Supporting Information

Strategic Utilization of Multifunctional Carbene for Direct Synthesis of Carboxylic–Phosphinic Mixed Anhydride from CO₂

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[1] General

All experiments were conducted under a nitrogen atmosphere by using standard Schlenk or dry box techniques unless otherwise noted. $^1$H, $^{11}$B, $^{13}$C, $^{19}$F, and $^{31}$P NMR spectra were recorded on a Bruker AVANCE III 400, JEOL AL-400, and Bruker AVANCE III 600 spectrometers at 25 °C unless otherwise noted. The chemical shifts in the $^1$H NMR spectra were recorded relative to Me$_4$Si or residual protonated solvents (C$_6$D$_5$H ($\delta$ 7.16), CHCl$_3$ (7.26), or CHDCl$_2$ (5.32), CHD$_2$CN (1.94)). The chemical shifts in the $^{13}$C spectra were recorded relative to Me$_4$Si or deuterated solvents (C$_6$D$_6$ ($\delta$ 128.06), CDCl$_3$ (77.16), or CD$_2$Cl$_2$ (53.84)). The chemical shifts in the $^{11}$B NMR spectra were recorded relative to BF$_3$. The chemical shifts in the $^{31}$P NMR spectra were recorded relative to $^{85}$% H$_3$PO$_4$ as an external standard. The chemical shifts in the $^{19}$F NMR spectra were recorded relative to $\alpha,\alpha,\alpha$-trifluorotoluene. Assignment of the resonances in $^1$H and $^{13}$C NMR spectra was based on $^1$H-$^1$H COSY, HMQC and HMBC experiments.

Analytical gas chromatography (GC) was carried out on a Shimadzu GC-2014 gas chromatograph, which is equipped with a flame ionization detector. Medium-pressure column chromatography was carried out on a Biotage Flash Purification System Isolera, which is equipped with a 254 nm UV detector. High resolution mass spectrometry (HRMS) was performed at Instrumental Analysis Center, Faculty of Engineering, Osaka University. ESI-MS analyses were performed with a Bruker Daltonics micrOTOF mass spectrometer. X-ray crystal data were collected with a Rigaku R-AXIS RAPID and Rigaku XtaLAB mini imaging Plate diffractometer.

[2] Materials

Benzene-$d_6$ was distilled from sodium benzophenone ketyl prior to use. CD$_2$Cl$_2$ and CD$_3$CN were distilled over CaH$_2$, and stored on molecular sieves (4 Å). All commercially available reagents including super dehydrated solvents (toluene, hexane, THF and CH$_2$Cl$_2$) were employed as received. PoxIm having N-2,6-diisopropylphenyl group (1h) was prepared according to our previous report.$^{51}$ 1-(2,6-Diethylphenyl)-1H-imidazole, 1-(2,6-diisopropylphenyl)-4,5-dihydro-1H-imidazole, ZnAr$_2$ (Ar = Ph, 4-OMeC$_6$H$_4$) were prepared according to the reported procedures.$^{52-5}$

Metrical data for the solid state structures are available from Cambridge Crystallographic Data Centre: CCDC 1507997 (1a), 1507988 (1c), 1507989 (1d), 1507990 (1e), 1507991 (1f), 1507992 (2a), 1507993 (2b), 1507994 (2g), 1507995 (2g•B(C$_6$F$_5$)$_3$).
[3] Synthesis of Poxlm·HOTf (1·HOTf) and PoxIm (1)

- Synthesis of 1a·HOTf

The literature procedure\textsuperscript{S1} was followed with 1-(2,6-diethylphenyl)-1H-imidazole (4.14 g, 20.67 mmol) to give 1a·HOTf as a white solid (9.23 g, 18.08 mmol, 87%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 8.66 (brs, 2H, Im-H), 7.83 (brs, 1H, Im-H), 7.53 (t, \(J = 7.6\) Hz, 1H, Ar-H), 7.31 (d, \(J = 7.6\) Hz, 2H, Ar-H), 2.32–2.29 (m, 4H, CH\textsubscript{2}CH\textsubscript{3}), 1.45 (d, \(J_{\text{H,P}} = 16.8\) Hz, 18H, tBu-H), 1.14 (t, \(J = 7.6\) Hz, 6H, CH\textsubscript{2}CH\textsubscript{3}). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 140.5, 139.8, 131.9, 131.3, 127.4, 127.0, 124.7, 120.5 (q, \(J_{C,F} = 319.0\) Hz), 37.6 (d, \(J_{C,P} = 60.0\) Hz), 25.4, 23.9, 14.6. \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}): \(\delta\) −81.5 (s). \textsuperscript{31}P\{\textsuperscript{1}H\} NMR (162 MHz, CDCl\textsubscript{3}): \(\delta\) 76.6 (s). HRMS (FAB\textsuperscript{+}): \(m/z\) Calcd for C\textsubscript{21}H\textsubscript{34}N\textsubscript{2}OP: ([M·OTf]\textsuperscript{+}) 361.2409, found 361.2404.

- Synthesis of 1b·HOTf

The literature procedure\textsuperscript{S1} was followed with 1-isopropylimidazole (5.08 g, 46.11 mmol) to give 1b·HOTf as a white solid (13.96 g, 33.20 mmol, 72%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 9.42 (brs, 1H, Im-H), 7.90 (brs, 1H, Im-H), 7.73 (brs, 1H, Im-H), 5.17–5.14 (m, 1H, CH(CH\textsubscript{3})\textsubscript{2}), 1.65 (d, \(J = 6.4\) Hz, 6H, CH(CH\textsubscript{3})\textsubscript{2}), 1.30 (d, \(J_{\text{H,P}} = 16.4\) Hz, 18H, tBu-H). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 136.9, 125.0, 123.8, 120.8 (q, \(J_{C,F} = 318.0\) Hz), 54.4, 38.1 (d, \(J_{C,P} = 60.0\) Hz), 26.0, 23.2. \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}): \(\delta\) −81.5 (s). \textsuperscript{31}P\{\textsuperscript{1}H\} NMR (162 MHz, CDCl\textsubscript{3}): \(\delta\) 75.6 (s). HRMS (FAB\textsuperscript{+}): \(m/z\) Calcd for C\textsubscript{14}H\textsubscript{28}N\textsubscript{2}OP: ([M·OTf]\textsuperscript{+}) 271.1939, found 271.1932.
• Synthesis of 1c-HOTf

NaOTf (1.2 eq.)
(‘Bu)2PCl (1.2 eq.)
THF, rt, 48 h
→
H2O2 aq. (20.0 eq.)
CH2Cl2
0 °C to rt, 12 h
→
1c-HOTf
77%

The literature procedure$^1$ was followed with 1-phenylimidazole (5.00 g, 34.68 mmol) to give 1c-HOTf as a white solid (12.06 g, 26.54 mmol, 77%). $^1$H NMR (400 MHz, CDCl3): $\delta$ 9.36 (brs, 1H, Im-H), 8.27 (brs, 1H, Im-H), 8.19 (brs, 1H, Im-H), 7.71–7.62 (m, 5H, Ar-H), 1.45 (d, $^3J_{H,P}$ = 16.8 Hz, 18H, 'Bu-H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl3): $\delta$ 136.9, 133.9, 131.1, 130.7, 125.0, 124.7, 122.7, 120.7 (q, $^1J_{C,F}$ = 319.0 Hz), 38.1 (d, $^1J_{C,P}$ = 59.0 Hz), 25.9. $^{19}$F NMR (376 MHz, CDCl3): $\delta$ –81.5 (s). $^{31}$P{$^1$H} NMR (162 MHz, CDCl3): $\delta$ 77.7 (s). HRMS (FAB$^+$): m/z Calcd for C17H26N2OP: ([M–OTf]$^+$) 305.1783, found 305.1785.

• Synthesis of 1f-HOTf

NaOTf (1.2 eq.)
(‘Bu)2PCl (1.2 eq.)
THF, rt, 48 h
→
H2O2 aq. (20.0 eq.)
CH2Cl2
0 °C to rt, 12 h
→
1f-HOTf
95%

The literature procedure$^1$ was followed with 1-(2,6-diisopropylphenyl)-4,5-dihydro-$^1$H-imidazole (2.18 g, 9.46 mmol) to give 1f-HOTf as a white solid (4.88 g, 9.03 mmol, 95%). $^1$H NMR (400 MHz, CDCl3): $\delta$ 8.34 (brs, 1H, Im-H), 7.47 (t, $J$ = 7.9 Hz, 1H, Ar-H), 7.26 (d, $J$ = 7.9 Hz, 2H, Ar-H), 4.91–4.86 (m, 2H, Im-H), 4.72–4.66 (m, 2H, Im-H), 2.86–2.79 (m, 2H, CH(CH$_3$)$_2$), 1.42 (d, $^3J_{H,P}$ = 16.0 Hz, 18H, 'Bu-H), 1.32 (d, $J$ = 6.8 Hz, 6H, CH(4CH$_3$)$_2$), 1.18 (d, $J$ = 6.8 Hz, 6H, CH(4CH$_3$)$_2$). $^{13}$C{$^1$H} NMR (100 MHz, CDCl3): $\delta$ 162.5 (d, $^2J_{C,P}$ = 5.0 Hz), 145.8, 131.9, 129.3, 125.2, 120.9 (q, $^1J_{C,F}$ = 318.0 Hz), 56.9, 51.2 (d, $^2J_{C,P}$ = 3.0 Hz), 37.9 (d, $^1J_{C,P}$ = 64.0 Hz), 29.0, 26.3, 25.2, 23.5. $^{19}$F NMR (376 MHz, CDCl3): $\delta$ –81.5 (s). $^{31}$P{$^1$H} NMR (162 MHz, CDCl3): $\delta$ 70.5 (s). HRMS (FAB$^+$): m/z Calcd for C23H$_{40}$N$_2$OP: ([M–OTf]$^+$) 391.2878, found 391.2871.
**Synthesis of 1g·HOTf**

To a solution of imidazole (1.00 g, 14.69 mmol) and triethylamine (1.70 g, 16.16 mmol) in THF (10 mL) was added (t-Bu)_2PCl (2.92 g, 16.16 mmol). The reaction mixture was stirred at room temperature for 11 h. Then, NaOTf (5.56 g, 32.32 mmol) was added with THF (15 mL) followed by addition of (t-Bu)_2PCl (5.84 g, 32.32 mmol). The reaction mixture was stirred at room temperature for 45 h. After removal of all volatiles in vacuo, the resultant was dissolved into CH_2Cl_2 (20 mL) followed by addition of H_2O_2 aq. (35% aq., 19.40 g, 200.00 mmol) very slowly at 0 °C (Caution! Exothermic process). The reaction mixture was stirred vigorously for 19 h, and then neutralized with saturated NaHCO_3 aq. The organic layer was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resultant was washed with ether, giving 1g·HOTf as a white solid (2.58 g, 4.79 mmol, 33%). 

**1H NMR** (400 MHz, CDCl_3): δ 9.12 (brs, 1H, Im-H), 8.39 (brs, 2H, Im-H), 1.39 (d, J_H,P = 16.4 Hz, 36H, t-Bu-H).  

**13C{1H} NMR** (151 MHz, CDCl_3): δ 145.0, 126.6, 120.9 (q, J_C,F = 320.1 Hz), 38.3 (d, J_C,P = 58.9 Hz), 26.0.  

**19F NMR** (376 MHz, CDCl_3): δ −81.5 (s).  

**31P{1H} NMR** (162 MHz, CDCl_3): δ 77.2 (s).  

**HRMS** (FAB⁺): m/z Calcd for C_19H_39N_2O_2P_2: [M−OTf]⁺ 389.2487, found 389.2489.

**Synthesis of PoxIm 1a**

The literature procedure was followed with 1a·HOTf (1.58 g, 3.09 mmol) to give 1a as a white solid (0.94 g, 2.61 mmol, 84%). A single crystal was prepared by recrystallization from THF/hexane at −30 °C. 

