

Supplementary material

S_NAr Reactions of 2,4-Diazidopyrido[3,2-*e*]pyrimidine and Azide-Tetrazole Equilibrium Studies of the Obtained 5-Substituted Tetrazolo[1,5-*a*]pyrido[2,3-*e*]pyrimidines

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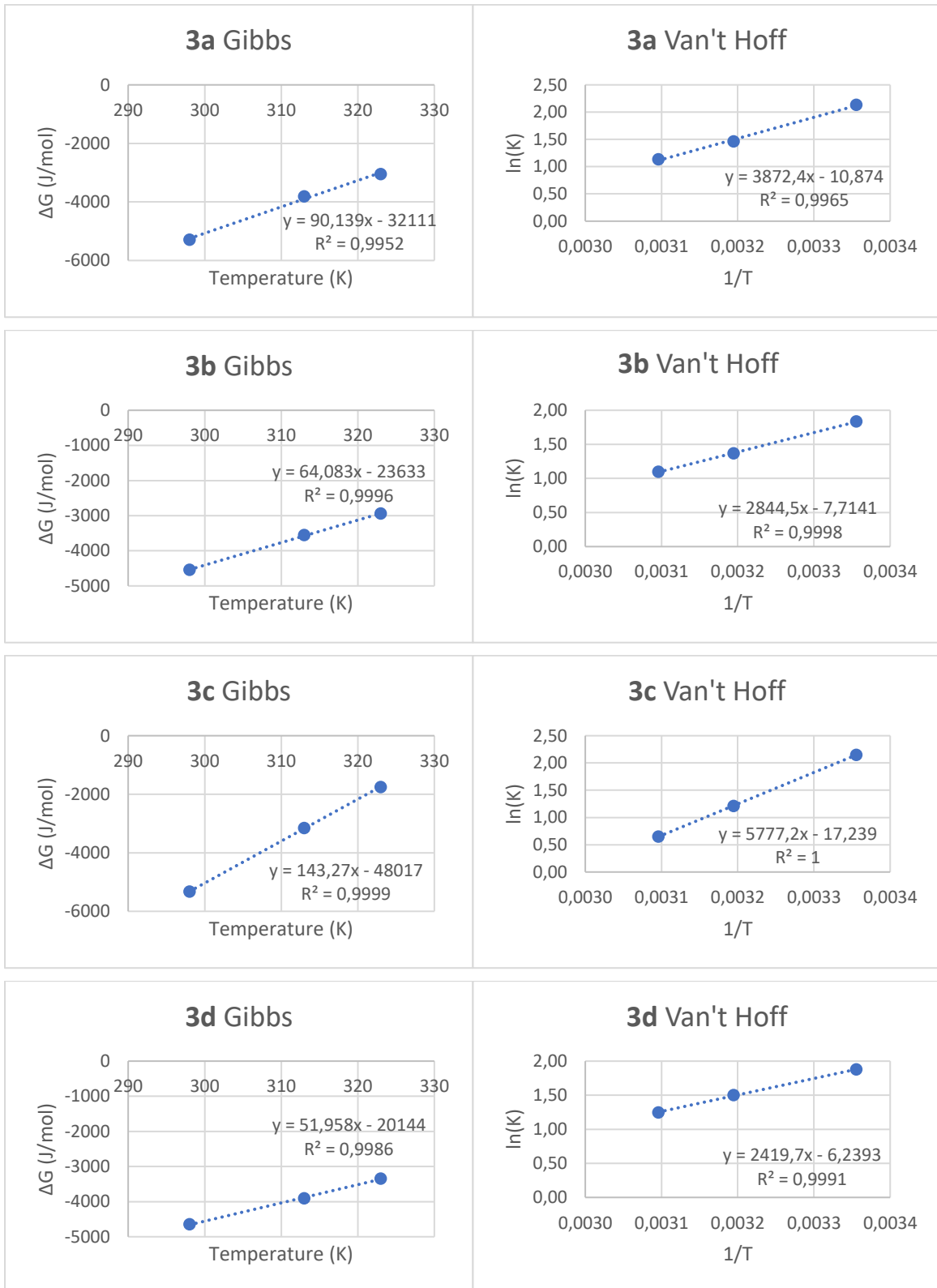
²Latvian Institute of Organic Synthesis, Aizkraukles str. 21, Riga, LV-1006, Latvia

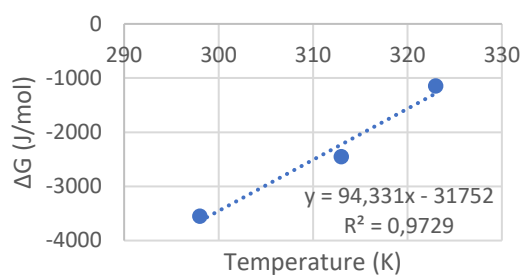
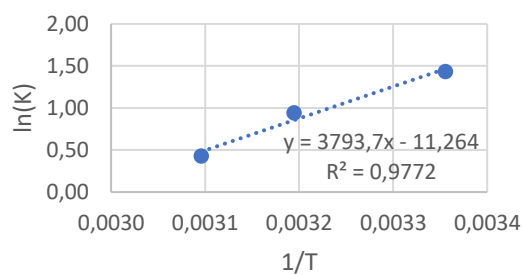
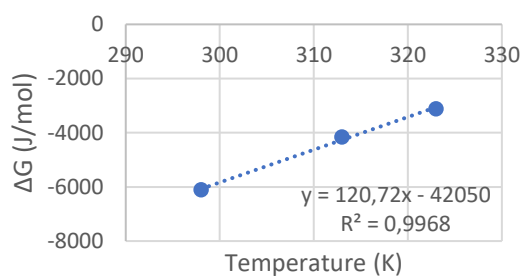
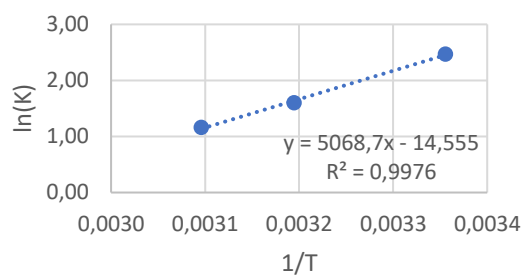
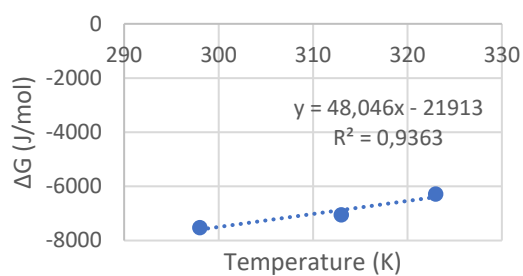
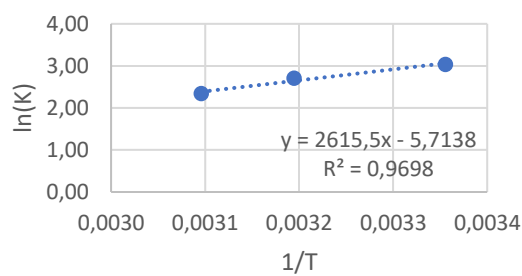
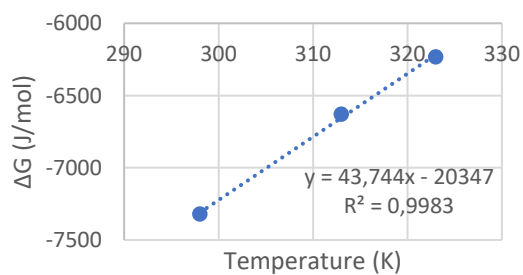
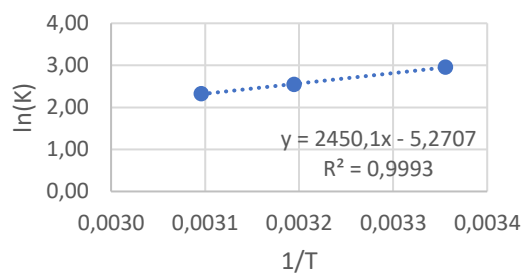
*Correspondence: Irina.Novosjolova@rtu.lv (I.N.); Maris.Turks@rtu.lv (M.T.)

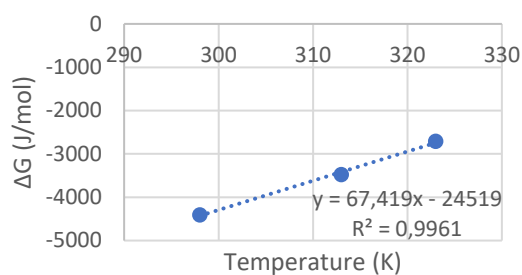
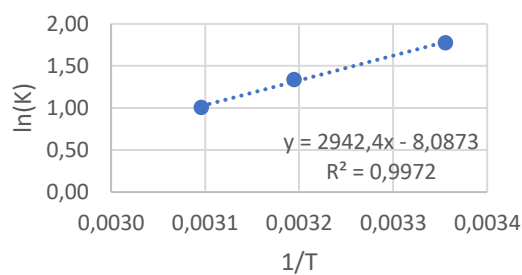
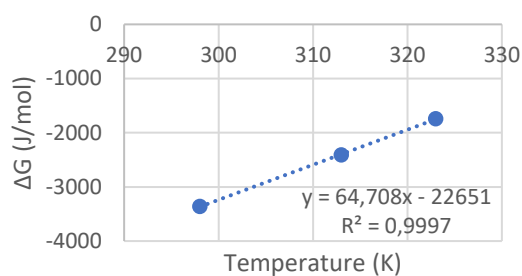
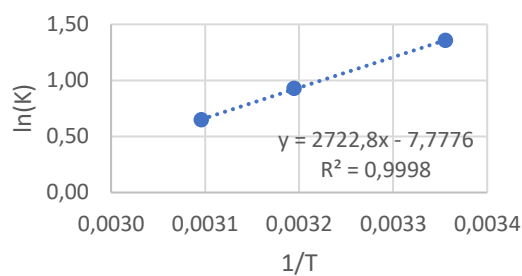
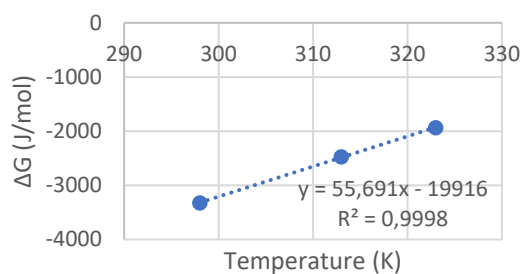
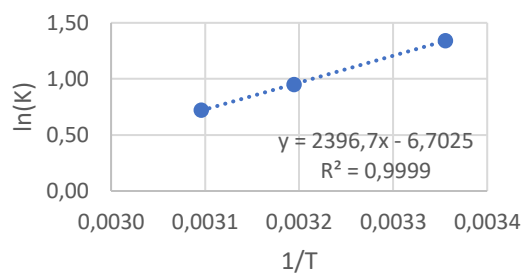
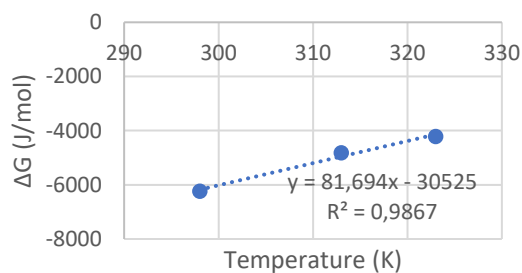
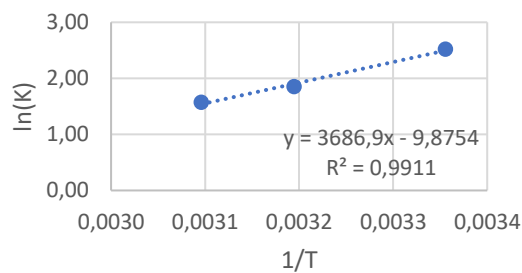
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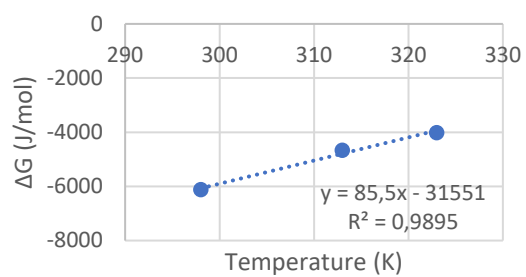
Gibbs and van't Hoff plots



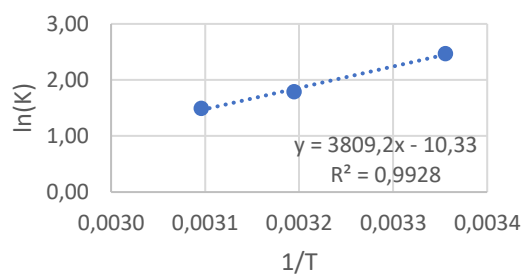
3e Gibbs**3e Van't Hoff****3f Gibbs****3f Van't Hoff****4a Gibbs****4a Van't Hoff****4b Gibbs****4b Van't Hoff**

4c Gibbs**4c Van't Hoff****4d Gibbs****4d Van't Hoff****4g Gibbs****4g Van't Hoff****5a Gibbs****5a Van't Hoff**

5b Gibbs



5b Van't Hoff

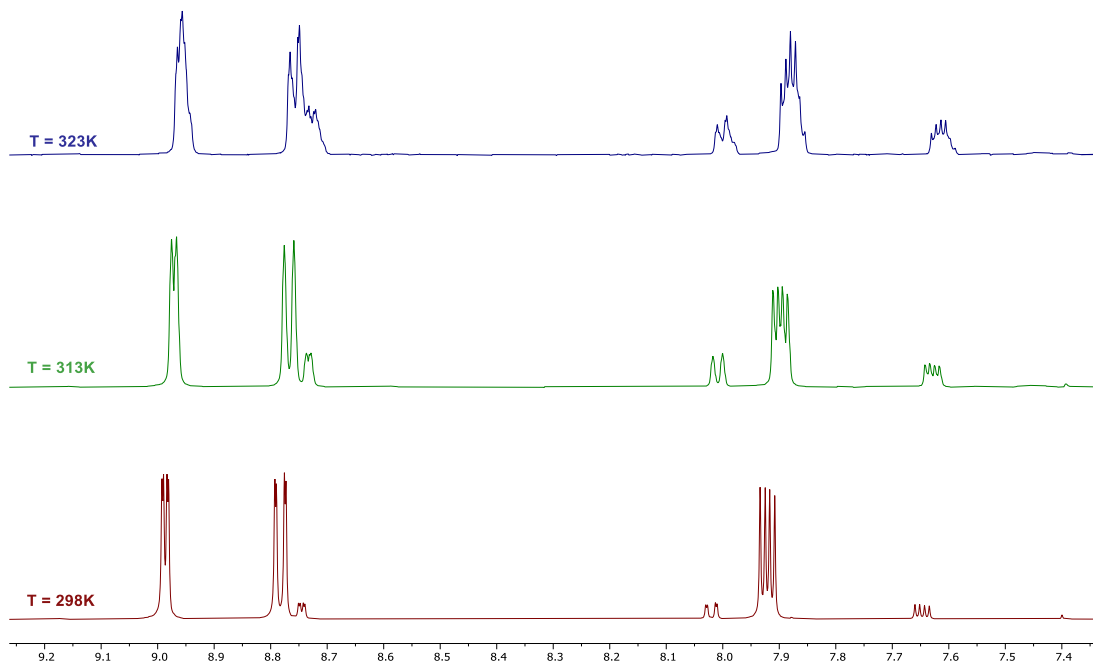


Gibbs and van' t Hoff plot derived thermodynamic values of tautomerization for compounds 3-5

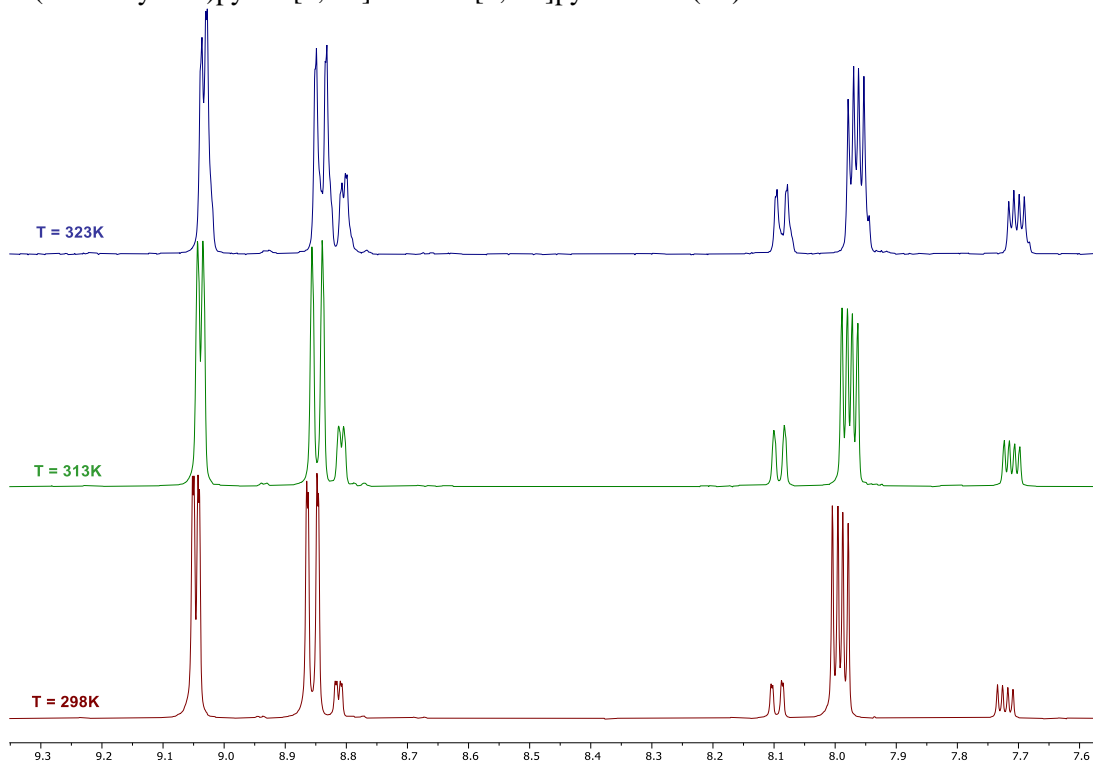
	T (K)	Gibbs plot values			Van't Hoff plot values		
		ΔG (kJ/mol)	ΔH_{298} (kJ/mol)	ΔS_{298} (J/mol·K)	ΔG (kJ/mol)	ΔH_{298} (kJ/mol)	ΔS_{298} (J/mol·K)
3a	298	-5.29			-5.25		
	313	-3.81	-32.11	-90.14	-3.90	-32.20	-90.41
	323	-3.05			-2.99		
3b	298	-4.54			-4.54		
	313	-3.56	-23.63	-64.08	-3.58	-23.65	-64.14
	323	-2.95			-2.93		
3c	298	-5.33			-5.32		
	313	-3.16	-48.02	-143.27	-3.17	-48.03	-143.33
	323	-1.75			-1.74		
3d	298	-4.65			-4.66		
	313	-3.91	-20.14	-51.96	-3.88	-20.12	-51.87
	323	-3.34			-3.36		
3e	298	-3.55			-3.63		
	313	-2.45	-31.75	-94.33	-2.23	-31.54	-93.65
	323	-1.15			-1.29		
3f	298	-6.12			-6.08		
	313	-4.17	-42.05	-120.72	-4.27	-42.14	-121.01
	323	-3.12			-3.06		
4a	298	-7.52			-7.59		
	313	-7.06	-21.91	-48.05	-6.88	-21.75	-47.50
	323	-6.29			-6.40		
4b	298	-7.32			-7.31		
	313	-6.63	-20.35	-43.74	-6.65	-20.37	-43.82
	323	-6.23			-6.22		
4c	298	-4.40			-4.43		
	313	-3.48	-24.52	-67.42	-3.42	-24.46	-67.24
	323	-2.71			-2.75		
4d	298	-3.36			-3.37		
	313	-2.41	-22.65	-64.71	-2.40	-22.64	-64.66
	323	-1.74			-1.75		
4g	298	-3.33			-3.32		
	313	-2.47	-19.92	-55.69	-2.49	-19.93	-55.72
	323	-1.94			-1.93		
5a	298	-6.24			-6.19		
	313	-4.82	-30.53	-81.69	-4.95	-30.65	-82.10
	323	-4.22			-4.13		
5b	298	-6.12			-6.08		
	313	-4.66	-31.55	-85.50	-4.79	-31.67	-85.88
	323	-4.01			-3.93		

^1H NMR spectra of tetrazoles 3-5 in CDCl_3 at variable temperatures

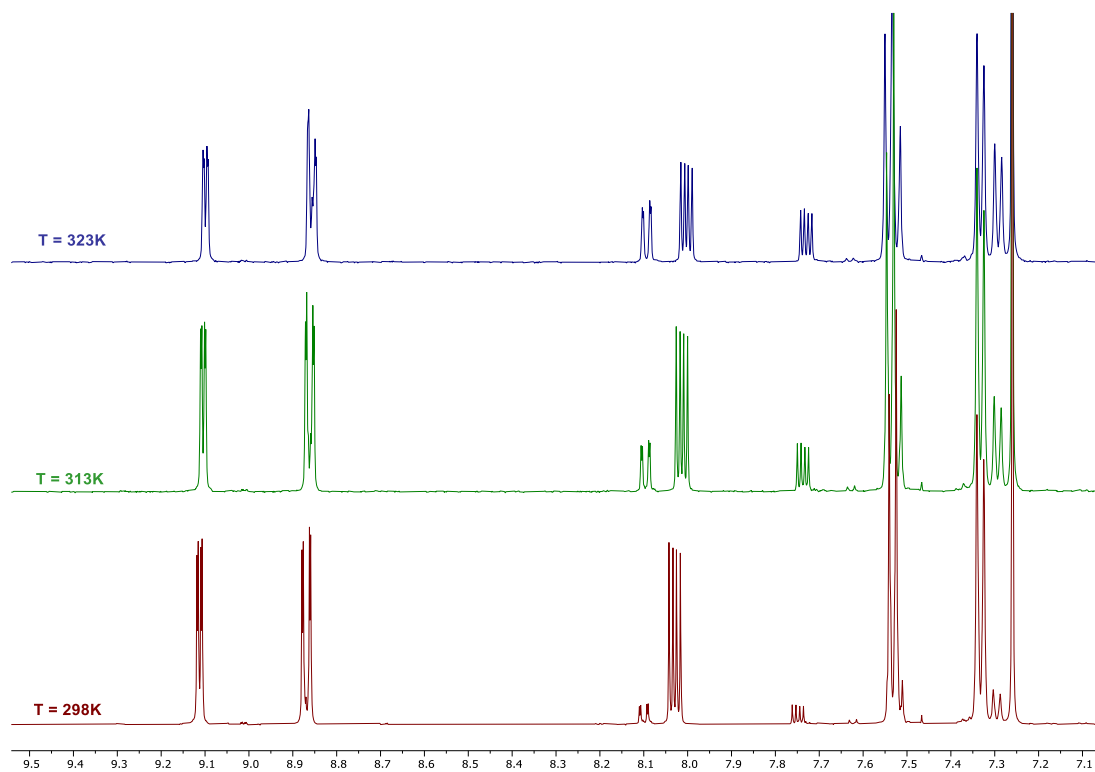
5-(Butylthio)pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidine (**3a**):



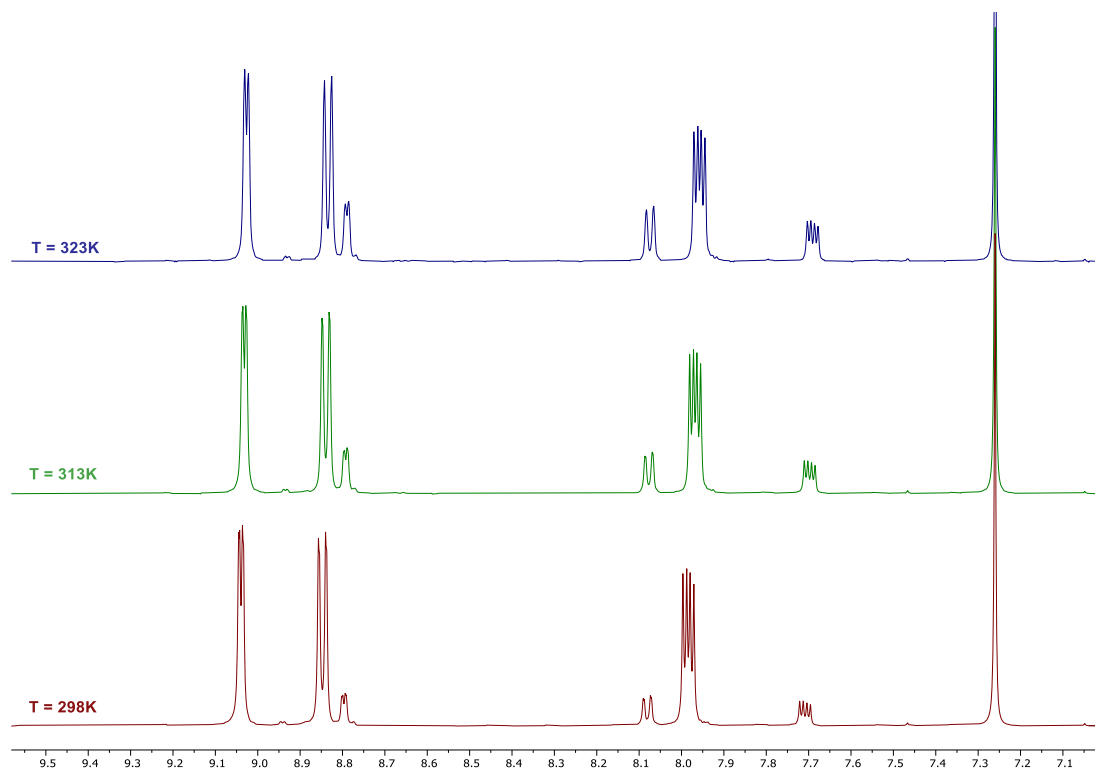
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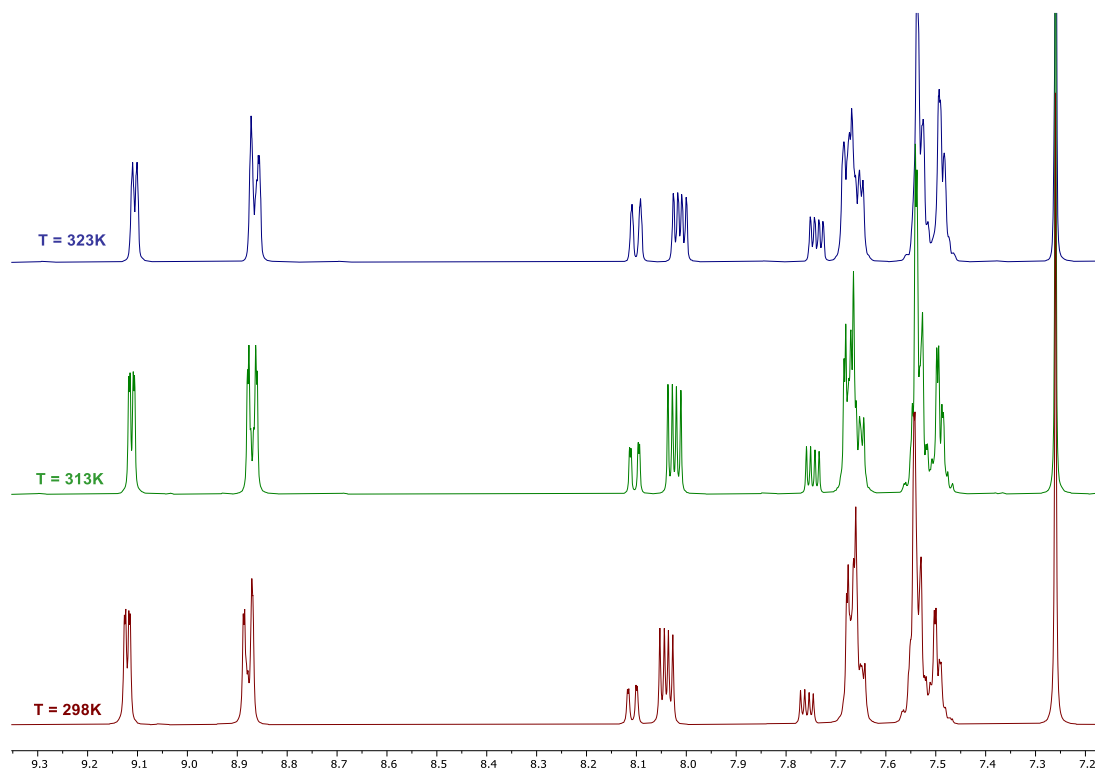
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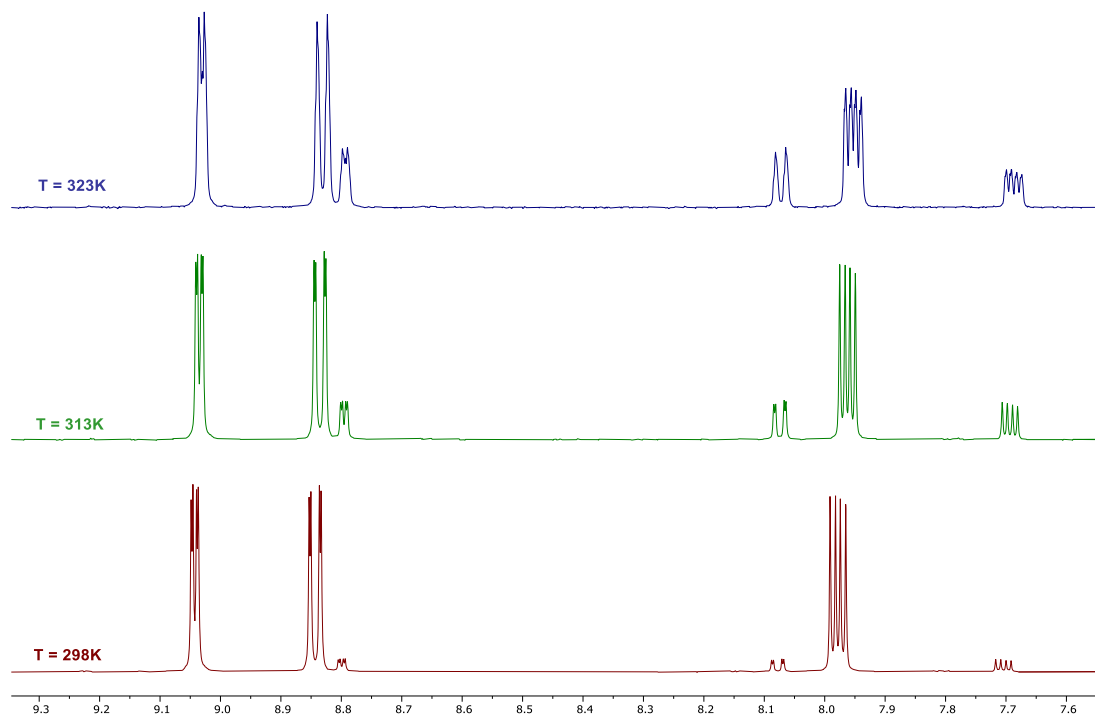
5-(Isopropylthio)pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidine (**3d**):



