Supporting Information

C–H Activation by Isolable Cationic Bis(phosphine)
Cobalt(III) Metallacycles

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I. General Considerations

All air- and moisture-sensitive manipulations were carried out using vacuum line, Schlenk and cannula techniques or in an MBraun inert atmosphere (nitrogen) dry box unless otherwise noted. All glassware was stored in a pre-heated oven prior to use. The solvents used for air- and moisture-sensitive manipulations were dried and deoxygenated using literature procedures. The following compounds were prepared according to literature procedures: (TMEDA)Co(CH\textsubscript{2}C(Me)\textsubscript{2}Ph)\textsubscript{2},\textsuperscript{2} (depe)Co(CH\textsubscript{2}SiMe\textsubscript{3})\textsubscript{2},\textsuperscript{3} FcBAr\textsuperscript{F}\textsubscript{4},\textsuperscript{4} N-Me-benzamide ring-d\textsubscript{5}.\textsuperscript{5}

\textsuperscript{1}H NMR spectra were recorded on Bruker AVANCE 300, 500, or Varian Inova spectrometers operating at 300.13 MHz, 500.46 MHz, and 399.80, respectively. \textsuperscript{13}C NMR spectra were recorded on Bruker AVANCE 500 spectrometer operating at 125.85 MHz. All \textsuperscript{1}H and \textsuperscript{13}C NMR chemical shifts are reported in ppm relative to SiMe\textsubscript{4} using the \textsuperscript{1}H (CDCl\textsubscript{3}: 7.26 ppm; C\textsubscript{6}D\textsubscript{6}: 7.16 ppm; THF-d\textsubscript{8}: 3.58 ppm) and \textsuperscript{13}C (CDCl\textsubscript{3}: 77.16 ppm; C\textsubscript{6}D\textsubscript{6}: 128.06 ppm; THF-d\textsubscript{8}: 67.21 ppm) chemical shifts of the solvent as a standard. \textsuperscript{1}H NMR data for diamagnetic compounds are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin. = quintet, hex. = hextet, hept. = heptet, br. = broad, m = multiplet, app = apparent), coupling constants (Hz), integration. \textsuperscript{1}H NMR data for paramagnetic compounds are reported as follows: chemical shift, peak width at half height (Hz), integration. \textsuperscript{13}C NMR data for diamagnetic compounds are reported as follows: chemical shift, multiplicity, coupling constants (Hz).

Elemental analyses were performed at Robinson Microlit Laboratories, Inc., in Ledgewood, NJ. High-resolution mass spectra were obtained at Princeton University mass spectrometry facilities using an Agilent 6210 TOF LC/MS.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox, transferred to a nylon loop and then quickly transferred to the goniometer head of a Bruker SMART APEX DUO diffractometer equipped with a molybdenum X-ray tube (\(\lambda = 0.71073\) Å) and a Cu X-ray tube (\(\lambda = 1.54178\) Å). Preliminary data revealed the crystal system. The data collection strategy was optimized for completeness and redundancy using the Bruker
COSMO software suite. The space group was identified, and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures.
II. Preparation of Cobalt Complexes

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\text{(depe)Co(cycloneophyl)(py)(Cl) (2). Note: Reaction of (TMEDA)Co(neophyl)}_2 \text{ (0.23 mmol scale) with 1 equivalent of depe forming (depe)Co(cycloneophyl) was reported by Walter and co-workers.}^2 \text{ A modified procedure using 1.5 equivalents of depe was developed, given that the formation of phosphine-bridged dinuclear cobalt complexes was found to give more reproducible reaction outcomes (yield, purity) when conducting reactions on larger scales. Structures of complexes S1 and S2 are proposed on the basis of } ^1\text{H and } ^{31}\text{P NMR spectroscopic data and by analogy with the observations of Walter and co-workers. Crystallization of these complexes proved unsuccessful due to their low solubility in aromatic and ethereal solvents.}
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In an N\(_2\)-filled glovebox, (TMEDA)Co(CH\(_2\)C(Me)\(_2\)Ph)\(_2\) (1, 566 mg, 1.28 mmol, 1 equiv) was dissolved in Et\(_2\)O (30 mL), cooled to –35 °C, and depe (397 mg, 1.92 mmol, 1.5 equiv) added. An orange precipitate was observed after 10 minutes, and the reaction was stirred for another 2 h at room temperature before being placed in a freezer (–35 °C) for 1 h. The reaction was filtered, and the precipitate washed with cold Et\(_2\)O to afford complex S1 as a yellow-orange powder (470 mg, 0.47 mmol, 73% yield). \( ^1\text{H NMR} \) (400 MHz, C\(_6\)D\(_6\), 23 °C): \( \delta \) 15.18 (br.}
s, $\Delta \nu = 236$ Hz), 3.26 (s, $\Delta \nu = 22$ Hz), 2.56 (br. s, $\Delta \nu = 150$ Hz), 1.48 – 0.87 (m), –0.48 (br. s, $\Delta \nu = 480$ Hz), –3.63 (br. s, $\Delta \nu = 430$ Hz).

In an N$_2$-filled glovebox, trityl chloride (393 mg, 1.41 mmol, 1.5 equiv) was added to a suspension of complex S1 (470 mg, 0.47 mmol, 1 equiv/Co) in Et$_2$O / MeCN (10:1, 20 mL) at room temperature. The reaction was stirred at room temperature for 2 h before evaporating the solvent, adding Et$_2$O (20 mL) and collecting the solid material by filtration (complex S2, yellow solid powder, 464 mg, 0.433 mmol, 92% yield). $^1$H NMR (400 MHz, C$_6$D$_6$, 23 °C): $\delta$ 8.60 (d, $J = 6.3$ Hz, 1H), 7.26 – 7.11 (m, 2H), 6.88 (br. s, 1H), 3.10 – 0.21 (m, 44H).

$^{31}$P{$^1$H} NMR (162 MHz, C$_6$D$_6$, 23 °C): $\delta$ 49.6 (d, $J = 250$ Hz), 39.3, 12.5 (d, $J = 250$ Hz).