**1H NMR** (400 MHz, C_6D_6): δ 7.81 (t, J = 1.6 Hz, 1H, Im-H), 7.14 (t, J = 7.5 Hz, 1H, Ar-H), 6.99 (d, J = 7.5 Hz, 2H, Ar-H), 6.33 (s,
$^1$H, Im-$H$, 2.36–2.27 (m, 4H, CH$_2$CH$_3$), 1.39 (d, $^3$J$_{H,P} = 14.8$ Hz, 18H, t-Bu-$H$), 1.03 (t, $J = 7.6$ Hz, 6H, CH$_2$CH$_3$). $^{13}$C{$^1$H} NMR (100 MHz, C$_6$D$_6$): $\delta$ 221.6 (d, $^2$J$_{C,P} = 26.0$ Hz, NCN), 141.6, 139.7, 129.3, 127.0, 121.1, 37.5 (d, $^1$J$_{C,P} = 69.0$ Hz), 26.6, 25.0, 15.5. $^{31}$P{$^1$H} NMR (162 MHz, C$_6$D$_6$): $\delta$ 61.4 (s). X-ray data for 1a: $M = 360.46$, colorless, monoclinic, $P2_1/c$ (#14), $a = 11.1582$ (5) Å, $b = 35.8205(18)$ Å, $c = 16.3494(9)$ Å, $\alpha = 90^\circ$, $\beta = 106.030(3)^\circ$, $\gamma = 90^\circ$, $V = 6280.6(6)$ Å$^3$, $Z = 12$, $D_{calcd} = 1.144$ g/cm$^3$, $T = -150$ °C, $R_1$ ($wR_2$) = 0.1736 (0.4625).

Figure S1. Molecular structures of 1a.

• Synthesis of PoxIm 1b

The literature procedure$^5$1 was followed with 1b-HOTf (6.47 g, 15.39 mmol) to give 1b as a white solid (3.67 g, 13.57 mmol, 88%). $^1$H NMR (400 MHz, C$_6$D$_6$): $\delta$ 7.74 (s, 1H, Im-$H$), 6.31 (s, 1H, Im-$H$), 4.37–4.30 (m, 1H, CH(CH$_3$)$_2$), 1.38 (d, $^3$J$_{H,P} = 14.8$ Hz, 18H, t-Bu-$H$), 1.13 (d, $^3$J$_{H,P} = 6.8$ Hz, 6H, CH(CH$_3$)$_2$). $^{13}$C{$^1$H} NMR (100 MHz, C$_6$D$_6$):
\[ \delta 218.1 \text{ (d, } J_{CP} = 25.0 \text{ Hz, NCN)}, \ 123.0, \ 115.3, \ 52.4, \ 37.4 \text{ (d, } J_{CP} = 70.0 \text{ Hz)}, \ 26.8, \ 23.9. \]

\[ ^{31}P\{^{1}H\} \text{ NMR (162 MHz, C}_{6}D_{6}): \delta 60.7 \ (s). \]

- **Synthesis of PoxIm 1c**

The literature procedure\(^{31}\) was followed with 1c·HOTf (3.10 g, 6.82 mmol) to give 1c as a white solid (2.03 g, 6.67 mmol, 98%). A single crystal suitable for the X-ray diffraction analysis was prepared by recrystallization from THF/hexane at \(-30^\circ C.\)

\[ ^{1}H \text{ NMR (400 MHz, C}_{6}D_{6}): \delta 7.79 \ (s, 1H, \text{Im-H}), \ 7.72 \ (d, J = 7.6 \text{ Hz, 2H, Ar-H}), \ 7.12 \ (t, J = 7.6 \text{ Hz, 2H, Ar-H}), \ 7.01 \ (t, J = 7.6 \text{ Hz, 1H, Ar-H}), \ 6.92 \ (s, 1H, \text{Im-H}), \ 1.35 \ (d, J_{HP} = 14.8 \text{ Hz, 18H, } ^{3} \text{Bu-H}). \]

\[ ^{13}C\{^{1}H\} \text{ NMR (100 MHz, C}_{6}D_{6}): \delta 221.0 \ (d, J_{CP} = 26.0 \text{ Hz, NCN}), \ 142.3, \ 129.3, \ 126.6, \ 124.0, \ 121.4, \ 116.8, \ 37.5 \ (d, J_{CP} = 69.0 \text{ Hz), 26.7}. \]

\[ ^{31}P\{^{1}H\} \text{ NMR (162 MHz, C}_{6}D_{6}): \delta 62.0 \ (s). \]

X-ray data for 1c: \( M = 304.36, \) colorless, triclinic, \( P1 \) (#1), \( a = 8.52761(17) \text{ Å, } b = 9.18592(19) \text{ Å, } c = 12.1630(3) \text{ Å, } \alpha = 67.8350(10)^\circ, \beta = 88.3290(10)^\circ, \gamma = 85.5640(10)^\circ, \ V = 879.72(3) \text{ Å}^3, \ Z = 2, \ Dealed = 1.149 \text{ g/cm}^3, \ T = -150 \text{ °C, } R_{I} (wR_{2}) = 0.0337 \text{ (0.0881).} \]

**Figure S2.** Molecular structures of 1c.
**Synthesis of PoxIm 1d**

To a solution of 1h (250.0 mg, 0.64 mmol) in THF (5 mL) was added CCl₄ (2.5 g, 16.06 mmol), and the reaction mixture was stirred at 40 °C for 23 h. Then, all volatiles were removed *in vacuo* to give a white solid including 1d (86%) and 1e (7%), which was calculated by the ¹H and ³¹P NMR. The resultant was dissolved into THF/hexane and cooled to −30 °C to afford 1d as a colorless crystal (110.5 mg, 0.26 mmol, 41%), which was suitable for the X-ray diffraction analysis. ¹H NMR (400 MHz, C₆D₆): δ 7.80 (s, 1H, Im-H), 7.26 (t, J = 7.7 Hz, 1H, Ar-H), 7.14 (d, J = 7.7 Hz, 2H, Ar-H), 2.67–2.61 (m, 2H, CH(CH₃)₂), 1.34 (d, ³J_H,P = 14.8 Hz, 18H, tBu-H), 1.17–1.14 (m, 12H, CH(CH₃)₂). ¹³C{¹H} NMR (151 MHz, C₆D₆): δ 224.0 (d, ²J_C,P = 24.2 Hz, NCN), 146.7, 134.9, 129.9, 123.9, 121.5, 119.2, 37.6 (d, ¹J_C,P = 68.0 Hz), 29.0, 26.6, 24.6, 22.9. ³¹P{¹H} NMR (162 MHz, C₆D₆): δ 62.0 (s). X-ray data for 1d: M = 422.96, colorless, triclinic, P-1 (#2), a = 8.440(5) Å, b = 10.401(5) Å, c = 14.132(8) Å, α = 98.396(18)°, β = 99.21(3)°, γ = 94.380(19)°, V = 1205.1(12) Å³, Z = 2, Dcalcd = 1.166 g/cm³, T = −100 °C, R₁ (wR₂) = 0.0653 (0.1685).

![Molecular structure of 1d](image-url)
**Synthesis of **Poxlm 1e

A solution of 1h (268.1 mg, 0.69 mmol) in CCl₄ (5 mL) was stirred at 40 °C for 68 h. Then all volatiles were removed in vacuo to give a white solid including 1d (9%) and 1e (87%), which was calculated by the ¹H and ³¹P NMR. The resultant was dissolved into THF/hexane and cooled to −30 °C to afford 1e as a colorless crystal (179.6 mg, 0.39 mmol, 57%), which was suitable for the X-ray diffraction analysis. ¹H NMR (400 MHz, C₆D₆): δ 7.23 (t, J = 7.8 Hz, 1H, Ar-H), 7.08 (d, J = 7.8 Hz, 2H, Ar-H), 2.60–2.54 (m, 2H, CH(CH₃)₂), 1.38 (d, ³J_H,P = 15.2 Hz, 18H, tBu-H), 1.13–1.08 (m, 12H, CH(CH₃)₂). ¹³C{¹H} NMR (151 MHz, C₆D₆): δ 223.4 (d, ²J_{C,P} = 25.7 Hz, NCN), 146.6, 134.8, 130.2, 124.1, 120.6, 119.2, 39.1(d, ¹J_{C,P} = 68.0 Hz), 28.9, 27.1, 24.7, 23.0. ³¹P{¹H} NMR (162 MHz, C₆D₆): δ 67.1 (s). X-ray data for 1e: M = 457.40, colorless, orthorhombic, P2₁2₁2₁ (#19), a = 10.818(5) Å, b = 13.170(6) Å, c = 17.361(8) Å, α = 90°, β = 90°, γ = 90°, V = 2473(2) Å³, Z = 4, D_{calcd} = 1.228 g/cm³, T = −100 °C, R₁ (wR₂) = 0.0591 (0.1323).

![Molecular structure of 1e](image-url)
• Synthesis of SPoxIm 1f

The literature procedure\textsuperscript{S1} was followed with 1f·HOTf (2.37 g, 4.38 mmol) to give 1f as a white solid (1.21 g, 3.10 mmol, 71%). A single crystal suitable for the X-ray diffraction analysis was prepared by recrystallization from THF/hexane at −30 °C. \textsuperscript{1}H NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}): \(\delta\) 7.22 (t, \(J\) = 7.6 Hz, 1H, Ar-\(H\)), 7.10 (d, \(J\) = 7.6 Hz, 2H, Ar-\(H\)), 3.79–3.74 (m, 2H, Im-\(H\)), 3.04–2.98 (m, 2H, Im-\(H\)), 2.97–2.88 (m, 2H, CH(CH\textsubscript{3})\textsubscript{2}), 1.42 (d, \(J_{H,P}\) = 14.0 Hz, 18H, tBu-\(H\)), 1.21 (d, \(J\) = 6.8 Hz, 6H, CH(CH\textsubscript{3})\textsubscript{2}), 1.16 (d, \(J\) = 6.8 Hz, 6H, CH(CH\textsubscript{3})\textsubscript{2}). \textsuperscript{13}C{\textsuperscript{1}H} NMR (100 MHz, C\textsubscript{6}D\textsubscript{6}): \(\delta\) 244.9 (d, \(J_{C,P}\) = 28.0 Hz, NCN), 146.6, 138.5, 124.1, 51.6 (d, \(J_{C,P}\) = 2.0 Hz), 49.8 (d, \(J_{C,P}\) = 3.0 Hz), 38.4 (d, \(J_{C,P}\) = 71.0 Hz), 28.8, 26.9, 25.2, 23.4 (Some peaks are obscured by a C\textsubscript{6}D\textsubscript{6} signal). \textsuperscript{31}P{\textsuperscript{1}H} NMR (162 MHz, C\textsubscript{6}D\textsubscript{6}): \(\delta\) 59.6 (s). X-ray data for 1f: \(M\) = 390.55, colorless, monoclinic, \(P2_1/c\) (#14), \(a\) = 11.684(9) Å, \(b\) = 12.083(8) Å, \(c\) = 17.744(13) Å, \(\alpha\) = 90°, \(\beta\) = 105.346(9)°, \(\gamma\) = 90°, \(V\) = 2416(3) Å\textsuperscript{3}, \(Z\) = 4, \textit{Dcalc} = 1.074 g/cm\textsuperscript{3}, \(T\) = 0 °C, \(R_1\) (w\(R_2\)) = 0.0711 (0.1619).

**Figure S5.** Molecular structure of 1f.
• Synthesis of PoxIm 1g

The literature procedure\textsuperscript{S1} was followed with 1g·HOTf (2.00 g, 3.71 mmol) to give 1g as a white solid (1.10 g, 2.83 mmol, 76%). \( ^1H \) NMR (600 MHz, C\textsubscript{6}D\textsubscript{6}): \( \delta \) 7.64 (s, 2H, Im-\( H \)), 1.28 (d, \( ^3J_{H,P} = 15.0 \) Hz, 36H, \( t-Bu-H \)). \( ^{13}C\{^1H\} \) NMR (151 MHz, C\textsubscript{6}D\textsubscript{6}): \( \delta \) 225.3 (t, \( ^2J_{C,P} = 25.7 \) Hz, NCN), 121.7 (t, \( ^2J_{C,P} = 4.5 \) Hz), 37.6 (d, \( ^1J_{C,P} = 69.5 \) Hz), 26.6. \( ^{31}P\{^1H\} \) NMR (243 MHz, C\textsubscript{6}D\textsubscript{6}): \( \delta \) 60.6 (s).

[4] Synthesis of carboxylic-phosphinic mixed anhydride (2)

• General Procedure

A solution of 1 in toluene (5 mL) was transferred into the autoclave reactor, and then, CO\textsubscript{2} (5 atm) was pressurized followed by stirring at room temperature for 5 minutes. All volatiles were removed \textit{in vacuo} to give 2.

