Supporting Information:

\[ \alpha\text{-Diimine Synthesis via Titanium-Mediated Multicomponent Diimination of Alkynes with C-Nitrosos} \]

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General Considerations

Addition of nitrosobenzene to 1 (NMR scale)

Figure S1. Stacked $^1$H NMR spectra (C$_6$D$_6$) of nitrosobenzene addition to 1; Bottom (red trace): nitrosobenzene (2a) prior to addition; Middle-bottom (green trace): p-tolunitrile, Middle-top (blue trace): 1 prior to addition of nitrosobenzene; Top (purple trace): After addition of nitrosobenzene to 1, $t = 0.5$ h at room temperature, showing 81% yield of 3a according to 1,3,5-trimethoxybenzene standard.

Figure S2. $^1$H NMR spectrum (C$_6$D$_6$) after nitrosobenzene addition to 1 after 0.5 h, showing 81% yield of 3a according to 1,3,5-trimethoxybenzene standard.

Scope of nitroso addition to py$_2$TiCl$_2$(ADA$^E$) (1) (Table 1, 3a – 3o) (isolation scale)

(2E,3E)-N$^a$N$^a$-diphenylpentane-2,3-diimine (3a)

Figure S3. $^1$H NMR spectrum of 3a in C$_6$D$_6$.

Figure S4. $^{13}$C NMR spectrum of 3a in C$_6$D$_6$.

Figure S5. $^1$H–$^{13}$N HMBC NMR spectrum of 3a in C$_6$D$_6$.

(2E,3E)-N$^a$-(3,5-dimethylphenyl)-N$^a$-phenylpentane-2,3-diimine (3b)

Figure S6. $^1$H NMR spectrum of 3b in C$_6$D$_6$.

Figure S7. $^{13}$C NMR spectrum of 3b in C$_6$D$_6$.

(2E,3E)-N$^a$-mesityl-N$^a$-phenylpentane-2,3-diimine (3c)

Figure S8. $^1$H NMR spectrum of 3c in C$_6$D$_6$.

Figure S9. $^{13}$C NMR spectrum of 3c in C$_6$D$_6$.

(2E,3E)-N$^a$-phenyl-N$^a$-(4-(trifluoromethyl)phenyl)pentane-2,3-diimine (3d)

Figure S10. $^1$H NMR spectrum of 3d in C$_6$D$_6$.

Figure S11. $^{13}$C NMR spectrum of 3d in C$_6$D$_6$, inset shows quartets from $^{13}$C–$^{19}$F coupling.

Figure S12. $^{19}$F NMR spectrum of 3d in C$_6$D$_6$ with trifluoroacetic acid (neat) reference capillary (δ -77.80).

(2E,3E)-N$^a$-(4-bromophenyl)-N$^a$-phenylpentane-2,3-diimine (3e)

Figure S13. $^1$H NMR spectrum of 3e in C$_6$D$_6$.

Figure S14. $^{13}$C NMR spectrum of 3e in C$_6$D$_6$.

(2E,3E)-N$^a$-(4-ethoxycarbonylphenyl)-N$^a$-phenylpentane-2,3-diimine (3f)

Figure S15. $^1$H NMR spectrum of 3f in C$_6$D$_6$.

Figure S16. $^{13}$C NMR spectrum of 3f in C$_6$D$_6$.

(2E,3E)-N$^a$-phenyl-N$^a$-(p-tolyl)pentane-2,3-diimine (3g)

Figure S17. $^1$H NMR spectrum of 3g in C$_6$D$_6$.

Figure S18. $^{13}$C NMR spectrum of 3g in C$_6$D$_6$.

(2E,3E)-N$^a$-(4-methoxyphenyl)-N$^a$-phenylpentane-2,3-diimine (3h)

Figure S19. $^1$H NMR spectrum of 3h in C$_6$D$_6$.

Figure S20. $^{13}$C NMR spectrum of 3h in C$_6$D$_6$.

(2E,3E)-N$^a$-(4-N,N-dimethyl)-N$^a$-phenylpentane-2,3-diimine (3i) (Not isolated)

Figure S21. $^1$H NMR spectrum of 3i in C$_6$D$_6$.

Figure S22. GC-MS of 3i reaction mixture after workup.
(2E,3E)-N²-(4-N,N-dimethyl)-N²-phenylpentane-2,3-diimine (3i) (NMR scale)

Figure S23. Stacked ¹H NMR spectra (CD₅D₆) of addition of 2i to 1; Bottom (green trace): 2i prior to addition; Middle (blue trace): 1 prior to addition; Top (purple trace): After addition of 2i to 1, t = 0.5 h at room temperature, showing 49% yield of 3i according to 1,3,5-trimethoxybenzene standard, with unidentified product also formed.

Figure S24. ¹H NMR spectrum (CD₅D₆) of addition of 2i to 1, showing 49% yield of 3i according to 1,3,5-trimethoxybenzene standard, with unidentified product also formed.

(2E,3E)-N²-phenyl-N²-(o-(trifluoromethyl)phenyl)pentane-2,3-diimine (3j)

Figure S25. ¹H NMR spectrum of 3j in CD₅D₆.

Figure S26. ¹³C NMR spectrum of 3j in CD₅D₆, inset shows quartets from ¹³C-¹⁹F coupling.

Figure S27. ¹⁹F NMR spectrum of 3j in CD₅D₆ with trifluoroacetic acid (neat) reference capillary (δ - 77.80).

(2E,3E)-N²-phenyl-N²-(o-tolyl)pentane-2,3-diimine (3k)

Figure S28. ¹H NMR spectrum of 3k in CD₅D₆.

Figure S29. ¹³C NMR spectrum of 3k in CD₅D₆.

(2E,3E)-N²-phenyl-N²-(o-methoxyphenyl)pentane-2,3-diimine (3l)

Figure S30. ¹H NMR spectrum of 3l in CD₅D₆ (Diimine denoted in red, enamine in blue).

Figure S31. ¹³C NMR spectrum of 3l in CD₅D₆.

(2E,3E)-N²-phenyl-N²-(pyridin-2-yl)pentane-2,3-diimine (3m) (NMR scale)

Figure S32. Stacked ¹H NMR spectra (CD₅D₆) of addition of 2m to 1; Bottom (red trace): pyridine, Middle-bottom (light green trace): p-tolunitrile; Middle (green trace): 2m prior to addition, Middle-top (blue trace): 1 prior to addition; Top (purple trace): reaction mixture showing 3m in 20% yield, p-tolunitrile (85%), and free pyridine versus 1,3,5-trimethoxybenzene standard.

Figure S33. ¹H NMR spectrum (CD₅D₆) of addition of 2m to 1, showing 3m in 20% yield, p-tolunitrile (85%), and free pyridine versus 1,3,5-trimethoxybenzene standard.

(2E,3E)-N²-(tert-butyl)-N²-phenylpentane-2,3-diimine (3n)

Figure S34. ¹H NMR spectrum of 3n in CD₅D₆ (Diimine denoted in red, enamine in blue).

Figure S35. ¹³C NMR spectrum of 3n in CD₅D₆ (Diimine denoted in red, enamine in blue).

(2E,3E)-N²-(adamantan-1-yl)-N²-phenylpentane-2,3-diimine (3o)

Figure S36. ¹H NMR spectrum of 3o in CD₅D₆ (Diimine denoted in red, enamine in blue).

Figure S37. ¹³C NMR spectrum of 3o in CD₅D₆ (Diimine denoted in red, enamine in blue).

Multicomponent coupling of [py₂TiCl₂(NPh)]₂, 3-hexyne, and acetonitrile with subsequent nitrosobenzene addition for the synthesis of N²,N²-diphenylbutane-2,3-diimine (5a) (NMR scale)

Figure S38. Stacked ¹H NMR spectra characterizing the multicomponent coupling of 3-hexyne (1 equiv.), MeCN (1 equiv.) and [py₂TiCl₂(NPh)]₂ in CD₅D₆Br; Bottom (red trace): t = 0; Middle (green trace): t = 4 h at 115 °C generating metallacycle 1b in 54% yield; Top (blue trace): t = 0.5 h after nitrosobenzene addition to give diimine 5b in 48% yield (90% with respect to 1b).

Figure S39. Full unstacked ¹H NMR (CD₅D₆Br) spectrum (middle trace); t = 4 h at 115 °C generating metallacycle 1b in 54% yield.

Figure S40. Full unstacked ¹H NMR (CD₅D₆Br) spectrum (top trace); t = 0.5 h after nitrosobenzene addition to give diimine 5b in 48% yield (90% with respect to 1b).
Scope of multicomponent coupling of \([\text{py}_2\text{TiCl}_2(\text{NPh})_2]\), alkynes, and acetonitrile with subsequent nitrosobenzene addition for the synthesis of \(\alpha\)-diimines (isolation scale) (Table 2, 5a – 5p)

\((2E,3E)-N^2,N^6\)-diphenylbutane-2,3-diimine (5a)

Figure S41. \(^1\text{H}\) NMR spectrum of 5a in C\(_6\)D\(_6\).

Figure S42. \(^{13}\text{C}\) NMR spectrum of 5a in C\(_6\)D\(_6\).

\((3E,4E)-N^2,N^4\)-diphenylhexane-3,4-diimine (5b)

Figure S43. \(^1\text{H}\) NMR spectrum of 5b in C\(_6\)D\(_6\).

Figure S44. \(^{13}\text{C}\) NMR spectrum of 5b in C\(_6\)D\(_6\).

\((5E,6E)-N^2,N^6\)-diphenyldecane-5,6-diimine (5c)

Figure S45. \(^1\text{H}\) NMR spectrum of 5c in C\(_6\)D\(_6\).

Figure S46. \(^{13}\text{C}\) NMR spectrum of 5c in C\(_6\)D\(_6\).

\((1E,2E)-N^1,N^4\)-1,2-tetraphenylethane-1,2-diimine (5d)

Figure S47. \(^1\text{H}\) NMR spectrum of 5d in C\(_6\)D\(_6\).

Figure S48. \(^{13}\text{C}\) NMR spectrum of 5d in C\(_6\)D\(_6\).

Synthesis of 5d using alternative method from \textit{in-situ} imido generation using TiCl\(_4\)(THF)\(_2\), Zn\(^6\), and azobenzene

\((2E,3E)-N^2,N^6\)-diphenylheptane-2,3-diimine (5e)

Figure S49. \(^1\text{H}\) NMR spectrum of 5e in C\(_6\)D\(_6\).

Figure S50. \(^{13}\text{C}\) NMR spectrum of 5e in C\(_6\)D\(_6\).

\(N^1,N^4\)-1-triphenylpropane-1,2-diimine (5f)

Figure S51. \(^1\text{H}\) NMR spectrum of 5f as a mixture of isomers in C\(_6\)D\(_6\).

Figure S52. \(^{13}\text{C}\) NMR spectrum of 5f as a mixture of isomers in C\(_6\)D\(_6\), with inset showing the imine region.

Figure S53. NOESY of methyl region (1.20 – 2.10 ppm) of 5f showing EXSY cross-peaks that indicate chemical exchange between different diimine isomers, as opposed to through-space interactions (NOEY); EXSY cross-peaks = same phase as diagonal, NOESY = opposite phase.

Figure S54. Full NOESY of 5f.

Figure S55. GC-MS of 5f (m/z = 298).

\((4\text{-trifluoromethyl})-N^1,N^6\)-diphenylpropane-1,2-diimine (5g)

Figure S56. \(^1\text{H}\) NMR spectrum of 5g as a mixture of isomers in C\(_6\)D\(_6\).

Figure S57. \(^{13}\text{C}\) NMR spectrum of 5g as a mixture of isomers in C\(_6\)D\(_6\), with insets showing ortho C quartets.

Figure S58. \(^{19}\text{F}\) NMR spectrum of 5g in C\(_6\)D\(_6\) with trifluoroacetic acid (neat) reference capillary (\(\delta_{-77.80}\), \(^{19}\text{F}\) signals for multiple isomers observed.

Figure S59. GC-MS of 5g (m/z = 366).

\((4\text{-methoxyethyl})-N^1,N^6\)-diphenylpropane-1,2-diimine (5h)

Figure S60. \(^1\text{H}\) NMR spectrum of 5h as a mixture of isomers in C\(_6\)D\(_6\).

Figure S61. \(^{13}\text{C}\) NMR spectrum of 5h as a mixture of isomers in C\(_6\)D\(_6\).

Figure S62. GC-MS of 5h (m/z = 328).

\(N^1,N^6\)-diphenyl-1-(trimethylsilyl)propane-1,2-diimine (5i) (Not isolated)

Figure S63. GC-MS of 5i reaction mixture after workup.
Addition of ZnCl₂ to asymmetric diimine isomers (Figure 3, 6f-6h, 6l) 93

ZnCl₂((1E,2E)-N²,N⁶-1-triphenylpropane-1,2-diimine)-0.5THF (6f) 94
Figure S83. ¹H NMR spectrum of 6f in CDCl₃. 94
Figure S84. ¹³C NMR spectrum of 6f in CDCl₃. 95
Figure S85. ¹H NMR spectrum of 6f in CDCl₃ after THF wash. 96
Figure S86. ¹³C NMR spectrum of 6f in CDCl₃ after THF wash. 97

ZnCl₂((1E,2E)-(4-trifluoromethyl)-N²,N⁶-diphenylpropane-1,2-diimine)-0.5THF (6g) 98
Figure S87. ¹H NMR spectrum of 6g in CDCl₃. 98
Figure S88. $^{13}$C NMR spectrum of 6g in CDCl$_3$.
Figure S89. $^{19}$F NMR spectrum of 6g in CDCl$_3$ with trifluoroacetic acid (neat) reference capillary ($\delta$ -77.80).

ZnCl$_2$((1E,2E)-(4-methoxyphenyl)-N$^1$,N$^2$-diphenylpropane-1,2-dimine)-0.5THF (6h)
Figure S90. $^1$H NMR spectrum of 6h in CDCl$_3$.
Figure S91. $^{13}$C NMR spectrum of 6h in CDCl$_3$.

