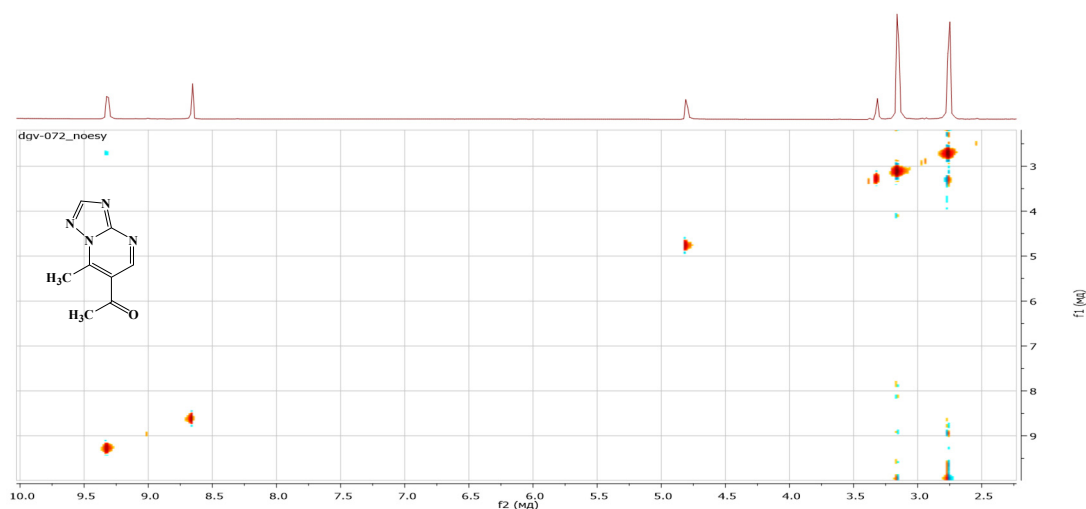
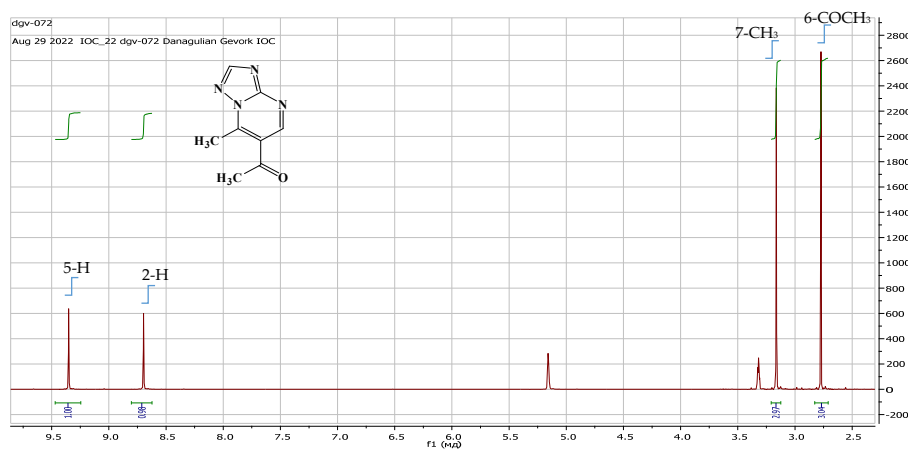


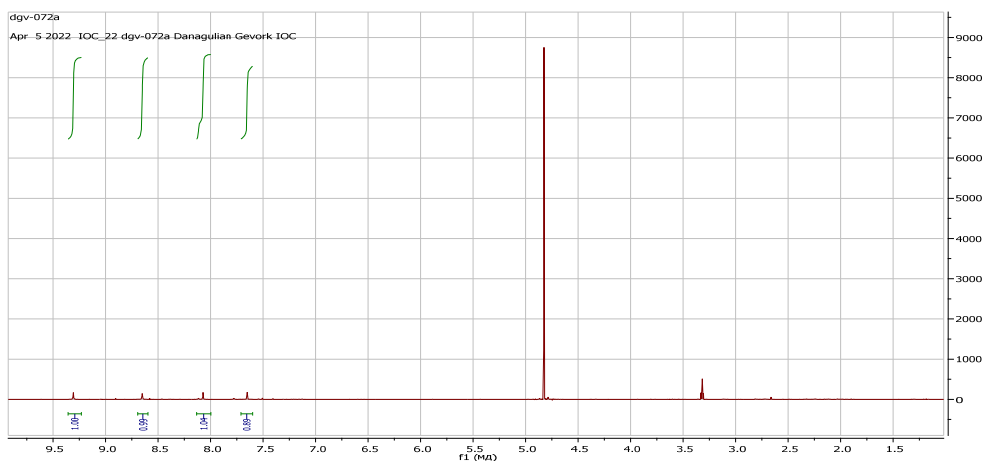
**Scheme S1.** Schematic representation of the dynamics of the decrease in the intensity of the peaks of methyl groups after the addition of CD<sub>3</sub>OD/CD<sub>3</sub>ONa to 6-acetyl-7-methyl-1,2,4-triazolo[1,5-*a*]pyrimidine (5) in a time interval of 0-110 minutes at a temperature of (-10°C).



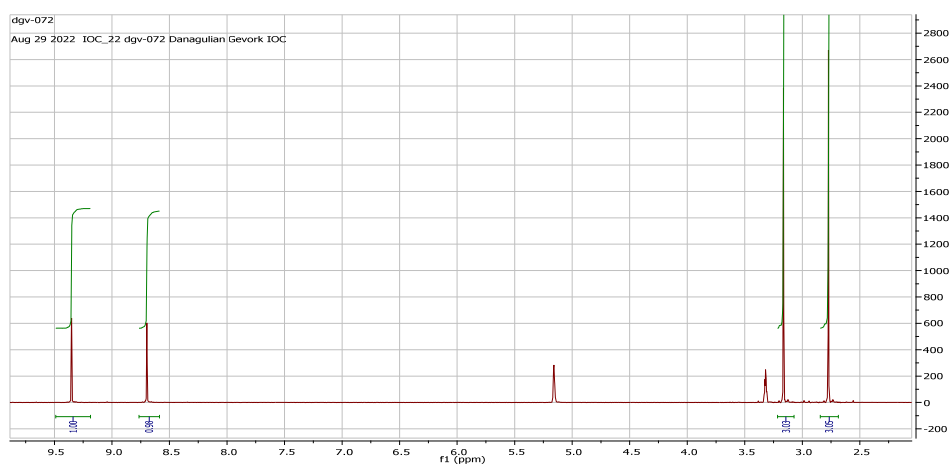
**Figure S1.** NOESY spectrum of 6-acetyl-7-methyl-1,2,4-triazolo [1,5-*a*]pyrimidine 5.



