

Supporting Information

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SUPPORTING INFORMATION

Application of Azide-Tetrazole Tautomerism and Sulfanyl Group Dance in the Synthesis of Thiosubstituted Tetrazoloquinazolines

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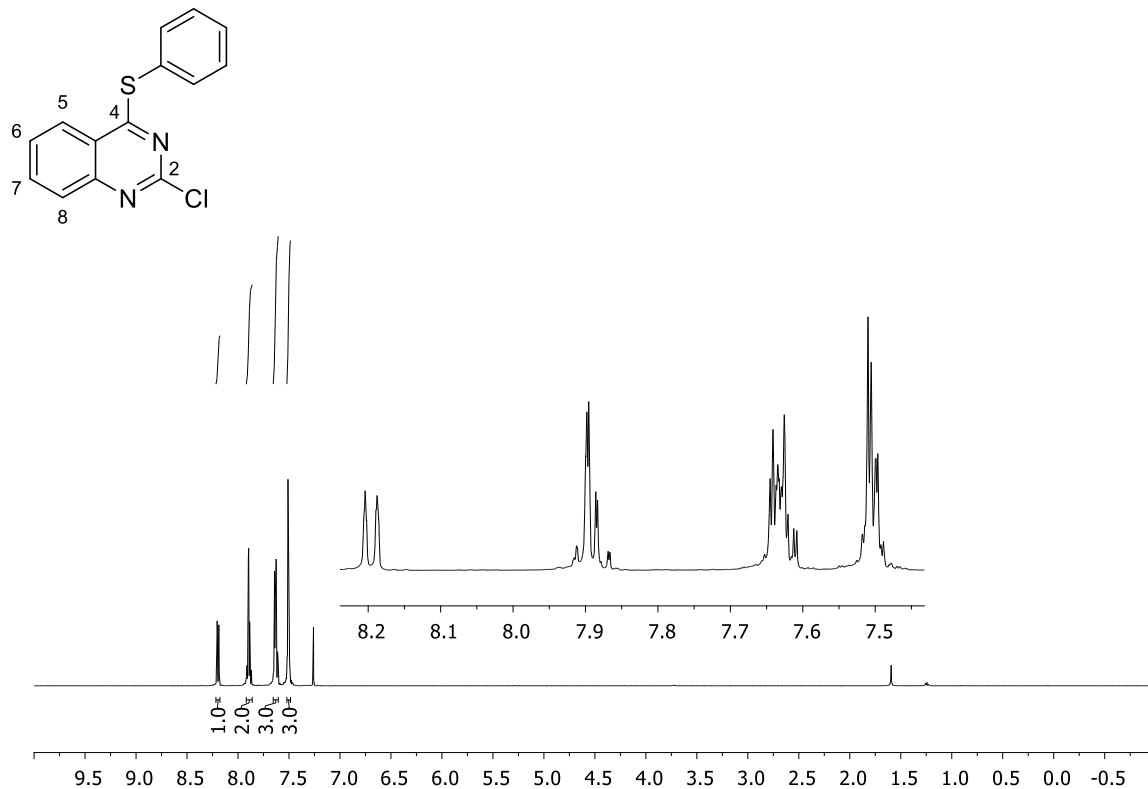
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NMR Spectra

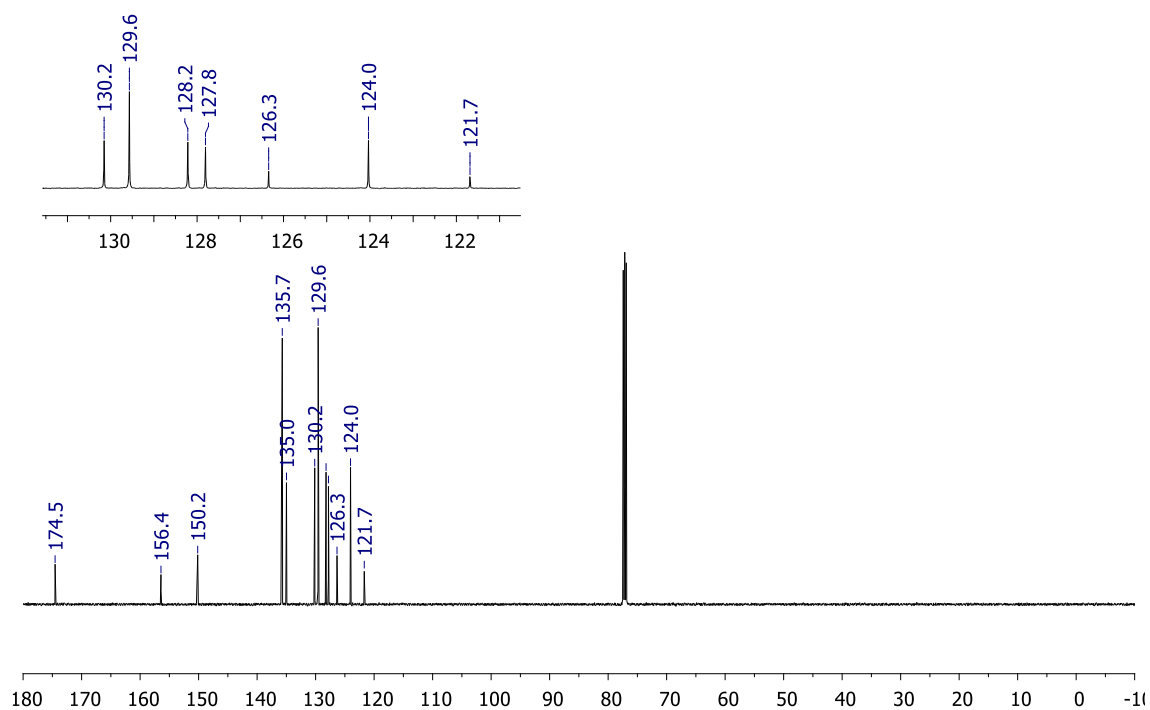
4-Arylthio-2-chloroquinazolines

2-Chloro-4-(phenylthio)quinazoline (2a)

^1H NMR (500 MHz, CDCl_3) spectrum of compound 2a:

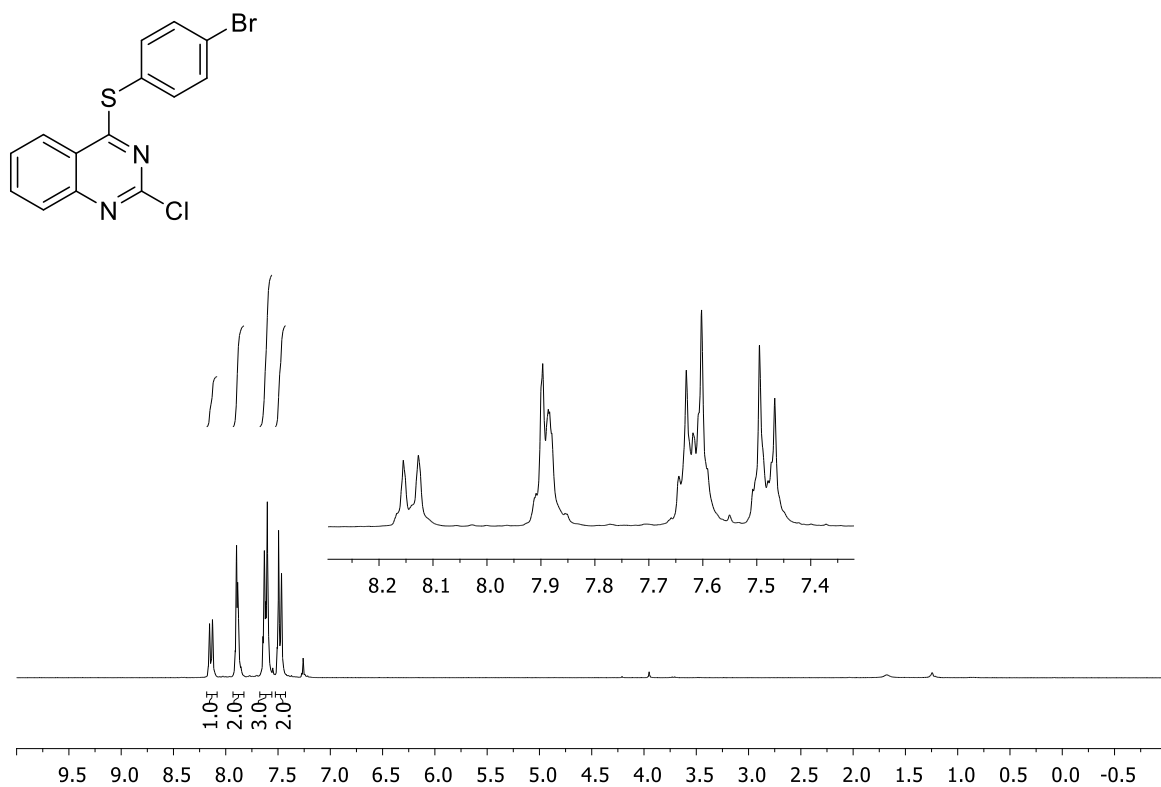


^{13}C NMR (125.7 MHz, CDCl_3) spectrum of compound 2a:

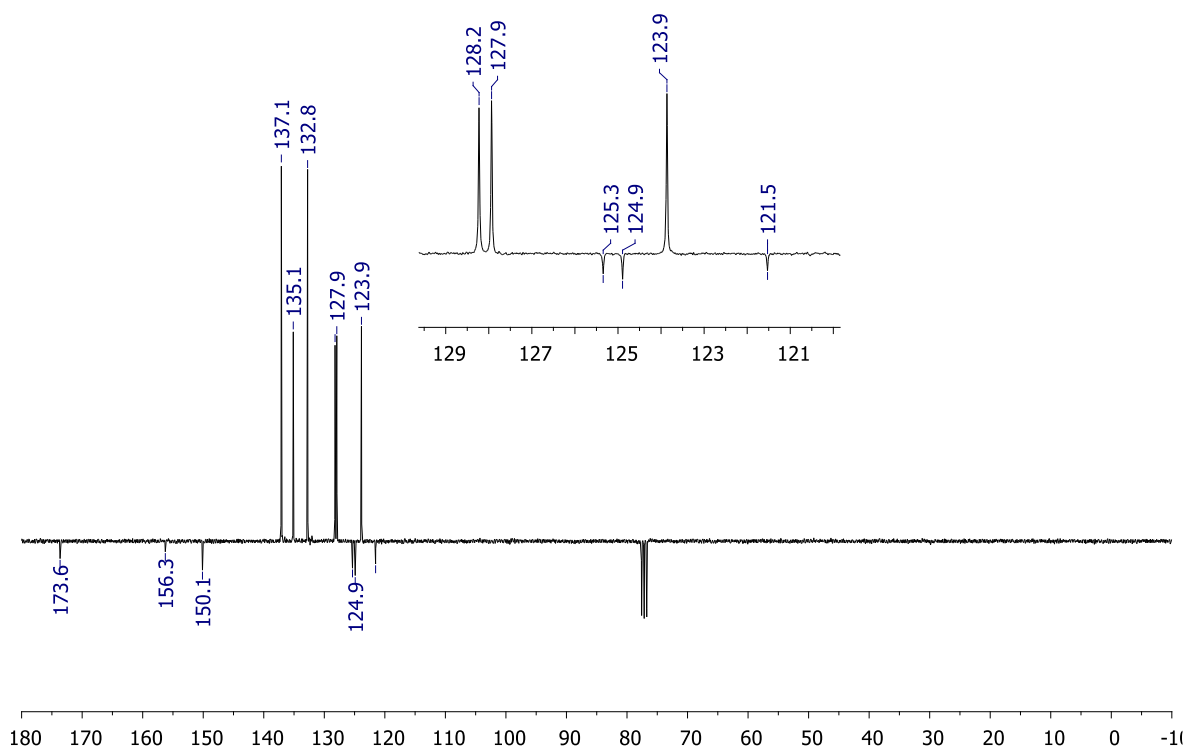


4-[(4-Bromophenyl)thio]-2-chloroquinazoline (2b)

^1H NMR (300 MHz, CDCl_3) spectrum of compound 2b:

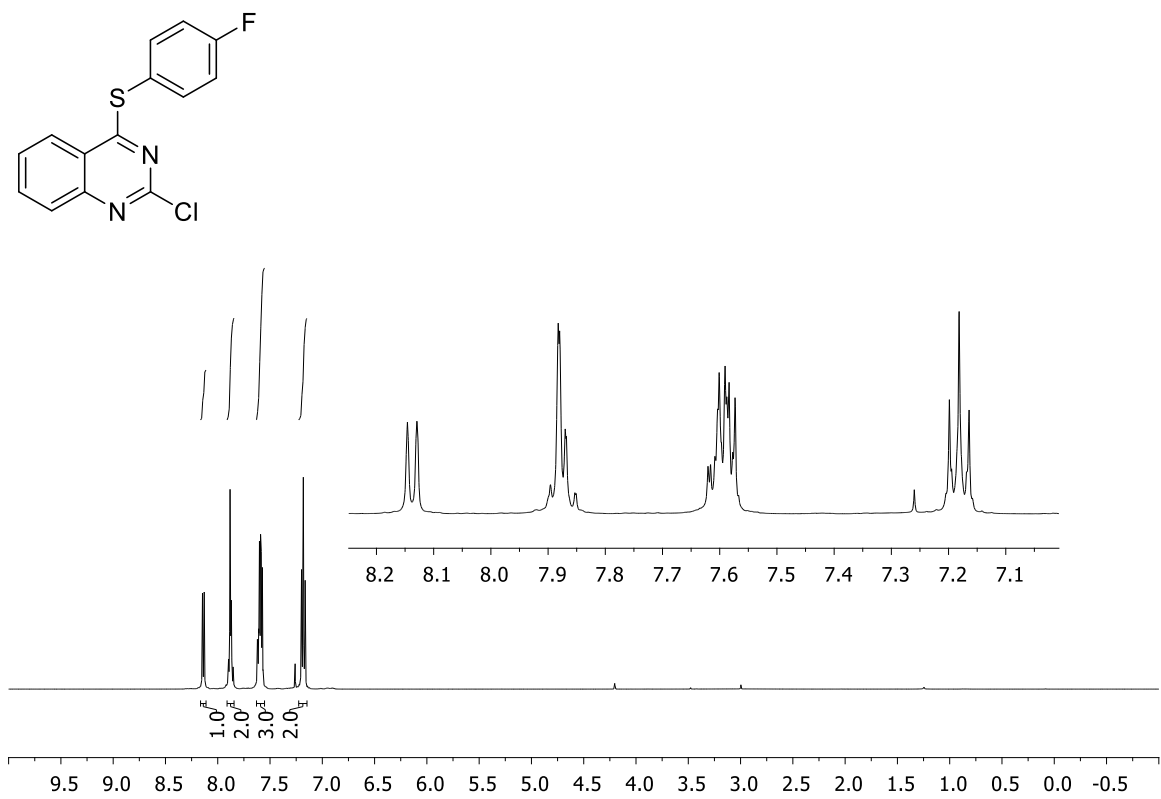


^{13}C NMR (75 MHz, CDCl_3) spectrum of compound 5b:

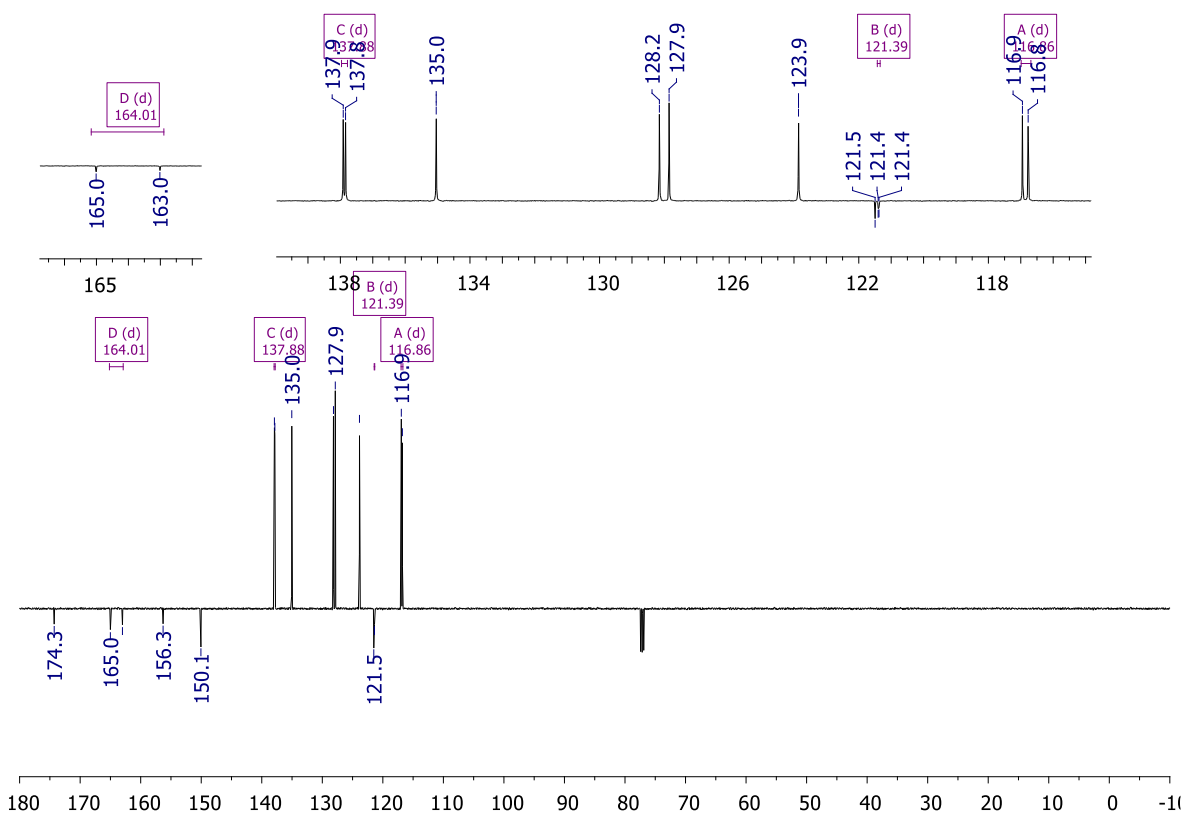


2-Chloro-4-[(4-fluorophenyl)thio]quinazoline (2c)

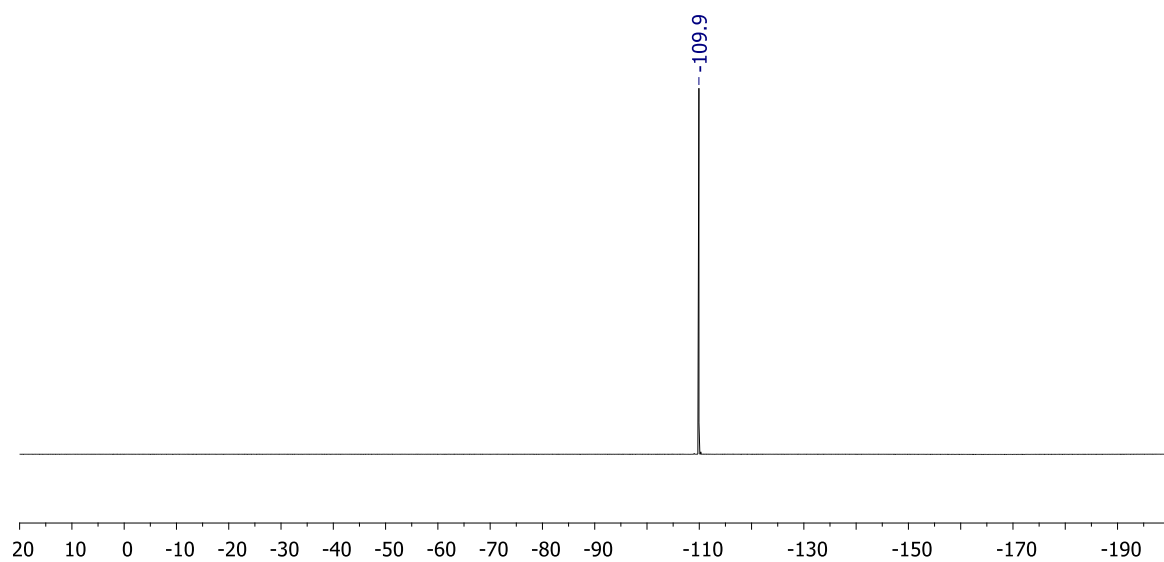
^1H NMR (500 MHz, CDCl_3) spectrum of compound 2c:



^{13}C NMR (125.7 MHz, CDCl_3) spectrum of compound 2c:

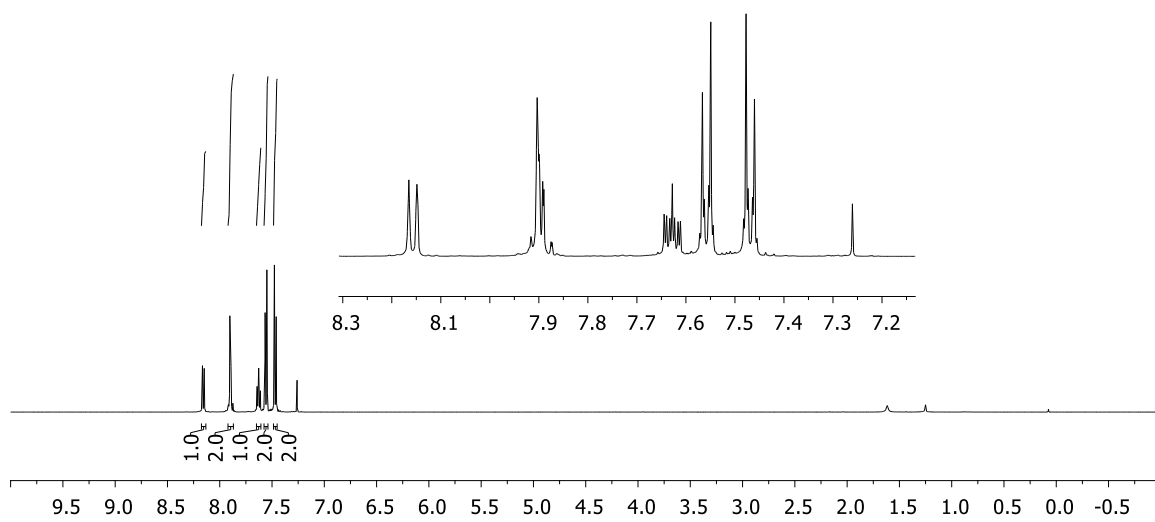
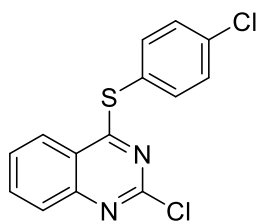


^{19}F NMR (470.5 MHz, CDCl_3) spectrum of compound 2c:

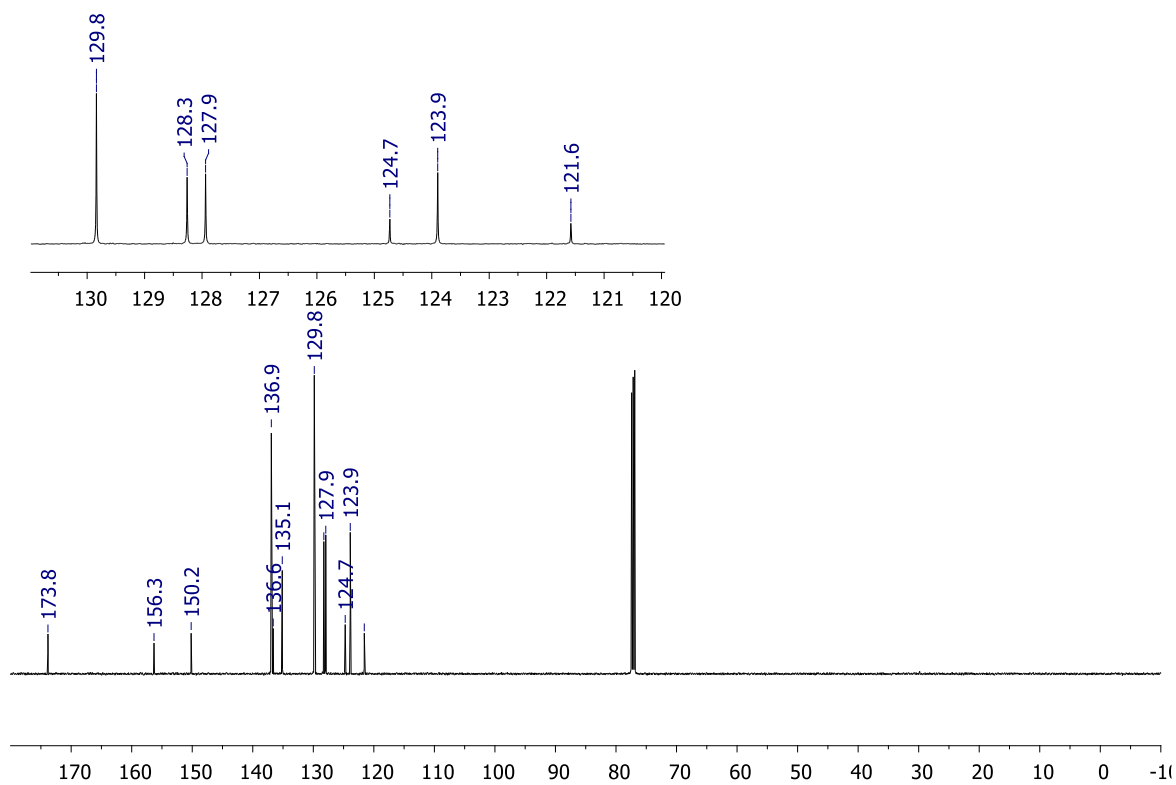


2-Chloro-4-[(4-chlorophenyl)thio]quinazoline (2d)

^1H NMR (500 MHz, CDCl_3) spectrum of compound 2d:

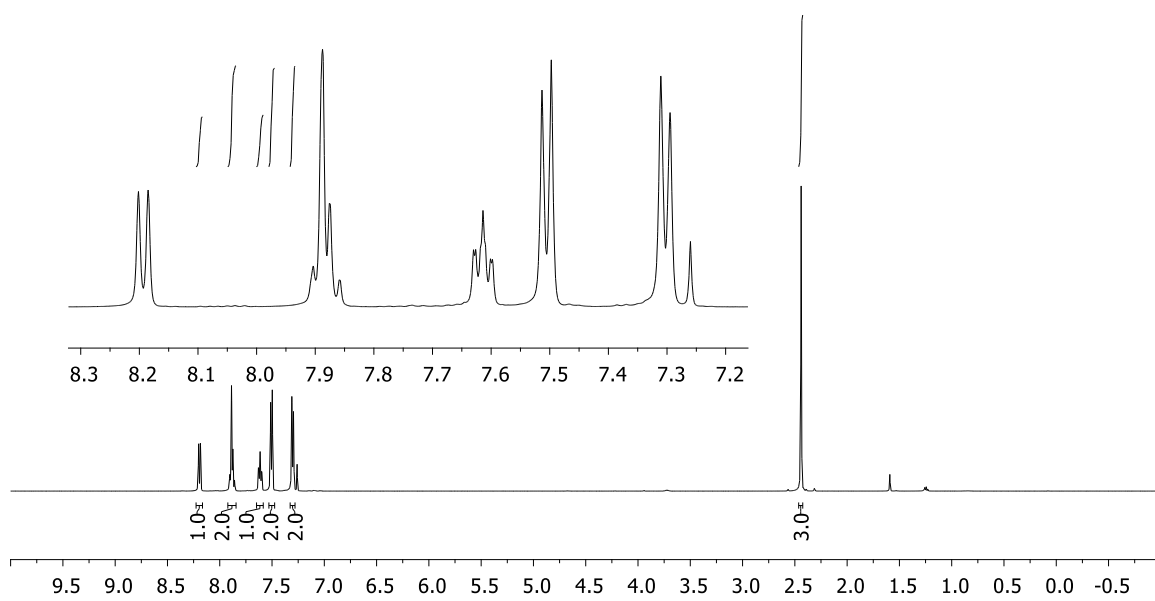
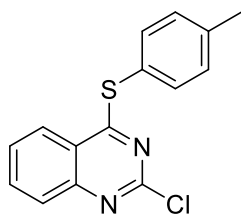


^{13}C NMR (125.7 MHz, CDCl_3) spectrum of compound 2d:

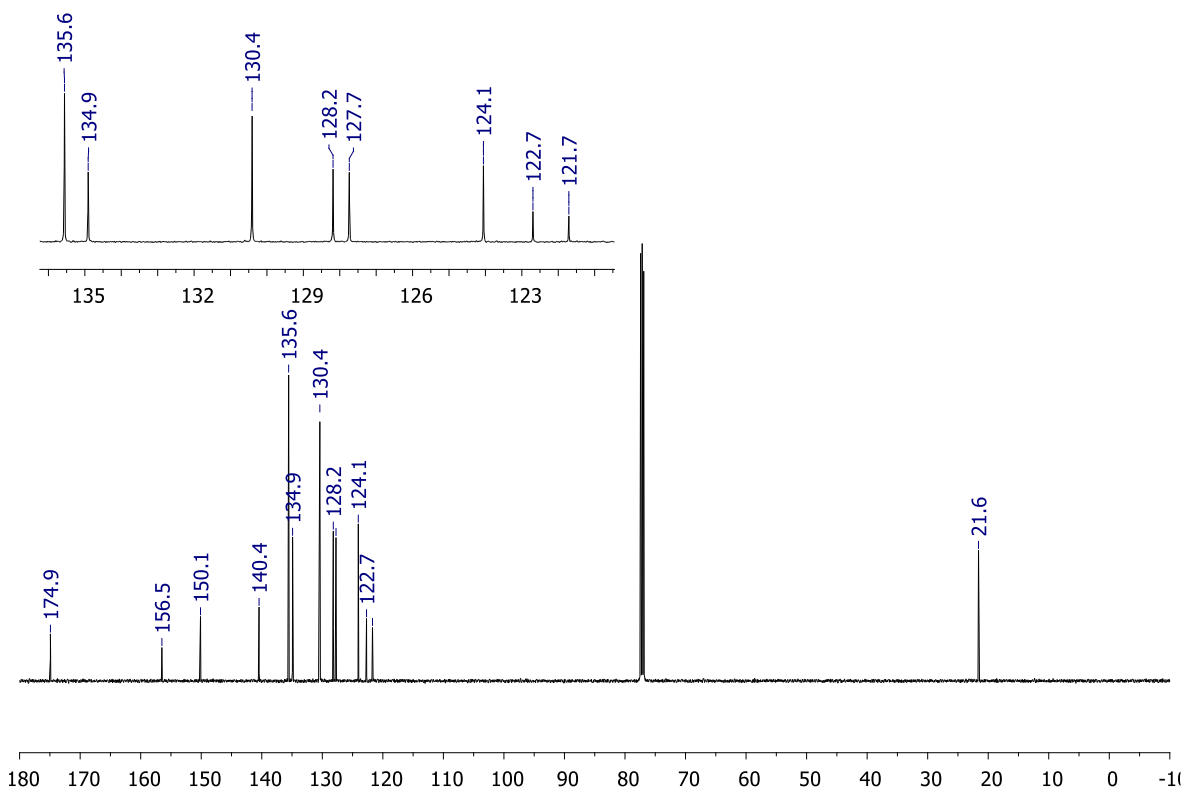


2-Chloro-4-(*p*-tolylthio)quinazoline (2e)

^1H NMR (500 MHz, CDCl_3) spectrum of compound 2e:



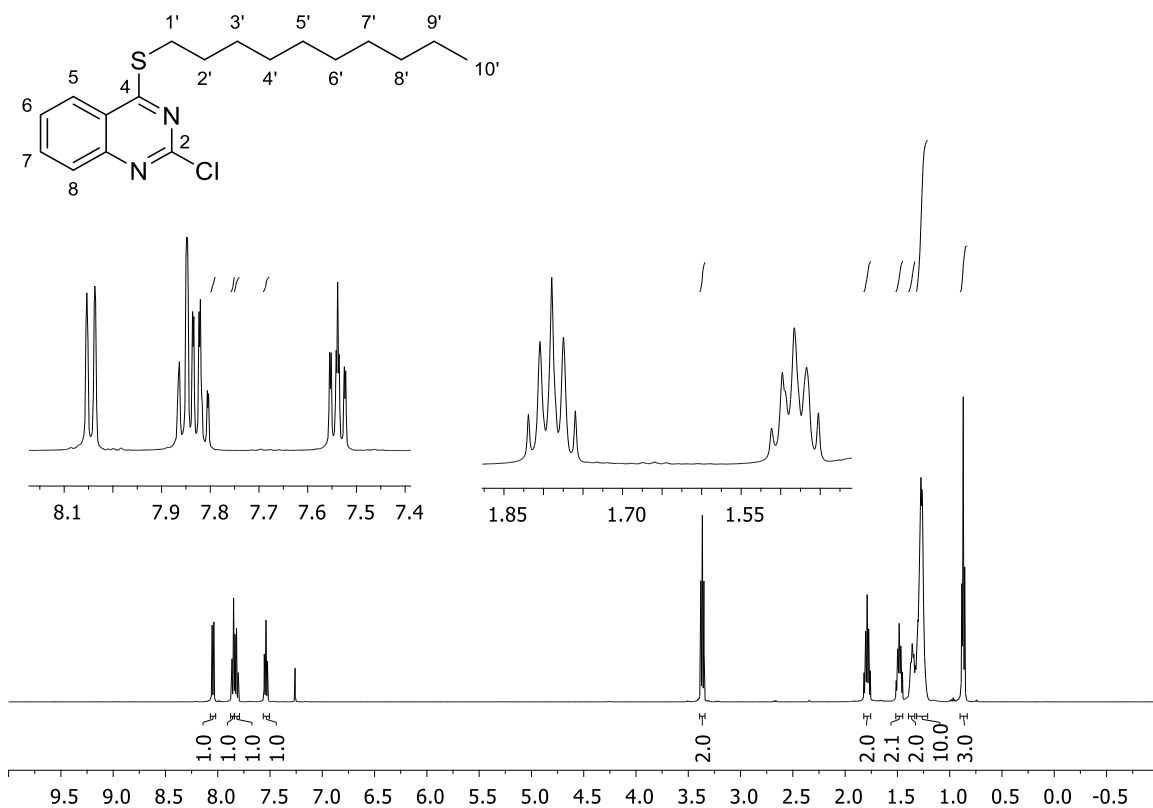
^{13}C NMR (125.7 MHz, CDCl_3) spectrum of compound 2e:



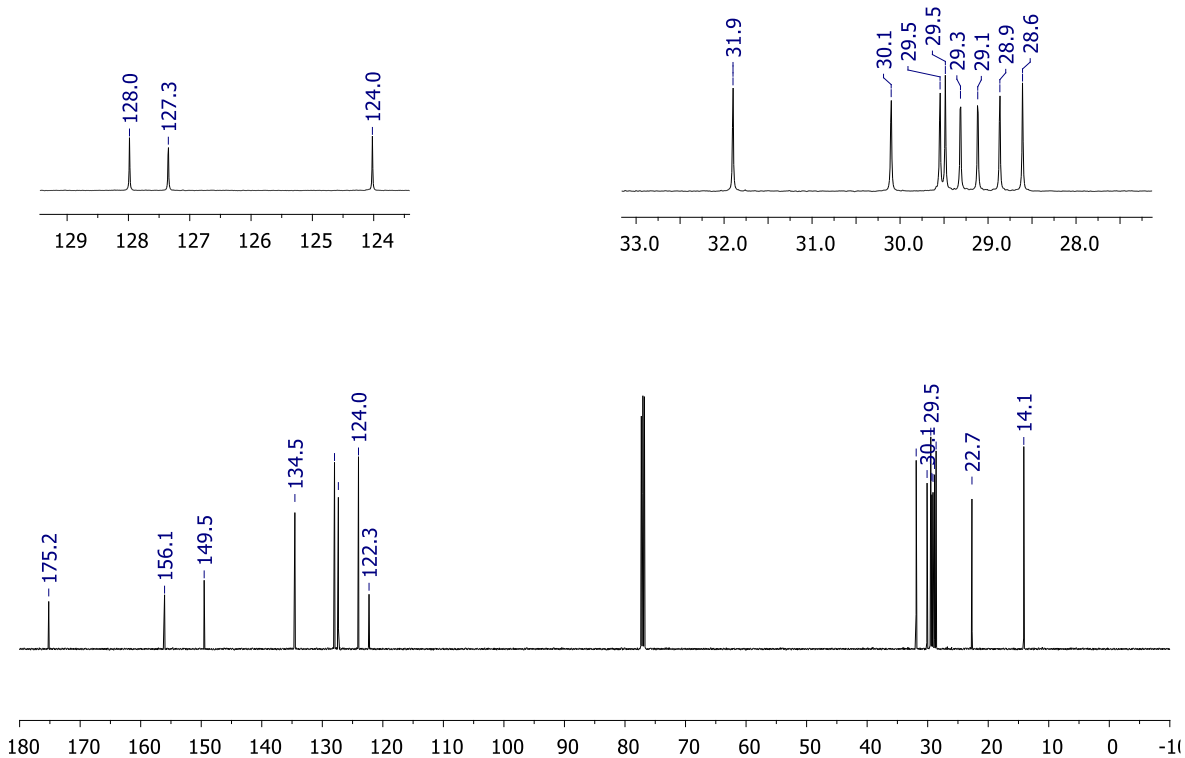
2-Chloro-4-(decylthio)quinazoline

2-Chloro-4-(decylthio)quinazoline (2f)

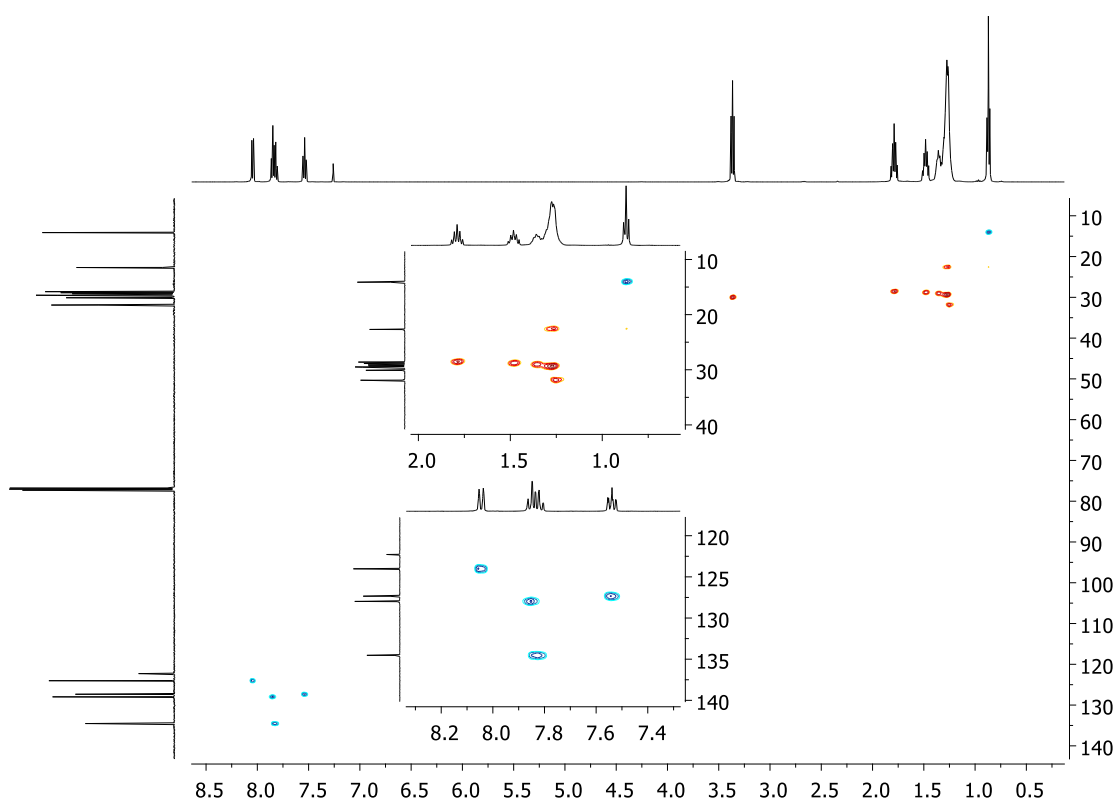
^1H NMR (500 MHz, CDCl_3) spectrum of compound 2f:



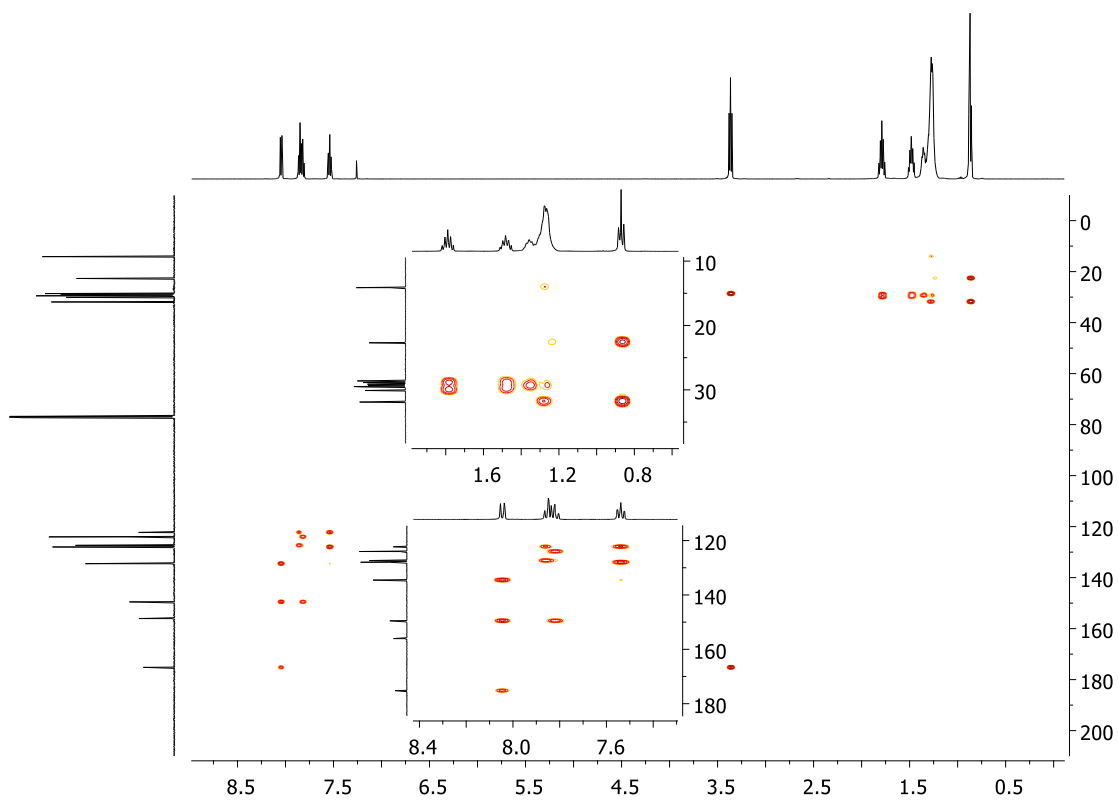
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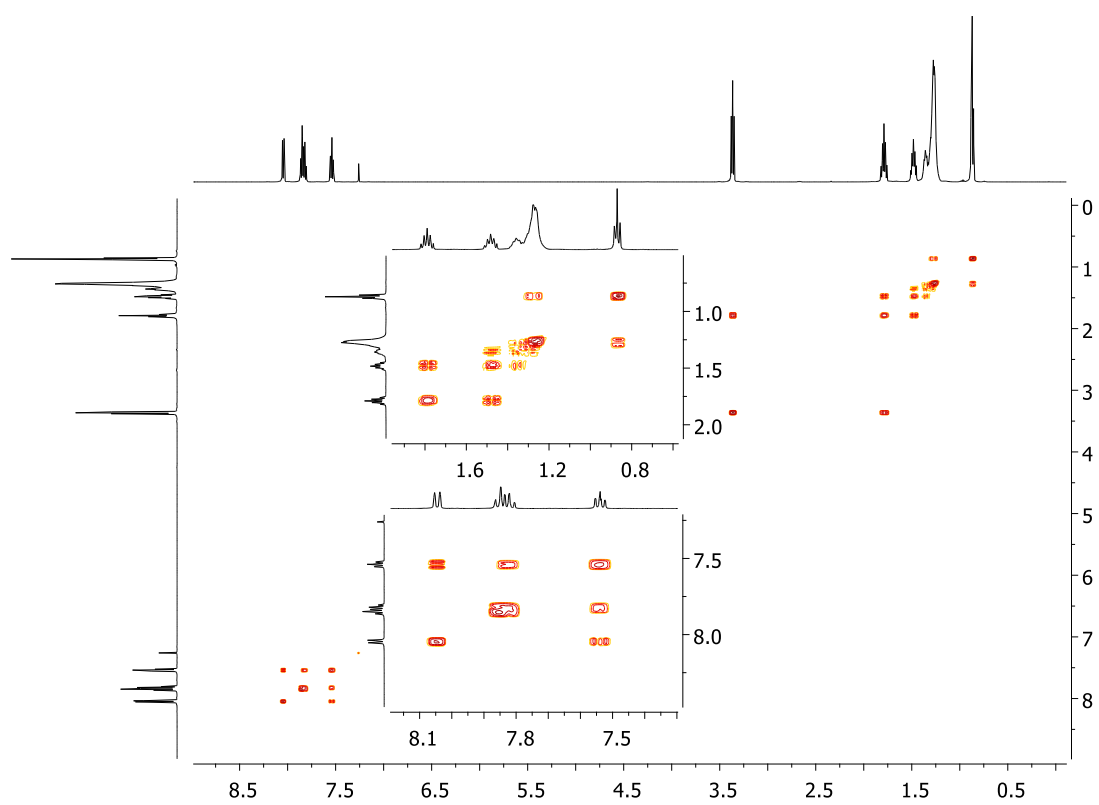
HSQC spectrum of compound 2f:



HMBC spectrum of compound 2f:



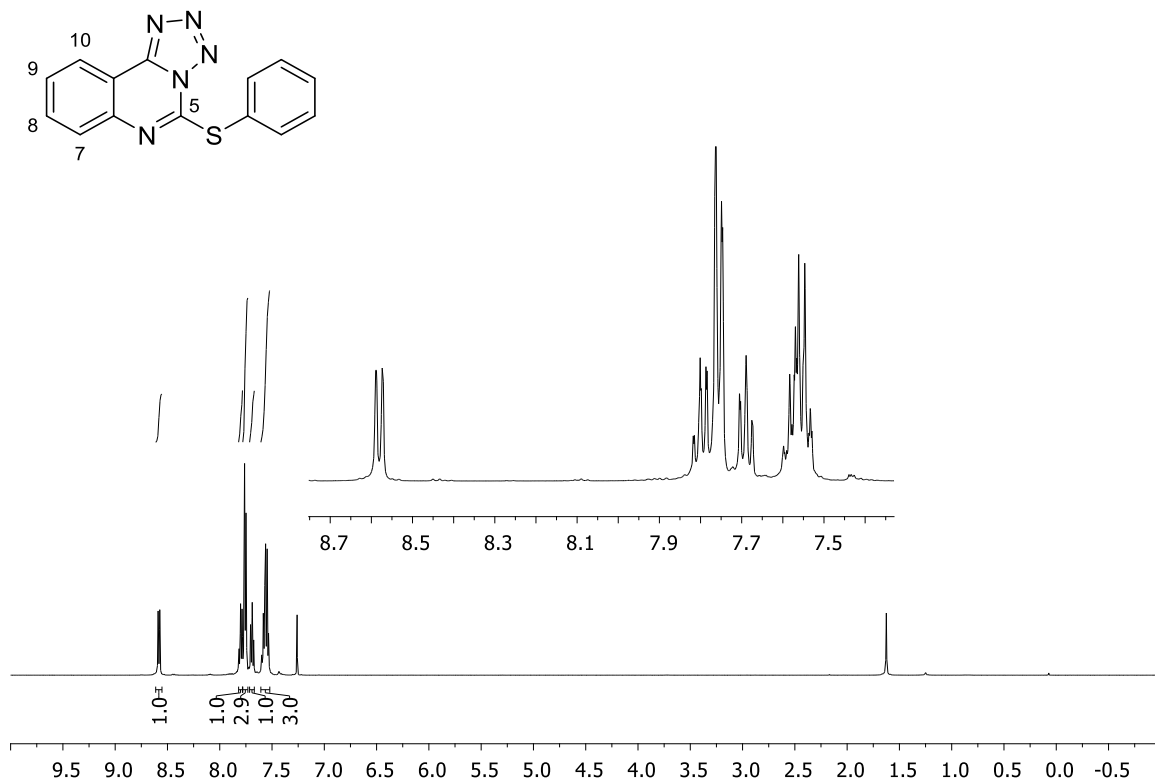
COSY spectrum of compound 2f:



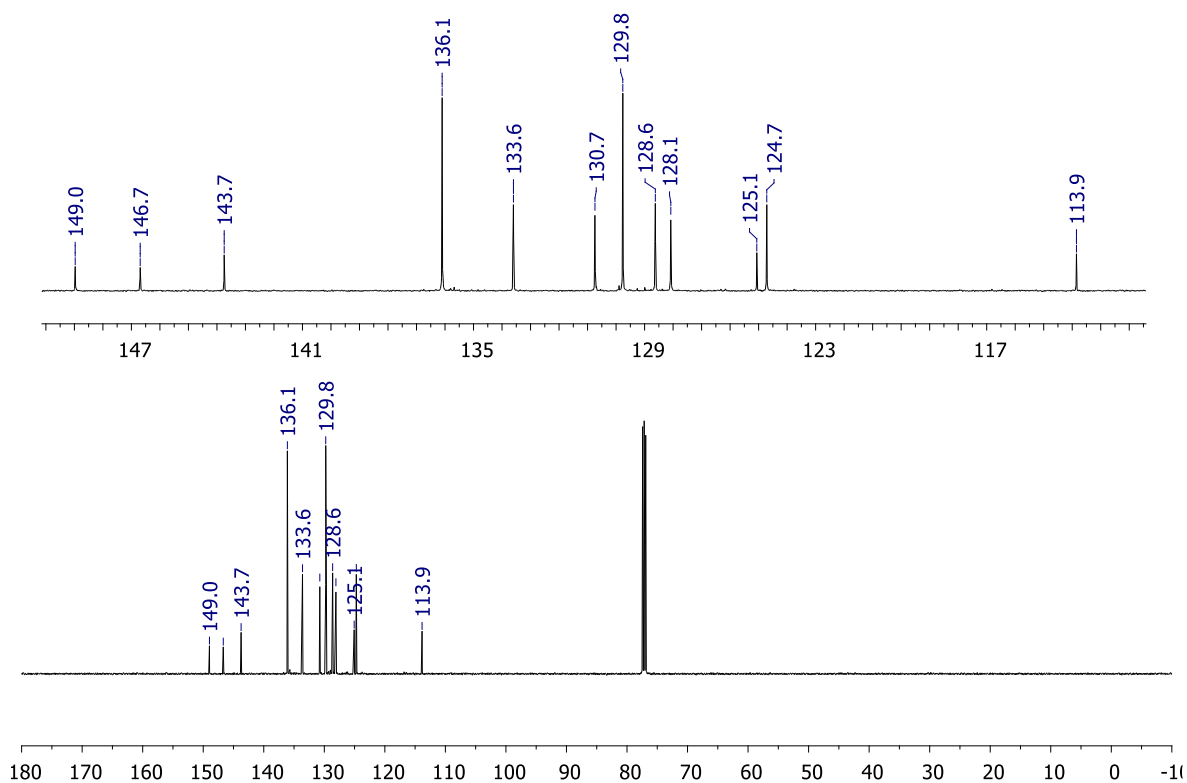
5-(Arylthio)tetrazolo[1,5-c]quinazolines

5-(Phenylthio)tetrazolo[1,5-c]quinazoline (3a)

^1H NMR (500 MHz, CDCl_3) spectrum of compound 3a:

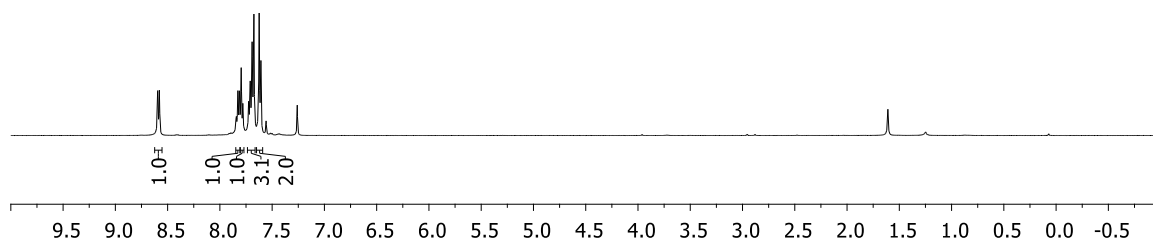
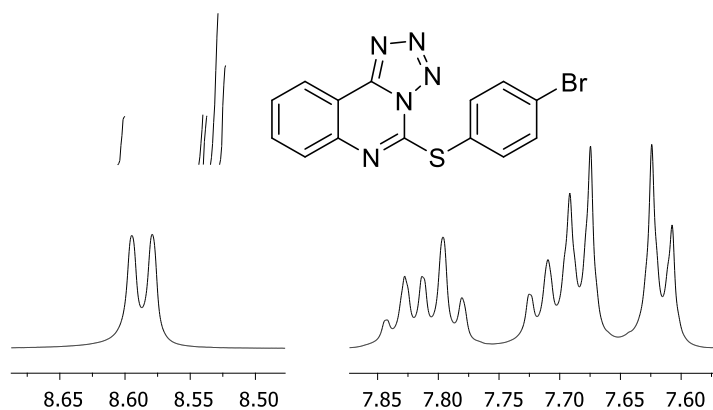


^{13}C NMR (125.7 MHz, CDCl_3) spectrum of compound 3a:

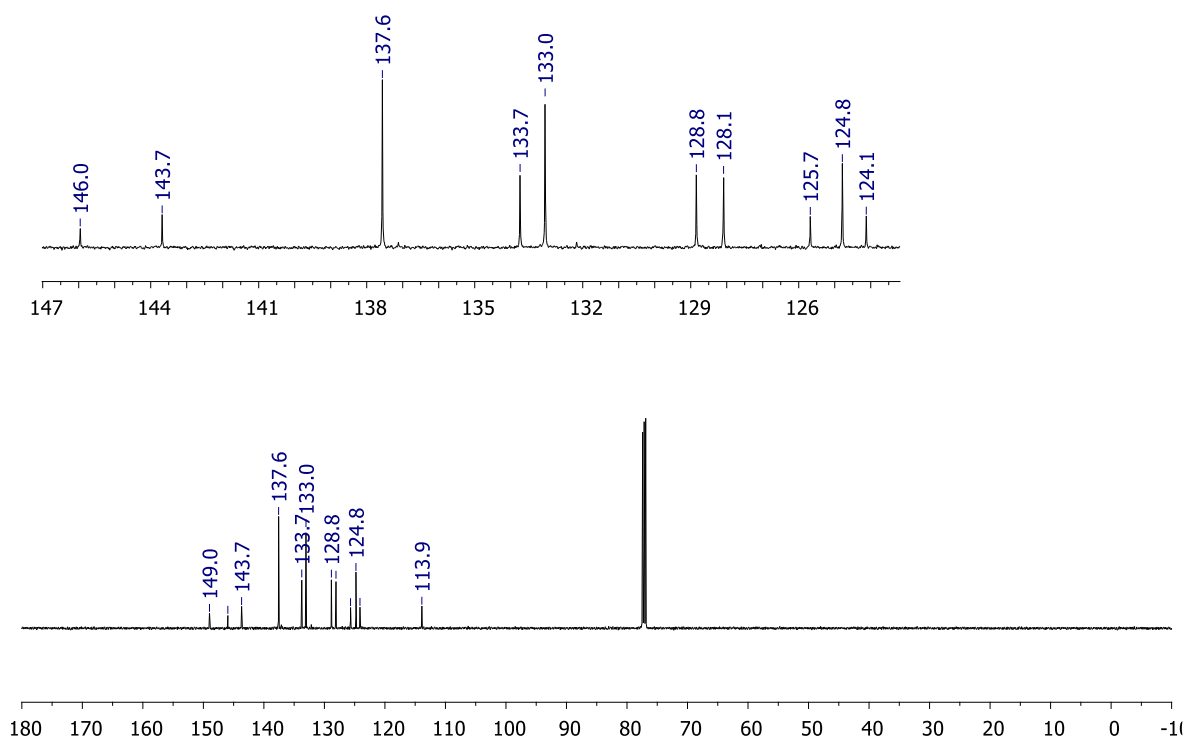


5-[(4-Bromophenyl)thio]tetrazolo[1,5-c]quinazoline (3b)

^1H NMR (500 MHz, CDCl_3) spectrum of compound 3b:

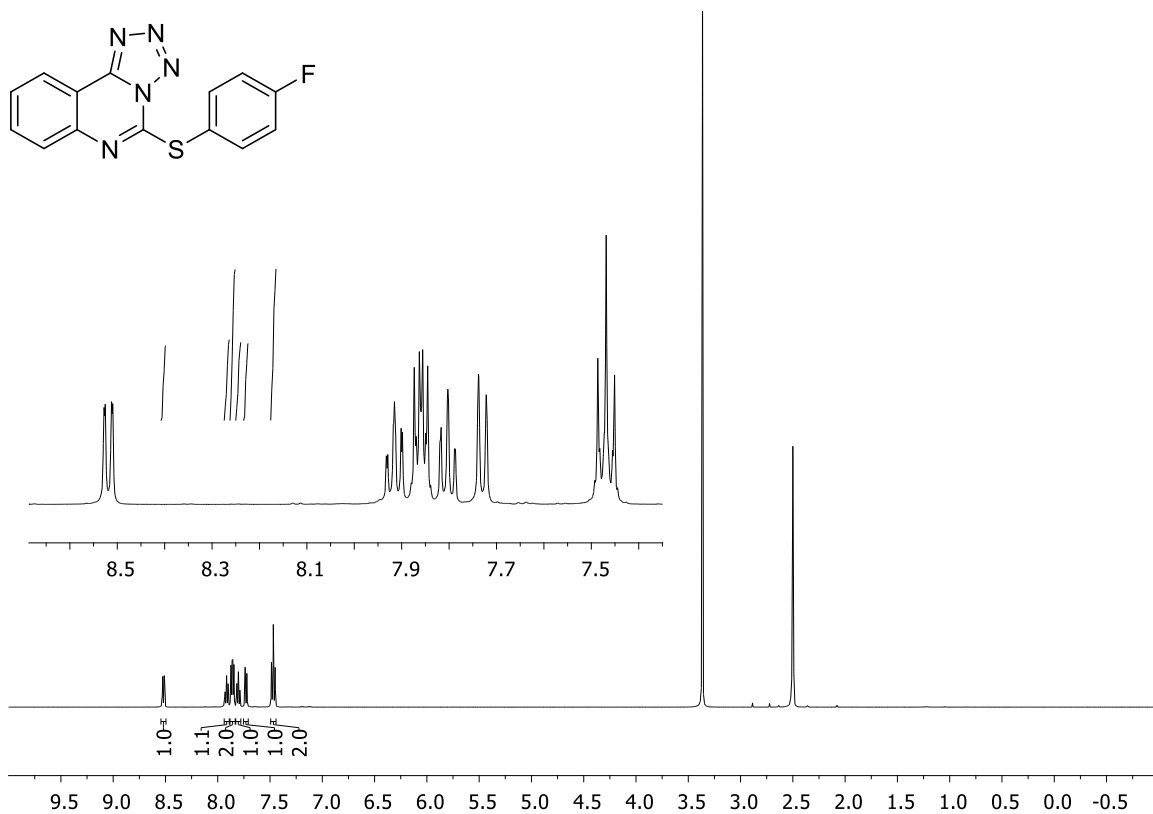


^{13}C NMR (125.7 MHz, CDCl_3) spectrum of compound 3b:

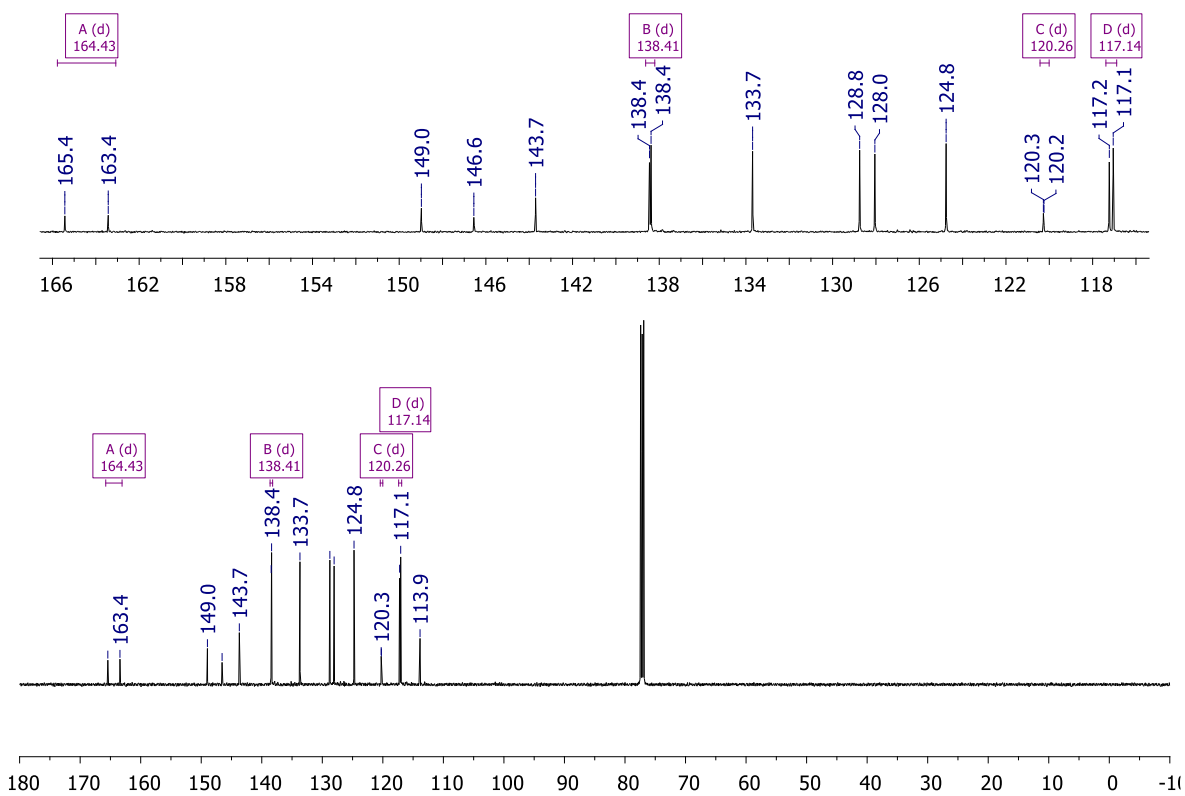


5-[(4-Fluorophenyl)thio]tetrazolo[1,5-c]quinazoline (3c)

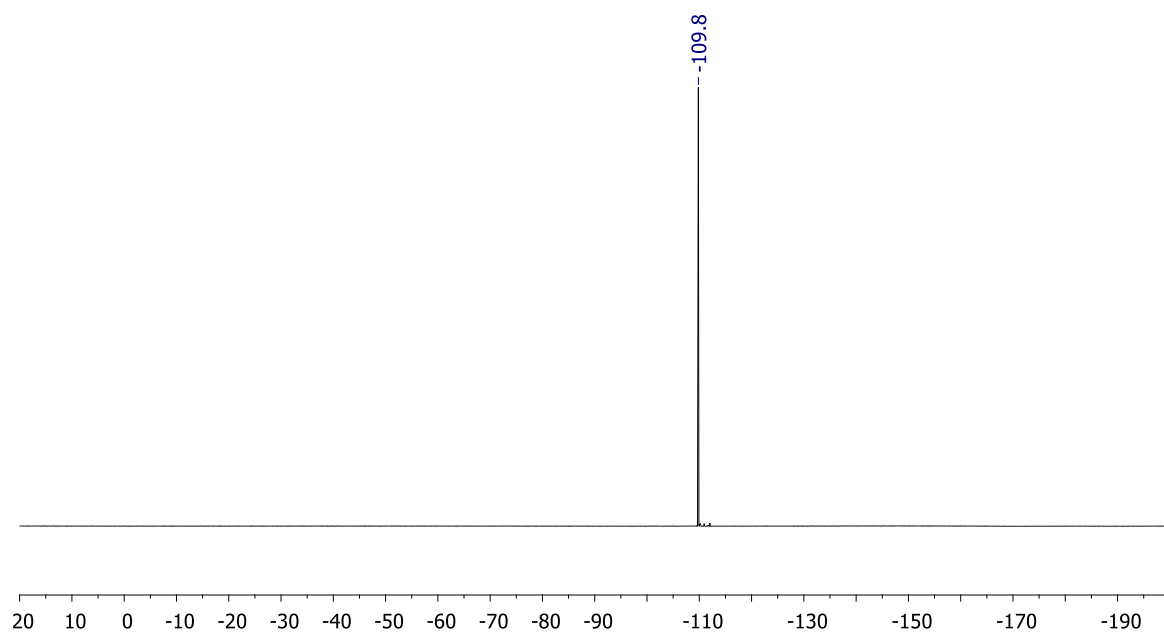
^1H NMR (500 MHz, DMSO-d_6) spectrum of compound 3c:



^{13}C NMR (125.7 MHz, CDCl_3) spectrum of compound 3c:

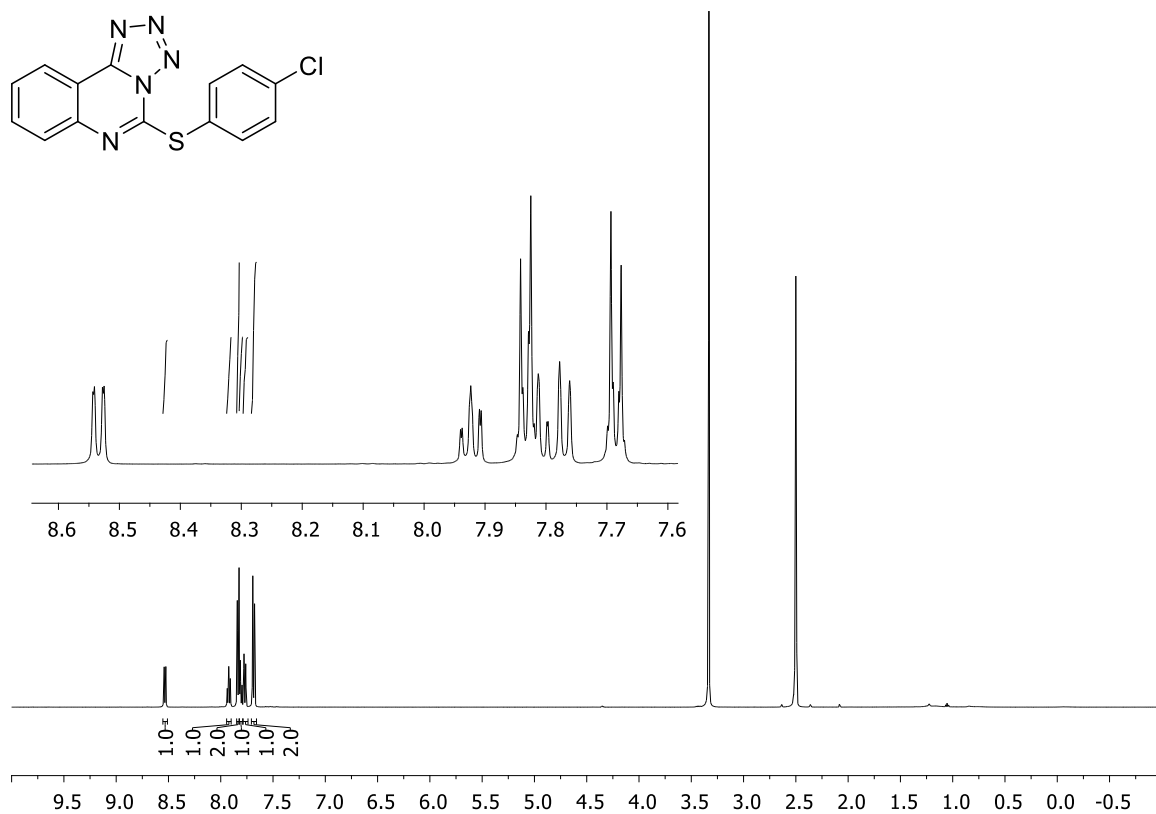


^{19}F NMR (470.5 MHz, DMSO-d_6) spectrum of compound 3c:

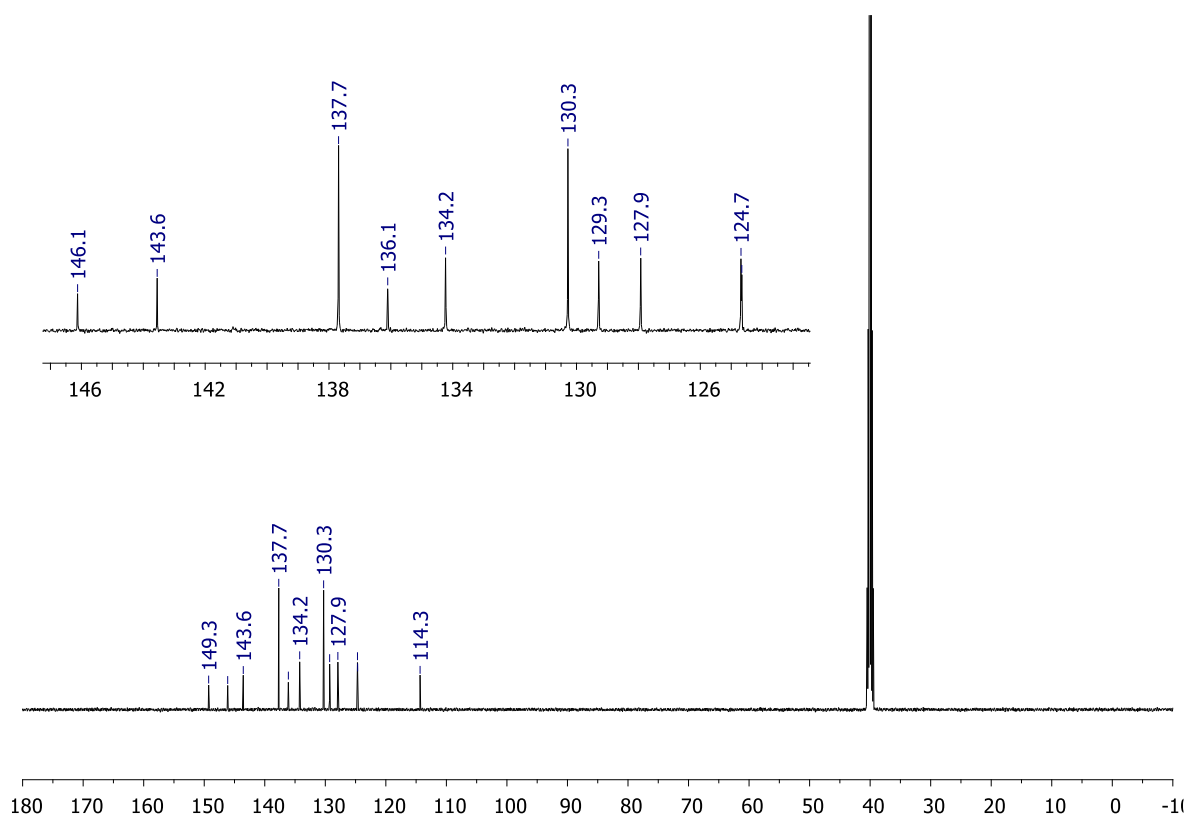


5-[(4-Chlorophenyl)thio]tetrazolo[1,5-c]quinazoline (3d)

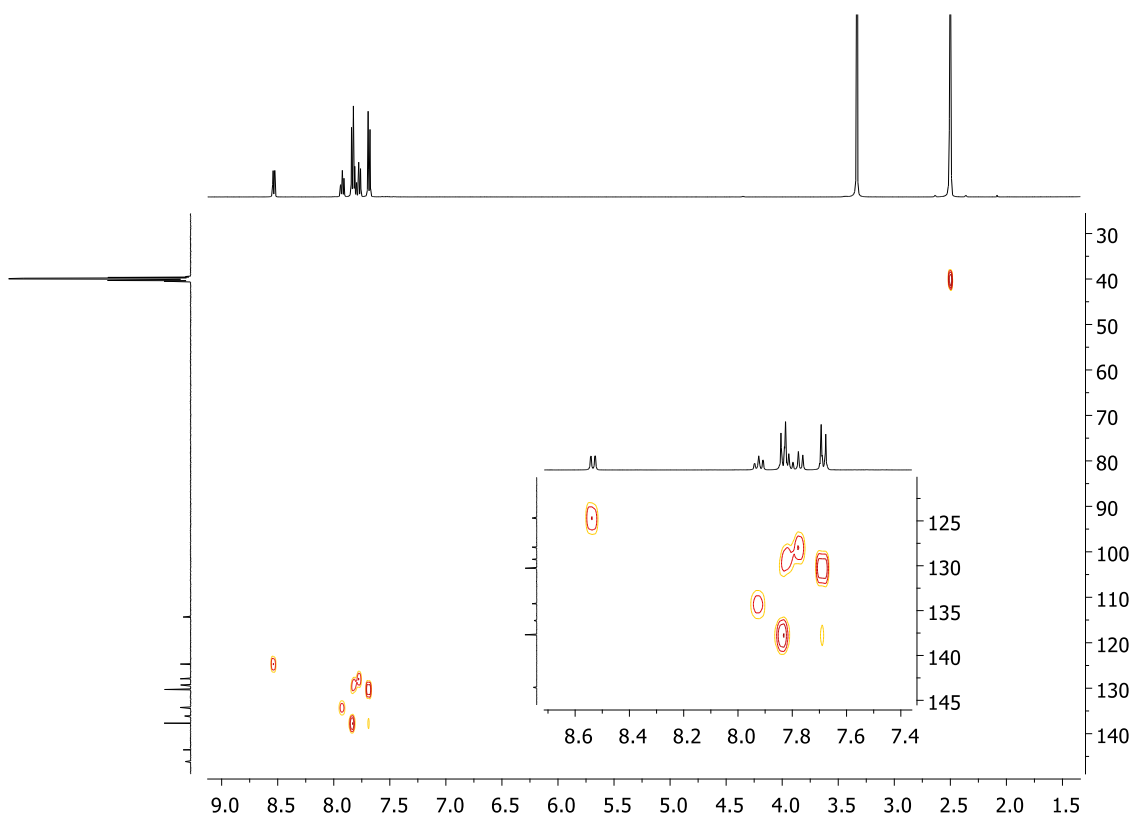
^1H NMR (500 MHz, DMSO-d_6) spectrum of compound 3d:



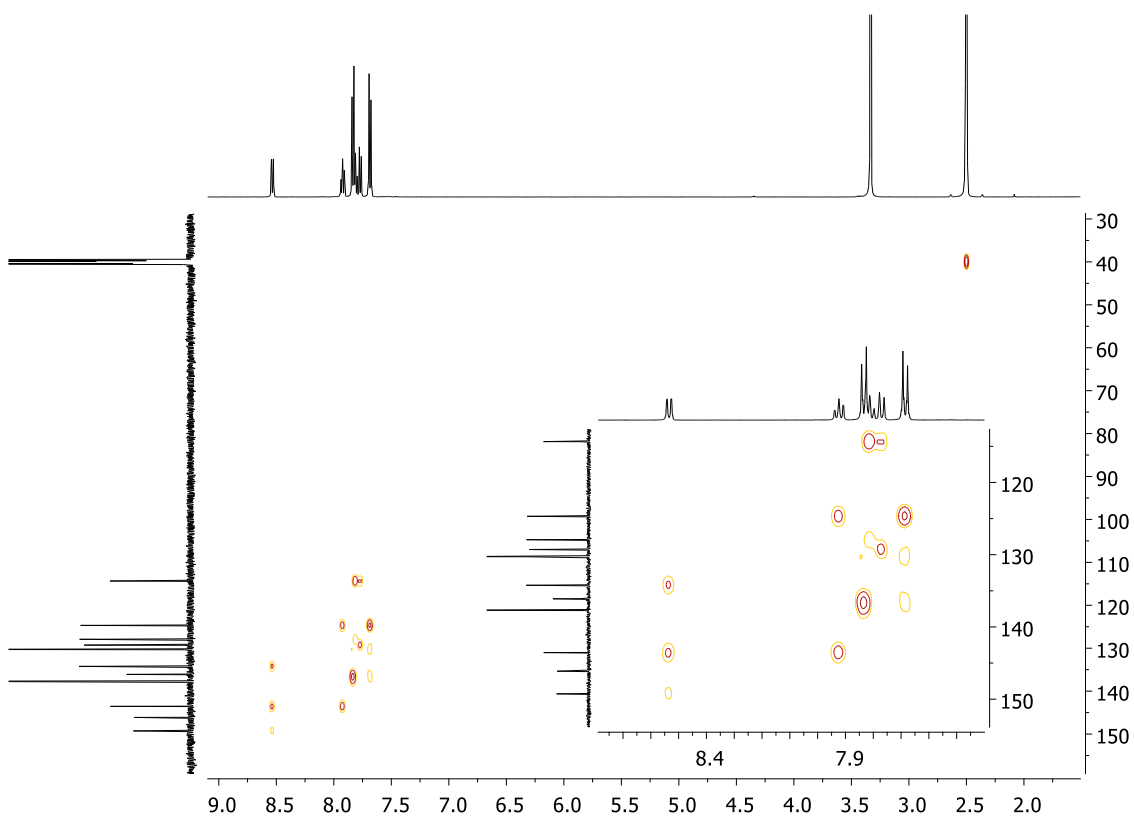
^{13}C NMR (125.7 MHz, DMSO-d_6) spectrum of compound 3d:



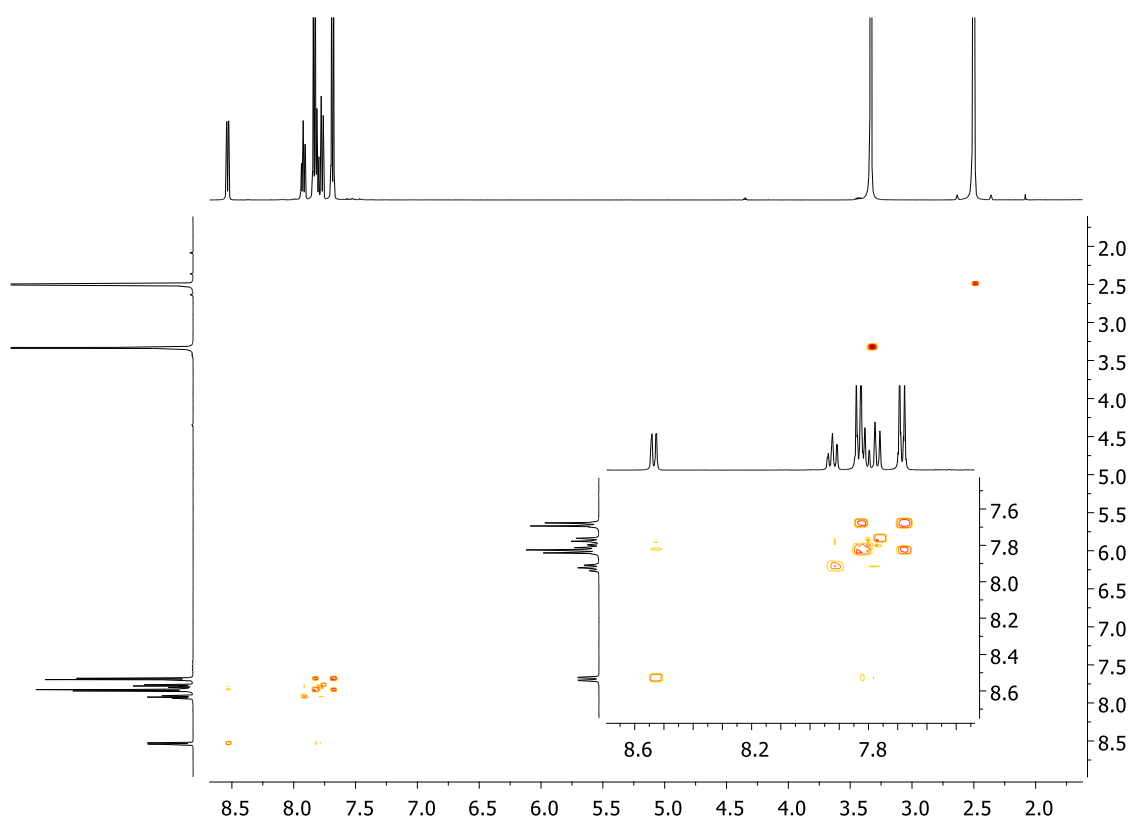
HSQC spectrum of compound 3d:



HMBC spectrum of compound 3d:

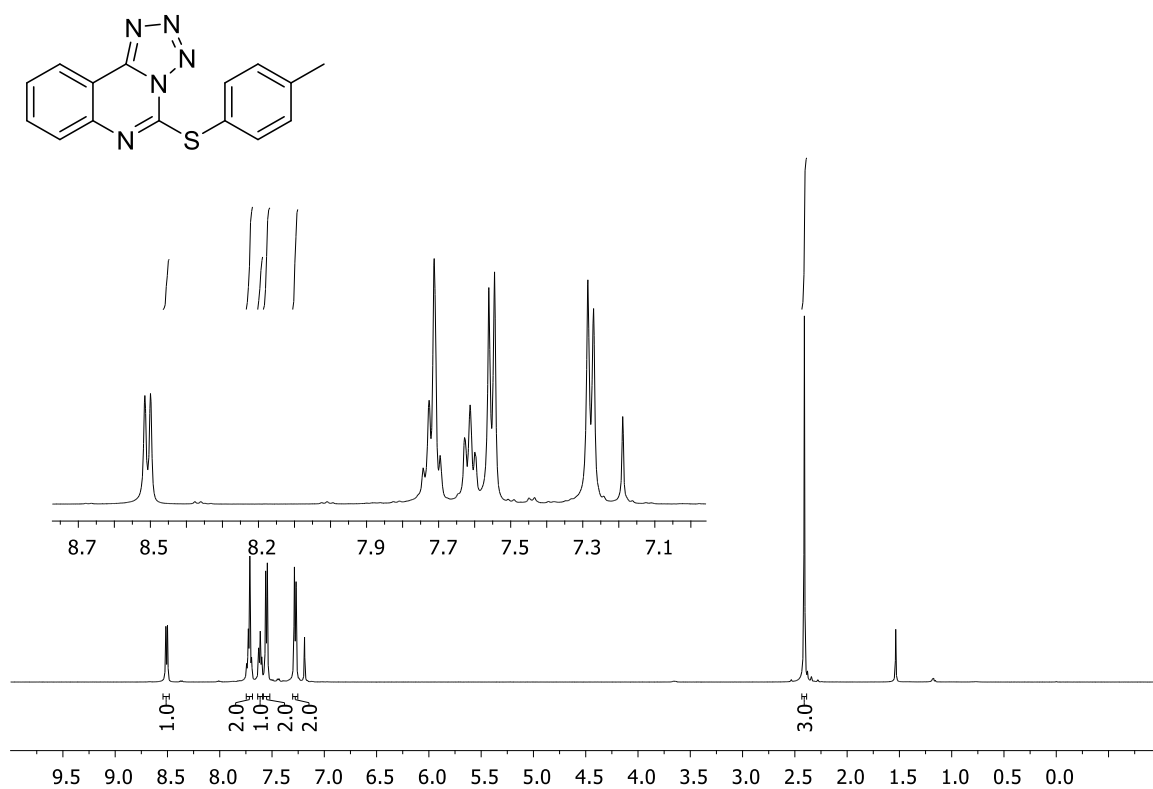


COSY spectrum of compound 3d:

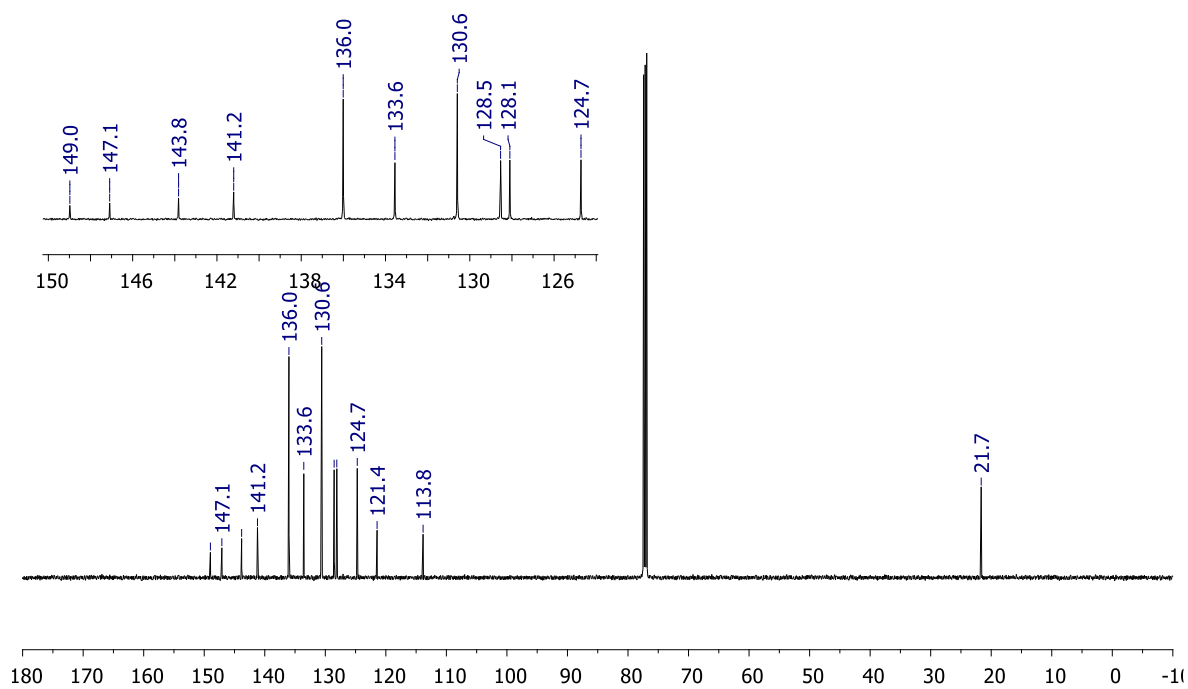


5-(*p*-Tolylthio)tetrazolo[1,5-*c*]quinazoline (3e)

¹H NMR (500 MHz, CDCl₃) spectrum of compound 3e:

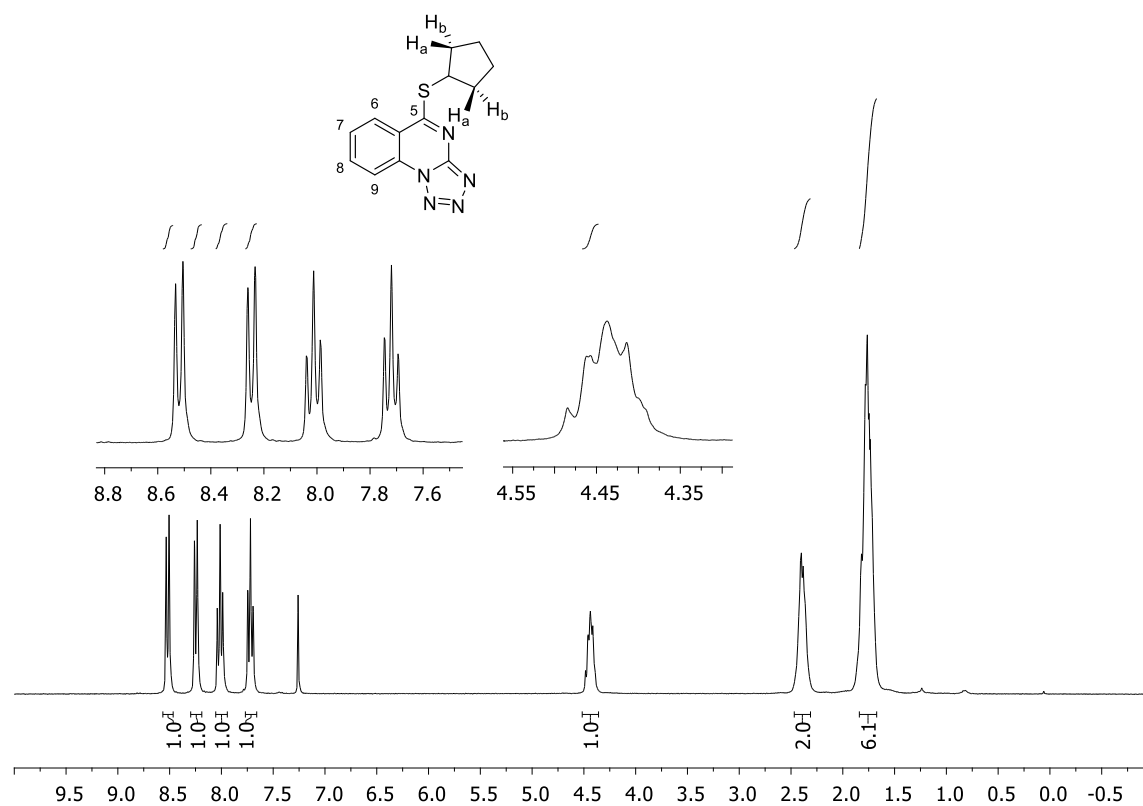


¹³C NMR (125.7 MHz, CDCl₃) spectrum of compound 3e:

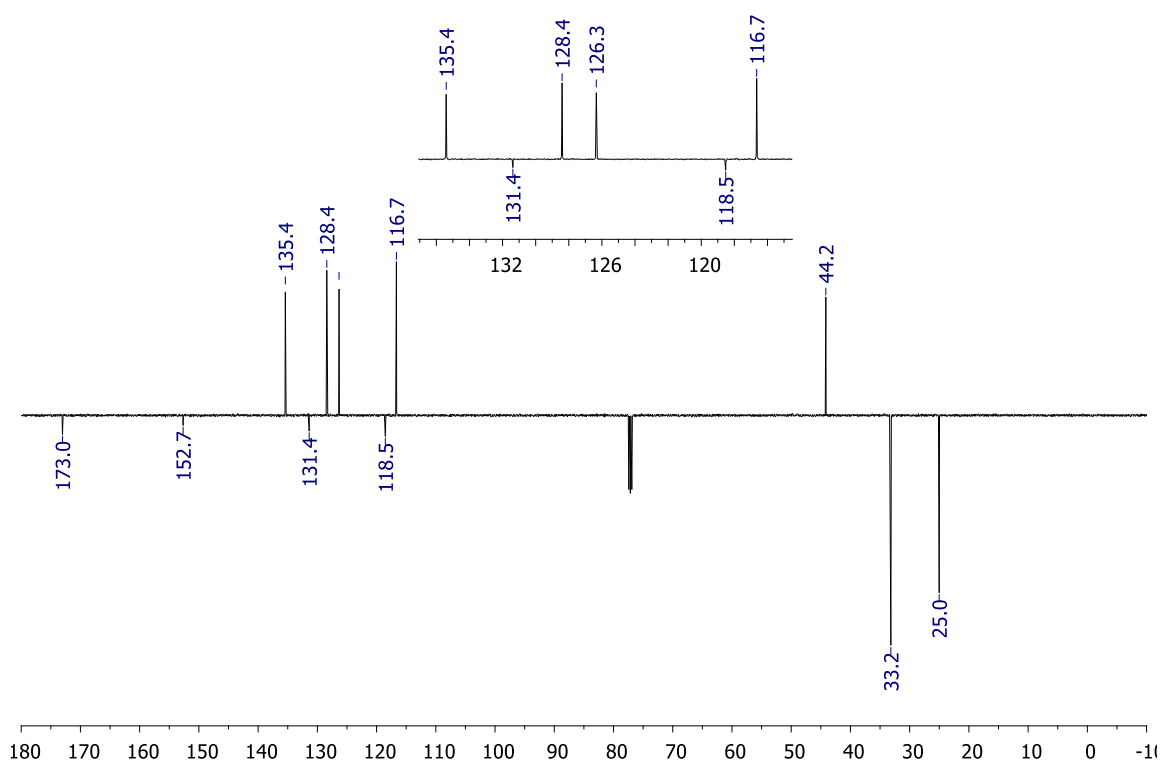


5-(Alkyl/Arylthio)tetrazolo[1,5-a]quinazolines

5-(Cyclopentylthio)tetrazolo[1,5-a]quinazoline (4a),
 ^1H NMR (300 MHz, CDCl_3) spectrum of compound 4a:

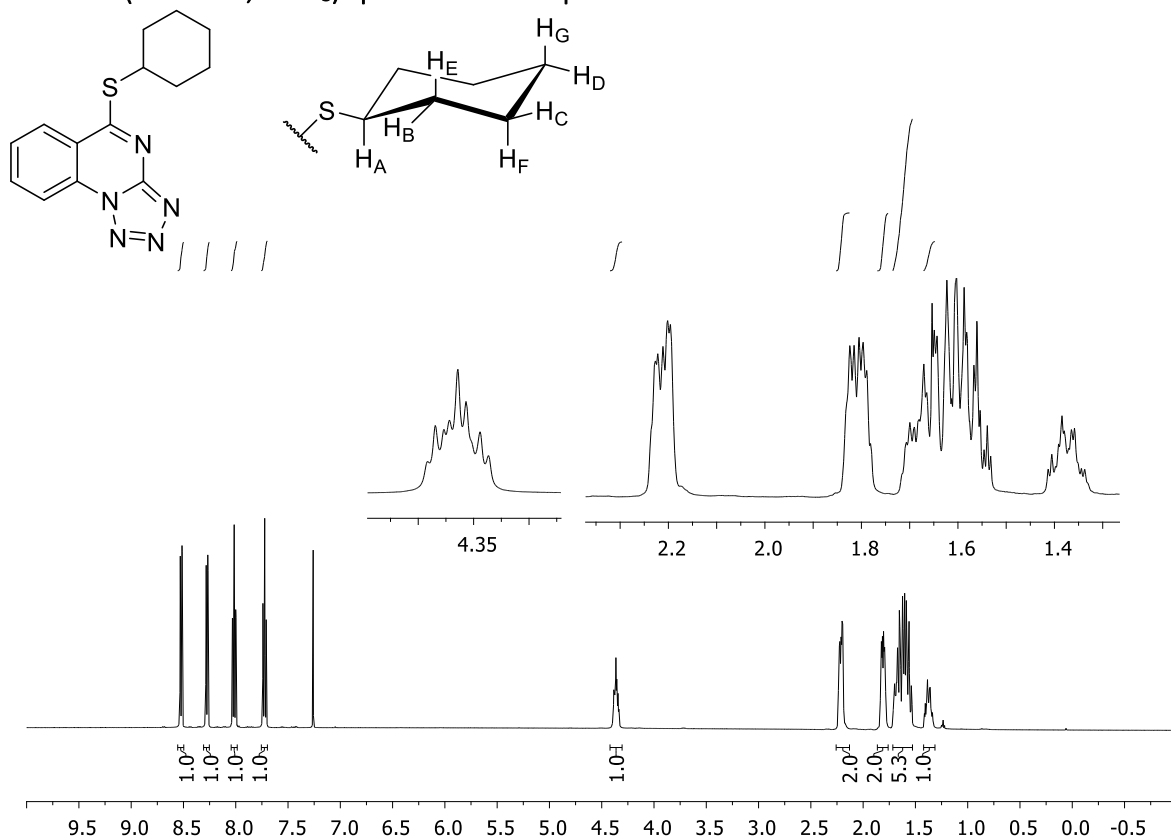


^{13}C NMR (125.7 MHz, CDCl_3) spectrum of compound 4a:

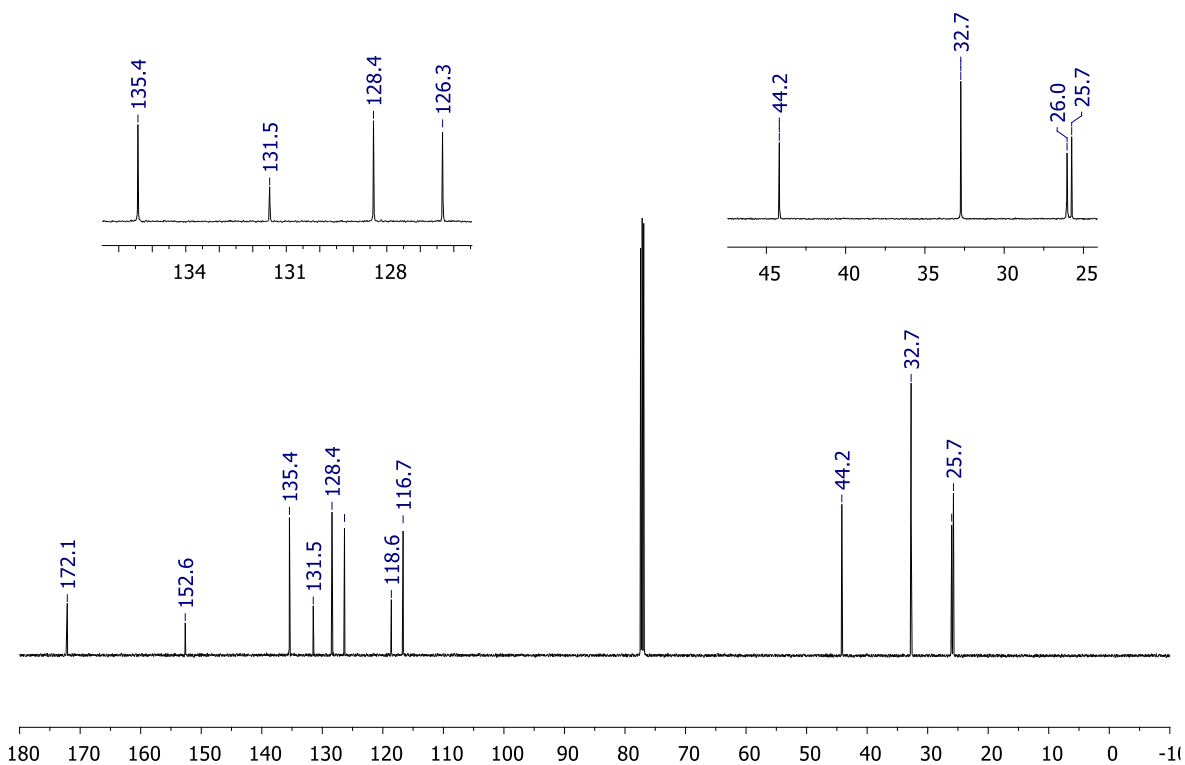


5-(Cyclohexylthio)tetrazolo[1,5-a]quinazoline (4b)

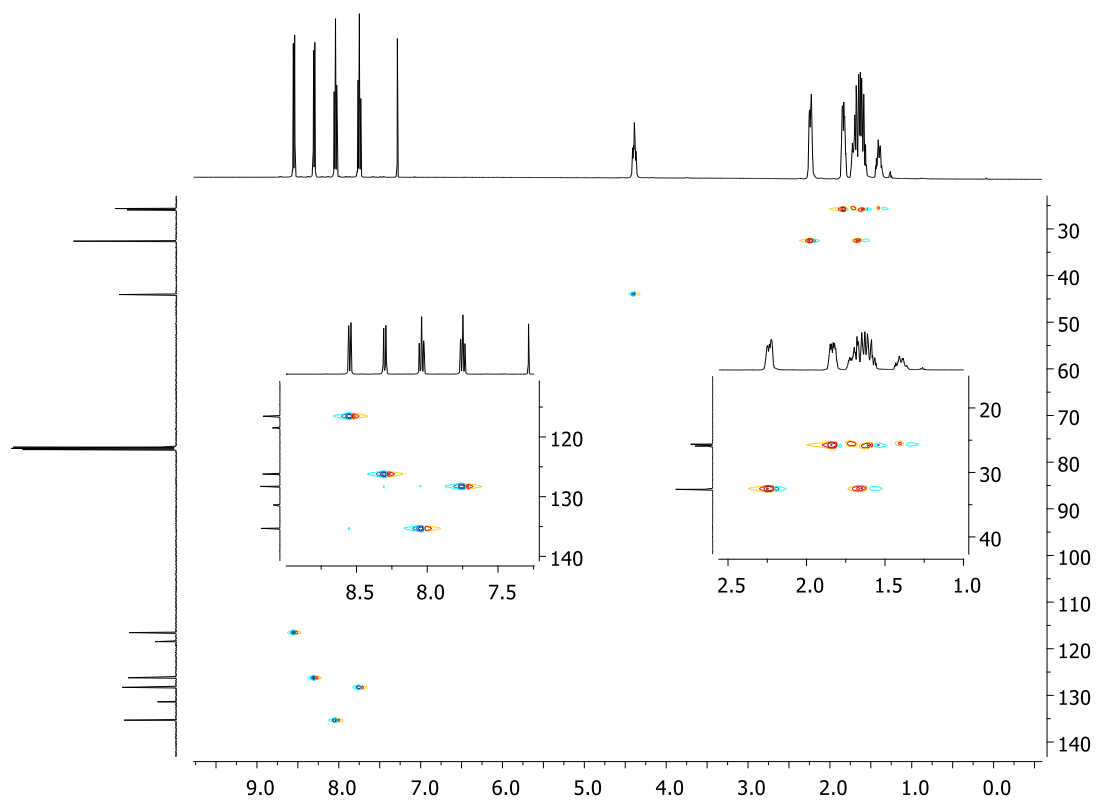
^1H NMR (500 MHz, CDCl_3) spectrum of compound 4b:



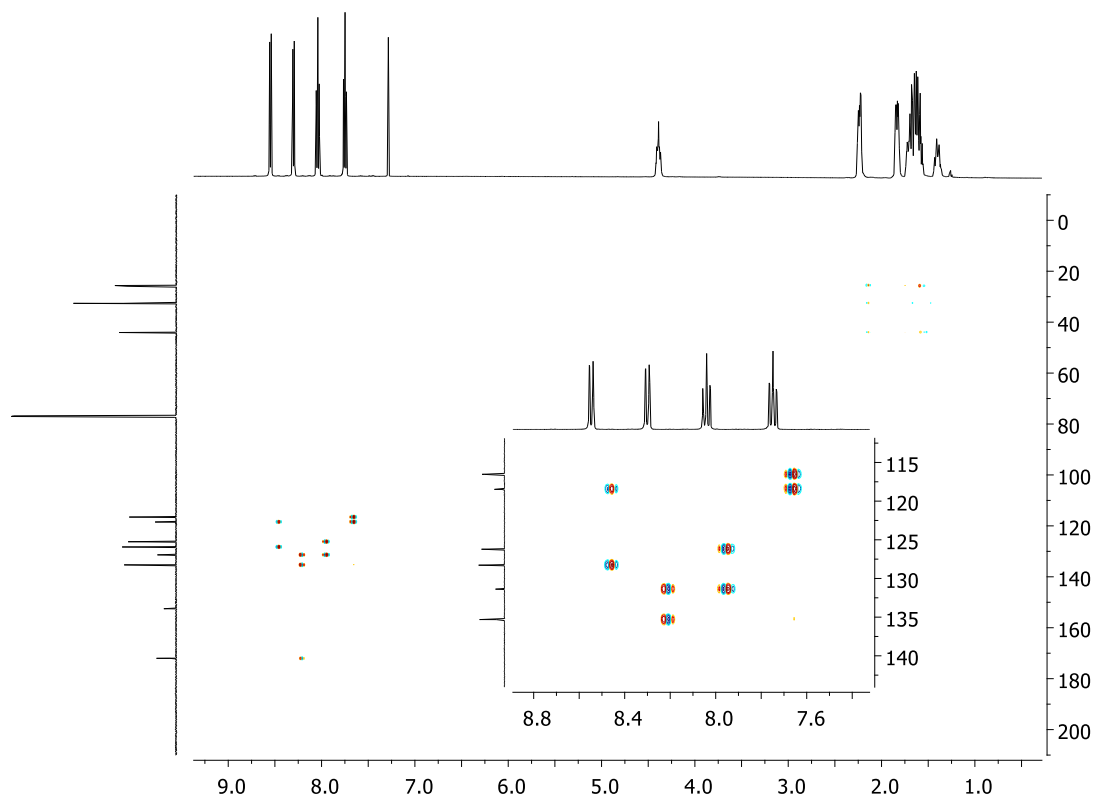
^{13}C NMR (125.7 MHz, CDCl_3) spectrum of compound 4b:



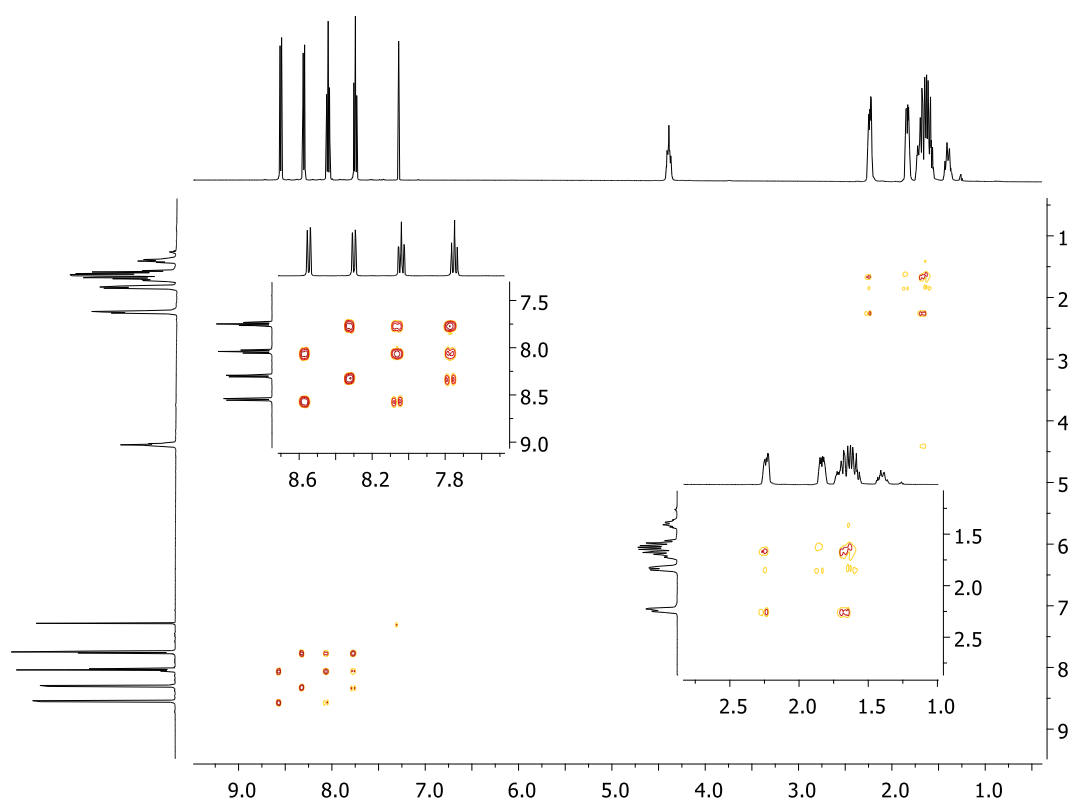
HSQC spectrum of compound 4b:



HMBC spectrum of compound 4b:

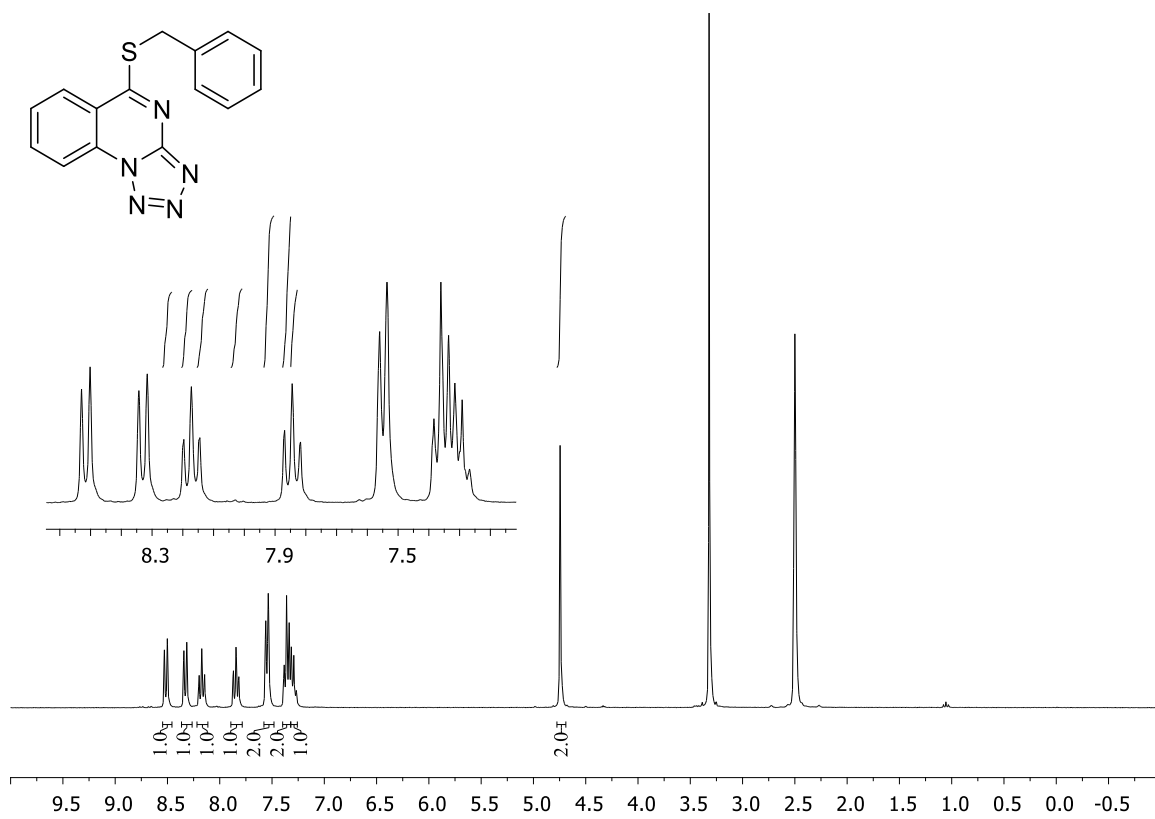


COSY spectrum of compound 4b:

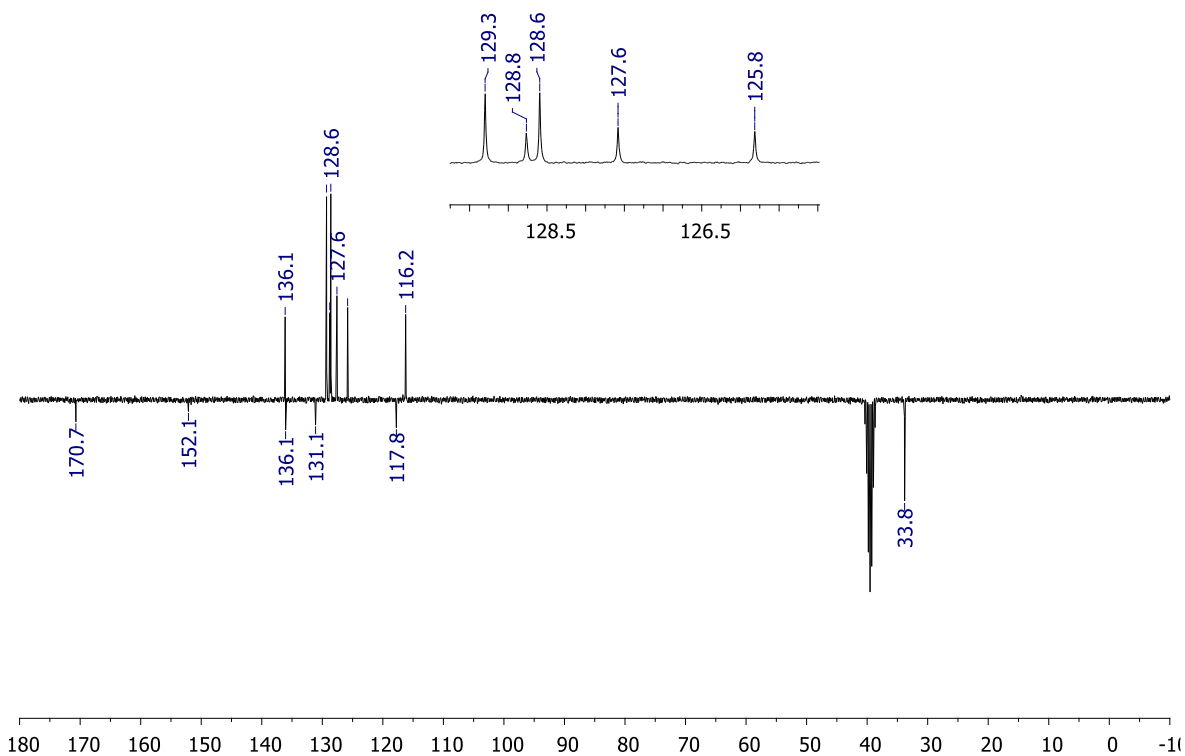


5-(Benzylthio)tetrazolo[1,5-a]quinazoline (4c)

^1H NMR (300 MHz, DMSO-d_6) spectrum of compound 4c:

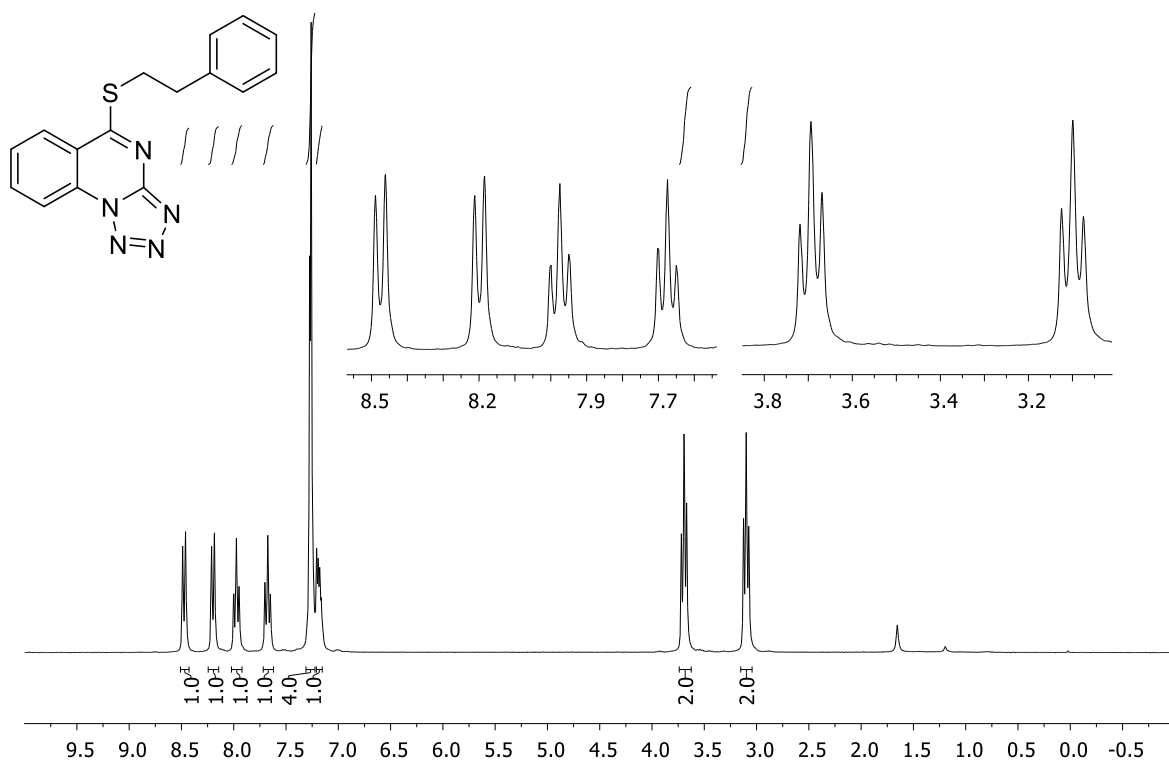


^{13}C NMR (75.5 MHz, DMSO-d_6) spectrum of compound 4c:

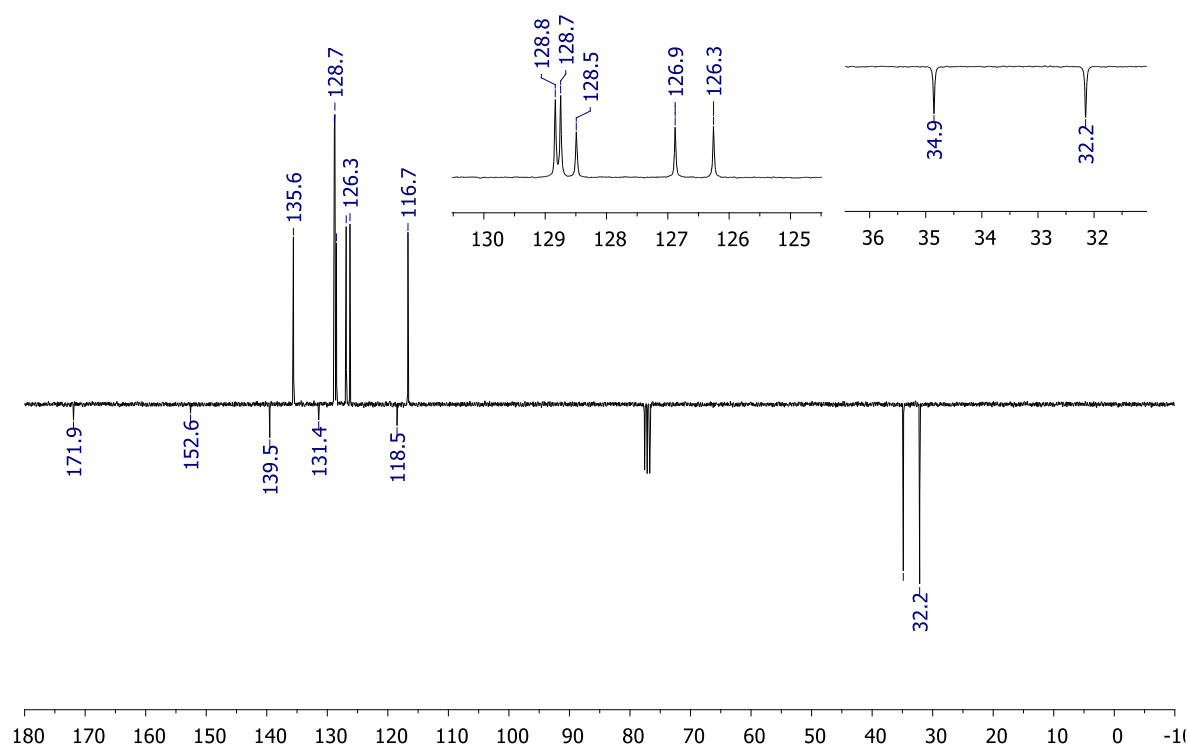


5-[(2-Phenyl)ethylthio]tetrazolo[1,5-a]quinazoline (4d)

^1H NMR (300 MHz, CDCl_3) spectrum of compound 4d:

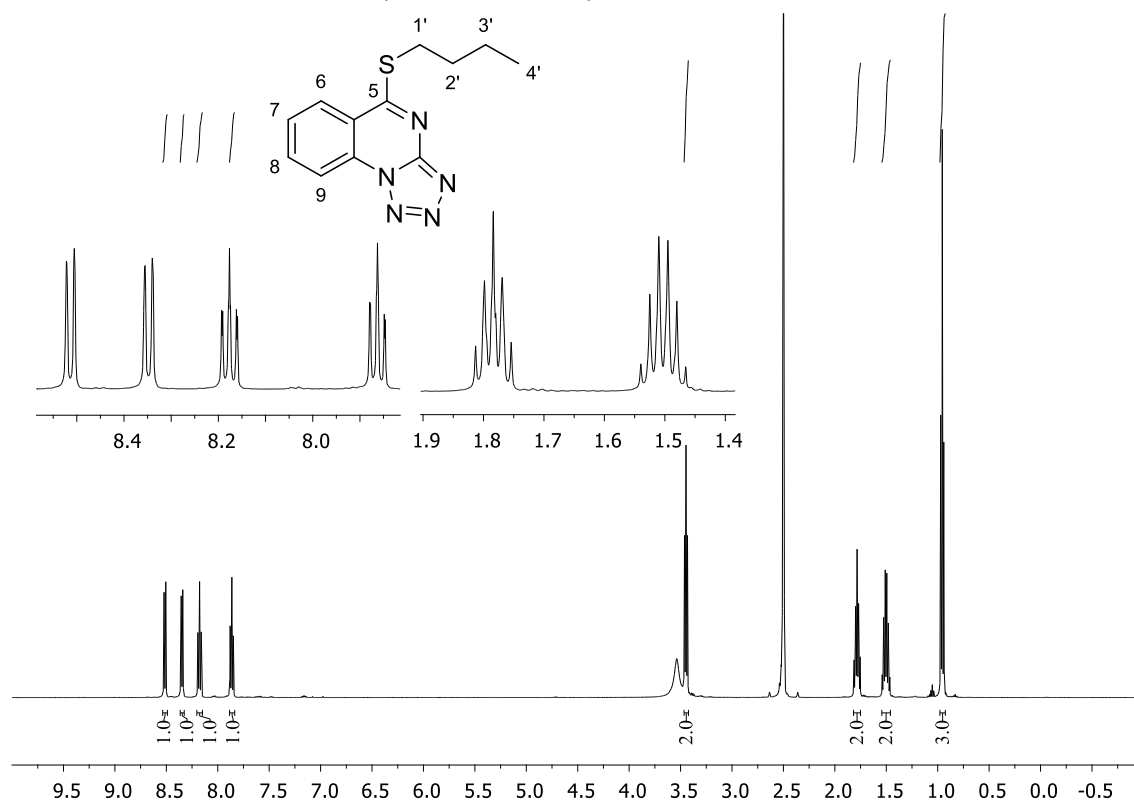


^{13}C NMR (75.5 MHz, CDCl_3) spectrum of compound 4d:

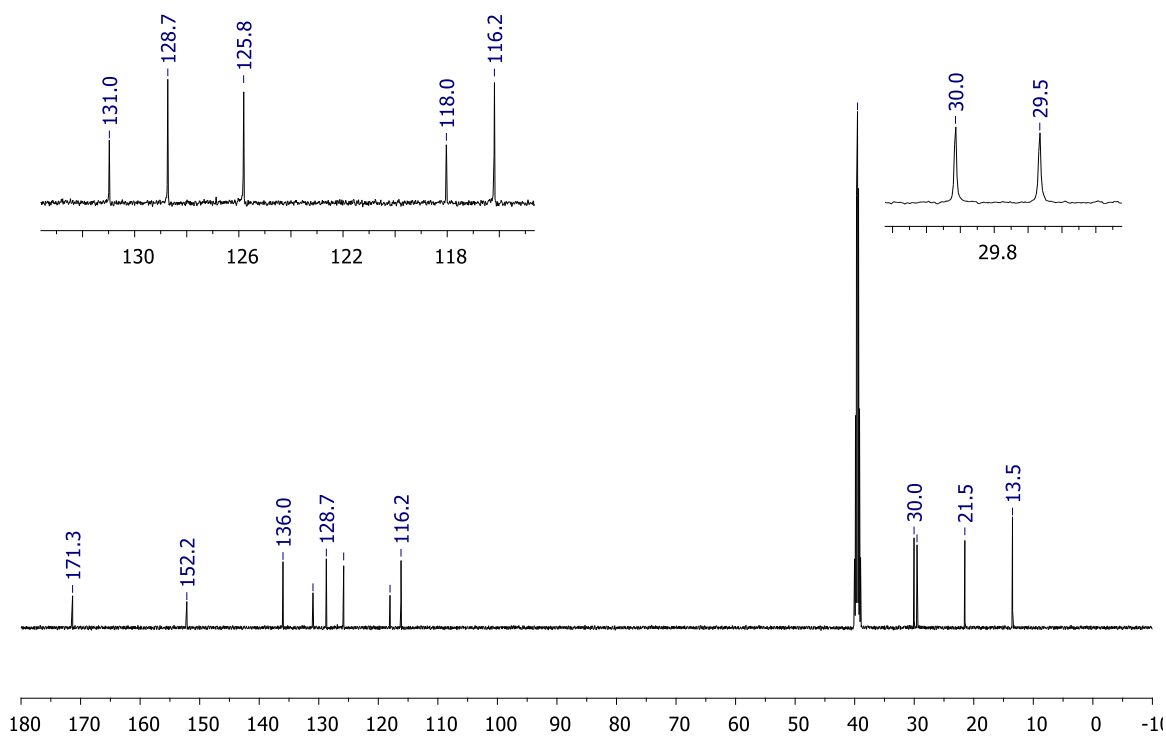


5-(Butylthio)tetrazolo[1,5-a]quinazoline (4e)

^1H NMR (500 MHz, DMSO-d_6) spectrum of compound 4e:

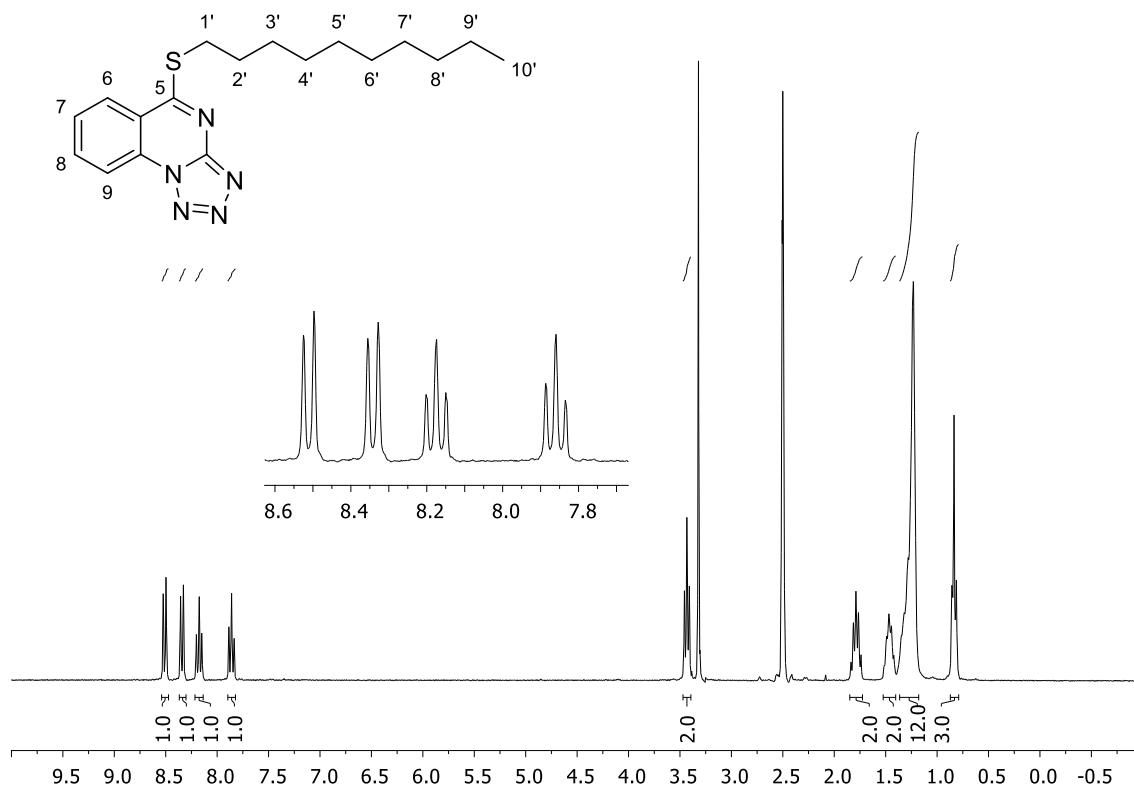


^{13}C NMR (125.7 MHz, DMSO-d_6) spectrum of compound 4e:

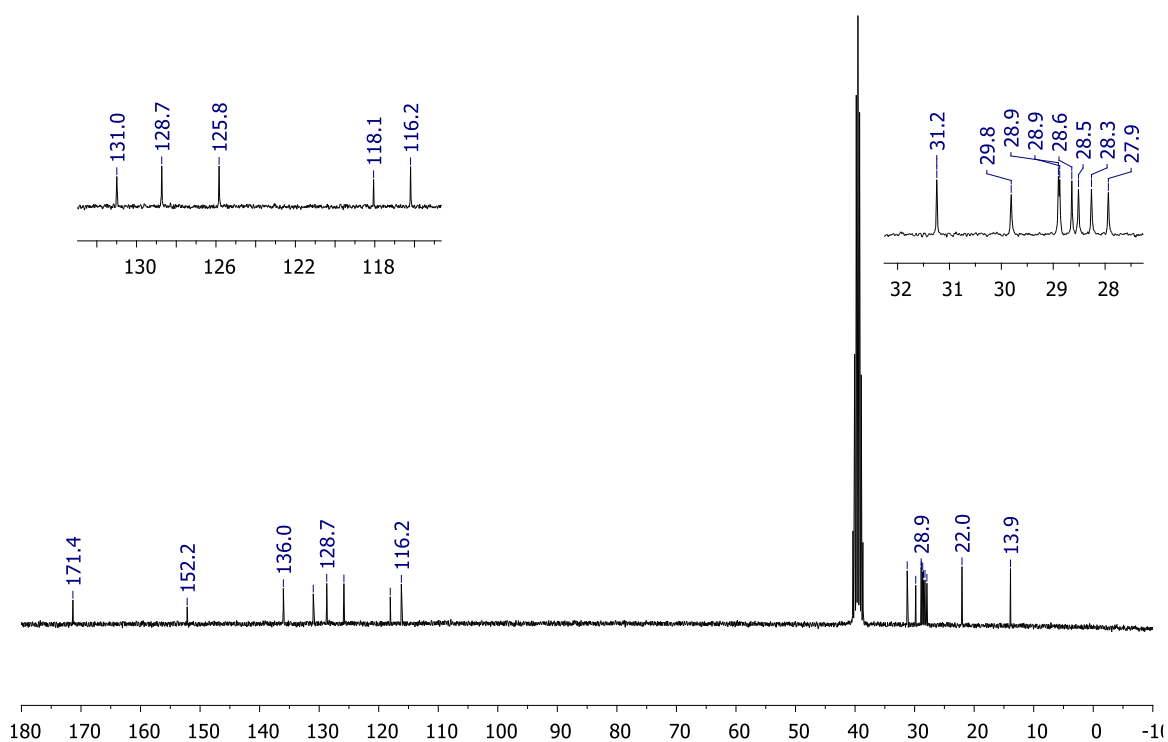


5-(Decylthio)tetrazolo[1,5-a]quinazoline (4f)

^1H NMR (300 MHz, DMSO-d_6) spectrum of compound 4f:

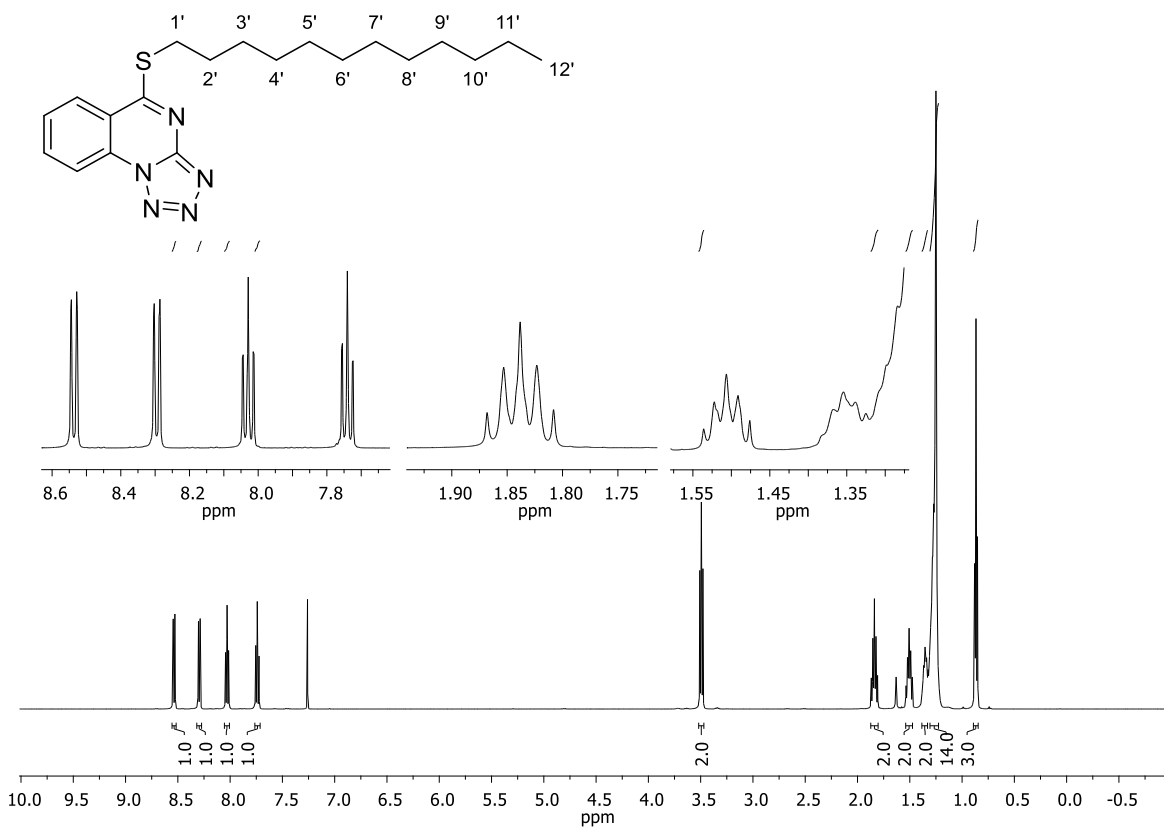


^{13}C NMR (75.5 MHz, DMSO-d_6) spectrum of compound 4f:

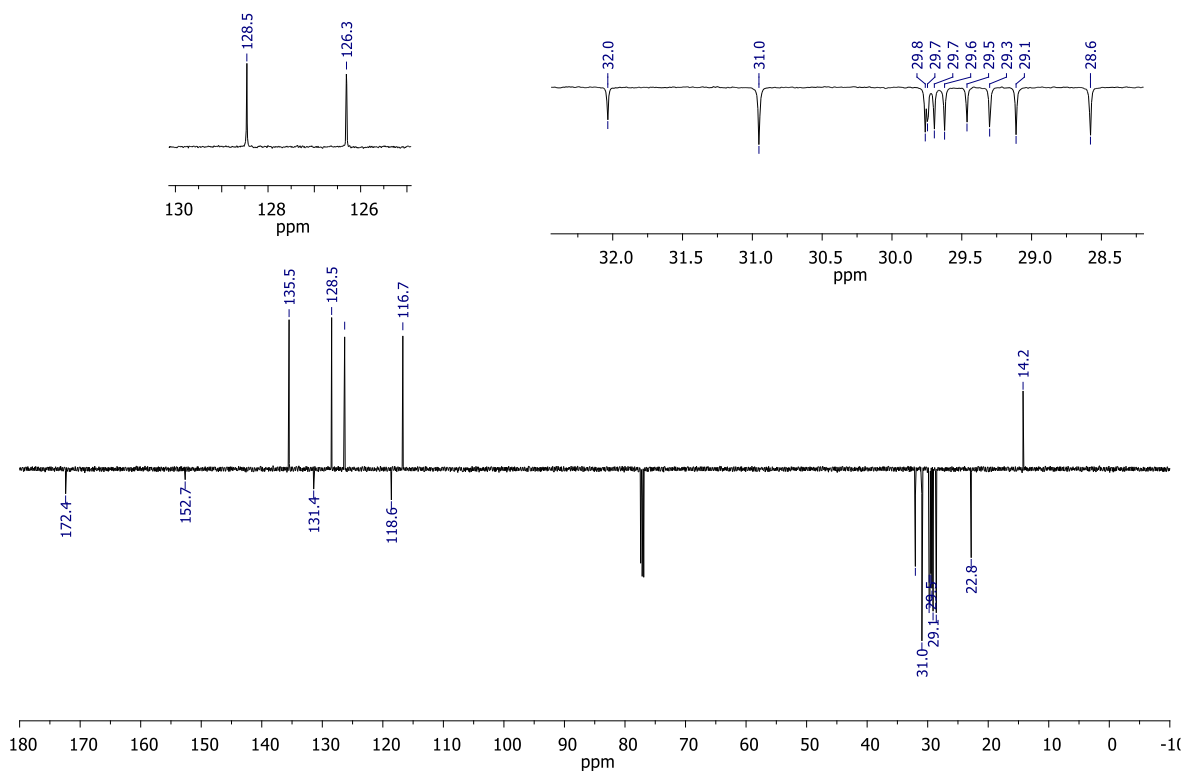


5-(Dodecylthio)tetrazolo[1,5-a]quinazoline (4g)

