SUPPLEMENTARY INFORMATION

Phosphonated bicycles with a nitrogen-nitrogen junction

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CONTENT

Characterization of the new compounds

Diethyl (1a, 2a, 6,9)-tetrahydro-4-methyl-1,2,4]triazolo[1a,2-*a*]pyridazinyl-6-phosphonate-3,5-dione (3b)

A mixture of 4-methyl-4*H*-1,2,4-triazole-3,5-dione (0.25 g, 2.2 mmol), diene **1** (0.42 g. 2.2 mmol, 1 equiv) and dichloroethane (3.5 mL) was stirred in a microwave oven under 500 W irradiation at 120 °C for 45 min. The reaction mixture was then concentrated under vacuum and purified by column chromatography (AcOEt : acetone 7/3) to afford a white gummy solid (0.5 g, 75%). Rf [acetone/AcOEt 3:7] = 0.4; mp (°C): 60.8-63.3; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.02-6.11 (m, C(2)-H and C(3)-H, 2H), 4.86 (dddt, $^{2}J_{1,P}$ = 15.2 Hz, $^{3}J_{1,2}$ = 4.7 Hz, $^{4}J_{1,3}$ = 3.1 Hz and $^{5}J_{1,4}$ = $^{5}J_{1,4'}$ = 1.5 Hz, C(1)-H, 1H), 4.31 (dddd, $^{2}J_{4,4'}$ = 16.8 Hz, $^{3}J_{3,4}$ = 6.9 Hz, $^{5}J_{4,P}$ = 3.5 Hz and $^{4}J_{2,4}$ = $^{5}J_{1,4}$ = 1.7 Hz, C(4)-H, 1H), 4.10-4.19 (m, PO(O$\underline{CH_2}$$CH_3$)$_2$, 4H), 3.95 (ddq, $^{2}J_{4,4'}$ = 16.8 Hz, $^{3}J_{3,4'}$ = 6.7 Hz and $^{4}J_{2,4'}$ = $^{5}J_{1,4'}$ = $^{5}J_{4',P}$ = 1.9 Hz, C(4)-H', 1H), 3.13 (s, Me, 3H), 1.33 (t, $^{3}J_{H,H}$ = 7.0 Hz, PO(OCH$_2$$\underline{CH_3}$)$_2$, 3H), 1.30 (t, $^{3}J_{H,H}$ = 7.3 Hz, PO(OCH$_2$$\underline{CH_3}$)$_2$, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.79 (s, C=O), 152.09 (s, C=O), 122.75 (d, $^{3}J_{3,P}$ = 9.8 Hz, C(3)), 119.55 (d, $^{2}J_{2,P}$ = 4.9 Hz, C(2)), 63.44 (d, $^{3}J_{C,P}$ = 7.1 Hz, PO(O$\underline{CH_2}$$CH_3$)$_2$), 63.29 (d, $^{3}J_{C,P}$ = 6.4 Hz, PO(O$\underline{CH_2}$$CH_3$)$_2$), 51.21 (d, $^{1}J_{1,P}$ = 140.6 Hz, C(1)), 44.24 (d, $^{4}J_{4,P}$ = 3.3 Hz, C(4)), 25.33 (s, Me), 16.50 (d, $^{3}J_{C,P}$ = 5.9 Hz, PO(OCH$_2$$\underline{CH_3}$)$_2$), 16.42 (d, $^{3}J_{C,P}$ = 5.9 Hz, PO(OCH$_2$$\underline{CH_3}$)$_2$); ^{31}P NMR (121 MHz, $CDCl_3$): δ 17.78; IR (cm^{-1}): ν 3564 (w), 3485 (w), 2984 (w), 2908 (w), 1774 (C=O, m), 1705 (C=O, s), 1470 (s), 1396 (m), 1252 (P=O, s), 1018 (P-O, s), 972 (P-O, m), 762 (m); MS (ESI, positive mode) m/z (%) 326.05 (100) [M+Na], 304.10 (5) [M+H]; HRMS m/z [M+Na^+]: Calcd for $C_{11}H_{18}N_3O_5PNa$: 326.0882, Found: 326.0880.

Diethyl 1,4,6,11-tetrahydro-6,11-dioxopyridazino[1,2-*b*]phthalazin-1-yl-1-phosphonate (11)

A mixture of phthalhydrazide (0.71 g, 4.38 mmol) in MeCN (33 mL) and diene **1** (0.5 g, 2.63 mmol) was stirred at 0 °C (ice bath). Lead tetraacetate (1.94 g, 4.38 mmol) was added (in small portions, over less than 20 min). The heterogeneous mixture was stirred at 0 °C. After 5 min, the mixture colour changed to yellow. As the reaction proceeds, the solution became cloudy and the colour changed from golden brown to lime green, then from green to yellow. The reaction mixture was filtered and the cake washed with MeCN to give a white precipitate and a cloudy filtrate. The filtrate was then concentrated in vacuum and purified by column chromatography [AcOEt: *i*-PrOH 95/5] to give **11** as a yellow oil (0.122 g, 38%). Rf [AcOEt :

i-PrOH 95/5] = 0.3; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (ddd, $^{3}J_{H,H}$ = 1.8 Hz, $^{4}J_{H,H}$ = 1.0 Hz and $^{5}J_{H,H}$ = 0.5 Hz, CH(Ph), 2H), 7.78-7.73 (m, CH(Ph), 2H), 6.19-6.13 (m, C(2)-H and C(3)-H, 2H), 5.99 (ddt, $^{2}J_{1,P}$ = 18.9 Hz, $^{3}J_{1,H}$ = 5.1 Hz and $^{5}J_{1,4}$ = $^{5}J_{1,4'}$ = 1.5 Hz, C(1)-H, 1H), 4.78 (ddq, $^{2}J_{4,4'}$ = 18.7 Hz, $^{3}J_{3,4}$ = 8.4 Hz and $^{4}J_{2,4}$ = $^{5}J_{1,4}$ = $^{5}J_{4,P}$ = 1.8 Hz, C(4)-H, 1H), 4.42-4.36 (m, $^{2}J_{4,4'}$ = 18.4 Hz, C(4)-H', 1H), 4.10-3.98 (m, $PO(O\underline{CH_2}CH_3)_2$, 4H), 1.15 (t, $^{3}J_{H,H}$ = 7.0 Hz, $PO(OCH_2\underline{CH_3})_2$, 3H) 1.11 (t, $^{3}J_{H,H}$ = 7.0 Hz, $PO(OCH_2\underline{CH_3})_2$, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.09 (s, C=O), 157.74 (s, C=O), 133.79 (s, CH(Ph)), 133.50 (s, CH(Ph)), 128.74 (s, Cq(Ph)), 128.68 (s, Cq(Ph)), 127.85 (s, CH(Ph)), 127.64 (s, CH(Ph)), 123.90 (d, $^{2}J_{2,P}$ = 10.1 Hz, C(2)), 118.96 (d, $^{3}J_{3,P}$ = 4.3 Hz, C(3)), 63.50 (d, $^{2}J_{C,P}$ = 5.9 Hz, $PO(O\underline{CH_2}CH_3)_2$), 63.32 (d, $^{2}J_{C,P}$ = 7.3 Hz, $PO(O\underline{CH_2}CH_3)_2$), 50.59 (d, $^{1}J_{1,P}$ = 144.9 Hz, C(1)), 45.63 (d, $^{4}J_{4,P}$ = 2.6 Hz, C(4)), 16.33 (d, $^{3}J_{C,P}$ = 5.7, $PO(OCH_2\underline{CH_3})_2$), 16.14 (d, $^{3}J_{C,P}$ = 6.2 Hz, $PO(OCH_2\underline{CH_3})_2$); ^{31}P NMR (121 MHz, $CDCl_3$): δ 18.12; IR (cm^{-1}): υ 3514 (w), 3474 (w), 2984 (m), 2931 (w), 2910 (w), 1776 (w), 1643 (s), 1634 (s), 1605 (s), 1470 (m), 1445 (w), 1408 (m), 1306 (s), 1244 (s), 1004 (s), 964 (s), 746 (s), 704 (s); MS (ESI, positive mode) m/z (%)373.28 (100) [M+Na^+], 213.26 (12) [M-$PO(OEt)_2$]; HRMS m/z [M+Na^+]: Calcd for $C_{16}H_{19}N_2O_5PNa$ 372.0929, Found: 373.0926.

Diethyl hexahydro-1,3-dioxo-2-phenyl-1*H*-[1,2,4]triazolo[1,2-*a*]pyridazin-5-yl-5-phosphonate (9a)

Reduction of the cycloadduct **3a** (0.338 g, 0.926 mmol) yielded the title compound **9a** as a white oil (0.332 g, 98%). Rf [AcOEt] = 0.4; ^{1}H NMR (500MHz, $CDCl_3$) δ : 7.48 (d, $^{3}J_{H,H}$ = 8.2 Hz, CH(Ph), 2H), 7.45 (t, $^{3}J_{H,H}$ = 8.0 Hz, CH(Ph), 2H), 7.36 (t, $^{3}J_{H,H}$ = 7.4 Hz, CH(Ph), 1H), 4.56 (dd, $^{2}J_{1,P}$ = 11.8 Hz and $^{3}J_{1,2}$ = 6.5 Hz, C(1)-H, 1H), 4.21-4.13 (m, $PO(C\underline{H_2}CH_3)_2$ and C(4)-H, 5H), 3.10 (dt, $^{2}J_{4,4'}$ = 12.5 Hz and $^{3}J_{3,4}$ = 3.7 Hz, C(4)-H, 1H), 2.41-2.34 (m, C(2)-H or/and C(3)-H), 2H), 2.01-1.94 (m, C(2)-H or/and C(3)-H), 1H), 1.94-1.85 (m, C(2)-H or/and C(3)-H), 1H), 1.32 (t, $^{3}J_{H,H}$ = 6.9 Hz, $PO(CH_2C\underline{H_3})_2$, 3H) , 1.28 (t, $^{3}J_{H,H}$ = 6.6 Hz, $PO(CH_2C\underline{H_3})_2$, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 153.07 (s, C=O), 151.45 (s, C=O), 131.40 (s, Cq(Ph)), 128.94 (s, CH(Ph)), 128.09 (s, CH(Ph)), 125.41 (s, CH(Ph)), 62.76 (d, $^{2}J_{C,P}$ = 6.5 Hz, $PO(O\underline{C}H_2CH_3)_2$), 62.73 (d, $^{2}J_{C,P}$ = 6.8 Hz, $PO(\underline{C}H_2CH_3)_2$,), 49.09 (d, $^{1}J_{1,P}$ = 142,0 Hz, C(1)), 44.28 (s, C(4)), 23.33 (s, C(3)), 19.62 (s, C(2)), 16.51 (d, $^{3}J_{C,P}$ = 5.6 Hz, $PO(OCH_2\underline{C}H_3)_2$), 16.42 (d, $^{3}J_{C,P}$ = 5.8 Hz, $PO(OCH_2\underline{C}H_3)_2$); ^{31}P NMR (121 MHz, $CDCl_3$) δ : 21.97; IR (υ, cm^{-1}) : 3554 (w), 2982 (w), 2923 (w), 1774 (w, C=O), 1713 (s, C=O), 1502 (w), 1418 (m), 1294 (w), 1248 (m, P=O), 1043 (m), 1020 (s, P-O), 966 (m, P-O), 767 (m); MS

(APCI, positive mode) m/z (%) = 367.94 (100) [M], 230.17 (90) [M-PO(OEt)$_2$]; HRMS m/z [M+Na]: Calcd for $C_{16}H_{22}N_3O_5NaP$: 390.1195, Found: 390.1191.

Diethyl hexahydro-1,3-dioxo-2-methyl-1*H*-[1,2,4]triazolo[1,2-*a*]pyridazin-5-yl-5-phosphonate (9b)

Reduction of the cycloadduct **3b** (0.217 g, 0.714 mmol) yielded the title compound **9b** as a yellow oil (0.198 g, 91%). Rf [AcOEt] = 0.3; ^{1}H NMR (300 MHz, $CDCl_3$) δ : 4.41 (app. q, $^1J_{1,P}$ = 11.4 Hz and $^3J_{1,2}$ = 5.6 Hz, C(1)-H), 1H), 4.12 (m, PO(OC$\underline{H_2}$CH$_3$)$_2$, 2H), 4.06 (m, PO(OC$\underline{H_2}$CH$_3$)$_2$, 2H), 4.0-3.97 (m, C(4)-H, 1H), 3.04 (s, Me, 3H), 2.94 (dt, $^2J_{4,4'}$ = 12.2 Hz and $^5J_{4,P}$ = 2.7 Hz, C(4)-H', 1H), 2.29-2.20 (m, C(3)-H and C(2)-H', 2H), 1.99-1.74 (m, C(3)-H and C(2)-H, 2H), 1.28 (t, $^3J_{H,H}$ = 6.8 Hz, PO(OCH$_2$C$\underline{H_3}$)$_2$, 3H), 1.24 (t, $^3J_{H,H}$ = 6.8 Hz, PO(OCH$_2$C$\underline{H_3}$)$_2$, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ : 154.46 (s, C=O), 152.33 (s, C=O), 62.32 (d, $^2J_{C,P}$ = 6.9 Hz, PO(O$\underline{C}$H$_2$CH$_3$)$_2$), 62.40 (d, $^2J_{C,P}$ = 7.3 Hz, PO(O$\underline{C}$H$_2$CH$_3$)$_2$), 48.55 (d, $^1J_{1,P}$ = 142.9 Hz, C(1)), 44.03 (s, C(4)), 24.9 (s, Me), 23.01 (d, $^3J_{3,P}$ = 1.9 Hz, C(3)), 20.66 (s, C(2)), 16.20 (d, $^3J_{C,P}$ = 5.8 Hz, PO(OCH$_2$$\underline{C}H_3$)$_2$); ^{31}P NMR (121 MHz, $CDCl_3$) δ : 21.50; IR (υ, cm^{-1}) : 3453-3556 (large, w), 3015 (w), 2866 (w), 1769 (s), 1697 (s), 1470 (w), 1447 (s), 1215 (s, P=O), 1097 (s, P-O), 964 (s, P-O), 908 (s), 1020 (s), 754 (s), 731 (s); MS (APCI, positive mode) m/z (%) 168.01 (100) [M-PO(OEt)$_2$], 306.90 (8) [M+H], 305.85 (63) [M], 275.90 (2) [M-H-CH$_2$=CH$_2$], 248.05 (3) [M-H-2 CH$_2$=CH$_2$], 169.00 (8) [M+H-PO(OEt)$_2$]; HRMS m/z [M+Na]: Calcd for $C_{11}H_{20}N_3O_5NaP$: 328.1038, Found : 328.1038.

Diethyl 1,2,3,4,6,11-hexahydro-6,11-dioxopyridazino[1,2-*b*]phtalazin-1-yl-1-phosphonate (12)

Reduction of the cycloadduct **11** (0.078 g, 0.223 mmol) yielded the title compound **12** as a colourless oil (0.063 g, 80 %). Rf [AcOEt] = 0.5; ^{1}H NMR (500MHz, $CDCl_3$) δ : 8.31-8.26 (m, CH(Ph), 2H), 7.79 (dddd, $^3J_{H,H}$ = 9.6 Hz, $^3J_{H,H}$ = 7.4 Hz, $^4J_{H,H}$ = 2.1 Hz and $^5J_{H,H}$ = 1.3 Hz, CH(Ph), 2H), 5.57 (ddd, $^2J_{1,P}$= 16.3 Hz, $^3J_{1,2}$= 5.8 Hz and $^4J_{1,3}$= 1.6 Hz, C(1)-H, 1H), 4.86 (dt, $^2J_{4,4'}$ = 12.6 Hz and $^5J_{4,P}$ = 4.1 Hz, C(4)-H, 1H), 4.08 (dq, $^3J_{H,H}$ = $^3J_{H,P}$ = 7.2 Hz, PO(OC$\underline{H_2}$CH$_3$)$_2$, 2H), 3.97 (dq, $^3J_{H,H}$ = $^3J_{H,P}$ = 7.1 Hz, PO(OC$\underline{H_2}$CH$_3$)$_2$,2H), 3.39 (ddd, $^2J_{4,4'}$ = 13.1 Hz, $^2J_{3,4}$ = 11.3 Hz and $^5J_{4,P}$ = 3.7 Hz, C(4)-H', 1H), 2.42-2.35 (m, C(3)-H or C(2)-H, 2H)), 2.34-2.10 (m, C(2)-H or C(3)-H, 1H), 1.86 (dt, $^3J_{2,P}$ = 13.1 Hz and $^3J_{1,2}$ = $^3J_{2,3}$ = 4.2 Hz, C(2)-H, 1H), 1.21 (t, $^3J_{H,H}$ = 7.1 Hz, PO(OCH$_2$C$\underline{H_3}$)$_2$, 3H), 1.07 (t, $^3J_{H,H}$ = 7.1 Hz, PO(OCH$_2$C$\underline{H_3}$)$_2$, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 133.87 (s, CH(Ph)), 133.59 (s, CH(Ph)), 129.03 (s, Cq(Ph)), 128.72 (s, Cq(Ph)), 128.06 (s, CH(Ph)), 127.98 (s, CH(Ph)),

62.99 (d, $^{2}J_{H,P}$ = 6.3 Hz, PO(O<u>C</u>H$_2$CH$_3$)$_2$), 62.58 (d, $^{2}J_{H,P}$ = 7.2 Hz, PO(O<u>C</u>H$_2$CH$_3$)$_2$), 49.61 (d, $^{1}J_{1,P}$ = 144,8 Hz, C(1)), 45.08 (s, C(4)), 22.68 (s, C(3)), 19.57 (s, C(2)), 16.35 (d, $^{3}J_{H,P}$ = 6.0 Hz, PO(OCH$_2$<u>C</u>H$_3$)$_2$); ^{31}P NMR (121 MHz, CDCl$_3$) δ : 21.89; IR (υ, cm^{-1}) : 3446 (m), 2982 (m), 2924 (m), 2855 (m), 1643 (s, C=O), 1604 (s, C=O), 1470 (m), 1396 (m), 1365 (s), 1312 (s), 1232 (s, P=O), 1043 (s), 1018 (s, P-O), 964 (s, P-O), 794 (s), 752 (s), 704 (s); MS (APCI, positive mode) m/z (%)230.17 (100) [M-PO(OEt)$_2$], 367.94 (90) [M]; HRMS m/z [M+Na]: Calcd for C$_{16}$H$_{21}$O$_5$N$_2$PNa: 375.10857, Found: 375.10796.

