Supplementary Information for

Alkaline Earth catalysis for the 100% Atom-Efficient Three Component Assembly of Imidazolidin-2-ones

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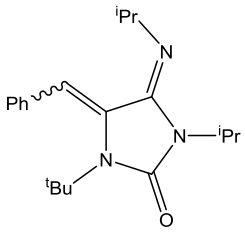
Synthesis of imidazolidin-2-ones

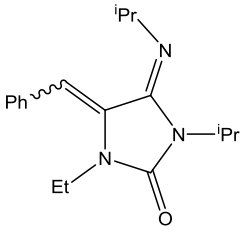
The relevant propargylamidines were prepared *in situ* in a sealed Youngs tap NMR tube using 21.9 μL of phenylacetylene (0.2 mmol) and 0.2 mmol of the relevant carbodiimide with 5 mol% of $[Sr\{N(SiMe_3)_2\}_2(THF)_2]$ in a 9:1 mixture of C_6D_6/d_8-THF at 80-100 ^oC overnight. After confirming full conversion to the amidine by ^1H NMR, 0.2 mmol of the relevant isocyanate was added to the NMR tube inside the glovebox. The sealed reaction mixtures were then immediately analysed by NMR spectroscopy to confirm conversion to the desired *N*-heterocyclic products. Unless specified otherwise, insertion/cyclisation was in each case instantaneous at room temperature under these reaction conditions.

4-benzylidene-1-*iso*propyl-5-(isopropylimino)-3-(*tert*-butyl)imidazolidin-2-one, 2



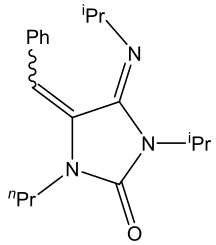
^1H NMR ppm (C_6D_6) Major isomer (*E*) 78%: 6.96-7.17 (m, 5H, Ph-*H*), 6.29 (s, 1H, C*H*Ph), 4.67 (sept, 1H, ^{i}Pr-C*H*, ^3J = 6.7 Hz), 3.38 (sept, 1H, ^{i}Pr-C*H*, ^3J = 6.7 Hz), 1.55 (s, 9H, ^{t}Bu-CH_3), 1.51 (d, 6H, ^{i}Pr-CH_3, ^3J = 6.7 Hz), 0.82 (d, 6H, ^{i}Pr-CH_3, ^3J = 6.7 Hz). Minor isomer (*Z*) 22%: 6.96-7.17 (m, 5H, Ph-*H*), 6.51 (s, 1H, C*H*Ph), 4.73 (sept, 1H, ^{i}Pr-C*H*, ^3J = 6.7 Hz), 4.25 (sept, 1H, ^{i}Pr-C*H*, ^3J = 6.7 Hz), 1.48 (d, 6H, ^{i}Pr-CH_3, ^3J = 6.7 Hz), 1.31 (s, 9H, ^{t}Bu-CH_3), 1.25 (d, 6H, ^{i}Pr-CH_3, ^3J = 6.7 Hz). $^{13}C\{^1H\}$ NMR ppm (C_6D_6) *E* isomer: 155.3 (*C*=O), 147.4 (*C*=N), 137.6, 130.9, 129.6, 129.4, 128.0, 112.9 (PhC*H*), 56.7 ($C(CH_3)_3$), 51.2, 44.5 (^{i}Pr-*C*H), 29.4 (^{t}Bu-*C*H_3), 24.8, 19.8 (^{i}Pr-*C*H_3). *Z* isomer: 160.8 (*C*=O), 149.7 (*C*=N), 138.0, 131.6, 130.1, 129.1, 129.0, 120.4 (PhC*H*), 62.0 ($C(CH_3)_3$), 49.7, 44.0 (^{i}Pr-*C*H), 29.0 (^{t}Bu-*C*H_3), 25.2, 19.8 (^{i}Pr-*C*H_3). FT-IR: $\nu_{C=O}$ 1726 cm^{-1}. ESI-MS for $[C_{20}H_{29}N_3O+Na]^+$: calc. 350.2208; found 350.2194.

4-benzylidene-3-ethyl-1-*iso*propyl-5-(isopropylimino)imidazolidin-2-one, 3



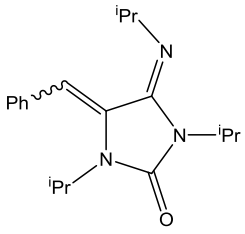
^{1}H NMR ppm (C_6D_6) Major isomer (*Z*) 83%: 6.91-7.15 (m, 5H, Ph-*H*), 6.51 (s, 1H, C*H*Ph), 4.84 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 7.1 Hz), 4.24 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.0 Hz), 3.43 (q, 2H, Et-CH_2, ^{3}J = 7.2 Hz), 1.47 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 7.1 Hz), 1.22 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.0 Hz), 0.60 (t, 3H, Et-CH_3, ^{3}J = 7.2 Hz). Minor isomer (*E*) 17%: 6.91-7.15 (m, 5H, Ph-*H*), 5.81 (s, 1H, C*H*Ph), 4.72 (broad, 1H, ^{i}Pr-C*H*), 3.40 (q, 2H, Et-CH_2, ^{3}J = 7.2 Hz), 3.31 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.0 Hz), 1.42 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.8 Hz), 0.91 (t, 3H, Et-CH_3, ^{3}J = 7.2 Hz), 0.85 (broad d, 6H, ^{i}Pr-CH_3). ^{13}C{^{1}H} NMR ppm (C_6D_6) *Z* isomer: 156.4 (*C*=O), 144.5 (*C*=N), 135.7, 130.6, 129.8, 129.1, 128.6, 110.3 (Ph*C*H), 51.0, 43.8 (^{i}Pr-*C*H), 37.2 (Et-*C*H_2), 24.8, 19.9 (^{i}Pr-*C*H_3), 13.5 (Et-*C*H_3). *E* isomer: 160.2 (*C*=O), 144.4 (*C*=N), 136.4, 129.6, 129.3, 128.5, 127.9, 107.7 (Ph*C*H), 49.7, 44.9 (^{i}Pr-*C*H), 35.0 (Et-*C*H_2), 25.2, 19.9 (^{i}Pr-*C*H_3), 12.5 (Et-*C*H_3). FT-IR: $\nu_{C=O}$ 1732 cm^{-1}. ESI-MS for $[C_{18}H_{25}N_3O+Na]^+$: calc. 322.1895; found 322.1893.

