Synthesis and structures of stable phosphorus zwitterions derived from mesoionic 4-trifluoroacetyl-1,3-oxazolium-5-olates

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Supplementary Information

Experimental Procedures and Analytical Data S2–S6

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General Information: Melting points were measured with a Yanaco MP-J3 melting point apparatus and are uncorrected. NMR spectra were recorded on a Bruker AVANCE500 (500 MHz for $^1$H, 126 MHz for $^{13}$C) with tetramethylsilane (Me$_4$Si) as an internal reference and CDCl$_3$ as the solvent. $^1$H and $^{13}$C NMR spectral data are reported in parts per million (δ) relative to Me$_4$Si. $^{31}$P NMR spectra were recorded on a Bruker AVANCE500 (202 MHz) and are reported relative to 85% H$_3$PO$_4$. Infrared spectra were recorded on a JASCO FT/IR-4100 spectrometer. Mass spectra were recorded on JEOL JMS-GC mate II spectrometer with a direct inlet system at 70 eV. X-ray crystallographic data were recorded on a Rigaku VariMax SaturnCCD724/α diffractometer using graphite monochromated Mo-Kα radiation at the Integrated Center for Science, Ehime University. Standard work-up means that the organic layers were finally dried over anhyd. Na$_2$SO$_4$, filtered, and concentrated in vacuo below 37 °C using a rotary evaporator.

Materials: The following compounds were prepared by employing the reported method.

$N$-(4-Bromobenzoyl)-$N$-phenylglycine: White crystals. mp 145–148 °C (ethyl acetate/hexane). IR (KBr) $\nu_{\text{max}}$ 3447, 3059, 2940, 1739, 1615, 1597, 1562, 1423, 1399, 1220, 1197, 759 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$) δ = 4.63 (s, 2H, NCH$_2$), 7.12 (d, J = 7.5 Hz, 2H, ArH), 7.21 (d, J = 8.3 Hz, 3H, ArH), 7.26 (t, J = 8.0 Hz, 2H, ArH), 7.31 (d, J = 8.5 Hz, 2H, ArH) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$) δ = 52.4, 124.8, 127.3, 127.5, 129.5, 130.6, 131.1, 133.5, 143.3, 170.1, 173.0 ppm. MS m/z: 335 (M$^{+}$+2, 18.9), 333 (M$^{+}$, 19.1), 185 (100), 183 (100). HRMS (EI) for C$_{15}$H$_{12}$BrNO$_3$ (M$^{+}$): Calcd, 333.0001. Found, 332.9989.

$N$-(4-Bromobenzoyl)-$N$-methylglycine: mp 147–150 °C (mp$^1$ 147–150 °C)


**N-Phenyl-N-pivaloylglycine:** mp 123–124 °C (mp\(^5\) 123–124 °C).

**General Procedure for Preparation of 4-Trifluoroacetyl-1,3-oxazolium-5-olates (1):** To a stirred suspension of N-acyl-N-alkylglycine (5.2 mmol) in ethyl acetate (10 mL) was added TFAA (2.2 mL, 15.6 mmol) at 0 °C, and the solution was stirred at 0 °C for 3 h. To the mixture was added hexane, and the precipitate was collected and recrystallized from hexane/ethyl acetate to give the product 1.

**2-(4-Bromophenyl)-4-trifluoroacetyl-3-phenyl-1,3-oxazolium-5-olate (1a):** Yellow crystals, 89% yield. mp 170–173 °C (ethyl acetate/hexane). IR (KBr) \(\nu_{\text{max}}\) 3435, 3108, 3085, 1780, 1638, 1261, 1205, 1152, 827, 702 cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta = 7.19 (d, J = 8.8 \text{ Hz}, 2H, \text{ArH}), 7.41 (d, J = 8.5 \text{ Hz}, 2H, \text{ArH}), 7.50 (d, J = 8.9 \text{ Hz}, 2H, \text{ArH}), 7.60 (t, J = 7.6 \text{ Hz}, 2H, \text{ArH}), 7.66 (t, J = 8.2 \text{ Hz}, 1H, \text{ArH}) \text{ ppm.} \) \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta = 98.1, 116.6 (q, J_{C,F} = 289.4 \text{ Hz, CF3}), 119.6, 126.3, 129.7, 130.4, 130.5, 131.4, 132.8, 134.3, 151.1, 157.3, 166.5 (q, \(^2J_{C,F} = 38.1 \text{ Hz, COCF3}) \text{ ppm.} \) MS \(m/z\): 413 (M\(^+\)+2, 0.7), 411 (M\(^+\), 0.7), 183 (100). HRMS (EI) for C\(_{175}\)H\(_9\)BrF\(_3\)NO\(_3\) (M\(^+\)): Calcd, 410.9718. Found, 410.9727.