^1H NMR (500 MHz, CDCl_3) spectrum of compound 4g:

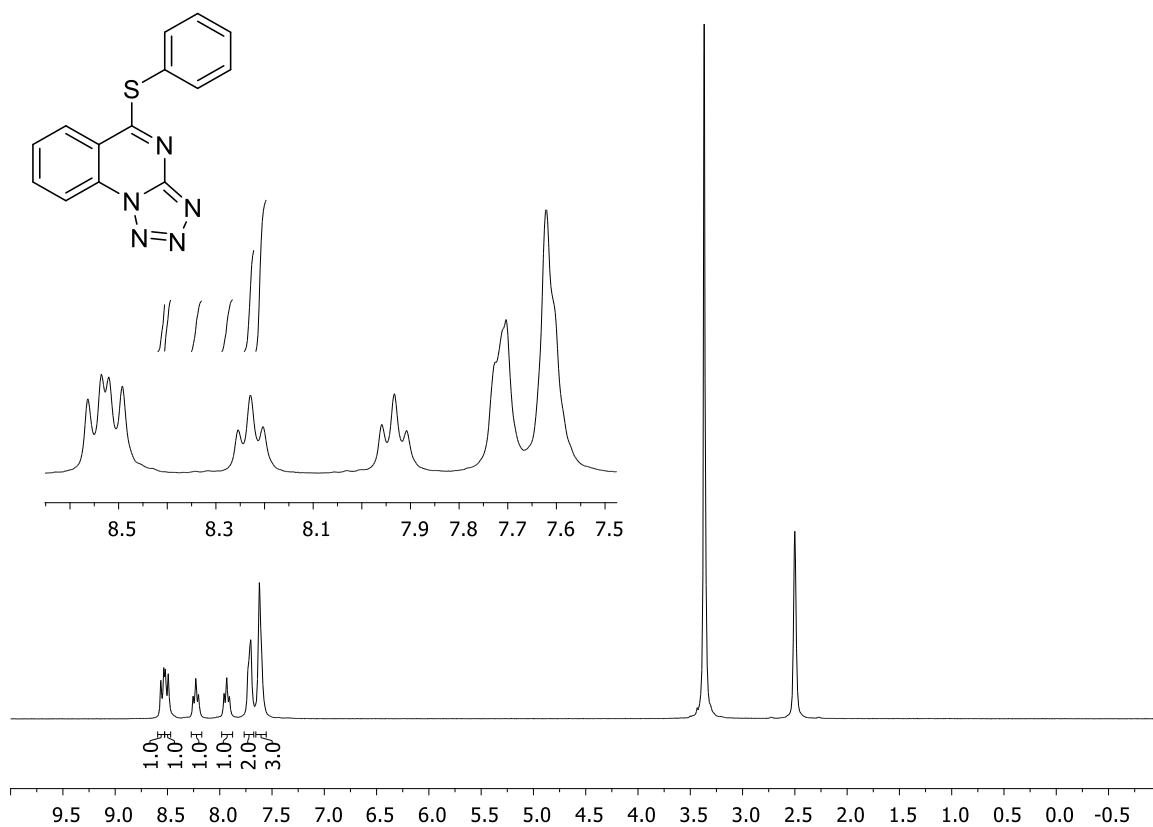


^{13}C NMR (125.7 MHz, CDCl_3) spectrum of compound 4g:

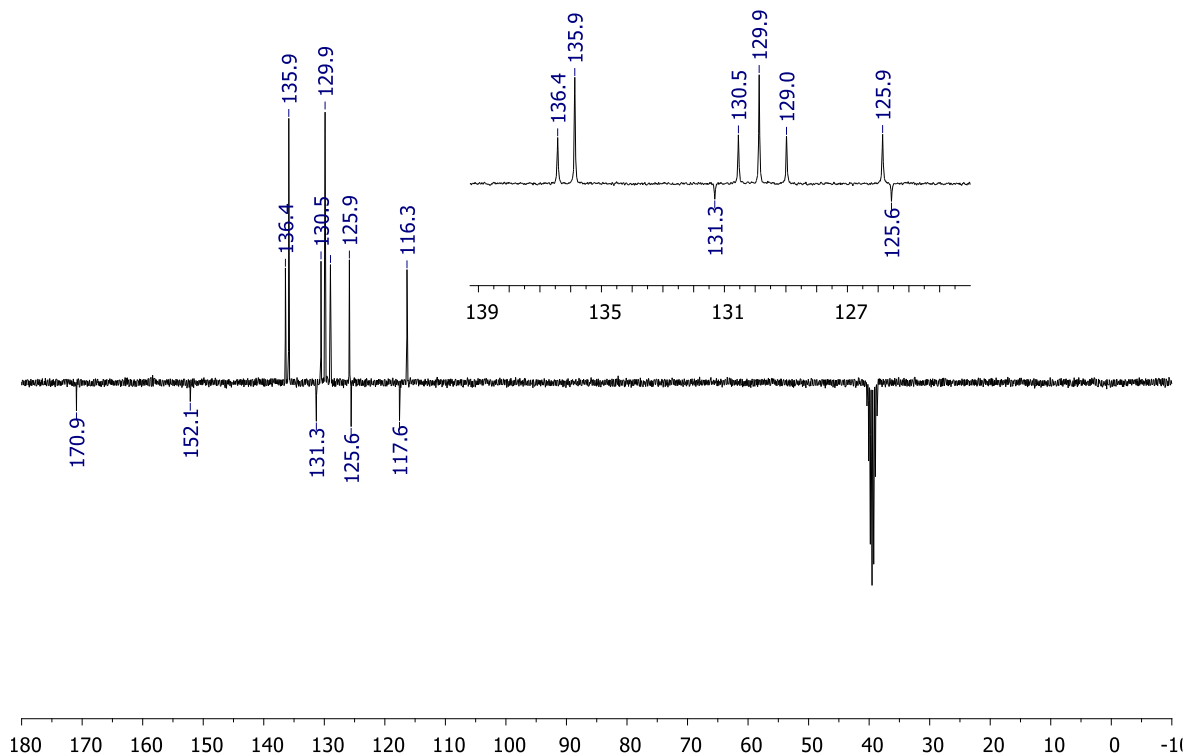


5-(Phenylthio)tetrazolo[1,5-a]quinazoline (4h)

^1H NMR (300 MHz, DMSO-d_6) spectrum of compound 4h:

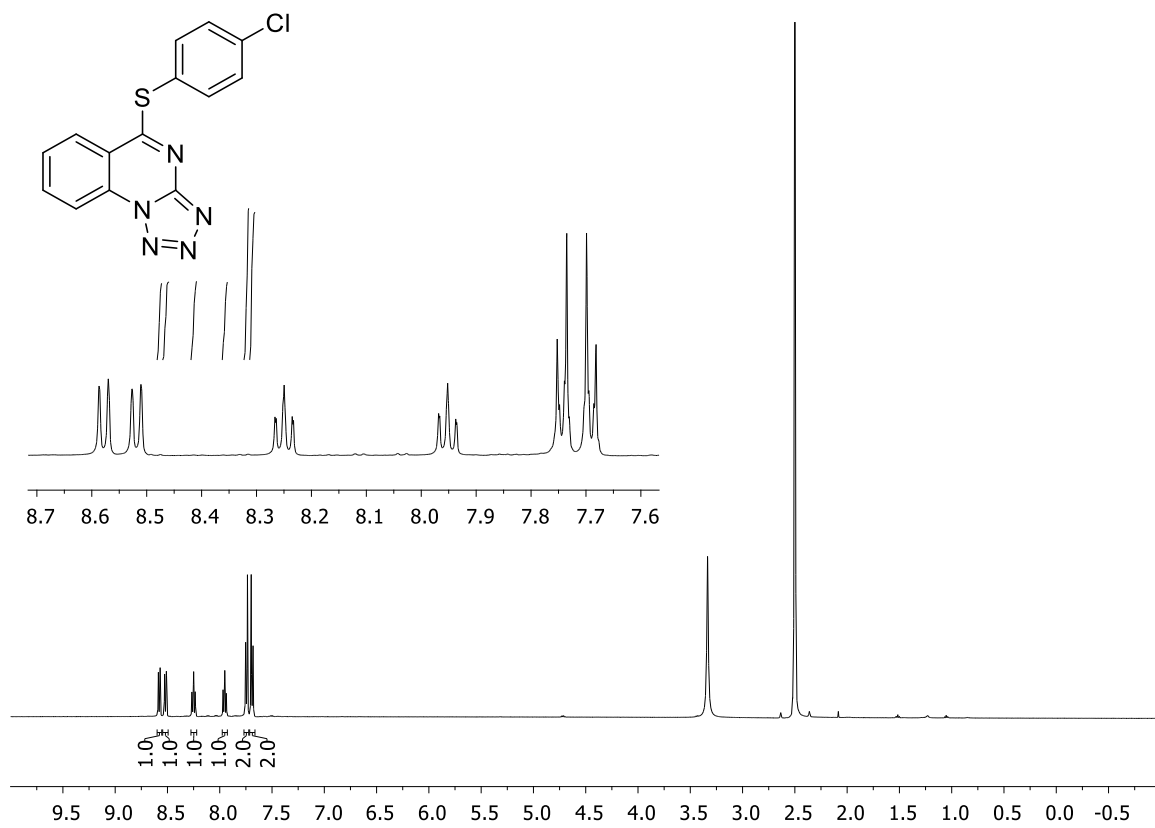


^{13}C NMR (75.5 MHz, DMSO-d_6) spectrum of compound 4h:

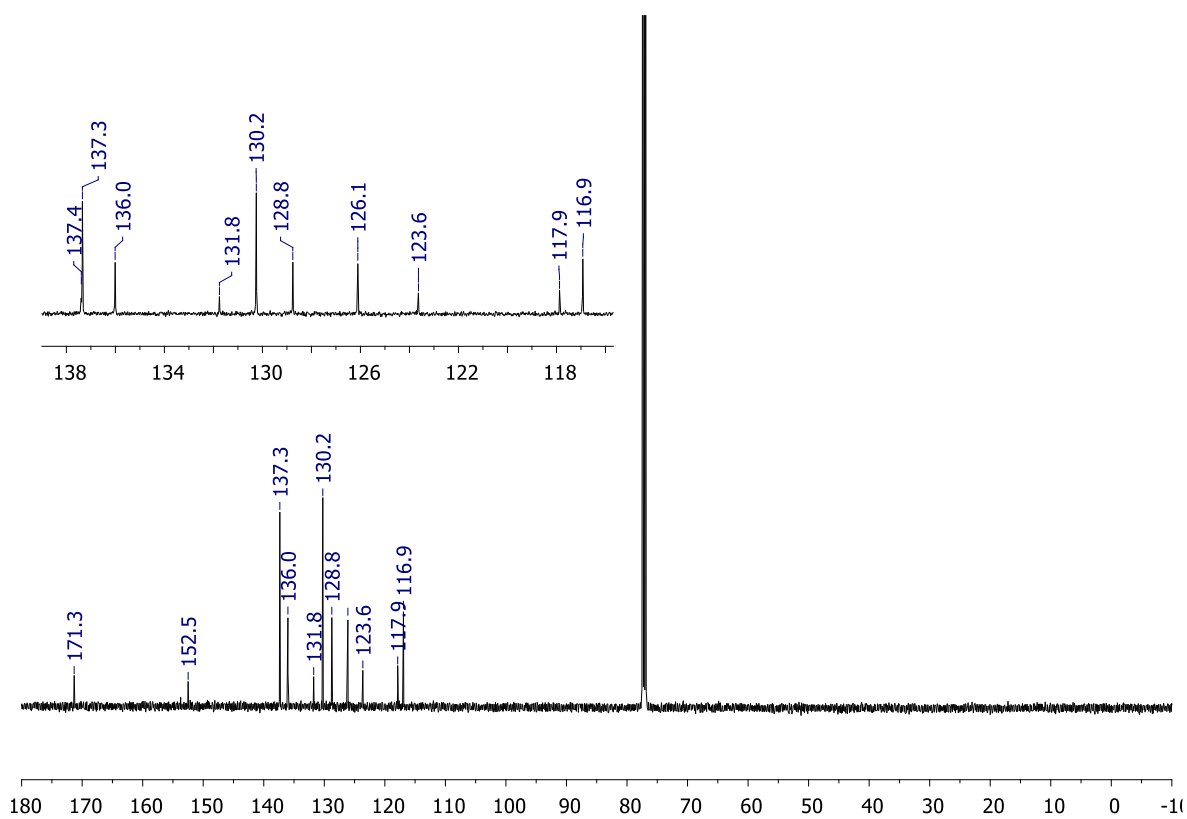


5-[(4-Chlorophenyl)thio]tetrazolo[1,5-a]quinazoline (4i)

^1H NMR (500 MHz, DMSO-d_6) spectrum of compound 4i:

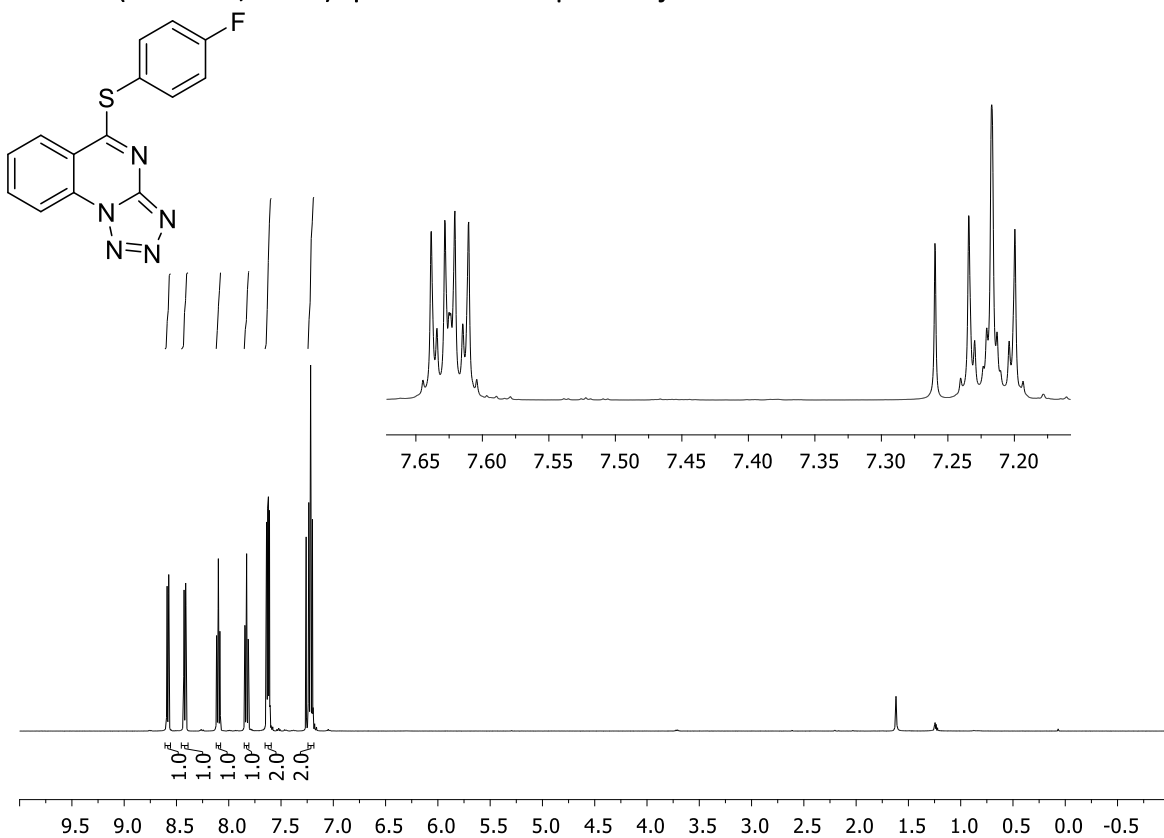


^{13}C NMR (125.7 MHz, CDCl_3) spectrum of compound 4i:

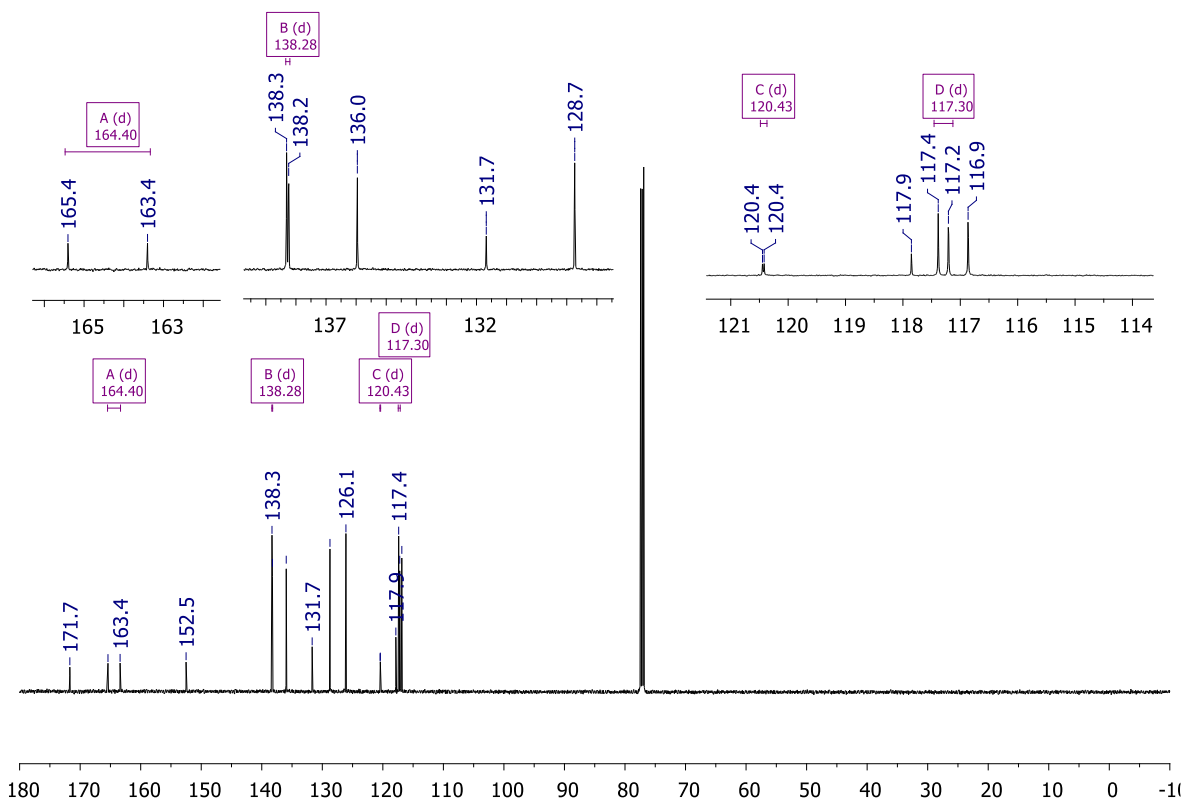


5-[(4-Fluorophenyl)thio]tetrazolo[1,5-a]quinazoline (4j)

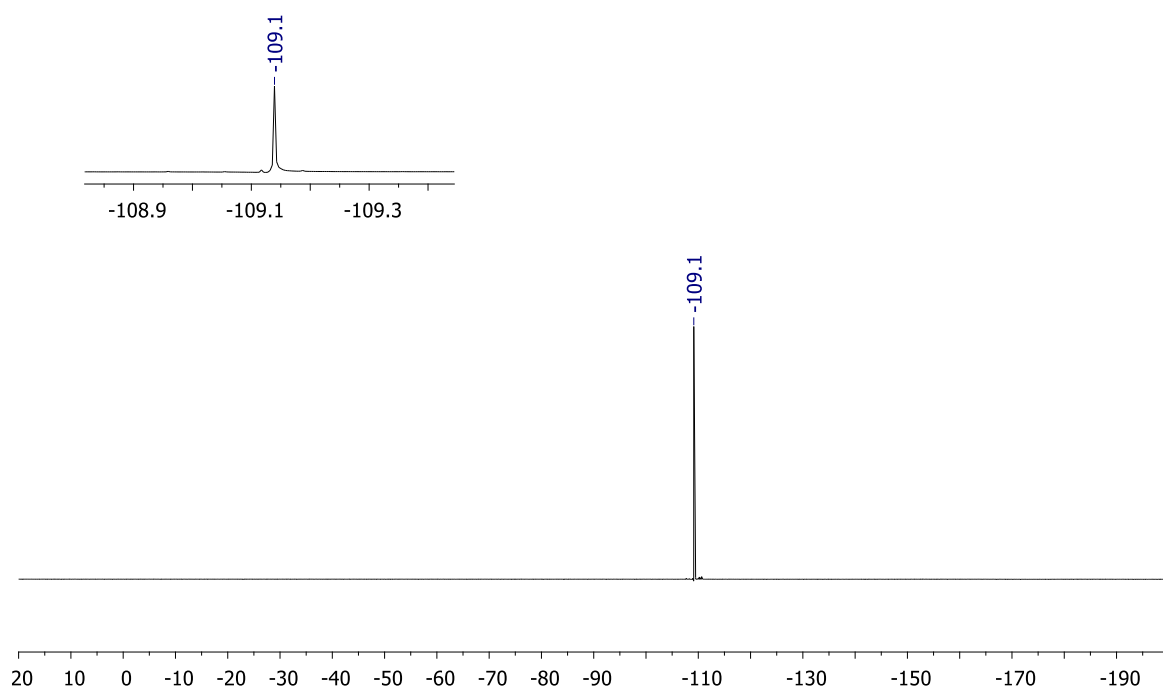
^1H NMR (500 MHz, CDCl_3) spectrum of compound 4j:



^{13}C NMR (125.7 MHz, CDCl_3) spectrum of compound 4j:

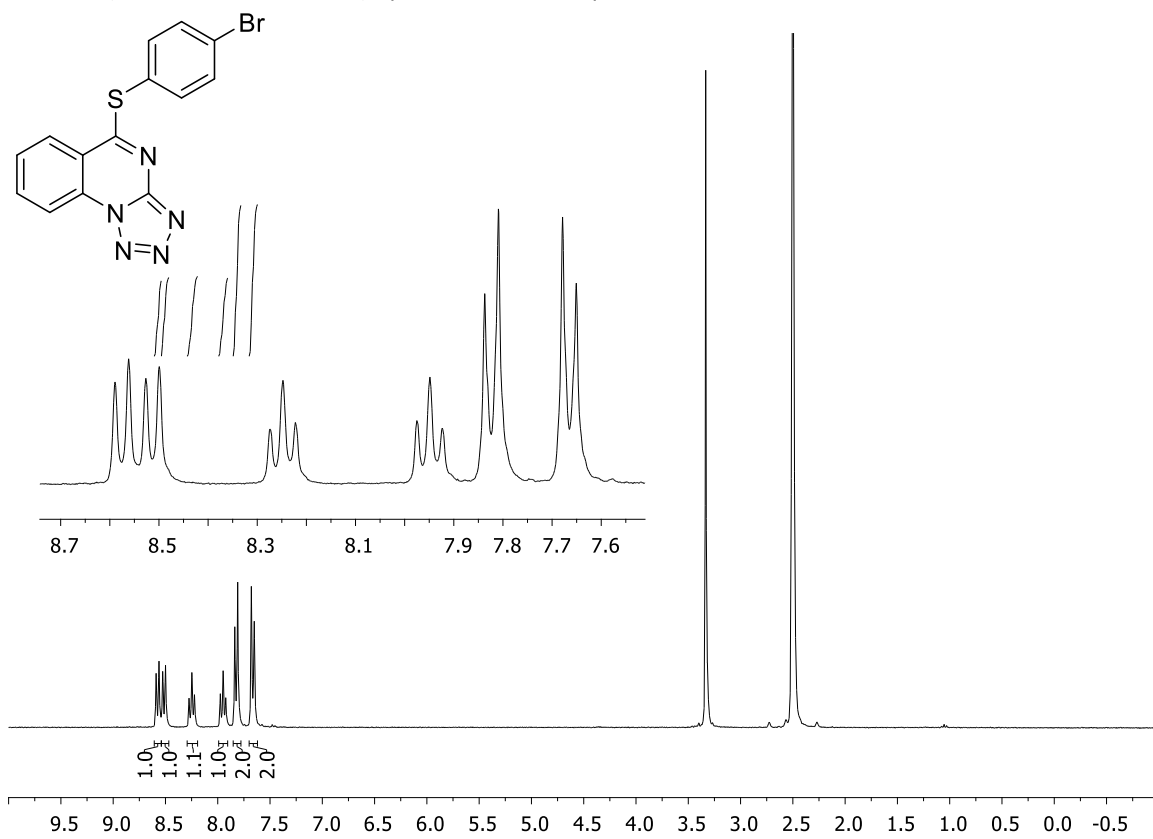


^{19}F NMR (470.5 MHz, CDCl_3) spectrum of compound 4j:

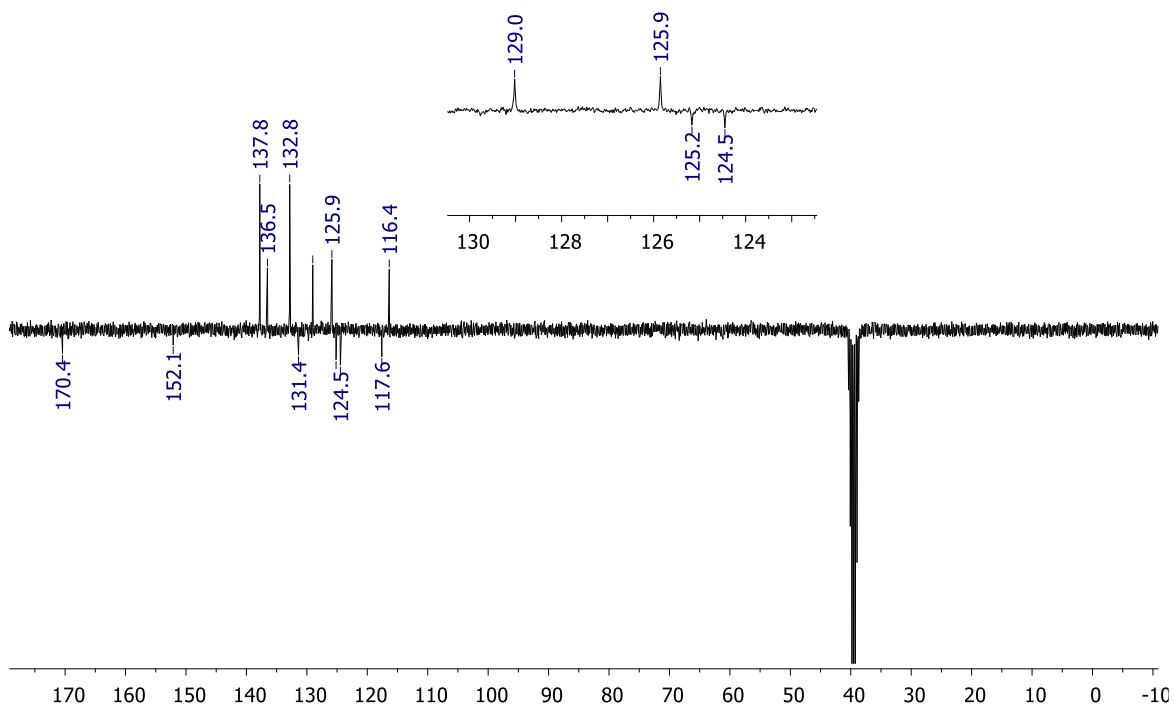


5-[(4-Bromophenyl)thio]tetrazolo[1,5-a]quinazoline (4k)

^1H NMR (300 MHz, DMSO-d_6) spectrum of compound 4k:

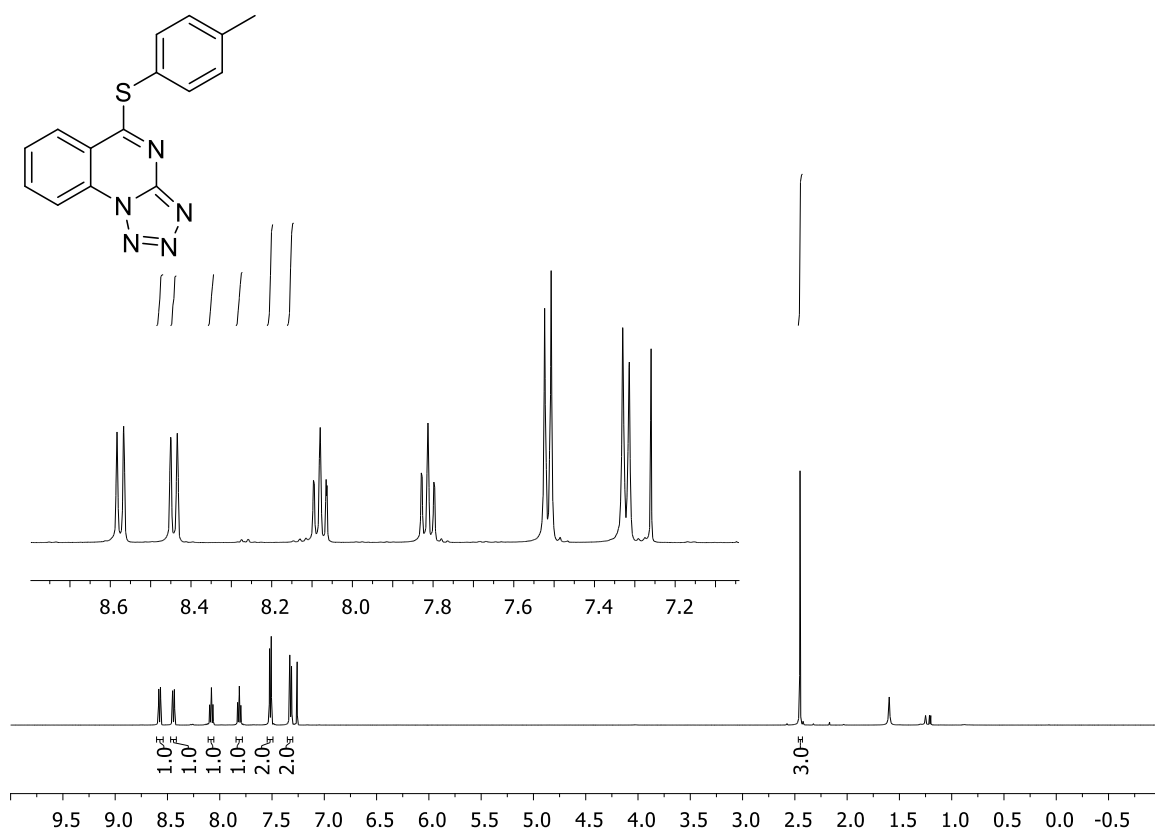


^{13}C NMR (75.5 MHz, DMSO-d_6) spectrum of compound 4k:

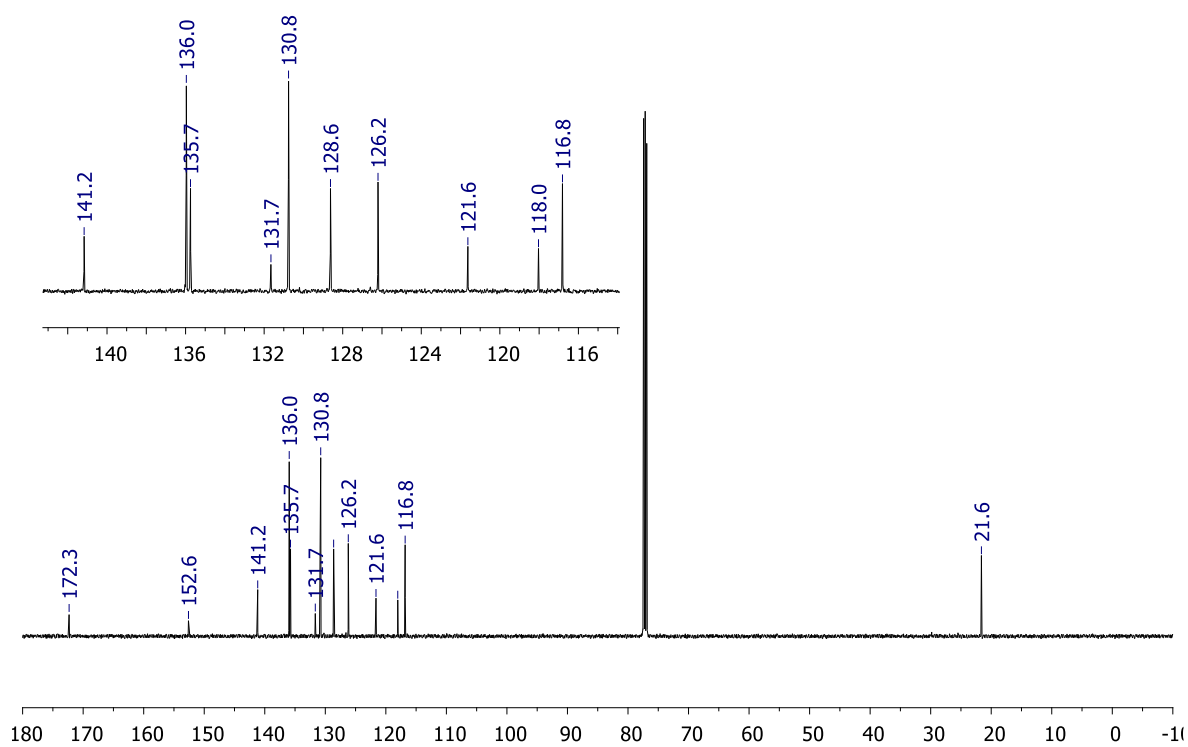


5-(*p*-Tolylthio)tetrazolo[1,5-*a*]quinazoline (4l)

^1H NMR (500 MHz, CDCl_3) spectrum of compound 4l:

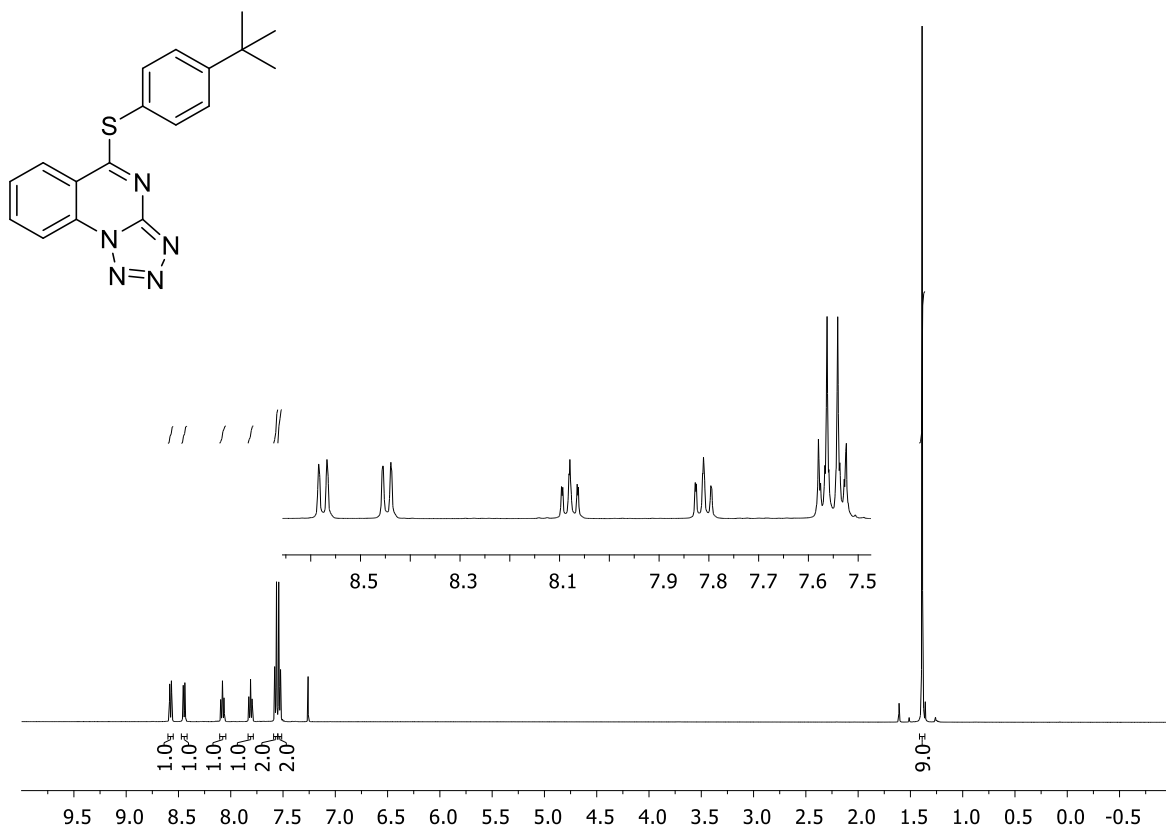


^{13}C NMR (125.7 MHz, CDCl_3) spectrum of compound 4l:

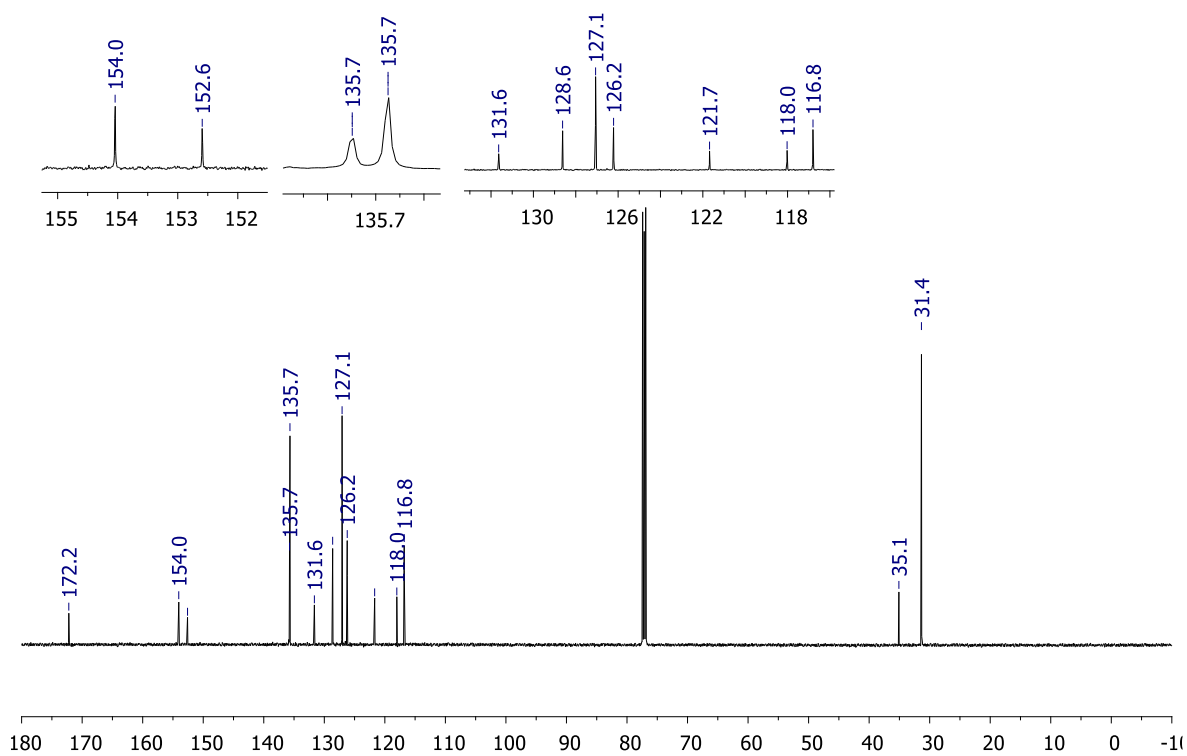


5-[(4-*tert*-Butylphenyl)thio]tetrazolo[1,5-*a*]quinazoline (4m)

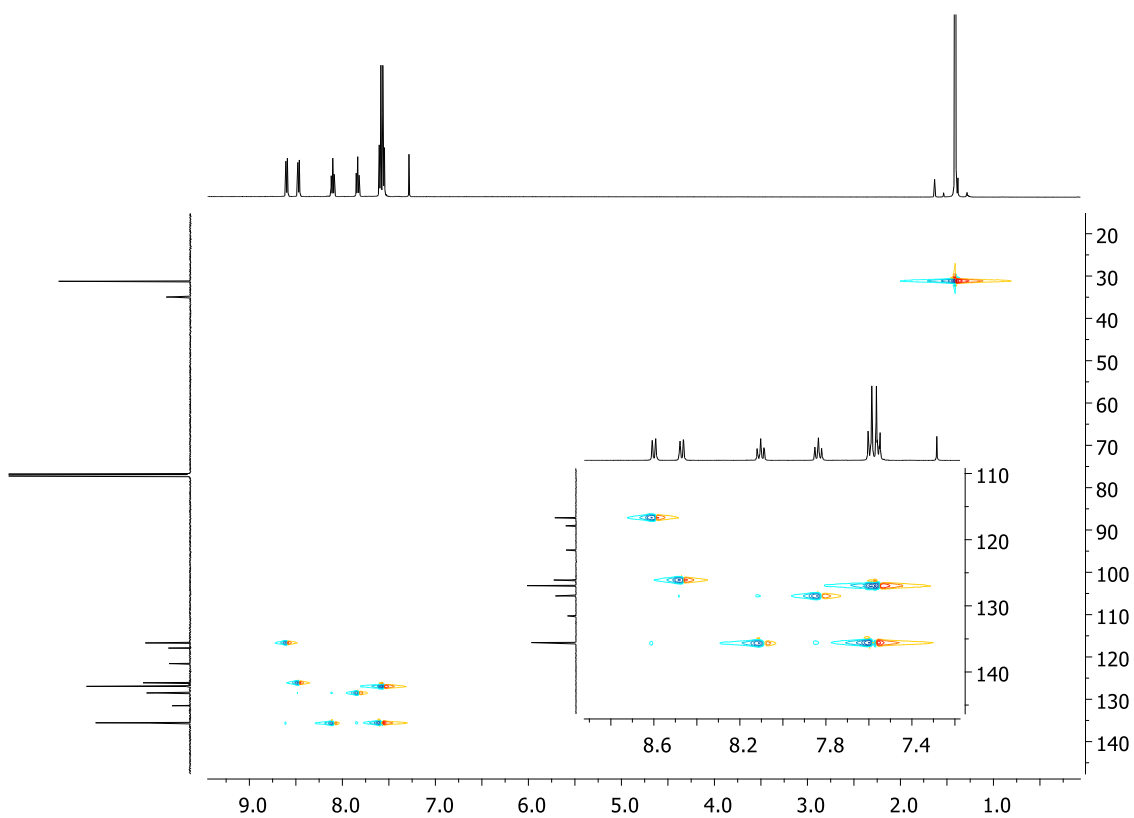
^1H NMR (500 MHz, CDCl_3) spectrum of compound 4m:



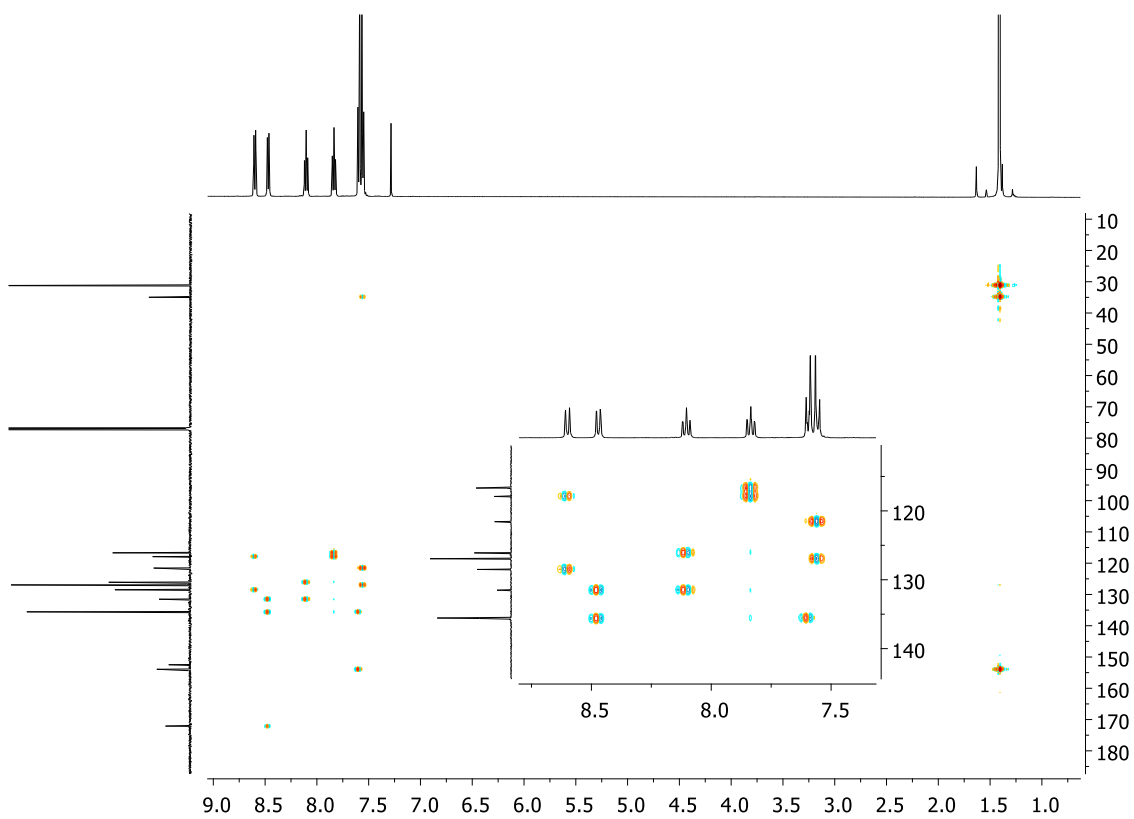
^{13}C NMR (125.7 MHz, CDCl_3) spectrum of compound 4m:



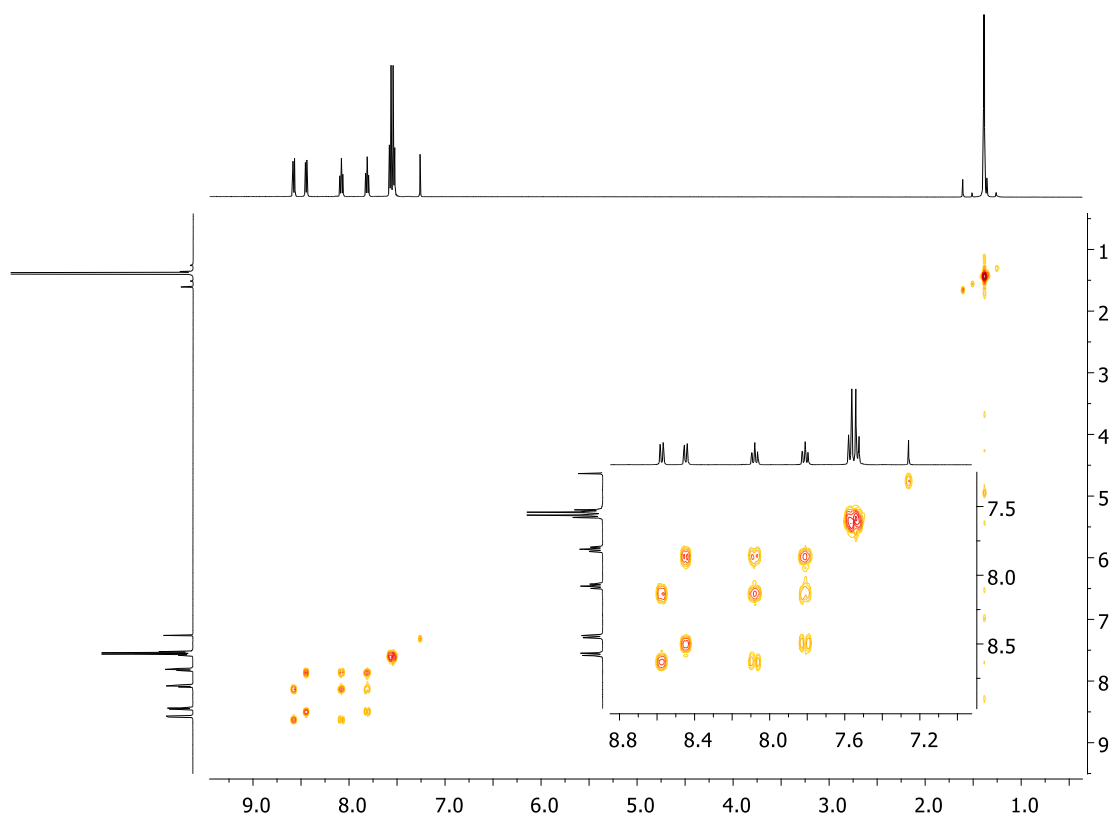
HSQC spectrum of compound 4m:



HMBC spectrum of compound 4m:



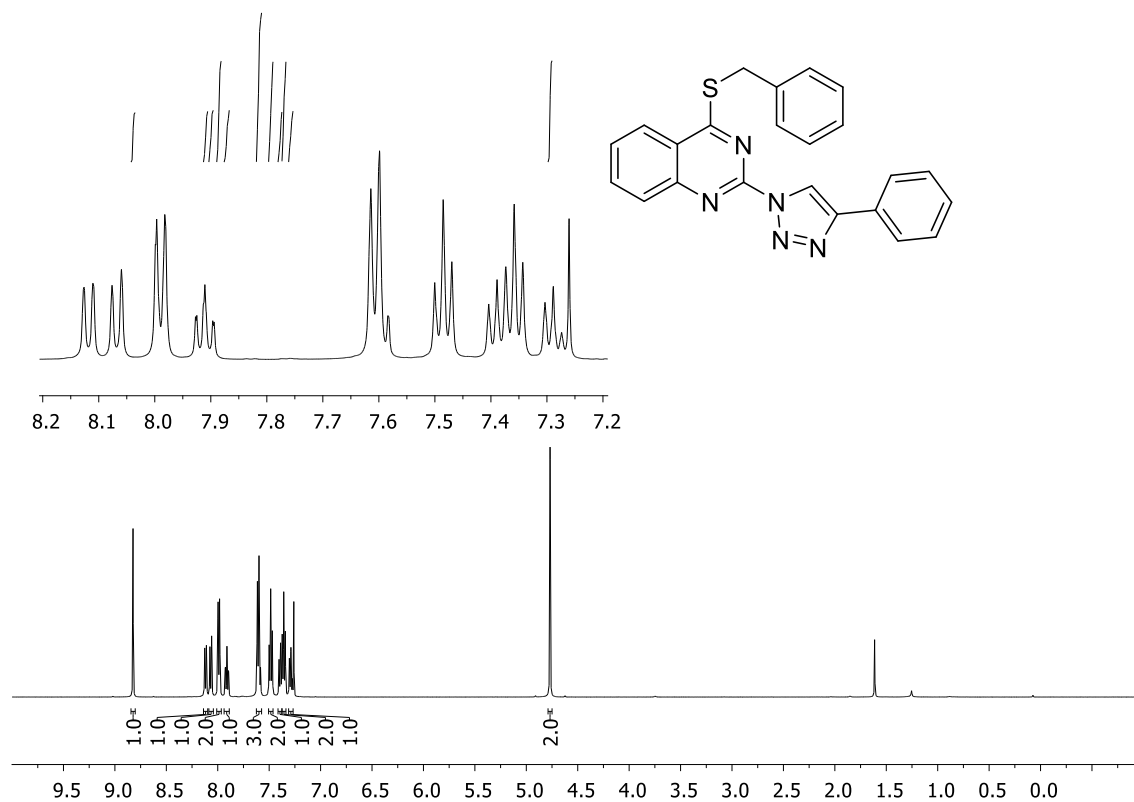
COSY spectrum of compound 4m:



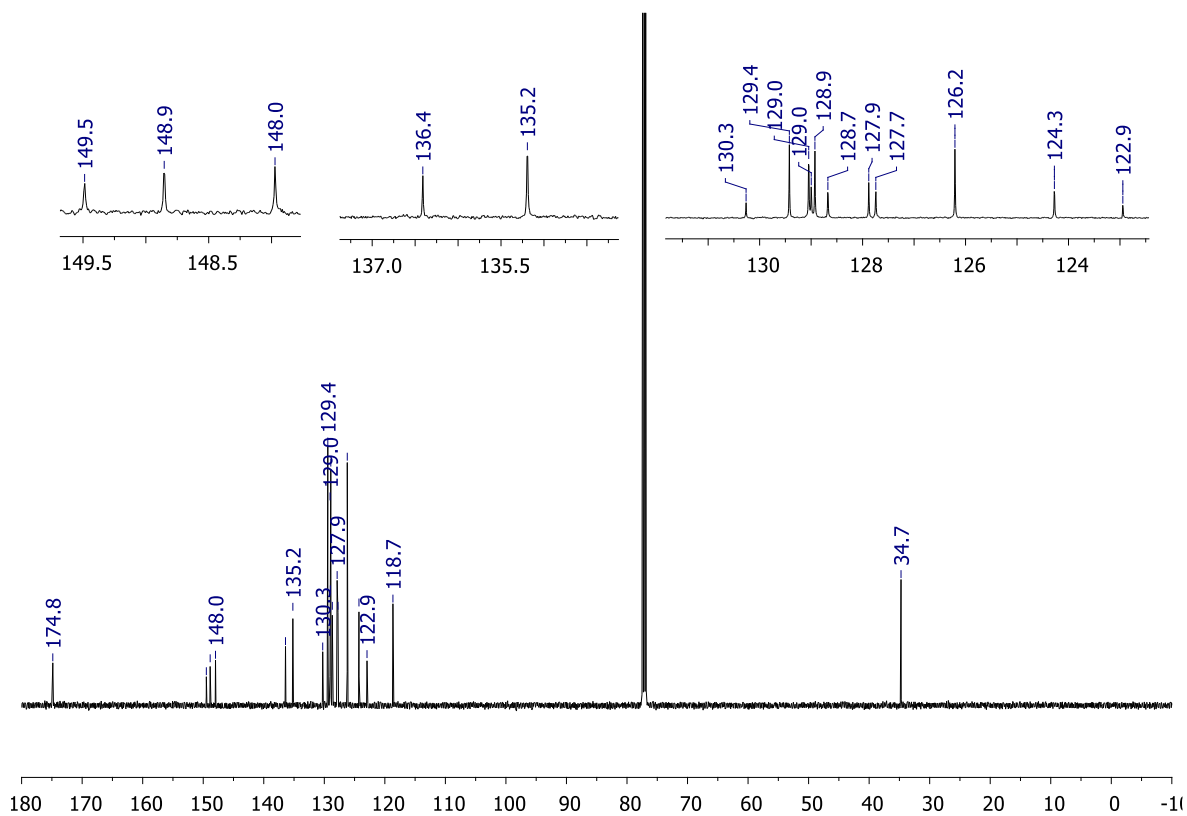
4-(alkyl/arylthio)-2-(1*H*-1,2,3-triazol-1-yl)quinazolines

4-(Benzylthio)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)quinazoline (7a)

¹H NMR (500 MHz, CDCl₃) spectrum of compound 7a:

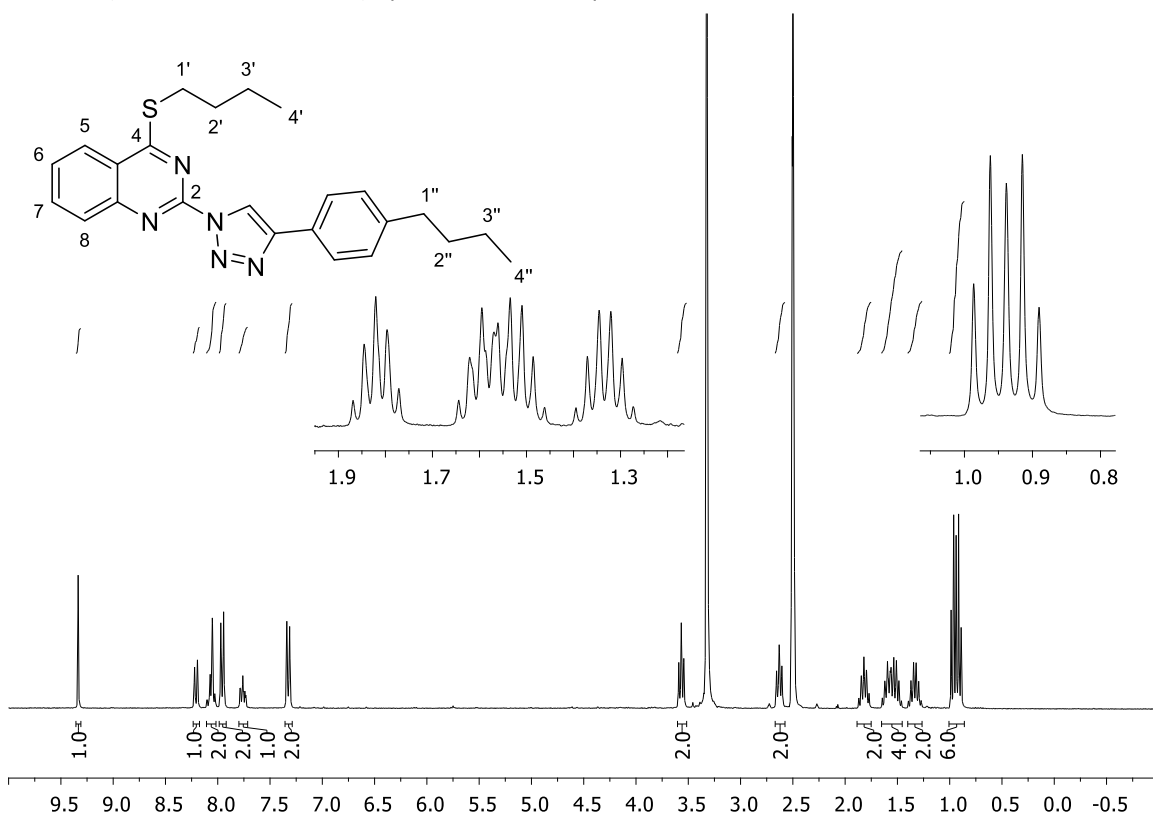


¹³C NMR (125.7 MHz, CDCl₃) spectrum of compound 7a:

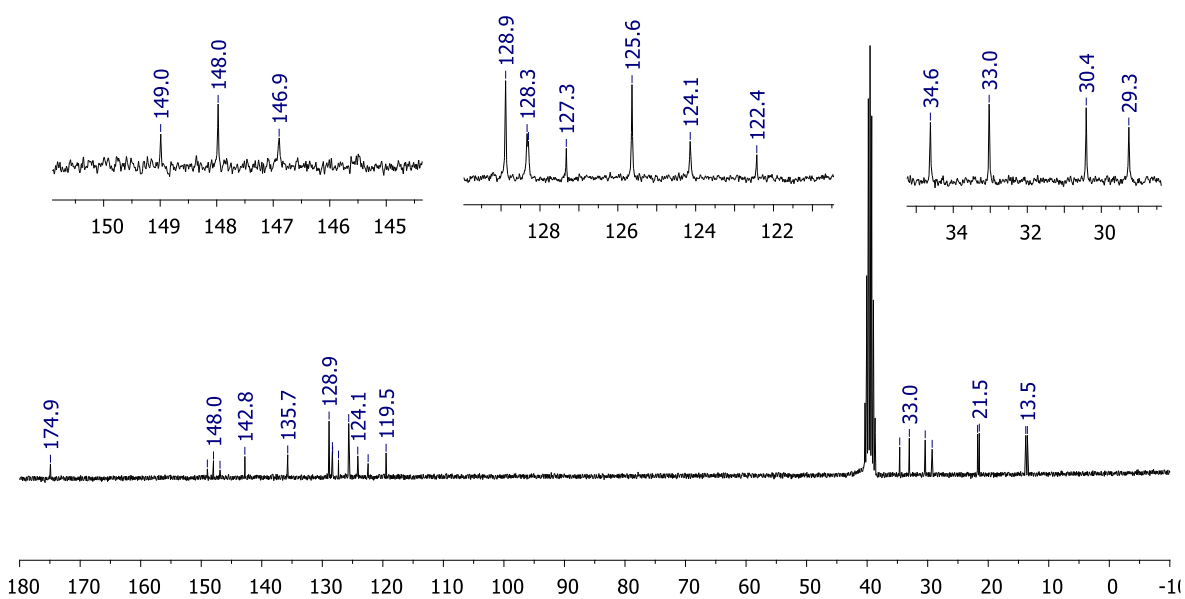


2-[4-(4-Butylphenyl)-1*H*-1,2,3-triazol-1-yl]-4-(butylthio)quinazoline (7b)

¹H NMR (300 MHz, DMSO-*d*₆) spectrum of compound 7b:

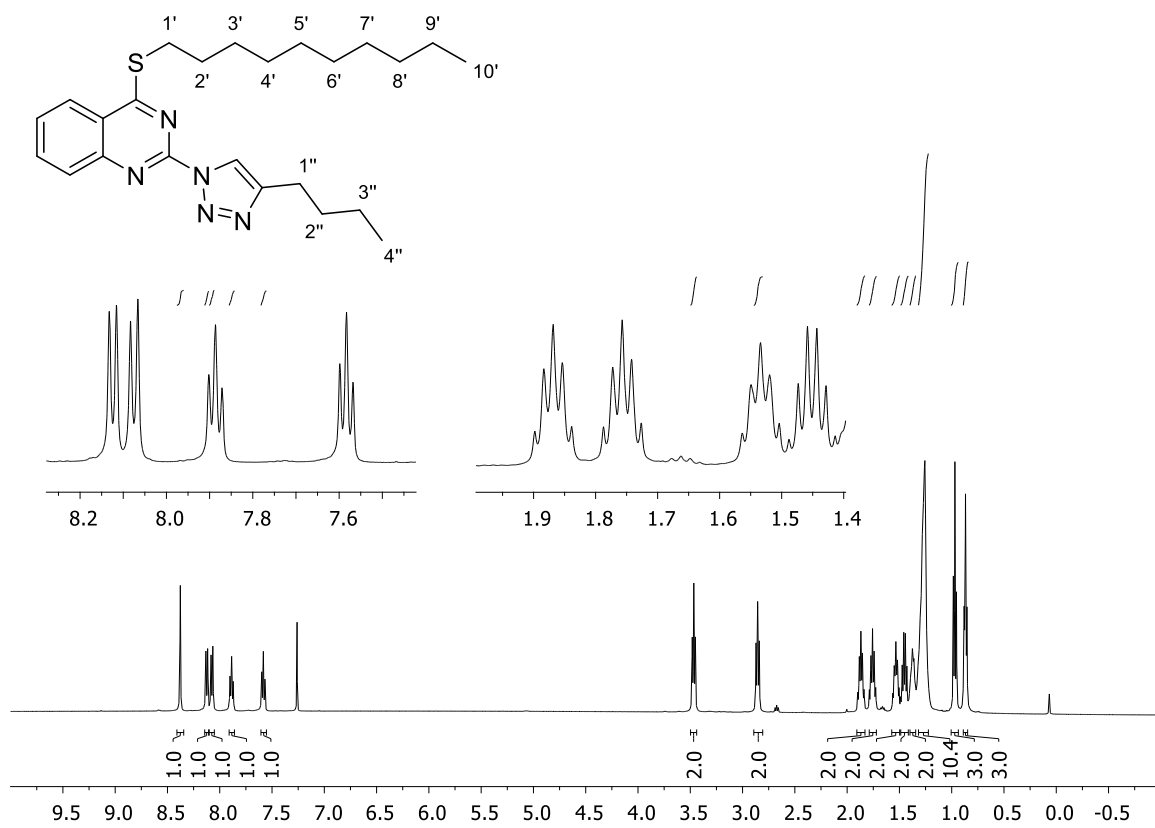


¹³C NMR (75.5 MHz, DMSO-*d*₆) spectrum of compound 7b:

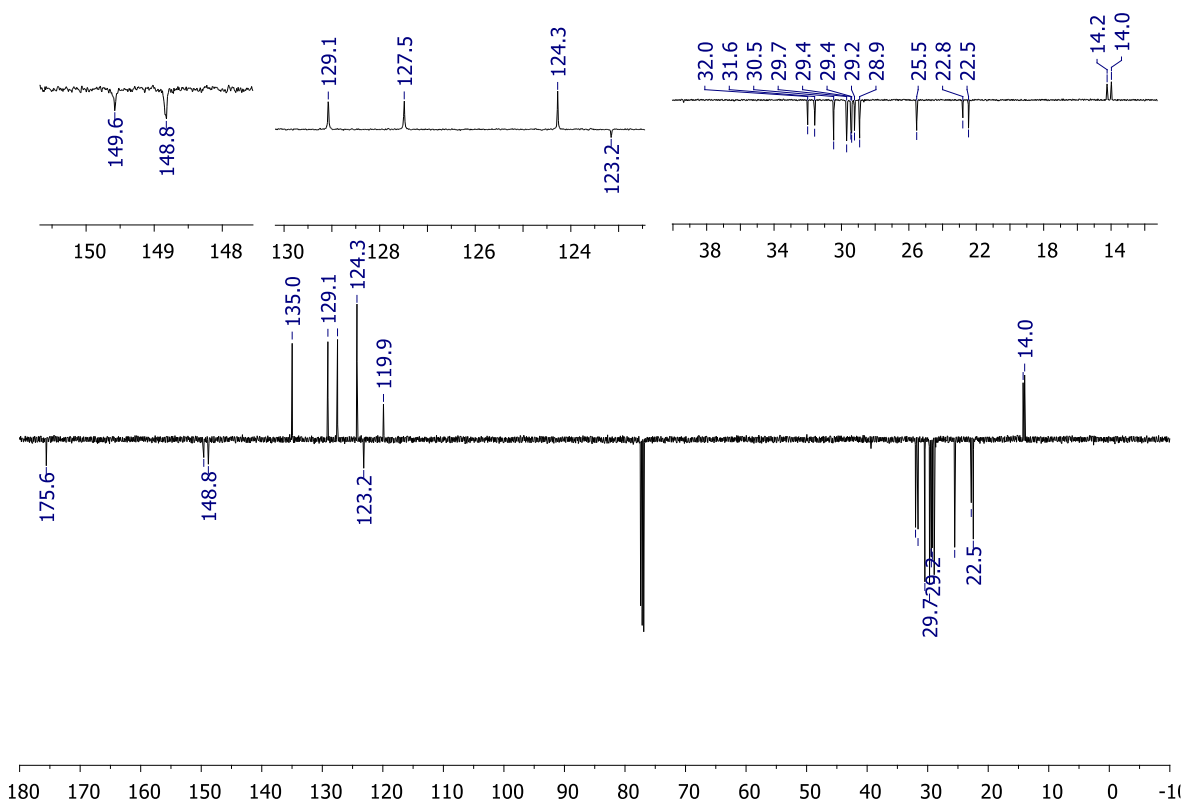


4-(Decylthio)-2-(4-butyl-1H-1,2,3-triazol-1-yl)quinazoline (7d)

^1H NMR (500 MHz, CDCl_3) spectrum of compound 7d:

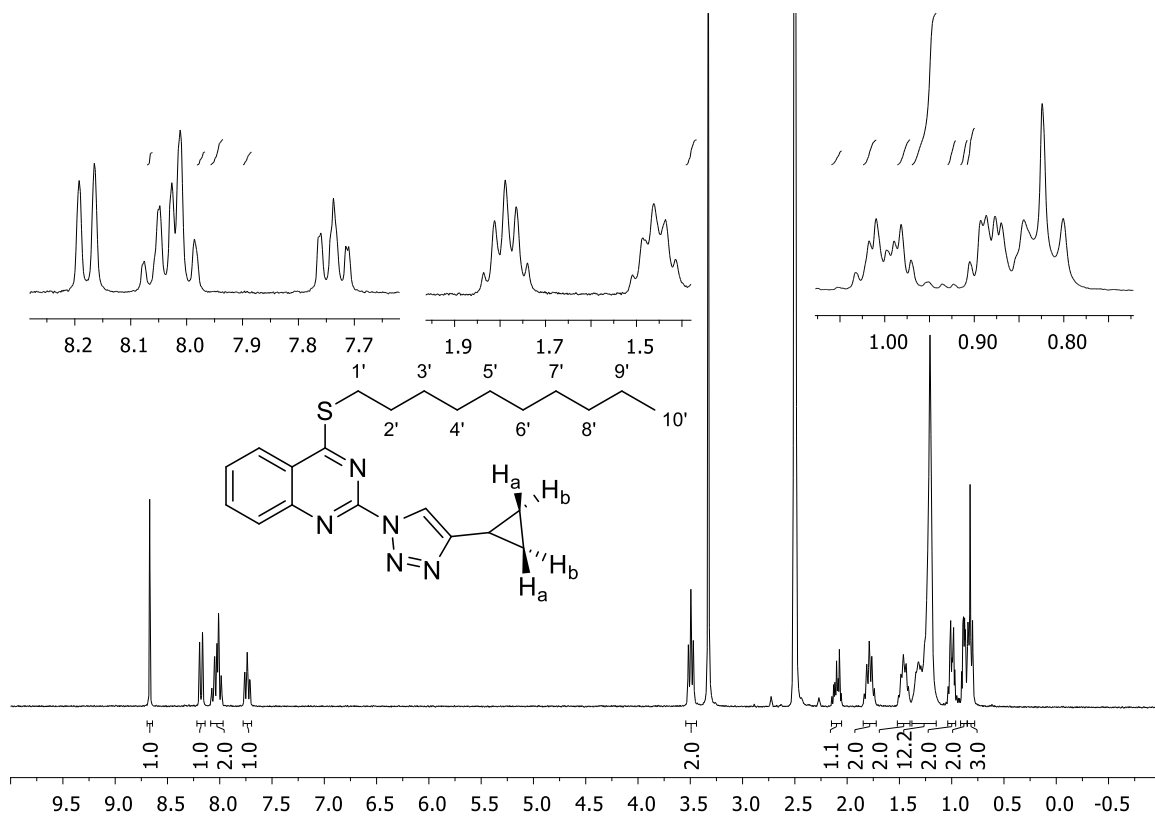


^{13}C NMR (125.7 MHz, CDCl_3) spectrum of compound 7d:

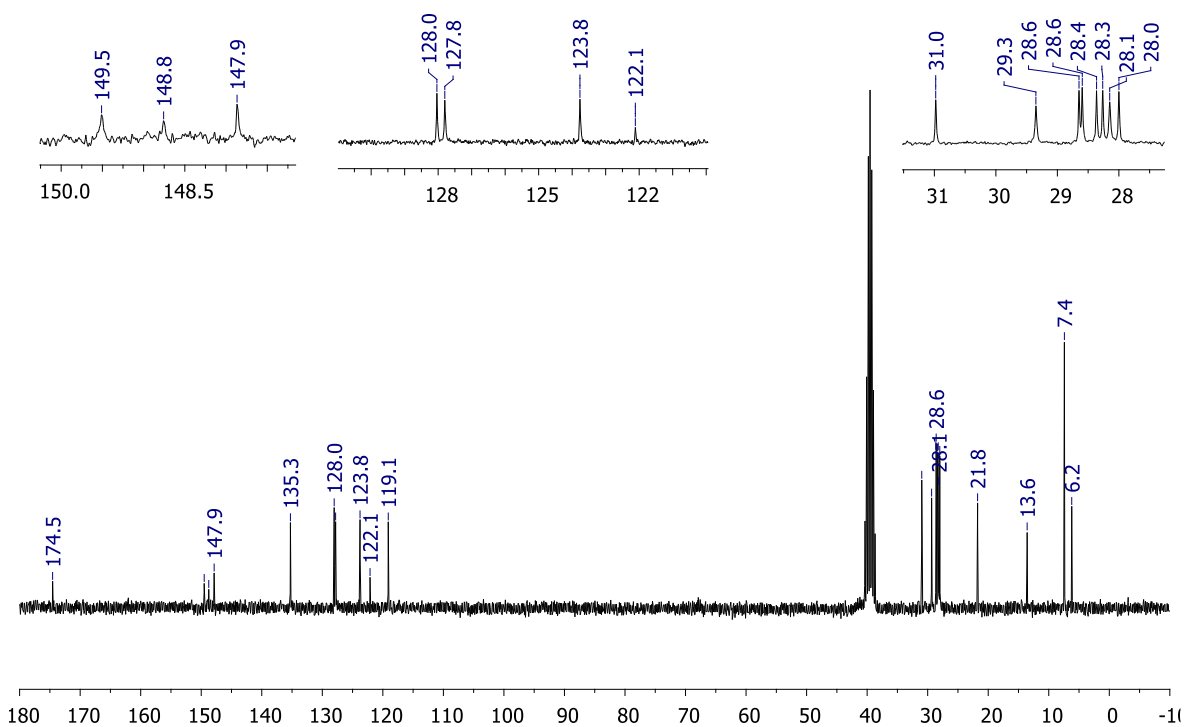


4-(Decylthio)-2-(4-cyclopropyl-1H-1,2,3-triazol-1-yl)quinazoline (7e)

^1H NMR (300 MHz, DMSO- d_6) spectrum of compound 7e:

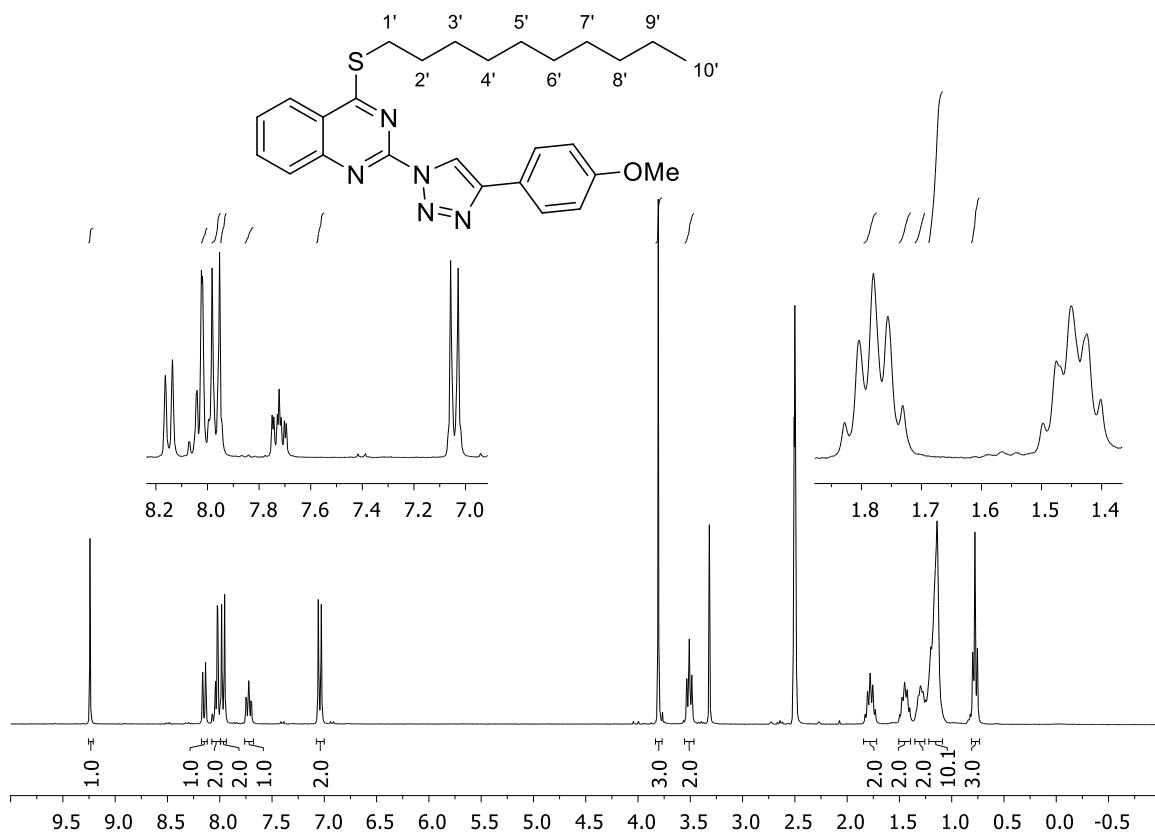


^{13}C NMR (75.5 MHz, DMSO- d_6) spectrum of compound 7e:

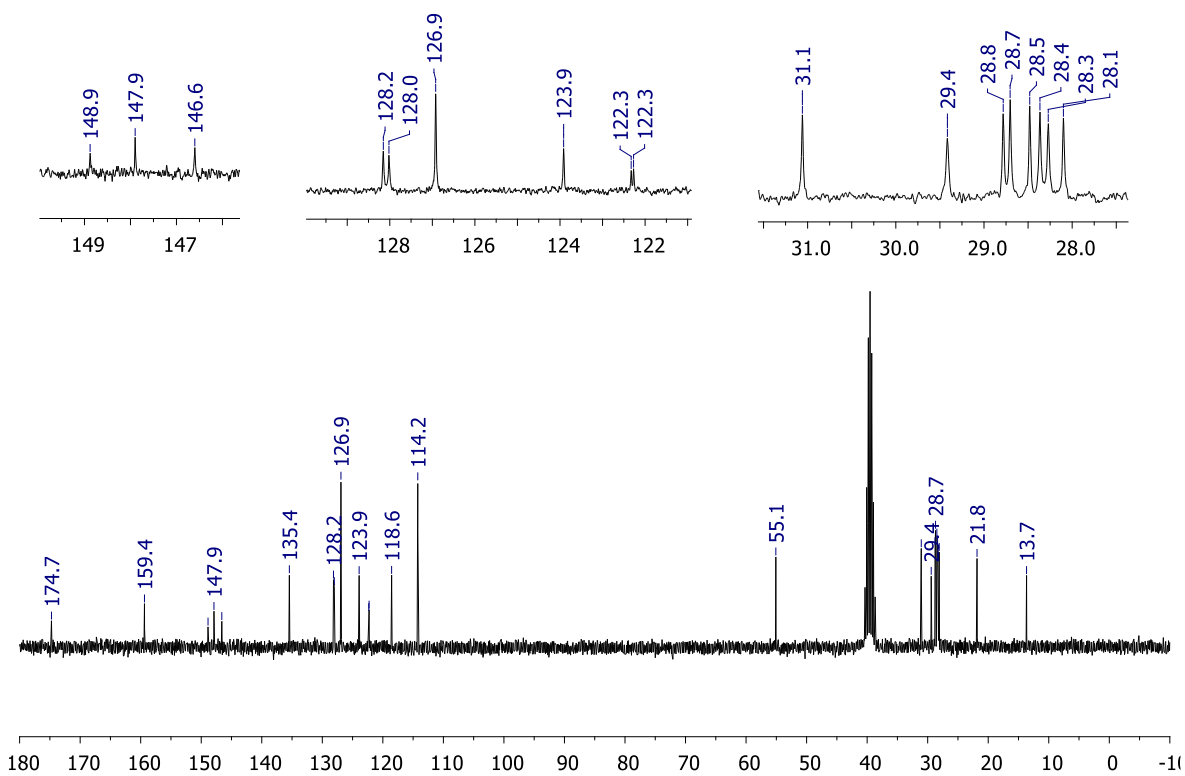


4-(Decylthio)-2-[4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-1-yl]quinazoline (7f)

¹H NMR (300 MHz, DMSO-*d*₆) spectrum of compound 7f:

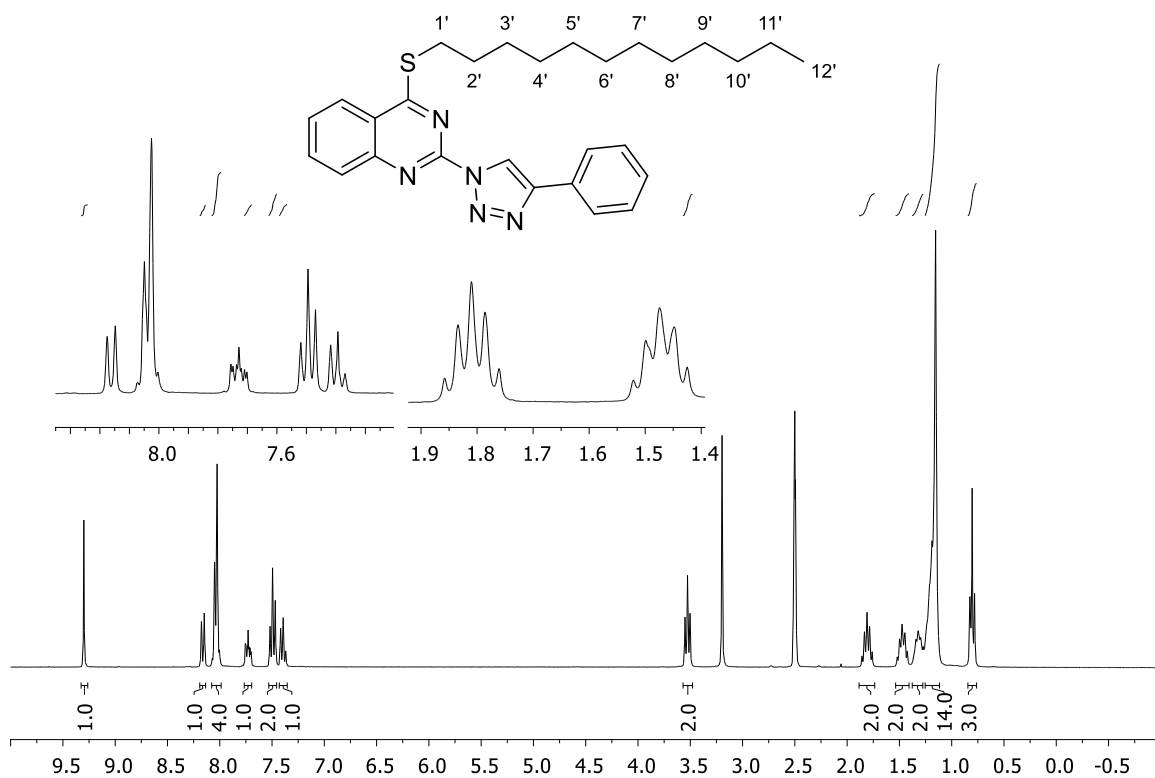


¹³C NMR (75.5 MHz, DMSO-*d*₆) spectrum of compound 7f:

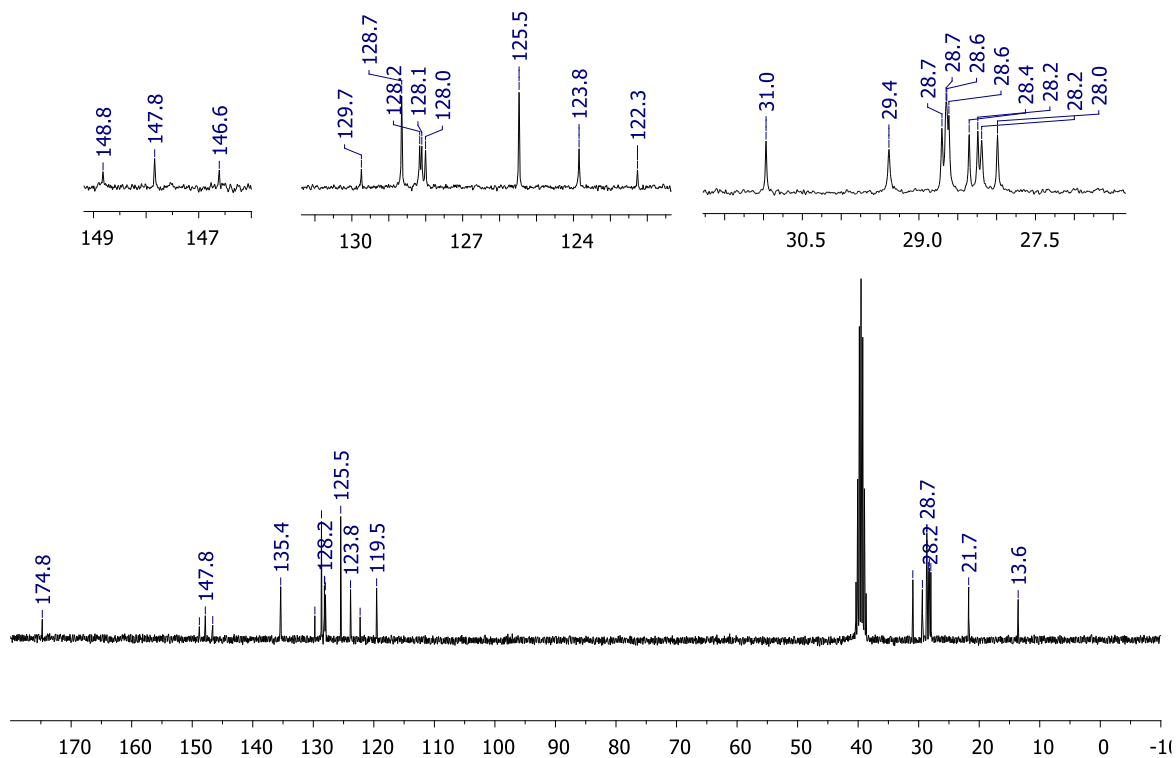


4-(Dodecylthio)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)quinazoline (7g)

¹H NMR (300 MHz, DMSO-d₆) spectrum of compound 7g:

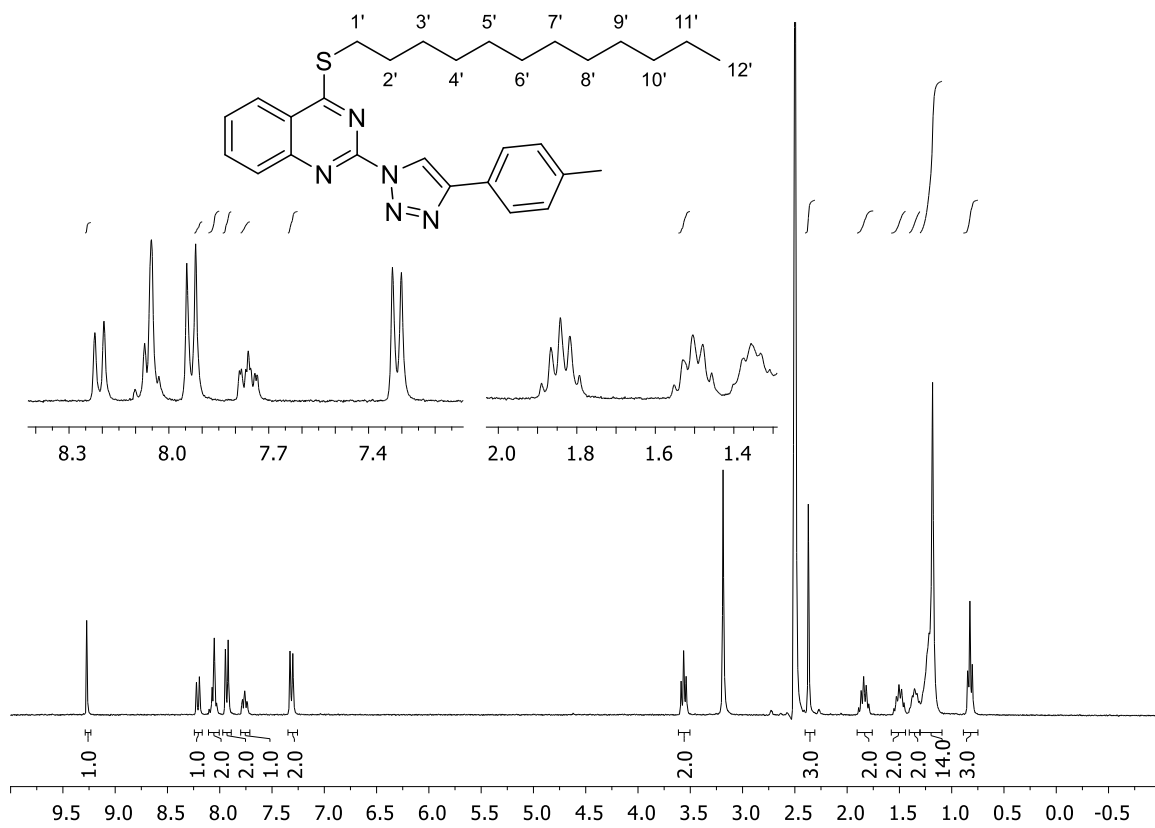


¹³C NMR (75.5 MHz, DMSO-d₆) spectrum of compound 7g:

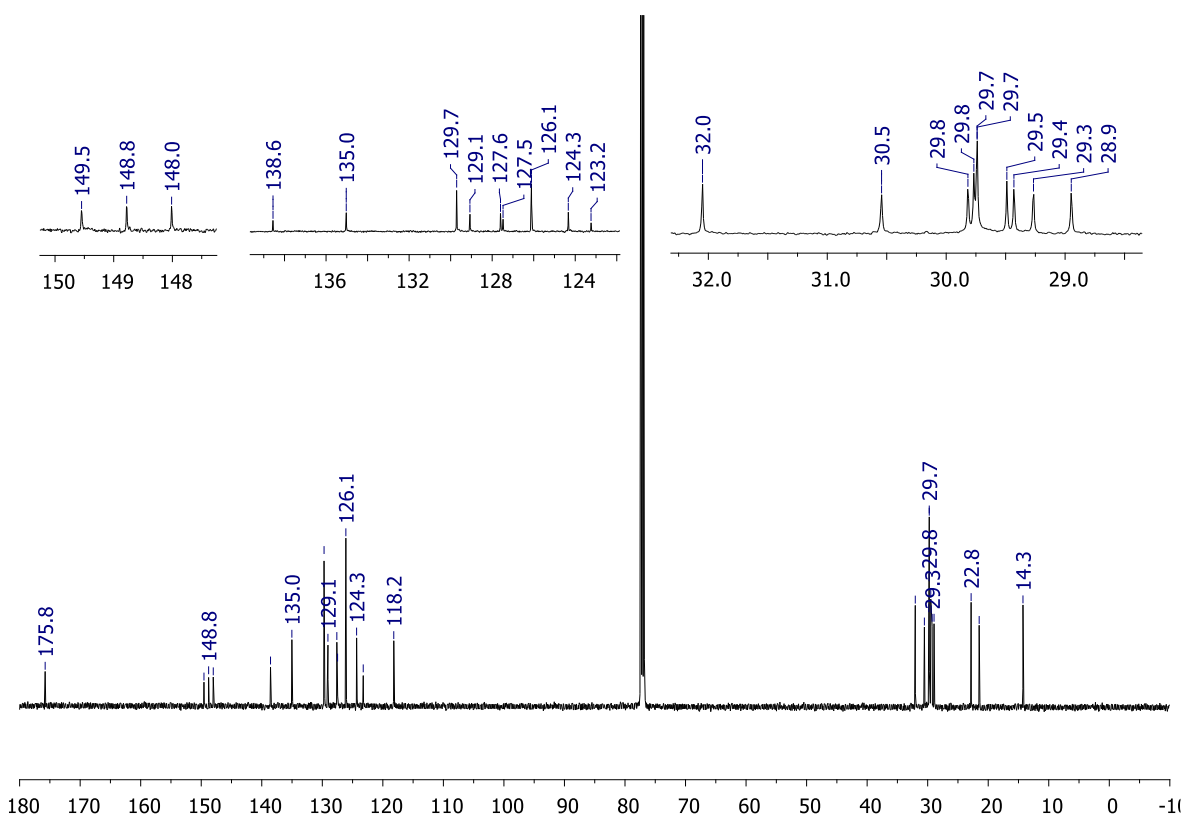


4-(Dodecylthio)-2-[4-(*p*-tolyl)-1*H*-1,2,3-triazol-1-yl]quinazoline (7h)

