Supporting Information

for

Synthesis of dinucleoside acylphosphonites by phosphonodiamidite chemistry and investigation of phosphorus epimerization

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Experimental

General methods. All reactions and sample analysis preparations were carried out in an inert-atmosphere glovebox with recirculating nitrogen, using oven-dried glassware. NMR spectra were recorded on 400 and 500 MHz Bruker spectrometers referenced to $CDCl_3$ solvent peaks [1,2] and for ^{31}P NMR to external PPh_3 at -5.25 ppm. Peak assignments were made where possible using 2D COSY and HETCOR or HSQC spectra, with ^{13}C-^{1}H correlations shown in the spectral data where needed, as well as by comparison to the thymidine starting materials. Reaction solvents were distilled under nitrogen and then dried over activated 3 Å molecular sieves [3]. Column chromatography was carried out in the glovebox on 230-400 mesh silica gel that had been dried several hours at 250 °C under vacuum. For the peak assignments in the ^{1}H NMR spectra of **12** and **13**, the 3′-phosphorylated thymidine and the 5′-phosphorylated thymidine are labeled T1 and T2, respectively.

$(iPr_2N)_2PC(O)CH_3$ (7). The starting material $(iPr_2N)_2PH$ (**4**) was prepared via a modification of the literature procedure [4]. In the glovebox, powdered $LiAlH_4$ (0.242 g, 6.37 mmol, 1.17 equiv) was added in one portion to 1.451 g (5.44 mmol) of $(iPr_2N)_2PCl$ [5] in 10 mL of THF, and the suspension was stirred vigorously for two hours; while it was stoppered, the stopper was removed periodically to release pressure. The grey suspension was filtered through a layer of dry Celite (*CAUTION: the grey solid smokes and occasionally briefly ignites when removed from the glovebox)*, and the solvent was then removed from the yellow solution using a vacuum pump. The resultant white solid suspended in a yellow oil was extracted with 7 × ~8 mL of hexanes, filtering each 8 mL extract through dried Celite. Solvent removal using a vacuum pump gave 1.16 g (5.00

mmol, 92% yield) of **4** as a white solid suspended in a clear oil, which on the basis of ^{1}H and ^{31}P NMR was ~93% pure. This material could be stored cold in the glovebox at –35 °C but was typically used immediately.

A sample of **4** (0.311 g, 1.34 mmol) was suspended in 7 mL CH_2Cl_2, the flask was fitted with a dropping funnel containing a solution of 0.119 g of $CH_3C(O)Cl$ (1.52 mmol, 1.13 equiv) in 3 mL of CH_2Cl_2, and the dropping funnel was then attached to a solenoid-controlled vacuum valve. The acetyl chloride solution was added dropwise over ~1 min, while periodically opening the reaction to vacuum in order to keep the reaction under partial vacuum. Gentle bubbling of the solution occurred, presumably due to release of HCl gas, giving a yellow solution. Solvent removal gave a yellow solid that was then extracted with 3 × 5 mL of hexanes (the last extract was clear), filtering each extract through Celite. Final solvent removal gave 0.234 g (0.852 mmol, 64% yield) of **7** as a yellow oil at room temperature; storage at –35 °C gave a crystalline mass but it quickly melted at room temperature. The material so produced was used as is with no further purification; on the basis of ^{31}P NMR it was > 95% pure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.29 (m, $(CH_3)_2CH$, 4H), 2.27 (d, $^{3}J_{PH}$ = 8.8 Hz, $CH_3C(O)$ 3H), 1.23 (d, J = 6.8 Hz, 12H), 1.18 (d, J = 6.4 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 227.9 (d, $^{1}J_{PC}$ = 22.4 Hz), 49.8 (br d, $(CH_3)_2CH$, $^{2}J_{PC}$ = 9.1 Hz), 30.7 (d, $CH_3C(O)$, $^{2}J_{PC}$ = 49.7 Hz), 24.4 (d, J = 6.2 Hz), 24.3 (d, J = 6.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 63.5; IR ($CDCl_3$) 2969, 1654 cm^{-1}. HRMS (ESI): Calcd for $C_{14}H_{32}N_2OP$ $[M+H]^+$ 275.2247, found 275.2247.

$(iPr_2N)_2PC(=CH_2)OC(O)CH_3$ (8). Reaction of **4** (0.876 g, 3.77 mmol), $CH_3C(O)Cl$ (0.319 g, 4.06 mmol, 1.08 equiv), and Et_3N (0.392 g, 3.87 mmol, 1.03 equiv) in 13 mL of CH_2Cl_2 gave a mixture of 43% **8**, 32% **7**, and 25% unreacted **4**, on the basis of

integration of the ^{1}H and ^{31}P NMR spectra. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48 (t, J_{HH} = J_{PH} = 1.1 Hz, 1H), 5.29 (dd, J_{HH} = 1.1 Hz, J_{PH} = 7.3 Hz, 1H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8 (s), 161.5 (d, J_{PC} = 8.8 Hz), 111.4 (d, J_{PC} = 16.8 Hz), 48.0 (d, J_{PC} = 12.0 Hz, *C*H$(CH_3)_2$); ^{31}P NMR (162 MHz, $CDCl_3$) δ 49.7. The iPr peaks could not be identified except as noted, and it appeared that the presumed OC(O)*C*H_3 carbon also overlapped the iPr region on the basis of the DEPT NMR.

$(iPr_2N)_2PC(O)C_6H_5$ (9). A sample of **4** (0.852 g, 3.67 mmol) prepared as described for the synthesis of **7** was suspended in 10 mL CH_2Cl_2 and Et_3N (0.402 g, 3.97 mmol, 1.08 equiv). The flask was fitted with a dropping funnel containing a solution of 0.563 g of $C_6H_5C(O)Cl$ (4.01 mmol, 1.09 equiv) in 4 mL of CH_2Cl_2, which was then attached to a solenoid-controlled vacuum valve. The benzoyl chloride solution was added dropwise over ~1 min, while periodically opening the reaction to vacuum in order to keep the reaction under partial vacuum. Gentle bubbling of the solution occurred, presumably due to release of some HCl gas, giving an orange solution. Solvent removal gave an orange solid that was then extracted with 4 $\times$ 5 mL of hexanes (the last extract was clear), filtering each extract through Celite. Final solvent removal gave 1.10 g (3.27 mmol, 89% yield) of **9** as a yellow-orange solid. The material so produced was used as is with no further purification; on the basis of ^{31}P NMR it was > 99.6% pure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (m, H_{ortho}, 2H), 7.46 (m, H_{para}, 1H), 7.38 (t, J = 7.8 Hz, H_{meta}, 2H), 3.32 (m, 4H), 1.21 (d, J = 6.8 Hz, 12H), 1.08 (d, J = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 220.9 (d, $^{1}J_{PC}$ = 23.7 Hz), 140.8 (d, $^{2}J_{PC}$ = 39.7 Hz, C_{ipso}), 132.3 (d, $^{5}J_{PC}$ = 1.5 Hz, C_{para}), 128.2 (C_{meta}), 127.9 (d, $^{3}J_{PC}$ = 11.8 Hz, C_{ortho}), 49.5 (br d, $^{2}J_{PC}$ = 8.1 Hz), 24.3 (d, $^{3}J_{PC}$ = 5.7 Hz), 23.9 (d, $^{3}J_{PC}$ = 6.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ

59.3; IR ($CDCl_3$) 2969, 1631 cm^{-1}HRMS (ESI): Calcd for $C_{19}H_{34}N_2OP$ $[M+H]^+$ 337.2403, found 337.2402.

3′-(5′-DMTr-OT)P(N(iPr)$_2$)C(O)CH$_3$ (10). Solid *N*-methylimidazolium triflate (NMI·Tf, 0.399 g, 1.72 mmol, 0.74 equiv) [6] was added to a suspension of **7** (0.639 g, 2.33 mmol,) and 5′-*O*-(4,4′-dimethoxytrityl)thymidine (5′-DMTr-OT) [7] (1.20 g, 2.21 mmol, 0.95 equiv) in 10 mL acetonitrile. After stirring for 1.25 h, only a small amount of solid remained and the solution was filtered through Celite. Solvent removal using a vacuum pump gave a foamy yellow solid that was taken up in 10 mL benzene, 20 mL ether was added to precipitate salts, the mixture was filtered, and the solvent was again removed using a vacuum pump to give a yellow solid. This was stirred with 10 mL hexane to remove some of the starting acyl, giving 1.56 g of product as a yellow powder (99% crude yield) that was 12% starting acyl and 85% product by ^{31}P NMR but also contained impurities of DMTr-OT and $iPr_2NH_2^+$ Tf^-. Significant purification was achieved by taking up 1.32 g of this material in 8 mL benzene, filtering, and then precipitating out the product by addition of 24 mL of hexane. After cooling for 1 hr at –35 °C, the solvent was poured off and the residue pumped under vacuum to give a sticky orange solid; final solvent removal was achieved by addition of a small amount of ether and pulling a vacuum again to give a yellow foam (1.26 g, 95% recovery) that was 89% pure by ^{31}P NMR.

Chromatography of 0.65 g of this material on 40 mL of silica gel on a 60 mL fritted funnel, eluting with 9:1 CH_2Cl_2:THF, gave a yellow band collected in three fractions (60 mL 9:1 CH_2Cl_2:THF, 20 mL 1:1 CH_2Cl_2:THF and 40 mL THF); all three fractions exhibited a spot with R_f = 0.5-0.55 on TLC (9:1 CH_2Cl_2:THF), with material at

the origin eluting at the end of the last fraction. Analysis by ^{31}P NMR showed that the first two fractions (97.8 mg) were ~95% pure and ~86% the "fast" isomer at 117.6 ppm, while the third fraction (429 mg; 81% total recovery) was ~81% pure and ~33:67 "fast": "slow" isomers at 117.6 and 116.8 ppm. The two samples were separately re-chromatographed.

The "fast" isomer was chromatographed on 10 mL of silica eluting only with 9:1 CH_2Cl_2:THF, and gave in the first two UV-active fractions 57.1 mg of material that was ~95% pure as a 93:7 mixture of "fast":"slow" isomers. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (br s, NH, 1H), 7.66 (~q, $^4J \approx 1.2$ Hz, H_6, 1H), 7.40 (m, Ph, 2H), 7.31 – 7.22 (m, Ph and 4H of $MeOC_6H_4$ AA′BB′, 3H), 6.83 (m, 4H of $MeOC_6H_4$ AA′BB′), 6.40 (dd, ^3J = 7.7, 5.9 Hz, H_1′, 1H), 4.65 (ddd, $^3J \approx 3.2$ Hz, H_3′, 1H), 4.32 (~ddd, $^3J \approx 1.3$ Hz, $H_{4'}$, 1H), 3.79 (s, *Me*OC_6H_4, 6H), 3.52 (dd, ^2J = 10.7 Hz, ^3J = 2.8 Hz, H_5′, 1H), 3.37 (dd, ^2J = 10.7 Hz, ^3J = 2.6 Hz, H_5′, 1H), 3.28 (m, C*H*$(CH_3)_2$, 2H), 2.51 (m, H_2′, 1H), 2.33 (m, H_2′, 1H), 2.24 (d, $^3J_{PH}$ = 5.4 Hz, C*H*$_3$C(O)P, 3H), 1.44 (d, ^4J = 1.0 Hz, C*H*$_3C_1$, 3H), 1.19 (br d, ^3J = 7.8 Hz, CH(C*H*$_3)_2$, 3H), 1.18 (br d, ^3J = 7.3 Hz, CH(C*H*$_3)_2$, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 226.9 (d, $^1J_{PC}$ = 25.3 Hz), 163.8, 158.9, 150.3, 144.4, 135.7 (*C*H_1), 135.5 (4°), 135.4 (4°), 130.27, 130.26 (Ar CH ~7.3; $MeOC_6H_4$ CH ~6.8), 128.3 (Ph CH ~7.4), 128.1, (Ar CH, ~7.3), 127.3 (Ar CH, ~7.25), 113.40, 113.38 (Ar CH, ~7.3; $MeOC_6H_4$ CH, ~6.8), 111.3 (4°), 87.1 (4°), 85.7 (d, $^3J_{PC4'}$ = 5.4 Hz, C_4′), 84.9 (*C*H_1′, 6.40), 77.6 (d, $^2J_{PC3'}$ = 19.9 Hz, *C*H_3′), 63.3 (*C*H_5′), 55.4 (*Me*O, 3.79), 46 (iPr *C*H, from HSQC cross peak with ^{1}H at δ 3.28), 40.5 (d, $^3J_{PC2'}$ = 3.9 Hz, *C*H_2′), 30.8 (d, $^2J_{PC}$ = 36.4 Hz, *C*H_3C(O)P), ~25 (broad, iPr Me at 1.19 and 1.18), 15.4 (iPr Me at 1.19 and 1.18), 11.9 (*C*H_3C_1); ^{31}P NMR (162

MHz, $CDCl_3$) δ 117.6, 116.8 (93.2:6.8); IR ($CDCl_3$) 3396, 2969, 1688 cm^{-1}. HRMS (ESI): Calcd for $C_{39}H_{49}N_3O_8P$ $[M+H]^+$ 718.3252, found 718.3252.

The 32:68 "fast":"slow" mixture was chromatographed on 30 mL of silica eluting only with 9:1 CH_2Cl_2:THF, giving three fractions as white foams consisting of isomeric mixtures of the "fast":"slow" isomers as follows: 46:54 (~96% pure, 81.5 mg), 25:75 (~91% pure, 40.0 mg), and 18:82 (~92% pure, 55.7 mg). Detailed spectra were obtained for the 46:54 mixture (only peaks for the "slow" isomer are given except as noted): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82, 8.77 (fast, slow, br s, NH), 7.60 (~q, ^4J ≈ 1.3 Hz, H_1), 7.39 (m, 2H, Ph), 7.30 – 7.26 (m, 3H, Ph and 4H of $MeOC_6H_4$ AA′BB′), 6.83 (m, 4H of $MeOC_6H_4$ AA′BB′), 6.48 (dd, ^3J = 8.2, 5.7 Hz, H_1′), 4.64 (m, H_3′), 4.19 (~q, ^3J ≈ 2.6 Hz, H_4′), 3.78 (s, 6H, *Me*OC_6H_4), 3.47 (dd, ^2J = 10.6 Hz, ^3J = 2.7 Hz, H_5′), 3.32 (dd, ^2J = 10.6 Hz, ^3J = 2.7 Hz, H_5′), 3.23 (m, C*H*$(CH_3)_2$, 2H), 2.65 (m, H_2′, 1H), 2.33 (m, H_2′, 1H), 2.34 (d, $^3J_{PH}$ = 5.4 Hz, C*H*$_3$C(O)P), 1.44 (br s (overlaps fast isomer), C*H*$_3C_1$), 1.40 (d, ^3J = 6.7 Hz, part of CH(C*H*$_3)_2$), 1.17 (br m, CH(C*H*$_3)_2$), 1.04 (br d, ^3J = 5.3 Hz, part of CH(C*H*$_3)_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 226.8 (d, $^1J_{PC}$ = 25.3 Hz), 163.9, 158.9, 150.4, 144.3, 135.7 (CH_1), 135.5 (4°), 135.4 (4°), 130.25, 130.21 (Ar CH ~7.3; $MeOC_6H_4$ CH ~6.8), 128.3 (Ph CH ~7.4), 128.1, (Ar CH, ~7.3), 127.3 (Ar CH, ~7.25), 113.39, 113.37 (Ar CH, ~7.3; $MeOC_6H_4$ CH, ~6.8), 111.4 (4°), 87.1 (4°), 85.8 (d, $^3J_{PC4}$′ = 4.7 Hz), 84.9 (CH_1′, 6.48), 78.0 (d, $^2J_{PC3}$′ = 19.0 Hz), 63.5 (C_5′), 55.3 (*Me*O, 3.79), 46.7 (iPr *C*H, from HSQC cross peak with ^{1}H at δ 3.3), 40.1 (d, $^3J_{PC2}$′ = 4.7 Hz), 30.83 (d, $^2J_{PC}$ = 36.8 Hz, *C*H_3C(O)P), ~25 (broad, iPr Me at 1.17, 1.04), 19.3 (iPr Me at 1.40), 11.9 (*C*H_3C_1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 117.6, 116.8 (46:54); IR ($CDCl_3$) 3396,

2969, 1688 cm^{-1}. HRMS (ESI): Calcd for $C_{39}H_{49}N_3O_8P$ $[M+H]^+$ 718.3252, found 718.3254.

3′-(5′-DMTr-OT)P(N(iPr)$_2$)C(O)C$_6$H$_5$ (11). An orange suspension of **9** (0.502 g, 1.49 mmol, 1.07 equiv), DMTr-OT (0.758 g, 1.39 mmol), and NMI·Tf (0.326 g, 1.40 mmol, 1.01 equiv) in 10 mL acetonitrile was stirred for 2 h to give a clear orange solution. Solvent removal using a vacuum pump gave an orange-yellow foam. Chromatography on 30 mL of silica gel on a 60 mL fritted funnel, eluting with 9:1 CH_2Cl_2:THF gave a yellow band in 60 mL of solvent, discarding a pale yellow tail; solvent removal gave 0.757 g (70% crude yield) of yellow foam consisting of product and starting material. Final purification was achieved by taking up the material in 4 mL ether, and precipitating out product by addition of 10 mL of hexane with swirling, cooling briefly to –35 °C, and filtration to give the product as a yellow solid. Addition of CH_2Cl_2 followed by solvent removal was required to remove the hexane, giving 0.632 g of yellow foam (58% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70, 8.62 (minor, major, br s, NH, 1H), 7.91 (m, 2H of Ph), 7.69, 7.62 (minor, major, ~q, $^4J \approx$ 1.6, 1.3 Hz, H_1, 1H), 7.62 – 7.2 (m, 8H of Ph and 4H of $MeOC_6H_4$ AA′BB′), 6.80 (m, 4H of $MeOC_6H_4$ AA′BB′), 6.51, 6.40 (major, minor, dd, ^3J = 7.8, 6.2, and 7.2, 6.2 Hz, H_1′, 1H), 4.70 (m, H_3′, 1H), 4.43, 4.26 (minor, major, ~q, $^3J \approx$ 3.0, 2.7 Hz, H_4′, 1H), 3.781, 3.779 and 3.73, 3.71 (major, minor, each two diastereotopic s, *Me*OC_6H_4, 6H), 3.52, 3.43 (m, $(H_5')_2$, 2H), 3.27 (m, C*H*$(CH_3)_2$, 2H), 2.73 (major, ddd, ^2J = 13.8 Hz, ^3J = 6.1, 2.7 Hz, H_2′, ~0.5 H), 2.58 (minor, ddd, ^2J = 13.6 Hz, ^3J = 5.9, 3.2 Hz, H_2′, ~0.5 H), 2.34 (m, H_2′, 1H), 1.45 (br s, C*H*$_3$C$_1$, 3H), 1.22, 1.09, 0.7 (br, CH(C*H*$_3$)$_2$, 6H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 217.2, 217.1 (major, minor, d, $^1J_{PC}$ = 30.6, 29.9 Hz), 163.94, 163.90, 163.86, 163.84, 163.82,

158.83, 158.81, 158.77, 158.73, 150.34, 150.30, 144.58, 144.46, 139.08, 139.02, 138.81, 138.75 (all 4°), 135.92 (CH_1 (major) 7.62), 135.82 (CH_1 (minor) 7.69), 135.55, 135.52, 135.51 (4°), 133.16, 133.08 (Ar CH ~7.5), 130.25, 130.22 ($MeOC_6H_4$ CH ~7.3), 128.5, 128.4, 128.3, 128.09, 128.06, 127.89, 127.83, 127.24, 127.17 (Ar CH 7.9-7.2), 113.36, 113.34, 113.32 ($MeOC_6H_4$ CH ~6.8), 111.22, 111.14 (4°), 86.99, 86.98 (4°), 85.8, 85.6 (d, $^3J_{PC4'}$ = 5.5, 4.3 Hz), 85.0, 84.8 (CH_1', major, minor), 77.32, 77.16, 76.96 (visible in DEPT45, $C_3'H$ 4.70), 63.5, 63.1, 55.4, 55.30, 55.28 (*Me*O, 3.78-3.71), 46.6, 40.2, ~24.5 (broad, iPr Me), 11.9 (CH_3C_1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 119.8, 116.7 (42.5:57.5); IR ($CDCl_3$) 3396, 2970, 1688 cm^{-1}. HRMS (ESI): Calcd for $C_{44}H_{51}N_3O_8P$ $[M+H]^+$ 780.34083, found 780.33935.

3′-(5′-DMTr-OT)-5′-(3′-*t*-BuMe$_2$Si-OT)PC(O)CH$_3$ (12). To a stirred solution of 69.4 mg of **10** (0.097 mmol, 1.46 equiv) and 23.6 mg of 3′-*O*-(*tert*-butyldimethylsilyl)thymidine [8,9] (3′-TBS-OT, 0.066 mmol, 1 equiv) in 1 mL of acetonitrile was added 0.95 g (1.2 mL) of 0.20 M/0.10 M pyridinium trifluoroacetate/*N*-methylimidazole (PTFA/NMI) in acetonitrile (0.24/0.12 mmol, 2.5/1.2 equiv relative to **10**), in one portion. The clear solution was stirred for 25 min, the solution was concentrated to about half its volume using a vacuum pump, and the solution was applied to a column of 6 mL of silica gel packed in THF. A UV-active band was eluted in about 10 mL of THF, the solvent was removed using a vacuum pump, and triturated with ether to give 105.4 mg of pale yellow foam. ^{31}P NMR indicated complete reaction of **10** and the presence of ~12% of unidentified material in the dinucleoside acyl region, and ^{1}H NMR indicated ~14% of unreacted 3′-TBS-OT. The mixture was applied in 2 mL of CH_2Cl_2 to a 15 mL column of silica packed in 5% THF in CH_2Cl_2. After elution with 20

mL of 5% THF in CH_2Cl_2 followed by 10 mL of 10% THF in CH_2Cl_2, unidentified weakly UV-active material (6.6 mg total) eluted in 5 mL of 10% THF in CH_2Cl_2 followed by 20 mL of 20% THF in CH_2Cl_2. The remaining UV-active material eluted in 30 mL of 20-30% THF in CH_2Cl_2 followed by 20 mL of THF, giving 54.5 mg of **12** (~85% yield) that was ~84% pure by ^{31}P NMR and contained ~14 mol% unreacted 3′-TBS-OT. Rechromatography of this material combined with similar fractions from prior syntheses (99 mg total) on a 15 mL column of silica packed in 10% THF in ethyl acetate gave after a 17 mL forerun an 8 mL UV-active fraction with virtually all the **12** recovered (55 mg), containing 6% of an unidentified impurity (^{31}P NMR: 142.9 ppm) and ~36 mol% of 3′-TBS-OT. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.57-9.35 (5 s, NH, 2H), 7.59, 7.55 (q, $^4J \approx$ 1.2, 1.1 Hz, H_6, 1H), 7.37 (m, 3H), 7.26 (m, 7H), 6.83 (d, J = 7.5 Hz, 4H of $MeOC_6H_4$ AA′BB′), 6.42, 6.39 (dd, ^3J = 8.5, 6.0 Hz and 7.5, 6.0 Hz, $^{T1}H_1$′, 1H), 6.29, 6.24 (t, ^3J = 6.5, 6.8 Hz, $^{T2}H_1$′, 1H), 4.80 (~q, $^3J \approx$ 6.8 Hz, $^{T1}H_3$′, 0.5 H), 4.38,4.21, 4.06 (m, ~2H), 3.93, 3.89 (m, 2H, overlapping with 3′-TBS-OT), 3.781, 3.778 (s, MeO, 6H), 3.52, 3.36 (m, $^{T1}H_5$′, 1.5H), 2.91 (m,$^{T1}H_5$′, 0.5 H), 2.6-2.2 (m, H_2′, 4H), 2.36, 2.28 (d, J = 4.0 and 4.0 Hz, CH_3C(O), 3H, with overlapping 3′-TBS-OT), 1.87, 1.83 (s, $^{T2}CH_3$C-5, 3H), 1.46, 1.45 (d, $^4J \approx$ 0.5 Hz, $^{T1}CH_3$C-5, 3H), 0.88 (s, *t*-Bu, 9H), 0.078, 0.054, 0.040 (s, Me_2Si, 6H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 223.28, 223.25 (d, $^1J_{PC}$ = 38.6, 41.4 Hz), 164.11, 164.04, 158.9, 150.68, 150.63, 150.51, 144.20, 144.16 (all 4°), 137.15, 136.0, 135.24 (*C*H_6 7.59, 7.55), 135.17 (*C*H_6 7.59, 7.55), 130.2, 128.2, 127.4, 113.4, ($MeOC_6H_4$ 6.83), 111. 7 (4°), 111.27 (4°), 111.20 (4°), 111.11 (4°), 87.7 (3′-TBS-OT, *C*H_1′), 87.33, 87.28, 87.0, 86.0, 85.7, 85.4, 85.1, 84.75, 84.69, 71.7, 71.36, 71.32, 68.4, 66.7, 63.2, 63.1, 62.1, 55.4 (MeO), 40.75, 40.59, 39.9, 30.2 (*C*H_3C(O)), 29.9 (*C*H_3C(O)), 25.83 (*t*-Bu),

25.79 (*t*-Bu), 18.06, 18.04, 18.00 (*t*-Bu 4° C), 12.63, 12.54 (^{T2}*C*H$_3$C-5), 11.99, 11.92 (^{T1}*C*H$_3$C-5), -4.52, -4.58, -4.72, -4.74 (*C*H$_3$Si); ^{31}P NMR (202 MHz, CDCl$_3$) δ 148.2, 145.2 (49:51); IR (CDCl$_3$) 3395, 2957, 2932, 1690 cm^{-1}. HRMS (ESI): Calcd for $C_{49}H_{62}N_4O_{13}PSi^+$ $[M+H]^+$ 973.38148, found 973.38100.

3′-(5′-DMTr-OT)-5′-(3′-*t*-BuMe$_2$Si-OT)PC(O)C$_6$H$_5$ (13). To a stirred solution of 118.0 mg of **11** (0.151 mmol, 1.34 equiv) and 40.0 mg of 3′-TBS-OT (0.112 mmol, 1 equiv) in 2 mL of acetonitrile was added 1.51 g (1.93 mL) of 0.20 M/0.10 M PTFA/NMI in acetonitrile (0.385/0.193 mmol, 2.6/1.3 equiv relative to **11**), in one portion. The yellow solution was stirred for 30 min, the solution was concentrated to about half its volume using a vacuum pump, and the solution was applied to a column of 7 mL of silica gel packed in THF. The yellow band was eluted in about 10 mL of THF, the solvent was removed using a vacuum pump, and triturated with ether to give 156.8 mg of yellow foam. ^{31}P NMR indicated the mixture contained 34 mol% of **11**. The mixture was applied in 3 mL of CH$_2$Cl$_2$ to a 15 mL column of silica packed in 5% THF in CH$_2$Cl$_2$. After elution with 32 mL of 5% THF in CH$_2$Cl$_2$ followed by 10 mL of 10% THF in CH$_2$Cl$_2$, unreacted **11** eluted in 45 mL of 10% THF in CH$_2$Cl$_2$, towards the end of which ~6 mg of **13** was eluted. The main yellow band eluted in 30 mL of 1:1 THF:CH$_2$Cl$_2$, giving 88 mg of **13** as a yellow solid, containing 7.5% of unidentified impurities (^{31}P NMR: 150.1, 148.0 ppm, 5.5% and 2% respectively), a trace of **11**, and ~12% of 3′-TBS-OT. ^{1}H NMR (500 MHz, CDCl$_3$) δ 9.19-9.05 (4 s, NH, 2H), 7.96-7.93 (m, Ar, 2H), 7.60-7.19 (m, Ar, ^{T1}H$_{6,}$ ^{T2}H$_6$, 14H), 6.84-6.81 (m, 4H of MeOC$_6$H$_4$ AA′BB′), 6.44, 6.40 (dd, ^3J = 7.8, 6.3 Hz and 8.5, 5.5 Hz, ^{T1}H$_1$′, 1H), 6.30 (m, ^{T2}H$_1$′, 1H), 4.86, 4.79 (~br dd, ^3J ≈ 6.9, 6.9 Hz, ^{T1}H$_3$′, 1 H), 4.43, 4.34 (~dd and m, ^3J ≈ 9.0, 5.0 Hz, ^{T2}H$_3$′, 1 H), 4.2-4.00 (m, 1H, ^{T1}H$_4$′, 2H,

$^{T2}H_5'$), 3.93 (m, 1H overlapping with 3′-TBS-OT, $^{T2}H_4'$), 3.786, 3.785, 3.77 (s, MeO, 6H), 3.44-3.34 (m, $^{T1}H_5'$, 1.5 H), 3.11 (dd, ^3J = 2.3 Hz, ^2J = 10.8 Hz,$^{T1}H_5'$, 0.5 H), 2.50, 2.42 (br dd, ^3J = 12.3, 5.3 Hz and 13.1, 5.8 Hz, $^{T1}H_2'$, 1H), 2.38-2.23 (m, $^{T1}H_2'$, 1H), 2.22-2.11 (m, $^{T2}H_2'$, 2H), 1.85, 1.79 (d, $^4J \approx 0.7$ Hz, $^{T2}CH_3C$-5, 3H), 1.45, 1.38 (d, $^4J \approx 0.7$ Hz, $^{T1}CH_3C$-5, 3H), 0.86 (s, *t*-Bu, 9H), 0.032, 0.028, 0.014, 0.003 (s, Me_2Si, 6H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 211.6, 211.1 (minor, major, d, $^1J_{PC}$ = 44.3, 42.4 Hz), 163.9, 158.9, 150.6, 150.4, 144.28, 144.22, 137.4 (all 4°), 137.17, 136.9 (4°), 136.3, 135.9, 135.4, 135.3, 135.22 (4°), 135.19 (4°), 135.18 (4°), 134.49, 134.41, 130.20, 130.13, 129.19, 129.16, 128.44, 128.37, 128.31, 128.19, 128.13, 127.38, 113.47 ($MeOC_6H_4$ 6.84-6.81), 113.42 ($MeOC_6H_4$ 6.84-6.81), 113.41 ($MeOC_6H_4$ 6.84-6.81), 111.67 (4°), 111.62 (4°), 111.4 (4°), 111.20 (4°), 111.16 (4°), 87.7, 87.3, 86.1, 85.8, 85.5, 85.4, 84.9 (C_{H1}'), 84.7 (C_{H1}'), 84.6 (C_{H1}'), 71.8, 71.6, 68.6, 68.5, 66.95, 66.91, 63.29 ($^{T1}CH_5'$), 63.17 ($^{T1}CH_5'$), 62.2 (CH_5' of 3′-TBS-OT), 55.39 (MeO), 55.37 (MeO), 40.67 (CH_2'), 40.58 (CH_2'), 39.94, 25.8 (*t*-Bu), 18.0 (*t*-Bu 4° C), 12.59, 12.56 ($^{T2}CH_3C$-5), 11.9, 11.8 ($^{T1}CH_3C$-5), -4.52, -4.59, -4.71, -4.76 (CH_3Si); ^{31}P NMR (202 MHz, $CDCl_3$) δ 151.5, 150.2 (46:54); IR ($CDCl_3$) 3395, 2955, 2932, 1690 cm^{-1}. HRMS (ESI): Calcd for $C_{54}H_{63}N_4NaO_{13}PSi^+$ $[M+Na]^+$ 1057.37907, found 1057.37949.

