SUPPLEMENTARY MATERIAL

Structural Study of Azide-Tetrazole Equilibrium in Pyrido[2,3-*d*]pyrimidines

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S1. NMR spectra

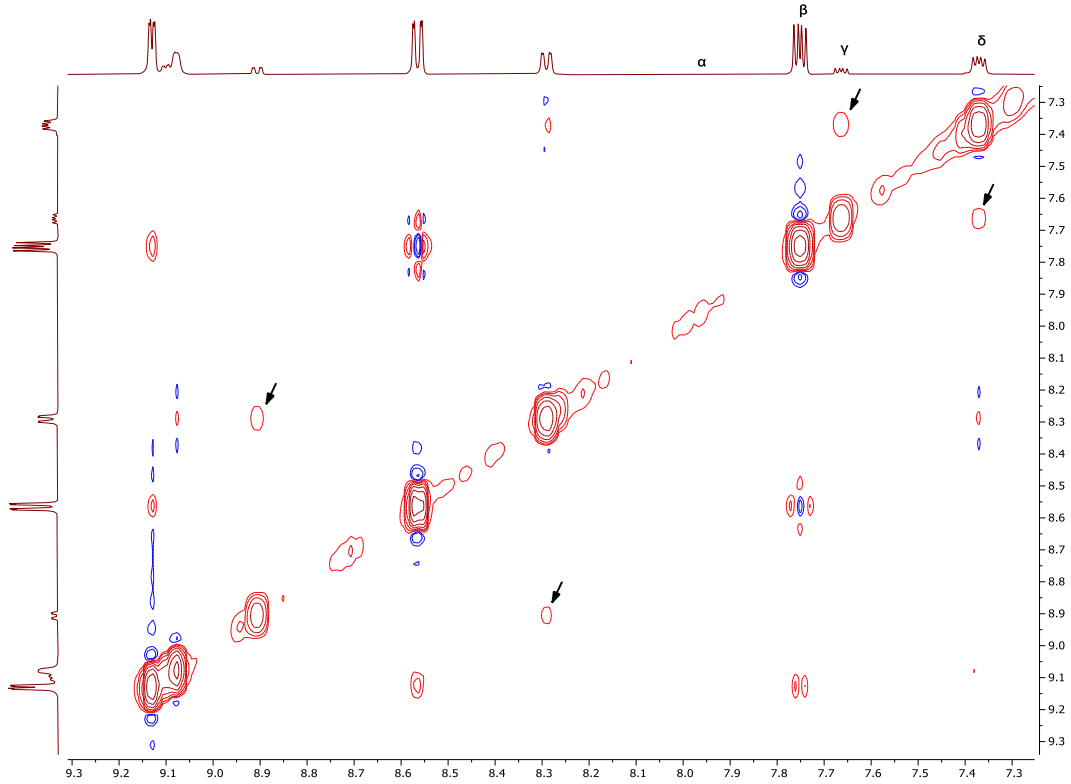


Figure S1. Diazide **2** 2D-EXSY spectrum in $CDCl_3$

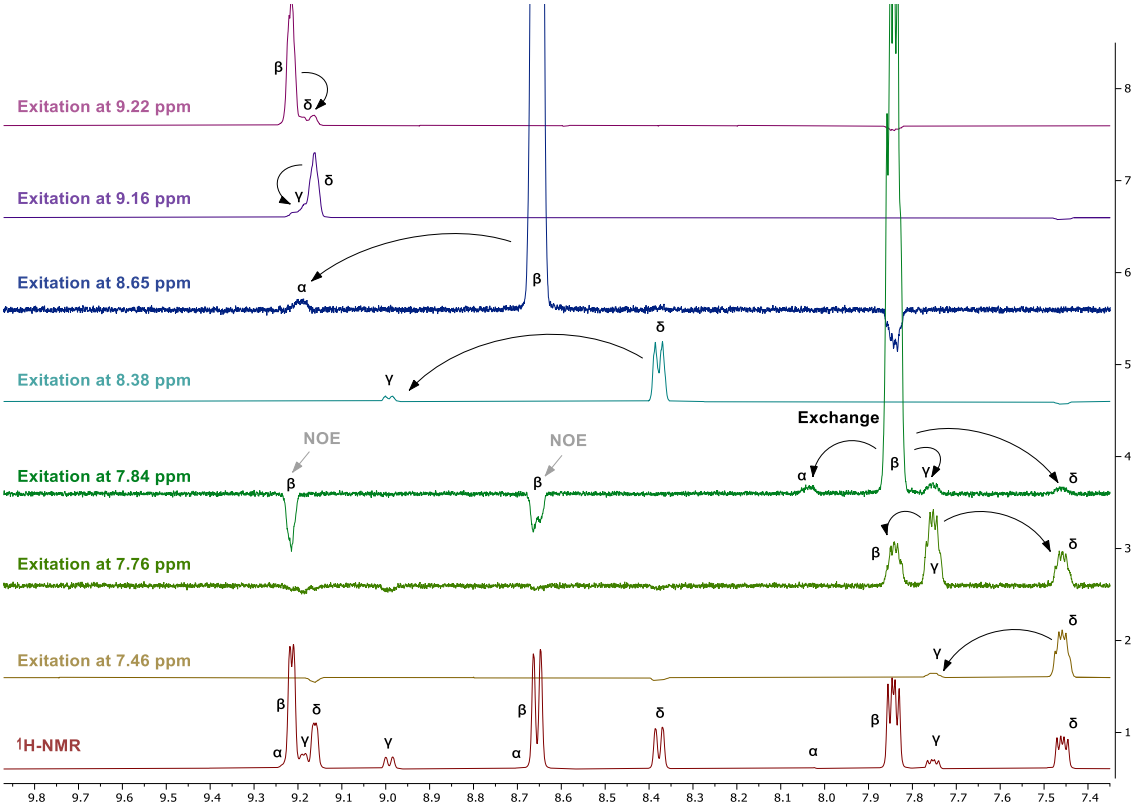


Figure S2. 1D-EXSY spectrum of diazide **2** in $CDCl_3$

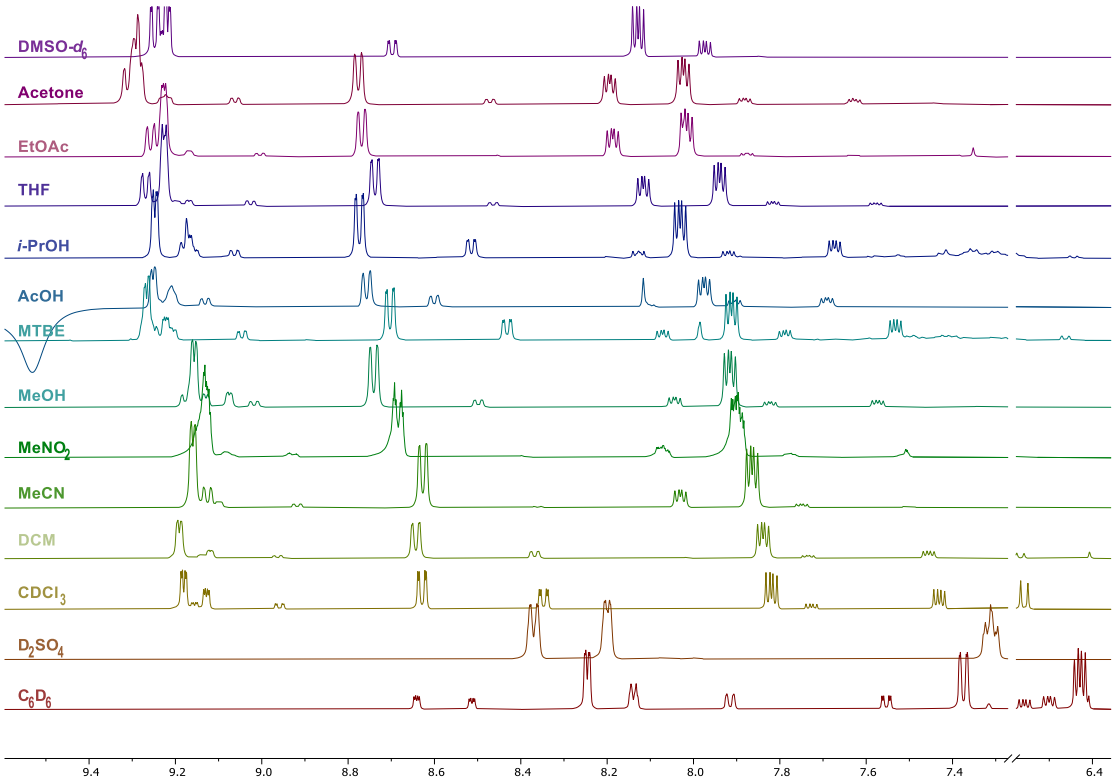


Figure S3. ^{1}H-NMR spectra of diazide **2** in various organic solvents (^{1}H-NMR shifts referenced to internal standard 1,2,3-trimetoxybenzene)

Table S1. Relative tautomer form ratios of diazide **2** in different solvents

			Relative tautomer ratio			
Entry	**Solvent**	**Dielectric constant**	**α**	**β**	**γ**	**δ**
1	DMSO-d_6	78.5	74	23	2	1
2	MeCN	36.6	21	72	5	2
3	$MeNO_2$	35.9	11	82	3	4
4	MeOH	32.6	14	65	10	11
5	Acetone	21.1	33	56	7	4
6	*i*-PrOH	18.3	3	77	2	18
7	DCM	9.1	2	75	7	16
8	THF	7.5	36	50	8	6
9	AcOH	6.2	5	55	18	22
10	EtOAc	6	34	53	7	6
11	$CDCl_3$	4.8	1	59	9	31
12	MTBE	4.5	9	57	10	24
13	C_6D_6	2.28	11	17	58	14

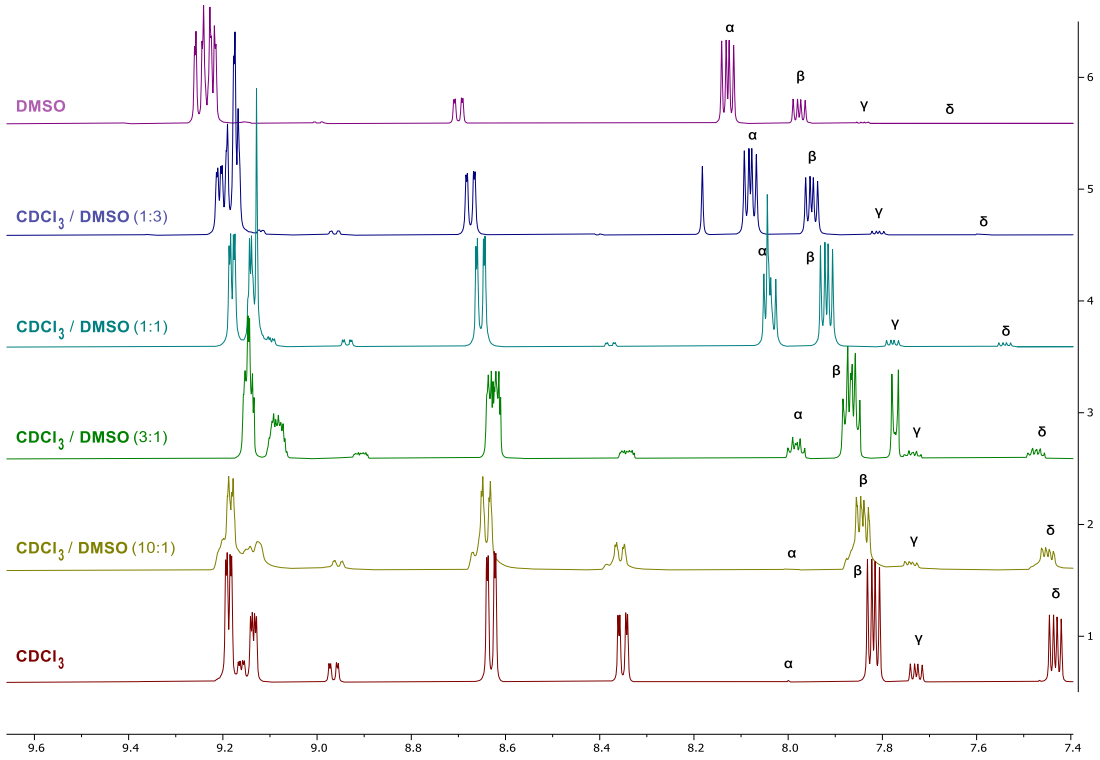


Figure S4. ^{1}H-NMR titration of diazide **2** in $CDCl_3$ solution with DMSO-d_6

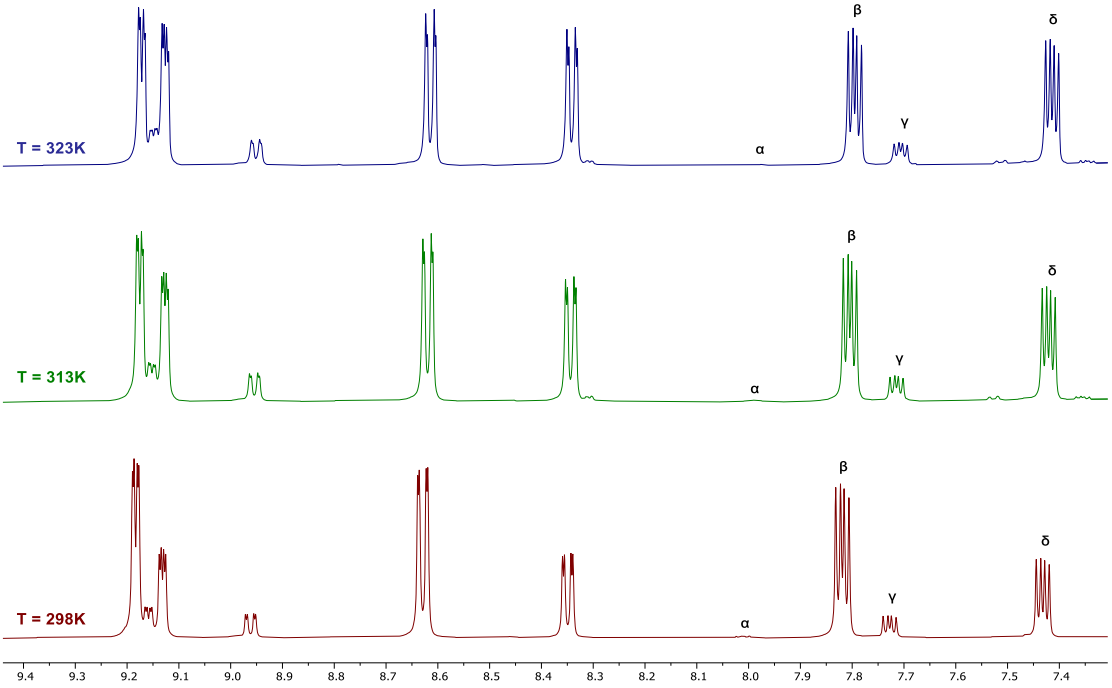


Figure S5 ^{1}H-NMR spectra of diazide **2** in $CDCl_3$ at different temperatures

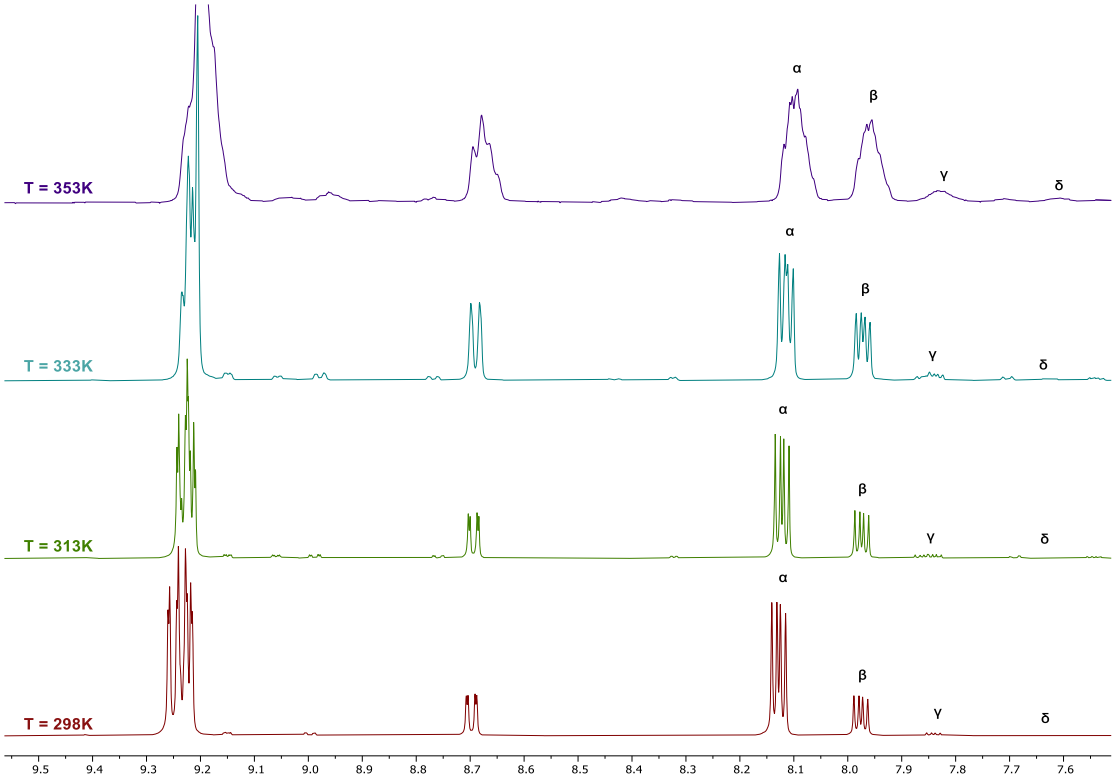


Figure S6. ^{1}H-NMR spectra of diazide **2** in DMSO-d_6 at different temperatures

