Pd-catalyzed Regioselective Asymmetric Addition Reaction of Unprotected Pyrimidines to Alkoxyallene

Supporting Information

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1. General information

Air and moisture sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of nitrogen. Similarly all solvents were dried and distilled according to the standard methods before use, then were transferred via syringe. Reactions were stirred using Teflon-coated magnetic stir bars. $Pd_2(dba)_3$ the Grubbs' catalysts were purchased form a Aldrich Chemical, Strem Chemical Inc. Chiral Trost ligands were purchased from Strem Chemical Inc. and stored in glove box. Reactions were monitored by thin-layer chromatography carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as a visualizing agent and acidic p-anisaldehyde, and heat as developing agent. Flash chromatography was carried out on Merck 60 silica gel (230-400 mesh). ^1H and ^{13}C NMR spectra were recorded on Bruker (300 MHz, 500MHz and 600MHz) spectrometer. ^1H NMR spectra were referenced to $CDCl_3$ (7.26 ppm), and reported as follows; chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). Chemical shifts of the ^{13}C NMR spectra were measured relative to $CDCl_3$ (77.23 ppm). Infrared spectra were recorded on a Bruker Vertex 70 spectrometer. Specific rotation data were measured on Rudolph Research Autopol IV polarimeter. HPLC was performed with an Agilent Technologies 1220 infinity LC system. Mass spectral datas were obtained from the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high resolution mass spectrometer (FAB, EI) and Organic Chemistry Research Center in Sogang University on a Bruker ultra High Resolution ESI Q-TOF MS / MS Compact System (ESI).

2. Optimization Table

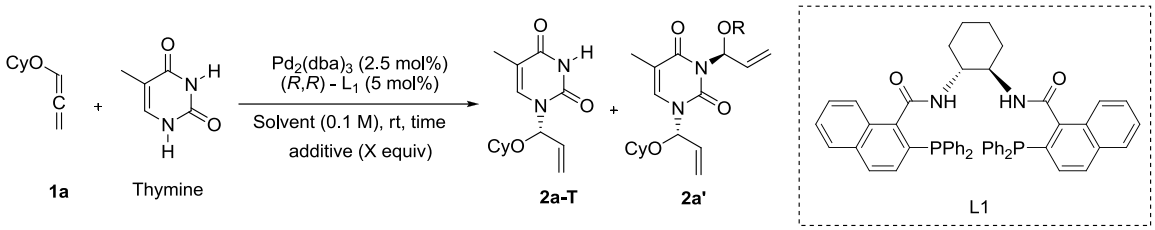


Table. Optimization Table

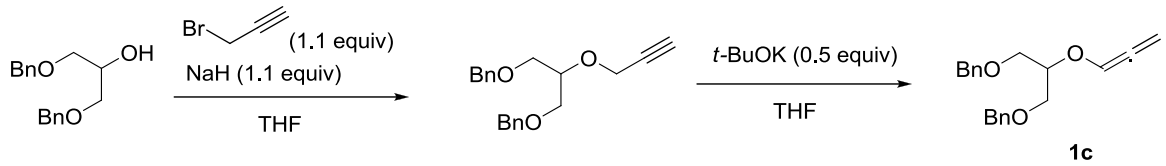
Entry	solvent	Additive (eq)	Time (h)	Yield (2a,%)[a]	Yield (2a',%)[b]	ee (2a,%)
1	CH_2Cl_2	-	1	9	41	58
2	CH_2Cl_2	Et_3N (1.0)	1	36	-	85
3	CH_2Cl_2	K_3PO_4 (0.25)	1	8	71	N.D.[c]
4	THF	-	4	35	25	81
5	Acetone	-	2.5	56	19	98
6	Acetone	Et_3N (1.5)	24	21	33	97
7	Acetone	K_3PO_4 (0.25)	2	25	38	99
8	DMF	-	4	96	<5	71
9	DMF	Et_3N (1.5)	5	80	15	99
10	DMF	K_3PO_4 (0.25)	4	59	15	98
11	Pyridine	-	20	38	2	91
12	Pyridine	K_3PO_4 (0.25)	1	94	Trace	96

[a] Isolated yield. [b] NMR yield. [c] not determined.

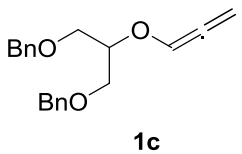
3. Substrate Synthesis for alkoxyallene

Compound 1a[1], 1b[2] have been prepared according to the literature procedure.

General procedure A : allene synthesis



To a suspension of NaH (810.0 mg, 20.3 mmol, 60% dispersion in mineral oil) in THF was added 1,3-Dibenzyloxy-2-propanol (5 g, 18.4 mmol) in THF (total concentration, 0.5 M) at 0℃ under nitrogen atmosphere. The reaction mixture was stirred for 5 min at room temperature. The solution of propargyl bromide (2.3 mL, 20.6 mmol, 80% wt% in Toluene) was added to a reaction mixture at 0℃. The resulting mixture was stirred at room temperature until TLC indicated complete conversion of starting material. The reaction was quenched with distilled water followed by extraction with Ethyl acetate. The organic layers were combined, dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The crude propargyl ether was filtered through a pad of celite and washed with Et_2O. The organic mixture was concentrated and diluted in THF (1.0 M), *t*-BuOK (1.0g, 9.2 mmol) was added. The resulting mixture was stirred at room temperature until TLC indicated complete conversion of propargyl ether. The reaction mixture was diluted with Et_2O and filtered through a celite pad, washing with Et_2O. The solution was then concentrated and purified by flash column chromatography (Hexane:EtOAc = 95:5) afforded **1c** (3.7 g, 12.4 mmol, 67.3% yield over two steps) as a colorless oil.



(2-(propa-1,2-dienyloxy)propane-1,3-diyl)bis(oxy)bis(methylene)dibenzene (1c) :

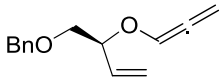
R_f 0.14 (Hexane:EtOAc = 95:5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27-7.36 (m, 10H), 6.75 (t, *J* = 6.04 Hz, 1H),

5.41 (d, J = 6.02 Hz, 2H), 4.56 (dd, J = 12.03, 16.57 Hz, 4H), 4.07-4.10 (m, 1H), 3.64-3.71 (m, 4H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.0, 138.3, 128.5, 127.8, 127.7, 121.1, 91.1, 76.5, 73.6, 68.8.; IR (KBr) ν 3031, 2903, 2860, 1952, 1453, 1196, 1090, 1023 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{22}O_3$ (M^+) 310.1569, found 310.1570.

3

(E)-1-(propa-1,2-dienyloxy)hex-2-ene (3) : Using the general procedure A and purified by Kugelrohor distillation under diminished pressure to afford **3** (3.4 g, 24.9 mmol, 50.0% yield over two steps) as a colorless liquid.

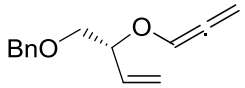
R_f 0.53 (Hexane:EtOAc = 95:5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.73 (t, J = 5.9 Hz, 1H), 5.79-5.70 (m, 1H), 5.65-5.55 (m, 1H), 5.44 (s, 1H), 5.42 (s, 1H), 4.03 (d, J = 6.0 Hz, 2H), 2.07-2.00 (m, 2H), 1.47-1.35 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.6, 135.9, 125.4, 121.4, 90.8, 69.7, 34.6, 22.4, 13.9.; IR (NaCl) ν 2960, 2931, 2874, 1954, 1730, 1673, 1445, 1379, 1350, 1195 cm^{-1}; HRMS (EI) calcd for $C_9H_{14}O$ (M+) 138.1045, found 138.1044.



6

(S)-((2-(propa-1,2-dienyloxy)but-3-enyloxy)methyl)benzene (6) : Based on a modified general procedure A, compound **6** was obtained from (S)-1-(benzyloxy)but-3-en-2-ol[3]. To a solution of propargyl ether (1.00 g, 4.62 mmol) in THF (4.6 mL, 1.0 M), t-BuOK (54.4 mg, 0.46 mmol) was added. The resulting reaction mixture was stirred for 3h at 0 ℃. The reaction mixture was passed through a pad of celite and concentrated under reduced pressure. The crude product was isolated by flash column chromatography (Hexane:Diehtyl ether = 97:3) to afford **6** (346.3 mg, 1.60 mmol, 34.6%) as colorless liquid, and recovered the starting material (556.1 mg, 2.57 mmol, 55.6%).

R_f 0.25 (Hexane:EtOAc = 95:5); $[\alpha]^{22}_D$ +1.25 (c 1.30, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28-7.35 (m, 5H), 6.70 (t, *J* = 5.95 Hz, 1H), 5.75-5.86 (m, 1H), 5.37-5.42 (m, 2H), 5.35-5.28 (m, 2H), 4.59 (dd, *J* = 12.22, 13.88 Hz, 2H), 4.34-4.39 (m, 1H), 3.52-3.63 (m, 2H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.7, 138.2, 134.9, 128.5, 127.81, 127.76, 120.6, 118.3, 90.8, 78.4, 73.5, 72.0.; IR (KBr) ν 3032, 2977, 2860, 1953, 1445, 1195 cm^{-1}; HRMS (FAB) calcd for $C_{13}H_{17}O_2$ ($M+H^+$) 205.1229, found 205.1235.

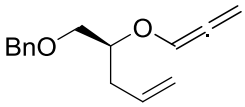


***ent*-6**

(R)-((2-(propa-1,2-dienyloxy)but-3-enyloxy)methyl)benzene (*ent*-6): Based on a modified general procedure A, compound ***ent*-6** was obtained from (S)-1-(benzyloxy)but-3-en-2-ol.

All spectral data matched a compound **6** except for the sign of specific rotation:

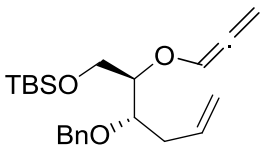
$[\alpha]^{28}_D$ -0.77 (c 0.52, $CHCl_3$)



13

(S)-((2-(propa-1,2-dienyloxy)pent-4-enyloxy)methyl)benzene (13) : Based on a modified general procedure A, compound **13** was obtained from (S)-1-(benzyloxy)pent-4-en-2-ol[4] and purified by flash column chromatography (Hexane: CH_2Cl_2 = 85:15) to afford **13** (2.5 g, 10.9 mmol, 39.0% yield over two steps) as a colorless liquid.

R_f 0.28 (Hexane:EtOAc = 95:5); $[\alpha]^{22}_D$ -11.86 (c 0.59, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.37 (m, 5H), 6.71 (t, *J* = 5.95 Hz, 1H), 5.75-5.83 (m, 1H), 5.39-5.45 (m, 2H), 5.06-5.12 (m, 2H), 4.57 (dd, *J* = 12.12, 18.60 Hz, 2H), 3.92-3.96 (m, 1H), 3.56 (d, *J* = 4.84 Hz, 2H), 2.41-2.44 (m, 2H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.4, 138.3, 133.9, 128.5, 127.8, 127.7, 120.9, 117.7, 90.7, 76.9, 73.5, 70.6, 35.4.; IR (KBr) ν 3032, 2977, 2860, 1952, 1445, 1195 cm^{-1}; HRMS (FAB) calcd for $C_{14}H_{19}O_2$ ($M+H^+$) 219.1385, found 219.1388.



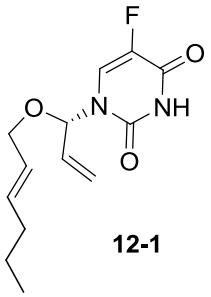
15

((2R,3S)-3-(benzyloxy)-2-(propa-1,2-dienyloxy)hex-5-enyloxy)(tert-butyl)dimethylsilane (15) : Based on a modified general procedure A, compound **15** was obtained from 3-(benzyloxy)-1-(tert-butyldimethylsilyloxy)hex-5-en-2-ol[5] and purified by flash column chromatography (Hexane:Et_2O = 98:2) afforded **15** (1.46 g, 3.89 mmol, 19.0% yield over two steps) as a colorless oil.

R_f 0.51 (Hexane:Et_2O = 95:5); $[\alpha]^{20}_D$ = +5.20 (c = 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26-7.37 (m, 1H), 6.70 (t, *J* = 6.0 Hz, 1H), 5.87 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.33-5.47 (m, 2H), 5.03-5.17 (m, 2H), 4.63 (d, *J* = 11.4 Hz, 1H), 4.58 (d, *J* = 11.4 Hz, 1H), 3.72-3.89 (m, 4H), 2.29-2.48 (m, 2H), 0.90 (s, 9H), 0.06 (s, 6H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.5, 138.8, 135.2, 128.5, 128.1, 127.7, 121.5, 117.4, 90.9, 80.4, 77.4, 72.8, 61.4, 35.5, 26.1, 18.5, -5.1.; IR (KBr) ν 3071, 2929, 2857, 1954, 1647, 1463, 1254, 1200, 1099, 836 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{34}NaO_3Si$ ($M+Na^+$) 397.2169, found 397.2169.

4. Synthesis N-glycosides

General procedure B : Pd-catalyzed hydroamination

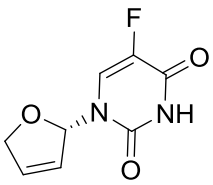


12-1

(S,E)-5-fluoro-1-(1-(hex-2-enyloxy)allyl)pyrimidine-2,4(1H,3H)-dione (12-1) : A solution of **3** (276 mg, 2.0 mmol) in distilled pyridine was added to a suspension of $Pd_2(dba)_3$ (45.8 mg, 50.0 μmol), *(R,R)*-L3 (98.6 mg, 0.125 mmol), K_3PO_4 (106.1 mg, 0.5 mmol) and 5-fluoro uracil (390.2 mg, 3.0 mmol) in distilled pyridine (total concentration of solvent, 0.1M) under nitrogen atmosphere. The reaction mixture was stirred at rt for 12h. The reaction mixture was filtered through a celite pad and washing with CH_2Cl_2. The solution was then concentrated and purified by flash column chromatography on silicagel (Hexane:EtOAc = 90:10) to afford **12-1** as a white solid (416.0 mg, 1.55 mmol, 77.6% yield).. Silica gel was deactivated with few drops of Et_3N and $CDCl_3$ was deactivated with K_2CO_3 before use.

R_f 0.27 (Hexane:EtOAc = 90:10); $[\alpha]^{21}_D$ = -68.5 (c = 0.50, $CHCl_3$); m.p.: 49-51 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.0 (br, s, 1H), 7.33 (d, *J* = 5.6 Hz, 1H), 6.23 (dd, *J* = 3.5, 1.6 Hz, 1H), 5.71-5.80 (m, 2H), 5.54 (d, *J* = 12.2 Hz, 1H), 5.26-5.46 (m, 1H), 5.42 (d, *J* = 10.6 Hz, 1H), 4.01 (ddd, *J* = 19.5, 7.1, 6.4 Hz, 2H), 2.01 (d, *J* = 7.15 Hz, 2H), 1.38 (q, *J* = 7.35 Hz, 2H), 0.88 (t, *J* = 7.35 Hz, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.4, 157.2, 150.0, 142.0, 140.1, 137.1, 133.0, 124.34, 124.28, 124.1, 120.2, 83.0, 70.2, 34.5, 22.2, 13.8.; IR (NaCl) ν 3435, 2961, 3435, 2961, 2091, 1660, 1465, 1383, 1341, 1245 cm^{-1}; HRMS (FAB) calcd for $C_{13}H_{18}FN_2O_3$ ($M+H^+$) 269.1301, found 269.1301.

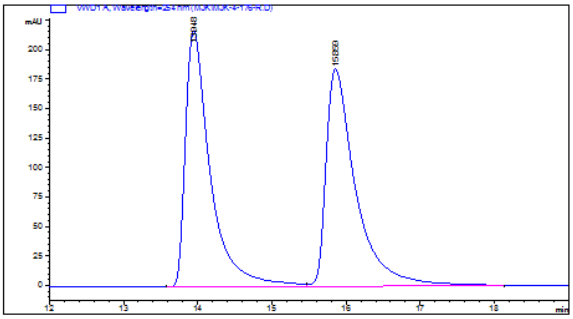
General procedure C : Ring Closing Metathesis

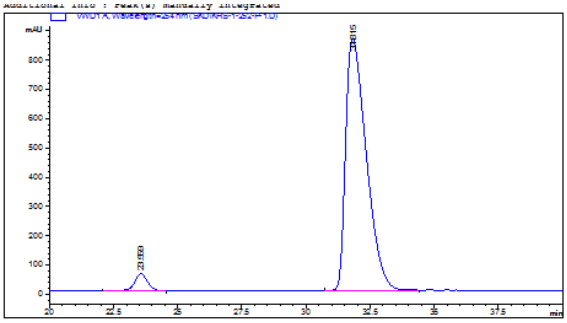


12

(S)-1-(2,5-dihydrofuran-2-yl)-5-fluoropyrimidine-2,4(1H,3H)-dione (12) : To a solution of **12-1** (416.0.0 mg, 1.55 mmol) dissolved in CH_2Cl_2 was added the Hoveyda Grubbs^{2nd} catalyst (48.6 mg, 0.08 mmol) at room temperature. The resulting reaction mixture was stirred at 40℃ for 10 min. The solvent was removed under reduced pressure and purified by flash column chromatography on silicagel (Hexane:EtOAc = 80:20) to afford **12** as a white solid (246.0 mg, 1.24 mmol, 80.1%). The enantiomeric excess (91.2% ee) was determined by HPLC on a chiral column (Chiralpak ID, Hexane: EtOAc = 60:40, flow rate = 1.5 mL/min, UV = 254 nm, retention time = 23.56 (minor), 31.82 (major)).

R_f 0.21 (Hexane:EtOAc = 50:50); $[\alpha]^{29}_D = -137.7$ (c = 1.0, $CHCl_3$); M.p. <260℃ decomp.; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (d, *J* = 5.6 Hz, 1H), 7.01 (s, 1H), 6.49 (d, *J* = 4.8 Hz, 1H), 5.86 (s, 1H), 4.86 (d, *J* =12.0 Hz, 1H), 4.75 (d, *J* = 13.9 Hz, 1H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.1, 156.9, 149.3, 141.9, 140.0, 134.2, 124.6, 123.9, 123.6, 91.5, 76.2.; IR (NaCl) ν 3171, 3051, 2923, 2831, 3171, 3051, 2923, 2831, 1801, 1658 cm^{-1}; HRMS (EI) calcd for $C_8H_7FN_2O_3$ (M^+) 198.0441, found 198.0443.





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Dilution: : 1.0000
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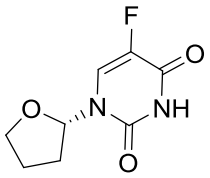
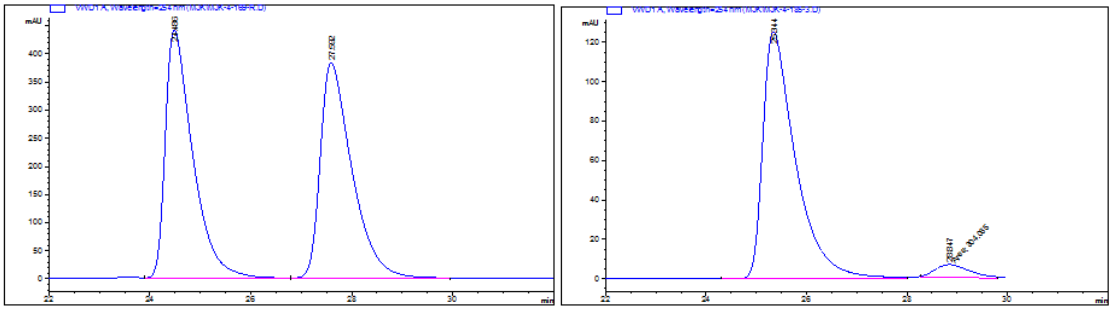


(-)-Tegafur

(S)-5-fluoro-1-(tetrahydrofuran-2-yl)pyrimidine-2,4(1H,3H)-dione ((-)-Tegafur) : Pd/C (2 mg, 10 w%) was added to a solution of **12** (20.0 mg, 0.10 mmol) in MeOH (1 mL). The resulting reaction mixture was stirred at rt under a hydrogen atmosphere (balloon) for 10 min. The mixture was passed through a pad of celite and the filtrate was concentrated under reduced pressure. The crude mixture was purified by flash column chromatography on silicagel(Hexane:EtOAc = 10:90) to afford **(-)-Tegafur** as a white solid (16.0 mg, 0.08 mmol, 78.0%). The enantiomeric excess (89.8% ee) was determined by HPLC on a chiral column (Chiralpak IB, Hexane: EtOAc = 90:10, flow rate = 1.0 mL/min, UV = 254 nm, retention time = 25.34 (major), 28.85 (minor)).

R_f 0.21 (Hexane:EtOAc = 50:50); $[\alpha]^{28}_D = -68.1$ (c = 0.7, $CHCl_3$) (lit. $[\alpha]^{23}_D = -70.0$ (c = 0.5, $CHCl_3$)[6]; m.p.: 170-171 ℃; ^{1}H NMR (500 MHz, MeOD) δ 7.74 (d, *J* = 6.6 Hz, 1H), 5.95 (ddd, *J* = 6.1, 3.3, 1.3 Hz, 1H), 4.26 (dt, *J* = 7.6, 5.1 Hz, 1H), 3.90-3.95 (m, 1H), 2.31-2.38 (m, 1H), 2.05-2.11 (m, 1H), 1.95-2.04 (m, 2H).; ^{13}C NMR (125 MHz, MeOD) δ 159.9, 159.7, 150.8, 142.8, 140.9, 126.2, 125.9, 88.9, 71.3, 33.4, 25.0.; IR (NaCl) ν 3419, 3179, 3049, 2824, 1707, 1427, 1406, 1181, 1107, 1073 cm^{-1}; HRMS (EI) calcd for $C_8H_9FN_2O_3$ (M^+) 200.0597, found 200.0601.



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Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

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Area Percent Report

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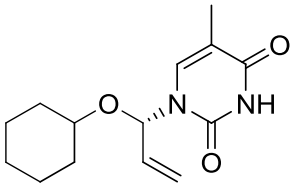
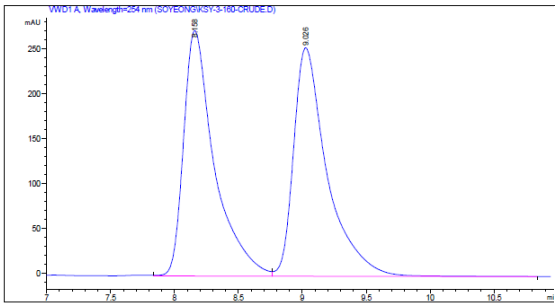


2a-T

(S)-1-(1-(cyclohexyloxy)allyl)-5-methylpyrimidine-2,4(1H,3H)-dione (2a-T) : Using the general procedure **B**, the mixture of **1a** (27.7 mg, 0.2 mmol) and Thymine (25.0 mg, 0.2 mmol) was reacted with $Pd_2(dba)_3$ (4.6 mg, 5.0 μmol), *(R,R)*-L1 (7.9 mg, 10.0 μmol) and K_3PO_4 (10.6 mg, 0.05 mmol) at room temperature for 1h. Flash column chromatography on silica gel (Hexane:EtOAc = 60:40) afforded **2a-T** as a white solid (49.8 mg, 0.19 mmol, 94.2% yield). The enantiomeric excess (96.8% ee) was determined by HPLC on a chiral column (Chiralpak ID, Hexane:iPrOH = 70:30, flow rate = 1.0 mL/min, UV = 254 nm, retention time = 8.04 (major), 9.02 (minor)). R_f 0.23 (Hexane:EtOAc = 70:30); M.p. 128.6-129.3 ºC; $[\alpha]^{22}_D$ = -85.5 (c = 0.37, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.54 (br, s, 1H), 7.13 (d, *J* = 1.32 Hz, 1H), 6.30-6.33 (m, 1H), 5.73-5.84 (m,1H), 5.52 (dt, *J* = 1.44, 17.07 Hz, 1H), 5.38 (dt, *J* = 1.75, 10.29 Hz, 1H), 3.41-3.48 (m,1H), 1.92-1.97 (m, 1H), 1.93 (d, *J* = 1.20 Hz, 3H), 1.70-1.73 (m, 3H), 1.51-1.52 (m, 1H), 1.22-1.39 (m, 5H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.0, 151.1, 136.1, 134.2, 119.2, 111.5, 80.8, 76.5, 33.0, 31.5, 25.6, 24.0, 23.8, 12.7.; IR (NaCl) ν 3180, 3050, 2931, 2857, 1708, 1684, 1464 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{20}N_2O_3$ (M^+) 264.1474, found 264.1477.



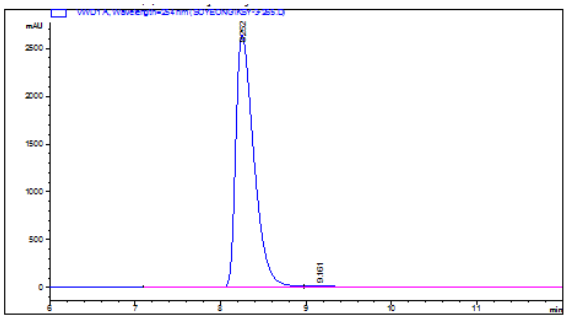
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.158	VV	0.2455	4578.55371	273.27731	49.7158
2	9.026	VB	0.2683	4630.89795	254.44316	50.2842

Totals : 9209.45166 527.72047



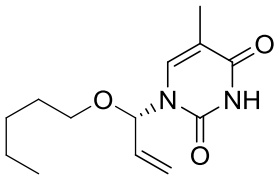
Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

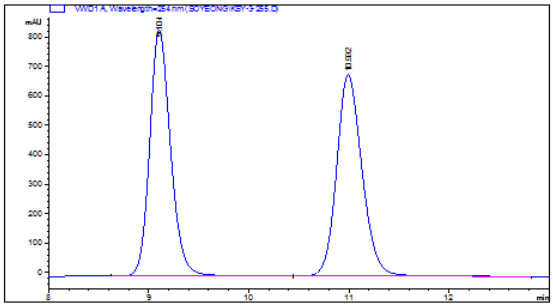
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.252	BV	0.2242	3.89581e4	2639.41748	98.4217
2	9.161	VV	0.4164	624.73090	20.45090	1.5783

Totals : 3.95829e4 2659.86839



2b-T

(S)-5-methyl-1-(1-(pentyloxy)allyl)pyrimidine-2,4(1H,3H)-dione (2b-T) : Using the general procedure **B**, the mixture of **1b** (31.6 mg, 0.25 mmol) and Thymine (47.4 mg, 0.38 mmol) was reacted with $Pd_2(dba)_3$ (5.7 mg, 6.3 μmol), *(R,R)*-L1 (9.9 mg, 13.0 μmol) and K_3PO_4 (13.3 mg, 0.063 mmol) at room temperature for 3h. Flash column chromatography on silica gel (Hexane:EtOAc = 80:20) afforded **2b-T** as a colorless oil (51.1 mg, 0.20 mmol, 81.0%). The enantiomeric excess (96.1% ee) was determined by HPLC on a chiral column (Chiralpak IA, Hexane:iPrOH = 90:10, flow rate = 1.0 mL/min, UV = 254 nm, retention time = 8.79 (major), 10.56 (minor)). R_f 0.49 (Hexane:EtOAc = 60:40); $[\alpha]^{28}_D = -59.5$ (c = 0.46, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48-8.62 (br, 1H), 7.07-7.08 (m, 1H), 6.17-6.19 (m, 1H), 5.79 (ddd, *J* = 3.71, 10.62, 17.20 Hz, 1H), 5.54 (td, *J* = 1.52, 17.20 Hz, 1H), 5.40 (td, *J* = 1.35, 10.62 Hz, 1H), 3.47-3.54 (m, 2H), 1.93 (d, *J* = 1.10 Hz, 3H), 1.57-1.63 (m, 2H), 0.89 (t, *J* = 6.74 Hz, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.5, 151.7, 135.7, 133.6, 119.5, 111.8, 83.1, 77.7, 77.2, 76.8, 69.2, 29.1, 28.3, 22.5, 14.1, 12.7.; IR (NaCl) ν 3185, 3049, 2931, 1694, 1466, 1377, 1251, 1220, 1098 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{20}N_2O_3$ (M^+) 252.1474, found 252.1478.



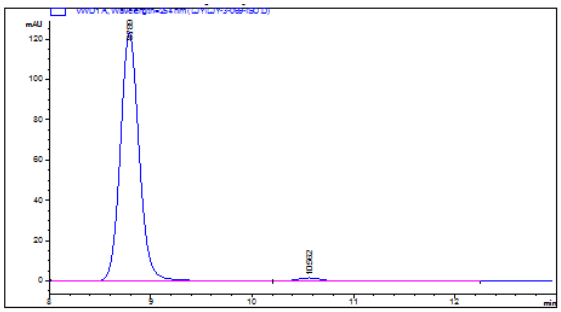
Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.104	VB	0.2215	1.21430e4	835.95679	50.1214
2	10.992	BB	0.2722	1.20842e4	683.87360	49.8786

Totals : 2.42271e4 1519.83038



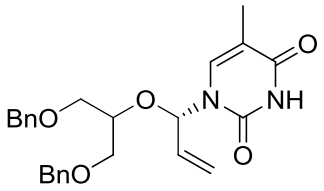
Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.789	BV	0.2013	1597.57178	123.16422	98.0339
2	10.562	VB	0.2797	32.04029	1.70132	1.9661

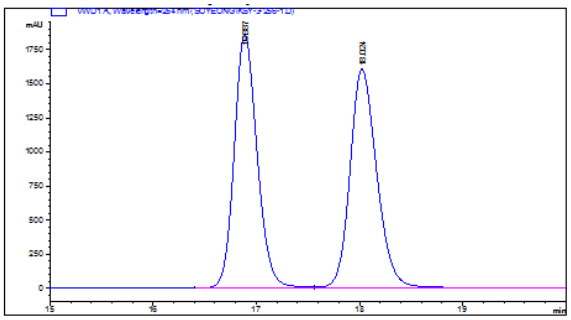
Totals : 1629.61207 124.86554



2c-T

(S)-1-(1-(1,3-bis(benzyloxy)propan-2-yloxy)allyl)-5-methylpyrimidine-2,4(1H,3H)-dione (2c-T) : Using the general procedure **B**, the mixture of **1c** (31.6 mg, 0.25 mmol) and Thymine (47.4 mg, 0.38 mmol) was reacted with $Pd_2(dba)_3$ (5.7 mg, 6.3 μmol), *(R,R)*-L1 (9.9 mg, 13.0 μmol) and K_3PO_4 (13.3 mg, 0.063 mmol) at room temperature for 4h. Flash column chromatography on silica gel (Hexane:EtOAc = 70:30) afforded **2c-T** as a colorless oil (86.1 mg, 0.20 mmol, 78.4%). The enantiomeric excess (87.9% ee) was determined by HPLC on a chiral column (Chiralpak ID, Hexane:iPrOH = 70:30, flow rate = 1.0 mL/min, UV = 254 nm, retention time = 16.93 (major), 19.61 (minor)).

R_f 0.33 (Hexane:EtOAc = 60:40); $[\alpha]^{28}_D = -41.5$ (c = 0.59, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (br s, 1H), 7.22-7.35 (m, 10H), 7.12-7.14 (m, 1H), 6.43-6.45 (m, 1H), 5.80 (ddd, *J* = 3.75, 10.54, 17.18 Hz, 1H), 5.53 (d, *J* = 17.18 Hz, 1H), 5.39 (d, *J* = 10.54 Hz, 1H), 4.54 (d, *J* = 4.29 Hz, 2H), 4.43 (s, 2H), 3.94-3.98 (m, 1H), 3.57-3.63 (m, 2H), 3.48-3.54 (m, 2H), 1.75 (d, *J* = 0.83 Hz, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4, 151.5, 138.0, 137.9, 136.5, 133.7, 128.5, 127.8, 127.76, 127.69, 127.6, 119.6, 111.2, 82.6, 77.6, 77.2, 76.84, 76.80, 73.43, 73.38, 70.1, 69.5.; IR (NaCl) ν 3185, 3031, 2926, 2861, 1690, 1495, 1371, 1251, 1075, 1028 cm^{-1}; HRMS (EI) calcd for $C_{25}H_{28}N_2O_5$ (M^+) 436.1998, found 436.2000.



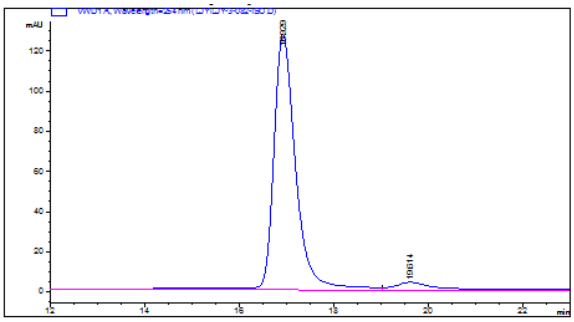
Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.887	VV	0.2365	2.88235e4	1862.82666	49.7155
2	18.024	VB	0.2799	2.91533e4	1605.38245	50.2845

Totals : 5.79768e4 3468.20911



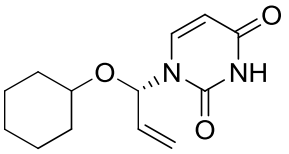
Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

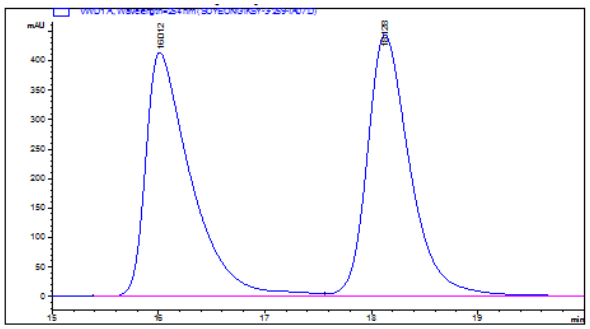
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.929	BV	0.4946	4178.03369	127.40030	93.9302
2	19.614	VB	0.9776	269.98761	3.79670	6.0698

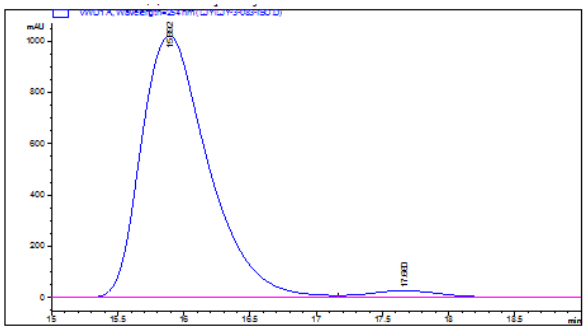
Totals : 4448.02130 131.19700



2a-U

(S)-1-(1-(cyclohexyloxy)allyl)pyrimidine-2,4(1H,3H)-dione (2a-U) : Using the general procedure **B**, the mixture of **1a** (34.6 mg, 0.25 mmol) and uracil (42.1 mg, 0.38 mmol) was reacted with $Pd_2(dba)_3$ (5.7 mg, 6.3 μmol), *(R,R)*-L1 (9.9 mg, 13.0 μmol) and K_3PO_4 (13.3 mg, 0.063 mmol) at room temperature for 1.5h. Flash column chromatography on silica gel (Hexane:EtOAc = 70:30) afforded **2a-U** as a white solid (55.0 mg, 0.22 mmol, 88.0%). The enantiomeric excess (94.0% ee) was determined by HPLC on a chiral column (Chiralpak IA, Hexane:iPrOH = 90:10, flow rate = 1.0 mL/min, UV = 254 nm, retention time = 15.89 (major), 17.66 (minor)). R_f 0.53 (Hexane:EtOAc = 60:40); M.p. 99.6-100.0 ºC; $[\alpha]^{28}_D = -57.4$ (c = 0.48, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.89-9.01 (br, 1H), 7.33 (d, *J* = 8.28 Hz, 1H), 6.31-6.33 (m, 1H), 5.75-5.82 (m, 2H), 5.52 (d, *J* = 17.11 Hz, 1H), 5.38 (d, *J* = 10.58 Hz, 1H), 3.44-3.48 (m, 1H), 1.92-1.95 (m, 1H), 1.65-1.72 (m, 3H), 1.49-1.54 (m, 1H), 1.19-1.42 (m, 5H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.4, 151.1, 140.5, 134.1, 119.4, 103.1, 81.3, 77.5, 77.2, 77.0, 35.0, 31.6, 25.7, 24.0, 23.8.; IR (NaCl) ν 3185, 3057, 2934, 2858, 1693, 1454, 1381, 1248, 1124, 1061, 1026 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{18}N_2O_3$ (M^+) 250.1317, found 250.1317.





Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

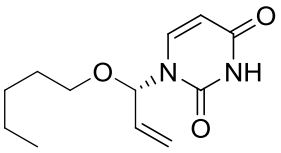
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.012	BV	0.4327	1.22384e4	414.27515	49.7727
2	18.128	VBA	0.4208	1.23502e4	443.54813	50.2273
Totals :				2.45886e4	857.82327	

Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

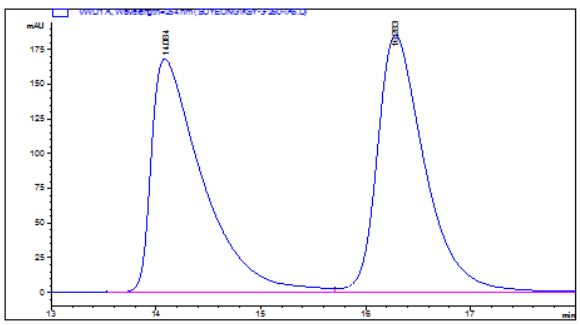
Signal 1: VWD1 A, Wavelength=254 nm

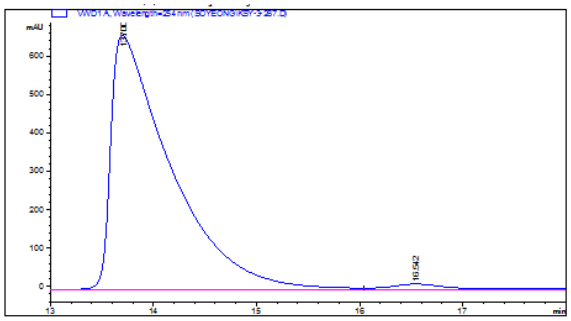
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.892	BV	0.5397	3.60161e4	1020.52216	97.0151
2	17.660	VBA	0.6157	1108.11060	27.17618	2.9849
Totals :				3.71242e4	1047.69833	



2b-U

(S)-1-(1-(pentyloxy)allyl)pyrimidine-2,4(1H,3H)-dione (2b-U) : Using the general procedure **B**, the mixture of **1b** (25.2 mg, 0.20 mmol) and uracil (22.4 mg, 0.20 mmol) was reacted with $Pd_2(dba)_3$ (4.6 mg, 5.0 μmol), *(R,R)*-L1 (7.9 mg, 10.0 μmol) and K_3PO_4 (10.6 mg, 0.05 mmol) at room temperature for 6h. Flash column chromatography on silica gel (Hexane:EtOAc = 70:30) afforded **2b-U** as a colorless oil (39.8 mg, 0.17 mmol, 83.5%). The enantiomeric excess (96.2% ee) was determined by HPLC on a chiral column (Chiralpak IA, Hexane:iPrOH = 95:5, flow rate = 1.5 mL/min, UV = 254 nm, retention time = 13.70 (major), 16.54 (minor)). R_f 0.52 (Hexane:EtOAc = 40:60); $[\alpha]^{23}_D = -65.7$ (c = 0.44, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.17 (br s, 1H), 7.28 (d, *J* = 8.04 Hz), 6.18-6.20 (m, 1H), 5.73-5.84 (m, 2H), 5.53 (dt, *J* = 1.32, 17.25 Hz), 5.41 (dt, *J* = 1.44, 10.51 Hz), 3.45-3.56 (m, 2H), 1.55-1.61 (m, 2H), 1.24-1.34 (m, 4H), 0.86-0.91 (m, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.6, 151.3, 140.1, 133.4, 119.7, 103.3, 83.4, 69.4, 29.1, 28.3, 22.5, 14.1.; IR (NaCl) ν 3194, 3058, 2957, 2933, 2872, 1692, 1457, 1381, 1250 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{18}N_2O_3$ (M^+) 238.1317, found 238.1316.





Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

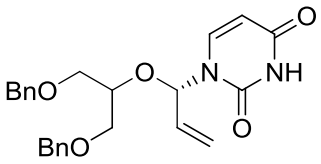
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.084	VV	0.4964	5749.55664	168.38275	49.4072
2	16.283	VBA	0.4761	5887.52539	185.57903	50.5928
Totals :				1.16371e4	353.96178	

Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

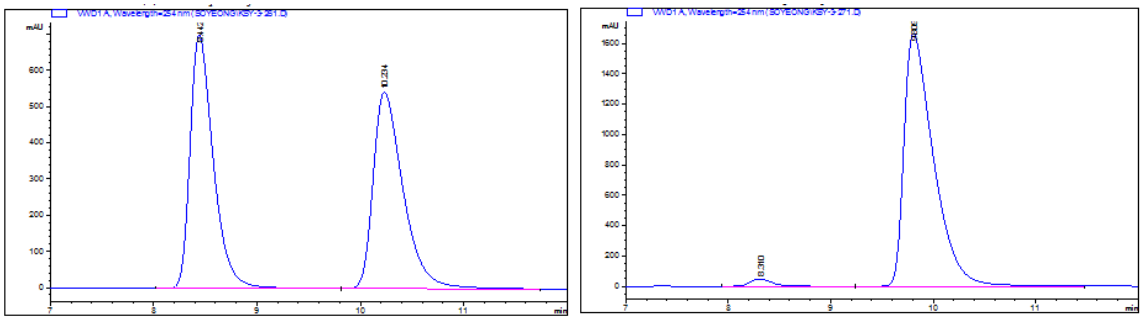
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.700	BV	0.5709	2.67446e4	662.63214	98.0862
2	16.542	VB	0.5584	521.81970	13.57629	1.9138
Totals :				2.72664e4	676.20843	



2c-U

(S)-1-(1-(1,3-bis(benzyloxy)propan-2-yloxy)allyl)pyrimidine-2,4(1H,3H)-dione (2c-U) : Using the general procedure **B**, the mixture of **1c** (62.1 mg, 0.20 mmol) and uracil (22.4 mg, 0.20 mmol) was reacted with $Pd_2(dba)_3$ (4.6 mg, 5.0 μmol), *(R,R)*-L1 (7.9 mg, 10.0 μmol) and K_3PO_4 (10.6 mg, 0.05 mmol) at room temperature for 24h. Flash column chromatography on silica gel (Hexane:EtOAc = 70:30) afforded **2c-U** as a colorless oil (69.3 mg, 0.16 mmol, 82.0%). The enantiomeric excess (95.8% ee) was determined by HPLC on a chiral column (Chiralpak IB, Hexane:iPrOH = 70:30, flow rate = 1.0 mL/min, UV = 254 nm, retention time = 8.31 (minor), 9.81 (major)). R_f 0.41 (Hexane:EtOAc = 40:60); $[\alpha]^{23}_D = -36.2$ (c = 0.58, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78 (br, s, 1H), 7.23-7.36 (m, 11H), 6.44-6.45 (m, 1H), 5.76-5.83 (m, 1H), 5.50-5.56 (m, 2H), 5.38-5.40 (m, 1H), 4.54 (dd, J = 12.29, 16.54 Hz, 2H), 4.43 (s, 2H), 3.94-3.97 (m, 1H), 3.56-3.62 (m, 2H), 3.49-3.50 (m, 2H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 151.1, 140.9, 138.0, 137.8, 133.5, 128.6, 128.0, 127.9, 127.7, 119.7, 102.6, 83.2, 77.3, 73.5, 70.1, 69.7.; IR (KBr) ν 3191, 3059, 2921, 2864, 1685, 1454, 1381, 1249, 1076 cm^{-1}; HRMS (FAB) calcd for $C_{24}H_{27}N_2O_5$ ($M+H^+$) 423.1920, found 423.1918.



Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

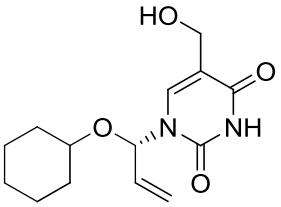
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.442	BB	0.2384	1.09238e4	698.84485	49.9667
2	10.234	BV	0.3076	1.09384e4	541.76318	50.0333
Totals :				2.18622e4	1240.60803	

Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

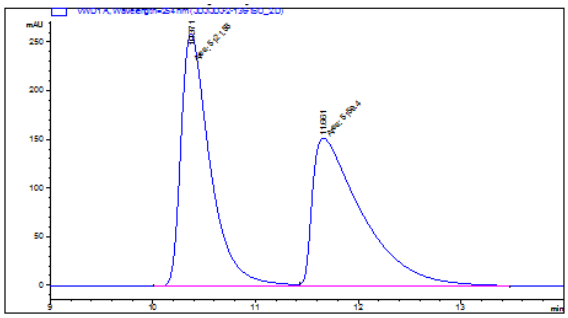
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.310	BB	0.2251	720.04657	48.51842	2.1163
2	9.809	BV	0.3016	3.33031e4	1662.96423	97.8837
Totals :				3.40232e4	1711.48265	



2a-HmU

(S)-1-(1-(cyclohexyloxy)allyl)-5-(hydroxymethyl)pyrimidine-2,4(1H,3H)-dione (2a-HmU) : Using the general procedure **B**, the mixture of **1a** (34.5mg, 0.25 mmol) and 5-hydroxy(methyl)uracil (53.3 mg, 0.375 mmol) was reacted with $Pd_2(dba)_3$ (5.8 mg, 6.3 μmol), *(R,R)*-L1 (9.9 mg, 13.0 μmol) and K_3PO_4 (13.3 mg, 0.063 mmol) at 0℃ for 7h. Flash column chromatography on silica gel (Hexane:EtOAc = 60:40) afforded **2a-HmU** as a colorless oil (55.8 mg, 0.20 mmol, 79.6%). The enantiomeric excess (98.2% ee) was determined by HPLC on a chiral column (Chiralpak IB, Hexane:iPrOH = 90:10, flow rate = 1.0 mL/min, UV = 254 nm, retention time = 10.31 (minor), 11.38 (major)).

R_f 0.38 (Hexane:EtOAc = 40:60); $[\alpha]^{27}_D = -53.8$ (c = 0.58, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.37 (s, 1H),6.32-6.34 (m, 1H), 5.72-5.83 (m, 1H), 5.53 (dt, *J* = 17.1, 1.3 Hz, 1H), 5.36 (dt, *J* = 10.4, 1.3 Hz, 1H) 4.40 (q, *J* = 13.1, 3.9 Hz, 2H), 3.13-3.48 (m, 2H), 1.91-1.95 (m, 1H), 1.70-1.72 (m, 2H), 1.49-1.51(m, 1H), 1.21-1.42(m, 6H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3, 151.0, 137.9, 134.0, 119.5, 114.6, 81.3, 76.7, 58.9, 33.0, 31.5, 25.6, 24.0, 23.8; IR (NaCl) ν 3433, 3065, 2934, 2858, 1685, 1468, 1252, 1137, 1094, 940 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{20}N_2O4$ (M^+) 280.1423, found 280.1426.



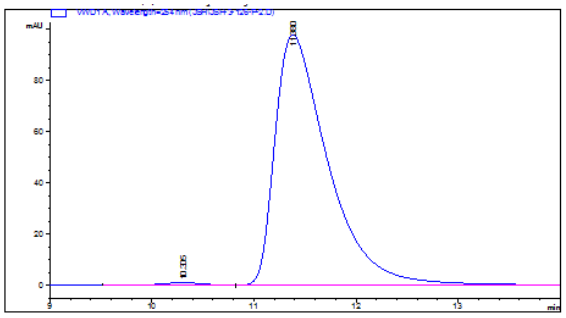
Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.371	MF	0.3286	5121.55762	259.77695	49.8160
2	11.661	FM	0.5646	5159.39795	152.29173	50.1840

Totals : 1.02810e4 412.06868



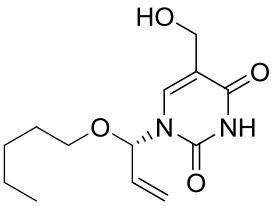
Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.305	BV	0.4866	33.15147	1.06083	0.9177
2	11.380	VB	0.5499	3579.15601	98.03619	99.0823

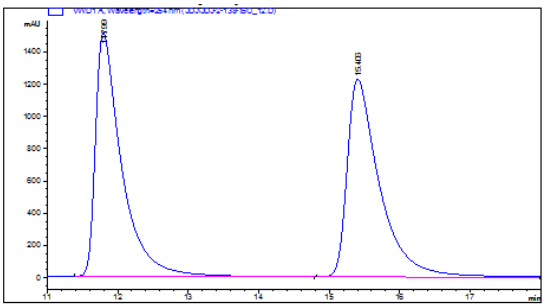
Totals : 3612.30748 99.09702



2b-HmU

(S)-5-(hydroxymethyl)-1-(1-(pentyloxy)allyl)pyrimidine-2,4(1H,3H)-dione (2b-HmU) : Using the general procedure **B**, the mixture of **1b** (32.0mg, 0.25 mmol) and 5-hydroxy(methyl)uracil (53.3 mg, 0.375 mmol) was reacted with $Pd_2(dba)_3$ (5.8 mg, 6.3 μmol), *(R,R)*-L1 (9.9 mg, 13.0 μmol) and K_3PO_4 (13.3 mg, 0.063 mmol) at 0℃ for 8h. Flash column chromatography on silica gel (Hexane:EtOAc = 40:60) afforded **2b-HmU** as a white solid (48.0 mg, 0.18 mmol, 71.5%). The enantiomeric excess (95.2% ee) was determined by HPLC on a chiral column (Chiralpak IA, Hexane:iPrOH = 90:10, flow rate = 1.0 mL/min, UV = 254 nm, retention time = 12.29 (major), 16.00 (minor)).

R_f 0.50 (Hexane:EtOAc = 40:60); M.p. 60.3-60.6 ºC; $[\alpha]^{27}_D = -65.6$ (c = 0.43, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.47 (s, 1H), 7.31 (s, 1H), 6.19-6.20 (m, 1H), 5.73-5.83 (m, 1H), 5.55 (dt, *J* = 16.3, 1.4 Hz, 1H), 5.41 (dt, *J* = 10.4, 1.4 Hz, 1H) 4.36-.4.45 (m, 2H), 3.51 (t, *J* = 6.6 Hz 2H), 2.97 (s, 1H), 1.55-1.62 (m, 2H), 1.25-1.33(m, 4H), 0.86-0.91(m, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.1, 151.2, 137.5, 133.4, 120.0, 114.8, 83.7, 69.6, 58.8, 29.1, 28.3, 22.6, 14.2; IR (NaCl) ν 3432, 3067, 2932, 2873, 1674, 1468, 1344, 1253, 1097, 763 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{20}N_2O_4$ (M^+) 268.1423, found 268.1424.