Conversion of 12 and 13 to 17. Sulfurization of **13** occurred by reaction in CD_3CN with excess phenylacetyl disulfide (PADS) [10] or DDTT [11] and gave new peaks at 66.4 and 66.0 ppm in the ^{31}P NMR spectrum consistent with formation of the tetravalent sulfides. Reaction with 2 M triethylammonium bicarbonate (TEAB) or with bis(trimethylsilyl)acetamide (BSA) [12] followed by TEAB gave material with only one major peak in the ^{31}P NMR spectrum at 113.3 ppm, and it could not be identified.

Oxidation of **13** in acetonitrile with anhydrous 3.3 M *tert*-butyl hydroperoxide [13] gave two peaks in the ^{31}P NMR spectrum for the diastereomeric oxides at -0.9 and -1.1 ppm. Treatment with TEAB gave the *H*-phosphonate (^{31}P NMR ($CDCl_3$): 8.8, 7.5 ppm [12]), and treatment with PADS gave the diastereomeric phosphorothioates (^{31}P NMR ($CDCl_3$): 58.0, 57.9 ppm [12]).

Oxidation of **12** in the same manner gave the diastereomeric oxides (^{31}P NMR ($CDCl_3$): -2.5, -2.7 ppm), and TEAB and PADS gave the same *H*-phosphonate and phosphorothioate spectra as for **13**.

Thermal decomposition of 12 and 13. Samples of **12** or **13** were dissolved in acetonitrile and added to a one-piece teflon vacuum stopcock-sealed heavy-walled glass vessel. The vessel was evacuated using a vacuum pump and then heated in a thermostatted oil bath. Periodically the solvent was removed under vacuum and the contents analyzed by NMR after extraction into $CDCl_3$ solution; after adding the NMR sample back to the vessel, the solvent was once again removed under vacuum and replaced with acetonitrile. Two samples of **12** were examined. A 1:1 mixture of diastereomers was heated for 12 h at 50 °C followed by 4 h at 75 °C, with no change in diastereomer ratio but extensive decomposition to unidentified materials that exhibited very broad bands in the ^{1}H and particularly the ^{31}P NMR spectra. A 42:58 sample of diastereomers was heated sequentially for 1.5 h at 100 °C, 1.5 h at 130°C, and 1.5 h at 150 °C. No change in diastereomer ratio occurred, but decomposition was nearly complete at the end. One sample of **13** was heated, for 2.5 h at 75 °C and 6 h at 100 °C, with no change in the 1:1 diastereomer ratio, and again with nearly complete decomposition.

X-ray structure of 9. A yellow fragment of **9** with approximate dimensions 0.31 mm x 0.37 mm x 0.41 mm, cleaved from a large crystal obtained by slow cooling of a saturated hexanes solution at –35 °C, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker Smart Breeze CCD system equipped with a graphite monochromator at 100(2) K, cooled by an Oxford Cryosystems 700 Series Cryostream. A total of 1464 frames were collected. The total exposure time was 12.20 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 21786 reflections to a maximum θ angle of 27.10° (0.78 Å resolution), of which 4311 were independent (average redundancy 5.054, completeness = 100.0%, R_{int} = 2.00%, R_{sig} = 1.47%) and 3921 (90.95%) were greater than $2\sigma(F^2)$. The final cell constants of *a* = 15.8768(8) Å, *b* = 9.2589(5) Å, *c* = 14.0614(7) Å, β = 108.8770(10)°, volume = 1955.87(17) $Å^3$, were based upon the refinement of the XYZ-centroids of 9998 reflections above 20 σ(I) with 5.168° < 2θ < 54.18°. Data were corrected for absorption effects using the numerical method (SADABS). The ratio of minimum to maximum apparent transmission was 0.927. The calculated minimum and maximum transmission coefficients (based on crystal size) were 0.9430 and 0.9550.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with Z = 4 for the formula unit, $C_{19}H_{33}N_2OP$. The final anisotropic full-matrix least-squares refinement on F^2 with 249 variables converged at R_1 = 3.11%, for the observed data and wR_2 = 8.21% for all data. The goodness-of-fit was 1.048. The largest peak in the final difference electron density synthesis was 0.412

$e^-/Å^3$ and the largest hole was -0.202 $e^-/Å^3$ with an RMS deviation of 0.041 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.143 g/cm^3 and F(000), 736 e^-.

Cambridge Crystallographic Data Centre deposition number for **9**: CCDC 1030743. The data can be obtained free from Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Calculations. All geometry and NMR calculations were carried out using *Gaussian 09 Revision A.02* and *D.01* [14] by first carrying out a geometry optimization (DFT, 6-31G(d), B3LYP) with modeling of solvation in chloroform using the polarization continuum model (IEFPCM), with calculation of vibrational frequencies to insure the finding of an energy minimum; NMR calculations (GIAO) were then carried out on the optimized structures using the 6-311+G(2d,p) basis set and the same IEFPCM solvation method.

Each of the inversion barrier calculations was carried out by optimizing using the 6-31+G(d) basis set, but without solvation modeling, with the exception of the phosphite triester where acetonitrile modeling was used. Following optimization, one of the groups was rotated to give the inverted structure, which was then reoptimized; **18** and **19** gave back the same structures but in the opposite configuration at phosphorus. For the transition state calculations, one enantiomer of each optimized structure was converted to a trigonal planar structure, and then used as the starting point for the transition state search. Both the QST3 option in *Gaussian* as well as the simpler Berny TS option ts=(opt,estmfc,noeigentest) described by the Collum group [15] were successfully used. The reported barriers are the smaller barrier from each ground state, as the sum of the electronic and thermal free energies at 298.15 K.

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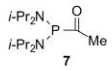
^{1}H NMR



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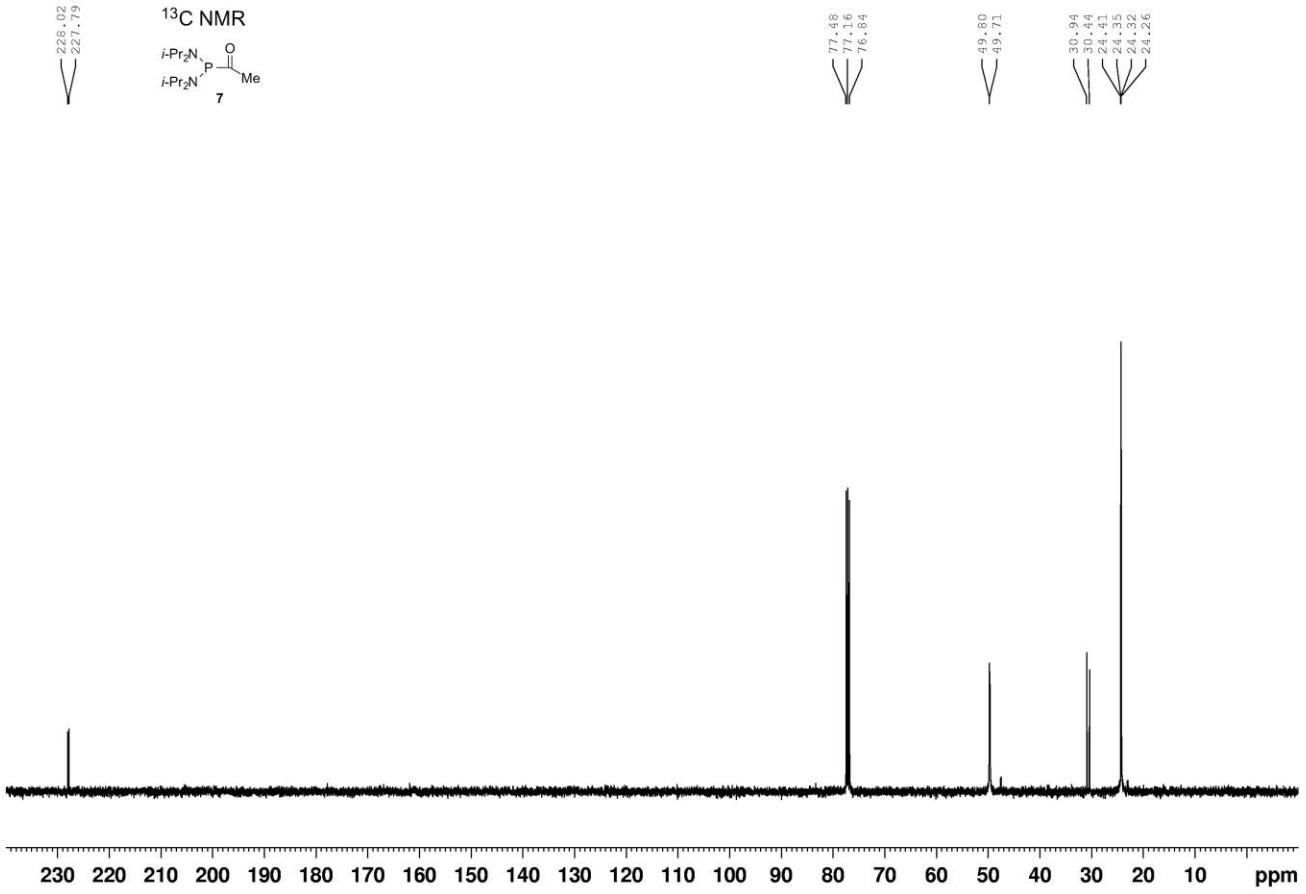

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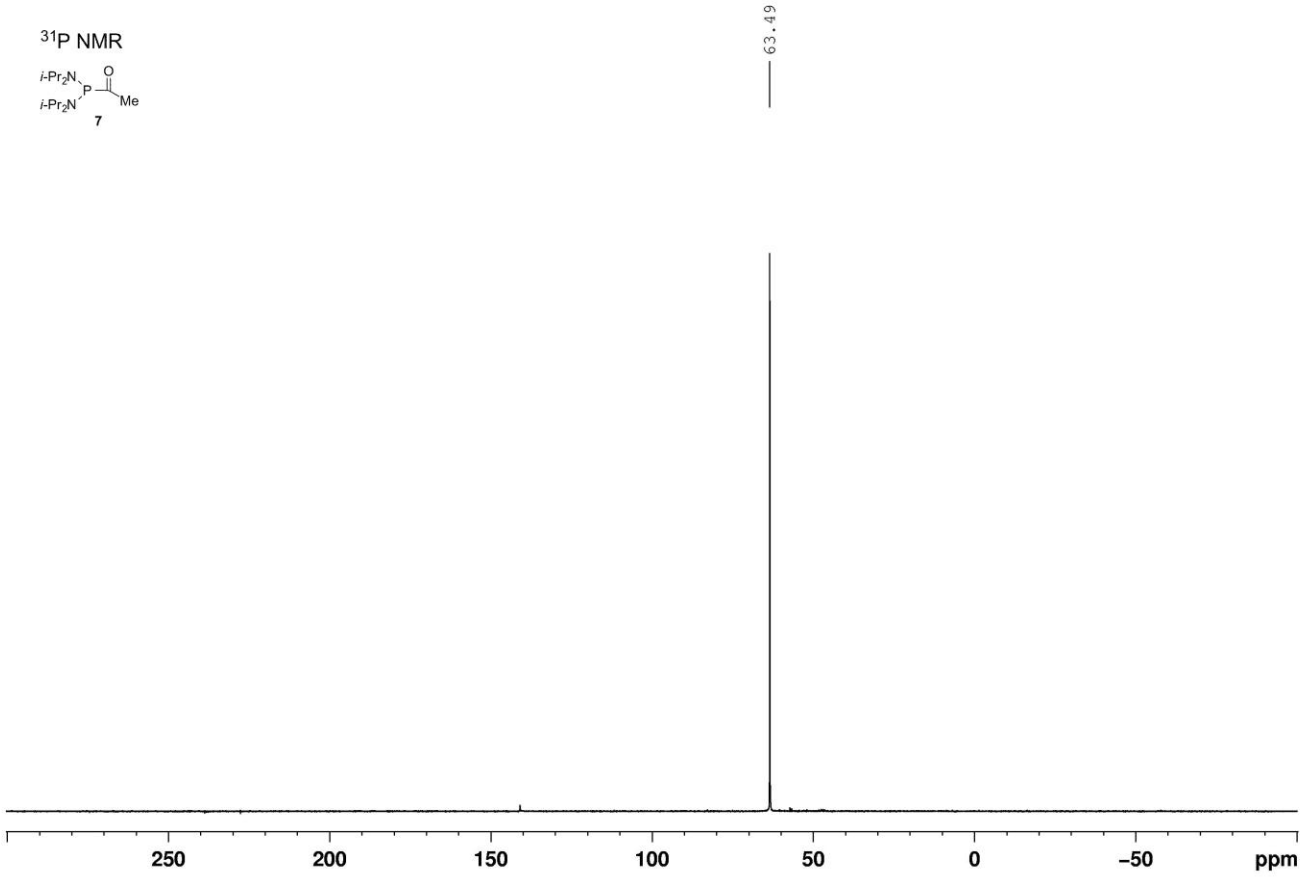


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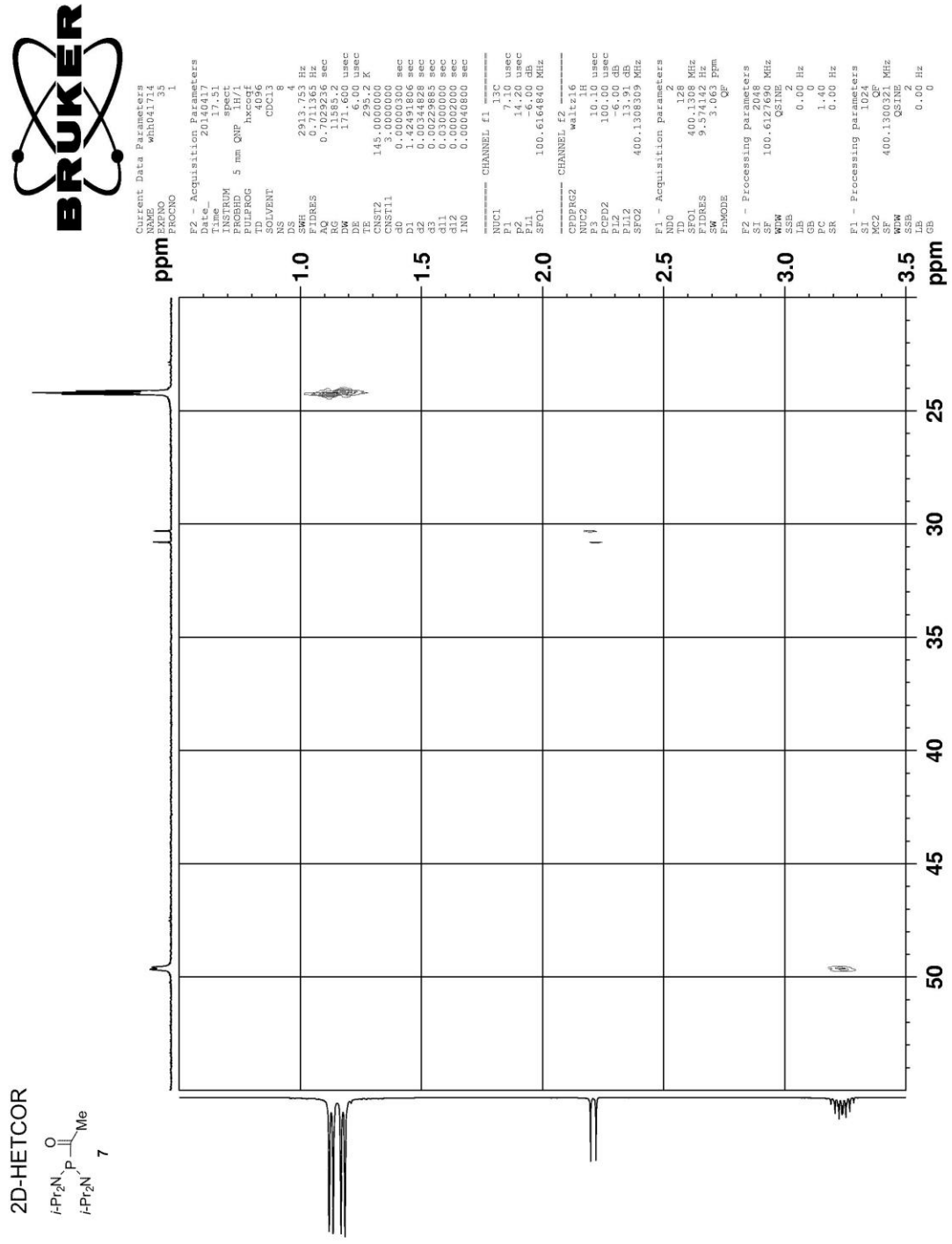
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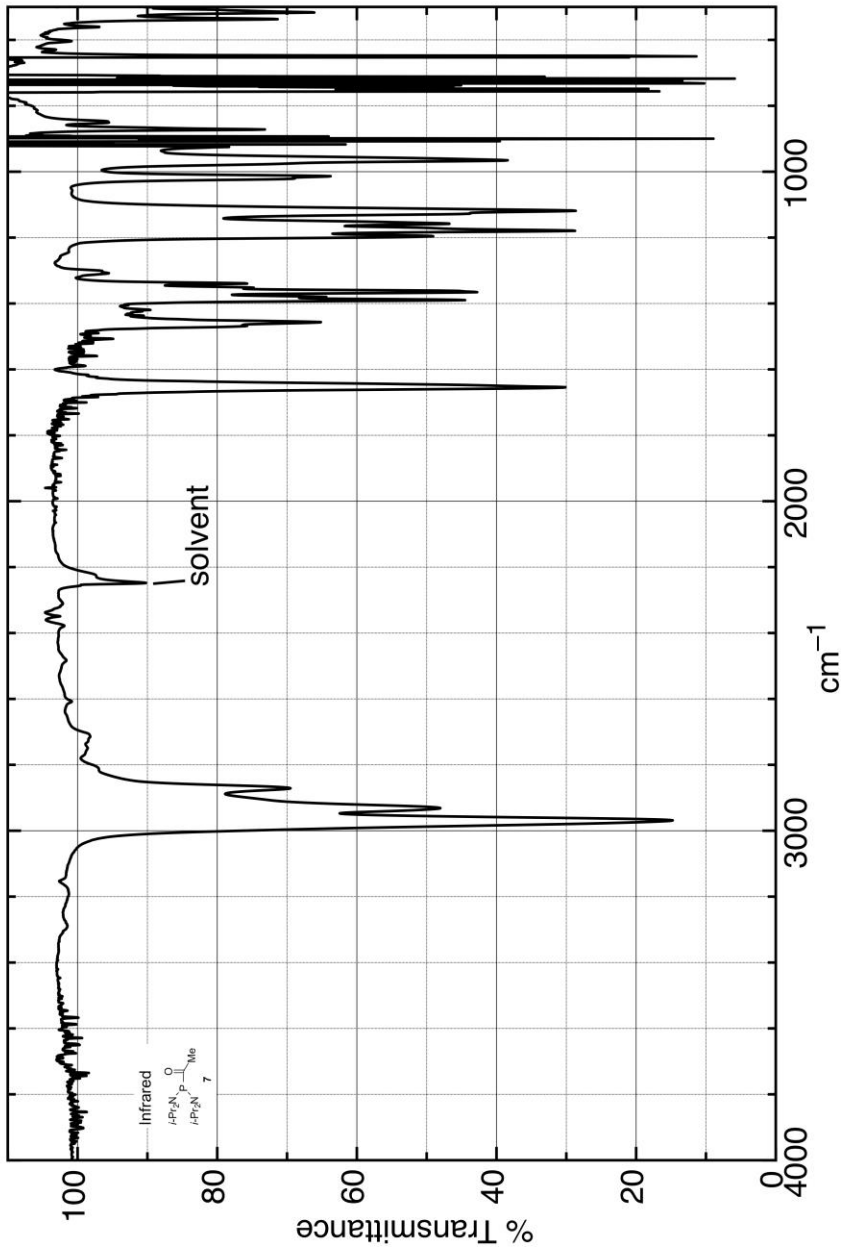
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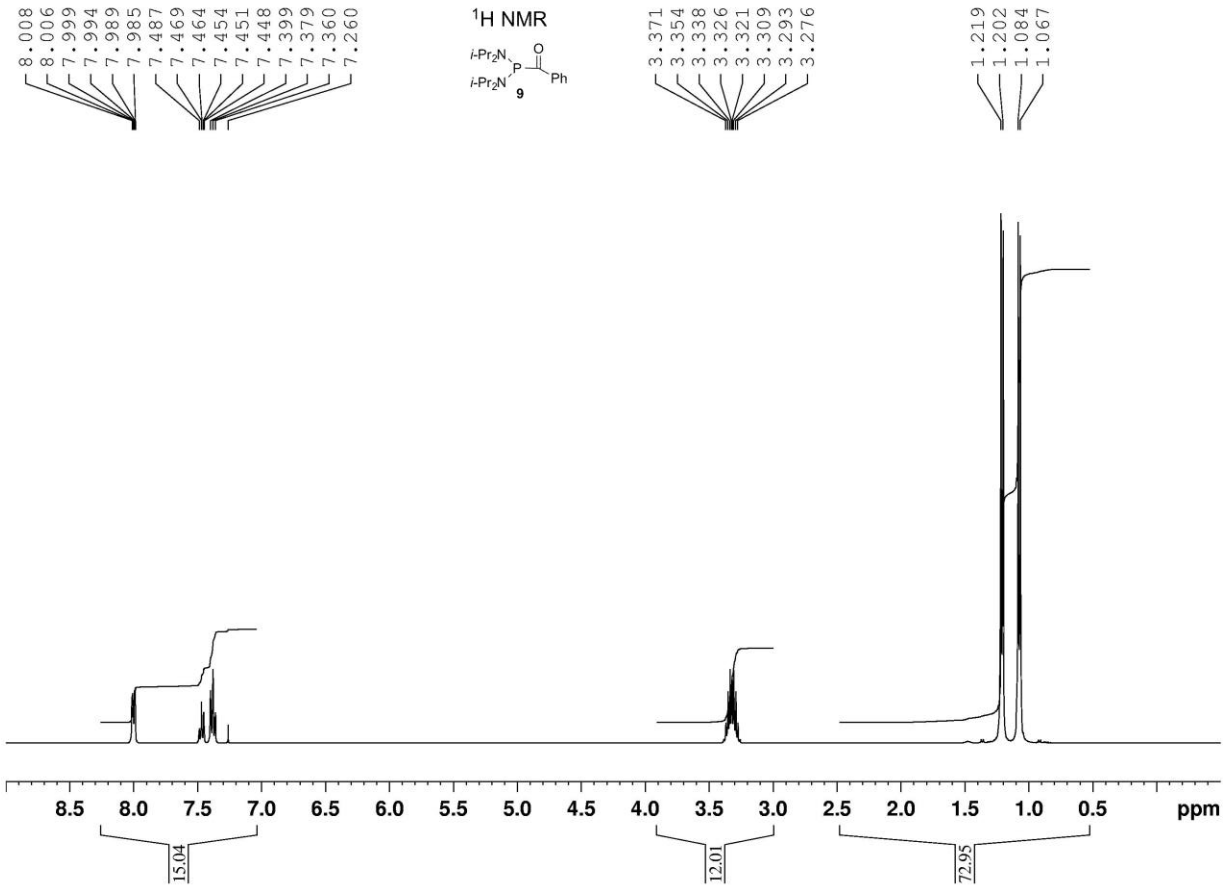


