

Supporting Information

Novel Water-Soluble Phosphatriazines: Versatile Ligands for Suzuki, Sonogashira and Heck reactions of Nucleosides

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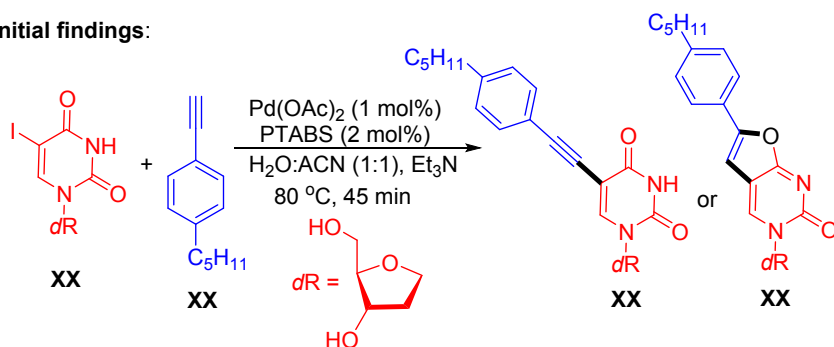
Felix-Hausdorff-Str. 4, 17489 Greifswald, Germany

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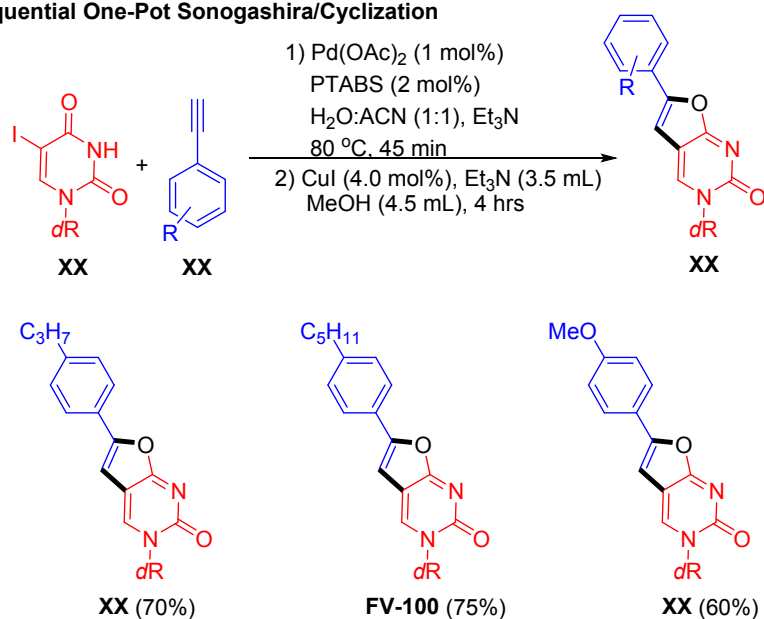
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Scheme 1: Sequential one-pot Sonogashira-cyclization protocol.

Initial findings:

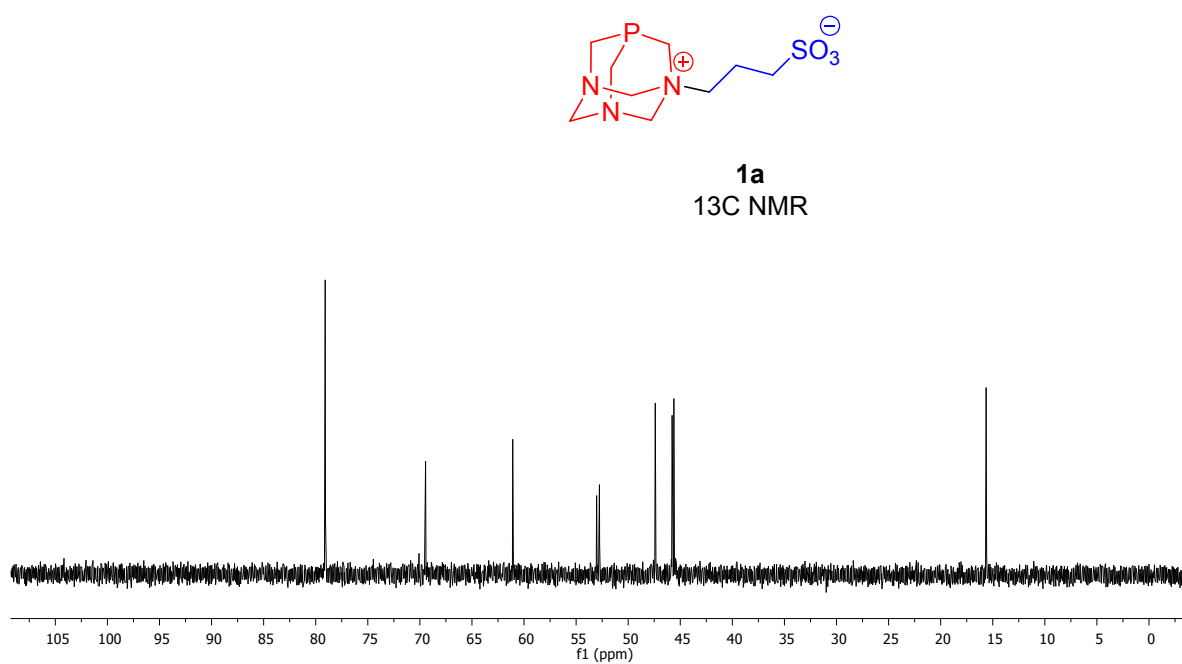
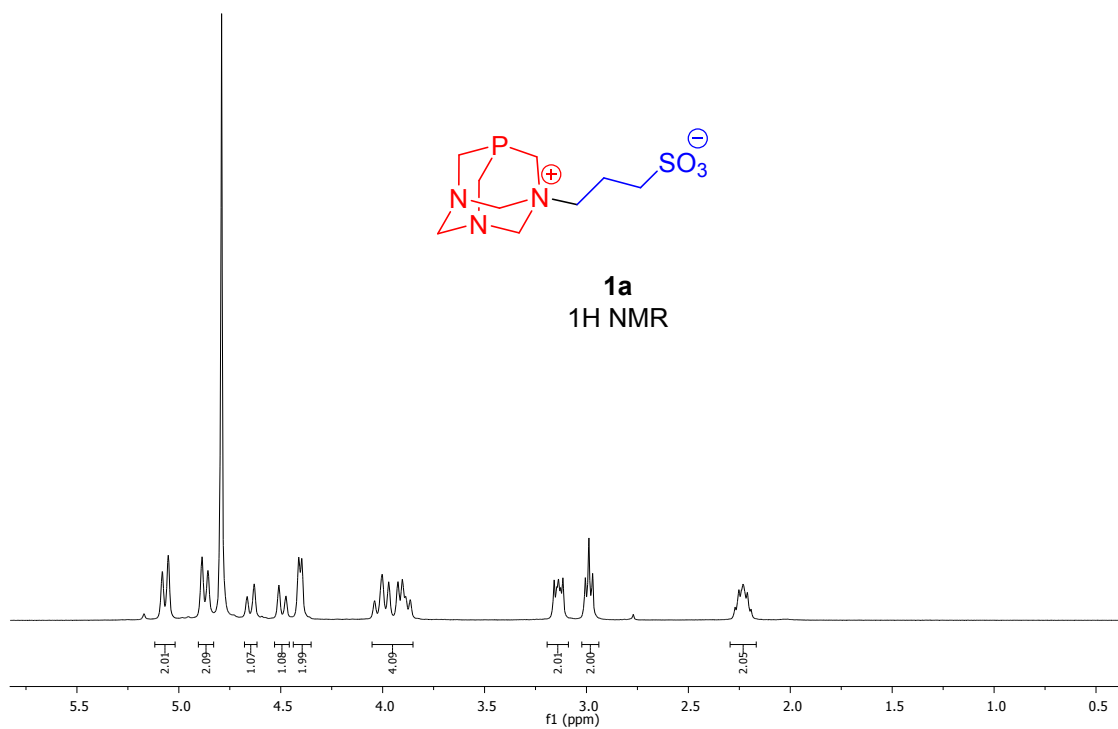


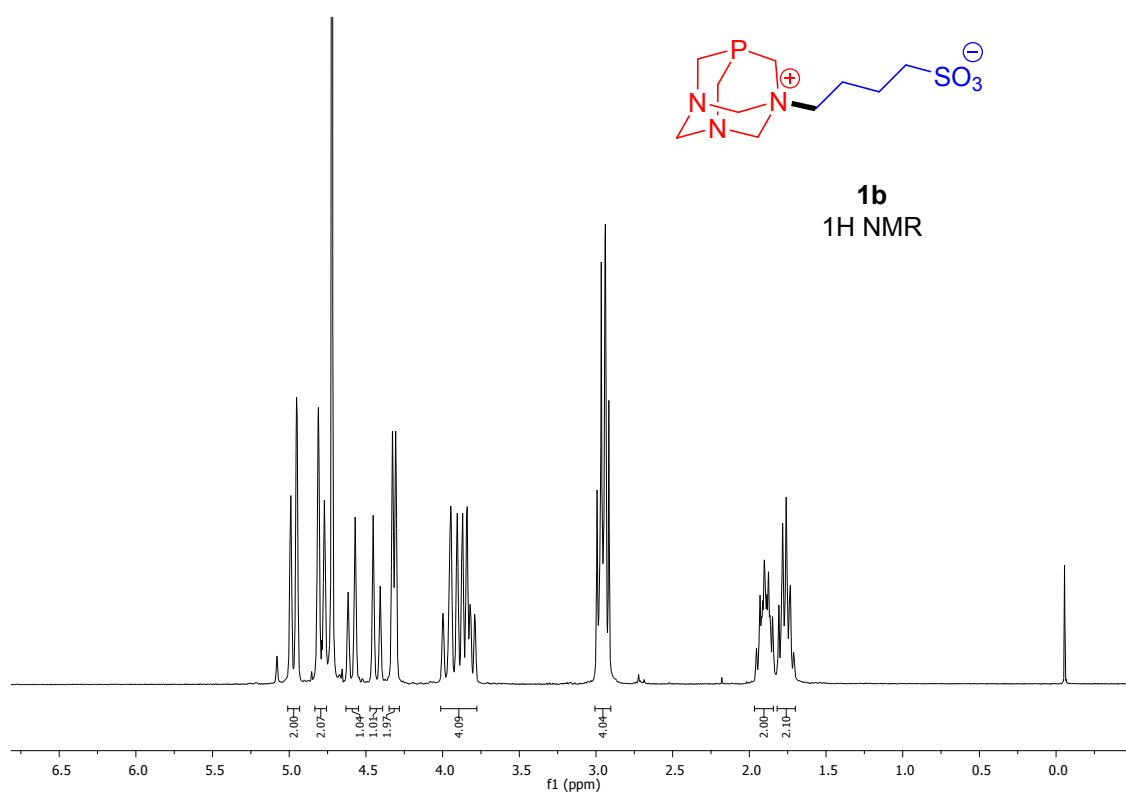
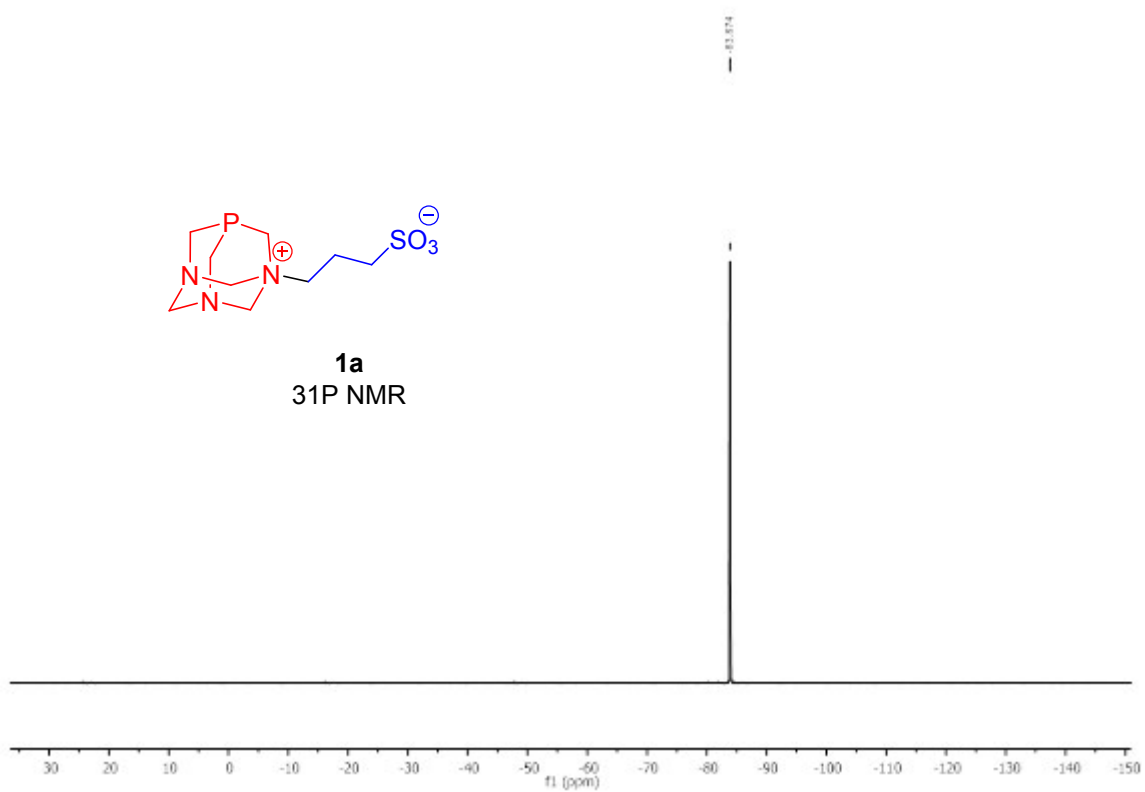
Sequential One-Pot Sonogashira/Cyclization

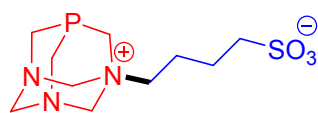


^aReaction conditions: 1) 0.5 mmol of 5-IdU, 1.0 mmol of alkyne, 1.0 mol% of Pd(OAc)₂, 2.0 mol% of PTABS, 1.0 mmol of triethylamine, 3 ml of H₂O:ACN(1:1), 2) CuI (4.0 mol%), Et₃N (3.5 mL), MeOH (4.5 mL) for 4 hrs. ^bisolated yields.

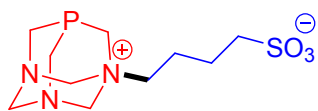
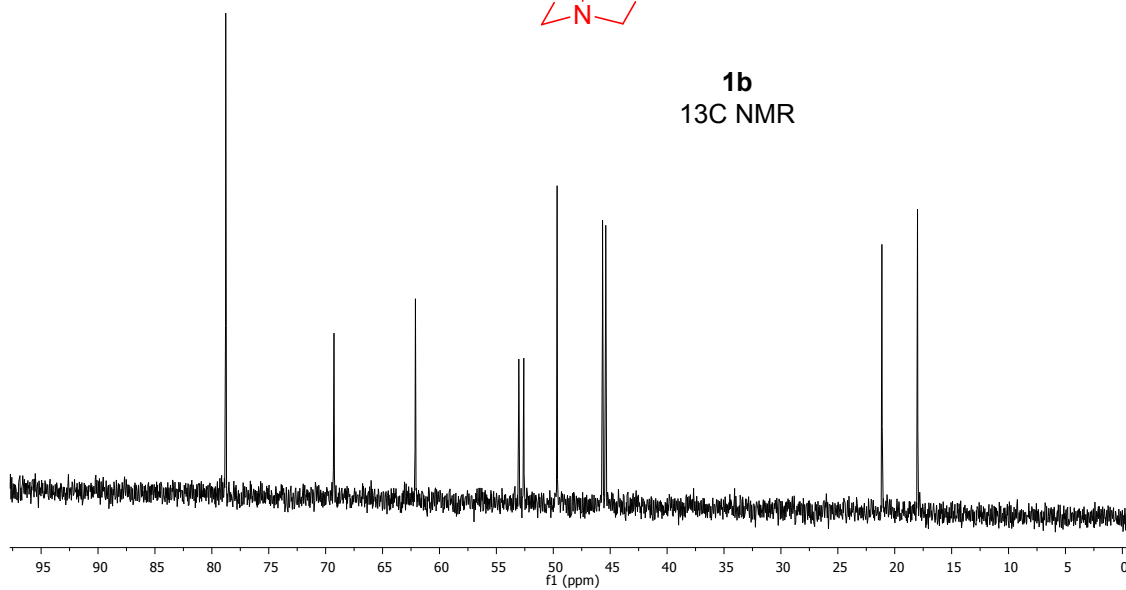
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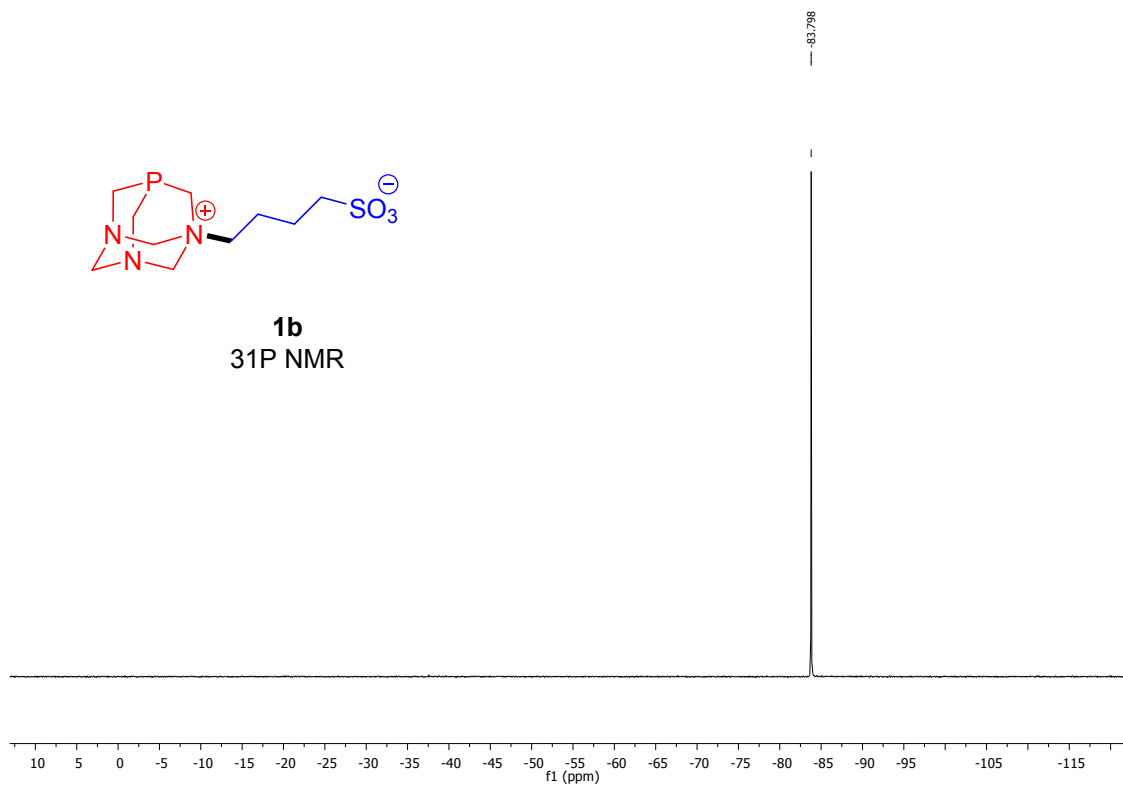


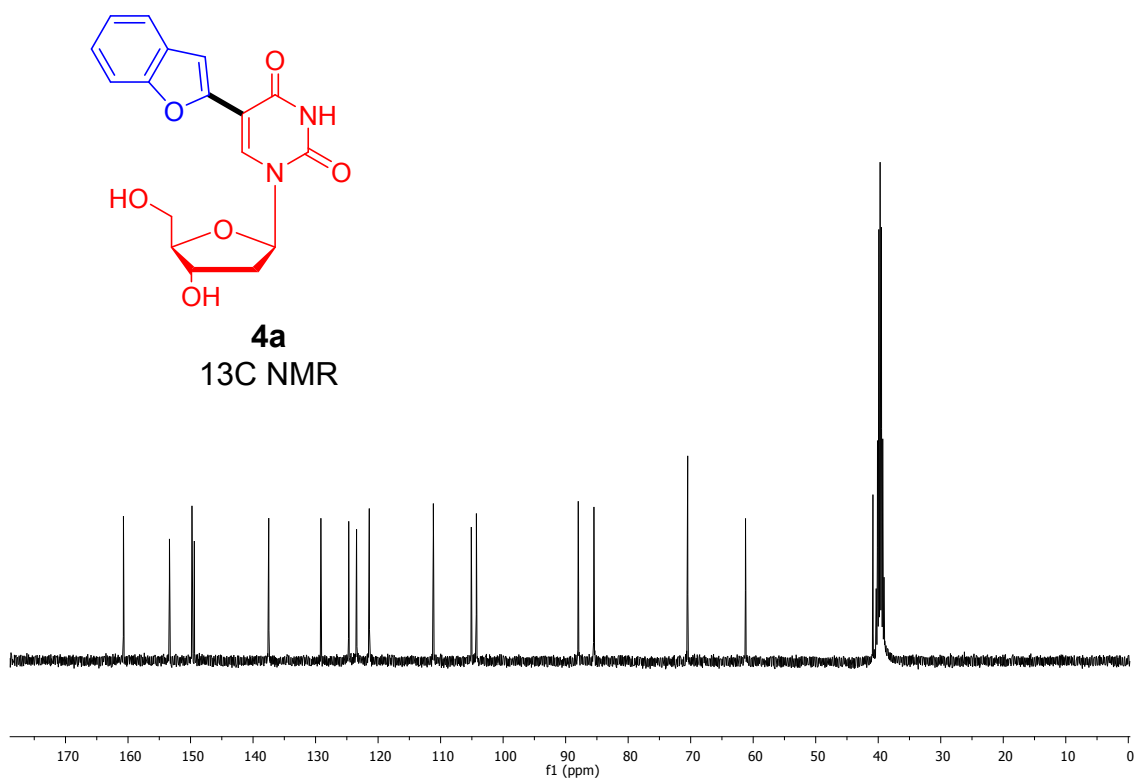
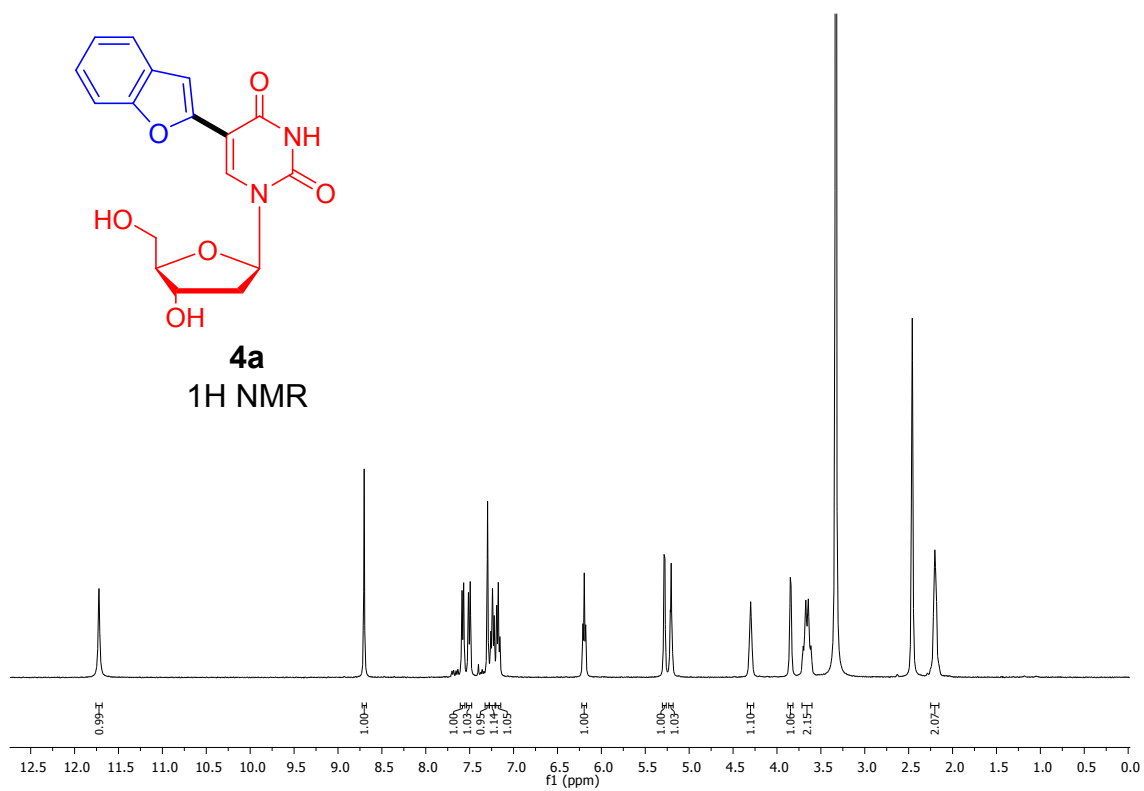