In an N$_2$-filled glovebox, complex S2 (464 mg, 0.433 mmol) was dissolved in pyridine (2 mL) forming an orange solution. Pentane (20 mL) was added with rapid stirring followed by cooling of the reaction mixture to –35 °C for 12 h. The mother liquor was decanted, leaving an orange crystalline solid from which a sample was taken for single-crystal X-ray crystallography. The bulk material was redissolved in Et$_2$O (50 mL), filtered through a pad of Celite, and the solvent removed in vacuo to give the title compound as an orange solid powder (337 mg, 0.658 mmol, 76% yield). Anal. calcd for C$_{25}$H$_{41}$Cl$_1$Co$_1$N$_1$P$_2$: C, 58.65; H, 8.07; N, 2.74; found: C, 58.61; H, 8.01; N, 2.74. $^1$H NMR (400 MHz, C$_6$D$_6$, 23 °C): $\delta$ 9.08 (d, $J = 7.6$ Hz, 1H; C$_6$–H), 9.04 (d, $J = 5.5$ Hz, 2H; py 2-CH), 7.41 (t, $J = 7.3$ Hz, 1H; C$_5$–H), 7.20 (td, $J = 7.3$, 1.2 Hz, 1H; C$_4$–H), 6.85 (d, $J = 7.4$ Hz, 1H; C$_5$–H), 6.63 (tt, $J = 7.5$, 1.3 Hz, 1H; py 4-CH), 6.27 (t, $J = 6.9$ Hz, 2H; py 3-CH), 2.88 – 2.70 (m, 1H; PCH$_2$CH$_3$), 2.15 – 1.72 (m, 4H; Co–CH$_2$ [1H], PCH$_2$CH$_3$ [3H]), 1.67 – 1.28 (m, 9H; Co–CH$_2$ [1H], PCH$_2$CH$_2$P [3H], PCH$_2$CH$_3$ [2H], CMe$_2$ [3H]), 1.22 – 1.09 (m, 1H; PCH$_2$CH$_3$), 1.07 – 0.84 (m, 4H; PCH$_2$CH$_3$ [1H], PCH$_2$CH$_3$ [3H]), 0.80 – 0.63 (m, 7H; PCH$_2$CH$_2$P [1H], PCH$_2$CH$_3$ [6H]), 0.50 (s, 3H; CMe$_2$), 0.32 – 0.20 (m, 3H; PCH$_2$CH$_3$). $^{13}$C{$^1$H} NMR (126 MHz, C$_6$D$_6$, 23 °C): $\delta$ 167.0 (dd, $^2J_{CP} = 70.0$, 47.7 Hz; C$_1$), 165.2 (C$_2$), 155.3 (py 2-CH), 140.0 (C$_6$), 135.1 (py 4-CH), 124.7 (C$_5$), 123.1 (C$_4$), 121.9 (py 3-CH), 121.6 (C$_3$), 48.3 (d, $^3J_{CP} = 10.4$ Hz; CMe$_2$), 34.7 (CMe$_2$), 32.7 (CMe$_2$), 31.7 (dd, $^2J_{CP} = 24.5$, 7.5 Hz; Co–CH$_2$), 21.3 (t, $^1J_{CP} = 19.2$ Hz; PCH$_2$CH$_2$P), 18.8 (dd, $^1J_{CP} = 23.5$, 10.5 Hz; PCH$_2$CH$_2$P), 15.9 (d, $^1J_{CP} = 29.7$ Hz; PCH$_2$CH$_3$), 14.7 (d, $^1J_{CP} = 13.8$ Hz; PCH$_2$CH$_3$), 14.0 (d,
$^{1}J_{CP} = 27.5$ Hz; PCH$_2$CH$_3$), 13.4 (d, $^{1}J_{CP} = 5.6$ Hz; PCH$_2$CH$_3$), 8.7 (PCH$_2$CH$_3$), 7.7 (d, $^{2}J_{CP} =$ 6.9 Hz; PCH$_2$CH$_3$), 7.6 (d, $^{2}J_{CP} = 9.2$ Hz; PCH$_2$CH$_3$), 6.9 (d, $^{2}J_{CP} = 5.0$ Hz; PCH$_2$CH$_3$). $^{31}$P{^1}H NMR (162 MHz, C$_6$D$_6$, 23 °C): δ 52.0, 36.1.

**Figure S1.** Crystal structure of (depe)Co(cycloneophyl)(py)(Cl) (2; ORTEP shown with 30% probability ellipsoids, H atoms omitted). CCDC 2193852.
[(depe)Co(cycloneophyl)(py)][BAR₄] (3). In an N₂-filled glovebox, NaBAR₄ (260 mg, 0.293 mmol, 1 equiv) was added to a solution of complex 2 (150 mg, 0.293 mmol, 1 equiv) in fluorobenzene (10 mL) at room temperature. The solution immediately changed color from yellow-orange to blue. After stirring for 30 minutes, the reaction was filtered through a pad of Celite, and the filtrate concentrated in vacuo to ca. 5 mL. Pentane (5 mL) was added and the reaction cooled to −35 °C for 18 h. The mother liquor was decanted to give the title compound as a blue crystalline solid (389 mg, 0.290 mmol, 99% yield). Anal. calcd for C₅₇H₅₃B₁Co₁F₂₄N₁P₂: C, 51.10; H, 3.99; N, 1.05; found: C, 50.82; H, 3.81; N, 1.04. ¹H NMR (400 MHz, THF-d₈, 23 °C): δ 8.69 (br. s, 2H; py 2-CH), 8.01 (t, J = 7.5 Hz, 1H; py 4-CH), 7.85–7.79 (m, 8H; BAR₄₂-CH), 7.64–7.55 (m, 6H; BAR₄₄-CH, py 3-CH), 7.42–7.38 (m, 1H; C₆-H), 7.13–7.01 (m, 2H; C₄-H, C₅-H), 6.79 (dt, J = 7.2, 1.6 Hz, 1H; C₃-H), 2.60–2.33 (m, 2H; PCH₂CH₂P), 2.18–1.77 (m, 8H; PCH₂CH₂P [2H], Co–CH₂ [1H], PCH₂CH₃ [5H]), 1.62–1.45 (m, 3H; Co–CH₂ [1H], PCH₂CH₃ [2H]), 1.38–1.03 (m, 10H; CMe₂ [3H], PCH₂CH₃ [1H], PCH₂CH₃ [6H]), 0.78–0.57 (m, 9H; CMe₂ [3H], PCH₂CH₃ [6H]). ¹³C{¹H} NMR (126 MHz, THF-d₈, 23 °C): δ 163.8 (dd, 2JCₗP = 59.0, 38.4 Hz; C₁), 162.5 – 161.2 (m, BAR₄ CF₃), 159.0 (d, 3JCₗP = 2.0 Hz; C₂), 149.2 (py 2-CH), 138.5 (py 4-CH), 134.6 (BAR₄ 2-CH), 133.1 (d, 3JCₗP = 2.0 Hz; C₆), 129.1 (qq, ¹JCₗB = 31.3, ⁴JCₗF 2.7 Hz; BAR₄ B–C), 125.9 (py 3-CH), 125.3 – 125.2 (m; C₃), 124.6 (q, ¹JCₗF = 272 Hz; BAR₄ CF₃), 124.1 (C₄), 122.2 – 122.0 (m; C₅), 117.4 – 117.1 (m; BAR₄ 4-CH), 50.3 (d, 3JCₗP = 10.5 Hz; CMe₂), 32.7 (CMe₂), 28.3 (CMe₂), 22.8 (dd, ¹²JCₗP = 24.4, 17.7 Hz; PCH₂CH₂P), 21.0 (d, ²JCₗP = 21.4 Hz; Co–CH₂), 17.1 (dd, ¹²JCₗP = 25.8, 8.2 Hz; PCH₂CH₂P), 16.5 (dd, ¹JCₗP = 33.7, ⁴JCₗP = 3.7 Hz; PCH₂CH₃), 14.8 (d, ¹JCₗP = 13.9 Hz; PCH₂CH₃), 14.2 (d, ¹JCₗP = 16.8 Hz; PCH₂CH₃), 10.4 (d, ¹JCₗP = 25.3 Hz; PCH₂CH₃), 7.8 (d, ²JCₗP = 3.7 Hz; PCH₂CH₃), 7.4 (PCH₂CH₃), 6.4 (d, ²JCₗP = 6.8 Hz; PCH₂CH₃), 6.2 (d, ²JCₗP = 6.8 Hz;
PCH₂CH₃). $^{31}P\{^1H\text{NMR} (162 \text{ MHz, THF-d}_8, 23 \degree C): \delta 59.4, 40.9.\text{ }^{19}F\text{NMR} (376 \text{ MHz, THF-d}_8, 23 \degree C): \delta –63.4.}$

**Figure S2.** Crystal structure of [(depe)Co(cycloneophyl)(py)][BAR$_4$] (3; ORTEP shown with 30% probability ellipsoids, H atoms omitted). CCDC 2193853.
**Conversion of five-coordinate to six-coordinate complexes.** In an N$_2$-filled glovebox, pivalonitrile (ca. 1 mg, 0.01 mmol, 1 equiv) was added to a solution of complex 3 (13 mg, 0.01 mmol, 1 equiv) in THF-$d_8$ (0.6 mL) in a J. Young NMR tube. An immediate color change from blue to yellow occurred. The $^{31}$P NMR spectrum indicated complete conversion of complex 3 to complex 4. The NMR tube was returned to the glovebox, the solvent removed *in vacuo*, and the sample re-dissolved in pivalonitrile (1 mL). The solvent was removed *in vacuo*, THF-$d_8$ added, and the resulting solution transferred to a J. Young NMR tube. The $^{31}$P NMR spectrum indicated formation of complex 5, with a small amount of 4 still present (95:5 5:4). Dissolution in pivalonitrile and solvent evaporation was repeated twice more. $^{31}$P NMR showed full conversion to complex 5.

