

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

Ryosuke Saijo,^a Hidemitsu Uno,^b Shigeki Mori^c and Masami Kawase*^a

^a*Faculty of Pharmaceutical Sciences, Matsuyama University, Matsuyama, Ehime 790-8578, Japan.*

^b*Department of Chemistry and Biology, Graduate School of Science and Engineerig, Ehime University, Matsuyama, 790-8577, Japan.*

^c*Advanced Research Support Center, Ehime University, Matsuyama, 790-8577, Japan.*

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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 ^1H , 126 MHz for ^{13}C) with tetramethylsilane (Me_4Si) as an internal reference and CDCl_3 as the solvent. ^1H and ^{13}C NMR spectral data are reported in parts per million (δ) relative to Me_4Si . ^{31}P NMR spectra were recorded on a Bruker AVANCE500 (202 MHz) and are reported relative to 85% H_3PO_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-K α radiation at the Integrated Center for Science, Ehime University. Standard work-up means that the organic layers were finally dried over anhyd. Na_2SO_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) ν_{max} 3447, 3059, 2940, 1739, 1615, 1597, 1562, 1423, 1399, 1220, 1197, 759 cm^{-1} . ^1H 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 ($\text{M}^+ + 2$, 18.9), 333 (M^+ , 19.1), 185 (100), 183 (100). HRMS (EI) for $\text{C}_{15}\text{H}_{12}\text{BrNO}_3$ (M^+): Calcd, 333.0001. Found, 332.9989.

***N*-(4-Bromobenzoyl)-*N*-methylglycine:** mp 147–150 °C (mp¹ 147–150 °C)

***N*-Benzoyl-*N*-phenylglycine:** mp 126–128 °C (mp² 127–129 °C).

***N*-Benzoyl-*N*-methylglycine:** mp 101–104 °C (mp² 102–104 °C).

***N*-Acetyl-*N*-phenylglycine:** mp 196–198 °C (mp³ 193–195 °C).

***N*-Benzoyl-*N*-benzylglycine:** mp 106–107 °C (mp⁴ 106–107 °C).

***N*-Phenyl-*N*-pivaloylglycine:** mp 123–124 °C (mp⁵ 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) ν_{\max} 3435, 3108, 3085, 1780, 1638, 1261, 1205, 1152, 827, 702 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ = 7.19 (d, *J* = 8.8 Hz, 2H, Ar*H*), 7.41 (d, *J* = 8.5 Hz, 2H, Ar*H*), 7.50 (d, *J* = 8.9 Hz, 2H, Ar*H*), 7.60 (t, *J* = 7.6 Hz, 2H, Ar*H*), 7.66 (t, *J* = 8.2 Hz, 1H, Ar*H*) ppm. ¹³C NMR (126 MHz, CDCl₃) δ = 98.1, 116.6 (q, ¹*J*_{C-F} = 289.4 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, ²*J*_{C-F} = 38.1 Hz, COCF₃) ppm. MS *m/z*: 413 (M⁺+2, 0.7), 411 (M⁺, 0.7), 183 (100). HRMS (EI) for C₁₇H₉BrF₃NO₃ (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 (mp¹ 188–191 °C).

4-Trifluoroacetyl-2,3-diphenyl-1,3-oxazolium-5-olate (1c): Yellow crystals, 94% yield. mp 194–196 °C (mp⁶ 194–196 °C).

4-Trifluoroacetyl-3-methyl-2-phenyl-1,3-oxazolium-5-olate (1d): Pale yellow crystals, 95% yield. mp 161–163 °C (mp⁶ 162–163 °C).

4-Trifluoroacetyl-2-methyl-3-phenyl-1,3-oxazolium-5-olate (1e): White crystals, 90% yield. mp 200–203 °C (mp⁶ 211–212 °C).

3-Benzyl-4-trifluoroacetyl-2-phenyl-1,3-oxazolium-5-olate (1f): White crystals, 83% yield. mp 143–145 °C (mp⁷ 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 μ L, 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**.

¹H, ¹³C and ³¹P 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) ν_{\max} = 2958, 2932, 2872, 1655, 1536, 1344, 1214, 1185, 1146, 893, 759 cm^{-1} . ¹H NMR (500 MHz, CDCl₃) δ = 0.91 (s, 9H, CH₃), 1.17–1.56 (br m, 12H, CH₂), 1.98–2.28 (br m, 6H, PCH₂), 7.02–7.40 (br m, 9H, ArH) ppm. ¹³C NMR (126 MHz, CDCl₃) δ = 13.3, 19.8 (d, ¹J_{C-P} = 43.1 Hz, PCH₂), 23.9 (d, ²J_{C-P} = 14.6 Hz, CH₂), 24.5, 27.2, 27.7, 117.1, 118.6 (q, ¹J_{C-F} = 295.7 Hz, CF₃), 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. ³¹P NMR (202 MHz, CDCl₃) δ = 29.7 ppm. MS *m/z*: 615 (M⁺², 2.2), 613 (M⁺, 2.0), 333 (100). HRMS (EI) for C₂₉H₃₆BrF₃NO₃P (M⁺): Calcd, 613.1568. Found, 613.1572.

Acylphosphonium zwitterion 2b: White crystals, 74% yield. mp 113–117 °C (ethyl acetate/hexane). IR (KBr) ν_{\max} = 2958, 2931, 2872, 1641, 1539, 1375, 1215, 1178, 1135, 1012, 938, 868, 756 cm^{-1} . ¹H NMR (500 MHz, CDCl₃) δ = 0.91 (t, *J* = 7.4 Hz, 9H, CH₃), 1.17–1.32 (m, 6H, CH₂), 1.36–1.43 (m, 6H, CH₂), 2.02–2.15 (m, 6H, PCH₂), 3.14 and 3.16 (s, 3H, NCH₃), 7.26 (d, *J* = 8.4 Hz, 2H, ArH), 7.35 (d, *J* = 8.5 Hz, 2H, ArH) ppm. ¹³C NMR (126 MHz, CDCl₃) δ = 13.3, 19.9 (d, ¹J_{C-P} = 45.5 Hz, PCH₂), 23.9 (d, ²J_{C-P} = 15.4 Hz, CH₂), 24.4 (d, ³J_{C-P} = 4.3 Hz, CH₂), 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), 173.1 (d, $^1J_{C-P} = 48.2$ Hz, PCO), 174.0 (qd, $^2J_{C-F} = 31.2$ Hz, $^3J_{C-P} = 3.6$ Hz, CF_3CO) 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 $C_{24}H_{34}BrF_3NO_3P$ (M^+): Calcd, 551.1412. Found, 551.1393.

Acylphosphonium zwitterion 2c: White crystals, 93% yield. mp 110–113 °C (ethyl acetate/hexane). IR (KBr) $\nu_{max} = 2960, 2933, 2874, 1658, 1543, 1337, 1323, 1210, 1183, 1137, 890, 701$ cm^{-1} . 1H NMR (500 MHz, $CDCl_3$) $\delta = 0.92$ (br m, 9H, CH_3), 1.24–1.67 (br m, 12H, CH_2), 1.93–2.29 (br m, 6H, PCH_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, 118.5 (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 $C_{29}H_{37}F_3NO_3P$ (M^+): Calcd, 535.2463. Found, 535.2464.

Acylphosphonium zwitterion 2d: White crystals, 89% yield. mp 113–115 °C (ethyl acetate/hexane). IR (KBr) $\nu_{max} = 2954, 2942, 2873, 1639, 1541, 1423, 1330, 1230, 1219, 1178, 1131, 943, 867, 705$ cm^{-1} . 1H NMR (500 MHz, $CDCl_3$) $\delta = 0.89$ and 0.96 (t, $J = 7.4$ Hz, 9H, CH_3), 1.15–1.29 (m, 6H, CH_2), 1.47–1.68 (m, 6H, CH_2), 1.96–2.14 (m, 6H, PCH_2), 3.05 and 3.18 (s, 3H, NCH_3), 7.20 (t, $J = 7.5$ Hz, 2H, ArH), 7.26 (t, $J = 7.1$ 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_3CO), 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 $C_{24}H_{35}F_3NO_3P$ (M^+): Calcd, 473.2307. Found, 473.2286.

Acylphosphonium zwitterion 2e: Pale yellow oil, 86% yield. IR (neat) ν_{\max} 2961, 2935, 2874, 1674, 1541, 1228, 1216, 1183, 1142, 883, 754 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ = 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) δ = 13.3, 20.0 (d, $^1J_{\text{C-P}}$ = 44.7 Hz, CH_2), 20.2 (d, $^1J_{\text{C-P}}$ = 45.0 Hz, PCH_2), 22.3, 22.7, 23.9 (d, $^2J_{\text{C-P}}$ = 14.5 Hz, CH_2), 24.6, 24.8, 117.1, 118.5 (q, $^1J_{\text{C-F}}$ = 282.3 Hz, CF_3), 119.1, 119.5, 119.8, 120.4 (d, $^2J_{\text{C-P}}$ = 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, $^1J_{\text{C-P}}$ = 51.0 Hz, PCO), 174.3, 174.9 (qd, $^2J_{\text{C-F}}$ = 31.8 Hz, $^3J_{\text{C-P}}$ = 2.5 Hz, CF_3CO) ppm, the broadening and the complexity signals were observed. ^{31}P NMR (202 MHz, CDCl_3) δ = 29.5 ppm. MS m/z : 473 (M^+ , 0.8), 218 (100). HRMS (EI) for $\text{C}_{24}\text{H}_{35}\text{F}_3\text{NO}_3\text{P}$ (M^+): Calcd, 473.2307. Found, 473.2286.

Acylphosphonium zwitterion 2f: White crystals, 89% yield. mp 85–88 °C (ethyl acetate/hexane). IR (KBr) ν_{\max} 2962, 2933, 2874, 1637, 1546, 1455, 1444, 1434, 1383, 1324, 1304, 1214, 1175, 1131, 934, 730, 696 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ = 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, J = 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) δ = 13.1, 20.2 (d, $^1J_{\text{C-P}}$ = 45.4 Hz, PCH_2), 23.8 (d, $^2J_{\text{C-P}}$ = 15.1 Hz, CH_2), 24.2 (d, $^3J_{\text{C-P}}$ = 4.3 Hz, CH_2), 52.4, 117.9 (d, $^2J_{\text{C-P}}$ = 62.5 Hz, NC), 118.4 (q, $^1J_{\text{C-F}}$ = 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, $^1J_{\text{C-P}}$ = 49.7 Hz, PCO), 173.9 (qd, $^2J_{\text{C-F}}$ = 30.5 Hz, $^3J_{\text{C-P}}$ = 2.9 Hz, CF_3CO) ppm. ^{31}P NMR (202 MHz, CDCl_3) δ = 28.5 ppm. MS m/z : 549 (M^+ , 2.3), 347 (100). HRMS (EI) for $\text{C}_{30}\text{H}_{39}\text{F}_3\text{NO}_3\text{P}$ (M^+): Calcd, 549.2620. Found, 549.2611.

Acylphosphonium zwitterion 2g: Pale yellow oil, 95% yield. IR (neat) ν_{\max} 2961, 2934, 2874, 1650, 1537, 1213, 1191, 1165, 1138, 867, 727 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ = 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, $^1J_{C-P}$ = 45.0 Hz, PCH₂), 23.9 (d, $^2J_{C-P}$ = 14.3 Hz, CH₂), 24.6 (d, $^3J_{C-P}$ = 4.1 Hz, CH₂), 29.6, 41.2, 118.8 (q, $^1J_{C-F}$ = 290.3 Hz, CF₃), 121.5 (d, $^2J_{C-P}$ = 62.8 Hz, NC), 126.7 and 126.8, 128.1 and 128.5, 129.4 and 129.4, 144.7, 173.2 (d, $^1J_{C-P}$ = 47.8 Hz, PCO), 174.3 (qd, $^2J_{C-F}$ = 30.7 Hz, $^3J_{C-P}$ = 3.4 Hz, CF₃CO), 180.0 ppm. ^{31}P 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. ^{13}C NMR (126 MHz, CDCl₃) δ = 20.2, 33.1, 120.7 (q, $^1J_{C-F}$ = 274.2 Hz, CF₃), 120.7 (q, $^2J_{C-F}$ = 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, 1071, 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, COCH), 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) δ = 18.6 and 18.7, 19.1, 33.3 and 33.9, 120.7 (q, $^1J_{\text{C-F}}$ = 271.7 Hz, CF_3), 120.7 (q, $^2J_{\text{C-F}}$ = 36.2 Hz, CCF_3), 126.1 (br, $\text{CH}=\text{C}$), 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 $\text{C}_{15}\text{H}_{16}\text{F}_3\text{NO}_3$ (M^+): Calcd, 315.1082. Found, 315.1068.

Trifluoromethylated enol ester 3c: Colorless oil, 41% yield. IR (neat) ν_{max} 2978, 2938, 1771, 1668, 1481, 1370, 1278, 1180, 1126, 1070, 1022, 794, 722 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ = 1.34 (s, 9H, CCH_3), 3.26 (s, 3H, NCH_3), 7.08 (br s, 1H, $\text{CH}=\text{C}$), 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) δ = 26.9, 33.4, 39.2, 120.8 (q, $^1J_{\text{C-F}}$ = 272.1 Hz, CF_3), 120.8 (q, $^2J_{\text{C-F}}$ = 36.1 Hz, CCF_3), 126.2 (q, $^3J_{\text{C-F}}$ = 5.5 Hz, $\text{CH}=\text{C}$), 128.6, 128.7, 131.5, 133.8, 171.0, 175.2 ppm. MS m/z : 329 (M^+ , 9), 105 (100). HRMS (EI) for $\text{C}_{16}\text{H}_{18}\text{F}_3\text{NO}_3$ (M^+): Calcd, 329.1239. Found, 329.1236.