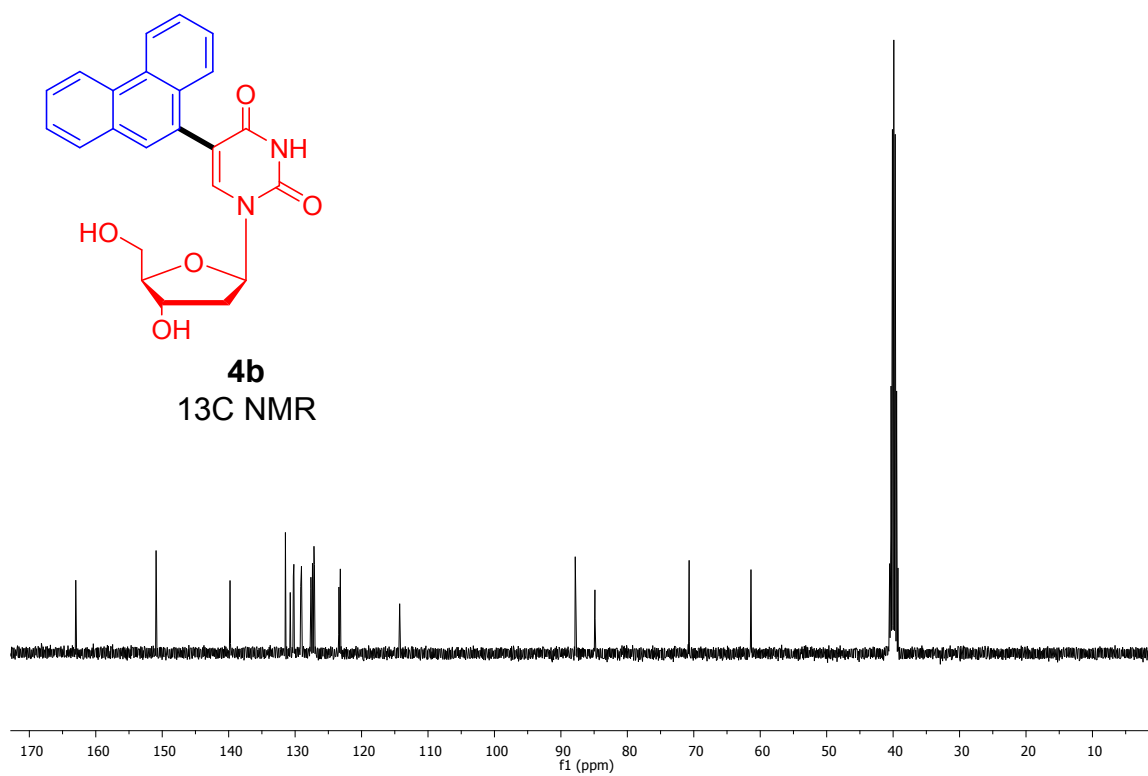
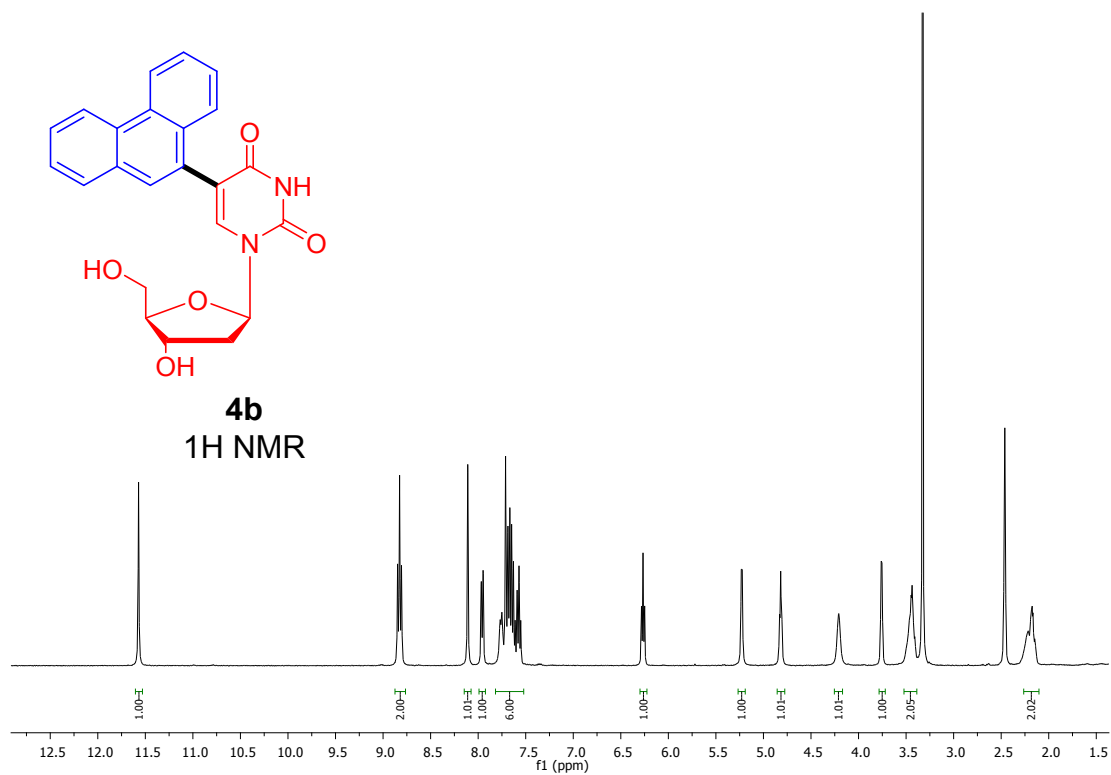
1b
¹³C NMR

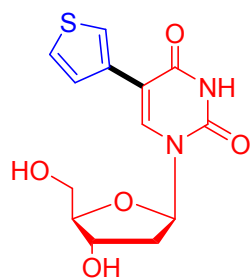


1b
³¹P NMR

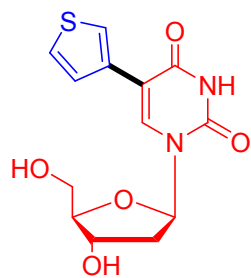
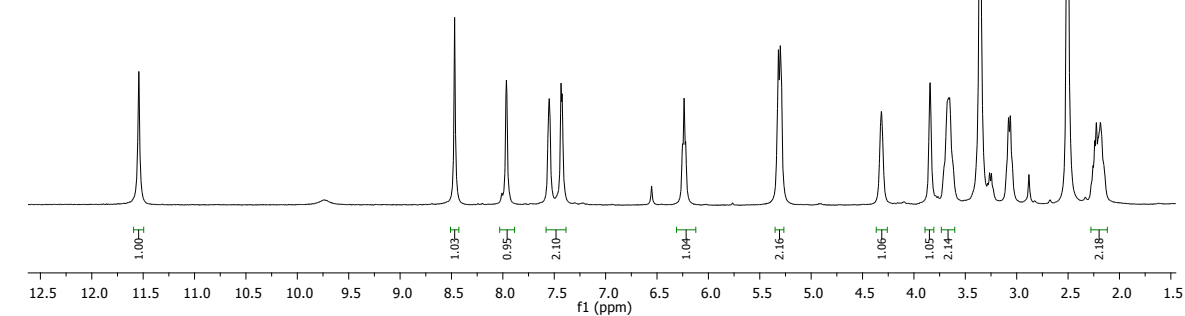




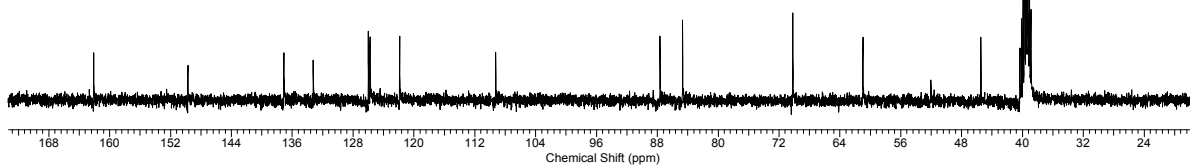


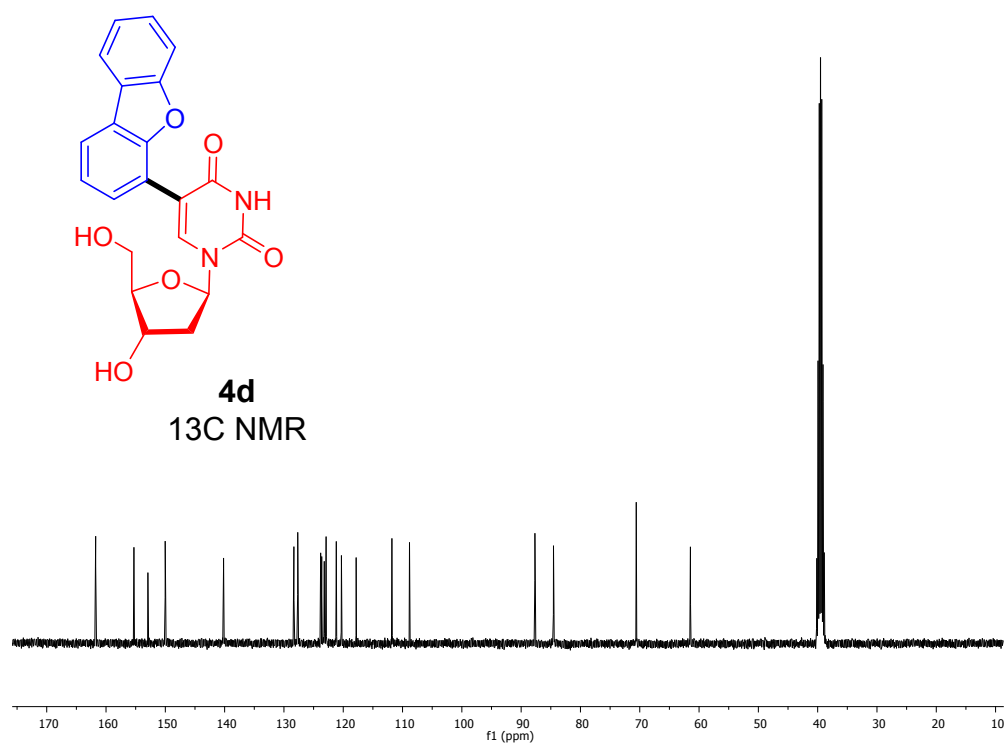
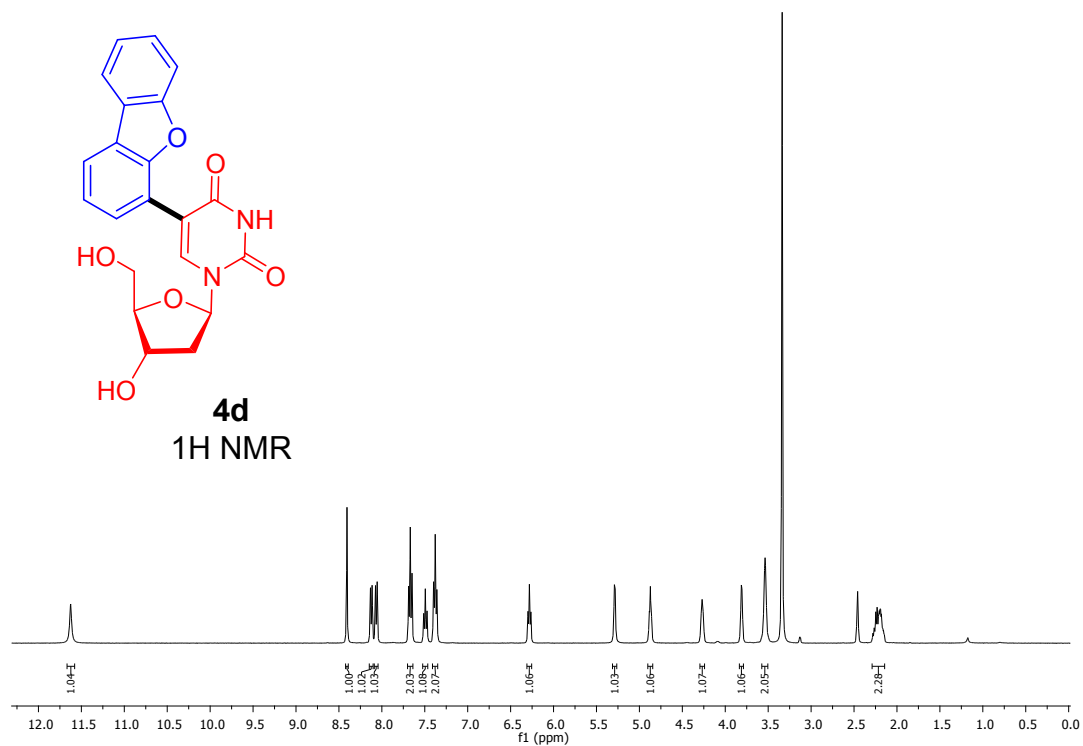


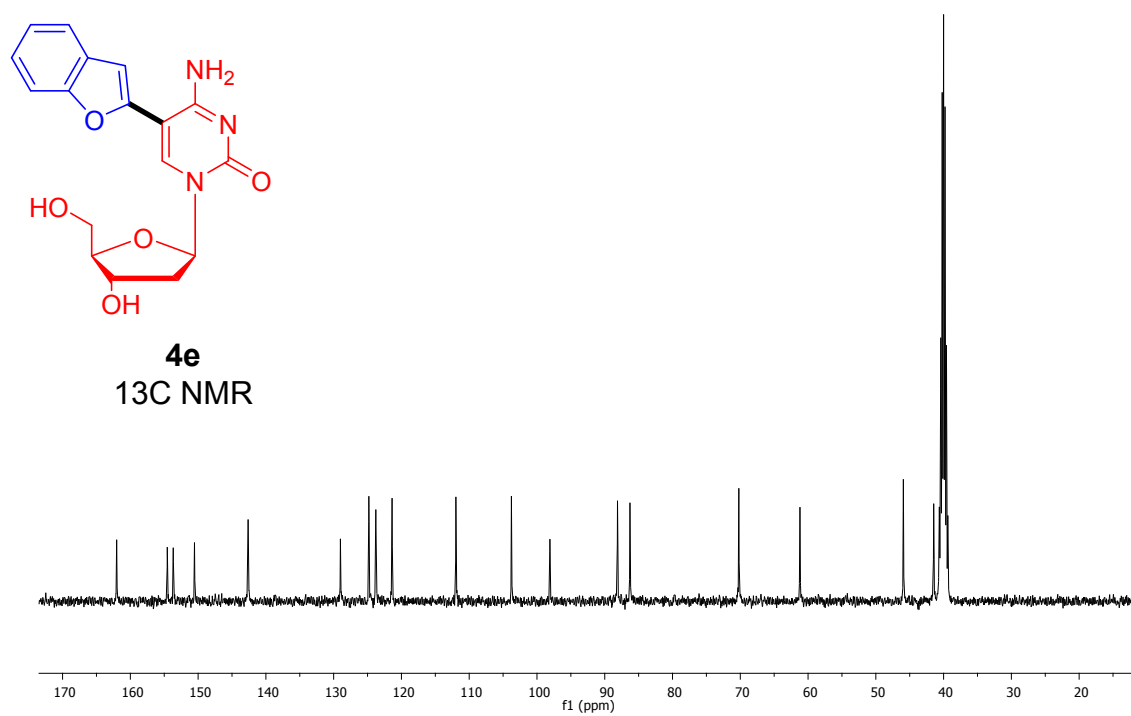
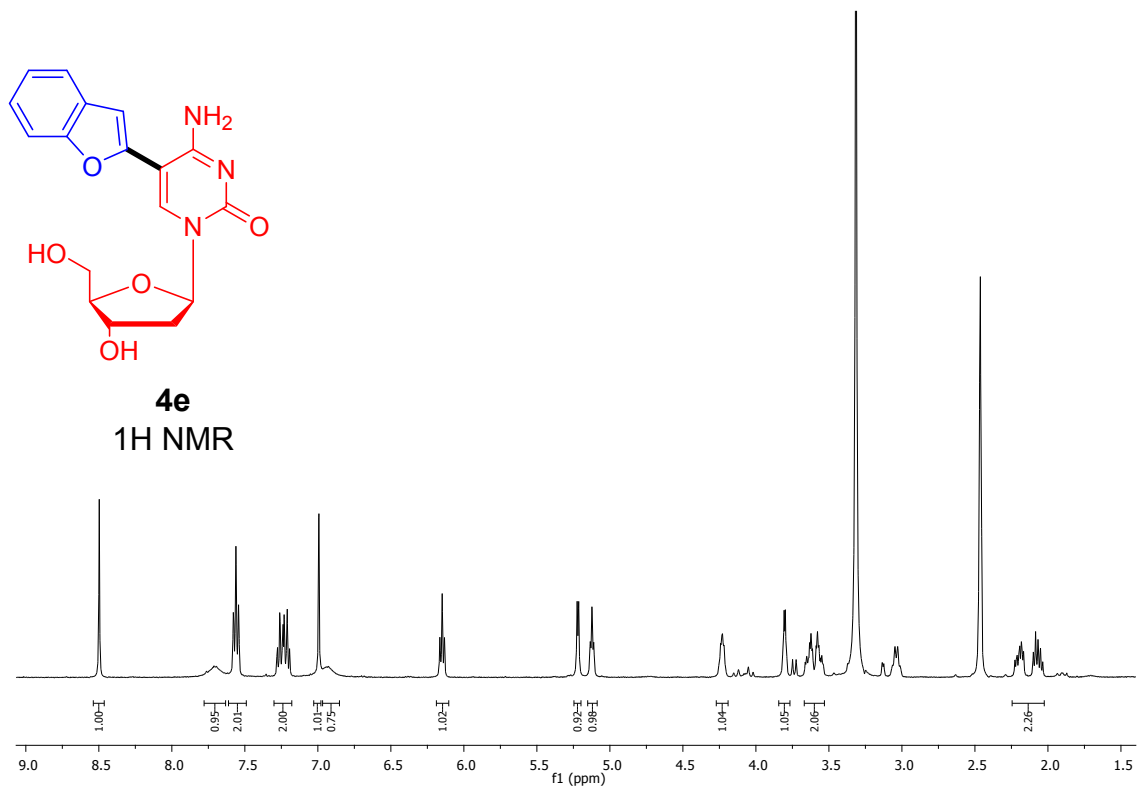
4c
¹H NMR

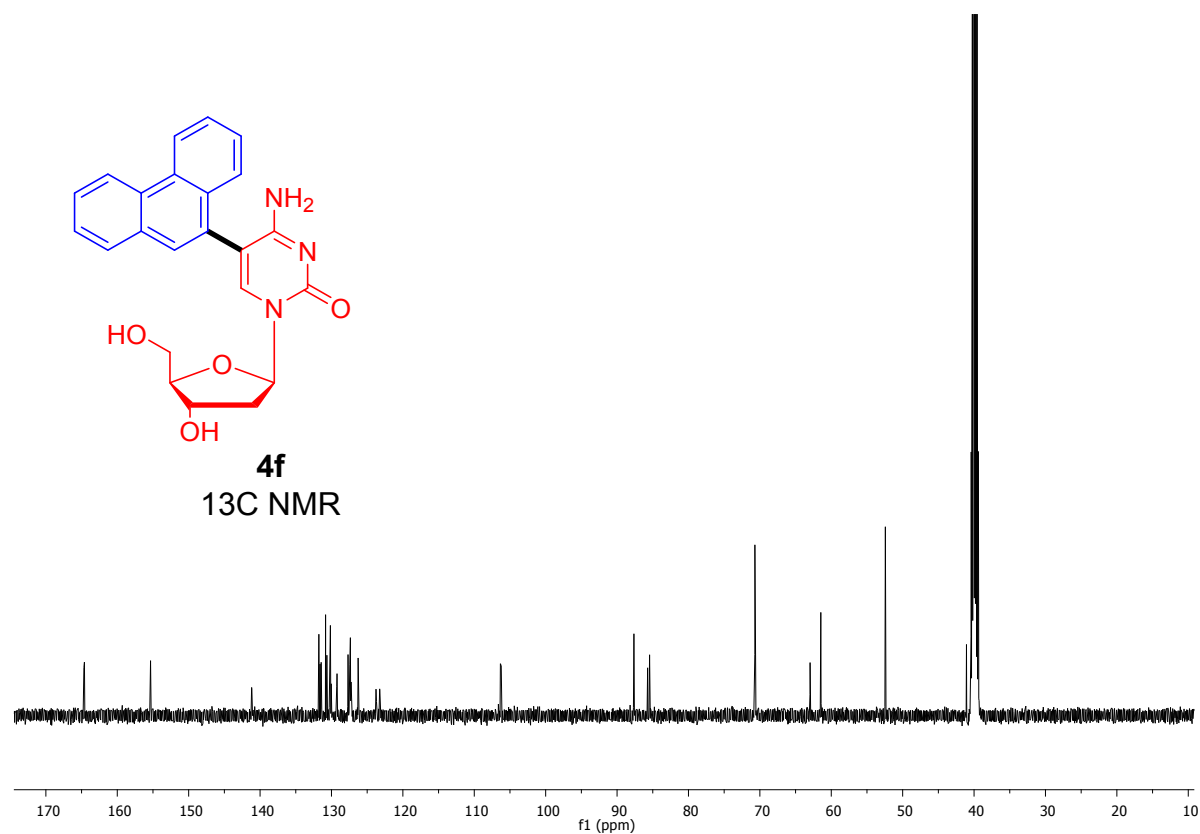
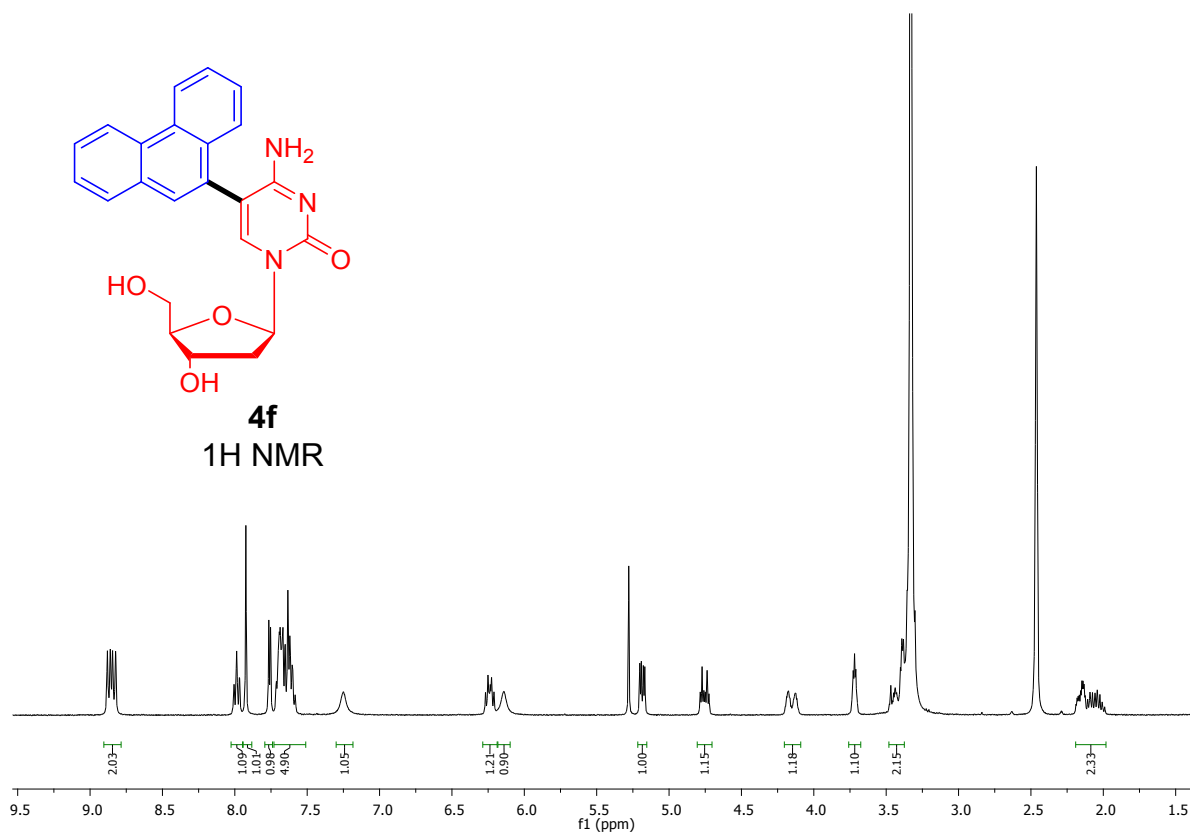