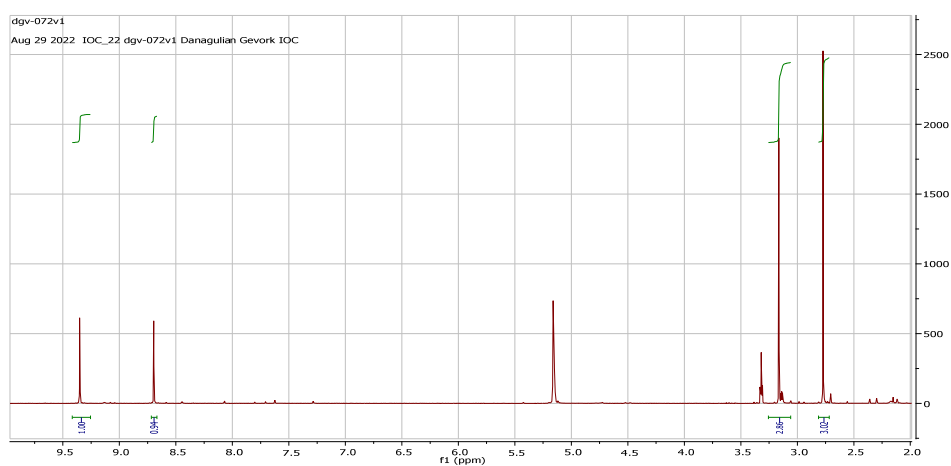
**Figure S2.** 6-Acetyl-7-methyl-1,2,4-triazolo[1,5-*a*]pyrimidine 5, T = 30°C.



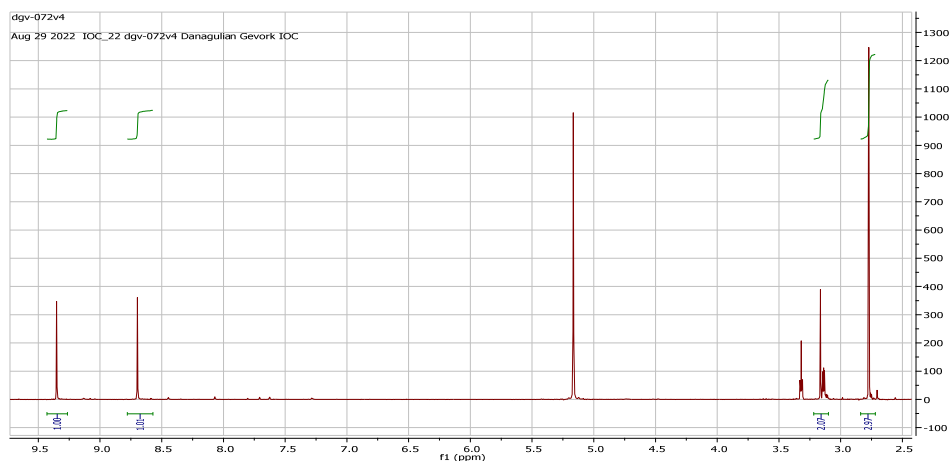
**Figure S3.** 6-d<sub>3</sub>-Acetyl-7-d<sub>3</sub>-methyl-1,2,4-triazolo[1,5-*a*]pyrimidine **6**, *T* = 30°C.



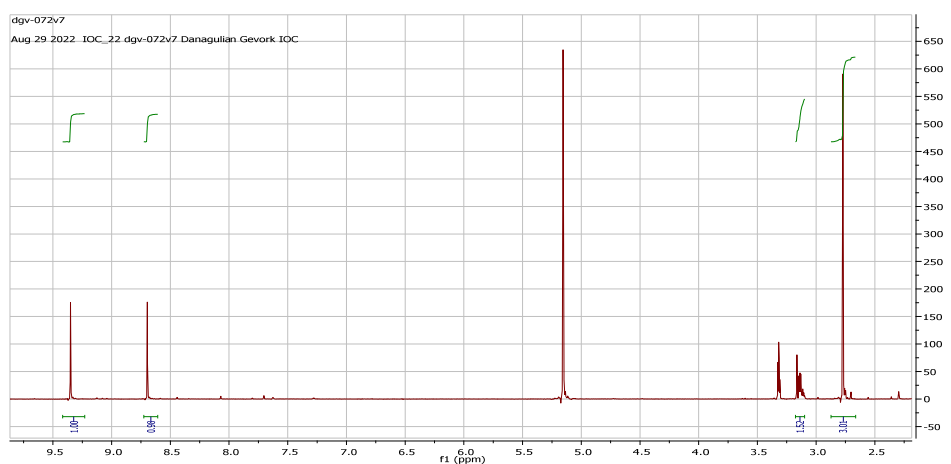
**Figure S4.** 6-Acetyl-7-methyl-1,2,4-triazolo[1,5-*a*]pyrimidine **5**, *T* = -10°C.



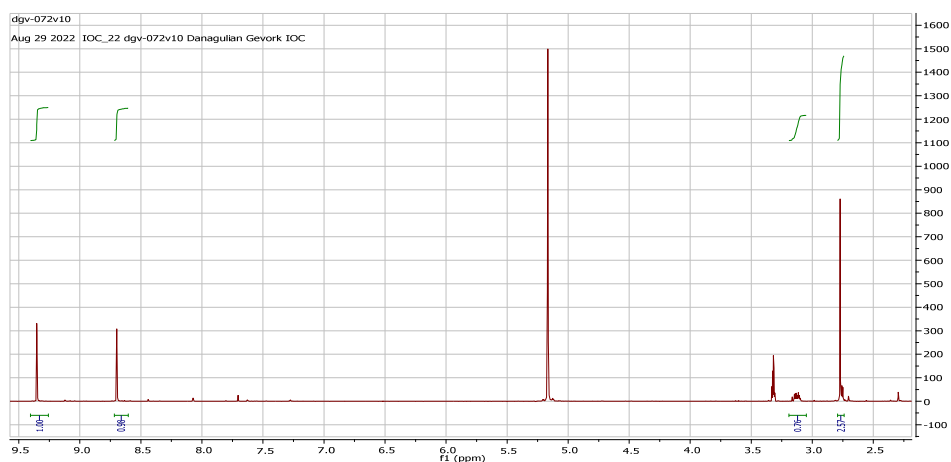
**Figure S5.** 6-d<sub>3</sub>-Acetyl-7-d<sub>3</sub>-methyl-1,2,4-triazolo[1,5-*a*]pyrimidine **6**, *T* = -10°C after 5 min.



**Figure S6.** 6-d<sub>3</sub>-Acetyl-7-d<sub>3</sub>-methyl-1,2,4-triazolo[1,5-*a*]pyrimidine **6**, *T* = -10°C after 20 min.



