Supplementary Information for:

Synthesis, Structural and Photophysical Studies of Mono- and Dinuclear Alkali Metal 2,6-dibenzhydryl-4-methylphenolates

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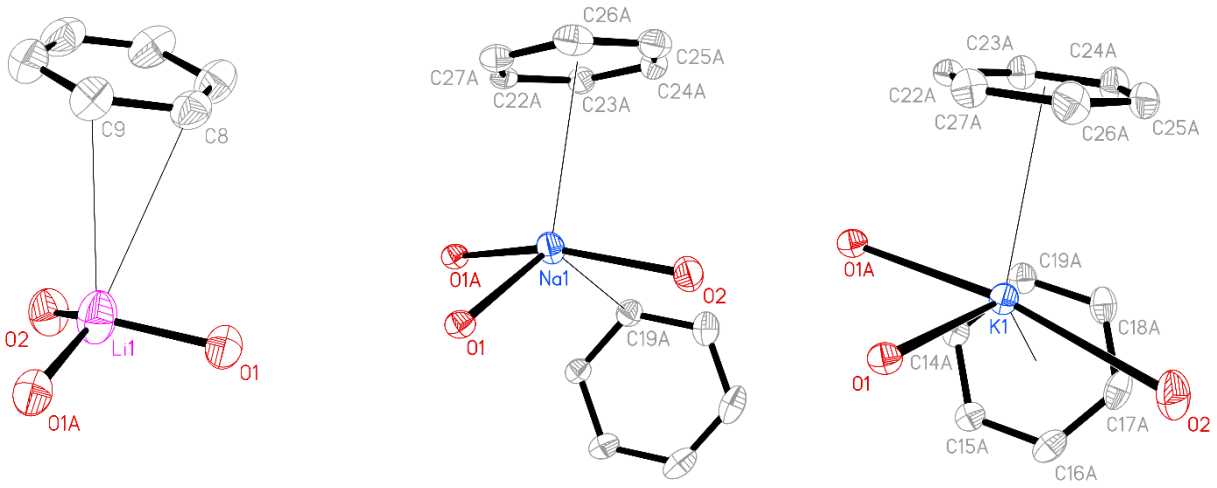
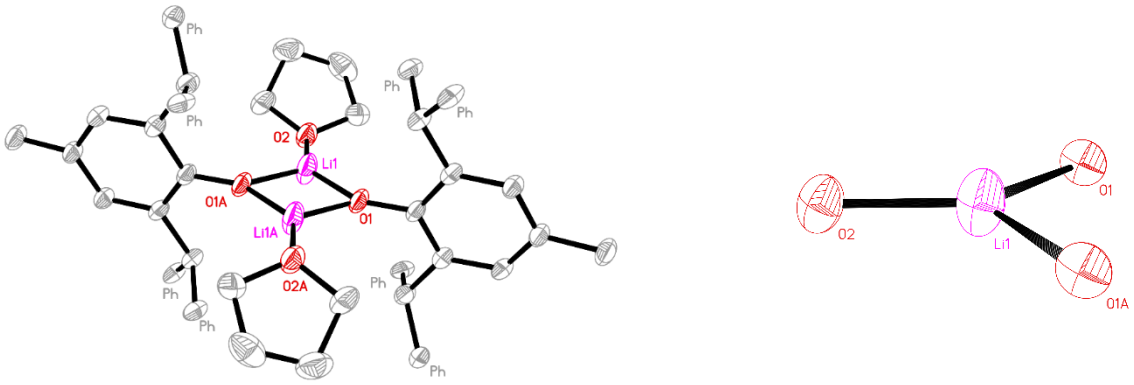


Additional Figures of Molecular Structures

Figure S1. Coordination environment of the alkali metal cations in **Li1** (left), **Na1** (center), **K1** (right).

Figure S2. Molecular structure of **Li1_Tol** molecule with the nearly planar lithium coordination environment (left), coordination environment of the lithium cation in **Li1_Tol** (right).



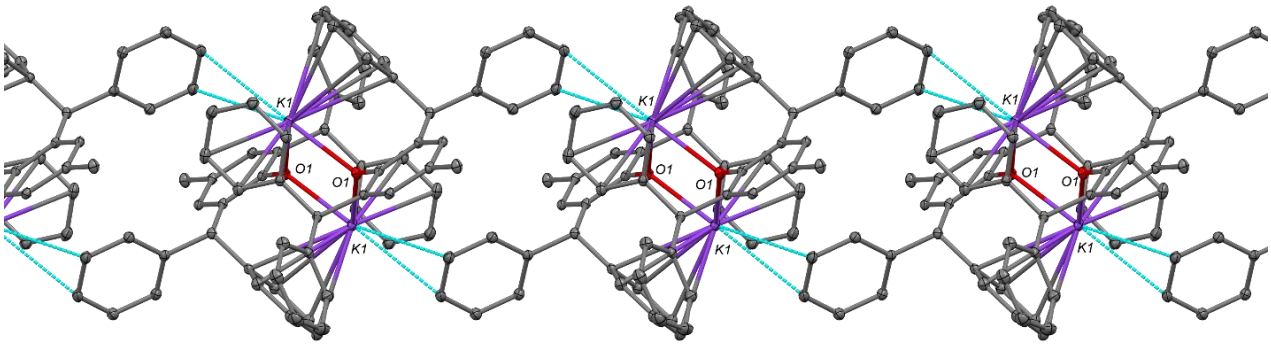


Figure S3. Fragment of crystal structure of **K1′**, illustrating short intermolecular K…C contacts.

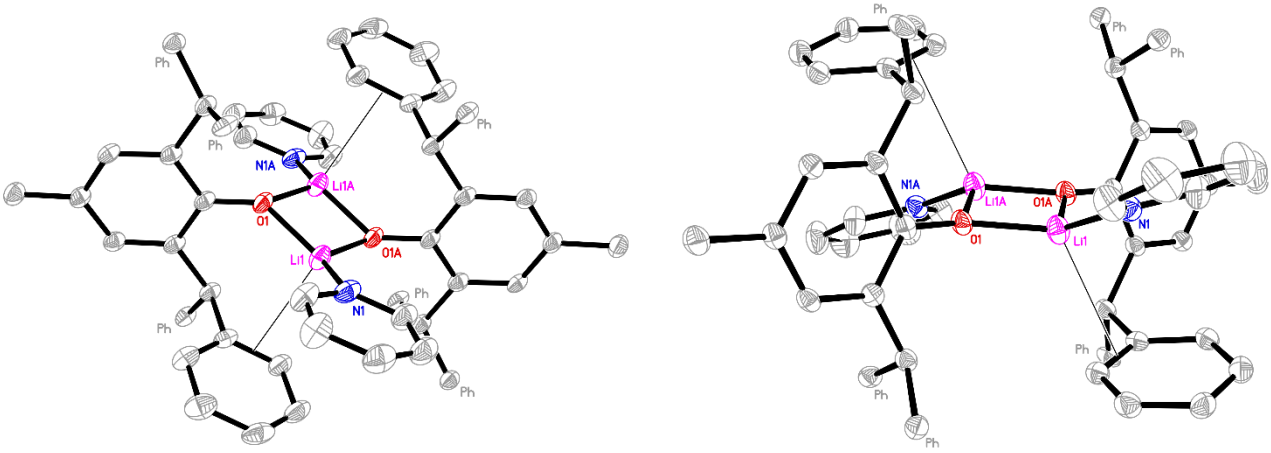


Figure S4. Molecular structures of **Li2** (left) and **Li2′** (right).

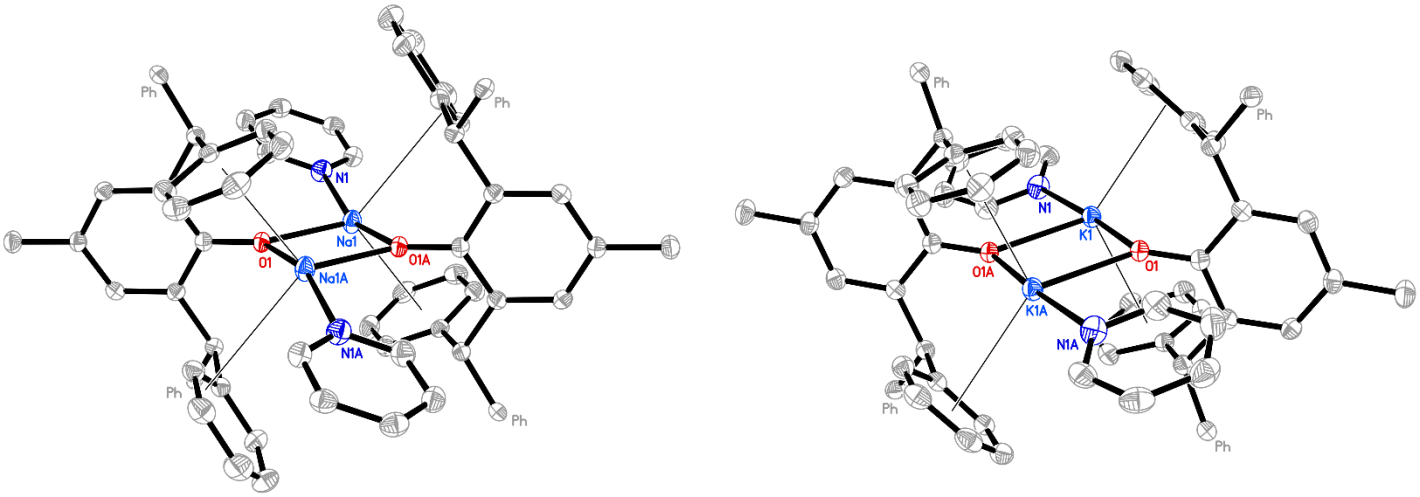


Figure S5. Molecular structures of **Na2** (left) and **K2** (right).

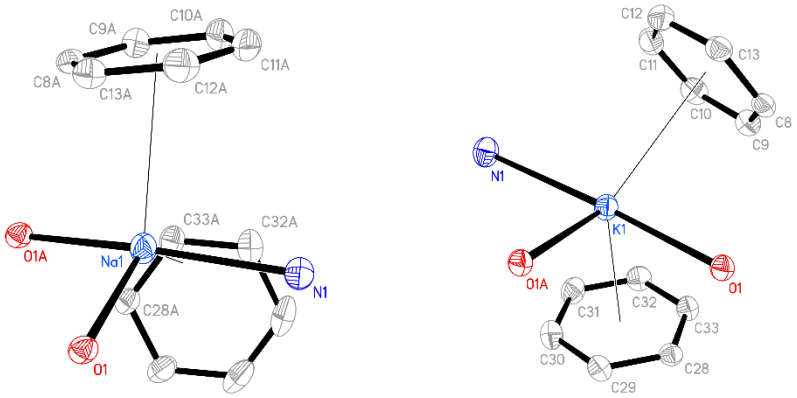


Figure S6. Coordination environment of the alkali metal cations in **Na2** (left), **K2** (right).

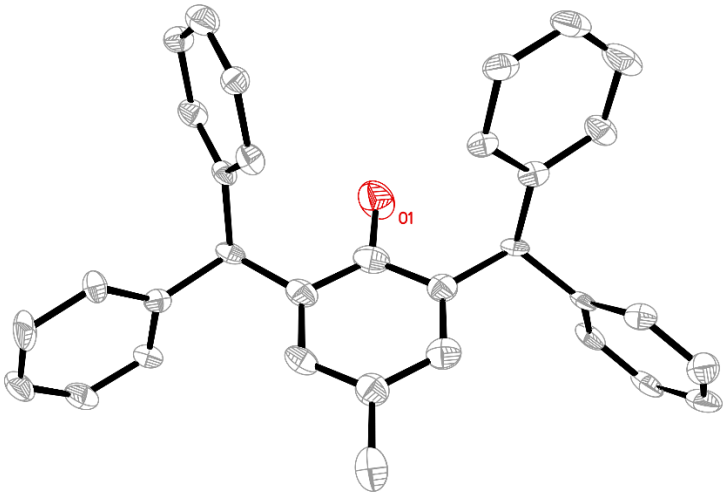


Figure S7. Molecular structure of one of the Ar*OH molecules in the unit cell.

NMR Spectra

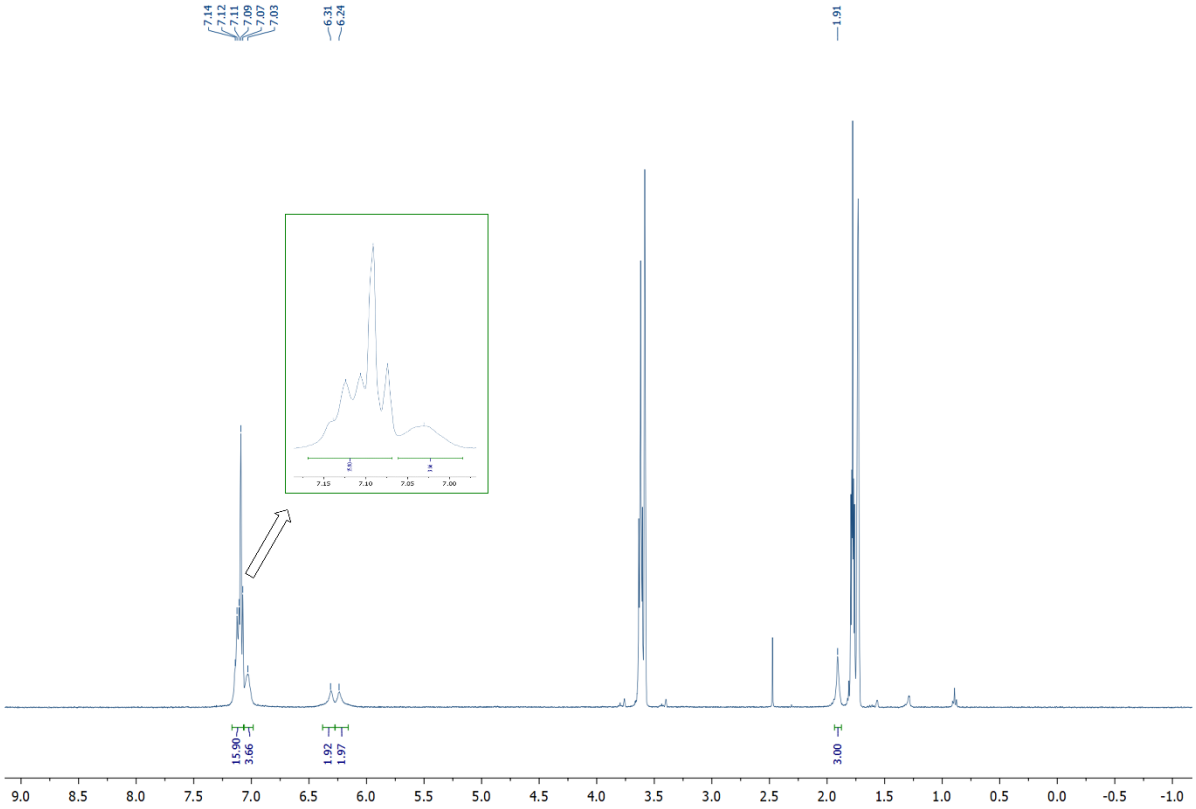


Figure S8. ^{1}H NMR spectrum of **Li1** recorded in THF-d_8.

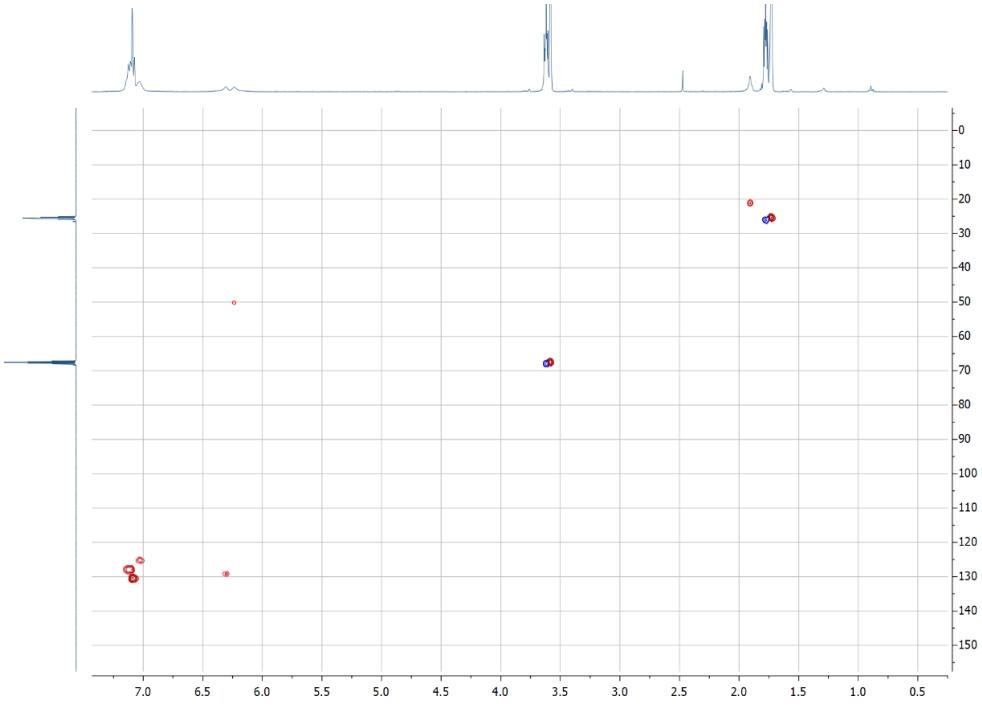


Figure S9. ^{1}H-^{13}C HSQC NMR spectrum of **Li1** recorded in THF-d_8.

