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Phosphoramidate synthesis via copper-catalysed aerobic oxidative coupling of amines and *H*-phosphonates

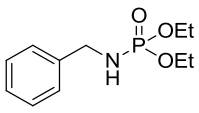
Jamie Fraser, Laura J. Wilson, Rebecca Blundell and Christopher J. Hayes*

School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, UK. Fax: +44(0)115 951 3564; Tel: +44(0)115 951 3045; E-mail: chris.hayes@nottingham.ac.uk

General procedure A for phosphoramidate synthesis

To a stirring suspension of CuI (38 mg, 0.20 mmol) in MeCN (2 mL) was added the *H*-phosphonate (1.00 mmol) and amine (2.00 mmol). The mixture was stirred at 55 °C for 4-18 h (see Table 2 for time) before cooling to room temperature and diluting with $CHCl_3$ (50 mL). The organic was washed with 2M HCl (30 mL), saturated $NaHCO_3$ (30 mL), then dried (Na_2SO_4). Removal of the volatiles *in vacuo* left the crude product which was purified by silica gel column chromatography (gradient: Et_2O to 5-10% MeOH in CH_2Cl_2).

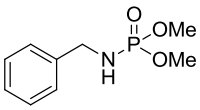
Diethyl benzylphosphoramidate 3



Following general procedure A, benzylamine (218 μL, 2.00 mmol) and diethyl phosphite (129 μL, 1.00 mmol) were used as coupling partners. The product was isolated as a yellow oil (138 mg, 67%). R_f – 0.46 (10% MeOH in CH_2Cl_2); υ_{max} /cm^{-1} ($CHCl_3$ soln) 3424, 2993, 1603, 1496, 1455, 1414, 1247, 1057, 1029 and 971; ^{1}H NMR (400 MHz, $CDCl_3$) 7.38 - 7.25 (5 H, m, *ArH*), 4.16 - 3.99 (6 H, m, *CH*$_2$ and O*CH*$_2$CH$_3$), 3.03 - 3.16 (1 H, m, *NH*), 1.32 (6 H, td, *J* 7.1 and 0.8, OCH$_2$*CH*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) 139.6 (C), 128.5 (CH), 127.3 (CH), 127.2 (CH), 62.3 (d, *J* 5, CH_2), 45.3 (CH_2) and 16.1 (d, *J* 7, CH_3); ^{31}P NMR

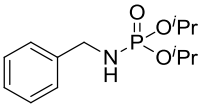
(161 MHz, $CDCl_3$) 8.49; HRMS *m/z* (ES^+) Found M + Na 266.0912. $C_{11}H_{18}NO_3PNa$ requires 266.0917.

Dimethyl benzylphosphoramidate 7



Following general procedure A, benzylamine (218 µL, 2.00 mmol) and dimethyl phosphite (92 µL, 1.00 mmol) were used as coupling partners. The product was isolated as a yellow oil (123 mg, 57%). R_f – 0.45 (10% MeOH in CH_2Cl_2); υ_{max} /cm^{-1} ($CHCl_3$ soln) 3424, 3001, 2954, 1455, 1414, 1252, 1063, 1038 and 853; ^1H NMR (400 MHz, $CDCl_3$) 7.36 - 7.25 (5 H, m, *ArH*), 4.10 (2 H, dd, *J* 10.0 and 7.0, *CH*$_2$), 3.70 (6 H, d, *J* 11.2, O*Me*) and 3.26 - 3.12 (1 H, m, *NH*); ^{13}C NMR (100 MHz, $CDCl_3$) 139.5 (C), 128.6 (CH), 127.4 (CH), 127.3 (CH), 53.0 (d, *J* 5, CH_3) and 45.3 (CH_2); ^{31}P NMR (161 MHz, $CDCl_3$) 11.13; HRMS *m/z* (ES^+) Found M + Na 238.0606. $C_9H_{14}NO_3PNa$ requires 238.0604.

Diisopropyl benzylphosphoramidate 8



Following general procedure A,.benzylamine (218 µL, 2.00 mmol) and diisopropyl phosphite (168 µL, 1.00 mmol) were used as coupling partners. The product was isolated as a yellow solid (151 mg, 56%). m.p. 48 – 50 °C. R_f – 0.44 (10% MeOH in CH_2Cl_2); υ_{max} /cm^{-1} ($CHCl_3$ soln) 3009, 2985, 1497, 1454, 1413, 1387, 1376, 1244, 1106, 1019 and 993; ^1H NMR (400 MHz, $CDCl_3$) 7.38 - 7.23 (5 H, m, *ArH*), 4.65 (2 H, dspt, *J* 7.5 and 6.2, O*CH*$(CH_3)_2$), 4.11 (2 H, dd, *J* 9.0 and 7.0, *CH*$_2$), 2.88 - 2.73 (1 H, m, *NH*), 1.36 (6 H, d, *J* 6.2, OCH(*CH*$_3$)$_2$) and 1.31 (6 H, d, *J* 6.2, OCH(*CH*$_3$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) 139.8 (C), 128.5 (CH), 127.3 (2CH [overlapping]), 70.9 (d *J* 6, CH), 45.5 (CH_2) and 23.8 (t, *J* 4, CH_3);

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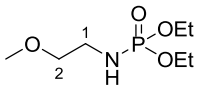
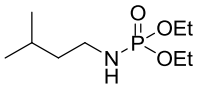
^{31}P NMR (161 MHz, $CDCl_3$) 6.52; HRMS *m/z* (ES^+) Found M + Na 294.1222. $C_{13}H_{22}NO_3PNa$ requires 294.1230.

Diethyl 2-methoxyethylphosphoramidate 9



Following general procedure A, 2-methoxyethylamine (174 μL, 2.00 mmol) and diethyl phosphite (129 μL, 1.00 mmol) were used as coupling partners. The product was isolated as a yellow oil (113 mg, 53%). R_f – 0.72 (10% MeOH in CH_2Cl_2); υ_{max} /cm^{-1} ($CHCl_3$ soln) 3421, 2993, 2932, 1602, 1416, 1393, 1245, 1058, 1030 and 970; ^{1}H NMR (400 MHz, $CDCl_3$) 4.10 - 3.99 (4 H, m, O*CH*$_2$CH$_3$), 3.41 (2 H, td, *J* 5.0 and 0.6, *C*^{2}*H*$_2$), 3.34 (3 H, s, *OMe*), 3.09 - 2.99 (3 H, m, *C*^{1}*H*$_2$ and *NH*) and 1.30 (6 H, td, *J* 7.1 and 0.8, OCH$_2$*CH*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) 72.6 (d, *J* 6, CH_2), 62.2 (d, *J* 5, CH_2), 58.7 (CH_3), 41.0 (CH_2) and 16.1 (d, *J* 7, CH_3); ^{31}P NMR (161 MHz, $CDCl_3$) 9.13; HRMS *m/z* (ES^+) Found M + Na 234.0873. $C_7H_{18}NO_4PNa$ requires 234.0866.

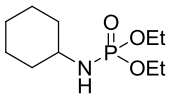
Diethyl isopentylphosphoramidate 10



Following general procedure A, isoamylamine (232 μL, 2.00 mmol) and diethyl phosphite (129 μL, 1.00 mmol) were used as coupling partners. The product was isolated as a yellow oil (120 mg, 54%). R_f – 0.40 (5% MeOH in CH_2Cl_2); υ_{max} /cm^{-1} ($CHCl_3$ soln) 3425, 2992, 2961, 2873, 1469, 1413, 1369, 1240, 1096, 1058, 1031 and 969; ^{1}H NMR (400 MHz, $CDCl_3$) 4.11 - 3.99 (4 H, m, O*CH*$_2$CH$_3$), 2.90 (2 H, dq, *J* 9.5 and 7.0, *CH*$_2$), 2.59 (1 H, m, *NH*), 1.63 (1 H, spt, *J* 7.0, *CH*), 1.37 (2 H, q, *J* 7.0, *CH*$_2$), 1.31 (6 H, t, *J* 7.0, *CH*$_3$) and 0.89 (6 H, d, *J* 6.7, OCH$_2$*CH*$_3$); ^{13}C NMR (400 MHz, $CDCl_3$) 62.1(d, *J* 5, CH_2), 40.7 (d, *J* 6, CH_2), 39.5

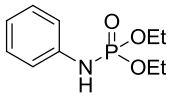
(CH_2), 25.4 (CH), 22.3 (CH_3) and 16.2 (d, *J* 7, CH_3); ^{31}P NMR (161 MHz, $CDCl_3$) 9.15; HRMS *m/z* (ES^+) Found M + Na 246.1231. $C_9H_{22}NO_3PNa$ requires 246.1230.

Diethyl cyclohexylphosphoramidate 11



Following general procedure A, cyclohexylamine (229 μL, 2.00 mmol) and diethyl phosphite (129 μL, 1.00 mmol) were used as coupling partners. The product was recovered as a tan waxy solid (104 mg, 44%). R_f – 0.17 (5% MeOH in CH_2Cl_2); υ_{max} /cm^{-1} ($CHCl_3$ soln) 3413, 2991, 2936, 2857, 1602, 1561, 1451, 1420, 1393, 1300, 1245, 1105, 1030 and 967; ^{1}H NMR (400 MHz, $CDCl_3$) 4.10 - 3.97 (4 H, m, O*CH*$_2$CH$_3$), 3.02 - 2.88 (1 H, m, *CH*), 2.55 (1 H, t, *J* 9.7, *NH*), 1.96 - 1.85 (3 H, m, *CyCH*$_2$), 1.68 (3 H, dt, *J* 13.0 and 3.7), 1.55 (1 H, dt, *J* 13.0 and 3.7, *CyCH*$_2$), 1.34 -1.22 (8 H, m, *CyCH*$_2$ and OCH$_2$*CH*$_3$) and 1.07 - 1.19 (3 H, m, *CyCH*$_2$); ^{13}C NMR (400 MHz, $CDCl_3$) 62.1 (d, *J* 5, CH_2), 50.5 (CH), 35.7 (CH_2), 25.3 (CH_2), 24.9 (CH_2) and 16.2 (d, *J* 7, CH_3); ^{31}P NMR (161 MHz, $CDCl_3$) 8.20; HRMS *m/z* (ES^+) Found M + Na 258.1228. $C_{10}H_{22}NO_3PNa$ requires 258.1230.

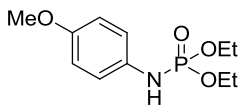
Diethyl phenylphosphoramidate 12



Following general procedure A, aniline (182 μL, 2.00 mmol) and diethyl phosphite (129 μL, 1.00 mmol) were used as coupling partners. The product was recovered as a black solid, (192 mg, 84%). R_f – 0.32 (5% MeOH in CH_2Cl_2); υ_{max} /cm^{-1} ($CHCl_3$ soln) 3692, 3607, 3412, 2998, 2361, 1602, 1500, 1479, 1398, 1298, 1252, 1026 and 976; ^{1}H NMR (400 MHz, $CDCl_3$) 7.26 (2 H, t, 8.6, *ArH*), 7.04 – 7.00 (2 H, m, *ArH*), 6.97 (1 H, tt, *J* 7.3 and 1.1, *ArH*), 6.17 (1 H, d, *J* 9.0, *NH*), 4.04 - 4.25 (4 H, m, O*CH*$_2$CH$_3$), 1.33 (6 H, td, *J* 7.2 and 0.8, OCH$_2$*CH*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) 139.7 (C), 129.2 (CH), 121.5 (CH), 117.3 (CH), 62.7 (d, *J* 5, CH_2)

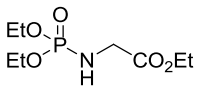
and 16.1 (d, *J* 7, CH_3); ^{31}P NMR (161 MHz, $CDCl_3$) 2.28; HRMS *m/z* (ES^+) Found M + Na 252.0759. $C_{10}H_{16}NO_3PNa$ requires 252.0760.

Diethyl *p*-anisidinephosphonate 13



Following general procedure A, *p*-anisidine (246 mg, 2.00 mmol) and diethyl phosphite (129 μL, 1.00 mmol) were used as coupling partners. The product was recovered as a black solid (198 mg, 76%). R_f – 0.37 (5% MeOH in CH_2Cl_2); υ_{max} /cm^{-1} ($CHCl_3$ soln) 3693, 3414, 3003, 2936, 2909, 2838, 1682, 1601, 1584, 1513, 1465, 1456, 1443, 1380, 1308, 1284, 1247, 1181, 1167, 1149, 1105, 1029, 978, 827; ^1H NMR (400 MHz, $CDCl_3$) 7.03-6.94 (1 H, m, *ArH*), 6.89 (1 H, br d, *J* 9.5, *ArH*), 6.82-6.72 (2 H, m, *ArH*), 4.22-3.98 (4 H, m, O*CH*$_2$CH$_3$), 3.74 (3 H, S, O*CH*$_3$), 1.28 (6 H, app br t, *J* 7.0, OCH$_2$*CH*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) 154.4 (C), 133.2 (C), 118.7 (d, *J* 7, CH), 114.4 (CH), 62.4 (d, *J* 5, CH_2), 55.4 (CH_3), 16.0 (d, *J* 8, CH_3); ^{31}P NMR (161 MHz, $CDCl_3$) 3.36; HRMS *m/z* (ES^+) Found M + Na 282.0864. $C_{11}H_{18}NO_4PNa$ requires 282.0866

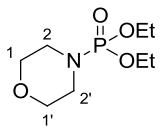
Ethyl 2-(diethoxyphosphorylamino)acetate 14



To a stirring suspension of CuI (38 mg, 0.20 mmol) in MeCN (2 mL) was added diethyl phosphite (129 μL, 1.00 mmol), glycine ethyl ester hydrochloride (280 mg, 2.00 mmol) and Et_3N (277 μL, 2.00 mmol). The mixture was stirred at 55 °C for 18 h before cooling to room temperature and diluting with $CHCl_3$ (50 mL). The organic was washed with 2M HCl (30 mL), saturated $NaHCO_3$ (30 mL), then dried (Na_2SO_4). Removal of the volatiles *in vacuo* left the crude product which was purified by column chromatography (gradient: Et_2O to 5% MeOH in CH_2Cl_2) yielding the product (189 mg, 79%) as a yellow oil. R_f – 0.46 (5 %

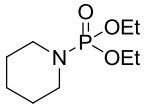
MeOH in CH_2Cl_2); υ_{max} /cm^{-1} ($CHCl_3$ soln) 3415, 2993, 2940, 2909, 1742, 1444, 1419, 1394, 1372, 1320, 1252, 1148, 1058, 1029 and 972; ^{1}H NMR (400 MHz, $CDCl_3$) 4.18 (2 H, q, *J* 7.2, $CO_2CH_2CH_3$), 4.11 - 4.01 (4 H, m, $P(O)OCH_2CH_3$), 3.67 (2 H, dd, *J* 9.9 and 6.3, CH_2), 3.32 - 3.20 (1 H, m, *NH*), 1.29 (6 H, td, *J* 7.0 and 0.8, $P(O)OCH_2CH_3$) and 1.25 (3 H, t, *J* 7.2, $CO_2CH_2CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) 170.9 (d, *J* 8, C), 62.5 (d, *J*, CH_2), 61.4 (CH_2), 43.0 (CH_2), 16.1 (d, *J* 7, CH_3) and 14.1 (CH_3); ^{31}P NMR (161 MHz, $CDCl_3$) 7.68; HRMS *m/z* (ES^+) Found M + Na 262.0811. $C_8H_{18}NO_5PNa$ requires 262.0815.

Diethyl morpholinophosphonate 15



Following general procedure A, morpholine (173 μL, 2.00 mmol) and diethyl phosphite (129 μL, 1.00 mmol) were used as coupling partners. The product was isolated as a yellow oil (71 mg , 32%), contaminated with tetraethyl hypodiphosphate (8% by ^{1}H NMR) as an inseparable impurity.. R_f – 0.61 (10% MeOH in CH_2Cl_2); υ_{max} /cm^{-1} ($CHCl_3$ soln) 3691, 3606, 2995, 2915, 2860, 1637, 1602, 1444, 1393, 1299, 1250, 1164, 1139, 1062, 1029 and 975; ^{1}H NMR (400 MHz, $CDCl_3$) 4.09 - 3.95 (4 H, m, OCH_2CH_3), 3.61 (4 H, td, *J* 4.7 and 1.1, C^1H_2 and $C^{1'}H_2$), 3.14 - 3.04 (4 H, m, C^2H_2 and $C^{2'}H_2$)and 1.28 (6 H, td, *J* 7.1 and 0.8, OCH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) 67.0 (d, *J* 6, CH_2), 62.4 (d, *J* 5, CH_2), 44.6 (CH_2) and 16.2 (d, *J* 7, CH_3); ^{31}P NMR (161 MHz, $CDCl_3$) 7.77; HRMS *m/z* (ES^+) Found M + Na 246.0869. $C_8H_{18}NO_4PNa$ requires 246.0866.

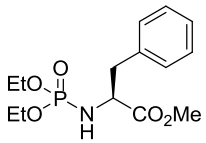
Diethyl piperidinephosphonate 16



Following general procedure A, piperidine (198 μL, 2.00 mmol) and diethyl phosphite (129 μL, 1.00 mmol) were used as coupling partners.

The product was recovered as a yellow oil (36 mg, 16%). R_f – 0.27 (5% MeOH in CH_2Cl_2); υ_{max} /cm^{-1} ($CHCl_3$ soln) 2990, 2940, 2855, 2473, 1665, 1478, 1466, 1453, 1444, 1392, 1383, 1368, 1342, 1243, 1167, 1119, 1099, 1059, 1028, 996, 910; ^{1}H NMR (400 MHz, $CDCl_3$) 4.10-3.93 (4 H, m, O*CH*$_2$CH$_3$), 3.14-3.03 (4 H, m, *CyCH*$_2$), 1.62-1.45 (6 H, m, *CyCH*$_2$), 1.30 (6 H, td, *J* 7.1 and 0.8, OCH$_2$*CH*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) 62.3 (d, *J* 5, CH_2), 45.7 (d, *J* 2, CH_2), 26.4 (d, *J* 5, CH_2), 24.8 (CH_2), 16.5 (d, *J* 7, CH_3); ^{31}P NMR (161 MHz, $CDCl_3$) 8.93; HRMS *m/z* (ES$^+$) Found M + Na 244.1072$C_9H_{20}NO_3PNa$ requires 244.1072.

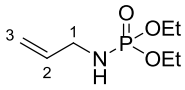
(*S*)-methyl 2-(diethoxyphosphorylamino)-3-phenylpropanoate 17



To a stirring suspension of CuI (38 mg, 0.20 mmol) in MeCN (2 mL) was added diethyl phosphite (129 µL, 1.00 mmol), *L*-phenylalanine methyl ester hydrochloride (432 mg, 2.00 mmol) and Et_3N (277 µL, 2.00 mmol). The mixture was stirred at 55 °C for 18 h before cooling to room temperature and diluting with $CHCl_3$ (50 mL). The organic was washed with 2M HCl (30 mL), saturated $NaHCO_3$ (30 mL), then dried (Na_2SO_4). Removal of the volatiles *in vacuo* left the crude product which was purified by column chromatography (gradient: Et_2O to 5% MeOH in CH_2Cl_2) yielding the product (310 mg, 98%) as a tan oil. R_f – 0.46 (5 % MeOH in CH_2Cl_2); υ_{max} /cm^{-1} ($CHCl_3$ soln) 3401, 2996, 1743, 1603, 1497, 1443, 1426, 1245, 1128, 1058, 1030 and 973; $[\alpha]_D^{22}$ +15.4 (c 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) 7.36 - 7.09 (5 H, m, *ArH*), 4.18 - 4.06 (1 H, m, *CH*), 4.04 - 3.86 (3 H, m, O*CH*$_2$CH$_3$), 3.82 - 3.69 (1 H, m, O*CH*$_2$CH$_3$), 3.72 (3 H, s, *OMe*), 3.19 (1 H, t, *J* 10.3, *NH*), 3.07 (1 H, ddd, *J* 13.6, 5.5 and 1.3, Ph*CH*$_2$), 2.97 (1 H, dd, *J* 13.6 and 7.0, Ph*CH*$_2$) and 1.24 (6 H, dtd, *J* 12.9, 7.0 and 0.8, OCH$_2$*CH*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) 173.1 (C), 136.0 (C), 129.4 (CH), 128.4 (CH), 127.0 (CH),

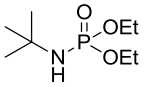
62.3 (d, *J* 5, CH_2), 55.6 (CH), 52.1 (CH_3), 40.5 (d, *J* 6, CH_2) and 16.0 (d, *J* 8, CH_3); ^{31}P NMR (161 MHz, $CDCl_3$) 6.79; HRMS *m/z* (ES^+) Found M + Na 338.1116. $C_{14}H_{22}NO_5PNa$ requires 338.1128.

Diethyl allylphosphoramidate 18



Following general procedure A, allylamine (149 μL, 2.00 mmol) and diethyl phosphite (129 μL, 1.00 mmol) were used as coupling partners. The product was isolated as as a yellow oil (111 mg, 58%). R_f – 0.61 (10% MeOH in CH_2Cl_2); υ_{max} /cm^{-1} ($CHCl_3$ soln) 3425, 3010, 1411, 1250, 1096, 1030 and 971; ^1H NMR (400 MHz, $CDCl_3$) 5.90 - 5.79 (1 H, m,C^2H), 5.20 (1 H, dq, *J* 17.1 and 1.6, C^3H_2), 5.07 (1 H, dq, *J* 10.3 and 1.4, C^3H_2), 4.09 - 3.98 (4 H, m, O$CH_2$$CH_3$), 3.50 (2 H, dddt, *J* 10.3, 6.9, 5.4 and 1.6, C^1H_2), 2.96 - 2.84 (1 H, m, *NH*)and 1.29 (6 H, td, *J* 7.1and 0.8. OCH$_2$$CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) 136.1 (CH), 115.3 (CH_2), 62.2 (d, *J* 5, CH_2), 43.7 (CH_2) and 16.1 (d, *J* 7, CH_3); ^{31}P NMR (161 MHz, $CDCl_3$) 8.81; HRMS *m/z* (ES^+) Found M + Na 216.0767. $C_7H_{16}NO_3PNa$ requires 216.0760.

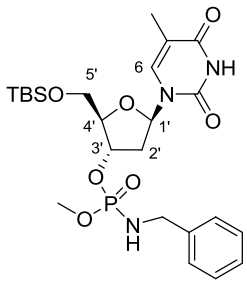
Diethyl tert-butylphosphoramidate 19



Following general procedure A, t*ert*-butylamine (210 μL, 2.00 mmol) and diethyl phosphite (129 μL, 1.00 mmol) were used as coupling partners. The product was recovered as a yellow oil (76 mg, 36%). R_f – 0.29 (5% MeOH in CH_2Cl_2); /cm^{-1} ($CHCl_3$ soln) 3404, 3010, 2986, 2908, 1408, 1390, 1244, 1031, 987 and 909; ^1H NMR (400 MHz, $CDCl_3$) 4.12 - 3.98 (4 H, m, O$CH_2$$CH_3$), 2.58 (1 H, d, *J* 6.8, *NH*), 1.30 (6 H, td, *J* 7.1 and 0.7, OCH$_2$$CH_3$) and 1.25 (9 H, d, *J* 0.8, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) 62.0 (d, *J* 5, CH_2), 50.6 (C), 31.3 (d, *J* 5,

CH_3) and 16.2 (d, *J* 8, CH_3); ^{31}P NMR (161 MHz, $CDCl_3$) 6.95; HRMS *m/z* (ES^+) Found M + Na 232.1076. $C_8H_{20}NO_3PNa$ requires 232.1073.