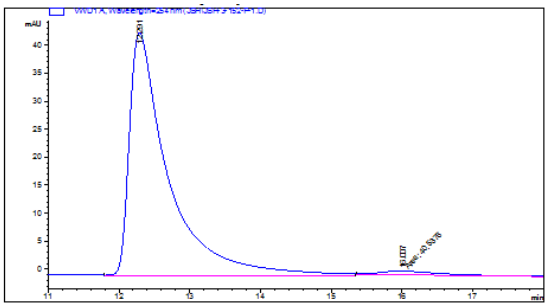
Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.799	BB	0.3744	3.88891e4	1510.10864	49.8350
2	15.406	BV	0.4644	3.91467e4	1226.39087	50.1650

Totals : 7.80358e4 2736.49951



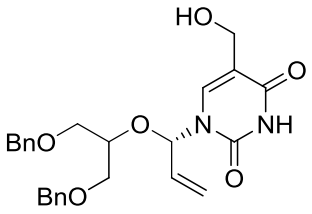
Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.291	BV	0.5395	1663.37878	43.36240	97.6209
2	16.007	MM	1.0428	40.53763	6.47871e-1	2.3791

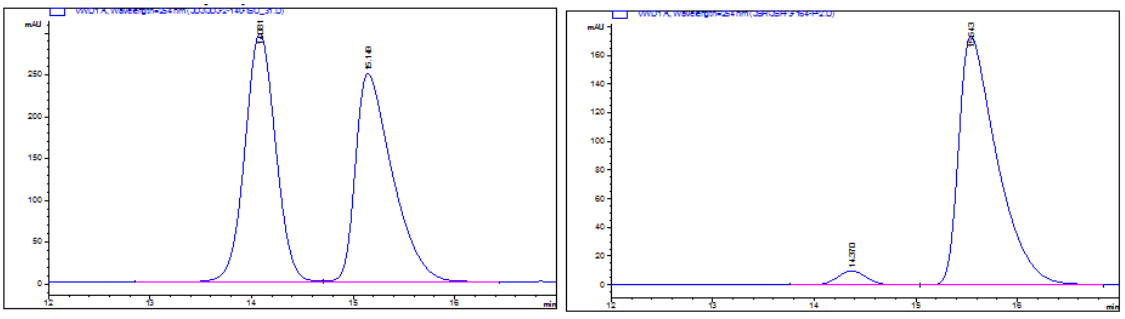
Totals : 1703.91642 44.01027



2c-HmU

(S)-1-(1-(1,3-bis(benzyloxy)propan-2-yloxy)allyl)-5-(hydroxymethyl)pyrimidine-2,4(1H,3H)-dione (2c-HmU) : Using the general procedure **B**, the mixture of **1c** (77.6mg, 0.25 mmol) and 5-hydroxy(methyl)uracil (53.3 mg, 0.375 mmol) was reacted with $Pd_2(dba)_3$ (5.8 mg, 6.3 μmol), *(R,R)*-L3 (9.8 mg, 13.0 μmol) and K_3PO_4 (13.3 mg, 0.063 mmol) at rt for 1h. Flash column chromatography on silica gel (Hexane:EtOAc = 40:60) afforded **2c-HmU** as a colorless oil (79.1 mg, 0.18 mmol, 70.0%). The enantiomeric excess (91.7% ee) was determined by HPLC on a chiral column (Chiralpak IB, Hexane:EtOH = 90:10, flow rate = 1.0 mL/min, UV = 254 nm, retention time = 14.37 (minor), 15.55 (major)).

R_f 0.44 (Hexane:EtOAc = 40:60); $[\alpha]^{27}_D = -49.3$ (c = 0.46, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.22-7.38 (m, 11H), 6.45-6.48 (m, 1H), 5.74-5.85 (m, 1H), 5.53 (dt, *J* = 17.1, 1.1 Hz, 1H), 5.39 (dt, *J* = 10.5, 1.2 Hz, 1H) 4.54 (q, *J* = 12.3, 1.5 Hz, 2H), 4.44 (s, 2H), 4.08-4.27 (m, 2H), 3.95-4.02 (m, 1H), 3.55-3.63(m, 2H), 3.48-3.54(m, 2H), 2.78(s, 1H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9, 151.1, 138.2, 138.0, 137.9, 133.5, 128.64, 128.60, 128.0, 127.9, 127.8, 119.9, 114.3, 83.3, 77.3, 73.6, 73.5, 70.3, 69.7, 58.6; IR (NaCl) ν 3440, 3064, 2926, 2866, 1679, 1496, 1252, 1074, 1028, 739 cm^{-1}; HRMS (FAB) calcd for $C_{25}H_{28}N_2O_6$ (M^+H^+) 453.2026, found 453.2027



Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.081	BV	0.3266	6297.16895	297.86667	49.8223
2	15.149	VV	0.3806	6342.07910	249.47015	50.1777

Totals : 1.26392e4 547.33682

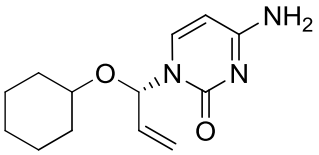
Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.370	BV	0.3076	196.27469	9.88917	4.1392
2	15.543	VV	0.3851	4545.52148	173.78749	95.8608

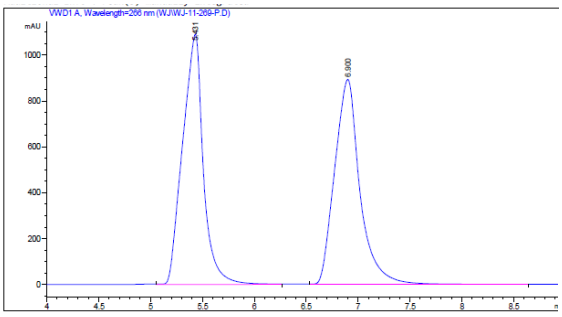
Totals : 4741.79617 183.67666

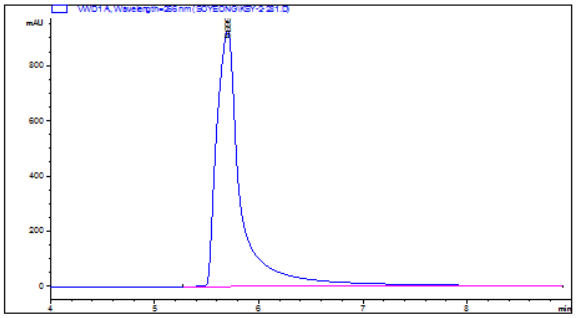


2a-C

(S)-4-amino-1-(1-(cyclohexyloxy)allyl)pyrimidin-2(1H)-one (2a-C) : Using the general procedure **B**, the mixture of **1a** (27.6 mg, 0.20 mmol) and cytosine (22.2 mg, 0.20 mmol) was reacted with $Pd_2(dba)_3$ (4.6 mg, 5.0 μmol), *(R,R)*-L2 (6.9 mg, 10.0 μmol) and K_3PO_4 (10.6 mg, 0.05 mmol) at rt for 24h. Flash column chromatography on silica gel (EtOAc:MeOH = 90:10) afforded **2a-C** as a white solid (49.1 mg, 0.20 mmol, 98.5%). The enantiomeric excess (99.9% ee) was determined by HPLC on a chiral column (Chiralpak ID, Hexane: iPrOH = 80:20, flow rate = 1.5 mL/min, UV = 266 nm, retention time = 5.43 (major), 6.90 (minor)).

R_f 0.27 (EtOAc:MeOH = 90:10); $[\alpha]^{17}_D = -79.4$ (c = 0.34, $CHCl_3$); M.p. 148.5-149.7 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.50 Hz, 1H), 6.46-6.47 (m, 1H), 5.77-5.84 (m, 2H), 5.45 (dt, *J* = 1.49, 17.08 Hz, 1H), 5.30 (dt, *J* = 1.37, 10.44 Hz, 1H), 3.43-3.48 (m, 1H), 1.95-1.97 (m, 1H), 1.67-1.73 (m, 3H), 1.48-1.51 (m, 1H), 1.15-1.40 (m, 5H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.6, 156.4, 141.8, 135.1, 118.2, 95.2, 81.7, 76.4, 33.1, 31.6, 25.6, 24.1, 23.9.; IR (NaCl) ν 3331, 3184, 2933, 2857, 2242, 1642, 1519, 1488 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{19}N_3O_2$ (M^+) 249.1477, found 249.1475.





Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=266 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.431	VV	0.2273	1.50675e4	1089.63000	49.9667
2	6.900	VB	0.2623	1.50876e4	892.22961	50.0333

Totals : 3.01551e4 1981.85962

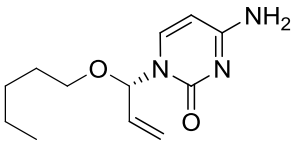
Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=266 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.699	BBA	0.2518	1.52350e4	926.53040	100.0000

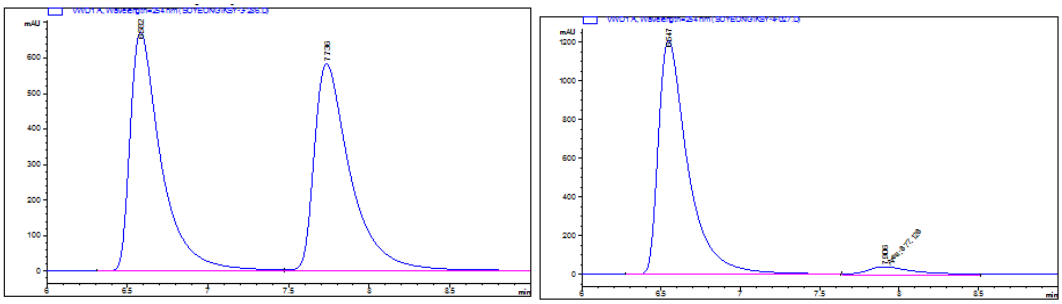
Totals : 1.52350e4 926.53040



2b-C

(S)-4-amino-1-(1-(pentyloxy)allyl)pyrimidin-2(1H)-one (2b-C) : Using the general procedure **B**, the mixture of **1b** (25.2 mg, 0.20 mmol) and cytosine (22.2 mg, 0.20 mmol) was reacted with $Pd_2(dba)_3$ (4.6 mg, 5.0 μmol), *(R,R)*-L3 (7.9 mg, 10.0 μmol) and K_3PO_4 (10.6 mg, 0.05 mmol) at rt for 24h. Flash column chromatography on silica gel (EtOAc:MeOH = 90:10) afforded **2b-C** as a colorless oil (46.4 mg, 0.20 mmol, 97.8%). The enantiomeric excess (89.5% ee) was determined by HPLC on a chiral column (Chiralpak IA, Hexane: EtOH = 80:20, flow rate = 1.0 mL/min, UV = 254 nm, retention time = 6.55 (major), 7.91 (minor)).

R_f 0.27 (EtOAc:MeOH = 90:10); $[\alpha]^{17}_D = -60.9$ (c = 0.35, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, J = 7.35 Hz, 1H), 6.33-6.35 (m, 1H), 5.77-5.84 (m, 2H), 5.47 (dt, J = 1.50, 17.30 Hz, 1H), 5.33 (dt, J = 1.39, 10.65 Hz, 1H), 3.45-3.54 (m, 2H), 1.54-1.58 (m, 2H), 1.25-1.32 (m, 4H), 0.86-0.89 (m, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 157.0, 140.7, 134.6, 118.4, 96.1, 83.7, 69.0, 29.1, 28.3, 22.5, 14.1.; IR (NaCl) ν 3329, 3190, 2956, 2933, 2872, 1627, 1489, 1391 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{19}N_3O_2Na^+$ ($M+Na^+$) 260.1369, found 260.1370.



Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.582	BV	0.1988	9048.08398	673.12866	49.5917
2	7.736	VB	0.2337	9197.06836	584.19025	50.4083

Totals : 1.82452e4 1257.31891

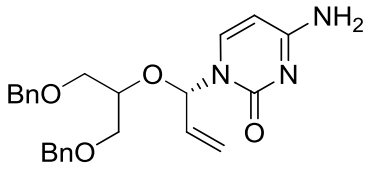
Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.547	BV	0.1924	1.57572e4	1205.90430	94.7270
2	7.906	MM	0.3552	877.12848	41.15801	5.2730

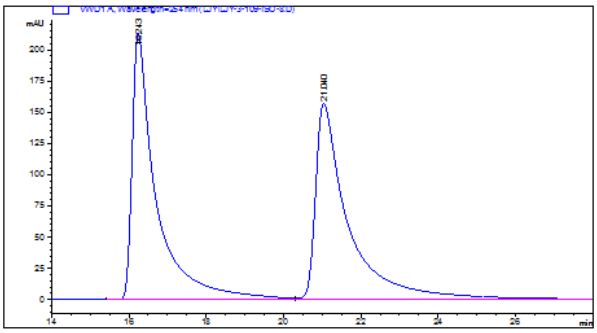
Totals : 1.66343e4 1247.06231

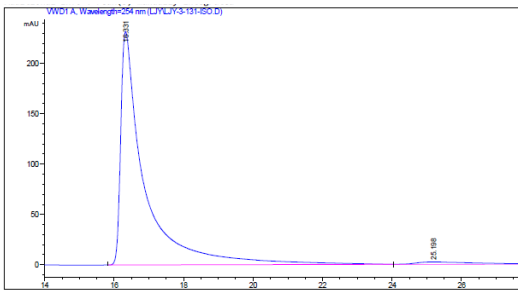


2c-C

(S)-4-amino-1-(1-(1,3-bis(benzyloxy)propan-2-yloxy)allyl)pyrimidin-2(1H)-one (2c-C) : Using the general procedure **B**, the mixture of **1c** (77.6 mg, 0.25 mmol) and cytosine (27.8 mg, 0.25 mmol) was reacted with $Pd_2(dba)_3$ (11.4 mg, 12.5 μmol), *(R,R)*-L3 (19.7 mg, 25.0 μmol) and K_3PO_4 (13.3 mg, 0.063 mmol) at 0℃ for 24h.

Flash column chromatography on silica gel (EtOAc:MeOH = 90:10) afforded **2c-C** as a colorless oil (76.8 mg, 0.18 mmol, 70.4%). The enantiomeric excess (95.1% ee) was determined by HPLC on a chiral column (Chiralpak IA, Hexane: EtOH = 90:10, flow rate = 1.0 mL/min, UV = 254 nm, retention time = 16.33 (major), 25.20 (minor)). R_f 0.56 (EtOAc : MeOH = 90 : 10); $[\alpha]^{28}_D = -27.8$ (c = 0.54, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23-7.45 (m, 11H), 6.56-6.58 (m, 1H), 5.82 (ddd, *J* = 3.65, 10.65, 17.45 Hz, 1H), 5.45-5.49 (m, 2H), 5.29-5.33 (m, 1H), 4.53 (s, 2H), 4.41 (s, 2H), 3.94 (pent, *J* = 4.69 Hz, 1H), 3.47-4.66 (m, 4H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 156.8, 141.7, 138.24, 138.18, 134.7, 128.5, 128.4, 127.76, 127.72, 127.70, 127.68, 118.6, 95.5, 83.1, 77.5, 77.2, 77.0, 76.4, 73.5, 73.3, 70.1, 69.6.; IR (NaCl) ν 3328, 3088, 3030, 2920, 2862, 1625, 1487, 1367, 1277, 1073 cm^{-1}; HRMS (FAB) calcd for $C_{24}H_{28}N_3O_4$ ($M+H^+$) 422.2080, found 422.2080.





Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.243	BV	0.5938	9265.15723	213.70695	49.8189
2	21.040	VB	0.8220	9332.53125	156.88919	50.1811

Totals : 1.85977e4 370.59615

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

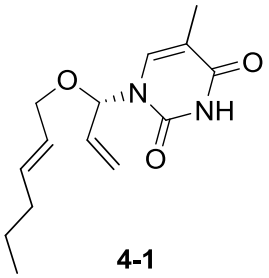
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.331	BB	0.6444	1.10725e4	231.75294	97.5774
2	25.198	BB	1.3977	274.90448	2.31115	2.4226

SYSTEM 3/17/2017 10:54:27 PM SYSTEM Page 1 of 2

a File C:\CHEM32\2\DATA\LJY\LJY-3-131-ISO.D
ple Name: LJY-3-131-iso

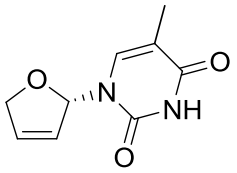
Totals : 1.13474e4 234.06410



4-1

(S,E)-1-(1-(hex-2-enyloxy)allyl)-5-methylpyrimidine-2,4(1H,3H)-dione (4-1) : Using the general procedure **B**, the mixture of **3** (34.6 mg, 0.25 mmol) and thymine (47.3 mg, 0.38 mmol) was reacted with $Pd_2(dba)_3$ (5.7 mg, 6.3 μmol), *(R,R)*-L1 (9.9 mg, 13.0 μmol) and K_3PO_4 (13.3 mg, 0.063 mmol) at rt for 2 h. Flash column chromatography on silica gel (Hexane:EtOAc = 70:30) afforded **4-1** as a colorless oil (52.0 mg, 0.20 mmol, 79.0%).

R_f 0.50 (Hexane:EtOAc = 60:40); $[\alpha]^{28}_D = -58.6$ (c = 0.43, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.53-9.70 (br, 1H), 7.11 (s, 1H), 6.26 (td. *J* = 1.61, 3.70 Hz, 1H), 5.72-5.84 (m, 2H), 5.48-5.55 (m, 2H), 5.39-5.41 (m, 1H), 3.97-4.04 (m, 2H), 2.02 (dd, *J* = 7.14, 14.66 Hz, 2H), 1.38-1.42 (m, 2H), 0.88-0.91 (m, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.3, 151.4, 136.7, 136.0, 133.6, 124.6, 119.7, 111.8, 82.3, 77.7, 77.2, 76.8, 70.0, 34.5, 22.2, 13.8, 12.7. ; IR (NaCl) ν 3185, 3049, 2959, 2930, 2872, 1694, 1465, 1377, 1251, 1136 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{20}N_2O_3$ (M^+) 264.1476, found 264.1474.

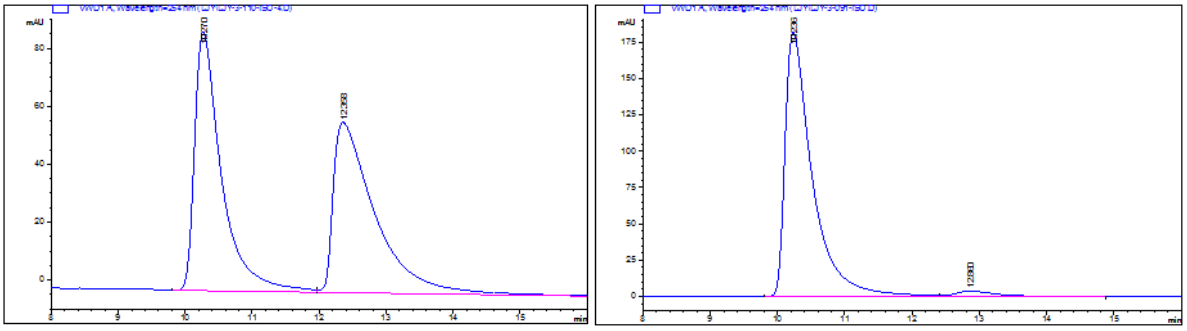


4

(S)-1-(2,5-dihydrofuran-2-yl)-5-methylpyrimidine-2,4(1H,3H)-dione (4) : Using the general procedure **C**, the solution of **4-1** (52.0 mg, 0.20 mmol) in CH_2Cl_2 was reacted with Grubbs catalyst at 40℃ for 4h. Flash column chromatography on silica gel (Hexane:EtOAc = 20:80) afforded **4** as a white solid (37.1 mg, 0.191 mmol, 97.0%). The enantiomeric excess (93.5% ee) was determined by HPLC on a chiral column (Chiralpak IB, Hexane: iPrOH = 70:30, flow rate = 1.0 mL/min, UV = 254 nm, retention time = 10.24 (major), 12.86 (minor)).

R_f 0.63 (Hexane:EtOAc = 40:60); M.p. 164.8-165.2ºC; $[\alpha]^{28}_D = -122.1$ (c = 0.51, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.17-9.29 (br, 1H), 7.01-7.03 (m, 1H), 6.86 (s, 1H), 6.42-6.44 (m, 1H), 5.80-5.83 (m, 1H), 4.83-4.86 (m, 1H), 4.70-4.74 (m, 1H), 1.89 (s, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 151.1, 135.4, 133.4, 125.0, 111.5, 90.7,

77.6, 77.2, 76.8, 75.9, 12.8.; IR (NaCl) ν 3185, 3049, 2927, 2868, 2825, 1690, 1468, 1223, 1067 cm^{-1}; HRMS (EI) calcd for $C_9H_{10}N_2O_3$ (M^+) 194.0691, found 194.0689.



Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

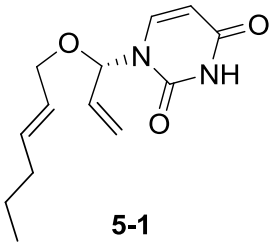
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.270	BV	0.4093	2494.81616	89.48742	49.2345
2	12.358	VB	0.6462	2572.39380	58.81876	50.7655
Totals :				5067.20996	148.30618	

Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

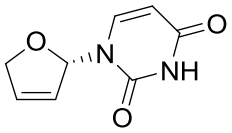
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.236	VV	0.4126	5134.70752	182.28882	96.7265
2	12.860	VB	0.6622	173.77240	3.82346	3.2735
Totals :				5308.47992	186.11228	



5-1

(S,E)-1-(1-(hex-2-enyloxy)allyl)pyrimidine-2,4(1H,3H)-dione (5-1) : Using the general procedure **B**, the mixture of **3** (34.6 mg, 0.25 mmol) and uracil (42.1 mg, 0.38 mmol) was reacted with $Pd_2(dba)_3$ (5.7 mg, 6.3 μmol), *(R,R)*-L1 (9.9 mg, 13.0 μmol) and K_3PO_4 (13.3 mg, 0.063 mmol) at rt for 2 h. Flash column chromatography on silica gel (Hexane:EtOAc = 50:50) afforded **5-1** as a colorless oil (48.3 mg, 0.19 mmol, 77.2%).

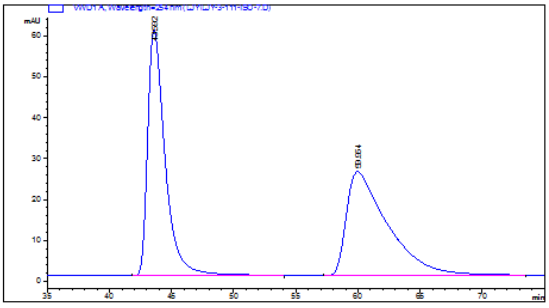
R_f 0.29 (Hexane:EtOAc = 60:40); $[\alpha]^{28}_D = -49.6$ (c = 0.42, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.76-9.97 (br, 1H), 7.29 (d, *J* = 8.04 Hz, 1H), 6.24 (td, *J* = 1.50, 3.46 Hz, 1H), 5.68-5.83 (m, 3H), 5.43-5.53 (m, 2H), 5.38 (d, *J* = 10.58Hz, 1H), 3.99 (d, *J* = 6.43 Hz, 2H), 2.00 (dd, *J* = 7.35, 14.08 Hz, 2H), 1.37 (sexet, *J* = 7.35 Hz, 2H), 0.87 (t, *J* = 7.35 Hz, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.7, 151.3, 140.4, 136.9, 133.4, 124.5, 119.8, 103.3, 82.6, 77.6, 77.2, 76.8, 70.1, 34.5, 22.2, 13.8. ; IR (NaCl) ν 3196, 3057, 2959, 2930, 2872, 1680, 1456, 1380, 1249, 1120, 1093, 1048 cm^{-1}; HRMS (FAB) calcd for $C_{13}H_{19}N_2O_3$ ($M+H^+$) 251.1396, found 251.1393.

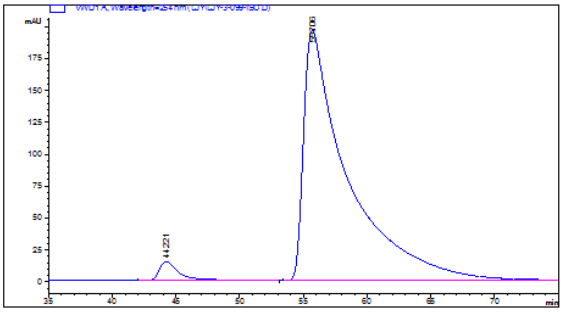


5

(S)-1-(2,5-dihydrofuran-2-yl)pyrimidine-2,4(1H,3H)-dione (5) : Using the general procedure **C**, the solution of **5-1** (45.0 mg, 0.18 mmol) in CH_2Cl_2 was reacted with Grubbs catalyst at 40℃ for 4h. Flash column chromatography on silica gel (Hexane:EtOAc = 20:80) afforded **5** as a white solid (30.3 mg, 0.17 mmol, 95.0%). The enantiomeric excess (93.3% ee) was determined by HPLC on a chiral column (Chiralpak IC, Hexane: iPrOH = 70:30, flow rate = 1.2 mL/min, UV = 254 nm, retention time = 44.71 (minor), 55.71 (major)).

R_f 0.17 (Hexane:EtOAc = 20:80); M.p. 140.8-141.2ºC; $[\alpha]^{28}_D = -114.7$ (c = 0.46, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.71-9.79 (br, 1H), 7.08 (d, *J* = 8.11 Hz, 1H), 7.00-7.02 (m, 1H) 6.43 (qd, *J* = 1.64, 8.11 Hz, 1H), 5.81-5.85 (m, 1H), 5.72 (d, *J* = 8.11 Hz, 1H), 4.79-4.87 (m, 1H), 4.68-4.75 (m, 1H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8, 150.9, 139.8, 133.6, 124.8, 103.1, 91.0, 77.7, 77.2, 76.8, 76.0.; IR (NaCl) ν 3185. 3094. 3057. 2926. 2872. 1686. 1459. 1388. 1116. 1014 cm^{-1}; HRMS (EI) calcd for $C_8H_8N_2O_3$ (M^+) 180.0535, found 180.0533.





Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.592	BB	1.4741	5910.53516	60.16654	50.1531
2	59.954	BB	3.1344	5874.43994	25.43630	49.8469

Totals : 1.17850e4 85.60284

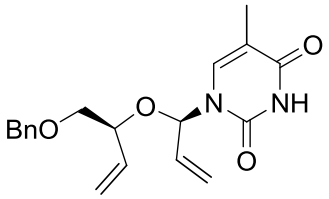
Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.221	BB	1.5793	1646.50098	15.06191	3.3599
2	55.706	BB	3.1898	4.73583e4	196.08264	96.6401

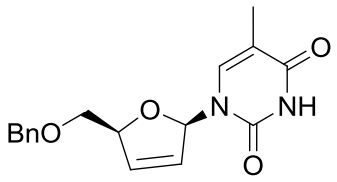
Totals : 4.90048e4 211.14455



7-1

1-((R)-1-((S)-1-(benzyloxy)but-3-en-2-yloxy)allyl)-5-methylpyrimidine-2,4(1H,3H)-dione (7-1) : Using the general procedure **B**, the mixture of **6** (563.7 mg, 2.61 mmol) and thymine (493.0 mg, 3.91 mmol) was reacted with $Pd_2(dba)_3$ (59.8 mg, 65.3 μmol), *(S,S)*-L3 (102.9 mg, 0.13 mmol) and K_3PO_4 (138.5 mg, 0.65 mmol) at rt for 8 h. Flash column chromatography on silica gel (Hexane:EtOAc = 70:30) afforded **7-1** as a colorless oil (842.0 mg, 2.46 mmol, 94.2%, d.r. = 1 : >25).

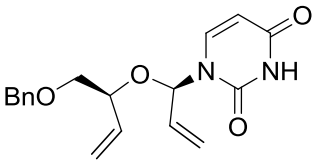
R_f 0.61 (Hexane:EtOAc = 50:50); $[\alpha]^{23}_D$ = +51.3 (c = 0.34, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.14 (br s, 1H), 7.25-7.36 (m, 5H), 7.19-7.20 (m, 1H), 6.24-6.27 (m, 1H), 5.66-5.86 (m, 2H), 5.34-5.55 (m, 4H), 4.49 (s, 2H), 4.05-4.12 (m, 1H), 3.44-3.57 (m, 2H), 1.74 (d, *J* = 1.18 Hz, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.1, 151.3, 138.0, 136.4, 133.6, 133.0, 128.6, 127.9, 127.6, 120.6, 119.4, 111.4, 80.8, 78.2, 73.4, 72.4, 12.4.; IR (NaCl) ν 3186, 3033, 2927, 2860, 1693, 1497, 1252, 1096 cm.$^{-1}$; HRMS (EI) calcd for $C_{19}H_{22}N_2O_4$ (M^+) 342.1580, found 342.1579.



7

1-((2R,5S)-5-(benzyloxymethyl)-2,5-dihydrofuran-2-yl)-5-methylpyrimidine-2,4(1H,3H)-dione (7) : Using the general procedure **C**, the solution of **7-1** (25.0 mg, 0.07 mmol) in CH_2Cl_2 was reacted with Grubbs catalyst at rt for 24h. Flash column chromatography on silica gel (Hexane:EtOAc = 20:80) afforded **7** as a white solid (26.0 mg, 0.09 mmol, 83.4%, d.r. = 1 : >25)

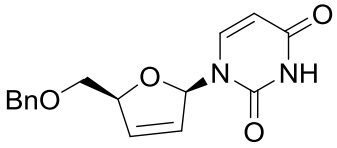
R_f 0.50 (Hexane:EtOAc = 20:80); $[\alpha]^{22}_D$ = −33.8 (c = 0.52, $CHCl_3$); M.p. 144.9-146.4 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (br, s, 1H), 7.51-7.52 (m, 1H), 7.28-7.38 (m, 5H), 7.03-7.05 (m, 1H), 6.31-6.34 (m, 1H), 5.80-5.83 (m, 1H), 4.95-4.99 (m, 1H), 4.56 (dd, *J* = 12.11, 15.61 Hz), 3.74 (ddd, *J* = 2.61, 11.02, 33.20 Hz, 2H), 1.53 (d, *J* = 1.20 Hz, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.0, 151.0, 137.6, 136.8, 134.3, 128.7, 128.1, 127.8, 126.6, 110.9, 89.6, 85.8, 73.6, 70.8, 12.0.; IR (NaCl) ν 3181, 3061, 2925, 2861, 1690, 1468, 1253, 1119 cm^{-1}; HRMS (FAB) calcd for $C_{17}H_{19}N_2O_4$ ($M+H^+$) 315.1345, found 315.1347.



8-1

1-((R)-1-((S)-1-(benzyloxy)but-3-en-2-yloxy)allyl)pyrimidine-2,4(1H,3H)-dione (8-1) : Using the general procedure **B**, the mixture of **6** (86.5 mg, 0.40 mmol) and uracil (67.3 mg, 0.60 mmol) was reacted with $Pd_2(dba)_3$ (9.2 mg, 10.0 μmol), *(S,S)*-L3 (15.8 mg, 20.0 μmol) and K_3PO_4 (21.2 mg, 0.10 mmol) at rt for 8 h. Flash column chromatography on silica gel (Hexane:EtOAc = 60:40) afforded **8-1** as a white solid (117.3 mg, 0.36 mmol, 89.3%, d.r. = 1 : >25).

R_f 0.14 (Hexane:EtOAc = 70:30); $[\alpha]^{23}_D$ = +57.6 (c = 0.47, $CHCl_3$); M.p. 63.8-65.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.70 (br, s, 1H), 7.41 (d, J = 8.11 Hz, 1H), 7.28-7.38 (m, 5H), 6.27-6.29 (m, 1H), 5.68-5.87 (m, 2H), 5.62 (dd, *J* = 1.95, 8.04 Hz, 1H), 5.49-5.56 (m, 1H), 5.35-5.46 (m, 3H), 4.51 (s, 2H), 4.07-4.13 (m, 1H), 3.45-3.57 (m, 2H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8, 151.3, 140.8, 137.9, 133.4, 132.9, 128.5, 127.9, 127.6, 120.5, 119.5, 102.8, 81.1, 78.4, 73.4, 72.2.; IR (NaCl) ν 3191, 3061, 2923, 2861, 1690, 1497, 1381, 1250 cm^{-1}; HRMS (FAB) calcd for $C_{18}H_{21}N_2O_4$ ($M+H^+$) 329.1501, found 329.1499.

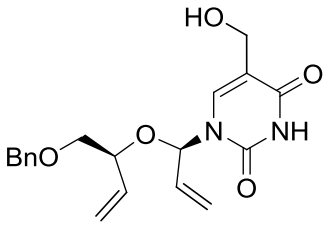


8

1-((2R,5S)-5-(benzyloxymethyl)-2,5-dihydrofuran-2-yl)pyrimidine-2,4(1H,3H)-dione (8) : Using the general procedure **C**, the solution of **8-1** (34.1 mg, 0.10 mmol) in CH_2Cl_2 was reacted with Grubbs catalyst at rt for 12h. Flash column chromatography on silica gel (Hexane:EtOAc = 20:80) afforded **8** as a white solid (26.0 mg, 0.09 mmol, 83.4%, d.r. = 1 : >25)

R_f 0.41 (Hexane:EtOAc = 20:80); $[\alpha]^{23}_D$ = −39.7 (c = 0.35, $CHCl_3$); M.p. 115.4-116.9 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.23 (br, s, 1H), 7.70 (d, *J* = 8.15 Hz, 1H), 7.26-7.38 (m, 5H), 7.02-7.04 (m, 1H), 6.29-6.32 (m, 1H), 5.76-5.79 (m, 1H), 5.21 (d, *J* = 8.14 Hz, 1H), 4.96-4.99 (m, 1H), 4.50 (dd, *J* = 11.26, 13.74 Hz, 2H), 3.76 (ddd, *J*

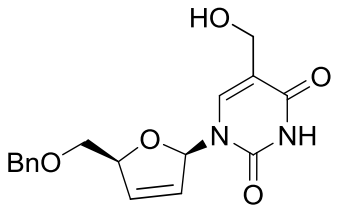
= 2.63, 10.93, 24.77 Hz, 2H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.6, 151.0, 141.5, 137.4, 134.4, 128.7, 128.3, 128.1, 126.3, 102.2, 89.7, 86.0, 73.8, 70.8.; IR (NaCl) ν 3192, 3060, 2865, 1688, 1625, 1496, 1381, 1249 cm^{-1}; HRMS (FAB) calcd for $C_{16}H_{17}N_2O_4$ ($M+H^+$) 301.1188, found 301.1190.



9-1

1-((R)-1-((S)-1-(benzyloxy)but-3-en-2-yloxy)allyl)-5-(hydroxymethyl)pyrimidine-2,4(1H,3H)-dione (9-1) : Using the general procedure **B**, the mixture of **6** (54.0 mg, 0.25 mmol) and 5-hydroxy(methyl)uracil (53.3 mg, 0.375 mmol) was reacted with $Pd_2(dba)_3$ (5.8 mg, 0.0063 mmol), *(S,S)*-L3 (9.8 mg, 0.013 mmol) and K_3PO_4 (13.3 mg, 0.063 mmol) at rt for 1.5 h. Flash column chromatography on silica gel (Hexane:EtOAc = 80:20) afforded **9-1** as a colorless oil (64.6 mg, 0.18 mmol, 72%, d.r. = 1 : 17).

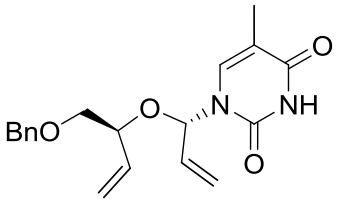
R_f 0.38 (Hexane:EtOAc = 40:60); $[\alpha]^{24}_D$ = +54.9 (c = 0.77, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.08 (s, 1H), 7.45 (s, 1H), 7.26-7.36 (m, 5H), 6.25-6.27 (m, 1H), 5.65-5.85 (m, 2H), 5.32-5.55 (m, 4H), 4.50 (s, 2H) 4.08-4.28 (m, 3H), 3.44-3.55 (m, 2H), 3.10 (s, 1H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.1, 151.2, 138.1, 138.0, 133.4, 133.0, 128.7, 128.0, 127.8, 120.6, 119.8, 114.5, 81.3, 78.5, 73.5, 72.4, 58.6.; IR (NaCl) ν , 3186, 3032, 2925, 2863, 1716, 1496, 1386, 1216, 991 cm.$^{-1}$; HRMS (ESI) calcd for $C_{19}H_{22}N_2NaO_5$ ($M+Na^+$) 381.1421, found 381.1420.



9

1-((2R,5S)-5-(benzyloxymethyl)-2,5-dihydrofuran-2-yl)-5-(hydroxymethyl)pyrimidine-2,4(1H,3H)-dione (9) : Using the general procedure **C**, the solution of **9-1** (29.0 mg, 0.08 mmol) in CH_2Cl_2 was reacted with Grubbs catalyst at 40^{o}C for 11h. Flash column chromatography on silica gel (Hexane:EtOAc = 0:100) afforded **9** as a colorless oil (17.0 mg, 0.05 mmol, 64%, d.r. = 1 : >25)

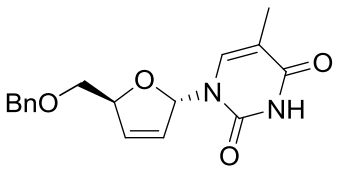
R_f 0.25 (Hexane:EtOAc = 20:80); $[\alpha]^{24}_D = -11.5$ (c = 0.85, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.78 (s, 1H), 7.75 (s, 1H), 7.26-7.40 (m, 5H), 7.03-7.05 (m, 1H), 6.32 (dt, *J* = 6.00, 1.65 Hz, 1H), 5.81-5.84 (m, 1H), 4.95-5.00 (m, 1H), 4.55 (q, *J* = 11.91, 8.34 Hz, 2H), 3.65-4.08 (m, 4H), 2.40 (s, 1H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8, 150.8, 138.6, 137.6, 134.6, 128.8, 128.3, 128.0, 126.4, 113.9, 89.9, 86.1, 73.7, 70.7, 58.7.; IR (NaCl) ν 3448, 3189, 3061, 2925, 2859, 1684, 1469, 1251, 1088, 738 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{18}N_2NaO_5$ ($M+Na^+$) 353.1108, found 353.1108.



10-1

1-((S)-1-((S)-1-(benzyloxy)but-3-en-2-yloxy)allyl)-5-methylpyrimidine-2,4(1H,3H)-dione (10-1) : Using the general procedure **B**, the mixture of **6** (86.5 mg, 0.4 mmol) and thymine (75.7 mg, 0.6 mmol) was reacted with $Pd_2(dba)_3$ (9.2 mg, 10.0 μmol), *(R,R)*-L3 (15.8 mg, 20.0 μmol) and K_3PO_4 (21.2 mg, 0.10 mmol) at rt for 8 h. Flash column chromatography on silica gel (Hexane:EtOAc = 60:40) afforded **10-1** as a colorless oil (131.7 mg, 0.38 mmol, 96.2%, d.r. = 15 : 1).

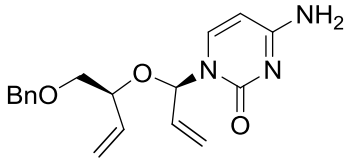
R_f 0.60 (Hexane:EtOAc = 50:50); $[\alpha]^{23}_D = -26.8$ (c = 0.52, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (br, s, 1H), 7.27-7.38 (m, 5H), 7.09-7.10 (m, 1H), 6.39-6.42 (m, 1H), 5.41-5.85 (m, 4H), 5.13-5.28 (m, 2H), 4.57 (m, 2H), 4.22-4.28 (m, 1H), 3.50-3.59 (m, 2H), 1.91 (d, *J* = 1.14 Hz, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9, 150.9, 138.1, 136.4, 134.8, 133.6, 128.5, 127.8, 127.7, 119.9, 118.3, 111.3, 82.9, 80.3, 73.5, 72.7, 12.6.; IR (NaCl) ν 3188, 3064, 2927, 1692, 1466, 1373, 1251, 1070 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{22}N_2O_4$ (M^+) 342.1580, found 342.1578.



10

1-((2S,5S)-5-(benzyloxymethyl)-2,5-dihydrofuran-2-yl)-5-methylpyrimidine-2,4(1H,3H)-dione (10) : Using the general procedure **C**, the solution of **10-1** (46.0 mg, 0.13 mmol) in CH_2Cl_2 was reacted with Grubbs catalyst at rt for 12h. Flash column chromatography on silica gel (Hexane:EtOAc = 20:80) afforded **10** as a white solid (38.0 mg, 0.12 mmol, 93.0%, d.r. = 19:1)

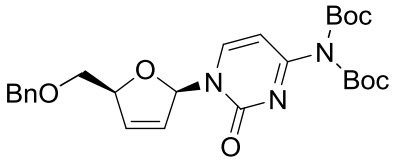
R_f 0.20 (Hexane:EtOAc = 50:50); $[\alpha]^{23}_D = -190.2$ (c = 0.37, $CHCl_3$); M.p. 123.9-125.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (br, s, 1H), 7.27-7.38 (m, 5H), 7.05-7.08 (m, 1H), 6.88-6.89 (m, 1H), 6.36-6.39 (m, 1H), 5.88-5.92 (m, 1H), 5.19-5.25 (m 1H), 4.59 (dd, *J* = 12.17, 14.49 Hz, 2H), 3.54-3.62 (m, 2H), 1.90 (d, *J* = 1.20 Hz, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8, 150.6, 137.8, 135.3, 134.4, 128.6, 128.0, 127.8, 126.7, 111.5, 90.5, 86.4, 73.8, 72.0, 12.7.; IR (NaCl) ν 3182, 3035, 2925, 2856, 1690, 1467, 1247, 1074 cm^{-1}; HRMS (FAB) calcd for $C_{17}H_{19}N_2O_4$ ($M+H^+$) 315.1345, found 315.1348.



11-1

4-amino-1-((R)-1-((S)-1-(benzyloxy)but-3-en-2-yloxy)allyl)pyrimidin-2(1H)-one (11-1) : Using the general procedure **B**, the mixture of **6** (43.3 mg, 0.20 mmol) and cytosine (22.2 mg, 0.20 mmol) was reacted with $Pd_2(dba)_3$ (4.6 mg, 5.0 μmol), *(S,S)*-L3 (7.9 mg, 10.0 μmol) and K_3PO_4 (10.6 mg, 0.05 mmol) at rt for 24 h. Flash column chromatography on silica gel (EtOAc:MeOH = 90:10) afforded **11-1** as a white solid (54.1 mg, 0.17 mmol, 82.6%, d.r. = 1 : 10).

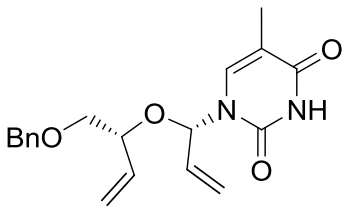
R_f 0.63 (EtOAc:MeOH = 95:5); $[\alpha]^{22}_D = +47.4$ (c = 0.27, MeOH); M.p. 72.8-74.4 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, J = 7.27 Hz, 1H), 7.22-7.34 (m, 5H), 6.37-6.38 (m, 1H), 5.65-5.85 (m, 3H), 5.26-5.44 (m, 4H), 4.47 (s, 2H), 4.03-4.09 (m, 1H), 3.39-3.53 (m, 2H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 156.6, 142.2, 138.2, 134.5, 133.3, 128.5, 127.73, 127.67, 120.2, 118.5, 95.0, 81.6, 77.8, 73.2, 72.4.; IR (NaCl) ν 3343, 3090, 2925, 2859, 1625, 1521 cm^{-1}; HRMS (FAB) calcd for $C_{18}H_{22}N_3O_3$ ($M+H^+$) 328.1661, found 328.1659.



11

***N,N*-Di-*tert*-butoxycarbonyl-1-((2R,5S)-5-(benzyloxymethyl)-2,5-dihydrofuran-2-yl)-cytosine (11)** : Using the general procedure **C**, The solution of boc protected **11-1** (38.8 mg, 0.07 mmol) in CH_2Cl_2 was reacted with Grubbs catalyst at rt for 24h. Flash column chromatography on silica gel (Hexane:EtOAc = 50:50) afforded **11** as a colorless oil (32.0 mg, 0.06 mmol, 87.1%, d.r. = 1 : >25)

R_f 0.32 (Hexane:EtOAc = 50:50); $[\alpha]^{22}_D$ = +31.4 (c = 0.26, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.63 Hz, 1H), 7.28-7.38 (m, 5H), 7.02-7.03 (m, 1H), 6.68 (d, *J* = 7.58 Hz, 1H), 6.19-6.20 (m, 1H), 5.94-5.95 (m, 1H), 5.03 (m, 1H), 4.53 (dd, *J* = 11.44, 17.57 Hz, 2H), 3.79 (dd, *J* = 3.04, 10.87 Hz, 1H), 3.66 (dd, *J* = 2.88, 11.03 Hz, 1H), 1.55 (s, 18H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6, 154.9, 149.7, 144.9, 137.5, 132.8, 128.7, 128.2, 128.1, 127.5, 96.4, 91.8, 86.5, 84.8, 73.7, 70.7, 27.8.; IR (NaCl) ν 3162, 3091, 3033, 2980, 2931, 2867, 1778, 1744, 1679 cm^{-1}; HRMS (EI) calcd for $C_{26}H_{33}N_3O_7$ (M^+) 499.2319, found 499.2316.

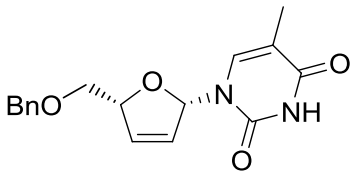


ent-**7-1**

1-((S)-1-((R)-1-(benzyloxy)but-3-en-2-yloxy)allyl)-5-methylpyrimidine-2,4(1H,3H)-dione (*ent*-7-1) : Using the general procedure **B**, the mixture of ***ent*-6** (54.1 mg, 0.25 mmol) and thymine (47.3 mg, 0.38 mmol) was reacted with $Pd_2(dba)_3$ (5.7 mg, 6.2 μmol), *(R,R)*-L3 (9.9 mg, 12.5 μmol) and K_3PO_4 (13.3 mg, 0.063 mmol) at rt for 8 h. Flash column chromatography on silica gel (Hexane:EtOAc = 50:50) afforded ***ent*-7-1** as a colorless oil (72.5 mg, 0.21 mmol, 84.7%, d.r. = 1 : >25).

R_f 0.69 (Hexane:EtOAc = 20:80); $[\alpha]^{28}_D$ = −65.2 (c = 0.75, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.13 (br, s, 1H), 7.26-7.35 (m, 5H), 7.19-7.20 (m, 1H), 6.24-6.27 (m, 1H), 5.66-5.86 (m, 2H), 5.34-5.55 (m, 4H), 4.49 (s, 2H), 4.05-4.12 (m, 1H), 3.44-3.57 (m, 2H), 1.74 (d, *J* = 1.07 Hz, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.1, 151.3,

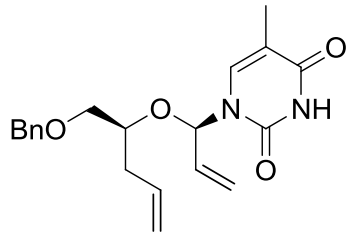
138.0, 136.4, 133.6, 133.0, 128.6, 127.9, 127.6, 120.6, 119.4, 111.4, 80.8, 78.2, 73.4, 72.4, 12.4.; IR (NaCl) ν 3192, 3065, 2927, 2857, 1692, 1497, 1252 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{22}N_2O_4$ (M^+) 342.1580, found 342.1581.



ent-**7**

1-((2S,5R)-5-(benzyloxymethyl)-2,5-dihydrofuran-2-yl)-5-methylpyrimidine-2,4(1H,3H)-dione (*ent*-7) : Using the general procedure **C**, the solution of ***ent*-7-1** (45.2 mg, 0.13 mmol) in CH_2Cl_2 was reacted with Grubbs catalyst at rt for 24h. Flash column chromatography on silica gel (Hexane:EtOAc = 50:50) afforded ***ent*-7** as a white solid (35.7 mg, 0.11 mmol, 87.4%, d.r. = >25:1)

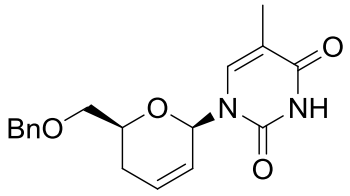
R_f 0.50 (Hexane:EtOAc = 20:80); $[\alpha]^{21}_D$ = +35.8 (c = 0.59, $CHCl_3$); M.p. 142.3-146.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (br, s, 1H), 7.51-7.52 (m, 1H), 7.28-7.38 (m, 5H), 7.03-7.05 (m, 1H), 6.31-6.34 (m, 1H), 5.81-5.82 (m, 1H), 4.96-4.98 (m, 1H), 4.56 (dd, *J* = 12.22, 15.79 Hz, 2H), 3.80 (dd, *J* = 2.63, 10.94 Hz, 1H), 3.69 (dd, *J* = 2.84, 10.94 Hz, 1H), 1.53 (d, J = 1.16 Hz, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8, 150.9, 137.6, 136.9, 134.3, 128.7, 128.2, 127.8, 126.5, 110.9, 89.6, 85.9, 73.6, 70.8, 12.0.; IR (NaCl) ν 3173, 3039, 2891, 2858, 1695, 1497 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{18}N_2O_4$ (M^+) 314.1267, found 314.1269.



14-1

1-((R)-1-((S)-1-(benzyloxy)pent-4-en-2-yloxy)allyl)-5-methylpyrimidine-2,4(1H,3H)-dione (14-1) : Using the general procedure **B**, the mixture of **13** (57.6 mg, 0.25 mmol) and thymine (47.3 mg, 0.38 mmol) was reacted with $Pd_2(dba)_3$ (5.8 mg, 6.3 μmol), *(S,S)*-L3 (9.8 mg, 13.0 μmol) and K_3PO_4 (13.3 mg, 0.063 mmol) at rt for 2 h. Flash column chromatography on silica gel (Hexane:EtOAc = 55:45) afforded **14-1** as a colorless oil (84.7 mg, 0.24 mmol, 95.0%, d.r. = 1 : >25).