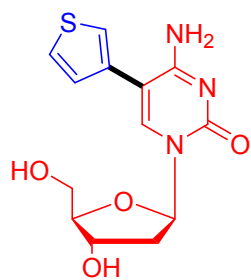
4c
¹³C NMR



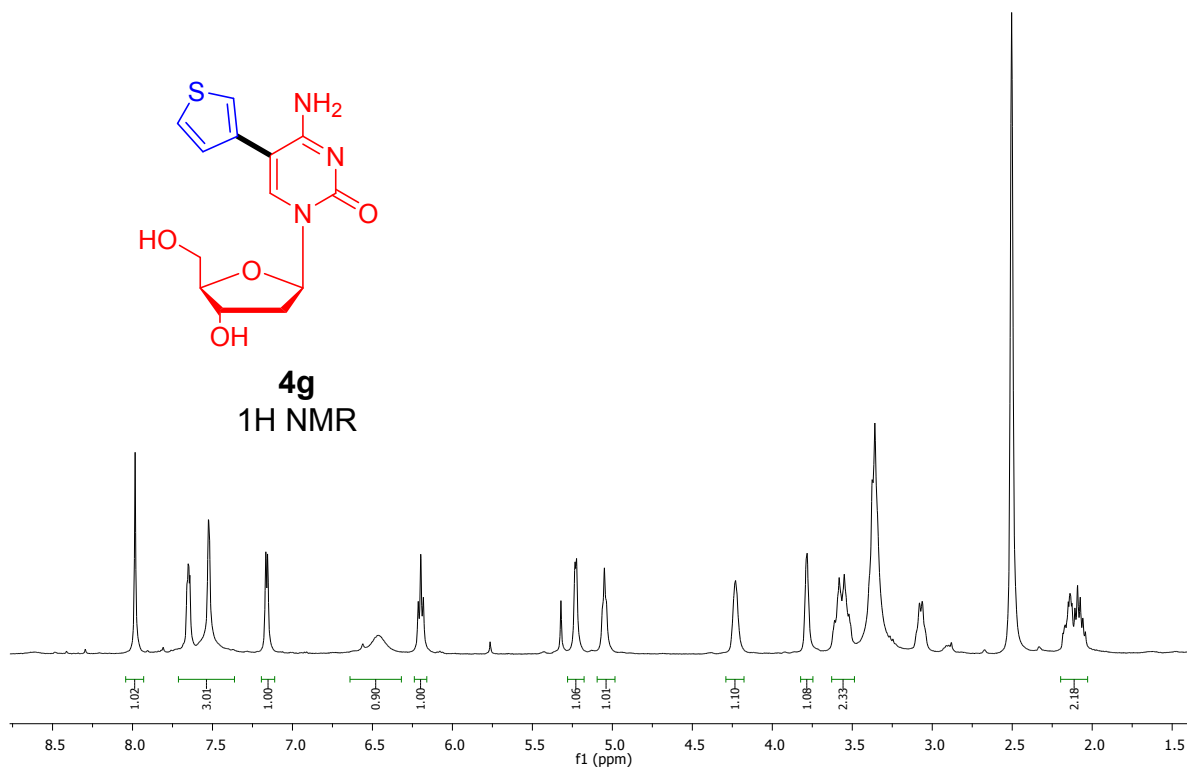




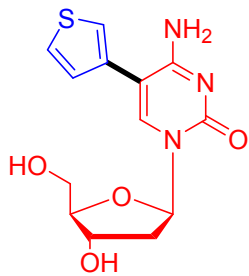




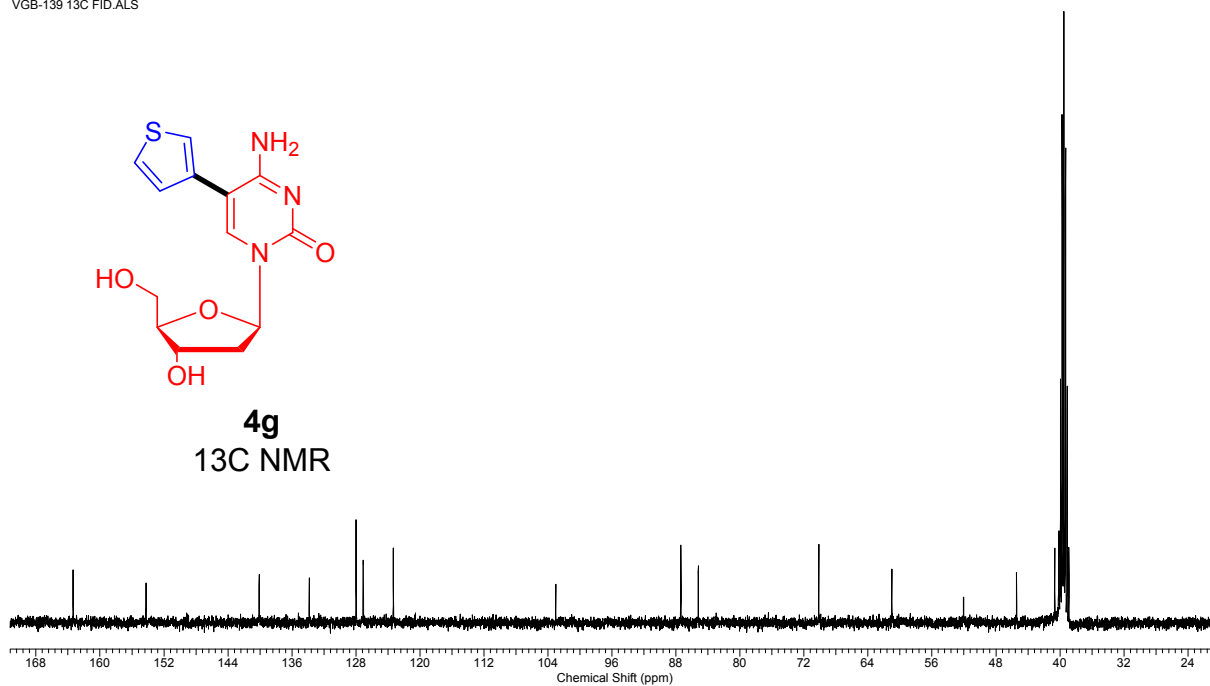
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1H NMR

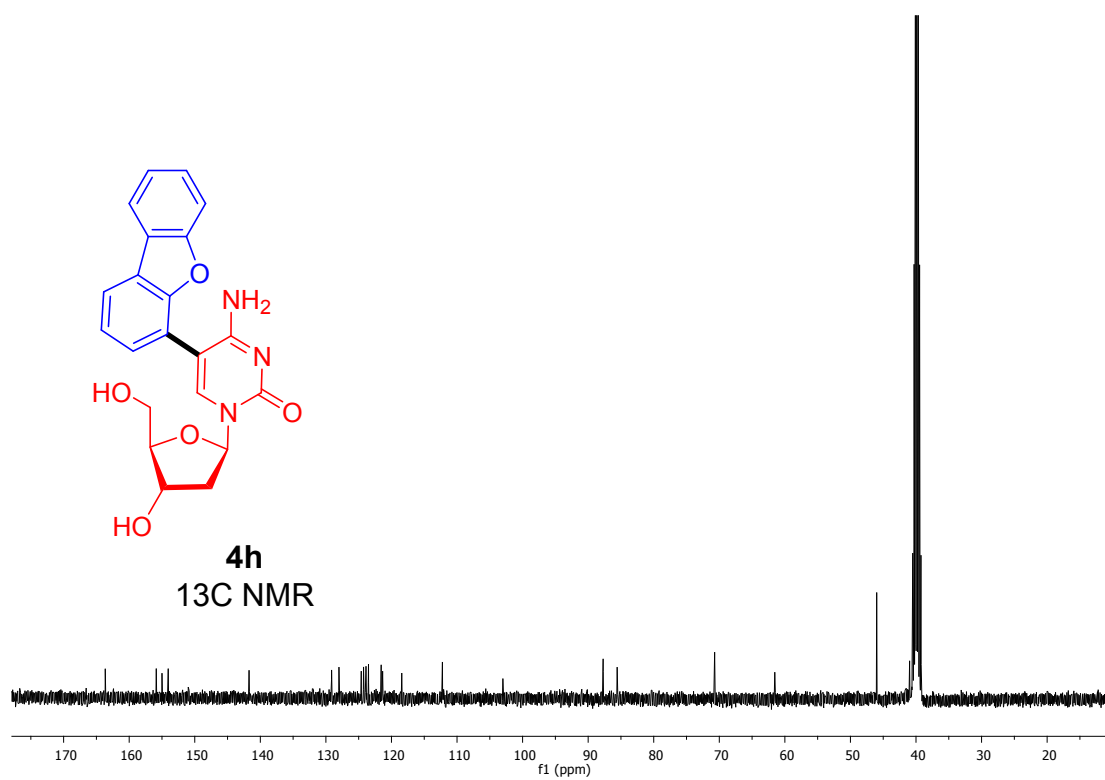
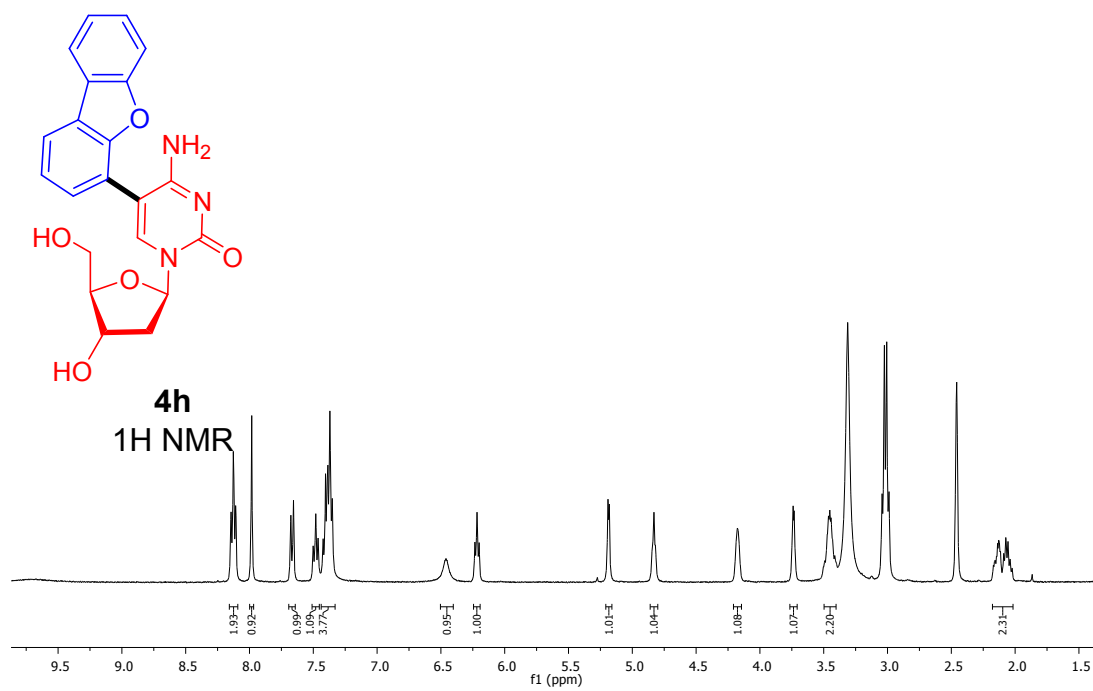


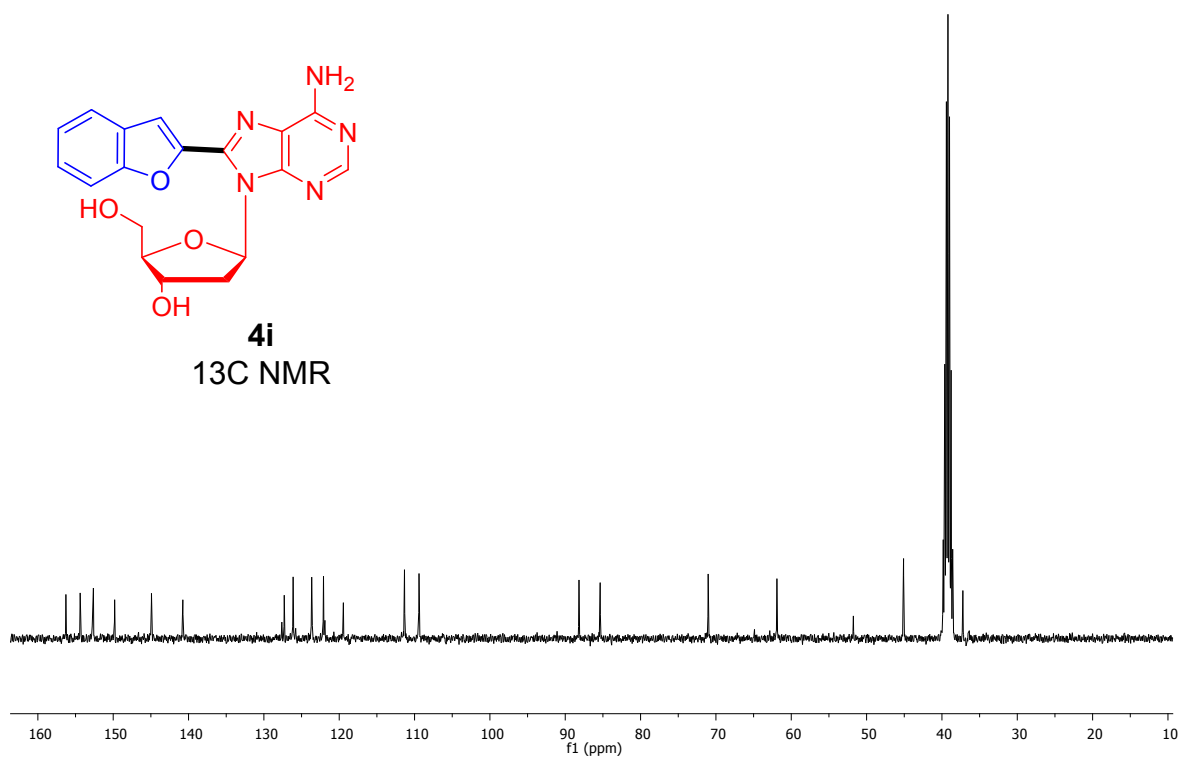
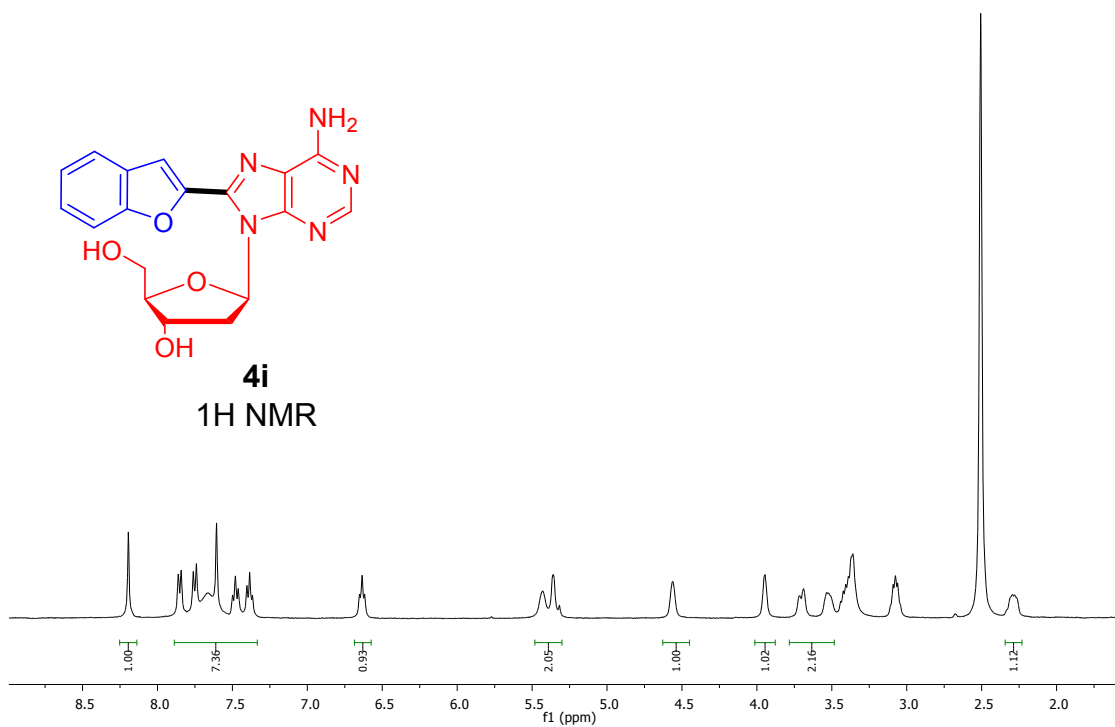
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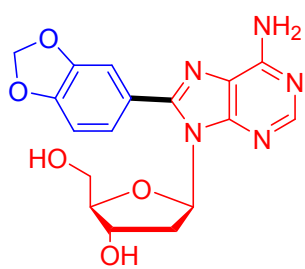


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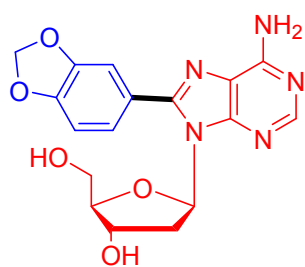
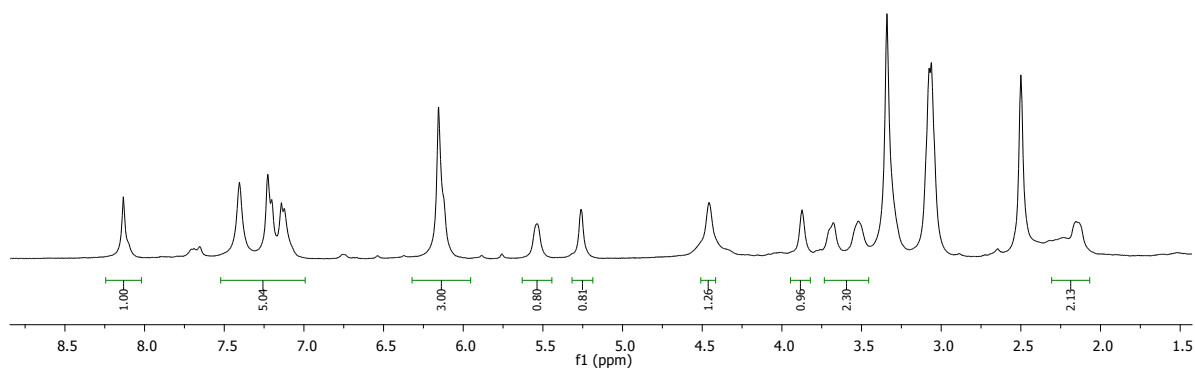




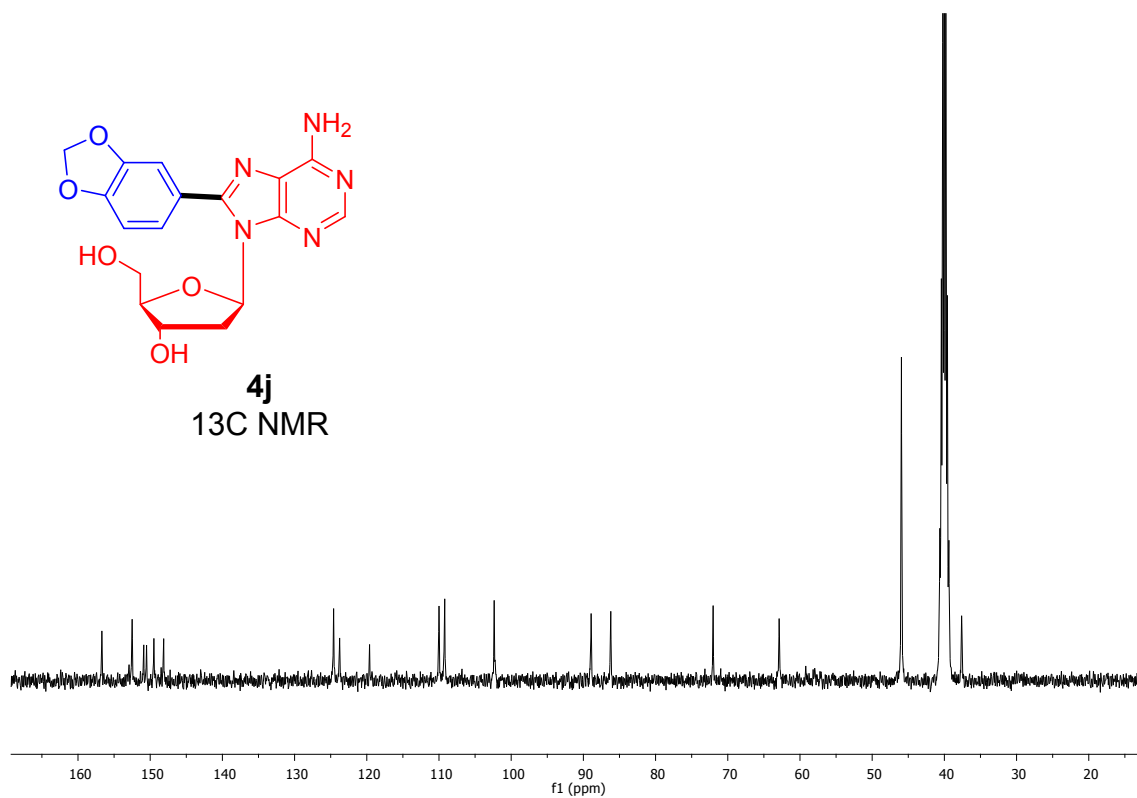


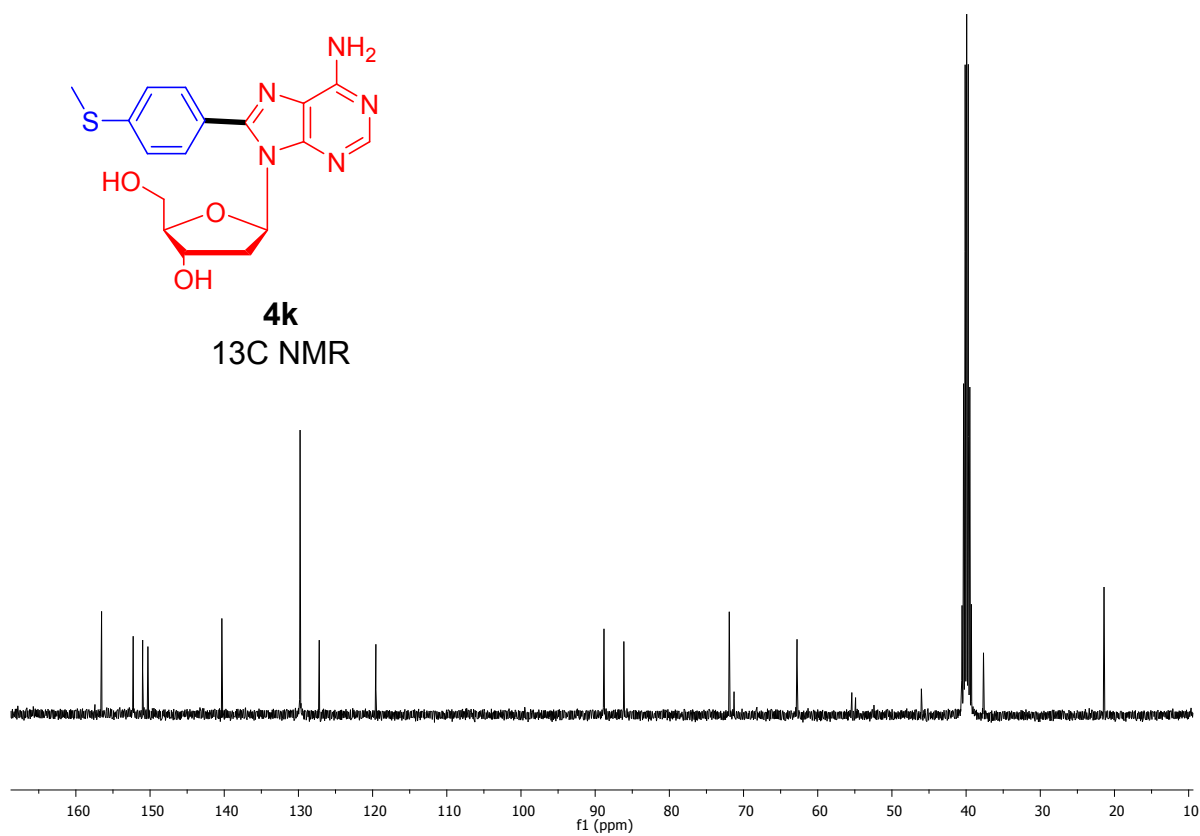
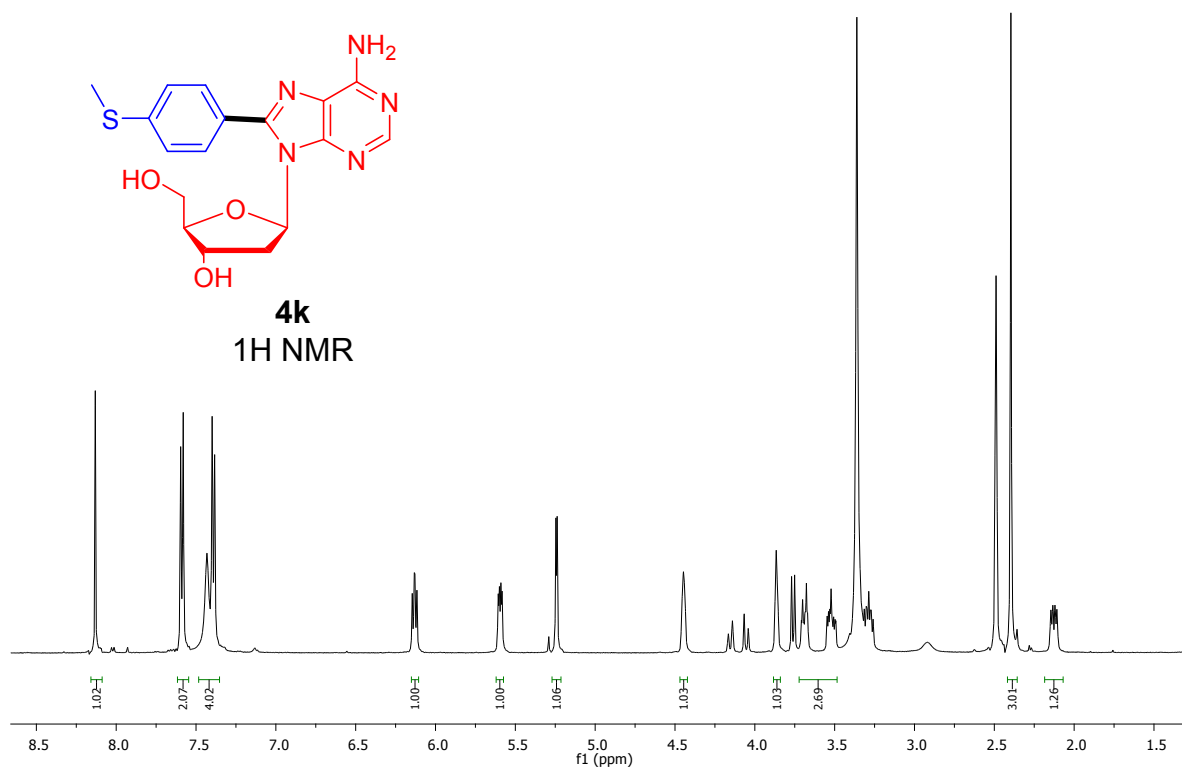


