37(3)	8(3)	11(3)	0(3)
C(15)	61(5)	78(5)	43(4)	5(4)	3(4)	-3(4)
C(16)	62(5)	56(4)	49(4)	14(3)	17(4)	-2(3)
C(17)	55(4)	56(4)	52(4)	11(3)	15(4)	9(3)
C(18)	38(4)	42(4)	43(4)	4(3)	19(3)	-8(3)
C(19)	41(4)	43(4)	44(4)	3(3)	11(3)	-6(3)
C(20)	43(4)	58(4)	46(4)	2(3)	12(3)	-19(3)
C(21)	39(4)	53(4)	56(4)	13(3)	9(3)	-8(3)
C(22)	31(3)	49(4)	55(4)	8(3)	13(3)	-1(3)
C(23)	61(5)	46(4)	65(5)	-4(4)	19(4)	-5(3)
C(24)	80(6)	89(6)	43(4)	-1(4)	9(4)	-26(5)
C(25)	46(4)	93(6)	82(6)	36(5)	-5(4)	-6(4)
C(26)	49(4)	60(5)	85(6)	7(4)	27(4)	9(4)
C(27)	60(5)	91(5)	53(4)	-7(4)	31(4)	-5(4)
C(28)	63(5)	63(5)	46(4)	22(3)	3(4)	-6(4)
C(29)	43(4)	37(3)	36(3)	2(3)	11(3)	8(3)
C(30)	44(4)	48(4)	38(3)	3(3)	14(3)	0(3)
C(31)	61(4)	58(4)	37(3)	-1(3)	3(3)	0(4)
C(32)	45(4)	70(5)	53(4)	-3(4)	1(4)	-4(3)
C(33)	42(4)	76(5)	59(5)	3(4)	16(4)	-2(4)
C(34)	41(4)	63(4)	36(3)	5(3)	13(3)	5(3)

C(35)	65(5)	51(4)	58(5)	-10(4)	31(4)	-4(4)
C(36)	99(6)	50(4)	53(4)	-7(4)	33(5)	-2(4)
C(37)	69(5)	64(5)	58(5)	-8(4)	9(4)	-16(4)
C(38)	75(5)	56(4)	51(4)	-2(3)	20(4)	-22(4)

Table 4. Bond lengths [Å] and angles [°] for **3**·1.5THF.