Trifluoromethylated enol ester 3d: Colorless oil, 43% yield. IR (neat) ν_{max} 3064, 2961, 2928, 1755, 1667, 1452, 1371, 1278, 1240, 1178, 1127, 1069, 1013, 705 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ = 3.26 (s, 3H, NCH_3), 7.20 (br s, 1H, $\text{CH}=\text{C}$), 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) δ = 33.3, 120.7 (q, $^2J_{\text{C-F}}$ = 36.6 Hz, CCF_3), 120.8 (q, $^1J_{\text{C-F}}$ = 271.8 Hz, CF_3), 126.4 (q, $^3J_{\text{C-F}}$ = 1.9 Hz, $\text{CH}=\text{C}$), 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 $\text{C}_{18}\text{H}_{14}\text{F}_3\text{NO}_3$ (M^+): Calcd, 349.0926. Found, 349.0939.

X-Ray Crystallographic Data

Data Collection: A colorless block crystal of $\text{C}_{29}\text{H}_{36}\text{BrF}_3\text{NO}_3\text{P}$ (**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 α 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: $a = 9.477(5) \text{ \AA}$, $b = 15.308(8) \text{ \AA}$, $c = 21.114(11) \text{ \AA}$, $\beta = 102.525(10)^\circ$, $V = 2990(3) \text{ \AA}^3$. 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: $P2_1/n$ (#14)

The data were collected at a temperature of $-172 \pm 1 \text{ }^\circ\text{C}$ to a maximum 2θ value of 62.5° . A total of 1440 oscillation images were collected. A sweep of data was done using ω oscillations from -110.0 to 70.0° in 0.5° steps. The exposure rate was $4.0 \text{ [sec./}^\circ\text{]}$. The detector swing angle was -19.85° . A second sweep was performed using ω oscillations from -110.0 to 70.0° in 0.5° steps. The exposure rate was $4.0 \text{ [sec./}^\circ\text{]}$. The detector swing angle was -19.85° . Another sweep was performed using ω oscillations from -110.0 to 70.0° in 0.5° steps. The exposure rate was $4.0 \text{ [sec./}^\circ\text{]}$. The detector swing angle was -19.85° . Another sweep was performed using ω oscillations from -110.0 to 70.0° in 0.5° steps. The exposure rate was $4.0 \text{ [sec./}^\circ\text{]}$. The detector swing angle was -19.85° . 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 ($R_{\text{int}} = 0.0553$). Data were collected and processed using CrystalClear (Rigaku).⁸

The linear absorption coefficient, μ , for Mo-K α 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 methods⁹ 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 refinement¹⁰ 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: $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.0717$, $wR2 = [\Sigma (w (F_o^2 - F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2} = 0.1968$.

The standard deviation of an observation of unit weight¹¹ was 1.17. Unit weights were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.98 and $-1.22 \text{ e}^-/\text{\AA}^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.¹² Anomalous dispersion effects were included in F_{calc} ;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 CrystalStructure¹⁶ crystallographic software package except for refinement, which was performed using SHELXL-97.¹⁷

Crystal Data and Structure Refinement for 3a

Crystal Data

Empirical Formula	$\text{C}_{29}\text{H}_{36}\text{BrF}_3\text{NO}_3\text{P}$
Formula Weight	614.48
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.200 x 0.200 x 0.150 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	$a = 9.477(5) \text{ \AA}$ $b = 15.308(8) \text{ \AA}$ $c = 21.114(11) \text{ \AA}$ $\beta = 102.525(10)^\circ$ $V = 2990(3) \text{ \AA}^3$
Space Group	$P2_1/n$ (#14)

Z value	4
D_{calc}	1.365 g/cm ³
F_{000}	1272.00
$\mu(\text{MoK}\alpha)$	14.805 cm ⁻¹

Intensity Measurements

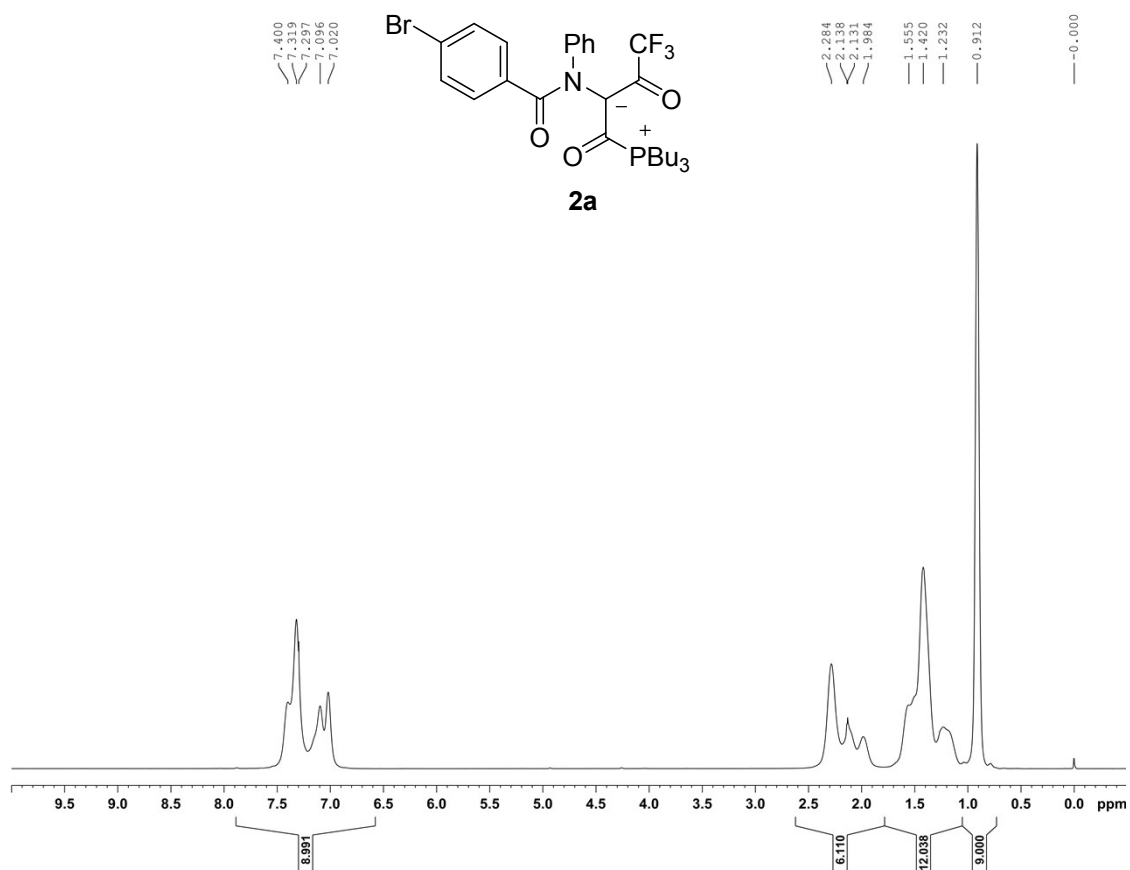
Diffractometer	Saturn724
Radiation	MoK α ($\lambda = 0.71075 \text{ \AA}$) multi-layer mirror monochromated
Voltage, Current	50 kV, 24 mA
Temperature	-172.8 °C
Detector Aperture	70 x 70 mm
Data Images	1440 exposures
ω oscillation Range	-110.0 – 70.0 °
Exposure Rate	4.0 sec./°
Detector Swing Angle	-19.85 °
ω oscillation Range	-110.0 – 70.0 °
Exposure Rate	4.0 sec./°
Detector Swing Angle	-19.85 °
ω oscillation Range	-110.0 – 70.0 °
Exposure Rate	4.0 sec./°
Detector Swing Angle	-19.85 °
Detector Position	45.15 mm
Pixel Size	0.141 mm
$2\theta_{\text{max}}$	62.5 °
No. of Reflections Measured	Total: 53268

	Unique: 8684 ($R_{\text{int}} = 0.0553$)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.710 – 0.801)

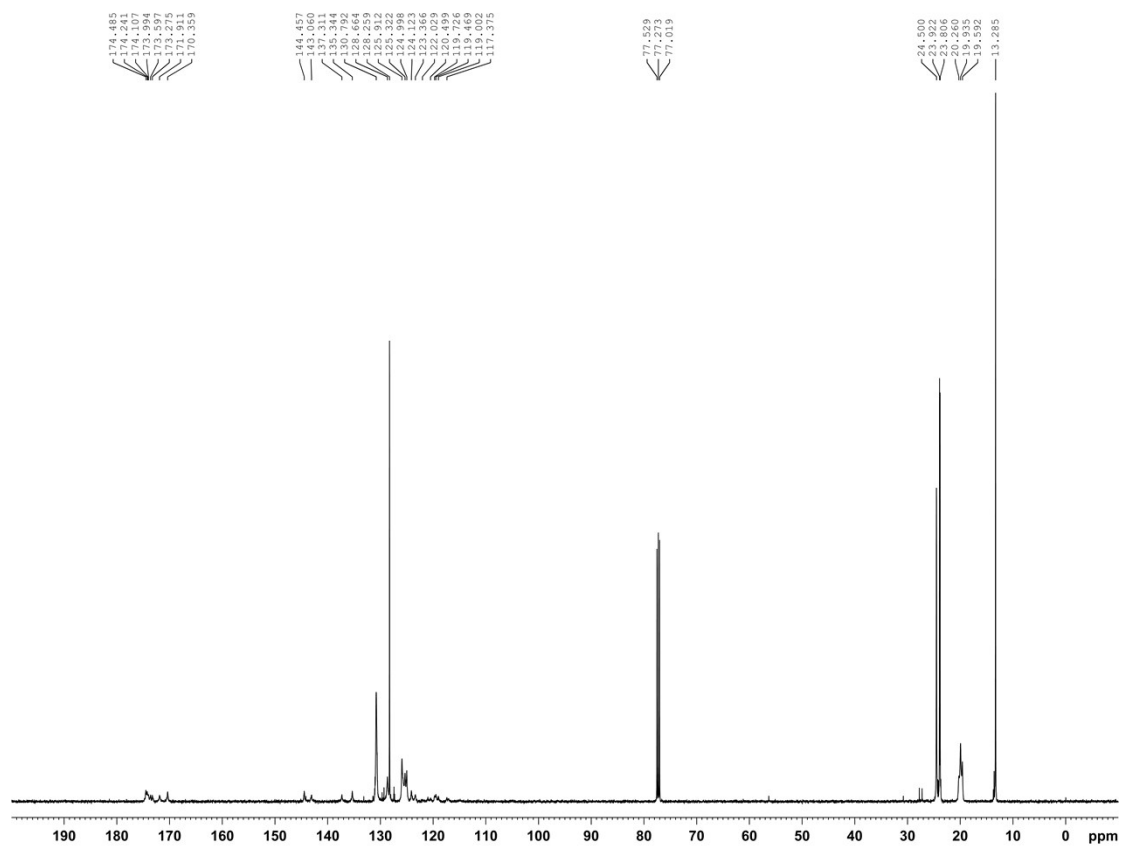
Structure Solution and Refinement

Structure Solution	Direct Methods
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma w (F_o^2 - F_c^2)^2$
Least Squares Weights	$w = 1/[\sigma^2(F_o^2) + (0.1041 \cdot P)^2 + 0.1945 \cdot P]$ where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$
$2\theta_{\text{max}}$ cutoff	60.0 °
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	8684
No. Variables	343
Reflection/Parameter Ratio	25.32
Residuals: R1 ($I > 2.00\sigma(I)$)	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/ \AA^3
Minimum peak in Final Diff. Map	-1.22 e/ \AA^3