4-benzylidene-1-*iso*propyl-5-(isopropylimino)-3-(*n*-propyl)imidazolidin-2-one, 4



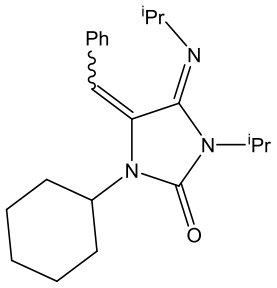
^{1}H NMR ppm (C_6D_6) Major isomer (*Z*) 90%: 6.89-7.10 (m, 5H, Ph-*H*), 6.51 (s, 1H, PhC*H*), 4.88 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.8 Hz), 4.26 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.3 Hz), 3.41 (m, 2H, NCH_2), 1.52 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.8 Hz), 1.23 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.8 Hz), 1.06-1.13 (m, 2H, ^{n}Pr-CH_2), 0.36 (t, 3H, ^{n}Pr-CH_3, ^{3}J = 7.2 Hz). Minor isomer (*E*) 10%: 6.89-7.10 (m, 5H, Ph-*H*), 5.82 (s, 1H, PhC*H*), 4.80 (broad, 1H, ^{i}Pr-C*H*), 3.38 (m, 1H, NCH_2), 3.34 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.5 Hz), 1.58 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 7.4 Hz), 1.06-1.13 (m, 2H, ^{n}Pr-CH_2), 1.04 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.5 Hz), 0.74 (t, 3H, ^{n}Pr-CH_3, ^{3}J = 7.2Hz). ^{13}C{^{1}H} NMR ppm (C_6D_6) *Z* isomer: 156.8 (*C*=O), 144.4 (*C*=N), 135.5, 129.9, 129.1, 128.5, 127.9, 110.4 (PhC*H*), 48.8 (^{i}Pr-*C*H), 43.9 (^{n}Pr-NCH$_2$), 43.6 (^{i}Pr-*C*H), 24.8 (^{i}Pr-*C*H$_3$), 21.0 (^{n}Pr-*C*H$_2$) 19.9 (^{i}Pr-*C*H$_3$), 10.9 (^{n}Pr-*C*H$_3$). The *E* isomer was not present in sufficient concentration to determine all its ^{13}C NMR resonances. An HMQC experiment enabled identification of the *E*-benzylic carbon at δ_{13C} at 107.7 ppm. FT-IR: $\nu_{C=O}$ 1733 cm^{-1}. ESI-MS for $[C_{19}H_{27}N_3O+Na]^+$: calc. 336.2052; found 336.2065.

4-benzylidene-1,3-di(*iso*propyl)-5-(isopropylimino)imidazolidin-2-one, 5



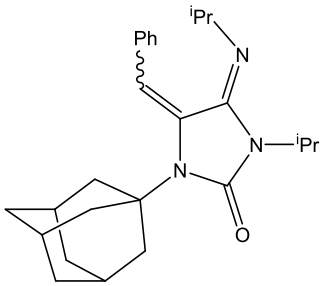
^{1}H NMR ppm (C_6D_6) Major isomer (*E*) 59%: 6.94-7.15 (m, 5H, Ph-*H*), 5.95 (s, 1H, C*H*Ph), 4.71 (broad, 1H, ^{i}Pr-C*H*), 3.99 (broad, 1H, ^{i}Pr-C*H*), 3.37 (broad, 1H, ^{i}Pr-C*H*), 1.49 (broad d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.3 Hz), 1.30 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 7.1 Hz), 0.85 (broad, 6H, ^{i}Pr-CH_3). Minor isomer (*Z*) 41%: 6.94-7.15 (m, 5H, Ph-*H*), 6.50 (s, 1H, C*H*Ph), 4.78 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.8 Hz), 4.24 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.1 Hz), 3.68 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.8 Hz), 1.46 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.8 Hz), 1.26 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.8 Hz), 1.23 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.1 Hz). ^{13}C{^{1}H} NMR ppm (C_6D_6) *E* isomer: 157.3 (*C*=O), 144.7 (*C*=N), 136.2, 130.2, 129.3, 128.9, 128.1, 110.6 (PhC*H*), 48.9, 48.7, 43.6 (^{i}Pr-*C*H), 24.8, 19.8, 19.5 (^{i}Pr-*C*H_3). *Z* isomer: 154.0 (*C*=O), 146.1 (*C*=N), 137.7, 130.9, 129.4, 129.3, 127.8, 108.5 (PhC*H*), 45.3, 44.5, 43.6 (^{i}Pr-*C*H), 24.8, 19.8, 19.7 (^{i}Pr-*C*H_3). FT-IR: $\nu_{C=O}$ 1728 cm^{-1}. ESI-MS for $[C_{19}H_{27}N_3O+Na]^+$: calc. 336.2052, found 336.2052.

