



Supporting Information

© Wiley-VCH 2007

69451 Weinheim, Germany

**A General Method for *meta*- and *para*-Functionalization of
Aromatics using $\text{TMP}_2\text{Mg}\cdot 2\text{LiCl}^{**}$**

Christoph J. Rohbogner, Giuliano C. Clososki and Paul Knochel*

Ludwig-Maximilians-Universität München, Department Chemie &
Biochemie

Butenandtstrasse 5-13, Haus F, 81377 München (Germany)

Fax: (+49) 089 21 80 776 80

e-mail: paul.knochel@cup.uni-muenchen.de

General All reactions were carried out under an argon atmosphere in flame-dried glassware. Syringes which were used to transfer anhydrous solvents or reagents were purged with argon prior to use. THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen. Yields refer to isolated yields of compounds estimated to be >95% pure as determined by ^1H -NMR (25 °C) and capillary GC. Column chromatography was performed using SiO_2 (0.040 – 0.063 mm, 230 – 400 mesh ASTM) from Merck.

Preparation of the reagent $\text{TMP}_2\text{Mg}\cdot 2\text{LiCl}$ (2) from $\text{TMPMgCl}\cdot \text{LiCl}$ (1):

In an argon flushed Schlenk-flask, 2,2,6,6-tetramethylpiperidine (TMPH, 5.07 mL, 30.0 mmol) was dissolved in THF (30 mL). This solution was cooled to -40 °C and *n*-BuLi (2.4 M in hexane, 12.5 mL, 30.0 mmol) was added dropwise.

After the addition was complete, the reaction mixture was warmed to 0 °C and stirred at this temperature for 30 min. Freshly titrated $\text{TMPMgCl}\cdot\text{LiCl}$ (**1**)^[1] (1 M in THF, 30 mL, 30.0 mmol) was then added dropwise to the LiTMP solution, the reaction mixture was stirred at 0 °C for 30 min, warmed to 25 °C and stirred for 1 h. The solvents were then removed *in vacuo* without heating, affording a yellowish solid. Freshly distilled THF was then slowly added under vigorous stirring, until a complete dissolution of the salts was observed. The fresh $\text{TMP}_2\text{Mg}\cdot 2\text{LiCl}$ solution was titrated^[2] prior to use at 0 °C with benzoic acid using 4-(phenylazo)-diphenylamine as indicator. A concentration of 0.6 M in THF was obtained.

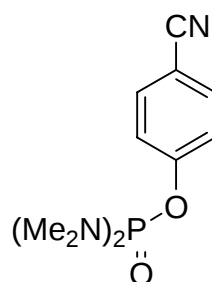
Preparation of the starting materials:

Typical Procedure 1 (TP1): synthesis of the phosphorodiamidates from phenols^[3]:

In a 100 mL round-bottom flask the phenol (20.0 mmol) and 4-DMAP (244 mg, 2.0 mmol) were dissolved in THF (20 mL), then $\text{Cl-P(=O)(NMe}_2)_2$ (4.50 g, 3.9 mL, 24.0 mmol) was carefully added, followed by the addition of triethylamine (2.43 g, 3.33 mL, 24.0 mmol). The resulting suspension was stirred at room temperature overnight. The reaction mixture was quenched by the addition of a half concentrated aq. NH_4Cl solution (20 mL) and extracted with ethyl acetate (3 x 20 mL). The combined

organic layers were washed with brine, dried over MgSO_4 , filtered and concentrated *in vacuo*.

Synthesis of 4-cyanophenyl-*N,N,N',N'*-tetramethyldiamido-phosphate (3a):



Prepared according to **TP1** from 4-cyanophenol (2.38 g, 20.0 mmol). The colorless oil was used without further purification (4.72 g, 93%).

$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ : 7.6 (d, J = 9.0 Hz, 2 H), 7.3 (dd, J = 8.9 Hz, J = 1.0 Hz, 2 H), 2.7 (d, J = 10.1 Hz, 12 H).

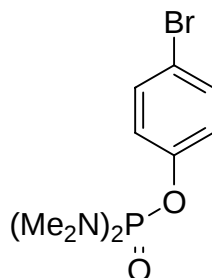
$^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ : 155.4, 134.2, 121.2, 118.8, 108.7, 36.8.

MS (70 eV, EI) m/z (%): 253 (27) [M^+], 209 (12), 155 (11), 145 (22), 136 (11), 135 (100), 102 (15), 92 (27), 90 (16), 76 (10).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3456, 2932, 2900, 2856, 2816, 2228, 1604, 1500, 1456, 1416, 1308, 1216, 1164, 1108, 1068, 988, 896, 848, 792, 760, 684, 664.

HRMS (ESI) for $\text{C}_{11}\text{H}_{16}\text{N}_3\text{O}_2\text{P}$ (253.0980): 253.1050.

Synthesis of 4-bromophenyl-*N,N,N',N'*-tetramethyldiamido-phosphate (3b):



Prepared according to **TP1** from 4-bromophenol (3.46 g, 20.0 mmol). The colorless oil was used without further purification (5.28 g, 86%).

¹H-NMR (300 MHz, CDCl₃) δ : 7.4 (d, J = 9.0 Hz, 2 H), 7.1 (m, 2 H), 2.7 (m, 12 H).

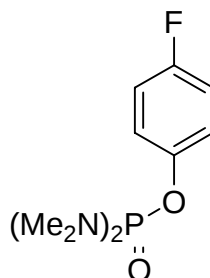
¹³C-NMR (75 MHz, CDCl₃) δ : 150.8, 132.9, 132.7, 122.2, 122.1, 117.1, 36.9.

MS (70 eV, EI) m/z (%): 309 (20), 308 (100), 307 (27), 306 (100) [M⁺], 293 (12), 291 (12), 264 (32), 262 (33), 220 (15), 218 (16), 201 (53), 200 (82), 199 (55), 198 (80), 174 (40), 173 (31), 172 (41), 171 (29), 157 (17), 155 (18), 145 (30), 143 (31), 136 (40), 135 (100), 92 (66), 91 (16), 64 (10), 63 (19).

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3452, 2928, 2896, 2852, 2812, 1580, 1484, 1456, 1400, 1304, 1272, 1208, 1164, 1096, 1068, 984, 900, 832, 768, 748, 700, 668.

HRMS (EI) for C₁₀H₁₆BrN₂O₂P (306.0133): 306.0124.

Synthesis of 4-fluorophenyl-*N,N,N',N'*-tetramethyldiamido-phosphate (3c):



Prepared according to **TP1** from 4-fluorophenol (2.24 g, 20.0 mmol). The colorless oil was used without further purification (2.23 g, 92%).

¹H-NMR (600 MHz, CDCl₃) δ : 7.1 (ddd, J = 9.0 Hz, J = 4.5 Hz, J = 1.2 Hz, 2 H), 7.0 (m, 2 H), 2.7 (d, J = 10.1 Hz, 12 H).

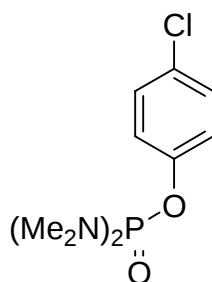
¹³C-NMR (150 MHz, CDCl₃) δ : 160.3, 158.7, 147.5, 121.7, 116.4, 115.8, 36.9.

MS (70 eV, EI) m/z (%): 246 (43) [M^+], 202 (19), 158 (10), 139 (19), 138 (44), 136 (20), 135 (100), 112 (21), 111 (31), 95 (20), 92 (66), 90 (12), 83 (33), 76 (12), 75 (16), 57 (12).

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3456, 3000, 2932, 2896, 2856, 2812, 1644, 1500, 1456, 1364, 1304, 1224, 1180, 1092, 1068, 984, 904, 840, 820, 760, 704, 664.

HRMS (EI) for C₁₀H₁₆FN₂O₂P (246.0933): 246.0925.

Synthesis of 4-chlorophenyl-*N,N,N',N'*-tetramethyldiamido-phosphate (3d):



Prepared according to **TP1** from 4-chlorophenol (2.57 g, 20.0 mmol). The colorless oil was used without further purification (4.73 g, 90%).

¹H-NMR (600 MHz, CDCl₃) δ : 7.3 (m, 2 H), 7.1 (d, J = 8.6 Hz, 2 H), 2.7 (d, J = 9.9 Hz, 12 H).

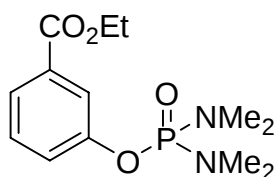
¹³C-NMR (150 MHz, CDCl₃) δ : 150.3, 129.7, 129.5, 121.7, 36.9.

MS (70 eV, EI) m/z (%): 262 (18) [M⁺], 218 (6), 155 (11), 154 (18), 136 (10), 135 (100), 127 (11), 99 (12), 92 (25), 75 (11).

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 2928, 2892, 2852, 2812, 1592, 1484, 1456, 1404, 1304, 1232, 1212, 1184, 1164, 1088, 1068, 984, 900, 832, 772, 752, 704, 672.

HRMS (EI) for C₁₀H₁₆ClN₂O₂P (262.0638): 262.0637.

Synthesis of ethyl 3-{[bis(dimethylamino)phosphoryl]oxy} benzoate (4a):



Prepared according to **TP1** from ethyl 3-hydroxybenzoate (3.32 g, 20.0 mmol). The colorless oil was used without further purification (5.57 g, 93%).

¹H-NMR (300 MHz, CDCl₃) δ : 7.8 – 7.7 (m, 2 H), 7.5 – 7.4 (m, 2 H), 4.4 (q, J = 7.1 Hz, 2 H), 2.8 (d, J = 10.1 Hz, 12 H) 1.4 (t, J = 7.1 Hz, 3 H).

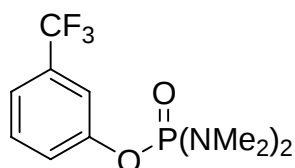
¹³C-NMR (75 MHz, CDCl₃) δ : 166.1, 151.7, 132.4, 129.8, 125.5, 124.9, 121.5, 61.4, 36.9, 14.5.

MS (70 eV, EI) m/z (%): 301 (11), 300 (65) [M^+], 255 (20), 226 (13), 192 (36), 135 (100), 92 (16), 44 (32).

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3435, 2997, 1715, 1584, 1483, 1440, 1366, 1268, 1229, 1203, 1097, 1072, 986, 947, 849, 752, 673.

HRMS (EI) for **C₁₃H₂₁N₂O₄P** (300.1239): 300.1247.

Synthesis of 3-(trifluoromethyl)phenyl *N,N,N',N'*-tetramethyldiamidophosphate (4b):



Prepared according to **TP1** from 3-(trifluoromethyl)phenol (3.24 g, 20.0 mmol). The colorless oil was used without further purification (5.33 g, 90%).

¹H-NMR (300 MHz, CDCl₃) δ : 7.4 (m, 4 H), 2.7 (d, J = 10.1 Hz, 12 H).

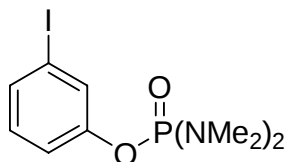
^{13}C -NMR (75 MHz, CDCl_3) δ : 151.9, 132.3 (q, $J(\text{C-F}) = 32.6$ Hz), 130.4, 123.9, 123.8 (q, $J(\text{C-F}) = 272.2$ Hz), 121.1, 117.6, 36.9.

MS (70 eV, EI) m/z (%): 296 (15) [M^+], 188 (13), 135 (100), 92 (18), 44 (49).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2932, 2900, 1596, 1492, 1448, 1324, 1308, 1280, 1228, 1208, 1164, 1120, 1092, 1064, 988, 928, 884, 796, 760, 732, 696, 676.

HRMS (ESI) for $\text{C}_{11}\text{H}_{16}\text{F}_3\text{N}_2\text{O}_2\text{P}$ (296.0901): 296.0896.

Synthesis of 3-iodophenyl N,N,N',N' -tetramethyldiamido-phosphate (4c):



Prepared according to **TP1** from 3-iodophenol (4.4 g, 20.0 mmol). Flash chromatography on silica (diethyl ether) furnished **4c** as a colorless solid (6.5 g, 92%).

m.p.: 75.0 – 77.2 °C.

^1H -NMR (300 MHz, CDCl_3) δ : 7.5 (m, 1H), 7.4 (d, $J = 7.9$ Hz, 1H), 7.0 (t, $J = 7.9$ Hz, 1H), 2.7 (d, $J = 10.1$ Hz, 12H).

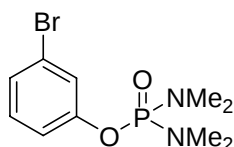
^{13}C -NMR (75 MHz, CDCl_3) δ : 151.7, 133.3, 130.8, 129.3, 119.6, 93.8, 36.6.

MS (70 eV, EI) m/z (%): 355 (2) $[M^+ + H]$, 354 (12) $[M^+]$, 246 (12), 135 (100), 92 (8), 44 (20).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3056, 2922, 2176, 1572, 1463, 1299, 1228, 1199, 1067, 991, 915, 794, 758, 687, 670, 584.

HRMS (ESI) for $\text{C}_{10}\text{H}_{17}\text{IN}_2\text{O}_2\text{P}$ (355.007): 355.007 $[M + H]^+$.

Synthesis of 3-bromophenyl *N,N,N',N'*-tetramethyldiamido-phosphate (4d):



Prepared according to **TP1** from 3-bromophenol (3.46 g, 20.0 mmol). The pale brown oil was used without further purification (5.52 g, 90%).

^1H -NMR (300 MHz, CDCl_3) δ : 7.33 (m, 1 H), 7.26-7.21 (m, 1 H), 7.17-7.15 (m, 2 H), 2.7 (d, J = 9 Hz, 12 H).

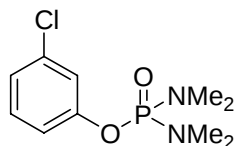
^{13}C -NMR (75 MHz, CDCl_3) δ : 130.6, 127.3, 123.5, 122.5, 118.9, 118.9, 36.6.

MS (70 eV, EI) m/z (%): 306 (47) $[M^+]$, 198 (40), 135 (30), 92 (68), 76 (9), 44 (100).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2894, 1583, 1471, 1297, 1205, 985, 914, 753, 671.

HRMS (ESI) for $\text{C}_{10}\text{H}_{16}\text{O}_2\text{N}_2\text{BrP}$ (306.0132): 306.0110.

Synthesis of 3-chlorophenyl *N,N,N',N'*-tetramethyldiamido-phosphate (4e):



Prepared according to **TP1** from 3-chlorophenol (2.57 g, 20.0 mmol). The pale brown oil was used without further purification (4.93 g, 94%).

¹H-NMR (300 MHz, CDCl₃) δ : 7.22 (dd, J = 8.3 Hz, J = 7.9 Hz, 1 H), 7.18 (m, 1 H), 7.11-7.08 (m, 2 H), 2.71 (d, J = 10.3 Hz, 12 H).

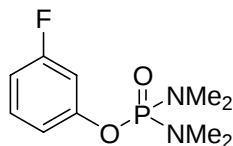
¹³C-NMR (75 MHz, CDCl₃) δ : 152.3, 134.6, 130.5, 124.6, 120.9, 118.7, 36.9.

MS (70 eV, EI) m/z (%): 262 (7) [M^+], 154 (10), 135 (76), 92 (23), 75 (6), 44 (100).

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 2895, 1587, 1473, 1300, 1208, 986, 924, 755, 680.

HRMS (ESI) for **C₁₀H₁₆O₂N₂ClP** (262.0637): 262.0624.

Synthesis of 3-fluorophenyl *N,N,N',N'*-tetramethyldiamido-phosphate (4f):



Prepared according to **TP1** from 3-fluorophenol (2.24 g, 20.0 mmol). The pale brown oil was used without further purification (4.38 g, 89%).

¹H-NMR (300 MHz, CDCl₃) δ : 7.3 (m, 1 H), 7.0 (m, 2 H), 6.8 (m, 1 H), 2.7 (d, J =10.2 Hz, 12 H).

¹³C-NMR (75 MHz, CDCl₃) δ : 163.1 (d, J (C-F)=246.9 Hz), 152.4 (dd, J (C-F)=11.3 Hz, 5.7 Hz), 130.3 (d, J (C-F)= 9.8 Hz), 115.9 (dd, J (C-F)=5.2 Hz, 3.1 Hz), 111.2 (d, J (C-F)=21.1 Hz), 108.1 (dd, J (C-F)=24.5 Hz, 5.4 Hz), 36.6.

MS (70 eV, EI) m/z (%): 246 (17) [M^+], 138 (17), 135 (100), 92 (20), 44 (45).

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 2932, 2896, 1600, 1484, 1456, 1304, 1264, 1220, 1160, 1124, 1068, 988, 960, 856, 836, 776, 760, 712, 684, 668, 520.

HRMS (ESI) for **C₁₀H₁₆FN₂O₂P** (246.0933): 246.0930.

Typical Procedure 2 (TP2): Cross-Coupling Reactions

In a dry argon flushed Schlenk-tube, the corresponding phosphorodiamidate (1.0 mmol) was dissolved in THF (1 mL) and then cooled to the indicated temperature. TMP₂Mg·2LiCl (0.6 M in THF, 1.83 mL, 1.1 mmol) was added dropwise and the mixture was stirred at the indicated temperature. Complete metalation was detected by GC-analysis of reaction aliquots, quenched with I₂ in THF. ZnCl₂ (1 M in THF, 1.2 mL, 1.2 mmol) was added

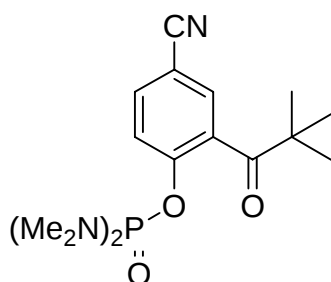
at -40 °C or below and the reaction mixture was stirred for 15 minutes. Pd(dba)₂ (2 mol%) and P(2-fur)₃ (4 mol %) were added as a solution in THF (0.5 mL), followed by the addition of the corresponding aryl iodide, and the reaction mixture was allowed to warm to room temperature overnight. The reaction mixture was quenched with sat. NH₄Cl solution (10 mL) and extracted with diethyl ether (3 x 20 mL). The combined organic layers were washed with brine, dried over MgSO₄ and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel.

Typical Procedure 3 (TP3): Acylations and allylations

In a dry argon flushed Schlenk-tube the corresponding phosphorodiamidate (1.0 mmol) was dissolved in THF (1 mL) and then cooled to the indicated temperature. (TMP)₂Mg·2LiCl (1.10 mmol) was added dropwise and the mixture was stirred at the indicated temperature. Complete metalation was detected by GC-analysis of reaction aliquots, quenched with I₂ in THF. ZnCl₂ (1 M in THF, 1.2 mL, 1.2 mmol) was added at -40 °C or below. The mixture was stirred for 15 minutes, then CuCN·2LiCl (1 M in THF, 0.5 mL, 0.5 mmol) and the corresponding acid chloride or allylbromide were added, and the mixture was allowed to warm to room temperature overnight. The reaction mixture was quenched with sat. NH₄Cl solution (10 mL) and was extracted with diethyl ether (3 x 20 mL). The combined organic

layers were washed with brine, dried over MgSO_4 and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel.

Synthesis of 4-cyano-2-(2,2-dimethylpropanoyl)phenyl *N,N,N',N'*-tetramethyldiamidophosphate (5a):



Prepared according to **TP3** from **3a** (1.27 g, 5.0 mmol), $\text{TMP}_2\text{Mg}\cdot 2\text{LiCl}$ (9.16 mL, 0.6 M in THF, 5.5 mmol) in THF (5 mL) at 0 °C. After 1 h, transmetalation using ZnCl_2 (1 M in THF, 6 mL, 6.00 mmol) was performed, followed by the addition of $\text{CuCN}\cdot 2\text{LiCl}$ (1 M in THF, 2.5 mL, 2.5 mmol) and pivaloyl chloride (664 mg, 5.5 mmol). The mixture was allowed to warm to 25 °C within 12 h. Flash chromatography on silica (ethyl acetate) furnished **5a** as a colorless solid (1.32 g, 78%).

m.p.: 65.4 – 67.9 °C.

$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ : 7.8 (m, 1 H), 7.6 (dd, $J = 8.7$ Hz, $J = 2.1$ Hz, 1 H), 7.4 (m, 1 H), 2.7 (d, $J = 10.4$ Hz, 12 H), 1.2 (s, 9 H).

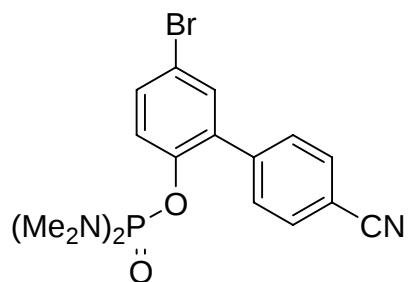
$^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ : 209.4, 151.5, 134.3, 133.7, 130.3, 120.8, 118.2, 107.2, 45.5, 36.9, 26.8.

MS (70 eV, EI) m/z (%): 338 (1) [M^+], 337 (1), 295 (47), 294 (100), 293 (10), 281 (85), 280 (100), 278 (13), 237 (18), 230 (19), 186 (59), 184 (10), 173 (12), 146 (10), 145 (23), 136 (12), 135 (100), 92 (34), 90 (10), 57 (19).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3392, 3196, 3076, 2228, 1696, 1600, 1484, 1408, 1364, 1300, 1224, 1132, 988, 892, 852, 764, 748, 692, 660.

HRMS (EI) for $\text{C}_{16}\text{H}_{24}\text{N}_3\text{O}_3\text{P}$ (337.1555): 337.1566.

Synthesis of 5-bromo-4'-cyanobiphenyl-2-yl *N,N,N',N'*-tetramethyldiamidophosphate (5b):



Prepared according to **TP2** from **3b** (1.54 g, 5.0 mmol), $\text{TMP}_2\text{Mg}\cdot 2\text{LiCl}$ (9.16 mL, 0.6 M in THF, 5.5 mmol) in THF (5 mL) at $-50\text{ }^\circ\text{C}$. After 7 h, transmetalation using ZnCl_2 (1 M in THF, 6 mL, 1.2 mmol) was performed, followed by the addition of $\text{Pd}(\text{dba})_2$ (55 mg, 2 mol%), $\text{P}(\text{2-fur})_3$ (45 mg, 4 mol%) in THF (5 mL) and 4-iodobenzonitrile (1.26 g, 5.50 mmol). The mixture was allowed to warm to $25\text{ }^\circ\text{C}$ within 12 h. Purification by flash chromatography on silica gel (ethyl acetate) furnished **5b** as a pale yellow solid (1.63 g, 80%).

m.p.: 128.8 – 129.8 °C.

¹H-NMR (300 MHz, CDCl₃) δ: 7.7 (d, *J* = 8.6 Hz, 2 H), 7.6 (d, *J* = 8.6 Hz, 2 H), 7.5 (m, 1 H), 7.4 (m, 2 H), 2.5 (d, *J* = 10.4 Hz, 12 H).

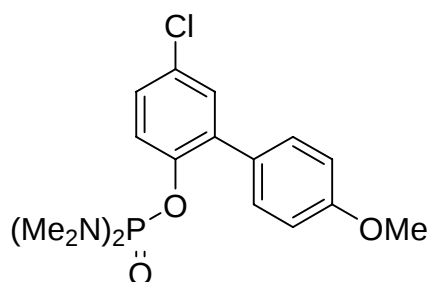
¹³C-NMR (75 MHz, CDCl₃) δ: 147.7, 141.7, 133.5, 132.9, 132.2, 130.5, 122.6, 118.8, 117.3, 111.8, 36.7.

MS (70 eV, EI) *m/z* (%): 407 (4) [M⁺], 193 (13), 164 (6), 135 (100).

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3076, 2928, 2904, 2856, 2808, 2224, 1608, 1508, 1468, 1452, 1408, 1384, 1300, 1260, 1228, 1212, 1184, 1124, 1108, 1068, 1028, 1016, 984, 904, 852, 816, 804, 768, 756, 728, 684.

HRMS (EI) for C₁₇H₁₉BrN₃O₂P (407.0398): 407.0386.

Synthesis of 5-chloro-4'-methoxybiphenyl-2-yl *N,N,N',N'*-tetramethyldiamidophosphate (5c):



Prepared according to **TP2** from **3d** (2.62 g, 8.0 mmol), TMP₂Mg·2LiCl (14.67 mL, 0.6 M in THF, 8.8 mmol) in THF (8 mL) at -40 °C. After 1.5 h, transmetalation using ZnCl₂ (1 M in THF, 9.6 mL, 9.6 mmol) was performed, followed by the addition

of Pd(dba)₂ (88 mg, 2 mol%), P(2-fur)₃ (72 mg, 4 mol%) in THF (8 mL) and 4-iodoanisole (2.06 g, 8.8 mmol). The mixture was allowed to warm to 25 °C within 12 h. Purification by flash chromatography on silica gel (ethyl acetate) furnished **5c** as an orange oil (2.78 g, 90%).

¹H-NMR (600 MHz, CDCl₃) δ: 7.5 (dd, *J* = 8.7 Hz, *J* = 1.2 Hz, 1 H), 7.4 (d, *J* = 8.8 Hz, 2 H), 7.3 (dd, *J* = 2.6 Hz, *J* = 1.1 Hz, 1 H), 7.2 (dd, *J* = 8.6 Hz, *J* = 2.6 Hz, 1 H), 6.9 (d, *J* = 8.8 Hz, 2 H), 3.8 (s, 3 H), 2.5 (d, *J* = 10.1 Hz, 12 H).

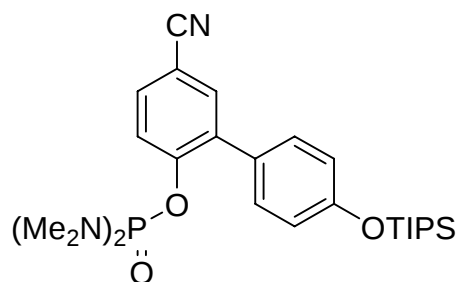
¹³C-NMR (150 MHz, CDCl₃) δ: 159.4, 147.3, 134.8, 134.7, 130.8, 129.5, 129.4, 128.2, 122.1, 113.7, 55.5, 36.7.

MS (70 eV, EI) *m/z* (%): 370 (29), 369 (17), 368 (100) [M⁺], 279 (27), 260 (21), 236 (18), 234 (61), 198 (14), 139 (17), 136 (13), 135 (64), 91 (10), 44 (47).

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3464, 3000, 2932, 2900, 2852, 2812, 1608, 1580, 1564, 1516, 1480, 1464, 1420, 1388, 1296, 1244, 1204, 1176, 1128, 1112, 1096, 1068, 1040, 1024, 984, 904, 816, 780, 756, 724, 696, 668.

HRMS (EI) for C₁₇H₂₂ClN₂O₃P (326.1559): 326.1574.

Synthesis of 5-cyano-4'-[(triisopropylsilyl)oxy]biphenyl-2-yl *N,N,N',N'*-tetramethyldiamidophosphate (5d):



Prepared according to **TP2** from **3a** (506 mg, 2.0 mmol), $\text{TMP}_2\text{Mg}\cdot 2\text{LiCl}$ (3.67 mL, 0.6 M in THF, 2.2 mmol) in THF (2 mL) at 0 °C. After 1 h, transmetalation using ZnCl_2 (1 M in THF, 2.4 mL, 2.4 mmol) was performed, followed the addition of $\text{Pd}(\text{dba})_2$ (22 mg, 2 mol%), $\text{P}(\text{2-fur})_3$ (18 mol%) in THF (2 mL) and (4-iodophenoxy)-(triisopropyl)silane (828 mg, 2.2 mmol) were added. The mixture was allowed to warm to 25 °C within 12 h. Purification by flash chromatography on silica gel (ethyl acetate) furnished **5d** as yellow oil (833 mg, 83%).

^1H -NMR (400 MHz, CDCl_3) δ : 7.6 (m, 3 H), 7.3 (d, J = 8.1 Hz, 2 H), 6.9 (d, J = 8.4 Hz, 2 H), 2.5 (d, J = 10.3 Hz, 12 H), 1.3 (m, 3 H), 1.1 (m, 18 H).

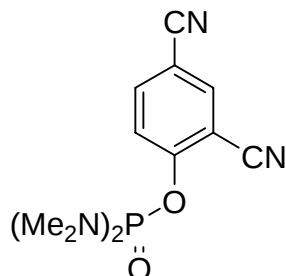
^{13}C -NMR (100 MHz, CDCl_3) δ : 156.4, 152.3, 135.0, 134.6, 132.4, 130.8, 128.7, 121.5, 120.0, 118.8, 108.1, 36.7, 18.1, 12.9.

MS (70 eV, EI) m/z (%): 501 (16) [M^+], 459 (30), 458 (100), 415 (10), 135 (40).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2944, 2892, 2868, 2228, 1604, 1512, 1484, 1464, 1420, 1392, 1260, 1216, 1172, 1132, 1104, 1068, 1040, 988, 900, 856, 836, 764, 740, 684, 660.

HRMS (ESI) for $\text{C}_{26}\text{H}_{41}\text{N}_3\text{O}_3\text{PSi}$ (502.2655): 502.2653 [$\text{M}+\text{H}$] $^+$.

Synthesis of 2,4-dicyanophenyl *N,N,N',N'*-tetramethyldiamidophosphate (5e):



4-Cyanophenyl *N,N,N',N'*-tetramethyldiamidophosphate (**3a**) (254 mg, 1.00 mmol) was reacted with $\text{TMP}_2\text{Mg} \cdot 2\text{LiCl}$ (0.6 M in THF, 1.83 mL, 1.10 mmol) at 0 °C for 1 h. Complete metalation was detected by GC-analysis of reaction aliquots, quenched with I_2 in THF. The mixture was cooled to -40 °C and ZnCl_2 (1 M in THF, 1.2 mL, 1.20 mmol) was added. The resulting mixture was stirred for 15 min at -40 °C, then $\text{CuCN} \cdot 2\text{LiCl}$ (1 M in THF, 1.3 mL, 1.30 mmol) was added. After 15 min at -40 °C, TsCN (199 mg, 1.10 mmol) was added and the reaction mixture was slowly warmed to 25 °C and stirred for 1 h. The reaction mixture was quenched with sat. aq. NH_4Cl solution (5 mL), extracted with diethyl ether (3 × 15 mL) and dried over anhydrous MgSO_4 . After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (ethyl acetate) furnished **5e** (209 mg, 77%) as a colorless solid.

m.p.: 143.0 – 144.2 °C.

$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ : 7.9 (d, J = 1.1 Hz, 1 H), 7.8 (m, 2 H), 2.8 (d, J = 10.4 Hz, 12 H).

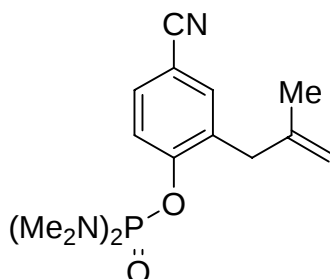
^{13}C -NMR (75 MHz, CDCl_3) δ : 156.9, 138.0, 137.4, 122.0, 116.7, 114.0, 108.7, 106.9, 36.8.

MS (70 eV, EI) m/z (%): 278 (66) [M^+], 207 (100), 206 (23), 135 (50), 97 (16), 95 (14), 83 (32), 73 (54), 57 (18), 55 (27), 43 (13), 41 (23).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3056, 2936, 2892, 2236, 1604, 1488, 1456, 1312, 1296, 1252, 1224, 1192, 1164, 1108, 1068, 1000, 984, 924, 912, 864, 844, 764, 744, 716, 684, 660.

HRMS (EI) for $\text{C}_{12}\text{H}_{15}\text{N}_4\text{O}_2\text{P}$ (278.0933): 278.0920.

Synthesis of 4-cyano-2-(2-methylprop-2-en-1-yl)phenyl N,N,N',N' -tetramethyldiamidophosphate (5f):



Prepared according to **TP3** from **3a** (254 mg, 1.0 mmol), $\text{TMP}_2\text{Mg}\cdot 2\text{LiCl}$ (0.6 M in THF, 1.83 mL, 1.1 mmol) in THF (1 mL) at 0 °C. After 1 h, transmetalation using ZnCl_2 (1 M in THF, 1.2 mL, 1.2 mmol) was performed, followed by the addition of $\text{CuCN}\cdot 2\text{LiCl}$ (1 M in THF, 0.50 mL, 0.5 mmol) and 3-bromo-2-methylpropene (156 mg, 1.2 mmol). The mixture was allowed to warm to 25 °C within 12 h. Purification by flash

chromatography on silica gel (ethyl acetate) furnished **5f** as a colorless oil (258 g, 84%).

¹H-NMR (300 MHz, CDCl₃) δ : 7.5 (m, 2 H), 7.5 (s, 1 H), 4.9 (d, J = 1.8 Hz, 1 H), 4.6 (d, J = 0.9 Hz, 1 H), 3.4 (s, 2 H), 2.7 (d, J = 10.1 Hz, 12 H) 1.7 (s, 3 H).

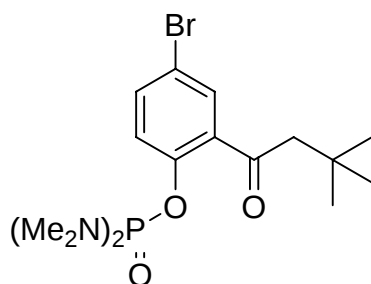
¹³C-NMR (75 MHz, CDCl₃) δ : 153.7, 142.8, 135.0, 132.2, 131.8, 120.1, 119.0, 113.3, 107.6, 38.0, 36.9, 22.7.

MS (70 eV, EI) m/z (%): 307 (29) [M^+], 306 (23), 263 (22), 200 (15), 199 (13), 173 (15), 156 (11), 154 (14), 136 (15), 135 (100), 92 (32).

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3460, 2932, 2904, 2856, 2812, 2228, 1652, 1600, 1580, 1492, 1456, 1412, 1376, 1304, 1248, 1212, 1180, 1112, 1068, 988, 940, 924, 876, 832, 756, 724, 704, 684, 664.

HRMS (EI) for C₁₅H₂₂N₃O₂P (307.1450): 307.1410.

Synthesis of 4-bromo-2-(3,3-dimethyl-2-oxobutyl)phenyl *N,N,N',N'*-tetramethyldiamidophosphate (5g)



Prepared according to **TP3** from **3b** (614 mg, 2.0 mmol), TMP₂Mg·2LiCl (3.6 mL, 0.6 M in THF, 2.2 mmol) in 1 mL THF at -50 °C. After 7 h, transmetalation using ZnCl₂ (1 M in THF, 2.4

mL, 2.4 mmol) was performed, followed by the addition of CuCN·2LiCl (1 M in THF, 1 mL, 1.0 mmol) and 3,3-dimethylbutanoyl chloride (323 mg, 2.4 mmol). The mixture was allowed to warm to 25 °C within 12 h. Purification by flash chromatography on silica gel (ethyl acetate) furnished **5g** as a colorless oil (293 mg, 72%).

¹H-NMR (300 MHz, CDCl₃) δ: 7.5 (m, 1 H), 7.5 (m, 2 H), 2.9 (s, 2 H), 2.7 (d, *J* = 10.3 Hz, 2 H), 1.1 (s, 9 H).

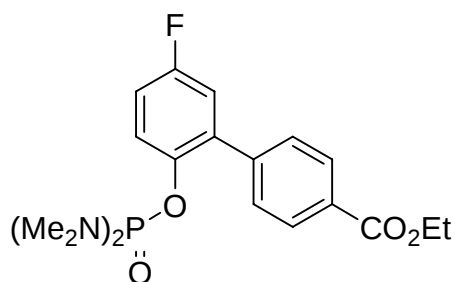
¹³C-NMR (75 MHz, CDCl₃) δ: 201.3, 148.2, 135.0, 131.8, 122.4, 116.8, 55.4, 36.9, 31.8, 30.0.

MS (70 eV, EI) *m/z* (%): 404 (5) [M⁺], 363 (10), 362 (62), 361 (17), 360 (62), 346 (20), 344 (20), 335 (34), 333 (35), 307 (45), 306 (100), 305 (52), 304 (100), 303 (19), 299 (11), 297 (11), 262 (12), 260 (11), 225 (21), 224 (11), 201 (10), 199 (11), 198 (12), 135 (100), 92 (19), 57 (17).

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3460, 2952, 2904, 2868, 2812, 1688, 1588, 1568, 1472, 1388, 1364, 1304, 1264, 1212, 1176, 1116, 1068, 988, 896, 820, 760, 744, 724, 676.

HRMS (EI) for C₁₆H₂₆N₂O₃P (404.0863): 404.0811.

Synthesis of ethyl 2'-{[bis(dimethylamino)phosphoryl]oxy}-5'-fluorobiphenyl-4-carboxylate (5h**):**



Prepared according to **TP2** from **3c** (246 mg, 1.0 mmol), $\text{TMP}_2\text{Mg}\cdot 2\text{LiCl}$ (1.83 mL, 0.6 M in THF, 1.1 mmol) in THF (1 mL) at $-40\text{ }^\circ\text{C}$. After 4 h, transmetalation using ZnCl_2 (1 M in THF, 1.2 mL, 1.2 mmol) was performed, followed by addition of $\text{Pd}(\text{dba})_2$ (11 mg, 2 mol%), $\text{P}(\text{2-fur})_3$ (9 mg, 4 mol%) in THF (2 mL) and ethyl-4-iodobenzoate (414 mg, 1.5 mmol). The mixture was allowed to warm to $25\text{ }^\circ\text{C}$ within 12 h. Purification by flash chromatography on silica gel (ethyl acetate) furnished **5h** as a pale yellow solid (307 mg, 78%).

m.p.: $77.0 - 78.6\text{ }^\circ\text{C}$.

^1H -NMR (600 MHz, CDCl_3) δ : 8.1 (d, $J = 8.4\text{ Hz}$, 2 H), 7.6 (d, $J = 8.6\text{ Hz}$, 2 H), 7.5 (dd, $J = 9.8\text{ Hz}$, $J = 5.4\text{ Hz}$, 1 H), 7.0 (m, 2 H), 4.4 (q, $J = 7.1\text{ Hz}$, 2 H), 2.7 (m, 2 H), 2.5 (d, $J = 10.1\text{ Hz}$, 10 H), 1.4 (t, $J = 7.2\text{ Hz}$, 3 H).

^{13}C -NMR (150 MHz, CDCl_3) δ : 166.6, 159.9, 158.3, 144.6, 141.9, 133.9, 129.9, 129.7, 129.6, 122.3, 117.5, 116.0, 115.8, 61.3, 36.9, 36.7, 14.5.

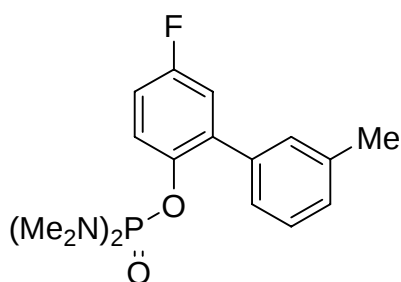
MS (70 eV, EI) m/z (%): 394 (3) [M^+], 286 (13), 260 (10), 186 (10), 157 (10), 135 (100).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3040, 3004, 2928, 2908, 2856, 2816, 1708, 1668, 1608, 1592, 1568, 1512, 1488, 1452, 1424, 1400, 1372,

1304, 1280, 1252, 1224, 1172, 1128, 1100, 1068, 1016, 992, 940, 912, 884, 860, 828, 772, 756, 732, 712, 700, 672.

HRMS (ESI) for **C₁₉H₂₅FN₂O₄P** (395.1536): 395.1529 [M+H]⁺.

Synthesis of 5-fluoro-3'-methylbiphenyl-2-yl *N,N,N',N'*-tetramethyldiamidophosphate (5i):



Prepared according to **TP2** from **3c** (1.23 g, 5.0 mmol), **TMP₂Mg·2LiCl** (3.67 mL, 0.6 M in THF, 5.5 mmol) in THF (5 mL) at -40 °C. After 4 h, transmetalation using **ZnCl₂** (1 M in THF, 6.0 mL, 6.0 mmol) was performed, followed by the addition of **Pd(dba)₂** (55 mg, 2 mol%), **P(2-fur)₃** (45 mg, 4 mol%) in THF (5 mL) and 3-iodotoluene (1.2 g, 5.5 mmol). The mixture was allowed to warm to 25 °C within 12 h. Purification by flash chromatography on silica gel (ethyl acetate) furnished **5i** as a pale yellow oil (1.26 g, 75%).

¹H-NMR (600 MHz, CDCl₃) δ: 7.4 (ddd, *J* = 9.0 Hz, *J* = 4.9 Hz, *J* = 1.2 Hz, 1 H), 7.3 (ddd, *J* = 15.2 Hz, *J* = 7.8 Hz, *J* = 7.7 Hz, 3 H), 7.1 (d, *J* = 7.6 Hz, 1 H), 7.0 (ddd, *J* = 9.0 Hz, *J* = 3.2 Hz, *J* = 1.0 Hz, 1 H), 7.0 (ddd, *J* = 9.0 Hz, *J* = 7.7 Hz, *J* =

3.2 Hz, 1 H), 2.7 (dd, $J = 11.4$ Hz, $J = 10.0$ Hz, 1 H), 2.5 (d, $J = 10.1$ Hz, 11 H), 2.4 (s, 3 H).

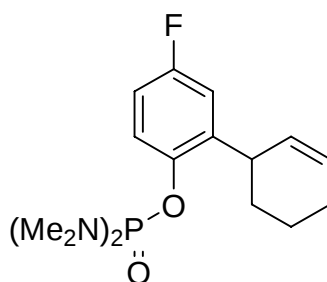
^{13}C -NMR (150 MHz, CDCl_3) δ : 159.9, 158.4, 144.6, 137.8, 137.2, 130.4, 128.6, 128.3, 126.7, 122.1, 117.5, 115.1, 36.9, 21.6.

MS (70 eV, EI) m/z (%): 337 (15), 336 (100) [M^+], 248 (12), 247 (14), 228 (83), 185 (13), 183 (12), 169 (10), 136 (12), 135 (42), 92 (11), 44 (71).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3464, 2992, 2924, 2896, 2852, 2812, 1608, 1584, 1496, 1476, 1412, 1396, 1304, 1220, 1164, 1116, 1096, 1068, 1044, 984, 936, 892, 816, 788, 760, 720, 700, 664.

HRMS (EI) for $\text{C}_{17}\text{H}_{22}\text{FN}_2\text{O}_2\text{P}$ (336.1403): 336.1377.

Synthesis of 2-cyclohex-2-en-1-yl-4-fluorophenyl N,N,N',N' -tetramethyldiamidophosphate (5j):



Prepared according to **TP3** from **3c** (246 mg, 1.0 mmol), $\text{TMP}_2\text{Mg} \cdot 2\text{LiCl}$ (0.6 M in THF, 1.83 mL, 1.1 mmol) in THF (1 mL) at 0 °C. After 1 h, transmetalation using ZnCl_2 (1 M in THF, 1.2 mL, 1.2 mmol) was performed, followed by the addition of $\text{CuCN} \cdot 2\text{LiCl}$ (1 M in THF, 0.5 mL, 0.5 mmol) and ethyl 3-bromocyclohexene (354 mg, 1.2 mmol). The mixture was allowed

to warm to 25 °C within 12 h. Purification by flash chromatography on silica gel (ethyl acetate) furnished **5j** as a colorless oil (277 mg, 85%).

¹H-NMR (600 MHz, CDCl₃) δ : 7.2 (ddd, J = 8.9 Hz, J = 4.9 Hz, J = 1.2 Hz, 1 H), 6.9 (ddd, J = 9.6 Hz, J = 3.2 Hz, J = 1.0 Hz, 1 H), 6.8 (ddd, J = 8.9 Hz, J = 7.7 Hz, J = 3.2 Hz, 1 H), 6.0 (m, 1 H), 5.6 (m, 1 H), 3.8 (s, 1 H), 2.7 (dd, J = 15.7 Hz, J = 10.1 Hz, 12 H), 2.1 (m, 2 H), 2.0 (m, 1 H), 1.7 (m, 1 H), 1.6 (m, 2 H).

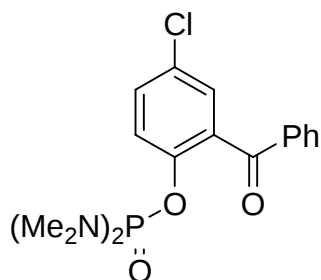
¹³C-NMR (150 MHz, CDCl₃) δ : 160.1, 145.2, 138.8, 129.8, 129.0, 120.3, 115.9, 113.6, 36.9, 35.1, 30.4, 25.1, 20.8.

MS (70 eV, EI) m/z (%): 327 (20), 326 (100) [M^+], 192 (12), 190 (12), 153 (23), 135 (95), 92 (15), 44 (39).

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3456, 3220, 3020, 2928, 2856, 2812, 1652, 1616, 1592, 1484, 1456, 1420, 1392, 1308, 1240, 1220, 1168, 1096, 1068, 984, 956, 900, 864, 816, 756, 736, 708, 664.

HRMS (EI) for C₁₆H₂₄FN₂O₂P (326.1559): 326.1574.

Synthesis of 2-benzoyl-4-chlorophenyl *N,N,N',N'*-tetramethyl-diamidophosphate (5k):



Prepared according to **TP3** from **3d** (1.31 g, 5.0 mmol), $\text{TMP}_2\text{Mg}\cdot 2\text{LiCl}$ (0.6 M in THF, 9.17 mL, 5.5 mmol) in THF (5 mL) at $-40\text{ }^\circ\text{C}$. After 1.5 h, transmetalation using ZnCl_2 (1 M in THF, 6.0 mL, 6.0 mmol) was performed, followed by the addition of $\text{CuCN}\cdot 2\text{LiCl}$ (1 M in THF, 2.5 mL, 2.5 mmol) and benzoyl chloride (773 mg, 5.5 mmol). The mixture was allowed to warm to $25\text{ }^\circ\text{C}$ within 12 h. Purification by flash chromatography on silica gel (ethyl acetate) furnished **5k** as a pale red oil (1.57 g, 85%).

^1H -NMR (600 MHz, CDCl_3) δ : 7.8 (m, 2 H), 7.6 (m, 1 H), 7.5 (dd, $J = 8.8\text{ Hz}$, $J = 0.9\text{ Hz}$, 1 H), 7.5 (t, $J = 7.8\text{ Hz}$, 2 H), 7.4 (m, 1 H), 7.4 (dd, $J = 2.7\text{ Hz}$, $J = 1.0\text{ Hz}$, 1 H), 2.4 (d, $J = 10.1\text{ Hz}$, 12 H).

