Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information for

Direct mono-insertion of isocyanides into terminal alkynes catalyzed by rare-earth silylamides

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Methods. ^{1}H and ^{13}C NMR spectra were recorded at 397.95 and 99.5 MHz, respectively. The stereochemistry of **3** was confirmed by NOE studies, and the ratio of *syn* and *anti* isomers was determined by ^{13}C NMR. Mass spectra (EI) were obtained at 70 eV on a GC-MS apparatus. Microanalyses were performed at our analytical laboratory. All reactions were carried out under argon.

Materials. Cyclohexane was distilled from sodium and stored under argon. The silylamide complexes were prepared by the reported method.[1] The terminal alkynes, 1-dibenzylaminoprop-2-yne (**1c**),[2] propargyloxy-*tert*-butyldimethylsilane (**1d**),[3] 1-ethynyl-4-methoxybenzene (**1f**)[4], 1-ethynyl-4-bromobenzene (**1g**)[4], and 1-ethynyl-4-(1,3-dioxoranyl)benzene (**1h**)[5] were obtained according to the literatures. Isocyanides, **2a-e**, were prepared based on the reported procedure.[6] All other materials were commercially available and used after drying and purification.

Representative experimental procedure. All reactions were carried out under Ar atmosphere. A solution of **1a** (99 μL, 0.67 mmol), **2e** (125 mg, 0.67 mmol), and amylamine (15.4 μL, 0.134 mmol) in cyclohexane (0.7 mL) was added into $Sm(btsa)_3$ (42 mg, 0.067 mmol). After 9 h of stirring at room temperature, the reaction mixture was quenched with distilled water and ether. Yield of **3ae** was measured by gas chromatography with dimethyl terephthalate as an internal standard. After extraction with ether, the combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and evaporated *in vacuo*. Kugelrohr distillation of the mixture (250 ºC/10^{-2} mmHg) gave 1-(2,6-diisopropylphenylimino)non-2-yne (**3ae**) (117 mg, 59%) as a yellow oil mixture of the *syn* and *anti*-isomers (65/35). MS *m/z* (70 eV) 297 (M^+, 36), 282 (100), 212 (35). ^{1}H NMR ($CDCl_3$) *anti isomer*: δ 0.91 (3H, t, *J* = 7.0 Hz), 1.01-1.49 (18 H, m), 1.61-1.69 (2H, m), 2.46 (2H, dt, *J* = 1.5, 7.2 Hz), 2.92 (2H, sept, *J* = 6.9 Hz), 7.03-7.14

(3H, m), 7.40 (1H, t, *J* = 1.5 Hz); *syn isomer* (assignable peaks only): δ 0.84 (3H, t, *J* = 7.2 Hz), 1.01-1.49 (18 H, m), 2.14 (2H, dt, *J* = 1.4, 6.9 Hz), 2.82 (2H, sept, *J* = 6.9 Hz), 7.03-7.14 (3H, m), 7.84 (1H, t, *J* = 1.4 Hz). ^{13}C NMR ($CDCl_3$) *anti isomer*: δ 14.01, 19.5, 22.5, 23.5, 27.71, 27.86, 28.0, 31.3, 78.9, 97.0, 123.0, 124.6, 137.5, 147.1, 148.6. *syn isomer*: δ 14.05, 19.0, 22.4, 23.3, 27.67, 27.84, 28.7, 31.2, 76.5, 100.3, 122.7, 124.1, 136.3, 145.2, 147.3. Anal. Calcd for $C_{21}H_{31}N$: C, 84.79; H, 10.50; N, 4.71. Found: C, 84.89; H, 10.62; N, 4.49.

Analytical data of the products 3.