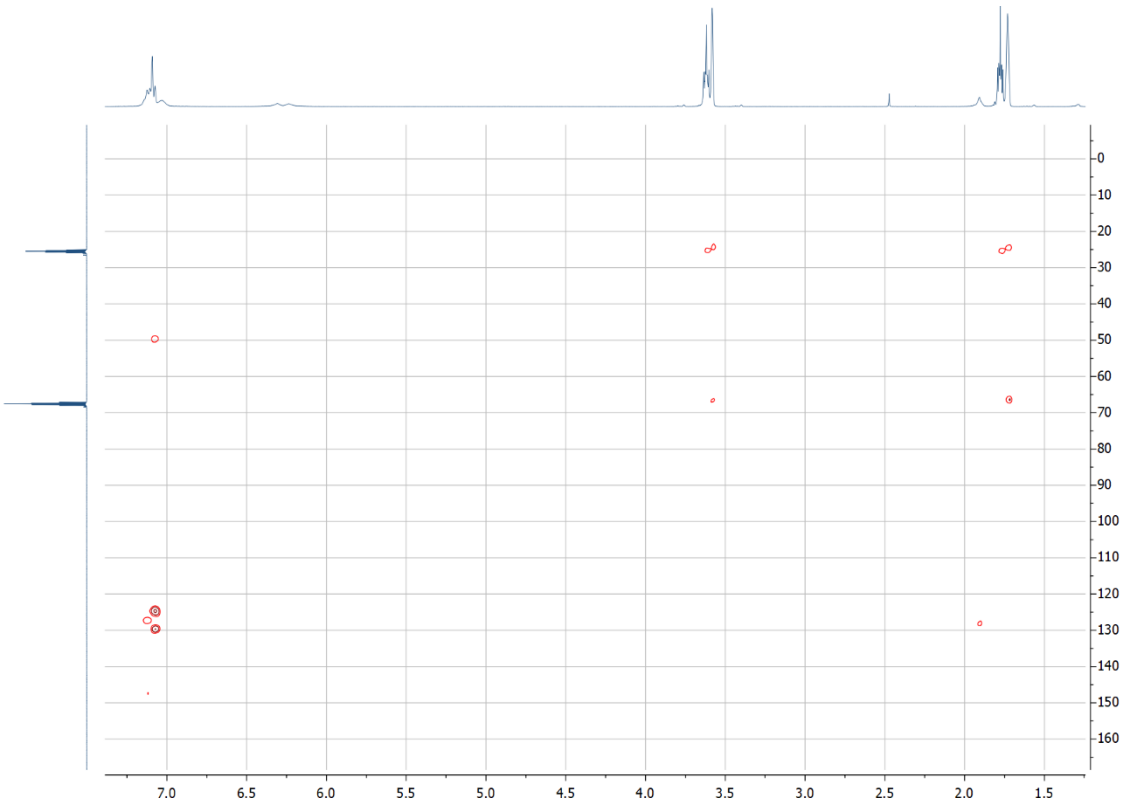


Figure S10. ^{1}H-^{13}C HMBC NMR spectrum of **Li1** recorded in THF-d_8.

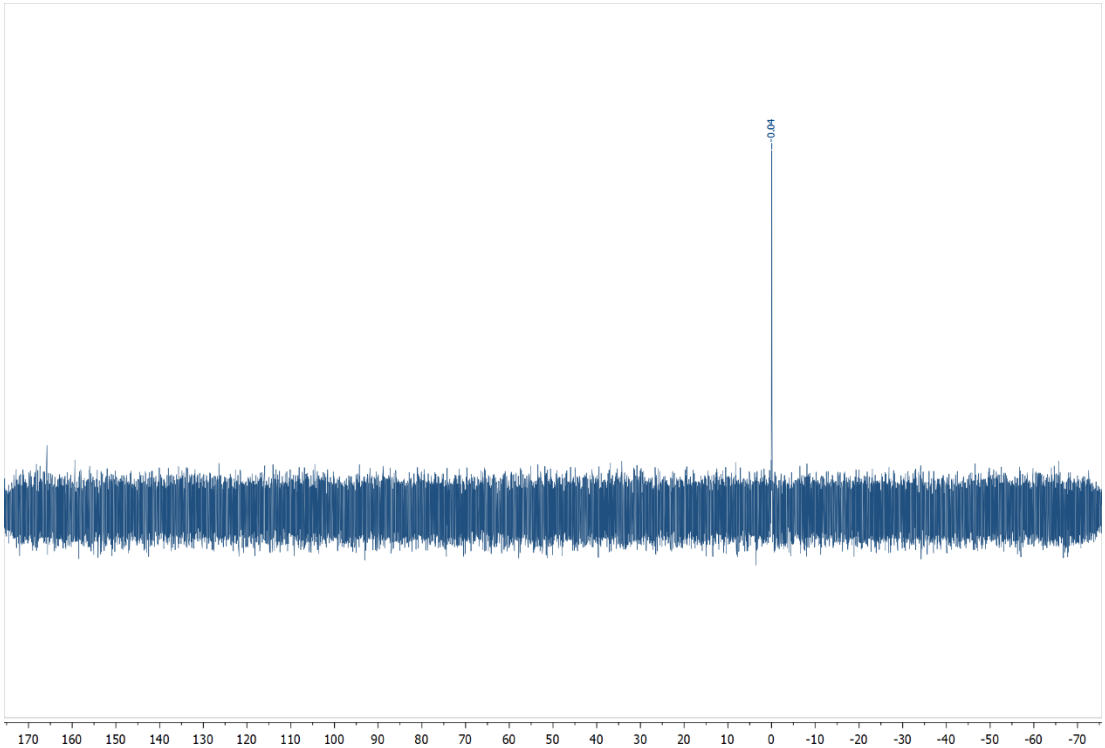


Figure S11. ^{7}Li NMR spectrum of **Li1** recorded in THF-d_8.

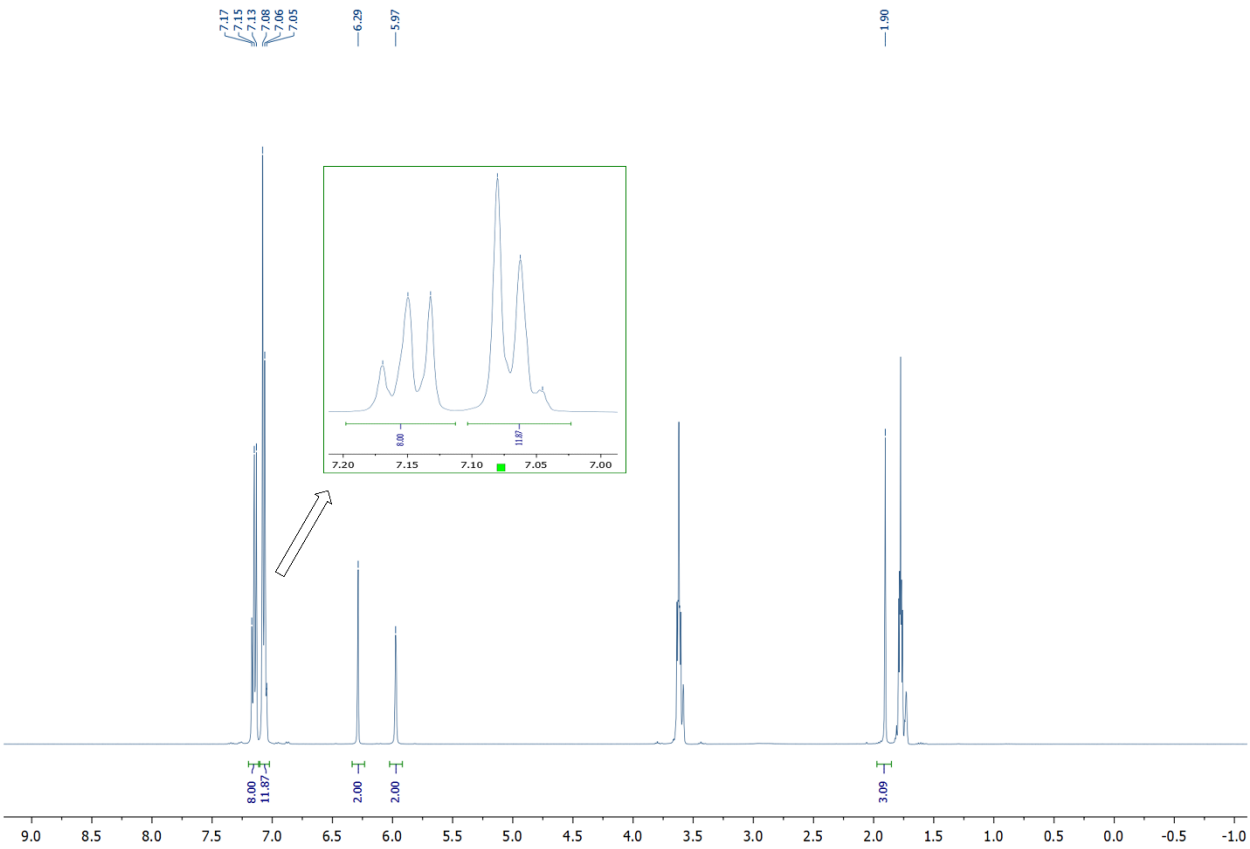


Figure S12. ^{1}H NMR spectrum of **Na1** recorded in THF-d_8.

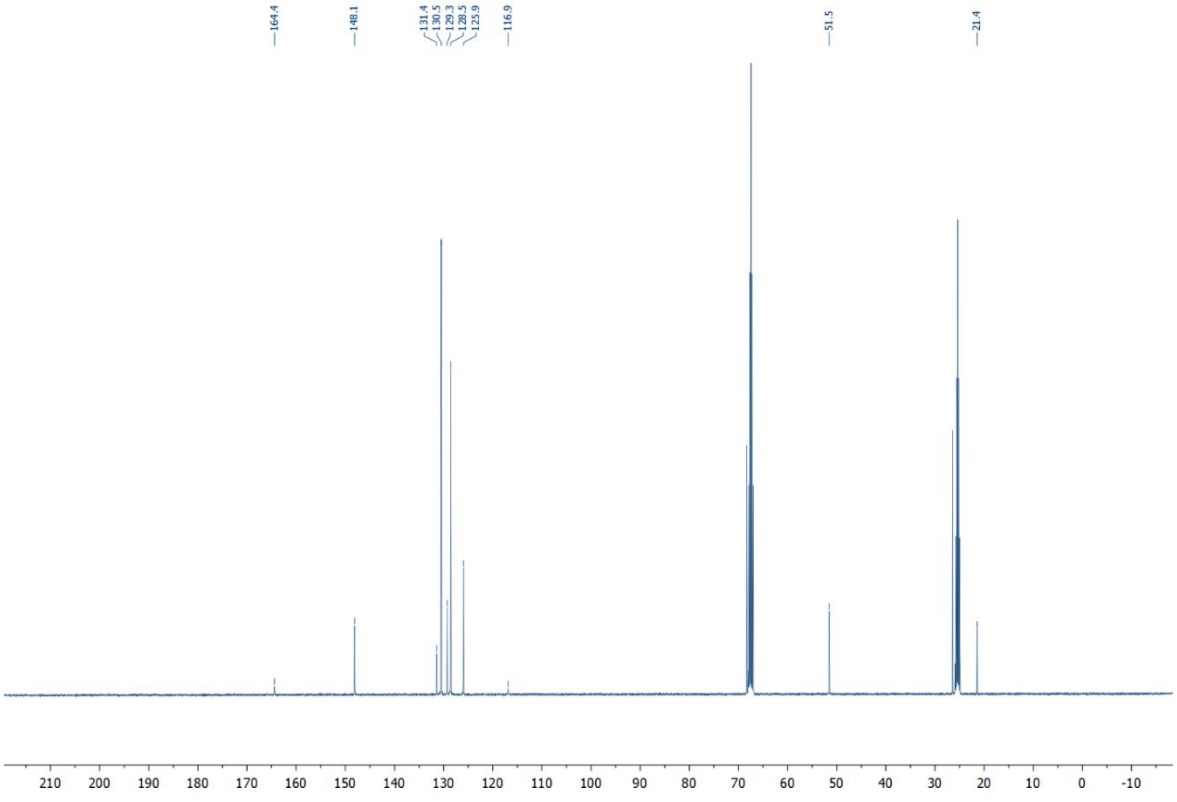


Figure S13. ^{13}C NMR spectrum of **Na1** recorded in THF-d_8.

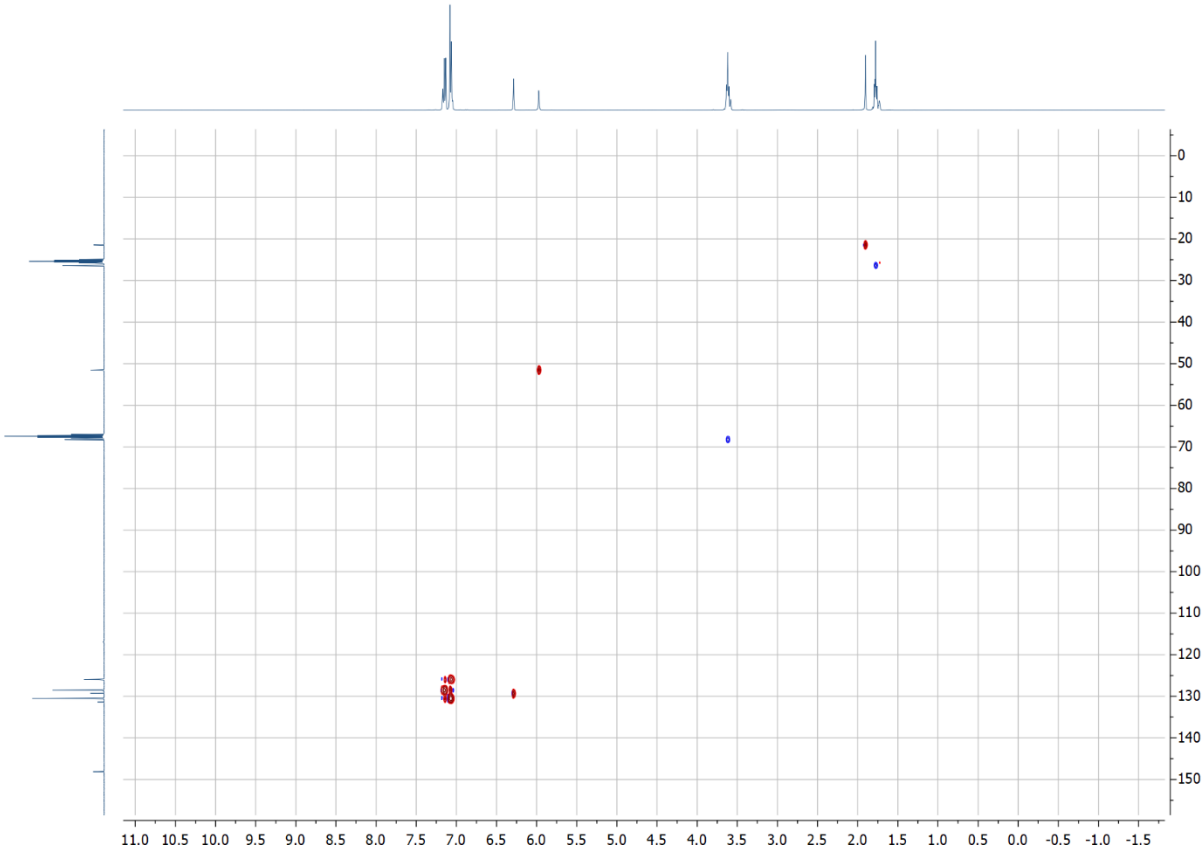


Figure S14. ^{1}H-^{13}C HSQC NMR spectrum of **Na1** recorded in THF-d_8.

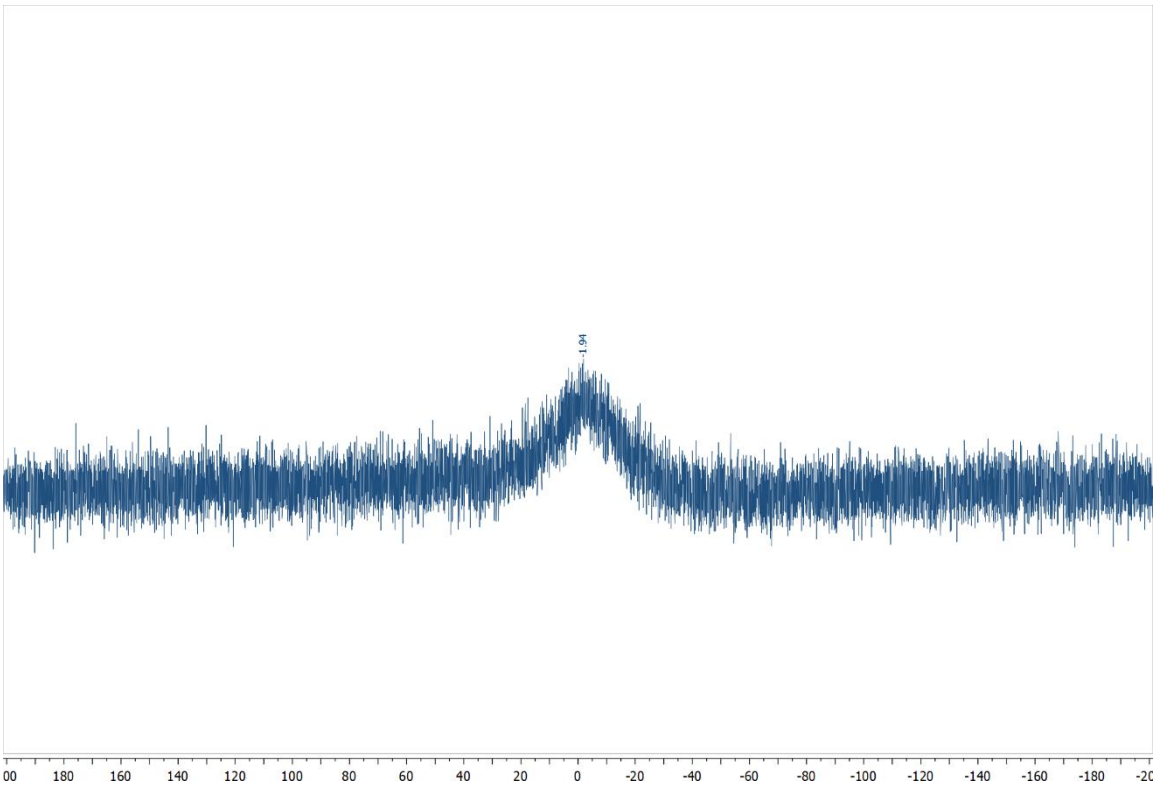


Figure S15. ^{23}Na NMR spectrum of **Na1** recorded in THF-d_8.