Diethyl hexahydro-6,7-dihydroxy-1,3-dioxo-2-phenyl-1*H*-[1,2,4]triazolo[1,2-*a*]pyridazin-5-yl-5-phosphonate (5a)

S*yn*-dihydroxylation of the cycloadduct **3a** (0.100 g, 0.274 mmol) yielded the title compound **5a** as a brown solid (0.104 g, 95%). Rf [AcOEt : *i*-PrOH 9/1] = 0.4; mp (°C) = 145.1-146.9; ^{1}H NMR (300MHz, CDCl$_3$) δ : 7.46-7.36 (m, CH(Ph), 4H), 7.25 (dd, $^{3}J_{H,H}$ = 7.5 Hz and $^{4}J_{H,H}$ = 1.5 Hz, CH(Ph), 1H), 4.73 (dd, $^{2}J_{1,P}$= 10.9 Hz and $^{3}J_{1,2}$ = 5.7 Hz, C(1)-H, 1H), 4.60-4.42 (m, C(2)-H and C(3)-H), 2H), 4.16 (m, PO(OC<u>H$_2$</u>CH$_3$)$_2$, 2H), 4.13 (m, PO(OC<u>H$_2$</u>CH$_3$)$_2$, 2H), 4.10-4.03 (m, C(4)-H, 1H), 3.27 (app q., $^{2}J_{4,4}$ = 17.3 Hz and $^{3}J_{3,4}$ = 7.3, C(4)-H', 1H), 2.94-2.80 (br s, OH), 1.32 (t, $^{3}J_{H,H}$ = 7.2 Hz, PO(OCH$_2$C<u>H$_3$</u>)$_2$, 3H), 1.24 (t, $^{3}J_{H,H}$ = 6.9 Hz, PO(OCH$_2$C<u>H$_3$</u>)$_2$, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ : 152.89 (s, C=O), 151.69 (s, C=O), 131.20 (s, Cq(Ph)), 129.29 (s, CH(Ph)), 128.41 (s, CH(Ph)), 125.50 (s, CH(Ph)), 66.07 (d, $^{2}J_{2,P}$ = 5.9 Hz, C(2)), 64.58 (s, C(3)), 63.76 (d, $^{2}J_{C,P}$ = 6.9 Hz, PO(O<u>C</u>H$_2$CH$_3$)$_2$), 63.74 (d, $^{2}J_{C,P}$ = 7.3 Hz, , PO(O<u>C</u>H$_2$CH$_3$)$_2$), 55.41 (d, $^{1}J_{1,P}$ = 138.7 Hz, C(1)), 44.77 (s, C(4)), 16.43 (d, $^{3}J_{C,P}$ = 6.2 Hz, , PO(OCH$_2$<u>C</u>H$_3$)$_2$), 16.42 (d, $^{3}J_{C,P}$ = 7.7 Hz, , PO(OCH$_2$<u>C</u>H$_3$)$_2$); ^{31}P NMR (121 MHz, CDCl$_3$) δ : 18.07; IR (υ, cm^{-1}) : 3471-3251 (large, m, OH), 2984 (m), 2927 (w), 2852 (w), 1776 (m, C=O), 1716 (s, C=O), 1643 (s), 1605 (s), 1412 (m), 1348 (m), 1246 (s, P=O), 1099 (m), 1018 (s, P-O), 964 (s, P-O), 851 (w), 748 (m) ; MS (APCI, positive mode) m/z (%) = 400.06 (100) [M], 261.99 (17) [M-PO(OEt)$_2$]; HRMS m/z [M+Na]: Calcd for C$_{16}$H$_{22}$N$_3$O$_7$NaP: 422.1093, Found: 422.1105.

Diethyl hexahydro-6,7-dihydroxy-1,3-dioxo-2-methyl-1*H*-[1,2,4]triazolo[1,2-*a*]pyridazin-5-yl-5-phosphonate (5b)

S*yn*-dihydroxylation of the cycloadduct **3b** (0.274 g, 0.816 mmol) yielded the title compound **5b** as a brown oil (0.179 g , 65%). Rf [AcOEt] = 0.2; ^{1}H NMR (500MHz, CDCl$_3$) δ : 4.58 (dd, $^{2}J_{1,P}$ = 13.8 Hz and $^{3}J_{1,2}$= 0.5 Hz, C(1)-H, 1H), 4.39-4.27 (m, C(2)-H and C(3)-H), 2H), 4.11 (m, PO(OC<u>H$_2$</u>CH$_3$)$_2$, 2H), 4.05 (m, PO(OC<u>H$_2$</u>CH$_3$)$_2$, 2H), 3.91-3.89 (m, C(4)-H, 1H), 3.11 (m,

C(4)-H', 1H), 3.01 (s, Me, 3H), 1.28 (t, $^{3}J_{H,H}$ = 7.8 Hz, PO(OCH$_2$C<u>H$_3$</u>)$_2$, 3H), 1.22 (t, $^{3}J_{H,H}$ = 7.4 Hz, PO(OCH$_2$C<u>H$_3$</u>)$_2$, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 154.42 (s, C=O), 152.73 (s, C=O), 65.78 (d, $^{2}J_{2,P}$ = 13.5 Hz, C(2)), 64.54 (s, C(3)), 63.61 (d, $^{2}J_{C,P}$ = 9.3 Hz, PO(O<u>C</u>H$_2$CH$_3$)$_2$), 63.50 (d, $^{2}J_{C,P}$ = 7.6 Hz, PO(O<u>C</u>H$_2$CH$_3$)$_2$), 55.19 (d, $^{1}J_{1,P}$ = 139.3 Hz, C(1)), 44.70 (s, C(4)), 25.38 (s, Me), 16.31 (d, $^{3}J_{C,P}$ = 5.8 Hz, PO(OCH$_2$<u>C</u>H$_3$)$_2$); ^{31}P NMR (121 MHz, $CDCl_3$) δ : 17.87 ; IR (υ, cm^{-1}) : 3404-3240 (large, m, OH), 3109 (w), 2987 (m), 1771 (s, C=O), 1693 (s, C=O), 1472 (s), 1398 (s), 1240 (s, P=O), 1161 (m), 1119 (m), 1016 (s, P-O), 862 (m, P-O), 794 (m), 731 (s); MS (APCI, positive mode) m/z (%) = 337.96 (100) [M], 338.91 (11) [M+H], 320.02 (17) [M- OH], 309.97 (5) [M- CH_2=CH_2], 200.02 (63) [M-PO(OEt)$_2$], 128.05 (9) [M-PO(OEt)$_2$-OH-2 CO]; HRMS m/z [M+Na]: Calcd for $C_{11}H_{20}N_3O_7NaP$: 360.0937, Found: 360.0949.

Diethyl 1,2,3,4,6,11-hexahydro-2,3-dihydroxy-6,11-dioxopyridazino-[1,2b]-phtalazin-1-yl-1-phosphonate (13)

S*yn*-dihydroxylation of the cycloadduct **11** (0.087 g, 0.248 mmol) yielded the title compound **13** as a yellow oil (0.063 g, 66 %). Rf [AcOEt : *i*-PrOH 95/5] = 0.5; ^{1}H NMR (500MHz, $CDCl_3$) δ : 8.29-8.25 (m, CH(Ph), 2H), 7.83-7.78 (m, CH(Ph), 2H), 5.72 (dd, $^{2}J_{1,P}$= 18.6 Hz and $^{3}J_{1,2}$ = 1.9 Hz, C(1)-H, 1H), 4.77 (dd, $^{2}J_{4,4'}$ = 12.6 Hz and $^{3}J_{3,4}$= 4.3 Hz, C(4)-H, 1H), 4.57-4.54 (m, C(2)-H and C(3)-H, 2H), 4.12 (dq, $^{3}J_{H,P}$ = $^{3}J_{H,H}$ = 7.1 Hz, PO(OC<u>H$_2$</u>CH$_3$)$_2$, 2H), 3.97 (dq, $^{3}J_{H,P}$ = $^{3}J_{H,H}$ = 7.3 Hz, PO(OC<u>H$_2$</u>CH$_3$)$_2$, 2H), 3.61 (dd, $^{2}J_{4,4'}$ = 12.6 Hz and $^{3}J_{3,4'}$= 9.7 Hz, C(4)-H', 1H), 3.42-3.20 (large s, OH), 1.23 (t, $^{3}J_{H,H}$ = 7.1 Hz, PO(OCH$_2$C<u>H$_3$</u>)$_2$, 3H), 1.06 (t, $^{3}J_{H,H}$ = 7.1 Hz, PO(OCH$_2$C<u>H$_3$</u>)$_2$, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 159.86 (s, C=O), 159.47 (s, C=O), 134.01 (s, CH(Ph)), 133.91 (s, CH(Ph)), 128.95 (s, Cq(Ph)), 128.64 (s, Cq(Ph)), 128.18 (s, CH(Ph)), 127.92 (s, CH(Ph)), 65.56 (d, $^{2}J_{2,P}$ = 13 .3 Hz, C(2)), 63.85 (d, $^{2}J_{C,P}$ = 6.3 Hz, PO(O<u>C</u>H$_2$CH$_3$)$_2$), 63.73 (s, C(3)), 63.38 (d, $^{2}J_{C,P}$ = 7.4 Hz, PO(O<u>C</u>H$_2$CH$_3$)$_2$), 56.76 (d, $^{1}J_{1,P}$ = 141.0Hz, C(1)), 45.20 (s, C(4)), 16.30 (d, $^{3}J_{C,P}$ = 6.1 Hz, PO(OCH$_2$<u>C</u>H$_3$)$_2$), 16.21 (d, $^{3}J_{C,P}$ = 5.9 Hz, PO(OCH$_2$<u>C</u>H$_3$)$_2$); ^{31}P NMR (121 MHz, $CDCl_3$) δ : 18.24; IR (υ, cm^{-1}) : 3423-3263 (large, m), 2924 (m), 2852 (w), 1706 (w, C=O), 1639 (s, C=O)), 1367 (m), 1313 (m), 1232 (m, P=O), 1018 (s, P-O), 973 (m), 912 (w), 842 (w, P-O), 794 (w), 706 (m); MS (APCI, positive mode) m/z (%) = 355.07 (100) [M-CH_2=CH_2], 161.26 (13) [M-CH=CH=CH=CH-PO(OEt)$_2$] ; HRMS m/z [M+Na]: Calcd for $C_{16}H_{21}N_2O_7NaP$: 407.0984, Found: 407.0994.

2,3,5,8-Tetrahydro-1,3-dioxo-2-phenyl-1*H*-[1,2,4]triazol-[1,2-*a*]pyridazin-5-yl-5-phosphonic acid (4a)

Diethyl phosphonate deprotection of the cycloadduct **3a** (0.10 g, 0.27 mmol) yielded the title compound **4a** as a yellow oil (0.083 g, 99 %). ^{1}H NMR (500 MHz, CD_3OD) δ : 7.53-7.49 (m, CH(Ph), 4H), 7.44-7.40 (t, $^{3}J_{H,H}$ = 6.4 Hz, CH(Ph), 1H), 6.17-6.10 (m, C(2)-H and C(3)-H, 2H), 4.97-4.94 (br d, $^{2}J_{1,P}$= 14.8 Hz, C(1)-H, 1H), 4.38-4.32 (m, C(4)-H, 1H), 4.15-4.09 (m, C(4)-H', 1H); ^{13}C NMR (125 MHz, CD_3OD) δ : 154.82 (s, C=O), 152.26 (s, C=O), 132.73 (s, Cq(Ph)), 130.07 (s, CH(Ph)), 129.49 (s, CH(Ph)), 127.40 (s, CH(Ph)), 123.43 (d, $^{2}J_{2,P}$ = 9.6 Hz, C(2)), 120.61 (d, $^{3}J_{3,P}$ = 4.7 Hz, C(3)), 53.38 (d, $^{1}J_{1,P}$ = 139.7 Hz, C(1)), 45.30 (d, $^{4}J_{4,P}$ = 2.8 Hz, C(4)); ^{31}P NMR (121 MHz, CD_3OD) δ : 15.75; MS (ESI, positive mode) m/z (%) = 309.83 (100) [M], 310.83 (13) [M+H], 229.05 (7) [M+H-$PO(OH)_2$], 228.04 (77) [M-$PO(OH)_2$]; HRMS m/z [M-H]: Calcd for $C_{12}H_{11}O_5N_3P$: 308.0421 Found: 308.0436.

2,3,5,8-Tetrahydro-2-methyl-1,3-dioxo-1*H*-[1,2,4]triazol-[1,2-*a*]pyridazin-5-yl-5-phosphonic acid (4b)

Diethyl phosphonate deprotection of the cycloadduct **3b** (0.10 g, 0.33 mmol) yielded the title compound **4b** as a yellow oil (0.065 g, 80 %). ^{1}H NMR (300MHz, CD_3OH) δ : 6.30-6.23 (m, C(2)-H and C(3)-H, 2H), 4.76 (d, $^{2}J_{1,P}$= 13.5 Hz, C(1)-H, 1H), 4.19 (dd, $^{2}J_{4,4'}$= 16.8 Hz and $^{3}J_{3,4}$ = 6.1 Hz, C(4)-H, 1H), 3.88 (ddd, $^{2}J_{4,4'}$= 16.8 Hz, $^{3}J_{3,4'}$ = 6.2 Hz and $^{4}J_{2,4'}$ or $^{5}J_{1,4'}$ = 2.5 Hz, C(4)-H', 1H), 2.97 (s, Me, 3H); ^{13}C NMR (75 MHz, CD_3OH) δ : 156.29 (s, C=O), 153.34 (s, C=O), 123.68 (d, $^{2}J_{2,P}$ = 15.2 Hz, C(2)), 120.48 (d, $^{3}J_{3,P}$ = 5.0 Hz, C(3)), 53.14 (d, $^{1}J_{1,P}$ = 140.3 Hz, C(1)), 45.22 (s, C(4)), 25.39 (s, Me); ^{31}P NMR (121 MHz, CD_3OH) δ : 16.23.