1-(2,6-Dimethylphenylimino)non-2-yne (3ac). Isolated as a yellow oil (78 mg, 30%, *anti*/*syn* = 54/46) by vacuum distillation (150-160 ºC/10^{-2} Torr). MS *m/z* 242 (M^+, 11), 241 (65), 184 (82), 170 (100). ^{1}H NMR ($CDCl_3$) *anti-isomer*: δ 0.86 (3H, t, *J* = 7.2 Hz), 1.10-1.33 (6H, m), 1.41-1.48 (2H, m), 2.06 (6H, s), 2.14 (2H, dt, *J* = 1.6, 6.8 Hz), 6.88-6.95 (1H, m), 7.00 (2H, d, *J* = 7.0 Hz), 7.43 (1H, t, *J* = 1.6 Hz); *syn-isomer* (assignable peaks only): δ 0.91 (3H, t, *J* = 7.0 Hz), 1.60-1.67 (2H, m), 2.12 (6H, s), 2.44 (2H, dt, *J* = 1.6, 7.2 Hz), 7.02 (2H, d, *J* = 7.2 Hz), 7.76 (1H, t, *J* = 1.6 Hz). ^{13}C NMR ($CDCl_3$) *anti-isomer*: δ14.0, 17.8, 19.5, 22.5, 27.7, 27.9, 31.2, 78.9, 97.2, 124.2, 126.9, 128.0, 144.83, 147.7, 150.8; *syn-isomer*: δ 14.0, 18.2, 19.0, 22.4, 27.9, 28.6, 31.3, 76.0, 99.5, 123.4, 125.8, 127.6, 144.76, 147.7, 149.6. Anal. Calcd for $C_{17}H_{23}N$: C, 84.59; H, 9.60; N; 5.80. Found: C, 84.45; H, 9.94; N, 5.60.

1-(2,4,6-Trimethylphenylimino)non-2-yne (3ad). Isolated as a yellow oil (94 mg, 57%, *anti*/*syn* = 55/45) by vacuum distillation (170-180 °C/10^{-2} Torr). MS *m/z* 255 (M^+, 31), 198 (28), 184 (43), 146 (20), 29 (100). ^{1}H NMR ($CDCl_3$) *anti-isomer*: δ 0.87 (3H, t, *J* = 7.2 Hz), 1.11-1.33 (6H, m), 1.41-1.48 (2H, m), 2.09 (6H, s), 2.16 (2H, dt, *J* = 1.6, 6.8 Hz), 2.26 (3H, s), 6.85 (2H, s), 7.42 (1H, t, *J* = 1.6 Hz); *syn-isomer*: δ 0.91 (3H, t, *J* = 7.1 Hz), 1.11-1.33 (6H, m), 1.59-1.67 (2H, m), 2.03 (6H, s), 2.26 (3H, s), 2.44 (2H, dt, *J* = 1.5, 7.2 Hz), 6.83 (2H, s), 7.76 (1H, t, *J* = 1.5 Hz). ^{13}C NMR ($CDCl_3$) *anti-isomer*: δ14.01, 18.2, 19.1, 20.66, 22.5, 27.8, 28.01, 31.3, 76.2, 99.3, 126.9, 128.7, 132.6, 144.9, 147.1; *syn-isomer*: δ14.04, 17.8, 19.5, 20.69, 22.4, 27.97, 28.6, 31.2, 79.0, 96.9, 125.7, 128.3, 133.5, 147.7, 148.4. Anal. Calcd for $C_{18}H_{25}N$: C, 84.65; H, 9.87; N, 5.48. Found: C, 84.46; H, 9.92; N, 5.62.

1-(2,6-Diisopropylphenylimino)-4,4-dimethylpent-2-yne (3be). Isolated as a yellow oil (152 mg, 53%, *syn*/*anti* = 57/43) by vacuum distillation (140 °C / 10^{-2} Torr). MS *m/z* 269 (M^+, 69), 254 (100), 212 (74). ^{1}H NMR ($CDCl_3$) *syn-isomer*: δ 0.95 (9H, s), 1.16 (12H, d, *J* = 6.9 Hz), 2.92 (2H, sept, *J* = 6.9 Hz), 7.01-7.13 (3H, m), 7.79 (1H, s); *anti-isomer:* δ 1.14 (12H, d, *J* = 7.0 Hz), 1.35 (9H, s), 2.81 (2H, sept, *J* = 7.0 Hz), 7.01-7.13 (3H, m), 7.40 (1H, s). ^{13}C NMR ($CDCl_3$) *syn-isomer*: δ22.4, 23.6, 27.6, 29.9, 75.2, 104.3, 122.6, 124.0, 137.5, 145.4, 147.6; *anti-isomer*: δ 22.6, (23.3, 23.5), 27.8, 30.4,

77.4, 107.8, 122.9, 124.6, 136.1, 147.1, 148.6. Anal. Calcd for $C_{19}H_{27}N$: C, 84.70; H, 10.10; N, 5.20. Found: C, 84.67; H, 10.26; N, 5.01.

