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Synthesis of a Novel Cyclopropyl Phosphonate Nucleotide as a Phosphate Mimic

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General. Commercially available 2'OMe Uridine was purchased from Chem Impex and used without further purification. Teledyne ISCO Combi-Flash systems were used where normal phase purification was needed. All NMR data was collected on a 400 MHz Varian instrument and chemical shifts (δ) are recorded in ppm. Single quadrupole mass spectrometry analyses were performed on a Waters instrument with ESI detection. High-resolution mass spectrometry was performed using an Agilent QTOF equipped with a 1290 Infinity II UHPLC. Mobile phases for the QTOF analysis were as follows: 2 mM ammonium formate pH 8.5 in water (mobile phase A), and 2 mM ammonium formate pH 8.5 in 90% acetonitrile/10% water (mobile phase B). Reaction progress was monitored at 254 nM on an analytical Shimadzu HPLC equipped with a Waters XBridge reverse phase C18 column. For most compounds, a 0.1% TFA-buffered mobile phase was used where mobile phase A was a 0.1% TFA in water solution and mobile phase B was a 0.1% TFA in acetonitrile solution. For analysis of acid labile phosphoramidites mobile phase A was an aqueous solution of 5mM ammonium bicarbonate buffer with mobile phase B consisting of acetonitrile. All compounds new to the literature were characterized with NMR and MS techniques.

Experimental Procedures.

*1-((2R,3R,4R,5R)-4-((tert-butyldimethylsilyl)oxy)-5-(hydroxymethyl)-3-methoxytetrahydrofuran-2-yl)pyrimidine-2,4(1H,3H)-dione **(3)***. To a solution of 2'OMe Uridine (10.0 g, 39.0 mmol) in DMF (30 mL) was added imidazole (5.80 g, 85.0 mmol) and the solution was cooled to 5 °C. To the solution was added TBSCl (12.8 g, 85.0 mmol) slowly over 15 minutes. The reaction was then warmed to 23 °C and found to reach completion within 20 hours. The reaction was added to a separatory funnel containing 100 mL ethyl acetate and washed 5 x 250 mL with water to remove the DMF. The organic layer was dried over sodium sulfate and concentrated to dryness. The white solids were redissolved in dichloromethane (100 mL) and treated with TFA (18.2 g, 160 mmol). After 20 hours, the reaction was poured into a flask containing 300 mL water and pH adjusted to pH = 8 with solid sodium bicarbonate. The dichloromethane layer was dried over sodium sulfate and concentrated to 30 mL or until solids begin to precipitate. The concentrated solution was then transferred to a flask equipped with overhead stirring and treated with 70 mL hexanes. The solution was aged for 3 hours and the solids were collected via filtration funnel and the cake was rinsed with 100 mL hexanes. The solids were dried in a vacuum oven resulting white solids (8.91 g, 62%). The crude solids were found to be 95% pure by HPLC and used without further purification. The identity was confirmed with proton NMR and MS analysis and found to be consistent with data in literature. (See A. V. Kel'in, I. Zlatev, J. Harp, M. Jayarman, A. Bisbe, J. O'Shea, N. Taneja, R. M. Monoharan, S. Khan, K. Charisse, M. A. Maier, M. Egli, K. G. Rajeev, M. Monoharan, *J. Org Chem*., 2016, **81**, 2261)

dimethyl hydroxymethylphosphonate. To a 500 mL round bottom flask, equipped with nitrogen bubbler and reflux condenser was added methanol (250 mL), paraformaldehyde (19.7 g, 0.63 mol) and triethylamine (6.4 g, 0.63 mol). The slurry was heated to 50 °C and dimethylphosphite (70.0 g, 0.63 mol) was charged dropwise over the course of 2 hours keeping the internal temperature less than 55 °C. The reaction was monitored by TLC and found to reach completion within 1 hour. The solvent was removed under vacuum at 40 °C and the residue was co-evaporated with ethyl acetate (2 x 200 mL) to remove residual methanol. To remove polar impurities, the crude oil was dissolved in ethyl acetate (100 mL) and passed through a silica

plug. The filtrate was collected and concentrated under vacuum resulting in a colorless oil (75.1 g, 84% yield).

*dimethyl((E)-2-((2R,3R,4R,5R)-3-((tert-butyldimethylsilyl)oxy)-5-(2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)-4-methoxytetrahydrofuran-2-yl)vinyl)phosphonate **(6)***.

Compound **3** (3.50 g, 9.0 mmol) was dissolved in 35 mL dichloromethane and cooled to 0 °C. To the reaction was added Dess-Martin periodinane (4.24 g, 10 mmol) over 5 minutes. The reaction was warmed to 23 °C and found to reach completion within 3 hours. Upon completion, undissolved solids were filtered through a pad of celite and the filter cake was rinsed with 10 mL dichloromethane. The filtrate was then transferred back to a clean flask, and stirred with ylide 5 (5.19 g, 13.5 mmol) at ambient temperature for 16 hours. Upon completion, the reaction mixture was washed with water, followed by brine, and the organic layer was dried over sodium sulfate. The solvent was removed under reduced pressure and the crude oil was purified via flash chromatography and eluted with 20% methanol/dichloromethane solvent system resulting in white solids (2.57 g, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 6.84 (ddd, *J* = 22.4, 17.2, 5.3 Hz, 1H), 6.01 (ddd, *J* = 19.3, 17.2, 1.6 Hz, 1H), 5.84 (d, *J* = 2.5 Hz, 1H), 5.78 (dd, *J* = 8.1, 2.1 Hz, 1H), 4.57 – 4.48 (m, 1H), 3.99 (dd, *J* = 7.4, 5.1 Hz, 1H), 3.77 (d, *J* = 1.2 Hz, 3H), 3.74 (d, *J* = 1.1 Hz, 3H), 3.52 (s, 3H), 0.90 (s, 9H), 0.09 (d, J = 5.5 Hz, 6H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.87 – 19.00 (m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.50, 150.08, 148.28 (d, *J* = 5.7 Hz), 139.75, 119.51, 117.63, 102.82, 89.83, 82.94 (d, *J* = 6.7 Hz), 82.74, 74.11 (d, *J* = 1.8 Hz), 58.56, 52.61 (d, *J* = 3.4 Hz), 52.57, 52.54, 25.60, 18.15 – 17.96 (m), -4.69, -4.88. HRMS (ESI) m/z [M-H]- calculated for $C_{19}H_{33}N_2O_8PSi$ 475.1666, found 475.1667.

*O,O-diethyl((E)-2-((2R,3R,4R,5R)-3-((tert-butyldimethylsilyl)oxy)-5-(2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)-4-methoxytetrahydrofuran-2-yl)vinyl)phosphonothioate **(10)***.

In-Situ Preparation of ylide (**9**): To a slurry of methyltriphenylphosphonium bromide (17.0 g, 47.7 mmol) in THF (120mL) was added LiHMDS (47.7 mL, 47.7 mmol) at ambient temperature. The slurry was stirred for 30 minutes eventually forming a solution. To the solution was added *O,O'*-diethyl chlorothiophosphate (3.0 g, 16.0 mmol) and the reaction was allowed to stir at ambient for 1 hour. After 1 hour, the reaction mixture was analyzed by proton NMR and found to contain 50% of the limiting reagent, *O,O'*-diethyl chlorothiophosphate. Two additional equivalents of LiHMDS (31.0 mL, 31.0 mmol) were added and the reaction was stirred for 1 hour. Upon completion, the reaction was diluted with methyl *tert*-butyl ether and washed with water (2 x 5 mL). The organic layer was dried over sodium sulfate and concentrated to an oil. The ylide was isolated as an oil and found to be unstable to chromatography. The crude oil was used in the next step without purification assuming 100% yield (16.0 mmol).

In-situ Preparation of Compound **4**: Compound **3** (5.0 g, 13.4 mmol) was dissolved in 50 mL dichloromethane and cooled to 0 °C. To the reaction was added Dess-Martin periodinane (5.68 g, 13.4 mmol) over 15 minutes. The reaction was stirred between 0 – 5 °C and found to reach completion within 3 hours. The crude reaction was passed through a celite pad and the filter cake was rinsed with 25 mL dichloromethane.

The filtrate from *in-situ* preparation of compound **4** was transferred to a flask containing crude ylide **9** from the previous step and stirred overnight at 23 °C. Upon completion, the reaction mixture was washed with water, followed by brine, and the organic layer was dried over sodium sulfate. The solvent was removed under reduced pressure and the crude oil was purified via flash chromatography and eluted with 20% methanol/dichloromethane solvent system resulting

in white solids (3.79 g, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.51 (s, 1H), 7.29 (d, *J* = 8.1 Hz, 1H), 6.80 (ddd, *J* = 24.7, 16.7, 5.0 Hz, 1H), 6.22 (ddd, *J* = 18.3, 16.7, 1.6 Hz, 1H), 5.83 (d, *J* = 2.1 Hz, 1H), 5.78 (dd, *J* = 8.2, 1.6 Hz, 1H), 4.53 (dddd, *J* = 6.6, 4.9, 2.9, 1.6 Hz, 1H), 4.16 – 4.04 (m, 4H), 3.95 (dd, *J* = 7.8, 5.1 Hz, 1H), 3.72 (ddd, *J* = 5.1, 2.2, 0.5 Hz, 1H), 3.53 (s, 3H), 1.30 (tdd, *J* = 7.1, 2.1, 0.4 Hz, 6H), 0.90 (s, 10H), 0.09 (d, *J* = 1.2 Hz, 6H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 84.04-83.65 (m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.89, 149.75, 145.66 (d, *J* = 10 Hz), 139.64, 125.63 (d, *J* = 153 Hz), 102.77, 90.09, 83.09, 82.43 (d, *J* = 23 Hz), 74.30 (d, *J* = 1 Hz), 62.63 (d, *J* = 2 Hz), 62.57 (d, *J* = 2 Hz), 58.71, 25.26, 18.12, 16.19 (d, *J* = 2 Hz), 16.11 (d, *J* = 2 Hz), -4.66, -4.79. HRMS (ESI) m/z [M-H]- calculated for $C_{21}H_{37}N_2O_7PSSi$ 519.1750, found 519.1752.

O,O-diethyl((1R,2S)-2-((2R,3R,4R,5R)-3-((tert-butyldimethylsilyl)oxy)-5-(2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)-4-methoxytetrahydrofuran-2-yl)cyclopropyl)phosphonothioate ***(11)***. To a solution of trimethylsulfoxonium iodide (634 mg, 2.9 mmol) in DMSO (2.5 mL) was added 60% weight percent NaH dispersion in mineral oil (115 mg, 2.9 mmol). The frothy mixture was stirred for 30 minutes or until a uniform solution was formed. The solution was then transferred to a separate flask containing a solution of vinyl thiophosphonate 10 (500 mg, 0.96 mmol) in 2.5 mL DMSO. After the transfer was complete, the reaction was held at 23 °C until complete conversion of starting material to a more polar intermediate, presumably 6a. The reaction was then heated to 35 °C for 2 – 3 hours. Upon completion, the reaction was cooled to room temperature and extracted with ethyl acetate (3 x 25 mL). The combined extracts were washed with water (3 x 25 mL) and brine (25 mL). The organic layer was dried over sodium sulfate, filtered and concentrated to dryness. The crude solids were found to exist in a 3:2 diastereomeric ratio but could not be separated by crystallization or chromatography. The solids were purified via flash chromatography and eluted with 20% methanol/dichloromethane solvent system resulting in a 3:2 diastereomeric ratio of the desired compound (333 mg, 65% yield). Major :^{1}H NMR (400 MHz, $CDCl_3$): δ 9.75 (s, 1H), 7.41 (d, J = 8.1 Hz, 1H), 5.81 – 5.75 (m, 2H), 4.16 – 4.02 (m, 4H), 4.00 (dd, J = 7.4, 5.1 Hz, 1H), 3.69 (dd, J = 5.1, 2.2 Hz, 1H) 3.51 (s, 3H), 3.41 (dd, J = 8.8, 7.4 Hz, 1H), 1.49 – 1.37 (m, 1H), 1.32 – 1.25 (m, 6H), 1.25 – 1.10 (m, 2H), 1.05 – 0.92 (m, 1H), 0.89 (s, 9H), 0.10 (s, 6H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 100.75. ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.67, 150.11, 139.40, 102.58, 88.97, 85.86 (d, J = 3 Hz), 83.76, 74.49, 62.75 (d, J = 6 Hz), 62.71 (d, J = 6 Hz), 58.52, 25.62, 20.05 (d, J = 3 Hz), 18.09, 16.23 (d, J = 4 Hz), 15.91 (d, J = 156 Hz), 8.38 (d, J = 4 Hz), 8.31 (d, J = 4 Hz), -4.67, -4.96. Minor: ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.65 (s, 1H), 7.33 (d, J = 8.1 Hz, 1H), 5.81 – 5.75 (m, 2H), 4.16 – 4.02 (m, 3H), 3.78 (dd, J = 5.1, 4.0 Hz, 1H), 3.65 (dd, J = 7.1, 5.5 Hz, 1H), 3.45 (s, 3H), 1.61 – 1.49 (m, 1H), 1.32 – 1.25 (m, 6H), 1.25 – 1.10 (m, 2H), 1.05 – 0.92 (m, 1H), 0.89 (s, 9H), 0.10 (s, 6H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 100.62. ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.58, 150.14, 140.22, 102.84, 88.83, 84.75 (d, J = 5 Hz), 82.85, 73.71, 62.97 (d, J = 6 Hz), 62.48 (d, J = 6 Hz), 58.25, 25.71, 19.71 (d, J = 3 Hz), 18.09, 16.16 (d, J = 3 Hz), 15.47 (d, J = 160 Hz), 8.31 (d, J = 4 Hz), -4.64, -4.76. HRMS (ESI) m/z [M-H]- calculated for $C_{22}H_{38}N_2O_7PSSi$ 533.1907, found 533.1907.

diethyl((1R,2S)-2-((2R,3R,4R,5R)-3-((tert-butyldimethylsilyl)oxy)-5-(2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)-4-methoxytetrahydrofuran-2-yl)cyclopropyl)phosphonate ***(12)***.