S2. FT-IR spectra

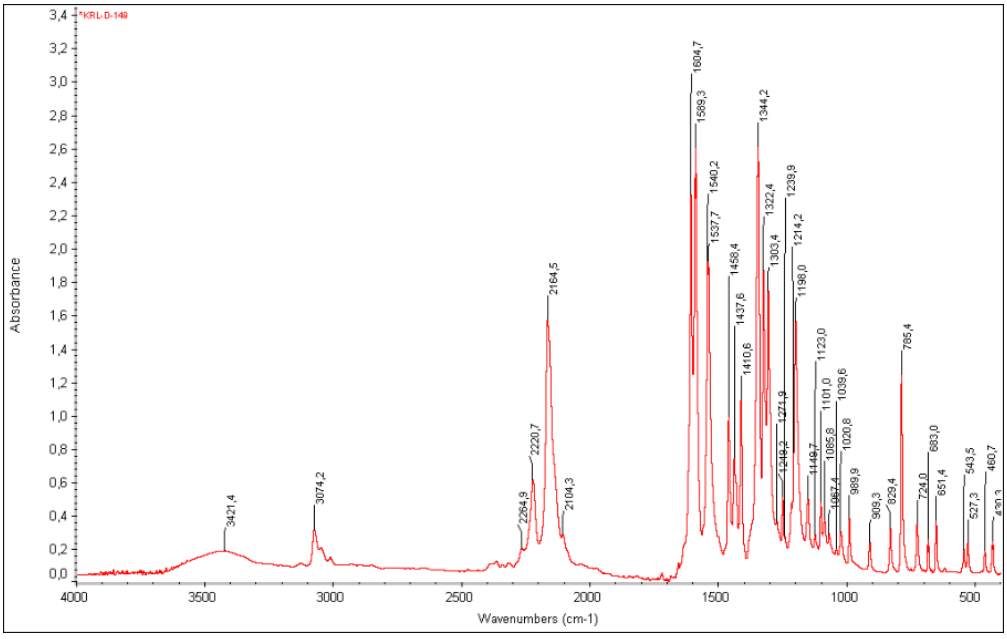


Figure S7. FT-IR spectra of diazide **2**

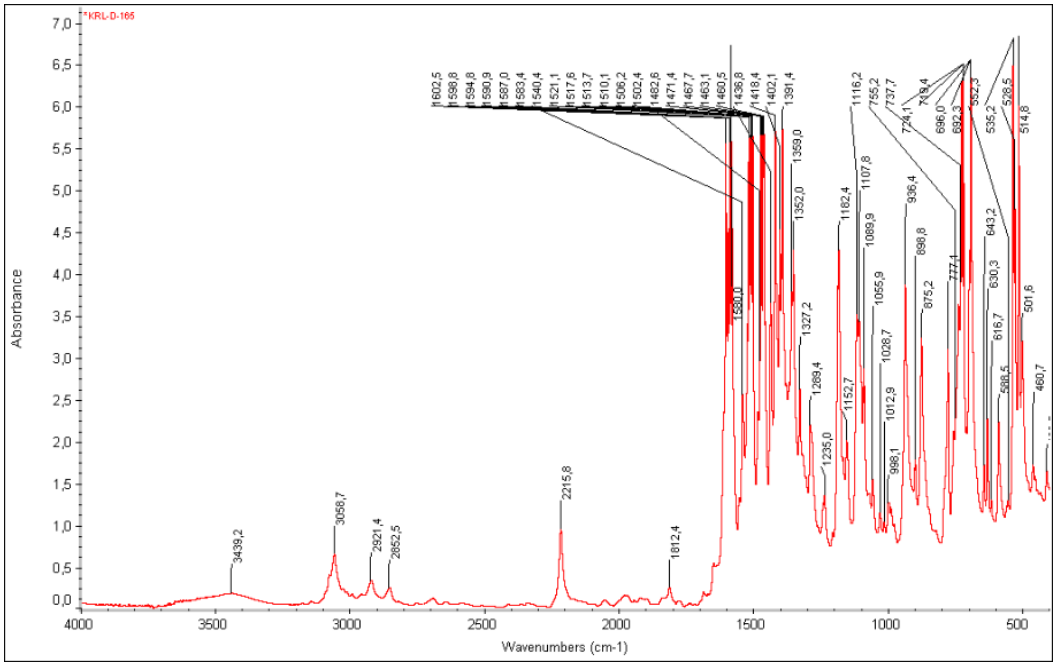


Figure S8. FT-IR spectra of phosphonimidate **12**

S3. Gibbs free energy plots

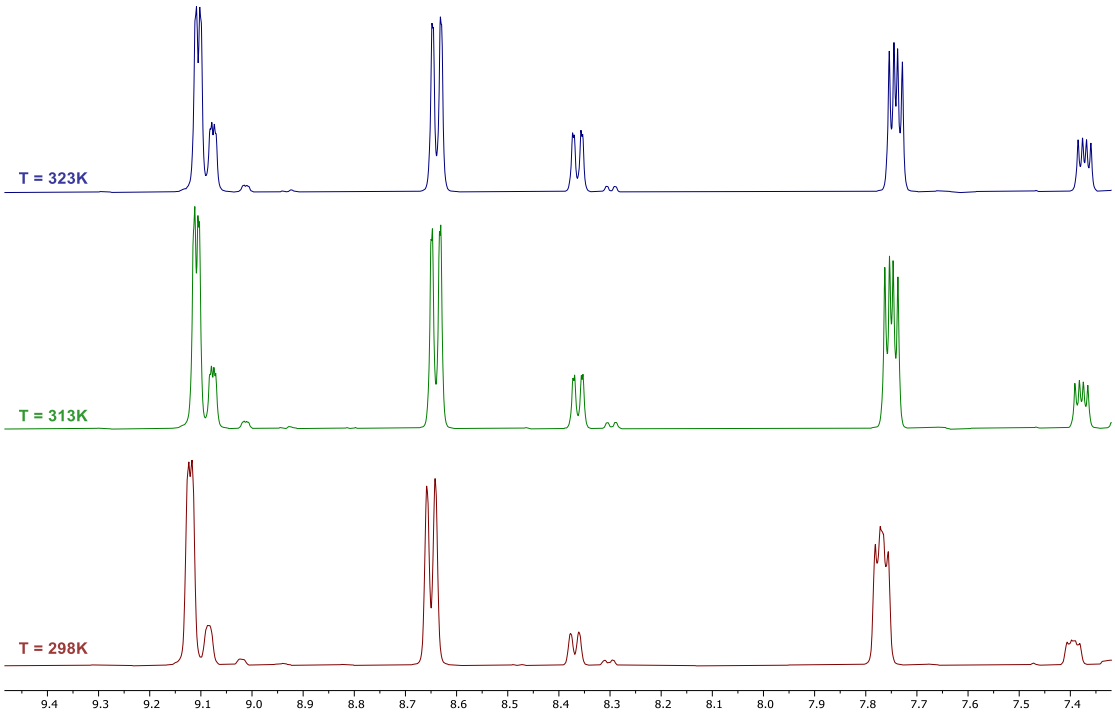


Figure S9. ^{1}H-NMR spectra of **4** in $CDCl_3$ at different temperatures

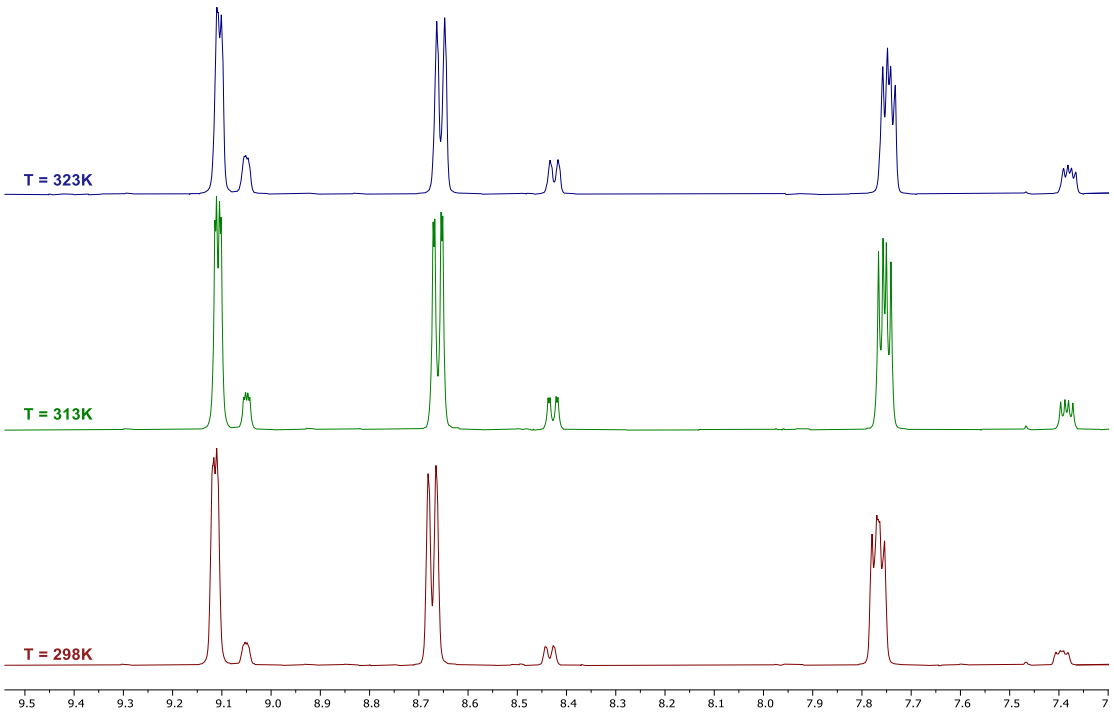


Figure S10. ^{1}H-NMR spectra of **7a** in $CDCl_3$ at different temperatures

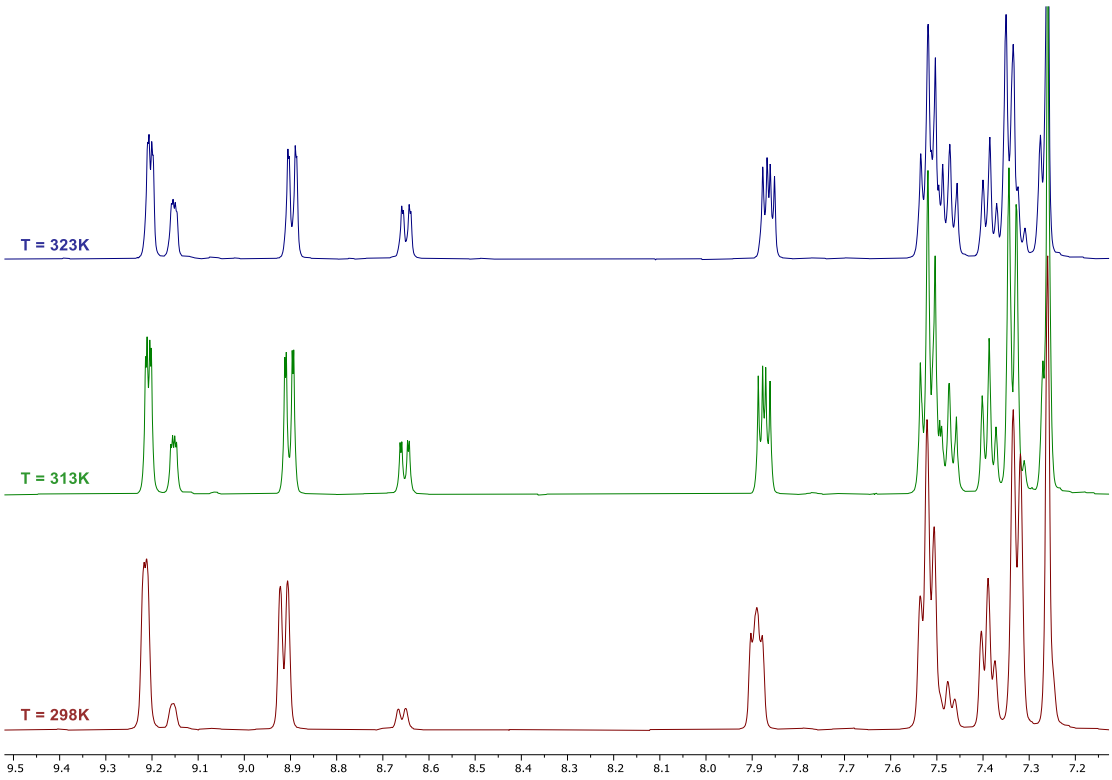


Figure S11. ^{1}H-NMR spectra of **7b** in $CDCl_3$ at different temperatures

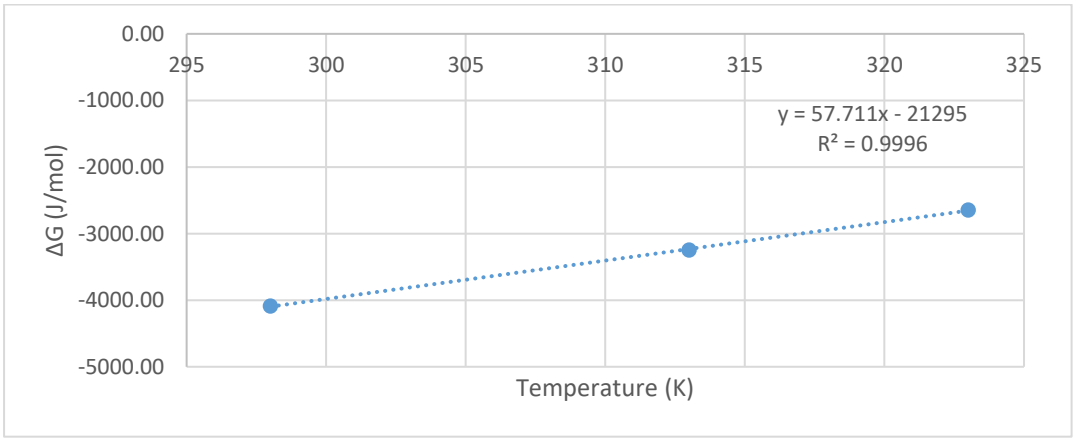


Figure S12. Gibbs free energy plot for **4**

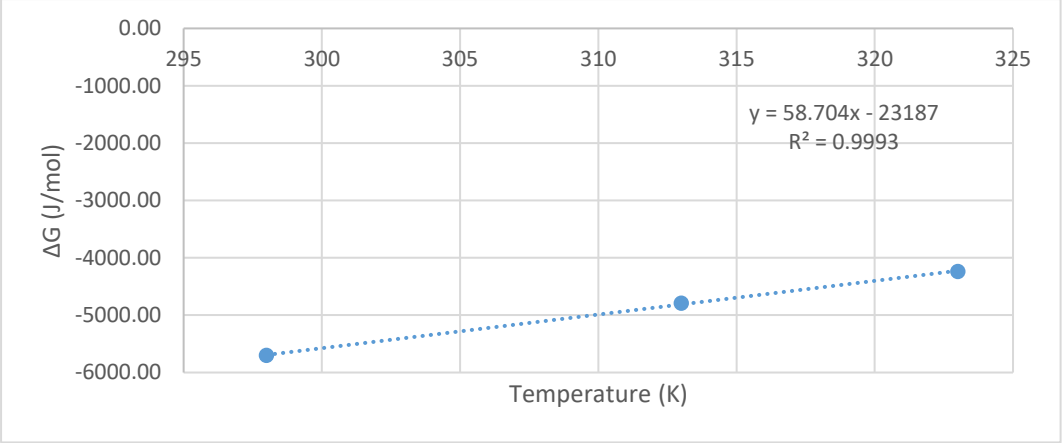


Figure S13. Gibbs free energy plot for **7a**

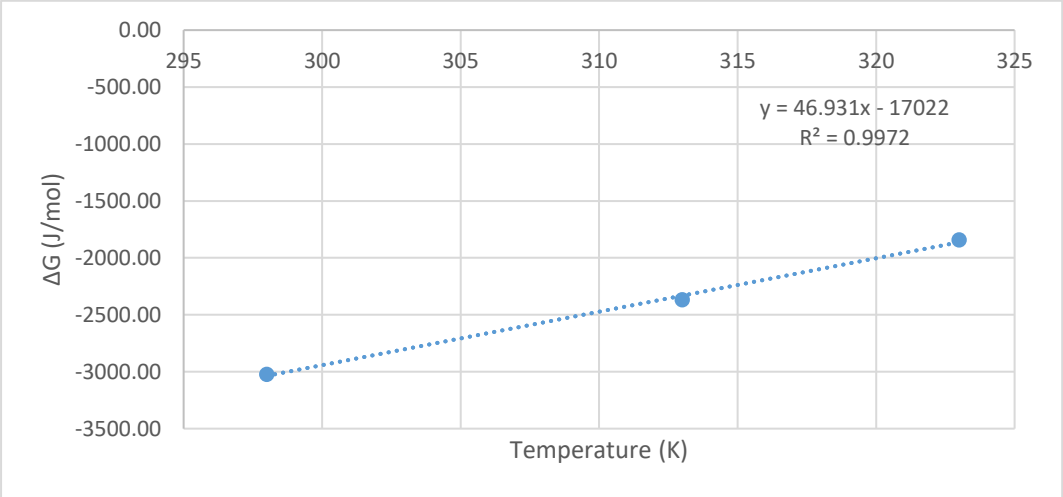


Figure S14. Gibbs free energy plot for **7b**

Table S2. Thermodynamic heats of equilibriation for **4**, **7a** and **7b** in $CDCl_3$ obtained using van't Hoff plot

Compound	ΔG_{298} (kJ/mol)	**ΔH** (kJ/mol)	**ΔS** (J/mol·K)
4	4.10	21.28	57.66
7a	5.69	23.21	58.77
7b	3.03	16.99	46.82

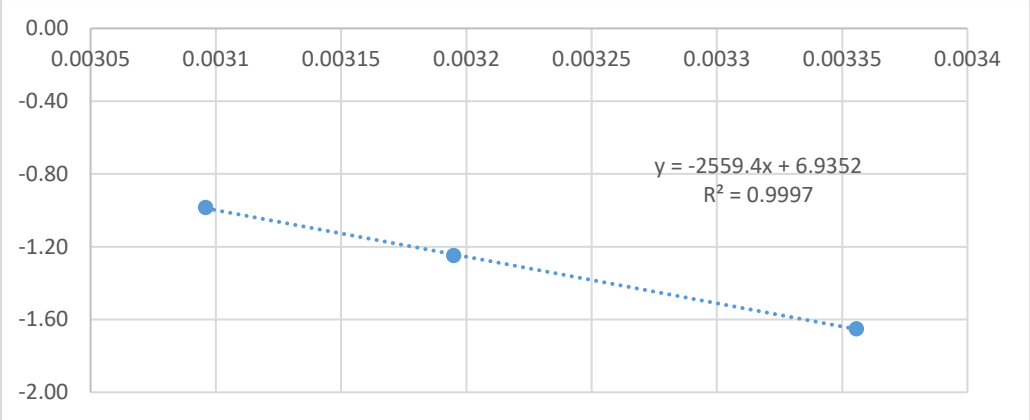


Figure S15. Van't Hoff plot for **4**

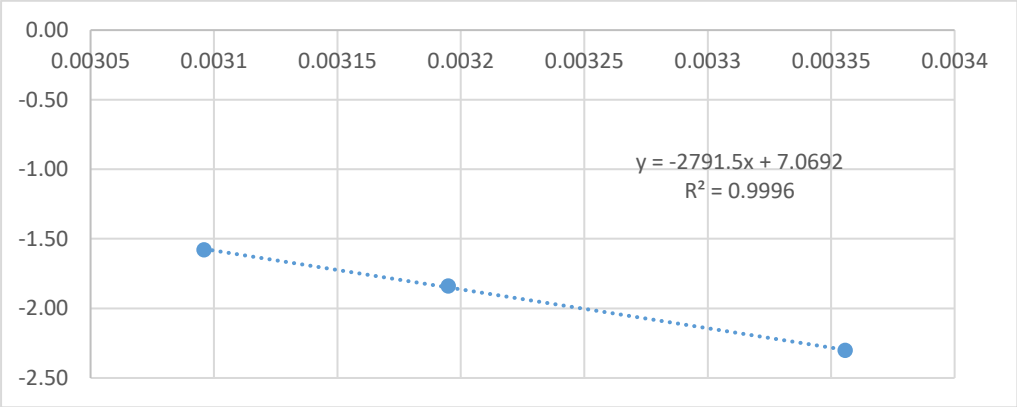


Figure S16. Van't Hoff plot for **7a**

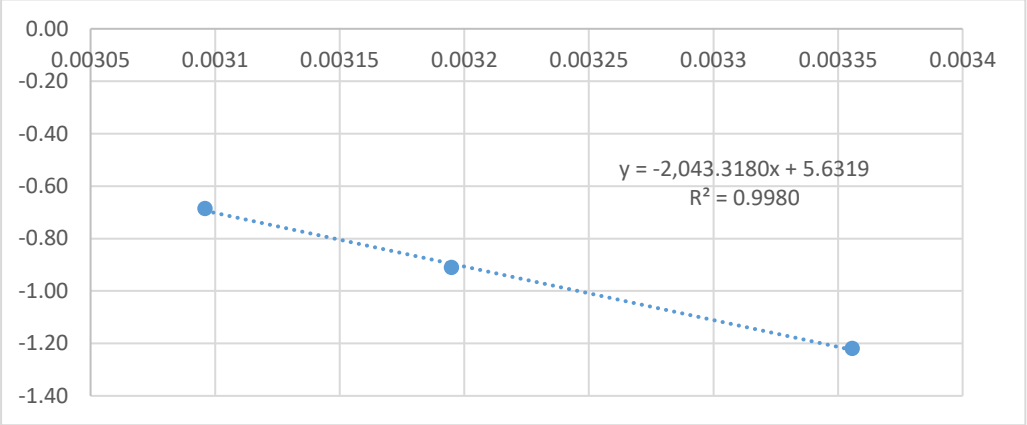
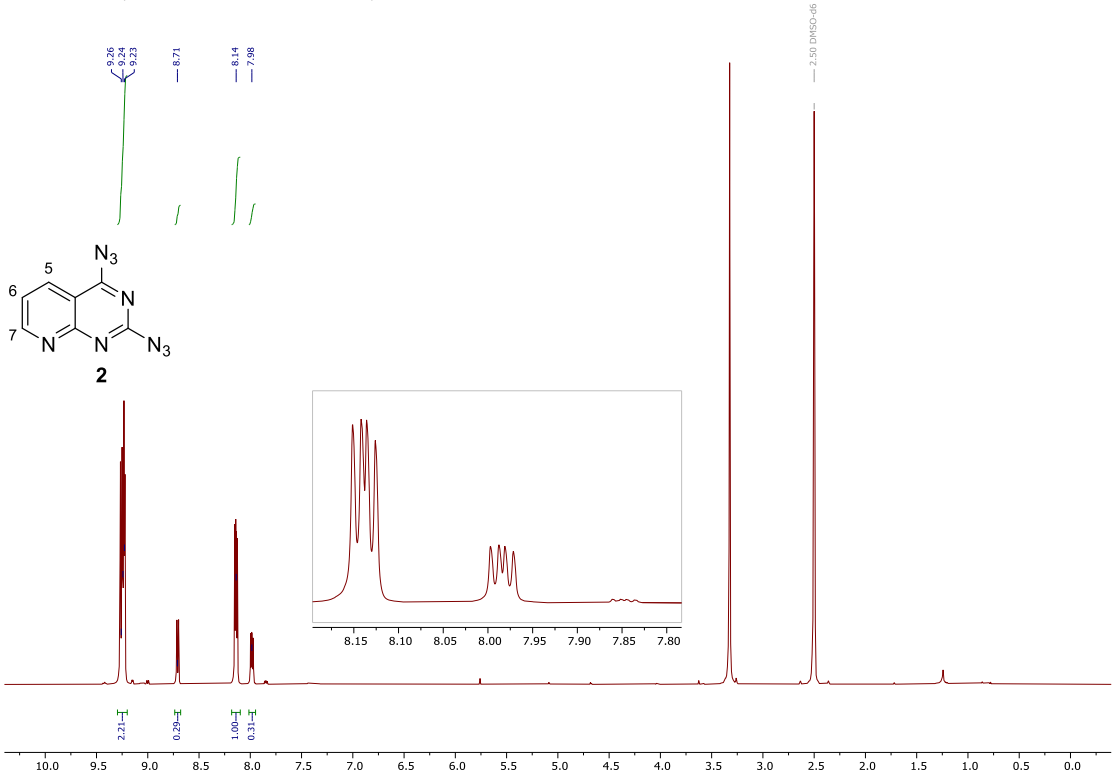


Figure S17. Van't Hoff plot for **7b**

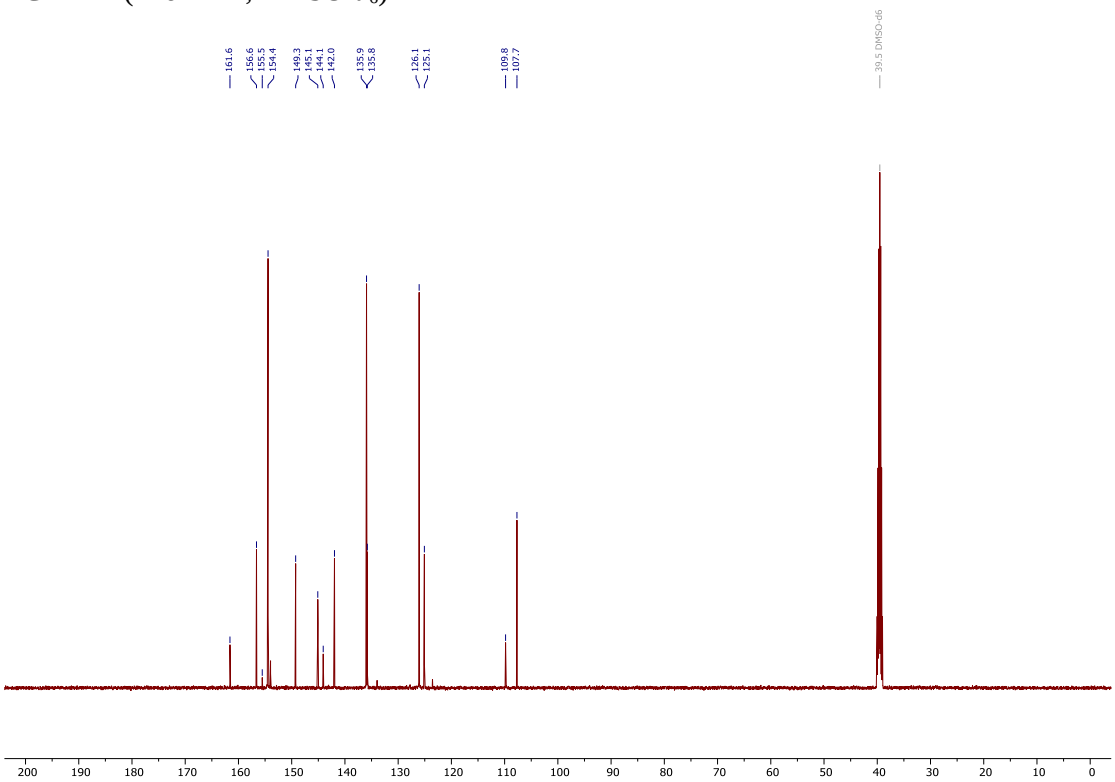
S4. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of characterized compounds

2,4-diazidopyrido[2,3-*d*]pyrimidine (**2**):

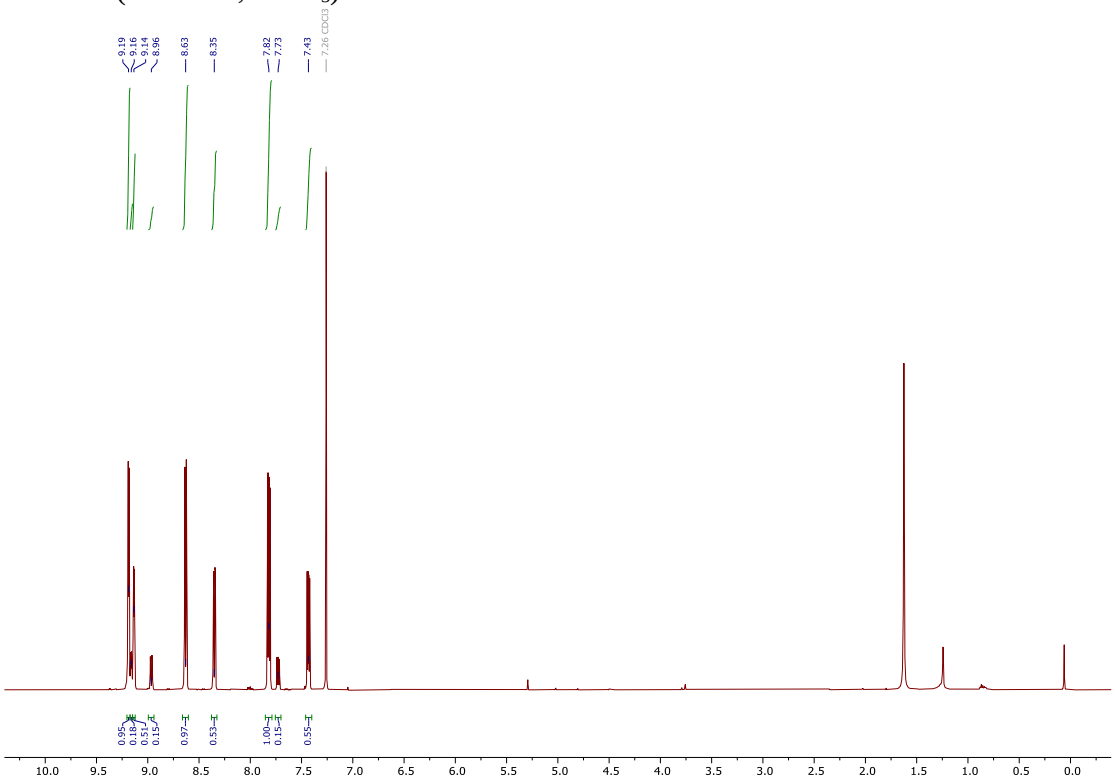
^{1}H NMR (500 MHz, DMSO-d_6)



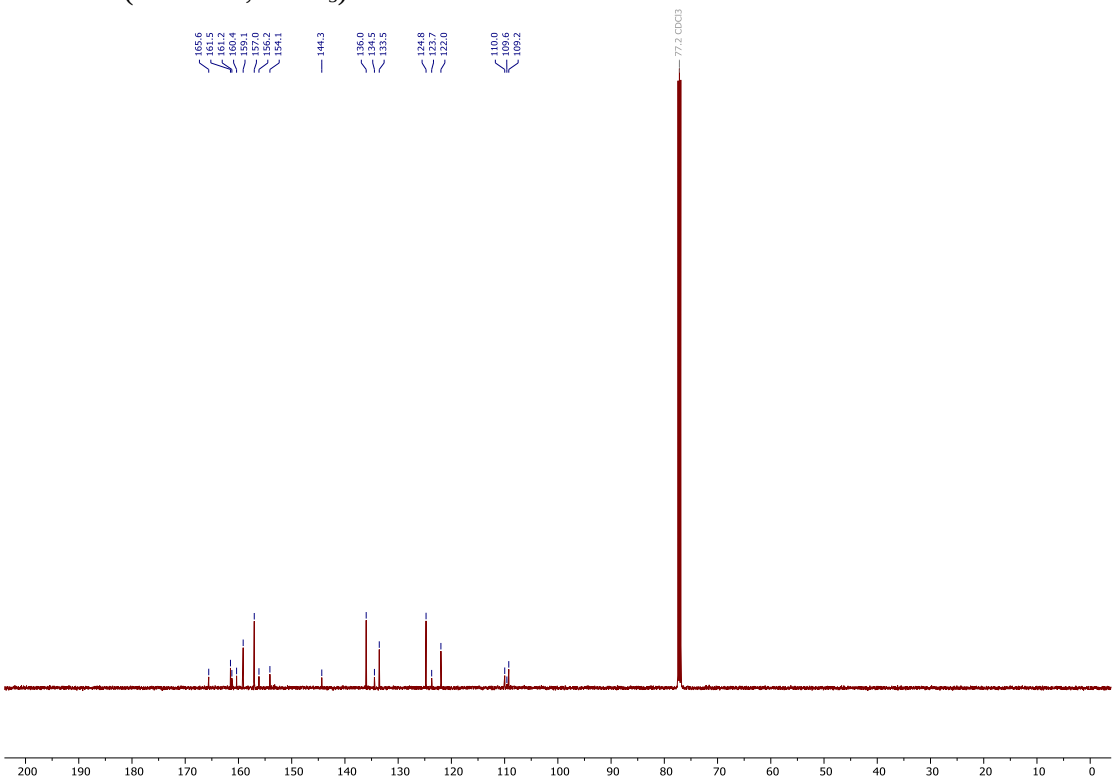
^{13}C NMR (126 MHz, DMSO-d_6)