3-*N*,*N*-Dibenzylamino-1-(2,6-Diisopropylphenylimino)prop-2-yne (3ce). Isolated as an orange oil (158 mg, 40%, *syn*/anti = 70/30) by MPLC on alumina with hexane containing 2% of ethylacetate. R_f = 0.43. Mass data was not obtained. ^{1}H NMR ($CDCl_3$) *syn-isomer*: δ1.18-1.28 (12H, m), 2.91 (2H, sept, *J* = 6.9 Hz), 3.21 (2H, d, *J* = 1.2 Hz), 3.23 (4H, s), 7.12-7.44 (13H, m), 7.95 (1H, t, *J* = 1.2 Hz); *anti-isomer*: δ1.18-1.28 (12H, m), 2.94 (2H, sept, *J* = 6.9 Hz), 3.53 (2H, d, *J* = 1.2 Hz), 3.78 (4H, s), 7.12-7.44 (13H, m), 7.49 (1H, t, *J* = 1.2 Hz). ^{13}C NMR ($CDCl_3$) *syn-isomer*: δ22.4, 23.2, 23.50, 23.54, 28.1, 41.5, 57.0, 80.7, 93.8, 123.0, 124.5, 127.1, 128.2, 128.9, 136.2, 138.4, 144.6. 147.8; *anti-isomer* (assignable peaks only): δ27.8, 42.2, 57.8, 83.6, 90.8, 123.1, 124.8, 127.3, 128.4, 129.0, 137.4, 138.5, 146.4, 148.6. Anal. Calcd for $C_{30}H_{34}N_2$: C, 85.26; H, 8.11; N, 6.63. Found: C, 85.01; H, 8.18; N, 6.81.

1-(2,6-Diisopropylphenylimino)-4-(*tert*-butyldimethylsilyloxy)but-2-yne (3de). Isolated as an orange oil (106 mg, 76%, *anti*/*syn* = 63/37) by vacuum distillation (>250 ^{o}C/10^{-2} Torr). MS *m/z* 357 (M^+, 94), 342 (100). ^{1}H NMR ($CDCl_3$) *anti-isomer*: δ0.19 (6H, s), 0.96 (9H, s), 1.17 (12H, d, *J* = 6.9 Hz), 2.91 (2H, sept, *J* = 6.9 Hz), 4.58 (2H, s), 7.08-7.18 (3H, m), 7.47 (1H, s); *syn-isomer* (assignable peaks only): δ -0.06 (6H, s), 0.82 (9H, s), 2.83 (2H, sept, *J* = 6.8 Hz), 4.26 (2H, s), 7.08-7.18 (3H, m), 7.95 (1H, s). ^{13}C NMR ($CDCl_3$) *anti-isomer*: δ-5.22, 18.3, 23.5, 25.8, 27.7, 52.0, 82.4, 92.9, 123.0, 124.8, 137.3, 146.3, 148.5; *syn-isomer*: δ-5.49, 18.1, 23.4, 25.6, 27.9, 51.5, 79.2, 96.4, 122.8, 136.1, 144.1, 146.9. Anal. Calcd for $C_{22}H_{35}NOSi$: C, 73.89; H, 9.87; N, 3.92. Found: C, 74.00; H, 9.90; N, 4.12.

1-(2,6-Diisopropylphenylimino)-3-phenylprop-2-yne (3ee). Isolated as a yellow oil (126 mg, 60%, *anti*/*syn* = 58/42) by vacuum distillation (>250 ^{o}C/10^{-2} Torr). MS *m/z* 289 (M^+, 82), 274 (95), 115 (100). ^{1}H NMR ($CDCl_3$) *anti-isomer*: δ 1.19 (12H, d, *J* = 6.9 Hz), 2.98 (2H, sept, *J* = 6.9 Hz), 7.12-7.64 (8H, m), 7.65 (1H, s); *syn-isomer* (assignable peaks only): δ2.89 (2H, sept, *J* = 6.9 Hz), 8.04 (1H, s), ^{13}C NMR ($CDCl_3$) *anti-isomer*: δ 23.6, 27.8, 86.8, 94.0, 120.8, 123.1, 124.9, 128.5, 129.9, 132.5, 137.5, 146.8, 148.6; *syn-isomer*: δ 23.5, 27.9, 83.8, 97.3, 121.1, 122.7, 124.3, 128.4, 129.8, 132.3, 136.5, 144.8, 147.4. Anal. Calcd for $C_{21}H_{23}N$: C, 87.15; H, 8.01; N, 4.84. Found: C, 86.91; H, 8.06; N, 5.10.