Y(1)-N(3)	2.285(5)	C(22)-C(26)	1.491(9)
Y(1)-N(2)	2.339(5)	C(29)-C(30)	1.396(8)
Y(1)-N(1)	2.393(5)	C(29)-C(34)	1.397(8)
Y(1)-O(1)	2.399(4)	C(30)-C(31)	1.369(9)
Y(1)-C(18)	2.564(5)	C(31)-C(32)	1.365(9)
Y(1)-C(22)	2.616(6)	C(32)-C(33)	1.376(9)
Y(1)-C(19)	2.647(6)	C(33)-C(34)	1.354(9)
Y(1)-C(21)	2.710(7)	C(35)-C(36)	1.461(9)
Y(1)-C(20)	2.715(6)	C(36)-C(37)	1.507(9)
Y(1)-C(1)	2.789(5)	C(37)-C(38)	1.452(9)
Y(1)-Si(1)	3.183(2)	C(39)-C(40)	1.445(10)
Si(1)-N(3)	1.707(5)	C(40)-C(40)#1	1.474(14)
Si(1)-C(18)	1.861(6)	C(41)-C(42)	1.401(15)
Si(1)-C(28)	1.870(7)	C(42)-C(43)	1.399(16)
Si(1)-C(27)	1.872(7)	C(43)-C(44)	1.476(15)
N(1)-C(1)	1.322(7)		
N(1)-C(14)	1.482(7)	N(3)-Y(1)-N(2)	104.15(17)
N(2)-C(1)	1.325(7)	N(3)-Y(1)-N(1)	146.18(17)
N(2)-C(10)	1.502(7)	N(2)-Y(1)-N(1)	56.48(17)
N(3)-C(29)	1.375(7)	N(3)-Y(1)-O(1)	81.40(16)
O(1)-C(35)	1.441(7)	N(2)-Y(1)-O(1)	113.95(16)
O(1)-C(38)	1.443(7)	N(1)-Y(1)-O(1)	82.77(15)
O(2)-C(39)	1.435(10)	N(3)-Y(1)-C(18)	66.96(18)
O(2)-C(39)#1	1.435(10)	N(2)-Y(1)-C(18)	127.56(19)
O(3)-C(44)	1.224(13)	N(1)-Y(1)-C(18)	146.65(19)
O(3)-C(41)	1.431(13)	O(1)-Y(1)-C(18)	115.21(16)
C(1)-C(2)	1.449(8)	N(3)-Y(1)-C(22)	88.52(19)
C(2)-C(3)	1.182(8)	N(2)-Y(1)-C(22)	147.28(19)
C(3)-C(4)	1.425(8)	N(1)-Y(1)-C(22)	123.17(19)
C(4)-C(9)	1.376(8)	O(1)-Y(1)-C(22)	97.55(17)
C(4)-C(5)	1.385(9)	C(18)-Y(1)-C(22)	31.95(18)
C(5)-C(6)	1.371(9)	N(3)-Y(1)-C(19)	85.53(18)
C(6)-C(7)	1.385(12)	N(2)-Y(1)-C(19)	98.76(18)
C(7)-C(8)	1.336(11)	N(1)-Y(1)-C(19)	122.23(18)
C(8)-C(9)	1.342(9)	O(1)-Y(1)-C(19)	146.82(16)
C(10)-C(12)	1.506(9)	C(18)-Y(1)-C(19)	32.21(18)
C(10)-C(13)	1.522(8)	C(22)-Y(1)-C(19)	51.56(19)
C(10)-C(11)	1.536(9)	N(3)-Y(1)-C(21)	117.19(18)
C(14)-C(17)	1.522(8)	N(2)-Y(1)-C(21)	122.2(2)
C(14)-C(16)	1.527(8)	N(1)-Y(1)-C(21)	96.35(18)
C(14)-C(15)	1.533(9)	O(1)-Y(1)-C(21)	110.81(18)
C(18)-C(22)	1.426(8)	C(18)-Y(1)-C(21)	51.82(19)
C(18)-C(19)	1.448(8)	C(22)-Y(1)-C(21)	30.63(19)
C(19)-C(20)	1.391(8)	C(19)-Y(1)-C(21)	50.21(19)
C(19)-C(23)	1.515(8)	N(3)-Y(1)-C(20)	114.77(18)
C(20)-C(21)	1.404(9)	N(2)-Y(1)-C(20)	97.16(19)
C(20)-C(24)	1.527(9)	N(1)-Y(1)-C(20)	96.24(18)
C(21)-C(22)	1.410(9)	O(1)-Y(1)-C(20)	140.70(18)
C(21)-C(25)	1.503(10)	C(18)-Y(1)-C(20)	51.68(19)