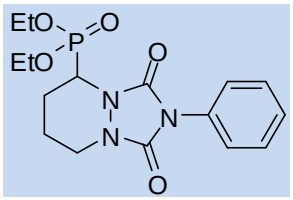
Hexahydro-6,7-dihydroxy-1,3-dioxo-2-phenyl-1*H*-[1,2,4]triazol-[1,2-*a*]pyridazin-5-yl-5-phosphonic acid (6a)

The reaction was performed at 90 °C during 8 h under MW activation (500 W). Diethyl phosphonate deprotection of the cycloadduct **5a** (0.199 g, 0.50 mmol) yielded the title compound **6a** as a yellow oil (0.094 g, 55 %). ^{1}H NMR (500 MHz, CD_3OH) δ : 7.64-7.61 (m, CH(Ph), 4H), 7.56 (dd, $^{3}J_{H,H}$ = 5.8 Hz and $^{4}J_{H,H}$ = 3.0 Hz, CH(Ph), 1H), 4.72 (dd, $^{2}J_{1,P}$ = 14.6 Hz and $^{3}J_{1,2}$ = 2.3 Hz, C(1)-H, 1H), 4.69 (m, C(3)-H, 1H), 4.53 (m, C(2)-H, 1H), 4.09 (dd, $^{2}J_{4,4'}$ = 10.8 Hz and $^{3}J_{3,4}$ = 5.5 Hz, C(4)-H, 1H), 3.46 (d, $^{2}J_{4,4'}$ = 11.1 Hz, C(4)-H', 1H); ^{13}C NMR (500 MHz, CD_3OD) δ : 154.55 (s, C=O), 153.08 (s, C=O), 132.68 (s, CqPh)), 130.08 (s, CH(Ph)), 129.51 (s, CH(Ph)), 127.34 (s, CH(Ph)), 67.21 (d, $^{2}J_{2,P}$ = 12.0 Hz, C(2)), 65.39 (s, C(3)), 58.68 (d, $^{1}J_{1,P}$ = 138.4 Hz, C(1)), 45.72 (s, C(4)); ^{31}P NMR (121 MHz, CD_3OD) δ :

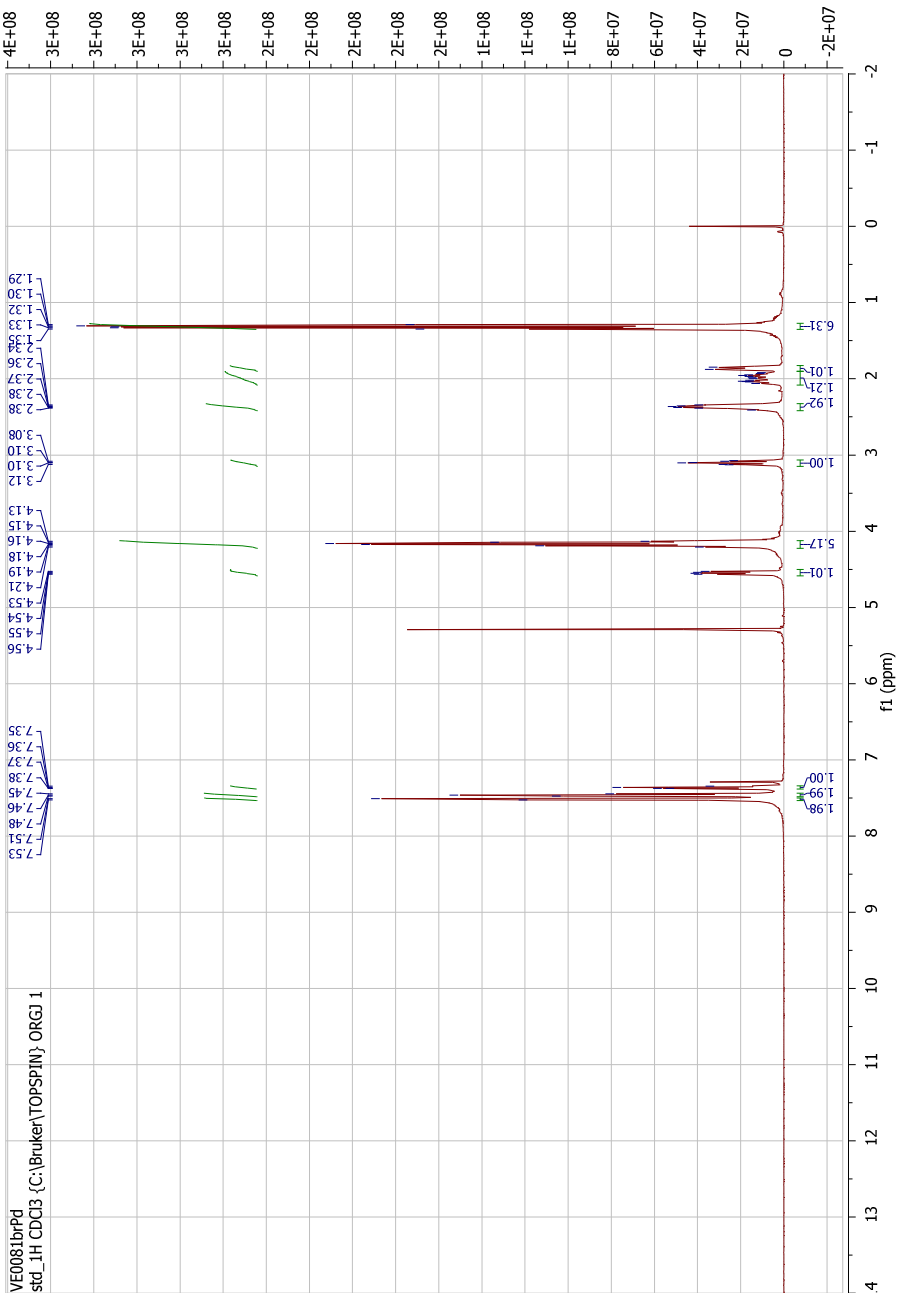
15.67; IR (υ, cm^{-1}) : 3696-3026 (large, w, OH), 2927 (w), 1772 (w), 1681 (s), 1434 (m), 1304 (w), 1144 (w, P=O), 943 (w, P-OH), 878 (w), 768 (w); MS (APCI, positive mode) m/z (%) = 260.24 (100) [M-$PO(OH)_2$], 263.13 (93) [M+H-$PO(OH)_2$], 228.17 (63) [M+H-$PO(OH)_2$-2OH].