To a solution of compound **11** (1.20 g, 2.2 mmol) in 12 mL THF was added concentrated HCl (2 mL) at 0 °C over 5 minutes. The solution was allowed to warm to ambient over 1 hour and found to be complete. The solution was concentrated to dryness under vacuum at 20 0°C and

then subjected to co-evaporation with acetonitrile (2 x 50 mL). After removal of solvent at reduced pressure the crude mixture was purified via flash chromatography and eluted with 20% methanol/dichloromethane solvent system resulting in a white foam (750 mg, 80% yield). *Major* ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.41 (s, 1H), 7.41 (d, *J* = 8 Hz, 1H), 5.83 – 5.78 (m, 2H), 4.19 – 4.05 (m, 4H), 4.02 (t, *J* = 8 Hz, 1H), 3.58 (s, 3H), 3.42 (t, *J* = 8 Hz, 1H), 2.67 (s), 1.62 – 1.49 (m, 1H), 1.34 – 1.27 (m, 6H), 1.27 – 1.18 (m, 2 H), 1.07 – 0.95 (m, 1H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 100.45.^{13}C NMR (100 MHz, $CDCl_3$) 163.19, 150.01, 139.24, 102.77, 88.08, 85.91 (d, *J* = 2.5 Hz), 83.44, 72.99, 62.81 (d, *J* = 6.6 Hz), 62.77 (d, *J* = 6.4 Hz), 58.85, 19.98 (d, *J* = 2.9 Hz), 16.25 (d, *J* = 6.9 Hz), 16.19 (d, *J* = 6.9 Hz), 15.94 (d, *J* =156.4 Hz), 8.24 (d, *J* = 4.1 Hz).HRMS (ESI) m/z [M-H]- calculated for $C_{16}H_{25}N_2O_7PS$ 419.1042, found 419.1067. *Minor:* ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.41 (s, 1H), 7.41 (d, *J* = 8 Hz, 1H), 5.83 – 5.78 (m, 2H), 4.19 – 4.05 (m, 4H), 3.93 (t, *J* = 8 H), 3.59 (s, 3H), 3.51 (t, *J* = 8 Hz, 1H), 2.67 (s), 1.62 – 1.49 (m, 1H), 1.34 – 1.27 (m, 6H), 1.27 – 1.18 (m, 2 H), 1.07 – 0.95 (m, 1H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 100.08.^{13}C NMR (100 MHz, $CDCl_3$) δ163.23, 149.96, 139.42, 102.77, 88.38, 84.93 (d, *J* = 5.0 Hz), 83.28, 72.62, 62.90 (d, *J* = 6.7 Hz), 62.80 (d, *J* = 6.5 Hz), 58.89, 19.19 (d, *J* = 2.7 Hz), 16.21 (d, *J* = 7.2z Hz), 16.19 (d, *J* = 7.8 Hz), 14.87 (d, *J* =157.0 Hz) 8.64 (d, *J* = 4.3 Hz). HRMS (ESI) m/z [M-H]- calculated for $C_{16}H_{25}N_2O_7PS$ 419.1042, found 419.1044.

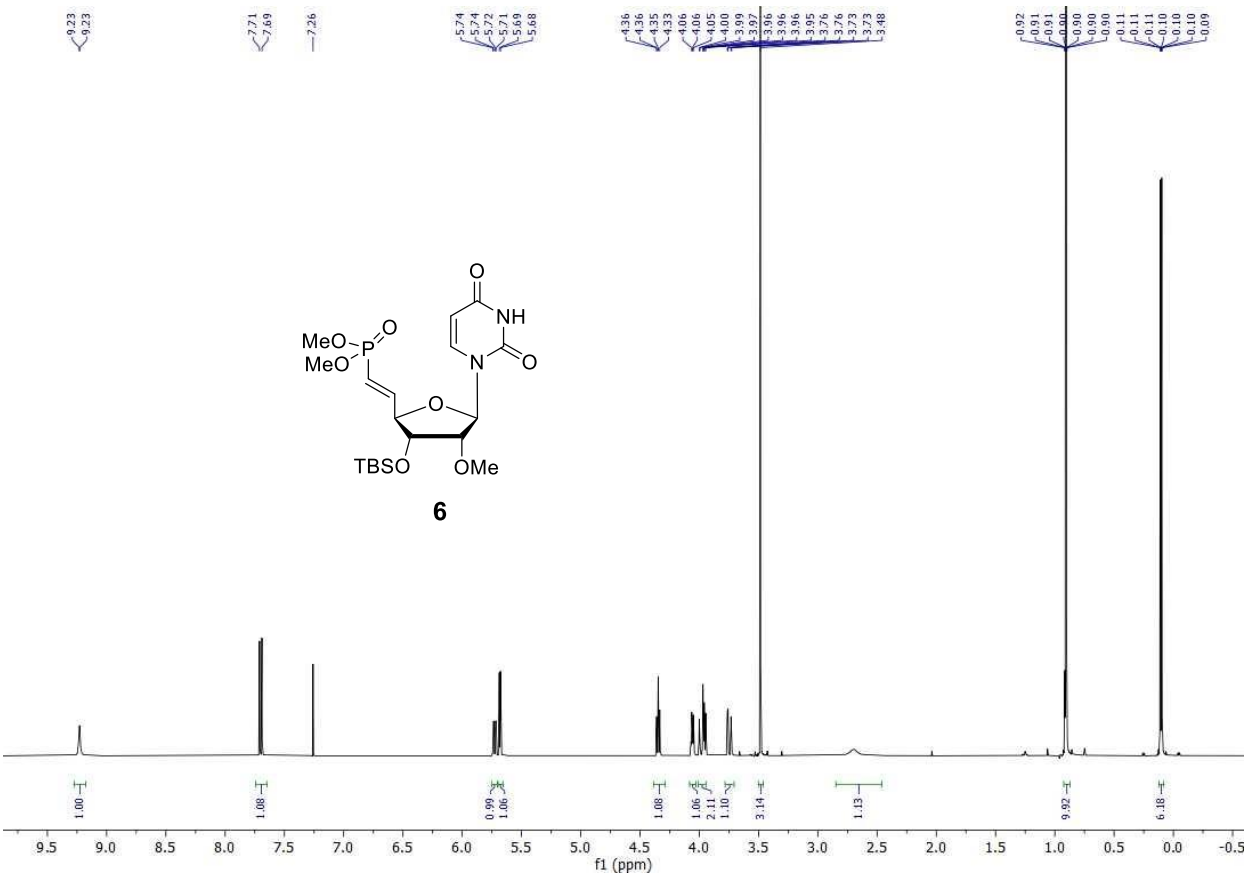
diethyl((1R,2S)-2-((2R,3R,4R,5R)-5-(2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)-3-hydroxy-4-methoxytetrahydrofuran-2-yl)cyclopropyl)phosphonate ***(13)***.

To a solution of thiophosphate **12** (2.1 g, 5.0 mmol) in 40 mL THF/water (1:1) was added Oxone (3.1 g, 10 mmol) and the resulting slurry was stirred for 4 hours at ambient, or until all starting material was consumed. The reaction mixture was extracted with ethyl acetate (7 x 25 mL) and the combined extracts were dried over sodium sulfate. The solvent was removed under vacuum resulting in recovery of a white solid. The solids were triturated with 12 mL ethyl acetate for 2 hours and filtered. The cake was rinsed with 5 mL cold ethyl acetate and the solids were dried under high vacuum resulting in a d.r. enrichment of the penultimate alcohol to 93:7 (655 mg, 32% yield). The solids were added to a vial containing 10 mL of 40% methanol/heptane solution and heated to 70 °C. After the solids dissolved, the heating was turned off and the solution was allowed to cool to 23 °C over 1 hour. The solids were aged for 16 hours and filtered resulting in penultimate alcohol as a single diastereomer (563 mg, 28% overall yield). The solids were found to be crystalline and were suitable for X-ray analysis. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 5.82 (d, *J* = 2.4 Hz, 1H), 5.76 (dd, *J* = 8.1, 1.8 Hz, 1H), 4.14 – 4.06 (m, 4H), 4.06 – 4.01 (m, 1H), 3.79 (dd, *J* = 5.4, 2.4 Hz, 1H), 3.56 (s, 3H), 3.34 (dd, *J* = 8.6, 7.2 Hz, 1H), 1.63 (tdd, *J* = 14.0, 8.5, 4.4 Hz, 1H), 1.30 (dtd, *J* = 12.6, 7.1, 0.5 Hz, 6H), 1.22 (ddd, *J* = 10.8, 5.8, 3.2 Hz, 1H), 1.02 (ddt, *J* = 12.0, 9.9, 5.1 Hz, 1H), 0.97 – 0.87 (m, 1H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.03. ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.47, 150.19, 139.39, 102.73, 88.00, 86.38 (d, *J* = 3 Hz, 83.52, 72.80, 62.20 (d, *J* = 6 Hz), 62.14 (d, J = 6 Hz), 58.77, 18.95 (d, *J* = 4 Hz), 16.43 (d, *J* = 2 Hz), 16.37 (d, *J* = 2 Hz), 8.76 (d, *J* = 193 Hz), 7.14 (d, *J* = 5 Hz) . HRMS (ESI-TOF) *m/z* : [M-H]- calculated for $C_{16}H_{24}N_2O_8P$ 403.1270; Found 403.1273.

2-cyanoethyl((2R,3R,4R,5R)-2-((1S,2R)-2-(diethoxyphosphoryl)cyclopropyl)-5-(2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)-4-methoxytetrahydrofuran-3-yl)diisopropylphosphoramidite ***(14)***.

Penultimate alcohol **13** (100 g, 247 mmol) was dissolved in acetonitrile (1 L) and concentrated to dryness under high vacuum. This was repeated twice, or until a KF reading of the solids was less than 100 ppm. The solids were then redissolved in DCM (500 mL) and to the solution was added diisopropylammonium tetrazolide (6.9 g, 98 mmol), and 2-cyanoethyl

N',N',N,N-tetraisopropylphosphoramidite (93.2 g, 309 mmol) at ambient temperature. The solution was stirred overnight. At 16 h, < 1% alcohol remained, and the reaction was quenched with 1:1 saturated bicarb/brine solution. The organic layer was washed with saturated bicarb and brine once more. The resulting dichloromethane solution was concentrated to 400 mL and poured into 6 L of 1:1 MTBE/hexanes. The solid cake was washed twice with the 1:1 mixture of MTBE/hexanes resulting in 143 g amidite **14** (95% yield, 98% purity). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 8.1, 0.9 Hz, 1H), 5.84 (dd, *J* = 7.0, 2.9 Hz, 1H), 5.72 (dd, *J* = 8.1, 1.8 Hz, 1H), 4.24 – 4.03 (m, 5H), 3.92 – 3.39 (m, 9H), 2.62 (tt, *J* = 6.1, 3.4 Hz, 2H), 1.66 – 1.48 (m, 1H), 1.29 (dtd, *J* = 11.4, 7.1, 1.7 Hz, 6H), 1.26 – 1.21 (m, 1H), 1.16 (td, *J* = 6.5, 2.1 Hz, 12H), 0.95 (tdd, *J* = 14.4, 7.4, 4.5 Hz, 2H). δ ^{31}P NMR (162 MHz, $CDCl_3$) δ 150.19, 150.02, 28.86, 28.69.^{13}C NMR (100 MHz, $CDCl_3$) δ 163.38, 163.37, 150.23, 150.18, 139.30, 139.20, 117.74, 117.66, 102.63, 88.62, 88.28, 85.69, 85.66, 85.63, 83.04, 83.02, 82.46, 82.43, 74.53, 74.40, 74.18, 74.03, 62.15, 62.10, 62.04, 58.75, 58.74, 58.52, 58.41, 58.40, 58.34, 57.97, 57.77, 43.32, 43.20, 24.70, 24.63, 24.60, 24.57, 24.52, 24.49, 20.42, 20.40, 20.35, 20.33, 19.07, 19.04, 19.03, 19.01, 16.45, 16.43, 16.39, 16.37, 10.07, 9.99, 8.13, 8.06, 7.78, 7.73, 7.55, 7.51. HRMS (ESI-TOF) *m/z* : [M-H]- calculated for $C_{25}H_{41}N_4O_9P_2$ 603.2349; Found 603.2353.