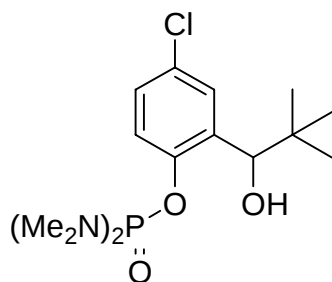
^{13}C -NMR (150 MHz, CDCl_3) δ : 194.2, 147.8, 137.2, 133.8, 132.6, 131.8, 130.1, 129.4, 128.8, 121.8, 36.5.

MS (70 eV, EI) m/z (%): 366 (3) [M^+], 324 (35), 323 (24), 322 (100), 321 (11), 280 (12), 278 (34), 258 (13), 228 (12), 135 (100), 105 (10), 77 (16), 44 (36).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3460, 3064, 2928, 2896, 2852, 2812, 1668, 1596, 1472, 1448, 1400, 1312, 1288, 1264, 1216, 1180, 1156, 1116, 1068, 988, 956, 900, 832, 808, 788, 760, 740, 712, 700, 668.

HRMS (EI) for $\text{C}_{17}\text{H}_{20}\text{ClN}_2\text{O}_3\text{P}$ (366.0900): 366.0900.

Synthesis of 4-chloro-2-(1-hydroxy-2,2-dimethylpropyl)phenyl N,N,N',N' -tetramethyldiamidophosphate (5l):



4-Chlorophenyl *N,N,N',N'*-tetramethyldiamidophosphate (**3d**) (525 mg, 2.0 mmol) was reacted with $\text{TMP}_2\text{Mg} \cdot 2\text{LiCl}$ (0.6 M in THF, 3.67 mL, 2.2 mmol) in THF (2 mL) at $-40\text{ }^\circ\text{C}$ for 1.5 h. Complete metalation was detected by GC-analysis of reaction aliquots, quenched with I_2 in THF. Then the mixture was cooled to $-80\text{ }^\circ\text{C}$ and pivaline aldehyde (215 mg, 2.5 mmol) was slowly added. The reaction mixture was slowly warmed to $25\text{ }^\circ\text{C}$ and stirred for 1 h. The reaction mixture was quenched with sat. aq. NH_4Cl solution (5 mL), extracted with diethyl ether ($3 \times 15\text{ mL}$) and dried over anhydrous MgSO_4 . After filtration, the solvent was evaporated *in vacuo*. Purification by flash chromatography (ethyl acetate) furnished **51** (550 mg, 79%) as a colorless solid.

m.p.: $158.3 - 160.5\text{ }^\circ\text{C}$.

$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ : 7.5 (d, $J = 2.0\text{ Hz}$, 1 H), 7.2 (m, 2 H), 4.8 (s, 1 H), 3.1 (br, 1 OH), 2.7 (dd, $J = 10.0\text{ Hz}$, $J = 6.1\text{ Hz}$, 12 H), 1.0 (s, 9 H).

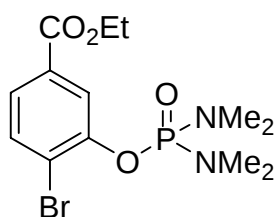
$^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ : 147.5, 136.3, 129.5, 129.4, 128.2, 120.6, 74.3, 36.9, 36.5, 26.1.

MS (70 eV, EI) m/z (%): 348 (2) [M^+], 290 (16), 189 (12), 288 (44), 247 (31), 246 (10), 245 (100), 153 (21), 135 (67), 91 (10), 44 (31).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3336, 2944, 2928, 2904, 2876, 1472, 1384, 1348, 1312, 1292, 1256, 1232, 1208, 1168, 1116, 1092, 1060, 1000, 984, 928, 908, 896, 868, 808, 752, 724, 672.

HRMS (EI) for $\text{C}_{15}\text{H}_{26}\text{ClN}_2\text{O}_3\text{P}$ (348.1370): 348.1354.

Synthesis of ethyl 3-[[bis(dimethylamino)phosphoryl]oxy} 4-bromobenzoate (6a):



Ethyl 3-[[bis(dimethylamino)phosphoryl]oxy]benzoate (**4a**) (300 mg, 1.0 mmol) was dissolved in THF (1 mL) and cooled to 0 °C. Then $\text{TMP}_2\text{Mg} \cdot 2\text{LiCl}$ (**2**) (0.6 M in THF, 1.83 mL, 1.1 mmol) was added dropwise. The mixture was stirred for 1 h, and after that $\text{BrCl}_2\text{CCl}_2\text{Br}$ (779 mg, 2.4 mmol), dissolved in dry THF (2 mL), was added dropwise at -40 °C and the resulting mixture was warmed to 25 °C and stirred for 1 h. The reaction mixture was quenched with sat. aq. NH_4Cl solution (5 mL), extracted with diethyl ether (3 × 15 mL) and dried over anhydrous Na_2SO_4 . After filtration, the solvent was evaporated *in vacuo*. Purification by flash chromatography (ethyl acetate) furnished **6a** (302 mg, 80%) as a pale yellow oil.

¹H-NMR (600 MHz, CDCl₃) δ : 8.0 (m, 1 H), 7.7 (m, 1 H), 7.6 (d, J = 7.9 Hz, 1 H), 4.4 (q, J = 7.1 Hz, 2 H), 2.8 (d, J = 10.4 Hz, 12 H), 1.4 (t, 7.2 Hz, 3 H).

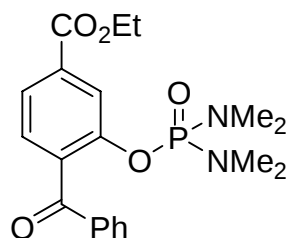
¹³C-NMR (150 MHz, CDCl₃) δ : 165.6, 150.0, 133.6, 131.4, 126.1, 121.8, 120.1, 61.6, 37.0, 14.5.

MS (70 eV, EI) m/z (%): 378 (1) [M⁺-H], 299 (39), 135 (100), 92 (17), 63 (8).

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 2929, 2811, 1717, 1589, 1573, 1475, 1405, 1366, 1279, 1212, 1101, 1068, 988, 954, 850, 754, 680, 663.

HRMS (EI) for C₁₃H₂₀N₂O₄BrP (378.0344): 378.0377.

Synthesis of ethyl 4-benzoyl-3-{[bis(dimethylamino)-phosphoryl]oxy}benzoate (6b):



Prepared according to **TP3** from **4a** (300 mg, 1.0 mmol), TMP₂Mg·2LiCl (0.6 M in THF, 1.83 mL, 1.1 mmol) in THF (1 mL) at 0 °C. After 1 h, transmetalation using ZnCl₂ (1 M in THF, 1.2 mL, 1.2 mmol) was performed, followed by the addition of CuCN·2LiCl (1 M in THF, 0.5 mL, 0.5 mmol) and benzoyl chloride (155 mg, 1.1 mmol). The mixture was allowed to warm to 25 °C within 12 h. Purification by flash chromatography on silica

gel (ethyl acetate) furnished **6b** as a greenish yellow oil (296 mg, 73%).

¹H-NMR (600 MHz, CDCl₃) δ : 8.1 (m, 1 H), 7.9 (dd, J = 7.9 Hz, 1.3 Hz, 1 H), 7.8 (m, 2 H), 7.6 (m, 1 H), 7.4 (m, 3 H), 4.4 (q, J = 7.1 Hz, 2 H), 2.5 (d, J = 10.1 Hz, 12 H), 1.4 (t, J = 7.2 Hz, 3 H).

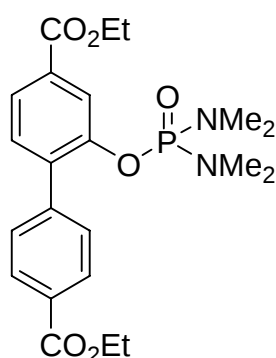
¹³C-NMR (150 MHz, CDCl₃) δ : 195.0, 165.5, 149.1, 137.1, 135.5, 134.0, 133.8, 130.2, 129.5, 128.9, 127.6, 125.1, 121.5, 61.7, 36.5, 14.5.

MS (70 eV, EI) m/z (%): 404 (1) [M⁺], 361 (23), 360 (100), 359 (15), 317 (35), 289 (15), 269 (10), 266 (14), 168 (13), 152 (11), 135 (45), 105 (26), 92 (16), 77 (39).

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 2929, 1718, 1668, 1596, 1405, 1281, 1205, 1089, 990, 964, 920, 851, 756, 703, 652.

HRMS (EI) for C₂₀H₂₅N₂O₅P (404.1501): 404.1493.

Synthesis of diethyl 2-[[bis(dimethylamino)phosphoryl]oxy]-biphenyl-4,4'-dicarboxylate (6c):



Prepared according to **TP2** from **4a** (300 mg, 1.0 mmol), $\text{TMP}_2\text{Mg}\cdot 2\text{LiCl}$ (0.6 M in THF, 1.83 mL, 1.1 mmol) in THF (1 mL) at 0 °C. After 1 h, transmetalation using 1.2 mL ZnCl_2 (1 M in THF) was performed, followed by the addition of $\text{Pd}(\text{dba})_2$ (11 mg, 2 mol%), $\text{P}(2\text{-fur})_3$ (9 mg, 4 mol%) in THF (1 mL) and ethyl 4-iodobenzoate (414 mg, 1.5 mmol). The mixture was allowed to warm to 25 °C within 12 h. Purification by flash chromatography on silica gel (ethyl acetate) furnished **6c** as a yellowish solid (351 mg, 78%).

m.p.: 53.0 – 55.9 °C.

^1H -NMR (600 MHz, CDCl_3) δ : 8.1 (m, 2 H), 8.0 (m, 1 H), 7.9 (m, 1 H), 7.6 (m, 2 H), 7.4 (dd, $J = 8.1$ Hz, $J = 1.0$ Hz, 1 H), 4.4 (m, 4 H), 2.5 (d, $J = 10.1$ Hz, 12 H), 1.4 (m, 6 H).

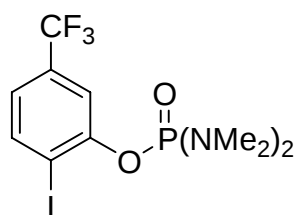
^{13}C -NMR (150 MHz, CDCl_3) δ : 166.6, 165.9, 148.6, 148.5, 142.1, 137.2, 137.1, 131.8, 131.1, 130.0, 129.8, 129.6, 125.6, 121.9, 61.5, 61.3, 36.7, 14.5.

MS (70 eV, EI) m/z (%): 448 (4) [M^+], 403 (3), 374 (10), 340 (24), 314 (31), 195 (11), 169 (7), 139 (15), 135 (100), 92 (8).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2987, 2901, 1707, 1605, 1556, 1518, 1474, 1392, 1366, 1272, 1235, 1181, 1197, 1124, 1099, 1070, 1026, 999, 958, 958, 906, 854, 845, 781, 757, 728, 675.

HRMS (EI) for $\text{C}_{22}\text{H}_{29}\text{N}_2\text{O}_6\text{P}$ (448.1763): 448.1777.

Synthesis of 2-iodo-5-(trifluoromethyl)phenyl N,N,N',N' -tetramethyldiamidophosphate(6d):



A solution of **4b** (592 mg, 2.0 mmol) in THF (2 mL) was cooled to -40 °C. Then $\text{TMP}_2\text{Mg} \cdot 2\text{LiCl}$ (0.6 M in THF, 3.67 mL, 2.2 mmol) was added dropwise and the resulting mixture was stirred for 2 h at -40 °C. Complete metalation was detected by GC-analysis of reaction aliquots, quenched with I_2 in THF. I_2 (558 mg, 2.2 mmol) in THF (2 mL) was added and the mixture was warmed to 25 °C within 12 h. The reaction mixture was quenched by the addition of sat. aq. $\text{Na}_2\text{S}_2\text{O}_3$ (10 mL) and sat. aq. NH_4Cl solution (10 mL). The mixture was extracted with diethyl ether (3 x 20 mL) and with ethyl acetate (3 x 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (diethyl ether:*n*-pentane = 3:1) furnishing **6d** as a colorless solid (749 mg, 88%).

m.p.: 85.3 – 86.1 °C.

$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ : 7.9 (d, J = 8.4 Hz, 1 H), 7.7 (s, 1 H), 7.1 (dd, J = 8.3 Hz, J = 2.1 Hz, 1 H), 2.8 (d, J = 10.4 Hz, 12 H).

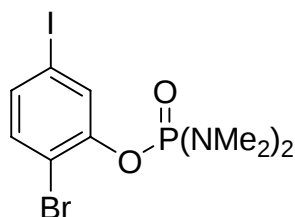
$^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ : 152.1, 140.3, 132.4 (q, $J(\text{C-F})$ = 33.3 Hz), 123.7 (q, $J(\text{C-F})$ = 272.2 Hz), 122.0, 116.6, 37.1.

MS (70 eV, EI) m/z (%): 423 (16), 422 (93), 378 (39), 314 (41), 296 (57), 295 (100), 287 (10), 276 (47), 252 (15), 250 (14), 232 (10), 207 (23), 188 (19), 160 (37), 145 (11), 144 (34), 141 (11), 136 (25), 135 (100), 132 (29), 92 (46), 91 (12), 90 (20), 76 (14), 63 (11).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2932, 2908, 2856, 1596, 1576, 1480, 1460, 1404, 1324, 1292, 1260, 1232, 1204, 1168, 1120, 1080, 1028, 1000, 980, 940, 892, 824, 764, 732, 716, 676.

HRMS (EI) for $\text{C}_{11}\text{H}_{15}\text{F}_3\text{IN}_2\text{O}_2\text{P}$ (421.9868): 421.9870.

Synthesis of 2-bromo-5-iodophenyl N,N,N',N' -tetramethyldiamidophosphate (6e).



3-Iodophenyl N,N,N',N' -tetramethyldiamidophosphate (**4c**) (400 mg, 1.0 mmol) was dissolved in THF (1 mL) and cooled to 0 °C. Then $\text{TMP}_2\text{Mg} \cdot 2\text{LiCl}$ (**2**) (0.6 M in THF, 1.83 mL, 1.1 mmol) was added dropwise. The mixture was stirred for 1 h, and after that $\text{BrCl}_2\text{CCl}_2\text{Br}$ (488 mg, 1.5 mmol), dissolved in dry THF (1 mL), was added dropwise at 0 °C and the resulting mixture was warmed to 25 °C and stirred for 1 h. The reaction mixture was quenched with sat. aq. NH_4Cl solution (5 mL), extracted with diethyl ether (3 × 15 mL) and dried over anhydrous Na_2SO_4 . After filtration, the solvent was evaporated *in vacuo*.

Purification by flash chromatography (ethyl acetate) furnished **6e** (329 mg, 76%) as a yellowish solid.

m.p.: 64.9 – 66.9 °C.

¹H-NMR (600 MHz, CDCl₃) δ: 7.7 (m, 1 H), 7.3 (dd, *J* = 1.2 Hz, *J* = 8.4 Hz, 1 H), 7.2 (dd, *J* = 0.9 Hz, *J* = 8.2 Hz, 1 H), 2.7 (d, *J* = 10.2 Hz, 12 H).

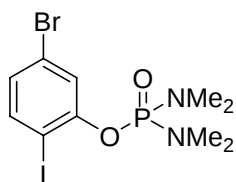
¹³C-NMR (150 MHz, CDCl₃) δ: 149.6, 134.9, 134.6, 130.2, 114.7, 92.5, 37.2.

MS (70 eV, EI) *m/z* (%): 432 (1) [M⁺+H], 353 (100), 135 (90), 92 (5), 63 (2), 44(11).

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 2931, 2884, 2845, 2811, 1566, 1467, 1383, 1310, 1290, 1215, 1172, 1068, 999, 983, 920, 799, 755, 675.

HRMS (EI) for C₁₀H₁₆N₂O₂BrIP (432.9178): 432.9178 [M+H]⁺.

Synthesis of 5-bromo-2-iodophenyl *N,N,N',N'*-tetramethyldiamidophosphate (**6f**):



A solution of **4d** (307 mg, 1.0 mmol) in THF (1 mL) was cooled to -30 °C. Then TMP₂Mg·2LiCl (0.6 M in THF, 1.84 mL, 1.1 mmol) was added dropwise and the resulting mixture was stirred for 2 h at -30 °C. Complete metalation was detected by GC-analysis of reaction aliquots, quenched with I₂ in THF. I₂ (279 mg,

1.1 mmol) in THF (1 mL) was added and the mixture was warmed to 25 °C within 2 h. The reaction mixture was quenched by the addition of sat. aq. Na₂S₂O₃ (10 mL) and sat. aq. NH₄Cl solution (10 mL). The mixture was extracted with diethyl ether (3 x 20 mL) and with ethyl acetate (3 x 20 mL). The combined organic layers were washed with brine, dried over Na₂SO₄ and the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (diethyl ether) furnishing the 5-bromo-2-iodophenyl *N,N,N',N'*-tetramethyldiamidophosphate **6f** (yellow solid, 190 mg, 44%) and the isomer 3-bromo-2-iodophenyl *N,N,N',N'*-tetramethyldiamidophosphate (yellow solid, 187 mg, 43%).

5-Bromo-2-iodophenyl *N,N,N',N'*-tetramethyldiamidophosphate:

m.p.: 108.4-110.1 °C.

¹H-NMR (600 MHz, CDCl₃) δ: 7.65 (dd, *J* = 2.1 Hz, *J* = 1 Hz, 1 H), 7.6 (dd, *J* = 8.5 Hz, *J* = 1 Hz, 1 H), 6.98 (dd, *J* = 8.5 Hz, *J* = 2.1 Hz, 1 H), 2.73 (d, *J* = 10.2 Hz, 12 H).

¹³C-NMR (150 MHz, CDCl₃) δ: 152.1, 140.1, 128.6, 122.9, 122.8, 86.6, 36.9.

MS (70 eV, EI) *m/z* (%): 432 (2) [M⁺], 307 (76), 207, 135 (100), 92 (12), 75 (5), 44 (24).

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 2897, 1563, 1458, 1376, 1203, 998, 980, 926, 759.

HRMS (EI) for C₁₀H₁₅N₂O₂BrIP (431.9099): 431.9096.

3-Bromo-2-iodophenyl *N,N,N',N'*-tetramethyldiamidophosphate:

m.p.: 75.0-77.8 °C.

¹H-NMR (600 MHz, CDCl₃) δ: 7.45 (dd, *J* = 8.2 Hz, *J* = 1.3 Hz, 1 H), 7.4 (dd, *J* = 8.2 Hz, *J* = 1.3 Hz, 1 H), 7.16 (t, *J* = 8.2 Hz, *J* = 2.1 Hz, 1 H), 2.75 (d, *J* = 10.2 Hz, 12 H).

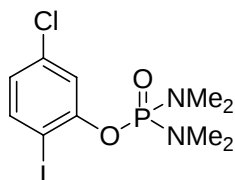
¹³C-NMR (150 MHz, CDCl₃) δ: 155.1, 129.8, 129.2, 126.9, 116.5, 95.7, 35.9.

MS (70 eV, EI) *m/z* (%): 432 (1) [M⁺], 307 (32), 207 (37), 135 (100), 92 (10), 75 (10), 44 (42).

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 2897, 1563, 1428, 1299, 1200, 1176, 991, 928, 791, 751.

HRMS (EI) for C₁₀H₁₅N₂O₂BrIP (431.9099): 431.9062.

Synthesis of 5-chloro-2-iodophenyl *N,N,N',N'*-tetramethyl-diamidophosphate (6g):



A solution of **4e** (262 mg, 1.0 mmol) in THF (1 mL) was cooled to -30 °C. Then TMP₂Mg·2LiCl (0.6 M in THF, 1.84 mL, 1.1 mmol) was added dropwise and the resulting mixture was stirred for 2 h at -30 °C. Complete metalation was detected by GC-analysis of reaction aliquots, quenched with I₂ in THF. I₂ (279 mg, 1.1 mmol) in THF (1 mL) was added and the mixture was warmed to 25 °C within 2 h. The reaction mixture was quenched by the addition of sat. aq. Na₂S₂O₃ (10 mL) and sat. aq. NH₄Cl solution

(10 mL). The mixture was extracted with diethyl ether (3 x 20 mL) and with ethyl acetate (3 x 20 mL). The combined organic layers were washed with brine, dried over Na₂SO₄ and the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (diethyl ether) furnishing the 5-chloro-2-iodophenyl *N,N,N',N'*-tetramethyldiamidophosphate **6g** (yellow solid, 113 mg, 29%) and the isomer 3-chloro-2-iodophenyl *N,N,N',N'*-tetramethyldiamidophosphate (**6f**) (yellow solid, 221 mg, 57%).

5-Chloro-2-iodophenyl *N,N,N',N'*-tetramethyldiamidophosphate:

m.p.: 78.7-82.6 °C.

¹H-NMR (600 MHz, CDCl₃) δ: 7.67 (dd, *J* = 8.5 Hz, *J* = 1 Hz, 1 H), 7.52 (dd, *J* = 2.3 Hz, *J* = 1 Hz, 1 H), 6.85 (dd, *J* = 8.5 Hz, *J* = 2.3 Hz, 1 H), 2.75 (d, *J* = 10.3 Hz, 12 H).

¹³C-NMR (150 MHz, CDCl₃) δ: 151.9, 139.7, 135.2, 125.7, 120.2, 85.7, 36.9.

MS (70 eV, EI) *m/z* (%): 388 (4) [M⁺], 261 (100), 135 (48), 92 (3), 44 (2).

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 2925, 1567, 1459, 1204, 997, 935, 808, 760, 682.

HRMS (EI) for C₁₀H₁₅N₂O₂ClIP (387.9604): 387.9591.

3-Chloro-2-iodophenyl *N,N,N',N'*-tetramethyldiamidophosphate:

m.p.: 74.7-76.6 °C.

¹H-NMR (600 MHz, CDCl₃) δ: 7.43-7.40 (m, 1 H), 7.22-7.20 (m, 2 H), 2.75 (d, *J* = 10.2 Hz, 12 H).

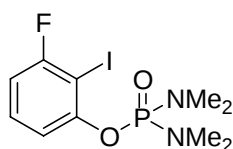
^{13}C -NMR (150 MHz, CDCl_3) δ : 153.3, 139.9, 130.1, 124.8, 117.4, 94.1, 37.2.

MS (70 eV, EI) m/z (%): 388 (3) [M^+], 261 (46), 135 (100), 92 (17), 75 (6), 44 (93).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2925, 1567, 1459, 1204, 997, 935, 808, 760, 682.

HRMS (EI) for $\text{C}_{10}\text{H}_{15}\text{N}_2\text{O}_2\text{ClIP}$ (387.9604): 387.9590.

Synthesis of 3-fluoro-2-iodophenyl N,N,N',N' -tetramethyl-diamidophosphate (6g):



A solution of **4f** (246 mg, 1.0 mmol) in THF (1 mL) was cooled to $-50\text{ }^{\circ}\text{C}$. Then $\text{TMP}_2\text{Mg}\cdot 2\text{LiCl}$ (0.6 M in THF, 1.84 mL, 1.1 mmol) was added dropwise and the resulting mixture was stirred for 30 min at $-50\text{ }^{\circ}\text{C}$. Complete metalation was detected by GC-analysis of reaction aliquots, quenched with I_2 in THF. I_2 (279 mg, 1.1 mmol) in THF (1 mL) was added and the mixture was warmed to $25\text{ }^{\circ}\text{C}$ within 12 h. The reaction mixture was quenched by the addition of sat. aq. $\text{Na}_2\text{S}_2\text{O}_3$ (10 mL) and sat. aq. NH_4Cl solution (10 mL). The mixture was extracted with diethyl ether (3 x 20 mL) and with ethyl acetate (3 x 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and the solvent was evaporated *in vacuo*. The residue was purified

by flash chromatography on silica gel (diethyl ether) furnishing **6g** as a colorless solid (272 mg, 73%).

m.p.: 86.9 – 86.4 °C.

¹H-NMR (600 MHz, CDCl₃) δ: 7.4 (m, 1 H), 7.3 (m, 1 H), 6.8 (m, 1 H), 2.8 (d, *J*=10.3 Hz, 12 H).

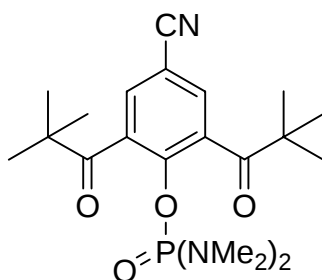
¹³C-NMR (150 MHz, CDCl₃) δ: 162.6 (d, *J*(C-F)=246.9 Hz), 153.1 (t, *J*(C-F)=5.6 Hz), 130.4 (d, *J*(C-F)= 9.6 Hz), 115.3 (t, *J*(C-F)=3.1 Hz), 111.1 (d, *J*(C-F)=21.1 Hz), 37.1.

MS (70 eV, EI) *m/z* (%): 373 (15), 372 (82) [M⁺], 355 (11), 281 (15), 246 (30), 245 (100), 208 (20), 207 (16), 168 (17), 149 (12), 135 (18), 118 (10), 73 (11), 71 (12), 68 (32), 57 (10), 55 (10), 44 (28), 43 (10), 41 (17).

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 2932, 2900, 1588, 1488, 1456, 1316, 1288, 1276, 1236, 1204, 1172, 1140, 1020, 1000, 972, 832, 772, 732, 700, 668, 616, 576, 532.

HRMS (EI) for C₁₀H₁₅FIN₂O₂P (371.9900): 371.9911.

Synthesis of 4-cyano-2,6-bis(2,2-dimethylpropanoyl)phenyl *N,N,N',N'*-tetramethyldiamidophosphate (**9a**):



Prepared according to **TP3** from **5a** (674 mg, 2.0 mmol), $\text{TMP}_2\text{Mg}\cdot 2\text{LiCl}$ (3.67 mL, 0.6 M in THF, 2.2 mmol) in 2 mL THF at $-60\text{ }^\circ\text{C}$. After 4 h, transmetalation using ZnCl_2 (1 M in THF, 2.4 mL, 2.4 mmol) was performed, followed by the addition of $\text{CuCN}\cdot 2\text{LiCl}$ (1 M in THF, 1.0 mL, 1.0 mmol) and pivaloyl chloride (265 mg, 2.2 mmol). The mixture was allowed to warm to $25\text{ }^\circ\text{C}$ within 12 h. Purification by flash chromatography on silica gel (*n*-pentane:diethyl ether = 1:1) furnished **9a** as a colorless solid (648 mg, 77%).

m.p.: 167.3 – 168.7 $^\circ\text{C}$.

^1H -NMR (300 MHz, CDCl_3) δ : 7.6 (s, 2 H), 2.6 (d, $J = 10.4\text{ Hz}$, 12 H), 1.3 (s, 18 H).

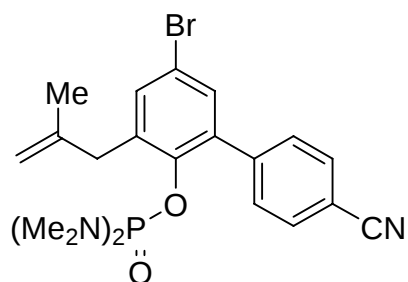
^{13}C -NMR (75 MHz, CDCl_3) δ : 208.1, 148.3, 148.2, 136.9, 136.9, 131.2, 117.7, 107.0, 45.1, 36.8, 27.8.

MS (70 eV, EI) m/z (%): 421 (1) [M^+], 378 (15), 377 (78), 365 (58), 364 (31), 319 (68), 135 (54), 46 (100).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2972, 2932, 2912, 2872, 2808, 2236, 1752, 1692, 1676, 1592, 1576, 1476, 1436, 1408, 1392, 1364, 1304, 1284, 1240, 1220, 1192, 1148, 1080, 1044, 1020, 996, 944, 904, 888, 872, 836, 800, 780, 752, 712, 696, 668.

HRMS (EI) for $\text{C}_{21}\text{H}_{32}\text{N}_3\text{O}_4\text{P}$ (421.2130): 421.2127.

Synthesis of 5-bromo-4'-cyano-3-(2-methylprop-2-en-1-yl)bi-phenyl-2-yl *N,N,N',N'*-tetramethyldiamidophosphate (9b):



Prepared according to **TP3** from **5b** (408 mg, 1.0 mmol), $\text{TMP}_2\text{Mg}\cdot 2\text{LiCl}$ (0.6 M in THF, 1.83 mL, 1.1 mmol) in THF (1 mL) at $-60\text{ }^\circ\text{C}$. After 0.5 h, transmetalation using ZnCl_2 (1 M in THF, 1.2 mL, 1.2 mmol) was performed, followed by the addition of $\text{CuCN}\cdot 2\text{LiCl}$ (1 M in THF, 0.5 mL, 0.5 mmol) and 3-bromo-2-methylpropene (150 mg, 1.1 mmol). The mixture was allowed to warm to $25\text{ }^\circ\text{C}$ within 12 h. Purification by flash chromatography on silica gel (ethyl acetate) furnished **9b** as a colorless solid (356 mg, 77%).

m.p.: $124.0 - 125.2\text{ }^\circ\text{C}$.

$^1\text{H-NMR}$ (600 MHz, CDCl_3) δ : 7.7 (d, $J = 7.9\text{ Hz}$, 2 H), 7.6 (d, $J = 8.2\text{ Hz}$, 2 H), 7.4 (d, $J = 2.4\text{ Hz}$, 1 H), 7.3 (d, $J = 2.4\text{ Hz}$, 1 H), 4.9 (s, 1 H), 4.6 (s, 1 H), 3.6 (s, 2 H), 2.3 (d, $J = 9.9\text{ Hz}$, 12 H), 1.8 (s, 3 H).

$^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ : 145.7, 143.7, 136.5, 135.3, 134.3, 132.3, 132.1, 130.6, 118.8, 118.3, 113.3, 111.5, 39.1, 36.4, 22.8.

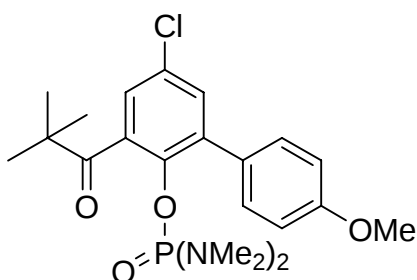
MS (70 eV, EI) m/z (%): 452 (1) [M^+], 410 (15), 409 (10), 408 (41), 397 (30), 396 (19), 395 (100), 135 (100), 44 (10).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3068, 2932, 2904, 2848, 2804, 2228, 1648, 1608, 1572, 1552, 1504, 1484, 1448, 1412, 1396, 1376, 1300,

1256, 1224, 1196, 1176, 1112, 1096, 1072, 1004, 988, 940, 912, 880, 844, 808, 776, 748, 688, 664.

HRMS (EI) for **C₂₁H₂₅BrN₃O₂P** (461.0868): 461.0865.

Synthesis of 5-chloro-3-(2,2-dimethylpropanoyl)-4'-methoxybiphenyl-2-yl *N,N,N',N'*-tetramethyldiamidophosphate (9c):



Prepared according to **TP3** from **5c** (738 mg, 2.0 mmol), **TMP₂Mg·2LiCl** (0.6 M in THF, 3.67 mL, 2.2 mmol) in THF (2 mL) at -60 °C. After 4 h, transmetalation using **ZnCl₂** (1 M in THF, 2.4 mL, 2.4 mmol) was performed, followed by the addition of **CuCN·2LiCl** (1 M in THF, 1.0 mL, 1.0 mmol) and pivaloyl chloride (265 mg, 2.2 mmol). The mixture was allowed to warm to 25 °C within 12 h. Purification by flash chromatography on silica gel (*n*-pentane:diethyl ether = 1:2) furnished **9b** as a colorless solid (744 mg, 82%).

m.p.: 155.2 – 156.3 °C.

¹H-NMR (300 MHz, CDCl₃) δ: 7.4 (d, *J* = 8.8 Hz, 2 H), 7.3 (m, 1H), 7.2 (d, *J* = 2.6 Hz, 1 H), 7.0 (d, *J* = 8.8 Hz, 2 H), 3.9 (s, 3 H), 2.3 (d, *J* = 10.1 Hz, 12 H), 1.4 (s, 9 H).

^{13}C -NMR (75 MHz, CDCl_3) δ : 209.1, 159.6, 143.7, 137.9, 137.0, 132.2, 131.0, 130.2, 128.9, 125.9, 114.0, 55.6, 44.8, 36.4, 28.6.

MS (70 eV, EI) m/z (%): 463 (10), 461 (10) [M^+], 135 (100), 44 (16).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2972, 2956, 2928, 2904, 2852, 2816, 1752, 1728, 1692, 1608, 1576, 1508, 1480, 1456, 1428, 1412, 1388, 1364, 1296, 1268, 1248, 1236, 1204, 1188, 1172, 1120, 1108, 1072, 1028, 988, 932, 900, 872, 832, 816, 796, 784, 756, 724, 692, 664.

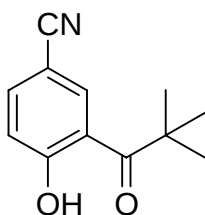
HRMS (EI) for $\text{C}_{22}\text{H}_{30}\text{ClN}_2\text{O}_4\text{P}$ (452.1632): 452.1650.

Typical procedure 4 (TP4): Microwave assisted deprotection of aryl phosphodiamidates

A mixture of the arylphosphoramidate (1.0 mmol), formic acid (2.5 mL), ethanol (2.5 mL) and H_2O (0.2 mL) were heated between 15 to 30 min in a 10 mL pressurized vial, by using a Discover BenchMate[®] Microwave system under the following conditions: Power = 100 W; Max. temperature = 120 °C; Max. pressure = 6.0 bar. After completion of the reaction (checked by GC-analysis), the reaction mixture was neutralized with sat. aq. NaHCO_3 and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 , filtered and the solvent was evaporated *in vacuo*. The crude material was

purified by flash chromatography on silica gel (eluting with diethyl ether/pentane mixtures).

Synthesis of 3-(2,2-dimethylpropanoyl)-4-hydroxybenzonitrile (10a):



Prepared according to **TP4** from **5b** (337 mg, 1.00 mmol), formic acid (2.5 mL), ethanol (2.5 mL) and H₂O (0.2 mL). Reaction time: 30 min. Purification by flash chromatography on silica gel (*n*-pentane:diethyl ether = 3:1) furnished **10b** as a colorless solid (160 mg, 79%).

m.p.: 78.2 – 80.5 °C.

¹H-NMR (300 MHz, CDCl₃) δ : 8.4 (d, J = 2.0 Hz, 1 H), 7.7 (dd, J = 8.8 Hz, J = 2.0 Hz, 1 H), 7.1 (d, J = 8.6 Hz, 1 H), 1.5 (s, 9 H).

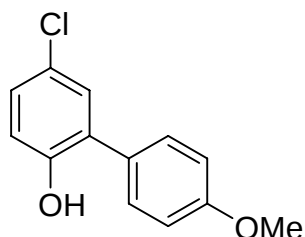
¹³C-NMR (75 MHz, CDCl₃) δ : 211.6, 167.1, 137.9, 136.1, 121.2, 118.7, 117.7, 101.8, 45.2, 28.8.

MS (70 eV, EI) m/z (%): 203 (16) [M⁺], 175 (14), 147 (10), 146 (69), 119 (21), 90 (1), 63 (12), 57 (100), 44 (24), 41 (42).

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 2976, 2228, 1640, 1608, 1580, 1476, 1344, 1296, 1260, 1196, 1148, 1124, 980, 960, 940, 928, 872, 836, 808, 796, 768, 732, 712, 676.

HRMS (EI) for $\text{C}_{12}\text{H}_{13}\text{NO}_2$ (203.0946): 203.0935.

Synthesis of 5-chloro-4'-methoxybiphenyl-2-ol (10b):



Prepared according to **TP4** from **5c** (368 mg, 1.0 mmol), formic acid (2.5 mL), ethanol (2.5 mL) and H_2O (0.2 mL). Reaction time: 30 min. Purification by flash chromatography on silica gel (*n*-pentane:diethyl ether = 3:1) furnished **10b** as a light yellow oil (183 mg, 78%).

^1H -NMR (300 MHz, CDCl_3) δ : 7.4 (d, J = 8.8 Hz, 2 H), 7.2 (m, 2 H), 7.0 (d, J = 9.0 Hz, 2 H), 6.9 (ddd, J = 8.9 Hz, J = 1.3 Hz, J = 1.2 Hz, 1 H), 5.2 (s, 1 H), 3.9 (s, 3 H).

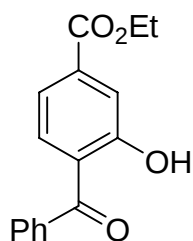
^{13}C -NMR (75 MHz, CDCl_3) δ : 159.9, 151.4, 130.4, 130.0, 129.5, 128.7, 128.2, 125.7, 117.2, 115.1, 55.6.

MS (70 eV, EI) m/z (%): 236 (28), 235 (12), 234 (100) [M^+], 219, (12), 128 (18), 127 (13).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3528, 3408, 2960, 2936, 2836, 1608, 1576, 1516, 1480, 1464, 1440, 1424, 1396, 1328, 1296, 1244, 1176, 1124, 1092, 1040, 1024, 884, 832, 816, 796, 740, 708.

HRMS (EI) for $\text{C}_{13}\text{H}_{11}\text{ClO}_2$ (234.0448): 234.0428.

Synthesis of ethyl 4-benzoyl-3-hydroxybenzoate (**10c**):



Prepared according to **TP4** from **6b** (404 mg, 1.0 mmol), formic acid (2.5 mL), ethanol (2.5 mL) and H₂O (0.2 mL). Reaction time: 15 min. Purification by flash chromatography on silica gel (*n*-pentane:diethyl ether = 10:1) furnished **10c** as a pale yellow solid (203 mg, 80 %).

m.p.: 63.2 – 64.8 °C.

¹H-NMR (300 MHz, CDCl₃) δ : 7.8 – 7.7 (m, 3 H), 7.6 (m, 1 H), 7.6 (m, 1 H), 7.5 (m, 3 H), 4.4 (q, J = 7.3 Hz, 2 H), 1.4 (t, J = 7.3 Hz, 3 H).

¹³C-NMR (75 MHz, CDCl₃) δ : 201.5, 165.7, 162.9, 137.7, 137.2, 133.7, 132.7, 129.5, 128.7, 121.9, 119.9, 119.4, 61.8, 14.5.

MS (70 eV, EI) m/z (%): 270 (100) [M⁺], 253 (5), 241 (25), 225 (28), 193 (25), 165 (30), 193 (13), 115 (14), 105 (83), 77 (71), 51 (16).

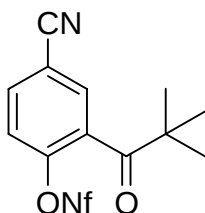
IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3252, 3084, 2984, 2936, 2904, 1712, 1640, 1600, 1564, 1496, 1464, 1448, 1424, 1400, 1364, 1332, 1292, 1264, 1224, 1192, 1172, 1112, 1092, 1020, 968, 936, 908, 896, 868, 844, 816, 768, 752, 712, 696, 660.

HRMS (ESI) for C₁₆H₁₅O₄ (271.0970): 271.0965.

Typical procedure 5 (TP5): Synthesis of the aryl nonaflates

A dry argon flushed round-bottom flask was charged with diethyl ether (4 mL) and NaH (31.2 mg, 1.3 mmol). The flask was cooled to 0 °C and a solution of the corresponding phenol (1.0 mmol) dissolved in diethyl ether (4 mL) was slowly added. After 30 min, nonafluorobutanesulfonic fluoride (0.25 mL, 1.4 mmol) was added dropwise, the solution was allowed to warm to room temperature and stirred for 12 h. To the reaction mixture was added water (30 mL) and extracted with diethyl ether (3 x 50 mL). The combined organic layers were washed with NaOH (5%) and brine (20 mL), dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The crude material was purified by flash chromatography on silica gel gel (eluting with diethyl ether/pentane mixtures).

Synthesis of 4-cyano-2-(2,2-dimethylpropanoyl)phenyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (11a):



Prepared according to **TP5** from **10a** (203 mg, 1.0 mmol), NaH (31.2 mg, 1.3 mmol), nonafluorobutanesulfonic fluoride (0.25 mL, 1.4 mmol) in THF (8 mL). Purification by flash

chromatography on silica gel (*n*-pentane:diethyl ether = 10:1) furnished **11a** as a colorless solid (427 mg, 88%).

m.p.: 67.2 – 68.5 °C.

¹H-NMR (600 MHz, CDCl₃) δ: 7.8 (dd, *J* = 8.6 Hz, *J* = 2.0 Hz, 1 H), 7.6 (d, *J* = 2.0 Hz, 1 H), 7.5 (d, *J* = 8.8 Hz, 1 H), 1.3 (s, 9 H).

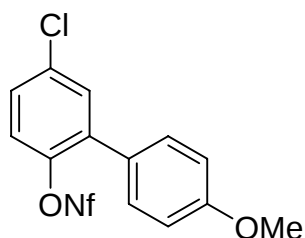
¹³C-NMR (150 MHz, CDCl₃) δ: 206.3, 147.9, 135.7, 134.7, 131.6, 122.9, 119.0-108.0 (m, 4C-F_n), 116.7, 112.5, 45.6, 26.8.

MS (70 eV, EI) *m/z* (%): 485 (10) [M⁺], 470 (30), 457 (35), 429 (11), 428 (100), 202 (3), 146 (10), 119 (6), 69 (6), 57 (100), 40 (17).

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 2976, 2240, 1704, 1604, 1476, 1428, 1396, 1356, 1292, 1248, 1216, 1200, 1168, 1140, 1104, 1032, 988, 964, 924, 872, 852, 840, 808, 768, 752, 736, 704, 688, 664.

HRMS (FIA/ESI) for C₁₆H₁₂F₉NO₄S (484.0265): 484.0271 [M-H]⁻.

Synthesis of 5-chloro-4'-methoxybiphenyl-2-yl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (11b):



Prepared according to **TP5** from **10b** (235 mg, 1.0 mmol), NaH (31.2 mg, 1.3 mmol), nonafluorobutanesulfonic fluoride (0.25

mL, 1.40 mmol) in THF (8 mL). Purification by flash chromatography on silica gel (*n*-pentane:diethyl ether = 40:1) furnished **11b** as a colorless oil (470 mg, 91%).

¹H-NMR (300 MHz, CDCl₃) δ : 7.5 (dd, J = 2.4 Hz, J = 0.5 Hz, 1 H), 7.4 (d, J = 8.9 Hz, 2 H), 7.3 (m, 2 H), 7.0 (d, J = 8.9 Hz, 2 H), 3.9 (s, 3 H).

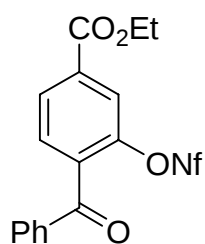
¹³C-NMR (75 MHz, CDCl₃) δ : 160.3, 145.7, 137.4, 134.3, 131.9, 130.7, 128.6, 127.0, 123.5, 114.4, 123.0-107.0 (m, 4C-F_n), 77.4, 55.6.

MS (70 eV, EI) m/z (%): 516 (26) [M⁺], 235 (20), 234 (13), 233 (63), 199 (18), 198 (100), 183 (24), 155 (11), 127 (12), 68 (16).

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 2964, 2940, 2840, 1612, 1580, 1564, 1516, 1464, 1424, 1388, 1352, 1296, 1236, 1224, 1200, 1180, 1140, 1112, 1040, 1008, 944, 884, 832, 812, 800, 776, 736, 720, 688.

HRMS (ESI) for C₁₇H₁₀ClF₉O₄S (515.9845): 515.9837 [M+H]⁺.

Synthesis of ethyl 4-benzoyl-3-[[nonafluorobutyl)sulfonyl]-oxy}benzoate (11c**):**



Prepared according to **TP5** from **10c** (270 mg, 1.0 mmol), NaH (31.2 mg, 1.3 mmol), nonafluorobutanesulfonic fluoride (0.25 mL, 1.4 mmol) in THF (8 mL). Purification by flash chromatography on silica gel (*n*-pentane:diethyl ether = 20:1) furnished **11c** as a colorless solid (519 mg, 94%).

m.p.: 102.0 – 103.6 °C.

¹H-NMR (600 MHz, CDCl₃) δ : 8.2 (dd, J = 7.9, 1.5 Hz, 1 H), 8.1 (d, J = 1.3 Hz, 1 H), 7.8 (dd, J = 8.4, 1.3 Hz, 2 H), 7.6 (d, J = 7.7 Hz, 2 H), 7.5 (m, 2 H), 4.5 (q, J = 7.1 Hz, 2 H), 1.4 (t, J = 7.2 Hz, 3 H).

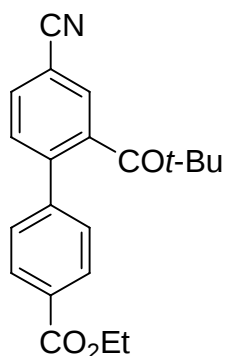
¹³C-NMR (150 MHz, CDCl₃) δ : 192.2, 164.9, 136.5, 136.2, 134.8, 134.4, 131.2, 130.4, 129.2, 128.9, 123.7, 120.0-105.5 (m, 4C-F_n), 62.5, 14.4.

MS (70 eV, EI) m/z (%): 533 (21), 507 (89), 475 (6), 411 (5), 317 (1), 269 (29), 223 (7), 196 (14), 169 (15), 139 (10), 105 (100), 77 (26).

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 2992, 1720, 1664, 1596, 1580, 1564, 1496, 1448, 1420, 1392, 1356, 1300, 1272, 1228, 1200, 1176, 1140, 1116, 1076, 1040, 1012, 964, 944, 912, 852, 836, 792, 780, 764, 740, 696, 664.

HRMS (ESI) for C₂₀H₁₇F₉NO₆S (570.0633): 570.0632 [M+NH₄]⁺.

Synthesis of ethyl 4'-cyano-2'-(2,2-dimethylpropanoyl)-biphenyl-4-carboxylate (12a):



A dry argon flushed 25 mL flask, equipped with a magnetic stirrer and a septum was charged with the organozinc reagent **13**^[4] (0.41 M in THF, 3.66 mL, 1.5 mmol) and NEP (*N*-ethylpyrrolidinone, 0.37 mL). To this mixture the nonaflate **11a** (0.552 g, 1.0 mmol) dissolved in THF (1 mL) was added, followed by NiCl₂(PPh₃)₂ (32.7 mg, 0.05 mmol). The mixture was stirred at 25 °C for 3 h. The reaction mixture was quenched with sat. aq. NH₄Cl solution (10 mL), extracted with diethyl ether (3 × 20 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvent was evaporated *in vacuo*. Purification by flash chromatography on silica gel (*n*-pentane/diethyl ether, 10:1) furnished compound **12a** as a colorless solid (302 mg, 90%).

m.p.: 119.3 – 120.6 °C.

