Supporting information

The Synthesis of Methoxyfumimycin Using 1,2-Addition to Ketimines

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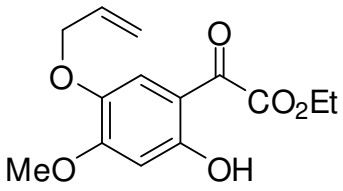
General

^{1}H-NMR spectra were recorded on a 400 MHz or a 500 MHz spectrometer as solutions. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to $CHCl_3$ (7.26 ppm), acetone-D_5 (2.05 ppm) and methanol-D_3 (3.31 ppm) as internal standards. All coupling constants are absolute values and *J* values are expressed in Hertz (Hz). The description of signals include: s = singlet, br. s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, m_c = centered multiplet, dd = doublet of doublets, ddd = doublet of dd, dt = doublet of triplets, dm = doublet of multiplets etc. The spectra were analyzed according to first order. ^{13}C-NMR spectra were recorded on a 100 MHz or a 125 MHz spectrometer as solutions. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to $CDCl_3$ (77.0 ppm) or to acetone-D_6 (sept., 30.8 ppm) and methanol-D_4 (sept., 49.1 ppm) as internal standards. MS (EI, 70 eV) electron impact mass spectrometry: The molecular fragments are quoted as the relation between mass and charge (*m/z*), the intensities as a percentaged value relative to the intensity of the base signal (100%). The abbreviation [M^+] refers to the Molecule-Ion. IR spectra of solids were recorded in KBr, and as thin films on KBr for oils and liquids. The deposit of the absorption band was given in wave numbers ν^{-1} in cm^{-1}. Routine monitoring of reactions were performed using Silica gel coated aluminium plates (silica gel 60) , which were analyzed under UV-light at 254 nm and/or dipped into a solution of molybdato phosphate (5% phosphor molybdic acid in ethanol, dipping solution) and/or $KMnO_4$-solution and heated with a heat gun. Solvent mixtures are understood as volume/volume. Solid materials were powdered. Tetrahydrofurane was distilled from sodium/potassium under argon prior to use. Dichloromethane was distilled from calcium hydride, toluene was destilled from sodium. All reactions involving moisture sensitive reactants were executed under an argon atmosphere using oven dried glassware. All other solvents, reagents and chemicals were used as purchased unless stated otherwise.

Experimental procedures

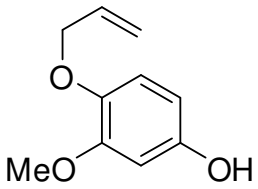
Ethyl (5-Allyloxy-2-hydroxy-4-methoxyphenyl)-oxoaceate



5

A solution of **6** (100 mg, 0.55 mmol, 1.00 eq.) and ethyl oxalyl chloride (0.074 mL, 91 mg, 0.67 mmol, 1.2 eq.) in CH_2Cl_2 (1.0 mL) was cooled to –15 °C. $TiCl_4$ (1.0 M in CH_2Cl_2, 0.67 mL, 0.67 mmol, 1.2 eq.) was added over 20 min. After additional stirring for 40 min, the mixture was poured into 0 °C cold 1 M HCl (15 mL). The aqueous layer was extracted with CH_2Cl_2 (4 × 15 mL). The combined organic extracts were washed with H_2O (20 mL) and brine (20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Flash chromatography (cyclohexane:EtOAc 5:1) afforded the phenol **5** as yellow solid (126 mg, 82%). Mp. 56-57 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.43 (t, *J* = 7.1 Hz, 3H), 3.94 (s, 3H), 4.44 (q, *J* = 7.1 Hz, 2H), 4.54 (dt, *J* = 5.6, 1.4 Hz, 2H), 5.32 (dq, *J* = 10.4, 1.3 Hz, 1H), 5.41 (dq, *J* = 17.2, 1.5 Hz, 1H), 6.05 (ddt, *J* = 17.2, 10.5, 5.5 Hz, 1H), 6.49 (s, 1H), 7.25 (s, 1H), 11.80 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 56.4, 62.5, 70.6, 100.5, 108.4, 114.4, 118.6, 132.8, 141.4, 159.2, 162.6, 162.7, 187.2. IR (KBr): ν^{-1} = 3089, 2912, 1725, 1511, 1201, 1007, 953, 757 cm^{-1}. MS (FAB), m/z (%): 281 (83) [M^+], 239 (46) [$C_{11}H_{11}O_6^+$], 207 (88), [$C_{11}H_{11}O_4^+$], 165 (36), [$C_8H_5O_4^+$]. HRMS (FAB, M+H) for $C_{14}H_{17}O_6$: calcd. 281.1025; found 281.1023.

4-Allyloxy-3-methoxyphenol

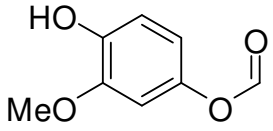


6

Boric acid (3.22 g, 52.0 mmol, 5.00 eq.) was suspended in THF (30 mL), H_2O_2 (30% in H_2O, 3.4 mL) and H_2SO_4 (1.5 mL). After stirring for 30 min, **9** (2.00 g, 10.4 mmol, 1.00 eq.) was added as solution in THF (10 mL) within 15 min. After additional stirring for 5 h, the mixture was filtrated. The filtrate was neutralized by addition of sat. $NaHCO_3$ solution (100 mL); the aqueous layer was extracted with EtOAc (3 × 50 mL). The combined organic extracts were washed with brine (50 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Flash chromatography (cyclohexane:EtOAc 4:1→3:1) afforded the phenol **6** as brown oil (1.48 g, 81%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 3.80 (s, 3H), 4.52 (dm, *J* = 5.6 Hz, 2H), 5.12 (br. s, 1H), 5.25 (dq, *J* = 10.4, 1.3 Hz, 1H), 5.36 (dq, *J* = 17.3, 1.5 Hz, 1H), 6.08 (ddt, *J* = 17.3, 10.5, 5.6 Hz, 1H), 6.31 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.46 (d, *J* = 2.8 Hz, 1H), 6.75 (dd, *J* = 8.6 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 55.8, 71.1, 100.7, 105.9, 115.5, 117.8, 133.7, 141.9, 150.5, 150.6. IR (KBr): ν^{-1} = 3360, 2940, 2603, 1607, 1455, 1217, 952, 722 cm^{-1}. MS (EI), m/z (%): 180 (44) [M^+], 139 (100) [$C_7H_7O_3^+$]. HRMS (EI) for $C_{10}H_{12}O_3$: calcd. 180.0786; found 180.0786.

4-Hydroxy-3-methoxyphenyl formate

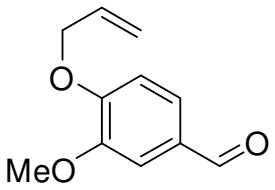


8

Vanilline (3.00 g, 19.7 mmol, 1.00 eq.) and *m*CPBA (9.72 g, 39.4 mmol, 2.00 eq.) were dissolved in $CHCl_3$ (90 mL) and heated to reflux for 1 h. The mixture was cooled to 0 °C, a sat. $Na_2S_2O_3$ solution (100 mL) was added. The aqueous layer was extracted with EtOAc (3 × 50 mL). The combined organic extracts were washed with sat. $Na_2S_2O_3$ solution (80 mL), sat. $NaHCO_3$ solution (80 mL) and brine (50 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Flash chromatography (cyclohexane:EtOAc 3:1→2:1) afforded the formate **10** as yellow oil (1.05 g, 32%).

^{1}H-NMR (400 MHz, acetone-D_6): δ = 3.85 (s, 3H), 6.64 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.83 (d, *J* = 2.6 Hz, 1H), 6.85 (d, *J* = 8.6 Hz, 1H), 7.72 (br.s, 1H), 8.39 (s, 1H). ^{13}C-NMR (100 MHz, acetone-D_6): δ = 57.4, 107.4, 114.9, 116.7, 145.0, 146.6, 149.8, 162.1. IR (KBr): ν^{-1} = 3385, 1736, 1511, 1193, 1157, 947, 796 cm^{-1}. MS (EI), m/z (%): 168 (10) [M+], 154 (20), 140 (100) [$C_7H_8O_3^+$]. HRMS (EI) for $C_8H_8O_4$: calcd. 168.0423; found 168.0420.

4-Allyloxy-3-methoxybenzaldehyde

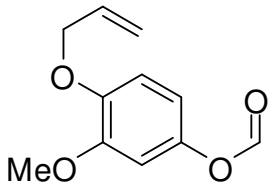


9

To a suspension of vanillin (1.00 g, 6.57 mmol, 1.00 eq.) and K_2CO_3 (1.82 g, 7.89 mmol, 2.00 eq.) in acetone (10.0 mL) allylbromide (0.69 mL, 0.95 g, 7.9 mmol, 1.2 eq.) was added. The mixture was heated to reflux for 6 h. After filtration, the filtrate was concentrated under reduced pressure. Flash chromatography (cyclohexane:EtOAc 5:1→3:1) afforded the allylether **9** as colorless oil (1.07 g, 85%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.93 (s, 3H), 4.70 (dm, *J* = 5.4 Hz, 2H), 5.34 (dq, *J* =10.5, 1.2 Hz, 1H), 5.44 (dq, *J* = 17.3, 1.4 Hz, 1H), 6,08 (ddt, *J* = 17.3, 10.5, 5.3 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 7.42 (br. s, 1H), 7.43 (dd, *J* = 7.5, 1.9 Hz, 1H), 9.85 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 55.9, 69.6, 109.2, 111.8, 118.6, 126.4, 130.0, 132.1, 149.7, 153.3, 190.7. IR (KBr): ν^{-1} = 3080, 2938, 2728, 1586, 1268, 1136, 935, 810, 732 cm^{-1}. MS (EI), m/z (%): 192 (100) [M_+], 152 (69) [$C_8H_7O_{3+}$]. HRMS (EI) for $C_{11}H_{12}O_3$: calcd. 192.0786; found 192.0790.

4-(Allyloxy)-3-methoxyphenyl formate



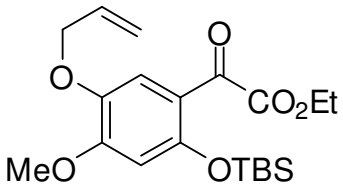
10

To a solution of **8** (109 mg, 0.650 mmol, 1.00 equiv.) in DMF (3.0 mL) was added allyl iodid (0.30 mL, 3.3 mmol, 5.0 equiv.) and BaO (100 mg, 0.650 mmol, 1.00 equiv.). The mixture was warmed to 40 °C under sonication. After 3 h the mixture was treated with water (15 mL) and extracted with EtOAc (3 × 15 mL). The combined organic extracts were washed with

H_2O (15 mL) and brine (15 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Flash chromatography (cyclohexane:EtOAc 7:1) afforded the formate **10** as colorless oil (65 mg, 48%).

^{1}H-NMR (400 MHz, acetone-D_6): δ = 3.83 (s, 3H), 4.57 (dt, *J* = 5.3, 1.5 Hz, 2H), 5.23 (dq, *J* = 10.5, 1.5 Hz, 1H), 5.42 (dq, *J* = 17.3, 1.5 Hz, 1H), 6.08 (ddt, *J* = 17.3, 10.5, 5.3 Hz, 1H), 6.70 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.85 (d, *J* = 2.7 Hz, 1H), 6.98 (d, *J* = 8.7 Hz, 1H), 8.40 (s, 1H). ^{13}C-NMR (100 MHz, acetone-D_6): δ = 57.3, 71.7, 108.0, 114.2, 116.1, 118.5, 135.8, 146.3, 148.3, 152.4, 162.0. IR (KBr): ν^{-1} = 3465, 2939, 1604, 1451, 1366, 1223, 1160, 1031, 959, 856 cm^{-1}. MS (EI), m/z (%): 208 (24) [M+], 167 (14) [$C_7H_7O_4$+], 139 (52). HRMS (EI) for $C_{11}H_{12}O_4$: calcd. 208.0736; found 208.0733.

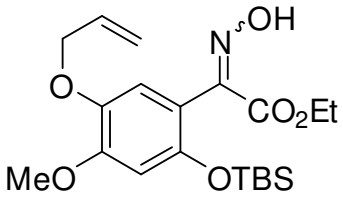
Ethyl (5-Allyloxy-2 *tert*-butyldimethylsilanyloxy-4-methoxyphenyl)-oxoacetate



12

A solution of **5** (11.57 g, 41.29 mmol, 1.00 eq.) and *tert*-butyldimethylchlorosilane (8.08 g, 53.7 mmol, 1.30 eq.) in CH_2Cl_2 (20 mL) was cooled to 0 °C. Diisopropylethylamine (10.6 mL, 8.02 g, 61.9 mmol, 1.50 eq.) were added within 5 min. The mixture was stirred at 0 °C for 4 h, followed by stirring at rt for 1 d. The reaction was quenched by addition of H_2O (300 mL), the aqueous layer was extracted with EtOAc (4 × 250 mL). The combined organic extracts were washed with H_2O (300 mL) and brine (300 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Flash chromatography (cyclohexane:EtOAc 7:1→4:1) afforded the silylether **12** as yellow oil (15.42 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.28 (s, 6H), 0.96 (s, 9H), 1.35 (t, *J* = 7.2 Hz, 3H), 3.87 (s, 3H), 4.33 (q, *J* = 7.2 Hz, 2H), 4.57 (dt, *J* = 4.6, 1.4 Hz, 2H), 5.29 (dq, *J* = 10.5, 1.4 Hz, 1H), 5.43 (dq, *J* = 17.2, 1.4 Hz, 1H), 6.06 (ddt, *J* = 17.2, 10.5, 5.5 Hz, 1H), 6.39 (s, 1H), 7.27 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = –3.8, 13.9, 19.0, 26.1, 56.0, 61.7, 70.1, 103.3, 113.4, 116.4, 118.5, 132.7, 142.8, 153.5, 155.8, 165.0, 185.6. IR (KBr): ν^{-1} = 3083, 2932, 1744, 1605, 1511, 1366, 1221, 1019, 886, 788 cm^{-1}. MS (EI), m/z (%): 394 (3) [M^+], 337 (100) [$C_{16}H_{21}O_6Si^+$], 321 (18) [$C_{17}H_{25}O_4Si^+$]. HRMS (EI) for $C_{20}H_{30}O_6Si$: calcd. 394.1812; found 394.1809.

Ethyl [5-Allyloxy-2-(*tert*-butyldimethylsilanyloxy)-4-methoxyphenyl]-(hydroxy imino) acetate

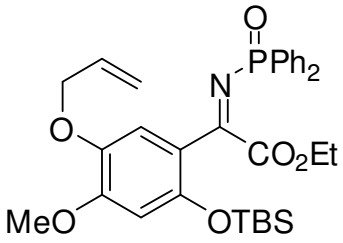


13

A mixture of **12** (20.82 g, 52.77 mmol, 1.00 eq), hydroxylamine hydrochloride (7.33 g, 106 mmol, 2.00 eq.), EtOH (175 mL) and pyridine (41.0 mL, 40.3 g, 509 mmol, 4.80 eq.) was heated to reflux for 70 min. The reaction was diluted with H_2O (300 mL) and extracted with EtOAc (4 × 250 mL). The combined organic extracts were washed with H_2O (200 mL) and brine (200 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Flash chromatography (cyclohexane:EtOAc 6:1→3:1) afforded the oxime **13** as 1:1 mixture of *E*:*Z* isomers as yellow oil (20.67 g, 96%).

Isomer 13a: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.19 (s, 6H), 0.93 (s, 9H), 1.29 (t, *J* = 7.1 Hz, 3H), 3.83 (s, 3H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.54 (dt, *J* = 5.5, 1.4 Hz, 2H), 5.26 (dq, *J* = 10.4, 1.4 Hz, 1H), 5.38 (dq, *J* = 17.3, 1.4 Hz, 1H), 6.05 (ddt, *J* = 17.3, 10.4, 5.5 Hz, 1H), 6.39 (s, 1H), 6.95 (s, 1H), 10.51 (br. s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = –4.1, 14.0, 18.4, 25.8, 55.8, 61.7, 70.4, 104.2, 114.2, 114.7, 118.1, 133.2, 142.5, 148.3, 148.6, 151.4, 162.8. IR (KBr): ν^{-1} = 3436, 2931, 1737, 1512, 1414, 1260, 1154, 1050, 944, 784 cm^{-1}. Isomer 13b: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.15 (s, 6H), 0.92 (s, 9H), 1.29 (t, *J* = 7.1 Hz, 3H), 3.84 (s, 3H), 4.28 (q, *J* = 7.1 Hz, 2H), 4.53 (dt, *J* = 5.6, 1.4 Hz, 2H), 5.25 (dq, *J* = 10.5, 1.4 Hz, 1H), 5.38 (dq, *J* = 17.2, 1.4 Hz, 1H), 6.07 (ddt, *J* = 17.2, 10.5, 5.6 Hz, 1H), 6.43 (s, 1H), 6.84 (s, 1H), 9.64 (br. s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = –4.5, 14.0, 18.0, 25.6, 55.8, 61.8, 70.6, 104.0, 112.0, 115.2, 118.0, 133.3, 142.1, 147.8, 148.7, 151.3, 163.3. IR (KBr): ν^{-1} = 3406, 2931, 1728, 1510, 1411, 1261, 1147, 993, 838 cm^{-1}. Mixture of isomers: MS (EI), m/z (%): 409 (54) [M^+], 368 (46) [$C_{17}H_{26}NO_6Si^+$], 352 (100) [$C_{16}H_{22}NO_6Si^+$]. HRMS (EI) for $C_{20}H_{31}NO_6Si$: calcd. 409.1921; found 409.1921.

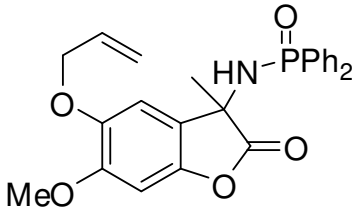
Ethyl [5-Allyloxy-2-(*tert*-butyl-dimethyl-silanyloxy)-4-methoxyphenyl]-(diphenyl phosphorylimino)acetate



14

A solution of **13** (1:1 mixture of *E*:*Z* isomers, 7.55 g, 18.4 mmol, 1.00 eq) in THF (40 mL) and NEt_3 (2.60 mL, 1.87 g, 18.4 mmol, 1.00 eq.) was cooled to –50 °C (acetonitrile/dry ice bath). Chlorodiphenylphosphine (3.38 mL, 4.07 g, 18.4 mmol, 1.00 eq.) was added as a solution in THF (8.0 mL) within 15 min. The dry ice was removed from the cool bath and the reaction was allowed to warm up slowly. After 4 h, H_2O (150 mL) was added, the mixture was extracted with EtOAc (4 × 100 mL). The combined organic extracts were washed with H_2O (100 mL) and brine (100 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Flash chromatography (cyclohexane:EtOAc 2:1→1:1) afforded the ketimine **14** as orange oil (7.85 g, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.26 (s, 6H), 0.91 (s, 9H), 1.28 (t, *J* = 7.2 Hz, 3H), 3.86 (s, 3H), 4.38 (q, *J* = 7.2 Hz, 2H), 4.60 (dt, *J* = 5.5, 1.4 Hz, 2H), 5.29 (dq, *J* = 10.5, 1.4 Hz, 1H), 5.38 (dq, *J* = 17.3, 1.4 Hz, 1H), 6.06 (ddt, *J* = 17.3, 10.5, 5.5 Hz, 1H), 6.39 (s, 1H), 7.40-7.50 (m, 6H), 7.52(s, 1H), 7.80-8.00 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = –3.6, 13.7, 19.2, 26.3, 56.0, 62.4, 70.4, 103.4, 114.4, 117.8 (d, J_P = 10.5 Hz), 118.3, 128.3 (d, J_P = 12.8 Hz), 131.4 (d, J_P = 2.5 Hz), 131.7 (J_P = 9.3 Hz), 133.3, 134.0 (d, J_P = 133.9 Hz), 142.8, 152.9, 155.2, 165.0 (d, J_P = 15.5 Hz), 169.0 (d, J_P = 7.6 Hz). IR (KBr): ν^{-1} = 3438, 3059, 2929, 2645, 1591, 1370, 1216, 983, 841 cm^{-1}. MS (EI), m/z (%): 552 (6) [M^+], 552 (22) [$C_{29}H_{35}NO_6PSi^+$], 536 (72) [$C_{28}H_{31}NO_6SiP^+$], 201 (100). HRMS (EI) for $C_{32}H_{40}NO_6SiP$: calcd. 593.2363, found 593.2365.

5-Allyloxy-3-diphenylphosphinoylamino-6-methoxy-3-methyl-3*H*-benzofuran-2-one

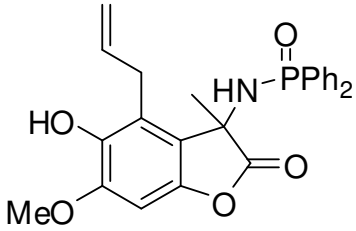


16

A solution of **15** (505 mg, 0.828 mmol) in DMF (5.0 mL) was heated to 120 °C for 19 h. The solvent was removed under reduced pressure. The lactone **16** was obtained as brown solid and used in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.69 (s,

3H), 3.77 (s, 3H), 4.43 (m_c, 2H), 5.28 (dq, J = 10.6, 1.4 Hz, 1H), 5.41 (dq, J = 17.3, 1.4 Hz, 1H), 6.06 (ddt, J = 17.3, 10.6, 5.5 Hz, 1H), 6.35 (s, 1H), 7.06 (s, 1H), 7.28-7.58 (m, 8H), 7.82-7.90 (m, 2H). ^{13}C NMR (100 MHz, acetone-D_6): δ = 27.7 (d, J_P = 5.2 Hz), 56.2, 59.0, 70.5, 95.8, 111.2, 118.0 (d, J_P = 2.0 Hz), 118.2, 128.3 (d, J_P = 12.9 Hz), 128.5 (d, J_P = 12.7 Hz), 131.4 (J_P = 10.1 Hz), 131.6 (d, J_P = 128.7 Hz), 131.6 (d, J_P = 2.5 Hz), 131.9 (J_P = 9.7 Hz), 132.1 (d, J_P = 2.7 Hz), 132.7 (d, J_P = 130.2 Hz), 133.0, 144.9, 146.7, 151.1, 179.0 (d, J_P = 4.2 Hz). IR (KBr): ν^{-1} = 3079, 2843, 1628, 1439, 1190, 1034, 856 cm^{-1}. MS (EI), m/z (%): 449 (36) [M^+], 408 (3) [$C_{22}H_{19}NO_5P^+$], 380 (100). HRMS (EI) for $C_{25}H_{24}NO_5P$: calcd. 449.1392, found 449.1394.

4-Allyl-3-diphenylphosphinoylamino-5-hydroxy-6-methoxy-3-methyl-3*H*-benzofuran-2-one



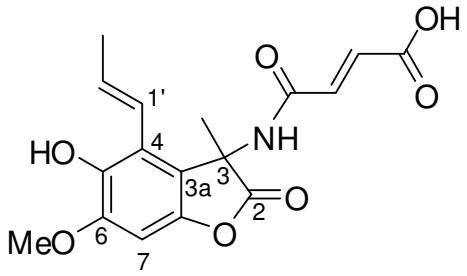
17

A solution of **15** (1.70 g, 2.79 mmol) in DMF (75 mL) was heated to reflux for 39 h. The solvent was removed under reduced pressure; the residue was dissolved in EtOAc (200 mL). The mixture was washed with half-saturated NaCl solution (3 × 175 mL) and with brine (175 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Flash chromatography (cyclohexane:EtOAc 2:1 + 5% MeOH) afforded the lactone **17** as brown solid (920 mg, 73%). Mp.: 200–202 °C. ^{1}H NMR (500 MHz, acetone-D_6): δ = 1.70 (s, 3H), 3.18 (dm, J = 15.3 Hz), 3.55 (ddm, J = 15.3, 7.1 Hz, 1H), 3.86 (s, 3H), 4.89 (dddd, J = 10.3, 1.5, 1.5, 1.5 Hz, 1H), 4.89 (dddd, J = 17.2, 1.6, 1.6, 1.6 Hz, 1H), 5.55 (d, 9.3 Hz), 5.95 (dddd, J = 17.2, 10.3, 7.1, 5.0 Hz, 1H), 6.58 (s, 1H), 7.21 (s, 1H), 7.36-7.44 (m, 4H), 7.46-7.54 (m, 2H), 7.72-7.80 (m, 4 H). ^{13}C NMR (100 MHz, acetone-D_6): δ = 27.5 (d, J_P = 8.0 Hz), 30.7, 57.7, 61.1 (d, J_P = 6.4 Hz), 95.7, 116.2, 120.6, 125.8, 129.8 (d, J_P = 12.9 Hz), 130.0 (d, J_P = 12.8 Hz), 133.4, 133.5 (J_P = 10.3 Hz), 133.6, 133.8 (J_P = 9.9 Hz), 134.8 (d, J_P = 129.3 Hz), 135.0 (d, J_P = 125.7 Hz), 138.5, 143.0, 147.4, 149.9, 180.8. IR (KBr): ν^{-1} = 3441, 2932, 2468, 1636, 1358, 1188, 1027, 943, 822 cm^{-1}. MS (EI): m/z (%): 449 (18) [M^+], 232 (22), 218 (100), 201 (84). HRMS (EI) for $C_{25}H_{24}NO_5P$: calcd. 449.1392, found 449.1395.

^{1}H and ^{13}C NMR spectra

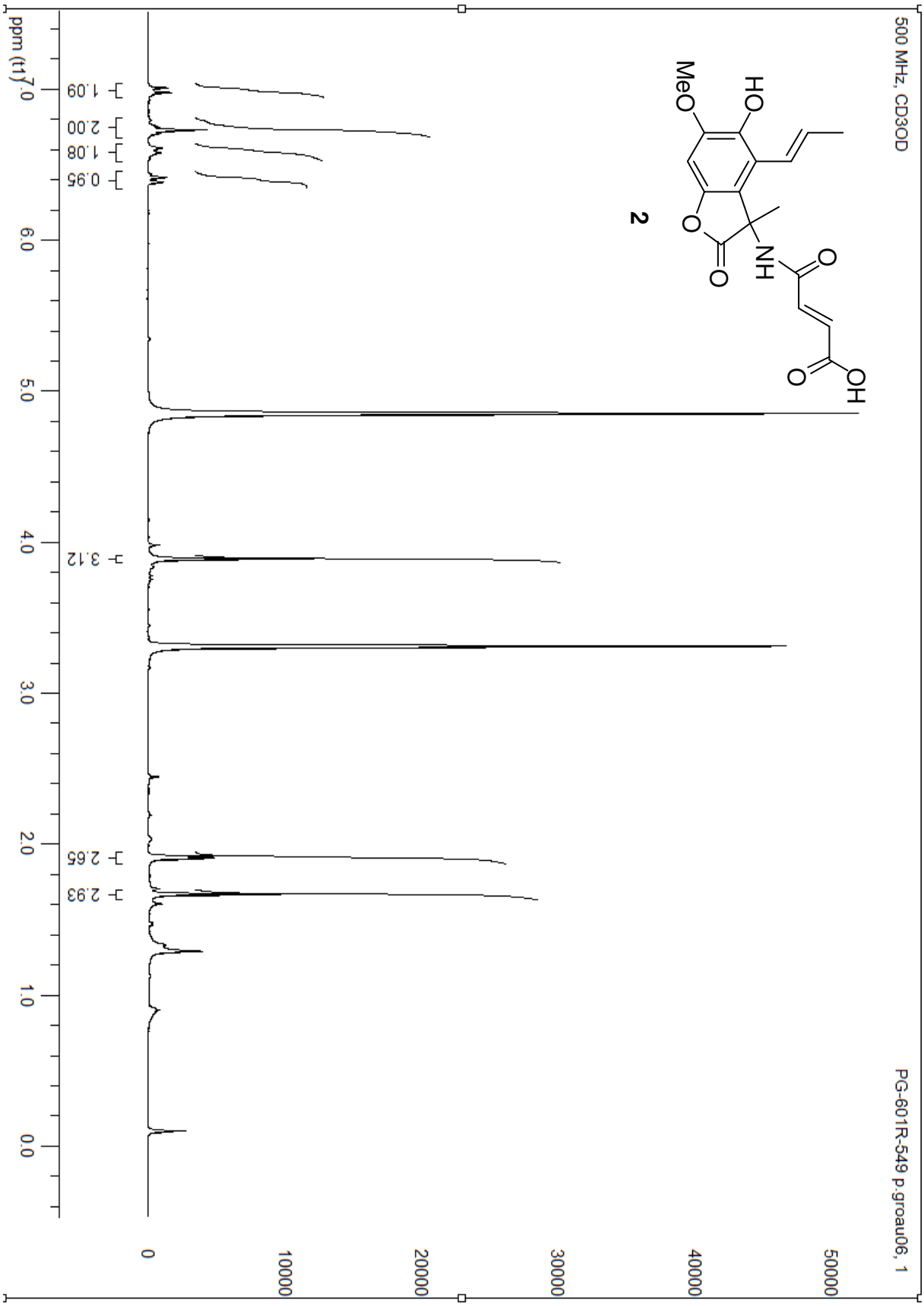
Table 1: Comparison of ^{13}C data for fumimycin and methoxyfumimycin