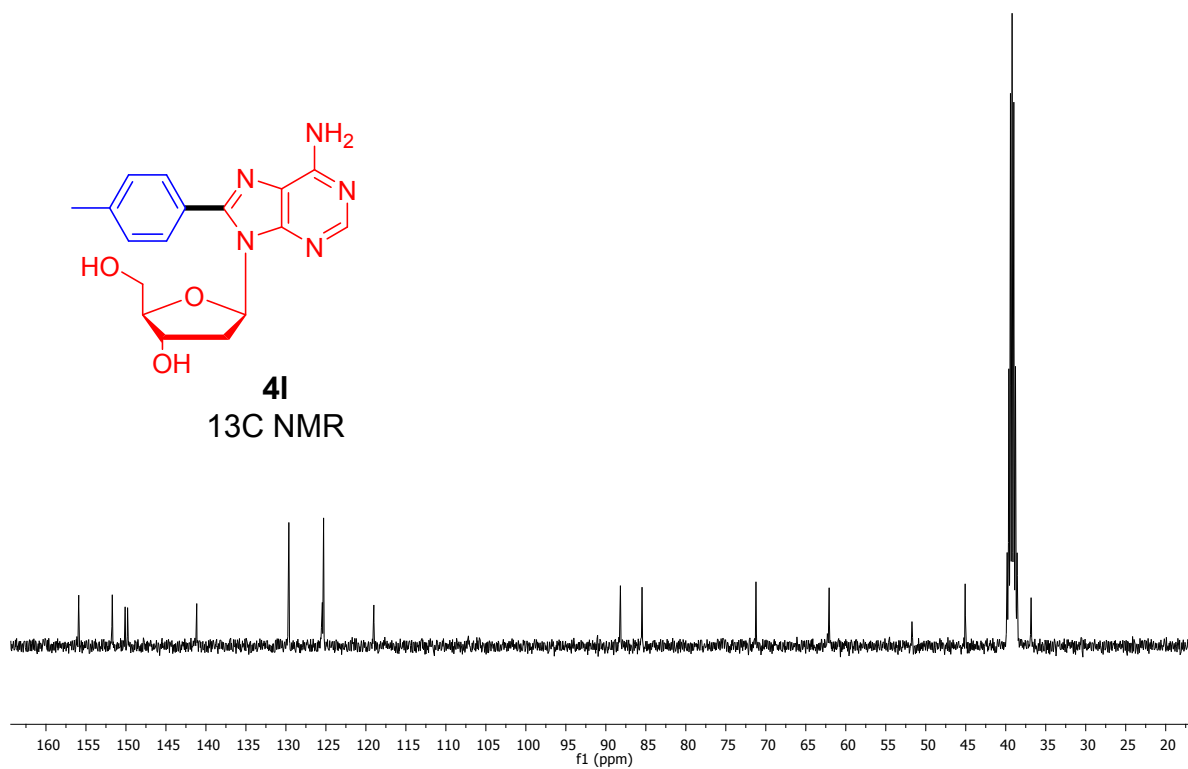
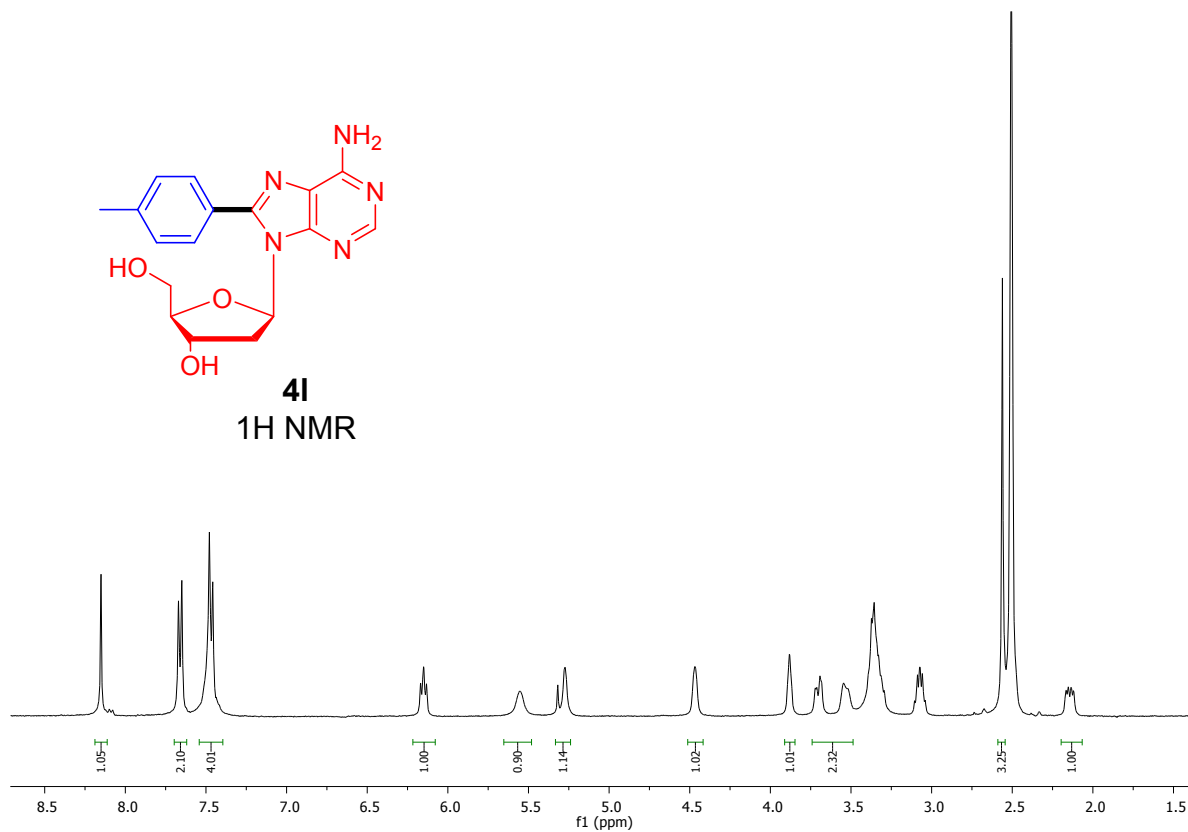
4j
¹H NMR

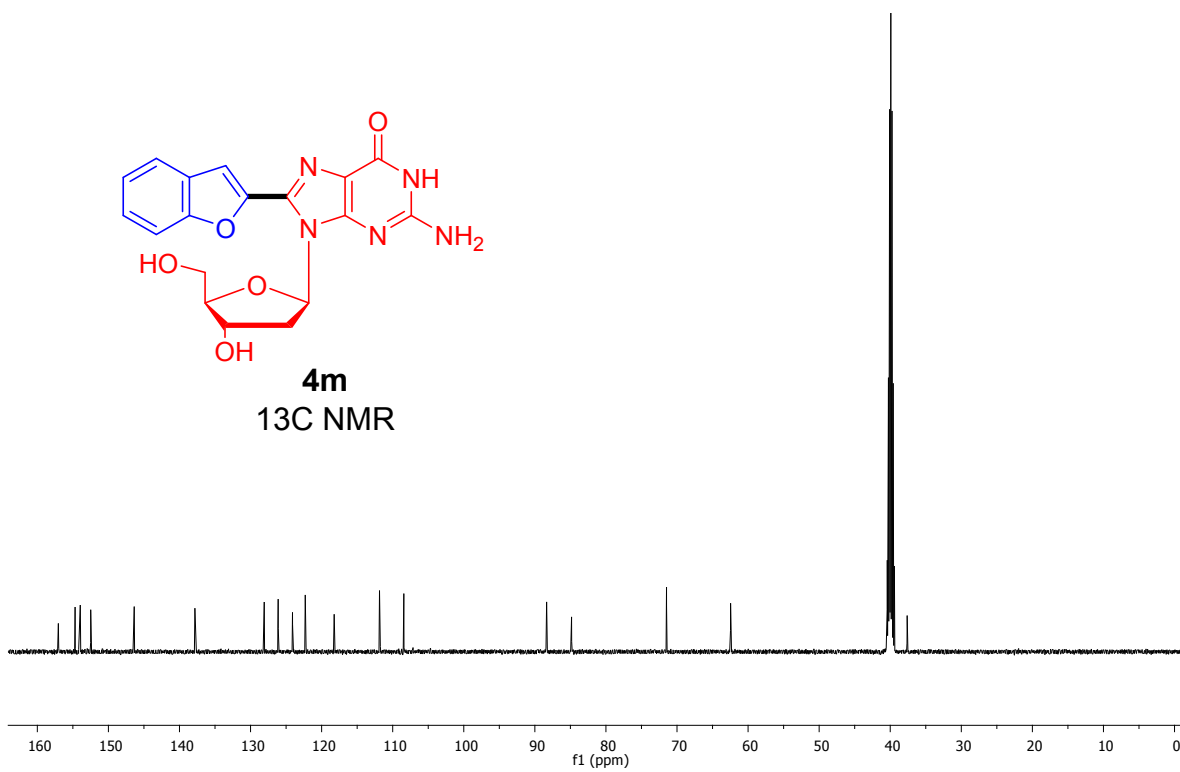
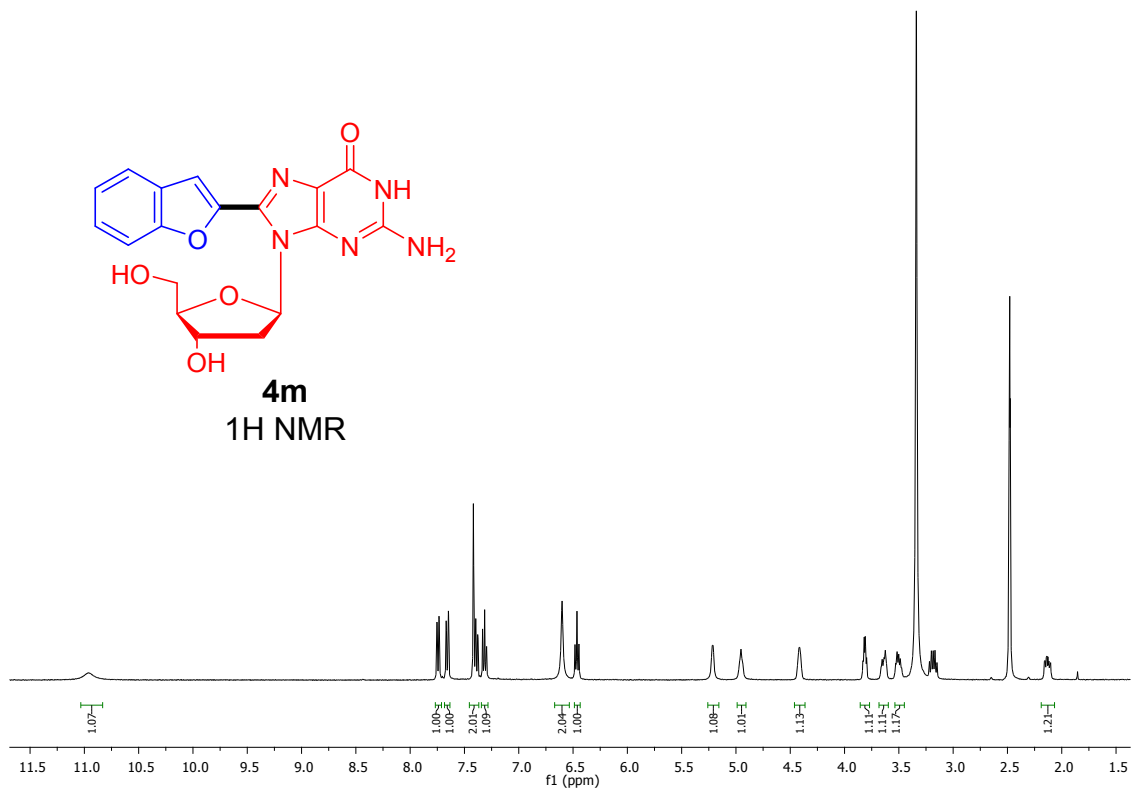


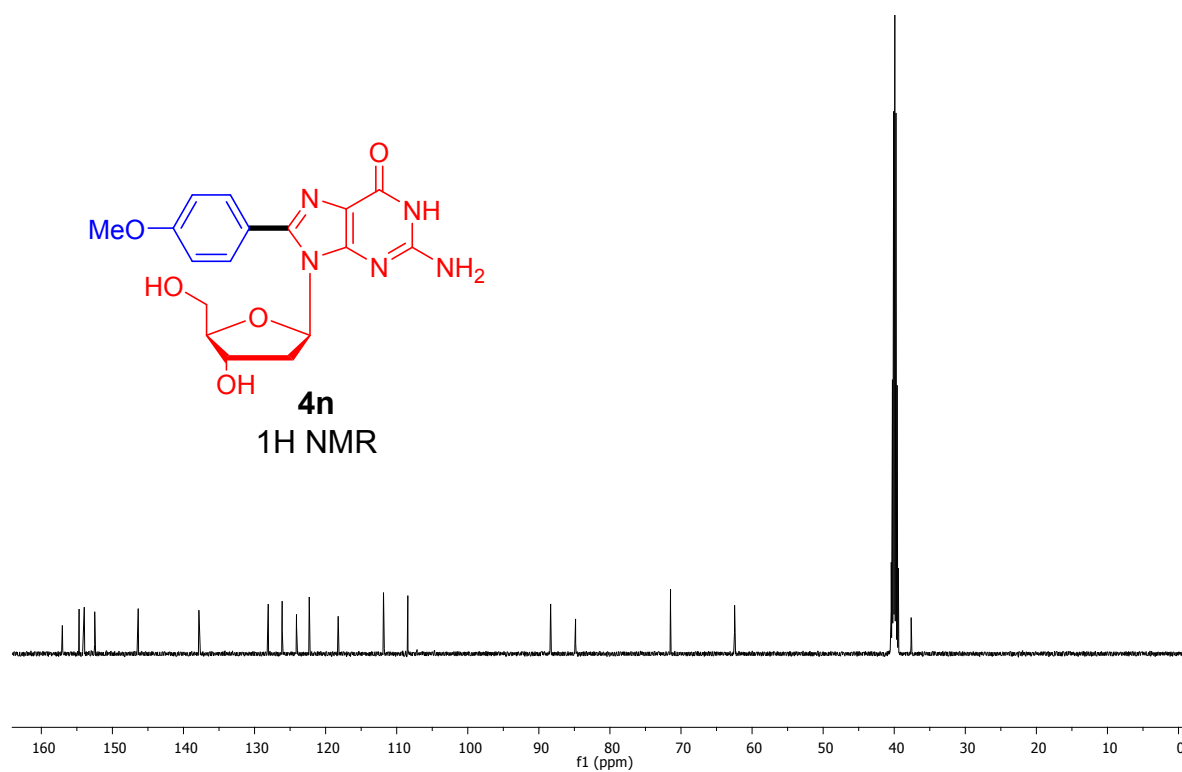
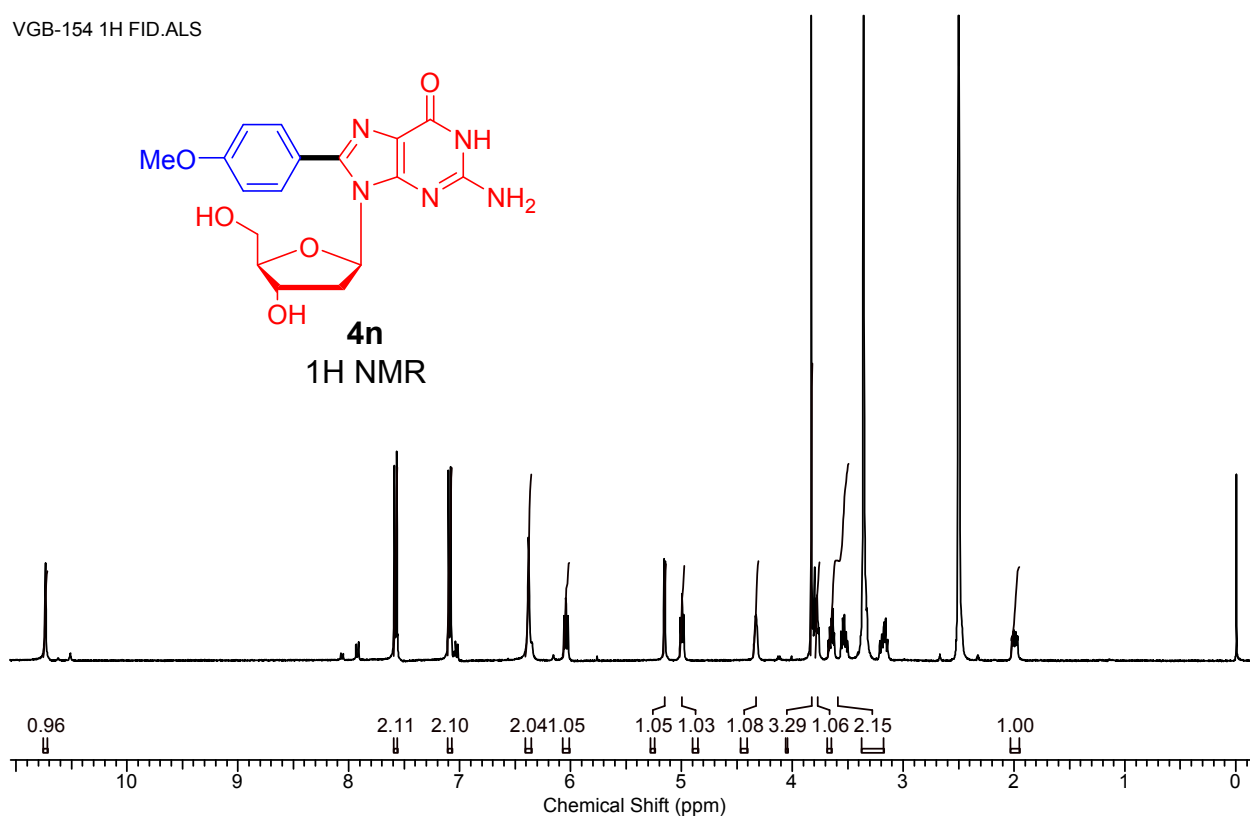
4j
¹³C NMR

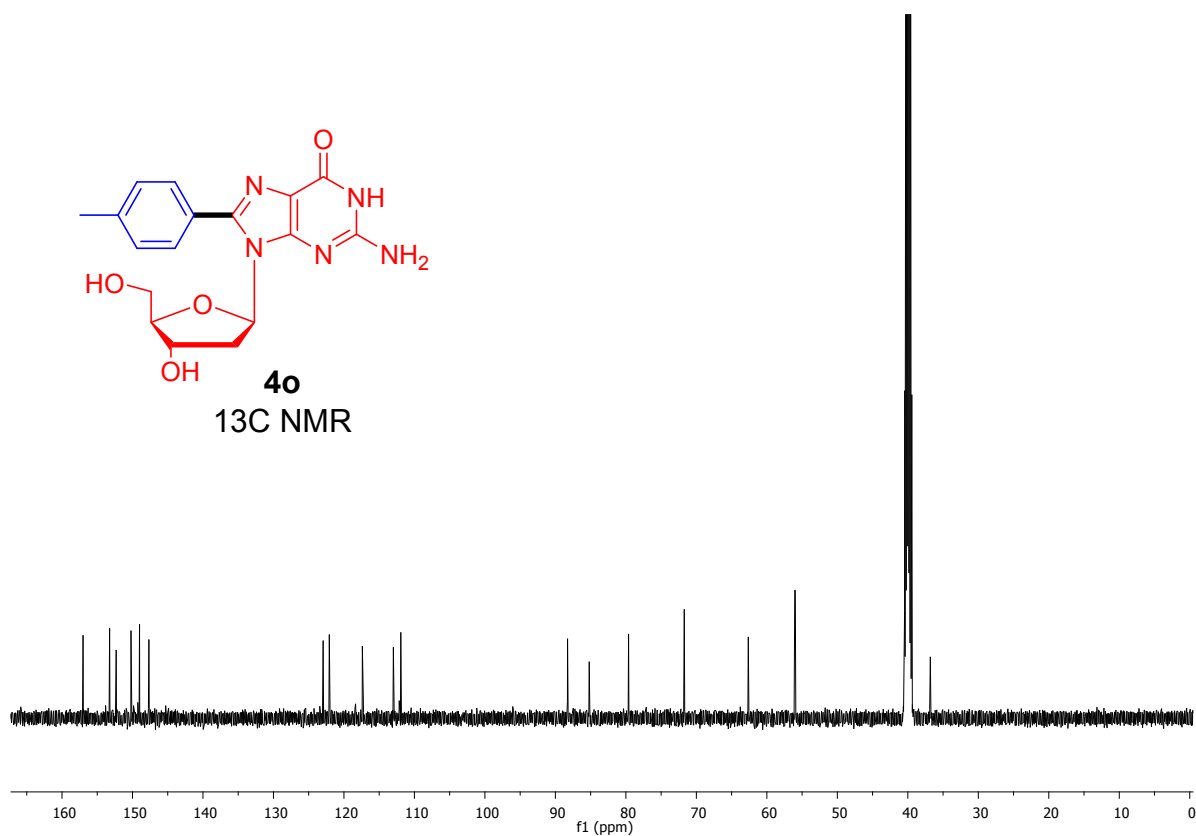
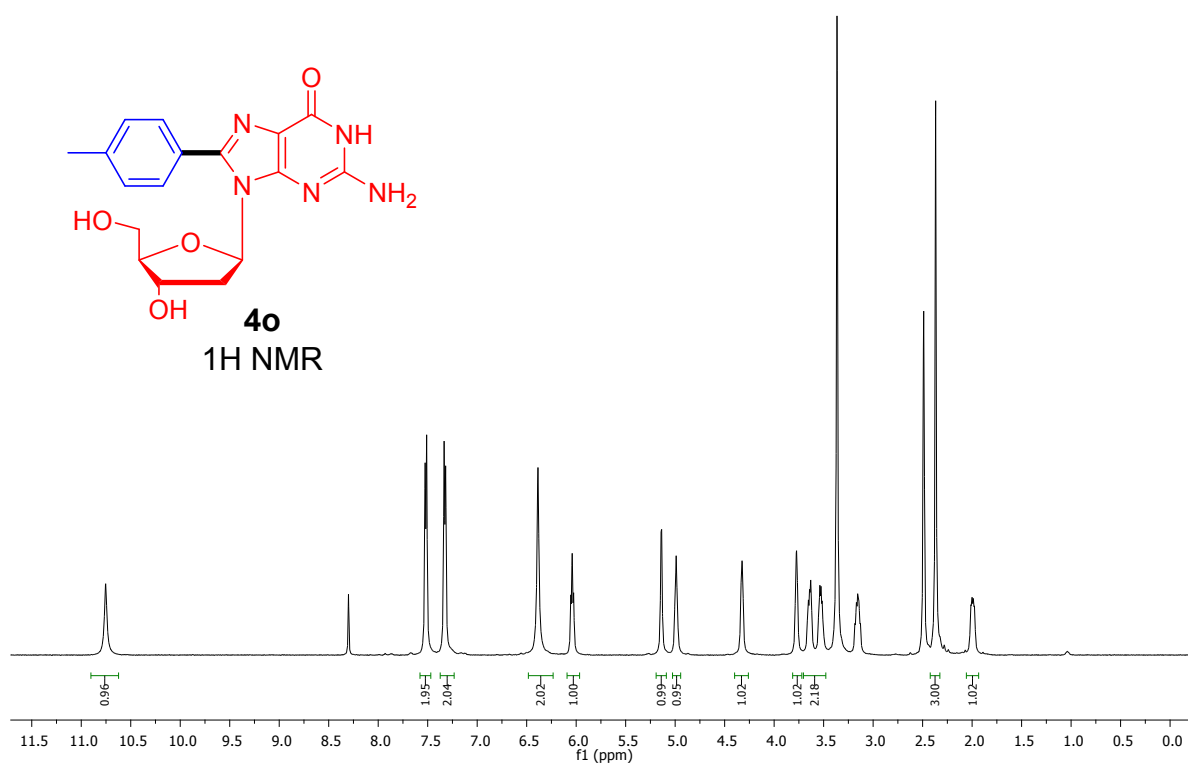