¹H-NMR (300 MHz, CDCl₃) δ: 8.1 (d, *J* = 8.6 Hz, 2 H), 7.8 (d, *J* = 1.8 Hz, 1 H), 7.5 (d, *J* = 7.9 Hz, 1 H), 7.4 (d, *J* = 1.8 Hz, 1 H), 7.3 (d, *J* = 8.6 Hz, 2 H), 4.4 (q, *J* = 7.1 Hz, 2 H), 1.4 (t, *J* = 7.2 Hz, 3 H), 0.9 (s, 9 H).

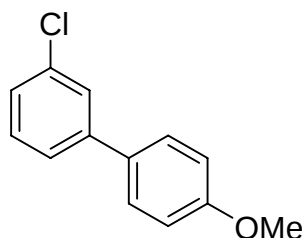
^{13}C -NMR (75 MHz, CDCl_3) δ : 213.5, 166.2, 143.6, 142.1, 141.9, 132.5, 131.0, 130.2, 129.8, 129.7, 118.1, 111.9, 61.5, 45.4, 27.3, 14.5.

MS (70 eV, EI) m/z (%): 335 (3) [M^+], 290 (17), 279 (28), 278 (24), 251 (38), 297 (15), 206 (100), 178 (11), 177 (25), 57 (58).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2964, 2936, 2908, 2868, 2228, 1720, 1696, 1612, 1600, 1572, 1476, 1444, 1412, 1396, 1368, 1276, 1184, 1164, 1120, 1104, 1040, 1024, 992, 936, 908, 860, 832, 804, 780, 748, 708.

HRMS (EI) for $\text{C}_{21}\text{H}_{21}\text{NO}_3$ (335.1521): 335.1521.

Synthesis of 3-chloro-4'-methoxybiphenyl (**12b**):



Borane·dimethylamine complex (59 mg, 1.0 mmol), nonaflate **11b** (254 mg, 1.0 mmol), $\text{Pd}(\text{PPh}_3)_4$ (58 mg, 0.05 mmol, 5 mol%) and K_2CO_3 (138 mg, 1.0 mmol) were weighed into an oven dried and argon flushed 10 mL-round bottomed flask. Dry acetonitrile (3.5 mL) was added via syringe and the reaction mixture was allowed to stir at 70 °C for 16 h (monitored by GC analysis). The reaction mixture was quenched with H_2O (10 mL), extracted

with diethyl ether (3 × 20 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (*n*-pentane/diethyl ether, 4:1) furnished compound **12b** (206 mg, 94%) as a colorless solid.

m.p.: 57.6 – 58.9 °C.

¹H-NMR (300 MHz, CDCl₃) δ: 7.6 (t, *J* = 1.9 Hz, 1 H), 7.5 (d, *J* = 9.0 Hz, 2 H), 7.4 (m, 1 H), 7.3 (t, *J* = 7.7 Hz, 1 H), 7.2 (m, 1 H), 7.0 (d, *J* = 8.8 Hz, 2 H), 3.9 (s, 3 H).

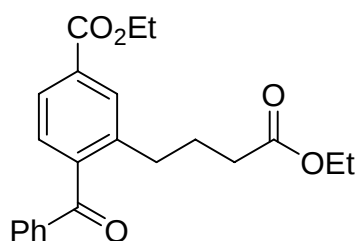
¹³C-NMR (75 MHz, CDCl₃) δ: 159.8, 142.9, 134.8, 132.5, 130.2, 128.4, 127.1, 126.9, 125.1, 114.6, 55.6.

MS (70 eV, EI) *m/z* (%): 220 (29), 219 (13), 218 (100) [M⁺], 205 (10), 203 (32), 175 (28), 139 (12).

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 2955, 2839, 1899, 1877, 1606, 1514, 1470, 1439, 1288, 1275, 1251, 1187, 1084, 1019, 835, 787, 684, 667.

HRMS (EI) for C₁₃H₁₁ClO (218.0498): 218.0497.

Synthesis of ethyl 4-benzoyl-3-(4-ethoxy-4-oxobutyl)benzoate (12c):



A dry argon flushed 25 mL flask, equipped with a magnetic stirrer and a septum was charged with the organozinc **14**^[4]

(0.75 M in THF, 2.0 mL, 1.5 mmol) and NEP (*N*-ethylpyrrolidinone, 0.2 mL). To this mixture the nonaflate **11c** (0.552 g, 1.00 mmol) dissolved in THF (1 mL) was added, followed by NiCl₂(PPh₃)₂ (32.7 mg, 0.05 mmol). The mixture was stirred at 25 °C for 3 h. The reaction mixture was quenched with sat. aq. NH₄Cl solution (10 mL), extracted with diethyl ether (3 × 20 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (*n*-pentane/diethyl ether, 4:1) furnished compound **12c** (350 mg, 95%) as a colorless oil.

¹H-NMR (600 MHz, CDCl₃) δ: 8.0 (d, *J* = 1.5 Hz, 1 H), 7.9 (dd, *J* = 7.9, *J* = 1.5 Hz, 1 H), 7.8 (dd, *J* = 8.3, *J* = 1.2 Hz, 2 H), 7.6 (t, *J* = 7.5 Hz, 1 H), 7.5 (t, *J* = 7.9 Hz, 2 H), 7.3 (d, *J* = 7.7 Hz, 1 H), 4.4 (q, *J* = 7.3 Hz, 2 H), 4.1 (q, *J* = 7.1 Hz, 2 H), 2.7 (m, 2 H), 2.3 (t, *J* = 7.5 Hz, 2 H), 1.9 (m, 2 H), 1.4 (t, *J* = 7.1 Hz, 3 H), 1.2 (t, *J* = 7.1 Hz, 3 H).

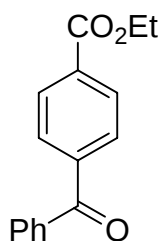
¹³C-NMR (150 MHz, CDCl₃) δ: 197.9, 173.3, 166.2, 142.9, 140.8, 137.3, 133.9, 132.1, 130.3, 128.8, 128.4, 126.9, 61.5, 60.5, 33.9, 32.6, 14.5.

MS (70 eV, EI) *m/z* (%): 369 (1) [M⁺], 339 (19) 322 (58), 281 (23), 266 (46), 251 (31), 221 (17), 194 (81), 165 (46), 129 (5), 105 (100), 77 (739, 51 (8)).

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 2980, 2936, 1716, 1668, 1596, 1580, 1568, 1492, 1448, 1408, 1392, 1368, 1316, 1276, 1252, 1188, 1148, 1116, 1096, 1024, 944, 908, 848, 804, 772, 744, 704, 660.

HRMS (EI) for C₂₂H₂₄O₅ (365.1624): 365.1695.

Synthesis of ethyl 4-benzoylbenzoate (**12d**):



Borane·dimethylamine complex (59 mg, 1.00 mmol), nonaflate **11c** (254 mg, 1.00 mmol), Pd(PPh₃)₄ (58 mg, 0.05 mmol, 5 mol%) and K₂CO₃ (138 mg, 1.00 mmol) were weighed into an oven dried and argon flushed 10 mL-round bottomed flask. Dry acetonitrile (3.5 mL) was added via syringe and the reaction was allowed to stir at 25 °C for 2 h (monitored by GC analysis). The reaction mixture was quenched with H₂O (10 mL), extracted with diethyl ether (3 × 20 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (*n*-pentane/diethyl ether, 4:1) furnished compound **12d** (188 mg, 74%) as a light yellow oil.

¹H-NMR (300 MHz, CDCl₃) δ: 8.2 (d, *J* = 8.6 Hz, 2 H), 7.8 (m, 4 H), 7.5 (m, 2 H) 7.6 (m, 1 H), 4.4 (q, *J* = 7.3 Hz, 2 H), 1.4 (t, *J* = 7.1 Hz, 3 H).

¹³C-NMR (75 MHz, CDCl₃) δ: 196.3, 166.1, 141.5, 137.2, 133.8, 133.1, 130.3, 130.0, 129.7, 128.7, 61.7, 14.5.

MS (70 eV, EI) m/z (%): 254 (49) [M^+], 226 (10), 209 (44), 180 (18), 176 (56), 151 (10), 148 (14), 104 (100), 77 (32), 76 (15), 51 (10).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2984, 1716, 1660, 1596, 1580, 1504, 1476, 1464, 1448, 1404, 1368, 1316, 1268, 1176, 1148, 1100, 1020, 1000, 976, 940, 924, 868, 852, 804, 768, 712, 696.

HRMS (EI) for $\text{C}_{16}\text{H}_{14}\text{O}_3$ (254.0943): 254.0939.

References:

[¹] a) A. Krasovskiy, V. Krasovskaya, P. Knochel, *Angew. Chem.* **2006**, *118*, 3024; *Angew. Chem. Int. Ed.* **2006**, *45*, 2958; b) W. Lin, O. Baron, P. Knochel, *Org. Lett.* **2006**, *8*, 5673.

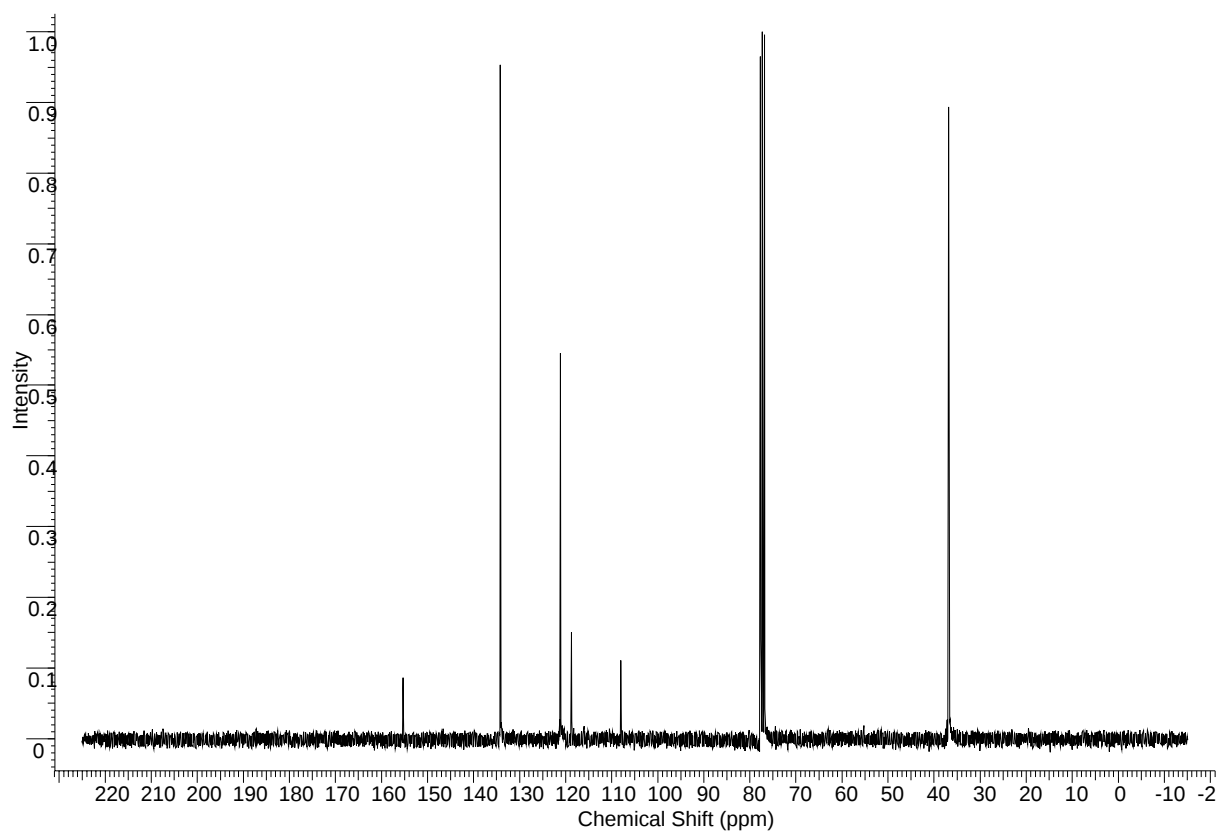
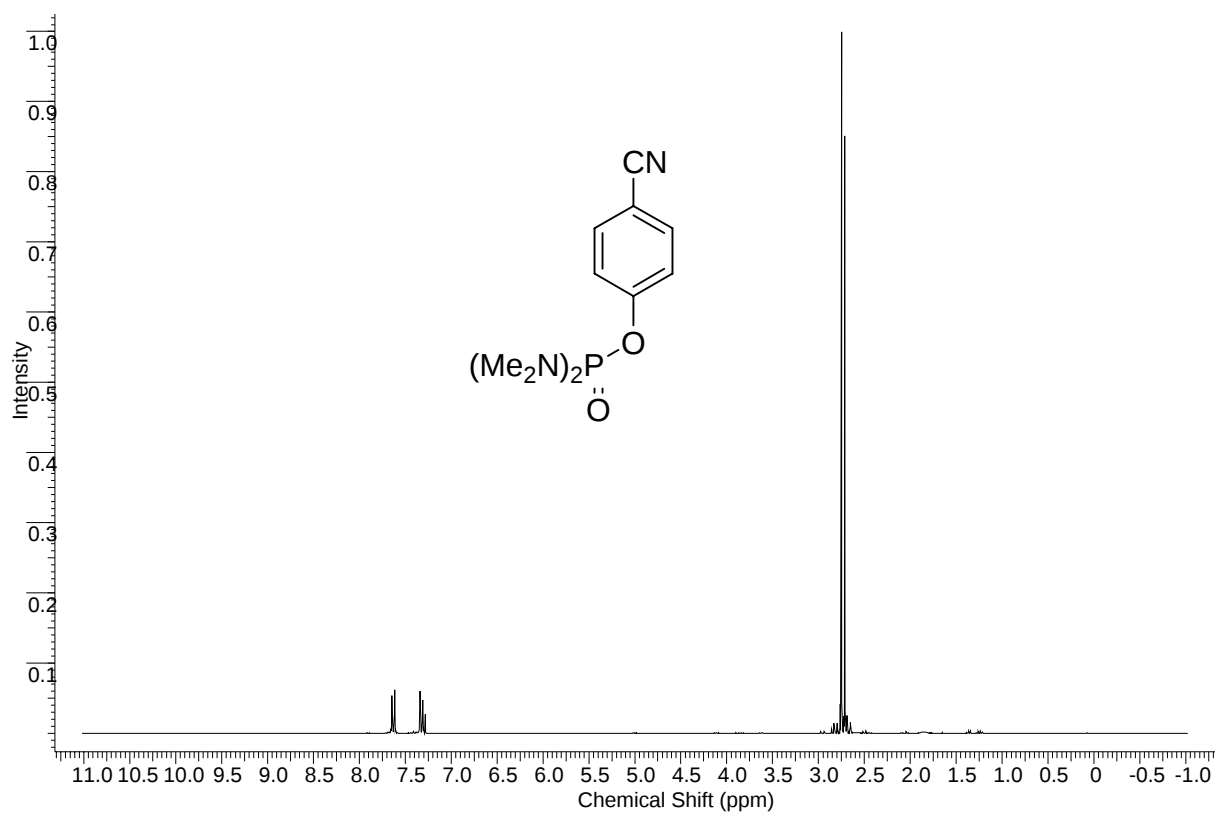
[²] L. P. Hammett, G. H. Walden, S. M. Edmonds *J. Am. Chem. Soc.* **1934**, *56*, 1092.

[3] C. C. Kofink, P. Knochel, *Org. Lett.* **2006**, *8*, 4121.

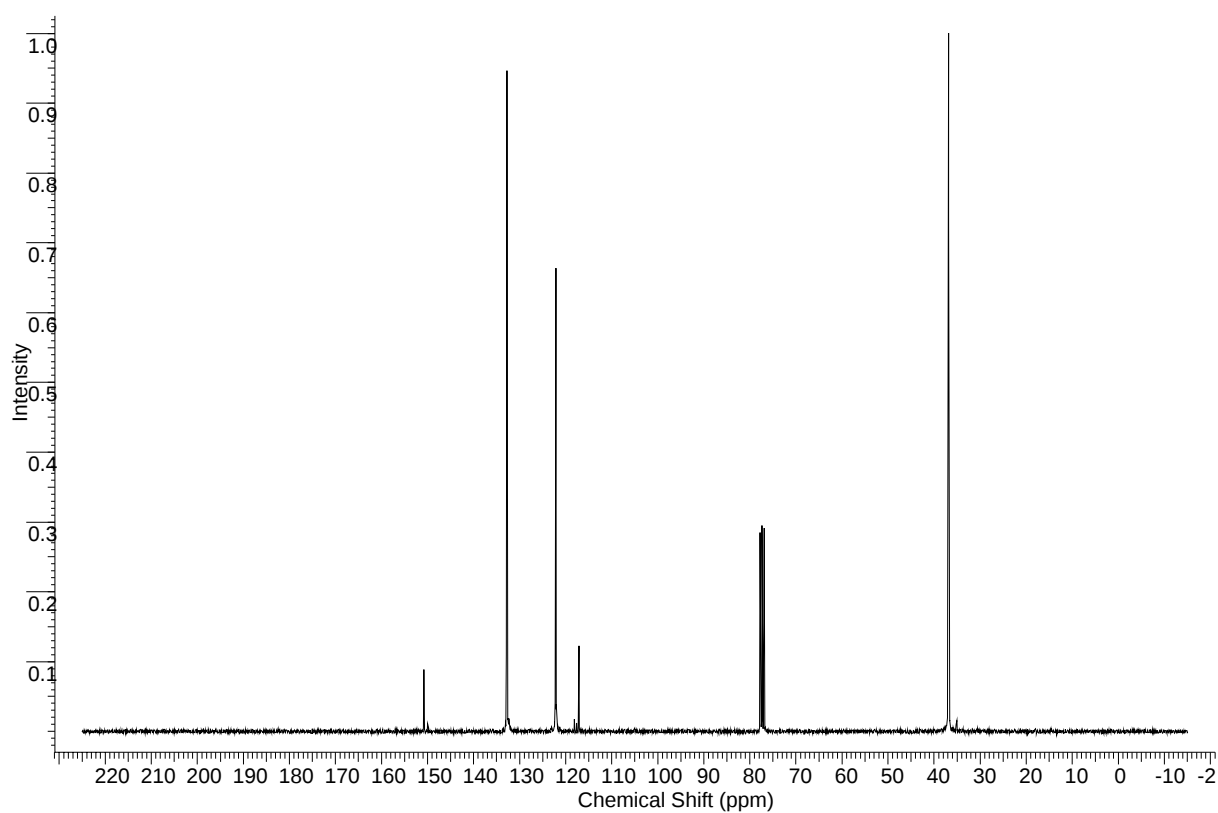
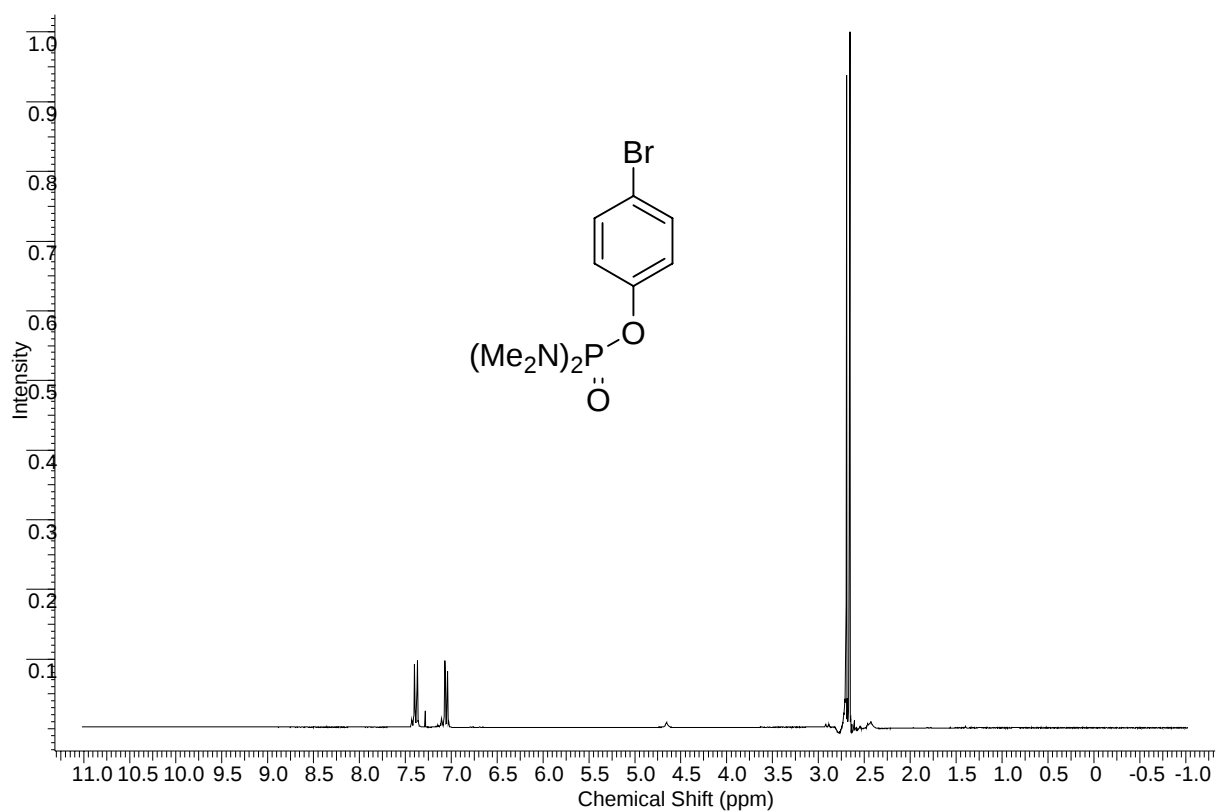
[4] For the preparation of the organozinc compounds **13** and **14** see: A. Krasovskiy, V. Malakhov, A. Gavryushin, P. Knochel, *Angew. Chem.* **2006**, *118*, 6186; *Angew. Chem. Int. Ed.* **2006**, *45*, 6040.

NMR Spectra of all compounds:

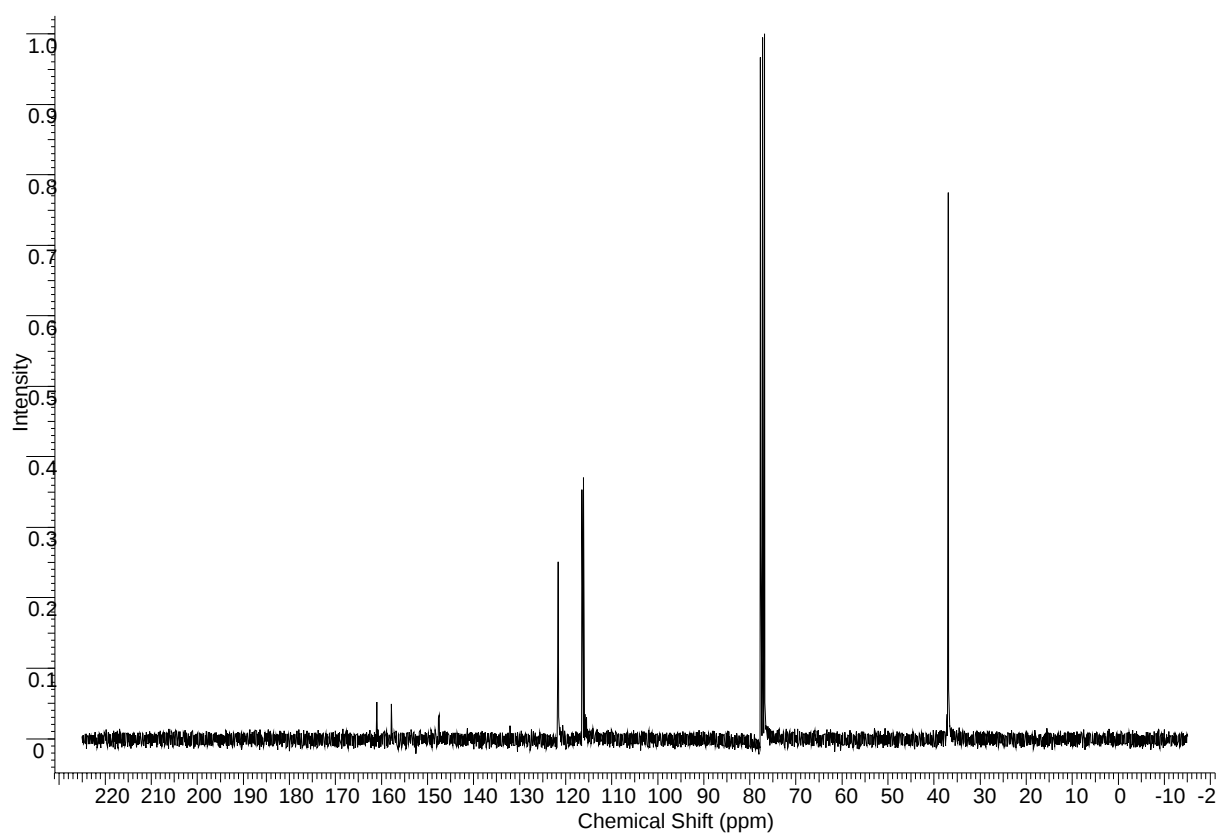
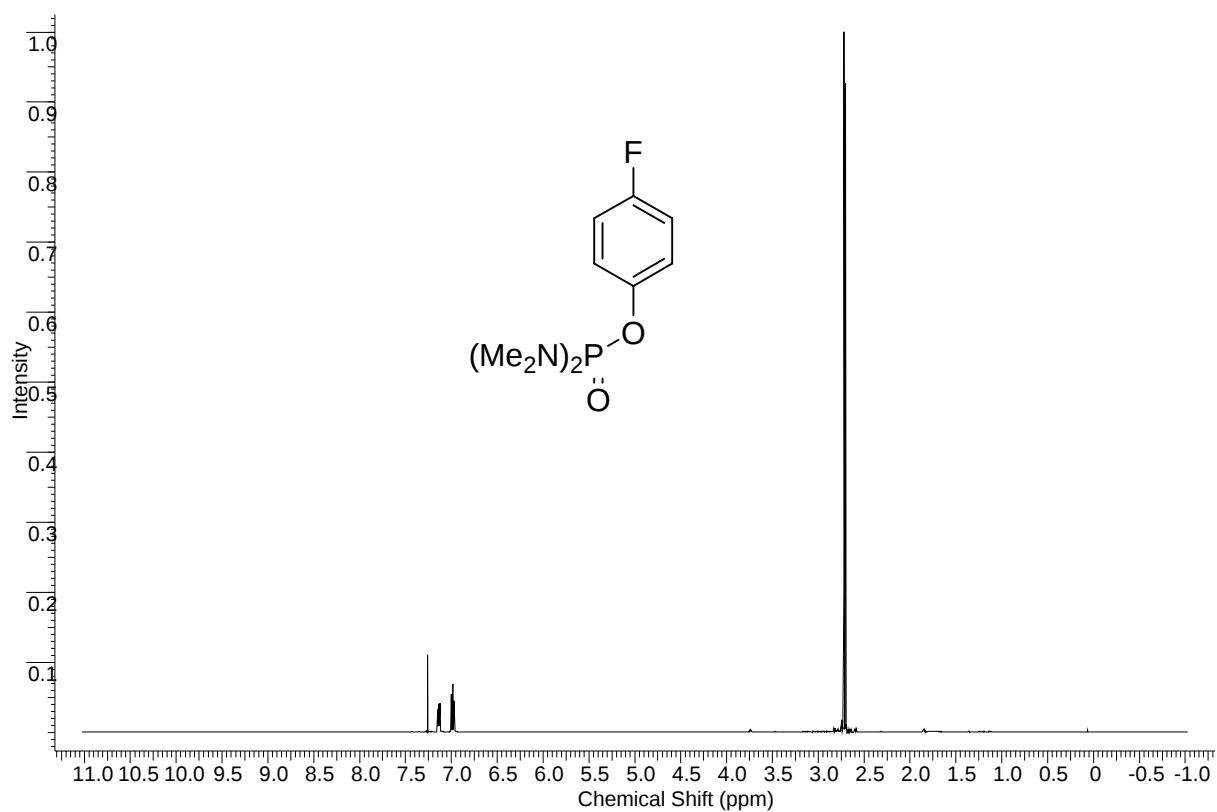
4-Cyanophenyl-*N,N,N',N'*-tetramethyldiamido-phosphate (3a)



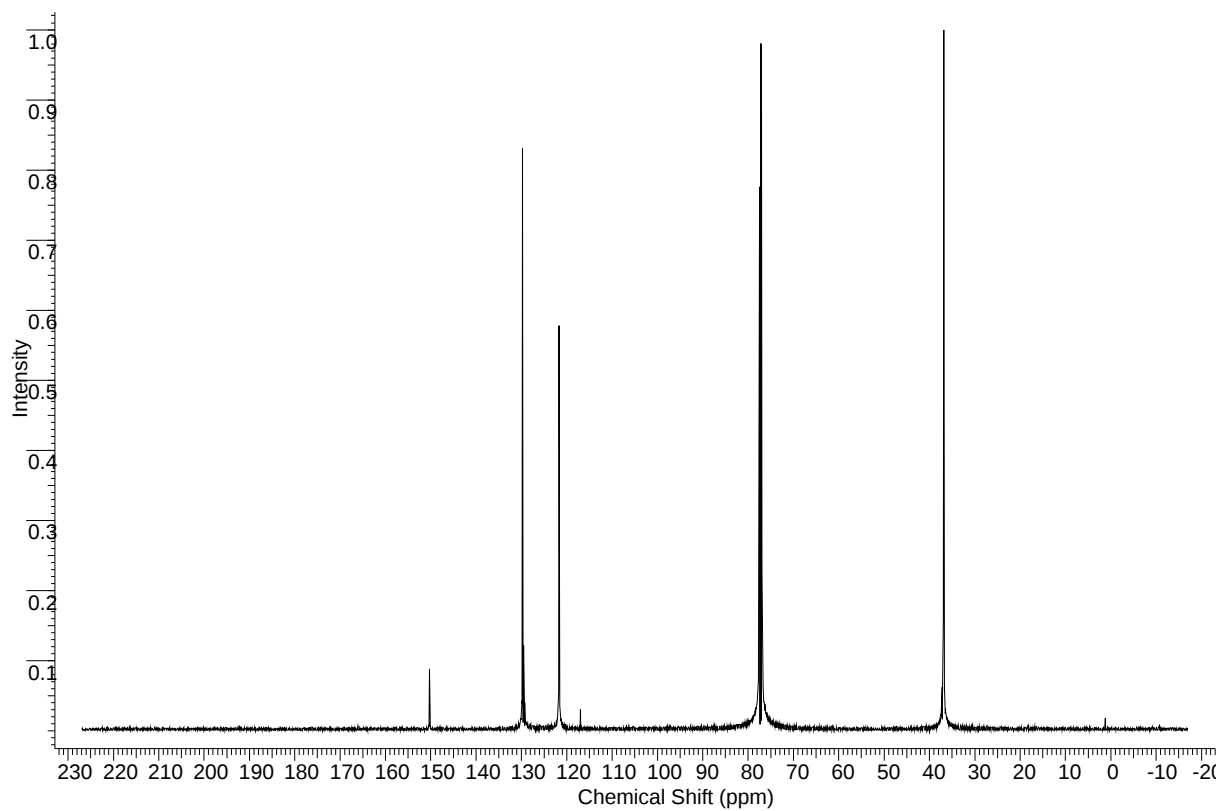
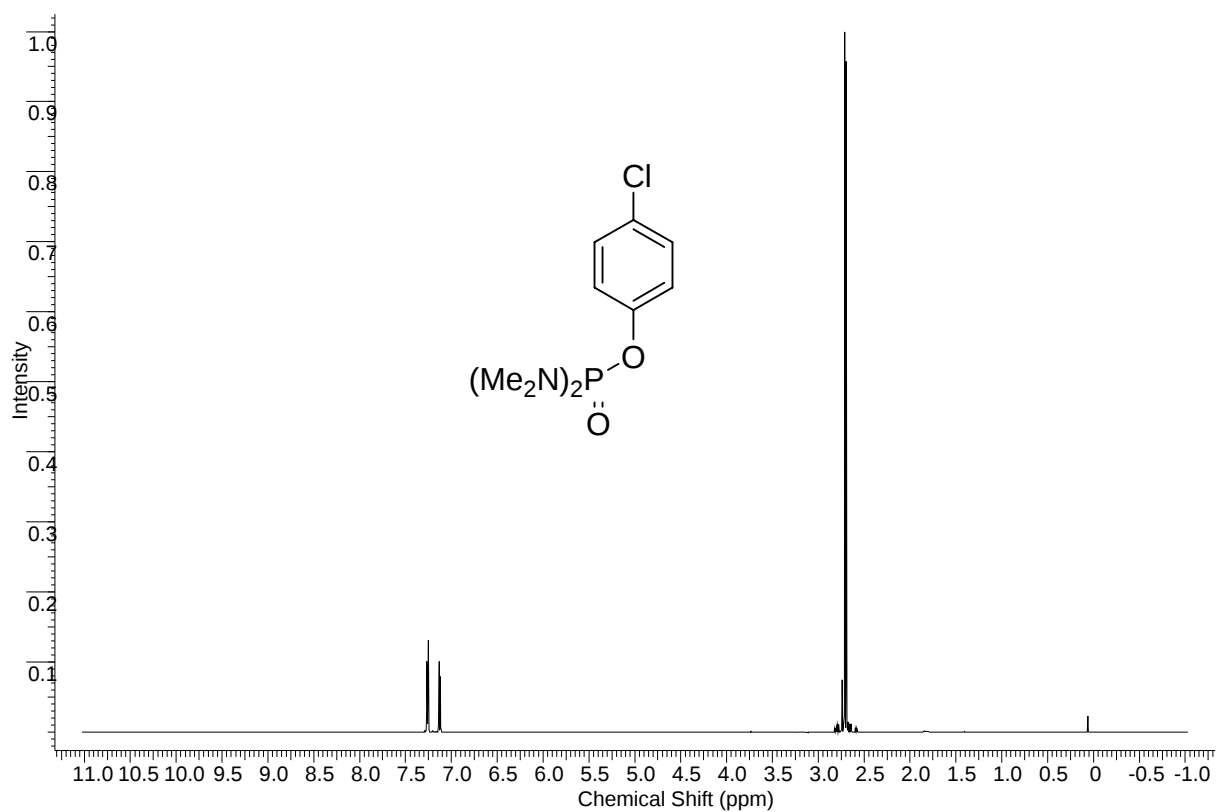
4-Bromophenyl-*N,N,N',N'*-tetramethyldiamido-phosphate (3b)



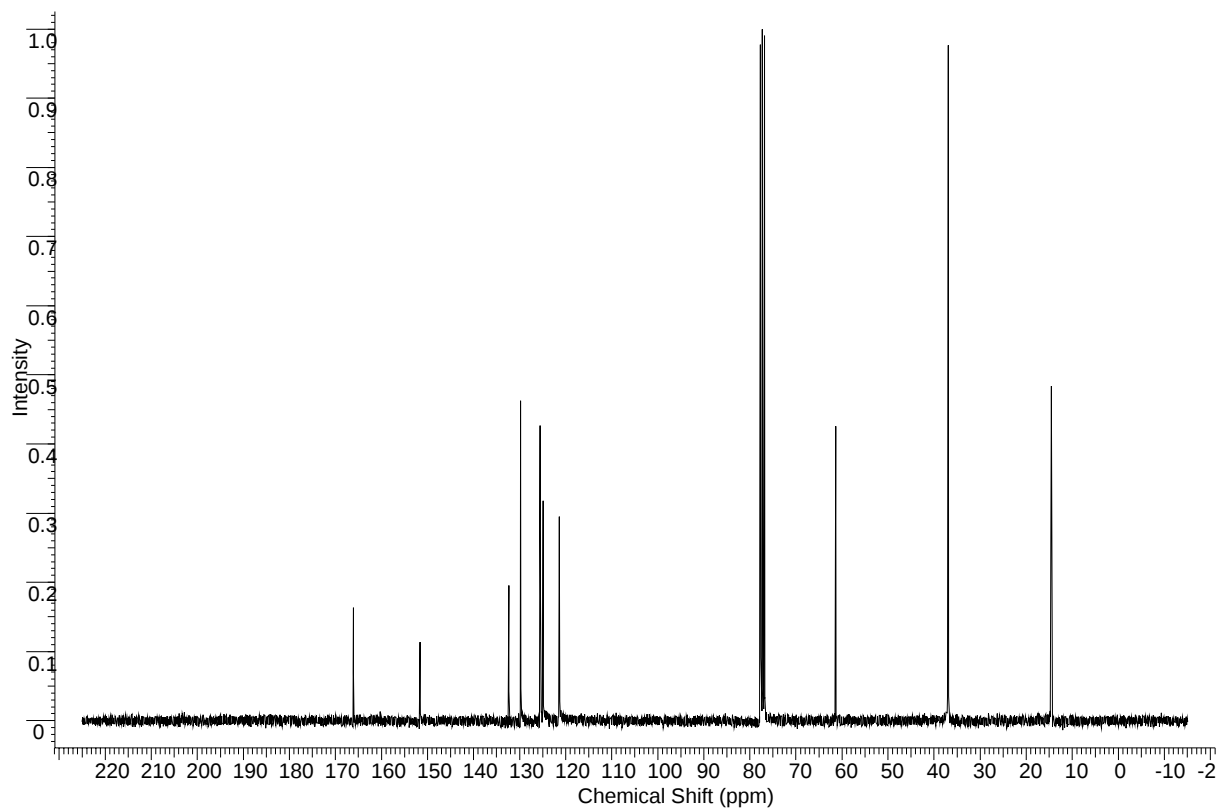
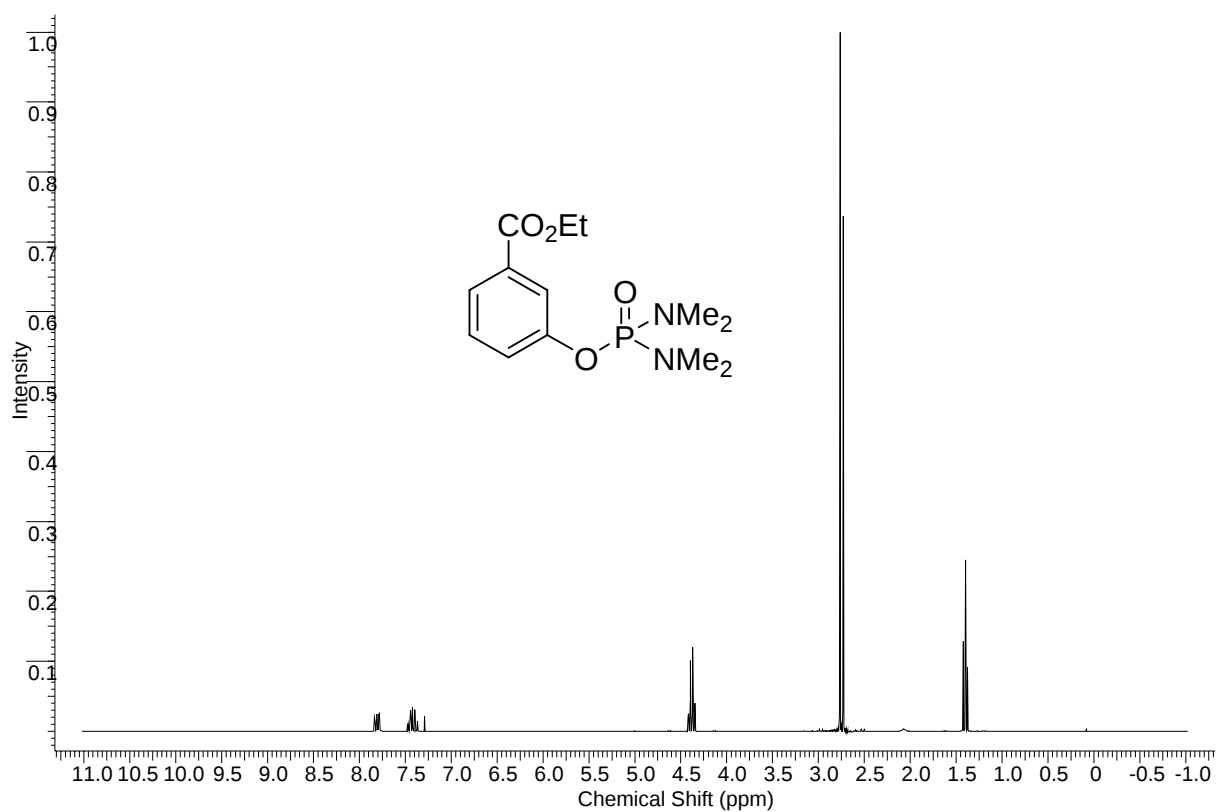
4-Fluorophenyl-*N,N,N',N'*-tetramethyldiamido-phosphate (3c)



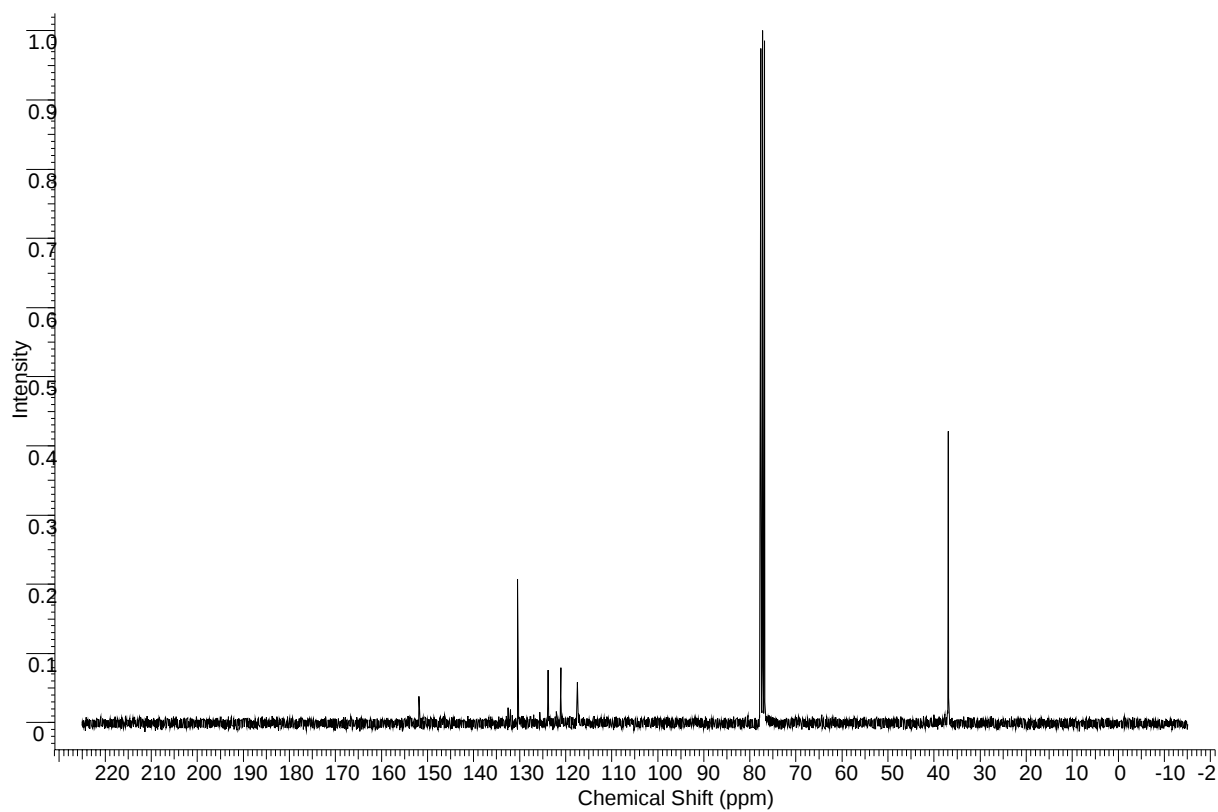
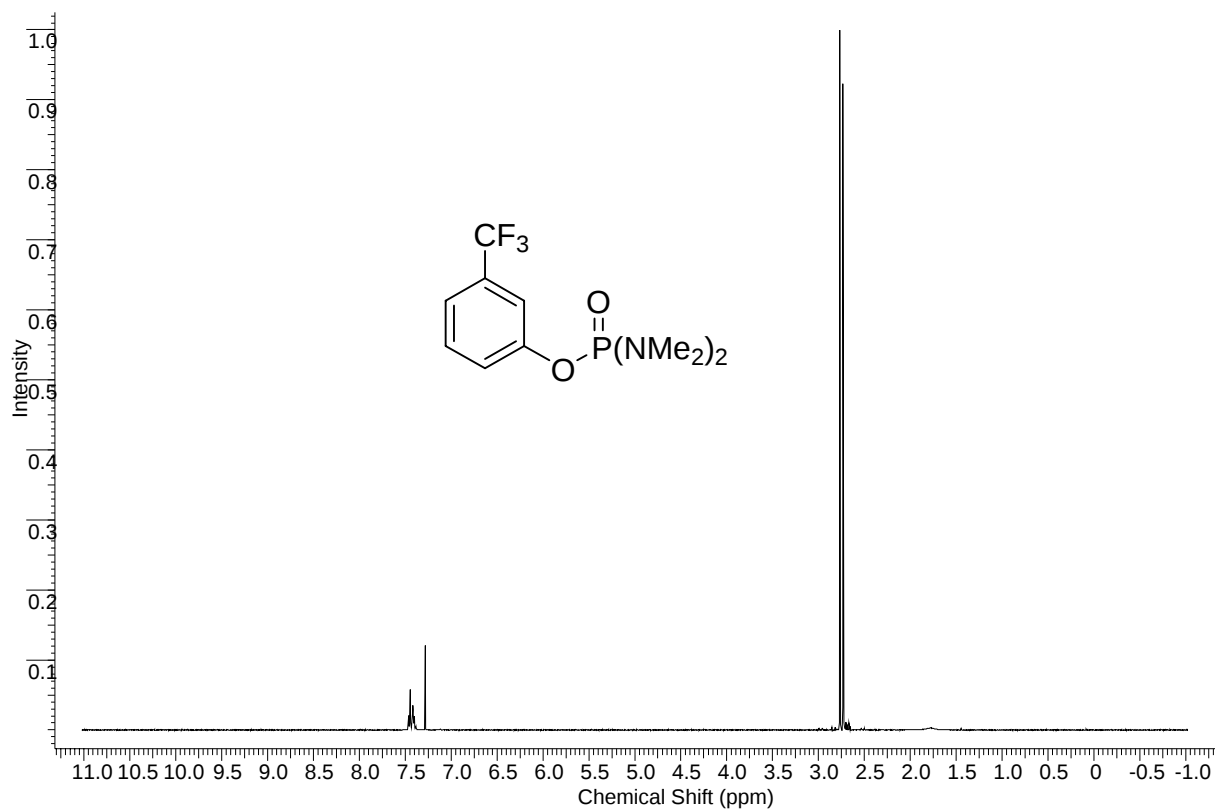
4-Chlorophenyl-*N,N,N',N'*-tetramethyldiamido-phosphate (3d)