In an N$_2$-filled glovebox, complex 3 (13 mg, 0.01 mmol, 1 equiv) in pyridine (0.6 mL) with cyclohexane-$d_{12}$ (50 μL) added was transferred to a J. Young NMR tube. An upfield shift in the $^{31}$P NMR signals relative to 3 indicated binding of a second pyridine to the complex (3-py). Removal of pyridine solvent *in vacuo*, trituration in pentane, and redissolving in THF-$d_8$ confirmed the re-formation of complex 3.
Figure S3. $^{31}P\{^1H\}$ NMR spectra (162 MHz, 23 °C, THF-$d_8$) monitoring the conversion of five-coordinate to six-coordinate complexes. aSolvent is pyridine/C$_6$D$_{12}$.
[(depe)Co(cycloneophyl)\(^{\text{tBuCN}}\)\(_2\)[BAr\(_4\)]\(^{\text{F}}\)\(_4\) (5). In an N\(_2\)-filled glovebox, NaBAr\(^{\text{F}}\)\(_4\) (353 mg, 0.398 mmol, 1 equiv) was added to a solution of complex 2 (204 mg, 0.398 mmol, 1 equiv) in Et\(_2\)O (10 mL) and pivalonitrile (2 mL) at room temperature. After stirring for 1 h, the solvent was evaporated \textit{in vacuo}, Et\(_2\)O added (20 mL), and the resulting suspension filtered through a pad of Celite. The filtrate was evaporated to dryness \textit{in vacuo}. Pivalonitrile (2 mL) was added, followed by evaporation of the solvent \textit{in vacuo}. Addition/removal of pivalonitrile was repeated five times. The yellow solid obtained was recrystallized from Et\(_2\)O/pentane (1:1) at –35 °C to give the title compound (470 mg, 0.329 mmol, 83% yield). Anal. calcd for C\(_{62}\)H\(_{66}\)B\(_1\)Co\(_1\)F\(_{24}\)N\(_2\)P\(_2\): C, 52.19; H, 4.66; N, 1.96; found: C, 52.13; H, 4.49; N, 1.99.

\(^1\)H NMR (400 MHz, THF-\(d_8\), 23 °C): \(\delta\) 7.87 – 7.77 (m, 8H; BAr\(_4\)\(^2\)-CH), 7.64 – 7.57 (m, 4H; BAr\(_4\)\(^4\)-CH), 7.55 – 7.48 (m, 1H; C\(_6\)-H), 7.02 – 6.85 (m, 3H; C\(_3\)-H, C\(_4\)-H, C\(_5\)-H), 2.24 – 1.13 (m, 44H; Co–CH\(_2\)\[2H\], PCH\(_2\)CH\(_3\)\[4H\]; PCH\(_3\)CH\(_3\)\[8H\], CMe\(_2\)\[6H\], PCH\(_2\)CH\(_3\)\[6H\]; CMe\(_3\)\[18H\]), 1.12 – 1.01 (m, 3H; PCH\(_2\)CH\(_3\)), 0.43 – 0.30 (m, 3H; PCH\(_2\)CH\(_3\)).

\(^{13}\)C\(_{\text{\{1H}}\) NMR (126 MHz, THF-\(d_8\), 23 °C): \(\delta\) 165.1 (C\(_2\)), 162.5 – 161.2 (m; BAr\(^{\text{F}}\)\(_4\) CCF\(_3\)), 158.6 (dd, \(^2\)J\(_{\text{CF}}\) = 64.2, 40.7 Hz; C\(_1\)), 136.6 (C\(_3\)), 134.6 (BAR\(^{\text{F}}\)\(_4\) 2-CH), 133.9 (CN), 132.5 (CN), 129.1 (qq, \(^1\)J\(_{\text{CB}}\) = 31.3 Hz, \(^4\)J\(_{\text{CF}}\) = 2.5 Hz; BAr\(^{\text{F}}\)\(_4\) B–C), 124.6 (d, \(^1\)J\(_{\text{CP}}\) = 3.6 Hz; C\(_3\)), 124.5 (q, \(^1\)J\(_{\text{CF}}\) = 272 Hz; BAr\(^{\text{F}}\)\(_4\) CF\(_3\)), 123.2(9) (C\(_4\)), 123.2(5) (C\(_3\)), 117.4 – 117.1 (m; BAr\(^{\text{F}}\)\(_4\) 4-CH), 48.2 (d, \(^3\)J\(_{\text{CP}}\) = 10.8 Hz; C\(_{\text{Me}}\)), 35.1 (C\(_{\text{Me}}\)), 33.2 (dd, \(^2\)J\(_{\text{CP}}\) = 25.7, 6.2 Hz; Co–CH\(_2\)), 32.4 (C\(_{\text{Me}}\)), 29.9(0) (C\(_{\text{Me}}\)), 29.8(6) (C\(_{\text{Me}}\)), 26.8 (C\(_{\text{Me}}\)), 26.6 (C\(_{\text{Me}}\)), 22.9 (dd, \(^1\)J\(_{\text{CP}}\) = 27.6, 20.0 Hz; PCH\(_2\)CH\(_2\)P), 19.1 (dd, \(^{1}\)J\(_{\text{CP}}\) = 24.5, 8.2 Hz; PCH\(_2\)CH\(_2\)P), 16.3 (d, \(^1\)J\(_{\text{CP}}\) = 14.9 Hz; PCH\(_2\)CH\(_3\)), 15.5 (dd, \(^1\)J\(_{\text{CP}}\) = 40.0 Hz, \(^4\)J\(_{\text{CP}}\) = 2.0 Hz; PCH\(_2\)CH\(_3\)), 14.5 (d, \(^1\)J\(_{\text{CP}}\) = 21.4 Hz; PCH\(_2\)CH\(_3\)), 13.7 (d, \(^1\)J\(_{\text{CP}}\) = 15.3 Hz; PCH\(_2\)CH\(_3\)), 7.5 (d, \(^2\)J\(_{\text{CP}}\) = 2.8 Hz; PCH\(_2\)CH\(_3\)), 6.9 (d, \(^2\)J\(_{\text{CP}}\) = 4.4 Hz; PCH\(_2\)CH\(_3\)), 6.6 (d, \(^2\)J\(_{\text{CP}}\) = 7.9 Hz; PCH\(_2\)CH\(_3\)), 6.0 (d,
[(depe)Co(cycloneophyl)(py)('BuCN)][BArF₄] (4). In an N₂-filled glovebox, pyridine (2 mL) was added to complex 5 (100 mg, 0.070 mmol) and the resulting solution stirred for 0.5 h at room temperature. The solvent was evaporated in vacuo and the residue obtained triturated in Et₂O/pentane (1:5) to give the title compound as a yellow solid powder (91 mg, 0.064 mmol, 91% yield). Crystals suitable for X-ray crystallography were grown from PhF/pentane (1:1) at –35 °C. Anal. calcd for C₆₂H₆₂B₁Co₁F₂₄N₂P₂: C, 52.34; H, 4.39; N, 1.97; found: C, 52.55; H, 4.00; N, 2.07. ¹H NMR (400 MHz, THF-d₈, 23 °C): δ 8.50 (d, J = 4.6 Hz, 2H; py 2-CH), 7.68 – 7.59 (m, 9H; py 4-CH, BArF₄ 2-CH), 7.55 – 7.49 (m, 1H; C₆-H), 7.45 – 7.41 (m, 4H; BArF₄ 4-CH), 7.13 (t, J = 6.8 Hz, 2H; py 3-CH), 6.89 (t, J = 7.2 Hz, 1H; C₅-H), 6.81 (t, J = 7.2 Hz, 1H; C₄-H), 6.55 (d, J = 7.3 Hz, 1H; C₃-H), 2.28 – 1.72 (m, 7H; Co–CH₂ [1H], PCH₂CH₂P [2H]), 1.70 – 1.04 (m, 22H; Co–CH₂ [1H], PCH₂CH₂P [2H], PCH₂CH₃ [4H]), 0.96 – 0.86 (m, 3H; 3H; PCH₂CH₃), 0.72 – 0.61 (m, 3H; PCH₂CH₃), 0.19 – 0.08 (m, 3H; PCH₂CH₃), 0.00 (s, 3H; CMe₂). ¹³C{¹H} NMR (126 MHz, THF-d₈, 23 °C): δ 164.8 (C₂), 162.8 (dd, J₀CP = 62.5, 45.0 Hz; C₁), 162.5 – 161.2 (m; BArF₄ 2-CH), 153.8 (d, J₀CP = 2.5 Hz; py 2-CH), 137.9 (py 4-CH), 136.6 (C₆), 134.6 (BAρF₄ 2-CH), 133.1 (CN), 129.1 (qq, J₄CF = 31.8, J₀CF = 3.0 Hz; BArF₄ B–C), 125.3 (d, J₀CP = 3.3 Hz; C₅), 124.5 (q, J₀CF = 272 Hz; BArF₄ CF₃), 124.4 (py 3-CH), 123.8 (C₄), 123.2 (C₃), 117.4 – 117.1 (m; BArF₄ 4-CH), 48.1 (d, J₀CP = 10.5 Hz; CMe₂), 37.3 – 36.7 (m; Co–CH₂), 33.3 (CMe₂), 32.5 (CMe₂), 30.0 (CMe₂), 26.5 (CMe₂), 21.3 (dd, J₀CP = 23.5, 18.2 Hz; PCH₂CH₂P), 18.0 (dd, J₀CP = 24.7, 9.3 Hz; PCH₂CH₂P), 15.9 (d, J₀CP = 13.7 Hz; PCH₂CH₃), 15.6 (dd, J₀CP = 36.6, J₀CP = 2.5 Hz; PCH₂CH₃).
$^{31}$P\{$^1$H\} NMR (162 MHz, THF-$d_8$, 23 °C): $\delta$ 58.3, 36.4. $^{19}$F NMR (376 MHz, THF-$d_8$, 23 °C): $\delta$ –63.4.