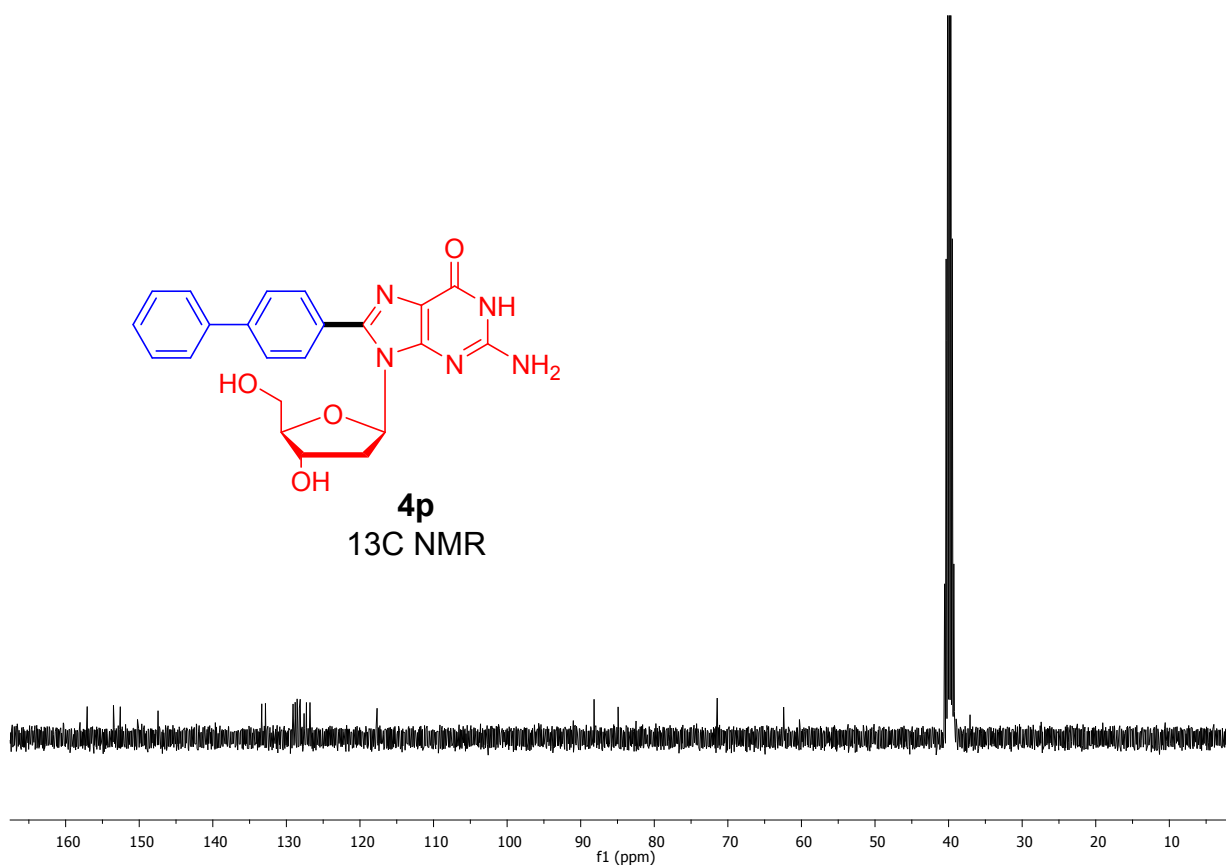
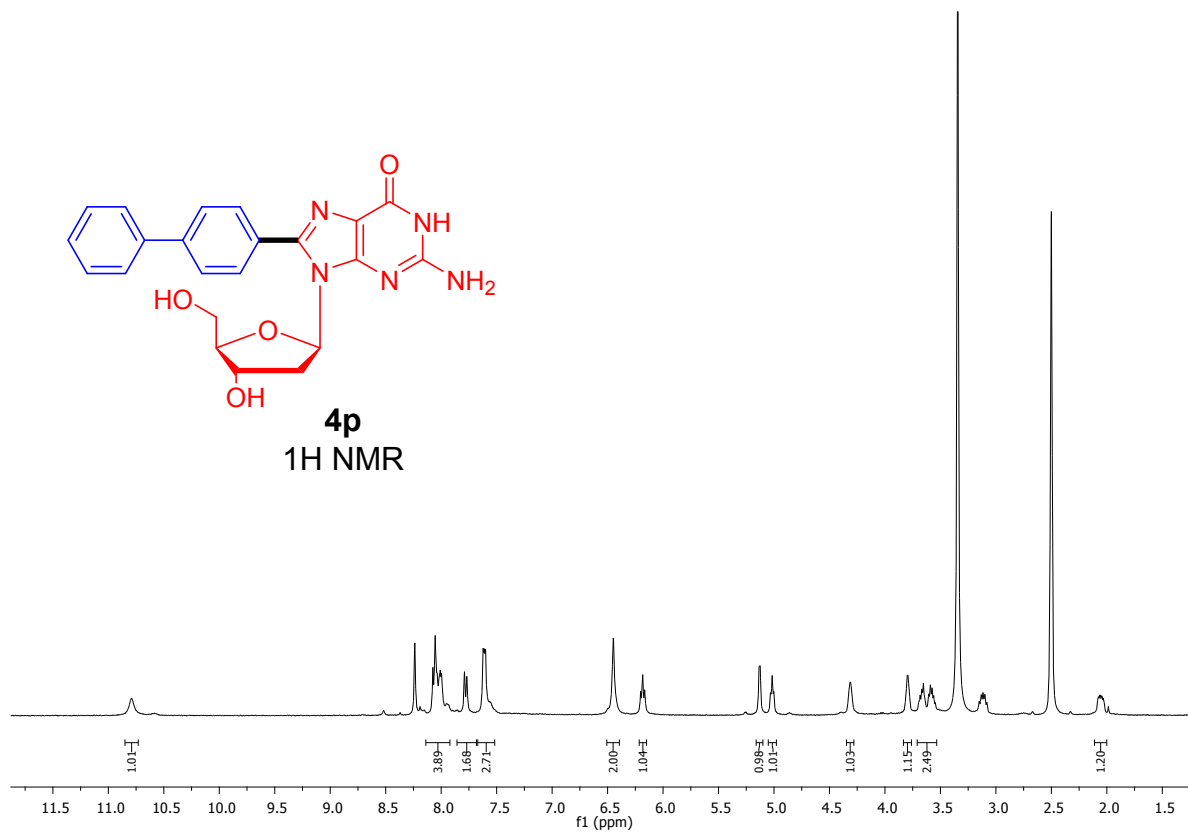


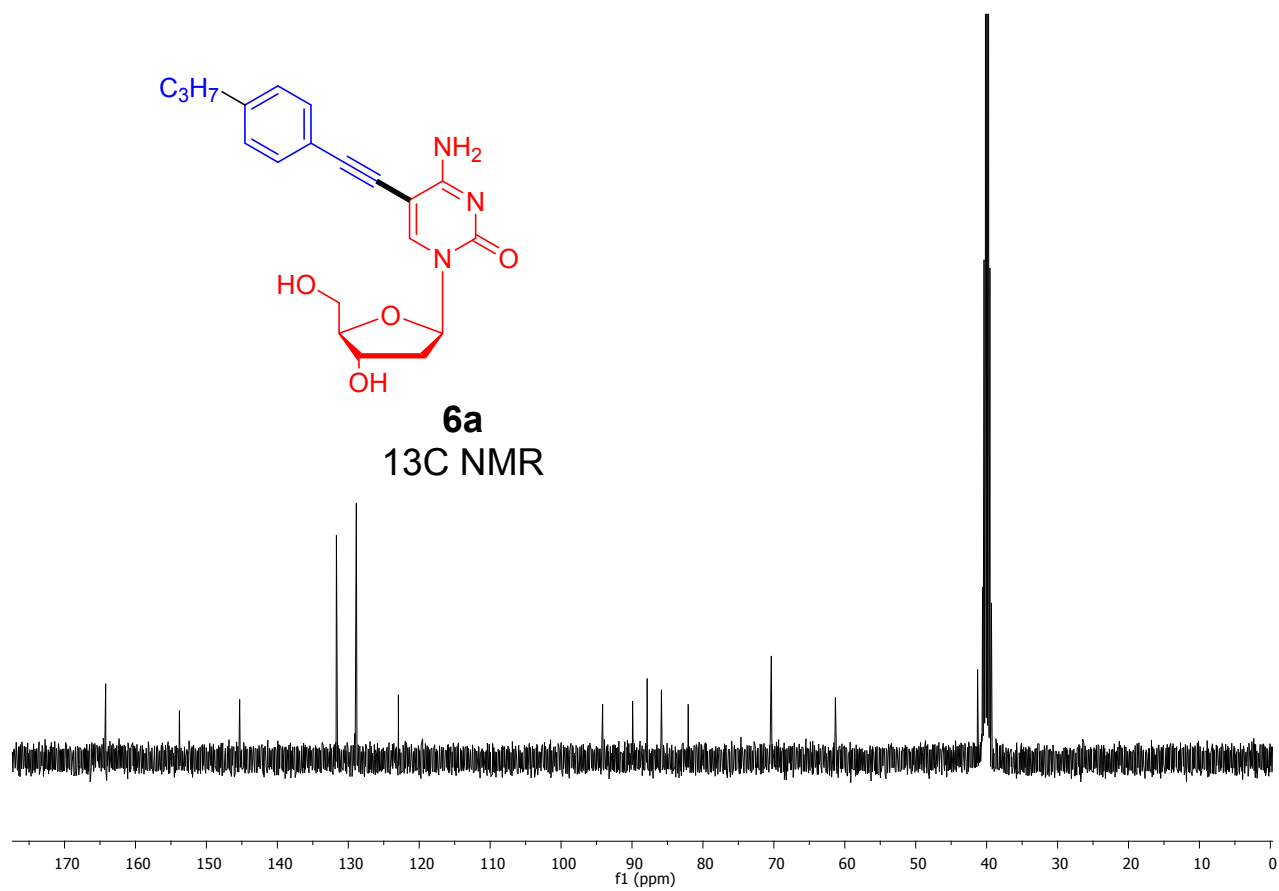
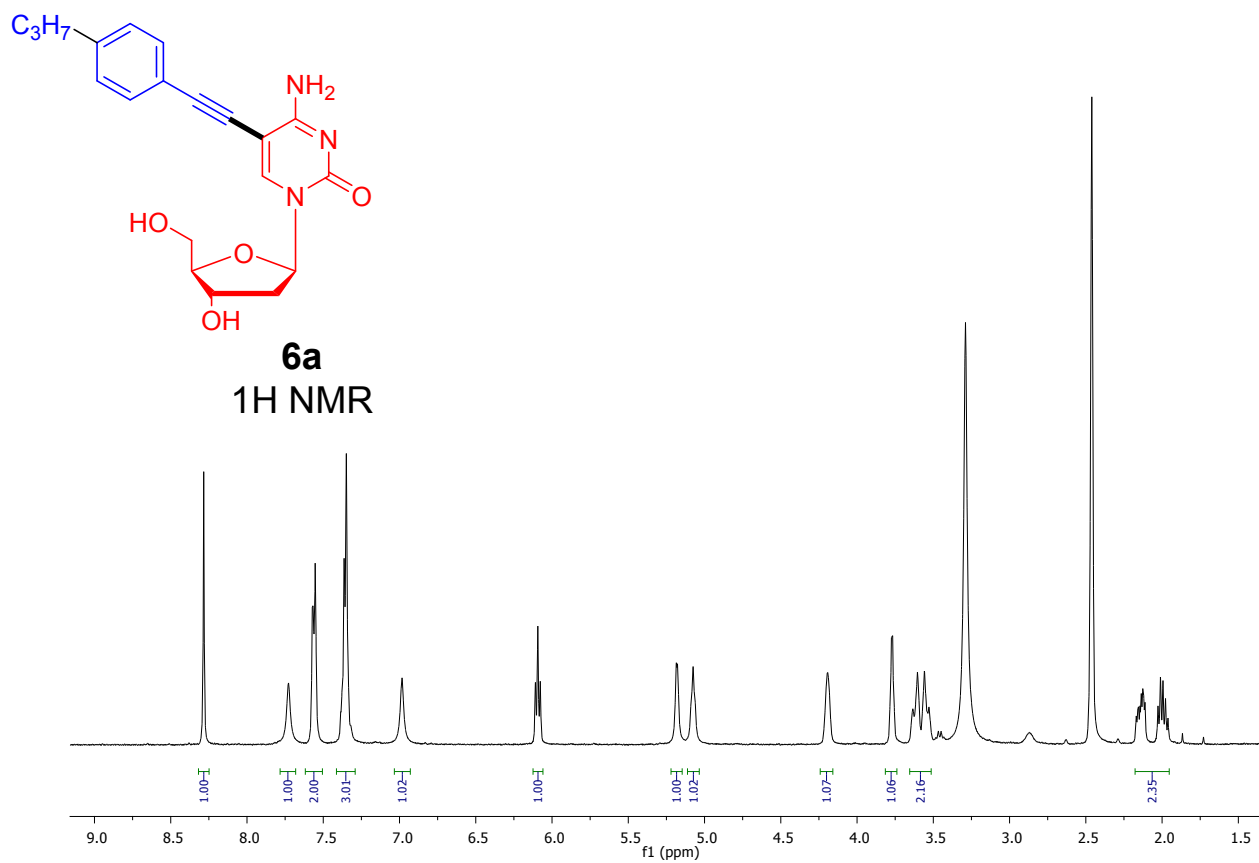


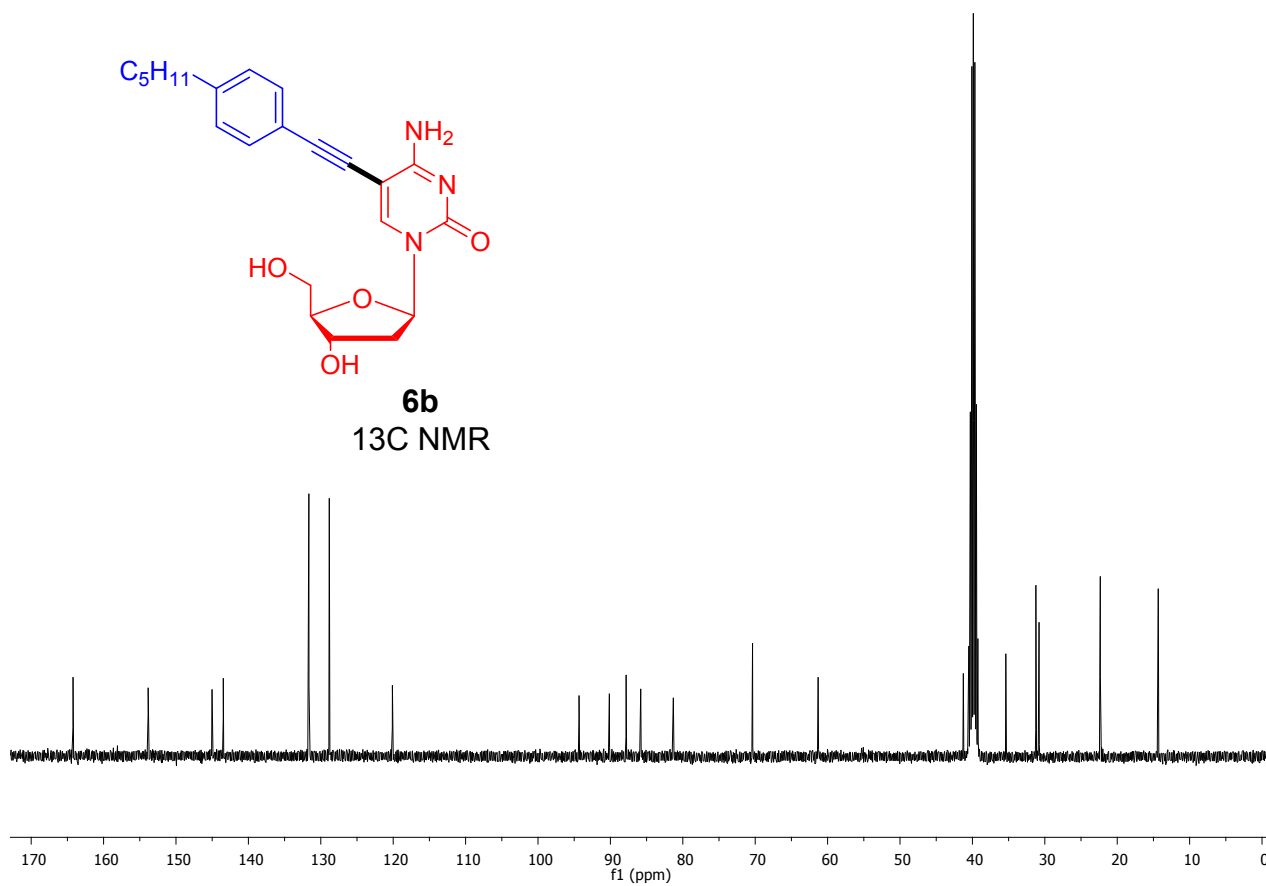
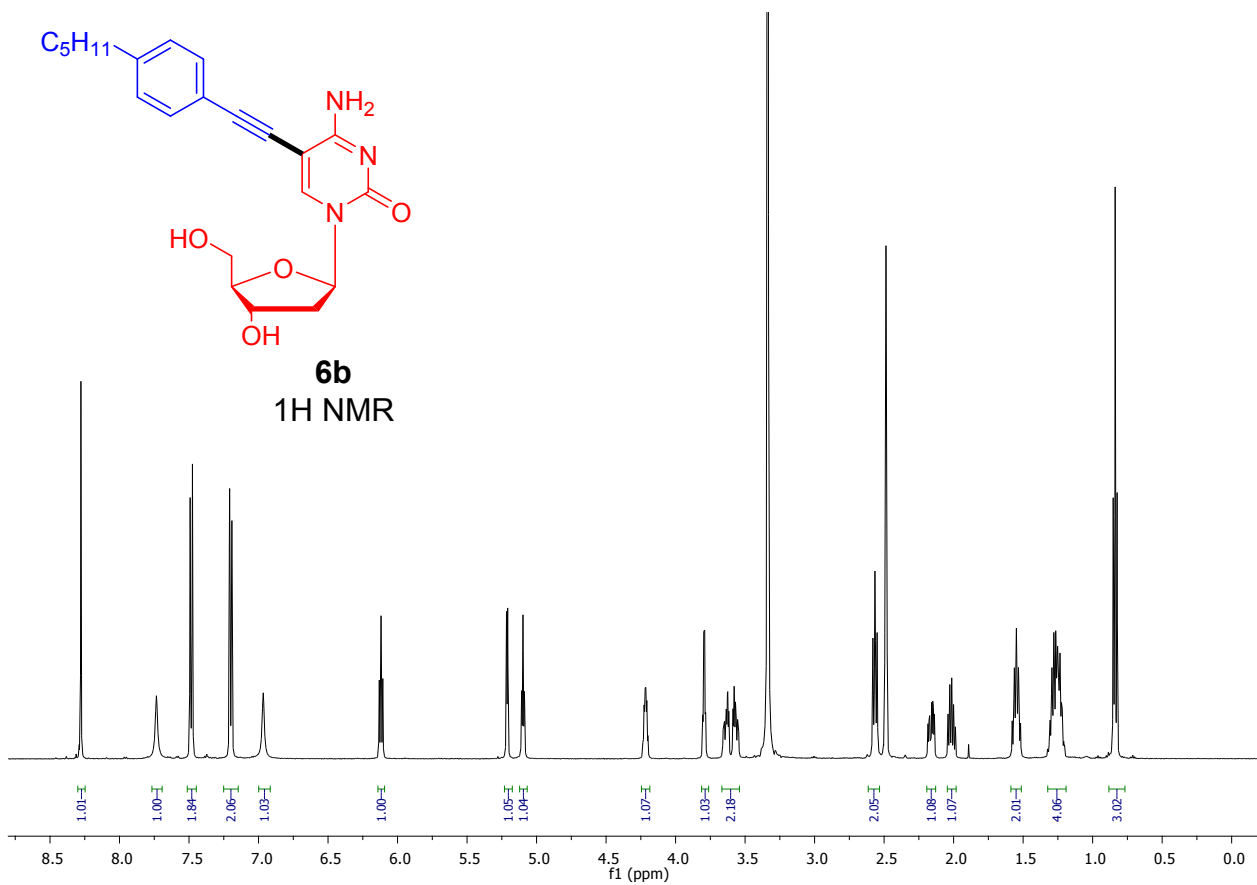


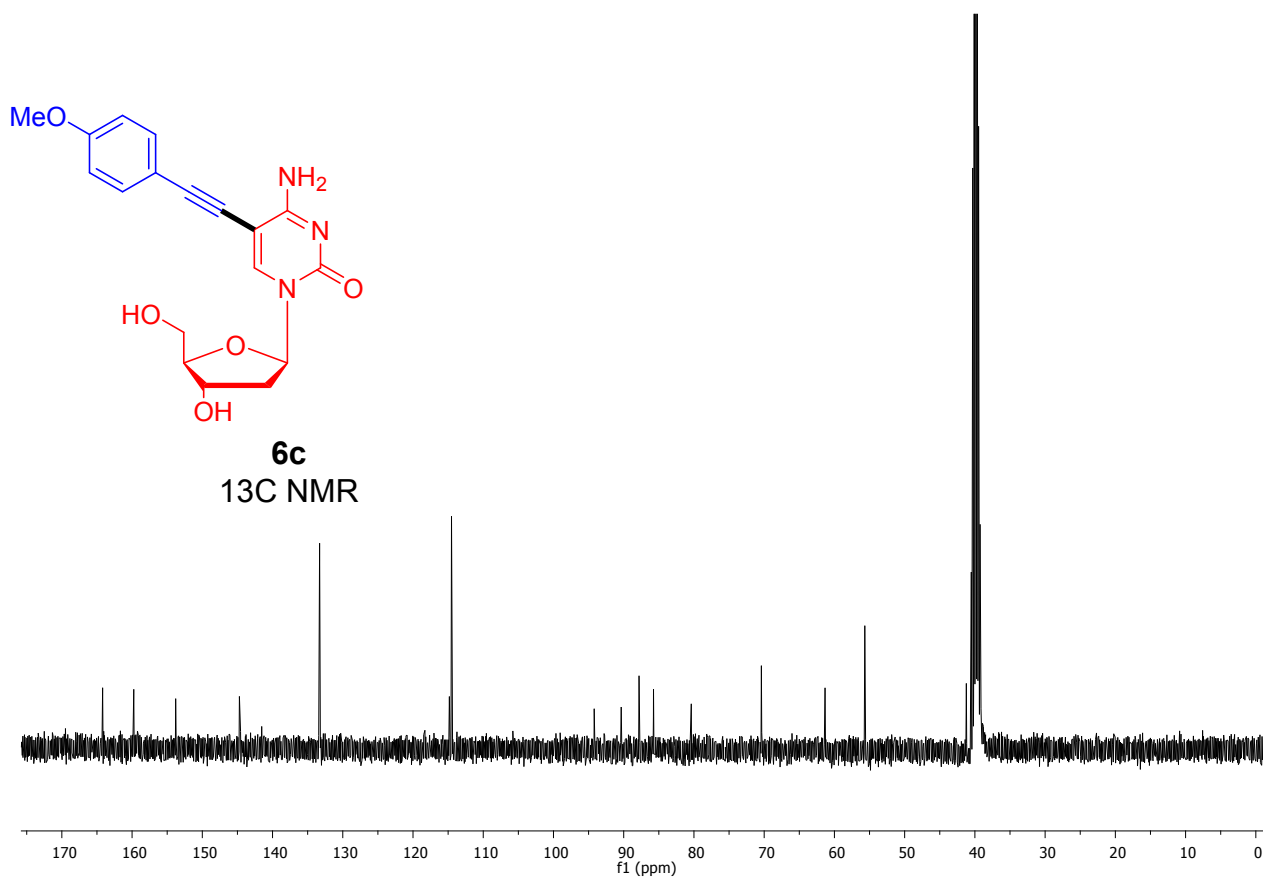
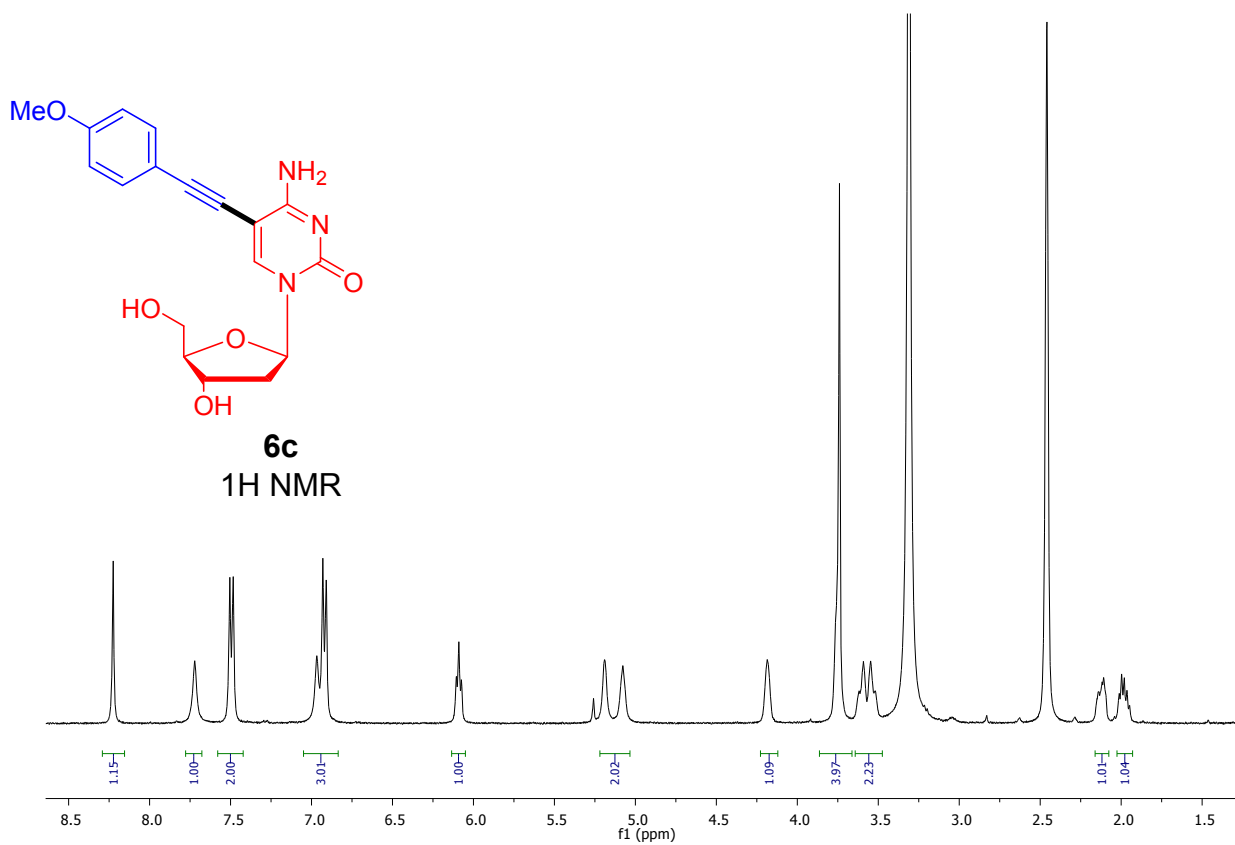


