Supporting Information

For

Microwave-Assisted Synthesis of Base-Modified Fluorescent 1,4-Dihydropyridine Nucleosides: Photophysical Characterization and Insights

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Experimental Part and NMR Spectra

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1. Experimental

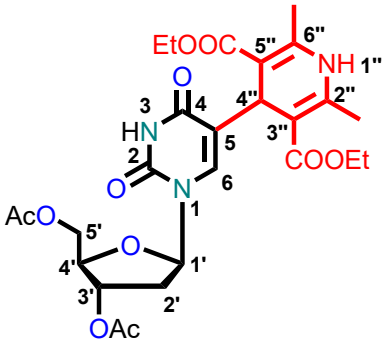
Unless otherwise noted, all chemicals and solvents were used directly without further purification and were acquired from Sigma-Aldrich Chemicals Pvt. Limited India and Alfa-Aesar (Thermo Fischer Scientific India Pvt. Limited), as well as from local commercial sources. Solvents used in column chromatography were dried and distilled prior to use. Solvents were removed using a rotary evaporator at low pressure, and the remaining solvent was removed thereafter under high vacuum. The column chromatography method used silica gel (100–200 mesh). Using a Buchi M-560 instrument that was not adjusted, melting points were determined. An Agilent G6530AA LC Q-TOF mass spectrometer was used to conduct the HRMS analysis using the ESI method. Using a PerkinElmer model 2000 FT-IR spectrometer, the IR spectra of various compounds were recorded and represented as wavenumbers (cm^{-1}). The compounds were visible under UV irradiation or by charring with a 5% alcoholic sulfuric acid solution. The R_f values of the compounds were reported from an analytical TLC examination utilizing the indicated solvents and 0.25 mm silica gel 60 F254 plates. Using tetramethylsilane (TMS) as an internal standard, the ^{1}H-, ^{13}C-, and other 2D NMR spectra were recorded on the JEOL alpha-400 and Bruker-Avance Neo 400 FT-NMR spectrometers. The coupling constant (*J*) is expressed in Hz while the chemical shift values are on the δ scale. All microwave assisted experiments were performed in a closed vial reaction vial applying a dedicated CEM-Discover monomode microwave apparatus operating at a frequency of 2.45 GHz with continuous irradiation power from 0 to 300 W (CEM Corporation, P.O. Box 200, Matthews, NC 28106).

1.1. General method for the synthesis of 3',5'-di-O-acetyl-5-(dialkyl 2'',6''-dimethyl-1'',4''-dihydropyridine-3'',5''-dicarboxylate)-4''-yl-2'-deoxyuridine (5a-h) and 3',5'-di-O-acetyl-5-(3'',5''-Diacetyl-2'',6''-dimethyl-1'',4''-dihydropyridine)-4''-yl-2'-deoxyuridine (5i)

A mixture of 3',5'-di-O-acetyl-5-formyl-2'-deoxyuridine (**3**, 1 mmol), β-keto ester (**4a-h**, 3 mmol) or acetyl acetone **4i**, ammonium acetate (1.2 mmol) and $Ba(NO_3)_2$ (0.1 mmol) was stirred in a microwave vial at 60 ˚C for 20 minutes under solvent-free conditions at 150 W and 1 atm pressure. After completion of the reaction (as indicated by TLC examination), the residue was extracted with chloroform (3 x 20 mL) and the organic layer was washed with brine solution (3 x 20 mL). The organic layer was dried over anhydrous sodium sulphate and excess

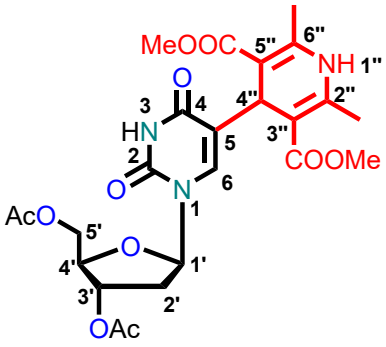
solvent was removed under reduced pressure. The crude product thus obtained was purified by column chromatography using MeOH in chloroform as the gradient solvent system to afford the desired products **5a-i** in 86-96% yields.

1.1.1. 3',5'-Di-O-acetyl-5-(diethyl 2'',6''-dimethyl-1'',4''-dihydropyridine-3'',5''-dicarboxylate)-4''-yl-2'-deoxyuridine (5a)



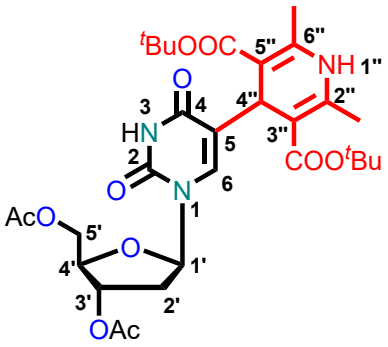
It was obtained as a white solid in 93% yield (0.52 g). R_f = 0.42 (5% MeOH in chloroform); Melting Point = 202-204 °C; IR (KBr, cm^{-1}): 3328, 2976, 1743, 1674, 1492, 1465, 1375, 1271, 1200, 1092, 1056, 1020, 774, 597, 552, 424; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.54 (brs, 1H, N-3H), 7.46 (brs, 1H, C-6H), 6.76 (s, 1H, N-1''H), 6.34-6.31 (m, 1H, C-1'H), 5.25-5.24 (m, 1H, C-3'H), 4.72 (s, 1H, C-4''H), 4.35-4.31 (m, 1H, C-4'H), 4.28-4.24 (m, 1H, C-5'H), 4.22-4.20 (m, 1H, C-5'H), 4.12-4.02 (m, 4H, 2 x C$\underline{H}_2$CH$_3$), 2.41-2.36 (m, 1H, C-2'H$_{a+b}$), 2.28-2.26 (m, 1H, C-2'H), 2.23 (s, 3H, CH$_3$), 2.22 (s, 3H, CH$_3$), 2.20 (s, 3H, CH$_3$), 2.10 (s, 3H, CH$_3$), 1.23 (t, J = 7.1 Hz, 3H, CH$_2$C$\underline{H}_3$), 1.17 (t, J = 7.1 Hz, 3H, CH$_2$C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.9 (OCOCH$_3$), 170.4 (OCOCH$_3$), 167.6 (COOEt), 167.4 (COOEt), 162.3 (CONH), 150.3 (CONH), 146.7 (C-2''), 146.3 (C-6''), 137.3 (C-6), 117.3 (C-5), 98.6 (C-5''), 98.4 (C-3''), 84.6 (C-1'), 81.9 (C-4'), 74.5 (C-3'), 64.2 (C-5'), 59.7 ($\underline{C}H_2$CH$_3$), 59.6 ($\underline{C}H_2$CH$_3$), 37.4 (C-2'), 36.1 (C-4''), 20.9 (CH$_3$), 20.9 (CH$_3$), 19.8 (CH$_3$), 19.3 (CH$_3$), 14.5 (CH$_2\underline{C}$H$_3$), 14.3 (CH$_2\underline{C}$H$_3$); HRMS (ESI): *m/z* calculated for $C_{26}H_{34}N_3O_{11}^+$ $[M+H]^+$: 564.2193, found: 564.2218.

1.1.2. 3',5'-Di-O-acetyl-5-(dimethyl 2'',6''-dimethyl-1'',4''-dihydropyridine-3'',5''-dicarboxylate)-4''-yl-2'-deoxyuridine (5b)



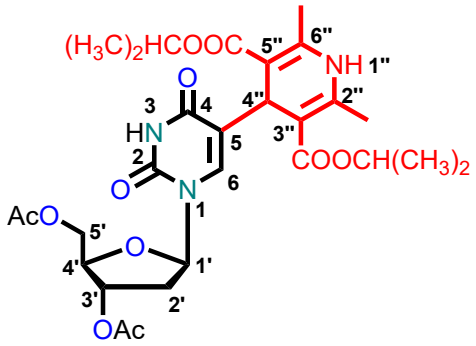
It was obtained as a white solid in 96% yield (0.51 g). R_f = 0.41 (5% MeOH in chloroform); Melting Point = 196-198 °C; IR (KBr, cm^{-1}): 3278, 2916, 1728, 1658, 1457, 1363, 1266, 1054, 1009, 761, 603, 562; ^1H NMR ($CDCl_3$, 400 MHz): δ 9.40 (brs, 1H, N-3H), 7.43 (brs, 1H, C-6H), 6.76 (s, 1H, N-1"H), 6.38-6.34 (m, 1H, C-1'H), 5.27-5.25 (m, 1H, C-3'H), 4.72 (s, 1H, C-4"H), 4.33-4.31 (m, 2H, C-4'H, C-5'H), 4.24-4.22 (m, 1H, C-5'H), 3.65 (s, 3H, CH_3), 3.59 (s, 3H, CH_3), 2.44-2.39 (m, 1H, C-2'H_a), 2.27-2.24 (m, 1H, C-2'H_b), 2.23 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.11 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.8 ($OCOCH_3$), 170.5 ($OCOCH_3$), 168.0 (COOMe), 167.8 (COOMe), 162.3 (CONH), 150.3 (CONH), 146.9 (C-2", C-6"), 137.0 (C-6), 117.3 (C-5), 98.5 (C-3", C-5"), 84.4 (C-1'), 81.9 (C-4'), 74.5 (C-3'), 64.3 (C-5'), 51.0 (CH_3), 50.9 (CH_3), 37.4 (C-2'), 35.9 (C-4"), 21.0 (CH_3), 20.8 (CH_3), 19.6 (CH_3), 19.3 (CH_3); HRMS (ESI): *m/z* calculated for $C_{24}H_{29}N_3O_{11}Na^+$ $[M+Na]^+$: 558.1700, found: 558.1729.

1.1.3. 3',5'-Di-O-acetyl-5-(di^{t}butyl 2",6"-dimethyl-1",4"-dihydropyridine-3",5"-dicarboxylate)-4"-yl-2'-deoxyuridine (5c)



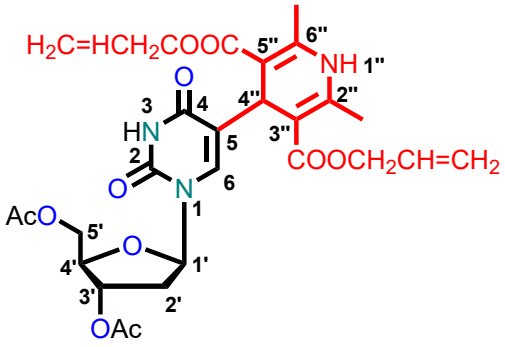
It was obtained as a white solid in 90% yield (0.56 g). R_f = 0.45 (5% MeOH in chloroform); Melting Point = 199-200 °C; IR (KBr, cm^{-1}): 3296, 2936, 1711, 1622, 1488, 1354, 1228, 1026, 785, 583, 548, 496; ^1H NMR ($CDCl_3$, 400 MHz): δ 9.46 (brs, 1H, N-3H), 7.48 (brs, 1H, C-6H), 6.38 (s, 1H, N-1"H), 6.36-6.32 (m, 1H, C-1'H), 5.26-5.24 (m, 1H, C-3'H), 4.65 (s, 1H, C-4"H), 4.36-4.31 (m, 1H, C-4'H), 4.22-4.21 (m, 1H, C-5'H), 4.21-4.19 (m, 1H, C-5'H), 2.36-2.31 (m, 1H, C-2'H_{a+b}), 2.23 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 2.01-2.00 (m, 1H, C-2H), 1.41 (s, 9H, $C(CH_3)_3$), 1.38 (s, 9H, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.0 ($OCOCH_3$), 170.4 ($OCOCH_3$), 166.9 (COOBu^t), 162.4 (CONH), 150.5 (CONH), 145.7 (C-2"), 144.9 (C-6"), 137.1 (C-6), 117.2 (C-5), 99.9 (C-3"), 99.5 (C-5"), 84.4 (C-1'), 81.9 (C-4'), 79.6 ($C(CH_3)_3$), 79.4 ($C(CH_3)_3$), 74.7 (C-3'), 64.2 (C-5'), 37.3 (C-2'), 36.5 (C-4"), 28.5 (CH_3), 28.4 (CH_3), 21.0 (CH_3), 20.9 (CH_3), 20.0 (CH_3), 19.3 (CH_3); HRMS (ESI): *m/z* calculated for $C_{30}H_{42}N_3O_{11}^+$ $[M+H]^+$: 620.2819, found: 620.2818.

1.1.4. 3',5'-Di-O-acetyl-5-(diisopropyl 2'',6''-dimethyl-1'',4''-dihydropyridine-3'',5''-dicarboxylate)-4''-yl-2'-deoxyuridine (5d)



It was obtained as a white solid in 92% yield (0.54 g). R_f = 0.43 (5% MeOH in chloroform); Melting Point = 208-209 °C; IR (KBr, cm^{-1}): 3324, 1710, 1683, 1656, 1584, 1557, 1512, 1458, 1412, 1304, 1277, 1232, 1169, 1105, 1051, 825, 780, 591; ^{1}H NMR ($CDCl_3$, 400MHz): δ 9.41 (brs, 1H, N-3H), 7.50 (brs, 1H, C-6H), 6.54 (s, 1H, N-1''H), 6.34-6.30 (m, 1H, C-1'H), 5.26-5.24 (m, 1H, C-3'H), 4.99-4.92 (m, 2H, C<u>H</u>$(CH_3)_2$), 4.69 (s, 1H, C-4''H), 4.37-4.33 (m, 1H, C-4'H), 4.28-4.24 (m, 1H, C-5'H), 4.23-4.20 (m, 1H, C-5'H), 2.39-2.34 (m, 1H, C-2'H_a), 2.30-2.26 (m, 1H, C-2'H_b), 2.22 (s, 6H, CH_3), 2.18 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 1.22-1.19 (m, 3H, CH_3), 1.19-1.17 (m, 6H, 2 x CH_3), 1.13-1.12 (m, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100MHz): δ 171.0 (O<u>C</u>OCH_3), 170.5 (O<u>C</u>OCH_3), 167.1 (<u>C</u>OOCH$(CH_3)_2$), 162.3 (CONH), 150.4 (CONH), 146.4 (C-2''), 145.8 (C-6''), 137.5 (C-6), 117.2 (C-5), 98.9 (C-3''), 98.6 (C-5''), 84.6 (C-1'), 82.0 (C-4'), 74.7 (C-3'), 67.0 (<u>C</u>H$(CH_3)_2$), 66.7 (<u>C</u>H$(CH_3)_2$), 64.2 (C-5'), 37.5 (C-2'), 36.3 (C-4''), 22.2 (CH_3), 22.2 (CH_3), 22.1 (CH_3), 22.0 (CH_3), 21.0 (CH_3), 20.9 (CH_3), 20.0 (CH_3), 19.4 (CH_3); HRMS (ESI): *m/z* calculated for $C_{28}H_{38}N_3O_{11}^+$ $[M+H]^+$: 592.2506, found: 592.2525.

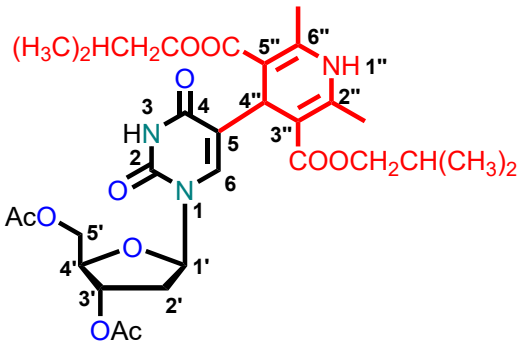
1.1.5. 3',5'-Di-O-acetyl-5-(diallyl 2'',6''-dimethyl-1'',4''-dihydropyridine-3'',5''-dicarboxylate)-4''-yl-2'-deoxyuridine (5e)



It was obtained as a white solid in 94% yield (0.55 g). R_f = 0.40 (5% MeOH in chloroform); Melting Point = 214-216 °C; IR (KBr, cm^{-1}): 3319, 2949, 1739, 1665, 1492, 1456, 1384, 1230,

1194, 1104, 1014, 783, 734, 597, 561, 434; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.50 (brs, 1H, N-3H), 7.46 (brs, 1H, C-6H), 6.83 (s, 1H, N-1"H), 6.34-6.31 (m, 1H, C-1'H), 5.95-5.89 (m, 1H, C-3'H), 5.88-5.82 (m, 1H, -C<u>H</u>=CH_2), 5.29-5.26 (m, 1H, -C<u>H</u>=CH_2), 5.24-5.21 (m, 2H, -CH=C<u>H</u>$_2$), 5.20-5.19 (m, 1H, -CH=CH_{2a}), 5.17-5.13 (m, 2H, -CH=CH_{2b}, C-4'H), 4.76 (s, 1H, C-4"H), 4.63-4.58 (m, 1H, CH_{2a}), 4.53-4.52 (m, 2H, CH_2), 4.36-4.32 (m, 1H, CH_{2b}), 4.27-4.24 (m, 1H, C-5'H), 4.22-4.20 (m, 1H, C-5'H), 2.38-2.33 (m, 1H, C-2'H_a), 2.27-2.25 (m, 1H, C-2'H_b), 2.24 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.10 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.8 ($OCOCH_3$), 170.4 ($OCOCH_3$), 167.1 ($COOCH_2CH$=CH), 167.0 ($COOCH_2CH$=CH), 162.3 (CONH), 150.3 (CONH), 147.1 (C-2"), 147.1 (C-6"), 137.3 (C-6), 133.1 (-<u>C</u>H=CH_2), 132.9 (-<u>C</u>H=CH_2), 117.7 (-CH=<u>C</u>H_2), 117.6 (-CH=<u>C</u>H_2), 116.9 (C-5), 98.2 (C-3", C-5"), 84.5 (C-1'), 81.9 (C-4'), 74.5 (C-3'), 64.6 (CH_2), 64.6 (CH_2), 67.0 ($CH(CH_3)_2$), 66.7 ($CH(CH_3)_2$), 64.2 (C-5'), 37.4 (C-2'), 36.2 (C-4"), 20.9 (CH_3), 20.9 (CH_3), 19.8 (CH_3), 19.5 (CH_3); HRMS (ESI): *m/z* calculated for $C_{28}H_{34}N_3O_{11}^+$ $[M+H]^+$: 588.2193, found: 588.2176.

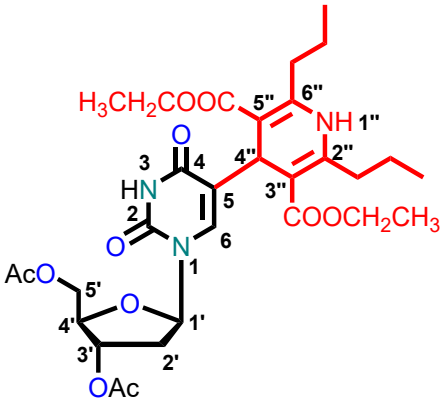
1.1.6. 3',5'-Di-O-acetyl-5-(diisobutyl 2",6"-dimethyl-1",4"-dihydropyridine-3",5"-dicarboxylate)-4"-yl-2'-deoxyuridine (5f)



It was obtained as a white solid in 92% yield (0.57 g). R_f = 0.46 (5% MeOH in chloroform); Melting Point = 204-205 °C; IR (KBr, cm^{-1}): 3314, 1717, 1675, 1641, 1529, 1422, 1297, 1214, 1151, 1101, 1069, 833, 786, 577; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.42 (brs, 1H, N-3H), 7.50 (brs, 1H, C-6H), 6.79 (s, 1H, N-1"H), 6.33-6.30 (m, 1H, C-1'H), 5.27-5.25 (m, 1H, C-3'H), 4.78 (s, 1H, C-4"H), 4.37-4.34 (m, 1H, C-4'H), 4.29-4.24 (m, 2H, 2 x C-5'H), 3.89-3.85 (m, 2H, CH_2), 3.83-3.78 (m, 2H, CH_2), 2.41-2.36 (m, 1H, C-2'H_a), 2.32-2.28 (m, 1H, C-2'H_b), 2.26 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 1.94-1.88 (m, 2H, 2 x C<u>H</u>$(CH_3)_2$), 0.94-0.93 (m, 6H, 2 x CH_3), 0.90-0.87 (m, 6H, 2 x CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.0 (O<u>C</u>OCH_3), 170.4 (O<u>C</u>OCH_3), 167.7 (<u>C</u>O$OCH_2CH(CH_3)_2$), 167.6 (<u>C</u>O$OCH_2CH(CH_3)_2$), 162.4 (CONH), 150.3 (CONH), 146.5 (C-2"), 146.0 (C-6"), 137.4 (C-6), 117.1 (C-5), 98.8 (C-3"), 98.6 (C-5"), 84.8 (C-1'), 82.0 (C-4'), 74.6 (C-3'), 70.3 (CH_2), 70.2

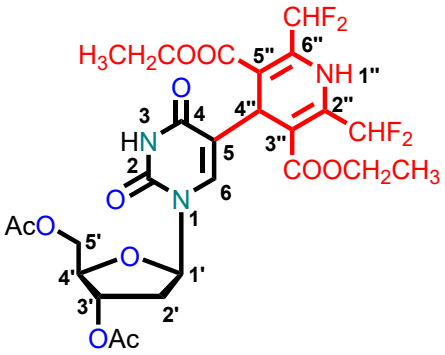
(CH_2), 64.2 (C-5'), 37.3 (C-2'), 36.0 (C-4''), 27.8 ($\underline{C}H(CH_3)_2$), 27.7 ($\underline{C}H(CH_3)_2$), 20.9 (CH_3), 20.9 (CH_3), 19.9 (CH_3), 19.4 (CH_3), 19.3 (CH_3); HRMS (ESI): *m/z* calculated for $C_{30}H_{42}N_3O_{11}^+$ $[M+H]^+$: 620.2819, found: 620.2821.

1.1.7. 3',5'-Di-O-acetyl-5-(diethyl 2'',6''-dipropyl-1'',4''-dihydropyridine-3'',5''-dicarboxylate)-4''-yl-2'-deoxyuridine (5g)



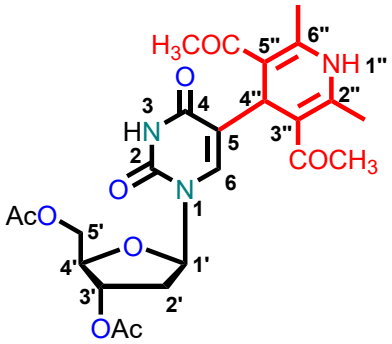
It was obtained as a white solid in 88% yield (0.55 g). R_f = 0.47 (5% MeOH in chloroform); Melting Point = 216-218 ˚C; IR (KBr, cm^{-1}): 3333, 2921, 1719, 1639, 1472, 1435, 1362, 1226, 1182, 1011, 771, 727, 596, 552; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.31 (brs, 1H, N-3H), 7.45 (brs, 1H, C-6H), 6.36-6.32 (m, 1H, C-1'H), 6.29 (s, 1H, N-1''H), 5.25-5.23 (m, 1H, C-3'H), 4.75 (s, 1H, C-4''H), 4.36-4.32 (m, 1H, C-4'H), 4.28-4.24 (m, 1H, C-5'H), 4.22-4.20 (m, 1H, C-5'H), 4.14-4.05 (m, 4H, 2 x $C\underline{H}_2CH_3$), 2.76-2.68 (m, 2H, CH_2), 2.47-2.43 (m, 1H, CH_{2a}), 2.41-2.35 (m, 2H, C-2'H_a, CH_{2b}), 2.27-2.25 (m, 1H, C-2'H_b), 2.23 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 1.62-1.52 (m, 4H, 2 x CH_2), 1.24 (t, J = 7.1 Hz, 3H, $CH_2C\underline{H}_3$), 1.18 (t, J = 7.1 Hz, 3H, $CH_2C\underline{H}_3$), 0.96-0.93 (m, 6H, 2 x CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.9 ($O\underline{C}OCH_3$), 170.4 ($O\underline{C}OCH_3$), 167.3 ($\underline{C}OOEt$), 167.0 ($\underline{C}OOEt$), 161.9 (CONH), 150.7 (CONH), 150.3 (C-2''), 150.3 (C-6''), 137.1 (C-6), 117.4 (C-5), 98.3 (C-5''), 98.1 (C-3''), 84.5 (C-1'), 81.9 (C-4'), 74.6 (C-3'), 64.2 (C-5'), 59.7 ($\underline{C}H_2CH_3$), 59.6 ($\underline{C}H_2CH_3$), 37.4 (C-2'), 36.2 (C-4''), 35.1 (CH_2), 34.5 (CH_2), 22.0 (CH_2), 21.9 (CH_2), 20.9 (CH_3), 20.9 (CH_3), 14.5 ($CH_2\underline{C}H_3$), 14.3 ($CH_2\underline{C}H_3$), 14.0 ($CH_2\underline{C}H_3$); HRMS (ESI): *m/z* calculated for $C_{30}H_{42}N_3O_{11}^+$ $[M+H]^+$: 620.2819, found: 620.2819.