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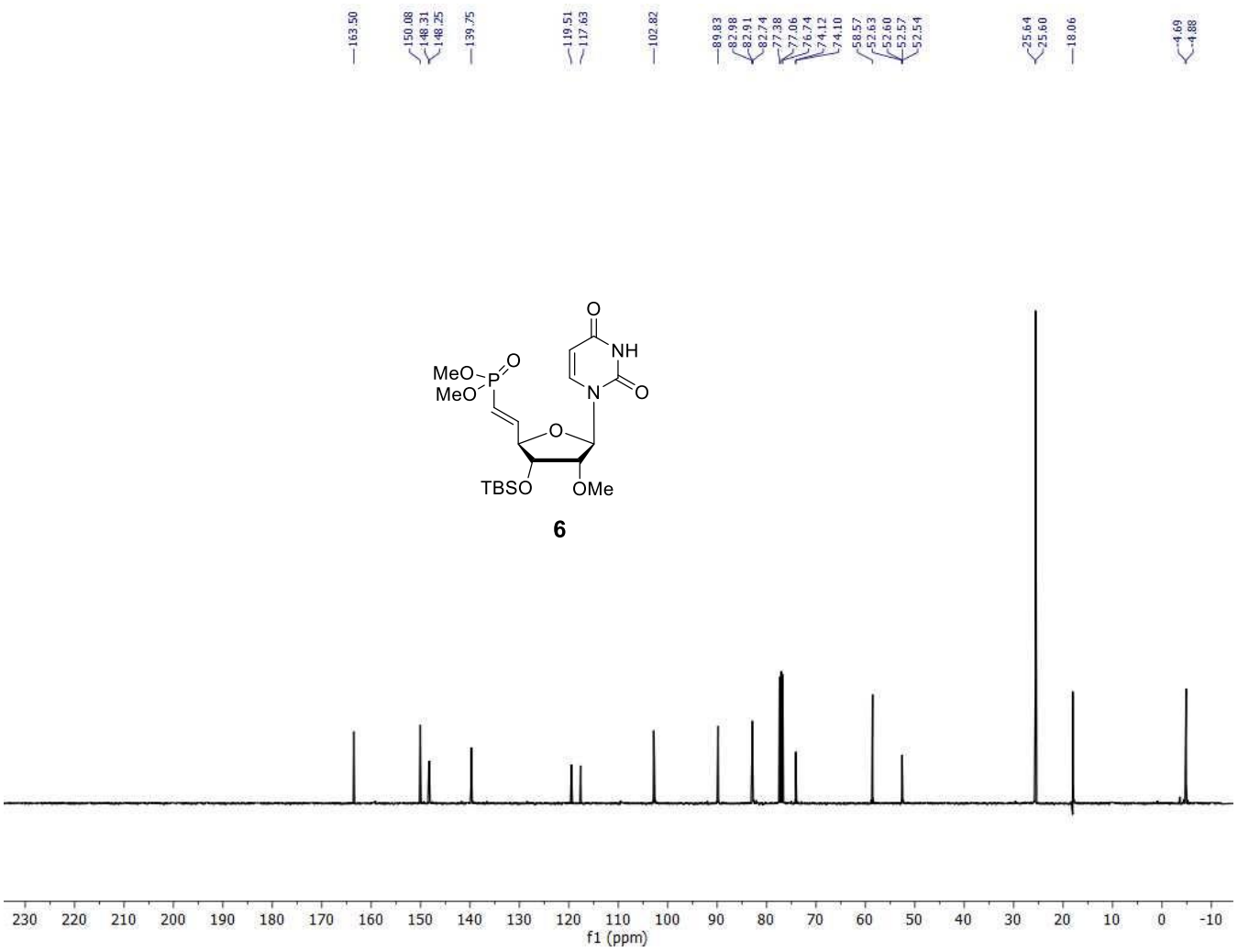
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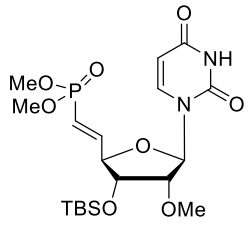
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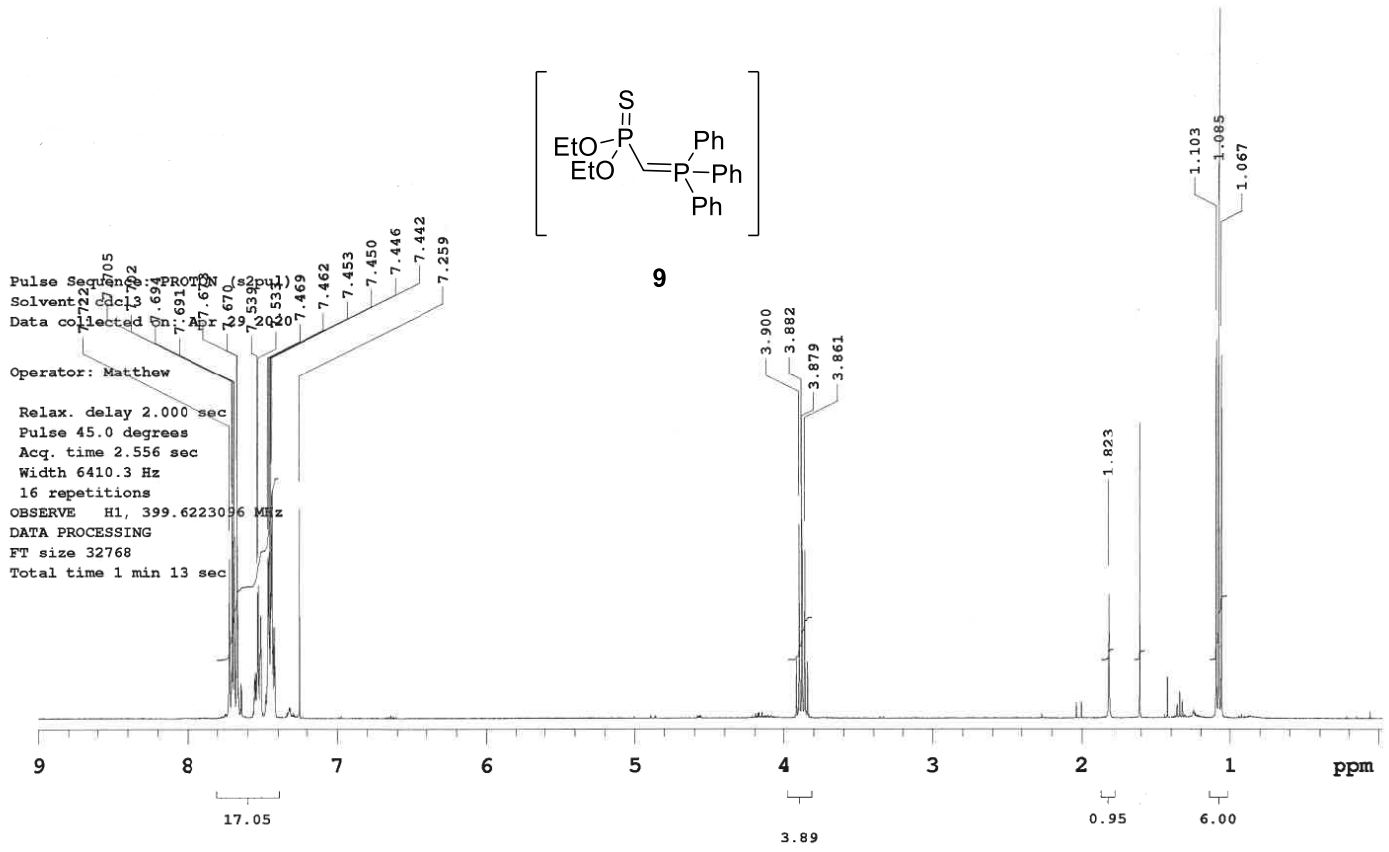
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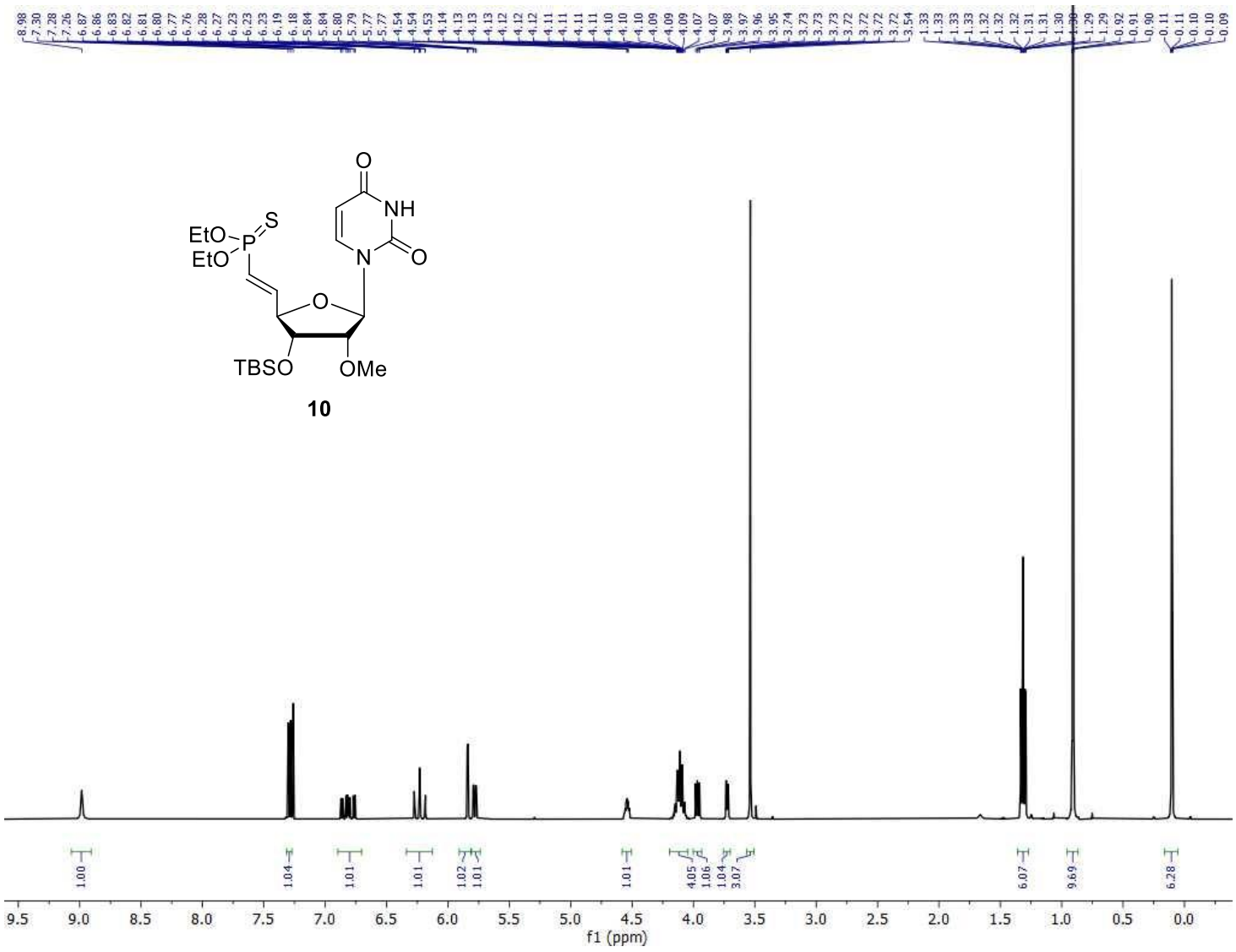
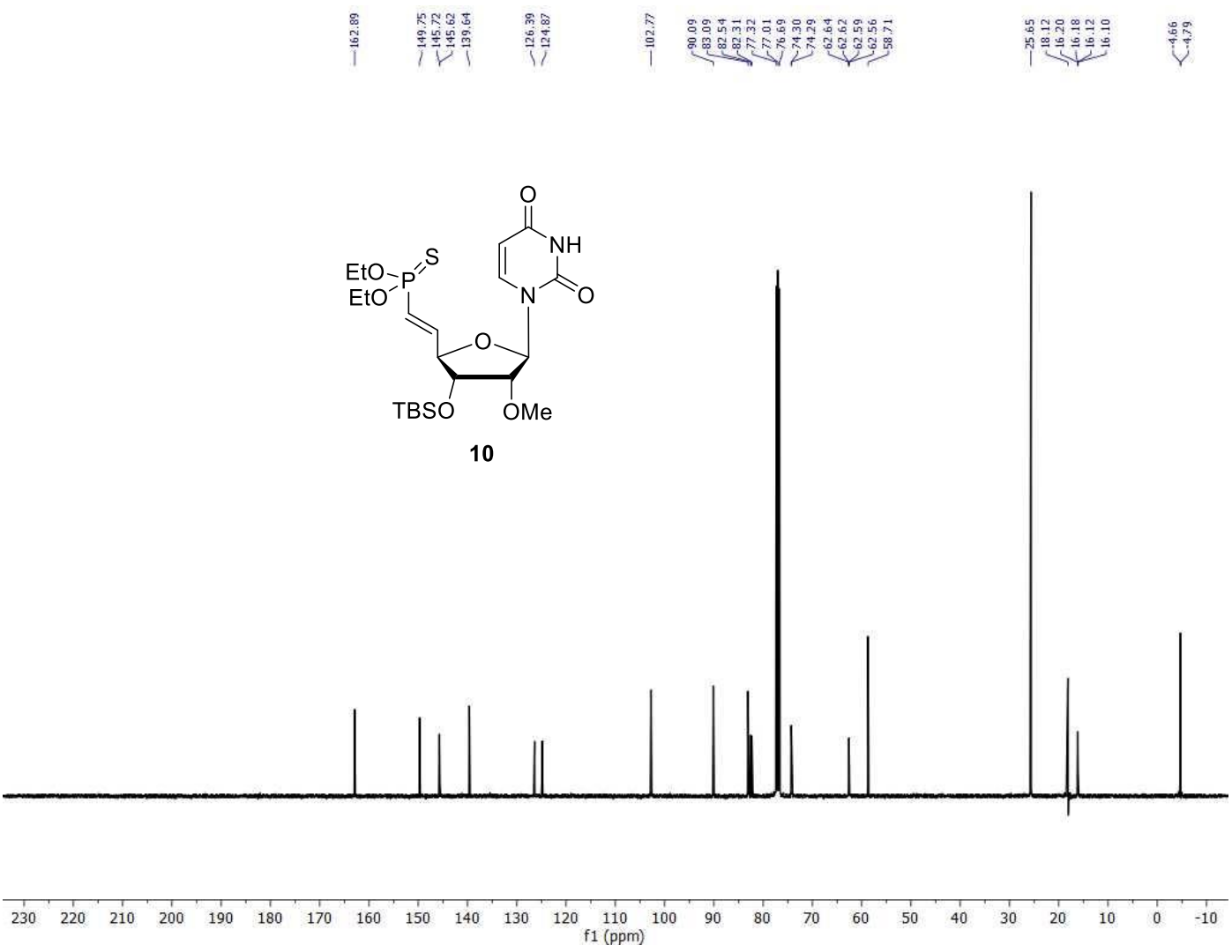

EtO
EtO
P
S
O
NH
N
O
O
TBSO
OMe
10
f1 (ppm)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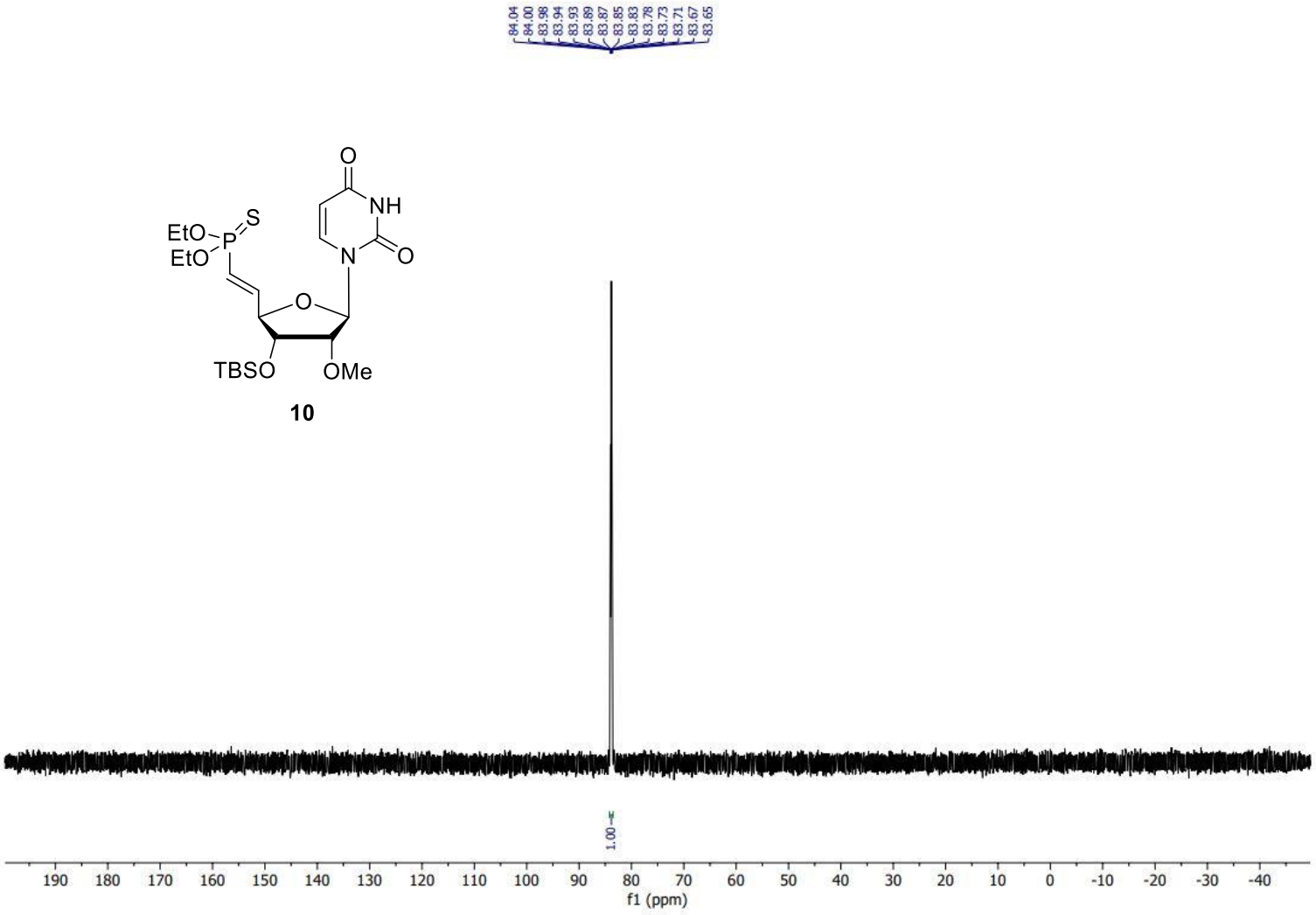
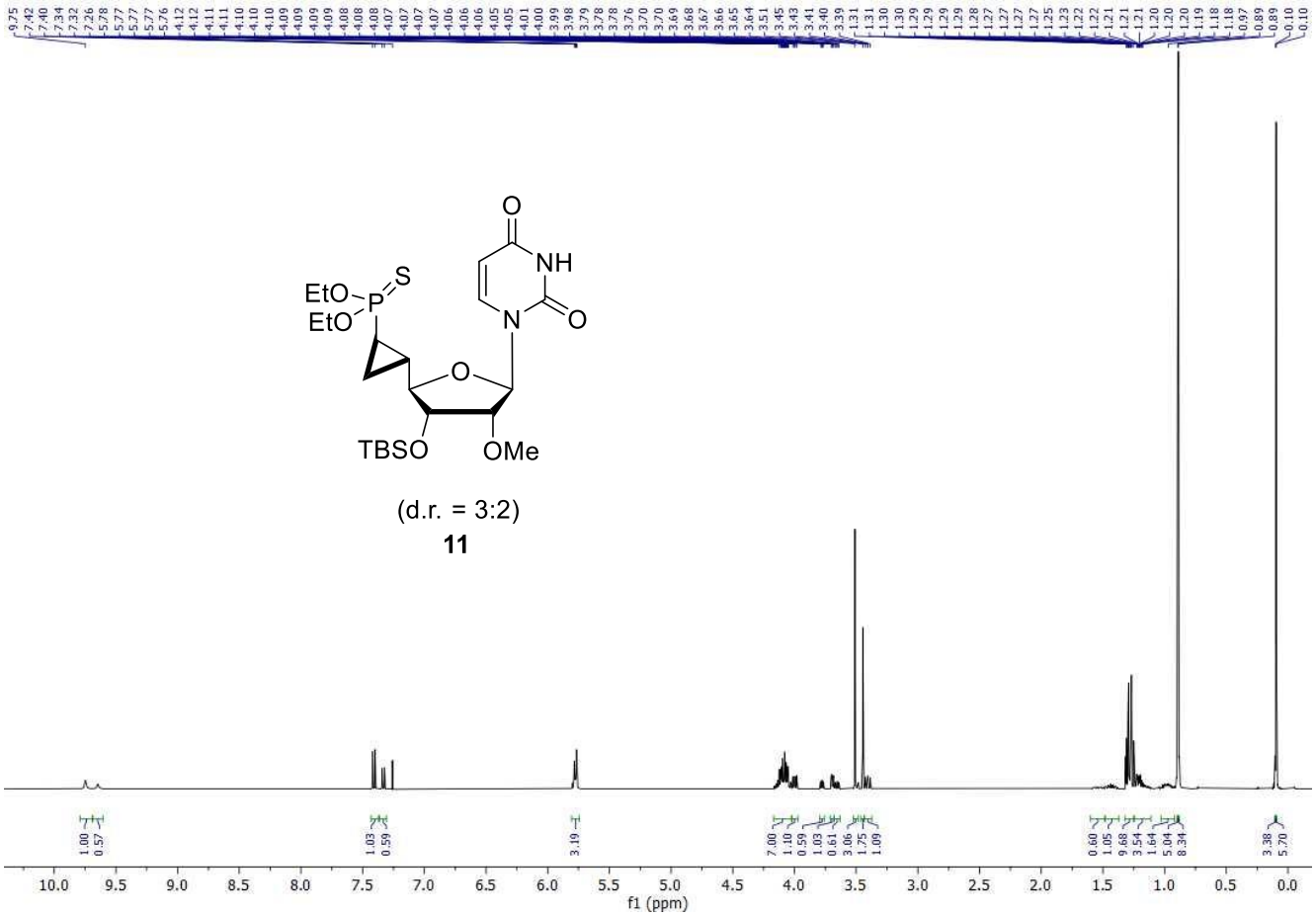
149.75
145.72
145.62
139.64
126.39
124.87
102.77
90.09
83.09
82.54
82.31
77.32
77.01
76.69
74.30
74.29
62.64
62.62
62.59
62.56
58.71
25.65
18.12
16.20
16.18
16.12
16.10
4.66
4.79
O
NH
N
O
EtO
EtO
P
S
O
TBSO
OMe
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