1-(2,6-Diisopropylphenylimino)-3-(4-methoxyphenyl)prop-2-yne (3fe). Isolated as a yellow oil (48 mg, 18%, *anti*/*syn* = 58/42) by vacuum distillation (>250 ºC / 10^{-2} Torr). MS *m/z* 319 (M^+, 82), 304 (100), 276 (45). ^{1}H NMR ($CDCl_3$) *anti-isomer*: δ1.185 (12H, d, *J* = 6.8 Hz), 3.00 (2H, sept, *J* = 6.8 Hz), 3.78 (3H, s), 6.71-7.58 (7H, m), 7.64 (1H, s); *syn-isomer*: δ1.176 (12H, d, *J* = 6.8 Hz), 2.91 (2H, sept, *J* = 6.8 Hz), 3.71 (3H, s),

6.71-7.58 (7H, m), 8.04 (1H, s). ^{13}C NMR ($CDCl_3$) *anti-isomer*: δ23.5, 27.7, 55.14, 86.2, 94.6, 113.0, 114.10, 122.9, 124.7, 134.1, 137.4, 146.7, 148.7, 160.81; *syn-isomer*: δ23.4, 27.8, 55.08, 83.5, 98.1, 112.6, 113.98, 122.6, 124.1, 134.0, 136.5, 144.8, 147.5, 160.76. Anal. Calcd for $C_{22}H_{25}NO$: C, 82.72; H, 7.89; N, 4.38. Found: C, 82.78; H, 8.12; N, 4.67.

1-(2,6-Diisopropylphenylimino)-3-(4-bromophenyl)prop-2-yne (3ge). Isolated as a yellow solid (144 mg, 60%, *anti*/*syn* = 62/38) by vacuum distillation (250 °C/10^{-2} Torr). MS *m/z* 369 (M^+ + 1, 46), 368 (M^+, 38), 367 (M^+ - 1, 39), 173 (100). ^{1}H NMR (400 MHz, CDCl3) anti-isomer: δ1.19 (12H, d, *J* = 6.8 Hz), 2.96 (2H, sept, *J* = 6.8 Hz), 6.93 -6.96 (1H, m), 7.10-7.17 (3H, m), 7.36-7.39 (1H, m), 7.47-7.54 (2H, m), 7.63 (1H, s); *syn-isomer*: δ 1.16 (12H, d, *J* = 7.0 Hz), 2.86 (2H, sept, *J* = 7.0 Hz), 6.93-6.96 (1H, m), 7.10-7.17 (3H, m), 7.36-7.39 (1H, m), 7.47-7.54 (2H, m), 8.07 (1H, s). ^{13}C NMR ($CDCl_3$) *anti-isomer*: δ23.5 (m), 27.9 (m), 87.7, 92.7, 120.2, 123.1, 124.5, 131.9 (m), 133.8 (m), 137.4, 146.4, 146.6, 148.6; *syn-isomer*: δ23.5 (m), 27.9 (m), 84.7, 96.0, 119.7, 122.8, 125.0, 131.9 (m), 133.8 (m), 136.5, 144.5, 144.6, 147.4. Anal. Calcd for $C_{21}H_{22}BrN$: C, 68.48; H, 6.02; N, 3.80. Found: C, 68.42; H, 5.85; N, 3.72.