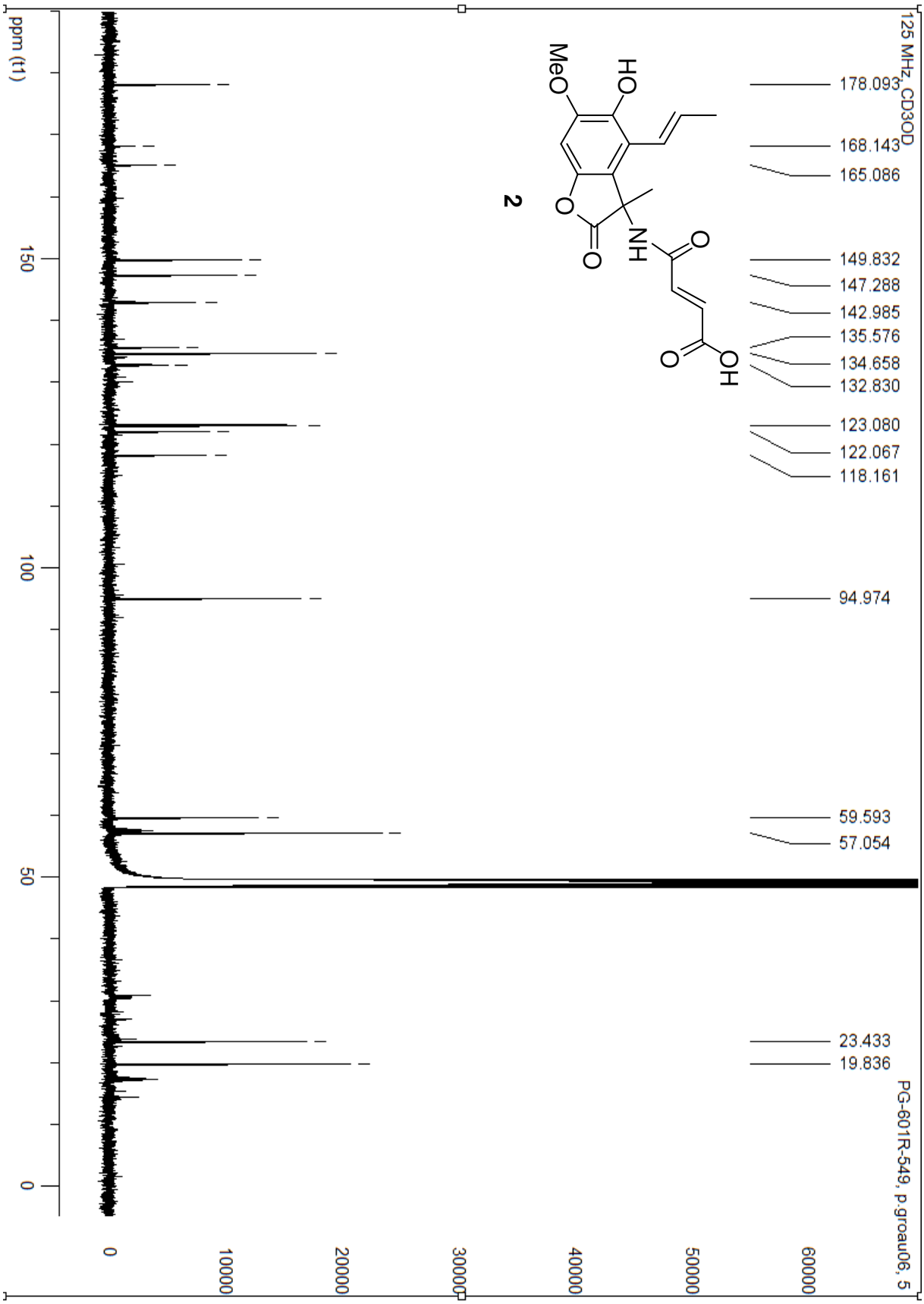
Numbering	literature δ_C for fumimycin[1] (CD_3OD:$CDCl_3$ 1:1)	δ_C for methoxyfumimycin (CD_3OD)
C-3‘	19.1	19.8
3-CH_3	22.4	23.4
OMe		57.1
C-3	58.1	59.6
C-7	96.9	95.0
C-3a	115.8	118.2
C-4	121.3	122.1
C-1‘	121.8	123.1
*C*CON	133.1	132.8
*C*COO	133.3	135.6
C-2‘	133.4	134.7
C-5	140.3	143.0
C-6	145.5	147.3
C-7a	145.8	149.8
CON	164.1	165.1
COO	168.5	168.1
C-2	177.5	178.1

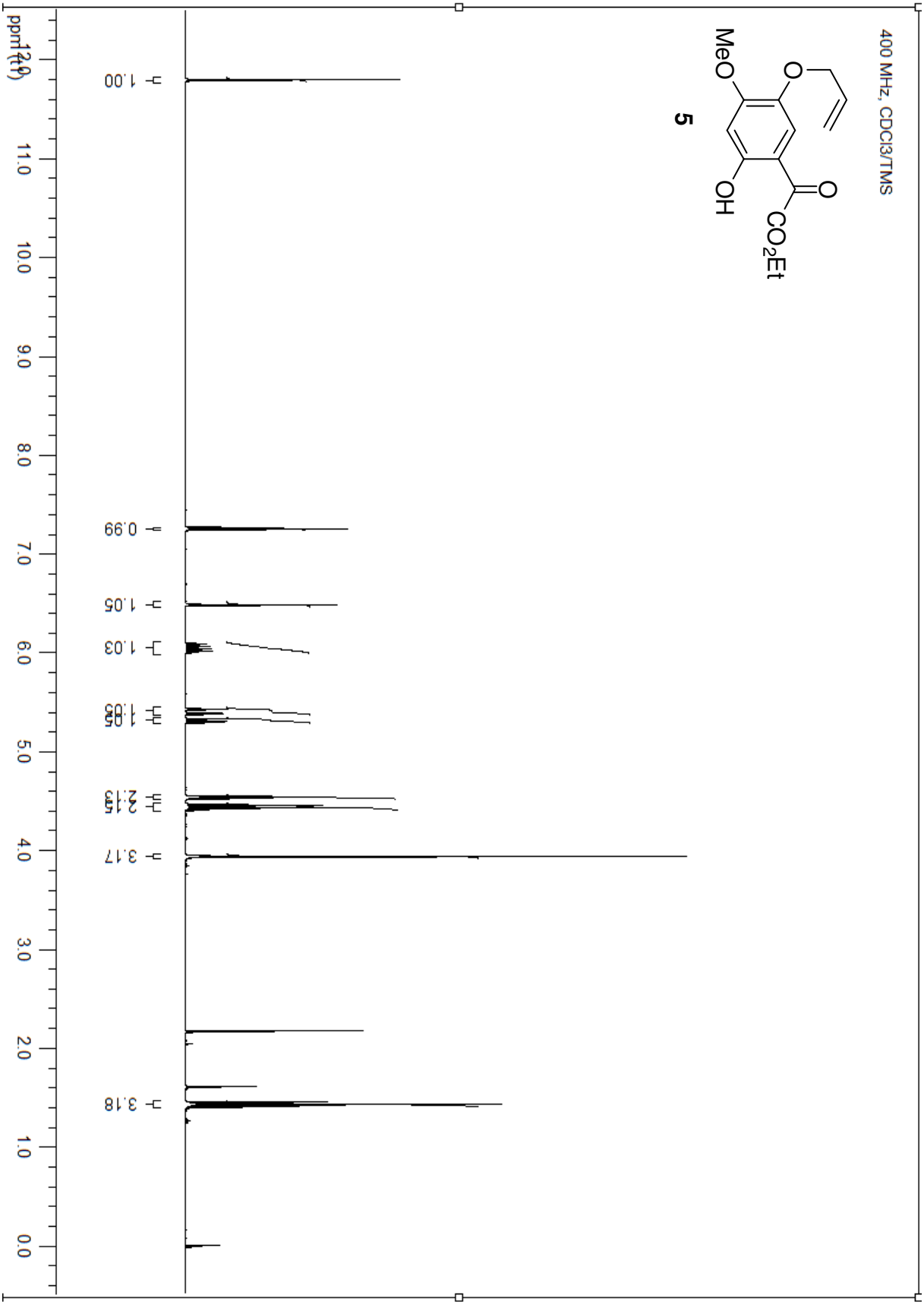


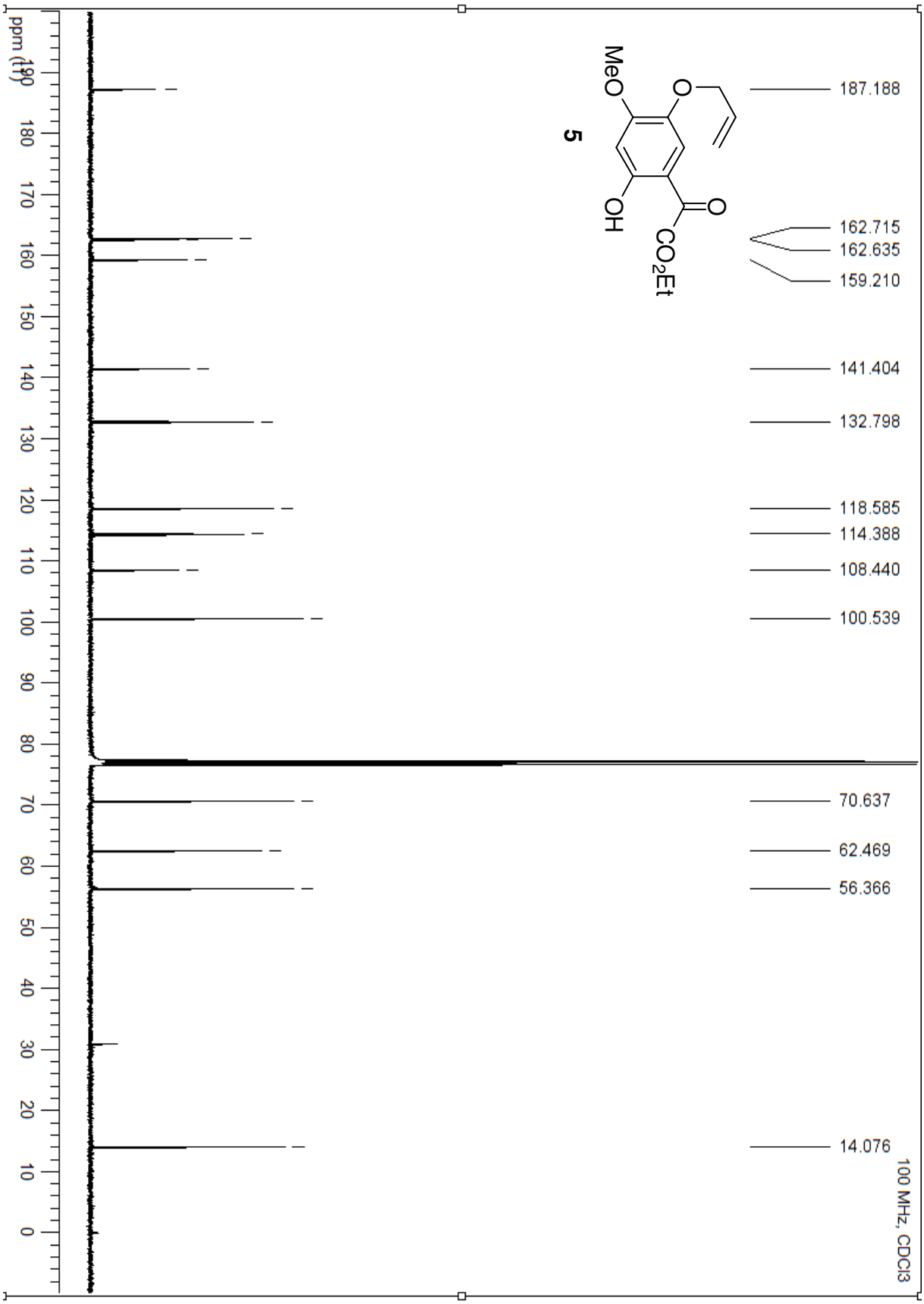
2

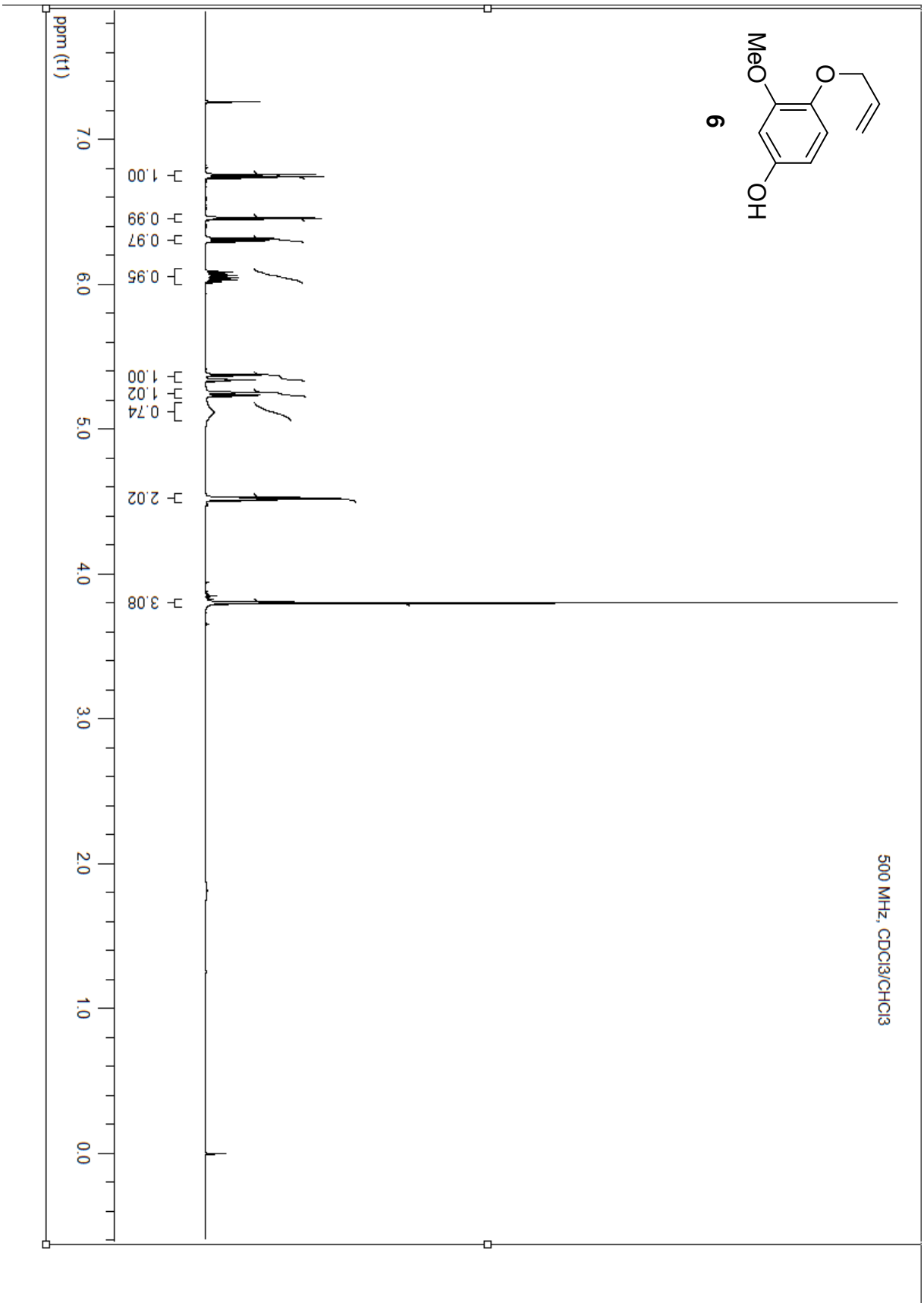
[1] Kwon,Y.-J.; Sohn, M.-J.; Zheng, C.-J.; Kim, W.-G. *Org. Lett.* **2007**, *9*, 2449–2451.

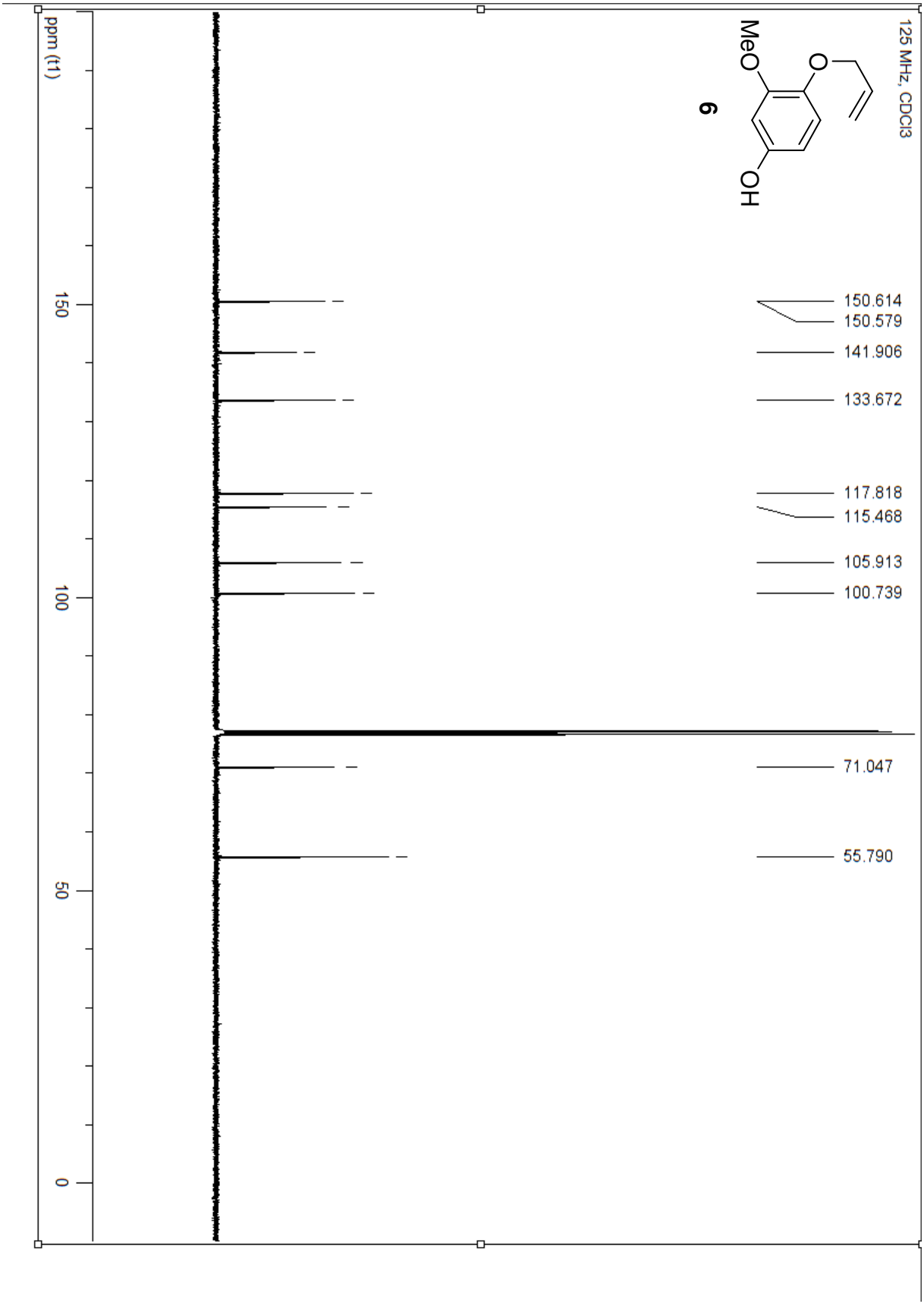

500 MHz, CD3OD
PG-601R-549 p.groau06, 1
MeO
HO
O
O
NH
O
O
OH
2
ppm (t1)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1.09
2.00
1.08
0.95
3.12
2.65
2.93
0
10000
20000
30000
40000
50000

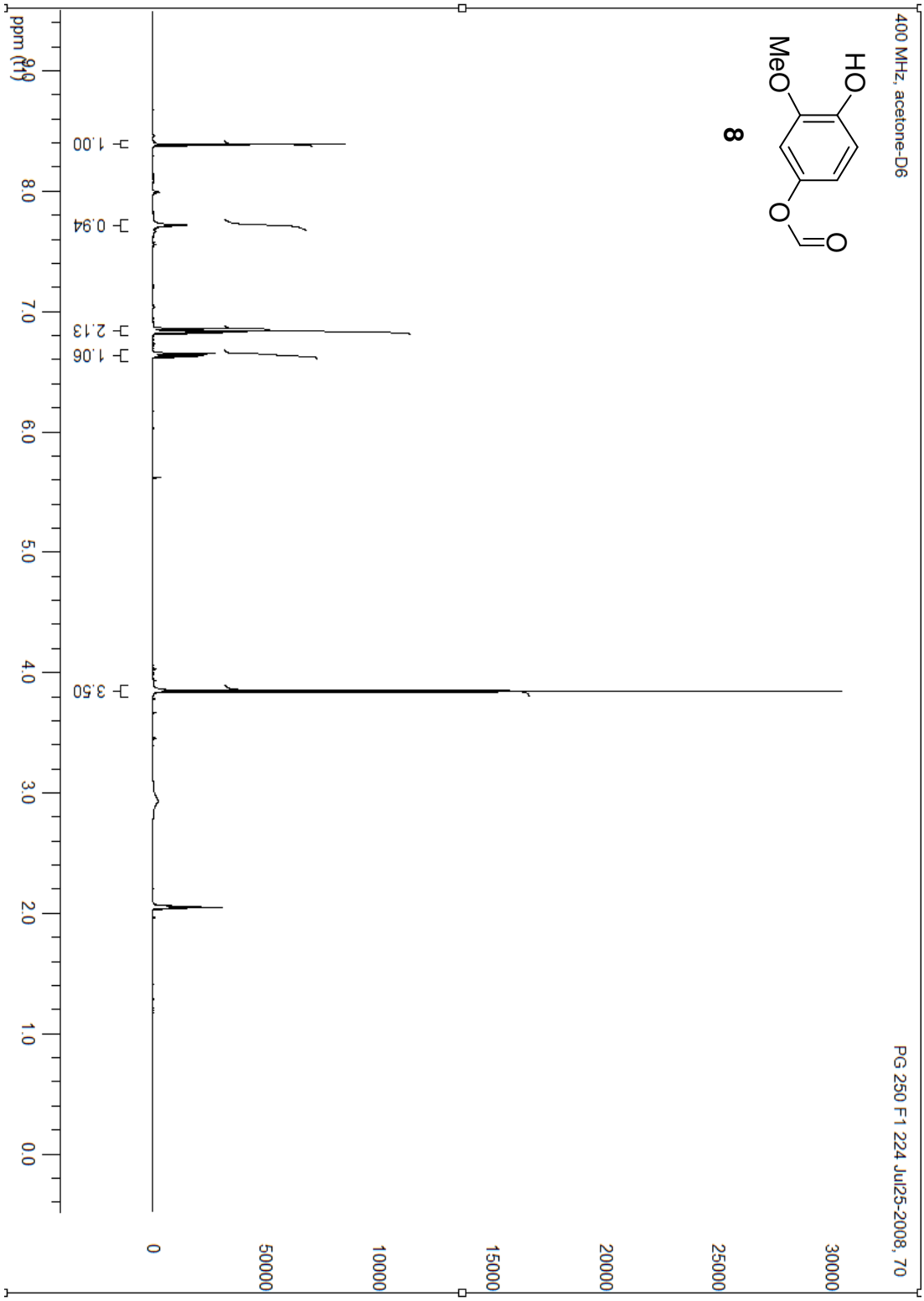

125 MHz, CD3OD
178.093
168.143
165.086
149.832
147.288
142.985
135.576
134.658
132.830
123.080
122.067
118.161
94.974
59.593
57.054
23.433
19.836
MeO
HO
NH
O
OH
2
ppm (t1)
0
50
100
150
0
10000
20000
30000
40000
50000
60000
PG-601R-549, p.groau06, 5

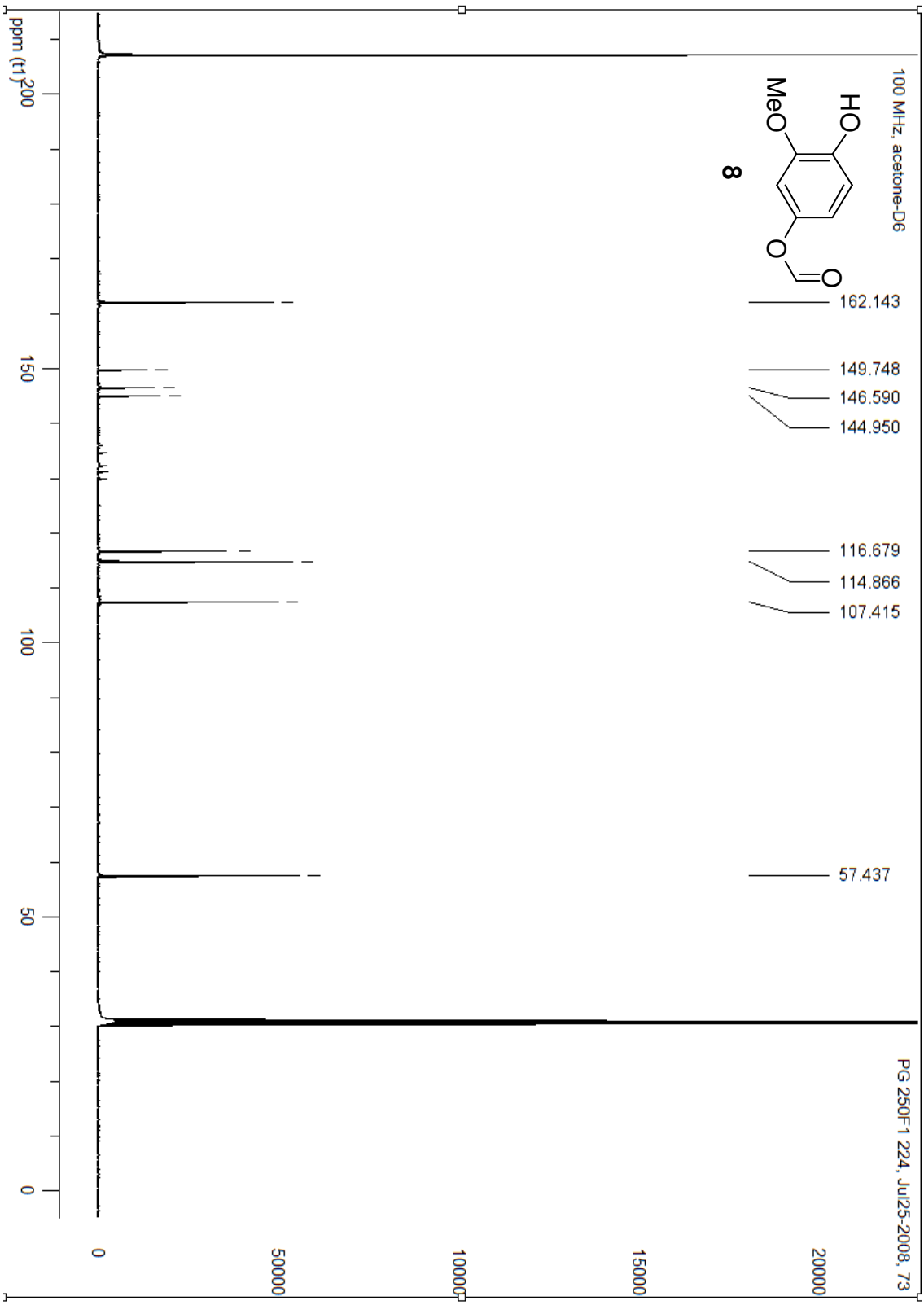

400 MHz, CDCl3/TMS
MeO
O
OH
O
CO2Et
5
ppm (t1)
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1.00
0.99
1.05
1.03
1.05
2.13
3.17
3.18

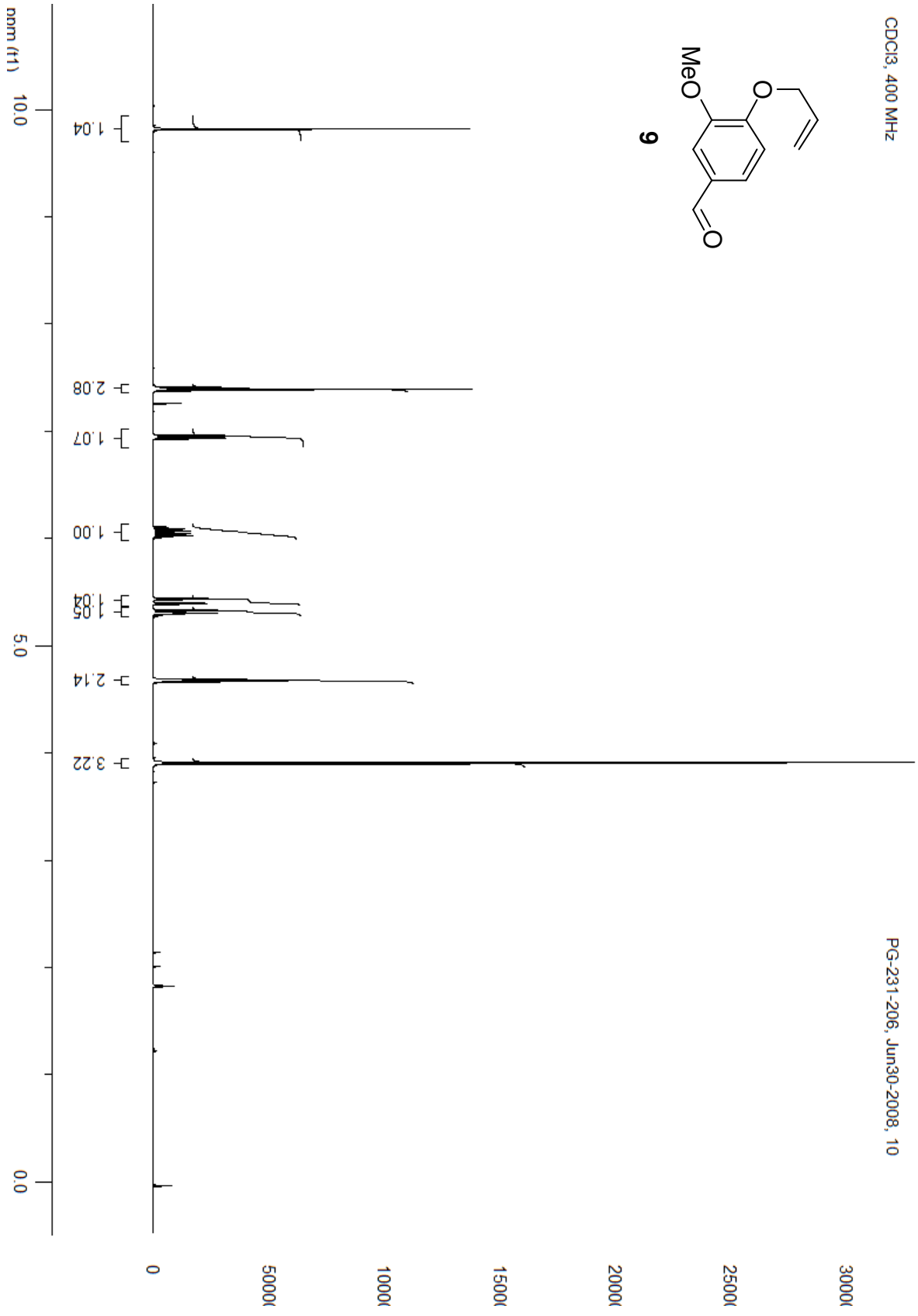

MeO
O
OH
O
CO2Et
5
187.188
162.715
162.635
159.210
141.404
132.798
118.585
114.388
108.440
100.539
70.637
62.469
56.366
14.076
ppm (t1)
100 MHz, CDCl3