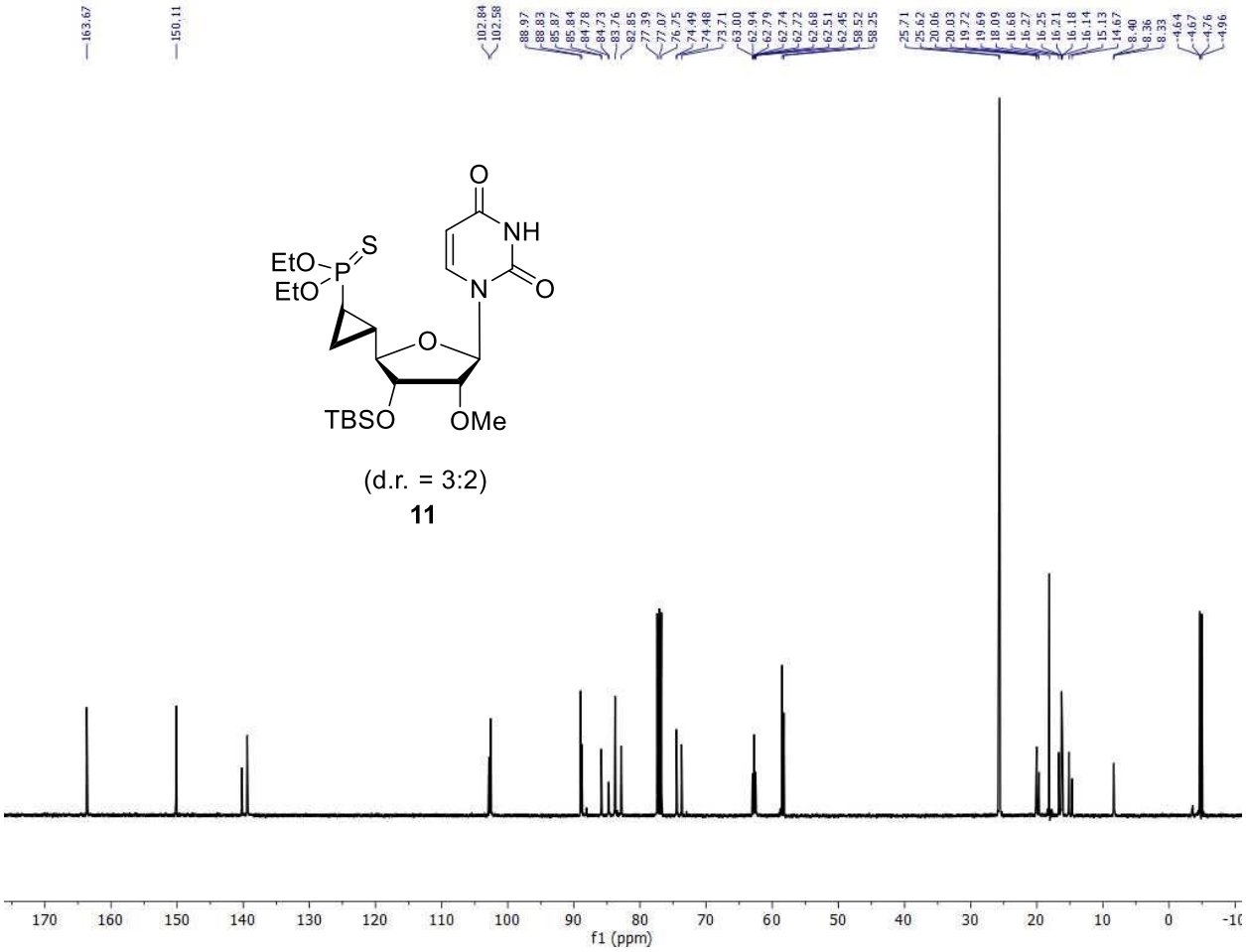
10


84.04
84.00
83.98
83.94
83.93
83.89
83.87
83.85
83.83
83.78
83.73
83.71
83.67
83.65
O
NH
EtO
P
S
EtO
N
O
O
TBSO
OMe
10
1.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)



(d.r. = 3:2)

11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150.11
102.84
102.58
88.97
88.83
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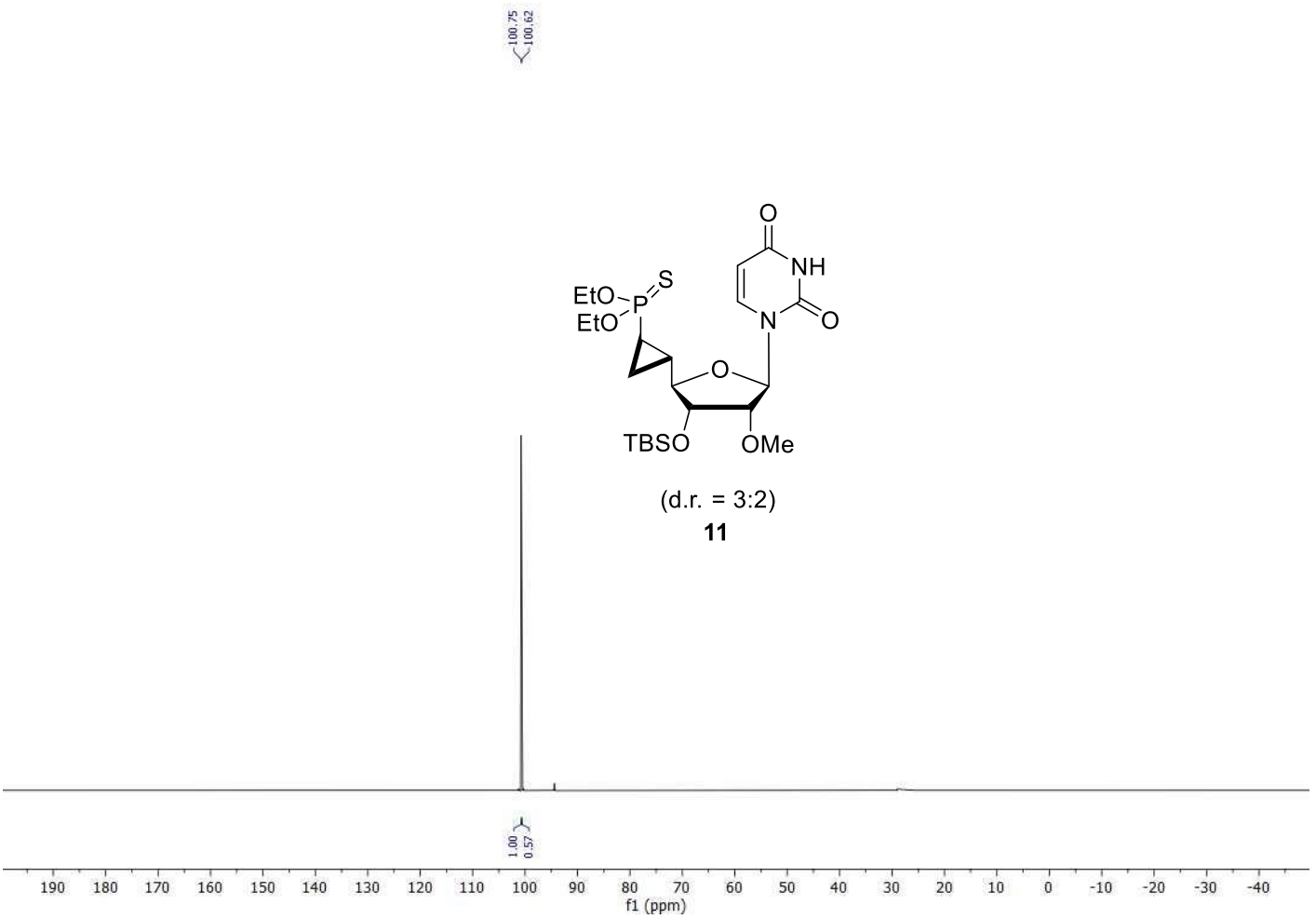
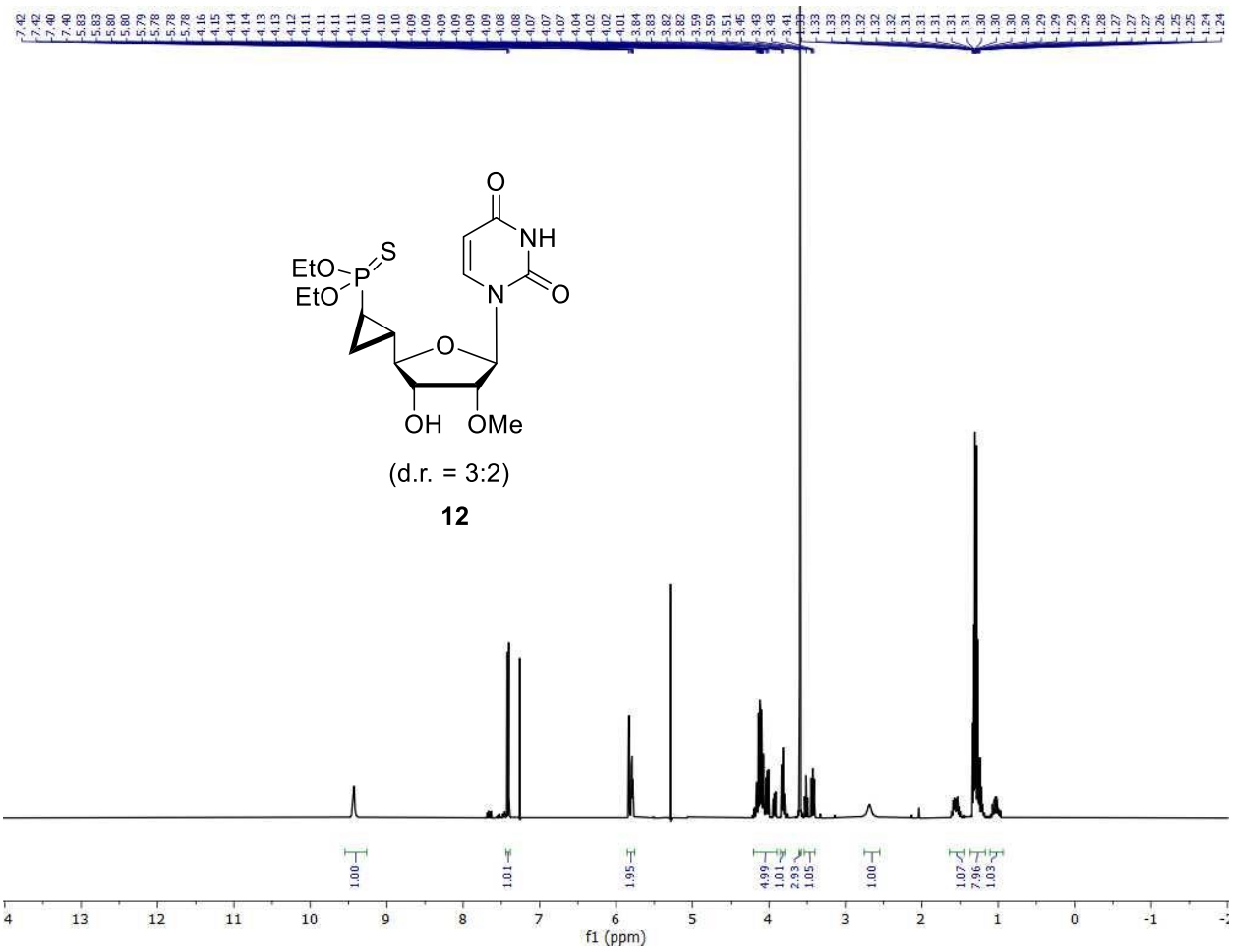
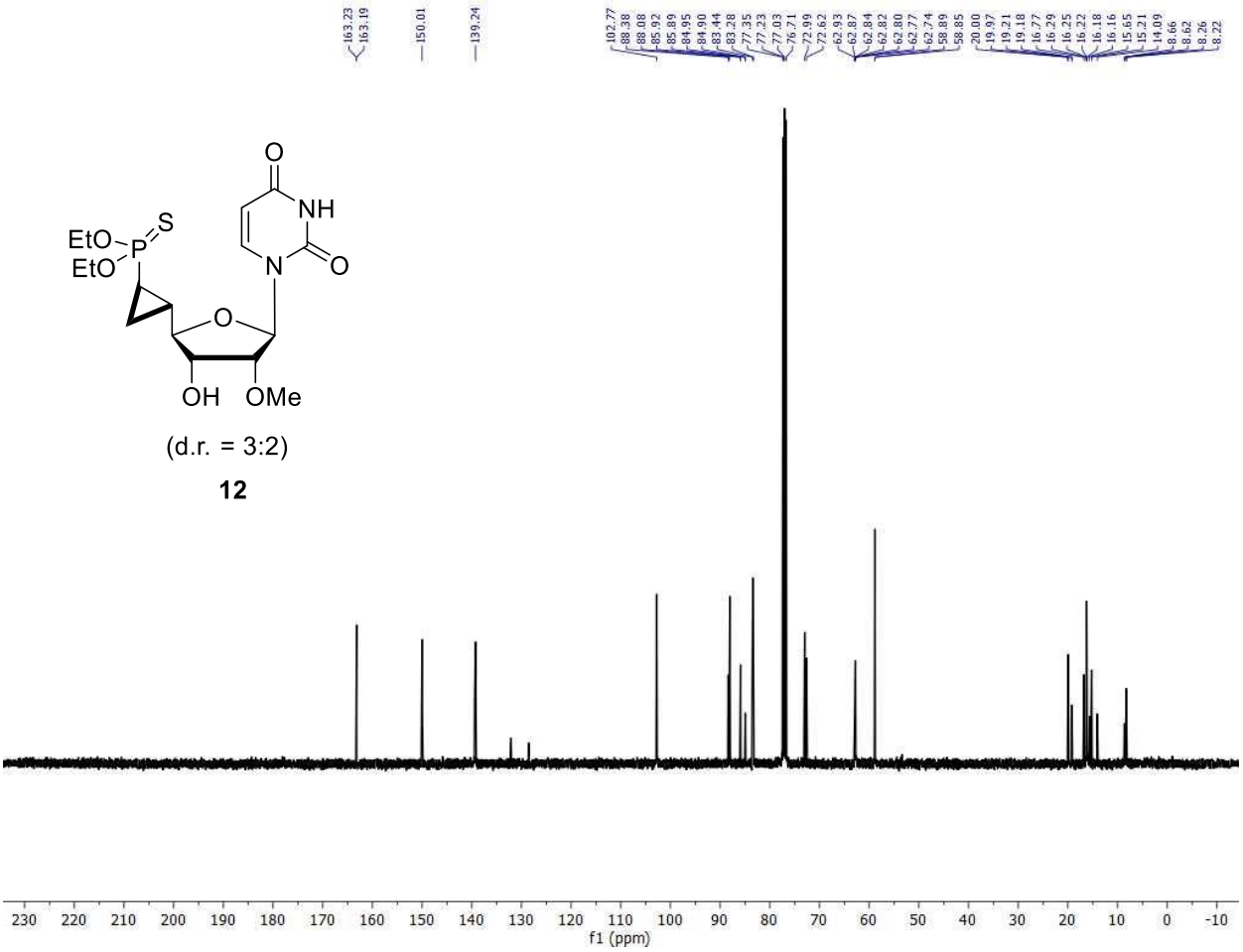
85.84
84.78
84.73
83.76
82.85
77.39
77.07
76.75
74.49
74.48
73.71
63.00
62.94
62.79
62.74
62.72
62.68
62.51
62.45
58.52
58.25
25.71
25.62
20.06
20.03
19.72
19.69
18.09
16.68
16.27
16.25
16.21
16.18
16.14
15.13
14.67
8.40
8.36
8.33
-4.64
-4.67
-4.76
-4.96
O
NH
N
O
EtO
EtO
P
S
O
TBSO
OMe
(d.r. = 3:2)
11
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


