Supporting Information for

Identifying the Imperative Role of Metal-Olefin Interactions in Catalytic C–O Reductive Elimination from Nickel(II)

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Table of Contents:

Materials and Methods ........................................................................................................... S2
List of Abbreviations ................................................................................................................ S2
Synthesis of β-Amino Alcohol Vinyl Iodide Substrates ........................................................... S3
Synthesis of Aryl Iodide Substrate ......................................................................................... S5
General Procedure for Nickel-Catalyzed Cycloetherification ................................................. S6
Synthetic Procedures and Characterization Data for Isolated Nickel Compounds .................. S8
Proposed Mechanisms of Formation for 4, 5, and 7 ............................................................... S14
X-Ray Crystallographic Procedures, Refinement Details, and Additional Figures ................ S16
Computational Methodologies ............................................................................................... S21
NMR Spectra of New Compounds and Key Experiments ...................................................... S43
References ............................................................................................................................... S66
Materials and Methods

Unless otherwise stated, catalytic and synthetic organometallic reactions were performed in a nitrogen glovebox using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon. Organic reagents were purchased from Sigma-Aldrich, Acros Organics, Strem, Oakwood Chemical, or Alfa Aesar and used as received unless otherwise stated. Ni(COD)$_2$ was purchased from Strem and used as received, or recrystallized at −40 °C from a 1:5 toluene/Et$_2$O mixture prior to use. Reaction progress was monitored by thin-layer chromatography (TLC) or Agilent 1290 UHPLC-MS. TLC was performed using E. Merck silica gel 60 F254 precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching or KMnO$_4$ staining. Silicycle SiliaFlash® P60 Academic Silica gel (particle size 40–63 μm) was used for flash column chromatography. $^1$H NMR spectra were recorded on a Bruker 400 MHz spectrometer and are reported relative to residual CHCl$_3$ (δ 7.26 ppm) or CHD$_3$ (δ 7.16 ppm). $^{13}$C NMR spectra were recorded on a Bruker 400 MHz spectrometer (100 MHz) and are reported relative to CDCl$_3$ (δ 77.16 ppm) or C$_6$D$_6$ (δ 128.06 ppm). $^{31}$P NMR spectra were recorded on a Bruker 400 MHz spectrometer (162 MHz) and are reported relative to a free PCy$_3$ internal standard. Data for $^1$H NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septuplet, m = multiplet. Data from $^{13}$C and $^{31}$P NMR spectra are reported in terms of chemical shifts (δ ppm). IR spectra were obtained by use of a Perkin Elmer Spectrum BXII spectrometer using thin films deposited on NaCl plates and reported in frequency of absorption (cm$^{-1}$). High resolution mass spectra (HRMS) of new organics were obtained from the Caltech Mass Spectral Facility.

List of Abbreviations:

TLC – thin-layer chromatography, COD – 1,5-cyclooctadiene, Et$_2$O – diethyl ether
Synthesis of β-Amino Alcohol Vinyl Iodide Substrates

New vinyl iodide substrates (1a, 1d) were synthesized by a two-pot procedure akin to that described in our previous report.1 A solution of cyclohexene oxide (1.0 equiv) and primary amine (1-2 equiv) in methanol ([amine] = 2 M) was heated in a sealed scintillation vial at 80 °C for 16–24 h, after which time the volatile components of the reaction mixture were removed by rotary evaporation to yield the desired β-amino alcohols, which were used in the following step without further purification.

To a solution of β-amino alcohol (1 equiv) dissolved in MeCN (5-8 mL) was added K₂CO₃ (5 equiv) followed by the appropriate allylic bromide (1 equiv). The resulting mixture was stirred at ambient temperature (ca. 23 °C) for 24 h. The reaction mixture was then filtered through Celite and concentrated by rotary evaporation. The resulting crude residues were purified by silica gel chromatography using hexanes/EtOAc as a mobile phase to yield β-amino alcohol vinyl iodides (1a, 1d).

Compound 3 was synthesized by this same procedure, employing cinnamyl bromide in the second step in place of an iodinated allylic bromide.

Compound 1a: Isolated as a colorless oil from a 2 mmol scale reaction. Yield: 115 mg, 19%. ¹H NMR (400 MHz, 298 K, CDCl₃): δ = 5.83 (q, J = 6.0 Hz, 1H), 4.02 (s, 1H), 3.41 (td, J = 4.7, 9.8 Hz, 1H), 3.27 (d, J = 13.4 Hz, 1H), 3.08 (d, J = 13.4 Hz, 1H), 2.15 (s, 3H), 2.12 (td, J = 1.9, 5.4 Hz, 1H), 1.80 (d, J = Hz, 3H), 1.78-1.62 (m, 4H), 1.33-1.08 (m, 4H). ¹³C NMR (100 MHz, 298 K, CDCl₃): δ = 132.2, 111.8, 69.5, 69.0, 65.3, 35.7, 33.4, 25.6, 24.3, 22.7, 21.9. FT-IR (neat film/NaCl): 3474, 2929, 2854, 1763, 1450, 1304, 1206, 1167, 1081, 1032 cm⁻¹. HRMS (MM: TOF-MS ES+): m/z calc’d for C₁₁H₂₁NOI, [M+H]^+ = 310.0668; found = 310.0662.
Compound 1d: Isolated as a yellow oil from a 1 mmol scale reaction. Yield: 50 mg, 15%. 

$^1$H NMR (400 MHz, 298 K, CDCl$_3$): $\delta = 5.92-5.78$ (m, 2H), 5.14 (d, $J = 26.2$ Hz, 1H), 5.13 (s, 1H), 3.90 (s, 1H), 3.48-3.36 (m, 2H), 3.26 (dt, $J = Hz$, 1H), 3.02 (d, $J = 13.8$ Hz, 1H), 2.91 (dd, $J = 7.4$, 14.0 Hz, 1H), 2.44-2.34 (m, 1H), 2.17-2.08 (m, 1H), 1.80 (dd, $J = 2.6$, 6.3 Hz, 3H), 1.78-1.66 (m, 3H), 1.32-1.00 (m, 4H). $^{13}$C NMR (100 MHz, 298 K, CDCl$_3$): $\delta = 136.8$, 132.8, 117.6, 111.8, 69.1, 64.7, 60.7, 52.2, 33.3, 25.7, 24.3, 23.4, 22.0. FT-IR (neat film/NaCl): 3485, 2932, 2857, 1447, 1300, 1206, 1080, 991, 917 cm$^{-1}$. HRMS (MM: TOF-MS ESI+): m/z calc’d for C$_{13}$H$_{23}$NOI, [M+H]$^+$ = 336.0824; found = 336.0813.

Compound 3: Isolated as a pale yellow semi-crystalline solid from a 1 mmol scale reaction. Yield: 165 mg, 67%. $^1$H NMR (400 MHz, 298 K, C$_6$D$_6$): $\delta = 7.28-7.23$ (m, 2H), 7.16-7.11 (m, 2H), 7.09-7.04 (m, 1H), 6.38 (d, $J = 15.9$ Hz, 1H), 6.07 (ddd, $J = 6.3$, 6.9, 15.9 Hz, 1H), 3.36 (td, $J = 4.5$, 10.4 Hz, 1H), 3.08 (ddd, $J = 1.4$, 6.2, 13.7 Hz, 1H), 2.83 (dd, $J = 1.1$, 7.0, 13.7 Hz, 1H), 2.29-2.21 (m, 2H), 2.00 (s, 3H), 1.55-1.43 (m, 3H), 1.42-1.30 (m, 1H), 1.08-0.92 (m, 2H), 0.91-0.79 (m, 1H). $^{13}$C NMR (100 MHz, 298 K, C$_6$D$_6$): $\delta = 137.8$, 132.6, 129.2, 129.1, 127.1, 69.8, 69.8, 56.9, 36.8, 34.4, 26.1, 24.8, 22.2. FT-IR (neat film/NaCl): 3447, 2931, 2857, 1450, 1079, 1030, 965, 743, 693 cm$^{-1}$. HRMS (MM: TOF-MS ESI+): m/z calc’d for C$_{16}$H$_{24}$NO, [M+H]$^+$ = 246.1858; found = 246.1854.
Synthesis of Aryl Iodide Substrate

In an adaptation of a reported procedure, cyclohexene oxide (197 mg, 2.01 mmol, 1.0 equiv) and N-methyl-2-iodoaniline (469 mg, 2.01 mmol, 1.0 equiv) were dissolved in dry Et₂O (10 mL). Cu(OTf)₂ (72 mg, 0.20 mmol, 0.1 equiv) was then added, and the reaction mixture was stirred at ca. 23 °C overnight. The reaction mixture was then filtered through Celite and concentrated by rotary evaporation. Following purification by silica gel chromatography with a hexanes/EtOAc mobile phase, compound 1e was isolated as a colorless oil (189 mg, 29%).