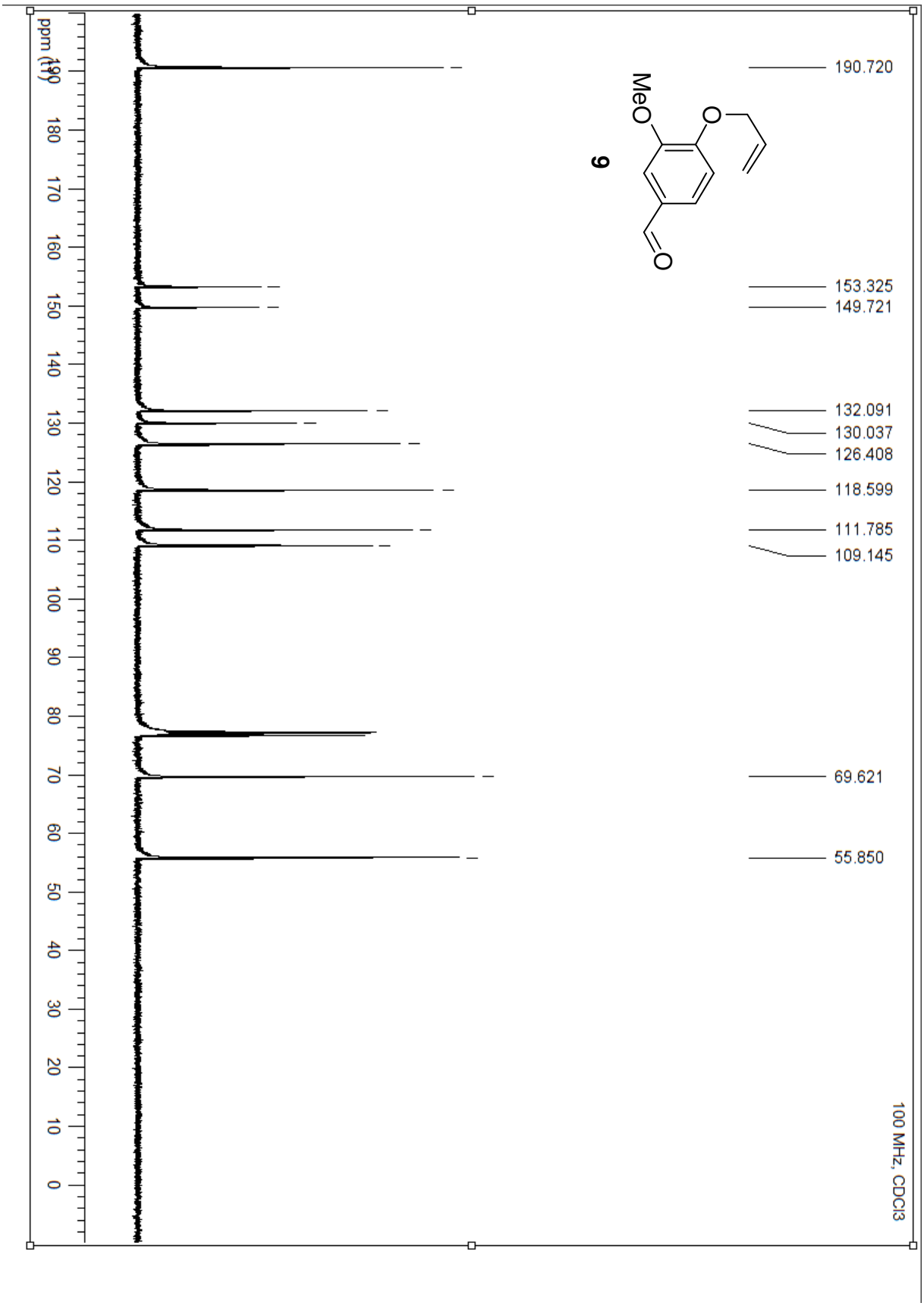

MeO
O
OH
6
500 MHz, CDCl3/CHCl3
ppm (t1)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1.00
0.99
0.97
0.95
1.00
1.02
0.74
2.02
3.08

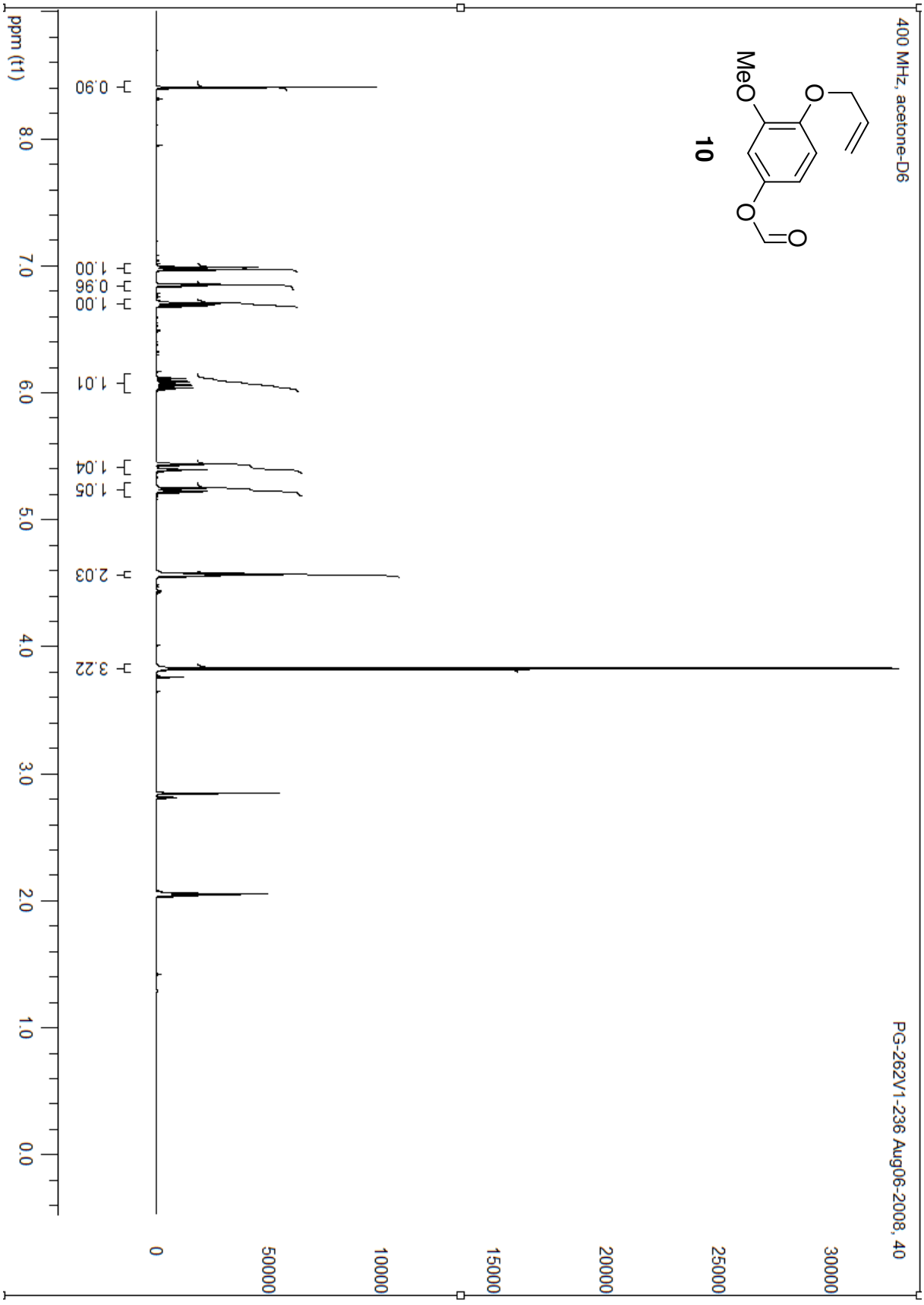

125 MHz, CDCl3
MeO
O
OH
6
150.614
150.579
141.906
133.672
117.818
115.468
105.913
100.739
71.047
55.790
ppm (t1)
150
100
50
0

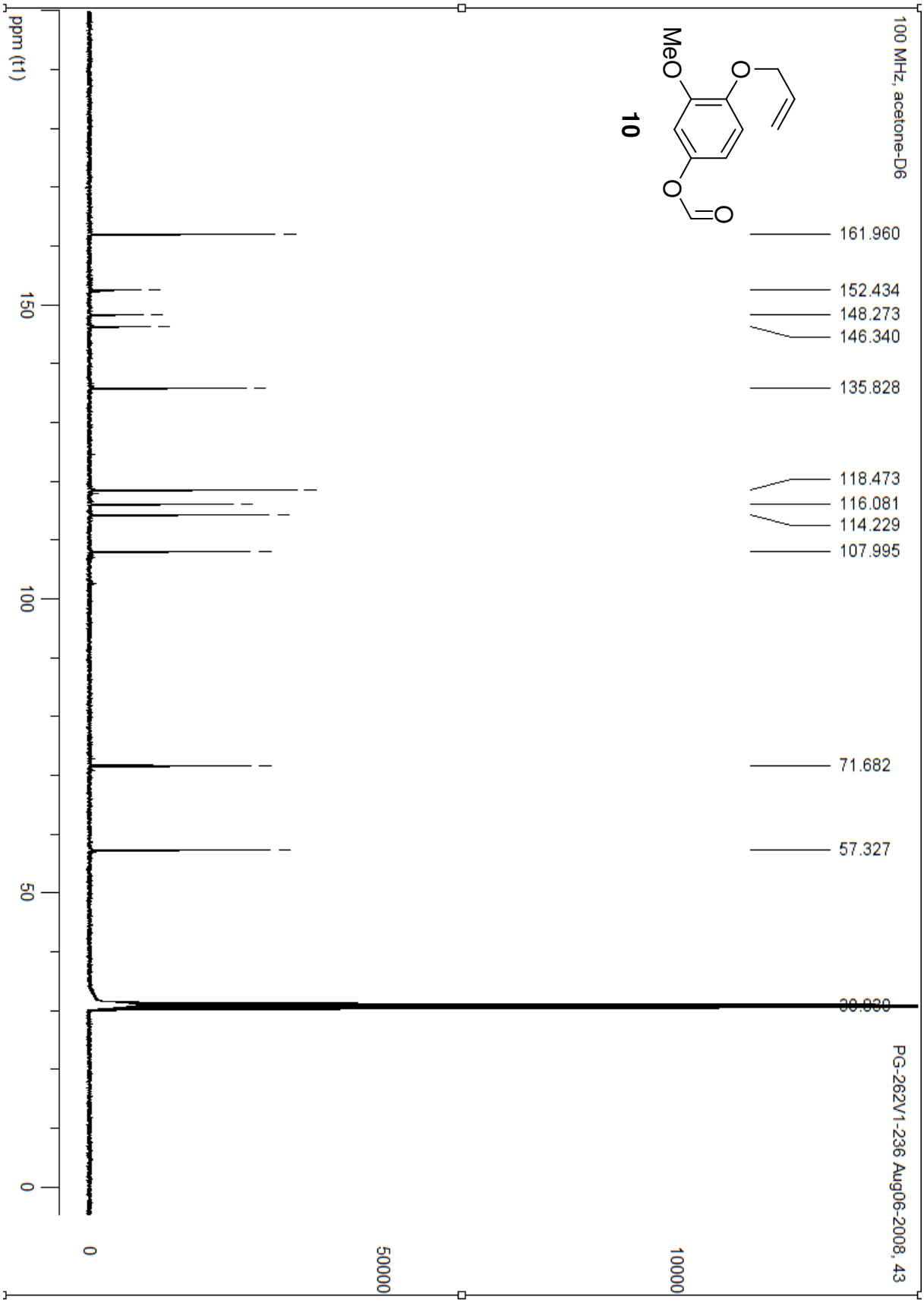

400 MHz, acetone-D6
PG 250 F1 224 Jul25-2008, 70
HO
MeO
O
O
8
3.50
1.06
2.13
0.94
1.00
ppm (t1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0
5000
10000
15000
20000
25000
30000

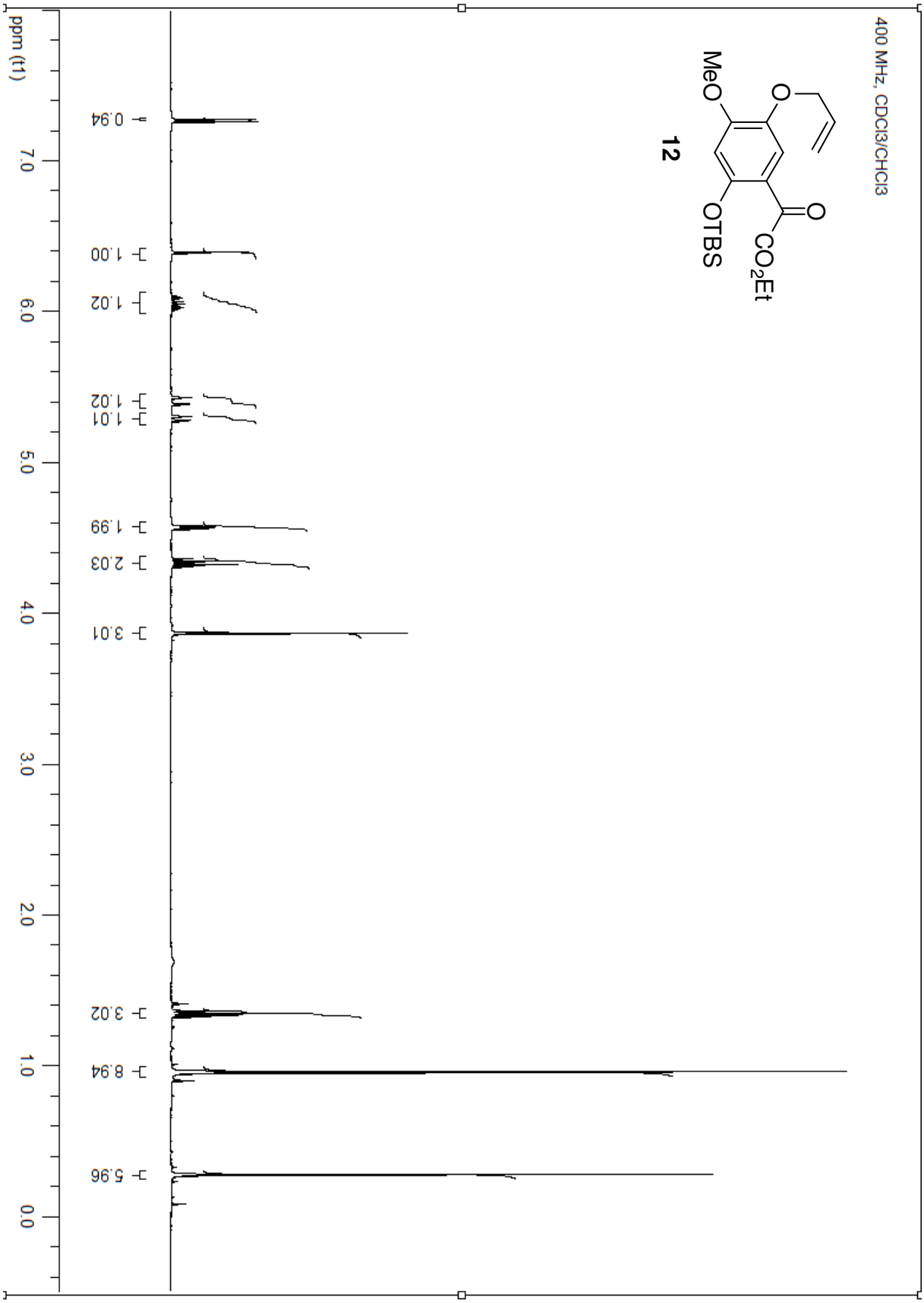

100 MHz, acetone-D6
8
MeO
HO
O
O
162.143
149.748
146.590
144.950
116.679
114.866
107.415
57.437
ppm (t1)
200
150
100
50
0
0
50000
10000
15000
20000
PG 250F1 224, Jul25-2008, 73

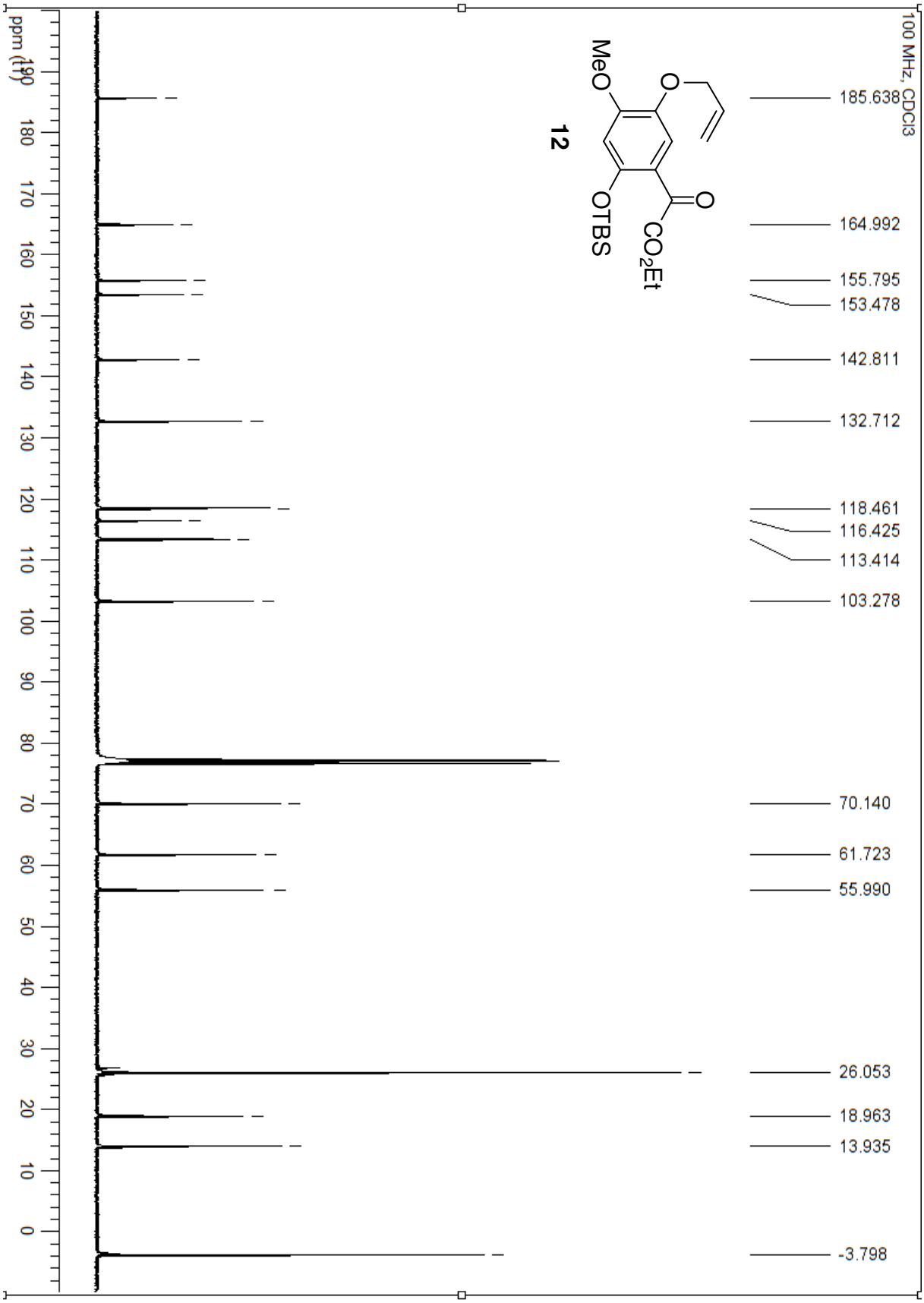

CDCl3, 400 MHz
MeO
O
O
9
PG-231-206, Jun30-2008, 10
ppm (f1)
10.0
5.0
0.0
1.04
2.08
1.07
1.00
1.05
1.04
2.14
3.22
0
5000
10000
15000
20000
25000
30000

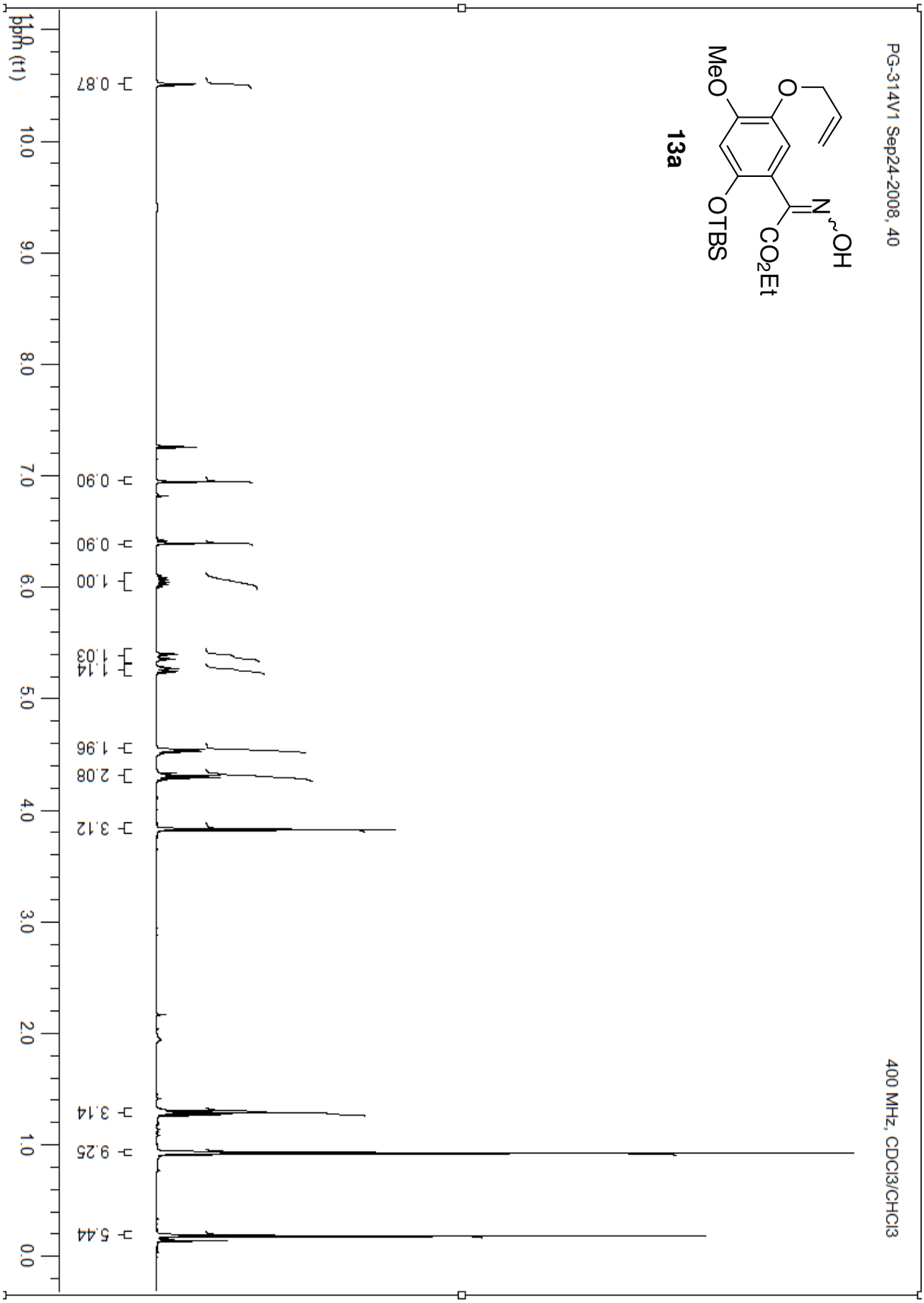

ppm (t1)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
MeO
O
O
9
190.720
153.325
149.721
132.091
130.037
126.408
118.599
111.785
109.145
69.621
55.850
100 MHz, CDCl3

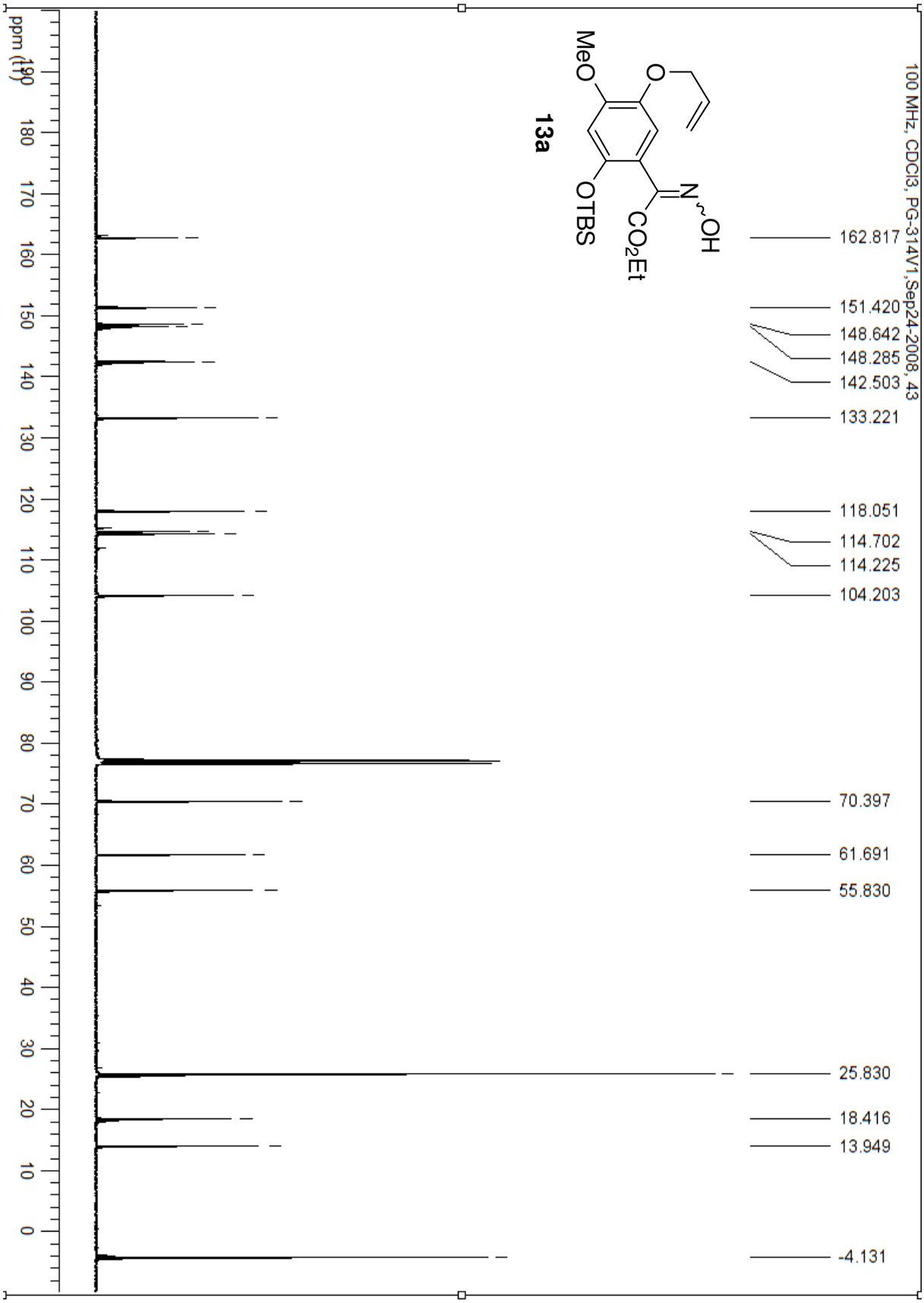

400 MHz, acetone-D6
PG-262V1-236 Aug06-2008, 40
10
MeO
O
O
O
ppm (t1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.90
1.00
0.96
1.00
1.01
1.04
1.05
2.03
3.22
0
50000
10000
15000
20000
25000
30000