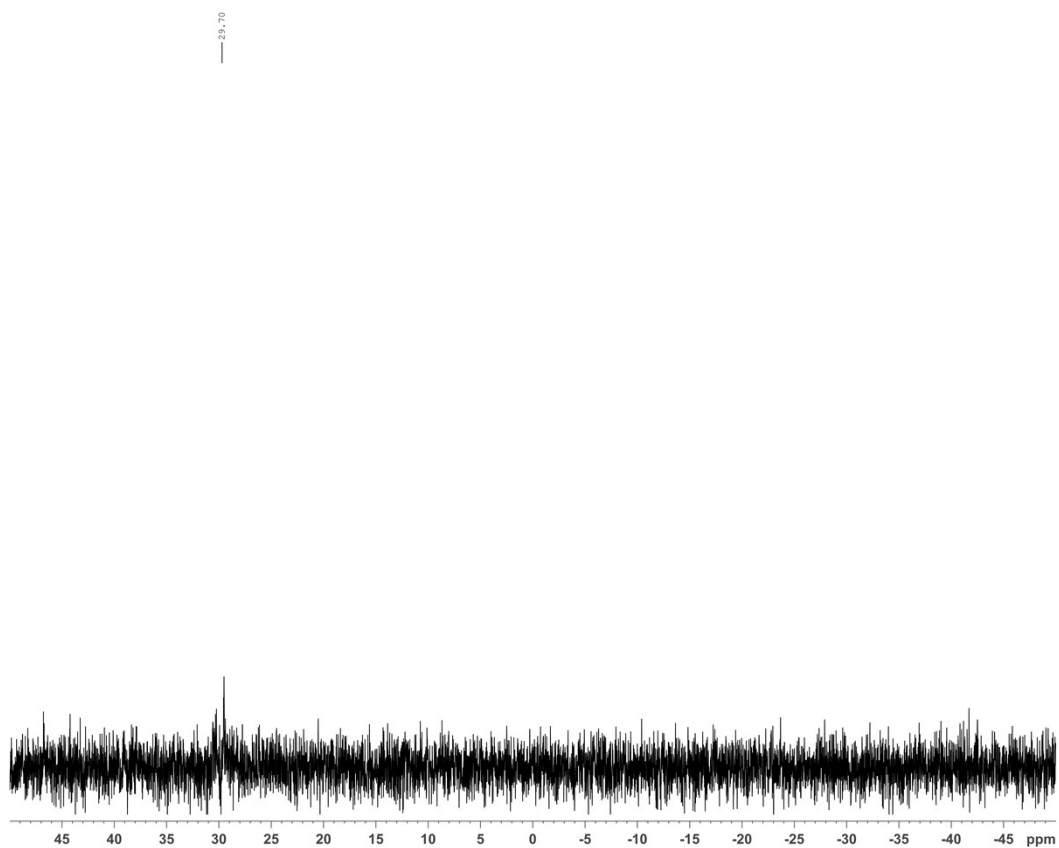
¹H NMR Spectra of 2a



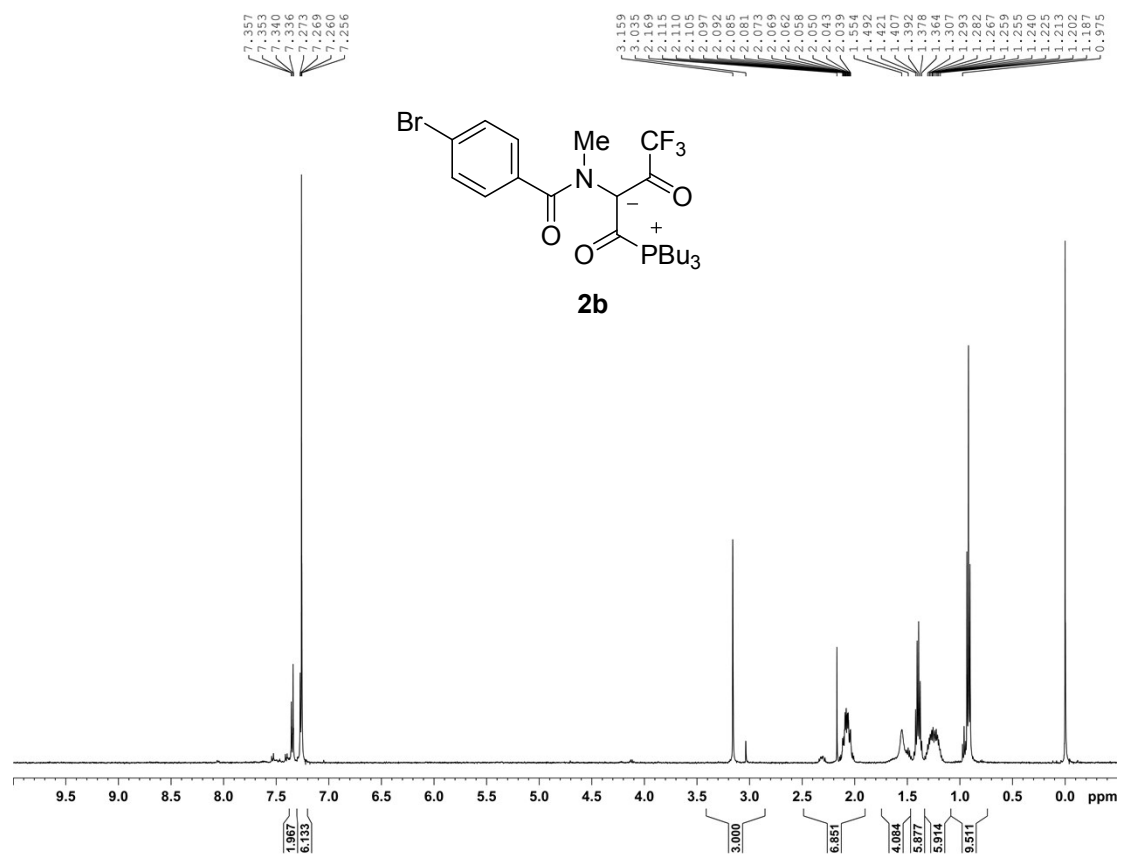
¹³C NMR Spectra of 2a



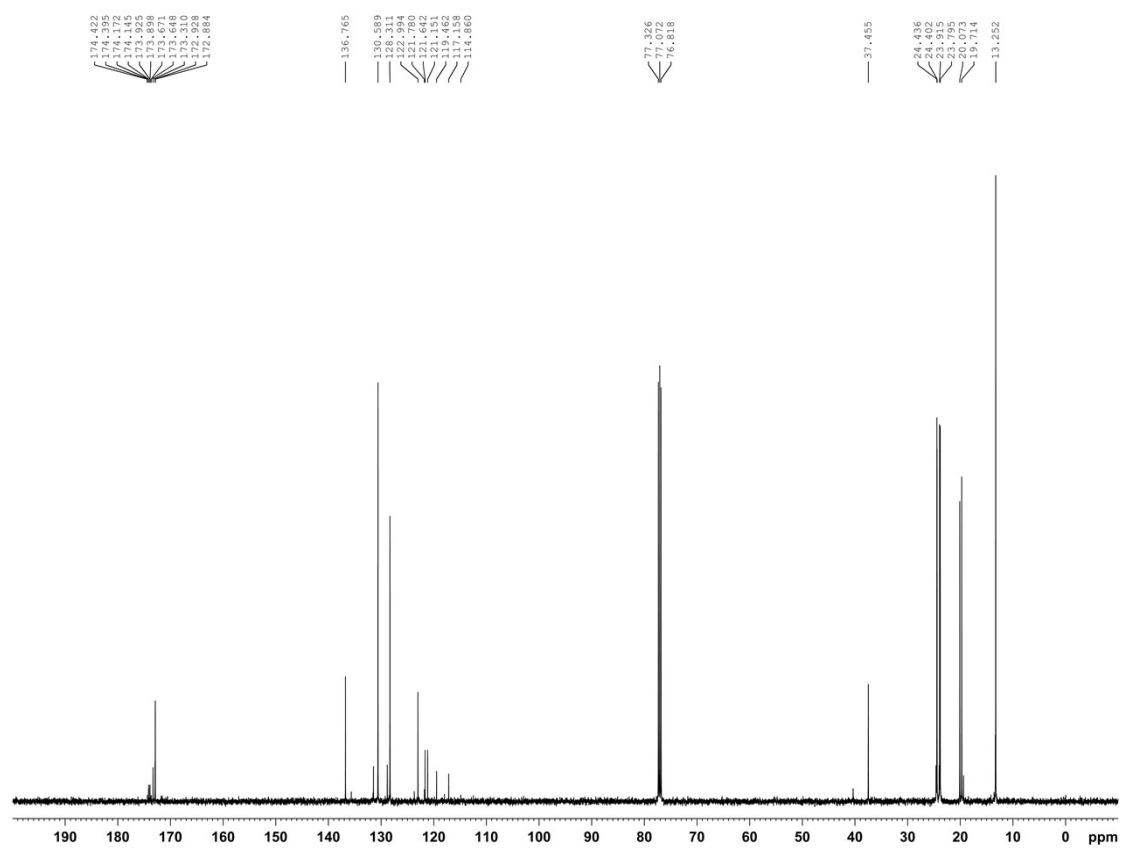
³¹P NMR Spectra of 2a



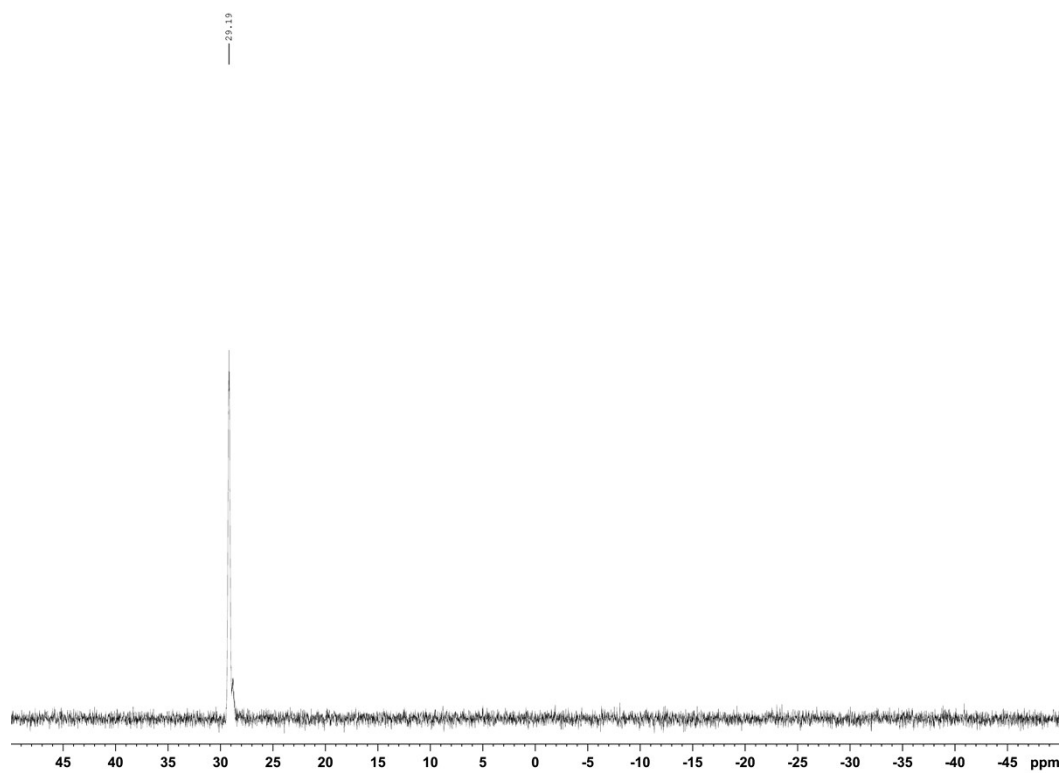
¹H NMR Spectra of 2b



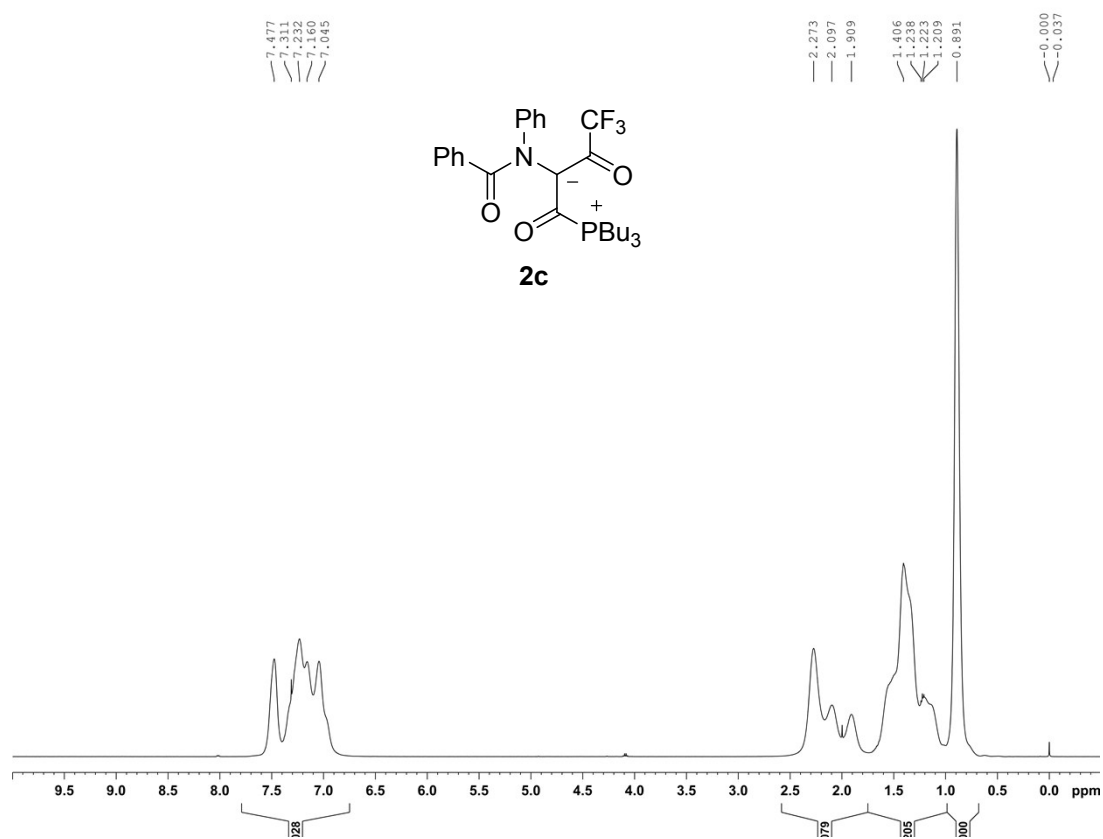
¹³C NMR Spectra of 2b