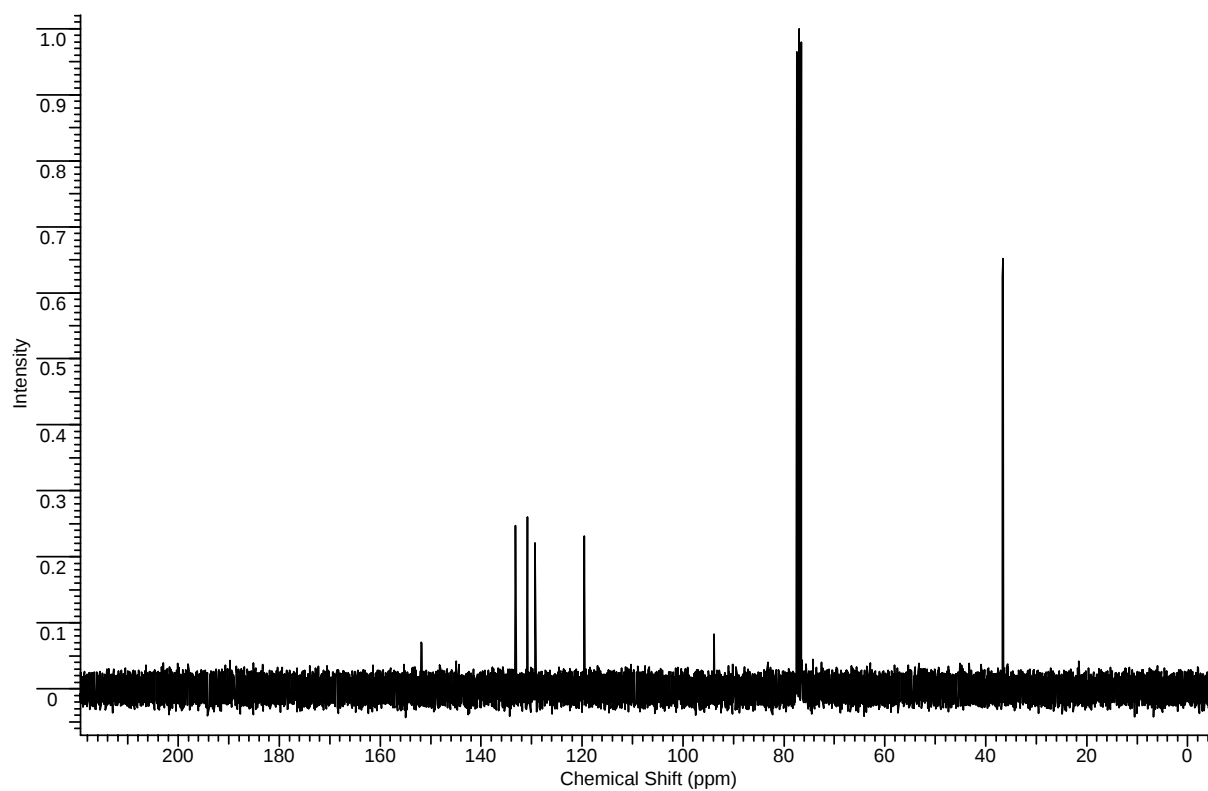
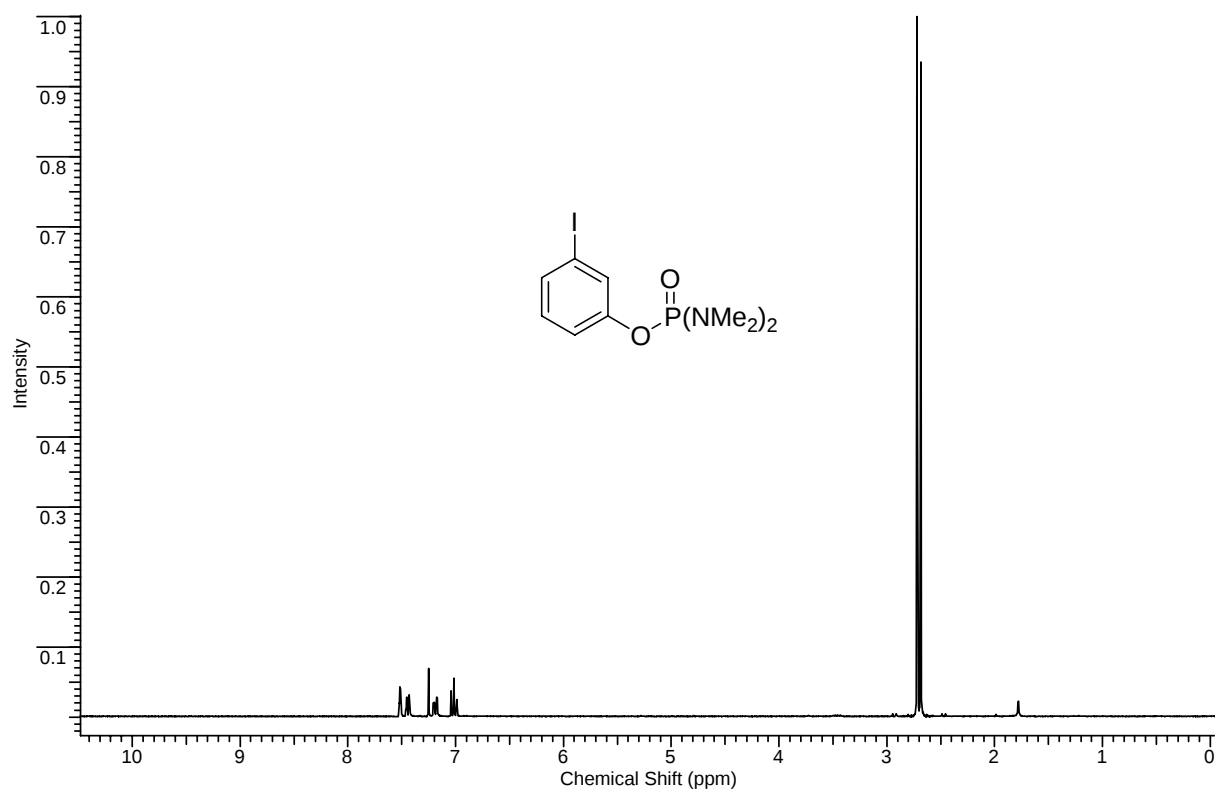
Ethyl 3-{[bis(dimethylamino)phosphoryl]oxy} benzoate (4a)



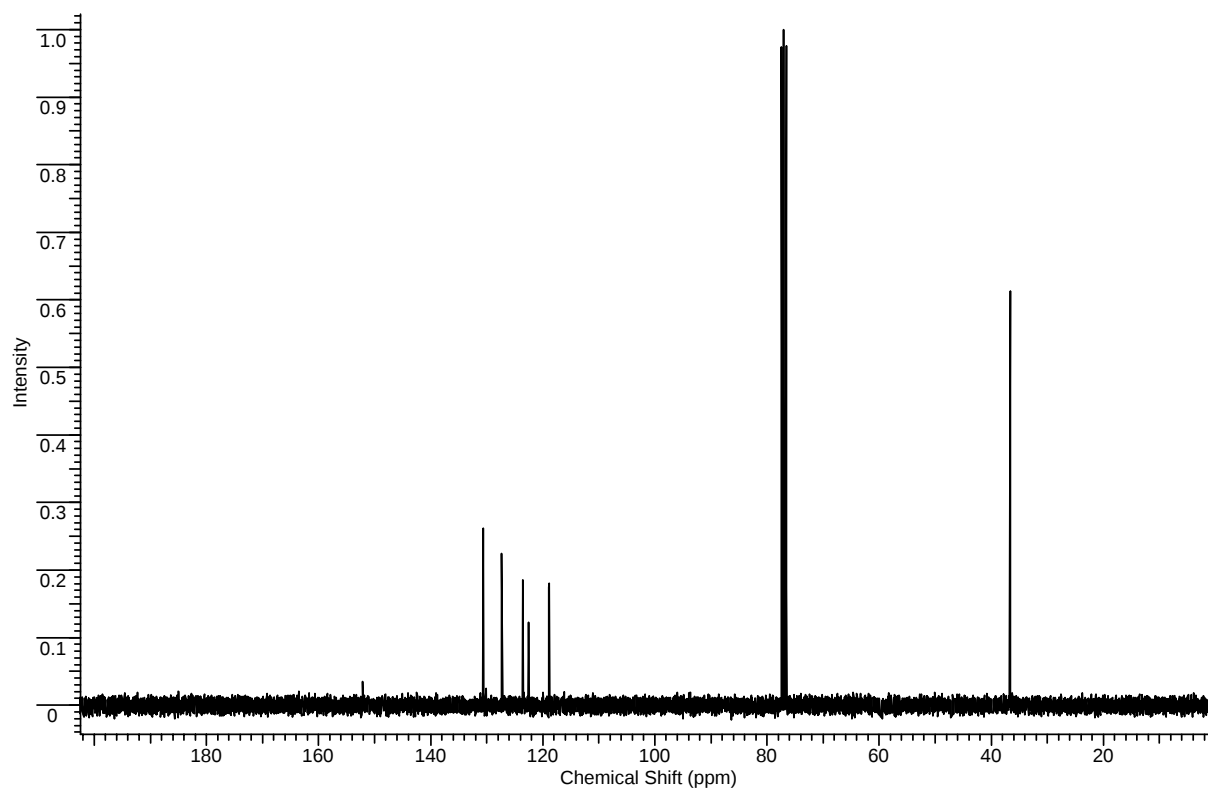
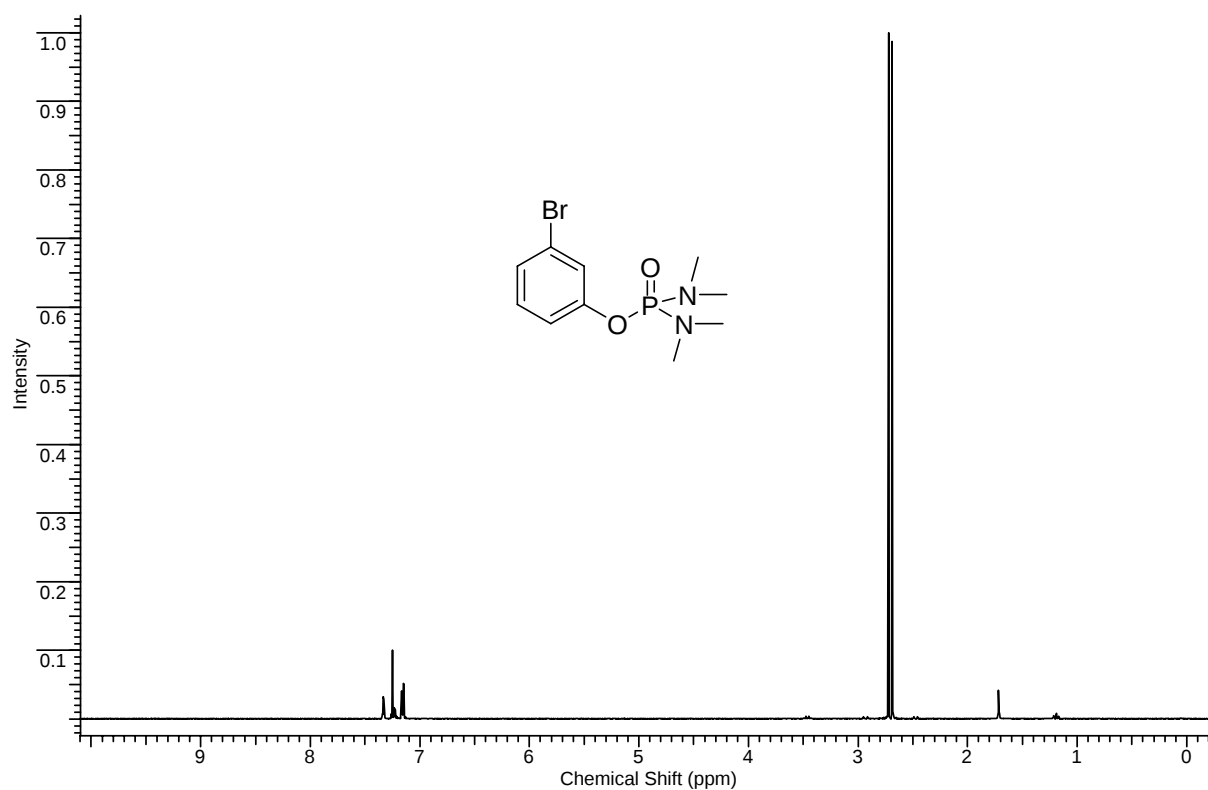
3-(Trifluoromethyl)phenyl *N,N,N',N'*-tetramethyldiamido-phosphate (4b)



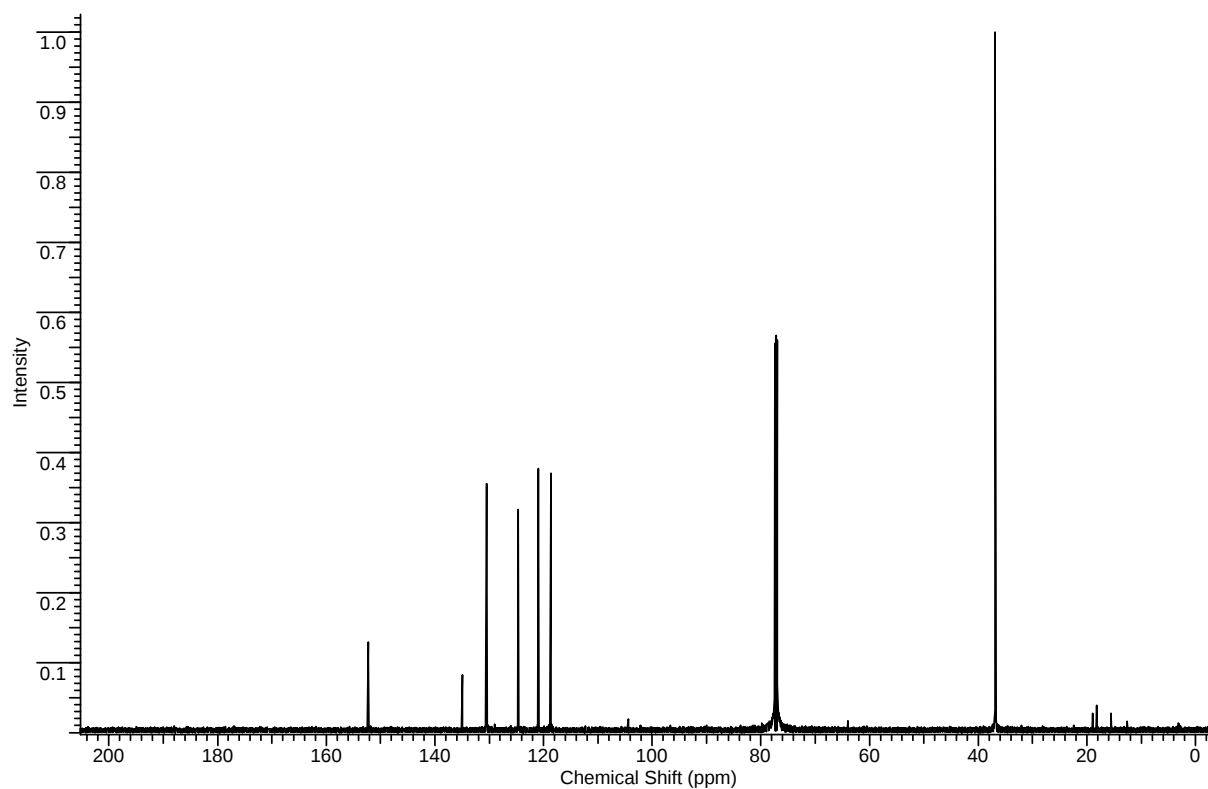
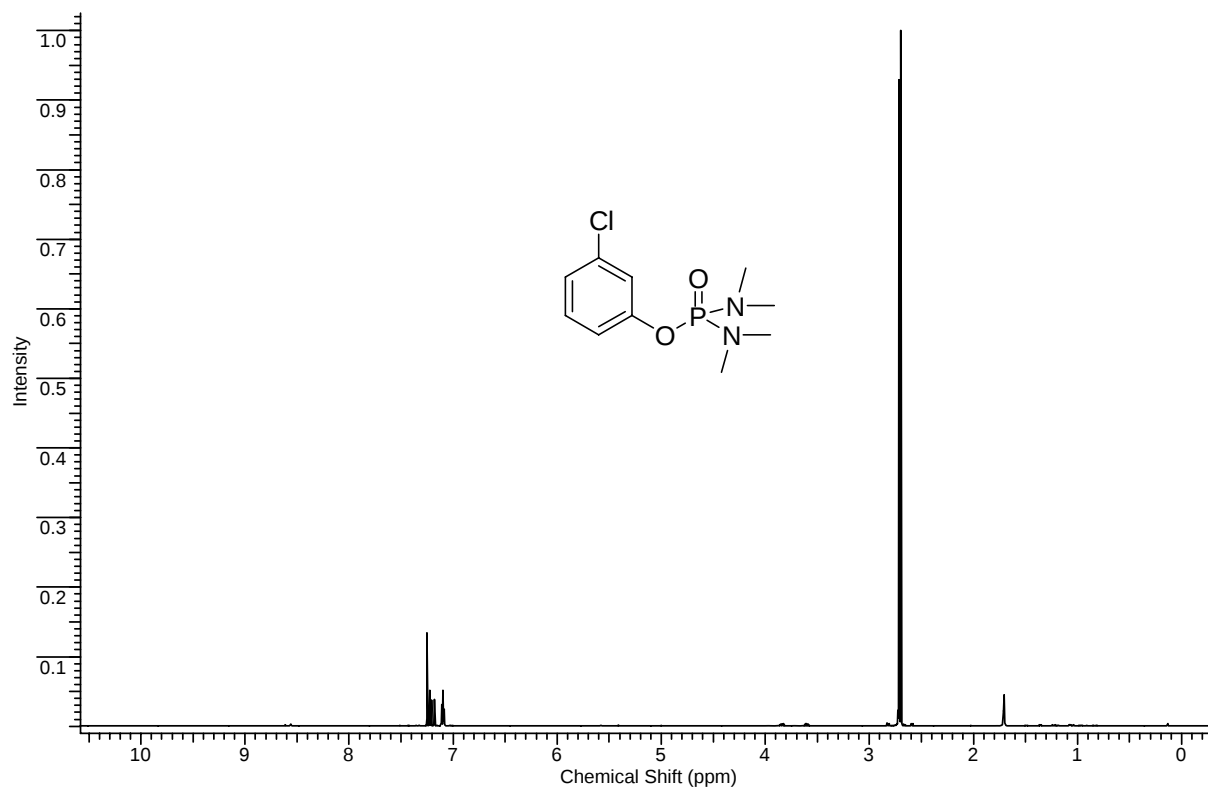
3-Iodophenyl N,N,N',N'-tetramethyldiamidophosphate (4c)



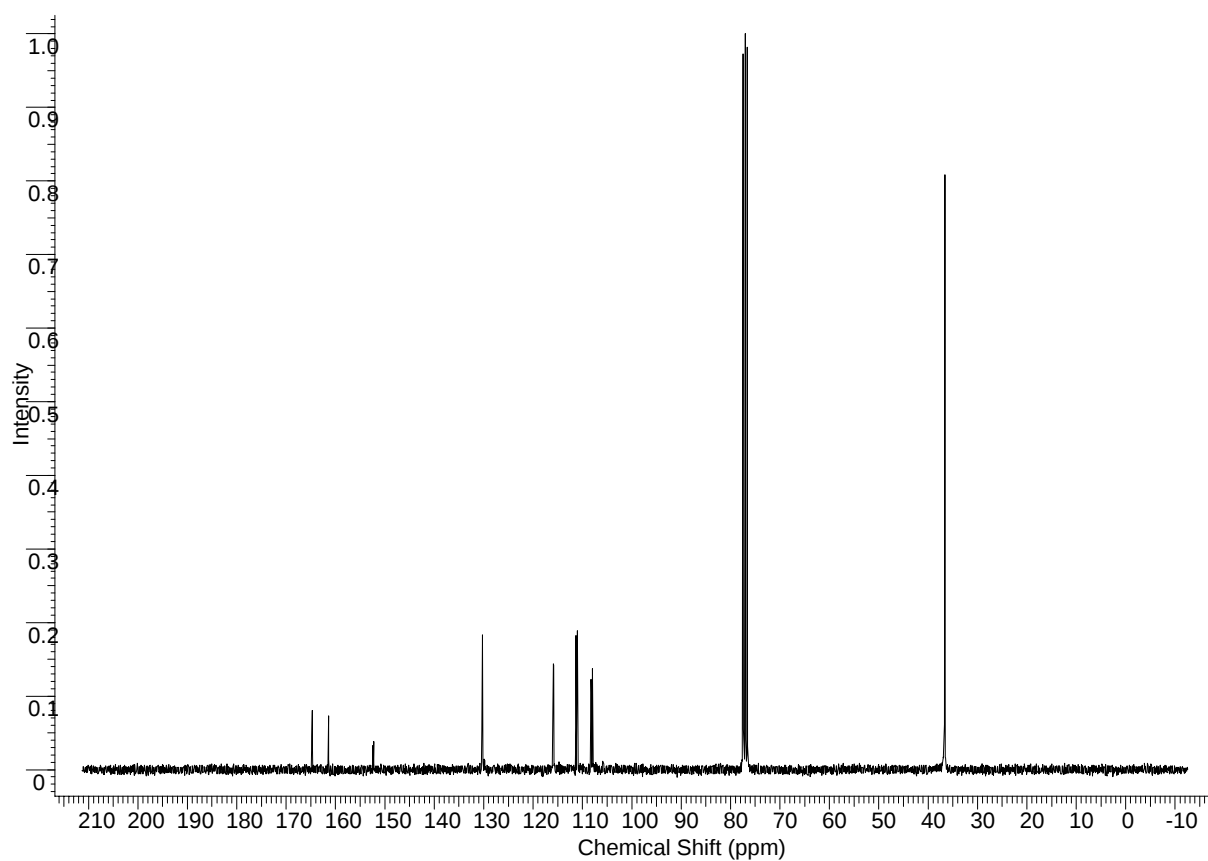
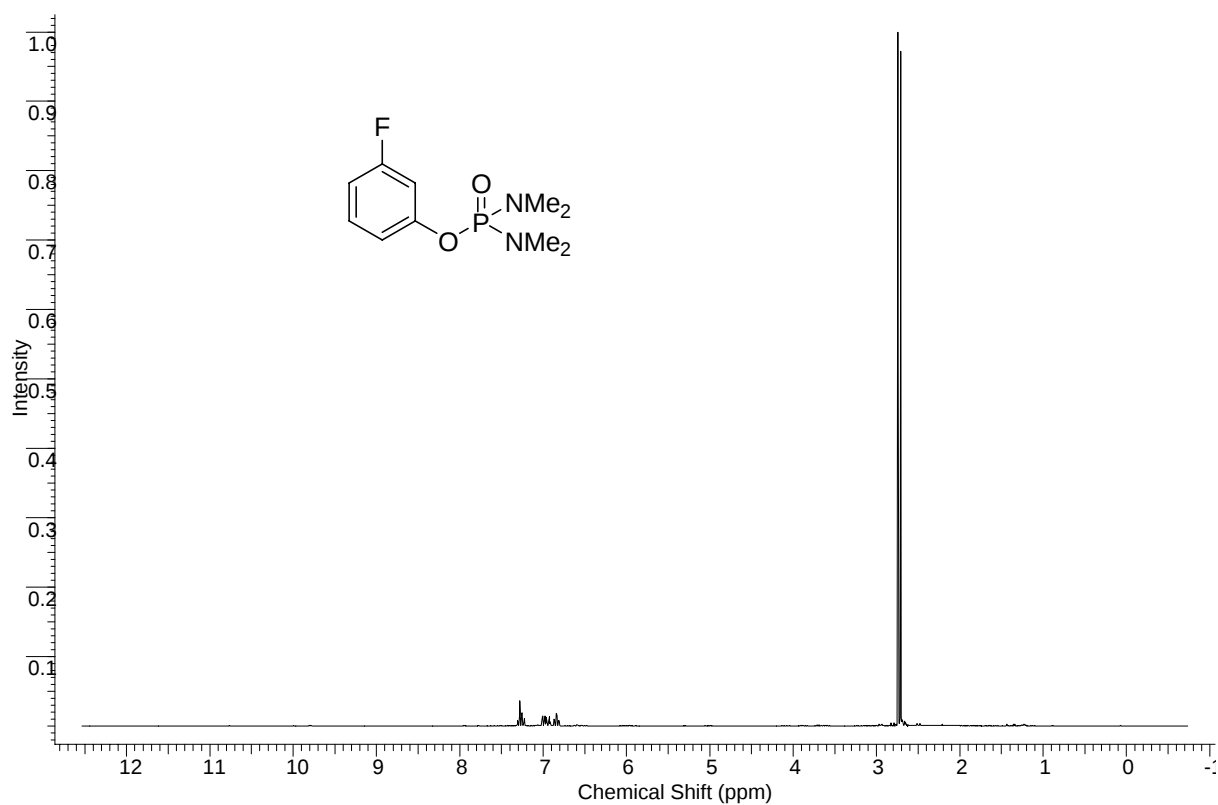
3-Bromophenyl *N,N,N',N'*-tetramethyldiamido-phosphate (4d)



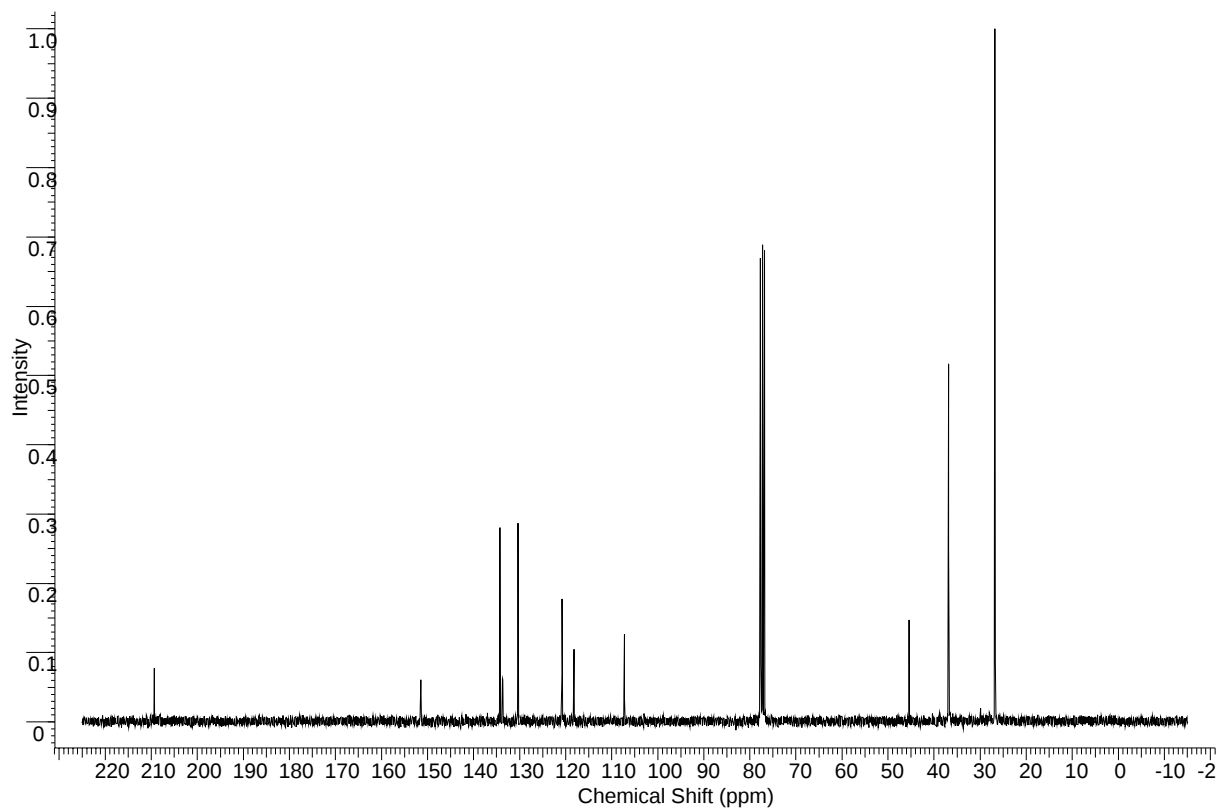
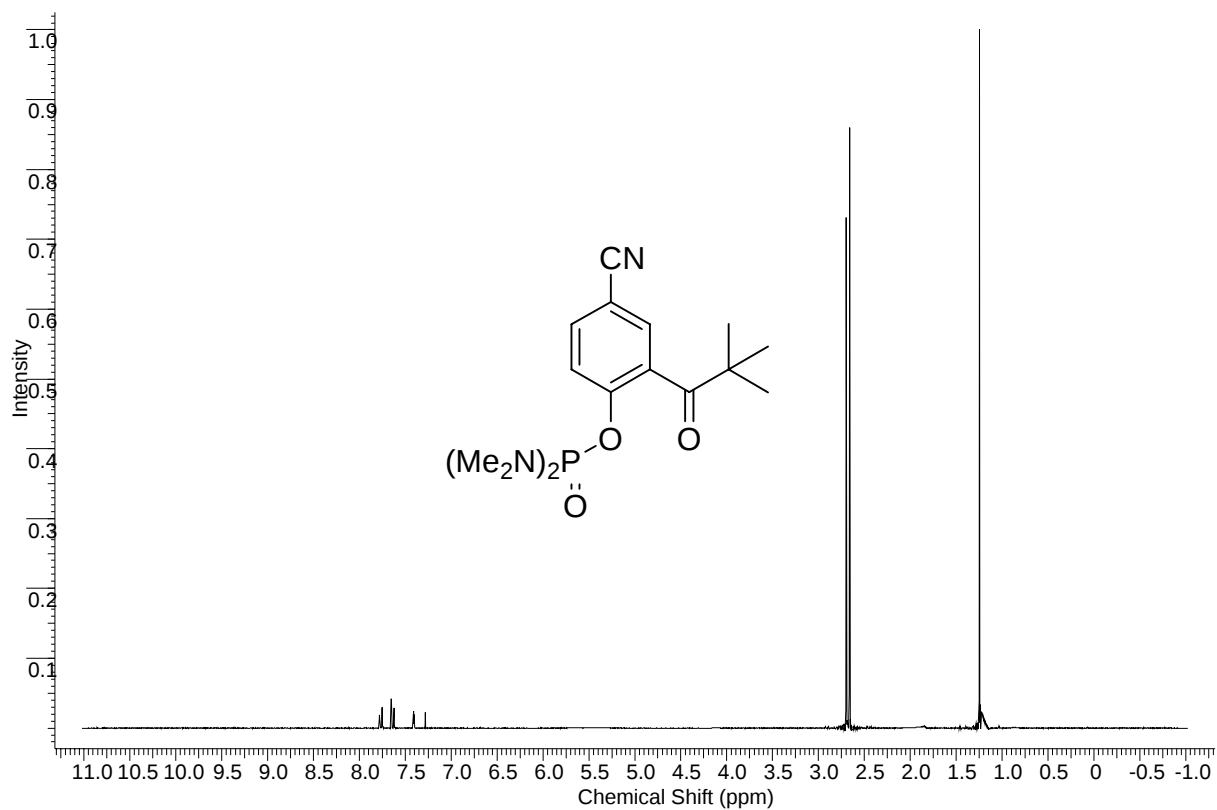
3-chlorophenyl *N,N,N',N'*-tetramethyldiamido-phosphate (4e)



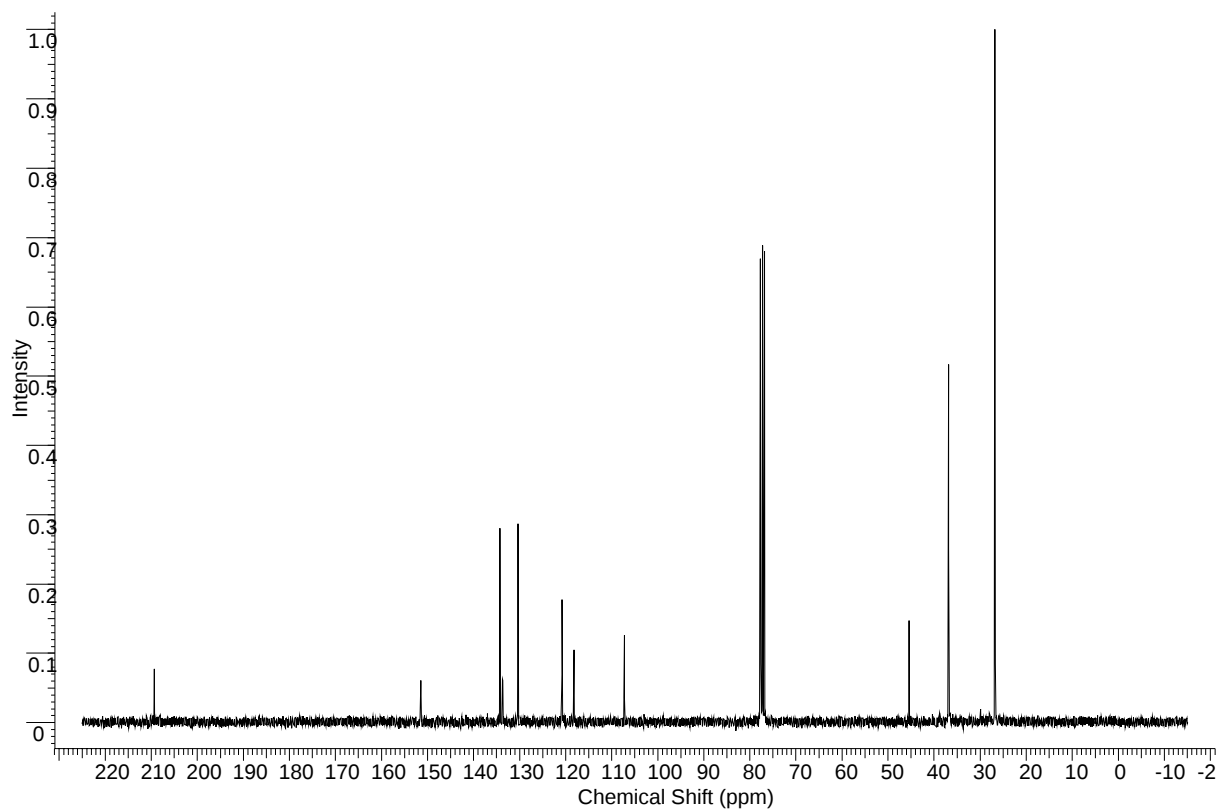
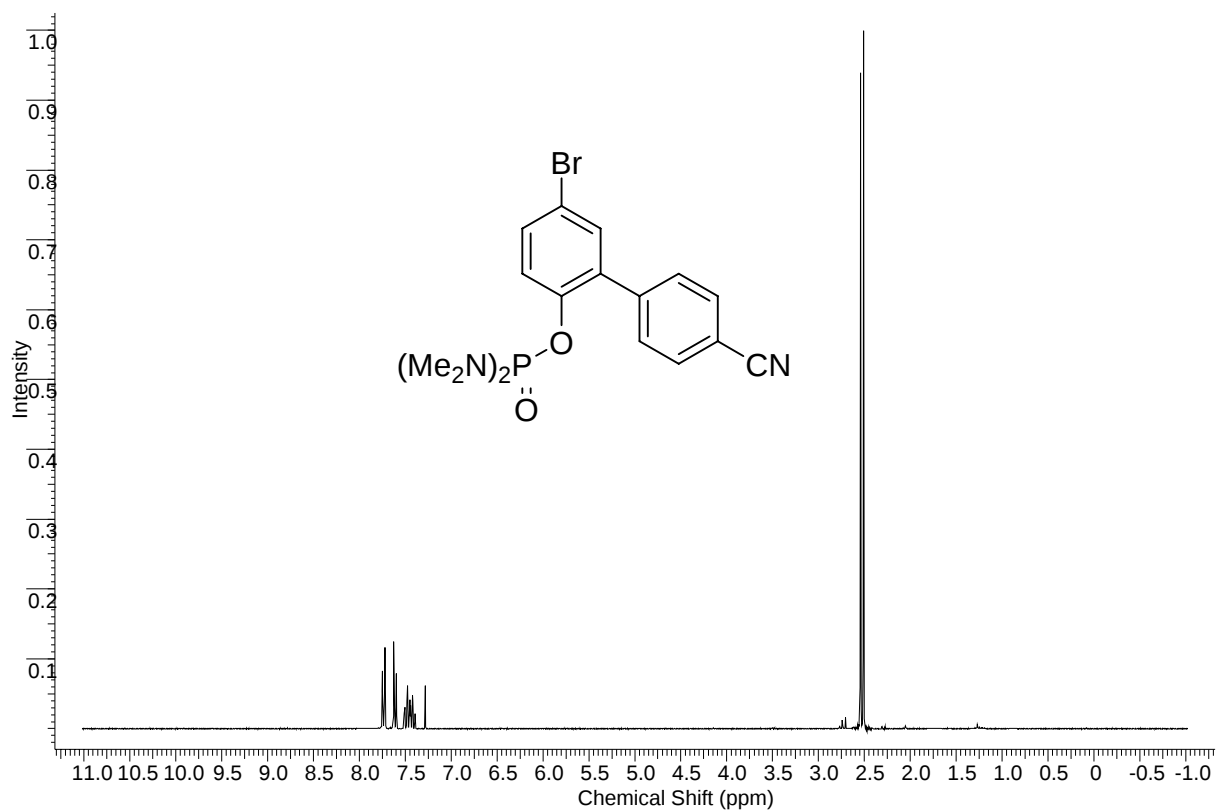
3-Fluorophenyl *N,N,N',N'*-tetramethyldiamidophosphate (4f)



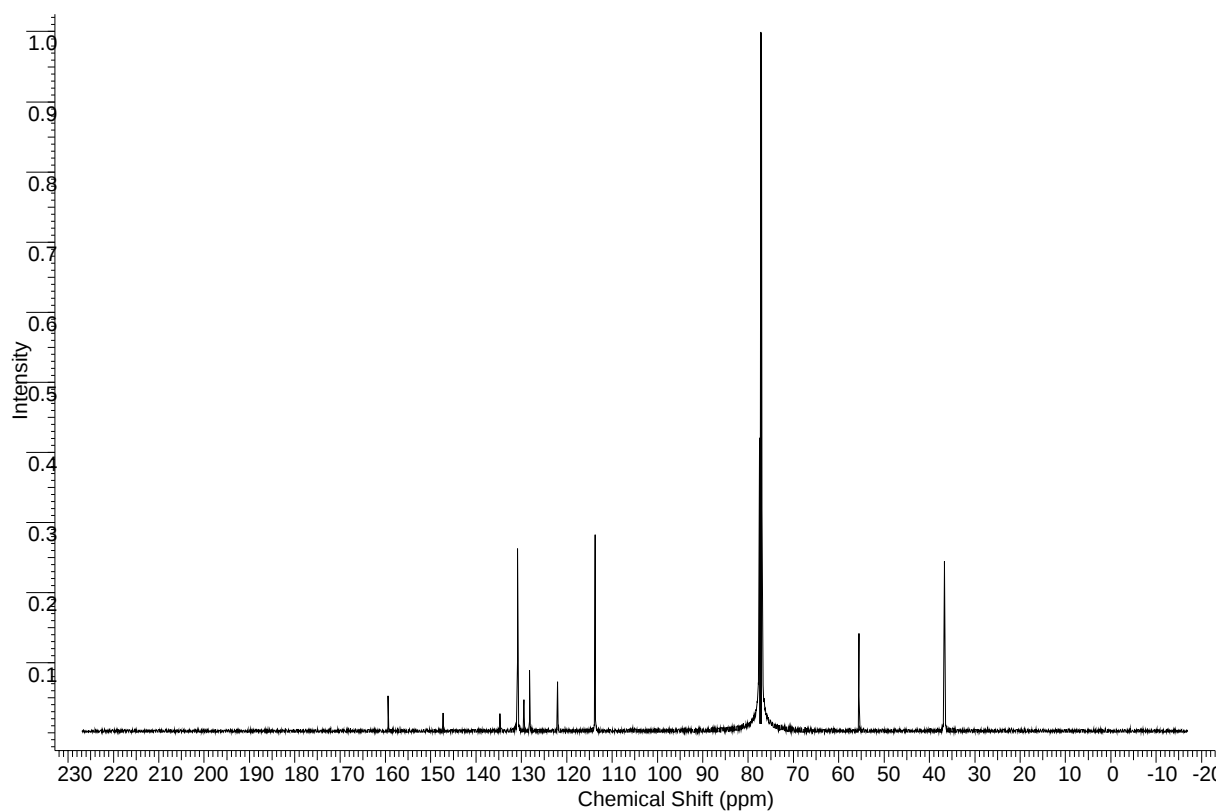
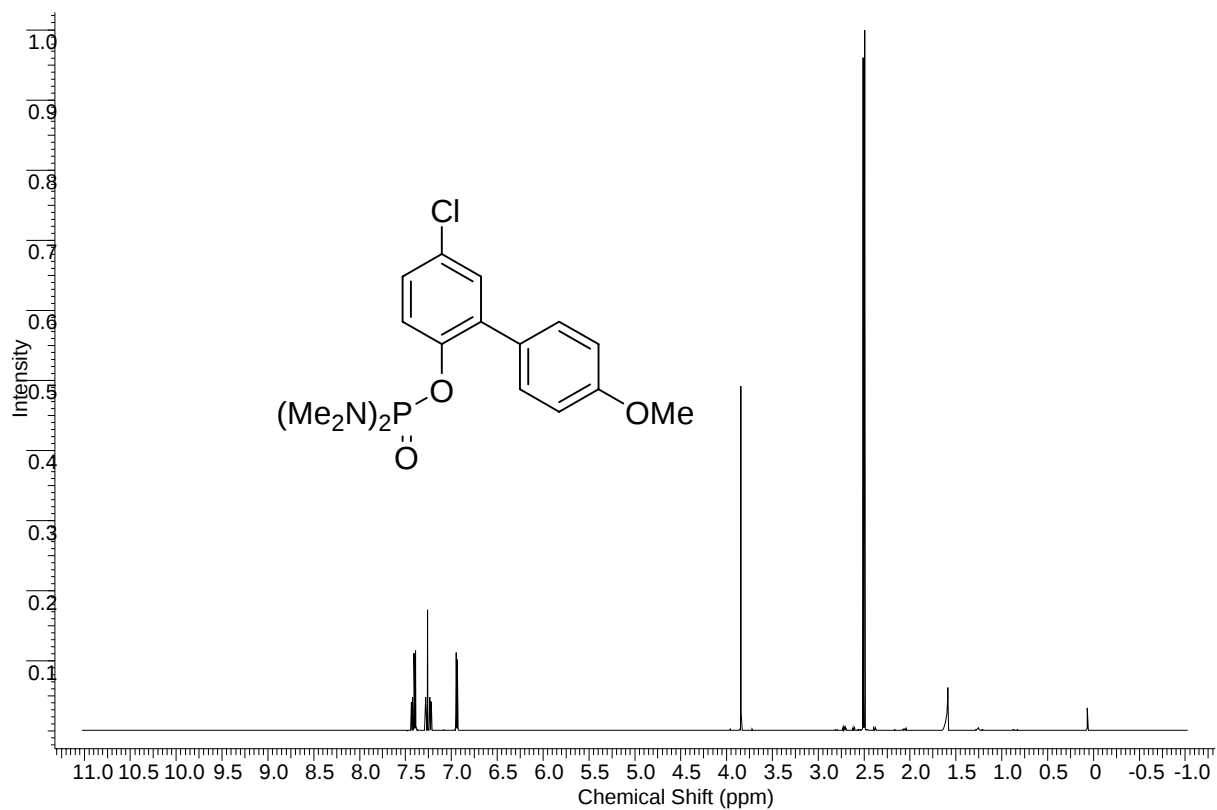
4-Cyano-2-(2,2-dimethylpropanoyl)phenyl *N,N,N',N'*-tetramethyl-diamidophosphate (5a)