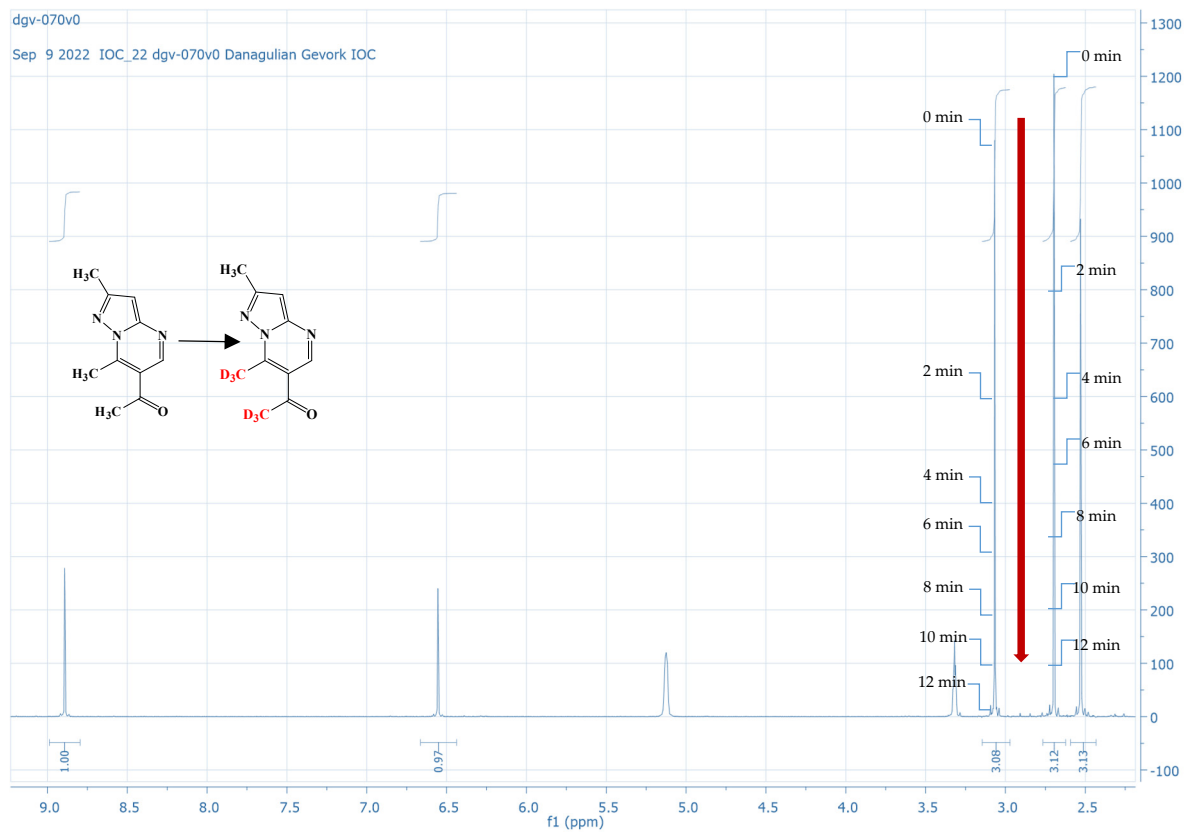
**Figure S7.** 6-d<sub>3</sub>-Acetyl-7-d<sub>3</sub>-methyl-1,2,4-triazolo[1,5-*a*]pyrimidine **6**, *T* = -10°C after 40 min.



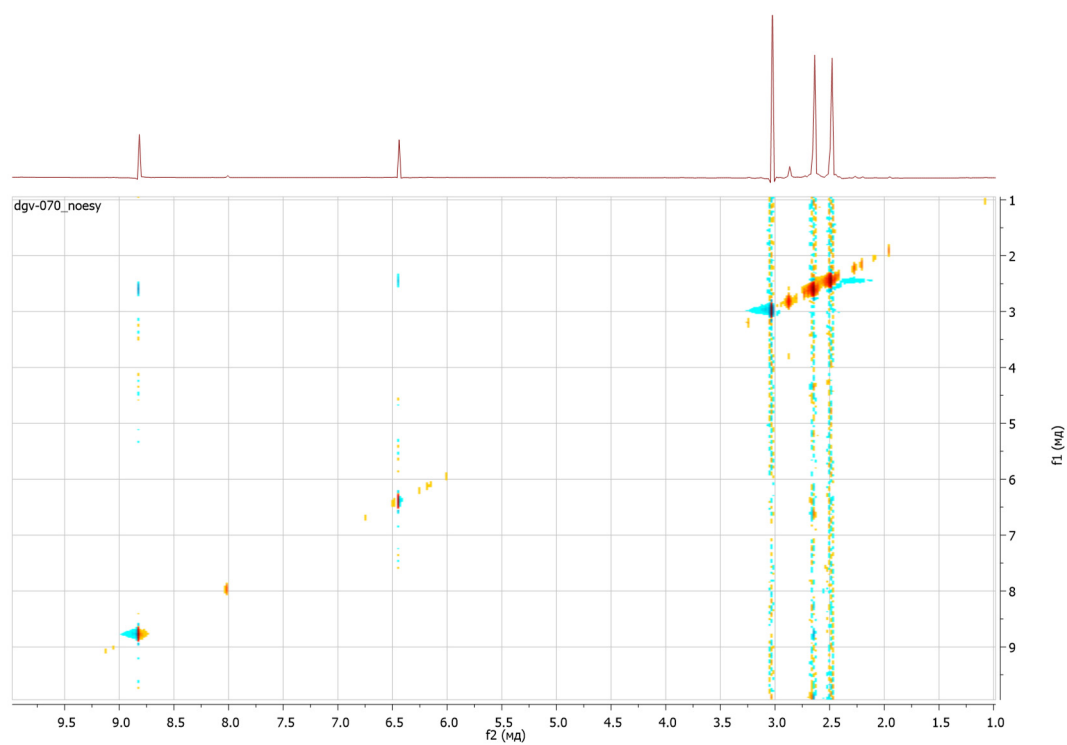
**Figure S8.** 6-d<sub>3</sub>-Acetyl-7-d<sub>3</sub>-methyl-1,2,4-triazolo[1,5-*a*]pyrimidine **6**, *T* = -10°C after 70 min.

**Table S1.** Kinetic study of the deuterium exchange from compound **5** to 6-d<sub>3</sub>-acetyl-7-d<sub>3</sub>-methyl-1,2,4-triazolo[1,5-*a*]pyrimidine **6** in CD<sub>3</sub>OD + CD<sub>3</sub>ONa at *T* = -10°C.