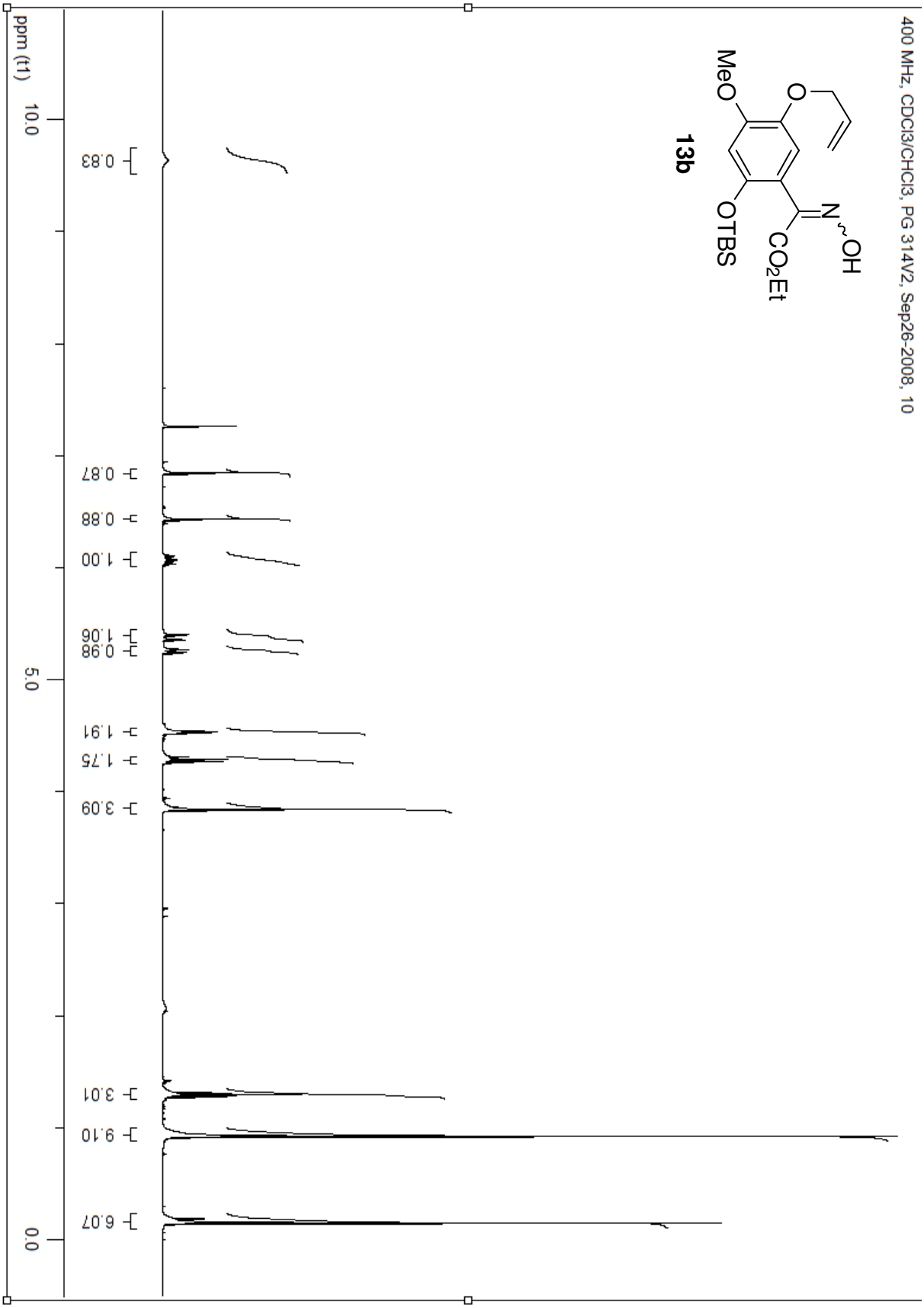

100 MHz, acetone-D6
10
MeO
O
O
O
161.960
152.434
148.273
146.340
135.828
118.473
116.081
114.229
107.995
71.682
57.327
39.939
ppm (t1)
150
100
50
0
0
50000
10000
PG-262V1-236 Aug06-2008, 43

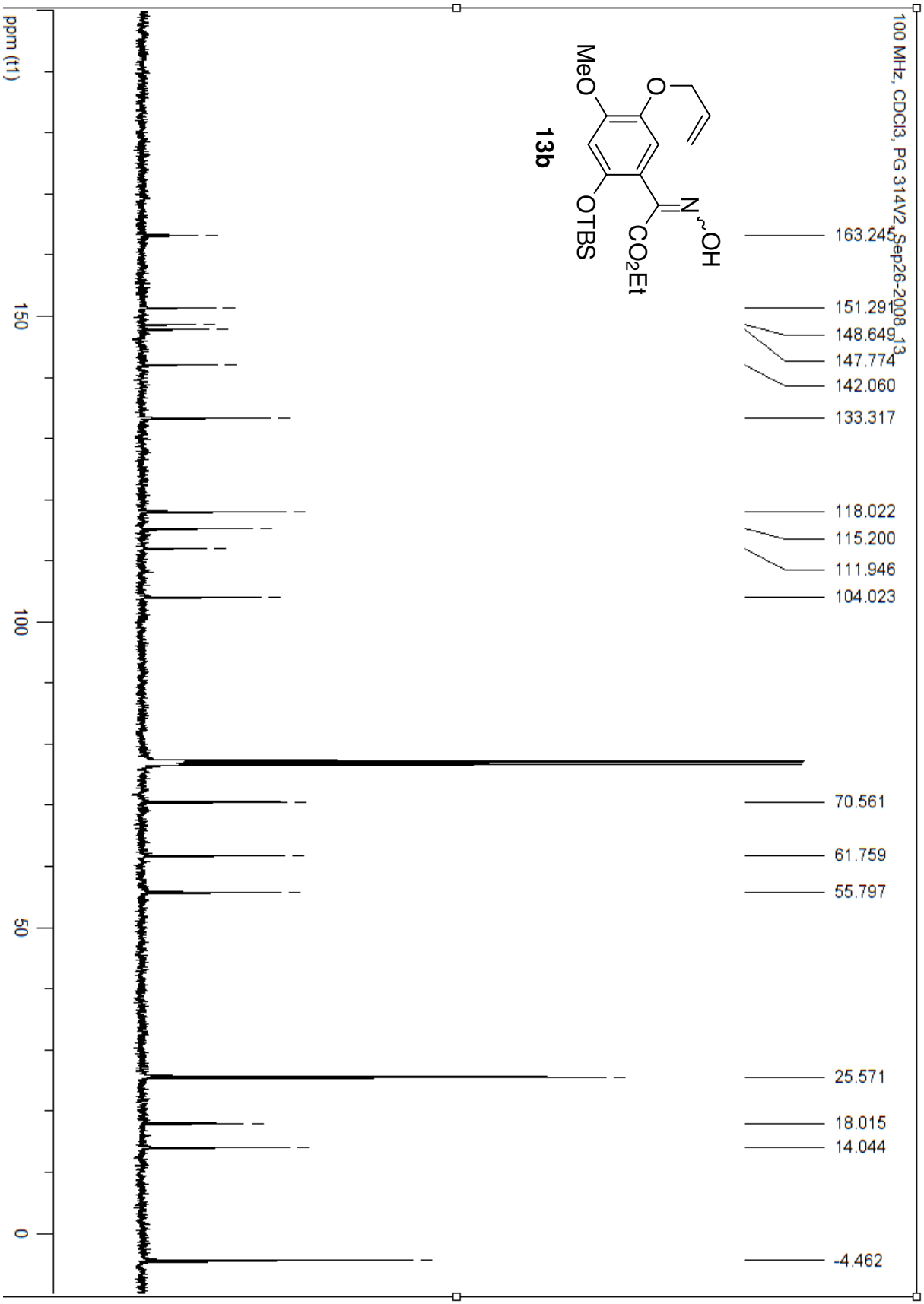

400 MHz, CDCl3/CHCl3
MeO
OTBS
O
O
CO2Et
12
ppm (t1)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.94
1.00
1.02
1.02
1.01
1.99
2.03
3.01
3.02
8.94
5.96

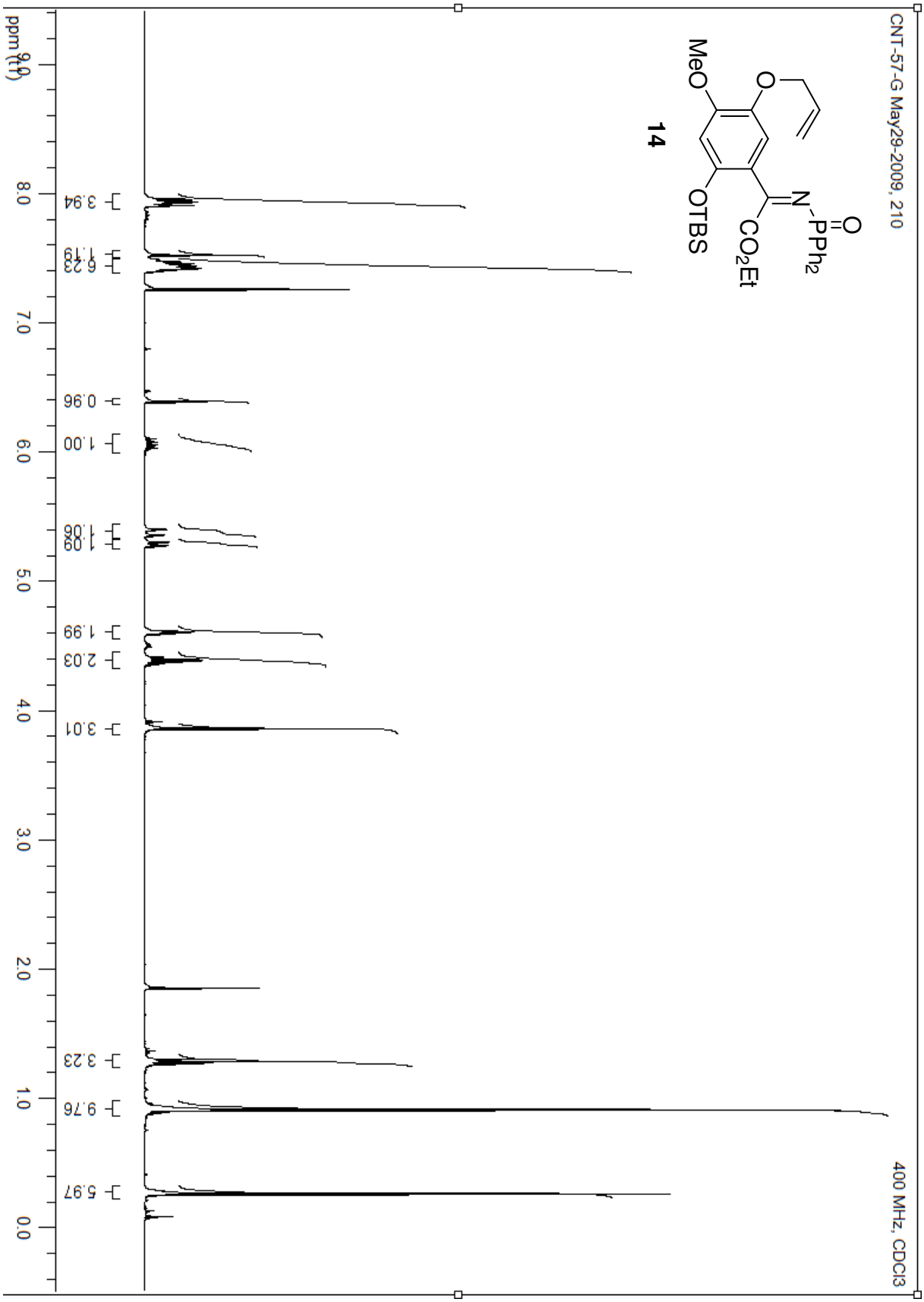

100 MHz, CDCl3
185.638
164.992
155.795
153.478
142.811
132.712
118.461
116.425
113.414
103.278
70.140
61.723
55.990
26.053
18.963
13.935
-3.798
MeO
OTBS
O
O
CO2Et
12
ppm (t1)

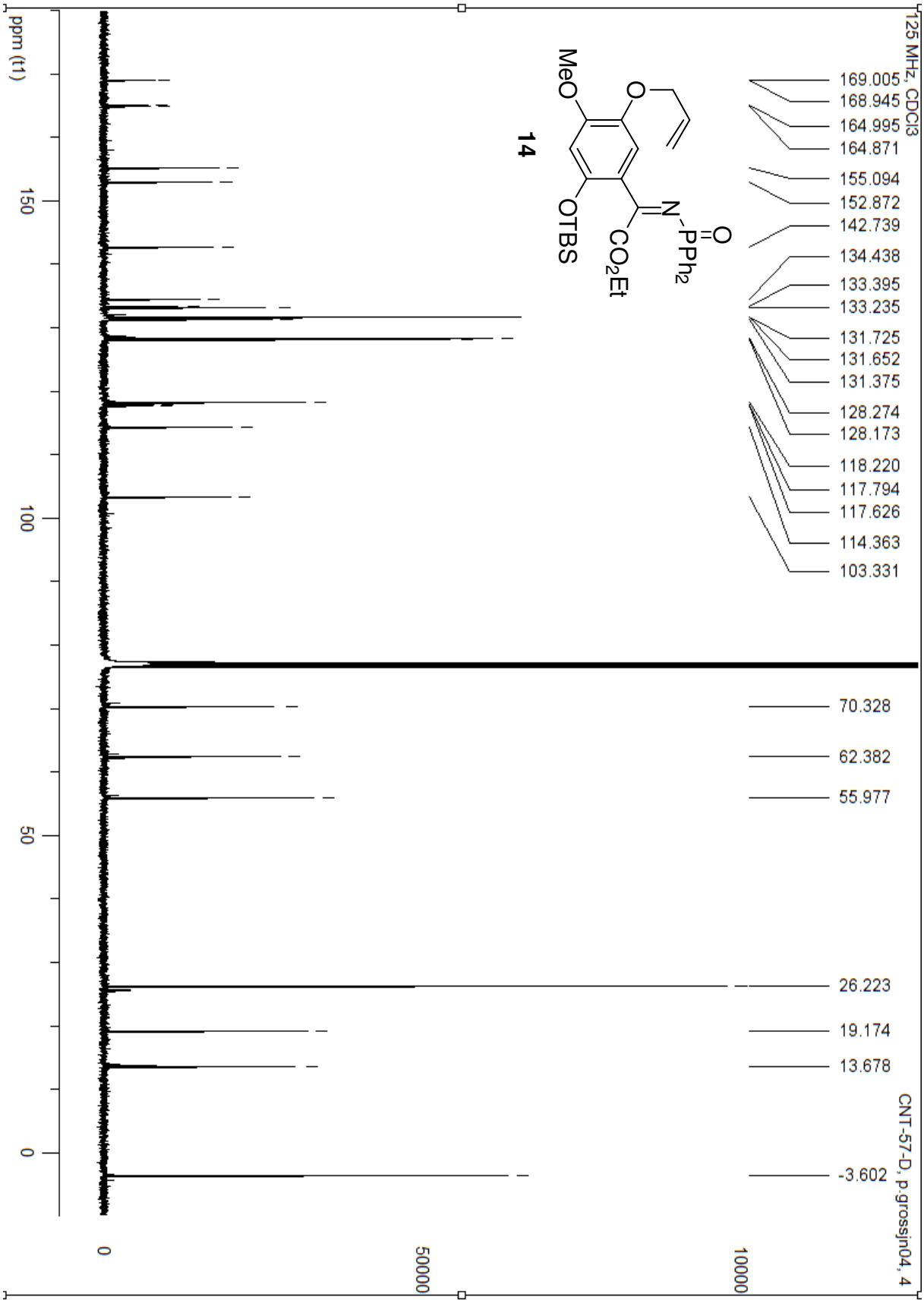

PG-314V1 Sep24-2008, 40
400 MHz, CDCl3/CHCl3
13a
MeO
OTBS
O
N
OH
CO2Et
ppm (t1)
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.87
0.90
0.90
1.00
1.03
1.14
1.96
2.08
3.12
3.14
9.25
5.44

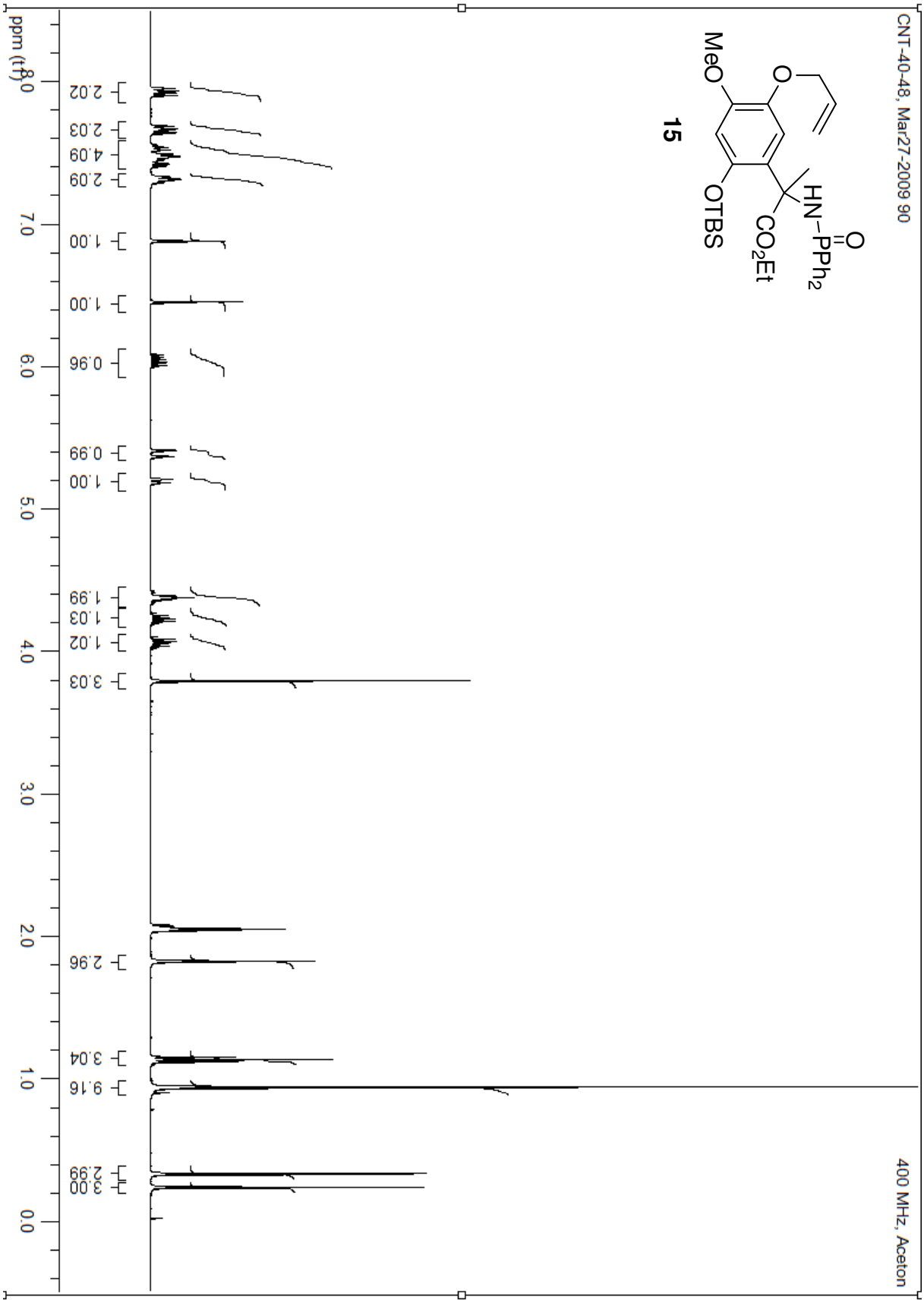

100 MHz, CDCl3, PG-314V1,Sep24-2008, 43
ppm (t1)
MeO
OTBS
O
N
OH
CO2Et
13a
162.817
151.420
148.642
148.285
142.503
133.221
118.051
114.702
114.225
104.203
70.397
61.691
55.830
25.830
18.416
13.949
-4.131

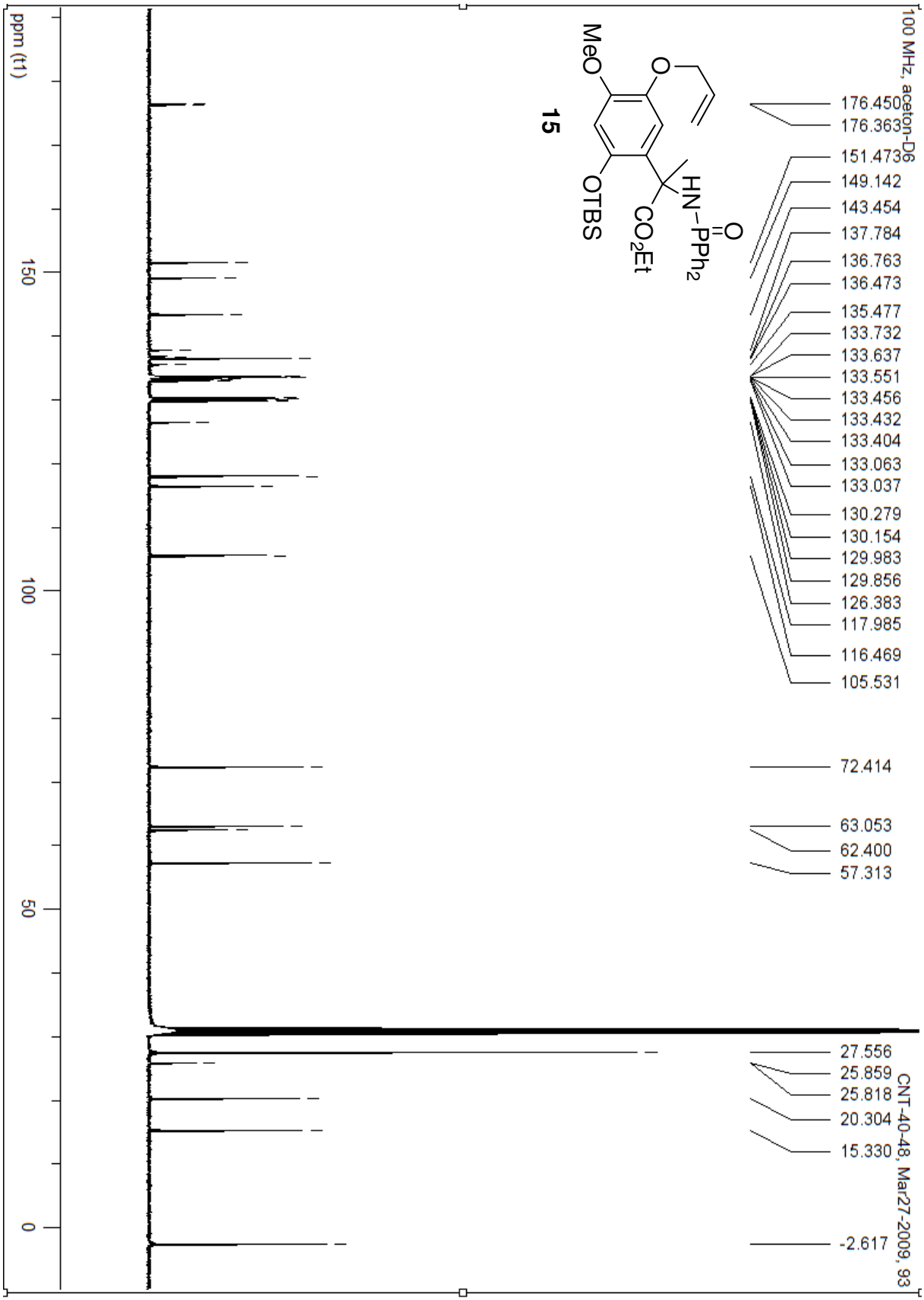

400 MHz, CDCl3/CHCl3, PG 314V2, Sep26-2008, 10
13b
MeO
OTBS
CO2Et
N
OH
O
ppm (t1)
10.0
5.0
0.0
0.83
0.87
0.88
1.00
0.98
1.06
1.91
1.75
3.09
3.01
9.10
6.07

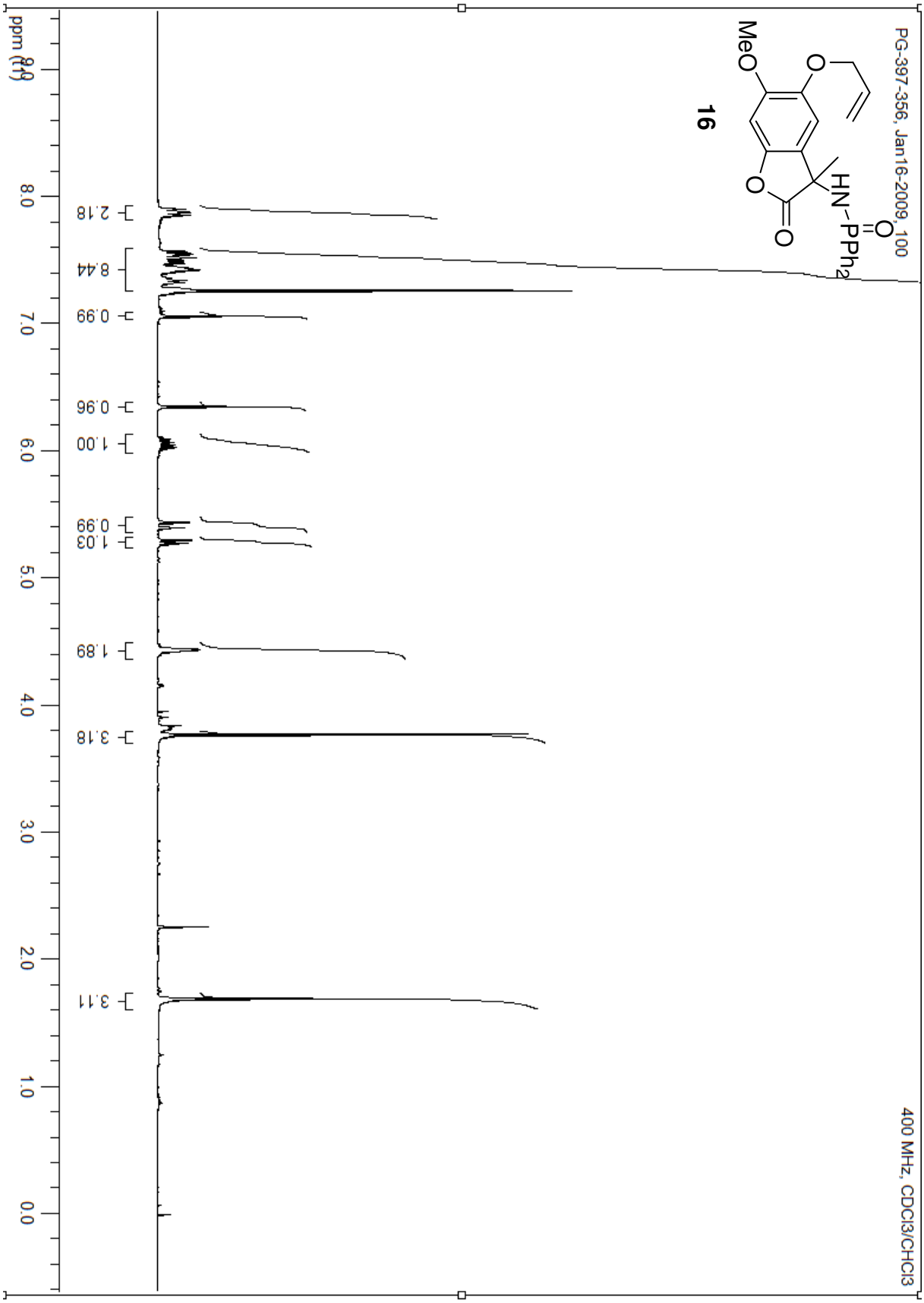

13b
MeO
OTBS
O
N
OH
CO2Et
100 MHz, CDCl3, PG 314V2, Sep26-2008, 13
ppm (t1)
0
50
100
150
163.245
151.291
148.649
147.774
142.060
133.317
118.022
115.200
111.946
104.023
70.561
61.759
55.797
25.571
18.015
14.044
-4.462

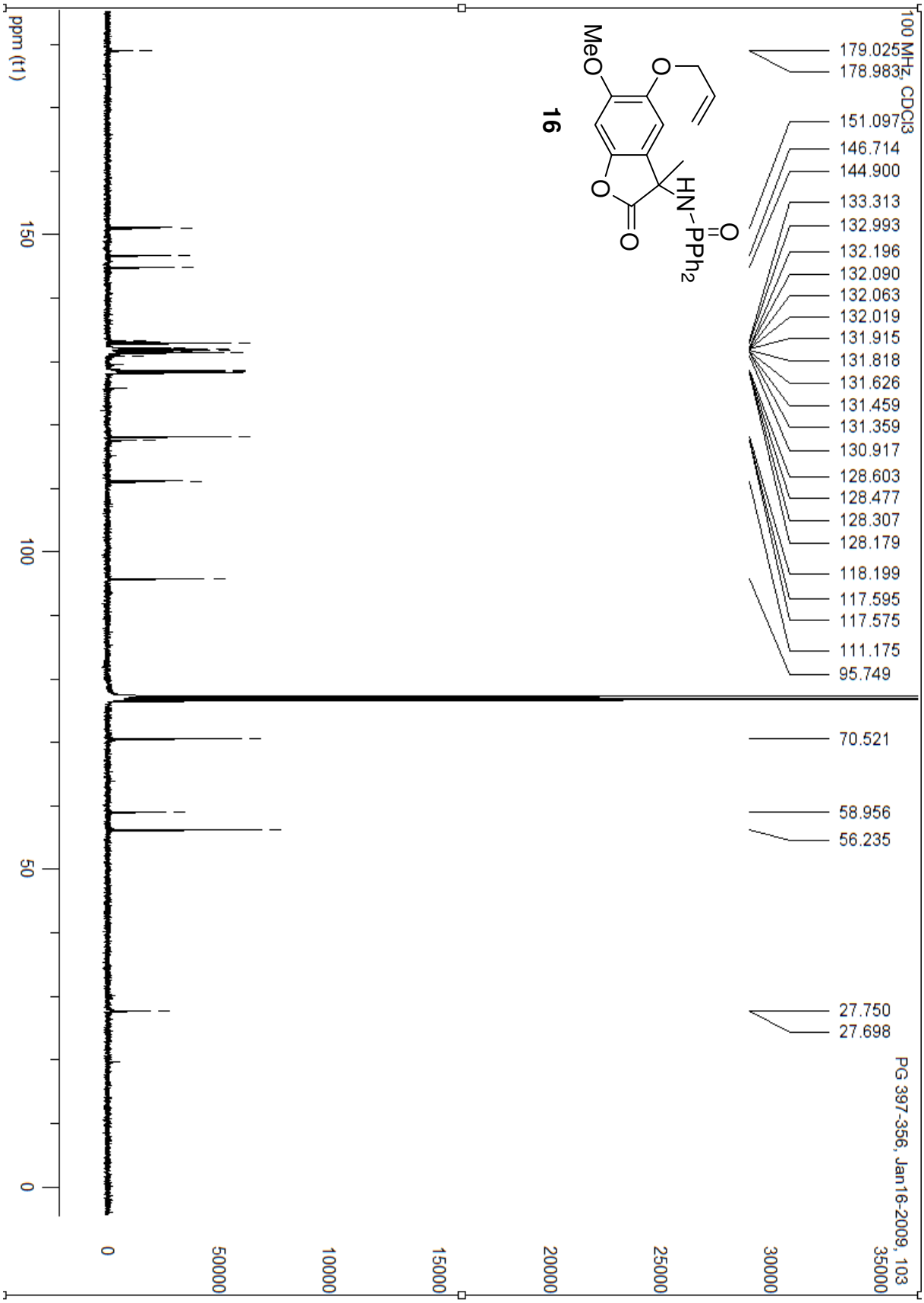

CNT-57-G May29-2009, 210
400 MHz, CDCl3
14
MeO
OTBS
CO2Et
O
N
PPh2
O
3.94
6.23
1.19
0.96
1.00
1.06
1.09
1.99
2.03
3.01
3.23
9.76
5.97
ppm (t1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