Compound 1e: ¹H NMR (400 MHz, 298 K, CDCl₃): δ = 7.85 (dd, J = 1.4, 7.9 Hz, 1H), 7.34-7.27 (m, 1H), 7.21 (dd, J = 1.2, 7.9 Hz, 1H), 6.82 (td, J = 1.5, 7.3 Hz, 1H), 3.83 (s, 1H), 3.65 (td, J = 4.2, 9.9 Hz, 1H), 2.89 (ddd, J = 3.4, 9.9, 11.7 Hz, 1H), 2.69 (s, 3H), 2.21-2.12 (m, 1H), 1.87-1.79 (m, 1H), 1.79-1.68 (m, 2H), 1.59-1.46 (m, 1H), 1.40-1.13 (m, 3H). ¹³C NMR (100 MHz, 298 K, CDCl₃): δ = 153.4, 140.3, 129.2, 126.3, 125.2, 99.9, 70.7, 68.2, 34.6, 33.8, 25.5, 24.5, 24.5. FT-IR (neat film/NaCl): 3486, 2933, 2858, 1578, 1468, 1285, 1076, 1045, 1013, 984, 754 cm⁻¹. HRMS (MM: TOF-MS ESI⁺): m/z calc’d for C₁₃H₁₉NOI, [M+H]⁺ = 332.0511; found = 332.0516.
General Procedure for Nickel-Catalyzed Cycloetherification

In an N₂-filled glovebox, to a vial containing vinyl iodide substrate (0.135 mmol) was added MeCN (0.9 mL, 0.15 M) and triethylamine (21 μL, 1.1 equiv). Once a homogeneous solution was obtained by gentle stirring, it was then added by pipette to a 1 dram vial containing Ni precatalyst (e.g. 1.8 mg/5 mol% of Ni(COD)₂) and a zinc additive (if applicable, e.g. 17.7 mg/2 equiv of Zn dust, or 12.3 mg/0.25 equiv of Zn(OTf)₂). The reaction mixture was then stirred in the glovebox at ca. 23 °C for 24 h (unless specified otherwise). The reaction mixture was then removed from the glovebox, exposed to ambient atmosphere, filtered through Celite, and concentrated by rotary evaporation. Enol ether products and unreacted starting material were then isolated by silica gel chromatography, using hexanes/EtOAc as a mobile phase. In all cases, the Rf values of the enol ether products were found to be significantly lower than those of the vinyl iodide starting materials.

Note that reactions conducted with other Ni precatalysts (e.g. 5, 6, 7) were carried out such that the total Ni content of the reaction equaled 5 mol%. Additionally, reactions conducted in solvents other than MeCN used the same quantity of solvent (0.9 mL) to maintain an identical starting concentration.

Compound 2a: Isolated as a yellow oil from a 0.135 mmol scale reaction. Reaction time: 24 h. Yield: 13.1 mg, 54%. ¹H NMR (400 MHz, 298 K, CDCl₃): δ = 4.65 (qd, J = 1.5, 6.7 Hz, 1H), 3.32 (qd, J = 4.3, 9.2 Hz, 1H), 3.16 (d, J = 12.3 Hz, 1H), 2.81 (d, J = 11.6 Hz, 1H), 2.26 (s, 3H), 2.12-1.99 (m, 2H), 1.91-1.82 (m, 1H) 1.58 (dd, J = 2.0, 7.7 Hz, 3H), 1.50-1.38 (m, 1H), 1.37-1.20 (m, 4H), 1.18-1.05 (m, 1H). ¹³C NMR (100 MHz, 298 K, CDCl₃): δ = 148.4, 103.8, 80.6, 67.5, 58.7, 41.5, 31.4, 28.0, 24.8, 24.4, 9.63. FT-IR (neat film/NaCl): 2926, 2861, 1680, 1454, 1361, 1330, 1070, 1026 cm⁻¹. HRMS (MM: TOF-MS ESI+): m/z calc’d for C₁₁H₂₀NO, [M+H]⁺ = 182.1545; found = 182.1539.
Compound 2d: Isolated as a red-brown oil from a 0.135 mmol scale reaction. Reaction time: 44h. Yield: 11.4 mg, 41%. 50% of the starting material was also recovered. $^1$H NMR (400 MHz, 298 K, CDCl$_3$): $\delta = 5.86$ (qdd, $J = 5.4$, 8.1, 16.0 Hz, 1H), 5.21 (m, 1H), 5.17 (s, 1H), 4.61 (qd, $J = 1.3$, 6.7 Hz, 1H), 3.49 (dd, $J = 5.4$, 13.6 Hz, 1H), 3.35 (qd, $J = 4.3$, 9.0 Hz, 1H), 3.24 (d, $J = 12.5$ Hz, 1H), 2.85-2.75 (m, 2H), 2.17-1.98 (m, 3H), 1.81-1.69 (m, 2H), 1.57 (dd, $J = 1.9$, 6.7 Hz, 3H), 1.50-1.38 (m, 1H), 1.37-1.19 (m, 3H), 1.18-1.07 (m, 1H). $^{13}$C NMR (100 MHz, 298 K, CDCl$_3$): $\delta = 148.7$, 134.2, 118.9, 103.3, 80.5, 65.3, 55.9, 54.8, 31.6, 28.1, 24.8, 24.4, 9.63. FT-IR (neat film/NaCl): 2937, 2864, 1734, 1678, 1451, 1418, 1330, 1202, 1070, 918 cm$^{-1}$. HRMS (MM: TOF-MS ESI+): m/z calc’d for C$_{13}$H$_{22}$NO, [M+H]$^+$ = 208.1701; found = 208.1692.

Table S1. Results of Ni-catalyzed cycloetherification carried out in various solvents.

<table>
<thead>
<tr>
<th>entry</th>
<th>Solvent</th>
<th>Yield(%)$^b$</th>
<th>Recovery 1f (%)</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>MeCN</td>
<td>93$^c$</td>
<td>n.d.</td>
</tr>
<tr>
<td>2</td>
<td>THF</td>
<td>11</td>
<td>51</td>
</tr>
<tr>
<td>3</td>
<td>Benzene</td>
<td>39</td>
<td>55</td>
</tr>
<tr>
<td>4</td>
<td>1,4-Dioxane</td>
<td>27</td>
<td>47</td>
</tr>
</tbody>
</table>

[a] Standard conditions: 1f (0.135 mmol), Ni(COD)$_2$ (5 mol%), triethylamine (1.1 equiv), Zn dust (2 equiv), Solvent (0.9 mL, 0.15 M). [b] Yield of isolated product. [c] Result taken from reference 1 of the Supporting Information.
Synthetic Procedures and Characterization Data for Isolated Nickel Compounds

**Compound 4**

In an N2-filled glovebox, solid Ni(COD)2 (37.0 mg, 0.135 mmol) was added to a stirred solution of 1f (50 mg, 0.135 mmol) in acetonitrile (3 mL). Within several minutes, the colorless solution began to take on an orange hue, followed by the precipitation of black solids and the formation of a silvery mirror on the interior of the reaction vial. After a total reaction time of 15 minutes all of the Ni(COD)2 had dissolved, at which point the volatile components of the reaction mixture were removed in vacuo. The crude residue was extracted with benzene (1 mL). The orange extracts were filtered through Celite into a clean scintillation vial, and the solution was allowed to stand at ambient temperature for several days. Removal of the mother liquor and brief washes with benzene (2 x 0.5 mL) yielded 4 as pale orange crystals (8.7 mg, 24%). X-ray quality single crystals of 4 were obtained by a repetition of this procedure. m.p.: 176-179 °C. 1H NMR (400 MHz, C6D6, 298K): δ 7.79 (bs), 7.27 (s), 5.54 (bs), 3.57 (bs), 2.91 (bs), 2.24 (bs), 1.84 (bs, overlapped), 1.41 (bs, overlapped), 1.31 (bs, overlapped), 1.23 (bs, overlapped), 0.90 (bm), 0.54 (bs). HRMS (MM: TOF-MS ESI–): m/z calc’d for NiI3, [NiI3-I]– = 438.6488; found = 438.6488.

Additional anions containing both organic and inorganic fragments were observed in a low resolution ESI– mass spectrum, including [NiI3C10H14N]– found at m/z = 713.7 (calc’d m/z = 713.6659) and [NiI3C10H13N]– found at m/z = 586.0 (calc’d m/z = 585.7536). Both of these anionic species are the result of cyclohexene oxide (C6H10O) loss from the parent ammonium/ammonia molecule. Given the susceptibility of 4 to hydrolysis, HRMS analysis of these anions was unsuccessful. LC-MS analysis of hydrolyzed 4 shows the presence of compound 3.
**Compound 5**

In an N$_2$-filled glovebox, Ni(COD)$_2$ (74.0 mg, 0.270 mmol) in Et$_2$O (3 mL) was added to a stirred solution of 1f (100 mg, 0.270 mmol) in Et$_2$O (5 mL). Within seconds, the solution began to take on an orange hue, and within several minutes, a pale orange precipitate began to form. Fine precipitate continued to form over the course of the reaction. After a reaction time of 45 minutes, the stir bar was removed and the reaction mixture was diluted with hexane, leading to the formation of additional precipitate. After storage of the resulting mixture overnight at -40 °C, the mother liquor was removed by pipette, and the isolated solids were washed vigorously with hexane (3 x 5 mL). Following the removal of residual volatile in vacuo, 5 was isolated as a fine orange powder. X-ray quality single crystals of 5-THF were grown from a THF/hexane solution stored at -40 °C. Yield: 104 mg, 82%. m.p.: decomp. without melting above ca. 160 °C. Anal. Calcd. for C$_{32}$H$_{44}$N$_2$O$_2$I$_2$Ni$_2$ (5): C, 44.70; H, 5.16; N, 3.26 %. Found: C, 45.08; H, 5.11; N, 3.19 %. Compound 5 displays a complex, paramagnetically-shifted $^1$H NMR spectrum that is not amenable to tabulation.
Compound 6