**Figure S4.** Crystal structure of [(depe)Co(cycloneophyl)(py)('BuCN)][BAr$_4$F$_4$] (4; ORTEP shown with 30% probability ellipsoids, H atoms omitted). CCDC 2193854.
[(depe)Co(η⁶-C₆H₆)][BArF₄] (8). In an N₂-filled glovebox, (depe)Co(CH₂SiMe₃)₂ (235 mg, 0.534 mmol, 1 equiv) was dissolved in benzene (10 mL) in a 20 mL scintillation vial. FcBArF₄ (560 mg, 0.534 mmol, 1 equiv) in Et₂O (10 mL) was added dropwise and the reaction stirred at room temperature for 2 h. The reaction was concentrated in vacuo and pentane (20 mL) added. The resulting suspension was filtered through a glass frit, and the solid washed with pentane. The solid was dissolved in Et₂O and filtered through a pad of Celite. The filtrate was concentrated in vacuo to give the title compound as a green solid (518 mg, 0.429 mmol, 80% yield). Anal. calcd for C₄₈H₄₂B₁Co₁F₂₄P₂: C, 47.78; H, 3.51; found: C, 46.54; H, 3.12. ¹H NMR (500 MHz, THF-d₈, 23 °C): δ 7.82 – 7.76 (m, 8H), 7.60 – 7.55 (m, 4H), 6.10 – 6.06 (m, 6H), 2.08 – 1.97 (m, 1H), 1.95 – 1.86 (m, 1H), 1.83 – 1.56 (m, 10H), 1.20 – 1.08 (m, 12H). ¹³C{¹H} NMR (126 MHz, THF-d₈, 23 °C): δ 162.4 – 161.1 (m), 134.6, 129.0 (qq, J = 31.4, 2.7 Hz), 124.5 (q, J = 272 Hz), 117.3 – 117.0 (m), 91.4, 23.6 – 23.1 (m), 22.7, 22.0, 9.1, 7.9. ³¹P{¹H} NMR (162 MHz, THF-d₈, 23 °C): δ 87.8. ¹⁹F NMR (376 MHz, THF-d₈, 23 °C): δ –63.4.
III. Reaction of 3, 4, and 5 with N-Methylbenzamide

In an N₂-filled glovebox, N-methylbenzamide (14 mg, 0.10 mmol, 10 equiv) was added to a solution of complex 3, 4, or 5 (0.01 mmol, 1 equiv) in THF-d₈ (0.6 mL) and C₆H₆ (0.1 mL) in a J. Young NMR tube, with pyridine or pivalonitrile added (0 or 10 equiv). Allowing the reaction to proceed at ambient temperature, progress was monitored by ¹H NMR spectroscopy and the yield of product 7a determined by integration with respect to the residual NMR solvent peak. A pure sample of 7a was obtained by combining the reaction mixtures and purifying by silica gel chromatography (20–40% ethyl acetate in hexanes).

![Figure S5. Product yield versus time plot for the reactions of complexes 3, 4, and 5 with N-methylbenzamide.](image-url)
No organometallic intermediates were observed during the course of the reactions. For example, $^{31}$P NMR spectra associated with the time points for the reaction between complex 5 and N-methylbenzamide are shown below:

**Figure S6.** Time-course plot by $^{31}$P NMR spectroscopy (162 MHz, THF-$d_8$/C$_6$H$_6$) for the reaction of complex 5 with N-methylbenzamide.
**N-Methyl-2-(2-methyl-2-phenylpropyl)benzamide (7a).** Isolated as a colorless solid. \(^1\)H NMR (400 MHz, CDCl\(_3\), 23 °C): \(\delta\) 7.26 – 7.11 (m, 8H), 6.95 (d, \(J = 7.5\) Hz, 1H), 4.95 (br. s, 1H), 3.16 (s, 2H), 2.73 (d, \(J = 4.9\) Hz, 3H), 1.37 (s, 6H). \(^13\)C\(^{\text{1H}}\) NMR (126 MHz, CDCl\(_3\), 23 °C): \(\delta\) 171.4, 148.6, 138.2, 137.0, 132.2, 128.9, 128.0, 126.8, 126.7, 126.1, 125.7, 46.5, 39.5, 28.8, 27.0. HRMS (ESI+): m/z calcd for C\(_{18}\)H\(_{21}\)N\(_1\)O\(_1\)\([M+H]^+\) 268.1696, found 268.1699.