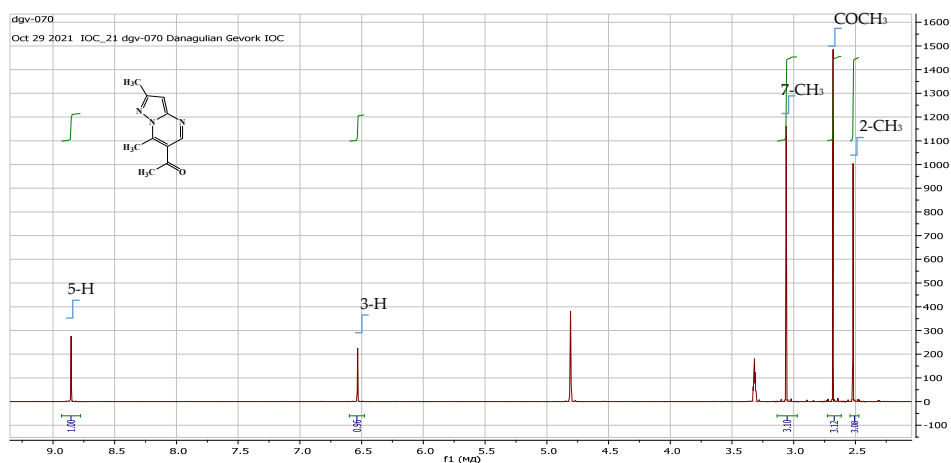
Time (min)	<sup>1</sup> H-NMR (300 MHz, δ, ppm):
5	2.78 (s, 3.02H); 3.18 (s, 2.86H); 8.62 (s, 1H); 9.25 (s, 1H)
20	2.78 (s, 2.97H); 3.18 (s, 2.07H); 8.62 (s, 1H); 9.25 (s, 1H)
40	2.78 (s, 3.01H); 3.18 (s, 1.52H); 8.62 (s, 1H); 9.25 (s, 1H)
70	2.78 (s, 2.57H); 3.18 (s, 0.76H); 8.62 (s, 1H); 9.25 (s, 1H)



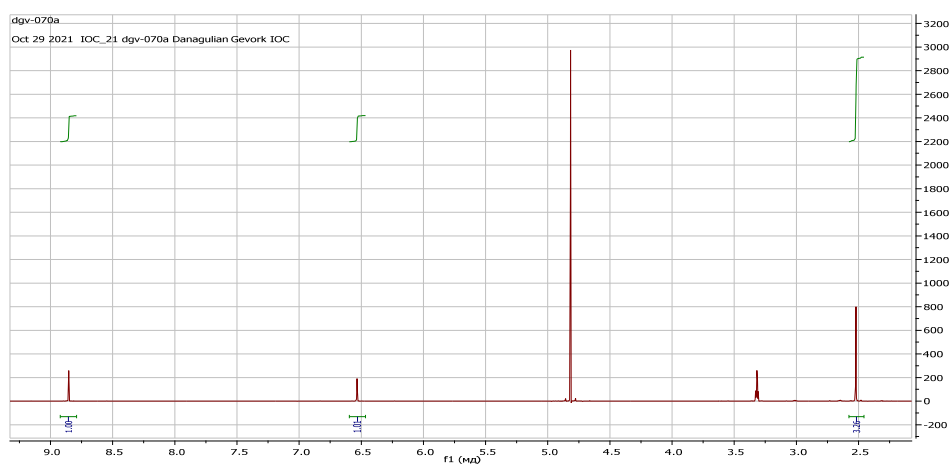
**Scheme S2.** Schematic representation of the dynamics of the decrease in the intensity of the peaks of methyl groups after the addition of CD<sub>3</sub>OD/CD<sub>3</sub>ONa to 2,7-dimethyl-6-acetylpyrazolo[1,5-a]pyrimidine (1) in a time interval of 0-12 minutes at a temperature of (-15°C).



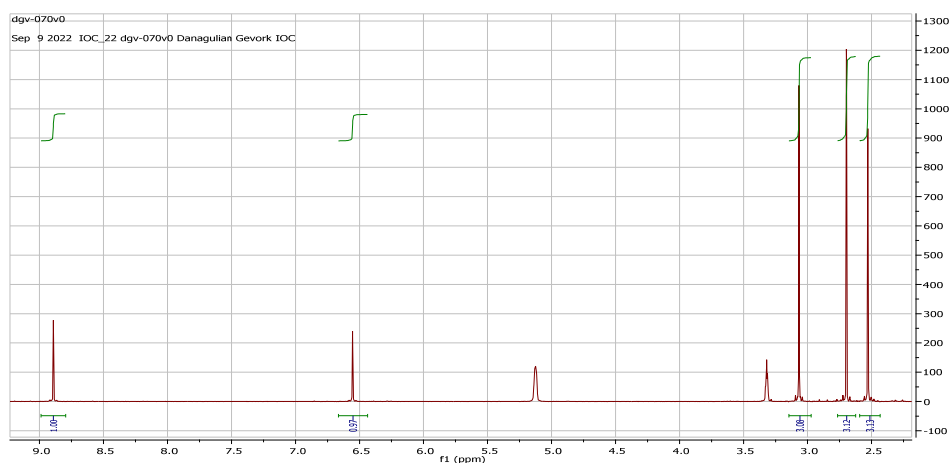
**Figure S9.** NOESY spectrum of 2,7-dimethyl-6-acetylpyrazolo[1,5-a]pyrimidine 1.



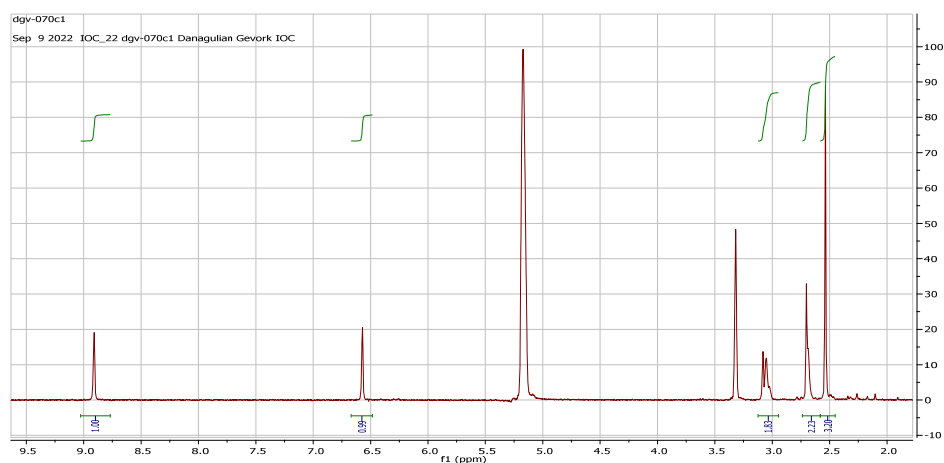
**Figure S10.** 6-Acetyl-2,7-dimethylpyrazolo[1,5-*a*]pyrimidine 1, T = 30°C.