1.1.8. 3',5'-di-O-acetyl-5-(diethyl 2'',6''-bisdifluoromethyl-1'',4''-dihydropyridine-3'',5''-dicarboxylate)-4''-yl-2'-deoxyuridine (5h)



It was obtained as a white solid in 86% yield (0.55 g). R_f = 0.42 (5% MeOH in chloroform); Melting Point = 212-213 ˚C; IR (KBr, cm^{-1}): 3338, 1712, 1650, 1583, 1517, 1422, 1313, 1267, 1228, 1164, 1121, 1049, 774, 563; ^1H NMR ($CDCl_3$, 400 MHz): δ 9.22-9.20 (m, 1H, N-3H), 7.39 (brs, 1H, N-1"H), 7.28-7.06 (m, 1H, C-6H), 6.35-6.30 (m, 1H, C-1'H), 5.95-5.72 (m, 1H, CHF_2), 5.67-5.54 (m, 1H, CHF_2), 5.24-5.19 (m, 1H, C-3'H), 4.43-4.38 (m, 1H, C-4"H), 4.28-4.23 (m, 2H, 2 x C-5'H), 4.18-4.11 (m, 4H, 2 x $C\underline{H}_2CH_3$), 4.05-4.00 (m, 1H, C-4'H), 2.47-2.39 (m, 1H, C-2'H_a), 2.18-2.16 (m, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.10-2.05 (m, 1H, C-2'H_b), 1.21-1.16 (m, 3H, $CH_2C\underline{H}_3$), 1.15-1.10 (m, 3H, $CH_2C\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.6 ($O\underline{C}OCH_3$), 172.4 ($O\underline{C}OCH_3$), 170.6-170.4 (m, $\underline{C}OOEt$), 164.9 (d, J = 18.8 Hz, $\underline{C}OOEt$), 161.6 (CONH), 150.1-149.9 (m, C-2" & C-6"), 137.2 (C-6), 116.3 (d, J = 7.8 Hz, CHF_2), 113.8 (d, J = 6.6 Hz, C-5), 111.3 (d, J = 6.8 Hz, C-5"), 109.3 (d, J = 6.6 Hz, C-3"), 103.3 (d, J = 5.0 Hz, CHF_2), 84.8 (C-1'), 82.3 (d, J = 7.6 Hz, C-4'), 74.3 (d, J = 42.1 Hz, C-3'), 63.9 (d, J = 32.3 Hz, C-5'), 62.3 (d, J = 20.7 Hz, $\underline{C}H_2CH_3$), 60.6 (d, J = 1.9 Hz, $\underline{C}H_2CH_3$), 37.5 (C-2'), 37.5 (C-4"), 20.9 (CH_3), 20.9-20.7 (m, CH_3), 14.1-13.9 (m, $CH_2\underline{C}H_3$); HRMS (ESI): *m/z* calculated for $C_{26}H_{29}F_4N_3O_{11}Na^+$ $[M+Na]^+$: 658.1636, found: 658.1635.

1.1.9. 3',5'-di-O-acetyl-5-(3",5"-Diacetyl-2",6"-dimethyl-1",4"-dihydropyridine)-4"-yl-2'-deoxyuridine (5i)



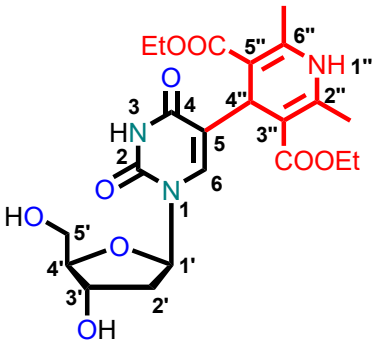
It was obtained as a yellow solid in 94% yield (0.47 g). R_f = 0.46 (5% MeOH in chloroform); Melting Point = 256-258 ˚C; IR (KBr, cm^{-1}): 3318, 1747, 1718, 1450, 1221, 1124, 1008, 786, 628; ^1H NMR ($CDCl_3$, 400 MHz): δ 9.40 (brs, 1H, N-3H), 7.15 (brs, 1H, C-6H), 6.75-6.67

(brs, 1H, N-1''H), 6.23-6.20 (m, 1H, C-1'H), 5.19-5.16 (m, 1H, C-3'H), 5.00 (s, 1H, C-4''H), 4.30-4.26 (m, 1H, C-4'H), 4.24-4.22 (m, 1H, C-5'H), 4.17-4.13 (m, 1H, C-5'H), 2.50-2.45 (m, 1H, C-2'H_a), 2.34 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 2.06-2.01 (m, 1H, C-2'H_b); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.3 (CO), 197.9 (CO), 171.1 (O<u>C</u>OCH_3), 170.4 (O<u>C</u>OCH_3), 162.7 (CONH), 150.0 (CONH), 144.0 (C-2''), 143.9 (C-6''), 136.8 (C-6), 117.6 (C-5), 110.6 (C-3''), 110.4 (C-3''), 85.3 (C-1'), 82.0 (C-4'), 74.3 (C-3'), 64.1 (C-5'), 37.3 (C-2'), 34.1 (C-4''), 29.9 (CH_3), 29.5 (CH_3), 20.9 (CH_3), 20.9 (CH_3), 19.9 (CH_3), 19.6 (CH_3); HRMS (ESI): *m/z* calculated for $C_{24}H_{30}N_3O_9^+$ $[M+H]^+$: 504.1982, found: 504.1901.

1.2. General method for the synthesis of 5-(diethyl 2'',6''-dimethyl-1'',4''-dihydropyridine-3'',5''-dicarboxylate)-4''-yl-2'-deoxyuridine (6a-h) and 5-(3'',5''-Diacetyl-2'',6''-dimethyl-1'',4''-dihydropyridine)-4''-yl-2'-deoxyuridine (6i)

To a solution of 3',5'-di-*O*-acetyl-5-(dialkyl 2'',6''-dimethyl-1'',4''-dihydropyridine-3'',5''-dicarboxylate)-2'-deoxyuridine (**5a-h**, 1mmol) or *3',5'-di-O-acetyl-5-(3'',5''-Diacetyl-2'',6''-dimethyl-1'',4''-dihydropyridine)-4''-yl-2'-deoxyuridine* (**5i**, 1mmol) in MeOH (10 mL), NaOMe (2.2 mmol) was added. The reaction mixture was stirred for 10-15 minutes at 25 ˚C. The progress of the reaction mixture was monitored through TLC. After completion of the reaction, the reaction mixture was neutralized with seralite (H^+) resin. The solution was then filtered through a cotton plug and removed under reduced pressure. The crude product thus obtained was purified by column chromatography using MeOH in chloroform as the solvent system to afford the desired products **6a-i** in 97-99% yields.

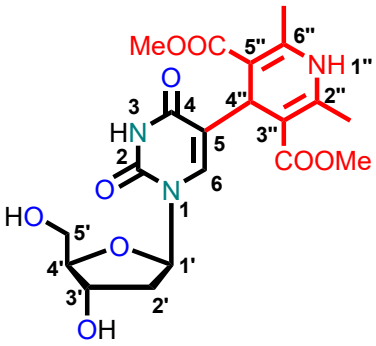
1.2.1. 5-(Diethyl 2'',6''-dimethyl-1'',4''-dihydropyridine-3'',5''-dicarboxylate)-4''-yl-2'-deoxyuridine (6a)



It was obtained as a white solid in 98% yield (0.47 g). R_f = 0.37 (10% MeOH in chloroform); Melting Point = 226-227 ˚C; IR (KBr, cm^{-1}): 3328, 3216, 1724, 1676, 1444, 1358, 1047, 775, 599, 556; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.05 (brs, 1H, N-3H), 8.76 (brs, 1H, N-1''H), 7.36 (s, 1H, C-6H), 6.17-6.14 (m, 1H, C-1'H), 5.27-5.26 (m, 1H, C-4'H), 4.93-4.91 (m, 1H, C-3'H), 4.66 (s, 1H, C-4''H), 4.21 (brs, 1H, OH), 4.06-4.02 (m, 2H, C$\underline{H}_2$CH$_3$), 4.00-3.93 (m, 2H, C$\underline{H}_2$CH$_3$), 3.79 (brs, 1H, OH), 3.55-3.51 (m, 1H, C-5'H), 3.51-3.47 (m, 1H, C-5'H), 2.17 (s, 3H, CH$_3$), 2.15 (s, 3H, CH$_3$), 2.10-2.06 (m, 1H, C-2'H$_a$), 1.90-1.87 (m, 1H, C-2'H$_b$), 1.17-1.15 (m, 3H, CH$_2$C$\underline{H}_3$), 1.15-1.13 (m, 3H, CH$_2$C$\underline{H}_3$); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 167.5 (COOEt), 167.4 (COOEt), 162.1 (CONH), 150.6 (CONH), 146.7 (C-2''), 146.4 (C-6''), 137.1 (C-6), 118.0 (C-5), 99.1 (C-5''), 98.9 (C-3''), 87.8 (C-1'), 84.3 (C-4'), 71.4 (C-3'), 62.3 (C-5'),

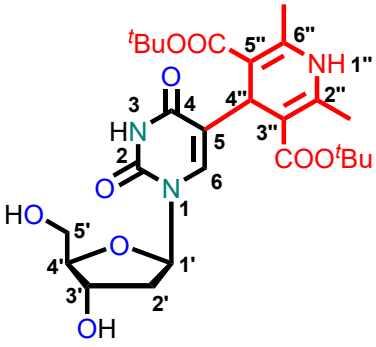
59.3 ($\underline{C}H_2CH_3$), 59.2 ($\underline{C}H_2CH_3$), 34.0 (C-2'), 18.6 (CH_3), 18.5 (CH_3), 14.8 ($CH_2\underline{C}H_3$), 14.7 ($CH_2\underline{C}H_3$); HRMS (ESI): *m/z* calculated for $C_{22}H_{30}N_3O_9^+$ $[M+H]^+$: 480.1982, found: 480.1992.

1.2.2. 5-(Dimethyl 2'',6''-dimethyl-1'',4''-dihydropyridine-3'',5''-dicarboxylate)-4''-yl-2'-deoxyuridine (6b)



It was obtained as a white solid in 97% yield (0.44 g). R_f = 0.38 (10% MeOH in chloroform); Melting Point = 222-224 ˚C; IR (KBr, cm^{-1}): 3278, 3196, 1718, 1648, 1450, 1353, 1256, 1054, 778, 610, 566; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.06 (brs, 1H, N-3H), 8.85 (brs, 1H, N-1''H), 7.32 (s, 1H, C-6H), 6.21-6.10 (m, 1H, C-1'H), 5.34-5.24 (m, 1H, C-4'H), 5.02-4.90 (m, 1H, C-3'H), 4.68 (s, 1H, C-4''H), 4.27-4.16 (m, 1H, C-5'H), 3.82-3.75 (m, 1H, C-5'H), 3.44-3.31 (m, 6H, 2 x CH_3), 2.17 (s, 6H, 2 x CH_3), 2.08-2.03 (m, 1H, C-2'H_a), 1.94-1.85 (m, 1H, C-2'H_b); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 167.9 ($\underline{C}$OOMe), 167.9 ($\underline{C}$OOMe), 162.3 (CONH), 150.6 (CONH), 146.8 (C-2''), 146.6 (C-6''), 136.9 (C-6), 117.6 (C-5), 98.9 (C-3''), 98.7 (C-5''), 87.8 (C-1'), 84.3 (C-4'), 71.4 (C-3'), 62.3 (C-5'), 51.0 (CH_3), 33.8 (C-2'), 18.4 (CH_3); HRMS (ESI): *m/z* calculated for $C_{20}H_{26}N_3O_9^+$ $[M+H]^+$: 452.1669, found: 452.1639.

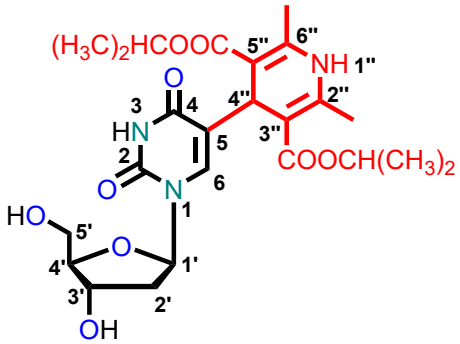
1.2.3. 5-(Di-^{t}butyl 2'',6''-dimethyl-1'',4''-dihydropyridine-3'',5''-dicarboxylate)-4''-yl-2'-deoxyuridine (6c)



It was obtained as a white solid in 98% yield (0.53 g). R_f = 0.42 (10% MeOH in chloroform); Melting Point = 229-231 ˚C; IR (KBr, cm^{-1}): 3210, 1720, 1638, 1464, 1319, 1229, 1008, 783, 577, 512; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.08 (brs, 1H, N-3H), 8.57 (brs, 1H, N-1''H), 7.10 (s, 1H, C-6H), 6.15-6.12 (m, 1H, C-1'H), 5.30-5.28 (m, 1H, C-4'H), 4.88 (brs, 1H, OH),

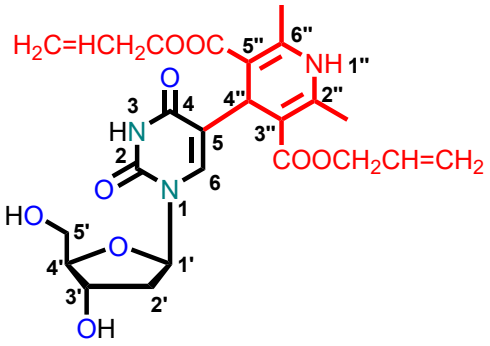
4.66 (s, 1H, C-4"H), 4.18-4.14 (m, 1H, C-3'H), 3.76 (brs, 1H, OH), 3.52-3.45 (m, 1H, C-5'H), 3.45-3.35 (m, 1H, C-5'H), 2.13 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.07-2.04 (m, 1H, C-2'H_a), 1.84-1.77 (m, 1H, C-2'H_b), 1.39 (s, 9H, $C(CH_3)_3$), 1.37 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 167.1 (COOBu^t), 167.0 (COOBu^t), 162.2 (CONH), 150.6 (CONH), 145.3 (C-2"), 144.4 (C-6"), 136.1 (C-6), 118.6 (C-5), 101.0 (C-3"), 100.4 (C-5"), 87.7 (C-1'), 84.2 (C-4'), 79.0 ($C(CH_3)_3$), 78.9 ($C(CH_3)_3$), 71.3 (C-3'), 62.4 (C-5'), 33.6 (C-2'), 28.5 (CH_3), 28.5 (CH_3), 18.5 (CH_3), 18.4 (CH_3); HRMS (ESI): *m/z* calculated for $C_{26}H_{38}N_3O_9^+$ $[M+H]^+$: 536.2608, found: 536.2582.

1.2.4. 5-(Diisopropyl 2",6"-dimethyl-1",4"-dihydropyridine-3",5"-dicarboxylate)-4"-yl-2'-deoxyuridine (6d)



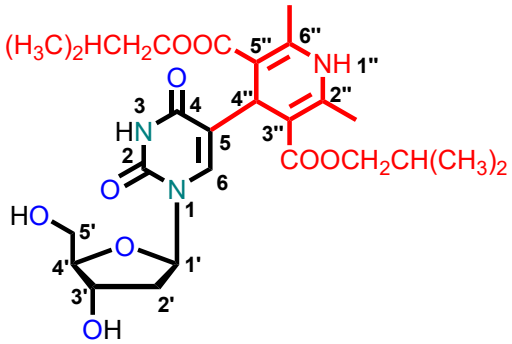
It was obtained as a white solid in 99% yield (0.50 g). R_f = 0.41 (10% MeOH in chloroform); Melting Point = 236-237 ˚C; IR (KBr, cm^{-1}): 3318, 3214, 1712, 1646, 1627, 1572, 1443, 1318, 1262, 1168, 781, 563; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.04 (brs, 1H, N-3H), 8.71 (brs, 1H, N-1"H), 7.25 (s, 1H, C-6H), 6.15-6.12 (m, 1H, C-1'H), 4.89-4.83 (m, 3H, C-4'H, 2 x C<u>H</u>$(CH_3)_2$), 4.65 (s, 1H, C-4"H), 4.20 (brs, 1H, OH), 3.78 (brs, 1H, OH), 3.54-3.52 (m, 1H, C-3'H), 3.48-3.45 (m, 1H, C-5'H), 3.18-3.16 (m, 1H, C-5'H), 2.16 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 2.10-2.06 (m, 1H, C-2'H_a), 1.89-1.83 (m, 1H, C-2'H_b), 1.18 (m, 3H, CH(C<u>H</u>$_3)_2$), 1.17 (m, 3H, CH(C<u>H</u>$_3)_2$), 1.14-1.12 (m, 3H, CH(C<u>H</u>$_3)_2$), 1.11-1.09 (m, 3H, CH(C<u>H</u>$_3)_2$); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 167.1 (<u>C</u>OOCH$(CH_3)_2$), 167.0 (<u>C</u>OOCH$(CH_3)_2$), 162.1 (CONH), 150.6 (CONH), 146.2 (C-2"), 145.8 (C-6"), 136.8 (C-6), 118.8 (C-5), 99.7 (C-3"), 99.4 (C-5"), 87.8 (C-1'), 84.4 (C-4'), 71.3 (C-3'), 66.4 (<u>C</u>H$(CH_3)_2$), 66.3 (<u>C</u>H$(CH_3)_2$), 62.3 (C-5'), 49.1 (C-4"), 33.6 (C-2'), 22.3 (CH_3), 22.2 (CH_3), 22.1 (CH_3), 18.7 (CH_3), 18.6 (CH_3); HRMS (ESI): *m/z* calculated for $C_{24}H_{34}N_3O_9^+$ $[M+H]^+$: 508.2295, found: 508.2282.

1.2.5. 5-(Diallyl 2",6"-dimethyl-1",4"-dihydropyridine-3",5"-dicarboxylate)-4"-yl-2'-deoxyuridine (6e)



It was obtained as a white solid in 97% yield (0.49 g). R_f = 0.40 (10% MeOH in chloroform); Melting Point = 220-222 °C; IR (KBr, cm^{-1}): 3269, 1727, 1635, 1482, 1456, 1368, 1246, 1074, 739, 592, 545; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.08 (brs, 1H, N-3H), 8.90 (brs, 1H, N-1"H), 7.27 (s, 1H, C-6H), 6.15-6.12 (m, 1H, C-1'H), 5.95-5.88 (m, 2H, 2 x -C<u>H</u>=CH_2), 5.27-5.26 (m, 1H, -CH=C<u>H</u>$_{2a}$), 5.25-5.22 (m, 1H, -CH=CH_{2b}), 5.20-5.17 (m, 1H, -CH=CH_{2a}), 5.17-5.14 (m, 1H, -CH=CH_{2b}), 5.14-5.11 (m, 1H, C-3'H), 4.90 (brs, 1H, OH), 4.75 (s, 1H, C-4"H), 4.53-4.50 (m, 3H, CH_2 & CH_{2a}), 4.21-4.16 (m, 1H, CH_{2b}), 3.80-3.76 (m, 1H, C-4'H), 3.53-3.45 (m, 2H, C-5'H), 3.36 (brs, 1H, OH), 2.19-2.18 (m, 6H, 2 x CH_3), 2.09-2.04 (m, 1H, C-2'H_a), 1.90-1.83 (m, 1H, C-2'H_b); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.1 (<u>C</u>OOCH$_2$CH=CH_2), 167.0 (<u>C</u>OOCH$_2$CH=CH_2), 162.2 (CONH), 150.6 (CONH), 147.2 (C-2"), 146.9 (C-6"), 136.9 (C-6), 134.0 (-<u>C</u>H=CH_2), 117.6 (-CH=CH_2), 117.4 (-CH=CH_2), 117.3 (C-5), 98.9 (C-3"), 98.5 (C-5"), 87.8 (C-1'), 84.4 (C-4'), 71.3 (C-3'), 64.1 (CH_2), 62.3 (CH_2), 33.8 (C-2'), 18.6 (CH_3); HRMS (ESI): *m/z* calculated for $C_{24}H_{30}N_3O_9^+$ $[M+H]^+$: 504.1982, found: 504.1975.

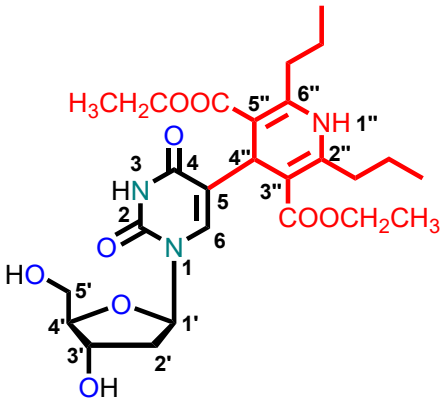
1.2.6. (5-(Diisobutyl 2",6"-dimethyl-1",4"-dihydropyridine-3",5"-dicarboxylate)-4"-yl-2'-deoxyuridine (6f)



It was obtained as a white solid in 98% yield (0.53 g). R_f = 0.43 (10% MeOH in chloroform); Melting Point = 231-232 °C; IR (KBr, cm^{-1}): 3280, 1732, 1616, 1534, 1411, 1252, 1212, 1126, 1043, 807, 556; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.07 (brs, 1H, N-3H), 8.84 (brs, 1H, N-1"H), 7.14 (s, 1H, C-6H), 6.14-6.11 (m, 1H, C-1'H), 5.30-5.25 (m, 1H, C-3'H), 4.86 (brs, 1H, OH), 4.80 (s, 1H, C-4"H), 4.19-4.15 (m, 1H, C-4'H), 3.80-3.73 (m, 5H, 2 x CH_2, OH), 3.51-3.48 (m,

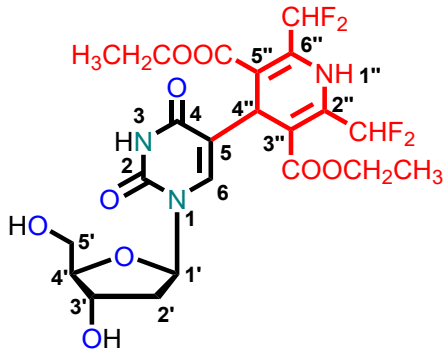
1H, C-5'H), 3.44-3.40 (m, 1H, C-5'H), 2.20 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.10-2.07 (m, 1H, C-2'H_a), 1.88-1.83 (m, 3H, C-2'H_b, 2 x C$\underline{H}(CH_3)_2$), 0.86-0.85 (m, 12H, 4 x CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.6 ($\underline{C}OOCH_2CH(CH_3)_2$), 167.4 ($\underline{C}OOCH_2CH(CH_3)_2$), 162.2 (CONH), 150.6 (CONH), 146.6 (C-2''), 145.9 (C-6''), 136.3 (C-6), 118.3 (C-5), 99.7 (C-3''), 99.1 (C-5''), 87.7 (C-1'), 84.3 (C-4'), 71.3 (C-3'), 69.7 (CH_2), 69.6 (CH_2), 62.4 (C-5'), 33.1 (C-2'), 27.8 ($\underline{C}H(CH_3)_2$), 27.7 ($\underline{C}H(CH_3)_2$), 19.6 (CH_3), 19.5 (CH_3), 19.5 (CH_3), 19.5 (CH_3), 18.4 (CH_3); HRMS (ESI): *m/z* calculated for $C_{26}H_{38}N_3O_9^+$ $[M+H]^+$: 536.2608, found: 536.2607.

1.2.7. 5-(Diethyl 2'',6''-propyl-1'',4''-dihydropyridine-3'',5''-dicarboxylate)-4''-yl-2'-deoxyuridine (6g)



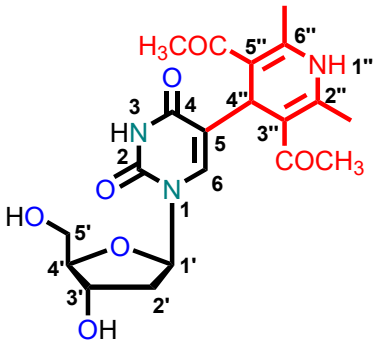
It was obtained as a white solid in 98% yield (0.53 g). R_f = 0.46 (10% MeOH in chloroform); Melting Point = 238-240 ˚C; IR (KBr, cm^{-1}): 3378, 3262, 1736, 1646, 1466, 1238, 1156, 1028, 732, 610, 559; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.05 (brs, 1H, N-3H), 8.99 (brs, 1H, N-1''H), 7.29 (s, 1H, C-6H), 6.16-6.12 (m, 1H, C-1'H), 5.31 (brs, 2H, OH), 4.71 (s, 1H, C-4''H), 4.20-4.19 (m, 1H, C-3'H), 4.05-3.96 (m, 4H, 2 x CH_2), 3.78-3.75 (m, 1H, C-4'H), 3.53-3.50 (m, 1H, C-5'H), 3.46-3.42 (m, 1H, C-5'H), 2.73-2.64 (m, 2H, C-2'H_{a+b}), 2.48-2.41 (m, 2H, CH_2), 2.10-2.04 (m, 1H, CH_{2a}), 1.88-1.82 (m, 1H, CH_{2b}), 1.51-1.44 (m, 4H, 2 x CH_2), 1.15 (t, 6H, J = 7.1 Hz, 2 x $OCH_2\underline{C}H_3$), 0.87 (t, 6H, J = 7.3 Hz, 2 x $CH_2\underline{C}H_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.2 (COOEt), 167.2 (COOEt), 162.0 (CONH), 150.7 (CONH), 150.6 (C-2'', C-6''), 136.8 (C-6), 119.3 (C-5), 99.3 (C-3'', C-5''), 87.7 (C-1'), 84.1 (C-4'), 71.4 (C-3'), 62.3 (C-5'), 59.3 ($\underline{C}H_2CH_3$), 59.3 ($\underline{C}H_2CH_3$), 33.2 (C-2'), 33.0 (CH_2), 32.9 (CH_2), 22.3 (CH_2), 14.7 ($CH_2\underline{C}H_3$), 14.6 ($CH_2\underline{C}H_3$), 14.2 ($CH_2\underline{C}H_3$); HRMS (ESI): *m/z* calculated for $C_{26}H_{38}N_3O_9^+$ $[M+H]^+$: 536.2608, found: 536.2601.