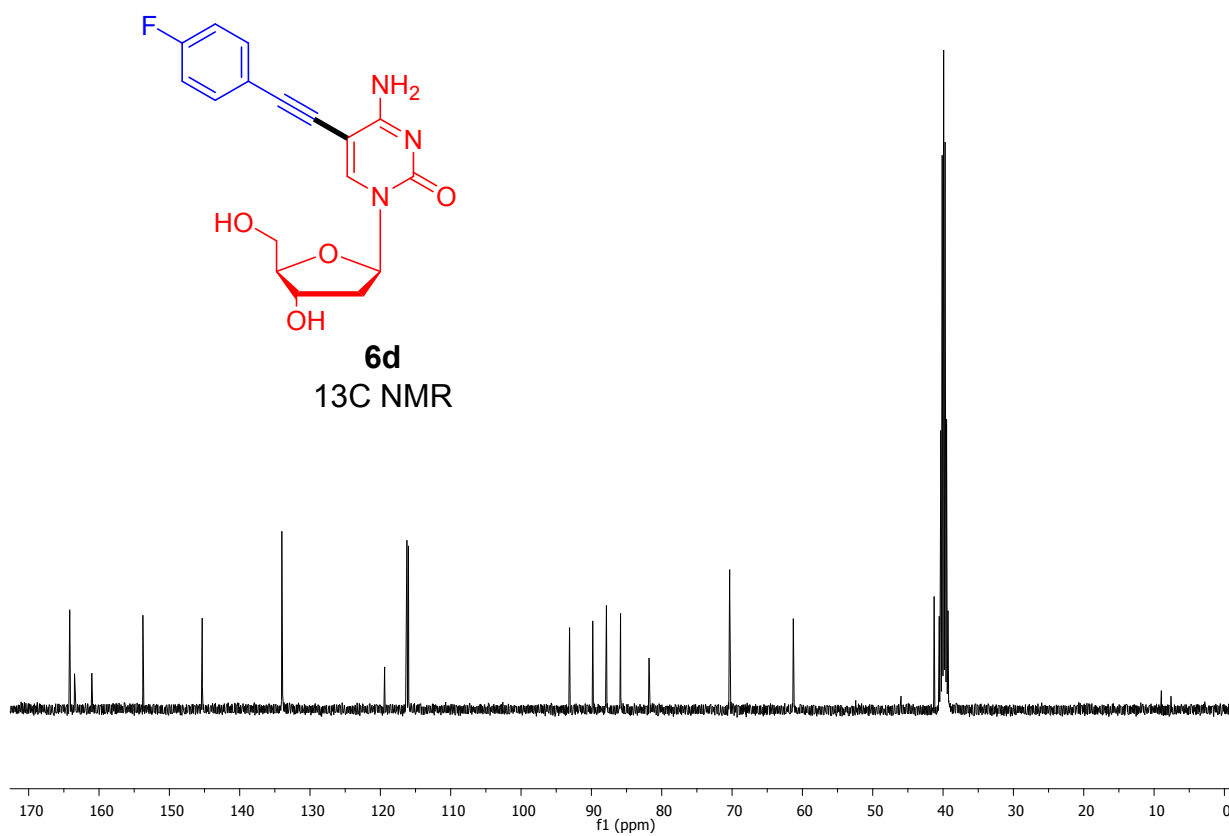
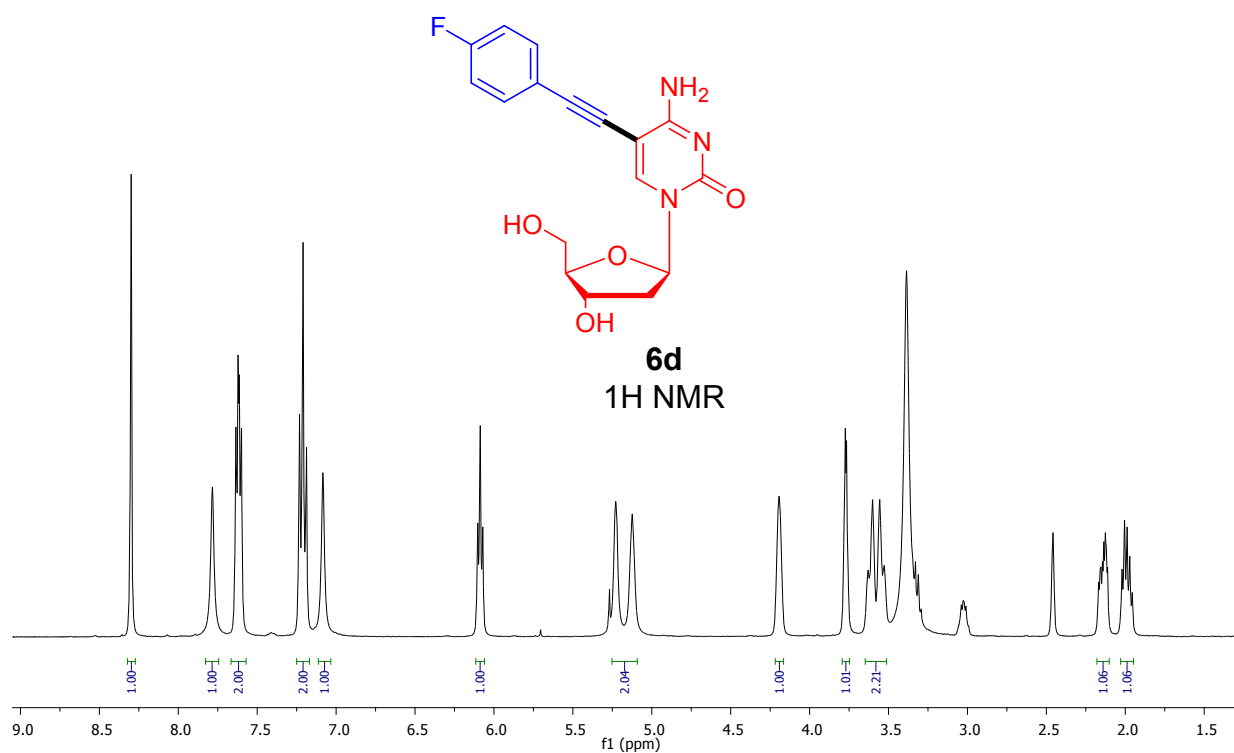


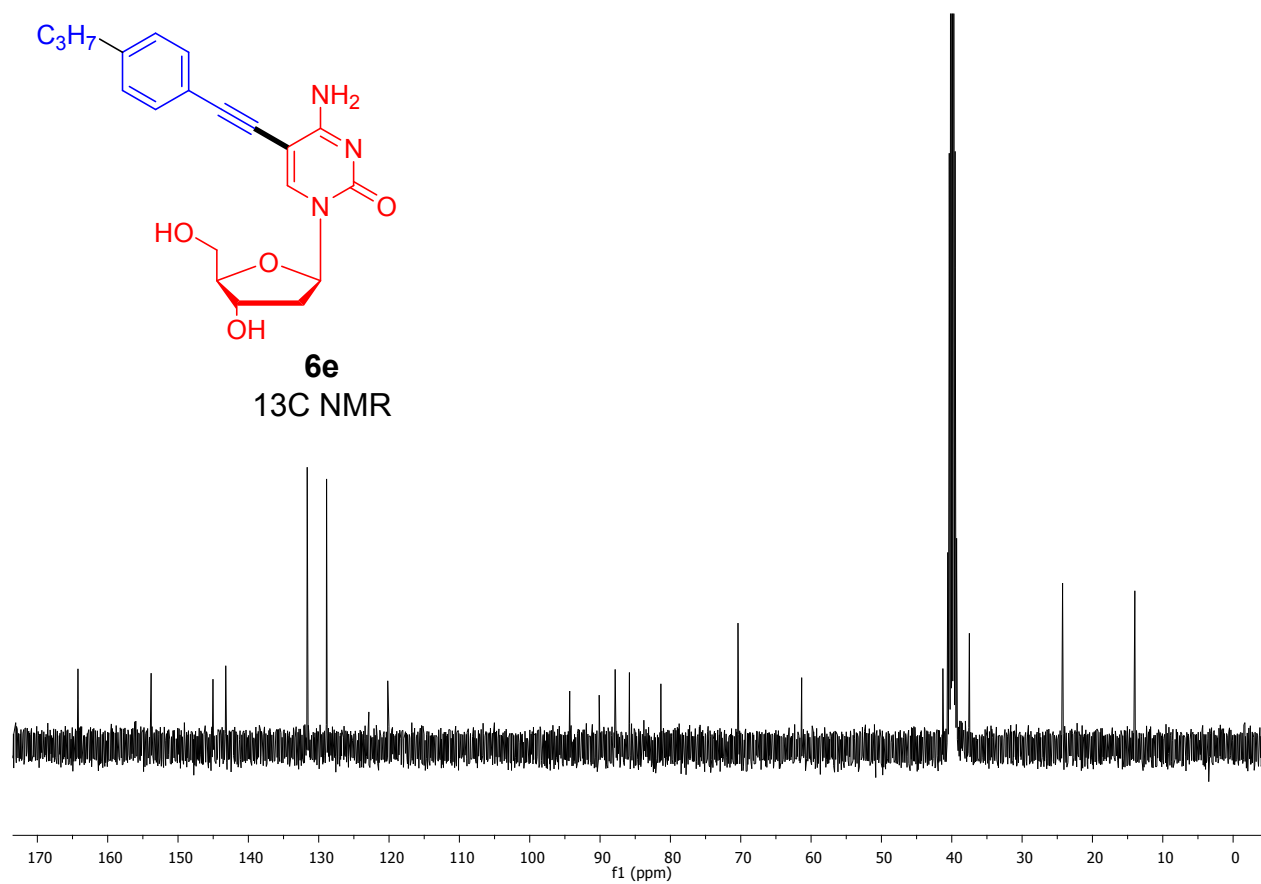
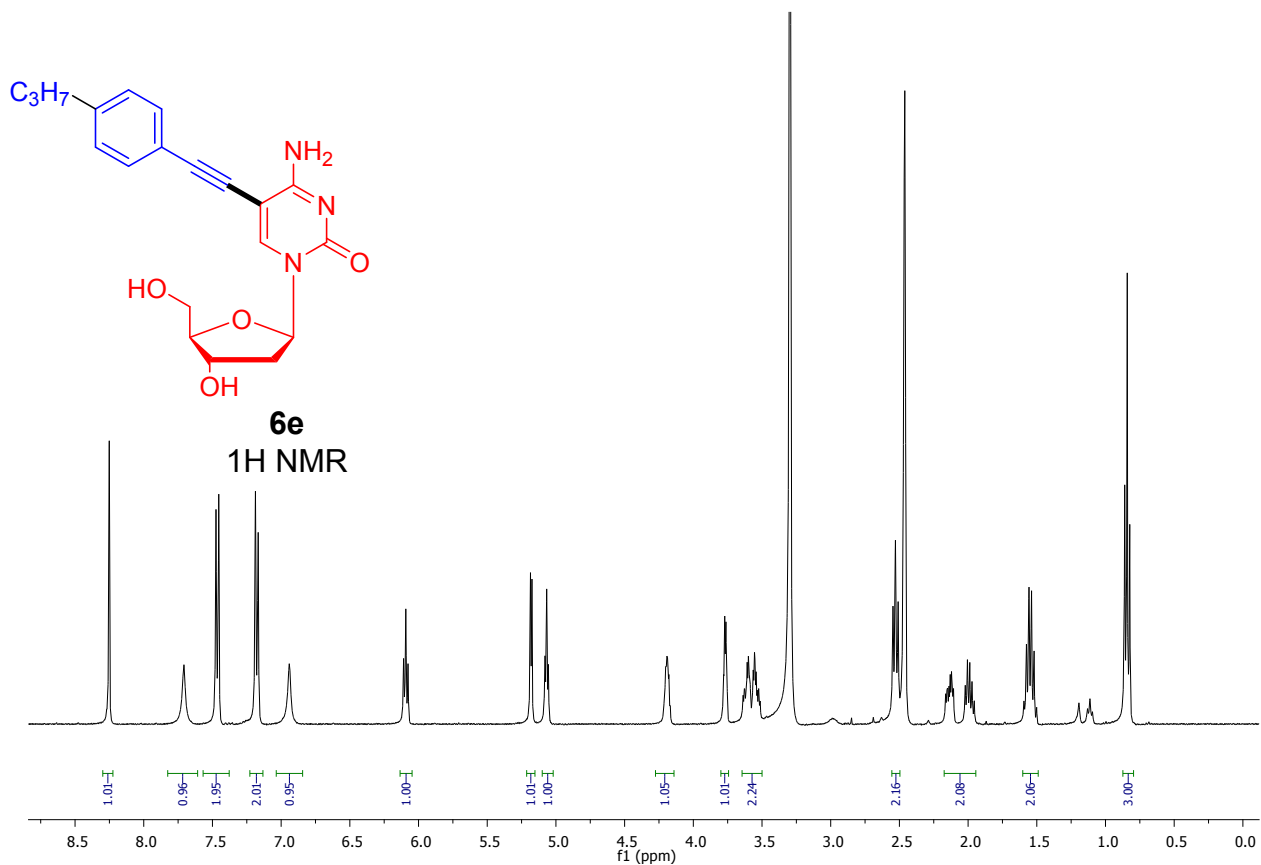


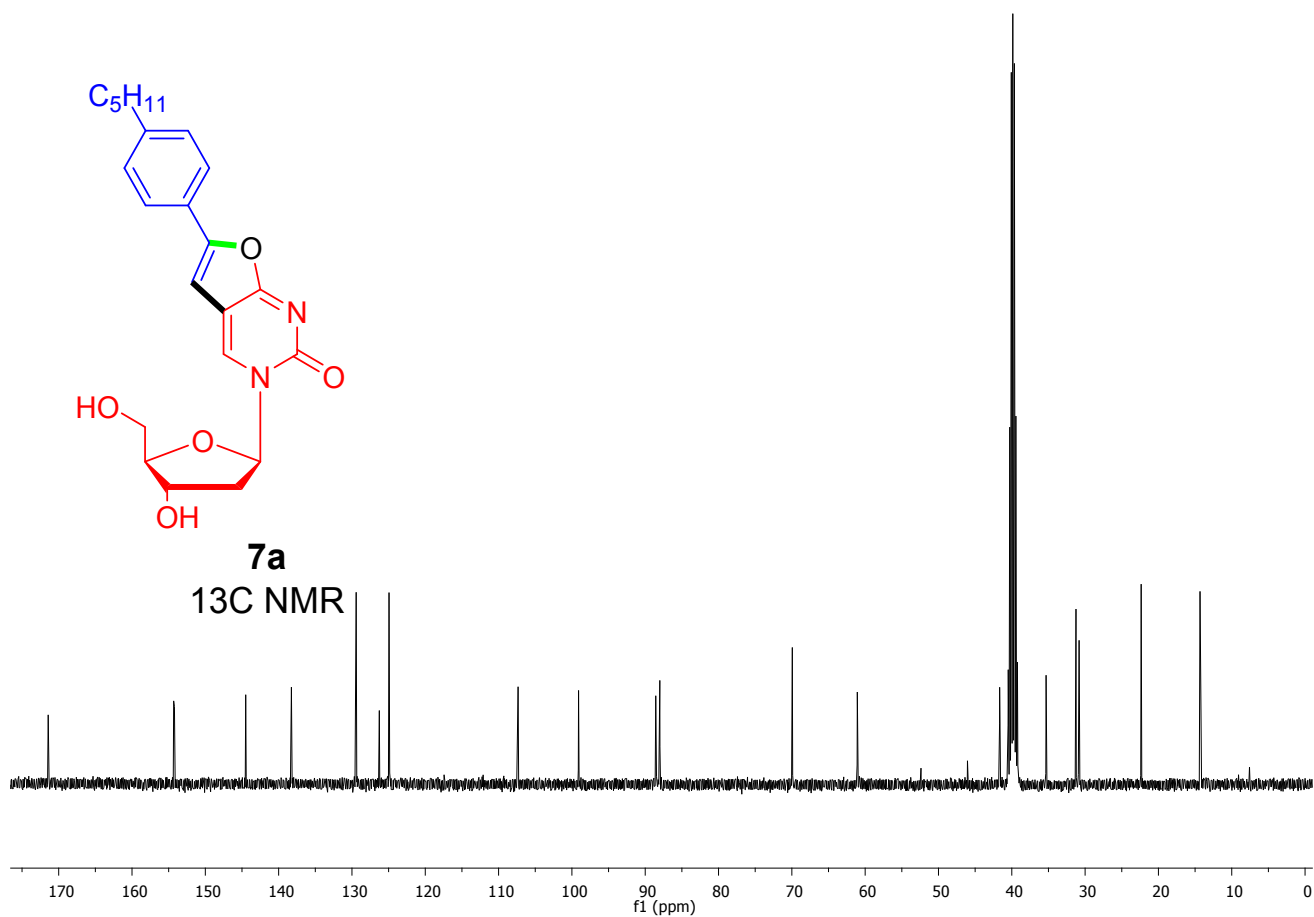
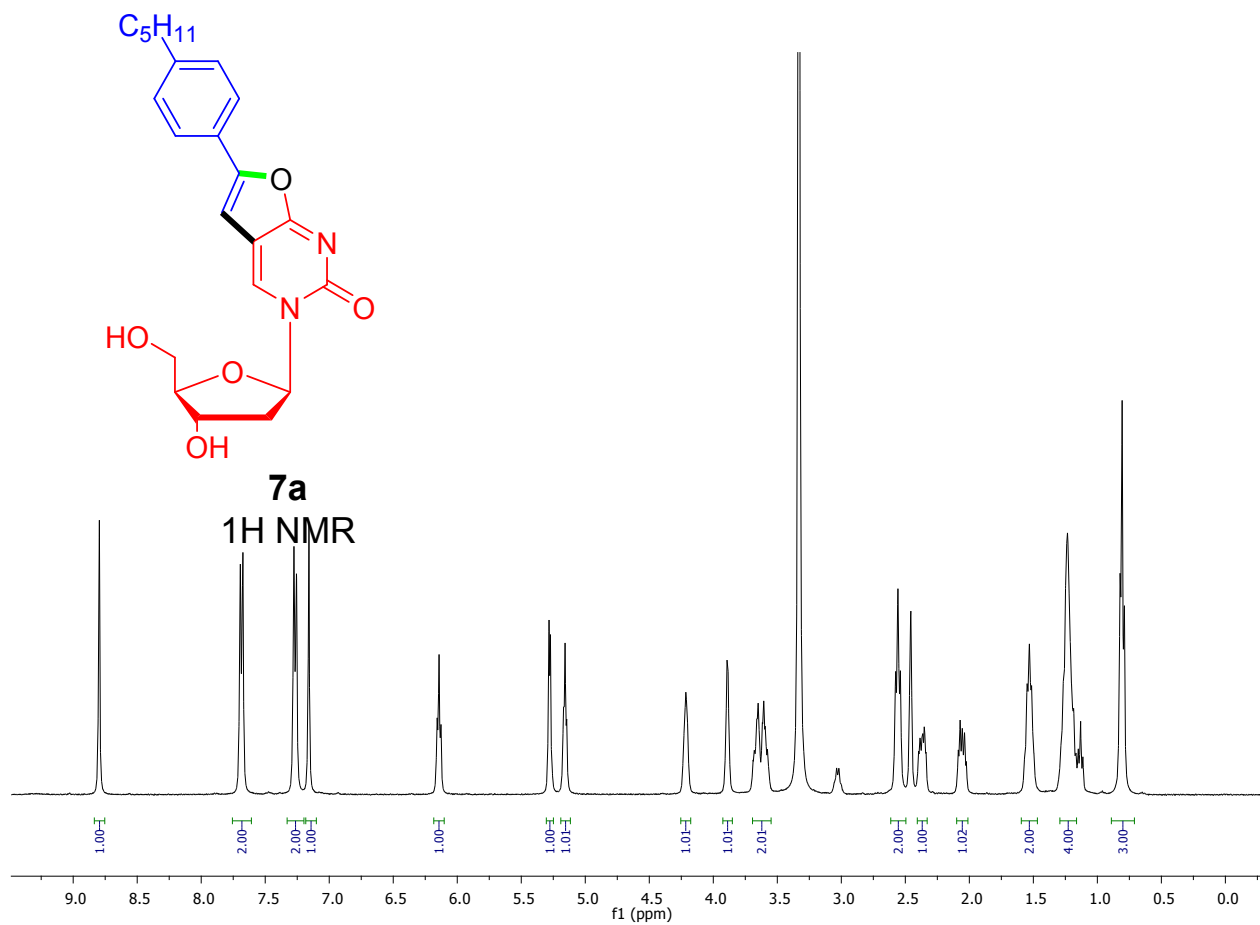


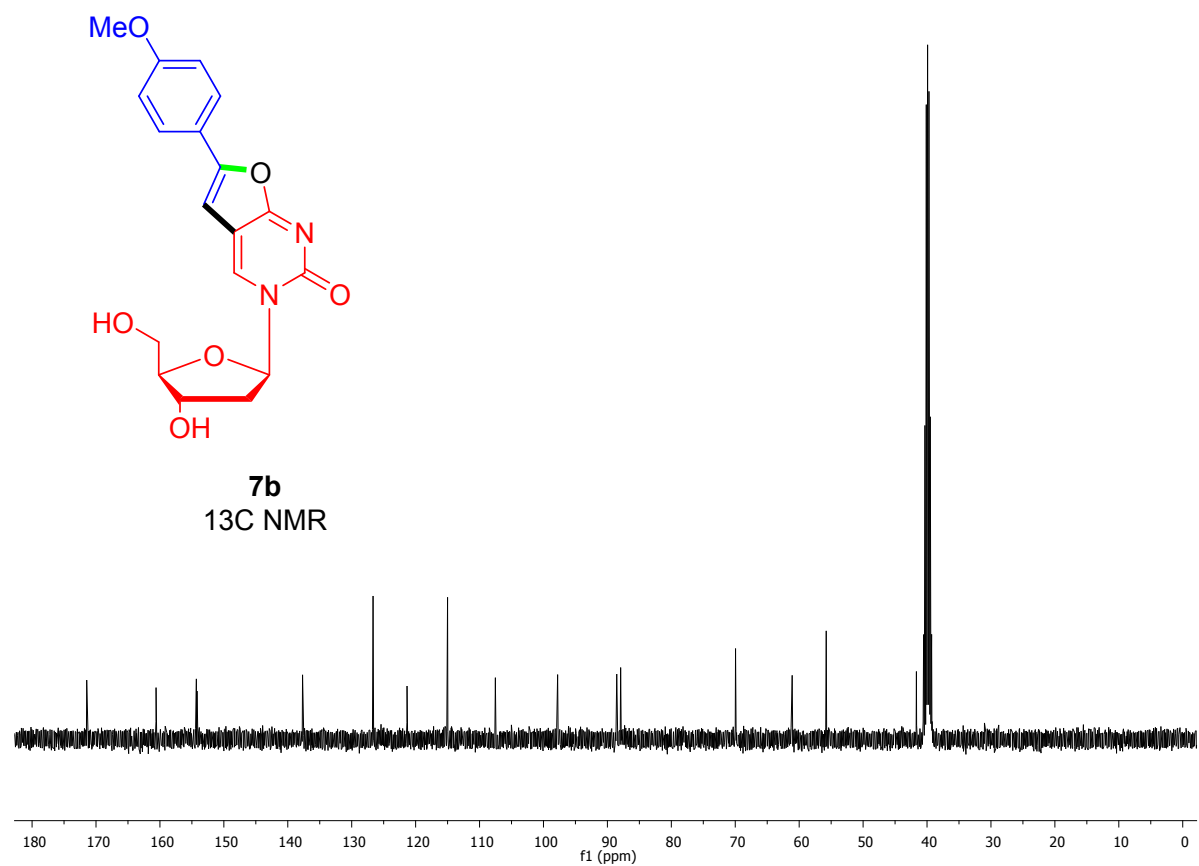
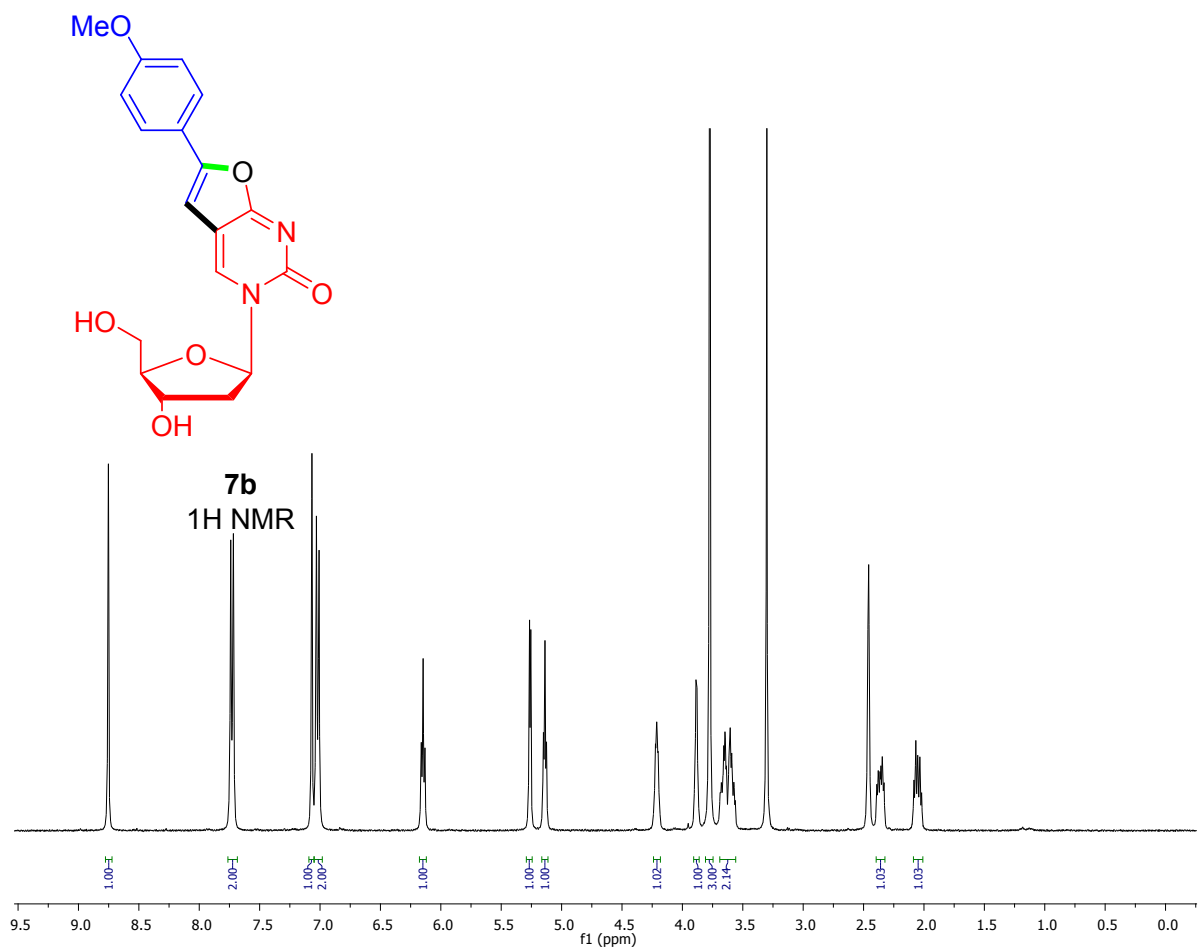