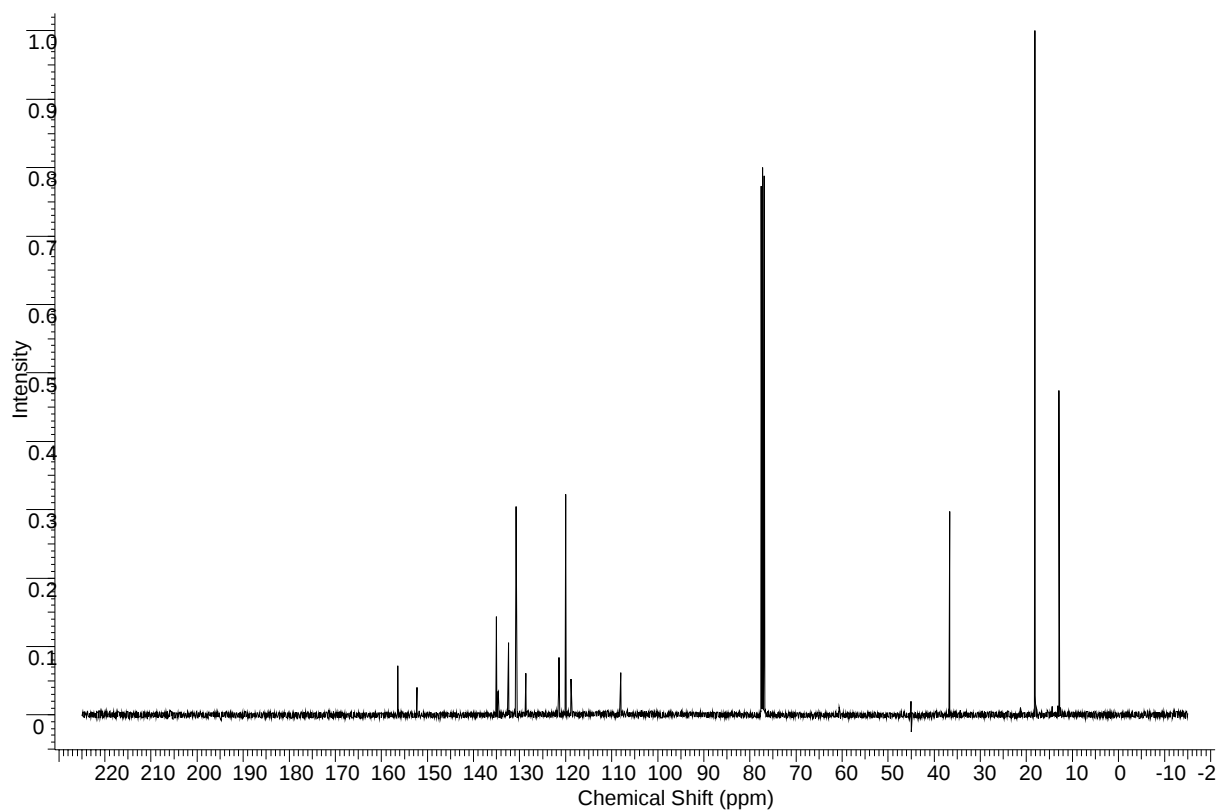
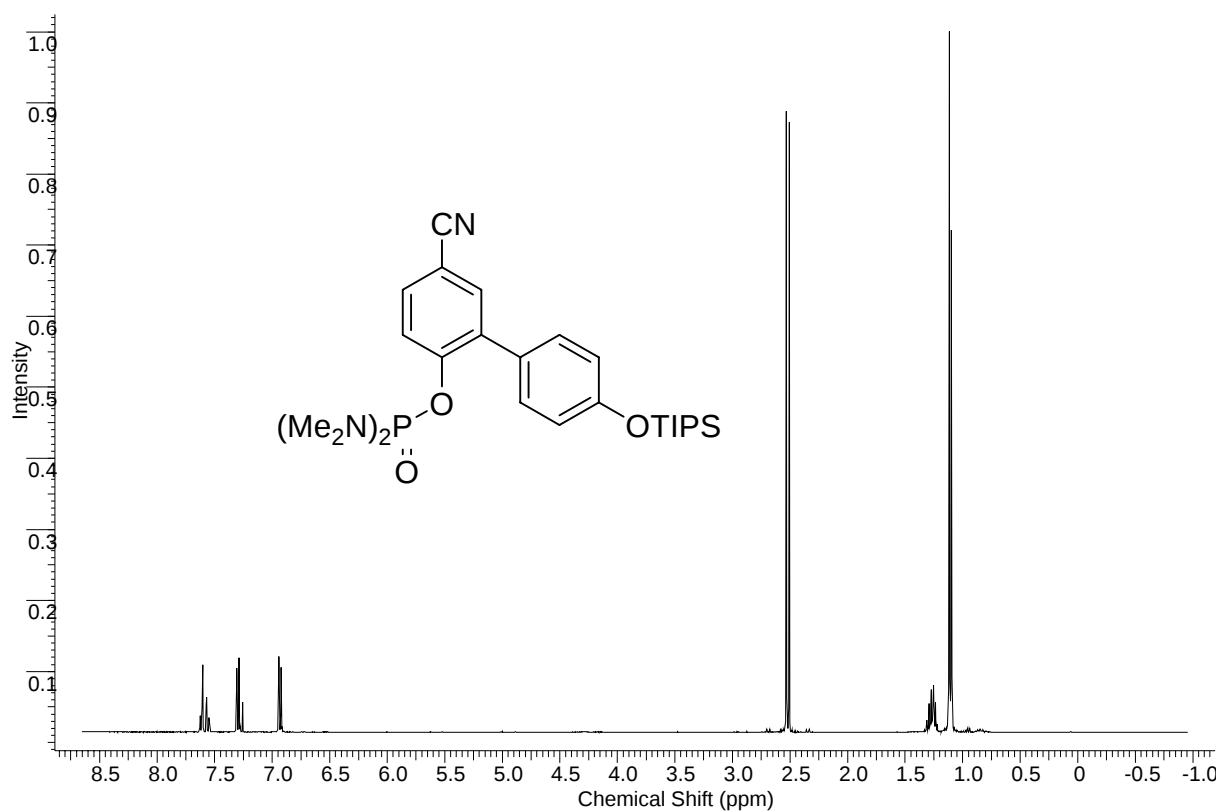
5-Bromo-4'-cyanobiphenyl-2-yl *N,N,N',N'*-tetramethyldiamido-phosphate (5b)



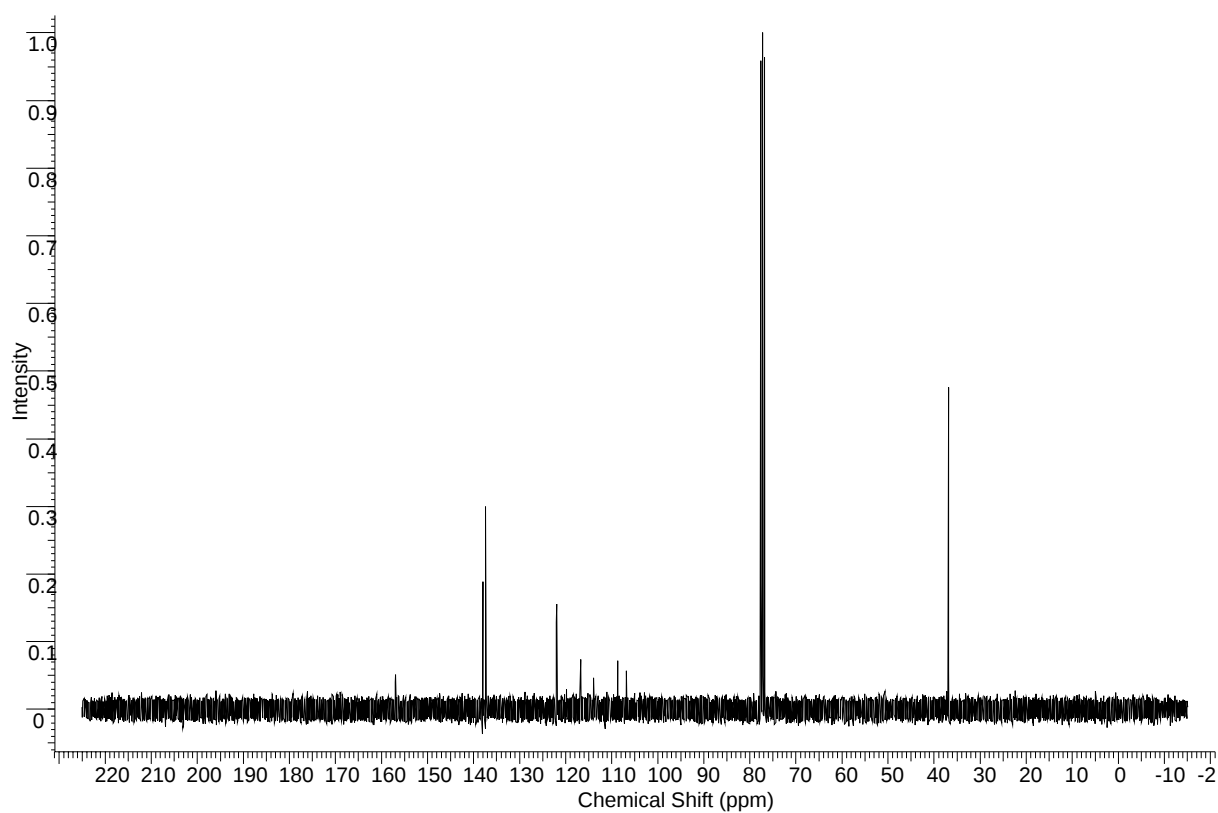
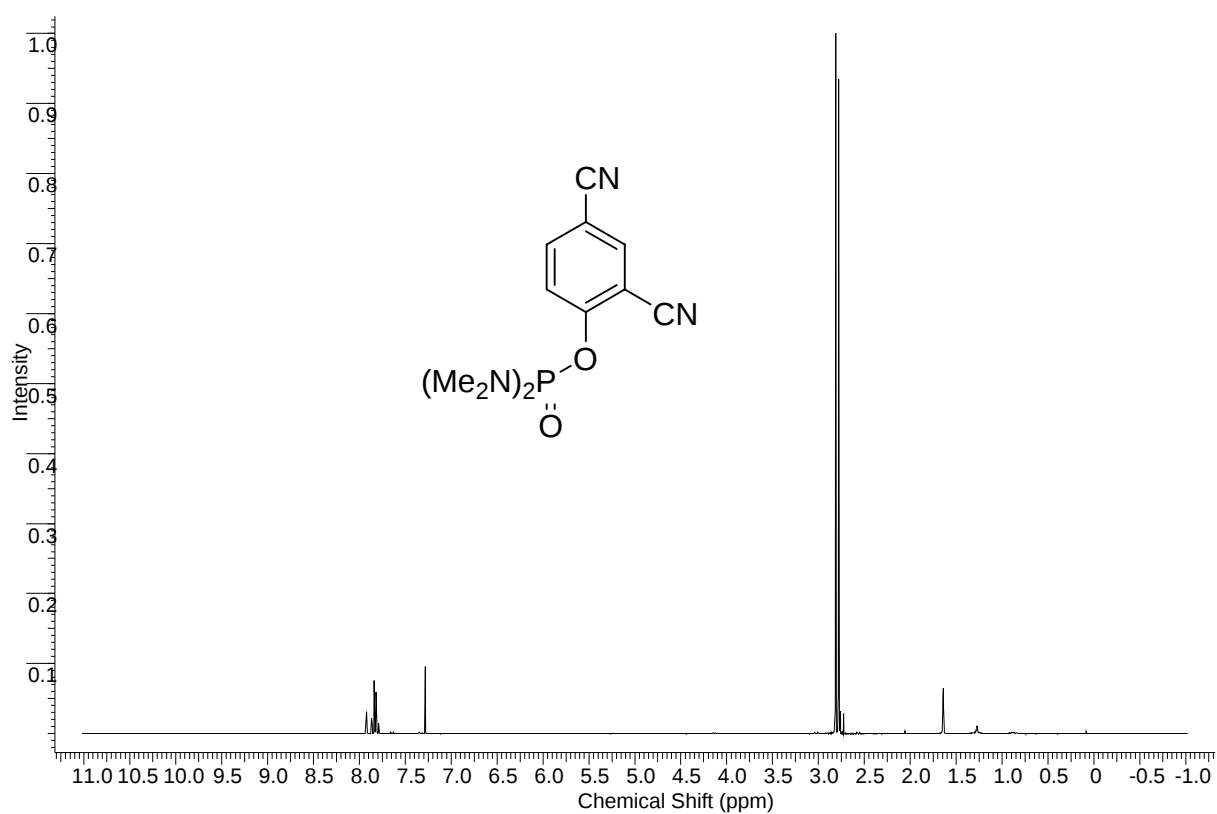
5-Chloro-4'-methoxybiphenyl-2-yl *N,N,N',N'*-tetramethyldiamido-phosphate (5c)



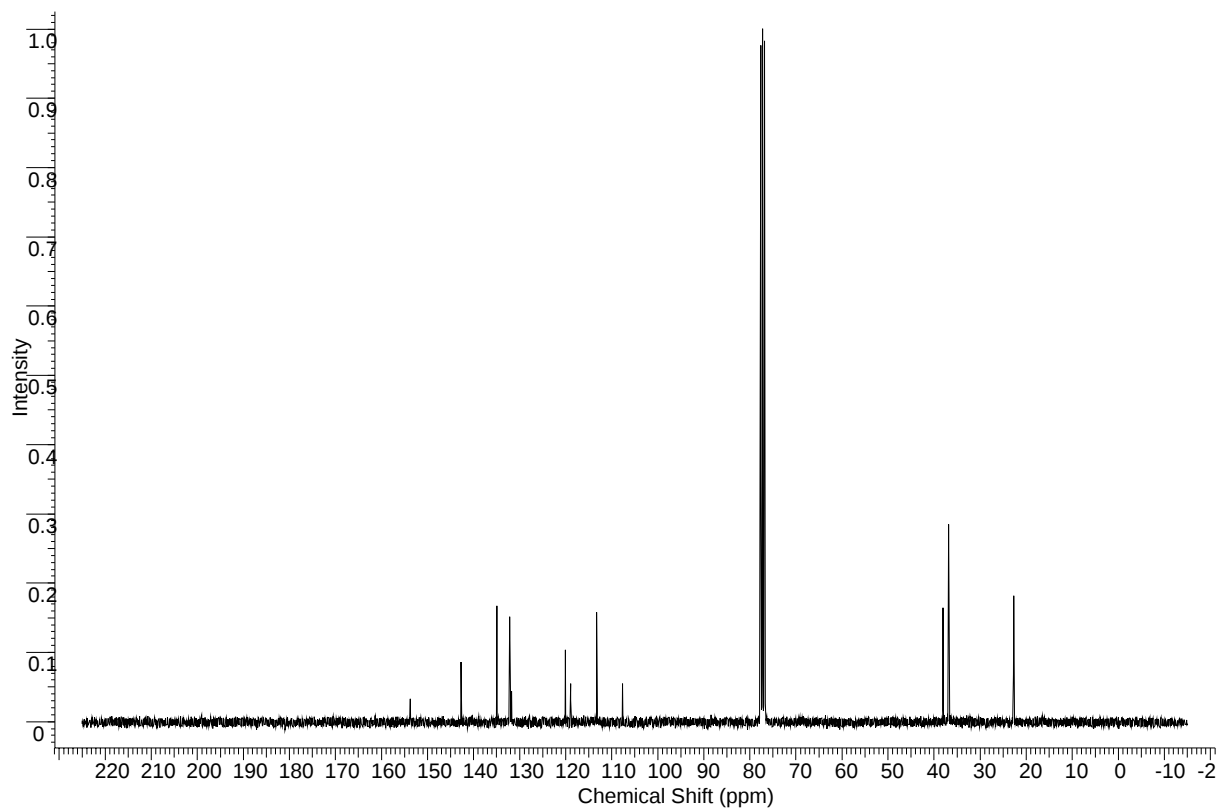
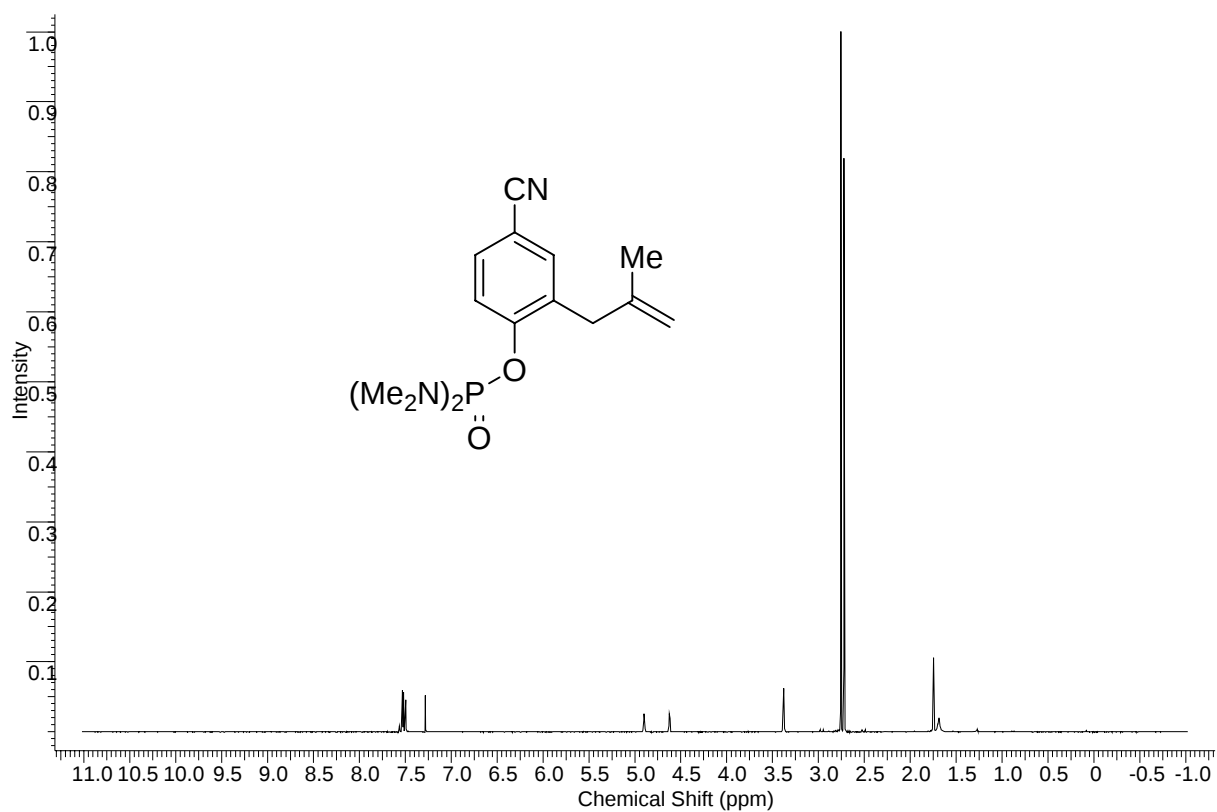
5-Cyano-4'-[(triisopropylsilyl)oxy]biphenyl-2-yl *N,N,N',N'*-tetramethyldiamidophosphate (5d)



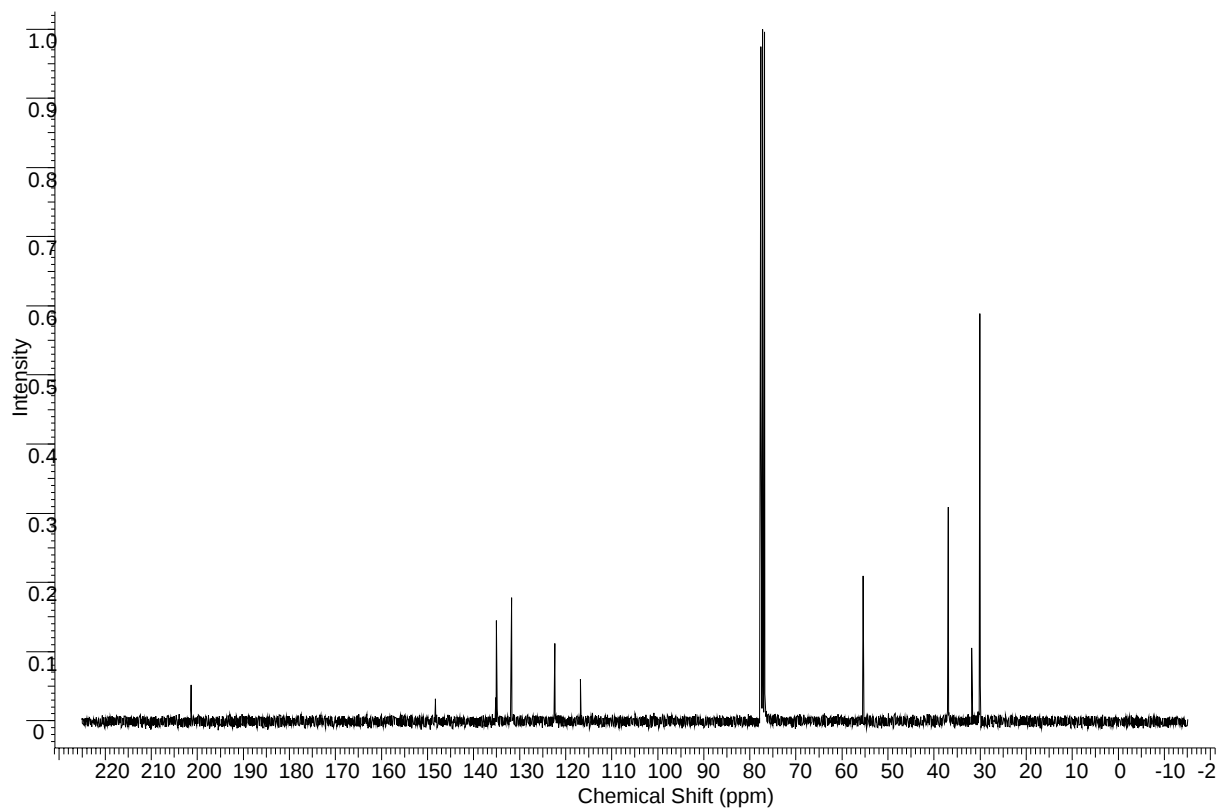
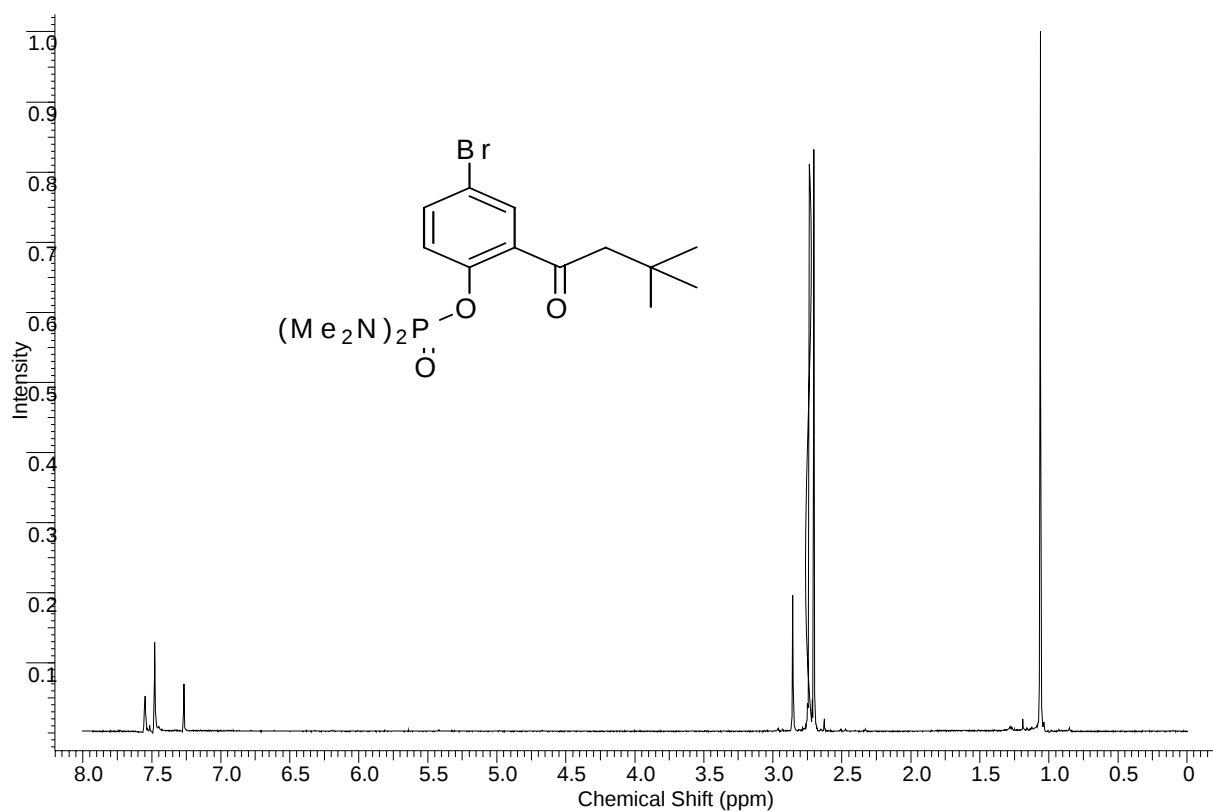
2,4-Dicyanophenyl *N,N,N',N'*-tetramethyldi-amidophosphate (5e)



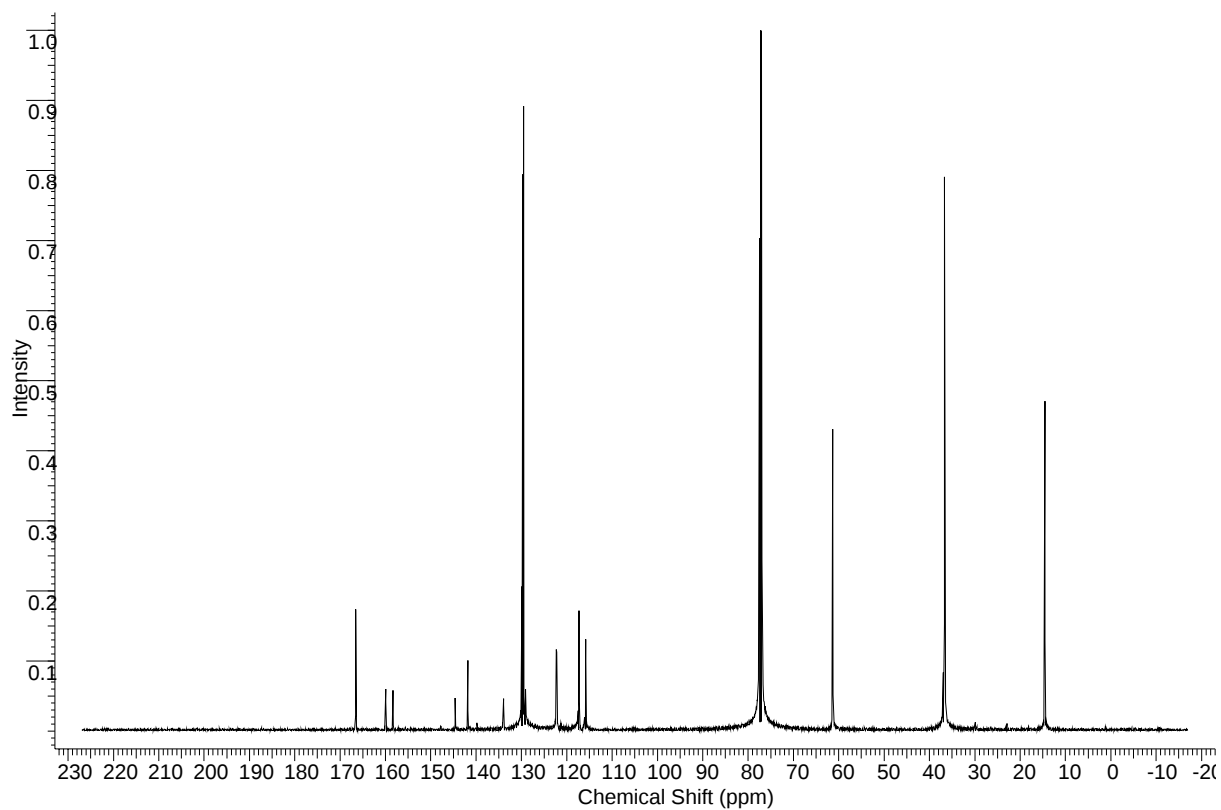
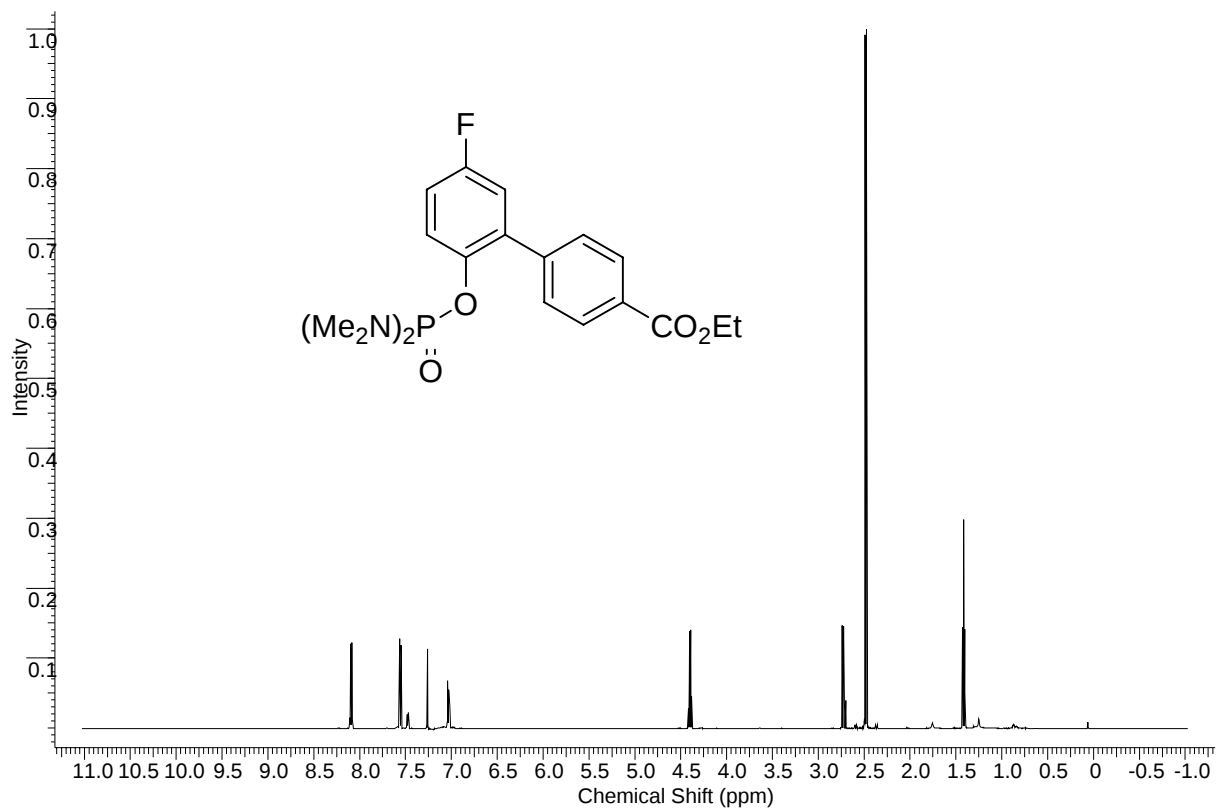
4-Cyano-2-(2-methylprop-2-en-1-yl)phenyl *N,N,N',N'*-tetramethyldiamidophosphate (5f)



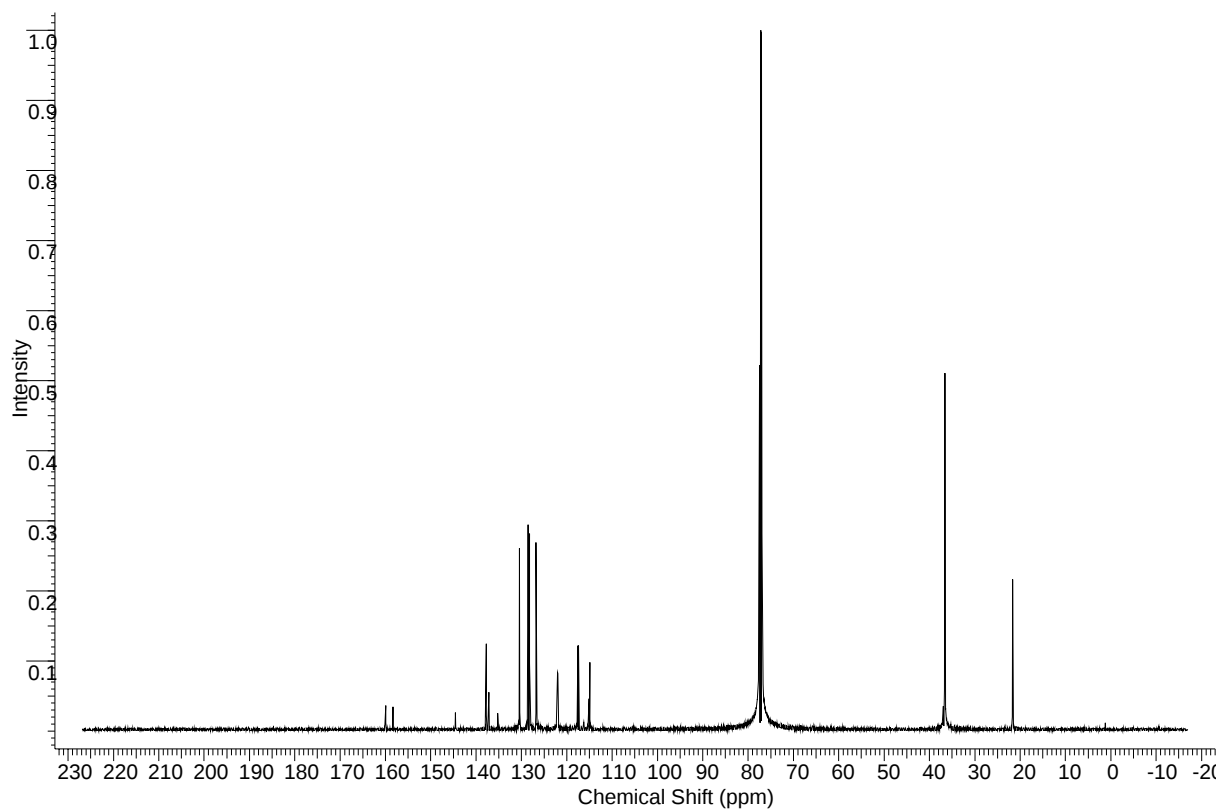
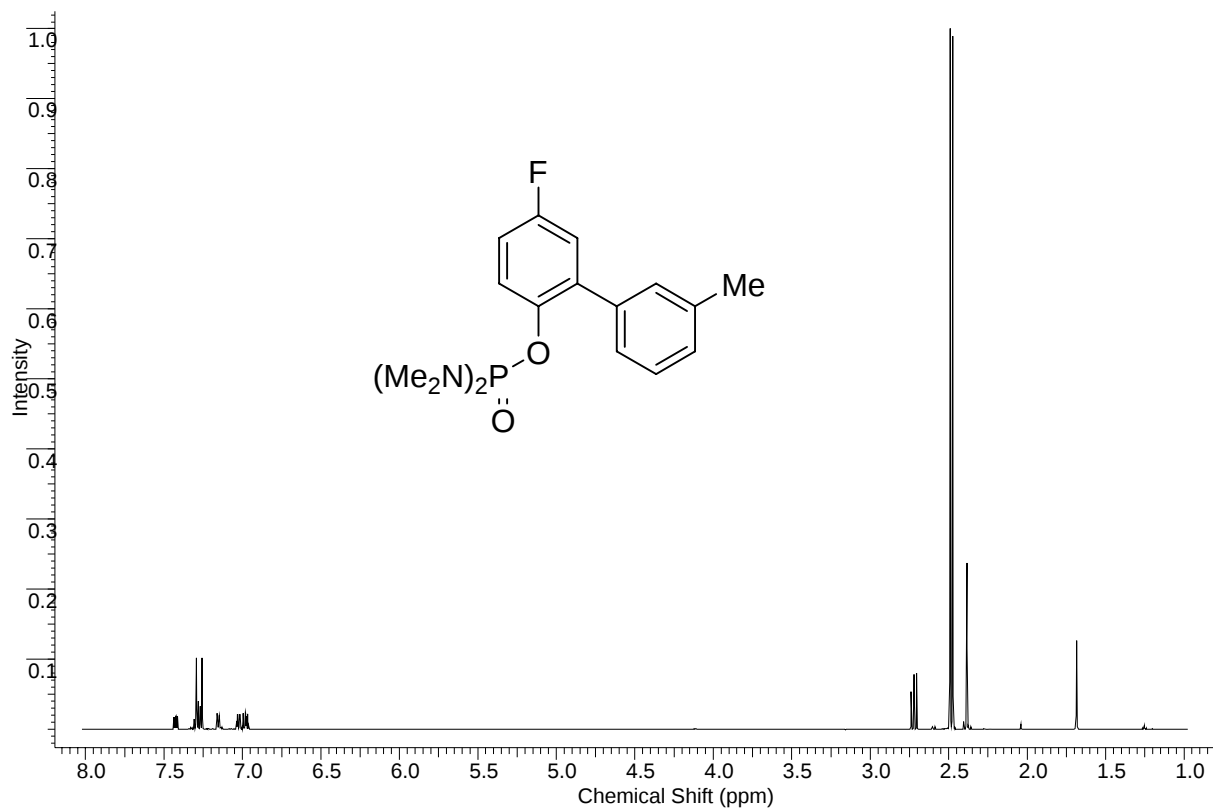
4-bromo-2-(3,3-dimethyl-2-oxobutyl)phenyl *N,N,N',N'*-tetramethyldiamidophosphate (5g)



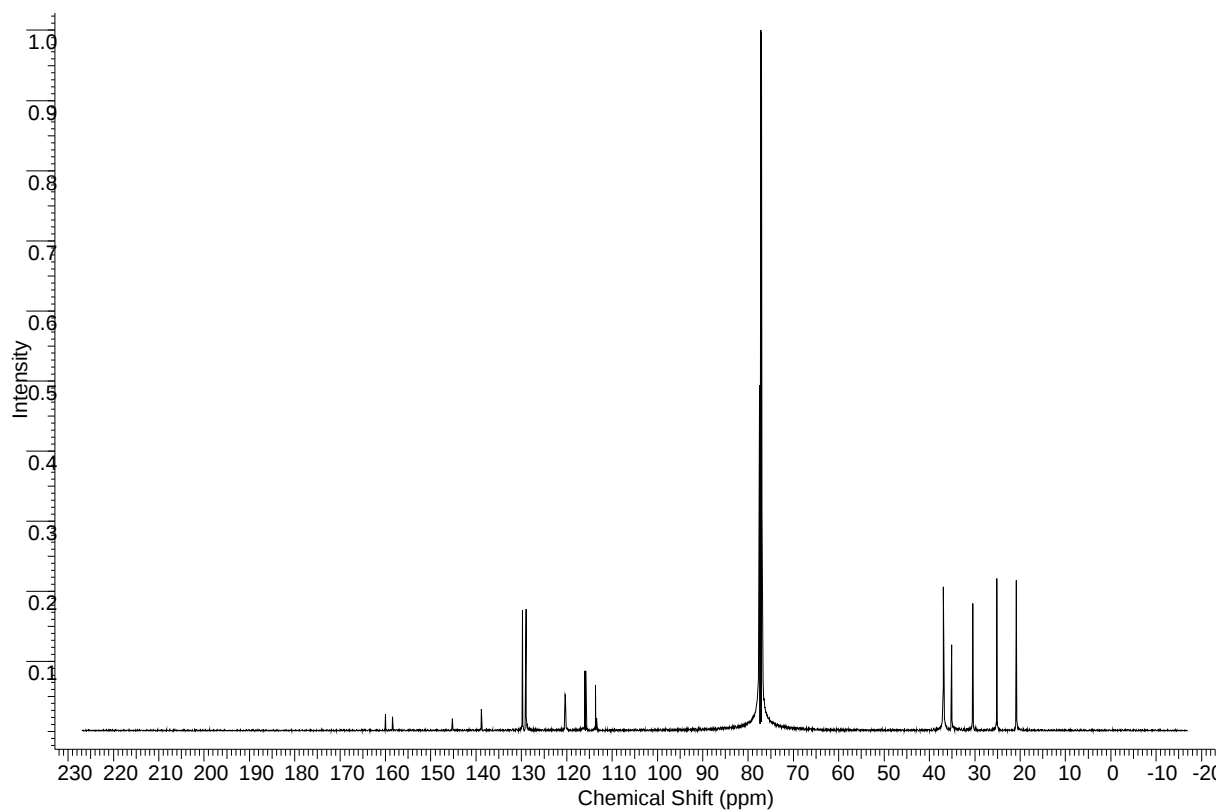
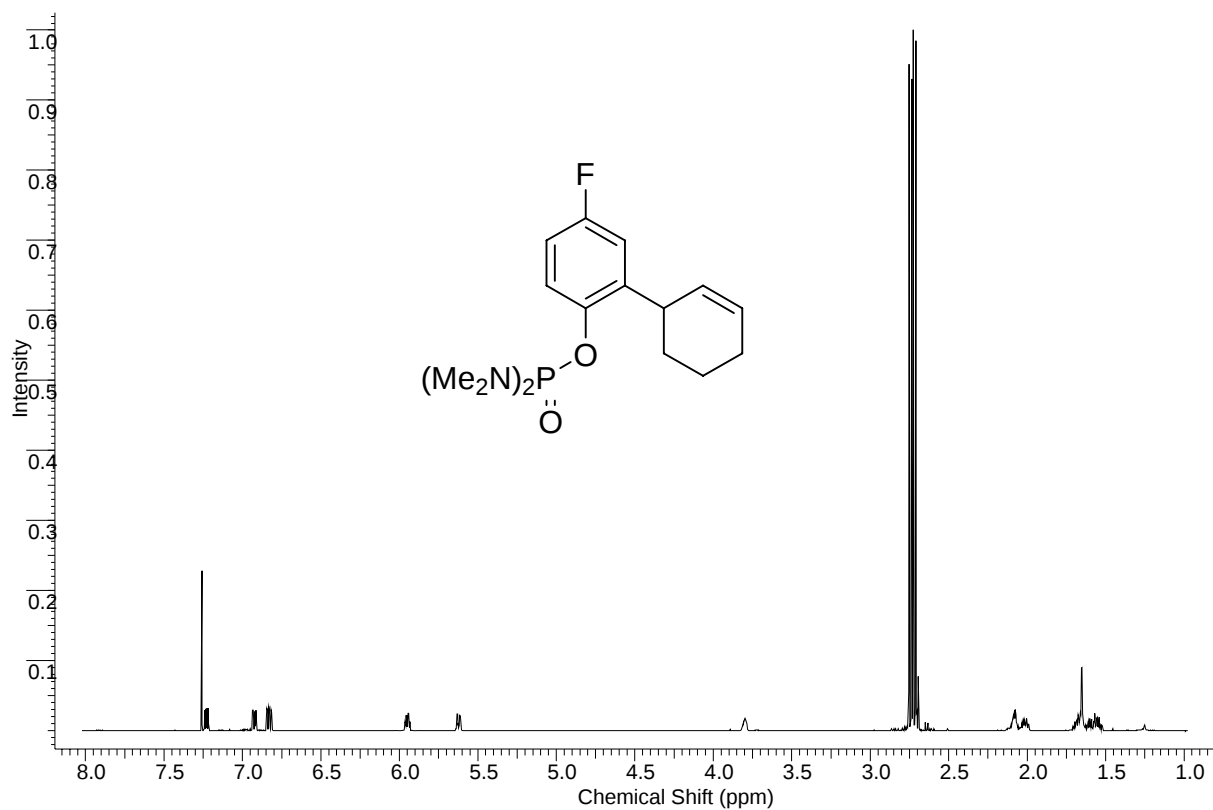
Ethyl 2'-{[bis(dimethylamino)phosphoryl]oxy}-5'-fluorobiphenyl-4-carboxylate (5h)



5-Fluoro-3'-methylbiphenyl-2-yl *N,N,N',N'*-tetra-methyldiamido-phosphate (5i)

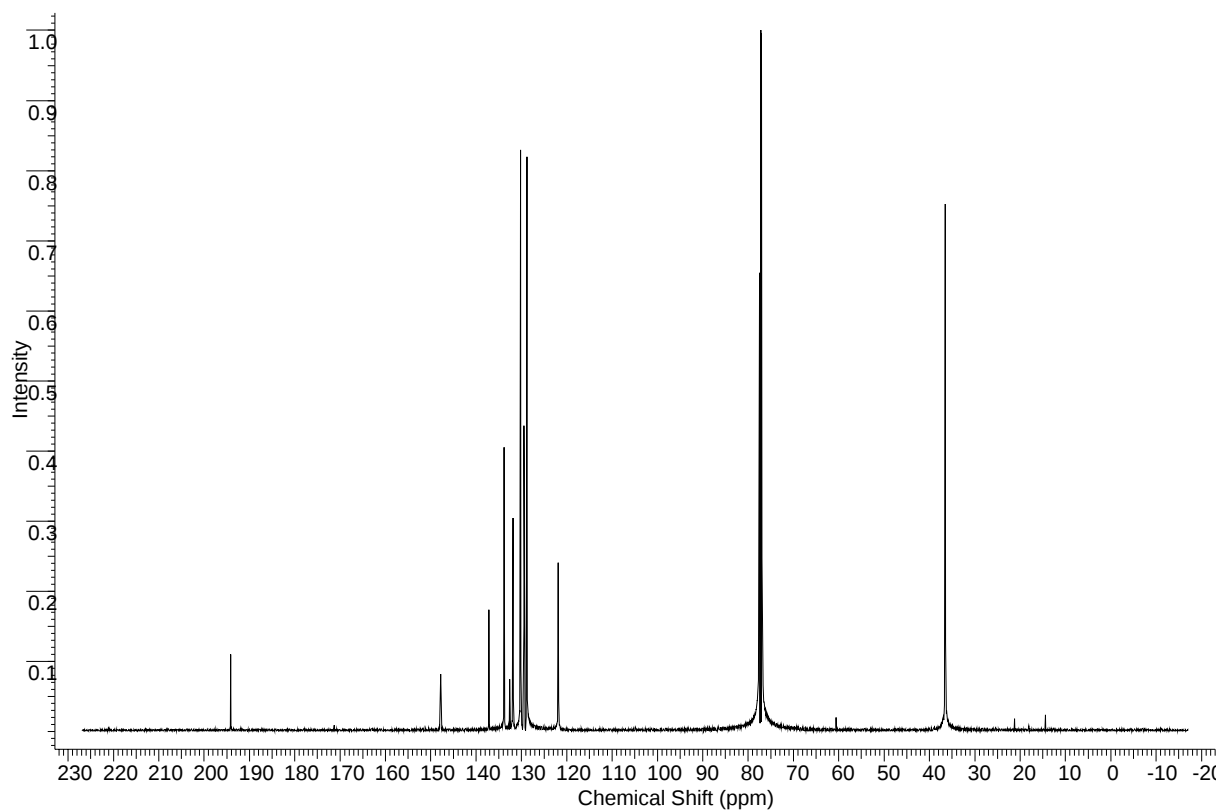
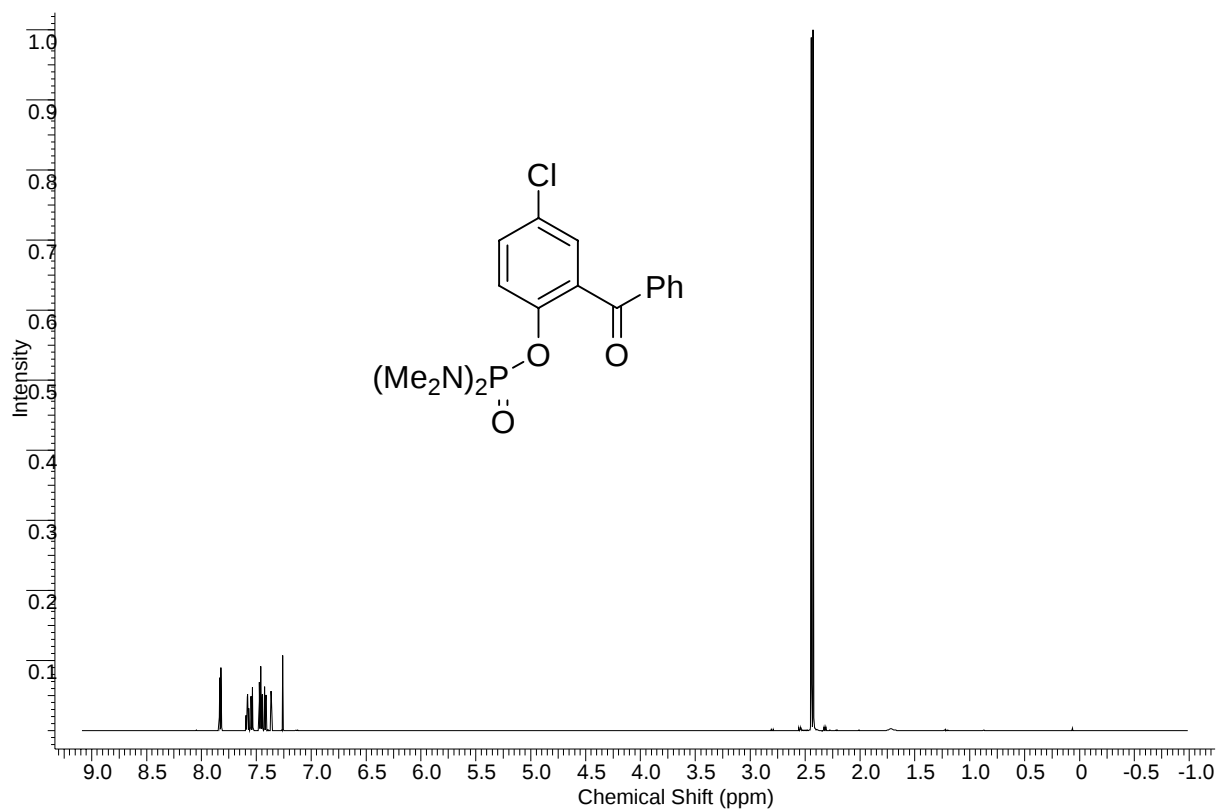