1.2.8. 5-(Diethyl 2'',6''-bisdifluorodimethyl-1'',4''-dihydropyridine-3'',5''-dicarboxylate)-4''-yl-2'-deoxyuridine (6h)



It was obtained as a white solid in 98% yield (0.54 g). R_f = 0.39 (10% MeOH in chloroform); Melting Point = 213-214 °C; IR (KBr, cm^{-1}): 3323, 1731, 1640, 1551, 1412, 1337, 1236, 1148, 1107, 1062, 756, 568; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.25 (brs, 1H, N-3H), 7.67-7.55 (m, 1H, C-6H), 7.45-7.33 (m, 1H, CHF_2), 7.24 (brs, 1H, N-1"H), 6.18-6.13 (m, 1H, CHF_2), 4.82 (brs, 2H, OH), 4.28-4.22 (m, 1H, C-1'H), 4.15-4.06 (m, 1H, C-3'H), 4.05-4.00 (m, 2H, C-5'H), 3.95-3.87 (m, 2H, $C\underline{H}_2CH_3$), 3.83-3.79 (m, 1H, C-4"H), 3.59-3.49 (m, 2H, $C\underline{H}_2CH_3$), 3.27-3.17 (m, 1H, C-4'H), 2.10-2.04 (m, 1H, C-2'H_a), 1-93-1.85 (m, 1H, C-2'H_b), 1.09-1.01 (m, 6H, $CH_2C\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.3-170.2 (m, $\underline{C}$OOEt), 165.9-165.5 (m, $\underline{C}$OOEt), 163.2 (d, J = 8.6 Hz, CONH), 162.1 (CONH), 150.5-150.4 (m, C-2" & C-6"), 138.2 (C-6), 115.3 (C-5), 114.5-114.2 (m, CHF_2), 112.6-110.0 (m, CHF_2), 109.4 (C-5"), 88.1 (d, J = 3.5 Hz, C-3"), 84.8 (d, J = 9.3 Hz, C-1'), 79.2-78.9 (m, C-4'), 71.5-71.2 (m, C-3'), 62.3-62.1 (m, C-5'), 61.1-60.7 (m, $\underline{C}H_2CH_3$), 60.0-59.9 (m, $\underline{C}H_2CH_3$), 33.7 (C-2'), 14.5-14.2 (m, $CH_2\underline{C}H_3$),; HRMS (ESI): *m/z* calculated for $C_{22}H_{26}F_4N_3O_9^+$ $[M+H]^+$: 552.1605, found: 552.1653.

1.2.9. 5-(3",5"-Diacetyl-2",6"-dimethyl-1",4"-dihydropyridine)-4"-yl-2'-deoxyuridine (6i)



It was obtained as a yellow solid in 98% yield (0.41 g). R_f = 0.44 (10% MeOH in chloroform); Melting Point = 224-225 °C; IR (KBr, cm^{-1}): 3334, 3274, 1719, 1616, 1448, 1223, 1147, 1022, 747, 619; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.23 (brs, 1H, N-3H), 8.97 (brs, 1H, N-1"H), 7.02 (s, 1H, C-6H), 6.13-6.10 (m, 1H, C-1'H), 5.28 (brs, 1H, OH), 5.03 (brs, 1H, OH), 4.87 (s, 1H, C-4"H), 4.18-4.15 (m, 1H, C-3'H), 3.78-3.75 (m, 1H, C-4'H), 3.51-3.47 (m, 1H, C-5'H), 3.44-3.40 (m, 1H, C-5'H), 2.26 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.19 (s, 3H, CH_3),

2.11-2.06 (m, 1H, C-2'H_a), 1.87-1.80 (m, 1H, C-2'H_b; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 197.7 (<u>CO</u>CH_3), 197.5 (<u>CO</u>CH_3), 163.1 (CONH), 150.4 (CONH), 144.5 (C-2''), 144.0 (C-6''), 136.3 (C-6), 117.5 (C-5), 110.4 (C-3''), 109.9 (C-5''), 87.9 (C-1'), 84.6 (C-4'), 71.3 (C-3'), 62.3 (C-5'), 32.7 (C-2'), 29.8 (CO<u>CH_3</u>), 18.9 (CH_3), 18.8 (CH_3); HRMS (ESI): *m/z* calculated for $C_{20}H_{26}N_3O_7^+$ $[M+H]^+$: 420.1771, found: 420.1751.

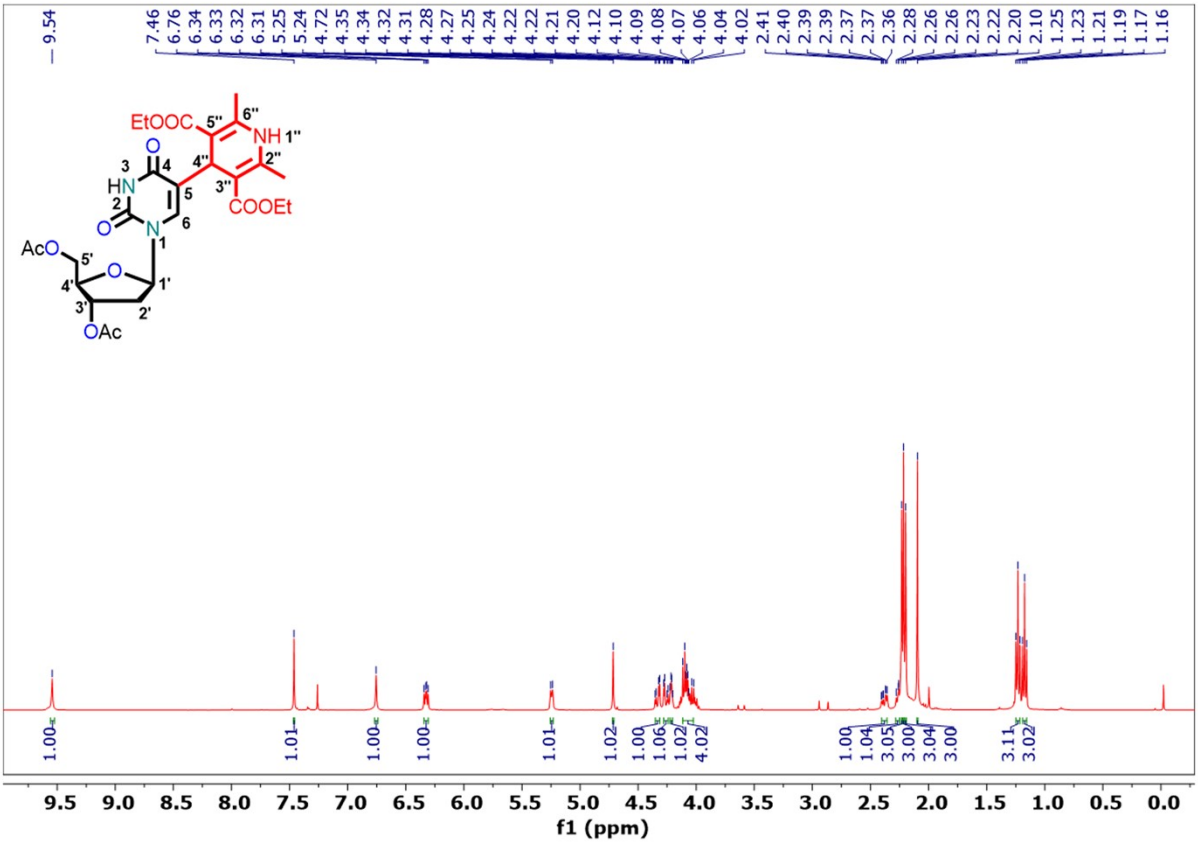


Figure S1: ^{1}H NMR Spectra of compound **5a** ($CDCl_3$, 400 MHz).

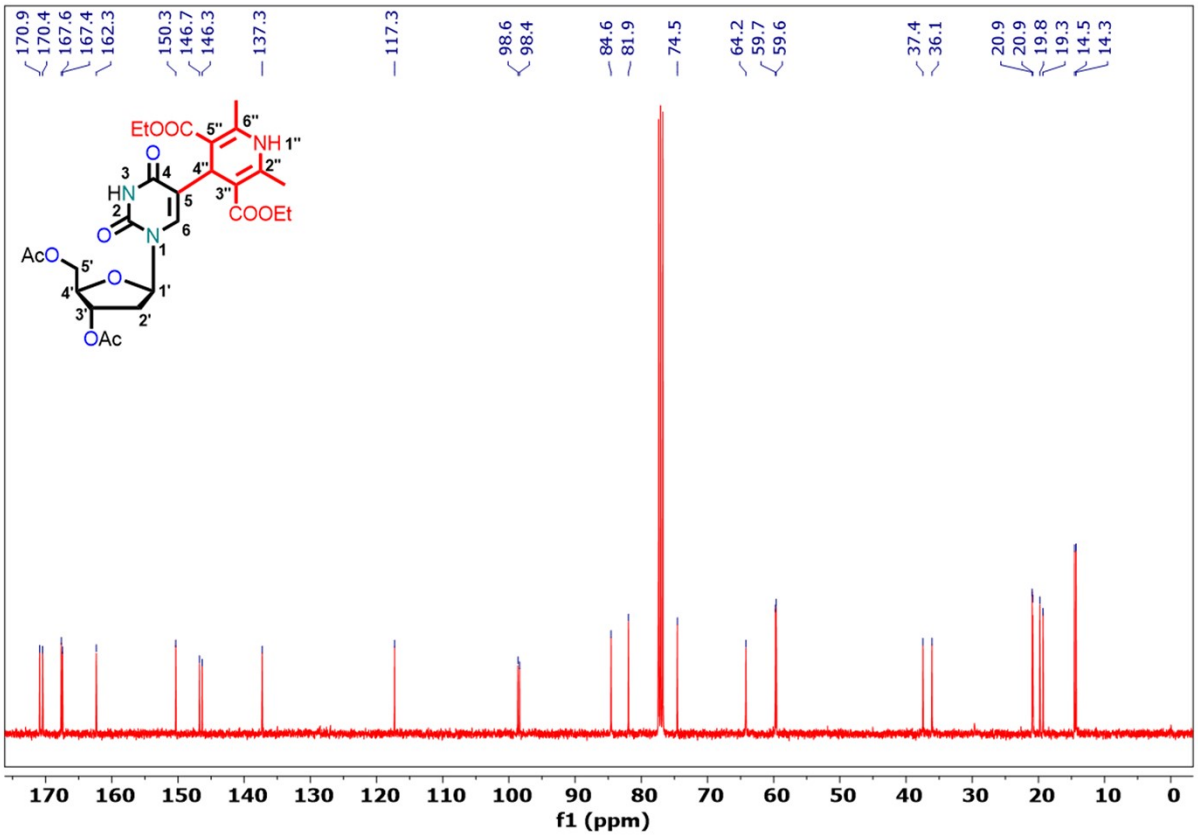


Figure S2: ^{13}C NMR Spectra of compound **5a** ($CDCl_3$, 100 MHz).

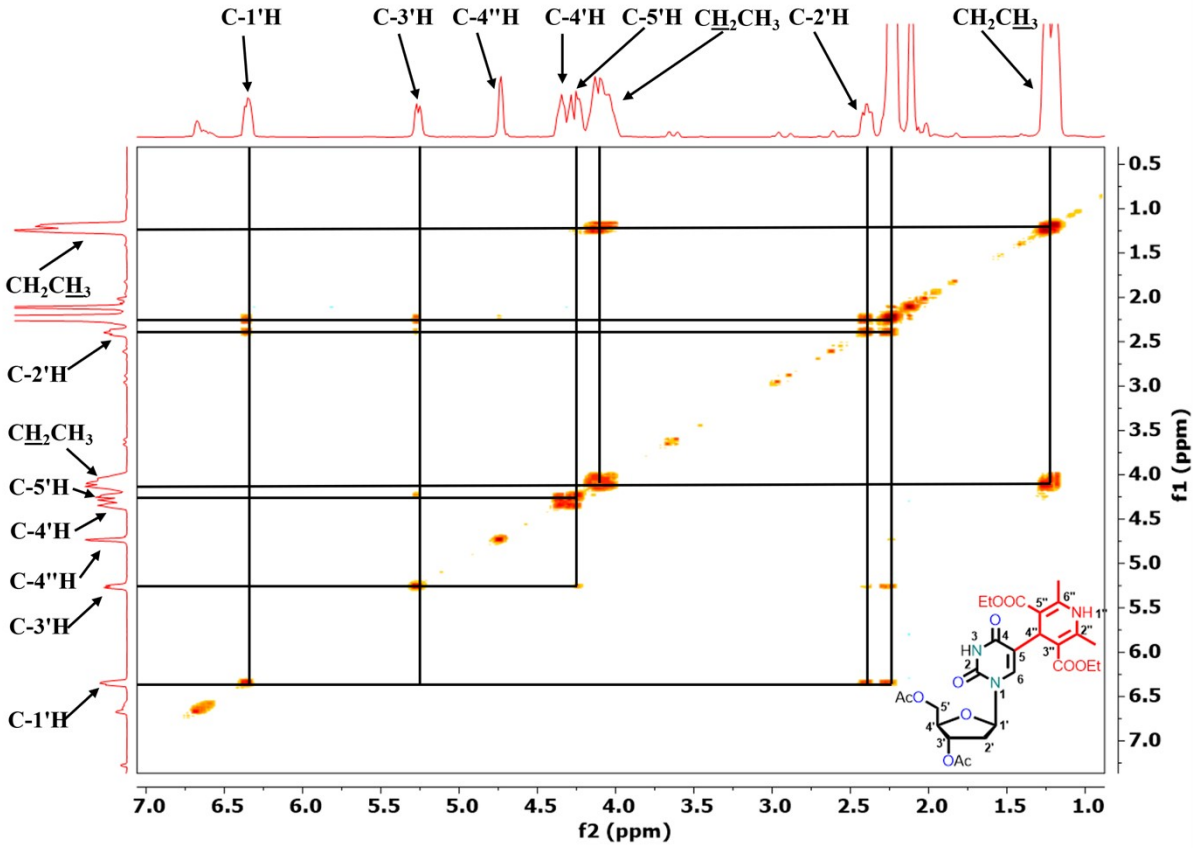


Figure S3: ^{1}H-^{1}H COSY NMR Spectra of compound **5a**.

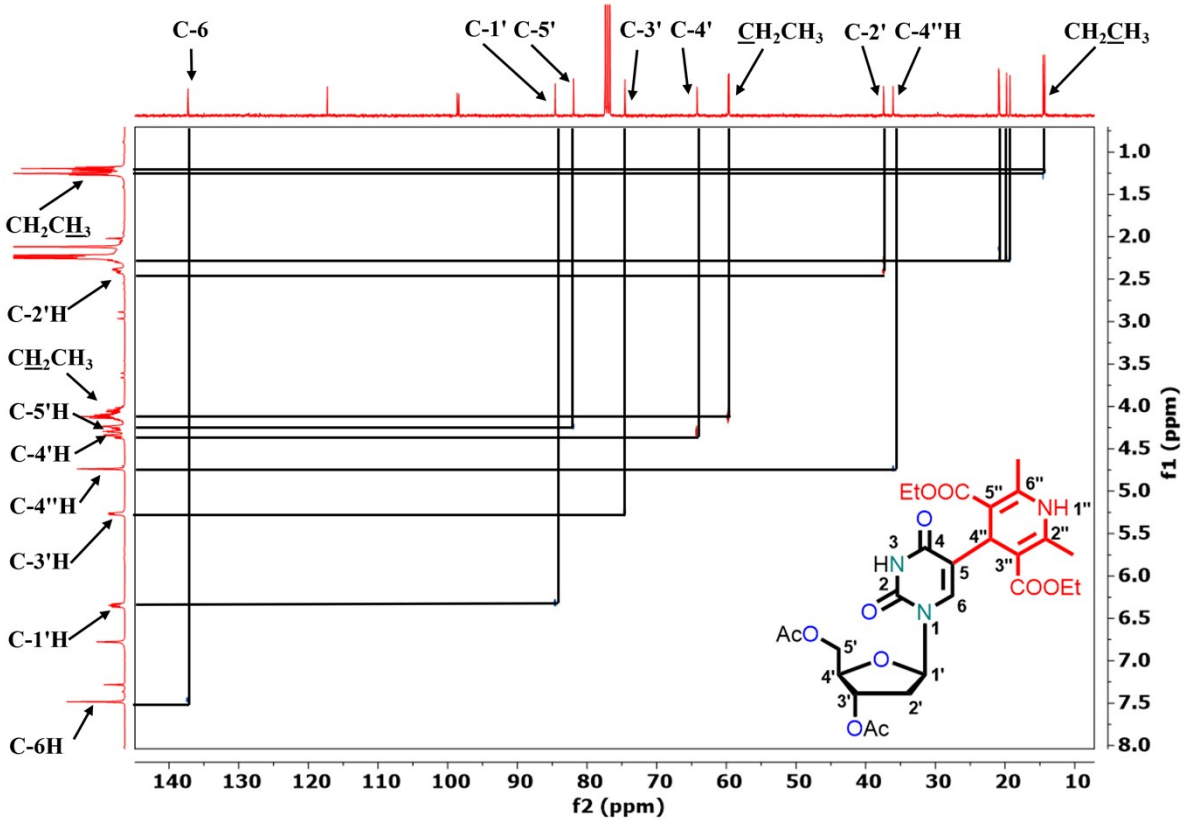


Figure S4: ^{1}H -^{13}C HETCOR NMR Spectra of compound **5a**.

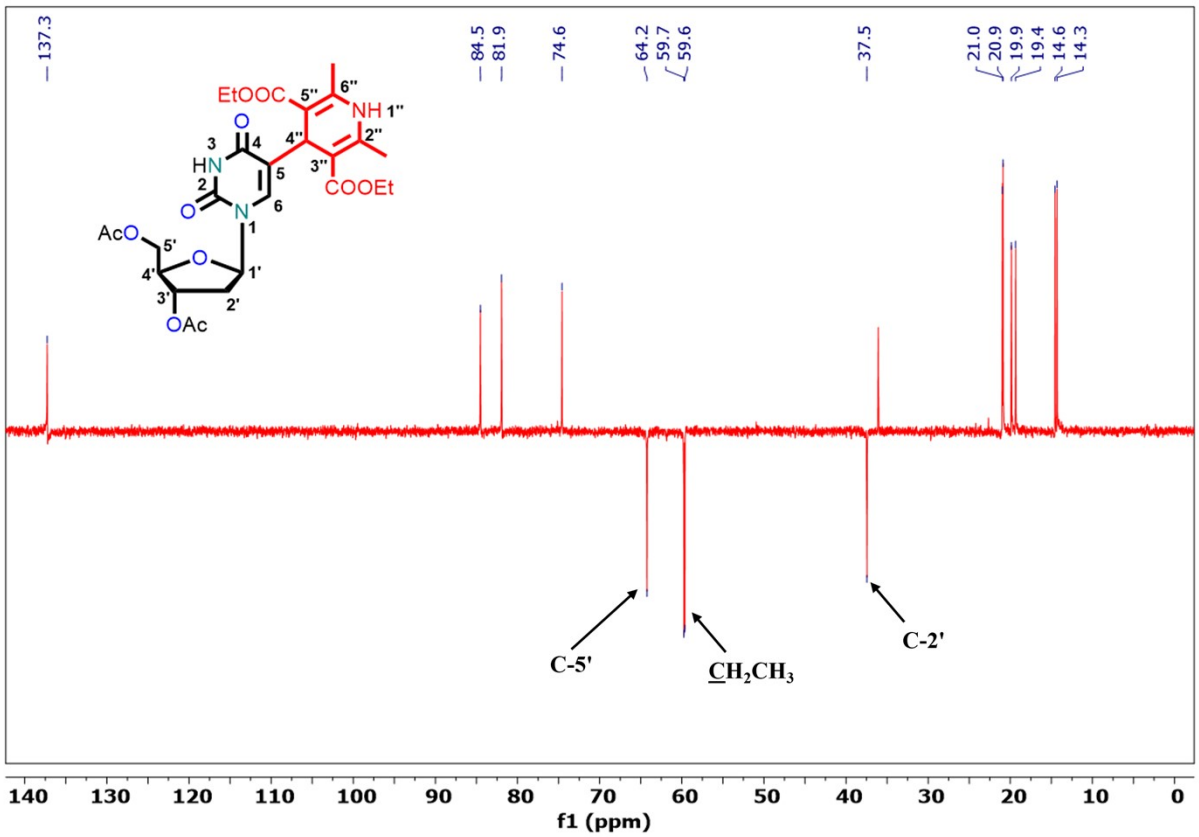


Figure S5: DEPT-135 NMR Spectra of compound **5a** ($CDCl_3$, 400 MHz).

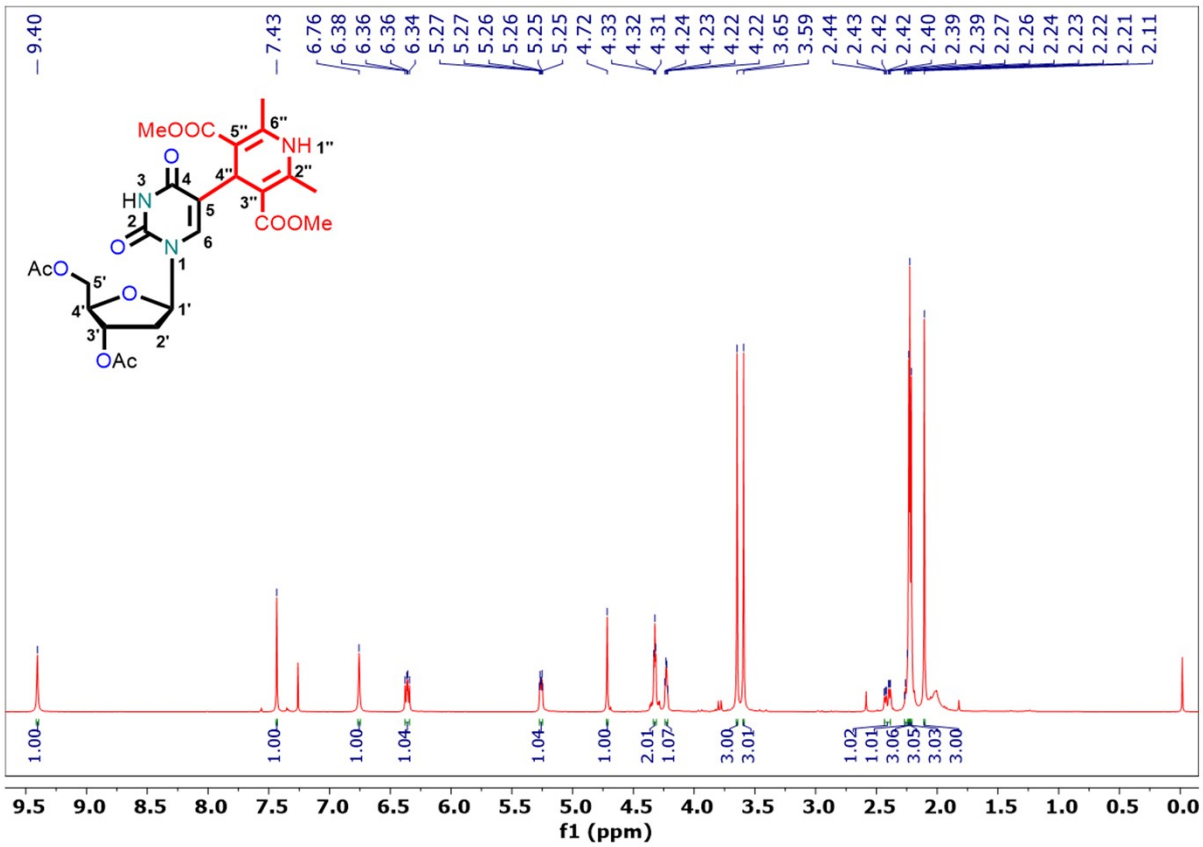


Figure S6: ^{1}H NMR Spectra of compound **5b** ($CDCl_3$, 400 MHz).