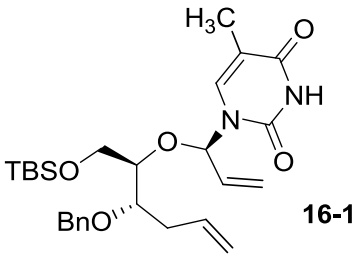
R_f 0.58 (Hexane:EtOAc = 60:40); $[\alpha]^{27}_D$ = +46.4 (c = 0.52, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.07 (s, 1H), 7.22-7.35 (m, 5H), 7.12-7.13 (m, 1H), 6.33-6.36 (m, 1H), 5.72-5.86 (m, 2H), 5.52 (dt, *J* = 17.1, 1.4 Hz, 1H) 5.38 (dt, *J* = 10.4, 1.4 Hz, 1H), 5.07-5.15 (m, 2H), 4.41 (s, 2H), 3.78-3.85 (m, 1H), 3.37-3.45 (m, 2H), 2.34-2.38 (m, 2H), 1.74(d, *J* = 1.1 Hz 3H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 153.1, 139.7, 138.4, 135.5, 135.0, 130.3, 129.6, 129.4, 121.3, 120.2, 112.9, 83.9, 79.3, 75.2, 73.7, 37.7, 14.2; IR (NaCl) ν 3190, 3065, 2927, 2856, 1694, 1497, 1252, 1076, 1029, 775 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{24}N_2O_4$ (M^+) 356.1736, found 356.1733



14

1-((2R,6S)-6-(benzyloxymethyl)-5,6-dihydro-2H-pyran-2-yl)-5-methylpyrimidine-2,4(1H,3H)-dione (14) : Using the general procedure **C**, the solution of **14-1** (59.0 mg, 0.17 mmol) in CH_2Cl_2 was reacted with Grubbs catalyst at 40℃ for 20h. Flash column chromatography on silica gel (Hexane:EtOAc = 20:80) afforded **14** as a colorless oil (45.2 mg, 0.137 mmol, 82.4%, d.r. = >25:1).

R_f 0.39 (Hexane:EtOAc = 60:40); $[\alpha]^{27}_D$ = +1.1 (c = 0.46, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.01 (s, 1H), 7.26-7.37 (m, 5H), 7.07 (d, *J* = 1.2 Hz , 1H), 6.48-6.49 (m, 1H), 6.22-6.27 (m, 1H), 5.55-5.59 (m, 1H), 4.56 (q, *J* = 12.2, 2.0 Hz, 2H), 4.06-4.13 (m, 1H), 3.61 (q, *J* = 5.5, 4.9 Hz, 1H), 3.51(q, *J* = 5.9, 4.6 Hz, 1H), 2.23-2.33 (m, 1H), 2.04-2.12 (m, 1H), 1.90 (d, *J* = 1.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.0, 150.8, 138.1, 136.4, 131.8, 128.6, 127.9, 125.5, 111.5, 78.9, 73.64, 73.60, 72.2, 27.1, 12.6.; IR (NaCl) ν 3188, 3043, 2925, 1689, 1496, 1374, 1253, 1118, 1078, 780 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{20}N_2O_4$ (M^+) 328.1423, found 328.1421.

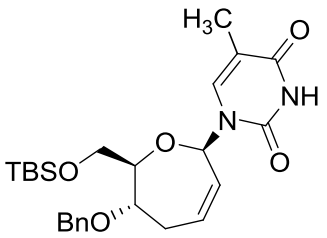


16-1

1-((R)-1-((2R,3S)-3-(benzyloxy)-1-(tert-butyldimethylsilyloxy)hex-5-en-2-yloxy)allyl)-5-methylpyrimidine-2,4(1H,3H)-dione (16-1) : Using the general procedure **B**, the mixture of **15** (49.0 mg, 0.13 mmol) and thymine

(16.5 mg, 0.13 mmol) was reacted with $Pd_2(dba)_3$ (4.2 mg, 4.6 μmol), *(S,S)*-L1 (7.3 mg, 9.2 μmol) and K_3PO_4 (7.0 mg, 0.033 mmol) at rt for 20 h. Flash column chromatography on silica gel (Hexane:EtOAc = 70:30) afforded **16-1** as a colorless oil (55.9 mg, 0.112 mmol, 85.3%, d.r. = 1:13).

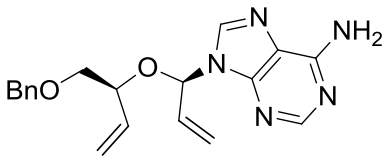
R_f 0.55 (Hexane:EtOAc = 70:30, twice); $[\alpha]^{27}_D$ = +9.8 (c = 1.57, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.14 (s, 1H), 7.21-7.39 (m, 5H), 7.10-7.17 (m, 1H), 6.49 (dt, *J* = 3.7, 1.5 Hz, 1H), 5.69-5.95 (m, 2H), 5.56 (dt, *J* = 17.2, 1.4 Hz, 1H), 5.40 (dt, *J* = 10.4, 1.4 Hz, 1H), 4.99-5.17 (m, 2H), 4.67 (d, *J* = 11.4 Hz, 1H), 4.54 (d, *J* = 11.4 Hz, 1H), 3.55-3.86 (m, 4H), 2.24-2.49 (m, 2H), 1.92 (d, *J* = 1.1 Hz, 3H), 0.84 (s, 9H), -0.10-0.04 (m, 6H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9, 151.1, 138.4, 136.6, 135.0, 133.8, 128.5, 128.1, 127.8, 119.8, 117.5, 111.4, 82.7, 80.6, 78.3, 72.5, 62.6, 35.1, 26.0, 18.5, 12.9, -5.2, -5.3.; IR (KBr) ν 3072, 2929, 2857, 1699, 1690, 1559, 1465, 1252, 1095 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{40}N_2NaO_5Si$ ($M+Na^+$) 523.2599, found 523.2598



16

1-((2R,6S,7R)-6-(benzyloxy)-7-((tert-butyldimethylsilyloxy)methyl)-2,5,6,7-tetrahydrooxepin-2-yl)-5-methylpyrimidine-2,4(1H,3H)-dione (16) : Using the general procedure **C**, the solution of **16-1** (25.0 mg, 0.05 mmol) in CH_2Cl_2 was reacted with Hoveyda-Grubbs catalyst 2nd generation (1.6 mg, 2.5 μmol) at 40℃ for 10h. Flash column chromatography on silica gel (Hexane:EtOAc = 70:30) afforded **16** as a sticky colorless oil (21.3 mg, 0.0453 mmol, 90.6%, d.r. = 1 : >25).

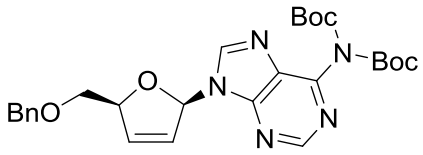
R_f 0.41 (Hexane:EtOAc = 70:30, twice); $[\alpha]^{20.2}_D$ = +13.3 (c = 1.50, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.27-7.39 (m, 5H), 7.12-7.18 (m, 1H), 6.45-6.55 (m, 1H), 5.87-6.03 (m, 1H), 5.54 (ddd, *J* = 11.1, 2.6, 2.0 Hz, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 4.48 (d, *J* = 12.0 Hz, 1H), 3.83-3.98 (m, 2H), 3.68 (dd, *J* = 10.7, 4.9 Hz, 1H), 3.54 (d, *J* = 10.7, 5.8 Hz, 1H), 2.61-2.76 (m, 1H), 2.53 (ddd, *J* = 16.4, 7.8, 4.9 Hz, 1H), 1.91 (d, *J* = 1.1 Hz, 3H), 0.85 (s, 9H), 0.00-0.04 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.0, 150.3, 138.3, 137.1, 131.2, 128.8, 127.81, 127.76, 111.1, 83.2, 82.5, 78.5, 70.9, 63.7, 28.0, 26.0, 18.4, 12.6, -5.18, -5.23..; IR (NaCl) ν 3033, 2928, 2856, 1698, 1465, 1252, 1092 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{36}N_2NaO_5Si$ ($M+Na^+$) 495.2286, found 495.2287.



17-1

9-((R)-1-((S)-1-(benzyloxy)but-3-en-2-yloxy)allyl)-9H-purin-6-amine (17-1) : Using the general procedure **B**, the mixture of **6** (86.5 mg, 0.40 mmol) and adenine (54.1 mg, 0.40 mmol) was reacted with $Pd_2(dba)_3$ (9.2 mg, 10.0 μmol), *(S,S)*-L3 (15.8 mg, 20.0 μmol) and K_3PO_4 (21.2 mg, 0.10 mmol) at rt for 8 h. Flash column chromatography on silica gel (EtOAc:MeOH = 90:10) afforded **17-1** as a white solid (112.1 mg, 0.32 mmol, 79.8%, d.r. = 1 : >25).

R_f 0.37 (Hexane:EtOAc = 50:80); $[\alpha]^{22}_D$ = +43.2 (c = 0.41, MeOH); M.p. 79.2-80.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.03 (s, 1H), 7.19-7.35 (m, 5H), 6.33-6.36 (m, 1H), 6.27 (br, s, 2H), 6.04-6.15 (m, 1H), 5.72-5.83 (m, 1H), 5.36-5.49 (m, 4H), 4.42 (s, 2H), 3.97-4.03 (m, 1H), 3.37-3.52 (m, 2H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.8, 153.3, 150.2, 139.1, 137.9, 134.0, 133.4, 128.4, 127.7, 127.6, 120.6, 119.4, 119.1, 80.4, 78.2, 73.3, 72.2.; IR (KBr) ν 3315, 3151, 2904, 2860, 1647, 1595 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{21}N_5O_2$ (M^+) 351.1695, found 351.1693.

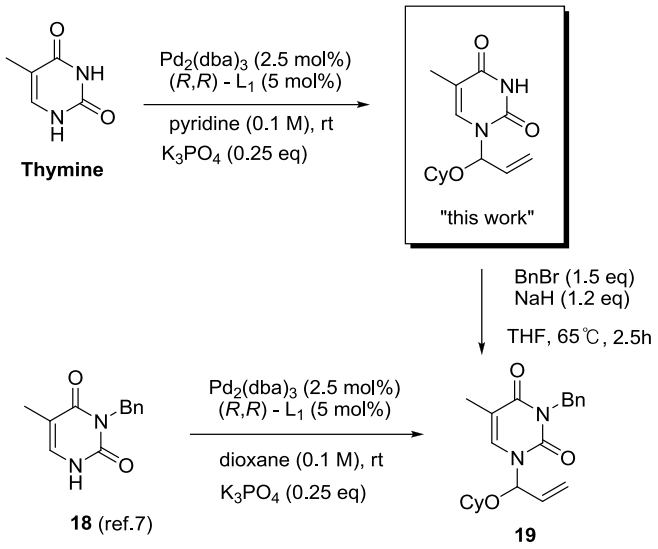


17

***N,N*-Di-*tert*-butoxycarbonyl-9-((2R,5S)-5-(benzyloxymethyl)-2,5-dihydrofuran-2-yl)-adenine (17)** : Using the general procedure **C**, The solution of boc protected **17-1** (45.2 mg, 0.08 mmol) in CH_2Cl_2 was reacted with Grubbs catalyst at 40℃ for 24h. Flash column chromatography on silica gel (Hexane:EtOAc = 50:50) afforded **17** as a colorless oil (37.9 mg, 0.07 mmol, 90.5%, d.r. = >25:1)

R_f 0.24 (Hexane:EtOAc = 50:50); $[\alpha]^{19}_D$ = −35.6 (c = 0.49, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.41 (s, 1H), 7.21-7.34 (m, 7H), 6.41-6.42 (m, 1H), 6.04-6.05 (m, 1H), 5.10 (m, 1H), 4.57 (d, *J* = 12.16 Hz, 1H), 4.46 (d, *J* = 12.33 Hz, 1H), 3.63-3.69 (m, 2H), 1.45 (s, 18H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 152.3, 150.6, 150.3, 144.0, 137.4, 134.7, 129.1, 128.7, 128.1, 128.0, 125.4, 88.4, 86.6, 83.8, 73.6, 70.7, 27.9.; IR (NaCl) ν 2980, 2929, 2862, 1789, 1756, 1599, 1577 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{33}N_5O_6Na$ (M^++Na) 546.2323, found 546.2323.

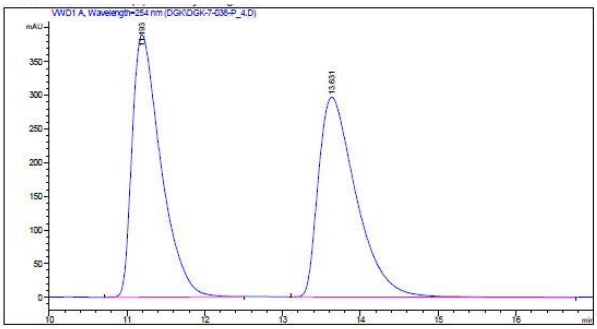
5. Determination of the Structure of 2a-T

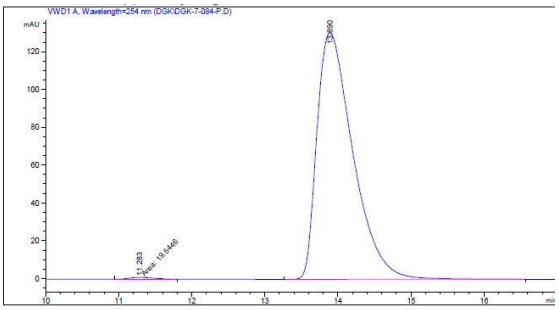


1) Synthesis of 19 from 18

(R)-3-benzyl-1-(1-(cyclohexyloxy)allyl)-5-methylpyrimidine-2,4(1H,3H)-dione (19) : Using the general procedure **B**, the mixture of **1a** (27.6 mg, 0.20 mmol) and *N*-benzylthymine[7] (42.5 mg 0.20 mmol) was reacted with $Pd_2(dba)_3$ (4.5 mg, 4.9 μmol), *(R,R)*-L1 (7.8 mg, 9.8 μmol) and K_3PO_4 (10.6 mg, 0.05 mmol) in 1,4-dioxane (2 mL, 0.1 M) at rt for 1 h. Flash column chromatography on silica gel (Hexane:EtOAc = 80:20) afforded **19** as a white solid (69.0 mg, 0.196 mmol, 99.9%). The enantiomeric excess (99.1% ee) was determined by HPLC on a chiral column (Chiralpak ID, Hexane: iPrOH = 95:5, flow rate = 1.0 mL/min, UV = 254 nm, retention time = 11.2 (minor), 13.9 (major)).

R_f 0.48 (Hexane:Et_2O = 95:5); $[\alpha]^{20}_D$ = −61.8 (c = 1.0, $CHCl_3$); m.p. 46-47 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41-7.51 (m, 2H), 7.21-7.34 (m, 3H), 7.11 (q, *J* = 1.2 Hz, 1H), 6.37 (dt, *J* = 3.6, 1.7 Hz, 1H), 5.77 (ddd, *J* = 17.1, 10.4, 3.7 Hz, 1H), 5.52 (dt, *J* = 17.2, 1.5 Hz, 1H), 5.36 (dt, *J* = 10.4, 1.5 Hz, 1H), 5.18 (d, *J* = 13.8 Hz, 1H), 5.12 (d, *J* = 13.8 Hz, 1H), 3.36-3.48 (m, 1H), 1.94 (d, *J* = 1.2 Hz, 3H), 1.88-2.00 (m, 1H), 1.58-1.80 (m, 3H), 1.45-1.55 (m, 1H), 1.15-1.40 (m, 5H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.6, 151.9, 137.2 134.4, 134.2, 129.1, 128.5, 127.7, 119.1, 110.8, 81.7, 76.5, 44.7, 33.0, 31.5, 25.6, 24.0, 23.9, 13.4; IR (NaCl) ν 3067, 3033, 2934, 2858, 1702, 1667, 1450, 1353, 1235, 768 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{26}N_2NaO_3$ ($M+Na^+$) 377.1836, found 377.1837.



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   2  13.631 BB    0.5156 9990.68750  296.92017  50.0666
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Use Multiplier & Dilution Factor with ISTDs


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Totals :                  4468.32679  131.31999
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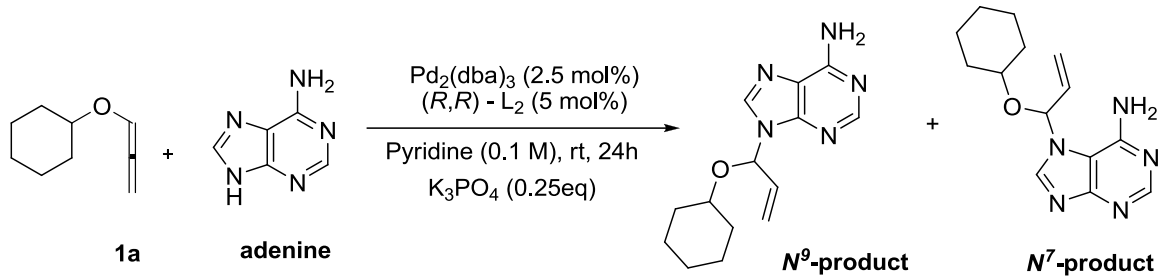
2) Synthesis of 19 from 2a-T

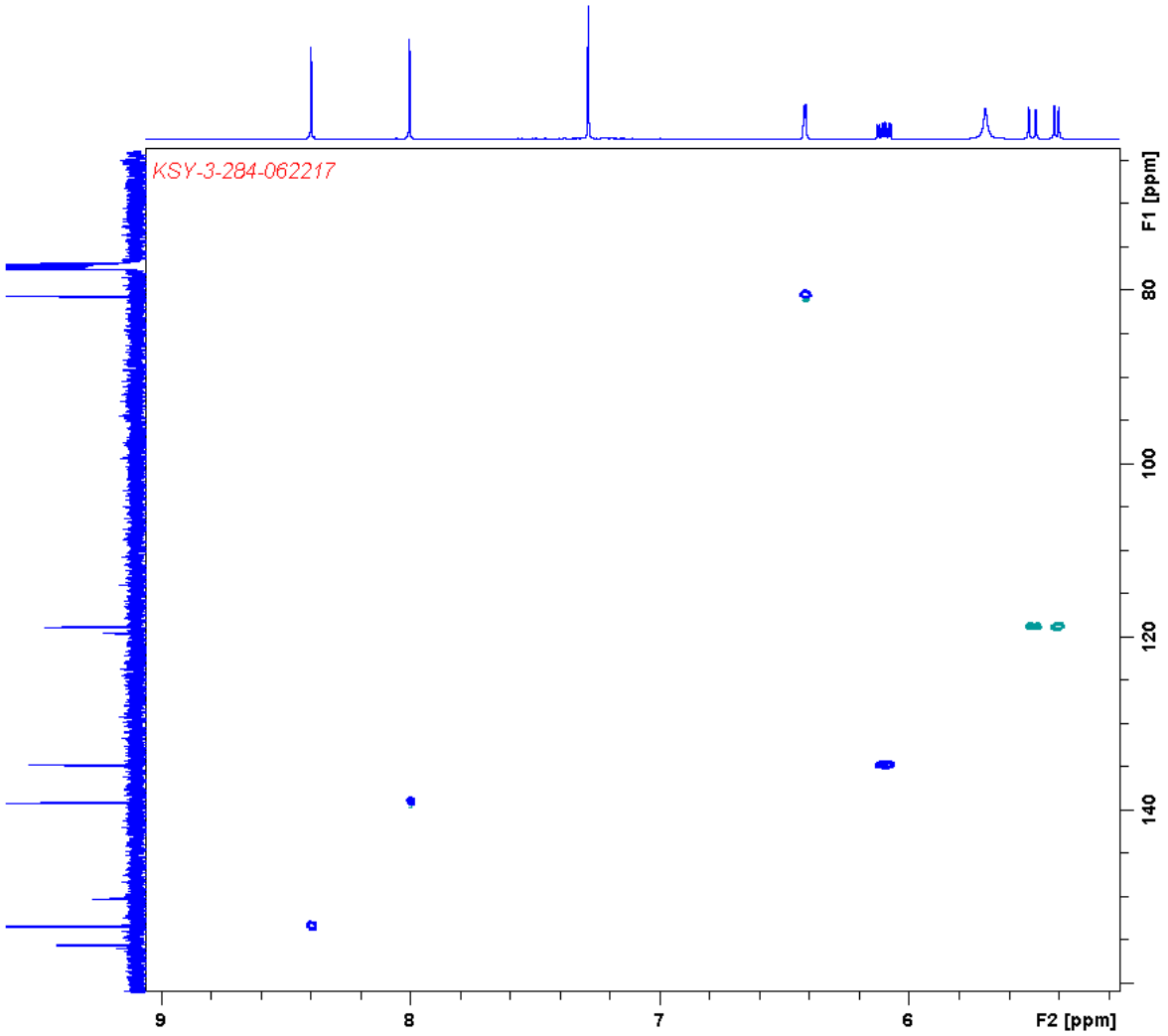
To a suspension of NaH (7.2 mg, 0.18 mmol, 60 wt% in mineral oil) in THF (0.5 mL) was added a solution of **2a-T** (39.5 mg, 0.15 mmol) in THF (1.0 mL) at 0℃. After stirring for 10 min at 0℃, benzyl bromide (27 mL, 0.22 mmol) was added. The reaction mixture was allowed to room temperature, then stirring for 2.5h at 65℃. The resulting solution was quenched with water followed by extraction with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The crude mixture was purified by flash column chromatography on silica gel (Hexane:EtOAc = 80:20) afforded **19** as a white solid (50.1 mg, 0.14 mmol, 94.2%). The spectral data are in complete accordance with the sample obtained from the previous experiment.

6. Structure determination of N^9/N^7 substituted adenine[8]



(90% yield, 92% ee)

1) HSQC experiment



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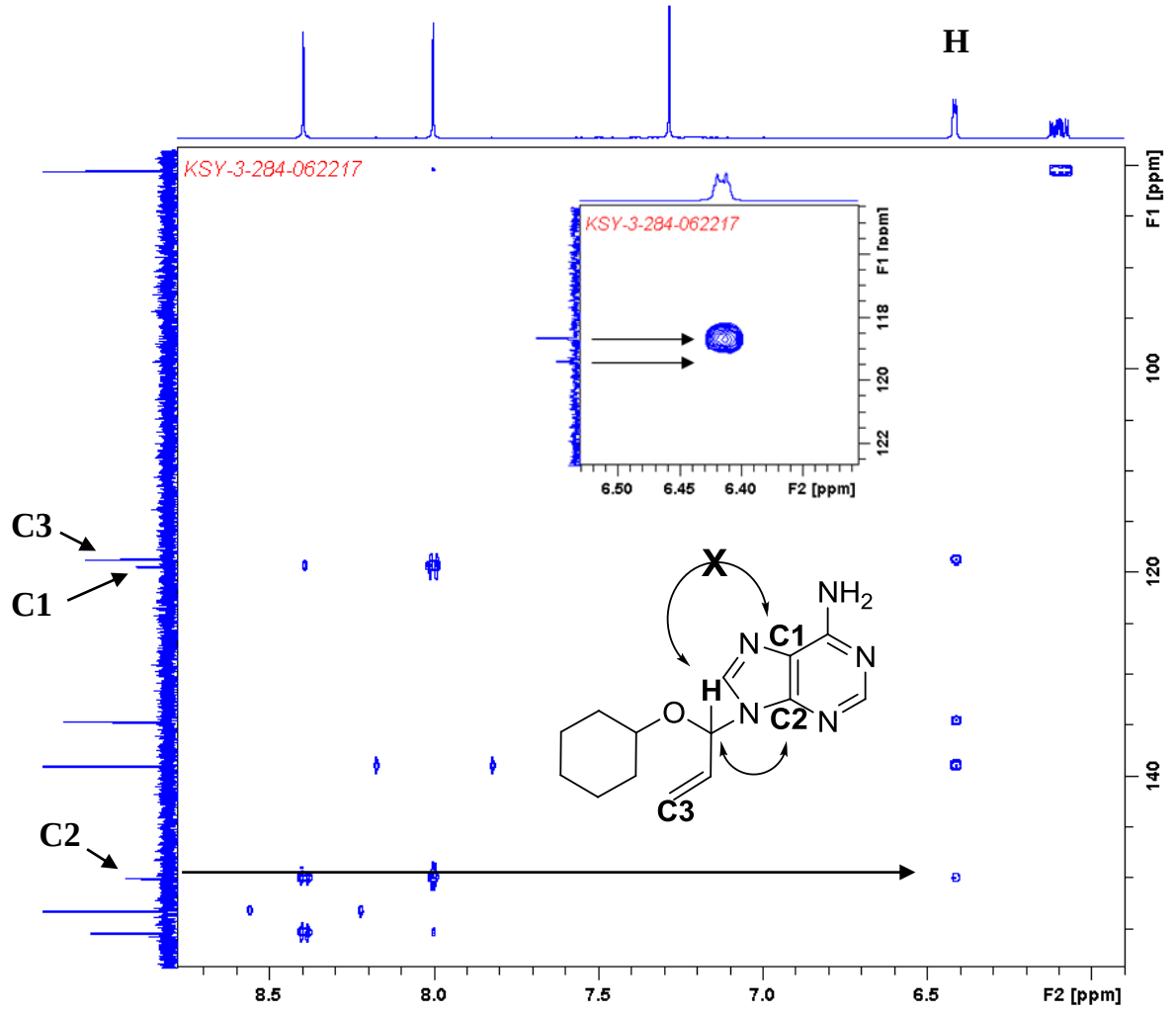
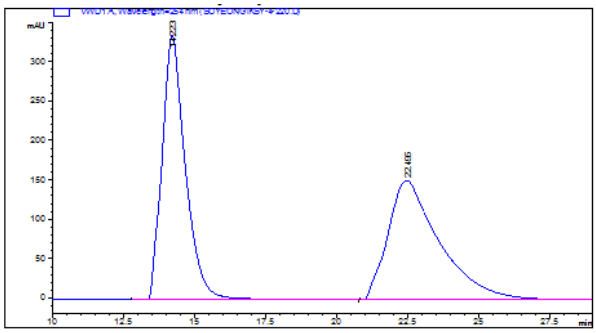
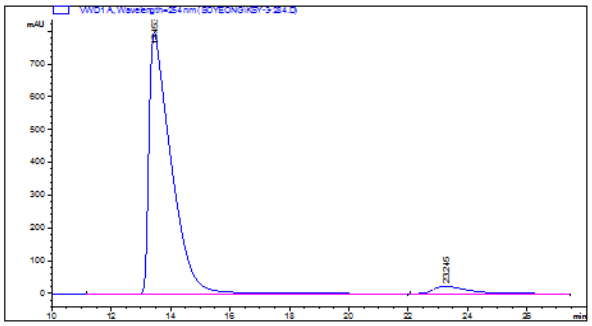


(S)-9-(1-(cyclohexyloxy)allyl)-9H-purin-6-amine : Using the general procedure **B**, the mixture of **1a** (27.0 mg, 0.20 mmol) and adenine (28.0 mg, 0.20 mmol) was reacted with $Pd_2(dba)_3$ (4.6 mg, 5.0 μmol), *(R,R)*-L2 (6.9 mg, 10.0 μmol) and K_3PO_4 (10.6 mg, 0.05 mmol) at rt for 24 h. Flash column chromatography on silica gel (EtOAc:MeOH = 90:10) afforded product as a white solid (49.3 mg, 0.18 mmol, 90.2%). The enantiomeric excess (91.7% ee) was determined by HPLC on a chiral column (Chiralpak ID, Hexane: iPrOH = 60:40, flow rate = 1.0 mL/min, UV = 254 nm, retention time = 13.45 (major), 23.25 (minor)).

R_f 0.67 (EtOAc:MeOH = 90:10); M.p. 127.8-128.9 ºC; $[\alpha]^{28}_D$ = +79.4 (c = 0.19, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.00 (s, 1H), 6.38-6.40 (m, 1H), 6.02-6.13 (m, 1H), 5.86 (br, s, 2H), 5.46-5.52 (m, 1H), 5.38-5.42 (m, 1H), 3.38-3.46 (m, 1H), 1.99-2.03 (m, 1H), 1.38-1.77 (m, 5H), 1.12-1.34 (m, 4H).; ^{13}C NMR (125

MHz, $CDCl_3$) δ 155.4, 153.1, 150.1, 139.1, 134.6, 119.4, 118.9, 80.6, 76.7, 32.9, 31.5, 25.6, 23.9, 23.8.; IR (NaCl) ν 3328, 3198, 2929, 2855, 1654, 1598 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{20}N_5O$ ($M+H^+$) 274.1662, found 274.1663.





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Area Percent Report

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Totals : 4.25871e4 818.57269

7. References

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2. Kim, H.; Rhee, Y. H. *J. Am. Chem. Soc.* **2012**, *134*, 4011.
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4. Nesbitt, C. L.; McErlean, C. S. P. *Org. Biomol. Chem.* **2011**, *9*, 2198.
5. Mohapatra, D. K.; Reddy, D. S.; Mallampudi, N. A.; Gaddam, J.; Polepalli, S.; Jain, N.; Yadav, J. S. *Org. Biomol. Chem.* **2014**, *12*, 9683.
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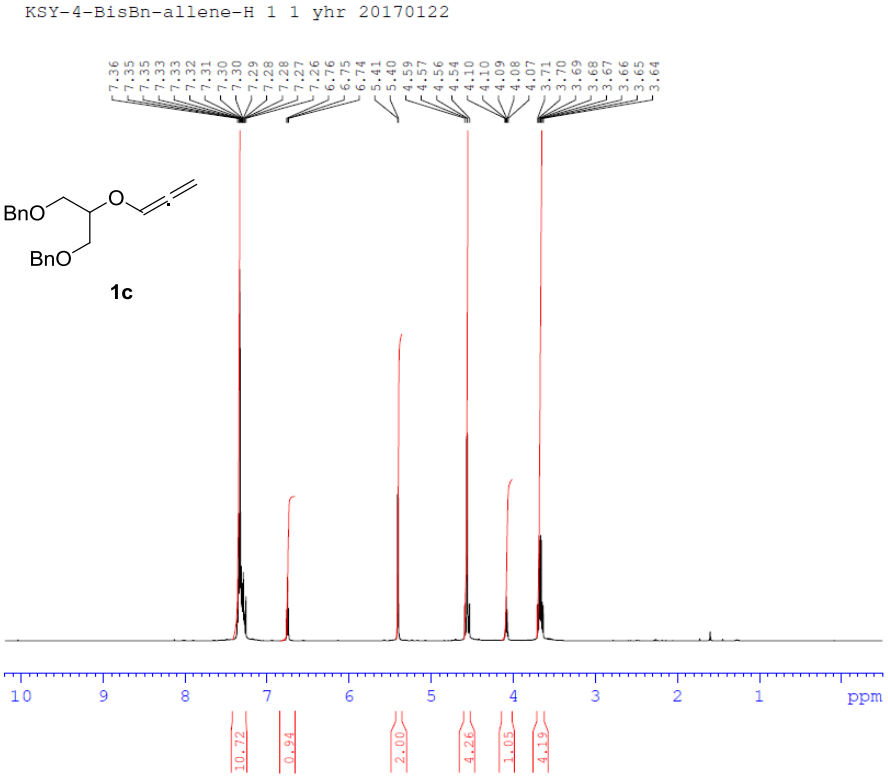
7. Jaime-Figueroa, S.; Zamilpa, A.; Guzmán, A.; Morgans, D. J. *Synth. Commun.* **2001**, *31*, 3739.
8. Webb, G. A. *Annual Reports on NMR Spectroscopy*; Elsevier Science, 2014.

8. ^{1}H NMR and ^{13}C Spectra

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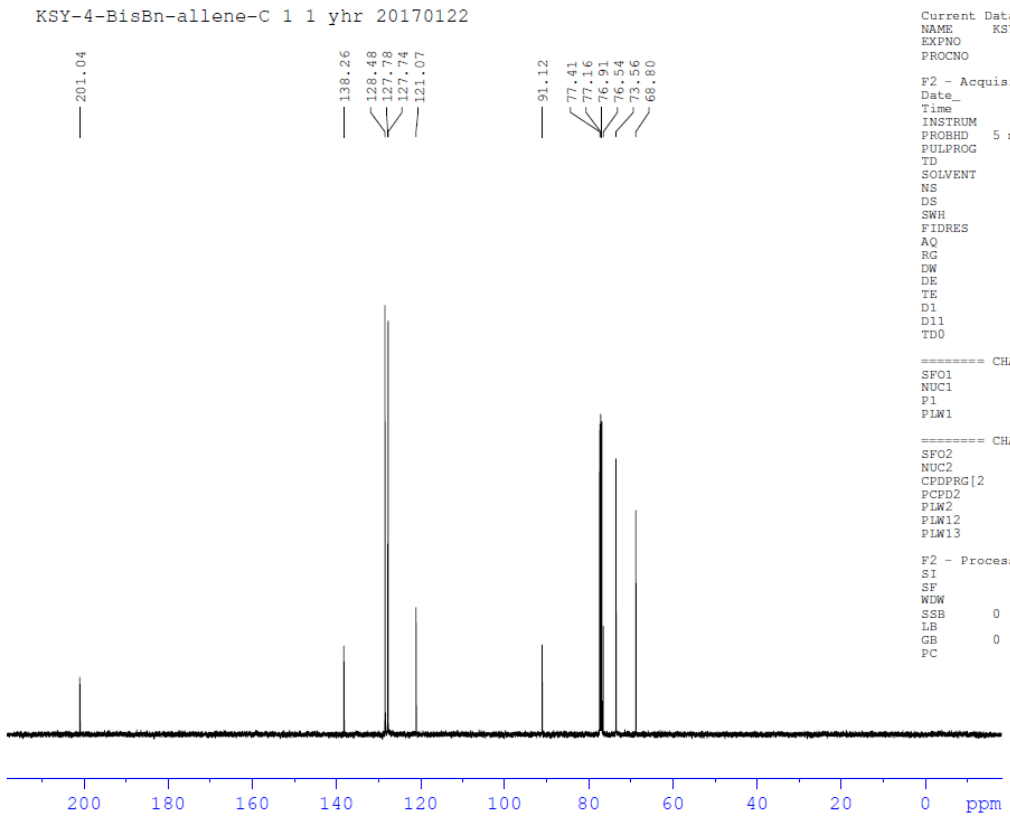


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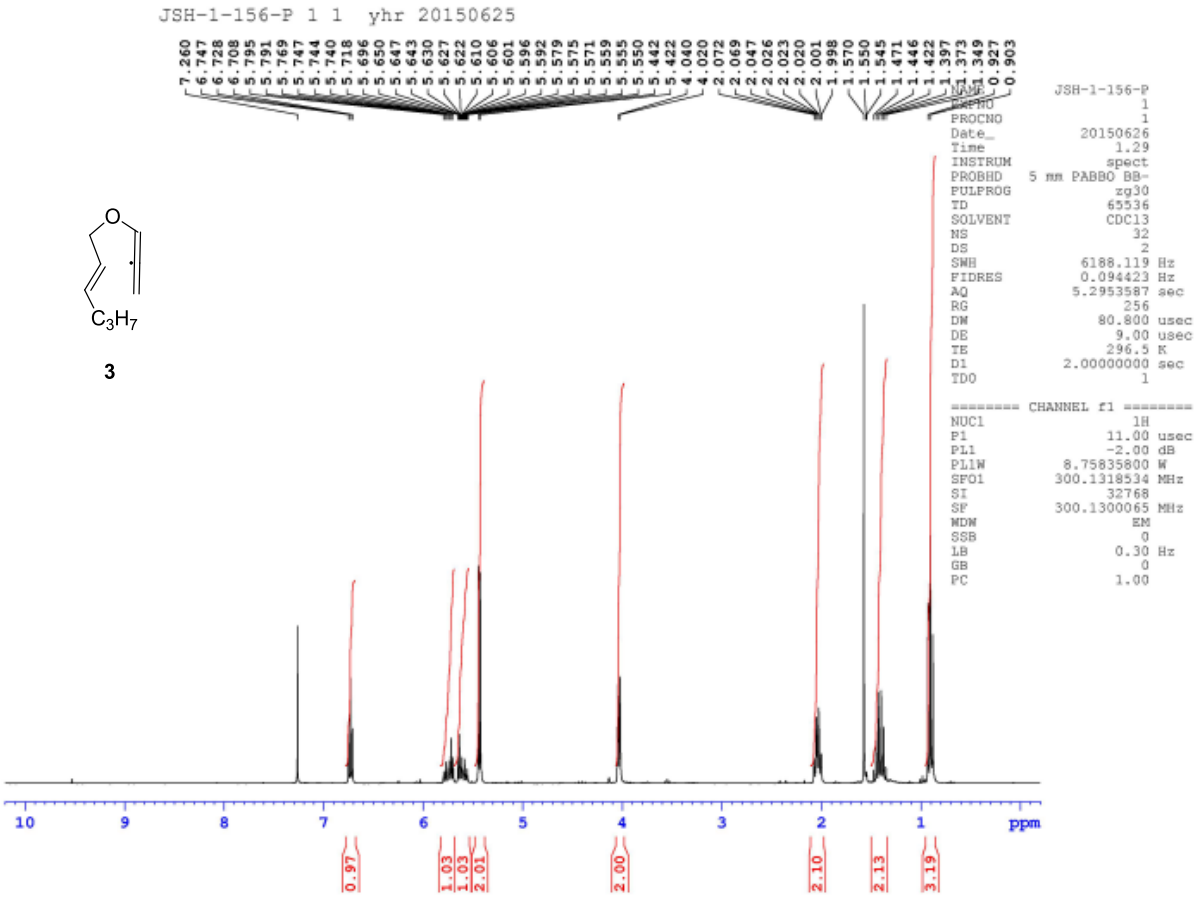
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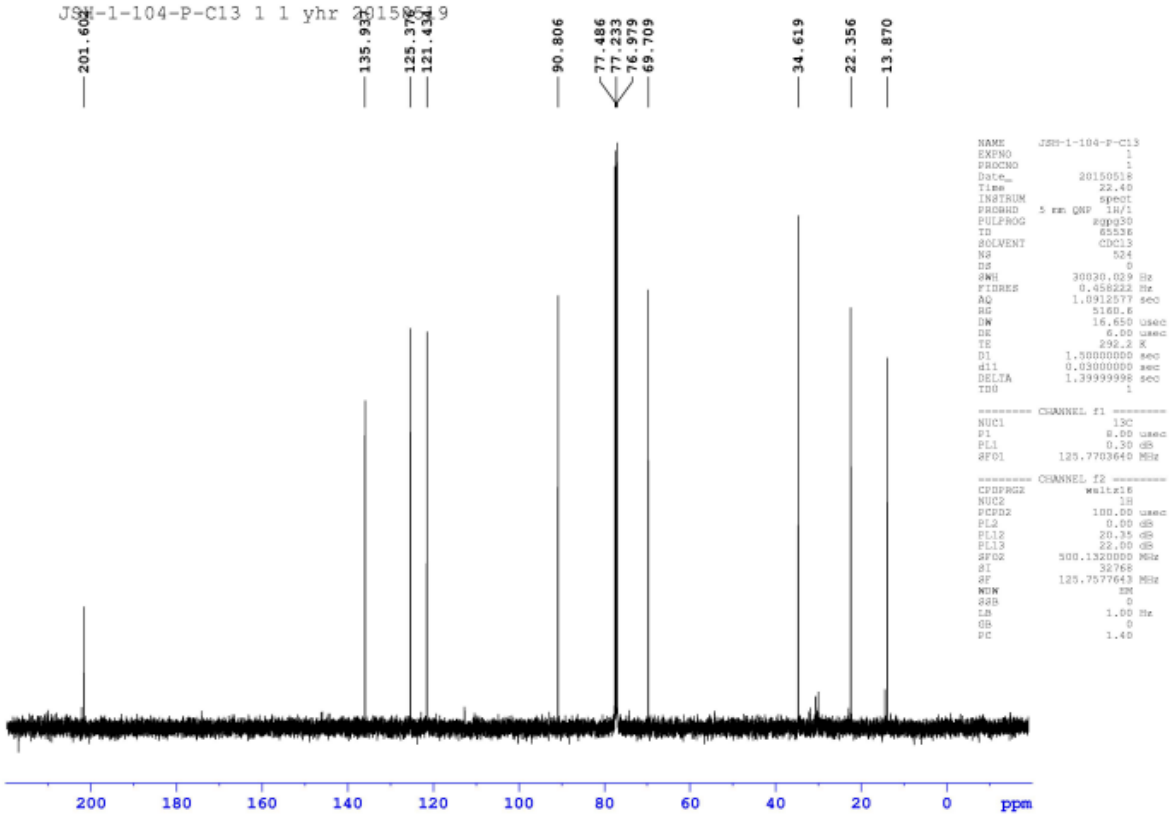
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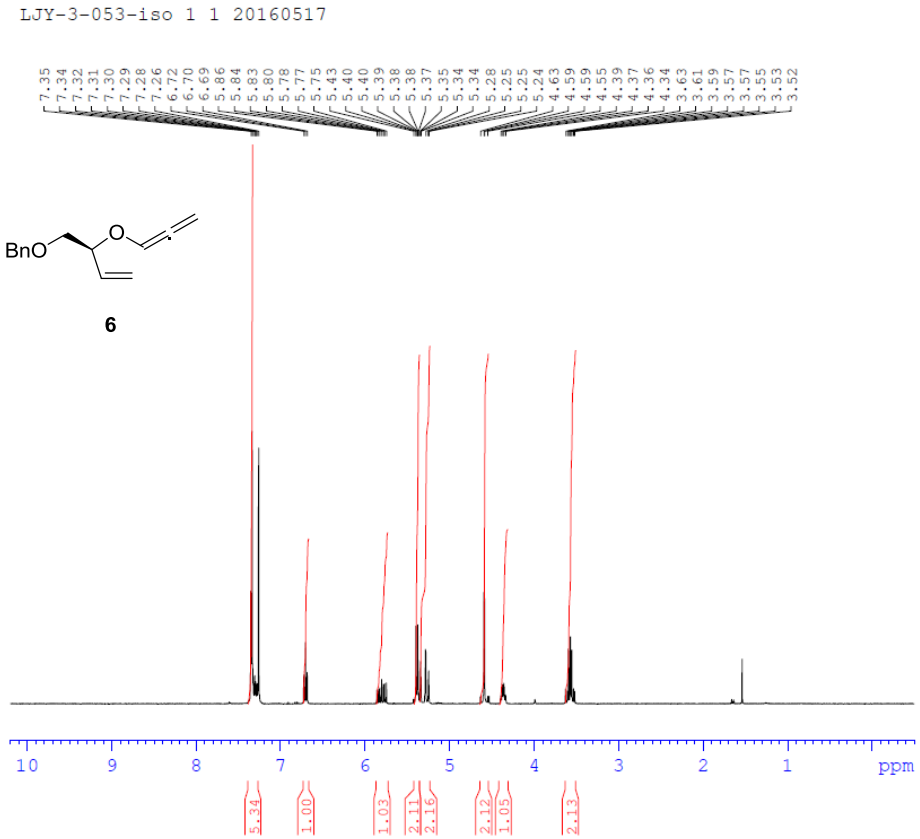


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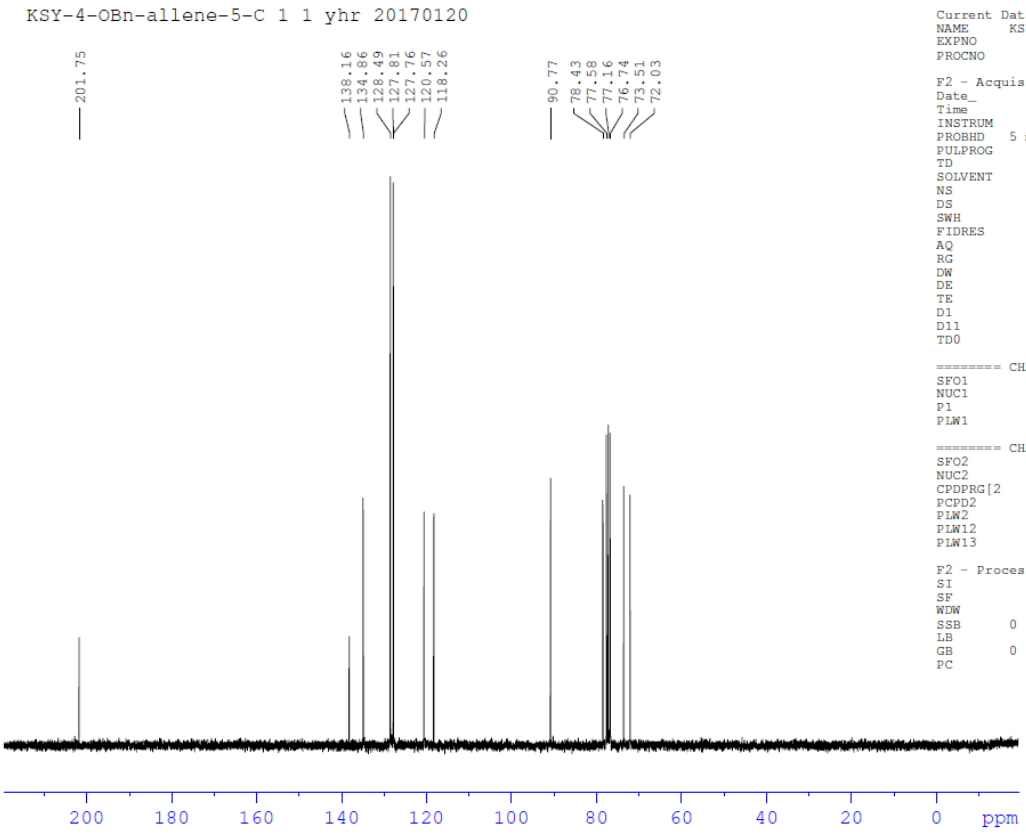


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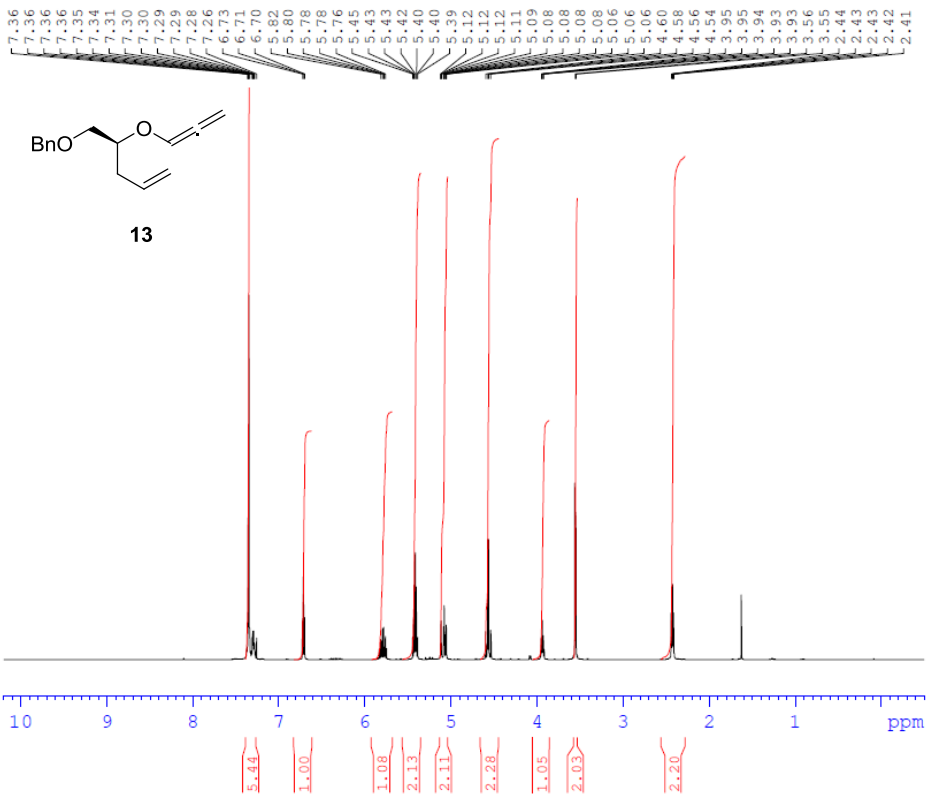
======== CHANNEL f1 ========
SFO1         75.4752953 MHz
NUC1                  13C
P1                10.20 usec
PLW1        18.97400093 W

======== CHANNEL f2 ========
SFO2        300.1312005 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2             90.00 usec
PLW2         8.75839996 W
PLW12        0.13083000 W
PLW13        0.10598000 W

F2 - Processing parameters
SI                  32768
SF           75.4677427 MHz
WDW                    EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

KSY-4-OBn-allene-6 1 1 yhr 20170122



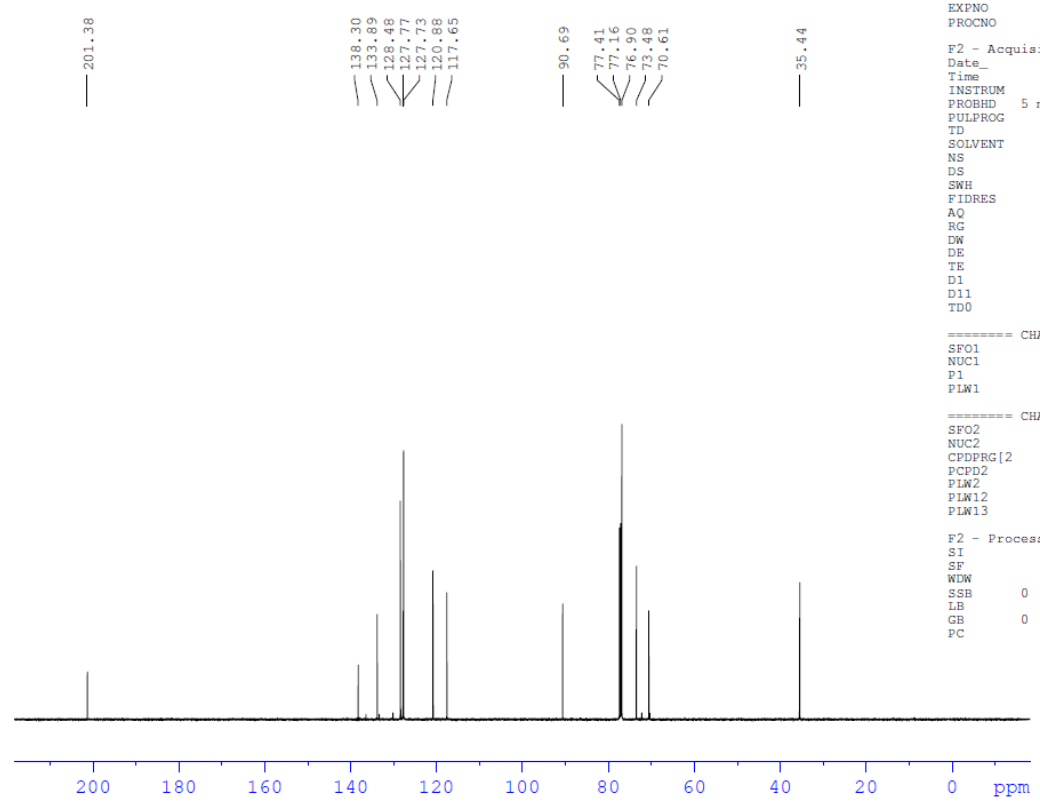

```
Current Data Parameters
NAME      KSY-4-OBn-allene-6
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20170123
Time                   1.51
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       25
DS                        2
SWH               10000.000 Hz
FIDRES                0.152588 Hz
AQ                3.2767999 sec
RG                     55.24
DW                  50.000 usec
DE                   6.50 usec
TE                   293.8 K
D1              2.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1            500.3030896 MHz
NUC1                      1H
P1                    11.20 usec
PLW1           21.00000000 W

F2 - Processing parameters
SI                        65536
SF                500.3000135 MHz
WDW                        EM
SSB                        0
LB                     0.30 Hz
GB                         0
PC                     1.00
```