To aid the characterization of deuterated isotopologues, NMR spectra of 7a were also recorded in C\(_6\)D\(_6\) (with assignments made). \(^1\)H NMR (500 MHz, C\(_6\)D\(_6\), 23 °C): \(\delta\) 7.17 (d, \(J = 8.1\) Hz, 2H; C\(_8\)–H), 7.09 (t, \(J = 7.4\) Hz, 2H; C\(_9\)–H), 6.99 (t, \(J = 7.2\) Hz, 1H; C\(_{10}\)–H), 6.96 – 6.91 (m, 2H; C\(_2\)–H, C\(_4\)–H), 6.87 (t, \(J = 7.4\) Hz, 1H; C\(_3\)–H), 6.73 (d, \(J = 7.4\) Hz, 1H; C\(_5\)–H), 4.37 (br. s, 1H; NH), 3.35 (s, 2H; ArCH\(_2\)), 2.43 (d, \(J = 4.8\) Hz, 3H; NMe), 1.27 (s, 6H; CMe\(_2\)). \(^13\)C\(^{\text{1H}}\) NMR (126 MHz, CDCl\(_3\), 23 °C): \(\delta\) 169.9 (C=O), 149.0 (C\(_7\)), 138.5 (C\(_1\)), 137.7 (C\(_6\)), 132.0 (C\(_3\)), 128.3 (C\(_4\)), 127.8 (overlapping with residual benzene peak, extracted from \(^1\)H–\(^13\)C HMBC; C\(_9\)), 126.8 (C\(_2\)), 126.5 (C\(_8\)), 125.6 (C\(_3\)), 125.4 (C\(_{10}\)), 45.9 (ArCH\(_2\)), 39.2 (CMe\(_2\)), 28.3 (CMe\(_2\)), 26.1 (NMe).
IV. Catalytic Competence of Complex 8 for C–H Functionalization

In a N2-filled glovebox, arene (0.50–1.00 mmol, 1–2 equiv), 1,6-ene/alkyne (0.50–1.25 mmol, 1–2.5 equiv), [(depe)Co(n⁶-C₆H₆)][BArF₄] (8, 0.025 mmol, 5 mol%), and THF (0.5 mL) were added to a 25 mL thick-walled glass vessel with a magnetic stir bar. The vessel was sealed with a Teflon-coated stopper and brought out of the glovebox. If ethylene was added, the solution was frozen in liquid nitrogen and ethylene (2.50 mmol, 5 equiv) transferred to the vessel using a calibrated gas bulb. The reaction was placed in a pre-heated oil bath at 40–50 °C. After stirring for 24 h, the vessel was opened to air and quenched by adding CHCl₃ (3 mL). The reaction was filtered through a short plug of silica gel, eluting with 1:2 hexanes:EtOAc (10 mL). The solvent was removed in vacuo, CDCl₃ and internal standard (trimethyl-p-tolysilane, 0.5 mmol, 1 equiv) added, and the reaction analyzed by ¹H NMR spectroscopy.

Reaction between acetophenone and a 1,6-ene gave the ortho-functionalized arene product (60% yield by NMR), in accordance with the literature. Conversely, reaction of N-methylbenzamide, ethylene, and 6-dodecyne gave no yield of the functionalized arene. Analysis of the crude reaction mixture by ¹H NMR spectroscopy showed the formation of
hydrovinylation products resulting from the two-component reaction between ethylene and the alkyne, indicating that β-H elimination was a more significant competing side-reaction with precatalyst 8 compared with our previous report using [(dcype)Co(η^6-C_7H_8)][BArF_4]. We hypothesized that the selectivity of product formation was likely affected by the number of β-H substituents within the putative metallacycle intermediate. In accordance with this hypothesis, ortho-C–H functionalization reactivity was restored when employing ethyl 2-pentynoate as coupling partner (69% yield by NMR), which we had previously shown as forming a putative metallacyclopentadiene intermediate containing no β-H substituents.
V. Deuterium Labeling

In an N₂-filled glovebox, N-methylbenzamide ring-d₅ (6a-d₅, 42 mg, 0.30 mmol, 10 equiv; >99% D at ring positions) was added to a solution of complex 3 (40 mg, 0.03 mmol, 1 equiv) in THF (1 mL). After stirring for 10 minutes at room temperature, the reaction mixture was concentrated and subjected to silica gel column chromatography (20–50% ethyl acetate in hexanes) to isolate the product (7a-d₅) and recover excess benzamide substrate. With respect to the neophyl phenyl group, two predominant isotopologues of the product were identified (7a-d₅:7a-d₆ in 88:12 ratio; C–D positions >99% D unless highlighted and stated otherwise).

Deuterated N-Methyl-2-(2-methyl-2-phenylpropyl)benzamide (7a-d₅). Isolated as a colorless solid (6 mg). Note: ¹³C NMR data are for the major d₅-labeled isotopologue; one signal is obscured by the residual benzene peak. ¹H NMR (500 MHz, C₆D₆, 23 °C): δ 7.19 – 7.17 (m, 0.12H), 7.09 (d, J = 7.3 Hz, 2H), 7.00 (t, J = 7.3 Hz, 1H), 6.93 (s, 0.07H), 4.39 (br. s, 1H), 3.37 – 3.30 (m, 1.97H), 2.44 (d, J = 4.7 Hz, 3H), 1.29 – 1.24 (m, 5.84H). ¹³C{¹H} NMR (126 MHz, C₆D₆, 23 °C): δ 169.9, 148.9, 138.7, 137.6, 131.6 (1:1:1 t, J = 24.1 Hz), 126.7 – 125.9 (m), 125.4, 125.1 (1:1:1 t, J = 24.5 Hz), 45.8, 39.2, 28.2, 26.1. ³H NMR (61 MHz, CH₂Cl₂, 23 °C): δ 7.55 – 6.82 (5.81 D), 3.19 (0.03 D), 1.35 (0.16 D). HRMS (ESI+): 7a-d₅ m/z calcd for C₁₈H₁₅D₅N₁O₁ [M+H]^+ 273.2010, found 273.2003; 7a-d₆ m/z calcd for C₁₈H₁₅D₆N₁O₁ [M+H]^+ 274.2073, found 274.2071.

Recovered N-methylbenzamide (6a-d₅). Isolated as a colorless solid (34 mg). ¹H NMR (500 MHz, CD₂Cl₂, 23 °C): δ 7.81 (s, 0.12H), 6.70 (br. s, 1H), 2.98 (d, J = 4.9 Hz, 3H). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂, 23 °C): δ 167.9 (1C), 134.7 (0.12C), 134.6 (0.88C), 130.7 (1:1:1 t, J = 24.3
Hz; 1C), 128.3 – 127.5 (m, 2C), 126.7 (0.12C), 126.4 (1:1:1 t, J = 24.4 Hz; 1.88C), 26.6 (1C).

$^2$H NMR (61 MHz, CH$_2$Cl$_2$, 23 °C): δ 7.86 (1.88D), 7.57 (1D), 7.49 (2D).
VI. Scope of Directed C–H Functionalization

In an N$_2$-filled glovebox, arene/alkene substrate (0.20 mmol, 10 equiv) was added to a solution of complex 3 (27 mg, 0.02 mmol, 1 equiv) in fluorobenzene (0.7 mL) in a J. Young NMR tube, with cyclohexane-$d_{12}$ (50 μL) and 4-(trimethylsilyl)toluene (0.02 mmol) added for NMR locking and as an internal standard, respectively. Allowing the reaction to proceed at ambient temperature, progress was monitored by $^1$H NMR spectroscopy and the product yield determined by integration with respect to the internal standard. Pure products were isolated by silica gel chromatography or preparative TLC.

1-(2-(2-Methyl-2-phenylpropyl)phenyl)ethan-1-one (7b). NMR yield: >98%. Isolated as a colorless solid (5 mg). $^1$H NMR (500 MHz, CDCl$_3$, 23 °C): $\delta$ 7.46 – 7.42 (m, 1H), 7.27 – 7.15 (m, 7H), 6.88 – 6.85 (m, 1H), 3.32 (s, 2H), 2.24 (s, 3H), 1.29 (s, 6H). $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$, 23 °C): $\delta$ 203.6, 148.6, 140.6, 137.9, 133.2, 130.0, 128.1, 127.9, 126.7, 125.9, 125.8, 45.5, 39.6, 29.9, 28.5. HRMS (ESI+): m/z calcd for C$_{18}$H$_{20}$O$_1$ [M+H]$^+$ 253.1587, found 253.1593.