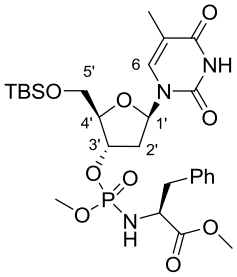
Phosphoramidate 20



To a stirring suspension of CuI (10 mg, 0.05 mmol) in MeCN (0.5 mL) was added 5'–OTBS–3'–methyl phosphonate thymidine (109 mg, 0.25 mmol) and benzylamine (56 μL, 0.5 mmol). The mixture was stirred at 55 °C for 18 h before cooling to room temperature and diluting with a mixtre of IPA : $CHCl_3$ (1:5, 30 mL). The organic was washed with 2M HCl (20 mL), saturated $NaHCO_3$ (20 mL), then dried (Na_2SO_4). Removal of the volatiles *in vacuo* left the crude product which was purified by column chromatography (gradient: Et_2O to 3% MeOH in Et_2O) yielding the product (76 mg, 56%) as a white solid (1:1 mixture of diastereoisomers). m.p. 47 - 50 °C; R_f – 0.15 (3% MeOH in Et_2O); υ_{max} /cm^{-1} ($CHCl_3$ soln) 3399, 3010, 2956, 2932, 2859, 1689, 1520, 1471, 1322, 1258, 1129, 1051, 1011, 976 and 834; [Diastereoisomer denoted with *] ^1H NMR (400 MHz, $CDCl_3$) 9.57 (0.5 H, br. s., *NH*), 9.55 (0.5 H, br. s., *NH**), 7.48 (0.5 H, d, *J* 1.1, C^6H), 7.47 (0.5 H, d, *J* 1.1, C^6H*), 7.37 – 7.24 (5 H, m, *ArH* and *ArH**), 6.35 (1 H, app. ddd, *J* 9.0, 5.2 and 3.7, $C^{1'}H$ and $C^{1'}H$*), 4.94 (0.5 H, t, *J* 6.3, $C^{4'}H$), 4.90 (0.5 H, t, *J* 6.5, $C^{4'}H$*), 4.28 (0.5 H, d, *J* 1.4, $C^{3'}H$), 4.17 (0.5 H, d, *J* 1.4, $C^{3'}H$*), 4.11 (2 H, app. dd, *J* 10.8 and 7.2, PhCH_2NH and PhCH_2NH*), 3.88 (2 H, app. dd, *J* 3.5 and 2.2, $C^{5'}H$ and $C^{5'}H$*), 3.73 (3 H, s, *OMe*), 3.70 (3 H, s, *OMe**), 3.70 - 3.62 (0.5 H, m, $PhCH_2NH$), 3.59 – 3.50 (0.5 H, m, $PhCH_2NH$*), 2.54 (0.5 H, dd, *J* 13.4 and 5.1, $C^{2'}H_2$), 2.35 (0.5 H, dd, *J* 13.2 and 5.5, $C^{2'}H_2$*), 2.15 – 2.03 (0.5 H, m, $C^{2'}H_2$), 2.03 – 1.93 (0.5 H, m, $C^{2'}H_2$*), 1.91 (3 H, s, CH_3 and CH_3*), 0.92 (9 H, s, $(CH_3)_3CSiMe_2$ and $(CH_3)_3CSiMe_2$*) and

0.11 (6 H, s, $(CH_3)_3CSi\mathit{Me}_2$ and $(CH_3)_3CSi\mathit{Me}_2$*); ^{13}C NMR (100 MHz, $CDCl_3$) 163.91 (C), 163.89 (C*), 150.4 (C and C*), 139.22 (C), 139.17 (C*), 134.99 (C), 134.96 (C*), 128.6 (CH and CH*), 127.4 (CH and CH*), 127.22 (CH), 127.18 (CH*), 111.04 (C), 111.02 (C*), 86.0 (d, *J* 4, CH), 85.7 (d, *J* 5, CH), 84.5 (CH and CH*), 77.5 (d, *J* 5, CH), 77.1(d, *J* 5, CH), 63.3 (CH_2 and CH_2*), 53.2 (dd, *J* 5 and 4, CH_3 and CH_3*), 45.21 (CH_2), 45.17 (CH_2*), 39.4 (d, *J* 5, CH_2), 39.2 (d, *J* 6, CH_2), 25.9 (CH_3 and CH_3*), 18.2 (C and C*) and 12.4 (CH_3 and CH_3*); ^{31}P NMR (161 MHz, $CDCl_3$) 9.67 and 9.42; HRMS *m/z* (ES^+) Found M + Na 562.2112. $C_{24}H_{38}N_3O_7PSiNa$ requires 562.2109.

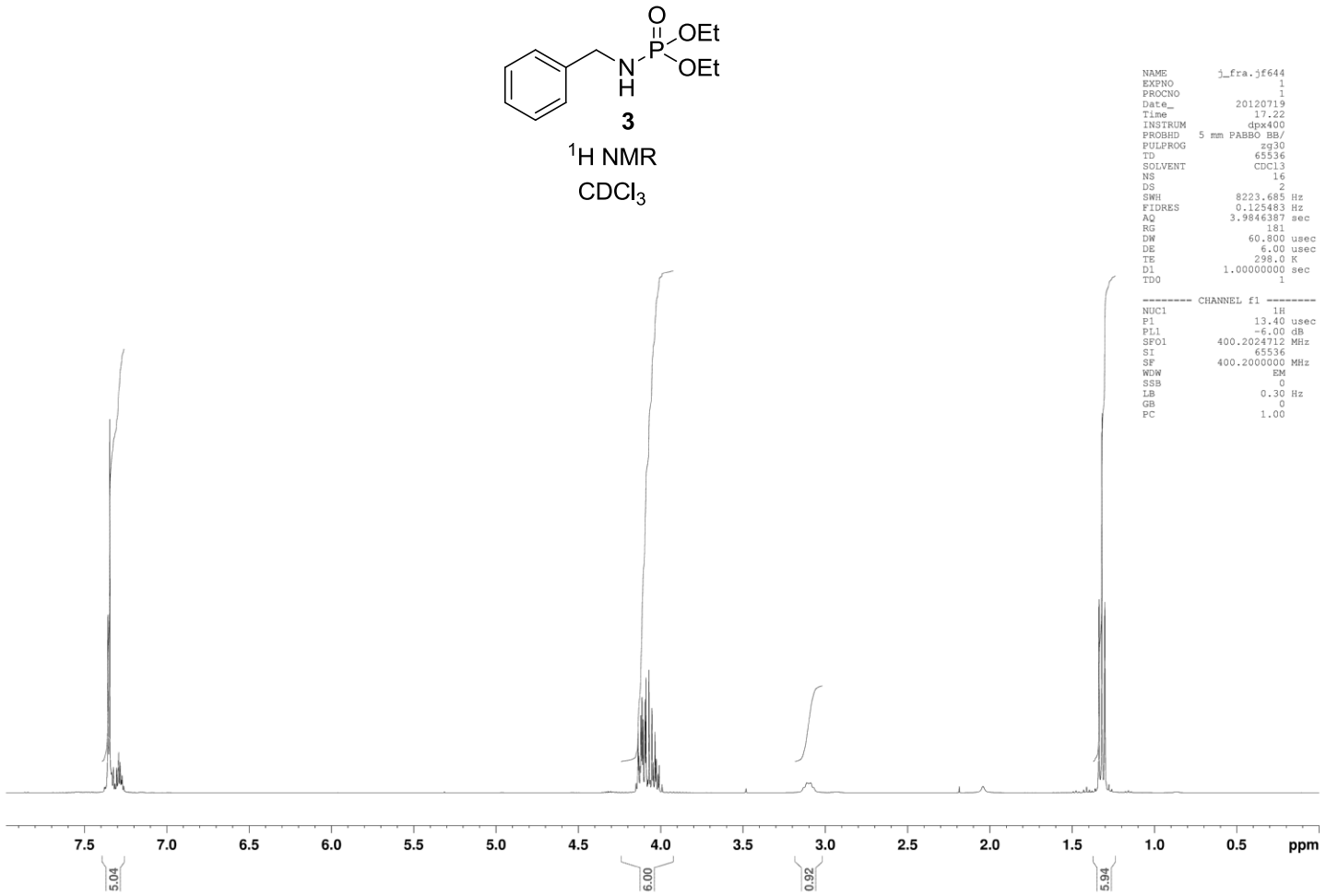
Phoshoramidate 21



To a stirring suspension of CuI (10 mg, 0.05 mmol) in MeCN (0.5 mL) was added 5'–OTBS–3'–methyl phosphonate thymidine (109 mg, 0.25 mmol), *L*-phenylalanine methyl ester hydrochloride (108 mg, 0.5 mmol) and Et_3N (64 μL, 0.5 mmol). The mixture was stirred at 55 °C for 18 h before cooling to room temperature and diluting with a mixture of IPA : $CHCl_3$ (1:5, 30 mL). The organic was washed with 2M HCl (20 mL), saturated $NaHCO_3$ (20 mL), then dried (Na_2SO_4). Removal of the volatiles *in vacuo* left the crude product which was purified by column chromatography (gradient: Et_2O to 5% MeOH in CH_2Cl_2) yielding the product (85 mg, 56%) as a white solid (1:1 mixture of diastereoisomers). m.p. 55 - 58 °C; R_f – 0.44 (5% MeOH in CH_2Cl_2); υ_{max} /cm^{-1} ($CHCl_3$ soln) 3396, 3043, 2956, 2932, 2859, 1743, 1689, 1520, 1470, 1322, 1259, 1129, 1050, 1011 and 835; [Diastereoisomer denoted with *] ^{1}H NMR (400 MHz, $CDCl_3$) 8.70 (1 H, br. s., *NH* and *NH**), 7.51 (0.5 H, d, *J* 1.1, $C^6\mathit{H}$), 7.47 (0.5 H, d, *J* 1.1, $C^6\mathit{H}$*), 7.37 – 7.15 (5 H, m, *ArH* and

*ArH**), 6.34 – 6.28 (1 H, m, $C^{1'}H$ and $C^{1'}H$*), 4.90 (0.5 H, t, *J* 6.0, $C^{4'}H$), 4.81 (0.5 H, t, *J* 6.5, $C^{4'}H$*), 4.21 (0.5 H, d, *J* 1.5, $C^{3'}H$), 4.15 (0.5 H, d, *J* 1.0, $C^{3'}H$*), 4.15 – 4.10 (0.5 H, m, *NH*), 4.09 – 4.00 (0.5 H, m, *NH*), 3.85 (1 H, app. td, *J* 5.9 and 2.1, PhCH_2 and PhCH_2*), 3.77 (1.5 H, s, CO_2Me), 3.75 (1.5 H, s, CO_2Me*), 3.60 (1.5 H, d, *J* 11.3, *OMe*), 3.45 (1.5 H, d, *J* 11.3, *OMe**), 3.33 (1 H, td, *J* 10.4 and 7.3, *CH* and *CH**), 3.13-3.04 (1 H, m, $C^{5'}H$ and $C^{5'}H$*), 3.01 – 2.89 (1 H, m, $C^{5'}H$ and $C^{5'}H$*), 2.48 (0.5 H, dd, *J* 13.4 and 5.3, $C^{2'}H_2$), 2.29 (0.5 H, dd, *J* 14.0 and 5.7, $C^{2'}H_2$*), 2.10 – 2.00 (0.5 H, m, $C^{2'}H_2$), 2.00-1.93 (0.5 H, m, $C^{2'}H_2$*), 1.93 (3 H, s, CH_3 and CH_3*), 0.94 (4.5 H, s, $(CH_3)_3CSiMe_2$), 0.93 (4.5 H, s, $(CH_3)_3CSiMe_2$*) and 0.14 – 0.11(6 H, m, $(CH_3)_3CSiMe_2$ and $(CH_3)_3CSiMe_2$*); ^{13}C NMR (100 MHz, $CDCl_3$) 173.0 (C and C*), 163.54 (C), 163.53 (C*), 150.19 (C), 150.16 (C*), 135.9 (C), 135.8 (C*), 135.1 (CH and CH*), 129.5 (CH), 129.4 (CH*), 128.63 (CH), 128.59 (CH*), 127.18 (CH and CH*), 111.05 (C and C*), 86.1 (d, *J* 4, CH), 85.8 (d, *J* 5, CH*), 84.55 (CH), 84.54 (CH*), 77.9 (d, *J* 6, CH), 77.4 (d, *J* 5, CH*), 63.4 (CH_2), 63.3 (CH_2*), 55.8 (C), 55.6 (CH*), 53.3 (d, *J* 5, CH_3), 53.1 (d, *J* 5, CH_3*), 52.4 (CH_3), 52.3 (CH_3*), 40.43 (CH_2), 40.36 (CH_2*), 39.4 (d, *J* 5, CH_2), 39.2 (d, *J* 5, CH_2*), 25.9 (CH_3 and CH_3*), 18.3 (C and C*) and 12.5 (CH_3 and CH_3*); ^{31}P NMR (161 MHz, $CDCl_3$) 8.06 and 7.63; HRMS *m/z* (ES^+) Found M + Na 634.2325. $C_{27}H_{42}N_3O_9PSiNa$ requires 634.2320.

ELECTRONIC SUPPORTING INFORMATION



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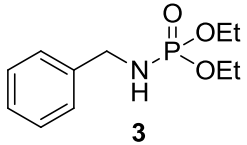
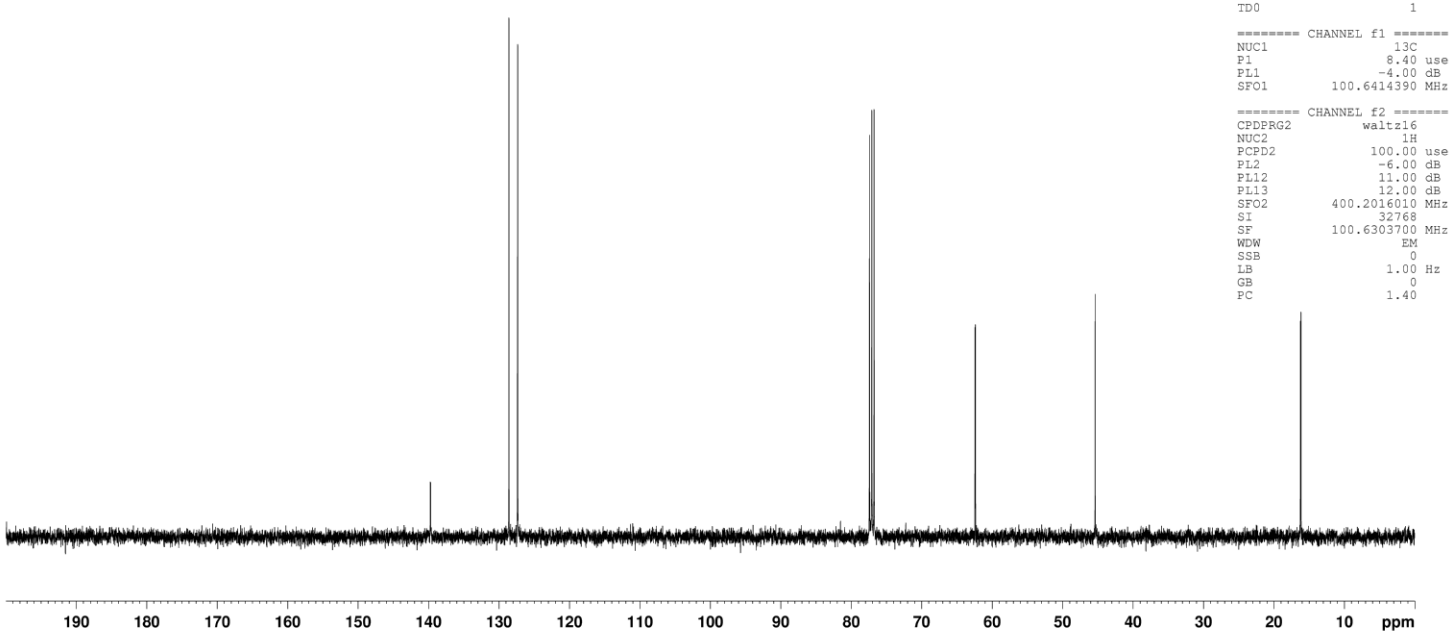


3

^{13}C NMR

$CDCl_3$

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NS                     128
DS                       2
SWH             25125.629 Hz
FIDRES          0.766773 Hz
AQ              0.6521332 sec
RG                 5160.6
DW                 19.900 use
DE                   6.00 use
TE                 298.0 K
D1            1.00000000 sec
d11           0.03000000 sec
DELTA         0.89999998 sec
TD0                     1

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PL1                 -4.00 dB
SFO1         100.6414390 MHz

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NUC2                  1H
PCPD2              100.00 use
PL2                 -6.00 dB
PL12                11.00 dB
PL13                12.00 dB
SFO2         400.2016010 MHz
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SSB                     0
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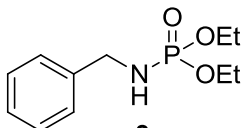
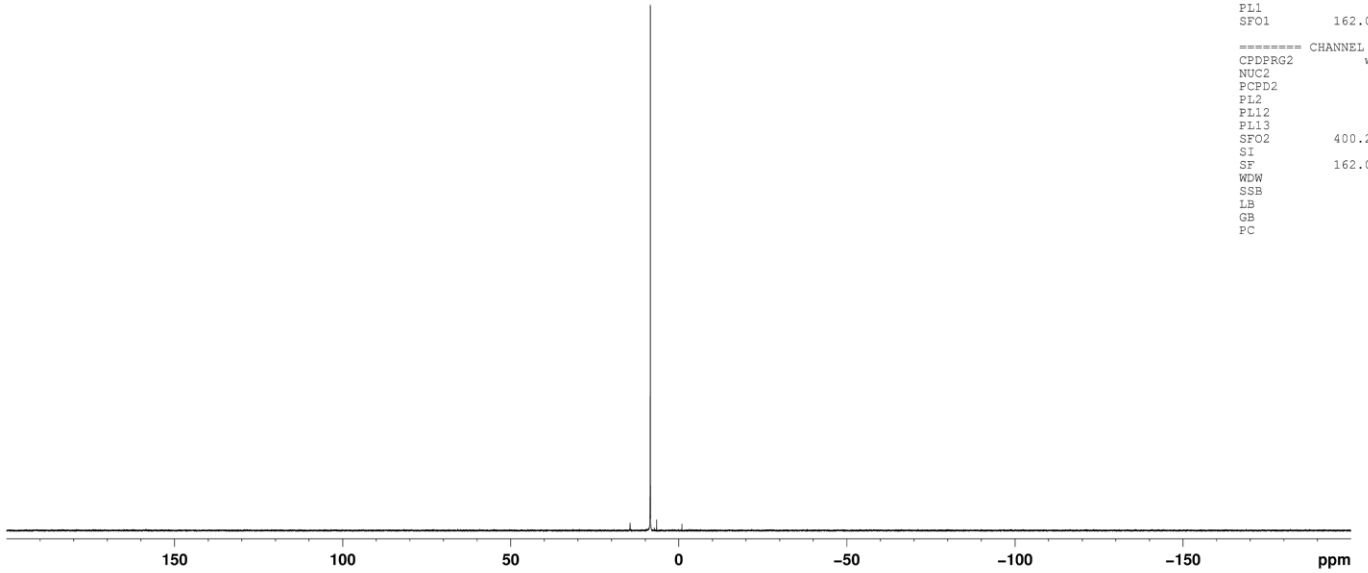
ELECTRONIC SUPPORTING INFORMATION



3

^{31}P NMR

$CDCl_3$

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SOLVENT             CDCl3
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DS                      2
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FIDRES          1.113780 Hz
AQ              0.4489716 sec
RG                20642.5
DW                  6.850 use
DE                  6.00 use
TE                298.1 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                     1

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P1                 11.80 use
PL1                 1.00 dB
SFO1         162.0039290 MHz

======== CHANNEL f2 =======
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NUC2                1H
PCPD2             100.00 use
PL2                -6.00 dB
PL12               11.00 dB
PL13               12.00 dB
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SI                  32768
SF           162.0039290 MHz
WDW                    EM
SSB                     0
LB                  1.00 Hz
GB                      0
PC                  1.40
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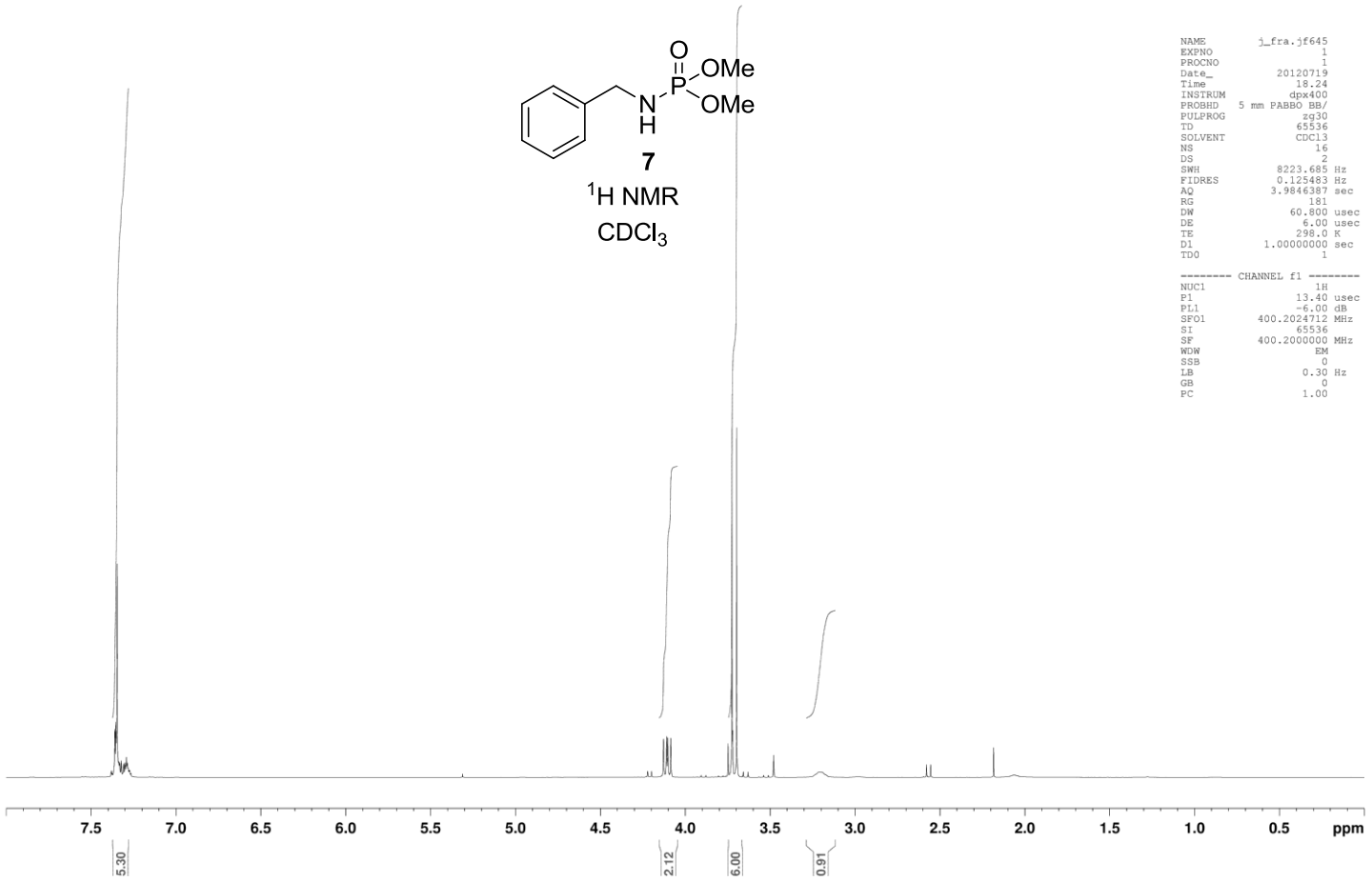