**2-(4-Bromophenyl)-4-trifluoroacetyl-3-methyl-1,3-oxazolium-5-olate (1b):** White crystals, 90% yield. mp 188–191 °C (mp\(^1\) 188–191 °C).

**4-Trifluoroacetyl-2,3-diphenyl-1,3-oxazolium-5-olate (1c):** Yellow crystals, 94% yield. mp 194–196 °C (mp\(^6\) 194–196 °C).

**4-Trifluoroacetyl-3-methyl-2-phenyl-1,3-oxazolium-5-olate (1d):** Pale yellow crystals, 95% yield. mp 161–163 °C (mp\(^6\) 162–163 °C).

**4-Trifluoroacetyl-2-methyl-3-phenyl-1,3-oxazolium-5-olate (1e):** White crystals, 90% yield. mp 200–203 °C (mp\(^6\) 211–212 °C).

**3-Benzyl-4-trifluoroacetyl-2-phenyl-1,3-oxazolium-5-olate (1f):** White crystals, 83% yield. mp 143–145 °C (mp\(^7\) 143–145 °C).

**2-tert-Butyl-4-trifluoroacetyl-3-phenyl-1,3-oxazolium-5-olate (1g):** White crystals, 72%
yield. mp 174–175 °C (mp5 174–175 °C).

**General Procedure for Synthesis of Acylphosphonium Zwitterions (2):** To a stirred solution of 1 (1.00 mmol) in THF (5 mL) was added n-tributylphosphine (380 μL, 1.50 mmol) at rt under atmosphere of argon, and the mixture was stirred for 2.5 to 6.5 h. The solvent was removed by evaporation, and the residue was recrystallized from ethyl acetate/hexane or purified by column chromatography (silica gel, hexane:ethyl acetate = 2:1) to give the product 2.

$^1$H, $^{13}$C and $^{31}$P NMR spectra of 2a, 2c and 2e showed intense broadening and considerable complexity due to their tautomeric and rotameric equilibria.

**Acylphosphonium zwitterion 2a:** Pale yellow crystals, 72% yield. mp 117–120 °C (ethyl acetate/hexane). IR (KBr) $\nu_{\text{max}} = 2958, 2932, 2872, 1655, 1536, 1344, 1214, 1185, 1146, 893, 759$ cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$) $\delta = 0.91$ (s, 9H, CH$_3$), 1.17–1.56 (br m, 12H, CH$_2$), 1.98–2.28 (br m, 6H, PCH$_2$), 7.02–7.40 (br m, 9H, ArH) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta = 13.3, 19.8$ (d, $^1J_{C-P} = 43.1$ Hz, PCH$_2$), 23.9 (d, $^2J_{C-P} = 14.6$ Hz, CH$_2$), 24.5, 27.2, 27.7, 117.1, 118.6 (q, $^1J_{C-F} = 295.7$ Hz, CF$_3$), 119.0, 119.5, 120.5, 121.0, 123.4, 124.1, 125.0, 125.3, 125.9, 128.3, 128.7, 130.8, 135.3, 137.3, 143.1, 144.5, 170.4, 171.9, 173.3, 173.6, 174.0, 174.1, 174.2, 174.5 ppm, the broadening and the complexity signals were observed in the downfield region. $^{31}$P NMR (202 MHz, CDCl$_3$) $\delta = 29.7$ ppm. MS $m/z$: 615 (M$^+2$, 2.2), 613 (M$^+$, 2.0), 333 (100). HRMS (EI) for C$_{29}$H$_{36}$BrF$_3$NO$_3$P (M$^+$): Calcd, 613.1568. Found, 613.1572.