ZnCl$_2$((1E,2E)-N$^1$,N$^2$-diphenyl-1-(p-tolyl)ethane-1,2-dimine)-1THF (6l)
Figure S92. $^1$H NMR spectrum of 6l in CDCl$_3$.
Figure S93. $^{13}$C NMR spectrum of 6l in CDCl$_3$.

Control reaction with [py$_2$TiCl$_2$NPh]$_2$, 3-hexyne, and PhNO
Figure S94. No-D $^1$H NMR spectrum in PhBr showing (bottom) 3-hexyne and TMB, (top) azobenzene formation and unreacted 3-hexyne after 1 hr of heating at 115 °C.

Evaluation of in situ sequential condensations from diketones

Symmetrical diimine - 2,3-butanedione
Figure S95. GC-FID of aliquot from reaction mixture 24 h following addition of aniline of 2,3-butanedione at 80 °C in toluene
Figure S96. GC-FID of aliquot from reaction mixture 24 h following second condensation step.

Unsymmetrical diimine - 1-phenyl-1,2-propanedione
Figure S97. GC-FID of aliquot from reaction mixture 24 h following addition of p-toluidine of 1-phenyl-1,2-propanedione at 80 °C in toluene.
Figure S98. GC-FID of aliquot from reaction mixture 24 h following second condensation step.

XRD Data
Figure S99. ORTEP diagram of 6f. Thermal ellipsoids are drawn at 50% probability.

Computational Methods
Figure S100. Relevant IBOs for intermediates and transition states of each reaction step (IM1 to IM8) are shown. The fraction of electrons in doubly occupied orbitals assigned to each atom are given in parenthesis (contributions that are ≤0.10 are omitted). Atom number labels correspond to line positions in respective cartesian coordinates (xyz).

XYZ coordinates (Å) of optimized structures with electronic, free, and frequency corrected free energies (a.u.) at 298.15 K and 1 atm using M06/6-311g(d,p)/ultrafine in bromobenzene

References
General Considerations

All air- and moisture-sensitive reactions were carried out in a nitrogen-filled glovebox (MBRAUN) unless otherwise specified. Standard solvents for air- and moisture-sensitive reactions were either degassed, dried over CaH₂, and filtered through basic alumina prior to use. Nitrosobenzene (2a), 2-nitrosopyridine (2m), and 2-methyl-2-nitrosopropane dimer (2o) were purchased from Sigma Aldrich. Other nitrosoarenes were synthesized by oxidation of their corresponding aniline using either Oxone® (2b, 2d-g, 2j) or Na₂WO₄⋅2H₂O/H₂O₂ (2c, 2h, 2i) by adaptation of established literature procedures. 1,3,5-trimethoxybenzene internal standard (acquisition time = 5 s, delay time = 30 s, dummy scans = 0, number of scans = 8). Qualitative GC-MS spectra were recorded on an Agilent GC6890N-MSD5975 gas chromatograph-mass spectrometer fitted with a 7683 autosampler. A HD-5 column (5% diphenyl siloxane in the polymer) was used in the gas chromatograph and electron ionization technique was used for mass spectrometry detection. GC-FID chromatographs were collected on an Agilent 7890B GC system equipped with an HP-5 column (30 m, 0.32 mm, 0.25 μm, 7 in cage), an oxidation-methanation reactor (Polyarc® System, Activated Research Company) and an FID detector for quantitative carbon detection. High-resolution electrospray mass spectrometry (ESI-MS) was performed on all isolated samples using a Bruker BioTOF II ESI/TOF-MS with PEG 300 as an internal mass standard.
Addition of nitrosobenzene to 1 (NMR scale)

*In situ* Procedure: Diazatitanacyclohexadiene 1 (19.6 mg, 0.035 mmol) and internal standard 1,3,5-trimethoxybenzene (TMB) (4.0 mg, 0.024 mmol) were added to an NMR tube and dissolved in 0.5 mL C₆D₆, then nitrosobenzene (2a) (3.9 mg, 0.036 mmol, 1 equiv.) was added. A ¹H NMR spectrum was recorded after 30 min. Diimine 3a was observed to have formed in an 81% yield, with 1:1 p-tolunitrile formation.

![Diagram](image)

*Figure S1.* Stacked ¹H NMR spectra (C₆D₆) of nitrosobenzene addition to 1; Bottom (red trace): nitrosobenzene (2a) prior to addition; Middle-bottom (green trace): p-tolunitrile, Middle-top (blue trace): 1 prior to addition of nitrosobenzene; Top (purple trace): After addition of nitrosobenzene to 1, t = 0.5 h at room temperature, showing 81% yield of 3a according to 1,3,5-trimethoxybenzene standard.
Figure S2. $^1$H NMR spectrum ($C_6D_6$) after nitrosobenzene addition to 1 after 0.5 h, showing 81% yield of 3a according to 1,3,5-trimethoxybenzene standard.
Scope of nitroso addition to py$_2$TiCl$_2$(ADA$^{Et}$) (1) (Table 1, 3a – 3o) (isolation scale)

**General procedure:** py$_2$TiCl$_2$(ADA$^{Et}$) (1) (110.7 mg, 0.2 mmol, 1 equiv.) and nitrosobenzene (2a) (21.4 mg, 0.2 mmol, 1 equiv.) were added to a 20 mL scintillation vial with 3 mL of C$_6$H$_6$. The reaction was stirred for 0.5 hours at room temperature. The dark yellow-brown mixture turned an opaque orange with visible white solid. The reaction was quenched by the addition of saturated Na$_2$CO$_3$ (aq). The layers were separated, and the aqueous layer was extracted with hexane. The organics were combined and dried over Na$_2$SO$_4$. After filtration, the volatiles (C$_6$H$_6$, hexanes) were reduced under vacuum. The removal of p-tolunitrile was achieved by heating at 35 °C under vacuum for 4 hours to afford 41.0 mg of pure 3a in an 82% yield.

This procedure was repeated for 3b – 3o. Diimines 3i and 3m were not able to be cleanly isolated, so NMR yields are instead reported (given below).
Yellow oil, 41.0 mg, 82% isolated yield. $^1$H NMR (500 MHz, C$_6$D$_6$) δ 7.22 – 7.17 (m, 4H, CH(CHCH$_2$CN)), 6.94 (t, J = 7.5 Hz, 2H, CH(CHCH$_2$CN)), 6.77 (d, J = 7.8 Hz, 2H, CH(CHCH$_2$CN)), 6.71 (d, J = 7.7 Hz, 2H, CH(CHCH$_2$CN)), 2.72 (q, J = 7.5 Hz, 2H, CH$_3$CH$_2$), 2.10 (s, 3H, CH$_3$), 1.08 (t, J = 7.5 Hz, 3H, CH$_3$CH$_2$). $^{13}$C NMR (126 MHz, C$_6$D$_6$) δ 172.71, 167.20, 151.62, 151.60, 129.29, 129.28, 124.00, 123.73, 119.13, 118.74, 22.04, 15.59, 13.27. ESI-HRMS (m/z): calcd. for C$_{17}$H$_{18}$N$_2$Na$^+$, 273.1368; found, 273.1368.

Figure S3. $^1$H NMR spectrum of 3a in C$_6$D$_6$. 
Figure S4. $^{13}$C NMR spectrum of 3a in C$_6$D$_6$.

Figure S5. $^1$H-$^{15}$N HMBC NMR spectrum of 3a in C$_6$D$_6$. 
(2E,3E)-N²-(3,5-dimethylphenyl)-N³-phenylpentane-2,3-diimine (3b)

Yellow oil, 42.8 mg, 77% isolated yield. $^1$H NMR (500 MHz, C$_6$D$_6$) δ 7.22 – 7.17 (m, 2H, CH(CHCH)$_2$CN), 6.95 (tt, J = 7.4, 1.2 Hz, 1H, CH(CHCH)$_2$CN), 6.79 (dd, J = 8.4, 1.2 Hz, 2H, CH(CHCH)$_2$CN), 6.63 (s, 1H, CH(CH$_3$)$_2$(CH)$_2$C), 6.43 (s, 2H, CH(CH$_3$)$_2$(CH)$_2$C), 2.76 (q, J = 7.6 Hz, 2H, CH$_2$CH$_3$), 2.16 (s, 3H, CH$_3$), 2.16 (s, 6H, CH(CH$_3$)$_2$(CH)$_2$C), 1.12 (t, J = 7.5 Hz, 3H, CH$_2$CH$_3$).

$^{13}$C NMR (126 MHz, C$_6$D$_6$) δ 172.83, 166.83, 151.78, 151.72, 138.71, 129.30, 125.70, 123.70, 118.77, 116.81, 22.06, 21.41, 15.67, 13.34. ESI-HRMS (m/z): calcd. for C$_{19}$H$_{22}$N$_2$H$^+$, 279.1861; found, 279.1849 (diff. 0.0012).

Figure S6. $^1$H NMR spectrum of 3b in C$_6$D$_6$. 
Figure S7. $^{13}$C NMR spectrum of 3b in C$_6$D$_6$. 
(2E,3E)-$N^2$-mesityl-$N^3$-phenylpentane-2,3-diimine (3c)

Yellow oil, 44.1 mg, 76% isolated yield. $^1$H NMR (500 MHz, C$_6$D$_6$) δ 7.20 – 7.17 (m, 2H, CH(CHCH)$_2$CN), 6.97 – 6.90 (m, 1H, CH(CHCH)$_2$CN), 6.83 (s, 2H, CH$_3$(CHCH)$_2$C), 6.77 (d, $J = 7.8$ Hz, 2H, CH(CHCH)$_2$CN), 2.80 (q, $J = 7.5$ Hz, 2H, CH$_2$CH$_3$), 2.22 (s, 3H, CH$_3$), 2.00 (s, 3H, CH$_3$(CHCH)$_2$C), 1.99 (s, 6H, CH$_3$(CHCH)$_2$C), 1.13 (t, $J = 7.5$ Hz, 3H, CH$_2$CH$_3$). $^{13}$C NMR (126 MHz, C$_6$D$_6$) δ 172.35, 167.83, 151.60, 146.90, 132.37, 129.27, 129.15, 124.53, 123.74, 118.85, 21.92, 20.86, 18.17, 15.91, 13.36. ESI-HRMS (m/z): calcd. for C$_{20}$H$_{24}$N$_2$Na$^+$, 315.1837; found, 315.1849 (diff. 0.0012).

Figure S8. $^1$H NMR spectrum of 3c in C$_6$D$_6$. 
Figure S9. $^{13}$C NMR spectrum of 3c in C$_6$D$_6$. 
(2E,3E)-N\textsuperscript{\text{Ph}}-N\textsuperscript{\text{2}(\text{4}-\text{(trifluoromethyl)}\text{Ph})\text{Ph}}\text{2,3-diimine (3d)}

Light orange crystalline solid, 56.6 mg, 65% isolated yield. \textsuperscript{1}H NMR (500 MHz, C\text{6}D\text{6})
\delta 7.34 (d, J = 8.3 Hz, 2H, CF\text{3}-C-(CHCH)\text{2}C), 7.23 – 7.18 (m, 2H, CH(CHCH)\text{2}CN), 6.96 (tt, J = 7.4, 1.3 Hz, 1H, CH(CHCH)\text{2}CN), 6.77 (d, J = 8.4 Hz, 2H, CH(CHCH)\text{2}CN), 6.43 (d, J = 8.2 Hz, 2H, CF\text{3}-C-(CHCH)\text{2}C), 2.64 (q, J = 7.5 Hz, 2H, CH\text{2}CH\text{3}), 1.92 (s, 3H), 1.03 (t, J = 7.5 Hz, 3H, CH\text{2}CH\text{3}). \textsuperscript{13}C NMR (126 MHz, C\text{6}D\text{6}) \delta 172.15, 168.04, 154.44, 151.30, 129.38, 126.58 (q, J = 32.5 Hz), 125.23 (q, J = 271.3 Hz), 118.97, 118.64, 21.96, 15.71, 13.17. \textsuperscript{19}F NMR (471 MHz, C\text{6}D\text{6}) \delta -62.07 \text{ (vs. TFA (neat), \delta -77.80)} \text{ ESI-HRMS (m/z): calcd. for C\textsubscript{18}H\textsubscript{17}F\textsubscript{3}N\textsubscript{2}Na\textsuperscript{+}, 319.1422; found, 314.1401 (diff. 0.0021).}

Figure S10. \textsuperscript{1}H NMR spectrum of 3d in C\textsubscript{6}D\textsubscript{6}. 

Figure S11. $^{13}$C NMR spectrum of 3d in $\text{C}_6\text{D}_6$, inset shows quartets from $^{13}$C-$^{19}$F coupling.
Figure S12. $^{19}$F NMR spectrum of 3d in C$_6$D$_6$ with trifluoroacetic acid (neat) reference capillary (δ - 77.80).
(2E,3E)-N²-(4-bromophenyl)-N³-phenylpentane-2,3-diimine (3e)

Brown crystalline solid, 55.2 mg, 85% isolated yield. $^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ 7.23 (d, $J = 8.5$ Hz, Br-C-(CHCH)$_2$C), 7.21 – 7.16 (m, 2H, CH(CHCH)$_2$CN), 6.95 (t, $J = 7.5$ Hz, 1H, CH(CHCH)$_2$CN), 6.77 (d, $J = 7.1$ Hz, 2H, CH(CHCH)$_2$CN), 6.31 (d, $J = 8.5$ Hz, 2H, Br-C-(CHCH)$_2$C), 2.66 (q, $J = 7.5$ Hz, 2H, CH$_2$CH$_3$), 1.97 (s, 3H), 1.03 (t, $J = 7.5$ Hz, 3H, CH$_3$). $^{13}$C NMR (126 MHz, C$_6$D$_6$) $\delta$ 172.43, 167.83, 151.45, 150.29, 132.32, 129.34, 123.89, 120.92, 118.66, 117.13, 21.96, 15.58, 13.22. ESI-HRMS (m/z): calcd. for C$_{17}$H$_{17}$BrN$_2$H$^+$, 329.0653; found, 329.0652 (diff. 0.0001).