^{1}H NMR (500 MHz, $CDCl_3$)

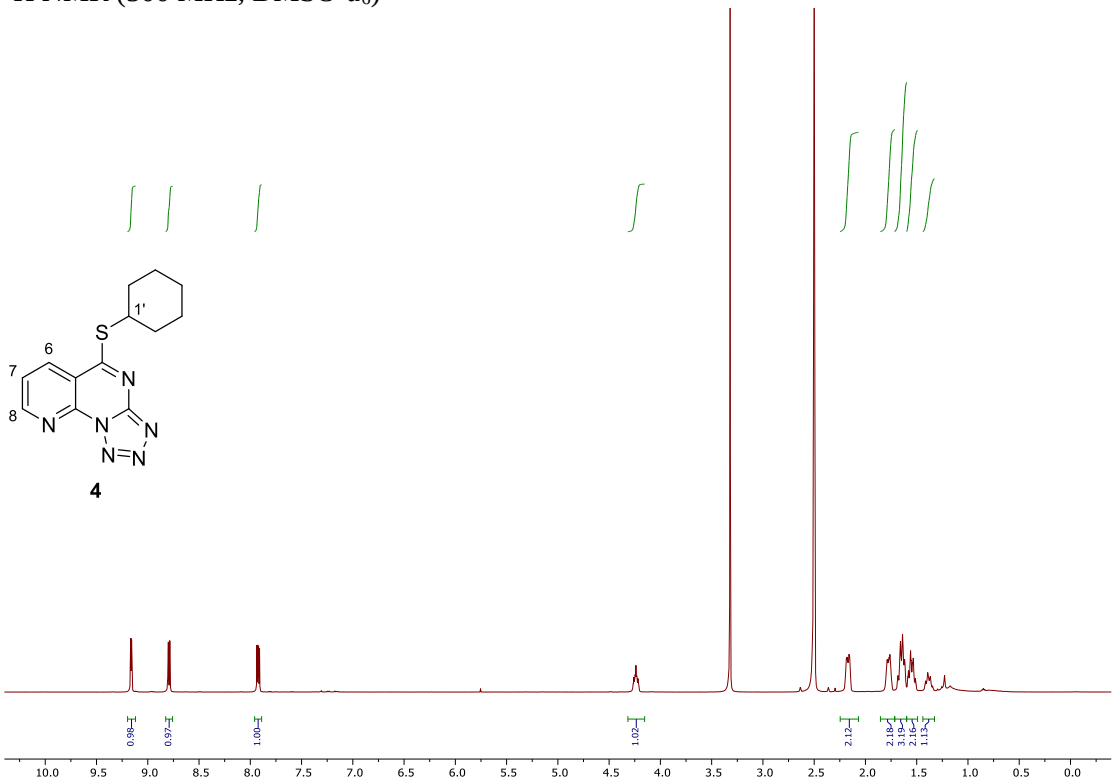


^{13}C NMR (126 MHz, $CDCl_3$)

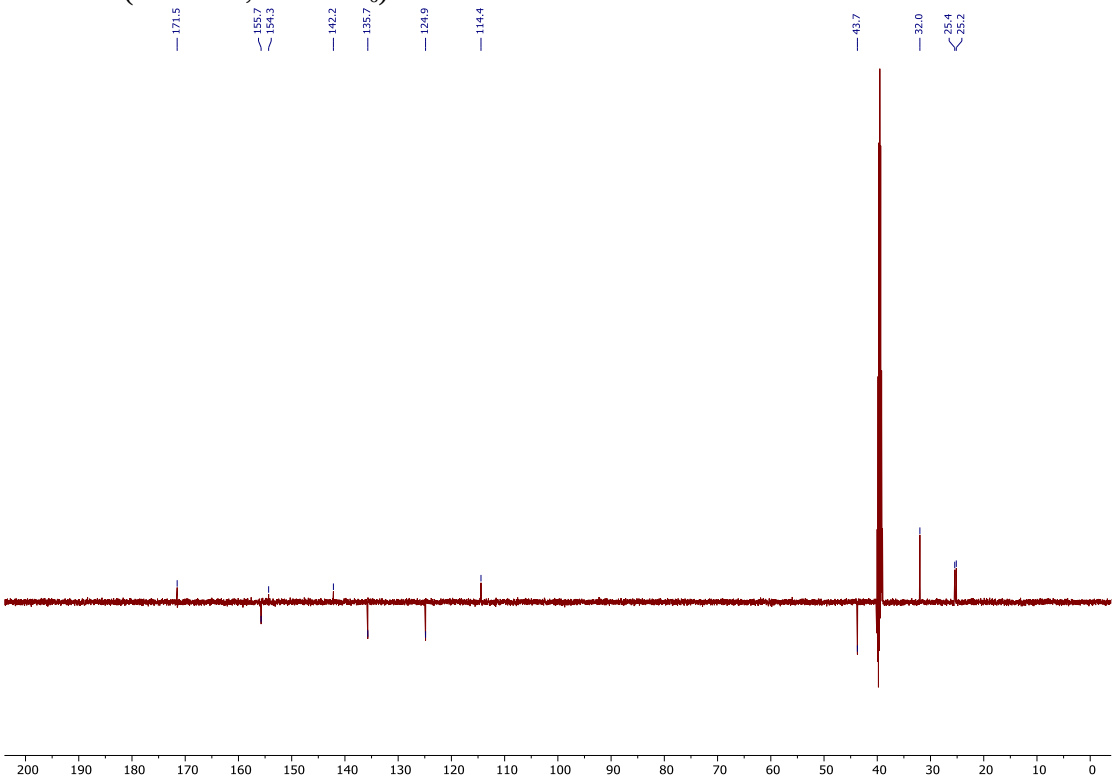


5-(cyclohexylthio)pyrido[3,2-*e*]tetrazolo[1,5-*a*]pyrimidine (**4**):

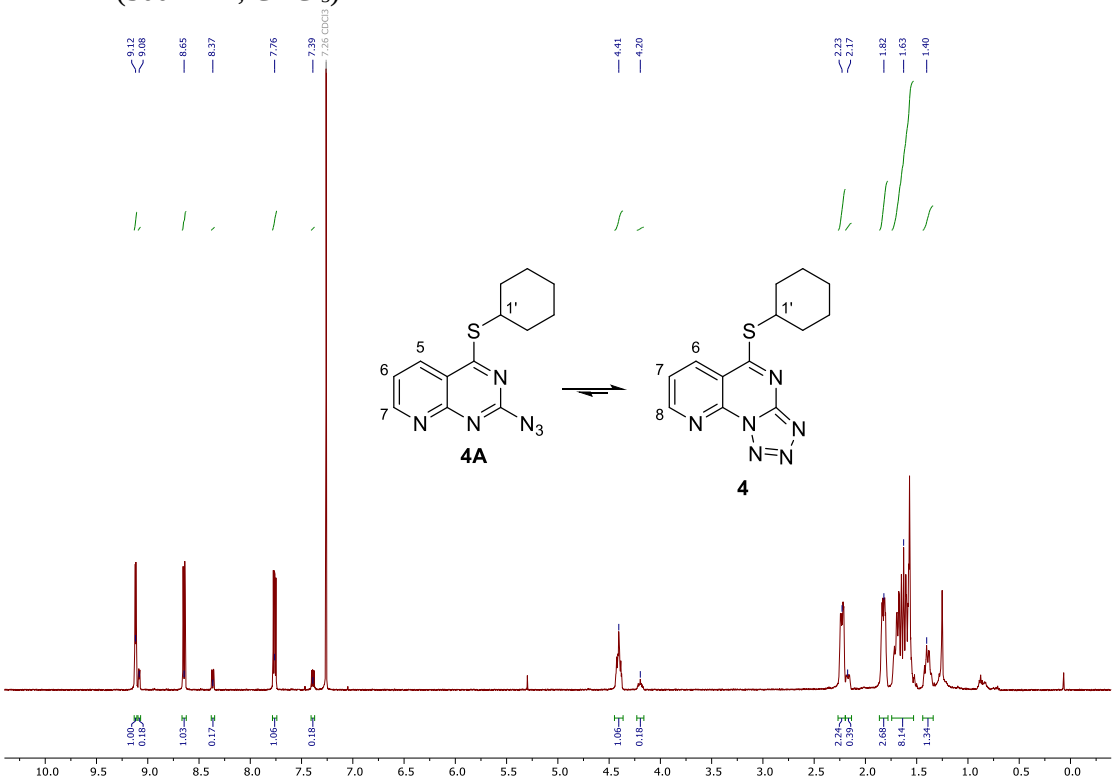
^{1}H NMR (500 MHz, DMSO-d_6)



^{13}C NMR (126 MHz, DMSO-d_6)

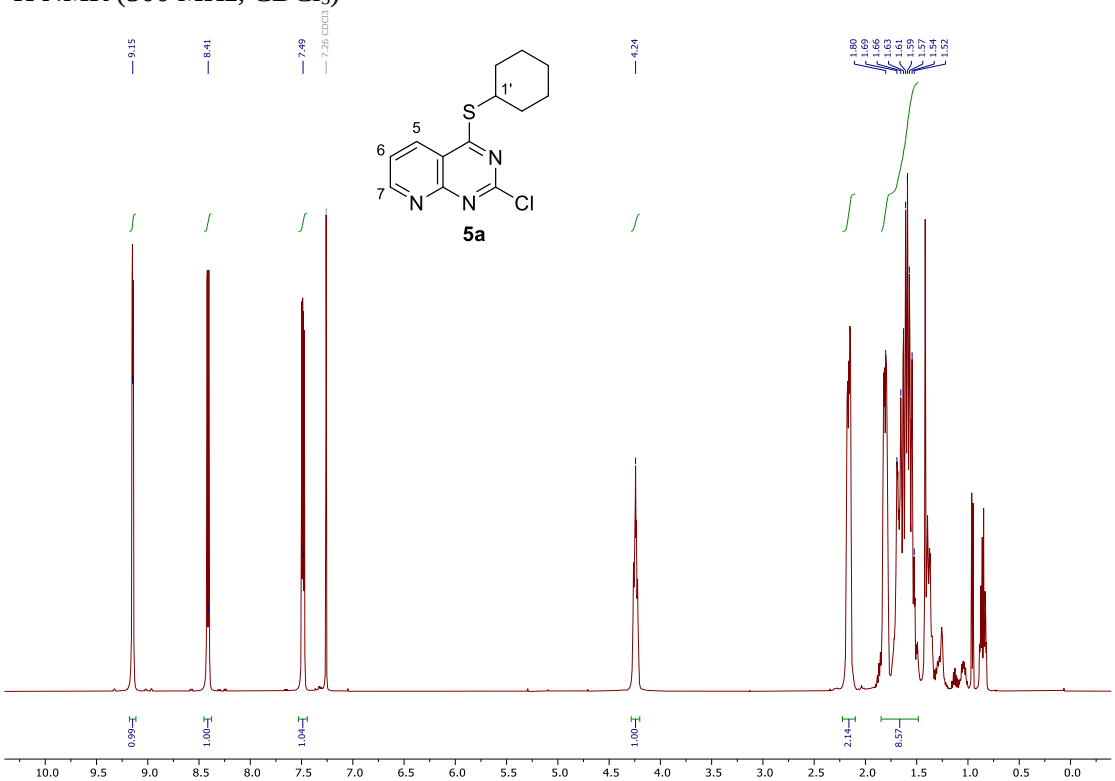


5-(cyclohexylthio)pyrido[3,2-*e*]tetrazolo[1,5-*a*]pyrimidine (**4**) and 2-azido-4-(cyclohexylthio)pyrido[2,3-*d*]pyrimidine (**4A**):
^{1}H NMR (500 MHz, $CDCl_3$)

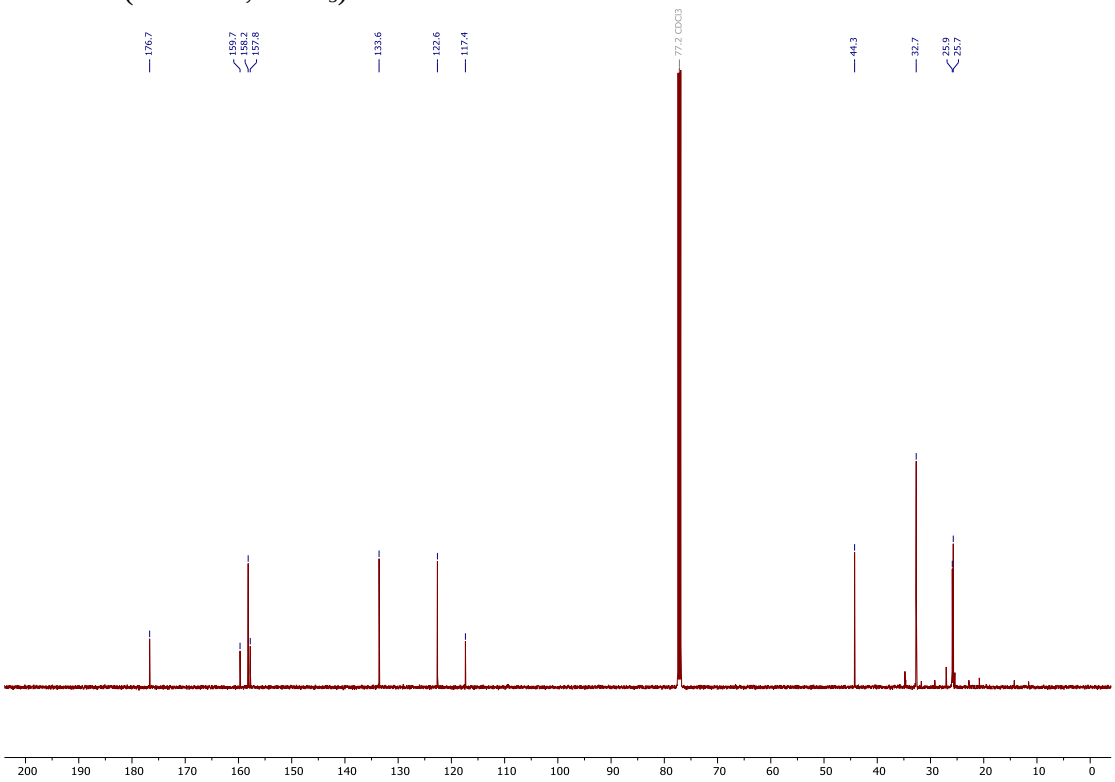


2-chloro-4-(cyclohexylthio)pyrido[2,3-*d*]pyrimidine (**5a**):

^{1}H NMR (500 MHz, $CDCl_3$)

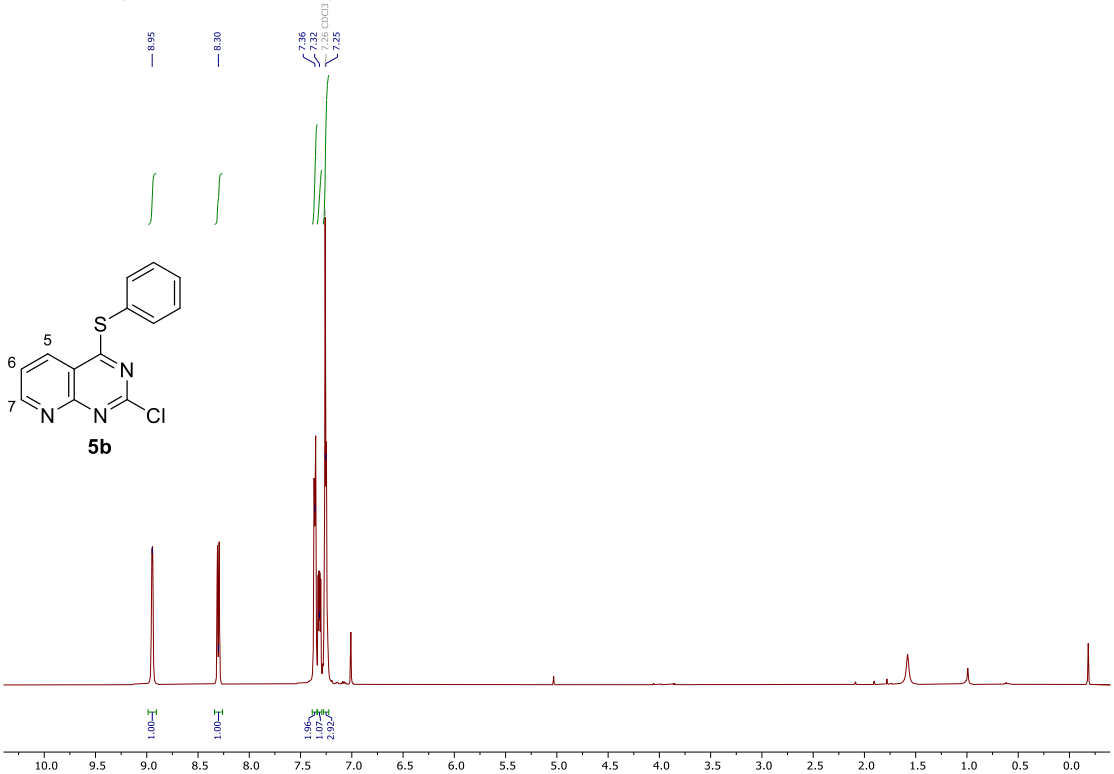


^{13}C NMR (126 MHz, $CDCl_3$)

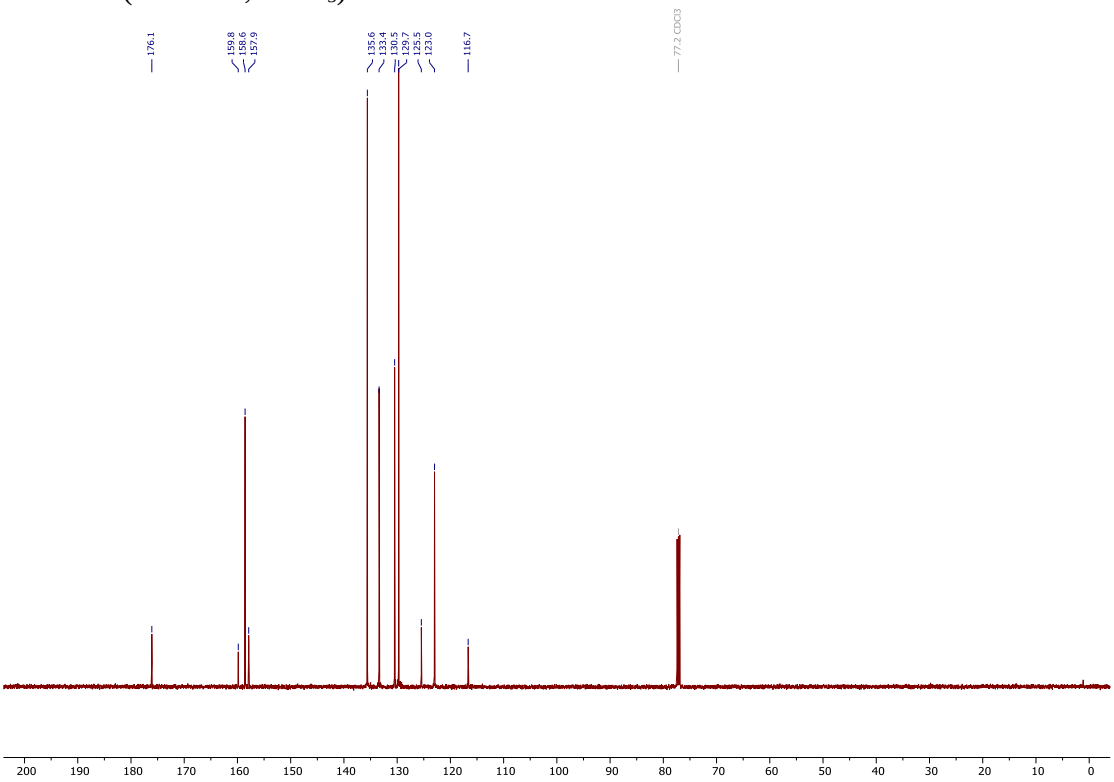


2-chloro-4-(phenylthio)pyrido[2,3-*d*]pyrimidine (**5b**):

^{1}H NMR (500 MHz, $CDCl_3$)

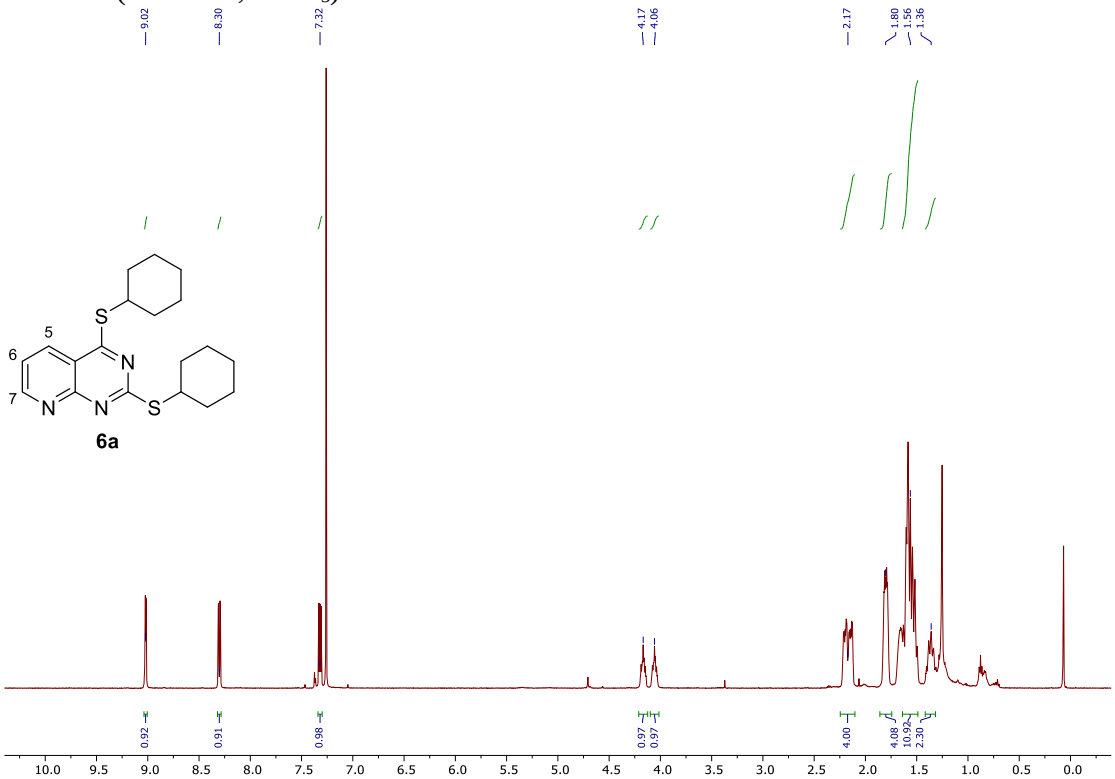


^{13}C NMR (126 MHz, $CDCl_3$)