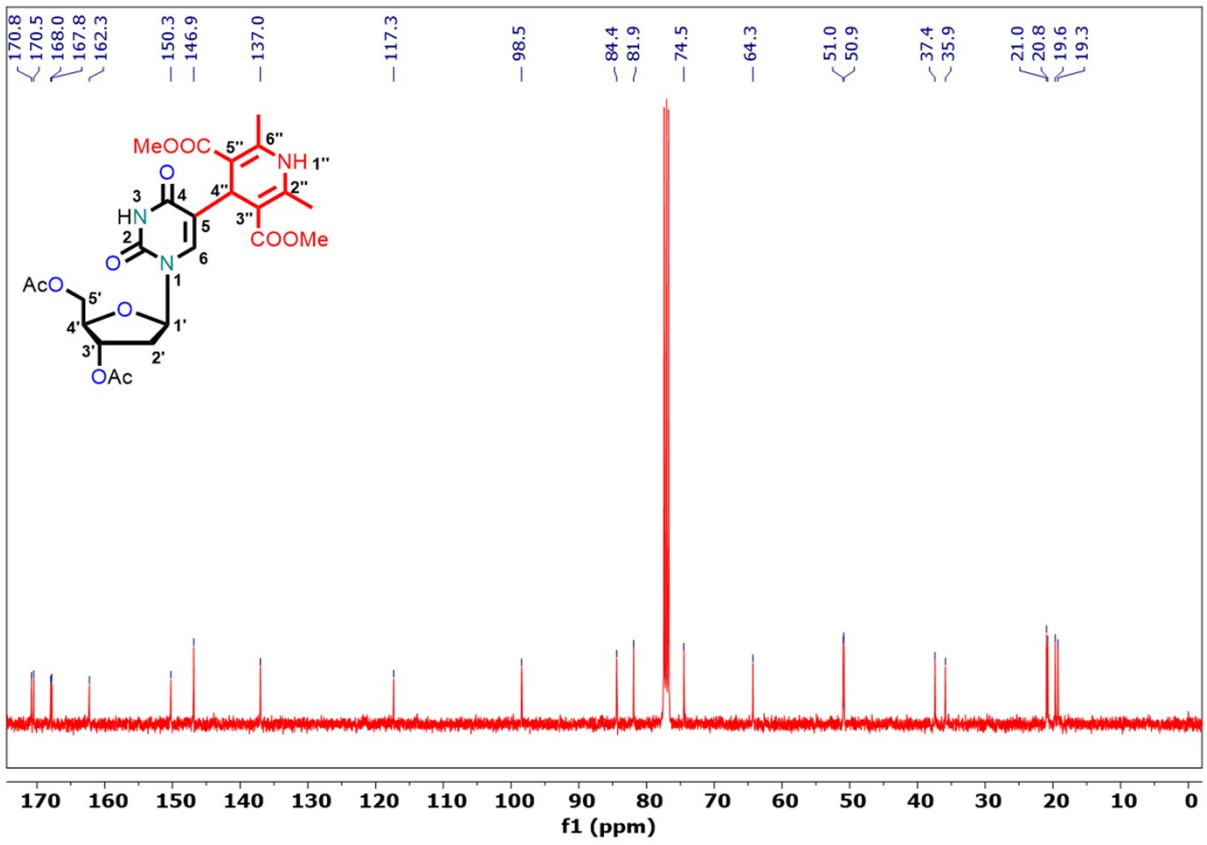


Figure S7: ^{13}C NMR Spectra of compound **5b** ($CDCl_3$, 100 MHz).

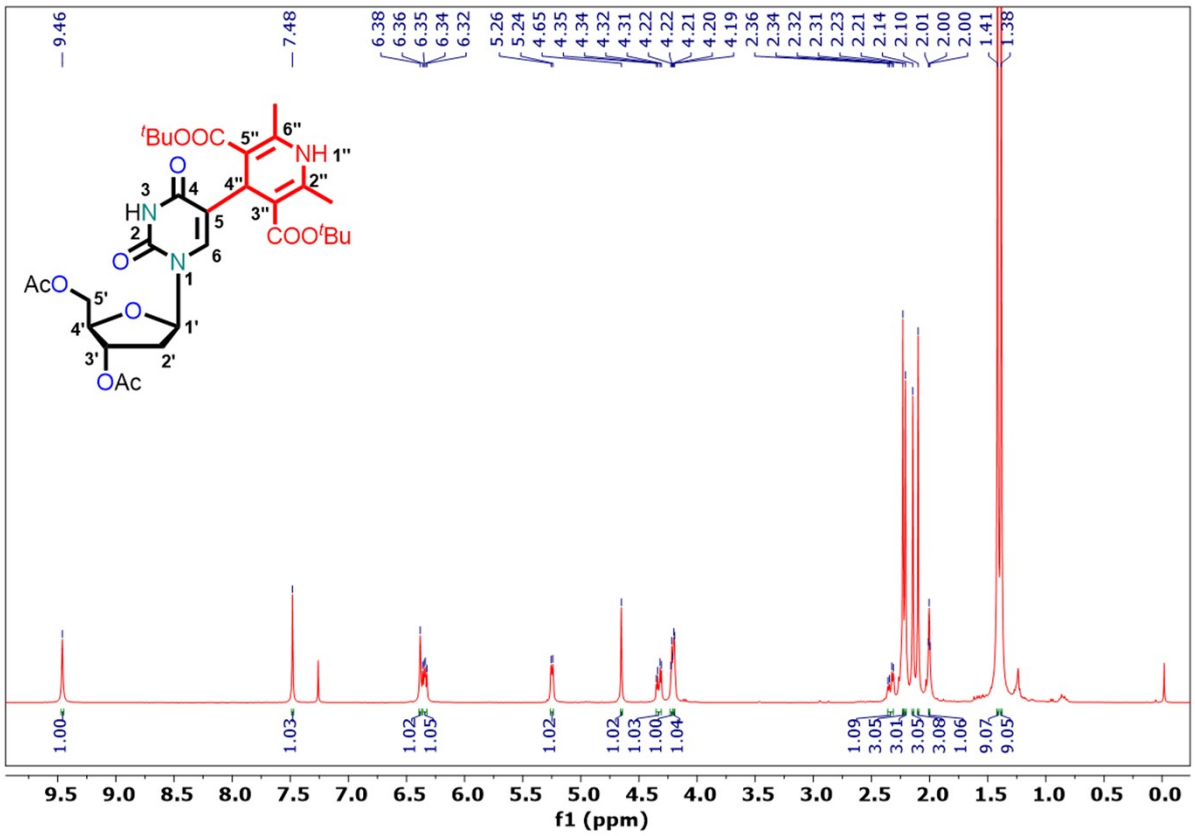


Figure S8: ^{1}H NMR Spectra of compound **5c** ($CDCl_3$, 400 MHz).

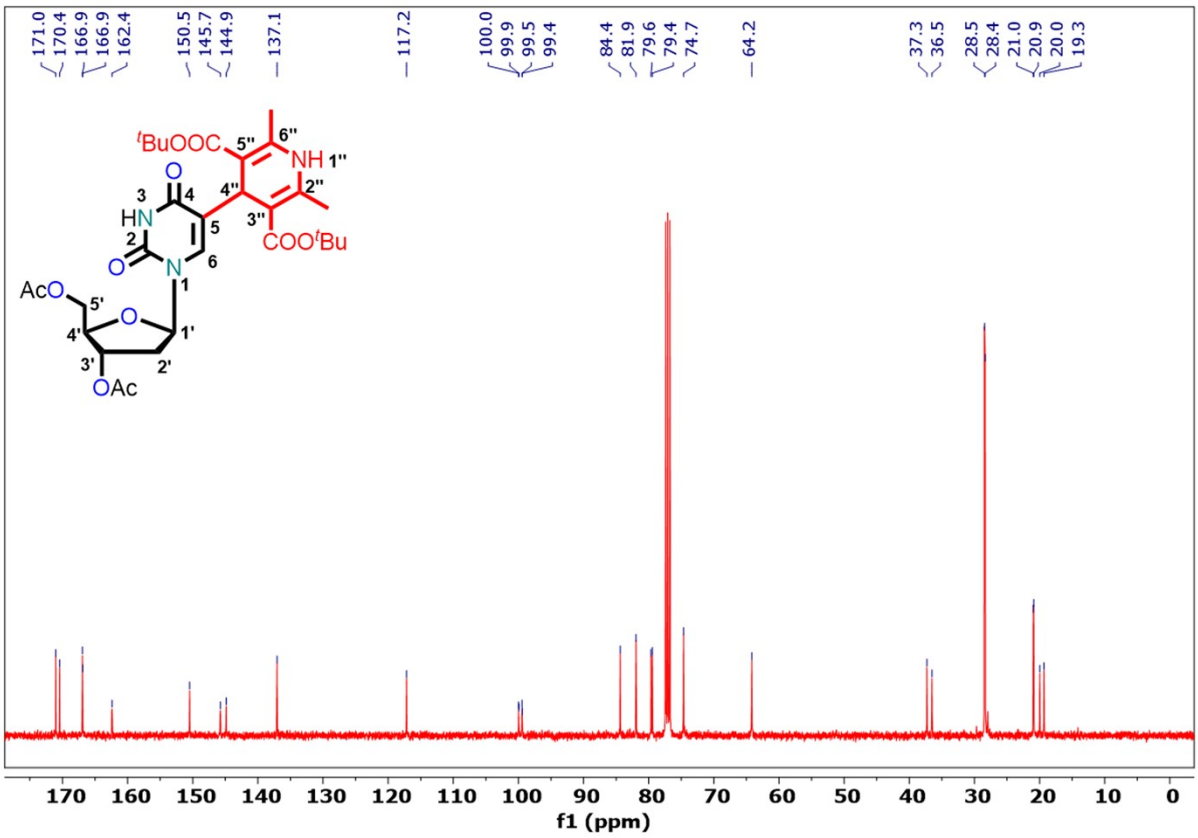


Figure S9: ^{13}C NMR Spectra of compound **5c** ($CDCl_3$, 100 MHz).

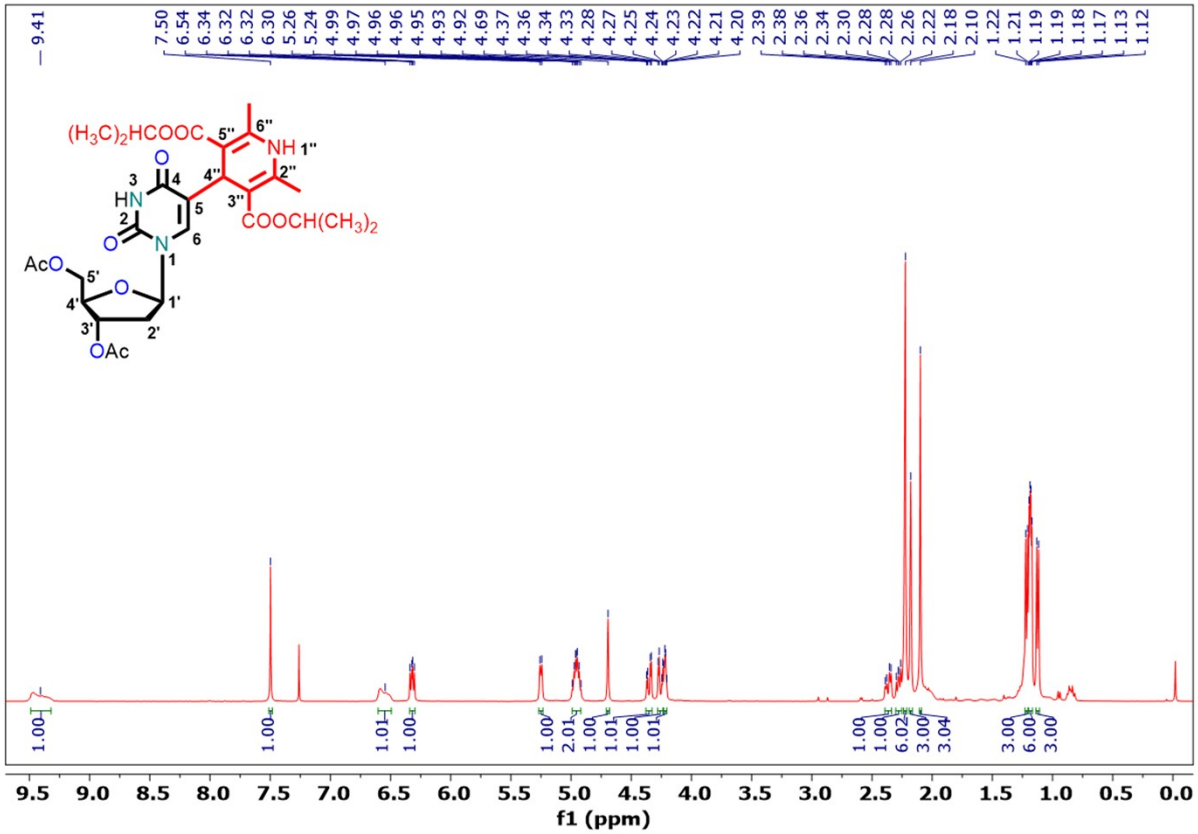


Figure S10: ^{1}H NMR Spectra of compound **5d** ($CDCl_3$, 400 MHz).

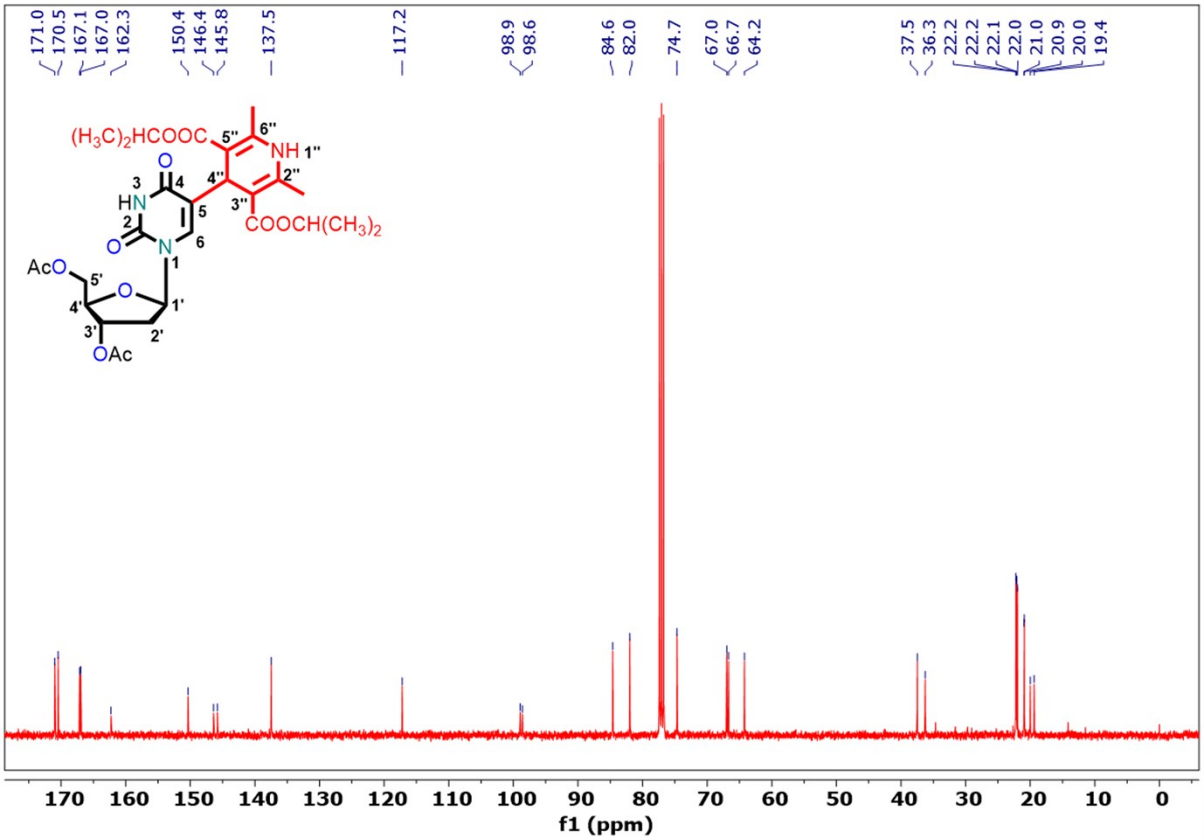


Figure S11: ^{13}C NMR Spectra of compound **5d** ($CDCl_3$, 100 MHz).

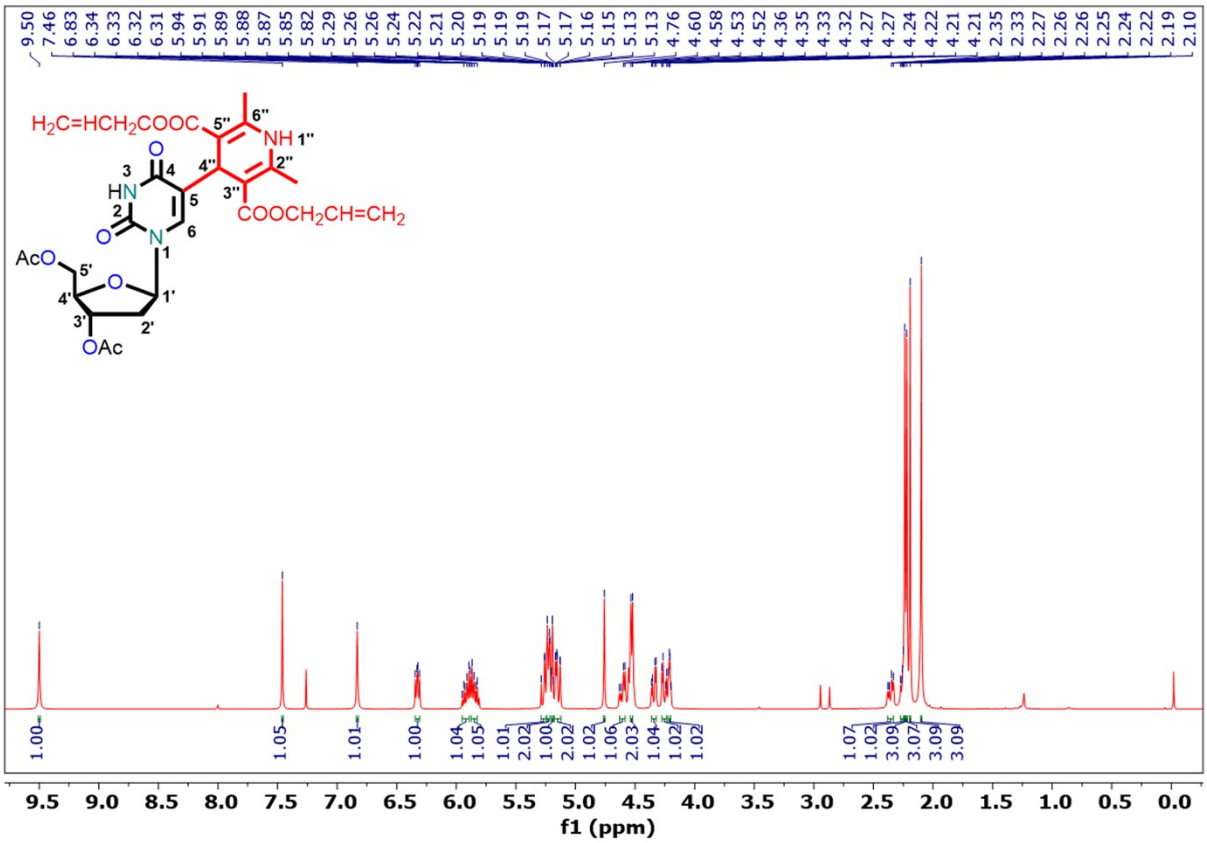


Figure S12: ^{1}H NMR Spectra of compound **5e** ($CDCl_3$, 400 MHz).

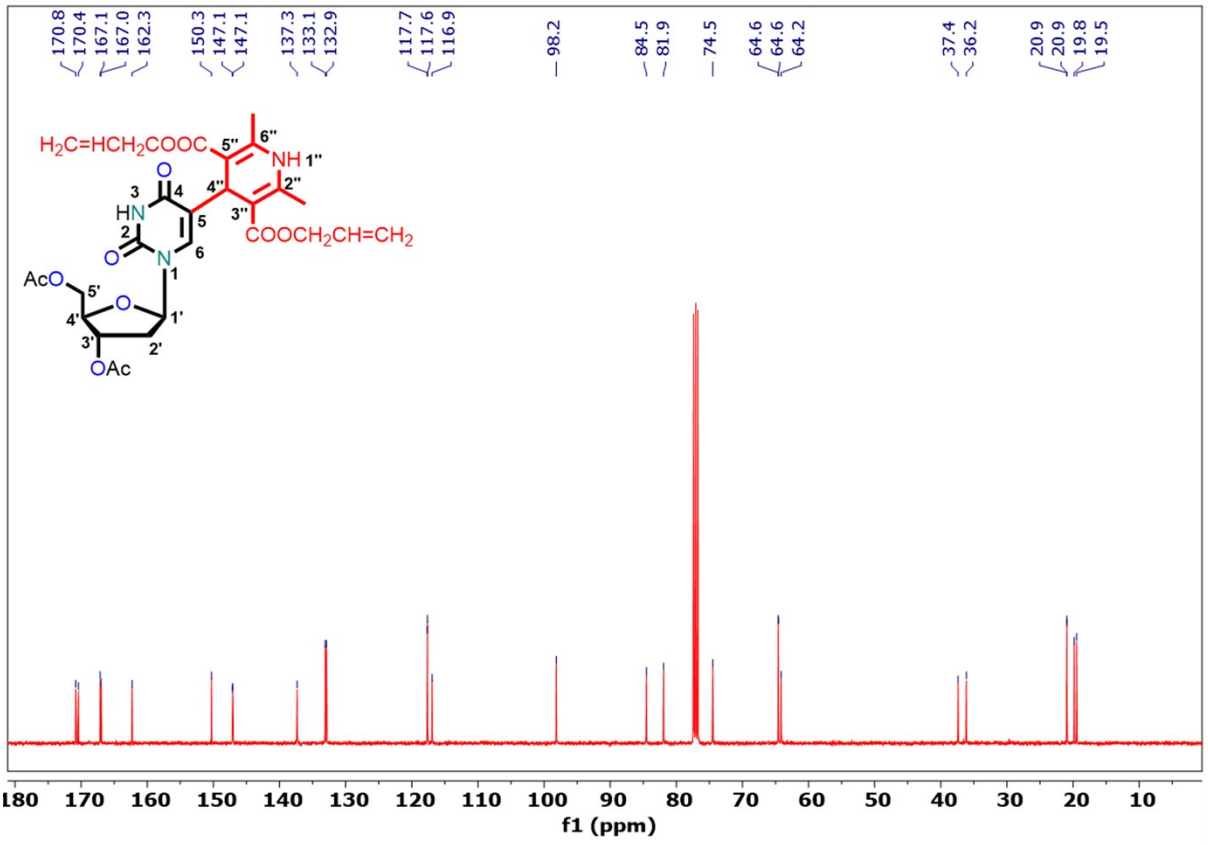


Figure S13: ^{13}C NMR Spectra of compound **5e** ($CDCl_3$, 100 MHz).

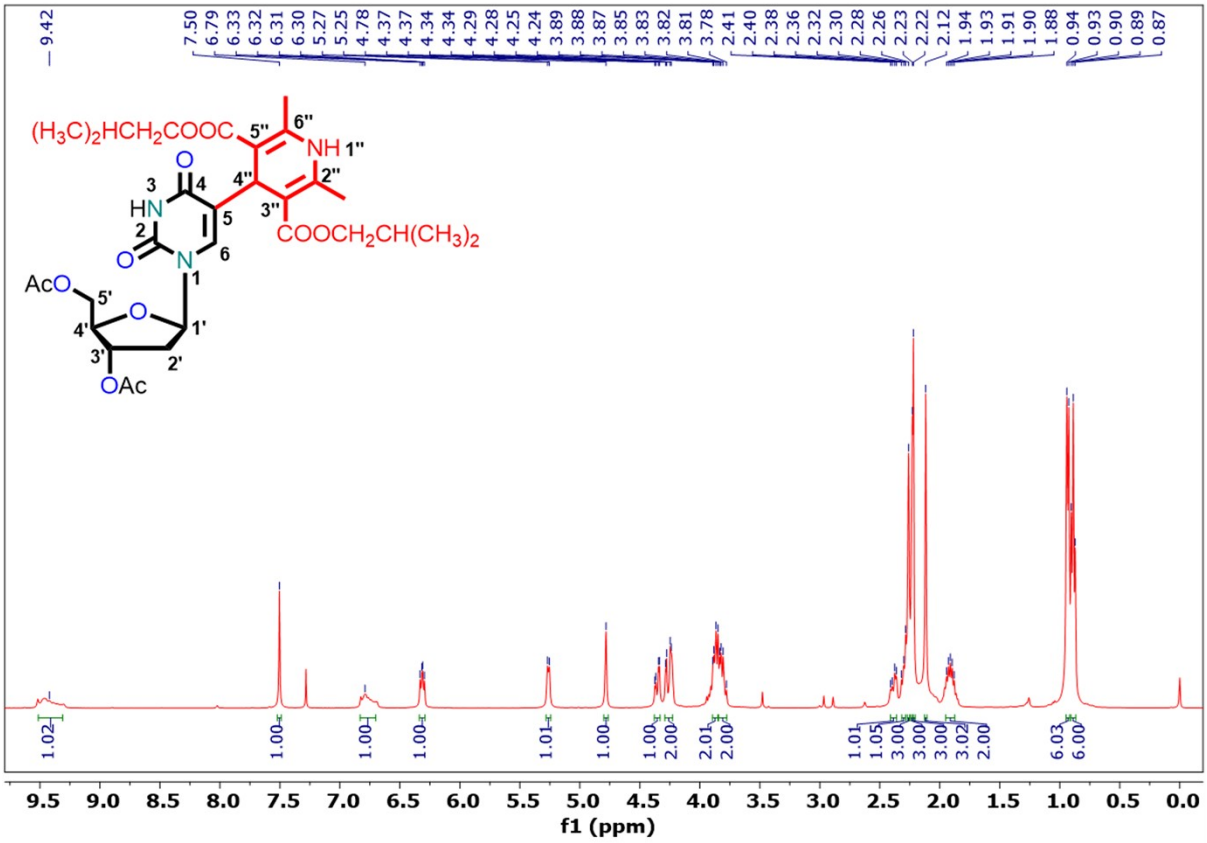


Figure S14: ^{1}H NMR Spectra of compound **5f** ($CDCl_3$, 400 MHz).