4-benzylidene-3-cyclohexyl-1-*iso*propyl-5-(isopropylimino)imidazolidin-2-one, 6



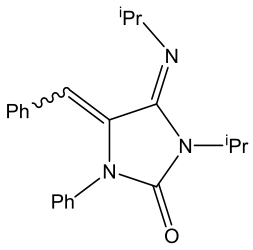
^{1}H NMR ppm (C_6D_6) Major isomer (*E*) 60%: 6.94-7.15 (m, 5H, Ph-*H*), 6.09 (s, 1H, PhC*H*), 4.77 (sept br, 1H, ^{i}Pr-C*H*), 3.66 (broad, 1H, Cy-NC*H*), 3.44 (sept br, 1H, ^{i}Pr-C*H*), 2.33 (qd br, 2H, Cy-CH_2), 1.58-1.62 (m, 4H, Cy-CH_2), 1.54 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.9 Hz), 1.00-1.07 (m, 2H, Cy-CH_2), 0.89 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.0 Hz), 0.57 (qt, 2H, Cy-CH_2, ^{3}J = 3.4, 13.3 Hz). Minor isomer (*Z*) 40%: 6.94-7.15 (m, 5H, Ph-*H*), 6.52 (s, 1H, PhC*H*), 4.85 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.8 Hz), 4.24 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 7.2 Hz), 3.22 (tt, 1H, Cy-NC*H*, ^{3}J = 3.8, 12.1 Hz), 2.47 (qd, 2H, Cy-CH_2, ^{3}J = 3.3, 12.5 Hz), 1.68-1.72 (m, 4H, Cy-CH_2), 1.50 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 7.2 Hz), 0.94-1.07 (m, 4H, Cy-CH_2), 1.25 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.0 Hz). ^{13}C{^{1}H} NMR ppm (C_6D_6) *E* isomer: 155.0, 145.3, 137.7, 131.2, 129.5, 129.4, 127.8, 108.3 (Ph*C*H), 54.0 (^{i}Pr-*C*H), 50.9 (Cy-N*C*H), 44.6 (^{i}Pr-*C*H), 29.6, 26.9 (Cy-*C*H_2), 24.8, 19.8 (^{i}Pr-*C*H_3). *Z* isomer: 156.5 (*C*=O), 144.6 (*C*=N), 136.4, 130.2, 129.1, 128.9, 127.9, 110.2 (Ph*C*H), 56.5 (^{i}Pr-*C*H), 48.8 (Cy-N*C*H), 43.6 (^{i}Pr-*C*H), 30.0, 26.0 (Cy-*C*H_2), 24.9, 19.9 (^{i}Pr-*C*H_3). FT-IR: $\nu_{C=O}$ 1726 cm^{-1}. ESI-MS for $[C_{22}H_{31}N_3O+Na]^+$: calc. 376.2365; found 376.2389.

3-adamantyl-4-benzylidene-1-*iso*propyl-5-(isopropylimino)imidazolidin-2-one, 7



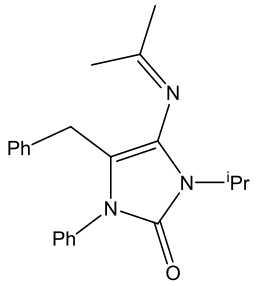
^{1}H NMR ppm (C_6D_6) Major isomer (*E*) 68%: 6.98-7.19 (m, 5H, Ph-*H*), 5.46 (s, 1H, C*H*Ph), 4.67 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.6 Hz), 3.39 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.0 Hz), 2.46 (d, 6H, Ad-CH_2, ^{3}J = 2.5 Hz), 1.98 (broad, 3H, Ad-C*H*), 1.57 (d, 3H, Ad-CH_2, ^{3}J = 12.0 Hz), 1.50 (d, 3H, Ad-CH_2, ^{3}J = 11.5 Hz), 1.49 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.6 Hz), 0.84 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.0 Hz). Minor isomer (*Z*) 32%: 6.98-7.19 (m, 5H, Ph-*H*), 6.52 (s, 1H, C*H*Ph), 4.73 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.9 Hz), 4.29 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.0 Hz), 2.22 (d, 6H, Ad-CH_2, ^{3}J = 2.8 Hz), 1.81 (broad, 3H, Ad-C*H*), 1.48 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.9 Hz), 1.38 (d, 3H, Ad-CH_2, ^{3}J = 13.0 Hz), 1.33 (d, 3H, Ad-CH_2, ^{3}J = 12.5 Hz), 1.28 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.0 Hz). ^{13}C{^{1}H} NMR ppm (C_6D_6) *E* isomer: 155.5 (*C*=O), 148.1 (*C*=N), 137.6, 130.3, 129.6, 129.4, 128.0, 115.0 (Ph*C*H), 59.1 (Ad-N*C*), 49.8, 44.6 (^{i}Pr-*C*H), 41., 36.9 (Ad-*C*H_2), 30.8 (Ad-*C*H), 24.9, 19.8 (^{i}Pr-*C*H_3). *Z* isomer: 159.8 (*C*=O), 149.8 (*C*=N), 138.2, 131.1, 130.3, 129.1, 128.6, 120.8 (Ph*C*H), 63.7 (Ad-N*C*), 51.2, 44.1 (^{i}Pr-*C*H), 40.8, 36.7 (Ad-*C*H_2), 31.0 (Ad-*C*H), 25.3, 19.9 (^{i}Pr-*C*H_3). FT-IR: $\nu_{C=O}$ 1719 cm^{-1}. ESI-MS for $[C_{26}H_{35}N_3O+Na]^+$: calc. 428.2678; found 428.2695.