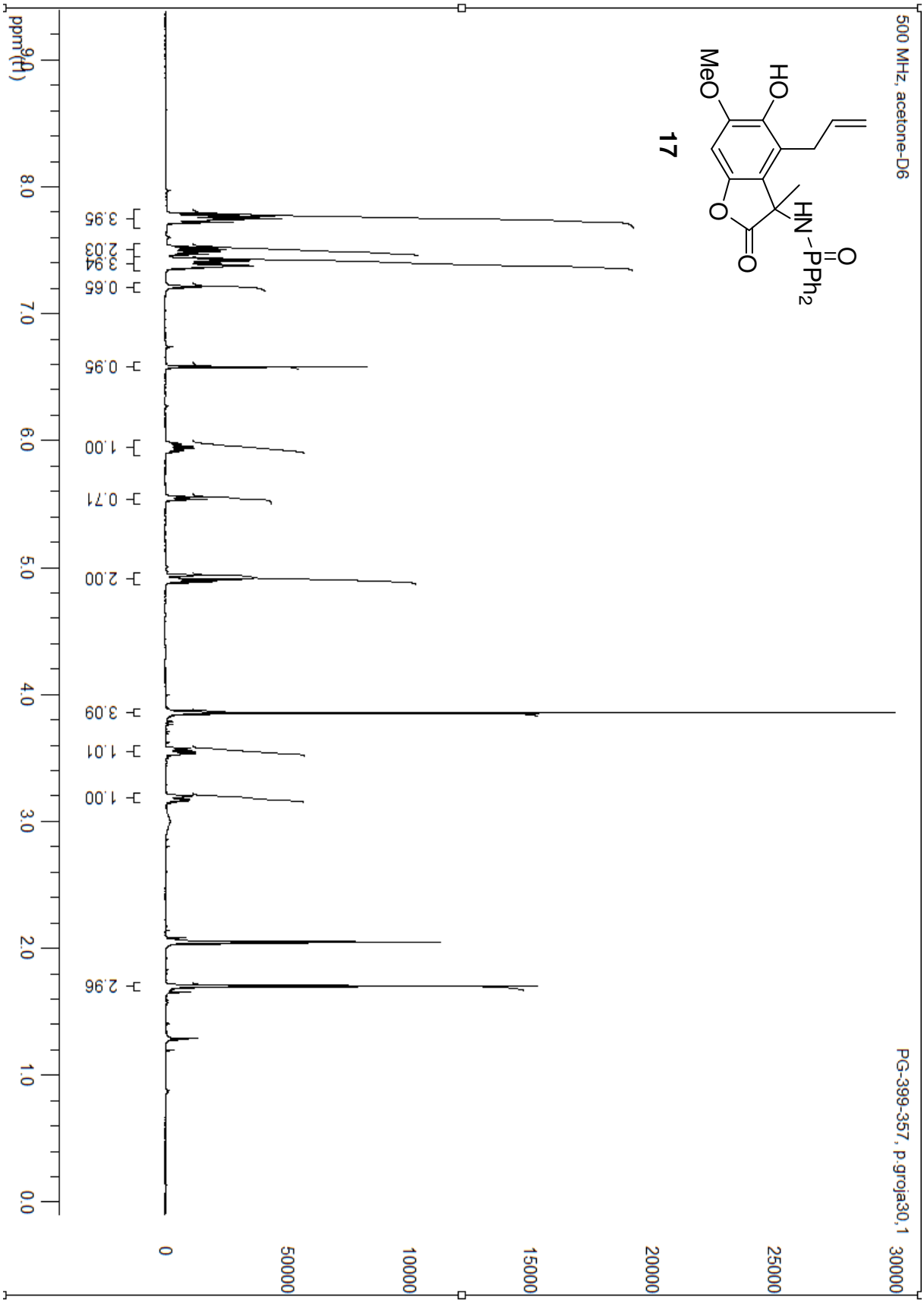

125 MHz, CDCl3
169.005
168.945
164.995
164.871
155.094
152.872
142.739
134.438
133.395
133.235
131.725
131.652
131.375
128.274
128.173
118.220
117.794
117.626
114.363
103.331
70.328
62.382
55.977
26.223
19.174
13.678
-3.602
14
MeO
OTBS
CO2Et
O
N
PPh2
ppm (t1)
0
50
100
150
0
50000
10000
CNT-57-D, p.grossjn04, 4


CNT-40-48, Mar27-2009 90
400 MHz, Aceton
15
MeO
OTBS
CO2Et
HN
PPh2
O
ppm (t1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
2.02
2.03
4.09
2.09
1.00
1.00
0.96
0.99
1.00
1.99
1.03
1.02
3.03
2.96
3.04
9.16
2.99
3.00


100 MHz, aceton-D6
ppm (t1)
150
100
50
0
MeO
OTBS
O
HN–PPh2
O
CO2Et
15
176.450
176.363
151.4736
149.142
143.454
137.784
136.763
136.473
135.477
133.732
133.637
133.551
133.456
133.432
133.404
133.063
133.037
130.279
130.154
129.983
129.856
126.383
117.985
116.469
105.531
72.414
63.053
62.400
57.313
27.556
25.859
25.818
20.304
15.330
-2.617
CNT-40-48, Mar27-2009, 93


PG-397-356, Jan16-2009, 100
400 MHz, CDCl3/CHCl3
16
MeO
O
HN
PPh2
ppm (t1)
2.18
8.44
0.99
0.96
1.00
0.99
1.03
1.89
3.18
3.11


100 MHz, CDCl3
179.025
178.983
151.097
146.714
144.900
133.313
132.993
132.196
132.090
132.063
132.019
131.915
131.818
131.626
131.459
131.359
130.917
128.603
128.477
128.307
128.179
118.199
117.595
117.575
111.175
95.749
70.521
58.956
56.235
27.750
27.698
MeO
O
HN
PPh2
O
O
O
16
ppm (t1)
0
50
100
150
0
50000
10000
15000
20000
25000
30000
35000
PG 397-356, Jan16-2009, 103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O
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8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
3.95
2.03
3.94
0.65
0.95
1.00
0.71
2.00
3.09
1.01
1.00
2.96
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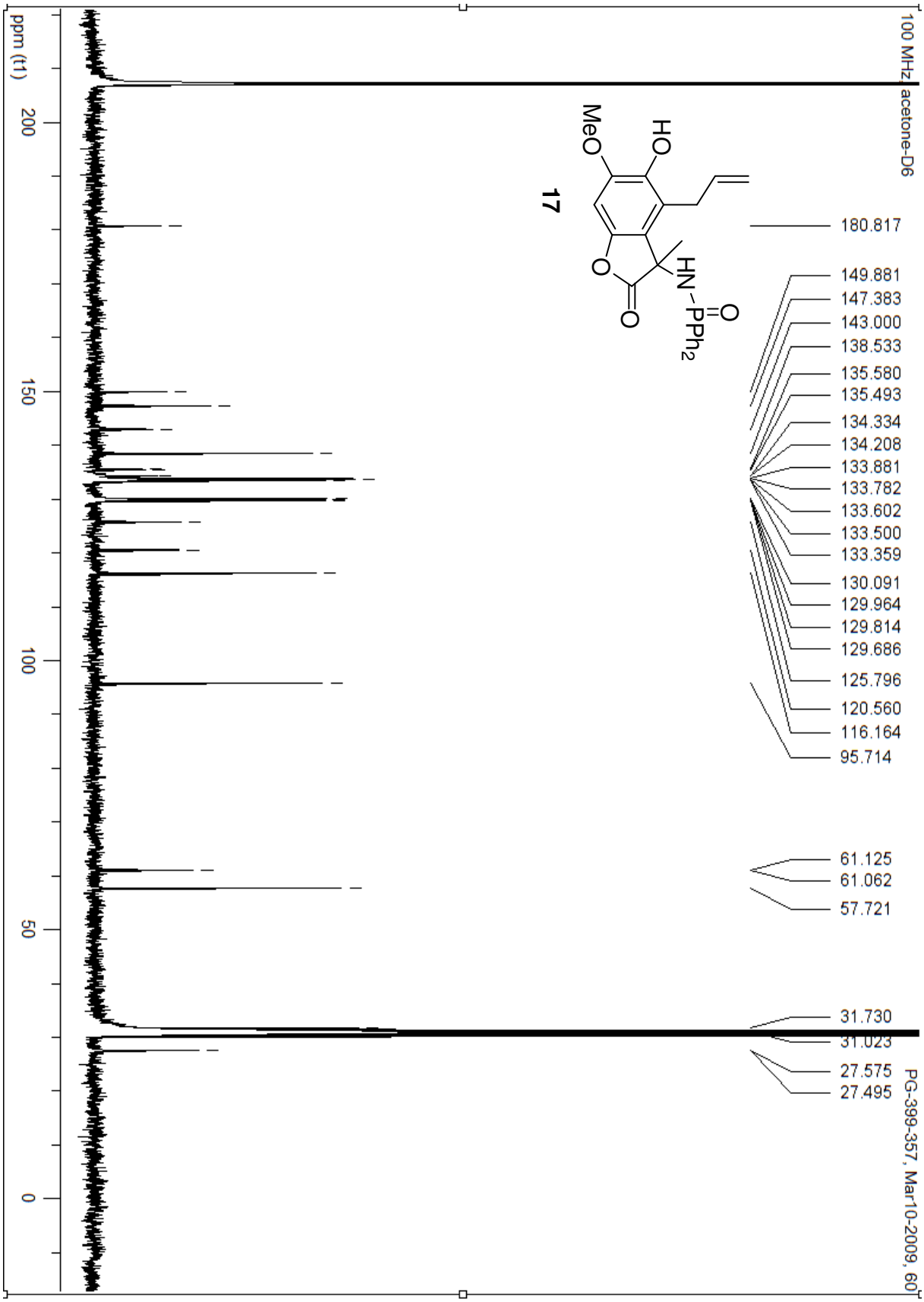
30000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HN
P
O
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149.881
147.383
143.000
138.533
135.580
135.493
134.334
134.208
133.881
133.782
133.602
133.500
133.359
130.091
129.964
129.814
129.686
125.796
120.560
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61.062
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27.575
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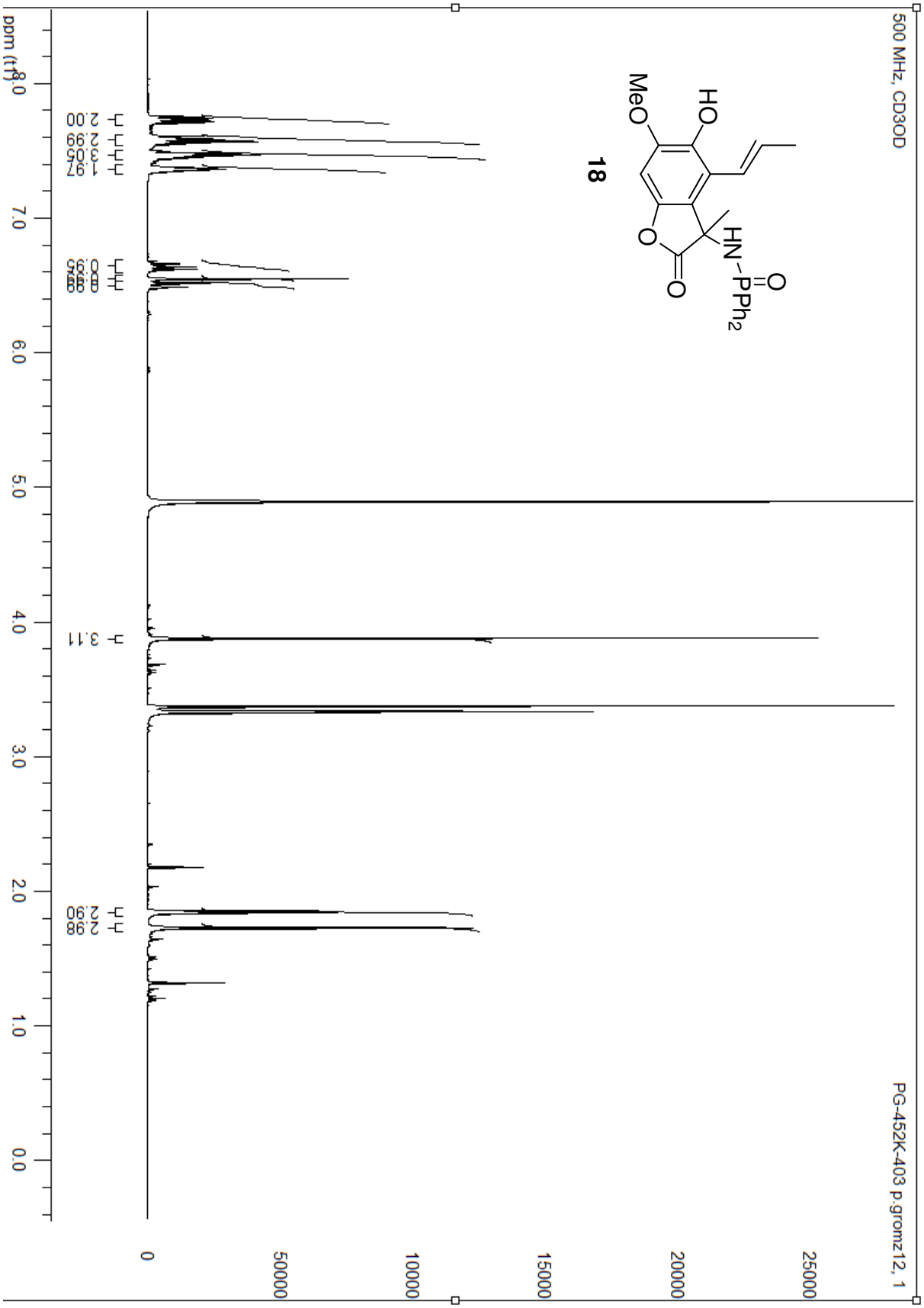
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P
Ph2
ppm (t1)
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7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
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25000
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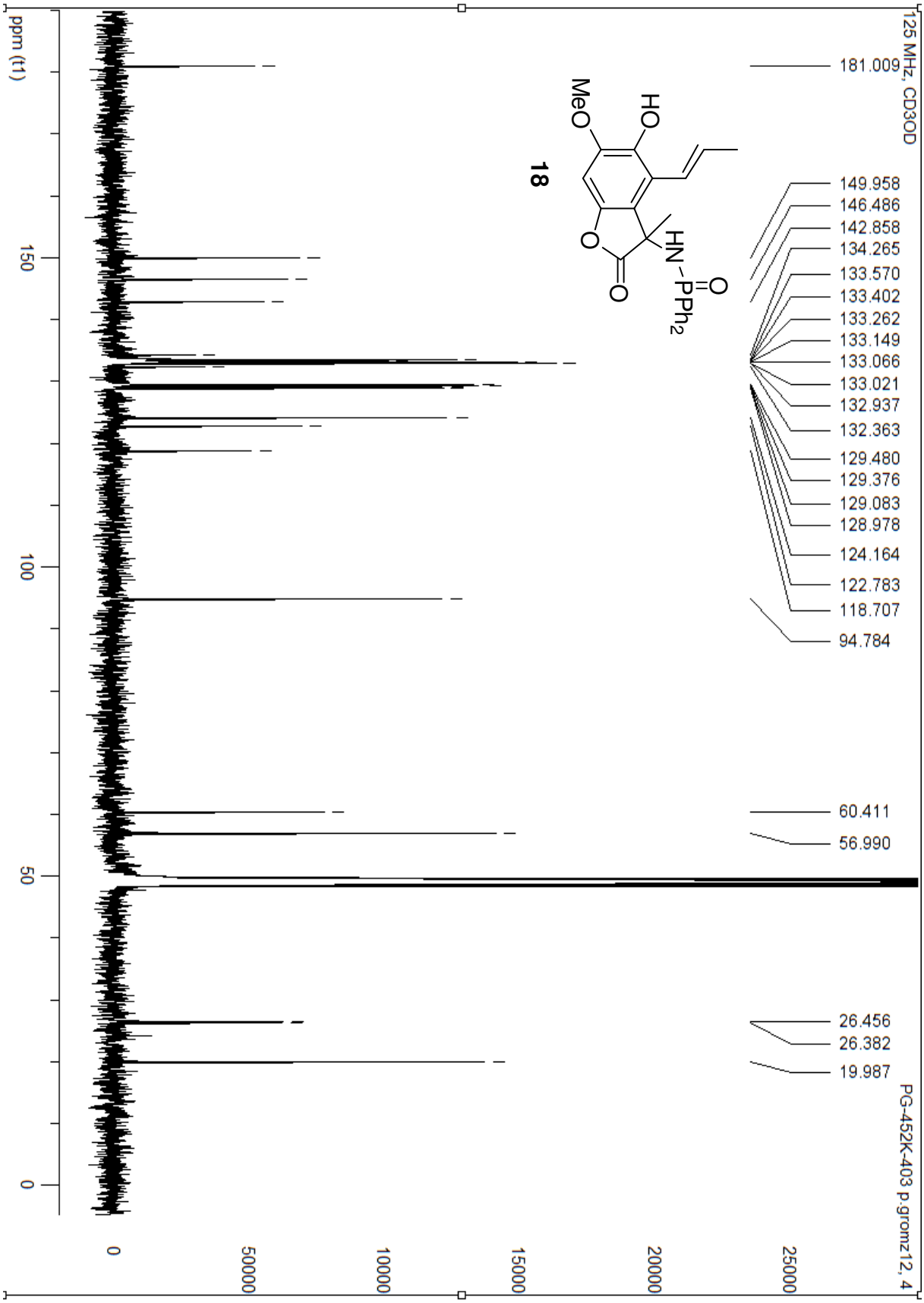
1.05
1.97
0.95
3.11
2.90
2.98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133.402
133.262
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133.066
133.021
132.937
132.363
129.480
129.376
129.083
128.978
124.164
122.783
118.707
94.784
60.411
56.990
26.456
26.382
19.987
MeO
HO
O
O
HN
P
O
Ph2
18
ppm (t1)
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100
150
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15000
20000
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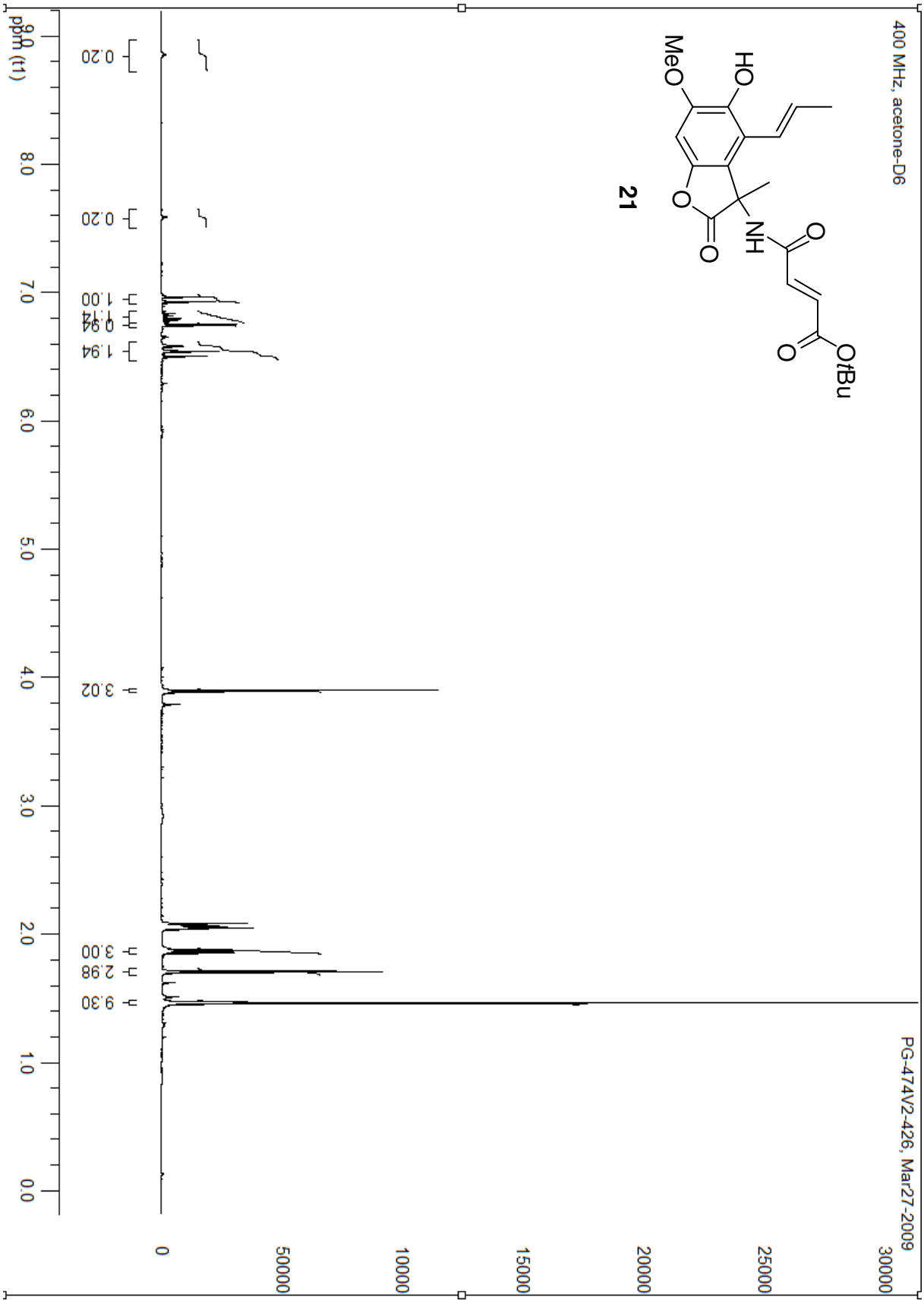
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HO
NH
O
OtBu
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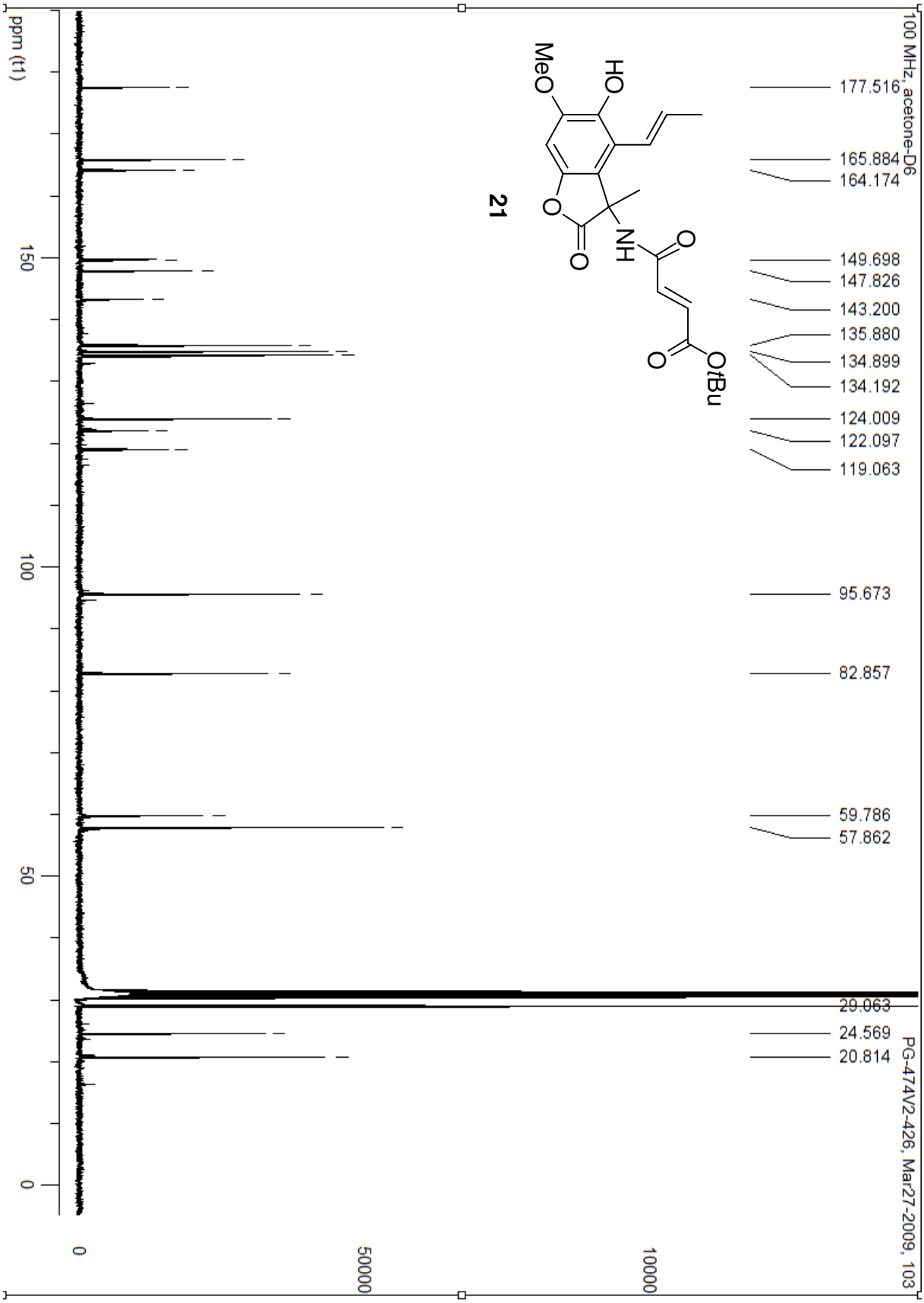
0.94
1.74
1.94
3.02
3.00
2.98
9.30


100 MHz, acetone-D6
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164.174
149.698
147.826
143.200
135.880
134.899
134.192
124.009
122.097
119.063
95.673
82.857
59.786
57.862
29.063
24.569
20.814
PG-474V2-426, Mar27-2009, 103
ppm (t1)
0
50
100
150
0
50000
10000
MeO
HO
NH
O
OtBu
21

Crystallographic data

The single-crystal X-ray diffraction study was carried out on a Nonius Kappa-CCD diffractometer at 123(2) K using MoKα radiation (λ = 0.71073 Å). Direct Methods (SHELXS-97)[2] were used for structure solution and refinement was carried out using SHELXL-97 (full-matrix least-squares on F^2). Hydrogen atoms were localized by difference electron density determination and refined using a riding model (H(N, O) free).
14: pale yellow crystals, $C_{32}H_{40}NO_6PSi$, M = 593.71, crystal size 0.50 x 0.35 x 0.25 mm, monoclinic, space group $P2_1/n$ (No. 14), a = 12.039(2) Å, b = 21.525(2) Å, c = 13.205(2) Å, β = 109.94(1)°, V = 3216.8(8) Å^3, Z = 4, ρ(calc) = 1.226 Mg m^{-3}, F(000) = 1264, μ = 0.165 mm^{-1}, 18988 reflexes ($2\theta_{max}$ = 55°), 7341 unique [R_{int} = 0.030], 371 parameters, $R1$ ($I > 2\sigma(I)$) = 0.046, *wR2 (all data)* = 0.106, S = 1.02, largest diff. peak and hole 0.584 and -0.291 e Å^{-3}.
18: colourless crystals, $C_{25}H_{24}NO_5P$, M = 449.42, crystal size 0.50 x 0.30 x 0.10 mm, triclinic, space group P-1 (No. 2), a = 10.199(1) Å, b = 13.332(1) Å, c = 17.800(1) Å, α = 99.86(1)°, β = 105.95(1)°, γ = 103.28(1)°, V = 2192.7(3) Å^3, Z = 4, ρ(calc) = 1.361 Mg m^{-3}, F(000) = 944, μ = 0.163 mm^{-1}, 22725 reflexes ($2\theta_{max}$ = 55°), 9958 unique [R_{int} = 0.043], 595 parameters, 4 restraints, $R1$ ($I > 2\sigma(I)$) = 0.047, *wR2 (all data)* = 0.123, S = 1.02, largest diff. peak and hole 0.795 and -0.478 e Å^{-3}.
Crystallographic data (excluding structure factors) for the structures reported in this work have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 743652 (**14**), and CCDC 743653 (**18**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge DB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

[2] G. M. Sheldrick, *Acta Crystallogr.* 2008, **A64**, 112-122.

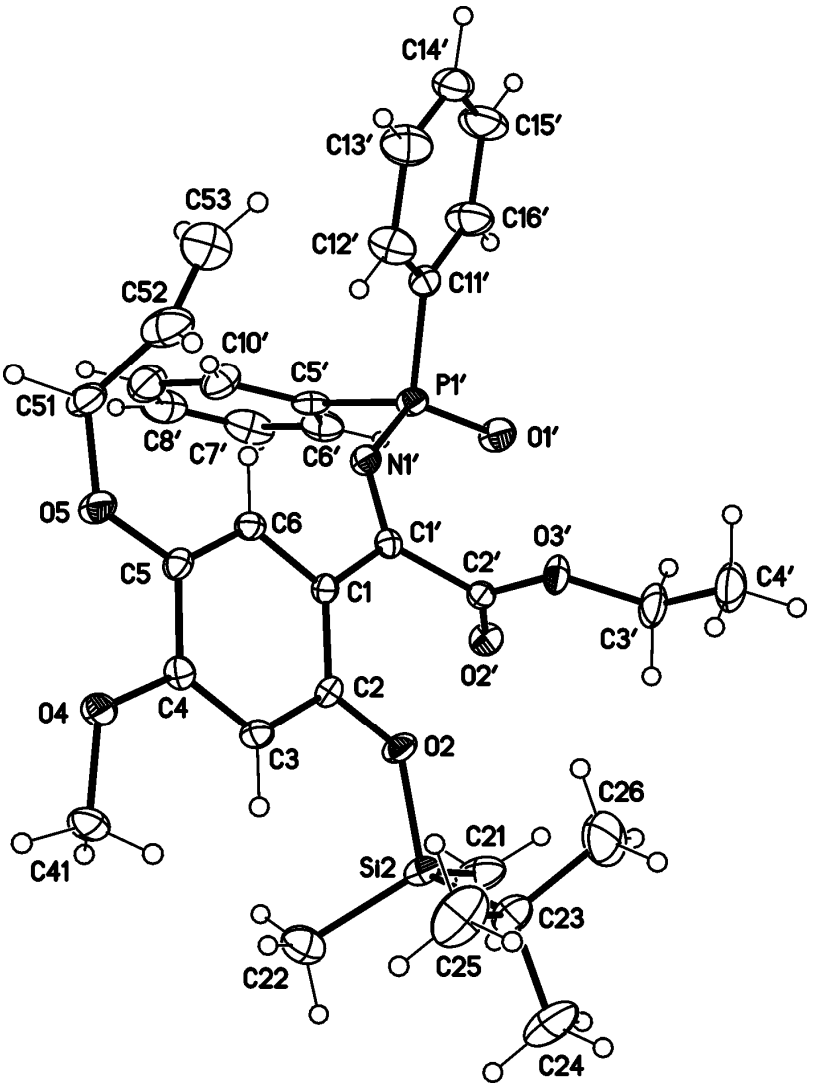

Fig. S1. Molecular structure of **14** (displacement parameters are drawn at 50% probability level).