**Acylphosphonium zwitterion 2b:** White crystals, 74% yield. mp 113–117 °C (ethyl acetate/hexane). IR (KBr) $\nu_{\text{max}} = 2958, 2931, 2872, 1641, 1539, 1375, 1215, 1178, 1135, 1012, 938, 868, 756$ cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$) $\delta = 0.91$ (t, $J = 7.4$ Hz, 9H, CH$_3$), 1.17–1.32 (m, 6H, CH$_2$), 1.36–1.43 (m, 6H, CH$_2$), 2.02–2.15 (m, 6H, PCH$_2$), 3.14 and 3.16 (s, 3H, NC$_3$H$_3$), 7.26 (d, $J = 8.4$ Hz, 2H, ArH), 7.35 (d, $J = 8.5$ Hz, 2H, ArH) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta = 13.3, 19.9$ (d, $^1J_{C-P} = 45.5$ Hz, PCH$_2$), 23.9 (d, $^2J_{C-P} = 15.4$ Hz, CH$_2$), 24.4 (d, $^3J_{C-P} = 4.3$ Hz, CH$_2$), 37.5
and 40.3, 118.3 (q, $^1J_{C-F} = 290.3$ Hz, CF$_3$), 121.4 (d, $^2J_{C-P} = 61.9$ Hz, NC), 123.0 and 123.7, 128.8 and 128.8, 130.6 and 131.4, 135.7 and 136.8, 172.9 (NC=O), 174.0 (qd, $^2J_{C-F} = 31.2$ Hz, $^3J_{C-P} = 3.6$ Hz, CF$_3$CO) ppm. $^{31}$P NMR (202 MHz, CDCl$_3$) $\delta = 29.2$ ppm. MS $m/z$: 553 (M$^+$$+2$, 0.8), 551 (M$^+$, 0.8), 202 (100). HRMS (EI) for C$_{24}$H$_{34}$BrF$_3$NO$_3$P (M$^+$): Calcd, 551.1412. Found, 551.1393.

**Acylphosphonium zwitterion 2c:** White crystals, 93% yield. mp 110–113 °C (ethyl acetate/hexane). IR (KBr) $\nu_{max} = 2960$, 2934, 2874, 1658, 1543, 1337, 1323, 1210, 1183, 1137, 890, 701 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$) $\delta = 0.92$ (br m, 9H, C$_3$H$_3$), 1.24–1.67 (br m, 12H, C$_2$H$_2$), 1.93–2.29 (br m, 6H, PC$_2$H$_2$), 7.03–7.65 (br m, 10H, ArH) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta = 13.3$, 19.9 (d, $^1J_{C-P} = 42.3$ Hz, PCH$_2$), 23.9 (d, $^2J_{C-P} = 14.6$ Hz, CH$_2$), 24.5, 118.4 (q, $^1J_{C-F} = 286.5$ Hz, CF$_3$), 125.0, 125.9, 126.9, 127.5, 128.1, 129.1, 136.4, 138.3, 143.4, 144.8, 171.4, 172.8, 174.3 ppm, the broadening and the complexity signals were observed in the downfield region. $^{31}$P NMR (202 MHz, CDCl$_3$) $\delta = 29.2$ ppm. MS $m/z$: 535 (M$^+$, 6), 333 (100). HRMS (EI) for C$_{29}$H$_{37}$F$_3$NO$_3$P (M$^+$): Calcd, 535.2463. Found, 535.2464.