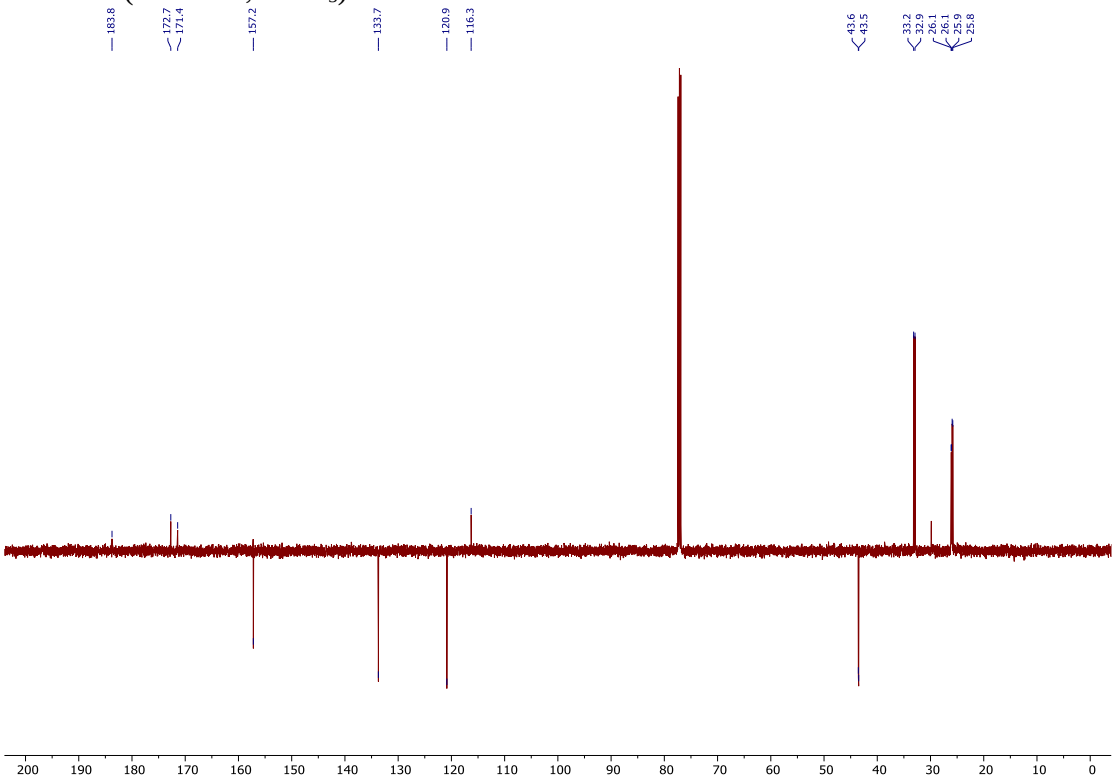


2,4-bis(cyclohexylthio)pyrido[2,3-*d*]pyrimidine (**6a**):

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



2,4-bis(phenylthio)pyrido[2,3-*d*]pyrimidine (**6b**):

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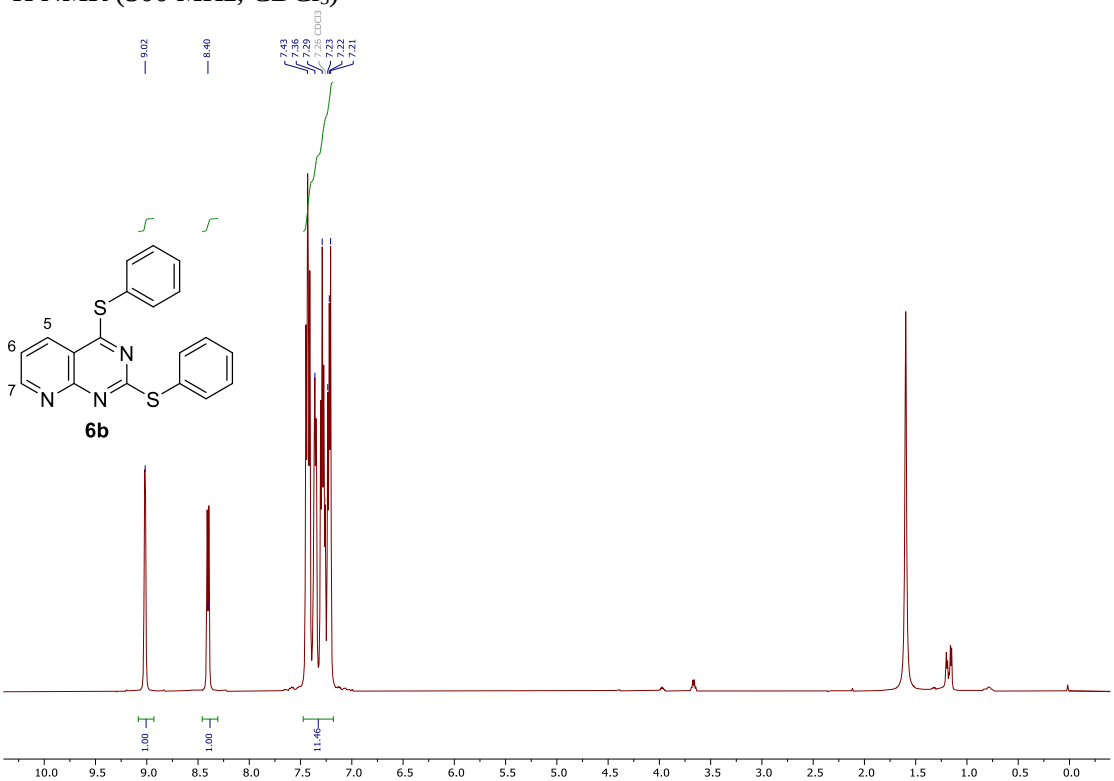
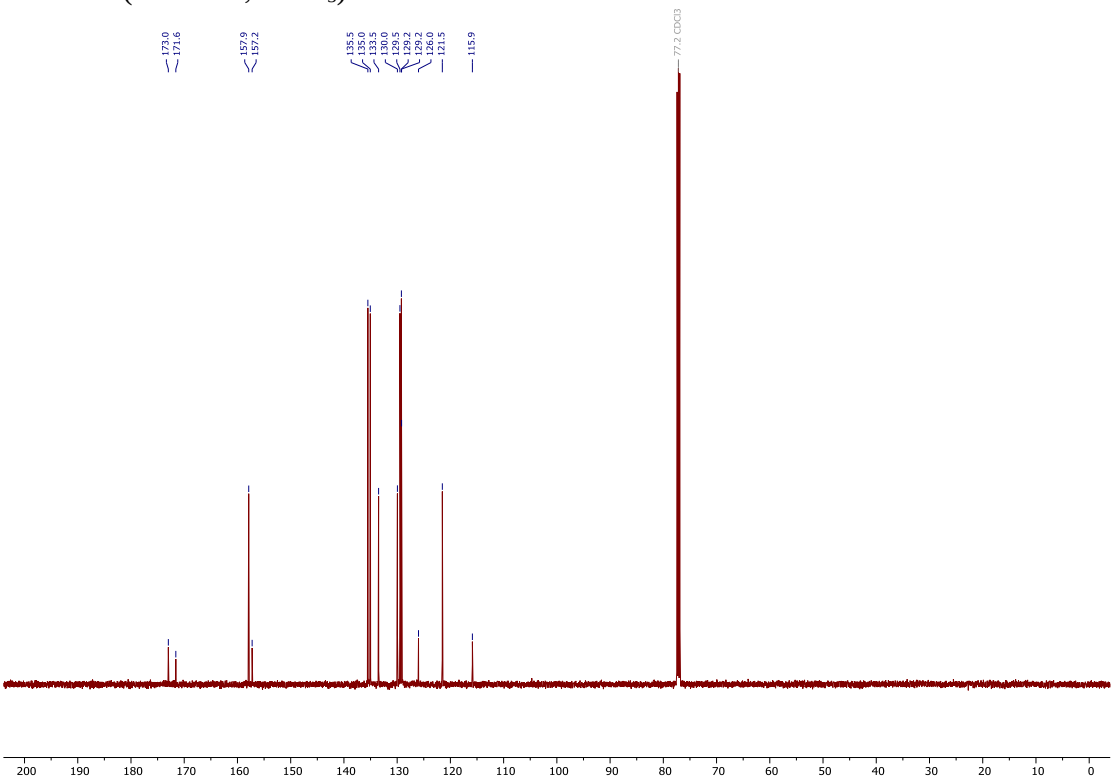
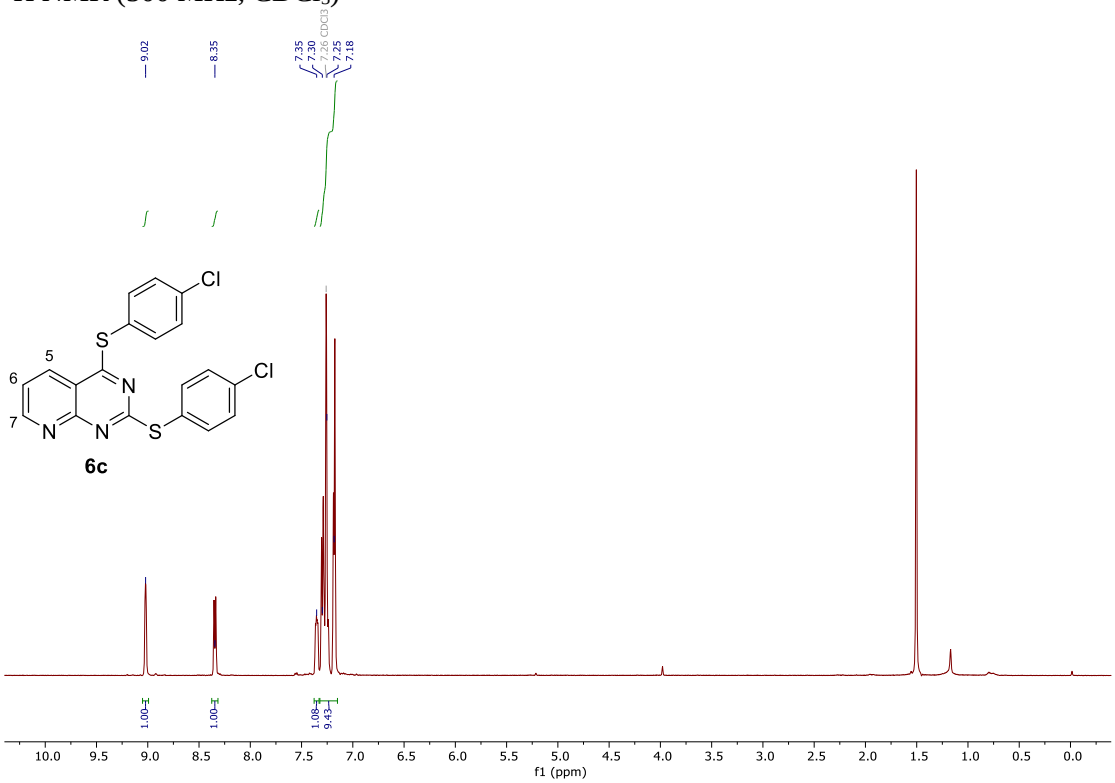


^{13}C NMR (126 MHz, $CDCl_3$)

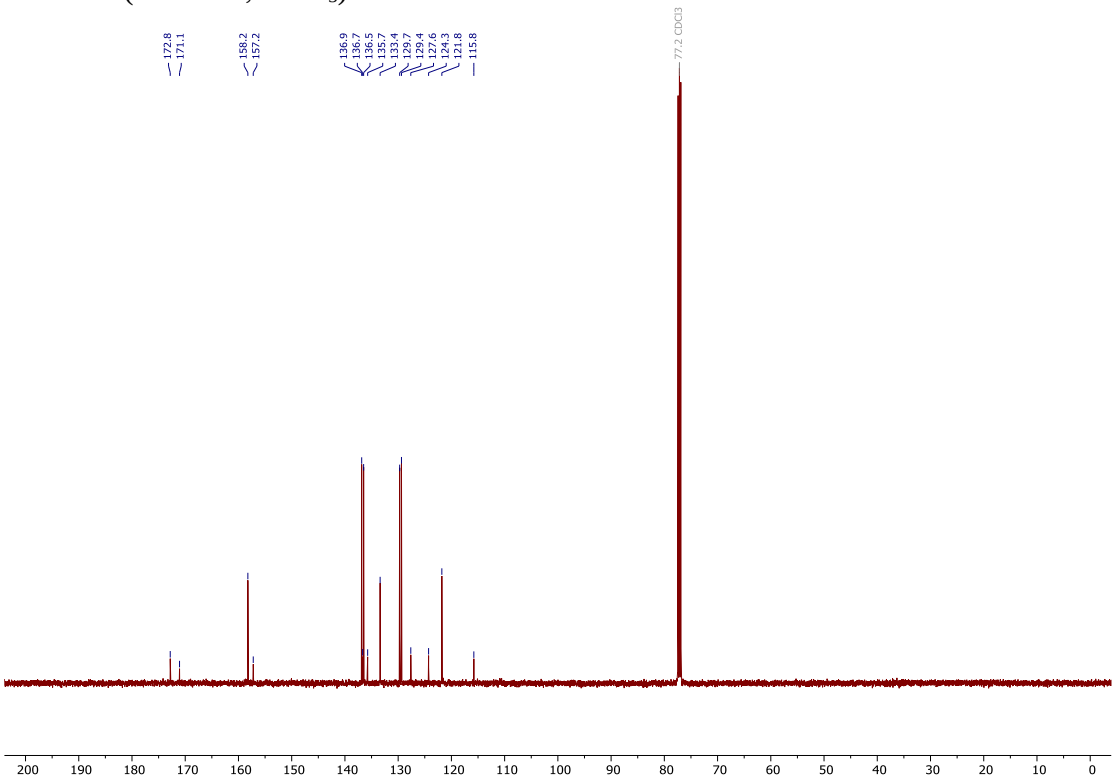


2,4-bis((4-chlorophenyl)thio)pyrido[2,3-*d*]pyrimidine (**6c**):

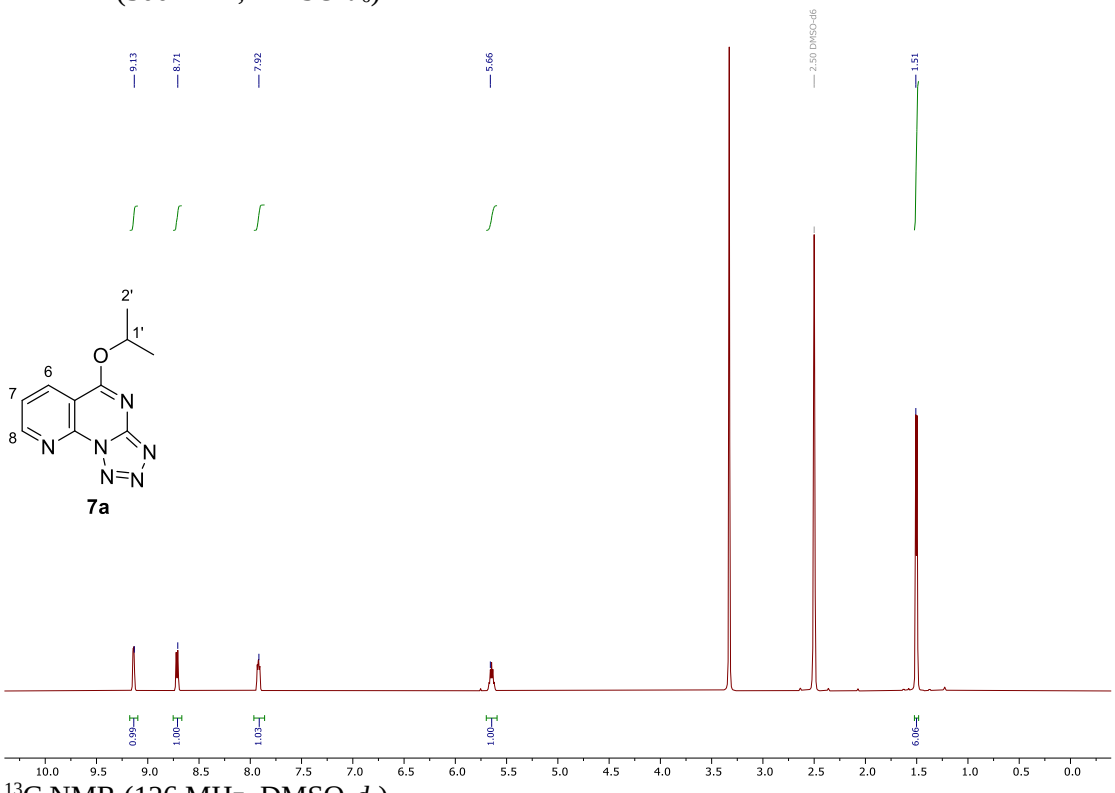
^{1}H NMR (500 MHz, $CDCl_3$)



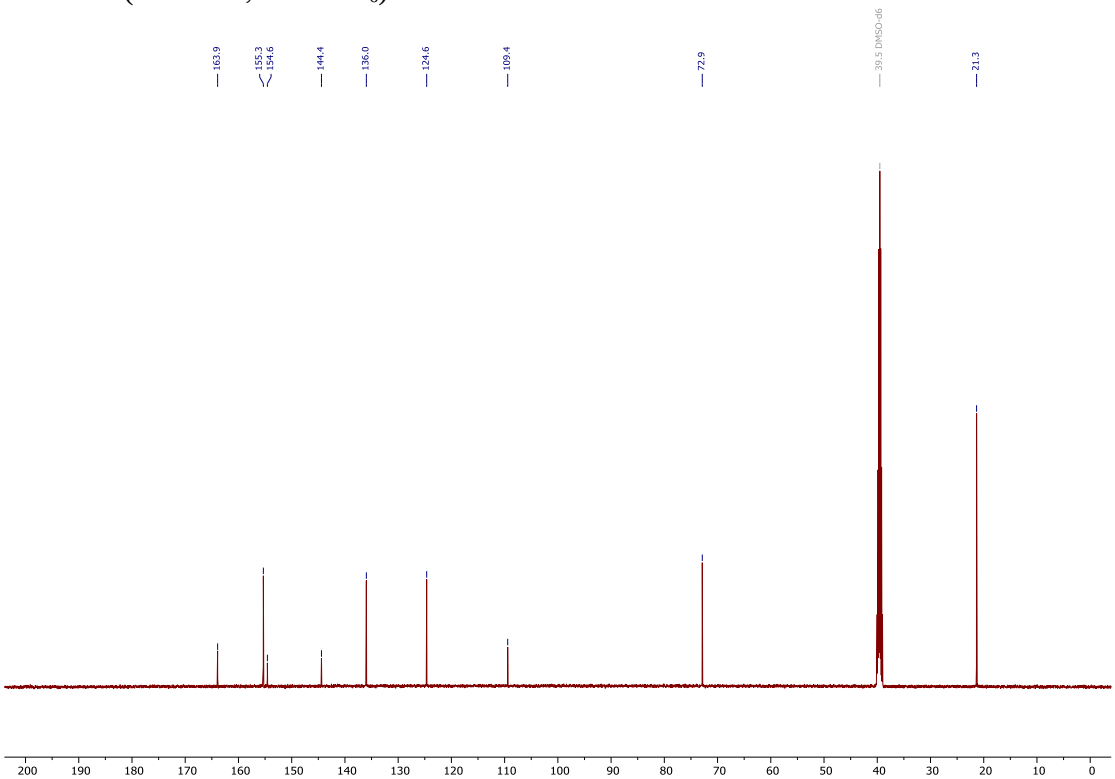
^{13}C NMR (126 MHz, $CDCl_3$)



5-isopropoxypyrido[3,2-*e*]tetrazolo[1,5-*a*]pyrimidine (**7a**):
^{1}H NMR (500 MHz, DMSO-d_6)

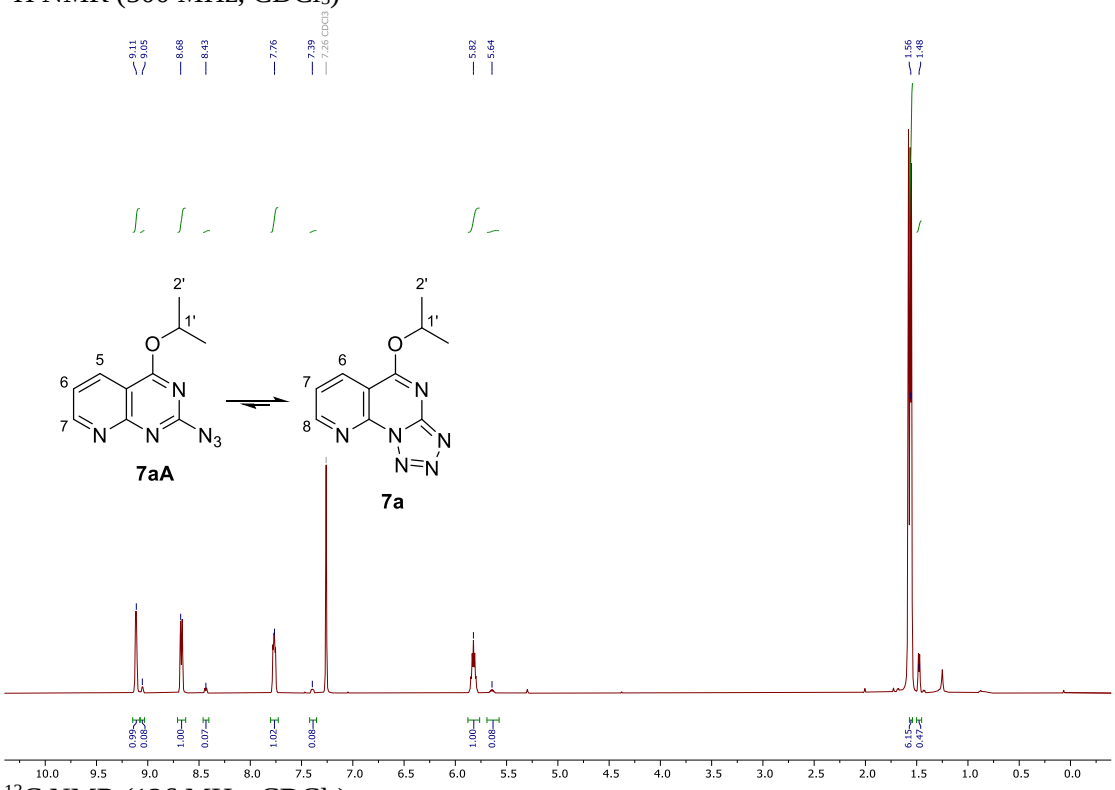


^{13}C NMR (126 MHz, DMSO-d_6)

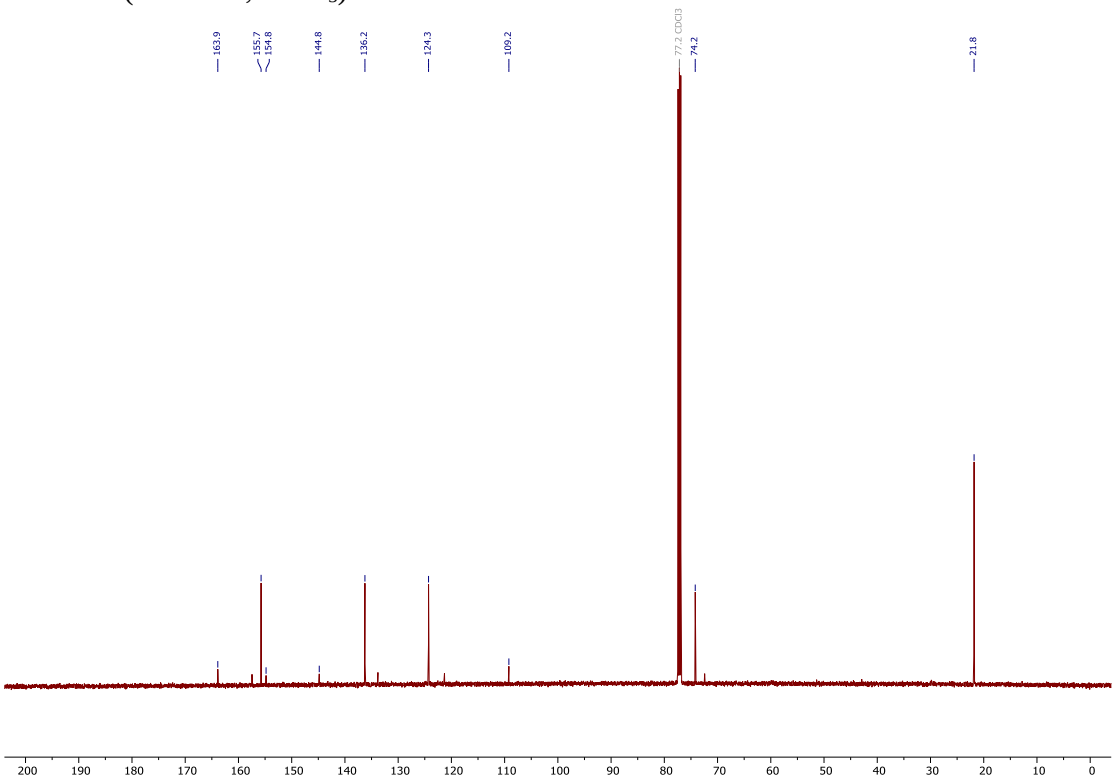


5-isopropoxypyrido[3,2-*e*]tetrazolo[1,5-*a*]pyrimidine (**7a**) and 2-azido-4-isopropoxypyrido[2,3-*d*]pyrimidine (**7aA**):

^{1}H NMR (500 MHz, $CDCl_3$)