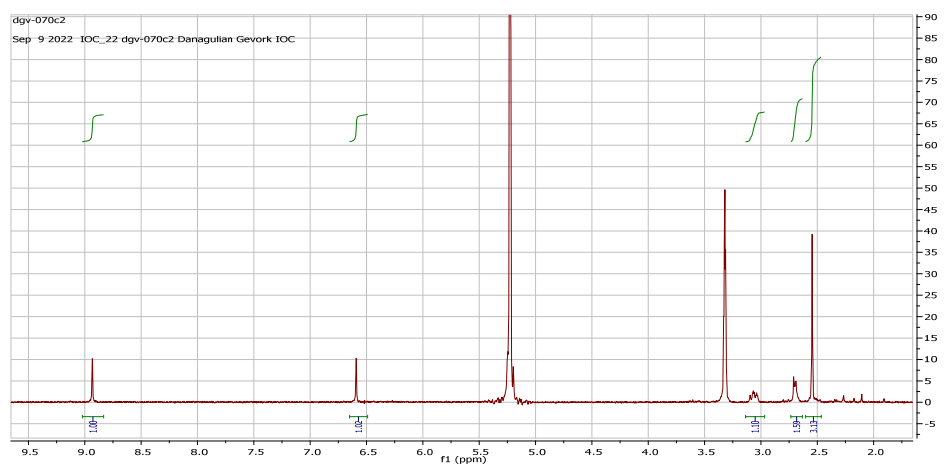
**Figure S11.** 6-d<sub>3</sub>-Acetyl-7-d<sub>3</sub>-methyl-2-methylpyrazolo[1,5-*a*]pyrimidine 3, T = 30°C.



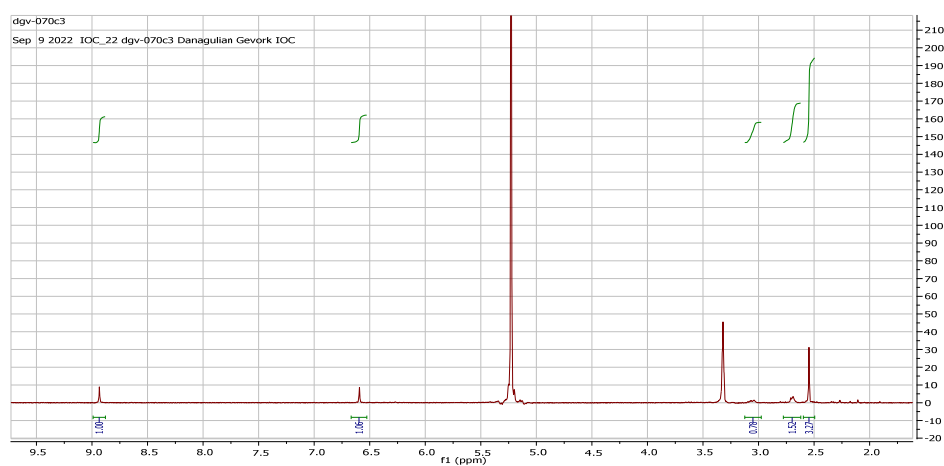
**Figure S12.** 6-Acetyl-2,7-dimethylpyrazolo[1,5-*a*]pyrimidine 1, T = -15°C.



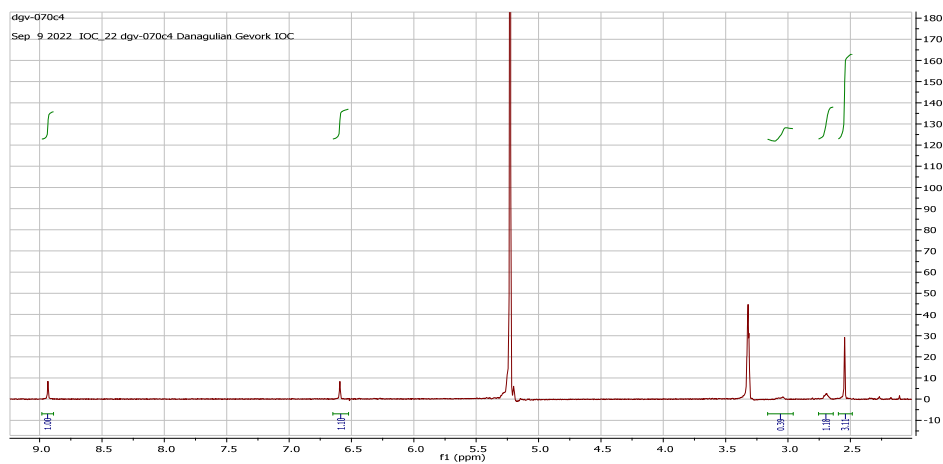
**Figure S13.** 6-d<sub>3</sub>-Acetyl-7-d<sub>3</sub>-methyl-2-methylpyrazolo[1,5-a]pyrimidine 3,  $T = -15^\circ\text{C}$  after 2 min.



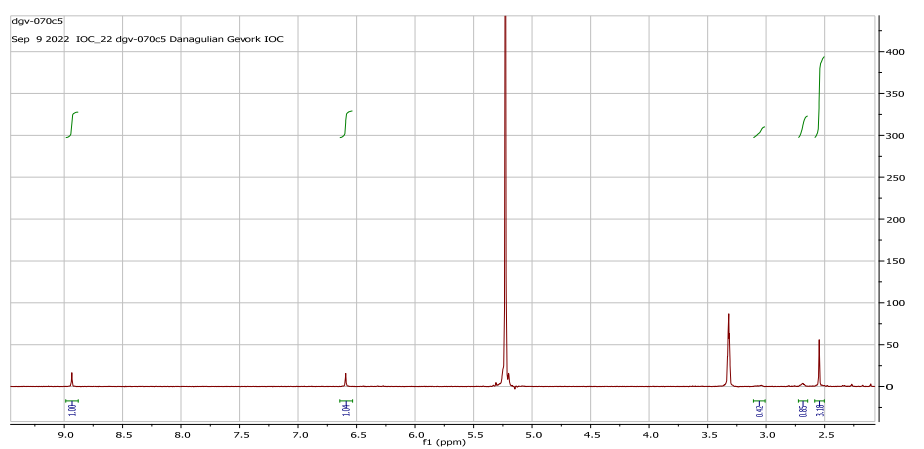
**Figure S14.** 6-d<sub>3</sub>-Acetyl-7-d<sub>3</sub>-methyl-2-methylpyrazolo[1,5-a]pyrimidine 3,  $T = -15^\circ\text{C}$  after 4 min.