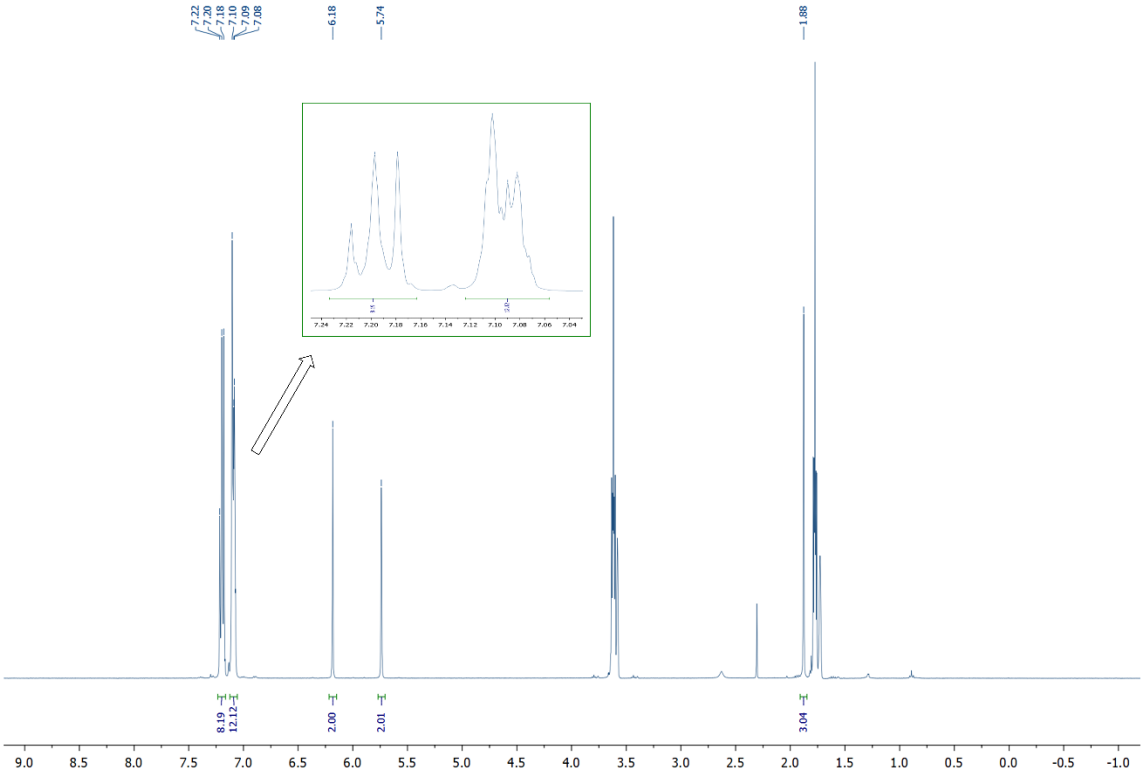


Figure S16. ^{1}H NMR spectrum of **K1** recorded in THF-d_8.

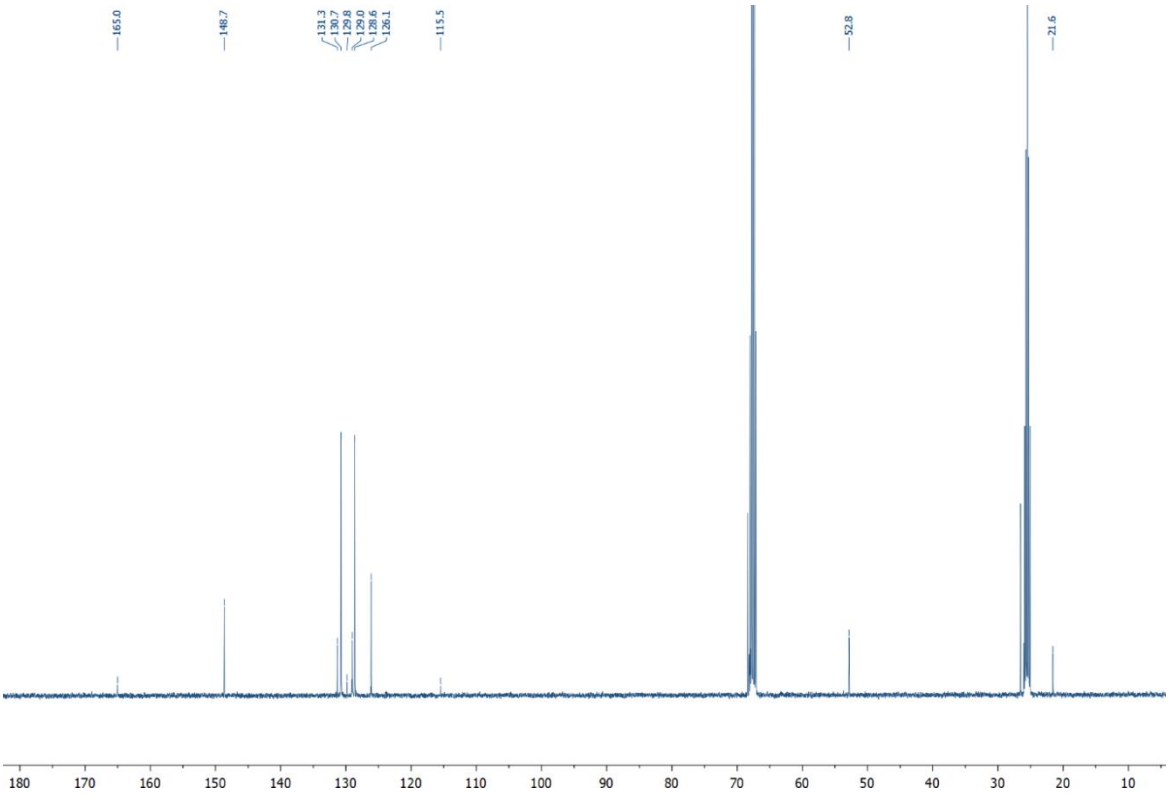


Figure S17. ^{13}C NMR spectrum of **K1** recorded in THF-d_8.

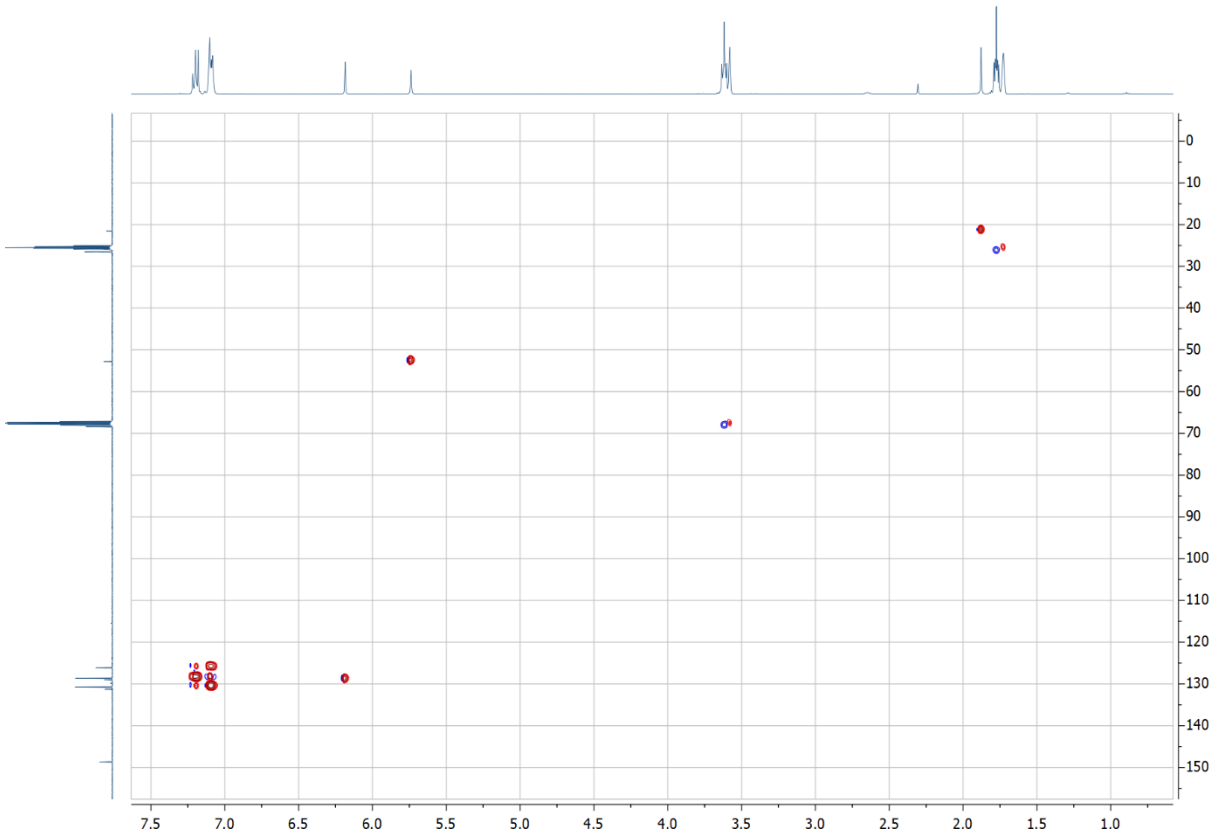


Figure S18. ^{1}H-^{13}C HSQC NMR spectrum of **K1** recorded in THF-d_8.

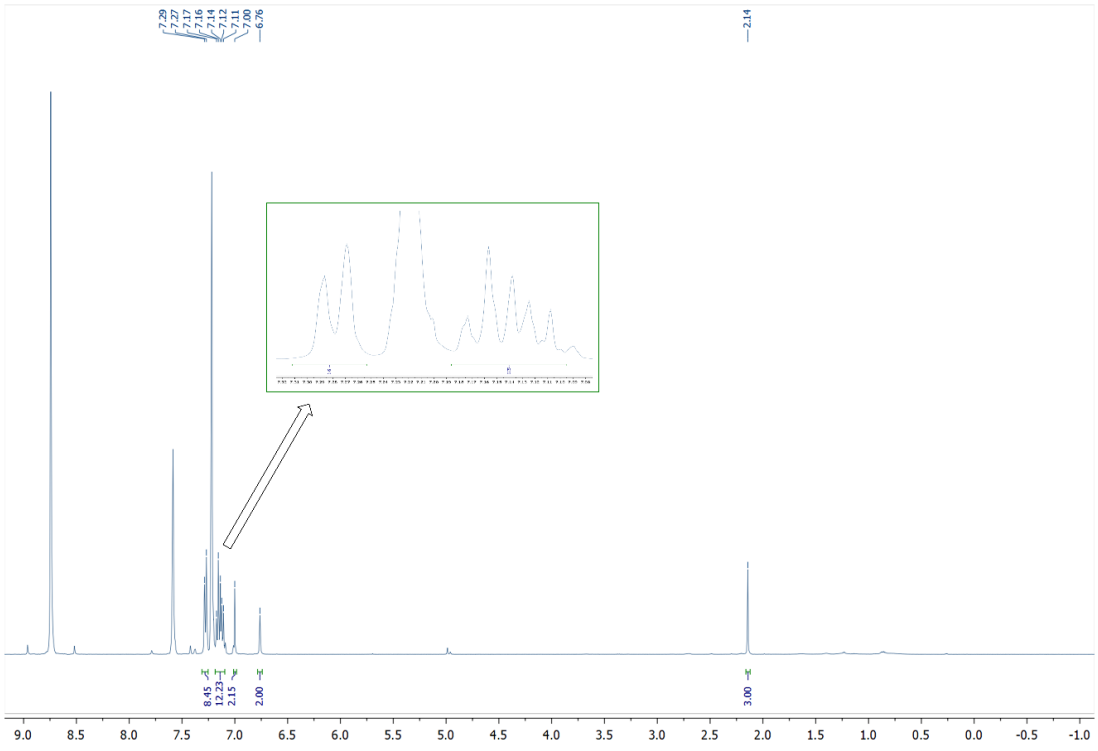


Figure S19. ^{1}H NMR spectrum of **Li2** recorded in pyridine-d_5.

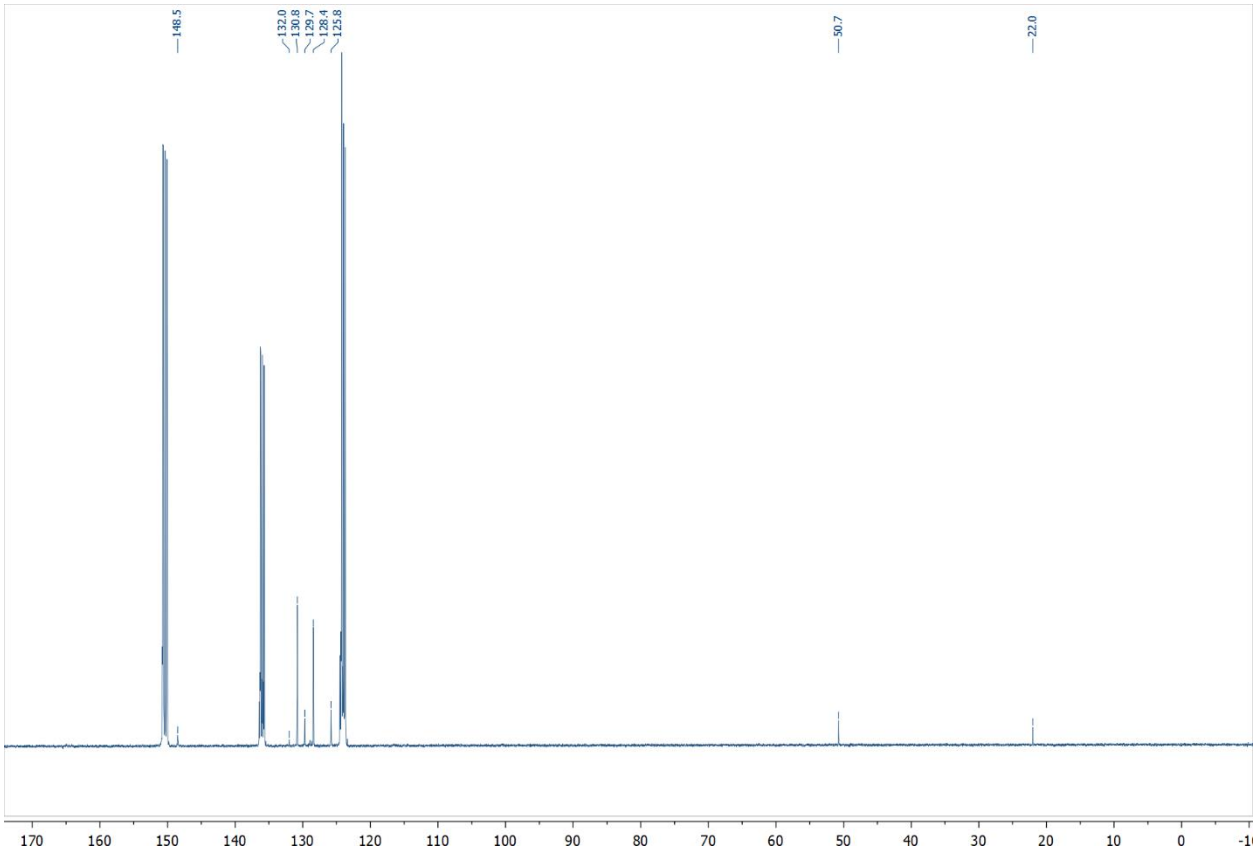


Figure S20. ^{13}C NMR spectrum of **Li2** recorded in pyridine-d_5.