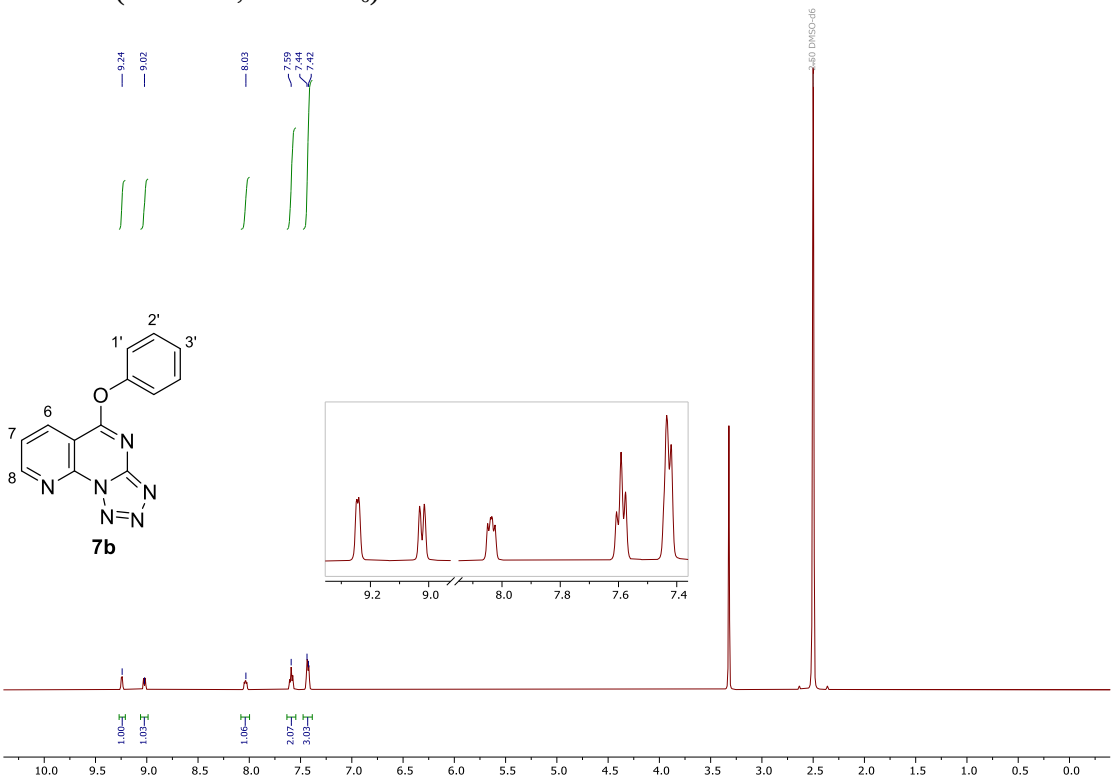


^{13}C NMR (126 MHz, $CDCl_3$)

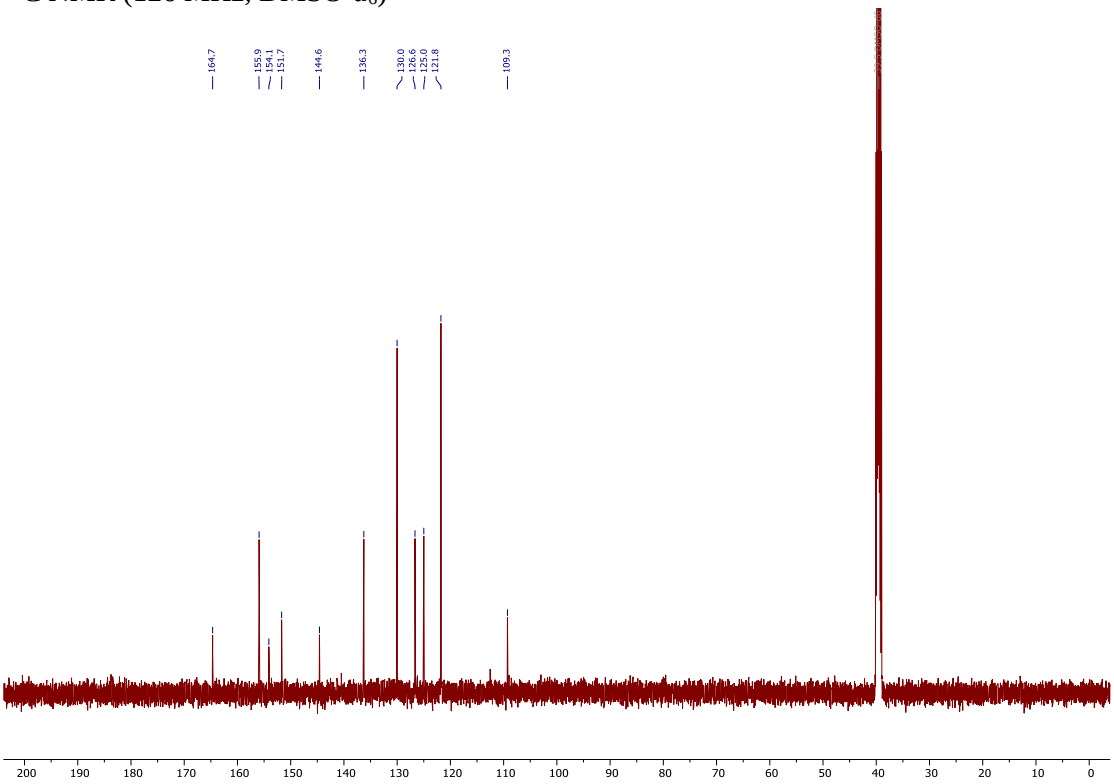


5-phenoxypyrido[3,2-*e*]tetrazolo[1,5-*a*]pyrimidine (**7b**):

^{1}H NMR (500 MHz, DMSO-d_6)

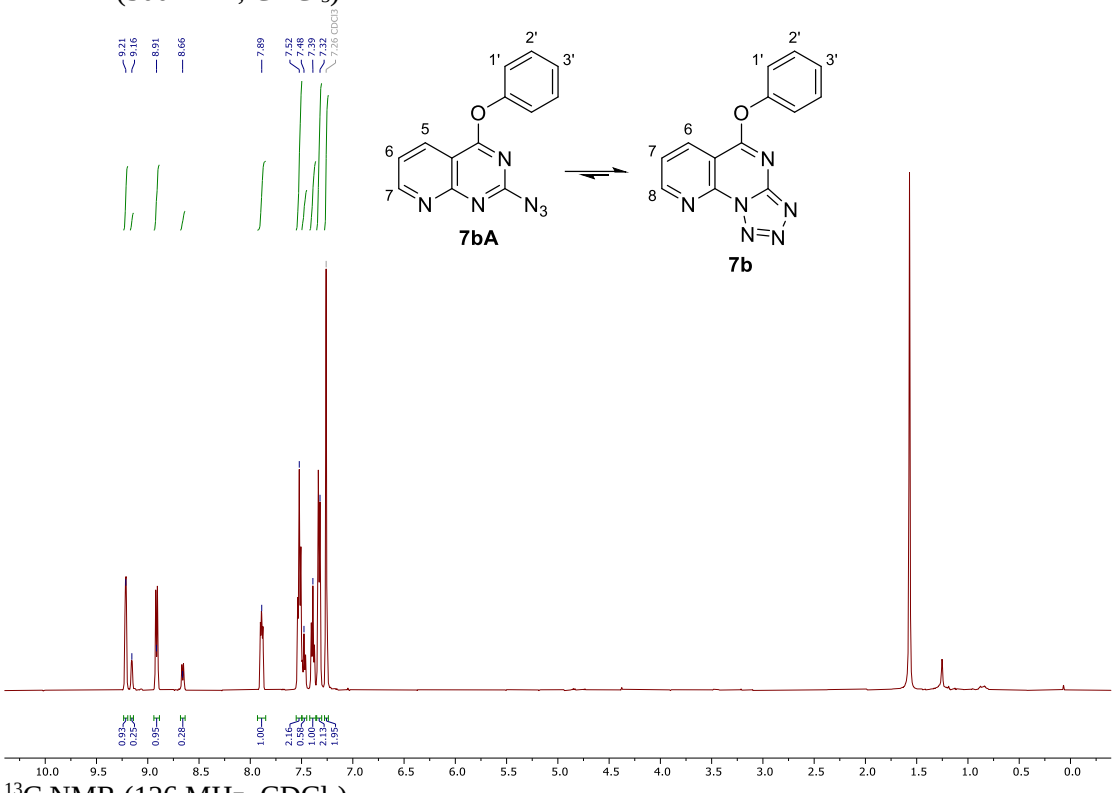


^{13}C NMR (126 MHz, DMSO-d_6)

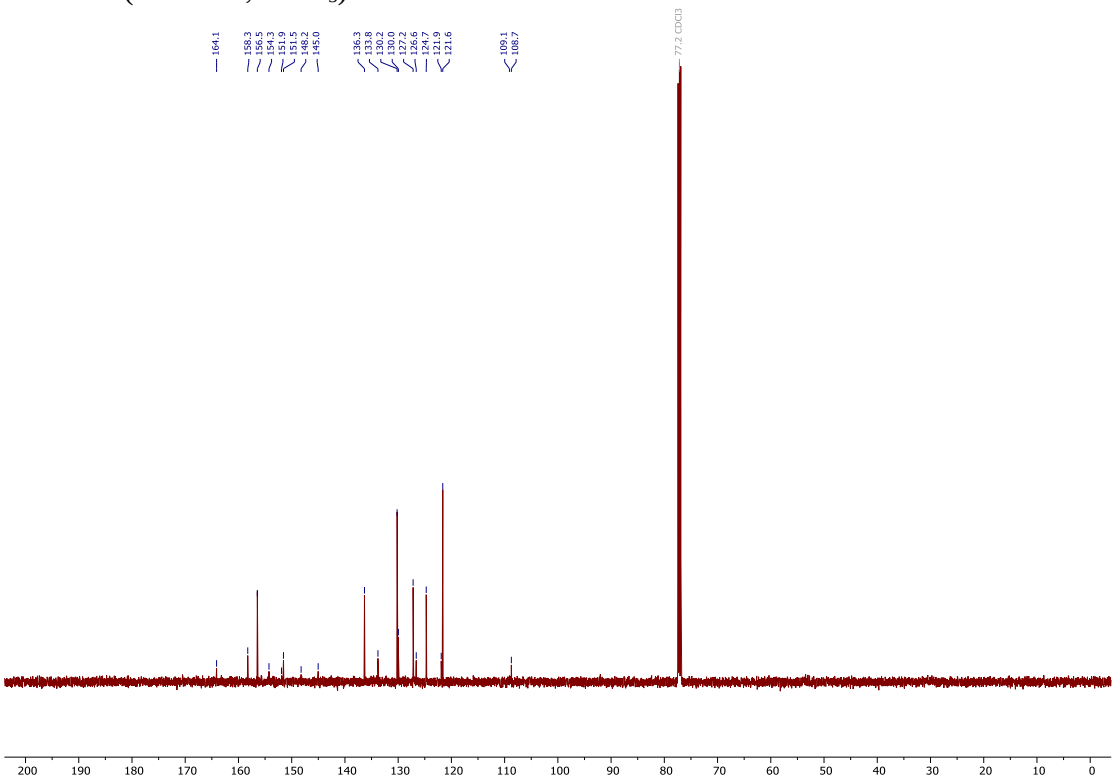


5-phenoxypyrido[3,2-*e*]tetrazolo[1,5-*a*]pyrimidine (**7b**) and 2-azido-4-phenoxypyrido[2,3-*d*]pyrimidine (**7bA**):

^{1}H NMR (500 MHz, $CDCl_3$)

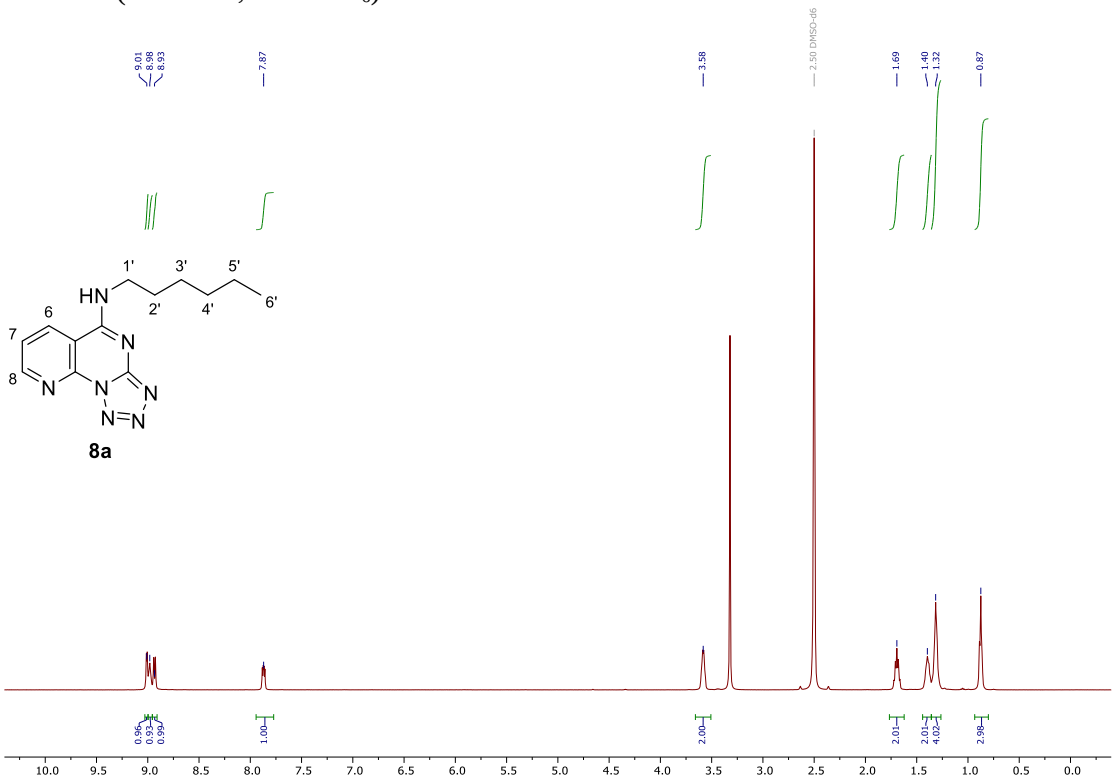


^{13}C NMR (126 MHz, $CDCl_3$)



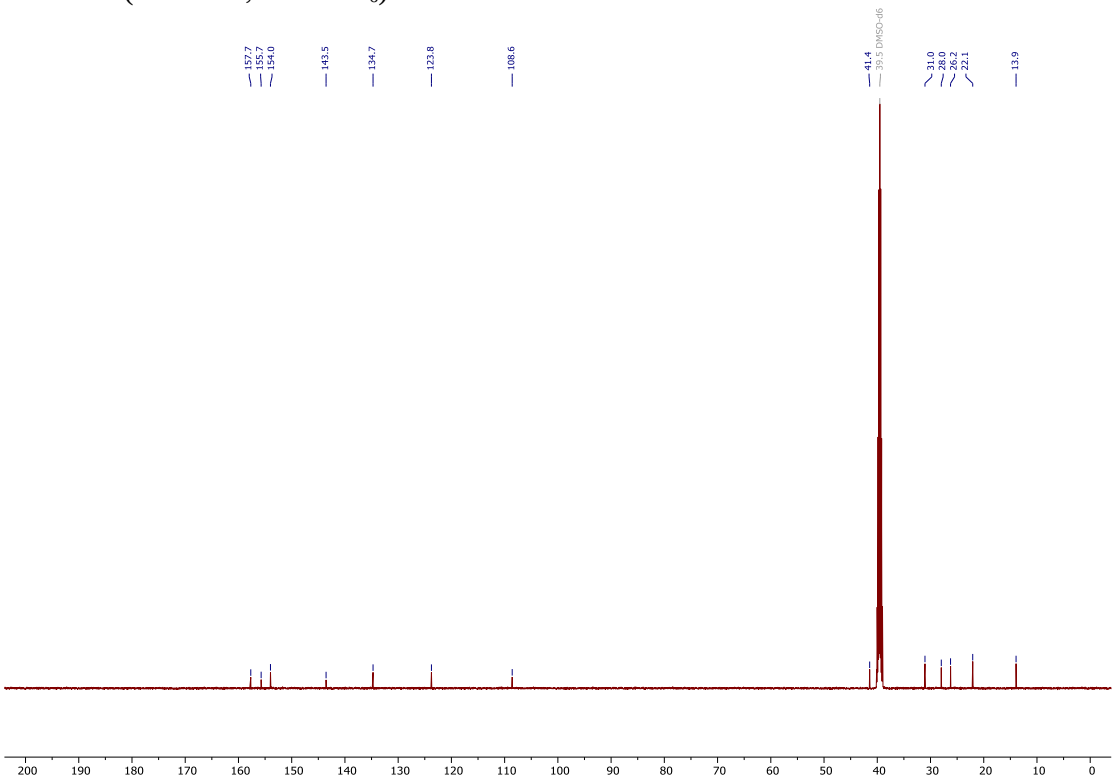
N-hexylpyrido[3,2-*e*]tetrazolo[1,5-*a*]pyrimidin-5-amine (**8a**):

^{1}H NMR (500 MHz, DMSO-d_6)



8a

^{13}C NMR (126 MHz, DMSO-d_6)



N-octylpyrido[3,2-*e*]tetrazolo[1,5-*a*]pyrimidin-5-amine (**8b**):
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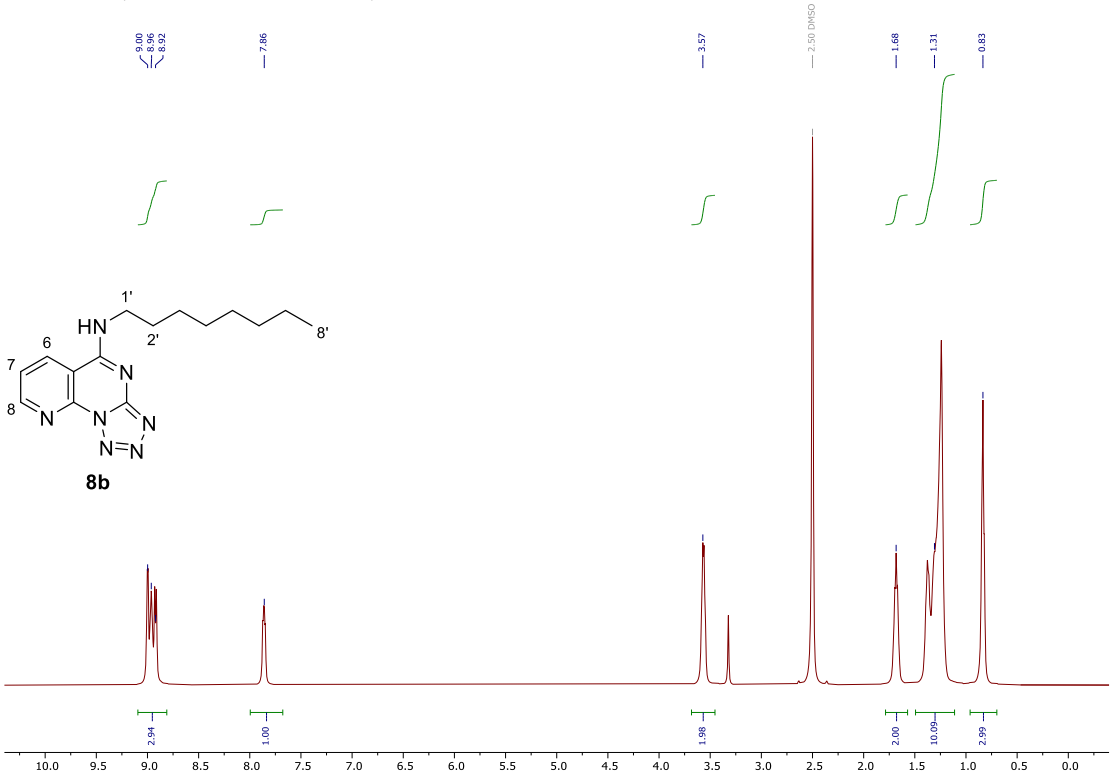
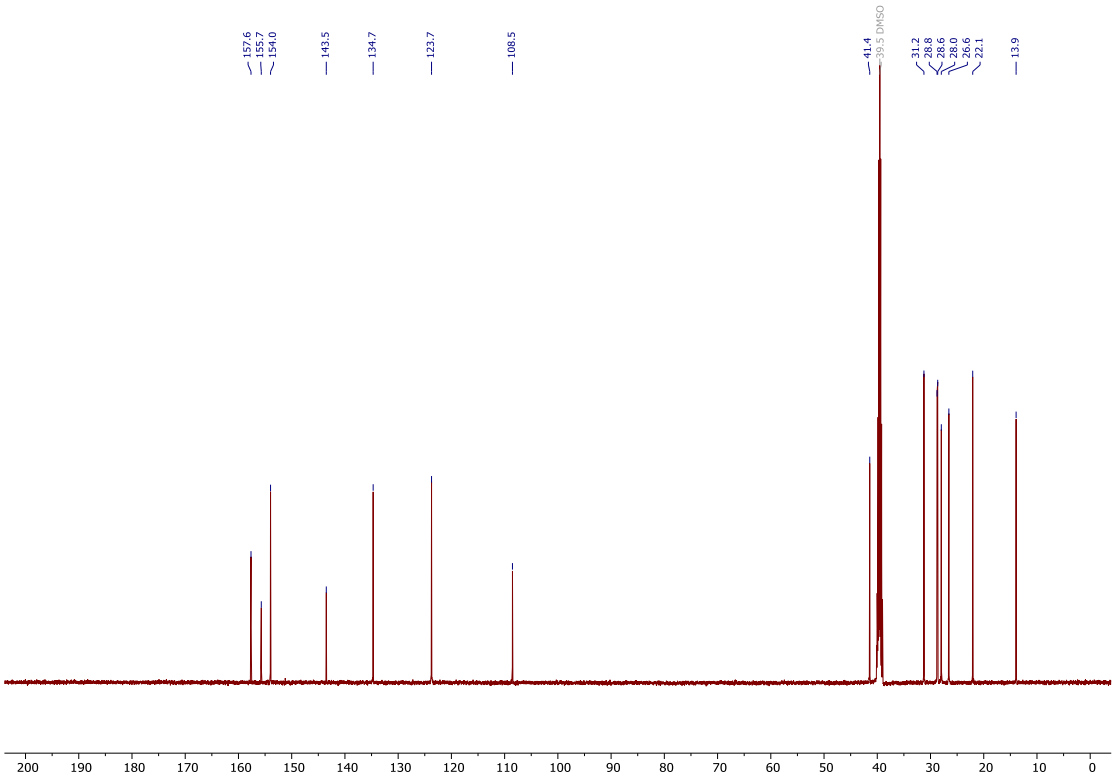
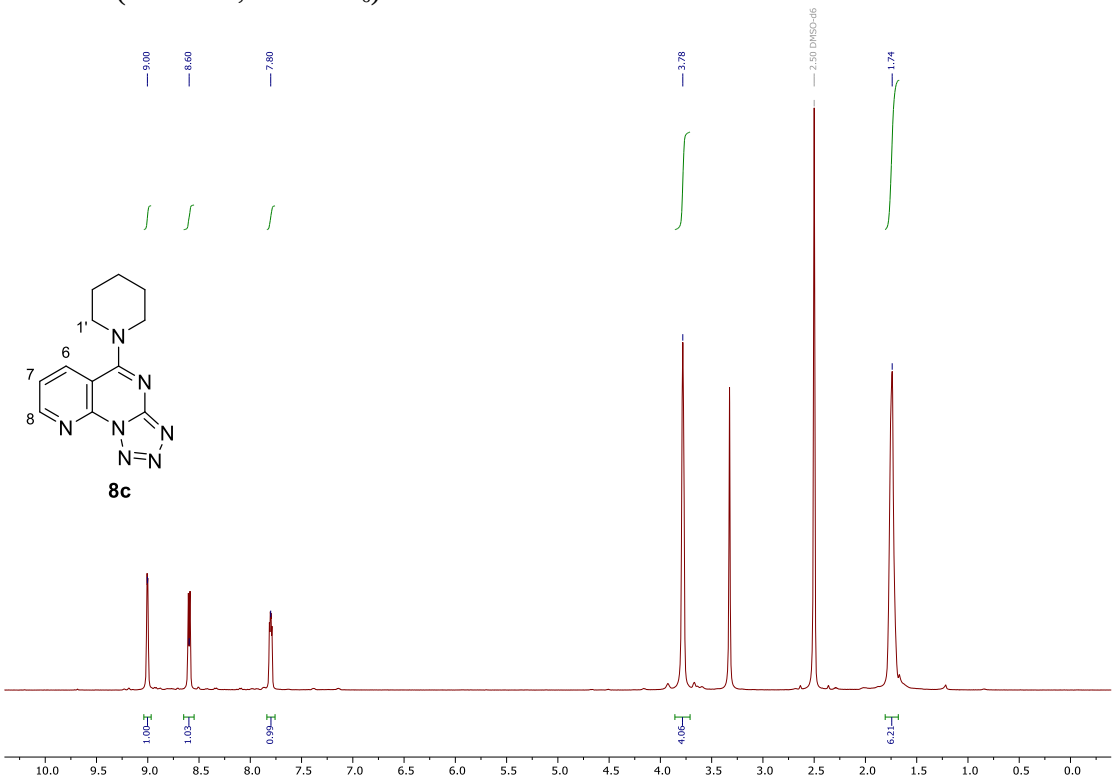