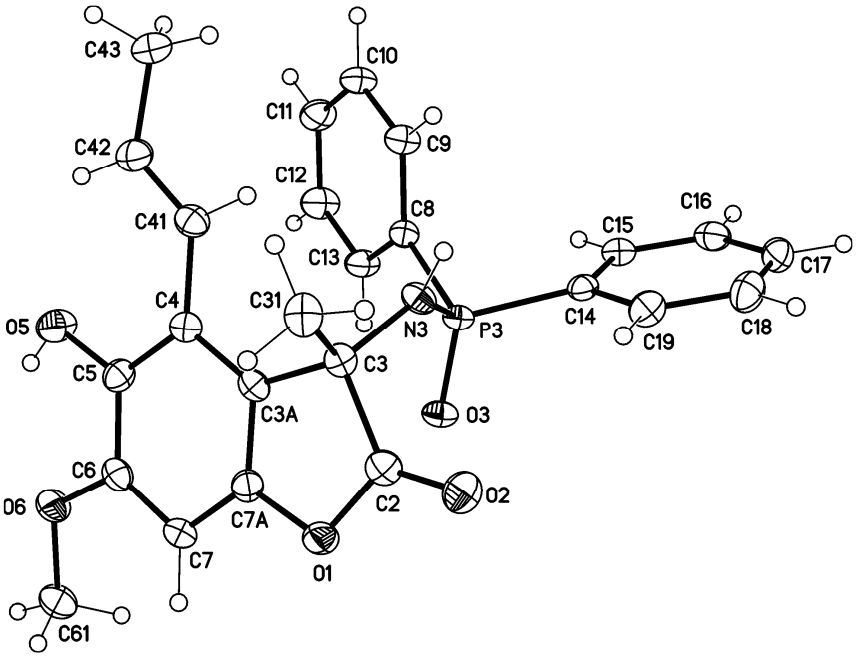

Fig. S2. Molecular structure of one the two crystallographic independent molecules of **18** (displacement parameters are drawn at 50% probability level).

Crystallographic data and pictures of **14**:

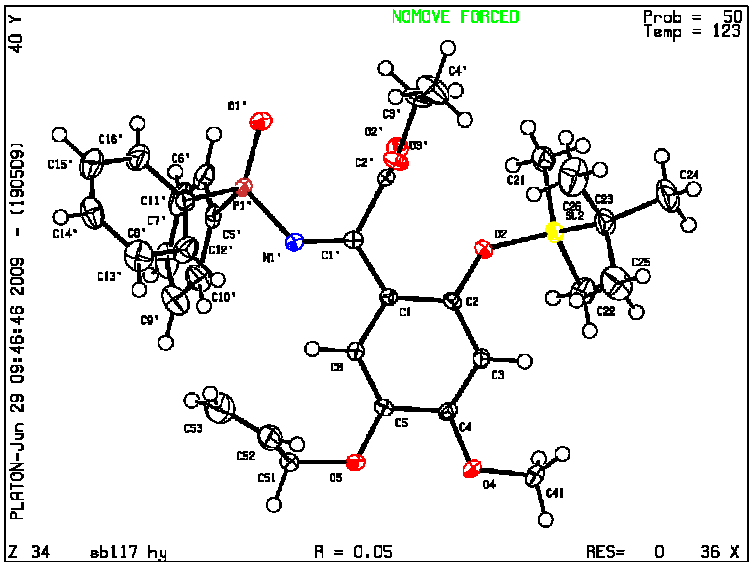

Table S1. Crystal data and structure refinement for 14.

Identification code	sb117_hy
Empirical formula	C32 H40 N O6 P Si
Formula weight	593.71
Temperature	123(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n (No.14)
Unit cell dimensions	a = 12.039(2) A alpha = 90 deg. b = 21.525(2) A beta = 109.94(1) deg. c = 13.205(2) A gamma = 90 deg.
Volume	3216.8(8) A^3
Z, Calculated density	4, 1.226 Mg/m^3
Absorption coefficient	0.165 mm^-1
F(000)	1264
Crystal size	0.50 x 0.35 x 0.25 mm
Theta range for data collection	2.97 to 27.48 deg.
Limiting indices	-15<=h<=15, -27<=k<=27, -17<=l<=17
Reflections collected / unique	18988 / 7341 [R(int) = 0.0295]
Completeness to theta = 27.48	99.6 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7341 / 0 / 371
Goodness-of-fit on F^2	1.021
Final R indices [I>2sigma(I)]	R1 = 0.0462, wR2 = 0.0977
R indices (all data)	R1 = 0.0660, wR2 = 0.1060
Largest diff. peak and hole	0.584 and -0.291 e.A^-3

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 14.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	4401(1)	6610(1)	2767(1)	14(1)
C(2)	4940(1)	7122(1)	2479(1)	15(1)
O(2)	4936(1)	7669(1)	2980(1)	21(1)
Si(2)	5256(1)	8407(1)	2790(1)	18(1)
C(21)	4281(2)	8858(1)	3340(2)	33(1)
C(22)	4871(2)	8590(1)	1338(2)	31(1)
C(23)	6857(2)	8524(1)	3590(2)	29(1)
C(24)	7164(2)	9217(1)	3617(2)	46(1)
C(25)	7656(2)	8170(1)	3108(2)	46(1)
C(26)	7087(2)	8296(1)	4746(2)	55(1)
C(3)	5437(2)	7064(1)	1673(1)	17(1)
C(4)	5409(1)	6502(1)	1159(1)	16(1)
O(4)	5824(1)	6413(1)	340(1)	20(1)
C(41)	6199(2)	6952(1)	-96(2)	26(1)
C(5)	4899(2)	5975(1)	1469(1)	16(1)
O(5)	4930(1)	5442(1)	917(1)	24(1)
C(51)	4332(2)	4907(1)	1123(2)	28(1)
C(52)	5034(2)	4592(1)	2176(2)	36(1)
C(53)	4567(3)	4302(1)	2780(2)	48(1)
C(6)	4402(1)	6038(1)	2249(1)	15(1)
C(1')	3777(1)	6640(1)	3541(1)	14(1)
N(1')	3087(1)	6198(1)	3579(1)	17(1)
P(1')	2162(1)	6133(1)	4260(1)	18(1)
O(1')	2110(1)	6597(1)	5066(1)	26(1)
C(2')	3966(1)	7184(1)	4320(1)	15(1)
O(2')	3315(1)	7616(1)	4216(1)	19(1)
O(3')	4938(1)	7074(1)	5164(1)	21(1)
C(3')	5137(2)	7503(1)	6064(2)	29(1)
C(4')	6322(2)	7351(1)	6873(2)	40(1)
C(5')	792(2)	6086(1)	3140(2)	20(1)
C(6')	-177(2)	6429(1)	3153(2)	27(1)
C(7')	-1229(2)	6398(1)	2290(2)	35(1)
C(8')	-1324(2)	6026(1)	1421(2)	37(1)
C(9')	-364(2)	5683(1)	1399(2)	35(1)
C(10')	687(2)	5710(1)	2254(2)	29(1)
C(11')	2475(2)	5364(1)	4821(1)	20(1)
C(12')	3236(2)	4949(1)	4596(2)	30(1)
C(13')	3424(2)	4368(1)	5078(2)	37(1)
C(14')	2860(2)	4201(1)	5780(2)	34(1)
C(15')	2101(2)	4609(1)	6004(2)	41(1)
C(16')	1906(2)	5190(1)	5530(2)	35(1)

Table S3. Bond lengths [A] and angles [deg] for 14.

C(1)-C(2)	1.395(2)
C(1)-C(6)	1.410(2)
C(1)-C(1')	1.462(2)
C(2)-O(2)	1.352(2)
C(2)-C(3)	1.393(2)
O(2)-Si(2)	1.6720(13)
Si(2)-C(21)	1.851(2)
Si(2)-C(22)	1.855(2)
Si(2)-C(23)	1.872(2)
C(23)-C(25)	1.526(3)
C(23)-C(24)	1.533(3)
C(23)-C(26)	1.537(3)
C(3)-C(4)	1.381(2)
C(4)-O(4)	1.351(2)
C(4)-C(5)	1.416(2)
O(4)-C(41)	1.435(2)
C(5)-C(6)	1.364(2)
C(5)-O(5)	1.366(2)
O(5)-C(51)	1.433(2)
C(51)-C(52)	1.517(3)
C(52)-C(53)	1.286(3)
C(1')-N(1')	1.276(2)
C(1')-C(2')	1.523(2)
N(1')-P(1')	1.6597(15)
P(1')-O(1')	1.4756(13)
P(1')-C(11')	1.7999(19)
P(1')-C(5')	1.8038(19)
C(2')-O(2')	1.193(2)
C(2')-O(3')	1.333(2)
O(3')-C(3')	1.460(2)
C(3')-C(4')	1.498(3)
C(5')-C(6')	1.386(3)
C(5')-C(10')	1.393(3)
C(6')-C(7')	1.386(3)
C(7')-C(8')	1.370(3)
C(8')-C(9')	1.380(3)
C(9')-C(10')	1.380(3)
C(11')-C(12')	1.382(3)
C(11')-C(16')	1.387(3)
C(12')-C(13')	1.386(3)
C(13')-C(14')	1.370(3)
C(14')-C(15')	1.371(3)
C(15')-C(16')	1.383(3)

C(2)-C(1)-C(6)	118.66(15)
C(2)-C(1)-C(1')	123.63(15)
C(6)-C(1)-C(1')	117.63(15)
O(2)-C(2)-C(3)	121.69(15)
O(2)-C(2)-C(1)	118.34(15)
C(3)-C(2)-C(1)	119.95(15)
C(2)-O(2)-Si(2)	135.64(12)
O(2)-Si(2)-C(21)	103.31(8)
O(2)-Si(2)-C(22)	111.59(8)
C(21)-Si(2)-C(22)	108.98(10)
O(2)-Si(2)-C(23)	106.82(8)
C(21)-Si(2)-C(23)	112.12(10)
C(22)-Si(2)-C(23)	113.56(10)
C(25)-C(23)-C(24)	108.31(19)
C(25)-C(23)-C(26)	109.2(2)
C(24)-C(23)-C(26)	109.12(19)
C(25)-C(23)-Si(2)	111.83(14)
C(24)-C(23)-Si(2)	109.80(15)
C(26)-C(23)-Si(2)	108.58(15)
C(4)-C(3)-C(2)	120.57(16)
O(4)-C(4)-C(3)	124.40(15)
O(4)-C(4)-C(5)	115.56(15)
C(3)-C(4)-C(5)	120.03(16)
C(4)-O(4)-C(41)	117.28(14)
C(6)-C(5)-O(5)	125.80(16)
C(6)-C(5)-C(4)	118.96(15)
O(5)-C(5)-C(4)	115.22(15)
C(5)-O(5)-C(51)	117.85(14)
O(5)-C(51)-C(52)	111.94(17)
C(53)-C(52)-C(51)	124.1(2)
C(5)-C(6)-C(1)	121.78(16)

N(1')-C(1')-C(1)	119.39(15)
N(1')-C(1')-C(2')	119.81(15)
C(1)-C(1')-C(2')	120.78(14)
C(1')-N(1')-P(1')	130.53(13)
O(1')-P(1')-N(1')	122.34(8)
O(1')-P(1')-C(11')	112.34(8)
N(1')-P(1')-C(11')	102.39(8)
O(1')-P(1')-C(5')	112.22(9)
N(1')-P(1')-C(5')	98.95(8)
C(11')-P(1')-C(5')	106.87(8)
O(2')-C(2')-O(3')	126.19(16)
O(2')-C(2')-C(1')	125.40(15)
O(3')-C(2')-C(1')	108.27(14)
C(2')-O(3')-C(3')	114.90(14)
O(3')-C(3')-C(4')	107.08(16)
C(6')-C(5')-C(10')	119.02(18)
C(6')-C(5')-P(1')	119.85(15)
C(10')-C(5')-P(1')	121.13(14)
C(7')-C(6')-C(5')	120.0(2)
C(8')-C(7')-C(6')	120.7(2)
C(7')-C(8')-C(9')	119.9(2)
C(10')-C(9')-C(8')	120.1(2)
C(9')-C(10')-C(5')	120.38(19)
C(12')-C(11')-C(16')	119.03(18)
C(12')-C(11')-P(1')	124.60(15)
C(16')-C(11')-P(1')	116.37(15)
C(11')-C(12')-C(13')	120.1(2)
C(14')-C(13')-C(12')	120.4(2)
C(13')-C(14')-C(15')	119.9(2)
C(14')-C(15')-C(16')	120.2(2)
C(15')-C(16')-C(11')	120.3(2)

Table S4. Anisotropic displacement parameters (A^2 x 10^3) for 14.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	13(1)	15(1)	13(1)	-1(1)	4(1)	0(1)
C(2)	14(1)	14(1)	16(1)	-3(1)	4(1)	-1(1)
O(2)	29(1)	14(1)	24(1)	-6(1)	15(1)	-6(1)
Si(2)	19(1)	14(1)	24(1)	-1(1)	9(1)	-2(1)
C(21)	39(1)	17(1)	52(1)	-4(1)	28(1)	0(1)
C(22)	30(1)	31(1)	30(1)	8(1)	9(1)	3(1)
C(23)	24(1)	29(1)	31(1)	-3(1)	6(1)	-10(1)
C(24)	39(1)	36(1)	63(2)	-13(1)	18(1)	-20(1)
C(25)	18(1)	51(2)	64(2)	-13(1)	7(1)	-1(1)
C(26)	40(1)	79(2)	33(1)	7(1)	-6(1)	-24(1)
C(3)	16(1)	16(1)	19(1)	0(1)	7(1)	-3(1)
C(4)	13(1)	19(1)	16(1)	0(1)	6(1)	0(1)
O(4)	26(1)	20(1)	22(1)	-2(1)	17(1)	-3(1)
C(41)	32(1)	25(1)	27(1)	2(1)	19(1)	-6(1)
C(5)	19(1)	14(1)	17(1)	-3(1)	7(1)	0(1)
O(5)	37(1)	15(1)	28(1)	-6(1)	23(1)	-4(1)
C(51)	45(1)	17(1)	33(1)	-9(1)	28(1)	-10(1)
C(52)	45(1)	21(1)	50(1)	-4(1)	29(1)	0(1)
C(53)	65(2)	40(1)	42(1)	2(1)	20(1)	-5(1)
C(6)	17(1)	14(1)	16(1)	1(1)	7(1)	-1(1)
C(1')	13(1)	15(1)	13(1)	1(1)	3(1)	3(1)
N(1')	19(1)	17(1)	18(1)	-2(1)	10(1)	-2(1)
P(1')	21(1)	16(1)	21(1)	-2(1)	13(1)	-2(1)
O(1')	36(1)	22(1)	29(1)	-6(1)	22(1)	-3(1)
C(2')	16(1)	16(1)	15(1)	-1(1)	8(1)	-2(1)
O(2')	19(1)	17(1)	23(1)	-1(1)	8(1)	4(1)
O(3')	22(1)	20(1)	15(1)	-6(1)	0(1)	4(1)
C(3')	37(1)	26(1)	19(1)	-11(1)	4(1)	1(1)
C(4')	46(1)	35(1)	23(1)	-6(1)	-8(1)	-1(1)
C(5')	20(1)	15(1)	28(1)	5(1)	11(1)	-3(1)
C(6')	26(1)	26(1)	36(1)	6(1)	19(1)	1(1)
C(7')	24(1)	37(1)	48(1)	18(1)	16(1)	6(1)
C(8')	26(1)	34(1)	42(1)	13(1)	1(1)	-4(1)
C(9')	36(1)	25(1)	34(1)	-1(1)	0(1)	-1(1)
C(10')	28(1)	20(1)	36(1)	-2(1)	7(1)	2(1)

C(11')	21(1)	20(1)	19(1)	0(1)	6(1)	-3(1)
C(12')	31(1)	30(1)	36(1)	8(1)	18(1)	6(1)
C(13')	34(1)	29(1)	46(1)	9(1)	12(1)	11(1)
C(14')	36(1)	25(1)	31(1)	9(1)	-1(1)	-5(1)
C(15')	58(2)	32(1)	41(1)	11(1)	27(1)	-5(1)
C(16')	47(1)	26(1)	43(1)	5(1)	28(1)	-1(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 14.

	x	y	z	U(eq)
H(21A)	4479	8763	4107	50
H(21B)	3455	8746	2953	50
H(21C)	4392	9303	3249	50
H(22A)	5387	8355	1042	46
H(22B)	4978	9036	1251	46
H(22C)	4046	8477	954	46
H(24A)	6660	9452	3926	69
H(24B)	7034	9363	2882	69
H(24C)	7995	9278	4059	69
H(25A)	7512	8314	2371	69
H(25B)	7485	7725	3100	69
H(25C)	8485	8244	3545	69
H(26A)	6572	8521	5057	83
H(26B)	7915	8372	5182	83
H(26C)	6920	7850	4736	83
H(3)	5797	7414	1474	20
H(41A)	5551	7253	-326	38
H(41B)	6423	6830	-716	38
H(41C)	6881	7139	457	38
H(51A)	4197	4607	525	34
H(51B)	3552	5033	1149	34
H(52)	5872	4612	2402	43
H(53A)	3731	4274	2576	58
H(53B)	5056	4115	3431	58
H(6)	4047	5686	2449	19
H(3'1)	4513	7454	6388	35
H(3'2)	5126	7938	5814	35
H(4'1)	6490	7632	7491	59
H(4'2)	6932	7400	6541	59
H(4'3)	6321	6921	7116	59
H(6')	-121	6687	3753	33
H(7')	-1889	6635	2301	42
H(8')	-2050	6005	835	44
H(9')	-428	5428	795	42
H(10')	1344	5470	2237	35
H(12')	3630	5062	4111	37
H(13')	3947	4084	4921	44
H(14')	2996	3803	6110	40
H(15')	1706	4491	6487	49
H(16')	1381	5471	5690	42

Table S6. Torsion angles [deg] for 14.

C(6)-C(1)-C(2)-O(2)	-179.97(14)
C(1')-C(1)-C(2)-O(2)	3.3(2)
C(6)-C(1)-C(2)-C(3)	1.8(2)
C(1')-C(1)-C(2)-C(3)	-174.96(15)
C(3)-C(2)-O(2)-Si(2)	9.9(3)
C(1)-C(2)-O(2)-Si(2)	-168.29(13)
C(2)-O(2)-Si(2)-C(21)	150.55(17)
C(2)-O(2)-Si(2)-C(22)	33.62(19)
C(2)-O(2)-Si(2)-C(23)	-91.03(17)
O(2)-Si(2)-C(23)-C(25)	69.59(17)
C(21)-Si(2)-C(23)-C(25)	-177.92(16)
C(22)-Si(2)-C(23)-C(25)	-53.85(19)
O(2)-Si(2)-C(23)-C(24)	-170.15(15)
C(21)-Si(2)-C(23)-C(24)	-57.67(18)
C(22)-Si(2)-C(23)-C(24)	66.41(18)
O(2)-Si(2)-C(23)-C(26)	-50.93(18)
C(21)-Si(2)-C(23)-C(26)	61.56(19)
C(22)-Si(2)-C(23)-C(26)	-174.37(17)
O(2)-C(2)-C(3)-C(4)	-178.72(15)
C(1)-C(2)-C(3)-C(4)	-0.5(2)
C(2)-C(3)-C(4)-O(4)	177.11(15)
C(2)-C(3)-C(4)-C(5)	-1.6(2)
C(3)-C(4)-O(4)-C(41)	-7.0(2)
C(5)-C(4)-O(4)-C(41)	171.75(15)
O(4)-C(4)-C(5)-C(6)	-176.40(15)
C(3)-C(4)-C(5)-C(6)	2.4(2)
O(4)-C(4)-C(5)-O(5)	1.9(2)
C(3)-C(4)-C(5)-O(5)	-179.29(15)
C(6)-C(5)-O(5)-C(51)	3.8(3)
C(4)-C(5)-O(5)-C(51)	-174.35(16)
C(5)-O(5)-C(51)-C(52)	-77.3(2)
O(5)-C(51)-C(52)-C(53)	148.4(2)
O(5)-C(5)-C(6)-C(1)	-179.24(15)
C(4)-C(5)-C(6)-C(1)	-1.1(2)
C(2)-C(1)-C(6)-C(5)	-0.9(2)
C(1')-C(1)-C(6)-C(5)	176.00(15)
C(2)-C(1)-C(1')-N(1')	164.09(16)
C(6)-C(1)-C(1')-N(1')	-12.7(2)
C(2)-C(1)-C(1')-C(2')	-17.6(2)
C(6)-C(1)-C(1')-C(2')	165.68(14)
C(1)-C(1')-N(1')-P(1')	-172.50(12)
C(2')-C(1')-N(1')-P(1')	9.1(2)
C(1')-N(1')-P(1')-O(1')	-7.2(2)
C(1')-N(1')-P(1')-C(11')	-134.01(16)
C(1')-N(1')-P(1')-C(5')	116.40(17)
N(1')-C(1')-C(2')-O(2')	-80.8(2)
C(1)-C(1')-C(2')-O(2')	100.9(2)
N(1')-C(1')-C(2')-O(3')	95.22(18)
C(1)-C(1')-C(2')-O(3')	-83.12(18)
O(2')-C(2')-O(3')-C(3')	5.3(3)
C(1')-C(2')-O(3')-C(3')	-170.62(15)
C(2')-O(3')-C(3')-C(4')	-173.85(17)
O(1')-P(1')-C(5')-C(6')	-4.74(18)
N(1')-P(1')-C(5')-C(6')	-135.23(15)
C(11')-P(1')-C(5')-C(6')	118.83(15)
O(1')-P(1')-C(5')-C(10')	175.09(15)
N(1')-P(1')-C(5')-C(10')	44.60(17)
C(11')-P(1')-C(5')-C(10')	-61.34(17)
C(10')-C(5')-C(6')-C(7')	-0.3(3)
P(1')-C(5')-C(6')-C(7')	179.54(15)
C(5')-C(6')-C(7')-C(8')	0.3(3)
C(6')-C(7')-C(8')-C(9')	-0.4(3)
C(7')-C(8')-C(9')-C(10')	0.5(3)
C(8')-C(9')-C(10')-C(5')	-0.5(3)
C(6')-C(5')-C(10')-C(9')	0.4(3)
P(1')-C(5')-C(10')-C(9')	-179.44(16)
O(1')-P(1')-C(11')-C(12')	-138.46(17)
N(1')-P(1')-C(11')-C(12')	-5.42(18)
C(5')-P(1')-C(11')-C(12')	98.06(18)
O(1')-P(1')-C(11')-C(16')	41.14(18)
N(1')-P(1')-C(11')-C(16')	174.18(15)
C(5')-P(1')-C(11')-C(16')	-82.35(17)
C(16')-C(11')-C(12')-C(13')	-0.1(3)
P(1')-C(11')-C(12')-C(13')	179.47(16)
C(11')-C(12')-C(13')-C(14')	-0.1(3)

C(12')-C(13')-C(14')-C(15')	0.3(3)
C(13')-C(14')-C(15')-C(16')	-0.4(4)
C(14')-C(15')-C(16')-C(11')	0.2(4)
C(12')-C(11')-C(16')-C(15')	0.0(3)
P(1')-C(11')-C(16')-C(15')	-179.59(18)

Table S7. Hydrogen bonds for 14 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(12')-H(12')...N(1')	0.95	2.57	2.983(3)	106.8
C(8')-H(8')...O(4)#1	0.95	2.57	3.343(3)	138.6
C(41)-H(41B)...O(2')#2	0.98	2.60	3.124(2)	113.6
C(51)-H(51A)...O(4)#3	0.99	2.47	3.403(2)	157.1
C(51)-H(51A)...O(5)#3	0.99	2.47	3.200(2)	130.2

Symmetry transformations used to generate equivalent atoms:
#1 x-1,y,z #2 x+1/2,-y+3/2,z-1/2 #3 -x+1,-y+1,-z

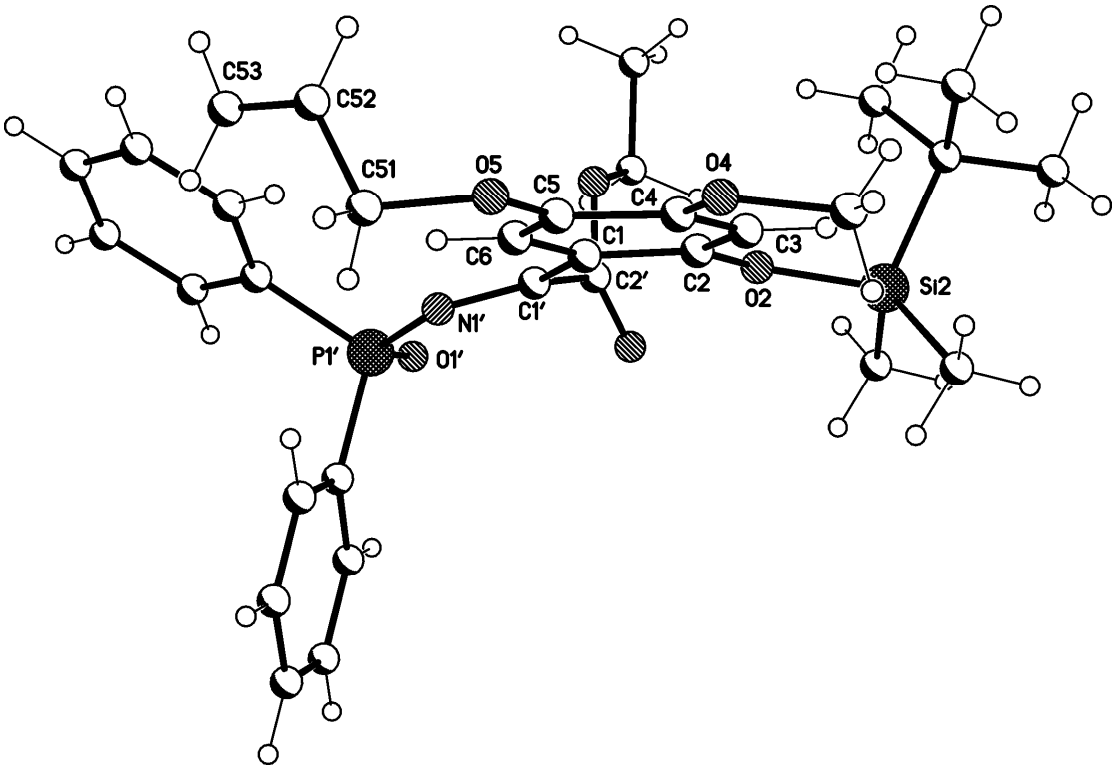

Fig. S3. Molecular structure of **14**.

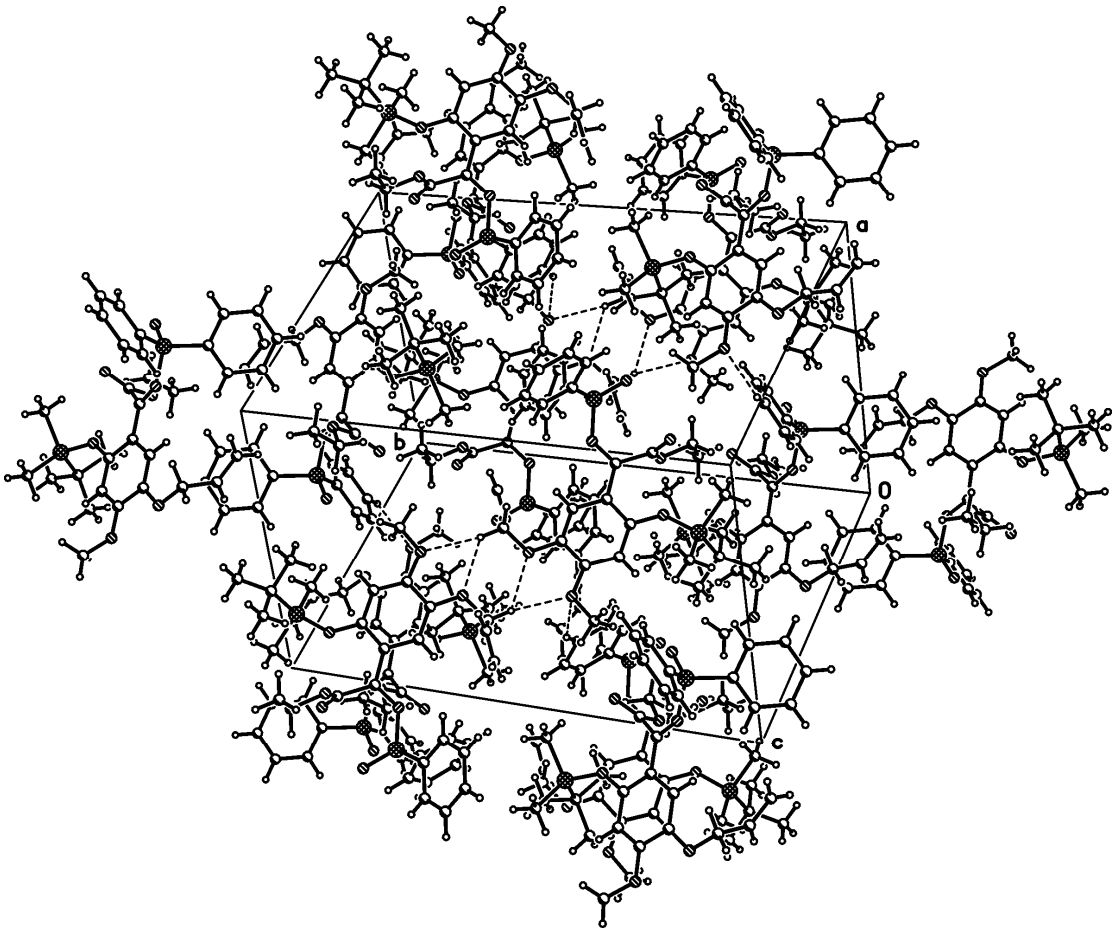

Fig. S4. Crystal packing of **14**.