Figure S13. $^1$H NMR spectrum of 3e in C$_6$D$_6$. 
Figure S14. $^{13}$C NMR spectrum of 3e in C$_6$D$_6$. 
(2E,3E)-N²-(4-ethoxycarbonylphenyl)-N⁰-phenylpentane-2,3-diimine (3f)

Red-orange oil, 45.9 mg. 71% isolated yield. ¹H NMR (500 MHz, C₆D₆) δ 8.18 (d, J = 8.5 Hz, 2H, CH₂CH₂OC(O)-C-(CHCH₂)₂C), 7.20 (t, J = 7.9 Hz, 2H, CH(CHCH₂)₂CN), 6.95 (t, J = 7.4 Hz, 1H, CH(CHCH₂)₂CN), 6.77 (d, J = 7.0 Hz, 2H, CH(CHCH₂)₂CN), 6.58 (d, J = 8.4 Hz, 2H, CH₃CH₂OC(O)-C-(CHCH₂)₂C), 4.18 (q, J = 7.1 Hz, 2H, CH₃CH₂OC(O)-C-(CHCH₂)₂C), 2.65 (q, J = 7.6 Hz, 2H, CH₂CH₃), 1.98 (s, 3H, CH₃), 1.07 (t, J = 7.1 Hz, 3H, CH₃CH₂OC(O)-C-(CHCH₂)₂C), 1.03 (t, J = 7.6 Hz, 3H, CH₂CH₃). ¹³C NMR (126 MHz, C₆D₆) δ 172.24, 167.54, 166.06, 155.51, 151.39, 131.27, 129.34, 126.70, 123.93, 118.67, 118.62, 60.71, 21.97, 15.74, 14.40, 13.21. ESI-HRMS (m/z): calcd. for C₂₀H₂₂N₂O₂H⁺, 345.1579; found, 345.1570 (diff. 0.0009).

Figure S15. ¹H NMR spectrum of 3f in C₆D₆.
Figure S16. $^{13}$C NMR spectrum of 3f in C$_6$D$_6$. 
(2E,3E)-N\textsuperscript{a}-phenyl-N\textsuperscript{b}-(p-tolyl)pentane-2,3-diimine (3g)

Yellow oil, 44.2 mg. 84% isolated yield. \textsuperscript{1}H NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}) \( \delta \) 7.22 – 7.16 (m, 2H, CH(CHCH\textsubscript{2})CN), 7.00 (d, \( J = 8.1 \) Hz, 2H, CH\textsubscript{2}-C-(CHCH\textsubscript{2})C), 6.94 (tt, \( J = 7.4, 1.1 \) Hz, 1H, CH(CHCH\textsubscript{2})CN), 6.78 (dd, \( J = 8.4 \) Hz, 1.1 Hz, 2H, CH(CHCH\textsubscript{2})CN), 6.69 (d, \( J = 8.1 \) Hz, 2H, CH\textsubscript{2}-C-(CHCH\textsubscript{2})C), 2.75 (q, \( J = 7.5 \) Hz, 2H, CH\textsubscript{2}CH\textsubscript{3}), 2.16 (s, 3H, CH\textsubscript{3}), 2.14 (s, 3H, CH\textsubscript{3}), 1.09 (t, \( J = 7.5 \) Hz, 3H, CH\textsubscript{2}CH\textsubscript{3}). \textsuperscript{13}C NMR (126 MHz, C\textsubscript{6}D\textsubscript{6}) \( \delta \) 172.86, 167.10, 151.71, 149.06, 133.31, 129.86, 129.29, 123.68, 119.36, 118.75, 22.05, 20.88, 15.58, 13.32. ESI-HRMS (m/z): calcd. for C\textsubscript{18}H\textsubscript{20}N\textsubscript{2}H\textsuperscript{+}, 265.1705; found, 265.1705.

Figure S17. \textsuperscript{1}H NMR spectrum of 3g in C\textsubscript{6}D\textsubscript{6}.
Figure S18. $^{13}$C NMR spectrum of 3g in C$_6$D$_6$. 
(2E,3E)-N²-(4-methoxyphenyl)-N⁶-phenylpentane-2,3-diimine (3h)

Yellow solid, 46.2 mg, 82% isolated yield. $^1$H NMR (500 MHz, C₆D₆) δ 7.19 (t, $J = 7.6$ Hz, 2H, CH(CHCH)₂-CN), 6.95 (t, $J = 7.5$ Hz, 1H, CH(CHCH)₂-CN), 6.79 (m, 4H, Ar-H), 6.72 (d, $J = 8.4$ Hz, 2H, CH₃-O-C-(CHCH)₂-C), 3.34 (s, 3H, CH₃-O-C-(CHCH)₂-C), 2.77 (q, $J = 7.5$ Hz, 2H, CH₃CH₂), 2.19 (s, 3H, CH₃), 1.11 (t, $J = 7.5$ Hz, 3H, CH₃CH₂). $^{13}$C NMR (126 MHz, C₆D₆) δ 173.00, 166.98, 157.14, 151.79, 144.47, 129.29, 123.65, 121.10, 118.77, 114.62, 55.01, 22.07, 15.60, 13.34. ESI-HRMS (m/z): calcd. for C₁₉H₂₀N₂ONa⁺, 303.1473; found, 303.1467 (diff. 0.0006).

Figure S19. $^1$H NMR spectrum of 3h in C₆D₆.
Figure S20. $^{13}\text{C}$ NMR spectrum of 3h in C$_6$D$_6$. 
(2E,3E)-N²-(4-N,N-dimethyl)-N¹-phenylpentane-2,3-diimine (3i) (Not isolated)

Red oil. Not isolated, but NMR and GC-MS of reaction mixture after workup is provided. The unknown product is likely to be a derivative of the protonated ligand precursor of 1, given its mass by GC-MS, which is the same mass but with a different fragmentation pattern.

Figure S21. ¹H NMR spectrum of 3i in C₆D₆.
Figure S22. GC-MS of 3i reaction mixture after workup.
(2E,3E)-N^2-(4-N,N-dimethyl)-N^2-phenylpentane-2,3-diimine (3i) (NMR scale)

In-situ Procedure: Diazatitanacyclohexadiene 1 (12.5 mg, 0.023 mmol) and internal standard 1,3,5-trimethoxybenzene (TMB) (4.5 mg, 0.027 mmol) were added to an NMR tube and dissolved in 0.5 mL C_6D_6, then 2i 4.4 mg, 0.029 mmol, 1.3 equiv.) was added. A ^1H NMR spectrum was recorded after 30 min. Diimine 3i was observed to have formed in an 49% yield, as well as some unidentified products.

Figure S23. Stacked ^1H NMR spectra (C_6D_6) of addition of 2i to 1: Bottom (green trace): 2i prior to addition; Middle (blue trace): 1 prior to addition; Top (purple trace): After addition of 2i to 1, t = 0.5 h at room temperature, showing 49% yield of 3i according to 1,3,5-trimethoxybenzene standard, with unidentified product also formed.
Figure S24. $^1$H NMR spectrum (C$_6$D$_6$) of addition of 2i to 1, showing 49% yield of 3i according to 1,3,5-trimethoxybenzene standard, with unidentified product also formed.
(2E,3E)-N<sup>Ph</sup>-phenyl-N<sup>Ph</sup>-(o-(trifluoromethyl)phenyl)pentane-2,3-diimine (3j)

Orange-yellow oil, 53.8 mg. 78% isolated yield. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.46 (d, J = 7.9 Hz, 1H, NCCCHCHCHCCF<sub>3</sub>), 7.20 – 7.12 (m, 2H, CH(CHCH)CN), 6.99 (t, J = 7.4 Hz, 1H, NCCCHCHCHCCF<sub>3</sub>), 6.93 (tt, J = 7.4, 1.2 Hz, 1H, CH(CHCH)CN), 6.72 (d, J = 7.2 Hz, 2H, CH(CHCH)CN), 6.72 – 6.67 (m, 1H, NCCCHCHCHCCF<sub>3</sub>), 6.32 (d, J = 7.9 Hz, 1H, NCCCHCHCHCCF<sub>3</sub>), 2.72 (q, J = 7.6 Hz, 2H, CH<sub>2</sub>CH<sub>3</sub>), 2.05 (s, 3H, CH<sub>3</sub>), 1.12 (t, J = 7.6 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>) δ 172.27, 169.19, 151.27, 149.82 (q, J = 1.7 Hz), 132.72, 129.28, 126.66 (q, J = 5.1 Hz), 124.76 (q, J = 272.5 Hz), 123.92, 123.49, 119.38 (q, J = 30.5 Hz), 119.25, 118.68, 21.93, 16.35, 12.77. <sup>19</sup>F NMR (471 MHz, C<sub>6</sub>D<sub>6</sub>) δ -61.69 (vs. TFA δ -77.80). ESI-HRMS (m/z): calcd. for C<sub>18</sub>H<sub>17</sub>F<sub>3</sub>N<sub>2</sub>H<sup>+</sup>, 319.1422; found, 319.1440 (diff. 0.0018).

Figure S25. <sup>1</sup>H NMR spectrum of 3j in C<sub>6</sub>D<sub>6</sub>. 

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Figure S26. $^{13}$C NMR spectrum of 3j in $\text{C}_6\text{D}_6$, inset shows quartets from $^{13}$C-$^{19}$F coupling.
Figure S27. $^{19}$F NMR spectrum of 3j in C$_6$D$_6$ with trifluoroacetic acid (neat) reference capillary (δ - 77.80).
(2E,3E)-N\textsuperscript{Ph}-phenyl-N\textsuperscript{otolyl}pentane-2,3-diimine (3k)

Red-orange oil, 39.0 mg. 74% isolated yield. \textsuperscript{1}H NMR (500 MHz, C\textsubscript{6}D\textsubscript{6}) \(\delta\) 7.21 – 7.16 (m, 2H, CH(CH\textsubscript{2})\textsubscript{2}CN), 7.13 – 7.02 (m, 2H, Ar-\textit{H}), 6.99 – 6.90 (m, 2H, Ar-\textit{H}), 6.77 (dd, \(J =\) 8.6, 1.2 Hz, 2H, CH(CH\textsubscript{2})\textsubscript{2}CN), 6.55 (dd, \(J =\) 7.7, 1.3 Hz, 1H, NCCCHCHCHCCH\textsubscript{3}), 2.75 (q, \(J =\) 7.5 Hz, 2H, CH\textsubscript{2}CH\textsubscript{3}), 2.06 (s, 3H, CH\textsubscript{3}), 2.05 (s, 3H, CH\textsubscript{3}), 2.09 (t, \(J =\) 7.5 Hz, 3H, CH\textsubscript{2}CH\textsubscript{3}), 1.09 (t, \(J =\) 7.5 Hz, 3H, CH\textsubscript{2}CH\textsubscript{3}). \textsuperscript{13}C NMR (126 MHz, C\textsubscript{6}D\textsubscript{6}) \(\delta\) 172.56, 166.95, 151.60, 150.29, 130.80, 129.28, 126.84, 126.79, 124.17, 123.75, 118.77, 117.93, 22.00, 18.05, 15.81, 13.29. ESI-HRMS (m/z): calcd. for C\textsubscript{18}H\textsubscript{20}N\textsubscript{2}H\textsubscript{+}, 265.1705; found, 287.1687 (diff. 0.018).

Figure S28. \textsuperscript{1}H NMR spectrum of 3k in C\textsubscript{6}D\textsubscript{6}. 
Figure S29. $^{13}$C NMR spectrum of 3k in C$_6$D$_6$. 
(2E,3E)-N\textsubscript{\textalpha}-phenyl-N\textsubscript{\textbeta}-(\textalpha-methoxyphenyl)pentane-2,3-diimine (3l)

Orange oil, 41.5 mg. 74\% isolated yield. Isolated as mixture of imine/enamine tautomers in a 6:1 ratio.

Diimine: \textsuperscript{1}H NMR (500 MHz, C\textsubscript{6}D\textsubscript{6}) \(\delta\) 7.19 – 7.16 (m, 2H, CH(CH\textsubscript{2})\textsubscript{2}CN), 7.16 – 7.14 (m, 1H, NC\textsubscript{\textalpha}CH\textsubscript{\textbeta}CH\textsubscript{\textgamma}CH\textsubscript{\textdelta}COCH\textsubscript{\textepsilon}), 6.99 – 6.87 (m, 4H, Ar-\textgamma\textdelta), 6.80 – 6.75 (m, 1H, NC\textsubscript{\textalpha}CH\textsubscript{\textbeta}CH\textsubscript{\textgamma}CH\textsubscript{\textdelta}COCH\textsubscript{\textepsilon}), 6.75 – 6.71 (m, 2H, CH(CH\textsubscript{2})\textsubscript{2}CN), 6.66 – 6.60 (m, 1H, NC\textsubscript{\textalpha}CH\textsubscript{\textbeta}CH\textsubscript{\textgamma}CH\textsubscript{\textdelta}COCH\textsubscript{\textepsilon}), 3.28 (s, 3H, OCH\textsubscript{\textgamma}), 2.80 (q, \textit{J} = 7.5 Hz, 2H, CH\textsubscript{\textbeta}CH\textsubscript{\textepsilon}), 2.18 (s, 3H, CH\textsubscript{\textgamma}), 1.17 (t, \textit{J} = 7.5 Hz, 3H, CH\textsubscript{\textdelta}CH\textsubscript{\textepsilon}). \textsuperscript{13}C NMR (126 MHz, C\textsubscript{6}D\textsubscript{6}) \(\delta\) 172.73, 168.48, 151.74, 148.63, 140.84, 129.22, 124.79, 123.61, 121.23, 120.06, 118.79, 111.96, 55.16, 22.21, 16.17, 13.27. ESI-HRMS (m/z): calcd. for C\textsubscript{18}H\textsubscript{20}N\textsubscript{2}H\textsubscript{+}, 281.1654; found, 281.1652 (diff. 0.0002).