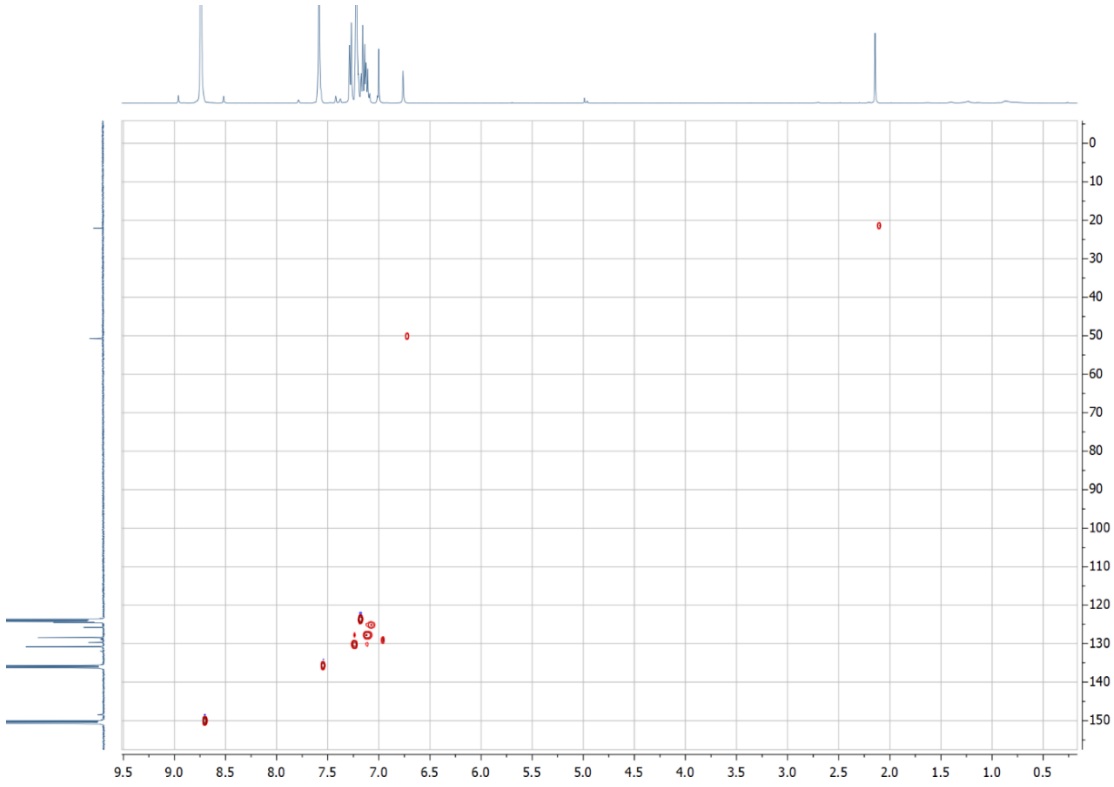


Figure S21. ^{1}H-^{13}C HSQC NMR spectrum of **Li2** recorded in pyridine-d_5.

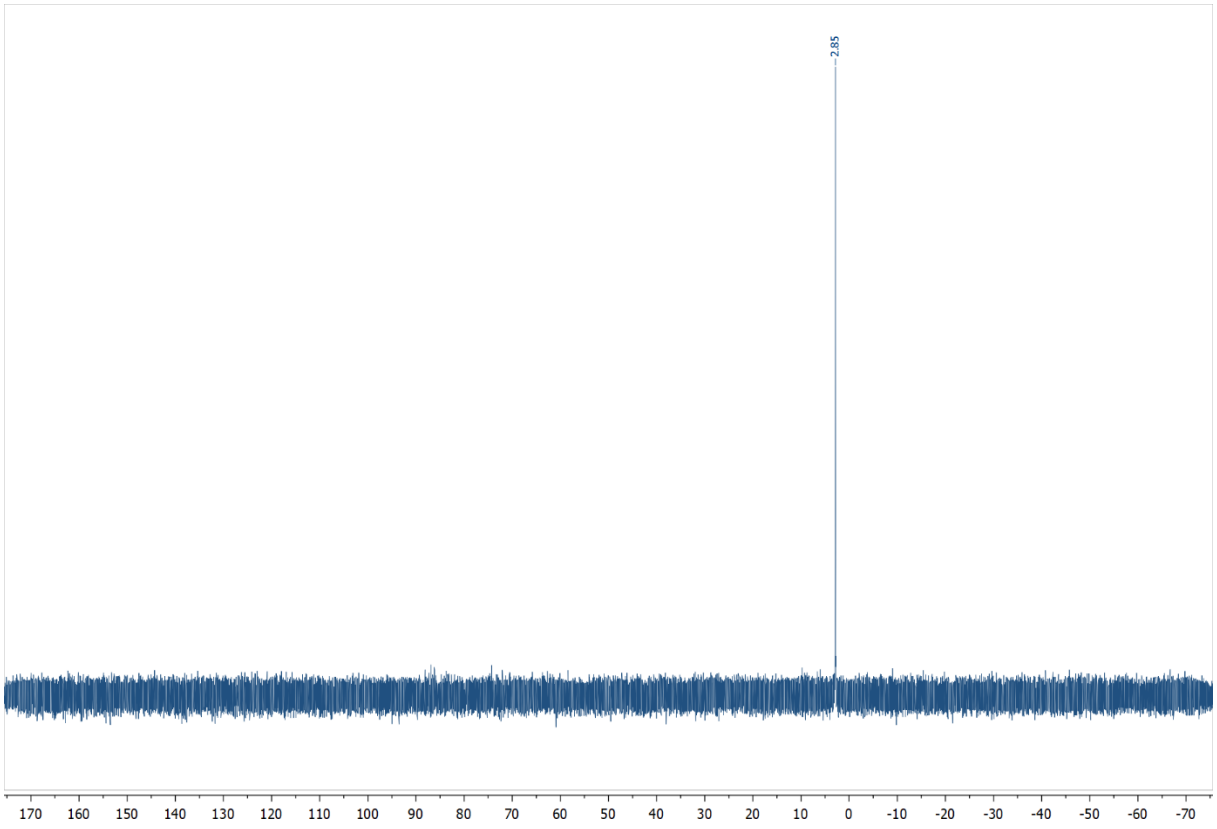


Figure S22. ^{7}Li NMR spectrum of **Li2** recorded in pyridine-d_5.

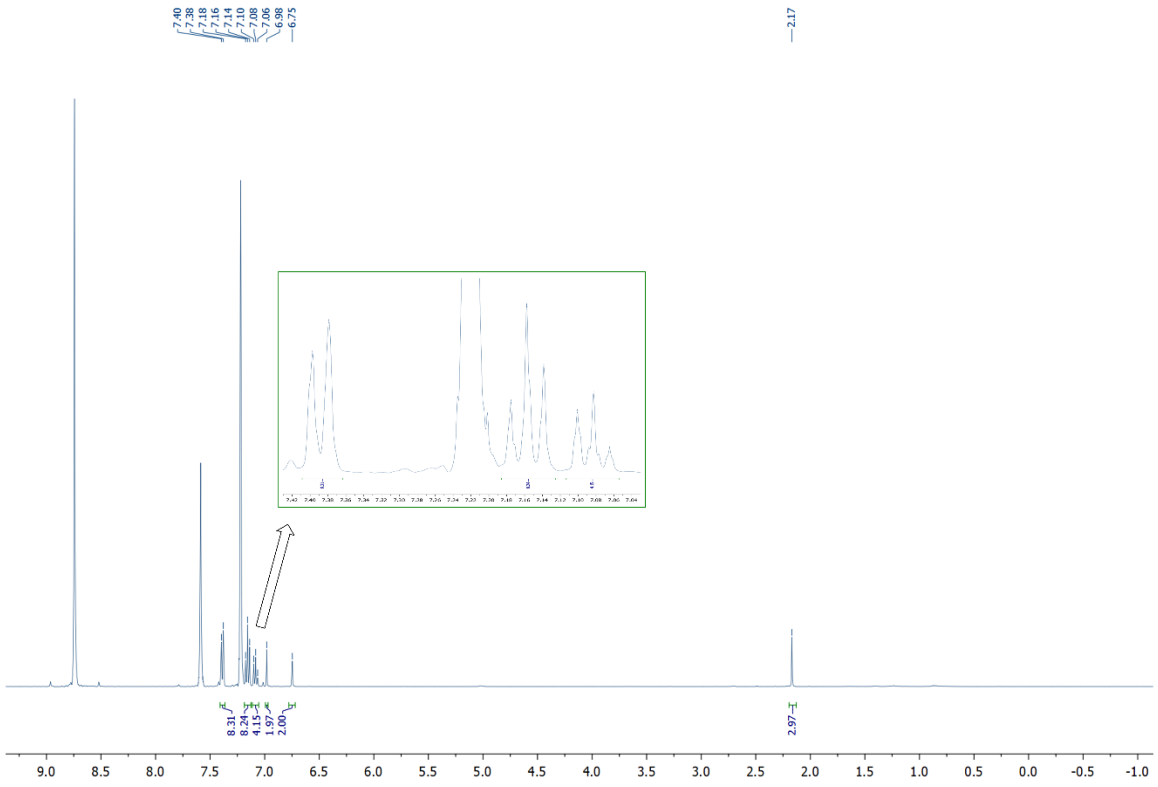


Figure S23. ^{1}H NMR spectrum of **Na2** recorded in pyridine-d_5.

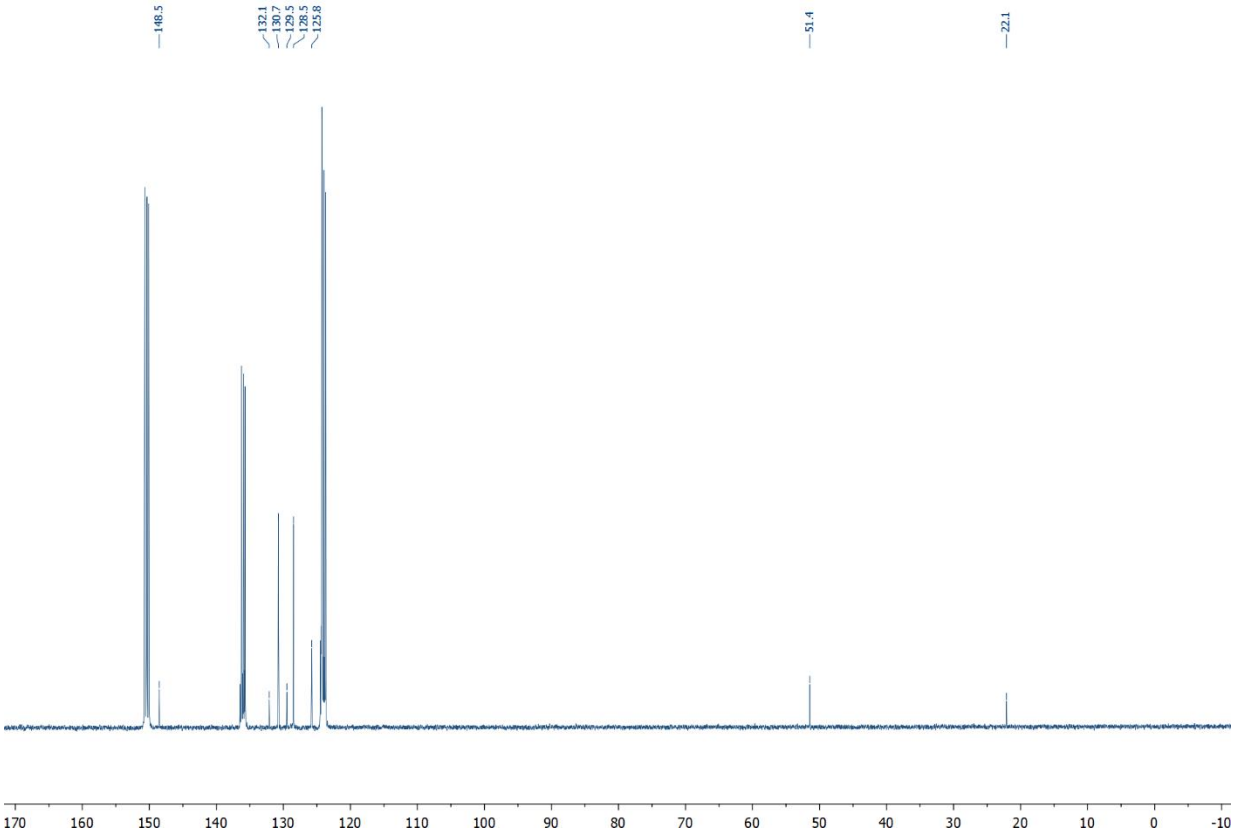


Figure S24. ^{13}C NMR spectrum of **Na2** recorded in pyridine-d_5.

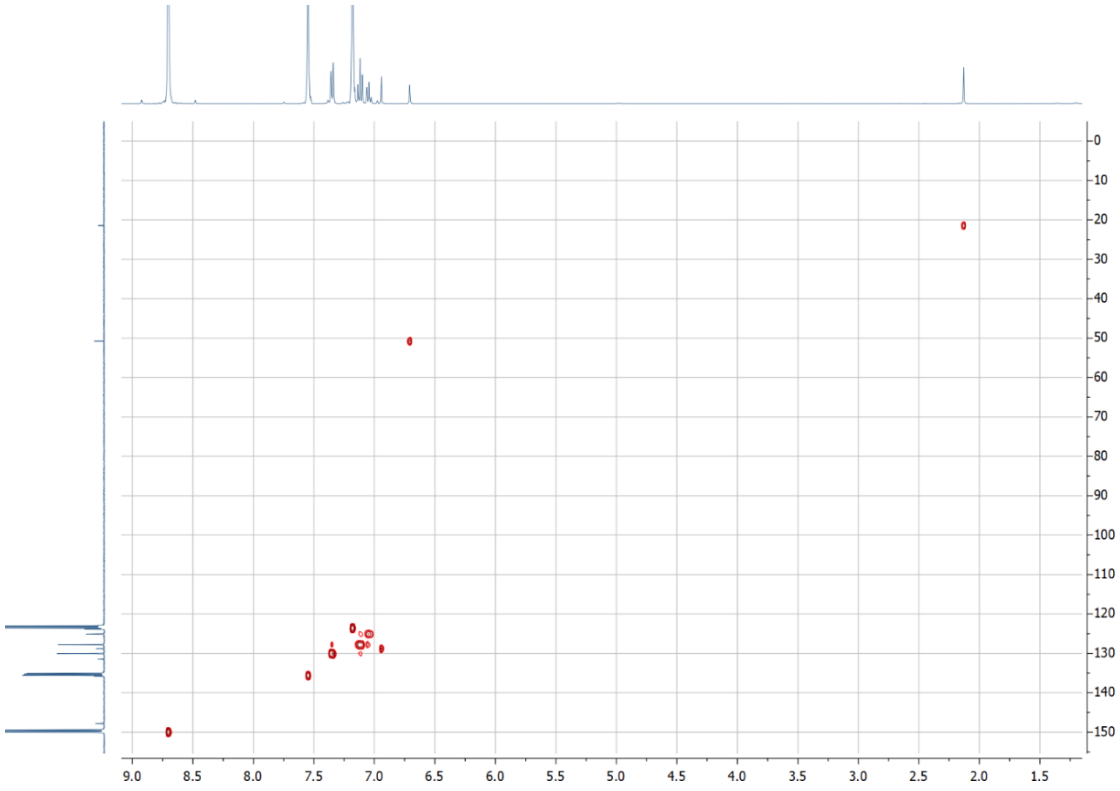


Figure S25. ^{1}H-^{13}C HSQC NMR spectrum of **Na2** recorded in pyridine-d_5.

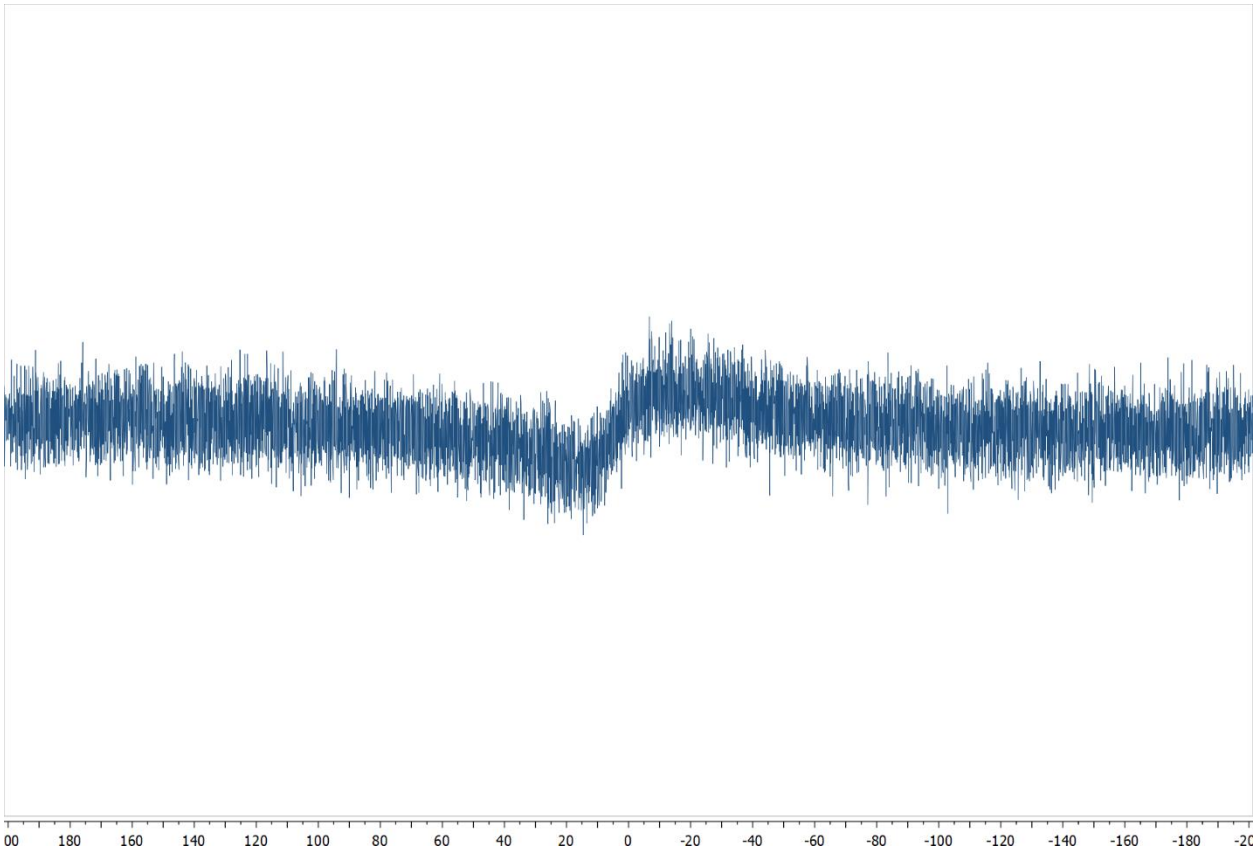


Figure S26. ^{23}Na NMR spectrum of **Na2** recorded in pyridine-d_5.