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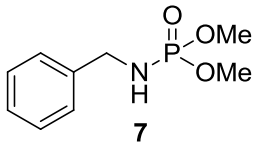
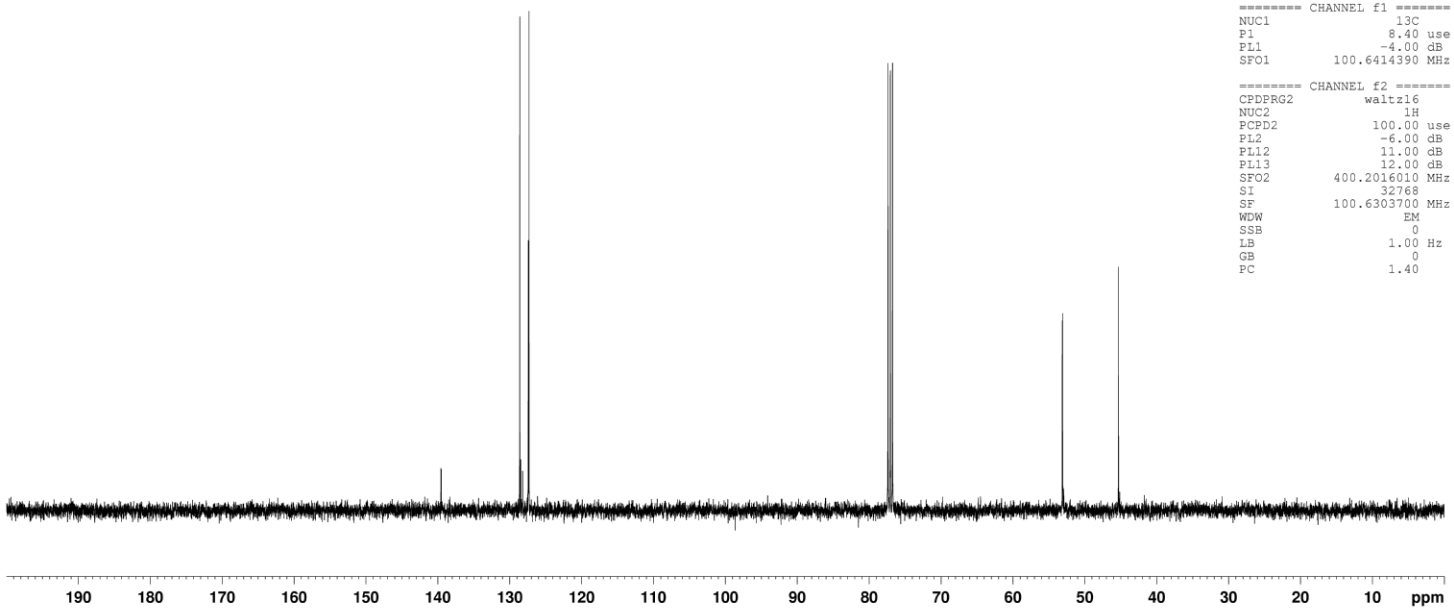


7

^{13}C NMR

$CDCl_3$

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Time                18.37
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PULPROG          zgpg30
TD                  32768
SOLVENT             CDCl3
NS                    128
DS                      2
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FIDRES          0.766773 Hz
AQ              0.6521332 sec
RG                   8192
DW                 19.900 use
DE                  6.00 use
TE                298.0 K
D1           1.00000000 sec
d11          0.03000000 sec
DELTA        0.89999998 sec
TD0                     1

======== CHANNEL f1 =======
NUC1                  13C
P1                   8.40 use
PL1                 -4.00 dB
SFO1         100.6414390 MHz

======== CHANNEL f2 =======
CPDPRG2           waltz16
NUC2                  1H
PCPD2              100.00 use
PL2                 -6.00 dB
PL12                11.00 dB
PL13                12.00 dB
SFO2         400.2016010 MHz
SI                  32768
SF           100.6303700 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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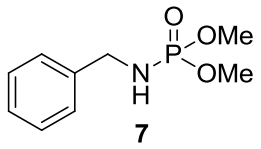
ELECTRONIC SUPPORTING INFORMATION



7

^{31}P NMR

$CDCl_3$

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PROCNO                  1
Date_            20120719
Time                18.31
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PULPROG          zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    128
DS                      2
SWH             72992.703 Hz
FIDRES          1.113780 Hz
AQ              0.4489716 sec
RG                20642.5
DW                  6.850 use
DE                  6.00 use
TE                298.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1

======== CHANNEL f1 =======
NUC1                31P
P1                 11.80 use
PL1                 1.00 dB
SFO1         162.0039290 MHz

======== CHANNEL f2 =======
CPDPRG2          waltz16
NUC2                1H
PCPD2             100.00 use
PL2                -6.00 dB
PL12               11.00 dB
PL13               12.00 dB
SFO2         400.2016008 MHz
SI                  32768
SF           162.0039290 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
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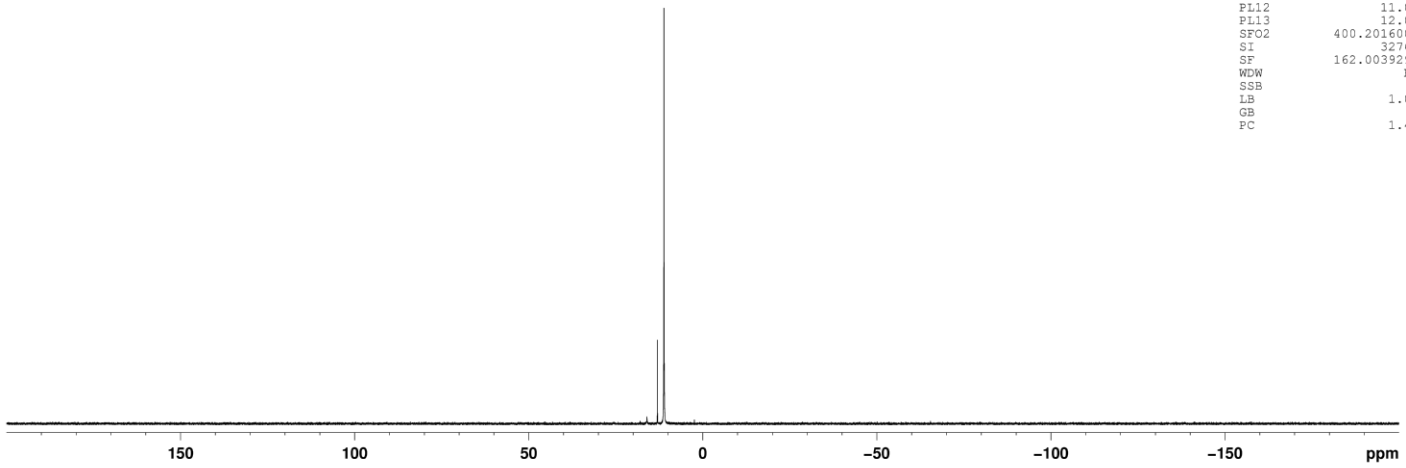

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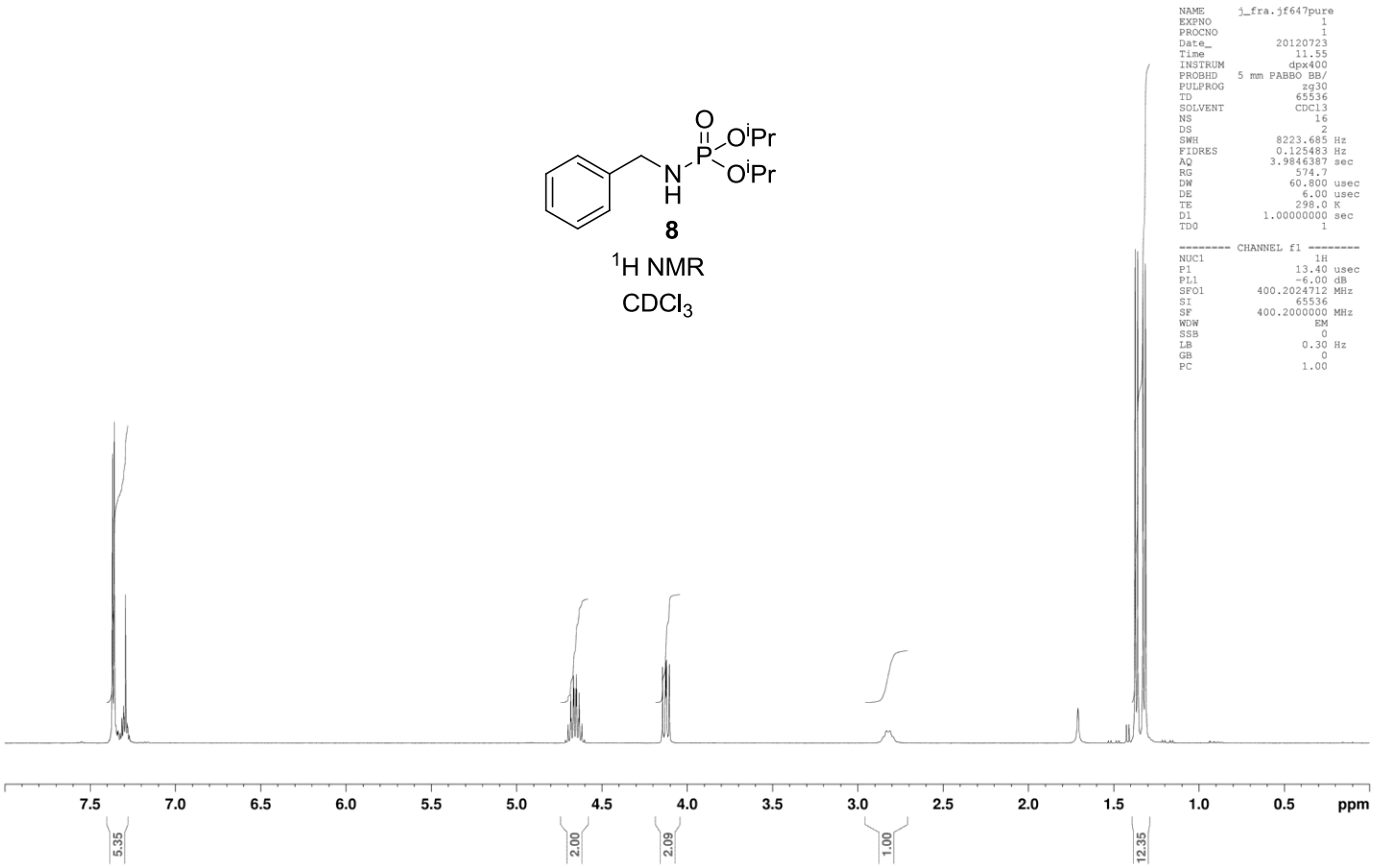

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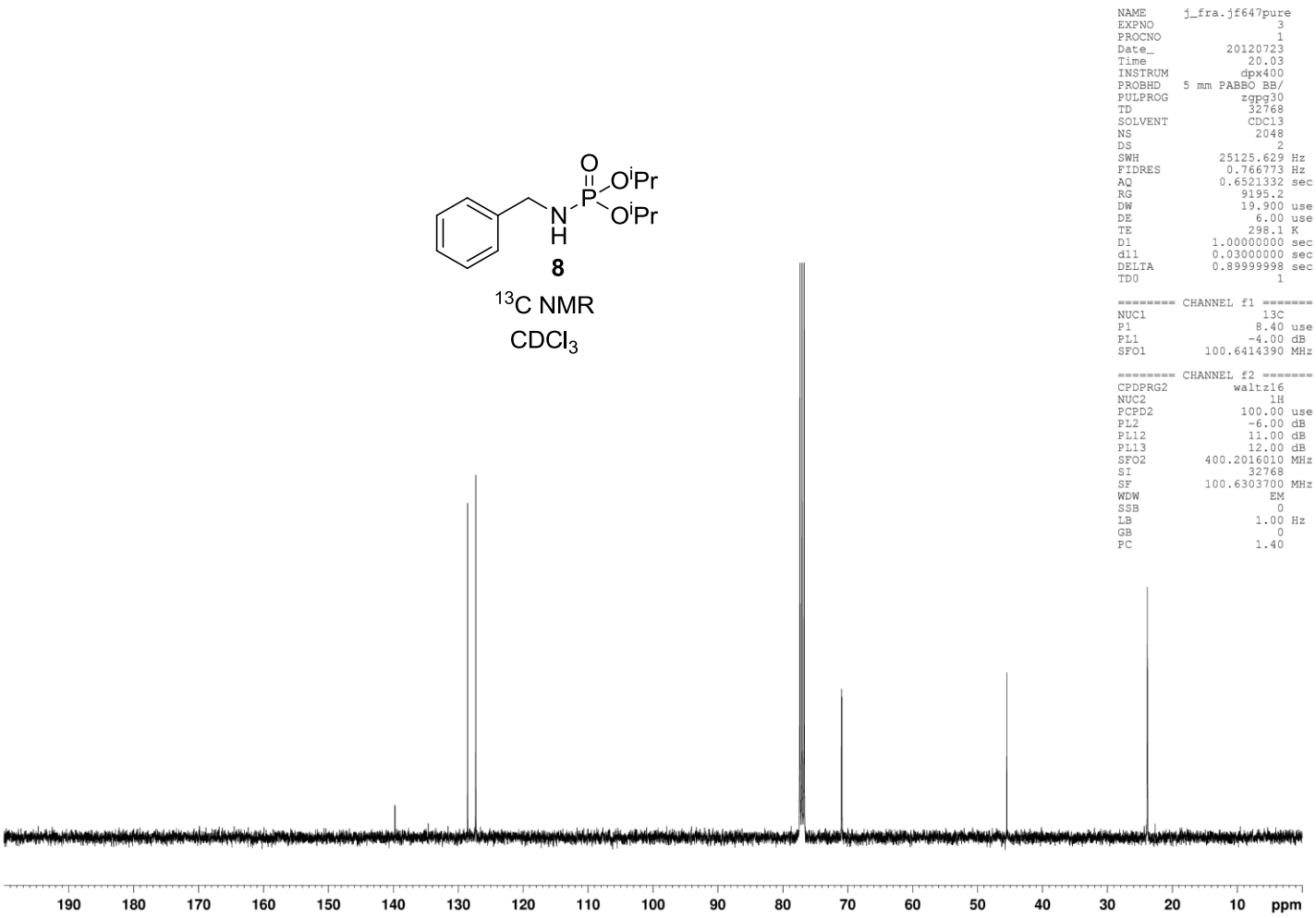

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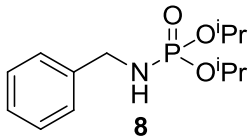

8

^{31}P NMR

$CDCl_3$

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PROCNO                      1
Date_                20120723
Time                    12.02
INSTRUM                 dpx400
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PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         128
DS                           2
SWH                  72992.703 Hz
FIDRES               1.113780 Hz
AQ                   0.4489716 sec
RG                     20642.5
DW                       6.850 use
DE                       6.00 use
TE                      298.1 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
TD0                         1

======== CHANNEL f1 =======
NUC1                       31P
P1                       11.80 use
PL1                       1.00 dB
SFO1              162.0039290 MHz

======== CHANNEL f2 =======
CPDPRG2                waltz16
NUC2                        1H
PCPD2                  100.00 use
PL2                     -6.00 dB
PL12                    11.00 dB
PL13                    12.00 dB
SFO2              400.2016008 MHz
SI                       32768
SF                162.0039290 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
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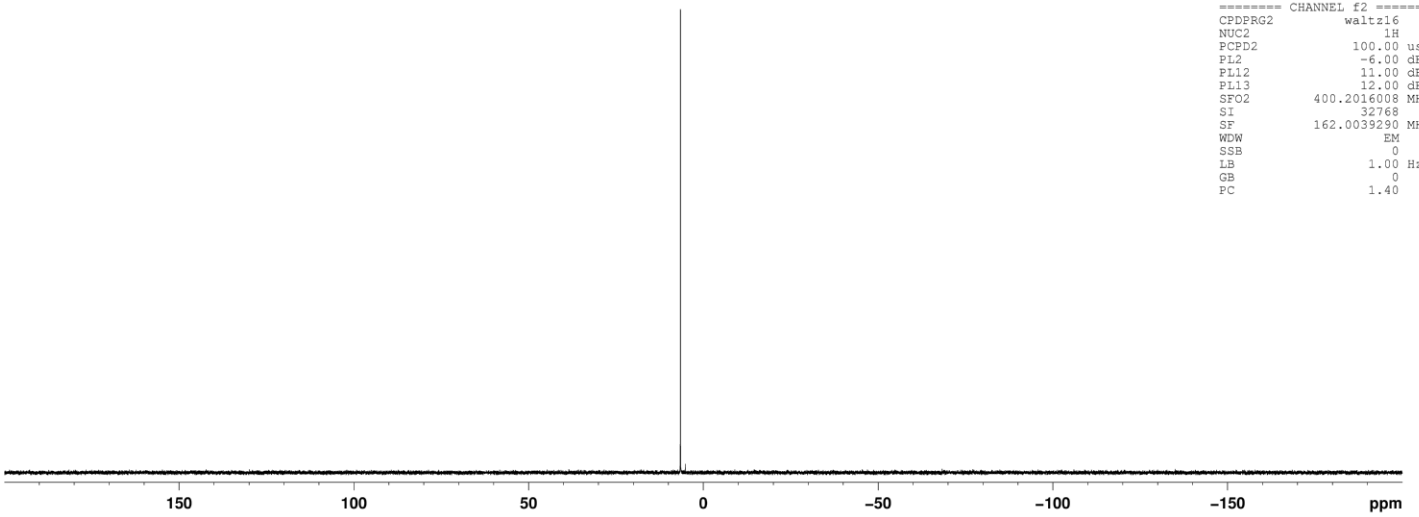

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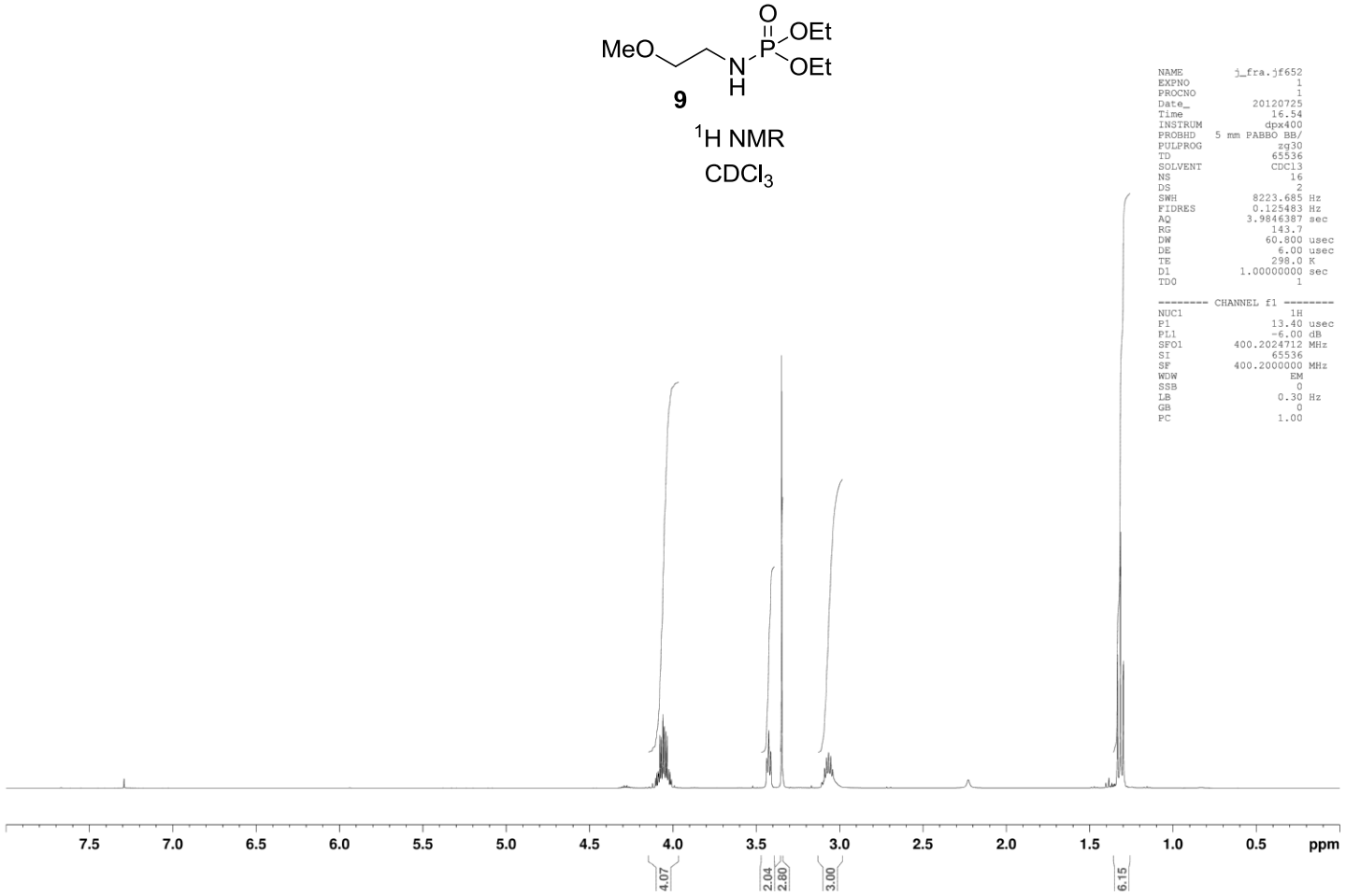