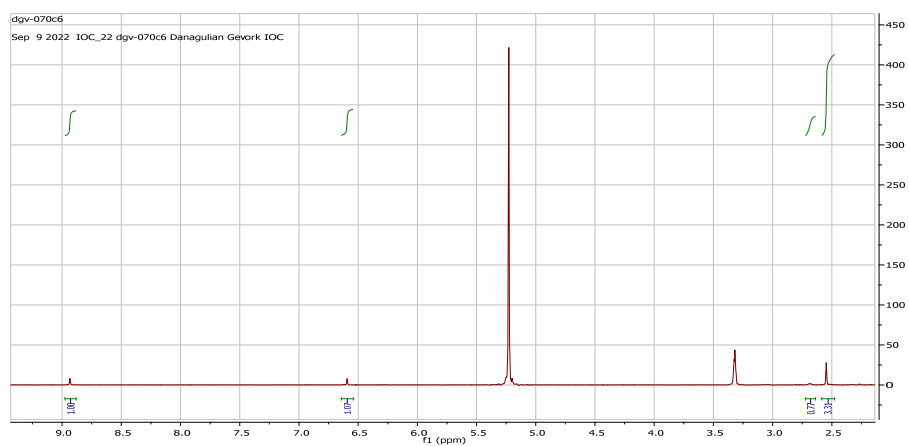
**Figure S15.** 6-d<sub>3</sub>-Acetyl-7-d<sub>3</sub>-methyl-2-methylpyrazolo[1,5-a]pyrimidine 3,  $T = -15^\circ\text{C}$  after 6 min.



**Figure S16.** 6-d<sub>3</sub>-Acetyl-7-d<sub>3</sub>-methyl-2-methylpyrazolo[1,5-*a*]pyrimidine **3**,  $T = -15^{\circ}\text{C}$  after 8 min.



**Figure S17.** 6-d<sub>3</sub>-Acetyl-7-d<sub>3</sub>-methyl-2-methylpyrazolo[1,5-*a*]pyrimidine **3**,  $T = -15^{\circ}\text{C}$  after 10 min.

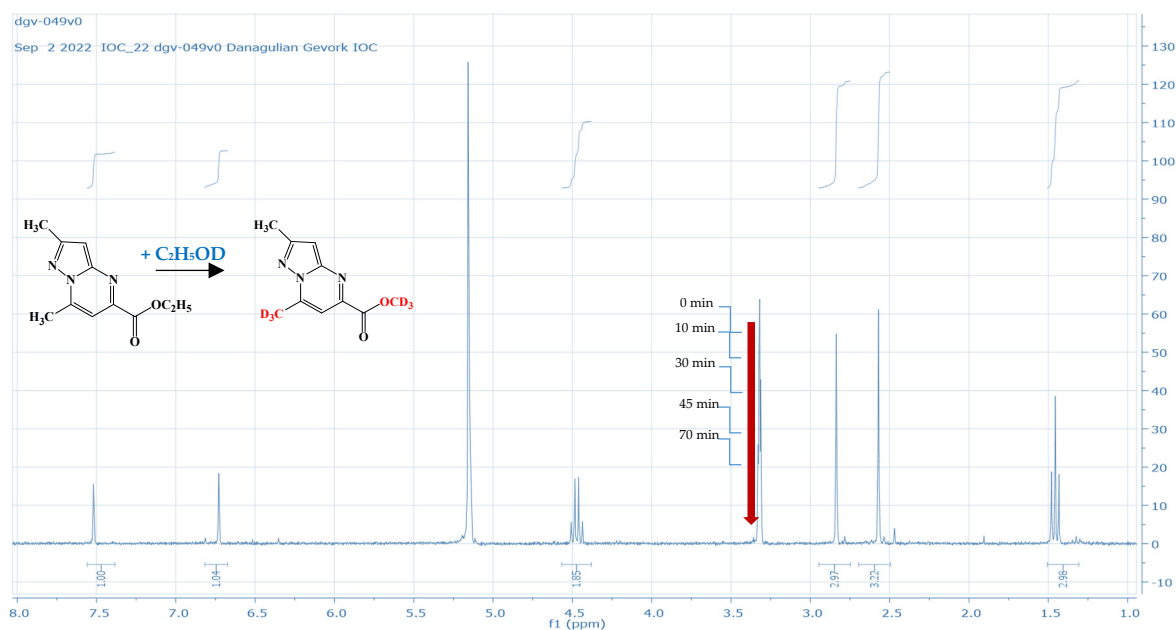


**Figure S18.** 6-d<sub>3</sub>-Acetyl-7-d<sub>3</sub>-methyl-2-methylpyrazolo[1,5-*a*]pyrimidine **3**,  $T = -15^{\circ}\text{C}$  after 12 min.

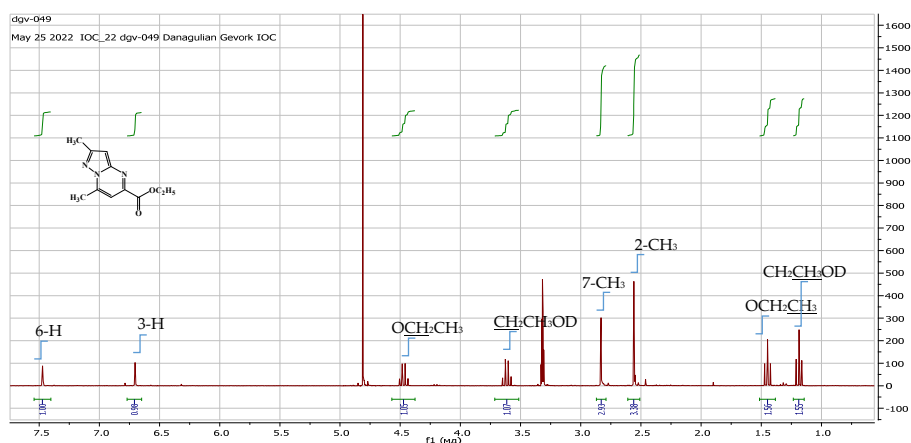
**Table S2.** Kinetic study of the deuterium exchange from compound **1** to 6-d<sub>3</sub>-acetyl-7-d<sub>3</sub>-methyl-2-methylpyrazolo[1,5-*a*]pyrimidine **3** in CD<sub>3</sub>OD + CD<sub>3</sub>ONa at T = -15°C.