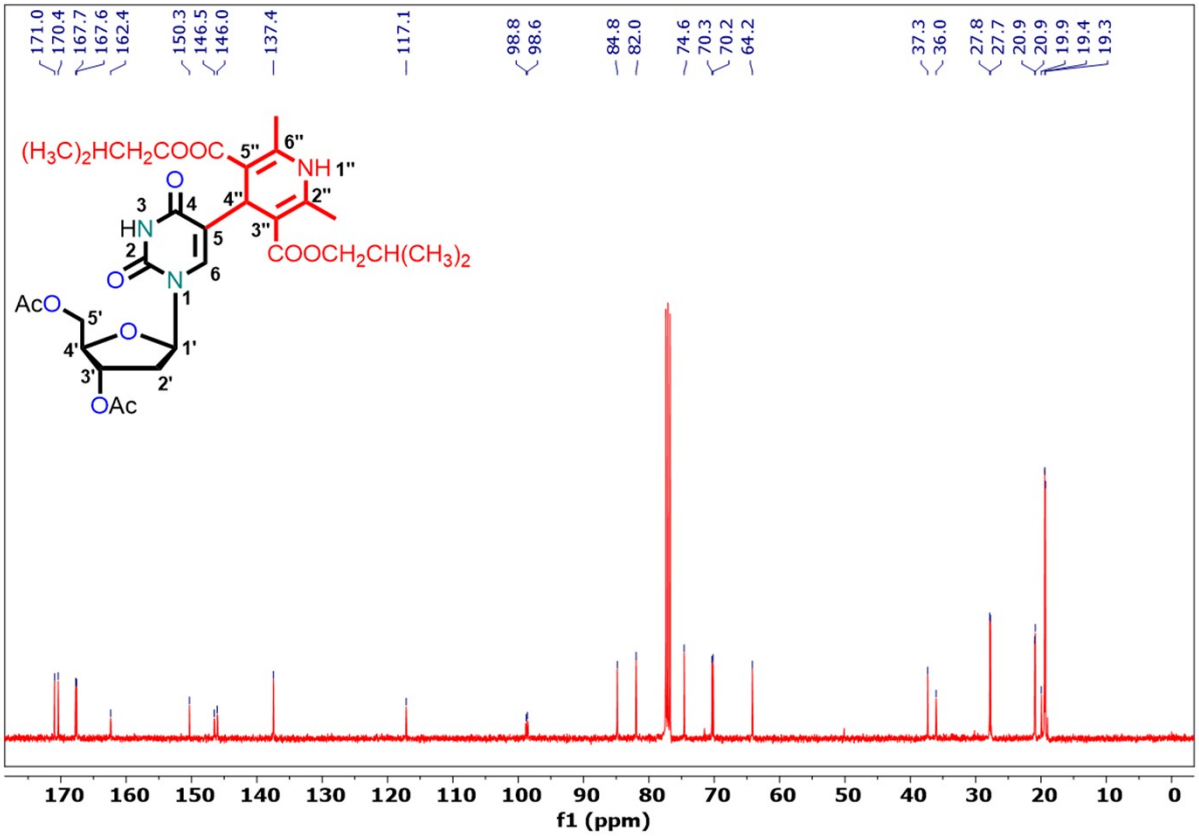


Figure S15: ^{13}C NMR Spectra of compound **5f** ($CDCl_3$, 100 MHz).

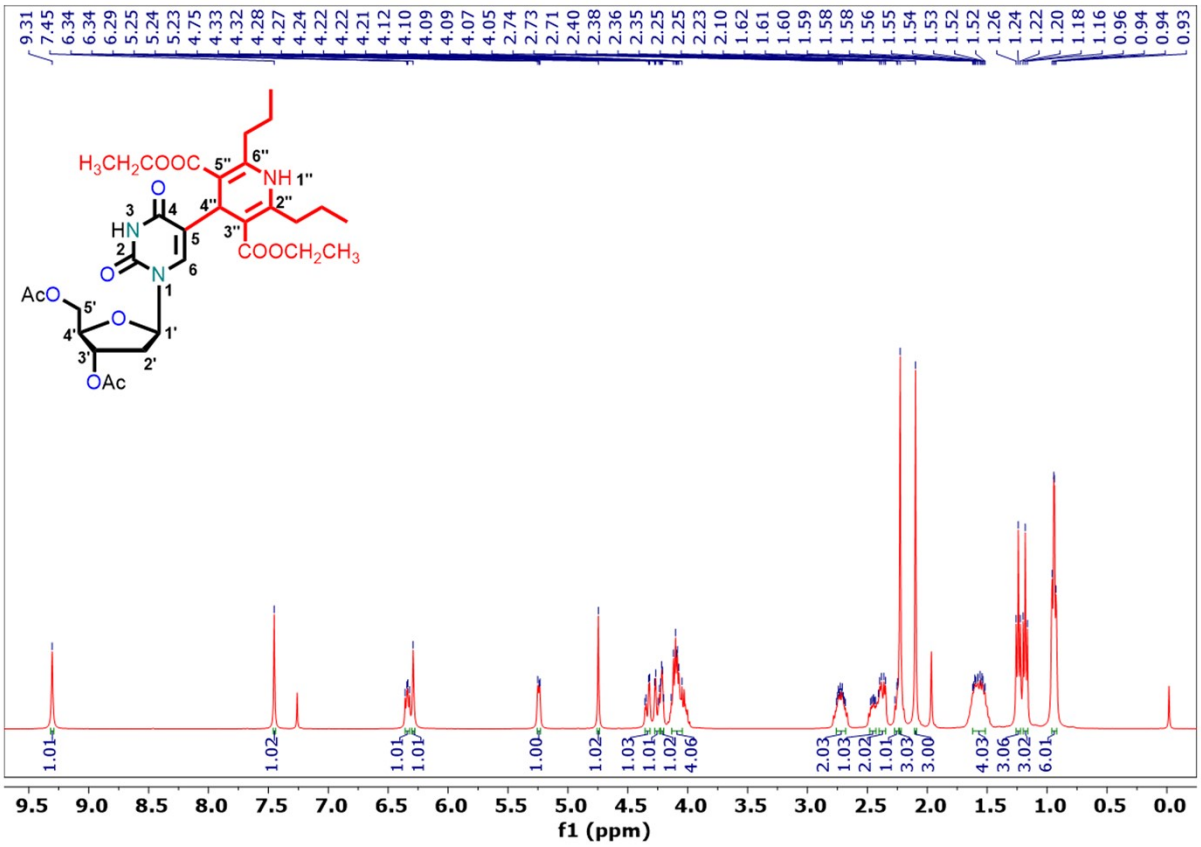


Figure S16: ^{1}H NMR Spectra of compound **5g** ($CDCl_3$, 400 MHz).

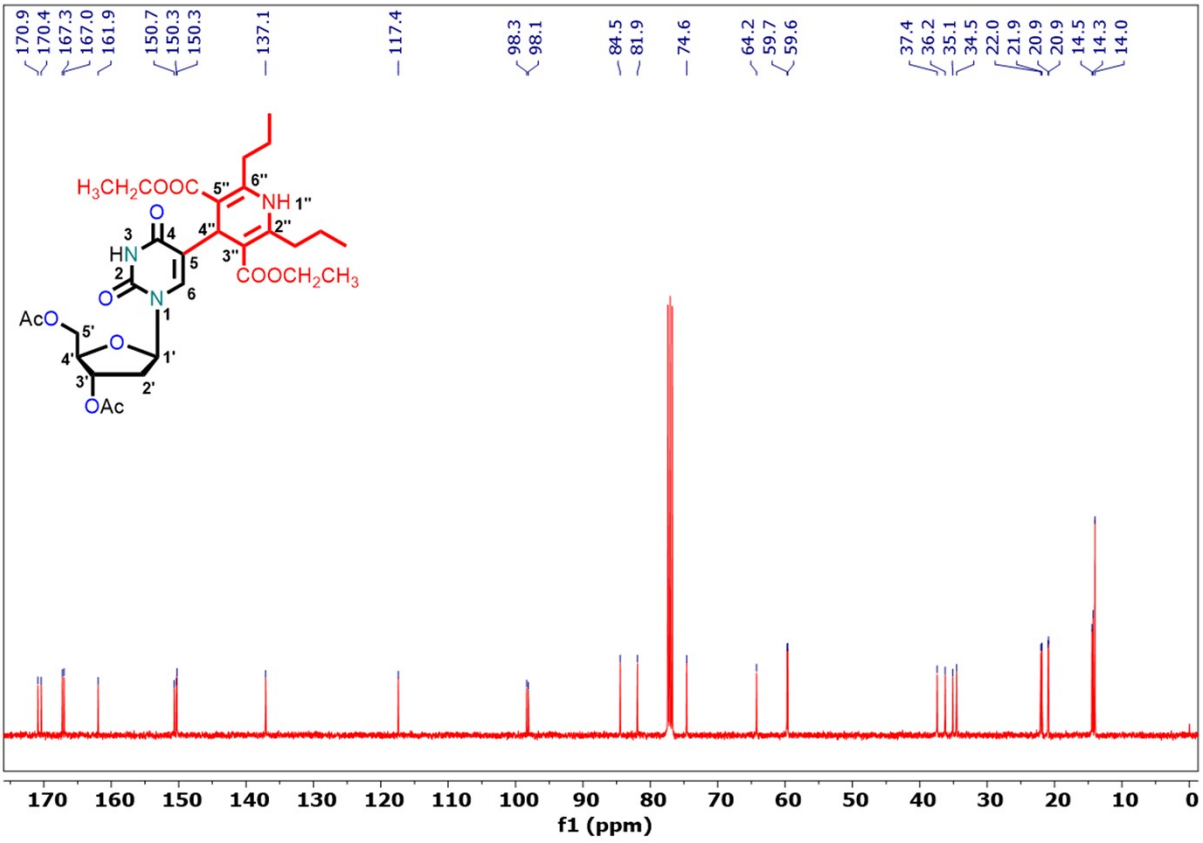


Figure S17: ^{13}C NMR Spectra of compound **5g** ($CDCl_3$, 100 MHz).

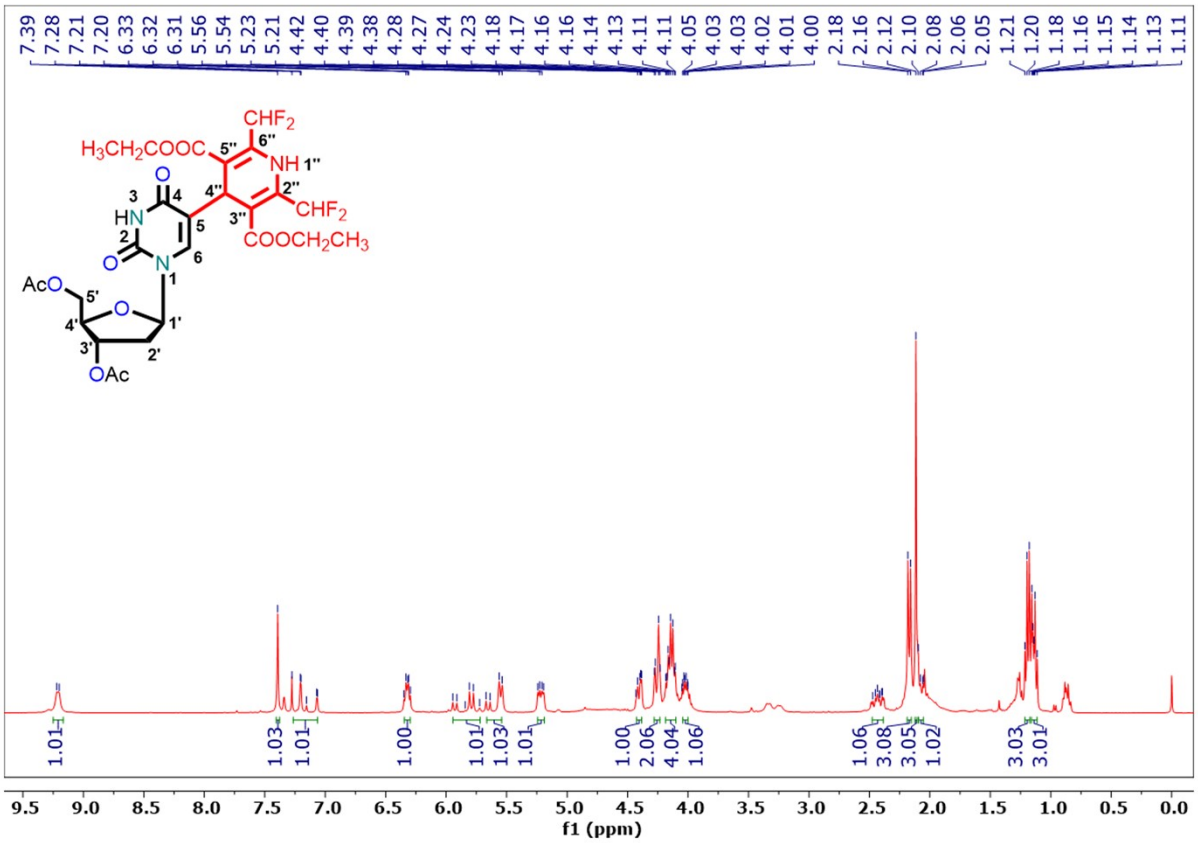


Figure S18: ^{1}H NMR Spectra of compound **5h** ($CDCl_3$, 400 MHz).

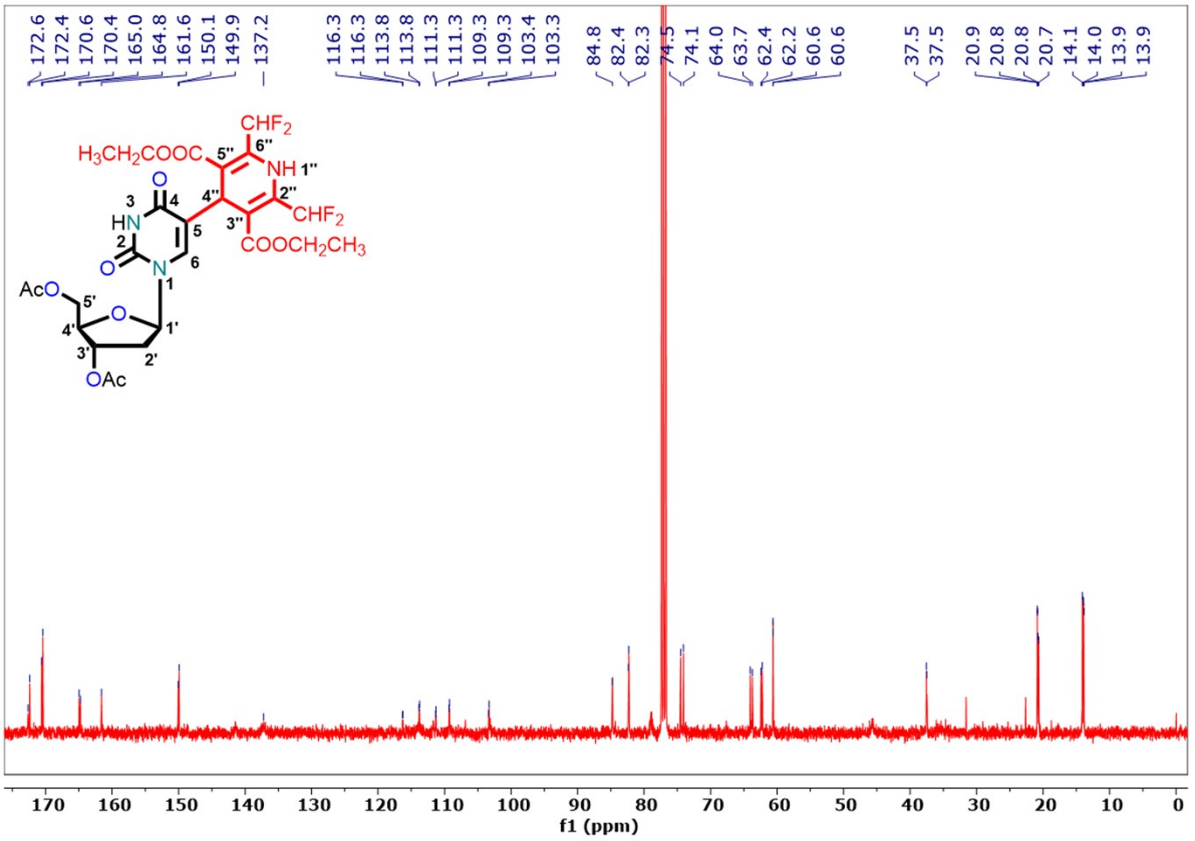


Figure S19: ^{13}C NMR Spectra of compound **5h** ($CDCl_3$, 100 MHz).

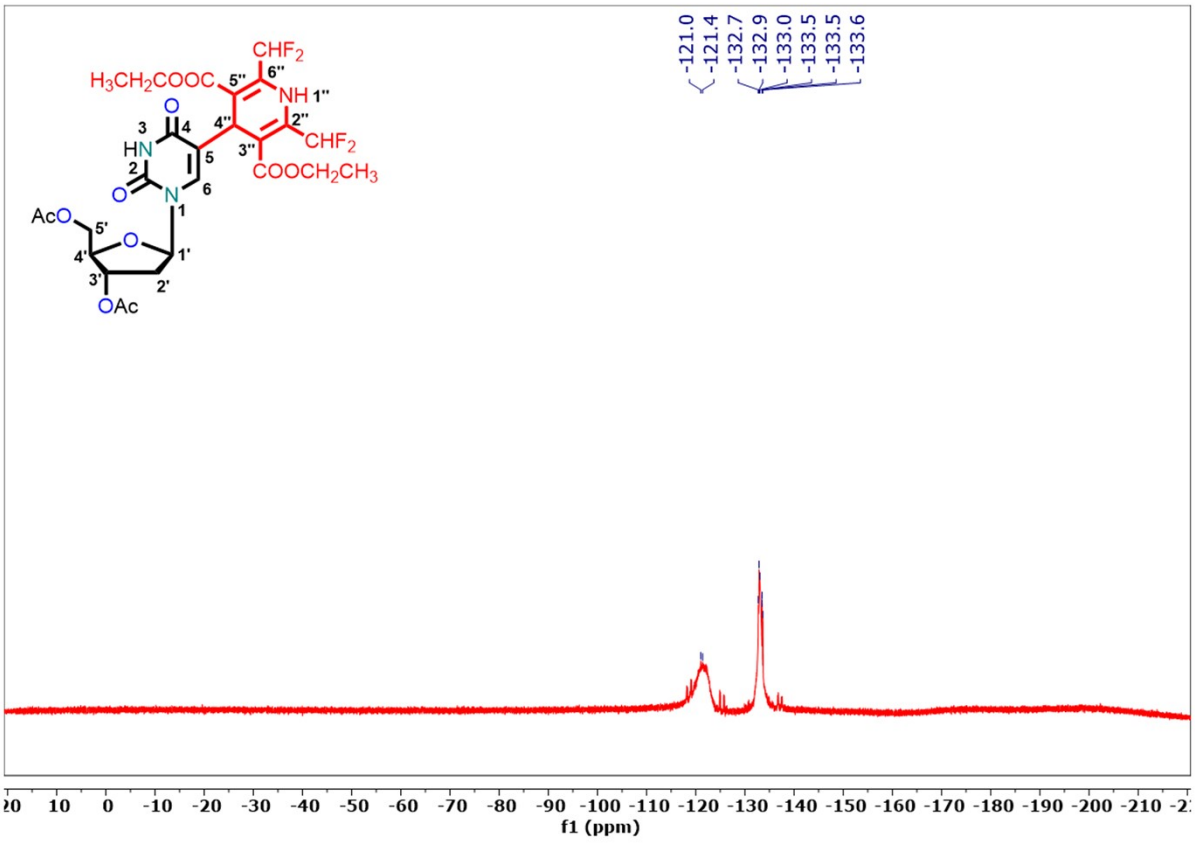


Figure S20: ^{19}F NMR Spectra of compound **5h** ($CDCl_3$, 377 MHz).

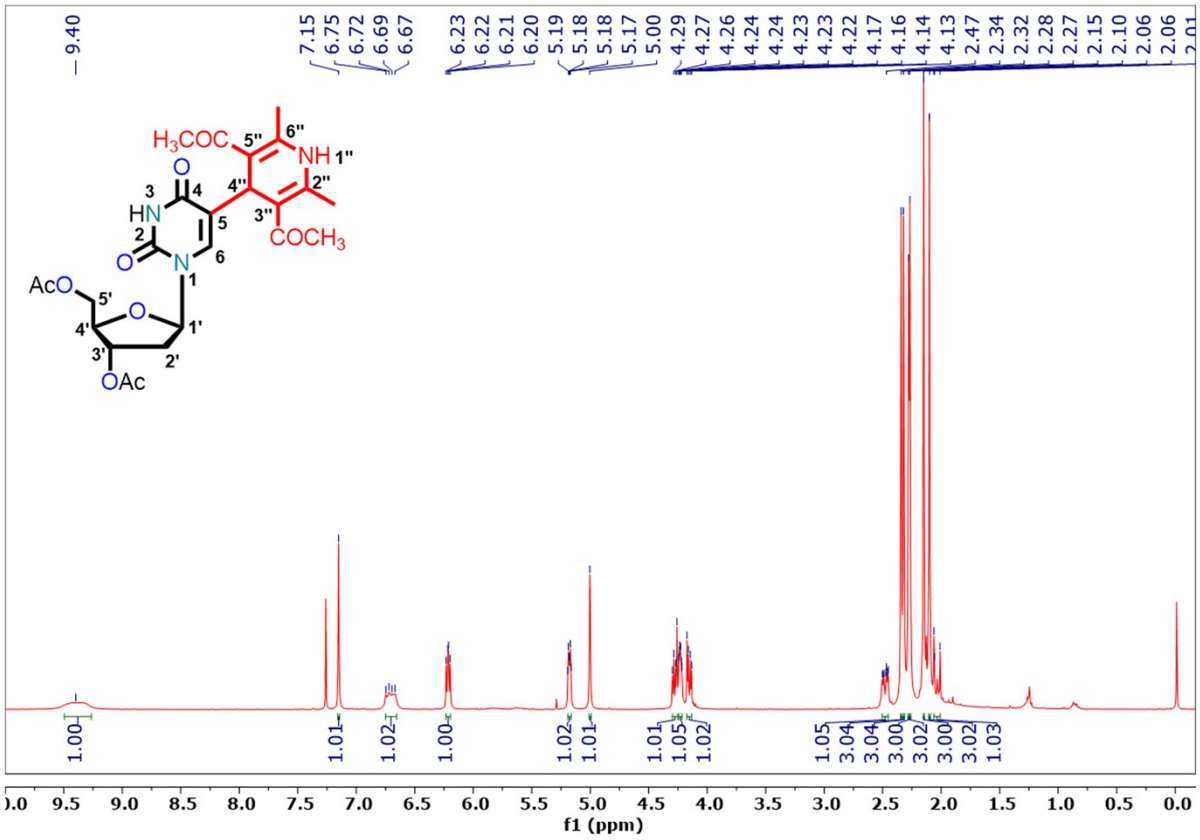


Figure S21: ^{1}H NMR Spectra of compound **5i** ($CDCl_3$, 400 MHz).

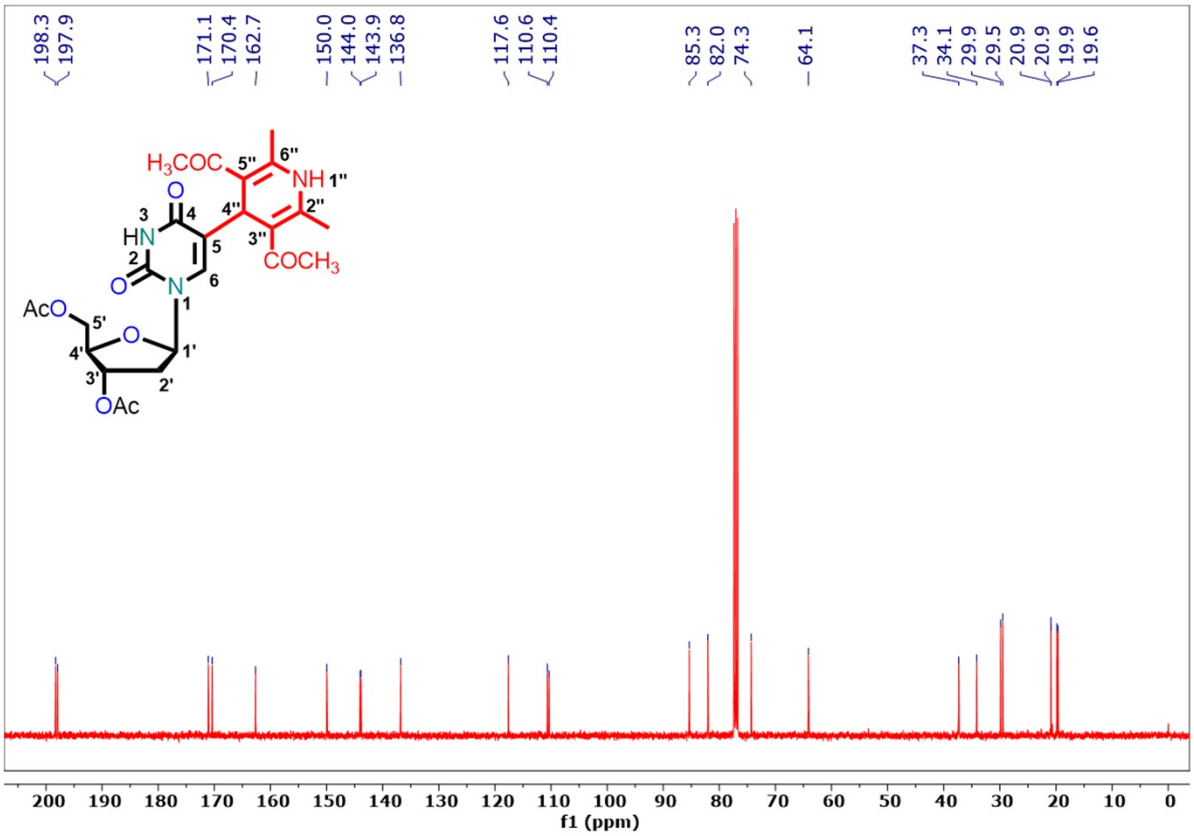


Figure S22: ^{13}C NMR Spectra of compound **5i** ($CDCl_3$, 100 MHz).