• Synthesis of 2a from 1a

The general procedure was followed with 1a (0.91 g, 2.52 mmol) to give 2a as
a white solid (1.02 g, 2.52 mmol, >99%). A single crystal suitable for the X-ray diffraction analysis was prepared by recrystallization from THF/hexane at –30 °C. 1H NMR (400 MHz, C6D6): δ7.19 (s, 1H, Im- H), 7.13 (t, J = 7.7 Hz, 1H, Ar-H), 6.94 (d, J = 7.7 Hz, 2H, Ar-H), 6.38 (s, 1H, Im-H), 2.14–1.99 (m, 4H, CH2CH3), 1.32 (d, JH,P = 14.8 Hz, 18H, tBu-H), 0.89 (t, J = 7.4 Hz, 6H, CH2CH3). 13C{1H} NMR (100 MHz, C6D6): δ 153.0 (d, JCP = 10.0 Hz), 140.6, 137.8 (d, JCP = 4.0 Hz), 136.1, 131.1, 129.5, 127.2, 126.7, 37.4 (d, JCP = 78.0 Hz), 26.7, 24.2, 14.7. 31P{1H} NMR (162 MHz, C6D6): δ 69.2 (s). HRMS (Cl–): m/z Calcld for C22H34N2O3P: ([M+H]+) 405.2307, found 405.2306. X-ray data for 2a: M = 404.47, colorless, monoclinic, P21/c (No.14), a = 9.9793(4) Å, b = 18.2234(6) Å, c = 12.3183(5) Å, α = 90°, β = 92.782(2)°, γ = 90°, V = 2237.52(14) Å³, Z = 4, Dcalc = 1.201 g/cm³, T = –150 °C, R1 (wR2) = 0.1190. (0.3231).

Figure S6. Molecular structure of 2a.

* Synthesis of 2b from 1b

The general procedure was followed with 1b (3.67 g, 13.57 mmol) to give 2b as a white solid (4.21 g, 13.39 mmol, 99%). A single crystal suitable for the X-ray diffraction
analysis was prepared by recrystallization from THF/hexane at −30 °C. $^1$H NMR (400 MHz, C$_6$D$_6$): $\delta$ 7.11 (s, 1H, Im-H), 6.46 (s, 1H, Im-H), 5.22–5.16 (m, 1H, CHCH$_3$), 1.41 (d, $^3$J$_{H,P}$ = 15.2 Hz, 18H, tBu-H), 0.80 (d, $J$ = 6.8 Hz, 6H, CHCH$_3$). $^{13}$C{$^1$H} NMR (100 MHz, C$_6$D$_6$): $\delta$ 154.3 (d, $^2$J$_{C,P}$ = 11.0 Hz), 135.9 (d, $^3$J$_{C,P}$ = 3.0 Hz), 130.6, 121.6, 49.3, 37.4 (d, $^1$J$_{C,P}$ = 78.0 Hz), 26.7, 23.1. $^{31}$P{$^1$H} NMR (162 MHz, C$_6$D$_6$): $\delta$ 69.1 (s). HRMS (FAB$^+$): m/z Calcd for C$_{15}$H$_{28}$N$_2$O$_3$P: ([M+H]$^+$) 315.1838, found 315.1834. X-ray data for 2b: $M$ = 314.36, colorless, monoclinic, P2$_1$/c (#14), $a$ = 8.19170(15) Å, $b$ = 15.9309(3) Å, $c$ = 13.2930(3) Å, $\alpha$ = 90°, $\beta$ = 90.2572(7)°, $\gamma$ = 90°, $V$ = 1734.73(6) Å$^3$, $Z$ = 4, $D$calcd = 1.204 g/cm$^3$, $T$ = −150 °C, $R_1$ (wR$_2$) = 0.0325 (0.0905).

![Molecular structure of 2b.](image)

**Synthesis of 2c from 1c**

![Diagram of the synthesis of 2c from 1c.](image)

The general procedure was followed with 1c (629.6 mg, 2.07 mmol) to give 2c as a white solid (703.0 mg, 2.02 mmol, 98%). $^1$H NMR (400 MHz, C$_6$D$_6$): $\delta$ 7.10 (s, 1H, Im-H), 6.98–6.90 (m, 3H, Ar-H), 6.73 (d, $J$ = 6.8 Hz, 2H, Ar-H), 6.43 (s, 1H, Im-H), 1.36 (d, $^3$J$_{H,P}$ = 14.8 Hz, 18H, tBu-H). $^{13}$C{$^1$H} NMR (151 MHz, C$_6$D$_6$): $\delta$ 153.1 (d, $^2$J$_{C,P}$ = 10.6 Hz), 138.2, 136.9 (d, $^3$J$_{C,P}$ = 3.0 Hz), 130.6, 128.9, 128.7, 127.6, 126.3, 37.4 (d, $^1$J$_{C,P}$...
= 78.0 Hz), 26.7. \[^{31}\text{P}\{^{1}\text{H}\}\text{NMR}\] (162 MHz, C\(_6\)D\(_6\)): \(\delta 69.5\) (s). \[^{1}\text{H}\text{NMR}\] (400 MHz, C\(_6\)D\(_6\)): \(\delta 7.19\) (t, \(J = 7.7\) Hz, 1H, Ar-H), 7.13 (s, 1H, Im-H), 7.02 (d, \(J = 7.7\) Hz, 2H, Ar-H), 2.24–2.17 (m, 2H, CH(CH\(_3\)\(_2\))\(_2\)), 1.31 (d, \(^3J_{\text{H,P}} = 14.8\) Hz, 18H, tBu-H), 1.06 (d, \(J = 6.8\) Hz, 6H, CH(CH\(_3\))\(_2\)), 1.00 (d, \(J = 6.8\) Hz, 6H, CH(CH\(_3\))\(_2\)). \[^{13}\text{C}\{^{1}\text{H}\}\text{NMR}\] (100 MHz, C\(_6\)D\(_6\)): \(\delta 152.4\) (d, \(^2J_{\text{C,P}} = 11.0\) Hz), 145.8, 137.6 (d, \(^3J_{\text{C,P}} = 3.0\) Hz), 131.1, 130.7, 126.0, 124.5, 37.3 (d, \(^1J_{\text{C,P}} = 77.0\) Hz), 29.1, 26.6, 23.9, 23.7 (Some peaks are obscured by a C\(_6\)D\(_6\) signal). \[^{31}\text{P}\{^{1}\text{H}\}\text{NMR}\] (162 MHz, C\(_6\)D\(_6\)): \(\delta 69.8\) (s). \[^{1}\text{H}\text{NMR}\] (400 MHz, C\(_6\)D\(_6\)): \(\delta 7.69\) (t, \(J = 7.6\) Hz, 1H, Ar-H), 6.99 (d, \(J = 7.6\) Hz, 2H, Ar-H), 2.15–2.09 (m, 2H, CH(CH\(_3\))\(_2\)), 1.28 (d, \(^3J_{\text{H,P}} = 15.2\) Hz, 18H, tBu-H), 1.00 (d, \(J = 6.4\) Hz, 6H, CH(CH\(_3\))\(_2\)), 0.92 (d, \(J = 6.4\) Hz, 6H, CH(CH\(_3\))\(_2\)). \[^{13}\text{C}\{^{1}\text{H}\}\text{NMR}\] (100 MHz, C\(_6\)D\(_6\)): \(\delta 151.7\) (d, \(^2J_{\text{C,P}} = 10.0\) Hz), 145.6,
135.1 (d, $^3J_{C,P} = 4.0$ Hz), 131.1, 131.0, 128.7, 124.6, 122.5, 37.4 (d, $^1J_{C,P} = 77.0$ Hz), 29.1, 26.5, 23.9, 23.7. $^{31}$P{$^1$H} NMR (162 MHz, C$_6$D$_6$): $\delta$ 71.1 (s). HRMS (FAB$^+$): m/z Calcd for C$_{24}$H$_{36}$ClN$_2$O$_3$P: ([M+H]$^+$) 501.1841, found 501.1845.

**Synthesis of 2f from 1f**

A solution of 1f (159.3 mg, 0.41 mmol) in toluene (5.0 mL) was stirred under CO$_2$ (5 atm) at 80 °C for 1 h. All volatiles were removed in vacuo to give 2f as a white solid (176.9 mg, 0.41 mmol, >99%). $^1$H NMR (600 MHz, C$_6$D$_6$): $\delta$ 7.15 (t, $J = 7.8$ Hz, 1H, Ar-H), 7.03 (d, $J = 7.8$ Hz, 2H, Ar-H), 3.80–3.77 (m, 2H, Im-H), 3.33–3.29 (m, 2H, Im-H), 3.15–3.10 (m, 2H, CH(CH$_3$)$_2$), 1.27 (d, $J = 6.6$ Hz, 6H, CH(CH$_3$)$_2$), 1.26 (d, $^3J_{H,P} = 15.0$ Hz, 18H, tBu-H), 1.11 (d, $J = 6.6$ Hz, 6H, CH(CH$_3$)$_2$). $^{13}$C{$^1$H} NMR (151 MHz, C$_6$D$_6$): $\delta$ 156.0 (d, $^3J_{C,P} = 3.0$ Hz), 154.2 (d, $^2J_{C,P} = 12.1$ Hz), 147.5, 135.8, 124.8, 124.5, 54.9, 54.1, 37.4 (d, $^1J_{C,P} = 78.5$ Hz), 28.7, 26.6, 24.9, 24.2. $^{31}$P{$^1$H} NMR (243 MHz, C$_6$D$_6$): $\delta$ 69.3 (s). HRMS (FAB$^+$): m/z Calcd for C$_{24}$H$_{40}$N$_2$O$_3$P: ([M+H]$^+$) 435.2777, found 435.2766.

[5] Reaction of 1g with CO$_2$

A solution of 1g (302.2 mg, 0.78 mmol) in toluene (5.0 mL) was transferred into the autoclave reactor, and then, CO$_2$ (5 atm) was pressurized followed by stirring at
100 °C for 1 h. All volatiles were removed in vacuo, and the resultant was dissolved into CD$_3$CN (0.5 mL), confirming the quantitative formation of 2g by $^1$H, $^{13}$C, and $^{31}$P NMR. A mixture of 2g (58%) and 2g´ (42%) was given after changing the solvent form CD$_3$CN to C$_6$D$_6$. Again, the quantitative formation of 2g was confirmed after changing the solvent from C$_6$D$_6$ to CD$_3$CN. A single crystal of 2g was prepared by recrystallization from THF/hexane at −30 °C.

The formation of 2g´ was rationalized by the NMR analyses in C$_6$D$_6$, showing the resonances attributed to the imidazolium moiety, as well as to ESI-MS analysis, showing the peaks attributed to 2g´ of n = 2. These results are shown in Figures S8–11.

**Figure S8.** The $^1$H NMR spectra for the reaction of 1g with CO$_2$. 

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**Diagram:**

- **1H NMR**
  - In CD$_3$CN
  - Changing the solvent from CD$_3$CN to C$_6$D$_6$
  - Changing the solvent from C$_6$D$_6$ to CD$_3$CN again

### Chemical Structures

- **2g**
- **2g´ (n > 1)**
Figure S9. The $^{31}$P NMR spectra for the reaction of 1g with CO$_2$.

Figure S10. The $^{13}$C NMR spectra for the reaction of 1g with CO$_2$. 

$^{31}$P NMR

In CD$_3$CN

$\delta$ C$_1$ 130.7 (d, $^2$J$_{C,P} = 8.0$ Hz)

$\delta$ C$_1$ 131.6 (d, $^2$J$_{C,P} = 4.0$ Hz)

$\delta$ C$_1$ 131.0 (d, $^3$J$_{C,P} = 7.0$ Hz)

$\delta$ C$_1$ 119.2 (d, $^2$J$_{C,P} = 3.0$ Hz)

$\delta$ C$_1$ 146.3 (d, $^2$J$_{C,P} = 4.0$ Hz)

Changing the solvent from CD$_3$CN to C$_6$D$_6$

C$_6$D$_6$

CO$_2$

$^{13}$C NMR
**Figure S11.** ESI-MS spectra for 2g′ (POS).

**1H NMR of 2g** (400 MHz, CD$_3$CN): δ 7.35 (s, 1H, Im-H), 7.18 (s, 1H, Im-H), 1.34–1.25 (m, 36H, tBu-H). **13C{1H} NMR of 2g** (100 MHz, CD$_3$CN): δ 157.2 (d, $^2$J$_{C,P}$ = 12.0 Hz), 150.0, 131.3 (d, $^3$J$_{C,P}$ = 7.0 Hz), 120.7, 38.5 (d, $^1$J$_{C,P}$ = 66.0 Hz), 37.9 (d, $^1$J$_{C,P}$ = 77.0 Hz), 26.6, 26.3. **31P{1H} NMR of 2g** (162 MHz, CD$_3$CN): δ 71.9 (s), 66.1 (s).