1-(2-Bromo-6-(2-methyl-2-phenylpropyl)phenyl)ethan-1-one (7c). NMR yield: 74%. Isolated as a colorless solid (5 mg). $^1$H NMR (500 MHz, CDCl$_3$, 23 °C): $\delta$ 7.35 (d, $J = 7.8$ Hz, 1H), 7.33 – 7.26 (m, 4H), 7.22 (tt, $J = 6.9, 1.4$ Hz, 1H), 6.91 (t, $J = 7.8$ Hz, 1H), 6.47 (d, $J = 7.8$ Hz, 1H), 2.86 (s, 2H), 2.39 (s, 3H), 1.31 (s, 6H). $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$, 23 °C): $\delta$ 205.1, 148.6, 143.9, 136.9, 130.6, 129.7, 129.1, 128.4, 126.5, 126.2, 117.0, 46.9, 39.3, 32.4, 28.9. HRMS (ESI+): m/z calcd for C$_{18}$H$_{19}$BrO$_1$ [M+H]$^+$ 331.0692, found 331.0688.
5-Chloro-N-methyl-2-(2-methyl-2-phenylpropyl)benzamide (7d). NMR yield: 96%. Isolated as a colorless solid (5 mg). \(^{1}H\) NMR (500 MHz, CDCl\(_3\), 23 °C): \(\delta\) 7.25 (t, \(J = 7.6\) Hz, 2H), 7.19 – 7.15 (m, 3H), 7.11 (d, \(J = 8.1\) Hz, 2H), 6.85 (d, \(J = 8.1\) Hz, 1H), 4.90 (q, \(J = 3.6\) Hz, 1H), 3.11 (s, 2H), 2.71 (d, \(J = 4.8\) Hz, 3H), 1.36 (s, 6H). \(^{13}C\)\(^{1}H\) NMR (126 MHz, CDCl\(_3\), 23 °C): \(\delta\) 169.8, 148.1, 139.6, 135.7, 133.5, 131.9, 128.9, 128.1, 126.9, 126.7, 125.8, 46.0, 39.5, 28.8, 27.0. HRMS (ESI+): m/z calcd for C\(_{18}\)H\(_{20}\)ClN\(_1\)O\(_1\) [M+H]\(^+\) 302.1306, found 302.1306.

1-(5-Methoxy-2-(2-methyl-2-phenylpropyl)phenyl)ethan-1-one (7f, major) & 1-(3-methoxy-2-(2-methyl-2-phenylpropyl)phenyl)ethan-1-one (7f, minor). NMR yield: >98% (70:30 mixture of regioisomers). Isolated as a colorless oil (5 mg). Major isomer: \(^{1}H\) NMR (500 MHz, CDCl\(_3\), 23 °C): \(\delta\) 7.27 – 7.13 (m, 5H), 6.94 (t, \(J = 1.4\) Hz, 1H), 6.76 (app. d, \(J = 1.5\) Hz,
Hexyl (Z)-2,5-dimethyl-5-phenylhex-2-enoate (7g). NMR yield: >98%. Isolated as a colorless oil (4 mg). $^1$H NMR (500 MHz, CDCl$_3$, 23 °C): $\delta$ 7.38 – 7.31 (m, 4H), 7.21 (tt, $J = 7.0$, 1.4 Hz, 1H), 5.66 (tq, $J = 7.1$, 1.4 Hz, 1H), 4.15 (t, $J = 6.6$ Hz, 2H), 2.88 (dq, $J = 7.1$, 1.3 Hz, 2H), 1.84 – 1.82 (m, 3H), 1.69 (quin., $J = 6.8$ Hz, 2H), 1.44 – 1.28 (m, 12H), 0.92 (t, $J = 6.8$ Hz, 3H). $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$, 23 °C): $\delta$ 168.4, 148.9, 139.7, 128.6, 128.3, 126.1, 125.8, 64.5, 43.4, 38.2, 31.6, 29.1, 28.8, 25.9, 22.7, 21.0, 14.2. HRMS (ESI+): m/z calcd for C$_{20}$H$_{30}$O$_2$ [M+H]$^+$ 303.2319, found 303.2315.

2-(2-(2-Methyl-2-phenylpropyl)phenyl)pyridine (7h). NMR yield: 92%. Isolated as a colorless solid (4 mg). $^1$H NMR (500 MHz, CDCl$_3$, 23 °C): $\delta$ 8.68 (d, $J = 4.6$ Hz, 1H), 7.69 (td, $J = 7.7$, 1.7 Hz, 1H), 7.30 – 7.22 (m, 3H), 7.21 – 7.16 (m, 4H), 7.14 (t, $J = 7.0$ Hz, 1H), 7.09 (d, $J = 7.6$ Hz, 2H), 6.89 (d, $J = 7.7$ Hz, 1H), 3.27 (s, 2H), 1.08 (s, 6H). $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$, 23 °C): $\delta$ 160.9, 149.1, 148.7, 141.5, 136.7, 136.3, 132.1, 130.0, 127.8, 127.3, 126.2, 125.8, 124.5, 119.5, 112.6, 55.2, 54.0, 36.6, 29.8, 28.3.
126.0, 125.4, 124.7, 121.4, 45.6, 39.5, 28.3. **HRMS** (ESI+): m/z calcd for C_{21}H_{21}N_{1} [M+H]^+ 288.1747, found 288.1748.

Figure S7. Time-course plot by $^{31}$P NMR spectroscopy (162 MHz, PhF/C_{6}D_{12}) for the reaction of complex 3 with 2-phenylpyridine.

8-(2-Methyl-2-phenylpropyl)quinoline (7i). NMR yield: >98%. Isolated as a colorless solid (4 mg). $^{1}$H NMR (500 MHz, CDCl$_3$, 23 °C): $\delta$ 8.86 (dd, $J = 4.1, 1.8$ Hz, 1H), 8.05 (dd, $J = 8.2, 1.8$ Hz, 1H), 7.58 (dd, $J = 8.1, 1.2$ Hz, 1H), 7.36 (d, $J = 8.3$ Hz, 2H), 7.32 – 7.20 (m, 4H), 7.16 (tt, $J = 7.2, 1.2$ Hz, 1H), 6.94 (dd, $J = 7.1, 1.2$ Hz, 1H), 3.67 (s, 2H), 1.31 (s, 6H). $^{13}$C($^{1}$H) NMR (126 MHz, CDCl$_3$, 23 °C): $\delta$ 149.9, 149.1, 147.9, 138.2, 136.3, 130.9, 128.3, 128.0, 126.5, 126.2, 125.7, 125.6, 120.6, 43.6, 40.0, 28.6. **HRMS** (ESI+): m/z calcd for C$_{19}$H$_{19}$N$_{1}$ [M+H]^+ 262.1590, found 262.1594.
VII. Thermolysis of Complex 3

In an N$_2$-filled glovebox, a solution of complex 3 (0.01 mmol, 1 equiv) in fluorobenzene (0.6 mL) was transferred to a J. Young NMR tube, with cyclohexane-$d_{12}$ (50 μL) and 4-(trimethylsilyl)toluene (ca. 1 mg) added for NMR locking and as an internal standard, respectively. After removal from the glovebox, the reaction was placed in a pre-heated oil bath at 80 °C. Progress was monitored by $^1$H NMR spectroscopy at time intervals and the consumption of starting material and yield of products determined by integration with respect to the internal standard. The protocol was repeated with 10 or 20 equivalents of pyridine added.

![Figure S8. $^1$H NMR spectra (400 MHz, PhF/C$_6$D$_{12}$, 23 °C) for the thermolysis of complex 3 at $t = 3$ h with 0 (bottom), 10 (middle), and 20 equivalents (top) of pyridine added. Integral assignments from right to left: internal standard, 10, 9.](image-url)
**Figure S9.** Plot of ln([3]) versus time (no added py): first-order decay of the cobalt complex.

\[
y = -0.01911x + 4.53245 \\
R^2 = 0.99509
\]

**Figure S10.** $^{31}\text{P}^{(1)}\text{H}$ NMR spectra (162 MHz, PhF/C$_6$D$_{12}$) of complex 3 with 20 equivalents of added pyridine at $T = 23$ °C (blue) and 70 °C (black).
The thermolysis of complex 3 was also conducted with 10 equivalents of pyridine-$d_5$ added. Note: %D incorporation in the organic products could not be accurately determined due to the low yield of labeled 9 and volatility of the benzocyclobutane.