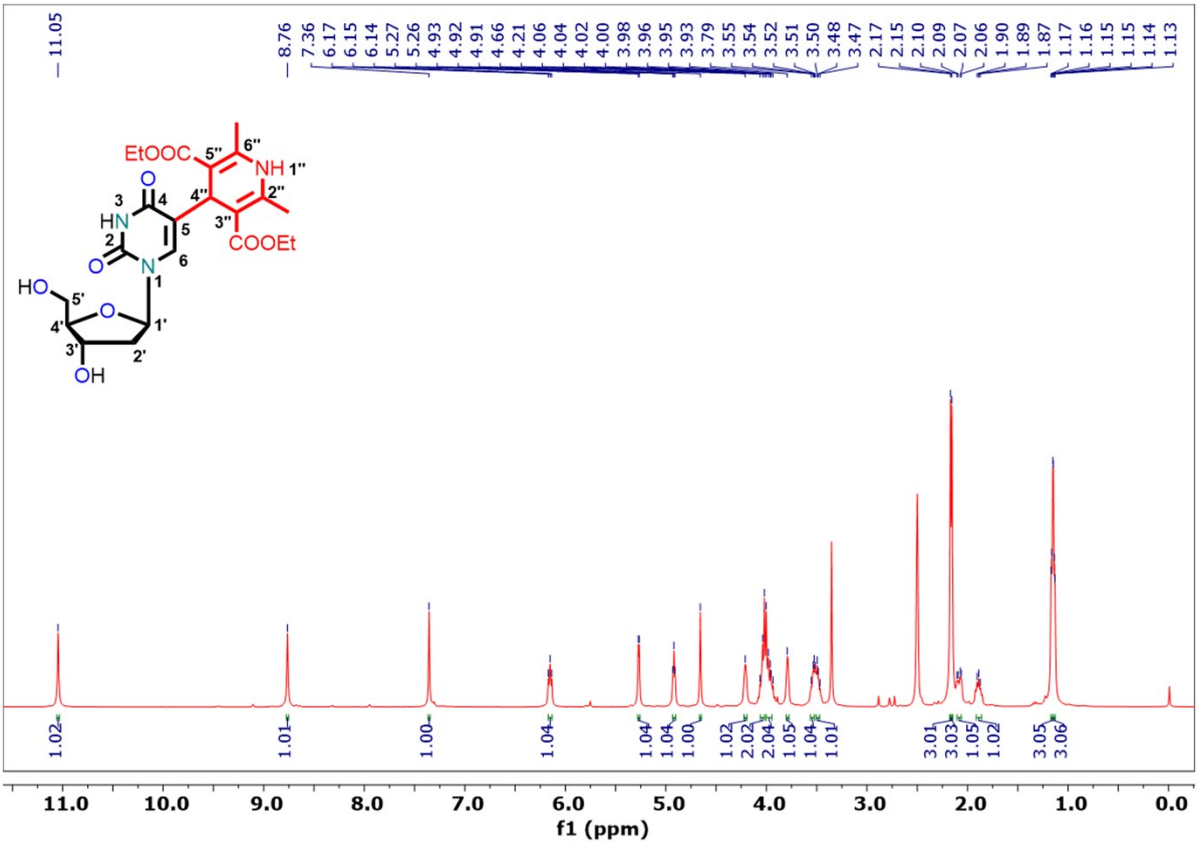


Figure S23: ^{1}H NMR Spectra of compound **6a** (DMSO-d_6, 400 MHz).

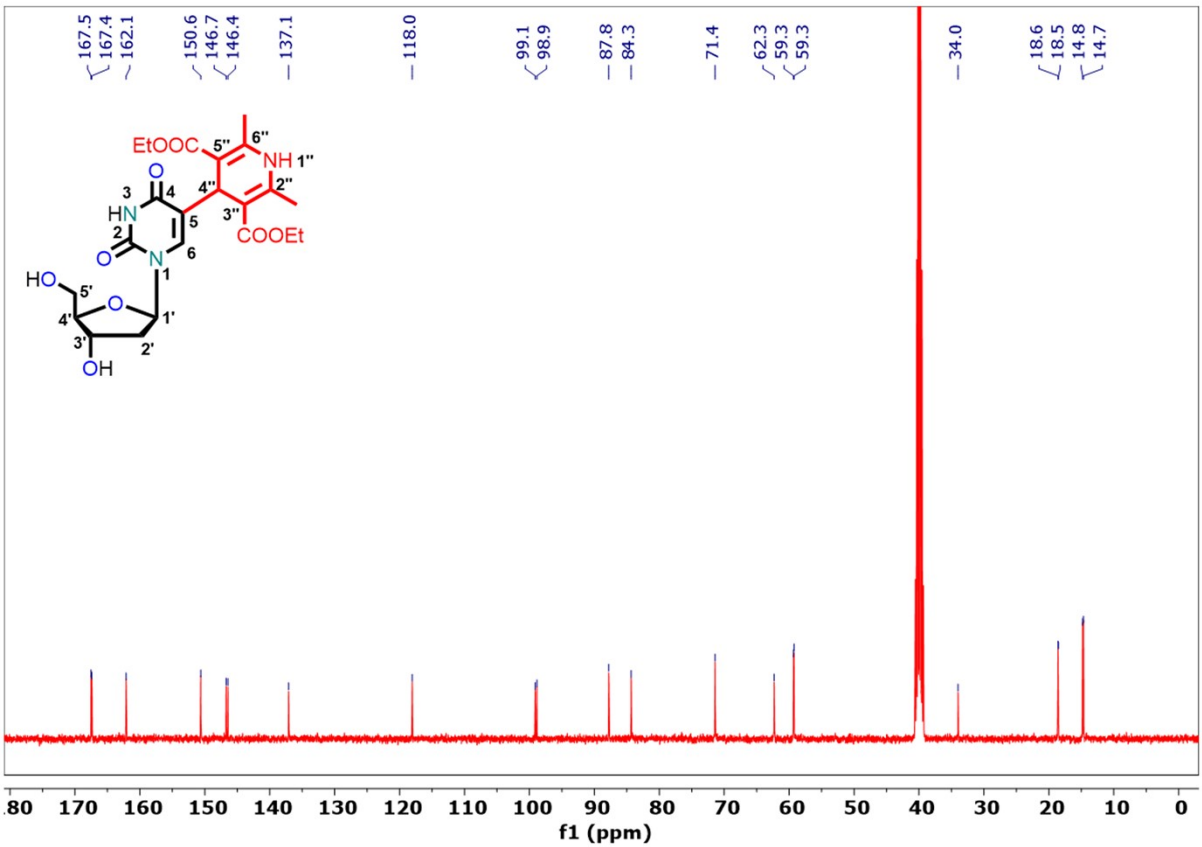


Figure S24: ^{13}C NMR Spectra of compound **6a** (DMSO-d_6, 100 MHz).

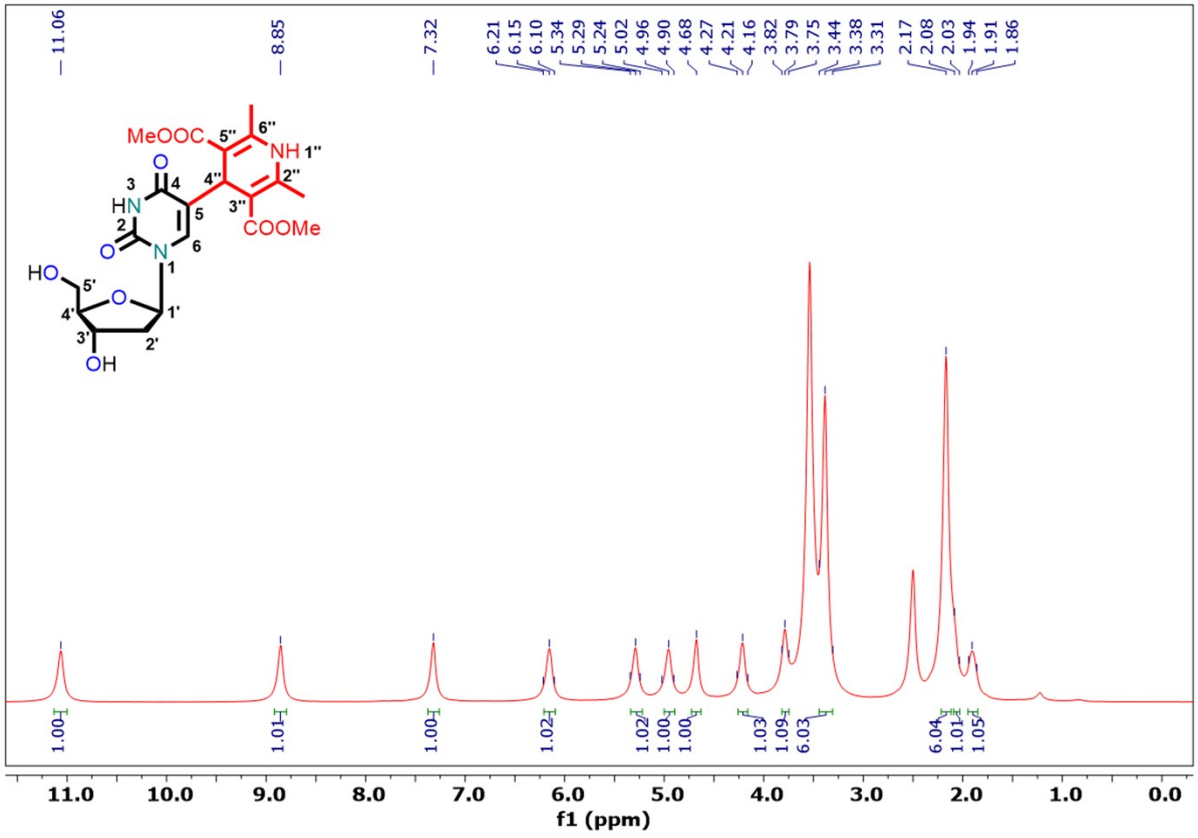


Figure S25: ^{1}H NMR Spectra of compound **6b** (DMSO-d_6, 400 MHz).

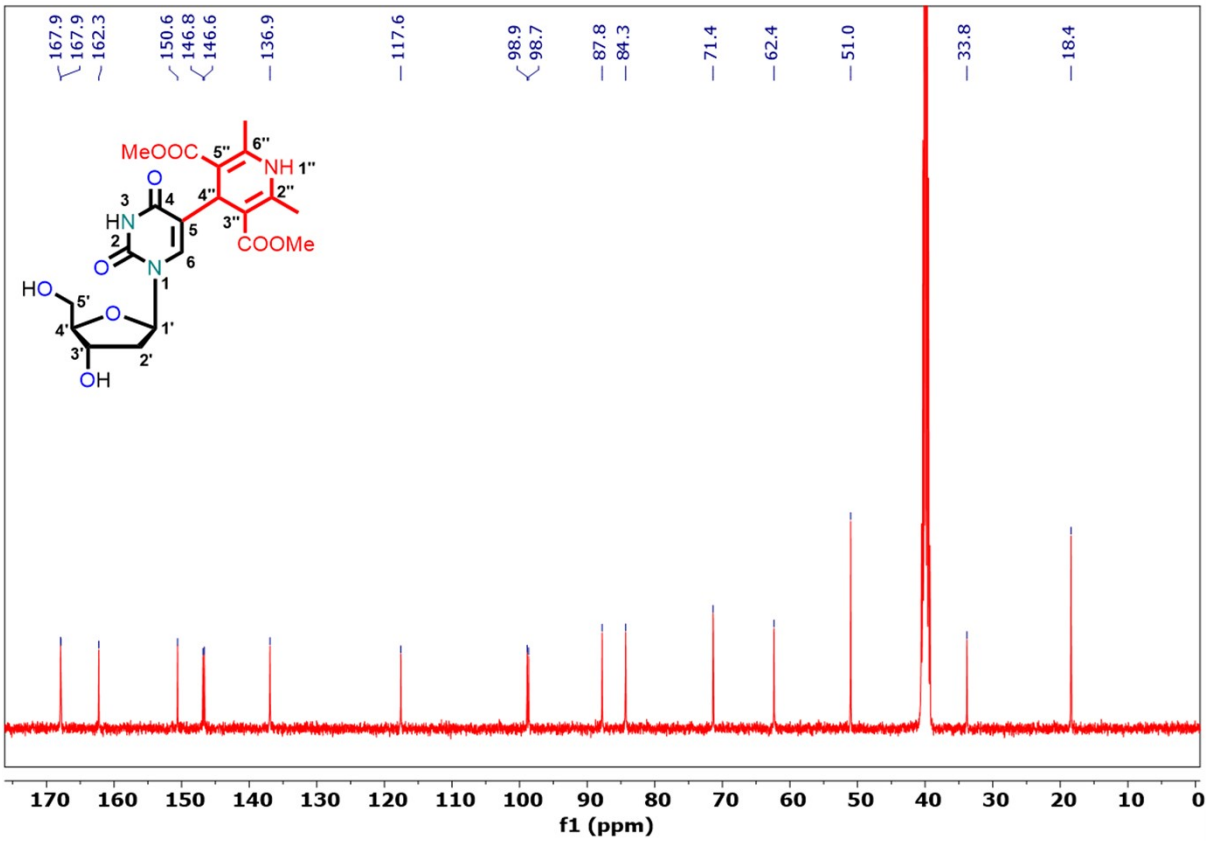


Figure S26: ^{13}C NMR Spectra of compound **6b** (DMSO-d_6, 100 MHz).

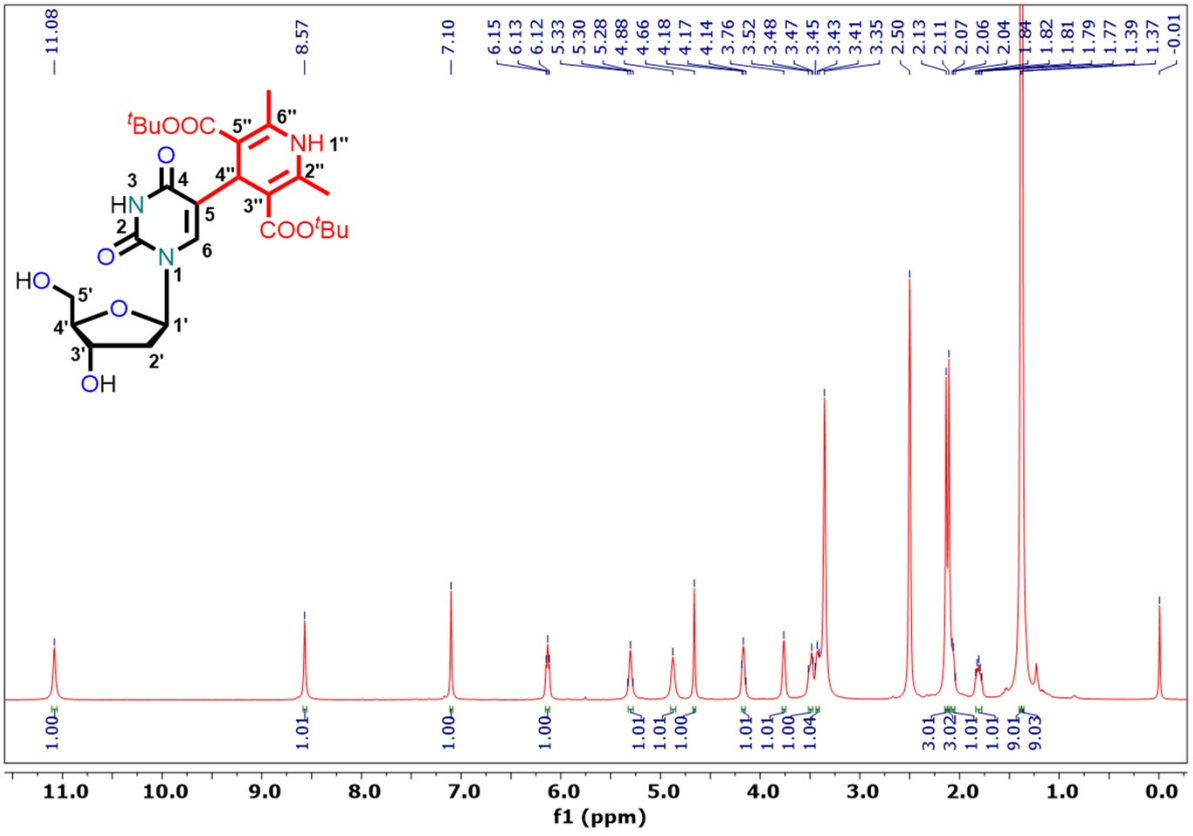


Figure S27: ^{1}H NMR Spectra of compound **6c** (DMSO-d_6, 400 MHz).

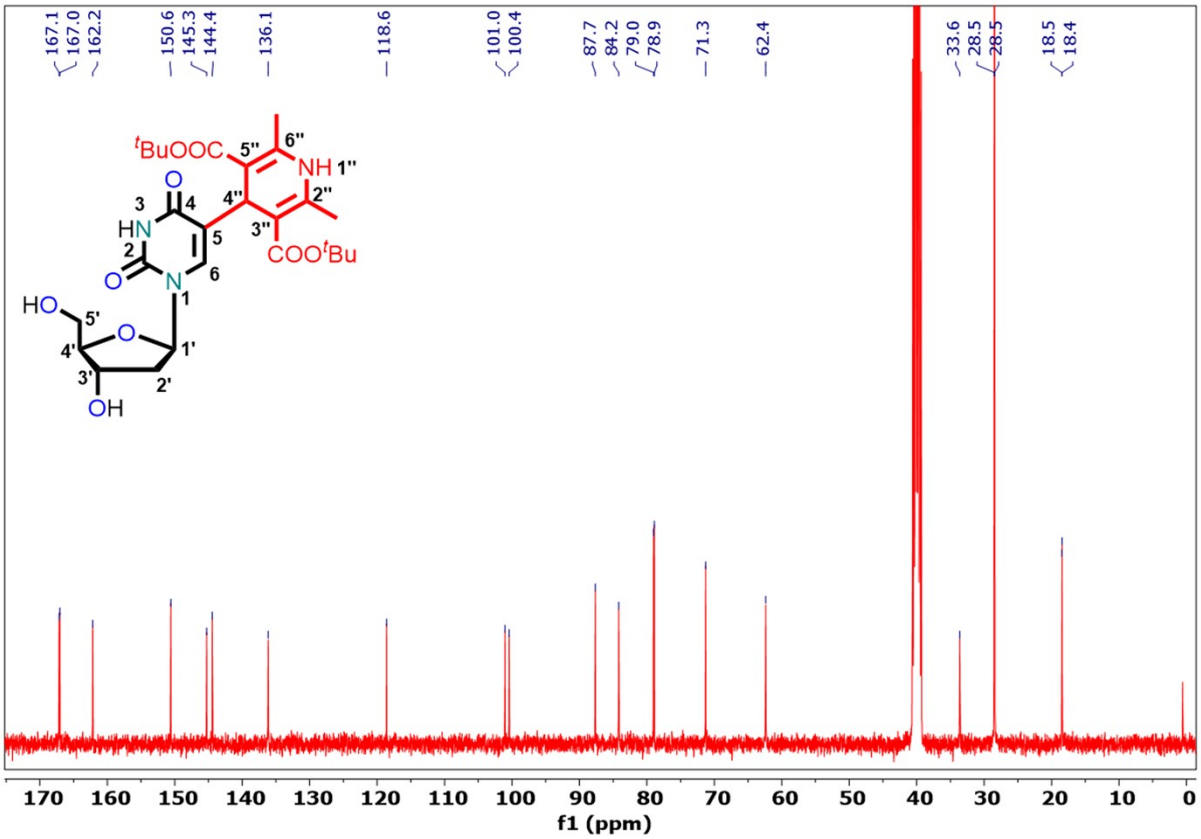


Figure S28: ^{13}C NMR Spectra of compound **6c** (DMSO-d_6, 100 MHz).

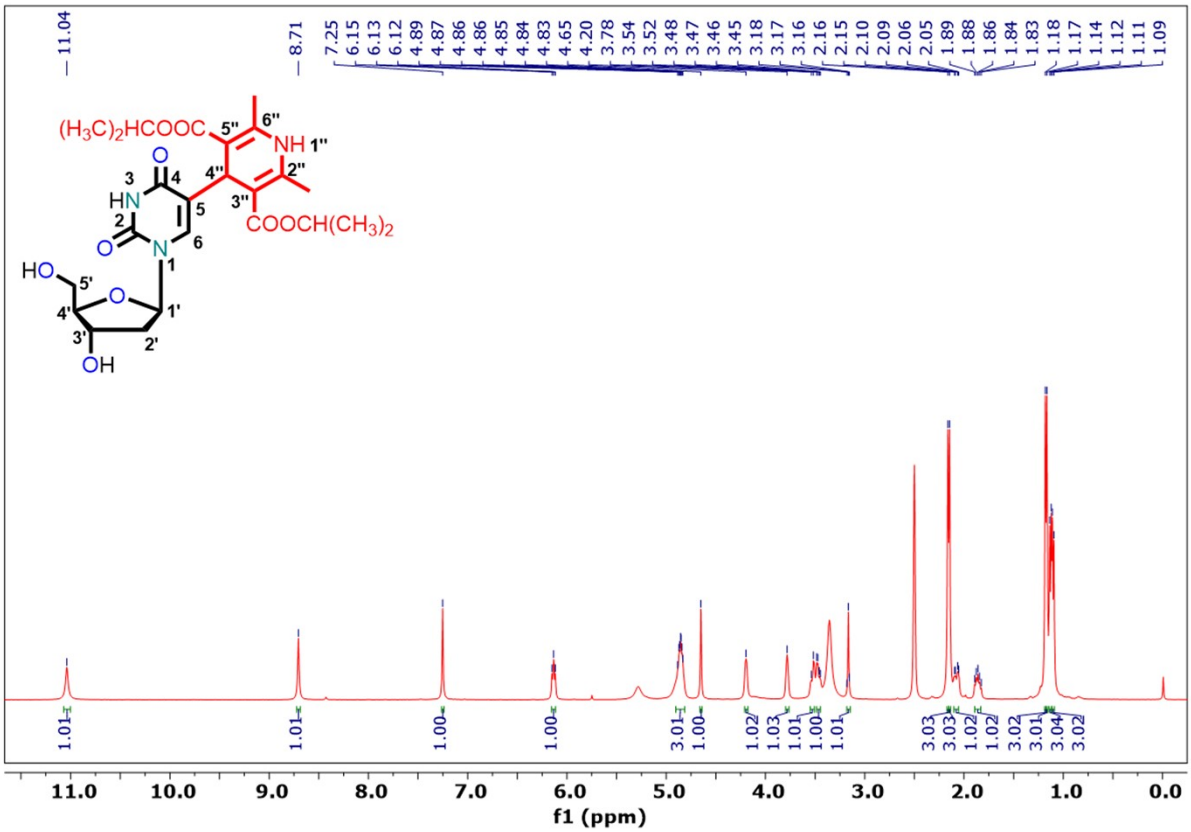


Figure S29: ^{1}H NMR Spectra of compound **6d** (DMSO-d_6, 400 MHz).

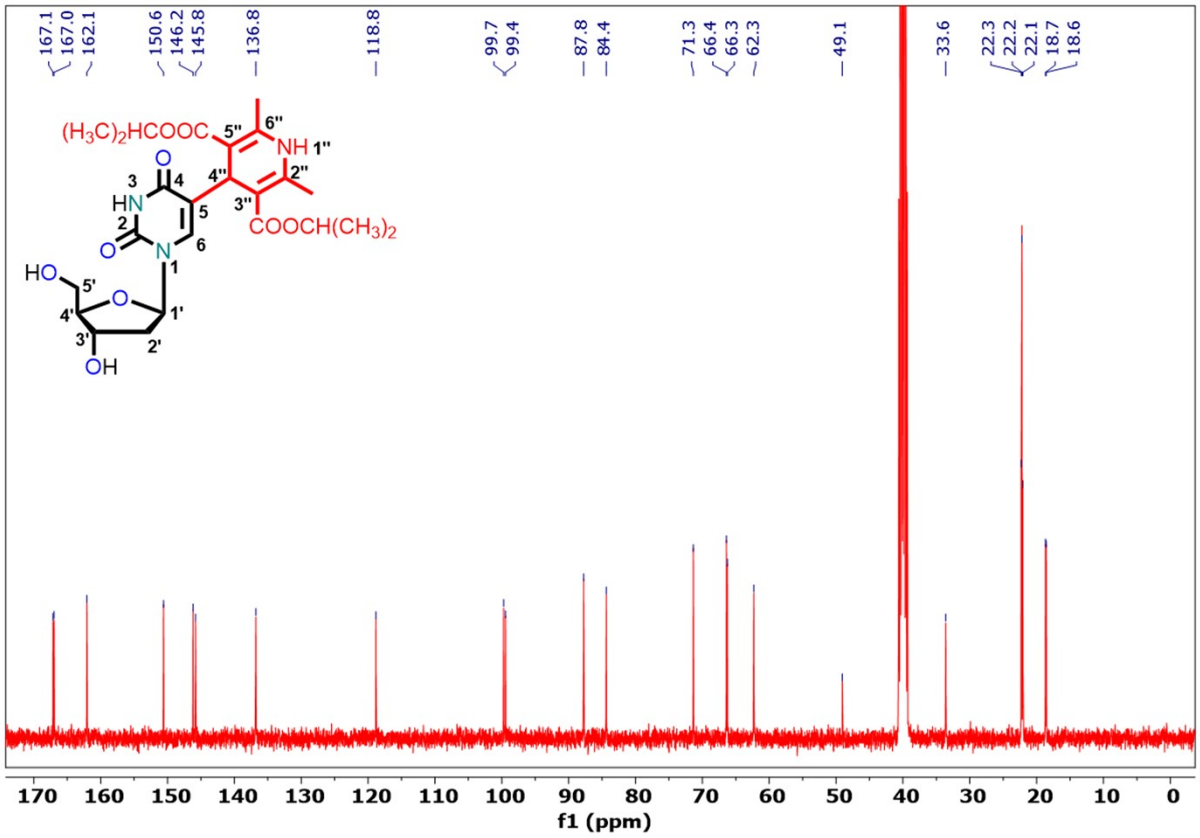


Figure S30: ^{13}C NMR Spectra of compound **6d** (DMSO-d_6, 100 MHz).