**Acylphosphonium zwitterion 2d:** White crystals, 89% yield. mp 113–115 °C (ethyl acetate/hexane). IR (KBr) $\nu_{max} = 2960$, 2942, 2873, 1639, 1541, 1423, 1330, 1230, 1199, 1178, 1131, 943, 867, 705 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$) $\delta = 0.89$ and 0.96 (t, $^1J = 7.4$ Hz, 9H, C$_3$H$_3$), 1.15–1.29 (m, 6H, C$_2$H$_2$), 1.47–1.68 (m, 6H, C$_2$H$_2$), 1.96–2.14 (m, 6H, PC$_2$H$_2$), 3.05 and 3.18 (s, 3H, NCH$_3$), 7.20 (t, $^1J = 7.5$ Hz, 2H, ArH), 7.26 (t, $^1J = 7.1$ Hz, 1H, ArH), 7.32–7.39 (m, 2H, ArH) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta = 13.2$, 19.9 (d, $^1J_{C-P} = 45.0$ Hz, PCH$_2$), 23.8 (d, $^2J_{C-P} = 15.2$ Hz, CH$_2$), 24.3 (d, $^3J_{C-P} = 4.3$ Hz, CH$_2$), 37.4 and 40.3, 118.4 (q, $^1J_{C-F} = 290.3$ Hz, CF$_3$), 121.6 (d, $^2J_{C-P} = 62.3$ Hz, NC), 126.5 and 127.0, 127.3 and 128.1, 128.8 and 129.4, 136.8 and 137.8, 173.3 (d, $^1J_{C-P} = 47.9$ Hz, PCO), 173.9 (qd, $^2J_{C-F} = 31.9$ Hz, $^3J_{C-P} = 3.6$ Hz, CF$_3$CO), 173.9 ppm. $^{31}$P NMR (202 MHz, CDCl$_3$) $\delta = 29.2$ ppm. MS $m/z$: 473 (M$^+$, 4.4), 271 (100). HRMS (EI) for C$_{24}$H$_{35}$F$_3$NO$_3$P (M$^+$): Calcd, 473.2307. Found, 473.2286.
**Acylphosphonium zwitterion 2e:** Pale yellow oil, 86% yield. IR (neat) $\nu_{\text{max}}$ 2961, 2935, 2874, 1674, 1541, 1228, 1216, 1183, 1142, 883, 754 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 0.93 (t, $J$ = 7.0 Hz, 9H, CH$_3$), 1.44–1.51 (br m, 12H, CH$_2$), 2.03 and 2.12 (s, 3H, CH$_3$), 2.29 (br s, 6H, PCH$_2$), 7.11–7.43 (br m, 5H, ArH) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ = 13.3, 20.0 (d, $^1J_{C-P}$ = 44.7 Hz, PCH$_2$), 22.6, 22.8, 23.9 (d, $^2J_{C-P}$ = 14.5 Hz, CH$_2$), 24.6, 24.8, 117.1, 118.5 (q, $^1J_{C-F}$ = 282.3 Hz, CF$_3$), 119.1, 119.5, 119.8, 120.4 (d, $^2J_{C-P}$ = 62.4 Hz, NC), 125.3, 125.4, 126.7, 127.6, 128.0, 128.4, 128.6, 129.8, 130.1, 143.4, 144.8, 171.5, 172.7, 173.4 (d, $^1J_{C-P}$ = 51.0 Hz, PCO), 174.3, 174.9 (qd, $^2J_{C-F}$ = 31.8 Hz, $^3J_{C-P}$ = 2.5 Hz, CF$_3$CO) ppm, the broadening and the complexity signals were observed. $^{31}$P NMR (202 MHz, CDCl$_3$) $\delta$ = 29.5 ppm. MS m/z: 473 (M$^+$, 0.8), 218 (100). HRMS (EI) for C$_{24}$H$_{35}$F$_3$NO$_3$P (M$^+$): Calcd, 473.2307. Found, 473.2286.

**Acylphosphonium zwitterion 2f:** White crystals, 89% yield. mp 85–88 °C (ethyl acetate/hexane). IR (KBr) $\nu_{\text{max}}$ 2962, 2933, 2874, 1637, 1546, 1455, 1444, 1434, 1383, 1324, 1304, 1214, 1175, 1131, 934, 730, 696 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 0.86 (t, $J$ = 7.4 Hz, 9H, CH$_3$), 0.91–1.05 (m, 6H, CH$_2$), 1.24–1.32 (m, 6H, CH$_2$), 1.72–1.90 (m, 6H, PCH$_2$), 4.25 and 5.50 (d, $^1J_{C-P}$ = 14.0 Hz, 2H, ArCH$_2$), 7.18–7.26 (m, 6H, ArH), 7.39–7.45 (m, 4H, ArH) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ = 13.1, 20.2 (d, $^1J_{C-P}$ = 45.4 Hz, PCH$_2$), 23.8 (d, $^2J_{C-P}$ = 15.1 Hz, CH$_2$), 24.2 (d, $^3J_{C-P}$ = 4.3 Hz, CH$_2$), 52.4, 117.9 (d, $^2J_{C-P}$ = 62.5 Hz, NC), 118.4 (q, $^1J_{C-F}$ = 289.8 Hz, CF$_3$), 126.6, 127.2, 127.3, 128.8, 130.6, 136.6 and 138.1, 173.3, 173.8 (d, $^1J_{C-P}$ = 49.7 Hz, PCO), 173.9 (qd, $^2J_{C-F}$ = 30.5 Hz, $^3J_{C-P}$ = 2.9 Hz, CF$_3$CO) ppm. $^{31}$P NMR (202 MHz, CDCl$_3$) $\delta$ = 28.5 ppm. MS m/z: 549 (M$^+$, 2.3), 347 (100). HRMS (EI) for C$_{30}$H$_{39}$F$_3$NO$_3$P (M$^+$): Calcd, 549.2620. Found, 549.2611.