In an N$_2$-filled glovebox, a solid mixture of compound 5 (25 mg, 0.029 mmol) and DMAP (7.0 mg, 0.058 mmol) was dissolved in benzene (4 mL). Within seconds, bright orange-yellow crystals began to form. The reaction mixture was allowed to stand at ambient temperature overnight. The following day, the accumulated crystals of 6 were isolated by removing the mother liquor and removing residual volatiles in vacuo. Yield: 27.6 mg, 86%. X-ray quality single crystals of 6 were obtained by repeating the reaction on a smaller scale and lower concentration, slowing the rate of crystallization. m.p. 164-170 °C (slow melting with decomp.). $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 298K): δ 34.61 (bs), 29.96 (bs), 24.81 (bs), 20.23 (bs), 18.67 (bs), 8.94 (bs), 7.98 (s), 7.22 (s), 6.79 (s), 6.54 (s), 6.28 (s), 5.76 (s), 5.54 (s), 3.44 (bm), 1.95 (s, overlapped), 1.82 (s, overlapped), 1.27 (s, overlapped), -1.22 (bs), -1.60 (s). Anal. Calcd. for C$_{64}$H$_{82}$Ni$_2$O$_2$I$_2$ (6 • 3 C$_6$H$_6$): C, 57.43; H, 6.17; N, 6.28 %. Found: C, 56.63; H, 6.18; N, 6.24 %.

We attribute the low C wt.% found in our elemental combustion analysis to the high benzene content of this highly crystalline compound and its incomplete combustion. The presence of three co-crystallized benzene molecules per molecule of 6 in the solid state is verified in the X-ray crystal structure. Given this consistency, these three benzene molecules were also accounted for in our calculation of the magnetic moment of this compound.
In an N$_2$-filled glovebox, compound 5 (25 mg, 0.029 mmol) was suspended in Et$_2$O (4 mL). A solution of tricyclohexylphosphine (16.3 mg, 0.058 mmol) in Et$_2$O (2 mL) was then added, and the resulting mixture stirred for 20 minutes. The volatile components of the reaction mixture were then removed in vacuo. The crude residue was washed with hexane (3 x 2 mL) and exposed to vacuum to remove residual volatiles. Compound 7 was isolated as pale purple-red solids. Yield: 21.3 mg, 52%. X-ray quality single crystals of 7 were obtained by recrystallizing isolated material from hexane at –40 °C. m.p.: 148-151 °C. $^1$H NMR (400 MHz, C$_6$D$_6$, 298 K): δ 8.35 (dq, J = Hz, 1H), 7.66 (d, J = Hz, 2H), 7.23 (t, J = Hz, 2H), 7.10 (t, J = Hz, 1H), 6.53 (d, J = Hz, 1H), 4.34 (ddd, J = Hz, 1H), 2.92 (td, J = Hz, 1H), 2.72 (s, 3H), 2.71-2.64 (m, 1H), 2.37-2.21 (m, 8H), 2.20-2.01 (m, 12H), 1.96-1.84 (m, 5H), 1.84-1.61 (m, 16H), 1.41-1.16 (m, 23H), 1.03-0.94 (m, 2H), 0.91-0.82 (m, 2H), 0.78-0.58 (m, 2H). $^{13}$C NMR (100 MHz, C$_6$D$_6$, 298 K): δ 137.4, 134.2, 129.0, 127.5, 127.0, 76.3 (d, J = 5.7 Hz), 70.2, 59.6, 39.6, 37.3, 34.6, 34.5 (d, J = 20.8 Hz), 30.6 (d, J = 12.7 Hz), 29.7, 28.2 (d, J = 5.0 Hz), 28.1 (d, J = 4.9 Hz), 28.1 (d, J = 8.3 Hz), 27.0, 25.6, 24.8, 22.7. $^{31}$P NMR (162 MHz, C$_6$D$_6$, 298 K): δ 27.3. Anal. Calcd. for C$_{34}$H$_{55}$NOPiNi (7): C, 57.49; H, 7.80; N, 1.97 %. Found: C, 57.26; H, 7.83; N, 1.82 %.

Compound 7 is isolated as a mixture of diastereomers, in approximately a 1.00:0.28 ratio, which readily co-crystallize (as apparent in the X-ray crystal structure). Based on the NMR spectral data, it appears these diastereomers display different behavior in solution: The major diastereomer of compound 7 displays sharp $^1$H NMR resonances, while the minor one appears dynamic, leading to broadened NMR peaks. Some $^1$H NMR resonances, particularly those associated with the PCy$_3$ ligand and cyclohexanol group, are broadened and overlapped: we have listed all of the resonances present in this region of the spectrum, as well as their integrations, which were shown to be reproducible between several batches of material, including after recrystallization or repeated washing of isolated material with hexane. In contrast, the $^{13}$C NMR spectrum of 7 can easily distinguish between the major and minor diastereomers, as the resonances of the major, non-fluxional diastereomer are of significantly greater intensity than those of the fluxional, minor diastereomer.
While a straightforward synthesis of (PCy$_3$)$_2$NiI is reported in the literature, the following is an account of our isolation of this material using a vinyl iodide as the halide source. In an N$_2$-filled glovebox, a solid mixture of Ni(COD)$_2$ (18.5 mg, 0.067 mmol) and tricyclohexylphosphine (37.8 mg, 0.135 mmol) was dissolved in Et$_2$O (5 mL), forming a clear orange solution. This solution was added to a stirred solution of 1f (25 mg, 0.067 mmol) in Et$_2$O (2 mL). After ca. 3 min, the reaction mixture began to become cloudy, and over the course of the reaction time (45 min), additional pale precipitate continued to form. The stir bar was then removed from the reaction vial, and the mixture was stored at -40 °C overnight. The following day, the mother liquor was removed and the isolated solids were washed with hexane (3 x 2 mL). The washed, pale yellow microcrystalline solids (23.7 mg) were then exposed to vacuum to remove residual volatiles. The combined mother liquor and hexane washes were again stored at -40 °C, leading to the formation of a small second crop of product (4.7 mg), which was isolated similarly. Yield: 28.4 mg, 56%. X-ray quality single crystals of (PCy$_3$)$_2$NiI were obtained by the slow evaporation of a Et$_2$O solution of isolated material. $^1$H NMR (400 MHz, C$_6$D$_6$, 298K): δ 15.50 (bs), 10.04 (bs), 7.54 (bs), 6.74 (bs), 4.15 (bs), 3.30 (bs), 2.97 (bs), 1.93 (bs), 1.67 (bs, overlapped), 1.56 (bs, overlapped), 1.36 (bs, overlapped), 1.08 (bs, overlapped), 0.37 (bs), -1.15 (bs). $^{31}$P NMR (162 MHz, C$_6$D$_6$, 298K): δ 46.8 (bs).

The identity of the isolated product as (PCy$_3$)$_2$NiI was established by X-ray crystallography. Given the lack of reported spectroscopic data for this compound, we herein include its $^1$H NMR spectrum and $^{31}$P NMR spectrum. The X-ray crystal structure of this compound was also previously unknown, and a finalized CIF is also included with this report.
[(COD)NiI]₂

The Ni(I) precatalyst [(COD)NiI]₂ was synthesized by an adaptation of a reported procedure.³ In a N₂-filled glovebox, Ni(COD)₂ (25.0 mg, 0.0909 mmol) was dissolved in a mixture of toluene (5 mL) and COD (0.5 mL). Separately, I₂ (11.5 mg, 0.0909 mmol) was dissolved in 1 mL toluene. Both solutions were chilled to -40 °C in the glovebox freezer. The iodine solution was then added dropwise to the Ni(COD)₂ solution with rapid stirring, leading to a change in color of the reaction mixture from light yellow to orange. After stirring for 2 minutes following the addition, the reaction mixture was stored at -40 °C overnight to ensure the reaction proceeded to completion without decomposition of the product. The following day, the volatile components of the reaction mixture (now a dark orange solution with notable precipitate) were removed in vacuo, and the resulting residue was washed with diethyl ether (3 x 2 mL). [(COD)NiI]₂ was isolated as orange-yellow microcrystalline solids following exposure to vacuum to remove residual volatiles. Yield: 21.8 mg, 82 %. X-ray quality single crystals were grown from a solution of isolated product in a toluene/hexane solution with trace COD at -40 °C.

While crystalline [(COD)NiI]₂ is somewhat stable at ambient temperature (similarly to Ni(COD)₂), we advise that great care must be taken when handling [(COD)NiI]₂ in solution. This highly reactive complex will significantly decompose upon dissolution in benzene or toluene at ambient temperature. The decomposition abates somewhat after an initial generation of dark solids, likely due to the stabilizing effect of free COD in solution. We suggest that any manipulations of this complex are carried out with pre-cooled solvents, with a significant quantity of COD added. We posit the instability of [(COD)NiI]₂ (particularly when compared to (PCy₃)₂NiI, which is generally stable in solution at room temperature) is due to the lability of COD, as well as the dimeric structure of this complex, which likely predisposes this compound to facile thermal or photoinitiated disproportionation.
Proposed Mechanisms of Formation for 4, 5, and 7

**Figure S1.** Plausible mechanism for the formation of 3, 4, and 2f from the stoichiometric reaction of Ni(COD)$_2$ with 1f in MeCN. [Ni] indicates a solvated Ni center beyond the ligands explicitly drawn. Note that the generation of 2f is dependent on the formation of 3 via protodemetalation, as the elimination of HI from intermediate B (to form C) necessitates the presence of a base to deprotonate the free alcohol group. Subsequently, the basic amine group of 3, in tandem with NiI$_2$ generated by protodemetalation, may further eliminate HI from additional equivalents of B, leading to additional quantities of 2f as well as the isolated ionic compound 4.