KSY-4-OBn-allene-6-C 1 1 yhr 20170122




```
Current Data Parameters
NAME      KSY-4-OBn-allene-6-C
EXPNO                      1
PROCNO                     1

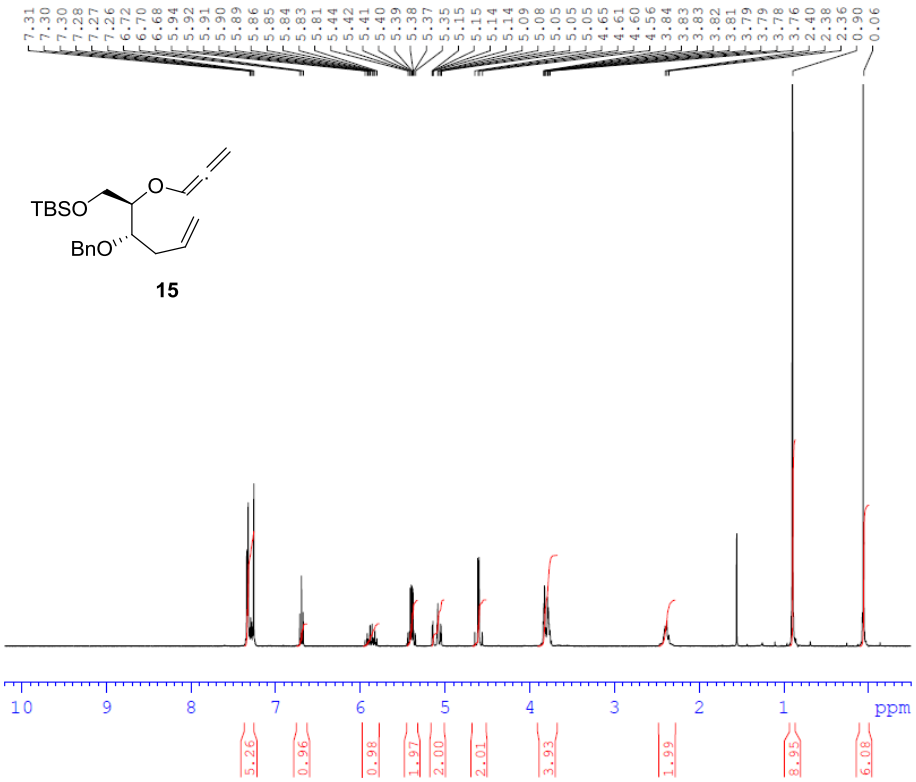
F2 - Acquisition Parameters
Date_              20170123
Time                   2.00
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG            zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      347
DS                        4
SWH               29761.904 Hz
FIDRES                0.454131 Hz
AQ                1.1010048 sec
RG                     2050
DW                  16.800 usec
DE                   6.50 usec
TE                   294.6 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1            125.8131145 MHz
NUC1                      13C
P1                    10.00 usec
PLW1           87.00000000 W

======== CHANNEL f2 ========
SFO2            500.3020012 MHz
NUC2                      1H
CPDPRG[2             waltz16
PCPD2                 80.00 usec
PLW2           21.50000000 W
PLW12           0.42140001 W
PLW13           0.26969999 W

F2 - Processing parameters
SI                        32768
SF                125.8005245 MHz
WDW                        EM
SSB                        0
LB                     1.00 Hz
GB                         0
PC                     1.40
```

DGK-9-050-P 1 1 yhr 20170120



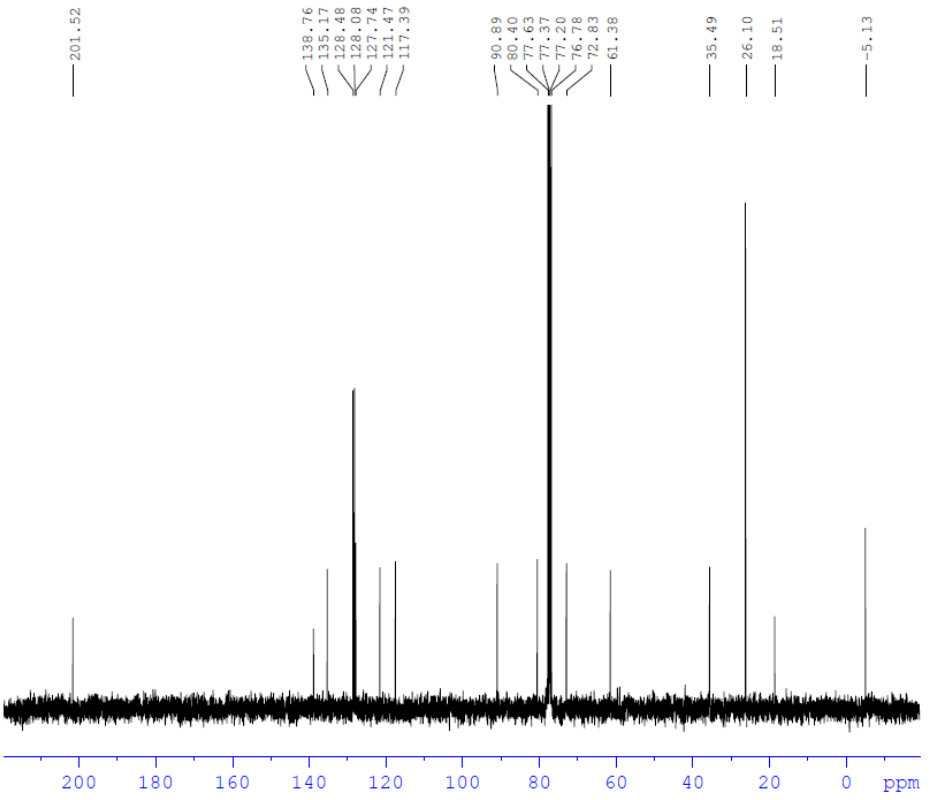

```
Current Data Parameters
NAME         DGK-9-050-P
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170125
Time                4.11
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                     8
DS                     2
SWH           6188.119 Hz
FIDRES        0.094423 Hz
AQ            5.2953086 sec
RG                   287
DW                80.800 usec
DE                 6.50 usec
TE                291.9 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         300.1314684 MHz
NUC1                 1H
P1                11.00 usec
PLW1          8.75839996 W

F2 - Processing parameters
SI                 32768
SF           300.1300062 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

DGK-9-050-P 13 1 yhr 20170120




```
Current Data Parameters
NAME         DGK-9-050-P
EXPNO                 13
PROCNO                 1

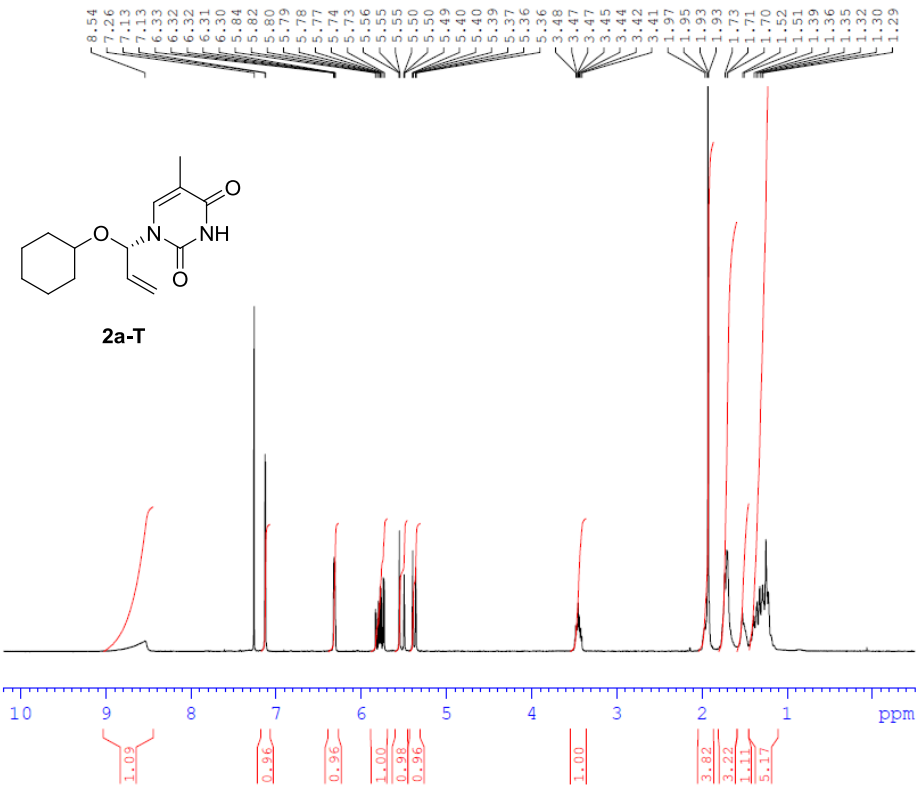
F2 - Acquisition Parameters
Date_           20170125
Time                4.22
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   919
DS                     2
SWH          18028.846 Hz
FIDRES        0.275098 Hz
AQ            1.8175317 sec
RG                  12.7
DW                27.733 usec
DE                 6.50 usec
TE                292.1 K
D1            1.50000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         75.4752953 MHz
NUC1                 13C
P1                10.20 usec
PLW1         18.97400093 W

======== CHANNEL f2 ========
SFO2         300.1312005 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2          8.75839996 W
PLW12         0.13083000 W
PLW13         0.10598000 W

F2 - Processing parameters
SI                 32768
SF           75.4677358 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

KSY-3-262-H 1 1 yhr 20161209



2a-T

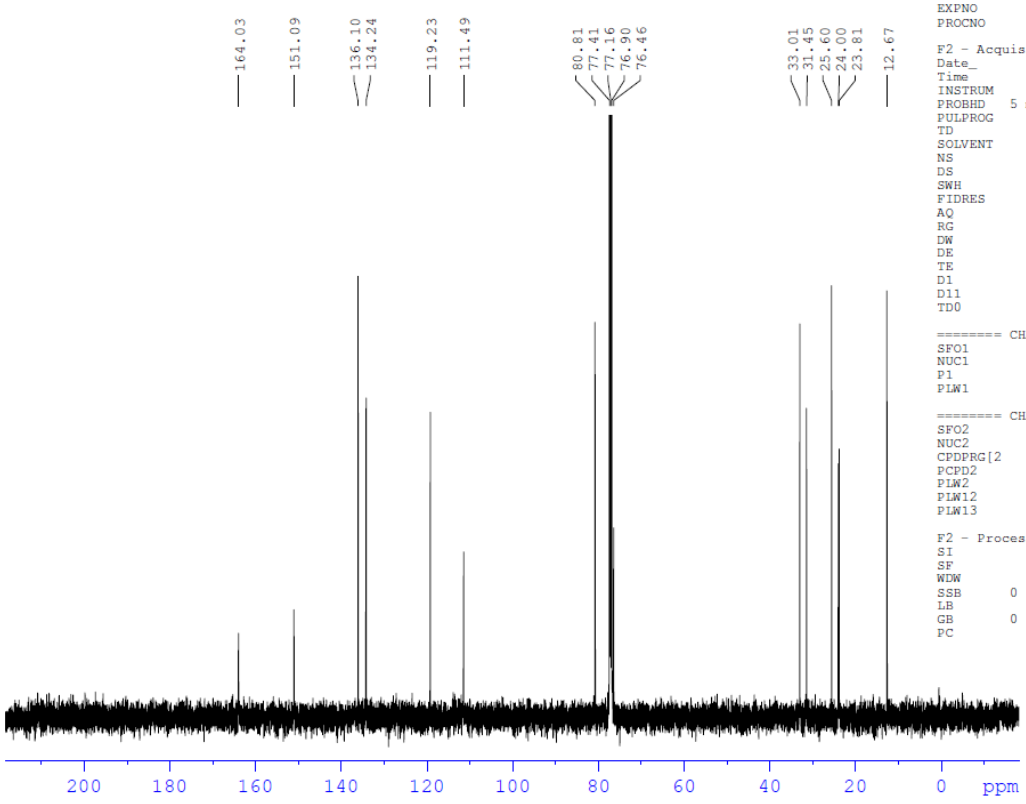
```
Current Data Parameters
NAME          KSY-3-262-H
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20161212
Time               17.53
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    18
DS                     2
SWH             6188.119 Hz
FIDRES          0.094423 Hz
AQ              5.2953086 sec
RG                   287
DW                80.800 usec
DE                 6.50 usec
TE                293.5 K
D1             2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          300.1314684 MHz
NUC1                  1H
P1                 11.00 usec
PLW1           8.75839996 W

F2 - Processing parameters
SI                 32768
SF            300.1300061 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

KSY-3-262-C 1 1 20161219 YHR




```
Current Data Parameters
NAME          KSY-3-262_C
EXPNO                   1
PROCNO                  1

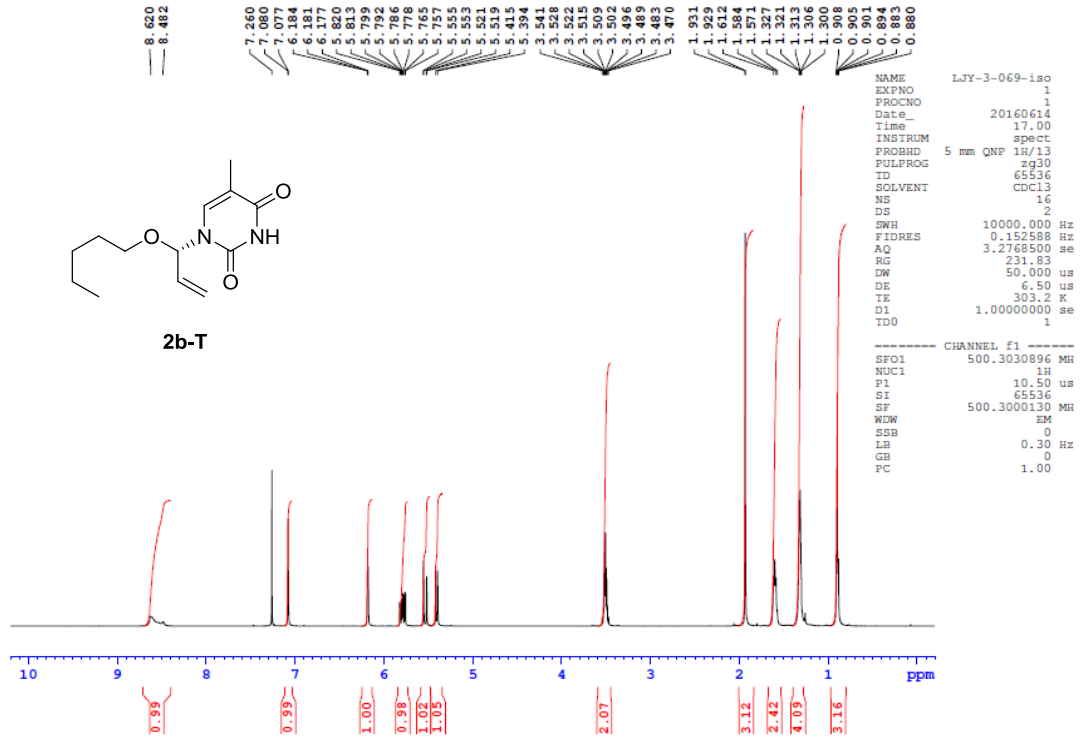
F2 - Acquisition Parameters
Date_           20161220
Time               23.24
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   446
DS                     4
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ              1.1010048 sec
RG                  2050
DW                16.800 usec
DE                 6.50 usec
TE                296.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          125.8131145 MHz
NUC1                  13C
P1                 10.00 usec
PLW1          87.00000000 W

======== CHANNEL f2 ========
SFO2          500.3020012 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              80.00 usec
PLW2          21.50000000 W
PLW12          0.42140001 W
PLW13          0.26969999 W

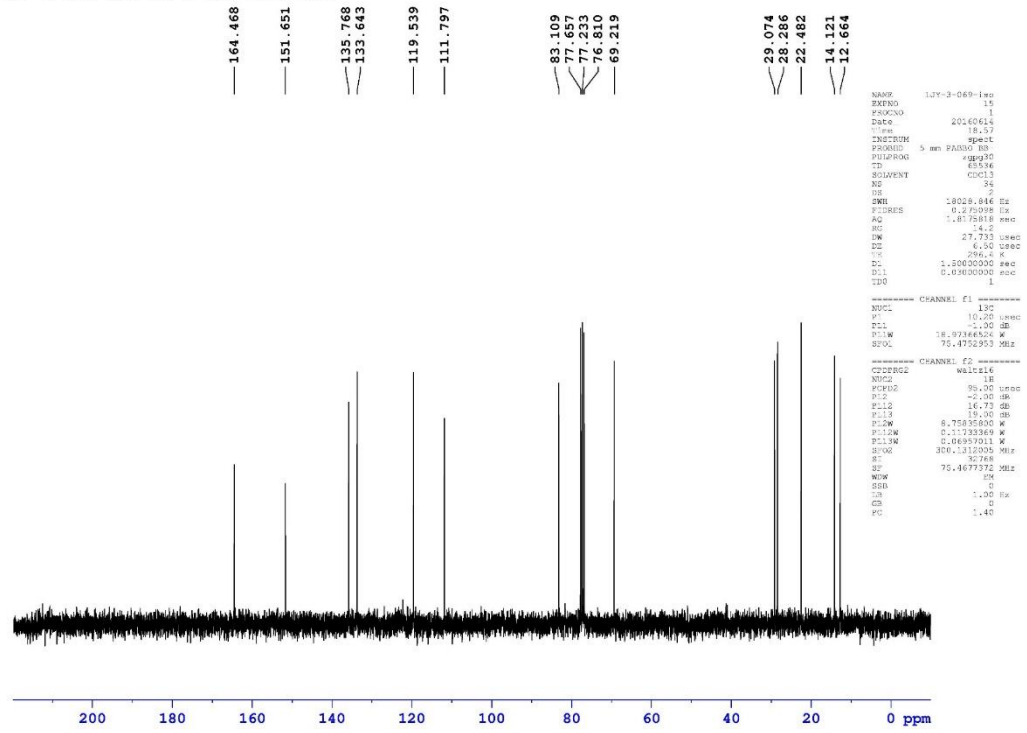
F2 - Processing parameters
SI                 32768
SF            125.8005199 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

LJY-3-069-iso

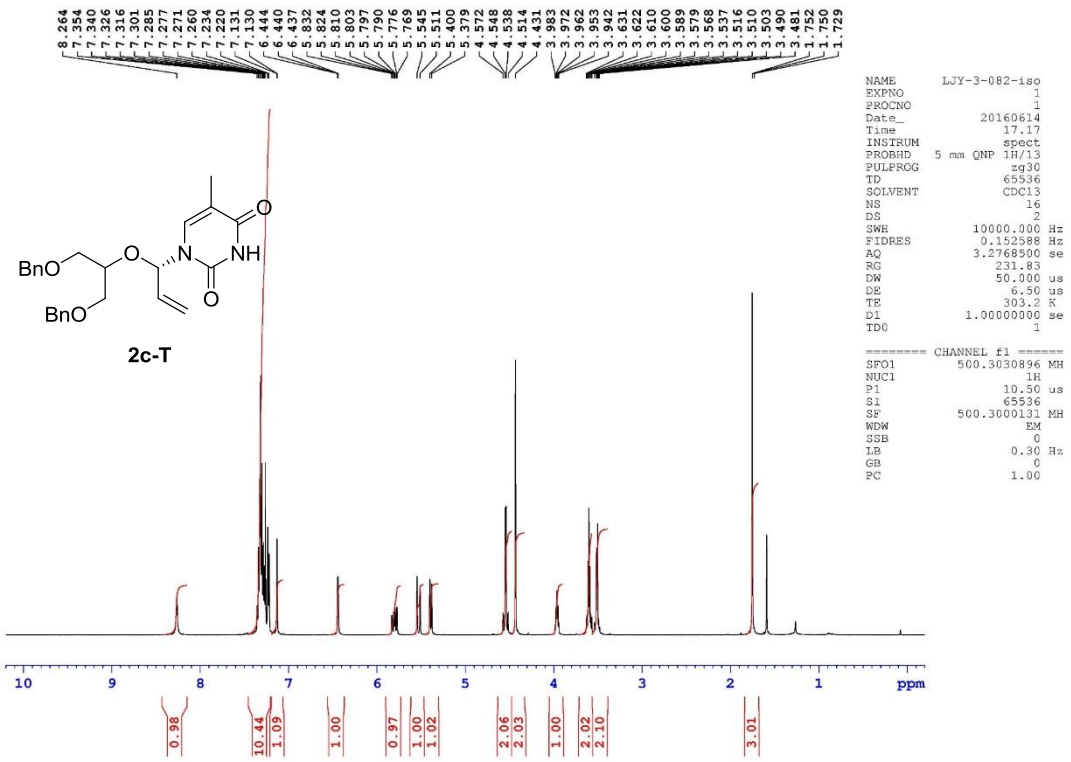


2b-T

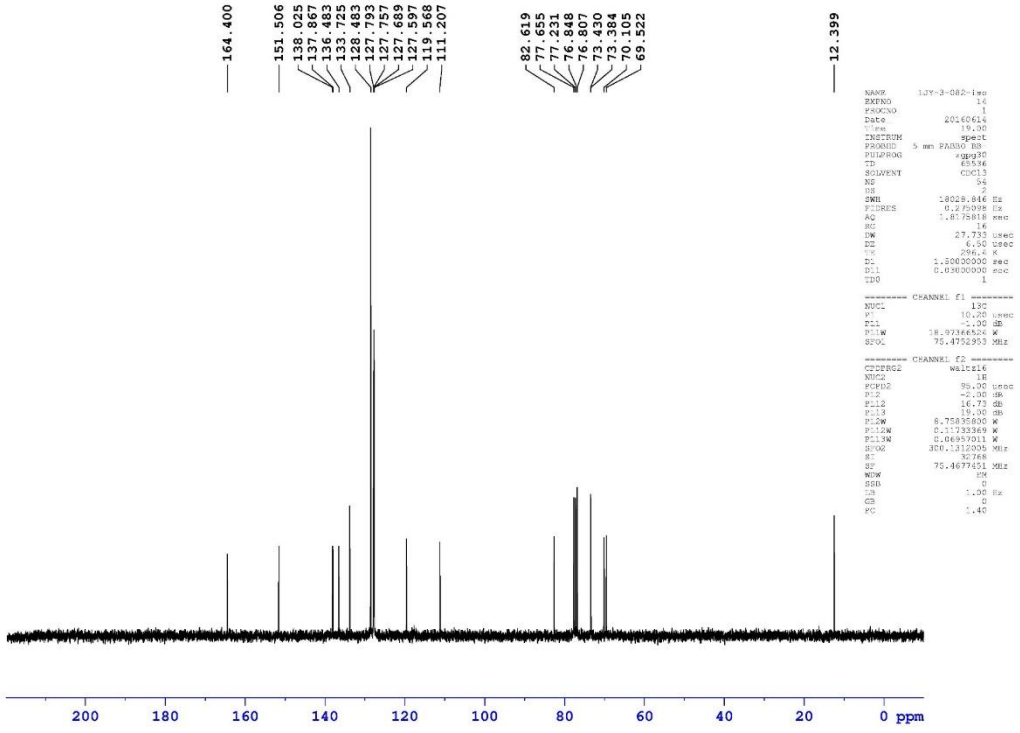
LJY-3-069-iso 15 1 yhr 20160615



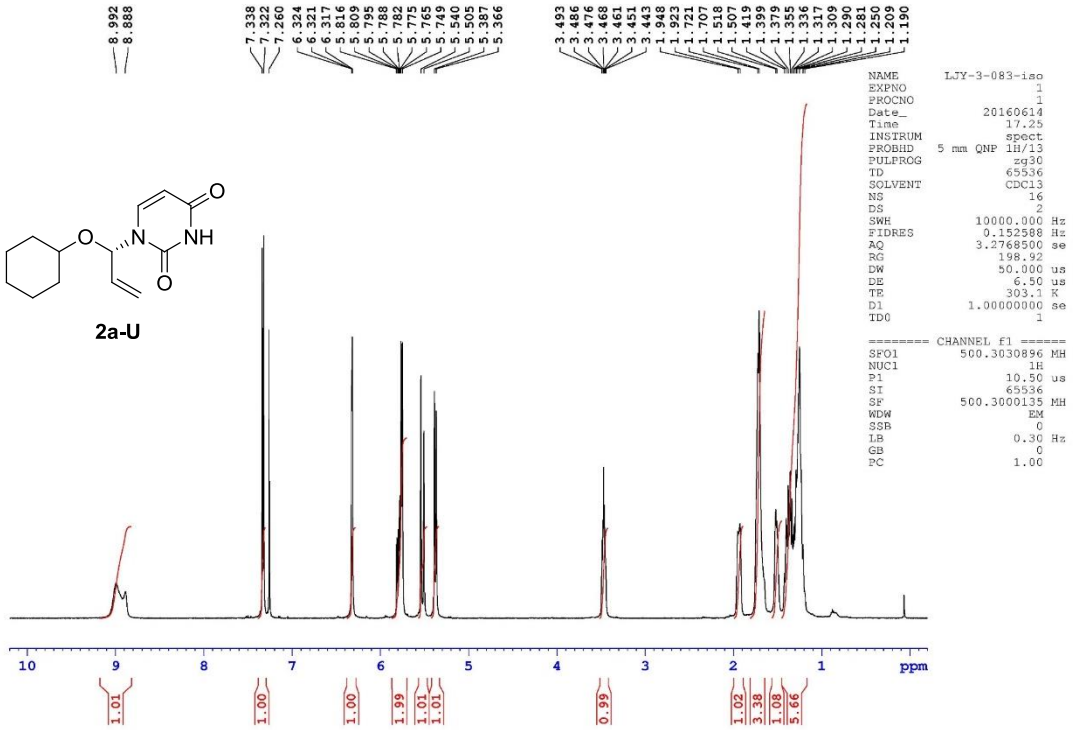
LJY-3-082-iso 1 1 yhr 20160614



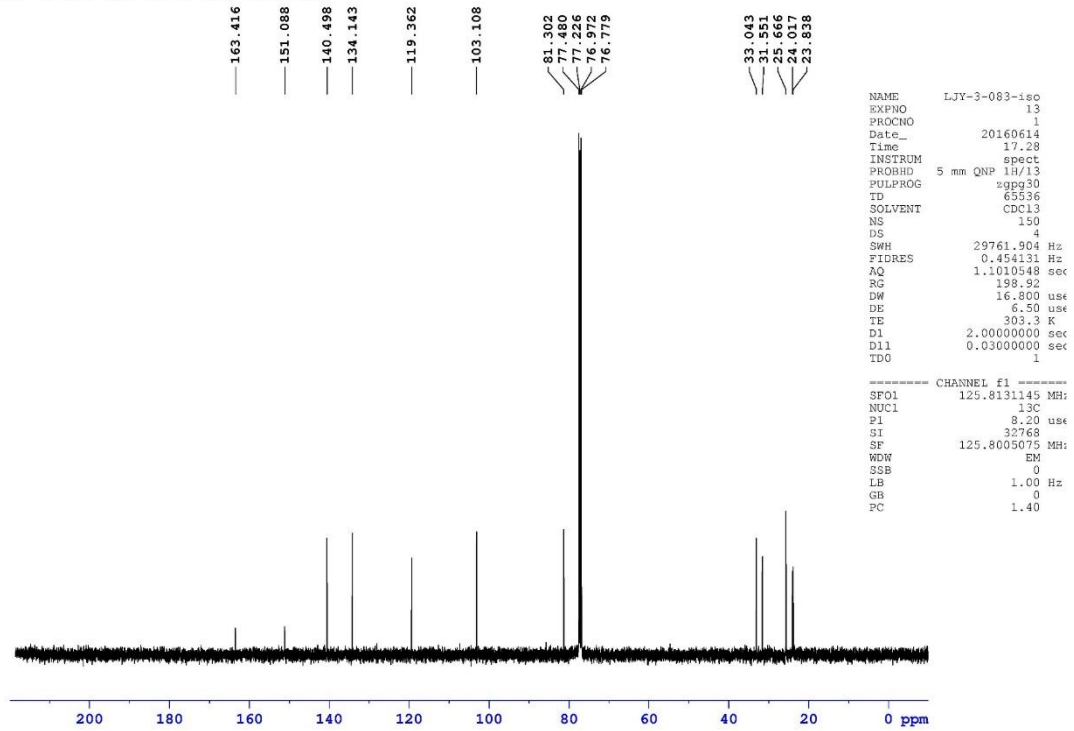
LJY-3-072-iso 14 1 yhr 20160615

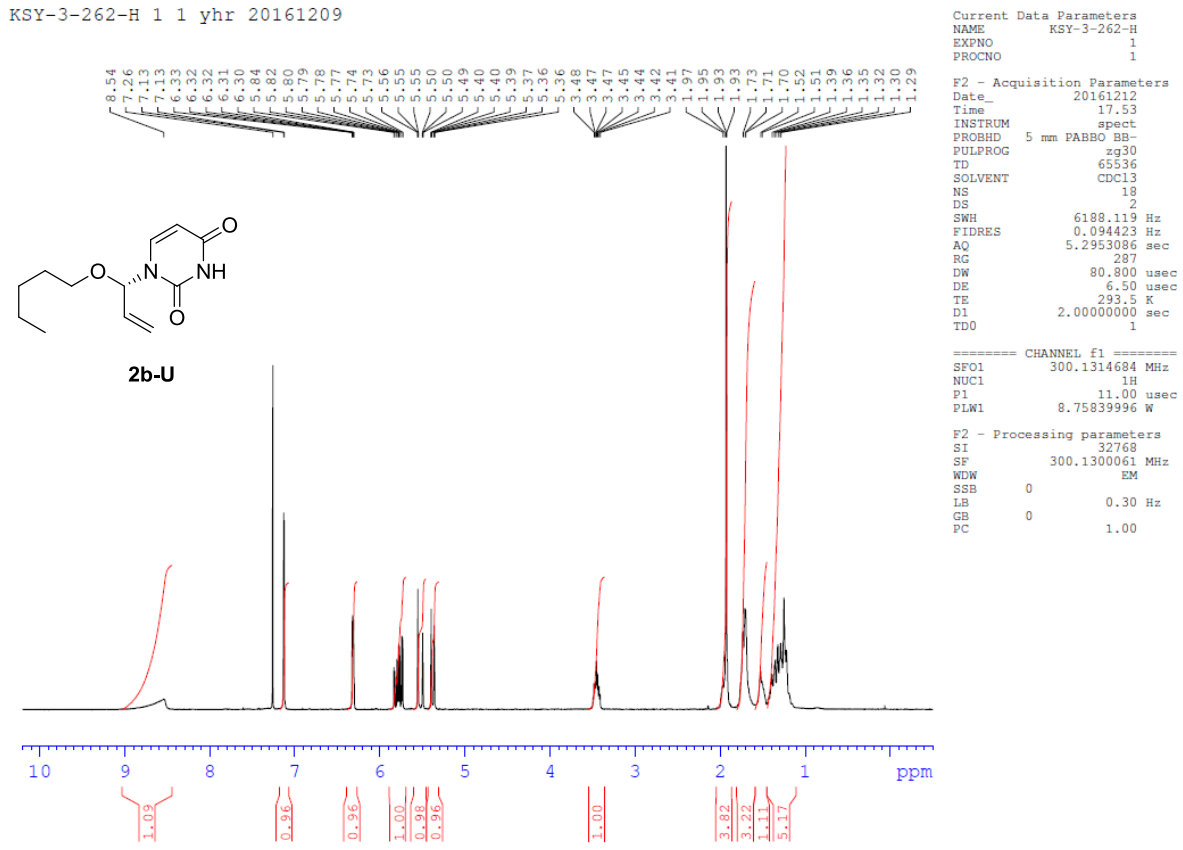


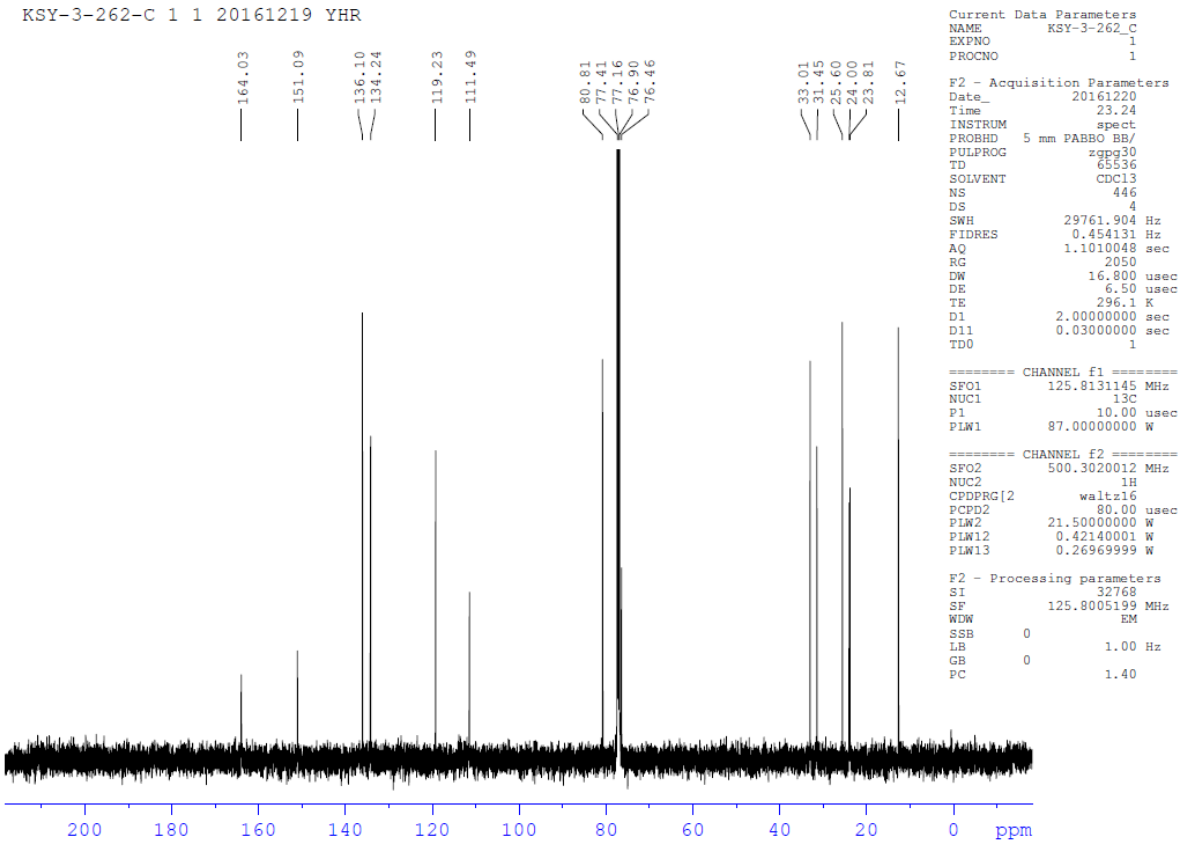
LJY-3-083-iso 1 1 yhr 20160614

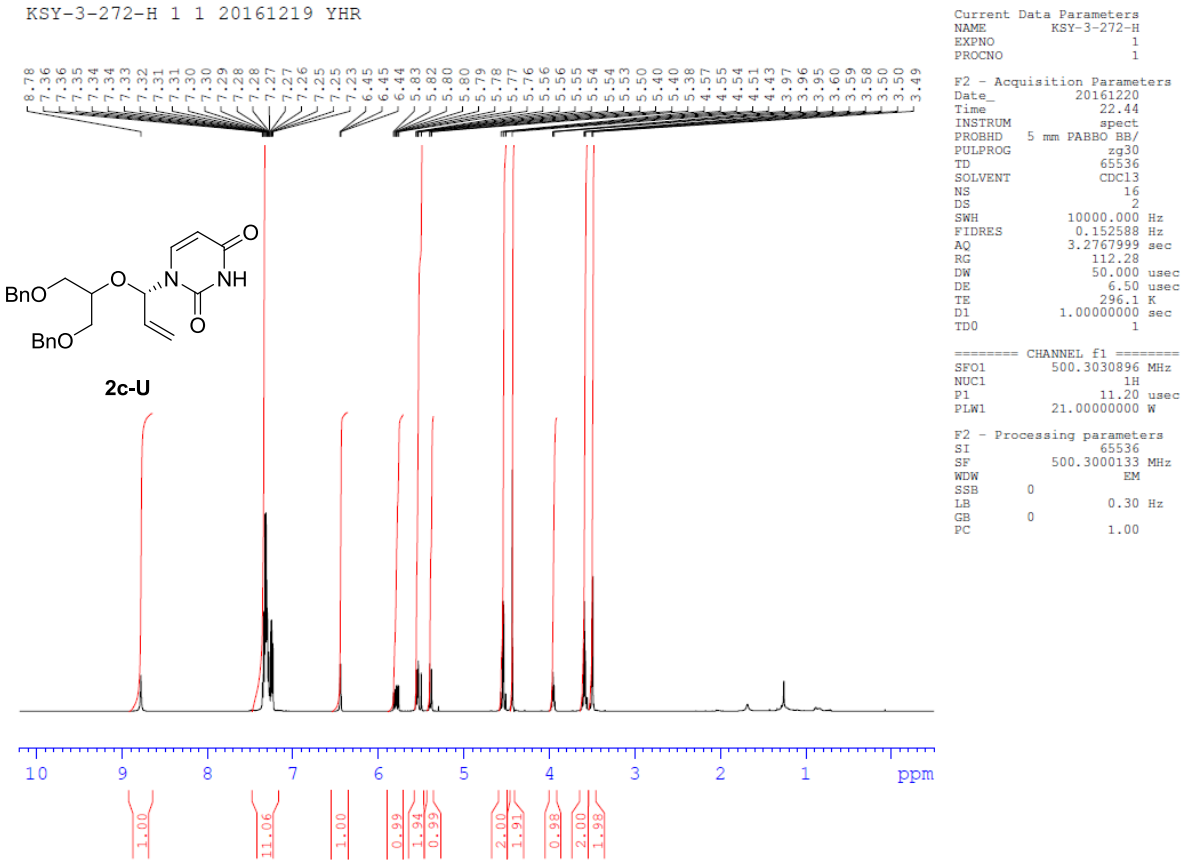


LJY-3-083-iso 13 1 yhr 20160614




KSY-3-262-H 1 1 yhr 20161209
8.54 7.26 7.13 7.13 6.33 6.32 6.32 6.31 6.30 5.84 5.82 5.80 5.79 5.78 5.77 5.74 5.73 5.56 5.55 5.55 5.50 5.50 5.49 5.40 5.40 5.39 5.37 5.36 5.36 3.48 3.47 3.47 3.45 3.44 3.42 3.41 1.97 1.95 1.93 1.93 1.73 1.71 1.70 1.52 1.51 1.39 1.36 1.35 1.32 1.30 1.29
O
NH
N
O
O
2b-U
10 9 8 7 6 5 4 3 2 1 ppm
1.09 0.96 0.96 1.00 0.98 0.96 1.00 3.82 3.22 1.11 5.17
Current Data Parameters
NAME KSY-3-262-H
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20161212
Time 17.53
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 18
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953086 sec
RG 287
DW 80.800 usec
DE 6.50 usec
TE 293.5 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 300.1314684 MHz
NUC1 1H
P1 11.00 usec
PLW1 8.75839996 W
F2 - Processing parameters
SI 32768
SF 300.1300061 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


KSY-3-262-C 1 1 20161219 YHR
164.03 151.09 136.10 134.24 119.23 111.49 80.81 77.41 77.16 76.90 76.46 33.01 31.45 25.60 24.00 23.81 12.67
200 180 160 140 120 100 80 60 40 20 0 ppm
Current Data Parameters
NAME KSY-3-262_C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20161220
Time 23.24
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 446
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 296.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.8131145 MHz
NUC1 13C
P1 10.00 usec
PLW1 87.00000000 W
======== CHANNEL f2 ========
SFO2 500.3020012 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 21.50000000 W
PLW12 0.42140001 W
PLW13 0.26969999 W
F2 - Processing parameters
SI 32768
SF 125.8005199 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

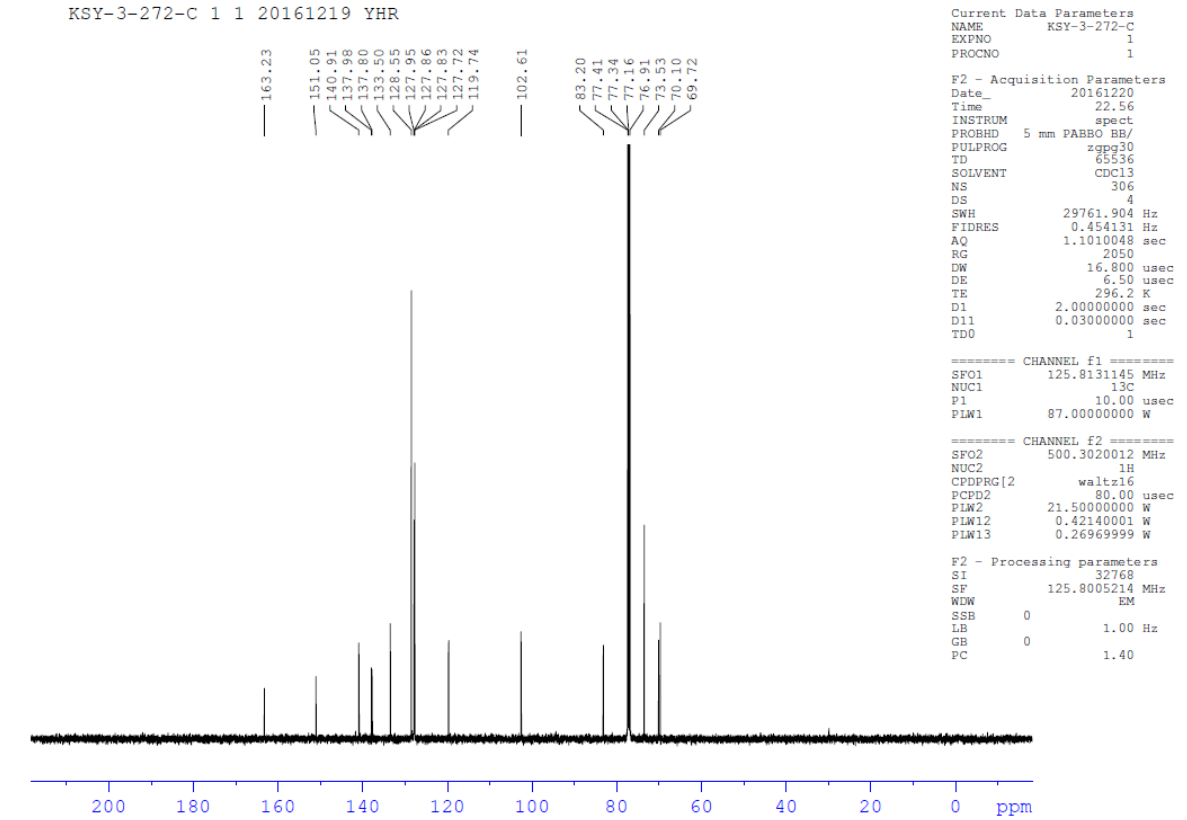



```
Current Data Parameters
NAME          KSY-3-272-H
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20161220
Time                22.44
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           10000.000 Hz
FIDRES            0.152588 Hz
AQ              3.2767999 sec
RG                 112.28
DW                 50.000 usec
DE                  6.50 usec
TE                296.1 K
D1              1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          500.3030896 MHz
NUC1                  1H
P1                 11.20 usec
PLW1          21.00000000 W

F2 - Processing parameters
SI                 65536
SF            500.3000133 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



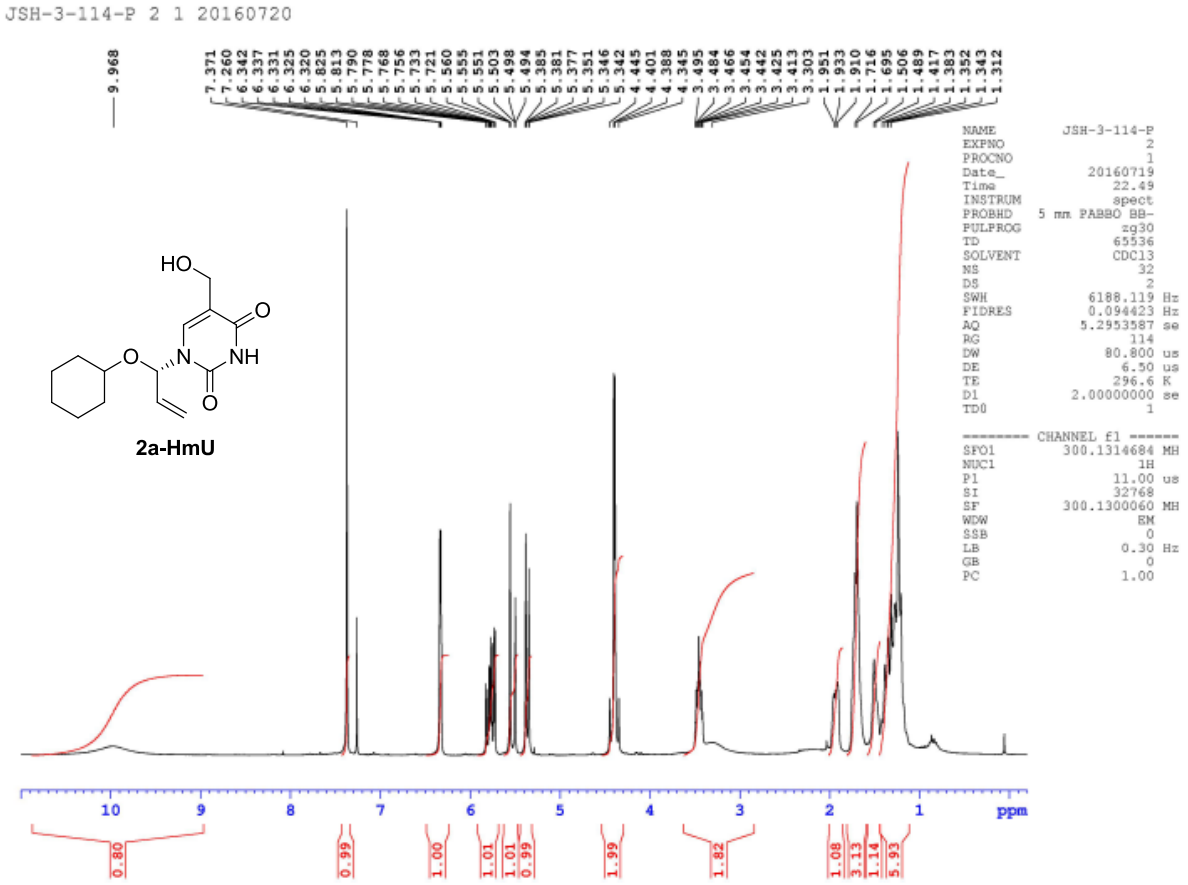

```
Current Data Parameters
NAME          KSY-3-272-C
EXPNO                   1
PROCNO                  1

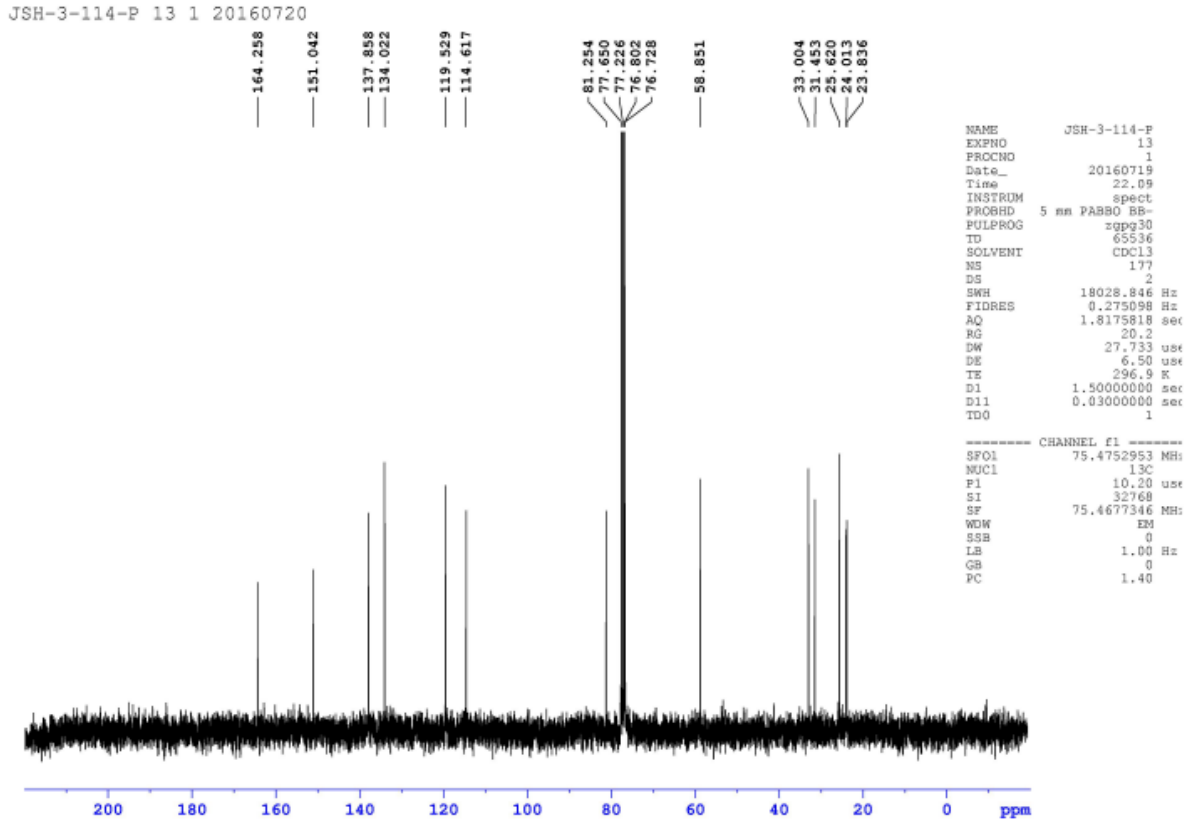
F2 - Acquisition Parameters
Date_            20161220
Time                22.56
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   306
DS                     4
SWH           29761.904 Hz
FIDRES            0.454131 Hz
AQ              1.1010048 sec
RG                 2050
DW                 16.800 usec
DE                  6.50 usec
TE                296.2 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                    1