4-benzylidene-1-*iso*propyl-5-(isopropylimino)-3-phenylimidazolidin-2-one, 8



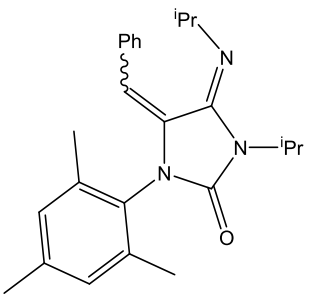
^{1}H NMR ppm (C_6D_6) Major isomer (*Z*) 85%: 6.96 (dm, 2H, *o*-Ph-*H*, ^{3}J = 8.1 Hz), 6.79 (t, 2H, Ph-H, ^{3}J = 8.1 Hz), 6.68-6.77 (m, 6H, Ph-*H*), 6.67 (s, 1H, C*H*Ph), 4.91 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.8 Hz), 4.38 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.1 Hz), 1.51 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.8 Hz), 1.33 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.1 Hz). Minor isomer (*E*) 15%: 6.97-7.26 (m, 10H, Ph-*H*), 6.05 (s, 1H, C*H*Ph), 4.86 (broad, 1H, ^{i}Pr-C*H*), 3.45 (broad, 1H, ^{i}Pr-C*H*), 1.58 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.8 Hz), 0.94 (broad d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.1 Hz). ^{13}C{^{1}H} NMR ppm (C_6D_6) *Z* isomer: 155.1 (*C*=O), 144.3 (*C*=N), 136.2, 134.3, 130.04(C-1 *C*=C), 129.5, 128.4, 127.8, 127.3, 127.0, 126.5, 112.3, 110.03, 49.0, 44.0, 24.9, 19.8. Due to solution fluxionality most ^{13}C NMR resonances for the *E* isomer were too broad to identify. An HMQC experiment enabled identification of the *E*-benzylic carbon at δ_{13C} at 110.0 ppm. FT-IR: $\nu_{C=O}$ 1731 cm^{-1}. ESI-MS for $[C_{22}H_{25}N_3O+Na]^+$: calc. 370.1895; found 370.1906.

4-benzyl-1-*iso*propyl-5-*iso*propylideneamino-3-phenylimidazol-2-one



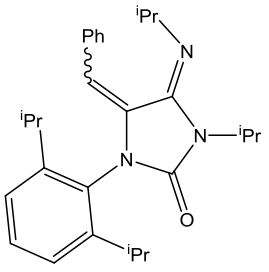
An *in situ* made solution of 4-benzylidene-1-*iso*propyl-5-(isopropylimino)-3-phenylimidazolidin-2-one was heated at 80 ^{o}C for 2 hours, leading to quantitative conversion to the corresponding imidazole-2-one. ^{1}H NMR ppm (C_6D_6): 7.18 (d, 2H, NPh-*H*, ^{3}J = 7.6 Hz), 7.00 (t, 2H, *m*-Ph-*H*, ^{3}J = 7.6 Hz), 6.90-6.95 (m, 4H, Ph-*H*), 6.81 (d, 2H, *o*-Ph-*H*, ^{3}J = 7.6 Hz), 4.57 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.8 Hz), 3.30 (s, 2H, PhCH_2), 1.75 (s, 3H, N=C(CH_3)$_2$), 1.61 (s, 3H, N=C(CH_3)$_2$), 1.44 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.8 Hz). ^{13}C{^{1}H} NMR ppm (C_6D_6): 173.8 (*C*=N), 152.1 (*C*=O), 138.7 (*i*-Ph-*C*), 136.9 (*i*-NPh-*C*), 130.2 (C=*C*N^{i}Pr), 129.1, 128.8, 128.8, 128.7, 127.1, 126.7, 103.8 (PhCH$_2$*C*), 45.6 (^{i}Pr-*C*H), 30.6 (Ph*C*H$_2$), 28.3 (^{i}Pr-*C*H$_3$), 22.2, 21.4 (N=C(*C*H$_3$)$_2$.

4-benzylidene-1-*iso*propyl-5-(isopropylimino)-3-mesitylimidazolidin-2-one, 9



^{1}H NMR ppm (C_6D_6) Major isomer (*Z*) > 99%: 6.76 (t, 1H, Ph-*p*-H, ^{3}J = 7.6 Hz), 6.71 (t, 2H, Ph-*m*-H, ^{3}J = 7.6 Hz), 6.66 (d, 2H, Ph-*o*-H, ^{3}J = 7.6 Hz), 6.61 (s, 1H, C*H*Ph*)*, 6.36 (s, 2H, Mes-*m*-H), 4.21 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.9 Hz), 4.32 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.0 Hz), 2.00 (s, 6H, Mes-*o*-CH_3), 1.95 (s, 6H, Mes-*p*-CH_3), 1.55 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.9 Hz), 1.31 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.0 Hz). ^{13}C{^{1}H} NMR ppm (C_6D_6) *Z* isomer: 154.3 (*C*=O), 144.2 (*C*=N), 138.2, 136.8, 133.7, 132.3, 129.3, 128.6, 128.1, 126.8, 111.2 (Ph*C*H), 48.9, 44.0 (^{i}Pr-*C*H), 24.9 (^{i}Pr-*C*H$_3$), 21.1 (Mes-*p*-*C*H$_3$), 19.9 (^{i}Pr-*C*H$_3$), 18.6 (Mes-*o*-*C*H$_3$). FT-IR: $\nu_{C=O}$ 1732 cm^{-1}. ESI-MS for $[C_{25}H_{31}N_3O+Na]^+$: calc. 412.2365, found 412.2384.

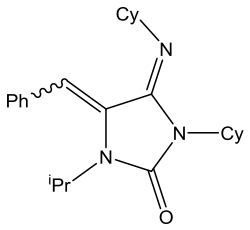
4-benzylidene-3-(2,6-di-*iso*propylphenyl)-1-*iso*propyl-5-(isopropylimino)imidazolidin-2-one, 10



^{1}H NMR ppm (C_6D_6) Major isomer (*Z*) 90%: 7.05 (t, 1H, Dipp-*p*-H, ^{3}J = 8.1 Hz), 6.83 (d, 2H, Dipp-*m*-H, ^{3}J = 8.1 Hz), 6.72-6.77 (m, 3H, Ph-*H*), 6.64 (d, 2H, Ph-*H*, ^{3}J = 7.3 Hz), 6.63 (s, 1H, C*H*Ph), 4.91 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.8 Hz), 4.34 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.1 Hz), 2.92 (sept, 2H, Dipp-^{i}Pr-C*H*, ^{3}J = 6.8 Hz), 1.54 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.8 Hz), 1.29 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.1 Hz), 1.19 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.8 Hz), 0.99 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.8 Hz). Minor isomer (*E*) 10%: 6.72-7.03 (m, 8H, Ar-*H*), 5.67 (s, 1H, C*H*Ph), 4.20 (two overlapping sept, 2H, Dipp/^{i}Pr-C*H*), 3.64 (sept, 1H, ^{i}Pr-C*H*, ^{3}J