**1H NMR of 2g** (400 MHz, C$_6$D$_6$): δ 7.03 (s, 1H, Im-H), 6.42 (s, 1H, Im-H), 1.43 (d, $^3$J$_{H,P}$ = 14.8 Hz, 18H, tBu-H), 0.91 (d, $^3$J$_{H,P}$ = 15.2 Hz, 18H, tBu-H). **13C{1H} NMR of 2g** (100 MHz, C$_6$D$_6$): δ 155.7 (d, $^2$J$_{C,P}$ = 12.0 Hz), 146.3 (d, $^2$J$_{C,P}$ = 4.0 Hz), 131.0 (d, $^3$J$_{C,P}$ = 7.0 Hz), 119.2 (d, $^2$J$_{C,P}$ = 3.0 Hz), 37.7 (d, $^1$J$_{C,P}$ = 66.5 Hz), 37.6 (d, $^1$J$_{C,P}$ = 77.8 Hz), 26.7, 25.9. **31P{1H} NMR of 2g** (162 MHz, C$_6$D$_6$): δ 69.6 (s), 63.0 (s).

**HRMS of 2g** (FAB$^+$): m/z Calcld for C$_{20}$H$_{39}$N$_2$O$_4$P$_2$: ([M+H]$^+$) 433.2385, found 433.2380. X-ray data for 2g: $M$ = 432.48, colorless, monoclinic, $P2_1/c$ (#14), $a = 8.03734(15)$ Å, $b = 27.4286(5)$ Å, $c = 11.1604(3)$ Å, $\alpha = 90^\circ$, $\beta = 105.5670(12)^\circ$, $\gamma = 90^\circ$, $V = 2370.09(8)$ Å$^3$, $Z = 4$, $D_{calc} = 1.212$ g/cm$^3$, $T = -150$ °C, $R_1$ ($wR_2$) = 0.0980 (0.3213).
Figure S12. Molecular structure of 2g.

The following data were identified as that of 2g′ from a mixture of 2g and 2g′.

$^1\text{H NMR}$ of 2g′ (400 MHz, C$_6$D$_6$): $\delta$ 8.22 (s, 1H, Im-H), 7.09 (s, 1H, Im-H), 1.33 (d, $^3J_{H,P} = 14.8$ Hz, 18H, 'Bu-H), 1.19 (d, $^3J_{H,P} = 16.4$ Hz, 18H, 'Bu-H). $^{13}\text{C}[^1\text{H}]$ NMR of 2g′ (100 MHz, C$_6$D$_6$): $\delta$ 154.9 (d, $^2J_{C,P} = 11.0$ Hz), 139.5 (t, $^2J_{C,P} = 4.0$ Hz), 131.6 (d, $^3J_{C,P} = 4.0$ Hz), 130.7 (d, $^2J_{C,P} = 8.0$ Hz), 40.3 (d, $^1J_{C,P} = 62.0$ Hz), 37.4 (d, $^1J_{C,P} = 77.0$ Hz), 27.1, 26.5. $^{31}\text{P}[^1\text{H}]$ NMR of 2g′ (162 MHz, C$_6$D$_6$): $\delta$ 75.4 (s), 70.4 (s). ESI-MS of 2g′ (POS): $m/z$ Calcd for C$_{40}$H$_{77}$N$_4$NaO$_8$P$_4$: ([M+Na]+) 887.4522, found 887.4206, $m/z$ Calcd for C$_{40}$H$_{77}$N$_4$O$_8$P$_4$: ([M+H]+) 865.4703, found 865.4357.

To a mixture of 2g and 2g′ (17.3 mg, 0.04 mmol) in C$_6$D$_6$ (0.5 mL) was added B(C$_6$F$_5$)$_3$ (20.5 mg, 0.04 mmol) at room temperature. The quantitative formation of 2g·B(C$_6$F$_5$)$_3$ was confirmed within 5 minutes by the $^1\text{H}$, $^{11}\text{B}$, and $^{31}\text{P}$ NMR. A single
crystal suitable for the X-ray diffraction analysis was prepared by recrystallization from C₆H₆ at room temperature. **¹H NMR** (400 MHz, C₆D₆): δ 7.14 (s, 1H, Im-H), 6.52 (s, 1H, Im-H), 1.20 (d, ³J₃₋₄ = 15.6 Hz, 18H, 'Bu-H), 0.85 (d, ³J₃₋₄ = 16.0 Hz, 18H, 'Bu-H). **¹¹B NMR** (128 MHz, C₆D₆): δ −5.7 (s). **¹³C{¹H} NMR** (100 MHz, C₆D₆): δ 151.8 (d, ²J₃₋₄ = 12.0 Hz), 150.7 (brs), 148.3 (brs), 144.8, 142.3 (brs), 139.1 (brs), 136.7 (brs), 129.1, 118.3, 38.4 (d, ¹J₃₋₄ = 61.0 Hz), 38.2 (d, ¹J₃₋₄ = 71.0 Hz), 26.7, 25.9. One fluorine resonances of C₆F₅ was not observed. **¹⁹F NMR** (376 MHz, C₆D₆): δ −130.3, −135.1, −158.7, −160.7, −164.9, −166.7. **³¹P{¹H} NMR** (162 MHz, C₆D₆): δ 79.8 (s), 73.2 (s). X-ray data for 2g·B(C₆F₅)₃·2C₆H₆: M = 1100.67, colorless, monoclinic, P2₁/c (#14), a = 14.7536(3) Å, b = 20.6115(4) Å, c = 18.7067(4) Å, α = 90°, β = 114.1354(11)°, γ = 90°, V = 5191.30(18) Å³, Z = 4, Dcalc = 1.408 g/cm³, T = −150 °C, R₁ (wR₂) = 0.0968 (0.2266).

**Figure S13.** Molecular structure of 2g·B(C₆F₅)₃·2C₆H₆.
In a pressure-tight NMR tube, a solution of 1b (21.6 mg, 0.08 mmol) in CD$_2$Cl$_2$ (0.5 mL) was cooled to −196 °C, and CO$_2$ (1 atm) was pressurized carefully (Note: solidification of CO$_2$ must be avoided). This NMR tube was transferred into the NMR apparatus at −90 °C. The formation of A (84%) and 2b (16%) were confirmed by the $^1$H, $^{13}$C, and $^{31}$P NMR at −90 °C. These results are shown in Figures S14–16. Then, the reaction mixture was allowed to warm to room temperature to confirm the quantitative production of 2b.

Figure S14. The $^1$H NMR spectra for the reaction of 1b with CO$_2$ at −90 °C.
Figure S15. The $^{13}$C NMR spectra for the reaction of 1b with CO$_2$ at $-90$ °C.

Figure S16. The $^{31}$P NMR spectra for the reaction of 1b with CO$_2$ at $-90$ °C.
H NMR (600 MHz, CD$_2$Cl$_2$): $\delta$ 7.69 (s, 1H, Im-H), 7.26 (d, $J = 1.8$ Hz, 1H, Im-H), 4.95–4.89 (m, 1H, CH$_2$), 1.44 (d, $J = 8.0$ Hz, 6H, CH$_3$), 1.33 (d, $^1J_{HP} = 16.8$ Hz, 18H, t-Bu-H). $^{13}$C$^{[1]}$H NMR (151 MHz, CD$_2$Cl$_2$): $\delta$ 156.3, 146.1 (d, $^2J_{C,P} = 3.0$ Hz), 122.8 (d, $^2J_{C,P} = 3.0$ Hz), 114.7 (d, $^3J_{C,P} = 4.5$ Hz), 51.9, 38.6 (d, $^1J_{C,P} = 58.9$ Hz), 25.3, 22.1.

$^{31}$P$^{[1]}$H NMR (243 MHz, CD$_2$Cl$_2$): $\delta$ 80.9 (s).

[7] Synthetic applications with 2b

- Synthesis of Imidazolium salt (3b)

To a solution of 2b (3.40 g, 10.82 mmol) in CH$_2$Cl$_2$ (15 mL) was added MeOTf (1.78 g, 10.85 mmol), and the reaction mixture was stirred for 2 h at room temperature. All volatiles were removed in vacuo, and the resultant was washed with hexane, and dried in vacuo to give 3b as a white solid (5.17 g, 10.81 mmol, 99%).

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ 7.87 (s, 1H, Im-H), 7.84 (s, 1H, Im-H), 5.45–5.38 (m, 1H, CH$_3$), 4.21 (s, 3H, CH$_3$), 1.61 (d, $J = 6.4$ Hz, 6H, CH$_3$), 1.40 (d, $^3J_{HP} = 16.0$ Hz, 18H, t-Bu-H). $^{13}$C$^{[1]}$H NMR (100 MHz, CD$_2$Cl$_2$): $\delta$ 149.9 (d, $^2J_{C,P} = 10.0$ Hz), 131.7, 128.7, 122.5, 54.7, 40.1, 38.2 (d, $^2J_{C,P} = 70.0$ Hz), 26.6, 23.2. $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$): $\delta$ –82.1 (s), $^{31}$P$^{[1]}$H NMR (162 MHz, CD$_2$Cl$_2$): $\delta$ 83.2 (s). HRMS (FAB$^+$): m/z Calcd for C$_{16}$H$_{30}$N$_2$O$_3$P: ([M–OTf]$^+$) 329.1994, found 329.1997.

- In situ observation of 4b by NMR

To a solution of 3b (19.1 mg, 0.04 mmol) in CD$_2$Cl$_2$ (0.5 mL) was added bis(4-
methoxyphenyl)zinc (11.2 mg, 0.04 mmol), and heated at 40 °C for 2 h. The quantitative formation of 4b and the zinc phosphinate salt was confirmed by the $^1$H and $^{31}$P NMR (Figure S17,18).

Figure S17. The $^1$H NMR spectra for the reaction of 3b with ZnAr$_2$. 
One-pot synthesis of methyl 4-methoxybenzoate (5) from 3b

To a solution of 3b (288.7 mg, 0.60 mmol) in CH$_2$Cl$_2$ (3.0 mL) was added bis(4-methoxyphenyl)zinc (167.8 mg, 0.60 mmol), and the reaction mixture was stirred at 40 °C for 2 h. To the reaction mixture was added MeOH (485 µL, 11.99 mmol) followed by stirring for 1 h at room temperature. The reaction mixture was concentrated in vacuo, and purified by the silica gel column chromatography (Et$_2$O). All volatiles were removed in vacuo, and the resultant was washed with hexane, and dried in vacuo to give 5 as a white solid (93.7 mg, 0.56 mmol, 93%). The compound was identified in comparison with the reported data.$^{56}$

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.99 (d, $J = 9.2$ Hz, 2H), 6.92 (d, $J = 9.2$ Hz, 2H), 3.89 (s, 3H), 3.86 (s, 3H).
One-pot synthesis of \(N\)-cyclohexyl-4-methoxybenzamide (6) from 3b

To a solution of 3b (239.1 mg, 0.50 mmol) in CH\(_2\)Cl\(_2\) (3.0 mL) was added bis(4-methoxyphenyl)zinc (139.8 mg, 0.50 mmol), and the reaction mixture was stirred at 40 °C for 2 h. To the reaction mixture was added cyclohexylamine (285 µL, 2.50 mmol), followed by stirring for 8 h at room temperature. The reaction mixture was concentrated in vacuo, and added Et\(_2\)O (10 mL) and 1 M HCl (2 mL), followed by stirring for 15 minutes at room temperature. The reaction mixture was poured into water (8 mL) and extracted with Et\(_2\)O. The combined organic layer was washed with saturated NaHCO\(_3\) aq. and brine, then dried over anhydrous Na\(_2\)SO\(_4\). All volatiles were removed in vacuo, and the resultant was washed with hexane, and dried in vacuo to give 6 as a white solid (107.3 mg, 0.46 mmol, 92%). The compound was identified in comparison with the reported data.\(^7\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.71 \ (d, J = 8.8 \ Hz, 2H), 6.91 \ (d, J = 8.8 \ Hz, 2H), 5.86 \ (d, J = 5.2 \ Hz, 1H), 3.97-3.94 \ (m, 1H), 3.84 \ (s, 3H), 2.04-2.00 \ (m, 2H), 1.77-1.73 \ (m, 2H), 1.67-1.62 \ (m, 2H), 1.48-1.38 \ (m, 2H), 1.27-1.19 \ (m, 3H).

One-pot synthesis of 2-nitro-1-phenylethan-1-one (7) from 3b

To a solution of 3b (100.0 mg, 0.209 mmol) in CH\(_2\)Cl\(_2\) (4.5 mL) was added diphenylzinc (45.8 mg, 0.21 mmol), and the reaction mixture was stirred at 40 °C for 2 h. The reaction mixture was cooled to room temperature and diluted with DMF (1 mL). To the reaction mixture was added a solution of (nitromethyl)sodium (0.25 mmol), which was prepared from reaction of CH\(_3\)NO\(_2\) (9.0 mg, 0.31 mmol) and NaH (16.0 mg, 0.25 mmol, 60% in paraffin oil) in DMF (2 mL) for 1 h at room temperature. After stirring for
2 h at room temperature, the reaction mixture was poured into ice-cold water (10 mL), acidified with 1 M HCl and extracted with EtOAc. The combined organic layer was washed with water and brine, then dried over anhydrous Na₂SO₄ and concentrated in vacuo. The product was purified by the silica gel column chromatography (EtOAc/hexane) to give 7 as a off white solid (31.1 mg, 0.188 mmol, 90%). The compound was identified in comparison with the reported data.¹⁻¹¹H NMR (400 MHz, CDCl₃) δ7.89–7.87 (m, 2H), 7.71–7.67 (m, 1H), 7.56–7.53 (m, 2H), 5.89 (s, 2H).