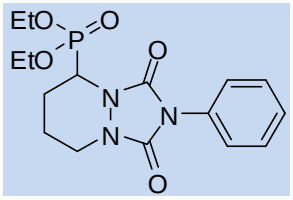
NMR spectra

A. Product 9a

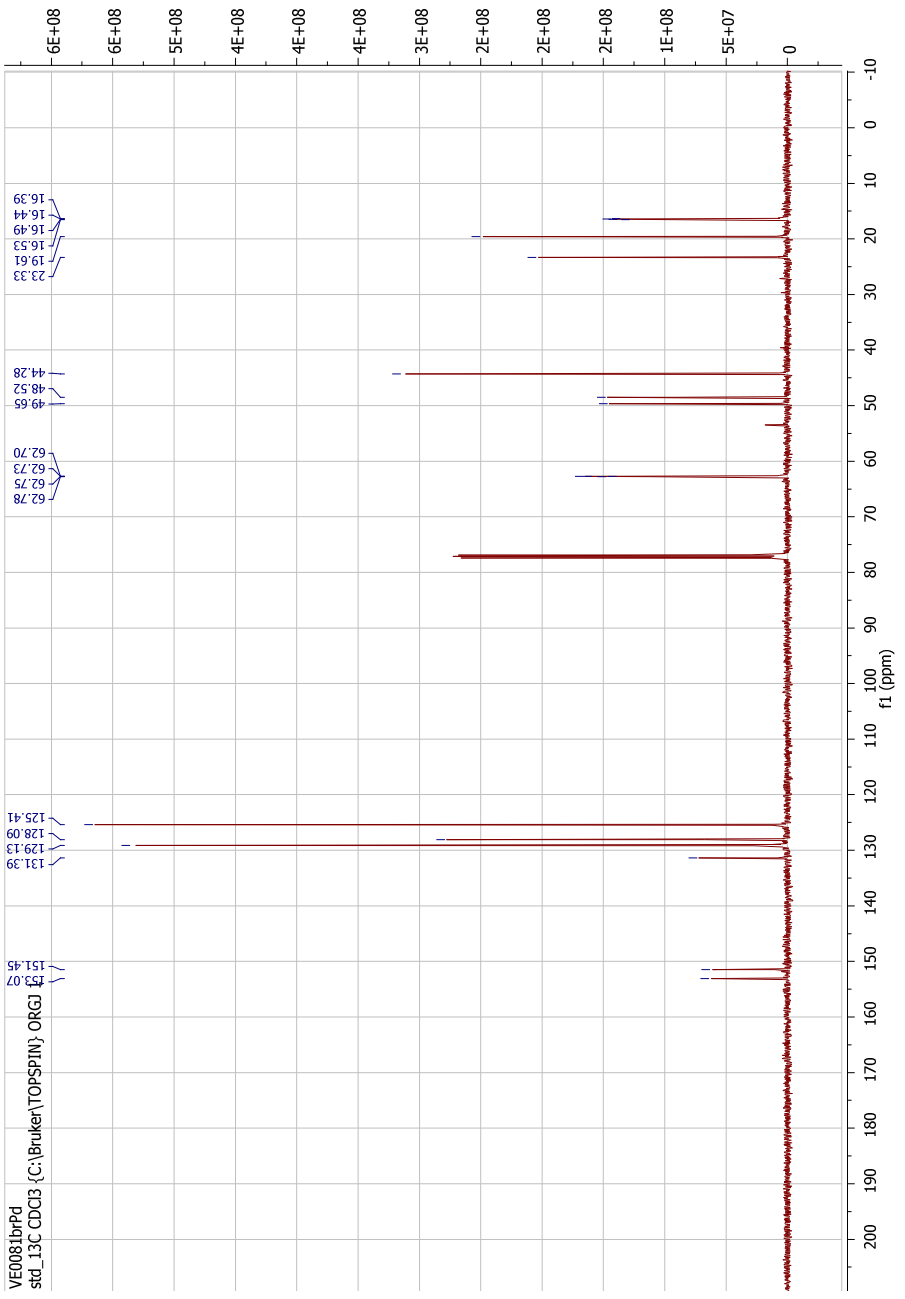


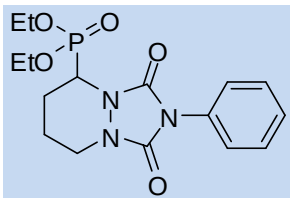
^{1}H NMR spectrum



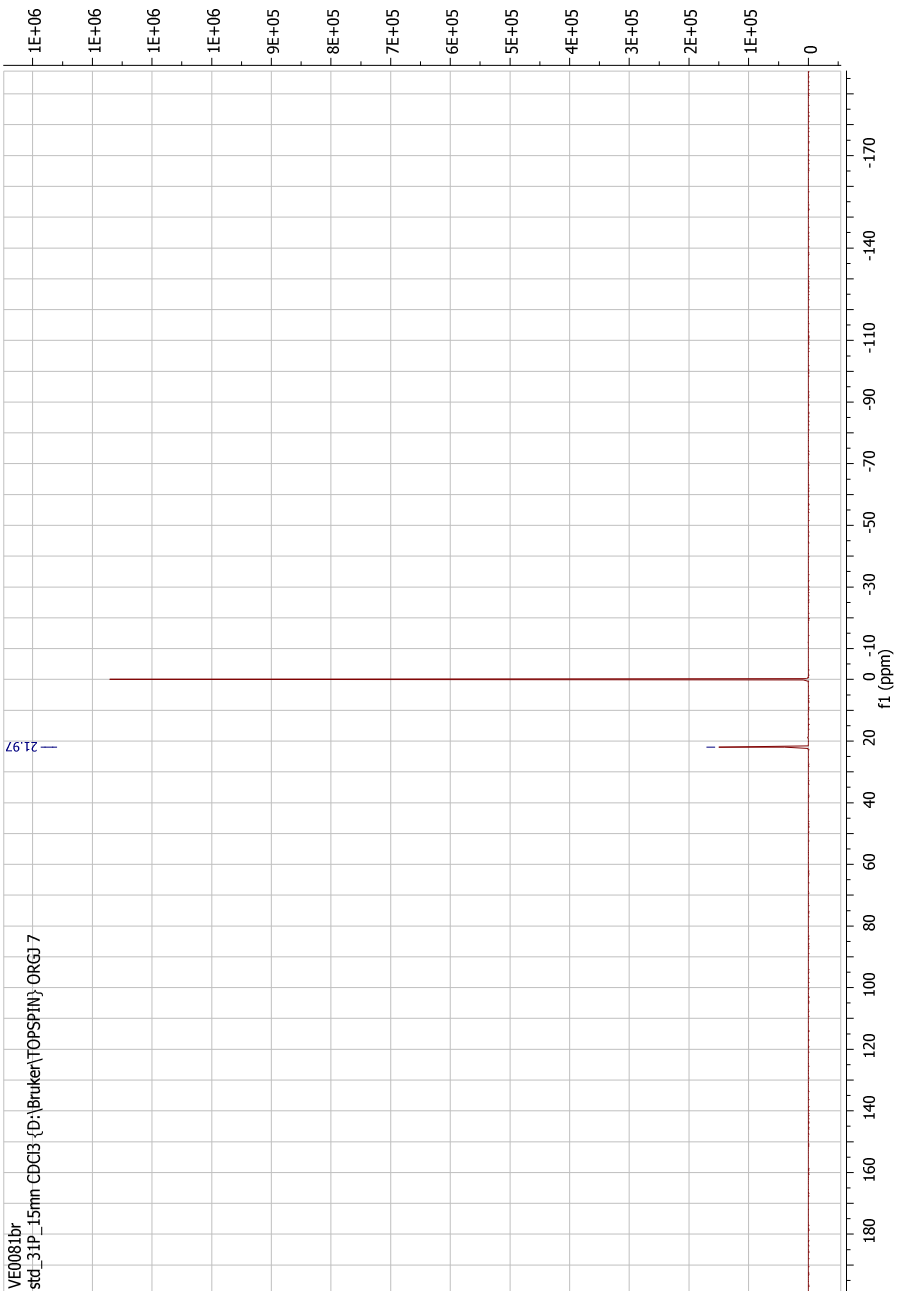


^{13}C NMR spectrum

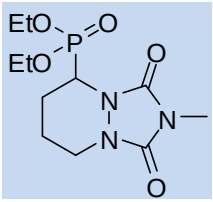




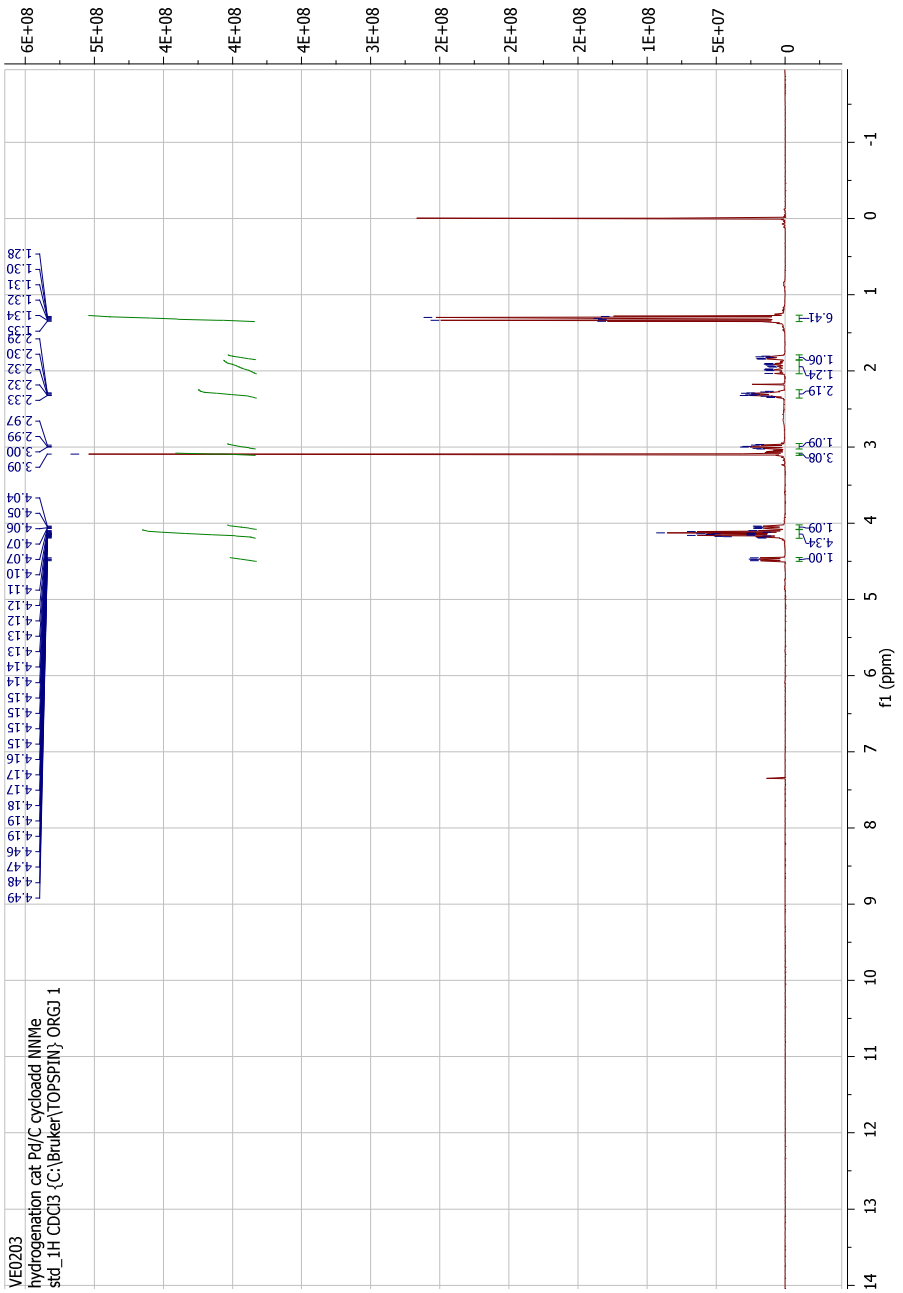
^{31}P NMR spectrum

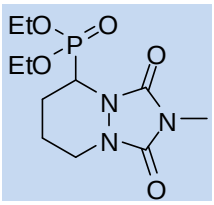


B. Product 9b

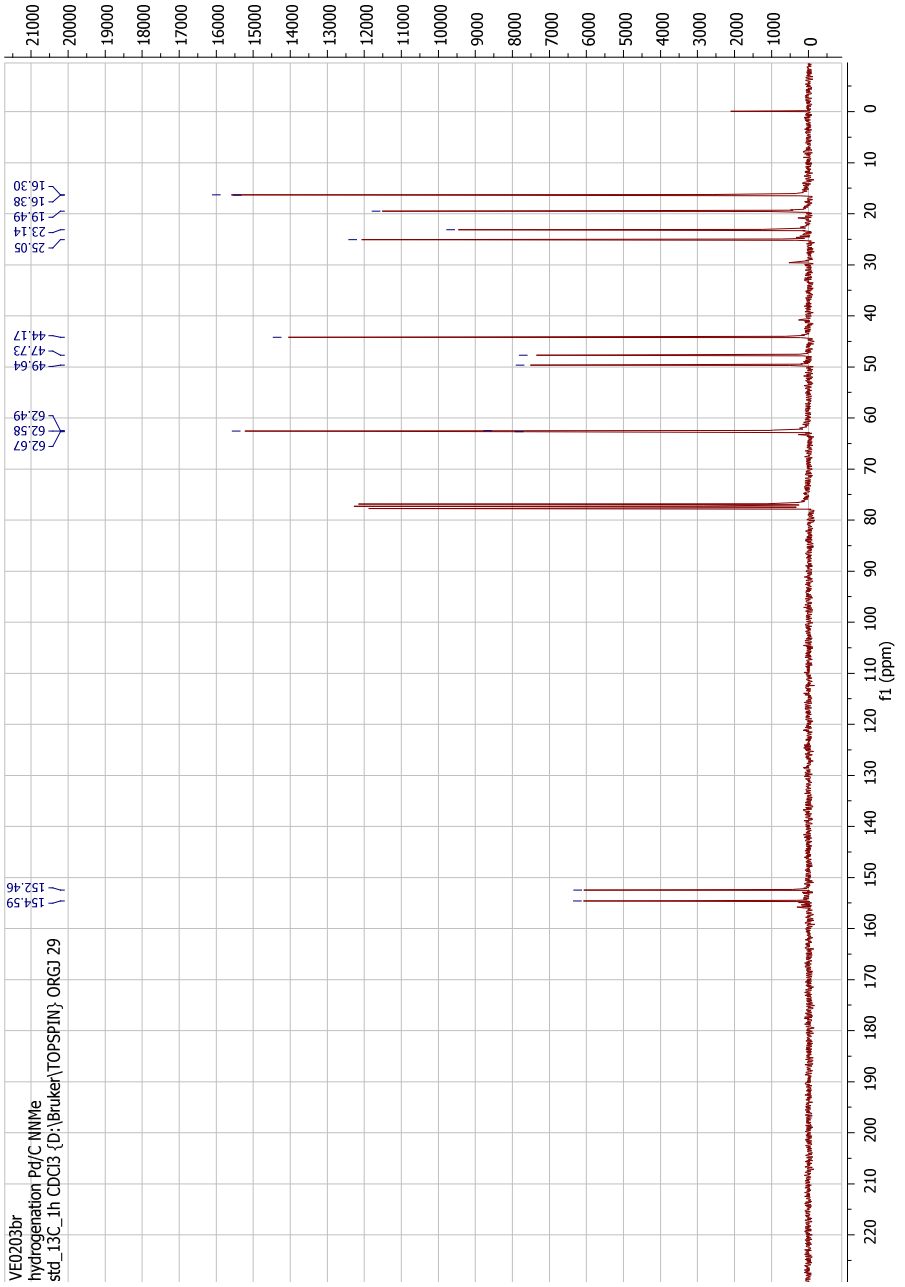


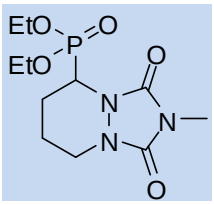
^{1}H NMR spectrum



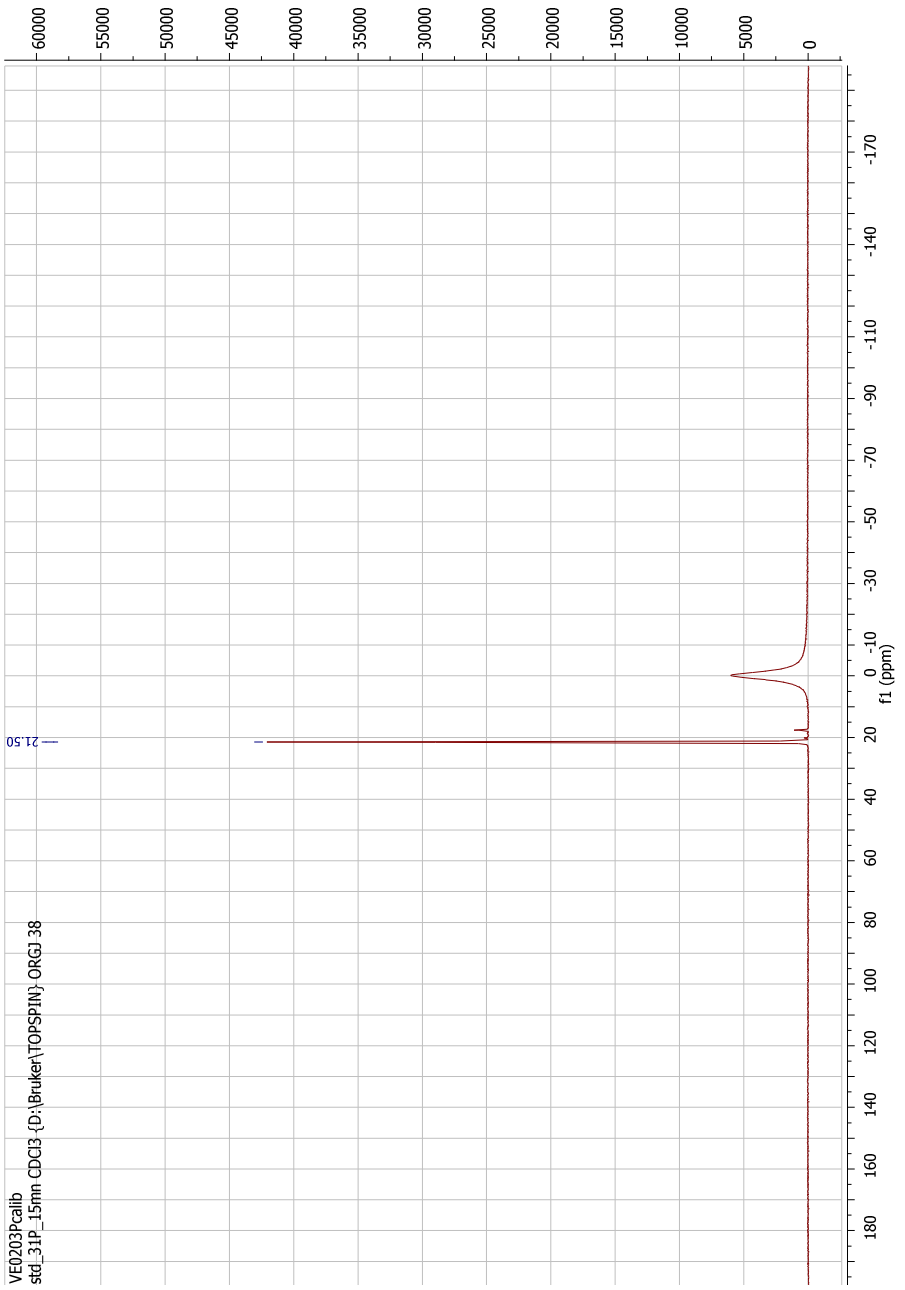


^{13}C NMR spectrum

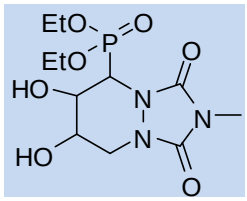




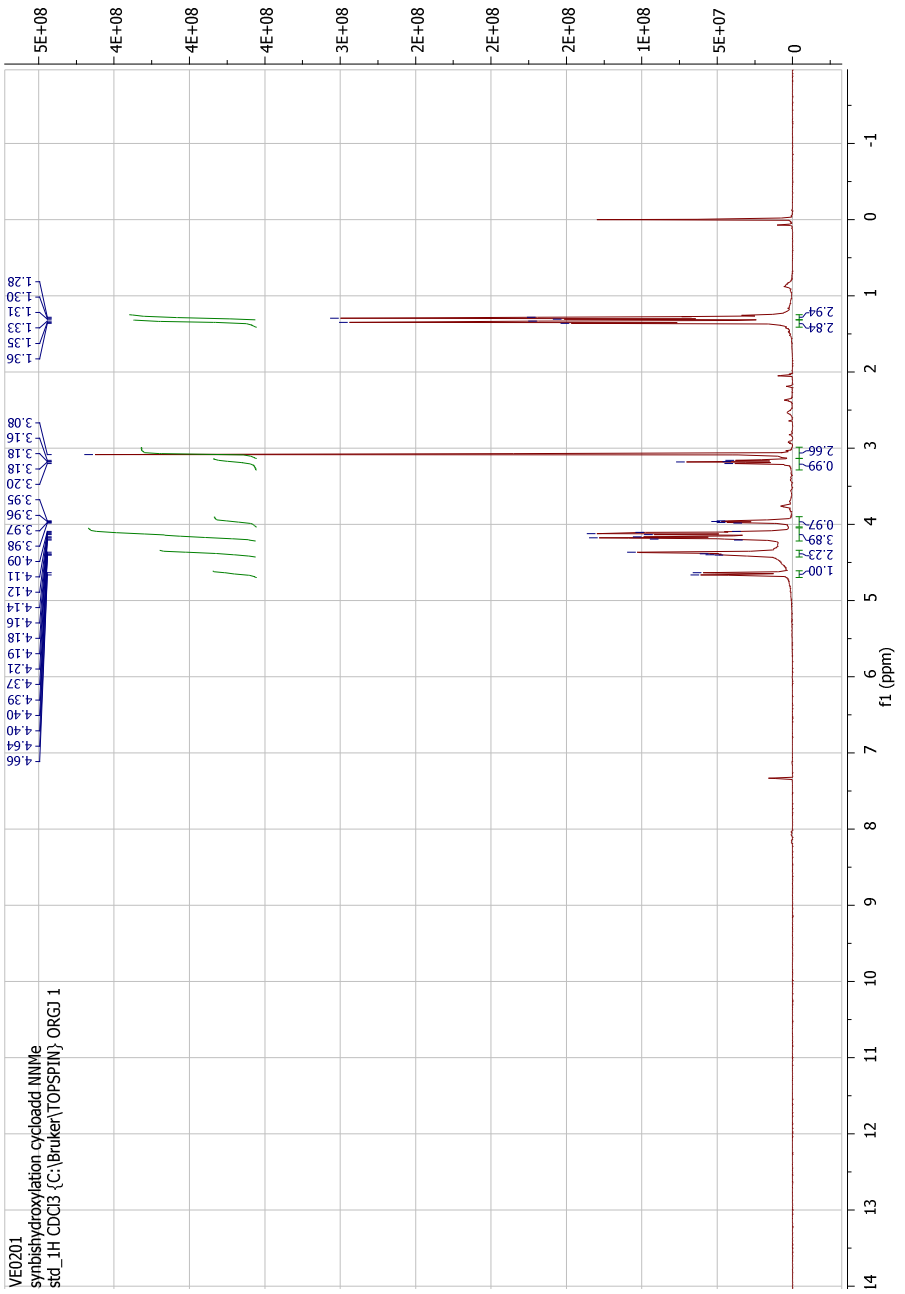
^{31}P NMR spectrum

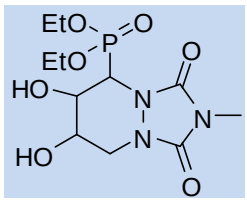


C. Product 5b

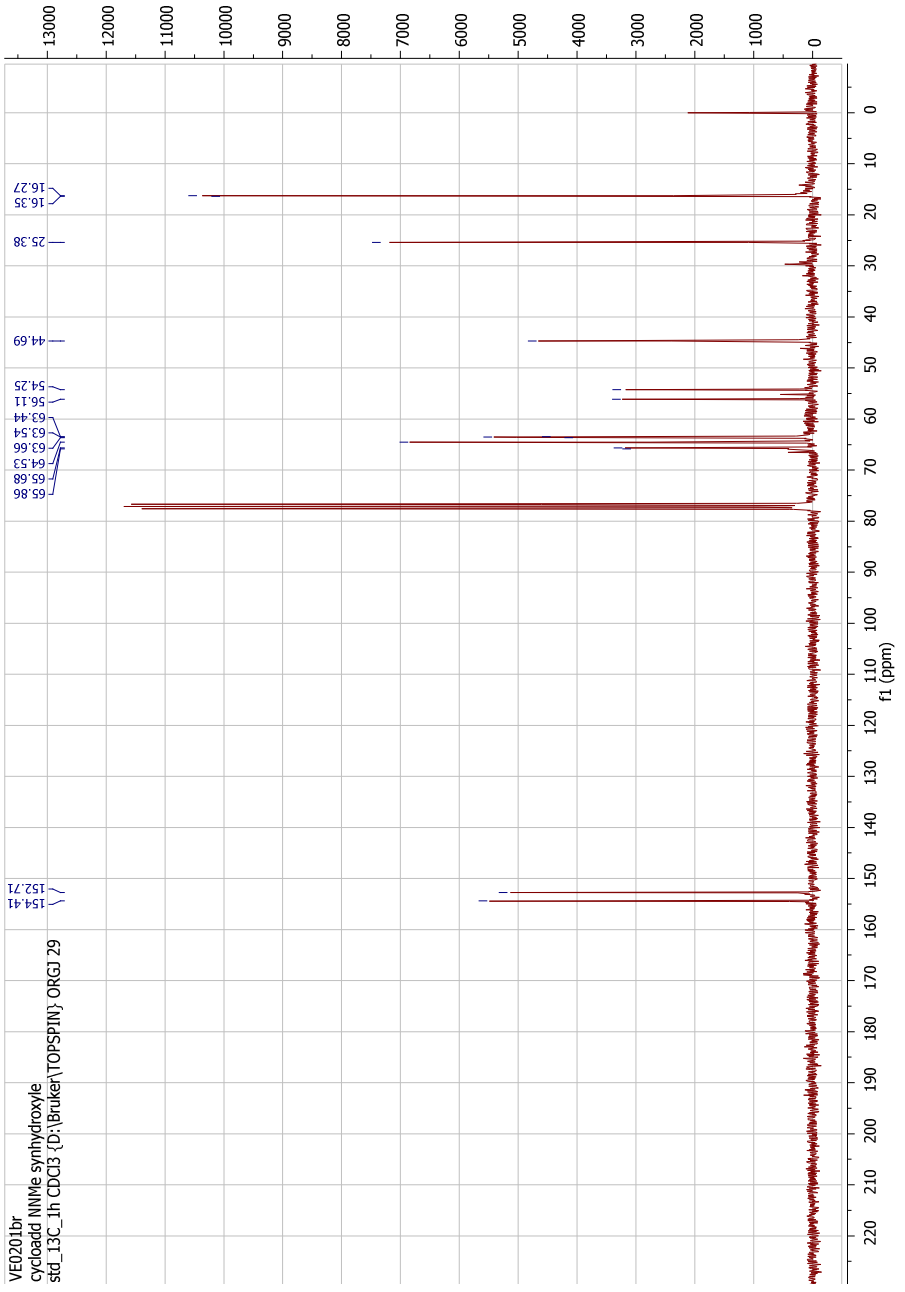


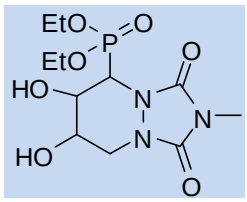
^{1}H NMR spectrum



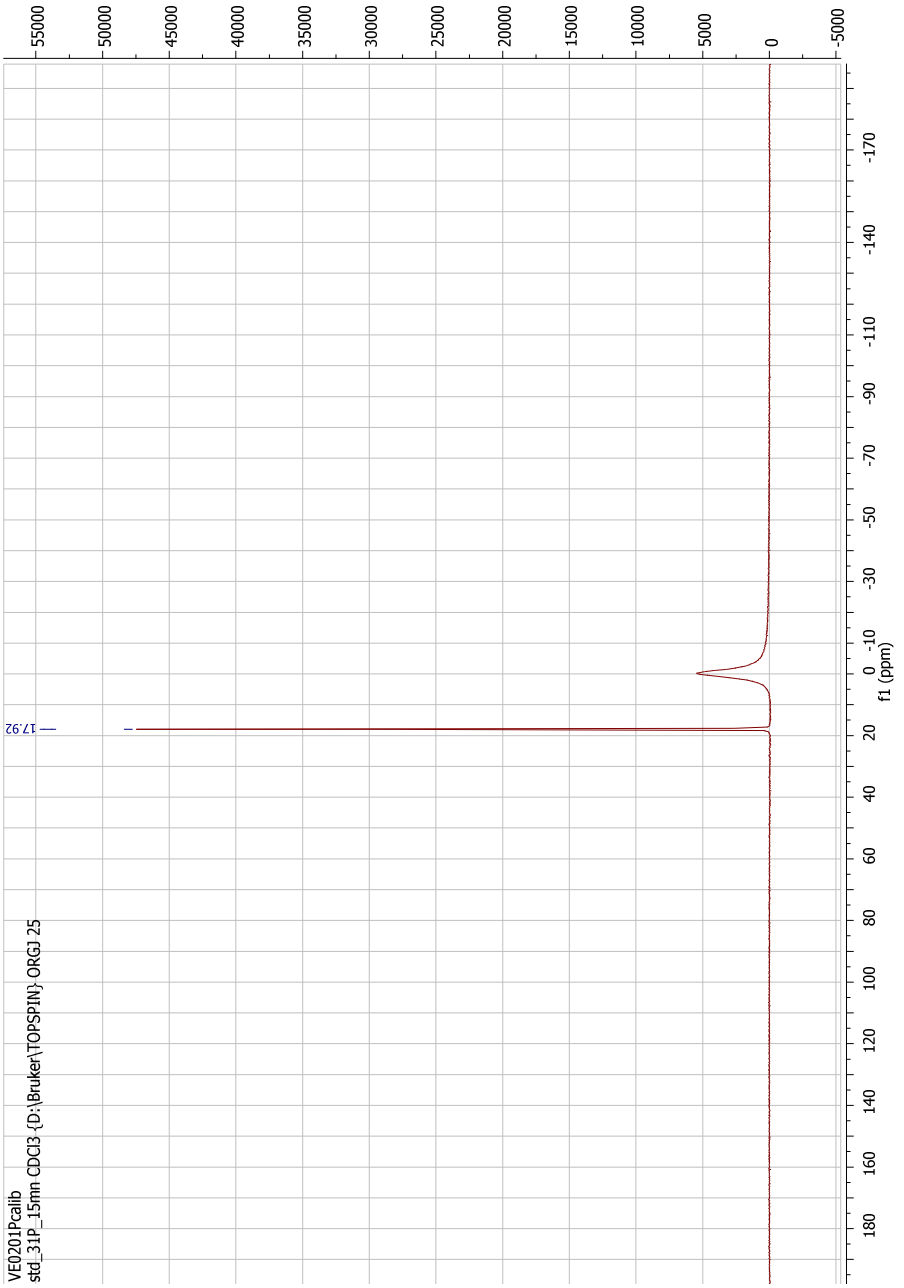


^{13}C NMR spectrum

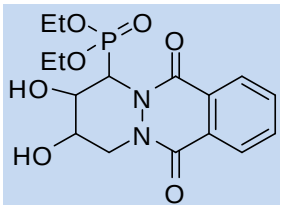




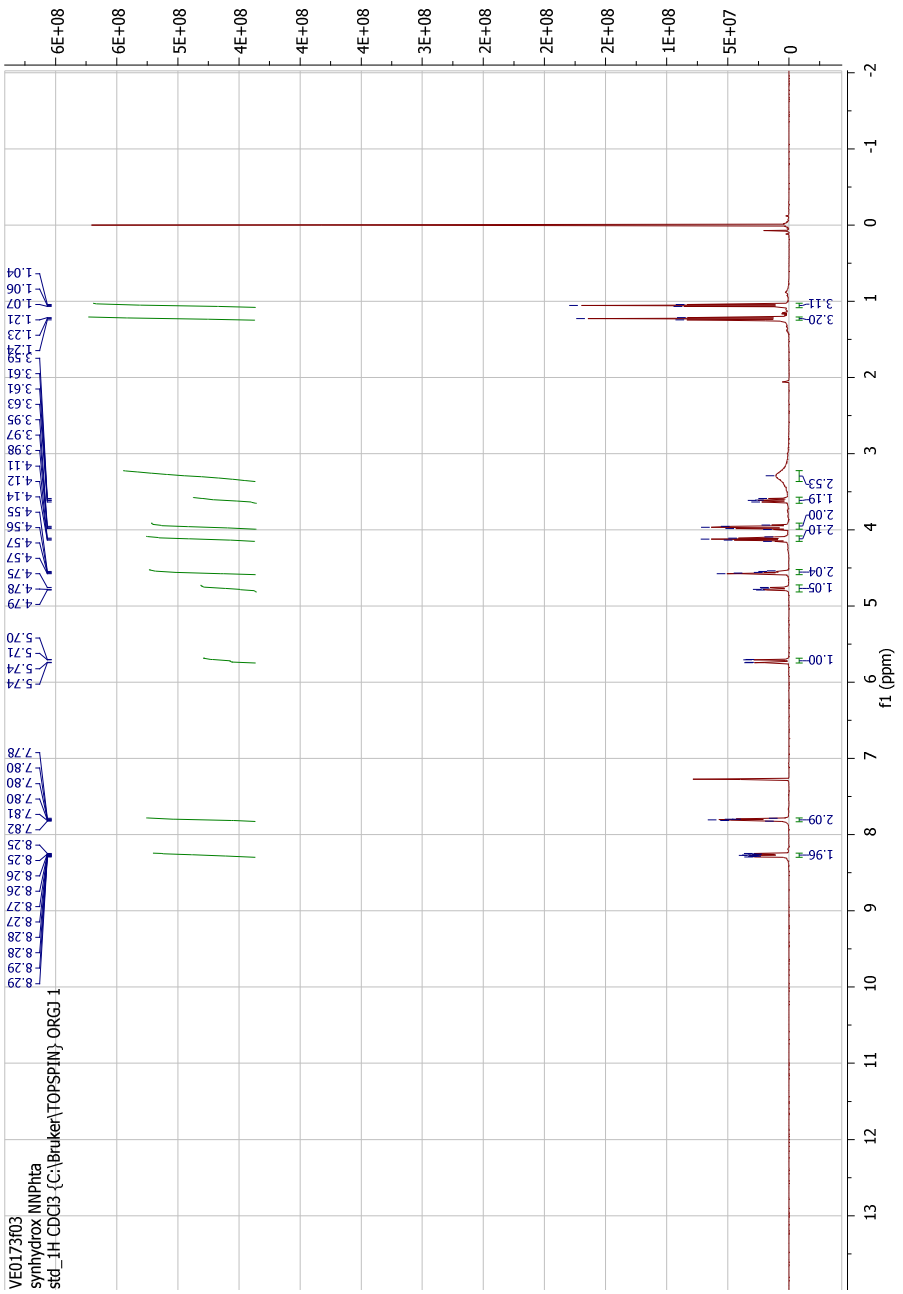
^{31}P NMR spectrum

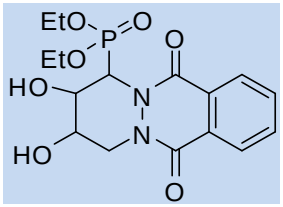


D. Product 13

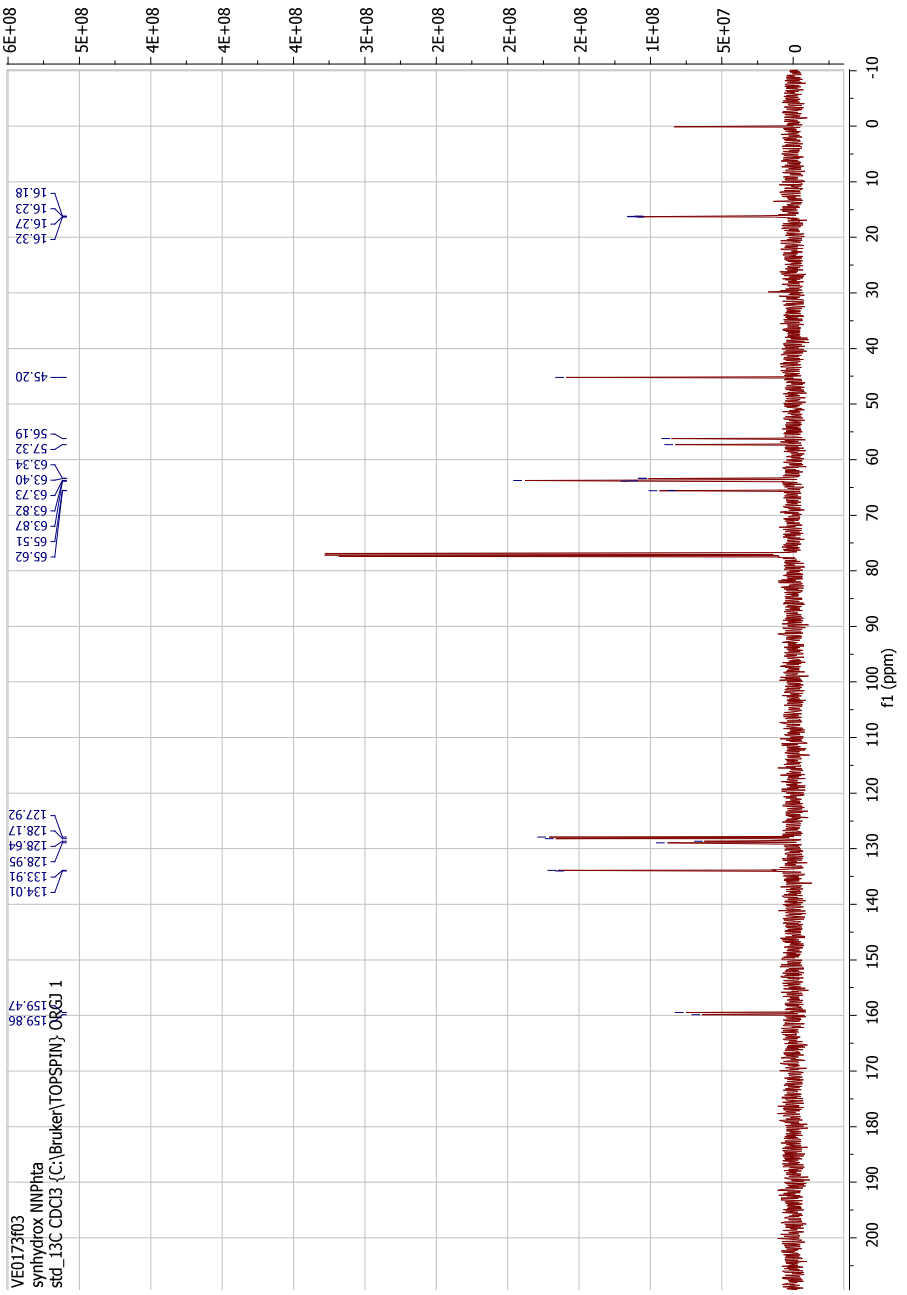


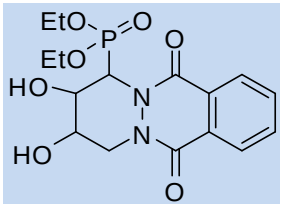
^{1}H NMR spectrum



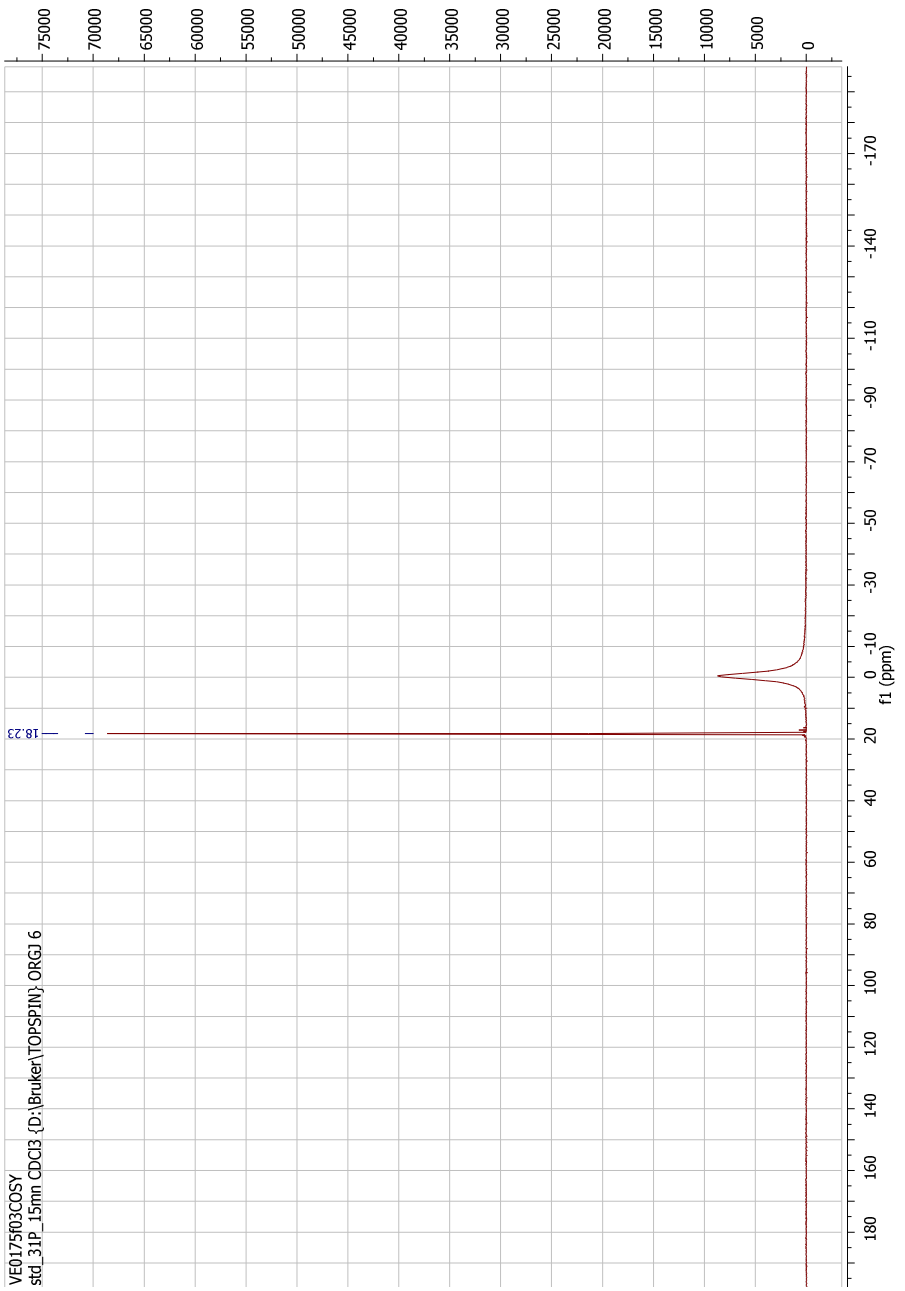


^{13}C NMR spectrum

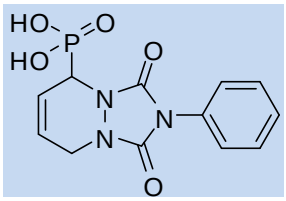




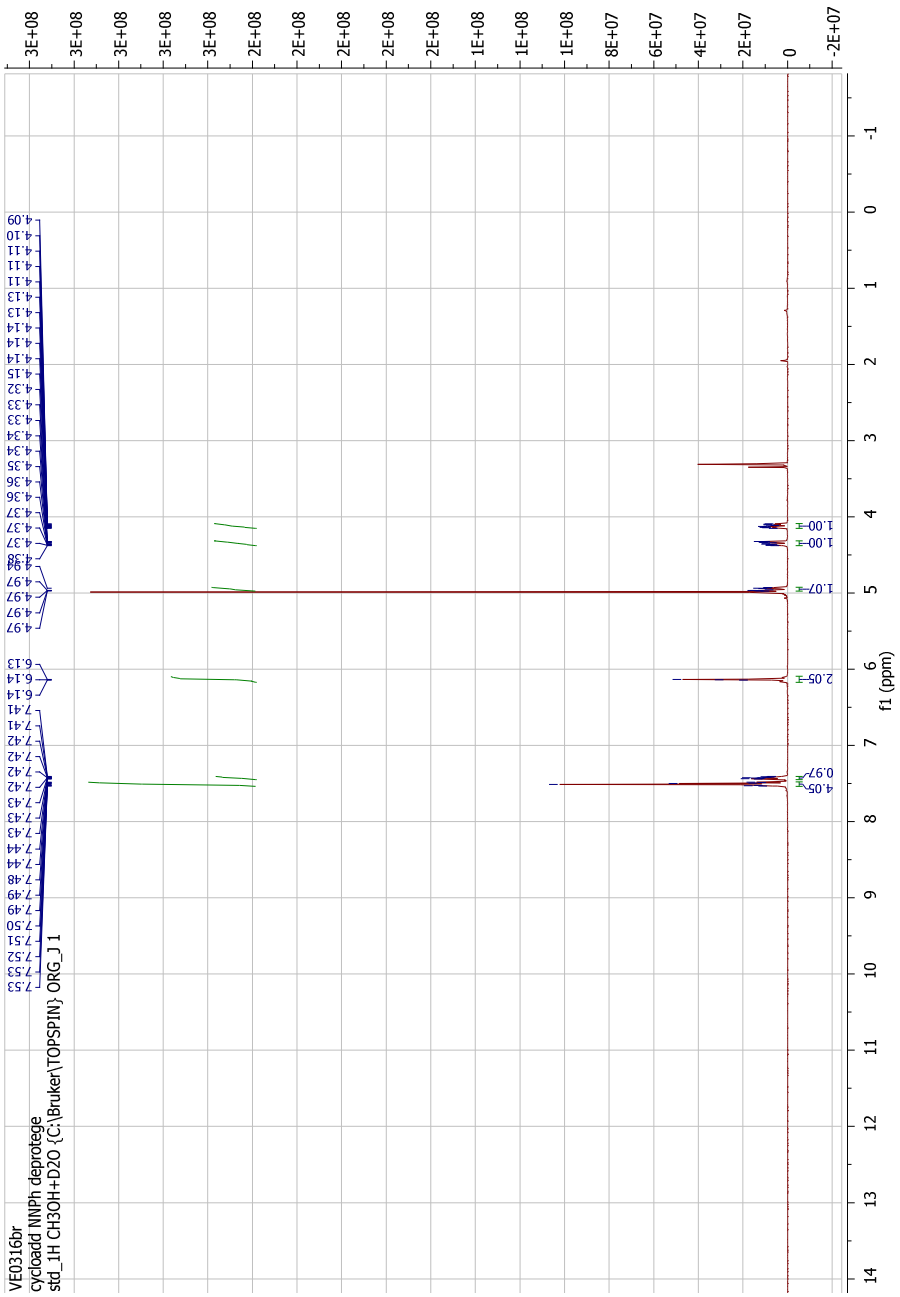
^{31}P NMR spectrum

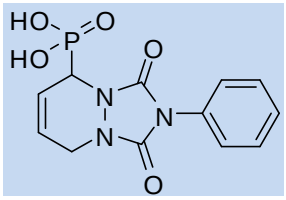


E. Product 4a

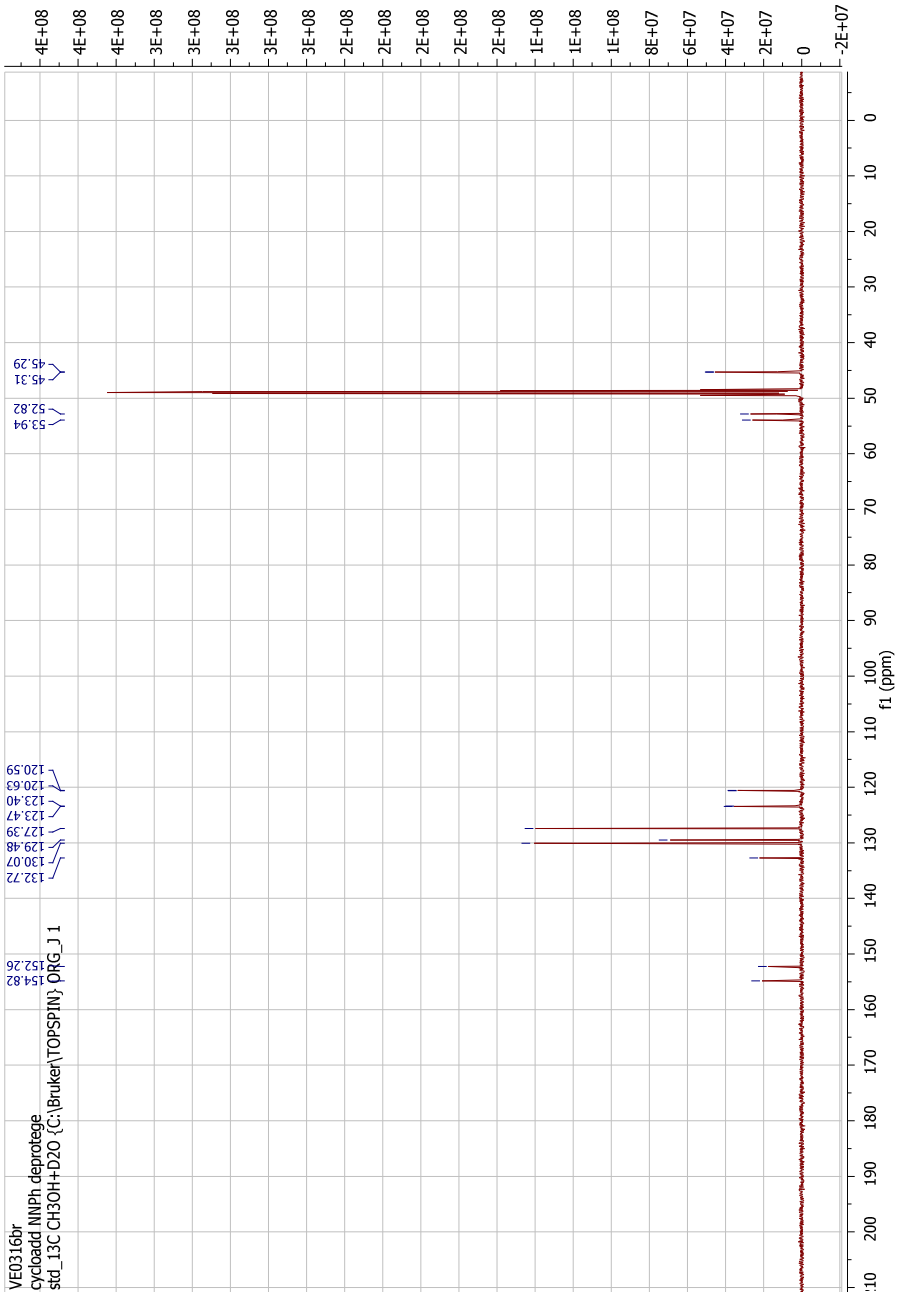


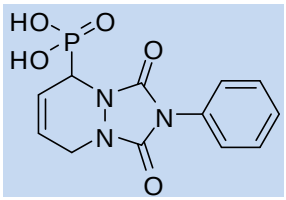
^{1}H NMR spectrum



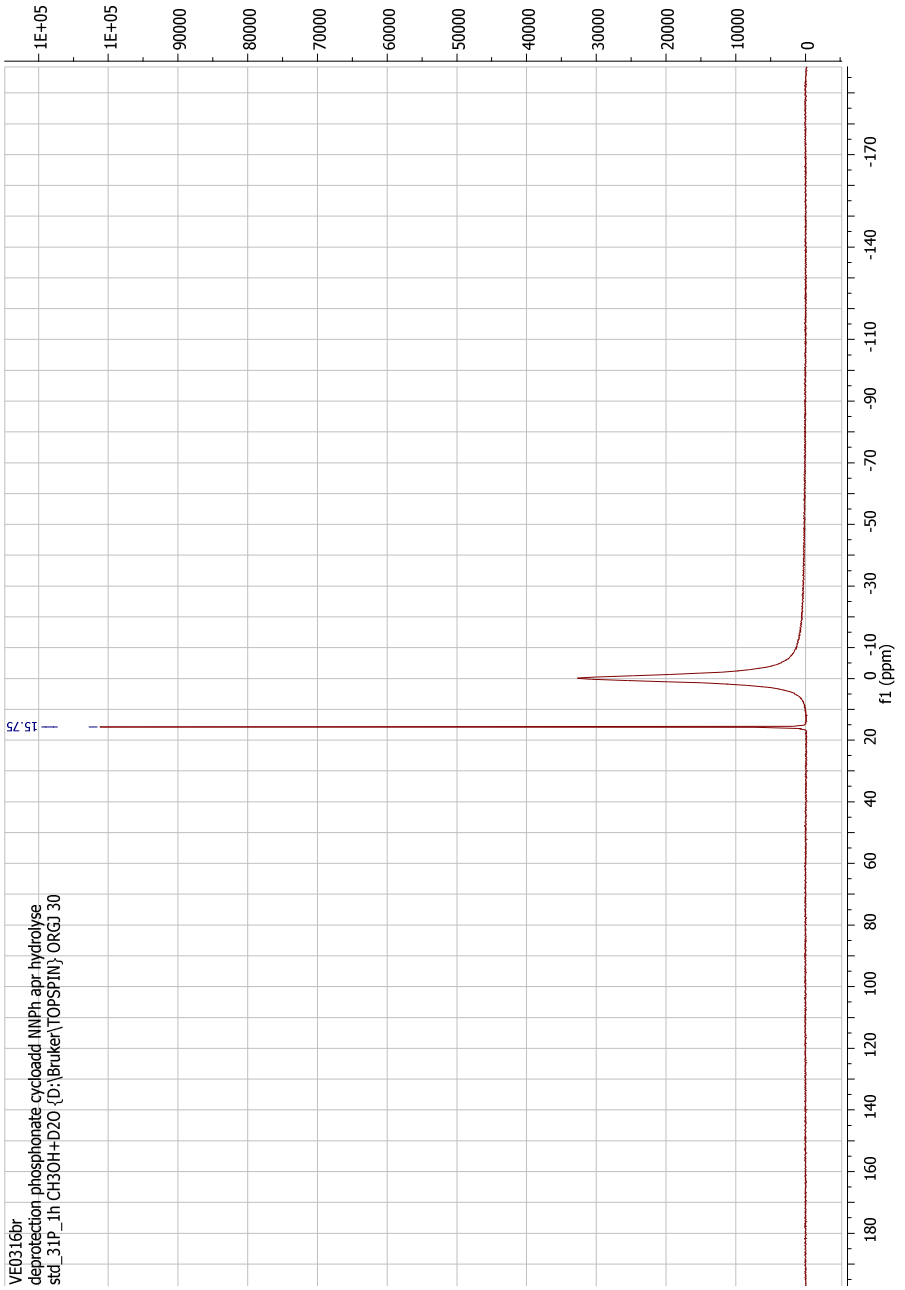


^{13}C NMR spectrum

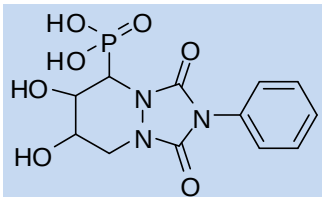