¹H NMR (300 MHz, DMSO-*d*₆) spectrum of compound 7h:

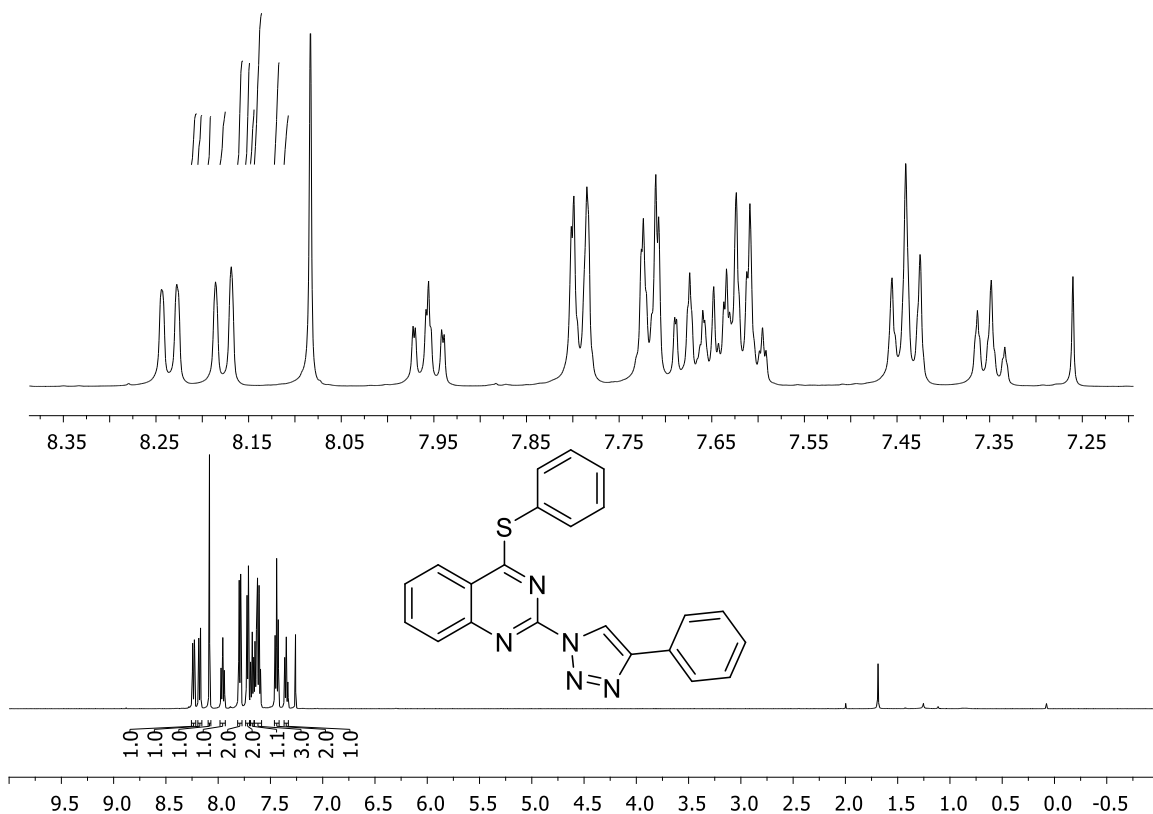


¹³C NMR (125.7 MHz, CDCl₃) spectrum of compound 7h:

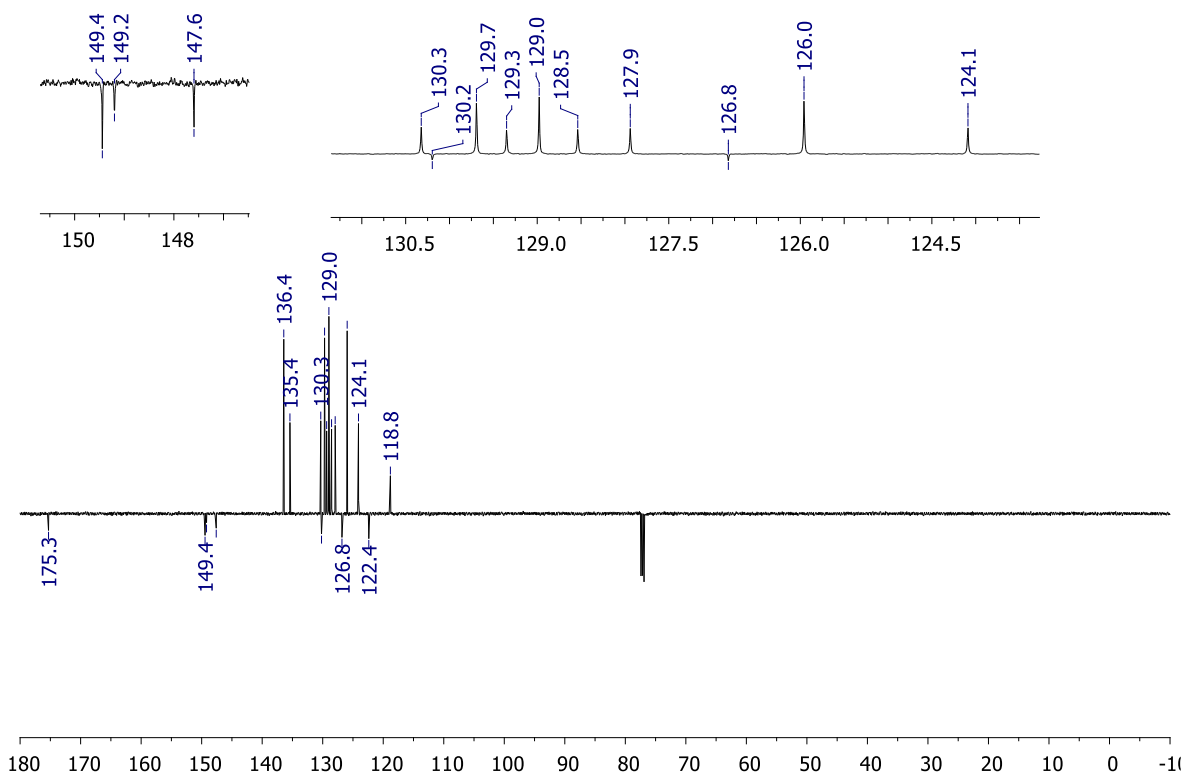


2-(4-Phenyl-1H-1,2,3-triazol-1-yl)-4-(phenylthio)quinazoline (7i)

¹H NMR (500 MHz, CDCl₃) spectrum of compound 7i:

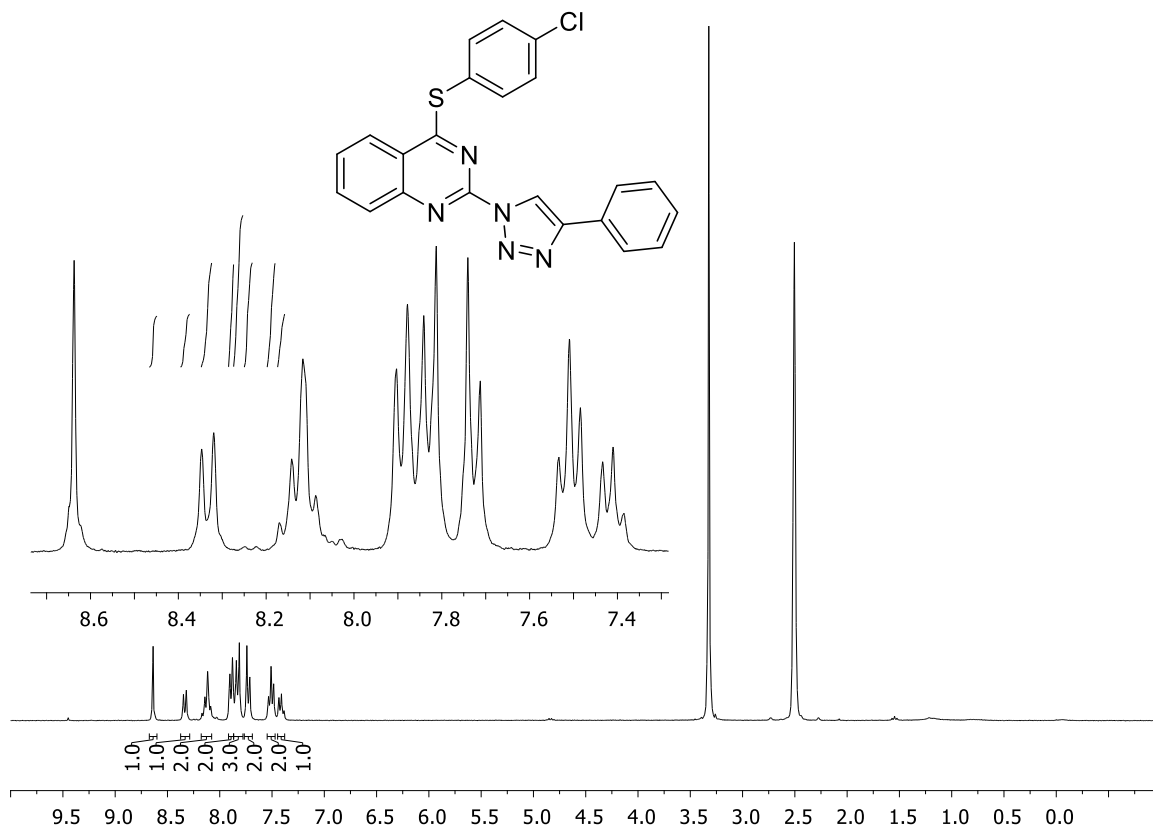


¹³C NMR (125.7 MHz, CDCl₃) spectrum of compound 7i:

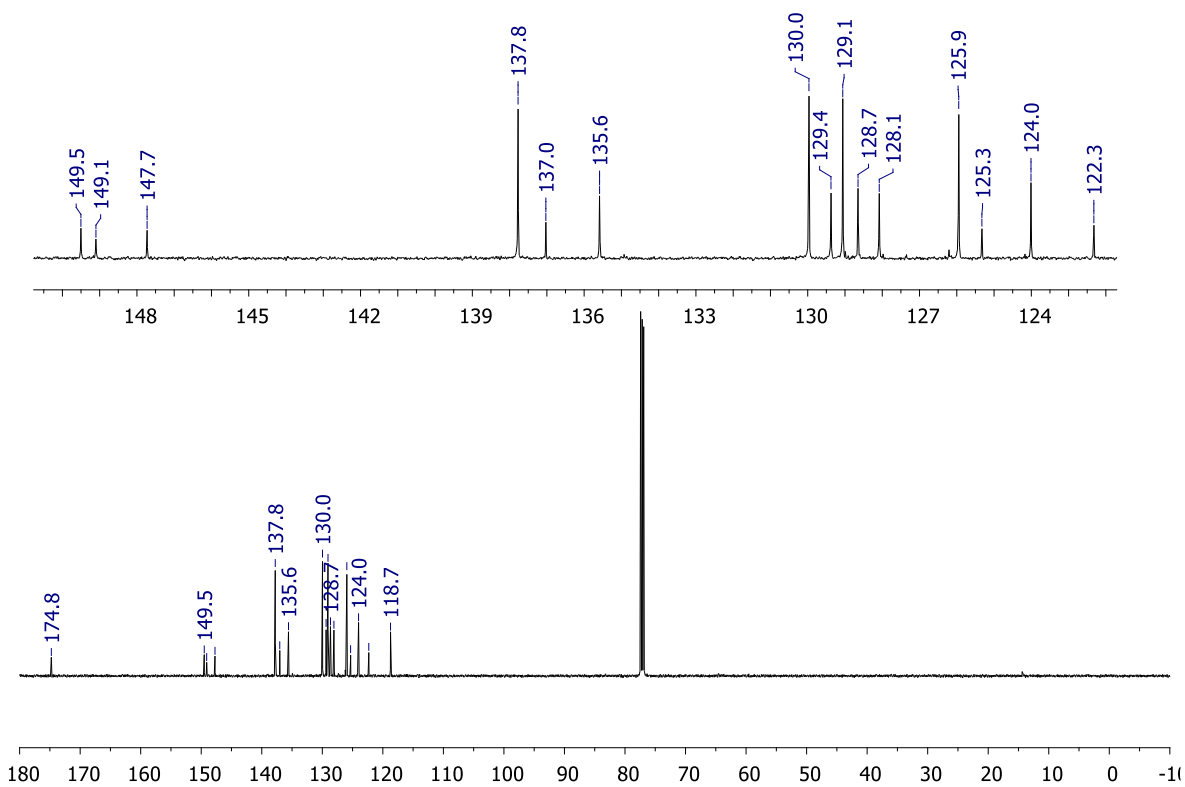


4-[(4-Chlorophenyl)thio]-2-(4-phenyl-1H-1,2,3-triazol-1-yl)quinazoline (7j)

^1H NMR (300 MHz, DMSO-d_6) spectrum of compound 7j:

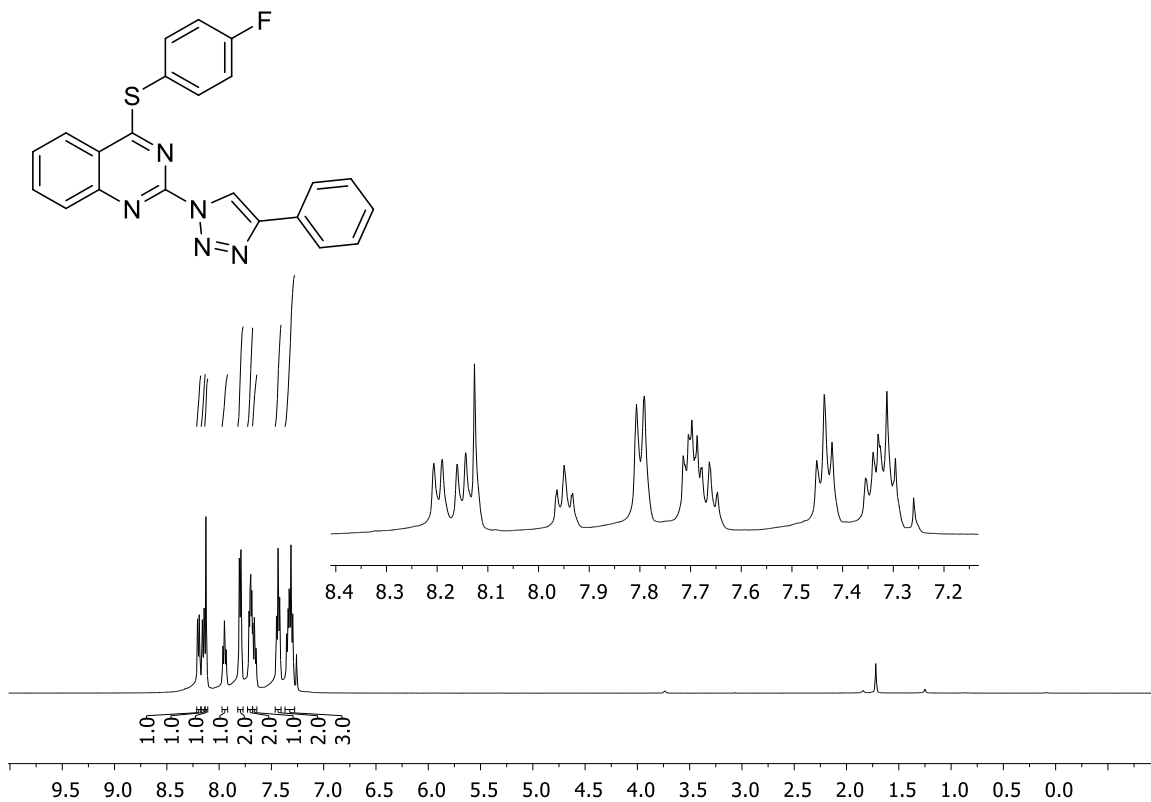


^{13}C NMR (125.7 MHz, CDCl_3) spectrum of compound 7j:

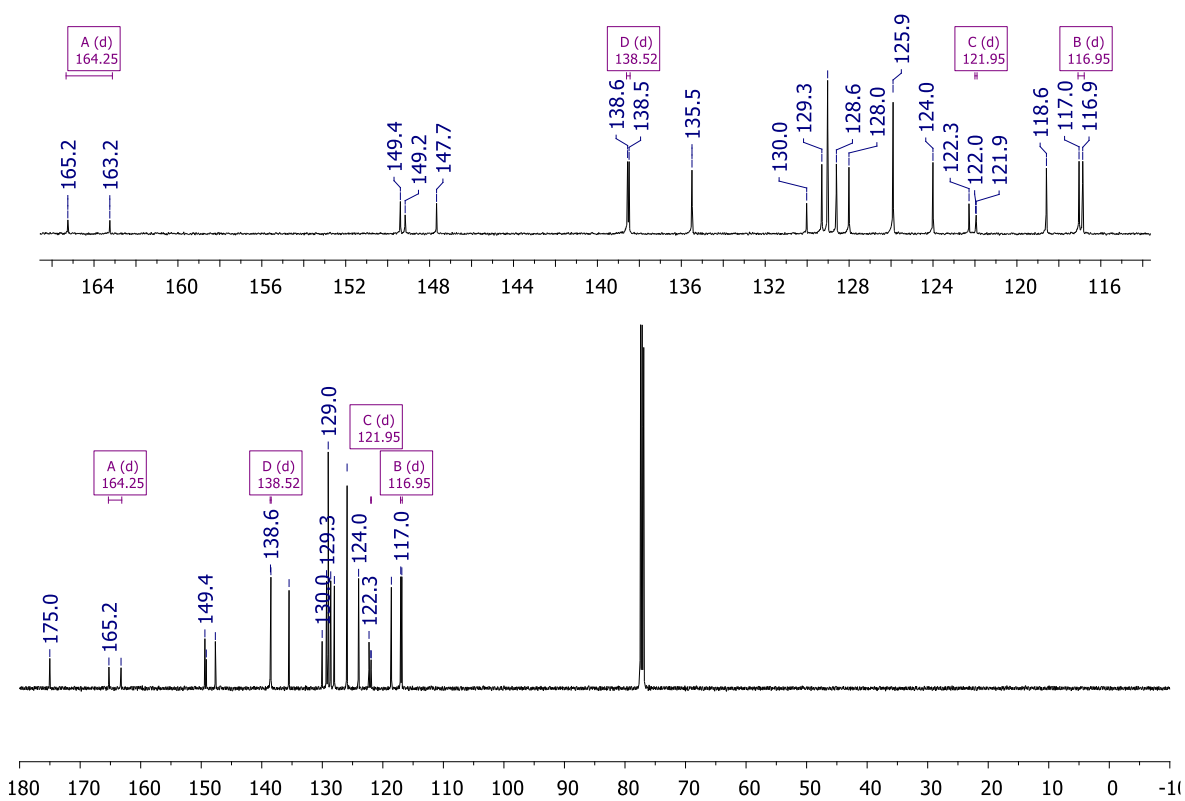


4-[(4-Fluorophenyl)thio]-2-(4-phenyl-1H-1,2,3-triazol-1-yl)quinazoline (7k)

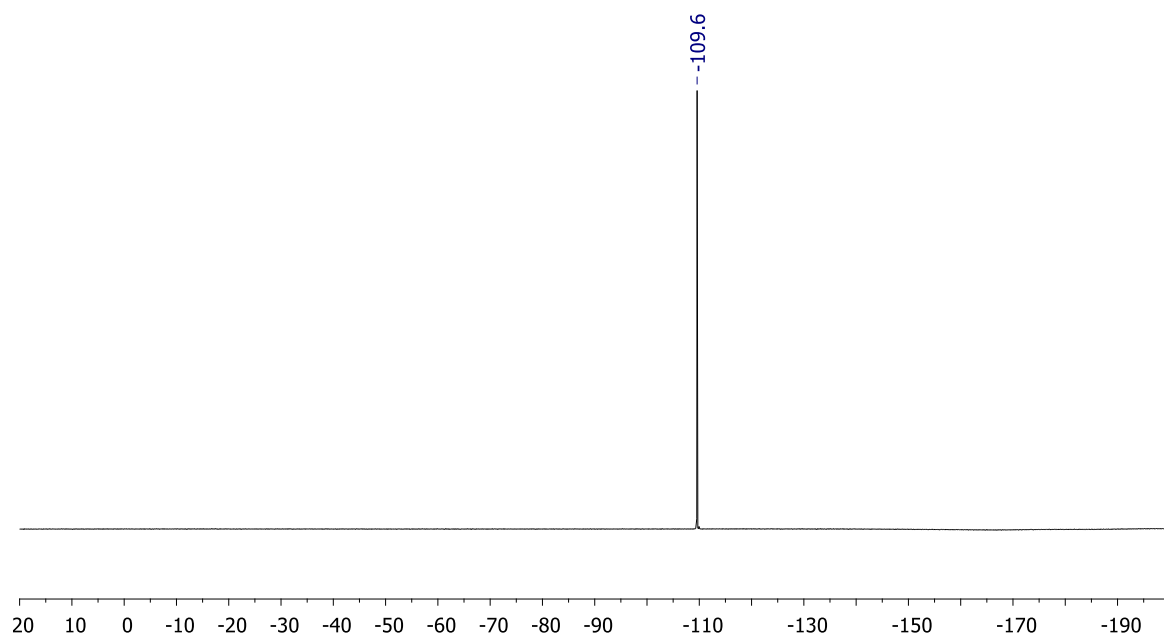
^1H NMR (500 MHz, CDCl_3) spectrum of compound 7k:



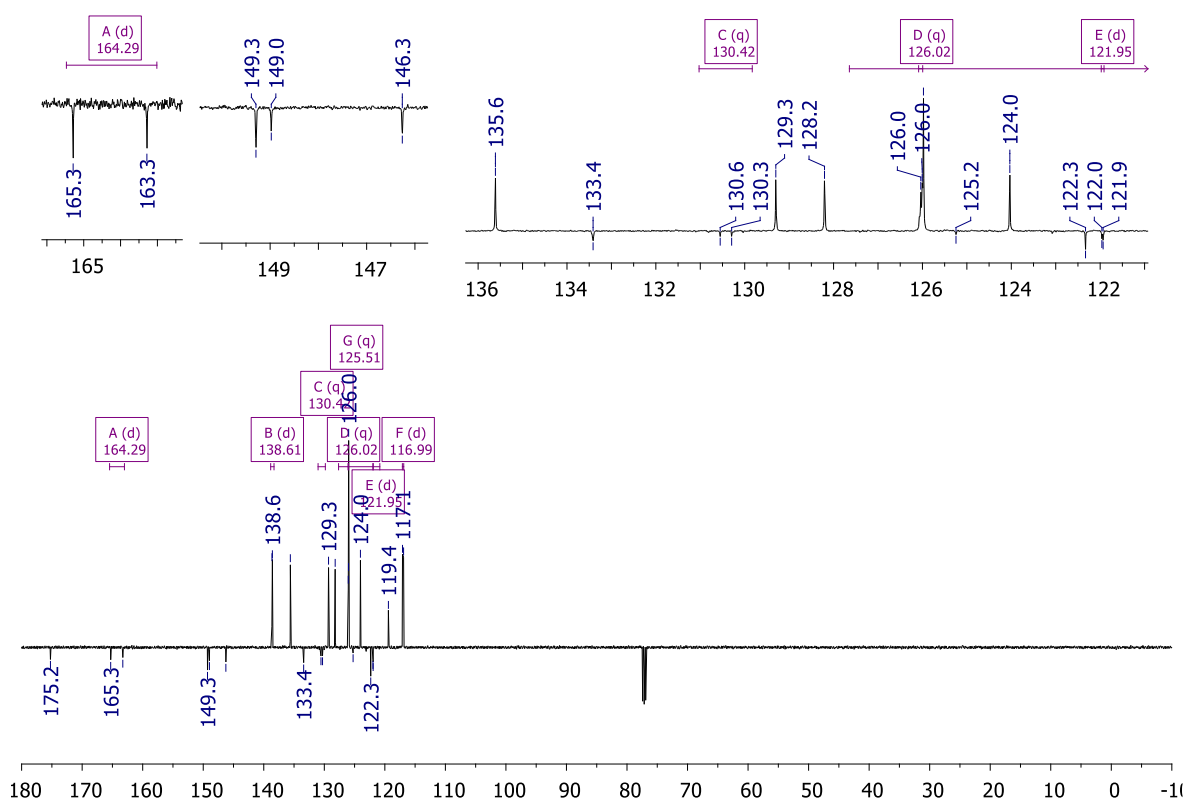
^{13}C NMR (125.7 MHz, CDCl_3) spectrum of compound 7k:



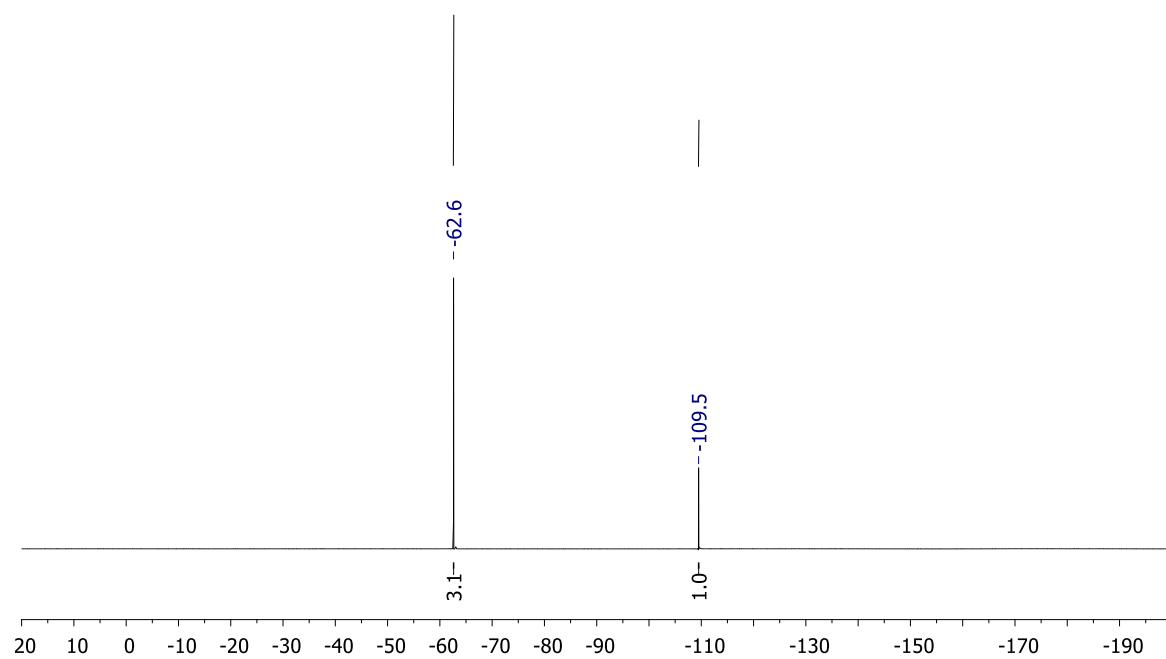
^{19}F NMR (470.5 MHz, CDCl_3) spectrum of compound 7k:



^{13}C NMR (125.7 MHz, CDCl_3) spectrum of compound 7l:

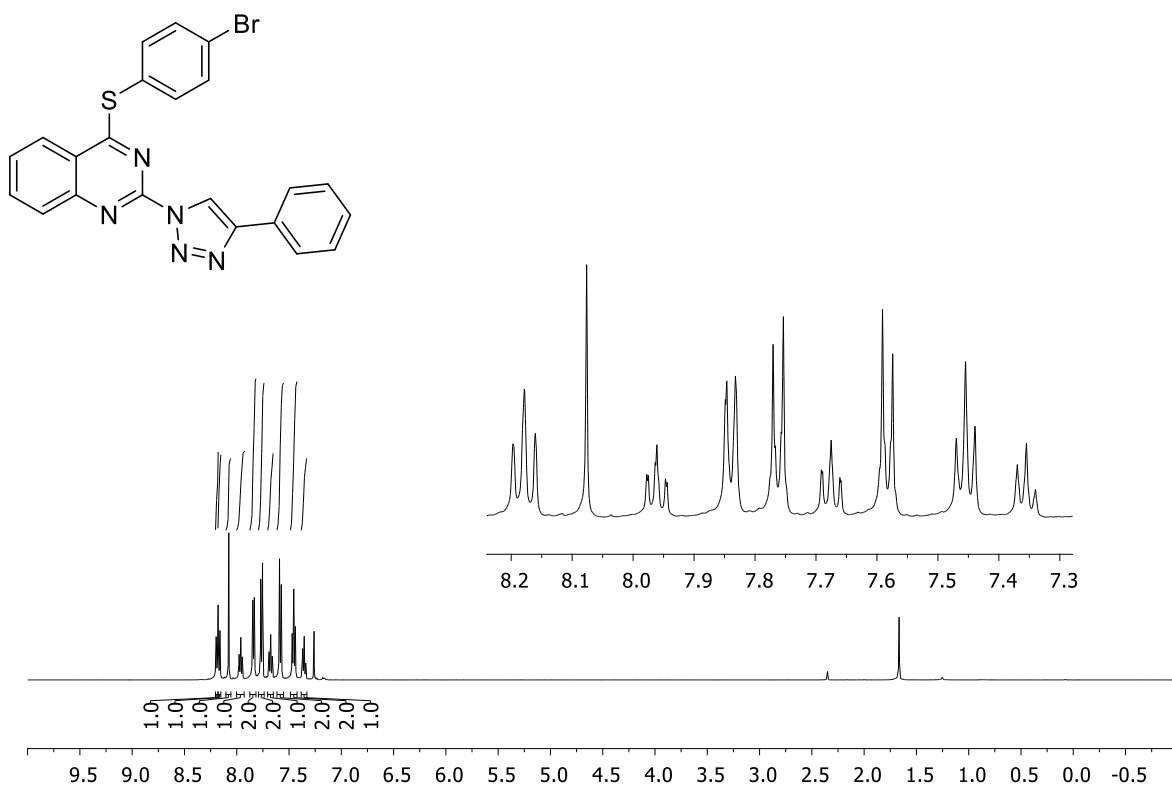


^{19}F NMR (470.5 MHz, CDCl_3) spectrum of compound 7l:

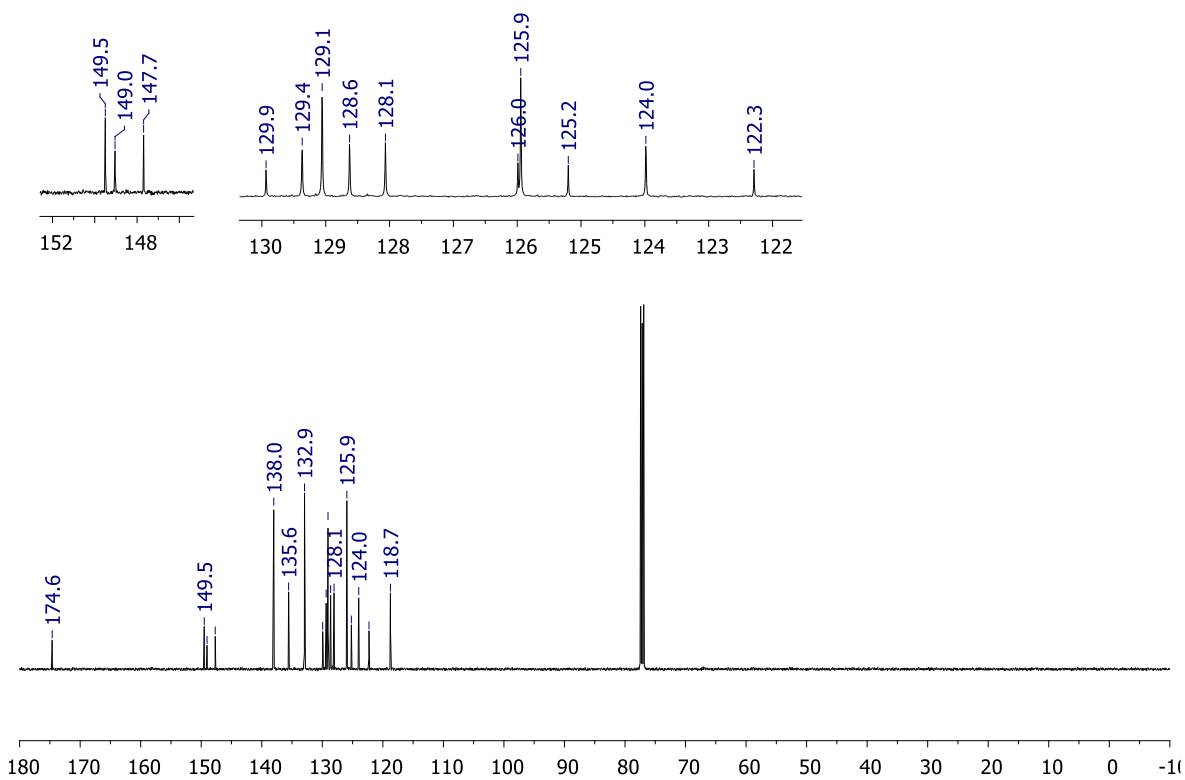


4-[(4-Bromophenyl)thio]-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)quinazoline (7m)

¹H NMR (500 MHz, CDCl₃) spectrum of compound 7m:

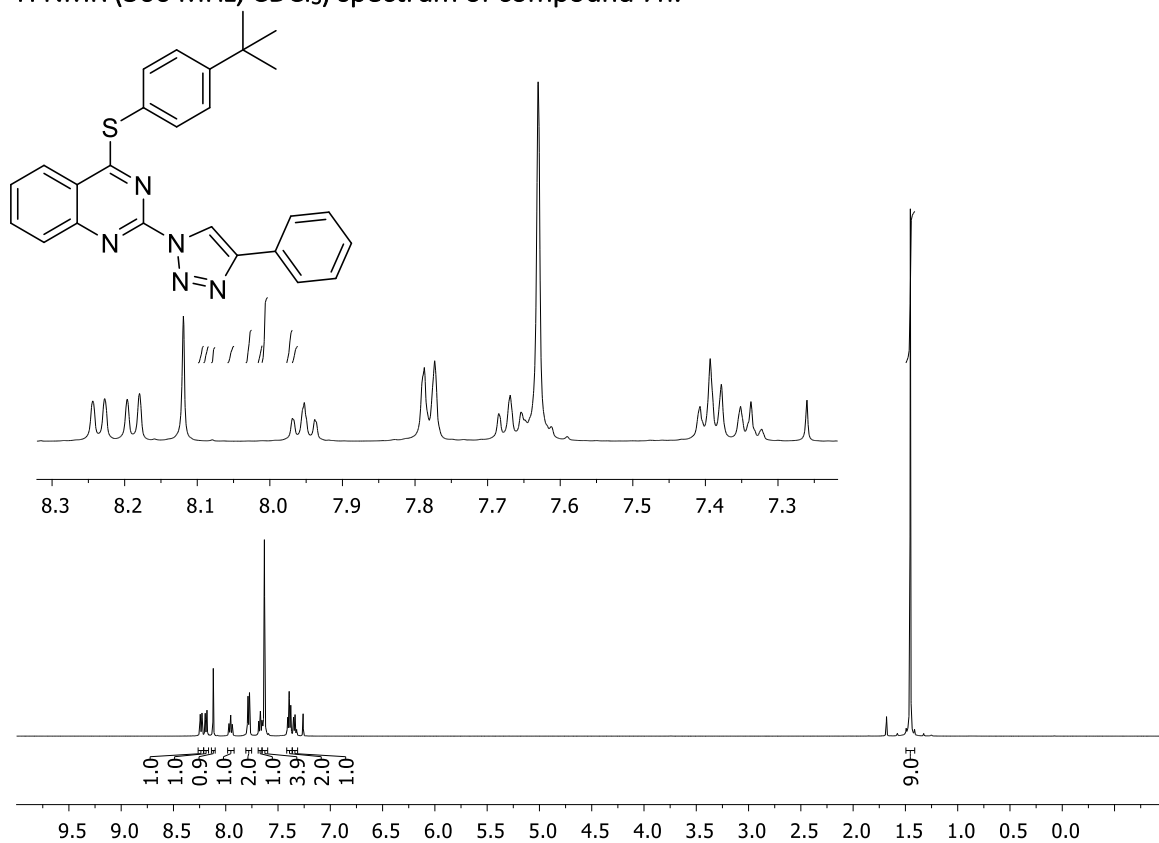


¹³C NMR (125.7 MHz, CDCl₃) spectrum of compound 7m:

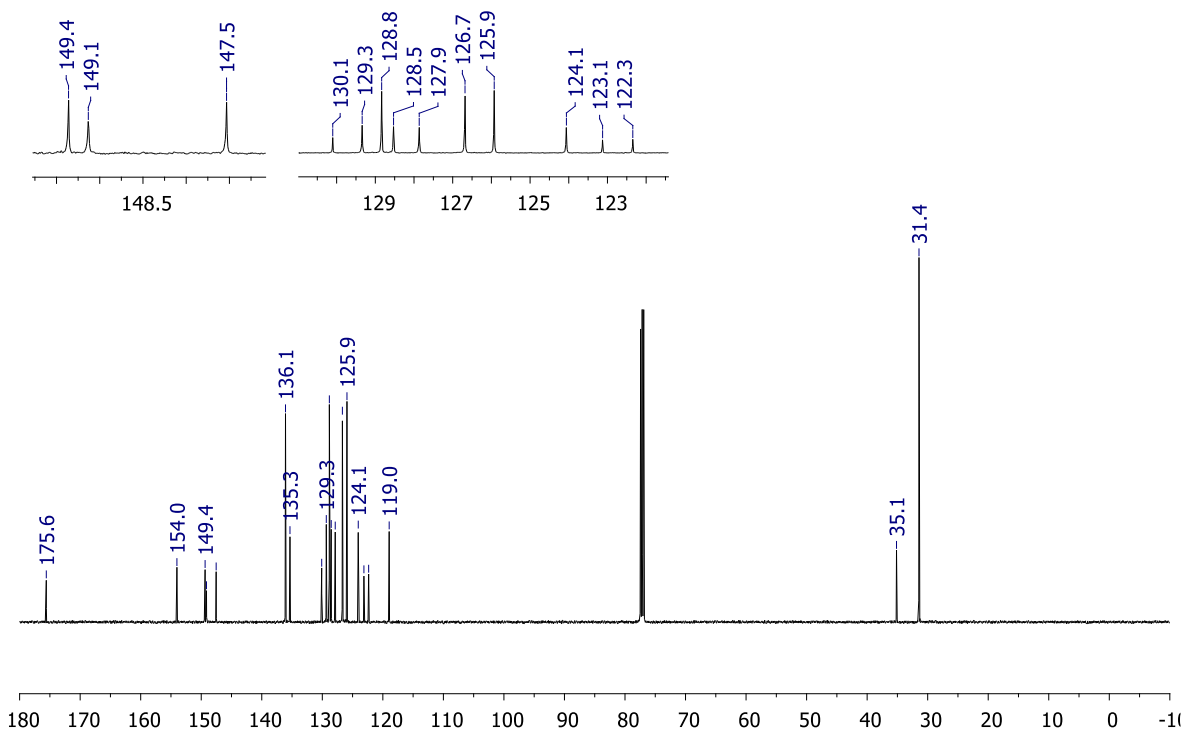


4-[(4-*tert*-Butylphenyl)thio]-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)quinazoline (7n)

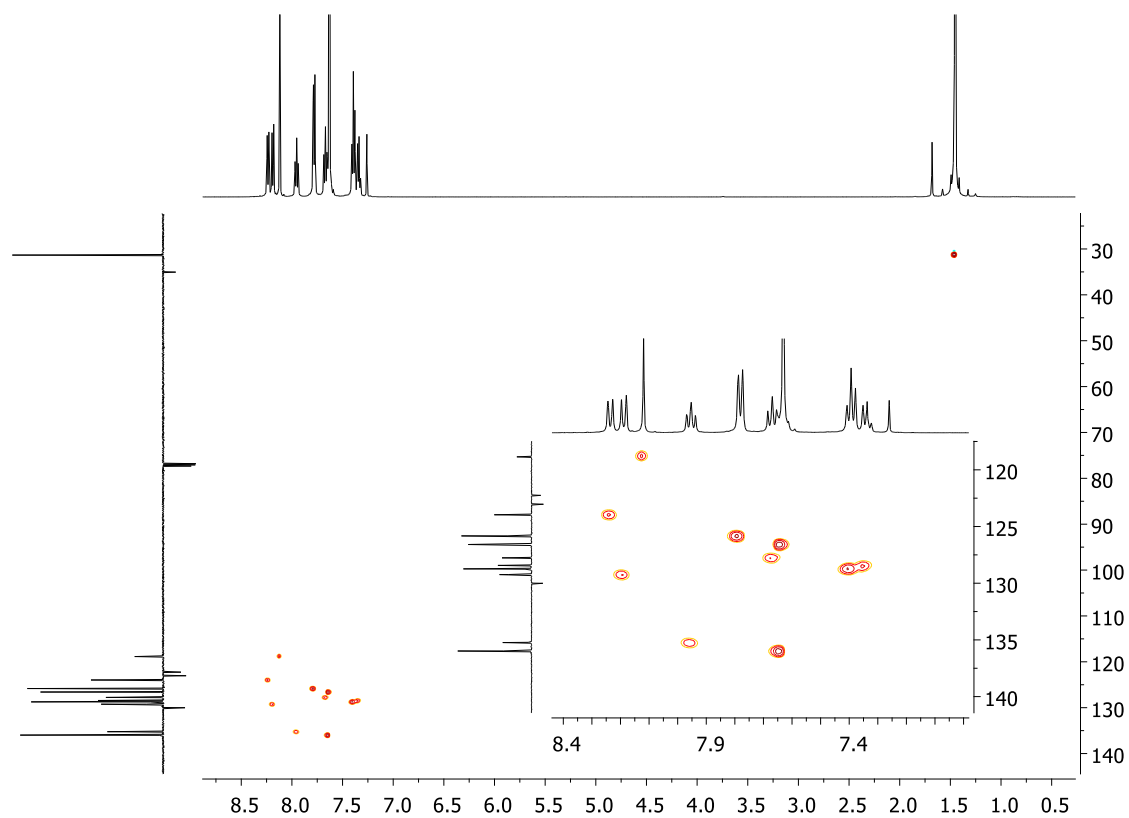
¹H NMR (500 MHz, CDCl₃) spectrum of compound 7n:



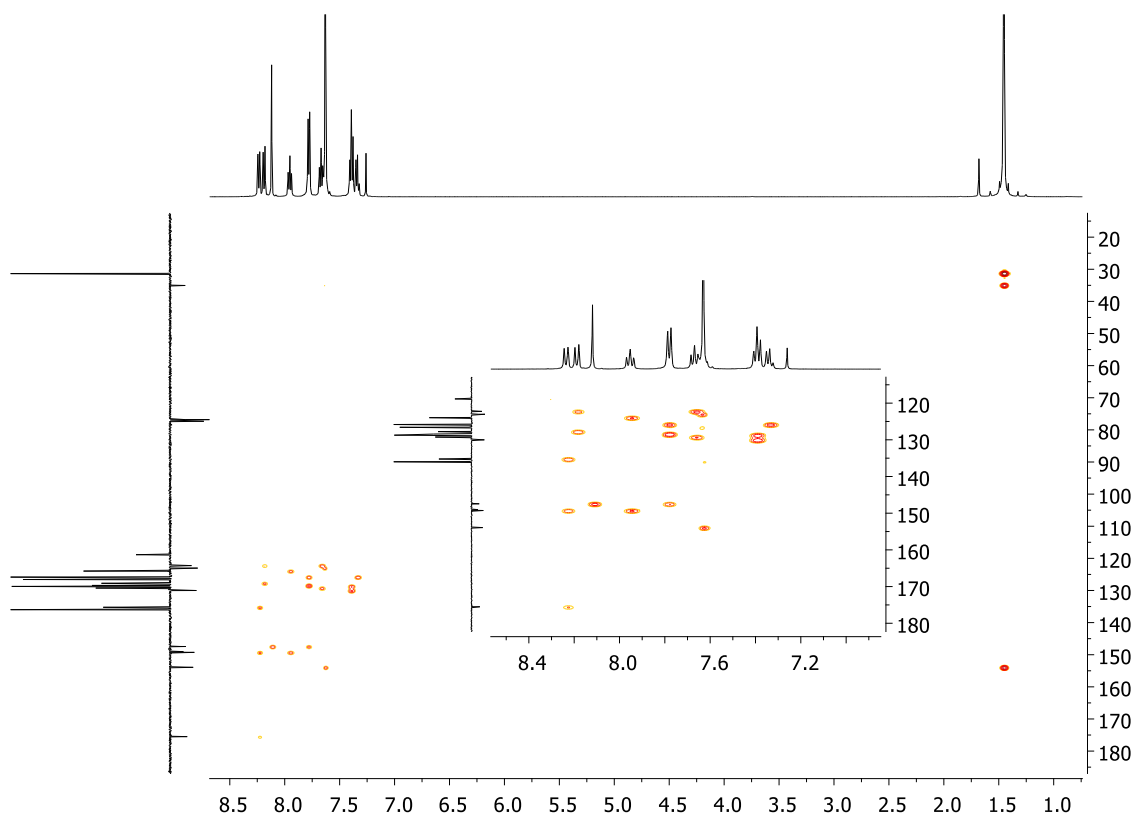
¹³C NMR (125.7 MHz, CDCl₃) spectrum of compound 7n:



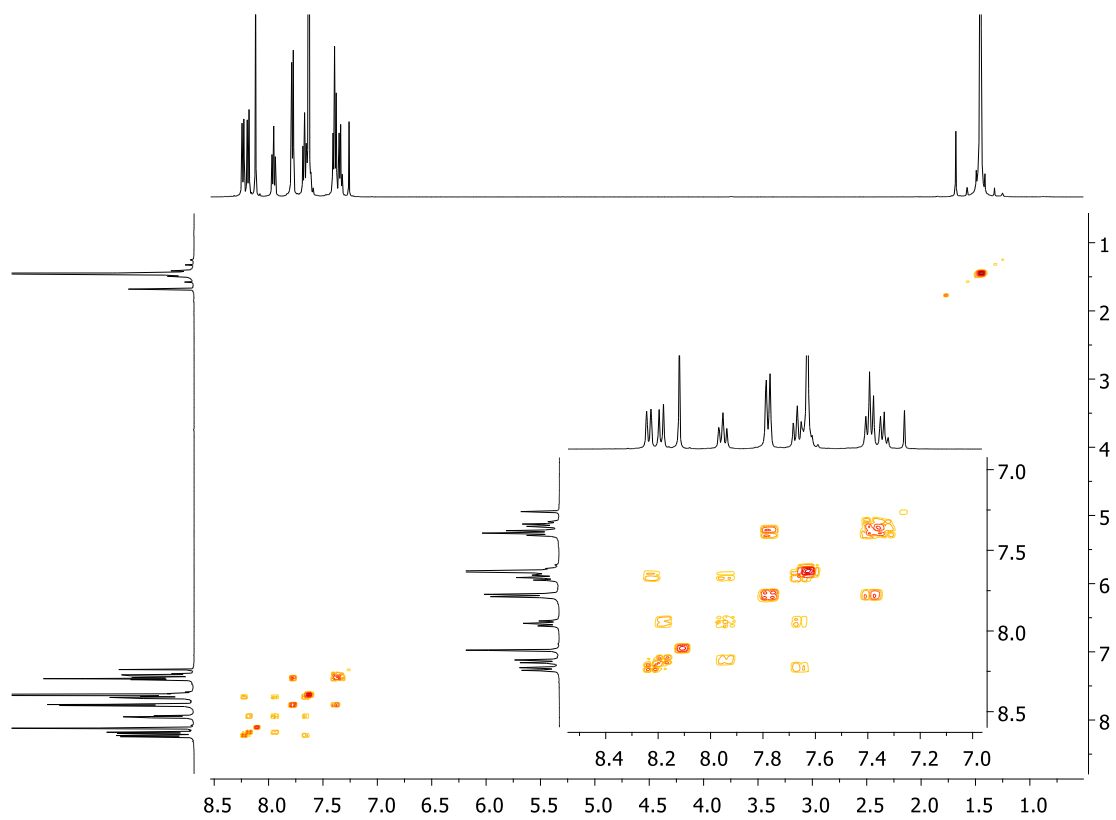
HSQC spectrum of compound 7n:



HMBC spectrum of compound 7n:

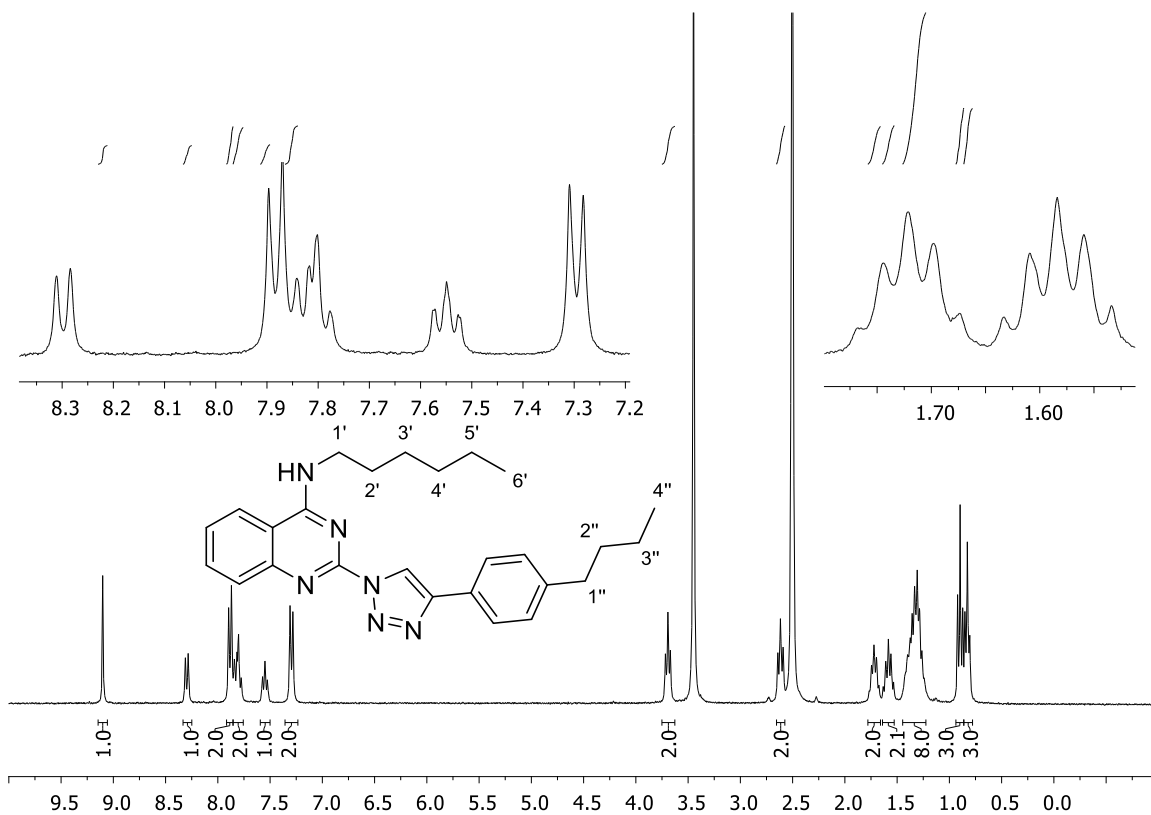


COSY spectrum of compound 7n:

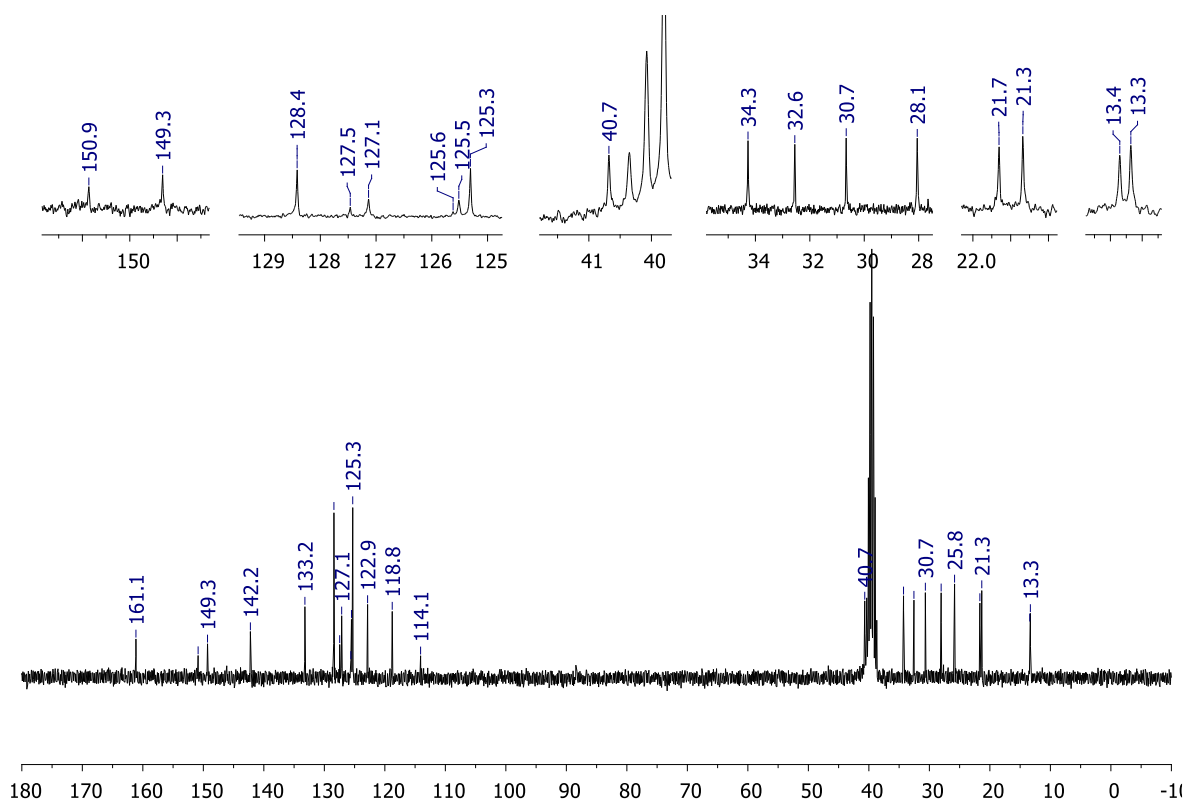


2-[4-(4-butylphenyl)-1H-1,2,3-triazol-1-yl]-4-(hexylamino)quinazoline (9)

^1H NMR (300 MHz, $\text{DMSO-d}_6 + \text{D}_2\text{O}$) spectrum of compound 9:

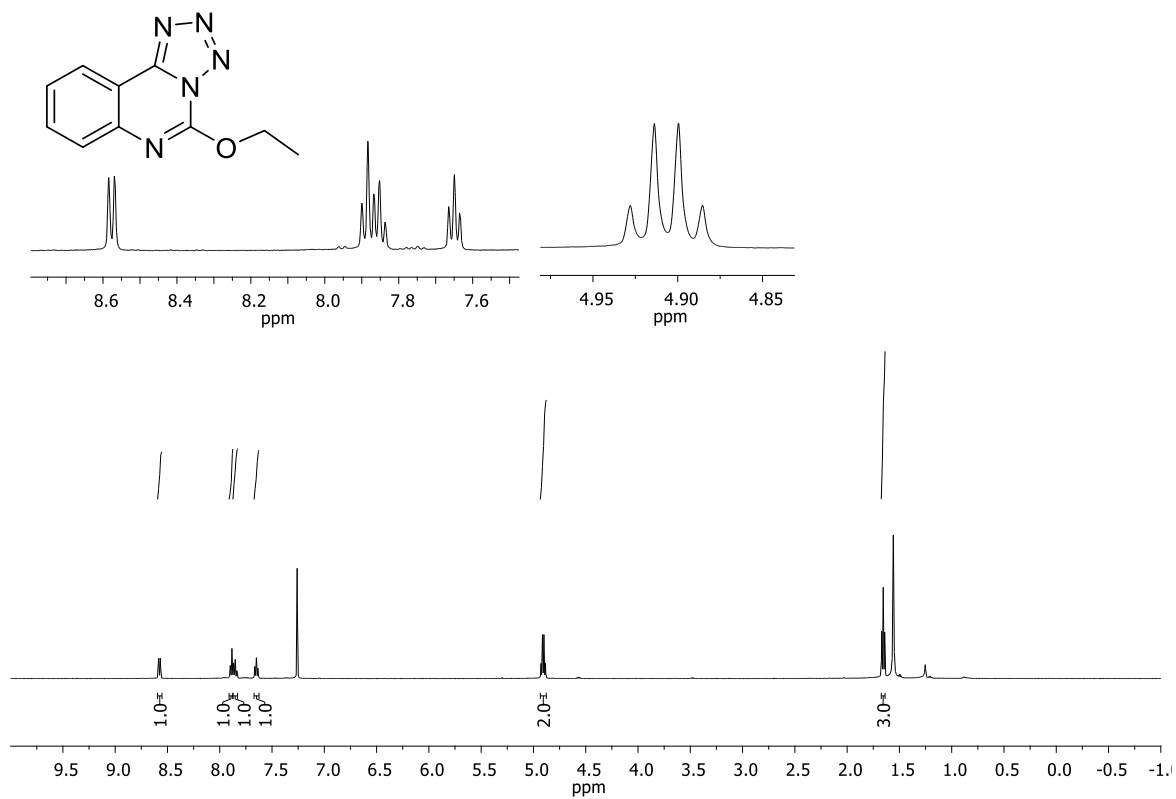


^{13}C NMR (75.5 MHz, DMSO-d_6) spectrum of compound 9:

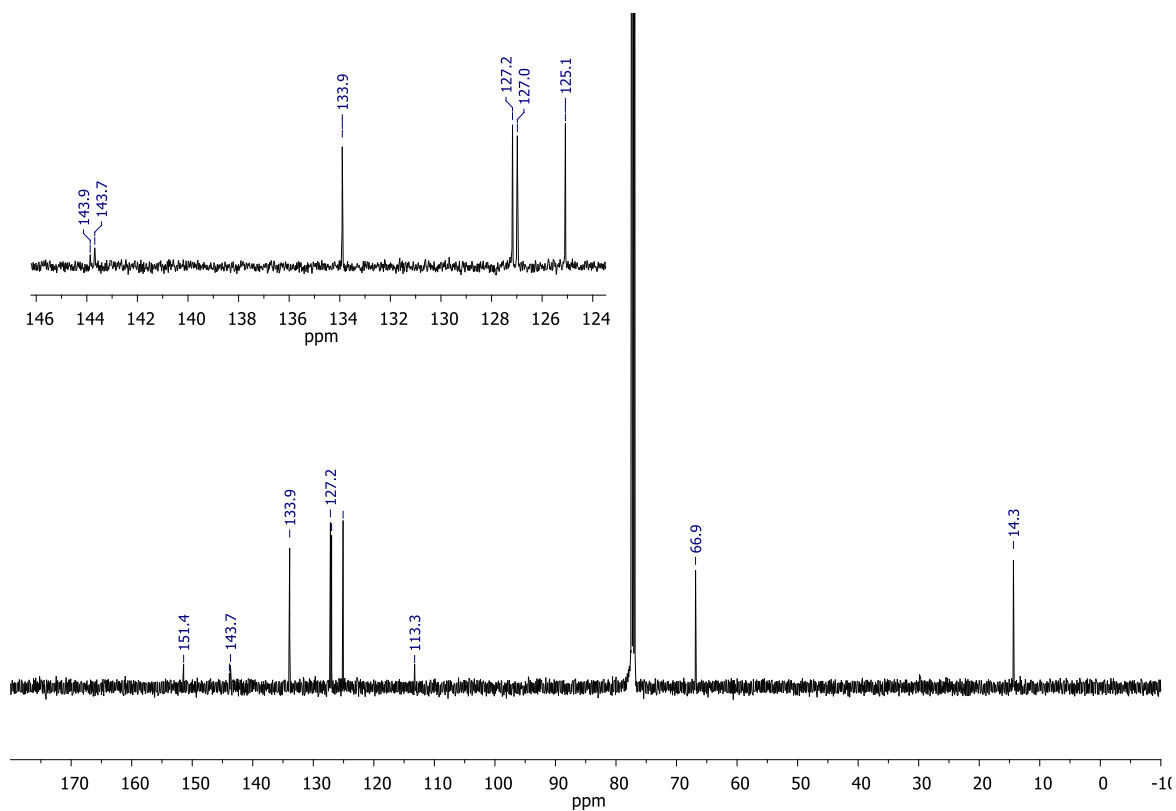


5-(Ethoxy)tetrazolo[1,5-c]quinazoline (11)

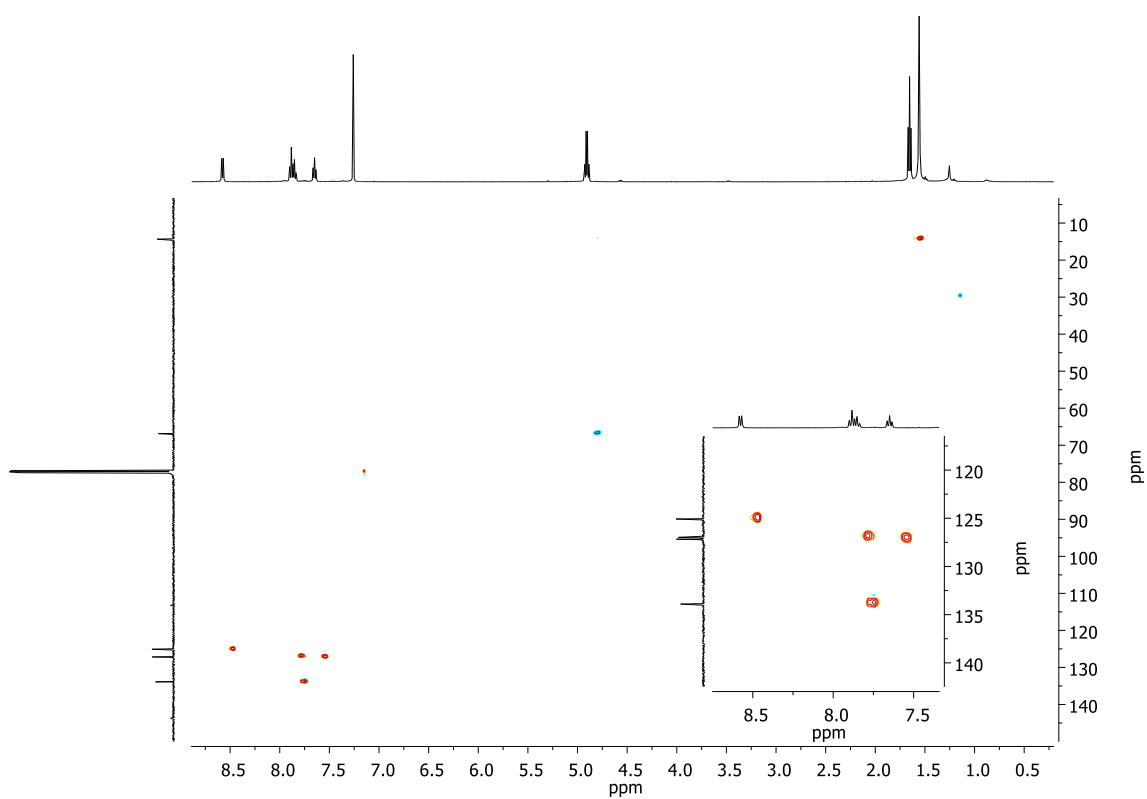
^1H NMR (500 MHz, CDCl_3) spectrum of compound 11:



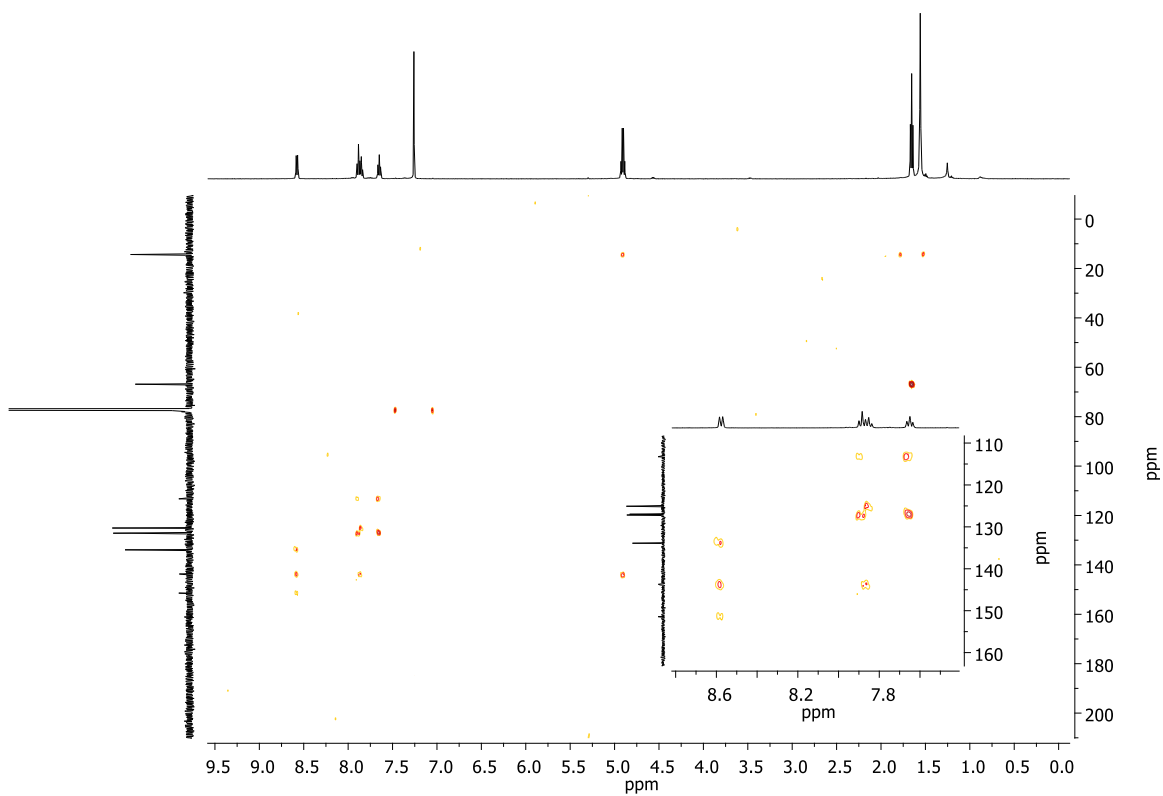
^{13}C NMR (125.7 MHz, CDCl_3) spectrum of compound 11:



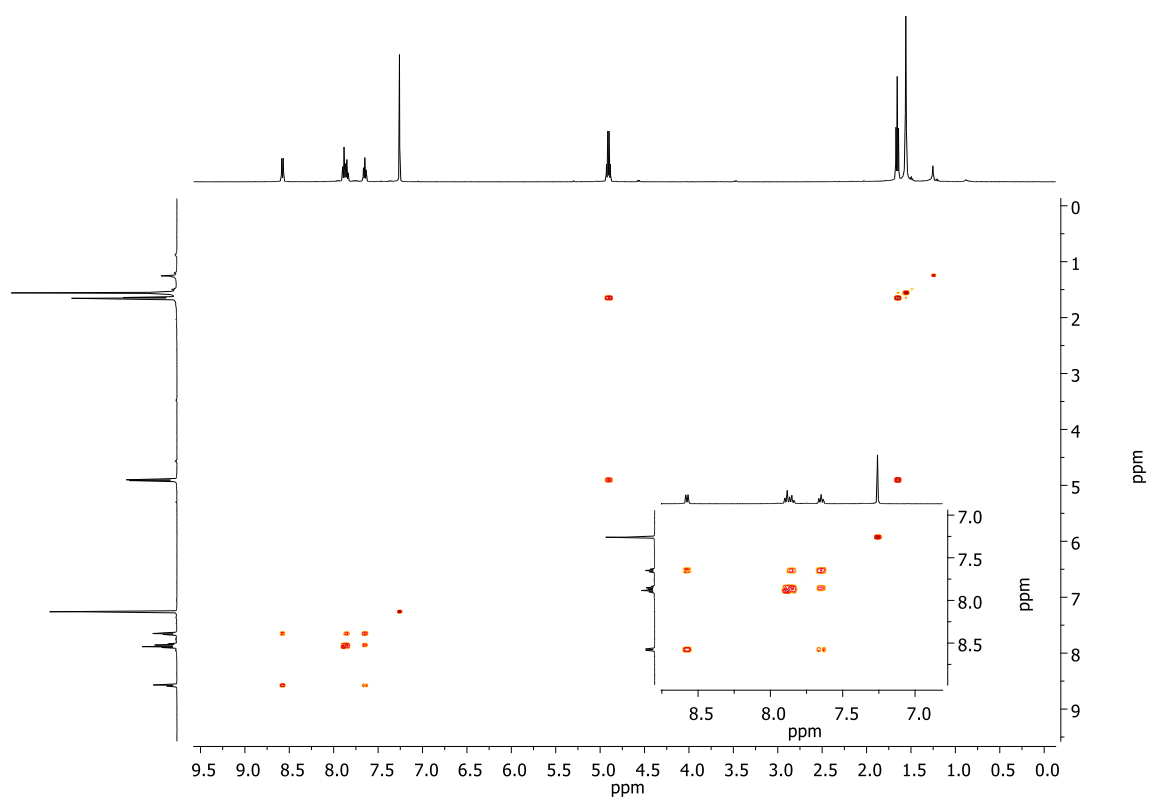
HSQC spectrum of compound 11:



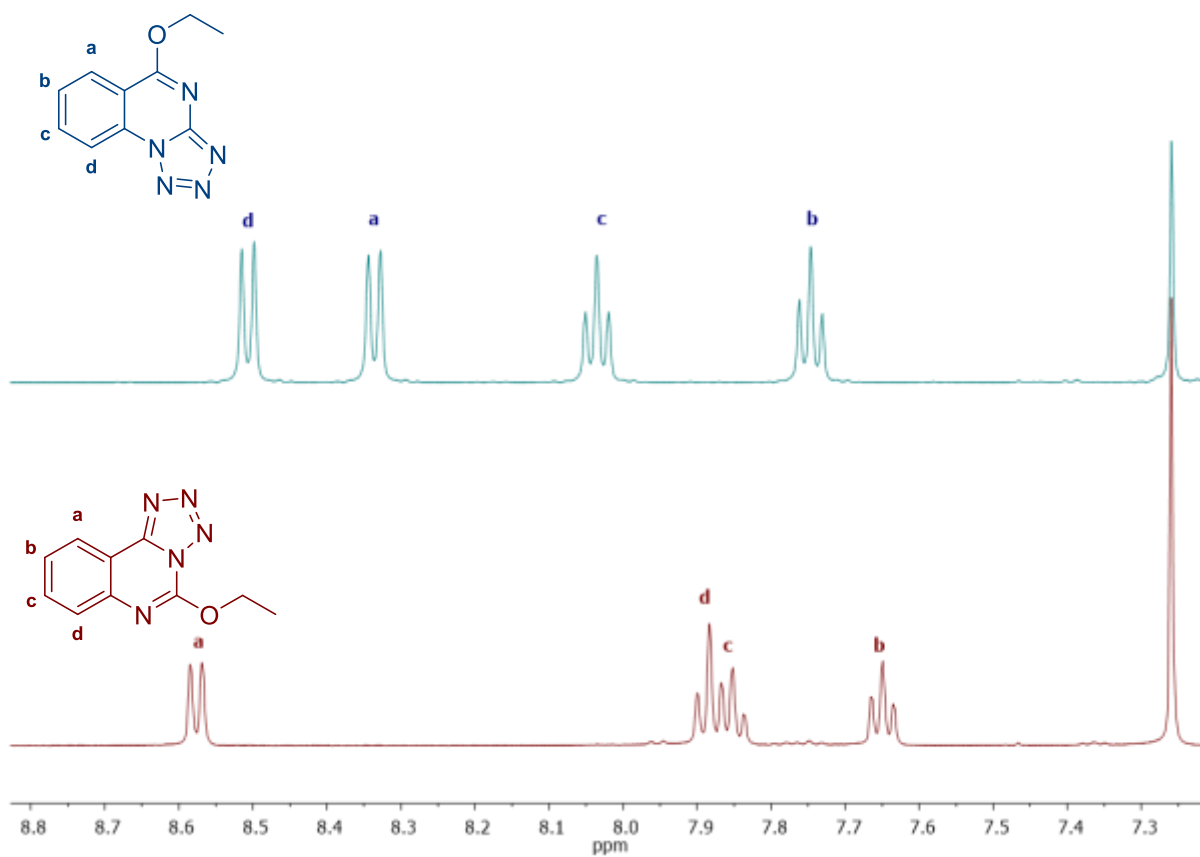
HMBC spectrum of compound 11:



COSY spectrum of compound 11:

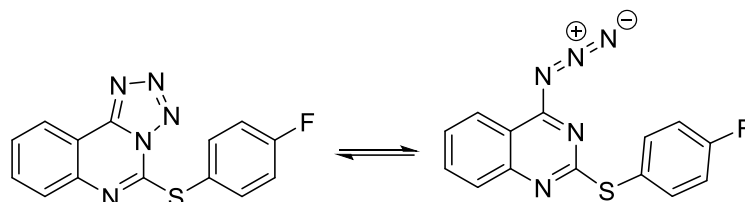


$^1\text{H-NMR}$ (500 MHz, DMSO-d_6) spectra comparison of compounds 10 and 11

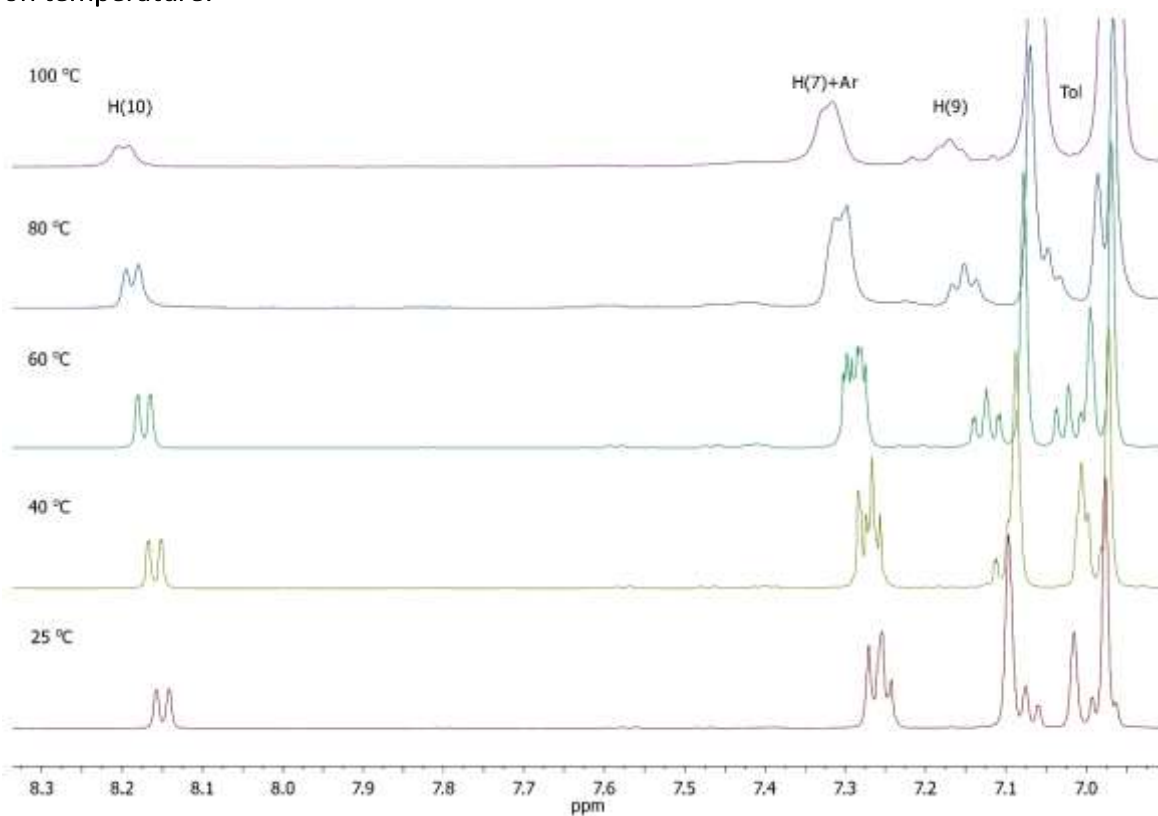


AZIDE-TETRAZOLE EQUILIBRIUM STUDIES

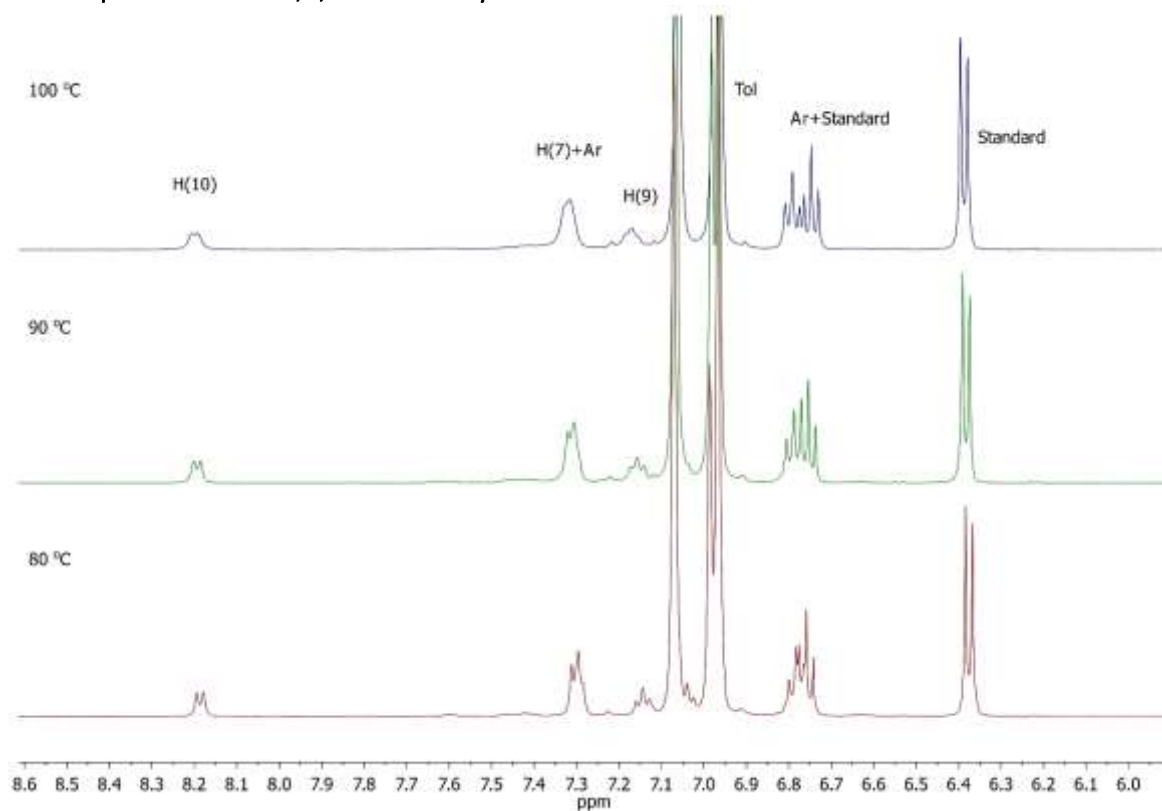
5-[(4-Fluorophenyl)thio]tetrazolo[1,5-c]quinazoline (3c-T) and
4-azido-2-[(4-fluorophenyl)thio]quinazoline (3c-A)



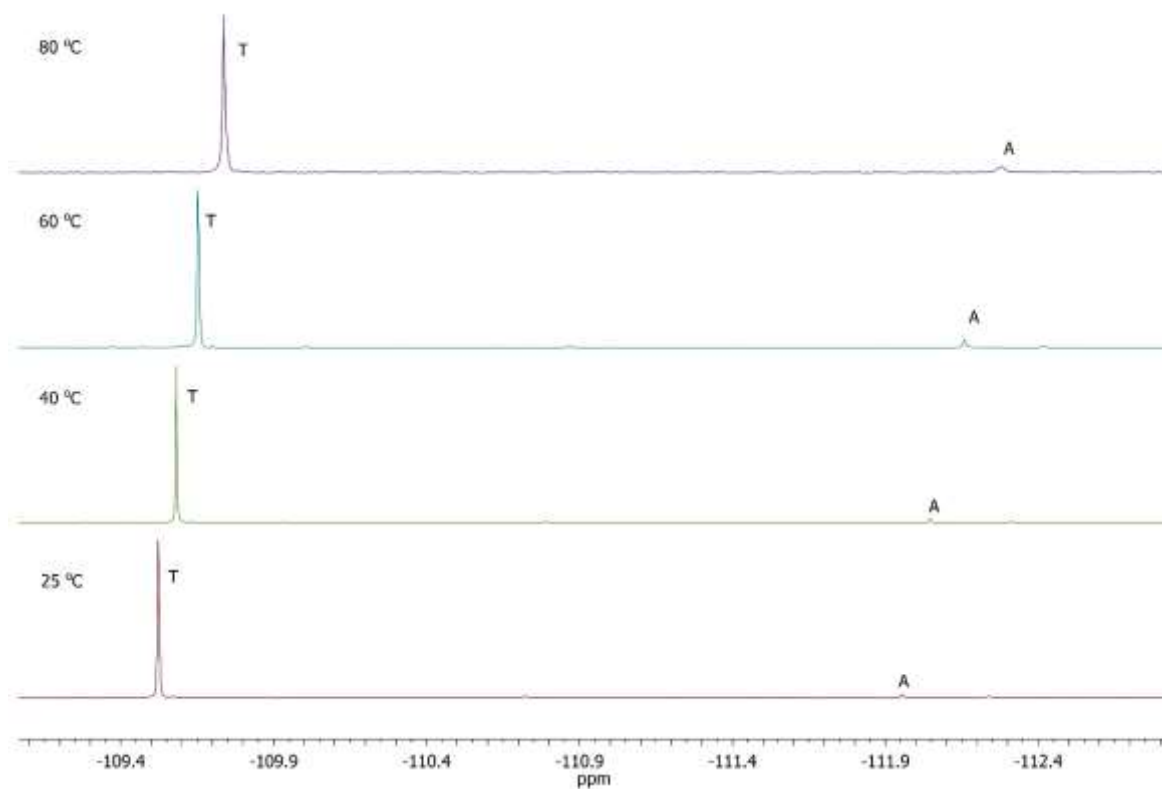
A test of azide-tetrazole equilibrium of compound 3c in Tol-*d*₈ (¹H NMR 500 MHz) depending on temperature:



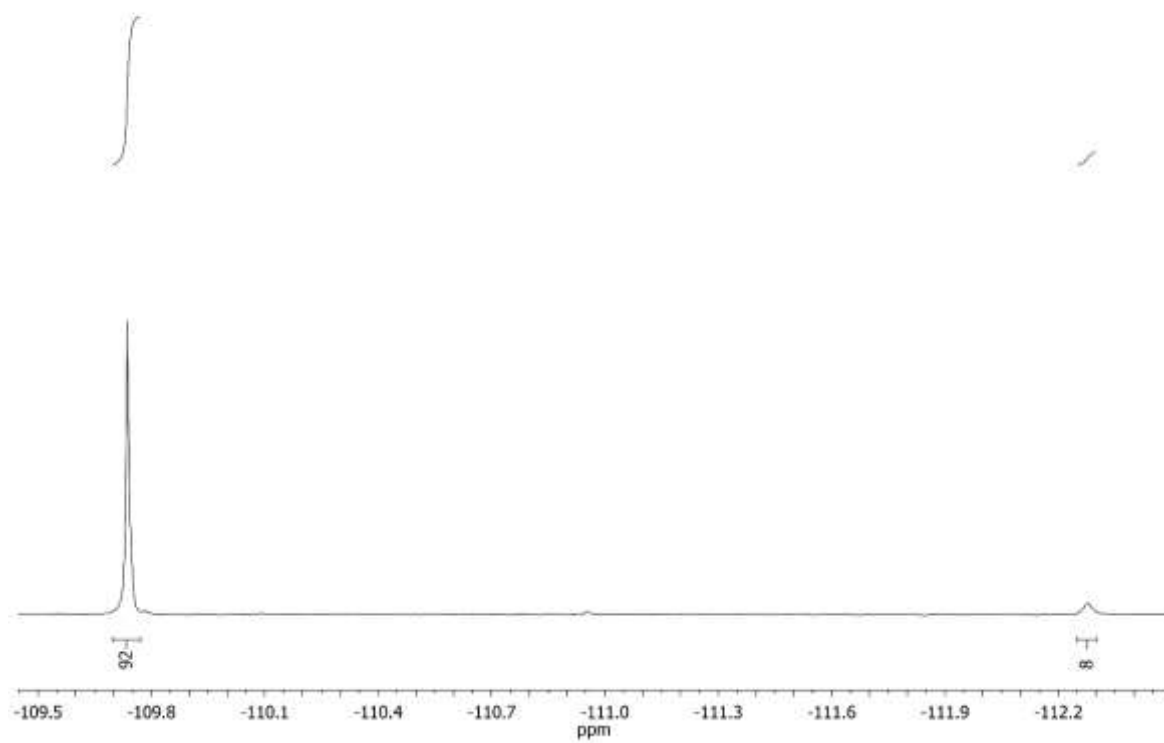
A test of azide-tetrazole equilibrium of compound 3c in Tol- d_8 (1H NMR 500 MHz) depending on temperature with 1,2,3-trimethoxybenzene as internal standard:



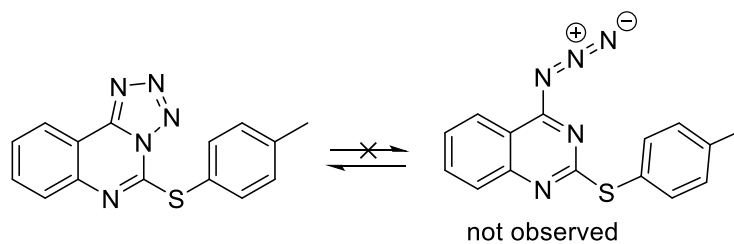
Azide-tetrazole equilibrium of compound 3c in Tol- d_8 (^{19}F NMR 470.5 MHz) depending on temperature:



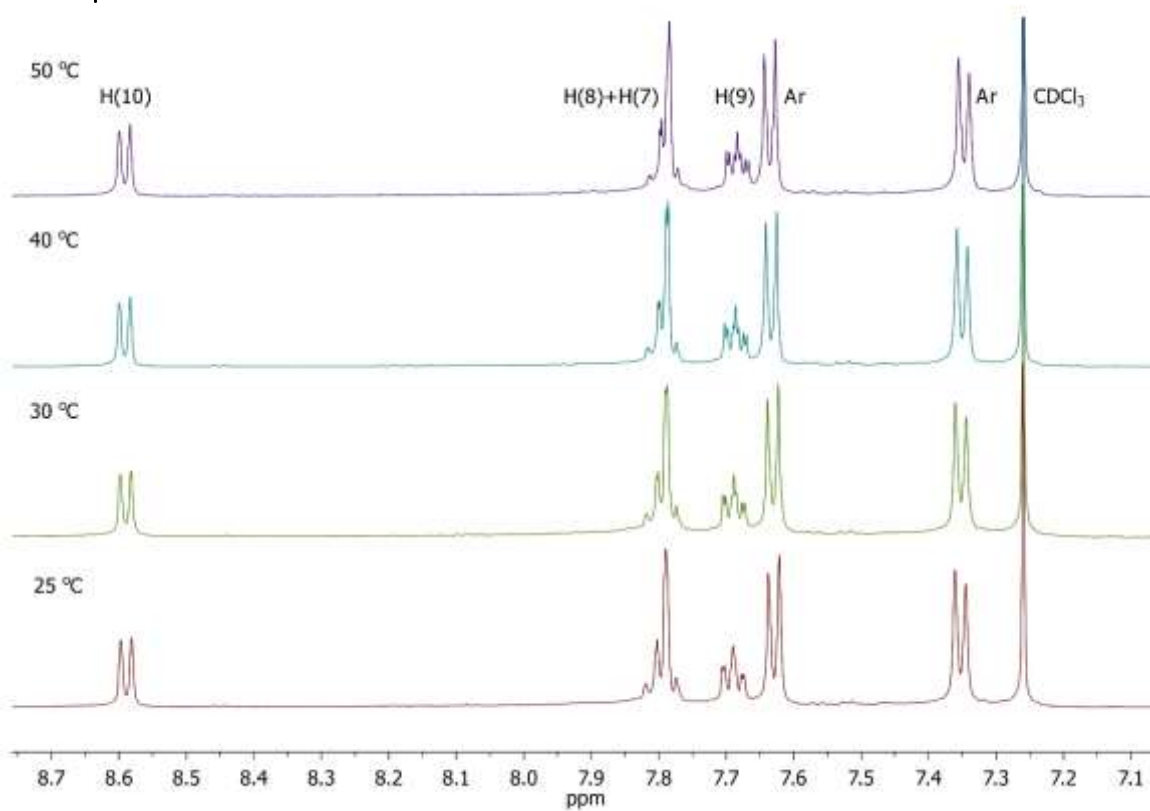
^{19}F NMR (470.5 MHz, ToI-d_8 , 80 $^\circ\text{C}$) spectrum of compound 3c:



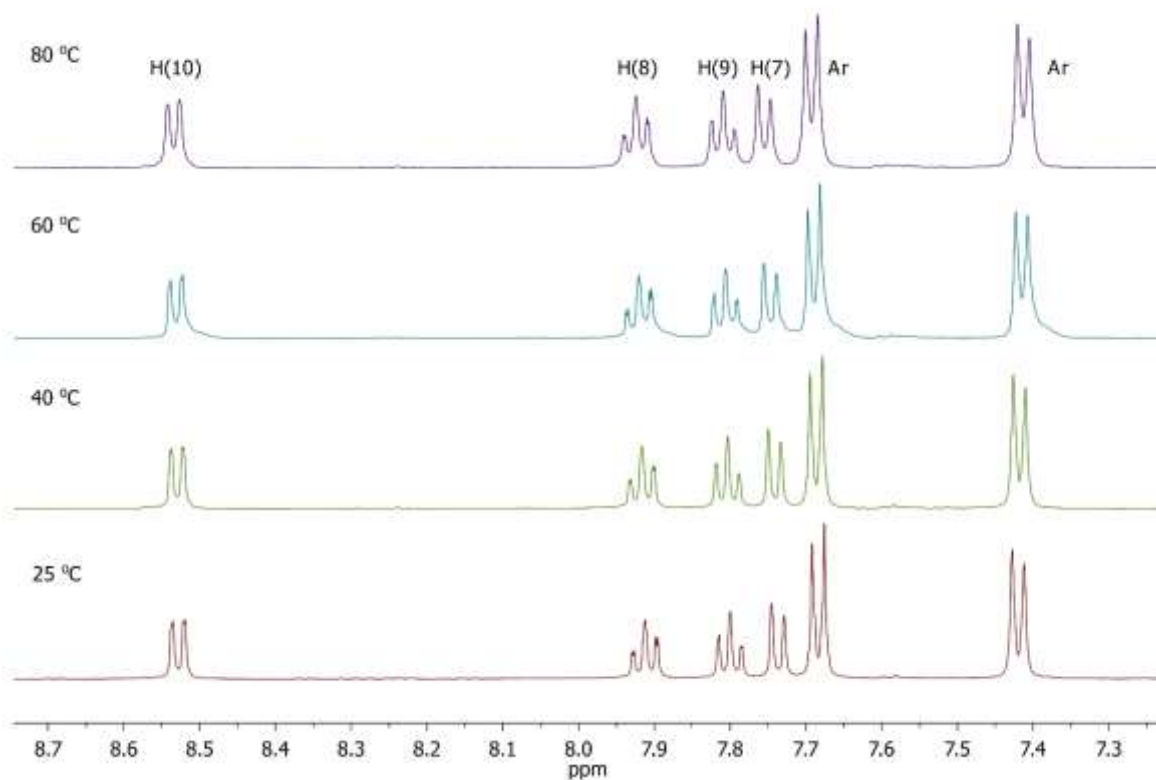
5-(*p*-Tolylthio)tetrazolo[1,5-*c*]quinazoline (3e-T) and
4-azido-2-(*p*-tolylthio)quinazoline (3e-A)



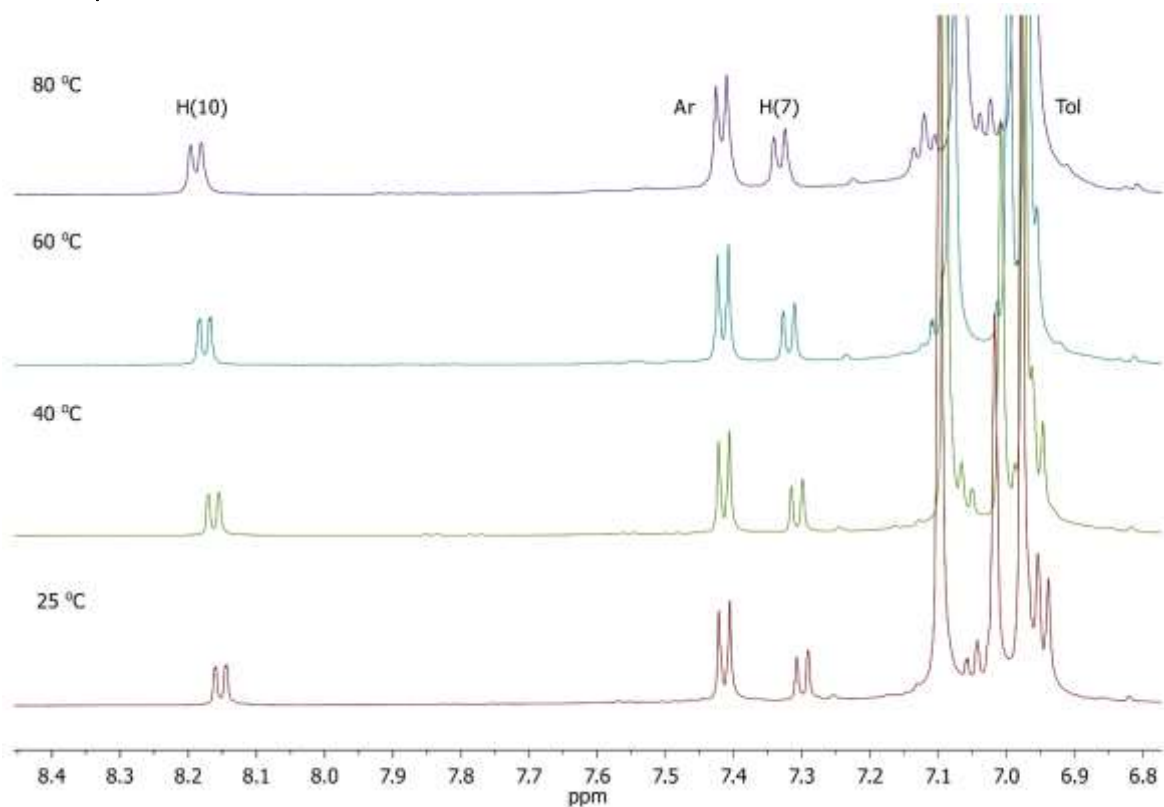
A test of azide-tetrazole equilibrium of compound 3e in CDCl₃ (¹H NMR 500 MHz) depending on temperature:



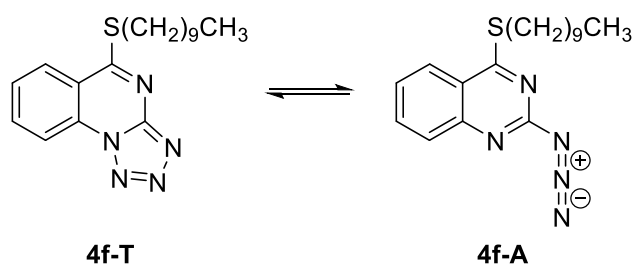
A test of azide-tetrazole equilibrium of compound 3e in DMSO-d₆ (¹H NMR 500 MHz) depending on temperature:



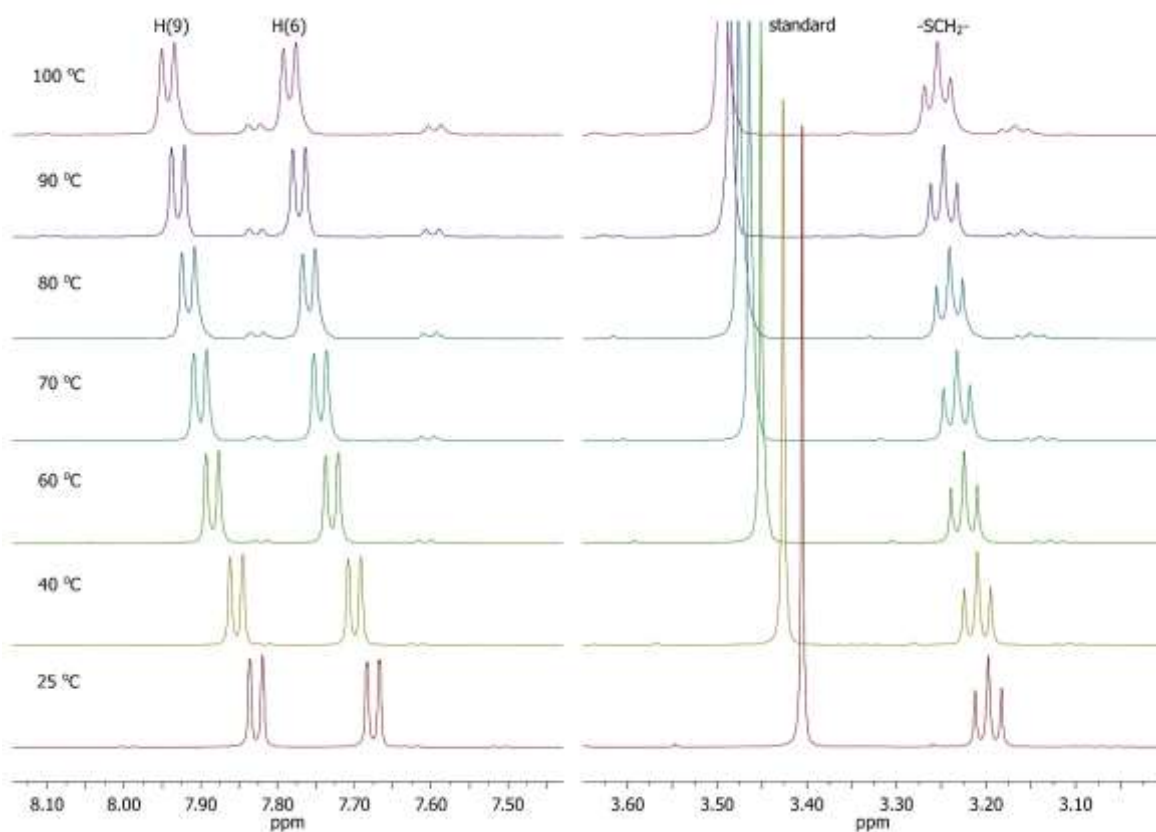
A test of azide-tetrazole equilibrium of compound 3e in Tol-d₈ (¹H NMR 500 MHz) depending on temperature:



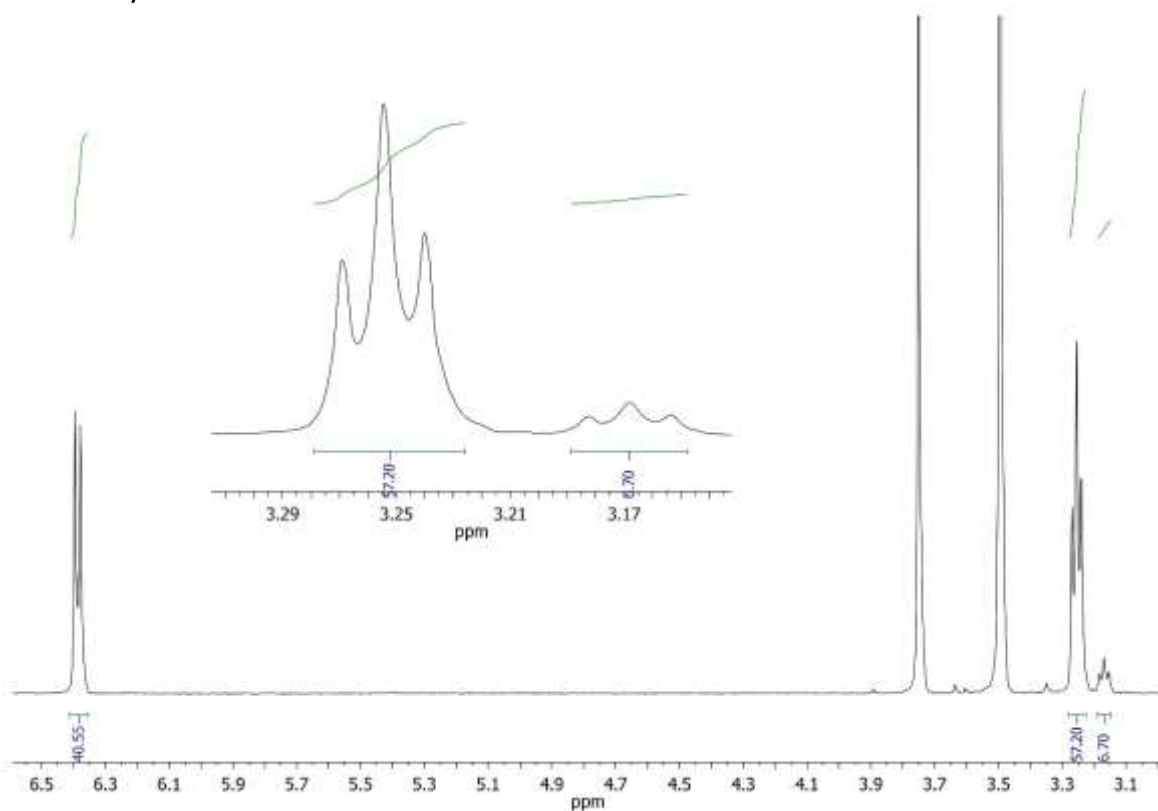
5-(Decylthio)tetrazolo[1,5-a]quinazoline (4f-T) and
2-azido-4-(decylthio)quinazoline (4f-A)



Azide-tetrazole equilibrium of compound 4f in Tol-d₈ (¹H NMR 500 MHz) depending on temperature with internal standard of 1,2,3-trimethoxybenzene:

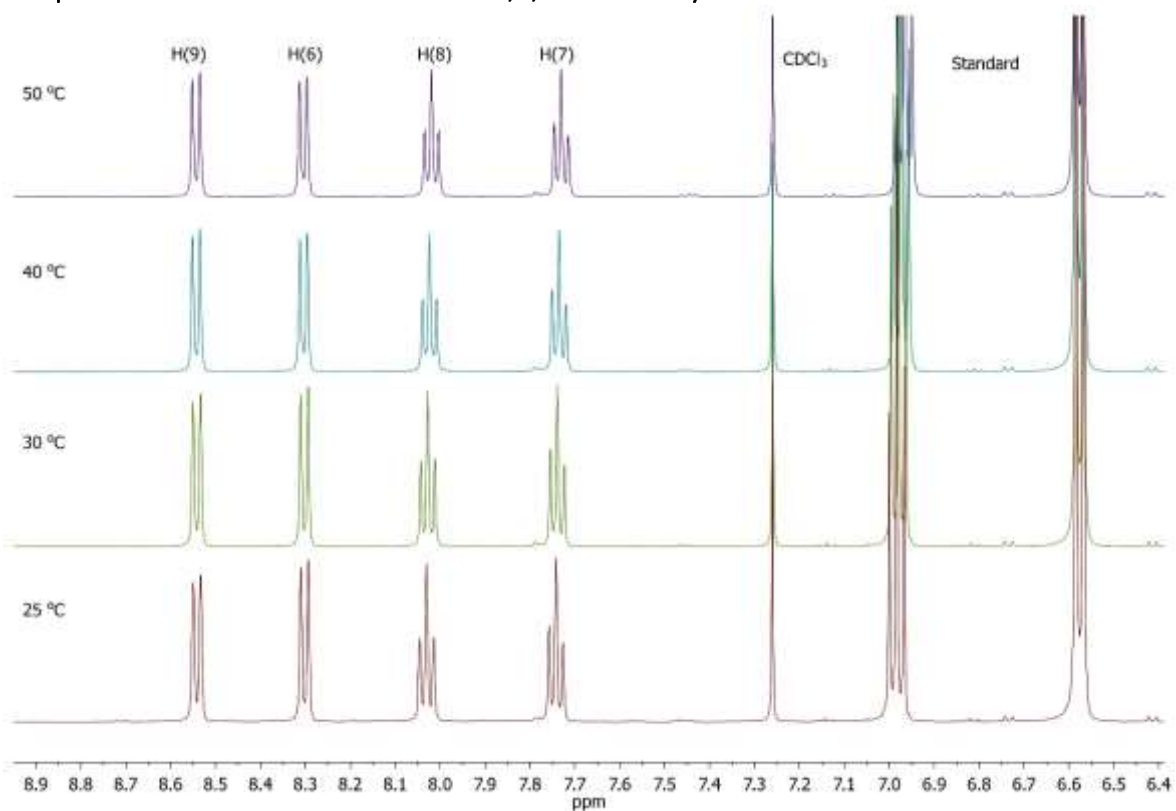


^1H NMR (500 MHz, CDCl_3 , 100 °C) spectrum of compound **4f** with internal standard of 1,2,3-trimethoxybenzene:

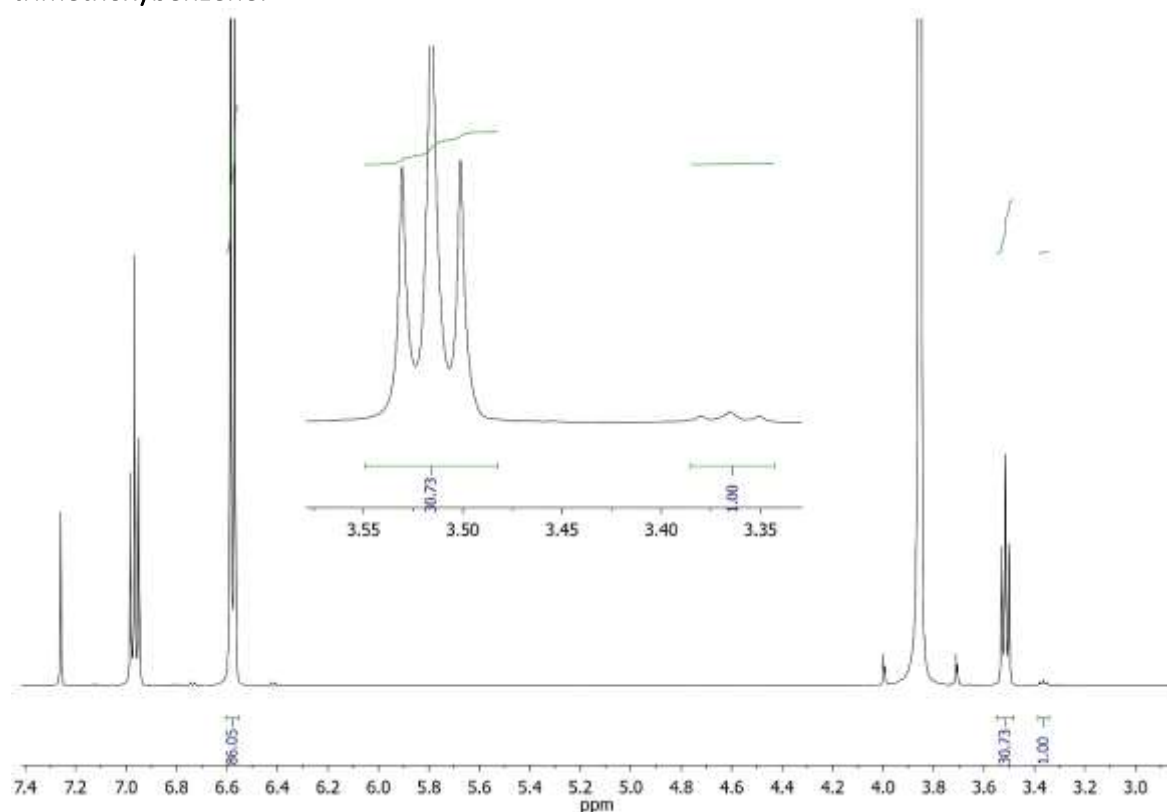


Weights: compound **4f** – 5.57 mg; 1,2,3-trimethoxybenzene – 1.73 mg. Azide-tetrazole forms proportions are calculated based on $-\text{SCH}_2-$ signal of compound **4f** and $2\times\text{H-C(Ar)}$ signal of 1,2,3-trimethoxybenzene. Results are showed in Table S1.

Azide-tetrazole equilibrium of compound 4f in CDCl_3 (^1H NMR 500 MHz) depending on temperature with internal standard of 1,2,3-trimethoxybenzene:



^1H NMR (500 MHz, CDCl_3 , 50 °C) spectrum of compound **4f** with internal standard of 1,2,3-trimethoxybenzene:

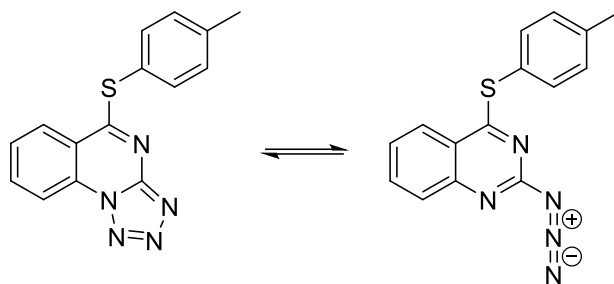


Weights: compound **4f** – 6.60 mg; 1,2,3-trimethoxybenzene – 8.68 mg. Azide-tetrazole forms proportions are calculated based on $-\text{SCH}_2-$ signal of compound **4f** and $2\times\text{H-C(Ar)}$ signal of 1,2,3-trimethoxybenzene. Results are showed in Table S1.

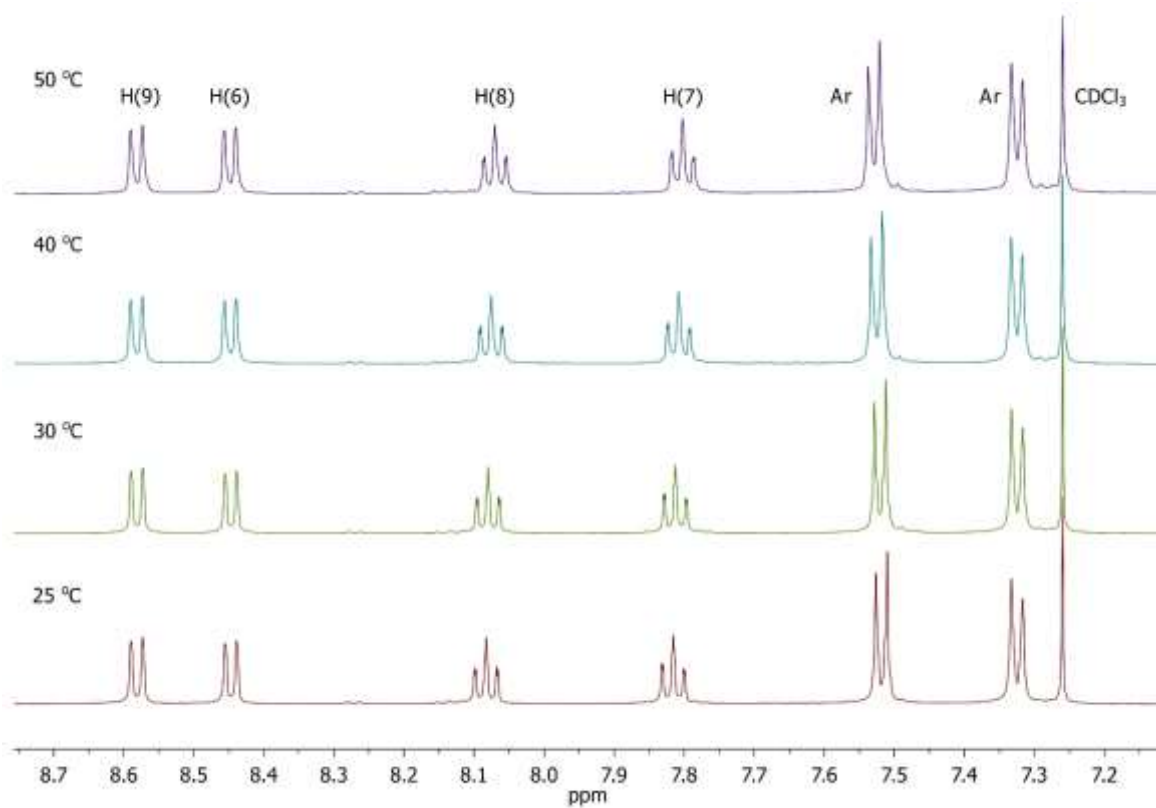
Table S1. Azide-tetrazole equilibrium of compound **4f** depending on temperature in Tol-d_8 and CDCl_3

Equilibrium in Tol-d_8		
Temperature, °C	A, %	T, %
25	1	99
40	2	98
60	4	96
70	5	95
80	7	93
90	9	91
100	10	90
Equilibrium in CDCl_3		
Temperature, °C	A, %	T, %
25	2.2	97.8
30	2.3	97.7
40	2.7	97.3
50	3.1	96.9

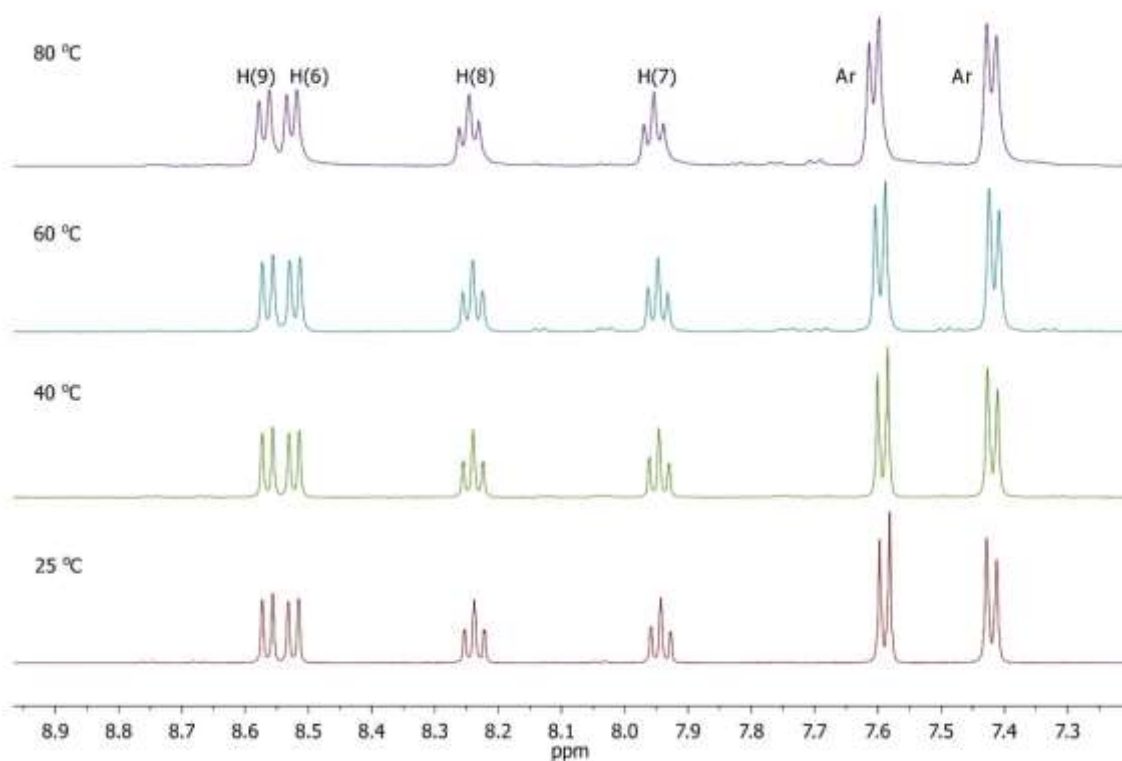
5-(*p*-Tolylthio)tetrazolo[1,5-*a*]quinazoline (4I-T) and
2-azido-4-(*p*-tolylthio)quinazoline (4I-A)



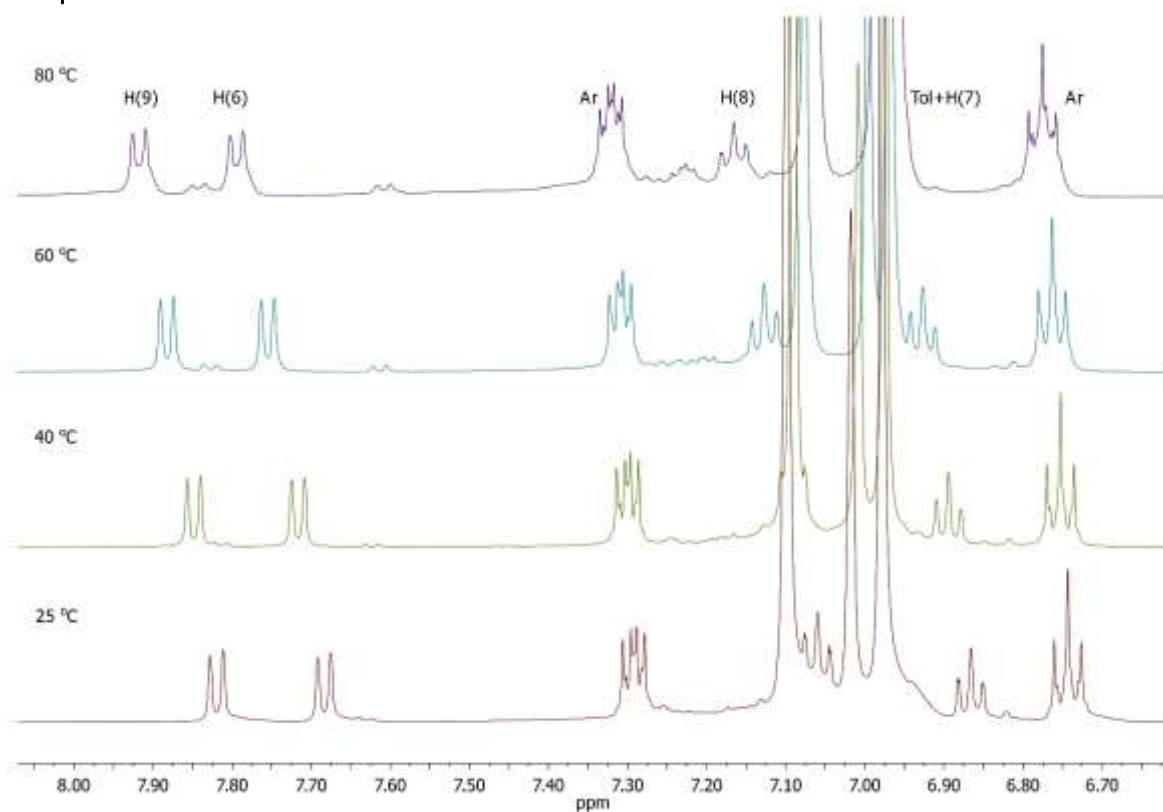
Test of azide-tetrazole equilibrium of compound 4I in CDCl₃ (¹H NMR 500 MHz) depending on temperature:



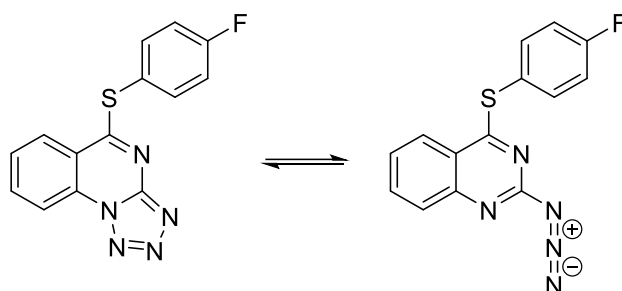
Azide-tetrazole equilibrium of compound 4I in DMSO-d₆ (¹H NMR 500 MHz) depending on temperature:



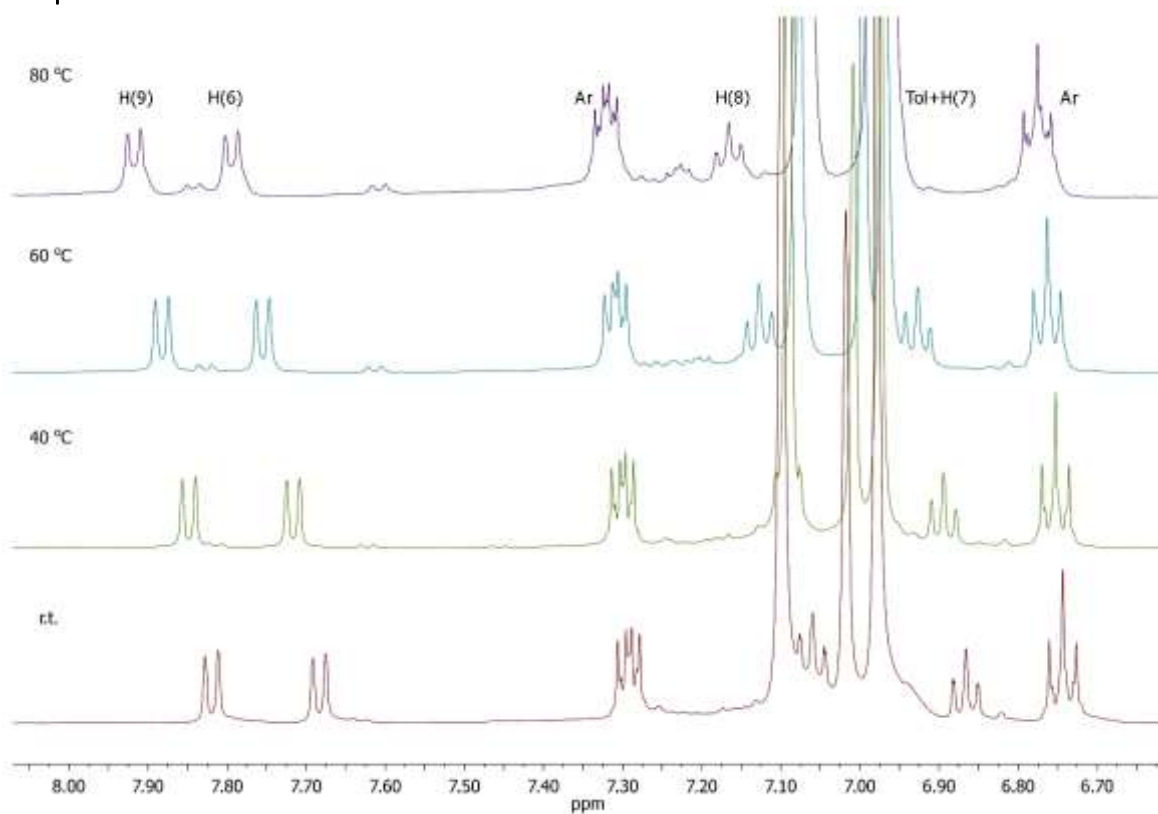
Azide-tetrazole equilibrium of compound 4I in Tol-d₈ (¹H NMR 500 MHz) depending on temperature:



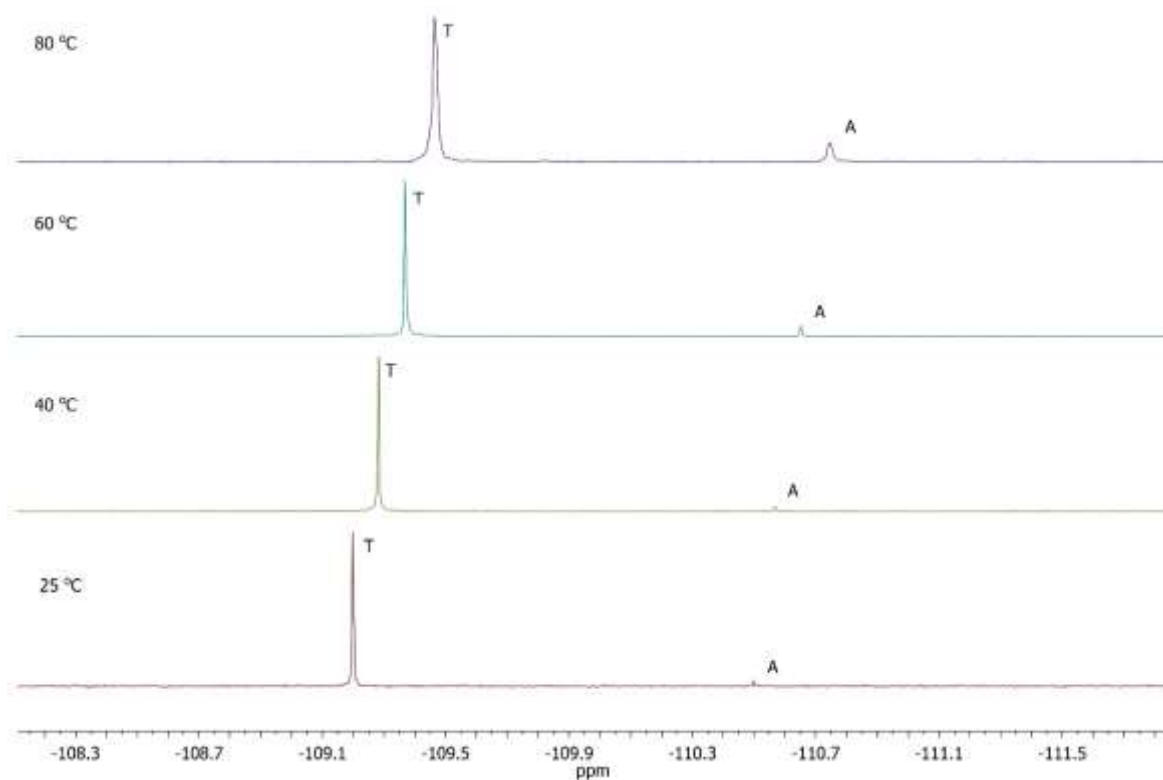
5-[(4-Fluorophenyl)thio]tetrazolo[1,5-a]quinazoline (4j-T) and
2-azido-4-[(4-fluorophenyl)thio]quinazoline (4j-A)



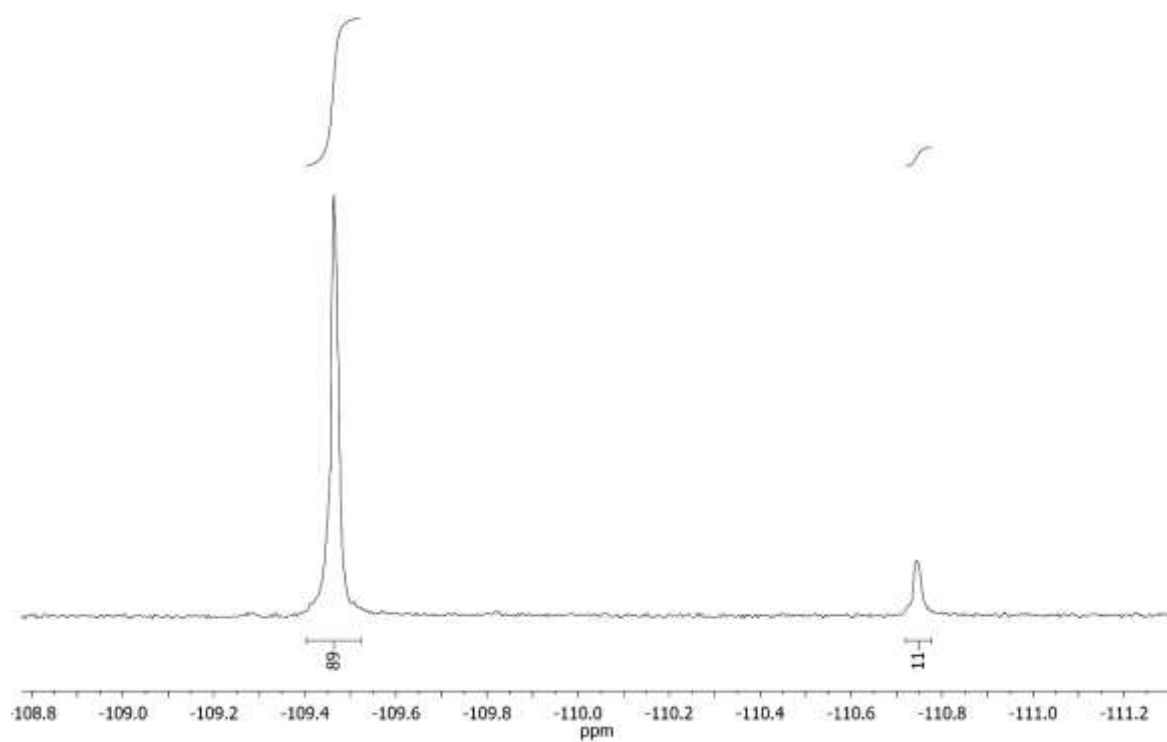
Azide-tetrazole equilibrium of compound 4j in Tol- d_8 (^1H NMR 500 MHz) depending on temperature:



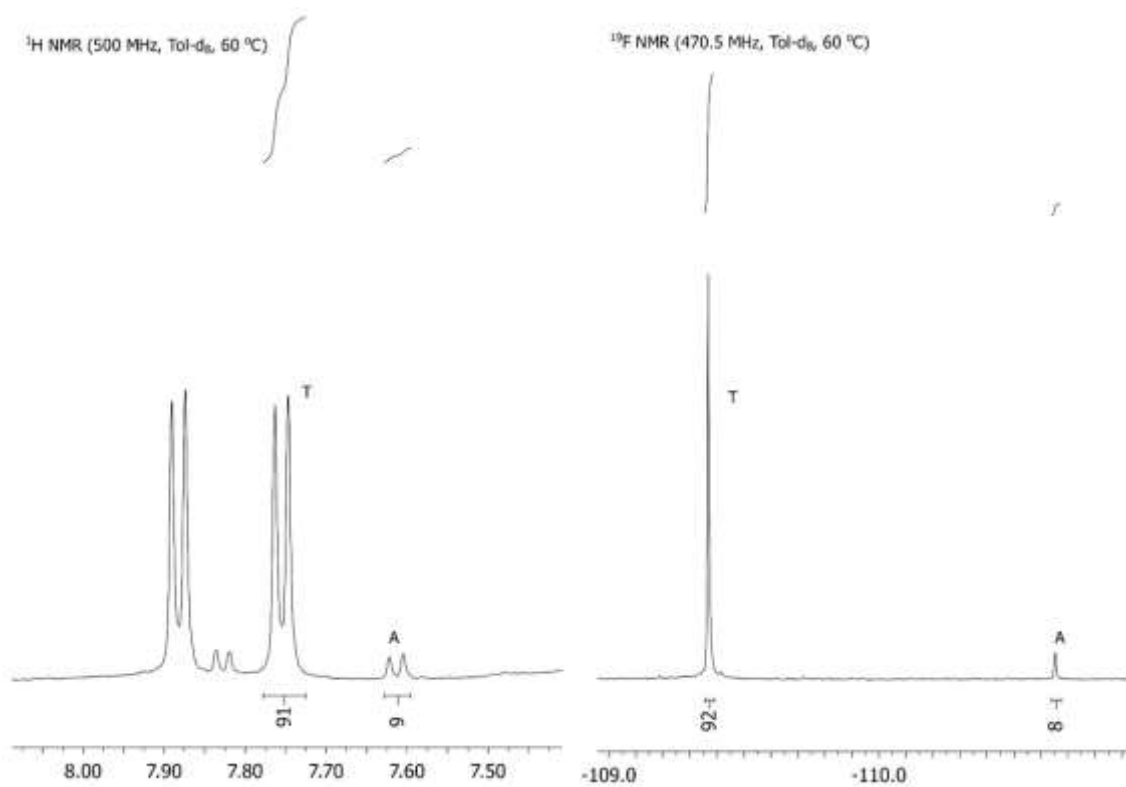
Azide-tetrazole equilibrium of compound 4j in Tol-d₈ (¹⁹F NMR 470.5 MHz) depending on temperature:



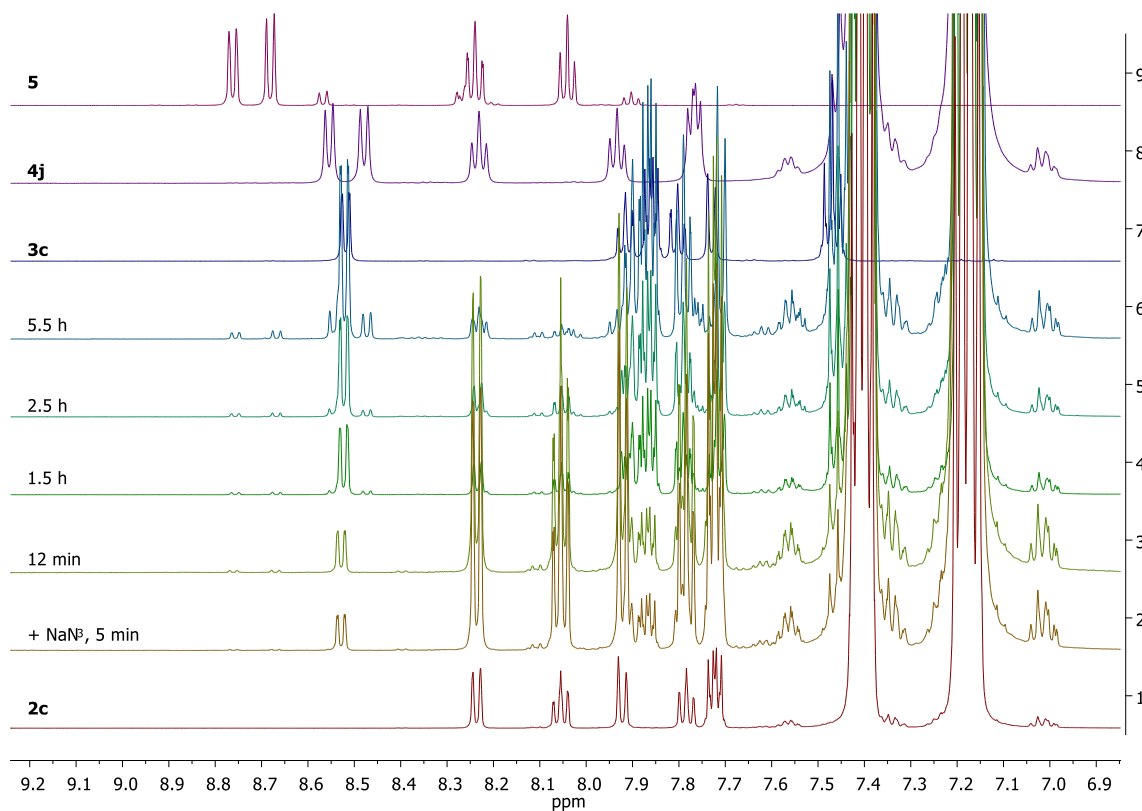
¹⁹F NMR (470.5 MHz, Tol-d₈, 80 °C) spectrum of compound 4j:



Comparison of integral values of azide and tetrazole forms of compound 4j:



NMR-monitoring of transformation 2c→3c (DMSO-d_6 , 500 MHz, 20 °C)



* Fluorbenzene was used as the internal standard