Enamine: \textsuperscript{1}H NMR (500 MHz, C\textsubscript{6}D\textsubscript{6}, aryl region buried, only <6 ppm assigned) \(\delta\) 5.61 (q, \textit{J} = 7.2, 1H, C=CH\textsubscript{\textgamma}CH\textsubscript{\textepsilon}), 3.23 (s, 3H, OCH\textsubscript{\textgamma}), 1.80 (s, 3H, CH\textsubscript{\textgamma}), 1.60 (d, \textit{J} = 7.2 Hz, 3H, C=CH\textsubscript{\textepsilon}). \textsuperscript{13}C NMR (126 MHz, C\textsubscript{6}D\textsubscript{6}) \(\delta\) 164.83, 149.31, 145.08, 140.62, 139.53, 129.13, 124.47, 121.33, 121.28, 119.67, 117.67, 117.28, 112.06, 55.20, 15.74, 15.56.

Figure S30. \textsuperscript{1}H NMR spectrum of 3l in C\textsubscript{6}D\textsubscript{6} (Diimine denoted in red, enamine in blue).
Figure S31. $^{13}$C NMR spectrum of 3I in C$_6$D$_6$. 
(2E,3E)-N\textsuperscript{a}-phenyl-N\textsuperscript{b}-(pyridin-2-yl)pentane-2,3-diimine (3m) \textbf{(NMR scale)}

\textit{In-situ} Procedure: Diazatitanacyclohexadiene 1 (12.8 mg, 0.023 mmol) and internal standard 1,3,5-trimethoxybenzene (TMB) (3.9 mg, 0.023 mmol) were added to an NMR tube and dissolved in 0.5 mL C\textsubscript{6}D\textsubscript{6}, then 2m 3.2 mg, 0.03 mmol, 1.3 equiv.) was added. A \textsuperscript{1}H NMR spectrum was recorded after 30 min. Diimine 3m was observed to have formed in an 20% yield, which is small compared to the observed amount of p-tolunitrile (85%) (1:1 in all other examples). Free pyridine is also evident in the free spectrum (unlike in reactions of 1 with 2a and other nitrosos). A large amount of insoluble brown solid was also observed to crash out of solution. It is possible the N of the heteronitroso fragment inhibits reactivity following p-tolunitrile elimination, perhaps through chelation, displacing the bound pyridine.

\textbf{Figure S32.} Stacked \textsuperscript{1}H NMR spectra (C\textsubscript{6}D\textsubscript{6}) of addition of 2m to 1; Bottom (red trace): pyridine, Middle-bottom (light green trace): p-tolunitrile; Middle (green trace): 2m prior to addition, Middle-top (blue trace): 1 prior to addition; Top (purple trace): reaction mixture showing 3m in 20% yield, p-tolunitrile (85%), and free pyridine versus 1,3,5-trimethoxybenzene standard.
Figure S33. $^1$H NMR spectrum (C$_6$D$_6$) of addition of 2m to 1, showing 3m in 20% yield, p-tolunitrile (85%), and free pyridine versus 1,3,5-trimethoxybenzene standard.
**(2E,3E)-N^2-(tert-butyl)-N^3-phenylpentane-2,3-diimine (3n)**

Polar yellow oil, 31.6 mg. 71% isolated yield of mixture of imine/enamine tautomers in 4.1:1 ratio.

Diimine: **1H NMR (500 MHz, C\textsubscript{6}D\textsubscript{6})** δ 7.20 – 7.16 (m, 2H, CH(CHCH)\textsubscript{2}CN), 6.91 (t, J = 7.4 Hz, 1H, CH(CHCH)\textsubscript{2}CN), 6.76 (d, J = 7.7 Hz, 2H, CH(CHCH)\textsubscript{2}CN), 2.68 (q, J = 7.5 Hz, 2H, CH\textsubscript{2}CH\textsubscript{3}), 2.26 (s, 3H, CH\textsubscript{3}), 1.57 (s, 9H, (CH\textsubscript{3})\textsubscript{3}CN), 1.01 (t, J = 7.5 Hz, 3H, CH\textsubscript{2}CH\textsubscript{3}). **13C NMR (126 MHz, C\textsubscript{6}D\textsubscript{6})** δ 174.12, 162.89, 152.24, 129.24, 123.25, 118.87, 55.81, 30.27, 22.13, 16.63, 13.41. **ESI-HRMS (m/z):** calcld. for C\textsubscript{15}H\textsubscript{22}N\textsubscript{2}Na\textsuperscript{+}, 253.1681; found, 253.1698 (diff. 0.0017).

Enamine: **1H NMR (500 MHz, C\textsubscript{6}D\textsubscript{6})** δ 7.10 (t, J = 7.3 Hz, 2H, CH(CHCH)\textsubscript{2}CN), 6.87 (t, J = 7.4 Hz, 1H, CH(CHCH)\textsubscript{2}CN), 6.67 (d, J = 7.7 Hz, 2H, CH(CHCH)\textsubscript{2}CN), 4.58 (s, 1H, C=CH\textsubscript{2}), 4.55 (s, 1H, C=CH\textsubscript{2}), 2.32 (q, J = 7.7 Hz, 2H, CH\textsubscript{2}CH\textsubscript{3}), 1.28 (s, 9H, CCH\textsubscript{3}), 0.95 (t, J = 7.6 Hz, 3H, CH\textsubscript{2}CH\textsubscript{3}). **13C NMR (126 MHz, C\textsubscript{6}D\textsubscript{6})** δ 168.89, 151.71, 143.56, 129.25, 123.29, 119.40, 87.05, 49.83, 28.84, 22.01, 14.53.

**Figure S34.** 1H NMR spectrum of 3n in C\textsubscript{6}D\textsubscript{6} (Diimine denoted in red, enamine in blue).
Figure S35. $^{13}$C NMR spectrum of 3n in C$_6$D$_6$ (Diimine denoted in red, enamine in blue).
(2E,3E)-N\textsuperscript{2}-(adamantan-1-yl)-N\textsuperscript{0}-phenylpentane-2,3-diimine (3o)

Light yellow oil, 43.3 mg. 70% isolated yield of mixture of imine/enamine tautomers in 3.3:1 ratio.

Diimine: \textsuperscript{1}H NMR (500 MHz, C\textsubscript{6}D\textsubscript{6}) \(\delta\) 7.21 – 7.16 (m, 1H, CH(CH\textsubscript{2}CN), 6.92 (tt, \(J = 7.5, 1.3\) Hz 1H, CH(CH\textsubscript{2}CN), 6.77 (dd, \(J = 8.4, 1.3\) Hz, 2H, CH(CH\textsubscript{2}CN), 2.71 (q, \(J = 7.5\) Hz, 2H, CH\textsubscript{2}CH\textsubscript{3}), 2.30 (s, 3H, CH\textsubscript{3}), 2.04 – 1.98 (m, 3H, NC(CH\textsubscript{2})\textsubscript{3}(CH\textsubscript{2})\textsubscript{3}), 1.98 – 1.96 (m, 6H, NC(CH\textsubscript{2})\textsubscript{3}(CH\textsubscript{2})\textsubscript{3}), 1.64 – 1.61 (m, 6H, NC(CH\textsubscript{2})\textsubscript{3}(CH\textsubscript{2})\textsubscript{3}), 1.06 (t, \(J = 7.5\) Hz, 3H, CH\textsubscript{2}CH\textsubscript{3}). \textsuperscript{13}C NMR (126 MHz, C\textsubscript{6}D\textsubscript{6}) \(\delta\) 174.32, 162.11, 152.34, 129.23, 123.22, 118.89, 57.11, 42.95, 36.92, 30.19, 22.20, 17.30, 13.56. ESI-HRMS (m/z): calcd. for C\textsubscript{15}H\textsubscript{22}N\textsubscript{2}Na\textsuperscript{+}, 253.1681; found, 253.1698 (diff. 0.0017).

Enamine: \textsuperscript{1}H NMR (500 MHz, C\textsubscript{6}D\textsubscript{6}) \(\delta\) 7.14 – 7.10 (m, 2H, CH(CHCH)\textsubscript{2}CN), 6.89 (t, \(J = 7.4\) Hz, 1H, CH(CHCH)\textsubscript{2}CN), 6.71 – 6.67 (m, 2H, CH(CHCH)\textsubscript{2}CN), 4.73 – 4.60 (m, 2H, C=CH\textsubscript{2}), 2.36 – 2.31 (m, 2H, CH\textsubscript{2}CH\textsubscript{3}), 1.96 – 1.90 (m, 6H, NC(CH\textsubscript{2})\textsubscript{3}(CH\textsubscript{2})\textsubscript{3}), 1.87 – 1.79 (m, 3H, NC(CH\textsubscript{2})\textsubscript{3}(CH\textsubscript{2})\textsubscript{3}), 1.55 – 1.51 (m, 6H, NC(CH\textsubscript{2})\textsubscript{3}(CH\textsubscript{2})\textsubscript{3}), 0.96 (t, \(J = 7.6\) Hz, 3H, CH\textsubscript{2}CH\textsubscript{3}). \textsuperscript{13}C NMR (126 MHz, C\textsubscript{6}D\textsubscript{6}) \(\delta\) 169.01, 151.80, 142.99, 129.26, 123.26, 119.40, 88.01, 50.78, 42.20, 36.99, 30.08, 21.98, 14.58.

Figure S36. \textsuperscript{1}H NMR spectrum of 3o in C\textsubscript{6}D\textsubscript{6} (Diimine denoted in red, enamine in blue).
Figure S37. $^{13}$C NMR spectrum of 3o in C$_6$D$_6$ (Diimine denoted in red, enamine in blue).
Multicomponent coupling of $[\text{py}_2\text{TiCl}_2(\text{NPh})_2]$, 3-hexyne, and acetonitrile with subsequent nitrosobenzene addition for the synthesis of $\text{N}^2,\text{N}^8$-diphenylbutane-2,3-diimine (5a) (NMR scale)

Procedure: $[\text{py}_2\text{TiCl}_2(\text{NPh})_2]$ (17.0 mg, 0.046 mmol, 1 equiv.), TMB (2.0 mg), and $\text{C}_6\text{D}_5\text{Br}$ (0.5 mL) were added to an NMR tube, followed by MeCN (2.5 μL, 0.047 mmol) and 3-hexyne (5.3 μL, 0.047 mmol). The tube was capped, sealed with electrical tape, and heated to 115 °C in an oil bath for 4 hours. After recording the $t = 4$ h $^1$H NMR spectrum, the tube was brought back into the glovebox, where nitrosobenzene (5.0 mg, 0.047 mmol, 1 equiv.) was added. The tube was resealed and a final $^1$H NMR spectrum was recorded after 30 minutes.

Figure S38. Stacked $^1$H NMR spectra characterizing the multicomponent coupling of 3-hexyne (1 equiv.), MeCN (1 equiv.) and $[\text{py}_2\text{TiCl}_2(\text{NPh})_2]$ in $\text{C}_6\text{D}_5\text{Br}$; Bottom (red trace): $t = 0$; Middle (green trace): $t = 4$ h at 115 °C generating metallacycle 1b in 54% yield; Top (blue trace): $t = 0.5$ h after nitrosobenzene addition to give diimine 5b in 48% yield (90% with respect to 1b).
Figure S39. Full unstacked $^1$H NMR (C$_6$D$_5$Br) spectrum (middle trace); $t = 4$ h at 115 °C generating metallacycle 1b in 54% yield.
**Figure S40.** Full unstacked $^1$H NMR (C$_6$D$_5$Br) spectrum (top trace); t = 0.5 h after nitrosobenzene addition to give diimine 5b in 48% yield (90% with respect to 1b).
Scope of multicomponent coupling of $[\text{py}_2\text{TiCl}_2(\text{NPh})]_2$, alkynes, and acetonitrile with subsequent nitrosobenzene addition for the synthesis of α-diimines (isolation scale) (Table 2, 5a – 5p)

**General procedure**: $[\text{py}_2\text{TiCl}_2(\text{NPh})]_2$ (147.2 mg, 0.400 mmol, 1 equiv.), PhBr (4 mL), and a stir bar were added to a 20 mL scintillation vial, followed by acetonitrile (208 μL, 4.00 mmol, 10 equiv.), and alkyne (0.400 mmol, 1.00 equiv). The vial was sealed with a Teflon cap, wrapped in electrical tape, brought out of the glovebox, and placed in a preheated oil bath at 115 °C for 4 h while stirring. The heterogeneous yellow-orange mixture turned dark brown-yellow upon heating. After the initial heating period, the vial was brought back into the glovebox, and nitrosobenzene (42.8 mg, 0.4 mmol, 1 equiv.) was added with an additional 0.5 mL PhBr. The mixture was allowed to stir for 30 minutes. The vial was then removed from the glovebox and was quenched by the addition of 10 mL of saturated Na$_2$CO$_3$ (aq). The layers were separated, and the aqueous layer was extracted with DCM. The organics were combined, dried over Na$_2$SO$_4$, and filtered. The volatiles (including bromobenzene, DCM, MeCN, and, in some cases, volatile alkyne) were reduced under vacuum. Any remaining azobenzene (from the metathesis of leftover imido with nitrosobenzene) was then removed through sublimation using a water-cooled cold finger with a ground glass joint fitted into a round bottom flask, which was heated at 70 °C under vacuum.

**Note on stability**: Diimines are highly sensitive to hydrolysis to the corresponding aniline and diketone, and as a result silica/alumina column chromatography was avoided.
(2E,3E)-N^0,N^0-diphenylbutane-2,3-diimine (5a)

Dark red solid, 59.8 mg, 63% isolated yield. \(^1\)H NMR (500 MHz, C\(_6\)D\(_6\)) \(\delta\) 7.18 (m, 4H, CH(CH\(\text{CH})\text{CH})\text{CN}), 6.95 (t, \(J\) = 7.5 Hz, 2H, CH(CH\(\text{CH})\text{CH})\text{CN}), 6.73 (d, \(J\) = 6.9 Hz, 4H, CH(CH\(\text{CH})\text{CH})\text{CN}), 2.11 (s, 6H, CH\(\text{CH})\text{CH})\text{CN}). \(^{13}\)C NMR (126 MHz, C\(_6\)D\(_6\)) \(\delta\) 168.29, 151.67, 129.28, 124.03, 119.17, 15.27. ESI-HRMS (m/z): calcd. for C\(_{16}\)H\(_{16}\)N\(_2\)Na\(^+\), 259.1211; found, 259.1208 (diff. 0.0003).