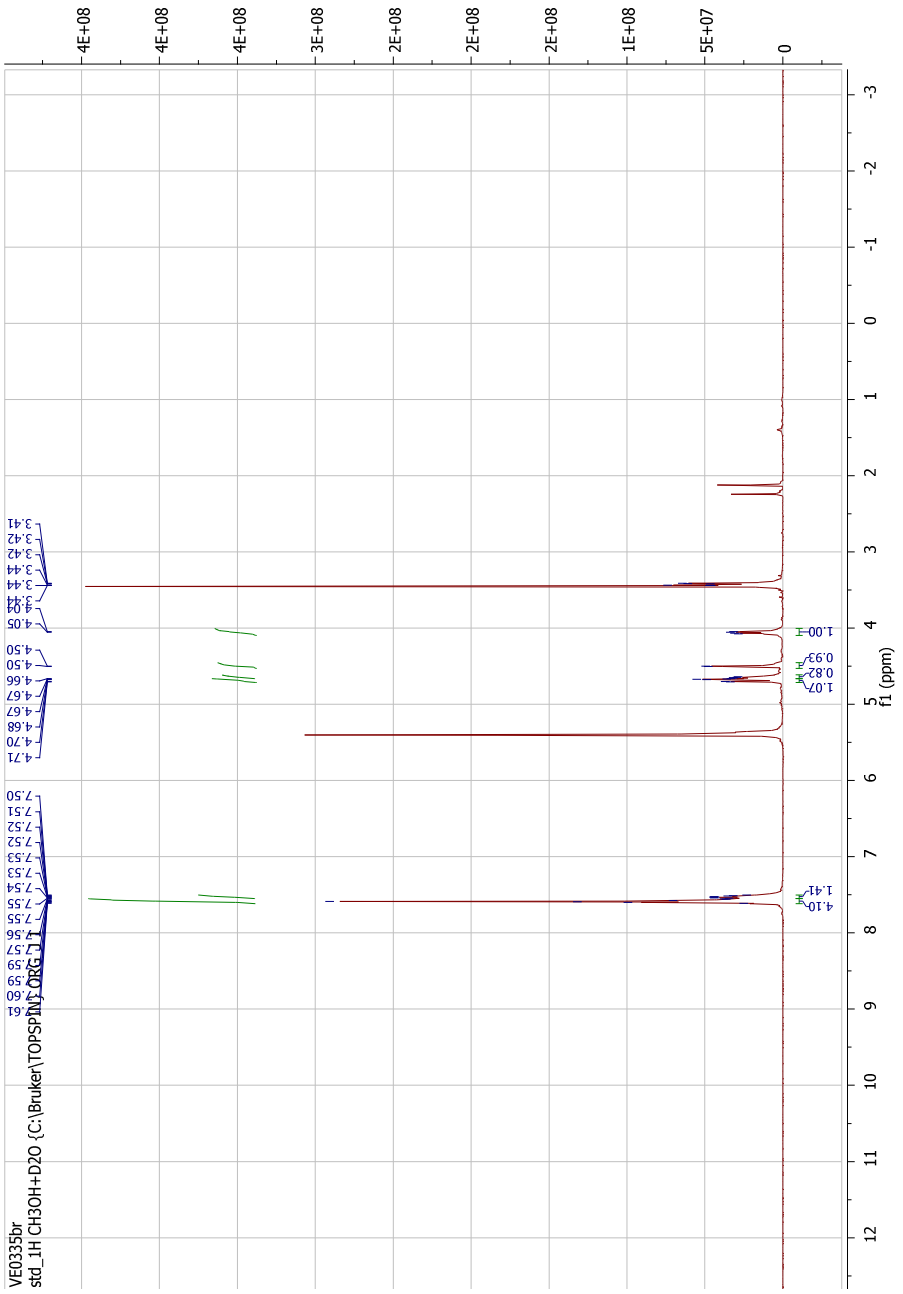
^{31}P NMR spectrum

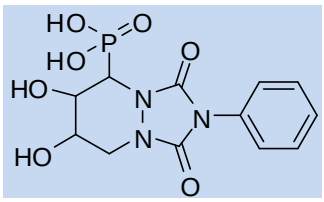


F. Product 6a

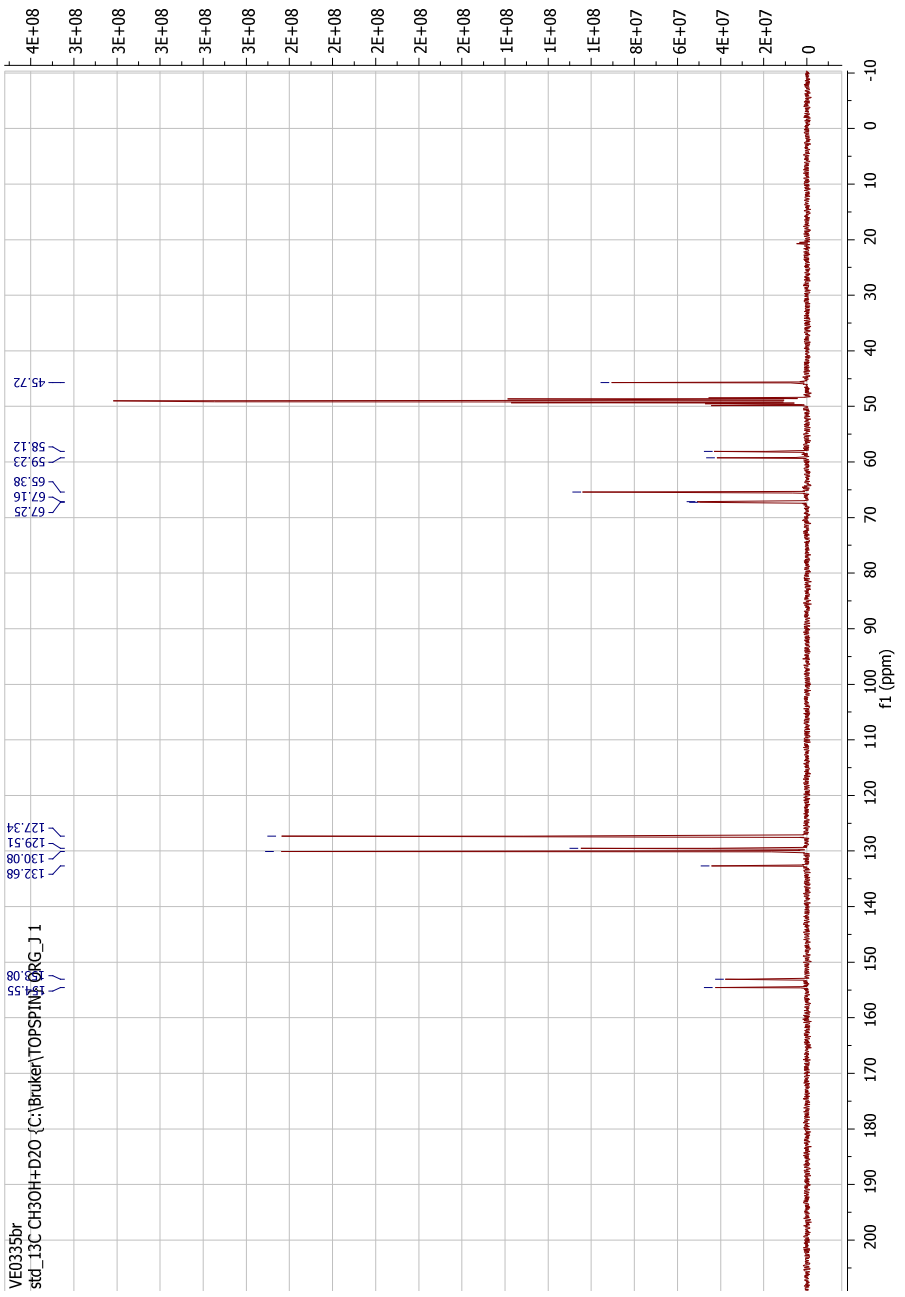


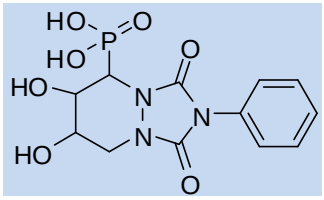
^{1}H NMR spectrum



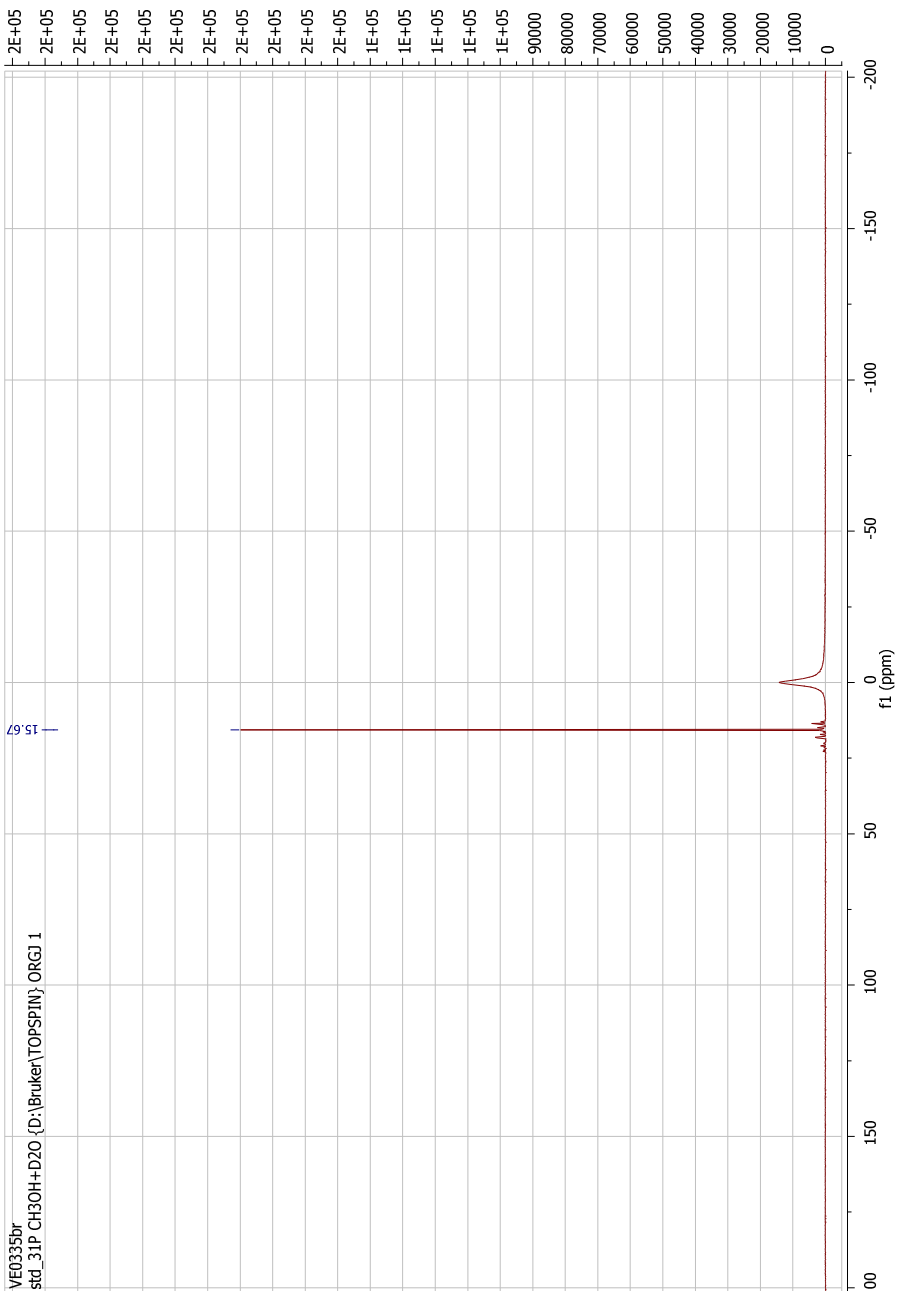


^{13}C NMR spectrum





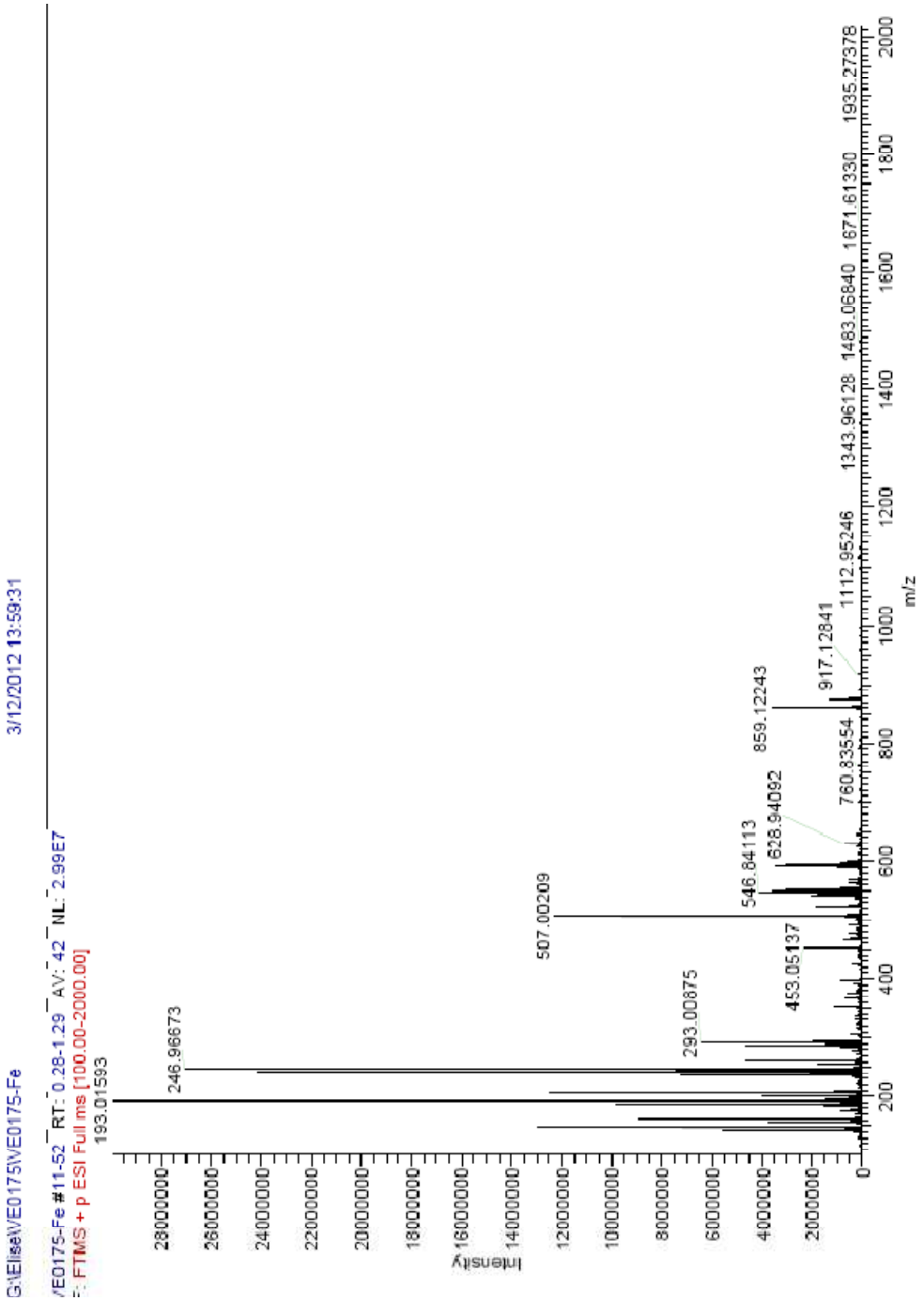
^{31}P NMR spectrum



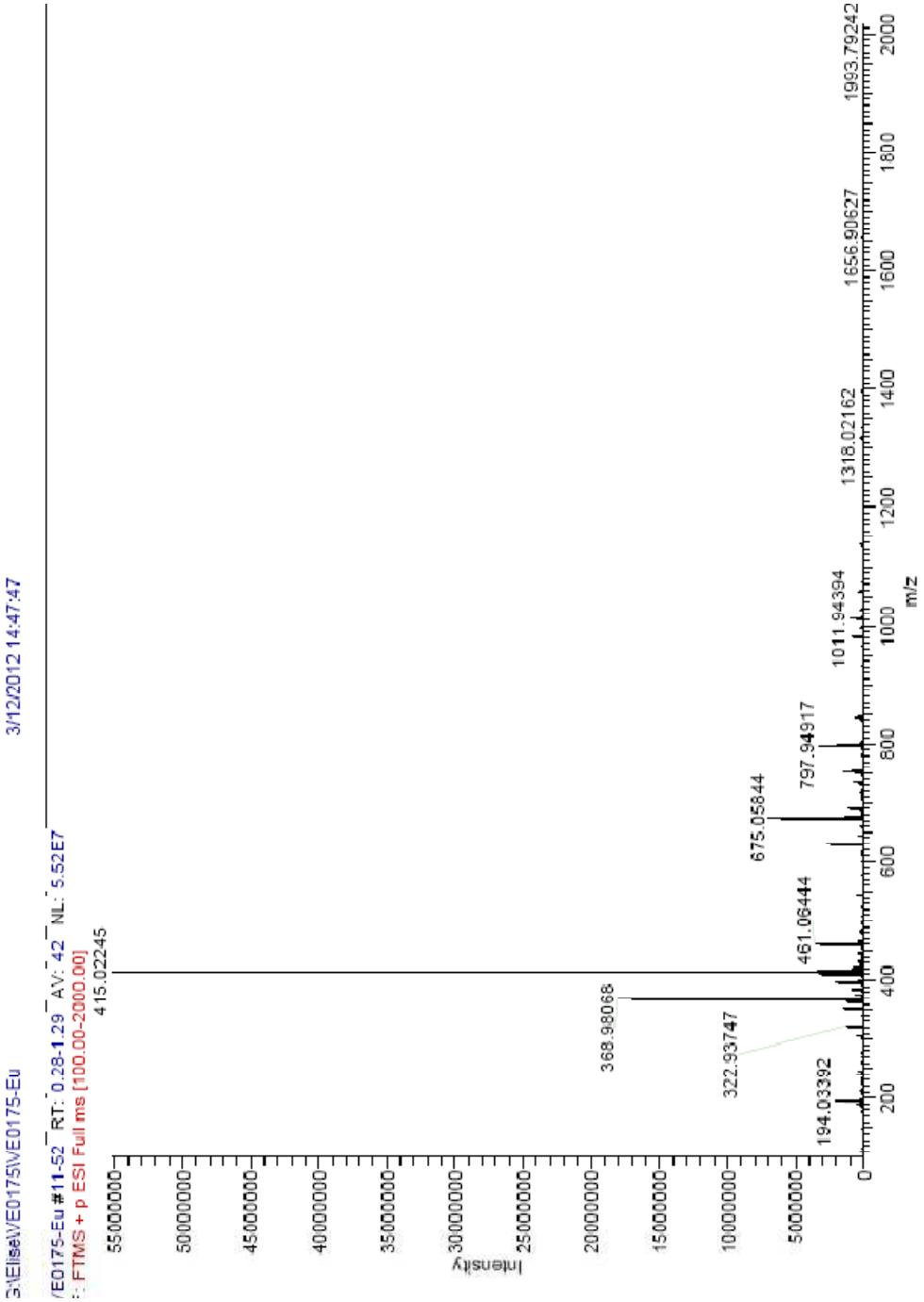
Mass spectra

A. Cycloadduct 12

Cycloadduct **12** with $Fe(ClO_4)_2$ in ethanol

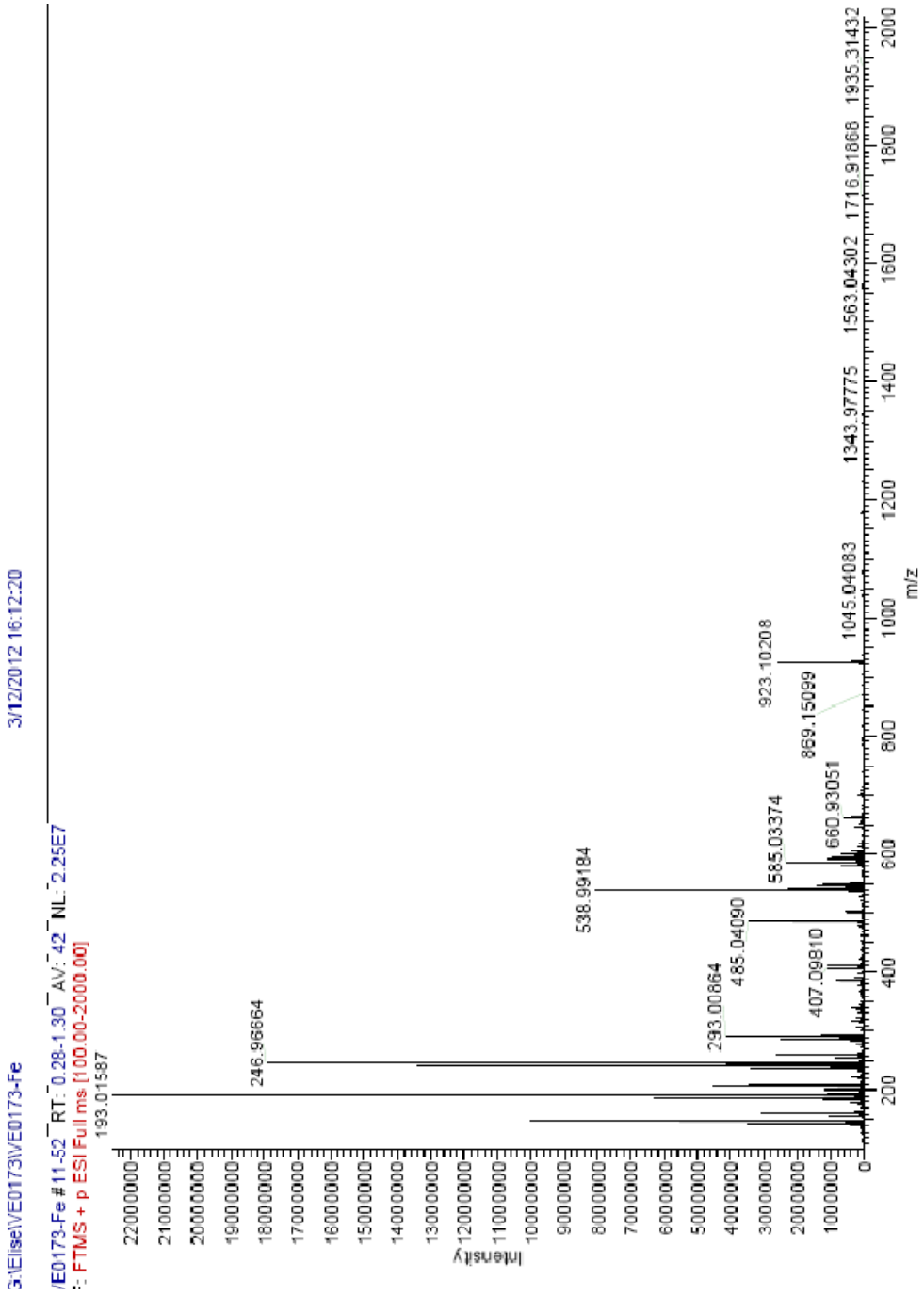


Cycloadduct **12** with $Eu(NO_3)_3$ in ethanol

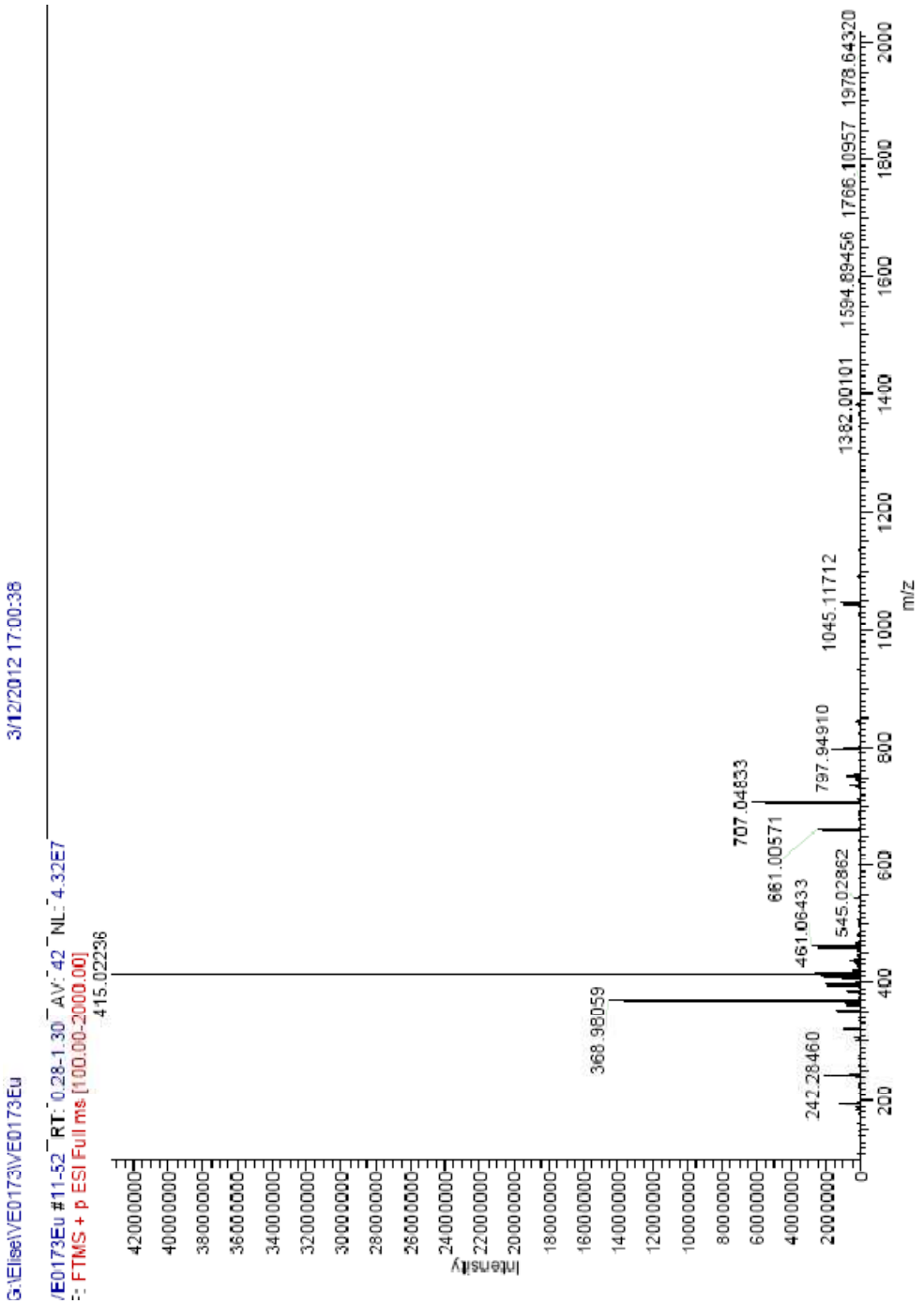


B. Cycloadduct 13

Cycloadduct **13** with $Fe(ClO_4)_2$ in ethanol



Cycloadduct **13**with $Eu(NO_3)_3$ in ethanol



Tables of masses

Atomic composition and exact masses of complexes observed in HRMS-ESI spectra of ligands (12) and (13)

Table S1a. Ligand **12** with divalent cations.

Cation	Exp. Mass	Theo. Mass	$\%I_{rel}$	Composition	Attribution
Ca^{2+}	491.03030	491.02992	39	$C_{16}H_{21}O_9N_2PCaCl$	$(LCaClO_4)^+$
	537.07123	537.07178	100	$C_{18}H_{27}O_{10}N_2PCaCl$	$(LCaClO_4EtOH)^+$
Co^{2+}	509.99981	510.00052	100	$C_{16}H_{21}O_9N_2PClCo$	$(LCoClO_4)^+$
	556.04156	556.04239	40	$C_{18}H_{27}O_{10}N_2PClCo$	$(LCoClO_4EtOH)^+$
	862.11976	862.11933	40	$C_{32}H_{42}O_{14}N_4P_2ClCo$	$(L_2CoClO_4)^+$
Fe^{2+}	507.00209	507.00226	100	$C_{16}H_{21}O_9N_2PClFe$	$(LFeClO_4)^+$
	553.04379	553.04413	24	$C_{18}H_{27}O_{10}N_2PClFe$	$(LFeClO_4EtOH)^+$
	859.12243	859.12243	29	$C_{32}H_{42}O_{14}N_4P_2ClFe$	$(L_2FeClO_4)^+$
Mg^{2+}	475.05218	475.05237	61	$C_{16}H_{21}O_9N_2PClMg$	$(LMgClO_4)^+$