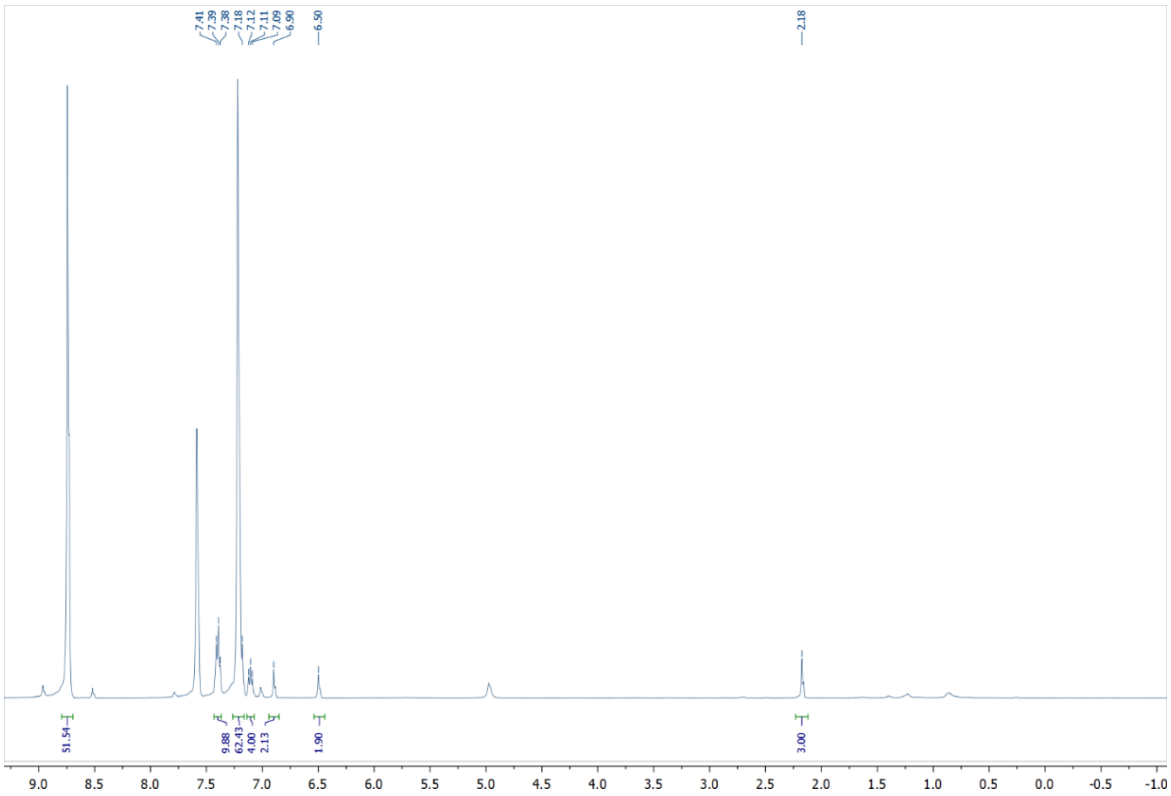


Figure S27. ^{1}H NMR spectrum of **K2** recorded in pyridine-d_5.

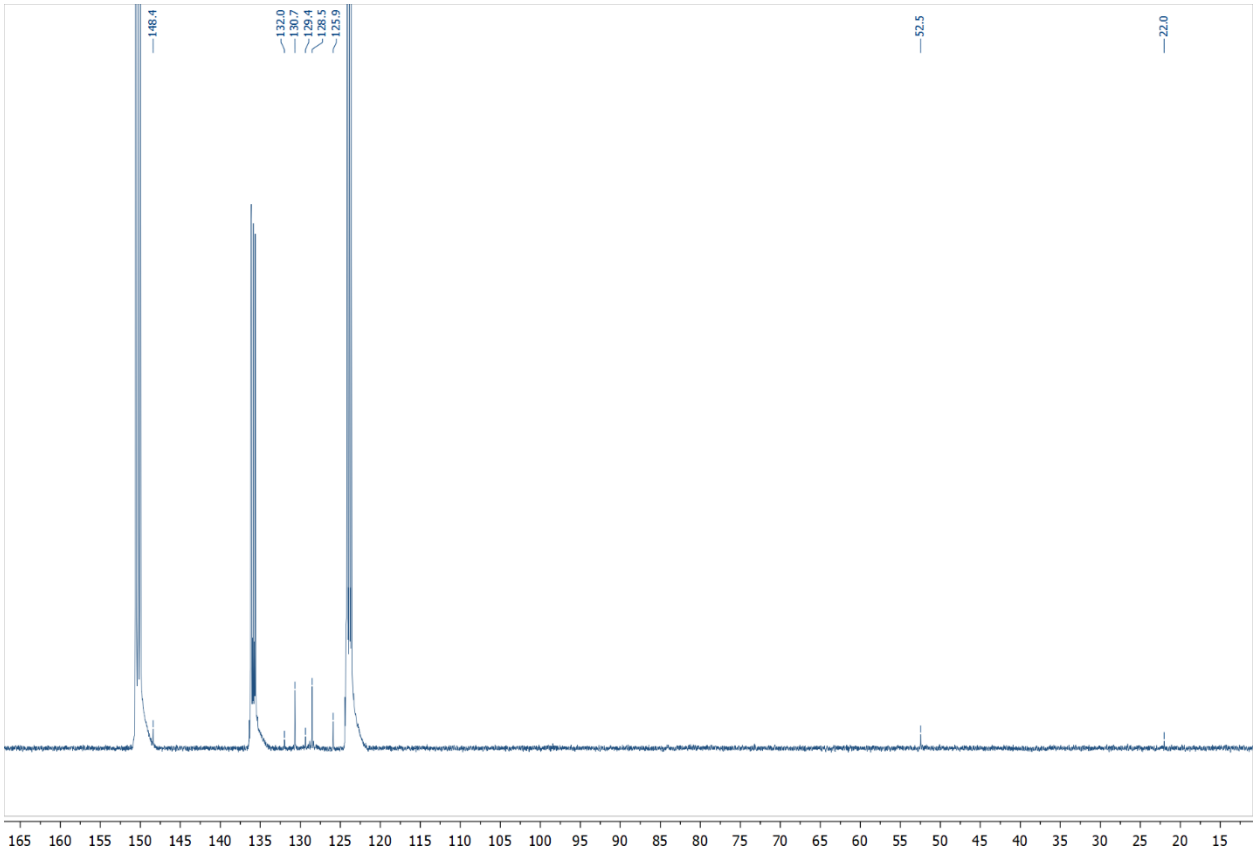


Figure S28. ^{13}C NMR spectrum of **K2** recorded in pyridine-d_5.

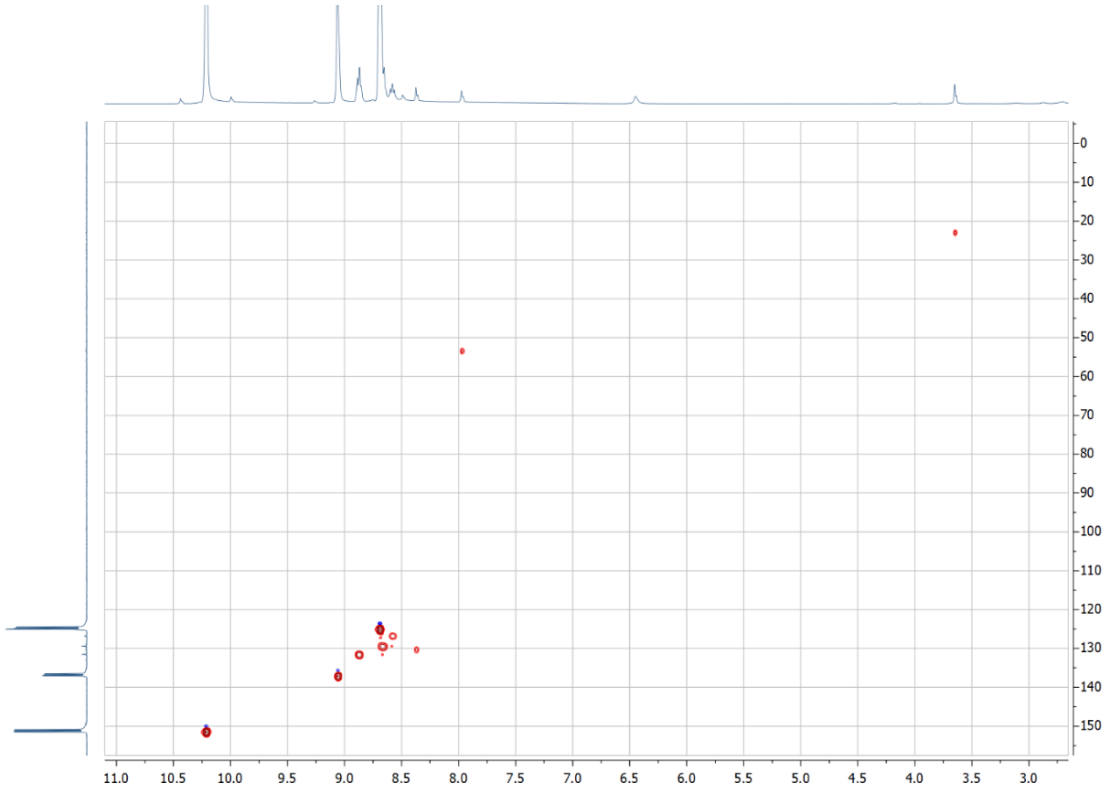


Figure S29. ^{1}H-^{13}C HSQC NMR spectrum of **K2** recorded in pyridine-d_5.

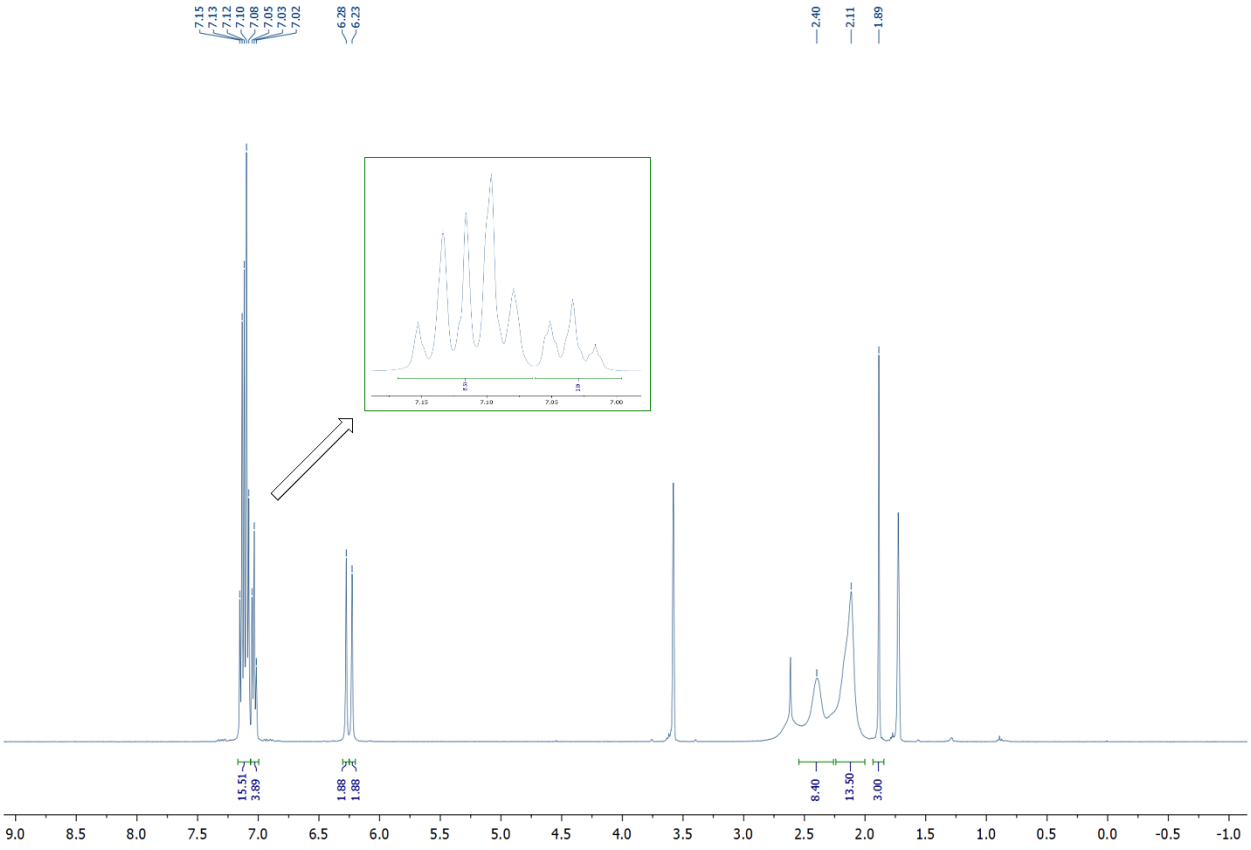


Figure S30. ^{1}H NMR spectrum of **Li3** recorded in THF-d_8.

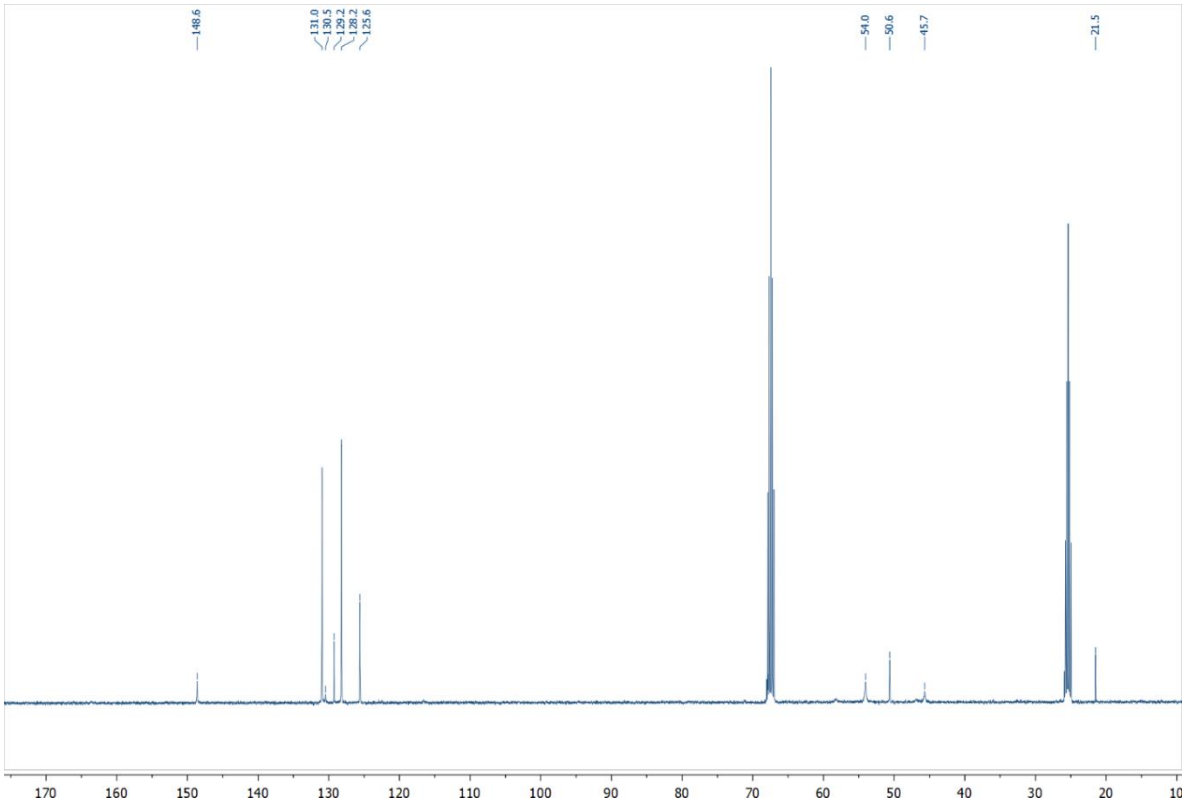


Figure S31. ^{13}C NMR spectrum of **Li3** recorded in THF-d_8.

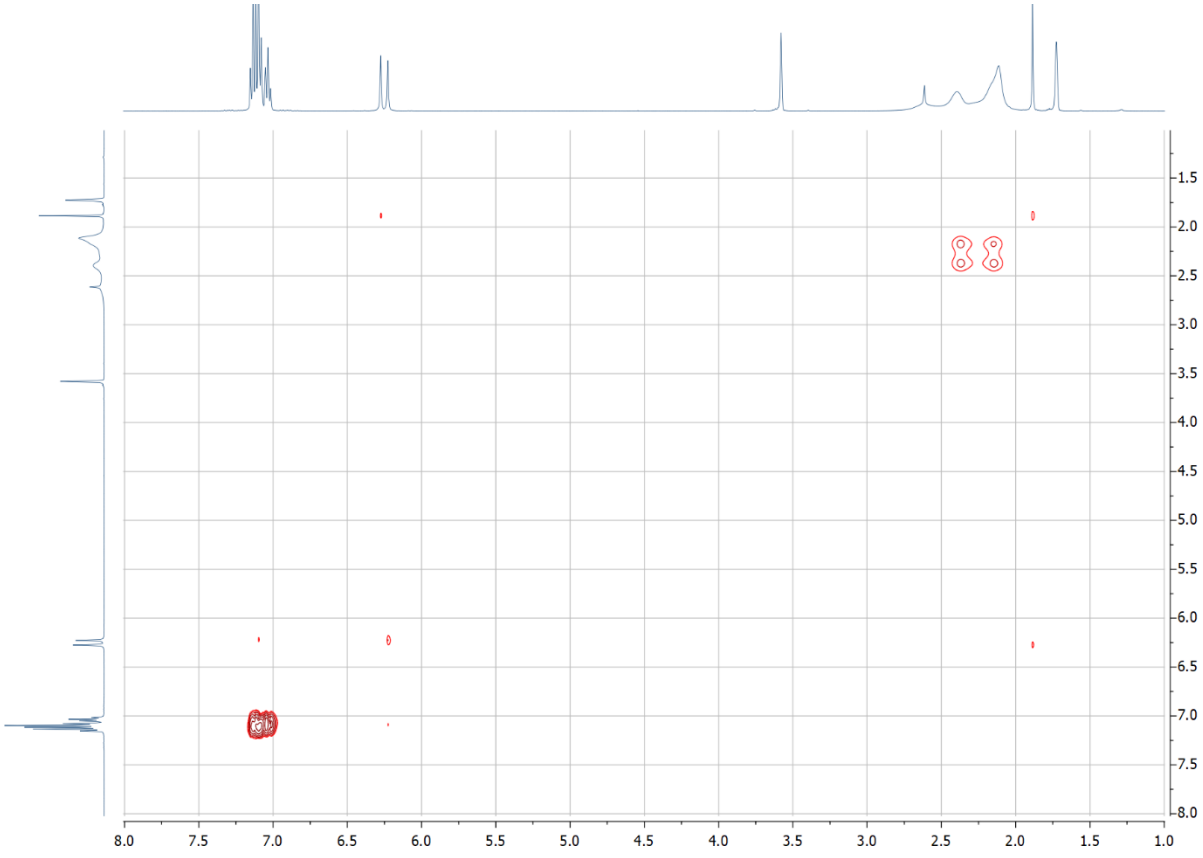


Figure S32. ^{1}H-^{1}H COSY NMR spectrum of **Li3** recorded in THF-d_8.