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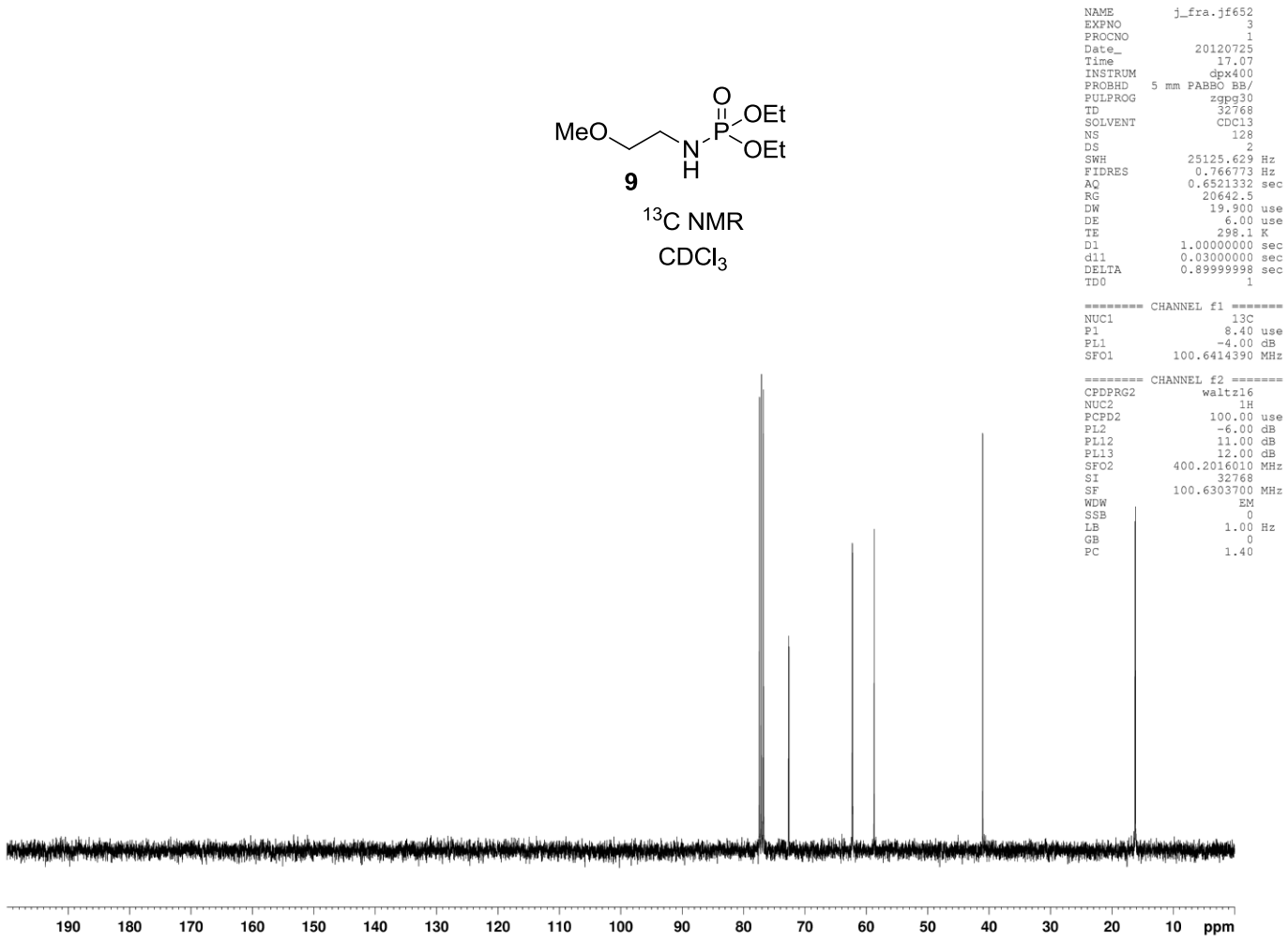

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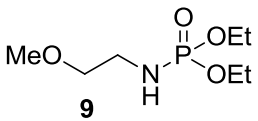

9

^{31}P NMR

$CDCl_3$

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PROCNO                  1
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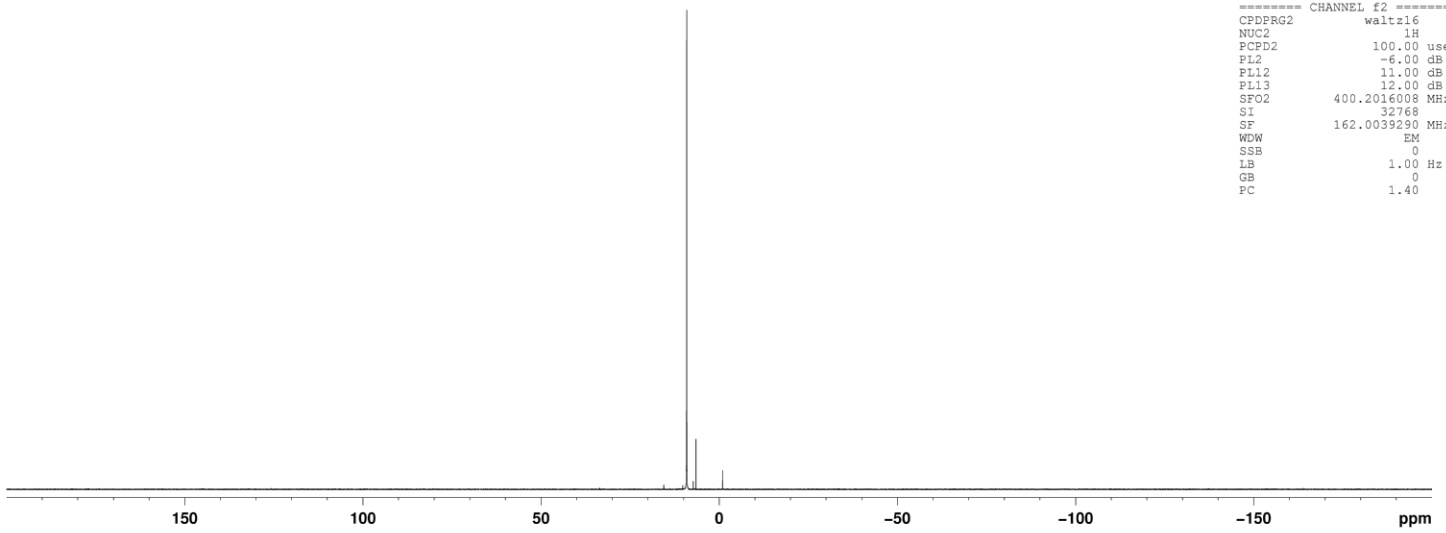
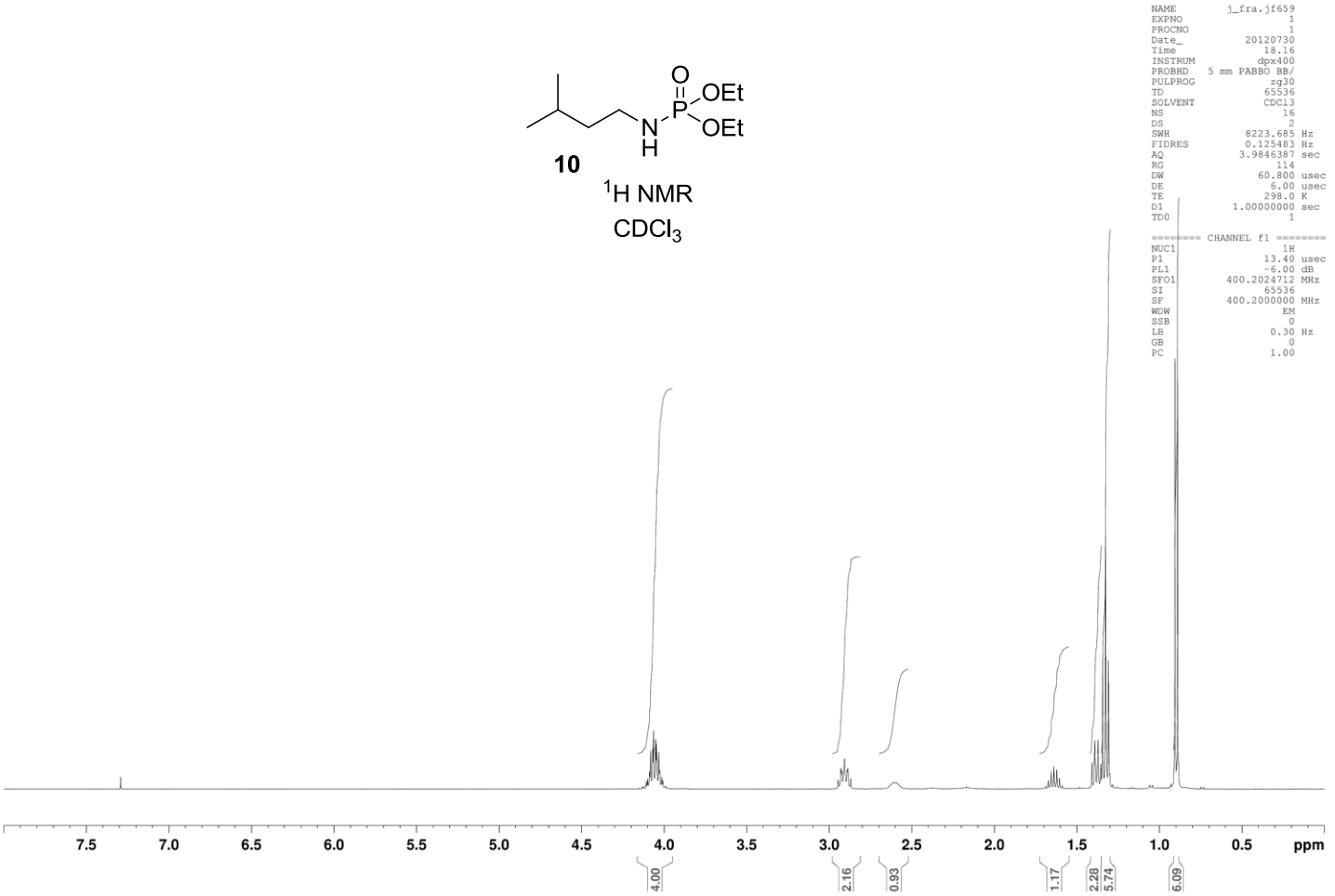
PULPROG           zgpg30
TD                 65536
SOLVENT             CDCl3
NS                    128
DS                      2
SWH             72992.703 Hz
FIDRES          1.113780 Hz
AQ              0.4489716 sec
RG                20642.5
DW                  6.850 use
DE                  6.00 use
TE                298.1 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                     1

======== CHANNEL f1 =======
NUC1                  31P
P1                  11.80 use
PL1                  1.00 dB
SFO1         162.0039290 MHz

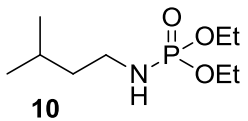
======== CHANNEL f2 =======
CPDPRG2           waltz16
NUC2                  1H
PCPD2              100.00 use
PL2                 -6.00 dB
PL12                11.00 dB
PL13                12.00 dB
SFO2         400.2016008 MHz
SI                  32768
SF           162.0039290 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



ELECTRONIC SUPPORTING INFORMATION



ELECTRONIC SUPPORTING INFORMATION



10

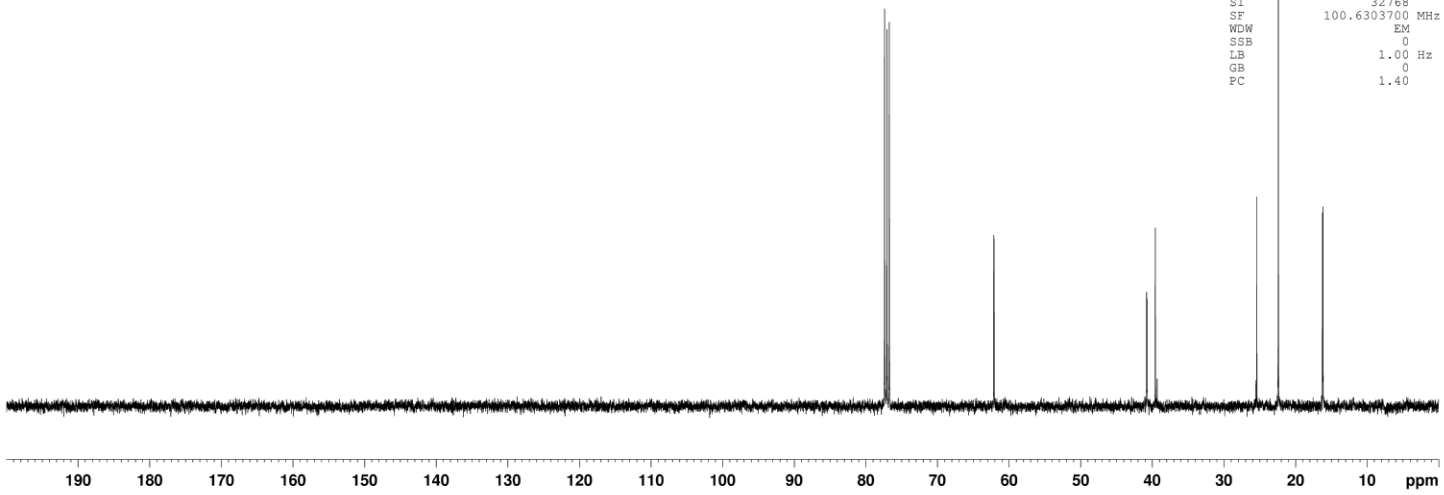
^{13}C NMR

$CDCl_3$

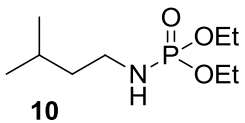
```
NAME          j_fra.jf659
EXPNO                   3
PROCNO                  1
Date_            20120730
Time                18.29
INSTRUM           dpx400
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 32768
SOLVENT             CDCl3
NS                    128
DS                      2
SWH             25125.629 Hz
FIDRES          0.766773 Hz
AQ              0.6521332 sec
RG                   6502
DW                 19.900 use
DE                  6.00 use
TE                298.0 K
D1             1.00000000 sec
d11            0.03000000 sec
DELTA          0.89999998 sec
TD0                     1

======== CHANNEL f1 =======
NUC1                  13C
P1                   8.40 use
PL1                 -4.00 dB
SFO1         100.6414390 MHz

======== CHANNEL f2 =======
CPDPRG2           waltz16
NUC2                  1H
PCPD2              100.00 use
PL2                 -6.00 dB
PL12                11.00 dB
PL13                12.00 dB
SFO2         400.2016010 MHz
SI                 32768
SF           100.6303700 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



ELECTRONIC SUPPORTING INFORMATION



10

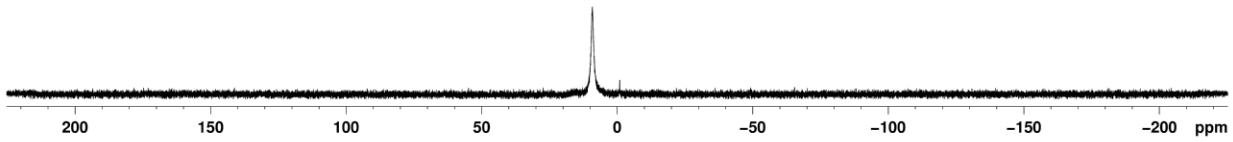
^{31}P NMR

$CDCl_3$

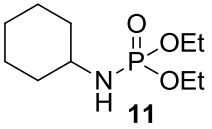
```
NAME          j_fra.jf659
EXPNO                   2
PROCNO                  1
Date_            20120730
Time                18.23
INSTRUM           dpx400
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     2
SWH            72992.703 Hz
FIDRES         1.113780 Hz
AQ             0.4489716 sec
RG               20642.5
DW                 6.850 use
DE                 6.00 use
TE                298.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 =======
NUC1                 31P
P1                 11.80 use
PL1                 1.00 dB
SFO1        162.0039290 MHz

======== CHANNEL f2 =======
CPDPRG2          waltz16
NUC2                 1H
PCPD2             100.00 use
PL2                -6.00 dB
PL12               11.00 dB
PL13               12.00 dB
SFO2        400.2016008 MHz
SI                 32768
SF          162.0039290 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