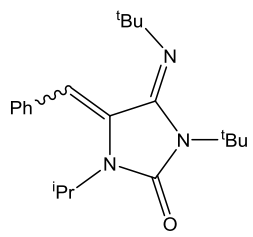
= 7.0 Hz), 3.12 (sept, 1H, Dipp-^{i}Pr-C*H*, ^{3}J = 6.1 Hz), 1.55 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 7.0 Hz), 1.12 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.6 Hz), 1.03 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.1 Hz), 0.89 (broad, 6H, ^{i}Pr-CH_3). ^{13}C{^{1}H} NMR ppm (C_6D_6) *Z* isomer: 155.6 (*C*=O), 148.0 (Dipp-*i*-C), 144.24 (*C*=N), 137.7, 133.4 (Dipp-*o*-C), 130.0, 129.9, 129.6, 127.7, 127.1, 124.1, 111.9 (Ph*C*H), 49.0, 43.9 (^{i}Pr-*C*H), 29.7 (Dipp-^{i}Pr-*C*H), 25.4, 25.0, 22.6, 19.8 (^{i}Pr-*C*H_3). *E* isomer: 157.2 (*C*=O), 149.0 (Dipp-*i*-C), 142.7 (*C*=N), 138.1, 133.3 (Dipp-*o*-C), 131.3, 130.6, 129.1, 128.8, 125.1, 123.4, 110.6 (Ph*C*H), 49.0, 44.8 (^{i}Pr-*C*H), 28.8 (Dipp-^{i}Pr-*C*H), 24.6, 24.2, 23.0, 19.7 (^{i}Pr-*C*H_3). FT-IR: $\nu_{C=O}$ 1740 cm^{-1}. ESI-MS for $[C_{28}H_{37}N_3O+Na]^+$: calc. 454.2834, found 454.2834.

4-benzylidene-1-cyclohexyl-5-cyclohexylimino-3-*iso*propylimidazolidin-2-one, 11



^{1}H NMR ppm (C_6D_6) Major isomer (*E*) 75%: 6.98-7.14 (m, 5H, Ph-*H*), 5.92 (s, 1H, C*H*Ph), 4.55, 4.05 (two tt, 1H each, Cy-C*H*, ^{3}J = 10.1, 3.7 Hz), 3.98 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.9 Hz), 2.64 (m, 2H, Cy-CH_2), 0.78-1.91 (m, 8H, Cy-CH_2), 1.31 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.9 Hz). Minor isomer (*Z*) 25%: 6.98-7.14 (m, 5H, Ph-*H*), 6.56 (s, 1H, C*H*Ph), 4.15, 4.02 (two tt, 1H each, Cy-C*H*, ^{3}J = 12.1, 3.9 Hz), 3.74 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.8 Hz), 3.04 (m, 2H, Cy-CH_2), 0.78-1.91 (m, 8H, Cy-CH_2), 1.32 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.8 Hz). ^{13}C{^{1}H} NMR ppm (C_6D_6) *E* isomer: 155.1 (*C*=O), 145.1 (*C*=N), 141.9 (PhCH=*C*), 138.0, 129.4, 129.3, 127.9, 108.2 (Ph*C*H), 58.8, 52.5 (Cy-*C*H), 45.3 (^{i}Pr-*C*H), 35.0, 34.9, 29.7, 27.0, 26.2, 25.0 (Cy-*C*H_2), 19.5 (^{i}Pr-*C*H_3). *Z* isomer: 154.3, 144.8, 143.9, 136.3, 130.4, 128.9, 127.9, 110.3, 57.9, 51.8, 45.7, 36.4, 34.9, 29.6, 27.1, 26.4, 25.1, 19.9. FT-IR: $\nu_{C=O}$ 1727 cm^{-1}. ESI-MS for $[C_{25}H_{35}N_3O+H]^+$: calc. 394.2858, found 394.2923; $[C_{25}H_{35}N_3O+Na]^+$: calc. 416.2678, found 416.2673.

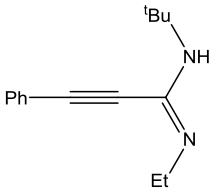
4-benzylidene-3-*iso*propyl-1-(*tert*-butyl)-5-(*tert*-butylimino)imidazolidin-2-one, 12



^{1}H NMR data showed instant and quantitative insertion of *iso*propylisocyanate into (*N*,*N*'-di-*tert*-butyl)phenylpropargylamidine at room temperature using 5 mol% of $[Sr\{N(SiMe_3)_2\}_2(THF)_2]$ to yield the corresponding *N*,*N*'-di(*tert*-butyl)-*N*-(*iso*propyl)carbamoyl-3-phenylprop-2-ynimidamide. ^{1}H NMR monitoring of the reaction mixture at room temperature showed 75% cyclization after 40 hours. A further 6 hours of heating at 80 ^{o}C provided the N-heterocyclic compound in 92% yield by ^{1}H NMR spectroscopy. ^{1}H NMR ppm (C_6D_6) Major isomer (*E*) 75%: 7.35-7.39 (m, 2H, Ph-*H*), 6.93-7.11 (m, 3H, Ph-H), 5.80 (s, 1H, C*H*Ph), 3.99 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 7.0 Hz), 1.82 (s, 9H,