**Figure S2.** Plausible mechanism for the formation of 5 and 5' from the stoichiometric reaction of Ni(COD)$_2$ with 1f in Et$_2$O. [Ni] indicates a solvated Ni center beyond the ligands explicitly drawn. The key feature of this reaction is the observation that the poorly coordinating nature of Et$_2$O leads to the aggregation of Ni(II) species, by virtue of the favorable chelation of the β-
amino cyclohexanol group (as well as the limited thermodynamic favorability of a single equivalent of If chelating to a single Ni center in a tridentate fashion). This dimerization process, which was not observed in MeCN (likely owing to its much greater coordination strength as compared to that of Et_{2}O), then leads to a rapid internal protodemetalation of one of the Ni-C bonds to generate compound 5, as isolated. Based on our combined experimental and computational findings, we propose that the slow decomposition of 5 at room temperature involves primarily a second protodemetalation, yielding the dimeric alkoxide-bridged Ni(II) complex 5' as a major product.

\[ \text{Figure S3. Plausible mechanism for the formation of 7 from the reaction of 5 with PCy}_{3}. \text{ Note that the allylic deprotonation likely depends on the formation of mononuclear Ni(II) intermediates, as the structures of compounds 5 and 6 indicate that bridging alkoxide groups are not amenable to promoting this process.} \]
X-Ray Crystallographic Procedures, Refinement Details, and Additional Figures

Single crystal X-ray diffraction data for 4, 5-THF, 6, 7, [(COD)NiI]2, and (PCy3)2NiI were collected at the Caltech XRCF, using either a Bruker AXS D8 Venture outfitted with a rotating anode Mo-Kα (λ = 0.71073 Å) micro-source, or a Bruker AXS D8 KAPPA with a sealed tube Mo-Kα X-ray source. All data collections were conducted at 100 K in a dry nitrogen cryostream. In an N2-filled glovebox, samples of single crystals were isolated from their mother liquor and coated in a thick hydrocarbon oil for transport to the diffraction facility. In the facility, samples were evaluated by polarized light microscopy, and candidate crystals were mounted on an appropriately-sized MiTiGen MicroLoop for X-ray diffraction analysis. Diffraction data were collected, integrated, and reduced using Bruker AXS APEX3 software, including its associated SAINT and SADABS programs.4 Structures were solved and refined using SHELXT and SHELXL-2014,5,6 as implemented within WinGX.7 The structural model for the allyl complex 7 required modeling of the cyclohexanol moiety over two positions (due to co-crystallization of diastereotopic Ni complexes containing different stereoisomers of the racemic trans-β-amino alcohol). The structural model for the asymmetric dinuclear Ni complex 5-THF required disorder modeling for multiple co-crystallized THF molecules. The PLATON squeeze program8 was used to remove electron density associated with a highly disordered Et2O molecule in the structure of (PCy3)2NiI oriented on a 3-fold screw axis (along c at a = b = 1/3, these void channels are readily observed in a packing diagram of the final model). Thermal ellipsoid plots were generated using Mercury.9 Finalized CIFs have been deposited to the Cambridge Crystallographic Data Centre (CCDC), with deposition numbers: 2078291 (4), 2078292 (5-THF), 2078293 (6), 2078294 (7), 2078295 ((PCy3)2NiI), and 2088878 ([((COD)NiI]2).
Table S2. Crystallographic details and refinement metrics.

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<th>[(COD)NiI]₂</th>
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Figure S4. X-ray crystal structure of compound 4 with 50% probability ellipsoids. A co-crystallized benzene molecule and hydrogen atoms (except those on the alcohol and ammonium groups) are excluded for clarity.

Figure S5. X-ray crystal structure of compound 5-THF with 50% probability ellipsoids. Co-crystallized THF molecules and hydrogen atoms (except that on the alcohol group) are excluded for clarity. Selected bond distances (Å) and angles (°): Ni1-I1 = 2.4936(9), Ni1-C1 = 1.890(6), Ni1-N1 = 2.043(5), Ni1-O1 = 1.886(4), Ni2-O1 = 1.988(4), Ni2-I2 = 2.6965(9), Ni2-N2 = 2.104(6), Ni2-O2 = 2.073(5), Ni2-O3 = 2.099(4), Ni1-O1-Ni2 = 111.9(2), O1-Ni1-N1 = 86.9(2), O1-Ni-C1 = 87.5(2), C1-Ni1-I1 = 87.65(19), I1-Ni1-N1 = 97.94(15), O2-Ni2-N2 = 80.3(2).
**Figure S6.** X-ray crystal structure of compound 6 with 50% probability ellipsoids. Co-crystallized benzene molecules and hydrogen atoms are excluded for clarity. Selected bond distances (Å) and angles (°): Ni1-I1 = 2.7099(3), Ni1-O1 = 1.9863(14), Ni1-O1’ = 1.9815(14), Ni1-N1 = 2.1649(18), Ni1-N2 = 2.0405(18), N1-Ni1-O1’ = 80.66(6), Ni1-O1-Ni1’ = 99.50(6).

**Figure S7.** X-ray crystal structure of compound 7 with 50% probability ellipsoids. Hydrogen atoms (except that bound to the alcohol group) are excluded for clarity. Selected bond distances (Å) and angles (°): Ni1-I1 = 2.5476(6), Ni1-P1 = 2.1812(11), Ni1-C8 = 2.473(4), Ni1-C9 = 2.004(4), Ni1-C10 = 1.959(4), P1-Ni1-I1 = 100.33(3).
Figure S8. X-ray crystal structure of (PCy$_3$)$_2$NiI with 50% probability ellipsoids. Hydrogen atoms are excluded for clarity. Selected bond distances (Å) and angles (°): Ni1-I1 = 2.4841(6), Ni1-P1 = 2.2212(7), P1-Ni1-P1’ = 118.45(4), P1-Ni1-I1 = 120.77(2).

Figure S9. X-ray crystal structure of [(COD)NiI]$_2$ with 50% probability ellipsoids. Hydrogen atoms are excluded for clarity. Selected bond distances (Å) and angles (°): Ni1-I1 = 2.6476(8), Ni1-I1’ = 2.6313(8), Ni1-C1 = 2.145(5), Ni1-C2 = 2.114(4), Ni1-C5 = 2.149(4), Ni1-C6 = 2.118(4), C1-C2 = 1.363(6), C5-C6 = 1.361(6), Ni1-I1-Ni1’ = 82.82(2), I1-Ni1-I1’ = 97.18(2).
Computational Methodologies

General Notes

All quantum mechanical calculations were carried out with the ORCA program.\textsuperscript{10} Geometry optimizations and harmonic frequency calculations were carried out with density functional theory (DFT). The PBE0 functional\textsuperscript{11} paired with Becke–Johnson damped D4 dispersion corrections\textsuperscript{12}, henceforth referred to as PBE0-D4, was used. Nickel is described by the def2-TZVP all electron basis set,\textsuperscript{13} while all other atoms are assigned the def2-TZVP(-f) basis. Diffuse functions are added to iodine (ma-def2-TZVP(-f)), as well as the ECP28MWB small-core (25 explicit valence electrons) quasi-relativistic pseudopotential.\textsuperscript{14} This composite basis set is termed BS1. For reactions carried out in MeCN, geometry optimizations and harmonic frequency calculations were conducted with the CPCM implicit solvation model (MeCN, $\varepsilon = 36.6$).\textsuperscript{15} For all calculations employing CPCM, surface charges are described by the improved Gaussian charge scheme of Neese and coworkers with a scaled Van der Waals cavity ($\alpha = 1.2$).\textsuperscript{16} Corrections for outlying charge are included in solvated energies. Gas phase geometries are used for reactions carried out in benzene. For gas phase species, the nuclear Hessians were computed analytically, while numerical Hessians were employed for solvated complexes. Stationary points are characterized by the correct number of imaginary vibrational modes (zero for minima and one for saddle points). Intrinsic reaction coordinate (IRC) analysis confirms the nature of transition states.\textsuperscript{17} Cartesian coordinates of all optimized structures are included as “.xyz” files are available online in a compressed zip file format.

For complexes with the tricyclohexylphosphine ligand (Cy$_3$P), the def2-TZVP and ma-def2-TZVP(-f) basis are used for nickel and iodine as mentioned above; however, the double-$\zeta$ split valence basis def2-SVP was employed for C, H, O, N, and P. As these complexes contain up to $>140$ atoms, this is necessary for the computations to remain tractable. This mixed basis set is henceforth referred to as BS3.