ELECTRONIC SUPPORTING INFORMATION

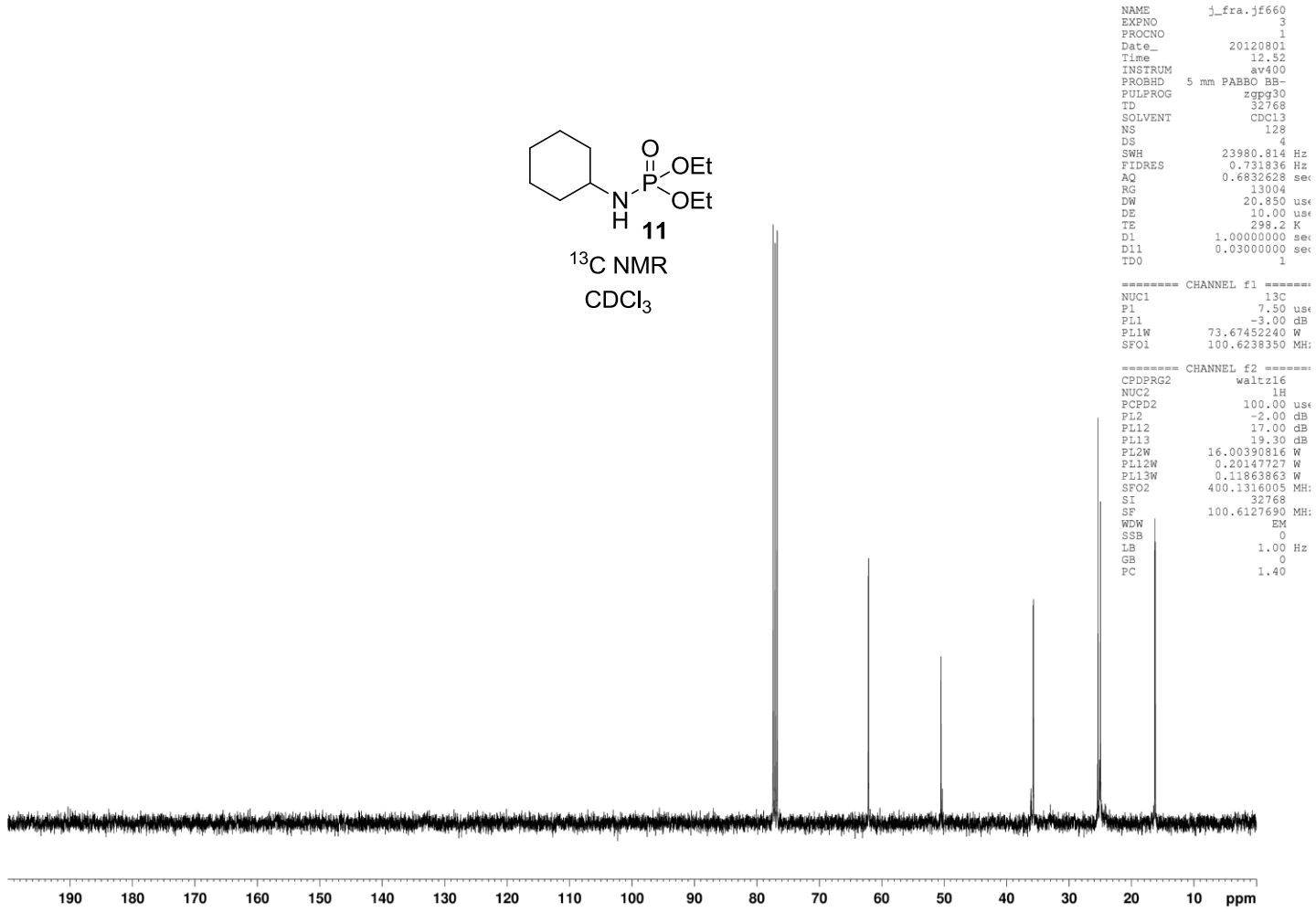


11

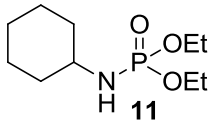
^{1}H NMR

$CDCl_3$

ELECTRONIC SUPPORTING INFORMATION



ELECTRONIC SUPPORTING INFORMATION



11

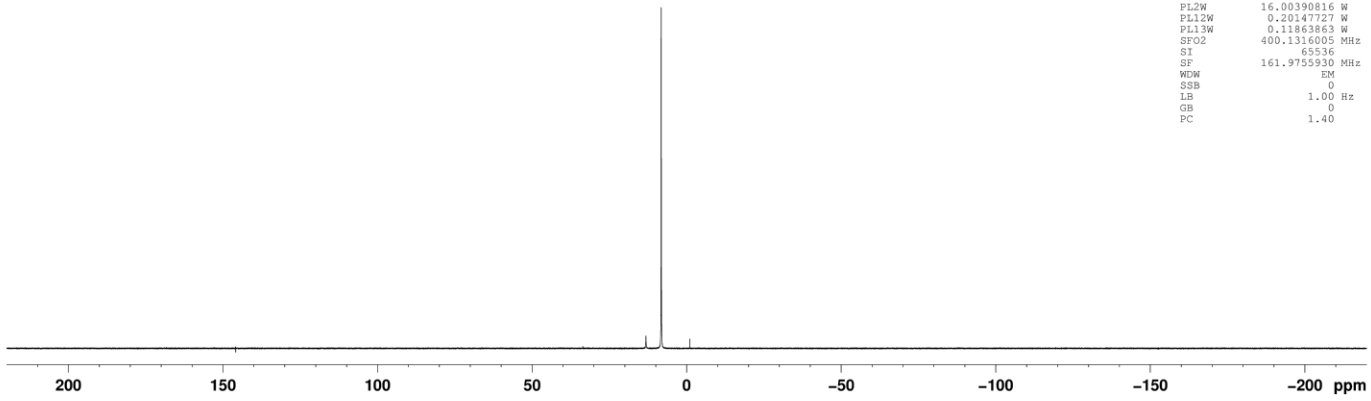
^{31}P NMR

$CDCl_3$

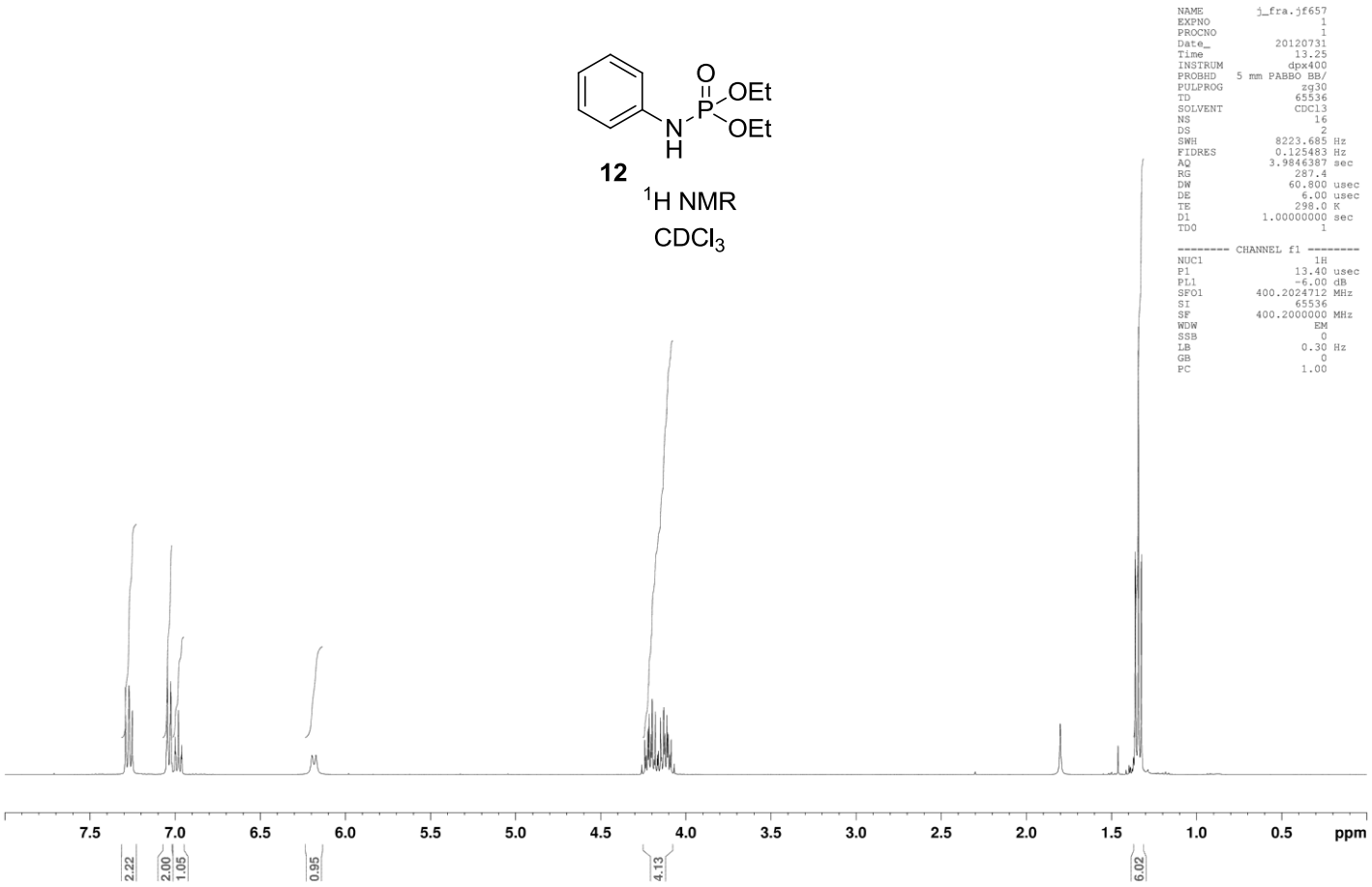
```
NAME          j_fra.jf660
EXPNO                   2
PROCNO                  1
Date_            20120801
Time                12.46
INSTRUM             av400
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    128
DS                      2
SWH             72992.703 Hz
FIDRES          1.113780 Hz
AQ              0.4489716 sec
RG                11585.2
DW                6.850 usec
DE                6.50 usec
TE                298.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

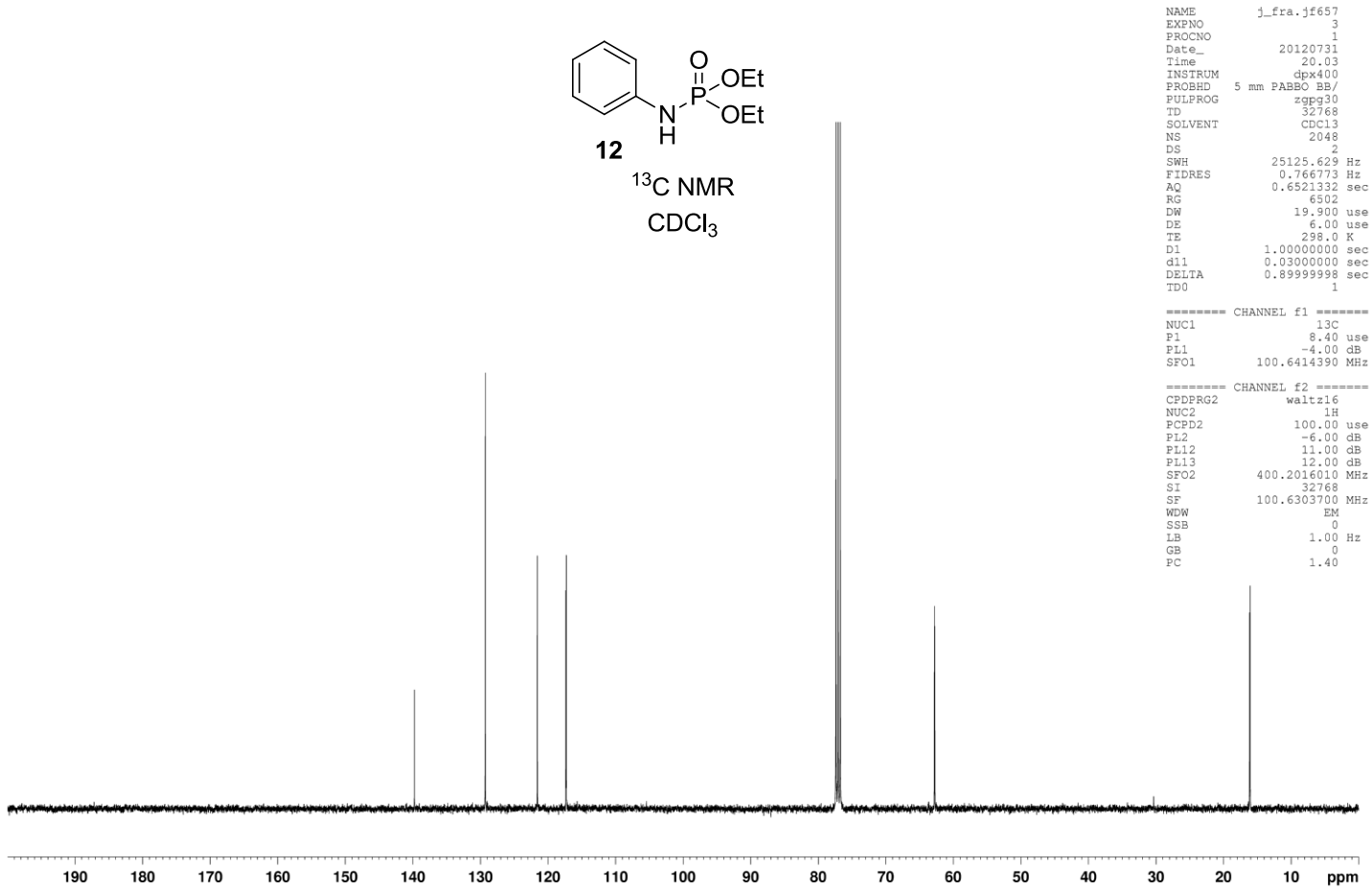
======== CHANNEL f1 ========
NUC1                   31P
P1                  9.00 usec
PL1                 0.00 dB
PL1W          27.88193893 W
SFO1          161.9755929 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2             100.00 usec
PL2                -2.00 dB
PL12               17.00 dB
PL13               19.30 dB
PL2W          16.00390816 W
PL12W          0.20147727 W
PL13W          0.11863863 W
SFO2          400.1316005 MHz
SI                  65536
SF            161.9755930 MHz
WDW                    EM
SSB                     0
LB                  1.00 Hz
GB                      0
PC                  1.40
```

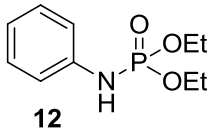


ELECTRONIC SUPPORTING INFORMATION





ELECTRONIC SUPPORTING INFORMATION



12

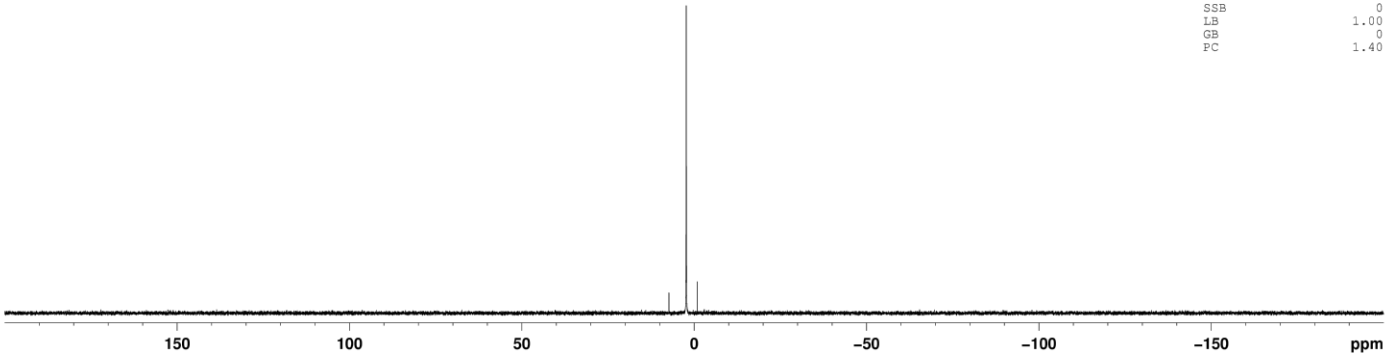
^{31}P NMR

$CDCl_3$

```
NAME            j_fra.jf657
EXPNO                     2
PROCNO                    1
Date_              20120731
Time                  13.32
INSTRUM             dpx400
PROBHD    5 mm PABBO BB/
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     128
DS                       2
SWH              72992.703 Hz
FIDRES           1.113780 Hz
AQ               0.4489716 sec
RG                 20642.5
DW                   6.850 use
DE                   6.00 use
TE                  297.9 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                      1

======== CHANNEL f1 =======
NUC1                   31P
P1                   11.80 use
PL1                   1.00 dB
SFO1         162.0039290 MHz

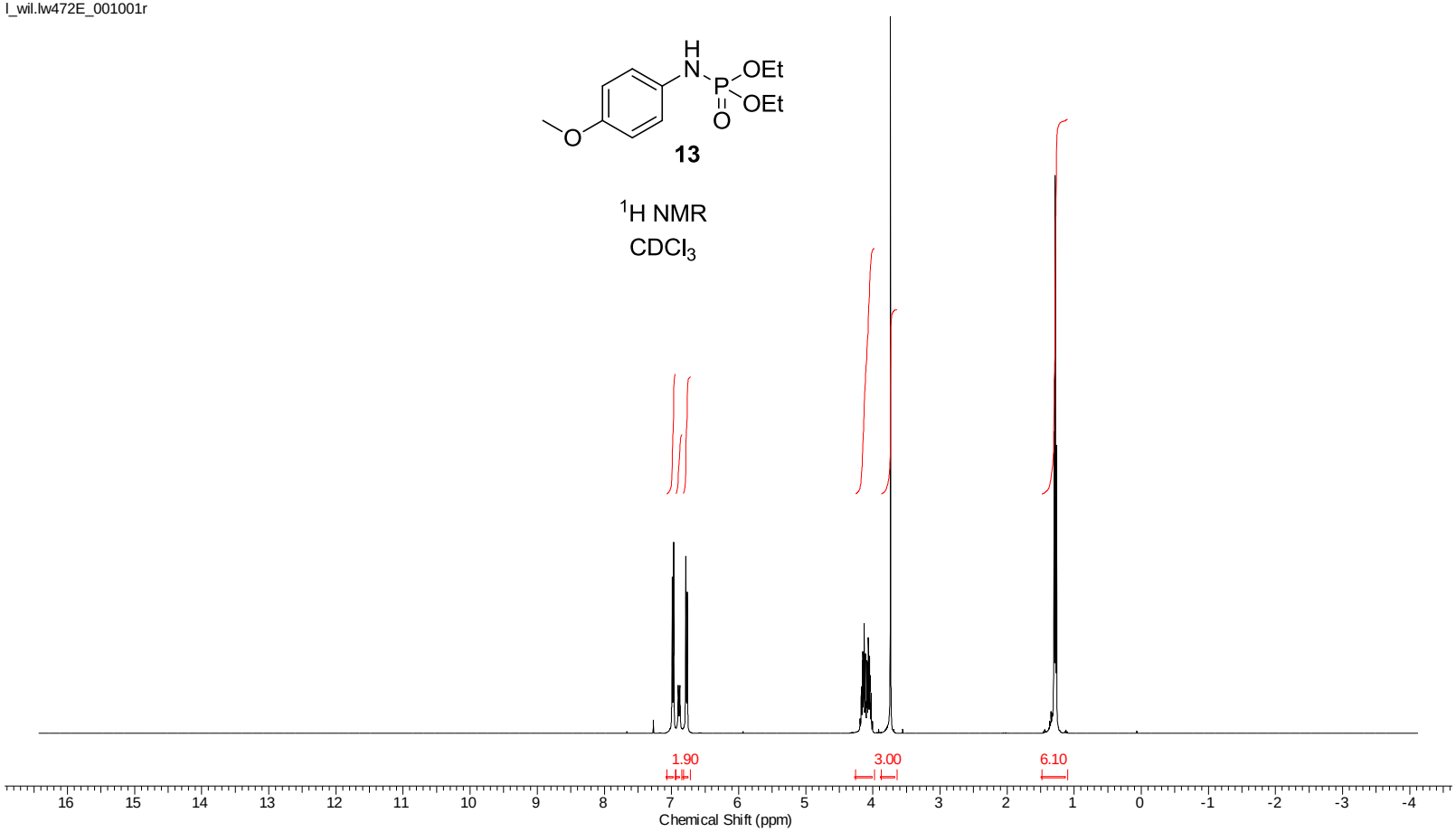
======== CHANNEL f2 =======
CPDPRG2            waltz16
NUC2                   1H
PCPD2               100.00 use
PL2                  -6.00 dB
PL12                 11.00 dB
PL13                 12.00 dB
SFO2         400.2016008 MHz
SI                   32768
SF           162.0039290 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



ELECTRONIC SUPPORTING INFORMATION

Acquisition Time (sec)	3.9846	***Comment***	Slot No. 2 Sample ID lw472E SupervisorID hayes Lab Phone No. 13536 UserID l_wil				
Date	27 Feb 2013 08:49:04			***Date Stamp***	27 Feb 2013 08:49:04		
File Name	\\brukdpx400\nmr_data\l_wil\nmr\l_wil.lw472E\1\pdata\1\1r			***Frequency (MHz)***	400.20	***Nucleus***	1H
Number of Transients	16	***Origin***	dpx400	***Original Points Count***	32768	***Owner***	nmruser
Points Count	65536	***Pulse Sequence***	zg30	***Receiver Gain***	64.00	***SW(cyclical) (Hz)***	8223.68
Solvent	CHLOROFORM-d			***Spectrum Offset (Hz)***	2462.7957	***Spectrum Type***	STANDARD
Sweep Width (Hz)	8223.56	***Temperature (degree C)***	25.000				

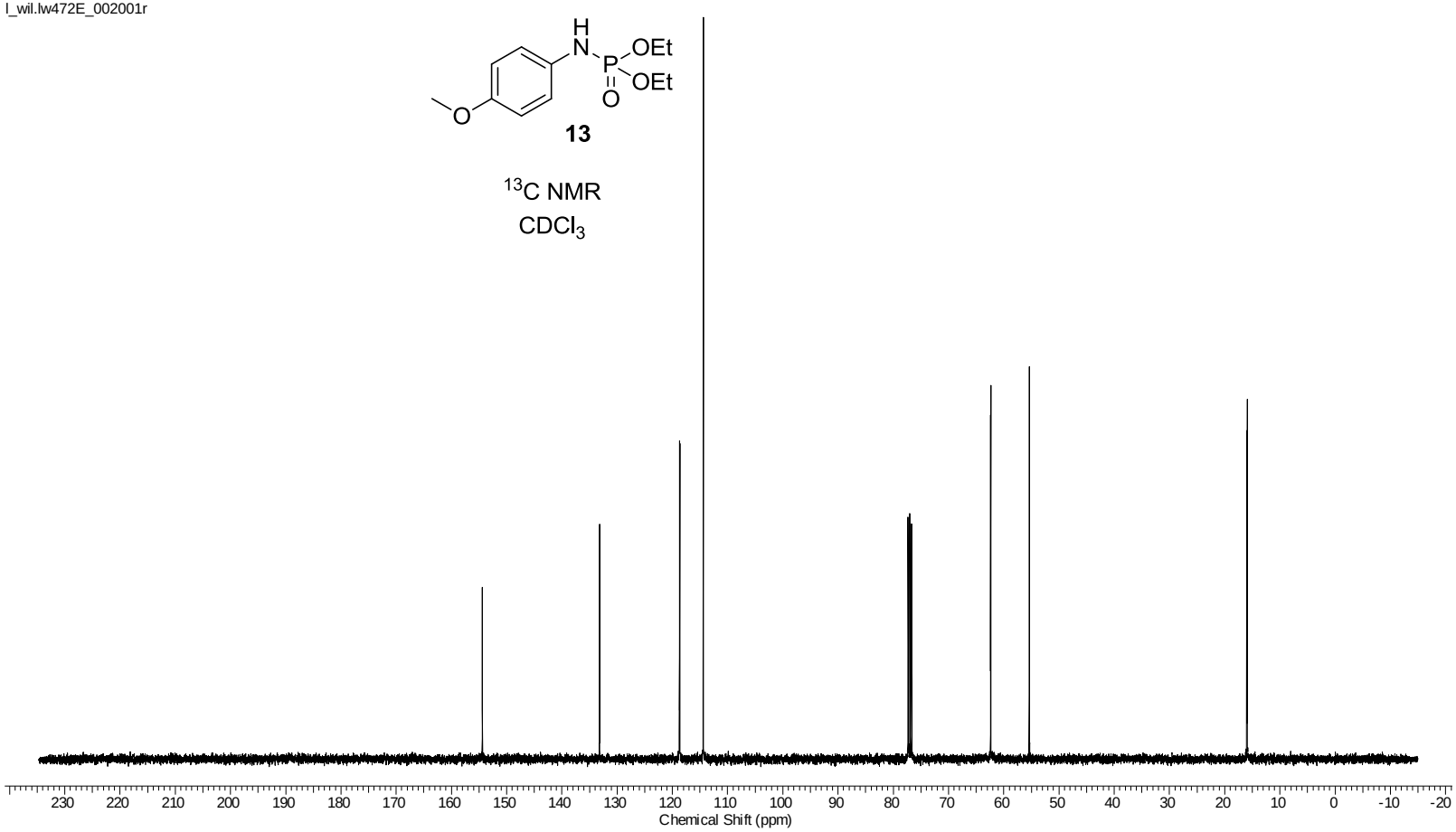
l_wil.lw472E_001001r



ELECTRONIC SUPPORTING INFORMATION

Acquisition Time (sec)	0.6521	***Comment***	Slot No. 55 Sample ID lw472E SupervisorID hayes Lab Phone No. 13536 UserID l_wil				
Date	27 Feb 2013 09:48:48			***Date Stamp***	27 Feb 2013 09:48:48		
File Name	\\brukdpx400\nmr_data\l_wil\nmr\l_wil.lw472E\2\pdata\1\1r			***Frequency (MHz)***	100.63	***Nucleus***	13C
Number of Transients	128	***Origin***	dpx400	***Original Points Count***	16384	***Owner***	nmruser
Points Count	32768	***Pulse Sequence***	zgpg30	***Receiver Gain***	20642.50	***SW(cyclical) (Hz)***	25125.63
Solvent	CHLOROFORM-d	***Spectrum Offset (Hz)***	11056.7822	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	25124.86
Temperature (degree C)	25.000						

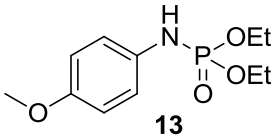
l_wil.lw472E_002001r



ELECTRONIC SUPPORTING INFORMATION

Acquisition Time (sec)	0.4489	***Comment***	Slot No. 55 Sample ID lw472E SupervisorID hayes Lab Phone No. 13536 UserID l_wil				
Date	27 Feb 2013 10:03:44			***Date Stamp***	27 Feb 2013 10:03:44		
File Name	\\brukdpx400\nmr_data\l_wil\nmr\l_wil.lw472E\5\pdata\1\1r			***Frequency (MHz)***	162.00	***Nucleus***	31P
Number of Transients	128	***Origin***	dpx400	***Original Points Count***	32768	***Owner***	nmruser
Points Count	32768	***Pulse Sequence***	zgpg30	***Receiver Gain***	9195.20	***SW(cyclical) (Hz)***	72992.70
Solvent	CHLOROFORM-d	***Spectrum Offset (Hz)***	0.0054	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	72990.48
Temperature (degree C)	25.000						

l_wil.lw472E_005001r

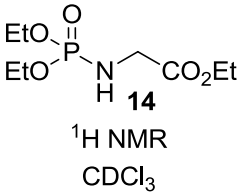


13

^{31}P NMR

$CDCl_3$

ELECTRONIC SUPPORTING INFORMATION

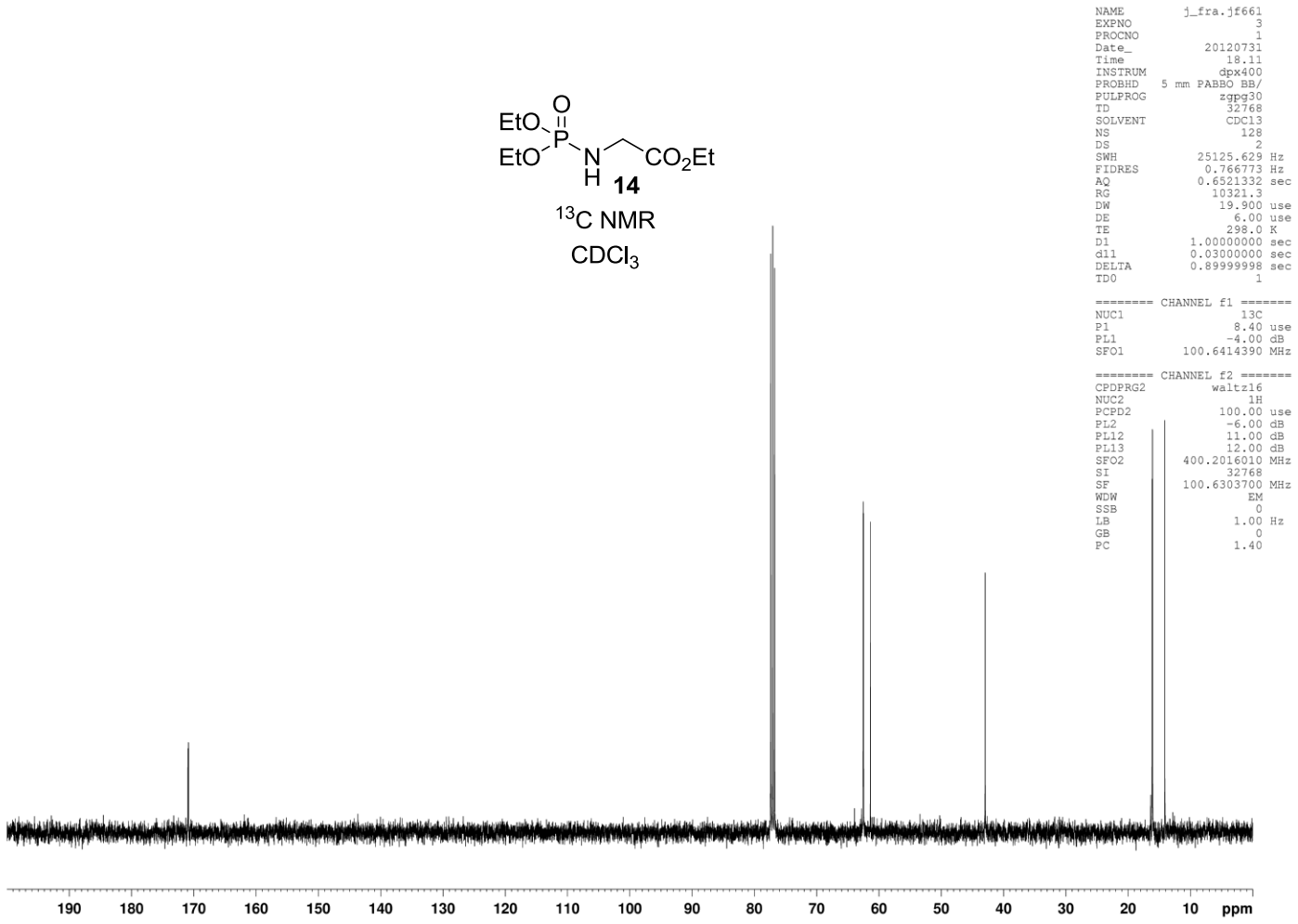


14

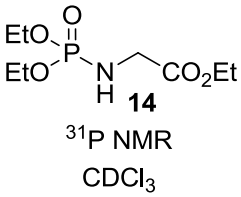
^{1}H NMR

$CDCl_3$

ELECTRONIC SUPPORTING INFORMATION



ELECTRONIC SUPPORTING INFORMATION



14

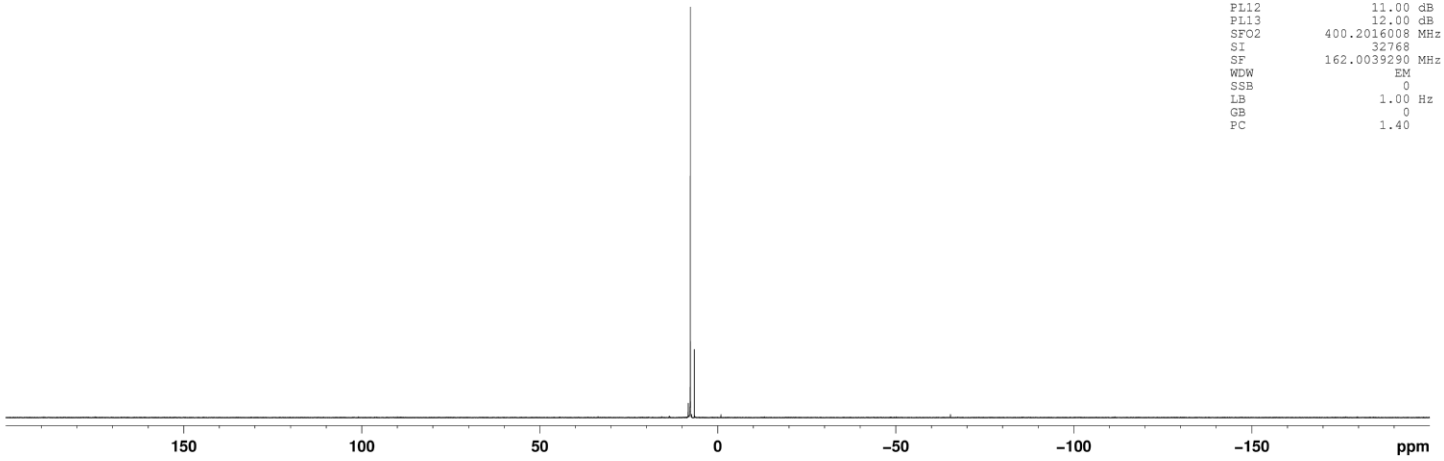
^{31}P NMR

$CDCl_3$

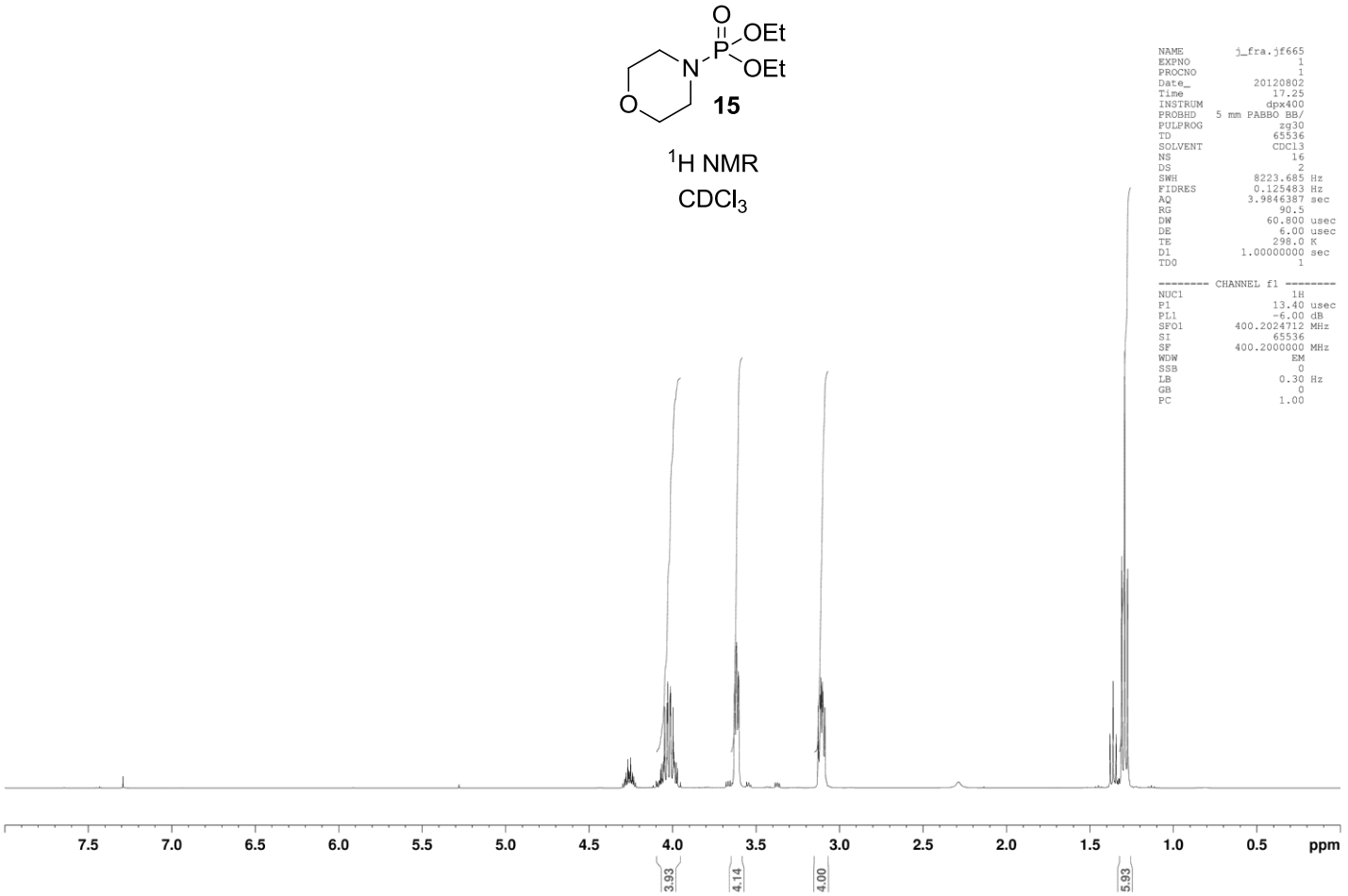
```
NAME          j_fra.jf661
EXPNO                   2
PROCNO                  1
Date_            20120731
Time                18.06
INSTRUM          dpx400
PROBHD    5 mm PABBO BB/
PULPROG          zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    128
DS                      2
SWH             72992.703 Hz
FIDRES          1.113780 Hz
AQ              0.4489716 sec
RG                20642.5
DW                  6.850 use
DE                  6.00 use
TE                298.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                     1