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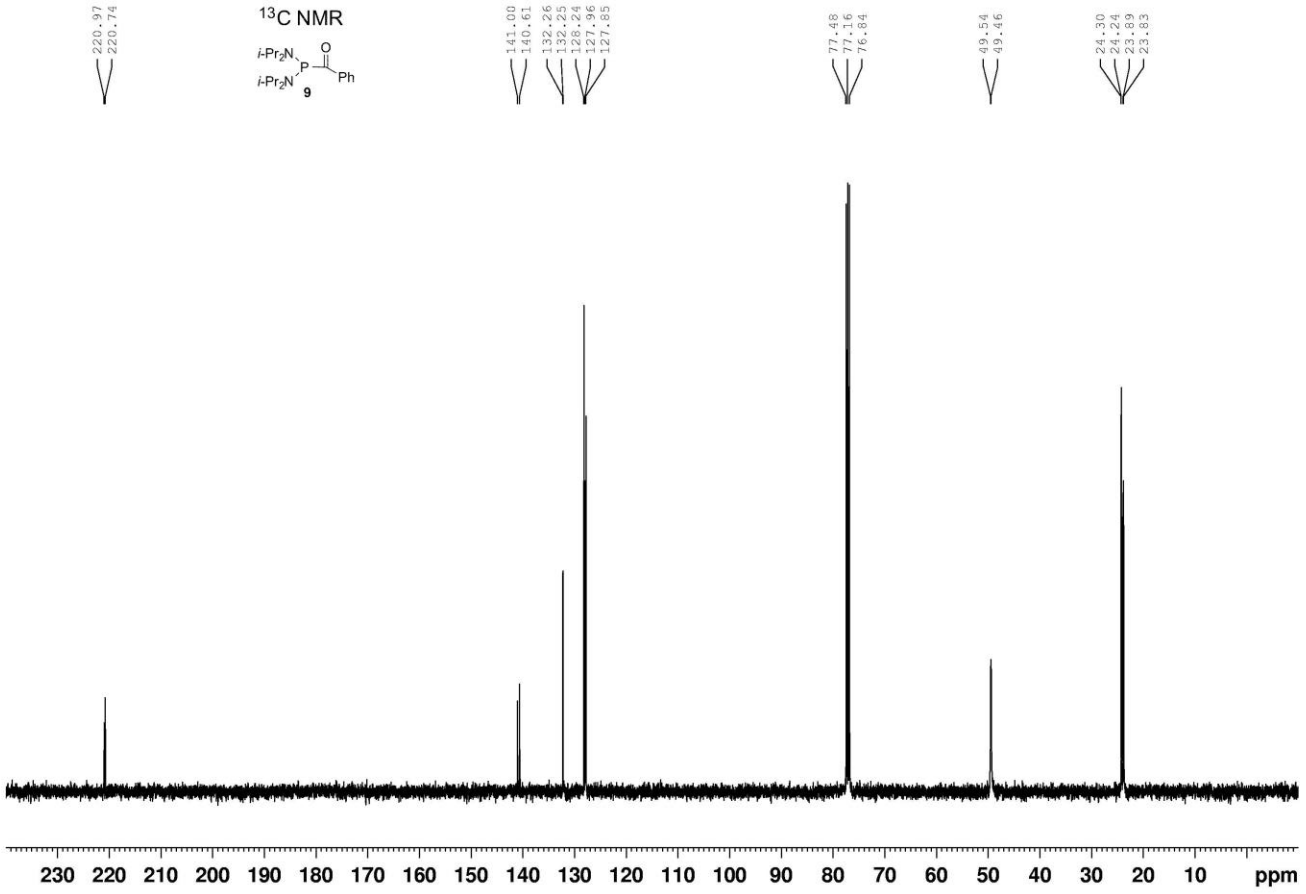
SR                  9.23 Hz
```



BRUKER

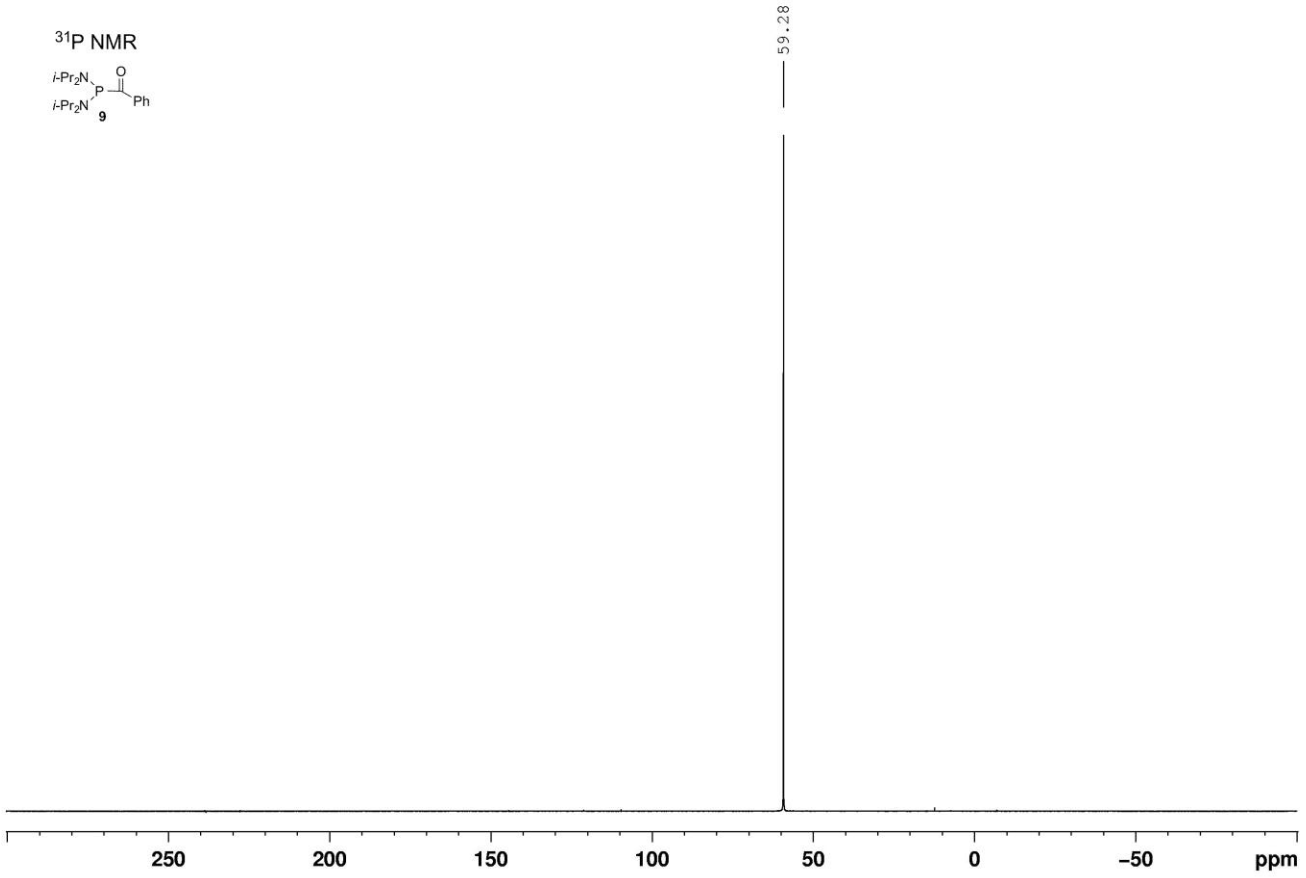
```
Current Data Parameters
NAME                 whh041714
EXPNO                       12
PROCNO                       1

F2 - Acquisition Parameters
Date_               20140417
Time                    13.12
INSTRUM                 spect
PROBHD    5 mm QNP  1H/1
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                        256
DS                          4
SWH                 28248.588 Hz
FIDRES              0.431039 Hz
AQ                  1.1600372 sec
RG                      143.7
DW                     17.700 usec
DE                      6.00 usec
TE                     295.2 K
D1                  2.00000000 sec
d11                 0.03000000 sec
DELTA               1.89999998 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                       7.10 usec
PL1                     -6.00 dB
SFO1             100.6238364 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                  100.00 usec
PL2                     -6.00 dB
PL12                    13.91 dB
PL13                   120.00 dB
SFO2             400.1316005 MHz

F2 - Processing parameters
SI                        32768
SF               100.6127568 MHz
WDW                          EM
SSB                           0
LB                       1.00 Hz
GB                            0
PC                       1.40
SR                     -12.24 Hz
```



BRUKER

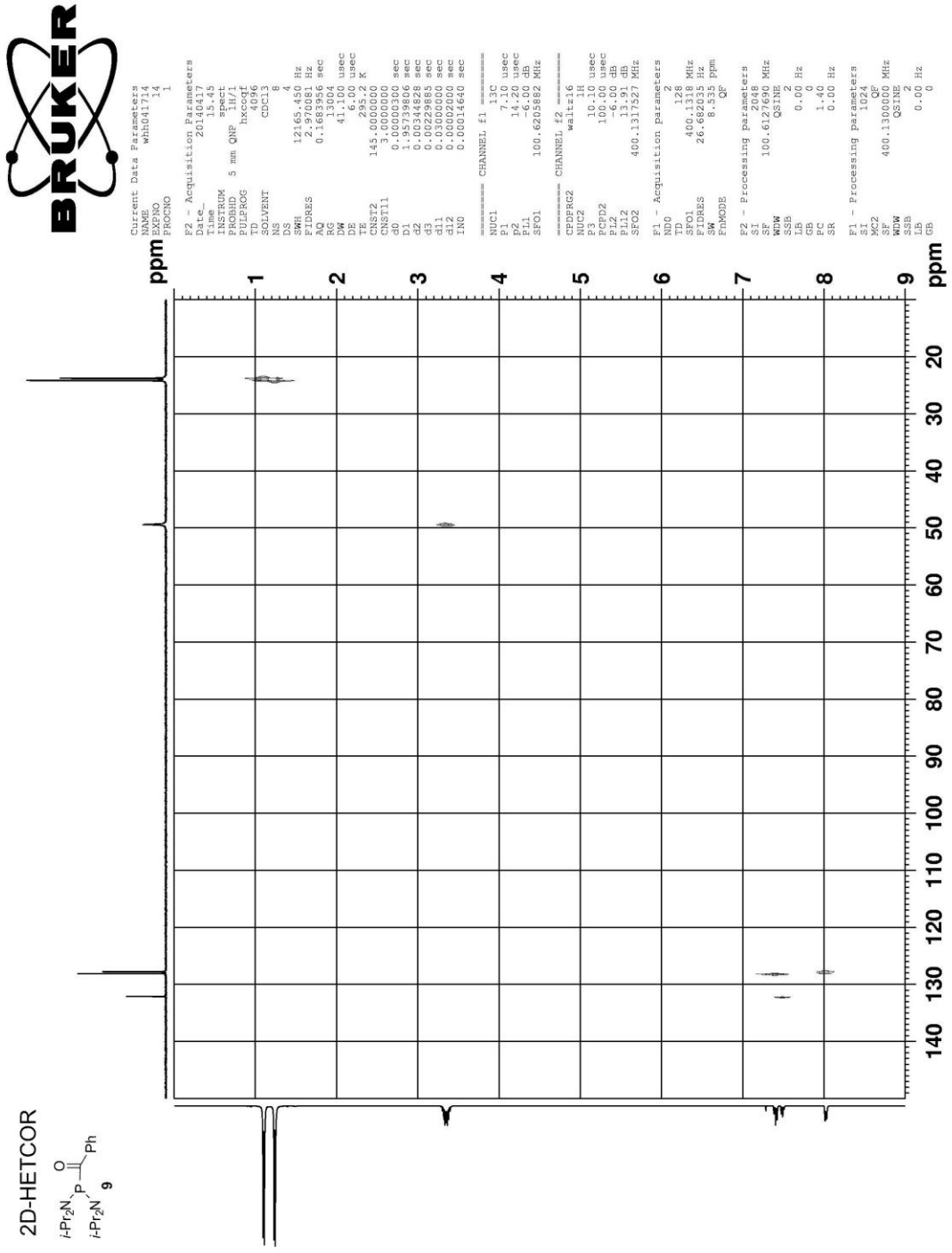
```
Current Data Parameters
NAME                 whh041814
EXPNO                       11
PROCNO                       1

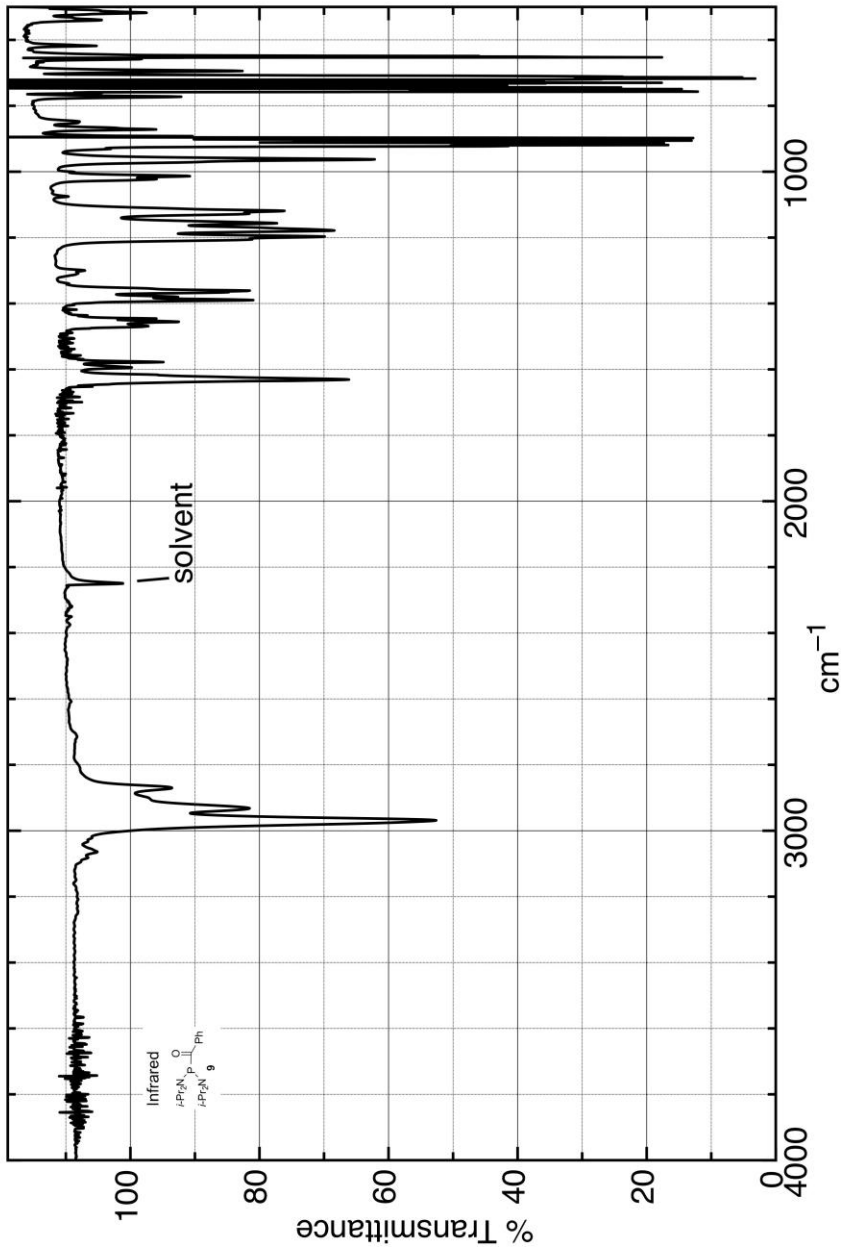
F2 - Acquisition Parameters
Date_               20140418
Time                    11.54
INSTRUM                 spect
PROBHD   5 mm QNP  1H/1
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                        512
DS                          4
SWH                 64935.066 Hz
FIDRES               0.990830 Hz
AQ                   0.5046772 sec
RG                     10321.3
DW                       7.700 usec
DE                       6.00 usec
TE                      295.2 K
D1                  2.00000000 sec
d11                 0.03000000 sec
DELTA               1.89999998 sec
TD0                         1

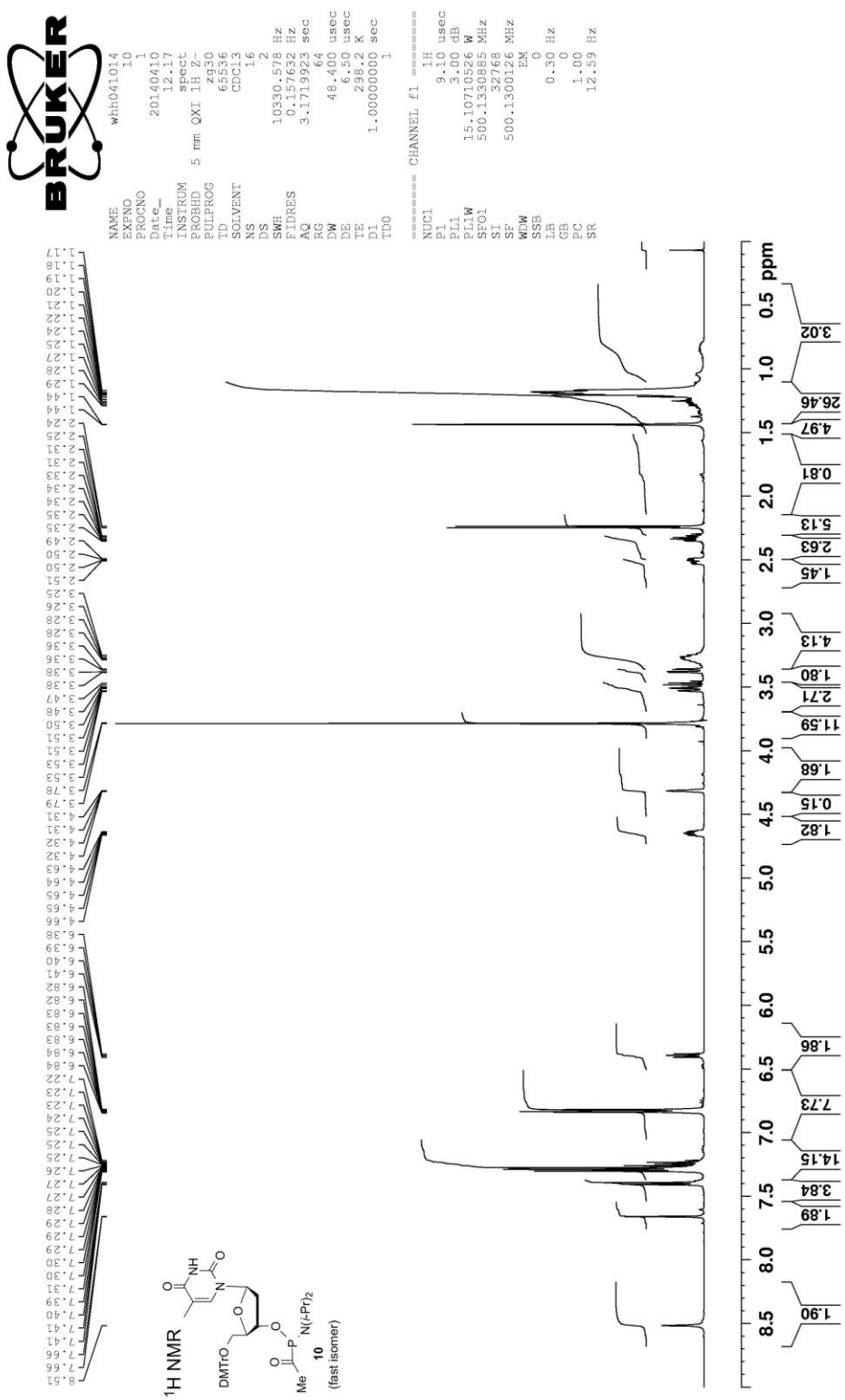
======== CHANNEL f1 ========
NUC1                       31P
P1                        4.65 usec
PL1                      -6.00 dB
SFO1               161.9917906 MHz

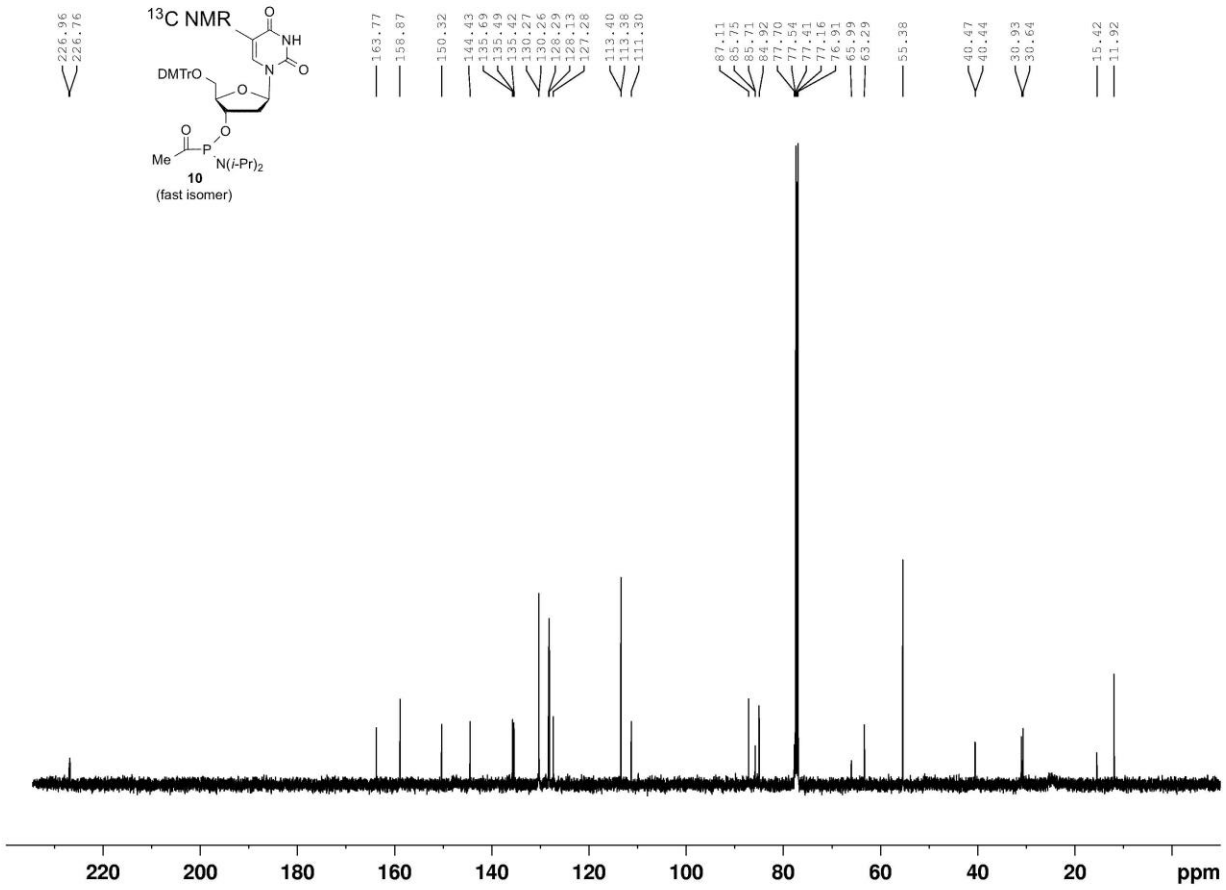
======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   100.00 usec
PL2                      -6.00 dB
PL12                     13.91 dB
PL13                    120.00 dB
SFO2               400.1316005 MHz

F2 - Processing parameters
SI                        32768
SF                 161.9755358 MHz
WDW                          EM
SSB                           0
LB                        1.00 Hz
GB                            0
PC                        1.40
SR                      -57.24 Hz
```

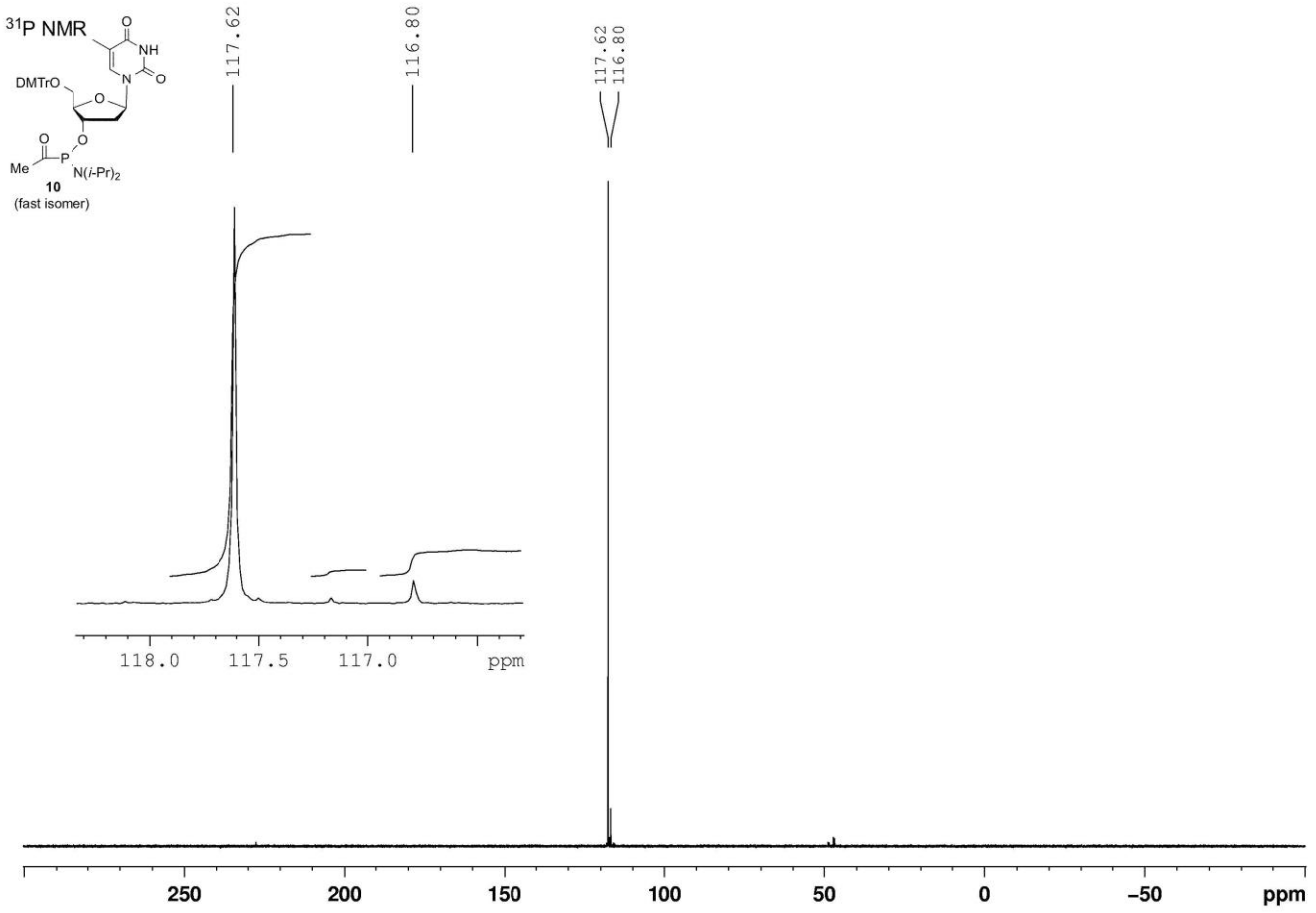

2D-HETCOR
i-Pr2N
P
O
Ph
i-Pr2N
9
ppm
1
2
3
4
5
6
7
8
9
ppm
20
30
40
50
60
70
80
90
100
110
120
130
140


Infrared
solvent
% Transmittance
cm−1
4000
3000
2000
1000
0
20
40
60
80
100


BRUKER
NAME whh041014
EXPNO 10
PROCNO 1
Date_ 20140410
Time 12.17
INSTRUM spect
PROBHD 5 mm QXI 1H Z-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 64
DW 48.400 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.10 usec
PL1 3.00 dB
PL1W 15.10710526 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300126 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
SR 12.59 Hz
1H NMR
DMTrO
Me
N(i-Pr)2
10
(fast isomer)
ppm
1.90
1.89
3.84
14.15
7.73
1.86
1.82
0.15
1.68
11.59
2.71
1.80
4.13
1.45
2.63
5.13
0.81
4.97
26.46
3.02



NAME	whh041014
EXPNO	11
PROCNO	1
Date_	20140410
Time	13.16
INSTRUM	spect
PROBHD	5 mm QXI 1H Z-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1024
DS	4
SWH	31250.000 Hz
FIDRES	0.476837 Hz
AQ	1.0486259 sec
RG	575
DW	16.000 usec
DE	6.50 usec
TE	298.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	14.50 usec
PL1	-1.00 dB
PL1W	132.81565857 W
SFO1	125.7716224 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	87.00 usec
PL2	3.00 dB
PL12	22.00 dB
PL13	22.00 dB
PL2W	15.10710526 W
PL12W	0.19018719 W
PL13W	0.19018719 W
SFO2	500.1320005 MHz
SI	32768
SF	125.7577722 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40
SR	-16.78 Hz



BRUKER

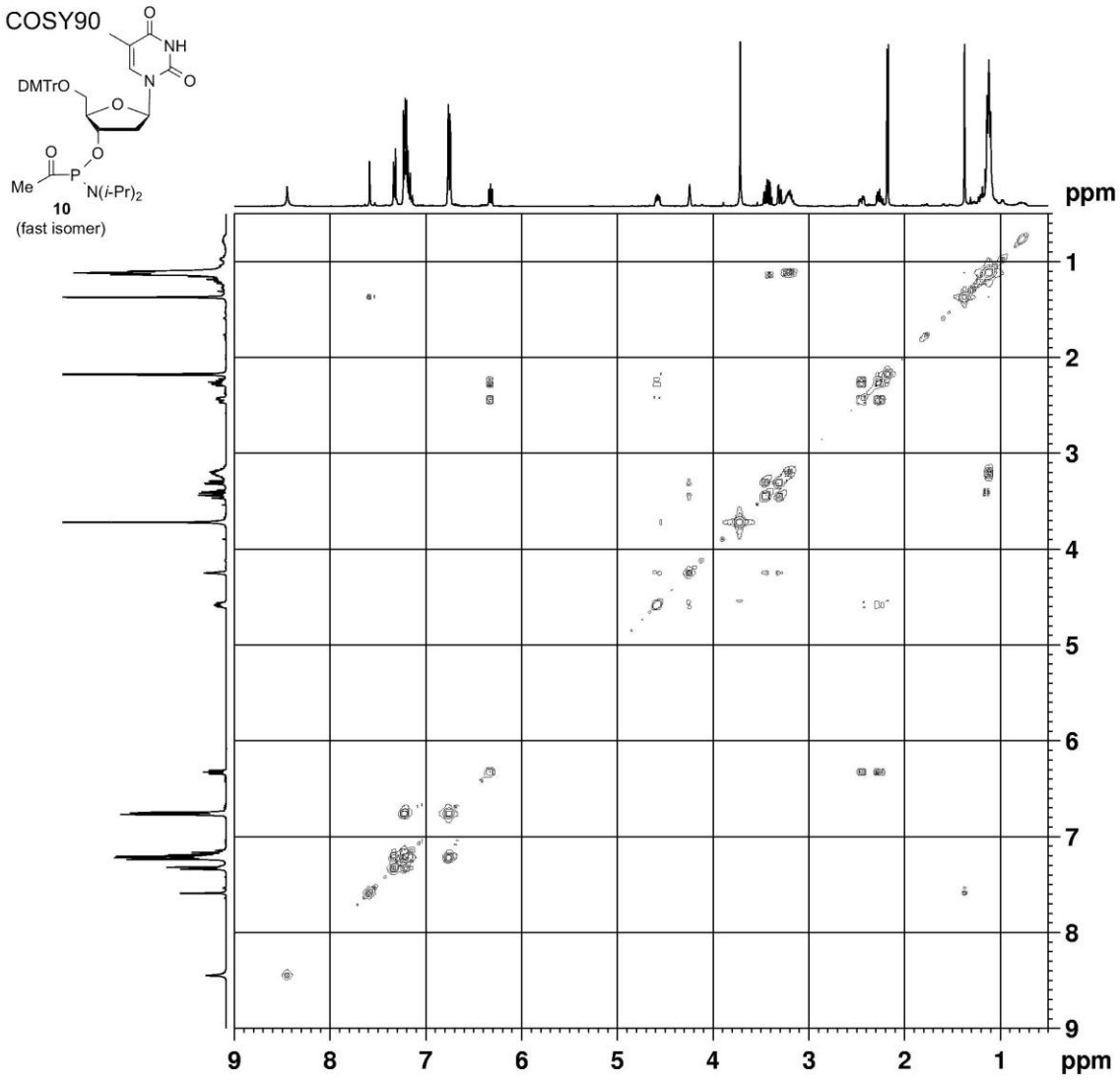
```
Current Data Parameters
NAME                 whh040114
EXPNO                       11
PROCNO                       1