Electronic energies are further refined with single point calculations employing the M06 functional\textsuperscript{18} and the def2-TZVPP basis set on all atoms with additional diffuse functions on I (ma-def2-TZVPP + ECP28MWB pseudopotential). This mixed basis is henceforth referred to as BS2. Solvation was accounted for with CPCM as mentioned above (MeCN, $\varepsilon = 36.6$; or benzene, $\varepsilon = 2.28$). Final Gibbs free energies were obtained by applying thermodynamic
corrections obtained at the optimization level of theory to these refined electronic energies. Thermodynamic corrections from harmonic frequency calculations employ the quasi-ridged rotor harmonic oscillator approach to correct for the breakdown of the harmonic oscillator approximation at low vibrational frequencies.\(^{19}\) Note that free energies are adjusted to a 1 M standard state. Acetonitrile is defined to a standard state of 19.15 M for reactions run in acetonitrile ($\Delta G_{0\rightarrow\ast} = 3.64 \text{ kcal/mol}$). The translational ($S_{\text{trans}}$) and rotational entropy ($S_{\text{rot}}$) contributions to the Gibbs free energy calculated for a complex in condensed phase are ca. 40–60% of the values obtained assuming an ideal gas.\(^{20}\) As suggested in the literature, $S_{\text{trans}}$ and $S_{\text{rot}}$ obtained by ideal gas treatment are scaled by a factor of 0.5 to obtain the final condensed phase values.\(^{21}\) Hence, the final Gibbs free energy at 298.15 K is calculated as:

$$G_{\text{solv}}^\ast = E_{el,solv}^{M06,BS2} + ZPE + E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + k_B T - T \left( S_{el} + S_{vib} + \frac{1}{2} S_{\text{trans}} + \frac{1}{2} S_{\text{rot}} \right) + \Delta G_{0\rightarrow\ast}$$

The resolution of identity (RI) and Chain-of-Spheres (COS) approximations are employed for efficient evaluation of Coulomb and exchange integrals, respectively.\(^{22}\) The def2/J auxiliary basis\(^{23}\) is employed for all atoms except iodine, for which a suitable auxiliary was obtained via the automatic generation algorithm in the ORCA program (keyword: AutoAux).\(^{24}\) Very fine grid settings are employed in all calculations (optimization/frequency calculations: Grid6 NoFinalGrid GridX6, single point calculations: Grid7 NoFinalGrid GridX9).

Calculations on open-shell systems employ unrestricted Kohn–Sham orbitals (UKS). Spin contamination is generally minor. Open-shell singlets are modeled using the broken-symmetry (BS) formalism. For an open-shell singlet, construction of a proper spin eigenfunction of $S^2$ cannot be achieved with a single Slater determinant. As such, BS-DFT does not properly describe the open-shell singlet as a pure singlet, but rather as a mixture of the corresponding singlet and triplet states.\(^{25}\) Various schemes for estimation of the singlet energy by removal of spin contamination have been developed. Here, we apply the formalism introduced by Yamaguchi and coworkers\(^{26}\):

$$E_S = \frac{2(E_{BS} - E_T)}{(S^2)_T - (S^2)_{BS}} + E_T$$

Along the minimum free energy path through the catalytic cycle as described in Figure 2 of the main text, high spin (triplet) Ni(II) intermediates were also considered. These were found to be higher in energy than their singlet counterparts (Figure S10).
Figure S10. Relative free energies between singlet and triplet vinyl Ni(II) species.

Nucleus Independent Chemical Shift (NICS) Calculations

NICS calculations were carried out by DFT with the PBE0-D4 functional and def2-TZVP basis set in the gas phase. In accordance with literature convention, the reported NICS values are the negative of the total isotropic shift (in ppm) from the chemical shielding tensor. The NICS value is measured at the geometric center of the ring in question. As such, a negative NICS value – additional shielding at the ring center – is indicative of a diatropic ring current, hence indicating aromaticity. Analogously, positive NICS values are obtained for antiaromatic compounds. In the ORCA code, these calculations were accomplished by placing a ghost atom at the site of interest, assigning a single Gaussian s function (one primitive, exponent = 10^6) with corresponding auxiliary to the ghost atom, and calculation of the NMR chemical shift (here using the gauge-independent atomic orbitals approach).
Table S3. NICS (in ppm) at ring centers along C–O bond formation reaction coordinates.  

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<th>ΔNICS (ppm)</th>
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*a* For naphthyl rings, second value in list is from second distal aryl ring.  

*<sup>b</sup> Dianion on neutral benzene geometry modeled with RKS for illustration purposes. ΔNICS defined to be NICS(transition state) – NICS(starting complex).  


Figure S11. Schematic representation of NICS values (given in ppm) along reaction coordinate for C–O bond forming pathways.

Figure S12. Plot of ΔNICS (ppm) versus calculated barrier height (kcal/mol). ΔNICS defined to be NICS(transition state) – NICS(starting complex). The ΔNICS value for naphthyl complexes is taken to be the average over the two aryl rings.
Coupled Cluster Calculations

Domain-based local pair natural orbital (DLPNO)-CCSD(T) calculations were performed to obtain further refined electronic energies.\textsuperscript{28} Coupled cluster (CC) calculations benefit from a degree of orbital relaxation of the reference determinant by the single orbital replacements from the T\textsubscript{1} operator; however, the reference wavefunction should still provide a suitable basis for the coupled cluster expansion.\textsuperscript{29} We consider both canonical Hartree–Fock (HF) orbitals as well as Kohn–Sham (KS) orbitals as references. The approach of using non-HF orbitals as a reference basis has been demonstrated to be particularly advantageous when the HF determinant is a less ideal zeroth order approximation for the reference state – as is often the case with transition metal complexes.\textsuperscript{30} This effect has also been observed within the context of DLPNO-based CC calculations.\textsuperscript{31} In accord with literature findings, we observe the use of KS orbitals (BP86) in place of HF orbitals reduces the T\textsubscript{1} diagnostic values\textsuperscript{32} in the C–O bond forming transition states to generally ≤ 0.02, compared to > 0.03 as obtained with HF references. The range of the T\textsubscript{1} diagnostic values with KS orbitals is reduced to 0.002, compared to 0.011 with HF references. As such, KS (BP86) orbitals are preferred as the reference for DLPNO-CCSD(T) calculations presented herein. We note that qualitatively similar results are obtained with both HF and KS references.

We then turned our attention to the accuracy cutoff parameters in the DLPNO-based method (T\textsubscript{CutPairs}, T\textsubscript{CutDO}, T\textsubscript{CutPNO}, and T\textsubscript{CutMKN}) as set by the keywords LoosePNO, NormalPNO, and TightPNO. While the NormalPNO settings capture the correct qualitative trends at affordable computational cost, we find deviations in barrier heights of up to 1.5 kcal/mol with respect to control calculations with the TightPNO settings (Table S4). As such, we elect to employ the TightPNO settings with BP86 reference orbitals for final energetics reported in this investigation.
Table S4. Effect of choice of reference orbitals (HF or BP86) and PNO accuracy settings (Normal/Tight) on calculated barrier heights.

<table>
<thead>
<tr>
<th>Transition State</th>
<th>HF/Normal</th>
<th>HF/Tight</th>
<th>BP86/Normal</th>
<th>BP86/Tight</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS(FG)\textsuperscript{\textit{im}}</td>
<td>28.4 [0.034]</td>
<td>28.1 [0.039]</td>
<td>30.6 [0.021]</td>
<td>29.3 [0.021]</td>
</tr>
<tr>
<td>TS(FG)\textsuperscript{\textit{im}}</td>
<td>30.0 [0.028]</td>
<td>28.5 [0.033]</td>
<td>28.1 [0.021]</td>
<td>27.5 [0.020]</td>
</tr>
<tr>
<td>TS(FG)\textsuperscript{\textit{phen}}</td>
<td>–</td>
<td>33.8 [0.036]</td>
<td>–</td>
<td>33.2 [0.020]</td>
</tr>
<tr>
<td>TS(FG)\textsuperscript{\textit{1nap}}</td>
<td>–</td>
<td>31.5 [0.034]</td>
<td>–</td>
<td>30.2 [0.019]</td>
</tr>
<tr>
<td>TS(FG)\textsuperscript{\textit{2nap}}</td>
<td>–</td>
<td>33.9 [0.033]</td>
<td>–</td>
<td>32.3 [0.019]</td>
</tr>
<tr>
<td>TS(FG)\textsuperscript{\textit{me}}</td>
<td>–</td>
<td>59.1 [0.028]</td>
<td>–</td>
<td>61.8 [0.019]</td>
</tr>
<tr>
<td>TS(DE)</td>
<td>23.2 [0.023]</td>
<td>22.0 [0.028]</td>
<td>–</td>
<td>21.0 [0.019]</td>
</tr>
</tbody>
</table>

T\textsubscript{1} diagnostic provided in brackets next to barrier heights (given in kcal/mol).