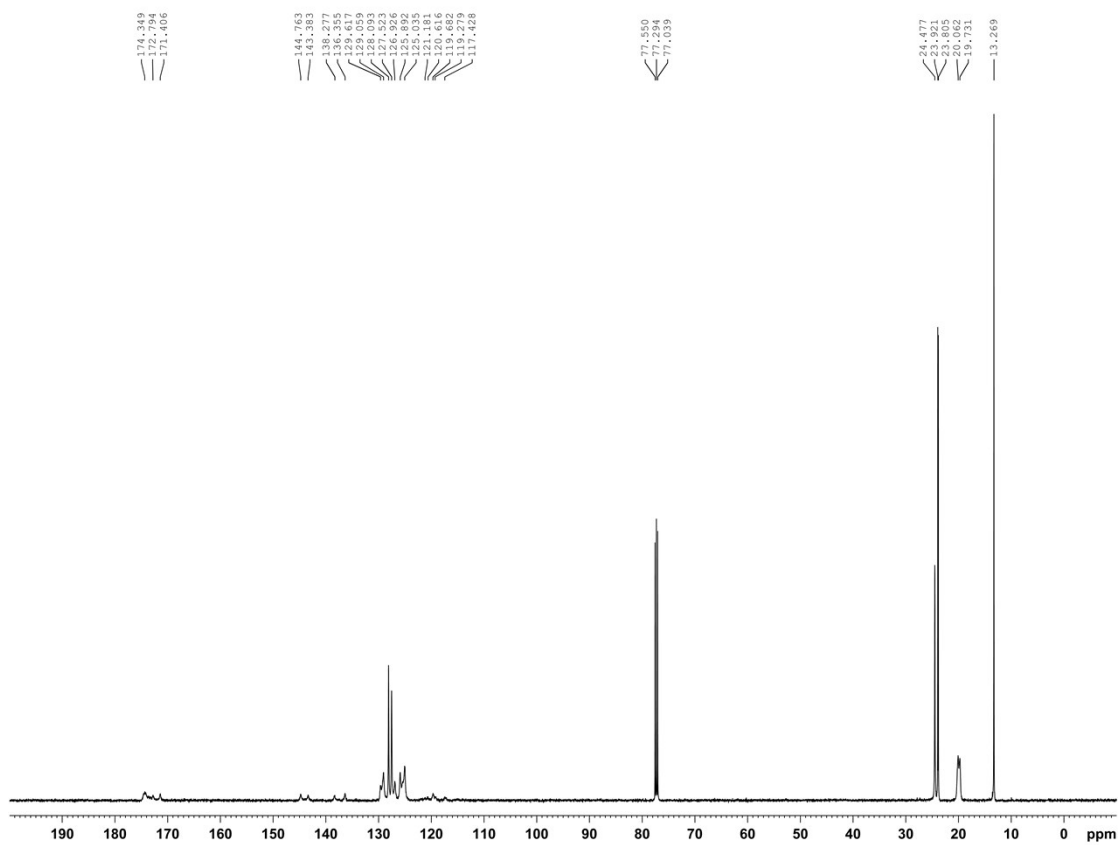
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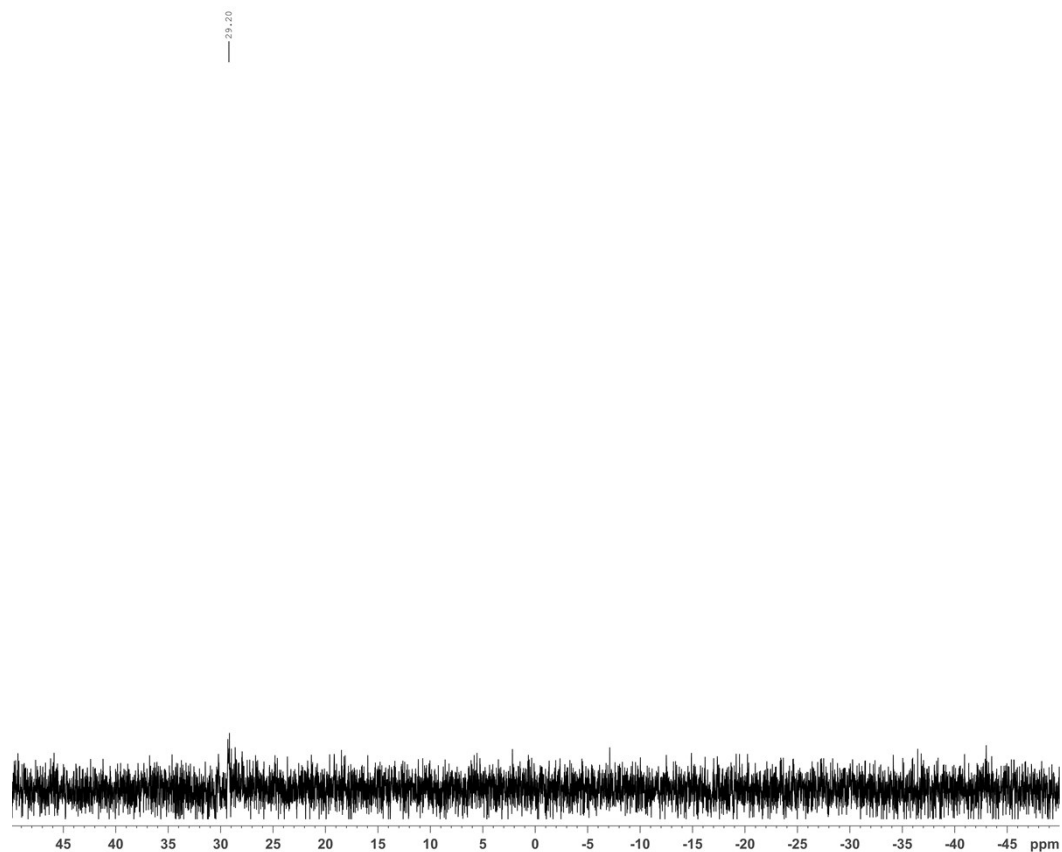
¹H NMR Spectra of 2c



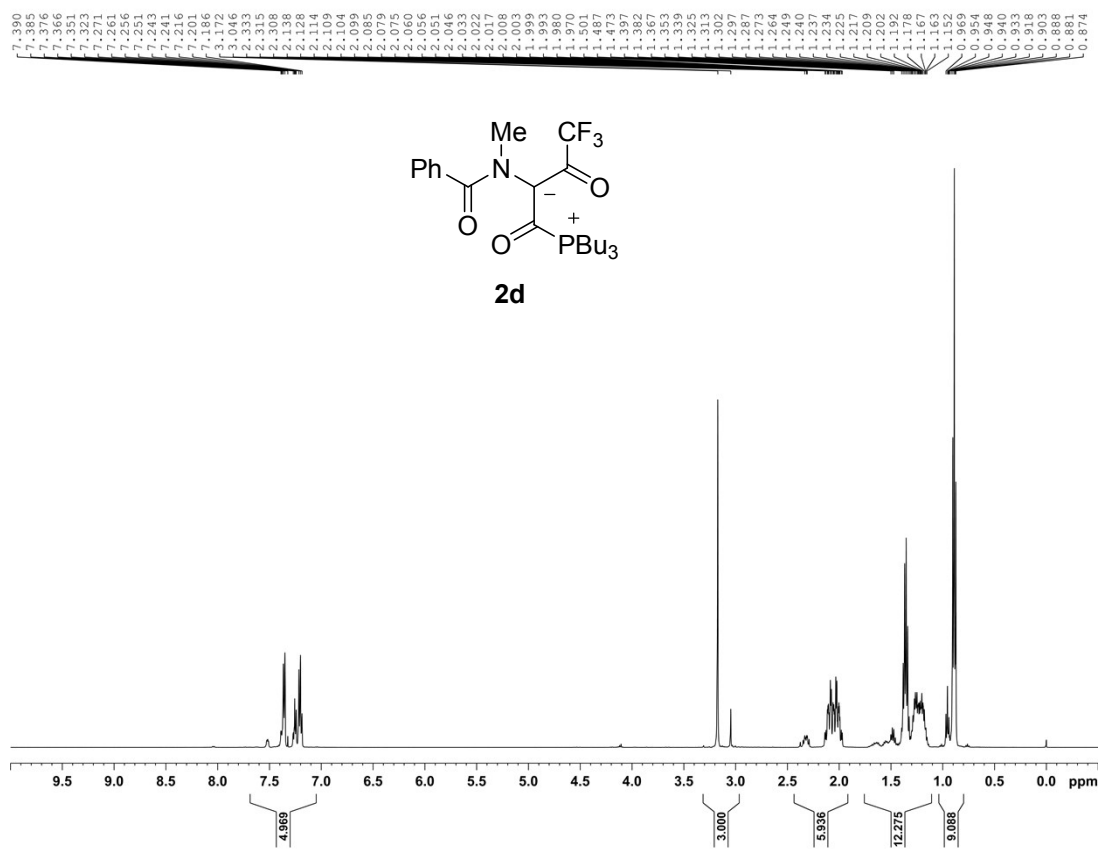
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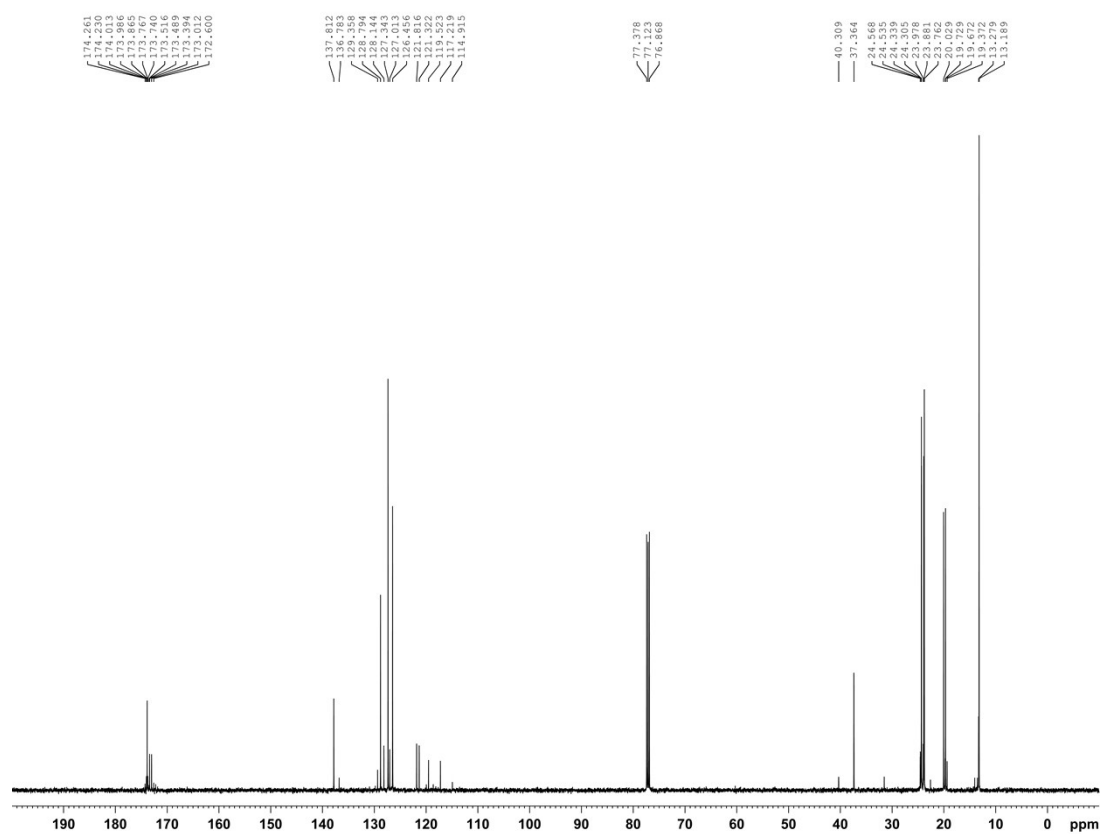
³¹P NMR Spectra of 2c