F2 - Acquisition Parameters
Date_               20140401
Time                    15.35
INSTRUM                 spect
PROBHD    5 mm QNP  1H/1
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                        512
DS                          4
SWH                 64935.066 Hz
FIDRES                0.990830 Hz
AQ                    0.5046772 sec
RG                      23170.5
DW                        7.700 usec
DE                        6.00 usec
TE                      298.2 K
D1                    2.00000000 sec
d11                   0.03000000 sec
DELTA                 1.89999998 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       31P
P1                        4.65 usec
PL1                      -6.00 dB
SFO1              161.9917906 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   100.00 usec
PL2                      -6.00 dB
PL12                     13.91 dB
PL13                    120.00 dB
SFO2              400.1316005 MHz

F2 - Processing parameters
SI                        32768
SF                161.9755358 MHz
WDW                          EM
SSB                           0
LB                        1.00 Hz
GB                            0
PC                        1.40
SR                      -57.24 Hz
```



BRUKER

```
Current Data Parameters
NAME                 whh041014
EXPNO                       11
PROCNO                       1

F2 - Acquisition Parameters
Date_               20140410
Time                    16.35
INSTRUM                 spect
PROBHD    5 mm QNP  1H/1
PULPROG              cosygf90
TD                       2048
SOLVENT                 CDCl3
NS                          8
DS                          4
SWH                  3654.971 Hz
FIDRES               1.784654 Hz
AQ                   0.2802164 sec
RG                       161.3
DW                     136.800 usec
DE                       6.00 usec
TE                      296.2 K
d0                   0.00000300 sec
D1                   1.96845996 sec
IN0                  0.00027360 sec

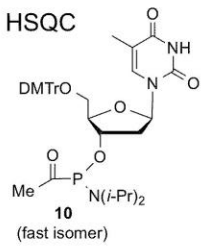
======== CHANNEL f1 ========
NUC1                        1H
P1                       10.10 usec
PL1                      -6.00 dB
SFO1               400.1318536 MHz

F1 - Acquisition parameters
ND0                         1
TD                        256
SFO1                400.1319 MHz
FIDRES             14.277229 Hz
SW                      9.134 ppm
FnMODE                     QF

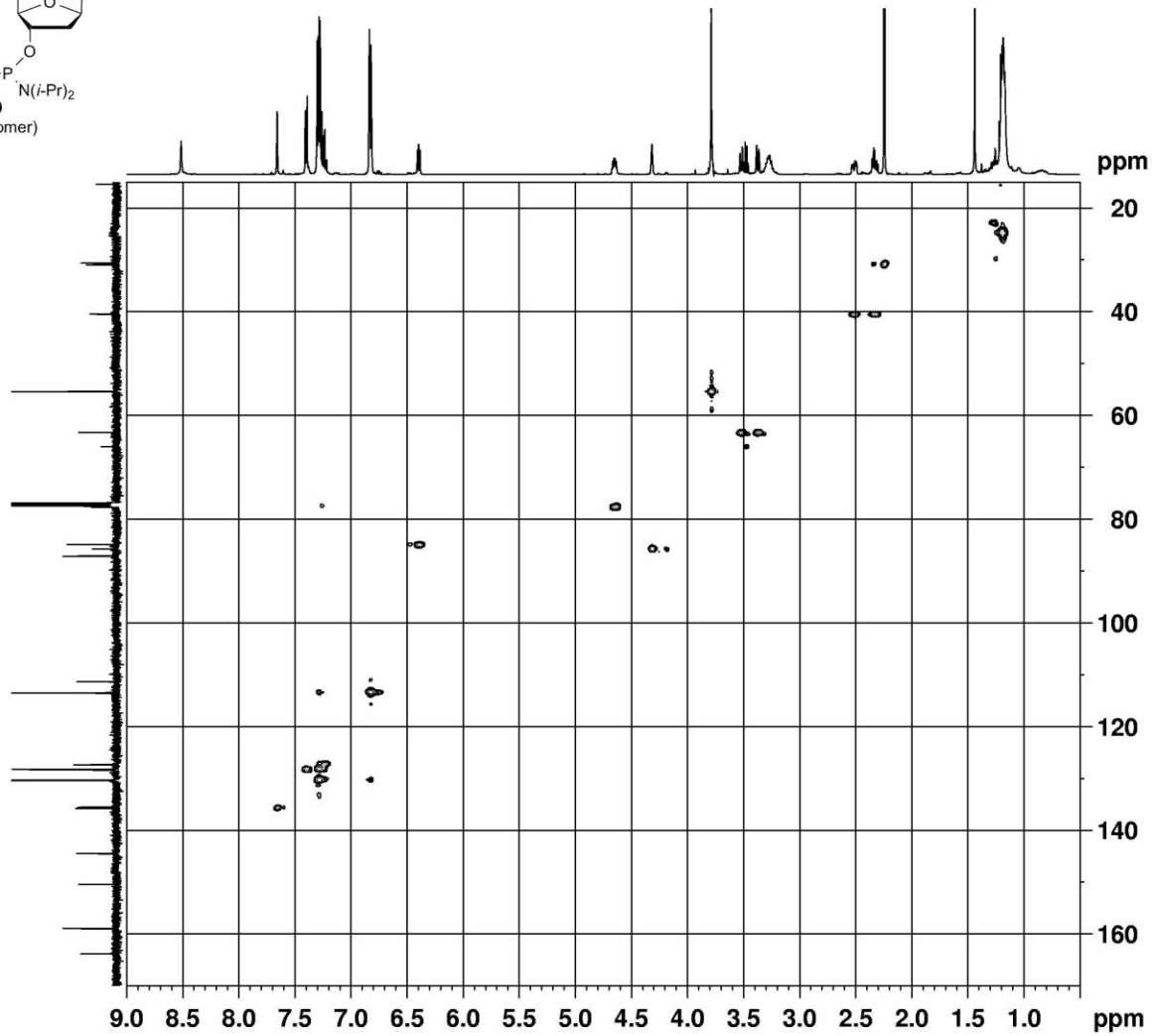
F2 - Processing parameters
SI                       1024
SF                 400.1300371 MHz
WDW                      SINE
SSB                         0
LB                       0.00 Hz
GB                          0
PC                       1.40
SR                      37.11 Hz

F1 - Processing parameters
SI                       1024
MC2                        QF
SF                 400.1300371 MHz
WDW                      SINE
SSB                         0
LB                       0.00 Hz
GB                          0
```

HSQC



10
(fast isomer)



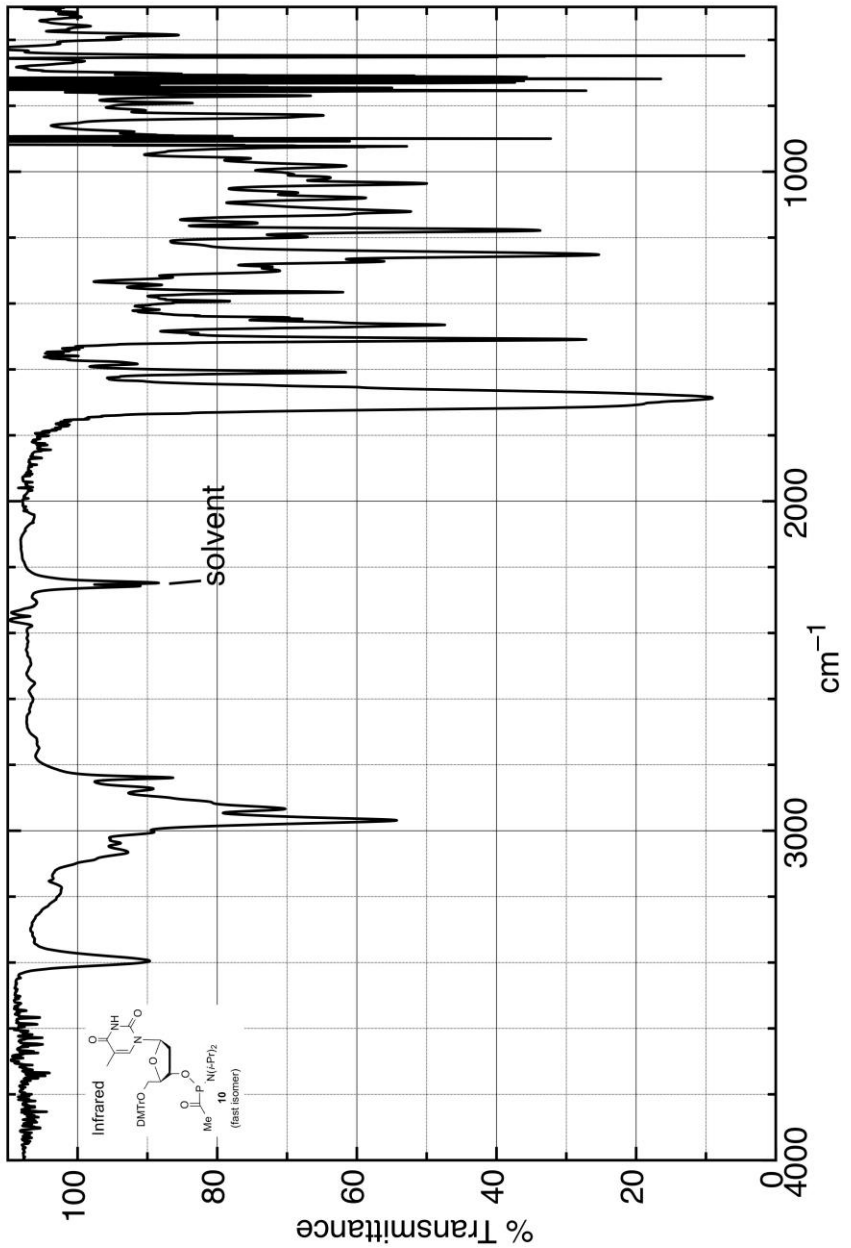
BRUKER

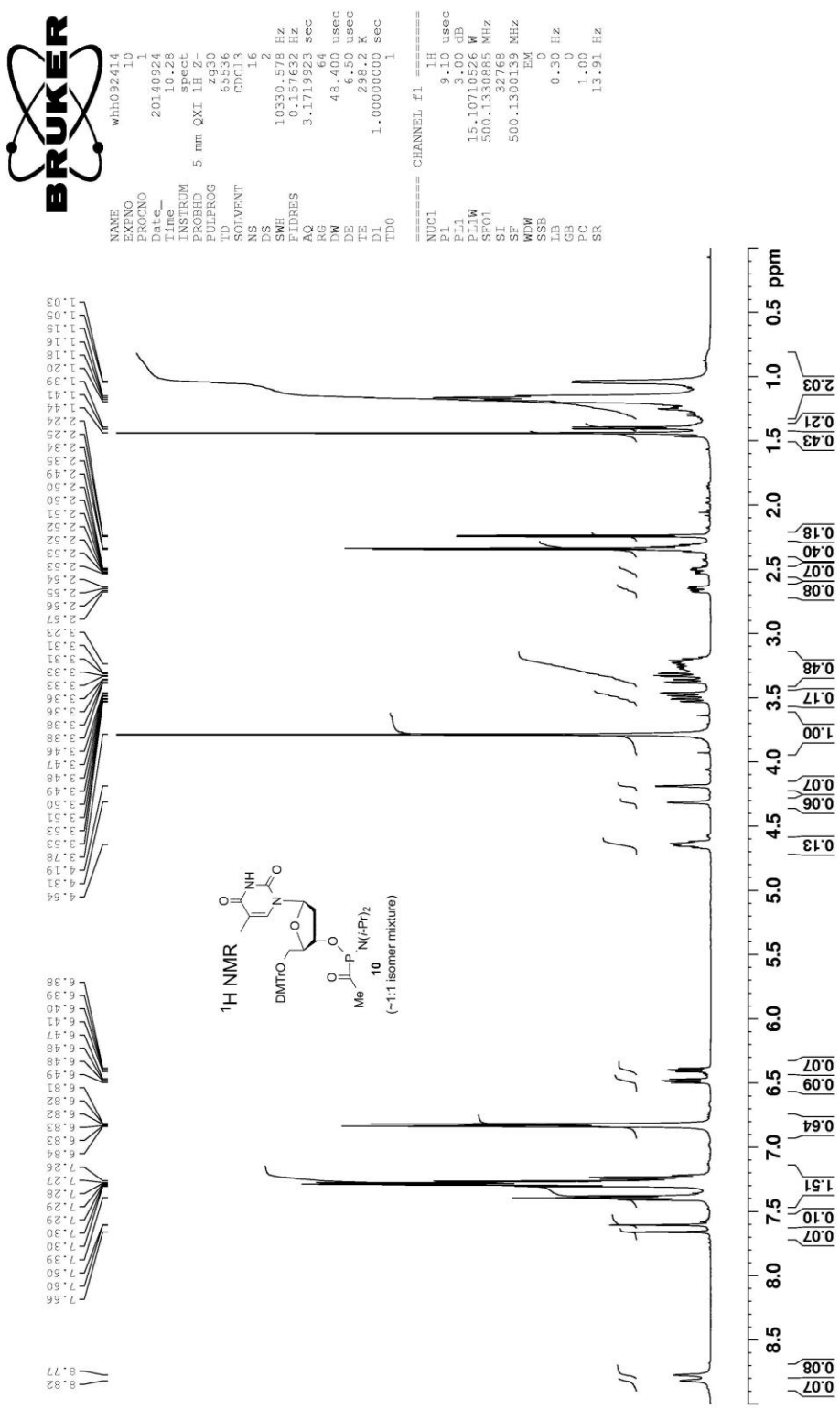
```
NAME                 WM041014
EXPNO                      14
PROCNO                      1
Date_              20140410
Time                    14.37
INSTRUM                 spect
PROBHD    5 mm QXI 1H Z-
PULPROG       hsqcetgpsi2
TD                       1024
SOLVENT                 CDCl3
NS                          2
DS                         16
SWH                  6666.667 Hz
FIDRES               6.510417 Hz
AQ                 0.0768500 sec
RG                        2050
DW                     75.000 usec
DE                      6.50 usec
TE                     298.3 K
CNST2              145.0000000
D0                 0.00000300 sec
D1                 1.50000000 sec
D4                 0.00172414 sec
D11                0.03000000 sec
D13                0.00000400 sec
D16                0.00020000 sec
D24                0.00086207 sec
IN0                0.00002400 sec
ZGOPTNS

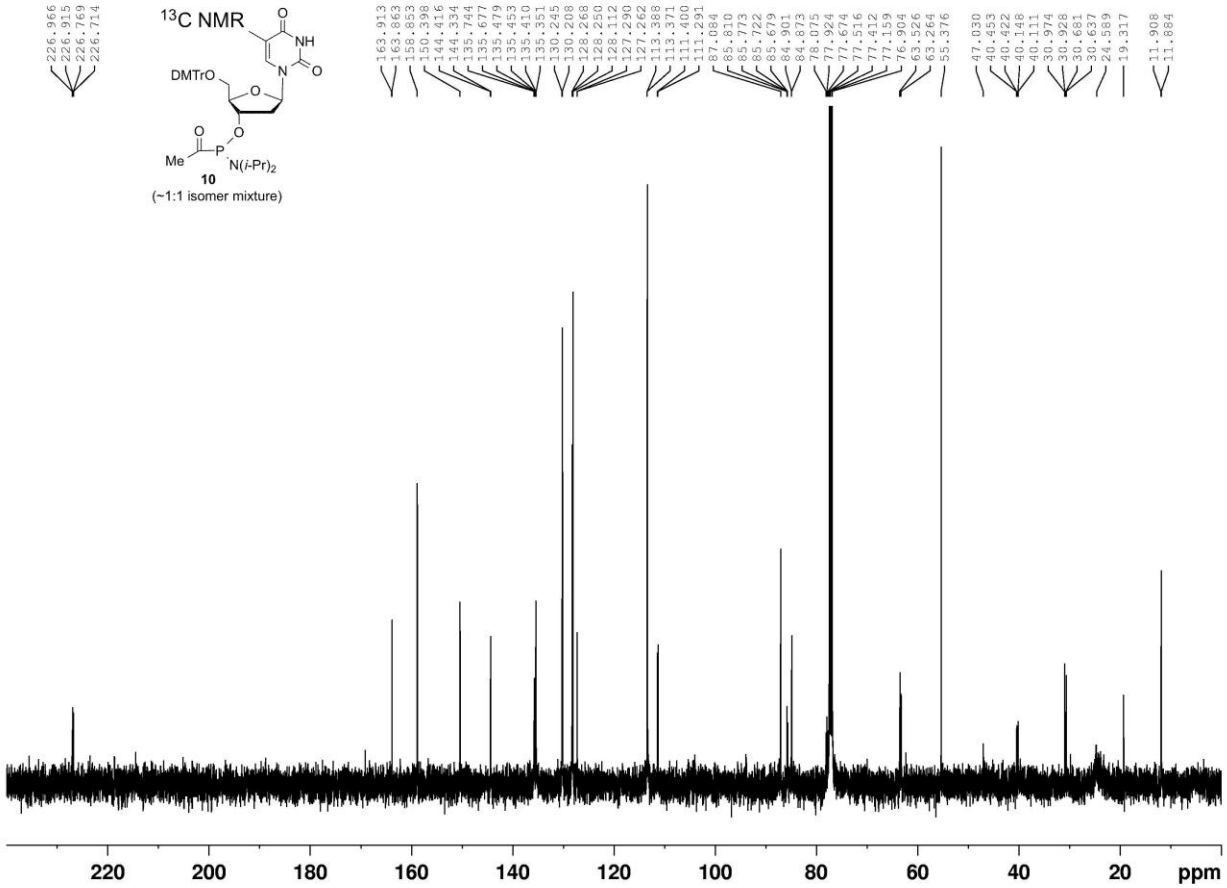
======== CHANNEL f1 ========
NUC1                       1H
P1                       9.10 usec
P2                      18.20 usec
P28                   1000.00 usec
PL1                      3.00 dB
PL1W               15.10710526 W
SFO1              500.1330069 MHz

======== CHANNEL f2 ========
CPDPRG2                 garp
NUC2                     13C
P3                      15.50 usec
P4                      31.00 usec
PCPD2                   65.00 usec
PL2                     -1.00 dB
PL12                    11.45 dB
PL2W              132.81565857 W
PL12W               7.55525827 W
SFO2              125.7672177 MHz

====== GRADIENT CHANNEL =====
GPNAM1                SINE.100
GPNAM2                SINE.100
GPNAM3                SINE.100
GPNAM4                SINE.100
GPZ1                    80.00 %
GPZ2                    20.10 %
GPZ3                    11.00 %
GPZ4                    -5.00 %
P16                   1000.00 usec
P19                    600.00 usec
ND0                         2
TD                        256
SFO1              125.7672 MHz
FIDRES             81.380234 Hz
SW                   165.650 ppm
FnMODE          Echo-Antiecho
SI                       1024
SF                500.1300126 MHz
WDW                     QSINE
SSB                         2
LB                       0.00 Hz
GB                          0
PC                       1.40
SR                      12.59 Hz
SI                       1024
MC2             echo-antiecho
SF                125.7577722 MHz
WDW                     QSINE
SSB                         2
LB                       0.00 Hz
GB                          0
```

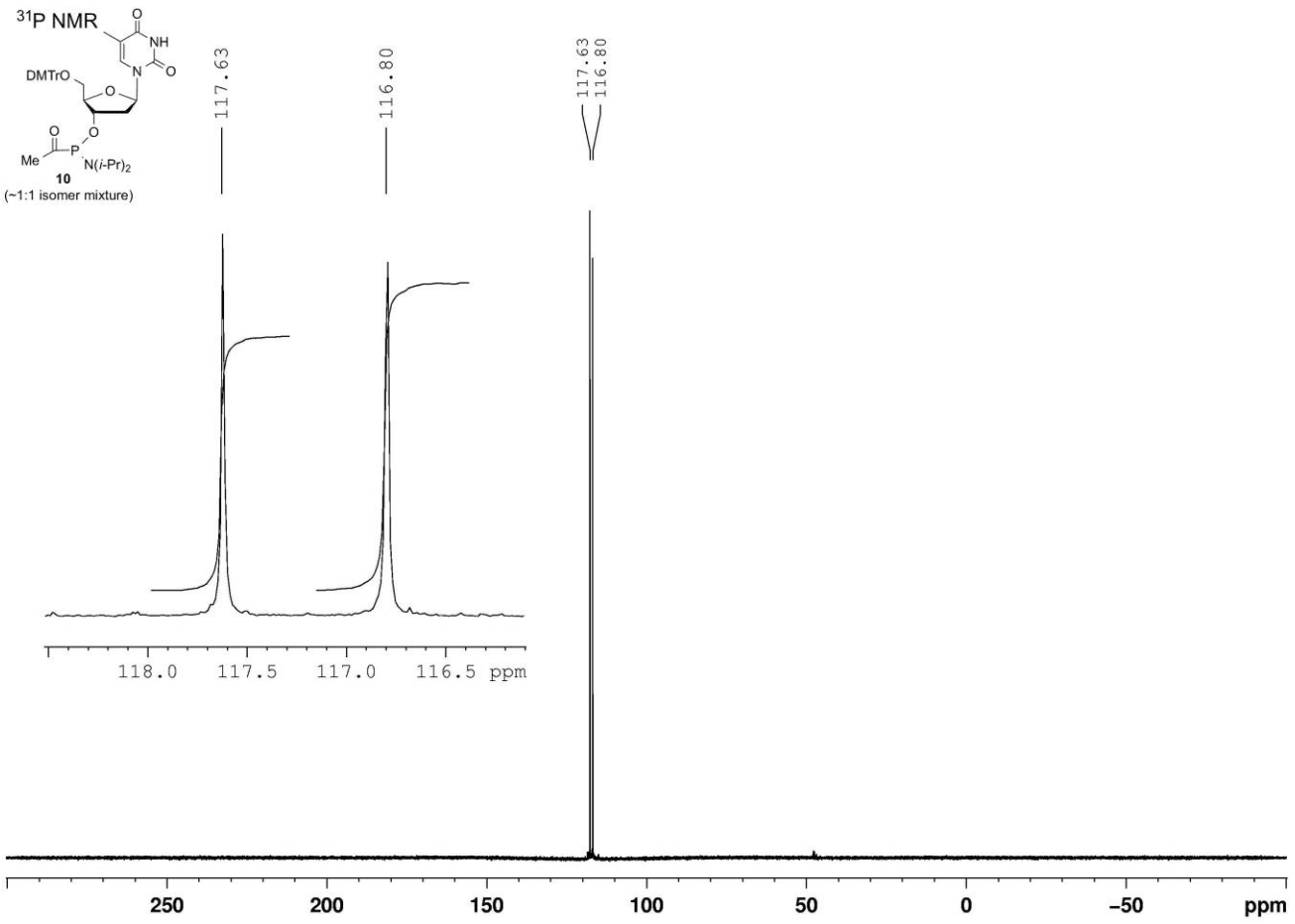

Infrared
DMTrO
Me
10
(fast isomer)
solvent
% Transmittance
cm−1
100
80
60
40
20
0
4000
3000
2000
1000


BRUKER
NAME whh092414
EXPNO 10
PROCNO 1
Date_ 20140924
Time 10.28
INSTRUM spect
PROBHD 5 mm QXI 1H Z-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 64
DW 48.400 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.10 usec
PL1 3.00 dB
PL1W 15.10710526 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300139 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
SR 13.91 Hz
^{1}H NMR
DMTrO
Me
N(i-Pr)$_2$
10
(~1:1 isomer mixture)
ppm



BRUKER

NAME	whh092414
EXPNO	11
PROCNO	1
Date_	20140924
Time	12.22
INSTRUM	spect
PROBHD	5 mm QXI 1H Z-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	2048
DS	4
SWH	35714.285 Hz
FIDRES	0.544957 Hz
AQ	0.9175540 sec
RG	456
DW	14.000 usec
DE	6.50 usec
TE	298.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	15.50 usec
PL1	-1.00 dB
PL1W	132.81565857 W
SFO1	125.7716224 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	3.00 dB
PL12	21.88 dB
PL13	120.00 dB
PL2W	15.10710526 W
PL12W	0.19551556 W
PL13W	0.00000000 W
SFO2	500.1320005 MHz
SI	32768
SF	125.7577745 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40
SR	-14.54 Hz



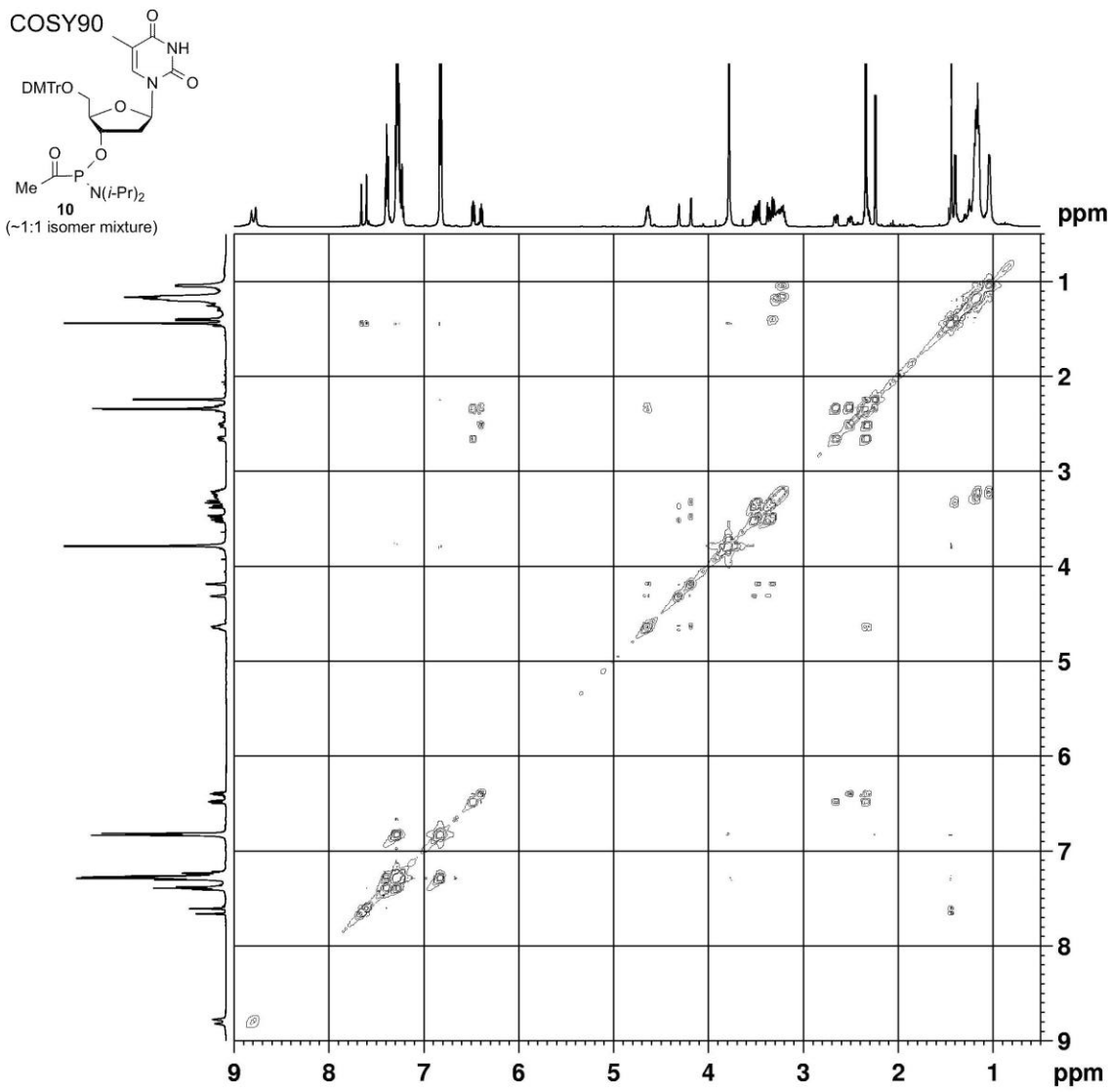

```
Current Data Parameters
NAME                 whh040214
EXPNO                       11
PROCNO                       1

F2 - Acquisition Parameters
Date_               20140402
Time                   21.59
INSTRUM                spect
PROBHD    5 mm QNP  1H/1
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      512
DS                        4
SWH                64935.066 Hz
FIDRES             0.990830 Hz
AQ                 0.5046772 sec
RG                   20642.5
DW                     7.700 usec
DE                     6.00 usec
TE                     299.2 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       31P
P1                        4.65 usec
PL1                      -6.00 dB
SFO1             161.9917906 MHz

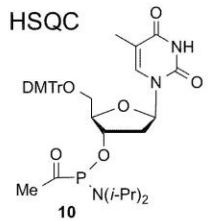
======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                  100.00 usec
PL2                      -6.00 dB
PL12                     13.91 dB
PL13                    120.00 dB
SFO2             400.1316005 MHz