**Figure S41.** \(^1\)H NMR spectrum of 5a in C\(_6\)D\(_6\).
Figure S42. $^{13}$C NMR spectrum of 5a in C$_6$D$_6$. 
(3E,4E)-N⁰,N⁴-diphenylhexane-3,4-diimine (5b)

Red oil, 60.3 mg. 57% isolated yield. ¹H NMR (500 MHz, C₆D₆) δ 7.24 – 7.16 (m, 4H, CH(CH(CH)₂CN), 6.94 (t, J = 7.5 Hz, 2H, CH(CH(CH)₂CN), 6.74 (dd, J = 8.3, 1.3 Hz, 4H, CH(CH(CH)₂CN), 2.70 (q, J = 7.5 Hz, 4H, CH₂CH₃), 1.04 (t, J = 7.5 Hz, 6H, CH₂CH₃). ¹³C NMR (126 MHz, C₆D₆) δ 171.66, 151.52, 129.29, 123.71, 118.73, 22.12, 12.90. ESI-HRMS (m/z): calcd. for C₁₈H₂₀N₂Na⁺, 287.1524; found, 287.1525 (diff. 0.0001).

Figure S43. ¹H NMR spectrum of 5b in C₆D₆.
Figure S44. $^{13}$C NMR spectrum of 5b in C$_6$D$_6$. 
(5E,6E)-N<sup>4</sup>,N<sup>6</sup>-diphenyldecane-5,6-diimine (5c)

Red solid, 59.9 mg. 51% isolated yield. \(^1\)H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) \(\delta 7.18 \text{ (d, } J = 7.4 \text{ Hz, } 2\text{H, CH(CHCH)}_2\text{CN), 6.93 \text{ (tt, } J = 7.3, 1.2 \text{ Hz, } 2\text{H, CH(CHCH)}_2\text{CN), 6.78 \text{ (d, } J = 8.3 \text{ Hz, } 2\text{H, CH(CHCH)}_2\text{CN), 2.84 – 2.78 \text{ (m, } 4\text{H, CH}_2\text{CH}_2\text{CH}_2\text{CH}_3, 1.61 \text{ (p, } J = 7.8 \text{ Hz, } 4\text{H, CH}_2\text{CH}_2\text{CH}_2\text{CH}_3), 1.18 \text{ (h, } J = 7.4 \text{ Hz, } 4\text{H, CH}_2\text{CH}_2\text{CH}_2\text{CH}_3), 0.74 \text{ (t, } J = 7.3 \text{ Hz, } 6\text{H, CH}_2\text{CH}_2\text{CH}_2\text{CH}_3). \(^1\)\(^3\)C NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>) \(\delta 171.14, 151.58, 129.25, 123.71, 118.82, 30.67, 28.44, 23.21, 13.91, 1.42. \) ESI-HRMS (m/z): calcd. for C<sub>22</sub>H<sub>28</sub>N<sub>2</sub>Na<sup>+</sup>, 343.2150; found, 343.2164. (diff. 0.0014).

Figure S45. \(^1\)H NMR spectrum of 5c in C<sub>6</sub>D<sub>6</sub>.
Figure S46. $^{13}$C NMR spectrum of 5c in C₆D₆.
(1E,2E)-N^1,N^2-1,2-tetraphenylethane-1,2-diimine (5d)

Light brown solid, 80.8 mg. 56% isolated yield using conditions A, 35% yield using conditions B (see below). \(^1\)H NMR (500 MHz, C\(_6\)D\(_6\)) \(\delta\) 8.11 – 8.03 (m, 4H, CH(CHCH)\(_2\)CC), 7.07 – 6.99 (m, 6H, CH(CHCH)\(_2\)CC & CH(CHCH)\(_2\)CC), 6.92 – 6.88 (m, 4H, CH(CHCH)CN), 6.81 (d, \(J = 7.6\) Hz, 6H, CH(CHCH)CN & CH(CHCH)CN). \(^{13}\)C NMR (126 MHz, C\(_6\)D\(_6\)) \(\delta\) 164.17, 150.19, 138.36, 131.25, 128.98, 128.80, 128.73, 125.17, 120.69. ESI-HRMS (m/z): calcd. for C\(_{26}\)H\(_{20}\)N\(_2\)Na\(^+\), 383.1524; found, 383.1512. (diff. 0.0012).

Figure S47. \(^1\)H NMR spectrum of 5d in C\(_6\)D\(_6\).
Figure S48. $^{13}$C NMR spectrum of 5d in C$_6$D$_6$.

Synthesis of 5d using alternative method from in-situ imido generation using TiCl$_4$(THF)$_2$, Zn$^0$, and azobenzene

Procedure for synthesis of 5d using conditions b: TiCl$_4$(THF)$_2$ (133.6 mg, 0.400 mmol, 1 equiv.), Zn$^0$ (65.4 mg, 0.48 mmol, 1.2 equiv.), and azobenzene (36.5 mg, 0.2 mmol, 0.5 equiv.), PhBr (4 mL), pyridine (64.4 μL, 0.8 mmol, 2 equiv.) and a stir bar were added to a 20 mL scintillation vial. The vial was heated for 3 hours at 115 °C. After allowing the vial to cool to room temperature, acetonitrile (208 μL, 4.00 mmol, 10 equiv.), and diphenylacetylene 4d (0.400 mmol, 1.00 equiv.) were added. The vial was sealed with a Teflon cap, wrapped in electrical tape, brought out of the glovebox, and placed in a preheated oil bath at 115 °C for 4 h while stirring. The heterogeneous yellow-orange mixture turned dark brown-yellow upon heating. After the initial heating period, the vial was brought back into the glovebox, and nitrosobenzene 2a (42.8 mg, 0.4 mmol, 1 equiv.) was added. The mixture was allowed to stir for 30 minutes. The vial was then removed from the glovebox and was quenched by the addition of 10 mL of saturated Na$_2$CO$_3$ (aq). The layers were separated, and the aqueous layer was extracted with DCM. The organics were combined, dried over Na$_2$SO$_4$, and filtered. The volatiles (including bromobenzene, DCM, MeCN) were reduced under vacuum. Any remaining azobenzene (from the metathesis of leftover imido with nitrosobenzene) was then removed through sublimation using a water-cooled cold finger with a ground glass joint fitted into a round bottom flask, which was heated at 70 °C under vacuum.
Any remaining diphenylacetylene was also be removed by prolonged heating under vacuum. Diimine 5d was obtained with a 35% yield using this alternative method (50.4 mg).
Red oil, 58.3 mg, 52% isolated yield. \(^1\)H NMR (500 MHz, C\(_6\)D\(_6\)) \(\delta\) 7.23 – 7.13 (m, 4H, CH(CHCH)\(_2\)CNC(CH\(_2\))\(_3\)CH\(_3\) \& CH(CHCH)\(_2\)CNCCH\(_3\)), 7.00 – 6.85 (m, 2H, CH(CHCH)\(_2\)CNC(CH\(_2\))\(_3\)CH\(_3\) \& CH(CHCH)\(_2\)CNCCH\(_3\)), 6.82 – 6.76 (m, 2H, CH(CHCH)\(_2\)CNC(CH\(_2\))\(_3\)CH\(_3\)), 6.75 – 6.69 (m, 2H, CH(CHCH)\(_2\)CNCCH\(_3\)), 2.83 – 2.75 (m, 2H, CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 2.13 (s, 3H, CH\(_3\)), 1.59 (p, \(J = 7.8\) Hz, 2H, CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 1.16 (h, \(J = 7.4\) Hz, 2H, CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 0.73 (t, \(J = 7.4\) Hz, 3H, CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)). \(^{13}\)C NMR (101 MHz, C\(_6\)D\(_6\)) \(\delta\) 171.87, 167.57, 151.67, 151.61, 129.30, 129.24, 124.00, 123.74, 119.11, 118.84, 30.90, 28.35, 23.26, 15.66, 13.92. ESI-HRMS (m/z): calcd. for C\(_{19}\)H\(_{22}\)N\(_2\)Na\(^{+}\), 301.1681; found, 301.1690. (diff. 0.0009).

**Figure S49.** \(^1\)H NMR spectrum of 5e in C\(_6\)D\(_6\).
Figure S50. $^{13}$C NMR spectrum of 5e in C$_6$D$_6$. 
**N',N'-1-triphenylpropane-1,2-dimine (5f)**

Brown oil, 67.5 mg. 57% isolated yield in a mixture of three isomers in a 3.2:1.8:1 ratio.

**ESI-HRMS (m/z):** calcd. for C_{21}H_{18}N_{2}Na^{+}, 321.1368; found, 321.1352. (diff. 0.0016).

The major isomer is likely to be E,E, and based on chemical shift arguments and DFT NMR Gauge-Independent Atomic Orbital (GIAO) calculations, Minor Isomer A and Minor Isomer B are tentatively assigned to be Z,E and E,Z, respectively.

The aryl region from 7.25 to 6.75 ppm in the ¹H NMR is too highly overlapped to be confidently assigned.

**¹H NMR (500 MHz, C_{6}D_{6})** δ 8.27 – 8.17 (m, 2H, Major Isomer), 7.96 – 7.85 (m, 1H, Minor Isomer B), 7.26 – 7.19 (m, 3H), 7.18 (d, J = 1.6 Hz, 1H), 7.15 – 7.07 (m, 8H), 7.07 – 7.04 (m, 1H), 7.03 – 6.83 (m, 7H), 6.83 – 6.76 (m, 3H), 6.72 – 6.67 (m, 1H, Minor Isomer B), 6.67 – 6.63 (m, 1H, Minor Isomer A), 6.63 – 6.59 (m, 2H, Major Isomer), 2.28 (s, 2H, Minor Isomer A), 2.15 (s, 1H, Minor Isomer B), 1.43 (s, 3H, Major Isomer).

Major Isomer (E,E): **¹³C NMR (126 MHz, C_{6}D_{6})** δ 167.28, 167.05, 151.35, 150.25, 136.43, 131.39, 130.31, 129.35, 129.17, 128.90, 128.87, 128.82, 120.93, 119.50, 20.16.

Minor Isomer A (Z,E): **¹³C NMR (126 MHz, C_{6}D_{6})** δ 168.52, 168.48, 151.64, 150.86, 135.24, 128.94, 128.88, 128.76, 128.35, 127.62, 124.24, 124.17, 121.01, 118.96, 16.28.

Minor Isomer B (E,Z): **¹³C NMR (126 MHz, C_{6}D_{6})** δ 166.11, 165.29, 150.59, 149.89, 136.61, 131.30, 128.97, 128.57, 125.07, 124.85, 124.21, 124.00, 120.78, 120.10, 27.90.
Figure S51. $^1$H NMR spectrum of 5f as a mixture of isomers in C$_6$D$_6$. 
Figure S52. $^{13}$C NMR spectrum of 5f as a mixture of isomers in C₆D₆, with inset showing the imine region.
Figure S53. NOESY of methyl region (1.20 – 2.10 ppm) of 5f showing EXSY cross-peaks that indicate chemical exchange between different diimine isomers, as opposed to through-space interactions (NOEY); EXSY cross-peaks = same phase as diagonal, NOESY = opposite phase.
Figure S54. Full NOESY of 5f.

Figure S55. GC-MS of 5f (m/z = 298).
(4-trifluoromethyl)-\(N^1,N^2\)-diphenylpropane-1,2-diimine (5g)

Dark red oil, 102.0 mg. 70% isolated yield. \(^1\text{H},^{13}\text{C},\) and \(^{19}\text{F}\) NMR show a mixture of isomers in solution (C\(_6\)D\(_6\)). GC-MS shows single product peak (m/z = 366), and the diimine was coordinated (6g) to ZnCl\(_2\) complex to obtain a single isomer and allow for full \(^1\text{H}\) and \(^{13}\text{C}\) assignments (see below).

\(^1\text{H}\) NMR (500 MHz, C\(_6\)D\(_6\)) (all isomers) \(\delta\) 8.05 – 7.99 (m, 2H), 7.70 (d, \(J = 8.1\) Hz, 1H), 7.39 (d, \(J = 8.3\) Hz, 2H), 7.28 (d, \(J = 8.2\) Hz, 1H), 7.15 – 7.10 (m, 7H), 7.10 – 7.05 (m, 3H), 7.00 (d, \(J = 8.0\) Hz, 2H), 6.98 – 6.89 (m, 7H), 6.88 – 6.83 (m, 1H), 6.76 (tt, \(J = 7.5, 1.2\) Hz, 1H), 6.72 (dd, \(J = 7.3, 1.3\) Hz, 1H), 6.71 – 6.66 (m, 3H), 6.66 – 6.61 (m, 4H), 2.25 (s, 3H), 2.06 (s, 1H), 1.36 (s, 3H), 1.18 (s, 1H).

\(^{13}\text{C}\) NMR (126 MHz, C\(_6\)D\(_6\)) (all isomers) \(\delta\) 168.08, 167.13, 166.90, 166.82, 165.77, 164.77, 164.52, 161.00, 152.02, 151.84, 151.19, 150.73, 150.11, 149.89, 149.87, 149.62, 146.76, 143.71, 142.49, 139.58, 138.89, 133.09, 132.98, 132.83, 132.68, 132.58, 132.32, 130.65, 130.31, 130.06, 130.05, 129.44, 129.29, 129.25, 129.13, 129.08, 129.03, 128.99, 128.86, 128.76, 128.25, 128.06, 127.87, 125.89, 125.86, 125.83, 125.79, 125.76, 125.73, 125.70, 125.67, 125.53, 125.45, 125.42, 125.32, 124.81, 124.74, 124.58, 124.55, 124.51, 124.49, 124.36, 121.57, 120.82, 120.74, 120.47, 120.20, 119.47, 118.95, 27.35, 21.86, 20.85, 19.90, 16.02. \(^{19}\text{F}\) NMR (471 MHz, C\(_6\)D\(_6\)) \(\delta\) -62.13, -62.69, -62.74, -62.76, -62.81 (vs. TFA) \(\delta\) -77.80. ESI-HRMS (m/z): calcd. for C\(_{22}\)H\(_{17}\)F\(_3\)N\(_2\)Na\(^+\), 389.1242; found, 389.1242.