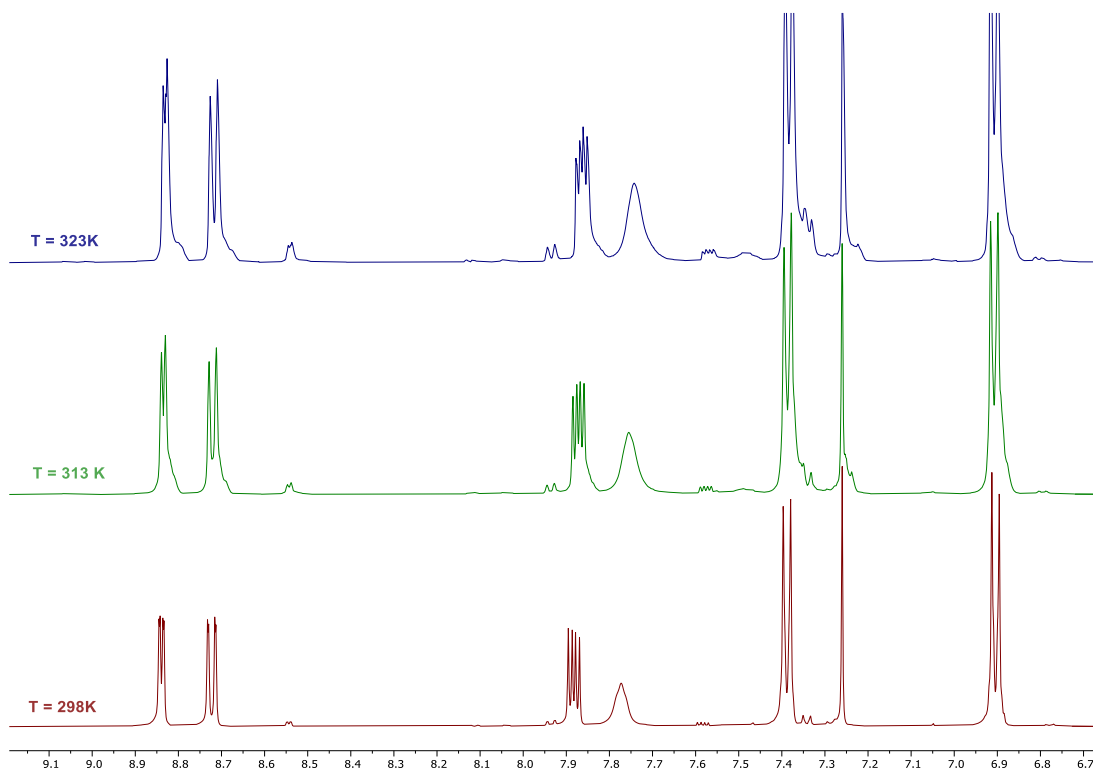
5-(Phenylthio)pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidine (**3e**):



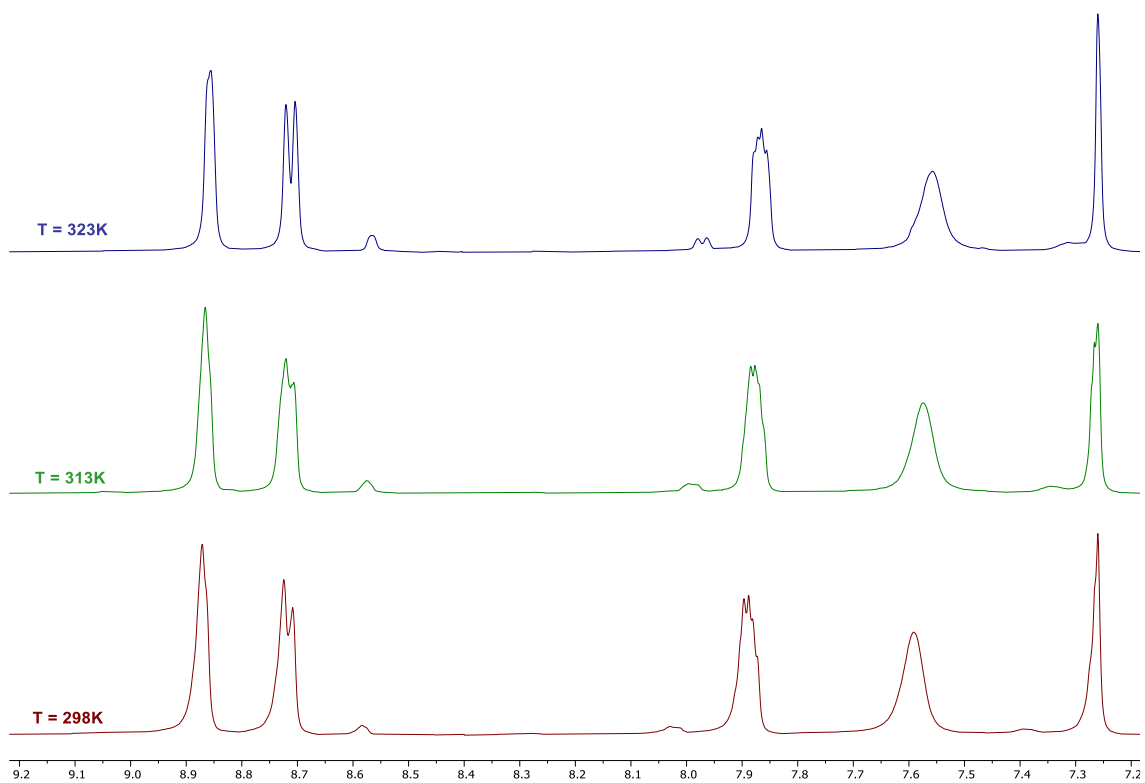
5-(Cyclohexylthio)pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidine (**3f**):



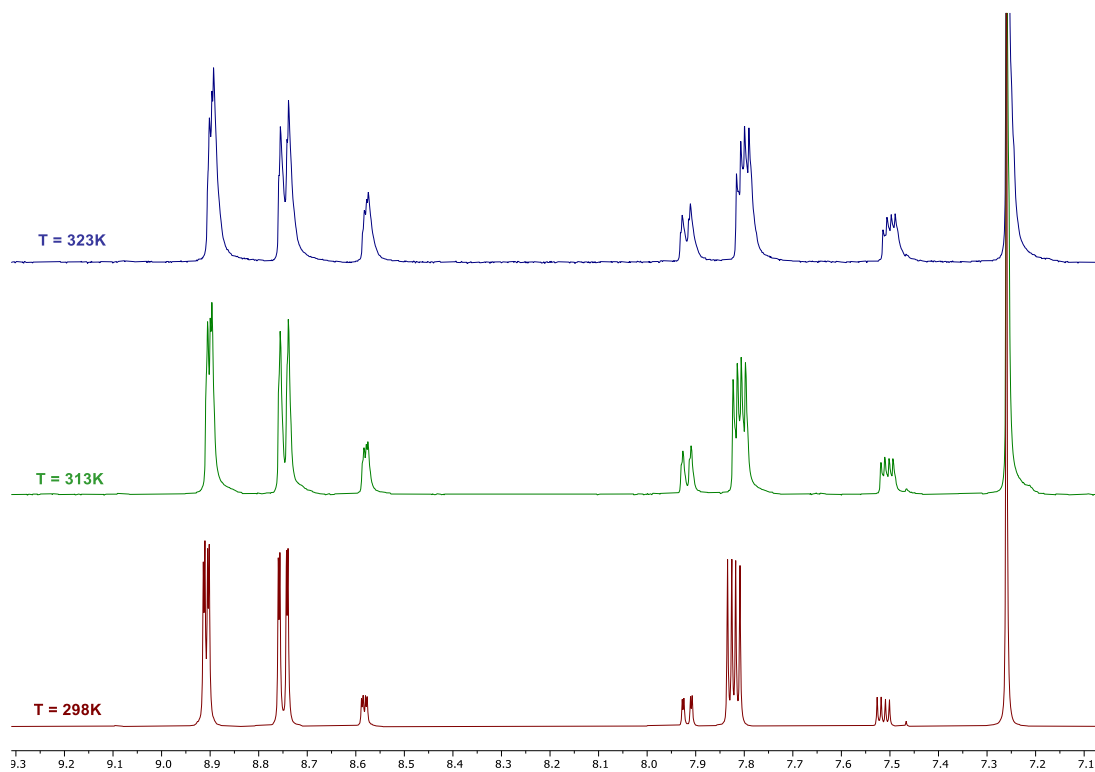
N-(4-Methoxybenzyl)pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidin-5-amine (**4a**):



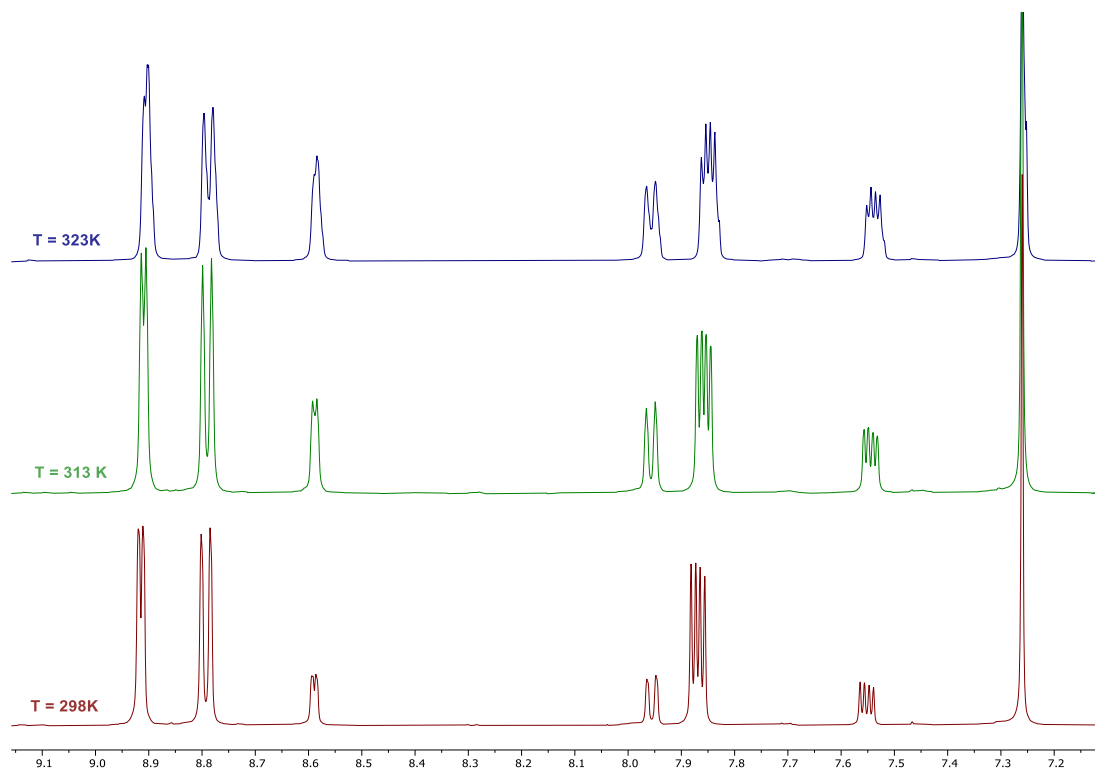
N-Hexylpyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidin-5-amine (**4b**):



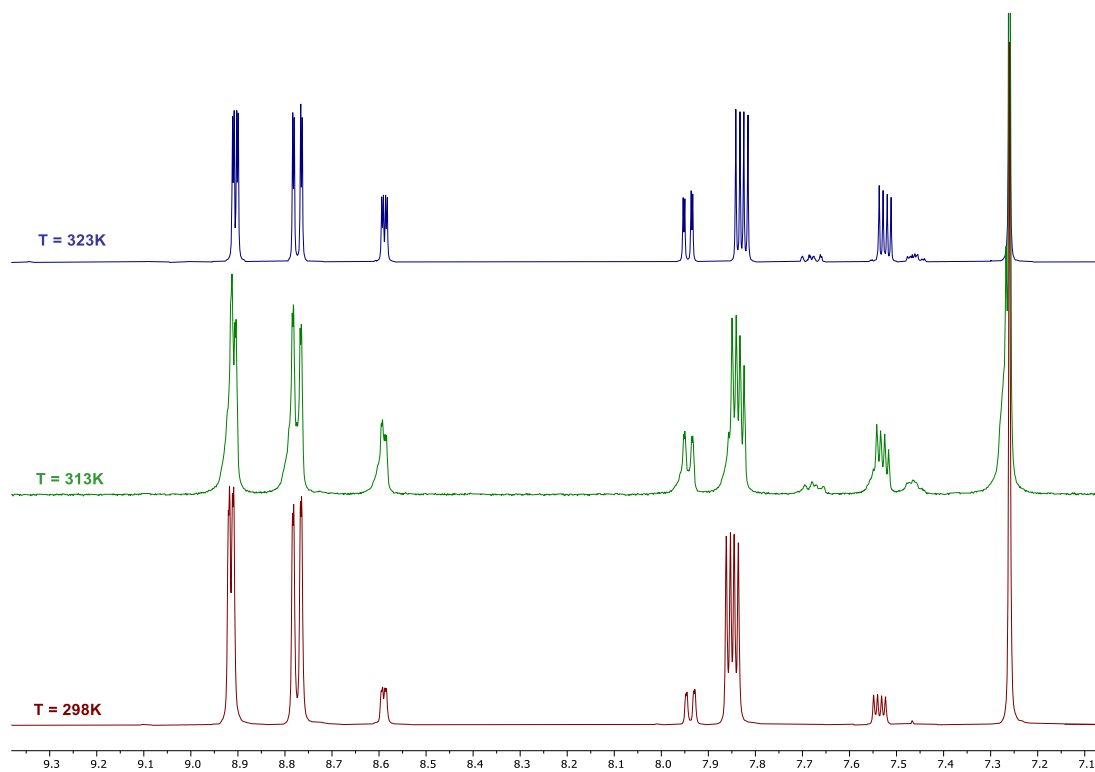
5-(Piperidin-1-yl)pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidine (**4c**):



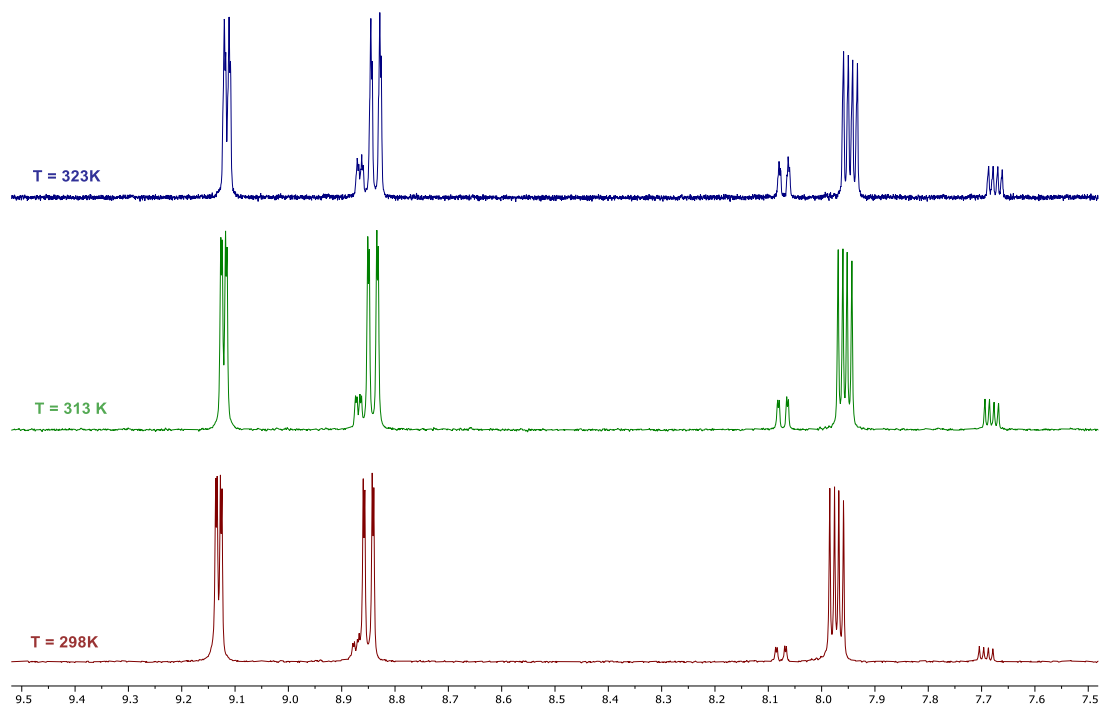
4-(Pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidin-5-yl)morpholine (**4d**):



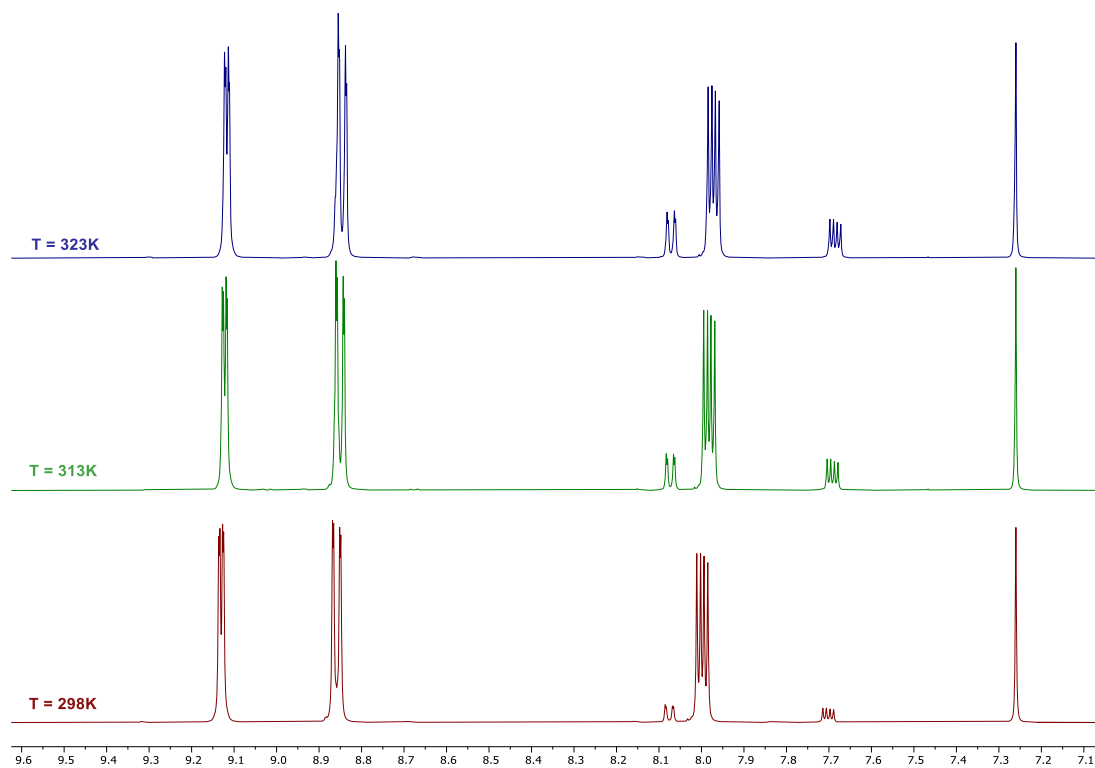
5-(4-Methylpiperazin-1-yl)pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidine (**4g**):



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



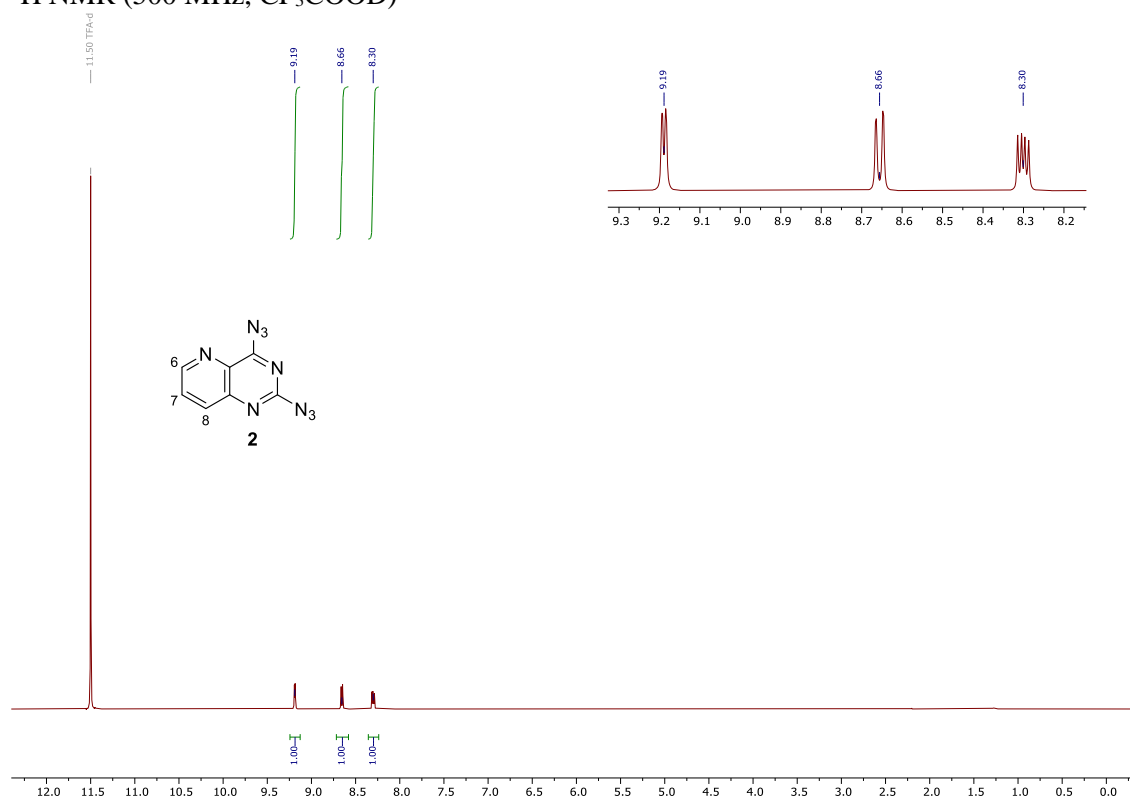
5-Propoxy-pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidine (**5b**):



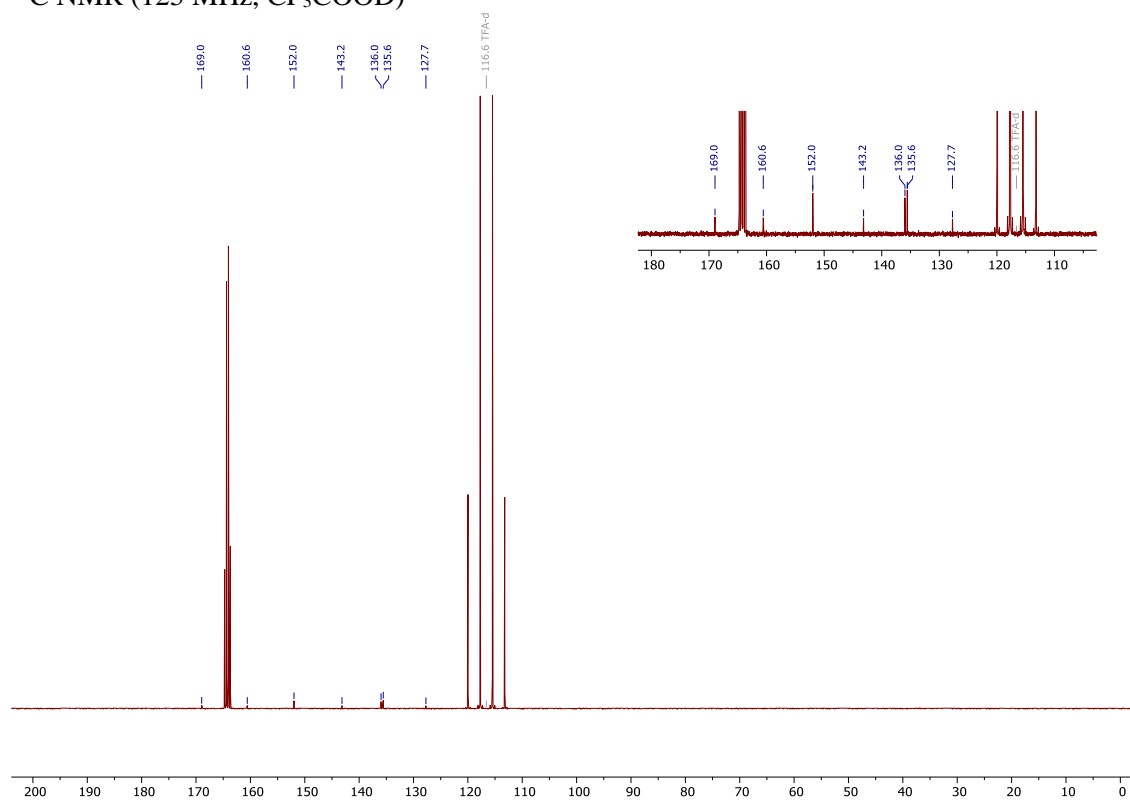
^1H , ^{13}C and ^{31}P NMR for obtained compounds

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

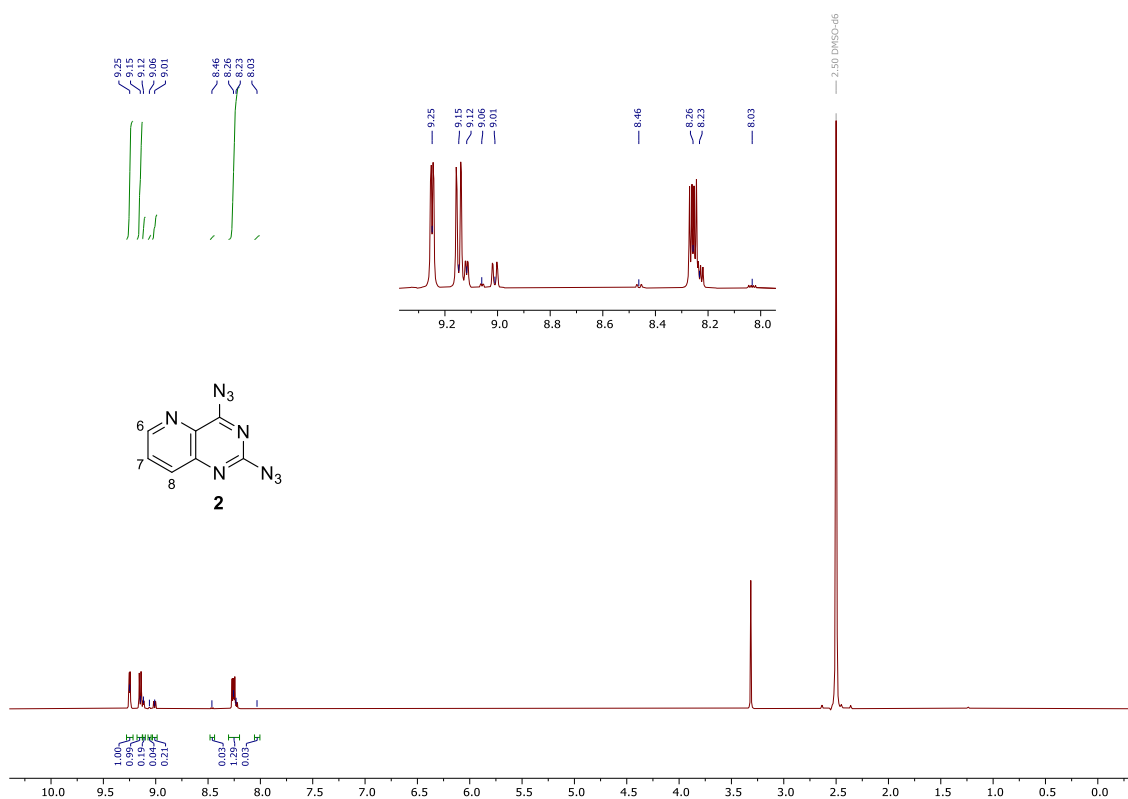
^1H NMR (500 MHz, CF_3COOD)