F2 - Processing parameters
SI                        32768
SF               161.9755358 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
SR                       -57.24 Hz
```



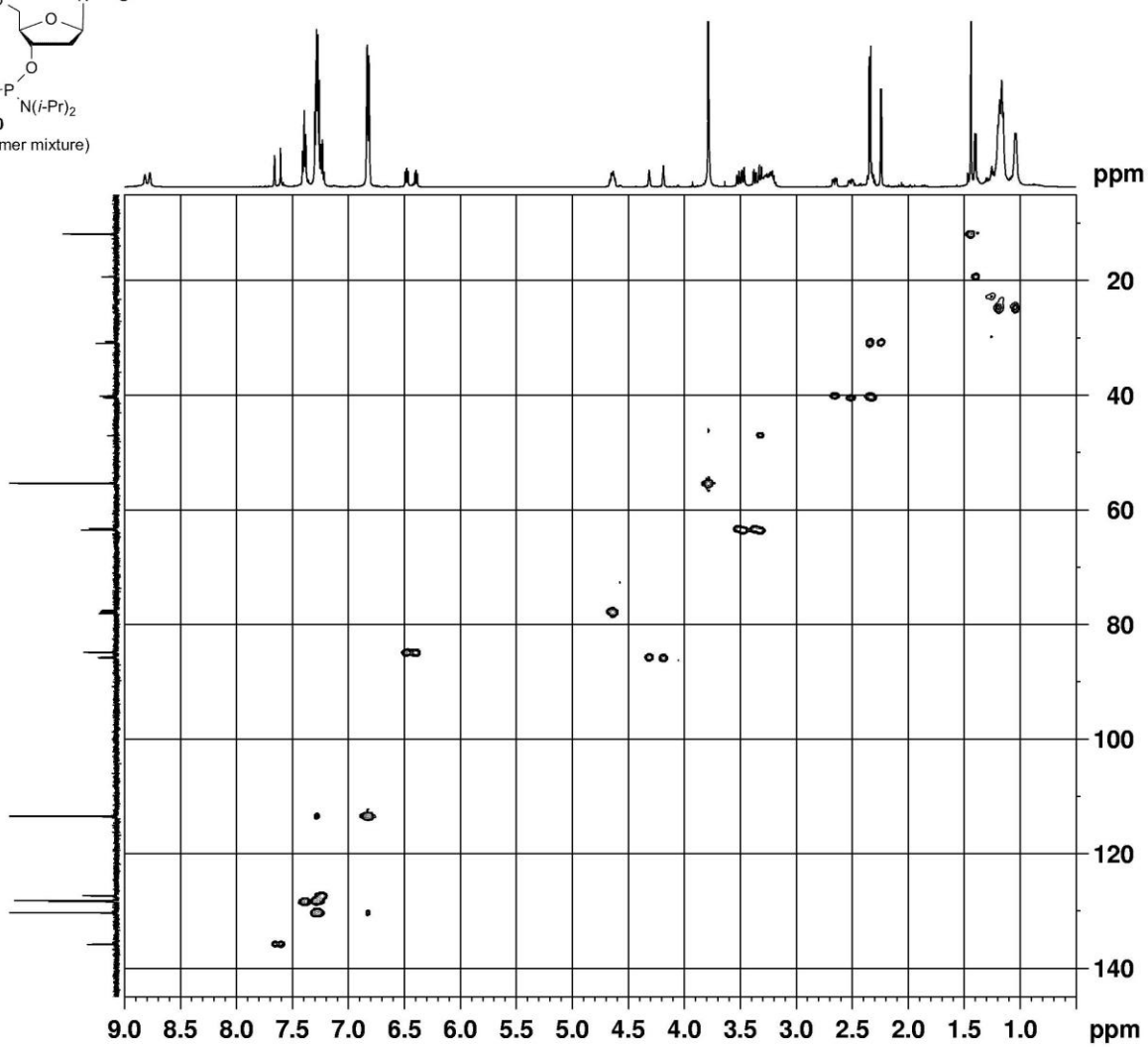
NAME	whh092414
EXPNO	14
PROCNO	1
Date_	20140924
Time	14.02
INSTRUM	spect
PROBHD	5 mm QXI 1H Z-
PULPROG	cosygf90
TD	2048
SOLVENT	CDCl3
NS	8
DS	4
SWH	5154.639 Hz
FIDRES	2.516914 Hz
AQ	0.1987060 sec
RG	71.8
DW	97.000 usec
DE	6.50 usec
TE	298.2 K
D0	0.00000300 sec
D1	2.00000000 sec
IN0	0.00019395 sec
======== CHANNEL f1 ========	
NUC1	1H
P1	9.10 usec
PL1	3.00 dB
PL1W	15.10710526 W
SFO1	500.1323164 MHz
ND0	1
TD	256
SFO1	500.1323 MHz
FIDRES	20.142307 Hz
SW	10.310 ppm
FnMODE	QF
SI	1024
SF	500.1300139 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.40
SR	13.91 Hz
SI	1024
MC2	QF
SF	500.1300139 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

HSQC



10

(~1:1 isomer mixture)



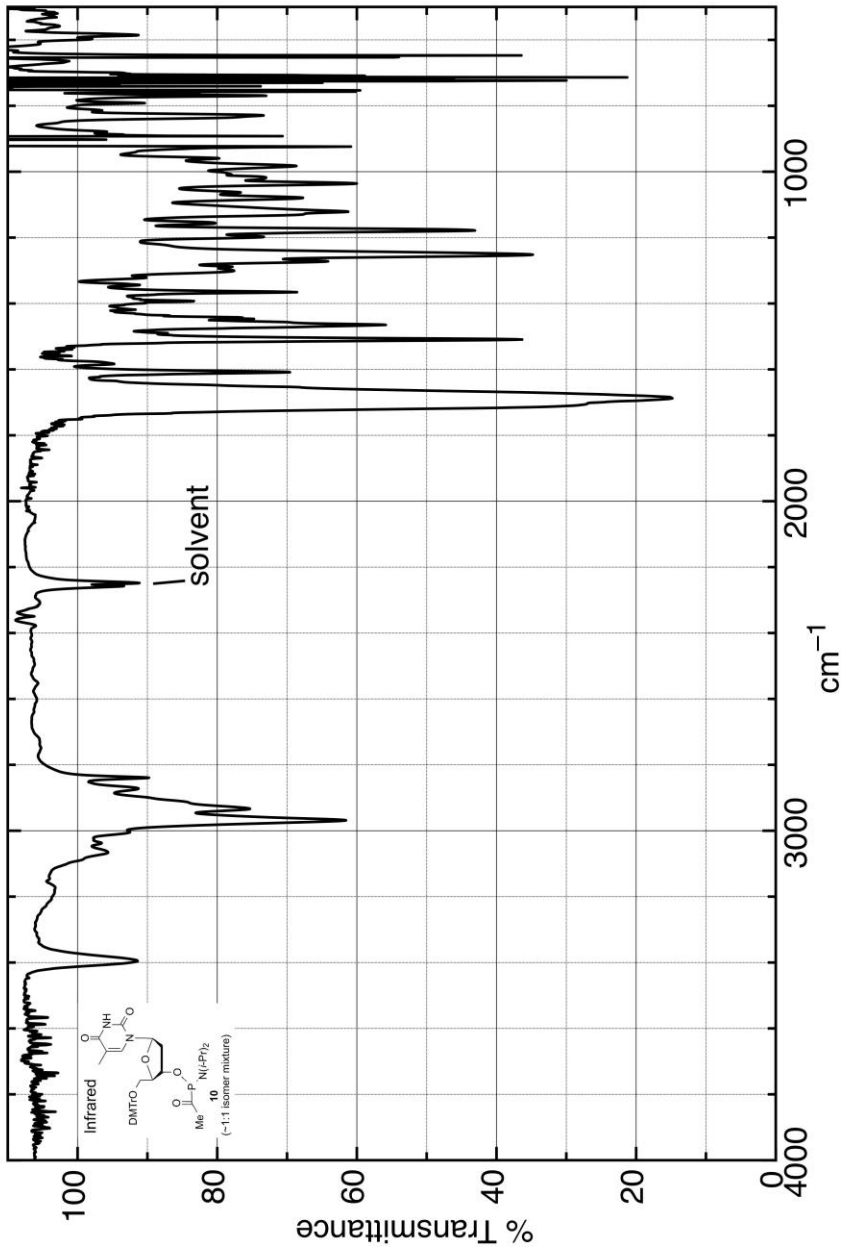
BRUKER

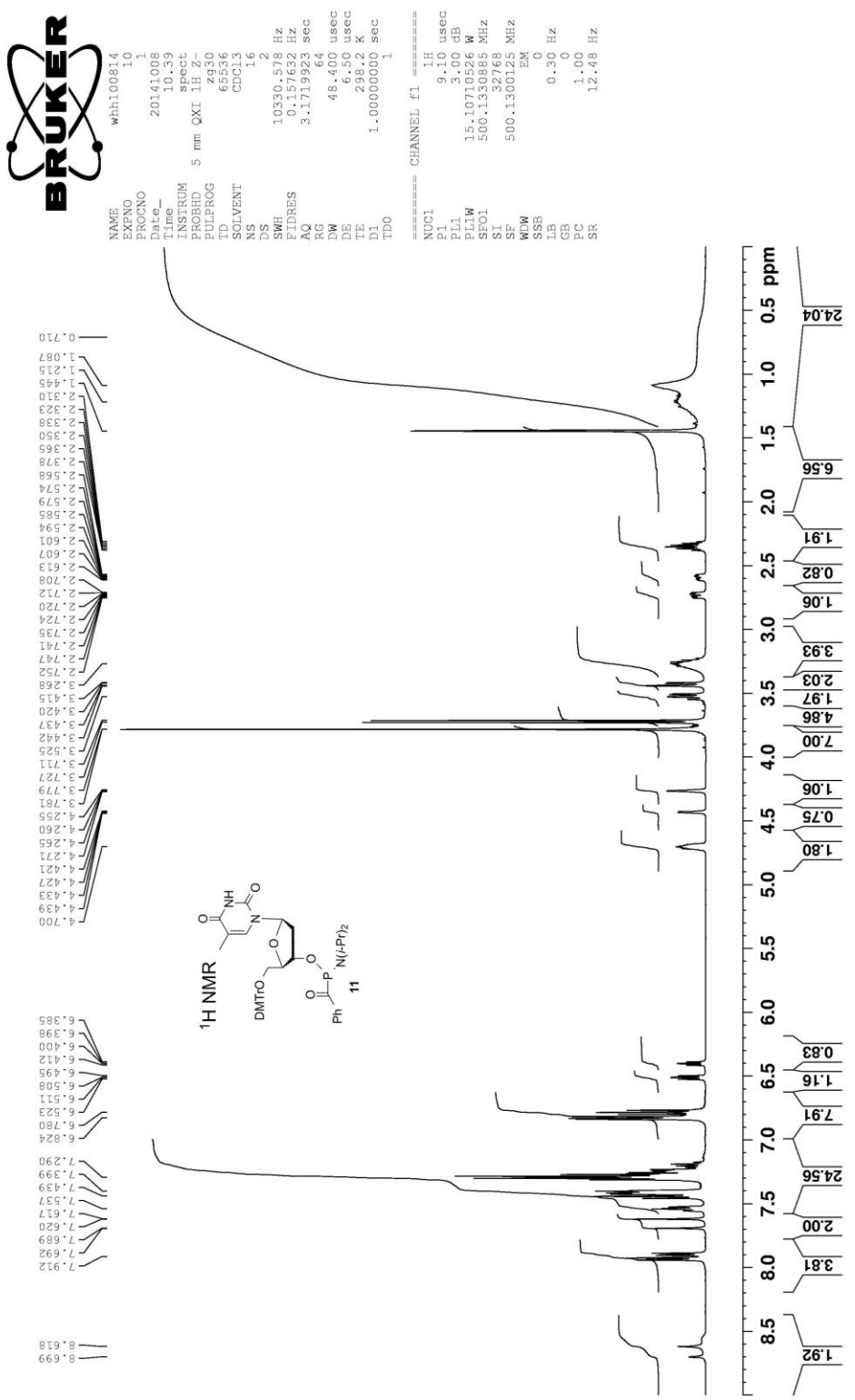
```
NAME                 WH092414
EXPNO                      13
PROCNO                      1
Date_              20140924
Time                    13.35
INSTRUM                  spect
PROBHD    5 mm QXI 1H Z-
PULPROG       hsqcetgpsi2
TD                       1024
SOLVENT                  CDCl3
NS                          2
DS                         16
SWH                 6666.667 Hz
FIDRES              6.510417 Hz
AQ                  0.0768500 sec
RG                       2050
DW                     75.000 usec
DE                      6.50 usec
TE                     298.4 K
CNST2              145.0000000
D0                  0.00000300 sec
D1                  1.50000000 sec
D4                  0.00172414 sec
D11                 0.03000000 sec
D13                 0.00000400 sec
D16                 0.00020000 sec
D24                 0.00086207 sec
IN0                 0.00002210 sec
ZGOPTNS

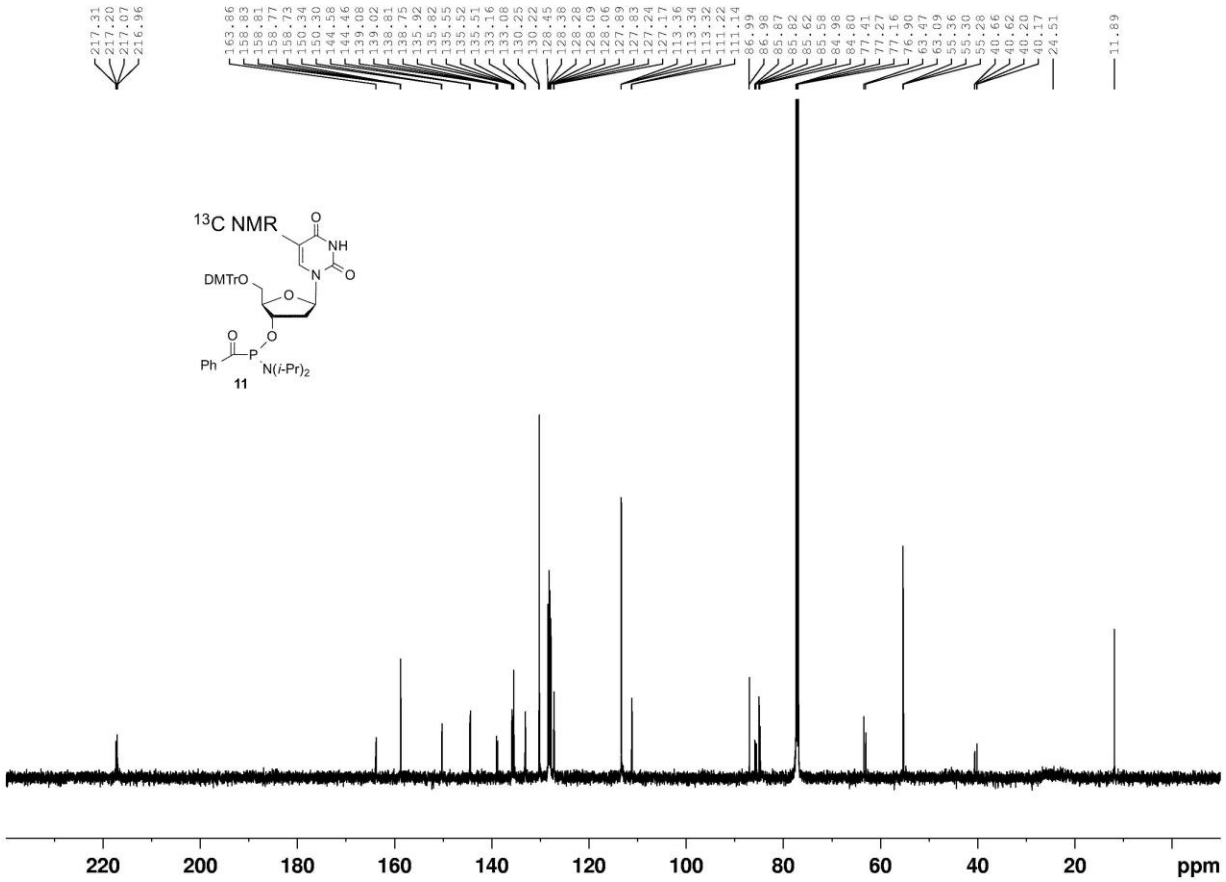
======== CHANNEL f1 ========
NUC1                       1H
P1                       9.10 usec
P2                      18.20 usec
P28                   1000.00 usec
PL1                      3.00 dB
PL1W               15.10710526 W
SFO1              500.1330069 MHz

======== CHANNEL f2 ========
CPDPRG2                 garp
NUC2                      13C
P3                      15.50 usec
P4                      31.00 usec
PCPD2                   70.00 usec
PL2                     -1.00 dB
PL12                    12.10 dB
PL2W               132.81565857 W
PL12W                6.50502920 W
SFO2              125.7672177 MHz

====== GRADIENT CHANNEL =====
GPNAM1                SINE.100
GPNAM2                SINE.100
GPNAM3                SINE.100
GPNAM4                SINE.100
GPZ1                    80.00 %
GPZ2                    20.10 %
GPZ3                    11.00 %
GPZ4                    -5.00 %
P16                   1000.00 usec
P19                    600.00 usec
ND0                         2
TD                        256
SFO1              125.7672 MHz
FIDRES             88.430077 Hz
SW                   180.000 ppm
FnMODE          Echo-Antiecho
SI                       1024
SF                500.1300139 MHz
WDW                     QSINE
SSB                         2
LB                      0.00 Hz
GB                          0
PC                       1.40
SR                      13.91 Hz
SI                       1024
MC2             echo-antiecho
SF                125.7577745 MHz
WDW                     QSINE
SSB                         2
LB                      0.00 Hz
GB                          0
```

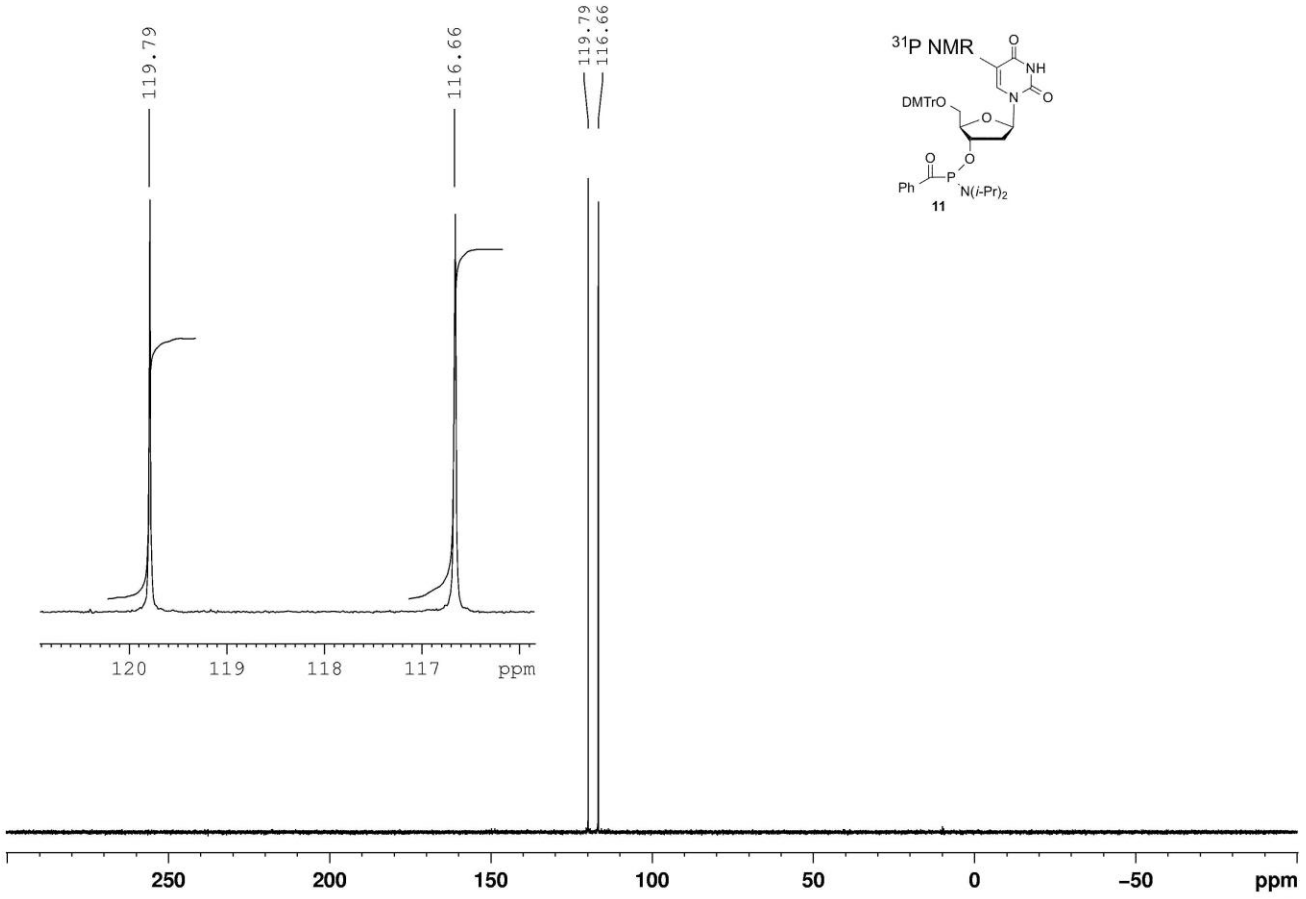

Infrared
DMTrO
Me
10
(~1:1 isomer mixture)
solvent
% Transmittance
cm−1
100
80
60
40
20
0
4000
3000
2000
1000


BRUKER
NAME whh100814
EXPNO 10
PROCNO 1
Date_ 20141008
Time 10.39
INSTRUM spect
PROBHD 5 mm QXI 1H Z-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 64
DW 48.400 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
TDO 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.10 usec
PL1 3.00 dB
PL1W 15.10710526 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300125 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
SR 12.48 Hz
1H NMR
11
DMTrO
Ph
N(i-Pr)2
ppm



BRUKER

NAME	whh100814
EXPNO	11
PROCNO	1
Date_	20141008
Time	14.10
INSTRUM	spect
PROBHD	5 mm QXI 1H Z-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	4096
DS	4
SWH	35714.285 Hz
FIDRES	0.544957 Hz
AQ	0.9175540 sec
RG	456
DW	14.000 usec
DE	6.50 usec
TE	298.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	15.50 usec
PL1	-1.00 dB
PL1W	132.81565857 W
SFO1	125.7716224 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	3.00 dB
PL12	21.88 dB
PL13	120.00 dB
PL2W	15.10710526 W
PL12W	0.19551556 W
PL13W	0.00000000 W
SFO2	500.1320005 MHz
SI	32768
SF	125.7577745 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40
SR	-14.52 Hz



^{31}P NMR

11

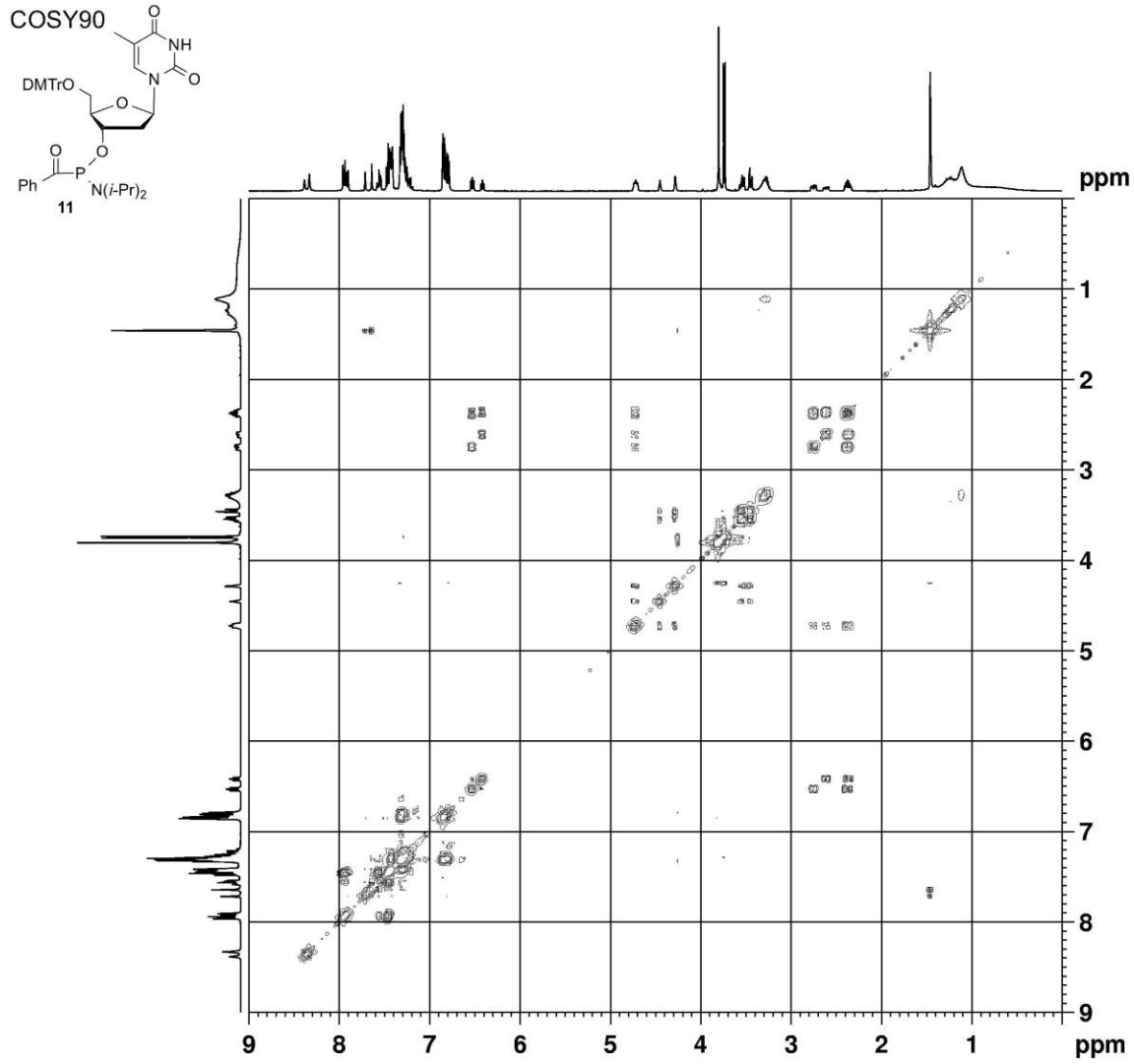
```
Current Data Parameters
NAME                 whh091814
EXPNO                       31
PROCNO                       1

F2 - Acquisition Parameters
Date_               20140919
Time                    16.16
INSTRUM                 spect
PROBHD   5 mm QNP  1H/1
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                        512
DS                          4
SWH                 64935.066 Hz
FIDRES                0.990830 Hz
AQ                    0.5046772 sec
RG                      18390.4
DW                        7.700 usec
DE                        6.00 usec
TE                      293.2 K
D1                    2.00000000 sec
d11                   0.03000000 sec
DELTA                 1.89999998 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       31P
P1                        4.65 usec
PL1                      -6.00 dB
SFO1              161.9917906 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   100.00 usec
PL2                      -6.00 dB
PL12                     14.09 dB
PL13                    120.00 dB
SFO2              400.1316005 MHz

F2 - Processing parameters
SI                         32768
SF                161.9755358 MHz
WDW                           EM
SSB                            0
LB                        1.00 Hz
GB                             0
PC                        1.40
SR                       -57.24 Hz
```



BRUKER

```
Current Data Parameters
NAME                 whh091814
EXPNO                       65
PROCNO                       1