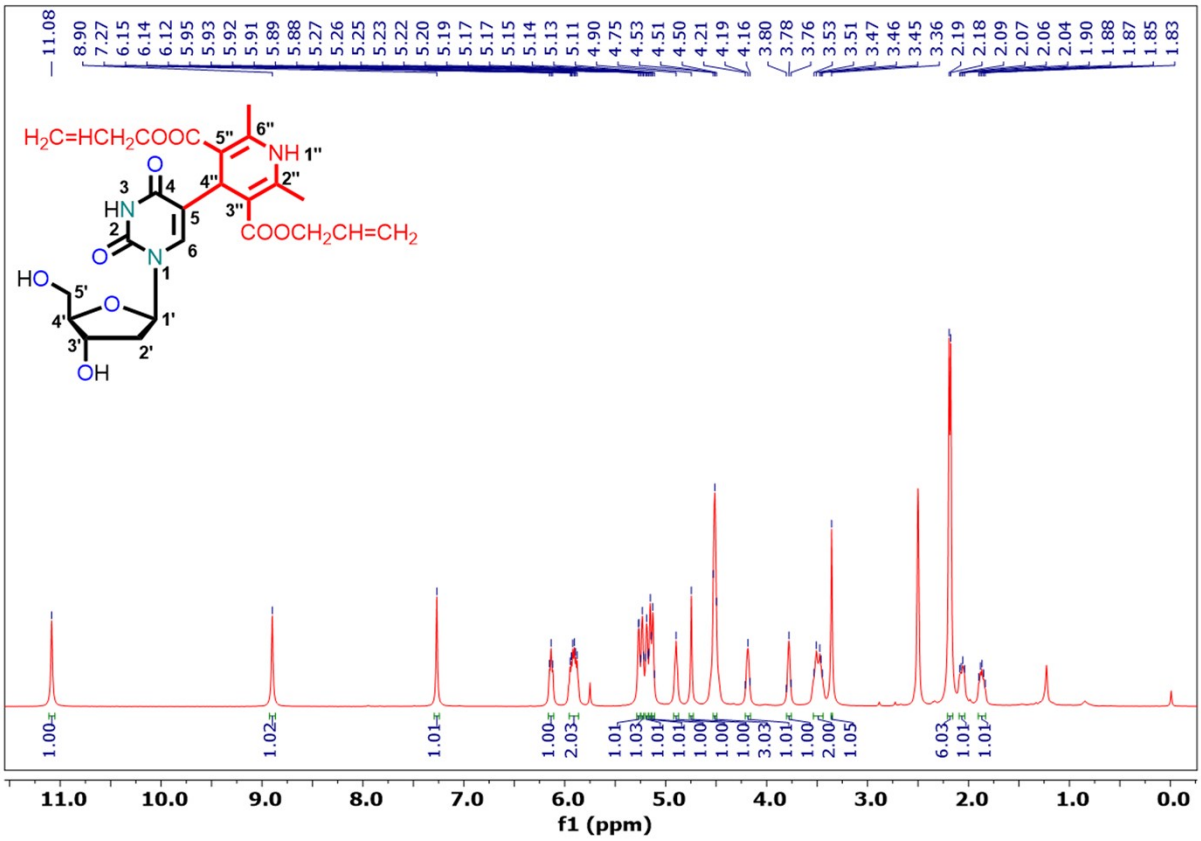


Figure S31: ^{1}H NMR Spectra of compound **6e** (DMSO-d_6, 400 MHz).

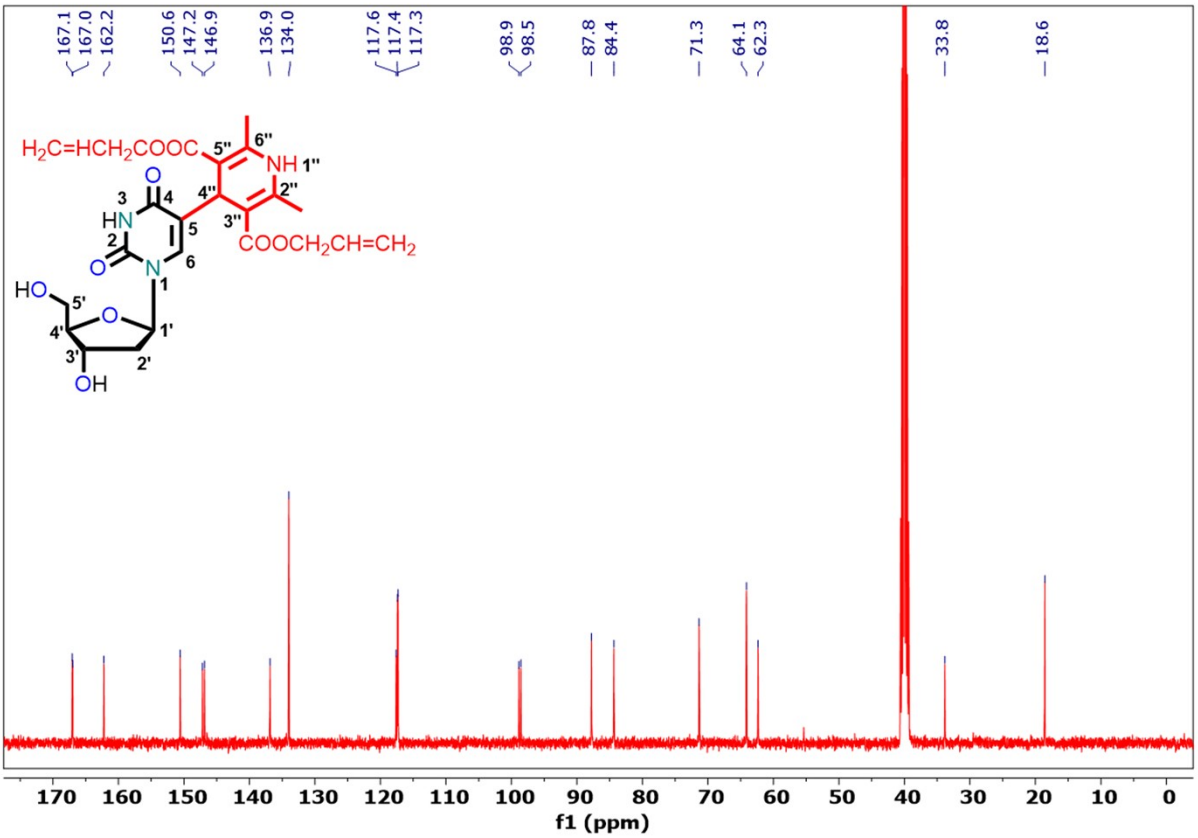


Figure S32: ^{13}C NMR Spectra of compound **6e** (DMSO-d_6, 100 MHz).

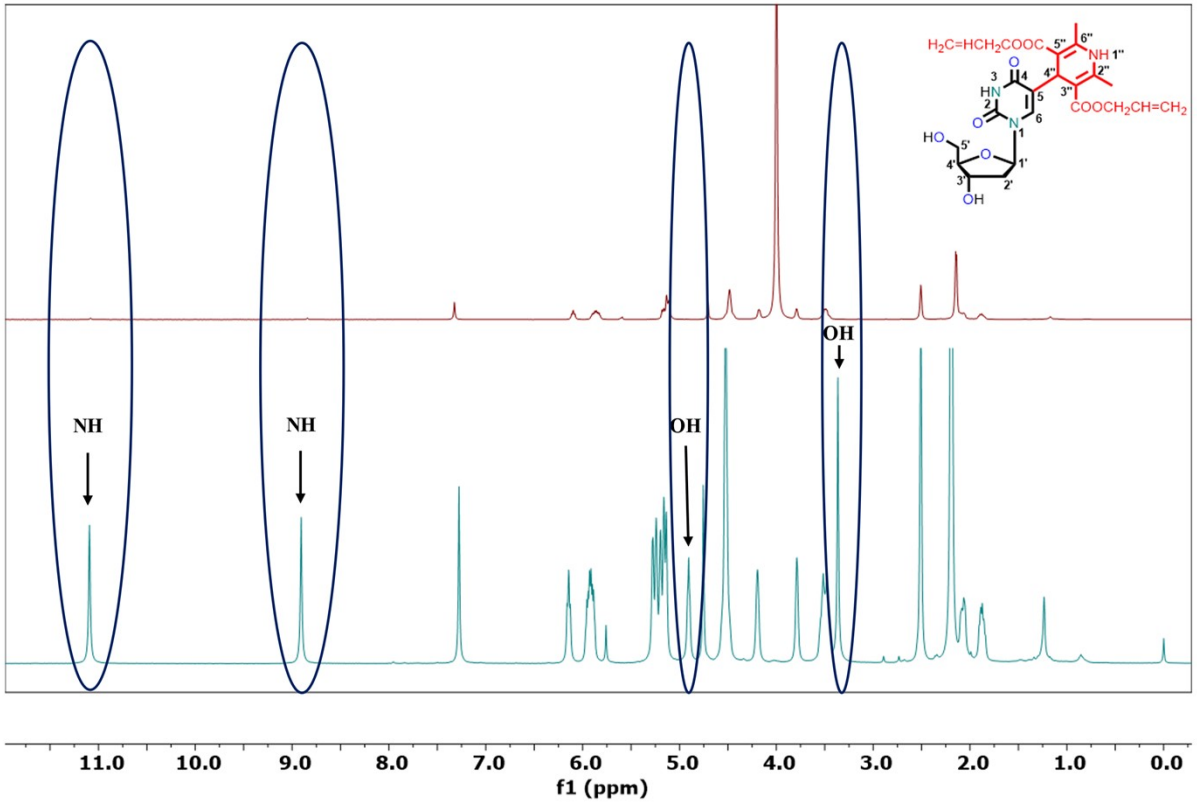


Figure S33: D_2O Exchange NMR Spectra of compound **6e** (DMSO-d_6, 100 MHz).

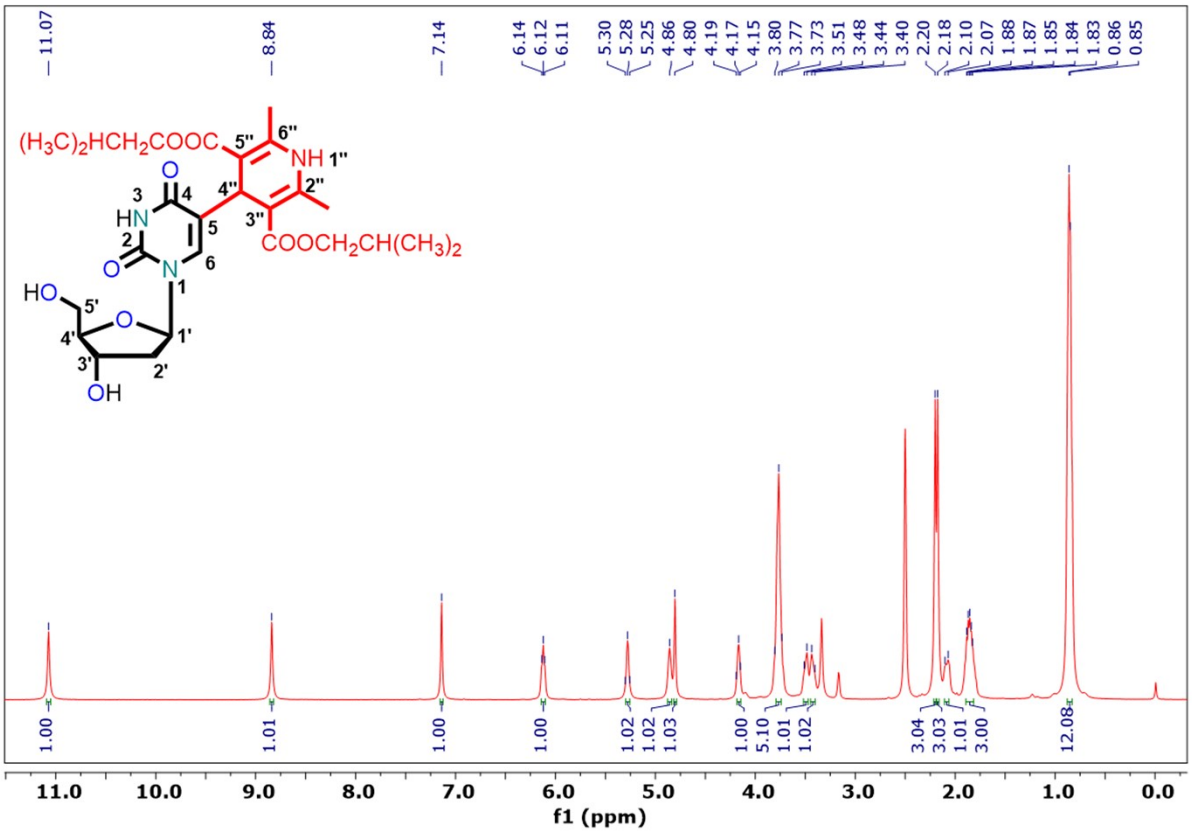


Figure S34: ^{1}H NMR Spectra of compound **6f** (DMSO-d_6, 400 MHz).

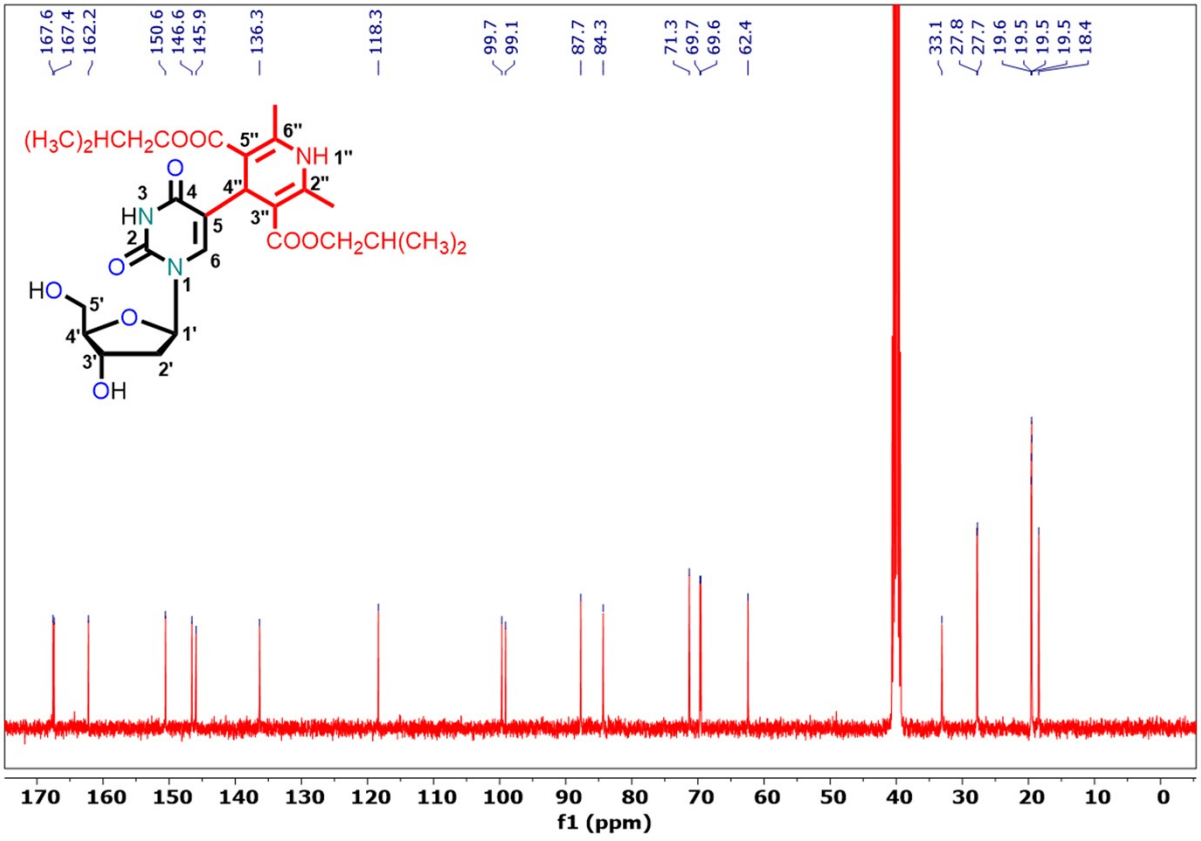


Figure S35: ^{13}C NMR Spectra of compound **6f** (DMSO-d_6, 100 MHz).

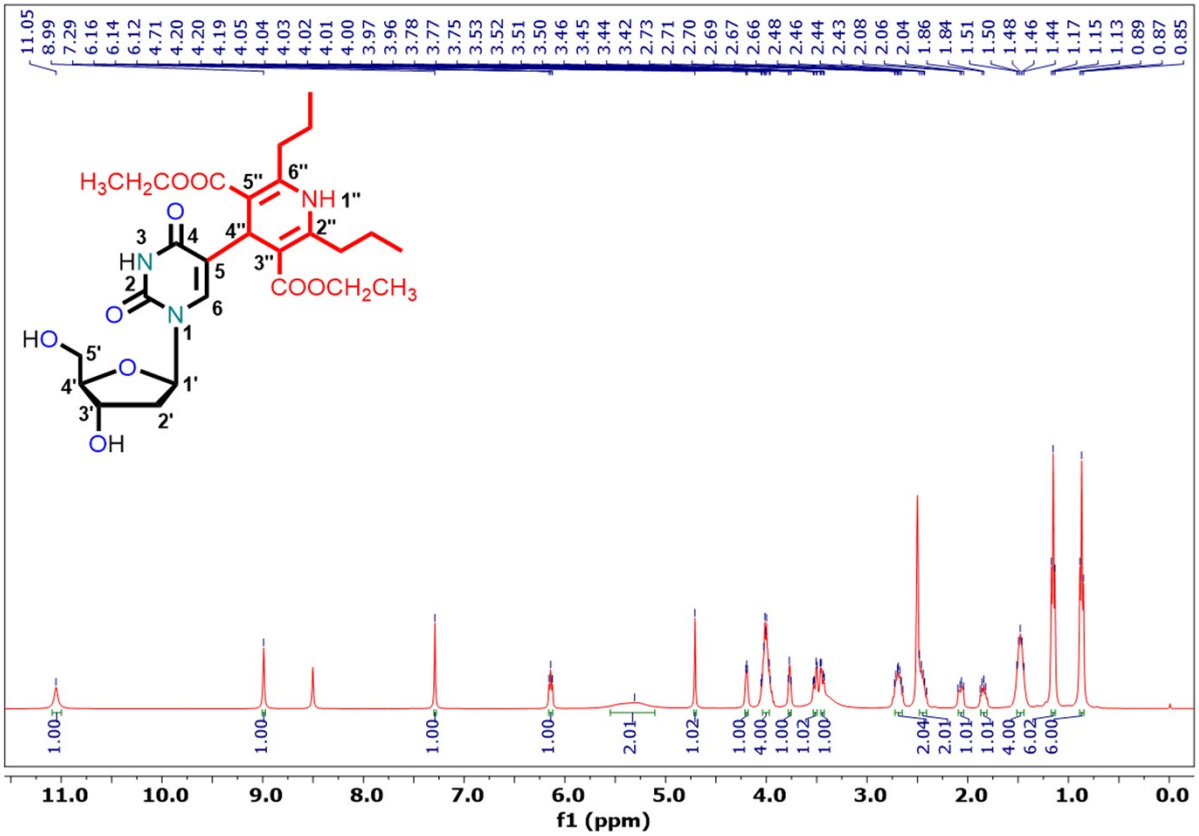


Figure S36: ^{1}H NMR Spectra of compound **6g** (DMSO-d_6, 400 MHz).

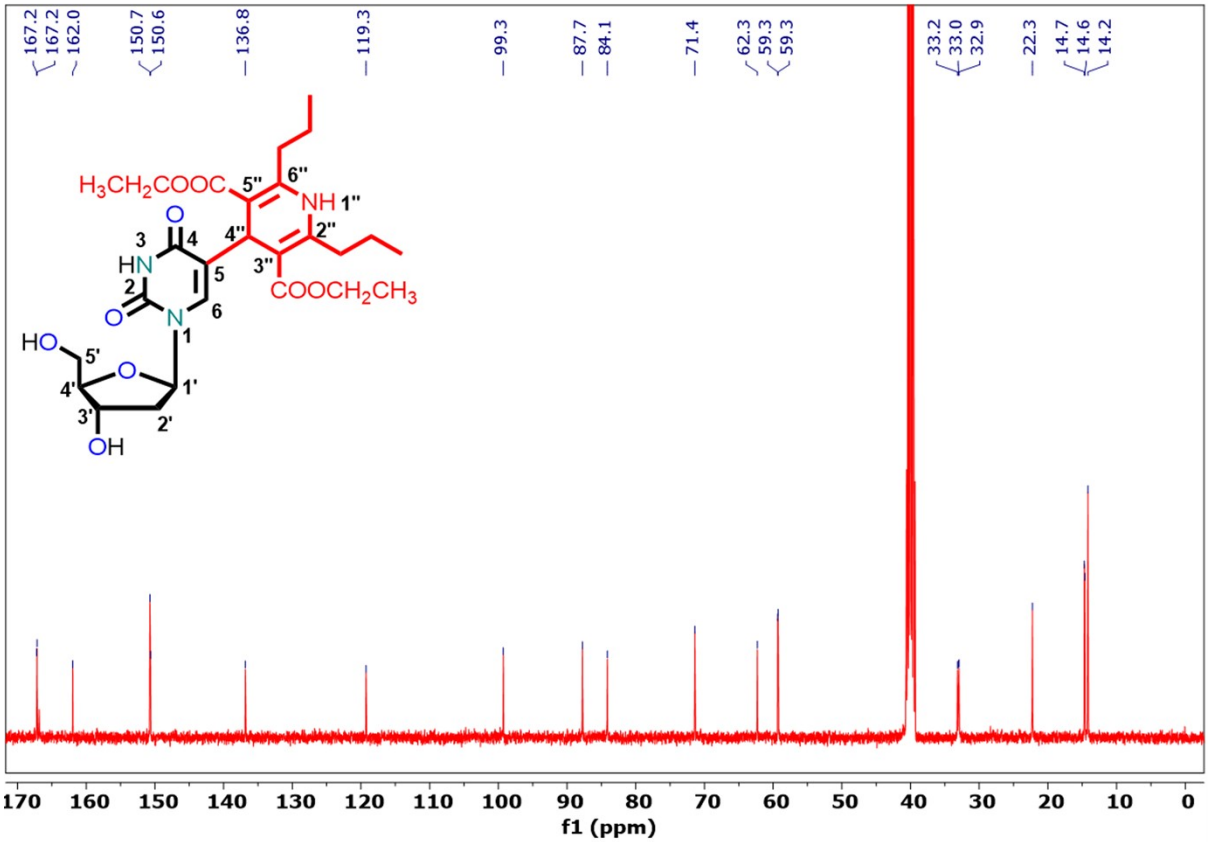


Figure S37: ^{13}C NMR Spectra of compound **6g** (DMSO-d_6, 100 MHz).