In the current ORCA implementation, CC amplitudes are not self-consistently optimized with respect to the solvation SCRF. As a result, solvation is taken into account by the addition of ∆G(solv) calculated by DFT to gas phase CC electronic energies. ∆G(solv) is calculated as \(E_{el}(M06/BS2/CPCM(MeCN)) - E_{el}(M06/BS2)\). Hence, final Gibbs free energies are calculated as:

\[
G_{solv}^* = E_{el,\text{gas}}^{CC} + E_{thermo}^{DFT} + \Delta G_{solv}^{DFT} + \Delta G^{0\rightarrow*}
\]

Comparison of density functional methods in calculation of the barrier height of the rate-determining C–O bond formation

Taking the barrier obtained by DLPNO-CCSD(T)[TightPNO/BP86]//(ma)-def2-TZVPP+∆G(solv) as a reference value (\(\Delta G^\dagger = 21.0\) kcal/mol), we then investigated the results obtained via a variety of DFT methods for comparison. M06\textsuperscript{18}, a commonly employed functional for evaluating energetics of transition metal containing systems, performs well with a \(\Delta G^\dagger\) of 18.2 kcal/mol. Less parameterized global hybrids (B3LYP\textsuperscript{33}, PBE0\textsuperscript{11}) as well as Head–Gordon’s range-separated hybrid \(\omega B97M-V\textsuperscript{34}\) accordingly produce similar results. Surprisingly, we find MN15\textsuperscript{35}, parameterized to perform well across a variety of single and multi-reference systems, substantially underestimates barrier to C–O bond formation (\(\Delta G^\dagger = 15.2\) kcal/mol).
Table S5. Comparison of DFT methods for computing barrier height for C–O reductive elimination, TS(FG).a

<table>
<thead>
<tr>
<th>Method</th>
<th>Barrier height (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DLPNO-CCSD(T)</td>
<td>21.0</td>
</tr>
<tr>
<td>M06</td>
<td>18.2</td>
</tr>
<tr>
<td>PBE0-D4</td>
<td>18.0</td>
</tr>
<tr>
<td>B3LYP-D4</td>
<td>20.9</td>
</tr>
<tr>
<td>ωB97M-V</td>
<td>22.7</td>
</tr>
<tr>
<td>MN15b</td>
<td>15.2</td>
</tr>
</tbody>
</table>

a Calculations performed on PBE0-D4/BS1/CPCM(MeCN) geometries. The def2-TZVPP basis set and CPCM(MeCN) models are used in the final single point calculations unless otherwise specified. b Calculation performed using the Jaguar program with the def2-TZVPP(-g) basis set and PBF solvation model for MeCN.

Notes on the Model System

Stability of the RKS solution:

Conducting stability analysis on the RKS (PBE0/BS1/CPCM(MeCN)) wavefunction at the C–O bond forming transition states reveals instability in some cases with respect to breaking of spin symmetry – favoring the UKS broken-symmetry (BS) solution, with ⟨S^2⟩ of up to 0.24. However, we find re-optimization along the broken-symmetry surface affords nearly identical geometries and final relative energies. Stability of the RKS density with respect to symmetry breaking is anticipated to be highly functional dependent. Control calculations with B3LYP-D4, M06, and PBE-D4 reveal minimal spin contamination and suggest the transition states are well described by a closed-shell KS determinant.
**Table S6.** Value of $\left\langle S^2 \right\rangle$ for broken-symmetry determinants (if exists) at the C–O bond forming transition states.

<table>
<thead>
<tr>
<th>Transition State</th>
<th>PBE0-D4</th>
<th>B3LYP-D4</th>
<th>M06</th>
<th>PBE-D4</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS(FG)$_{\text{vin}}$</td>
<td>0.124</td>
<td>0.003</td>
<td>0.001</td>
<td>0.000</td>
</tr>
<tr>
<td>TS(FG)$_{\text{cin}}$</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>TS(FG)$_{\text{phen}}$</td>
<td>0.243</td>
<td>0.030</td>
<td>0.010</td>
<td>0.000</td>
</tr>
<tr>
<td>TS(FG)$_{\text{1nap}}$</td>
<td>0.205</td>
<td>0.013</td>
<td>0.008</td>
<td>0.000</td>
</tr>
<tr>
<td>TS(FG)$_{\text{2nap}}$</td>
<td>0.209</td>
<td>0.014</td>
<td>0.007</td>
<td>0.000</td>
</tr>
<tr>
<td>TS(FG)$_{\text{me}}$</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>

We became curious as to whether the stability of a broken-symmetry wavefunction is an artifact of the PBE0-D4 functional or an indicator of chemically relevant non-dynamical correlation. Plotting the $\alpha – \beta$ spin density for the PBE0-D4 broken-symmetry determinant of TS(FG)$_{\text{phen}}$ reveals net $\alpha$ spin density on Ni (predominantly in the $d_{x^2-y^2}$ orbital), with a buildup of $\beta$ spin density in the $\pi$ system of the phenyl ring (Figure S13). Vertical excitation energies were evaluated with time-dependent DFT (TD-DFT) calculations (B3LYP-D4/def2-TZVPP/CPCM(MeCN)) to check for low lying excited states (possibly involving the $\pi$ system of the vinyl/aryl substituents) in the vicinity of the transition state. However, the lowest vertical singlet excitations [$d_{x^2-y^2}/\pi^*$ (aryl/vinyl) $\rightarrow \pi^*$ MeCN ligand] occur from 1.6 to $>3.0$ eV for the six transition states, with the corresponding (spin-adapted) triplets $>1.0$ eV above the closed-shell singlet ground state. Hence, the ground state singlet surface is well isolated from other excited states, particularly MLCT states, in the vicinity of the transition state, pointing to a suitable description within a single-reference framework. Similar TD-DFT results were obtained using the M06 functional. As discussed in the text, the aryl/vinyl $\pi/\pi^*$ systems are indeed involved in bond formation; however, this appears to be from the aforementioned $\sigma/\pi$ mixing rather than introduction of low-lying charge transfer excited states in the region of the TS.
To further probe this, multiconfigurational SCF calculations were carried out using complete active space self-consistent field (CASSCF) theory, including the bonding/antibonding orbital pairs as prompted by the broken-symmetry DFT calculations (Figure S14). The natural orbitals from the resulting (2,2) active space mirror the Ni $d_{x^2-y^2}$/phenyl $\pi^*$ character of the broken-symmetry calculations. The ground state configuration interaction (CI) vector is comprised of 84% of the [20] (doubly occupied bonding) and 16% [02] (doubly occupied antibonding) configurations, indicating diradical character to be minimal. Moreover, CC calculations (vide supra) afford $T_1$ diagnostics of $\leq 0.021$, further suggesting an adequate single reference description.

In summary, these results suggest the dominance of a single configuration in the ground state, while highlighting the importance of the aryl/vinyl $\pi$ systems in the reductive elimination process. Moreover, we expect the DLPNPO-CCSD(T) calculations with TightPNO settings and BP86 reference orbitals are well suited for evaluating the energies at these transition states.
Comparing CC to DFT in calculating barrier heights

Barrier heights calculated with M06 are systematically lower than those obtained with DLPNO-CCSD(T); however, the two methods show the same trends in reactivity (Table S7).

Table S7. DFT and CC barrier heights for C–O reductive elimination.

<table>
<thead>
<tr>
<th>Transition State</th>
<th>M06</th>
<th>DLPNO-CCSD(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS(FG)\text{vin}</td>
<td>25.4</td>
<td>29.3</td>
</tr>
<tr>
<td>TS(FG)\text{cin}</td>
<td>24.9</td>
<td>27.5</td>
</tr>
<tr>
<td>TS(FG)\text{phen}</td>
<td>28.7</td>
<td>33.2</td>
</tr>
<tr>
<td>TS(FG)\text{1nap}</td>
<td>26.8</td>
<td>30.2</td>
</tr>
<tr>
<td>TS(FG)\text{2nap}</td>
<td>28.9</td>
<td>32.3</td>
</tr>
<tr>
<td>TS(FG)\text{me}</td>
<td>53.8</td>
<td>61.8</td>
</tr>
</tbody>
</table>

Calculations performed on PBE0-D4/BS1/CPCM(MeCN) geometries. The def2-TZVPP basis set and CPCM(MeCN) models are used in the final single point calculations. DLPNO-CCSD(T) calculations employ TightPNO settings with a BP86 reference as discussed above.

C–H Bond Dissociation Energies as Metric for Disruption of π Bonding

For C–O bond formation via reductive elimination (TS(DE) and TS(FG)), the key role of \(\sigma/\pi\) mixing at the transition state in facilitating bond formation is discussed in the main text. The degree of stabilization experienced at the transition state depends on the ability of the ligand-based \(\pi^*\) to serve as an acceptor in the HOMO/LUMO mixing. For example, \(F\text{vin}\) undergoes reductive elimination more readily than \(F\text{phen}\), as partially occupying the phenyl \(\pi^*\) is detrimental to the resonance stabilization of the \(\pi\) system of the aryl ligand, whereas this does not apply to the vinyl \(\pi\) system. Above, we investigate this from the viewpoint of NICS. Here, we the energetic cost of breaking a C=C bond by virtue of the ability for a \(\pi\) system to accept H\(^*\), generating the corresponding radical. We define C–H bond dissociation energy (BDE) to be the change in electronic energy from the organic radical to the closed-shell \(\pi\) system and H\(^*\) (the reverse of the process stated above). A high C–H BDE indicates less penalty for breaking the C=C bond (Figure S15). A lower energetic penalty for lowering the bond order of the \(\pi\) system would correlate with a more facile \(\sigma/\pi\) mixing at the transition state (in which the ligand \(\pi^*\) serves as an acceptor to a M–L \(\sigma\) donor). As hypothesized, a correlation between C–H BDE and barrier height for C–O reductive elimination exists (Figure S16).
Figure S15. C–H bond dissociation energy (BDE) from organic radical compounds (in kcal/mol). Calculated at the PBE0-D4/def2-TZVP(-f) level of theory.