100.75
100.62
O
NH
EtO
EtO
P
S
N
O
O
TBSO
OMe
1.00
0.57
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

(d.r. = 3:2)

11


O
NH
EtO
EtO
P
S
N
O
O
OH
OMe
(d.r. = 3:2)
12
1.00
1.01
1.95
4.99
1.01
2.93
1.05
1.00
1.07
7.96
1.03
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)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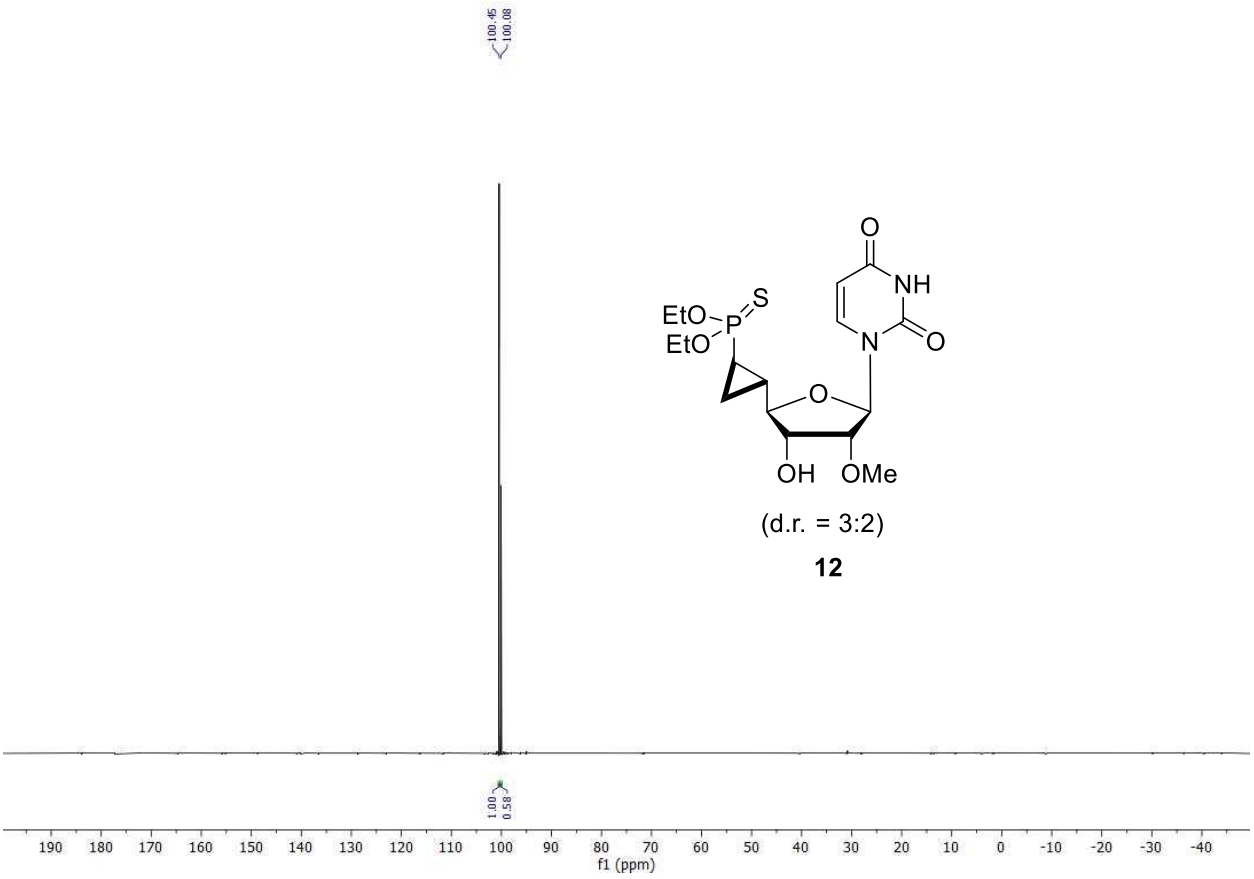
163.19
150.01
139.24
102.77
88.38
88.08
85.92
85.89
84.95
84.90
83.44
83.28
77.35
77.23
77.03
76.71
72.99
72.62
62.93
62.87
62.84
62.82
62.80
62.77
62.74
58.89
58.85
20.00
19.97
19.21
19.18
16.77
16.29
16.25
16.22
16.18
16.16
15.65
15.21
14.09
8.66
8.62
8.26
8.22
O
NH
EtO
P
S
EtO
N
O
O
OH
OMe
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

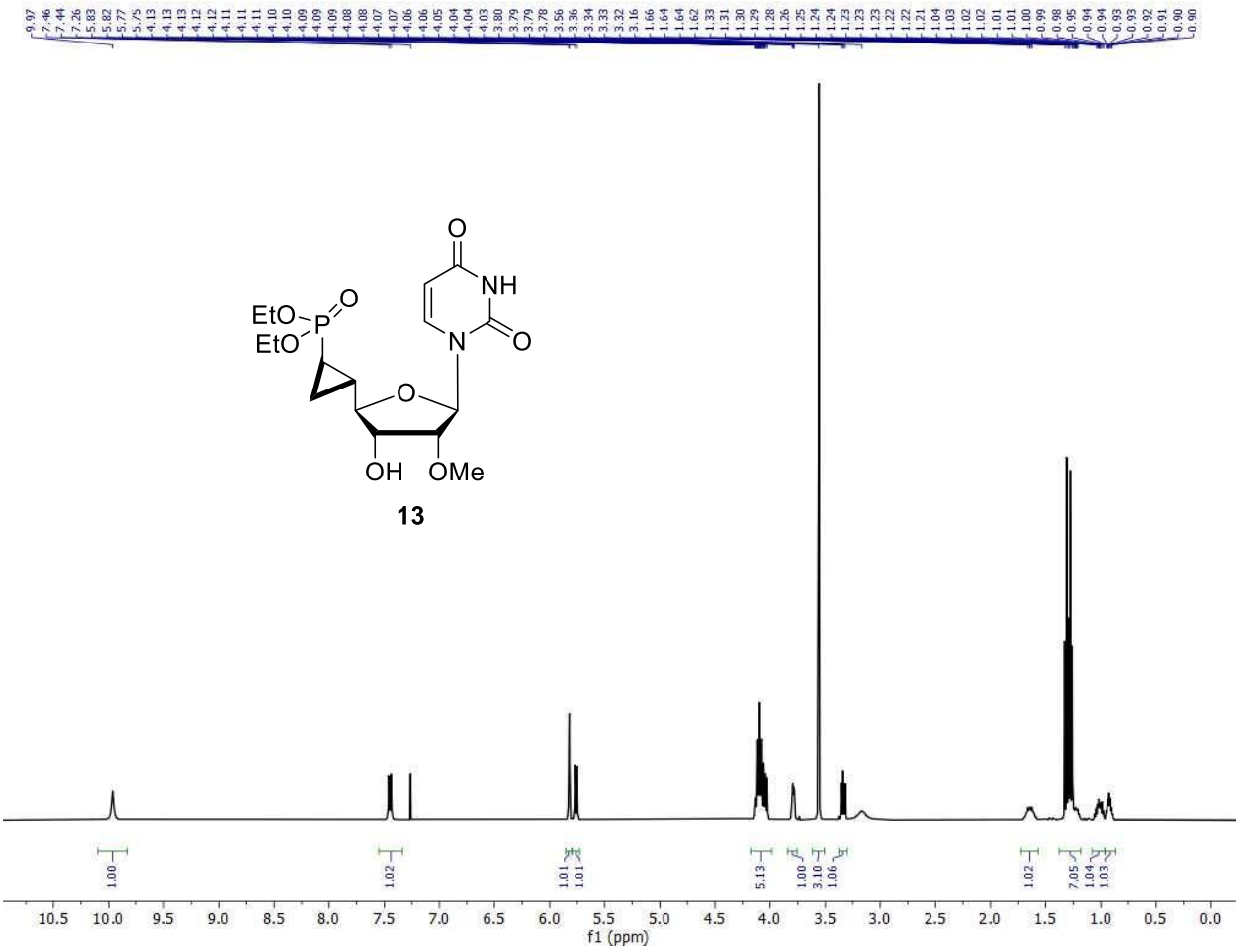
(d.r. = 3:2)

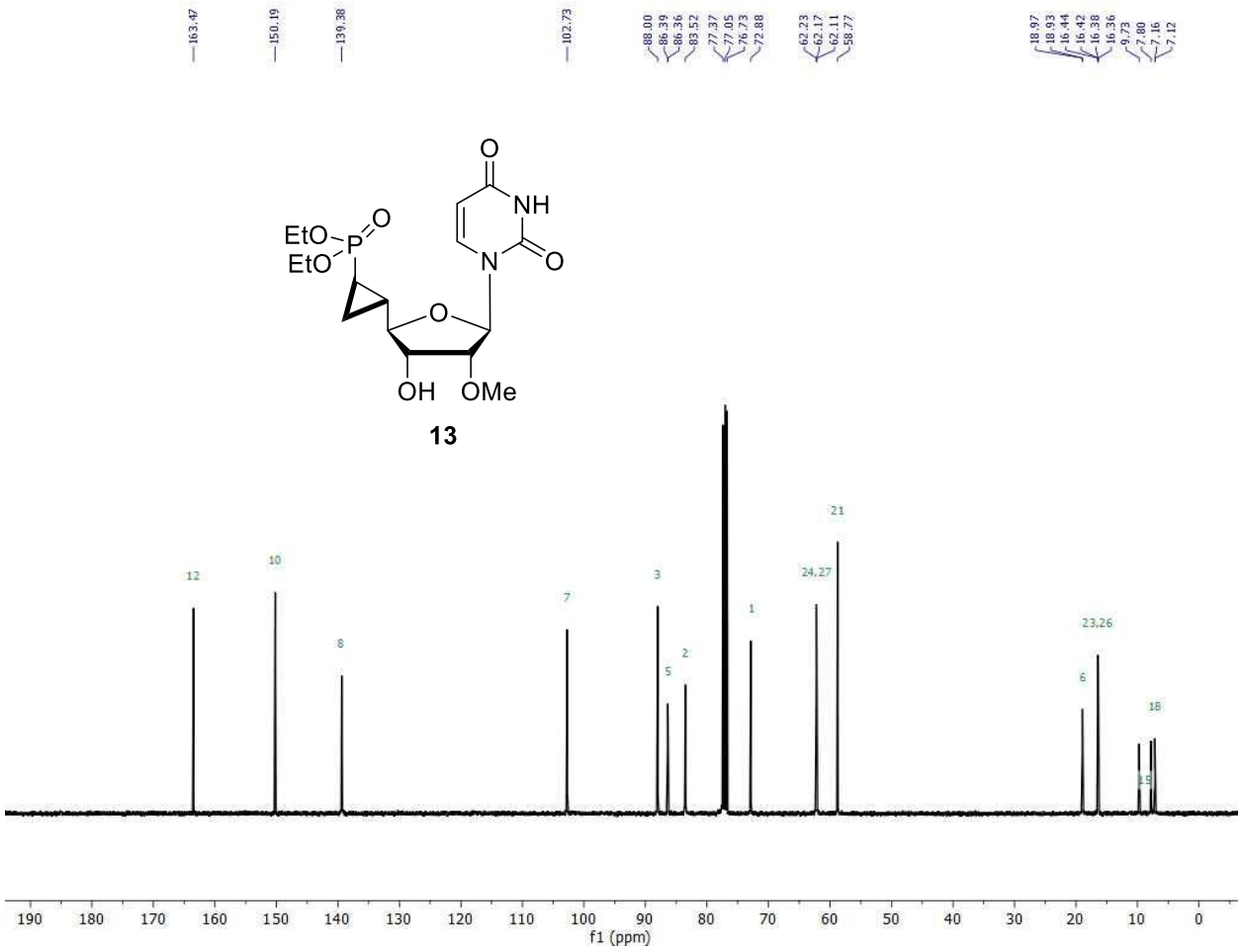
12


100.45
100.08
EtO
EtO
P
S
O
NH
N
O
O
OH
OMe
1.00
0.58
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)

(d.r. = 3:2)

12


EtO
EtO
P
O
O
NH
N
O
O
OH
OMe
13
f1 (ppm)