**Acylphosphonium zwitterion 2g:** Pale yellow oil, 95% yield. IR (neat) $\nu_{\text{max}}$ 2961, 2934, 2874, 1650, 1537, 1213, 1191, 1165, 1138, 867, 727 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 0.87 (t, $J$ = 7.1 Hz, 9H, CH$_3$), 1.10 (s, 9H, CH$_3$), 1.34–1.47 (m, 12H, CH$_2$), 2.12–2.26 (m, 6H, PCH$_2$), 7.20 (t, $J$ = 7.4 Hz, 1H, ArH), 7.27 (t, $J$ = 7.6 Hz, 2H, ArH), 7.47 (d, $J$ = 7.9 Hz, 2H, ArH) ppm. $^{13}$C
NMR (126 MHz, CDCl₃) δ = 13.3, 20.0 (d, J_C-P = 45.0 Hz, PCH₂), 23.9 (d, J_C-P = 14.3 Hz, CH₂), 24.6 (d, J_C-P = 4.1 Hz, CH₂), 29.6, 41.2, 118.8 (q, J_C-F = 290.3 Hz, CF₃), 121.5 (d, J_C-P = 62.8 Hz, NC), 126.7 and 126.8, 128.1 and 128.5, 129.4 and 129.4, 144.7, 173.2 (d, J_C-P = 47.8 Hz, PCO), 174.3 (qd, J_C-F = 30.7 Hz, J_C-P = 3.4 Hz, CF₃CO), 180.0 ppm.  

^31P NMR (202 MHz, CDCl₃) δ = 27.5 ppm.  

MS m/z: 515 (M⁺, 3.8), 202 (100).  HRMS (EI) for C₂₇H₄₁F₃NO₃P (M⁺): Calcd, 515.2776.  Found, 515.2781.

**General Procedure for Reaction of Acylphosphonium Zwitterion with Acyl Chloride:** To a stirred suspension of 2d (142 mg, 0.30 mmol) and potassium carbonate (124 mg, 0.90 mmol) in dry toluene (3 mL) was added acyl chloride (0.45 mmol) at 0 °C, and the mixture was heated at 80 °C for 8 to 14 h. After acidified with 10% aq HCl, the mixture was extracted with ethyl acetate (x3). The combined organic layers were washed with brine, dried over anhyd MgSO₄, and evaporated. The residue was purified by column chromatography (silica gel, hexane:ethyl acetate = 6:1) to give the product 3.

**Trifluoromethylated enol ester 3a:** Colorless oil, 23% yield.  IR (neat) ν_max 2929, 2855, 1784, 1667, 1371, 1277, 1175, 1126, 1052, 897, 839, 795, 724 cm⁻¹.  ¹H NMR (500 MHz, CDCl₃) δ = 2.31 (s, 3H, COCH₃), 3.28 (s, 3H, NCH₃), 7.06 (br s, 1H, CH=C), 7.46 (t, J = 7.7 Hz, 2H, ArH), 7.52 (t, J = 7.1 Hz, 1H, ArH), 7.59 (d, J = 7.1 Hz, 2H, ArH) ppm.  ¹³C NMR (126 MHz, CDCl₃) δ = 20.2, 33.1, 120.7 (q, J_C-F = 274.2 Hz, CF₃), 120.7 (q, J_C-P = 37.4 Hz, CCF₃), 126.1 (br, CH=C), 128.6, 128.6, 131.6, 133.7, 167.3, 171.0 ppm.  MS m/z: 287 (M⁺, 41.7), 245 (100).  HRMS (EI) for C₁₃H₁₂F₃NO₃ (M⁺): Calcd, 287.0769.  Found, 287.0779.

**Trifluoromethylated enol ester 3b:** Colorless oil, 62% yield.  IR (neat) ν_max 2979, 2940, 1776, 1668, 1370, 1277, 1179, 1126, 1043, 794, 723, 652 cm⁻¹.  ¹H NMR (500 MHz, CDCl₃) δ = 1.31 (d, J = 7.0 Hz, 6H, CH₃), 2.81 (sep, J = 7.0 Hz, 1H, COCH₃), 3.14 (s, 3H, NCH₃), 7.07 (br s, 1H, CH=C), 7.45 (t, J = 7.6 Hz, 2H, ArH), 7.51 (t, J = 7.3 Hz, 1H, ArH), 7.61 (d, J = 7.0 Hz, 2H,
ArH) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ = 18.6 and 18.7, 19.1, 33.3 and 33.9, 120.7 (q, $^1$J$_{C-F}$ = 271.7 Hz, CF$_3$), 120.7 (q, $^2$J$_{C-F}$ = 36.2 Hz, CCF$_3$), 126.1 (br, CH=C), 128.6, 128.7, 131.5, 133.8, 171.0, 173.6 ppm. MS $m/z$: 315 (M$^+$, 2.9), 105 (100). HRMS (EI) for C$_{15}$H$_{16}$F$_3$NO$_3$ (M$^+$): Calcd, 315.1082. Found, 315.1068.