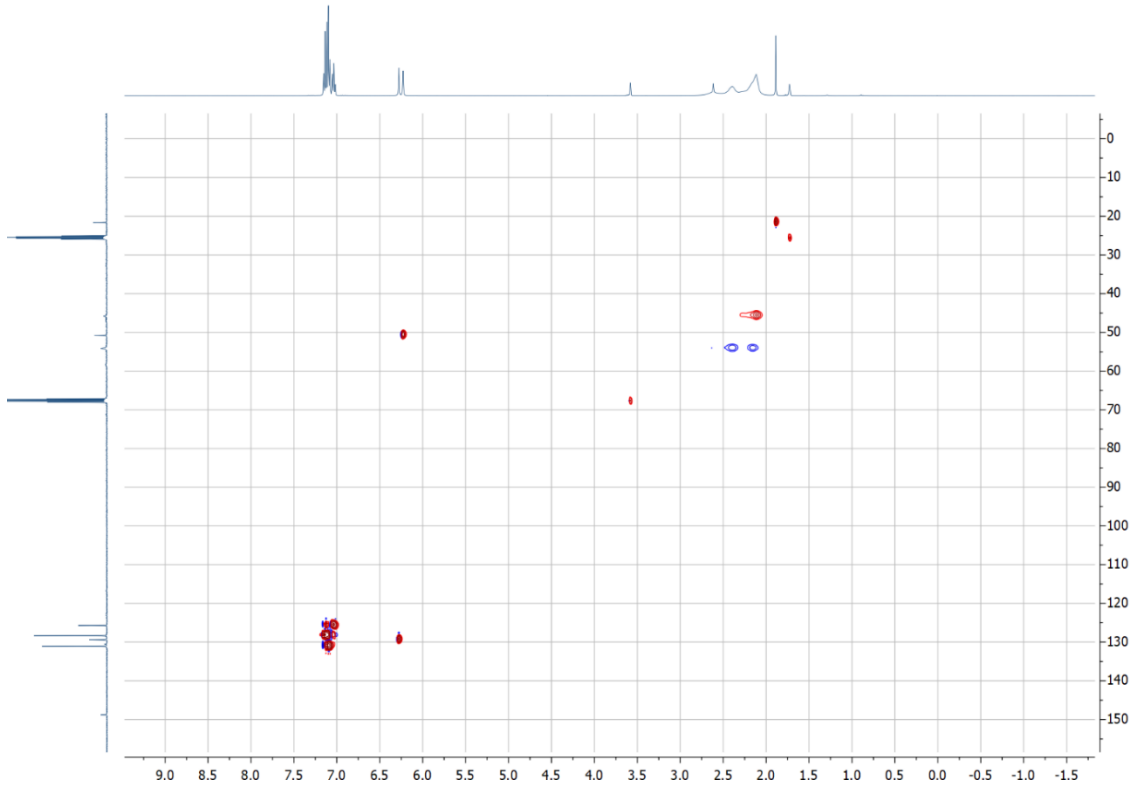


Figure S33. ^{1}H-^{13}C HSQC NMR spectrum of **Li3** recorded in THF-d_8.

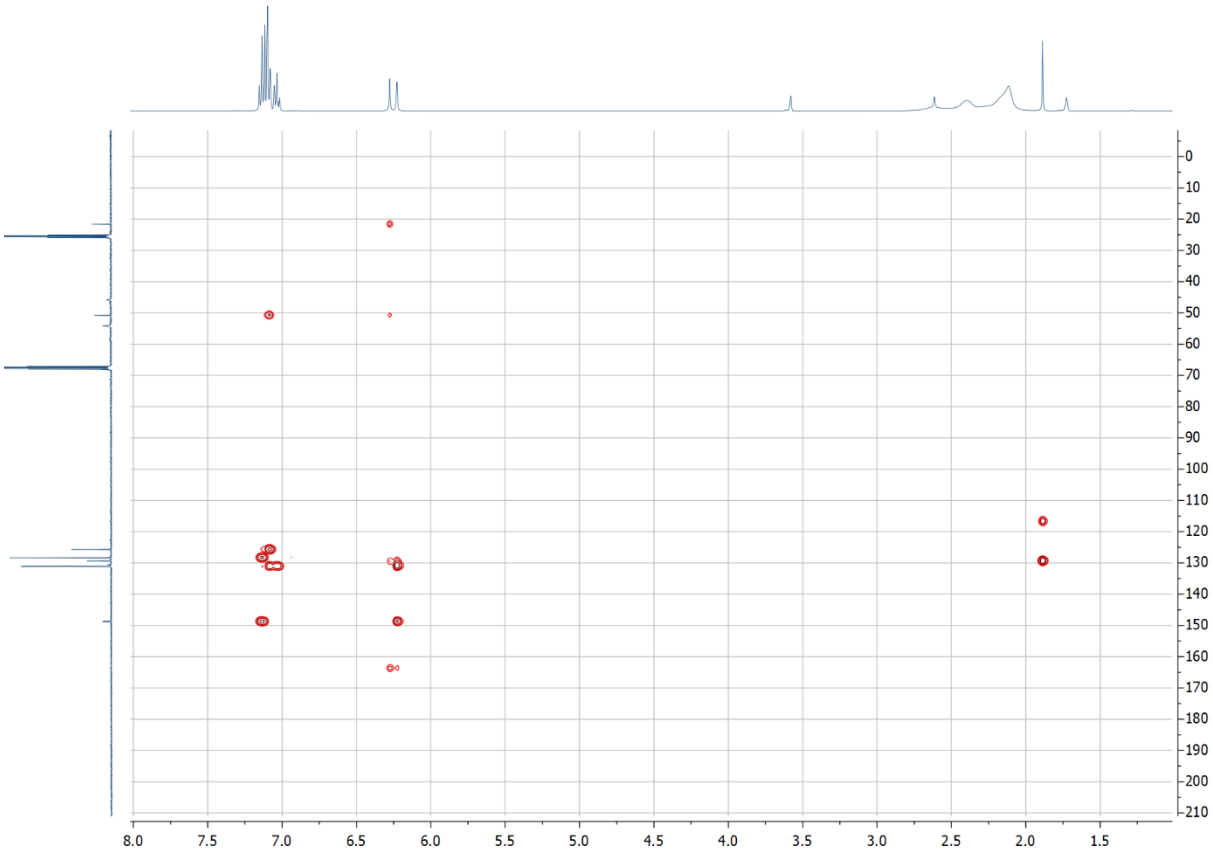


Figure S34. ^{1}H-^{13}C HMBC NMR spectrum of **Li3** recorded in THF-d_8.

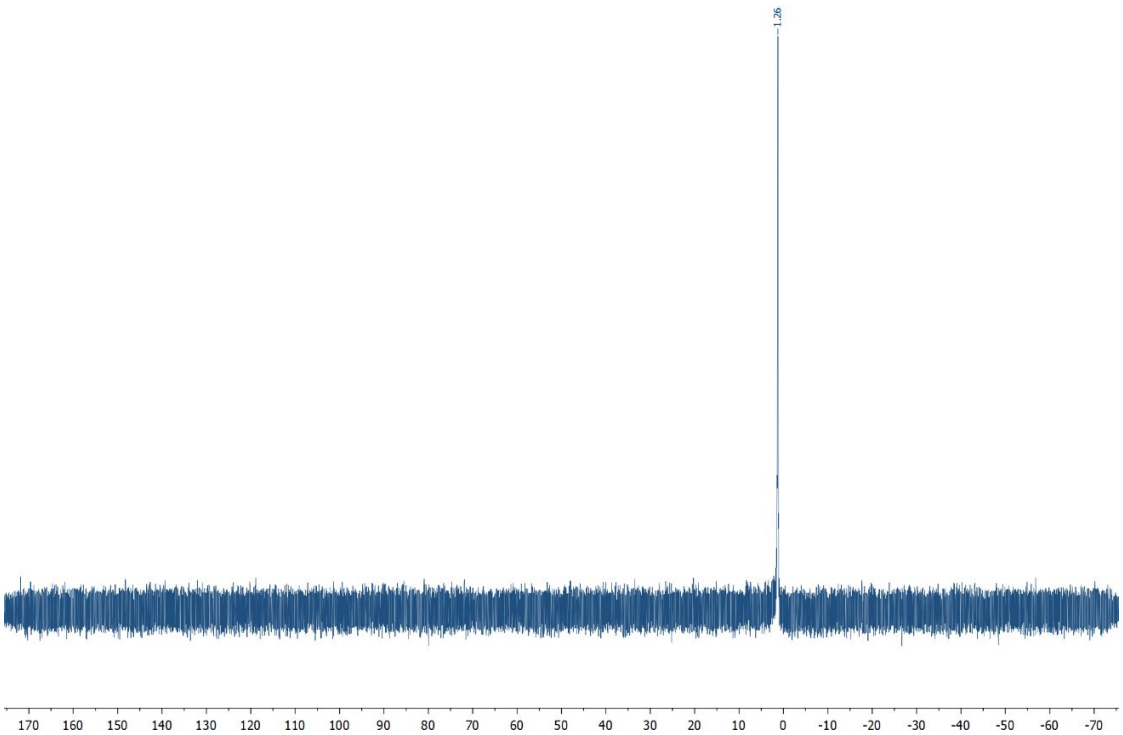


Figure S35. ^{7}Li NMR spectrum of **Li3** recorded in THF-d_8.

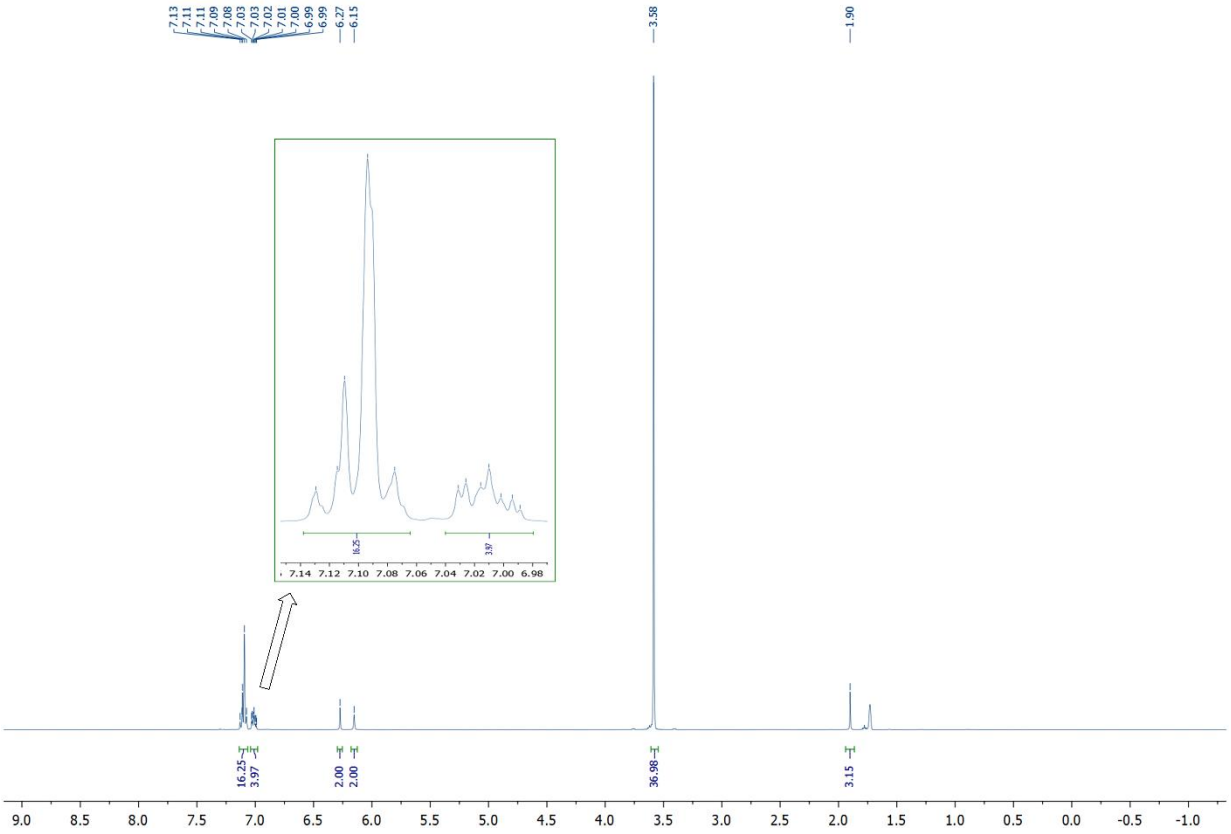


Figure S36. ^{1}H NMR spectrum of **Na4** recorded in THF-d_8.

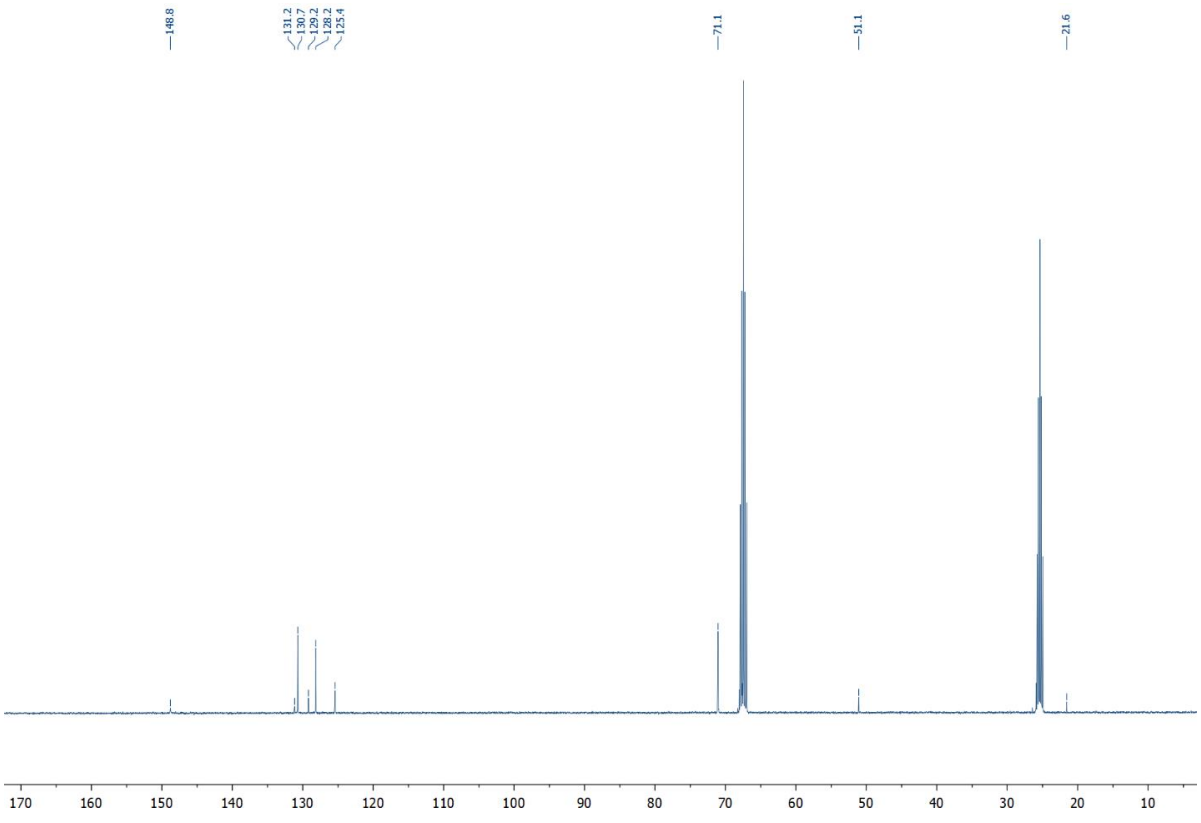


Figure S37. ^{13}C NMR spectrum of **Na4** recorded in THF-d_8.