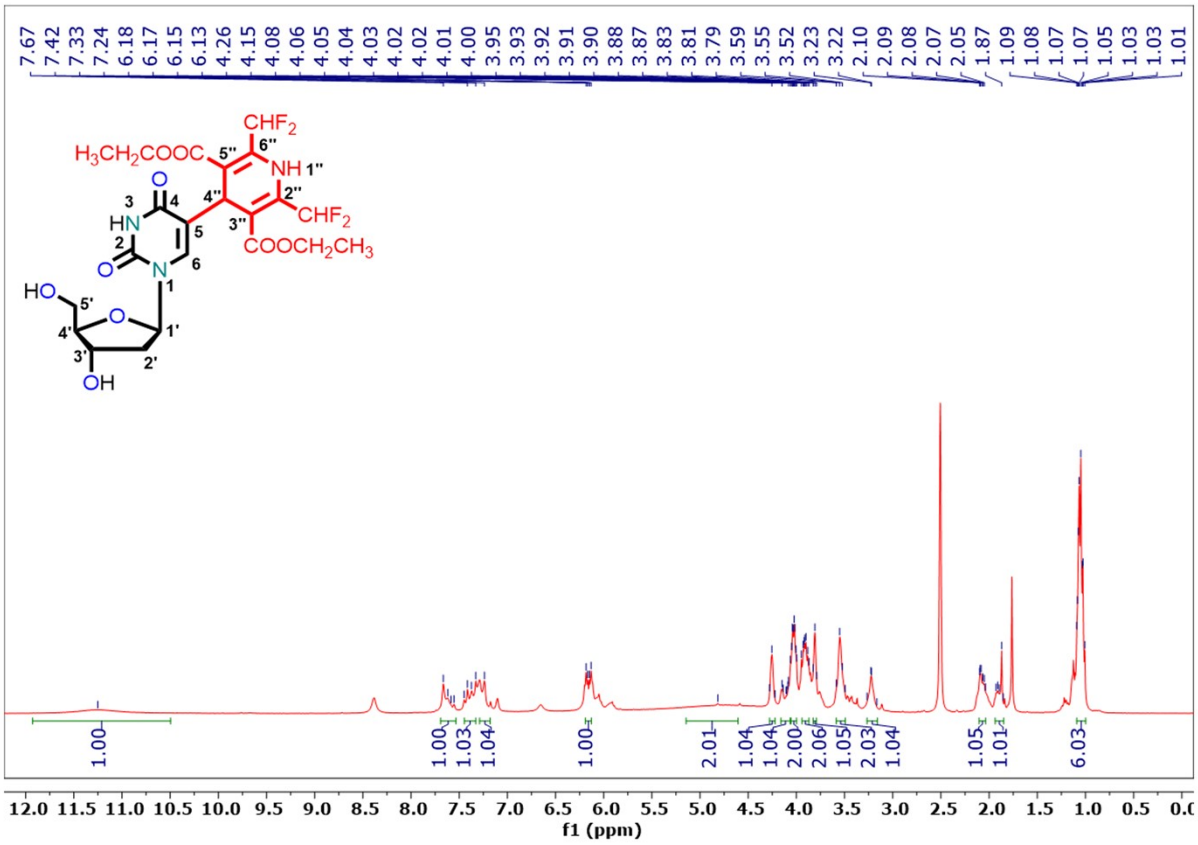


Figure S38: ^{1}H NMR Spectra of compound **6h** (DMSO-d_6, 400 MHz).

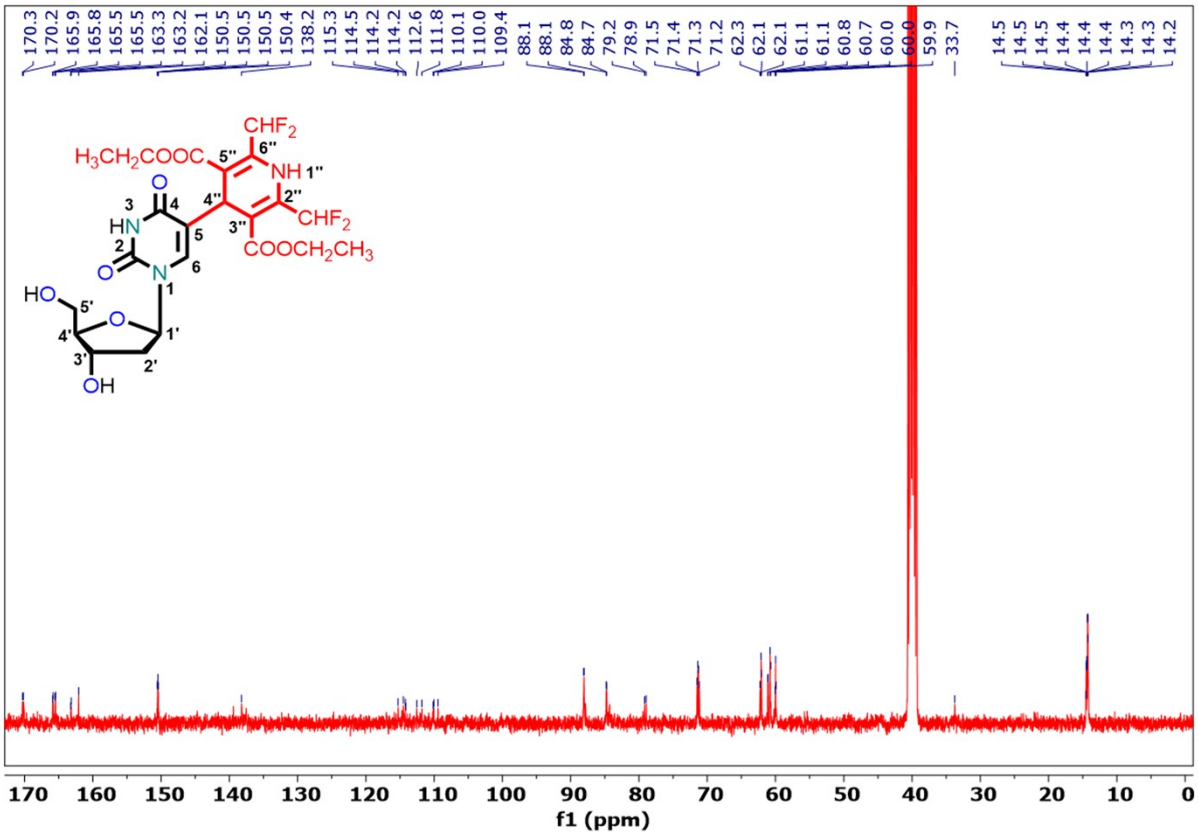


Figure S39: ^{13}C NMR Spectra of compound **6h** (DMSO-d_6, 100 MHz).

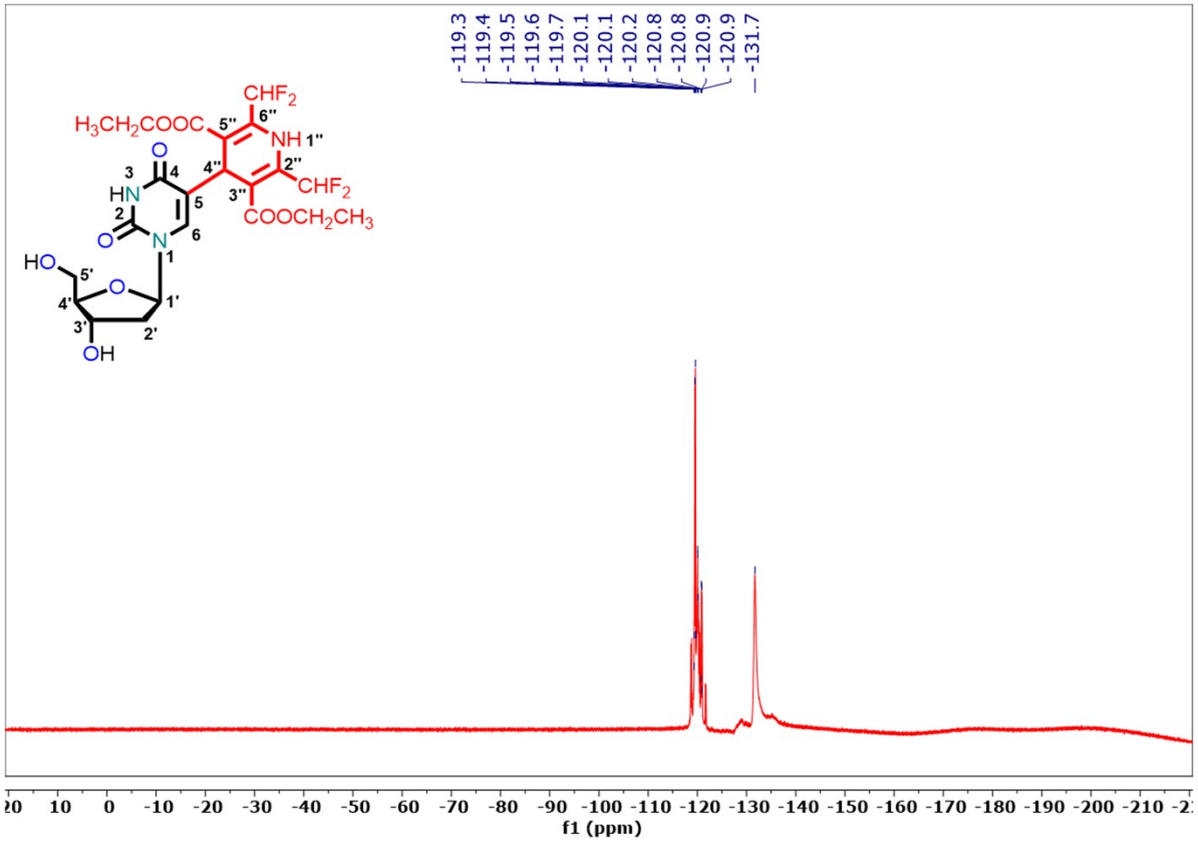


Figure S40: ^{19}F NMR Spectra of compound **6h** (DMSO-d_6, 377 MHz).

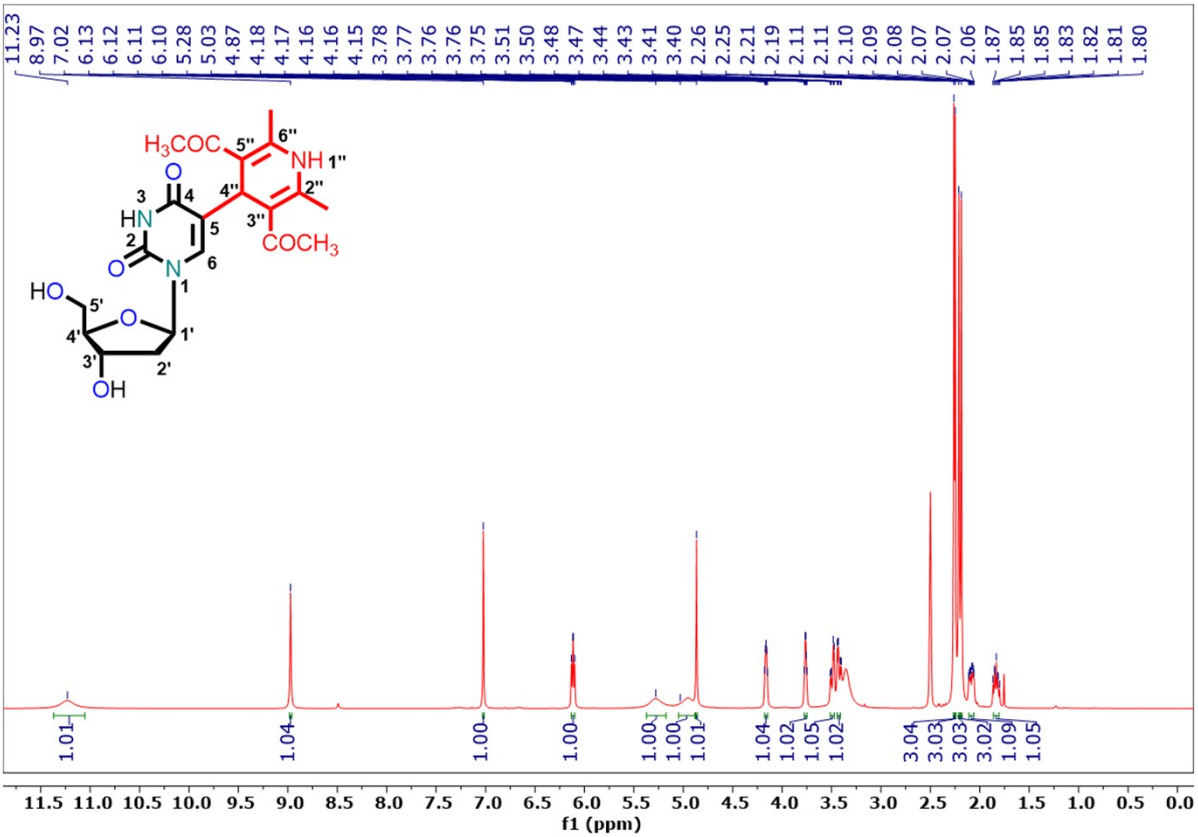


Figure S41: ^{1}H NMR Spectra of compound **6i** (DMSO-d_6, 400 MHz).

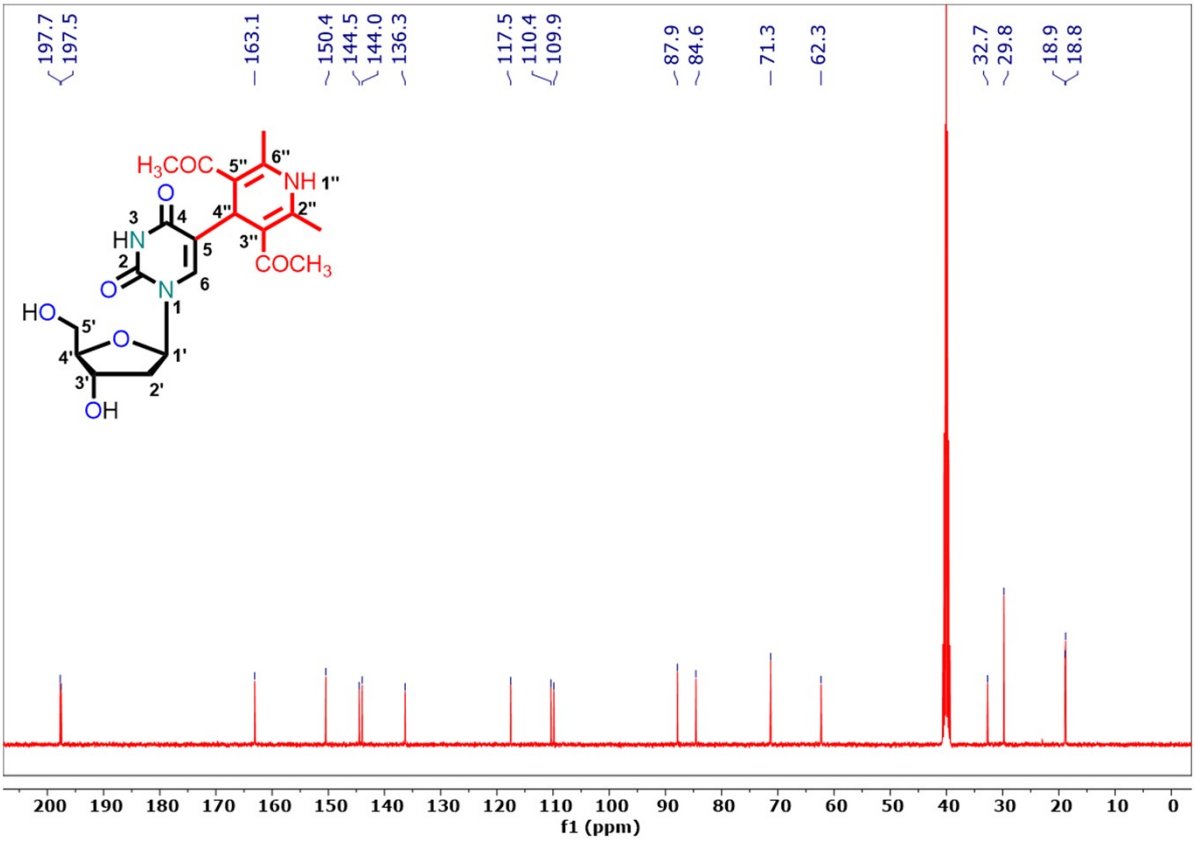


Figure S42: ^{13}C NMR Spectra of compound **6i** (DMSO-d_6, 100 MHz).

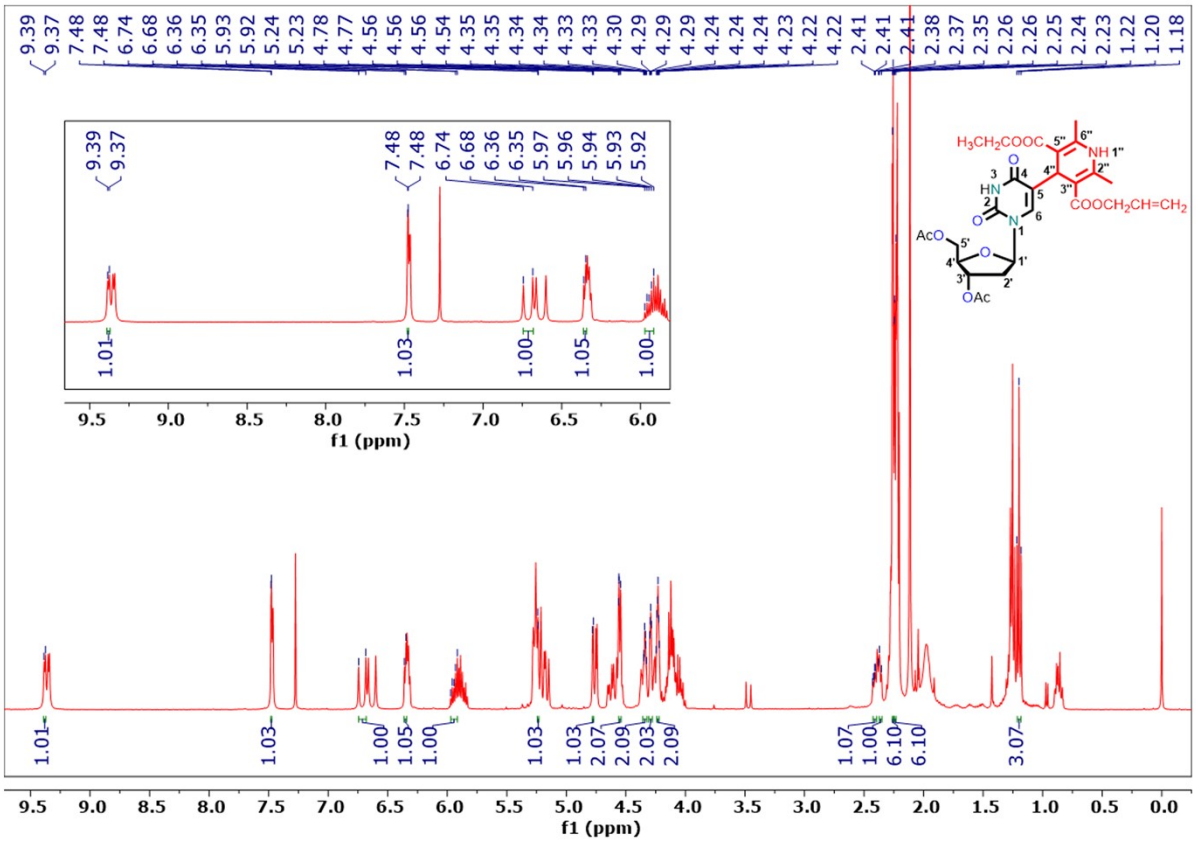


Figure S43: ^{1}H NMR Spectra of unsymmetrical 1,4-dihydropyridine ($CDCl_3$, 400 MHz).

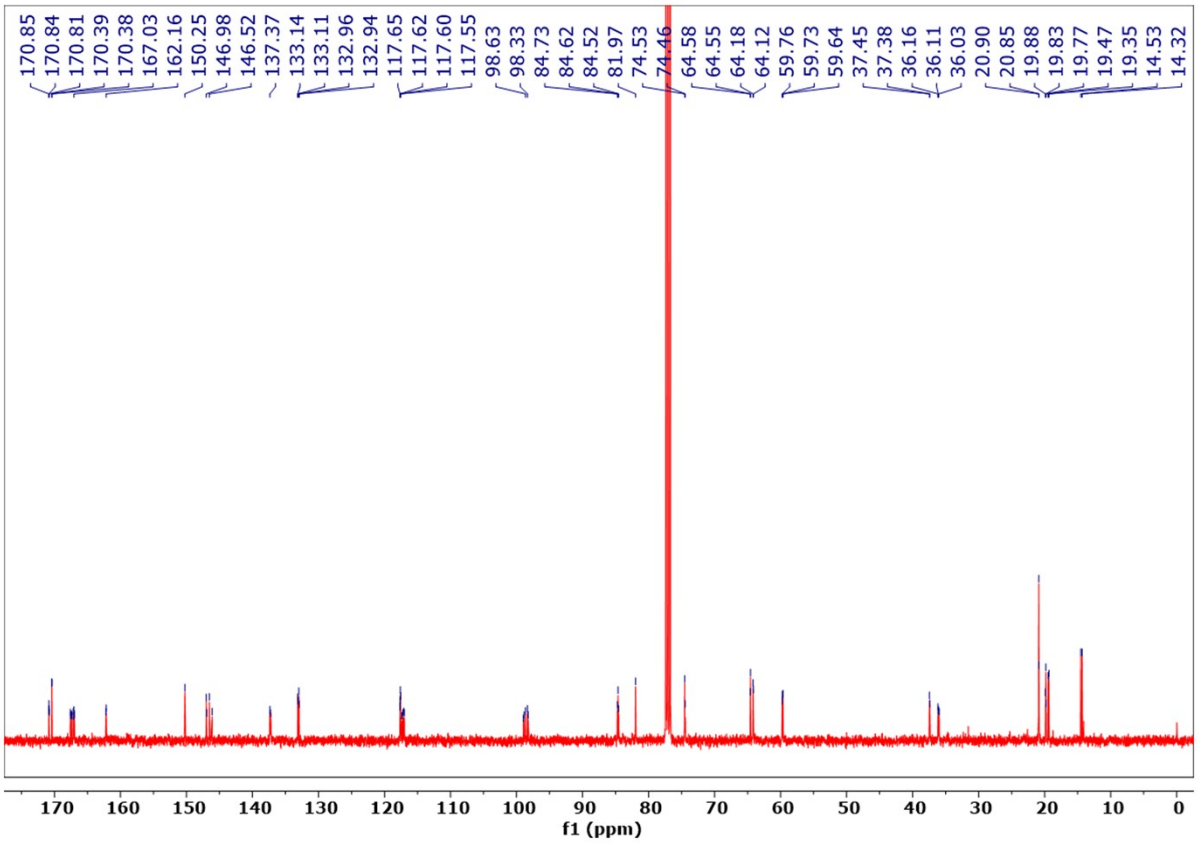


Figure S44: ^{13}C NMR Spectra of unsymmetrical 1,4-dihydropyridine ($CDCl_3$,100 MHz).

2. Absorption and Emission Spectra of Compounds 6a-i.

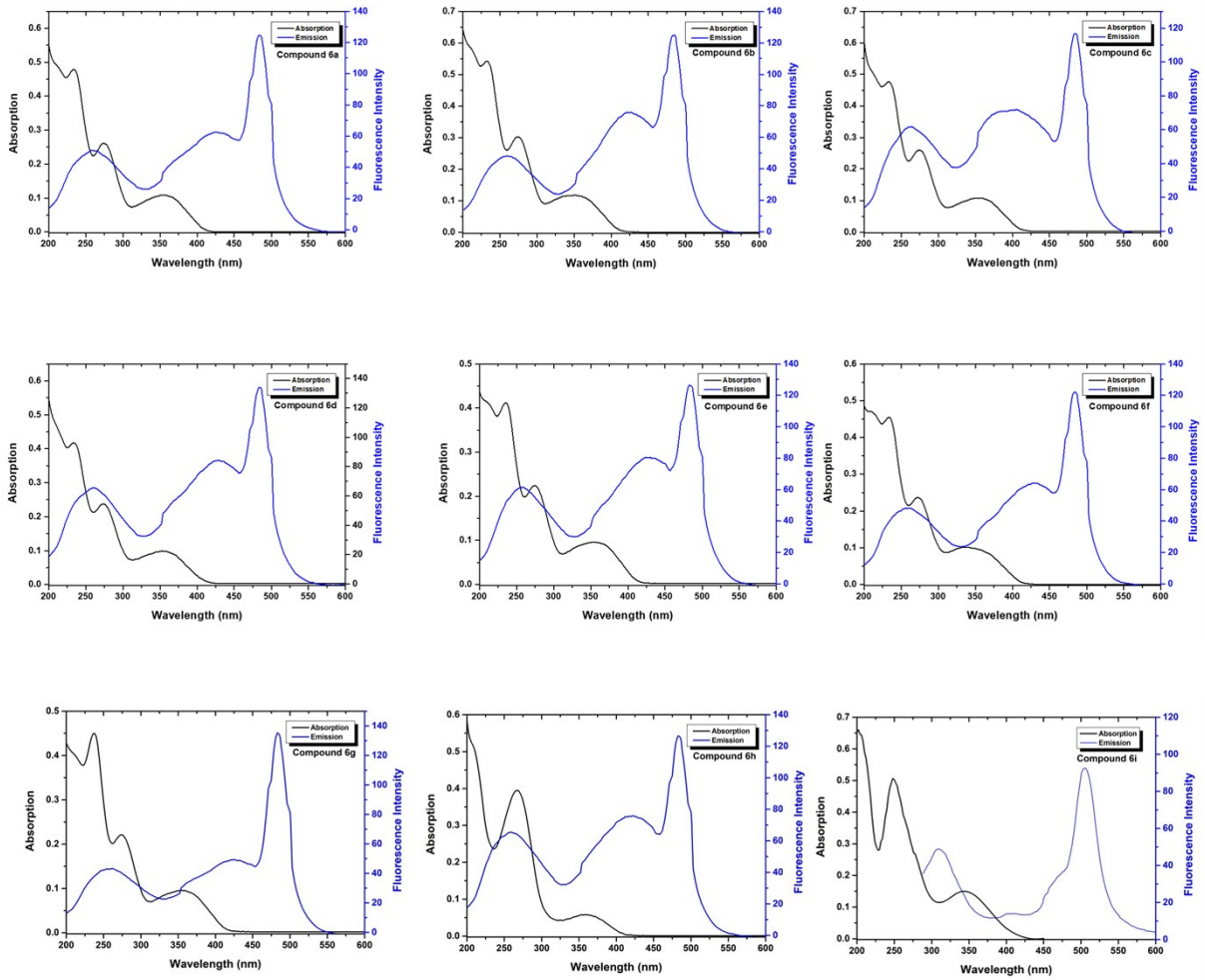


Figure S45: Absorption and Emission Spectra for compounds **6a-i**.