Trifluoromethylated enol ester 3c: Colorless oil, 41% yield. IR (neat) $\nu$$_{max}$ 2978, 2938, 1771, 1668, 1481, 1370, 1278, 1180, 1126, 1070, 1022, 794, 722 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 1.34 (s, 9H, CC$_3$H$_3$), 3.26 (s, 3H, NC$_3$H$_3$), 7.08 (br s, 1H, CH=C), 7.45 (t, $J$ = 7.6 Hz, 2H, ArH), 7.51 (t, $J$ = 7.3 Hz, 1H, ArH), 7.62 (d, $J$ = 6.9 Hz, 2H, ArH) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ = 26.9, 33.4, 39.2, 120.8 (q, $^1$J$_{C-F}$ = 272.1 Hz, CF$_3$), 120.8 (q, $^2$J$_{C-F}$ = 36.1 Hz, CCF$_3$), 126.2 (q, $^3$J$_{C-F}$ = 5.5 Hz, CH=C), 128.6, 128.7, 131.5, 133.8, 171.0, 175.2 ppm. MS $m/z$: 329 (M$^+$, 9), 105 (100). HRMS (EI) for C$_{16}$H$_{18}$F$_3$NO$_3$ (M$^+$): Calcd, 329.1239. Found, 329.1236.

Trifluoromethylated enol ester 3d: Colorless oil, 43% yield. IR (neat) $\nu$$_{max}$ 3064, 2961, 2928, 1755, 1667, 1452, 1371, 1278, 1240, 1178, 1127, 1069, 1013, 705 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 3.26 (s, 3H, NC$_3$H$_3$), 7.20 (br s, 1H, CH=C), 7.47 (t, $J$ = 7.6 Hz, 2H, ArH), 7.53 (t, $J$ = 7.0 Hz, 1H, ArH), 7.54 (t, $J$ = 7.6 Hz, 2H, ArH), 7.65 (d, $J$ = 7.0 Hz, 2H, ArH), 7.68 (t, $J$ = 7.5 Hz, 1H, ArH), 8.16 (d, $J$ = 7.3 Hz, 2H, ArH) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ = 33.3, 120.7 (q, $^2$J$_{C-F}$ = 36.6 Hz, CCF$_3$), 120.8 (q, $^1$J$_{C-F}$ = 271.8 Hz, CF$_3$), 126.4 (q, $^3$J$_{C-F}$ = 1.9 Hz, CH=C), 127.5, 128.7, 128.7, 129.0, 130.6, 131.6, 133.8, 134.6, 163.3, 171.0 ppm. MS $m/z$: 315 (M$^+$, 2.9), 105 (100). HRMS (EI) for C$_{18}$H$_{14}$F$_3$NO$_3$ (M$^+$): Calcd, 349.0926. Found, 349.0939.

X-Ray Crystallographic Data

Data Collection: A colorless block crystal of C$_{29}$H$_{36}$BrF$_3$NO$_3$P (2a; CCDC no. 1440729) having approximate dimensions of 0.200 x 0.200 x 0.150 mm was mounted on a glass fiber. All measurements were made on a Rigaku Saturn 724 diffractometer using multi-layer mirror monochromated Mo-K$\alpha$ radiation. The crystal-to-detector distance was 45.15 mm.
Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions: \( a = 9.477(5) \) Å, \( b = 15.308(8) \) Å, \( c = 21.114(11) \) Å, \( \beta = 102.525(10)^\circ \), \( V = 2990(3) \) Å\(^3\). For \( Z = 4 \) and F.W. = 614.48, the calculated density is 1.365 g/cm\(^3\). The reflection conditions of: \( h0l: h+l = 2n, 0k0: k = 2n \), uniquely determine the space group to be: \( \text{P2}_1/n \) (#14)

The data were collected at a temperature of \(-172 \pm 1 \) °C to a maximum 2θ value of 62.5°. A total of 1440 oscillation images were collected. A sweep of data was done using \( \omega \) oscillations from \(-110.0 \) to 70.0° in 0.5° steps. The exposure rate was 4.0 [sec./°]. The detector swing angle was \(-19.85^\circ\). A second sweep was performed using \( \omega \) oscillations from \(-110.0 \) to 70.0° in 0.5° steps. The exposure rate was 4.0 [sec./°]. The detector swing angle was \(-19.85^\circ\). Another sweep was performed using \( \omega \) oscillations from \(-110.0 \) to 70.0° in 0.5° steps. The exposure rate was 4.0 [sec./°]. The detector swing angle was \(-19.85^\circ\). Another sweep was performed using \( \omega \) oscillations from \(-110.0 \) to 70.0° in 0.5° steps. The exposure rate was 4.0 [sec./°]. The detector swing angle was \(-19.85^\circ\). The crystal-to-detector distance was 45.15 mm. Readout was performed in the 0.141 mm pixel mode.