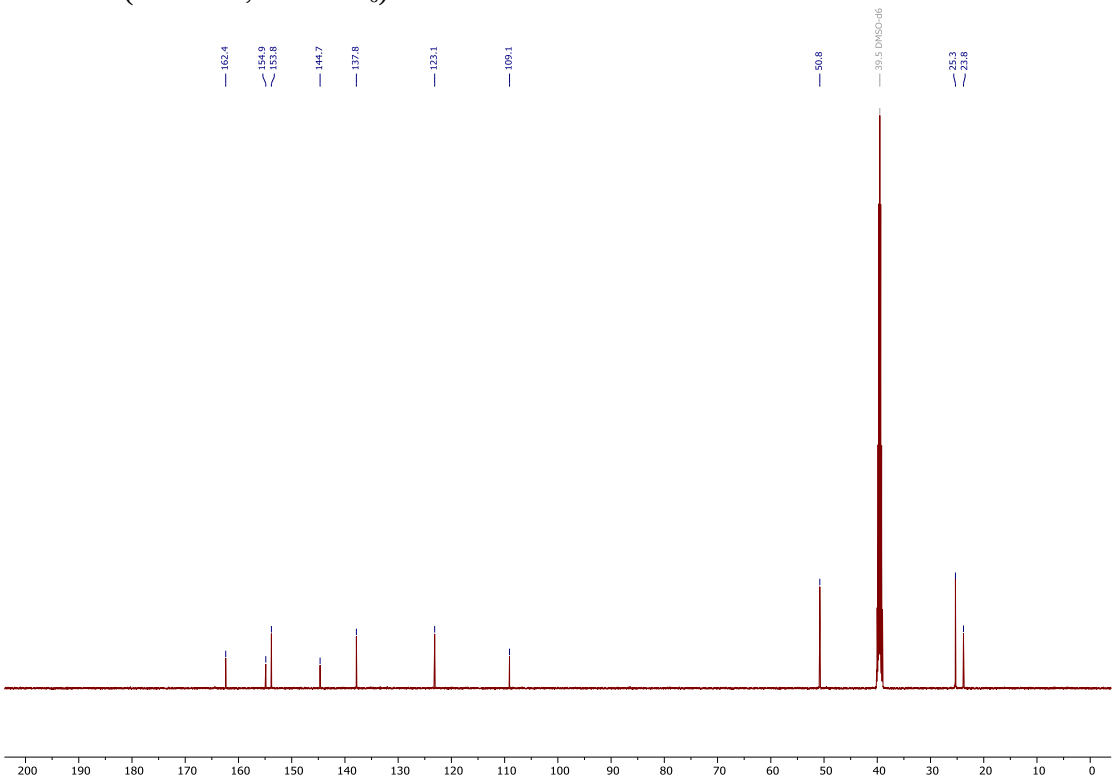
^{13}C NMR (126 MHz, DMSO-d_6)



5-(piperidin-1-yl)pyrido[3,2-*e*]tetrazolo[1,5-*a*]pyrimidine (**8c**):
^{1}H NMR (500 MHz, DMSO-d_6)

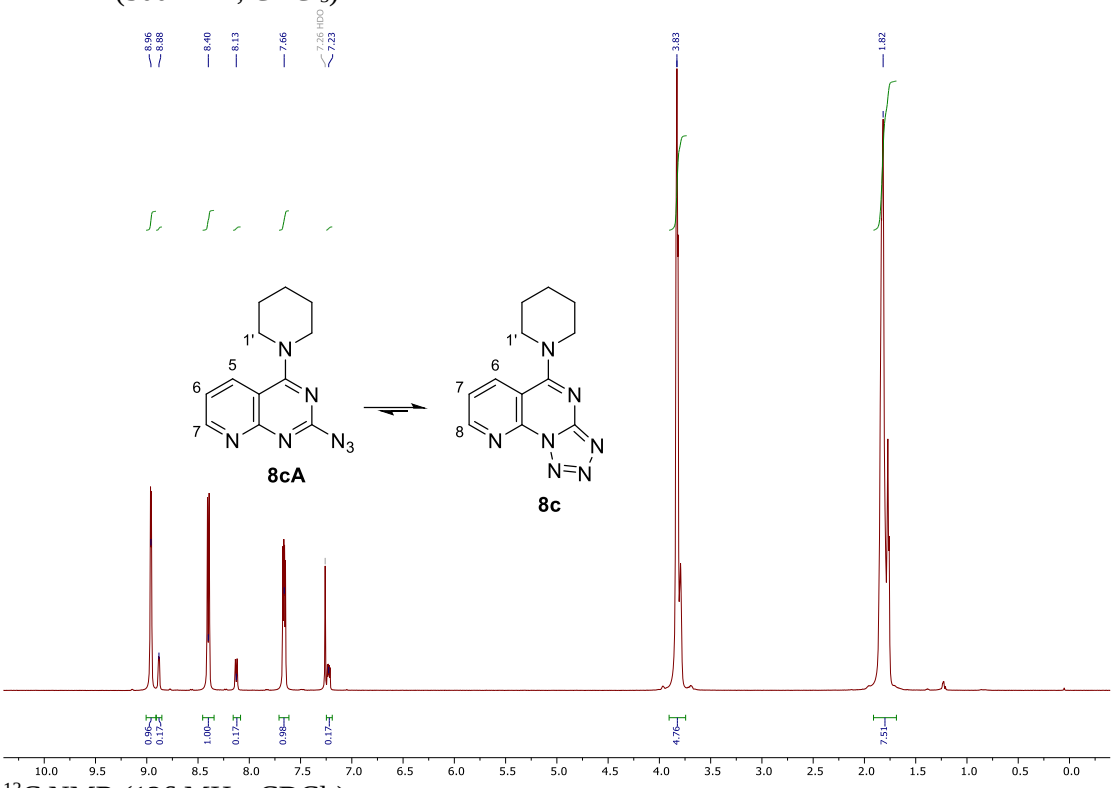


^{13}C NMR (126 MHz, DMSO-d_6)

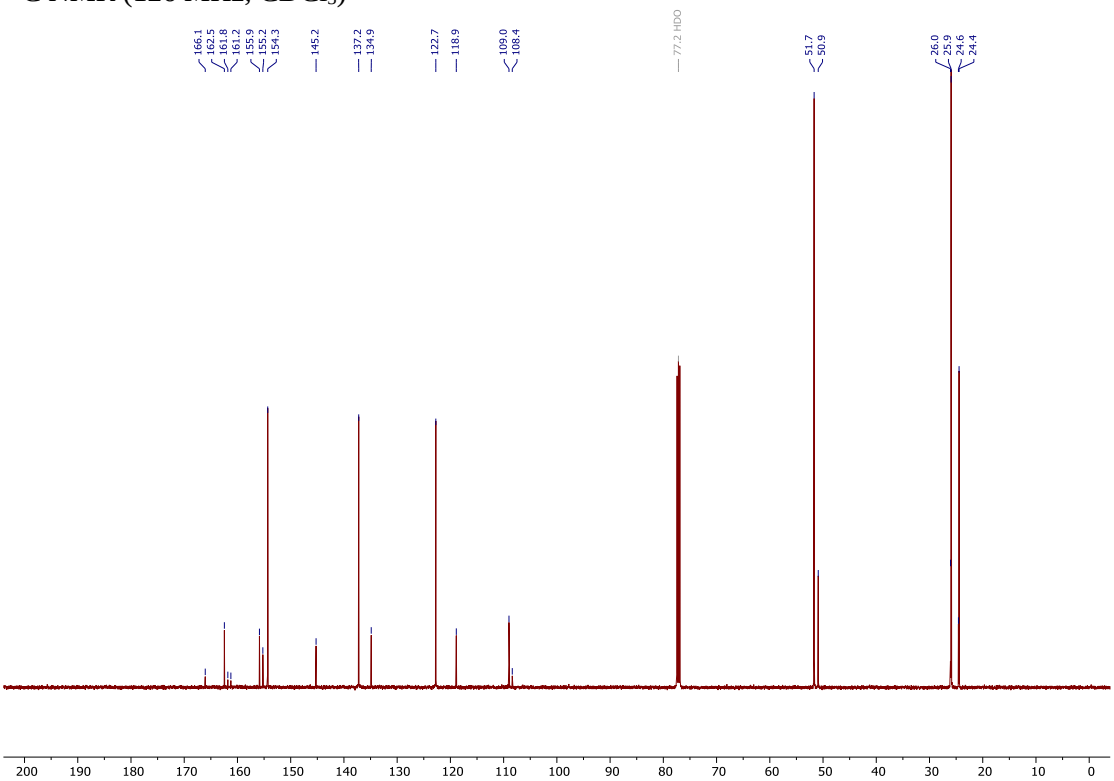


5-(piperidin-1-yl)pyrido[3,2-*e*]tetrazolo[1,5-*a*]pyrimidine (**8c**) and 2-azido-4-(piperidin-1-yl)pyrido[2,3-*d*]pyrimidine (**8cA**):

^{1}H NMR (500 MHz, $CDCl_3$)

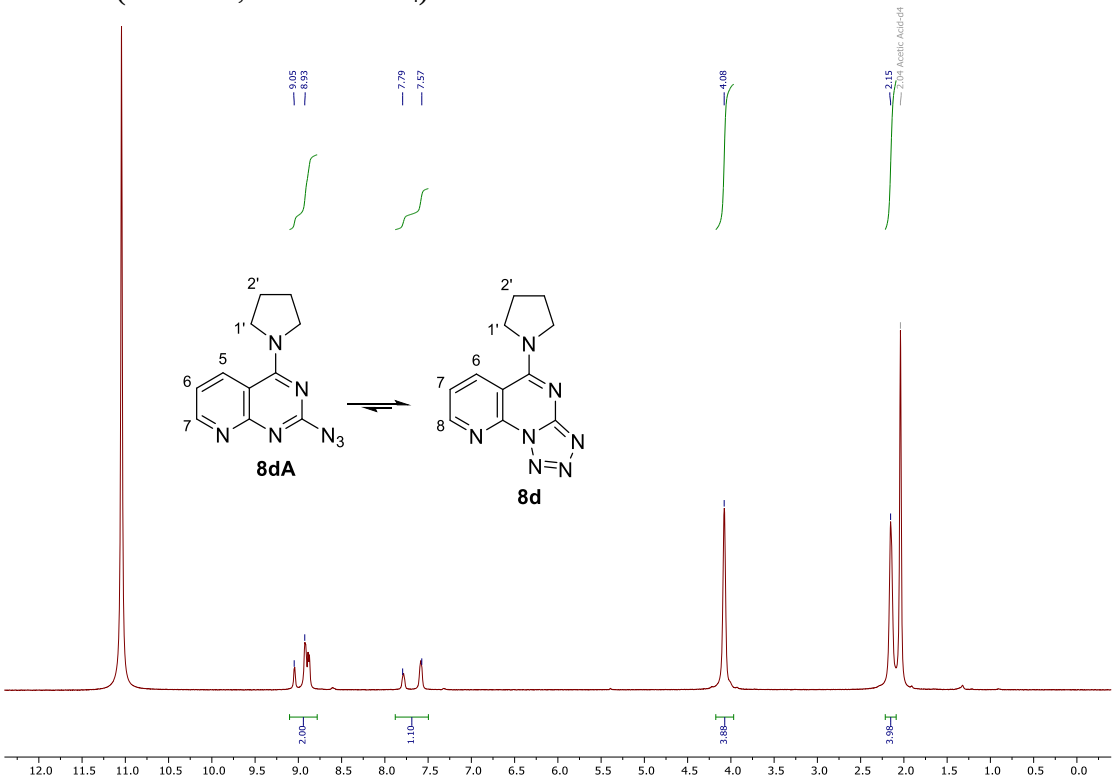


^{13}C NMR (126 MHz, $CDCl_3$)

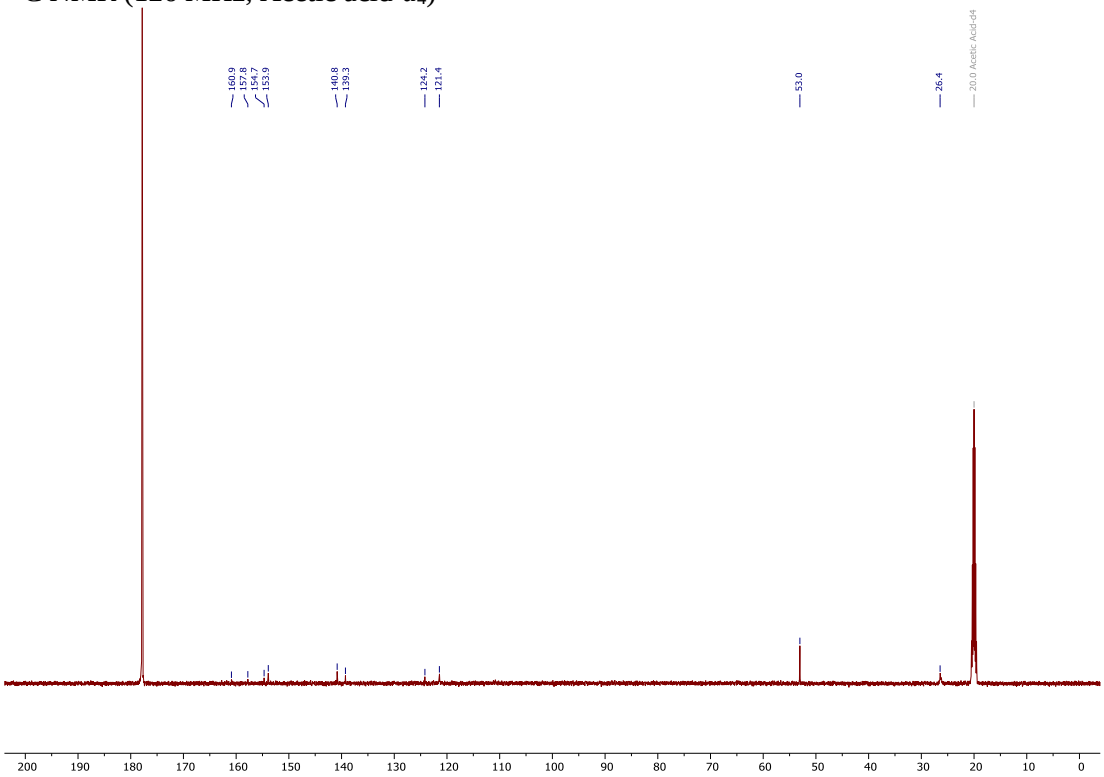


5-(pyrrolidin-1-yl)pyrido[3,2-*e*]tetrazolo[1,5-*a*]pyrimidine (**8d**):

^{1}H NMR (500 MHz, Acetic acid-d_4)

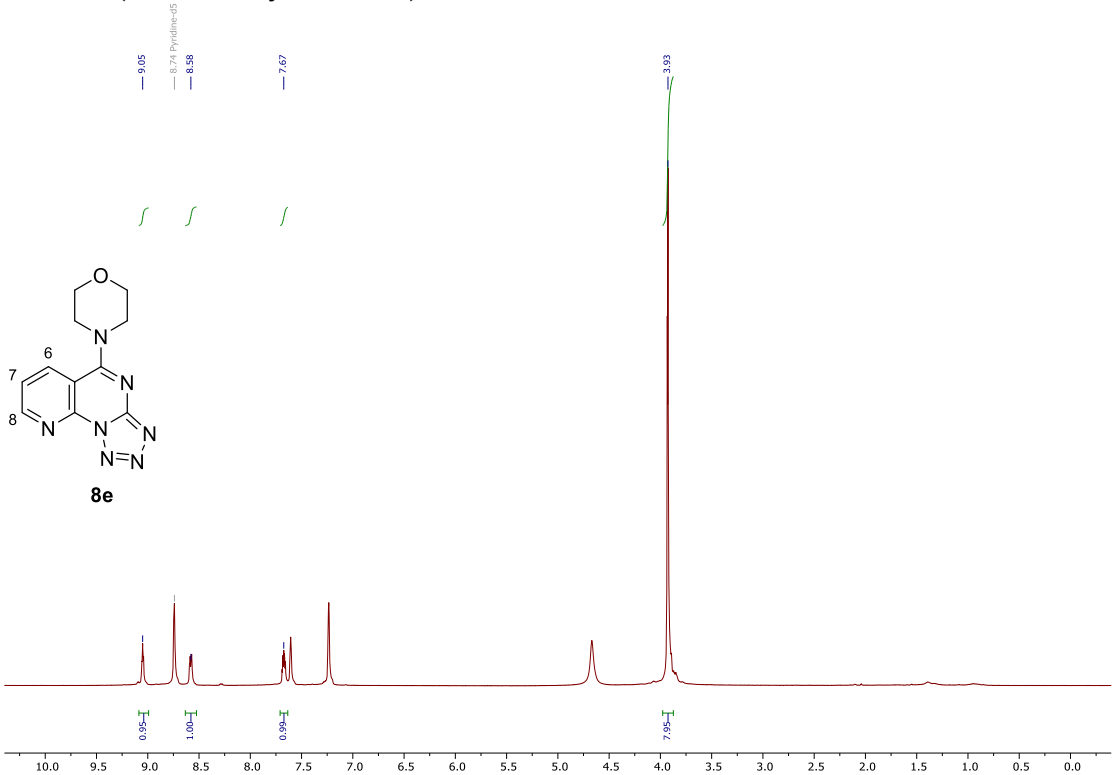


^{13}C NMR (126 MHz, Acetic acid-d_4)



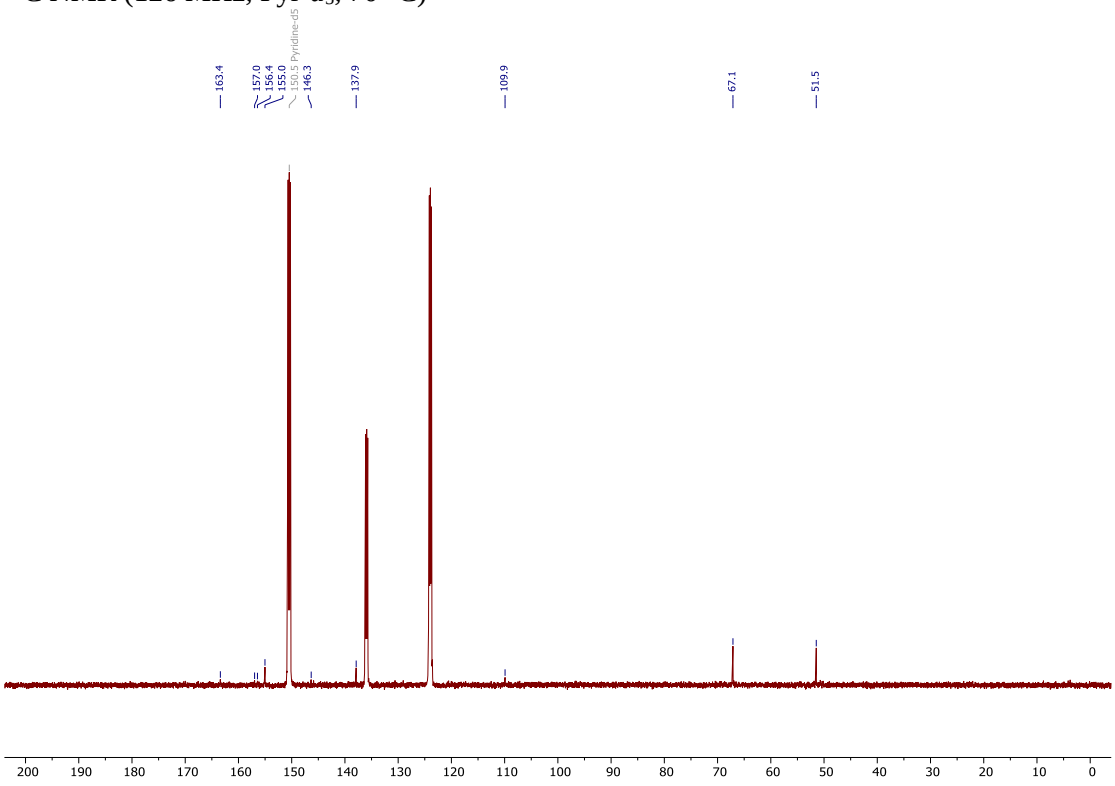
4-(pyrido[3,2-*e*]tetrazolo[1,5-*a*]pyrimidin-5-yl)morpholine (**8e**):

^{1}H NMR (500 MHz, Pyr-d_5, 70 °C)

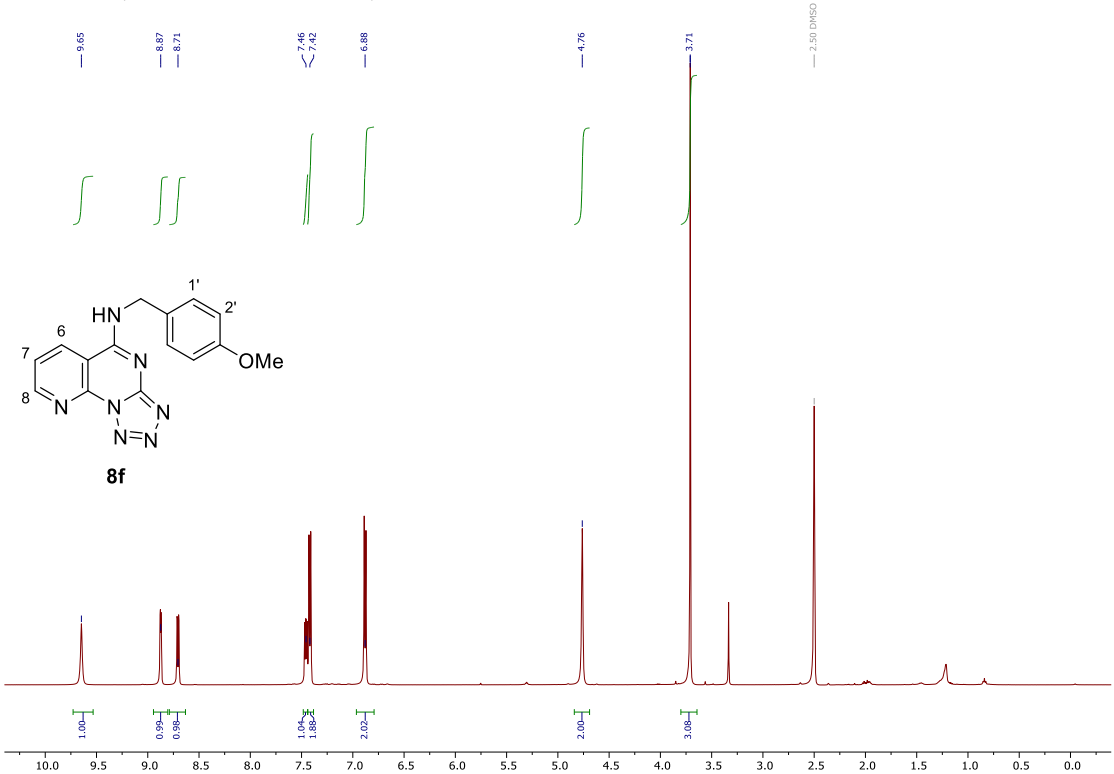


8e

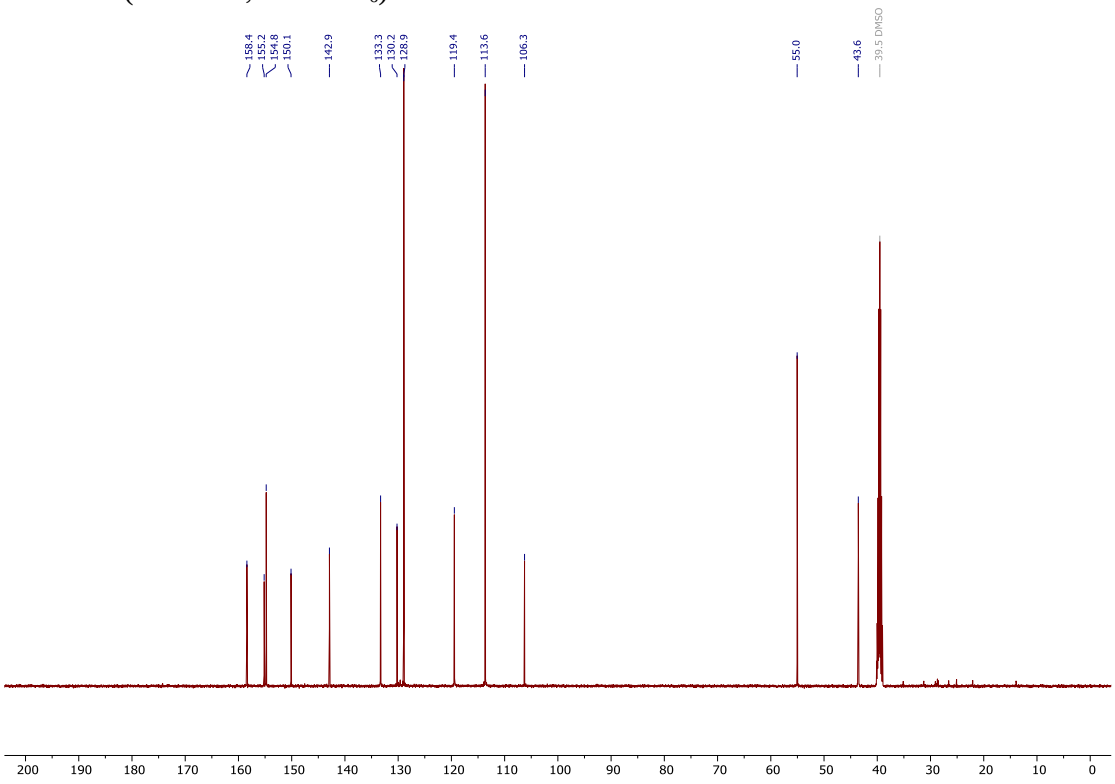
^{13}C NMR (126 MHz, Pyr-d_5, 70 °C)