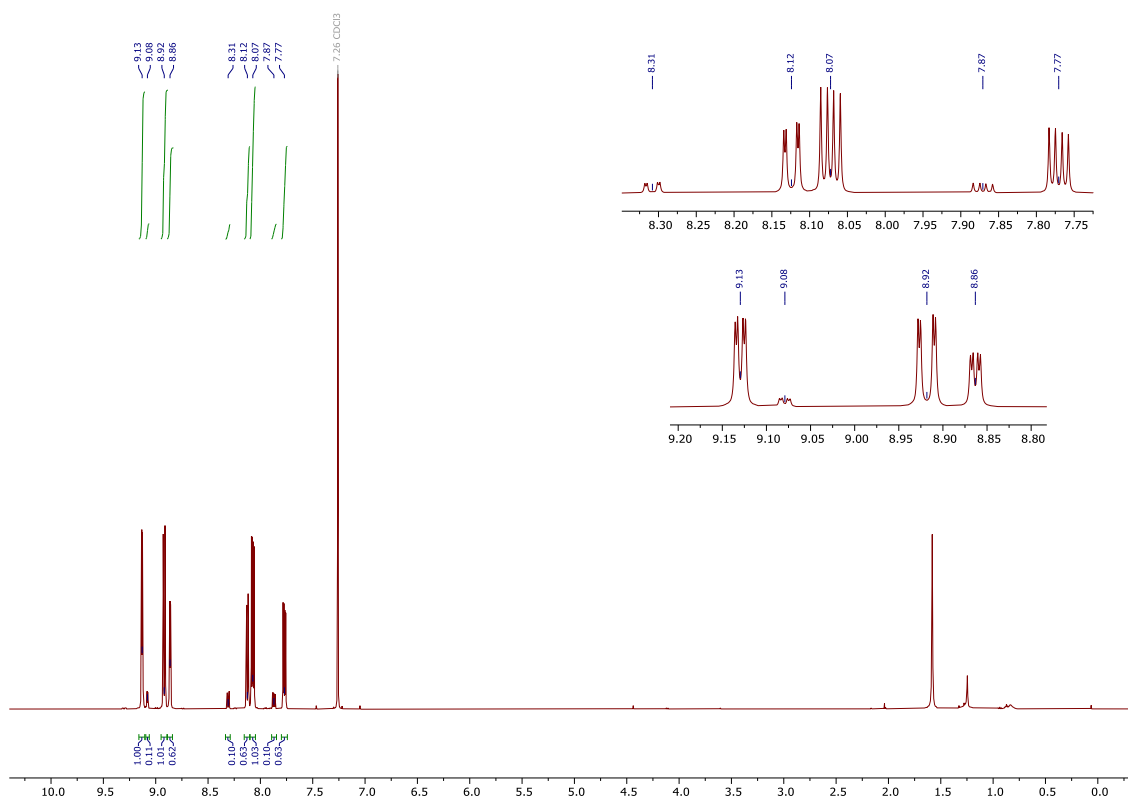
^{13}C NMR (125 MHz, CF_3COOD)



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

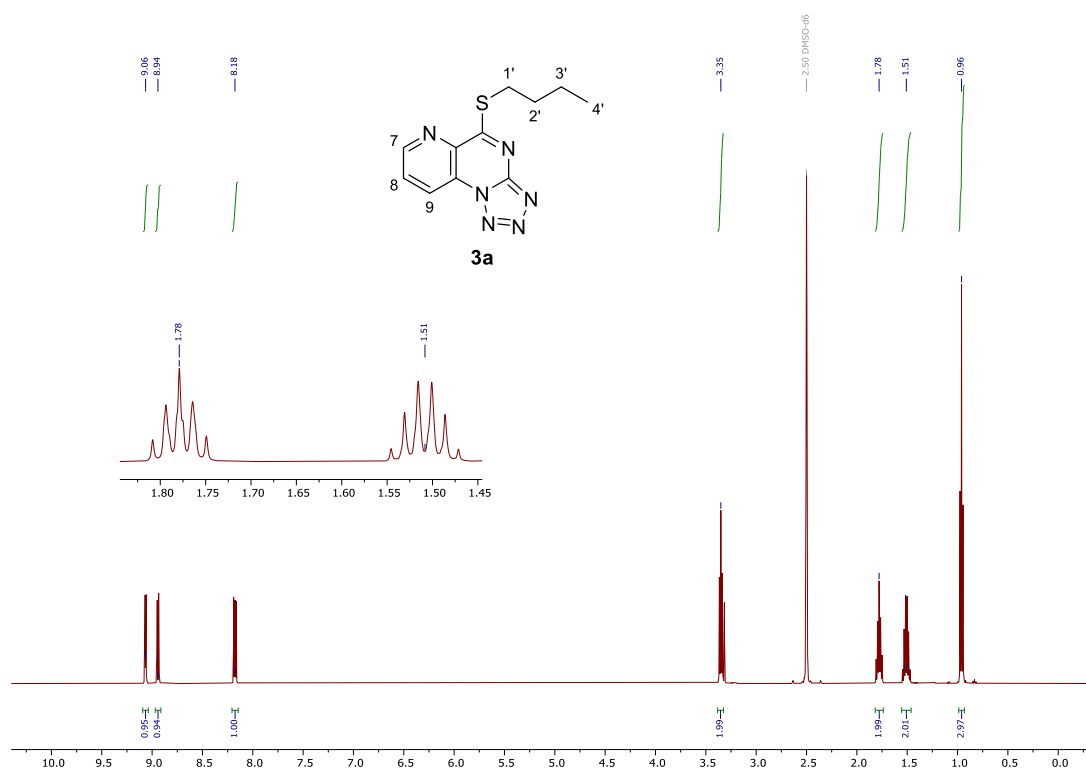


^1H NMR (500 MHz, CDCl_3)

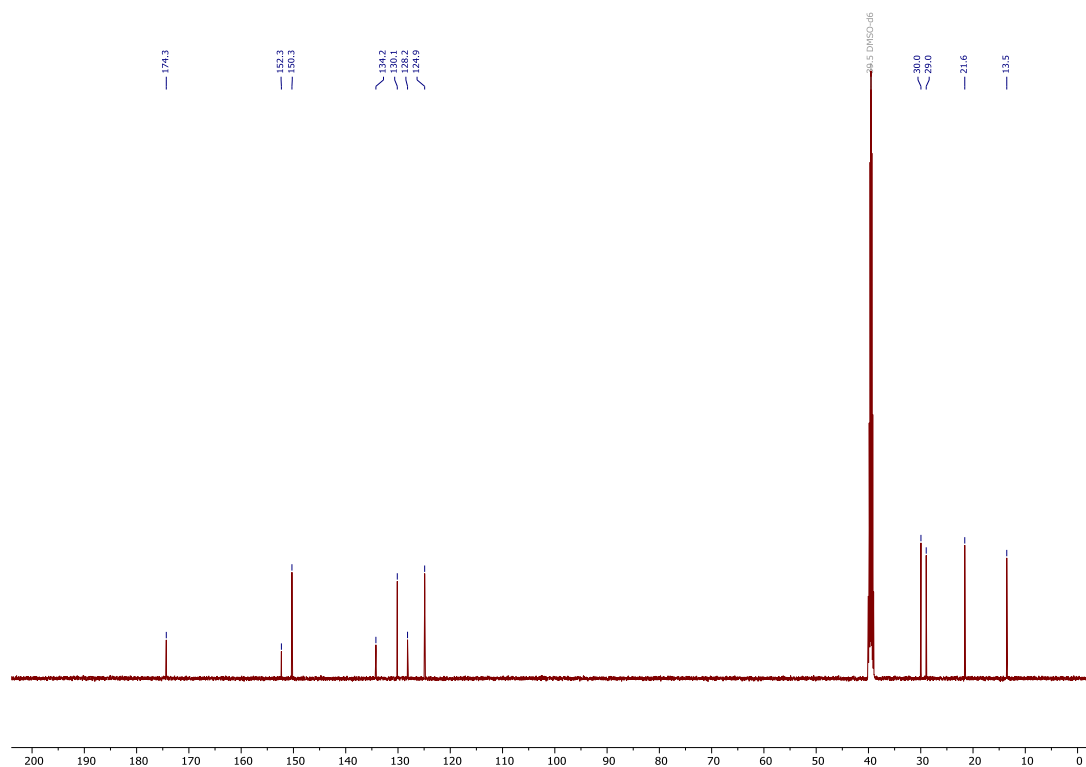


5-(Butylthio)pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidine (**3a**):

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

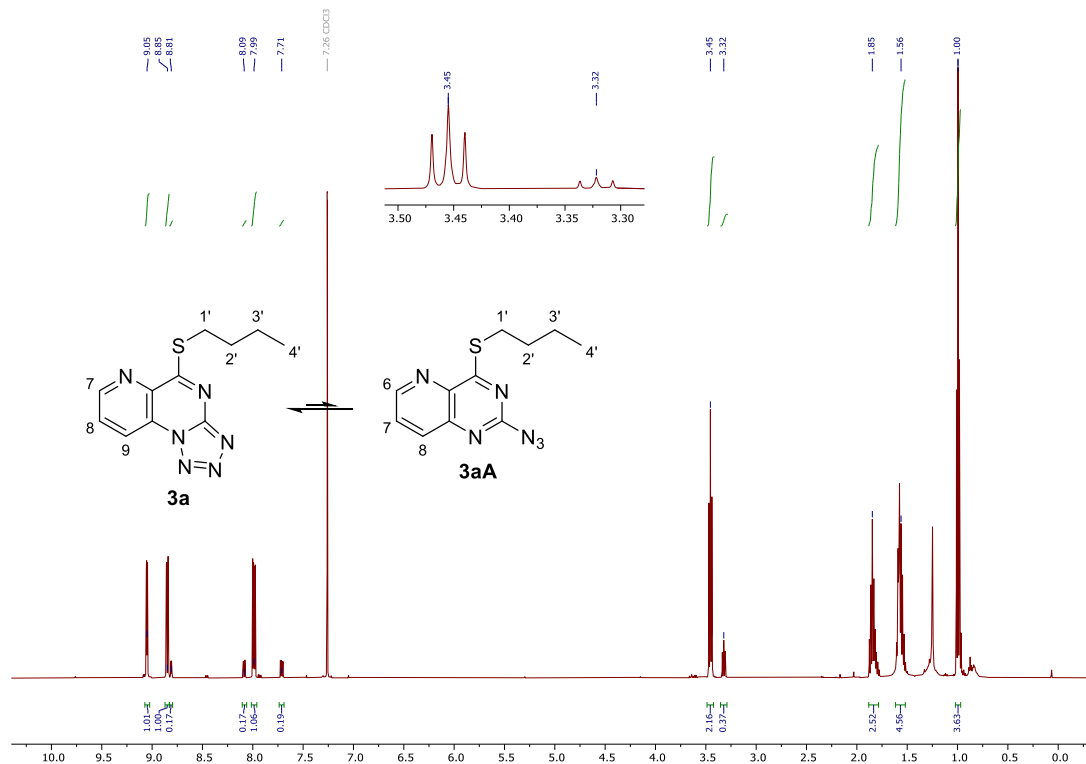


^{13}C NMR (125 MHz, $\text{DMSO-}d_6$)



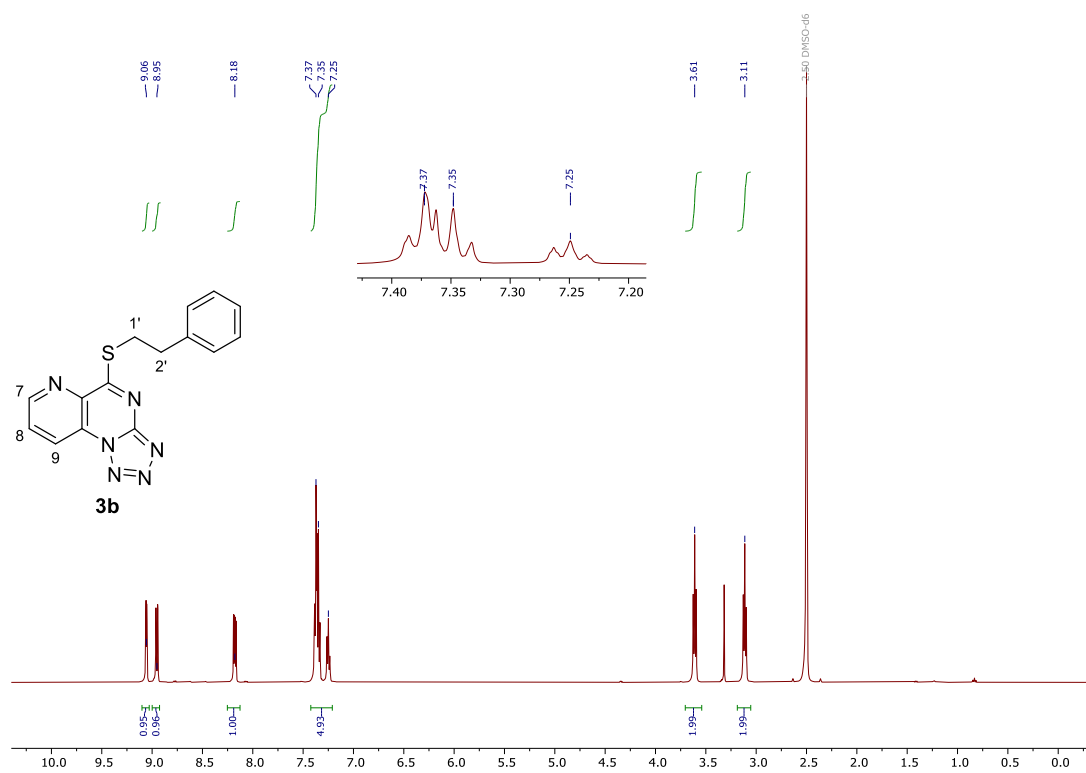
5-(Butylthio)pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidine (**3a**) and 2-azido-4-(butylthio)pyrido[3,2-*d*]pyrimidine (**3aA**):

^1H NMR (500 MHz, CDCl_3)

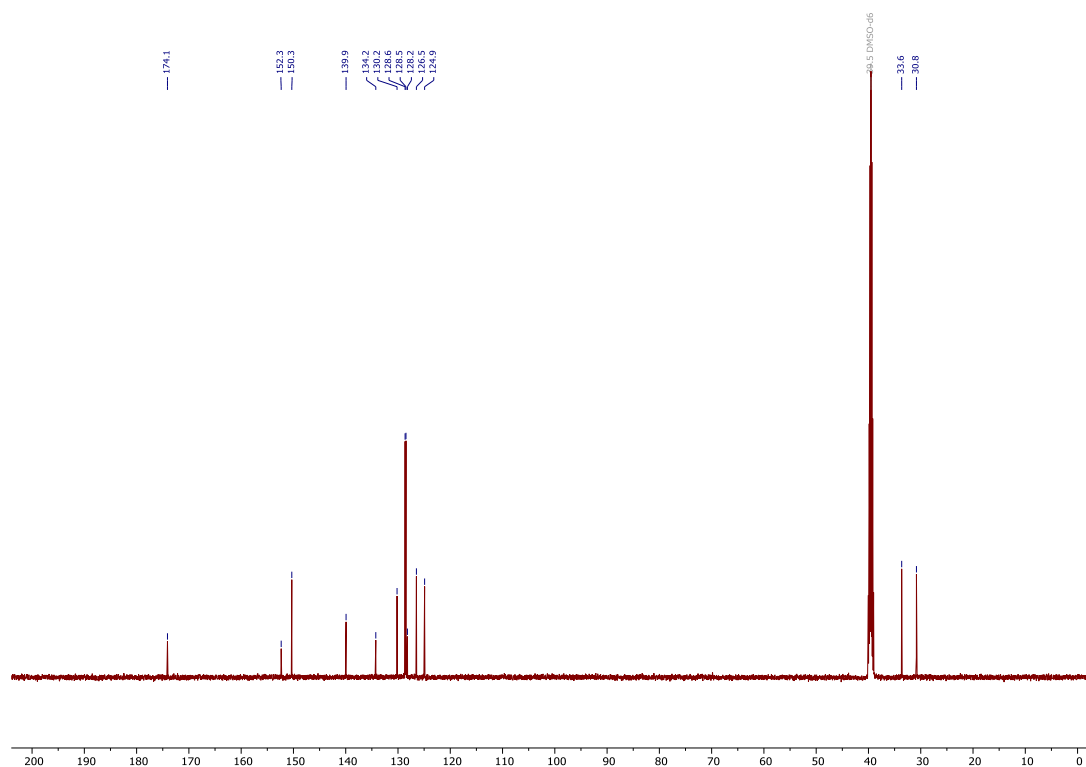


5-(Phenethylthio)pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidine (**3b**):

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

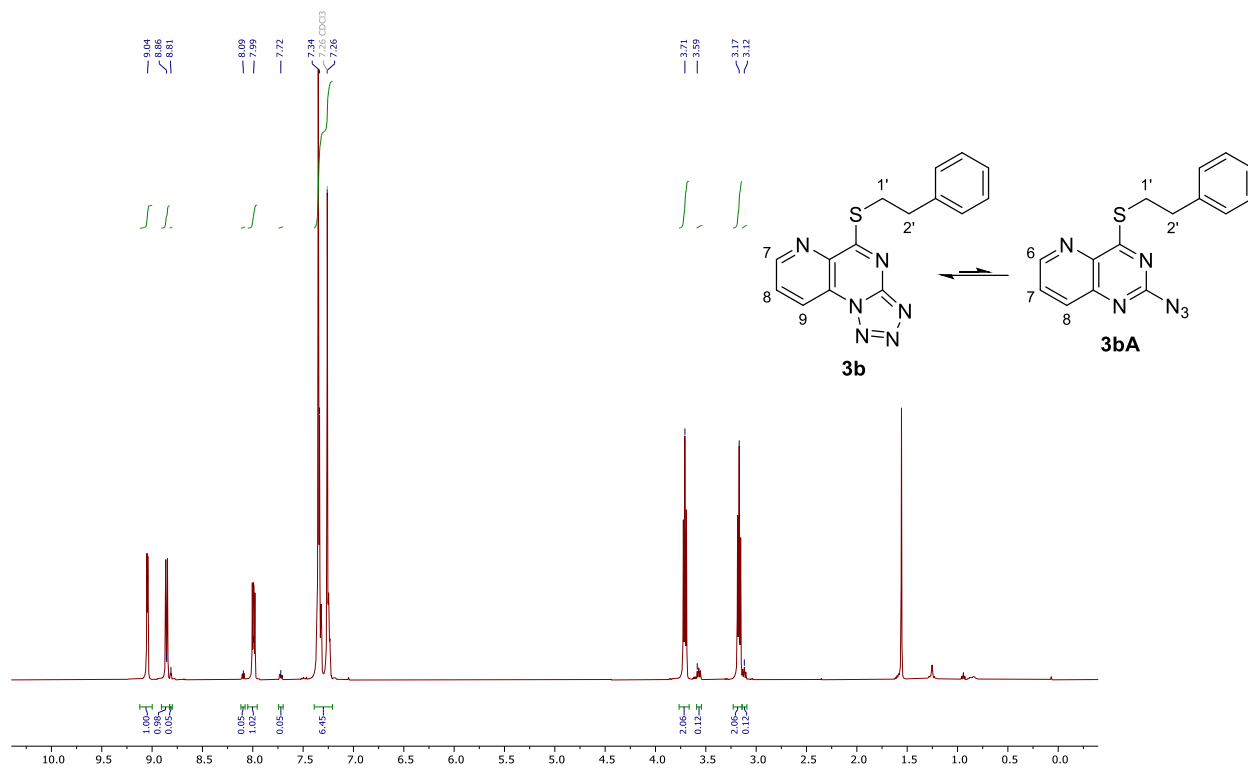


^{13}C NMR (125 MHz, $\text{DMSO-}d_6$)



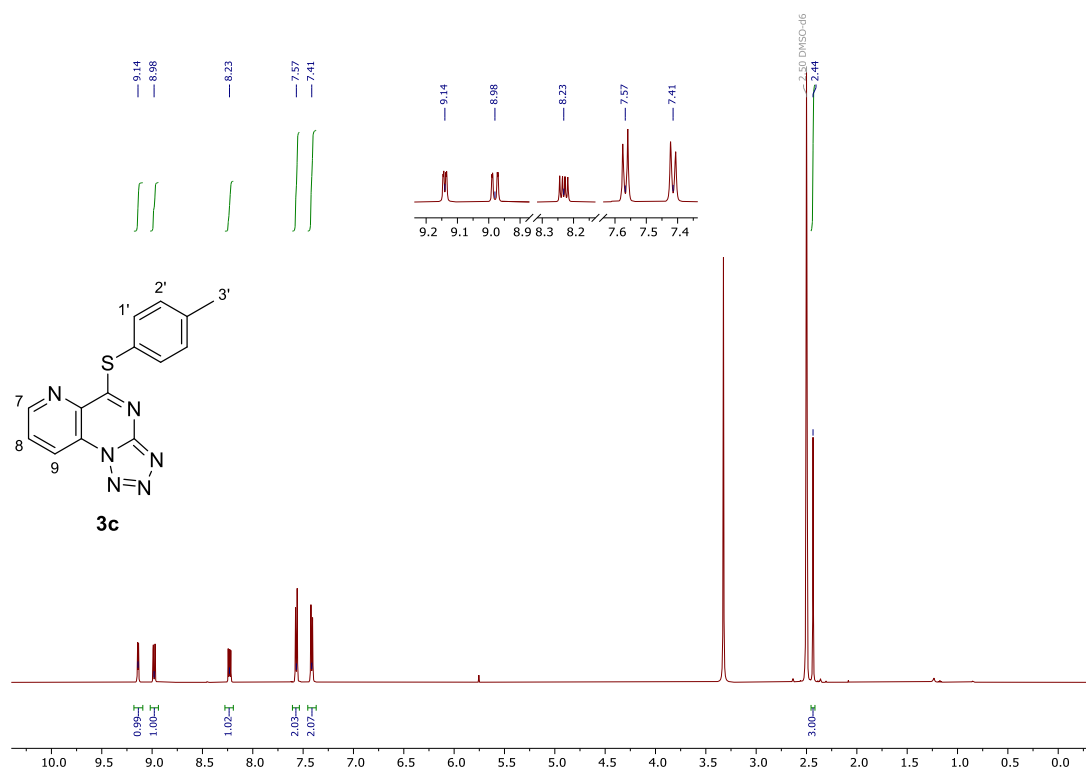
5-(Phenethylthio)pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidine (**3b**) and 2-azido-4-(phenethylthio)pyrido[3,2-*d*]pyrimidine (**3bA**):

¹H NMR (500 MHz, CDCl₃)

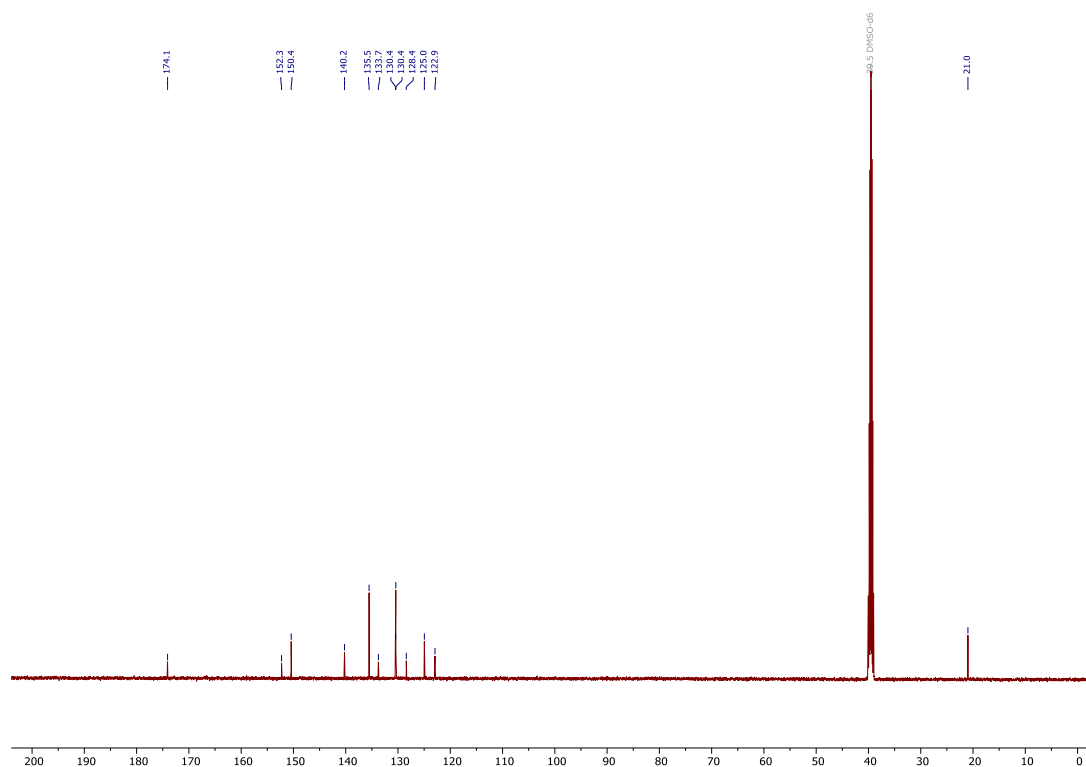


5-(*p*-Tolylthio)pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidine (**3c**):

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



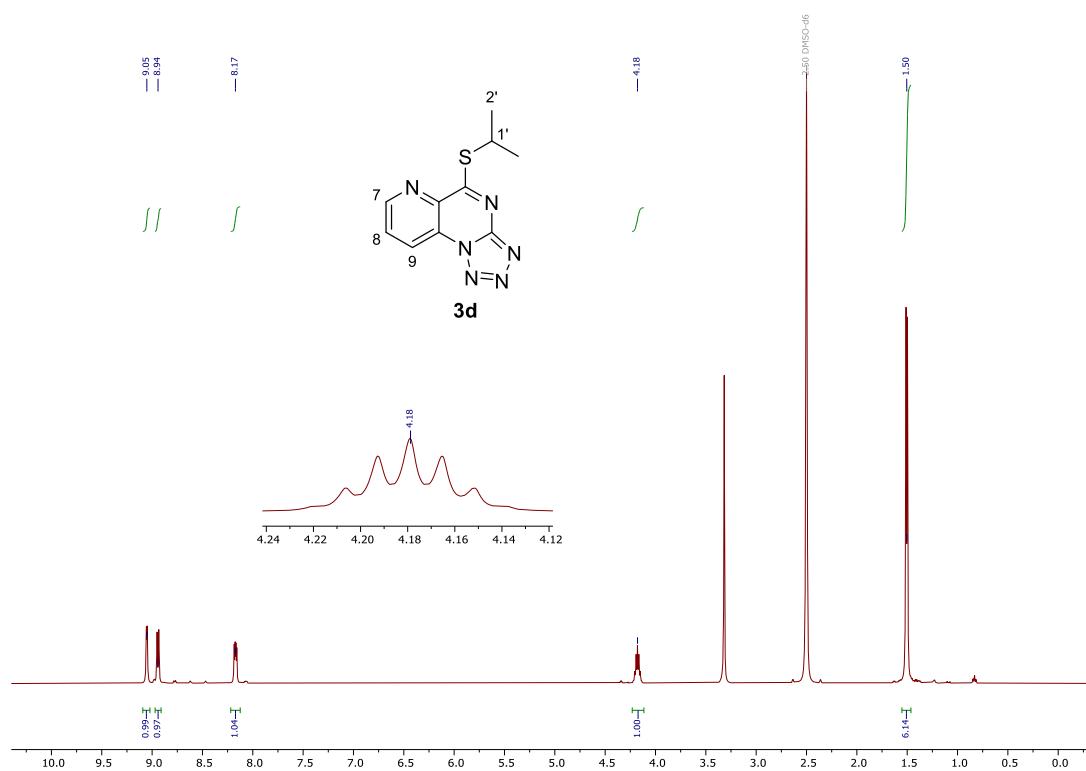
^{13}C NMR (125 MHz, $\text{DMSO-}d_6$)



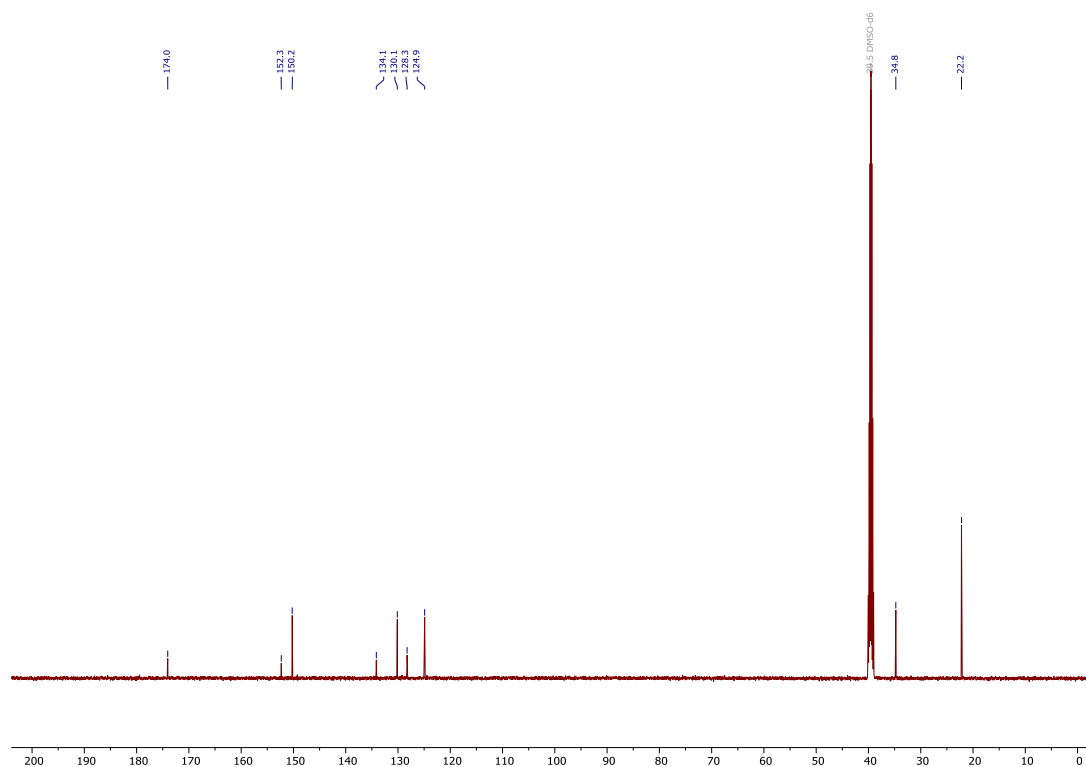
¹H NMR (500 MHz, CDCl₃)