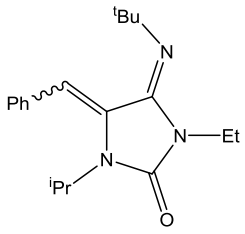
^{t}Bu-CH_3), 1.28 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 7.0 Hz), 0.98 (s, 9H, ^{t}Bu-CH_3). Minor isomer (*Z*) 25% : 7.35-7.39 (m, 2H, Ph-*H*), 6.93-7.11 (m, 3H, Ph-H), 6.43 (s, 1H, C*H*Ph), 3.63 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.6 Hz), 1.81 (s, 9H, ^{t}Bu-CH_3), 1.45 (s, 9H, ^{t}Bu-CH_3), 1.32 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.6 Hz). ^{13}C{^{1}H} NMR ppm (C_6D_6) *E* isomer: 155.3 (*C*=O), 144.2 (*C*=N), 137.5, 130.9, 129.4, 127.9, 108.7 (Ph*C*H), 68.2 (*C*=N)*C*Me$_3$), 56.6 (N*C*Me$_3$), 45.2 (^{i}Pr-*C*H), 30.2, 29.0 (^{t}Bu-*C*H$_3$), 19.5 (^{i}Pr-*C*H$_3$). *Z* isomer: 154.9, 143.8, 136.0, 132.0, 129.6, 128.9, 112.6, 71.8, 52.1, 49.9, 29.4, 29.3, 20.2. FT-IR: $\nu_{C=O}$ 1731 cm^{-1}. ESI-MS for $[C_{21}H_{31}N_3O+H]^+$: calc. 342.2545, found 342.2555; $[C_{21}H_{31}N_3O+Na]^+$: calc. 364.2365, found 364.2385.

(N-ethyl-N'-tert-butyl)phenylpropargylamidine



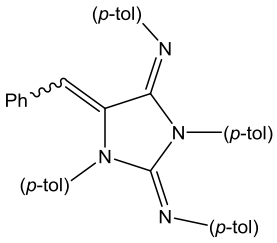
^{1}H NMR ppm (C_6D_6): 7.36-7.39 (m, 2H, Ph-*H*), 6.92-6.97 (m, 3H, Ph-*H*), 4.11 (broad singlet, N*H*), 3.80 (broad q, 2H, Et-CH_2), 1.32-1.45 (broad, 12H, ^{t}Bu/Et-CH_3). ^{13}C{^{1}H} NMR ppm (C_6D_6): 132.4, 129.6, 129.1, 122.6, 115.2 (Ph*C*≡C), 81.8 (PhC≡*C*), 52.2 (^{t}Bu-*C*), 47.8 (Et-*C*H$_2$), 29.9 (^{t}Bu-*C*H$_3$), 17.9 (Et-*C*H$_3$). ESI-MS for $[C_{15}H_{10}N_2+H]^+$: calc. 229.1705; found 229.1699.

4-benzylidene-1-ethyl-3-*iso*propyl-5-(*tert*-butylimino)imidazolidin-2-one, 13



The regioselectivity of the isocyanate insertion into the *N*-ethyl moiety was determined by HMBC and NOESY NMR experiments. ^{1}H NMR ppm (C_6D_6) Major isomer (*E*) 66%: 7.61 (d, 2H, *o*-Ph-*H*, ^{3}J = 7.8 Hz), 7.22 (t, 2H, *m*-Ph-*H*, ^{3}J = 7.8 Hz), 7.05 (t, 1H, *p*-Ph-*H*, ^{3}J = 7.8 Hz), 5.85 (s, 1H, C*H*Ph), 4.04 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.8 Hz), 3.63 (q, 2H, Et-CH_2, ^{3}J = 7.0 Hz), 1.30 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.8 Hz), 1.08 (s, 9H, ^{t}Bu-CH_3), 1.03 (t, 3H, Et-CH_3, ^{3}J = 7.0 Hz). Minor isomer (*Z*) 34%: 6.90-7.15 (m, 5H, Ph-*H*), 6.61 (s, 1H, C*H*Ph), 4.04 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.8 Hz), 3.72 (q, 2H, Et-CH_2, ^{3}J = 7.1 Hz), 1.44 (s, 9H, ^{t}Bu-CH_3), 1.28 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.8 Hz), 1.16 (t, 3H, Et-CH_3, ^{3}J = 7.1 Hz). ^{13}C{^{1}H} NMR ppm (C_6D_6) *E* isomer: 156.4 (*C*=O), 137.4 (*C*=N), 137.1, 134.2, 131.1, 128.0, 126.9, 107.9 (Ph*C*H), 53.5 (^{t}Bu-*C*), 45.0 (^{i}Pr-*C*H), 38.7 (Et-*C*H$_2$), 31.9 (^{t}Bu-*C*H$_3$), 19.8 (^{i}Pr-*C*H$_3$), 14.5 (Et-*C*H$_3$). *Z* isomer: 157.2, 142.7, 136.0, 131.4, 129.8, 129.0, 128.1, 113.0, 53.0, 49.4, 34.7, 31.1, 20.0, 14.5. FT-IR: $\nu_{C=O}$ 1730 cm^{-1}. ESI-MS for $[C_{19}H_{27}N_3O+H]^+$: calc. 314.223238; found 314.2246.