**Data Reduction:** Of the 53268 reflections that were collected, 8684 were unique (\( R_{int} = 0.0553 \)). Data were collected and processed using CrystalClear (Rigaku).\(^8\)

The linear absorption coefficient, \( \mu \), for Mo-K\(\alpha \) radiation is 14.805 cm\(^{-1}\). An empirical absorption correction was applied which resulted in transmission factors ranging from 0.710 to 0.801. The data were corrected for Lorentz and polarization effects.

**Structure Solution and Refinement:** The structure was solved by direct methods\(^9\) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement\(^10\) on \( F^2 \) was based on 8684 observed reflections and 343 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement.
factors of: \( R_1 = \Sigma |F_o| - |F_c| / \Sigma |F_o| = 0.0717, \ wR_2 = \left[ \Sigma (w(F_o^2 - F_c^2)^2) / \Sigma (wF_o^2)^2 \right]^{1/2} = 0.1968. \)

The standard deviation of an observation of unit weight\(^{11}\) was 1.17. Unit weights were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.98 and \(-1.22\) e\(^{-}/\text{Å}\(^3\), respectively.

Neutral atom scattering factors were taken from Cromer and Waber.\(^{12}\) Anomalous dispersion effects were included in Fcalc;\(^{13}\) the values for \(\Delta f'\) and \(\Delta f''\) were those of Creagh and McAuley.\(^{14}\) The values for the mass attenuation coefficients are those of Creagh and Hubbell.\(^{15}\) All calculations were performed using the CrystalStructure\(^{16}\) crystallographic software package except for refinement, which was performed using SHELXL-97.\(^{17}\)

### Crystal Data and Structure Refinement for 3a

**Crystal Data**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>(\text{C}<em>{29}\text{H}</em>{36}\text{BrF}_3\text{NO}_3\text{P})</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>614.48</td>
</tr>
<tr>
<td>Crystal Color, Habit</td>
<td>colorless, block</td>
</tr>
<tr>
<td>Crystal Dimensions</td>
<td>0.200 x 0.200 x 0.150 mm</td>
</tr>
<tr>
<td>Crystal System</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Lattice Type</td>
<td>Primitive</td>
</tr>
<tr>
<td>Lattice Parameters</td>
<td>(a = 9.477(5) \text{ Å})</td>
</tr>
<tr>
<td></td>
<td>(b = 15.308(8) \text{ Å})</td>
</tr>
<tr>
<td></td>
<td>(c = 21.114(11) \text{ Å})</td>
</tr>
<tr>
<td></td>
<td>(\beta = 102.525(10) ^\circ)</td>
</tr>
<tr>
<td></td>
<td>(V = 2990(3) \text{ Å}^3)</td>
</tr>
<tr>
<td>Space Group</td>
<td>(\text{P}2_1/\text{n} \ (#14))</td>
</tr>
<tr>
<td>Property</td>
<td>Value</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>Z value</td>
<td>4</td>
</tr>
<tr>
<td>$D_{\text{calc}}$</td>
<td>1.365 g/cm$^3$</td>
</tr>
<tr>
<td>$F_{000}$</td>
<td>1272.00</td>
</tr>
<tr>
<td>$\mu(\text{MoK}\alpha)$</td>
<td>14.805 cm$^{-1}$</td>
</tr>
</tbody>
</table>