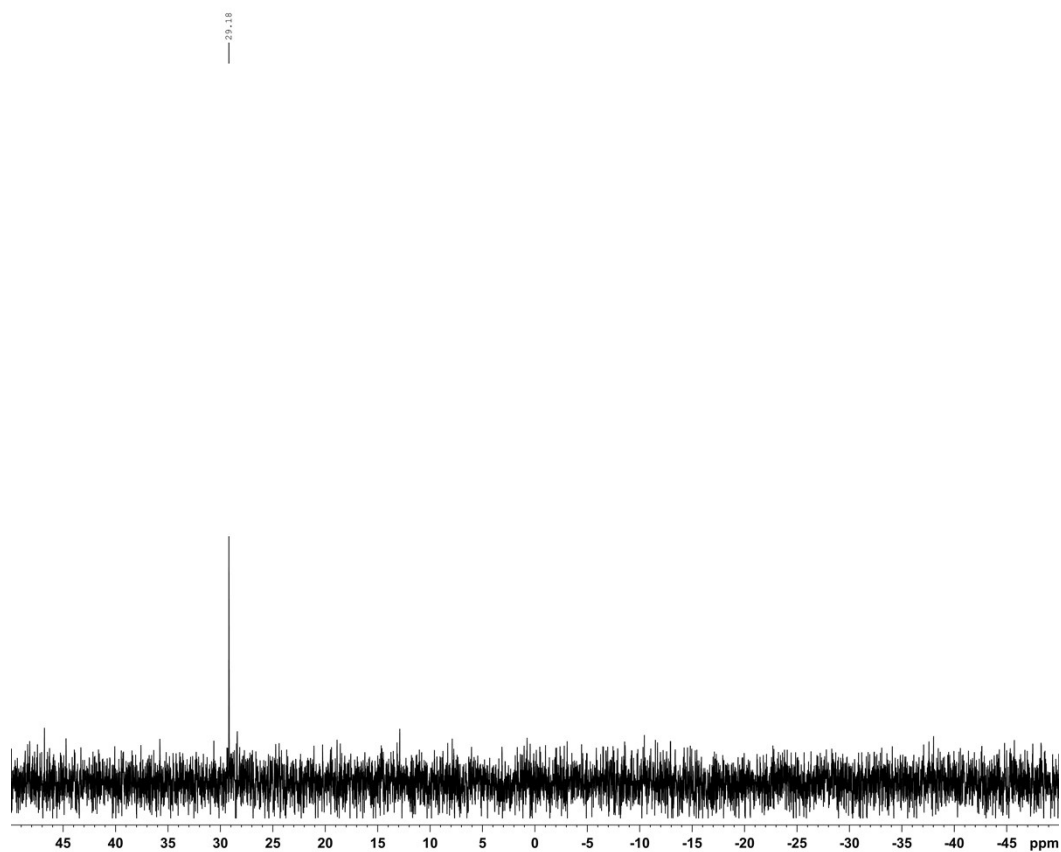
¹H NMR Spectra of 2d



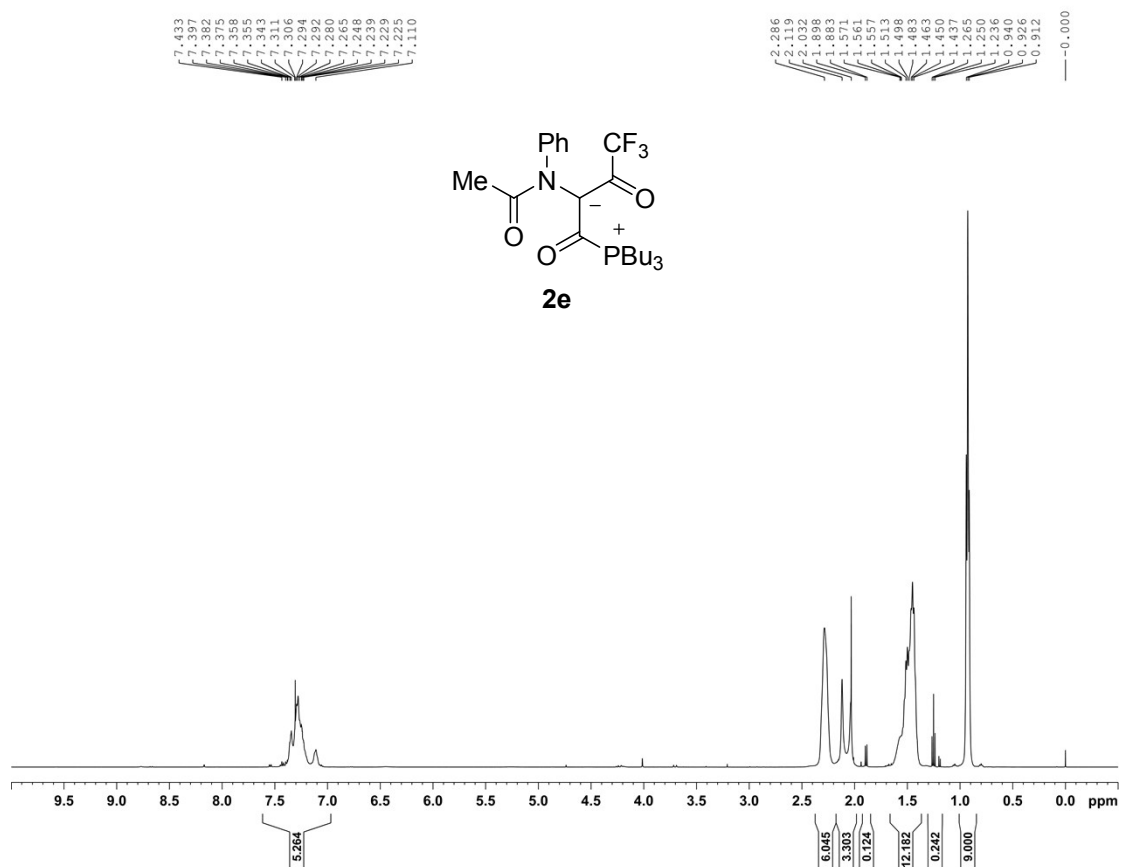
¹³C NMR Spectra of 2d



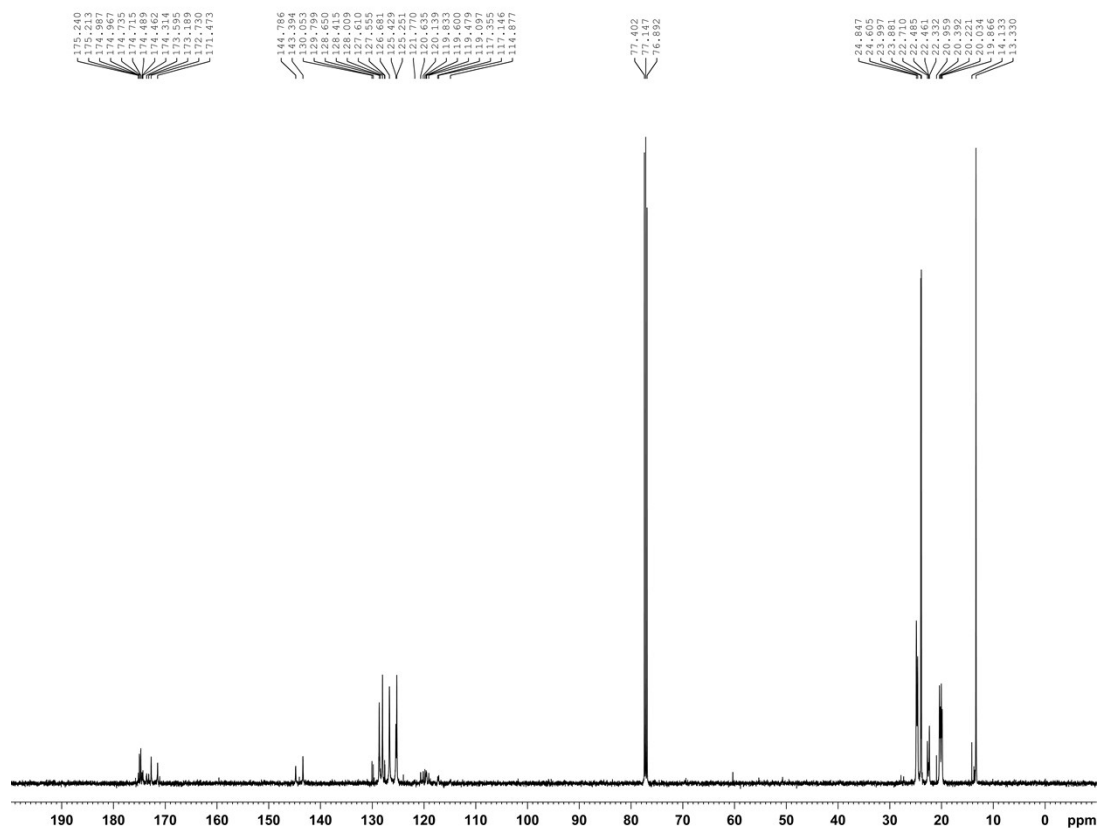
³¹P NMR Spectra of 2d



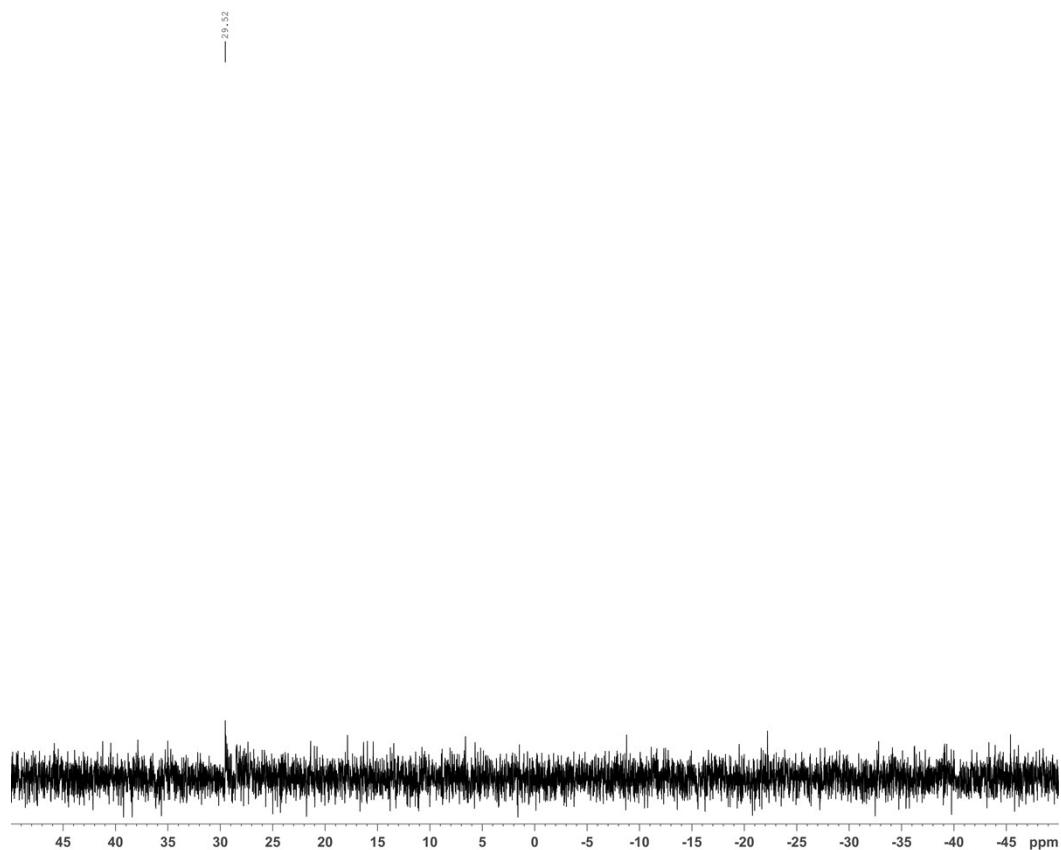
¹H NMR Spectra of 2e



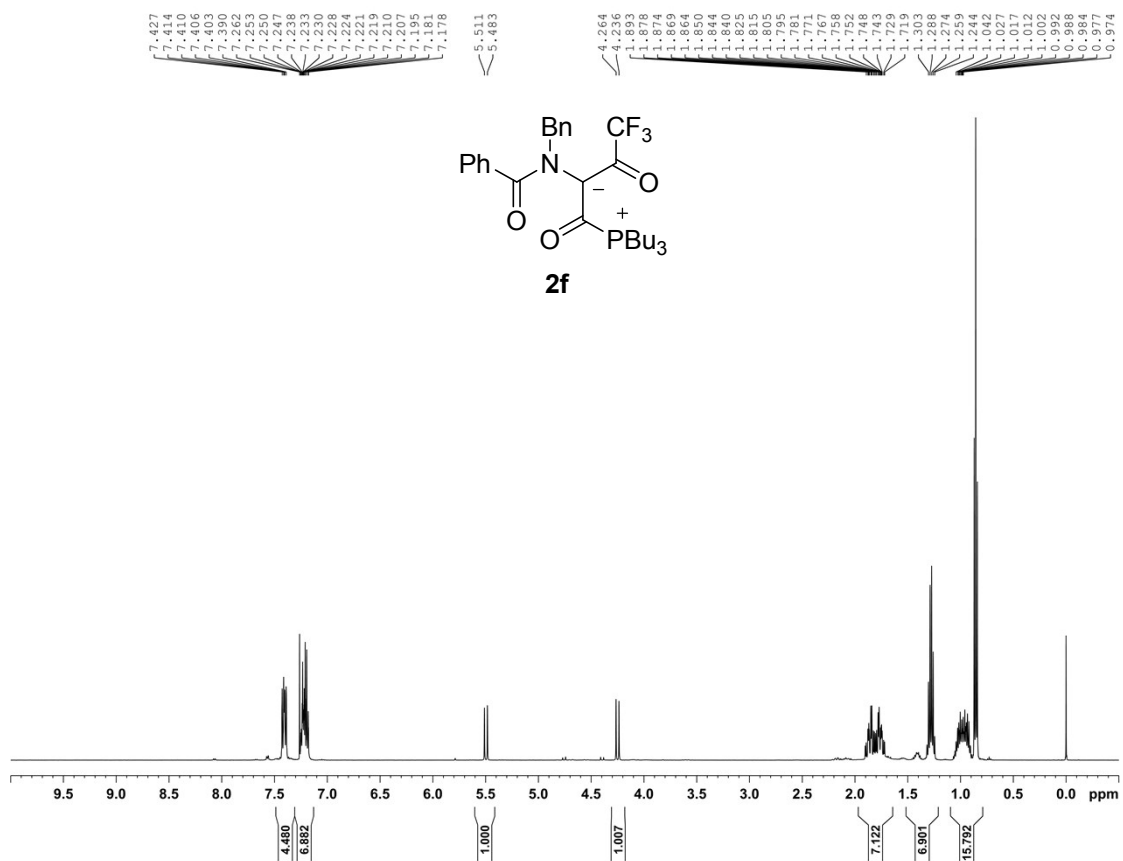
¹³C NMR Spectra of 2e