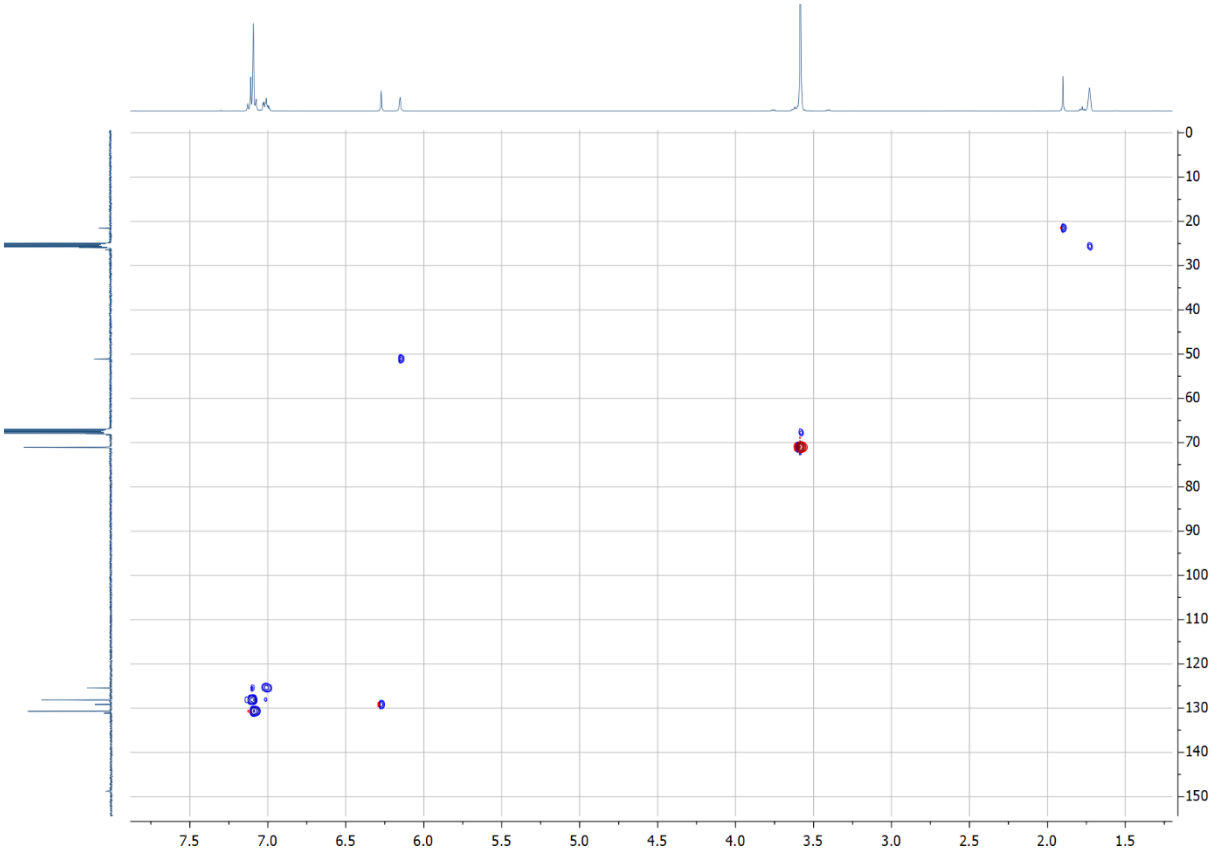


Figure S38. ^{1}H-^{13}C HSQC NMR spectrum of **Na4** recorded in THF-d_8.

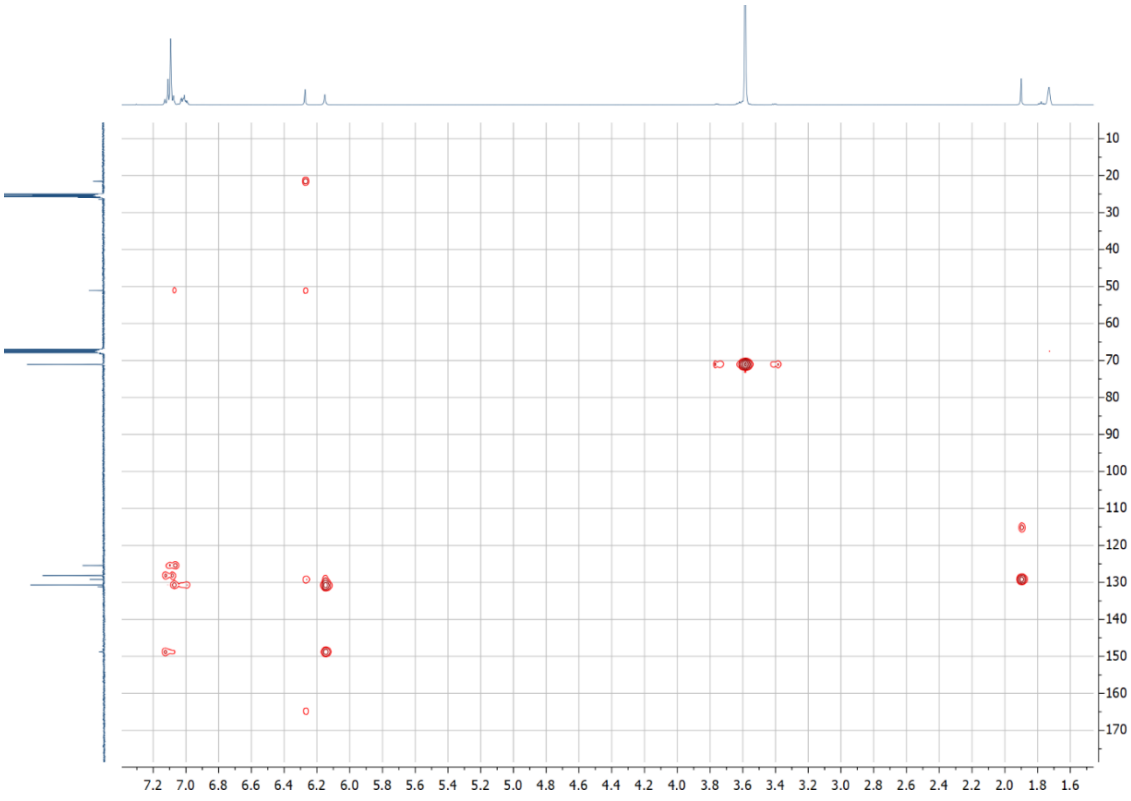


Figure S39. ^{1}H-^{13}C HMBC NMR spectrum of **Na4** recorded in THF-d_8.

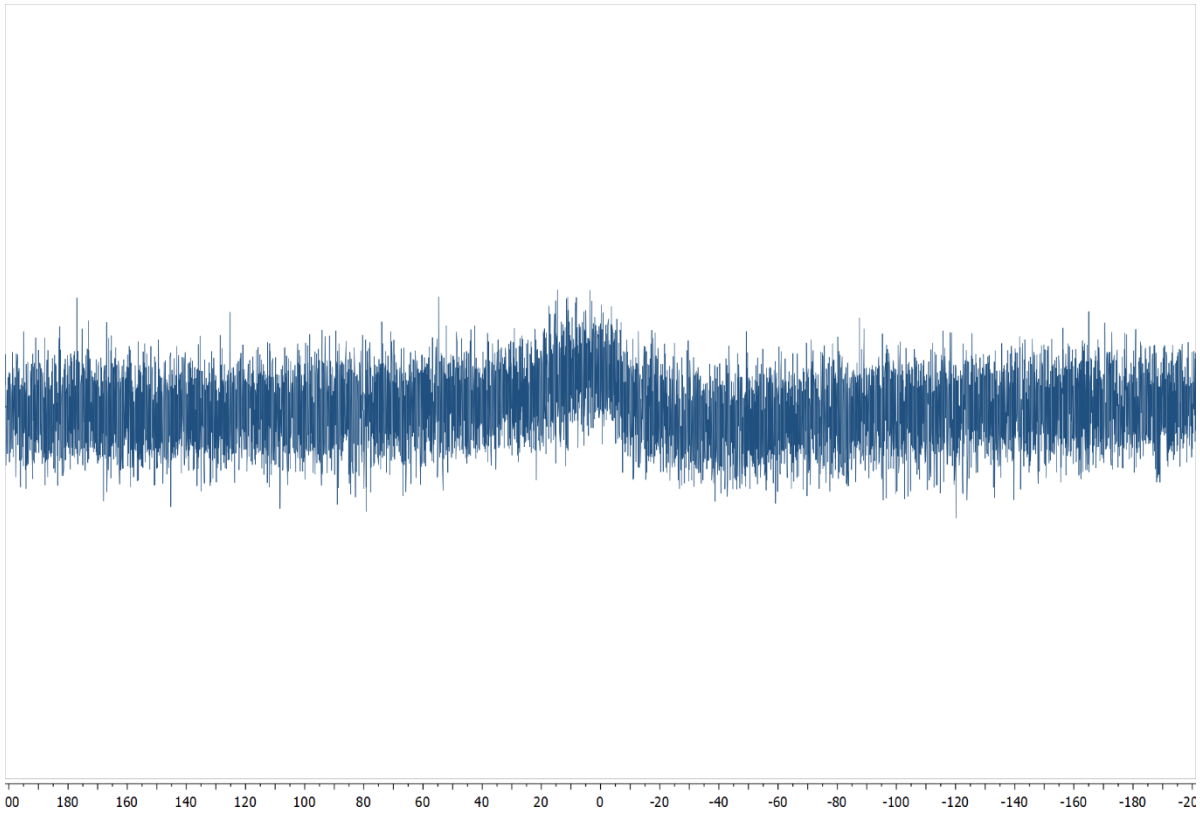


Figure S40. ^{23}Na NMR spectrum of **Na4** recorded in THF-d_8.

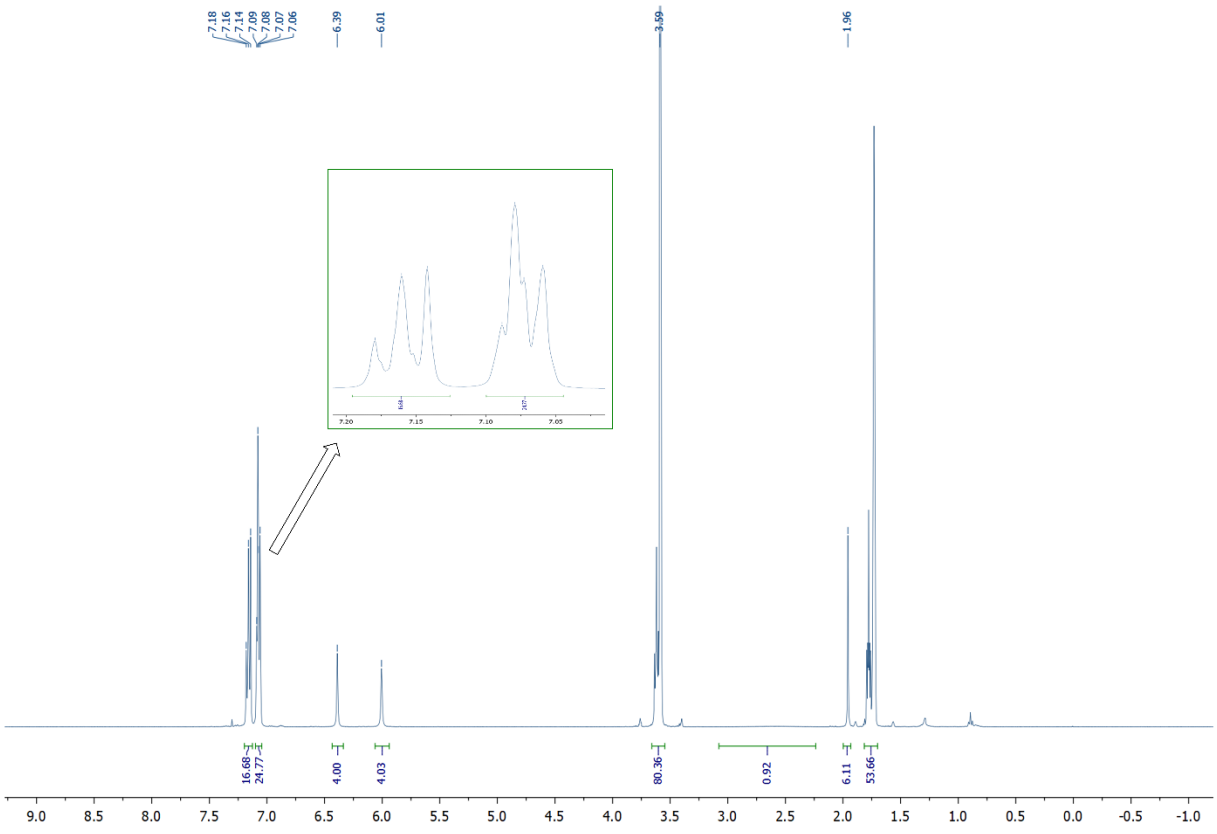


Figure S41. ^{1}H NMR spectrum of **Na5** recorded in THF-d_8.

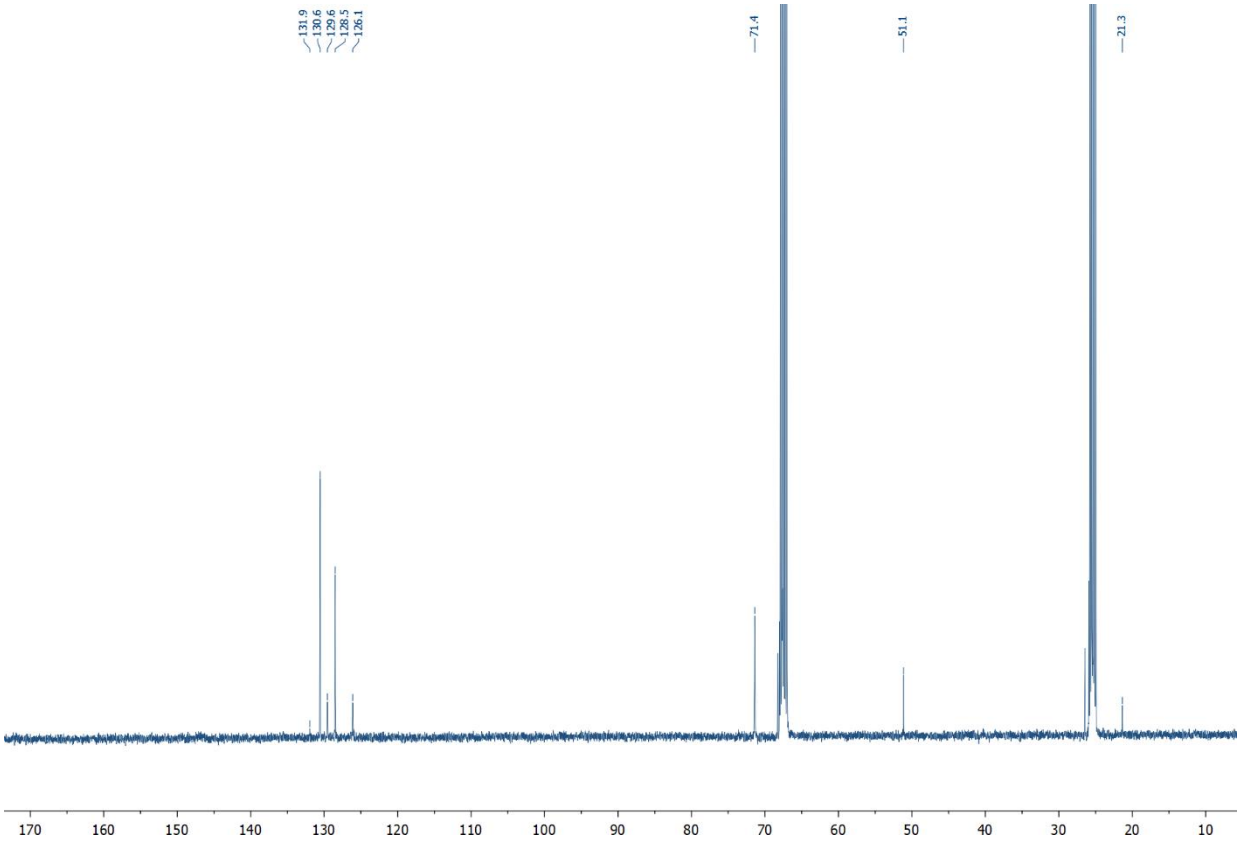


Figure S42. ^{13}C NMR spectrum of **Na5** recorded in THF-d_8.

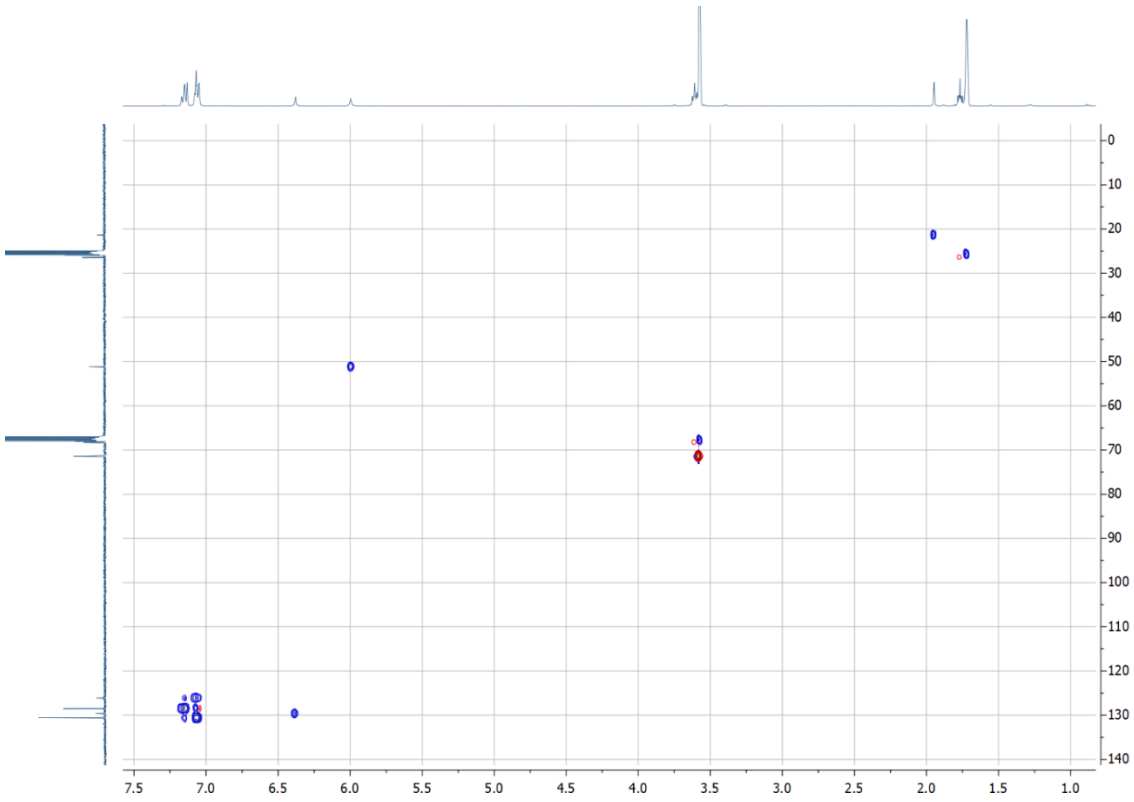


Figure S43. ^{1}H-^{13}C HSQC NMR spectrum of **Na5** recorded in THF-d_8.