C(22)-Y(1)-C(20)	50.5(2)	C(6)-C(5)-C(4)	119.8(7)
C(19)-Y(1)-C(20)	30.03(18)	C(5)-C(6)-C(7)	119.2(8)
C(21)-Y(1)-C(20)	29.99(19)	C(8)-C(7)-C(6)	120.6(7)
N(3)-Y(1)-C(1)	127.92(17)	C(7)-C(8)-C(9)	120.4(8)
N(2)-Y(1)-C(1)	28.24(16)	C(8)-C(9)-C(4)	121.5(7)
N(1)-Y(1)-C(1)	28.25(16)	N(2)-C(10)-C(12)	112.5(5)
O(1)-Y(1)-C(1)	99.56(15)	N(2)-C(10)-C(13)	106.1(5)
C(18)-Y(1)-C(1)	144.63(18)	C(12)-C(10)-C(13)	109.0(6)
C(22)-Y(1)-C(1)	141.56(19)	N(2)-C(10)-C(11)	110.2(5)
C(19)-Y(1)-C(1)	112.45(18)	C(12)-C(10)-C(11)	111.5(6)
C(21)-Y(1)-C(1)	110.96(19)	C(13)-C(10)-C(11)	107.2(6)
C(20)-Y(1)-C(1)	97.10(18)	N(1)-C(14)-C(17)	107.2(5)
N(3)-Y(1)-Si(1)	31.23(12)	N(1)-C(14)-C(16)	112.8(5)
N(2)-Y(1)-Si(1)	121.04(13)	C(17)-C(14)-C(16)	107.6(5)
N(1)-Y(1)-Si(1)	177.02(13)	N(1)-C(14)-C(15)	110.4(5)
O(1)-Y(1)-Si(1)	97.27(11)	C(17)-C(14)-C(15)	108.1(5)
C(18)-Y(1)-Si(1)	35.77(14)	C(16)-C(14)-C(15)	110.5(5)
C(22)-Y(1)-Si(1)	59.80(15)	C(22)-C(18)-C(19)	105.6(5)
C(19)-Y(1)-Si(1)	58.95(14)	C(22)-C(18)-Si(1)	125.7(5)
C(21)-Y(1)-Si(1)	86.43(14)	C(19)-C(18)-Si(1)	122.4(5)
C(20)-Y(1)-Si(1)	85.63(14)	C(22)-C(18)-Y(1)	76.0(3)
C(1)-Y(1)-Si(1)	149.28(13)	C(19)-C(18)-Y(1)	77.1(3)
N(3)-Si(1)-C(18)	97.5(2)	Si(1)-C(18)-Y(1)	90.6(2)
N(3)-Si(1)-C(28)	111.9(3)	C(20)-C(19)-C(18)	108.6(5)
C(18)-Si(1)-C(28)	115.7(3)	C(20)-C(19)-C(23)	125.1(6)
N(3)-Si(1)-C(27)	115.9(3)	C(18)-C(19)-C(23)	125.9(6)
C(18)-Si(1)-C(27)	111.9(3)	C(20)-C(19)-Y(1)	77.7(3)
C(28)-Si(1)-C(27)	104.3(3)	C(18)-C(19)-Y(1)	70.7(3)
N(3)-Si(1)-Y(1)	43.94(16)	C(23)-C(19)-Y(1)	123.7(4)
C(18)-Si(1)-Y(1)	53.65(17)	C(19)-C(20)-C(21)	108.9(6)
C(28)-Si(1)-Y(1)	129.4(2)	C(19)-C(20)-C(24)	126.4(6)
C(27)-Si(1)-Y(1)	125.9(3)	C(21)-C(20)-C(24)	124.2(6)
C(1)-N(1)-C(14)	124.4(5)	C(19)-C(20)-Y(1)	72.3(4)
C(1)-N(1)-Y(1)	92.8(3)	C(21)-C(20)-Y(1)	74.8(4)
C(14)-N(1)-Y(1)	142.3(4)	C(24)-C(20)-Y(1)	125.0(4)
C(1)-N(2)-C(10)	124.4(5)	C(20)-C(21)-C(22)	107.9(6)
C(1)-N(2)-Y(1)	95.1(3)	C(20)-C(21)-C(25)	125.7(7)
C(10)-N(2)-Y(1)	140.5(4)	C(22)-C(21)-C(25)	125.3(7)
C(29)-N(3)-Si(1)	127.8(4)	C(20)-C(21)-Y(1)	75.2(4)
C(29)-N(3)-Y(1)	127.3(4)	C(22)-C(21)-Y(1)	71.0(4)
Si(1)-N(3)-Y(1)	104.8(2)	C(25)-C(21)-Y(1)	129.1(4)
C(35)-O(1)-C(38)	105.2(5)	C(21)-C(22)-C(18)	108.9(6)
C(35)-O(1)-Y(1)	125.8(4)	C(21)-C(22)-C(26)	122.6(6)
C(38)-O(1)-Y(1)	125.9(4)	C(18)-C(22)-C(26)	128.3(6)
C(39)-O(2)-C(39)#1	107.0(12)	C(21)-C(22)-Y(1)	78.4(4)
C(44)-O(3)-C(41)	104.4(11)	C(18)-C(22)-Y(1)	72.0(3)
N(1)-C(1)-N(2)	115.6(5)	C(26)-C(22)-Y(1)	119.5(4)
N(1)-C(1)-C(2)	122.6(5)	N(3)-C(29)-C(30)	124.9(5)
N(2)-C(1)-C(2)	121.8(5)	N(3)-C(29)-C(34)	120.7(5)
N(1)-C(1)-Y(1)	59.0(3)	C(30)-C(29)-C(34)	114.4(6)
N(2)-C(1)-Y(1)	56.7(3)	C(31)-C(30)-C(29)	122.7(6)
C(2)-C(1)-Y(1)	177.8(4)	C(32)-C(31)-C(30)	120.7(6)
C(3)-C(2)-C(1)	175.1(7)	C(31)-C(32)-C(33)	118.3(7)
C(2)-C(3)-C(4)	178.5(7)	C(34)-C(33)-C(32)	120.7(6)
C(9)-C(4)-C(5)	118.4(6)	C(33)-C(34)-C(29)	123.1(6)
C(9)-C(4)-C(3)	121.1(6)	O(1)-C(35)-C(36)	106.6(5)
C(5)-C(4)-C(3)	120.4(6)	C(35)-C(36)-C(37)	104.5(6)