• One-pot synthesis of diethyl 2-benzoylmalonate (8) from 3b

![Diagram of the reaction](image)

To a solution of 3b (100.0 mg, 0.209 mmol) in CH₂Cl₂ (4.5 mL) was added diphenylzinc (45.8 mg, 0.21 mmol), and the reaction mixture was stirred at 40 °C for 2 h. The reaction mixture was cooled to room temperature and diluted with DMF (1 mL). To the reaction mixture was added a solution of sodium(1,3-diethoxy-1,3-dioxopropan-2-ide) (45.6 mg, 0.25 mmol) in DMF (2 mL). After stirring at room temperature for 1 h, the reaction mixture was poured into water (10 mL), acidified with 1 M HCl and extracted with EtOAc. The combined organic layer was washed with water and brine, then dried over anhydrous Na₂SO₄ and concentrated in vacuo. The product was purified by the silica gel column chromatography (EtOAc/hexane) to give 8 as a colorless oil (51.4 mg, 0.194 mmol, 93%). The compound was identified in comparison with the reported data.¹⁻¹¹H NMR (400 MHz, CDCl₃) δ13.39 (s, 1H), 7.90–7.45 (m, 5H), 5.28 (s, 1H), 4.27–3.97 (m, 4H), 1.16 (t, J = 6.8 Hz, 6H).

• One-pot synthesis of diaryl ketone (9) from 3b

![Diagram of the reaction](image)

[Ar = p-OMeC₆H₄]
To a solution of 3b (239.1 mg, 0.50 mmol) in ClCH₂CH₂Cl (3.0 mL) was added diphenylzinc (109.8 mg, 0.50 mmol), and the reaction mixture was stirred at 40 °C for 2 h. To the reaction mixture was added bis(4-methoxyphenyl)zinc (279.6 mg, 1.00 mmol), followed by stirring at 100 °C for 24 h. The reaction mixture was concentrated in vacuo, and added Et₂O (10 mL) and 1 M HCl (2 mL), followed by stirring for 15 minutes at room temperature. The reaction mixture was poured into water (8 mL) and extracted with Et₂O. The combined organic layer was washed with saturated NaHCO₃ aq. and brine, then dried over anhydrous Na₂SO₄. The product was purified by the silica gel column chromatography (EtOAc/hexane) to give 9 as a white solid (38.8 mg, 0.18 mmol, 36%). The compound was identified in comparison with the reported data.¹¹ ¹H NMR (400 MHz, CDCl₃) δ 7.83−7.82 (m, 2H), 7.77−7.74 (m, 2H), 7.57−7.55 (m, 1H), 7.49−7.45 (m, 2H), 6.98−6.95 (m, 2H), 3.89 (s, 3H).

- Reaction of 3b with organometallic reagents

| Entry | Reagent         | x (eq.) | Temp.       | Yields | 10ᵃ | 11ᵇ | 12ᵇ |
|-------|----------------|---------|-------------|--------|-----|-----|-----|
| 1     | PhMgBr         | 1.0     | rt          | n.d.   | 24% | 0%  |
| 2     | PhMgBr         | 2.0     | rt          | -      | 22% | 19% |
| 3     | PhLi           | 1.0     | −78 °C to rt| n.d.   | 14% | 0%  |
| 4     | PhLi           | 2.0     | −78 °C to rt| -      | 31% | 2%  |
| 5ᵇ    | ZnPh₂          | 1.0     | 40 °C       | quant  | n.d. | n.d. |

ᵃDetermined by NMR. ᵇDetermined by GC using n-pentadecane as an internal standard. ᶜThe reaction was performed in CD₂Cl₂.

**Entry 1:** To a solution of 3b (19.1 mg, 0.04 mmol) and n-pentadecane (10.4 mg, 0.05 mmol; internal standard) in THF (1.5 mL) was added phenyl magnesium bromide (1.0 M in THF, 40 µL, 0.04 mmol). The reaction mixture was stirred for 2 h at room
temperature. Then, all volatiles were removed in vacuo, and the resultant was dissolved into CD$_2$Cl$_2$ (0.5 mL), confirming that 13 was not formed by NMR analyses. The reaction mixture was poured into 1 M HCl and extracted with EtOAc. The yields of 10 and 11 were determined by GC.

**Entry 2**: To a solution of 3b (100.0 mg, 0.21 mmol) and n-pentadecane (47.7 mg, 0.24 mmol; internal standard) in THF (3.0 mL) was added phenyl magnesium bromide (1.0 M in THF, 418 µL, 0.42 mmol). The reaction mixture was stirred for 2 h at room temperature, and then, poured into 1 M HCl and extracted with EtOAc. The yields of 10 and 11 were determined by GC.

**Entry 3**: To a solution of 3b (191.4 mg, 0.40 mmol) and n-pentadecane (70.8 mg, 0.33 mmol; internal standard) in THF (6.0 mL) was added phenyl lithium (1.6 M in butyl ether, 250 µL, 0.40 mmol) at −78 °C. The reaction mixture was stirred for 2 h at room temperature. Then all volatiles were removed in vacuo, and the resultant was dissolved into CD$_2$Cl$_2$ (0.5 mL), confirming that 12 was not formed by NMR analyses. The reaction mixture was poured into 1 M HCl and extracted with EtOAc. The yields of 10 and 11 were determined by GC.

**Entry 4**: To a solution of 3b (100.0 mg, 0.21 mmol) and n-pentadecane (46.2 mg, 0.24 mmol; internal standard) in THF (3.0 mL) was added phenyl lithium (1.6 M in butyl ether, 262 µL, 0.42 mmol) at −78 °C. The reaction mixture was stirred for 2 h at room temperature, and then, poured into 1 M HCl and extracted with EtOAc. The yields of 10 and 11 were determined by GC.

**Entry 5**: To a solution of 3b (19.1 mg, 0.04 mmol) in CD$_2$Cl$_2$ (0.5 mL) was added diphenylzinc (8.8 mg, 0.04 mmol), the reaction mixture was heated at 40 °C for 2 h. The quantitative formation of 12 and the zinc phosphinate salt was confirmed by the $^1$H and $^{31}$P NMR. The reaction mixture was poured into 1 M HCl and extracted with EtOAc. The formation of 10 and 11 was not confirmed by GC.
Additional synthetic applications with 2b giving 14 and 15

To a solution of 2b (157.5 mg, 0.50 mmol) in CH₂Cl₂ (2.0 mL) was added benzimidazole (59.1 mg, 0.50 mmol), and the reaction mixture was stirred for 2 h at room temperature. The reaction mixture was washed with saturated NaHCO₃ aq. The organic layer was extracted with CH₂Cl₂, dried over anhydrous Na₂SO₄ and concentrated _in vacuo_ to give 13 as a yellow oil (118.2 mg, 0.46 mmol, 92%). ¹H NMR (400 MHz, CDCl₃): δ 9.62 (s, 1H, Im-H), 8.36–8.34 (m, 1H, Ar-H), 7.84–7.81 (m, 1H, Ar-H), 7.43–7.32 (m, 3H), 7.32 (s, 1H, Im-H), 5.58–5.52 (m, 1H, CH(CH₃)₂), 1.57 (d, J = 6.8 Hz, 6H, CH(CH₃)₂). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 156.7, 145.3, 143.8, 137.0, 132.6, 130.3, 125.6, 125.2, 122.1, 120.6, 116.0, 49.9, 24.0. HRMS (FAB⁺): m/z Calcd for C₁₄H₁₅N₄O: ([M+H]⁺) 255.1246, found 255.1242.

A solution of 2b (157.7 mg, 0.50 mmol) in CH₃OH (5.0 mL) was stirred for 18 h at room temperature. The reaction mixture was washed with saturated NaHCO₃ aq. The organic layer was extracted with CH₂Cl₂, dried over anhydrous Na₂SO₄ and concentrated _in vacuo_ to give 14 as a yellow oil (46.4 mg, 0.28 mmol, 56%). ¹H NMR (400 MHz, CDCl₃): δ 7.24 (s, 1H, Im-H), 7.17 (s, 1H, Im-H), 5.57–5.50 (m, 1H, CH(CH₃)₂), 3.94 (s, 3H, CH₃), 1.47 (d, J = 6.8 Hz, 6H, CH(CH₃)₂). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 159.7, 135.7, 130.0, 120.7, 52.3, 49.2, 23.8. HRMS (FAB⁺): m/z Calcd for C₈H₁₃N₂O₂: ([M+H]⁺) 169.0977, found 169.0974.
[9] A one-pot synthesis of 8 from CO$_2$

\[
\begin{align*}
\text{CO}_2 \quad \text{(ballon)} & \quad 1) 1b, 5 \text{ min} \\
& \quad 2) \text{MeOTf, 2 h} \\
& \quad \text{CICH}_2\text{CH}_2\text{Cl} \quad \text{rt} \\
& \quad 3) \text{ZnPh}_2, 40 ^\circ\text{C}, 2 \text{ h} \\
& \quad 4) \text{NaCH(CO}_2\text{Et})_2 \quad (1.2 \text{ equiv in DMF}) \\
& \quad \text{rt, 2 h} \\
\end{align*}
\]
\[\Rightarrow 8 \quad 75\%\]

A reaction vessel with a J. Young screw-cap was filled with a solution of 1b (108.1 mg, 0.40 mmol) in CICH$_2$CH$_2$Cl (3.0 mL) and CO$_2$ (from balloon) at room temperature, giving yellow solution (Figure S19). After stirring for 5 min, CO$_2$ balloon was removed, and the system was purged by N$_2$. Then, to a reaction mixture was added MeOTf (65.6 mg, 0.40 mmol) followed by stirring for 2 h at room temperature. Then, diphenylzinc (87.9 mg, 0.40 mmol) was added, and the reaction mixture was stirred at 40 $^\circ$C for 2 h. After cooling to room temperature, NaCH(COEt)$_2$ (87.4 mg, 0.48 mmol) in DMF (3.0 mL) was added. After stirring at room temperature for 2 h, the reaction mixture was poured into water (10 mL), acidified with 1 M HCl and extracted with EtOAc. The combined organic layer was washed with water and brine, then dried over anhydrous Na$_2$SO$_4$ and concentrated in vacuo. The product was purified by the silica gel column chromatography (EtOAc/hexane) to give 8 as colorless oil (78.8 mg, 0.30 mmol, 75%).
Theoretical study

All calculations were performed with the Gaussian 09, Revision A.02\textsuperscript{11} of programs with the hybrid B3LYP\textsuperscript{12} function. The 6-31G+(d) basis set was used. Geometry optimizations were performed without any symmetry constraint followed by analytical frequency calculations to confirm that a minimum or a transition state had been reached. The gas-phase Gibbs energies were calculated at 298.15 K and 1 atm from the harmonic approximation for frequencies. Potential energies were also obtained by performing single point calculations using the above optimized geometries with the same basis sets. Solvent effects (toluene; $\varepsilon = 2.379$) were introduced through the single-point calculation at the optimized gas-phase geometries for all the minima and transition states by means of the SMD model implemented in Gaussian 09.\textsuperscript{13} These calculations involve a certain margin error.
Table S1. Computed Cartesian coordinates \((x, y, z)\) for the optimized structures.