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

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

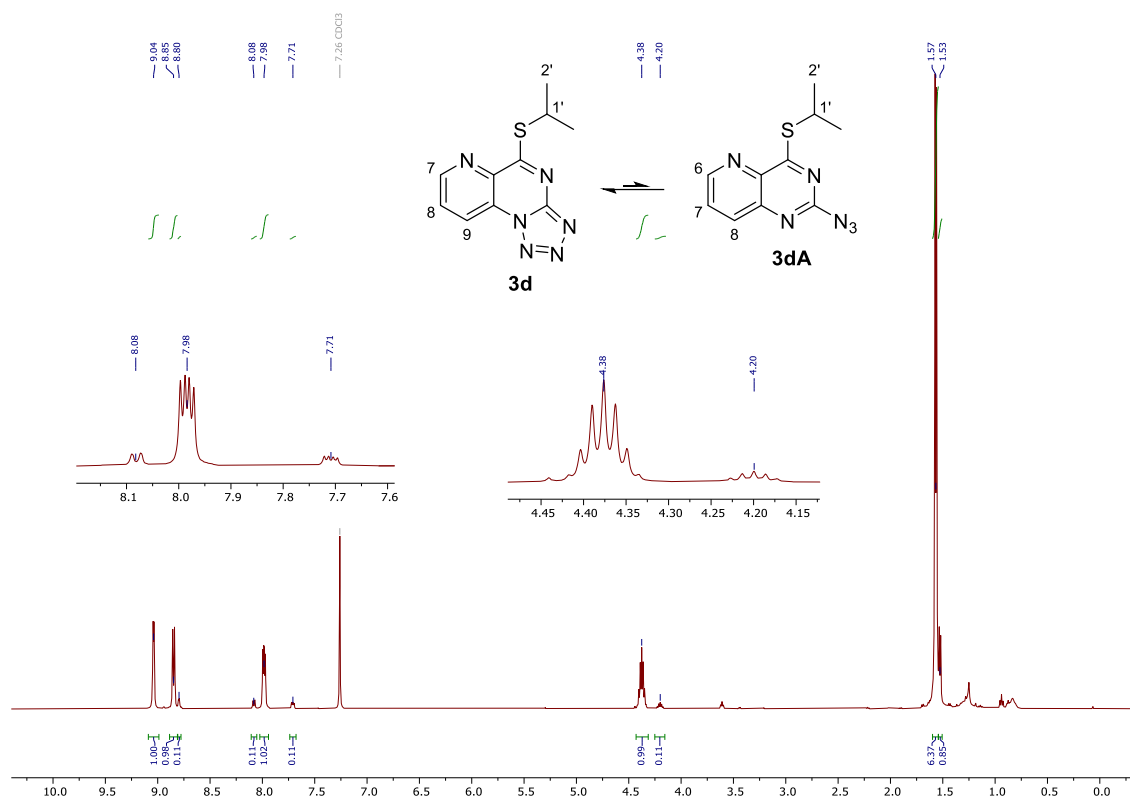


^{13}C NMR (125 MHz, $\text{DMSO-}d_6$)



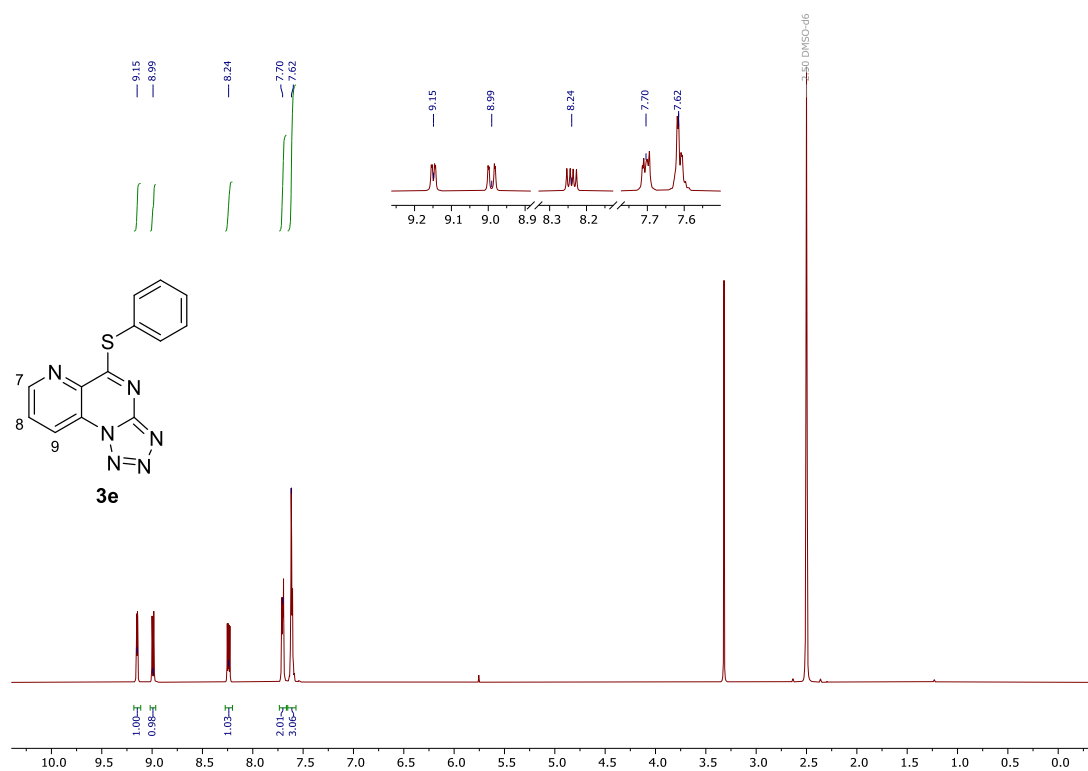
5-(Isopropylthio)pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidine (**3d**) and 2-azido-4-(isopropylthio)pyrido[3,2-*d*]pyrimidine (**3dA**):

^1H NMR (500 MHz, CDCl_3)

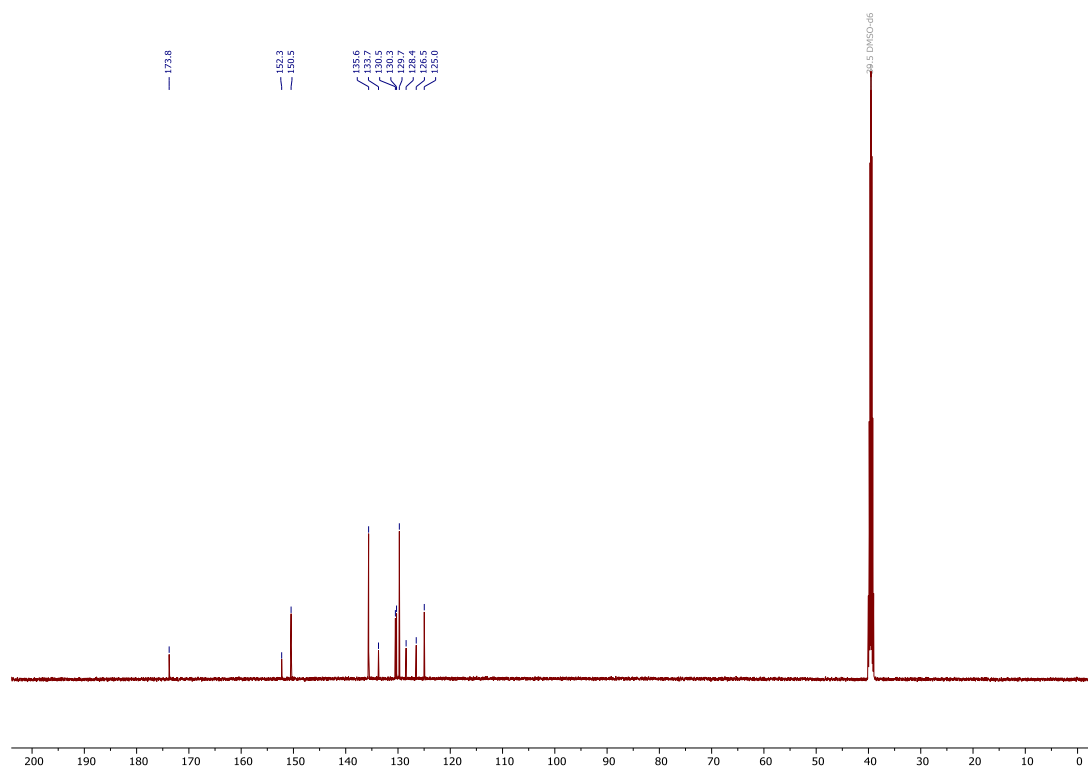


5-(Phenylthio)pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidine (**3e**):

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

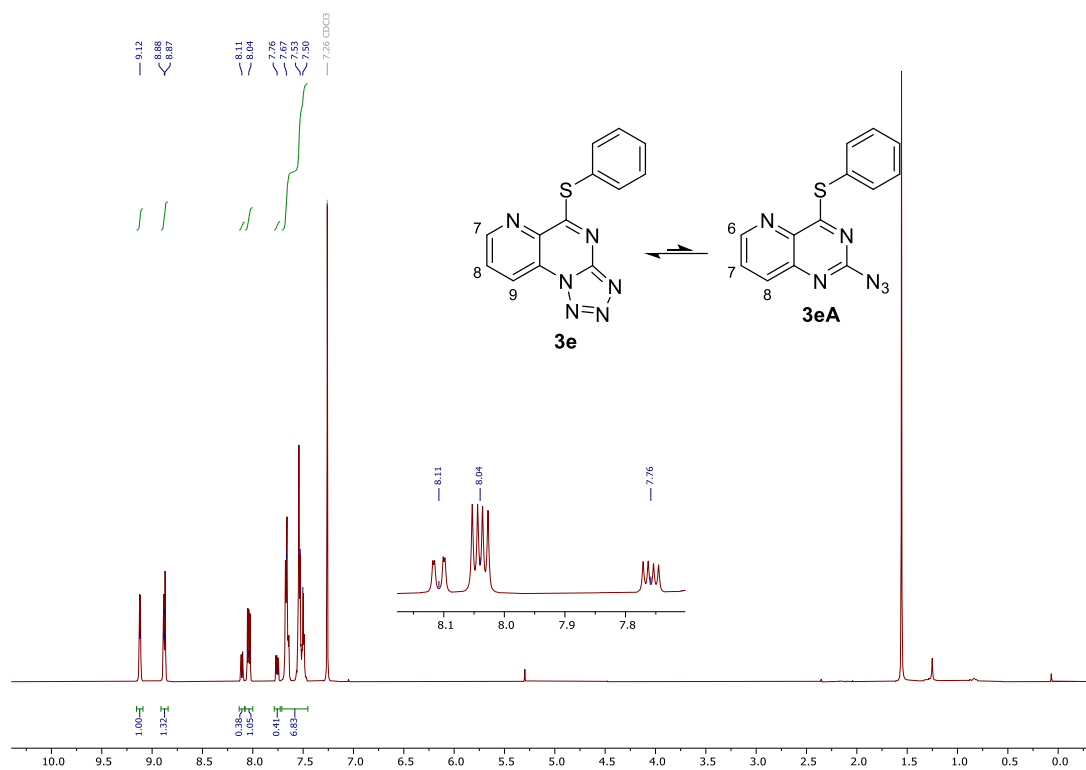


^{13}C NMR (125 MHz, $\text{DMSO-}d_6$)



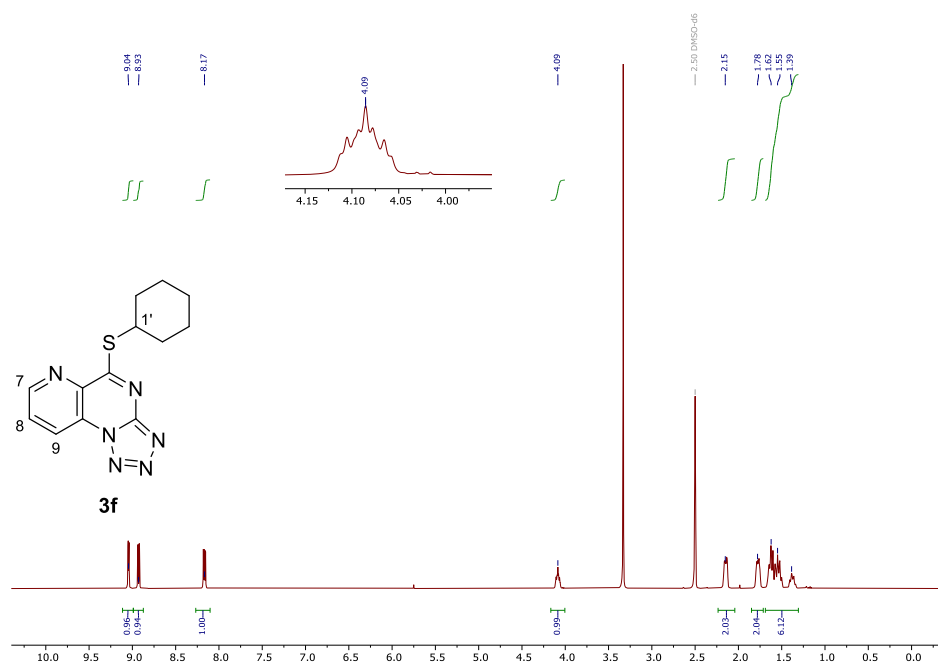
5-(Phenylthio)pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidine (**3e**) and 2-azido-4-(phenylthio)pyrido[3,2-*d*]pyrimidine (**3eA**):

¹H NMR (500 MHz, CDCl₃)

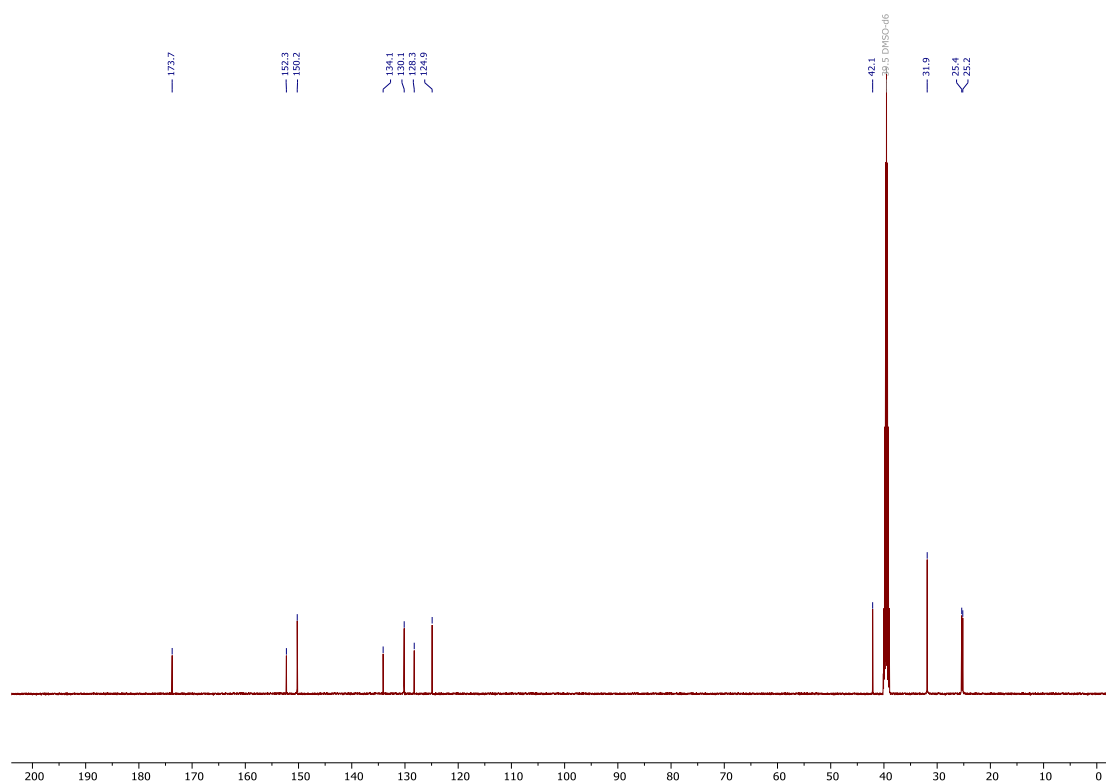


5-(Cyclohexylthio)pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidine (**3f**):

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

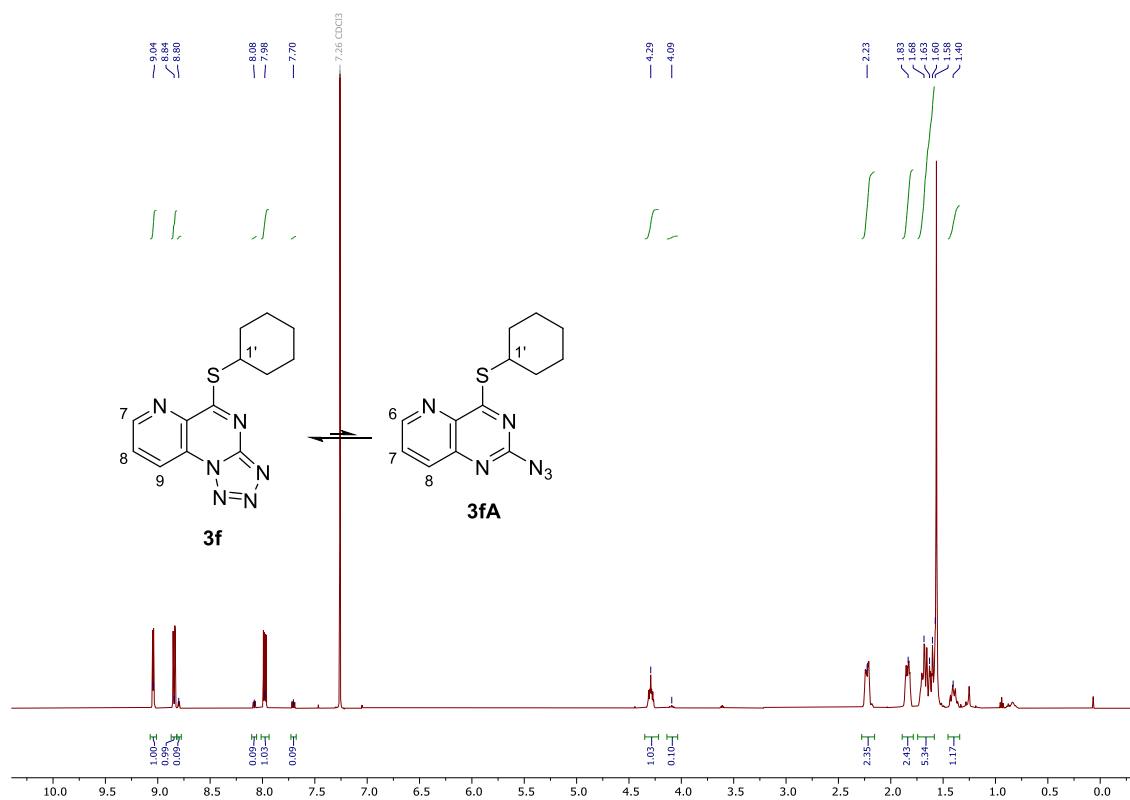


^{13}C NMR (125 MHz, $\text{DMSO-}d_6$)



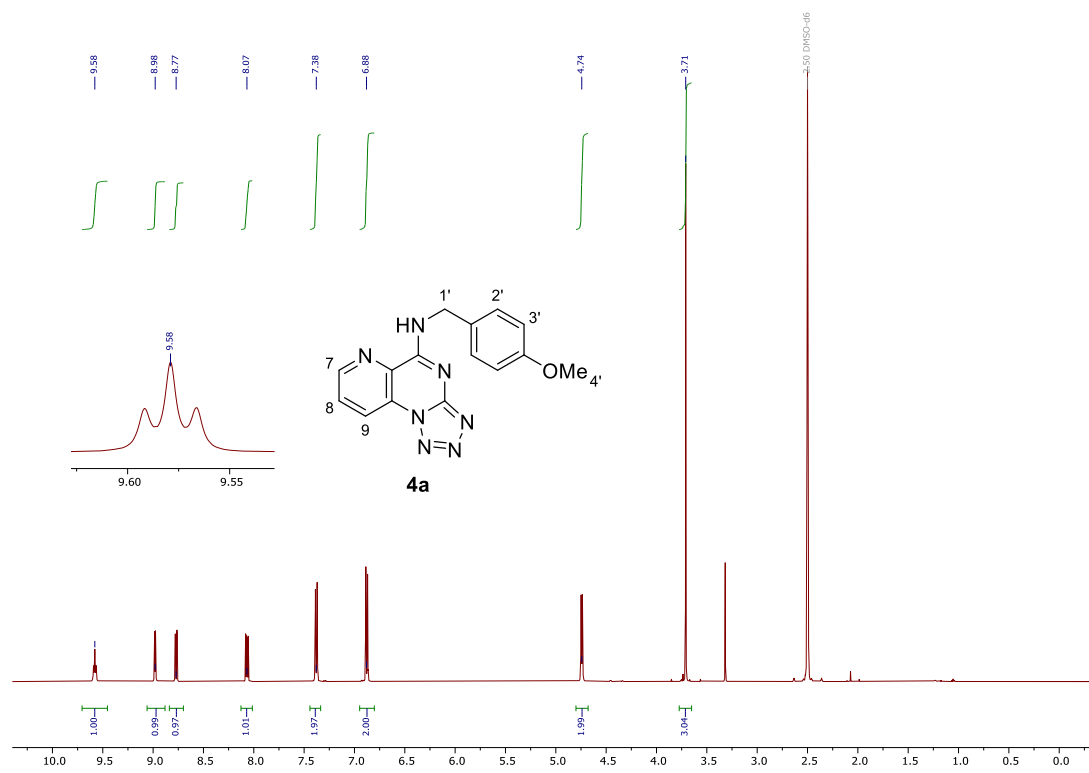
5-(Cyclohexylthio)pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidine (**3f**) and 2-azido-4-(cyclohexylthio)pyrido[3,2-*d*]pyrimidine (**3fA**):

¹H NMR (500 MHz, CDCl₃)

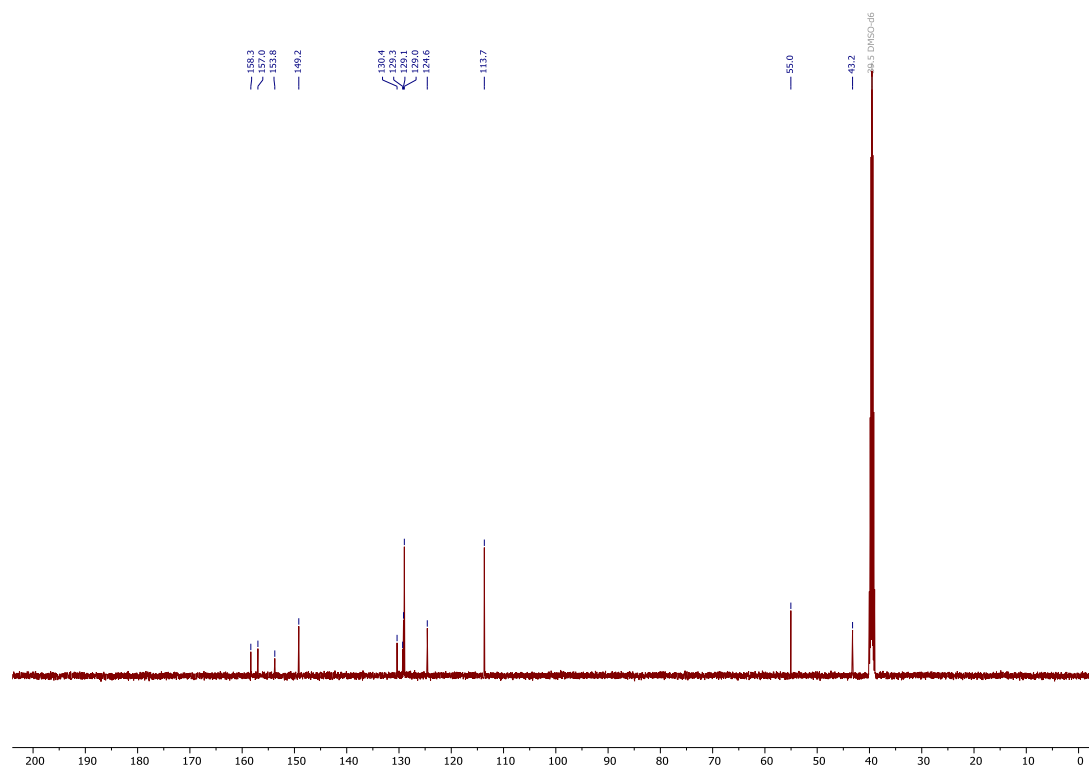


N-(4-Methoxybenzyl)pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidin-5-amine (**4a**):

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

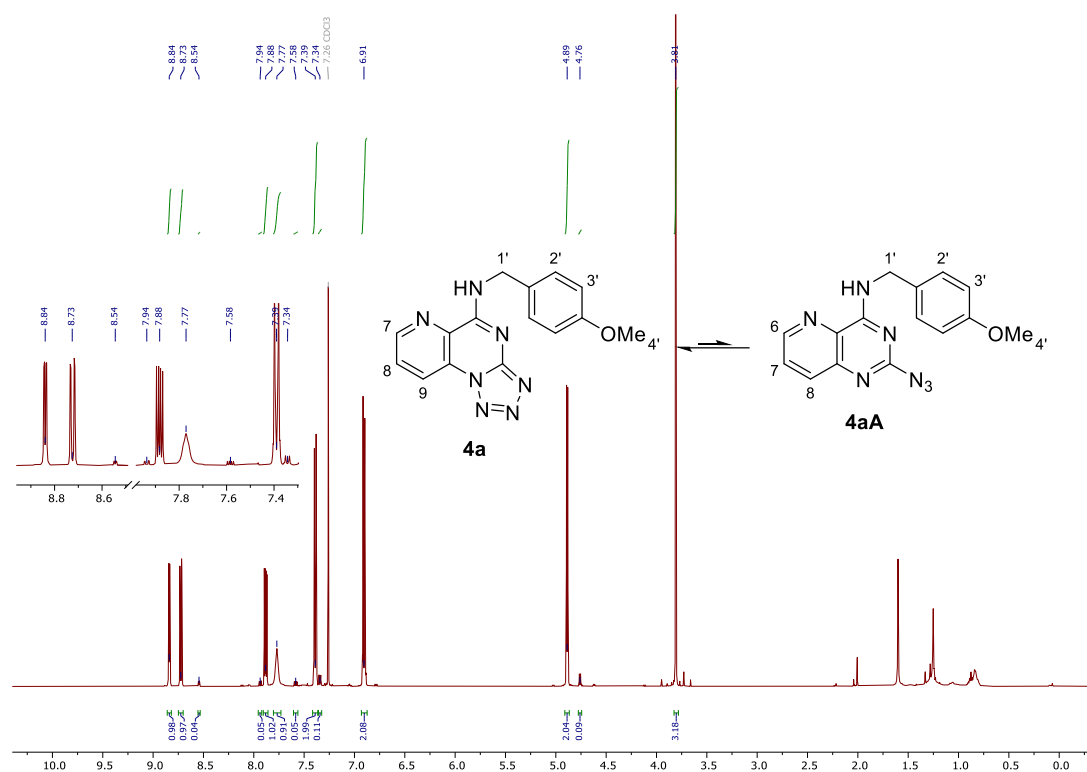


^{13}C NMR (125 MHz, $\text{DMSO-}d_6$)



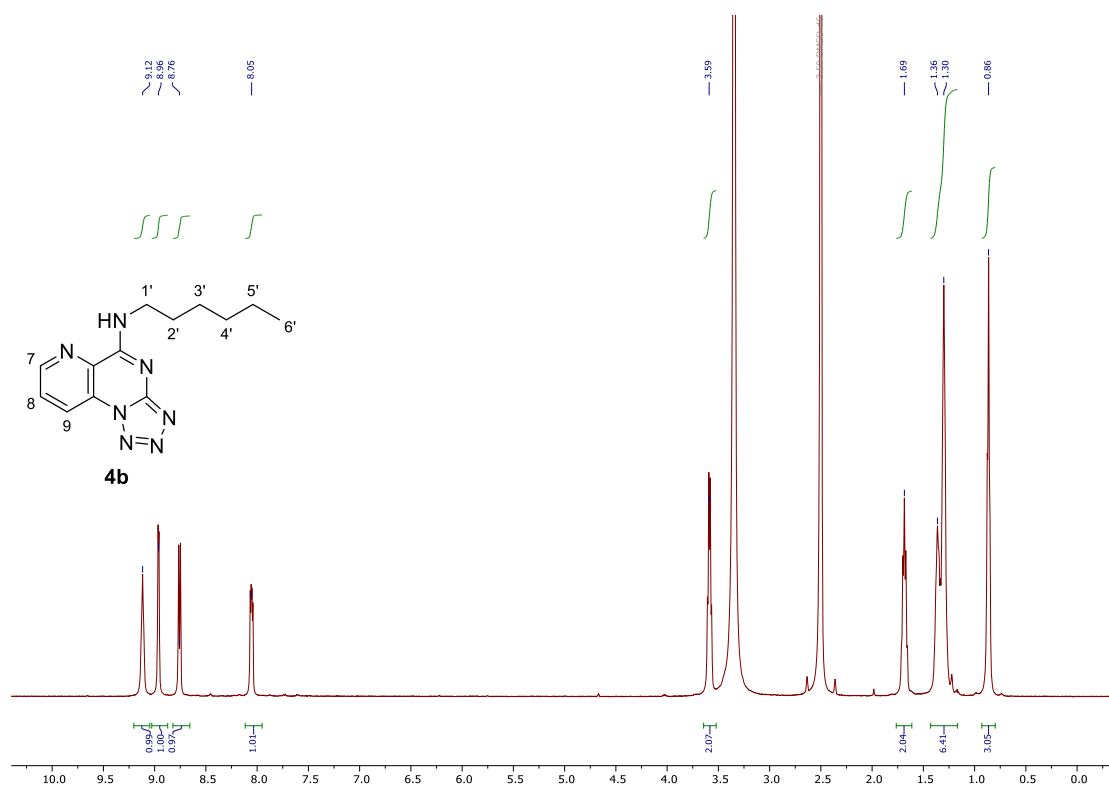
N-(4-Methoxybenzyl)pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidin-5-amine (**4a**) and 2-azido-*N*-(4-methoxybenzyl)pyrido[3,2-*d*]pyrimidin-4-amine (**4aA**):

¹H NMR (500 MHz, CDCl₃)