Figure S16. Plot of barrier height to C–O reductive elimination from Ni(II) complexes F versus C–H bond dissociation energy (BDE), in kcal/mol, from organic radical compounds corresponding to the C(sp²) fragments of complexes F.
Oxidative Addition Mechanisms

In the minimum free energy path presented in Figure 2 of the main text, four mechanisms of oxidative addition from A to B/C/D are considered: (1) A three-centered transition state leading to B, (2) an anti-displacement-type mechanism leading to cationic Ni(II) intermediate C, (3) halide abstraction affording a Ni(I) iodide and organic radical, and (4) outer-sphere electron transfer, followed by radical recombination (Figure S17). With an apparent barrier height of 10.3 kcal/mol, anti-displacement (TS(BC)) represents the lowest energy pathway for C–I bond cleavage. Oxidative addition via a canonical three-centered transition state is competitive, with a ΔG‡ of 13.5 kcal/mol. As a control, geometries were also obtained in the gas phase. These calculations slightly favor the less polar three-centered transition state. Halide abstraction (TS(HI)) proceeds with a higher barrier of 22.8 kcal/mol. Tris(acetonitrile) complexes were also considered.

Figure S17. Oxidative addition mechanisms considered herein.
The barrier height for outer-sphere electron transfer is evaluated by Marcus theory. Vertical reorganization energies ($\lambda$) approximated by Nelsen’s four-point model using electronic energies at the M06/BS2/CPCM(MeCN) level of theory (Figure S17).\textsuperscript{37} Hence, reorganization energy is calculated as the electronic energy of the initial state (D+A) at the optimized geometry of the initial state (D+A) subtracted from the electronic energy of the initial state (D+A) at the geometry of the final state (D•+A•−). Change in free energy ($\Delta G^0$) is calculated at the M06/BS2/CPCM(MeCN)//PBE0-D4/BS1/CPCM(MeCN) level of theory. Note that single electron reduction of substrate If leads to concomitant cleavage of the C–I bond to afford a C-centered radical and iodide (Figure S17).

![Model reaction coordinate for outer-sphere electron transfer.](image)

**Figure S18.** Model reaction coordinate for outer-sphere electron transfer.

The corresponding free energy barrier is calculated as:

$$\Delta G^\ddagger = \frac{(\lambda_0 + \Delta G^0)^2}{4\lambda_0}$$

A reorganization energy ($\lambda$) of 83.9 kcal/mol paired with a reaction free energy ($\Delta G^0$) of 10.9 kcal/mol affords $\Delta G^\ddagger$ of 26.8 kcal/mol.
Thermodynamics of reorganization to π-alloy complex M

**Figure S19.** Free energy change for the reaction of Ni(COD)$_2$ and substrate 1f to give π-alloy complex 7. Gibbs free energies give in kcal/mol at the M06/(ma)-def2-TZVPP/PCPM(Et$_2$O)//PBE0-D4/BS3 level of theory.

In stoichiometric experiments, pre-mixing PCy$_3$ and Ni(COD)$_2$ followed by addition of 1f yields predominantly halide abstraction, producing (PCy$_3$)$_2$NiI (see Figure 7 and 8 in the main text). We suspect this is due to the formation of sterically encumbered PCy$_3$-ligated Ni(0) complexes which undergo halide abstraction with 1f preferentially to $2e^-$ oxidative addition (see Figure 8 in main text). Instead, if substrate 1f is first reacted with 1 equivalent of Ni(COD)$_2$ followed by addition of PCy$_3$, π-alloy complex 7 is formed. As such, we suspected that Ni(COD)$_2$ undergoes facile oxidative addition with 1f and the resultant Ni(II) vinyl iodide L is thermodynamically preferred to its Ni(0) precursors. Our computations corroborate this hypothesis, finding the formation of Ni(II) vinyl iodide L is accompanied by a free energy change of −6.9 kcal/mol (Figure S19). In the absence of a vinyl iodide or base with zinc (II) salts, treatment of intermediate L with PCy$_3$ affords π-alloy complex 7 with a $\Delta G$ of −50.3 kcal/mol.

Despite extensive efforts, starting from the crystallographic structure of 7, optimizations at the PBE0-D4/BS3 level of theory return one small imaginary mode (<100 cm$^{-1}$) corresponding to the rocking of the ally group/Ni center. Control optimizations and Hessian calculations with PBE-D4/BS3 level of theory afford nearly superimposable structures with no imaginary modes. Regardless, these observations bear no effect on the final conclusions.

**Disproportionation from Ni(II)/Ni(II) to Ni(I)/Ni(III)**

We have further investigated the possibility for a disproportionation event between two Ni(II) species to give Ni(I) and Ni(III) intermediates. From the catalyst resting state (D) in MeCN, outer-sphere electron transfer affords anionic Ni(I) and cationic Ni(III) intermediates M and N, respectively. Geometric relaxation and solvent exchange afford a $\Delta G$ of 41.5 kcal/mol,
disfavoring the formation of the Ni(I)/Ni(III) products (Figure S20). Although already 3.6 kcal/mol higher in energy than the resting state (D), disproportionation from Ni(II) iodide complex B was also considered. Even allowing anion exchange for charge equilibration, disproportionation to Ni(I) and Ni(III) complexes O and P is disfavored by 53.6 kcal/mol. Note that the lowest energy isomers and ligation environments are depicted. In summary, disproportionation from Ni(II)/Ni(II) to Ni(I)/Ni(III) is thermodynamically inaccessible. These results are in accord with prior literature.38

Figure S20. Thermodynamics of disproportionation of Ni(II)/Ni(II) to Ni(I)/Ni(III) from Ni(II) intermediates B and D. Energies referenced from 2 mol Ni(II) to 1 mol Ni(I) plus 1 mol Ni(III).

Electronic structure of dinuclear Ni complex 5

Complex 5 is a dinuclear nickel species bearing a square planar nickel center (Ni\textsuperscript{II}) and a distorted tetrahedral nickel (Ni\textsuperscript{II}) center. Given the ligand field environment, 5 was anticipated to present a triplet ground state with both nickel centers formally in the (II) oxidation state and with Ni\textsuperscript{II} in a high spin configuration. An effective magnetic moment (\(\mu_{\text{eff}}\)) of 3.57 B.M. (with
diamagnetic correction) is found via Evan’s method (see text). This is consistent with the presence of one high spin Ni(II) center. We sought to further explore the spin state assignment of 5 by computational analysis. The X-ray crystal structure of 5 contains a Ni-bound molecule of THF which hydrogen bonds to the pendant alcohol coordinated to Ni(2). Elemental analysis of the bulk material suggests the THF molecule is indeed an artifact of subsequent crystallization conditions (THF/hexanes) employed for obtaining X-ray quality crystals. (Note that bulk 5 is isolated without exposure to THF). Indeed, when THF is present a ∆G of 1.0 kcal/mol is calculated favoring the formation of 5•THF from 5 and THF (Figure S21).

**Figure S21.** Coordination of THF to 5 to give 5•THF is favorable by 1.0 kcal/mol.

To obtain a representative structure of 5, the Ni-bound molecule of THF was removed from the complex and the coordinates were relaxed. This was performed for the lowest energy closed-shell singlet (CSS), open-shell singlet (OSS), triplet, and quintet states. The optimization was carried out with DFT using the PBE0-D4 functional with the def2-TZVP basis set for Ni, ma-def2-SVP with ECP28MWB small-core pseudopotential for iodine, and def2-SVP for all other atoms. Single point calculations were then carried out on 5 at the M06/BS2/PCPM(benzene) level of theory for the lowest singlet, triplet, and quintet spin states. The triplet (low spin at Ni(1) and high spin at Ni(2)) is lowest in energy with the CSS [two low spin Ni(II)], OSS [antiferromagnetically-coupled high spin Ni(II) centers], and quintet [two high spin Ni(II)] at 15.4, 13.9 and 13.9 kcal/mol higher in energy, respectively. While bond distances and angles vary, the ligation of 5 remained the same across the relaxed geometries in different electronic configurations. The coordinates for all four complexes are available in the coordinate data file, labeled as 5, 5_CSS, 5_OSS, and 5_HS. For high-spin Ni(II) centers, Löwdin spin populations of 1.603–1.570 were found (lower than the value of 2 from Ni–L covalency – the unpaired spin-bearing orbitals, d_\(_{z^2}\) and d_\(_{x^2-y^2}\), have character on ligating atoms) (Table S8). Analysis of intrinsic atomic orbitals (IAOs)\(^{39}\) reveals 13 α and 13 β spin electrons are localized
to Ni\(^{(1)}\), while 14 \(\alpha\) and 12 \(\beta\) spin electrons are localized to Ni\(^{(2)}\). These results further corroborate the formal oxidation state assignments in complex 5 as two Ni(II) centers, Ni\(^{(1)}\) low spin and Ni\(^{(2)}\) high spin.

Table S8. Löwdin atomic spin populations for 5 optimized in different spin states.\(^a\)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Löwdin spin population on Ni(^{(1)})</th>
<th>Löwdin spin population on Ni(^{(2)})</th>
<th>(\langle S^2 \rangle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.024</td>
<td>1.603</td>
<td>2.238</td>
</tr>
<tr>
<td>5_CSS</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>5_OSS(^b)</td>
<td>1.573</td>
<td>-1.571</td>
<td>2.021</td>
</tr>
<tr>
<td>5_HS</td>
<td>1.566</td>
<td>1.570</td>
<td>6.023</td>
</tr>
</tbody>
</table>

\(^a\) Löwdin atomic spin populations and \(\langle S^2 \rangle\) calculated with M06/BS2/CPCM(benzene). \(^b\) Net \(\alpha\)--\(\beta\) signed spin density for an OSS is a consequence of the broken-symmetry formalism, i.e. the necessarily improper description of open-shell singlet states by a single Slater determinant. The opposite signed \(\alpha\)--\(\beta\) spin density and each Ni center indicates the desired “OSS” state (broken-symmetry state) was captured, however we remind the reader that a \(\alpha\)--\(\beta\) spin density for a proper singlet state is unphysical as a pure singlet state is defined as having \(\langle S^2 \rangle = 0\).