Figure S11. $^1$H NMR spectra (400 MHz, PhF/C$_6$D$_{12}$, 23 °C) for the thermolysis of complex 3 at $t = 3$ h with 10 equivalents of pyridine-$d_5$ added. Integral assignments from right to left: internal standard, 10, 9.
VIII. Functionalization of Heteroarenes

In an N₂-filled glovebox, a solution of complex 3 (0.01 mmol, 1 equiv) and substituted pyridine (4-OMe, 4-CF₃, or 2-Me; 0.10 mmol, 10 equiv) in fluorobenzene (0.6 mL) was transferred to a J. Young NMR tube, with cyclohexane-d₁₂ (50 μL) and 4-(trimethylsilyl)toluene (ca. 1 mg) added for NMR locking and as an internal standard, respectively. After removal from the glovebox, the reaction was placed in a pre-heated oil bath at 80 °C. Progress was monitored by ¹H NMR spectroscopy and yield of products determined by integration with respect to the internal standard. Identities of the functionalized pyridines in the reaction mixtures were confirmed by spiking with authentic samples synthesized by Ni-catalyzed Kumada coupling.

Figure S12. ¹H NMR spectra (400 MHz, PhF/C₆D₁₂, 23 °C) for the thermolysis of complex 3 with 10 equiv 4-OMe-py (bottom, \( t = 3 \) h), 4-CF₃-py (middle, \( t = 3 \) h), and 2-Me-py (top, \( t = 1 \) h). Integral assignments from right to left: internal standard, 10, functionalized pyridines.
Ni-catalyzed Kumada coupling of bromopyridines and (neophyl)MgCl. In an N₂-filled glovebox, (neophyl)MgCl (3 mL, 1.50 mmol, 3 equiv; 0.5 M in Et₂O) was added to a suspension of 2-bromopyridine (R = H, 4-OMe, 4-CF₃, 2-Me; 0.50 mmol, 1 equiv) and (dpf)NiCl₂ (34 mg, 0.05 mmol, 10 mol%) in Et₂O (10 mL). The reaction was removed from the glovebox and placed in a heating block at 40 °C. After stirring overnight, the reaction was cooled, diluted with Et₂O (50 mL) and washed with brine (20 mL). The organic phase was separated, dried over MgSO₄, filtered, and the solvent evaporated. The crude residue was purified by silica gel chromatography.

2-(2-Methyl-2-phenylpropyl)pyridine (9). Isolated by silica gel chromatography (0–10% Et₂O in CH₂Cl₂) as a colorless oil (68 mg, 0.32 mmol, 64% yield). ¹H NMR (500 MHz, CDCl₃, 23 °C): δ 8.49 (d, J = 4.9 Hz, 1H), 7.37 (td, J = 7.7, 1.8 Hz, 1H), 7.34 – 7.27 (m, 4H), 7.19 (tt, J = 6.9, 1.5 Hz, 1H), 7.05 (dd, J = 7.4, 4.9 Hz, 1H), 6.55 (d, J = 7.8 Hz, 1H), 3.08 (s, 6H). ¹³C{¹H} NMR (126 MHz, CDCl₃, 23 °C): δ 159.5, 149.0, 148.7, 135.5, 128.1, 126.2, 125.9, 124.6, 121.2, 53.1, 39.1, 28.4. HRMS (ESI⁺): m/z calcd for C₁₅H₁₇N₁ [M+H]⁺ 212.1434, found 212.1433.

4-Methoxy-2-(2-methyl-2-phenylpropyl)pyridine (11a). Isolated by silica gel chromatography (0–50% ethyl acetate in hexanes) as a colorless oil (105 mg, 0.44 mmol, 87% yield). ¹H NMR (500 MHz, CDCl₃, 23 °C): δ 8.31 (d, J = 5.9 Hz, 1H), 7.37 – 7.30 (m, 4H), 7.22
2-(2-Methyl-2-phenylpropyl)-4-(trifluoromethyl)pyridine (11b). Isolated by silica gel chromatography (0–10% Et₂O in toluene) as a pale yellow oil (50 mg, 0.18 mmol, 36% yield).

\[ 1^H \text{NMR} \ (500 \text{ MHz, CDCl}_3, 23 \degree \text{C}): \delta 8.68 \ (d, J = 5.1 \text{ Hz}, 1H), 7.34 – 7.27 \ (m, 5H), 7.23 \ (tt, J = 7.0, 1.5 \text{ Hz}, 1H), 6.64 \ (s, 1H), 3.16 \ (s, 2H), 1.42 \ (s, 6H). \]

\[ 1^{13}C\{^1H\} \text{NMR} \ (126 \text{ MHz, CDCl}_3, 23 \degree \text{C}): \delta 161.0, 149.5, 147.8, 137.5 \ (q, J = 33.9 \text{ Hz}), 128.2, 126.1, 126.0, 122.8 \ (q, J = 273 \text{ Hz}), 120.0 \ (q, J = 3.8 \text{ Hz}), 116.6 \ (q, J = 3.7 \text{ Hz}), 53.1, 39.2, 28.2. \]

\[ 1^9F \text{NMR} \ (376 \text{ MHz, CDCl}_3, 23 \degree \text{C}): \delta –65.1. \]

HRMS (ESI+): m/z calcd for C₁₆H₁₉F₃N₁ [M+H]\(^+\) 280.1308, found 280.1314.

2-Methyl-6-(2-methyl-2-phenylpropyl)pyridine (11c). Isolated by silica gel chromatography (0–5% Et₂O in CH₂Cl₂) as a colorless oil (70 mg, 0.31 mmol, 62% yield).

\[ 1^H \text{NMR} \ (500 \text{ MHz, CDCl}_3, 23 \degree \text{C}): \delta 7.37 – 7.29 \ (m, 4H), 7.27 \ (t, J = 7.7 \text{ Hz}, 1H), 7.21 \ (tt, J = 7.0, 1.4 \text{ Hz}, 1H), 6.93 \ (d, J = 7.5 \text{ Hz}, 1H), 6.37 \ (d, J = 7.8 \text{ Hz}, 1H), 3.08 \ (s, 2H), 2.53 \ (s, 3H), 1.39 \ (s, 6H). \]

\[ 1^{13}C\{^1H\} \text{NMR} \ (126 \text{ MHz, CDCl}_3, 23 \degree \text{C}): \delta 158.7, 157.1, 149.1, 135.5, 128.0, 126.1, 125.7, 121.3, 120.5, 52.8, 38.9, 28.3, 24.6. \]

HRMS (ESI+): m/z calcd for C₁₆H₁₉N₁ [M+H]\(^+\) 226.1590, found 226.1593.
2-(2-Methyl-2-phenylpropyl)benzofuran (12). In an N$_2$-filled glovebox, a solution of complex 5 (28 mg, 0.02 mmol) in benzofuran (0.25 mL) and fluorobenzene (0.25 mL) was transferred to a J. Young NMR tube, with cyclohexane-d$_{12}$ (50 μL) added. The reaction was taken out of the glovebox and placed in a pre-heated oil bath at 80 °C for 48 h. Product yield was determined by integration with respect to the BArF$_4$ anion peaks. Product 12 was isolated (5 mg, colorless oil) by silica gel chromatography (10% ethyl acetate in hexanes). $^1$H NMR (500 MHz, CDCl$_3$, 23 °C): δ 7.44 (m, 4H), 7.32 (t, $J = 7.3$ Hz, 2H), 7.24 – 7.12 (m, 3H), 6.08 (s, 1H), 3.07 (s, 2H), 1.43 (s, 6H). $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$, 23 °C): δ 157.1, 154.6, 148.9, 129.0, 128.3, 126.0, 125.9, 123.2, 122.4, 120.4, 110.9, 104.4, 43.3, 38.7, 28.7. Spectral data are in accordance with the literature.$^9$
IX. Spectroscopic Data

Figure S13. $^1$H NMR spectrum (400 MHz, C$_6$D$_6$, 23 °C) of complex S1.
Figure S14. $^1$H NMR spectrum (400 MHz, C$_6$D$_6$, 23 °C) of complex S2.