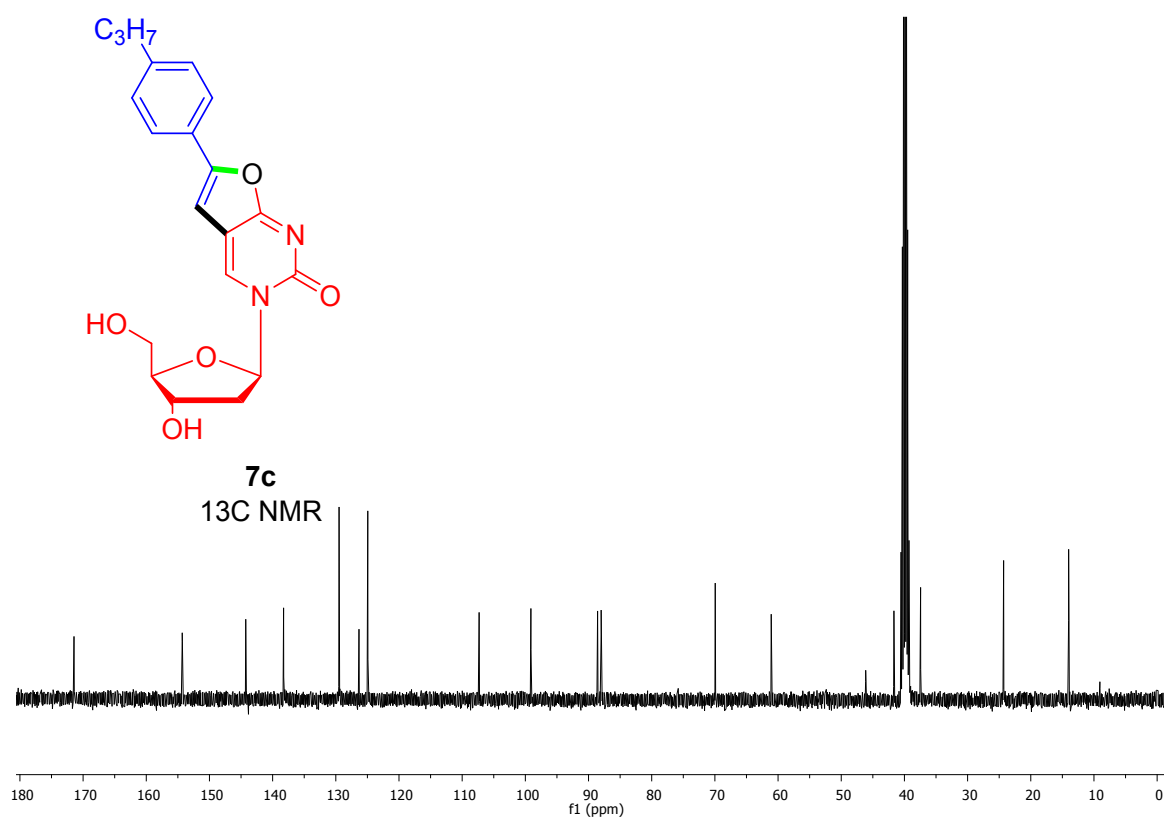
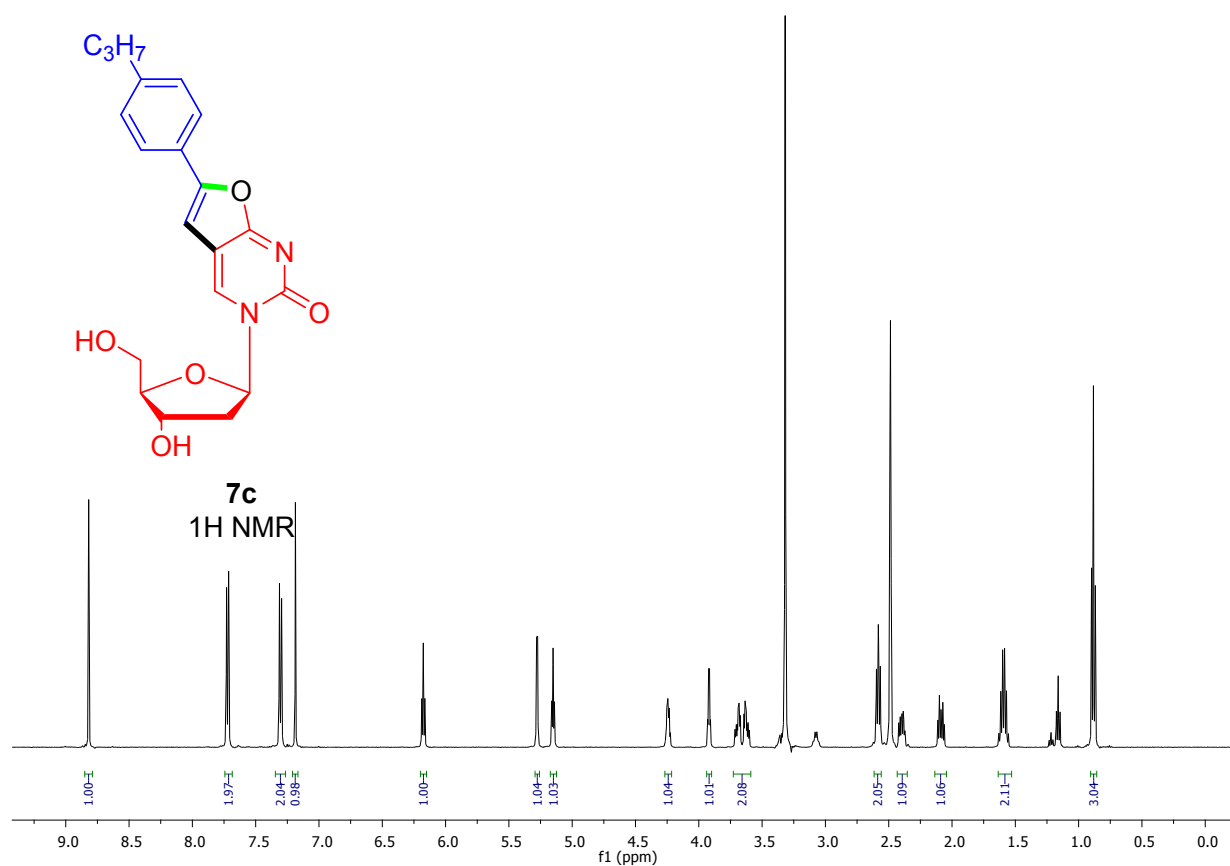


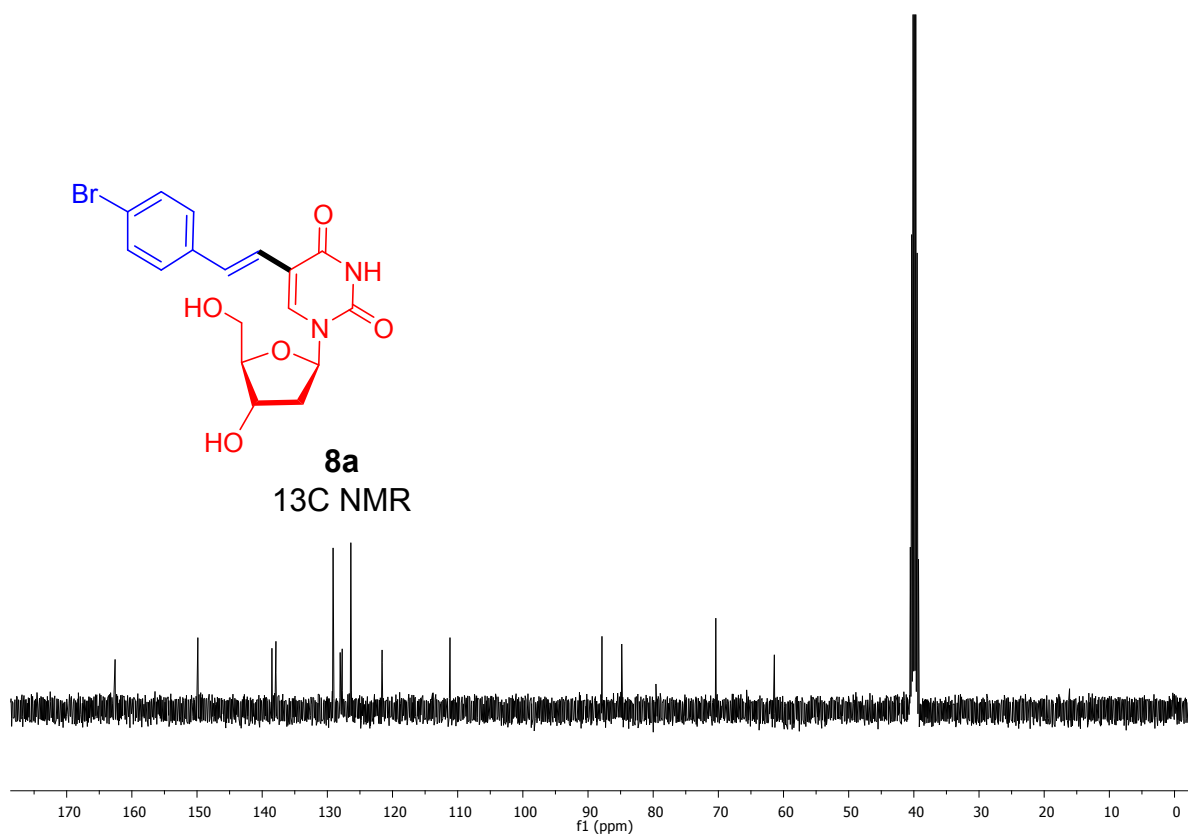
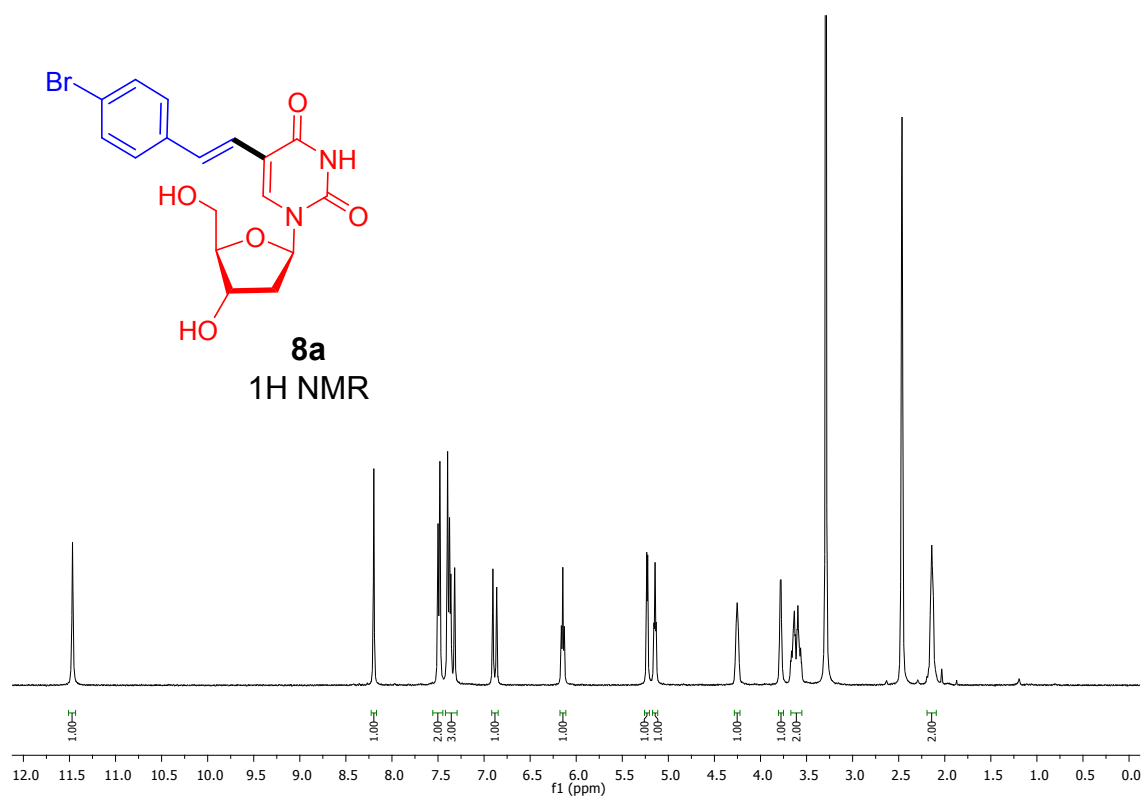


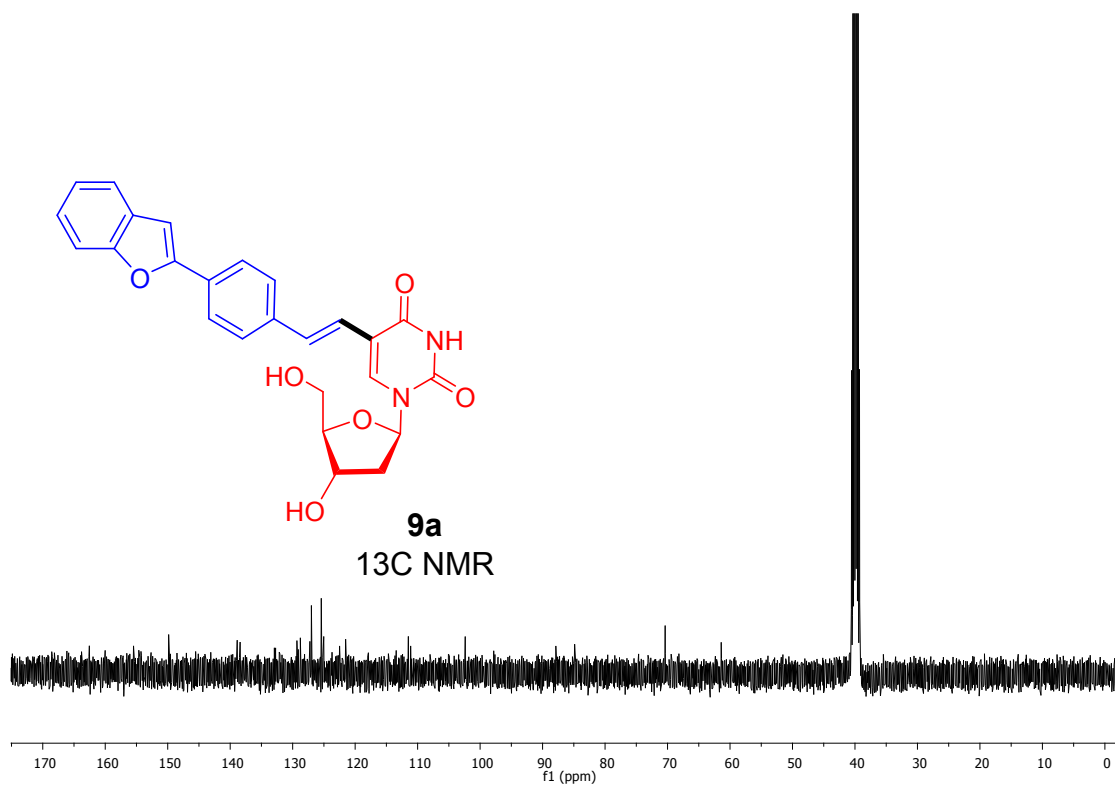
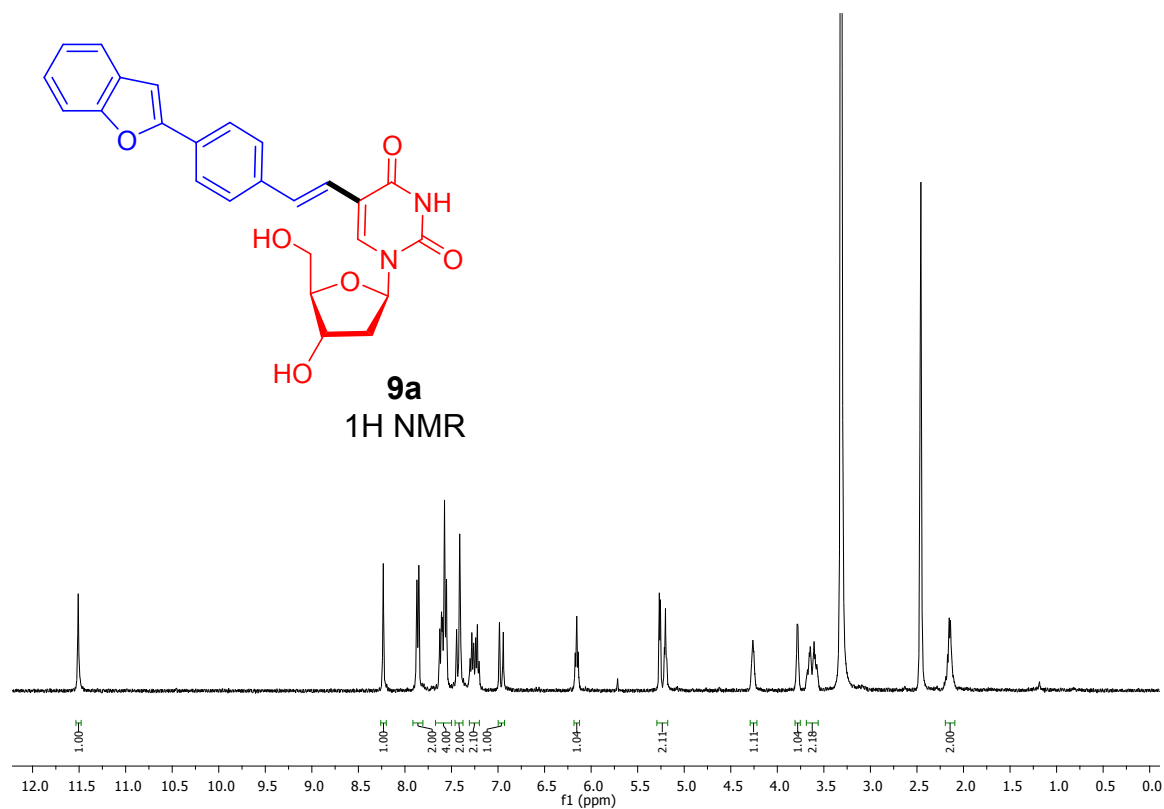


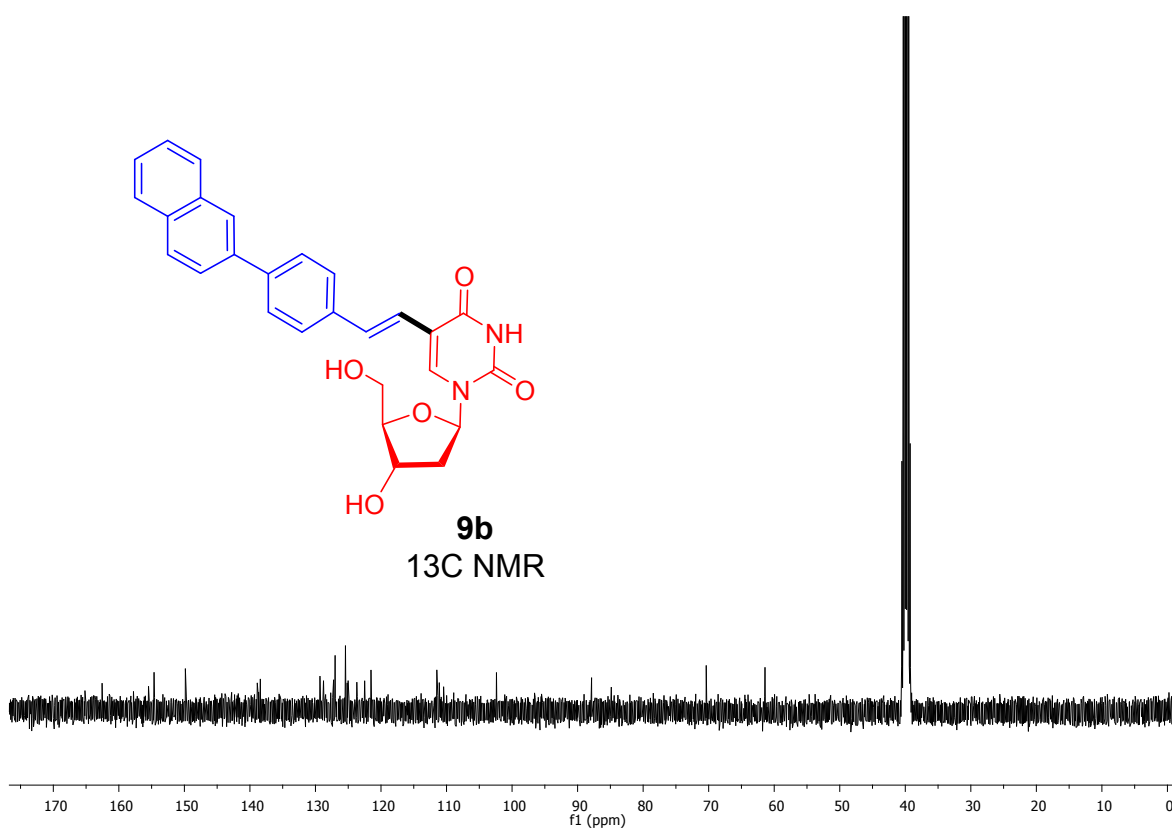
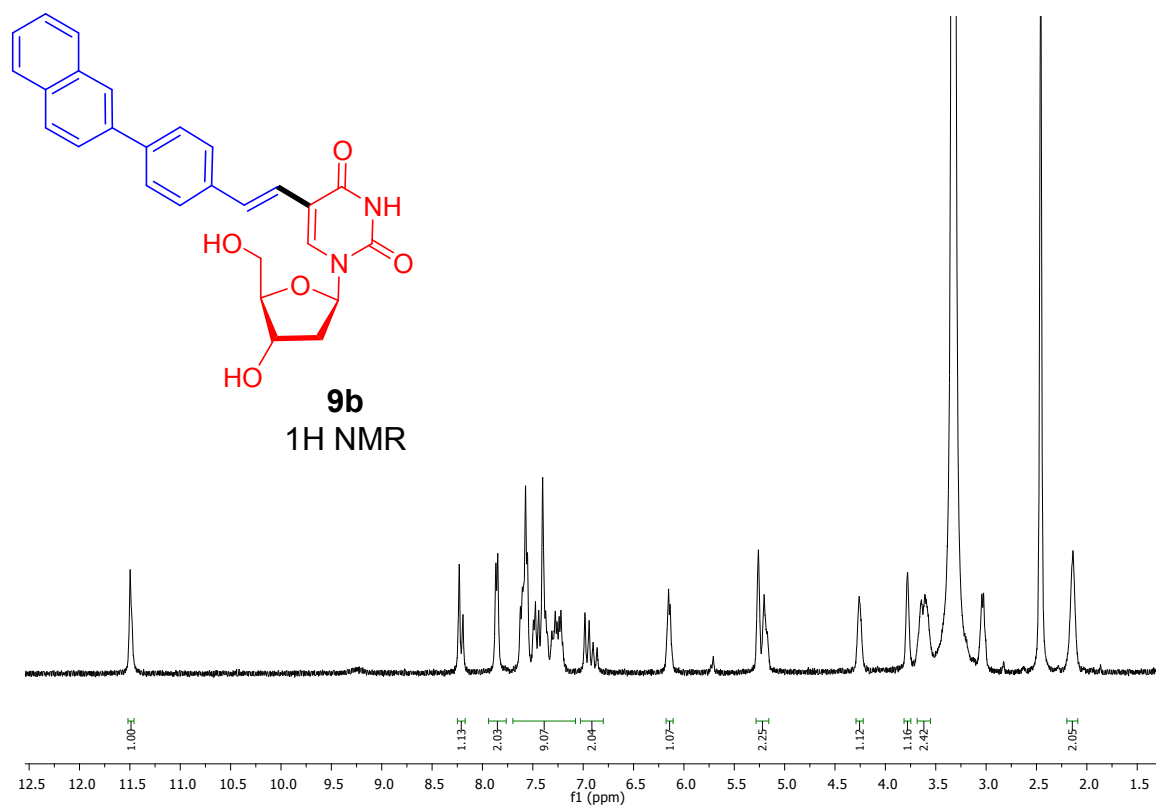