While these results suggest a ground state with formally Ni(II)/Ni(II) oxidation states, we were curious as to whether facile electron transfer could occur between the nickel centers to afford a Ni(I)/Ni(III) species. Time-dependent density functional theory (TD-DFT) calculations were carried out from the triplet ground state of 5 with the M06/BS2/CPCM(benzene) level of theory. The first 12 excitations (0.48–2.00 eV) are d-d excitations within the ligand field of single nickel centers. The first inter-nickel charge-transfer (CT) excitation found is at 2.16 eV and is characterized by CT from Ni\(^{(1)}\)/L to Ni\(^{(2)}\). Natural Transition Orbitals (NTOs) were utilized in this analysis. The NTO donor/acceptor pair describing 99\% of the transition (\(n = 0.990\)) character is depicted below (Figure S22). Note that the donor NTO has significant character on the iodine ligand on Ni\(^{(1)}\). While the TD-DFT description of the energetics of CT states is often not quantitatively accurate, these initial calculations qualitatively highlight the significant preference for the Ni(II)/Ni(II) configuration over Ni(I)/Ni(III).
**Figure S22.** Donor (left) and acceptor (right) NTOs for 12th root.

**Thermodynamics of the formation of complexes 6 and 7**

Complex 6 is high spin \((S = 2)\) in the ground state. The open-shell singlet (antiferromagnetically-coupled high spin Ni(II) centers) and closed-shell singlet are found to be 3.7 and 30.3 kcal/mol higher in energy than the high spin complex. As with 5, the relaxed geometries for each spin state are available in the structure data file (6, 6_CSS, and 6_OSS).

Given the small difference in energy between the high spin and low spin states of 5', the assignment of spin state becomes increasingly dependent on the method employed. B3LYP-D4 and M06-L find the singlet and triplet state complexes to be less than 0.5 kcal/mol different in
energy. PBE0-D4 affords a preference of 6.5 kcal/mol for the low spin 5' while M06 and TPSSH predict a closed-shell singlet by 8.2 and 8.3 kcal/mol (Table S9). These calculations highlight the known challenges of computing energy differences between different spin states in transition metal complexes. Regardless, we find the subsequent formation of DMAP and PCy₃ adducts 6 and 7 to be highly thermodynamically favorable and their formations from 5/5’ irreversible.

**Table S9.** Comparison of relative energies of high-spin and low-spin 5’ computed across different density functionals.

<table>
<thead>
<tr>
<th>Method</th>
<th>Low-spin R</th>
<th>High-spin R</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE0-D4</td>
<td>6.5</td>
<td>0.0</td>
</tr>
<tr>
<td>B3LYP-D4</td>
<td>0.0</td>
<td>0.3</td>
</tr>
<tr>
<td>M06-L</td>
<td>0.0</td>
<td>0.4</td>
</tr>
<tr>
<td>M06</td>
<td>0.0</td>
<td>8.2</td>
</tr>
<tr>
<td>TPSSH</td>
<td>0.0</td>
<td>8.3</td>
</tr>
</tbody>
</table>

**Acid/Base equilibrium and importance of Zn(II) salt additives**

Throughout our experimental and computational investigations, we find that Zn(II) salts play an important role in sequestering iodide produced after oxidative addition. These may be produced either from reduction of sacrificial Ni iodide species or from the reaction of Zn⁰ with the HI formed in the reaction after oxidative addition. Modeling the exact speciation of Zn(II) salts in the reaction is challenging and this matter is further complicated by (in)solubility of some of these potential adducts. Likewise, Zn(OTf)₂ is used in the modified reaction conditions due to its improved solubility over ZnI₂. For simplicity, we highlight in a general case how solvated ZnI₂ may aid in sequestration of iodide through formation of zinc-ate (ZnI₄²⁻) derived intermediates. The computed ΔG of –29.5 kcal/mol for formation of [Et₃NH]₂ZnI₄ from ZnI₂ and Et₃NHI demonstrates this point (Figure S24). The corresponding process with Zn(OTf)₂ should be similar, if not even more favorable.
Figure S24. Impact of ZnI$_2$ on sequestration of iodide and formation of stable adducts.

**Alternative C–O bond forming mechanistic hypotheses**

Throughout the course of our investigation numerous mechanistic hypotheses were considered for C–O bond formation. While in the full context of experimental and computational investigation it is now clear that π-allyl complex 7 is not catalytically relevant, we initially suspected C–O bond formation may occur from nucleophilic attack of the electrophilic β carbon of the π-allyl moiety (Figure S25). Our initial investigations highlight a thermodynamic preference of 13.8 kcal/mol for π-allyl intermediate R over metallacyclobutane S. Critically, given the geometric constraints of S, β-hydride elimination is not anticipated to be facile. Accordingly, a barrier of 32.0 kcal/mol is found for this step (TS(ST)). Note that high spin S was found to have a relative free energy of 39.8 kcal/mol. These preliminary results we obtained with the PBE-D4/def2-TZVP [Ni], ma-def2-SV(P) [I], def2-SV(P) level of theory.

**Figure S25.** Alternative mechanistic hypothesis for C–O bond formation. Relative free energies given in kcal/mol.
An oxa-Heck type mechanism was also considered starting from a protodemetalated olefin. Syn-addition of a nickel alkoxide can be eliminated on a basis of stereochemical outcome of the observed product – the enol ether after subsequent β-hydride elimination would bear the $E$ olefin geometry when starting from the $Z$ styrene. The charge separated intermediates required for an anti-addition are found to be high in energy or unstable on the PES. When olefin 3 is subjected to the reaction conditions (with or without strong exogenous base), no productive reaction is experimentally observed.
NMR Spectra of New Compounds and Key Experiments

Figure S26. $^1$H NMR spectrum of 1a in CDCl$_3$. 
Figure S27. $^{13}$C NMR spectrum of 1a in CDCl$_3$. 
Figure S28. $^1$H NMR spectrum of 1d in CDCl$_3$. 
Figure S29. $^{13}$C NMR spectrum of 1d in CDCl$_3$. 
Figure S30. $^1$H NMR spectrum of 1e in CDCl$_3$. 
Figure S3. $^{13}$C NMR spectrum of 1e in CDCl$_3$. 
Figure S32. $^1$H NMR spectrum of 2a in CDCl$_3$. 
Figure S3. $^{13}$C NMR spectrum of 2a in CDCl$_3$. 
Figure S34. $^1$H NMR spectrum of 2d in CDCl$_3$. 
Figure S35. $^{13}$C NMR spectrum of 2d in CDCl$_3$. 
Figure S36. $^1$H NMR spectrum of 3 in C$_6$D$_6$. 
Figure S37. $^{13}$C NMR spectrum of 3 in C$_6$D$_6$. 
Figure S38. $^1$H NMR spectrum of 4 in C$_6$D$_6$. 
Figure S39. $^1$H NMR spectrum of 5 in C$_6$D$_6$. 
Figure S40. Stacked $^1$H NMR spectra of compound 5 (top) and its decomposition products(s) 5’ in C$_6$D$_6$. 
Figure S41. $^1$H NMR spectrum of 6 in CD$_2$Cl$_2$. 
Figure S42. $^1$H NMR spectrum of 7 in C$_6$D$_6$. 
Figure S43. $^{13}$C NMR spectrum of 7 in C$_6$D$_6$. 
Figure S44. $^{31}$P NMR spectrum of compound 7 in C$_6$D$_6$. The small, broadened upfield peak is associated with the minor diastereomer, which displayed broadened resonances in the $^1$H NMR spectrum.
Figure S45. $^1$H NMR spectrum of (PCy$_3$)$_2$NiI in C$_6$D$_6$. 
Figure 46. $^{31}$P NMR spectrum of (PCy$_3$)$_2$NiI in C$_6$D$_6$. 
Figure S47. $^1$H NMR spectrum of 5 following exposure to ca. 120 equiv of Et$_3$N in C$_6$D$_6$ for 30 minutes at 23 °C. Key resonances assigned to 2f and a triphenylmethane internal standard are identified with arrows. Quantities: 8.0 mg of 5, 1.0 mg of HCPh$_3$. Equivalents of Et$_3$N are estimated based on the relative integration of its resonances to that of HCPh$_3$. 
Figure S48. Stacked $^1$H NMR spectra of $5'$ before and after the addition of ca. 15 equivalents of Et$_3$N. 5.0 mg of $5'$ were allowed to decompose at ca. 23 °C for 16 h with 1.1 mg of a HCPh$_3$ internal standard. The second spectrum was collected ca. 2 h following the addition of base. The ratio of $2f$ to HCPh$_3$ is ca. 0.22:1.00 in both spectra, indicating a 19% spectroscopic yield.
References
4. APEX3, SADABS, and SAINT. Bruker AXS. Madison, WI, USA.
32. T; diagnostic defined as the norm of the singles amplitude vector divided by the square root of the number of electrons