======== CHANNEL f1 =======
NUC1                  31P
P1                 11.80 use
PL1                 1.00 dB
SFO1         162.0039290 MHz

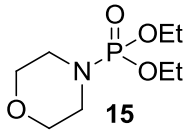
======== CHANNEL f2 =======
CPDPRG2           waltz16
NUC2                  1H
PCPD2              100.00 use
PL2                -6.00 dB
PL12               11.00 dB
PL13               12.00 dB
SFO2         400.2016008 MHz
SI                  32768
SF           162.0039290 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



ELECTRONIC SUPPORTING INFORMATION



ELECTRONIC SUPPORTING INFORMATION



15

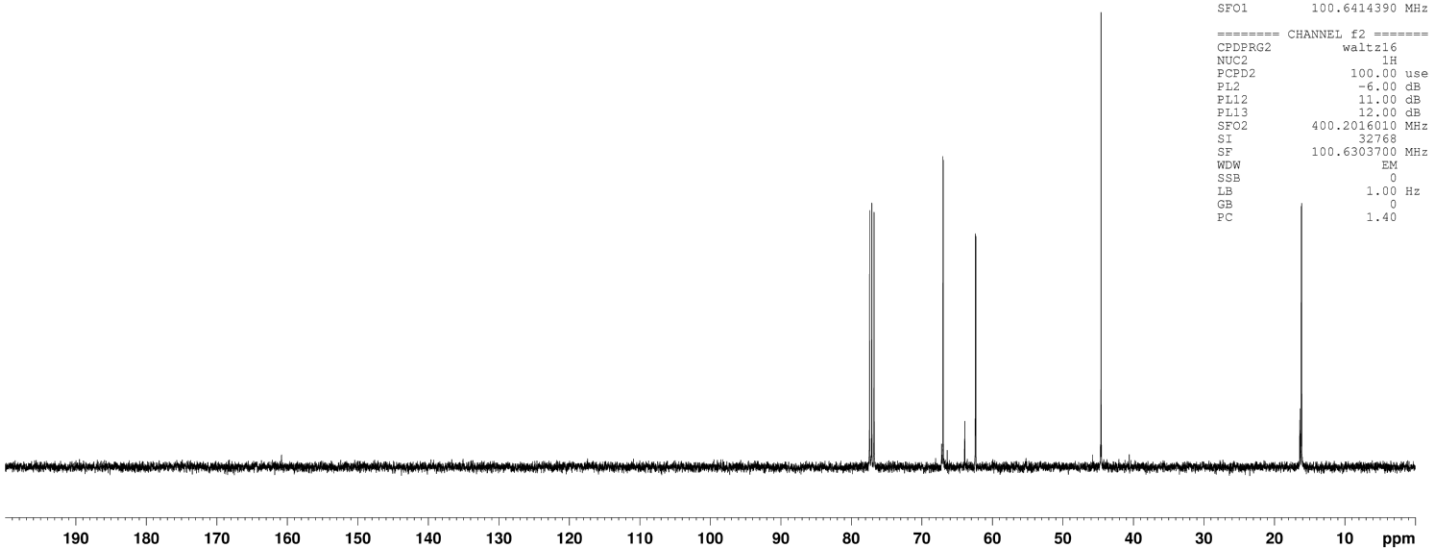
^{13}C NMR

$CDCl_3$

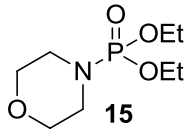
```
NAME          j_fra.jf665
EXPNO                   3
PROCNO                  1
Date_            20120802
Time                17.37
INSTRUM          dpx400
PROBHD    5 mm PABBO BB/
PULPROG          zgpg30
TD                 32768
SOLVENT            CDCl3
NS                   128
DS                     2
SWH            25125.629 Hz
FIDRES         0.766773 Hz
AQ             0.6521332 sec
RG               11585.2
DW                19.900 use
DE                 6.00 use
TE                298.0 K
D1           1.00000000 sec
d11          0.03000000 sec
DELTA        0.89999998 sec
TD0                    1

======== CHANNEL f1 =======
NUC1                  13C
P1                  8.40 use
PL1                -4.00 dB
SFO1         100.6414390 MHz

======== CHANNEL f2 =======
CPDPRG2           waltz16
NUC2                  1H
PCPD2             100.00 use
PL2                -6.00 dB
PL12               11.00 dB
PL13               12.00 dB
SFO2         400.2016010 MHz
SI                 32768
SF           100.6303700 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



ELECTRONIC SUPPORTING INFORMATION



15

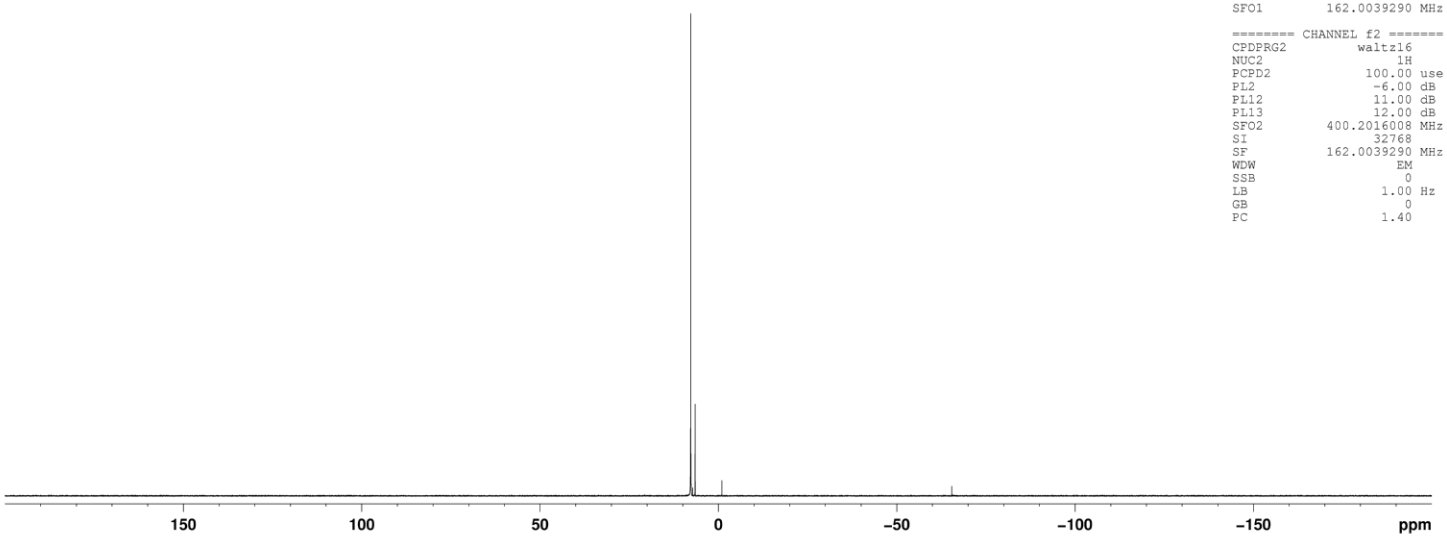
^{31}P NMR

$CDCl_3$

```
NAME          j_fra.jf665R
EXPNO                    2
PROCNO                   1
Date_             20120803
Time                 17.22
INSTRUM              dpx400
PROBHD    5 mm PABBO BB/
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    128
DS                      2
SWH              72992.703 Hz
FIDRES           1.113780 Hz
AQ               0.4489716 sec
RG                 20642.5
DW                   6.850 use
DE                   6.00 use
TE                  298.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                     1

======== CHANNEL f1 =======
NUC1                   31P
P1                   11.80 use
PL1                   1.00 dB
SFO1          162.0039290 MHz

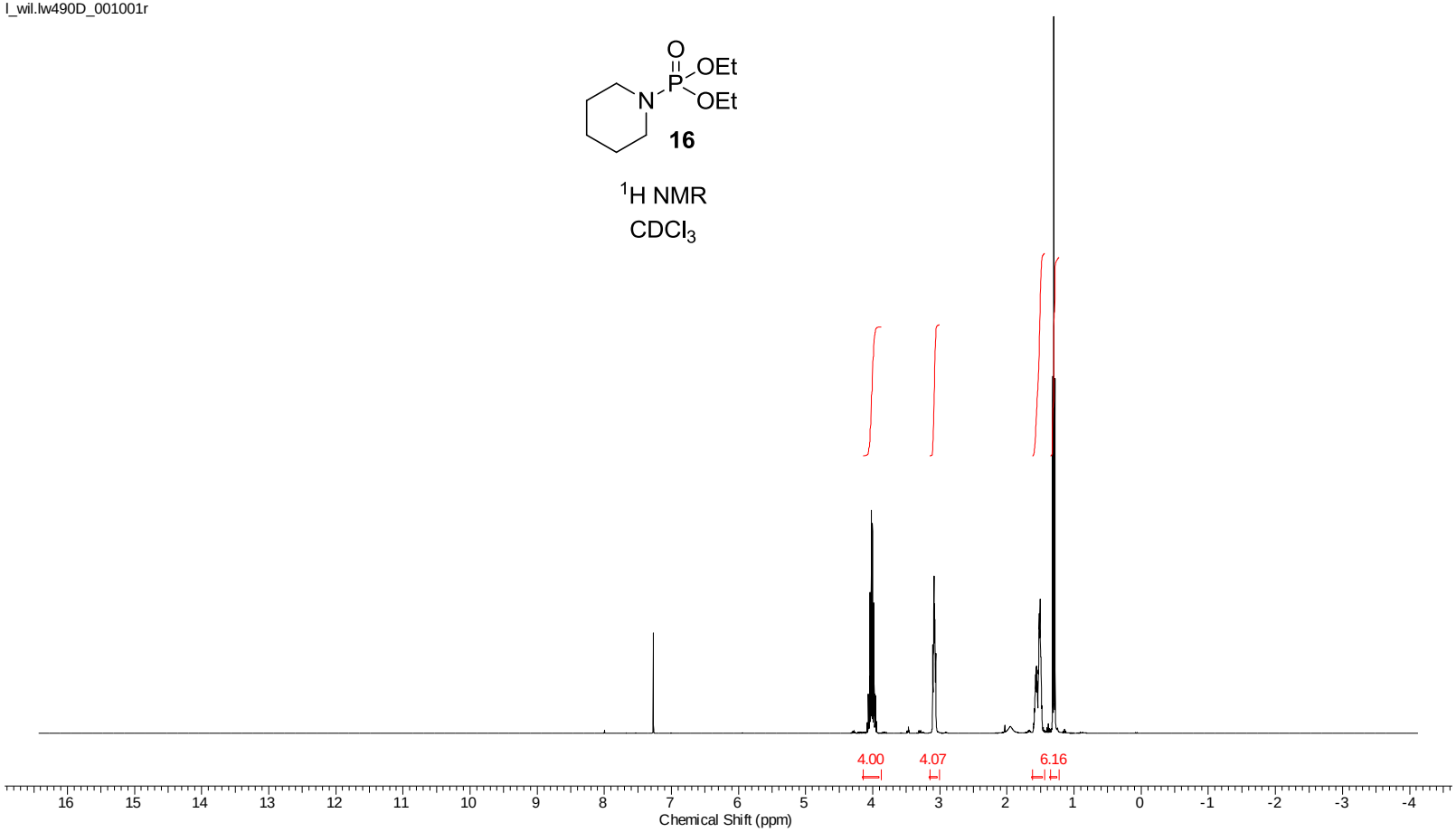
======== CHANNEL f2 =======
CPDPRG2            waltz16
NUC2                    1H
PCPD2               100.00 use
PL2                  -6.00 dB
PL12                 11.00 dB
PL13                 12.00 dB
SFO2          400.2016008 MHz
SI                   32768
SF            162.0039290 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```



ELECTRONIC SUPPORTING INFORMATION

Acquisition Time (sec)	3.9846	***Comment***	Slot No. 25 Sample ID lw490D SupervisorID hayes Lab Phone No. 13536 UserID l_wil				
Date	22 Mar 2013 10:48:32			***Date Stamp***	22 Mar 2013 10:48:32		
File Name	\\brukdpx400\nmr_data\l_wil\nmr\l_wil.lw490D\1\pdata\1\1r			***Frequency (MHz)***	400.20	***Nucleus***	1H
Number of Transients	16	***Origin***	dpx400	***Original Points Count***	32768	***Owner***	nmruser
Points Count	65536	***Pulse Sequence***	zg30	***Receiver Gain***	203.20	***SW(cyclical) (Hz)***	8223.68
Solvent	CHLOROFORM-d	***Spectrum Offset (Hz)***	2462.2937	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	8223.56
Temperature (degree C)	25.000						