C(38)-C(37)-C(36)	106.3(6)	C(42)-C(41)-O(3)	108.9(12)
O(1)-C(38)-C(37)	107.6(5)	C(43)-C(42)-C(41)	101.4(13)
O(2)-C(39)-C(40)	106.9(8)	C(42)-C(43)-C(44)	104.7(12)
C(39)-C(40)-C(40)#1	103.4(5)	O(3)-C(44)-C(43)	104.7(12)

Symmetry transformations used to generate equivalent atoms:

#1 -x,y,-z+1/2

STable 5. Crystal data and structure refinement for **4g**.

Identification code	4g	
Empirical formula	C17 H23 Cl N2	
Formula weight	290.82	
Temperature	173(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 8.8524(13) Å	$\alpha = 90^\circ$.
	b = 11.2198(17) Å	$\beta = 100.444(3)^\circ$.
	c = 17.538(3) Å	$\gamma = 90^\circ$.
Volume	1713.0(4) Å ³	
Z	4	
Density (calculated)	1.128 Mg/m ³	
Absorption coefficient	0.216 mm ⁻¹	
F(000)	624	
Crystal size	0.75 x 0.6 x 0.5 mm ³	
Theta range for data collection	2.17 to 25.05°.	
Index ranges	-10 ≤ h ≤ 10, -13 ≤ k ≤ 12, -14 ≤ l ≤ 20	
Reflections collected	8256	
Independent reflections	3021 [R(int) = 0.0245]	
Completeness to theta = 25.05°	99.5 %	
Absorption correction	Empirical	
Max. and min. transmission	0.86 and 0.64	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3021 / 0 / 187	
Goodness-of-fit on F ²	1.026	
Final R indices [I > 2sigma(I)]	R1 = 0.0389, wR2 = 0.1023	
R indices (all data)	R1 = 0.0498, wR2 = 0.1077	
Largest diff. peak and hole	0.183 and -0.282 e.Å ⁻³	

STable 6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4g**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	6686(1)	-187(1)	1417(1)	57(1)
N(1)	100(1)	5629(1)	1883(1)	39(1)
N(2)	708(1)	6957(1)	971(1)	39(1)
C(1)	952(2)	5974(1)	1339(1)	33(1)
C(2)	2107(2)	5065(1)	1278(1)	38(1)
C(3)	2954(2)	4237(2)	1285(1)	40(1)
C(4)	3903(2)	3194(1)	1301(1)	38(1)
C(5)	3586(2)	2338(2)	721(1)	44(1)
C(6)	4429(2)	1304(2)	755(1)	45(1)
C(7)	5619(2)	1124(1)	1370(1)	40(1)
C(8)	5973(2)	1962(2)	1951(1)	47(1)
C(9)	5109(2)	2989(2)	1915(1)	46(1)
C(10)	-1160(2)	6284(1)	2137(1)	38(1)
C(11)	-2495(2)	6445(2)	1468(1)	64(1)
C(12)	-1651(2)	5520(2)	2768(1)	62(1)
C(13)	-598(2)	7485(2)	2478(1)	58(1)
C(14)	1663(2)	7359(1)	409(1)	41(1)
C(15)	1581(3)	6506(2)	-270(1)	69(1)
C(16)	3301(2)	7572(2)	810(1)	71(1)
C(17)	973(3)	8552(2)	103(1)	70(1)
H(1)	332	4950	2101	47
H(5)	2790	2467	304	53
H(6)	4199	732	368	54
H(8)	6784	1836	2360	57
H(9)	5335	3553	2307	55
H(11A)	-2172	6923	1072	96
H(11B)	-3326	6835	1651	96
H(11C)	-2829	5680	1258	96
H(12A)	-1987	4755	2559	92
H(12B)	-2477	5906	2958	92
H(12C)	-796	5418	3187	92
H(13A)	243	7366	2901	87
H(13B)	-1420	7885	2663	87
H(13C)	-262	7962	2086	87
H(15A)	2062	5766	-90	103
H(15B)	2103	6848	-651	103
H(15C)	525	6365	-496	103
H(16A)	3310	8115	1234	107
H(16B)	3877	7907	448	107
H(16C)	3757	6830	1003	107
H(17A)	-67	8433	-158	106
H(17B)	1566	8879	-255	106
H(17C)	987	9093	528	106