\[
E [\text{a.u.}] = -1188.975261 \\
G [\text{a.u.}] = -1188.631625
\]

| Element | X     | Y     | Z     | X     | Y     | Z     |
|---------|-------|-------|-------|-------|-------|-------|
| P       | -2.024000 | -0.131000 | -0.422000 | H     | 6.265000   | -1.394000   | -0.468000   |
| O       | -2.721000 | -0.481000 | -1.713000 | H     | -0.650000  | -2.739000  | 0.160000   |
| N       | -0.285000 | -0.171000 | -0.746000 | H     | -2.168000  | -2.976000  | -0.736000   |
| N       | 1.852000  | -0.110000 | -0.620000 | H     | -1.993000  | -3.615000  | 0.908000   |
| C       | 0.732000  | 0.068000  | 0.150000  | H     | -0.587000  | -1.013000  | 2.158000   |
| C       | 1.544000  | -0.448000 | -1.945000 | H     | -1.773000  | -2.138000  | 2.850000   |
| C       | 0.195000  | -0.486000 | -2.027000 | H     | -0.402000  | -2.531000  | 1.661000   |
| C       | 3.186000  | 0.012000  | -0.121000 | H     | -4.292000  | -0.789000  | 1.563000   |
| C       | 3.491000  | 0.993000  | 0.831000  | H     | -4.351000  | -1.778000  | 0.088000   |
| C       | 4.795000  | 1.106000  | 1.315000  | H     | -2.331000  | 1.626000   | 2.262000   |
| C       | 5.803000  | 0.255000  | 0.848000  | H     | -0.748000  | 1.885000   | 1.502000   |
| C       | 5.494000  | -0.720000 | -0.105000 | H     | -1.958000  | 3.183000   | 1.520000   |
| C       | 4.188000  | -0.849000 | -0.586000 | H     | -4.380000  | 1.513000   | -0.833000   |
| C       | -2.397000 | 1.654000  | 0.064000  | H     | -4.167000  | 2.888000   | 0.219000   |
| C       | -1.818000 | 2.098000  | 1.418000  | H     | -4.416000  | 1.267000   | 0.874000   |
| C       | -1.807000 | 2.533000  | -1.064000 | H     | -2.124000  | 3.571000   | -0.899000   |
| C       | -3.933000 | 1.826000  | 0.066000  | H     | -0.713000  | 2.518000   | -1.070000   |
| C       | -2.312000 | -1.475000 | 0.872000  | H     | -2.131000  | -0.412000  | 2.790000   |
| C       | -1.656000 | -1.231000 | 2.242000  | H     | -2.166000  | 2.226000   | -2.052000   |
| C       | -1.741000 | -2.772000 | 0.251000  | H     | 3.948000   | -1.629000  | -1.302000   |
| C       | -3.839000 | -1.641000 | 1.046000  | H     | 2.708000   | 1.657000   | 1.182000   |
| H       | 2.299000  | -0.598000 | -2.701000 |       |        |        |        |
| H       | -0.469000 | -0.693000 | -2.852000 |       |        |        |        |
| H       | 5.025000  | 1.869000  | 2.053000  |       |        |        |        |
| H       | 6.818000  | 0.350000  | 1.223000  |       |        |        |        |
**Table S2.** Computed Cartesian coordinates (x, y, z) for the optimized structures. sPxm

![Diagram of optimized structure](image)

\[ E \text{ [a.u.]} = -1188.965765 \]
\[ G \text{ [a.u.]} = -1188.622928 \]

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| P | 1.792000 | -0.046000 | -0.563000 | H | -5.558000 | -1.228000 | -2.208000 |
| O | 1.688000 | -0.254000 | -2.044000 | H | 0.624000 | 2.656000 | -0.838000 |
| N | 0.185000 | -0.057000 | 0.201000 | H | 1.805000 | 2.396000 | -2.130000 |
| N | -1.952000 | -0.065000 | 0.394000 | H | 2.082000 | 3.660000 | -0.912000 |
| C | -0.967000 | -0.025000 | -0.557000 | H | 1.266000 | 2.195000 | 1.594000 |
| C | -1.444000 | -0.116000 | 1.697000 | H | 2.762000 | 3.111000 | 1.412000 |
| C | -0.098000 | -0.111000 | 1.578000 | H | 4.327000 | 2.741000 | -0.495000 |
| C | -3.349000 | -0.047000 | 0.089000 | H | 4.595000 | 1.102000 | 0.105000 |
| C | -4.237000 | 0.642000 | 0.924000 | H | 4.129000 | 1.367000 | -1.591000 |
| C | -5.604000 | 0.644000 | 0.634000 | H | 3.988000 | -0.462000 | 1.684000 |
| C | -6.088000 | -0.027000 | -0.493000 | H | 2.484000 | -1.091000 | 2.388000 |
| C | -5.193000 | -0.703000 | -1.329000 | H | 3.787000 | -2.193000 | 1.962000 |
| C | -3.827000 | -0.722000 | -1.041000 | H | 3.554000 | -2.006000 | -1.745000 |
| C | 2.712000 | -1.507000 | 0.224000 | H | 4.385000 | -2.748000 | -0.361000 |
| C | 3.263000 | -1.281000 | 1.644000 | H | 4.649000 | -1.042000 | -0.739000 |
| C | 1.745000 | -2.713000 | 0.221000 | H | 2.303000 | -3.612000 | 0.517000 |
| C | 3.894000 | -1.834000 | -0.721000 | H | 0.917000 | -2.590000 | 0.925000 |
| C | 2.477000 | 1.668000 | -0.165000 | H | 2.827000 | 1.453000 | 2.010000 |
| C | 2.317000 | 2.113000 | 1.301000 | H | 1.323000 | -2.894000 | -0.774000 |
| C | 1.694000 | 2.646000 | -1.072000 | H | -3.130000 | -1.249000 | -1.682000 |
| C | 3.969000 | 1.706000 | -0.562000 | H | -3.864000 | 1.193000 | 1.783000 |
| H | -2.071000 | -0.184000 | 2.574000 | H | -6.288000 | 1.183000 | 1.285000 |
| H | 0.658000 | -0.146000 | 2.345000 | H | -7.151000 | -0.021000 | -0.719000 |
Table S3. Computed Cartesian coordinates (x, y, z) for the optimized structures.

**aPxm-CO2**

\[
E \text{ [a.u.]} = -1377.574045 \\
G \text{ [a.u.]} = -1377.220243
\]

|    | x    | y    | z    |    | x    | y    | z    |
|----|------|------|------|----|------|------|------|
| P  | 2.167000 | -0.238000 | -0.550000 | H  | -5.397000 | 2.297000 | 0.517000 |
| O  | 2.688000 | -0.756000 | -1.863000 | H  | 0.638000 | 2.467000 | -0.672000 |
| N  | 0.338000 | -0.342000 | -0.770000 | H  | 1.523000 | 2.082000 | -2.179000 |
| N  | -1.848000 | -0.337000 | -0.767000 | H  | 2.004000 | 3.464000 | -1.188000 |
| C  | -0.758000 | -0.016000 | -0.037000 | H  | 1.689000 | 1.992000 | 1.626000 |
| C  | -1.447000 | -0.882000 | -1.984000 | H  | 2.928000 | 3.141000 | 1.120000 |
| C  | -0.094000 | -0.890000 | -1.985000 | H  | 4.325000 | 2.779000 | -0.883000 |
| C  | -3.223000 | -0.144000 | -0.383000 | H  | 4.785000 | 1.134000 | -0.424000 |
| C  | -4.075000 | -1.251000 | -0.359000 | H  | 4.044000 | 1.430000 | -2.006000 |
| C  | -5.418000 | -1.068000 | -0.023000 | H  | 2.272000 | -0.159000 | 2.617000 |
| C  | -5.896000 | 0.208000  | 0.292000  | H  | 0.872000 | -1.161000 | 2.208000 |
| C  | -5.031000 | 1.305000  | 0.268000  | H  | 2.307000 | -1.896000 | 2.919000 |
| C  | -3.688000 | 1.137000  | 0.078000  | H  | 4.620000 | -1.635000 | 0.000000 |
| C  | 2.588000  | -1.432000 | 0.843000  | H  | 4.427000 | -2.204000 | 1.666000 |
| C  | 1.964000  | -1.127000 | 2.215000  | H  | 4.514000 | -0.471000 | 1.343000 |
| C  | 2.129000  | -2.829000 | 0.366000  | H  | 2.462000 | -3.570000 | 1.104000 |
| C  | 4.131000  | -1.422000 | 0.956000  | H  | 1.039000 | -2.905000 | 0.297000 |
| C  | 2.619000  | 1.586000  | -0.329000 | H  | 3.422000 | 1.557000  | 1.718000 |
| C  | 2.658000  | 2.077000  | 1.130000  | H  | 2.561000 | -3.095000 | -0.603000 |
| C  | 1.623000  | 2.436000  | -1.147000 | H  | -3.011000 | 1.985000  | -0.100000 |
| C  | 4.030000  | 1.724000  | -0.954000 | H  | -3.687000 | -2.241000 | -0.581000 |
| H  | -2.164000 | -1.189000 | -2.730000 | C  | -0.867000 | 0.614000  | 1.375000 |
| H  | 0.619000  | -1.218000 | -2.724000 | O  | -0.551000 | 1.822000  | 1.414000 |
| H  | -6.086000 | -1.925000 | 0.003000  | O  | -1.282000 | -0.172000 | 2.247000 |
| H  | -6.940000 | 0.345000  | 0.560000  |    |        |        |     |
Table S4. Computed Cartesian coordinates (x, y, z) for the optimized structures. sPxm-CO2

![Diagram of sPxm-CO2 molecule]

\[ E \text{ [a.u.]} = -1377.565835 \]
\[ G \text{ [a.u.]} = -1377.211301 \]

|   | x   | y   | z   |   | x   | y   | z   |
|---|-----|-----|-----|---|-----|-----|-----|
| P | -1.996000 | -0.035000 | 0.378000 | H | 5.690000 | -1.635000 | 1.283000 |
| O | -1.811000 | -0.173000 | 1.854000 | H | -0.809000 | 2.643000 | 0.620000 |
| N | -0.360000 | -0.095000 | -0.422000 | H | -2.067000 | 2.496000 | 1.844000 |
| N | 1.807000 | -0.143000 | -0.698000 | H | -2.243000 | 3.682000 | 0.532000 |
| C | 0.830000 | -0.047000 | 0.233000 | H | -1.416000 | 2.127000 | -1.861000 |
| C | 1.235000 | -0.249000 | -1.964000 | H | -2.932000 | 3.018000 | -1.751000 |
| C | -0.106000 | -0.218000 | -1.794000 | H | -4.509000 | 2.740000 | 0.154000 |
| C | 3.230000 | -0.099000 | -0.470000 | H | -4.769000 | 1.080000 | -0.391000 |
| C | 3.988000 | 0.834000 | -1.184000 | H | -4.335000 | 1.409000 | 1.303000 |
| C | 5.373000 | 0.865000 | -1.010000 | H | -4.189000 | -0.569000 | -1.831000 |
| C | 5.989000 | -0.024000 | -0.124000 | H | -2.698000 | -1.253000 | -2.513000 |
| C | 5.217000 | -0.947000 | 0.588000 | H | -4.005000 | -2.315000 | -2.070000 |
| C | 3.831000 | -0.996000 | 0.416000 | H | -3.728000 | -1.923000 | 1.681000 |
| C | -2.905000 | -1.540000 | -0.325000 | H | -4.574000 | -2.736000 | 0.348000 |
| C | -3.471000 | -1.391000 | -1.750000 | H | -4.831000 | -1.011000 | 0.634000 |
| C | -1.937000 | -2.742000 | -0.260000 | H | -2.501000 | -3.656000 | -0.485000 |
| C | -4.078000 | -1.805000 | 0.652000 | H | -1.126000 | -2.668000 | -0.992000 |
| C | -2.655000 | 1.661000 | -0.104000 | H | -2.955000 | 1.335000 | -2.273000 |
| C | -2.472000 | 2.036000 | -1.586000 | H | -1.495000 | -2.858000 | 0.735000 |
| C | -1.891000 | 2.672000 | 0.780000 | H | 3.224000 | -1.699000 | 0.975000 |
| C | -4.156000 | 1.706000 | 0.265000 | H | 3.498000 | 1.538000 | -1.851000 |
| H | 1.837000 | -0.358000 | -2.833000 | C | 1.129000 | 0.155000 | 1.748000 |
| H | -0.893000 | -0.283000 | -2.525000 | O | 1.334000 | -0.903000 | 2.368000 |
| H | 5.966000 | 1.593000 | -1.557000 | O | 1.188000 | 1.359000 | 2.061000 |
| H | 7.066000 | 0.006000 | 0.016000 |
Table S5. Computed Cartesian coordinates (x, y, z) for the optimized structures.