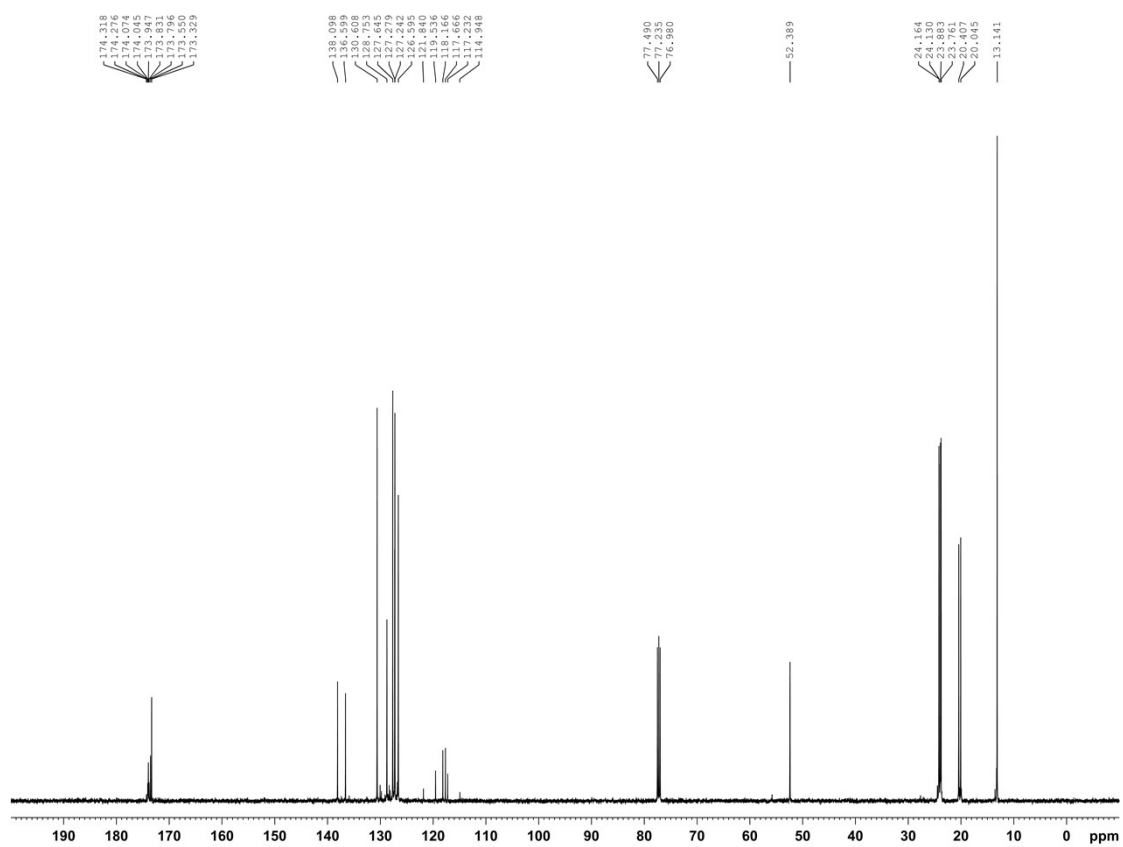
^{31}P NMR Spectra of **2e**



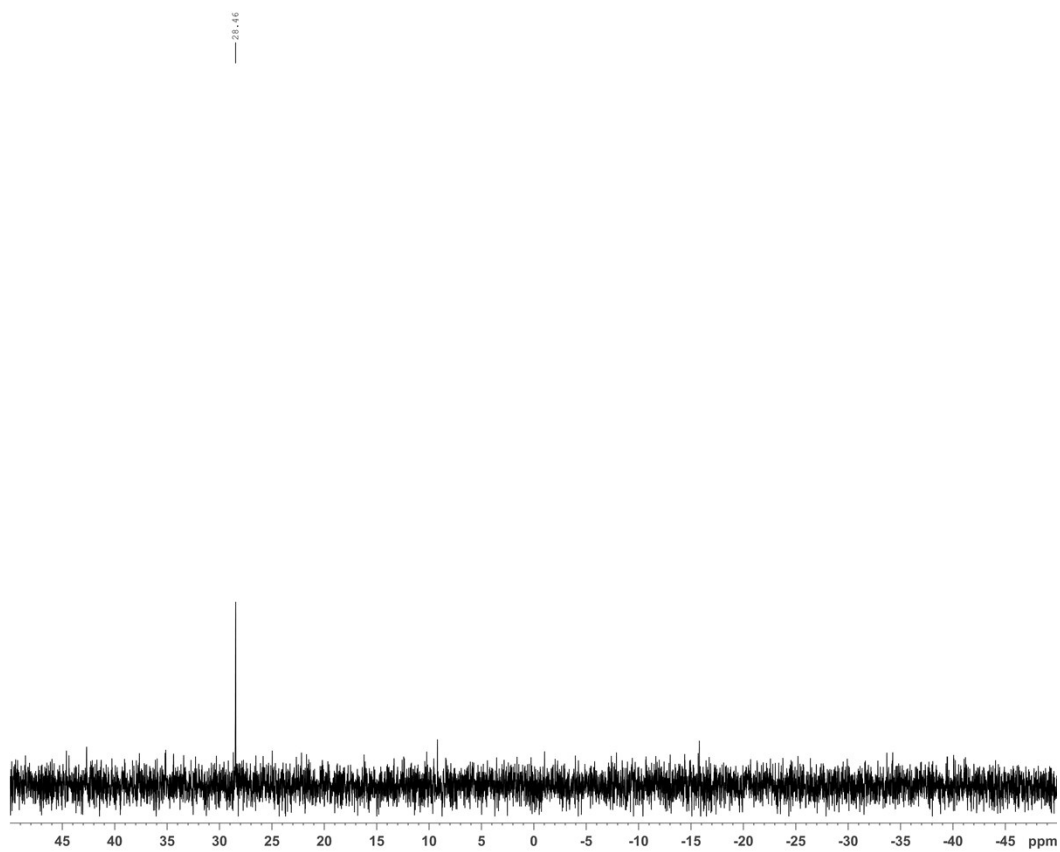
^1H NMR Spectra of **2f**



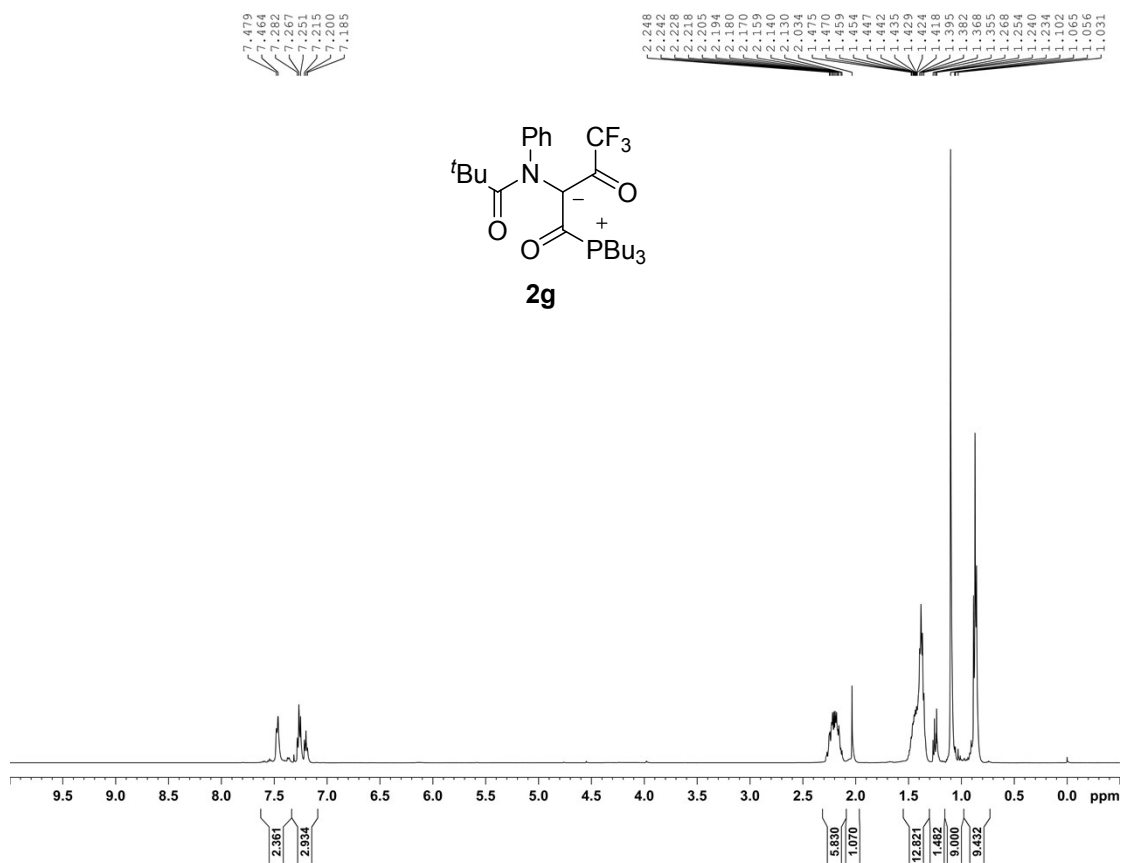
¹³C NMR Spectra of 2f



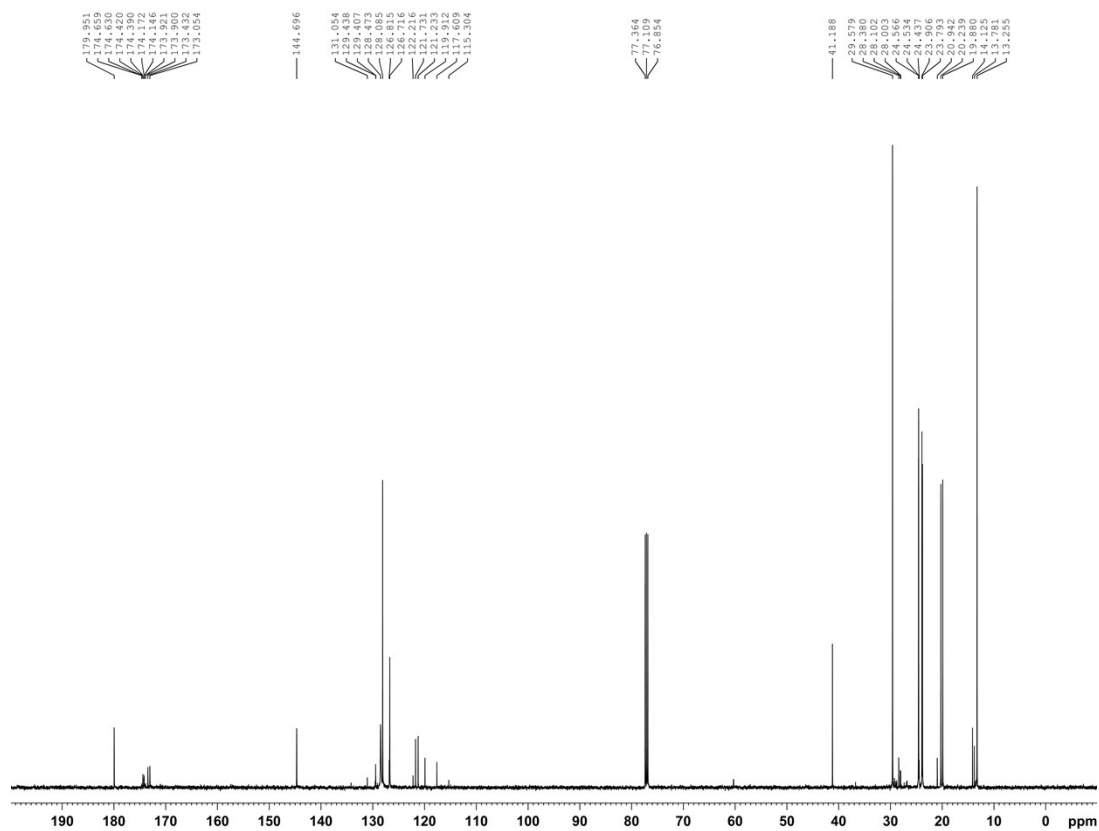
³¹P NMR Spectra of 2f



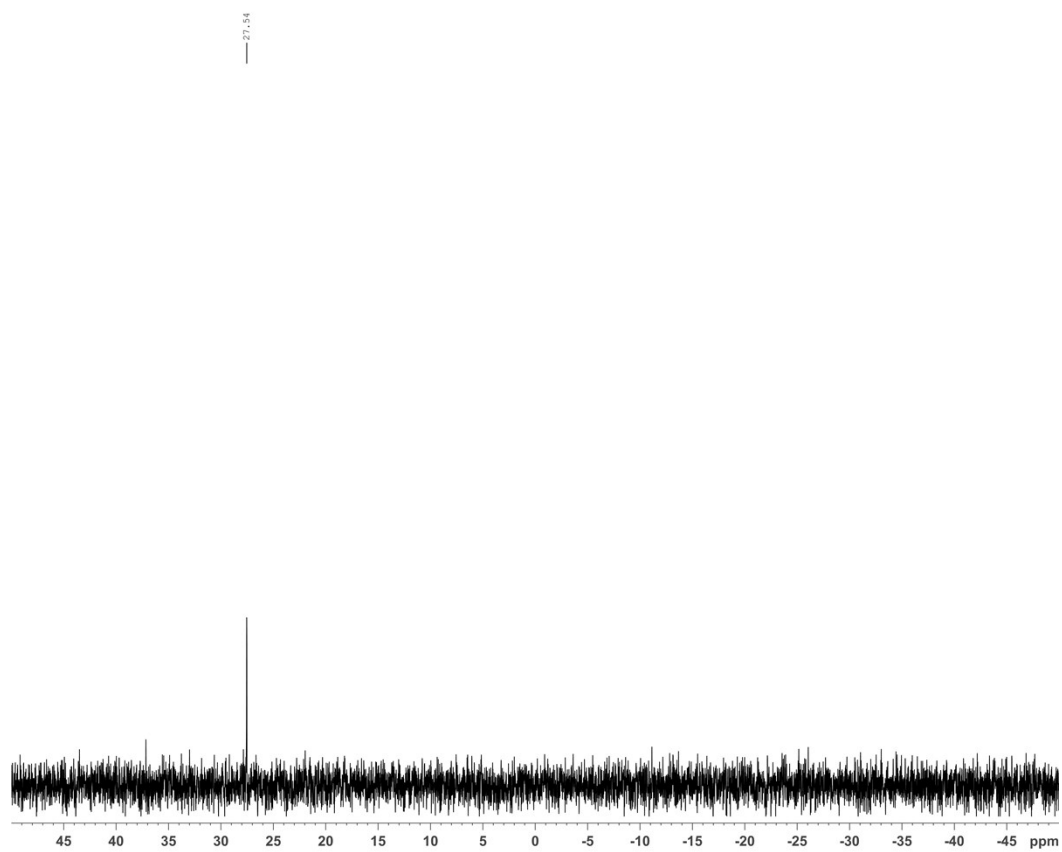