Time (min)	<sup>1</sup> H-NMR (300 MHz, δ, ppm):
2	2.50 (s, 3H); 2.65 (s, 2.23H); 3.14 (s, 1.83H); 6.55 (s, 1H); 8.82 (s, 1H)
4	2.50 (s, 3H); 2.65 (s, 1.59H); 3.14 (s, 1.1H); 6.55 (s, 1H); 8.82 (s, 1H)
6	2.50 (s, 3H); 2.65 (s, 1.52H); 3.14 (s, 0.78H); 6.55 (s, 1H); 8.82 (s, 1H)
8	2.50 (s, 3H); 2.65 (s, 1.18H); 3.14 (s, 0.39H); 6.55 (s, 1H); 8.82 (s, 1H)
10	2.50 (s, 3H); 2.65 (s, 0.45H); 3.14 (s, 0.042H); 6.55 (s, 1H); 8.82 (s, 1H)
12	2.50 (s, 3H); 2.65 (s, 0.77H); 3.14 (s, 0.0H); 6.55 (s, 1H); 8.82 (s, 1H)

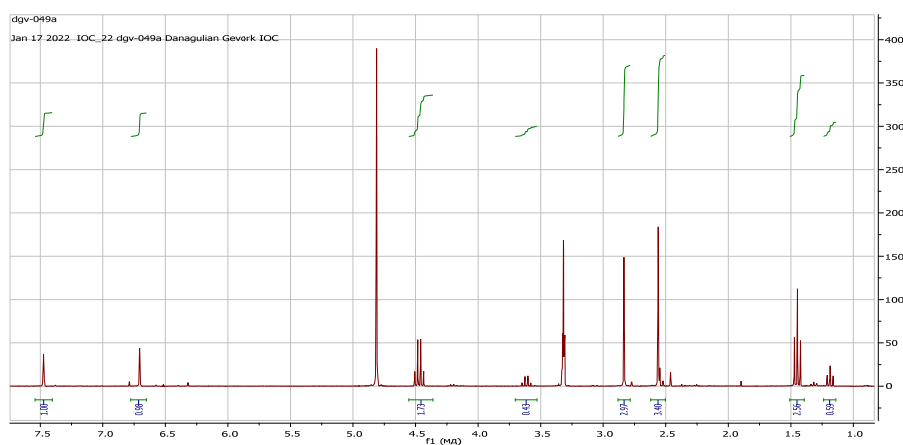




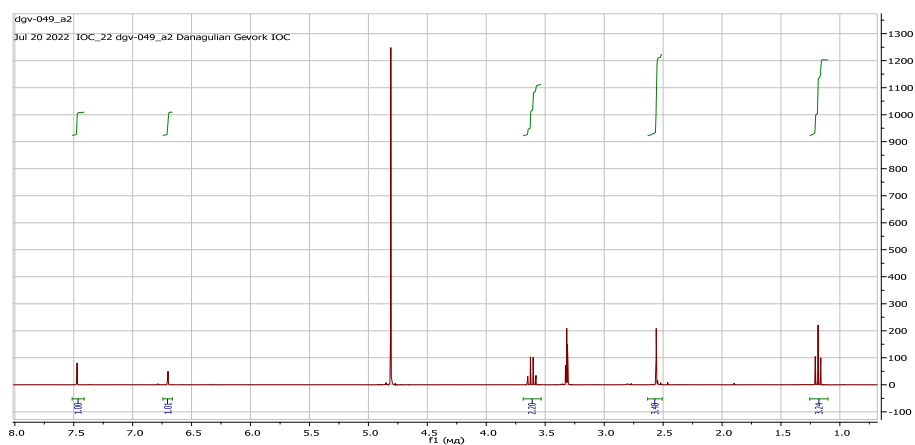
**Scheme S3.** Schematic representation of the dynamics of the decrease in the intensity of the peaks of methyl groups after the addition of CD<sub>3</sub>OD/CD<sub>3</sub>ONa to 2,7-dimethyl-5-ethoxycarbonylpyrazolo[1,5-*a*]pyrimidine (**10**) in a time interval of 0-70 minutes at a temperature of (-10°C).



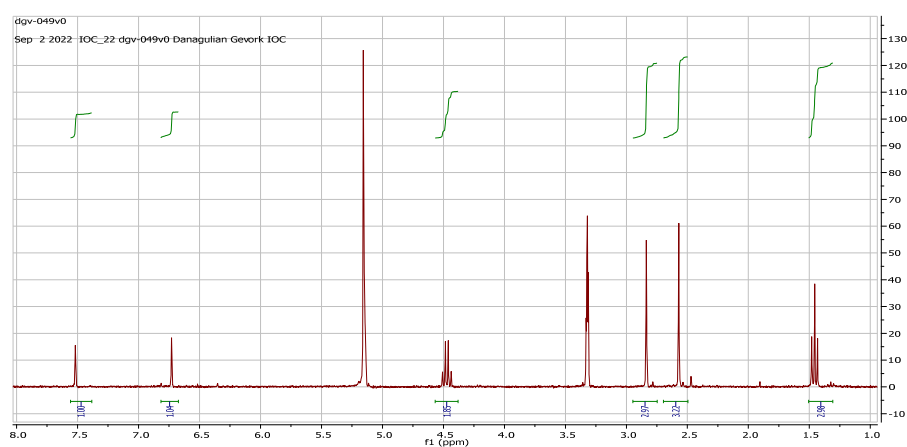
**Figure S20.** 2,7-Dimethyl-5-ethoxycarbonylpyrazolo[1,5-*a*]pyrimidine **10**, T = 30°C.



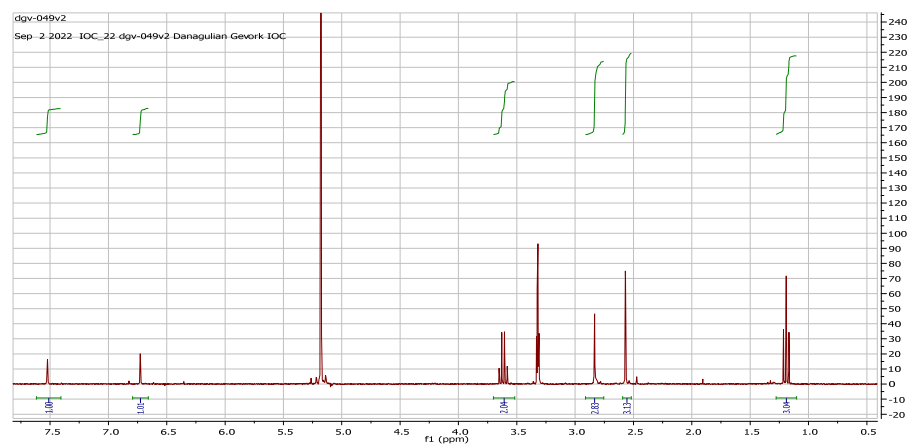
**Figure S21.** 2,7-Dimethyl-5-ethoxycarbonylpyrazolo[1,5-*a*]pyrimidine **10**, T = 30°C.