1-(2,6-Diisopropylphenylimino)-3-[4-(1,3-dioxolanyl)phenyl]prop-2-yne (3he). Isolated as a yellow oil (305 mg, 68%, *anti*/*syn* = 62/38) by vacuum distillation (>250 °C / 10^{-2} Torr). MS *m/z* 361 (M^+, 75), 360 (26), 73 (100). ^{1}H NMR ($CDCl_3$) *anti-isomer*: δ1.19 (12H, d, *J* = 6.9 Hz), 2.98 (2H, sept, *J* = 6.9 Hz), 3.95-4.14 (4H, m), 5.82 (1H, s), 7.10-7.17 (3H, m), 7.34-7.66 (4H, m), 7.65 (1H, s); *syn-isomer*: δ 1.16 (12H, d, *J* = 7.0 Hz), 2.88 (2H, sept, *J* = 7.0 Hz), 3.95-4.14 (4H, m), 5.74 (1H, s), 7.10-7.17 (3H, m), 7.34-7.66 (4H, m), 8.08 (1H, s). ^{13}C NMR ($CDCl_3$) *anti-isomer*: δ23.52, 23.54, 27.7, 27.8, 65.3, 87.1, 93.5, 103.0, 121.4, 123.0, 124.9, 126.6, 132.4, 137.4, 139.6, 144.7, 148.6; *syn-isomer*: δ 23.3, 23.4, 27.8, 27.9, 65.2, 84.2, 96.9, 102.8, 121.8, 122.7, 124.3, 126.4, 132.3, 136.4, 139.7, 146.6, 147.4. Anal. Calcd for $C_{24}H_{27}NO_2$: C, 79.74; H, 7.53; N, 3.87. Found: C, 79.61; H, 7.72; N, 3.75.

References

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(3) The compound **1d** was obtained by the reaction of propargyl alcohol with *tert*-butyldimethylsilyl chloride in the presence of imidazole.

(4) The alkynes **1f** and **1g** were prepared by the treatment of 4-methoxystyrene and 4-bromostyrene with bromine, followed by dehydrobromination, according to the reported method: X. K. Jiang, G. Z. Ji, D. Z. R. Wang, *J. Fluorine. Chem*., 1996, **79**,

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(5) The alkyne **1h** was prepared as follows. A mixture of 2-(4-bromophenyl)-1,3-oxolane (5.9 g, 25.8 mmol), 2-methylbut-3-yn-2-ol (2.6 g, 31.0 mmol), $PdCl_2(PPh_3)_2$ (9.1 mg, 13 μmol), CuI (8.8 mg, 46 μmol), and PPh_3 (17 mg, 65 μmol) in triethylamine (25 mL) was stirred at reflux temperature. The reaction was monitored by TLC until the substrates were completely consumed. After stirring for 20 h, the reaction mixture was diluted with ether (100 mL), washed with saturated NH_4Cl aq. (50 mL×2) and NaCl aq. (50 mL×2), dried over $MgSO_4$, evaporated *in vacuo* to give 5.48 g (91% yield) of the Sonogashira coupling product. Without further purification, the product was used for the next step. The material, thus obtained, (5.48 g, 23.6 mmol) was deprotected in toluene (60 mL) with a catalytic amount of NaH (3.1 mmol) under reflux conditions (6h). The reaction mixture was diluted with dichloromethane, filtered, washed with saturated aqueous Na_2CO_3 and brine, and evaporated *in vacuo*. The crude product was chromatographed on silica-gel with chloroform as an eluent to give 2.0 g (49% yield) of **1h** as a white solid. IR (CCl_4) 2108, 2889, 2954, 3286 cm^{-1}. MS *m/z* 174 (M^+, 21), 173 (70), 129 (39), 102 (62), 101 (31), 73 (59), 29 (100). ^1H NMR ($CDCl_3$) δ 3.09 (1H, s), 4.00-4.15 (4H, m,), 5.81 (1H, s), 7.44 (2H, d, J = 8.5 Hz), 7.51 (2H, d, J = 8.2 Hz). ^{13}C NMR ($CDCl_3$) δ77.7, 65.3, 77.7, 83.3, 103.2, 126.4, 132.1, 138.5: (a) E. T. Sabourin, A. J. Omopchenko, *J. Org. Chem*., 1983, **48**, 5135. (b) H. Iwamura, N. Koga, N. Sasagawa, *Jpn. Kokai Tokkyo Koho*, 1991, JP 03188040 A2 (to Mitsubishi Kasei Co., Japan).

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