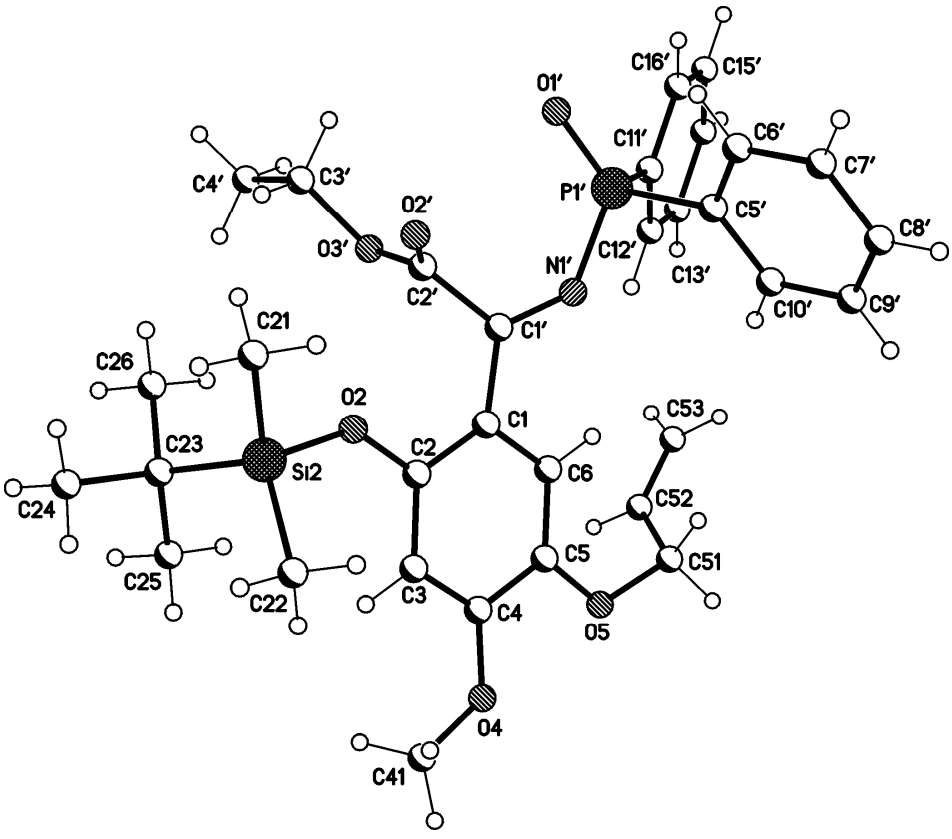

Fig. S5. Molecular structure of **14**.

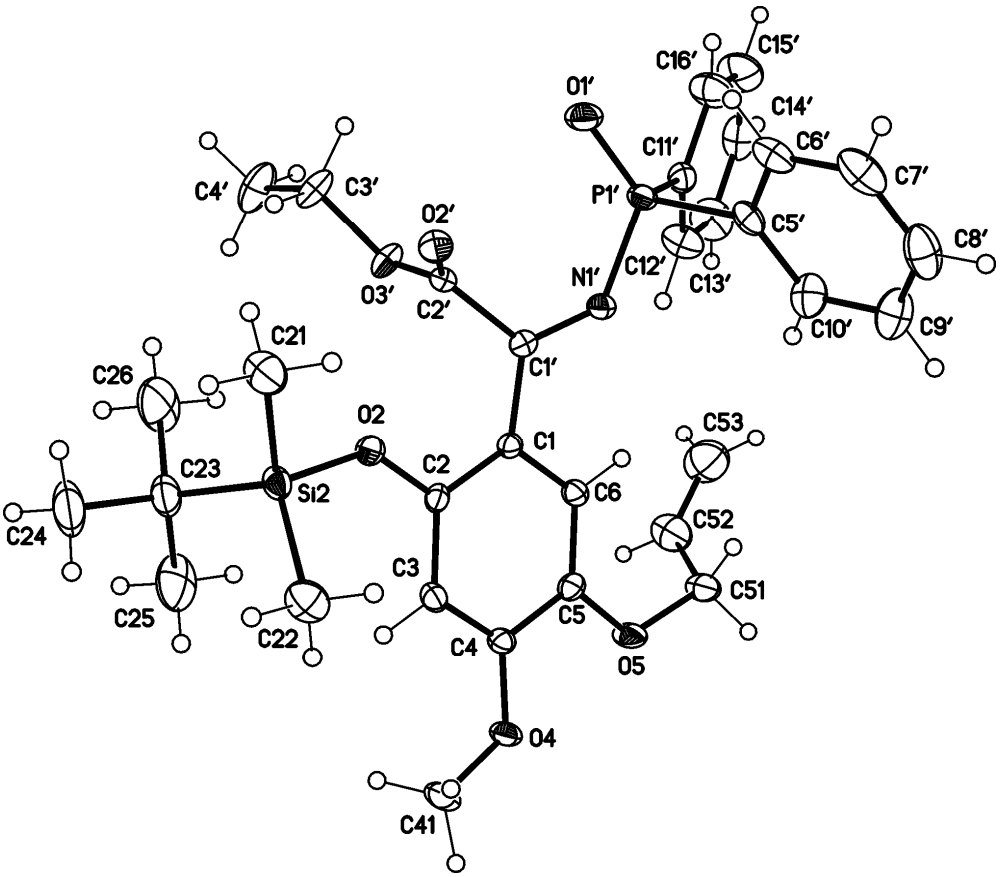

Fig. S6. Molecular structure of **14** (displacement parameters are drawn at 50% probability level).

Crystallographic data and pictures of **18**:

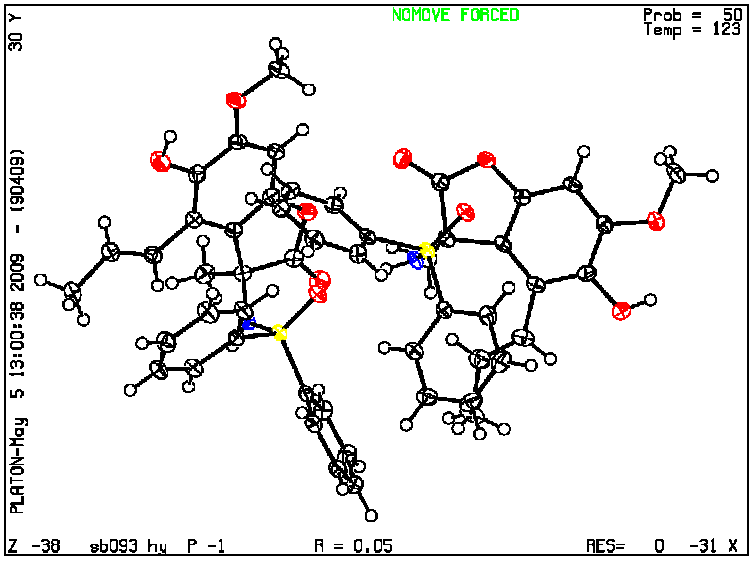

Table S8. Crystal data and structure refinement for 18.

Identification code	sb093_hy
Empirical formula	C25 H24 N O5 P
Formula weight	449.42

Temperature	123(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1 (No.2)
Unit cell dimensions	a = 10.199(1) A alpha = 99.86(1) deg. b = 13.332(1) A beta = 105.95(1) deg. c = 17.800(1) A gamma = 103.28(1) deg.
Volume	2192.7(3) A^3
Z, Calculated density	4, 1.361 Mg/m^3
Absorption coefficient	0.163 mm^-1
F(000)	944
Crystal size	0.50 x 0.30 x 0.10 mm
Theta range for data collection	3.07 to 27.48 deg.
Limiting indices	-13<=h<=12, -17<=k<=16, -19<=l<=23
Reflections collected / unique	22725 / 9958 [R(int) = 0.0427]
Completeness to theta = 25.00	99.3 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9958 / 4 / 595
Goodness-of-fit on F^2	1.021
Final R indices [I>2sigma(I)]	R1 = 0.0469, wR2 = 0.1115
R indices (all data)	R1 = 0.0680, wR2 = 0.1231
Largest diff. peak and hole	0.795 and -0.478 e.A^-3

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 18.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	4500(2)	7131(1)	447(1)	24(1)
C(2)	3457(2)	6797(2)	773(1)	21(1)
O(2)	2911(2)	5871(1)	689(1)	27(1)
C(3)	3134(2)	7762(2)	1219(1)	19(1)
C(31)	1649(2)	7761(2)	727(1)	25(1)
N(3)	3145(2)	7646(1)	2019(1)	19(1)
P(3)	4618(1)	7755(1)	2738(1)	16(1)
O(3)	5758(1)	7569(1)	2414(1)	21(1)
C(8)	5157(2)	9053(2)	3415(1)	18(1)
C(9)	4152(2)	9421(2)	3691(1)	22(1)
C(10)	4542(2)	10441(2)	4177(1)	25(1)
C(11)	5921(2)	11097(2)	4383(1)	27(1)
C(12)	6913(2)	10739(2)	4111(1)	28(1)
C(13)	6540(2)	9712(2)	3630(1)	23(1)
C(14)	4128(2)	6827(1)	3310(1)	18(1)
C(15)	4849(2)	7057(2)	4134(1)	21(1)
C(16)	4571(2)	6316(2)	4573(1)	25(1)
C(17)	3572(2)	5339(2)	4194(1)	26(1)
C(18)	2848(2)	5098(2)	3374(1)	28(1)
C(19)	3119(2)	5834(2)	2930(1)	24(1)
C(3A)	4287(2)	8670(2)	1168(1)	18(1)
C(4)	4623(2)	9780(2)	1450(1)	19(1)
C(41)	3813(2)	10219(2)	1917(1)	22(1)
C(42)	3877(2)	11225(2)	2196(1)	29(1)

C(43)	2953(3)	11531(2)	2666(2)	36(1)
C(5)	5747(2)	10389(2)	1260(1)	21(1)
O(5)	6155(2)	11473(1)	1526(1)	31(1)
C(6)	6480(2)	9914(2)	812(1)	21(1)
O(6)	7598(2)	10630(1)	718(1)	26(1)
C(61)	8516(2)	10195(2)	375(2)	32(1)
C(7)	6107(2)	8821(2)	515(1)	22(1)
C(7A)	4999(2)	8242(2)	707(1)	20(1)
O(1')	9147(2)	5781(1)	737(1)	21(1)
C(2')	8263(2)	6296(2)	972(1)	23(1)
O(2')	8024(2)	7034(1)	727(1)	32(1)
C(3')	7680(2)	5785(2)	1574(1)	19(1)
C(31')	6072(2)	5275(2)	1166(1)	26(1)
N(3')	7948(2)	6635(1)	2287(1)	18(1)
P(3')	9562(1)	7321(1)	2897(1)	16(1)
O(3')	10701(1)	7126(1)	2573(1)	21(1)
C(8')	9717(2)	6979(1)	3847(1)	18(1)
C(9')	8658(2)	7028(2)	4197(1)	22(1)
C(10')	8760(2)	6757(2)	4924(1)	27(1)
C(11')	9898(3)	6425(2)	5301(1)	30(1)
C(12')	10942(2)	6367(2)	4952(1)	31(1)
C(13')	10856(2)	6646(2)	4229(1)	24(1)
C(14')	9602(2)	8702(2)	3103(1)	18(1)
C(15')	10381(2)	9369(2)	3869(1)	22(1)
C(16')	10522(2)	10453(2)	4018(1)	24(1)
C(17')	9892(2)	10873(2)	3403(1)	23(1)
C(18')	9122(2)	10216(2)	2641(1)	24(1)
C(19')	8974(2)	9131(2)	2490(1)	22(1)
C(3A')	8488(2)	4966(1)	1682(1)	18(1)
C(4')	8487(2)	4188(2)	2126(1)	19(1)
C(41')	7627(2)	3945(2)	2652(1)	28(1)
C(42')	6925(2)	4506(2)	2951(1)	31(1)
C(43')	6026(2)	4132(2)	3448(2)	36(1)
C(5')	9358(2)	3539(2)	2024(1)	21(1)
O(5')	9445(2)	2776(1)	2456(1)	30(1)
C(6')	10175(2)	3639(2)	1512(1)	20(1)
O(6')	10988(2)	2946(1)	1516(1)	29(1)
C(61')	11998(3)	3098(2)	1096(2)	40(1)
C(7')	10143(2)	4378(2)	1060(1)	20(1)
C(7A')	9279(2)	5008(1)	1167(1)	18(1)

Table S10. Bond lengths [A] and angles [deg] for 18.

O(1)-C(2)	1.370(2)
O(1)-C(7A)	1.399(2)
C(2)-O(2)	1.196(2)
C(2)-C(3)	1.544(3)
C(3)-N(3)	1.454(3)
C(3)-C(3A)	1.516(3)
C(3)-C(31)	1.527(3)
N(3)-P(3)	1.6421(17)
N(3)-H(3)	0.853(15)
P(3)-O(3)	1.4828(13)
P(3)-C(8)	1.7983(19)
P(3)-C(14)	1.801(2)
C(8)-C(13)	1.389(3)
C(8)-C(9)	1.399(3)
C(9)-C(10)	1.384(3)
C(10)-C(11)	1.385(3)
C(11)-C(12)	1.378(3)
C(12)-C(13)	1.391(3)
C(14)-C(15)	1.392(3)
C(14)-C(19)	1.398(3)
C(15)-C(16)	1.388(3)
C(16)-C(17)	1.379(3)
C(17)-C(18)	1.384(3)
C(18)-C(19)	1.388(3)
C(3A)-C(7A)	1.372(3)
C(3A)-C(4)	1.406(3)
C(4)-C(5)	1.402(3)
C(4)-C(41)	1.466(3)
C(41)-C(42)	1.329(3)
C(42)-C(43)	1.499(3)
C(5)-O(5)	1.366(2)
C(5)-C(6)	1.404(3)

O(5)-H(5)	0.829(17)
C(6)-O(6)	1.378(2)
C(6)-C(7)	1.385(3)
O(6)-C(61)	1.425(2)
C(7)-C(7A)	1.376(3)
O(1')-C(2')	1.362(2)
O(1')-C(7A')	1.395(2)
C(2')-O(2')	1.190(3)
C(2')-C(3')	1.542(3)
C(3')-N(3')	1.465(2)
C(3')-C(3A')	1.519(3)
C(3')-C(31')	1.530(3)
N(3')-P(3')	1.6468(16)
N(3')-H(3')	0.855(15)
P(3')-O(3')	1.4845(13)
P(3')-C(8')	1.800(2)
P(3')-C(14')	1.8034(19)
C(8')-C(13')	1.384(3)
C(8')-C(9')	1.396(3)
C(9')-C(10')	1.384(3)
C(10')-C(11')	1.379(3)
C(11')-C(12')	1.383(3)
C(12')-C(13')	1.385(3)
C(14')-C(19')	1.387(3)
C(14')-C(15')	1.395(3)
C(15')-C(16')	1.390(3)
C(16')-C(17')	1.382(3)
C(17')-C(18')	1.385(3)
C(18')-C(19')	1.391(3)
C(3A')-C(7A')	1.378(3)
C(3A')-C(4')	1.408(3)
C(4')-C(5')	1.399(3)
C(4')-C(41')	1.475(3)
C(41')-C(42')	1.294(3)
C(42')-C(43')	1.503(3)
C(5')-O(5')	1.381(2)
C(5')-C(6')	1.397(3)
O(5')-H(5')	0.836(17)
C(6')-C(7')	1.375(3)
C(6')-O(6')	1.376(2)
O(6')-C(61')	1.429(3)
C(7')-C(7A')	1.376(3)

C(2)-O(1)-C(7A)	107.49(14)
O(2)-C(2)-O(1)	121.37(18)
O(2)-C(2)-C(3)	128.26(19)
O(1)-C(2)-C(3)	110.36(16)
N(3)-C(3)-C(3A)	117.60(15)
N(3)-C(3)-C(31)	109.64(16)
C(3A)-C(3)-C(31)	111.62(17)
N(3)-C(3)-C(2)	109.44(16)
C(3A)-C(3)-C(2)	100.65(15)
C(31)-C(3)-C(2)	107.08(15)
C(3)-N(3)-P(3)	122.32(13)
C(3)-N(3)-H(3)	116.2(16)
P(3)-N(3)-H(3)	121.5(16)
O(3)-P(3)-N(3)	112.08(8)
O(3)-P(3)-C(8)	111.85(8)
N(3)-P(3)-C(8)	107.79(9)
O(3)-P(3)-C(14)	113.06(8)
N(3)-P(3)-C(14)	106.06(9)
C(8)-P(3)-C(14)	105.55(9)
C(13)-C(8)-C(9)	119.91(17)
C(13)-C(8)-P(3)	120.41(14)
C(9)-C(8)-P(3)	119.58(14)
C(10)-C(9)-C(8)	119.81(18)
C(9)-C(10)-C(11)	119.98(18)
C(12)-C(11)-C(10)	120.42(18)
C(11)-C(12)-C(13)	120.22(19)
C(8)-C(13)-C(12)	119.65(18)
C(15)-C(14)-C(19)	118.91(19)
C(15)-C(14)-P(3)	119.72(14)
C(19)-C(14)-P(3)	121.12(16)
C(16)-C(15)-C(14)	120.67(18)
C(17)-C(16)-C(15)	120.1(2)
C(16)-C(17)-C(18)	119.9(2)
C(17)-C(18)-C(19)	120.48(19)
C(18)-C(19)-C(14)	119.99(19)
C(7A)-C(3A)-C(4)	120.32(17)

C(7A)-C(3A)-C(3)	107.74(16)
C(4)-C(3A)-C(3)	131.77(17)
C(5)-C(4)-C(3A)	115.94(17)
C(5)-C(4)-C(41)	124.77(17)
C(3A)-C(4)-C(41)	119.28(17)
C(42)-C(41)-C(4)	129.8(2)
C(41)-C(42)-C(43)	122.6(2)
O(5)-C(5)-C(4)	119.42(17)
O(5)-C(5)-C(6)	118.86(17)
C(4)-C(5)-C(6)	121.71(17)
C(5)-O(5)-H(5)	107(2)
O(6)-C(6)-C(7)	124.44(18)
O(6)-C(6)-C(5)	113.77(17)
C(7)-C(6)-C(5)	121.77(18)
C(6)-O(6)-C(61)	116.62(16)
C(7A)-C(7)-C(6)	115.33(18)
C(3A)-C(7A)-C(7)	124.83(18)
C(3A)-C(7A)-O(1)	113.36(17)
C(7)-C(7A)-O(1)	121.81(17)
C(2')-O(1')-C(7A')	107.91(15)
O(2')-C(2')-O(1')	121.82(19)
O(2')-C(2')-C(3')	127.90(18)
O(1')-C(2')-C(3')	110.28(17)
N(3')-C(3')-C(3A')	117.13(16)
N(3')-C(3')-C(31')	109.70(15)
C(3A')-C(3')-C(31')	112.61(16)
N(3')-C(3')-C(2')	107.80(15)
C(3A')-C(3')-C(2')	101.12(15)
C(31')-C(3')-C(2')	107.65(17)
C(3')-N(3')-P(3')	122.99(12)
C(3')-N(3')-H(3')	116.1(15)
P(3')-N(3')-H(3')	118.1(15)
O(3')-P(3')-N(3')	113.04(8)
O(3')-P(3')-C(8')	112.55(9)
N(3')-P(3')-C(8')	106.17(9)
O(3')-P(3')-C(14')	112.96(8)
N(3')-P(3')-C(14')	106.94(9)
C(8')-P(3')-C(14')	104.54(9)
C(13')-C(8')-C(9')	119.3(2)
C(13')-C(8')-P(3')	121.06(15)
C(9')-C(8')-P(3')	119.65(15)
C(10')-C(9')-C(8')	120.1(2)
C(11')-C(10')-C(9')	120.3(2)
C(10')-C(11')-C(12')	119.7(2)
C(11')-C(12')-C(13')	120.4(2)
C(8')-C(13')-C(12')	120.2(2)
C(19')-C(14')-C(15')	119.45(18)
C(19')-C(14')-P(3')	120.69(14)
C(15')-C(14')-P(3')	119.60(16)
C(16')-C(15')-C(14')	120.24(19)
C(17')-C(16')-C(15')	119.90(18)
C(16')-C(17')-C(18')	120.15(18)
C(17')-C(18')-C(19')	120.2(2)
C(14')-C(19')-C(18')	120.08(18)
C(7A')-C(3A')-C(4')	118.88(17)
C(7A')-C(3A')-C(3')	106.96(17)
C(4')-C(3A')-C(3')	133.95(17)
C(5')-C(4')-C(3A')	115.78(17)
C(5')-C(4')-C(41')	116.52(19)
C(3A')-C(4')-C(41')	127.63(18)
C(42')-C(41')-C(4')	129.1(2)
C(41')-C(42')-C(43')	123.4(2)
O(5')-C(5')-C(6')	117.86(18)
O(5')-C(5')-C(4')	119.21(18)
C(6')-C(5')-C(4')	122.91(19)
C(5')-O(5')-H(5')	111(2)
C(7')-C(6')-O(6')	124.95(18)
C(7')-C(6')-C(5')	121.30(18)
O(6')-C(6')-C(5')	113.74(18)
C(6')-O(6')-C(61')	116.94(17)
C(6')-C(7')-C(7A')	114.95(17)
C(7')-C(7A')-C(3A')	126.10(19)
C(7')-C(7A')-O(1')	120.36(17)
C(3A')-C(7A')-O(1')	113.54(16)

Table S11. Anisotropic displacement parameters (A^2 x 10^3) for 18.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	29(1)	18(1)	22(1)	0(1)	12(1)	3(1)
C(2)	21(1)	22(1)	17(1)	2(1)	3(1)	4(1)
O(2)	27(1)	19(1)	29(1)	1(1)	7(1)	0(1)
C(3)	18(1)	18(1)	17(1)	3(1)	4(1)	2(1)
C(31)	19(1)	26(1)	25(1)	8(1)	2(1)	3(1)
N(3)	13(1)	25(1)	18(1)	5(1)	6(1)	3(1)
P(3)	14(1)	17(1)	16(1)	1(1)	5(1)	4(1)
O(3)	17(1)	24(1)	21(1)	1(1)	8(1)	6(1)
C(8)	20(1)	18(1)	17(1)	3(1)	7(1)	6(1)
C(9)	19(1)	24(1)	22(1)	1(1)	8(1)	5(1)
C(10)	27(1)	27(1)	24(1)	2(1)	13(1)	11(1)
C(11)	32(1)	21(1)	25(1)	-2(1)	10(1)	6(1)
C(12)	21(1)	24(1)	32(1)	-2(1)	10(1)	0(1)
C(13)	20(1)	23(1)	26(1)	1(1)	11(1)	5(1)
C(14)	17(1)	18(1)	21(1)	4(1)	8(1)	8(1)
C(15)	20(1)	22(1)	20(1)	2(1)	7(1)	8(1)
C(16)	27(1)	31(1)	21(1)	7(1)	10(1)	14(1)
C(17)	28(1)	27(1)	33(1)	15(1)	15(1)	14(1)
C(18)	25(1)	21(1)	36(1)	7(1)	7(1)	4(1)
C(19)	22(1)	22(1)	23(1)	2(1)	4(1)	5(1)
C(3A)	16(1)	21(1)	16(1)	4(1)	5(1)	3(1)
C(4)	17(1)	20(1)	17(1)	3(1)	5(1)	5(1)
C(41)	18(1)	25(1)	22(1)	6(1)	7(1)	6(1)
C(42)	29(1)	27(1)	38(1)	11(1)	18(1)	13(1)
C(43)	42(1)	37(1)	47(2)	16(1)	28(1)	24(1)
C(5)	21(1)	17(1)	24(1)	4(1)	6(1)	4(1)
O(5)	28(1)	18(1)	47(1)	3(1)	21(1)	2(1)
C(6)	18(1)	24(1)	21(1)	8(1)	8(1)	5(1)
O(6)	25(1)	25(1)	34(1)	10(1)	18(1)	5(1)
C(61)	30(1)	38(1)	40(1)	15(1)	24(1)	12(1)
C(7)	26(1)	24(1)	18(1)	5(1)	10(1)	8(1)
C(7A)	23(1)	17(1)	17(1)	3(1)	5(1)	4(1)
O(1')	28(1)	20(1)	18(1)	3(1)	12(1)	8(1)
C(2')	29(1)	21(1)	16(1)	0(1)	7(1)	8(1)
O(2')	49(1)	30(1)	27(1)	12(1)	18(1)	22(1)
C(3')	20(1)	20(1)	15(1)	-1(1)	6(1)	5(1)
C(31')	21(1)	27(1)	23(1)	-2(1)	2(1)	6(1)
N(3')	16(1)	19(1)	18(1)	-2(1)	6(1)	7(1)
P(3')	14(1)	17(1)	15(1)	0(1)	6(1)	5(1)
O(3')	17(1)	23(1)	23(1)	1(1)	9(1)	6(1)
C(8')	19(1)	15(1)	16(1)	-1(1)	5(1)	3(1)
C(9')	22(1)	23(1)	22(1)	3(1)	9(1)	6(1)
C(10')	32(1)	23(1)	24(1)	3(1)	14(1)	3(1)
C(11')	43(1)	23(1)	21(1)	7(1)	9(1)	5(1)
C(12')	34(1)	28(1)	29(1)	10(1)	3(1)	11(1)
C(13')	23(1)	23(1)	25(1)	2(1)	7(1)	7(1)
C(14')	15(1)	18(1)	20(1)	2(1)	9(1)	4(1)
C(15')	22(1)	22(1)	20(1)	3(1)	5(1)	7(1)
C(16')	24(1)	19(1)	24(1)	-1(1)	7(1)	2(1)
C(17')	25(1)	16(1)	29(1)	4(1)	13(1)	3(1)
C(18')	26(1)	23(1)	25(1)	10(1)	9(1)	7(1)
C(19')	23(1)	22(1)	18(1)	2(1)	7(1)	4(1)
C(3A')	16(1)	18(1)	15(1)	-3(1)	6(1)	2(1)
C(4')	17(1)	21(1)	16(1)	0(1)	6(1)	1(1)
C(41')	24(1)	36(1)	23(1)	8(1)	10(1)	6(1)
C(42')	33(1)	30(1)	29(1)	6(1)	13(1)	7(1)
C(43')	29(1)	50(2)	32(1)	6(1)	19(1)	9(1)
C(5')	22(1)	20(1)	19(1)	5(1)	6(1)	3(1)
O(5')	37(1)	29(1)	38(1)	18(1)	22(1)	15(1)
C(6')	21(1)	18(1)	20(1)	0(1)	7(1)	5(1)
O(6')	36(1)	31(1)	33(1)	11(1)	20(1)	20(1)
C(61')	48(1)	55(2)	43(1)	22(1)	31(1)	35(1)
C(7')	21(1)	19(1)	18(1)	0(1)	10(1)	3(1)
C(7A')	20(1)	14(1)	15(1)	0(1)	6(1)	1(1)

Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 18.

	x	y	z	U(eq)
H(31A)	950	7097	689	38
H(31B)	1638	7819	184	38
H(31C)	1407	8367	991	38
H(3)	2336(19)	7495(17)	2090(14)	23
H(9)	3204	8972	3544	27
H(10)	3865	10690	4370	30
H(11)	6183	11798	4714	32
H(12)	7856	11195	4254	34
H(13)	7229	9462	3448	28
H(15)	5540	7729	4399	25
H(16)	5069	6482	5136	30
H(17)	3382	4831	4495	32
H(18)	2161	4424	3114	34
H(19)	2620	5663	2367	29
H(41)	3141	9705	2039	26
H(42)	4534	11773	2094	35
H(43A)	2309	10887	2706	54
H(43B)	2391	11947	2391	54
H(43C)	3554	11959	3209	54
H(5)	6900(20)	11700(20)	1425(17)	46
H(61A)	8847	9699	674	48
H(61B)	9338	10771	405	48
H(61C)	7995	9816	-191	48
H(7)	6583	8494	200	26
H(31D)	5670	4945	1536	39
H(31E)	5896	4730	674	39
H(31F)	5621	5822	1026	39
H(3')	7260(20)	6902(16)	2295(14)	22
H(9')	7866	7247	3937	27
H(10')	8043	6800	5164	32
H(11')	9964	6237	5799	36
H(12')	11723	6134	5209	38
H(13')	11581	6609	3994	29
H(15')	10817	9081	4291	26
H(16')	11051	10905	4540	29
H(17')	9987	11614	3504	28
H(18')	8694	10508	2219	29
H(19')	8444	8682	1966	26
H(41')	7583	3284	2791	33
H(42')	6981	5190	2851	37
H(43D)	6096	3431	3519	54
H(43E)	5030	4081	3172	54
H(43F)	6366	4640	3977	54
H(5')	10010(30)	2450(20)	2356(17)	45
H(61D)	11492	2965	517	60
H(61E)	12569	2603	1181	60
H(61F)	12626	3831	1299	60
H(7')	10678	4450	701	23

Table S13. Torsion angles [deg] for 18.