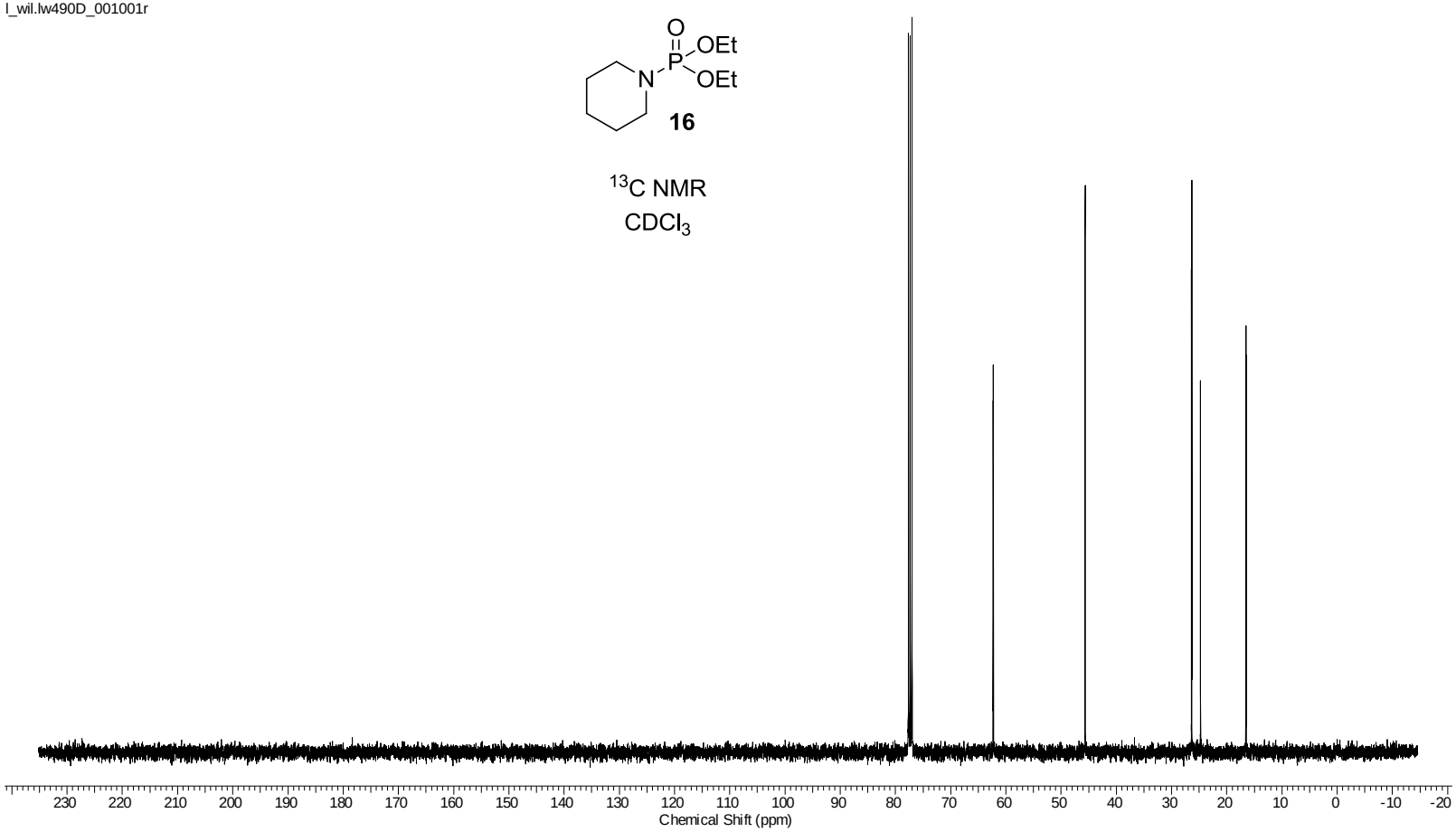
l_wil.lw490D_001001r



ELECTRONIC SUPPORTING INFORMATION

Acquisition Time (sec)	0.6521	***Comment***	UserID l_wil SampleID lw490D SupervisorID hayes Lab Phone No. 13536 Slot Number 9				
Date	23 Mar 2013 06:41:04			***Date Stamp***	23 Mar 2013 06:41:04		
File Name	\\brukav400\nmr_data\l_wil\nmr\l_wil.lw490D\1\pdata\1\1r			***Frequency (MHz)***	100.61	***Nucleus***	13C
Number of Transients	512	***Origin***	av400	***Original Points Count***	16384	***Owner***	nmruser
Points Count	32768	***Pulse Sequence***	zgpg30	***Receiver Gain***	5792.60	***SW(cyclical) (Hz)***	25125.63
Solvent	CHLOROFORM-d	***Spectrum Offset (Hz)***	11094.5332	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	25124.86
Temperature (degree C)	25.160						

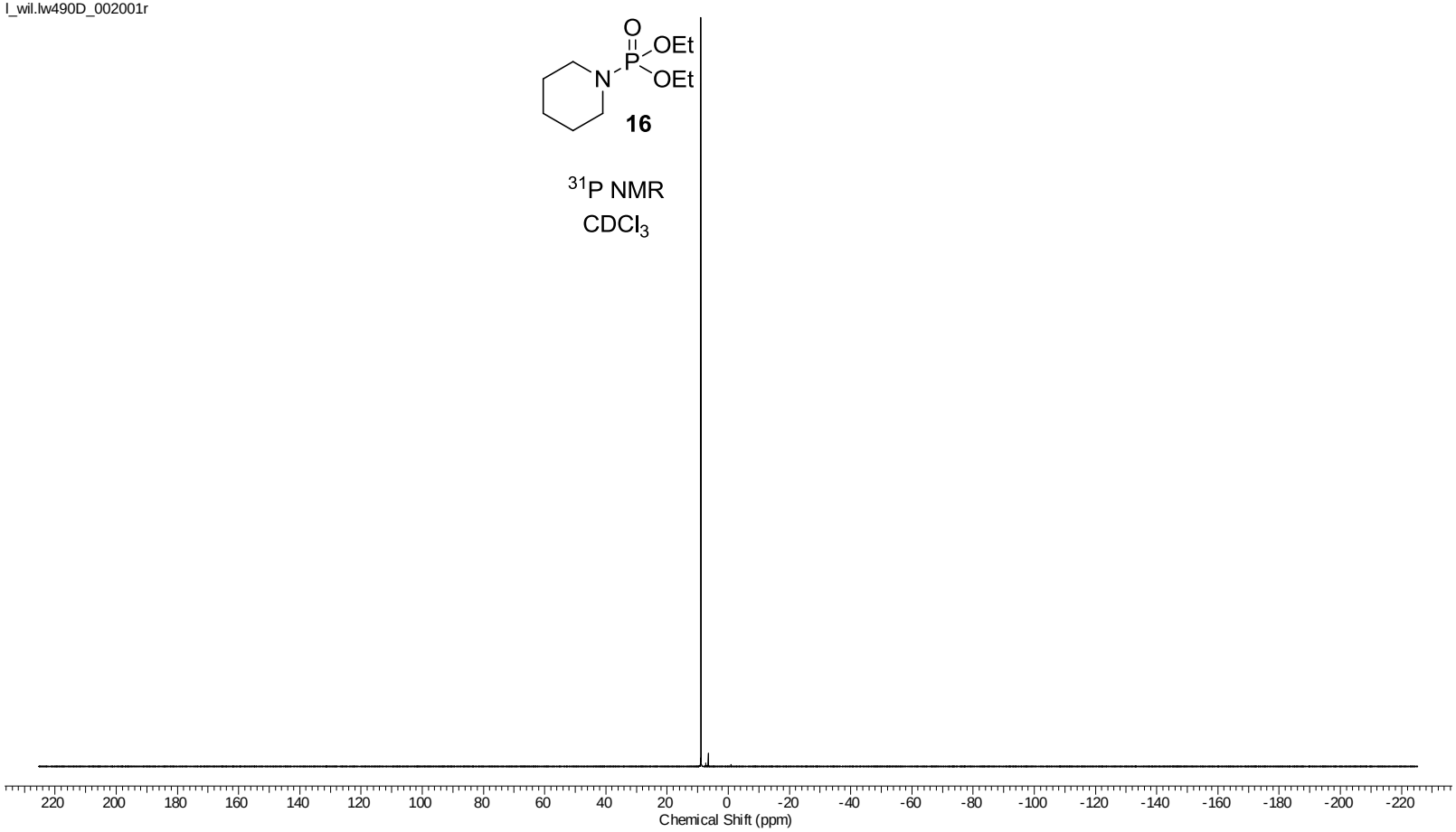
l_wil.lw490D_001001r



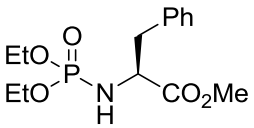
ELECTRONIC SUPPORTING INFORMATION

Acquisition Time (sec)	0.4489	***Comment***	UserID l_wil SampleID lw490D SupervisorID hayes Lab Phone No. 13536 Slot Number 9				
Date	23 Mar 2013 07:04:32			***Date Stamp***	23 Mar 2013 07:04:32		
File Name	\\brukav400\nmr_data\l_wil\nmr\l_wil.lw490D\2\pdata\1\1r			***Frequency (MHz)***	161.98	***Nucleus***	31P
Number of Transients	512	***Origin***	av400	***Original Points Count***	32768	***Owner***	nmruser
Points Count	65536	***Pulse Sequence***	zgpg30	***Receiver Gain***	16384.00	***SW(cyclical) (Hz)***	72992.70
Solvent	CHLOROFORM-d	***Spectrum Offset (Hz)***	-0.1102	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	72991.59
Temperature (degree C)	25.160						

l_wil.lw490D_002001r



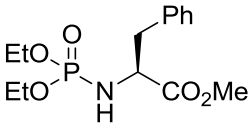
ELECTRONIC SUPPORTING INFORMATION



17 ^{1}H NMR

$CDCl_3$

ELECTRONIC SUPPORTING INFORMATION



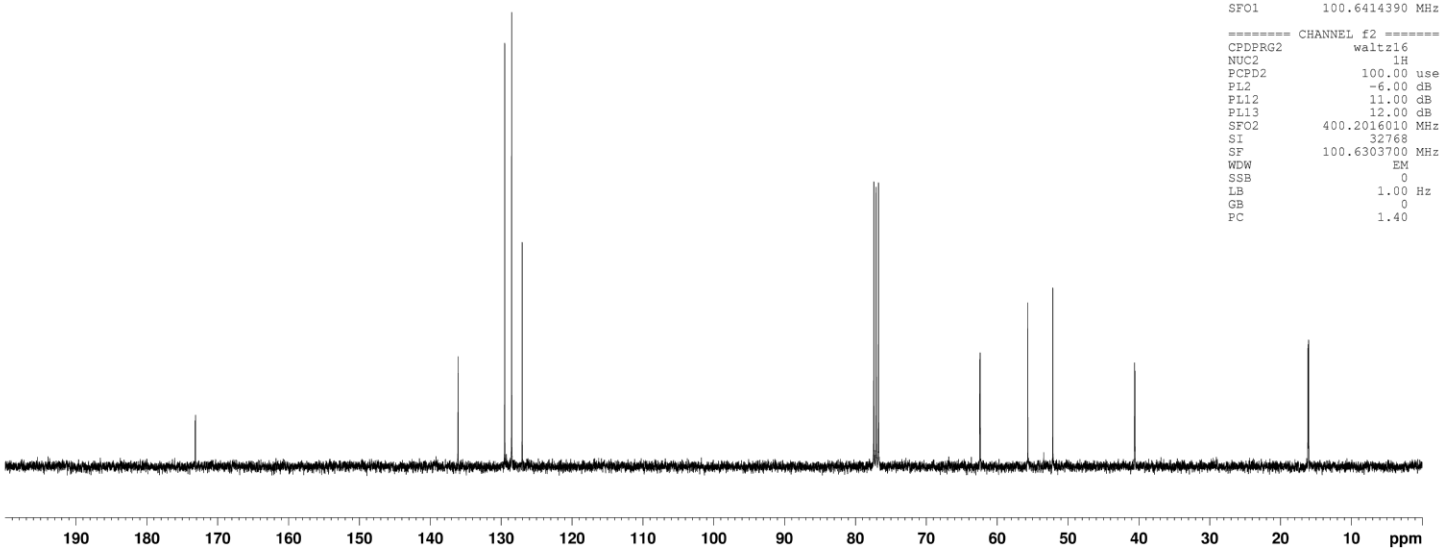
17 ^{13}C NMR

$CDCl_3$

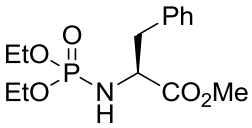
```
NAME          j_fra.jf653
EXPNO                   3
PROCNO                  1
Date_            20120726
Time                15.27
INSTRUM            dpx400
PROBHD    5 mm PABBO BB/
PULPROG           zgpg30
TD                 32768
SOLVENT             CDCl3
NS                    128
DS                      2
SWH            25125.629 Hz
FIDRES          0.766773 Hz
AQ              0.6521332 sec
RG                18390.4
DW                 19.900 use
DE                  6.00 use
TE                298.0 K
D1           1.00000000 sec
d11          0.03000000 sec
DELTA        0.89999998 sec
TD0                     1

======== CHANNEL f1 =======
NUC1                  13C
P1                   8.40 use
PL1                 -4.00 dB
SFO1         100.6414390 MHz

======== CHANNEL f2 =======
CPDPRG2           waltz16
NUC2                  1H
PCPD2              100.00 use
PL2                 -6.00 dB
PL12                11.00 dB
PL13                12.00 dB
SFO2         400.2016010 MHz
SI                 32768
SF           100.6303700 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



ELECTRONIC SUPPORTING INFORMATION



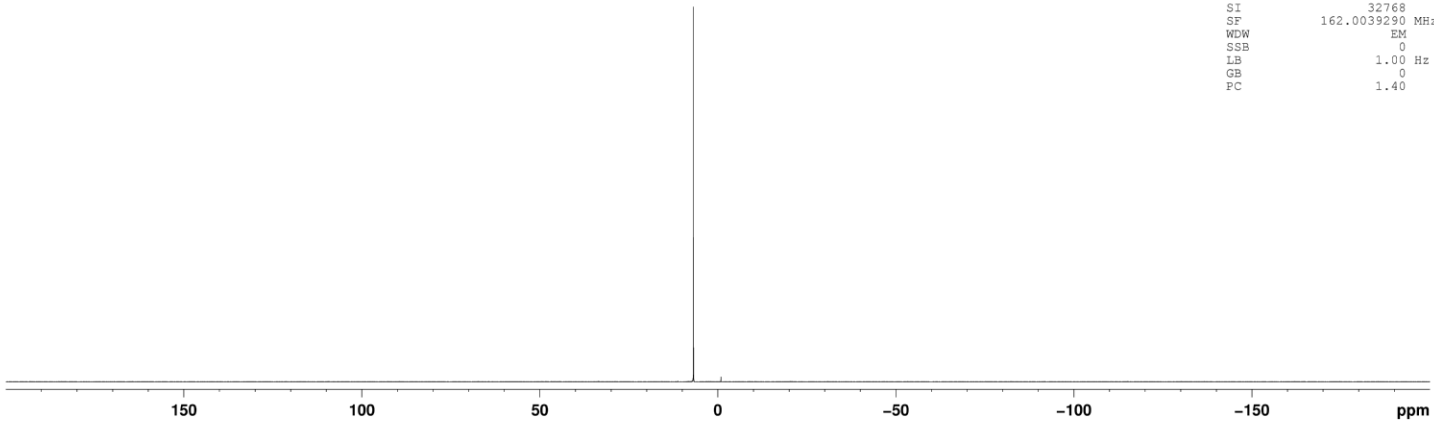
17 ^{31}P NMR

$CDCl_3$

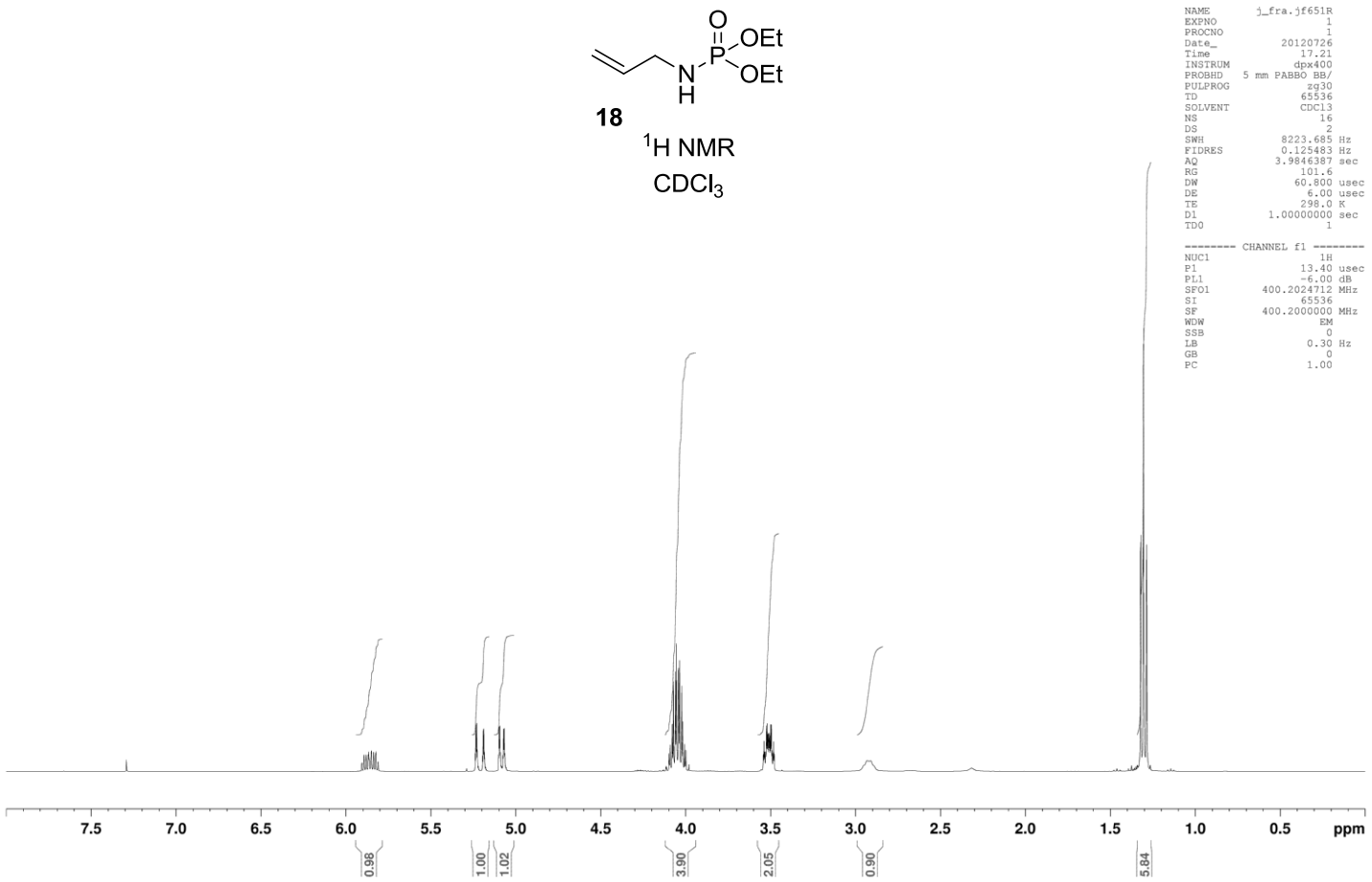
```
NAME          j_fra.jf653
EXPNO                   2
PROCNO                  1
Date_            20120726
Time                15.21
INSTRUM           dpx400
PROBHD    5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT             CDCl3
NS                    128
DS                      2
SWH             72992.703 Hz
FIDRES          1.113780 Hz
AQ              0.4489716 sec
RG                20642.5
DW                  6.850 use
DE                  6.00 use
TE                298.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                     1

======== CHANNEL f1 =======
NUC1                  31P
P1                 11.80 use
PL1                 1.00 dB
SFO1         162.0039290 MHz

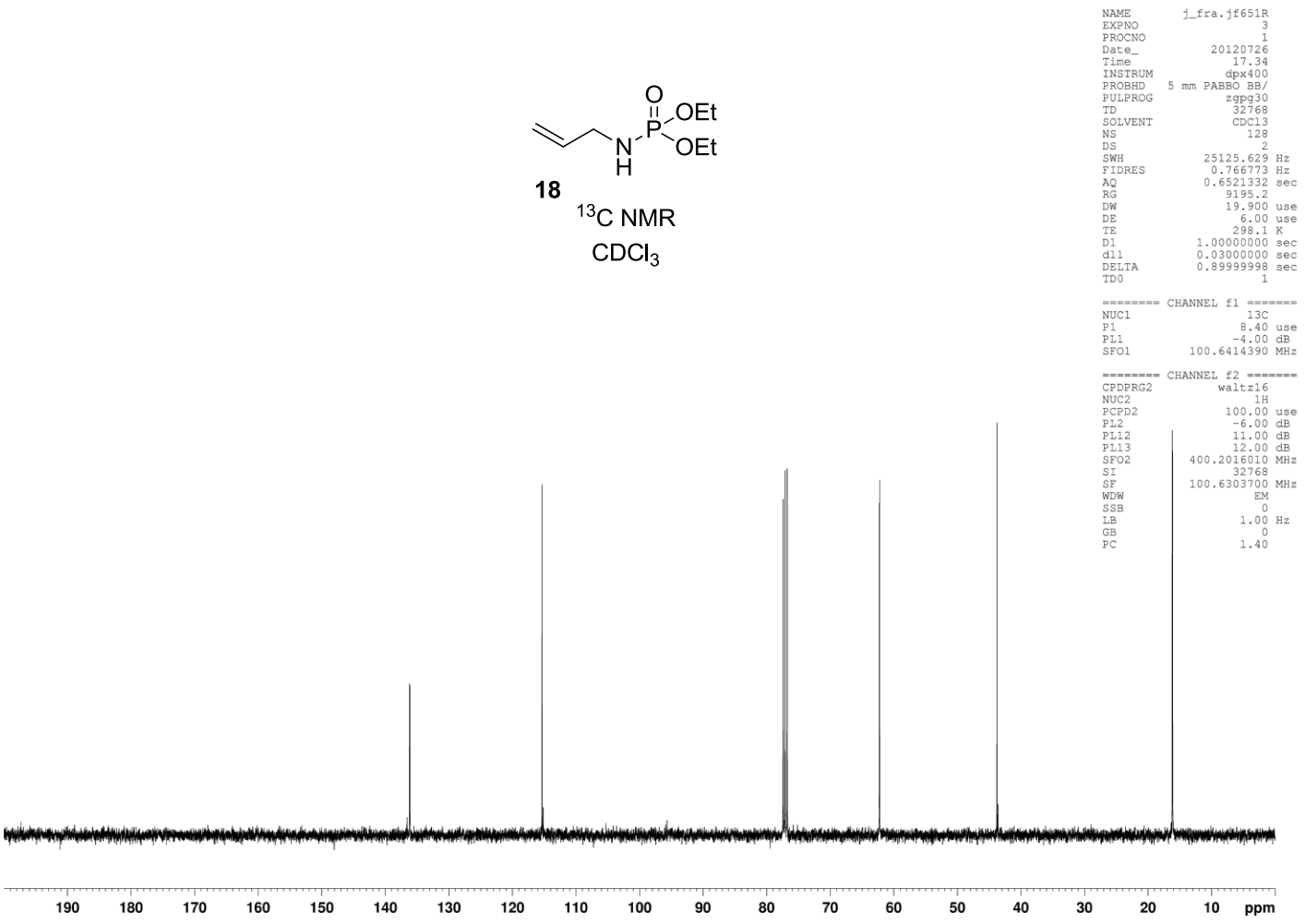
======== CHANNEL f2 =======
CPDPRG2           waltz16
NUC2                  1H
PCPD2             100.00 use
PL2                -6.00 dB
PL12               11.00 dB
PL13               12.00 dB
SFO2         400.2016008 MHz
SI                  32768
SF           162.0039290 MHz
WDW                    EM
SSB                     0
LB                  1.00 Hz
GB                      0
PC                  1.40
```



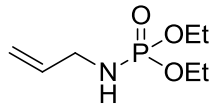
ELECTRONIC SUPPORTING INFORMATION



ELECTRONIC SUPPORTING INFORMATION



ELECTRONIC SUPPORTING INFORMATION



18

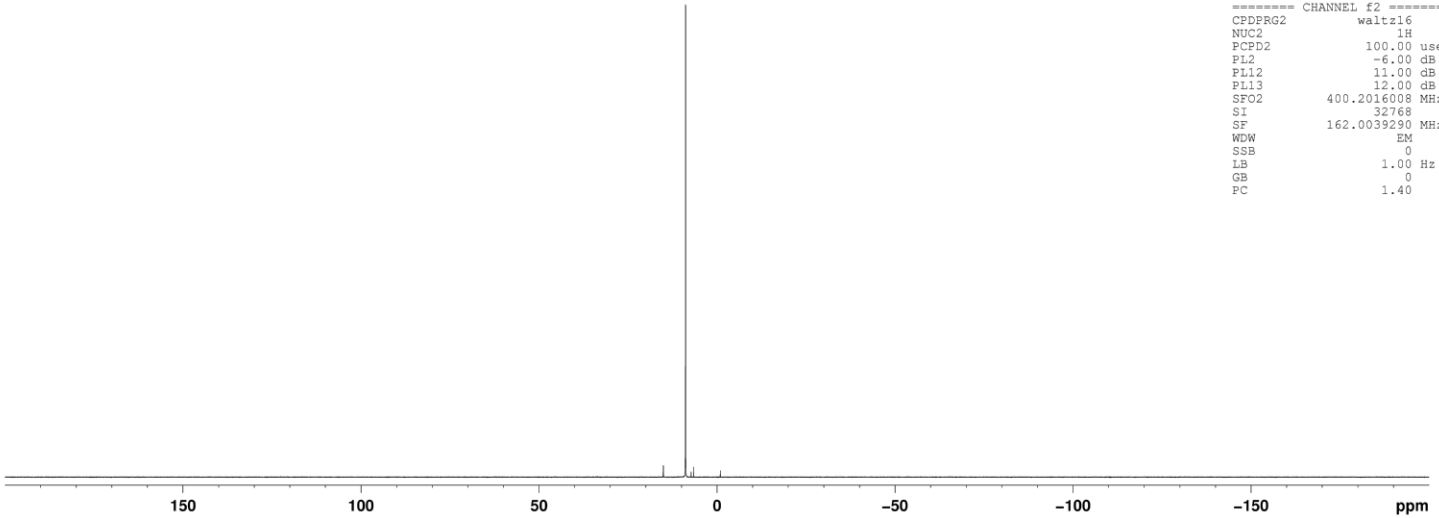
^{31}P NMR

$CDCl_3$

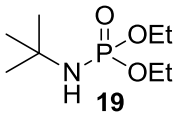
```
NAME          j_fra.jf651R
EXPNO                    2
PROCNO                   1
Date_             20120726
Time                 17.28
INSTRUM              dpx400
PROBHD    5 mm PABBO BB/
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    128
DS                      2
SWH              72992.703 Hz
FIDRES           1.113780 Hz
AQ               0.4489716 sec
RG                 10321.3
DW                   6.850 use
DE                   6.00 use
TE                  298.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1