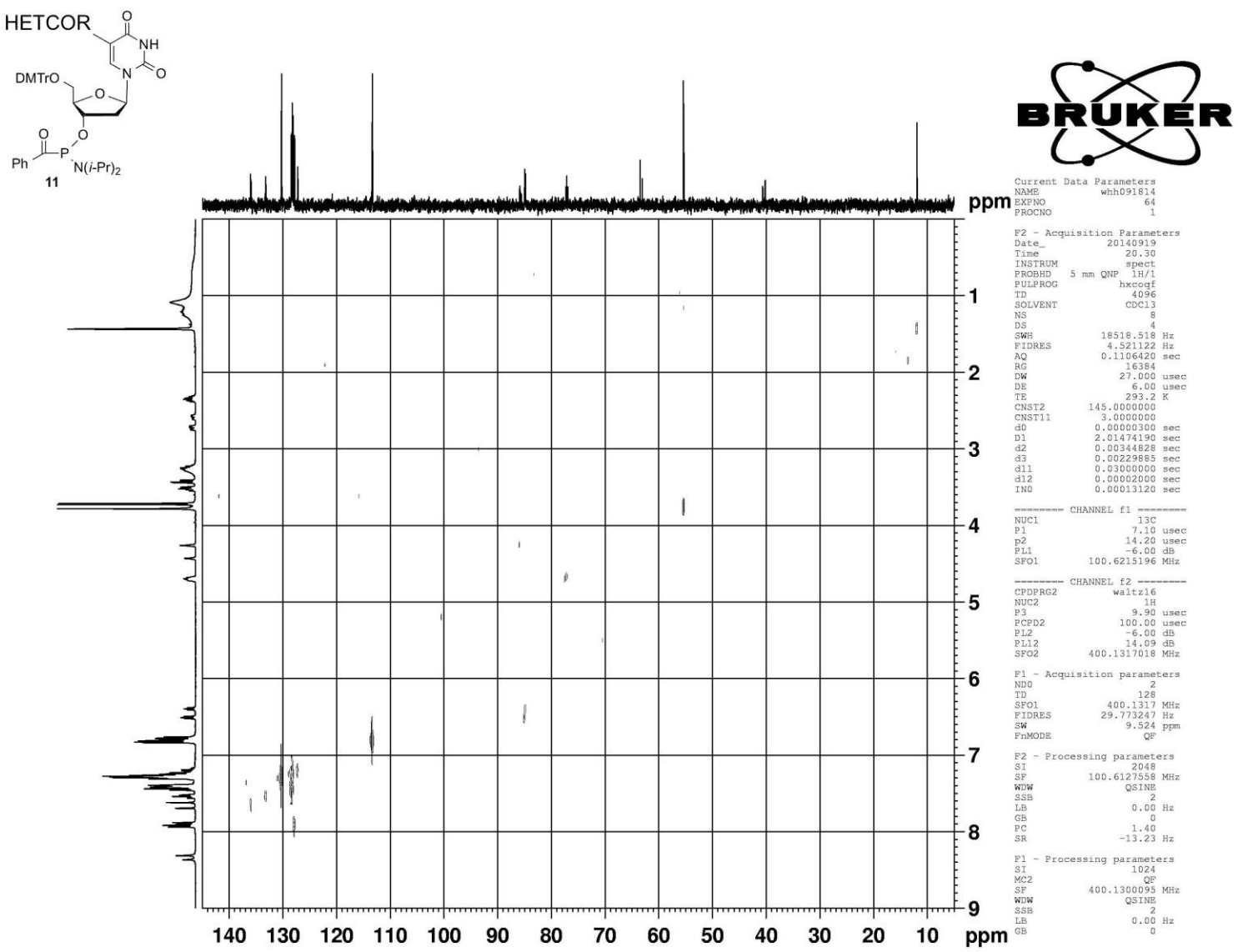
F2 - Acquisition Parameters
Date_               20140919
Time                    21.08
INSTRUM                 spect
PROBHD    5 mm QNP  1H/1
PULPROG              cosyqf90
TD                       2048
SOLVENT                 CDCl3
NS                          8
DS                          4
SWH                 3810.976 Hz
FIDRES              1.860828 Hz
AQ                  0.2687476 sec
RG                      203.2
DW                  131.200 usec
DE                    6.00 usec
TE                    293.2 K
d0                0.00000300 sec
D1                1.98074806 sec
IN0               0.00026240 sec

======== CHANNEL f1 ========
NUC1                        1H
P1                       9.90 usec
PL1                     -6.00 dB
SFO1             400.1317018 MHz

F1 - Acquisition parameters
ND0                         1
TD                        256
SFO1               400.1317 MHz
FIDRES            14.886623 Hz
SW                     9.524 ppm
FnMODE                     QF

F2 - Processing parameters
SI                       1024
SF               400.1300000 MHz
WDW                      SINE
SSB                         0
LB                    0.00 Hz
GB                          0
PC                       1.40
SR                    0.00 Hz

F1 - Processing parameters
SI                       1024
MC2                        QF
SF               400.1300000 MHz
WDW                      SINE
SSB                         0
LB                    0.00 Hz
GB                          0
```



BRUKER

```
Current Data Parameters
NAME                 whh091814
EXPNO                       64
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20140919
Time                     20.30
INSTRUM                  spect
PROBHD    5 mm QNP  1H/1
PULPROG                hxcoqf
TD                       4096
SOLVENT                  CDCl3
NS                          8
DS                          4
SWH                 18518.518 Hz
FIDRES                4.521122 Hz
AQ                    0.1106420 sec
RG                       16384
DW                       27.000 usec
DE                        6.00 usec
TE                       293.2 K
CNST2                145.0000000
CNST11                 3.0000000
d0                    0.00000300 sec
D1                    2.01474190 sec
d2                    0.00344828 sec
d3                    0.00229885 sec
d11                   0.03000000 sec
d12                   0.00002000 sec
IN0                   0.00013120 sec

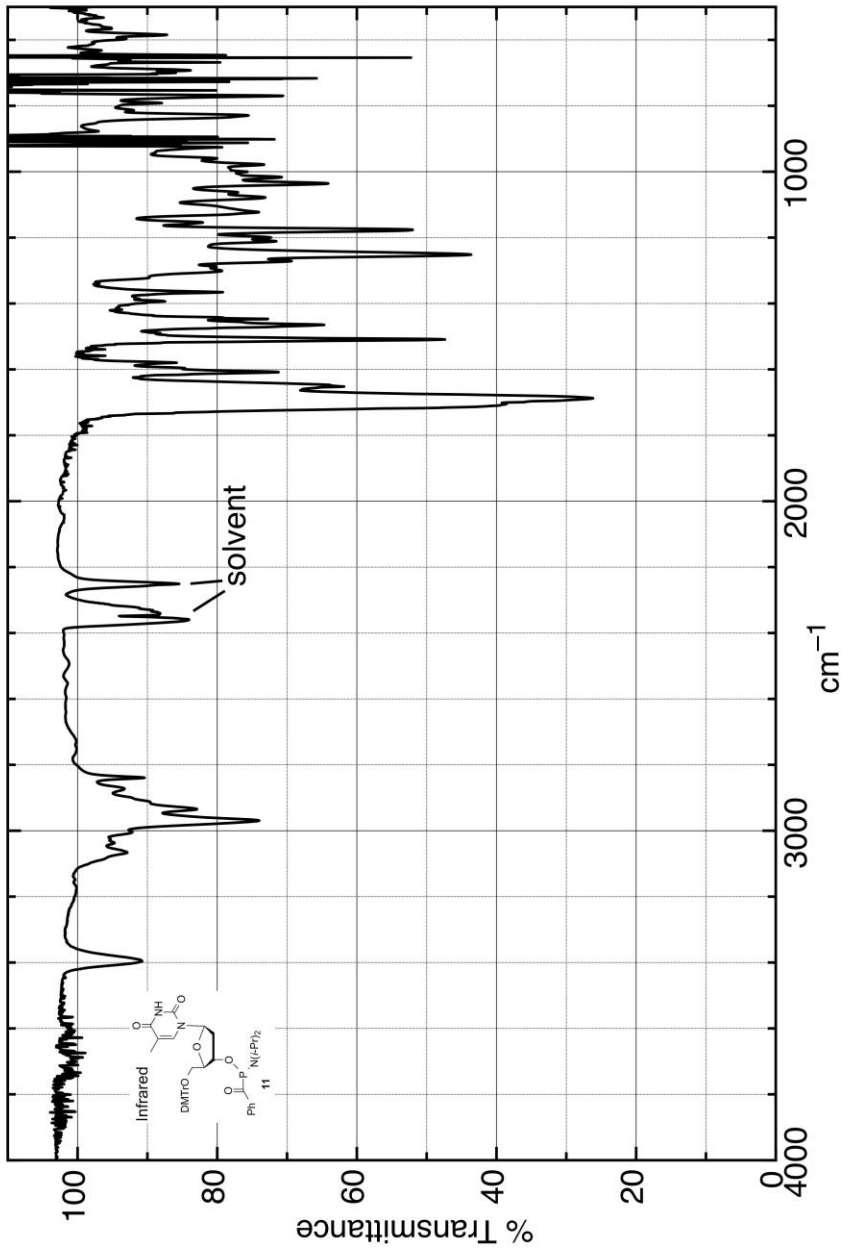
======== CHANNEL f1 ========
NUC1                        13C
P1                         7.10 usec
p2                        14.20 usec
PL1                       -6.00 dB
SFO1                100.6215196 MHz

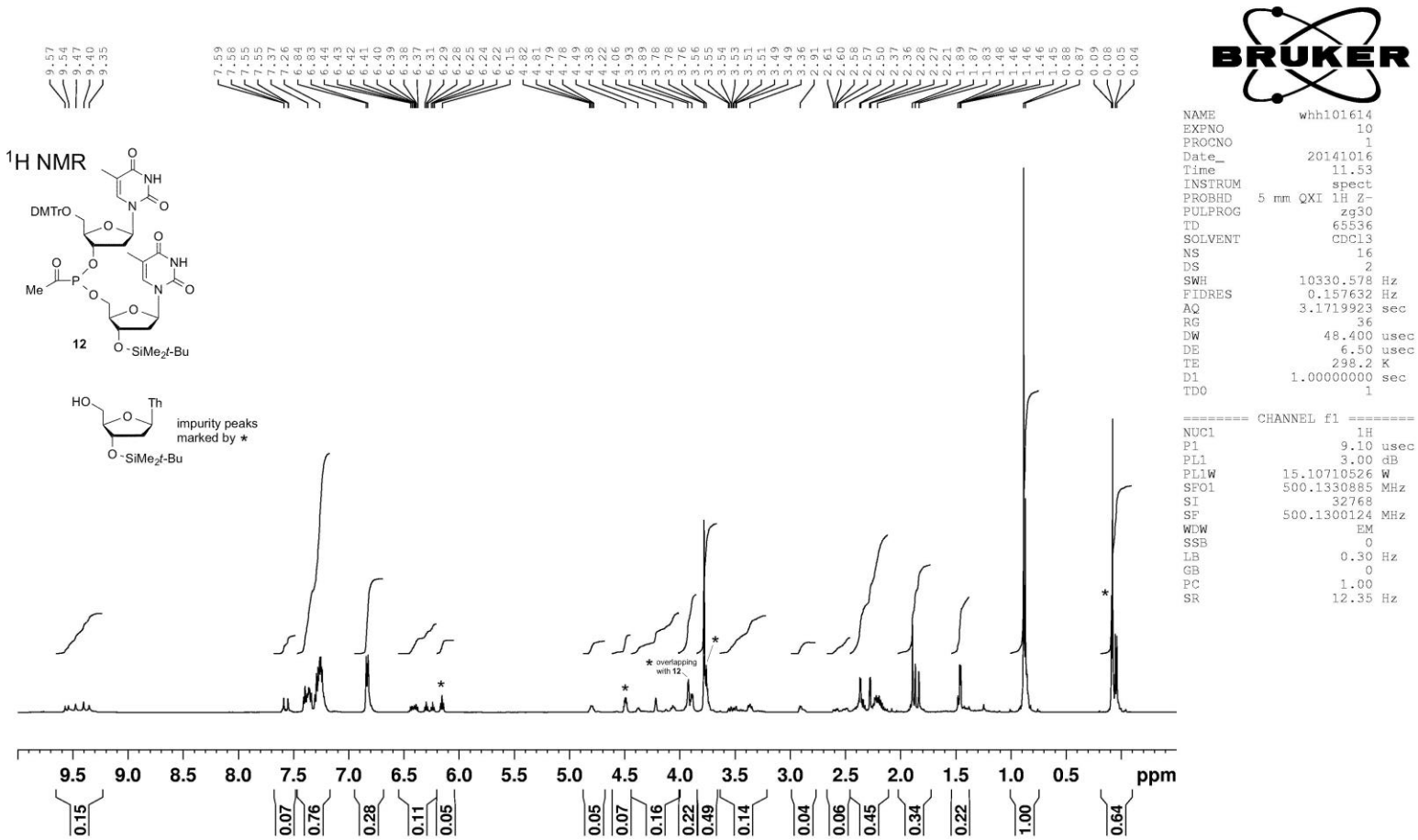
======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                        1H
P3                         9.90 usec
PCPD2                    100.00 usec
PL2                       -6.00 dB
PL12                      14.09 dB
SFO2                400.1317018 MHz

F1 - Acquisition parameters
ND0                         2
TD                        128
SFO1                 400.1317 MHz
FIDRES               29.773247 Hz
SW                        9.524 ppm
FnMODE                       QF

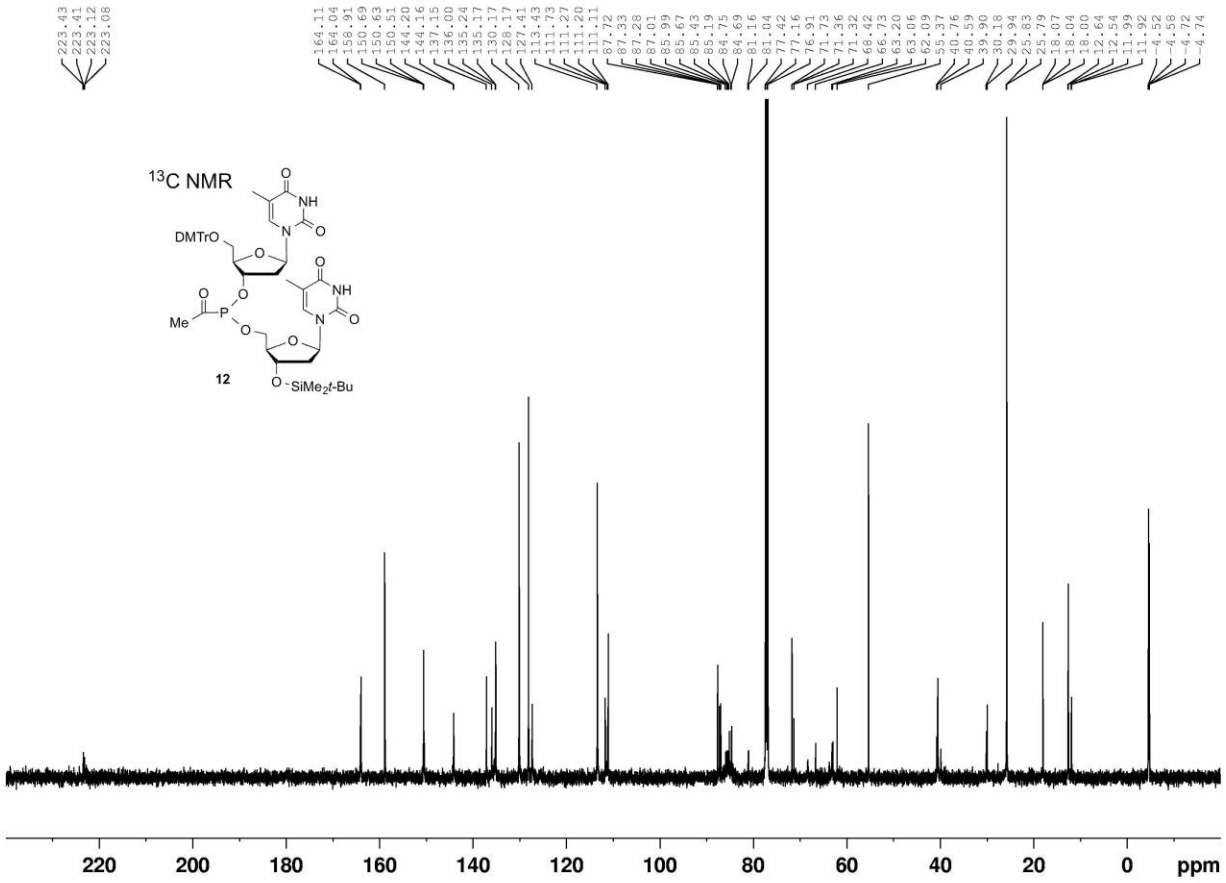
F2 - Processing parameters
SI                       2048
SF                 100.6127558 MHz
WDW                      QSINE
SSB                         2
LB                        0.00 Hz
GB                           0
PC                        1.40
SR                      -13.23 Hz

F1 - Processing parameters
SI                       1024
MC2                         QF
SF                 400.1300095 MHz
WDW                      QSINE
SSB                         2
LB                        0.00 Hz
GB                           0
```

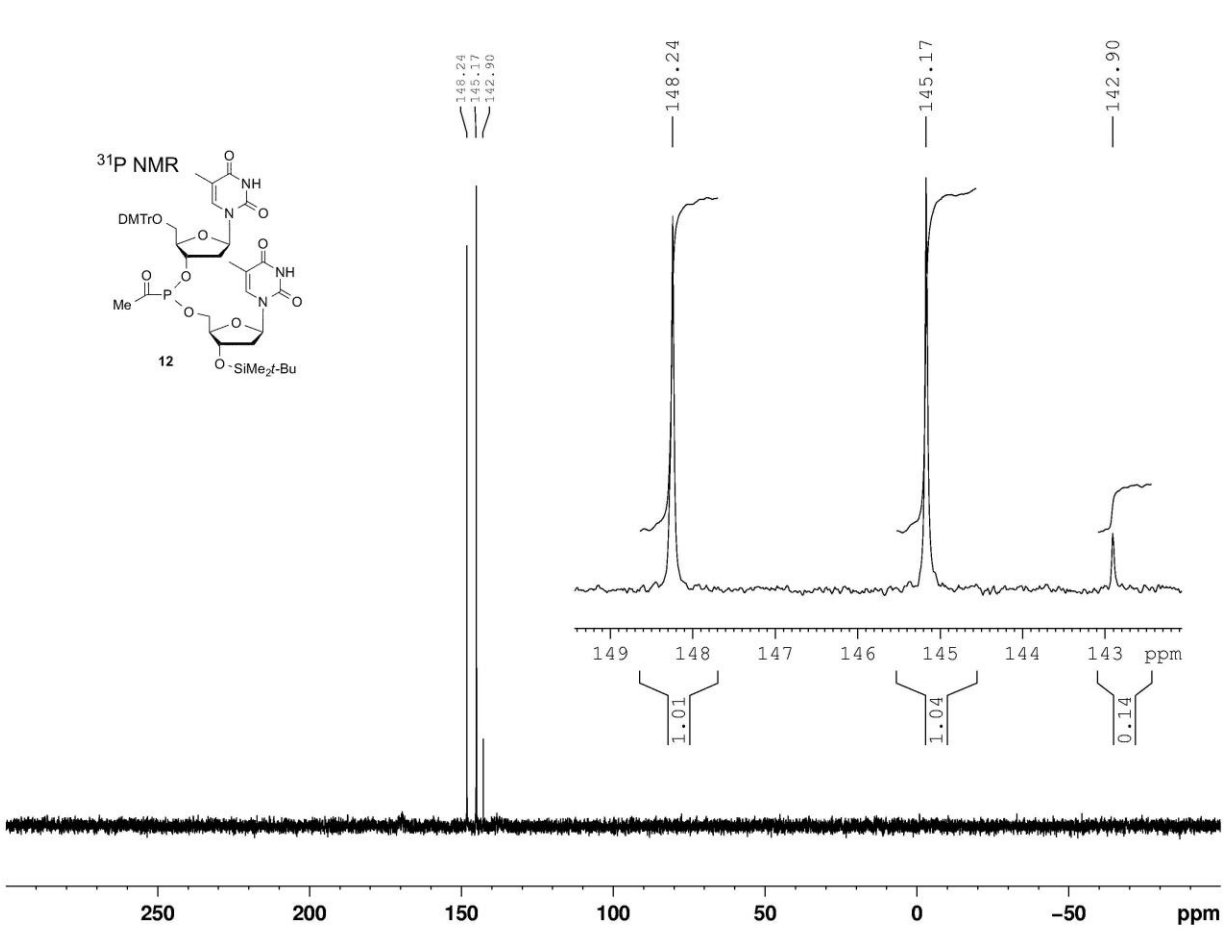

Infrared
solvent
% Transmittance
cm^{-1}
4000
3000
2000
1000
0
20
40
60
80
100
DMTrO
Ph
Ni(i-Pr)$_2$
11



NAME	whh101614
EXPNO	10
PROCNO	1
Date_	20141016
Time	11.53
INSTRUM	spect
PROBHD	5 mm QXI 1H Z-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	10330.578 Hz
FIDRES	0.157632 Hz
AQ	3.1719923 sec
RG	36
DW	48.400 usec
DE	6.50 usec
TE	298.2 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	9.10 usec
PL1	3.00 dB
PL1W	15.10710526 W
SFO1	500.1330885 MHz
SI	32768
SF	500.1300124 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00
SR	12.35 Hz

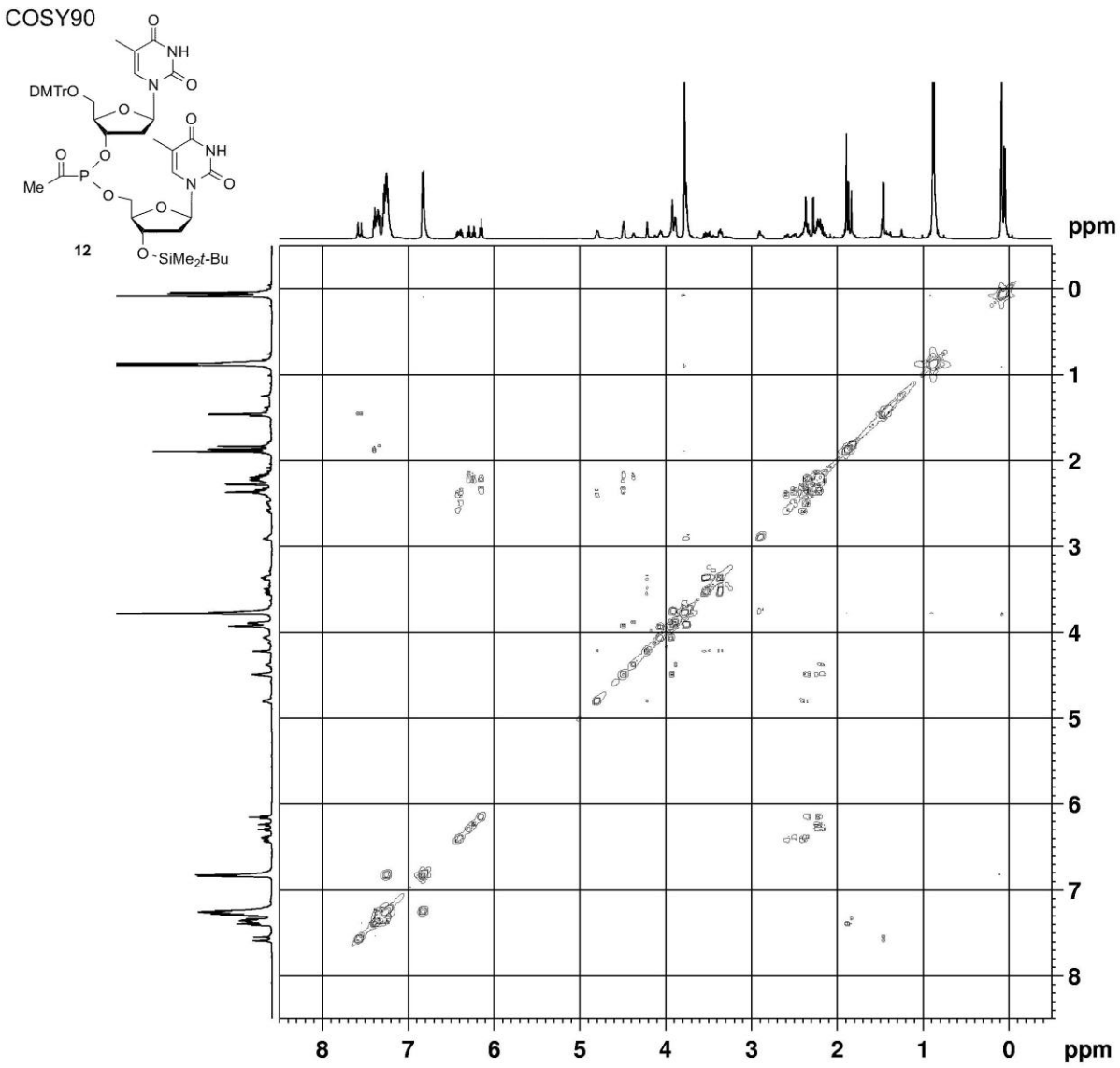


NAME	whh101614
EXPNO	13
PROCNO	1
Date_	20141016
Time	16.24
INSTRUM	spect
PROBHD	5 mm QXI 1H Z-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	4096
DS	4
SWH	35714.285 Hz
FIDRES	0.544957 Hz
AQ	0.9175540 sec
RG	322
DW	14.000 usec
DE	6.50 usec
TE	298.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	15.50 usec
PL1	-1.00 dB
PL1W	132.81565857 W
SFO1	125.7716224 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	3.00 dB
PL12	21.88 dB
PL13	120.00 dB
PL2W	15.10710526 W
PL12W	0.19551556 W
PL13W	0.00000000 W
SFO2	500.1320005 MHz
SI	32768
SF	125.7577767 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40
SR	-12.34 Hz



BRUKER

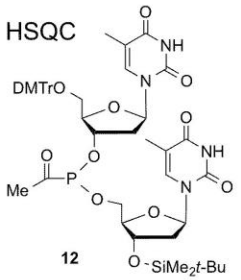
NAME	whh101614
EXPNO	15
PROCNO	1
Date_	20141016
Time	18.07
INSTRUM	spect
PROBHD	5 mm QXI 1H Z-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	128
DS	4
SWH	81521.742 Hz
FIDRES	1.243923 Hz
AQ	0.4020041 sec
RG	2050
DW	6.133 usec
DE	6.50 usec
TE	298.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	31P
P1	38.75 usec
PL1	0.00 dB
PL1W	90.17671967 W
SFO1	202.4765806 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	3.00 dB
PL12	21.88 dB
PL13	120.00 dB
PL2W	15.10710526 W
PL12W	0.19551556 W
PL13W	0.00000000 W
SFO2	500.1320005 MHz
SI	32768
SF	202.4563071 MHz
WDW	EM
SSB	0
LB	4.00 Hz
GB	0
PC	1.40
SR	-27.94 Hz

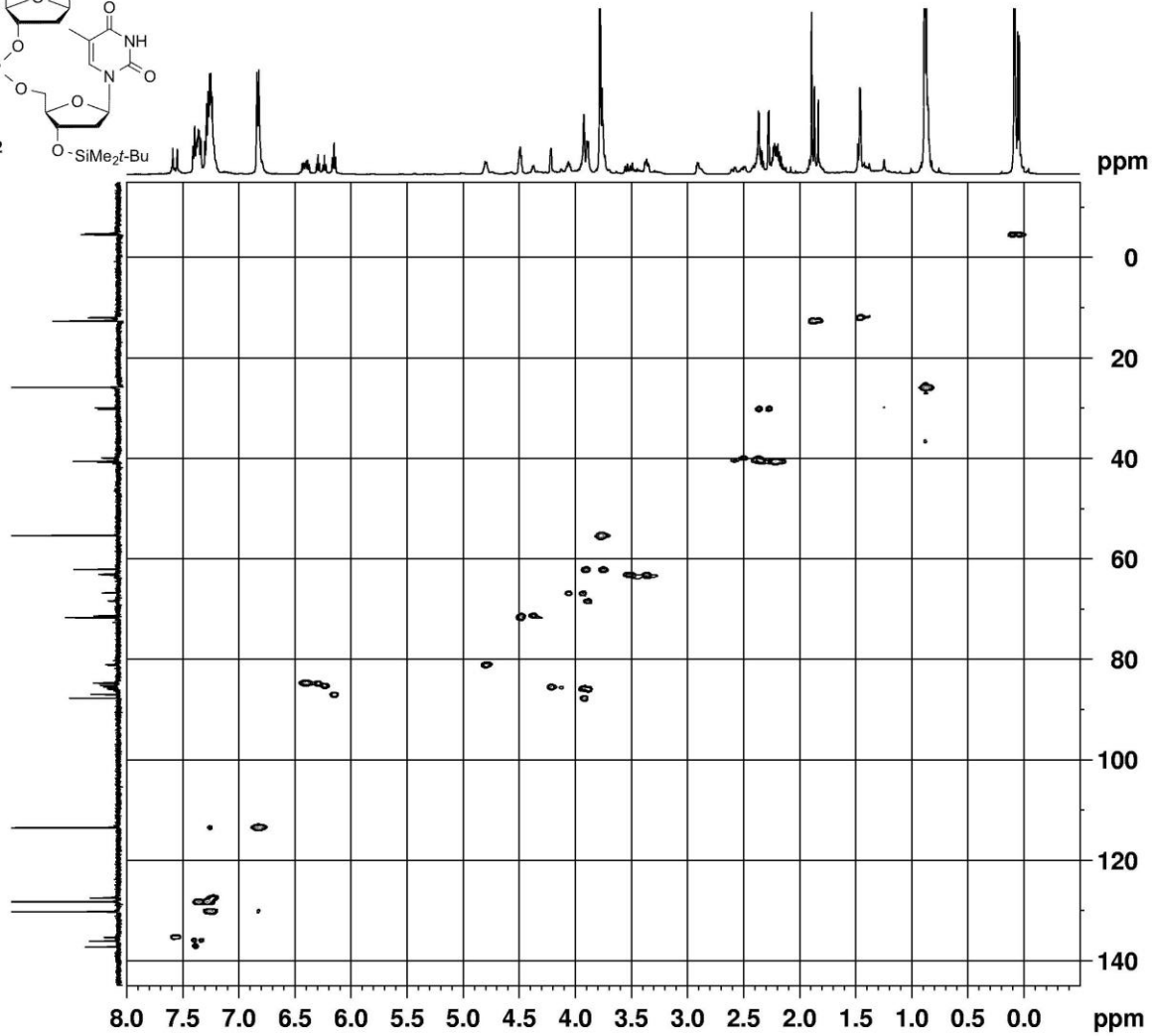


BRUKER

NAME	whh101614	
EXPNO	14	
PROCNO	1	
Date_	20141016	
Time	16.35	
INSTRUM	spect	
PROBHD	5 mm QXI 1H Z-	
PULPROG	cosygf90	
TD	2048	
SOLVENT	CDCl3	
NS	8	
DS	4	
SWH	5154.639	Hz
FIDRES	2.516914	Hz
AQ	0.1987060	sec
RG	28.5	
DW	97.000	usec
DE	6.50	usec
TE	298.2	K
D0	0.00000300	sec
D1	2.00000000	sec
IN0	0.00019395	sec
======== CHANNEL f1 ========		
NUC1	1H	
P1	9.10	usec
PL1	3.00	dB
PL1W	15.10710526	W
SFO1	500.1323164	MHz
ND0	1	
TD	256	
SFO1	500.1323	MHz
FIDRES	20.142307	Hz
SW	10.310	ppm
FnMODE	QF	
SI	1024	
SF	500.1300124	MHz
WDW	SINE	
SSB	0	
LB	0.00	Hz
GB	0	
PC	1.40	
SR	12.35	Hz
SI	1024	
MC2	QF	
SF	500.1300124	MHz
WDW	SINE	
SSB	0	
LB	0.00	Hz
GB	0	

HSQC





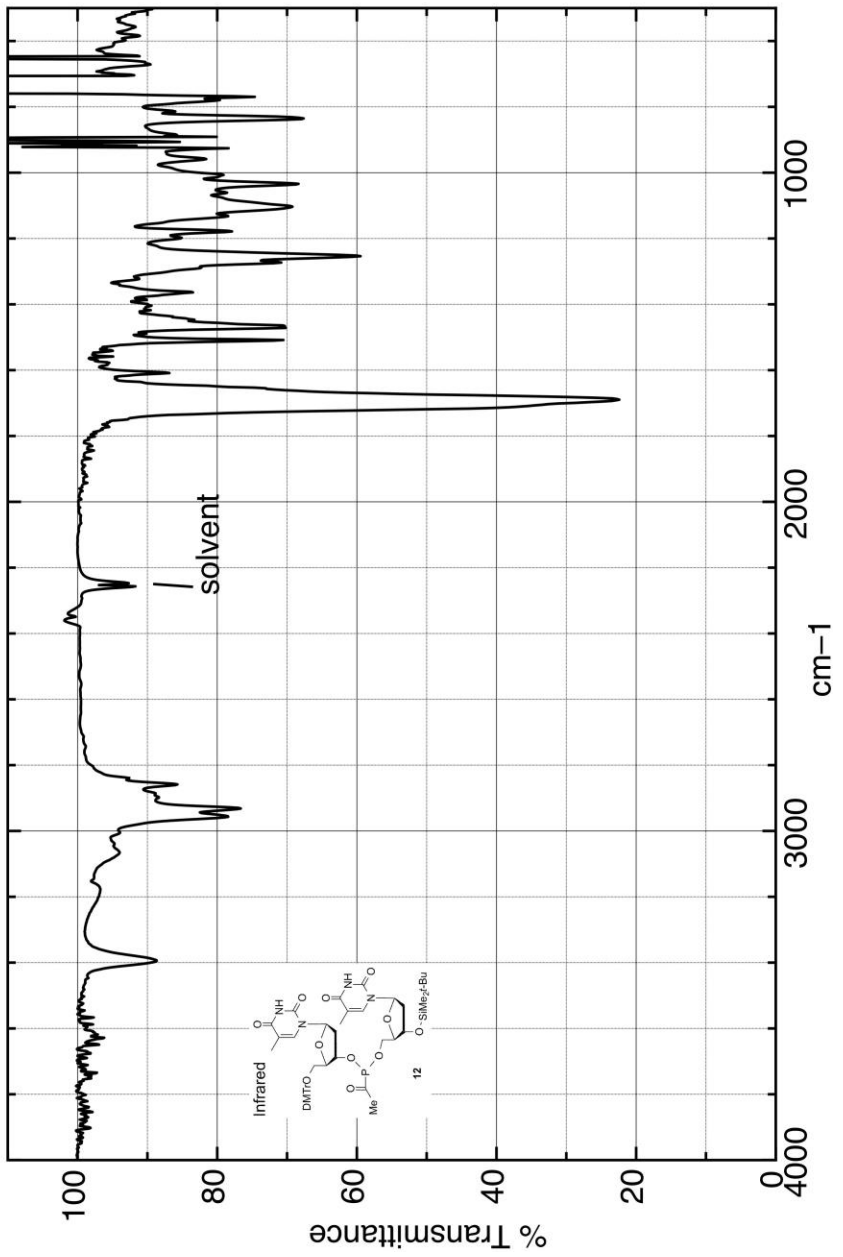
BRUKER

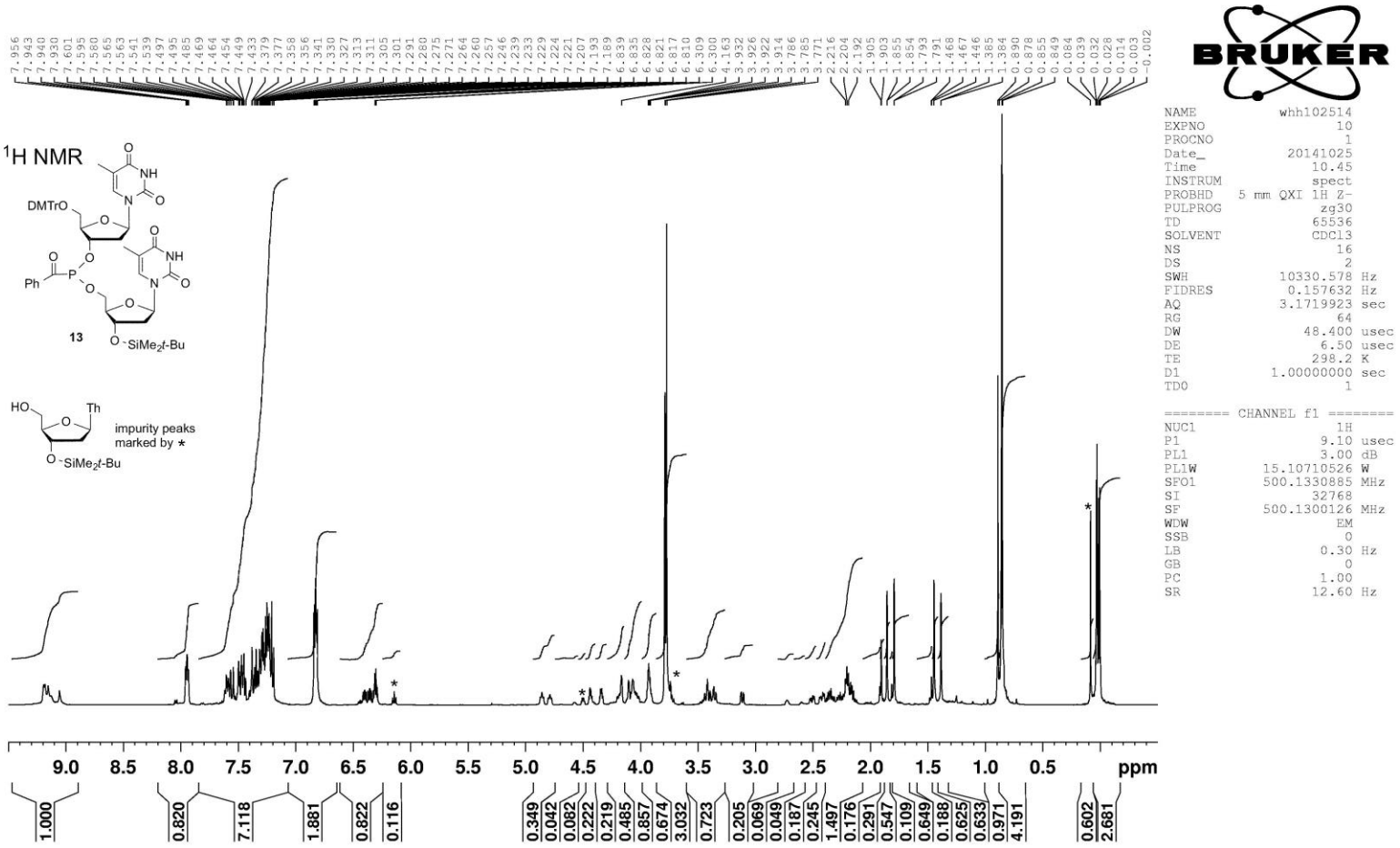
```
NAME                 WH101614
EXPNO                      12
PROCNO                      1
Date_              20141016
Time                    12.36
INSTRUM                 spect
PROBHD    5 mm QXI 1H Z-
PULPROG       hsqcetgpsi2
TD                       1024
SOLVENT                 CDCl3
NS                          2
DS                         16
SWH                  6666.667 Hz
FIDRES               6.510417 Hz
AQ                 0.0768500 sec
RG                        2050
DW                     75.000 usec
DE                      6.50 usec
TE                     298.4 K
CNST2             145.0000000
D0                 0.00000300 sec
D1                 1.50000000 sec
D4                 0.00172414 sec
D11                0.03000000 sec
D13                0.00000400 sec
D16                0.00020000 sec
D24                0.00086207 sec
IN0                0.00002400 sec
ZGOPTNS