**2-Cyclohex-2-en-1-yl-4-fluorophenyl *N,N,N',N'*-tetramethyldi-
amidophate (5j)**



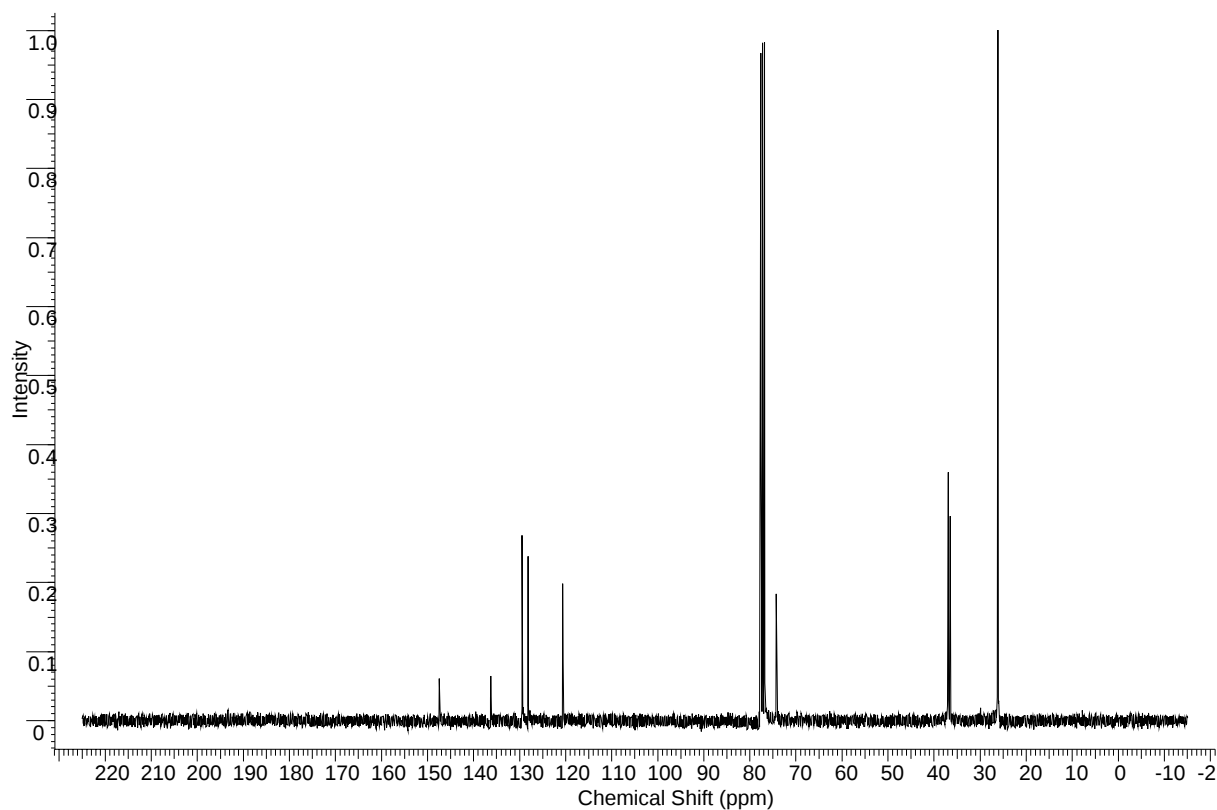
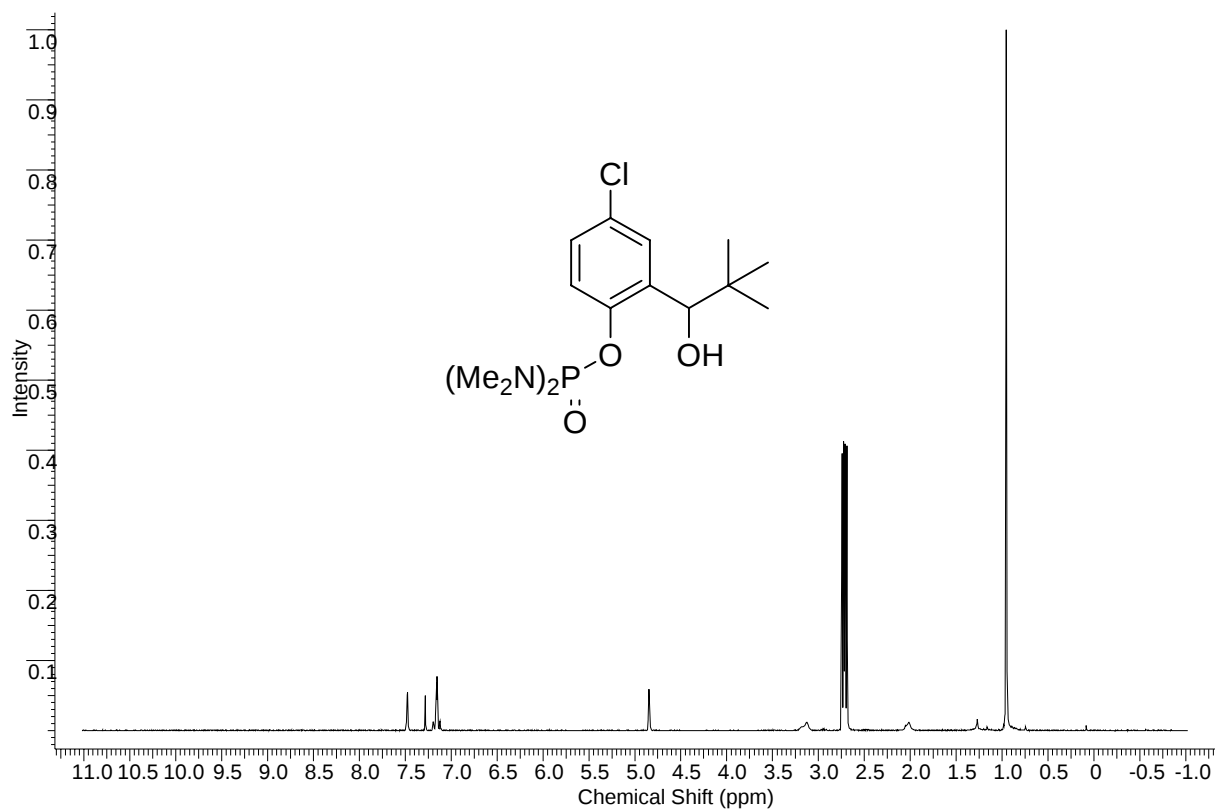
**2-Benzoyl-4-chlorophenyl
phate (5k)**

***N,N,N',N'*-tetramethyl-diamidophos-**



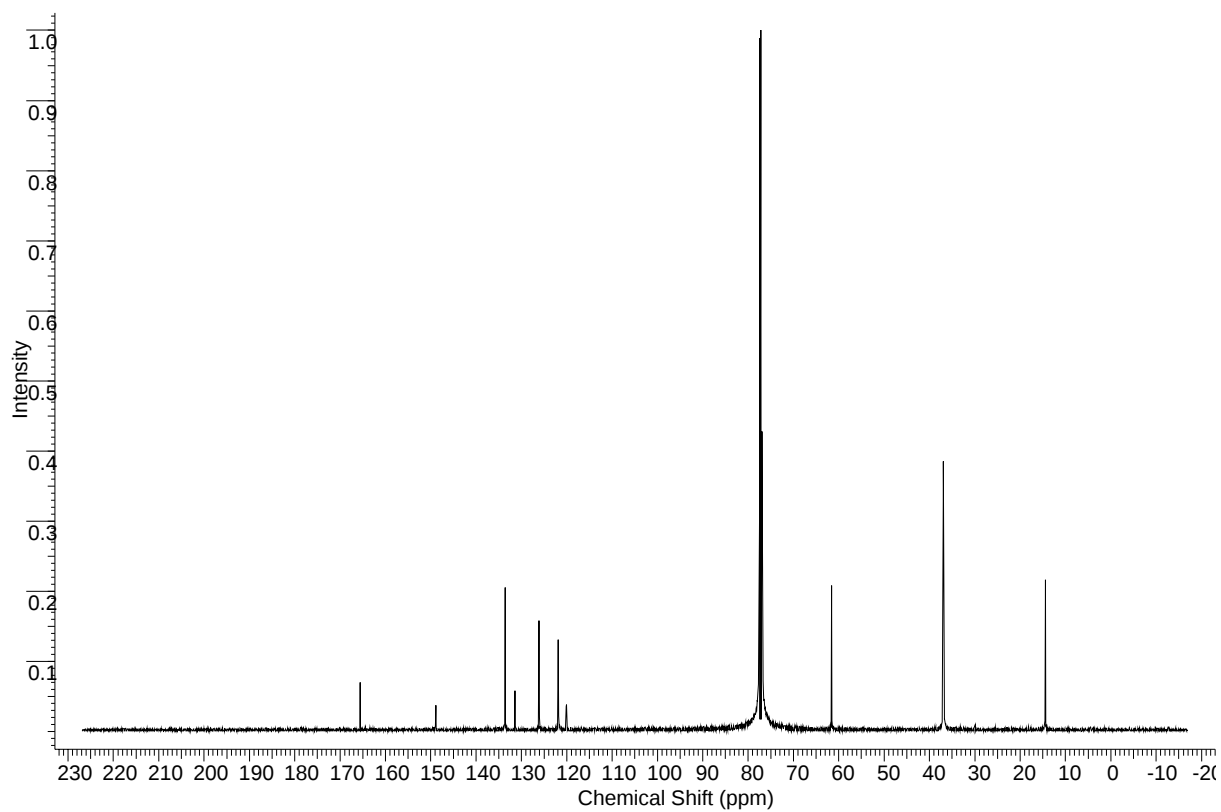
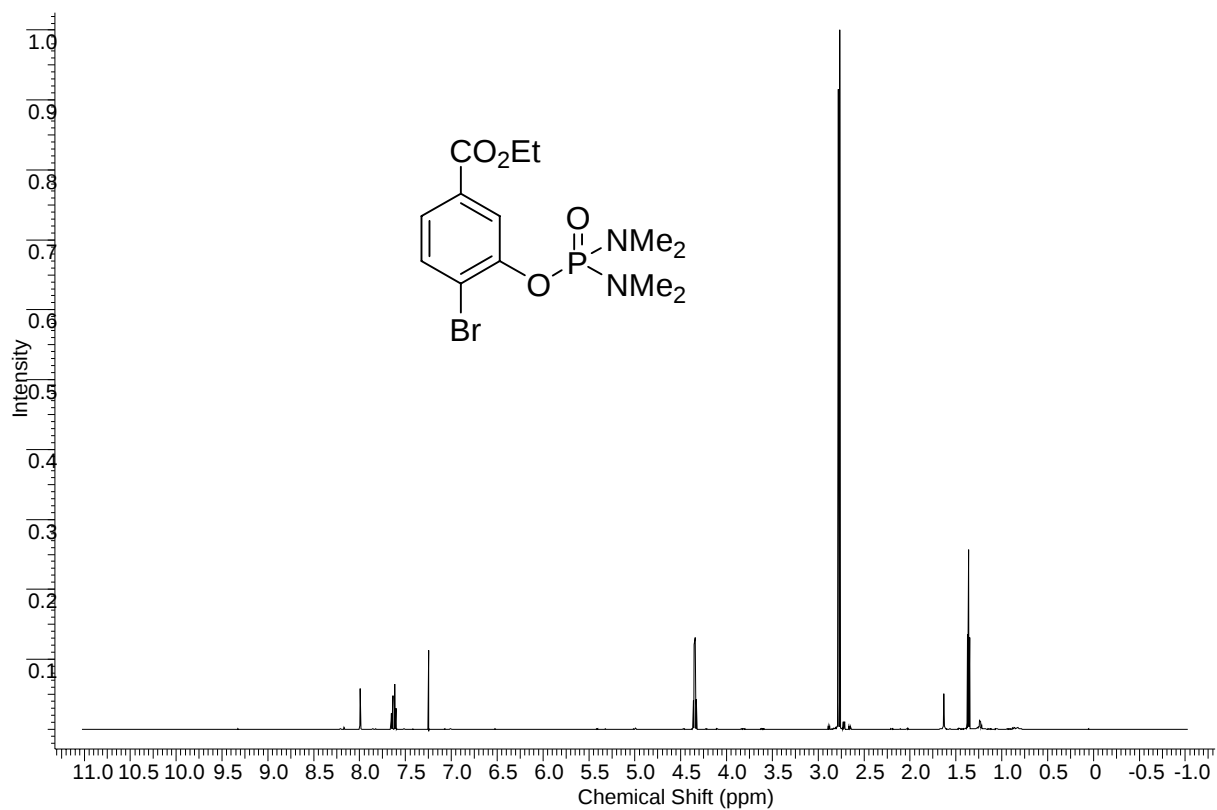
**4-Chloro-2-(1-hydroxy-2,2-dimethylpropyl)phenyl
tetramethyldiamidophosphate (51)**

N,N,N',N' -

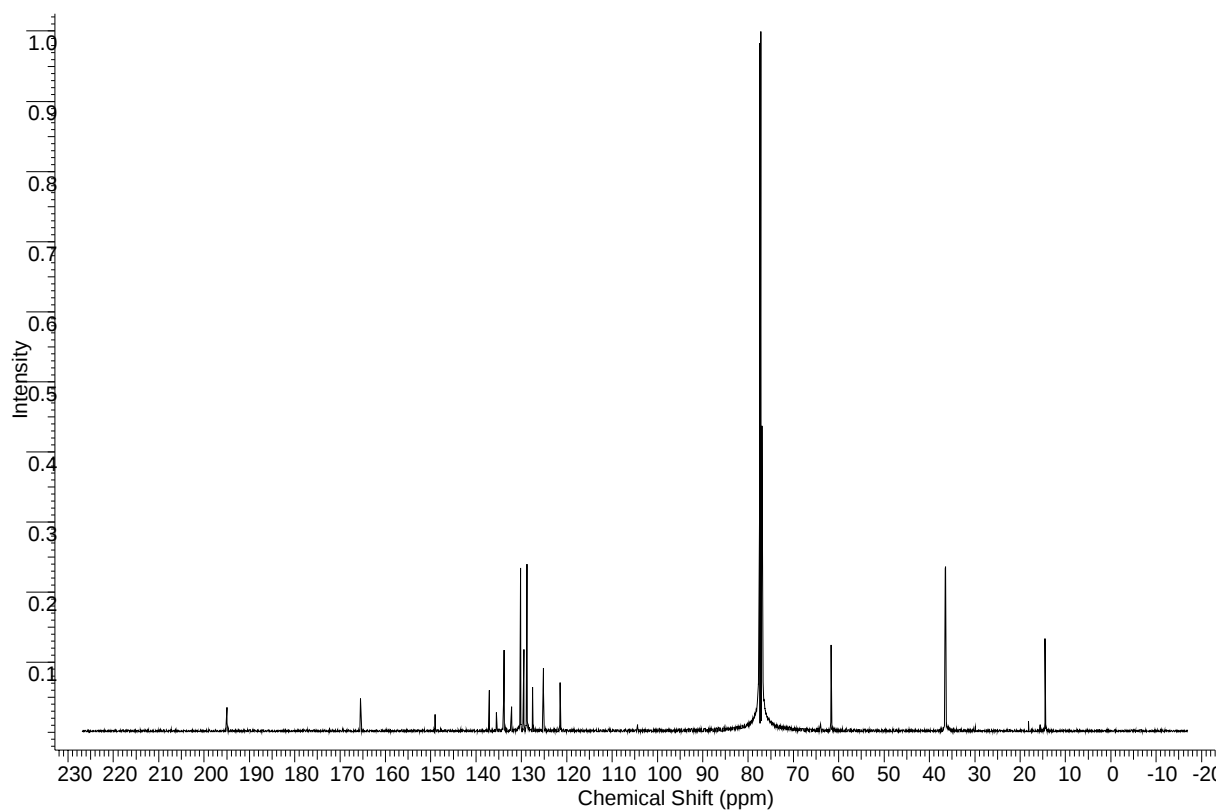
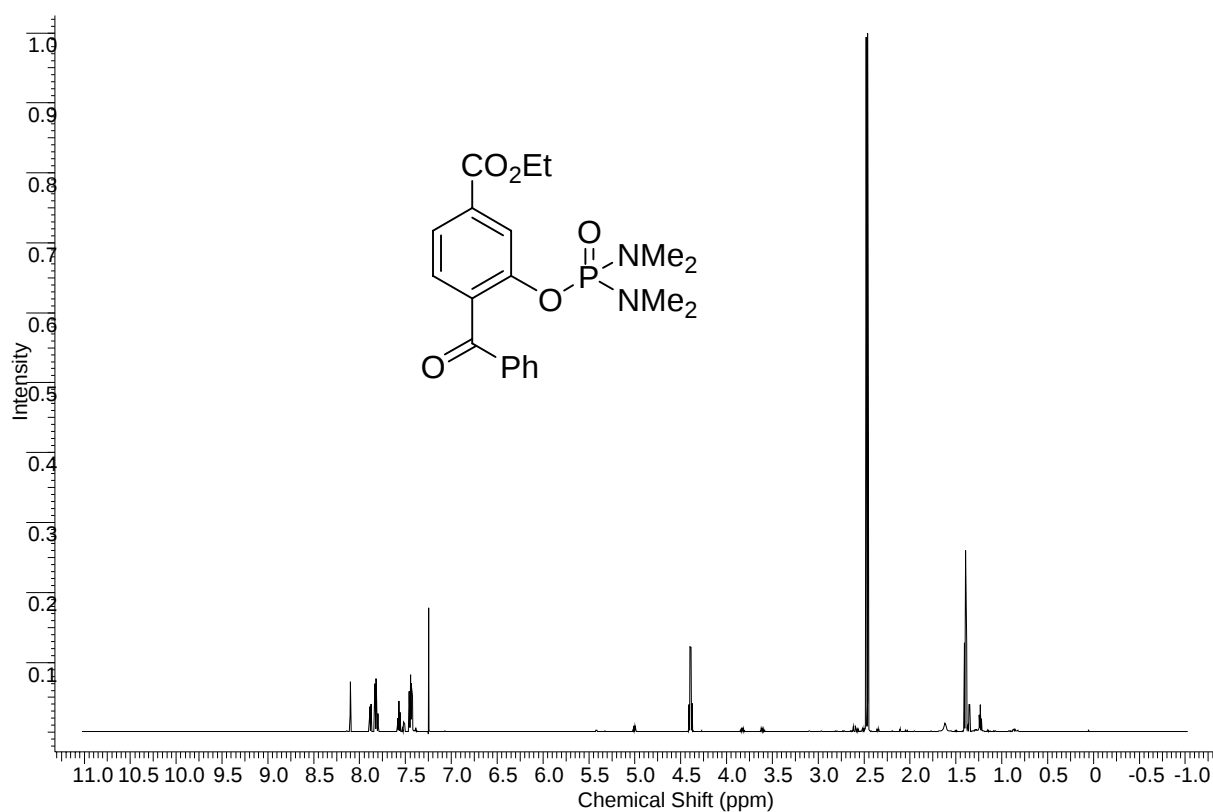


Ethyl 3-[[bis(dimethylamino)phosphoryl]oxy] 4-bromobenzoate

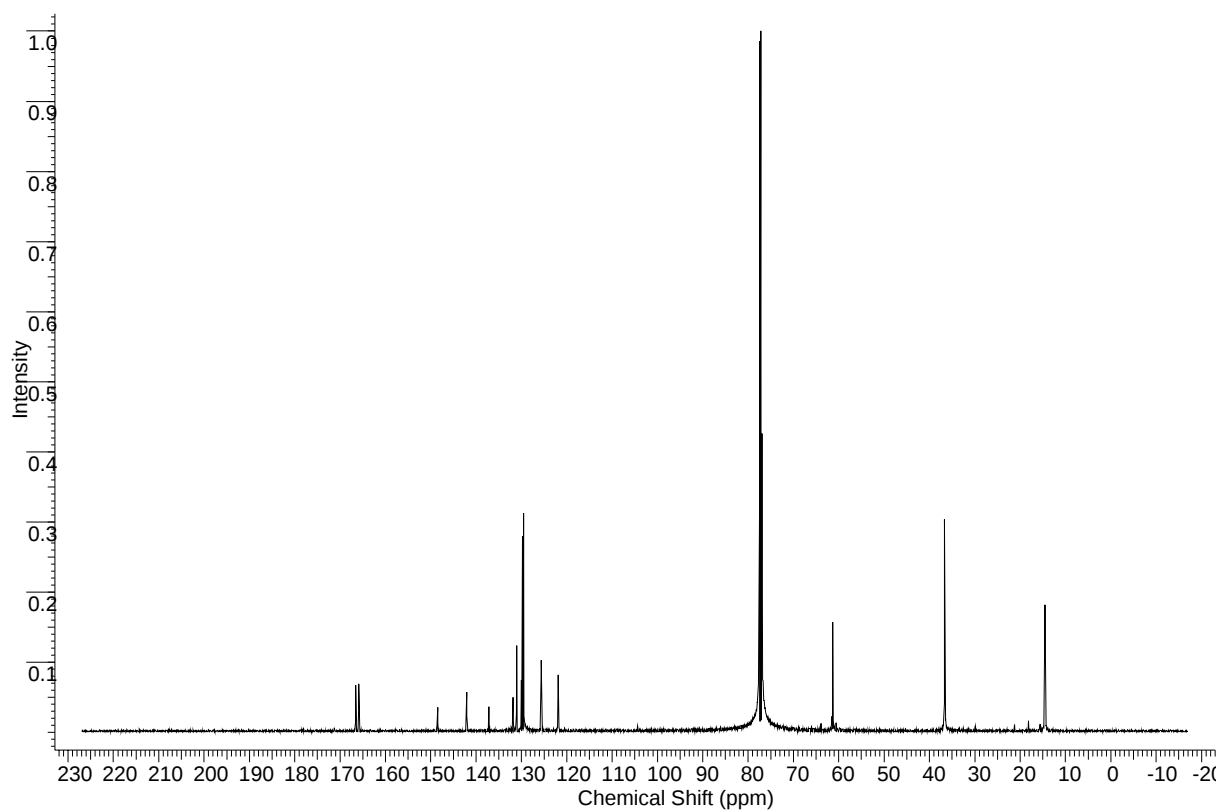
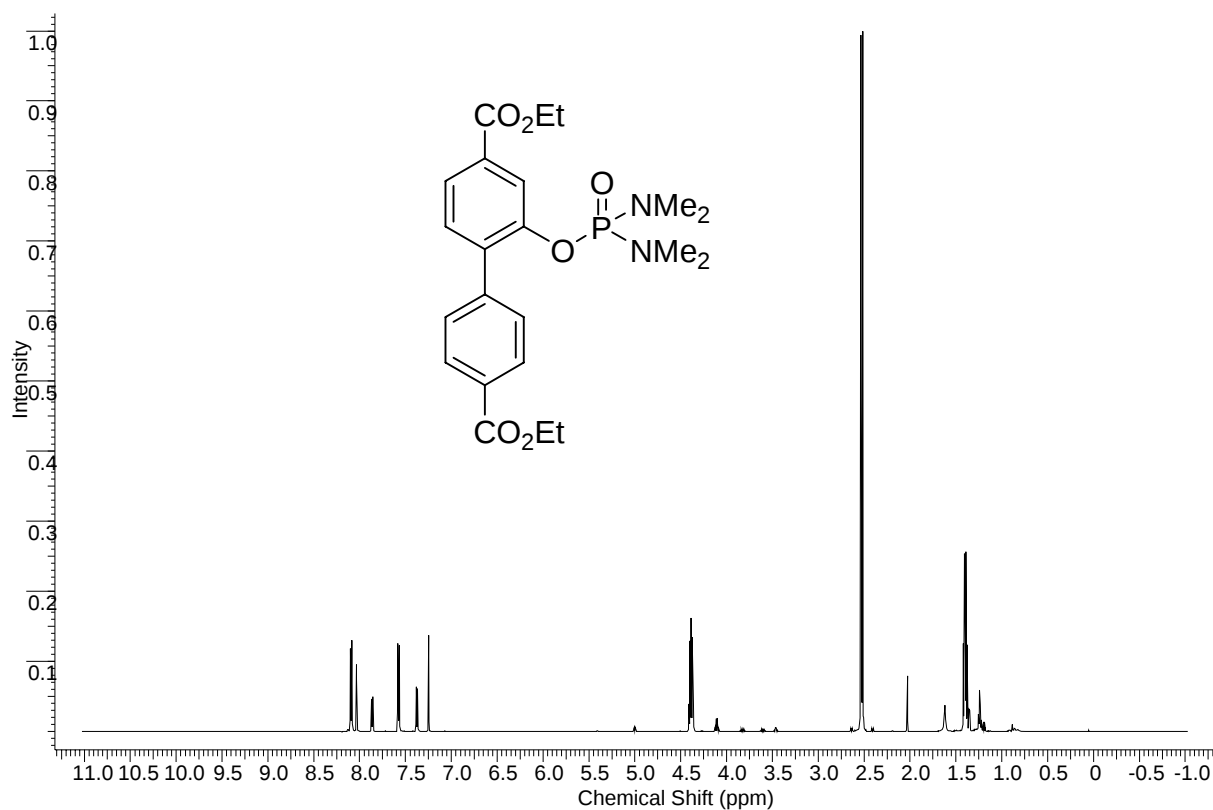
(6a)



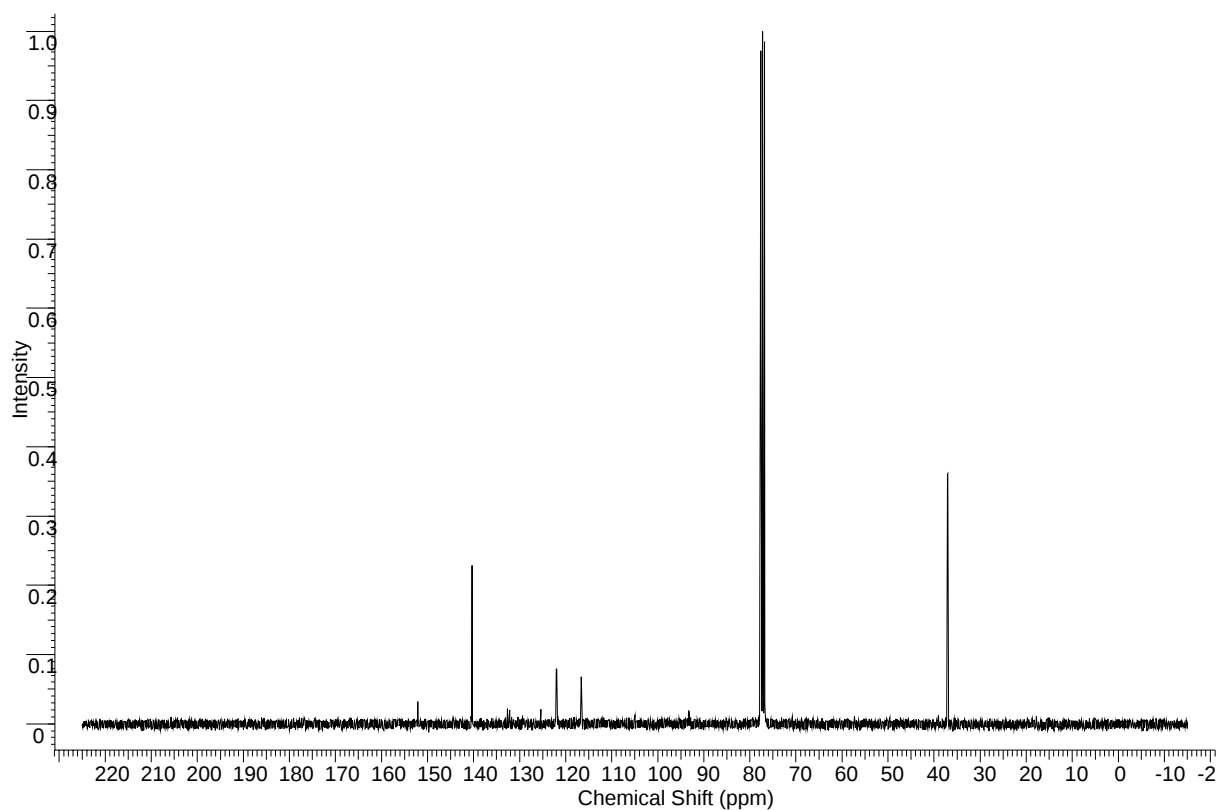
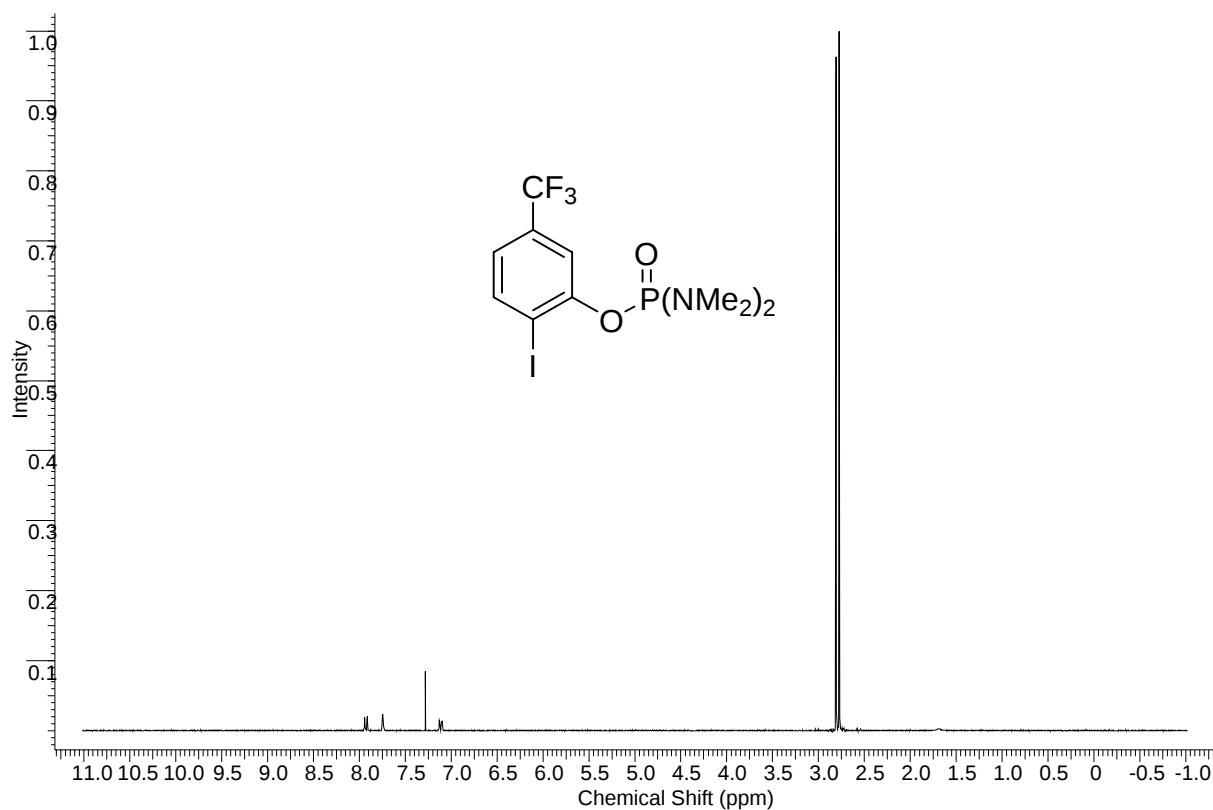
Ethyl 4-benzoyl-3-{[bis(dimethylamino)-phosphoryl]oxy}benzoate
(6b)



Diethyl 2-[[bis(dimethylamino)phosphoryl]oxy]-biphenyl-4,4'-dicarboxylate (6c)

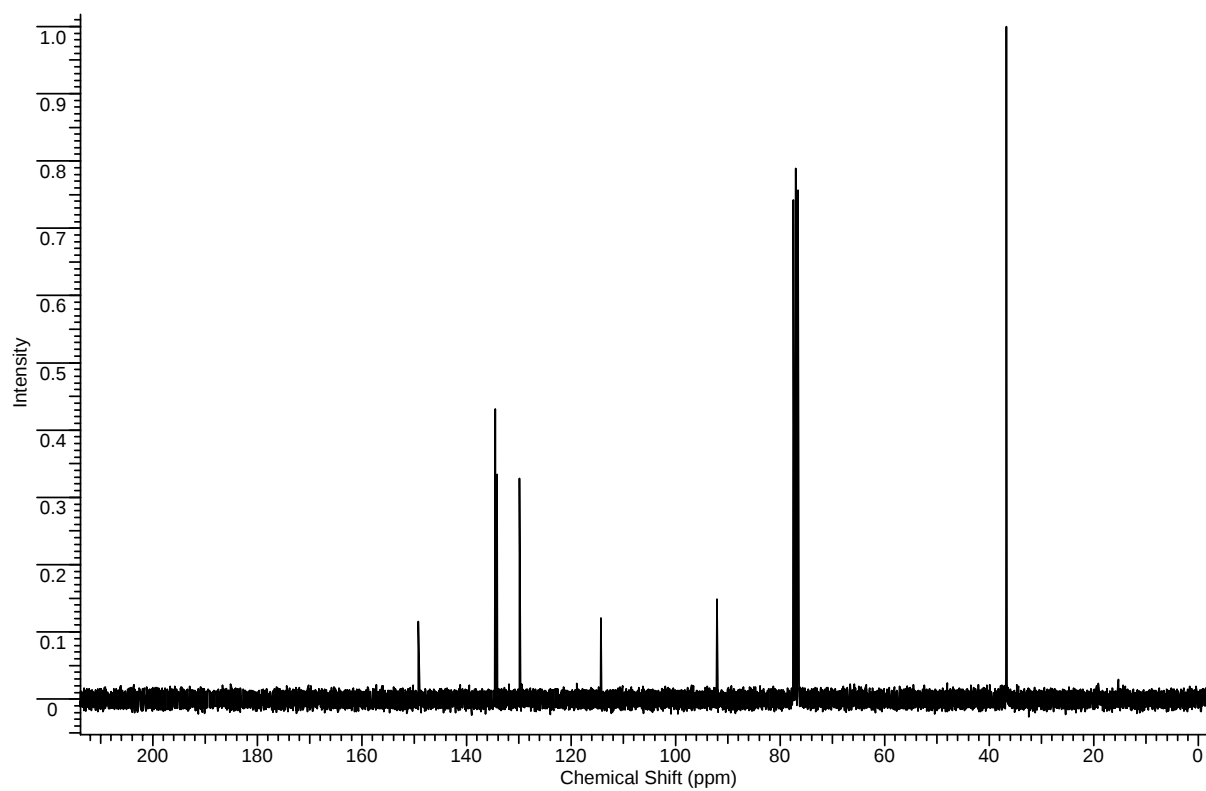
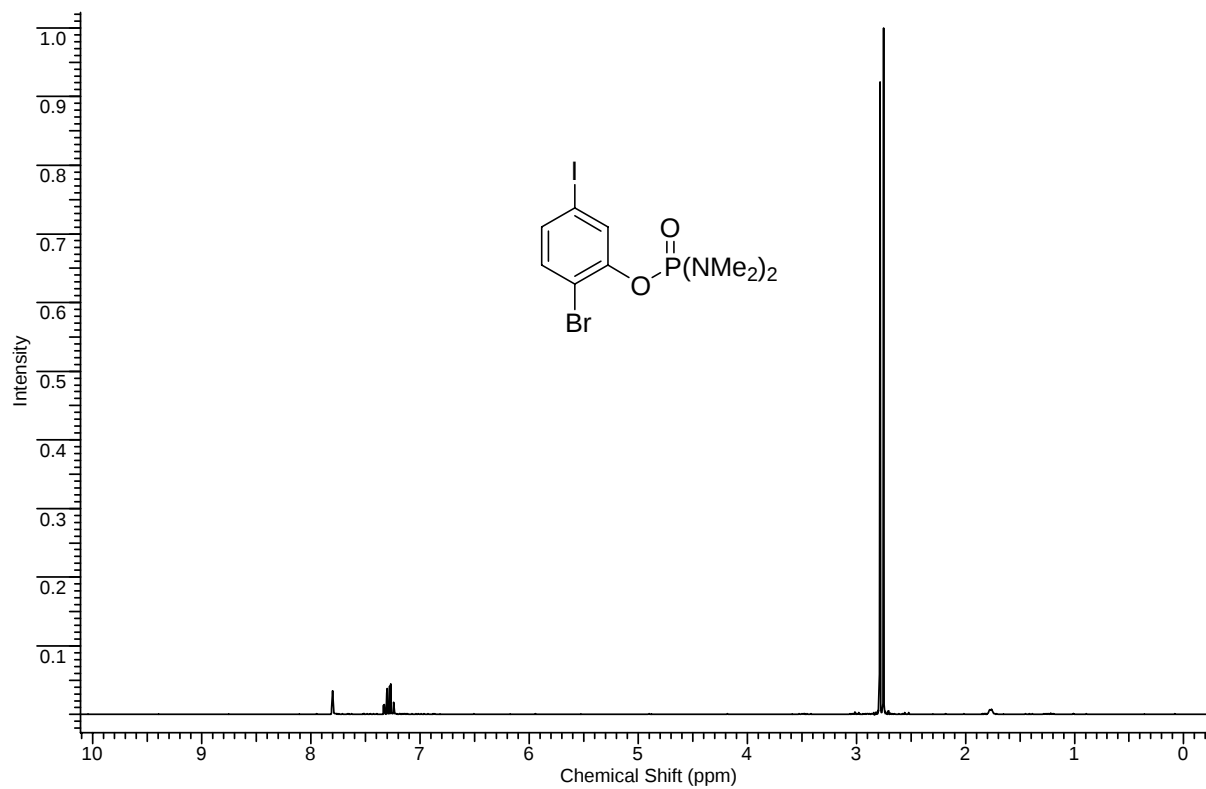


2-Iodo-5-(trifluoromethyl)phenyl *N,N,N',N'*-tetramethyldiamido-phosphate(6d)



2-Bromo-5-iodophenyl
(6e)

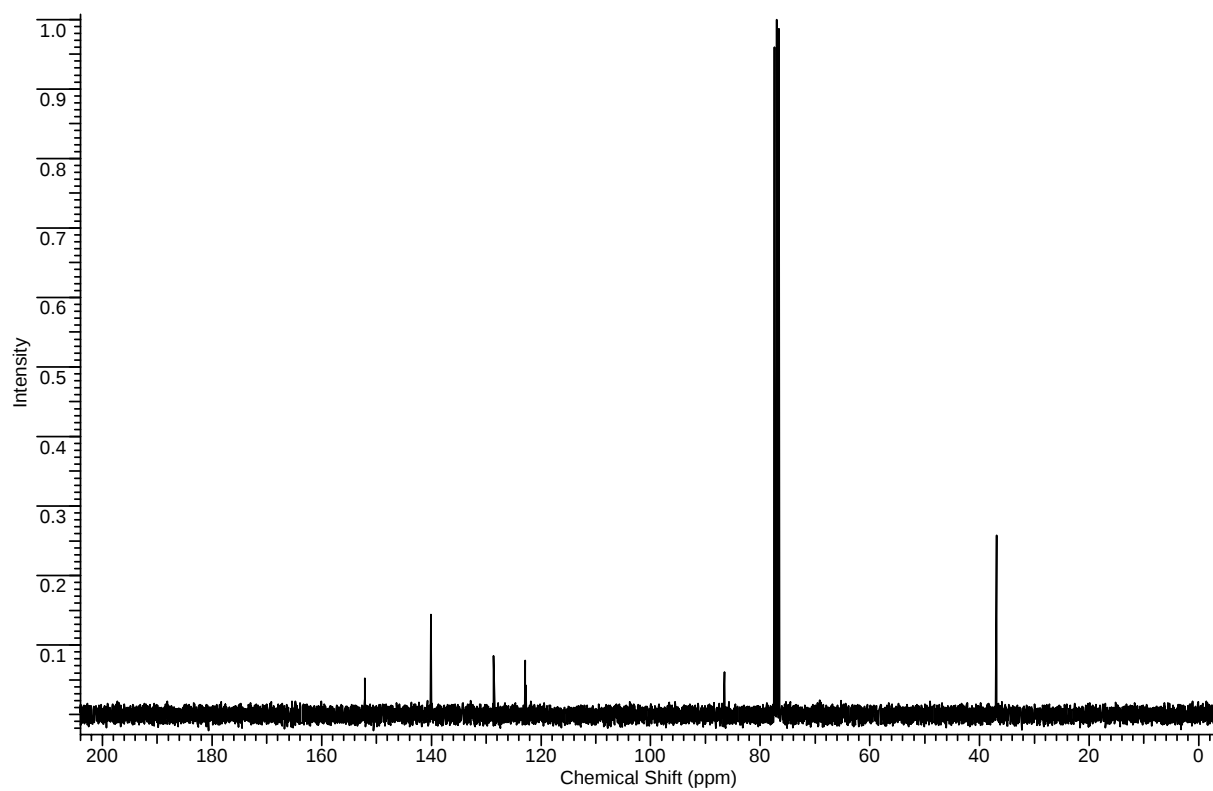
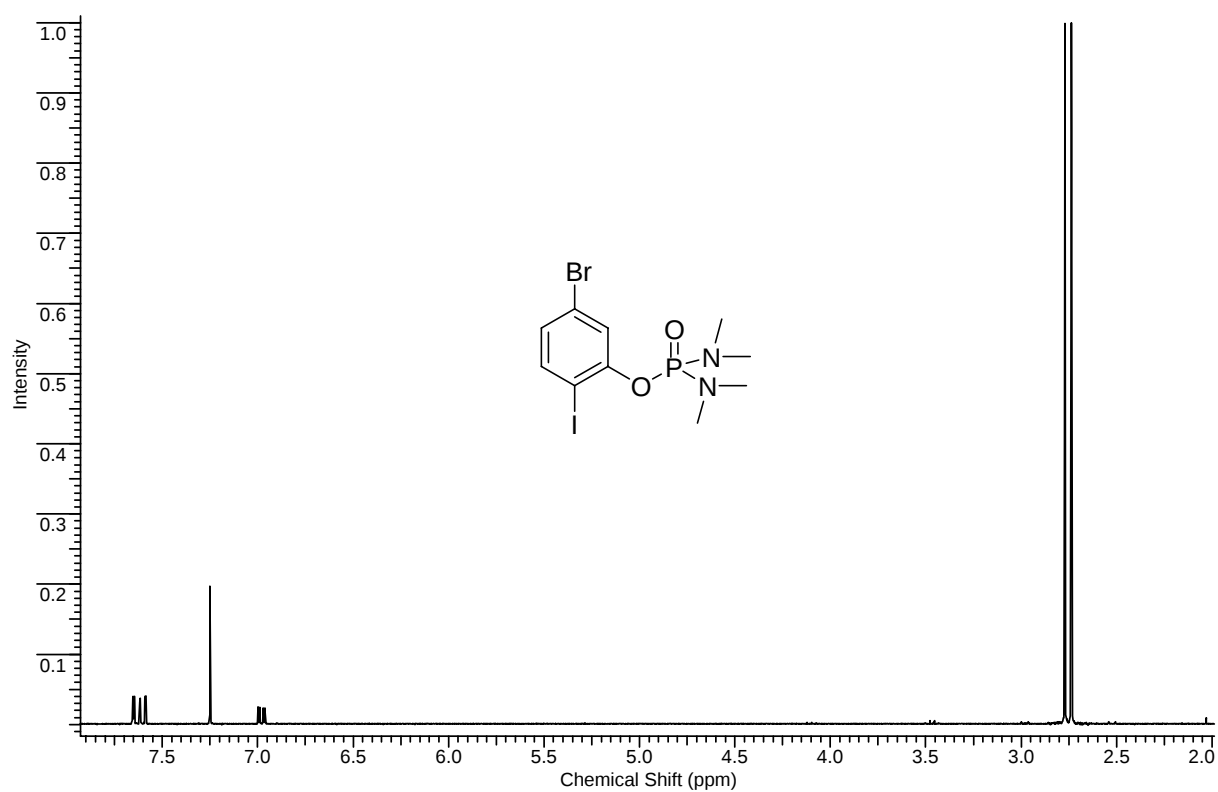
***N,N,N',N'*-tetra-methyldiamidophosphate**