\[
E \text{ [a.u.]} = -1377.601996 \\
G \text{ [a.u.]} = -1377.249896
\]

| Element | x       | y       | z       | Element | x       | y       | z       |
|---------|---------|---------|---------|---------|---------|---------|---------|
| P       | 2.196000| -0.382000| 0.497000| H       | -4.172000| 2.757000| -0.623000|
| O       | -0.867000| -0.997000| 0.141000| H       | -4.809000| -1.533000| 2.692000|
| O       | 0.867000 | 0.451000 | -0.154000| H       | -6.022000| -2.711000| 0.867000|
| O       | 1.964000 | -0.901000| 1.884000| H       | -5.658000| -2.038000| -1.502000|
| N       | -2.684000| 1.253000 | -0.294000| H       | 4.231000 | 0.881000 | -1.534000|
| N       | -0.870000| 2.508000 | -0.667000| H       | 4.318000 | 2.501000 | -0.838000|
| C       | -1.301000| 1.293000 | -0.344000| H       | 2.774000 | 1.900000 | -1.457000|
| C       | -1.985000| 3.273000 | -0.832000| H       | 3.398000 | 3.031000 | 1.421000 |
| C       | -3.119000| 2.517000 | -0.604000| H       | 2.433000 | 1.851000 | 2.324000 |
| C       | -3.567000| 0.159000 | 0.026000 | H       | 1.790000 | 2.570000 | 0.830000 |
| C       | -3.769000| -0.203000| 1.359000 | H       | 5.311000 | 1.560000 | 1.333000 |
| C       | -4.654000| -1.241000| 1.657000 | H       | 5.265000 | -0.068000| 0.652000 |
| C       | -5.335000| -1.903000| 0.630000 | H       | 4.479000 | 0.263000 | 2.207000 |
| C       | -5.132000| -1.526000| -0.701000| H       | 2.069000 | -3.328000| 0.701000 |
| C       | -4.244000| -0.491000| -1.008000| H       | 1.928000 | -3.806000| -1.005000|
| C       | -0.445000| 0.119000 | -0.083000| H       | 0.674000 | -2.798000| -0.247000|
| C       | 3.378000 | 1.079000 | 0.490000 | H       | 2.368000 | -2.192000| -2.860000|
| C       | 3.685000 | 1.607000 | -0.924000| H       | 2.629000 | -0.470000| -2.552000|
| C       | 2.695000 | 2.195000 | 1.317000 | H       | 1.039000 | -1.194000| -2.256000|
| C       | 4.681000 | 0.669000 | 1.211000 | H       | 4.204000 | -2.995000| -1.360000|
| C       | 2.546000 | -1.751000| -0.753000| H       | 4.410000 | -2.345000| 0.269000 |
| C       | 1.749000 | -2.992000| -0.290000| H       | 4.674000 | -1.307000| -1.151000|
| C       | 2.118000 | -1.364000| -2.182000| H       | -3.232000| 0.315000 | 2.148000 |
| C       | 4.050000 | -2.104000| -0.737000| H       | -4.068000| -0.194000| -2.039000|
| H       | -1.924000| 4.319000 | -1.101000|         |         |         |         |
**Table S6.** Computed Cartesian coordinates (x, y, z) for the optimized structures. TS1

\[ E \text{ [a.u.] } = -1188.956444 \]
\[ G \text{ [a.u.] } = -1188.611715 \]
\[ 45.54i \text{ [cm}^{-1}\text{]} \]

|     | x         | y         | z         |     | x         | y         | z         |
|-----|-----------|-----------|-----------|-----|-----------|-----------|-----------|
| P   | 1.862000  | 0.155000  | -0.517000 | H   | -5.440000 | 2.047000  | -1.272000 |
| O   | 2.071000  | 0.352000  | -1.995000 | H   | 0.040000  | 2.511000  | -0.572000 |
| N   | 0.246000  | -0.553000 | -0.184000 | H   | 1.496000  | 2.935000  | -1.455000 |
| N   | -1.906000 | -0.644000 | -0.100000 | H   | 1.078000  | 3.798000  | 0.040000  |
| C   | -0.876000 | 0.251000  | -0.144000 | H   | 0.236000  | 1.469000  | 1.828000  |
| C   | -1.461000 | -1.969000 | -0.124000 | H   | 1.375000  | 2.742000  | 2.292000  |
| C   | -0.113000 | -1.916000 | -0.189000 | H   | 3.245000  | 3.441000  | 0.740000  |
| C   | -3.285000 | -0.267000 | -0.034000 | H   | 3.917000  | 1.894000  | 1.238000  |
| C   | -4.171000 | -1.003000 | 0.762000  | H   | 3.833000  | 2.319000  | -0.489000 |
| C   | -5.520000 | -0.641000 | 0.815000  | H   | 2.762000  | -0.935000 | 2.292000  |
| C   | -5.986000 | 0.458000  | 0.087000  | H   | 1.780000  | -2.214000 | 1.571000  |
| C   | -5.092000 | 1.193000  | -0.699000 | H   | 3.515000  | -2.454000 | 1.802000  |
| C   | -3.745000 | 0.833000  | -0.768000 | H   | 4.780000  | 0.006000  | -0.715000 |
| C   | 3.093000  | -1.151000 | 0.129000  | H   | 5.232000  | -1.392000 | 0.262000  |
| C   | 2.752000  | -1.715000 | 1.523000  | H   | 4.682000  | 0.077000  | 1.060000  |
| C   | 3.163000  | -2.272000 | -0.941000 | H   | 3.848000  | -3.050000 | -0.579000 |
| C   | 4.522000  | -0.558000 | 0.187000  | H   | 2.212000  | -2.754000 | -1.170000 |
| C   | 1.867000  | 1.823000  | 0.403000  | H   | 1.841000  | 1.049000  | 2.467000  |
| C   | 1.291000  | 1.750000  | 1.829000  | H   | 3.557000  | -1.880000 | -1.883000 |
| C   | 1.053000  | 2.820000  | -0.460000 | H   | -3.050000 | 1.392000  | -1.384000 |
| C   | 3.310000  | 2.379000  | 0.471000  | H   | -3.809000 | -1.840000 | 1.352000  |
| H   | -2.130000 | -2.816000 | -0.125000 |     |           |           |           |
| H   | 0.585000  | -2.730000 | -0.242000 |     |           |           |           |
| H   | -6.203000 | -1.214000 | 1.436000  |     |           |           |           |
| H   | -7.034000 | 0.739000  | 0.132000  |     |           |           |           |
Table S7. Computed Cartesian coordinates (x, y, z) for the optimized structures.

| Atom | x   | y   | z   | Atom | x   | y   | z   |
|------|-----|-----|-----|------|-----|-----|-----|
| P    | 1.943000 | 0.226000 | 0.225000 | H   | -5.617000 | 1.967000 | -0.236000 |
| O    | 1.722000 | 1.341000 | 1.201000 | H   | 0.750000  | -1.730000 | 2.111000  |
| N    | 0.364000 | -0.333000 | -0.407000 | H   | 1.804000  | -0.617000 | 2.995000  |
| N    | -1.772000 | -0.533000 | -0.615000 | H   | 2.201000  | -2.348000 | 2.916000  |
| C    | -0.823000 | 0.135000  | 0.097000  | H   | 1.613000  | -2.934000 | 0.036000  |
| C    | -1.203000 | -1.402000 | -1.549000 | H   | 3.107000  | -3.393000 | 0.849000  |
| C    | 0.137000  | -1.277000 | -1.422000 | H   | 4.467000  | -1.779000 | 2.158000  |
| C    | -3.190000 | -0.397000 | -0.430000 | H   | 4.786000  | -0.921000 | 0.647000  |
| C    | -3.971000 | -1.548000 | -0.283000 | H   | 4.170000  | -0.038000 | 2.064000  |
| C    | -5.354000 | -1.427000 | -0.127000 | H   | 4.274000  | -0.819000 | -1.649000 |
| C    | -5.951000 | -0.162000 | -0.107000 | H   | 2.791000  | -0.917000 | -2.624000 |
| C    | -5.160000 | 0.982000  | -0.249000 | H   | 4.034000  | 0.264000  | -3.020000 |
| C    | -3.778000 | 0.871000  | -0.419000 | H   | 3.584000  | 2.585000  | -0.137000 |
| C    | 2.882000  | 0.852000  | -1.296000 | H   | 4.507000  | 2.244000  | -1.616000 |
| C    | 3.522000  | -0.231000 | -2.185000 | H   | 4.749000  | 1.250000  | -0.173000 |
| C    | 1.898000  | 1.702000  | -2.130000 | H   | 2.460000  | 2.206000  | -2.928000 |
| C    | 3.995000  | 1.785000  | -0.759000 | H   | 1.119000  | 1.097000  | -2.605000 |
| C    | 2.653000  | -1.300000 | 1.081000  | H   | 3.187000  | -2.528000 | -0.685000 |
| C    | 2.632000  | -2.601000 | 0.255000  | H   | 1.412000  | 2.476000  | -1.527000 |
| C    | 1.794000  | -1.500000 | 2.350000  | H   | -3.160000 | 1.754000  | -0.542000 |
| C    | 4.104000  | -0.976000 | 1.503000  | H   | -3.499000 | -2.527000 | -0.272000 |
| H    | -1.799000 | -2.000000 | -2.230000 | C   | -1.179000 | 1.747000  | 1.536000  |
| H    | 0.929000  | -1.765000 | -1.965000 | O   | -1.203000 | 2.715000  | 0.837000  |
| H    | -5.960000 | -2.321000 | -0.007000 | O   | -1.297000 | 1.196000  | 2.586000  |
| H    | -7.026000 | -0.070000 | 0.021000  |      |            |            |            |

\(E\) [a.u.] = −1377.549608
\(G\) [a.u.] = −1377.197019
173.43 \(i\) [cm\(^{-1}\)]
Table S8. Computed Cartesian coordinates (x, y, z) for the optimized structures.

**TS2b**

\[
E [\text{a.u.}] = -1377.553402 \\
G [\text{a.u.}] = -1377.203501 \\
184.42 i [\text{cm}^{-1}]
\]

|   |   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|---|
| P | 2.202000 | -0.279000 | -0.566000 | H | -5.211000 | 2.375000 | 0.156000 |
| O | 2.846000 | -0.912000 | -1.772000 | H | 0.589000 | 2.196000 | -1.417000 |
| N | 0.435000 | -0.494000 | -0.801000 | H | 1.795000 | 1.708000 | -2.631000 |
| N | -1.719000 | -0.460000 | -0.816000 | H | 1.953000 | 3.257000 | -1.790000 |
| C | -0.648000 | -0.033000 | -0.091000 | H | 1.207000 | 2.156000 | 1.117000 |
| C | -1.328000 | -1.179000 | -1.948000 | H | 2.419000 | 3.356000 | 0.660000 |
| C | 0.023000 | -1.198000 | -1.944000 | H | 4.214000 | 2.844000 | -1.013000 |
| C | -3.095000 | -0.199000 | -0.499000 | H | 4.696000 | 1.360000 | -0.185000 |
| C | -3.992000 | -1.269000 | -0.414000 | H | 4.246000 | 1.304000 | -1.899000 |
| C | -5.336000 | -1.017000 | -0.128000 | H | 1.872000 | 0.163000 | 2.523000 |
| C | -5.778000 | 0.293000 | 0.082000 | H | 0.748000 | -1.147000 | 2.113000 |
| C | -4.873000 | 1.355000 | -0.003000 | H | 2.179000 | -1.482000 | 3.084000 |
| C | -3.530000 | 1.114000 | -0.302000 | H | 4.760000 | -1.220000 | 0.408000 |
| C | 2.632000 | -1.241000 | 0.994000 | H | 4.442000 | -1.701000 | 2.082000 |
| C | 1.801000 | -0.891000 | 2.240000 | H | 4.338000 | 0.002000 | 1.632000 |
| C | 2.405000 | -2.729000 | 0.640000 | H | 2.687000 | -3.340000 | 1.508000 |
| C | 4.133000 | -1.015000 | 1.283000 | H | 1.353000 | -2.943000 | 0.417000 |
| C | 2.523000 | 1.581000 | -0.554000 | H | 2.910000 | 1.934000 | 1.581000 |
| C | 2.240000 | 2.279000 | 0.786000 | H | 3.011000 | -3.044000 | -0.214000 |
| C | 1.654000 | 2.208000 | -1.666000 | H | -2.825000 | 1.935000 | -0.387000 |
| C | 4.012000 | 1.767000 | -0.936000 | H | -3.636000 | -2.286000 | -0.551000 |
| H | -2.043000 | -1.577000 | -2.652000 | C | -1.186000 | 0.685000 | 1.929000 |
| H | 0.738000 | -1.621000 | -2.631000 | O | -0.897000 | 1.841000 | 1.977000 |
| H | -6.033000 | -1.848000 | -0.056000 | O | -1.645000 | -0.311000 | 2.398000 |
| H | -6.823000 | 0.484000 | 0.312000 |   |   |   |   |
Table S9. Computed Cartesian coordinates (x, y, z) for the optimized structures.