Figure S56. \(^1\text{H}\) NMR spectrum of 5g as a mixture of isomers in C\(_6\)D\(_6\).
Figure S57. $^{13}$C NMR spectrum of 5g as a mixture of isomers in $C_6D_6$, with insets showing ortho C quartets.
Figure S58. $^{19}$F NMR spectrum of 5g in C$_6$D$_6$ with trifluoroacetic acid (neat) reference capillary (δ - 77.80), $^{19}$F signals for multiple isomers observed.
Figure S59. GC-MS of 5g (m/z = 366).
Brown oil, 89.1 mg, 68% isolated yield. \(^1\)H and \(^{13}\)C NMR show a mixture of isomers in solution (C\(_6\)D\(_6\)). GC-MS shows single product peak (m/z = 328), and the diimine was coordinated (6h) to ZnCl\(_2\) complex to obtain a single isomer and allow for full proton and carbon assignments (see below).

\(^1\)H NMR (500 MHz, C\(_6\)D\(_6\)) (all isomers) \(\delta 8.25 - 8.15\) (m, 2H), \(8.02 - 7.98\) (m, 1H), \(7.92 - 7.84\) (m, 1H), \(7.28 - 7.18\) (m, 1H), \(7.15\) (d, \(J = 2.0\) Hz, 4H), \(7.11\) (d, \(J = 7.9\) Hz, 2H), \(7.09 - 6.99\) (m, 2H), \(6.95 - 6.88\) (m, 4H), \(6.83 - 6.79\) (m, 2H), \(6.78 - 6.74\) (m, 1H), \(6.74 - 6.71\) (m, 1H), \(6.70 - 6.67\) (m, 1H), \(6.67 - 6.63\) (m, 2H), \(6.57 - 6.54\) (m, 1H), \(3.33\) (s, 1H), \(3.28\) (s, 3H), \(3.20\) (s, 1H), \(3.13\) (s, 1H), \(2.89\) (s, 1H), \(2.29\) (s, 1H), \(1.74\) (s, 1H), \(1.48\) (s, 3H), \(1.44\) (s, 1H). \(^{13}\)C NMR (101 MHz, C\(_6\)D\(_6\)) (all isomers) \(\delta 168.76, 168.18, 167.88, 167.55, 165.69, 165.51, 162.66, 162.49, 160.02, 158.65, 153.21, 152.55, 152.09, 151.77, 151.61, 151.29, 150.85, 150.38, 149.97, 134.98, 133.48, 132.24, 131.76, 131.44, 131.38, 131.18, 130.65, 130.36, 130.33, 130.24, 129.38, 129.32, 129.22, 129.20, 129.02, 128.93, 128.90, 128.86, 128.76, 128.30, 128.06, 127.82, 125.09, 124.57, 124.14, 124.01, 123.95, 123.34, 121.72, 121.18, 121.00, 120.94, 120.27, 119.53, 118.93, 114.47, 114.34, 114.15, 113.26, 54.97, 54.91, 54.85, 54.75, 54.57, 28.15, 22.17, 21.01, 20.27, 16.55. ESI-HRMS (m/z): calcd. for C\(_{22}\)H-20N\(_2\)OH\(^+\), 329.1654; found, 329.1647. (diff. 0.0007)
Figure S60. $^1$H NMR spectrum of 5h as a mixture of isomers in C$_6$D$_6$. 

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Figure S61. $^{13}$C NMR spectrum of 5h as a mixture of isomers in C$_6$D$_6$. 
Figure S62. GC-MS of 5h (m/z = 328).
$N'^1, N'^2$-diphenyl-1-(trimethylsilyl)propane-1,2-diimine (5i) (Not isolated)

Not isolated, but reaction mixture GC-MS is given. Trace amount of 5i observed in GC-MS.

Figure S63. GC-MS of 5i reaction mixture after workup.
Yellow-brown residue, 31.9 mg. Isolated as a mixture of diimine (26% yield) with some pyrrole impurity (2.4%) (91% pure). $^1$H and $^{13}$C NMR show a mixture of isomers in solution ($\text{C}_6\text{D}_6$). Efforts to coordinate to ZnCl$_2$ were unsuccessful. $^1$H NMR (500 MHz, $\text{C}_6\text{D}_6$) (both isomers) $\delta$ 8.31 (s, 1H), 8.12 (s, 1H), 7.14 – 7.07 (m, 7H), 7.07 – 7.02 (m, 4H), 6.98 (m, 6H), 6.95 – 6.86 (m, 10H), 6.79 (m, 5H), 0.57 (s, 9H), 0.17 (s, 6H). $^{13}$C NMR (126 MHz, $\text{C}_6\text{D}_6$) $\delta$ 185.41, 184.59, 166.27, 155.94, 154.19, 152.50, 150.99, 129.47, 129.42, 129.06, 128.99, 127.49, 127.18, 124.77, 124.53, 121.54, 121.30, 120.24, 118.22, 3.00, 1.53, 0.96, -0.94. ESI-HRMS (m/z): calcd. for C$_{17}$H$_{20}$N$_2$SiNa+, 303.1293; found, 303.1271 (diff. 0.0022).

Figure S64. $^1$H NMR spectrum of 5j in $\text{C}_6\text{D}_6$. 

\[N^1,N^2\text{-diphenyl-1-}(\text{trimethylsilyl})\text{ethane-1,2-diimine} \ (5j)\]
Figure S65. $^{13}$C NMR spectrum of 5j in C$_6$D$_6$. 
(1E,2E)-3,3-dimethyl-N₁,N₂-diphenylbutane-1,2-diimine (5k)

Yellow oil. 68% isolated yield, 67.2 mg. ¹H NMR (400 MHz, C₆D₆) δ 7.87 (s, 1H, CH), 7.04 (t, J = 7.7 Hz, 2H, Ar-H), 7.01 – 6.95 (m, 2H, Ar-H), 6.94 – 6.90 (m, 1H, Ar-H), 6.90 – 6.83 (m, 3H, Ar-H), 6.80 – 6.74 (m, 2H, CH(CHCH₂)₂CNC(CH₃)₃), 1.60 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, C₆D₆) δ 173.68, 155.60, 151.27, 150.21, 129.41, 129.04, 127.09, 124.28, 123.35, 121.23, 40.66, 28.85. ESI-HRMS (m/z): calcd. for C₁₈H₂₀N₂Na⁺, 265.1705; found, 265.1704. (diff. 0.0001).

Figure S66. ¹H NMR spectrum of 5k in C₆D₆.
Figure S67. $^{13}$C NMR spectrum of 5k in C$_6$D$_6$. 
$N^1,N^2$-diphenyl-1-(p-tolyl)ethane-1,2-diimine (5I)

Brown solid, 94.1 mg. Isolated as a mixture of diimine (66% yield) and pyrrole (12%) (84% pure). $^1$H and $^{13}$C NMR show a mixture of two major isomers in solution ($C_6D_6$). **ESI-HRMS (m/z):** calcd. for $C_{21}H_{18}N_2H^+$, 299.1548; found, 299.1544 (diff. 0.0004).

$^1$H NMR (500 MHz, $C_6D_6$) (both isomers) δ 8.59 (s, 1H), 8.31 (d, $J = 8.2$ Hz, 2H), 8.13 (s, 1H), 7.22 – 7.14 (m, 2H), 7.14 – 6.87 (m, 23H), 6.84 – 6.80 (m, 2H), 2.12 (s, 3H), 1.93 (s, 2H). $^{13}$C NMR (126 MHz, $C_6D_6$) (both isomers and pyrrole) δ 166.69, 162.87, 162.55, 155.37, 150.84, 150.76, 150.57, 150.03, 140.75, 138.49, 134.41, 131.06, 130.71, 130.48, 130.01, 129.46, 129.35, 129.33, 129.14, 129.09, 128.80, 128.76, 128.63, 128.37, 127.08, 126.99, 125.69, 125.67, 125.24, 124.51, 124.22, 123.74, 122.99, 122.28, 121.14, 121.13, 120.87, 120.83, 21.05, 20.86, 20.74.

**Figure S68.** $^1$H NMR spectrum of 5I in $C_6D_6$. 
Figure S69. $^{13}$C NMR spectrum of 5I in C$_6$D$_6$. 
(5E,6E)-N₅,N⁰-diphenyldec-1-ene-5,6-diimine (5m)

Reddish-brown oil, 64.3 mg. 50% isolated yield. ¹H NMR (500 MHz, C₆D₆) δ 7.22 – 7.17 (m, 2H), 7.16 – 7.14 (m, 2H), 6.97 – 6.90 (m, 2H), 6.82 – 6.70 (m, 4H), 5.64 (ddt, J = 16.9, 10.1, 6.8 Hz, 1H, CH₂CH₂CH=CH₂), 4.94 (dd, J = 17.0, 1.7 Hz, 1H, CH₂CH₂CH=CH₂), 4.86 (dd, J = 10.1, 1.7 Hz, 1H, CH₂CH₂CH=CH₂), 2.92 – 2.83 (m, 2H, CH₂CH₂CH=CH₂), 2.83 – 2.71 (m, 2H, CH₂CH₂CH₂CH₃), 2.35 (q, J = 7.5 Hz, 2H, CH₂CH₂CH₂CH₃), 1.58 (p, J = 7.3 Hz, 2H, CH₂CH₂CH₂CH₃), 1.16 (h, J = 7.4 Hz, 2H, CH₂CH₂CH₂CH₃), 0.73 (t, J = 7.4 Hz, 3H, CH₃CH₂CH₂CH₃). ¹³C NMR (101 MHz, C₆D₆) δ 170.99, 170.14, 151.46, 151.34, 137.80, 129.27, 129.25, 123.81, 123.77, 118.81, 118.78, 115.23, 32.67, 30.67, 28.41, 28.11, 23.16, 13.90. ESI-HRMS (m/z): calcd. for C₂₂H₂₆N₂Na⁺, 341.1994; found, 341.1999. (diff. 0.0005).

Figure S70. ¹H NMR spectrum of 5m in C₆D₆.
Figure S71. $^{13}$C NMR spectrum of 5m in C$_6$D$_6$. 
(1E,2E)-N¹,N²-1-triphenyleth-6-ene-1,2-dilmine (5n) (Not isolated)

Not isolated, 10% yield of diimine, with 6% combined yield of two carboamination products as determined by GC-FID (Figure S71) using 1,3,5-trimethoxybenzene as an internal standard (45.8 mg). Product identities determined by GC-MS (Figure S70).

Figure S72. GC-MS of 5n reaction mixture in C₆D₆.
Figure S73. GC-FID of 5n reaction mixture.
(3E,4E)-2-methyl-\(N^3,N^4\)-diphenylhex-1-ene-3,4-diimine (5o) (Not isolated)

Not isolated, but reaction mixture GC-MS is given. Trace amount of 5o observed in GC-MS, alongside some hydrolyzed 5o.

**Figure S74.** \(^{13}\)C NMR spectrum of 5n in C\(_6\)D\(_6\).
(1E,2E)-N¹,N²-diphenylcyclooctane-1,2-diimine (5p) (Not isolated or detected)

Not isolated, but reaction mixture NMR and GC-MS is given. Trimer was the major reaction product, with a small amount of pyrrole. A trace amount of 5p was observed in the baseline of the GC-MS.

Figure S75. \(^1\)H NMR spectrum of 5p reaction mixture after workup (top) and cyclooctyne 4p (bottom) in C₆D₆.
Figure S76. GC-MS of 5p reaction mixture after workup (m/z = 290).
Modular synthesis of diimine regioisomers (5q-5r)

For 5q: [py2TiCl2(Np-tol)]2 (152.8 mg, 0.400 mmol, 1 equiv.), PhBr (4 mL), and a stir bar were added to a 20 mL scintillation vial, followed by acetonitrile (208 μL, 4.00 mmol, 10 equiv.), and tert-butylacetylene (0.400 mmol, 1.00 equiv, 50 μL). The vial was sealed with a Teflon cap, wrapped in electrical tape, brought out of the glovebox, and placed in a preheated oil bath at 115 °C for 4 h while stirring. The heterogeneous yellow-orange mixture turned dark brown-yellow upon heating. After the initial heating period, the vial was brought back into the glovebox, and nitrosobenzene (2a) (42.8 mg, 0.4 mmol, 1 equiv.) was added with an additional 0.5 mL PhBr. The mixture was allowed to stir for 30 minutes. The vial was then removed from the glovebox and was quenched by the addition of 10 mL of saturated Na2CO3 (aq). The layers were separated, and the aqueous layer was extracted with DCM. The organics were combined, dried over Na2SO4, and filtered. The volatiles (including bromobenzene, DCM, MeCN, and any remaining tert-butylacetylene) were reduced under vacuum. Any remaining diazene (from the metathesis of leftover imido with nitrosobenzene) was then removed through sublimation using a water-cooled cold finger with a ground glass joint fitted into to a round bottom flask, which was heated at 70 °C under vacuum. 45.8 mg of an orange solid (41% yield) was isolated and a 1H NMR spectrum was recorded.