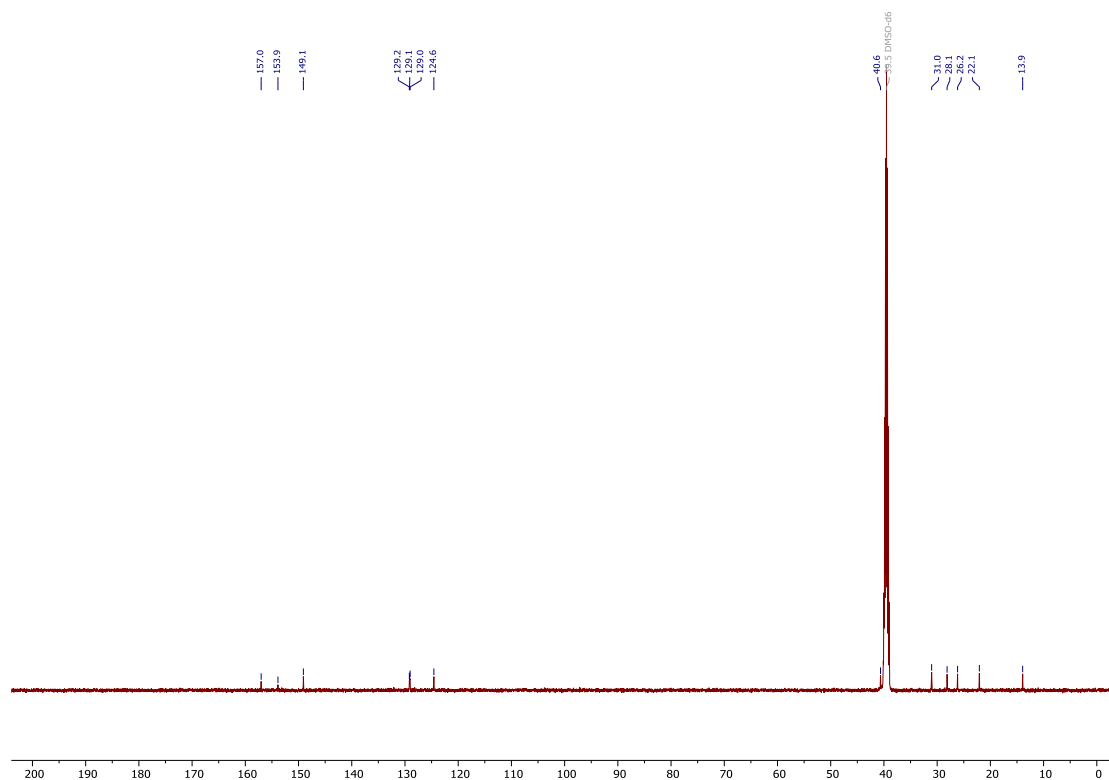


N-Hexylpyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidin-5-amine (**4b**):

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

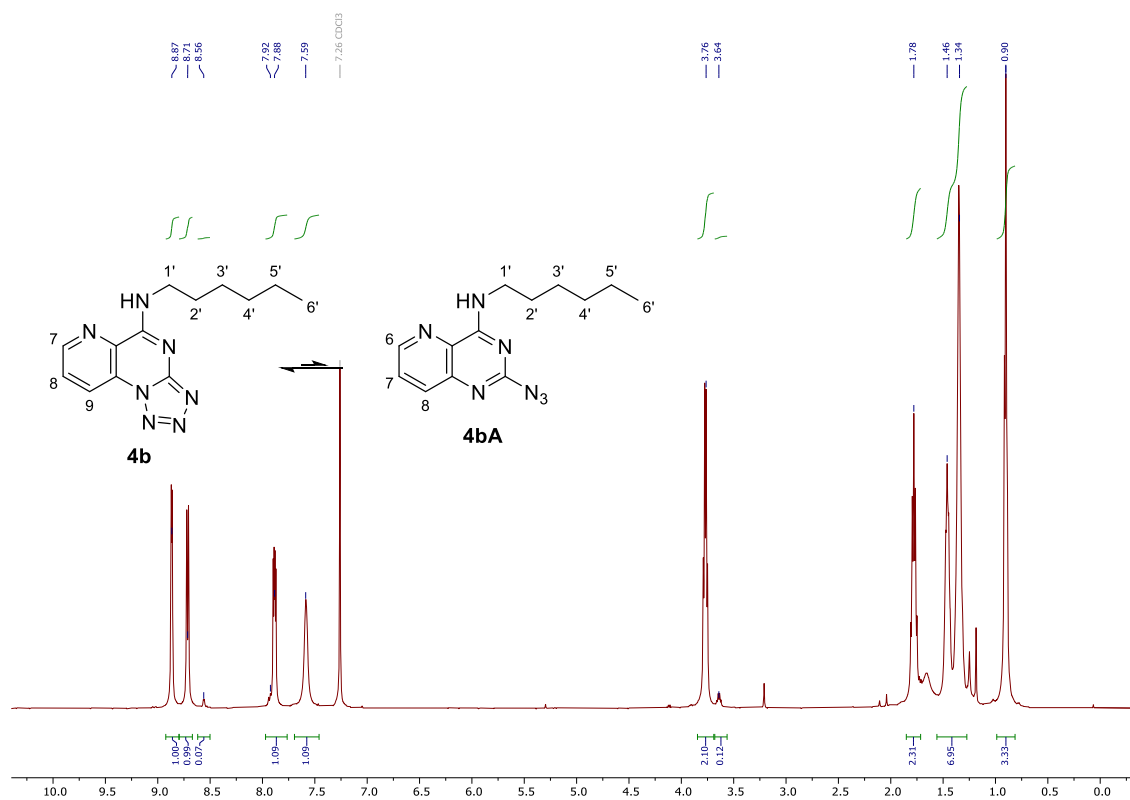


^{13}C NMR (125 MHz, $\text{DMSO}-d_6$)



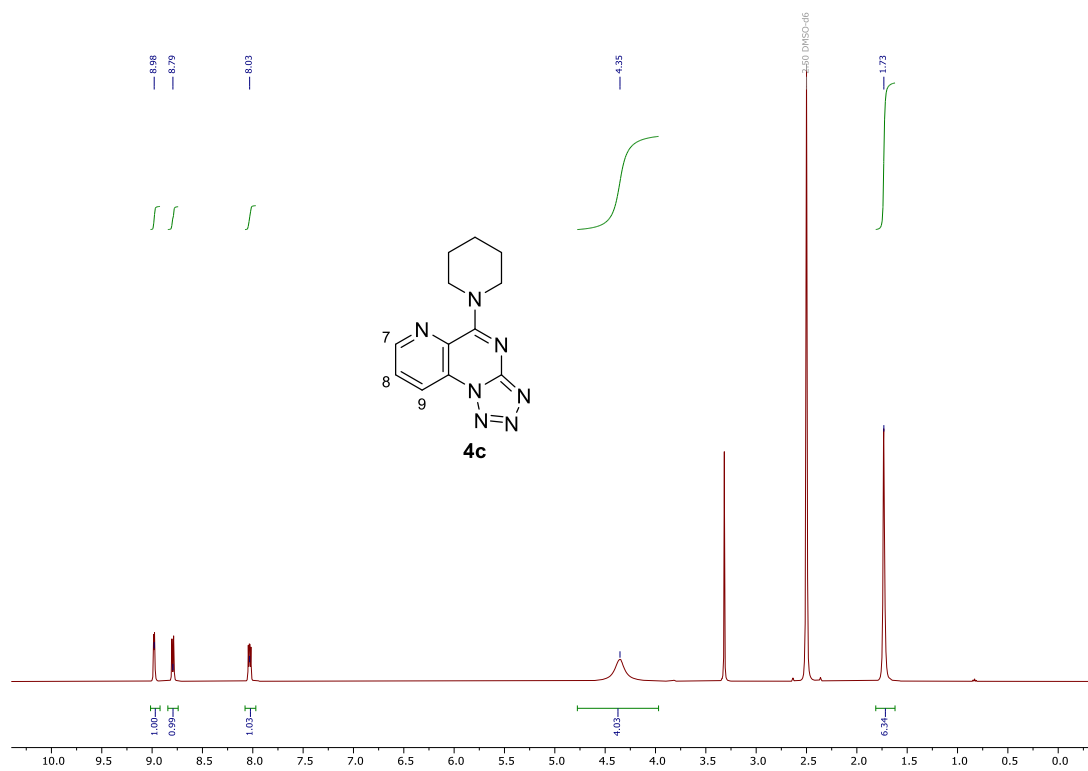
2-Azido-*N*-hexylpyrido[3,2-*d*]pyrimidin-4-amine (**4bA**) and *N*-hexylpyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidin-5-amine (**4b**):

^1H NMR (500 MHz, CDCl_3)

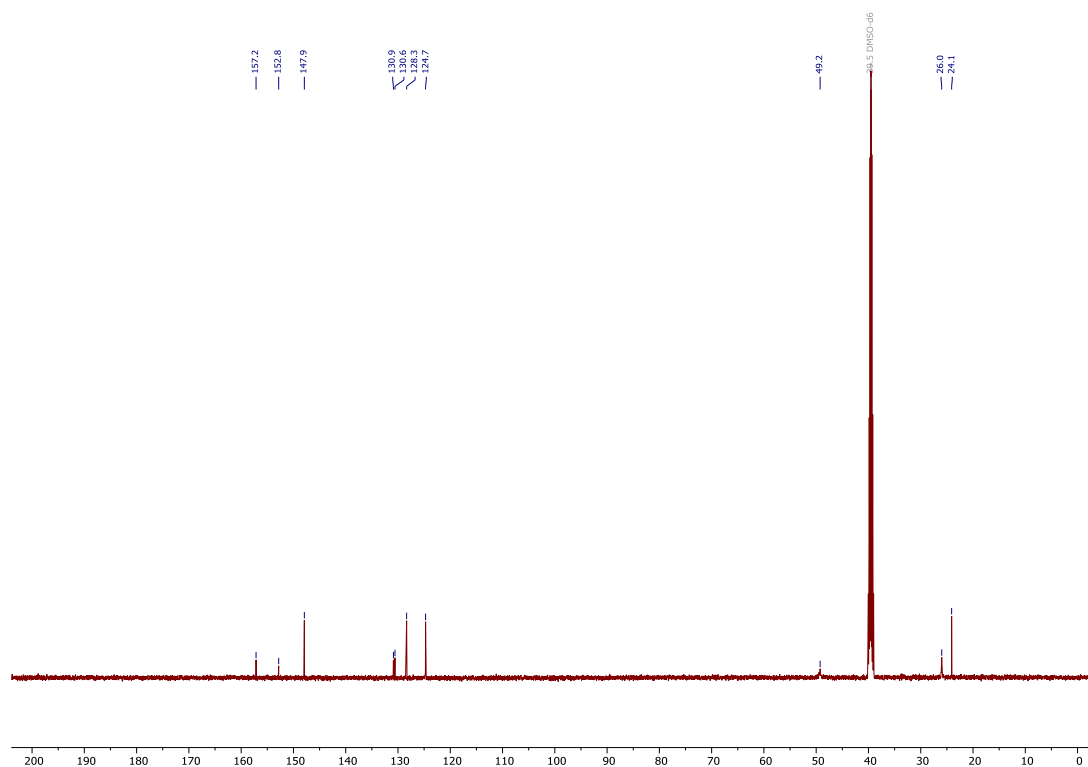


5-(Piperidin-1-yl)pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidine (**4c**):

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

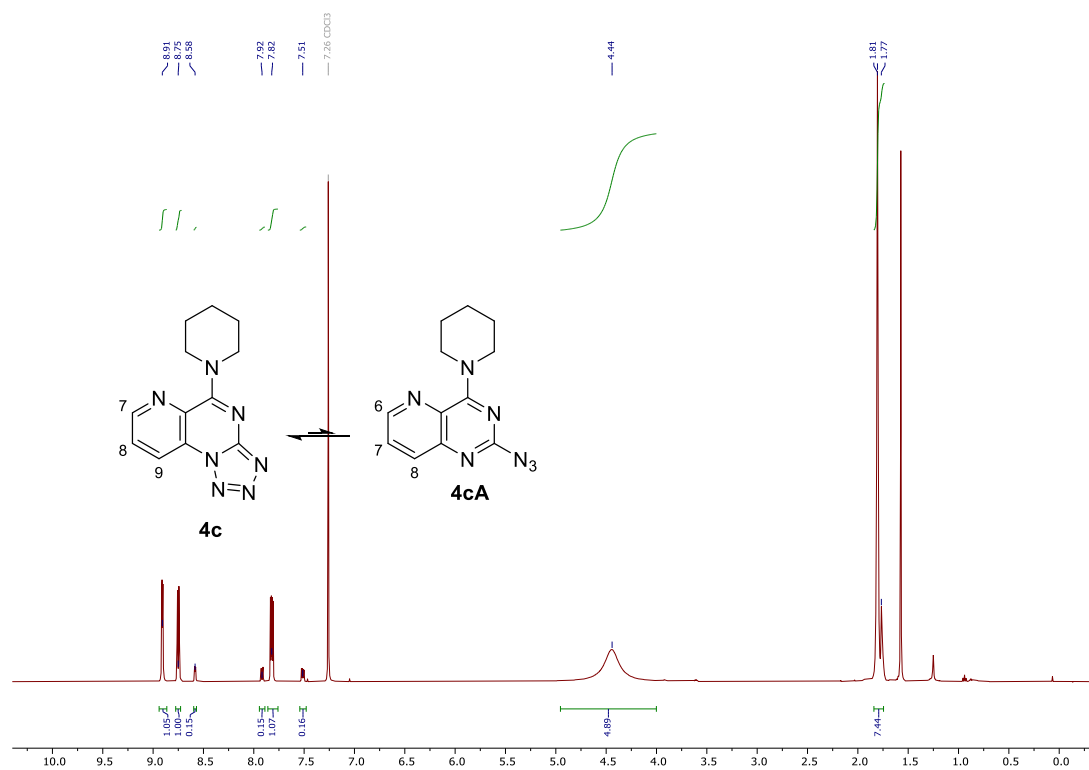


^{13}C NMR (125 MHz, $\text{DMSO-}d_6$)



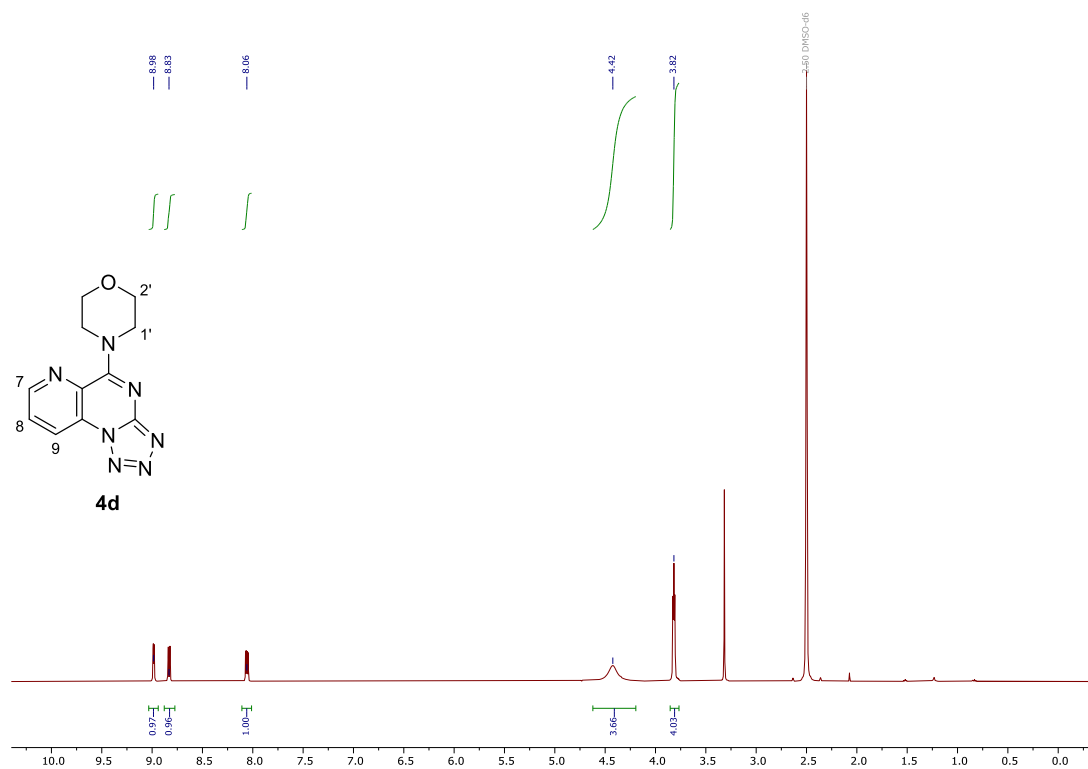
4-(Pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidin-5-yl)morpholine (**4c**) and 2-azido-4-(piperidin-1-yl)pyrido[3,2-*d*]pyrimidine (**4cA**):

^1H NMR (500 MHz, CDCl_3)

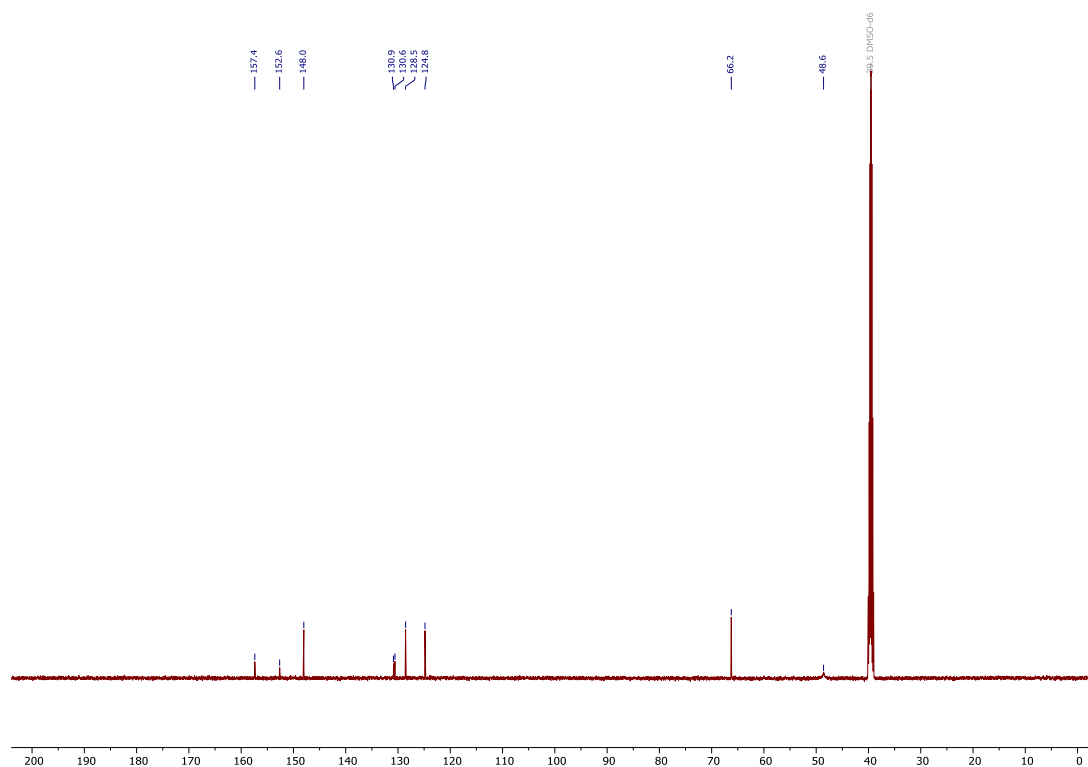


4-(Pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidin-5-yl)morpholine (**4d**):

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

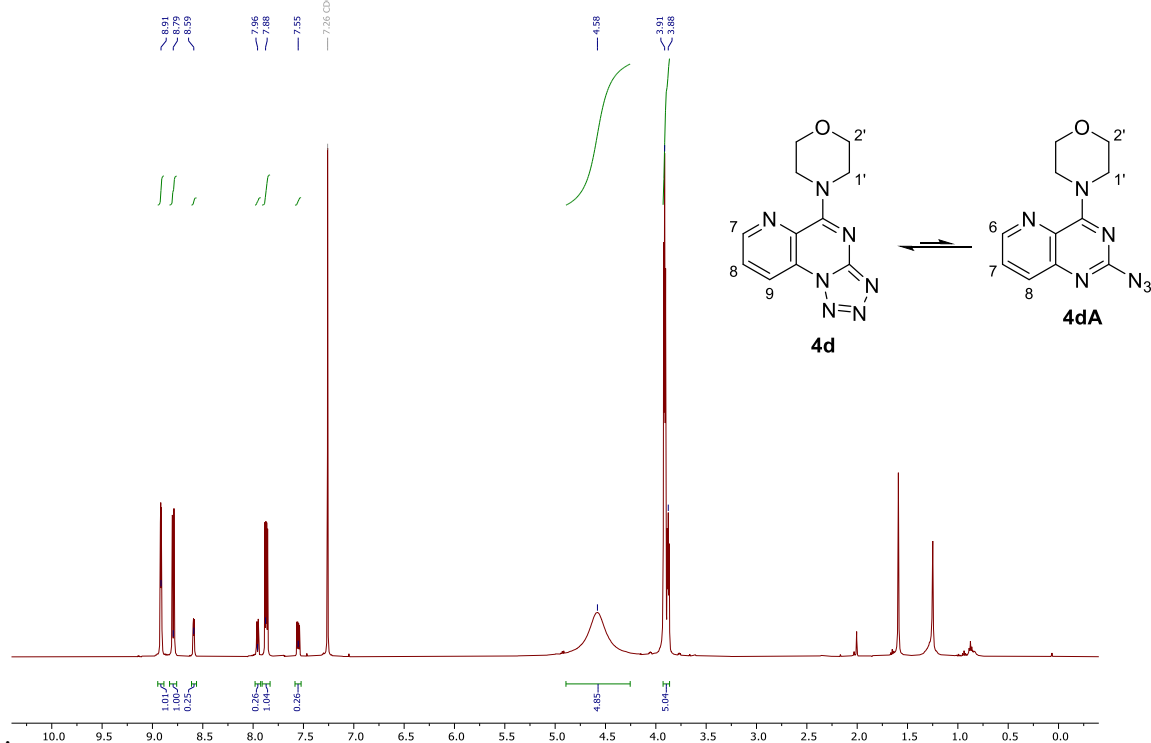


^{13}C NMR (125 MHz, $\text{DMSO-}d_6$)



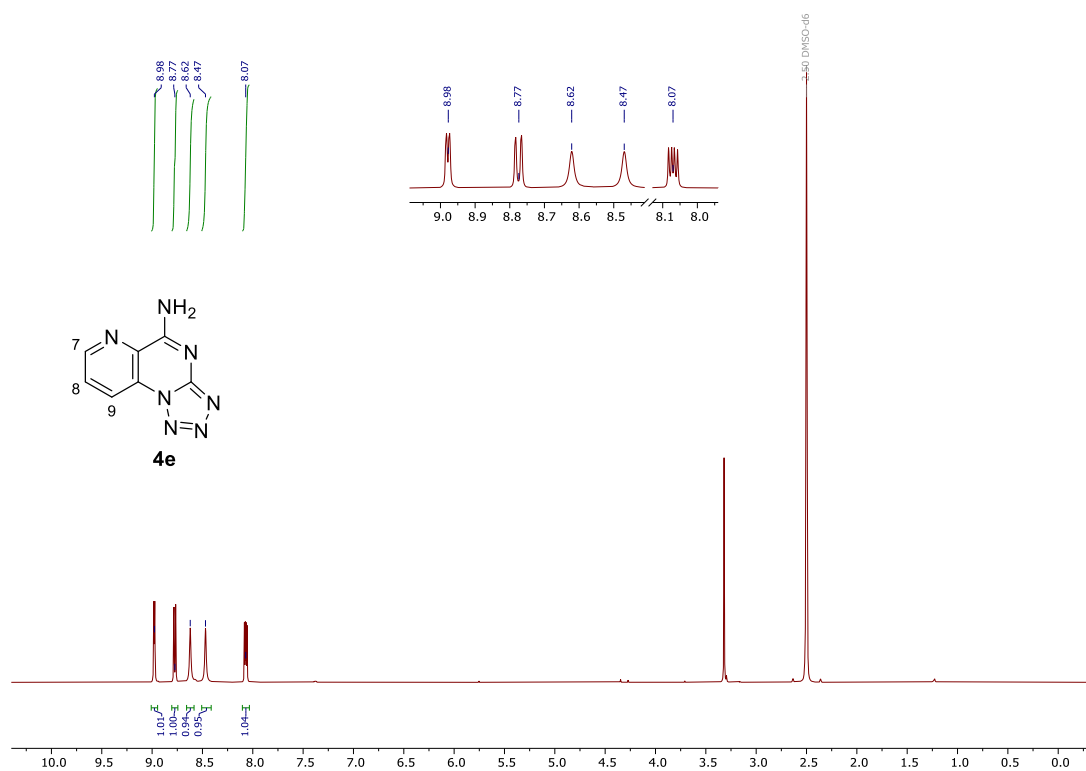
4-(Pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidin-5-yl)morpholine (**4d**) and 4-(2-azidopyrido[3,2-*d*]pyrimidin-4-yl)morpholine (**4dA**):

¹H NMR (500 MHz, CDCl₃)

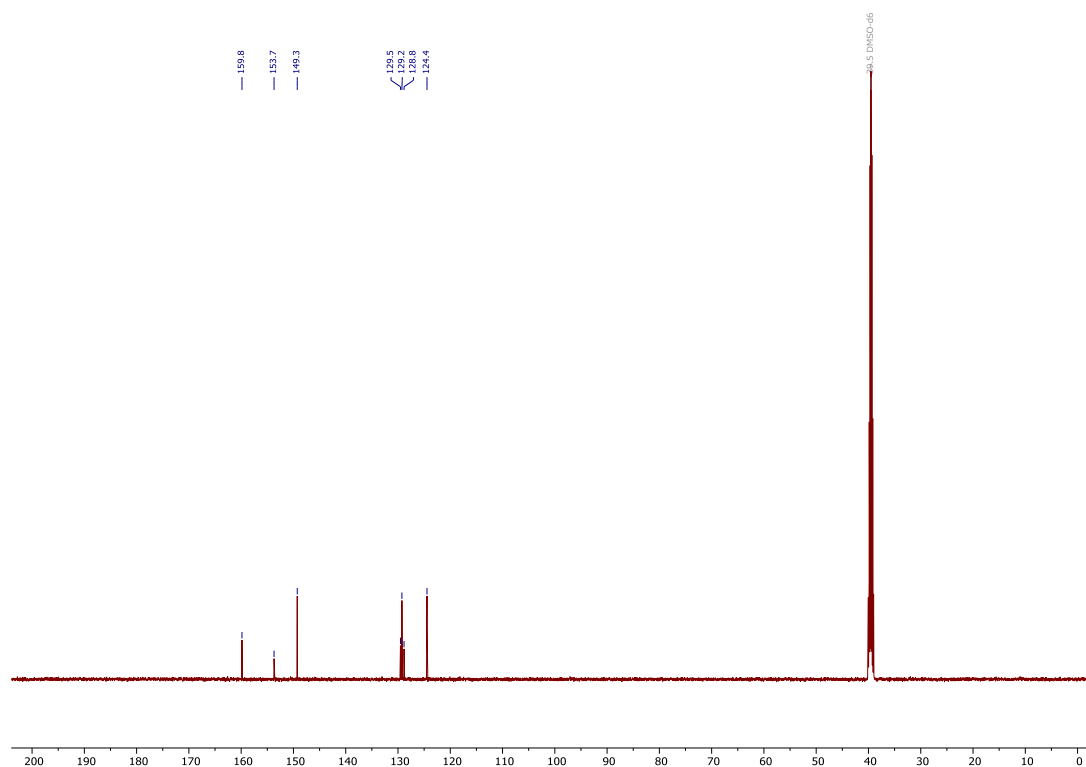


Pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidin-5-amine (**4e**):

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

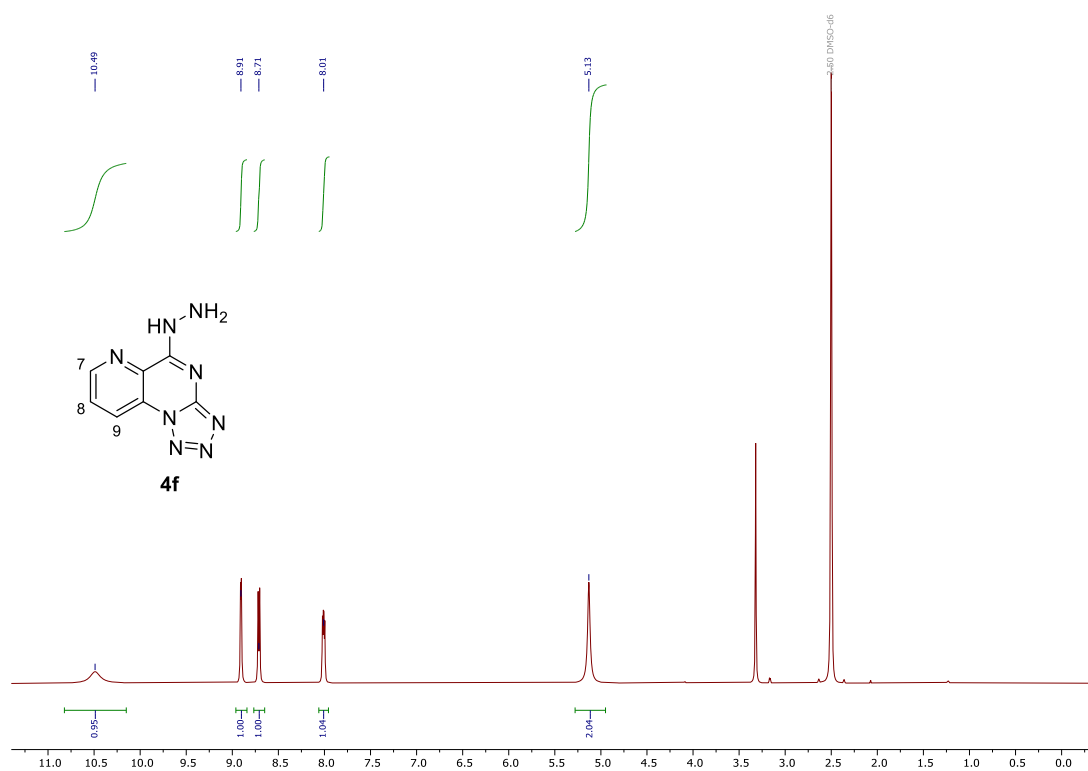


^{13}C NMR (125 MHz, $\text{DMSO-}d_6$)