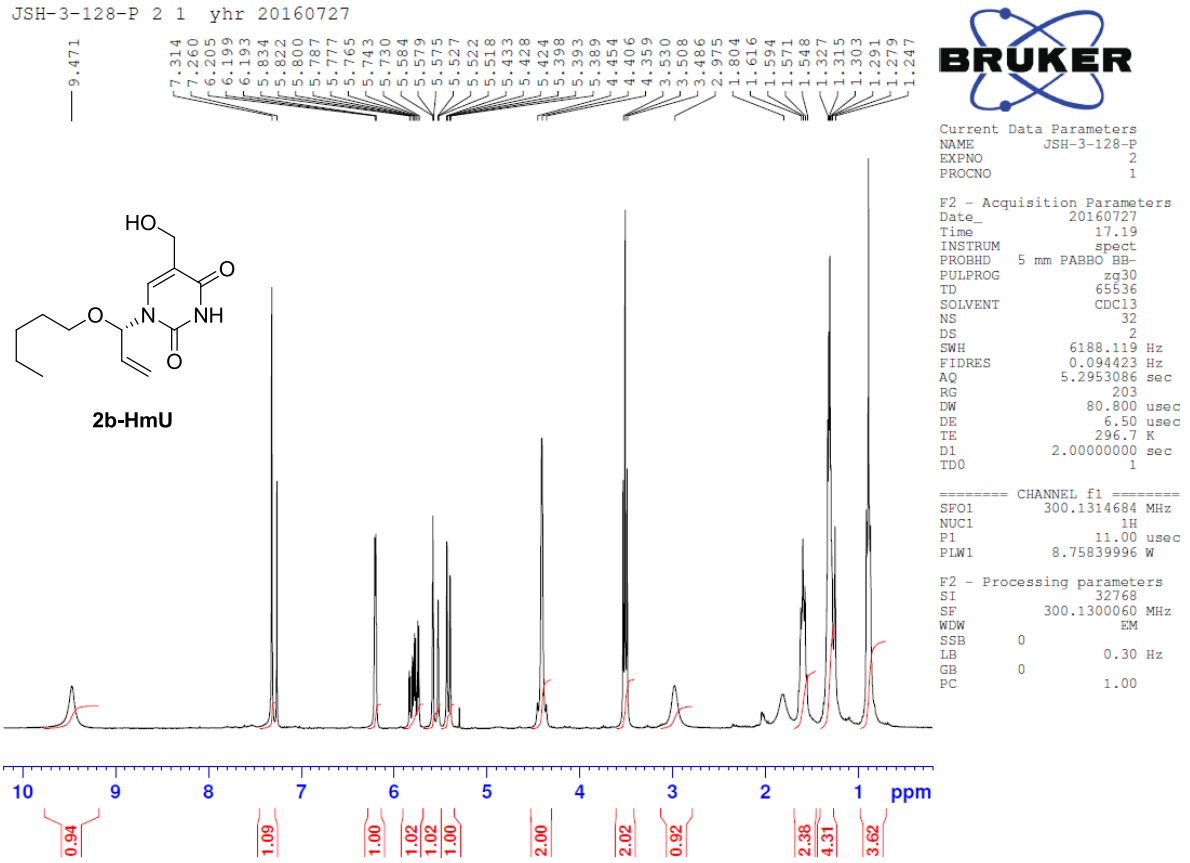
======== CHANNEL f1 ========
SFO1          125.8131145 MHz
NUC1                  13C
P1                 10.00 usec
PLW1          87.00000000 W

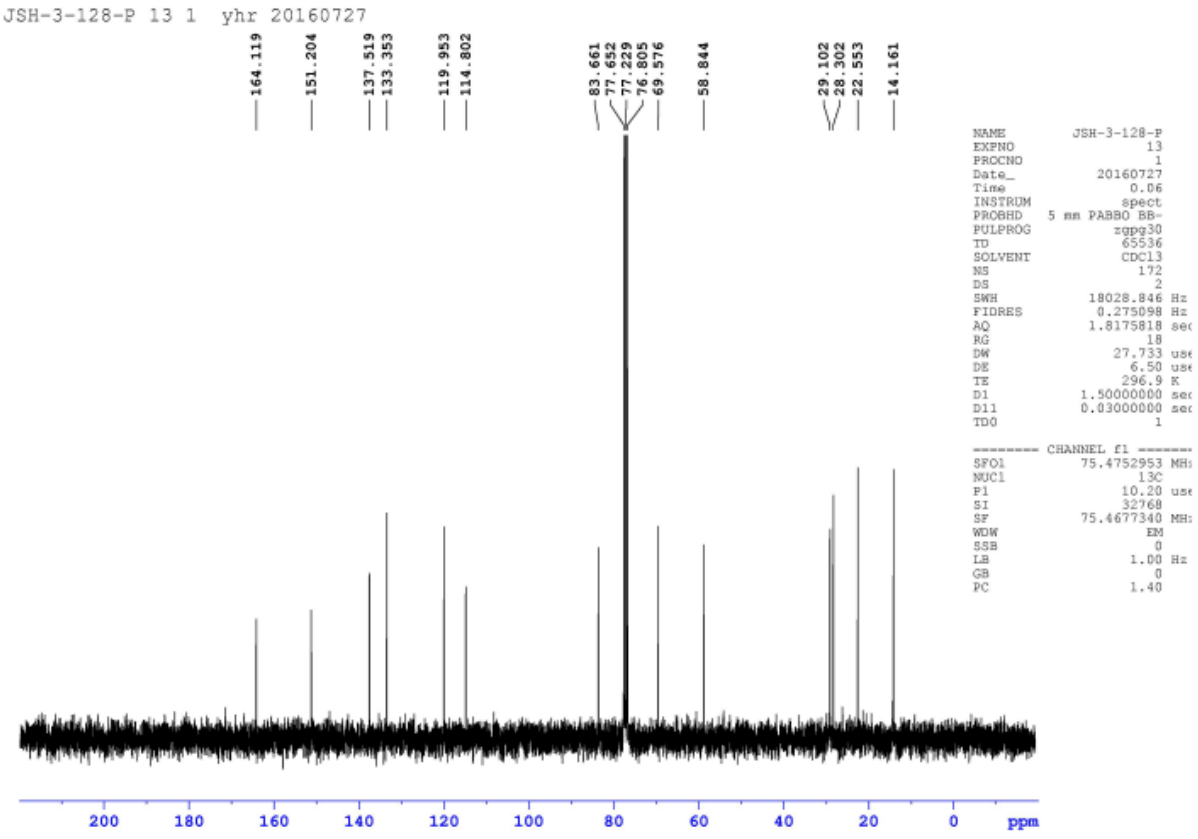
======== CHANNEL f2 ========
SFO2          500.3020012 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              80.00 usec
PLW2          21.50000000 W
PLW12          0.42140001 W
PLW13          0.26969999 W

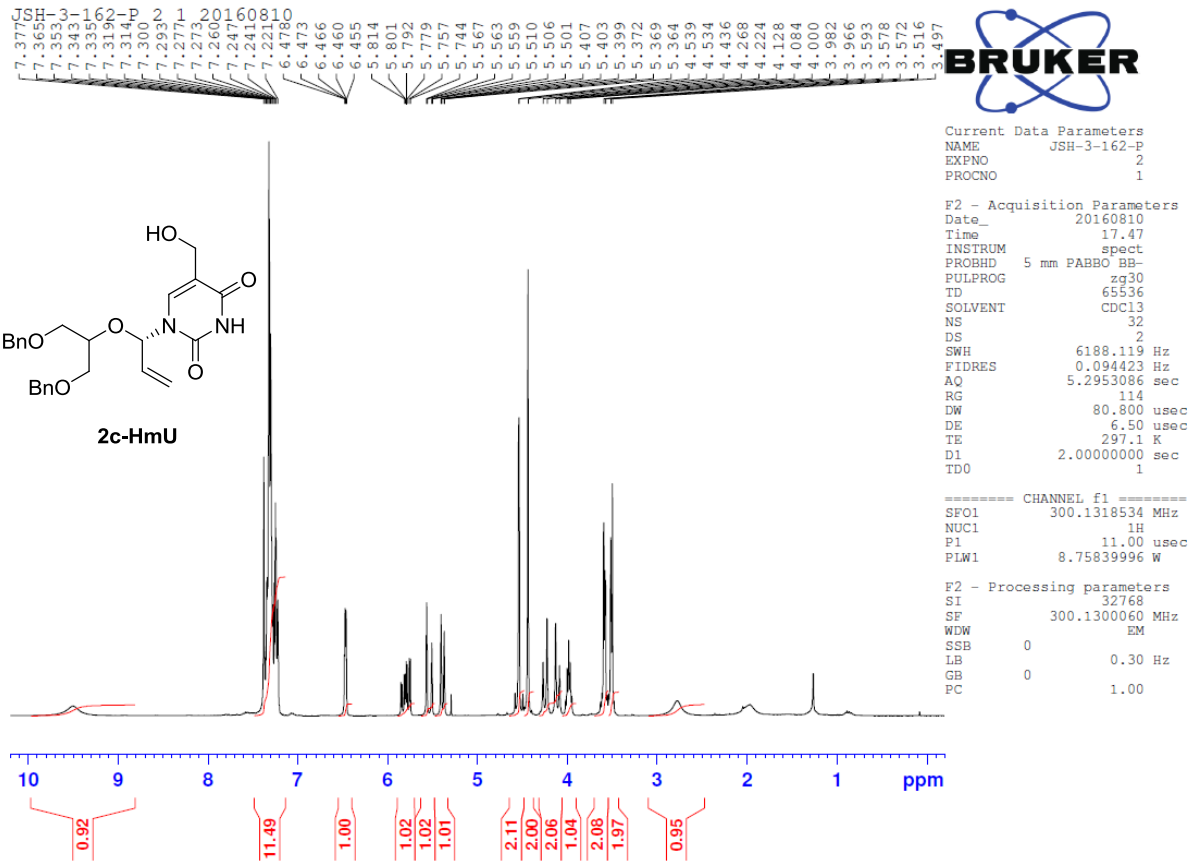
F2 - Processing parameters
SI                 32768
SF            125.8005214 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

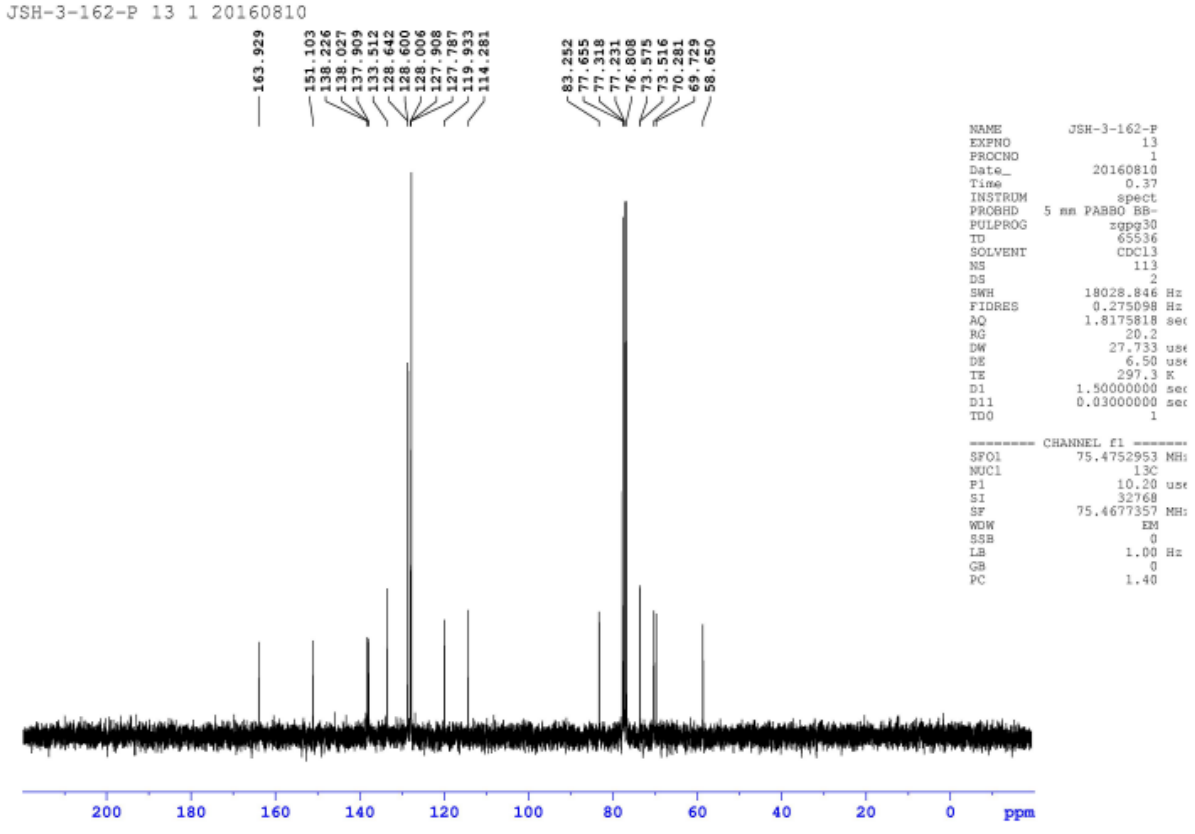

JSH-3-114-P 2 1 20160720
9.968
7.371
7.260
6.342
6.337
6.331
6.325
6.320
5.825
5.813
5.790
5.778
5.768
5.756
5.733
5.721
5.560
5.555
5.551
5.503
5.498
5.494
5.385
5.381
5.377
5.351
5.346
5.342
4.445
4.401
4.388
4.345
3.495
3.484
3.466
3.454
3.442
3.425
3.413
3.303
1.951
1.933
1.910
1.716
1.695
1.506
1.489
1.417
1.383
1.352
1.343
1.312
HO
O
N
NH
O
O
2a-HmU
NAME JSH-3-114-P
EXPNO 2
PROCNO 1
Date_ 20160719
Time 22.49
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 se
RG 114
DW 80.800 us
DE 6.50 us
TE 296.6 K
D1 2.00000000 se
TD0 1
======== CHANNEL f1 ======
SFO1 300.1314684 MH
NUC1 1H
P1 11.00 us
SI 32768
SF 300.1300060 MH
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10
9
8
7
6
5
4
3
2
1
ppm
0.80
0.99
1.00
1.01
1.01
0.99
1.99
1.82
1.08
3.13
1.14
5.93

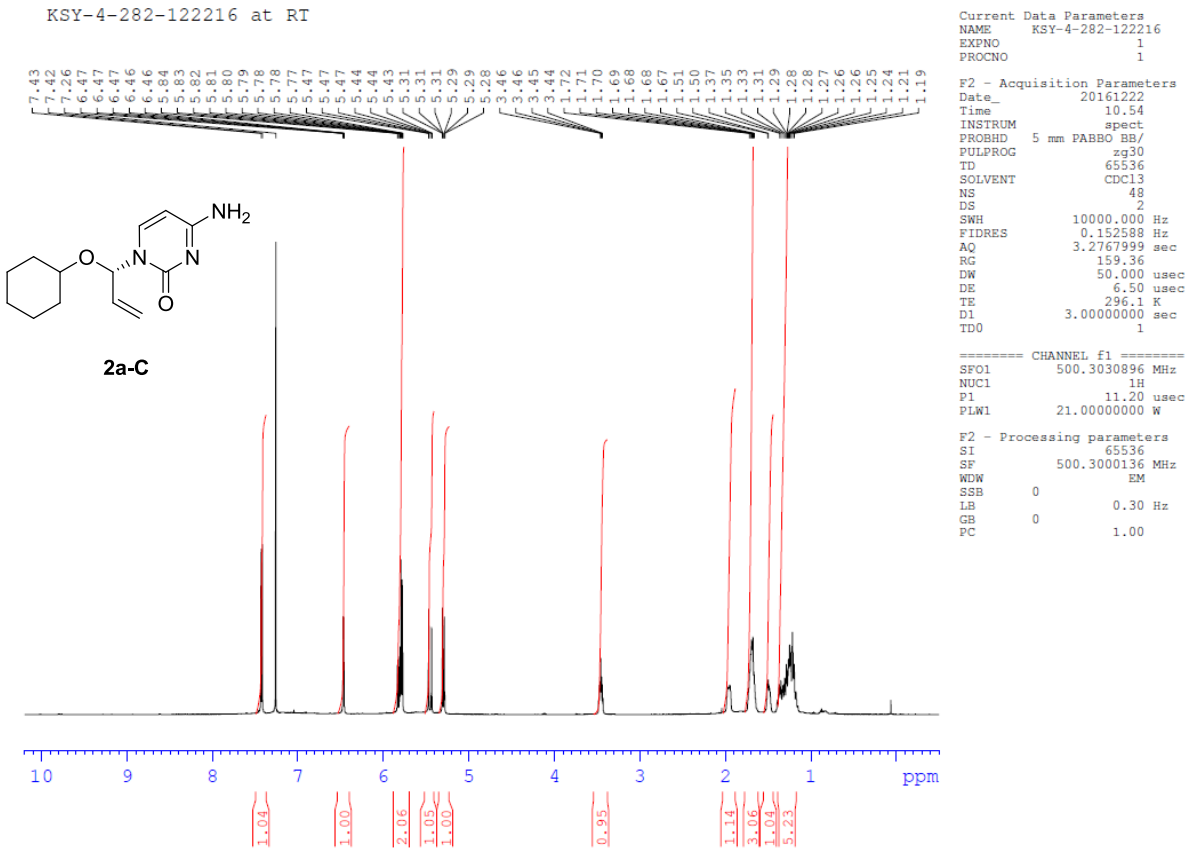

JSH-3-114-P 13 1 20160720
164.258
151.042
137.858
134.022
119.529
114.617
81.254
77.650
77.226
76.802
76.728
58.851
33.004
31.453
25.620
24.013
23.836
NAME JSH-3-114-P
EXPNO 13
PROCNO 1
Date_ 20160719
Time 22.09
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 177
DS 2
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 20.2
DW 27.733 use
DE 6.50 use
TE 296.9 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ======
SFO1 75.4752953 MH
NUC1 13C
P1 10.20 use
SI 32768
SF 75.4677346 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
0
ppm


JSH-3-128-P 2 1 yhr 20160727
9.471
7.314
7.260
6.205
6.199
6.193
5.834
5.822
5.800
5.787
5.777
5.765
5.743
5.730
5.584
5.579
5.575
5.527
5.522
5.518
5.433
5.428
5.424
5.398
5.393
5.389
4.454
4.406
4.359
3.530
3.508
3.486
2.975
1.804
1.616
1.594
1.571
1.548
1.327
1.315
1.303
1.291
1.279
1.247
HO
O
N
NH
O
O
2b-HmU
BRUKER
Current Data Parameters
NAME JSH-3-128-P
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160727
Time 17.19
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953086 sec
RG 203
DW 80.800 usec
DE 6.50 usec
TE 296.7 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 300.1314684 MHz
NUC1 1H
P1 11.00 usec
PLW1 8.75839996 W
F2 - Processing parameters
SI 32768
SF 300.1300060 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10
9
8
7
6
5
4
3
2
1
ppm
0.94
1.09
1.00
1.02
1.02
1.00
2.00
2.02
0.92
2.38
4.31
3.62


JSH-3-128-P 13 1 yhr 20160727
164.119
151.204
137.519
133.353
119.953
114.802
83.661
77.652
77.229
76.805
69.576
58.844
29.102
28.302
22.553
14.161
NAME JSH-3-128-P
EXPNO 13
PROCNO 1
Date_ 20160727
Time 0.06
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 172
DS 2
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 18
DW 27.733 usec
DE 6.50 usec
TE 296.9 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 75.4752953 MHz
NUC1 13C
P1 10.20 usec
SI 32768
SF 75.4677340 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
0
ppm


JSH-3-162-P 2 1 20160810
BRUKER
HO
O
NH
N
O
O
BnO
BnO
2c-HmU
Current Data Parameters
NAME JSH-3-162-P
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160810
Time 17.47
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953086 sec
RG 114
DW 80.800 usec
DE 6.50 usec
TE 297.1 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 300.1318534 MHz
NUC1 1H
P1 11.00 usec
PLW1 8.75839996 W
F2 - Processing parameters
SI 32768
SF 300.1300060 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10 9 8 7 6 5 4 3 2 1 ppm
0.92 11.49 1.00 1.02 1.02 1.01 2.11 2.00 2.06 1.04 2.08 1.97 0.95


JSH-3-162-P 13 1 20160810
163.929
151.103
138.226
138.027
137.909
133.512
128.642
128.600
128.006
127.908
127.787
119.933
114.281
83.252
77.655
77.318
77.231
76.808
73.575
73.516
70.281
69.729
58.650
NAME JSH-3-162-P
EXPNO 13
PROCNO 1
Date_ 20160810
Time 0.37
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 113
DS 2
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 20.2
DW 27.733 usec
DE 6.50 usec
TE 297.3 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 75.4752953 MHz
NUC1 13C
P1 10.20 usec
SI 32768
SF 75.4677357 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 180 160 140 120 100 80 60 40 20 0 ppm

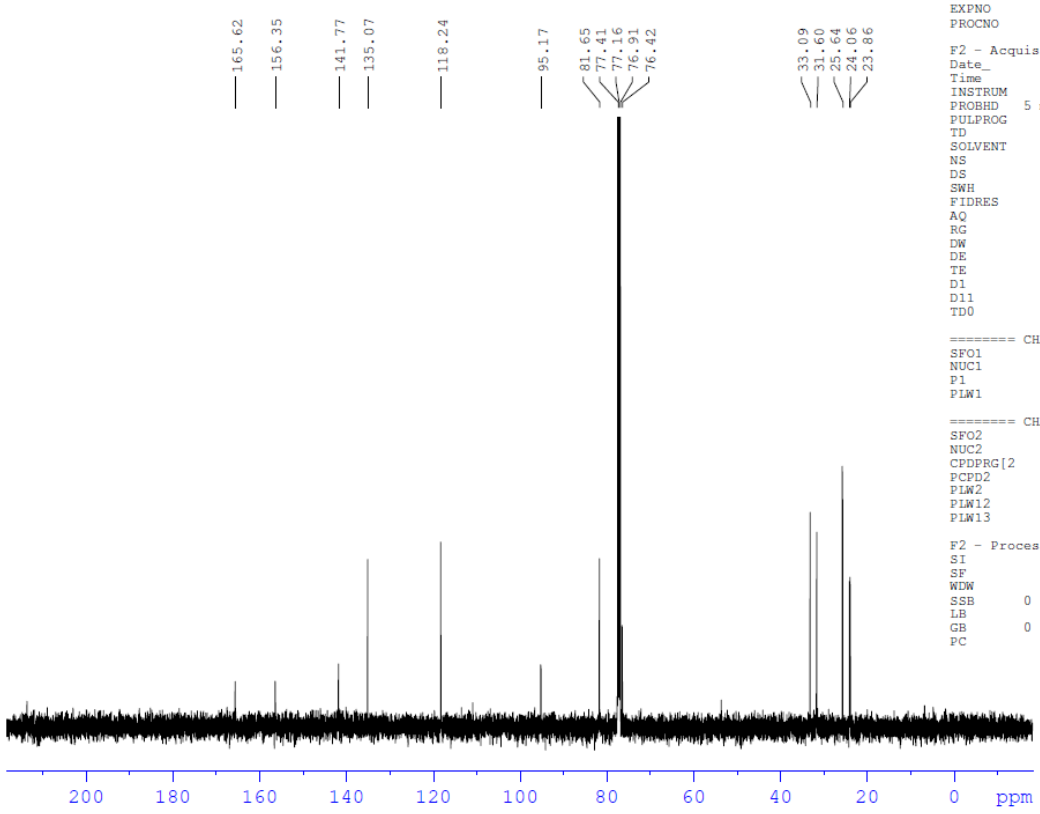



```
Current Data Parameters
NAME      KSY-4-282-122216
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_            20161222
Time                10.54
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    48
DS                     2
SWH            10000.000 Hz
FIDRES             0.152588 Hz
AQ               3.2767999 sec
RG                 159.36
DW                 50.000 usec
DE                  6.50 usec
TE                 296.1 K
D1              3.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1           500.3030896 MHz
NUC1                   1H
P1                  11.20 usec
PLW1           21.00000000 W

F2 - Processing parameters
SI                 65536
SF             500.3000136 MHz
WDW                   EM
SSB          0
LB                  0.30 Hz
GB           0
PC                  1.00
```




```
Current Data Parameters
NAME          KSY-3-282-C
EXPNO                    1
PROCNO                   1

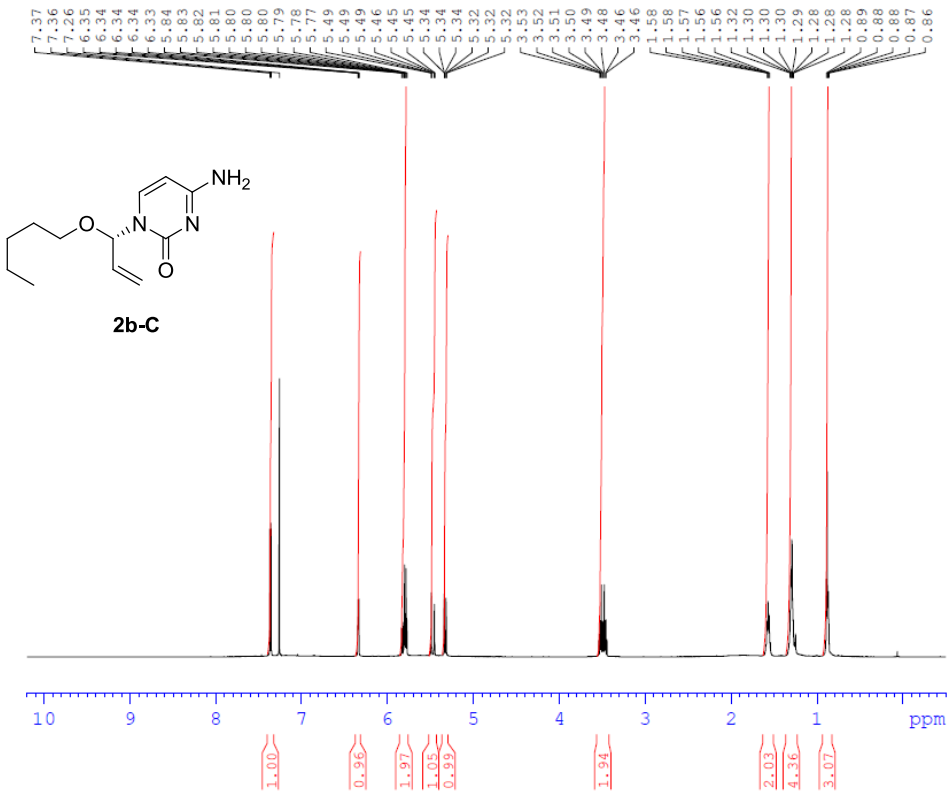
F2 - Acquisition Parameters
Date_            20161220
Time                21.09
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   352
DS                     4
SWH            29761.904 Hz
FIDRES             0.454131 Hz
AQ               1.1010048 sec
RG                  2050
DW                 16.800 usec
DE                  6.50 usec
TE                 296.2 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1           125.8131145 MHz
NUC1                   13C
P1                  10.00 usec
PLW1           87.00000000 W

======== CHANNEL f2 ========
SFO2           500.3020012 MHz
NUC2                   1H
CPDPRG[2            waltz16
PCPD2               80.00 usec
PLW2           21.50000000 W
PLW12           0.42140001 W
PLW13           0.26969999 W

F2 - Processing parameters
SI                 32768
SF             125.8005199 MHz
WDW                   EM
SSB          0
LB                  1.00 Hz
GB           0
PC                  1.40
```

KSY-4-027-122216 at RT



2b-C

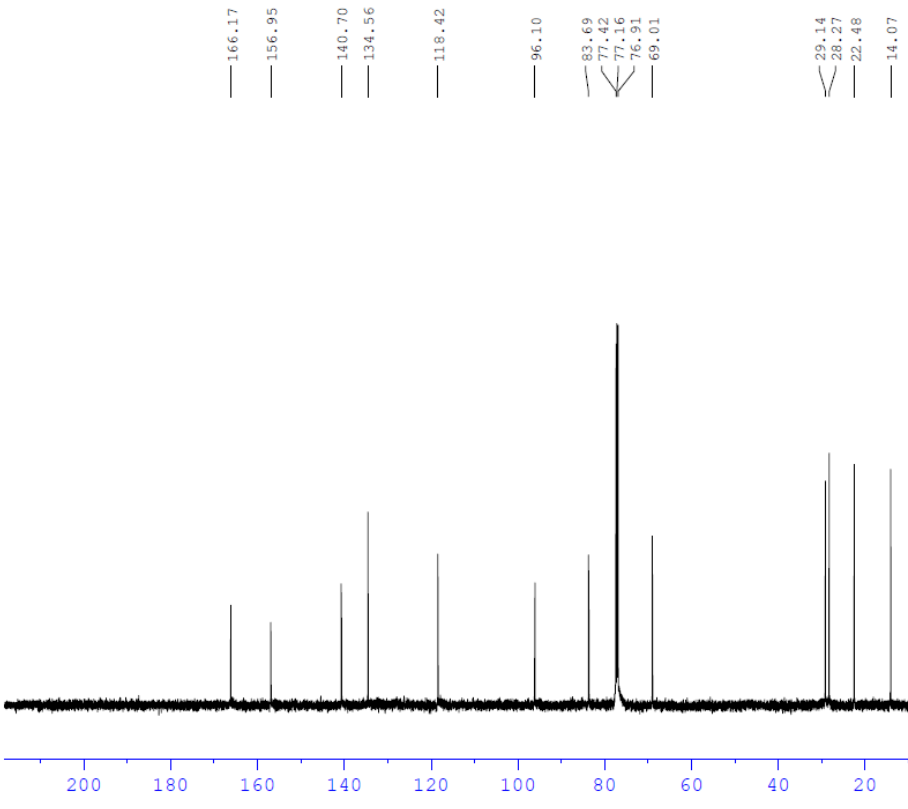
```
Current Data Parameters
NAME          KSY-4-027-122216
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_               20161222
Time                   13.33
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       30
DS                        2
SWH               10000.000 Hz
FIDRES                0.152588 Hz
AQ                 3.2767999 sec
RG                     179.08
DW                     50.000 usec
DE                      6.50 usec
TE                     297.6 K
D1                 4.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1              500.3030896 MHz
NUC1                       1H
P1                      11.20 usec
PLW1              21.00000000 W

F2 - Processing parameters
SI                        65536
SF                500.3000133 MHz
WDW                         EM
SSB                  0
LB                      0.30 Hz
GB                   0
PC                      1.00
```

KSY-4-027-C 1 1 yhr 20161221




```
Current Data Parameters
NAME          KSY-4-027-C
EXPNO                       1
PROCNO                      1

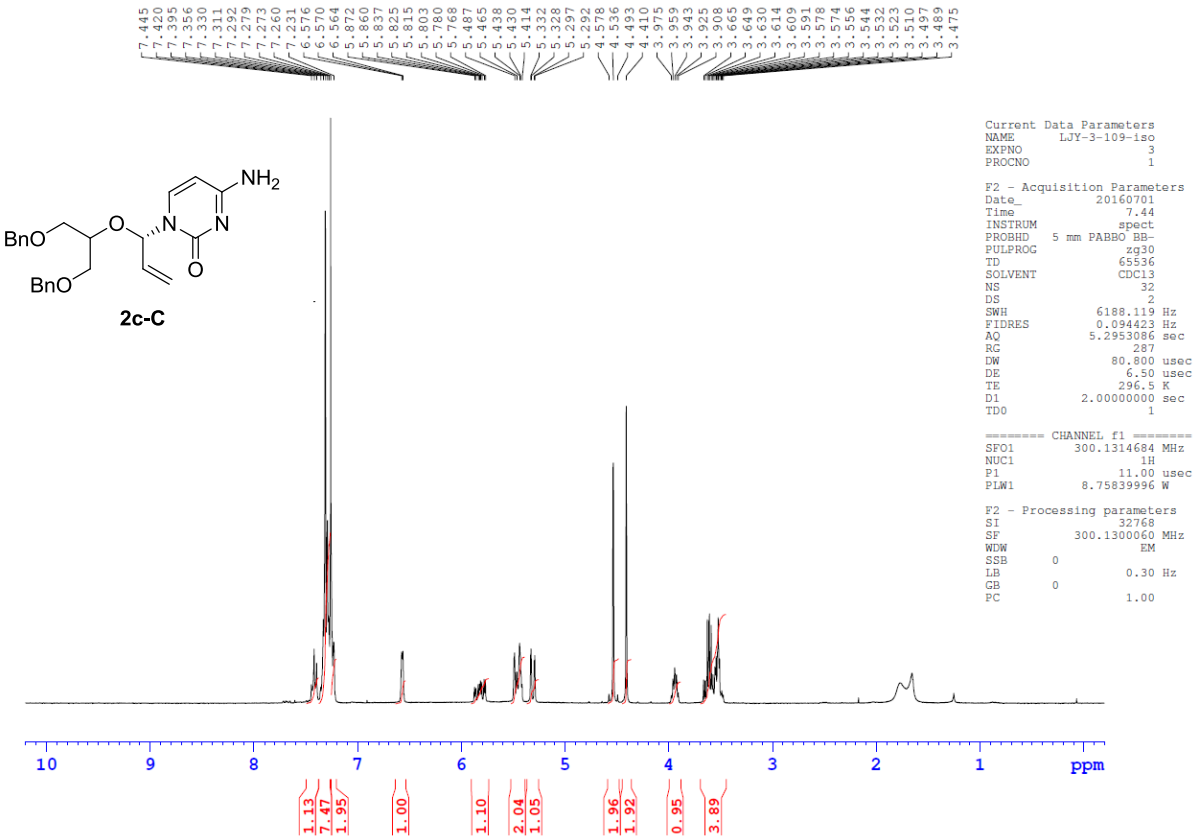
F2 - Acquisition Parameters
Date_               20161221
Time                   19.10
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      133
DS                        4
SWH               29761.904 Hz
FIDRES                0.454131 Hz
AQ                 1.1010048 sec
RG                     2050
DW                     16.800 usec
DE                      6.50 usec
TE                     296.4 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1              125.8131145 MHz
NUC1                       13C
P1                      10.00 usec
PLW1              87.00000000 W

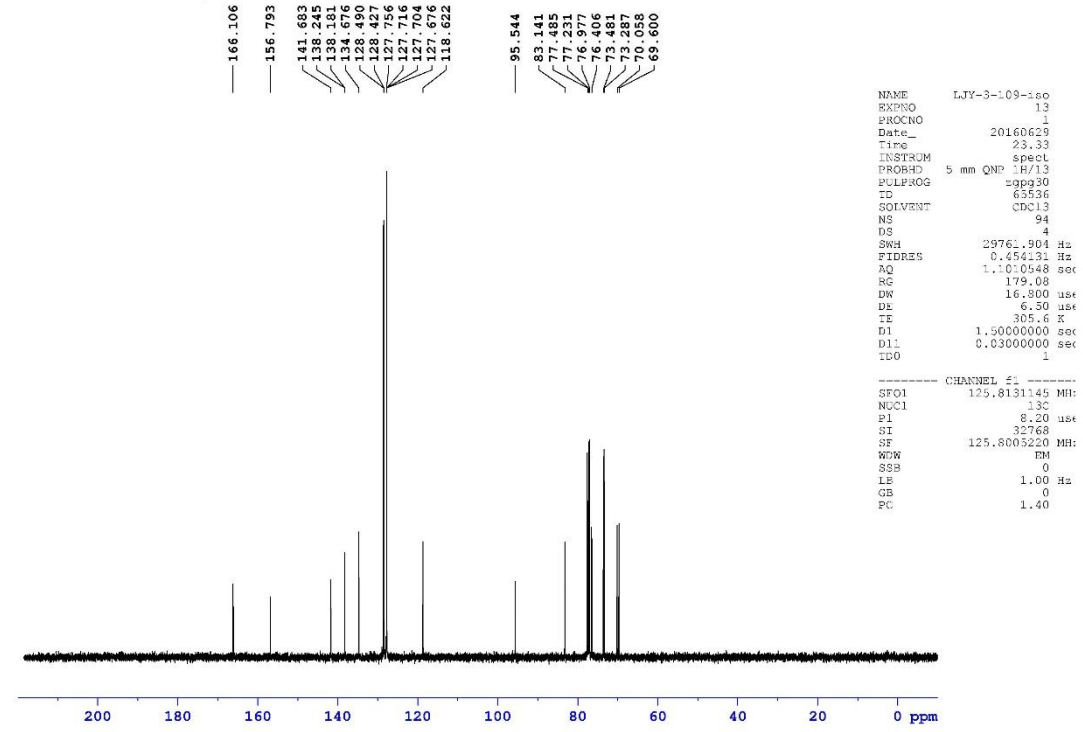
======== CHANNEL f2 ========
SFO2              500.3020012 MHz
NUC2                       1H
CPDPRG[2              waltz16
PCPD2                   80.00 usec
PLW2              21.50000000 W
PLW12              0.42140001 W
PLW13              0.26969999 W

F2 - Processing parameters
SI                        32768
SF                125.8005245 MHz
WDW                         EM
SSB                  0
LB                      1.00 Hz
GB                   0
PC                      1.40
```