STable 7. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4g**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	61(1)	45(1)	66(1)	4(1)	11(1)	19(1)
N(1)	44(1)	31(1)	45(1)	8(1)	16(1)	9(1)
N(2)	41(1)	35(1)	40(1)	3(1)	9(1)	1(1)
C(1)	32(1)	33(1)	34(1)	-2(1)	3(1)	1(1)
C(2)	37(1)	40(1)	39(1)	2(1)	10(1)	1(1)
C(3)	37(1)	42(1)	42(1)	5(1)	11(1)	3(1)
C(4)	36(1)	38(1)	41(1)	5(1)	14(1)	6(1)
C(5)	41(1)	56(1)	34(1)	2(1)	4(1)	11(1)
C(6)	50(1)	48(1)	38(1)	-4(1)	9(1)	7(1)
C(7)	40(1)	37(1)	45(1)	5(1)	13(1)	7(1)
C(8)	41(1)	49(1)	48(1)	0(1)	-3(1)	9(1)
C(9)	43(1)	43(1)	50(1)	-8(1)	1(1)	4(1)
C(10)	37(1)	35(1)	44(1)	-1(1)	12(1)	4(1)
C(11)	42(1)	83(2)	64(1)	-5(1)	3(1)	12(1)
C(12)	67(1)	57(1)	71(1)	7(1)	40(1)	7(1)
C(13)	65(1)	48(1)	66(1)	-16(1)	24(1)	-3(1)
C(14)	44(1)	42(1)	38(1)	4(1)	9(1)	-3(1)
C(15)	100(2)	68(1)	41(1)	-2(1)	21(1)	-9(1)
C(16)	55(1)	95(2)	63(1)	19(1)	7(1)	-27(1)
C(17)	85(2)	57(1)	73(1)	26(1)	26(1)	6(1)

STable 8. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for **4g**.

Cl(1)-C(7)	1.7422(16)	N(1)-C(1)-C(2)	109.45(12)
N(1)-C(1)	1.3756(18)	C(3)-C(2)-C(1)	171.80(16)
N(1)-C(10)	1.4704(18)	C(2)-C(3)-C(4)	176.63(16)
N(2)-C(1)	1.2763(19)	C(5)-C(4)-C(9)	118.48(14)
N(2)-C(14)	1.4811(19)	C(5)-C(4)-C(3)	120.55(14)
C(1)-C(2)	1.460(2)	C(9)-C(4)-C(3)	120.89(14)
C(2)-C(3)	1.193(2)	C(6)-C(5)-C(4)	121.03(15)
C(3)-C(4)	1.438(2)	C(5)-C(6)-C(7)	119.24(15)
C(4)-C(5)	1.389(2)	C(8)-C(7)-C(6)	121.12(15)
C(4)-C(9)	1.391(2)	C(8)-C(7)-Cl(1)	119.48(13)
C(5)-C(6)	1.375(2)	C(6)-C(7)-Cl(1)	119.39(13)
C(6)-C(7)	1.379(2)	C(9)-C(8)-C(7)	119.11(15)
C(7)-C(8)	1.379(2)	C(8)-C(9)-C(4)	121.01(15)
C(8)-C(9)	1.378(2)	N(1)-C(10)-C(11)	110.68(13)
C(10)-C(11)	1.517(2)	N(1)-C(10)-C(13)	110.48(13)
C(10)-C(13)	1.522(2)	C(11)-C(10)-C(13)	110.62(15)
C(10)-C(12)	1.525(2)	N(1)-C(10)-C(12)	105.67(13)
C(14)-C(16)	1.511(2)	C(11)-C(10)-C(12)	110.13(15)
C(14)-C(15)	1.518(2)	C(13)-C(10)-C(12)	109.13(15)
C(14)-C(17)	1.528(2)	N(2)-C(14)-C(16)	110.68(13)
		N(2)-C(14)-C(15)	112.21(14)
C(1)-N(1)-C(10)	127.65(12)	C(16)-C(14)-C(15)	111.73(17)
C(1)-N(2)-C(14)	122.32(13)	N(2)-C(14)-C(17)	105.11(14)
N(2)-C(1)-N(1)	121.99(13)	C(16)-C(14)-C(17)	108.29(16)
N(2)-C(1)-C(2)	128.55(14)	C(15)-C(14)-C(17)	108.50(16)