¹H NMR Spectra of 2g



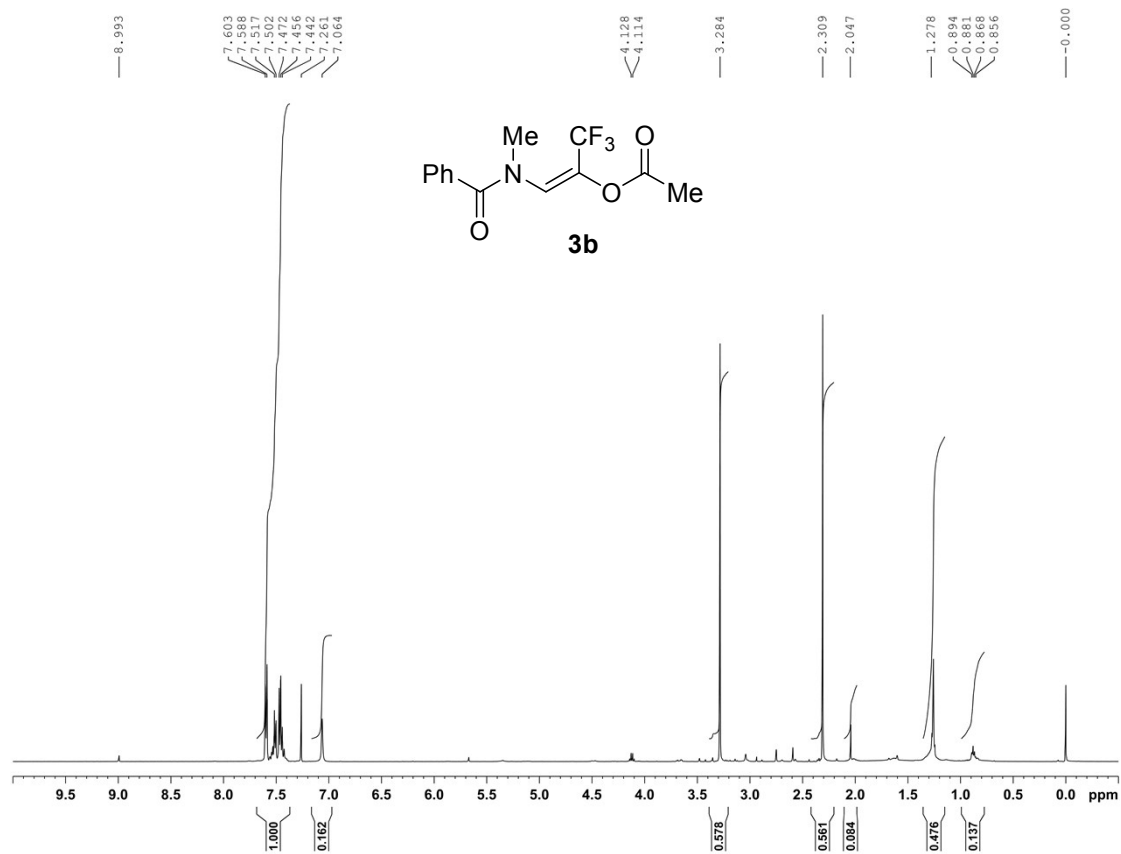
¹³C NMR Spectra of 2g



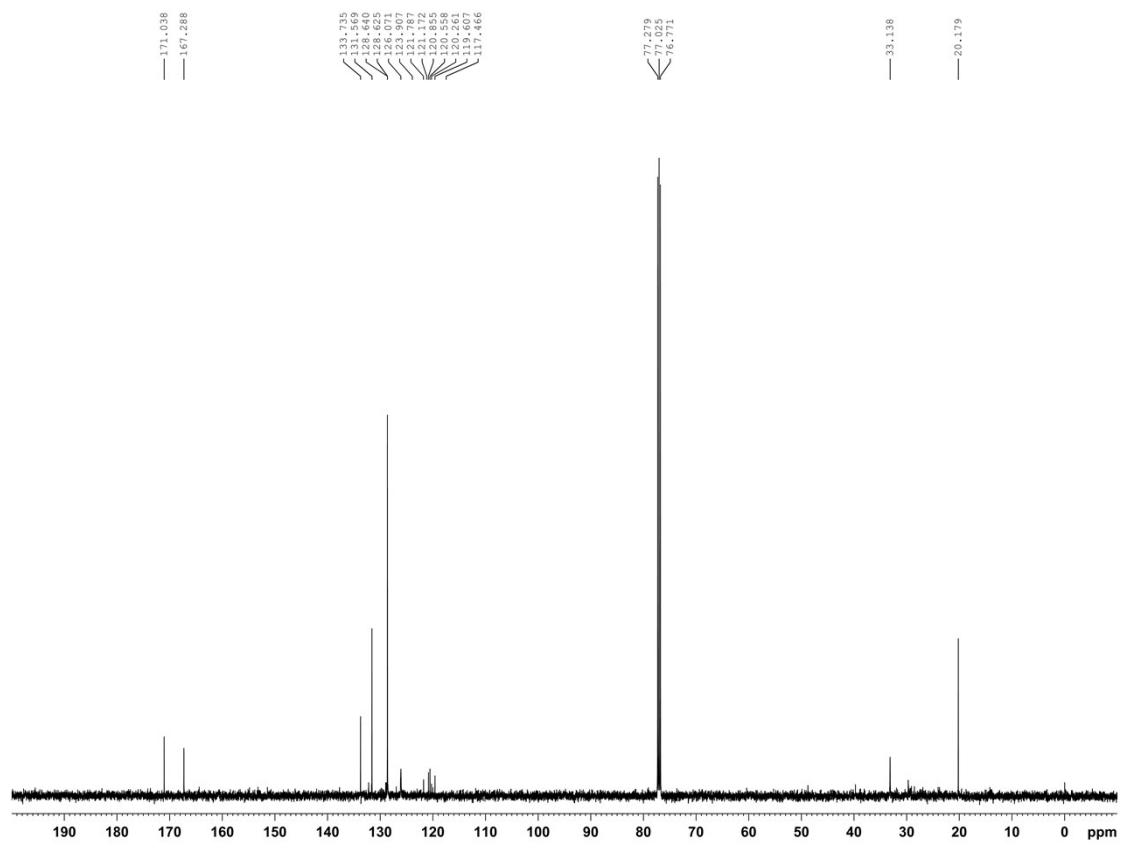
³¹P NMR Spectra of 2g



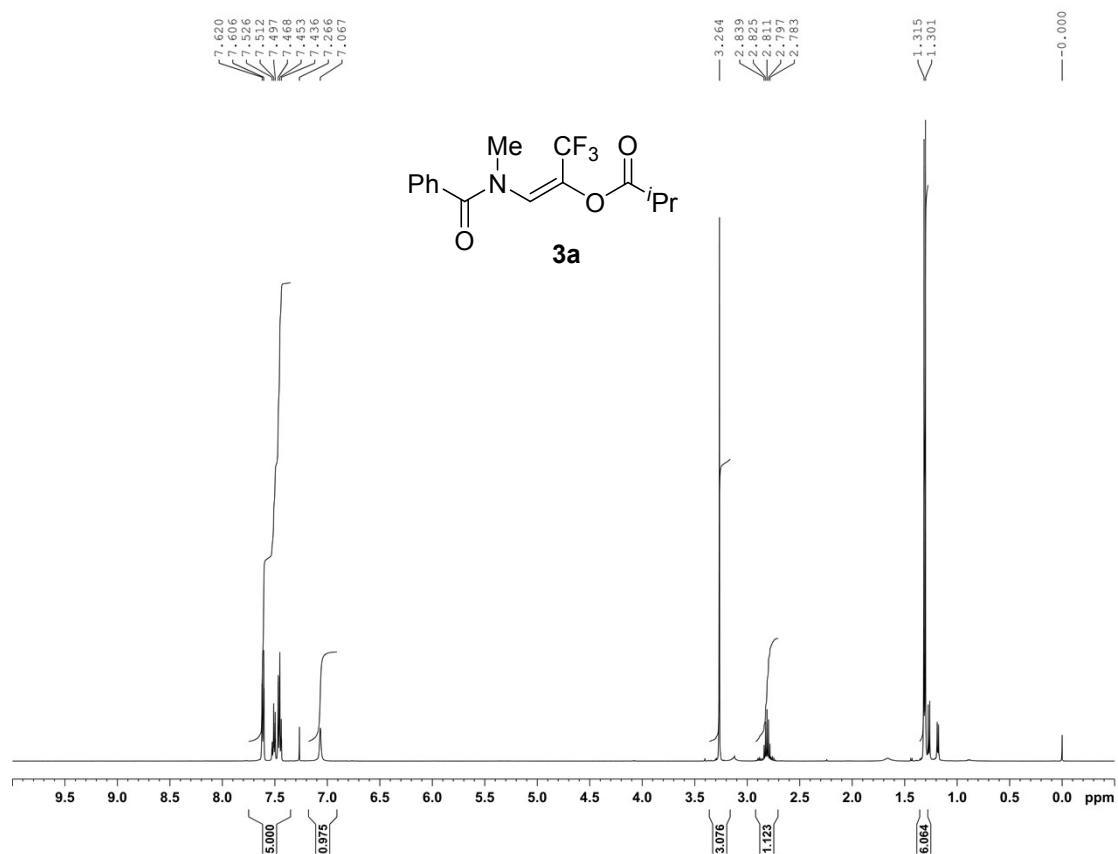
¹H NMR Spectra of 3a



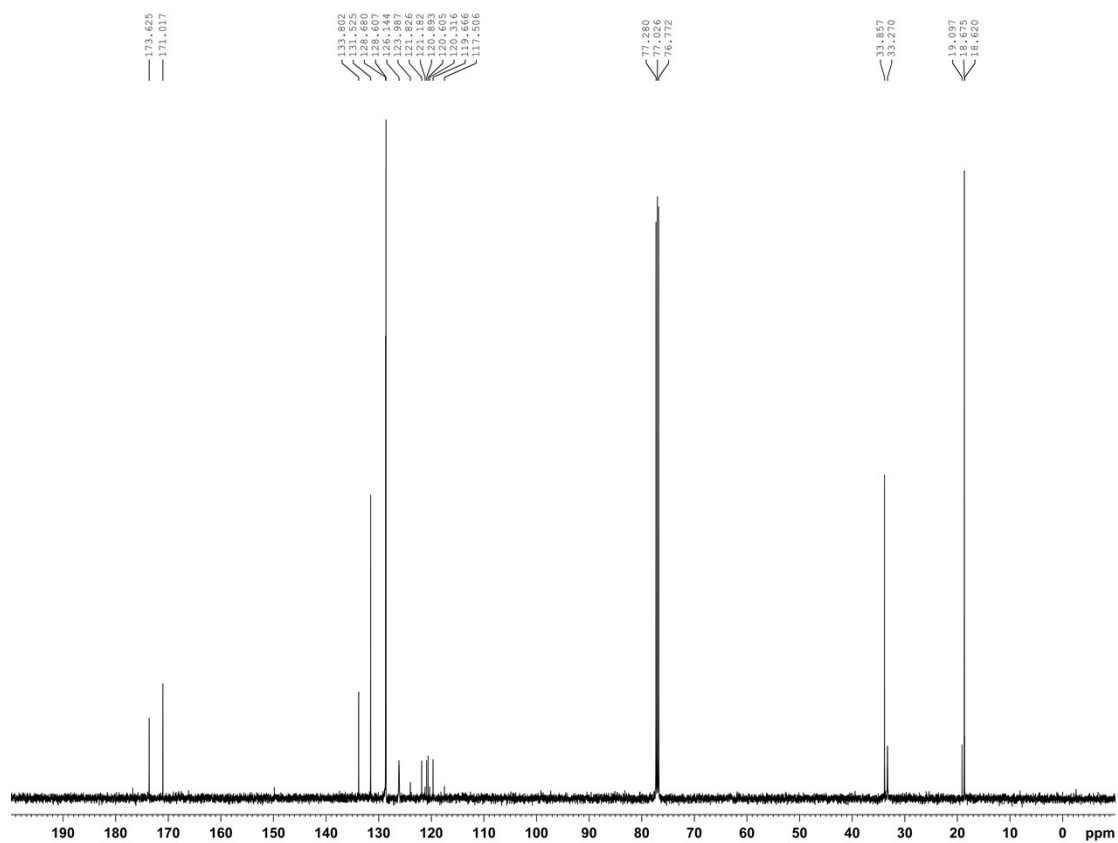
¹³C NMR Spectra of 3a



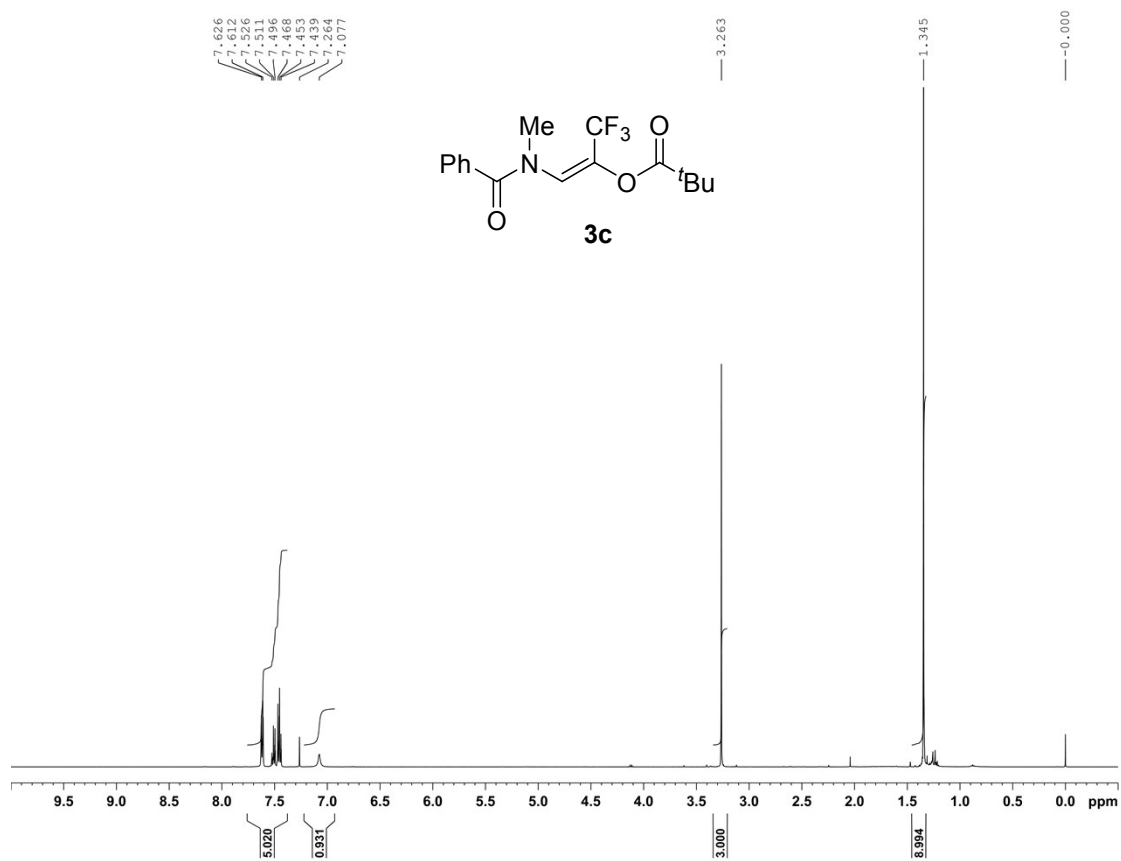