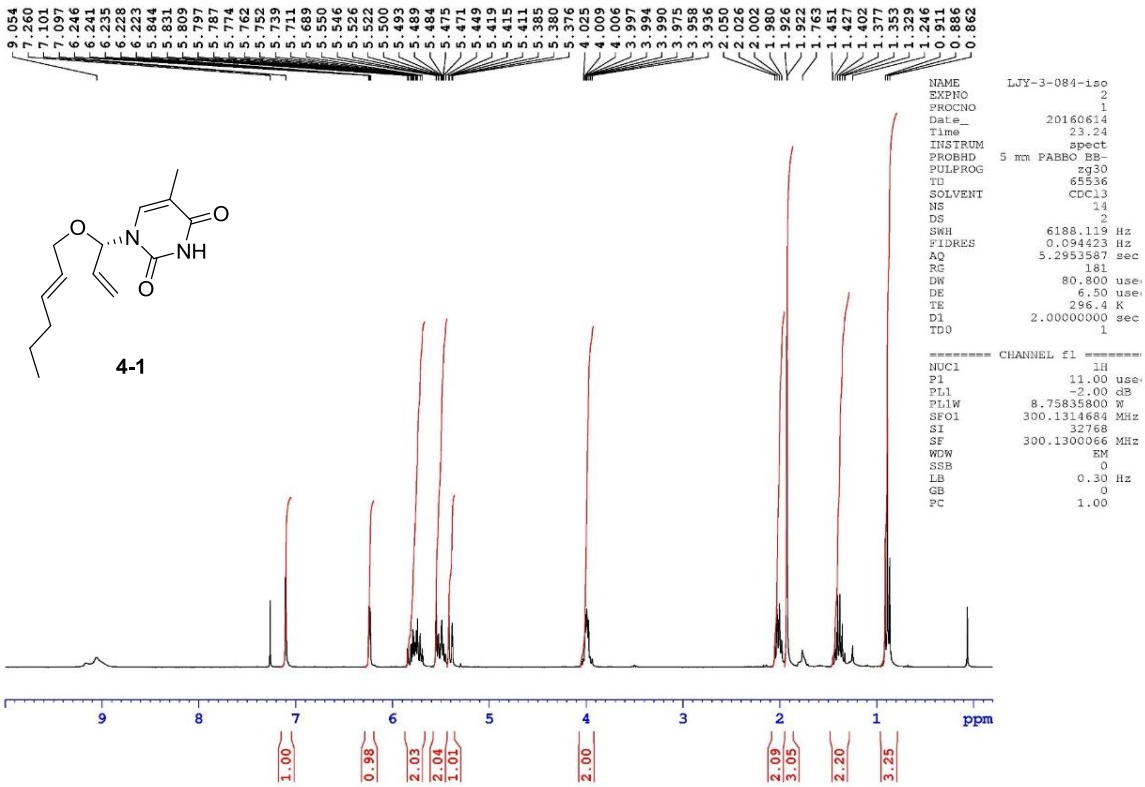
LJY-3-109-iso 3 1 20160701



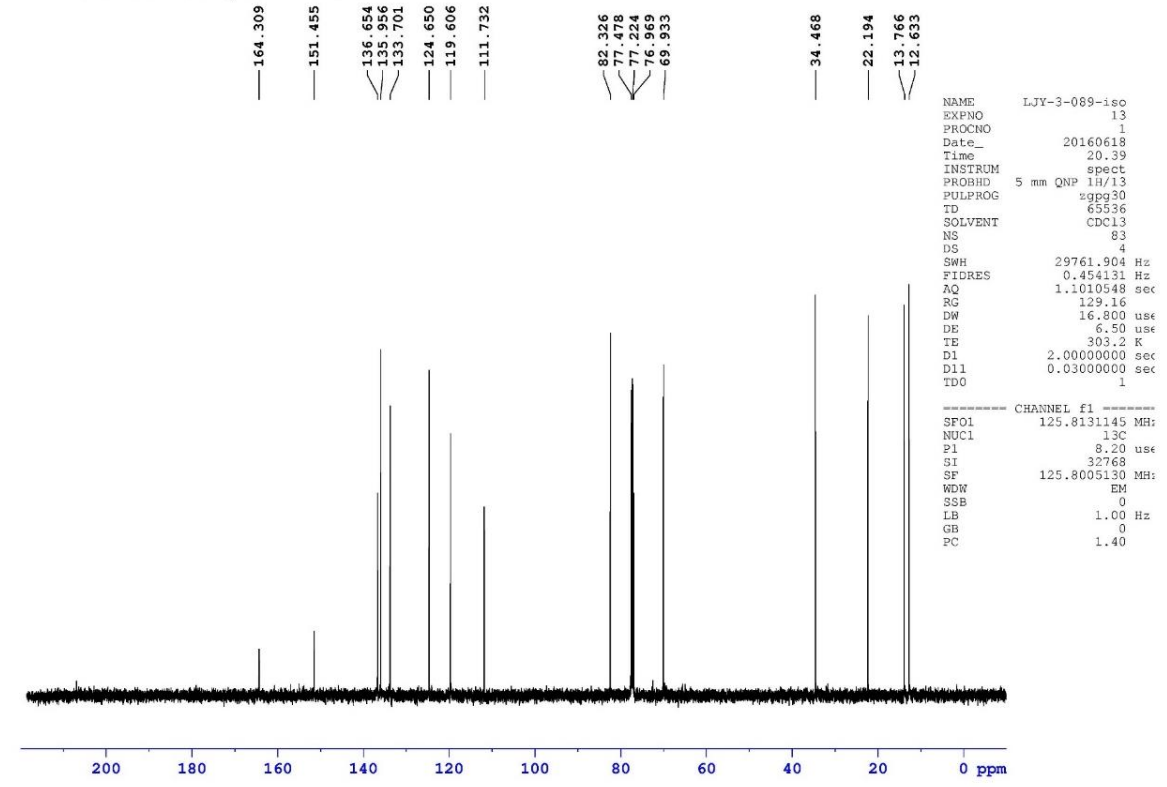
LJY-3-109-iso 1 1 yhr 20160623



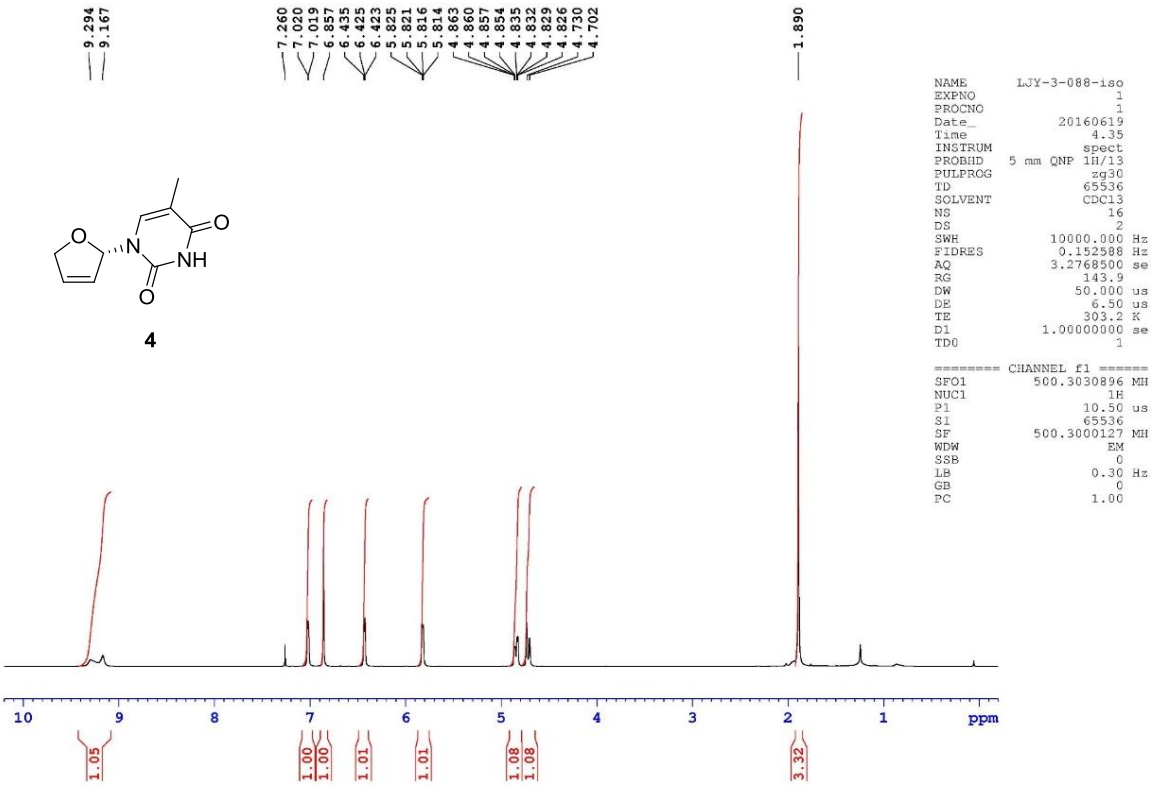
LJY-3-084-iso 2 1 yhr 20160615



LJY-3-089-iso 13 1 yhr 20160619

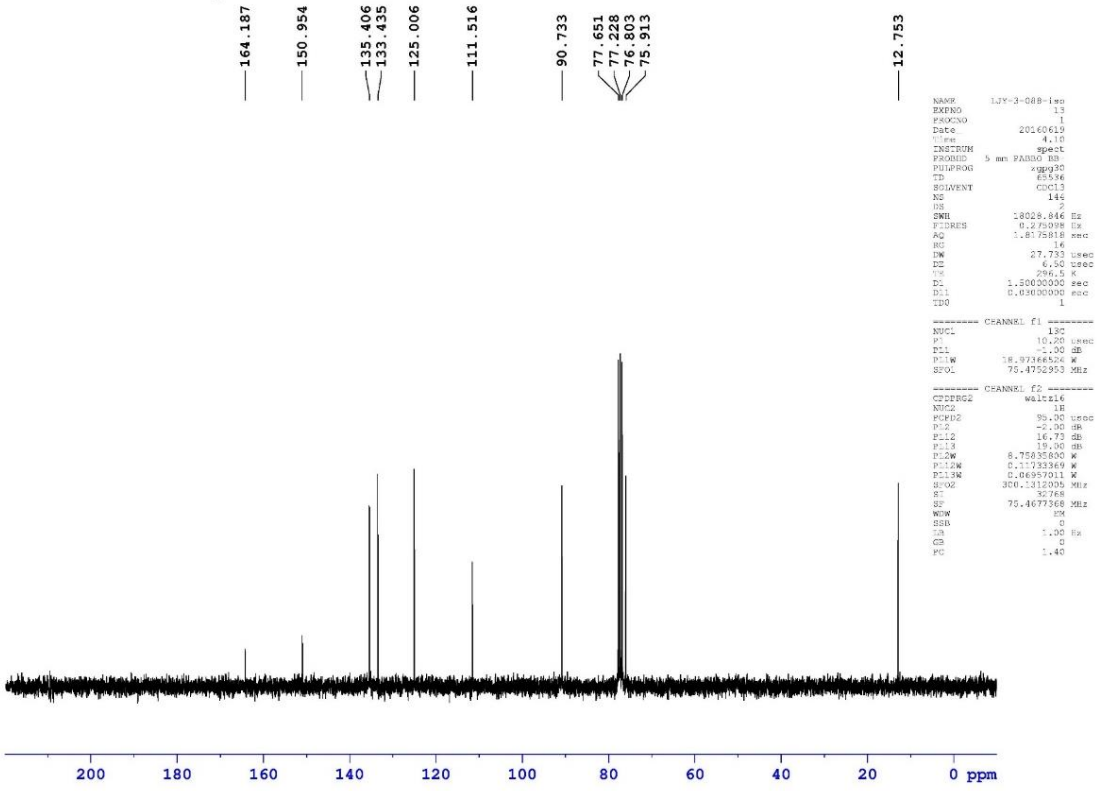


LJY-3-088-iso 1 1 yhr 20160619

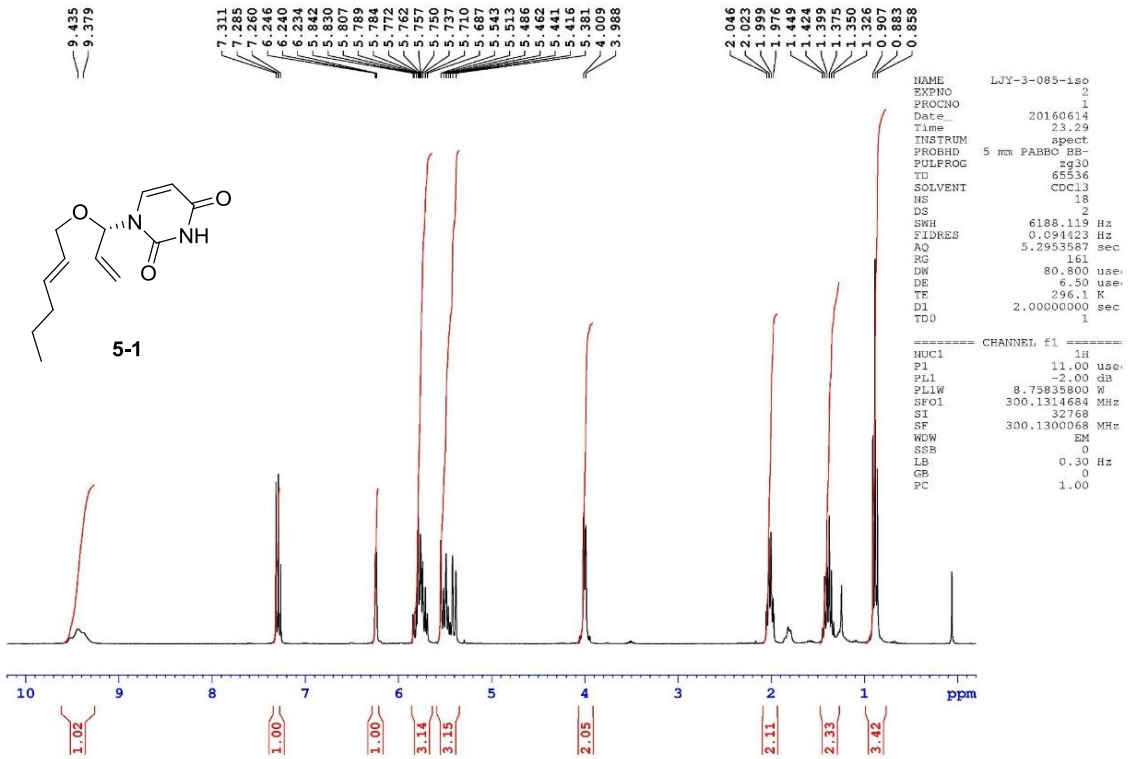


4

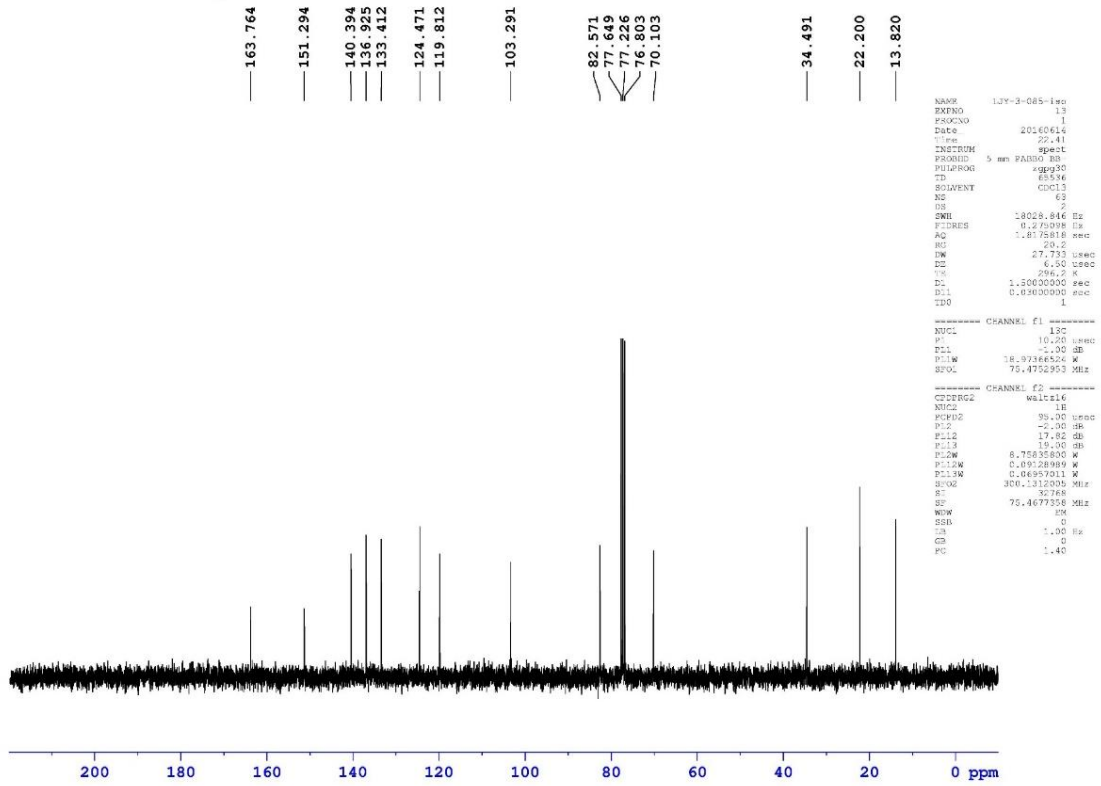
LJY-3-088-iso 13 1 yhr 20160619



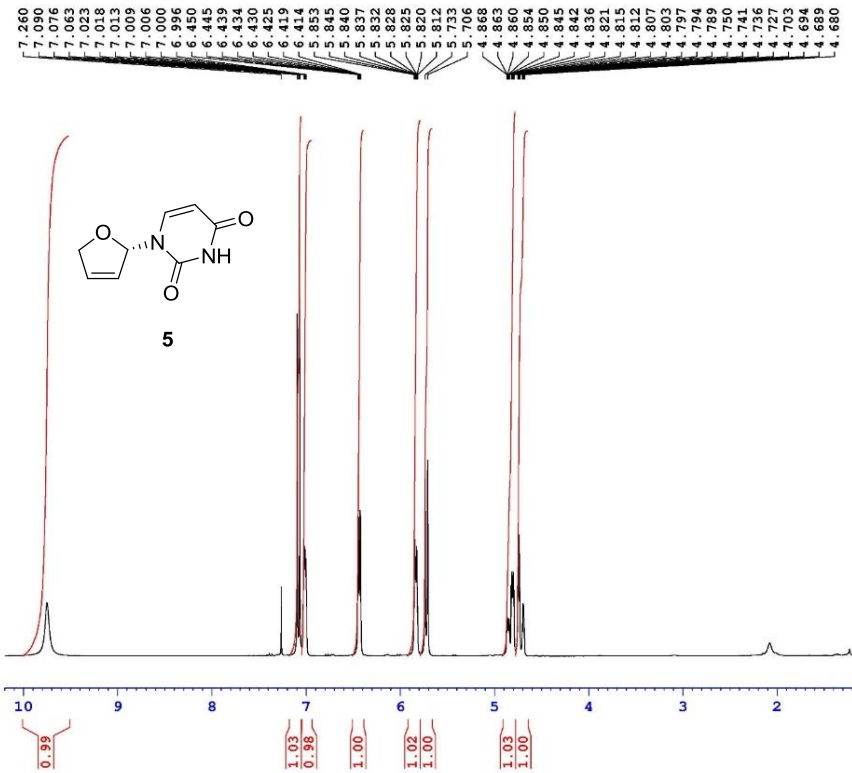
LJY-3-085-iso 2 1 yhr 20160615



LJY-3-085-iso 13 1 yhr 20160615

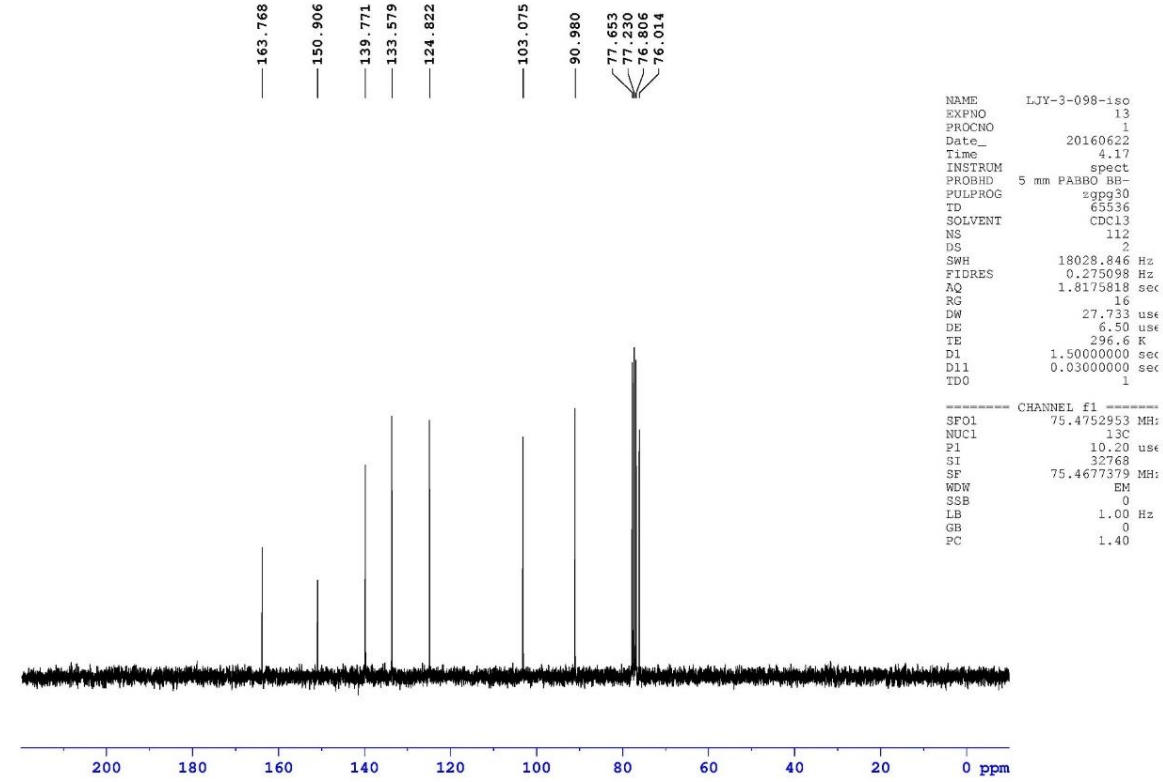


LJY-3-098-iso 2 1 20160622

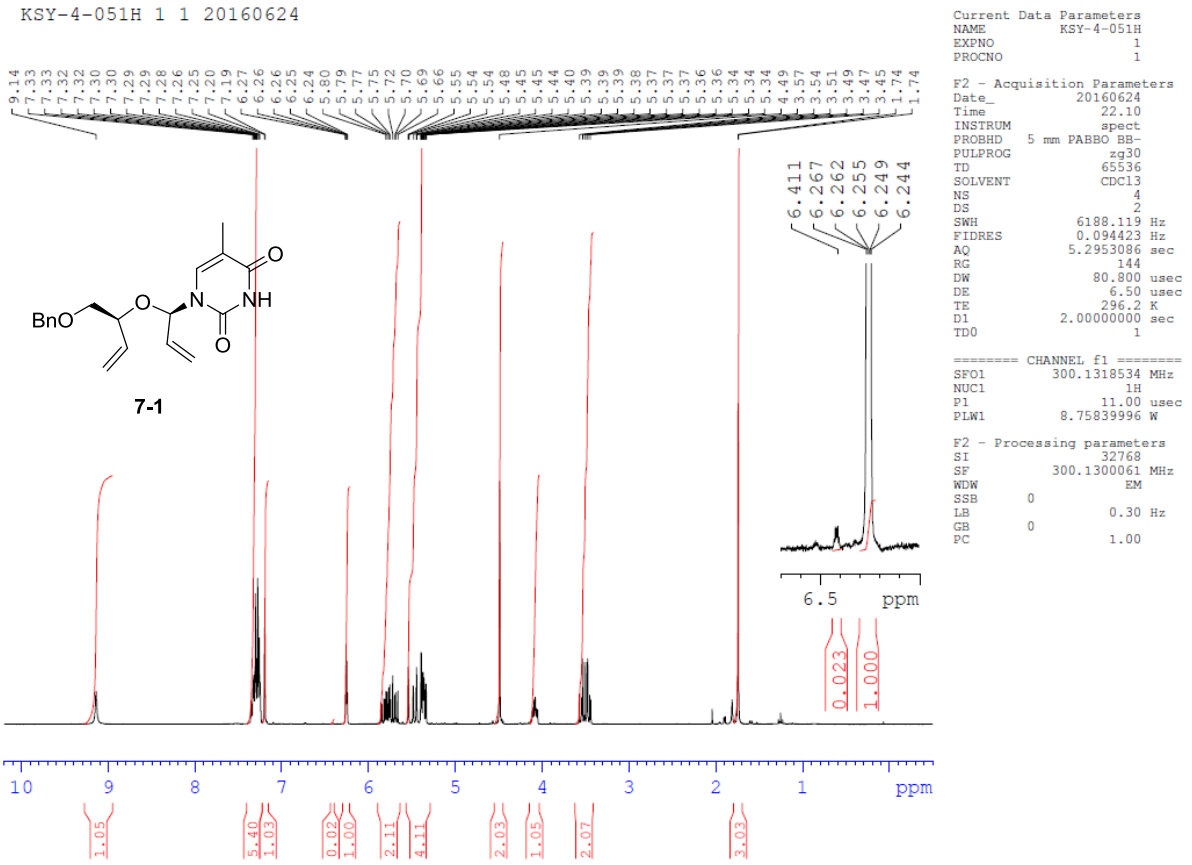


NAME	LJY-3-098-iso
EXPNO	2
PROCNO	1
Date_	20160622
Time	4.25
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	28
DS	2
SWH	6188.119 Hz
FIDRES	0.094423 Hz
AQ	5.2953587 se
RG	161
DW	80.800 us
DE	6.50 us
TE	296.2 K
D1	2.00000000 se
TD0	1
========	CHANNEL f1 ======
SFO1	300.1314684 MH
NUC1	1H
P1	11.00 us
SI	32768
SF	300.1300058 MH
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

LJY-3-098-iso 13 1 20160622



NAME	LJY-3-098-iso
EXPNO	13
PROCNO	1
Date_	20160622
Time	4.17
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	112
DS	2
SWH	18028.846 Hz
FIDRES	0.275098 Hz
AQ	1.8175818 sec
RG	16
DW	27.733 use
DE	6.50 use
TE	296.6 K
D1	1.50000000 sec
D11	0.03000000 sec
TD0	1
========	CHANNEL f1 ======
SFO1	75.4752953 MH:
NUC1	13C
P1	10.20 use
SI	32768
SF	75.4677379 MH:
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

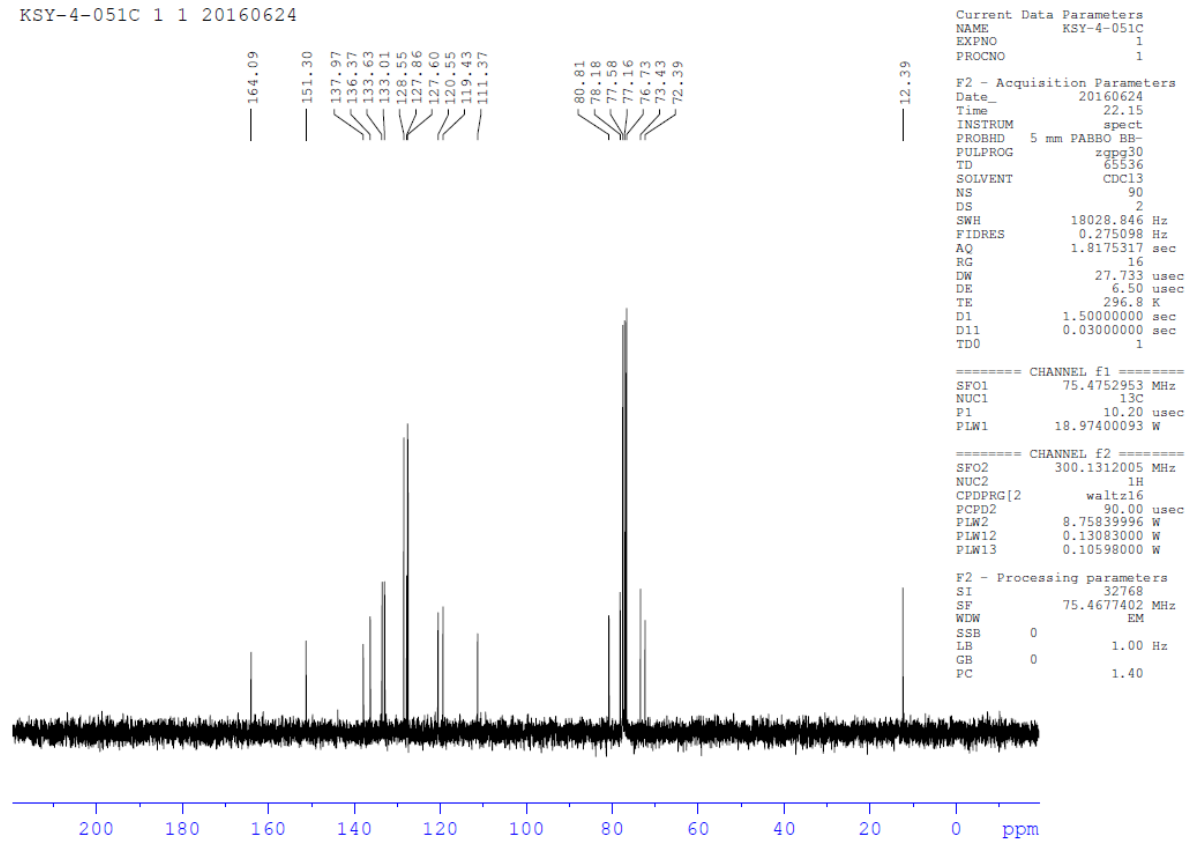



```
Current Data Parameters
NAME                 KSY-4-051H
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_               20160624
Time                   22.10
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                         4
DS                         2
SWH                 6188.119 Hz
FIDRES              0.094423 Hz
AQ                  5.2953086 sec
RG                       144
DW                    80.800 usec
DE                     6.50 usec
TE                    296.2 K
D1                  2.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             300.1318534 MHz
NUC1                       1H
P1                     11.00 usec
PLW1              8.75839996 W

F2 - Processing parameters
SI                       32768
SF                  300.1300061 MHz
WDW                         EM
SSB                  0
LB                        0.30 Hz
GB                   0
PC                        1.00
```



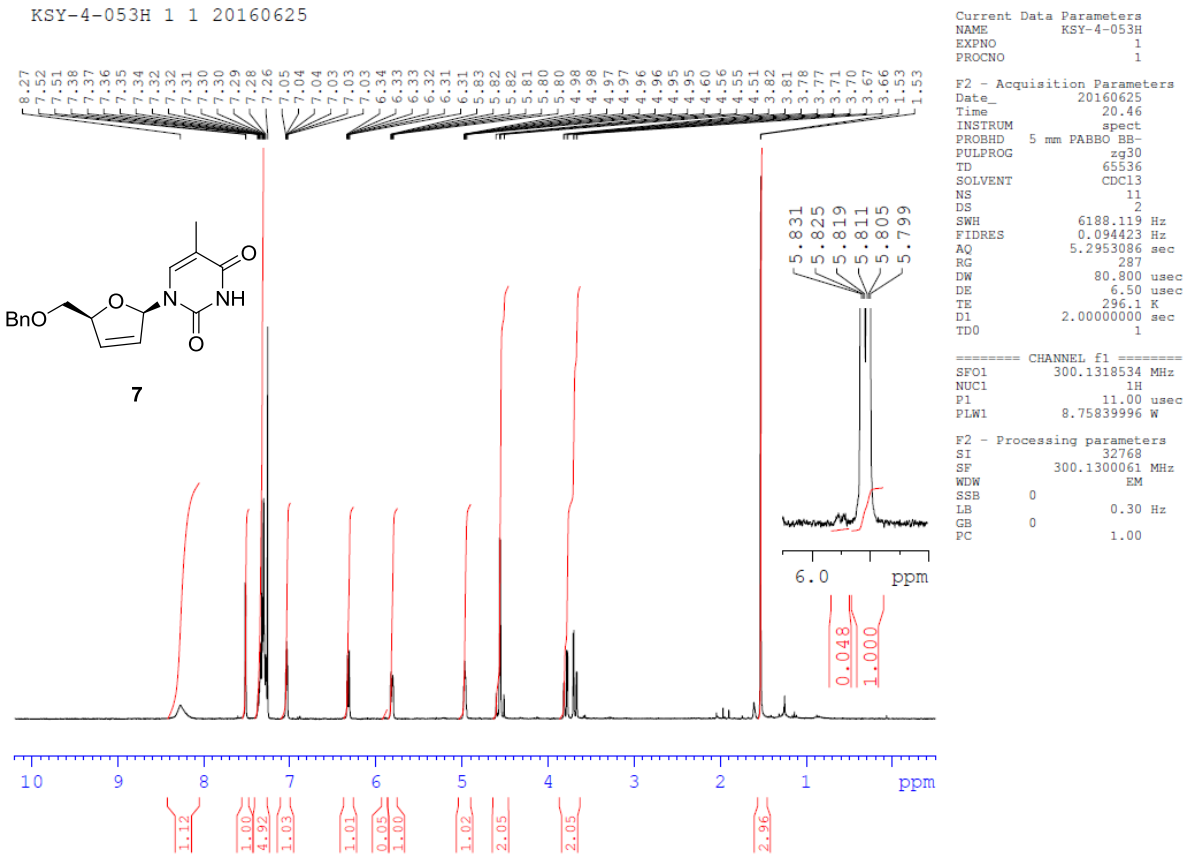

```
Current Data Parameters
NAME                 KSY-4-051C
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_               20160624
Time                   22.15
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                     65536
SOLVENT                CDCl3
NS                        90
DS                         2
SWH                18028.846 Hz
FIDRES              0.275098 Hz
AQ                  1.8175317 sec
RG                        16
DW                    27.733 usec
DE                     6.50 usec
TE                    296.8 K
D1                  1.50000000 sec
D11                 0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             75.4752953 MHz
NUC1                       13C
P1                     10.20 usec
PLW1             18.97400093 W

======== CHANNEL f2 ========
SFO2            300.1312005 MHz
NUC2                       1H
CPDPRG[2              waltz16
PCPD2                  90.00 usec
PLW2              8.75839996 W
PLW12             0.13083000 W
PLW13             0.10598000 W

F2 - Processing parameters
SI                       32768
SF                  75.4677402 MHz
WDW                         EM
SSB                  0
LB                        1.00 Hz
GB                   0
PC                        1.40
```

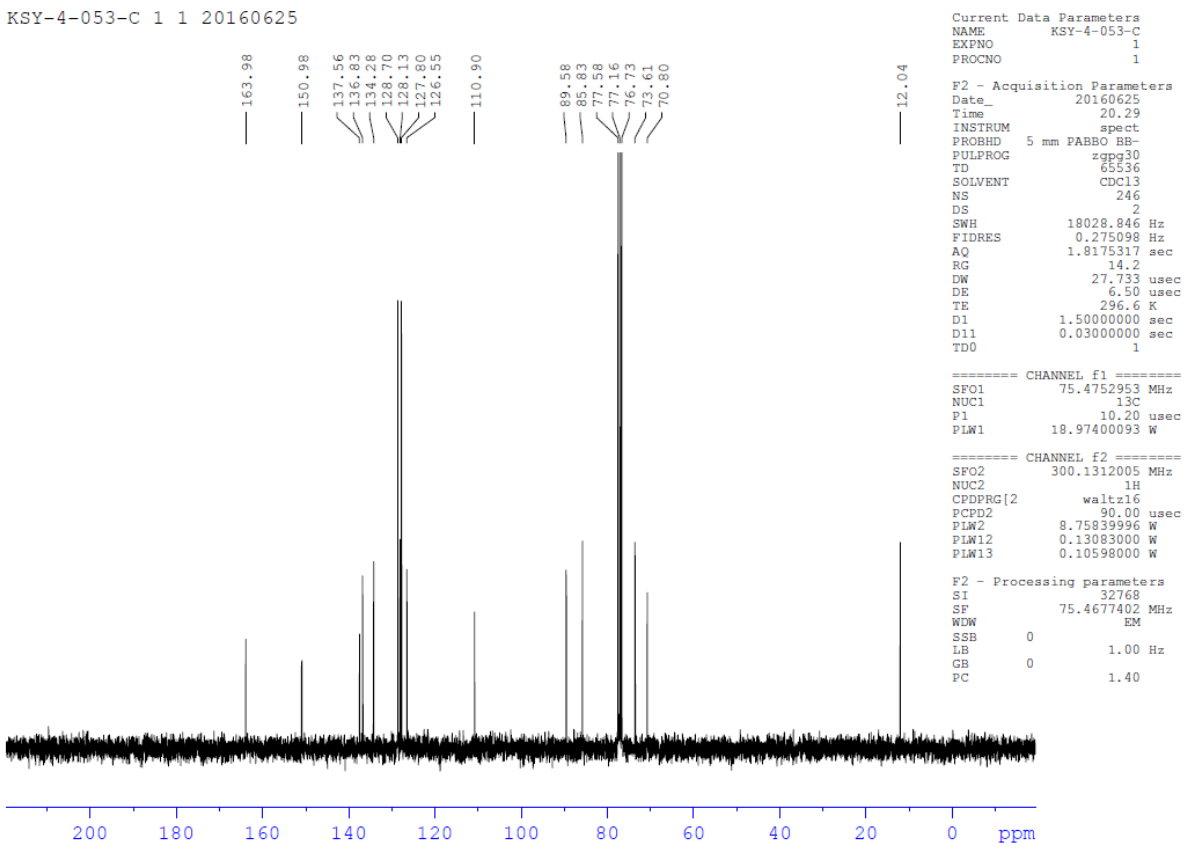



```
Current Data Parameters
NAME                 KSY-4-053H
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_               20160625
Time                   20.46
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        11
DS                         2
SWH                6188.119 Hz
FIDRES             0.094423 Hz
AQ                 5.2953086 sec
RG                       287
DW                    80.800 usec
DE                     6.50 usec
TE                    296.1 K
D1                 2.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1            300.1318534 MHz
NUC1                      1H
P1                     11.00 usec
PLW1             8.75839996 W

F2 - Processing parameters
SI                     32768
SF                300.1300061 MHz
WDW                       EM
SSB                    0
LB                     0.30 Hz
GB                     0
PC                     1.00
```



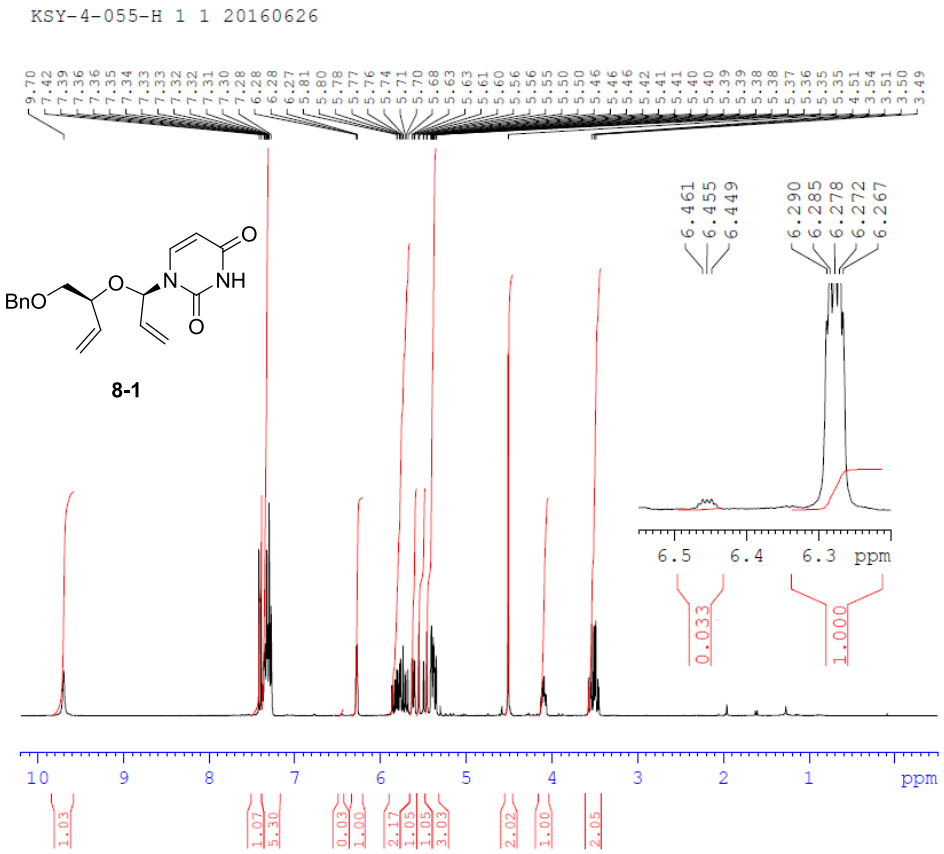

```
Current Data Parameters
NAME               KSY-4-053-C
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_               20160625
Time                   20.29
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                     65536
SOLVENT                CDCl3
NS                       246
DS                         2
SWH               18028.846 Hz
FIDRES             0.275098 Hz
AQ                 1.8175317 sec
RG                      14.2
DW                    27.733 usec
DE                     6.50 usec
TE                    296.6 K
D1                 1.50000000 sec
D11                0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1            75.4752953 MHz
NUC1                      13C
P1                     10.20 usec
PLW1            18.97400093 W

======== CHANNEL f2 ========
SFO2           300.1312005 MHz
NUC2                      1H
CPDPRG[2             waltz16
PCPD2                 90.00 usec
PLW2             8.75839996 W
PLW12            0.13083000 W
PLW13            0.10598000 W

F2 - Processing parameters
SI                     32768
SF                75.4677402 MHz
WDW                       EM
SSB                    0
LB                     1.00 Hz
GB                     0
PC                     1.40
```

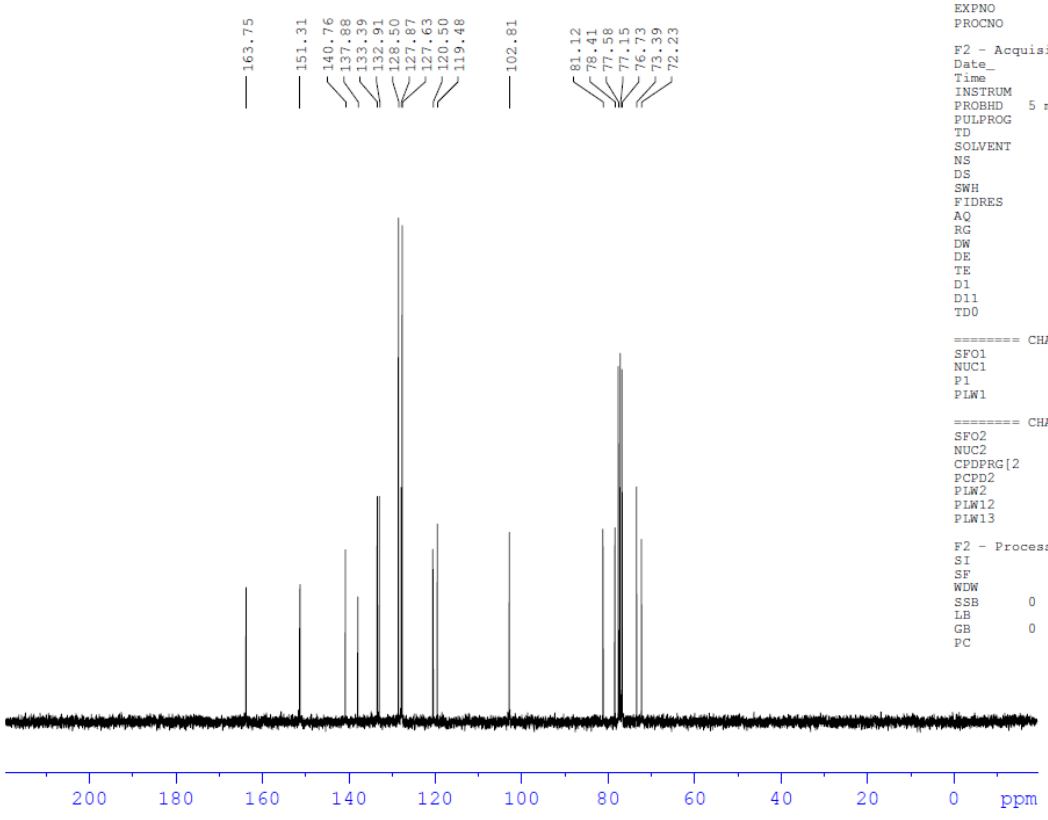


Current Data Parameters
NAME KSY-4-055-H
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160627
Time 5.33
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 4
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953086 sec
RG 101
DW 80.800 usec
DE 6.50 usec
TE 296.8 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 300.1318534 MHz
NUC1 1H
P1 11.00 usec
PLW1 8.75839996 W

F2 - Processing parameters
SI 32768
SF 300.1300001 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME KSY-4-055-C
EXPNO 1
PROCNO 1

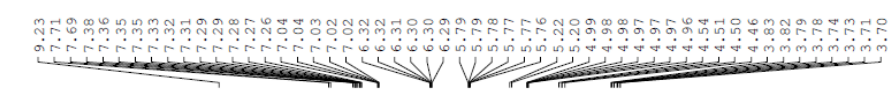
F2 - Acquisition Parameters
Date_ 20160627
Time 20.09
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 249
DS 2
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175317 sec
RG 16
DW 27.733 usec
DE 6.50 usec
TE 296.8 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1

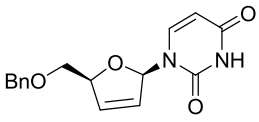
======== CHANNEL f1 ========
SFO1 75.4752953 MHz
NUC1 13C
P1 10.20 usec
PLW1 18.97400093 W

======== CHANNEL f2 ========
SFO2 300.1312005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 8.75839996 W
PLW12 0.13083000 W
PLW13 0.10598000 W

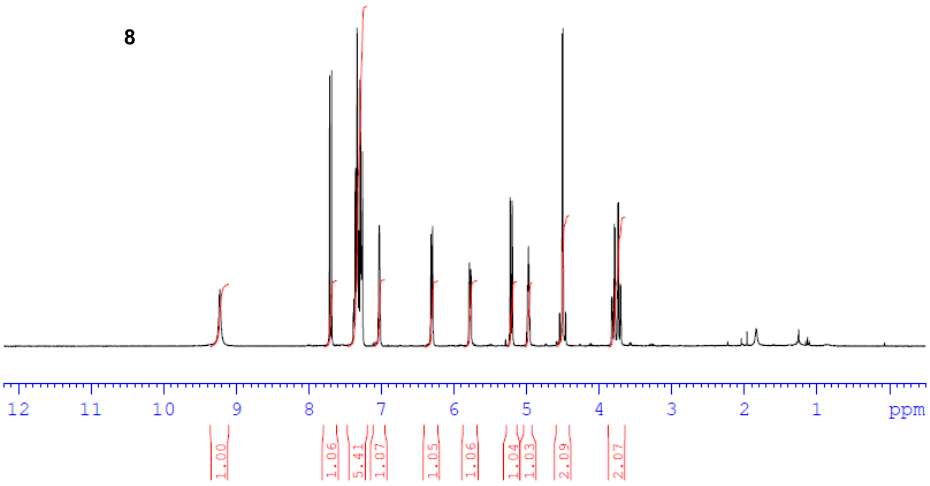
F2 - Processing parameters
SI 32768
SF 75.4677435 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

KSY-4-061 1 1 20160701





8



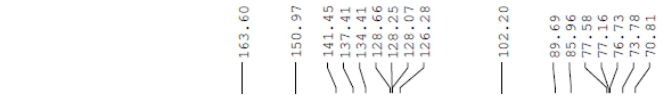

```
Current Data Parameters
NAME            KSY-4-061
EXPNO                   1
PROCNO                  1

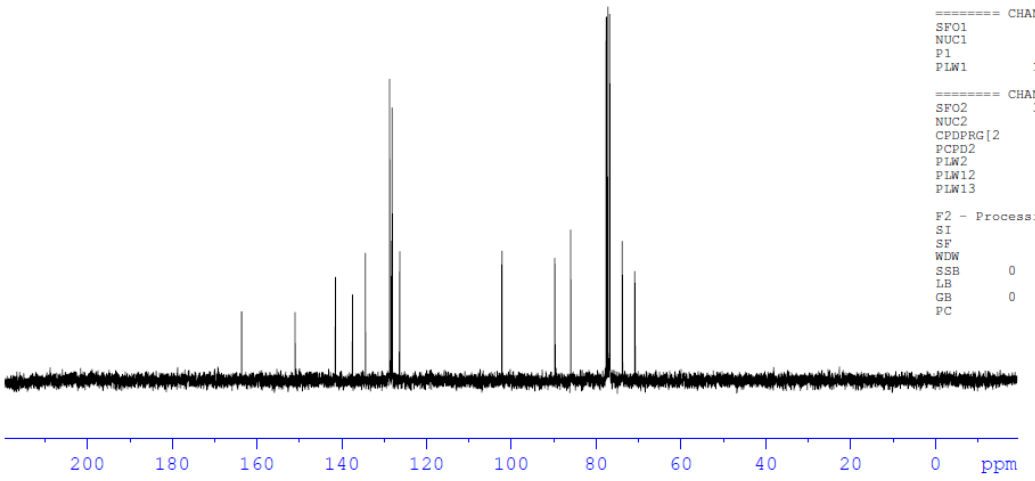
F2 - Acquisition Parameters
Date_            20160701
Time                21.17
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      4
DS                      2
SWH              6188.119 Hz
FIDRES           0.094423 Hz
AQ               5.2953086 sec
RG                    161
DW                 80.800 usec
DE                  6.50 usec
TE                 296.5 K
D1              2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          300.1314684 MHz
NUC1                  1H
P1                 11.00 usec
PLW1           8.75839996 W

F2 - Processing parameters
SI                  32768
SF            300.1300063 MHz
WDW                    EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

KSY-4-061-C 1 1 20160701





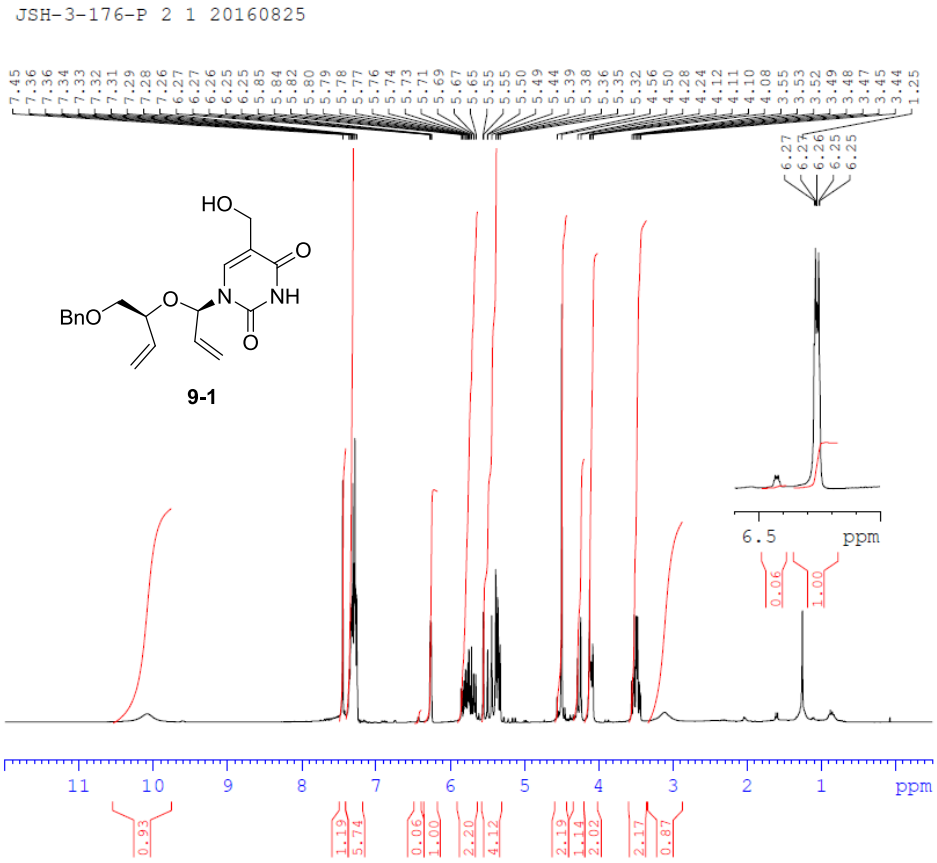

```
Current Data Parameters
NAME          KSY-4-061-C
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160701
Time                21.27
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    151
DS                      2
SWH             18028.846 Hz
FIDRES           0.275098 Hz
AQ               1.8175317 sec
RG                     18
DW                 27.733 usec
DE                  6.50 usec
TE                 297.2 K
D1              1.50000000 sec
D11             0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          75.4752953 MHz
NUC1                  13C
P1                 10.20 usec
PLW1          18.97400093 W

======== CHANNEL f2 ========
SFO2          300.1312005 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              90.00 usec
PLW2           8.75839996 W
PLW12          0.13083000 W
PLW13          0.10598000 W

F2 - Processing parameters
SI                  32768
SF            75.4677419 MHz
WDW                    EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

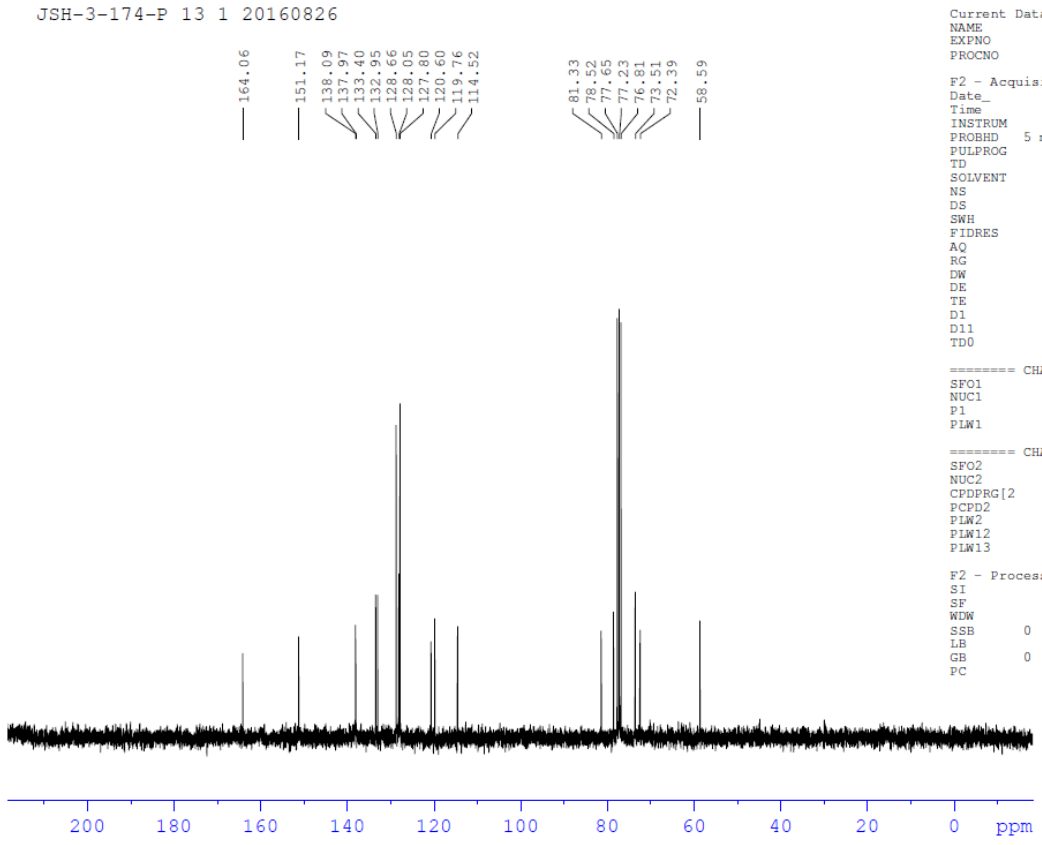



```
Current Data Parameters
NAME          JSH-3-176-P
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_              20160825
Time                 16.27
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      32
DS                       2
SWH               6188.119 Hz
FIDRES            0.094423 Hz
AQ                5.2953086 sec
RG                    40.3
DW                  80.800 usec
DE                   6.50 usec
TE                  295.7 K
D1              2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          300.1314684 MHz
NUC1                    1H
P1                  11.00 usec
PLW1           8.75839996 W

F2 - Processing parameters
SI                   32768
SF          300.1300060 MHz
WDW                     EM
SSB                  0
LB                   0.30 Hz
GB                   0
PC                   1.00
```



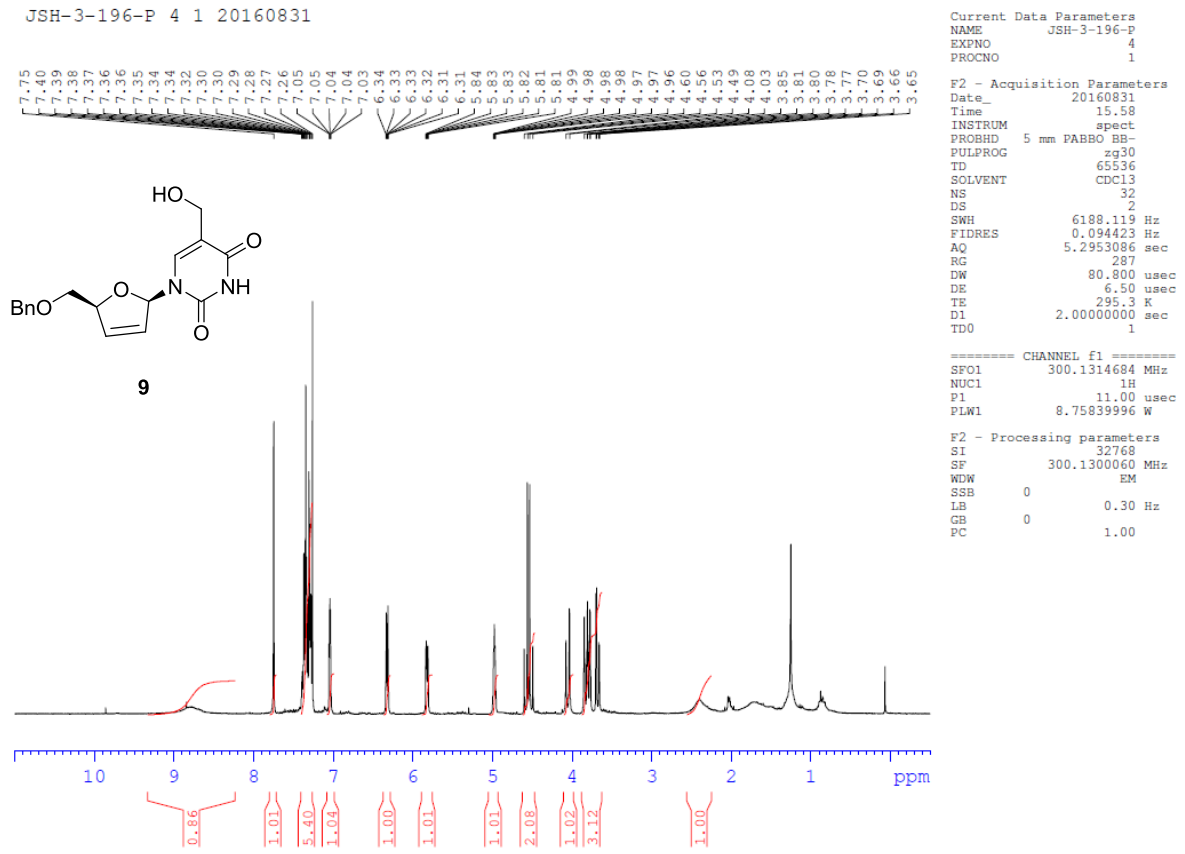

```
Current Data Parameters
NAME          JSH-3-174-P
EXPNO                  13
PROCNO                  1

F2 - Acquisition Parameters
Date_              20160826
Time                 16.19
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG           zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     102
DS                       2
SWH              18028.846 Hz
FIDRES            0.275098 Hz
AQ                1.8175317 sec
RG                    20.2
DW                  27.733 usec
DE                   6.50 usec
TE                  296.7 K
D1              1.50000000 sec
D11             0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          75.4752953 MHz
NUC1                   13C
P1                  10.20 usec
PLW1          18.97400093 W

======== CHANNEL f2 ========
SFO2          300.1312005 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2               90.00 usec
PLW2           8.75839996 W
PLW12          0.13083000 W
PLW13          0.10598000 W

F2 - Processing parameters
SI                   32768
SF           75.4677357 MHz
WDW                     EM
SSB                  0
LB                   1.00 Hz
GB                   0
PC                   1.40
```