Symmetry transformations used to generate equivalent atoms:

STable 9. Crystal data and structure refinement for **4i**.

Identification code	4i	
Empirical formula	C ₁₅ H ₁₉ Cl N ₂	
Formula weight	262.77	
Temperature	173(1) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 17.097(2) Å	α = 90°.
	b = 9.3950(13) Å	β = 90°.
	c = 18.607(3) Å	γ = 90°.
Volume	2988.9(7) Å ³	
Z	8	
Density (calculated)	1.168 Mg/m ³	
Absorption coefficient	0.241 mm ⁻¹	
F(000)	1120	
Crystal size	0.75 x 0.6 x 0.15 mm ³	
Theta range for data collection	2.19 to 25.07°.	
Index ranges	-18 ≤ h ≤ 20, -11 ≤ k ≤ 9, -21 ≤ l ≤ 22	
Reflections collected	14008	
Independent reflections	2634 [R(int) = 0.0356]	
Completeness to theta = 25.07°	99.4 %	
Absorption correction	Empirical	
Max. and min. transmission	0.96 and 0.83	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2634 / 0 / 179	
Goodness-of-fit on F ²	1.015	
Final R indices [I > 2σ(I)]	R1 = 0.0343, wR2 = 0.0854	
R indices (all data)	R1 = 0.0536, wR2 = 0.0910	
Largest diff. peak and hole	0.135 and -0.158 e.Å ⁻³	

STable 10. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4i**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	4531(1)	1245(1)	4506(1)	61(1)
N(1)	2408(1)	1011(2)	1937(1)	45(1)
N(2)	3373(1)	-633(2)	2222(1)	42(1)
C(1)	3028(1)	561(2)	2334(1)	37(1)
C(2)	3238(1)	1547(2)	2907(1)	38(1)
C(3)	3380(1)	2307(2)	3401(1)	36(1)
C(4)	3543(1)	3247(2)	3988(1)	36(1)
C(5)	4056(1)	2870(2)	4538(1)	39(1)
C(6)	4204(1)	3778(2)	5106(1)	49(1)
C(7)	3843(1)	5080(2)	5131(1)	56(1)
C(8)	3337(1)	5484(2)	4589(1)	56(1)
C(9)	3189(1)	4576(2)	4027(1)	48(1)
C(10)	2107(1)	247(2)	1314(1)	41(1)
C(11)	1926(1)	1307(2)	720(1)	54(1)
C(12)	1401(1)	-638(2)	1506(1)	59(1)
C(13)	4090(1)	-934(2)	2632(1)	47(1)
C(14)	4707(1)	-1408(3)	2115(1)	100(1)
C(15)	3926(1)	-2029(3)	3202(1)	97(1)
H(6)	4546	3507	5469	59
H(7)	3940	5693	5513	67
H(8)	3097	6372	4605	67
H(9)	2845	4855	3667	57
H(11A)	1538	1969	885	81
H(11B)	1732	808	307	81
H(11C)	2394	1813	593	81
H(12A)	1524	-1241	1907	89
H(12B)	1255	-1215	1102	89
H(12C)	974	-22	1631	89
H(14A)	4514	-2195	1838	150
H(14B)	5164	-1697	2376	150
H(14C)	4838	-635	1799	150
H(15A)	3520	-1689	3514	146
H(15B)	4393	-2198	3477	146
H(15C)	3761	-2901	2979	146
H(1)	2234(9)	1814(18)	2023(8)	42(5)
H(10)	2509(10)	-365(17)	1174(8)	37(4)
H(13)	4296(9)	-83(18)	2867(9)	45(5)