======== CHANNEL f1 =======
NUC1                   31P
P1                   11.80 use
PL1                   1.00 dB
SFO1          162.0039290 MHz

======== CHANNEL f2 =======
CPDPRG2            waltz16
NUC2                   1H
PCPD2               100.00 use
PL2                  -6.00 dB
PL12                 11.00 dB
PL13                 12.00 dB
SFO2          400.2016008 MHz
SI                   32768
SF            162.0039290 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



ELECTRONIC SUPPORTING INFORMATION

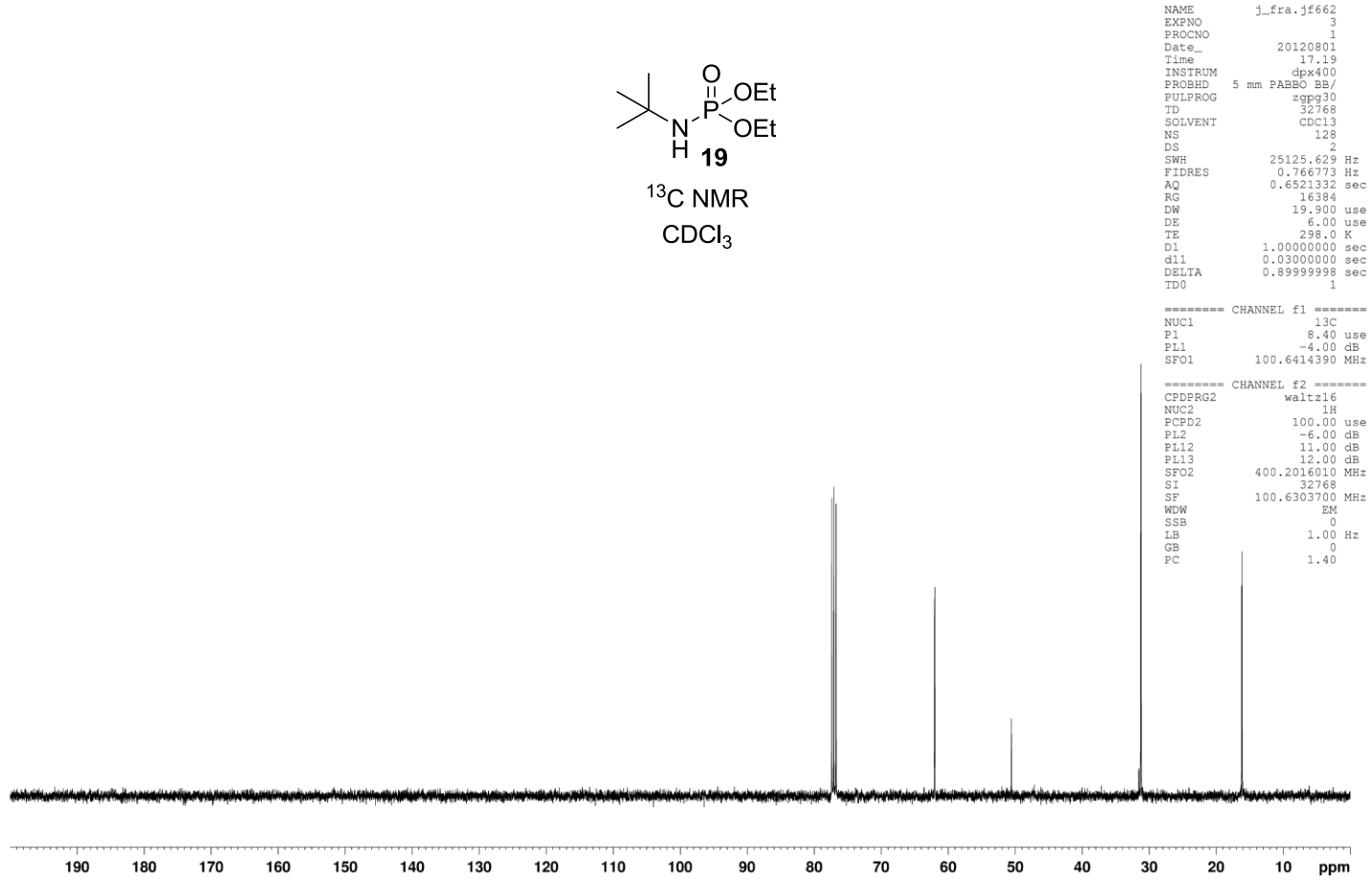


19

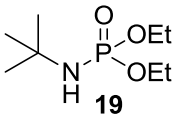
^{1}H NMR

$CDCl_3$

ELECTRONIC SUPPORTING INFORMATION



ELECTRONIC SUPPORTING INFORMATION



19

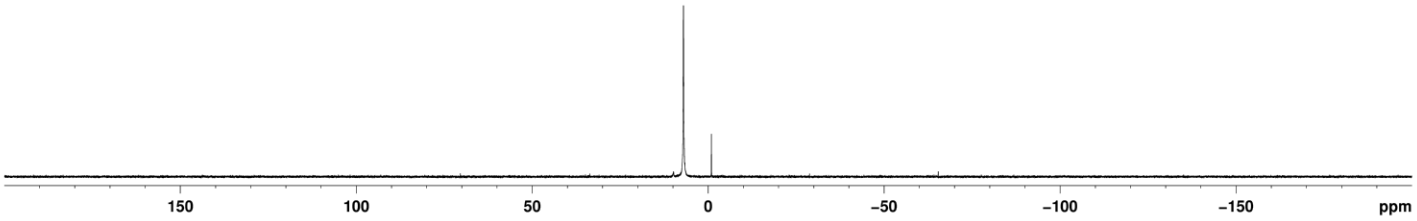
^{31}P NMR

$CDCl_3$

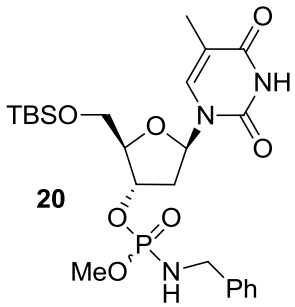
```
NAME          j_fra.jf662
EXPNO                   2
PROCNO                  1
Date_            20120801
Time                17.13
INSTRUM             dpx400
PROBHD    5 mm PABBO BB/
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     128
DS                       2
SWH              72992.703 Hz
FIDRES           1.113780 Hz
AQ               0.4489716 sec
RG                   16384
DW                  6.850 use
DE                  6.00 use
TE                 298.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                     1

======== CHANNEL f1 =======
NUC1                  31P
P1                 11.80 use
PL1                 1.00 dB
SFO1         162.0039290 MHz

======== CHANNEL f2 =======
CPDPRG2           waltz16
NUC2                  1H
PCPD2             100.00 use
PL2                -6.00 dB
PL12               11.00 dB
PL13               12.00 dB
SFO2         400.2016008 MHz
SI                  32768
SF           162.0039290 MHz
WDW                    EM
SSB                     0
LB                  1.00 Hz
GB                      0
PC                  1.40
```



ELECTRONIC SUPPORTING INFORMATION

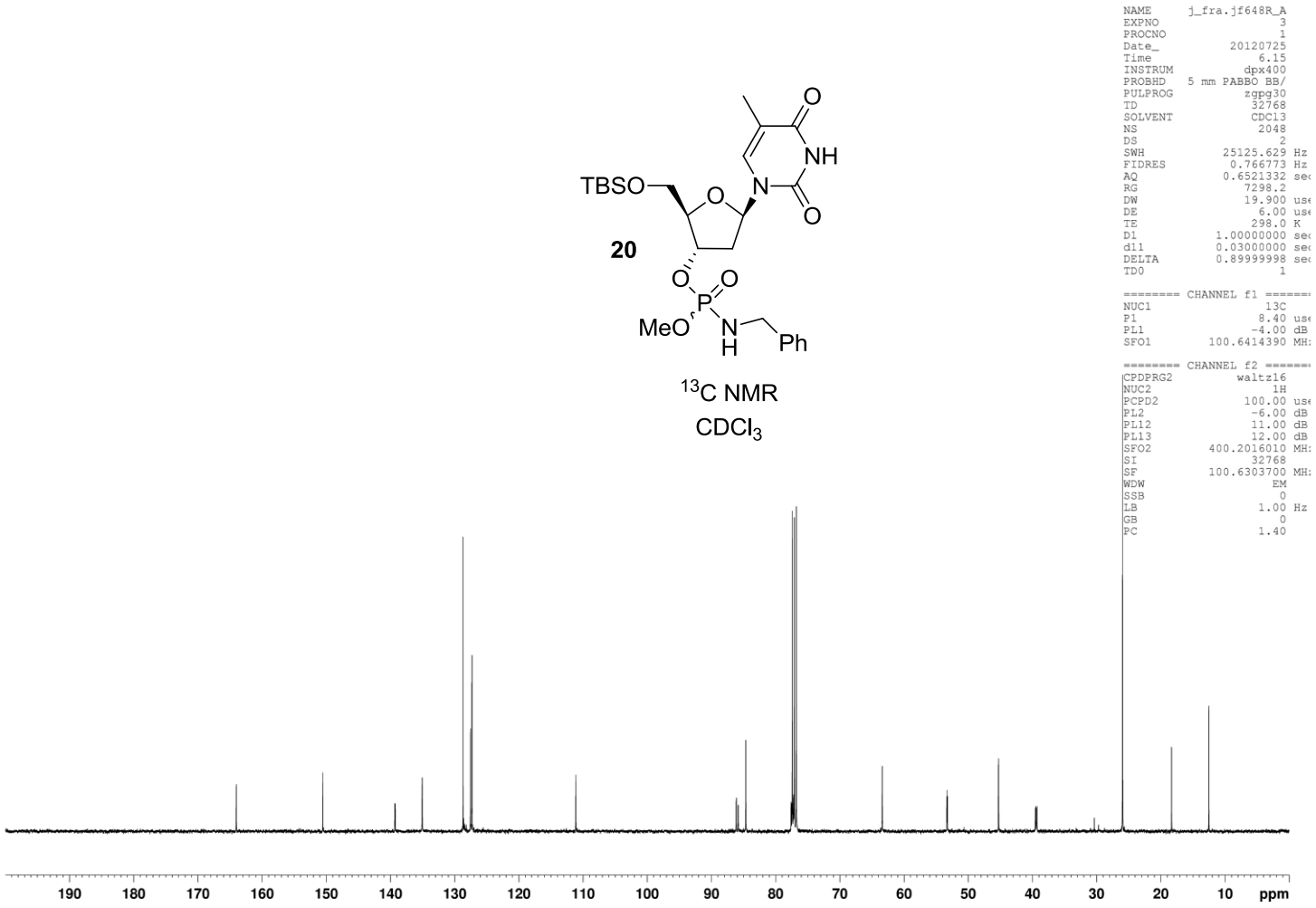


20

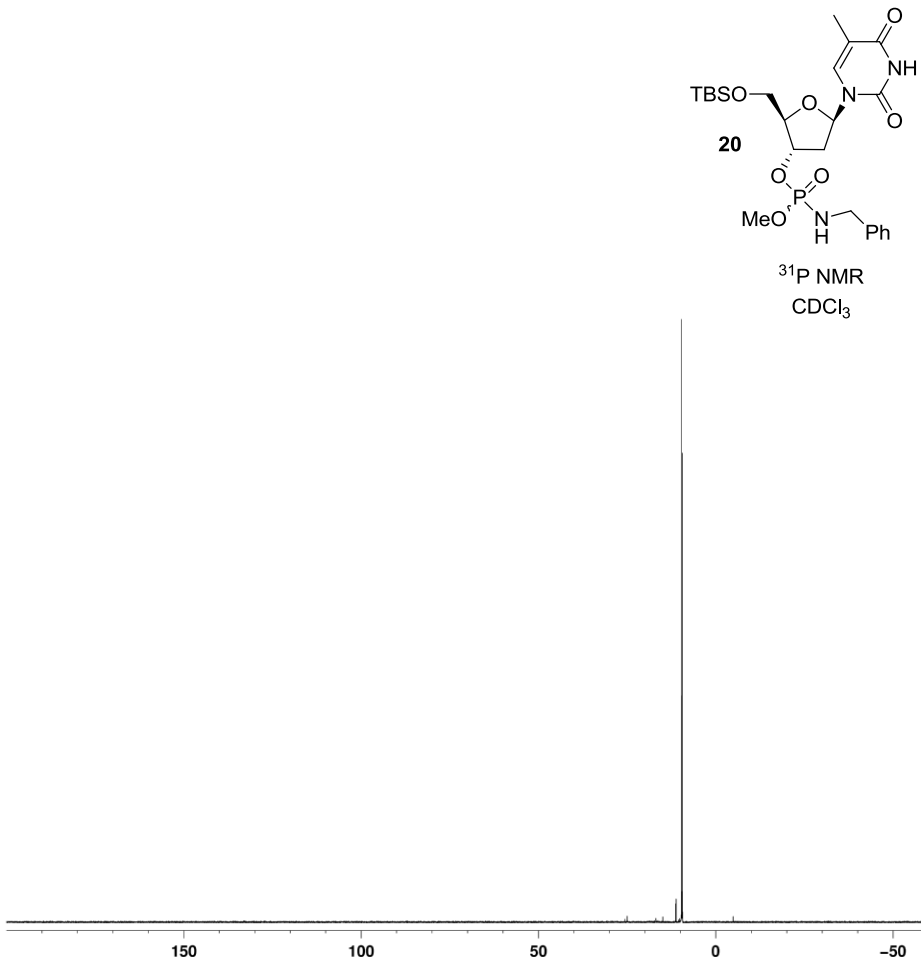
^{1}H NMR

$CDCl_3$

ELECTRONIC SUPPORTING INFORMATION



ELECTRONIC SUPPORTING INFORMATION

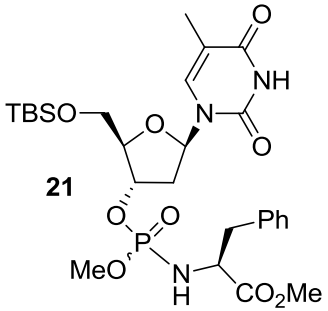



```
NAME          j_fra.jf648R_A
EXPNO                      2
PROCNO                     1
Date_               20120724
Time                   15.56
INSTRUM                dpx400
PROBHD     5 mm PABBO BB/
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                        128
DS                          2
SWH                 72992.703 Hz
FIDRES              1.113780 Hz
AQ                  0.4489716 sec
RG                    20642.5
DW                      6.850 use
DE                      6.00 use
TE                     298.0 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
TD0                         1

======== CHANNEL f1 =======
NUC1                      31P
P1                     11.80 use
PL1                     1.00 dB
SFO1             162.0039290 MHz

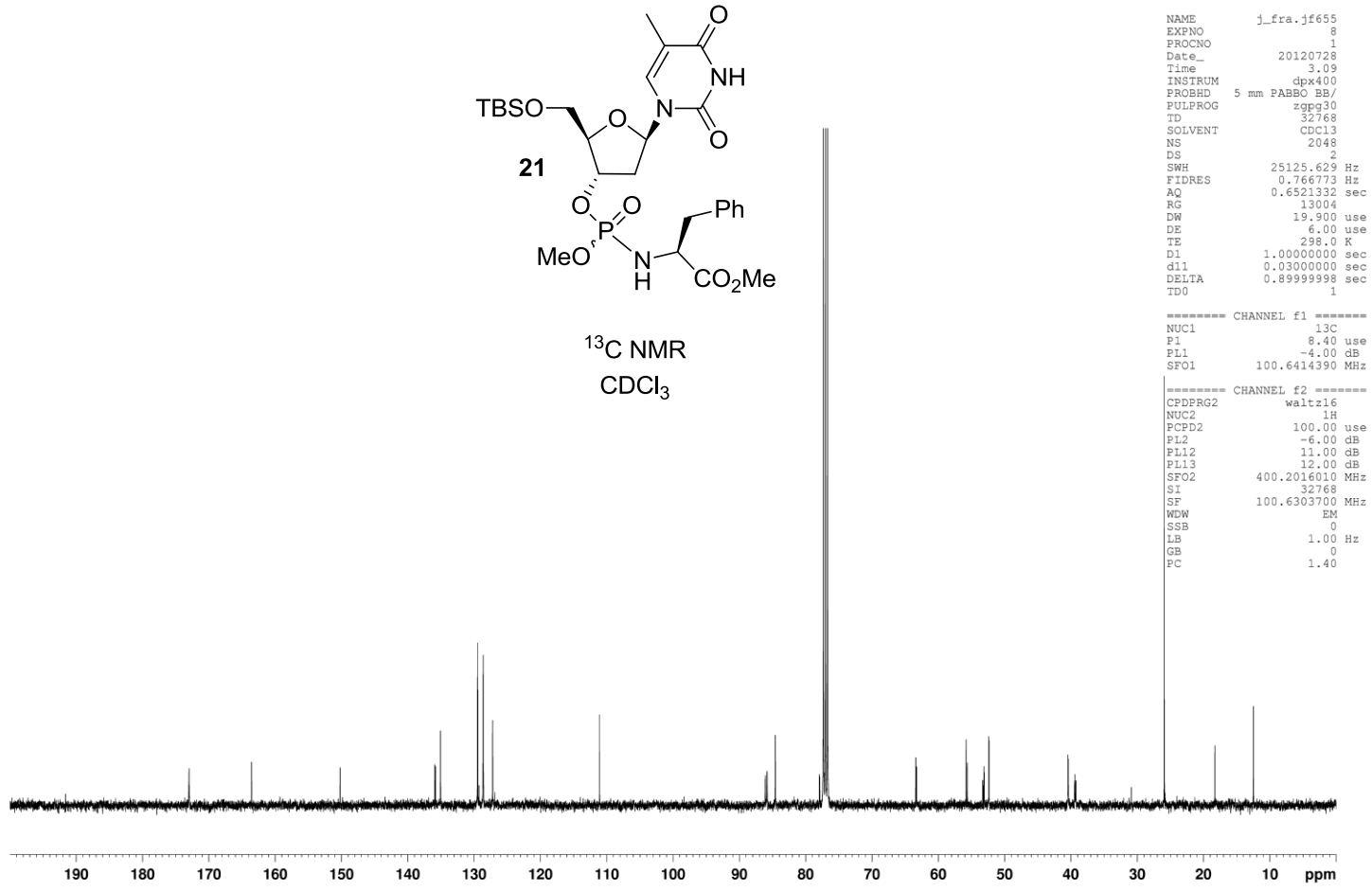
======== CHANNEL f2 =======
CPDPRG2               waltz16
NUC2                      1H
PCPD2                 100.00 use
PL2                    -6.00 dB
PL12                   11.00 dB
PL13                   12.00 dB
SFO2             400.2016008 MHz
SI                      32768
SF               162.0039290 MHz
WDW                        EM
SSB                         0
LB                      1.00 Hz
GB                          0
PC                      1.40
```

ELECTRONIC SUPPORTING INFORMATION

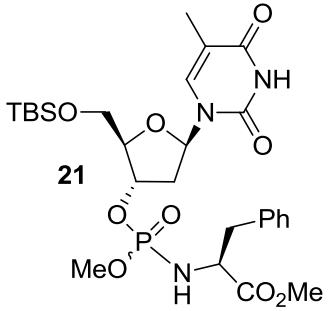


^{1}H NMR
$CDCl_3$

ELECTRONIC SUPPORTING INFORMATION



ELECTRONIC SUPPORTING INFORMATION



^{31}P NMR

$CDCl_3$

```
NAME          j_fra.jf655
EXPNO                   2
PROCNO                  1
Date_            20120727
Time                13.57
INSTRUM          dpx400
PROBHD    5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     2
SWH            72992.703 Hz
FIDRES         1.113780 Hz
AQ             0.4489716 sec
RG               20642.5
DW                 6.850 use
DE                 6.00 use
TE                298.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                    1

======== CHANNEL f1 =======
NUC1                 31P
P1                 11.80 use
PL1                 1.00 dB
SFO1         162.0039290 MHz

======== CHANNEL f2 =======
CPDPRG2          waltz16
NUC2                 1H
PCPD2             100.00 use
PL2                -6.00 dB
PL12               11.00 dB
PL13               12.00 dB
SFO2         400.2016008 MHz
SI                 32768
SF           162.0039290 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```