	521.09388	521.09423	100	$C_{18}H_{27}O_{10}N_2PClMg$	$(LMgClO_4EtOH)^+$
	827.17237	827.17118	46	$C_{32}H_{42}O_{14}N_4P_2ClMg$	$(L_2MgClO_4)^+$
Ni^{2+}	509.00234	509.00267	100	$C_{16}H_{21}O_9N_2PClNi$	$(LNiClO_4)^+$
	555.04425	555.04454	68	$C_{18}H_{27}O_{10}N_2PClNi$	$(LNiClO_4EtOH)^+$
	861.16192	861.12148	26	$C_{32}H_{42}O_{14}N_4P_2ClNi$	$(L_2NiClO_4)^+$
Zn^{2+}	514.99636	514.99647	100	$C_{16}H_{21}O_9N_2PClZn$	$(LZnClO_4)^+$
	561.03813	561.03833	37	$C_{18}H_{27}O_{10}N_2PClZn$	$(LZnClO_4EtOH)^+$
	867.11694	867.11528	33	$C_{32}H_{42}O_{14}N_4P_2ClZn$	$(L_2ZnClO_4)^+$

Table S1b. Ligand **12** with trivalent cations.

Cation	Exp. Mass	Theo. Mass	$\%I_{rel}$	Composition	Attribution
Eu^{3+}	629.01599	629.01569	33	$C_{16}H_{21}O_{11}N_4PEu$	$(LEu\ (NO_3)_2)^+$
	675.05844	675.05756	100	$C_{18}H_{27}O_{12}N_4PEu$	$(LEu\ (NO_3)_2EtOH)^+$
	981.13766	981.13450	17	$C_{32}H_{42}O_{16}N_6P_2Eu$	$(L_2Eu\ (NO_3)_2)^+$
Gd^{3+}	634.01912	634.01856	33	$C_{16}H_{21}O_{11}N_4PGd$	$(LGd(NO_3)_2)^+$
	680.06189	680.06043	100	$C_{18}H_{27}O_{12}N_4PGd$	$(LGd(NO_3)_2EtOH)^+$
	986.14095	986.13737	8	$C_{32}H_{42}O_{16}N_6P_2Gd$	$(L_2Gd\ (NO_3)_2)^+$
La^{3+}	615.00111	615.00080	50	$C_{16}H_{21}O_{11}N_4PLa$	$(LLa(NO_3)_2)^+$
	661.04371	661.04267	100	$C_{18}H_{27}O_{12}N_4PLa$	$(LLa(NO_3)_2EtOH)^+$
	967.12212	967.11962	10	$C_{32}H_{42}O_{16}N_6P_2La$	$(L_2La(NO_3)_2)^+$
Lu^{3+}	651.03589	651.03523	53	$C_{16}H_{21}O_{11}N_4PLu$	$(LLu(NO_3)_2)^+$
	697.07860	697.07860	100	$C_{18}H_{27}O_{12}N_4PLu$	$(LLu(NO_3)_2EtOH)^+$
	1003.15731	1003.15405	13	$C_{32}H_{42}O_{16}N_6P_2Lu$	$(L_2Lu(NO_3)_2)^+$