STable 11. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4i**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	69(1)	60(1)	55(1)	7(1)	-5(1)	25(1)
N(1)	46(1)	45(1)	45(1)	-9(1)	-11(1)	12(1)
N(2)	38(1)	48(1)	40(1)	-4(1)	-6(1)	4(1)
C(1)	34(1)	44(1)	33(1)	0(1)	2(1)	-4(1)
C(2)	37(1)	42(1)	35(1)	5(1)	2(1)	0(1)
C(3)	34(1)	40(1)	35(1)	5(1)	3(1)	2(1)
C(4)	36(1)	40(1)	31(1)	2(1)	4(1)	-1(1)
C(5)	36(1)	45(1)	37(1)	5(1)	3(1)	1(1)

C(6)	46(1)	64(1)	38(1)	2(1)	-6(1)	-3(1)
C(7)	66(1)	57(1)	44(1)	-14(1)	-1(1)	-5(1)
C(8)	70(1)	45(1)	52(1)	-7(1)	4(1)	10(1)
C(9)	54(1)	48(1)	41(1)	2(1)	-6(1)	9(1)
C(10)	42(1)	44(1)	36(1)	-3(1)	-5(1)	6(1)
C(11)	62(1)	57(1)	44(1)	8(1)	-5(1)	1(1)
C(12)	62(1)	57(1)	58(1)	8(1)	-8(1)	-10(1)
C(13)	41(1)	53(1)	48(1)	-9(1)	-12(1)	6(1)
C(14)	49(1)	169(3)	81(2)	-47(2)	-17(1)	38(2)
C(15)	82(2)	105(2)	104(2)	43(2)	-41(2)	-4(2)

STable 12. Bond lengths [Å] and angles [°] for **4i**.

Cl(1)-C(5)	1.7304(17)	N(2)-C(1)-N(1)	122.82(15)
N(1)-C(1)	1.358(2)	N(2)-C(1)-C(2)	124.07(15)
N(1)-C(10)	1.457(2)	N(1)-C(1)-C(2)	113.07(14)
N(2)-C(1)	1.285(2)	C(3)-C(2)-C(1)	176.08(17)
N(2)-C(13)	1.472(2)	C(2)-C(3)-C(4)	178.76(18)
C(1)-C(2)	1.457(2)	C(9)-C(4)-C(5)	117.62(15)
C(2)-C(3)	1.189(2)	C(9)-C(4)-C(3)	120.66(15)
C(3)-C(4)	1.432(2)	C(5)-C(4)-C(3)	121.72(15)
C(4)-C(9)	1.389(2)	C(6)-C(5)-C(4)	121.32(16)
C(4)-C(5)	1.394(2)	C(6)-C(5)-Cl(1)	119.07(13)
C(5)-C(6)	1.381(2)	C(4)-C(5)-Cl(1)	119.60(13)
C(6)-C(7)	1.371(3)	C(7)-C(6)-C(5)	119.65(17)
C(7)-C(8)	1.381(3)	C(6)-C(7)-C(8)	120.17(17)
C(8)-C(9)	1.373(2)	C(9)-C(8)-C(7)	120.01(17)
C(10)-C(12)	1.510(3)	C(8)-C(9)-C(4)	121.22(16)
C(10)-C(11)	1.520(2)	N(1)-C(10)-C(12)	111.43(15)
C(13)-C(14)	1.495(3)	N(1)-C(10)-C(11)	109.17(14)
C(13)-C(15)	1.504(3)	C(12)-C(10)-C(11)	111.71(15)
		N(2)-C(13)-C(14)	108.05(15)
C(1)-N(1)-C(10)	123.67(15)	N(2)-C(13)-C(15)	110.02(15)
C(1)-N(2)-C(13)	117.79(14)	C(14)-C(13)-C(15)	112.4(2)

Symmetry transformations used to generate equivalent atoms:

Figure 1. ORTEP drawing of **4g**. Selected bond length (Å): N(1)–C(1) 1.3756(18), N(2)–C(1) 1.2763(19), C(1)–C(2) 1.460(2), C(2)–C(3) 1.193(2).

Figure 2. ORTEP drawing of **4i**. Selected bond length (Å): N(1)–C(1) 1.358(2), N(2)–C(1) 1.285(2), C(1)–C(2) 1.457(2), C(2)–C(3) 1.189(2).