5-Bromo-2-iodophenyl

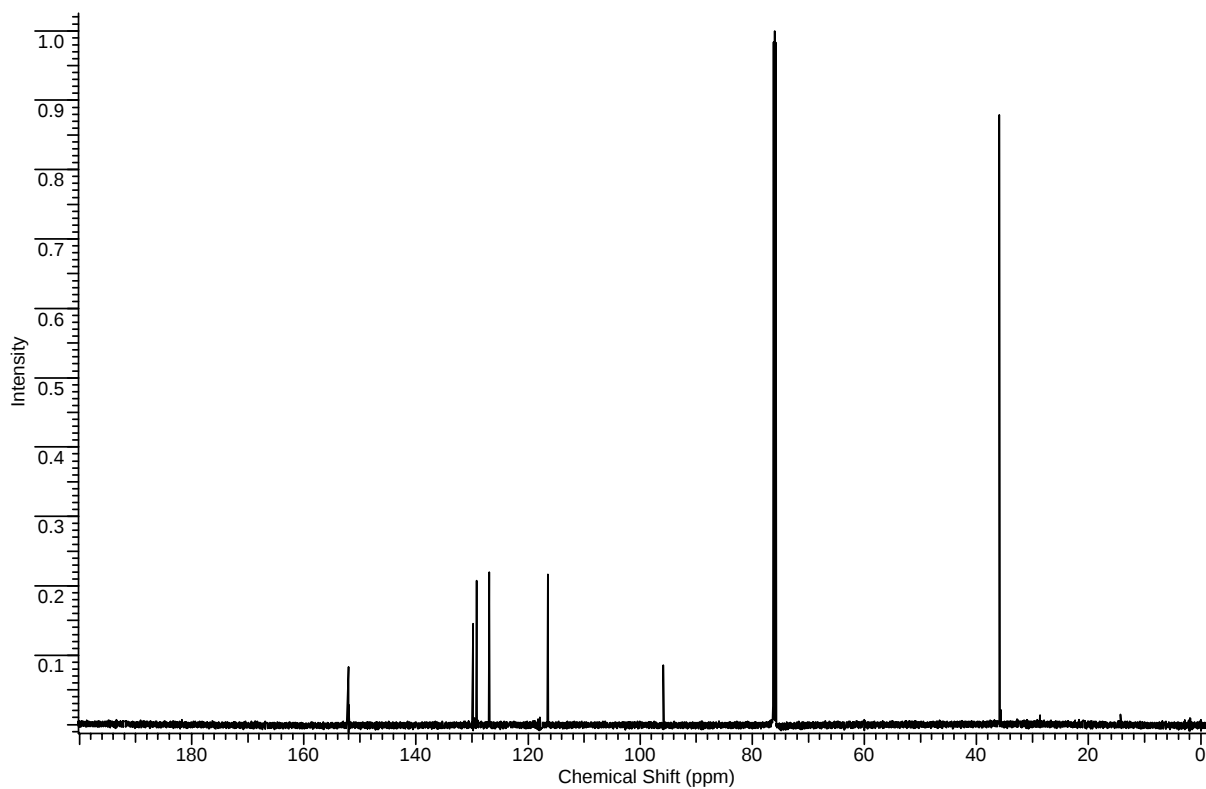
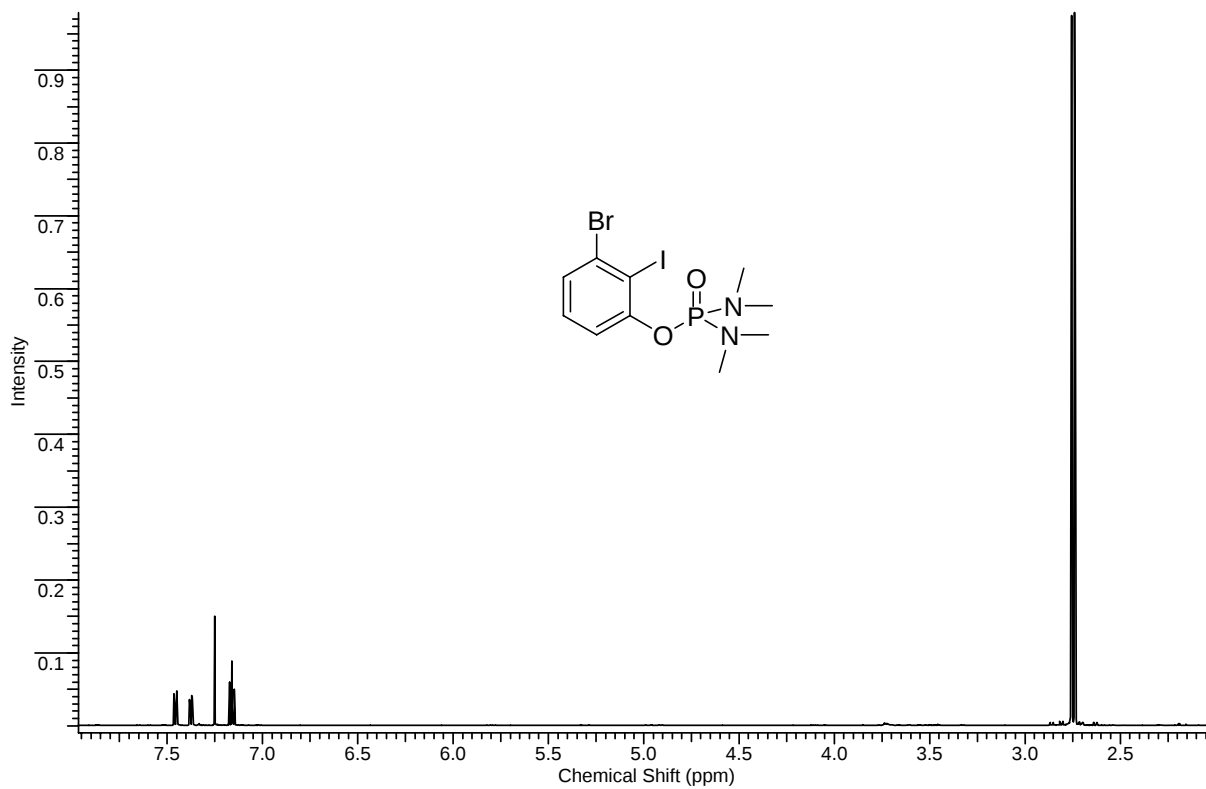
N,N,N',N'-tetra-methyldiamidophosphate

(6f)



3-Bromo-2-iodophenyl
(6g)

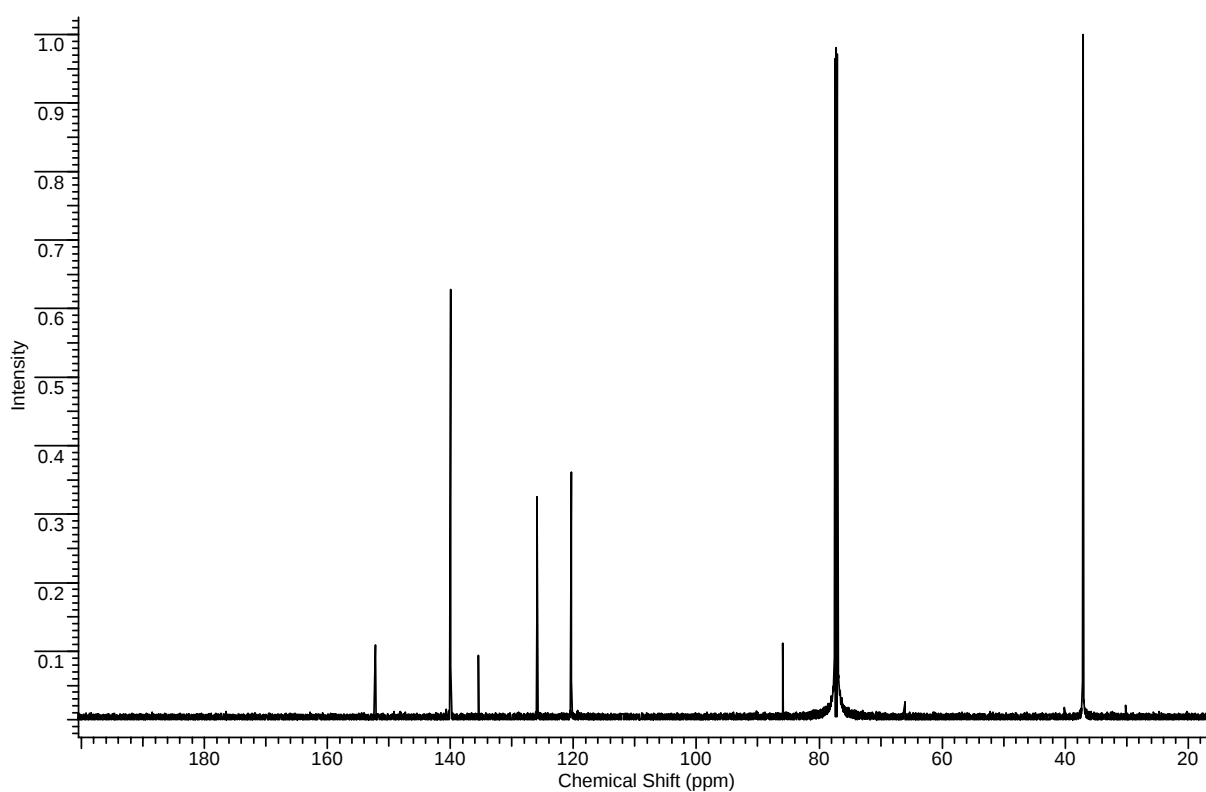
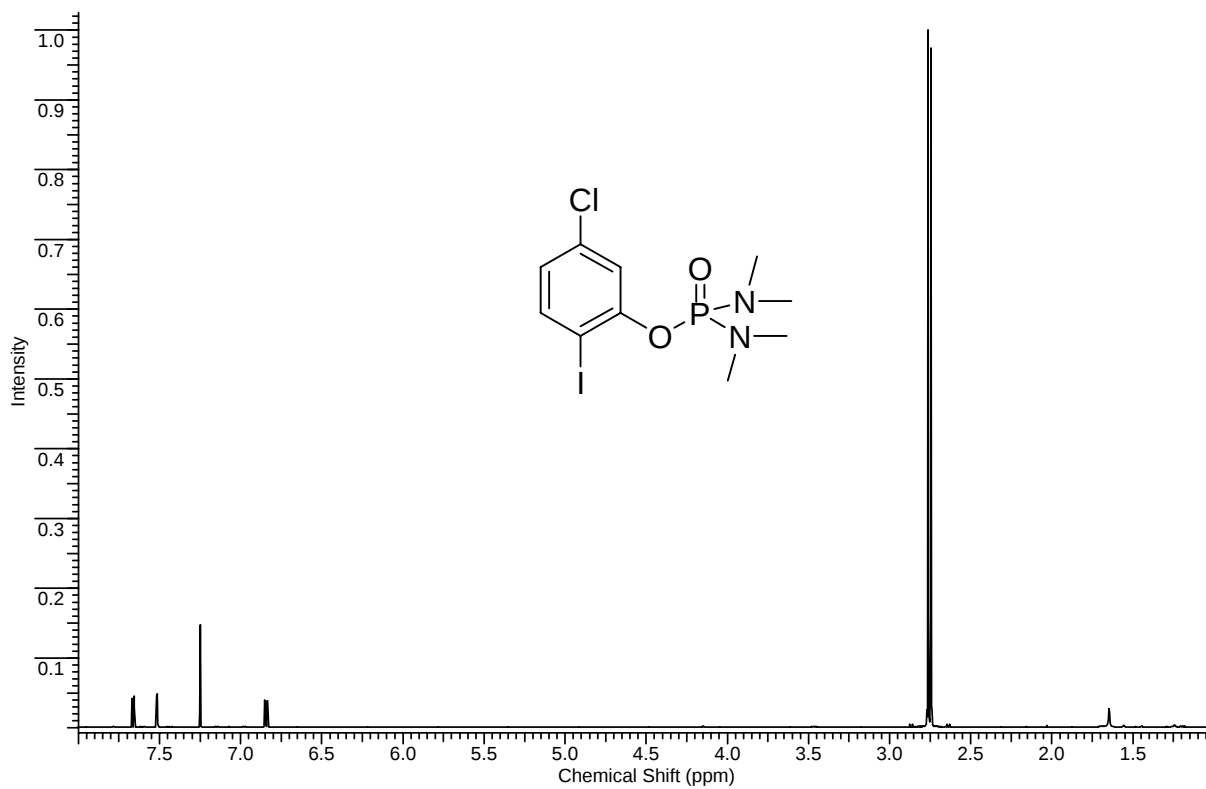
***N,N,N',N'*-tetramethyldiamidophosphate**



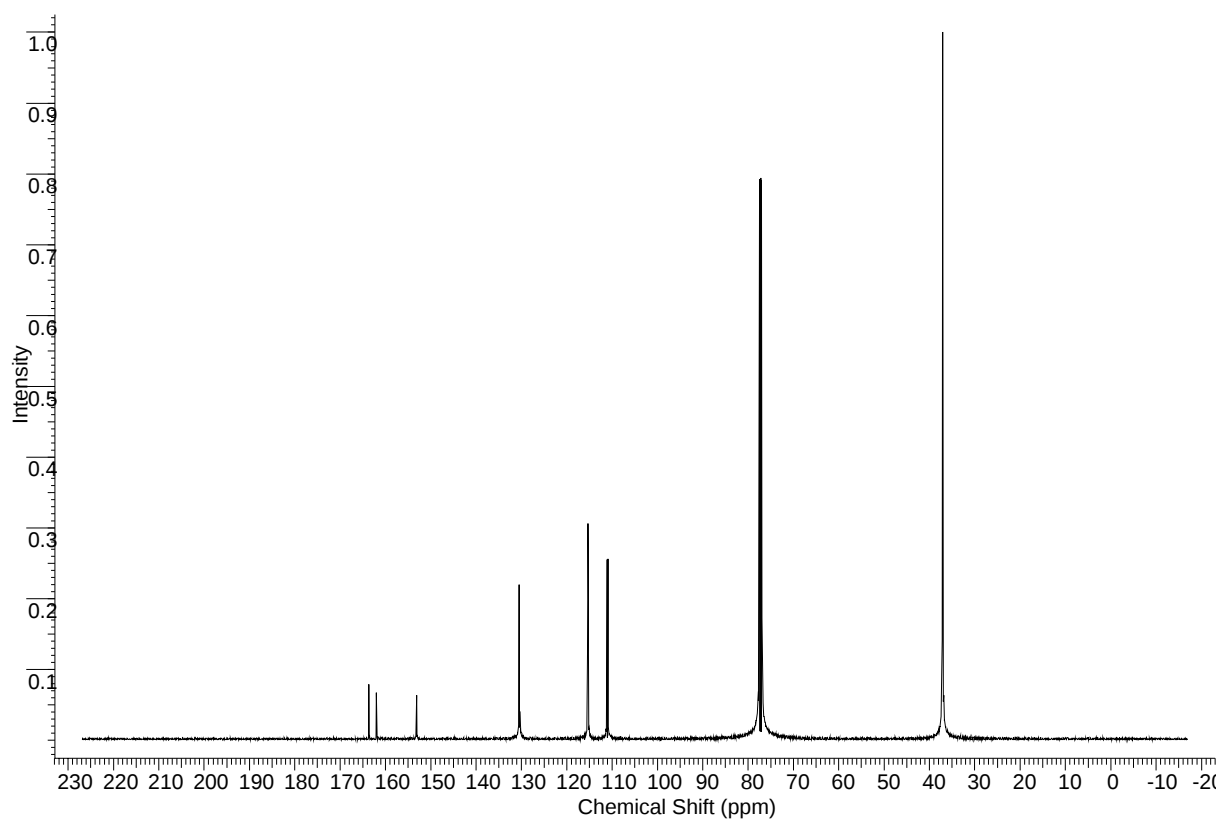
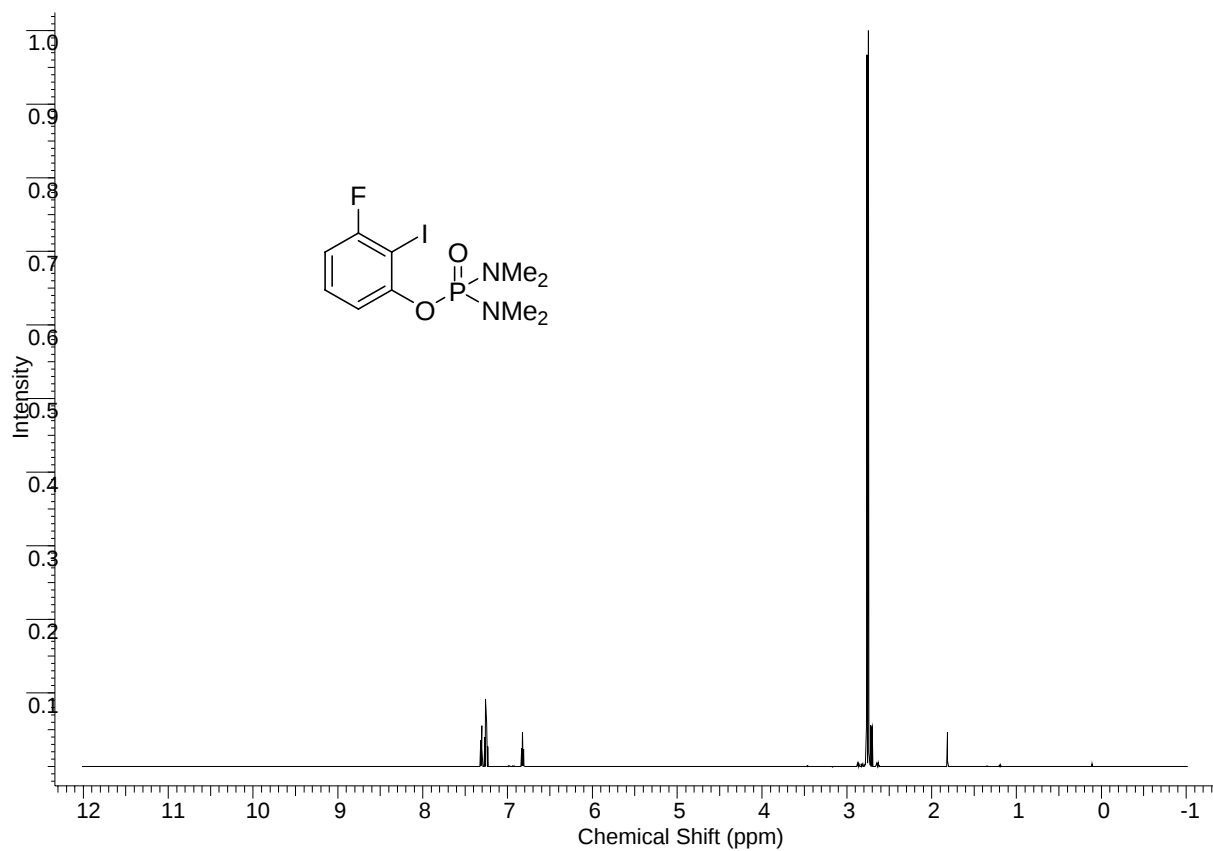
5-Chloro-2-iodophenyl

N,N,N',N'-tetramethyldiamidophosphate

(6g)

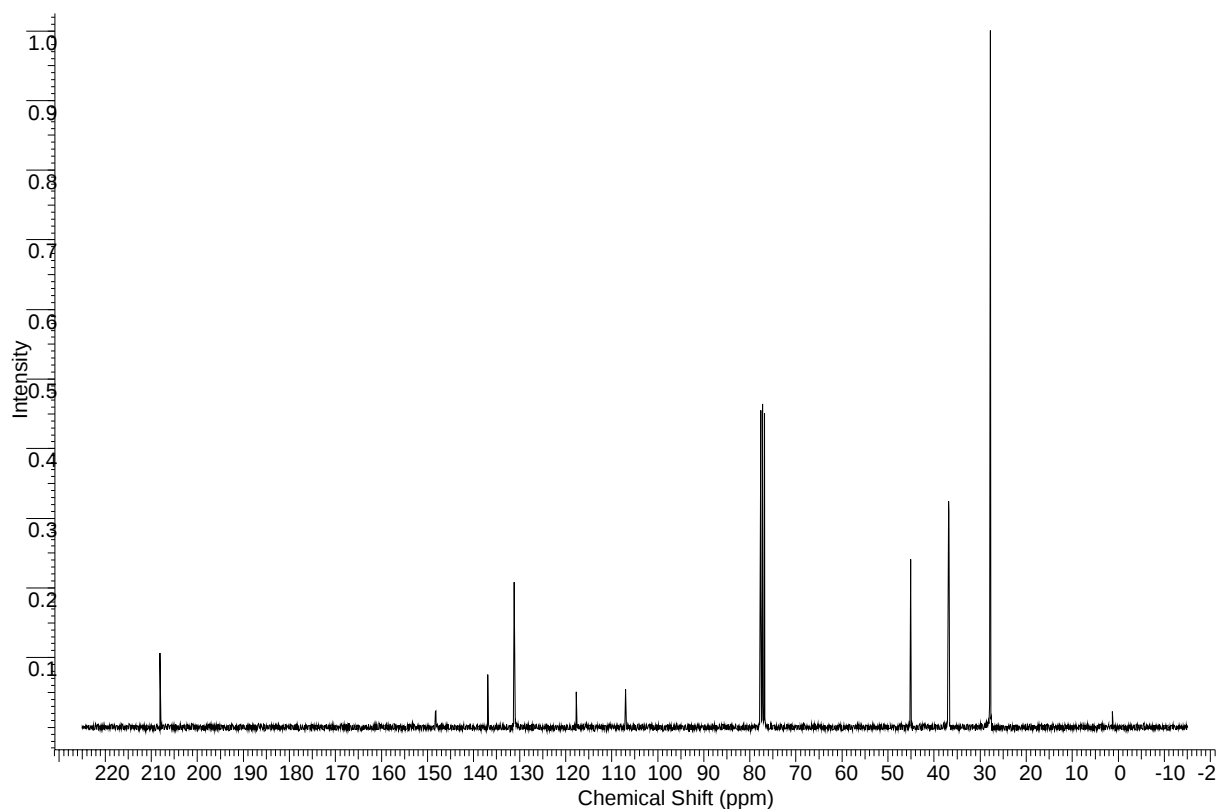
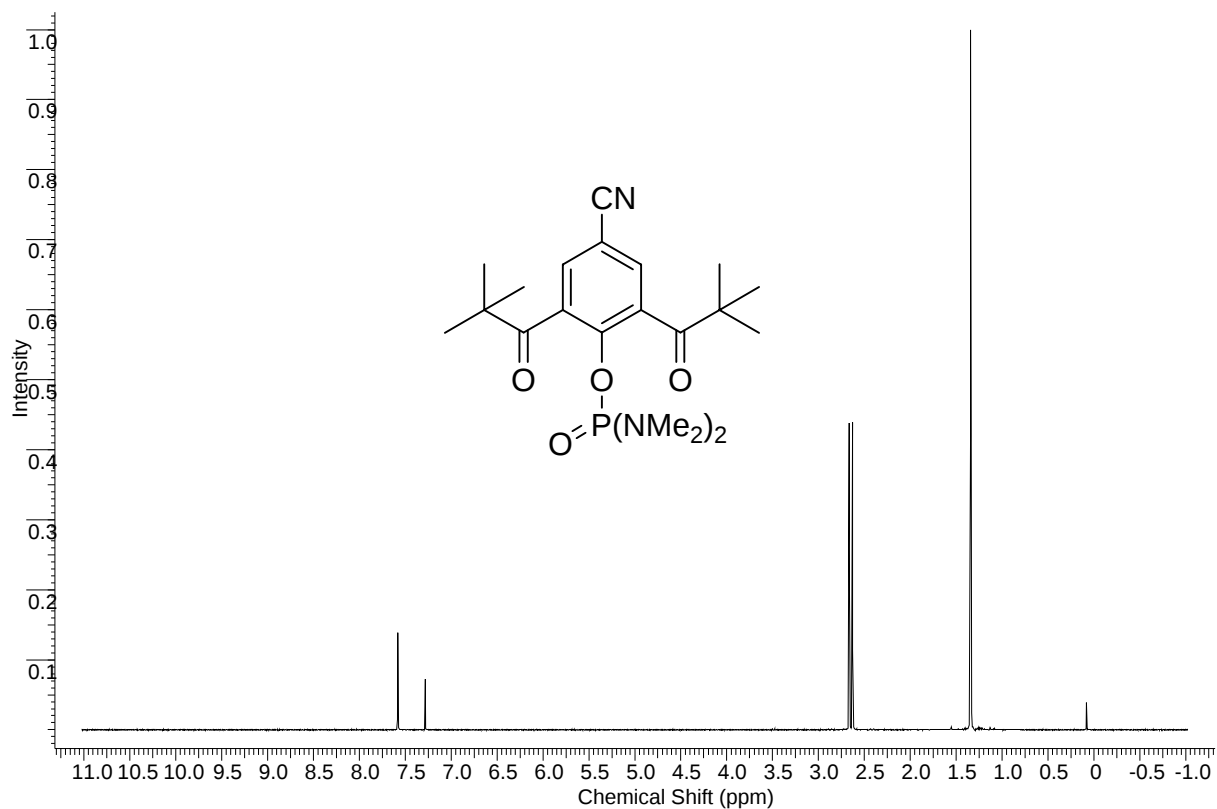


3-fluoro-2-iodophenyl *N,N,N',N'*-tetramethyl-diamidophosphate (6g):



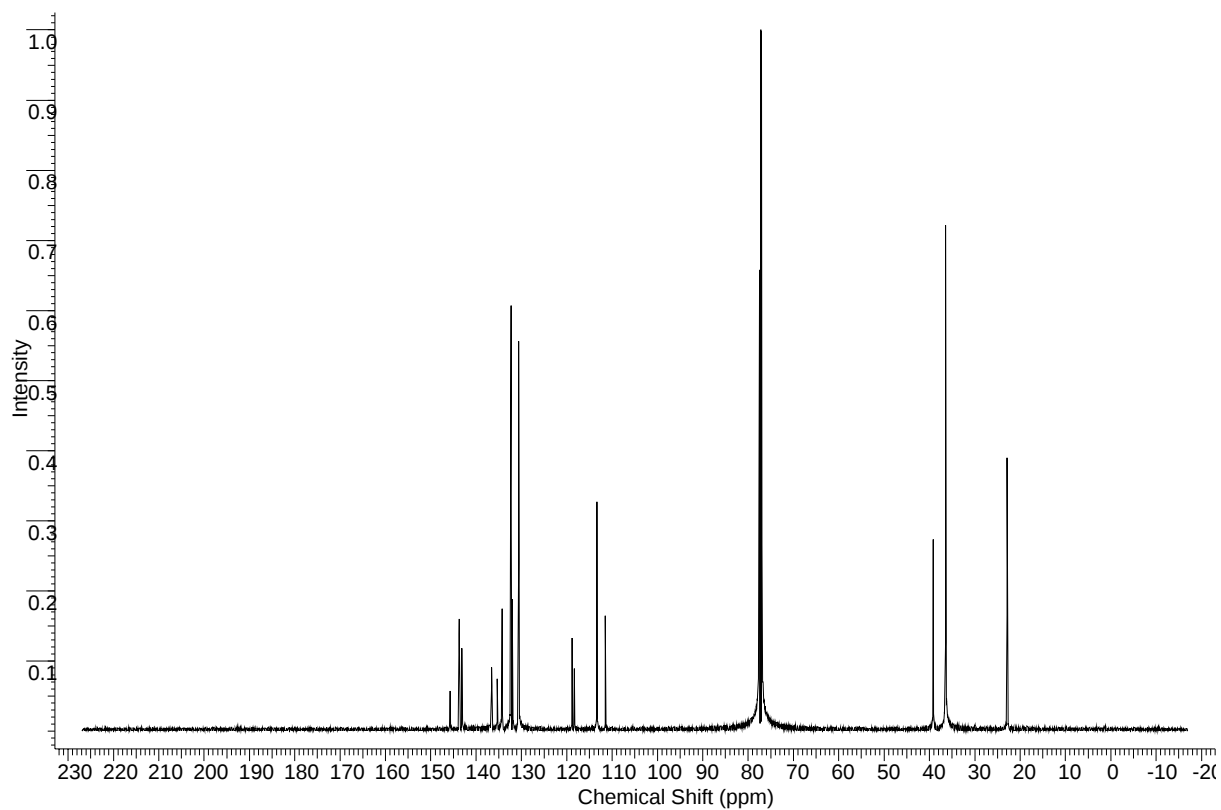
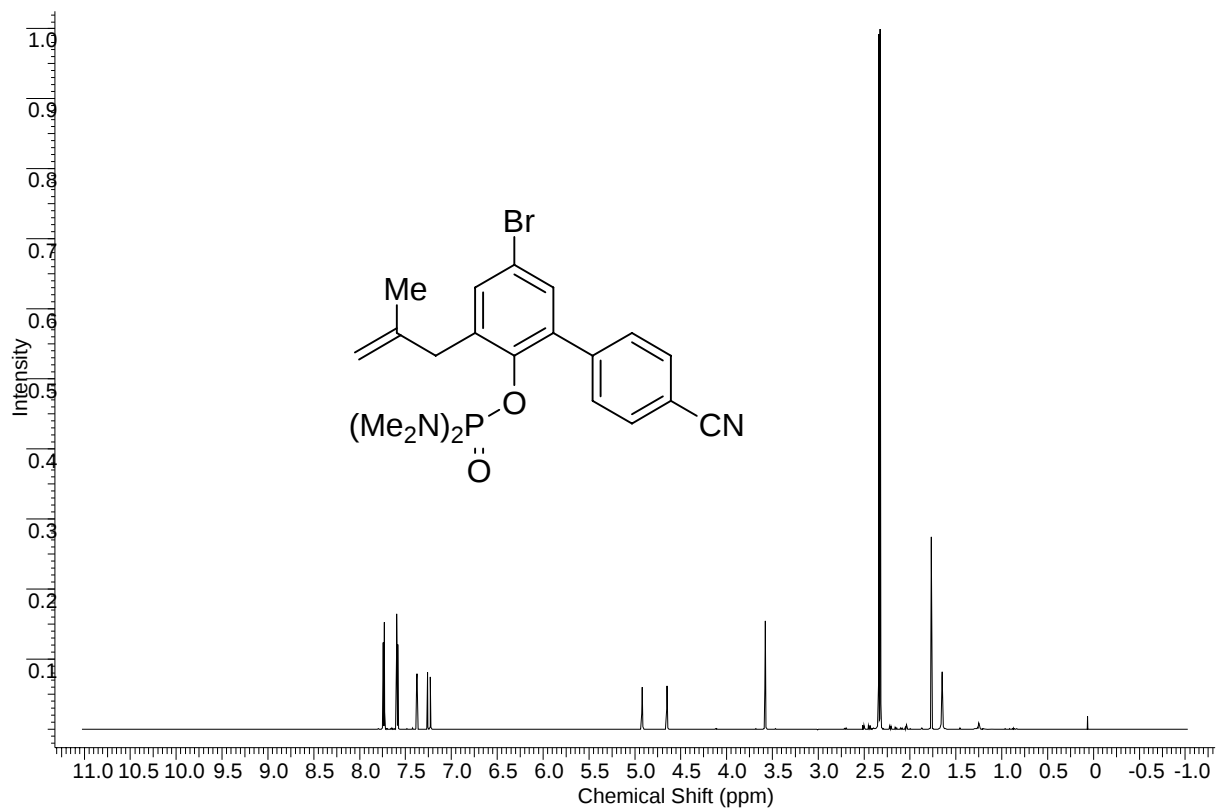
**Cyano-2,6-bis(2,2-dimethylpropanoyl)phenyl
methyldiamidophosphate (9a)**

***N,N,N',N'*-tetra-**



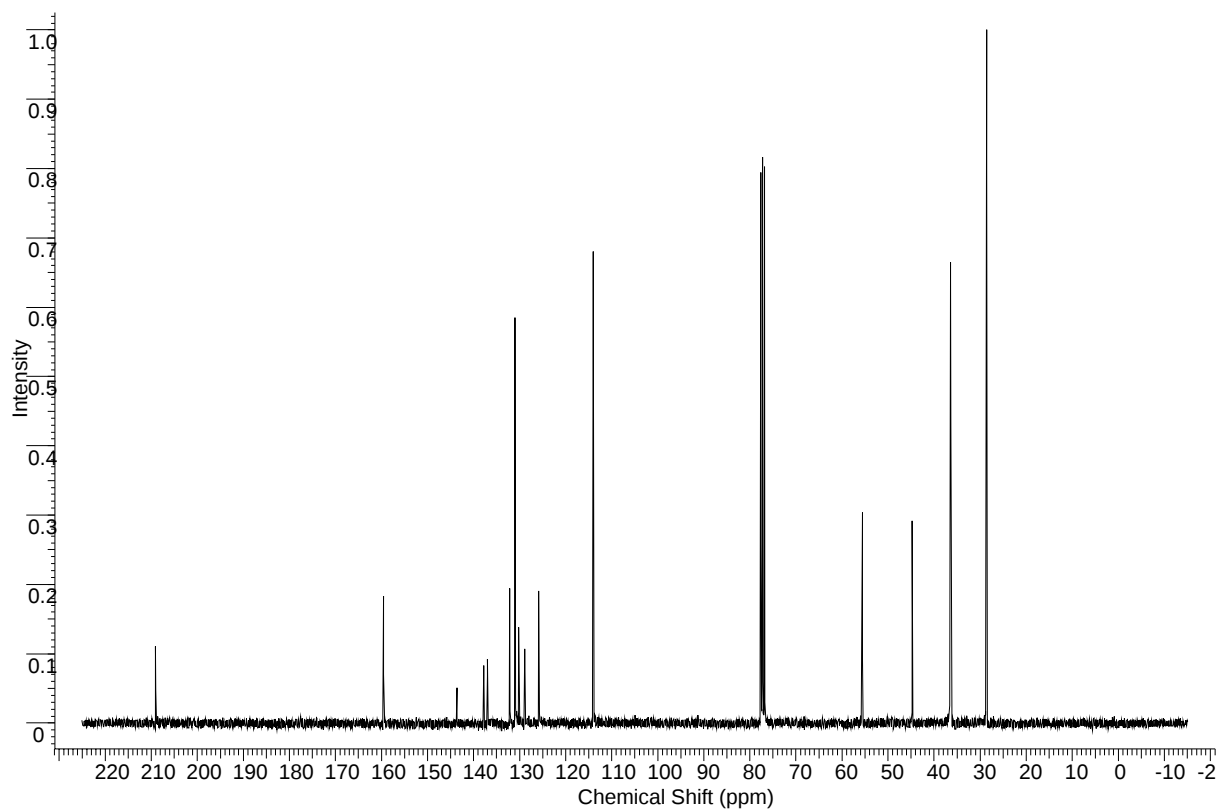
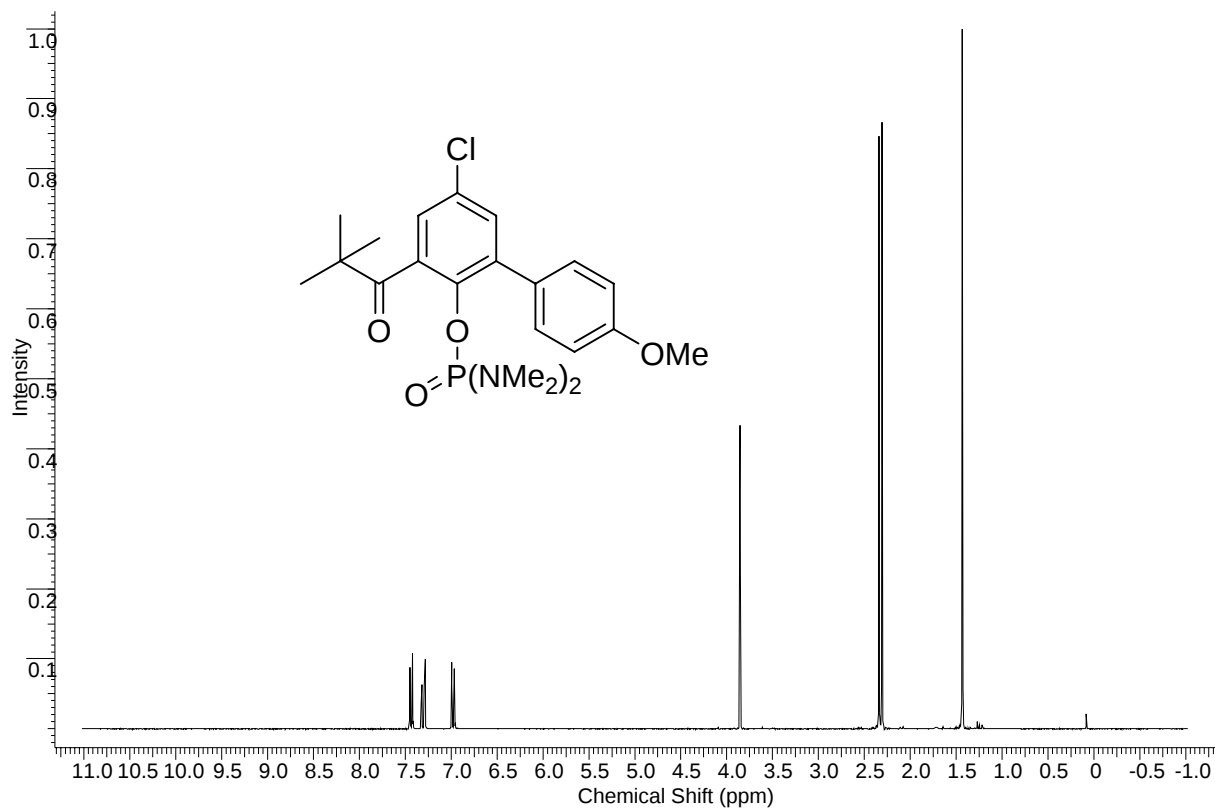
5-Bromo-4'-cyano-3-(2-methylprop-2-en-1-yl)bi-phenyl-2-yl

***N,N,N',N'*-tetramethyldiamidophosphate (9b)**

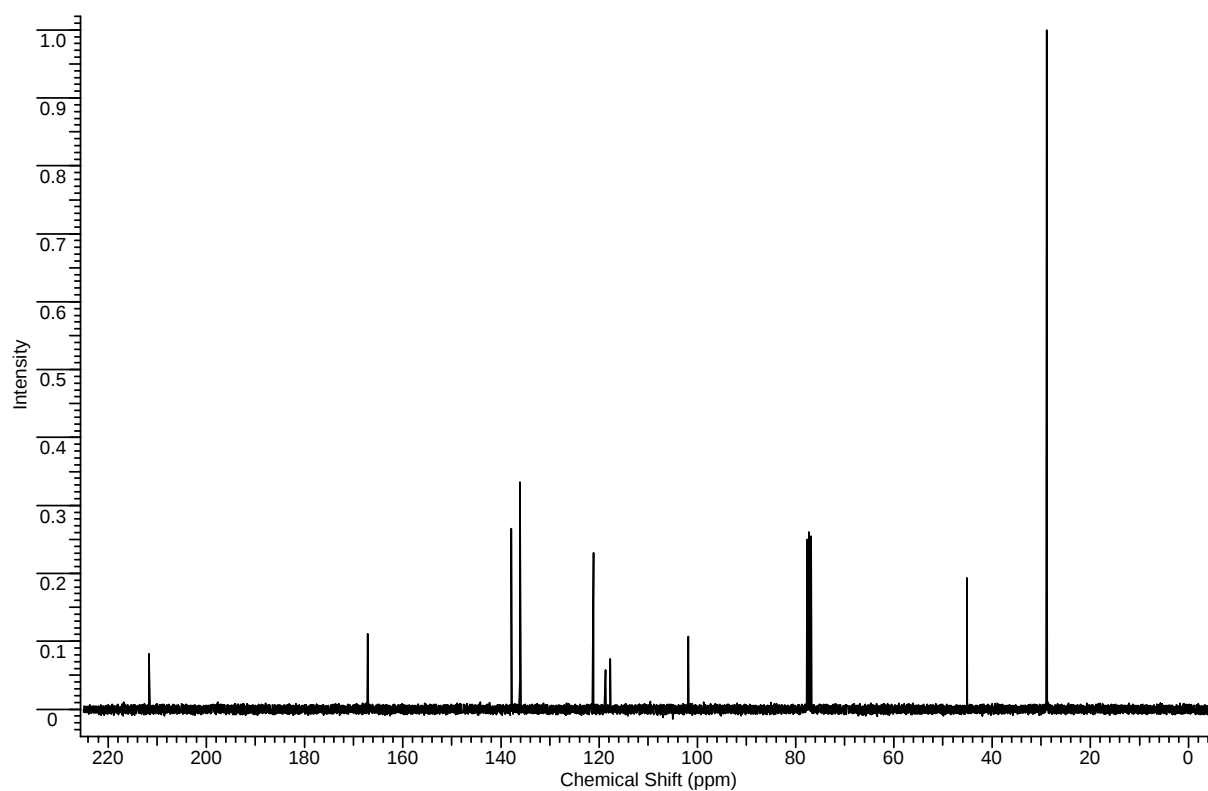
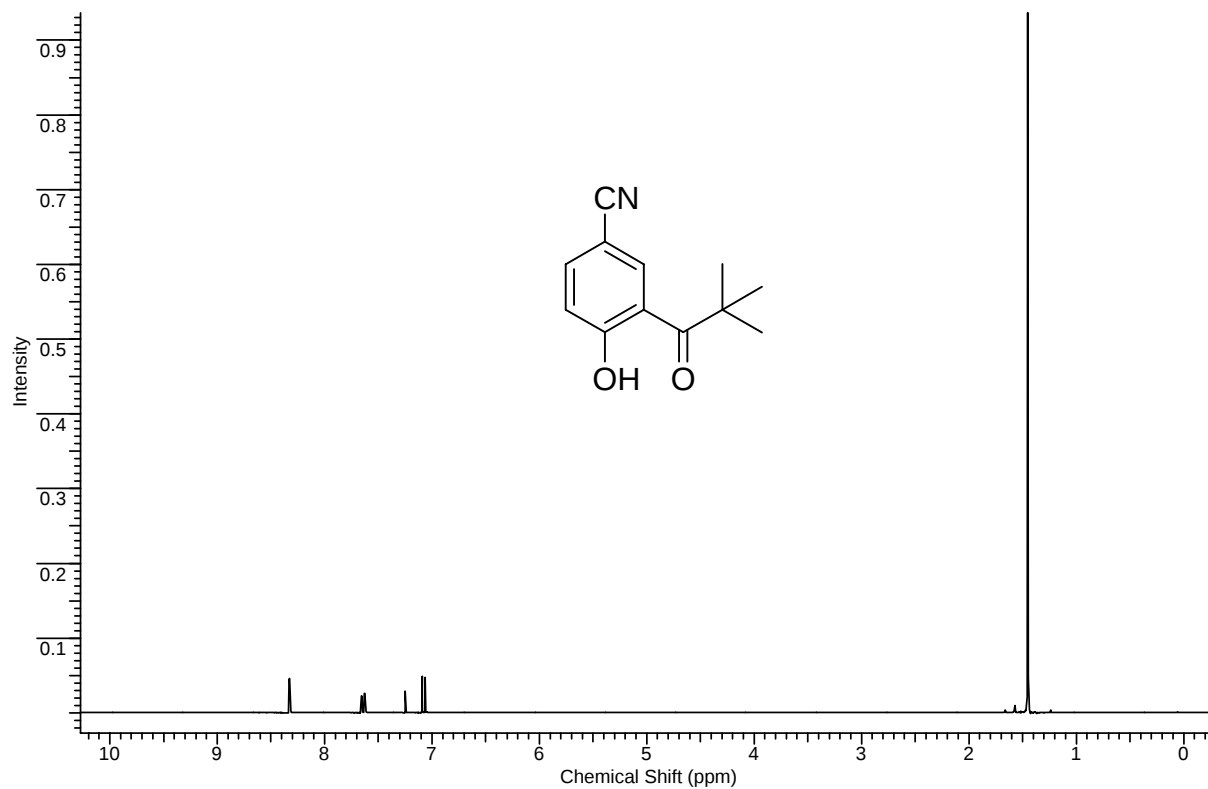


5-Chloro-3-(2,2-dimethylpropanoyl)-4'-methoxybi-phenyl-2-yl

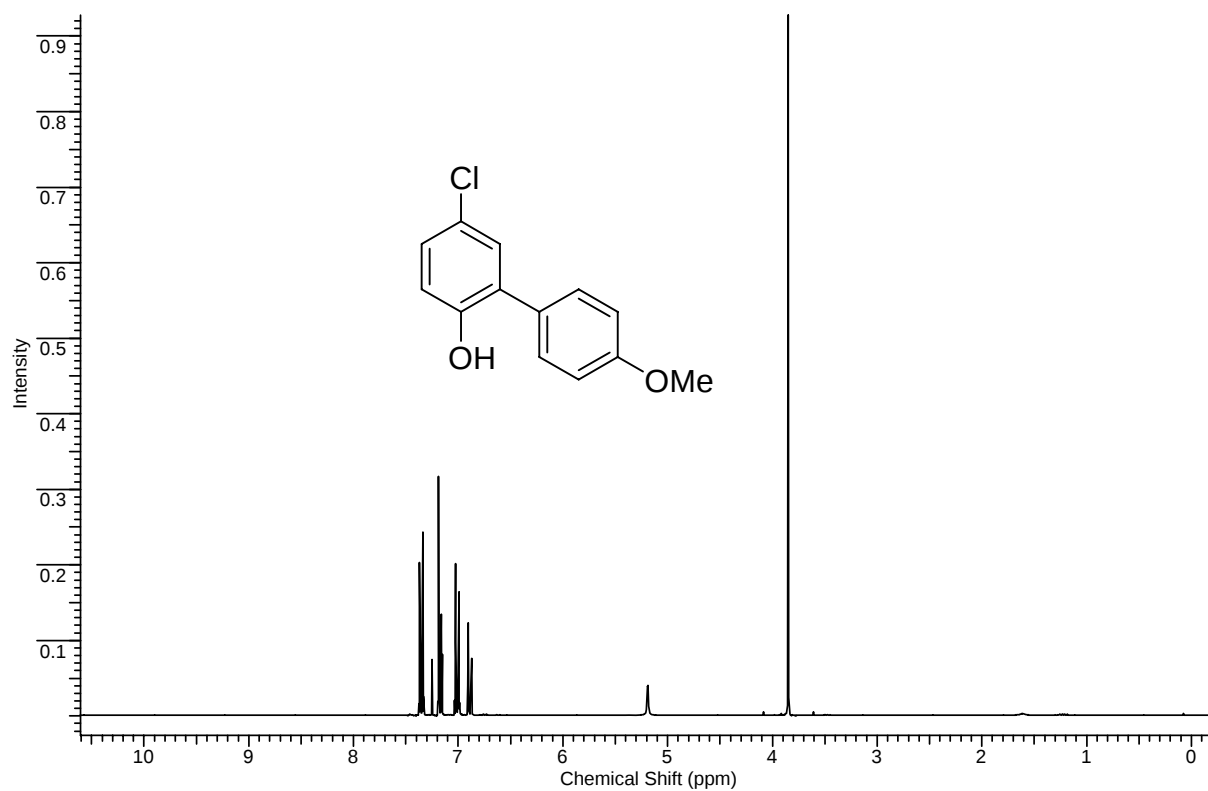
***N,N,N',N'*-tetramethyldiamidophosphate (9c)**