163.47
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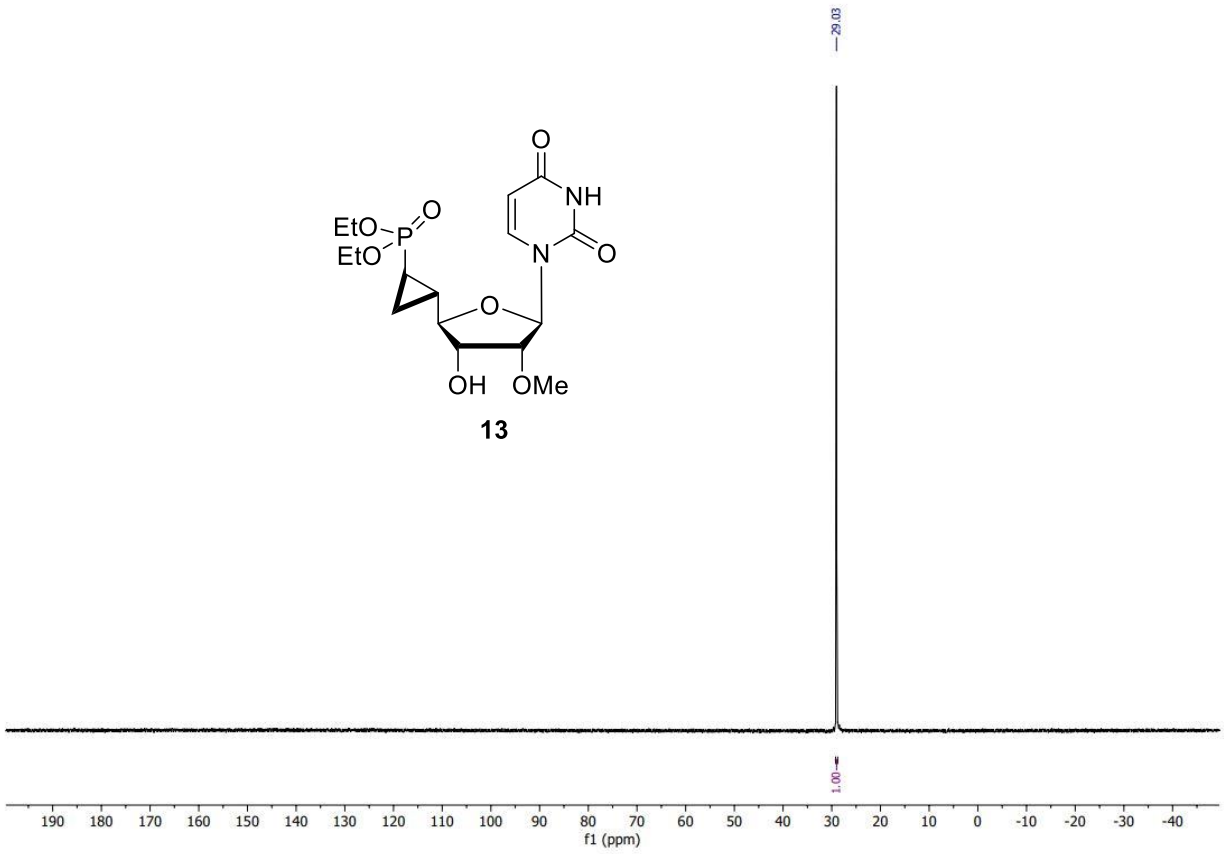
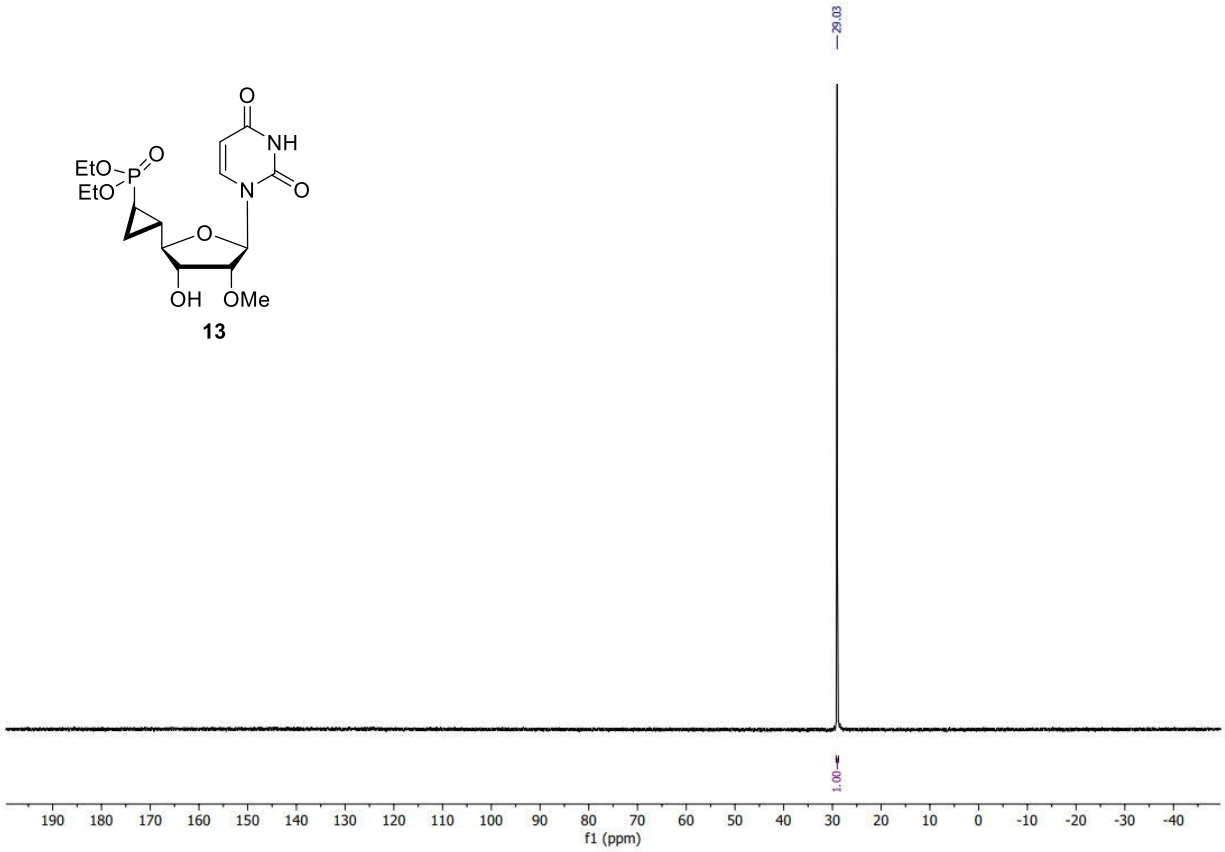
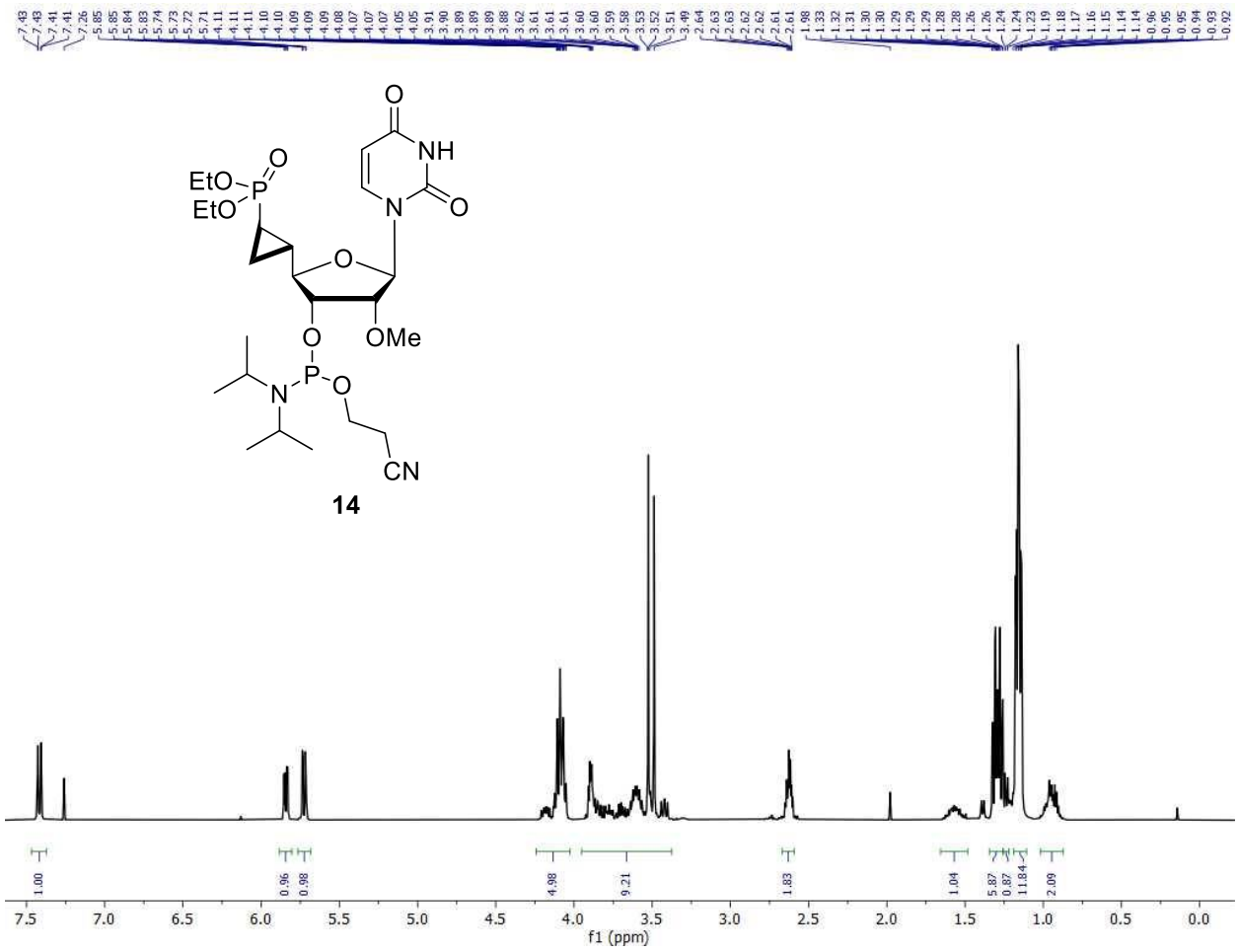
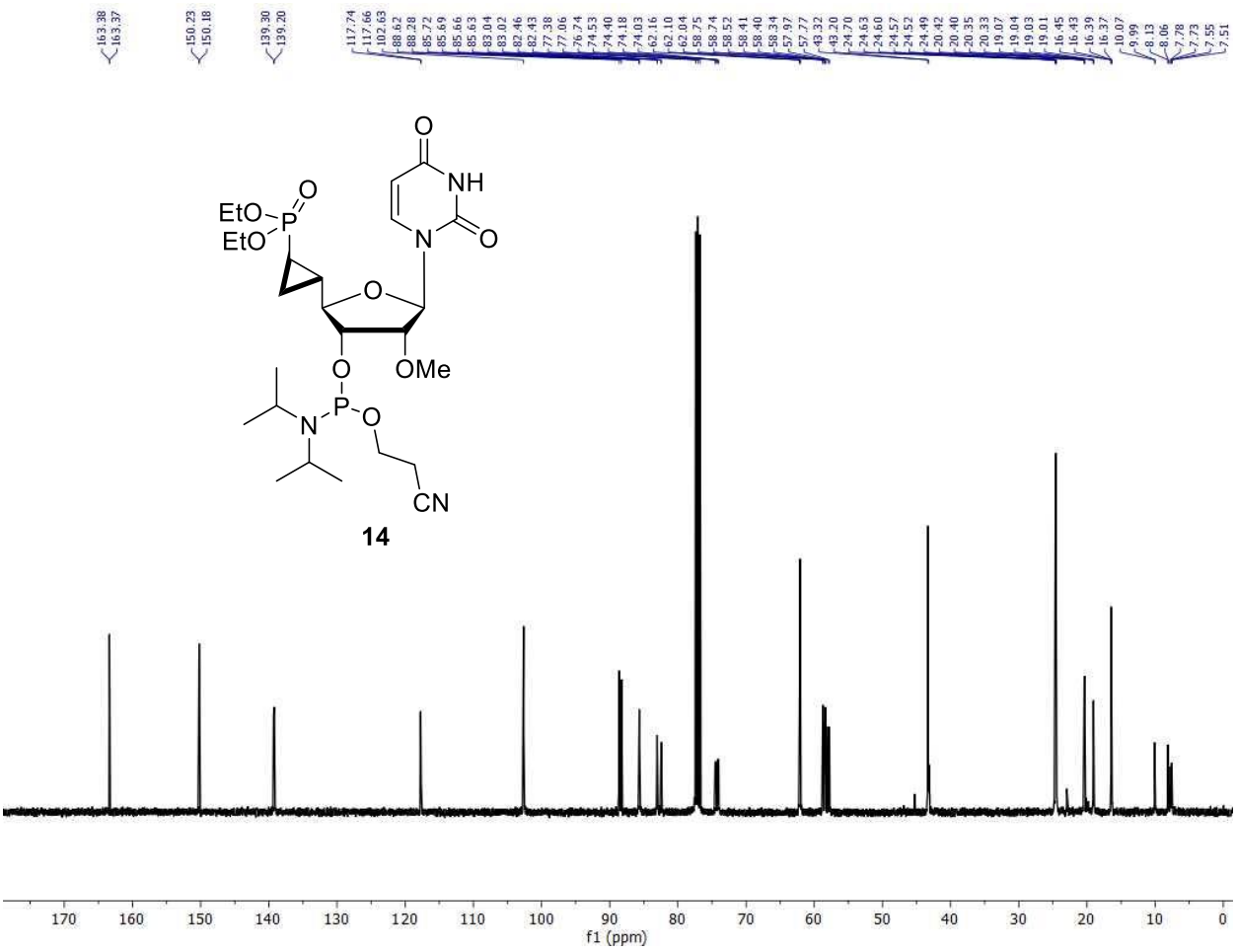
139.38
102.73
88.00
86.39
86.36
83.52
77.37
77.05
76.73
72.88
62.23
62.17
62.11
58.77
18.97
18.93
16.44
16.42
16.38
16.36
9.73
7.80
7.16
7.12
O
NH
EtO
EtO
P
O
N
O
O
OH
OMe
13
12
10
8
7
3
5
2
1
24,27
21
6
23,26
18
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