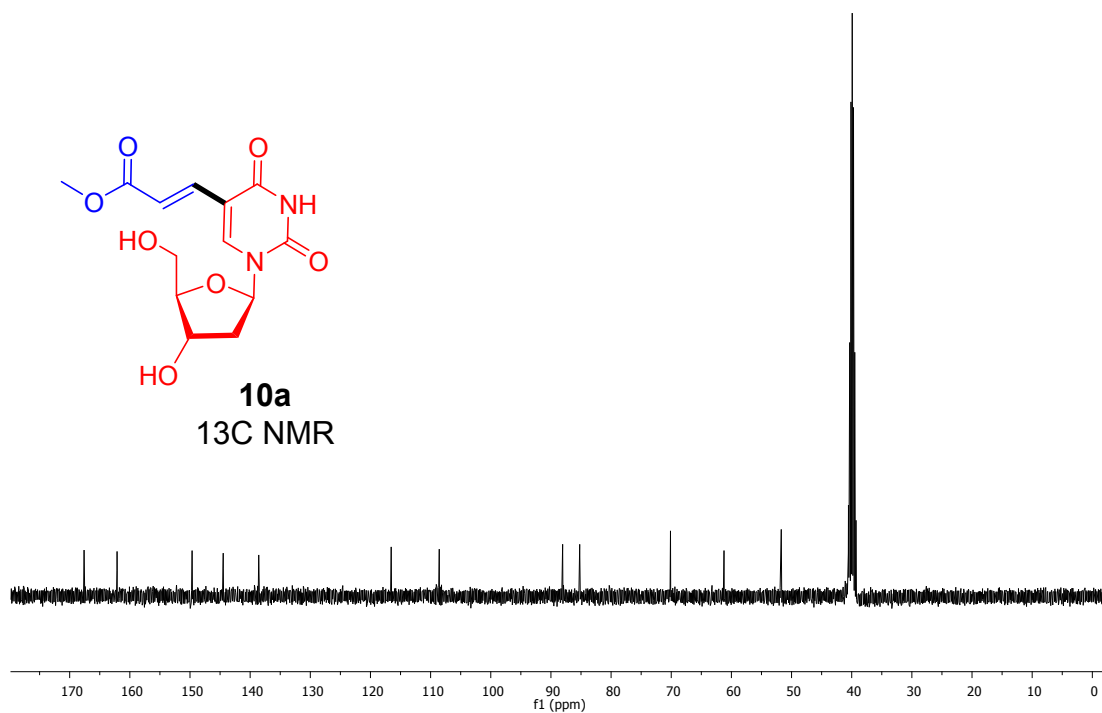
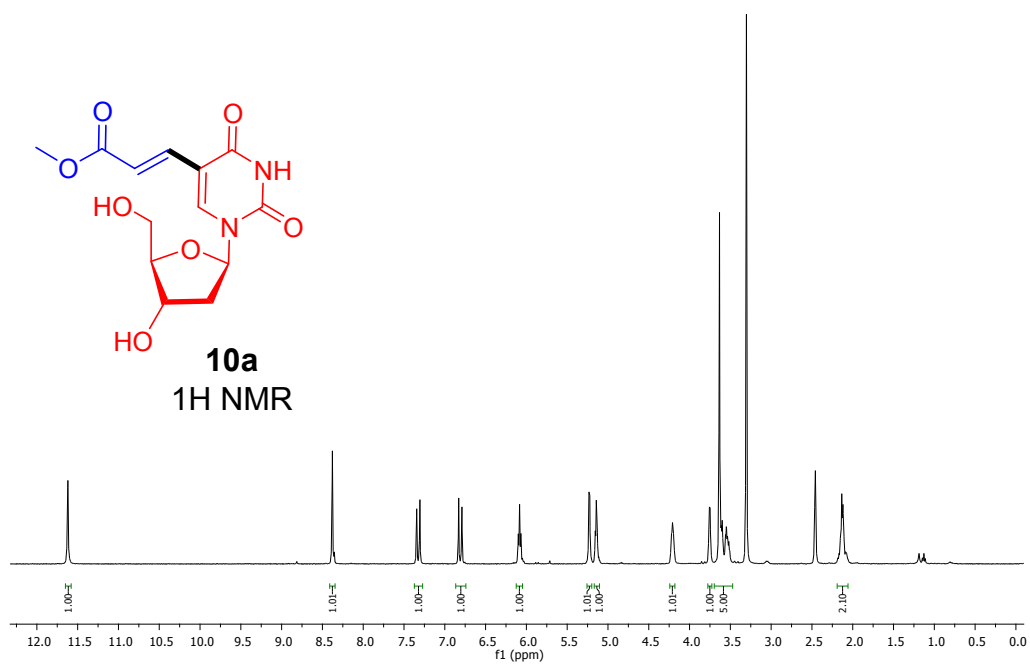


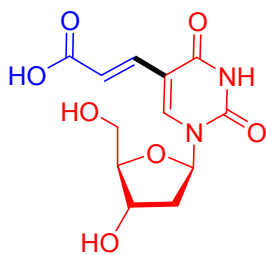




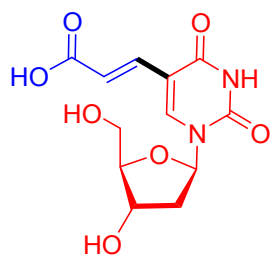
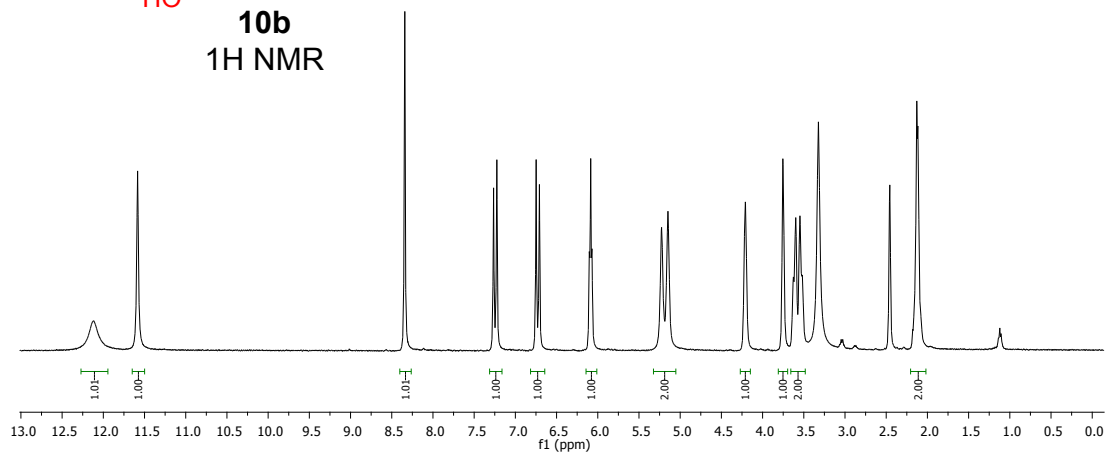




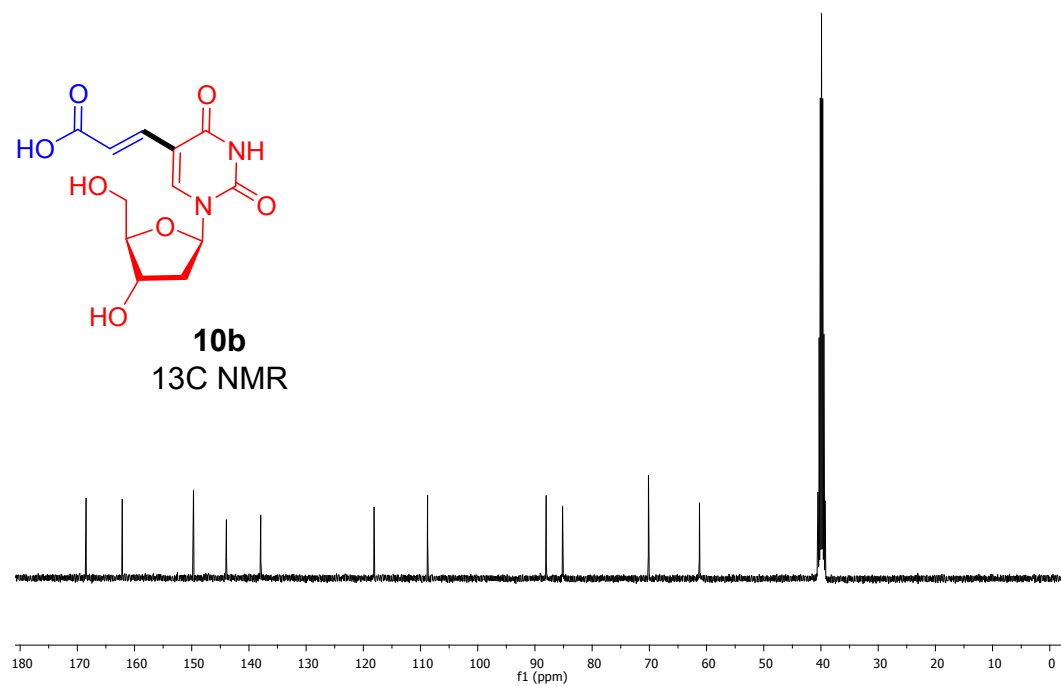




10b
1H NMR



10b
13C NMR



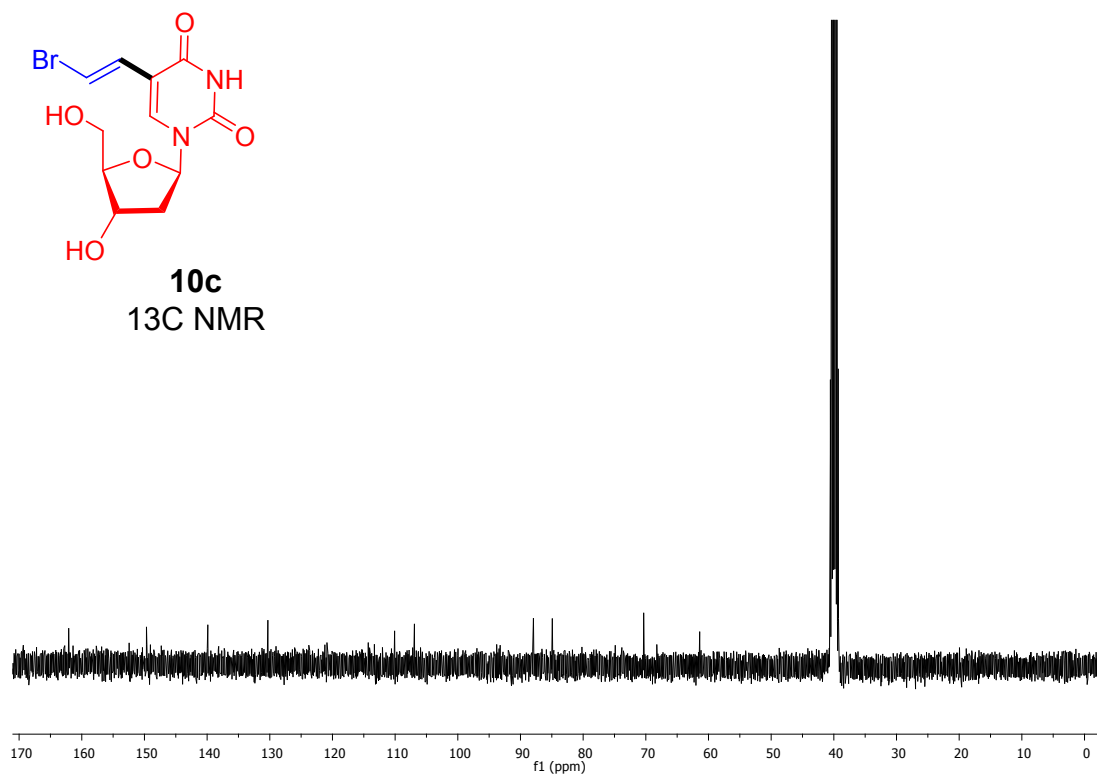
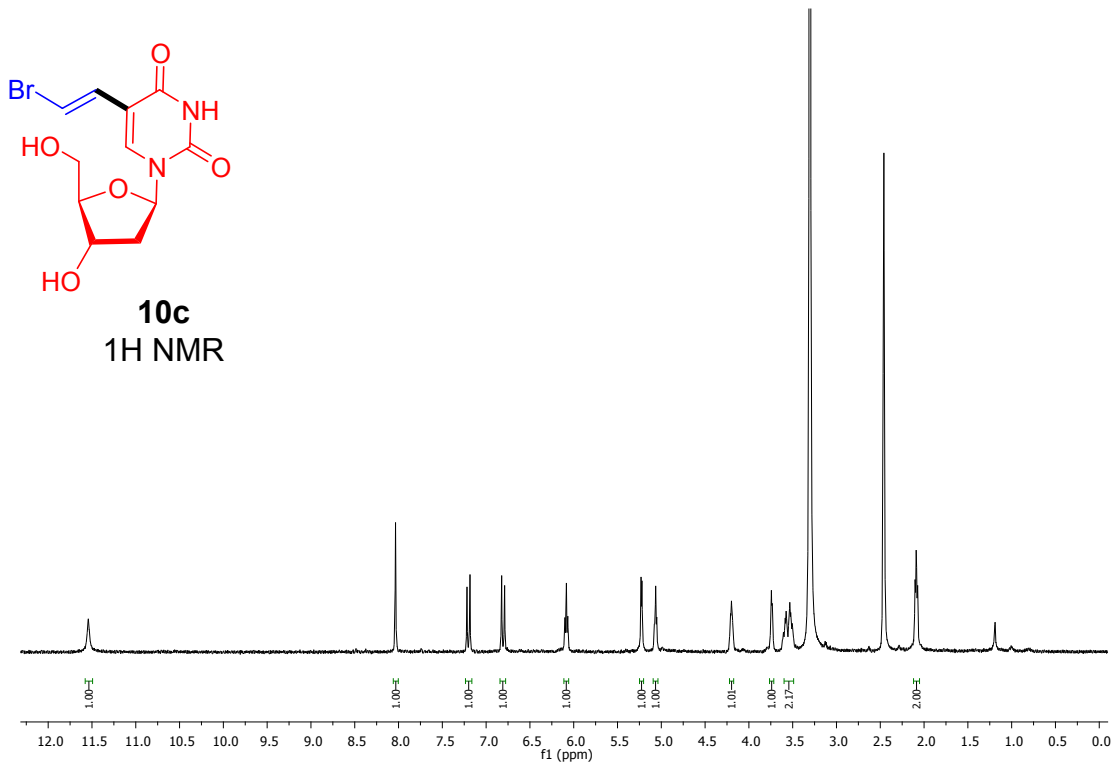


Table 1. Crystal data and structure refinement for **1a**. (CCDC 1489309)

Identification code	shelx
Empirical formula	C ₉ H ₂₄ N ₃ O ₆ P S
Formula weight	333.34
Temperature	170(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 2 ₁ /c
Unit cell dimensions	a = 10.321(2) Å alpha = 90 deg. b = 6.3748(13) Å beta = 98.65(3) deg. c = 22.799(5) Å gamma = 90 deg.
Volume	1482.9(5) Å ³
Z, Calculated density	4, 1.493 Mg/m ³
Absorption coefficient	0.355 mm ⁻¹
F(000)	712
Crystal size	0.434 x 0.301 x 0.198 mm
Theta range for data collection	3.321 to 29.253 deg.
Limiting indices	-14 ≤ h ≤ 13, -8 ≤ k ≤ 8, -30 ≤ l ≤ 31
Reflections collected / unique	15778 / 4007 [R(int) = 0.0423]
Completeness to theta = 25.242	99.7 %
Absorption correction	Numerical
Max. and min. transmission	0.9261 and 0.7377
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4007 / 18 / 205
Goodness-of-fit on F ²	1.113
Final R indices [I > 2sigma(I)]	R1 = 0.0345, wR2 = 0.0901
R indices (all data)	R1 = 0.0423, wR2 = 0.1050
Extinction coefficient	n/a
Largest diff. peak and hole	0.335 and -0.636 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for vg24. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	8217(2)	-93(3)	7680(1)	24(1)
C(2)	8477(2)	989(3)	7114(1)	24(1)
C(3)	7553(1)	55(2)	6599(1)	20(1)
C(4)	7099(1)	3351(2)	6011(1)	18(1)
C(5)	8959(1)	1029(2)	5847(1)	18(1)
C(6)	6645(1)	-129(2)	5548(1)	18(1)
C(7)	8184(2)	4602(2)	5217(1)	20(1)
C(8)	6022(1)	2986(2)	5022(1)	20(1)
C(9)	7671(1)	721(2)	4694(1)	20(1)
N(1)	7598(1)	1084(2)	6010(1)	16(1)
N(2)	6924(1)	4265(2)	5433(1)	18(1)
N(3)	6480(1)	828(2)	4976(1)	18(1)
O(1)	8712(1)	-62(2)	8823(1)	33(1)
O(2)	10451(1)	990(2)	8290(1)	29(1)
O(3)	8615(1)	3293(2)	8315(1)	32(1)
O(5)	3839(1)	3425(2)	6232(1)	35(1)
O(4)	5392(2)	6361(3)	6903(1)	43(1)
O(6)	3860(2)	-91(2)	6954(1)	41(1)
P(1)	9084(1)	2148(1)	5108(1)	19(1)
S(1)	9070(1)	1132(1)	8326(1)	21(1)

Table 3. Bond lengths [Å] and angles [deg] for vg24.

C(1)-C(2)	1.523(2)
C(1)-S(1)	1.7796(16)
C(2)-C(3)	1.517(2)
C(3)-N(1)	1.5010(17)
C(4)-N(2)	1.4270(18)
C(4)-N(1)	1.5346(19)
C(5)-N(1)	1.5068(18)
C(5)-P(1)	1.8509(15)
C(6)-N(3)	1.4269(18)
C(6)-N(1)	1.5378(18)
C(7)-N(2)	1.4743(19)
C(7)-P(1)	1.8549(16)
C(8)-N(3)	1.4637(19)
C(8)-N(2)	1.4657(19)
C(9)-N(3)	1.4713(19)
C(9)-P(1)	1.8521(16)
O(1)-S(1)	1.4571(12)
O(2)-S(1)	1.4433(12)
O(3)-S(1)	1.4545(14)
C(2)-C(1)-S(1)	112.05(11)
C(3)-C(2)-C(1)	107.91(12)
N(1)-C(3)-C(2)	114.81(12)
N(2)-C(4)-N(1)	112.31(11)
N(1)-C(5)-P(1)	114.28(10)
N(3)-C(6)-N(1)	112.80(11)
N(2)-C(7)-P(1)	113.97(10)
N(3)-C(8)-N(2)	112.84(12)
N(3)-C(9)-P(1)	113.56(10)
C(3)-N(1)-C(5)	111.49(11)
C(3)-N(1)-C(4)	110.80(11)
C(5)-N(1)-C(4)	110.33(11)
C(3)-N(1)-C(6)	106.92(11)
C(5)-N(1)-C(6)	110.06(11)
C(4)-N(1)-C(6)	107.09(10)
C(4)-N(2)-C(8)	110.09(12)
C(4)-N(2)-C(7)	111.91(12)
C(8)-N(2)-C(7)	111.95(12)
C(6)-N(3)-C(8)	109.36(11)
C(6)-N(3)-C(9)	112.80(12)
C(8)-N(3)-C(9)	111.99(12)
C(5)-P(1)-C(9)	96.76(7)
C(5)-P(1)-C(7)	95.68(7)
C(9)-P(1)-C(7)	96.35(7)
O(2)-S(1)-O(3)	112.18(8)
O(2)-S(1)-O(1)	112.32(8)
O(3)-S(1)-O(1)	112.93(8)
O(2)-S(1)-C(1)	107.13(8)
O(3)-S(1)-C(1)	106.44(8)
O(1)-S(1)-C(1)	105.22(8)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for vg24.
The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
C(1)	28(1)	26(1)	16(1)	2(1)	0(1)	-5(1)
C(2)	25(1)	28(1)	16(1)	2(1)	1(1)	-7(1)
C(3)	21(1)	22(1)	16(1)	3(1)	2(1)	-3(1)
C(4)	20(1)	17(1)	18(1)	-2(1)	4(1)	1(1)
C(5)	14(1)	22(1)	19(1)	1(1)	2(1)	2(1)
C(6)	18(1)	16(1)	18(1)	-2(1)	0(1)	-3(1)
C(7)	23(1)	19(1)	19(1)	2(1)	3(1)	-2(1)
C(8)	17(1)	20(1)	22(1)	-1(1)	-2(1)	2(1)
C(9)	21(1)	21(1)	18(1)	-3(1)	4(1)	0(1)
N(1)	16(1)	17(1)	15(1)	0(1)	2(1)	-1(1)
N(2)	19(1)	17(1)	20(1)	0(1)	1(1)	2(1)
N(3)	17(1)	19(1)	18(1)	-1(1)	1(1)	0(1)
O(1)	33(1)	47(1)	17(1)	4(1)	2(1)	-7(1)
O(2)	20(1)	36(1)	29(1)	1(1)	0(1)	1(1)
O(3)	32(1)	30(1)	31(1)	-7(1)	-1(1)	6(1)
O(5)	32(1)	35(1)	38(1)	-1(1)	9(1)	0(1)
O(4)	36(1)	37(1)	55(1)	-5(1)	3(1)	-2(1)
O(6)	34(1)	31(1)	54(1)	1(1)	-4(1)	-4(1)
P(1)	17(1)	22(1)	19(1)	0(1)	5(1)	0(1)
S(1)	20(1)	26(1)	16(1)	0(1)	0(1)	0(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for vg24.

	x	y	z	U(eq)
H(1A)	8492	-1579	7671	28
H(1B)	7265	-65	7698	28
H(2A)	8322	2516	7139	28
H(2B)	9398	765	7055	28
H(3A)	7766	-1451	6566	23
H(3B)	6647	148	6690	23
H(4A)	6253	3373	6166	22
H(4B)	7733	4205	6280	22
H(5A)	9263	-445	5856	22
H(5B)	9556	1814	6150	22
H(6A)	6976	-1576	5516	21
H(6B)	5781	-220	5686	21
H(7A)	8746	5502	5504	24
H(7B)	8018	5366	4835	24
H(8A)	5155	2964	5157	24
H(8B)	5911	3643	4624	24
H(9A)	7475	1313	4289	24
H(9B)	7916	-769	4657	24
H(5O)	3018(19)	3850(40)	6206(12)	56(8)
H(5P)	3890(30)	2260(40)	6440(14)	79(10)
H(4O)	4890(30)	5460(40)	6691(13)	83(11)
H(6O)	3060(20)	-600(50)	6902(14)	83(11)
H(4P)	4940(30)	7520(40)	6912(15)	77(10)
H(6P)	4020(40)	310(80)	7328(11)	150(20)

Table 6. Hydrogen bonds for vg24 [A and deg.].

Donor	--- H....	Acceptor	[ARU]	D - H	H...A	D...A	D - H...A
O4	--H4O	..O5	[1565.03]	0.87(3)	1.90(3)	2.771(2)	178(4)
O4	--H4P	..O6	[]	0.88(3)	1.90(3)	2.772(2)	176(3)
O5	--H5O	..O1	[2645.01]	0.88(2)	1.91(2)	2.789(2)	176(2)
O5	--H5P	..O6	[]	0.88(3)	1.91(3)	2.780(2)	173(3)
O6	--H6O	..O3	[2655.01]	0.88(2)	1.86(2)	2.737(2)	172(3)
O6	--H6P	..O4	[2645.02]	0.88(3)	1.89(3)	2.764(2)	171(4)
C3	--H3A	..O2	[2755.01]	0.99	2.44	3.296(2)	144
C4	--H4A	..O5	[]	0.99	2.52	3.476(2)	163
C4	--H4B	..O2	[2745.01]	0.99	2.28	3.248(2)	164
C6	--H6B	..N3	[3665.01]	0.99	2.61	3.297(2)	127
C7	--H7B	..O1	[4554.01]	0.99	2.52	3.3171(19)	137

Translation of ARU-Code to CIF and Equivalent Position Code

[2745.] =	2-x,-1/2+y,1/2-z
[4554.] =	x,1/2-y,-1/2+z
[2755.] =	2-x,1/2+y,1/2-z
[3665.] =	1-x,1-y,-z
[1565.] =	x,1+y,z
[2645.] =	1-x,-1/2+y,1/2-z
[2655.] =	1-x,1/2+y,1/2-z