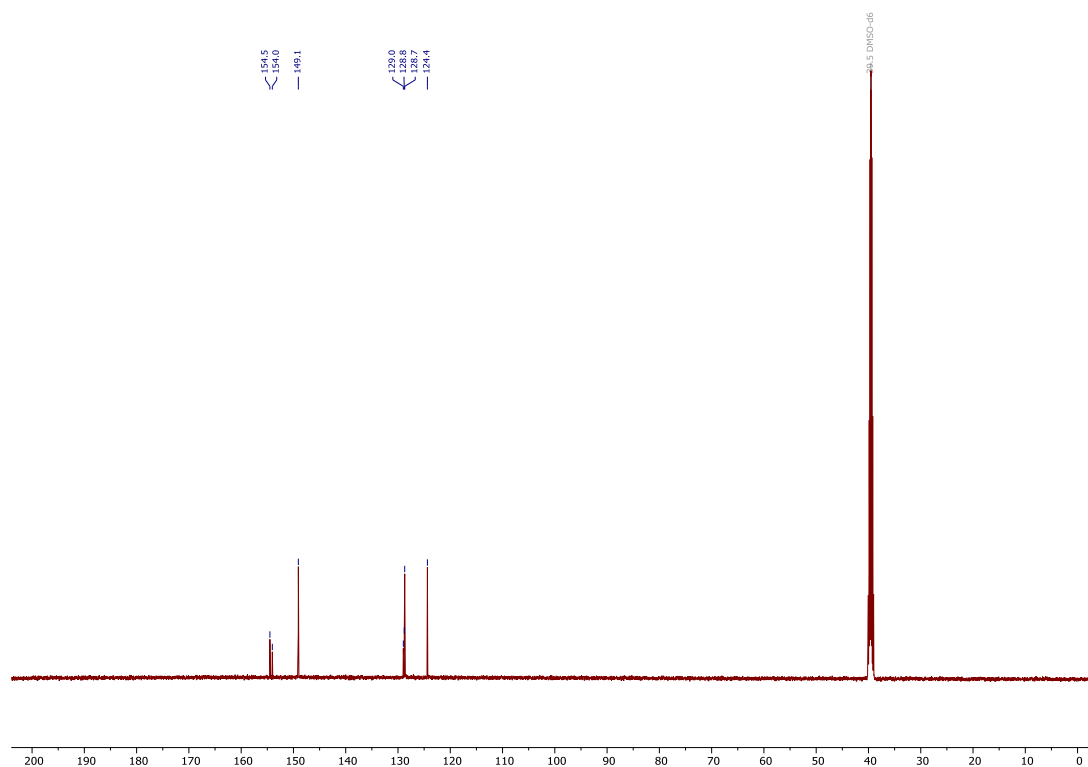


5-Hydrazinylpyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidine (**4f**):

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

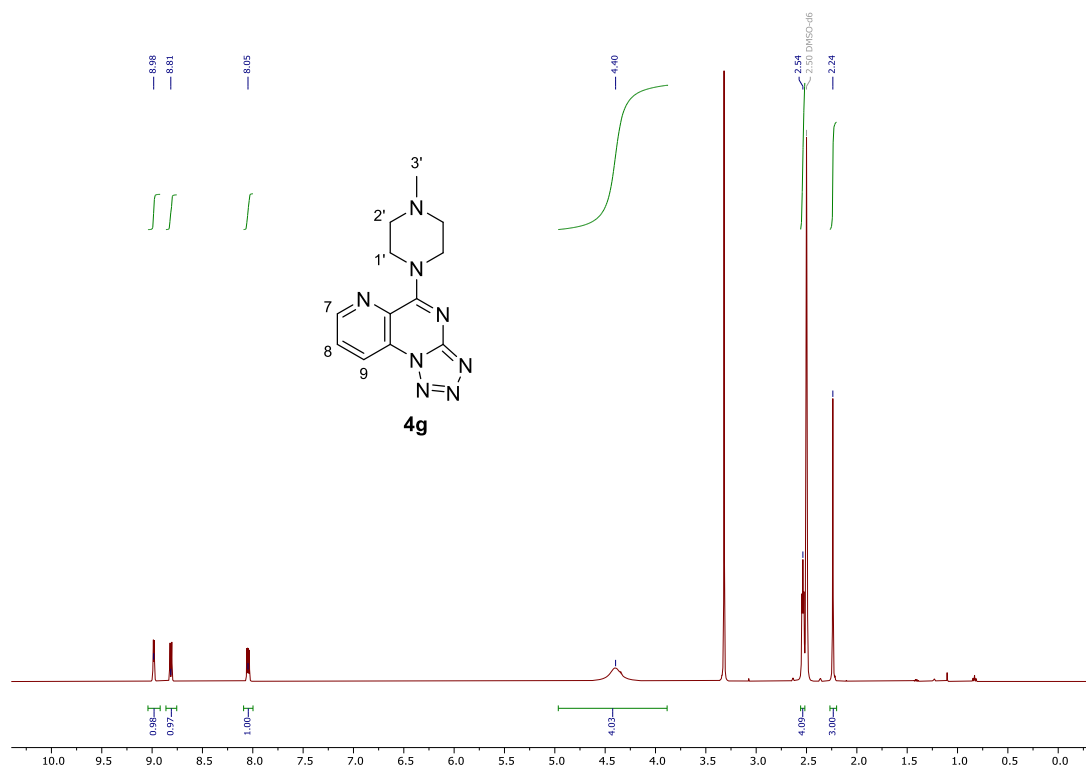


^{13}C NMR (125 MHz, $\text{DMSO-}d_6$)

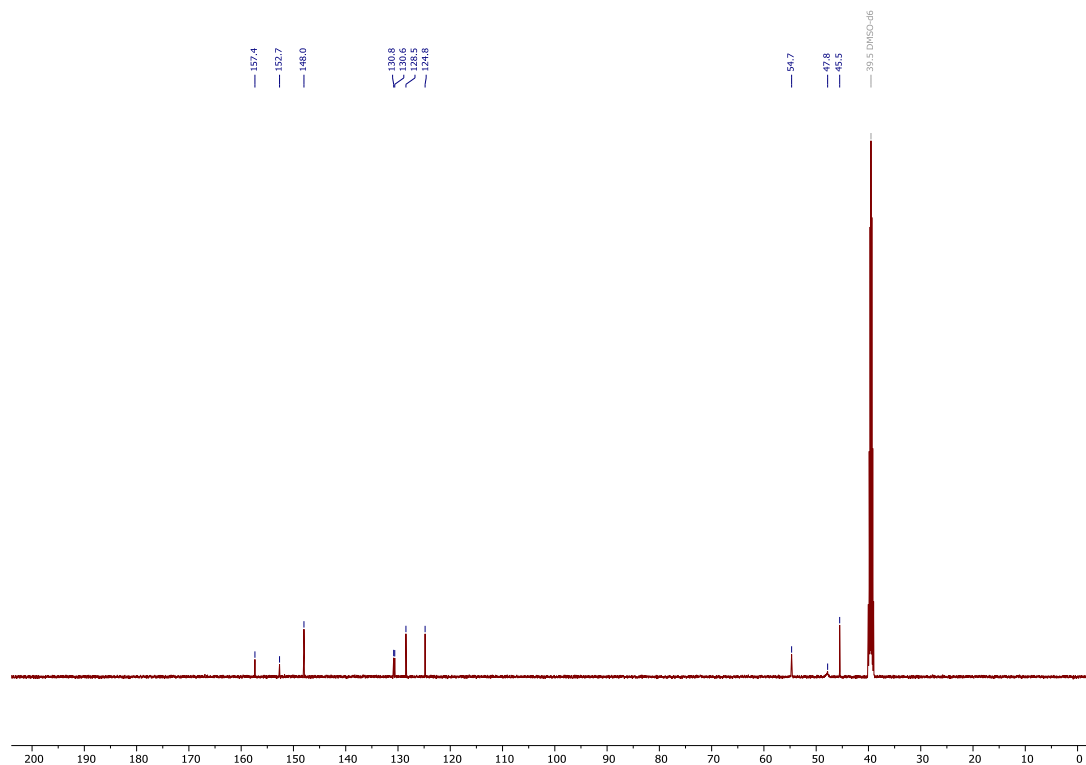


5-(4-Methylpiperazin-1-yl)pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidine (**4g**):

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

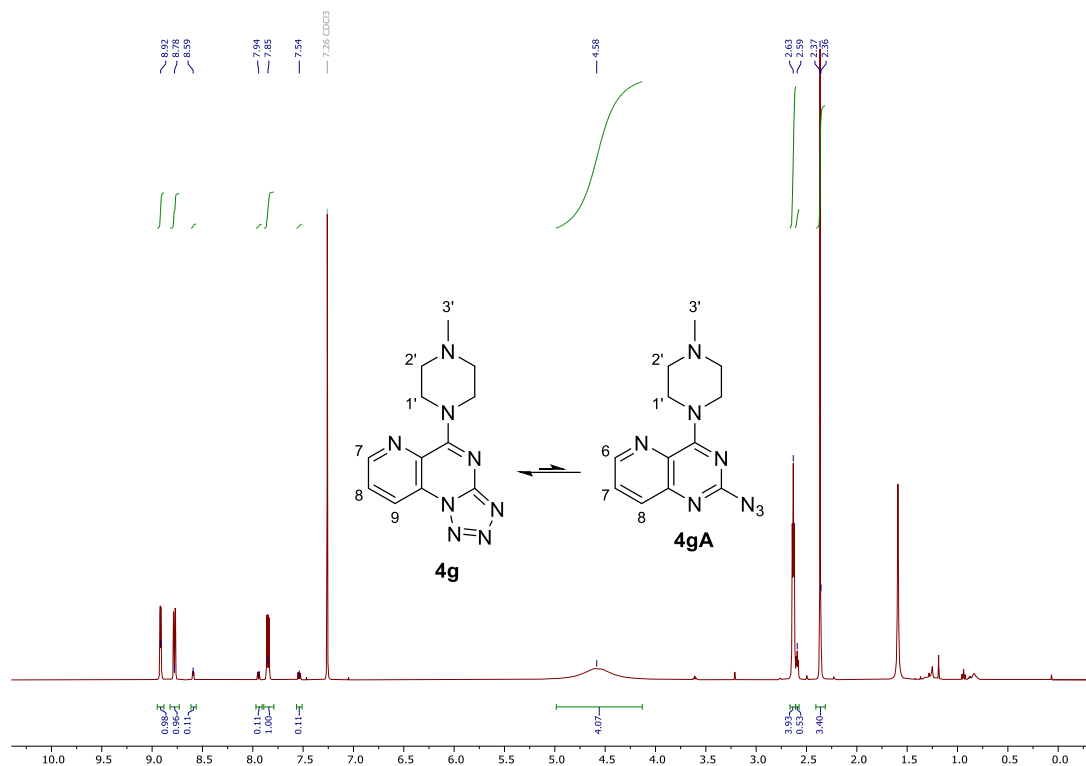


^{13}C NMR (125 MHz, $\text{DMSO-}d_6$)



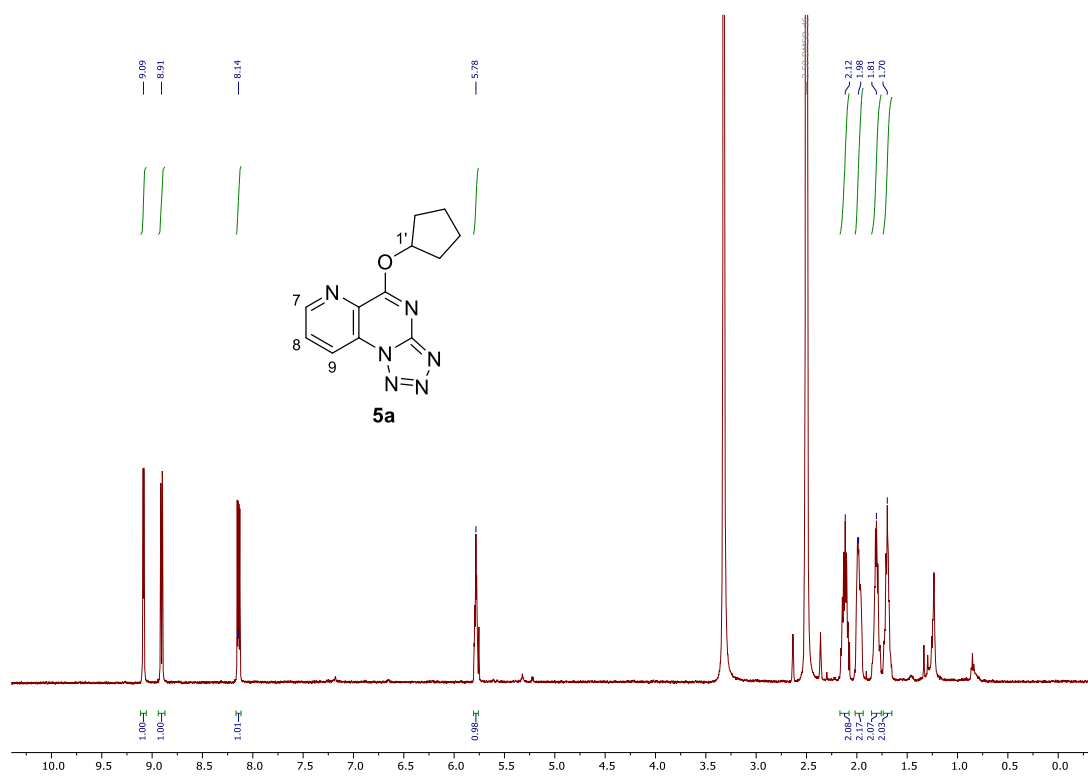
5-(4-Methylpiperazin-1-yl)pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidine (**4g**) and 2-azido-4-(4-methylpiperazin-1-yl)pyrido[3,2-*d*]pyrimidine (**4gA**):

¹H NMR (500 MHz, CDCl₃)

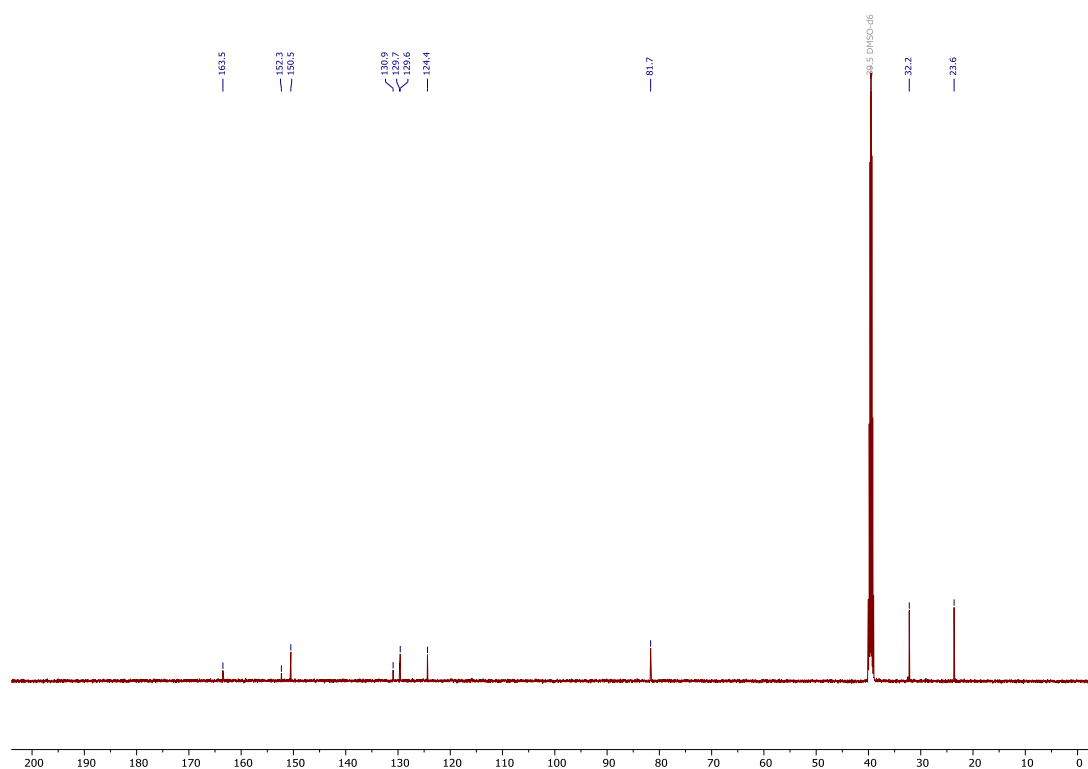


5-(Cyclopentyloxy)pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidine (**5a**):

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

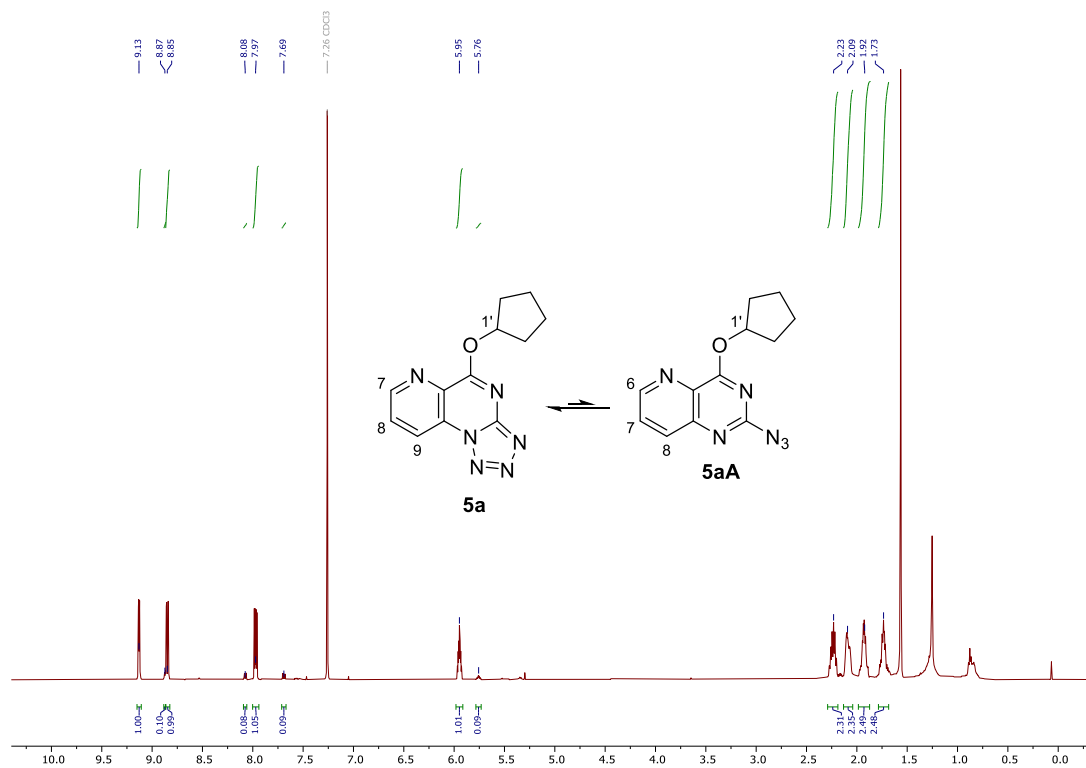


^{13}C NMR (125 MHz, $\text{DMSO}-d_6$)



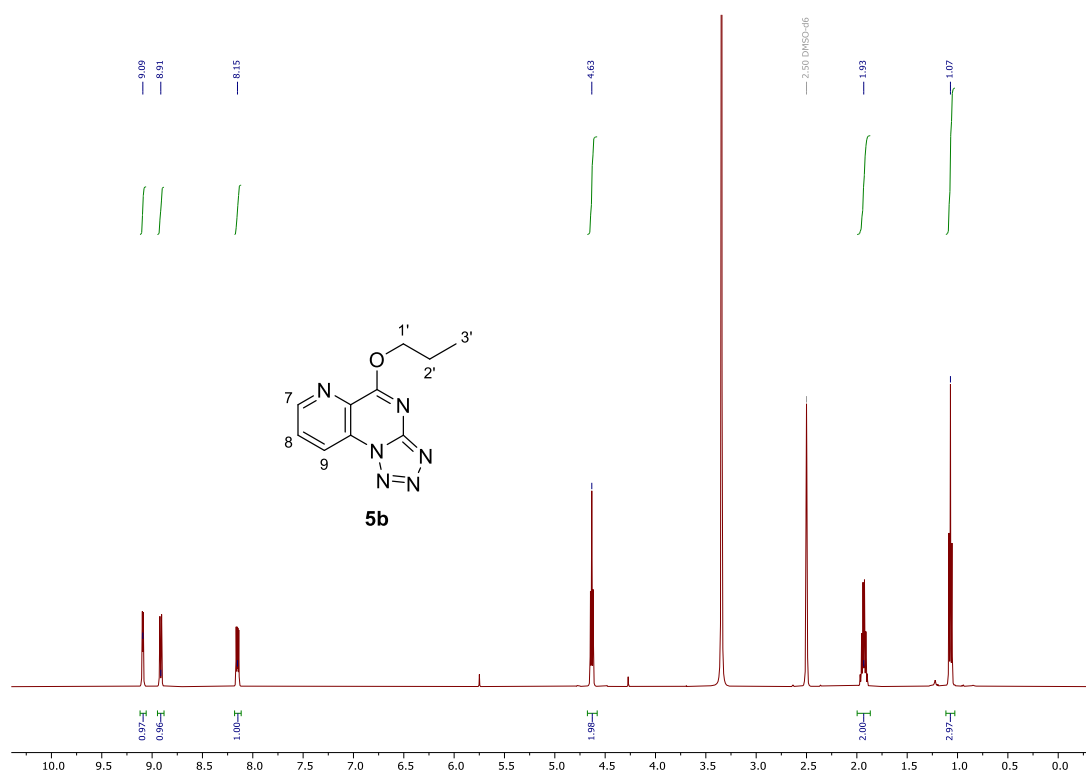
5-(Cyclopentyloxy)pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidine (**5a**) and 2-azido-4-(cyclopentyloxy)pyrido[3,2-*d*]pyrimidine (**5aA**):

^1H NMR (500 MHz, CDCl_3)

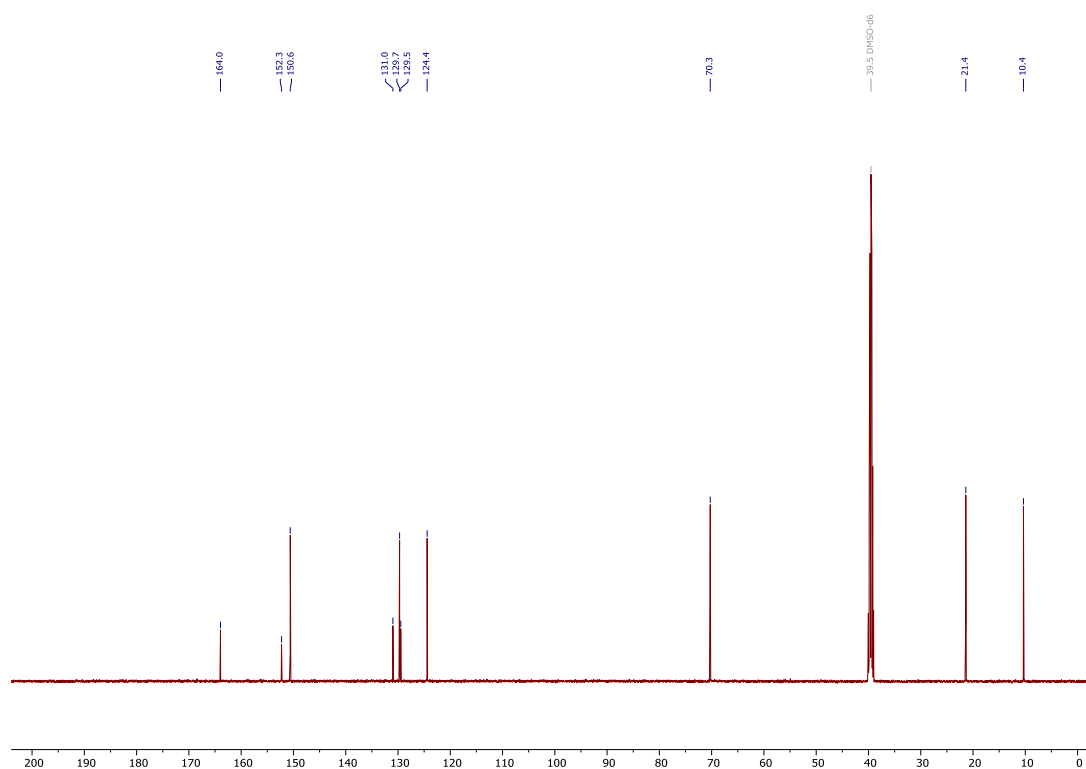


5-Propoxyprido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidine (**5b**):

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

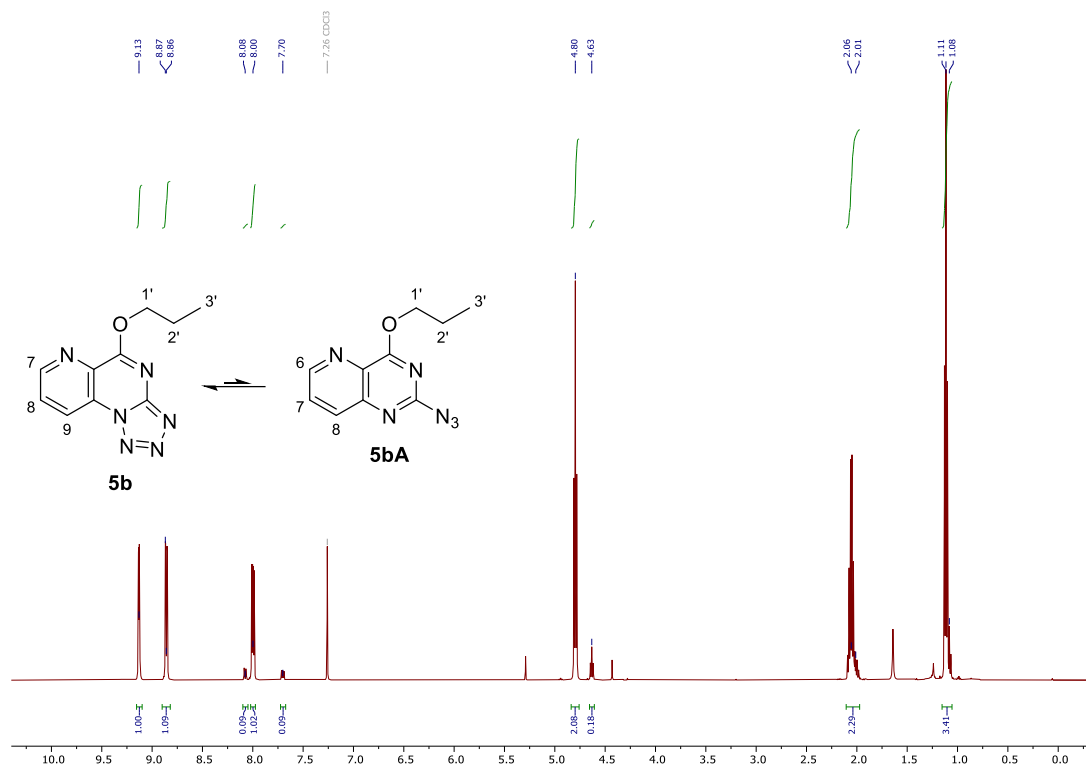


^{13}C NMR (125 MHz, $\text{DMSO-}d_6$)



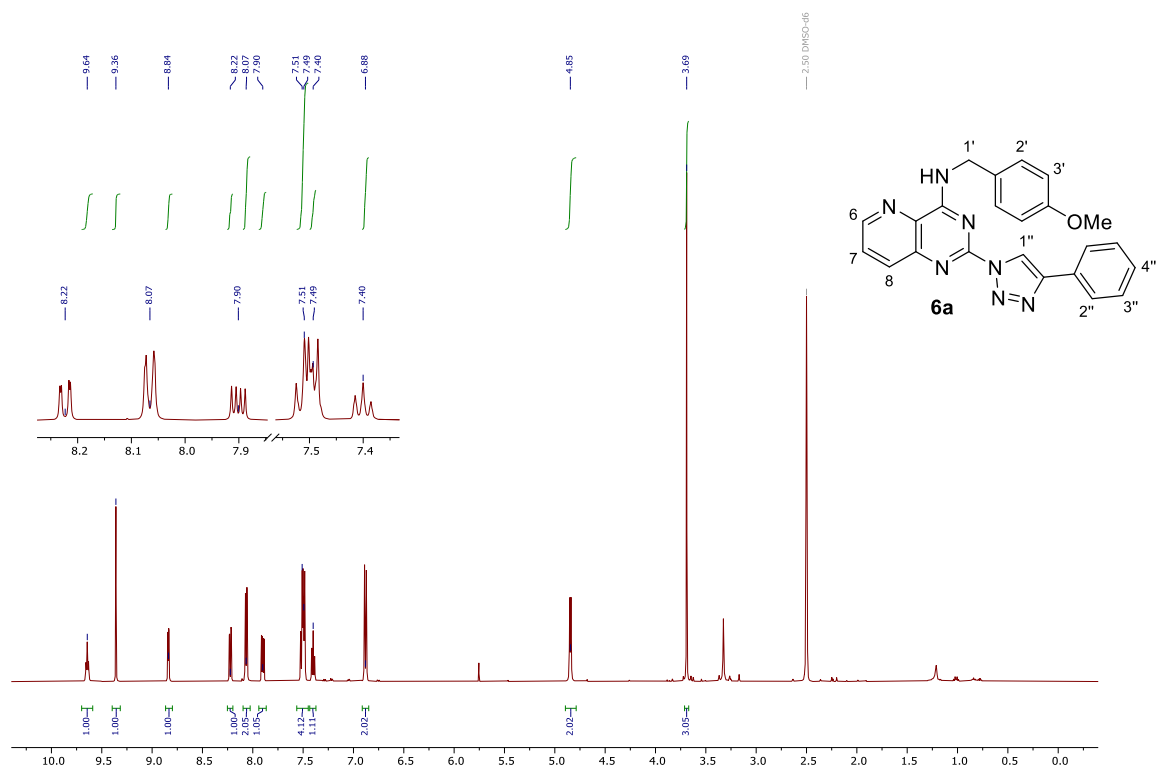
5-Propoxy-pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrimidine (**5b**) and 2-azido-4-propoxy-pyrido[3,2-*d*]pyrimidine (**5bA**):