Figure S15. $^{31}$P NMR spectrum (162 MHz, C$_6$D$_6$, 23 °C) of complex S2.
Figure S16. $^1$H NMR spectrum (400 MHz, C$_6$D$_6$, 23 °C) of complex 2.

Figure S17. $^{13}$C NMR spectrum (126 MHz, C$_6$D$_6$, 23 °C) of complex 2.
Figure S18. $^{31}\text{P}$ NMR spectrum (162 MHz, C$_6$D$_6$, 23 °C) of complex 2.
Figure S19. $^1$H NMR spectrum (400 MHz, THF-$_2$H$_8$, 23 °C) of complex 3.

Figure S20. $^{13}$C NMR spectrum (126 MHz, THF-$_2$H$_8$, 23 °C) of complex 3.
Figure S21. $^{31}$P NMR spectrum (162 MHz, THF-$d_8$, 23 °C) of complex 3.

Figure S22. $^{19}$F NMR spectrum (376 MHz, THF-$d_8$, 23 °C) of complex 3.
Figure S23. $^1$H NMR spectrum (400 MHz, THF-$d_8$, 23 °C) of complex 5.

Figure S24. $^{13}$C NMR spectrum (126 MHz, THF-$d_8$, 23 °C) of complex 5.
Figure S25. $^{31}$P NMR spectrum (162 MHz, THF-$d_8$, 23 °C) of complex 5.

Figure S26. $^{19}$F NMR spectrum (376 MHz, THF-$d_8$, 23 °C) of complex 5.
Figure S27. $^1$H NMR spectrum (400 MHz, THF-$d_8$, 23 °C) of complex 4.

Figure S28. $^{13}$C NMR spectrum (126 MHz, THF-$d_8$, 23 °C) of complex 4.
Figure S29. $^{31}$P NMR spectrum (162 MHz, THF-$d_8$, 23 °C) of complex 4.

Figure S30. $^{19}$F NMR spectrum (376 MHz, THF-$d_8$, 23 °C) of complex 4.
Figure S31. $^1$H NMR spectrum (500 MHz, THF-$d_8$, 23 °C) of complex 8.

Figure S32. $^{13}$C NMR spectrum (126 MHz, THF-$d_8$, 23 °C) of complex 8.
Figure S33. $^{31}$P NMR spectrum (162 MHz, THF-$d_8$, 23 °C) of complex 8.

Figure S34. $^{19}$F NMR spectrum (376 MHz, THF-$d_8$, 23 °C) of complex 8.
Figure S35. $^1$H NMR spectrum (400 MHz, CDCl$_3$, 23 °C) of 7a.

Figure S36. $^{13}$C NMR spectrum (126 MHz, CDCl$_3$, 23 °C) of 7a.
Figure S37. $^1$H NMR spectrum (500 MHz, C₆D₆, 23 °C) of 7a.

Figure S38. $^{13}$C NMR spectrum (126 MHz, C₆D₆, 23 °C) of 7a.
Figure S39. $^1$H NMR spectrum (500 MHz, C$_6$D$_6$, 23 °C) of deuterated 7a.

Figure S40. Quantitative $^{13}$C NMR spectrum (126 MHz, C$_6$D$_6$, 23 °C) of deuterated 7a.
Figure S41. $^2$H NMR spectrum (61 MHz, CH$_2$Cl$_2$, 23 °C) of deuterated 7a.
Figure S42. $^1$H NMR spectrum (500 MHz, CD$_2$Cl$_2$, 23 °C) of recovered 6a-d$_5$.

Figure S43. Quantitative $^{13}$C NMR spectrum (126 MHz, CD$_2$Cl$_2$, 23 °C) of recovered 6a-d$_5$. 
Figure S44. $^2$H NMR spectrum (61 MHz, CH$_2$Cl$_2$, 23 °C) of recovered 6a-$d_5$. 
Figure S45. $^1$H NMR spectrum (500 MHz, CDCl$_3$, 23 °C) of 7b.

Figure S46. $^{13}$C NMR spectrum (126 MHz, CDCl$_3$, 23 °C) of 7b.
**Figure S47.** $^1$H NMR spectrum (500 MHz, CDCl$_3$, 23 °C) of 7c.

**Figure S48.** $^{13}$C NMR spectrum (126 MHz, CDCl$_3$, 23 °C) of 7c.
Figure S49. $^1$H NMR spectrum (500 MHz, CDCl$_3$, 23 °C) of 7d.

Figure S50. $^{13}$C NMR spectrum (126 MHz, CDCl$_3$, 23 °C) of 7d.
Figure S51. $^1$H NMR spectrum (500 MHz, CDCl$_3$, 23 °C) of 7e.

Figure S52. $^{13}$C NMR spectrum (126 MHz, CDCl$_3$, 23 °C) of 7e.
Figure S53. $^1$H NMR spectrum (500 MHz, CDCl$_3$, 23 °C) of 7f.

Figure S54. $^{13}$C NMR spectrum (126 MHz, CDCl$_3$, 23 °C) of 7f.
**Figure S55.** $^1$H NMR spectrum (500 MHz, CDCl$_3$, 23 °C) of 7g.

**Figure S56.** $^{13}$C NMR spectrum (126 MHz, CDCl$_3$, 23 °C) of 7g.
Figure S57. $^1$H–$^1$H NOESY NMR spectrum (500 MHz, CDCl$_3$, 23 °C) of 7g.

Figure S58. Zoom-in of $^1$H–$^1$H NOESY NMR spectrum of 7g.
Figure S59. $^1$H NMR spectrum (500 MHz, CDCl$_3$, 23 °C) of 7h.

Figure S60. $^{13}$C NMR spectrum (126 MHz, CDCl$_3$, 23 °C) of 7h.
Figure S61. $^1$H NMR spectrum (500 MHz, CDCl$_3$, 23 °C) of 7i.

Figure S62. $^{13}$C NMR spectrum (126 MHz, CDCl$_3$, 23 °C) of 7i.
Figure S63. $^1$H NMR spectrum (500 MHz, CDCl$_3$, 23 °C) of 9.

Figure S64. $^{13}$C NMR spectrum (126 MHz, CDCl$_3$, 23 °C) of 9.
Figure S65. $^1$H NMR spectrum (500 MHz, CDCl$_3$, 23 °C) of 11a.

Figure S66. $^{13}$C NMR spectrum (126 MHz, CDCl$_3$, 23 °C) of 11a.
Figure S67. $^1$H NMR spectrum (500 MHz, CDCl$_3$, 23 °C) of 11b.

Figure S68. $^{13}$C NMR spectrum (126 MHz, CDCl$_3$, 23 °C) of 11b.
Figure S69. $^{19}$F NMR spectrum (376 MHz, CDCl$_3$, 23 °C) of 11b.
Figure S70. $^1$H NMR spectrum (500 MHz, CDCl$_3$, 23 °C) of 11c.

Figure S71. $^{13}$C NMR spectrum (126 MHz, CDCl$_3$, 23 °C) of 11c.
Figure S72. $^1$H NMR spectrum (500 MHz, CDCl$_3$, 23 °C) of 12.

Figure S73. $^{13}$C NMR spectrum (126 MHz, CDCl$_3$, 23 °C) of 12.
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