***N,N'*-[5-benzylidene-1,3-bis(*p*-tolyl)imidazolidine-2,4-diylidene]bis(*p*-toluidine), 14**



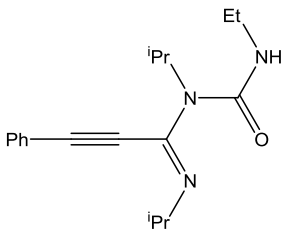
To 0.5 mL of a 1.0 mM solution of **1a** in a 9:1 C_6D_6/d_8-THF mixture were added 44.5 mg (0.2 mmol) of di-(*p*-tolyl)carbodiimide followed by 11 μL (0.1 mmol) of phenylacetylene in the glovebox. The reaction mixture was transferred into a sealed Young's tap NMR tube. 80% conversion by ^{1}H NMR spectroscopy to compound **7** was reached after heating for 4 hours at 80 ^{o}C. The reaction mixture was then carefully hydrolyzed with 0.5 mL of water, extracted with 1 mL of toluene and the organic phase dried over $MgSO_4$ prior to filtration. The imidazolidine was recrystallized by slow evaporation of toluene in the fridge over 2 days, isolated as a pale yellow compound, washed with hexanes and dried *in vacuo* (33 mg, 50 μmol, 50% yield). In solution the compound was highly fluxional at room temperature and had to be cooled to 228 K to resolve the NMR resonances of the *E* and *Z* isomers present in solution in a 3:1 ratio. ^{1}H NMR ppm ($CDCl_3$, 228 K) Major isomer (*Z*) 75%: 7.07, 7.05, 6.98, 6.84, 6.82, 6.77, 6.54, 6.30 (eight doublets, 2H each, *o*/*m*-tol-*H*, ^3J = 8.0 Hz), 5.82 (s, 1H, PhC*H*=C), 2.27, 2.19, 2.15, 2.08 (four singlets, 3H each, tol-CH_3). Minor isomer (*E*) 25%: 7.56, 7.34, 7.92, 7.89, 7.59, 7.44, 7.40, 7.20 (eight d, 2H each, *o*/*m*-tol-*H*, ^3J = 8.0 Hz), 5.86 (s, 1H, PhC*H*=C), 2.36, 2.23, 2.05, 1.99 (four s, 3H each, tol-CH_3). ^{13}C{^{1}H} NMR ppm ($CDCl_3$, 228 K) *Z* isomer: 148.7, 146.0, 145.9, 144.0, 141.8, 137.1, 136.1, 136.0, 133.2, 133.1, 131.8, 129.9, 129.8, 128.7, 128.4, 128.3, 128.1, 127.7, 126.8, 126.5, 125.8, 121.6, 119.0, 110.1 (Ph*C*H=C), 21.1, 21.0, 20.9, 20.6 (tol-*C*H_3). The *E* isomer was not present in sufficient concentration to determine all its ^{13}C NMR resonances. ESI-MS for $[C_{48}H_{34}N_4+H]^+$: calc. 547.2862; found 547.2908.

Synthesis of (*N*-carbamoyl)alkynylimidamides

The addition of 0.2 mmol of various isocyanates to a C_6D_6 solution of 0.2 mmol of isolated (*N*,*N'*-di-*iso*propyl)phenylpropargylamidine did not result in any reactivity. In the case of ethylisocyanate instant and quantitative insertion was observed at room temperature upon addition of 0.1 mol% of $[Sr\{N(SiMe_3)_2\}_2(THF)_2]$, without any evidence of cyclization. In the case of (2,6-di-*iso*propylphenyl)isocyanate addition of 0.1 mol% of $[Sr\{N(SiMe_3)_2\}_2(THF)_2]$ resulted in slow insertion over a period of 18 hours at room temperature, without any evidence of cyclization. In all cases turnover to the N-heterocyclic product was only observed when catalyst loadings were increased to 0.5 mol%, with the ethyl derivative reaching 91% conversion after 20 minutes and the 2,6-di-*iso*propylphenyl derivative only reaching 78%

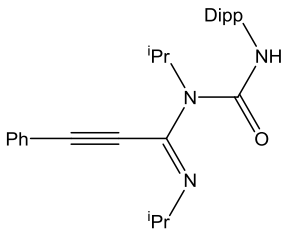
conversion after 18 hours at room temperature. The (*N*-carbamoyl)alkynylimidamides all proved highly air-sensitive and underwent rapid de-insertion/hydrolysis.

_N,N'_-di(*iso*propyl)-*N*-ethylcarbamoyl-3-phenylprop-2-ynimidamide



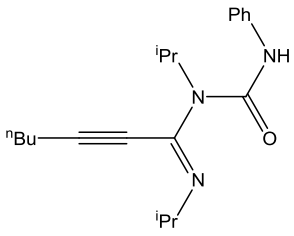
^{1}H NMR ppm (C_6D_6): 10.30 (broad, 1H, N*H*), 7.28 (dd, 2H, Ph-*H*, ^{3}J = 7.7, ^{4}J = 1.7 Hz), 6.92-7.00 (m, 3H, Ph-*H*), 4.94 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 7.0 Hz), 4.12 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.3 Hz), 3.40 (dq, 2H, Et-CH_2, ^{3}J = 7.3, 5.1 Hz), 1.70 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 7.0 Hz), 1.21 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.3 Hz), 1.05 (t, 3H, Et-CH_3, ^{3}J = 7.3 Hz). ^{13}C{^{1}H} NMR ppm (C_6D_6): 156.1 (*C*=O), 144.2 (*C*=N), 132.5 (*o*-Ph-*C*), 130.4 (*p*-Ph-*C*), 129.2 (*m*-Ph-*C*), 121.6 (*i*-Ph-*C*), 98.2 (Ph*C*≡C), 79.0 (PhC≡*C*), 53.8, 51.9 (N^{i}Pr-*C*H), 35.6 (Et-*C*H_2), 24.7, 21.9 (^{i}Pr-*C*H_3), 15.6 (Et-*C*H_3). ESI-MS for $[C_{18}H_{25}N_3O+Na]^+$: calc. 322.1895; found 322.1893.