Table S2a. Ligand **13** with divalent cations.

Cation	Exp. Mass	Theo. Mass	$\%I_{rel}$	Composition	Attribution
Ca^{2+}	523.01963	523.01975	25	$C_{16}H_{21}N_2O_{11}PCaCl$	$(LCaClO_4)^+$
	569.06145	569.06161	100	$C_{18}H_{27}N_2O_{12}PCaCl$	$(LCaClO_4EtOH)^+$
	907.12986	907.12839	25	$C_{32}H_{42}N_4O_{18}P_2CaCl$	$(L_2CaClO_4)^+$
Co^{2+}	541.98993	541. 99035	100	$C_{16}H_{21}N_2O_{11}PClCo$	$(LCoClO_4)^+$
	588.03193	588.03222	50	$C_{18}H_{27}N_2O_{12}PClCo$	$(LCoClO_4EtOH)^+$
	926.10009	926.09899	44	$C_{32}H_{42}N_4O_{18}P_2ClCo$	$(L_2CoClO_4)^+$
Fe^{2+}	538.99184	538.99209	100	$C_{16}H_{21}N_2O_{11}PFeCl$	$(LFeClO_4)^+$
	585.03374	585.033958	28	$C_{18}H_{27}N_2O_{12}PFeCl$	$(LFeClO_4EtOH)^+$
	923.10208	923.10073	31	$C_{32}H_{42}N_4O_{18}P_2FeCl$	$(L_2FeClO_4)^+$
Mg^{2+}	507.04221	507.042209	20	$C_{16}H_{21}N_2O_{11}PClMg$	$(LMgClO_4)^+$
	553.08392	553.084064	100	$C_{18}H_{27}N_2O_{12}PClMg$	$(LMgClO_4EtOH)^+$
	891.15236	891.15084	27	$C_{32}H_{42}N_4O_{18}P_2ClMg$	$(L_2MgClO_4)^+$
Ni^{2+}	540.99214	540.99250	62	$C_{16}H_{21}N_2O_{11}PClNi$	$(LNiClO_4)^+$
	587.03408	587.03437	100	$C_{18}H_{27}N_2O_{12}PClNi$	$(LNiClO_4EtOH)^+$
	925.10241	925.10114	31	$C_{32}H_{42}N_4O_{18}P_2ClNi$	$(L_2NiClO_4)^+$
Zn^{2+}	546.98635	546.98630	100	$C_{16}H_{21}N_2O_{11}PClZn$	$(LZnClO_4)^+$
	593.02846	593.02816	50	$C_{18}H_{27}N_2O_{12}PClZn$	$(LZnClO_4EtOH)^+$
	931.09713	931.09494	44	$C_{32}H_{42}N_4O_{18}P_2ClZn$	$(L_2ZnClO_4)^+$

Table S2b. Ligand **13** with trivalent cations.

Cation	Exp. Mass	Theo. Mass	$\%I_{rel}$	Composition	Attribution
Eu^{3+}	661.00571	661.00552	43	$C_{16}H_{21}N_4O_{13}PEu$	$(LEu\ (NO_3)_2)^+$