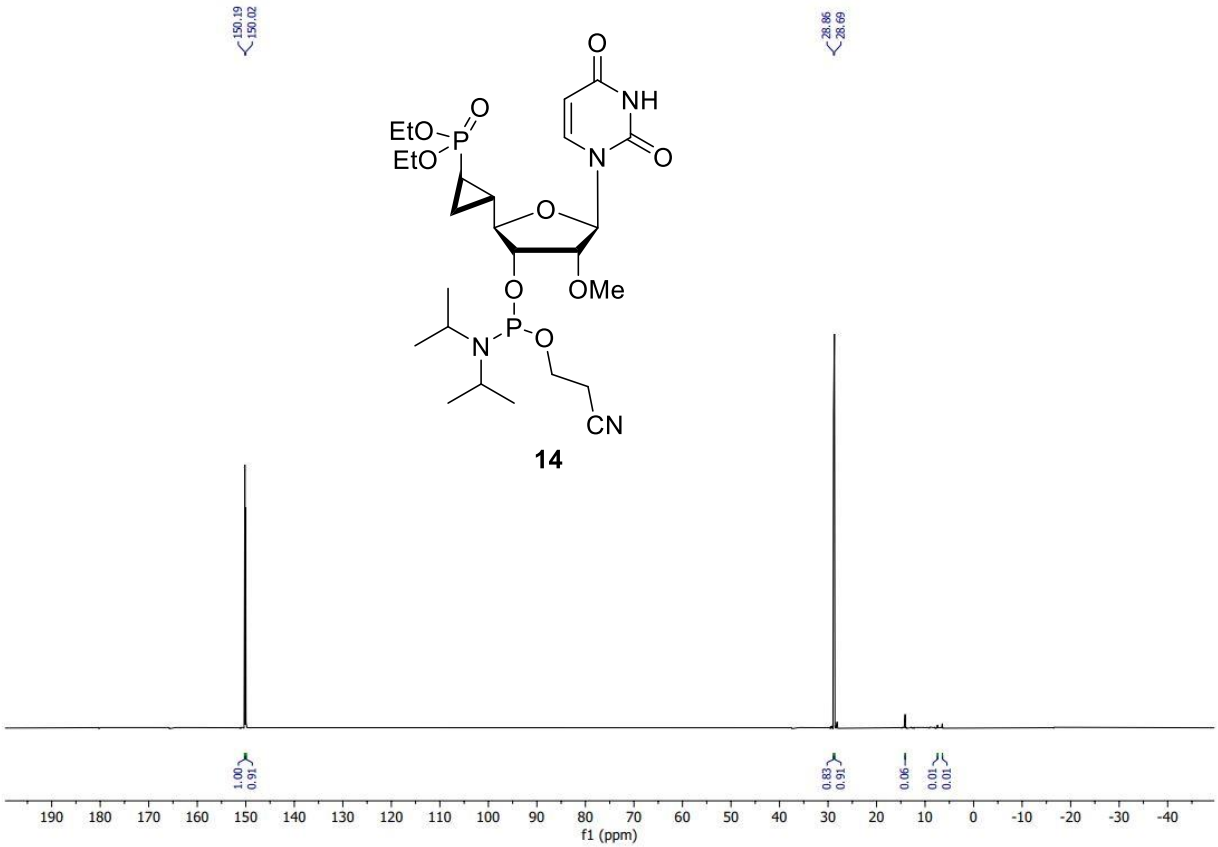

29.03
O
NH
EtO
P
O
EtO
N
O
O
OH
OMe
1.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

13


29.03
O
NH
N
O
EtO
EtO
P
O
O
OH
OMe
13
1.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

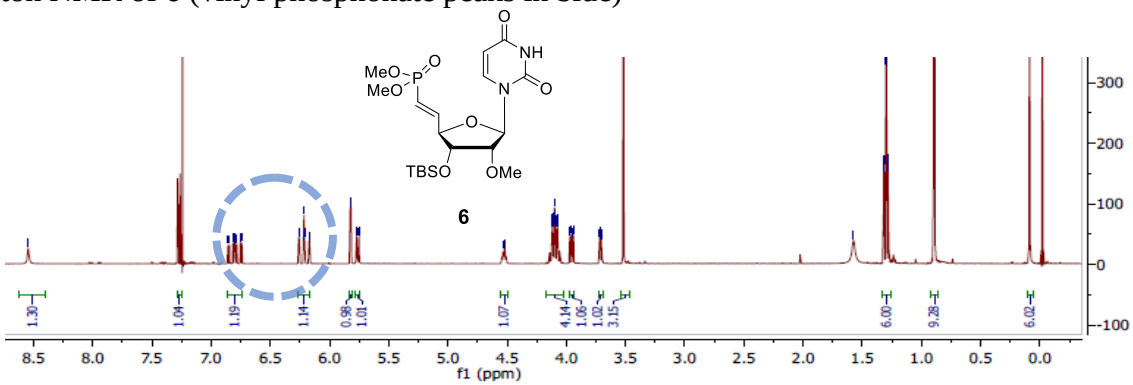

EtO
EtO
P
O
NH
N
O
O
OMe
O
P
O
N
CN
14
1.00
0.96
0.98
4.98
9.21
1.83
1.04
5.87
0.87
11.84
2.09
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


163.38
163.37
150.23
150.18
139.30
139.20
117.74
117.66
102.63
88.62
88.28
85.72
85.69
85.66
85.63
83.04
83.02
82.46
82.43
77.38
77.06
76.74
74.53
74.40
74.18
74.03
62.16
62.10
62.04
58.75
58.74
58.52
58.41
58.40
58.34
57.97
57.77
43.32
43.20
24.70
24.63
24.60
24.57
24.52
24.49
20.42
20.40
20.35
20.33
19.07
19.04
19.03
19.01
16.45
16.43
16.39
16.37
10.07
9.99
8.13
8.06
7.78
7.73
7.55
7.51
EtO
EtO
P
O
NH
N
O
O
O
OMe
O
P
N
O
CN
14
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

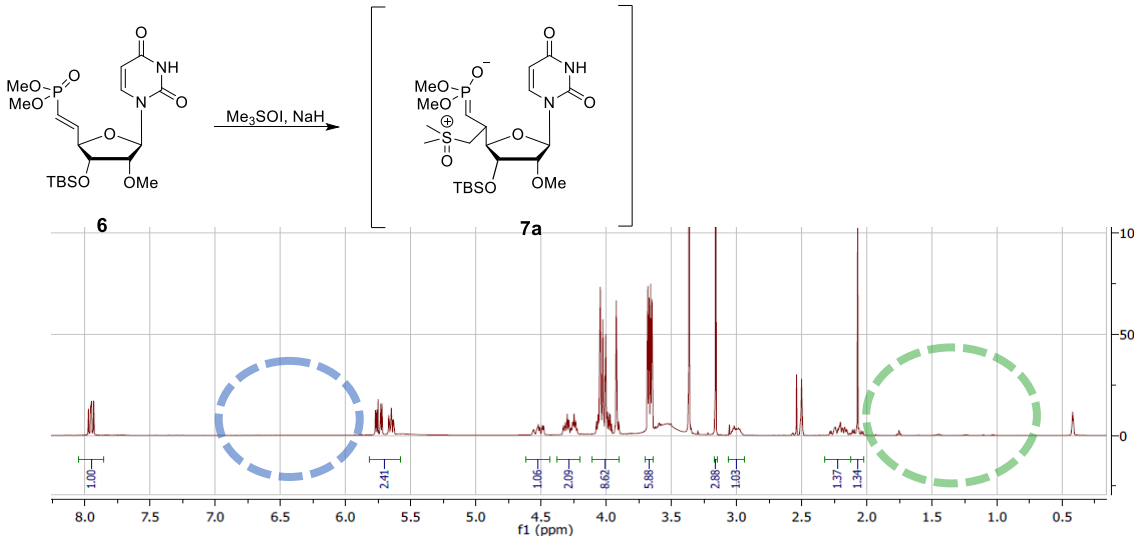

150.19
150.02
28.86
28.69
O
NH
EtO
EtO
P
O
N
O
O
OMe
O
P
N
O
CN
1.00
0.91
0.83
0.91
0.06
0.01
0.01
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

14

Proton NMR of **6** (vinyl phosphonate peaks in blue)



Crude NMR of **7a** (disappearance of vinyl phosphonate protons blue, absence of cp protons green)



Crystallographic Data.

A blocky crystal with a diameter of roughly 1 mm in all three directions was mounted using vacuum grease and analyzed on a Bruker X8 Prospector SCXRD equipped with an IμS microfocus Cu Kα source (λ = 1.54178 Å; beam power = 45 kV, 0.65 mA).

Table 1. Crystal data and structure refinement for Cp-U.

Identification code	s1	
Empirical formula	C16 H25 N2 O8 P	
Formula weight	404.35	
Temperature	298(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12$	
Unit cell dimensions	a = 11.4700(4) Å	α= 90°.
	b = 23.4314(8) Å	β= 90°.
	c = 7.3958(3) Å	γ = 90°.
Volume	1987.68(13) $Å^3$	
Z	4	
Density (calculated)	1.351 Mg/m^3	
Absorption coefficient	1.633 mm^{-1}	
F(000)	856	
Crystal size	1.2 x 1 x 0.88 mm^3	
Theta range for data collection	3.773 to 72.555°.	
Index ranges	-14<=h<=13, -28<=k<=28, -9<=l<=9	
Reflections collected	45084	
Independent reflections	3941 [R(int) = 0.0468]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.3859 and 0.2310	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3941 / 3 / 270	
Goodness-of-fit on F^2	1.052	
Final R indices [I>2sigma(I)]	R1 = 0.0617, wR2 = 0.1638	
R indices (all data)	R1 = 0.0632, wR2 = 0.1661	
Absolute structure parameter	0.029(10)	
Extinction coefficient	0.022(2)	
Largest diff. peak and hole	0.345 and -0.417 $e.Å^{-3}$	

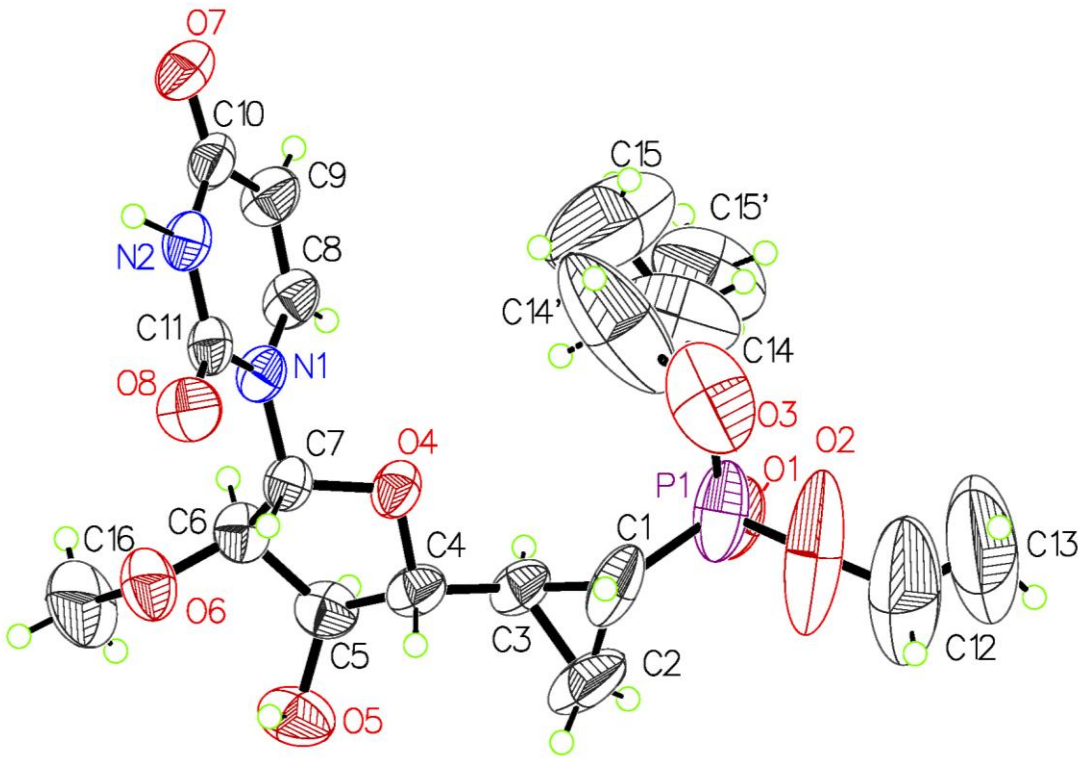


Figure 1: Labeled 50% probability ellipsoid plot of asymmetric/formula unit for Cp-U.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Cp-U. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	5828(1)	8783(1)	8422(2)	96(1)
O(4)	9111(2)	8966(1)	5618(3)	51(1)
O(8)	12355(2)	9187(1)	5842(5)	66(1)
O(7)	13084(3)	7301(1)	6643(5)	71(1)
O(6)	10449(3)	9298(2)	1505(4)	70(1)
O(1)	4993(3)	8483(2)	7237(6)	87(1)
N(2)	12705(3)	8242(1)	6213(5)	50(1)
N(1)	10914(2)	8555(1)	5123(4)	45(1)
C(11)	12023(3)	8697(1)	5730(5)	45(1)
C(10)	12387(3)	7669(2)	6206(6)	52(1)
C(8)	10531(3)	7998(2)	5133(6)	54(1)

O(5)	8207(3)	9663(2)	1567(5)	81(1)
C(1)	6680(3)	9273(2)	7215(8)	77(2)
C(4)	8237(3)	9295(2)	4690(6)	52(1)
C(7)	10127(3)	9001(1)	4539(4)	45(1)
C(6)	9700(3)	8958(2)	2585(5)	54(1)
C(3)	7068(3)	9116(2)	5358(6)	56(1)
C(9)	11203(3)	7567(2)	5676(7)	61(1)
C(5)	8437(4)	9186(2)	2665(6)	58(1)
C(2)	6148(4)	9551(2)	5603(13)	103(2)
O(3)	6677(5)	8398(3)	9540(9)	143(2)
O(2)	5277(5)	9137(4)	9975(10)	210(5)
C(16)	10388(8)	9155(3)	-382(7)	110(2)
C(12)	4177(13)	9211(7)	10470(20)	232(8)
C(13)	3695(16)	9003(11)	11620(20)	283(11)
C(14)	6950(30)	7869(9)	9080(40)	144(11)
C(14')	7600(50)	8001(13)	8630(40)	250(30)
C(15)	7950(40)	7480(20)	8910(50)	250(20)
C(15')	6590(30)	7553(13)	9190(30)	165(10)

Table 3. Bond lengths [Å] and angles [°] for Cp-U.