N-(4-methoxybenzyl)pyrido[3,2-*e*]tetrazolo[1,5-*a*]pyrimidin-5-amine (**8f**):
^{1}H NMR (500 MHz, DMSO-d_6)

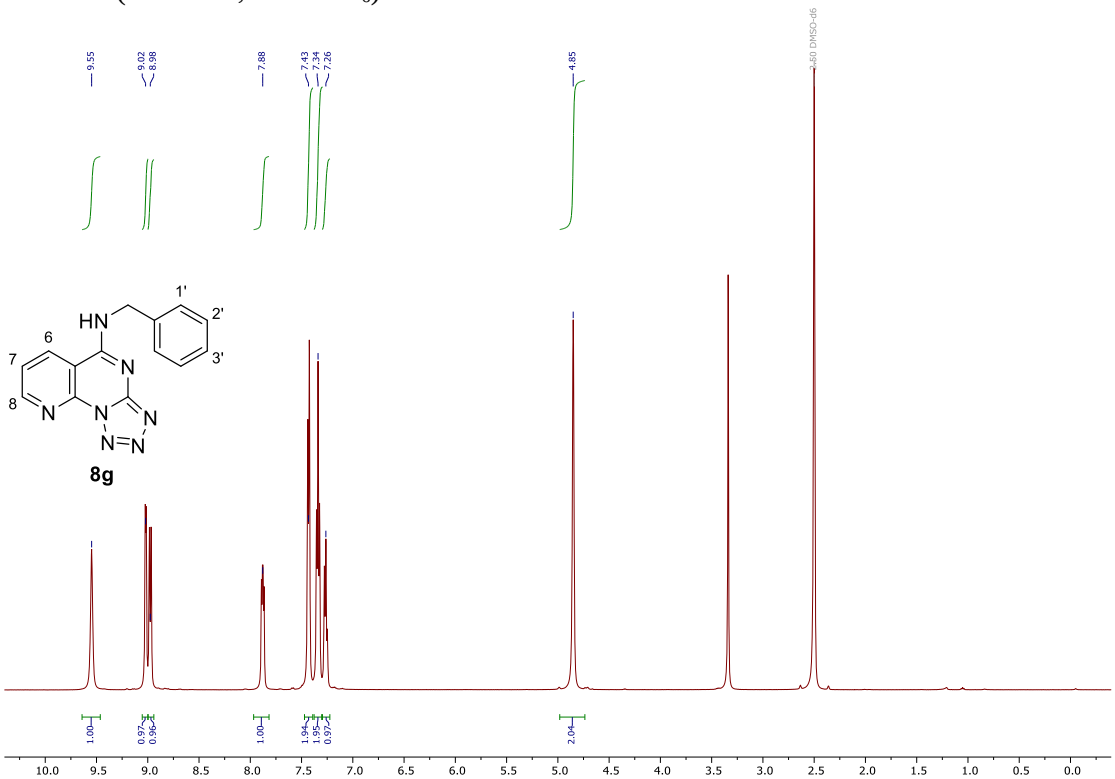


^{13}C NMR (126 MHz, DMSO-d_6)

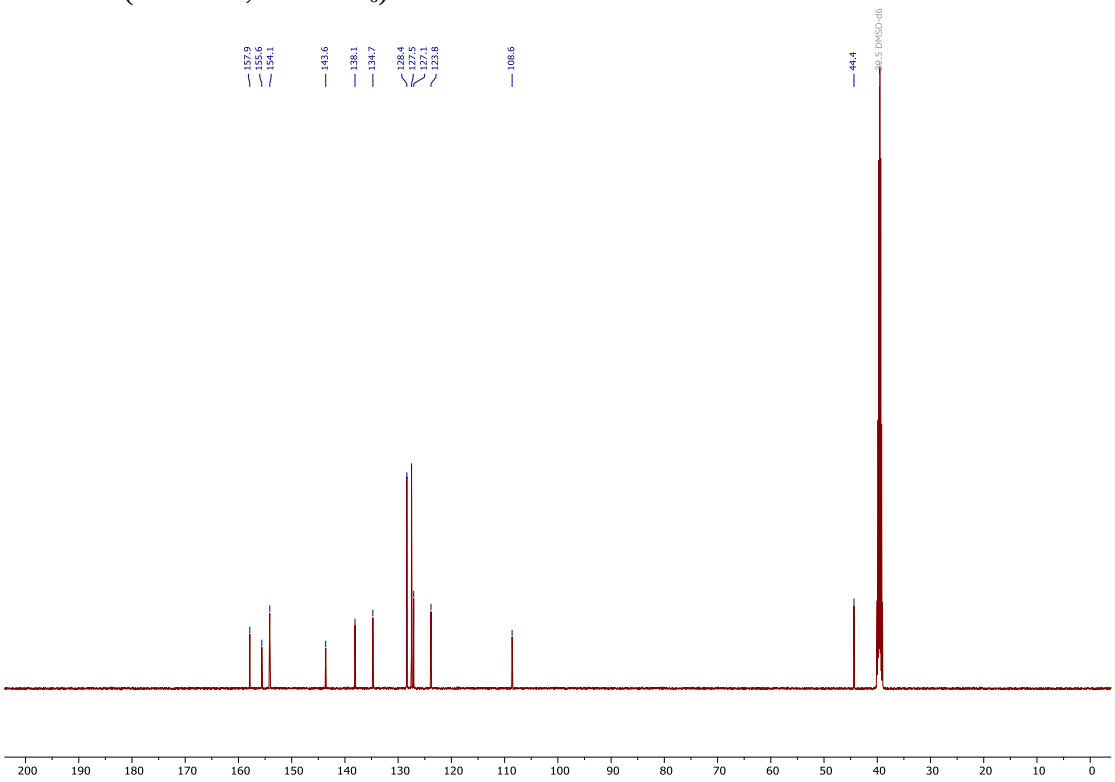


N-benzylpyrido[3,2-*e*]tetrazolo[1,5-*a*]pyrimidin-5-amine (**8g**):

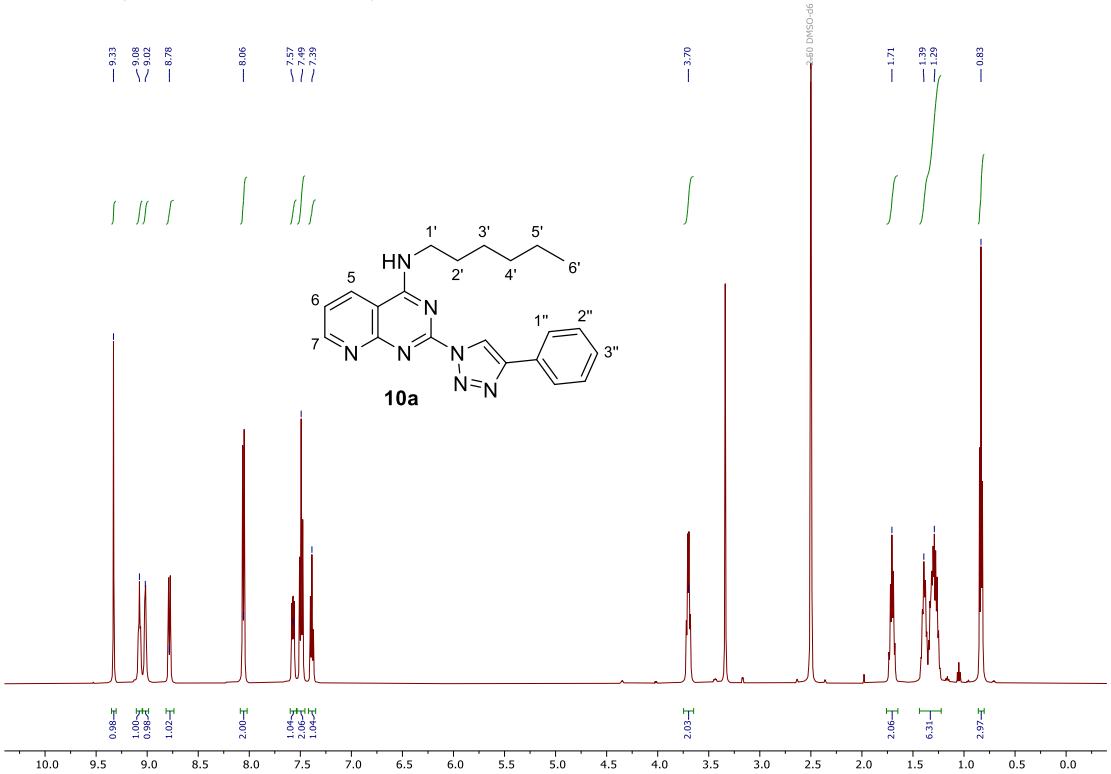
^{1}H NMR (500 MHz, DMSO-d_6)



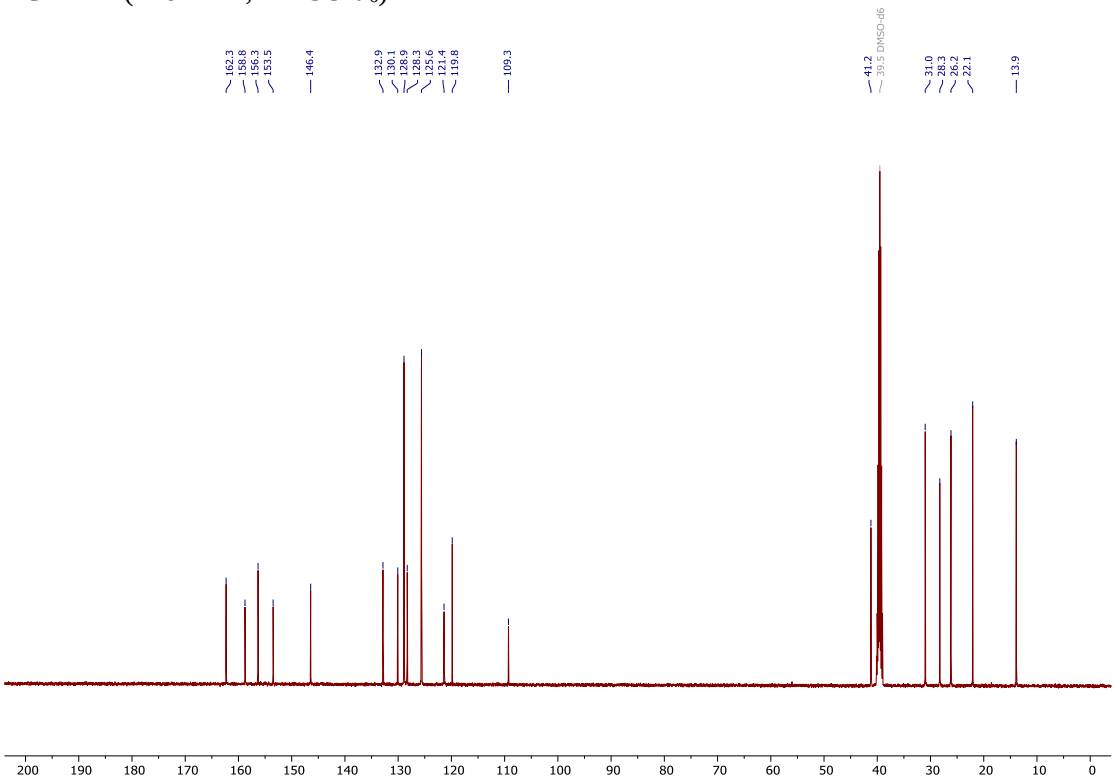
^{13}C NMR (126 MHz, DMSO-d_6)



N-hexyl-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)pyrido[2,3-*d*]pyrimidin-4-amine (**10a**):
^{1}H NMR (500 MHz, DMSO-d_6)

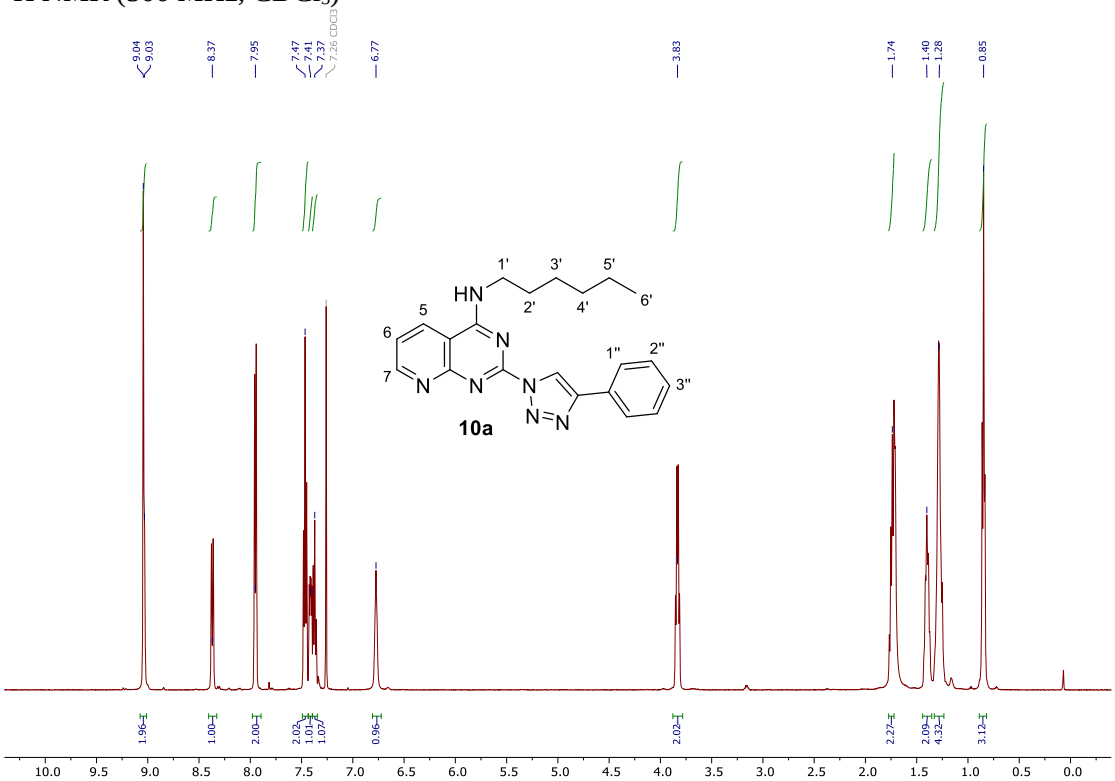


^{13}C NMR (126 MHz, DMSO-d_6)

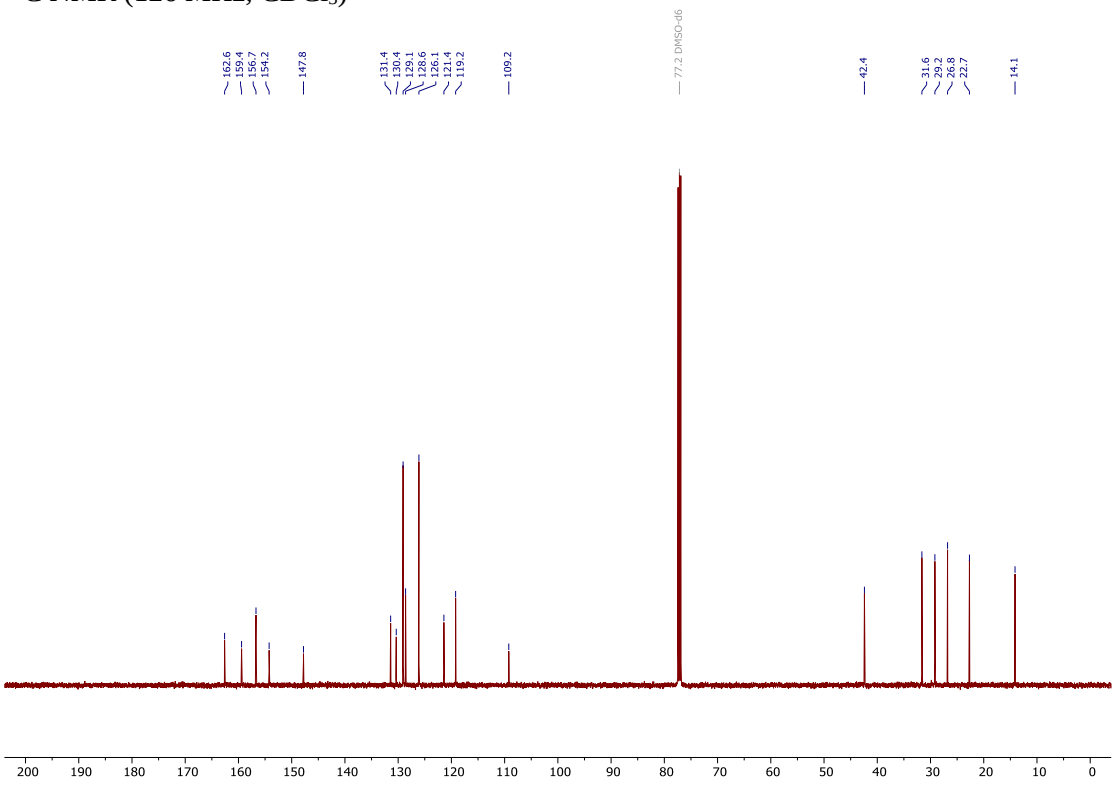


N-hexyl-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)pyrido[2,3-*d*]pyrimidin-4-amine (**10a**):

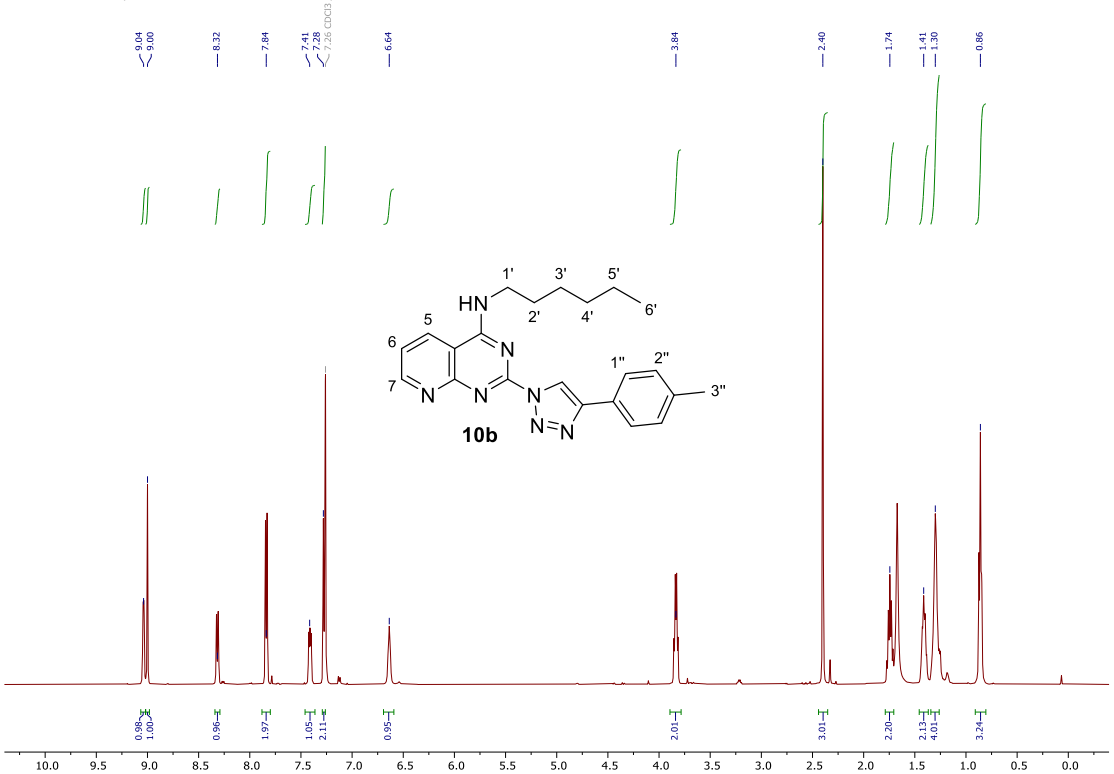
^{1}H NMR (500 MHz, $CDCl_3$)



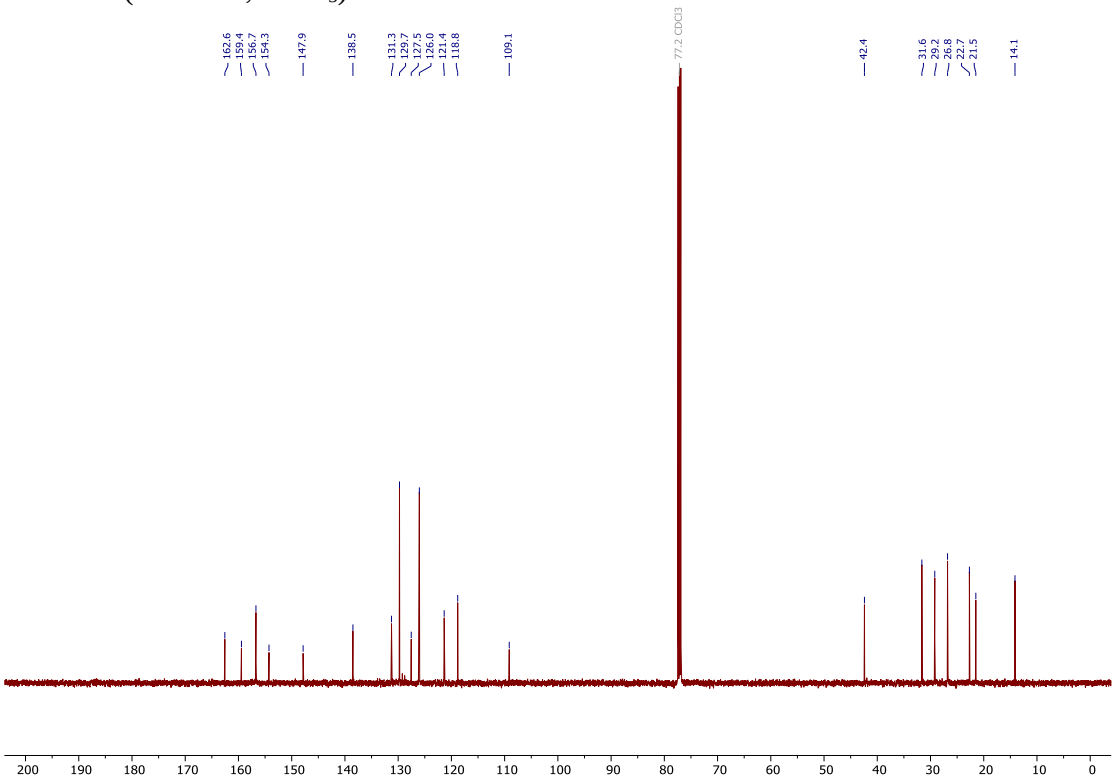
^{13}C NMR (126 MHz, $CDCl_3$)



N-hexyl-2-(4-(p-tolyl)-1*H*-1,2,3-triazol-1-yl)pyrido[2,3-d]pyrimidin-4-amine (**10b**):
^{1}H NMR (500 MHz, $CDCl_3$)