C(7A)-O(1)-C(2)-O(2)	-175.06(19)
C(7A)-O(1)-C(2)-C(3)	5.8(2)
O(2)-C(2)-C(3)-N(3)	50.0(3)
O(1)-C(2)-C(3)-N(3)	-130.89(16)
O(2)-C(2)-C(3)-C(3A)	174.5(2)
O(1)-C(2)-C(3)-C(3A)	-6.4(2)
O(2)-C(2)-C(3)-C(31)	-68.8(3)
O(1)-C(2)-C(3)-C(31)	110.34(18)
C(3A)-C(3)-N(3)-P(3)	-43.9(2)
C(31)-C(3)-N(3)-P(3)	-172.77(13)
C(2)-C(3)-N(3)-P(3)	70.06(18)
C(3)-N(3)-P(3)-O(3)	-21.64(17)
C(3)-N(3)-P(3)-C(8)	101.87(16)
C(3)-N(3)-P(3)-C(14)	-145.46(15)
O(3)-P(3)-C(8)-C(13)	-5.3(2)
N(3)-P(3)-C(8)-C(13)	-128.94(17)
C(14)-P(3)-C(8)-C(13)	118.05(18)
O(3)-P(3)-C(8)-C(9)	171.20(16)
N(3)-P(3)-C(8)-C(9)	47.55(19)
C(14)-P(3)-C(8)-C(9)	-65.46(18)
C(13)-C(8)-C(9)-C(10)	-0.1(3)
P(3)-C(8)-C(9)-C(10)	-176.59(17)
C(8)-C(9)-C(10)-C(11)	0.7(3)
C(9)-C(10)-C(11)-C(12)	-0.5(3)
C(10)-C(11)-C(12)-C(13)	-0.2(4)
C(9)-C(8)-C(13)-C(12)	-0.7(3)
P(3)-C(8)-C(13)-C(12)	175.83(18)
C(11)-C(12)-C(13)-C(8)	0.8(3)
O(3)-P(3)-C(14)-C(15)	88.83(16)
N(3)-P(3)-C(14)-C(15)	-147.96(15)
C(8)-P(3)-C(14)-C(15)	-33.74(17)
O(3)-P(3)-C(14)-C(19)	-85.38(17)
N(3)-P(3)-C(14)-C(19)	37.83(18)
C(8)-P(3)-C(14)-C(19)	152.05(16)
C(19)-C(14)-C(15)-C(16)	-0.2(3)
P(3)-C(14)-C(15)-C(16)	-174.59(14)
C(14)-C(15)-C(16)-C(17)	0.1(3)
C(15)-C(16)-C(17)-C(18)	0.0(3)
C(16)-C(17)-C(18)-C(19)	0.0(3)
C(17)-C(18)-C(19)-C(14)	-0.1(3)
C(15)-C(14)-C(19)-C(18)	0.3(3)
P(3)-C(14)-C(19)-C(18)	174.51(15)
N(3)-C(3)-C(3A)-C(7A)	123.32(18)
C(31)-C(3)-C(3A)-C(7A)	-108.71(19)
C(2)-C(3)-C(3A)-C(7A)	4.6(2)
N(3)-C(3)-C(3A)-C(4)	-61.5(3)
C(31)-C(3)-C(3A)-C(4)	66.5(3)
C(2)-C(3)-C(3A)-C(4)	179.8(2)
C(7A)-C(3A)-C(4)-C(5)	-2.8(3)
C(3)-C(3A)-C(4)-C(5)	-177.4(2)
C(7A)-C(3A)-C(4)-C(41)	177.87(18)
C(3)-C(3A)-C(4)-C(41)	3.2(3)
C(5)-C(4)-C(41)-C(42)	5.5(4)
C(3A)-C(4)-C(41)-C(42)	-175.2(2)
C(4)-C(41)-C(42)-C(43)	179.8(2)
C(3A)-C(4)-C(5)-O(5)	-178.82(18)
C(41)-C(4)-C(5)-O(5)	0.5(3)
C(3A)-C(4)-C(5)-C(6)	0.5(3)
C(41)-C(4)-C(5)-C(6)	179.80(19)
O(5)-C(5)-C(6)-O(6)	2.4(3)
C(4)-C(5)-C(6)-O(6)	-176.91(18)
O(5)-C(5)-C(6)-C(7)	-179.01(19)
C(4)-C(5)-C(6)-C(7)	1.7(3)
C(7)-C(6)-O(6)-C(61)	-7.7(3)
C(5)-C(6)-O(6)-C(61)	170.91(18)
O(6)-C(6)-C(7)-C(7A)	176.99(19)
C(5)-C(6)-C(7)-C(7A)	-1.5(3)
C(4)-C(3A)-C(7A)-C(7)	3.2(3)
C(3)-C(3A)-C(7A)-C(7)	179.00(19)
C(4)-C(3A)-C(7A)-O(1)	-177.45(17)
C(3)-C(3A)-C(7A)-O(1)	-1.6(2)
C(6)-C(7)-C(7A)-C(3A)	-0.9(3)
C(6)-C(7)-C(7A)-O(1)	179.71(18)
C(2)-O(1)-C(7A)-C(3A)	-2.7(2)
C(2)-O(1)-C(7A)-C(7)	176.74(19)

C(7A')-O(1')-C(2')-O(2')	176.12(19)
C(7A')-O(1')-C(2')-C(3')	-3.61(19)
O(2')-C(2')-C(3')-N(3')	-51.7(3)
O(1')-C(2')-C(3')-N(3')	127.99(16)
O(2')-C(2')-C(3')-C(3A')	-175.2(2)
O(1')-C(2')-C(3')-C(3A')	4.54(19)
O(2')-C(2')-C(3')-C(31')	66.5(3)
O(1')-C(2')-C(3')-C(31')	-113.74(17)
C(3A')-C(3')-N(3')-P(3')	47.2(2)
C(31')-C(3')-N(3')-P(3')	177.17(15)
C(2')-C(3')-N(3')-P(3')	-65.9(2)
C(3')-N(3')-P(3')-O(3')	10.26(19)
C(3')-N(3')-P(3')-C(8')	-113.61(16)
C(3')-N(3')-P(3')-C(14')	135.19(16)
O(3')-P(3')-C(8')-C(13')	4.15(18)
N(3')-P(3')-C(8')-C(13')	128.32(15)
C(14')-P(3')-C(8')-C(13')	-118.81(16)
O(3')-P(3')-C(8')-C(9')	-174.44(14)
N(3')-P(3')-C(8')-C(9')	-50.27(16)
C(14')-P(3')-C(8')-C(9')	62.60(16)
C(13')-C(8')-C(9')-C(10')	0.8(3)
P(3')-C(8')-C(9')-C(10')	179.40(15)
C(8')-C(9')-C(10')-C(11')	-0.8(3)
C(9')-C(10')-C(11')-C(12')	0.2(3)
C(10')-C(11')-C(12')-C(13')	0.4(3)
C(9')-C(8')-C(13')-C(12')	-0.2(3)
P(3')-C(8')-C(13')-C(12')	-178.75(15)
C(11')-C(12')-C(13')-C(8')	-0.4(3)
O(3')-P(3')-C(14')-C(19')	82.55(17)
N(3')-P(3')-C(14')-C(19')	-42.44(18)
C(8')-P(3')-C(14')-C(19')	-154.75(15)
O(3')-P(3')-C(14')-C(15')	-91.56(17)
N(3')-P(3')-C(14')-C(15')	143.46(15)
C(8')-P(3')-C(14')-C(15')	31.14(17)
C(19')-C(14')-C(15')-C(16')	0.3(3)
P(3')-C(14')-C(15')-C(16')	174.49(15)
C(14')-C(15')-C(16')-C(17')	-0.2(3)
C(15')-C(16')-C(17')-C(18')	-0.1(3)
C(16')-C(17')-C(18')-C(19')	0.2(3)
C(15')-C(14')-C(19')-C(18')	-0.1(3)
P(3')-C(14')-C(19')-C(18')	-174.23(15)
C(17')-C(18')-C(19')-C(14')	-0.2(3)
N(3')-C(3')-C(3A')-C(7A')	-120.53(18)
C(31')-C(3')-C(3A')-C(7A')	110.88(18)
C(2')-C(3')-C(3A')-C(7A')	-3.73(18)
N(3')-C(3')-C(3A')-C(4')	65.0(3)
C(31')-C(3')-C(3A')-C(4')	-63.6(3)
C(2')-C(3')-C(3A')-C(4')	-178.25(19)
C(7A')-C(3A')-C(4')-C(5')	2.5(2)
C(3')-C(3A')-C(4')-C(5')	176.50(18)
C(7A')-C(3A')-C(4')-C(41')	-174.30(18)
C(3')-C(3A')-C(4')-C(41')	-0.3(3)
C(5')-C(4')-C(41')-C(42')	167.7(2)
C(3A')-C(4')-C(41')-C(42')	-15.5(4)
C(4')-C(41')-C(42')-C(43')	176.7(2)
C(3A')-C(4')-C(5')-O(5')	178.22(16)
C(41')-C(4')-C(5')-O(5')	-4.6(3)
C(3A')-C(4')-C(5')-C(6')	-0.5(3)
C(41')-C(4')-C(5')-C(6')	176.66(18)
O(5')-C(5')-C(6')-C(7')	179.86(17)
C(4')-C(5')-C(6')-C(7')	-1.4(3)
O(5')-C(5')-C(6')-O(6')	-0.6(2)
C(4')-C(5')-C(6')-O(6')	178.17(17)
C(7')-C(6')-O(6')-C(61')	8.0(3)
C(5')-C(6')-O(6')-C(61')	-171.60(19)
O(6')-C(6')-C(7')-C(7A')	-178.36(17)
C(5')-C(6')-C(7')-C(7A')	1.2(3)
C(6')-C(7')-C(7A')-C(3A')	1.0(3)
C(6')-C(7')-C(7A')-O(1')	-179.41(16)
C(4')-C(3A')-C(7A')-C(7')	-2.9(3)
C(3')-C(3A')-C(7A')-C(7')	-178.42(17)
C(4')-C(3A')-C(7A')-O(1')	177.46(15)
C(3')-C(3A')-C(7A')-O(1')	2.0(2)
C(2')-O(1')-C(7A')-C(7')	-178.59(16)
C(2')-O(1')-C(7A')-C(3A')	1.1(2)

Table S14 Hydrogen bonds for 18 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(3)-H(3)...O(3')#1	0.853(15)	2.078(17)	2.909(2)	164(2)
O(5)-H(5)...O(6)	0.829(17)	2.12(3)	2.620(2)	119(2)
O(5)-H(5)...O(5')#2	0.829(17)	2.63(2)	3.210(2)	128(2)
N(3')-H(3')...O(3)	0.855(15)	1.984(16)	2.837(2)	175(2)
O(5')-H(5')...O(6')	0.836(17)	2.12(3)	2.597(2)	116(2)
C(7')-H(7')...O(1')#3	0.95	2.58	3.450(2)	151.6
C(31)-H(31A)...O(1')#1	0.98	2.26	3.229(3)	168.5
C(31')-H(31F)...O(1)	0.98	2.51	3.480(3)	170.8
C(41')-H(41')...O(5')	0.95	2.34	2.736(3)	104.1
C(42)-H(42)...O(5)	0.95	2.24	2.870(3)	123.3
C(42')-H(42')...N(3')	0.95	2.45	3.317(3)	150.9
C(43)-H(43B)...O(6')#4	0.98	2.57	3.545(3)	173.0
C(61')-H(61D)...O(2')#3	0.98	2.40	3.212(3)	140.1

Symmetry transformations used to generate equivalent atoms:
#1 x-1,y,z #2 x,y+1,z #3 -x+2,-y+1,-z #4 x-1,y+1,z

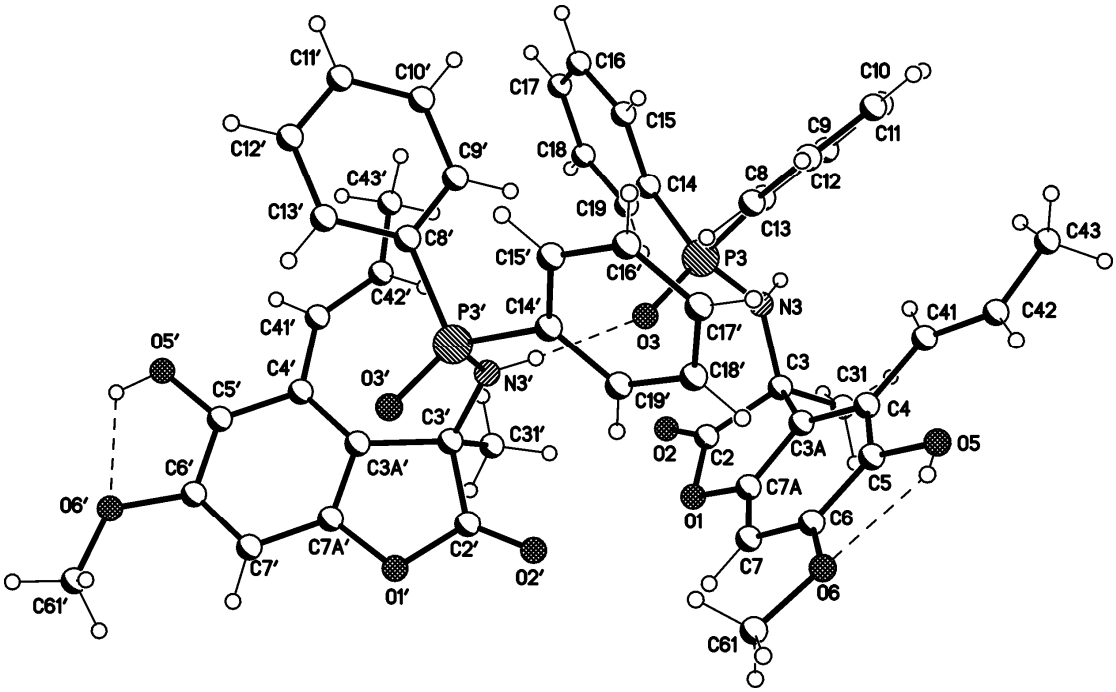

Fig. S11. Molecular structure of **18** (both independent molecules are shown).

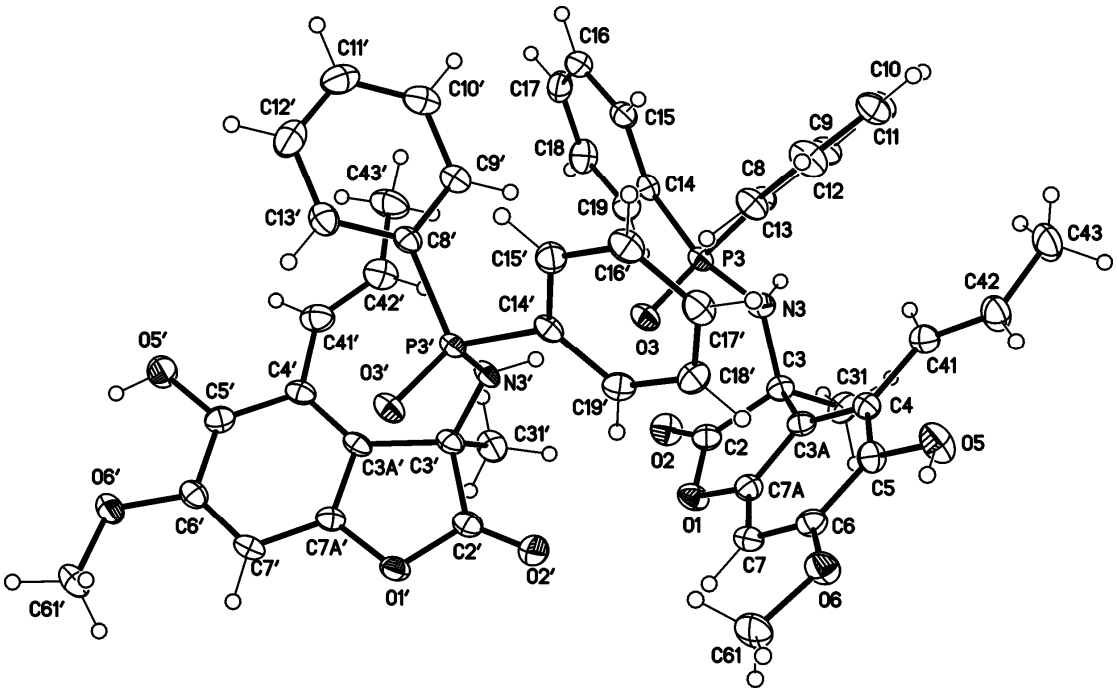

Fig. S12. Molecular structure of **18** (both independent molecules are shown ,displacement parameters are drawn at 50% probability level).

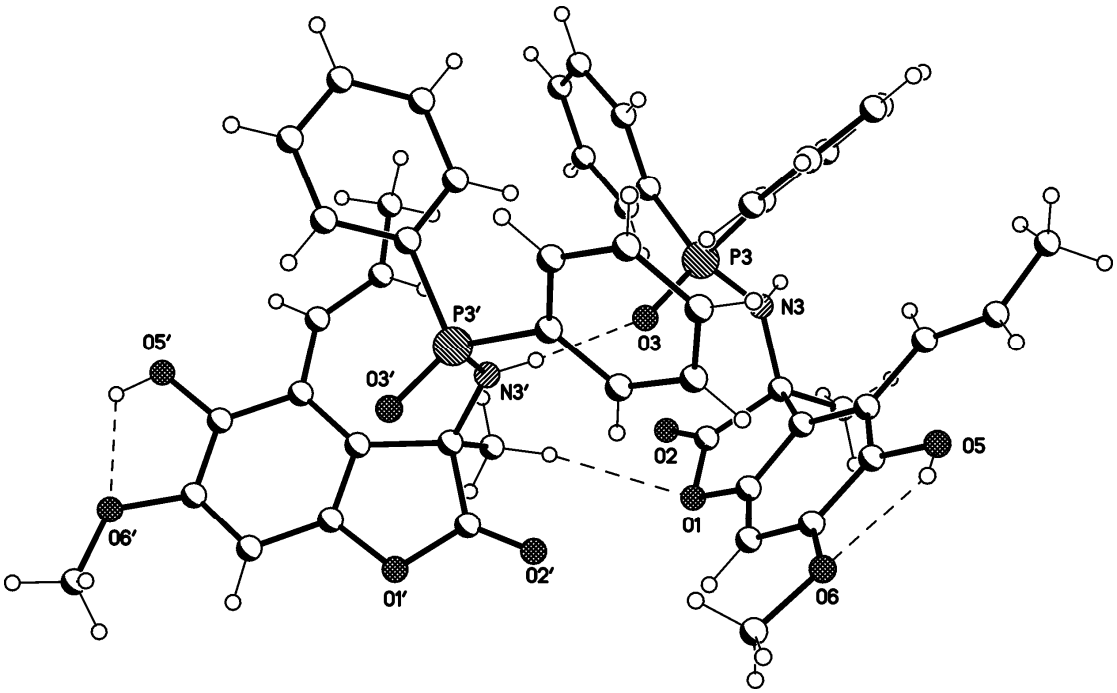

Fig. S13. Molecular structure of **18** showing the hydrogen bond pattern (both independent molecules are shown).

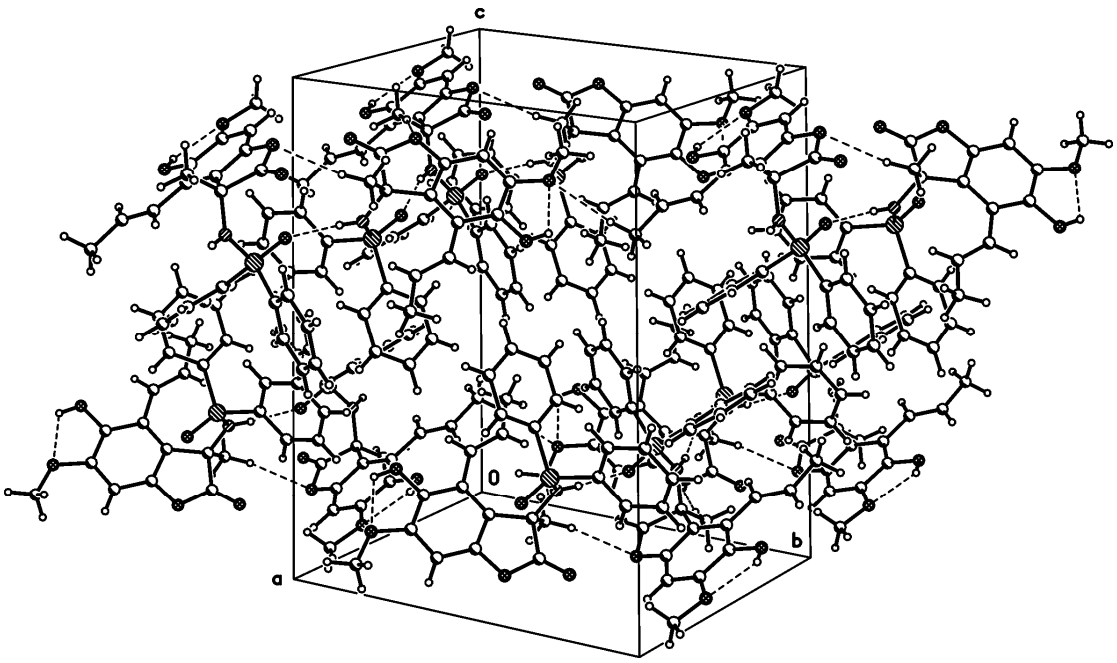

Fig. S14. Crystal packing of **18**.

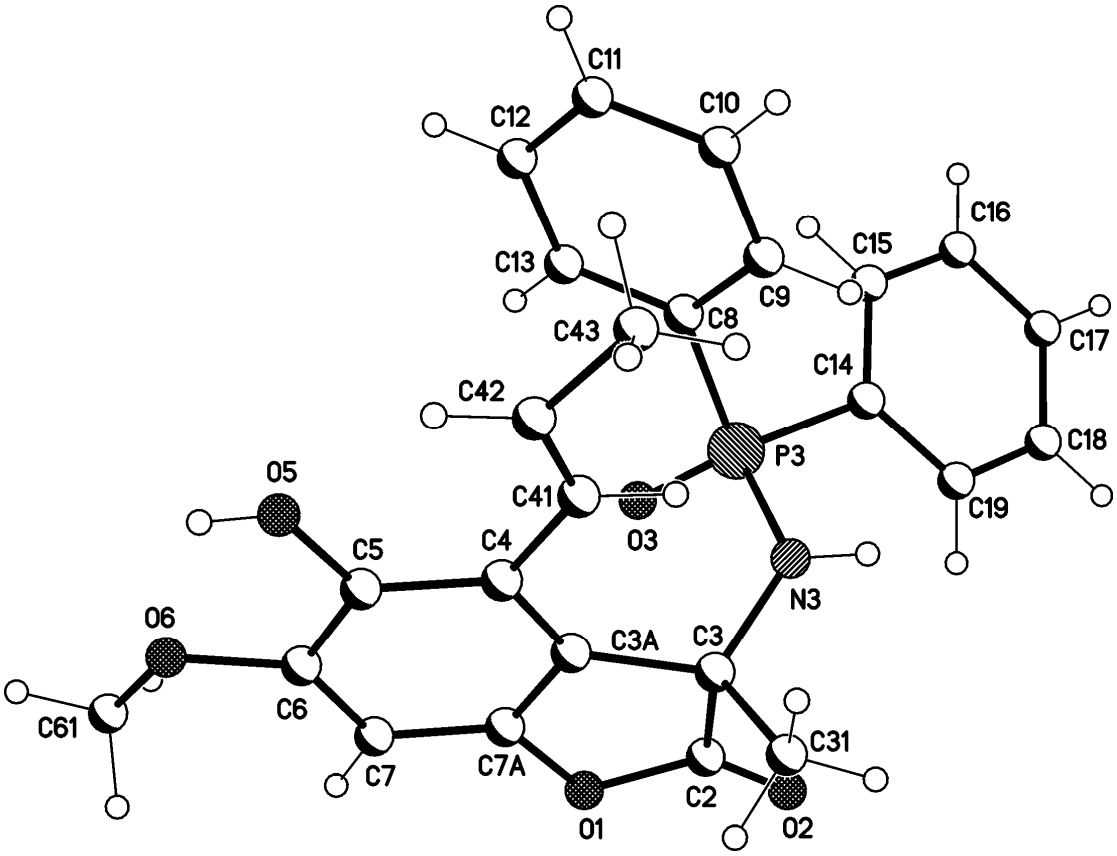

Fig. S15. Molecular structure of first of the two crystallographic independent molecules of **18**.

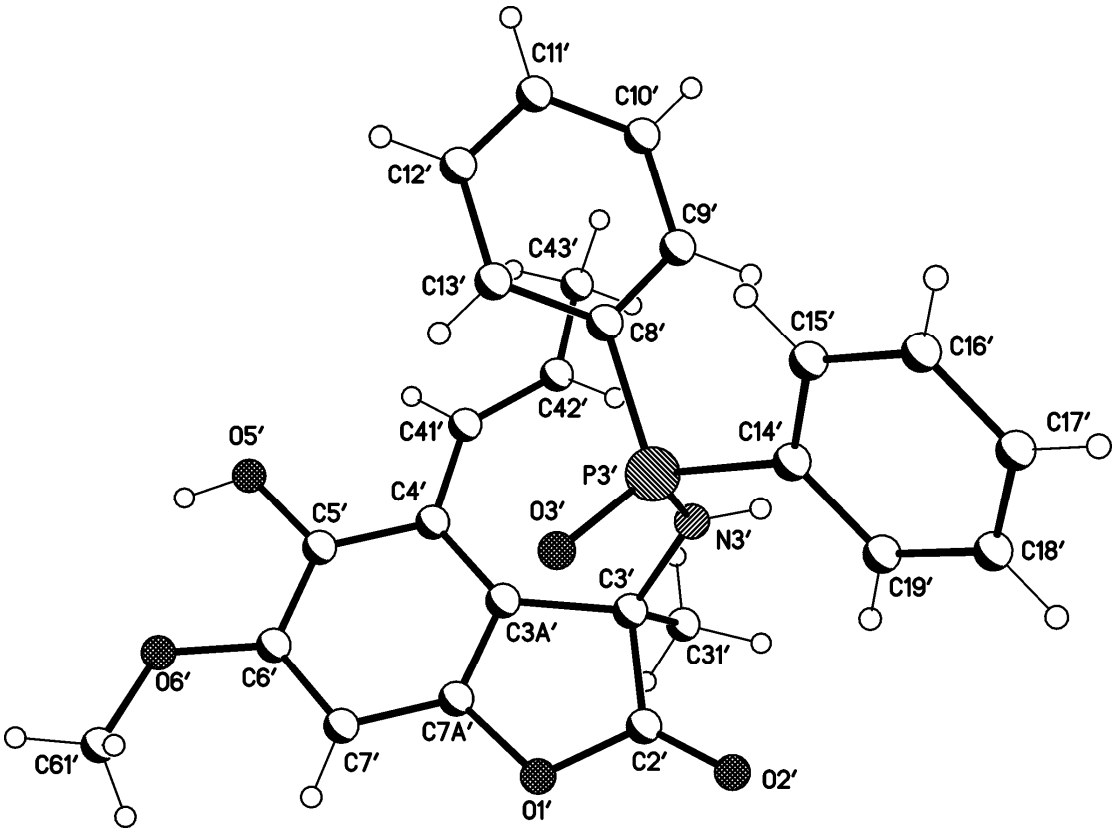

Fig. S16. Molecular structure of second of the two crystallographic independent molecules of **18**.

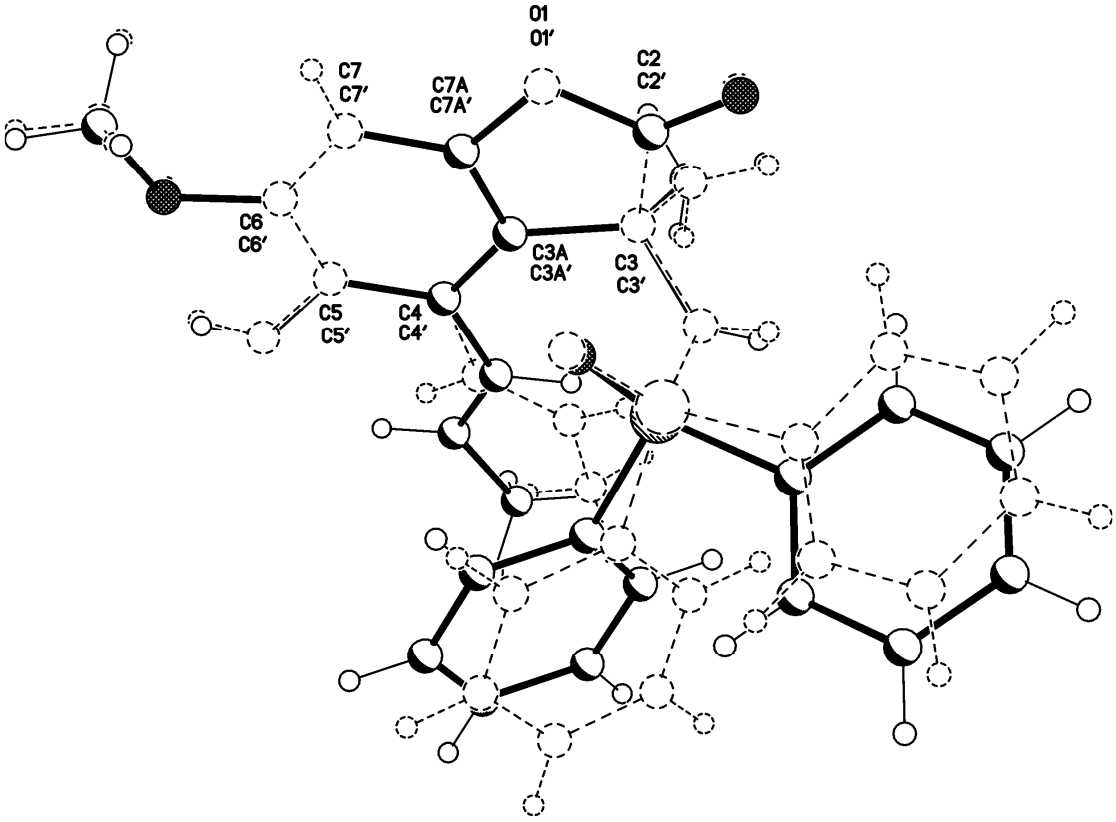

Fig. S17. L.S. fit of the two independent molecules of **18**.