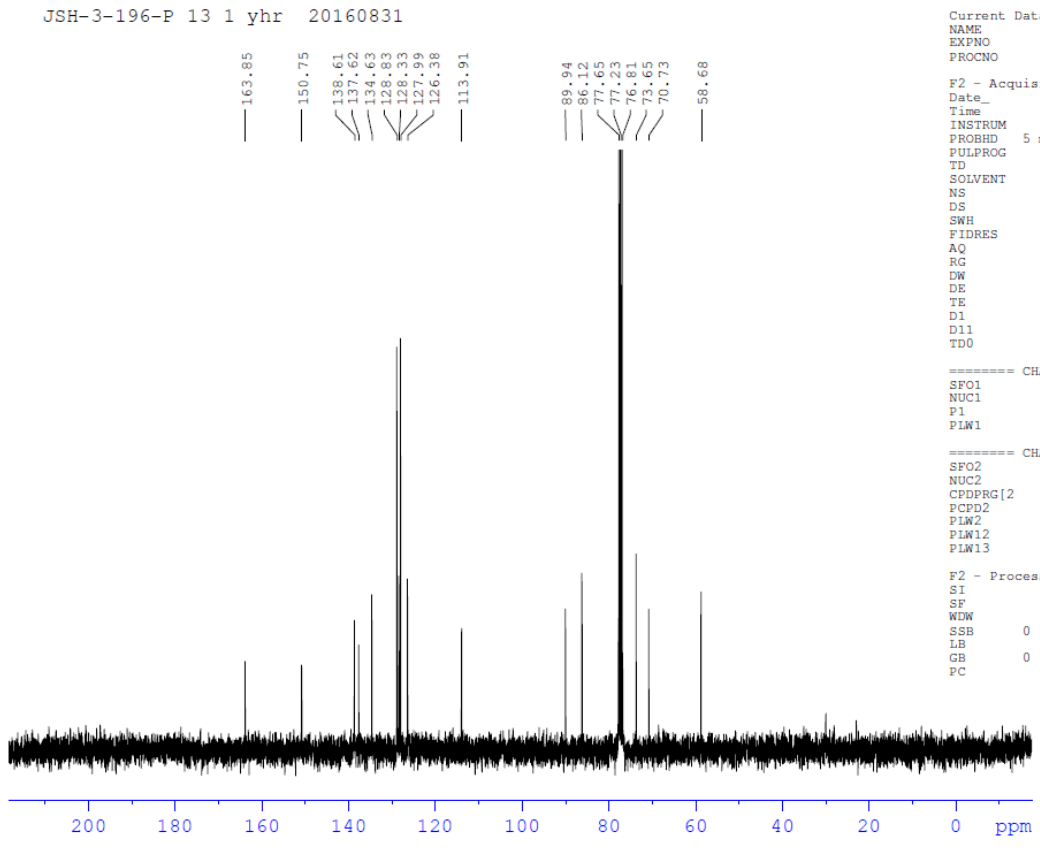



```
Current Data Parameters
NAME          JSH-3-196-P
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160831
Time                15.58
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH             6188.119 Hz
FIDRES          0.094423 Hz
AQ              5.2953086 sec
RG                   287
DW                80.800 usec
DE                 6.50 usec
TE                295.3 K
D1             2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          300.1314684 MHz
NUC1                  1H
P1                 11.00 usec
PLW1           8.75839996 W

F2 - Processing parameters
SI                 32768
SF            300.1300060 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



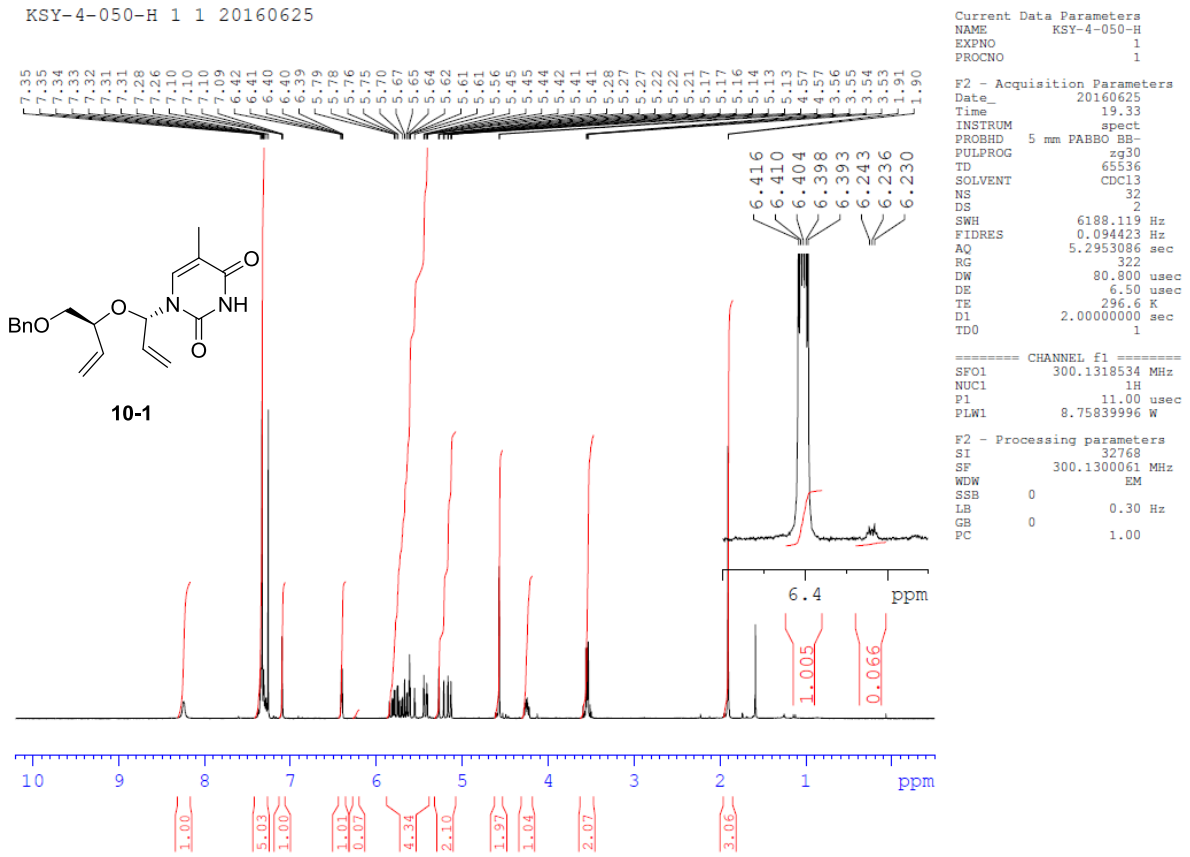

```
Current Data Parameters
NAME          JSH-3-196-P
EXPNO                  13
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160831
Time                14.06
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   331
DS                     2
SWH            18028.846 Hz
FIDRES          0.275098 Hz
AQ              1.8175317 sec
RG                  20.2
DW                27.733 usec
DE                 6.50 usec
TE                296.2 K
D1             1.50000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          75.4752953 MHz
NUC1                  13C
P1                 10.20 usec
PLW1          18.97400093 W

======== CHANNEL f2 ========
SFO2          300.1312005 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              90.00 usec
PLW2           8.75839996 W
PLW12          0.13083000 W
PLW13          0.10598000 W

F2 - Processing parameters
SI                 32768
SF             75.4677341 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

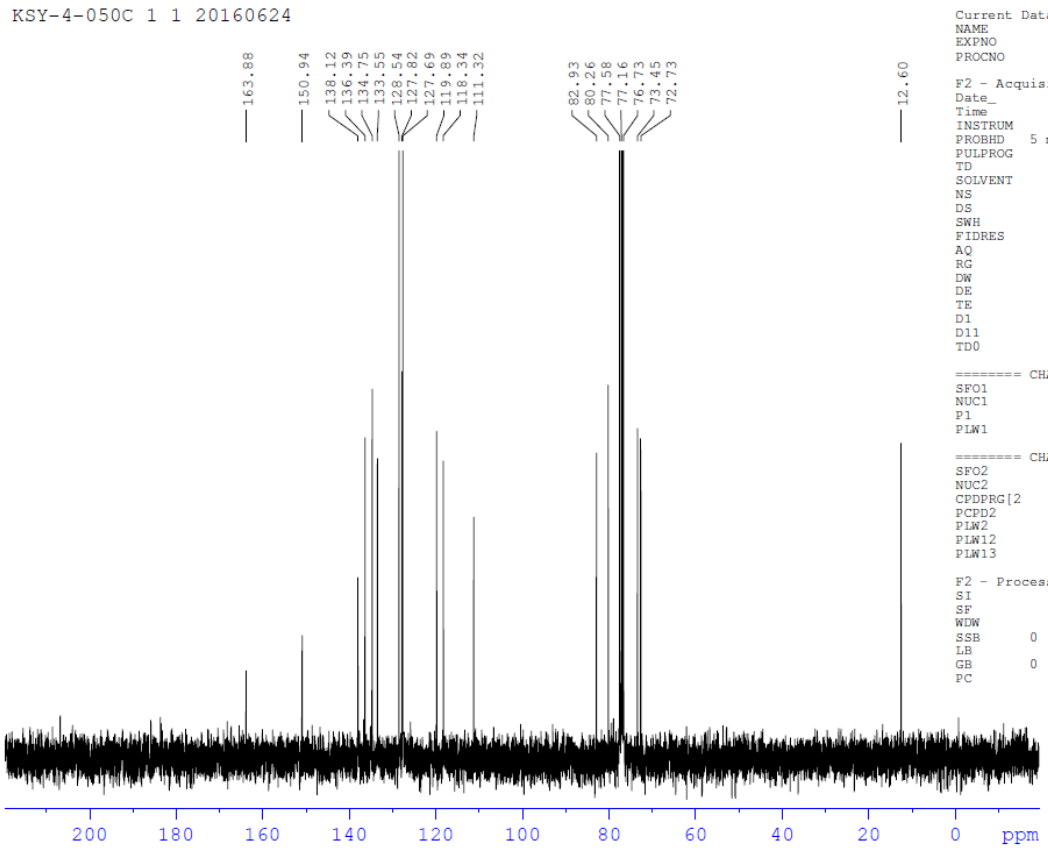



```
Current Data Parameters
NAME          KSY-4-050-H
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160625
Time                19.33
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH              6188.119 Hz
FIDRES           0.094423 Hz
AQ               5.2953086 sec
RG                    322
DW                 80.800 usec
DE                  6.50 usec
TE                 296.6 K
D1              2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          300.1318534 MHz
NUC1                  1H
P1                 11.00 usec
PLW1          8.75839996 W

F2 - Processing parameters
SI                  32768
SF            300.1300061 MHz
WDW                    EM
SSB          0
LB                  0.30 Hz
GB           0
PC                  1.00
```



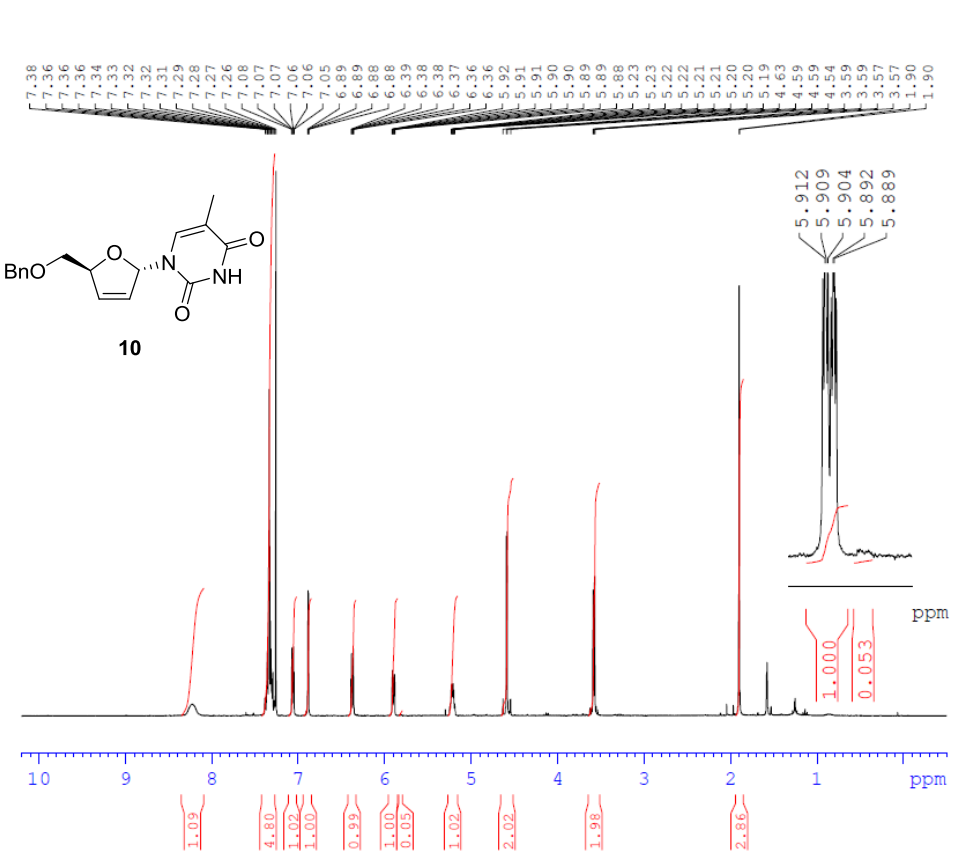

```
Current Data Parameters
NAME          KSY-4-050C
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160624
Time                21.18
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    663
DS                      2
SWH             18028.846 Hz
FIDRES           0.275098 Hz
AQ               1.8175317 sec
RG                     16
DW                 27.733 usec
DE                  6.50 usec
TE                 296.6 K
D1              1.50000000 sec
D11             0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          75.4752953 MHz
NUC1                  13C
P1                 10.20 usec
PLW1         18.97400093 W

======== CHANNEL f2 ========
SFO2         300.1312005 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              90.00 usec
PLW2          8.75839996 W
PLW12         0.13083000 W
PLW13         0.10598000 W

F2 - Processing parameters
SI                  32768
SF            75.4677391 MHz
WDW                    EM
SSB          0
LB                  1.00 Hz
GB           0
PC                  1.40
```

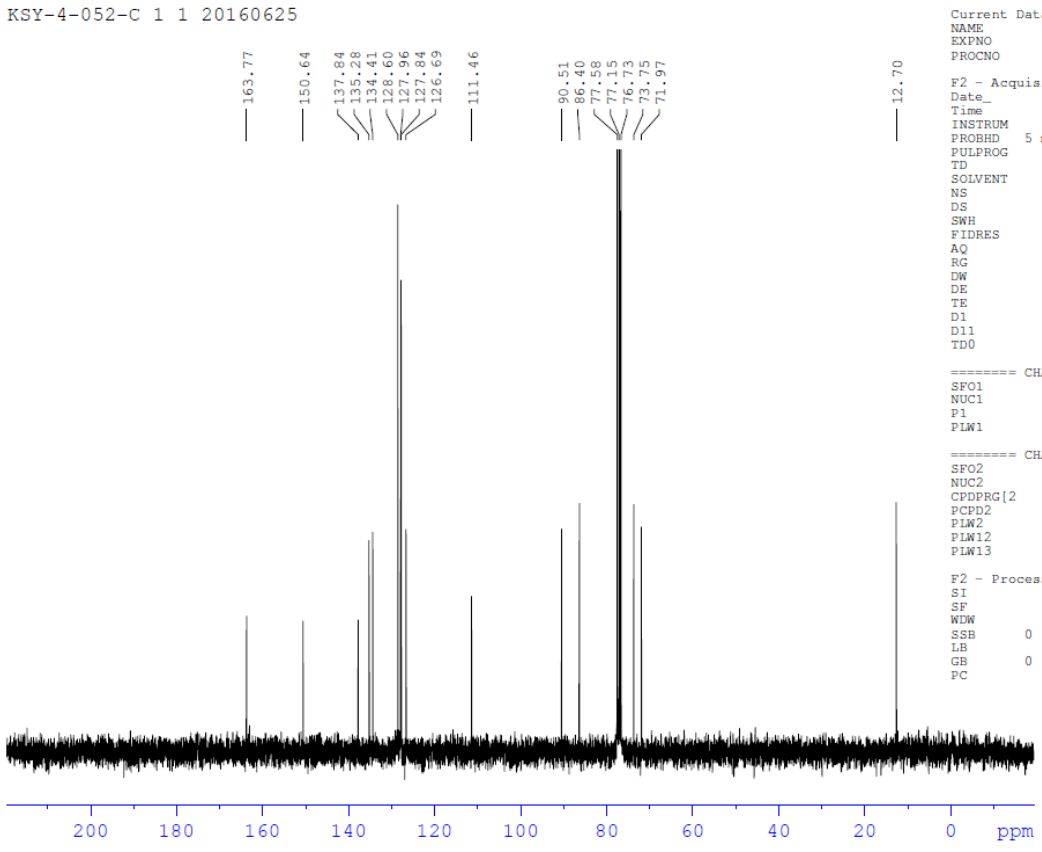


Current Data Parameters
NAME KSY-4-052-H
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160625
Time 20.39
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953086 sec
RG 322
DW 80.800 usec
DE 6.50 usec
TE 296.7 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 300.1318534 MHz
NUC1 1H
P1 11.00 usec
PLW1 8.75839996 W

F2 - Processing parameters
SI 32768
SF 300.1300061 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



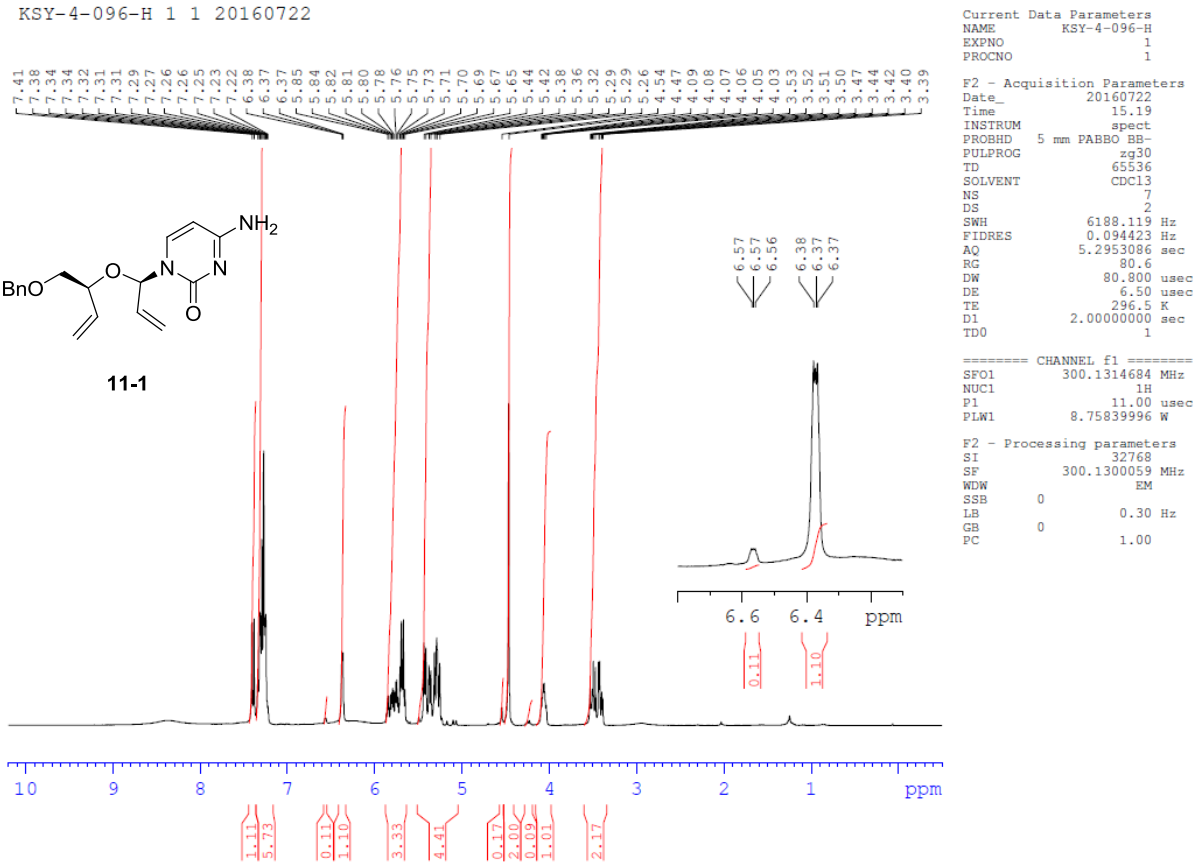
Current Data Parameters
NAME KSY-4-052-C
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160625
Time 19.52
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 560
DS 2
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175317 sec
RG 14.2
DW 27.733 usec
DE 6.50 usec
TE 297.0 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 75.4752953 MHz
NUC1 13C
P1 10.20 usec
PLW1 18.97400093 W

======== CHANNEL f2 ========
SFO2 300.1312005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 8.75839996 W
PLW12 0.13083000 W
PLW13 0.10598000 W

F2 - Processing parameters
SI 32768
SF 75.4677396 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

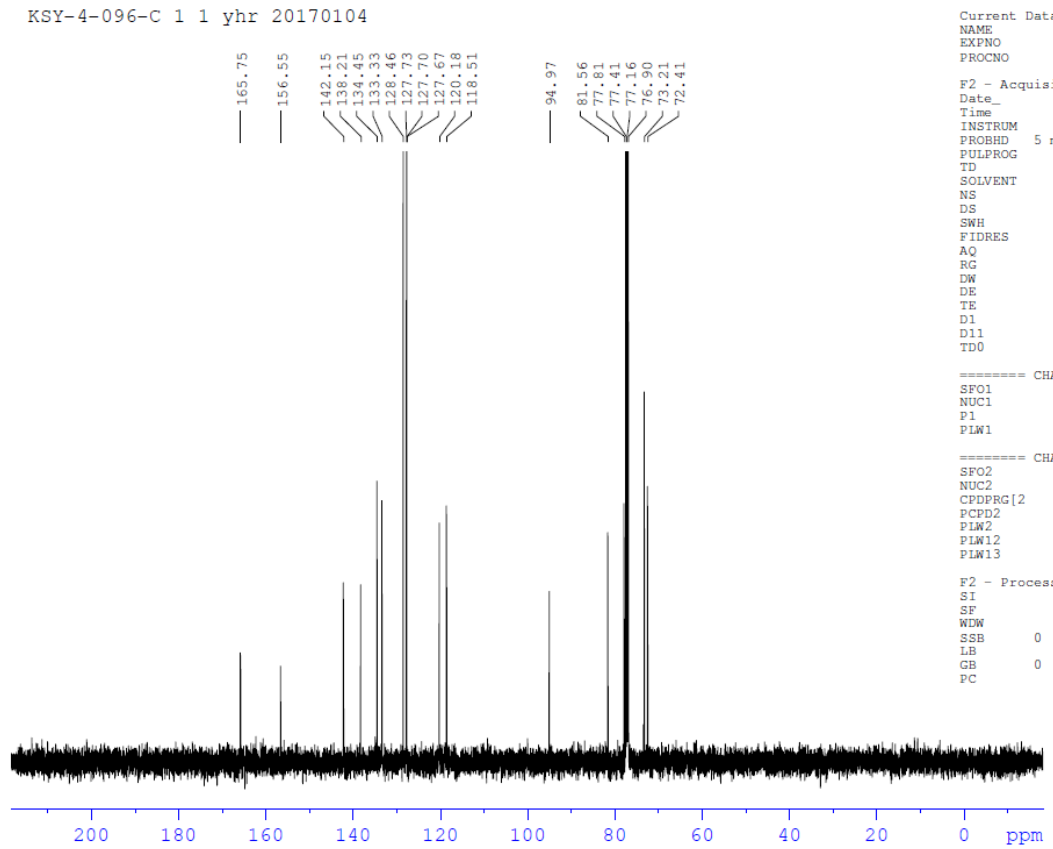



```
Current Data Parameters
NAME          KSY-4-096-H
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160722
Time                15.19
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     7
DS                     2
SWH             6188.119 Hz
FIDRES          0.094423 Hz
AQ              5.2953086 sec
RG                  80.6
DW                80.800 usec
DE                 6.50 usec
TE                296.5 K
D1             2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          300.1314684 MHz
NUC1                  1H
P1                 11.00 usec
PLW1           8.75839996 W

F2 - Processing parameters
SI                 32768
SF            300.1300059 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```




```
Current Data Parameters
NAME          KSY-4-096-C
EXPNO                   1
PROCNO                  1

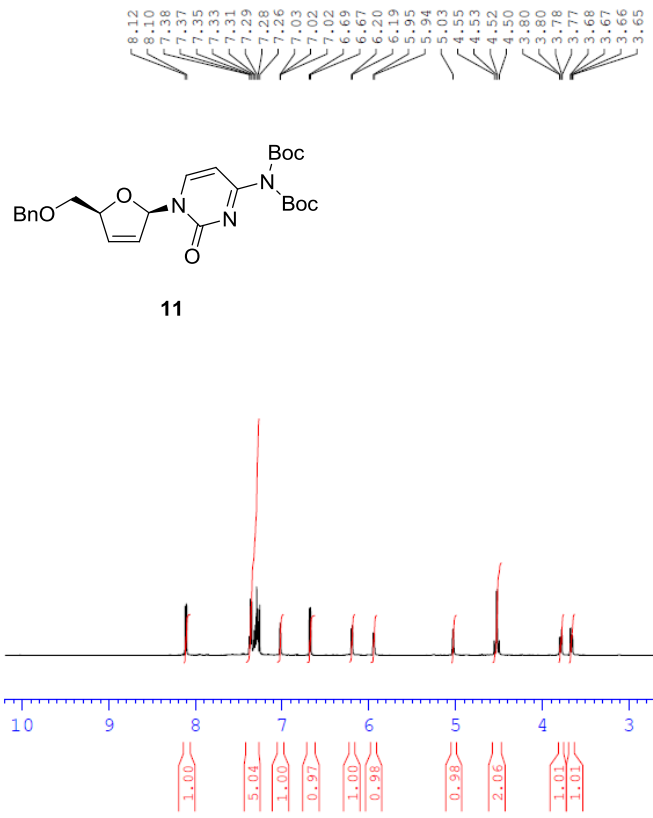
F2 - Acquisition Parameters
Date_            20170104
Time                17.29
INSTRUM             spect
PROBHD    5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   226
DS                     4
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ              1.1010048 sec
RG                  2050
DW                16.800 usec
DE                 6.50 usec
TE                296.6 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          125.8131145 MHz
NUC1                  13C
P1                 10.00 usec
PLW1          87.00000000 W

======== CHANNEL f2 ========
SFO2          500.3020012 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              80.00 usec
PLW2          21.50000000 W
PLW12          0.42140001 W
PLW13          0.26969999 W

F2 - Processing parameters
SI                 32768
SF            125.8005213 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

KSY-4-099-H 1 1 yhr 20160725



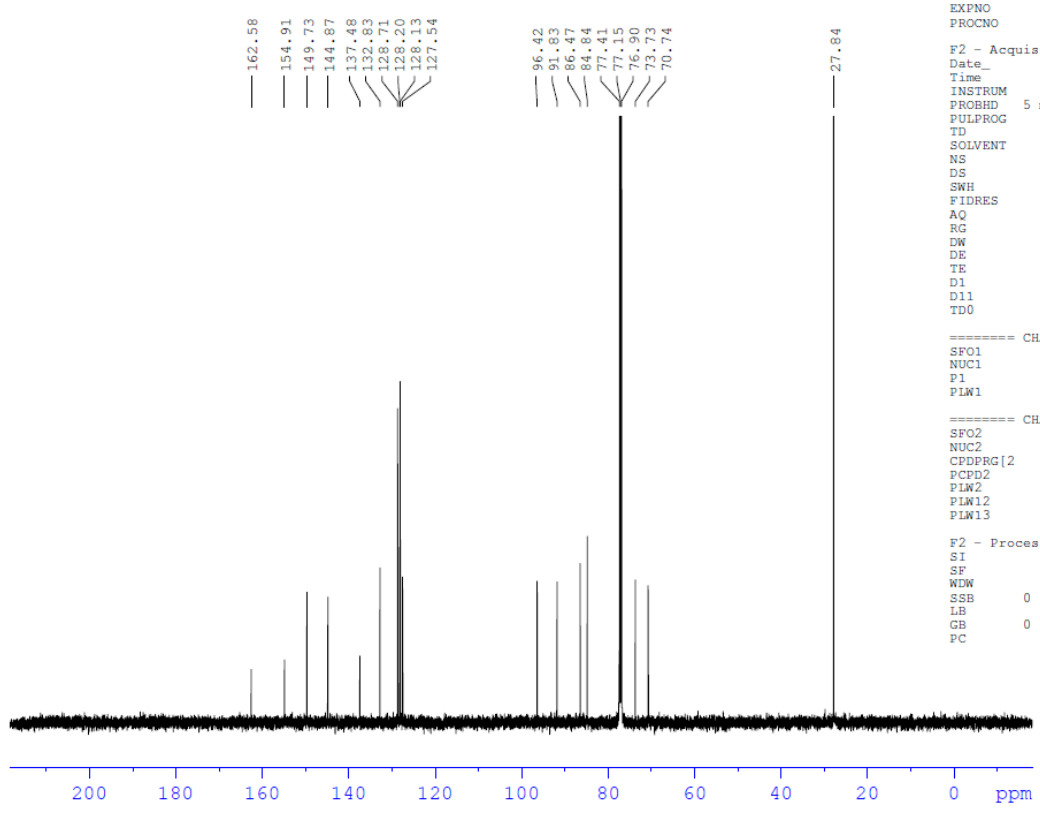

```
Current Data Parameters
NAME          KSY-4-099-H
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20160725
Time               17.38
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    10
DS                     2
SWH           10000.000 Hz
FIDRES            0.152588 Hz
AQ                3.2767999 sec
RG                   143.9
DW                  50.000 usec
DE                   6.50 usec
TE                  300.9 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          500.3030896 MHz
NUC1                   1H
P1                  10.50 usec
PLW1          22.50000000 W

F2 - Processing parameters
SI                 65536
SF            500.3000133 MHz
WDW                   EM
SSB          0
LB                  0.30 Hz
GB           0
PC                  1.00
```

KSY-4-099-C 1 1 yhr 20160725



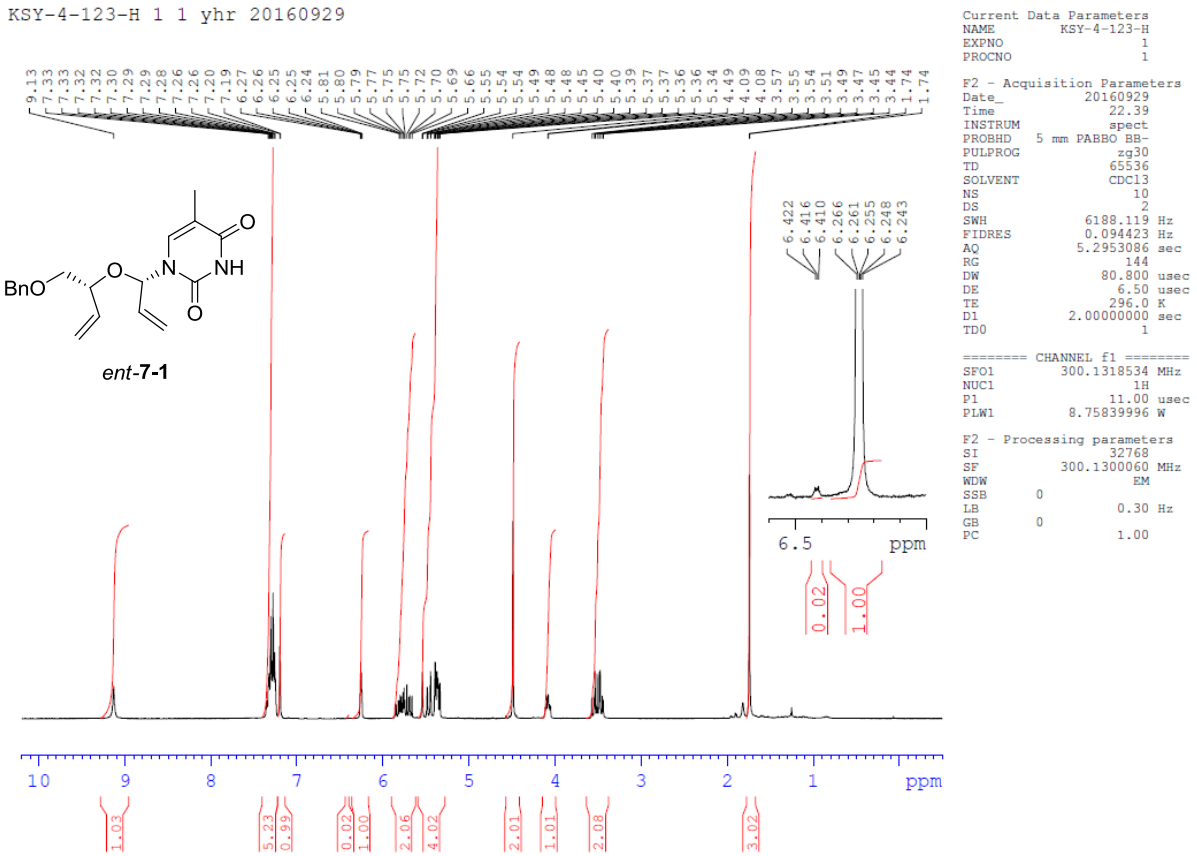

```
Current Data Parameters
NAME          KSY-4-099-C
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20160725
Time               17.58
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   339
DS                     4
SWH           29761.904 Hz
FIDRES            0.454131 Hz
AQ                1.1010048 sec
RG                   143.9
DW                  16.800 usec
DE                   6.50 usec
TE                  300.9 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          125.8131145 MHz
NUC1                   13C
P1                   8.20 usec
PLW1          90.00000000 W

======== CHANNEL f2 ========
SFO2          500.3020012 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2               80.00 usec
PLW2          22.50000000 W
PLW12          0.44100001 W
PLW13          0.28224000 W

F2 - Processing parameters
SI                 32768
SF            125.8005195 MHz
WDW                   EM
SSB          0
LB                  1.00 Hz
GB           0
PC                  1.40
```

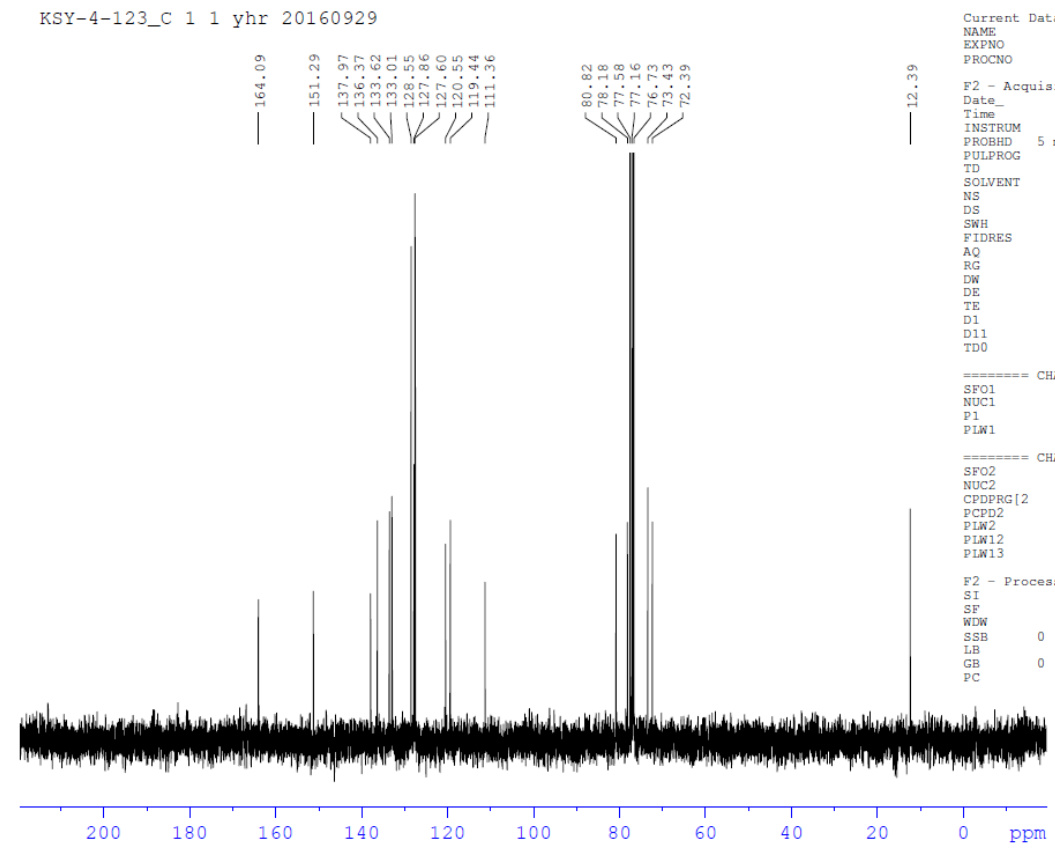



```
Current Data Parameters
NAME          KSY-4-123-H
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_              20160929
Time                 22.39
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      10
DS                       2
SWH               6188.119 Hz
FIDRES            0.094423 Hz
AQ                5.2953086 sec
RG                     144
DW                  80.800 usec
DE                   6.50 usec
TE                  296.0 K
D1              2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          300.1318534 MHz
NUC1                    1H
P1                   11.00 usec
PLW1           8.75839996 W

F2 - Processing parameters
SI                   32768
SF            300.1300060 MHz
WDW                     EM
SSB                  0
LB                   0.30 Hz
GB                   0
PC                   1.00
```




```
Current Data Parameters
NAME          KSY-4-123_C
EXPNO                   1
PROCNO                  1

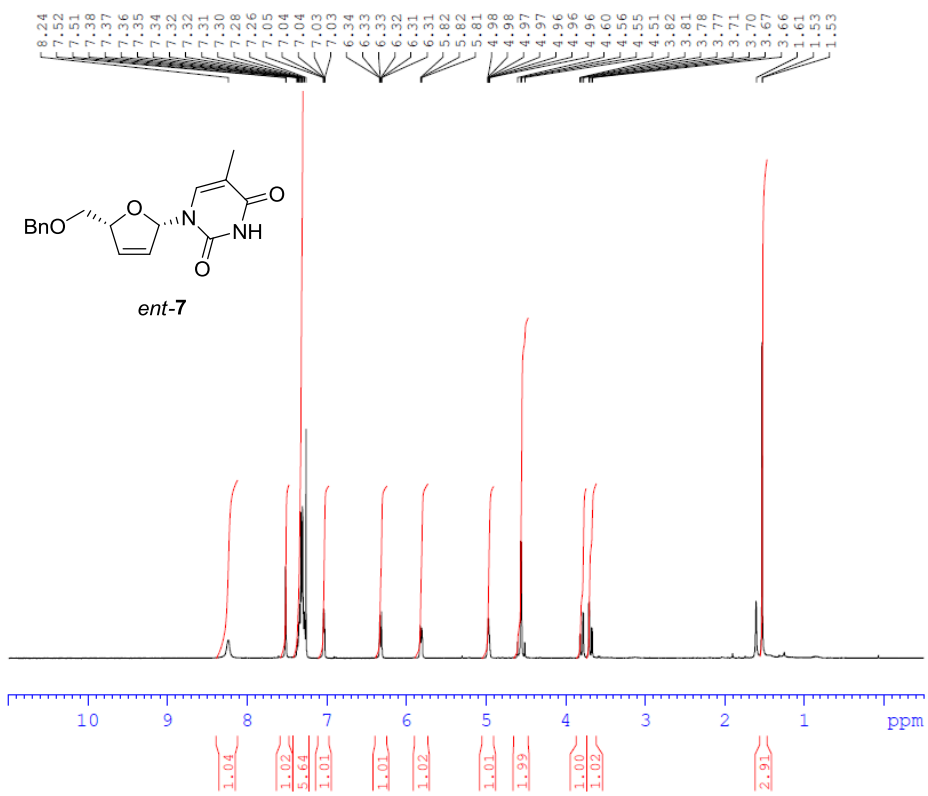
F2 - Acquisition Parameters
Date_              20160929
Time                 22.46
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      92
DS                       2
SWH              18028.846 Hz
FIDRES            0.275098 Hz
AQ                1.8175317 sec
RG                    20.2
DW                  27.733 usec
DE                   6.50 usec
TE                  296.6 K
D1              1.50000000 sec
D11             0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          75.4752953 MHz
NUC1                    13C
P1                   10.20 usec
PLW1          18.97400093 W

======== CHANNEL f2 ========
SFO2          300.1312005 MHz
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                90.00 usec
PLW2           8.75839996 W
PLW12          0.13083000 W
PLW13          0.10598000 W

F2 - Processing parameters
SI                   32768
SF            75.4677404 MHz
WDW                     EM
SSB                  0
LB                   1.00 Hz
GB                   0
PC                   1.40
```

KSY-4-126-H 1 1 yhr 20160929



ent-**7**

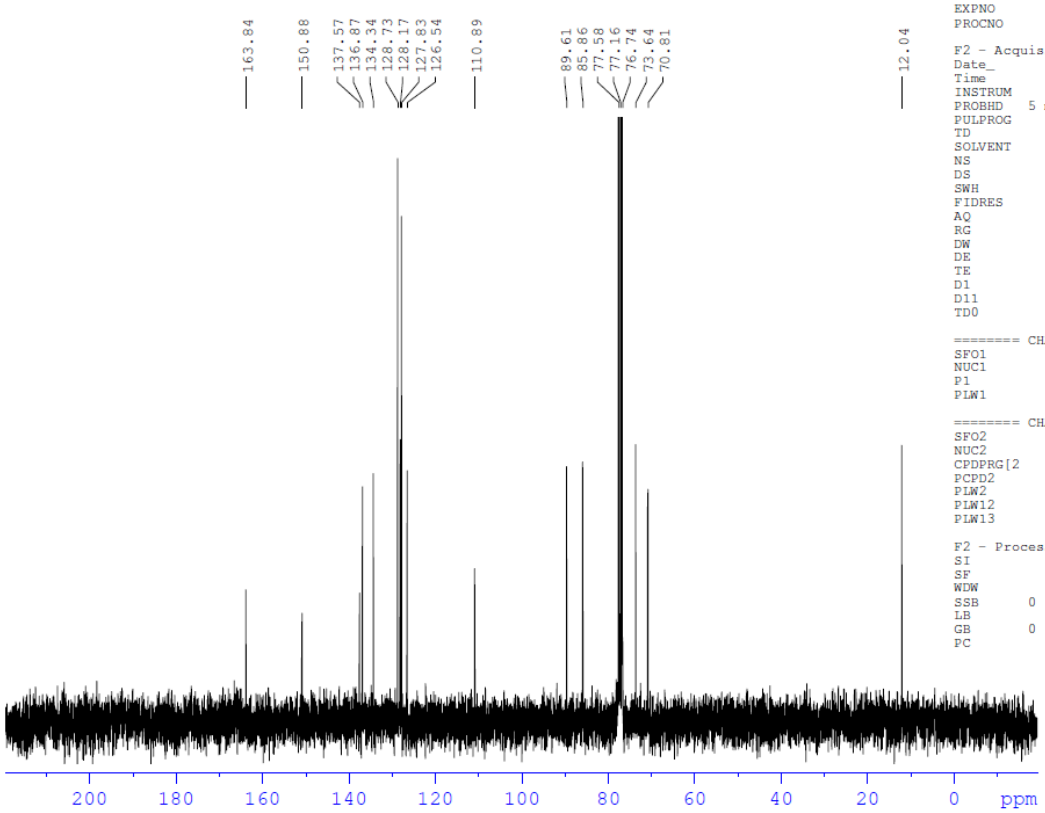
```
Current Data Parameters
NAME          KSY-4-126-H
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160929
Time                22.20
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     19
DS                      2
SWH              6188.119 Hz
FIDRES           0.094423 Hz
AQ               5.2953086 sec
RG                    287
DW                 80.800 usec
DE                  6.50 usec
TE                 296.1 K
D1              2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          300.1314684 MHz
NUC1                   1H
P1                  11.00 usec
PLW1           8.75839996 W

F2 - Processing parameters
SI                  32768
SF            300.1300060 MHz
WDW                    EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

KSY-4-126-C 1 1 yhr 20160929




```
Current Data Parameters
NAME          KSY-4-126-C
EXPNO                   1
PROCNO                  1

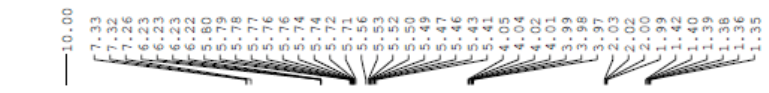
F2 - Acquisition Parameters
Date_            20160929
Time                19.52
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG          zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    521
DS                      2
SWH             18028.846 Hz
FIDRES           0.275098 Hz
AQ               1.8175317 sec
RG                   20.2
DW                 27.733 usec
DE                  6.50 usec
TE                 296.4 K
D1              1.50000000 sec
D11             0.03000000 sec
TD0                     1

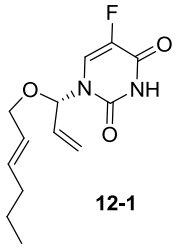
======== CHANNEL f1 ========
SFO1          75.4752953 MHz
NUC1                   13C
P1                  10.20 usec
PLW1          18.97400093 W

======== CHANNEL f2 ========
SFO2         300.1312005 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2               90.00 usec
PLW2           8.75839996 W
PLW12          0.13083000 W
PLW13          0.10598000 W

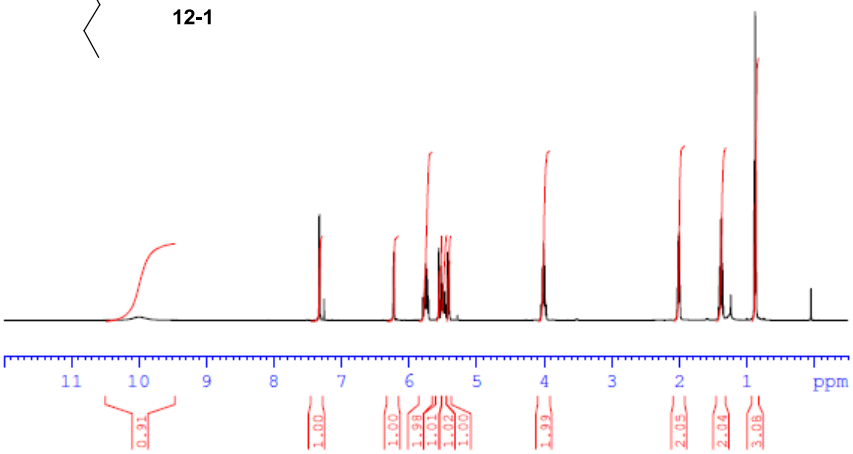
F2 - Processing parameters
SI                  32768
SF            75.4677388 MHz
WDW                    EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

MJK-4-142 11 1 YHR 160719





12-1



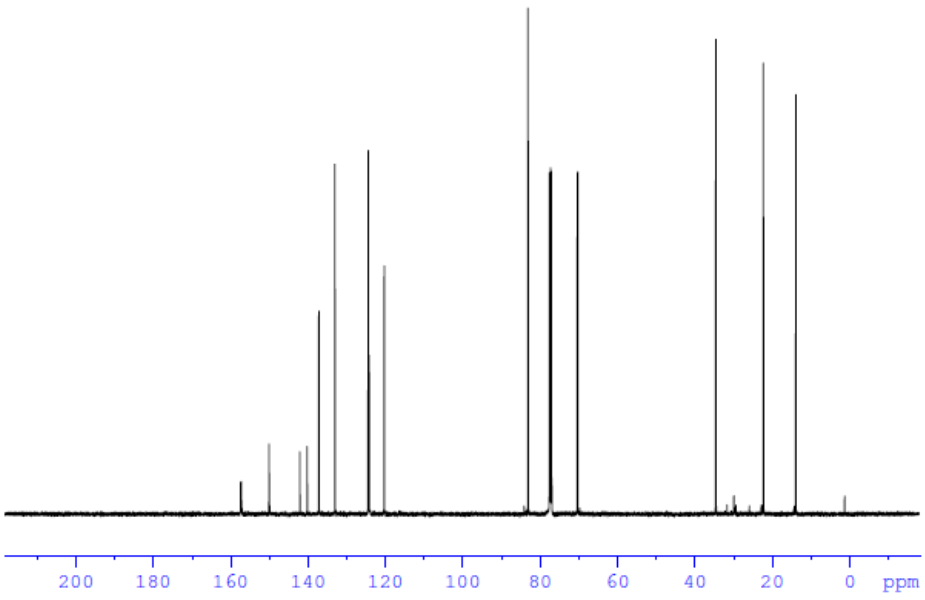

```
Current Data Parameters
NAME                  MJK-4-142
EXPNO                        11
PROCNO                        1

F2 - Acquisition Parameters
Date_                 20160720
Time                      10.55
INSTRUM                   spect
PROBHD     5 mm QNP 1H/13
PULPROG                   zg30
TD                       65536
SOLVENT                  CDCl3
NS                           17
DS                            2
SWH                 10000.000 Hz
FIDRES                0.152588 Hz
AQ                    3.2767999 sec
RG                        99.44
DW                       50.000 usec
DE                        6.50 usec
TE                       299.1 K
D1                    2.00000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1                500.3030896 MHz
NUC1                        1H
P1                       10.50 usec
PLW1                22.50000000 W

F2 - Processing parameters
SI                        65536
SF                  500.3000134 MHz
WDW                          EM
SSB                   0
LB                        0.30 Hz
GB                    0
PC                        1.00
```

MJK-4-142 1 1 YHR 160719




```
Current Data Parameters
NAME                  MJK-4-142
EXPNO                        13
PROCNO                        1

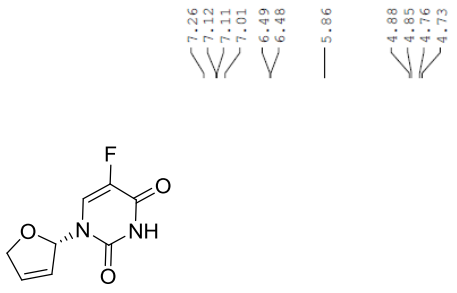
F2 - Acquisition Parameters
Date_                 20160719
Time                      1.41
INSTRUM                   spect
PROBHD     5 mm QNP 1H/13
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         2229
DS                            4
SWH                 29761.904 Hz
FIDRES                0.454131 Hz
AQ                    1.1010048 sec
RG                       198.92
DW                       16.800 usec
DE                        6.50 usec
TE                       298.8 K
D1                    1.50000000 sec
D11                   0.03000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1                125.8131145 MHz
NUC1                        13C
P1                        8.20 usec
PLW1                90.00000000 W

======== CHANNEL f2 ========
SFO2                500.3020012 MHz
NUC2                        1H
CPDPRG[2                waltz16
PCPD2                     80.00 usec
PLW2                22.50000000 W
PLW12                0.44100001 W
PLW13                0.28224000 W

F2 - Processing parameters
SI                        32768
SF                  125.8005153 MHz
WDW                          EM
SSB                   0
LB                        1.00 Hz
GB                    0
PC                        1.40
```