^1H NMR (500 MHz, CDCl_3)

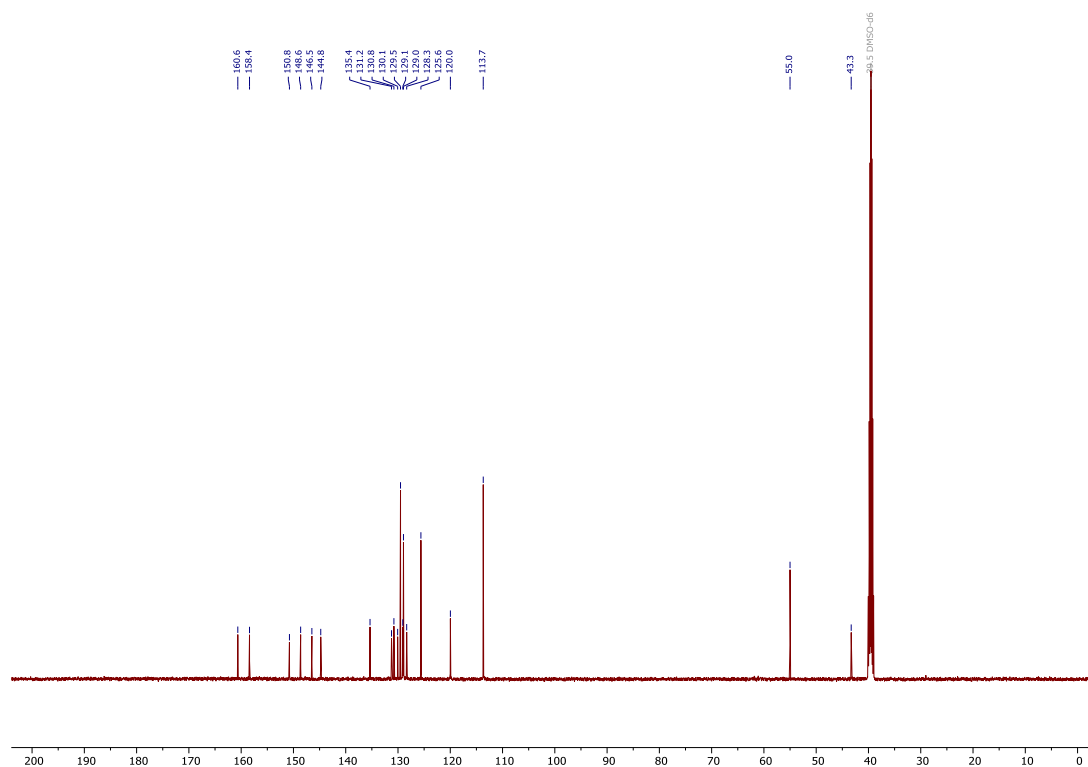


N-(4-Methoxybenzyl)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)pyrido[3,2-*d*]pyrimidin-4-amine (**6a**):

¹H NMR (500 MHz, DMSO-*d*₆)

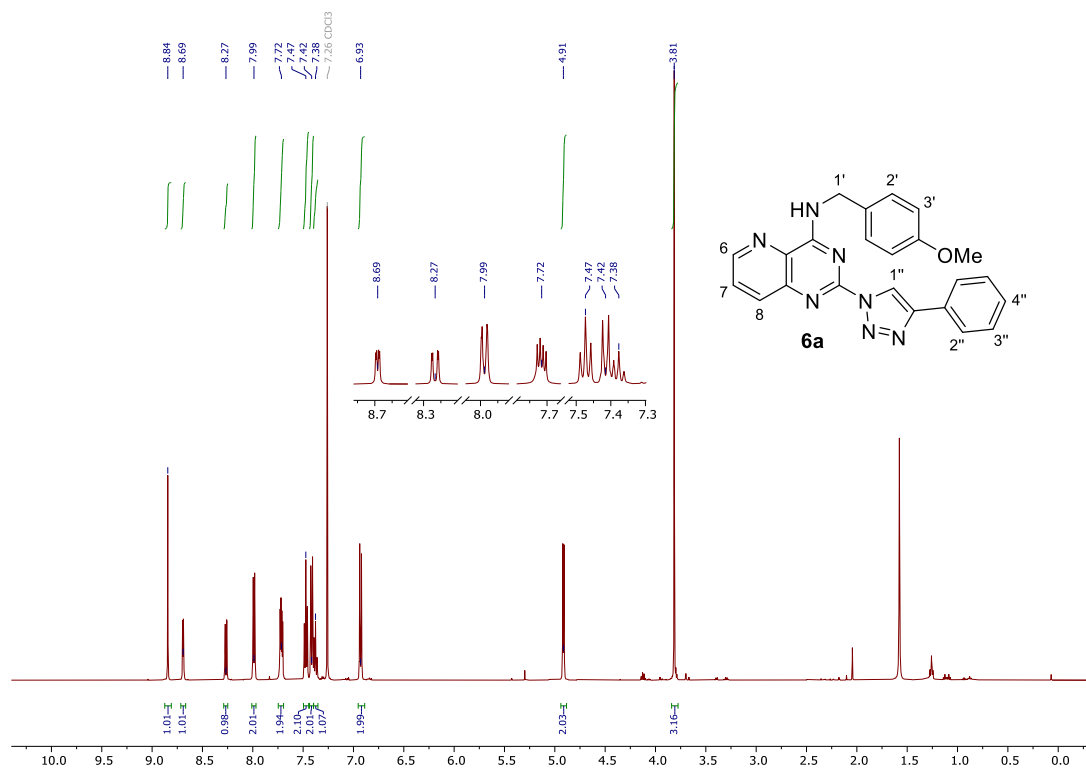


¹³C NMR (125 MHz, DMSO-*d*₆)

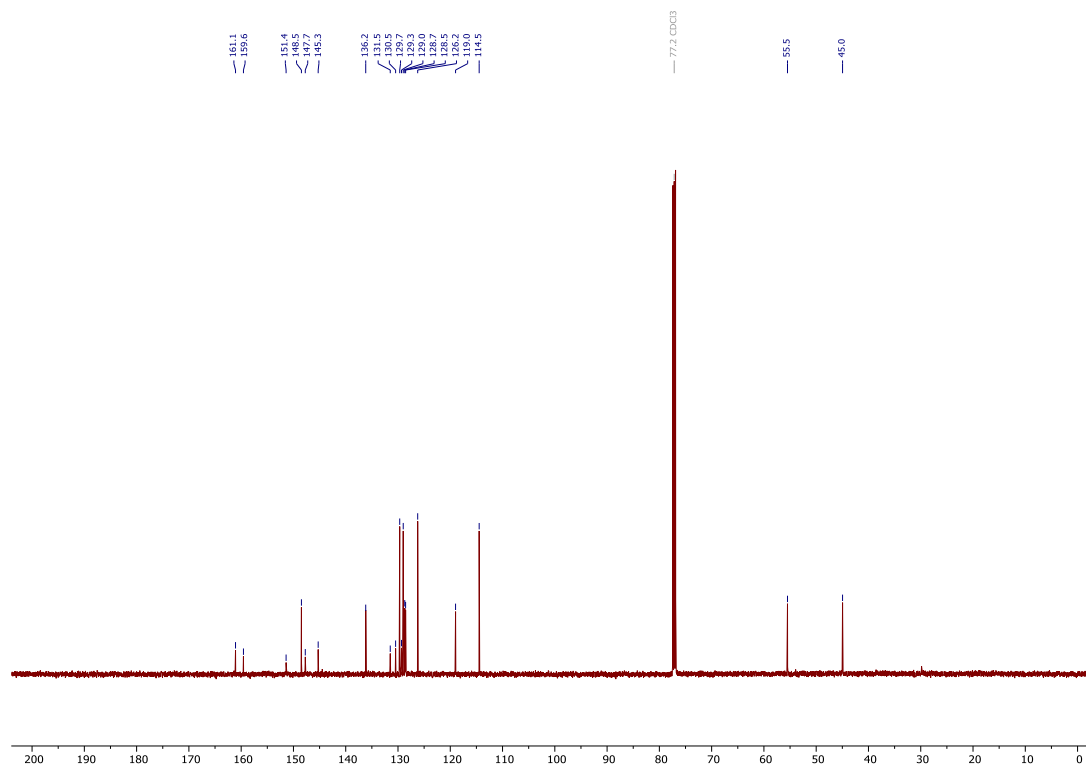


N-(4-Methoxybenzyl)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)pyrido[3,2-*d*]pyrimidin-4-amine (**6a**):

¹H NMR (500 MHz, CDCl₃)

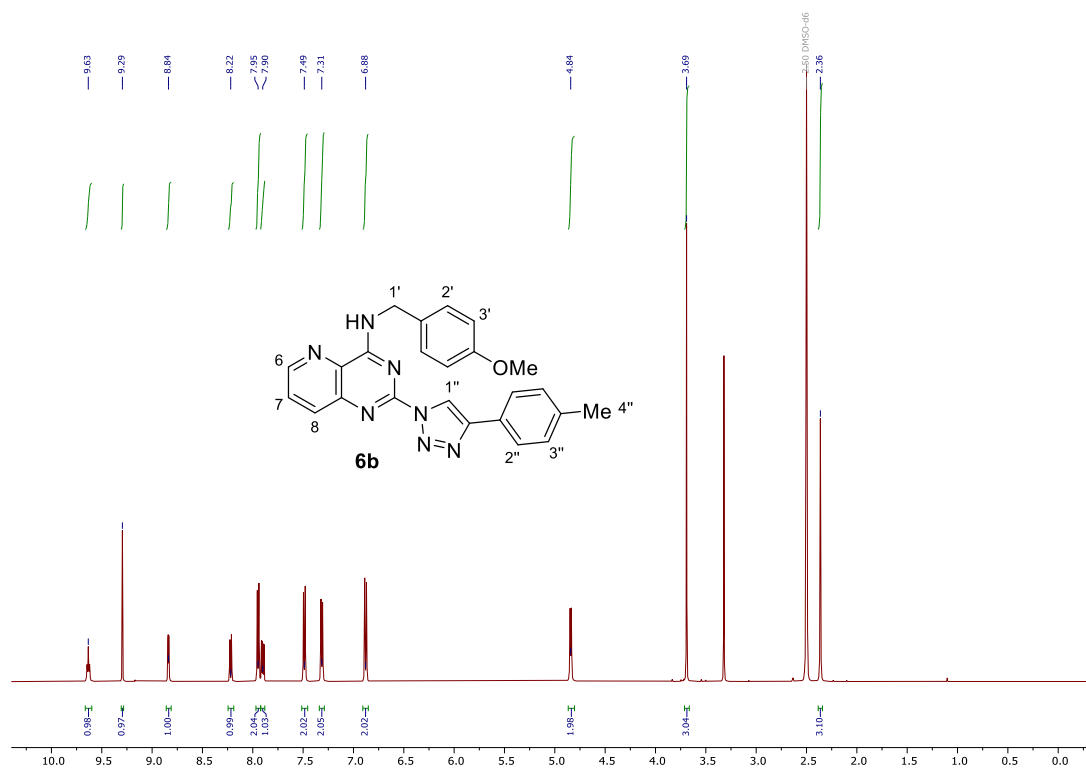


¹³C NMR (125 MHz, CDCl₃)

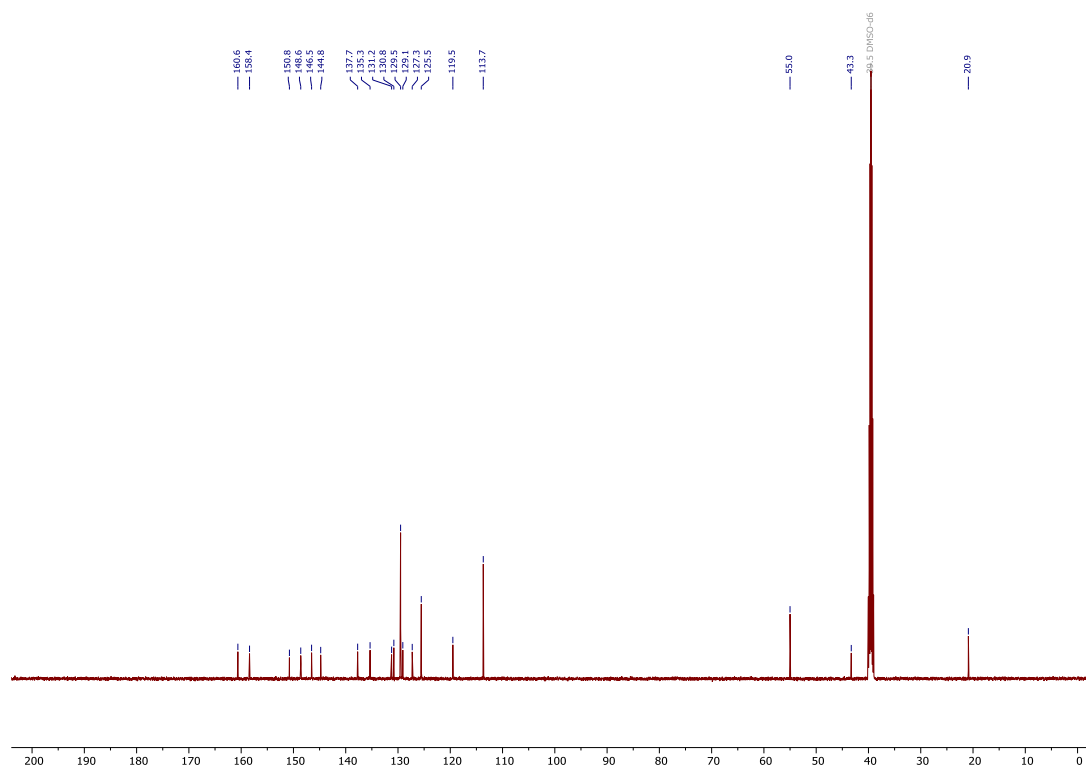


N-(4-Methoxybenzyl)-2-(4-(*p*-tolyl)-1*H*-1,2,3-triazol-1-yl)pyrido[3,2-*d*]pyrimidin-4-amine (**6b**):

¹H NMR (500 MHz, DMSO-*d*₆)

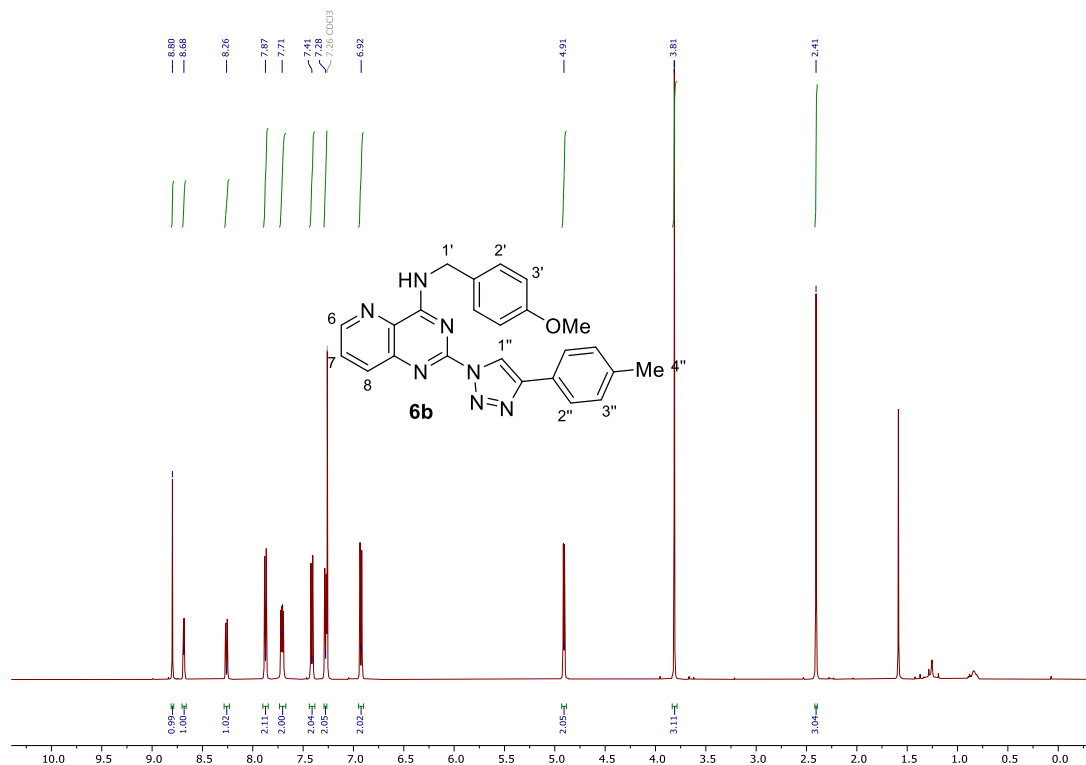


¹³C NMR (125 MHz, DMSO-*d*₆)

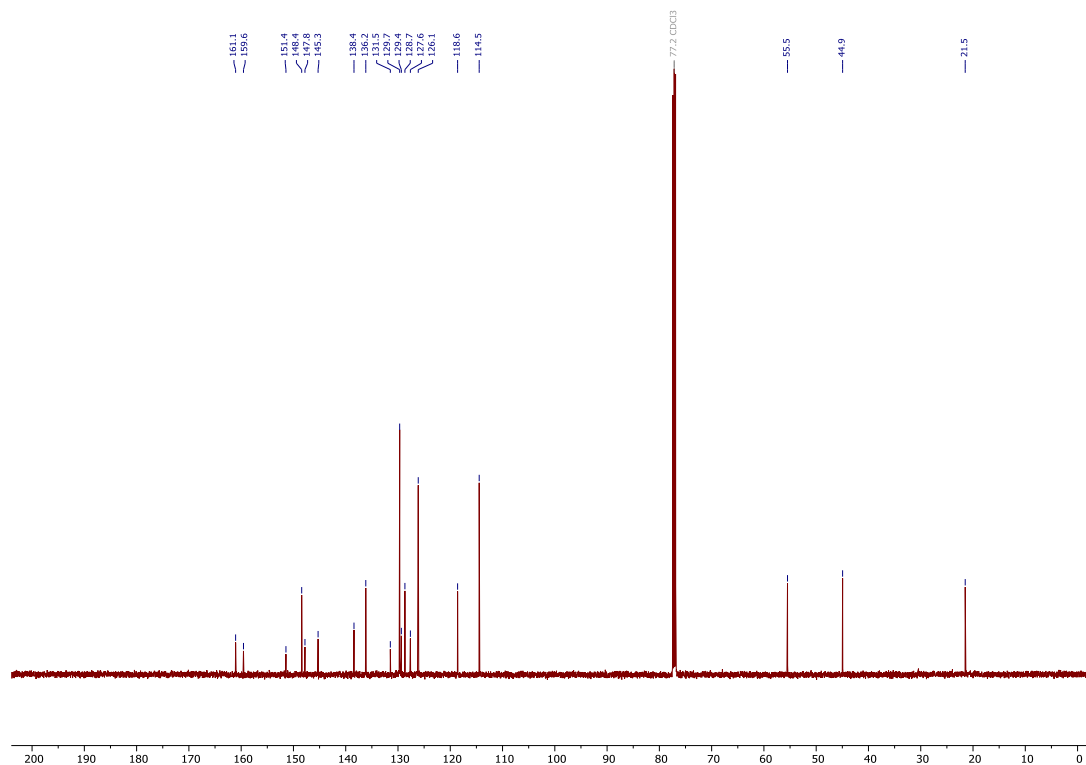


N-(4-Methoxybenzyl)-2-(4-(*p*-tolyl)-1*H*-1,2,3-triazol-1-yl)pyrido[3,2-*d*]pyrimidin-4-amine (**6b**):

¹H NMR (500 MHz, CDCl₃)

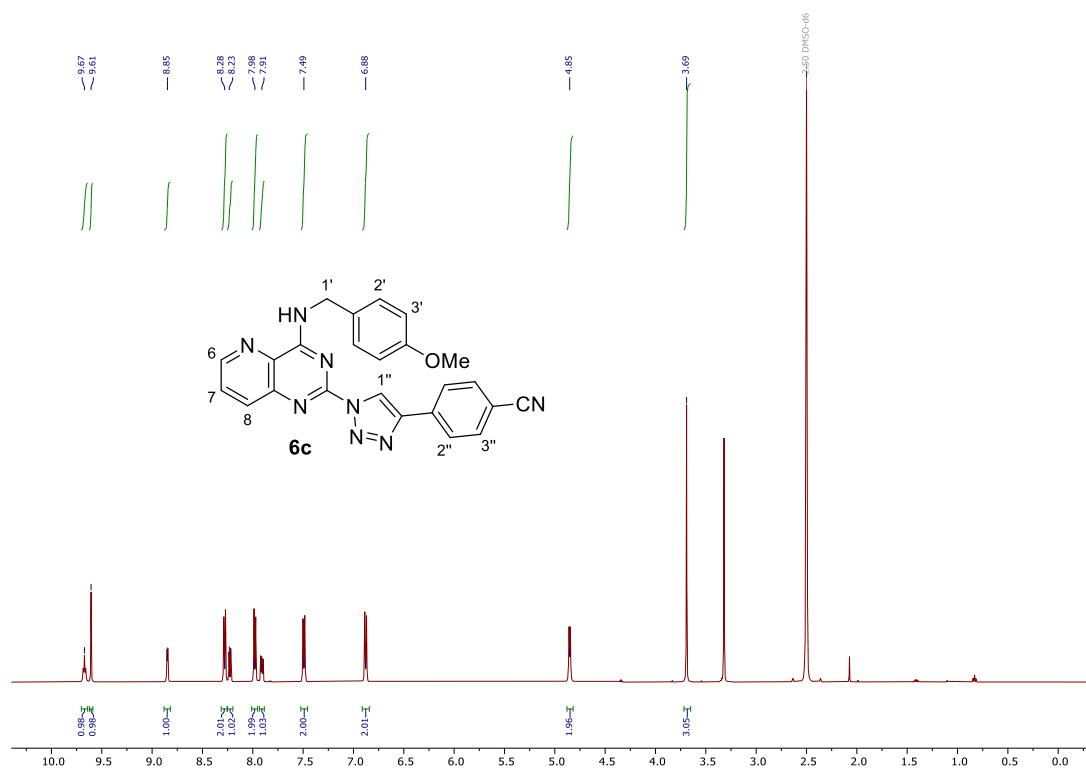


¹³C NMR (125 MHz, CDCl₃)

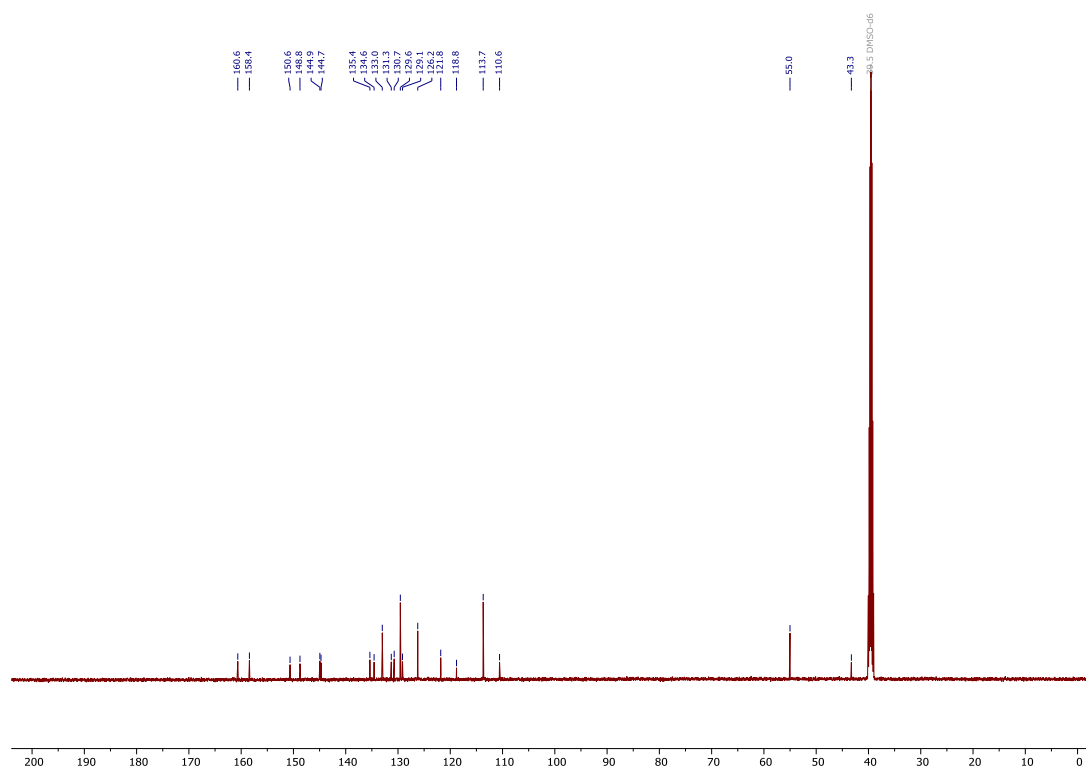


4-(1-(4-((4-Methoxybenzyl)amino)pyrido[3,2-*d*]pyrimidin-2-yl)-1*H*-1,2,3-triazol-4-yl)benzonitrile (**6c**):

¹H NMR (500 MHz, DMSO-*d*₆)

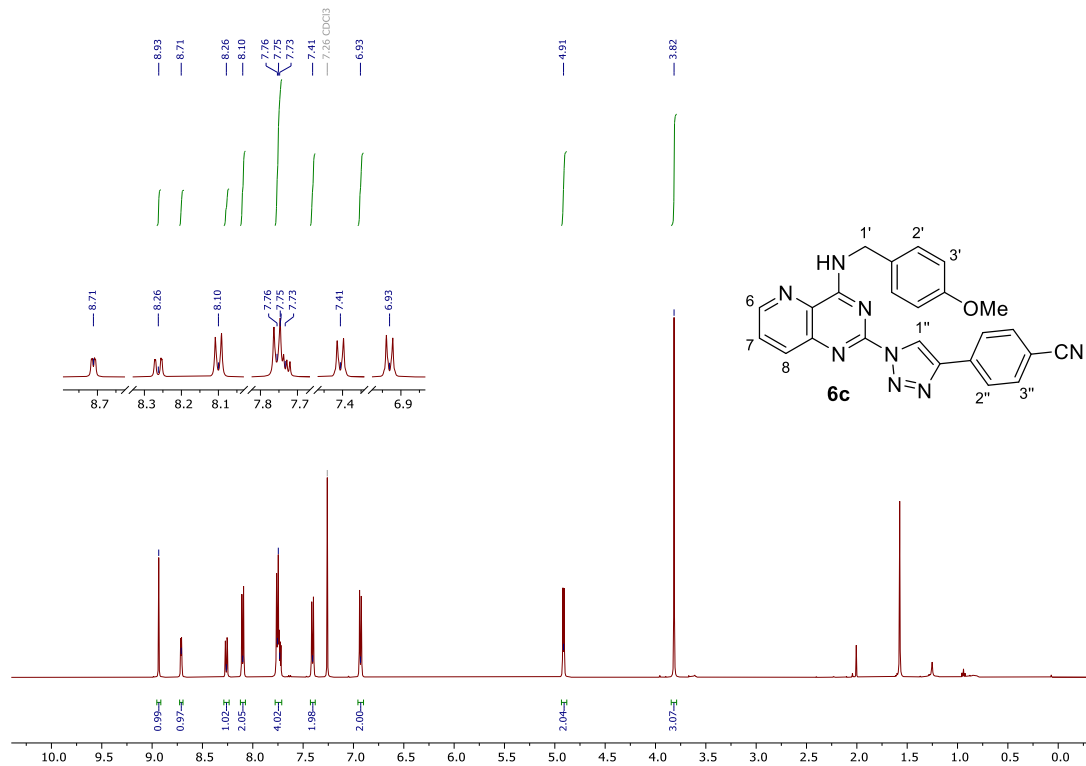


¹³C NMR (125 MHz, DMSO-*d*₆)

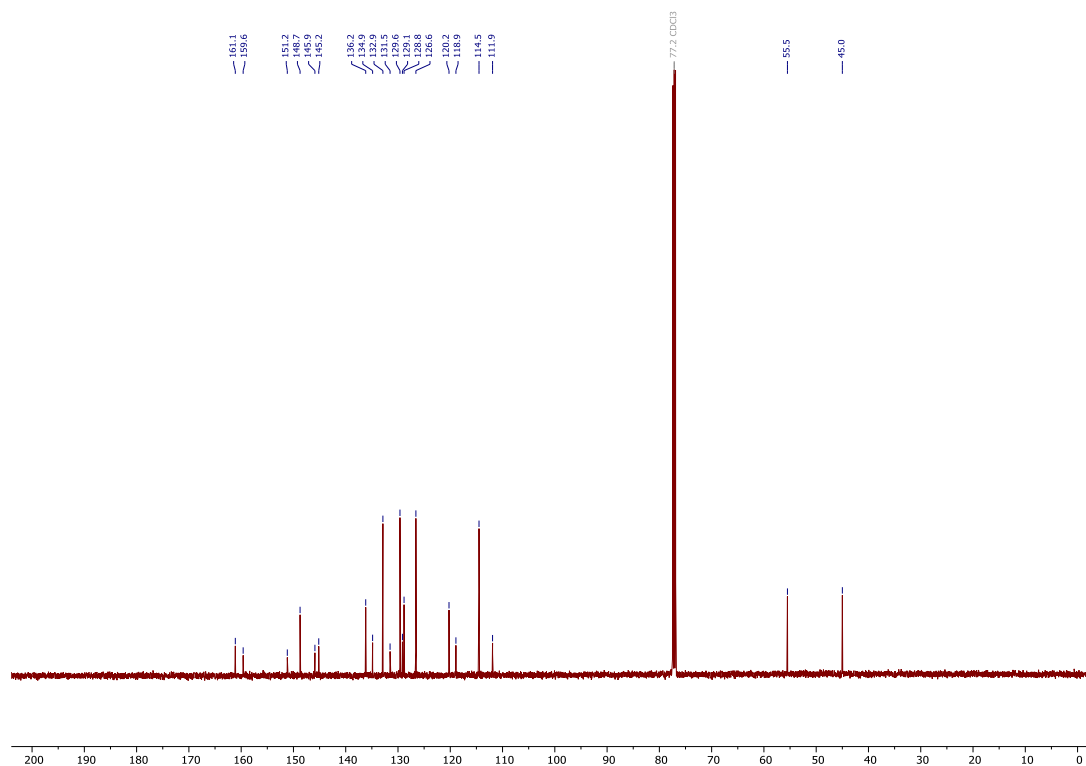


4-(1-(4-((4-Methoxybenzyl)amino)pyrido[3,2-*d*]pyrimidin-2-yl)-1*H*-1,2,3-triazol-4-yl)benzonitrile (**6c**):