¹H NMR Spectra of 3b



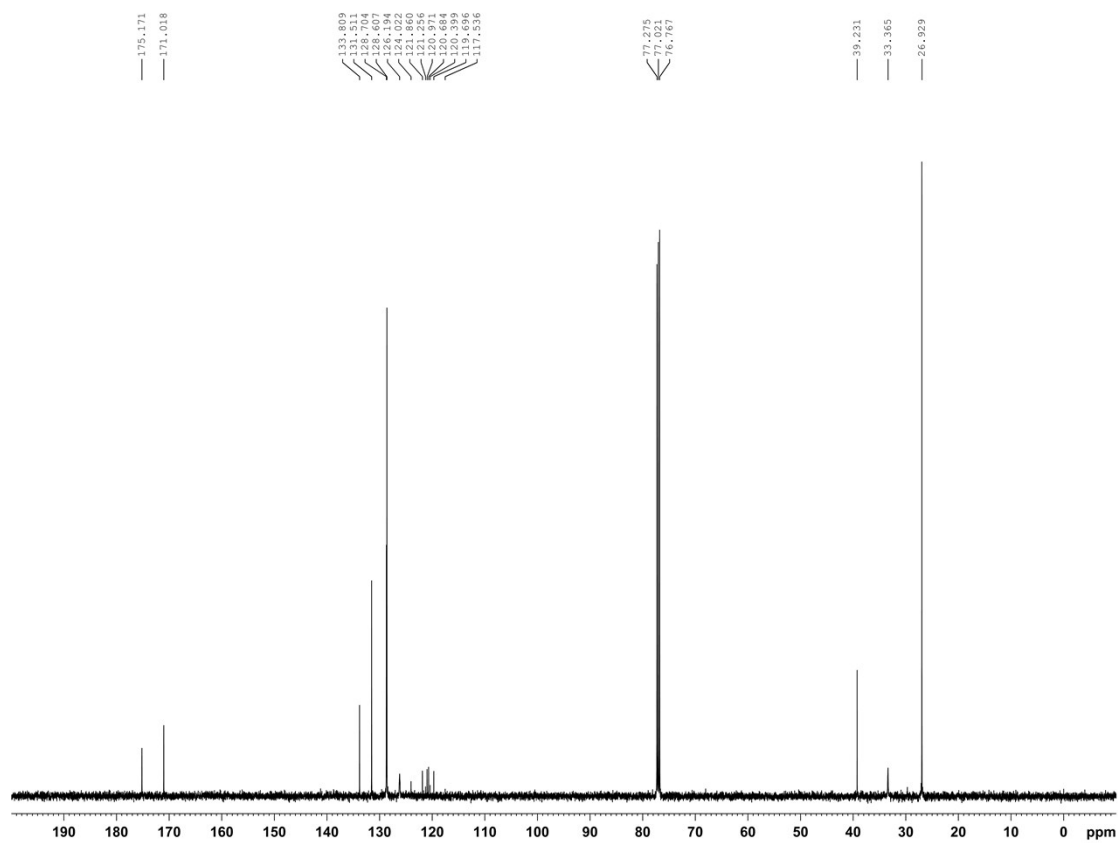
¹³C NMR Spectra of 3b



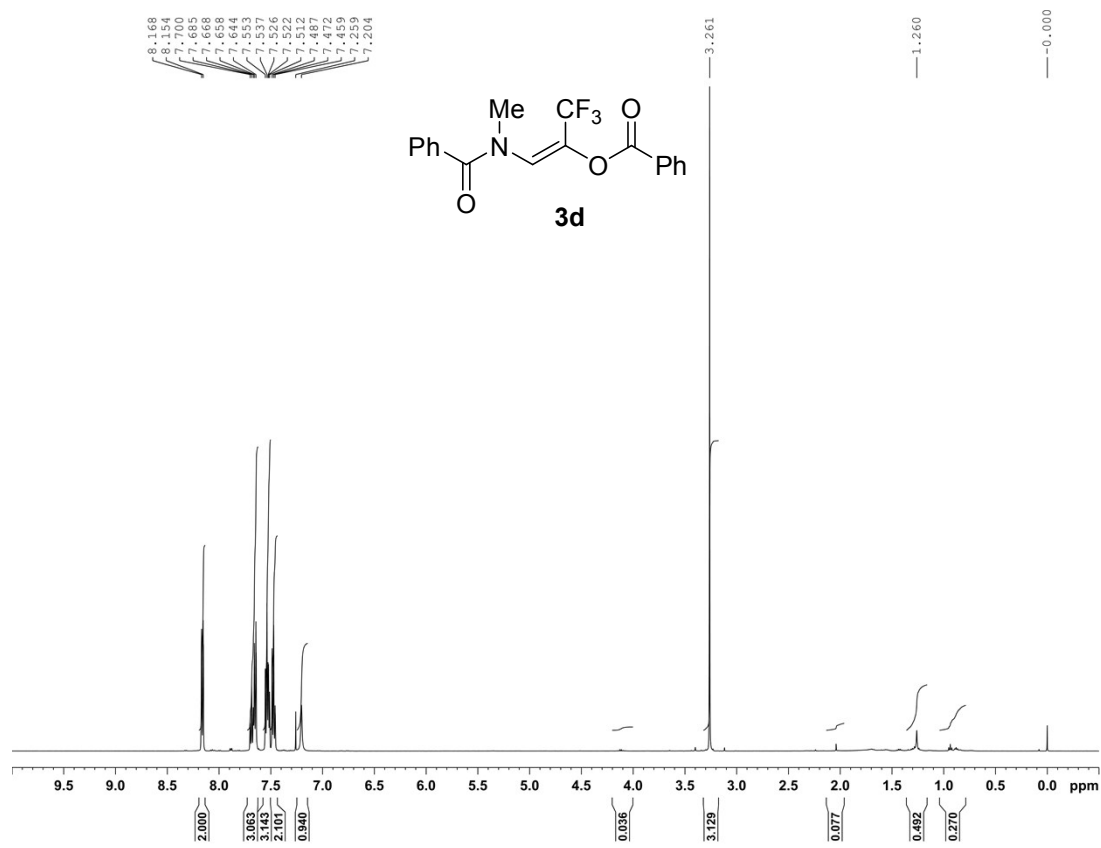
¹H NMR Spectra of 3c



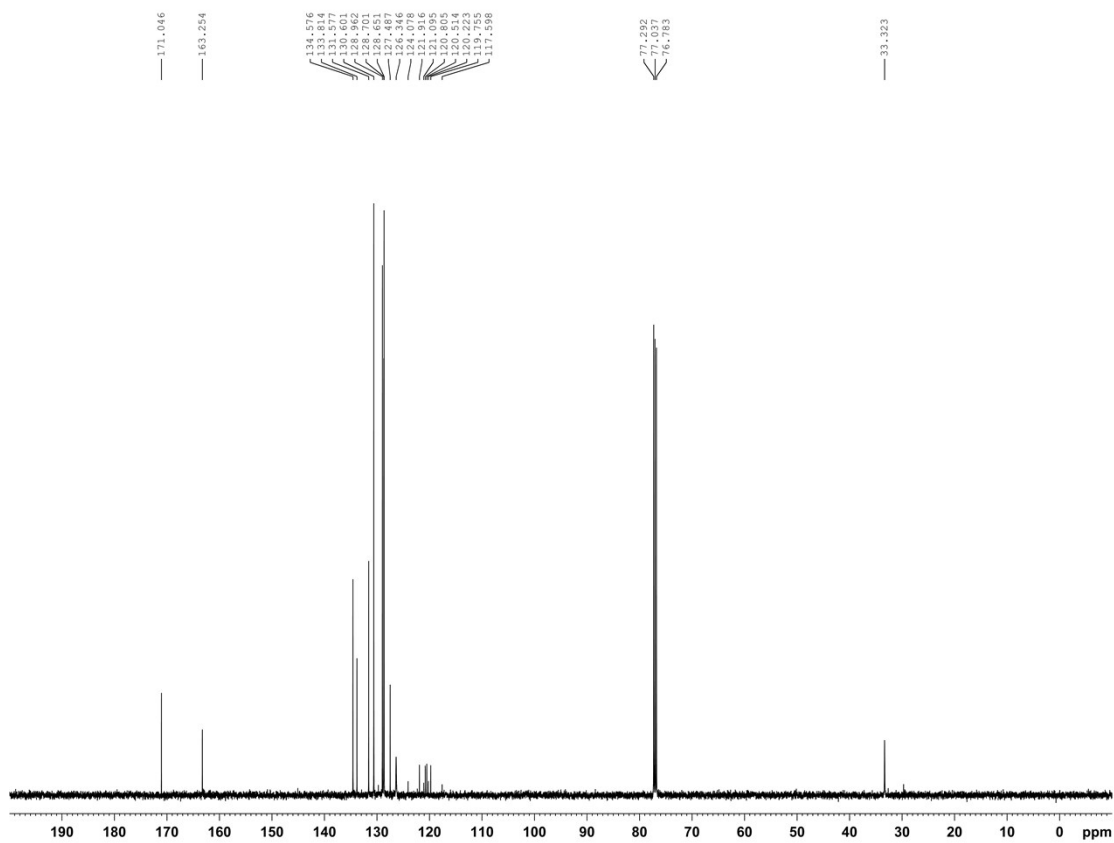
¹³C NMR Spectra of 3c



¹H NMR Spectra of 3d



¹³C NMR Spectra of 3d



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