For 5r: [py2TiCl2(NPh)]2 (147.2 mg, 0.400 mmol, 1 equiv.), PhBr (4 mL), and a stir bar were added to a 20 mL scintillation vial, followed by acetonitrile (208 μL, 4.00 mmol, 10 equiv.), and tert-butylacetylene (0.400 mmol, 1.00 equiv, 50 μL). The vial was sealed with a Teflon cap, wrapped in electrical tape, brought out of the glovebox, and placed in a preheated oil bath at 115 °C for 4 h while stirring. The heterogeneous yellow-orange mixture turned dark brown-yellow upon heating. After the initial heating period, the vial was brought back into the glovebox, and p-tolNO (2g) (42.8 mg, 0.4 mmol, 1 equiv.) was added with an additional 0.5 mL PhBr. The mixture was allowed to stir for 30 minutes. The vial was then removed from the glovebox and was quenched by the addition of 10 mL of saturated Na2CO3 (aq). The layers were separated, and the aqueous layer was extracted with DCM. The organics were combined, dried over Na2SO4, and filtered. The volatiles (including bromobenzene, DCM, MeCN, and any remaining tert-butylacetylene) were reduced under vacuum. Any remaining diazene (from the metathesis of leftover imido with 2g) was then removed through sublimation using a water-cooled cold finger with a ground glass joint fitted into to a round bottom flask, which was heated at 70 °C under vacuum. 49.4 mg of an orange oil (44% yield) was isolated and a 1H NMR spectrum was recorded.

For 5s: [py2TiCl2(N’Bu)]2 (139.2 mg, 0.400 mmol, 1 equiv.), PhBr (4 mL), and a stir bar were added to a 20 mL scintillation vial, followed by acetonitrile (208 μL, 4.00 mmol, 10 equiv.), and p-tolacetylene (0.400 mmol, 1.00 equiv, 51 μL). The vial was sealed with a Teflon cap, wrapped in electrical tape, brought out of the glovebox, and placed in a preheated oil bath at 115 °C for 4 h while stirring. The heterogeneous orange-pink mixture turned dark brown upon heating. After the initial heating period, the vial was brought back into the glovebox, and nitrosobenzene (2a) (42.8 mg, 0.4 mmol, 1 equiv.) was added with an additional 0.5 mL PhBr. The mixture was allowed to stir for 30 minutes. The vial was then removed from the glovebox and was quenched by the addition of 10 mL of saturated Na2CO3 (aq). The layers were separated, and the aqueous layer was extracted with DCM. The organics were combined, dried over Na2SO4, and filtered. The volatiles (including bromobenzene, DCM, MeCN, and any remaining p-tolacetylene) were reduced under vacuum. Any remaining diazene was then removed through sublimation using a water-cooled cold finger with a ground glass joint fitted into to a round bottom flask, which was heated at 70 °C under vacuum. 60.2 mg of an orange oil (50% yield of diimine, 4% yield of pyrrole) was isolated and a 1H NMR spectrum was recorded.
(1E,2E)-3,3-dimethyl-N\textsuperscript{2}-phenyl-N\textsuperscript{1}-(p-tolyl)butane-1,2-diimine (5q)

Orange solid. 45.8 mg. 41% isolated yield. \textsuperscript{1}H NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}) \(\delta\) 7.95 (s, 1H, CH), 7.08 – 7.02 (m, 2H, CH(CH\textsubscript{3})\textsubscript{2}CN), 6.91 – 6.83 (m, 3H, CH\textsubscript{3}C(CH\textsubscript{3})\textsubscript{2}CN & CH(CH\textsubscript{3})\textsubscript{2}CN), 6.82 – 6.76 (m, 4H, CH(CH\textsubscript{3})\textsubscript{2}CN & CH\textsubscript{3}C(CH\textsubscript{3})\textsubscript{2}CN), 2.00 (s, 3H, CH\textsubscript{3}), 1.63 (s, 9H, C(CH\textsubscript{3})\textsubscript{3}). \textsuperscript{13}C NMR (101 MHz, C\textsubscript{6}D\textsubscript{6}) \(\delta\) 173.76, 154.48, 150.37, 148.76, 137.04, 130.07, 129.04, 124.18, 121.34, 120.46, 40.68, 28.91, 20.90. ESI-HRMS (m/z): calcd. for C\textsubscript{19}H\textsubscript{22}N\textsubscript{2}Na\textsuperscript{+}, 301.1681; found, 301.1681.

Figure S77. \textsuperscript{1}H NMR spectrum of 5q in C\textsubscript{6}D\textsubscript{6}.
Figure S78. $^{13}$C NMR spectrum of 5q in C$_6$D$_6$. 
(1E,2E)-3,3-dimethyl-N1-phenyl-N2-(p-tolyl)butane-1,2-diimine (5r)

Orange oil, 49.4 mg. 44% isolated yield. 1H NMR (500 MHz, C6D6) δ 7.95 (s, 1H, CH), 7.02 – 6.97 (m, 2H, CH(CHCH)2CN), 6.93 – 6.89 (m, 3H, CH3C(CHCH)2CN & CH(CHCH)2CN), 6.87 (d, J = 8.1 Hz, 2H, CH2C(CHCH)2CN), 6.77 (d, J = 8.2 Hz, 2H, CH(CHCH)2CN), 2.04 (s, 3H, CH3), 1.64 (s, 9H, C(CH3)3). 13C NMR (126 MHz, C6D6) δ 173.46, 155.72, 151.34, 147.59, 133.79, 129.68, 129.42, 127.04, 121.27, 120.77, 40.73, 28.91, 20.86. ESI-HRMS (m/z): calcd. for C19H22N2Na+, 301.1681; found, 301.1673. (diff. 0.0008).

Figure S79. 1H NMR spectrum of 5r in C6D6.
Figure S80. $^{13}$C NMR spectrum of 5r in C$_6$D$_6$. 
$N^2$-(tert-butyl)-$N^1$-phenyl-1-(p-tolyl)ethane-1,2-diimine (5s)

Orange oil, 60.2 mg. Isolated as a mixture of diimine (50% yield) with some pyrrole impurity (4%) (92% pure). $^1$H and $^{13}$C NMR show a mixture of two major isomers in solution (C$_6$D$_6$). **ESI-HRMS (m/z):** calcd. for C$_{19}$H$_{22}$N$_2$Na$,^+$, 301.1681; found, 301.1688. (diff. 0.0007).

$^1$H NMR (500 MHz, C$_6$D$_6$) (both isomers) $\delta$ 8.43, 8.29, 8.27, 7.91, 7.18, 7.13, 7.11, 7.10, 7.07, 7.06, 7.03, 7.02, 7.00, 6.95, 6.94, 6.93, 6.91, 6.89, 6.88, 6.82, 6.80, 6.78, 6.77, 2.08, 1.89, 1.12, 1.01. $^{13}$C NMR (126 MHz, C$_6$D$_6$) (both isomers and pyrrole) $^{13}$C NMR (126 MHz, C$_6$D$_6$) $\delta$ 167.36, 163.91, 158.93, 152.27, 151.25, 150.84, 140.84, 138.52, 135.06, 132.14, 131.21, 130.54, 130.19, 129.73, 129.34, 128.98, 128.94, 128.48, 128.35, 128.25, 128.06, 127.97, 127.87, 125.36, 124.32, 124.10, 121.18, 121.04, 58.88, 58.27, 31.84, 30.46, 30.22, 29.36, 29.04, 21.34, 21.16.

**Figure S81.** $^1$H NMR spectrum of 5s in C$_6$D$_6$. 
Figure S82. $^{13}$C NMR spectrum of 5s in C$_6$D$_6$. 
Addition of ZnCl$_2$ to asymmetric diimine isomers (Figure 3, 6f-6h, 6l)

General procedure: 5 mL of THF was added to a 20 mL scintillon vial containing diimine (0.25 mmol), along with a stirbar. ZnCl$_2$ (0.25 mmol) in 5 mL THF was then added, and the reaction was stirred for 2 h at room temperature. The volatiles were reduced to obtain a brown powder, which was washed with hexanes and dried. A $^1$H and $^{13}$C NMR spectrum was then recorded in CDCl$_3$. Crystals suitable for XRD were grown from this CDCl$_3$ solution (Figure S97).

The resulting ZnCl$_2$(diimine)$\cdot$0.5THF complex was then washed with THF to remove the half equivalent of THF that was not able to be removed by vacuum (only demonstrated for 6f, Figure S83-84).
ZnCl$_2$((1$E$,2$E$)-$N^1,N^2$-1,2-triphenylpropane-1,2-diimine)$\cdot$0.5THF (6f)

Brown powder, 136.6 mg, 93% isolated yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.49 – 7.30 (m, 10H, Ar-H), 7.23 – 7.15 (m, 5H, Ar-H), 3.80 (s, 2H, O(CH$_2$)$_2$(CH$_2$)$_2$), 2.20 (s, 3H, CH$_3$), 1.86 (s, 2H, O(CH$_2$)$_2$(CH$_2$)$_2$). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 169.38, 167.98, 143.85, 143.61, 131.63, 131.16, 129.95, 129.45, 129.40, 128.53, 128.43, 123.72, 122.18, 68.75, 25.63, 21.35.

After THF wash $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.50 – 7.39 (m, 5H), 7.37 (d, J = 7.9 Hz, 2H), 7.30 (d, J = 7.0 Hz, 2H), 7.23 – 7.10 (m, 5H), 2.19 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 168.93, 167.58, 143.94, 143.67, 131.71, 131.18, 129.95, 129.40, 128.55, 128.45, 128.41, 123.73, 122.13, 77.41, 77.36, 77.16, 76.91, 21.28.

Figure S83. $^1$H NMR spectrum of 6f in CDCl$_3$. 
Figure S84. $^{13}$C NMR spectrum of 6f in CDCl$_3$. 
Figure S85. $^1$H NMR spectrum of 6f in CDCl$_3$ after THF wash.
Figure S86. $^{13}$C NMR spectrum of 6f in CDCl$_3$ after THF wash.
ZnCl₂((1E,2E)-(4-trifluoromethyl)-N¹,N²-diphenylpropane-1,2-diimine)-0.5THF (6g)

Light tan powder, 136.9 mg. 91% isolated yield. ¹H NMR (500 MHz, CDCl₃) δ 7.67 (d, \( J = 8.1 \) Hz, 2H, CF₃(CHCH)CC), 7.52 (d, \( J = 8.1 \) Hz, 2H, CF₃(CHCH)CC), 7.44 – 7.39 (m, 3H, Ar-H), 7.39 – 7.34 (m, 3H, Ar-H), 7.23 – 7.17 (m, 3H, Ar-H), 7.16 – 7.10 (m, 2H, Ar-H), 3.83 – 3.68 (m, 2H, O(CH₂)₂(CH₂)₂), 2.16 (s, 3H, CH₃), 1.90 – 1.82 (m, 2H, O(CH₂)₂(CH₂)₂). ¹³C NMR (126 MHz, CDCl₃) δ 168.05, 166.52, 143.61, 143.21, 135.29, 133.05 (q, \( J = 276.6 \) Hz), 129.86, 129.50, 129.16, 128.71, 128.39, 126.32 (q, \( J = 3.7 \) Hz), 123.31, 122.01, 68.05, 25.70, 21.20. (note, most of the CF₃ quartet (133.05) is buried in noise, and the ipso quartet was not observed).

Figure S87. ¹H NMR spectrum of 6g in CDCl₃.
Figure S88. $^{13}$C NMR spectrum of 6g in CDCl$_3$. 
Figure S89. $^{19}$F NMR spectrum of 6g in CDCl$_3$ with trifluoroacetic acid (neat) reference capillary ($\delta$ - 77.80).
ZnCl$_2$(1E,2E)-(4-methoxyphenyl)-$N'$,$N''$-diphenylpropane-1,2-diimine)-0.5THF (6h)

Brown powder, 117.8 mg, 93% isolated yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.49 – 7.42 (m, 2H, Ar-$H$), 7.41 – 7.32 (m, 3H, CHC(CHCH)CN&CCH$_3$ & Ar-$H$), 7.22 (d, $J = 8.5$ Hz, 4H, CH$_3$OC(CHCH)CC & Ar-$H$), 7.11 – 7.15 (m, 3H, CHC(CHCH)CN & Ar-$H$), 6.90 (d, $J = 8.9$ Hz, 2H, CH$_3$OC(CHCH)CC), 3.82 (s, 3H, OCH$_3$), 3.79 – 3.75 (m, 2H, O(CH$_2$)$_2$(CH$_2$)$_2$), 2.23 (s, 3H, CH$_3$), 1.88 – 1.84 (m, 2H, O(CH$_2$)$_2$(CH$_2$)$_2$). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 169.62, 167.42, 161.71, 144.05, 143.98, 130.64, 129.95, 129.49, 128.37, 128.36, 123.77, 123.29, 122.12, 114.95, 68.35, 55.59, 25.72, 21.36.

Figure S90. $^1$H NMR spectrum of 6h in CDCl$_3$. 
Figure S91. $^{13}$C NMR spectrum of 6h in CDCl$_3$. 
ZnCl$_2$($1E,2E$)-$N^1,N^2$-diphenyl-1-(p-tolyl)ethane-1,2-diimine$\cdot$1THF (6I)

Brown powder, 114.8 mg, 86% isolated yield (some pyrrole impurity remaining). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.69 (s, 1H, CH), 7.88 – 7.78 (m, 2H, CH$_3$CHCH$_2$CH), 7.61 – 7.51 (m, 3H, Ar-H), 7.35 – 7.27 (m, 7H, Ar-H), 7.25 – 7.24 (m, 2H, Ar-H), 3.87 – 3.66 (m, 4H, O(CH$_2$)$_2$(CH$_2$)$_2$), 2.41 (s, 3H, CH$_3$), 1.99 – 1.76 (m, 4H, O(CH$_2$)$_2$(CH$_2$)$_2$). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.18, 155.67, 143.99, 143.71, 143.19, 132.24, 130.56, 130.52, 129.92, 129.21, 128.92, 128.76, 123.62, 123.54, 77.48, 77.16, 76.84, 68.31, 25.72, 21.91.

Figure S92. $^1$H NMR spectrum of 6I in CDCl$_3$. 
Figure S93. $^{13}$C NMR spectrum of 6I in CDCl$_3$. 
Control reaction with $[\text{py}_2\text{TiCl}_2\text{NPh}]_2$, 3-hexyne, and PhNO

**Procedure:** $[\text{py}_2\text{TiCl}_2(\text{NPh})]_2$ (17.6 mg, 0.048 mmol, 1 equiv.) and 0.5 mL of 0.020 M TMB in PhBr were added to an NMR tube, followed by 3-hexyne (4.8 mg, 0.059 mmol, 1 equiv.) and nitrosobenzene (5.5 mg, 0.050 mmol, 1 equiv.). The tube was capped, sealed with electrical tape, and heated to 115 °C in an oil bath for 1 hour. A $^1$H NMR spectrum was recorded. Azobenzene formation was observed without formation of any diimine.