_N,N'_-di(*iso*propyl)-*N*-(2,6-di-*iso*propylphenyl)carbamoyl-3-phenylprop-2-ynimidamide



^{1}H NMR ppm (C_6D_6): 12.03 (s, 1H, N*H*), 7.18-7.30 (m, 4H, Ar-*H*), 6.89-7.00 (m, 4H, Ar-*H*), 5.02 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.8 Hz), 4.19 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.4 Hz), 3.53 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.4 Hz), 1.72 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.8 Hz), 1.37 (broad d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.8 Hz), 1.25 (broad d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.4 Hz), 1.21 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.8 Hz). ^{13}C{^{1}H} NMR ppm (C_6D_6): 155.1 (*C*=N), 146.9 (*o*-Dipp-*C*), 144.8 (PhC≡C*C*), 133.9 (*i*-Dipp-*C*), 132.4 (*o*-Ph-*C*), 130.6 (*p*-Ph-*C*), 129.3 (*m*-Ph-*C*), 128.0 (*p*-Dipp-*C*), 123.9 (*m*-Dipp-*C*), 121.3 (*i*-Ph-*C*), 99.3 (Ph*C*≡C), 78.6 (PhC≡*C*), 53.9, 52.7 (N^{i}Pr-*C*H), 29.8 (Dipp-^{i}Pr-*C*H), 25.0, 24.6, 23.9, 21.8 (^{i}Pr-*C*H_3). ESI-MS for $[C_{28}H_{37}N_3O+Na]^+$: calc. 454.2834, found 454.2834.

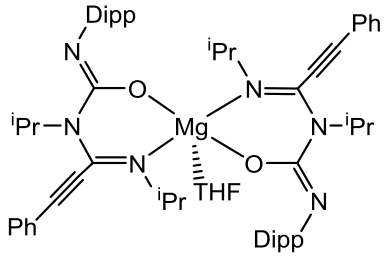
_N,N'_-di(*iso*propyl)-*N*-phenylcarbamoyl-3-hept-2-ynimidamide, 17



^{1}H NMR ppm (C_6D_6): 13.29 (s, 1H, N*H*), 7.85 (dm, 2H, *o*-Ph-*H*, ^{3}J = 8.5 Hz), 7.16-7.21 (m, 2H, *m*-Ph-*H*), 6.98 (tt, 1H, *p*-Ph-*H*, ^{3}J = 7.5, ^{2}J = 1.2 Hz), 4.85 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.8 Hz), 3.97 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.4 Hz), 1.96 (t, 2H, CH_2C≡C, ^{3}J = 6.8 Hz), 1.63 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.8 Hz), 1.10-1.24 (m, 4H, ^{n}Bu-CH_2), 1.04 (d, 6H, ^{i}Pr-CH_3, ^{3}J = 6.4 Hz), 0.73 (t, 2H, ^{n}Bu-CH_3, ^{3}J = 6.9 Hz). ^{13}C{^{1}H} NMR ppm (C_6D_6): 153.5 (*C*=O), 144.8 (*C*=N), 140.8 (*i*-Ph-*C*), 129.5, 123.3, 120.2, 101.9 (Ph*C*≡C), 70.8 (PhC≡*C*),

53.6, 52.4 (^{i}Pr-*C*H), 30.5, 26.2 (^{n}Bu-*C*H$_2$), 24.4, 21.6 (^{i}Pr-*C*H$_3$), 19.1 (^{n}Bu-*C*H$_2$), 13.8 (^{n}Bu-*C*H$_3$). ESI-MS for $[C_{20}H_{30}N_3O+H]^+$: calc. 328.2389; found 328.2364.

Magnesium bis(*N*-{[2,6-di-*iso*propylphenyl]carbamoyl}-3-phenyl-*N*,*N*'-(di-*iso*propyl)-prop-2-ynimidamidate} THF adduct, 18



Phenylacetylene (28.6 µL, 0.26 mmol) and di(*iso*propyl)carbodiimide (40.7 µL, 0.26mol) were added to a d$_8$-toluene solution of [Mg{CH$_2$Ph}$_2$(THF)$_2$] (50 mg, 0.13 mmol). The reaction mixture was heated at 60 ^{o}C for 5h after which (2,6-di-isopropylphenyl)isocyanate (55.6 µL, 0.26 mmol) was added. NMR data confirmed full conversion of the homoleptic bis(propargylamidinate) to the desired isocyanate insertion product, complex **4**. Colourless crystals of **4** were obtained through slow evaporation of a saturated toluene/hexanes 1:1 solution in the glovebox (86 mg, 90 µmol, 69% yield). ^{1}H NMR (C$_6$D$_6$): 7.20-7.26 (m, 4H, Ph-*H*), 6.88-6.99 (m, 4H, Ph-*H*), 4.91 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.8 Hz), 4.14 (sept, 1H, ^{i}Pr-C*H*, ^{3}J = 6.8 Hz), 3.56 (m, 4H, THF), 3.48 (sept, 2H, Dipp-^{i}Pr-C*H*, ^{3}J = 6.4 Hz), 1.91 (d, 6H, ^{i}Pr-C*H$_3$*, ^{3}J = 6.8 Hz), 1.40 (m, 4H, THF), 1.37 (d, 12H, Dipp-^{i}Pr-C*H$_3$*, ^{3}J = 6.4 Hz), 1.24 (d, 6H, ^{i}Pr-C*H$_3$*, ^{3}J = 6.8 Hz). ^{13}C{^{1}H} NMR ppm (C$_6$D$_6$): 151.4 (O*C*=NDipp), 151.0 (^{i}PrN-*C*=N^{i}Pr), 147.4 (*i*-Dipp-*C*), 140.1 (*o*-Dipp-*C*), 132.5, 129.3, 126.8, 122.9, 122.1, 121.3 (*i*-Ph-*C*), 100.3 (Ph*C*≡C), 80.7 (PhC≡*C*), 55.0, 54.6 (N^{i}Pr-*C*H), 29.3 (Dipp-^{i}Pr-*C*H), 25.1, 23.4, 22.5 (^{i}Pr-*C*H$_3$). Elemental analysis for [C$_{60}$H$_{79}$MgN$_6$O$_3$] (M$_w$ = 956.6): calc. %C 75.33, %H 8.32, %N 8.79; found %C 75.45 , %H 8.56, %N 8.51.

Figure S1: Representative ^{1}H, $^{13}C\{^{1}H\}$ and NOESY spectra of *E/Z*-4-benzylidene-1-*iso*propyl-5-(isopropylimino)-3-(*tert*-butyl)imidazolidin-2-one, **2**