MJK-4-136-P 1 1 yhr 20160715



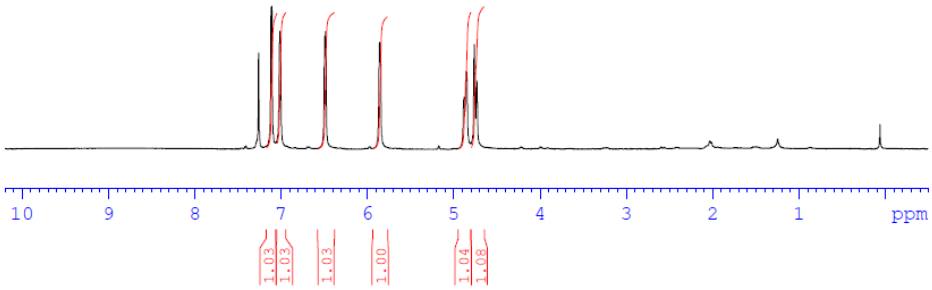
12

```
Current Data Parameters
NAME         MJK-4-136-P
EXPNO                  2
PROCNO                 1

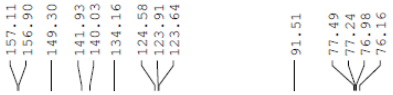
F2 - Acquisition Parameters
Date_           20160715
Time               12.08
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    17
DS                     2
SWH           10000.000 Hz
FIDRES        0.152588 Hz
AQ            3.2767999 sec
RG                322.66
DW               50.000 usec
DE                6.50 usec
TE                298.5 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         500.3030896 MHz
NUC1                   1H
P1                10.50 usec
PLW1        22.50000000 W

F2 - Processing parameters
SI                 65536
SF           500.3000140 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```



MJK-4-136-P 1 1 yhr 20160715



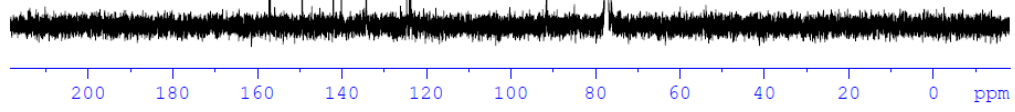

```
Current Data Parameters
NAME         MJK-4-136-P
EXPNO                 14
PROCNO                 1

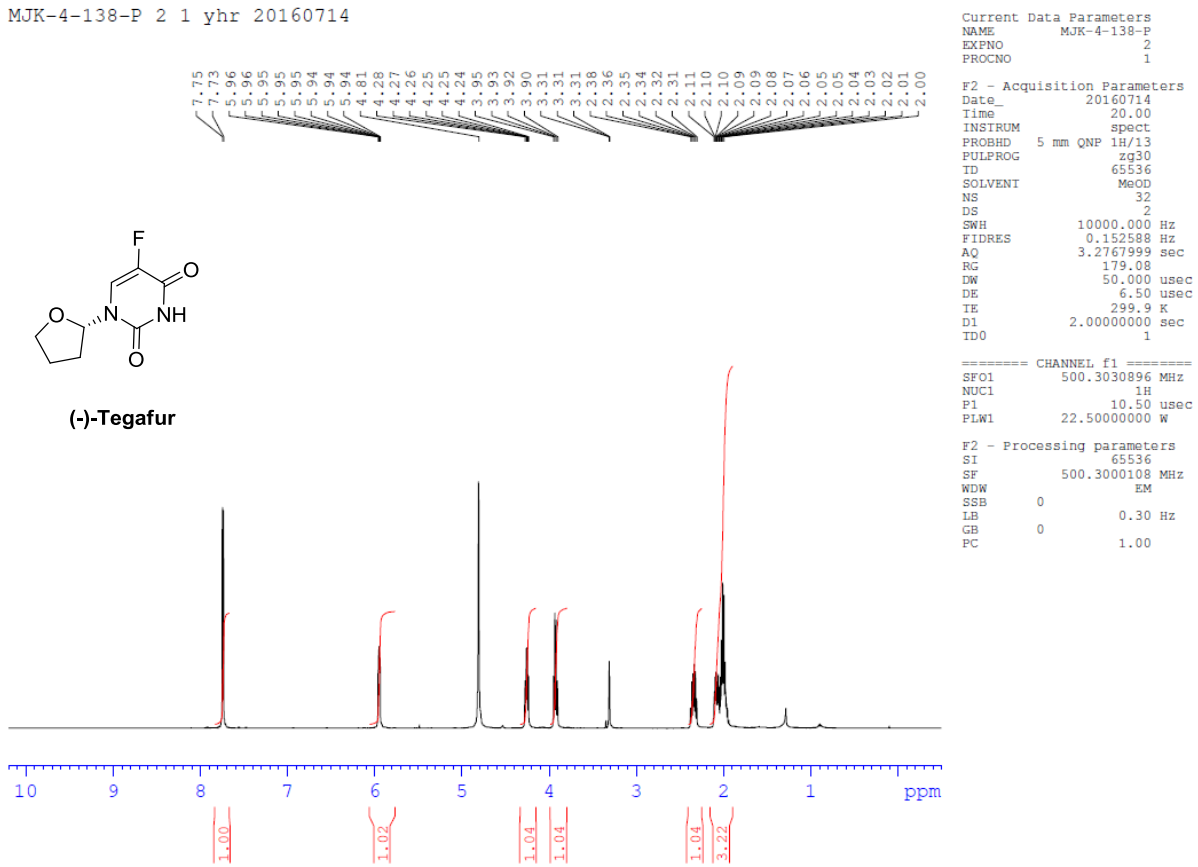
F2 - Acquisition Parameters
Date_           20160715
Time               12.10
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1770
DS                     4
SWH           29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010048 sec
RG                198.92
DW               16.800 usec
DE                6.50 usec
TE                298.6 K
D1            1.50000000 sec
D11           0.03000000 sec
TD0                    1

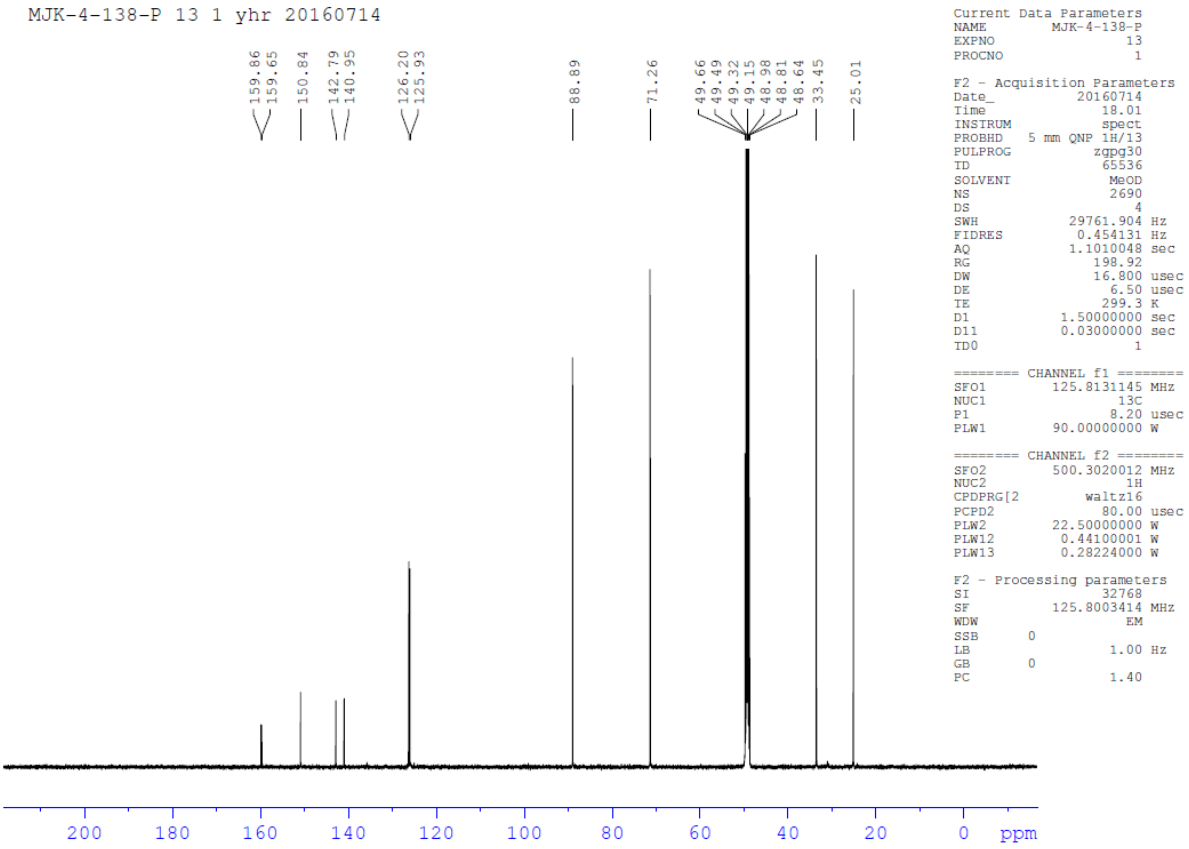
======== CHANNEL f1 ========
SFO1         125.8131145 MHz
NUC1                  13C
P1                8.20 usec
PLW1        90.00000000 W

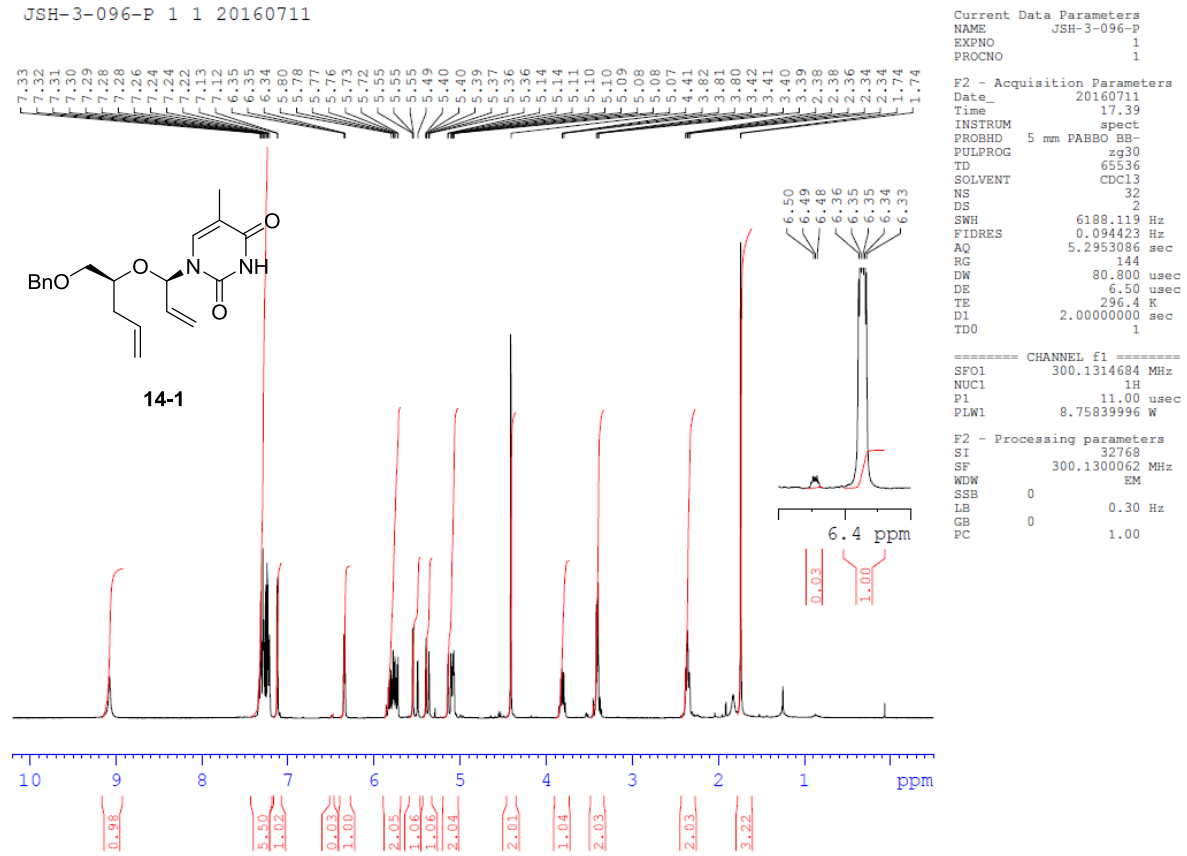
======== CHANNEL f2 ========
SFO2         500.3020012 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2             80.00 usec
PLW2        22.50000000 W
PLW12        0.44100001 W
PLW13        0.28224000 W

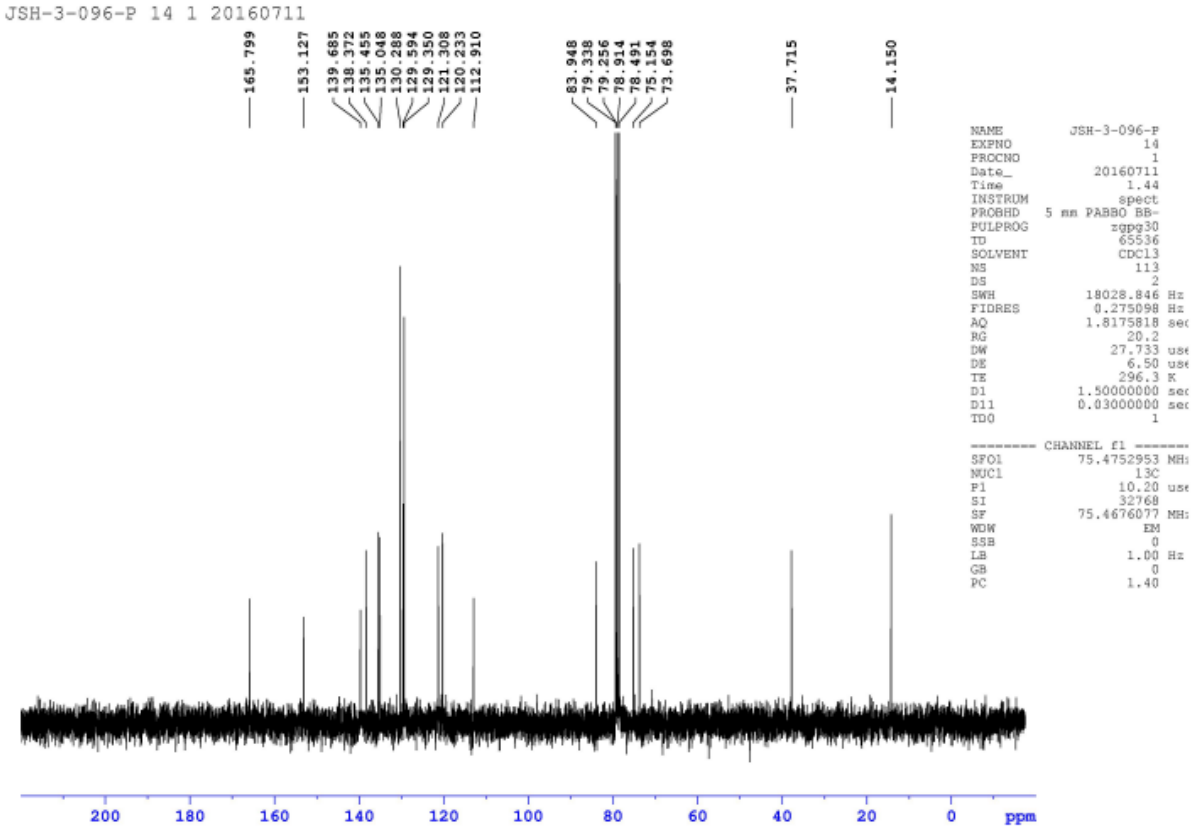
F2 - Processing parameters
SI                 32768
SF           125.8005089 MHz
WDW                   EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

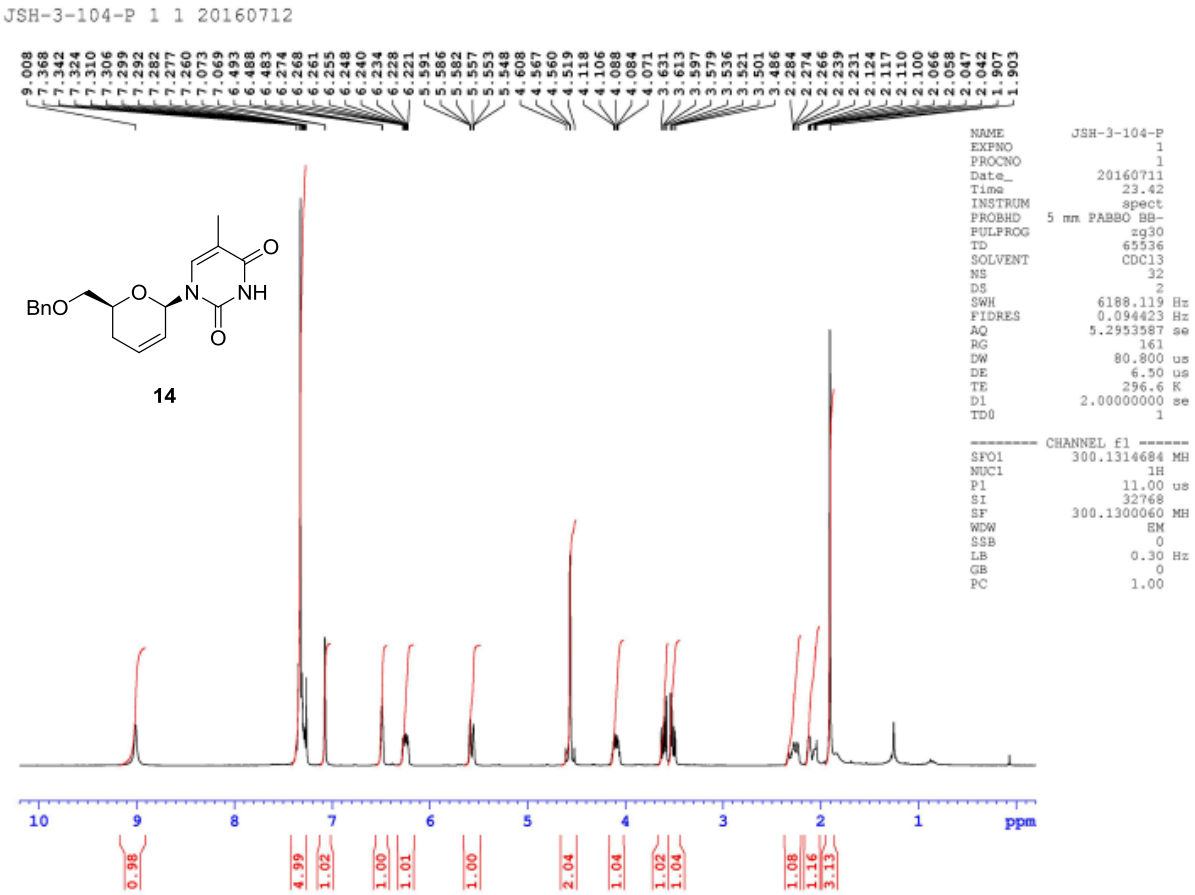


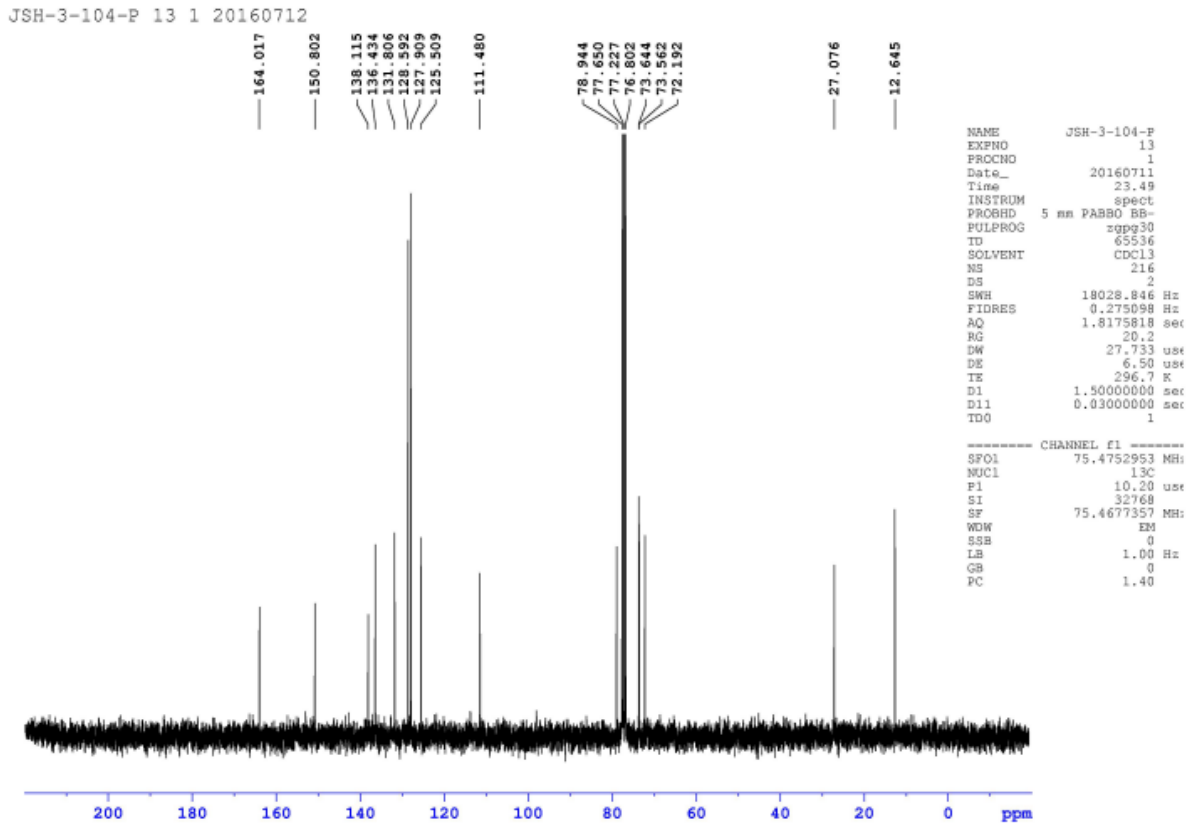

MJK-4-138-P 2 1 yhr 20160714
7.75 7.73 5.96 5.95 5.95 5.95 5.94 5.94 5.94 4.81 4.28 4.27 4.26 4.25 4.25 4.24 3.95 3.93 3.92 3.90 3.31 3.31 3.31 2.38 2.36 2.35 2.34 2.32 2.31 2.11 2.10 2.10 2.09 2.09 2.08 2.07 2.06 2.05 2.05 2.04 2.03 2.02 2.01 2.00
F
O
O
N
NH
O
(-)-Tegafur
10 9 8 7 6 5 4 3 2 1 ppm
1.00 1.02 1.04 1.04 1.04 3.22
Current Data Parameters
NAME MJK-4-138-P
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160714
Time 20.00
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT MeOD
NS 32
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 179.08
DW 50.000 usec
DE 6.50 usec
TE 299.9 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 500.3030896 MHz
NUC1 1H
P1 10.50 usec
PLW1 22.50000000 W
F2 - Processing parameters
SI 65536
SF 500.3000108 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


MJK-4-138-P 13 1 yhr 20160714
159.86 159.65 150.84 142.79 140.95 126.20 125.93 88.89 71.26 49.66 49.49 49.32 49.15 48.98 48.81 48.64 33.45 25.01
200 180 160 140 120 100 80 60 40 20 0 ppm
Current Data Parameters
NAME MJK-4-138-P
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160714
Time 18.01
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 2690
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 198.92
DW 16.800 usec
DE 6.50 usec
TE 299.3 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.8131145 MHz
NUC1 13C
P1 8.20 usec
PLW1 90.00000000 W
======== CHANNEL f2 ========
SFO2 500.3020012 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 22.50000000 W
PLW12 0.44100001 W
PLW13 0.28224000 W
F2 - Processing parameters
SI 32768
SF 125.8003414 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

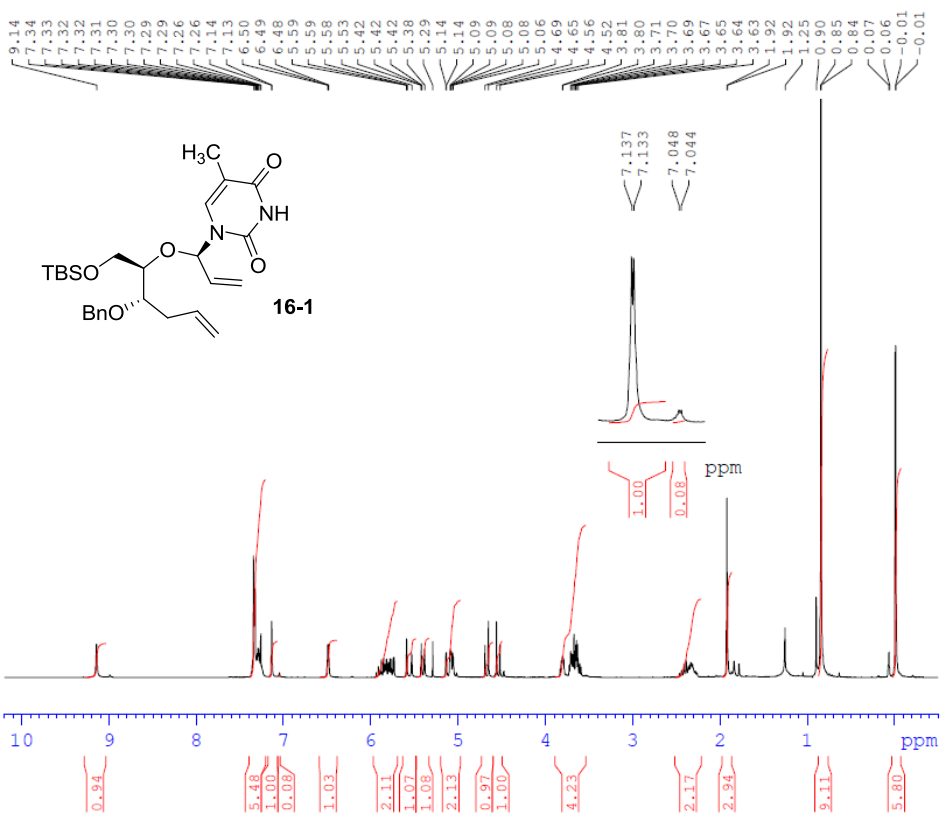

JSH-3-096-P 1 1 20160711
BnO
O
N
NH
O
O
14-1
6.4 ppm
ppm


JSH-3-096-P 14 1 20160711
ppm


JSH-3-104-P 1 1 20160712
9.008
7.368
7.342
7.324
7.310
7.306
7.299
7.292
7.282
7.277
7.260
7.073
7.069
6.493
6.488
6.483
6.274
6.268
6.261
6.255
6.248
6.240
6.234
6.228
6.221
5.591
5.586
5.582
5.557
5.553
5.548
4.608
4.567
4.560
4.519
4.118
4.106
4.088
4.084
4.071
3.631
3.613
3.597
3.579
3.536
3.521
3.501
3.486
2.284
2.274
2.266
2.239
2.231
2.124
2.117
2.110
2.100
2.066
2.058
2.047
2.042
1.907
1.903
BnO
O
N
NH
O
O
14
NAME JSH-3-104-P
EXPNO 1
PROCNO 1
Date_ 20160711
Time 23.42
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 se
RG 161
DW 80.800 us
DE 6.50 us
TE 296.6 K
D1 2.00000000 se
TD0 1
======== CHANNEL f1 ======
SFO1 300.1314684 MH
NUC1 1H
P1 11.00 us
SI 32768
SF 300.1300060 MH
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10
9
8
7
6
5
4
3
2
1
ppm
0.98
4.99
1.02
1.00
1.01
1.00
2.04
1.04
1.02
1.04
1.08
1.16
3.13


JSH-3-104-P 13 1 20160712
164.017
150.802
138.115
136.434
131.806
128.592
127.909
125.509
111.480
78.944
77.650
77.227
76.802
73.644
73.562
72.192
27.076
12.645
NAME JSH-3-104-P
EXPNO 13
PROCNO 1
Date_ 20160711
Time 23.49
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 216
DS 2
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 20.2
DW 27.733 use
DE 6.50 use
TE 296.7 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ======
SFO1 75.4752953 MHz
NUC1 13C
P1 10.20 use
SI 32768
SF 75.4677357 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
0
ppm

DGK-9-070-P (S,S) 2 1 yhr 20160609



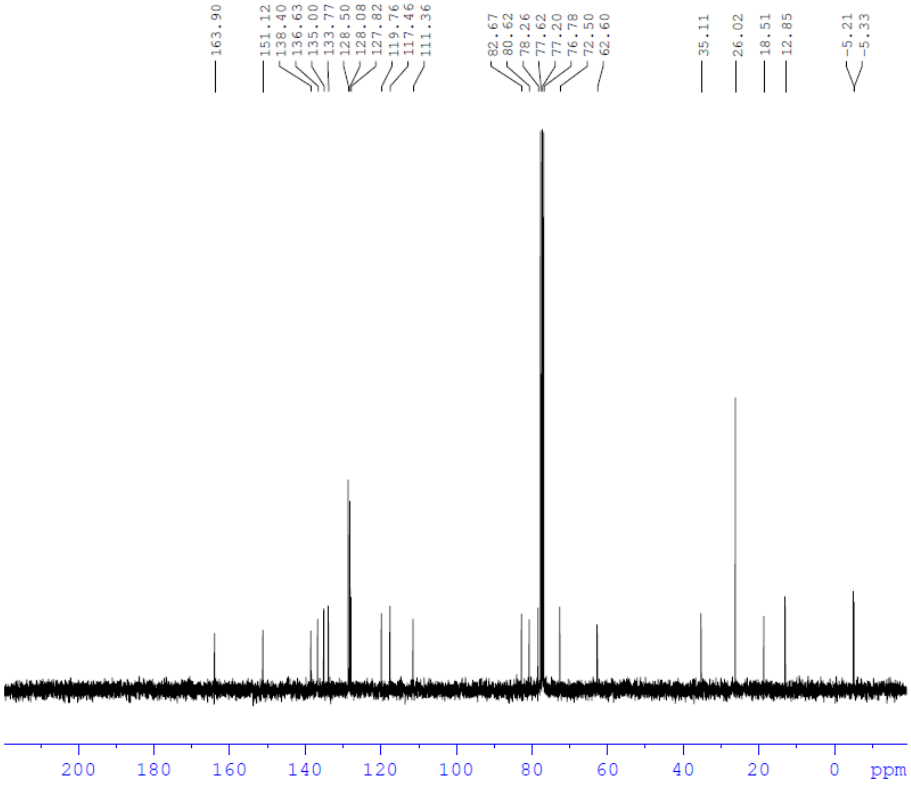
Current Data Parameters
NAME DGK-9-070-P
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160611
Time 4.38
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953086 sec
RG 80.6
DW 80.800 usec
DE 9.00 usec
TE 296.4 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 -2.00 dB
PL1W 8.75835800 W
SFO1 300.1318534 MHz

F2 - Processing parameters
SI 32768
SF 300.1300068 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

DGK-9-094-P 13 1 yhr 20160629



Current Data Parameters
NAME DGK-9-094-P
EXPNO 13
PROCNO 1

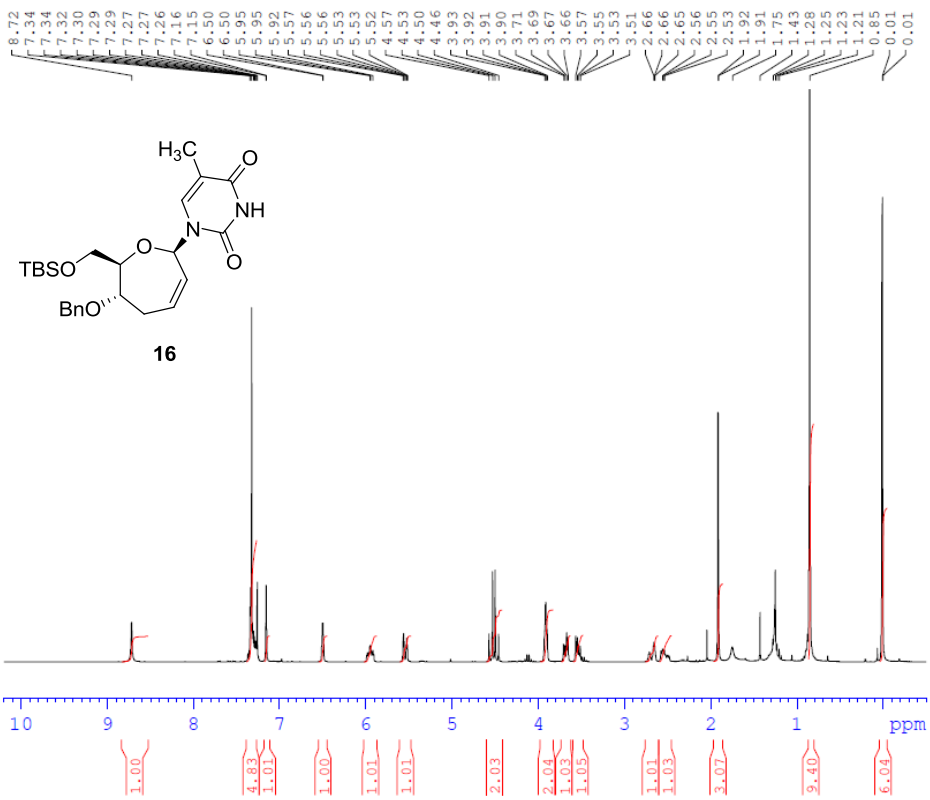
F2 - Acquisition Parameters
Date_ 20170125
Time 5.22
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 286
DS 2
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175317 sec
RG 12.7
DW 27.733 usec
DE 6.50 usec
TE 292.8 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 75.4752953 MHz
NUC1 13C
P1 10.20 usec
PLW1 18.97400093 W

======== CHANNEL f2 ========
SFO2 300.1312005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 8.75839996 W
PLW12 0.13083000 W
PLW13 0.10598000 W

F2 - Processing parameters
SI 32768
SF 75.4677369 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

DGK-9-101-P 1 1 20160704



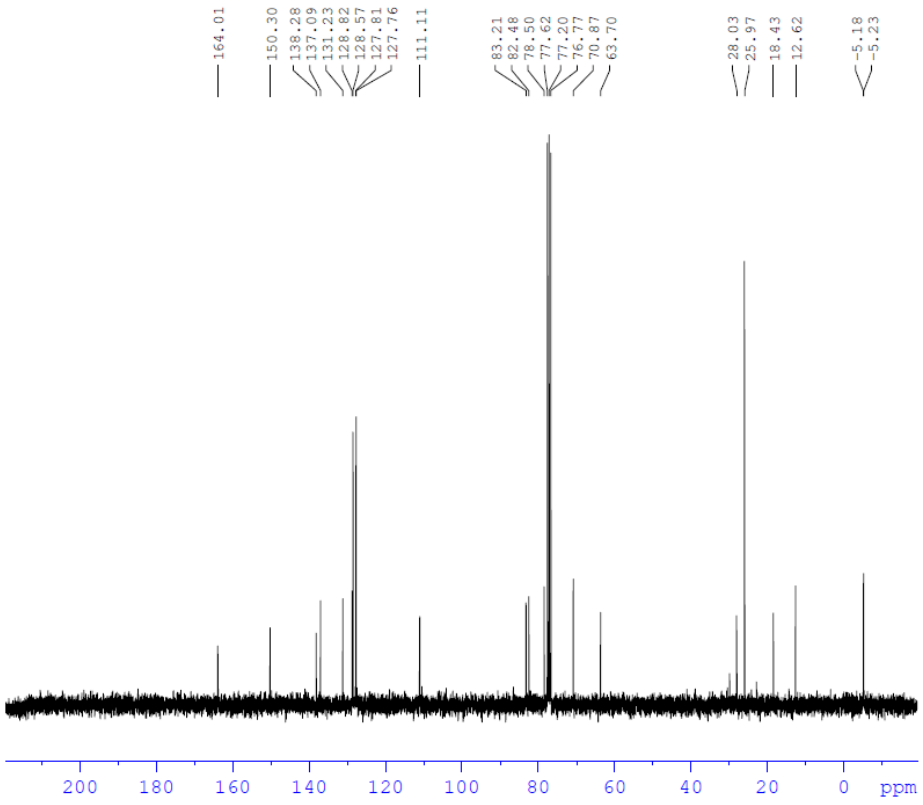

```
Current Data Parameters
NAME         DGK-9-101-P
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160705
Time                4.34
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH              6188.119 Hz
FIDRES           0.094423 Hz
AQ               5.2953086 sec
RG                   128
DW                80.800 usec
DE                 6.50 usec
TE                295.4 K
D1             2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          300.1314684 MHz
NUC1                  1H
P1                 11.00 usec
PLW1           8.75839996 W

F2 - Processing parameters
SI                 32768
SF            300.1300060 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

DGK-9-101-P 13 1 20160704



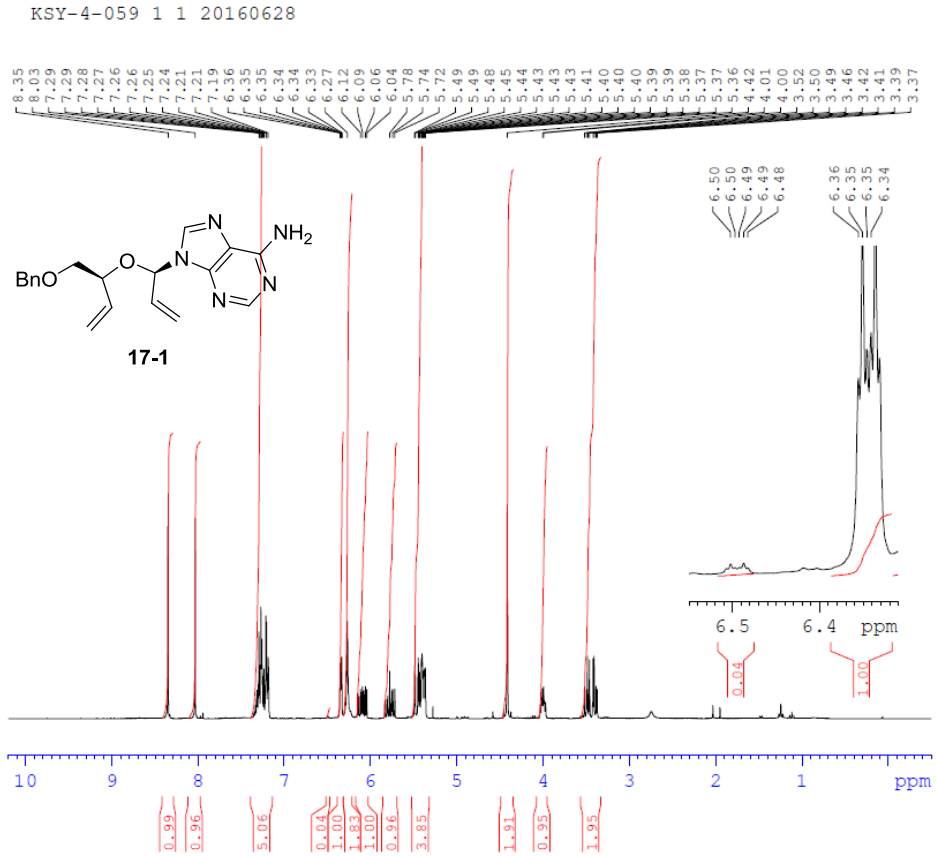

```
Current Data Parameters
NAME         DGK-9-101-P
EXPNO                 13
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160705
Time                4.41
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   194
DS                     2
SWH             18028.846 Hz
FIDRES           0.275098 Hz
AQ               1.8175317 sec
RG                    18
DW                27.733 usec
DE                 6.50 usec
TE                295.7 K
D1             1.50000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          75.4752953 MHz
NUC1                  13C
P1                 10.20 usec
PLW1          18.97400093 W

======== CHANNEL f2 ========
SFO2          300.1312005 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              90.00 usec
PLW2           8.75839996 W
PLW12          0.13083000 W
PLW13          0.10598000 W

F2 - Processing parameters
SI                 32768
SF            75.4677369 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

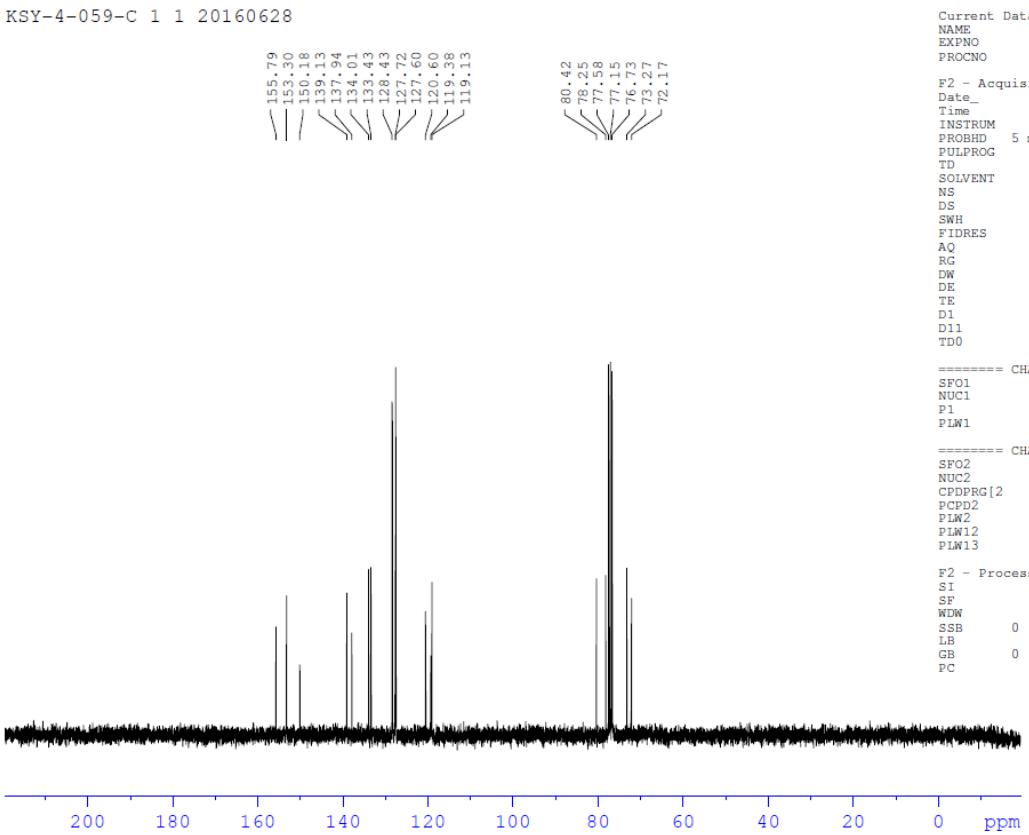



```
Current Data Parameters
NAME            KSY-4-059
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160628
Time                17.16
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    13
DS                     2
SWH             6188.119 Hz
FIDRES          0.094423 Hz
AQ              5.2953086 sec
RG                   101
DW                80.800 usec
DE                 6.50 usec
TE                296.0 K
D1             2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          300.1318534 MHz
NUC1                  1H
P1                 11.00 usec
PLW1          8.75839996 W

F2 - Processing parameters
SI                 32768
SF            300.1300061 MHz
WDW                   EM
SSB        0
LB                 0.30 Hz
GB         0
PC                 1.00
```




```
Current Data Parameters
NAME          KSY-4-059-C
EXPNO                   1
PROCNO                  1

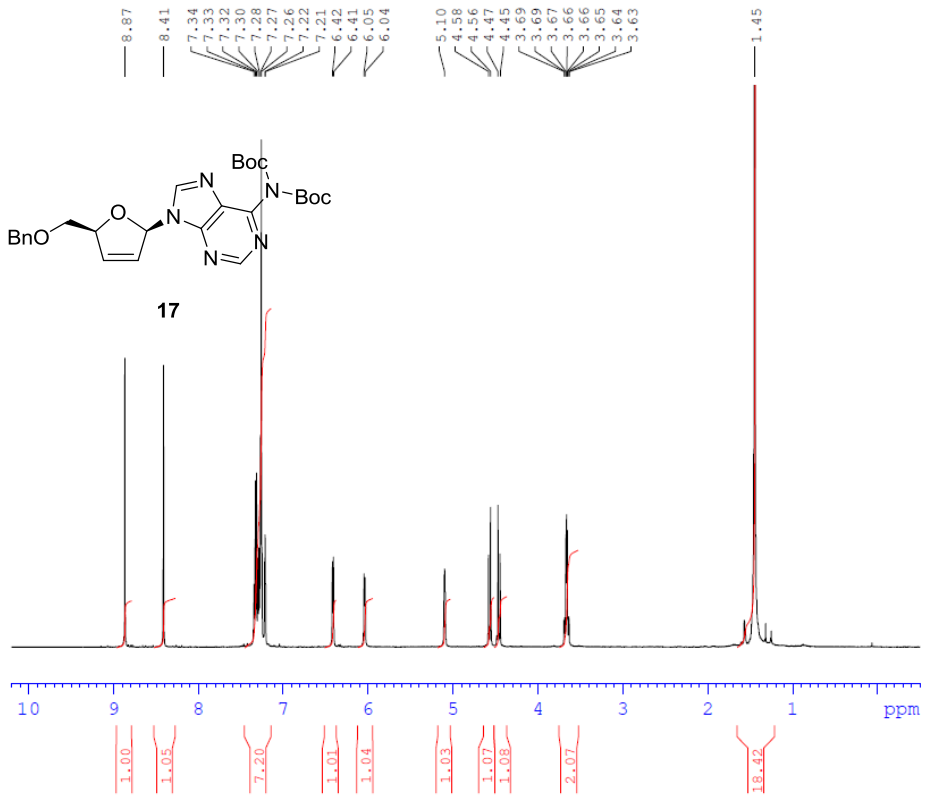
F2 - Acquisition Parameters
Date_            20160628
Time                17.25
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   171
DS                     2
SWH            18028.846 Hz
FIDRES          0.275098 Hz
AQ              1.8175317 sec
RG                    16
DW                27.733 usec
DE                 6.50 usec
TE                297.0 K
D1             1.50000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          75.4752953 MHz
NUC1                  13C
P1                 10.20 usec
PLW1          18.97400093 W

======== CHANNEL f2 ========
SFO2          300.1312005 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              90.00 usec
PLW2          8.75839996 W
PLW12         0.13083000 W
PLW13         0.10598000 W

F2 - Processing parameters
SI                 32768
SF            75.4677424 MHz
WDW                   EM
SSB        0
LB                 1.00 Hz
GB         0
PC                 1.40
```

KSY-4-069-H 1 1 yhr 20170112



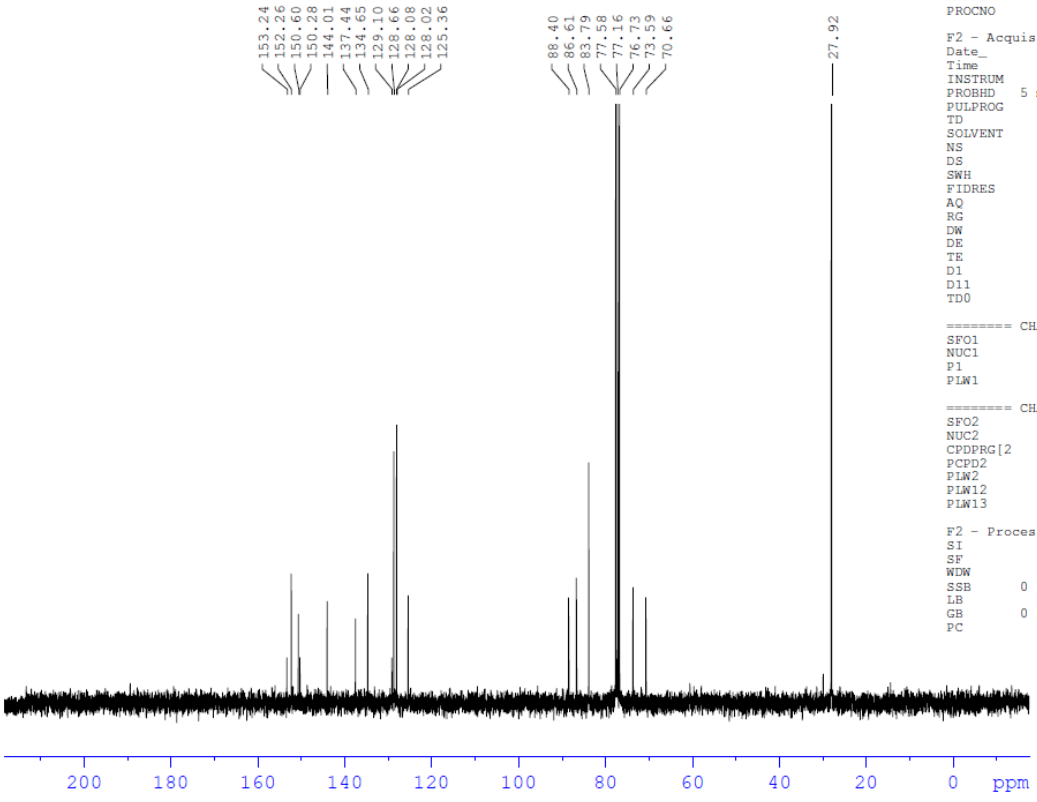

```
Current Data Parameters
NAME         KSY-4-069-H
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170125
Time               22.25
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    11
DS                     2
SWH            10000.000 Hz
FIDRES             0.152588 Hz
AQ                 3.2767999 sec
RG                   143.9
DW                  50.000 usec
DE                   6.50 usec
TE                  299.1 K
D1              2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1           500.3030896 MHz
NUC1                   1H
P1                  11.20 usec
PLW1           21.00000000 W

F2 - Processing parameters
SI                 65536
SF             500.3000138 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

KSY-4-069C 1 1 yhr 20170120




```
Current Data Parameters
NAME         KSY-4-069C
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170124
Time               15.36
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   226
DS                     2
SWH            18028.846 Hz
FIDRES             0.275098 Hz
AQ                 1.8175317 sec
RG                   12.7
DW                  27.733 usec
DE                   6.50 usec
TE                  293.1 K
D1              1.50000000 sec
D11             0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1           75.4752953 MHz
NUC1                  13C
P1                  10.20 usec
PLW1           18.97400093 W

======== CHANNEL f2 ========
SFO2          300.1312005 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               90.00 usec
PLW2           8.75839996 W
PLW12          0.13083000 W
PLW13          0.10598000 W

F2 - Processing parameters
SI                 32768
SF            75.4677410 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```