TS3

\[ E \text{ [a.u.]} = -1377.544914 \]
\[ G \text{ [a.u.]} = -1377.188315 \]
\[ 56.69i \text{ [cm}^{-1}\text{]} \]

|     | x     | y     | z     |     | x     | y     | z     |
|-----|-------|-------|-------|-----|-------|-------|-------|
| H   | -5.821000 | 0.637000 | -1.859000 |
| H   | 0.674000  | 2.518000 | -0.874000 |
| H   | 2.292000  | 2.879000 | -1.448000 |
| H   | 1.663000  | 3.675000 | 0.011000  |
| H   | 0.702000  | 1.496000 | 1.840000  |
| H   | 1.974000  | 2.640000 | 2.241000  |
| H   | 3.885000  | 3.117000 | 0.635000  |
| H   | 4.384000  | 1.536000 | 1.223000  |
| H   | 4.365000  | 1.881000 | -0.527000 |
| H   | 4.998000  | -0.409000 | -0.633000 |
| H   | 4.841000  | -0.370000 | 1.141000  |
| H   | 5.291000  | -1.861000 | 0.325000  |
| H   | 2.257000  | -2.920000 | -1.301000 |
| H   | 3.787000  | -3.402000 | -0.564000 |
| H   | 3.743000  | -2.182000 | -1.851000 |
| H   | 3.521000  | -2.744000 | 1.825000  |
| H   | 2.799000  | -1.200000 | 2.281000  |
| H   | 2.285000  | 0.913000  | 2.424000  |
| H   | 1.801000  | -2.460000 | 1.558000  |
| H   | -3.362000 | 0.260000  | -1.988000 |
| H   | -3.392000 | -1.321000 | 2.013000  |
| C   | -1.249000 | 1.592000  | -0.047000 |
| O   | -1.499000 | 2.070000  | -1.170000 |
| O   | -1.328000 | 2.060000  | 1.104000  |
| H   | -7.065000 | 0.028000  | 0.207000  |
Table S10. Computed Cartesian coordinates (x, y, z) for the optimized structures.
TS4a

\[ E \text{ [a.u.]} = -1377.529768 \]
\[ G \text{ [a.u.]} = -1377.173811 \]
\[ 158.16 \text{ i [cm}^{-1}] \]

|   | x     | y     | z     |   | x     | y     | z     |
|---|-------|-------|-------|---|-------|-------|-------|
| P | 2.089000 | 0.218000 | -0.552000 | H | -5.839000 | -0.121000 | -2.201000 |
| O | 2.485000 | 0.488000 | -1.976000 | H | 1.718000 | 3.252000 | -0.315000 |
| N | 0.175000 | -0.712000 | 0.256000 | H | 3.365000 | 2.851000 | -0.819000 |
| N | -2.034000 | -0.730000 | 0.323000 | H | 3.092000 | 3.628000 | 0.751000 |
| C | -0.930000 | -0.067000 | -0.110000 | H | 0.578000 | 1.920000 | 1.568000 |
| C | -1.596000 | -1.855000 | 0.998000 | H | 1.915000 | 2.384000 | 2.626000 |
| C | -0.228000 | -1.837000 | 0.947000 | H | 4.228000 | 2.006000 | 2.057000 |
| C | -3.423000 | -0.377000 | 0.165000 | H | 4.030000 | 0.267000 | 1.870000 |
| C | -4.165000 | -0.056000 | 1.304000 | H | 4.755000 | 1.235000 | 0.564000 |
| C | -5.524000 | 0.242000 | 1.173000 | H | 3.943000 | -1.869000 | 1.649000 |
| C | -6.128000 | 0.218000 | -0.088000 | H | 2.246000 | -1.479000 | 1.866000 |
| C | -5.373000 | -0.107000 | -1.220000 | H | 2.720000 | -3.071000 | 1.260000 |
| C | -4.016000 | -0.411000 | -1.099000 | H | 4.415000 | -1.130000 | -1.837000 |
| C | 2.926000 | -1.509000 | -0.262000 | H | 4.849000 | -2.401000 | -0.673000 |
| C | 2.948000 | -1.998000 | 1.209000 | H | 4.997000 | -0.704000 | -0.217000 |
| C | 2.218000 | -2.517000 | -1.197000 | H | 2.771000 | -3.466000 | -1.170000 |
| C | 4.384000 | -1.411000 | -0.782000 | H | 1.185000 | -2.732000 | -0.917000 |
| C | 2.583000 | 1.537000 | 0.762000 | H | 1.479000 | 0.678000 | 2.466000 |
| C | 1.570000 | 1.621000 | 1.916000 | H | 2.222000 | -2.159000 | -2.231000 |
| C | 2.686000 | 2.898000 | 0.038000 | H | -3.422000 | -0.659000 | -1.973000 |
| C | 3.980000 | 1.217000 | 1.335000 | H | -3.679000 | -0.025000 | 2.275000 |
| H | -2.990000 | -2.561000 | 1.431000 | C | -0.817000 | 1.252000 | -0.812000 |
| H | 0.457000 | -2.561000 | 1.353000 | O | -1.818000 | 1.904000 | -1.121000 |
| H | -6.104000 | 0.499000 | 2.054000 | O | 0.415000 | 1.551000 | -0.987000 |
| H | -7.183000 | 0.456000 | -0.189000 |
Table S11. Computed Cartesian coordinates (x, y, z) for the optimized structures.

**TS4b**

![molecular structure diagram]

\[
E \text{ [a.u.]} = -1377.549855 \\
G \text{ [a.u.]} = -1377.195079 \\
158.18i \text{ [cm}^{-1}\text{]} 
\]

|   | x   | y   | z   |   | x   | y   | z   |
|---|-----|-----|-----|---|-----|-----|-----|
| C | -5.641000 | 0.845000 | -0.708000 | H | -3.238000 | -1.017000 | 1.715000 |
| C | -6.073000 | 0.500000 | 0.576000 | H | -3.992000 | 0.810000 | -2.109000 |
| C | -5.207000 | -0.168000 | 1.448000 | H | 0.817000 | -2.825000 | 0.384000 |
| C | -3.913000 | -0.499000 | 1.043000 | H | 2.093000 | -2.952000 | -0.847000 |
| C | -3.492000 | -0.145000 | -0.241000 | H | 2.334000 | -3.649000 | 0.765000 |
| C | -4.344000 | 0.527000 | -1.122000 | H | 1.122000 | -1.327000 | 2.416000 |
| N | -2.171000 | -0.498000 | -0.693000 | H | 2.635000 | -2.164000 | 2.788000 |
| C | -0.967000 | -0.157000 | -0.159000 | H | 2.604000 | -0.399000 | 2.651000 |
| N | 0.012000 | -0.657000 | -0.891000 | H | 4.366000 | -1.750000 | -0.469000 |
| C | -0.522000 | 0.677000 | 0.994000 | H | 4.612000 | -0.767000 | 0.991000 |
| O | -1.280000 | 1.180000 | 1.817000 | H | 4.410000 | -2.514000 | 1.129000 |
| O | 0.776000 | 0.776000 | 0.972000 | H | 4.758000 | 2.502000 | -1.007000 |
| P | 2.019000 | -0.072000 | -0.413000 | H | 4.951000 | 0.775000 | -0.685000 |
| O | 2.357000 | -0.455000 | -1.843000 | H | 4.040000 | 1.302000 | -2.107000 |
| C | 2.540000 | -1.499000 | 0.742000 | H | 2.445000 | 2.119000 | 1.860000 |
| C | 2.958000 | 1.610000 | -0.219000 | H | 3.995000 | 1.269000 | 1.693000 |
| C | 1.899000 | -2.801000 | 0.220000 | H | 3.862000 | 2.956000 | 1.200000 |
| C | 2.199000 | -1.323000 | 2.231000 | H | 1.760000 | 2.444000 | -1.866000 |
| C | 4.075000 | -1.625000 | 0.578000 | H | 1.152000 | 2.873000 | -0.247000 |
| C | 4.251000 | 1.528000 | -1.060000 | H | 2.614000 | 3.643000 | -0.885000 |
| C | 3.324000 | 1.997000 | 1.226000 | C | -0.536000 | -1.326000 | -1.951000 |
| C | 2.054000 | 2.698000 | -0.841000 | C | -1.902000 | -1.241000 | -1.835000 |
| H | -6.306000 | 1.371000 | -1.387000 | H | 0.073000 | -1.804000 | -2.702000 |
| H | -7.079000 | 0.753000 | 0.897000 | H | -2.702000 | -1.644000 | -2.439000 |
| H | -5.537000 | -0.435000 | 2.448000 |   |   |   |   |
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[12] NMR spectra

1a·HOTf, CDCl₃, 400 MHz
$^{1}H$NMR, CDCl$_{3}$, 100 MHz

1a·HOTf, CDCl$_{3}$, 100 MHz
1a·HOTf, CDCl₃, 376 MHz
1a·HOTf, CDCl₃, 162 MHz
1b·HOTf, CDCl₃, 400 MHz
1b·HOTf, CDCl₃, 100 MHz
$^{1}b$-HOTf, CDCl$_3$, 162 MHz
$^{1}c$-HOTf, CDCl$_3$, 400 MHz
1c·HOTf, CDCl₃, 100 MHz
1c-HOTf, CDCl$_3$, 376 MHz
$^{1}c\cdot\text{HOTf}$, CDCl$_3$, 162 MHz
$^{1}f$-HOTf, CDCl$_3$, 400 MHz
$1f \cdot$HOTf, CDCl$_3$, 376 MHz
$^{1}f$-HOTf, CDCl$_3$, 162 MHz
$^{1}{\text{H}}\text{OTf}$, CDCl$_3$, 400 MHz
$^{1}g \cdot HOTf$, CDCl$_3$, 151 MHz
$^{1}g\cdot$HOTf, CDCl$_3$, 376 MHz
$\text{1g\cdot HOTf, CDCl}_3$, 162 MHz
1a, C₆D₆, 400 MHz
1a, C₆D₆, 100 MHz
1a, C₆D₆, 162 MHz
$1b$, C$_6$D$_6$, 400 MHz
$1b$, C$_6$D$_6$, 100 MHz
$1b, C_6D_6, 162$ MHz
$1c$, C$_6$D$_6$, 400 MHz
1c, C₆D₆, 100 MHz
1c, C₆D₆, 162 MHz
1d, C₆D₆, 400 MHz
1d, C₆D₆, 151 MHz
$1d, \text{C}_6\text{D}_6, 162 \text{ MHz}$
$1e, C_6D_6, 151$ MHz
$1e$, C$_6$D$_6$, 162 MHz
$1f, \text{C}_6\text{D}_6, 100 \text{ MHz}$
$^{13}$C-NMR, $^{1}$H-NMR, 600 MHz
$^{1}g$, C$_6$D$_6$, 151 MHz
2a, C₆D₆, 400 MHz
$2a$, C$_6$D$_6$, 100 MHz
2b, C₆D₆, 400 MHz
$2c$, $\text{C}_6\text{D}_6$, 400 MHz
$2c, \text{C}_6\text{D}_6, 151 \text{ MHz}$
$2c$, $C_6D_6$, 162 MHz
2d, C₆D₆, 400 MHz
2d, C₆D₆, 100 MHz
2d, C₆D₆, 162 MHz
$2e$, $C_6D_6$, 400 MHz
$2e, C_6D_6, 100 \text{ MHz}$
$2e, C_6D_6, 162$ MHz
$2f$, C$_6$D$_6$, 600 MHz

[Chemical structure image]
$2f$, $C_6D_6$, 151 MHz
$\text{2f, C}_6\text{D}_6, 243 \text{ MHz}$
$2g$, CD$_2$CN, 400 MHz
$2g$, CD$_3$CN, 100 MHz
$\text{C}_6\text{D}_6$, 400 MHz
C₆D₆, 100 MHz

[Chemical structures of 2g and 2g']

C₆D₆
$\text{C}_6\text{D}_6$, 162 MHz
2g \cdot B(C_6F_3)_3, C_6D_6, 400 MHz
$2g \cdot B(C_6F_3)_3$, $C_6D_6$, 128 MHz
$\text{Phosphorus NMR spectrum of } \text{BuP}_{3} \text{BuPOC(Bu)}_{2} \text{ Bu}$

$2\text{g} \cdot \text{B}(\text{C}_6\text{F}_3)_3, \text{C}_6\text{D}_6, 100 \text{ MHz}$
$\text{2g} \cdot \text{B(C}_6\text{F}_3)_3$, C$_6$D$_6$, 376 MHz
$2g\cdot B(C_6F_3)_3$, C$_6$D$_6$, 162 MHz
A, CD$_2$Cl$_2$, 600 MHz
A, CD$_2$Cl$_2$, 151 MHz
A, CD$_2$Cl$_2$, 162 MHz
$3b$, $\text{CD}_2\text{Cl}_2$, 400 MHz
$3b$, $\text{CD}_2\text{Cl}_2$, 376 MHz
$3b$, $\text{CD}_2\text{Cl}_2$, 162 MHz
13, CDCl$_3$, 400 MHz
13, CDCl₃, 100 MHz
14, CDCl₃, 400 MHz