P(1)-O(1)	1.475(4)
P(1)-C(1)	1.753(6)
P(1)-O(3)	1.563(7)
P(1)-O(2)	1.552(6)
O(4)-C(4)	1.439(4)
O(4)-C(7)	1.415(4)
O(8)-C(11)	1.212(4)
O(7)-C(10)	1.220(5)
O(6)-C(6)	1.418(5)
O(6)-C(16)	1.437(6)
N(2)-C(11)	1.369(5)
N(2)-C(10)	1.392(5)
N(1)-C(11)	1.390(4)
N(1)-C(8)	1.375(5)
N(1)-C(7)	1.447(4)
C(10)-C(9)	1.433(5)
C(8)-C(9)	1.333(6)
O(5)-C(5)	1.407(5)
C(1)-C(3)	1.489(7)
C(1)-C(2)	1.489(10)
C(4)-C(3)	1.489(5)
C(4)-C(5)	1.536(6)
C(7)-C(6)	1.529(5)
C(6)-C(5)	1.545(6)
C(3)-C(2)	1.478(5)
O(3)-C(14)	1.322(19)
O(3)-C(14')	1.56(5)
O(2)-C(12)	1.325(13)
C(12)-C(13)	1.129(19)
C(14)-C(15)	1.46(4)
C(14')-C(15')	1.62(4)
O(1)-P(1)-C(1)	111.8(3)

O(1)-P(1)-O(3)	116.4(3)
O(1)-P(1)-O(2)	115.5(3)
O(3)-P(1)-C(1)	107.4(3)
O(2)-P(1)-C(1)	104.7(4)
O(2)-P(1)-O(3)	99.8(5)
C(7)-O(4)-C(4)	105.9(3)
C(6)-O(6)-C(16)	112.7(4)
C(11)-N(2)-C(10)	126.9(3)
C(11)-N(1)-C(7)	119.6(3)
C(8)-N(1)-C(11)	121.2(3)
C(8)-N(1)-C(7)	119.1(3)
O(8)-C(11)-N(2)	122.7(3)
O(8)-C(11)-N(1)	122.5(3)
N(2)-C(11)-N(1)	114.8(3)
O(7)-C(10)-N(2)	120.7(3)
O(7)-C(10)-C(9)	125.2(4)
N(2)-C(10)-C(9)	114.2(3)
C(9)-C(8)-N(1)	122.3(3)
C(3)-C(1)-P(1)	118.3(3)
C(2)-C(1)-P(1)	117.8(3)
C(2)-C(1)-C(3)	59.5(4)
O(4)-C(4)-C(3)	108.6(3)
O(4)-C(4)-C(5)	105.8(3)
C(3)-C(4)-C(5)	114.3(3)
O(4)-C(7)-N(1)	107.7(3)
O(4)-C(7)-C(6)	105.4(3)
N(1)-C(7)-C(6)	115.8(3)
O(6)-C(6)-C(7)	107.5(3)
O(6)-C(6)-C(5)	113.3(3)
C(7)-C(6)-C(5)	103.9(3)
C(1)-C(3)-C(4)	120.4(3)
C(2)-C(3)-C(1)	60.2(4)
C(2)-C(3)-C(4)	119.3(4)
C(8)-C(9)-C(10)	120.3(3)
O(5)-C(5)-C(4)	113.8(3)

O(5)-C(5)-C(6)	115.4(4)
C(4)-C(5)-C(6)	103.6(3)
C(3)-C(2)-C(1)	60.3(3)
P(1)-O(3)-C(14')	122.7(15)
C(14)-O(3)-P(1)	123.5(9)
C(12)-O(2)-P(1)	131.4(8)
C(13)-C(12)-O(2)	128(2)
O(3)-C(14)-C(15)	142(4)
O(3)-C(14')-C(15')	78(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for Cp-U. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	49(1)	143(1)	97(1)	-40(1)	16(1)	-30(1)
O(4)	37(1)	66(1)	49(1)	-2(1)	-1(1)	7(1)
O(8)	50(1)	60(2)	88(2)	0(1)	-10(1)	-14(1)
O(7)	49(2)	73(2)	92(2)	6(2)	8(2)	17(1)
O(6)	72(2)	93(2)	46(1)	1(1)	5(1)	-7(2)
O(1)	40(1)	106(2)	116(3)	-18(2)	-1(2)	-16(2)
N(2)	33(1)	60(2)	58(2)	-1(1)	2(1)	-2(1)
N(1)	33(1)	51(1)	52(2)	-4(1)	-2(1)	-3(1)
C(11)	32(1)	57(2)	45(2)	-1(1)	3(1)	-7(1)
C(10)	38(2)	58(2)	61(2)	-2(2)	9(2)	6(1)
C(8)	36(2)	54(2)	73(2)	-8(2)	-5(2)	-4(1)
O(5)	78(2)	85(2)	79(2)	24(2)	-28(2)	-2(2)
C(1)	37(2)	85(3)	109(4)	-42(3)	11(2)	-5(2)
C(4)	43(2)	47(2)	68(2)	-3(2)	-7(2)	4(1)
C(7)	37(2)	50(2)	48(2)	-3(1)	0(1)	-1(1)
C(6)	54(2)	61(2)	46(2)	-4(2)	-5(2)	-2(2)
C(3)	37(2)	54(2)	76(2)	-7(2)	-9(2)	5(1)
C(9)	43(2)	48(2)	91(3)	-6(2)	2(2)	-4(1)
C(5)	55(2)	61(2)	59(2)	4(2)	-15(2)	-4(2)
C(2)	42(2)	65(2)	200(7)	-4(4)	0(3)	14(2)
O(3)	102(4)	225(7)	102(4)	15(4)	-43(3)	-65(4)
O(2)	114(4)	329(11)	187(7)	-151(8)	88(5)	-100(6)
C(16)	148(7)	136(5)	45(2)	-4(3)	10(3)	3(5)
C(12)	236(15)	252(16)	209(13)	-94(13)	134(13)	-67(13)
C(13)	260(20)	390(30)	201(16)	32(17)	140(16)	-10(20)
C(14)	210(30)	90(11)	129(17)	5(12)	-94(19)	-46(14)
C(14')	450(70)	170(20)	123(17)	-24(18)	40(30)	-190(40)
C(15)	270(40)	290(40)	200(30)	-40(30)	-60(30)	160(40)
C(15')	230(30)	170(20)	94(11)	11(14)	-61(16)	-20(20)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Cp-U.

	x	y	z	U(eq)
H(8)	9776	7920	4747	65
H(1)	7220	9506	7927	92
H(4)	8354	9701	4950	63
H(7)	10498	9373	4724	54
H(6)	9710	8560	2173	65
H(3)	6797	8744	4924	67
H(9)	10903	7199	5710	73
H(5A)	7914	8878	2289	70
H(2A)	5356	9446	5289	123
H(2B)	6350	9946	5365	123
H(16A)	10933	9384	-1045	165
H(16B)	9613	9225	-821	165
H(16C)	10575	8759	-540	165
H(12A)	4094	9619	10663	279
H(12B)	3720	9125	9398	279
H(13A)	2906	9140	11650	425
H(13B)	3695	8597	11461	425
H(13C)	4074	9097	12742	425
H(14A)	6608	7843	7885	173
H(14B)	6433	7650	9850	173
H(14C)	8333	7960	9283	296
H(14D)	7717	8056	7346	296
H(15A)	7678	7115	8497	382
H(15B)	8495	7634	8062	382
H(15C)	8315	7438	10070	382
H(15D)	6813	7175	8828	247
H(15E)	6473	7562	10473	247
H(15F)	5874	7656	8591	247
H(2)	13580(100)	8290(40)	6330(180)	198

H(5)	8860(80)	9870(50)	2030(180)	247

Table 6. Torsion angles [°] for Cp-U.

P(1)-C(1)-C(3)-C(4)	-144.2(3)
P(1)-C(1)-C(3)-C(2)	107.3(4)
P(1)-C(1)-C(2)-C(3)	-108.2(4)
P(1)-O(3)-C(14)-C(15)	135(4)
P(1)-O(3)-C(14')-C(15')	-102.2(13)
P(1)-O(2)-C(12)-C(13)	102(2)
O(4)-C(4)-C(3)-C(1)	71.4(5)
O(4)-C(4)-C(3)-C(2)	142.1(5)
O(4)-C(4)-C(5)-O(5)	-145.1(3)
O(4)-C(4)-C(5)-C(6)	-19.0(4)
O(4)-C(7)-C(6)-O(6)	146.8(3)
O(4)-C(7)-C(6)-C(5)	26.5(4)
O(7)-C(10)-C(9)-C(8)	-176.5(4)
O(6)-C(6)-C(5)-O(5)	4.5(5)
O(6)-C(6)-C(5)-C(4)	-120.5(3)
O(1)-P(1)-C(1)-C(3)	-37.7(4)
O(1)-P(1)-C(1)-C(2)	30.7(5)
O(1)-P(1)-O(3)-C(14)	23(2)
O(1)-P(1)-O(3)-C(14')	63.5(15)
O(1)-P(1)-O(2)-C(12)	1.8(18)
N(2)-C(10)-C(9)-C(8)	4.2(6)
N(1)-C(8)-C(9)-C(10)	-2.6(7)
N(1)-C(7)-C(6)-O(6)	-94.4(4)
N(1)-C(7)-C(6)-C(5)	145.3(3)
C(11)-N(2)-C(10)-O(7)	178.8(4)
C(11)-N(2)-C(10)-C(9)	-1.8(6)
C(11)-N(1)-C(8)-C(9)	-1.7(6)
C(11)-N(1)-C(7)-O(4)	-121.7(3)
C(11)-N(1)-C(7)-C(6)	120.7(3)
C(10)-N(2)-C(11)-O(8)	177.1(4)
C(10)-N(2)-C(11)-N(1)	-2.1(5)
C(8)-N(1)-C(11)-O(8)	-175.2(4)
C(8)-N(1)-C(11)-N(2)	3.9(5)

C(8)-N(1)-C(7)-O(4)	55.7(4)
C(8)-N(1)-C(7)-C(6)	-61.8(4)
C(1)-P(1)-O(3)-C(14)	-103(2)
C(1)-P(1)-O(3)-C(14')	-62.6(15)
C(1)-P(1)-O(2)-C(12)	125.1(16)
C(4)-O(4)-C(7)-N(1)	-164.0(3)
C(4)-O(4)-C(7)-C(6)	-39.9(3)
C(4)-C(3)-C(2)-C(1)	-110.3(5)
C(7)-O(4)-C(4)-C(3)	160.2(3)
C(7)-O(4)-C(4)-C(5)	37.1(3)
C(7)-N(1)-C(11)-O(8)	2.2(5)
C(7)-N(1)-C(11)-N(2)	-178.6(3)
C(7)-N(1)-C(8)-C(9)	-179.1(4)
C(7)-C(6)-C(5)-O(5)	120.9(4)
C(7)-C(6)-C(5)-C(4)	-4.1(4)
C(3)-C(4)-C(5)-O(5)	95.5(4)
C(3)-C(4)-C(5)-C(6)	-138.4(3)
C(5)-C(4)-C(3)-C(1)	-170.8(4)
C(5)-C(4)-C(3)-C(2)	-100.1(6)
C(2)-C(1)-C(3)-C(4)	108.6(4)
O(3)-P(1)-C(1)-C(3)	91.2(5)
O(3)-P(1)-C(1)-C(2)	159.6(5)
O(3)-P(1)-O(2)-C(12)	-123.8(16)
O(2)-P(1)-C(1)-C(3)	-163.4(5)
O(2)-P(1)-C(1)-C(2)	-94.9(5)
O(2)-P(1)-O(3)-C(14)	148(2)
O(2)-P(1)-O(3)-C(14')	-171.5(15)
C(16)-O(6)-C(6)-C(7)	161.2(5)
C(16)-O(6)-C(6)-C(5)	-84.6(5)

Symmetry transformations used to generate equivalent atoms:

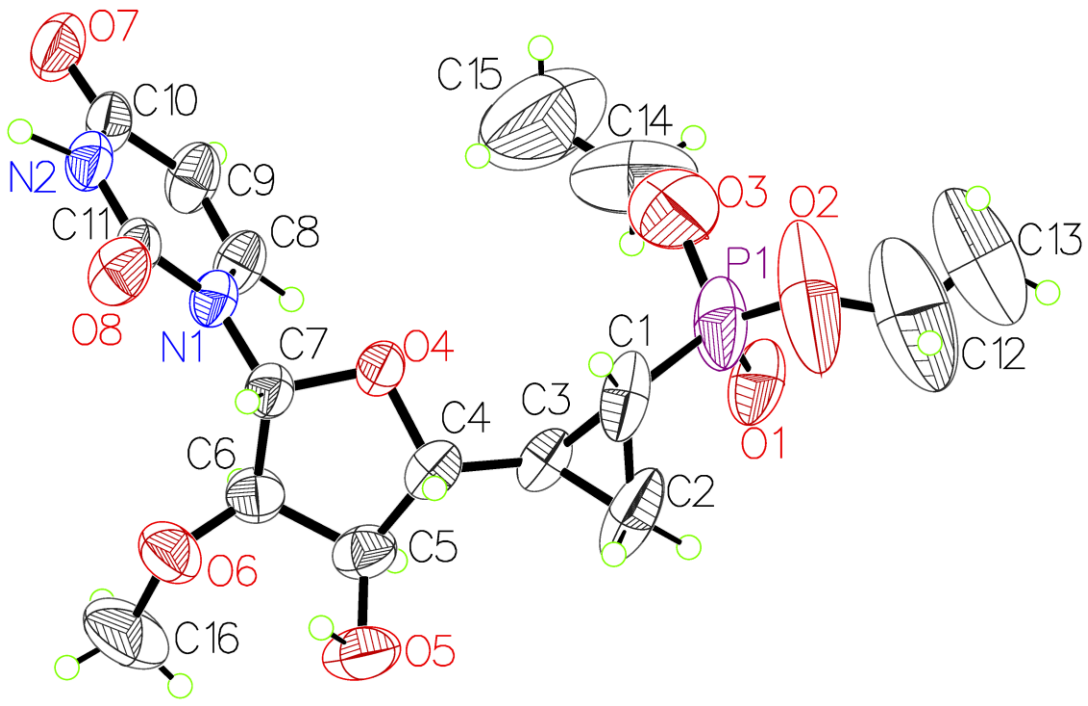
Table 7. Hydrogen bonds for Cp-U [Å and °].

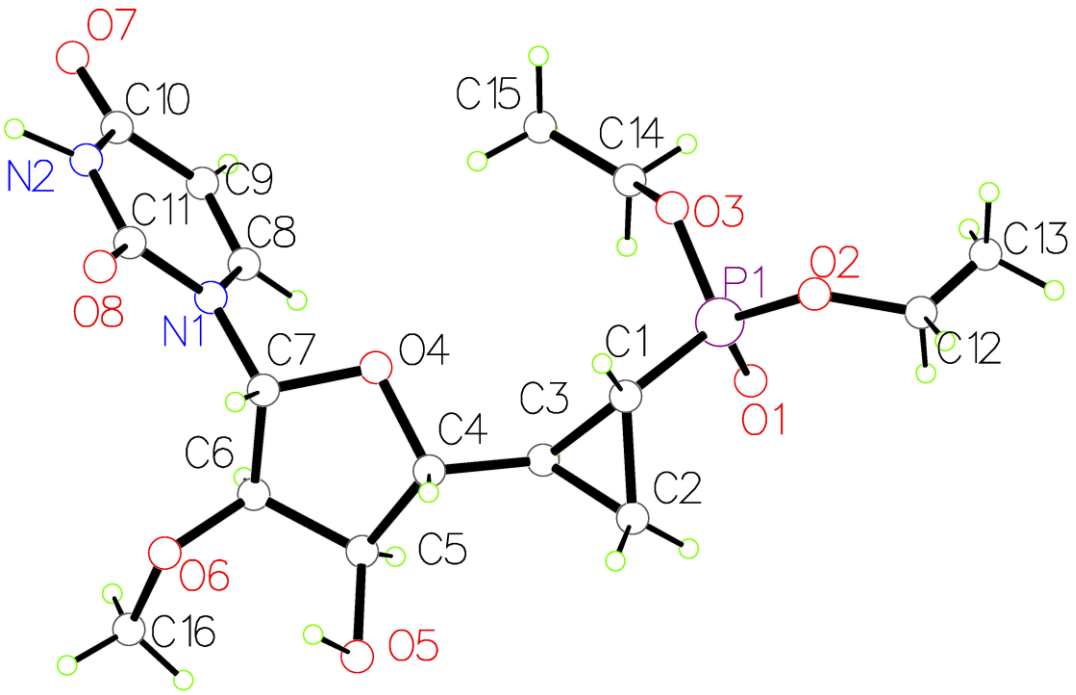
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(8)-H(8)...O(7)#1	0.93	2.26	3.177(5)	170.4
N(2)-H(2)...O(1)#2	1.01(12)	1.81(12)	2.789(4)	161(11)
O(5)-H(5)...O(6)#3	0.95(3)	2.15(10)	2.881(5)	133(11)

Symmetry transformations used to generate equivalent atoms:

#1 x-1/2,-y+3/2,-z+1 #2 x+1,y,z #3 -x+2,-y+2,z

ORTEP Representation




O7
C10
N2
C9
C11
C8
O8
N1
C7
O4
C6
C4
C5
O6
C16
O5
C15
C14
O3
P1
O2
C13
C12
C1
C3
O1
C2

X-ray Crystal Structure of 13 (CCDC Deposition Number 2048176)