	707.04833	707.04739	100	$C_{18}H_{27}N_4O_{14}PEu$	$(LEu\ (NO_3)_2EtOH)^+$
	1045.11712	1045.11416	14	$C_{32}H_{42}N_6O_{20}P_2Eu$	$(L_2Eu\ (NO_3)_2)^+$
Gd^{3+}	666.00879	666.00839	33	$C_{16}H_{21}N_4O_{13}PGd$	$(LGd(NO_3)_2)^+$
	712.05144	712.05026	100	$C_{18}H_{27}N_4O_{14}PGd$	$(LGd(NO_3)_2EtOH)^+$
	1050.12061	1050.11703	13	$C_{32}H_{42}N_6O_{20}P_2Gd$	$(L_2Gd\ (NO_3)_2)^+$
La^{3+}	646.99062	646.99063	54	$C_{16}H_{21}N_4O_{13}PLa$	$(LLa(NO_3)_2)^+$
	693.03319	693.03250	100	$C_{18}H_{27}N_4O_{14}PLa$	$(LLa(NO_3)_2EtOH)^+$
	1031.10179	1031.09928	15	$C_{32}H_{42}N_6O_{20}P_2La$	$(L_2La(NO_3)_2)^+$
Lu^{3+}	683.02530	683.02506	50	$C_{16}H_{21}N_4O_{13}PLu$	$(LLu(NO_3)_2)^+$
	729.06805	729.06693	100	$C_{18}H_{27}N_4O_{14}PLu$	$(LLu(NO_3)_2EtOH)^+$
	1067.13968	1067.13371	13	$C_{32}H_{42}N_6O_{20}P_2Lu$	$(L_2Lu(NO_3)_2)^+$

Percentage of complexes versus "free" metal. [a, b]

Table S3. Ligand **12**.

Mg	45 %	Eu	11 %
Ca	6 %	La	10 %
Zn	30 %	Gd	11 %
Fe	23 %	Lu	15 %
Co	43 %		
Ni	42 %		

[a] $\% = \frac{ML(ClO4) + ML(EtOH)(ClO4) + ML2(ClO4)}{ML(ClO4) + ML(EtOH)(ClO4) + ML2(ClO4) + M(ClO4)(EtOH)n}$ x 100 where n = 2, 3

[b] $\% = \frac{ML(NO3)2 + ML(EtOH)(NO3)2 + ML2(NO3)2}{ML(NO3)2 + ML(EtOH)(NO3)2 + ML2(NO3)2 + M(NO3)2(EtOH)n}$ x 100 where n = 2, 3, 4

Table S4. Ligand **13**.

Mg	18 %	Eu	14 %
Ca	14 %	La	13 %
Zn	27 %	Gd	14 %
Fe	37 %	Lu	16 %
Co	36 %		
Ni	33 %		

[a] $\% = \frac{ML(ClO4) + ML(EtOH)(ClO4) + ML2(ClO4)}{ML(ClO4) + ML(EtOH)(ClO4) + ML2(ClO4) + M(ClO4)(EtOH)n}$ where n = 2, 3

[b] $\% = \frac{ML(NO3)2 + ML(EtOH)(NO3)2 + ML2(NO3)2}{ML(NO3)2 + ML(EtOH)(NO3)2 + ML2(NO3)2 + M(NO3)2(EtOH)n}$ where n = 2, 3, 4