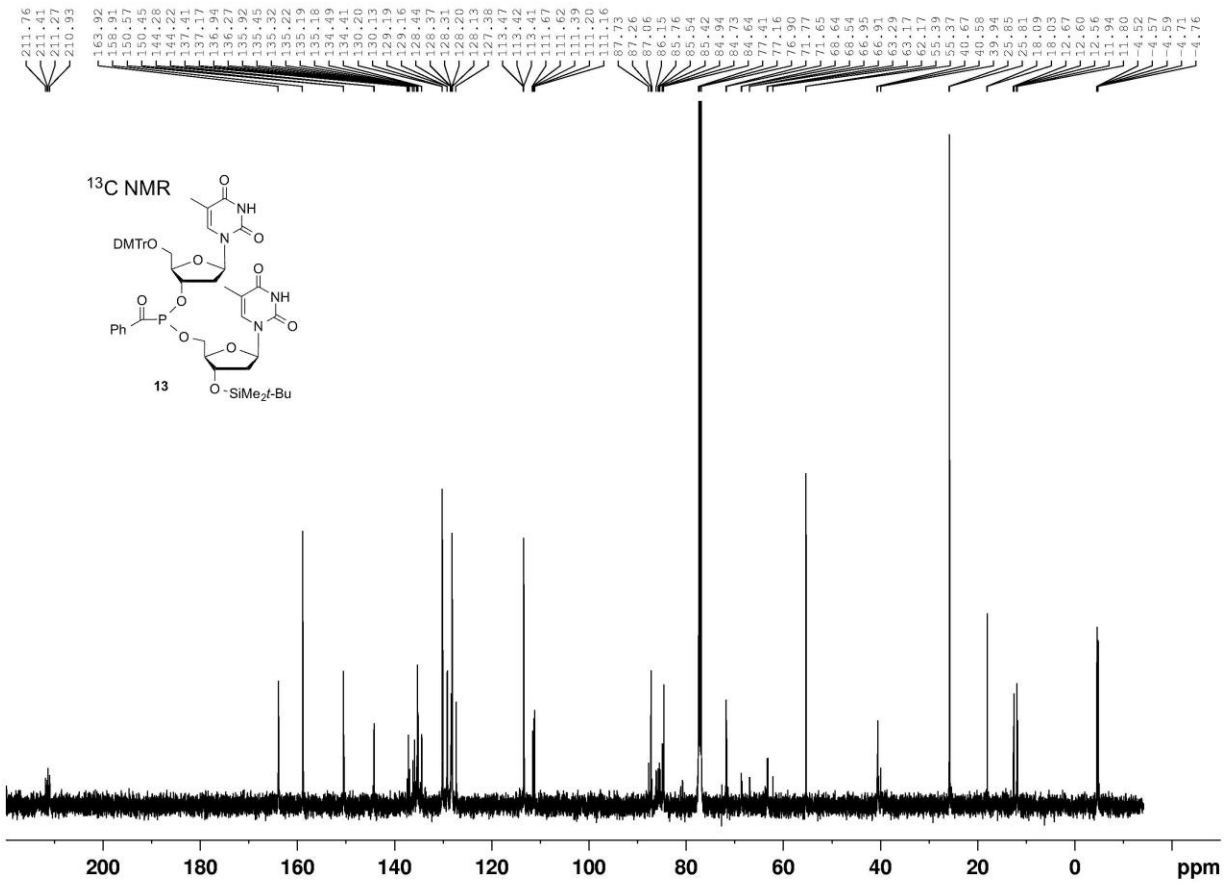
======== CHANNEL f1 ========
NUC1                       1H
P1                       9.10 usec
P2                      18.20 usec
P28                   1000.00 usec
PL1                      3.00 dB
PL1W              15.10710526 W
SFO1              500.1330069 MHz

======== CHANNEL f2 ========
CPDPRG2                 garp
NUC2                     13C
P3                      15.50 usec
P4                      31.00 usec
PCPD2                   70.00 usec
PL2                     -1.00 dB
PL12                    12.10 dB
PL2W             132.81565857 W
PL12W              6.50502920 W
SFO2              125.7672177 MHz

====== GRADIENT CHANNEL =====
GPNAM1               SINE.100
GPNAM2               SINE.100
GPNAM3               SINE.100
GPNAM4               SINE.100
GPZ1                    80.00 %
GPZ2                    20.10 %
GPZ3                    11.00 %
GPZ4                    -5.00 %
P16                   1000.00 usec
P19                    600.00 usec
ND0                         2
TD                        256
SFO1              125.7672 MHz
FIDRES             81.380234 Hz
SW                   165.650 ppm
FnMODE      Echo-Antiecho
SI                       1024
SF                500.1300124 MHz
WDW                     QSINE
SSB                         2
LB                       0.00 Hz
GB                          0
PC                       1.40
SR                      12.35 Hz
SI                       1024
MC2         echo-antiecho
SF                125.7577767 MHz
WDW                     QSINE
SSB                         2
LB                       0.00 Hz
GB                          0
```

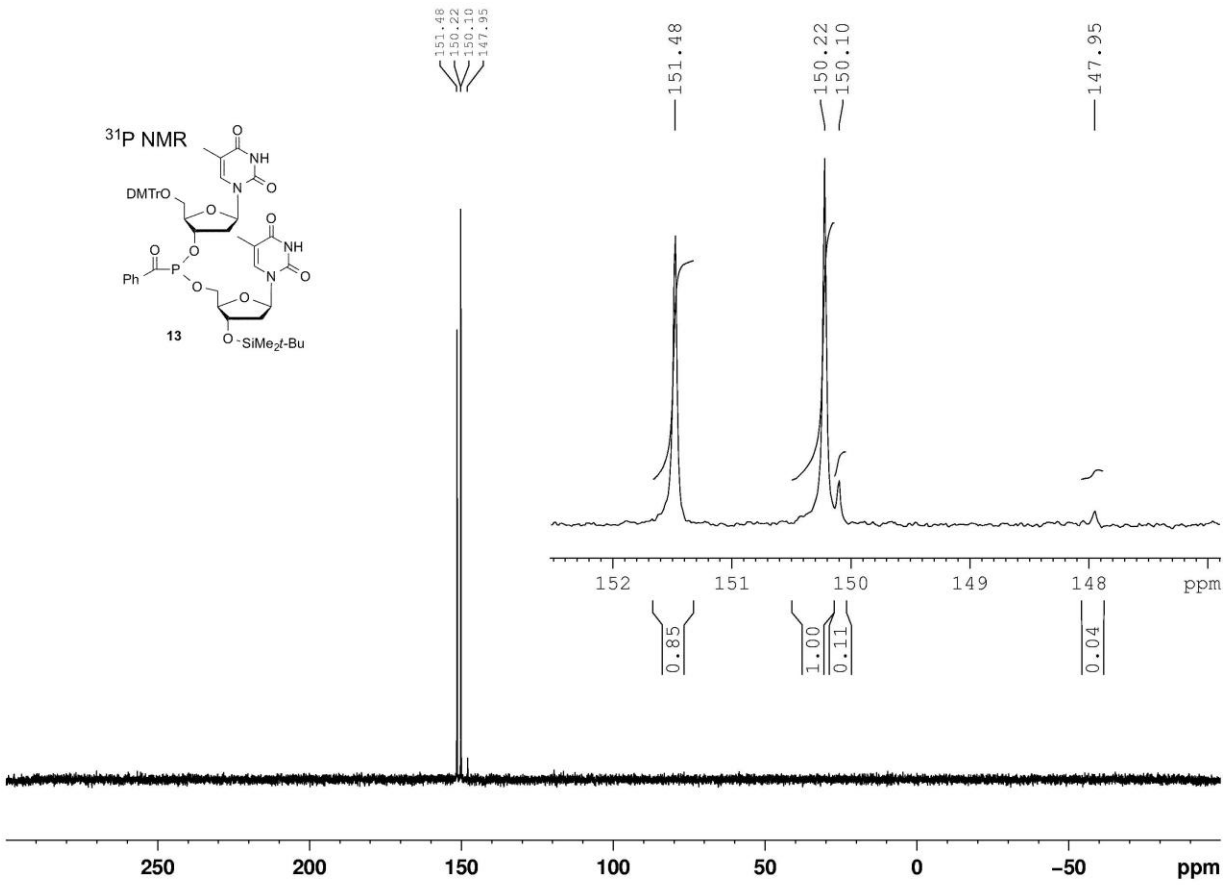

% Transmittance
100
80
60
40
20
0
4000
3000
2000
1000
cm−1
solvent
Infrared
DMTrO
Me
12
O-SiMe2-t-Bu


^{1}H NMR
DMTrO
Ph
13
O-SiMe$_2$t-Bu
HO
Th
impurity peaks
marked by *
O-SiMe$_2$t-Bu
BRUKER
NAME whh102514
EXPNO 10
PROCNO 1
Date_ 20141025
Time 10.45
INSTRUM spect
PROBHD 5 mm QXI 1H Z-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 64
DW 48.400 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.10 usec
PL1 3.00 dB
PL1W 15.10710526 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300126 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
SR 12.60 Hz
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000 0.820 7.118 1.881 0.822 0.116 0.349 0.042 0.082 0.222 0.219 0.485 0.857 0.674 3.032 0.723 0.205 0.069 0.049 0.187 0.245 1.497 0.176 0.291 0.547 0.109 0.649 0.188 0.625 0.633 0.971 4.191 0.602 2.681



BRUKER

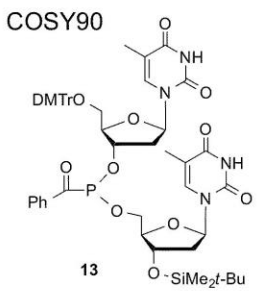
NAME	whh102514	
EXPNO	13	
PROCNO	1	
Date_	20141025	
Time	15.14	
INSTRUM	spect	
PROBHD	5 mm QXI 1H Z-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	4096	
DS	4	
SWH	31250.000	Hz
FIDRES	0.476837	Hz
AQ	1.0486259	sec
RG	322	
DW	16.000	usec
DE	6.50	usec
TE	298.2	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	15.50	usec
PL1	-1.00	dB
PL1W	132.81565857	W
SFO1	125.7716224	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	3.00	dB
PL12	21.88	dB
PL13	120.00	dB
PL2W	15.10710526	W
PL12W	0.19551556	W
PL13W	0.00000000	W
SFO2	500.1320005	MHz
SI	32768	
SF	125.7577747	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	
SR	-14.31	Hz

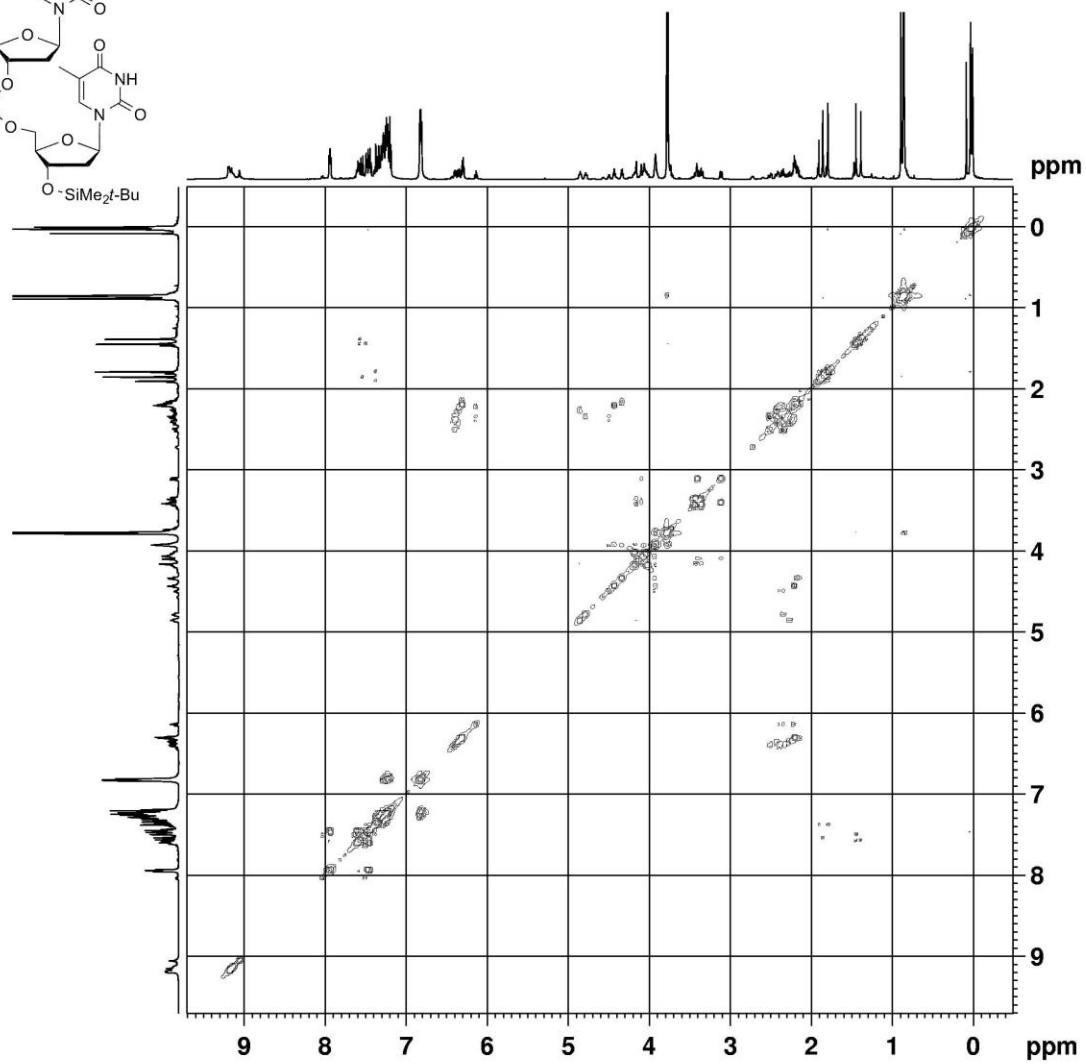


BRUKER

NAME	whh102514	
EXPNO	11	
PROCNO	1	
Date_	20141025	
Time	11.00	
INSTRUM	spect	
PROBHD	5 mm QXI 1H Z-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	256	
DS	4	
SWH	81521.742	Hz
FIDRES	1.243923	Hz
AQ	0.4020041	sec
RG	2050	
DW	6.133	usec
DE	6.50	usec
TE	298.2	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	31P	
P1	38.75	usec
PL1	0.00	dB
PL1W	90.17671967	W
SFO1	202.4765806	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	3.00	dB
PL12	21.88	dB
PL13	120.00	dB
PL2W	15.10710526	W
PL12W	0.19551556	W
PL13W	0.00000000	W
SFO2	500.1320005	MHz
SI	32768	
SF	202.4563071	MHz
WDW	EM	
SSB	0	
LB	4.00	Hz
GB	0	
PC	1.40	
SR	-27.94	Hz

COSY90

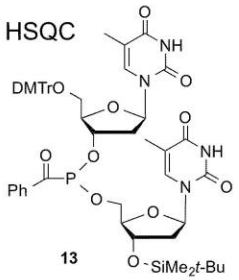


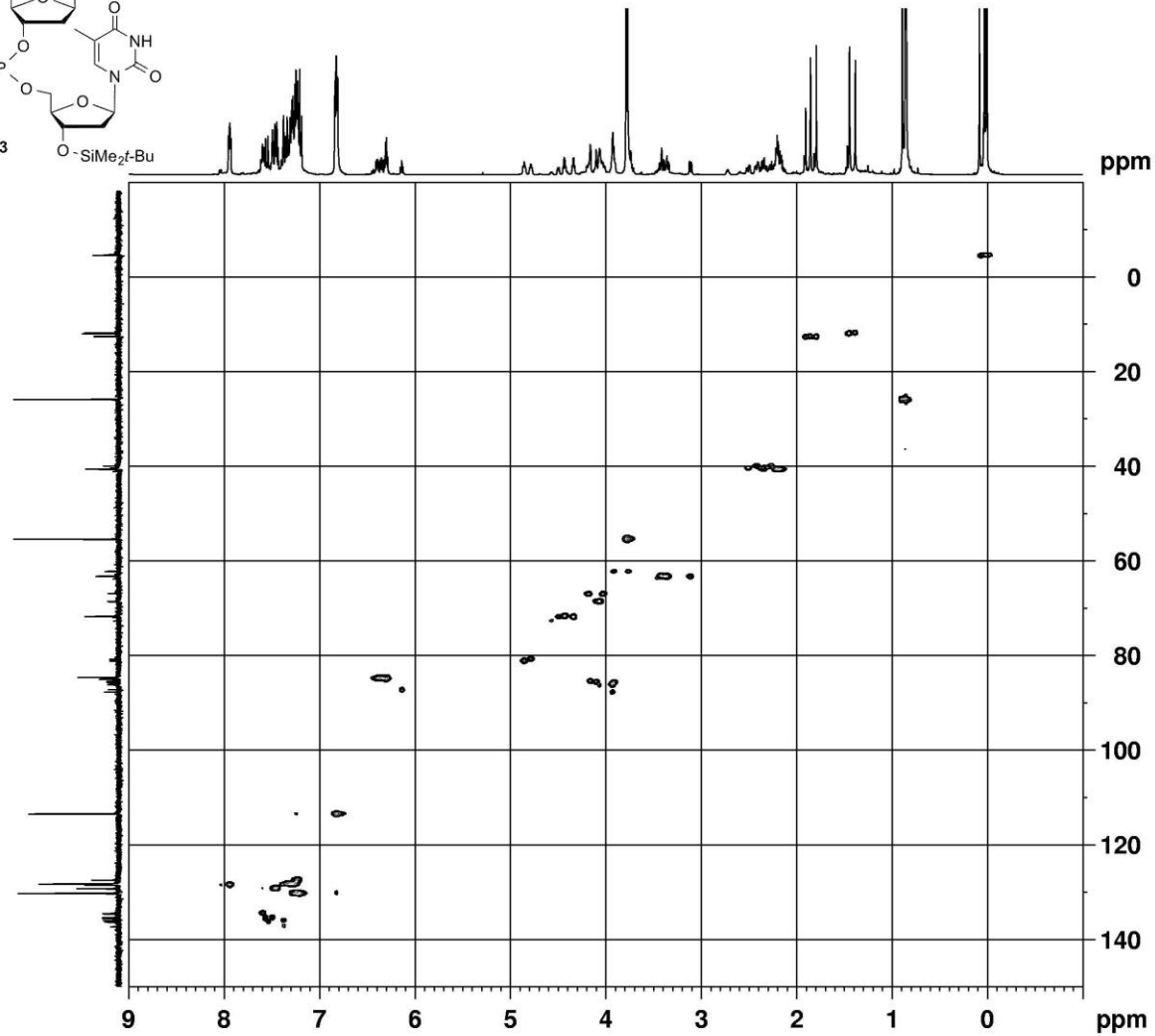


BRUKER

NAME	whh102514	
EXPNO	14	
PROCNO	1	
Date_	20141025	
Time	15.23	
INSTRUM	spect	
PROBHD	5 mm QXI 1H Z-	
PULPROG	cosygf90	
TD	2048	
SOLVENT	CDCl3	
NS	8	
DS	4	
SWH	5154.639	Hz
FIDRES	2.516914	Hz
AQ	0.1987060	sec
RG	57	
DW	97.000	usec
DE	6.50	usec
TE	298.2	K
D0	0.00000300	sec
D1	2.00000000	sec
IN0	0.00019395	sec
======== CHANNEL f1 ========		
NUC1	1H	
P1	9.10	usec
PL1	3.00	dB
PL1W	15.10710526	W
SFO1	500.1323164	MHz
ND0	1	
TD	256	
SFO1	500.1323	MHz
FIDRES	20.142307	Hz
SW	10.310	ppm
FnMODE	QF	
SI	1024	
SF	500.1300126	MHz
WDW	SINE	
SSB	0	
LB	0.00	Hz
GB	0	
PC	1.00	
SR	12.60	Hz
SI	1024	
MC2	QF	
SF	500.1300126	MHz
WDW	SINE	
SSB	0	
LB	0.00	Hz
GB	0	

HSQC



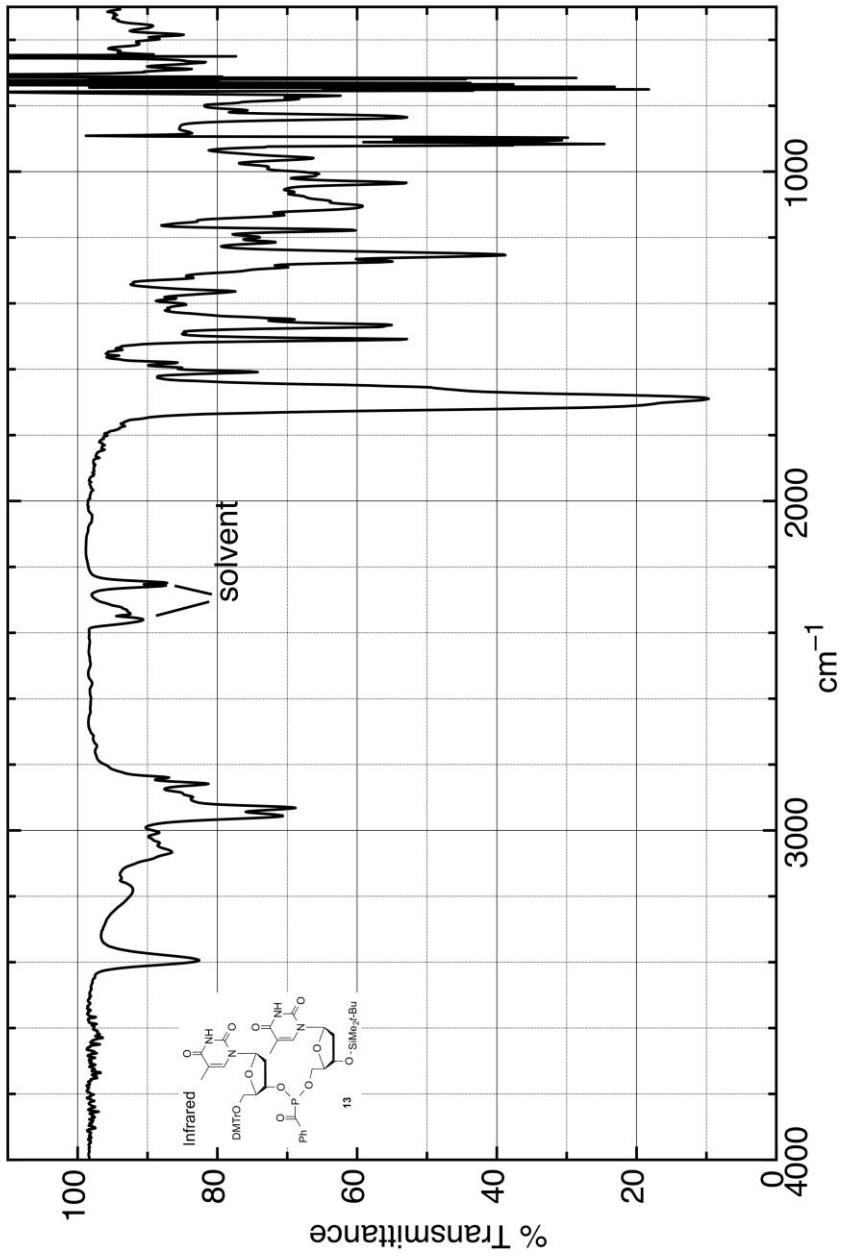


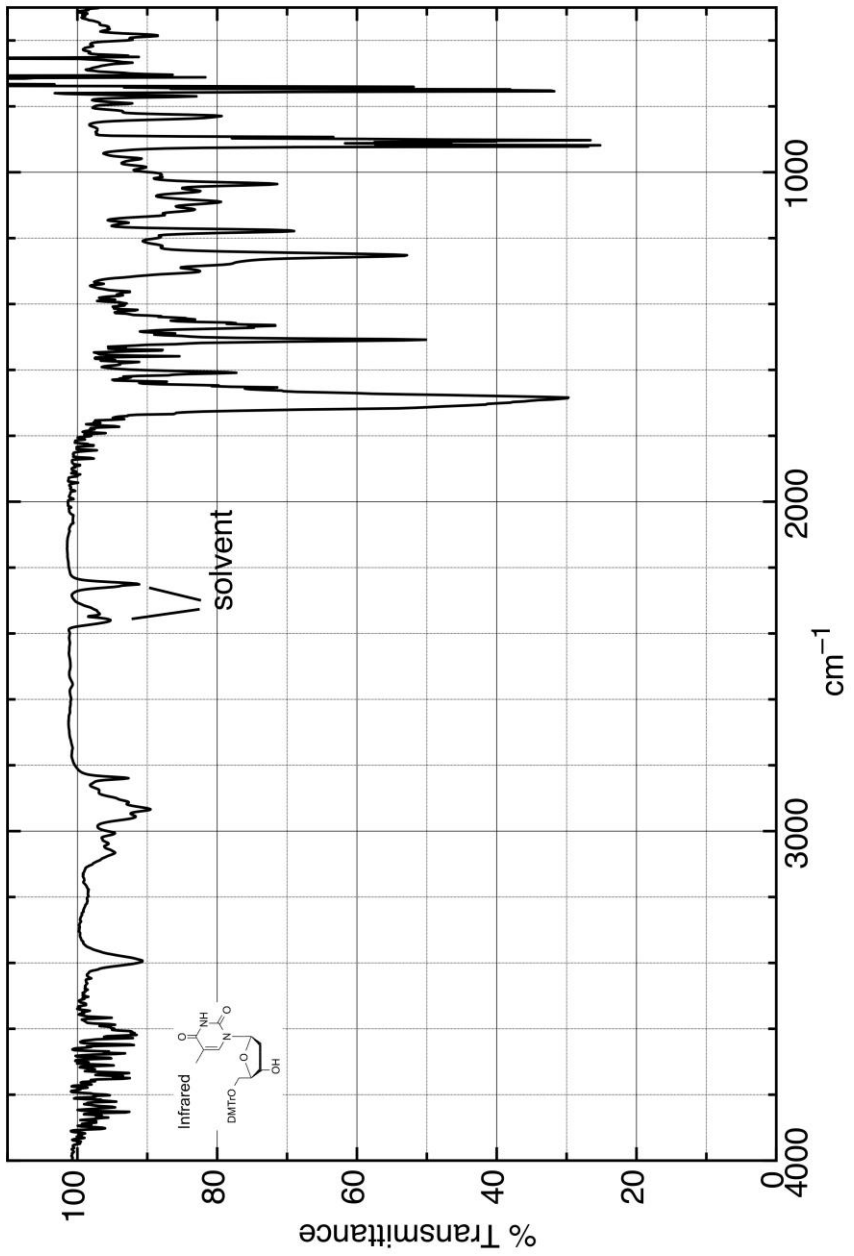