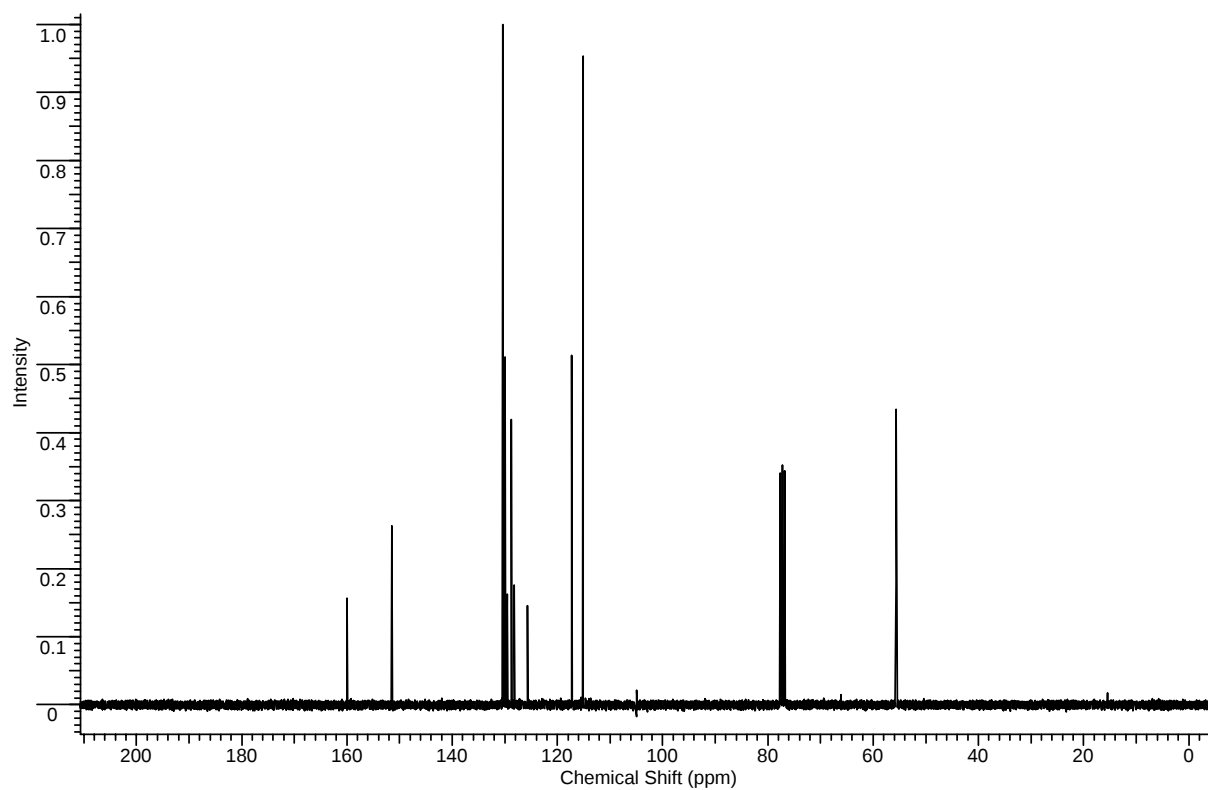


3-(2,2-Dimethylpropanoyl)-4-hydroxybenzonitrile (10a)

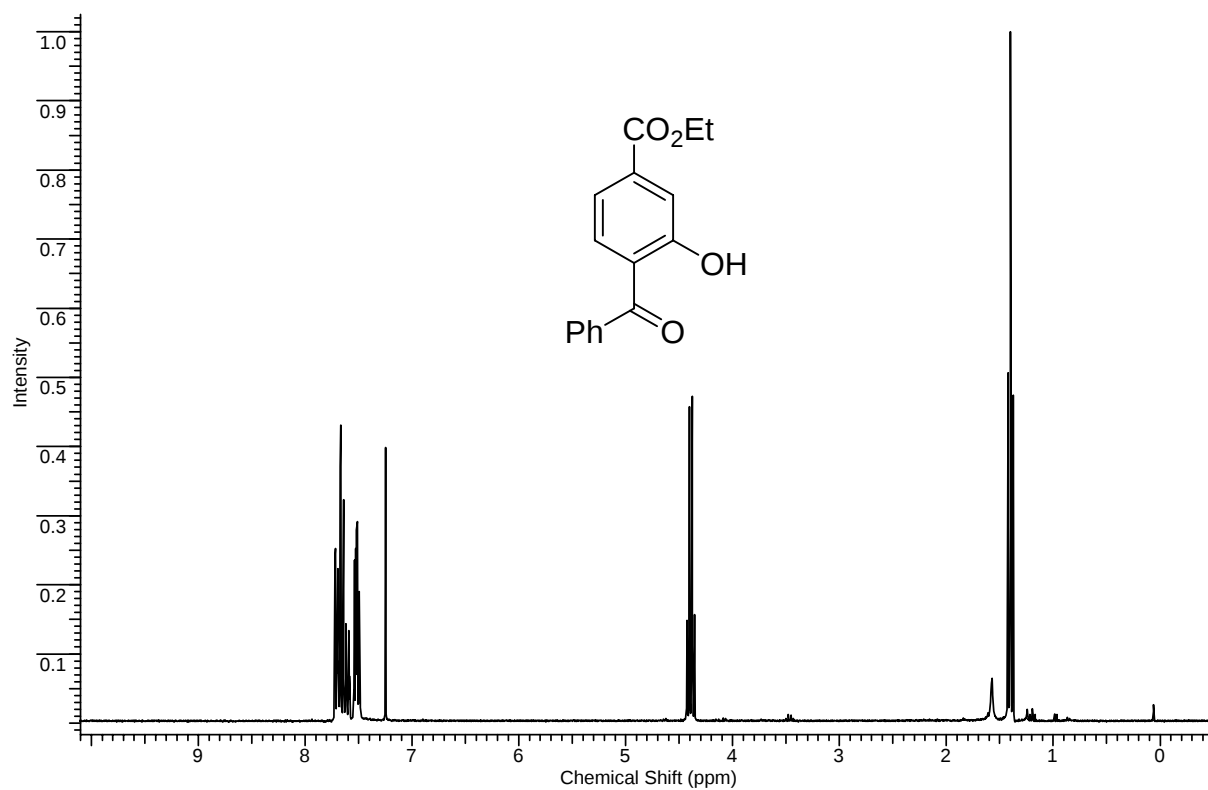


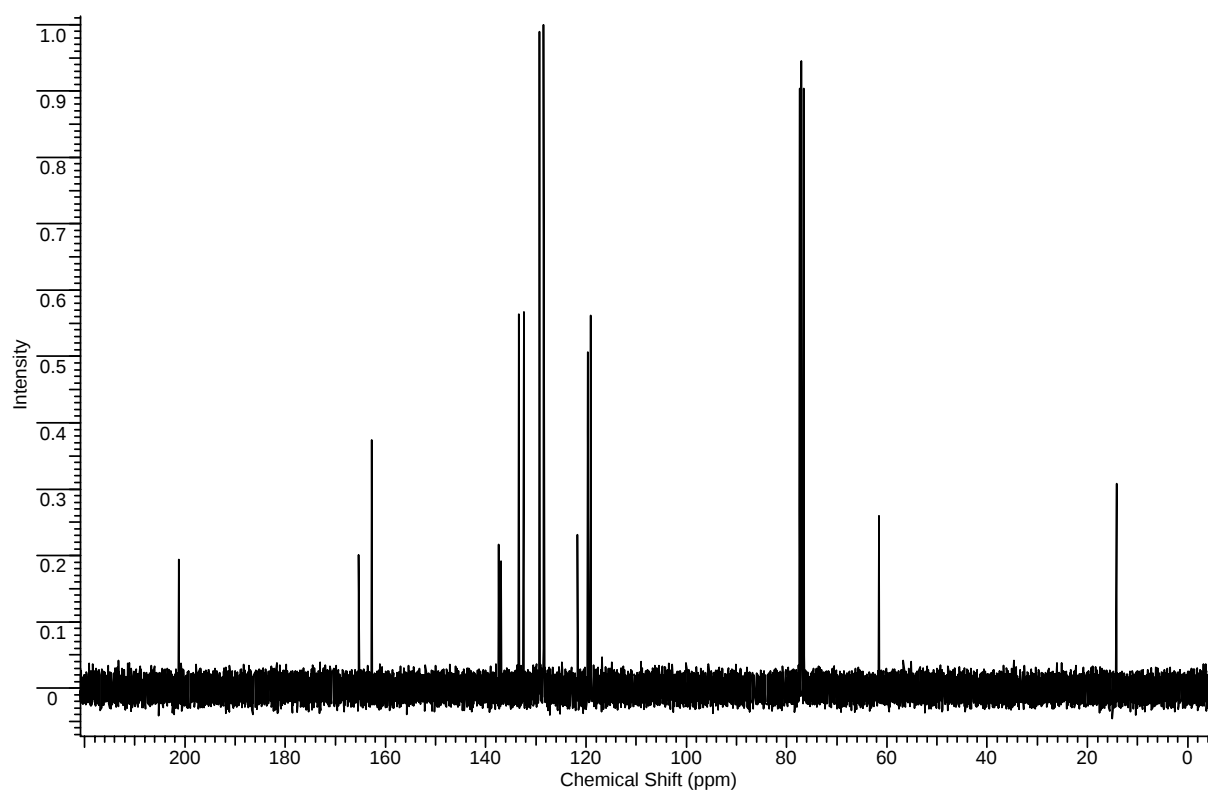
5-Chloro-4'-methoxybiphenyl-2-ol (10b)



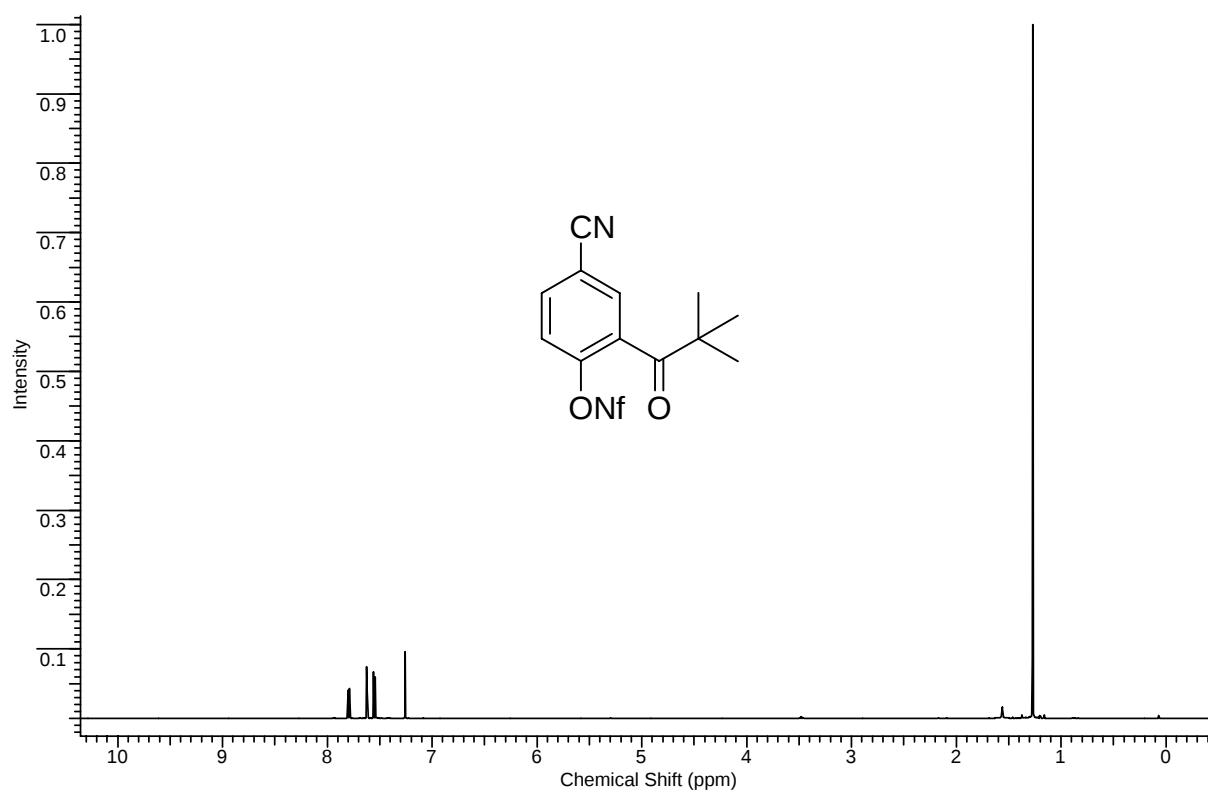


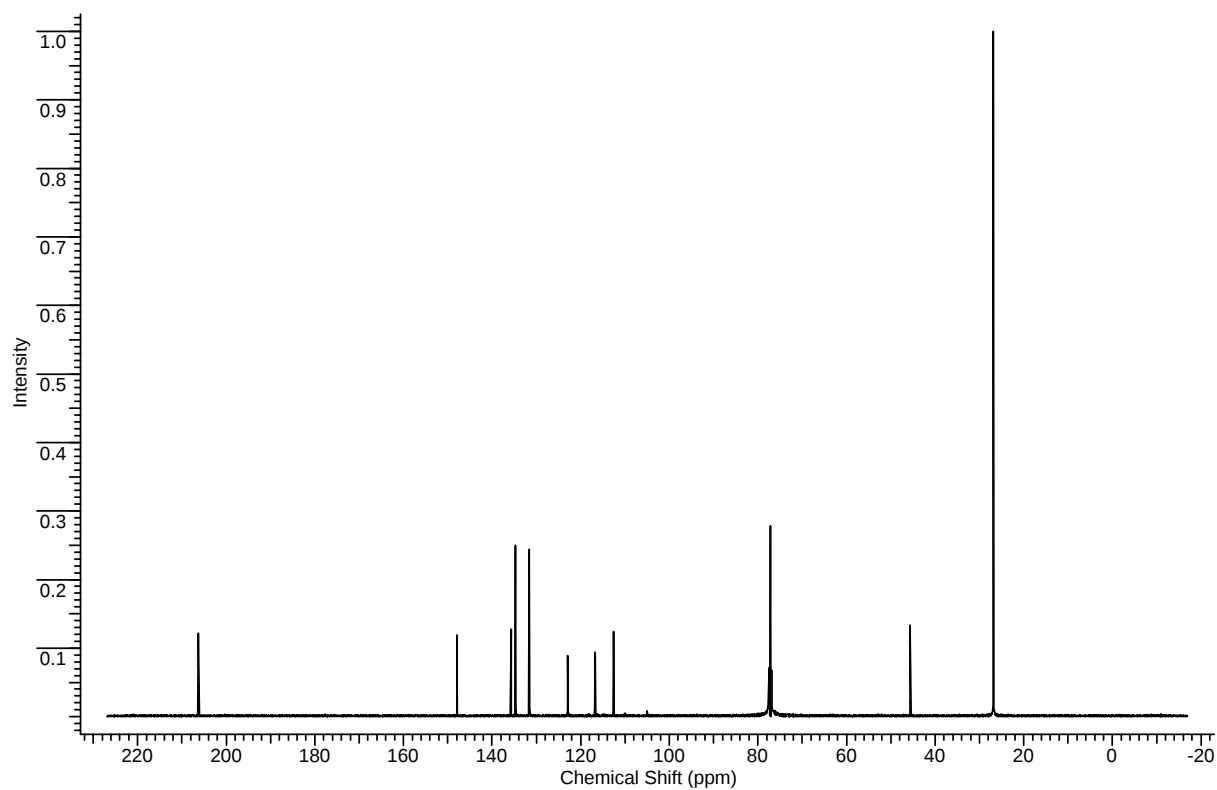
Ethyl 4-benzoyl-3-hydroxybenzoate (10c)



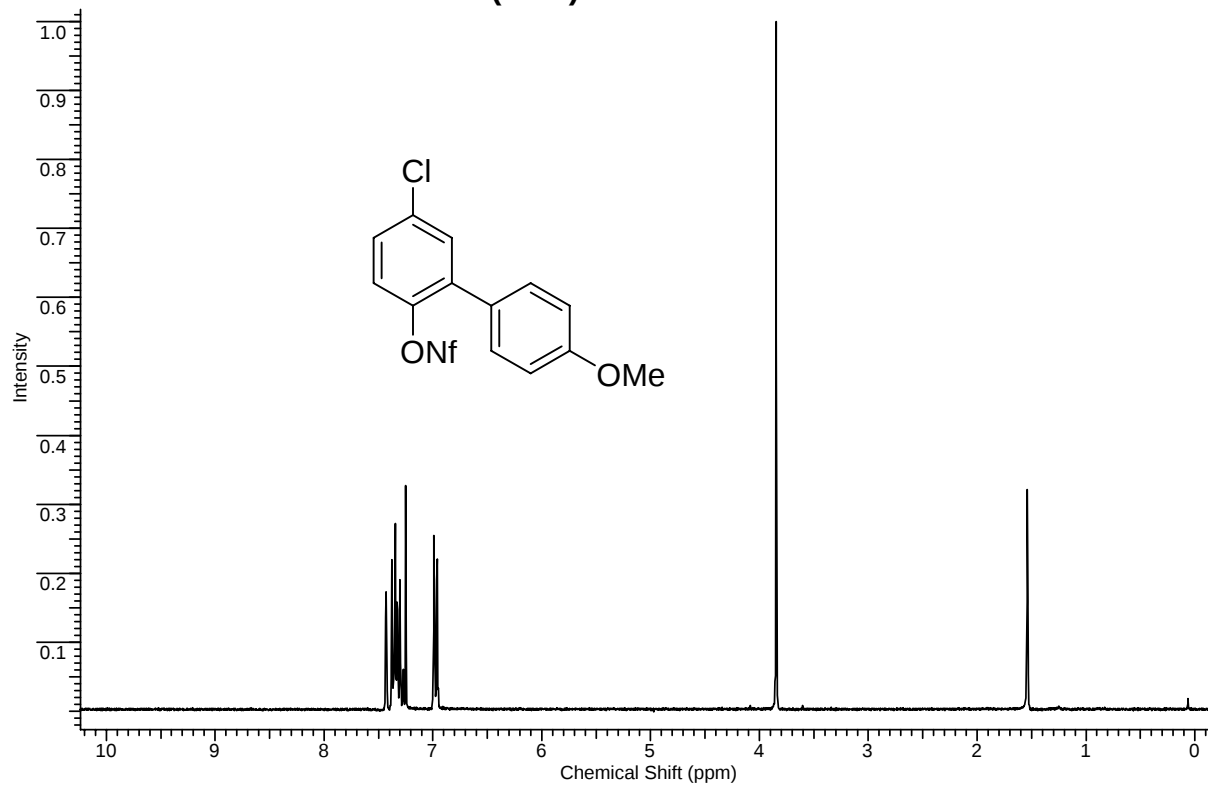


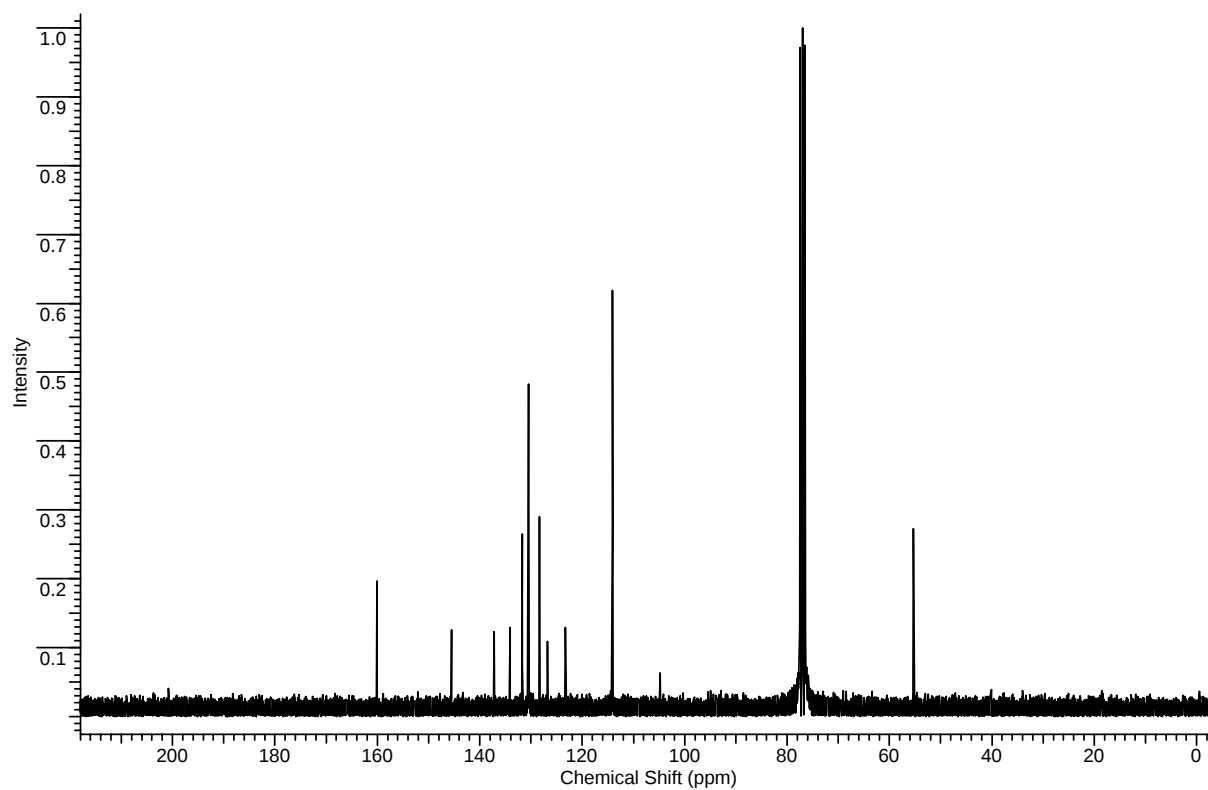
4-Cyano-2-(2,2-dimethylpropanoyl)phenyl 1,1,2,2, 3,3,4,4,4-nonafluorobutane-1-sulfonate (11a)



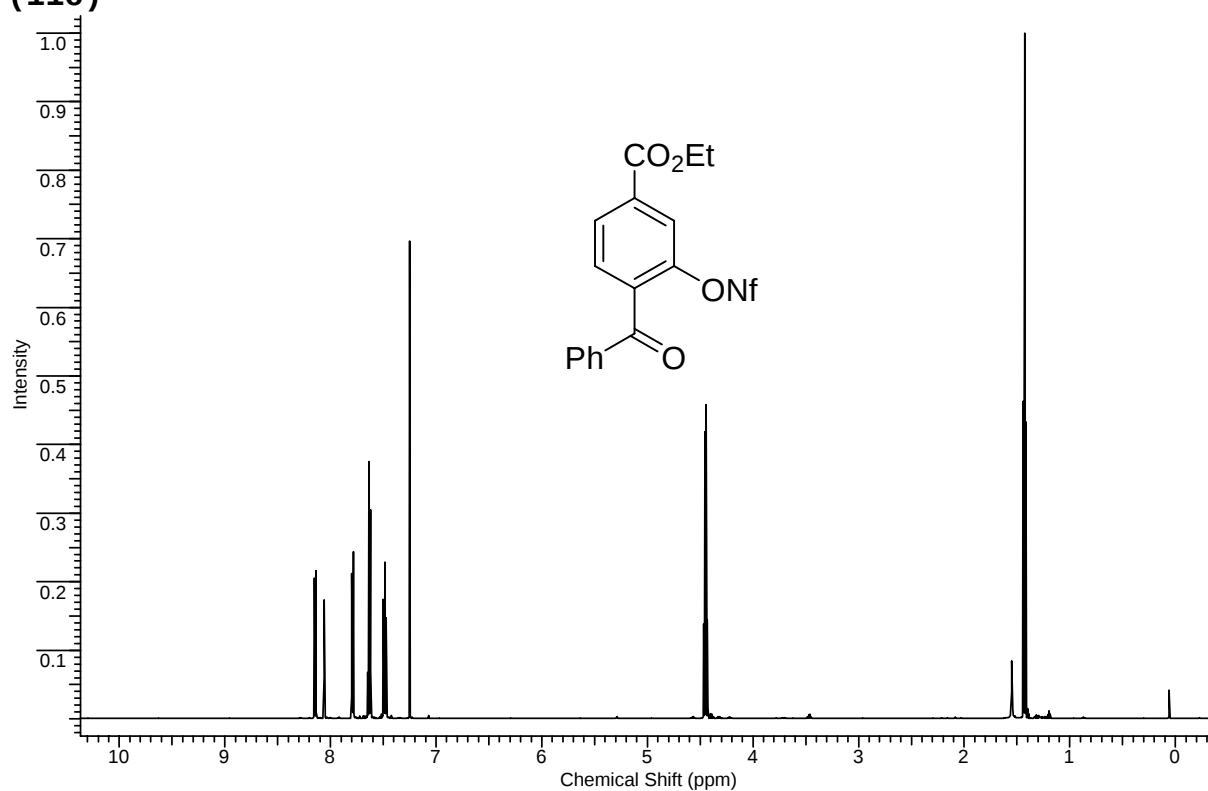


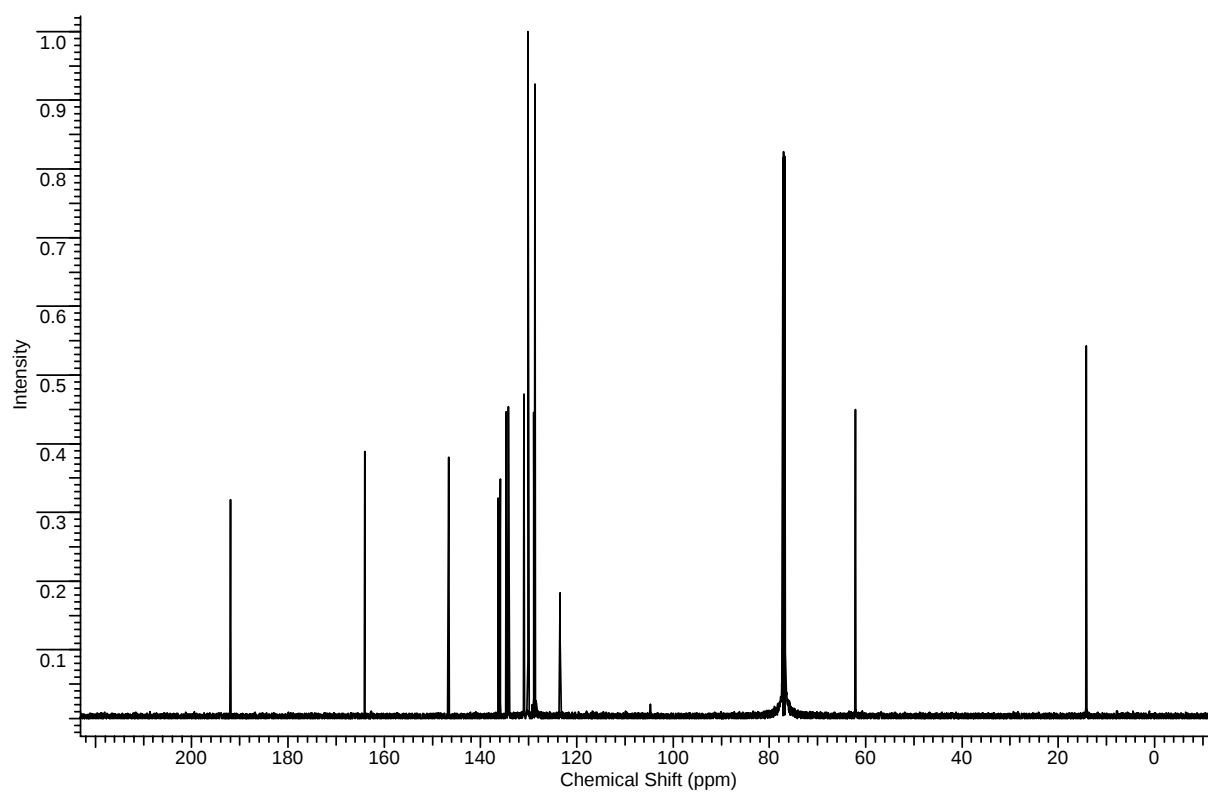
5-Chloro-4'-methoxybiphenyl-2-yl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (11b)



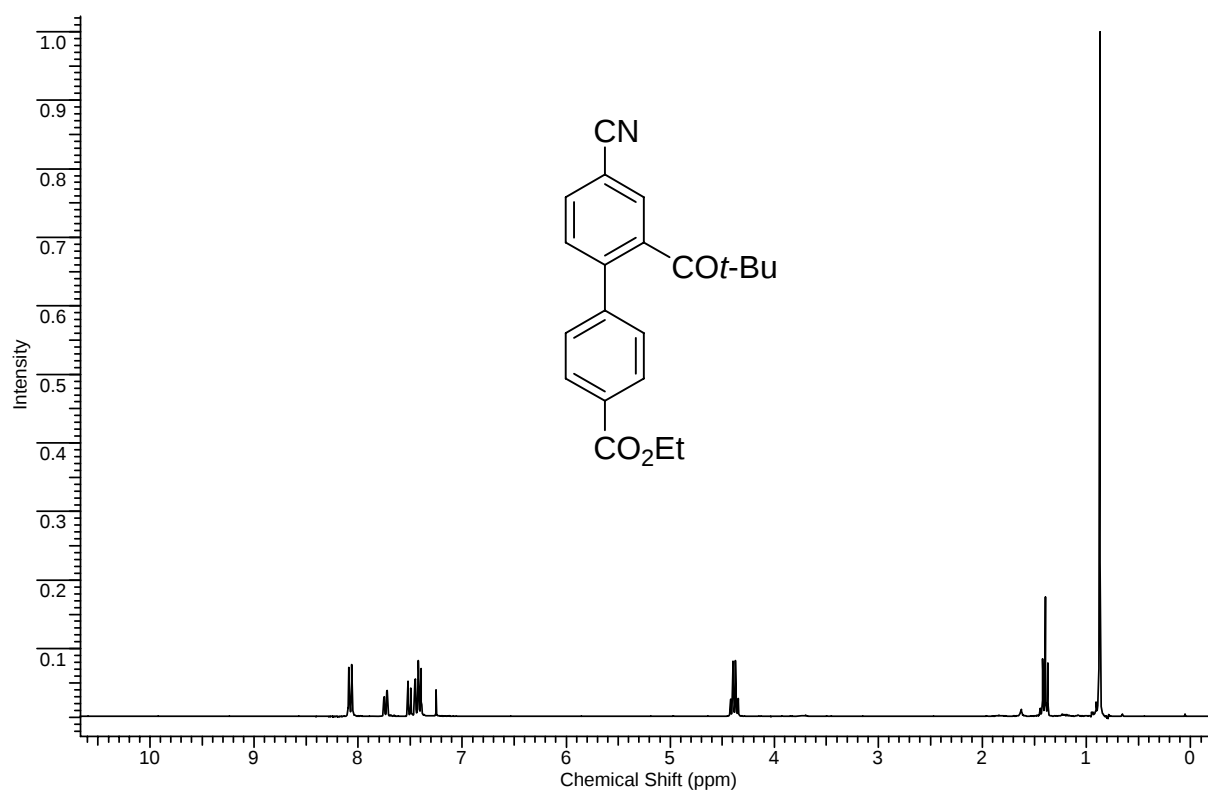


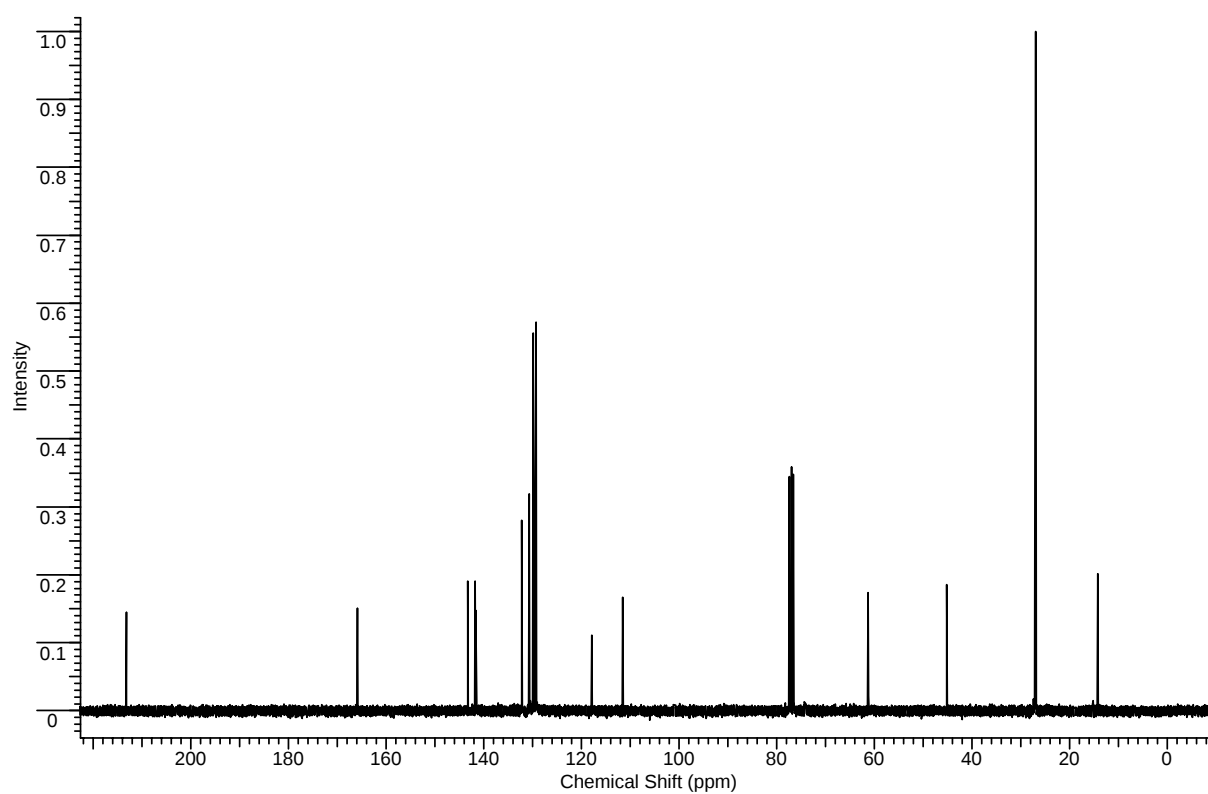
Ethyl 4-benzoyl-3-[(nonafluorobutyl)sulfonyl]-oxy}benzoate (11c)



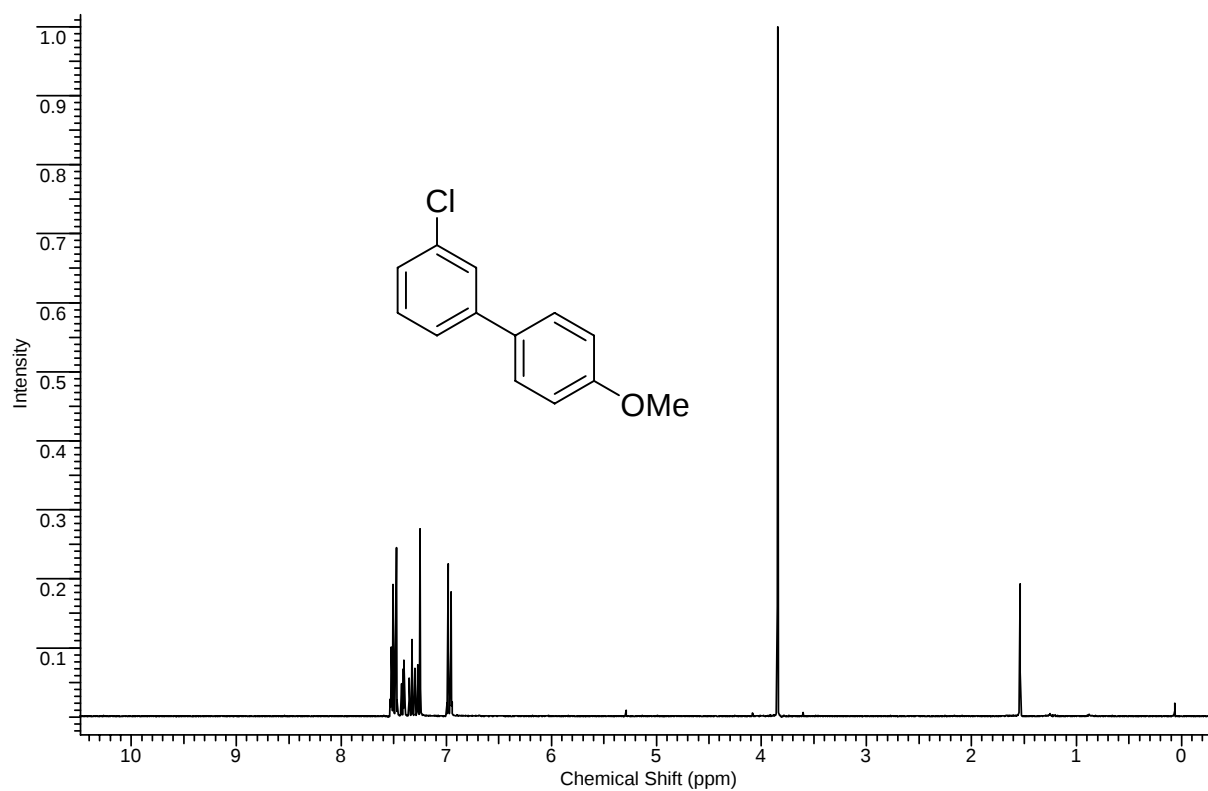


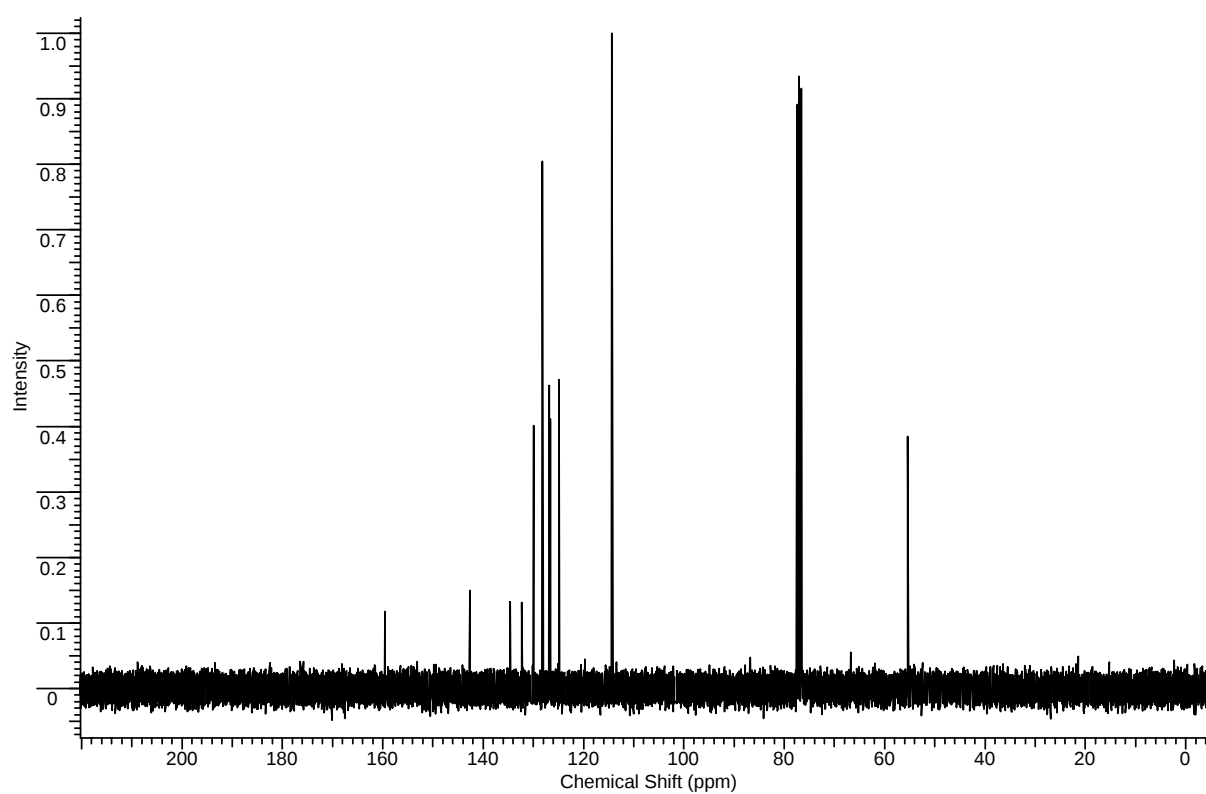
4' -Cyano-2' - (2,2-dimethylpropanoyl) -biphenyl-4-carboxylate (12a)



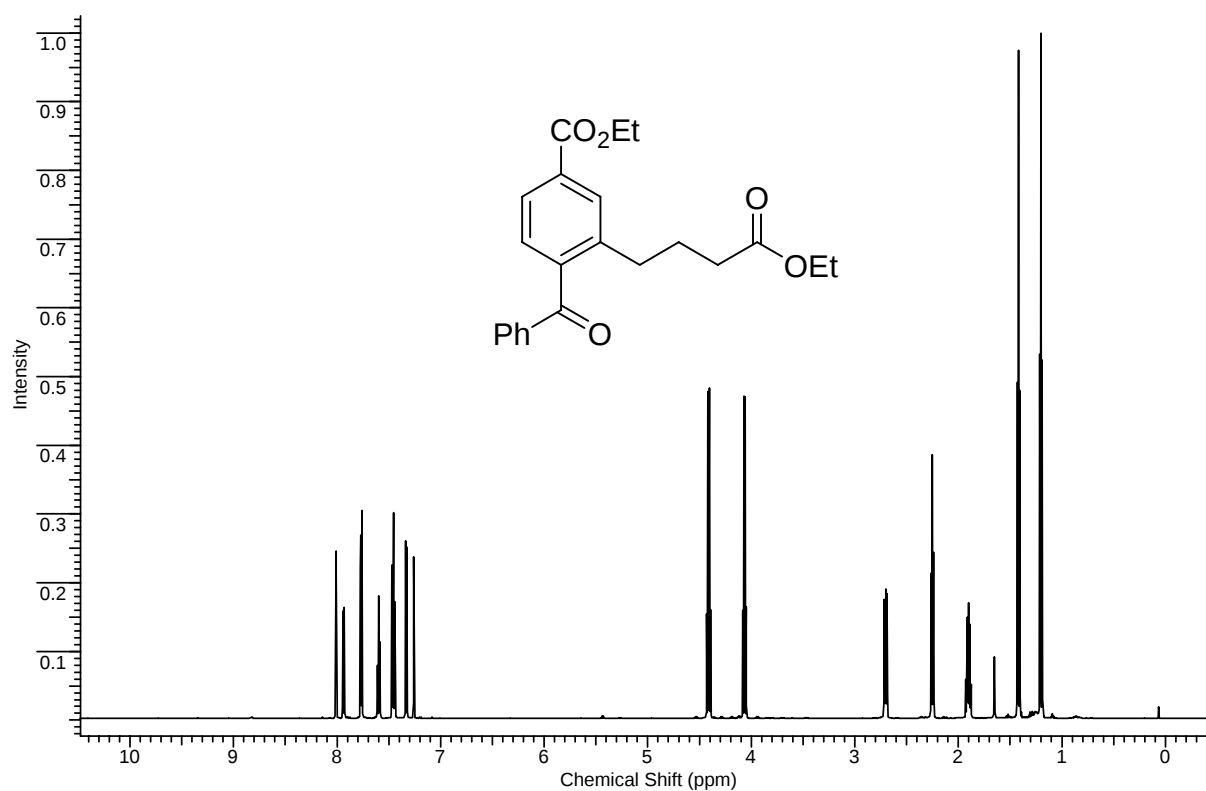


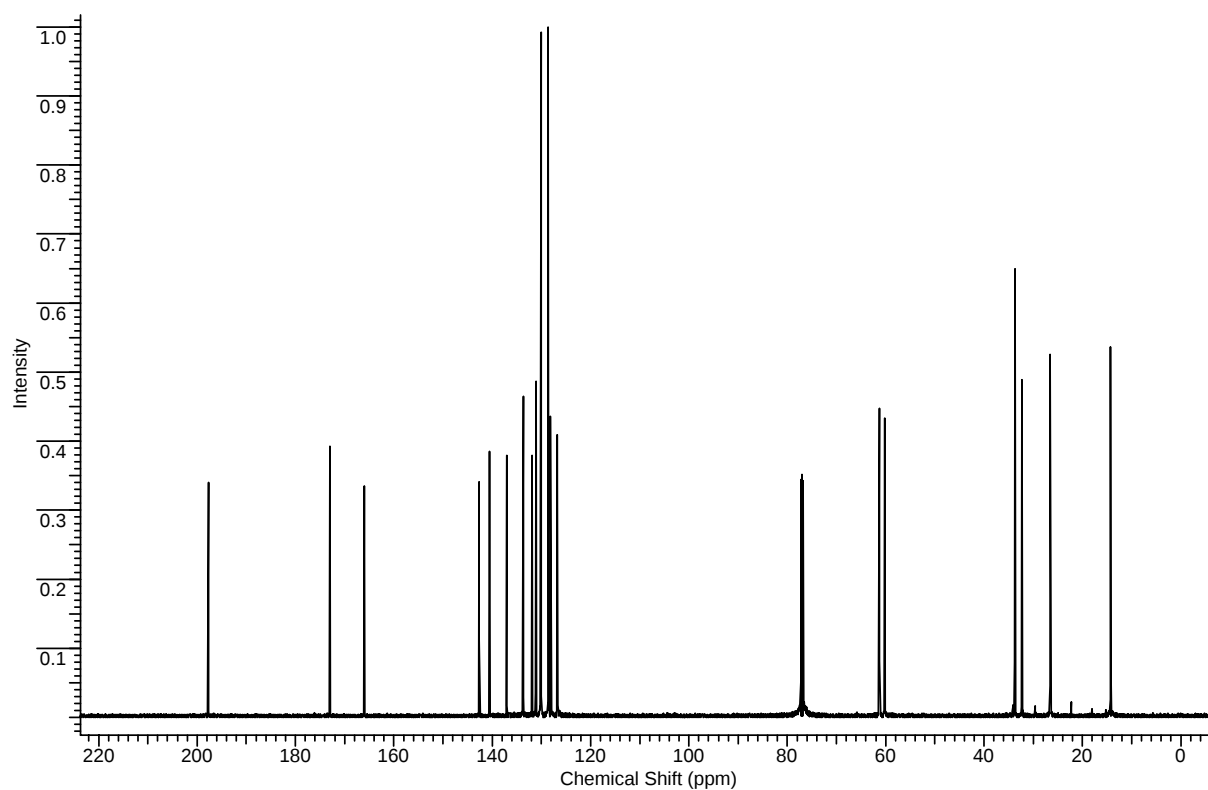
3-Chloro-4'-methoxybiphenyl (12b)





Ethyl 4-benzoyl-3-(4-ethoxy-4-oxobutyl)benzoate (12c)





Ethyl 4-benzoylbenzoate (12d)