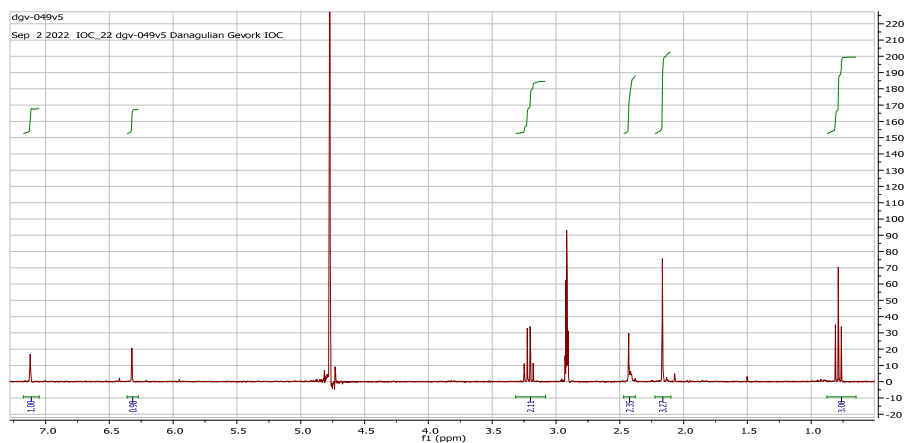
**Figure S22.** 7-d<sub>3</sub>-Methyl-2-methyl-5-d<sub>3</sub>-metoxycarbonylpyrazolo[1,5-a]pyrimidine **10**,  $T = 30^\circ\text{C}$ .



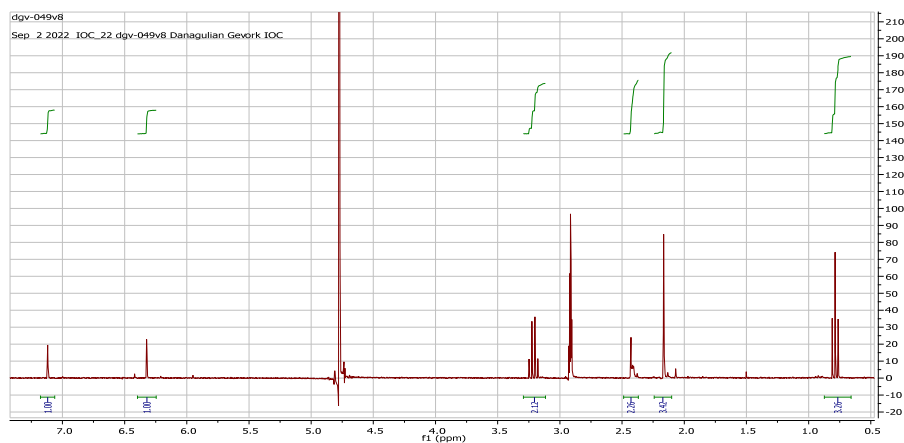
**Figure S23.** 2,7-Dimethyl-5-ethoxycarbonylpyrazolo[1,5-a]pyrimidine **10**,  $T = -10^\circ\text{C}$ .



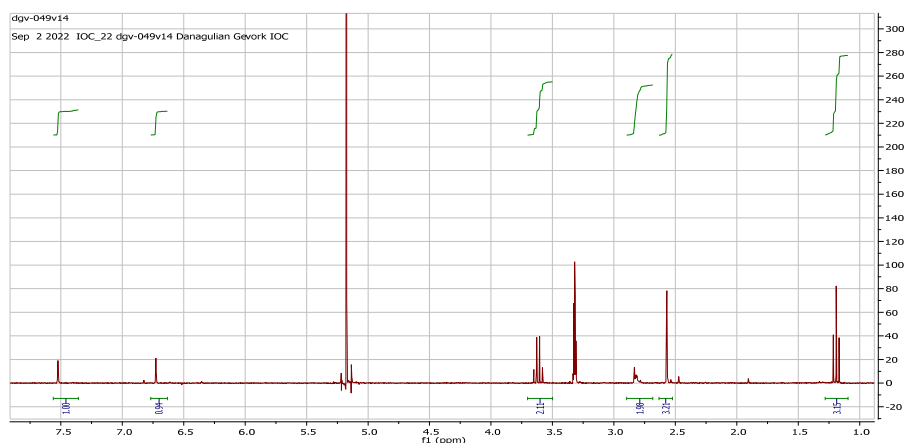
**Figure S24.** 7-d<sub>3</sub>-Methyl-2-methyl-5-d<sub>3</sub>-metoxycarbonylpyrazolo[1,5-a]pyrimidine **14**,  $T = -10^\circ\text{C}$  after 10 min.



**Figure S25.** 7-d<sub>3</sub>-Methyl-2-methyl-5-d<sub>3</sub>-metoxycarbonylpyrazolo[1,5-*a*]pyrimidine **14**, T = -10°C after 30 min.



**Figure S26.** 7-d<sub>3</sub>-Methyl-2-methyl-5-d<sub>3</sub>-metoxycarbonylpyrazolo[1,5-*a*]pyrimidine **14**, T = -10°C after 45 min.



**Figure S27.** 7-d<sub>3</sub>-Methyl-2-methyl-5-d<sub>3</sub>-metoxycarbonylpyrazolo[1,5-*a*]pyrimidine **14**, T = -10°C after 70 min.

**Table S3.** Kinetic study of the deuterium exchange from compound **10** to 7-d<sub>3</sub>-methyl-2-methyl-5-d<sub>3</sub>-methoxycarbonylpyra-zolo[1,5-*a*]pyrimidine **14** in CD<sub>3</sub>OD + CD<sub>3</sub>ONa at T = -10°C.

Time (min)	<sup>1</sup> H-NMR (300 MHz, δ, ppm):
5	1.2 (t, 3H); 2.55 (s, 3H); 3.6 (q, 2H); 6.7 (s, 1H); 7.45 (s, 1H)
10	1.42(t, 3H); 2.55 (s, 3H); 2.82 (s, 2.83H); 4.45 (q, 2H); 6.7 (s, 1H); 7.45 (s, 1H)
30	1.42(t, 3H); 2.55 (s, 3H); 2.82 (s, 2.35H); 4.45 (q, 2H); 6.7 (s, 1H); 7.45 (s, 1H)
45	1.42(t, 3H); 2.55 (s, 3H); 2.82 (s, 2.26H); 4.45 (q, 2H); 6.7 (s, 1H); 7.45 (s, 1H)
70	1.42(t, 3H); 2.55 (s, 3H); 2.82 (s, 1.98H); 4.45 (q, 2H); 6.7 (s, 1H); 7.45 (s, 1H)