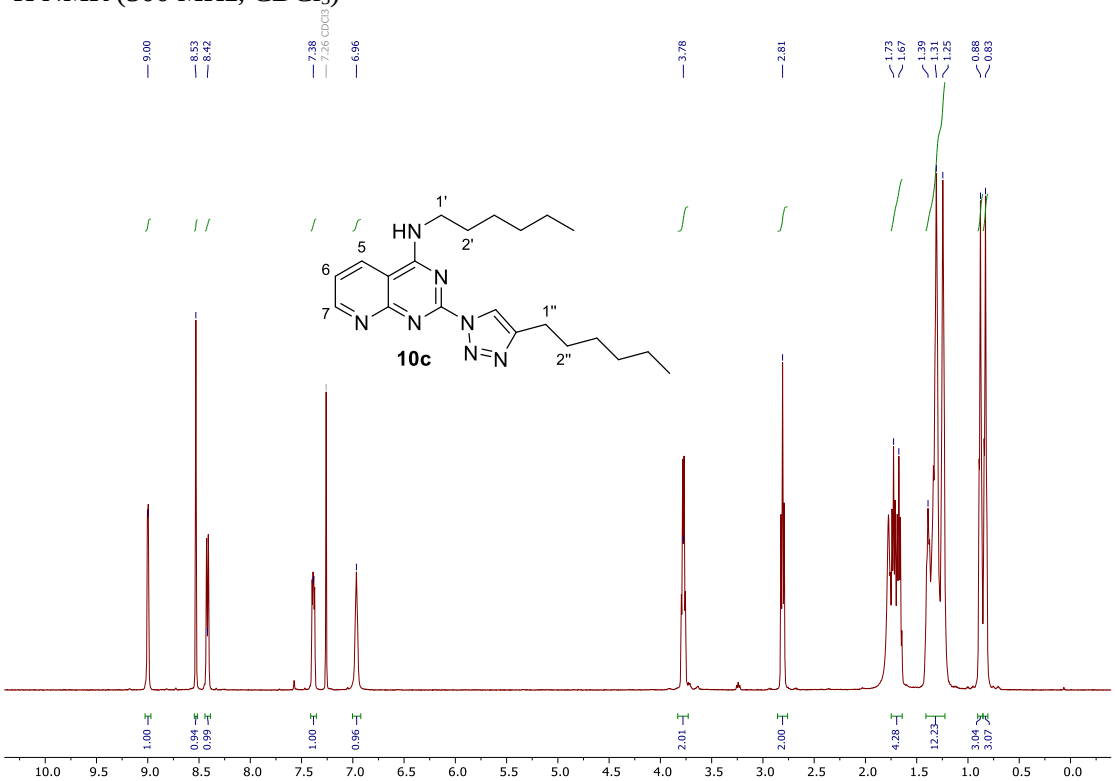


^{13}C NMR (126 MHz, $CDCl_3$)

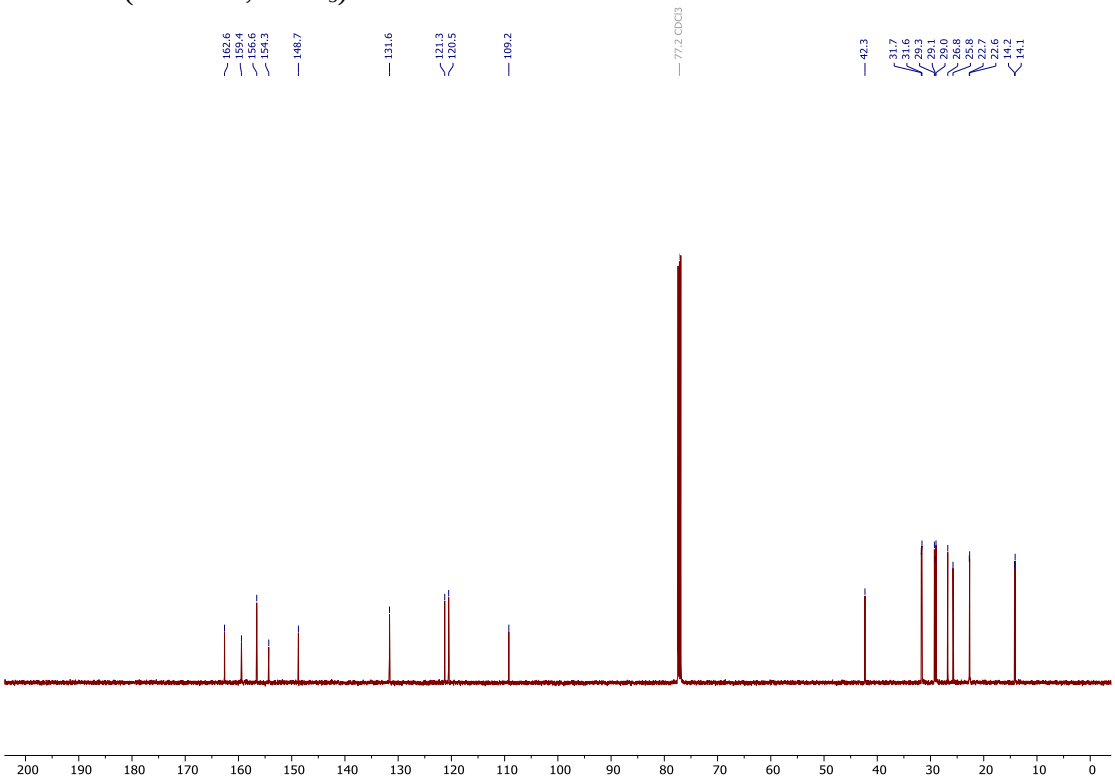


N-hexyl-2-(4-hexyl-1H-1,2,3-triazol-1-yl)pyrido[2,3-d]pyrimidin-4-amine (**10c**):

^{1}H NMR (500 MHz, $CDCl_3$)

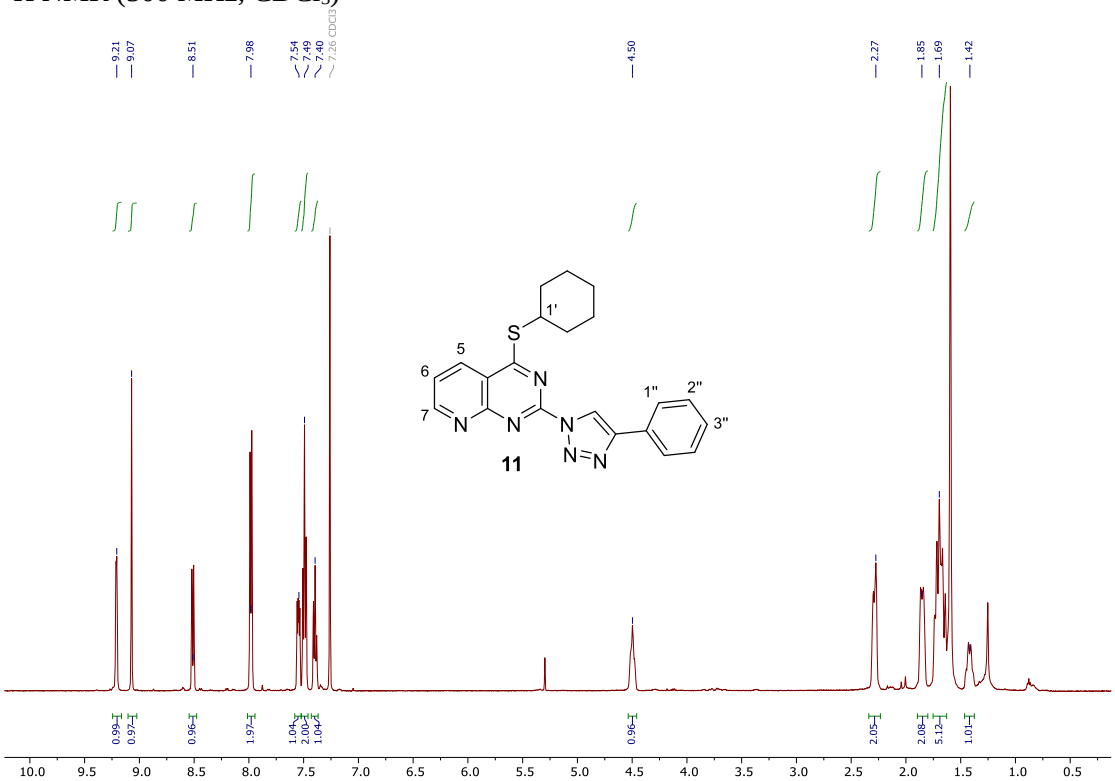


^{13}C NMR (126 MHz, $CDCl_3$)

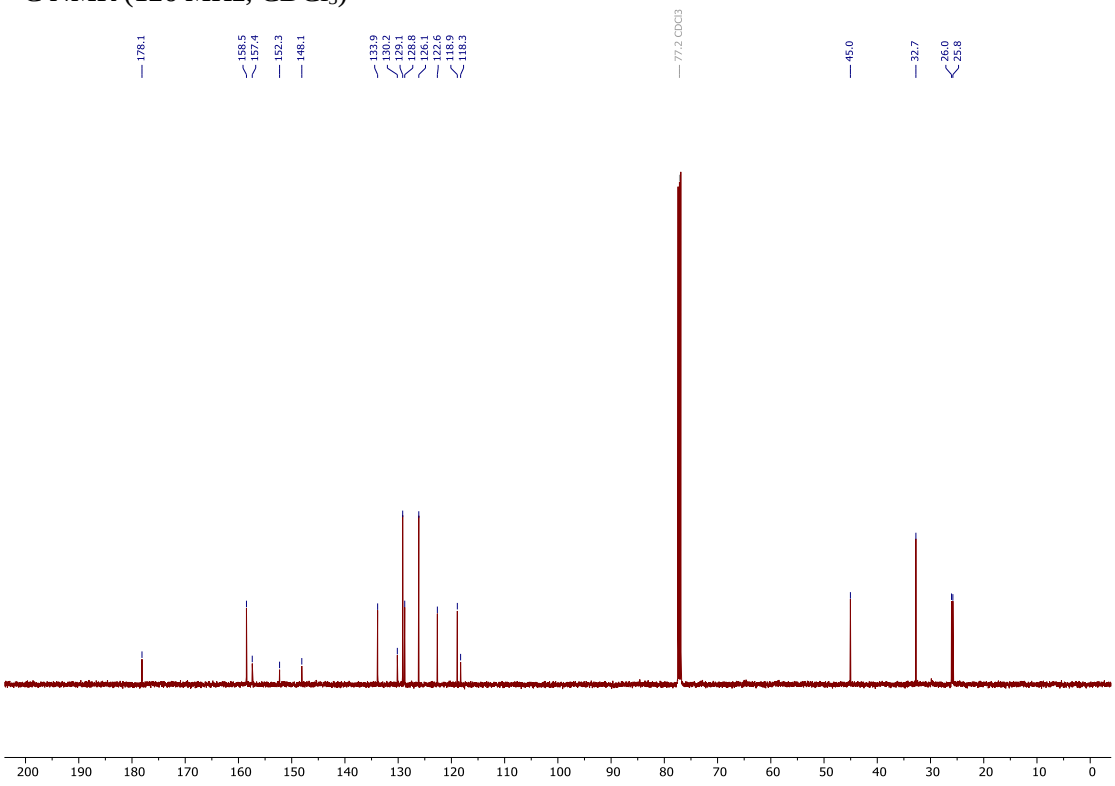


4-(cyclohexylthio)-2-(4-phenyl-1H-1,2,3-triazol-1-yl)pyrido[2,3-d]pyrimidine (**11**):

^{1}H NMR (500 MHz, $CDCl_3$)

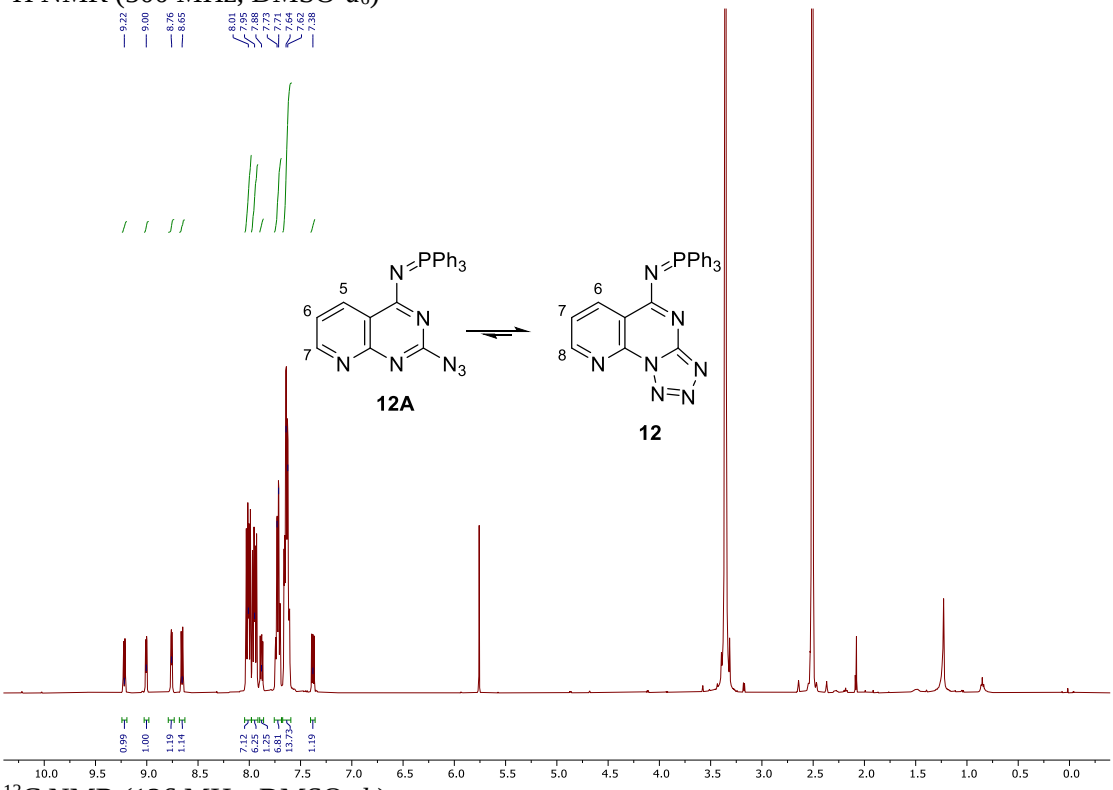


^{13}C NMR (126 MHz, $CDCl_3$)

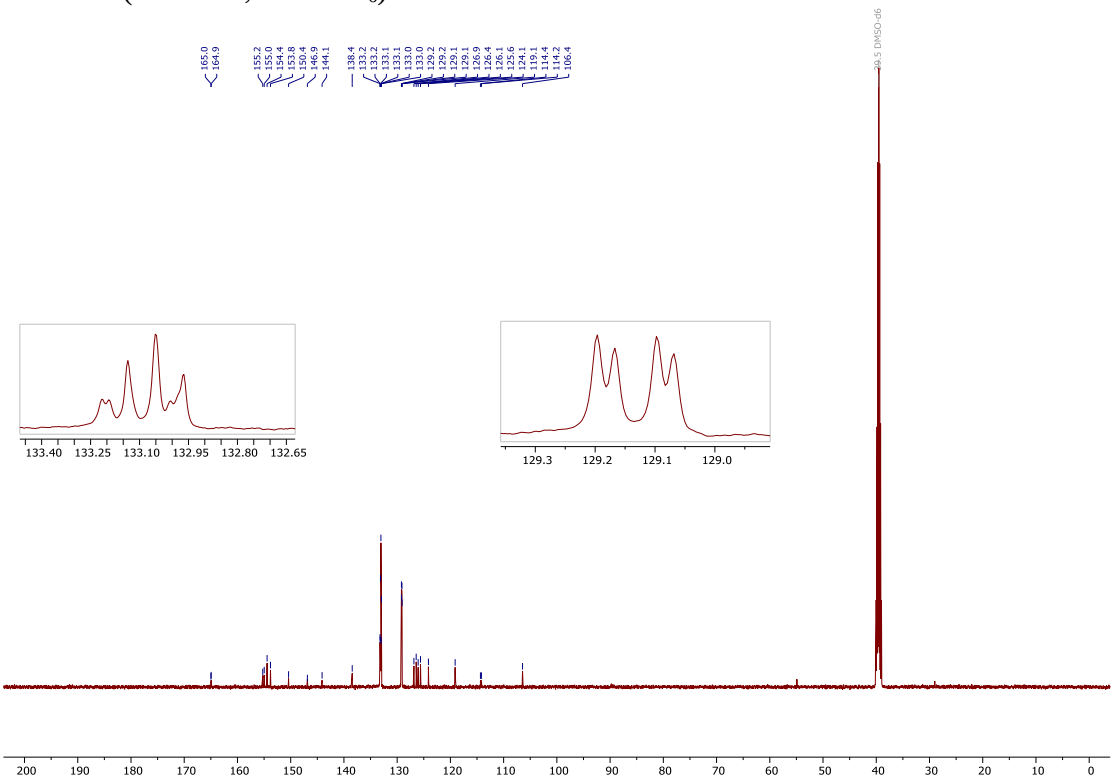


1,1,1-triphenyl-*N*-(pyrido[3,2-*e*]tetrazolo[1,5-*a*]pyrimidin-5-yl)-phosphonimine (**12**) and *N*-(triphenylphosphorylidene)-2-azidopyrido[2,3-*d*]pyrimidin-4-yl-amine (**12A**):

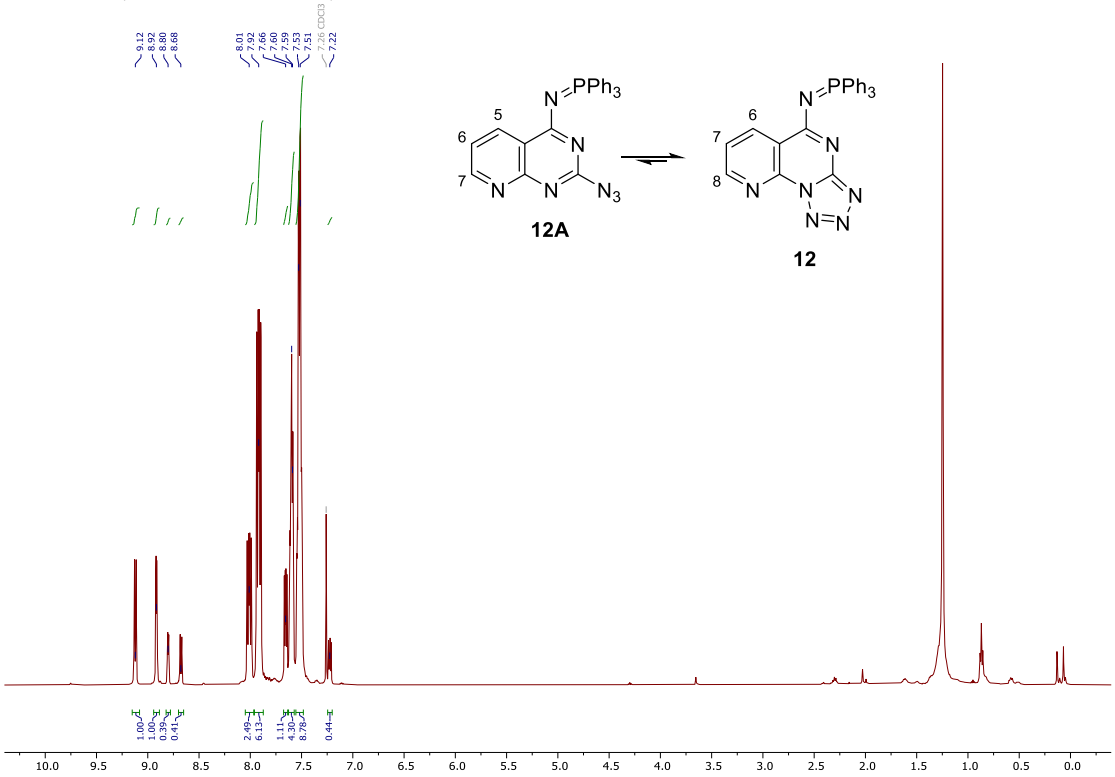
^{1}H NMR (500 MHz, DMSO-d_6)



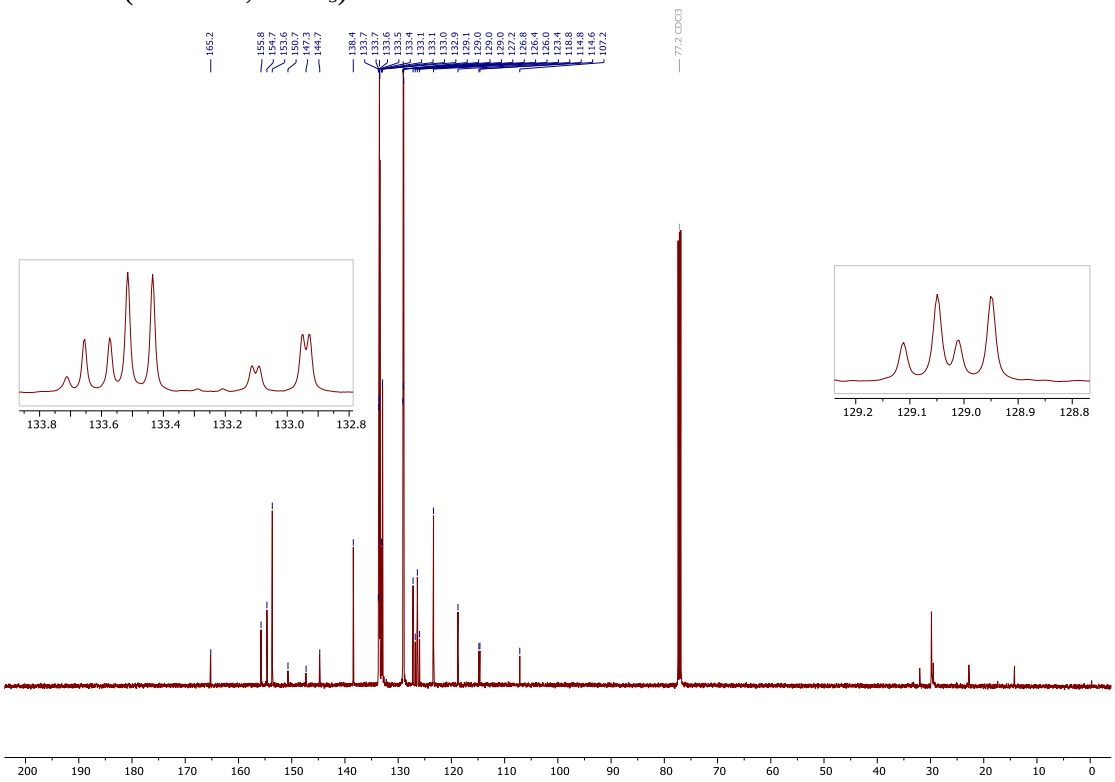
^{13}C NMR (126 MHz, DMSO-d_6)



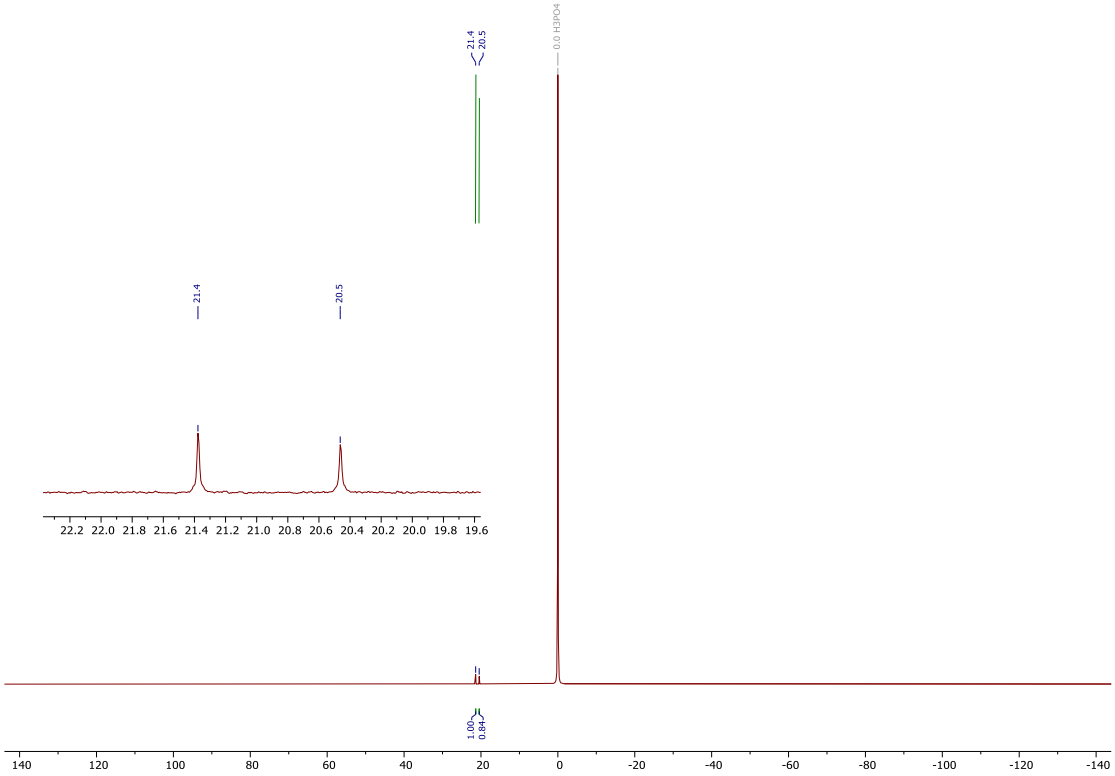
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



^{31}P NMR (202 MHz, DMSO-d_6)



^{31}P NMR (202 MHz, $CDCl_3$)