¹H NMR (500 MHz, CDCl₃)

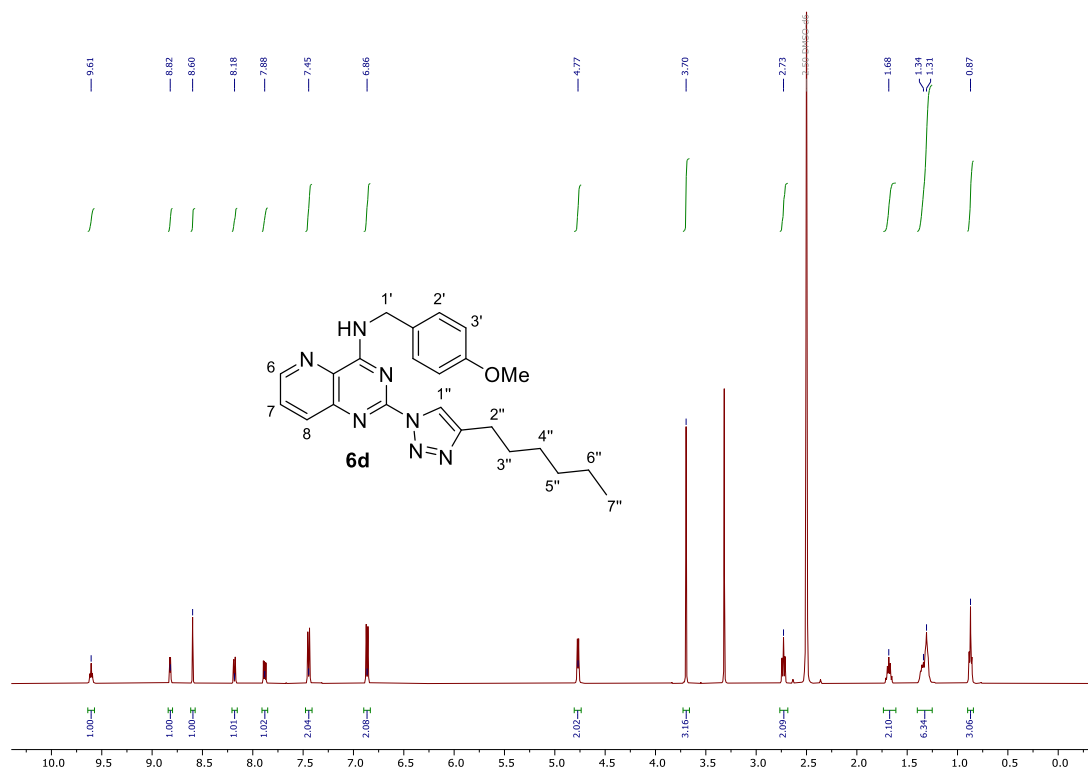


¹³C NMR (125 MHz, CDCl₃)



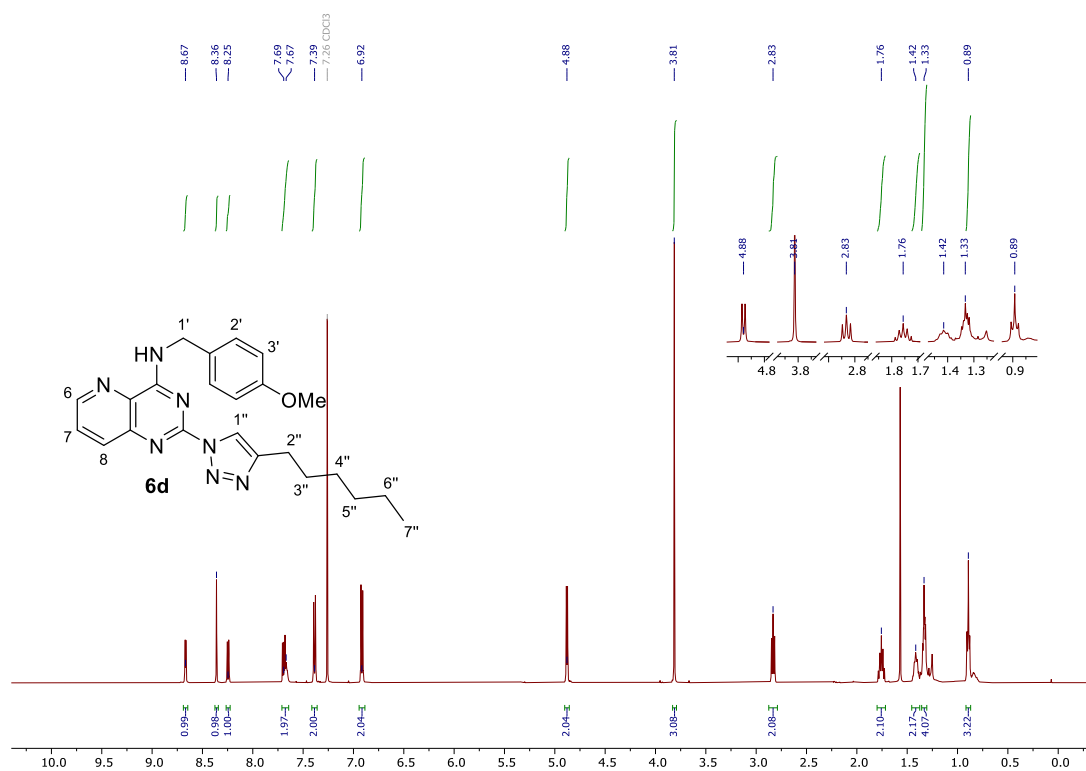
2-(4-Hexyl-1*H*-1,2,3-triazol-1-yl)-*N*-(4-methoxybenzyl)pyrido[3,2-*d*]pyrimidin-4-amine (**6d**):

¹H NMR (500 MHz, DMSO-*d*₆)

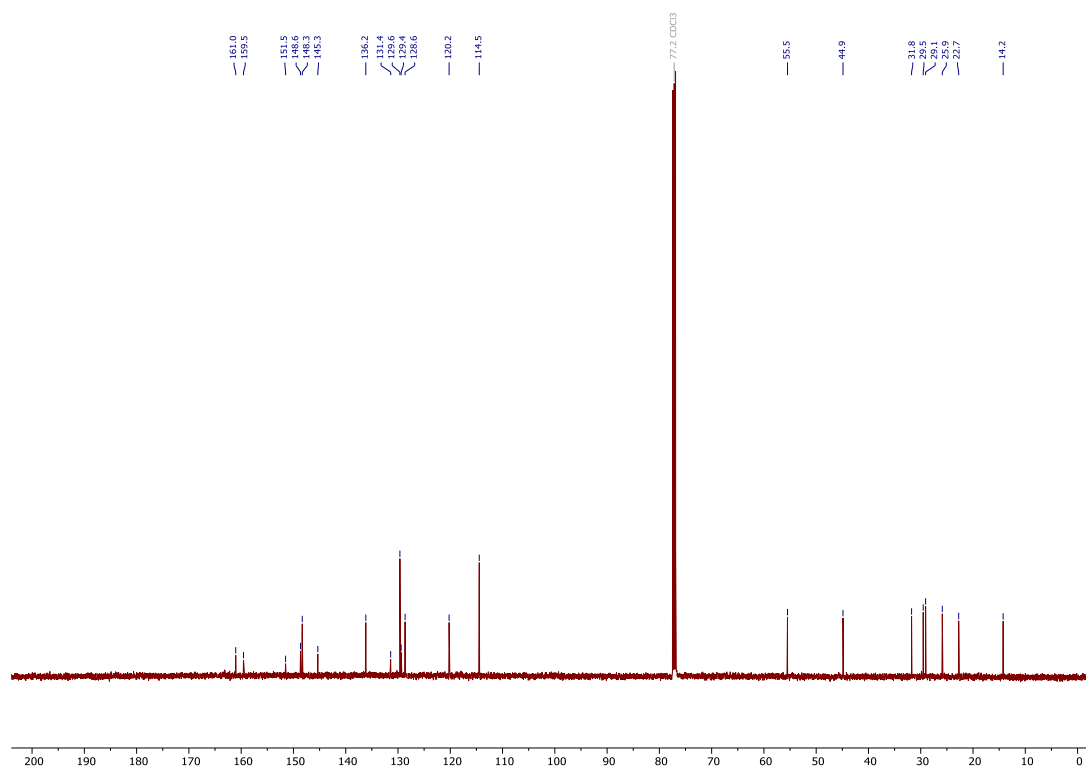


2-(4-Hexyl-1*H*-1,2,3-triazol-1-yl)-*N*-(4-methoxybenzyl)pyrido[3,2-*d*]pyrimidin-4-amine (**6d**):

¹H NMR (500 MHz, CDCl₃)

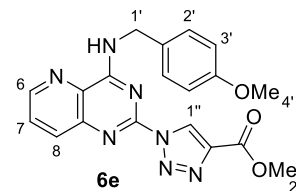
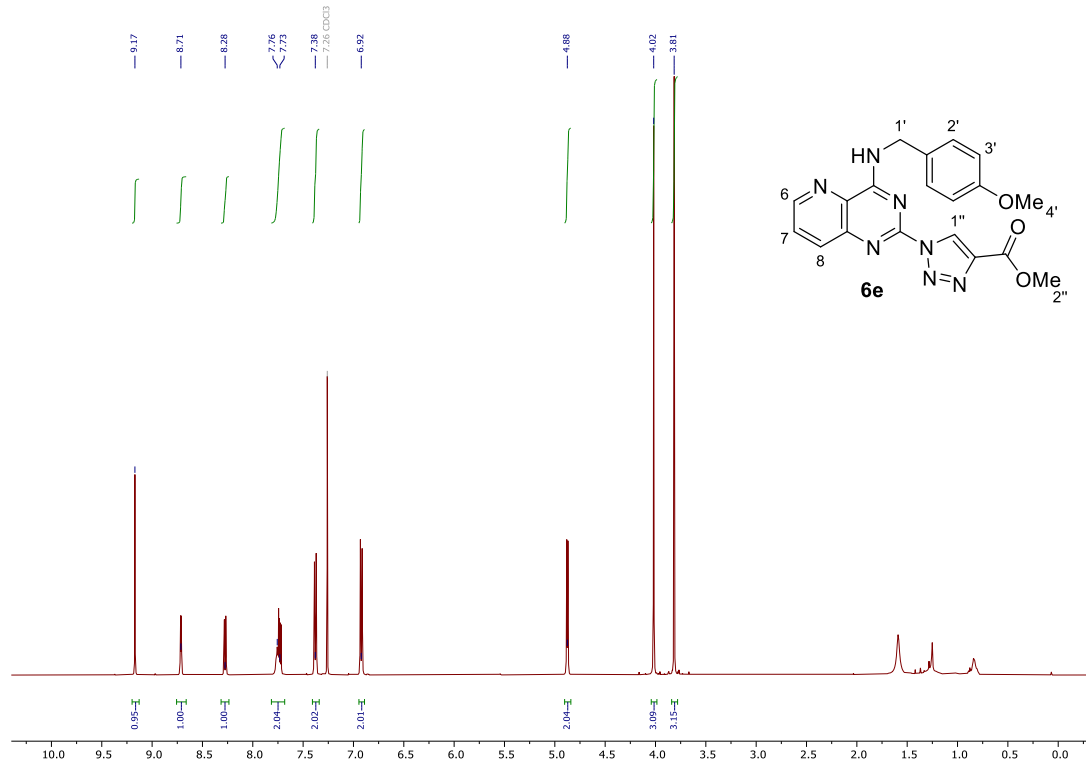


¹³C NMR (125 MHz, CDCl₃)

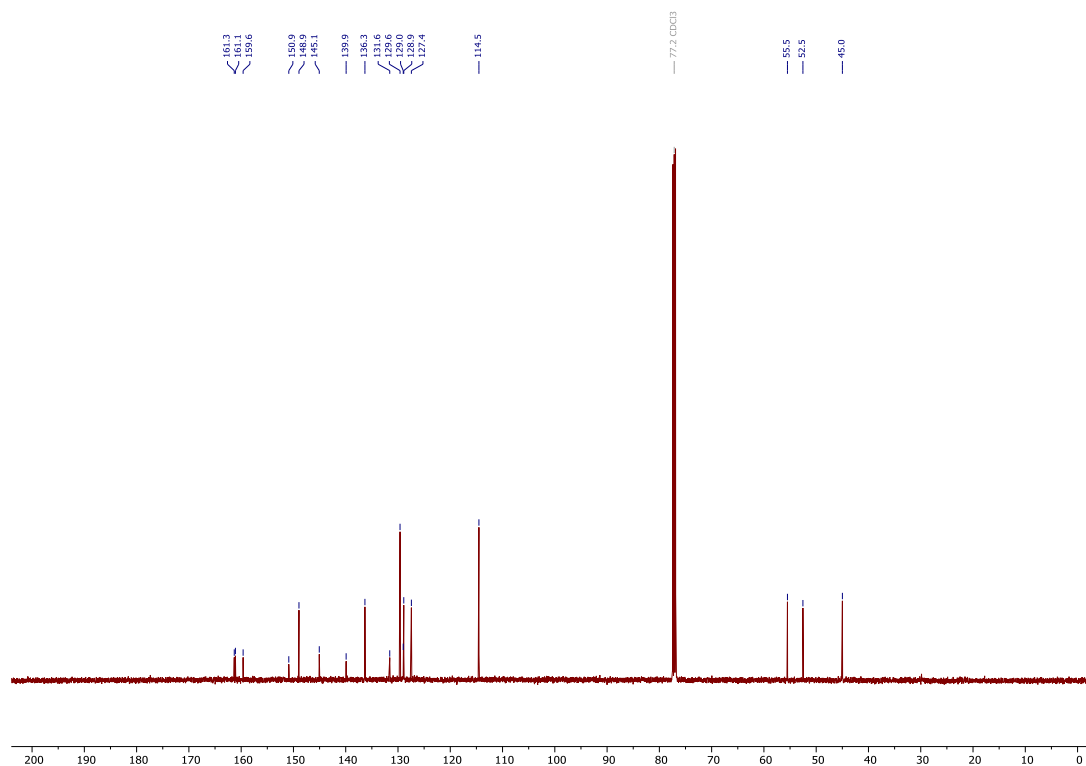


Methyl-1-(4-((4-methoxybenzyl)amino)pyrido[3,2-*d*]pyrimidin-2-yl)-1*H*-1,2,3-triazole-4-carboxylate (**6e**):

^1H NMR (500 MHz, CDCl_3)

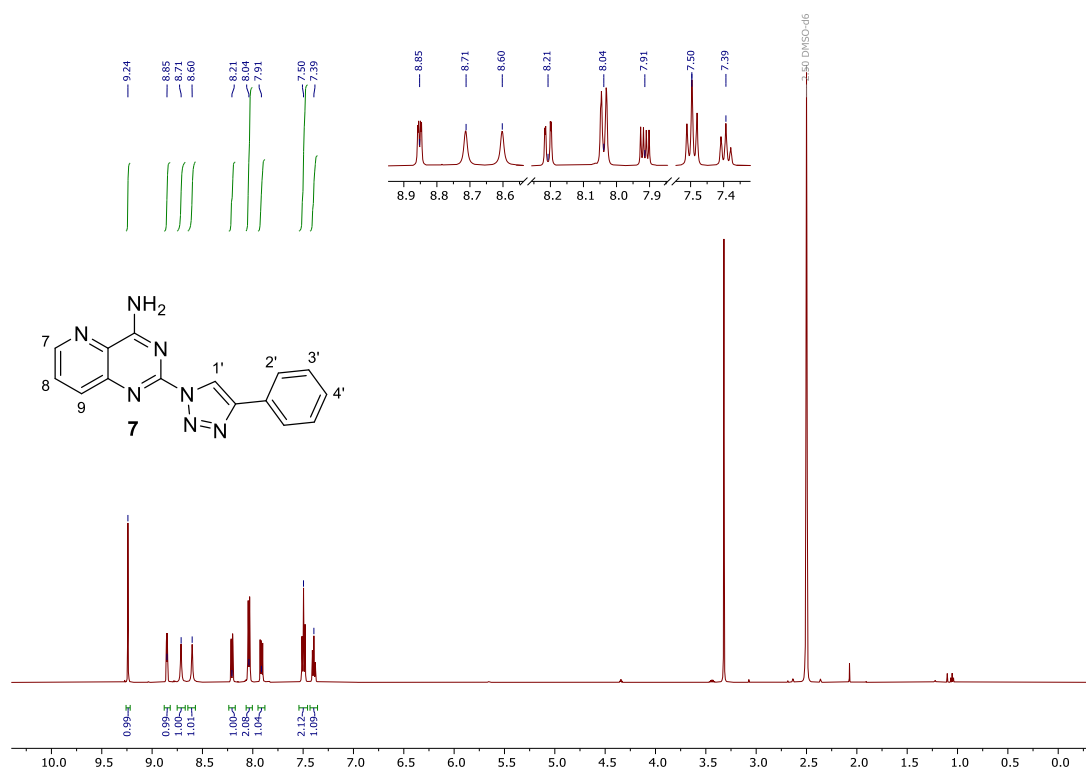


^{13}C NMR (125 MHz, CDCl_3)

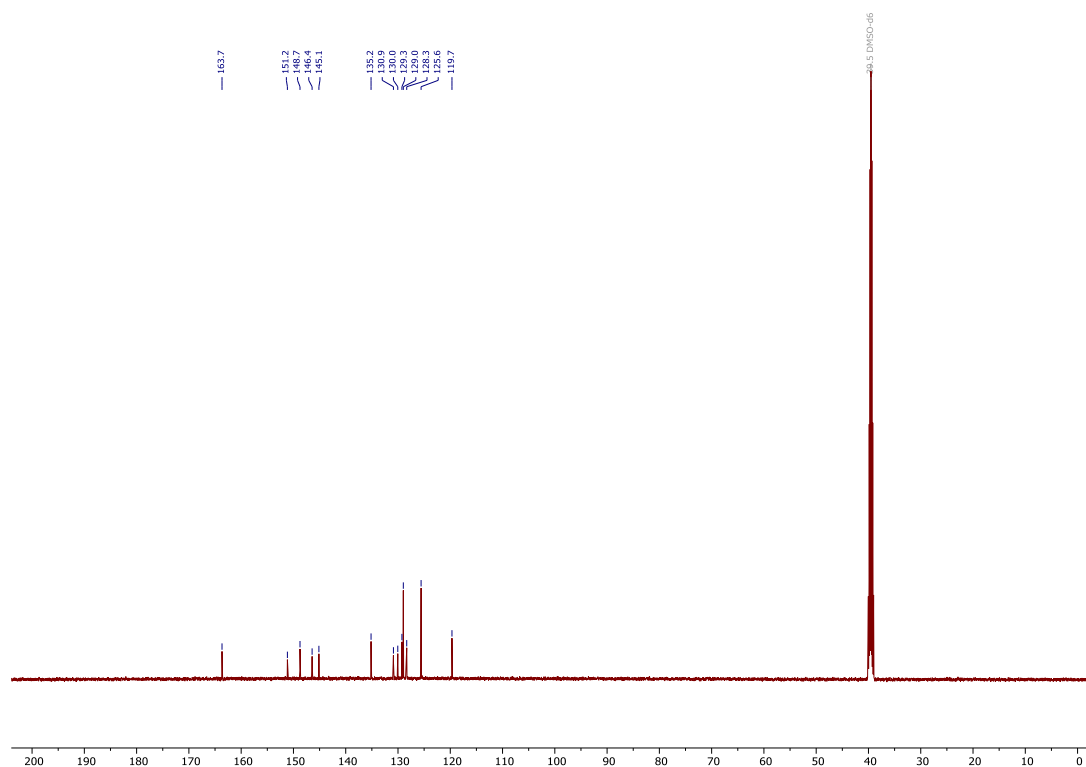


2-(4-Phenyl-1*H*-1,2,3-triazol-1-yl)pyrido[3,2-*d*]pyrimidin-4-amine (**7**):

¹H NMR (500 MHz, DMSO-*d*₆)

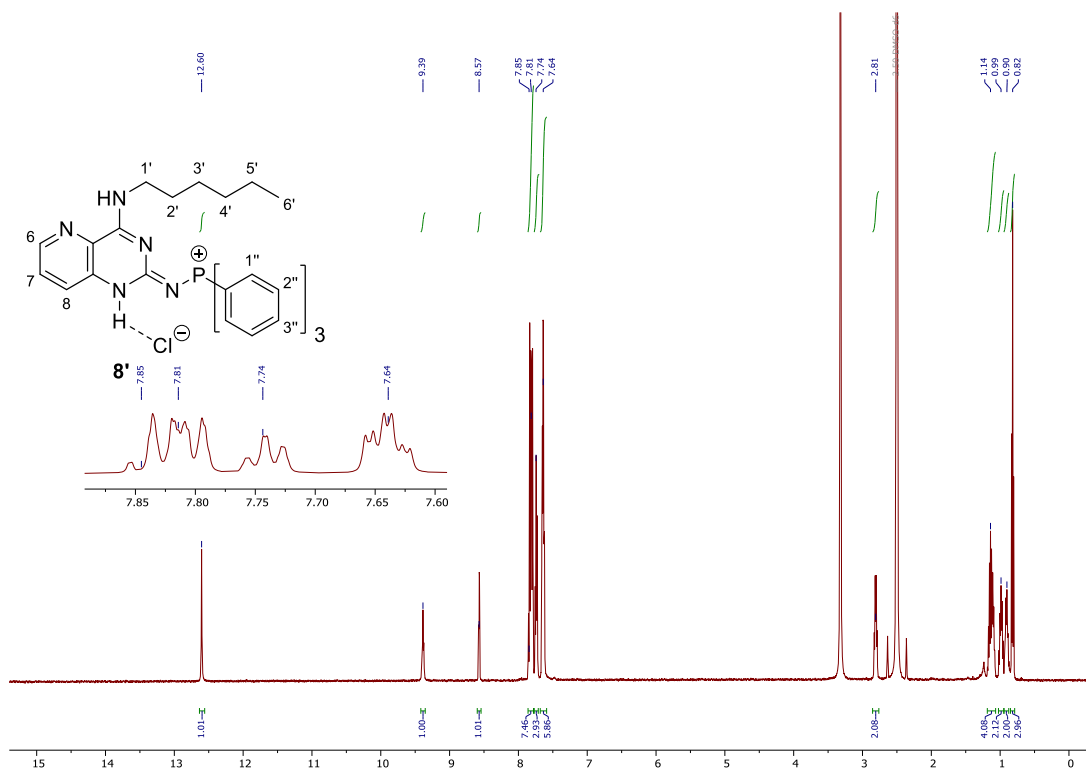


¹³C NMR (125 MHz, DMSO-*d*₆)

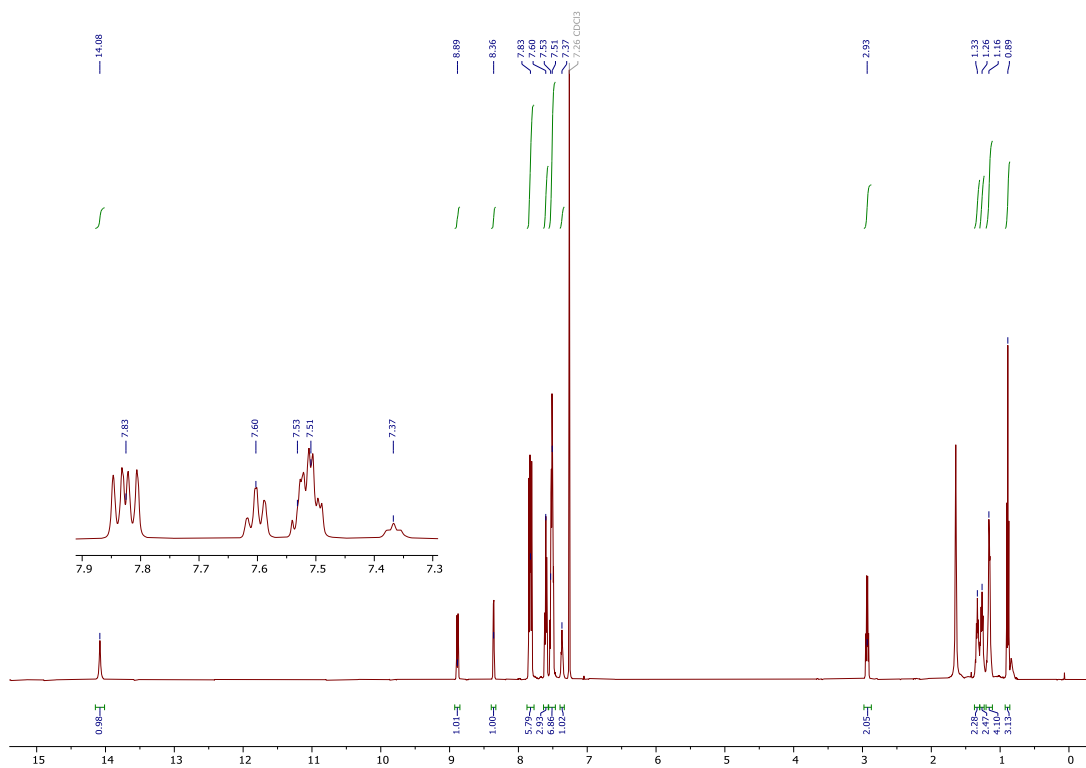


((4-(Hexylamino)pyrido[3,2-*d*]pyrimidin-2(1*H*)-ylidene)amino)triphenylphosphonium chloride (**8'**):

¹H NMR (500 MHz, DMSO-*d*₆)



¹H NMR (500 MHz, CDCl₃)



13C NMR spectrum of compound 10 in CDCl₃.

Chemical Shifts (ppm):

- 159.2
- 156.9
- 145.3
- 137.9
- 133.3
- 133.2
- 133.0
- 132.9
- 129.1
- 129.1
- 129.0
- 127.6
- 127.3
- 126.8
- 126.3
- 77.2 (CDCl₃)
- 41.0
- 31.5
- 29.0
- 26.7
- 22.7
- 14.2

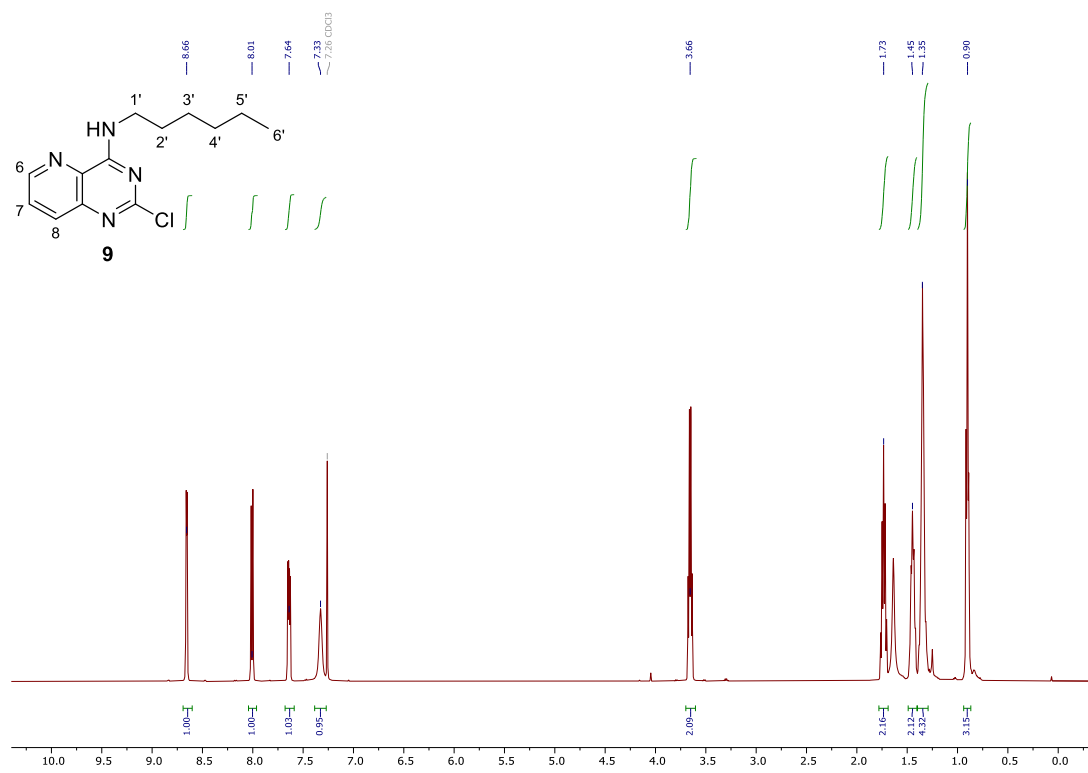
Inset (Aromatic Region):

- 133.3
- 133.2
- 133.0
- 132.9
- 129.1
- 129.1
- 129.0

The plot shows the 1D momentum distribution function $g(p)$ as a function of momentum p in GeV/c . The x-axis spans from -150 to 150 GeV/c , and the y-axis spans from 0.0 to 1.0. Two data series are shown: a blue line for the 19.6 GeV collision system and a red line for the 0.0 HEPc4 collision system. Both distributions are highly peaked at $p = 0$, with the 0.0 HEPc4 peak reaching a value of 1.0. A small blue vertical tick mark is present on the x-axis at approximately $p = 19.6$.

2-Chloro-*N*-hexylpyrido[3,2-*d*]pyrimidin-4-amine (**9**):

^1H NMR (500 MHz, CDCl_3)



^{13}C NMR (125 MHz, CDCl_3)