```
NAME                 WH102614
EXPNO                      11
PROCNO                      1
Date_              20141026
Time                    9.55
INSTRUM                 spect
PROBHD    5 mm QXI 1H Z-
PULPROG       hsqcetgpsi2
TD                       1024
SOLVENT                 CDCl3
NS                          2
DS                         16
SWH                6666.667 Hz
FIDRES             6.510417 Hz
AQ                 0.0768500 sec
RG                      2050
DW                    75.000 usec
DE                     6.50 usec
TE                    298.4 K
CNST2             145.0000000
D0                 0.00000300 sec
D1                 1.50000000 sec
D4                 0.00172414 sec
D11                0.03000000 sec
D13                0.00000400 sec
D16                0.00020000 sec
D24                0.00086207 sec
IN0                0.00002400 sec
ZGOPTNS

======== CHANNEL f1 ========
NUC1                       1H
P1                       9.10 usec
P2                      18.20 usec
P28                   1000.00 usec
PL1                      3.00 dB
PL1W              15.10710526 W
SFO1              500.1330069 MHz

======== CHANNEL f2 ========
CPDPRG2                 garp
NUC2                     13C
P3                      15.50 usec
P4                      31.00 usec
PCPD2                   70.00 usec
PL2                     -1.00 dB
PL12                    12.10 dB
PL2W             132.81565857 W
PL12W              6.50502920 W
SFO2              125.7672177 MHz

====== GRADIENT CHANNEL =====
GPNAM1               SINE.100
GPNAM2               SINE.100
GPNAM3               SINE.100
GPNAM4               SINE.100
GPZ1                    80.00 %
GPZ2                    20.10 %
GPZ3                    11.00 %
GPZ4                    -5.00 %
P16                   1000.00 usec
P19                    600.00 usec
ND0                         2
TD                        256
SFO1              125.7672 MHz
FIDRES             81.380234 Hz
SW                   165.650 ppm
FnMODE          Echo-Antiecho
SI                       1024
SF                500.1300126 MHz
WDW                     QSINE
SSB                         2
LB                       0.00 Hz
GB                          0
PC                       1.00
SR                      12.60 Hz
SI                       1024
MC2             echo-antiecho
SF                125.7577747 MHz
WDW                     QSINE
SSB                         2
LB                       0.00 Hz
GB                          0
```


Infrared
solvent
% Transmittance
cm^{-1}
100
80
60
40
20
0
4000
3000
2000
1000
DMTrO
Ph
O-SiMe$_2$-t-Bu
13


% Transmittance
100
80
60
40
20
0
4000
3000
2000
1000
cm−1
solvent
Infrared
DMTrO
OH
NH
O
N

XYZ Coordinates for **7** from DFT optimization;
E(6-311G+(2d,p))= -1078.49563987 au

Atom Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	15	-0.023368	0.169733	-0.826094
2	8	-0.734670	2.771713	-0.257079
3	7	1.421462	-0.241278	0.007741
4	7	-1.433560	-0.180628	0.076356
5	6	0.110745	2.055204	-0.770891
6	6	1.954595	0.457598	1.206204
7	1	1.265477	1.285959	1.401025
8	6	1.230538	2.668374	-1.604044
9	6	-2.595677	-0.749460	-0.660859
10	1	-3.379189	-0.882476	0.091785
11	6	-1.855706	-1.127351	2.350269
12	1	-2.792431	-1.634746	2.091102
13	1	-1.905181	-0.875026	3.416413
14	1	-1.036204	-1.837205	2.199139
15	6	1.979011	-0.427224	2.465267
16	1	0.992353	-0.847254	2.677949
17	1	2.295303	0.163317	3.333244
18	1	2.686572	-1.257599	2.360206
19	6	-2.779004	1.157441	1.746813
20	1	-2.595511	2.066033	1.170573
21	1	-2.825313	1.416214	2.811931
22	1	-3.758830	0.751448	1.469363
23	6	2.194976	-1.423811	-0.461701
24	1	3.064451	-1.485386	0.199956
25	6	-2.317140	-2.137115	-1.256476
26	1	-1.558304	-2.085880	-2.044680
27	1	-3.231916	-2.549515	-1.699533
28	1	-1.966114	-2.830066	-0.485131
29	6	-1.647562	0.143043	1.506400
30	1	-0.723446	0.615459	1.849028
31	6	3.342222	1.078660	0.960888
32	1	4.107956	0.313744	0.789077
33	1	3.652009	1.658062	1.838532
34	1	3.331079	1.748489	0.096710
35	6	-3.151826	0.212103	-1.724480
36	1	-3.361303	1.194693	-1.291130
37	1	-4.079940	-0.183996	-2.155062
38	1	-2.434737	0.346880	-2.542690
39	6	1.428934	-2.746677	-0.313775
40	1	1.066611	-2.878333	0.711023
41	1	2.081359	-3.593516	-0.559514

42	1	0.566770	-2.784276	-0.987567
43	6	2.733424	-1.246437	-1.889358
44	1	1.914131	-1.176311	-2.612892
45	1	3.360623	-2.100986	-2.170585
46	1	3.338972	-0.337066	-1.968068
47	1	0.787828	3.091280	-2.514708
48	1	1.690793	3.492920	-1.049588
49	1	1.993525	1.942694	-1.892081

XYZ Coordinates for **8** from DFT optimization;
E(6-311G+(2d,p))= -1231.17406507 au

Atom	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z
1	15	-0.029622	-0.290573	0.388031
2	7	0.331583	1.370506	0.127581
3	7	-1.665212	-0.645341	-0.027312
4	6	0.948391	-1.059218	-0.988680
5	6	0.515259	2.018791	-1.196116
6	1	0.261494	1.256220	-1.938670
7	6	-2.398183	-1.560601	0.891703
8	1	-3.421917	-1.602572	0.507199
9	6	-3.469202	1.043516	-0.454945
10	1	-4.234176	0.527592	0.137127
11	1	-3.986613	1.599798	-1.246116
12	1	-2.961397	1.759847	0.197151
13	6	-0.430970	3.213073	-1.412570
14	1	-1.476769	2.926987	-1.271244
15	1	-0.315832	3.602647	-2.431171
16	1	-0.209777	4.036209	-0.722980
17	6	-3.187529	-0.907068	-2.031617
18	1	-2.496339	-1.610535	-2.504175
19	1	-3.673304	-0.327311	-2.825358
20	1	-3.969733	-1.488157	-1.530399
21	6	0.680811	2.191272	1.319254
22	1	0.898673	3.191351	0.931461
23	6	-2.492367	-1.055986	2.341422
24	1	-1.508460	-1.038454	2.821093
25	1	-3.139745	-1.718740	2.928592
26	1	-2.912087	-0.045719	2.380395
27	6	-2.463810	0.047196	-1.062340
28	1	-1.749262	0.620925	-1.657532
29	6	1.974576	2.429447	-1.467459
30	1	2.313301	3.208932	-0.775176

31	1	2.065252	2.833771	-2.482869
32	1	2.642088	1.569402	-1.376100
33	6	-1.838643	-2.991325	0.836174
34	1	-1.861574	-3.379073	-0.187521
35	1	-2.429280	-3.662000	1.472369
36	1	-0.799797	-3.023443	1.184191
37	6	-0.490264	2.343202	2.300574
38	1	-1.375630	2.741327	1.794033
39	1	-0.221149	3.029831	3.112482
40	1	-0.757130	1.381892	2.752040
41	6	1.948122	1.702488	2.040345
42	1	1.791508	0.710440	2.477222
43	1	2.217343	2.390716	2.850957
44	1	2.793477	1.641553	1.347396
45	6	0.548557	-1.809192	-2.014184
46	1	1.263581	-2.292130	-2.674668
47	1	-0.505062	-1.966246	-2.201659
48	8	2.340169	-0.863668	-0.804673
49	6	3.029303	-1.764048	-0.040757
50	8	2.531789	-2.746786	0.458431
51	6	4.473258	-1.344323	0.080382
52	1	4.903194	-1.164968	-0.909633
53	1	4.538705	-0.406831	0.642977
54	1	5.036622	-2.120544	0.599067

XYZ Coordinates for **18** from DFT optimization;
Sum of electronic and thermal Free Energies(6-31G+(d))= -691.998977 au

Atom Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.395875	1.348909	-0.250561
2	6	-3.305990	0.289175	-0.329180
3	6	-2.852673	-1.023242	-0.180918
4	6	-1.494845	-1.272653	0.045765
5	6	-0.567901	-0.220820	0.125882
6	6	-1.041285	1.094246	-0.025389
7	15	1.215158	-0.658838	0.419399
8	6	3.553367	0.041777	-1.053137
9	6	2.026509	0.204764	-1.039799
10	6	1.656013	0.528174	1.795329
11	1	-2.742049	2.373614	-0.364742
12	1	-4.360560	0.487733	-0.503957
13	1	-3.552962	-1.853029	-0.239194
14	1	-1.147473	-2.296842	0.162938

15	1	-0.351959	1.933442	0.032885
16	1	3.984167	0.490486	-1.956763
17	1	3.841327	-1.016119	-1.034616
18	1	4.022421	0.530313	-0.190679
19	1	1.756573	1.269799	-1.057032
20	1	1.596510	-0.246131	-1.943274
21	1	2.720822	0.425393	2.032063
22	1	1.088554	0.264030	2.694096
23	1	1.453351	1.577912	1.549333

XYZ Coordinates for **18** transition state from DFT optimization;
Sum of electronic and thermal Free Energies(6-31G+(d))= -691.947172 au

Atom Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.834870	0.855352	0.234687
2	6	3.291750	-0.457361	0.077929
3	6	2.356301	-1.472865	-0.150160
4	6	0.993569	-1.189413	-0.220144
5	6	0.521841	0.135172	-0.067570
6	6	1.474714	1.154192	0.164504
7	15	-1.211261	0.519598	-0.172081
8	6	-2.907505	-1.648502	0.691271
9	6	-2.448595	-0.806549	-0.510153
10	6	-1.747138	2.266628	0.029452
11	1	3.543851	1.660685	0.413915
12	1	4.352566	-0.684755	0.134037
13	1	2.688778	-2.501371	-0.272497
14	1	0.293032	-2.002527	-0.392960
15	1	1.151979	2.184737	0.289689
16	1	-3.630047	-2.411115	0.367984
17	1	-2.062127	-2.159287	1.164162
18	1	-3.384740	-1.022485	1.452597
19	1	-3.304314	-0.295947	-0.969505
20	1	-2.033203	-1.451322	-1.294621
21	1	-2.831058	2.284109	-0.127840
22	1	-1.545628	2.658341	1.032032
23	1	-1.289018	2.927039	-0.714681

XYZ Coordinates for **19** from DFT optimization;
Sum of electronic and thermal Free Energies(6-31G+(d))= -766.036587 au

Atom Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.332829	0.055021	1.437940
2	6	-3.290100	0.279684	0.442357
3	6	-2.916996	0.225074	-0.902225
4	6	-1.591192	-0.054336	-1.249886
5	6	-0.619296	-0.279242	-0.261478
6	6	-1.009530	-0.221243	1.088513
7	15	1.115680	-0.640195	-0.806029
8	6	2.067601	0.734962	0.082548
9	6	1.611924	-2.080081	0.258289
10	8	3.045519	0.467672	0.759838
11	6	1.636892	2.166326	-0.180619
12	1	-2.616854	0.097075	2.486675
13	1	-4.320150	0.494524	0.715388
14	1	-3.655643	0.394879	-1.681664
15	1	-1.307673	-0.102437	-2.298680
16	1	-0.278035	-0.389503	1.875496
17	1	2.673771	-2.281415	0.089696
18	1	1.036429	-2.959498	-0.048406
19	1	1.463815	-1.902480	1.327786
20	1	2.364152	2.854252	0.259292
21	1	0.646606	2.350259	0.252646
22	1	1.555374	2.348894	-1.259133

XYZ Coordinates for **19** transition state from DFT optimization;
Sum of electronic and thermal Free Energies(6-31G+(d))= -766.002998 au

Atom Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.989774	0.765051	-0.679087
2	6	-3.506502	-0.367112	-0.041367
3	6	-2.644195	-1.224481	0.647920
4	6	-1.277615	-0.945800	0.715989
5	6	-0.742794	0.176661	0.054693
6	6	-1.619274	1.026889	-0.648425
7	15	1.026577	0.550220	0.110624
8	6	2.354735	-0.621259	-0.172889
9	6	1.551401	2.259579	0.518064
10	8	3.522774	-0.254005	-0.063112
11	6	1.989009	-2.043502	-0.557687
12	1	-3.651756	1.436440	-1.220293

13	1	-4.572147	-0.576967	-0.078483
14	1	-3.037867	-2.100738	1.156927
15	1	-0.625946	-1.591314	1.297599
16	1	-1.227132	1.888269	-1.182403
17	1	2.644123	2.216647	0.576362
18	1	1.153176	2.581012	1.484519
19	1	1.270230	2.980497	-0.254727
20	1	2.297413	-2.719490	0.248935
21	1	2.557659	-2.313064	-1.454613
22	1	0.921460	-2.178716	-0.751557

XYZ Coordinates for **20** from DFT optimization;
Sum of electronic and thermal Free Energies(6-31G+(d))= -936.138233 au

Atom Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.054739	0.044486	-0.300289
2	6	-2.940209	-0.973618	0.436752
3	6	-4.354482	-0.822392	0.088488
4	7	-5.473514	-0.692587	-0.196166
5	8	-0.715862	-0.157069	0.161113
6	15	0.549743	0.223342	-0.890229
7	6	2.194851	-1.760140	-0.121028
8	8	1.762588	-0.374544	0.055362
9	8	0.768444	1.827666	-0.628002
10	6	0.941617	2.429625	0.686626
11	1	-2.376141	1.066377	-0.070372
12	6	3.679172	-1.744192	-0.465997
13	1	1.632212	-2.195611	-0.958582
14	6	1.879371	-2.532016	1.155251
15	1	-2.124125	-0.106865	-1.384949
16	1	-2.830468	-0.843861	1.519349
17	1	-2.623123	-1.992938	0.190102
18	6	0.911972	3.938642	0.525724
19	1	1.897357	2.090180	1.097187
20	1	0.135627	2.082099	1.340833
21	1	2.189290	-3.578210	1.047850
22	1	4.046169	-2.767518	-0.606859
23	1	0.806554	-2.509073	1.370993
24	1	4.255394	-1.279126	0.342726
25	1	3.858506	-1.182683	-1.389140
26	1	2.416489	-2.099480	2.007732
27	1	1.048171	4.414954	1.503946
28	1	-0.046243	4.270960	0.111374
29	1	1.716107	4.277961	-0.136549

XYZ Coordinates for **20** after rotation to opposite configuration, from DFT optimization;
Sum of electronic and thermal Free Energies(6-31G+(d))= -936.137960 au

Atom Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.038365	-0.332346	-0.240296
2	6	3.087921	0.468896	0.548525
3	6	4.451315	0.020820	0.257507
4	7	5.528094	-0.343814	0.017209
5	8	0.752412	0.148930	0.158980
6	15	-0.469082	0.263299	-0.999639
7	6	-1.769137	-1.737475	0.390085
8	8	-1.269116	-1.154859	-0.863489
9	8	-1.476091	1.214423	-0.089394
10	6	-1.168394	2.624497	0.038825
11	1	2.118076	-1.399170	-0.005565
12	6	-3.291884	-1.751465	0.329960
13	1	-1.435138	-1.103132	1.216732
14	6	-1.160049	-3.127471	0.525561
15	1	2.191481	-0.200461	-1.318705
16	1	2.905330	0.360018	1.623658
17	1	3.006766	1.533670	0.303516
18	6	-2.384660	3.333245	0.607938
19	1	-0.904939	3.031720	-0.946485
20	1	-0.302105	2.736384	0.700578
21	1	-1.508658	-3.600495	1.451239
22	1	-3.699301	-2.185614	1.250883
23	1	-0.066781	-3.075602	0.557092
24	1	-3.638513	-2.355275	-0.517218
25	1	-3.686643	-0.736653	0.221907
26	1	-1.455285	-3.762723	-0.317953
27	1	-2.166838	4.401092	0.726783
28	1	-2.649296	2.924937	1.589570
29	1	-3.247082	3.228355	-0.059309

XYZ Coordinates for **20** transition state from DFT optimization;
Sum of electronic and thermal Free Energies(6-31G+(d))= -936.072122 au

Atom Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.370958	-0.332605	0.000023
2	6	3.536484	-1.341651	0.000325
3	6	4.840569	-0.675170	0.000196
4	7	5.865295	-0.126270	0.000115
5	8	1.155797	-1.069680	0.000426

6	15	-0.536825	-0.545341	0.000407
7	6	-3.223424	-0.973199	0.000676
8	8	-2.184035	0.022650	0.000989
9	8	0.000101	0.997639	-0.000165
10	6	-0.767950	2.228594	-0.000602
11	1	2.423502	0.309689	-0.886804
12	6	-4.053260	-0.816593	1.273541
13	1	-2.752368	-1.970932	0.002711
14	6	-4.049600	-0.820113	-1.274994
15	1	2.423697	0.310476	0.886274
16	1	3.472559	-1.986210	-0.883712
17	1	3.472473	-1.985763	0.884681
18	6	0.213817	3.386153	-0.000764
19	1	-1.409293	2.237631	0.884513
20	1	-1.409090	2.237196	-0.885869
21	1	-4.840708	-1.578746	-1.309858
22	1	-4.845200	-1.574380	1.307758
23	1	-3.417420	-0.940361	-2.161764
24	1	-4.521580	0.174390	1.310023
25	1	-3.423811	-0.935455	2.162437
26	1	-4.518758	0.170334	-1.315103
27	1	-0.343179	4.330532	-0.003147
28	1	0.853411	3.362735	-0.889739
29	1	0.850608	3.365511	0.890284

XYZ Coordinates for **21** from DFT optimization;
Sum of electronic and thermal Free Energies(6-31G+(d))= -842.668118 au

Atom Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.417580	2.965013	0.584131
2	8	-1.854501	2.326648	0.122276
3	1	-0.021325	3.905237	0.930003
4	6	-0.671930	2.036281	0.104336
5	15	-0.234200	0.359015	-0.690536
6	6	2.076795	-0.948312	-0.244079
7	8	1.188423	0.141491	0.130612
8	8	-1.273562	-0.595438	0.194031
9	6	-2.430370	-1.164635	-0.454690
10	1	0.984150	2.484599	1.390053
11	6	3.467341	-0.359128	-0.453263
12	1	1.717047	-1.377673	-1.191180
13	6	2.031773	-2.012664	0.848426
14	1	1.132742	3.159813	-0.225472

15	6	-2.878663	-2.378034	0.342805
16	1	-2.176721	-1.441602	-1.487980
17	1	-3.219776	-0.404858	-0.488009
18	1	2.684174	-2.855288	0.587872
19	1	4.178706	-1.146032	-0.731236
20	1	1.012475	-2.386666	0.984270
21	1	3.822519	0.116982	0.468183
22	1	3.456692	0.393111	-1.249421
23	1	2.372610	-1.593265	1.802190
24	1	-3.778320	-2.812063	-0.110710
25	1	-3.113867	-2.095651	1.374481
26	1	-2.096144	-3.144612	0.363668

XYZ Coordinates for **21** after rotation to opposite configuration, from DFT optimization; Sum of electronic and thermal Free Energies(6-31G+(d))= -842.668984 au

Atom Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.203875	-2.883460	0.605711
2	8	-2.288031	-1.829577	0.045501
3	1	-0.833309	-3.694144	0.983372
4	6	-1.071232	-1.791765	0.019087
5	15	-0.207857	-0.382810	-0.949807
6	6	2.258944	0.466609	-0.258749
7	8	1.035201	-0.200323	0.157097
8	8	-1.226791	0.881889	-0.693503
9	6	-1.755834	1.274144	0.598913
10	1	0.489900	-3.270217	-0.151996
11	6	2.209174	1.936934	0.149920
12	1	2.330849	0.394450	-1.354175
13	6	3.421097	-0.287633	0.377602
14	1	0.412596	-2.469757	1.412216
15	6	-2.491640	2.591130	0.423588
16	1	-0.923033	1.374861	1.304831
17	1	-2.430248	0.488949	0.952252
18	1	4.375615	0.169691	0.091203
19	1	3.130944	2.448328	-0.153256
20	1	3.430087	-1.334494	0.056135
21	1	2.106926	2.028068	1.237886
22	1	1.363926	2.447995	-0.322829
23	1	3.341383	-0.262169	1.470843
24	1	-2.915317	2.911199	1.383559
25	1	-3.309599	2.482887	-0.296466
26	1	-1.815692	3.374834	0.064331

XYZ Coordinates for **21** transition state from DFT optimization;
Sum of electronic and thermal Free Energies(6-31G+(d))= -842.601643 au

Atom Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.495296	3.064340	0.146405
2	8	1.842796	2.421002	0.257126
3	1	-0.537962	3.485847	1.157291
4	6	0.675162	2.104010	0.067021
5	15	0.248203	0.420344	-0.364057
6	6	-2.065146	-0.832641	0.334162
7	8	-1.265434	-0.115225	-0.672690
8	8	1.433060	-0.680735	-0.578212
9	6	2.034054	-1.350955	0.570492
10	1	-0.312104	3.884990	-0.556750
11	6	-3.476388	-0.266813	0.253700
12	1	-1.625936	-0.618516	1.317330
13	6	-1.997499	-2.325226	0.036178
14	1	-1.450141	2.590396	-0.095224
15	6	3.222689	-2.146085	0.065840
16	1	1.280585	-2.002751	1.030266
17	1	2.337103	-0.590808	1.297488
18	1	-0.966589	-2.692094	0.080269
19	1	-4.130162	-0.777711	0.970548
20	1	-2.392330	-2.533157	-0.964714
21	1	-3.888864	-0.407929	-0.751758
22	1	-3.484175	0.803656	0.484008
23	1	-2.592642	-2.885608	0.767380
24	1	3.700070	-2.669410	0.903321
25	1	3.961262	-1.482838	-0.395788
26	1	2.910014	-2.889352	-0.675379