**Intensity Measurements**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffractometer</td>
<td>Saturn724</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoK$\alpha$ ($\lambda = 0.71075$ Å)</td>
</tr>
<tr>
<td>multi-layer mirror monochromated</td>
<td></td>
</tr>
<tr>
<td>Voltage, Current</td>
<td>50 kV, 24 mA</td>
</tr>
<tr>
<td>Temperature</td>
<td>$-172.8$ °C</td>
</tr>
<tr>
<td>Detector Aperture</td>
<td>70 x 70 mm</td>
</tr>
<tr>
<td>Data Images</td>
<td>1440 exposures</td>
</tr>
<tr>
<td>$\omega$ oscillation Range</td>
<td>$-110.0$ – $70.0$ °</td>
</tr>
<tr>
<td>Exposure Rate</td>
<td>4.0 sec./°</td>
</tr>
<tr>
<td>Detector Swing Angle</td>
<td>$-19.85$ °</td>
</tr>
<tr>
<td>$\omega$ oscillation Range</td>
<td>$-110.0$ – $70.0$ °</td>
</tr>
<tr>
<td>Exposure Rate</td>
<td>4.0 sec./°</td>
</tr>
<tr>
<td>Detector Swing Angle</td>
<td>$-19.85$ °</td>
</tr>
<tr>
<td>$\omega$ oscillation Range</td>
<td>$-110.0$ – $70.0$ °</td>
</tr>
<tr>
<td>Exposure Rate</td>
<td>4.0 sec./°</td>
</tr>
<tr>
<td>Detector Swing Angle</td>
<td>$-19.85$ °</td>
</tr>
<tr>
<td>Detector Position</td>
<td>45.15 mm</td>
</tr>
<tr>
<td>Pixel Size</td>
<td>0.141 mm</td>
</tr>
<tr>
<td>$2\theta_{\text{max}}$</td>
<td>62.5 °</td>
</tr>
<tr>
<td>No. of Reflections Measured</td>
<td>Total: 53268</td>
</tr>
</tbody>
</table>
Unique: 8684 ($R_{int} = 0.0553$)

Corrections
Lorentz-polarization
Absorption
(trans. factors: 0.710 – 0.801)

Structure Solution and Refinement

Structure Solution
Direct Methods

Refinement
Full-matrix least-squares on $F^2$

Function Minimized
$\Sigma w (Fo^2 - Fc^2)^2$

Least Squares Weights
$w = 1/[\sigma^2(Fo^2) + (0.1041 \cdot P)^2$
$+ 0.1945 \cdot P]$

where $P = (\text{Max}(Fo^2,0) + 2Fc^2)/3$

$2\theta_{\text{max}}$ cutoff
60.0 °

Anomalous Dispersion
All non-hydrogen atoms

No. Observations (All reflections)
8684

No. Variables
343

Reflection/Parameter Ratio
25.32

Residuals: $R1$ (I > 2.00σ(I))
0.0717

Residuals: $R$ (All reflections)
0.0874

Residuals: $wR2$ (All reflections)
0.1968

Goodness of Fit Indicator
1.167

Max Shift/Error in Final Cycle
0.001

Maximum peak in Final Diff. Map
1.98 e/$\text{Å}^3$

Minimum peak in Final Diff. Map
$-1.22$ e/$\text{Å}^3$
$^1$H NMR Spectra of 2a

$^{13}$C NMR Spectra of 2a
$^{31}$P NMR Spectra of 2a

$^1$H NMR Spectra of 2b
$^{13}$C NMR Spectra of 2b

$^{31}$P NMR Spectra of 2b
H NMR Spectra of 2c

\[ \text{NMR Spectra} \]

C NMR Spectra of 2c

\[ \text{NMR Spectra} \]
$^{31}$P NMR Spectra of 2c

$^1$H NMR Spectra of 2d
$^{13}$C NMR Spectra of 2d

$^{31}$P NMR Spectra of 2d
$^1$H NMR Spectra of 2e

$^{13}$C NMR Spectra of 2e
$^{31}\text{P NMR Spectra of } 2e$

$^1\text{H NMR Spectra of } 2f$
$^{13}$C NMR Spectra of 2f

$^{31}$P NMR Spectra of 2f
$^1$H NMR Spectra of 2g

$^{13}$C NMR Spectra of 2g
$^{31}$P NMR Spectra of 2g
$^1$H NMR Spectra of 3a

$^{13}$C NMR Spectra of 3a
$^{1}H$ NMR Spectra of 3b

![H NMR Spectra of 3b](image)

$^{13}C$ NMR Spectra of 3b

![C NMR Spectra of 3b](image)
$^1$H NMR Spectra of 3c

$^{13}$C NMR Spectra of 3c
References:


(10) Least Squares function minimized (SHELXL97):
\[ \sum w(F_0^2-F_c^2)^2 \] where w = Least Squares weights.

(11) Standard deviation of an observation of unit weight:
\[ [\sum w(F_0^2-F_c^2)^2/(N_o-N_v)]^{1/2} \] where: \( N_o \) = number of observations, \( N_v \) = number of variables.