**Figure S94.** No-D $^1$H NMR spectrum in PhBr showing (bottom) 3-hexyne and TMB, (top) azobenzene formation and unreacted 3-hexyne after 1 hr of heating at 115 °C.
Evaluation of *in situ* sequential condensations from diketones

Symmetrical diimine - 2,3-butanedione

**Procedure:** 2,3-butanedione (86.1 mg, 1.0 mmol), aniline (93.1 mg, 1.0 mmol, 1.0 equiv.), and 1-2 mg of p-toluenesulfonic acid (p-TsOH) was added to a 20 mL scintillation vial with 10.0 mL of dry toluene and 43.0 mg of 1,3,5-trimethoxybenzene as an internal standard. The yellow-orange solution was allowed to stir at 80 °C for 24 h. An aliquot of the dark red solution was extracted for analysis by GC-FID. p-Toluidine (107 mg, 1.0 mmol, 1.0 equiv.) and another 1-2 mg of p-TsOH was added and the reaction was stirred for an additional 24 h at 80 °C. A second aliquot was extracted for GC-FID analysis.

**Analysis of reaction mixture after step 1 (yields vs. TMB internal standard):**

![Graph showing GC-FID of aliquot from reaction mixture 24 h following addition of aniline of 2,3-butanedione at 80 °C in toluene]

Figure S95. GC-FID of aliquot from reaction mixture 24 h following addition of aniline of 2,3-butanedione at 80 °C in toluene
Analysis of reaction mixture after step 2 (yields vs. TMB internal standard):

Figure S96. GC-FID of aliquot from reaction mixture 24 h following second condensation step.

Unsymmetrical diimine - 1-phenyl-1,2-propanedione

Procedure: 1-phenyl-1,2-propanedione (148.0 mg, 1.0 mmol), aniline (93.1 mg, 1.0 mmol, 1.0 equiv.), and 1-2 mg of p-toluenesulfonic acid (p-TsOH) was added to a 20 mL scintillation vial with 10.0 mL of dry toluene and 43.0 mg of 1,3,5-trimethoxybenzene as an internal standard. The reaction was allowed to stir at 80 °C for 24 h. An aliquot was extracted for analysis by GC-FID. p-Toluidine (107 mg, 1.0 mmol, 1.0 equiv.) and another 1-2 mg of p-TsOH was added and the reaction was stirred for an additional 24 h at 80 °C. A second aliquot was extracted for GC-FID analysis.

Analysis of reaction mixture after step 1 (yields vs. TMB internal standard):
Figure S97. GC-FID of aliquot from reaction mixture 24 h following addition of p-toluidine of 1-phenyl-1,2-propanedione at 80 °C in toluene.

Analysis of reaction mixture after step 2 (yields vs. TMB internal standard)

Figure S98. GC-FID of aliquot from reaction mixture 24 h following second condensation step.
XRD Data

Figure S99. ORTEP diagram of 6f. Thermal ellipsoids are drawn at 50% probability.

| Property                  | Value                  |
|---------------------------|------------------------|
| CCDC Number               | 2072232                |
| Empirical Formula         | C_{21}H_{18}Cl_{2}N_{2}Zn (CDCl_{3}) |
| Formula Weight            | 554.01                 |
| Temperature (K)           | 125(2)                 |
| a, Å                      | 23.376(2)              |
| b, Å                      | 10.6352(9)             |
| c, Å                      | 20.2506(19)            |
| α, °                      | 90                     |
| β, °                      | 106.848(4)             |
| γ, °                      | 90                     |
| Volume, Å³                | 4818.4(8)              |
| Z                         | 8                      |
| Crystal System            | Monoclinic             |
| Space Group               | P2_1/c                 |
| d_{calc}, g/cm³           | 1.527                  |
| θ Range, °               | 2.034 to 27.944        |
| μ, mm⁻¹                   | 1.586                  |
| Abs. Correction           | Multi-scan             |
| GooF                       | 1.053                  |
| R_{1}^a                   | 0.0687                 |
| wR_{2}^b [l>2σ(l)]       | 0.1758                 |

\[ a R_1 = \Sigma |F_0|-|F_c|/|F_0|. \]
\[ b wR_2 = [\Sigma (w(F_o^2-F_c^2))^2]/[\Sigma w(F_o^2)^2]^{1/2}. \]
Computational Methods

The employed computational methods were adapted from previous work on similar systems. All geometry optimizations and frequency calculations were performed with the Gaussian 16 package (Rev. C.016). Structures were optimized using the M06 functional with 6-311G(d,p) as a basis set. A SMD continuum solvation model for bromobenzene was used for the best approximation of the experimental conditions. The ultrafine grid setting was used for all calculations to avoid integration errors, as is suggested with M06 functionals. Frequency calculations were performed on the optimized geometries at the same level of theory to obtain free energies and verify the structure as either a minima with no imaginary frequencies or as a transition state with a single imaginary frequency. To mitigate fictitious contributions by small frequencies, thermal energies were calculated at 298.15 K and 1 atm using a frequency correction calculation that scales any frequencies lower than 50 cm$^{-1}$ to 50 cm$^{-1}$. A graphical representation as well as the cartesian coordinates for all optimized geometries are given below with their electronic and free energy (before and after the frequency correction). A sample Gaussian input file with the settings described above has also been provided.

Intrinsic bond orbital (IBO) calculations were performed with MOLPRO 2019 and visualized with IBOView. All calculations were performed with the M06 functional and def2-TZVP basis set (IBOView does not support the previous used 6-31G-family of basis sets). Density fitting with def2-TZVP JK-fitting was used to accelerate MOLPRO calculations.

Sample Gaussian input:

```
# opt=(CalcFC) freq m06/6-311g(d,p) integral(grid=ultrafinegrid)
SCRF(SMD,Solvent=Bromobenzene) Temperature=298.15
PhNO

0 1
C  0.550971  -0.219292  -0.000020
C  -0.333310  -1.292700  -0.000010
C  -1.697780  -1.052119   0.000010
C  -2.159348   0.257752   0.000020
C  -1.267677   1.331301  -0.000010
C   0.092483   1.097859  -0.000030
H  -1.647025   2.348151  -0.000010
H   0.815324   1.907118  -0.000030
H   0.076198  -2.298761  -0.000020
H  -2.400101  -1.878988   0.000040
H  -3.227918   0.450544   0.000050
N   1.935581  -0.576234  -0.000030
O   2.715302   0.346095   0.000050
```
Intrinsic bond orbital analysis

(a) Loss of pyridine

(b) [4+2] cycloaddition of PhNO

(c) retro-[4+2] cycloaddition to eliminate MeCN

(d) Rearrangement to eto2(H2O)

(e) retro-[4+2] cycloaddition to Ti oxo

Figure S100. Relevant IBOs for intermediates and transition states of each reaction step (IM1 to IM8) are shown. The fraction of electrons in doubly occupied orbitals assigned to each atom are given in parenthesis (contributions that are ≤ 0.10 are omitted). Atom number labels correspond to line positions in respective cartesian coordinates (xyz).

Sample Molpro input:

```
memory.200,m;
geometry={
C 0.550971 -0.219292 -0.000020
C -0.333310 -1.292700 -0.000010
C -1.697780 -1.052119 0.000010
C -2.159348 0.257752 0.000020
C -1.267677 1.331301 -0.000010
C 0.092483 1.097859 -0.000030
}```
H  -1.647025  2.348151  -0.000010
H   0.815324  1.907118  -0.000030
H   0.076198 -2.298761  -0.000020
H  -2.400101 -1.878988  0.000040
H  -3.227918  0.450544  0.000050
N   1.935581 -0.576234  -0.000030
O   2.715302  0.346095  0.000050
}

basis=def2-TZVP
(df-rks,XC-m06,maxit=100; save, 2101.2)
(ibba,MAXIT_IB=100; orbital,2101.2; save,2103.2)
(put,xml,'PhNO.xml'; orbital,2103.2; keepspherical; skipvirt)
XYZ coordinates (Å) of optimized structures with electronic, free, and frequency corrected free energies (a.u.) at 298.15 K and 1 atm using M06/6-311g(d,p)/ultrafine in bromobenzene

IM1
Electronic energy: -2841.319854
Gibbs free energy: -2840.967609
Corrected free energy: -2840.965493

IM2
Electronic energy: -2593.136684
Gibbs free energy: -2592.866668
Corrected free energy: -2592.865142
**IM5**

Electronic energy: -2954.565283  
Gibbs free energy: -2954.208628  
Corrected free energy: -2954.205857

**IM6**

Electronic energy: -2821.841276  
Gibbs free energy: -2821.526602  
Corrected free energy: -2821.524094

Gibbs free energy:

IM5

H       0.249990       3.946185  
C
C
H
H
C
H
C
Cl       1.297967       1.094035  
Cl       1.857067       2.094141       1.176315  
Ti       0.554411       0.785146  
H       3.648547       0.233281  
C       5.210256       0.018031  
C       3.918587  
H
N
C
G

IM6

C       2.280261       -3.055308       1.103448  
C       1.187651       -2.105686       -0.867146  
H       1.862737       -4.007143       -1.824831  
N       1.597687       -0.841052       -0.456404  
C       -0.125889       -2.426411       -1.072436  
C       -0.724917       0.527673       2.497509  
N       -0.296743       0.001560       1.572626  
C       -0.554411       3.758146       -1.621268  
H       -0.338421       4.588559       -0.940325  
H       -0.044612       3.967158       -2.567539  
H       -1.624771       3.772687       -1.830161  
C       2.944843       -0.729422       0.022390  
C       3.918587       0.129068       -0.70722  
C       3.274969       -1.196768       1.29285  
C       5.465833       -1.049001       1.774315  
C       5.535899       -0.435958       0.989746  
C       5.210256       0.180031       -0.280335  
H       6.545109       -0.312594       1.370787  
H       5.964936       0.495939       -0.897805  
H       2.501915       -1.622745       1.899890  
C       4.814720       -1.405963       2.769174  
H       3.648547       0.233281       -1.754582  
Ti       0.559670       0.784704       -0.313631  
Cl       1.862737       2.094141       1.176315  
Cl
C       -1.269095       -1.889222       3.651249  
C       -0.785146       1.499957       -0.917940  
H       -2.343469       1.342028       3.516913  
H       -1.098941       -0.580403       4.542596  
H       -4.262736       -3.862131       1.430506  
H       -1.938573       3.426788       0.737310  
C       -4.052855       3.037276       0.755605  
C       -2.744949       2.803455       0.357804  
C       -5.084376       2.216173       0.318712  
H       -6.104818       -2.399145       0.639601  
C       -3.458165       1.747780       -0.512876  
C       -4.794200       -1.156206       -0.534396  
C       -3.496354       -0.921696       -0.955069  
H       -5.591763       -0.590144       -0.887398  
H       -3.270173       -0.103981       -1.631044  
N       -1.143681       -1.489957       -0.917940  
O       -0.839565       -0.717952       -1.045008  
C       -3.003807       4.386158       0.189372  
C       -0.769899       3.717368       -0.308681  
C       -2.290905       2.112999       0.281337  
C       -1.712040       4.721806       -0.183749  
C       -3.301654       3.054023       0.427593  
N       -1.051674       2.427232       -0.084306  
H       -3.765962       5.151833       0.283932  
H       -2.498947       1.061153       0.455281  
H       0.249990       3.946185       -0.601309  
H       -1.428272       5.749303       -0.380097  
H       -4.296050       2.737543       0.722891

S116
TS3
Electronic energy: -2821.840769
Gibbs free energy: -2821.524205
Corrected free energy: -2821.522527

IM7
Electronic energy: -2821.863095
Gibbs free energy: -2821.546380
Corrected free energy: -2821.544636
TS4
Electronic energy: -2821.855518
Gibbs free energy: -2821.540278
Corrected free energy: -2821.538276

IM8
Electronic energy: -2821.930796
Gibbs free energy: -2821.614194
Corrected free energy: -2821.613251
pyridine
Electronic energy: -248.159196
Gibbs free energy: -248.098400
Corrected free energy: -248.098400

\[
\begin{array}{ccc}
\text{py} & \\
\text{C} & 0.718138 & 1.137600 \\
\text{C} & -0.668412 & 1.192430 \\
\text{C} & -1.375862 & 0.000000 \\
\text{C} & -0.668412 & -1.192430 \\
\text{N} & 1.410788 & -0.000000 \\
\text{H} & 1.299888 & -2.058260 \\
\text{H} & -1.177562 & -2.150450 \\
\text{H} & 1.299888 & 2.058260 \\
\text{H} & -1.177552 & 2.150450 \\
\end{array}
\]

PhNO
Electronic energy: -361.381435
Gibbs free energy: -361.314959
Corrected free energy: -361.314959

\[
\begin{array}{ccc}
\text{PhNO} & \\
\text{C} & 0.550971 & -0.219292 \\
\text{C} & -0.333310 & -1.292700 \\
\text{C} & -1.697780 & -1.052119 \\
\text{C} & -2.159348 & 0.257752 \\
\text{C} & -1.267677 & 1.331301 \\
\text{N} & 1.935581 & -0.576234 \\
\text{O} & 2.715302 & 0.346095 \\
\end{array}
\]

MeCN
Electronic energy: -132.699549
Gibbs free energy: -132.678363
Corrected free energy: -132.678363

\[
\begin{array}{ccc}
\text{MeCN} & \\
\text{N} & 1.426808 & -0.000010 \\
\text{C} & 0.275288 & 0.000010 \\
\text{C} & -1.167782 & -0.000000 \\
\text{H} & -1.544191 & -0.116926 \\
\text{H} & -1.544313 & -0.824031 \\
\text{H} & -1.544192 & 0.940967 \\
\end{array}
\]
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