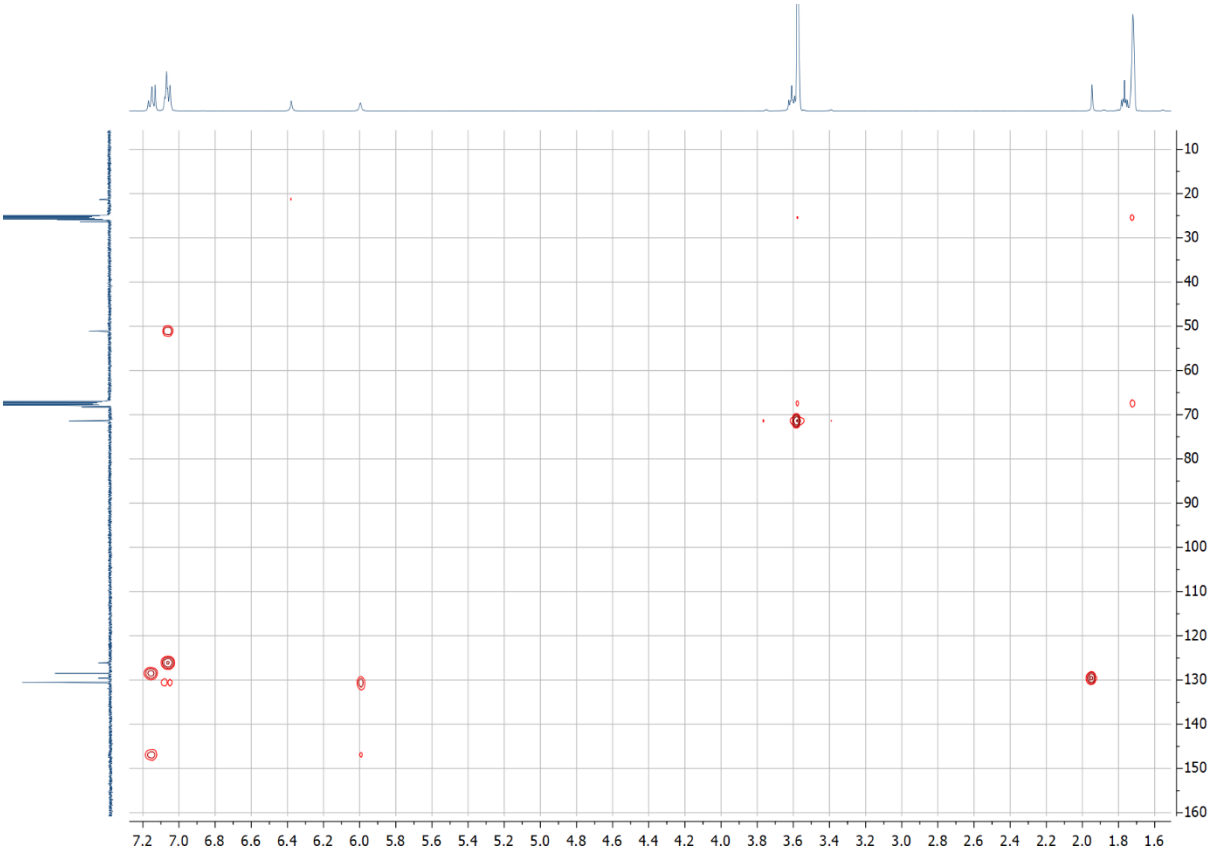


Figure S44. ^{1}H-^{13}C HMBC NMR spectrum of **Na5** recorded in THF-d_8.

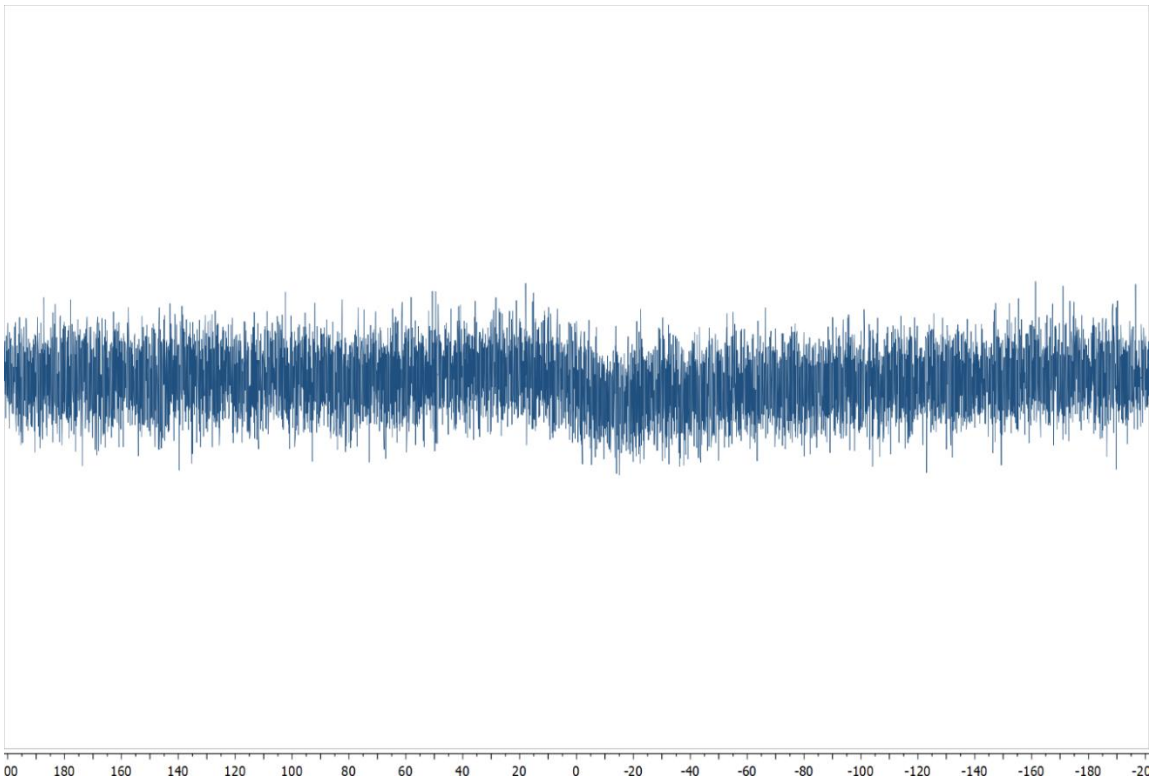


Figure S45. ^{23}Na NMR spectrum of **Na5** recorded in THF-d_8.

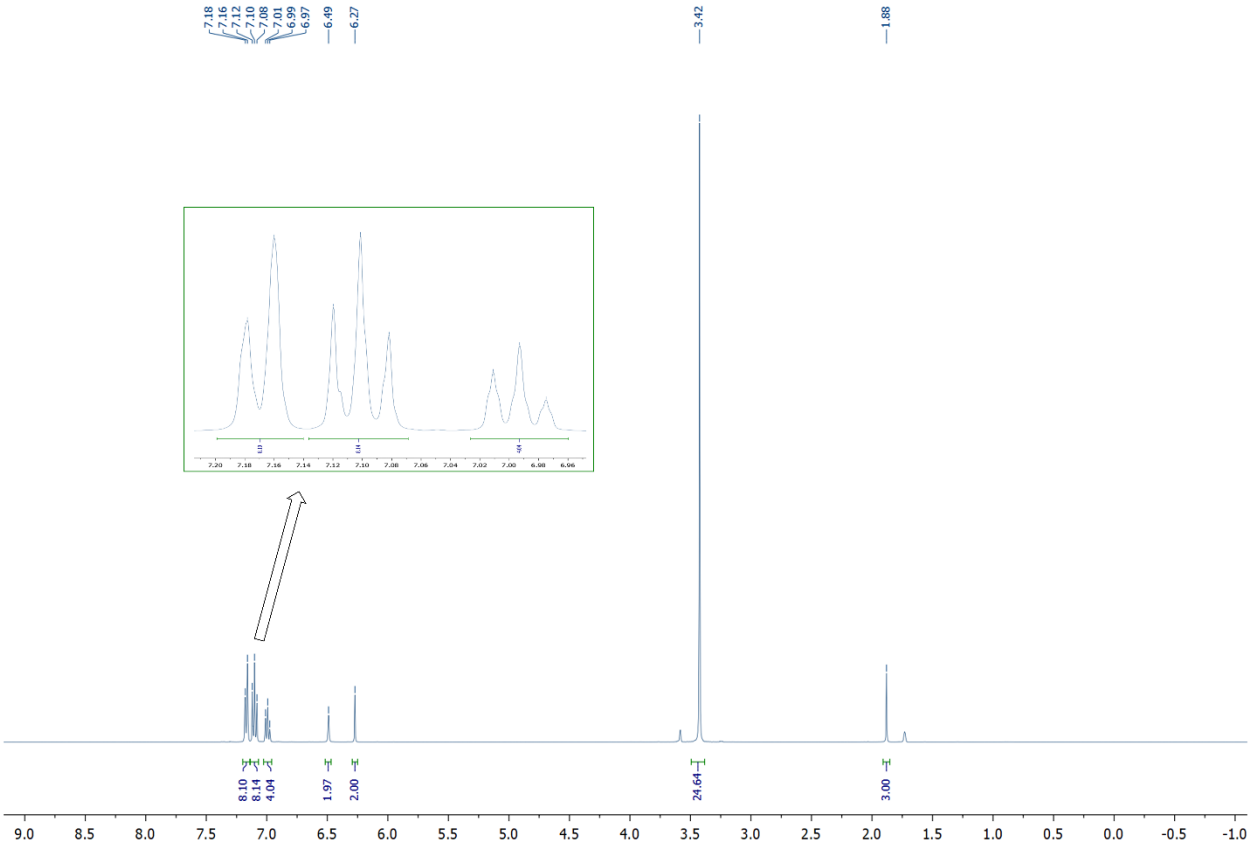


Figure S46. ^{1}H NMR spectrum of **Na6** recorded in THF-d_8.

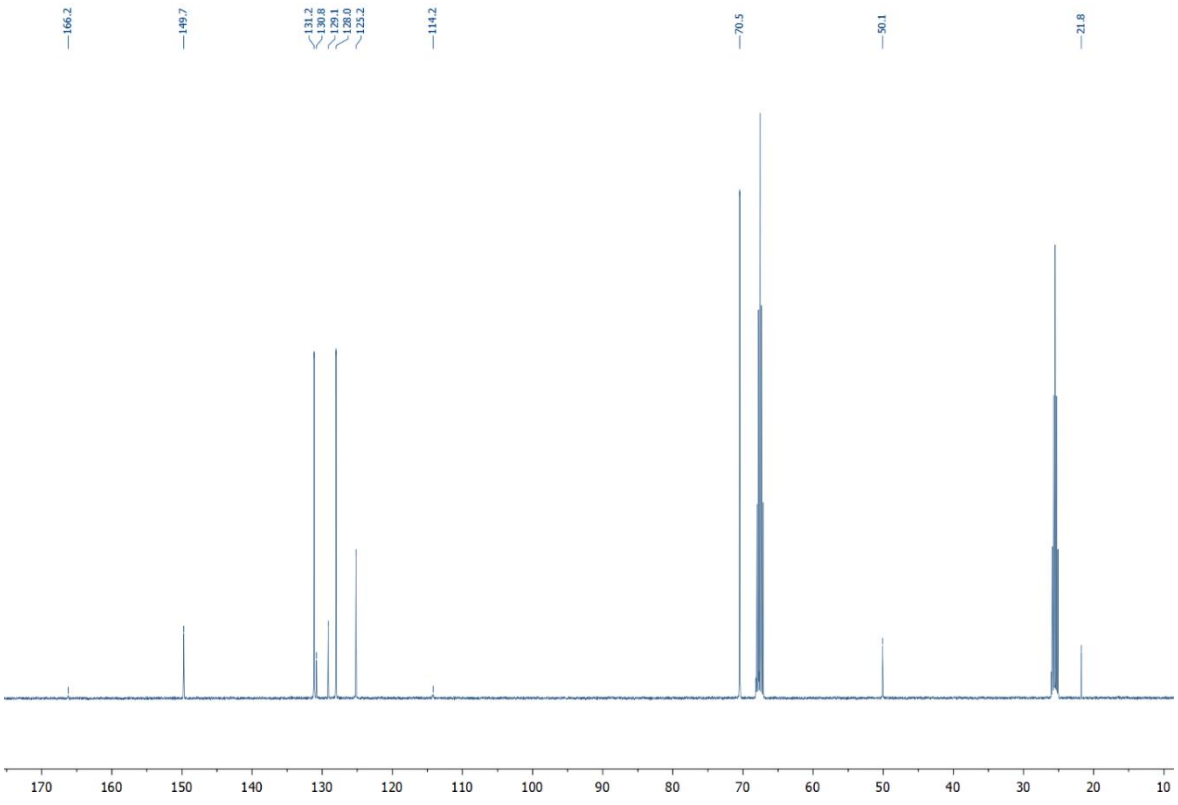


Figure S47. ^{13}C NMR spectrum of **Na6** recorded in THF-d_8.

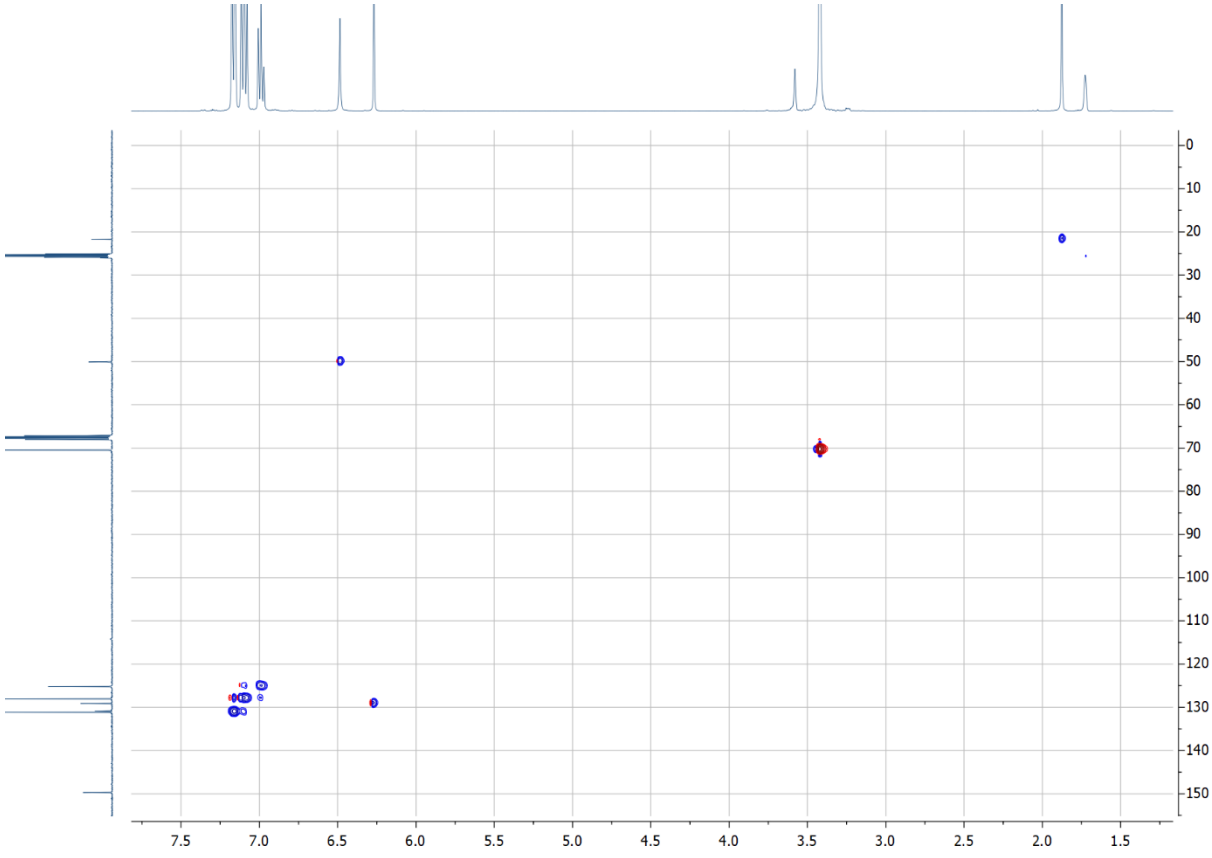


Figure S48. ^{1}H-^{13}C HSQC NMR spectrum of **Na6** recorded in THF-d_8.

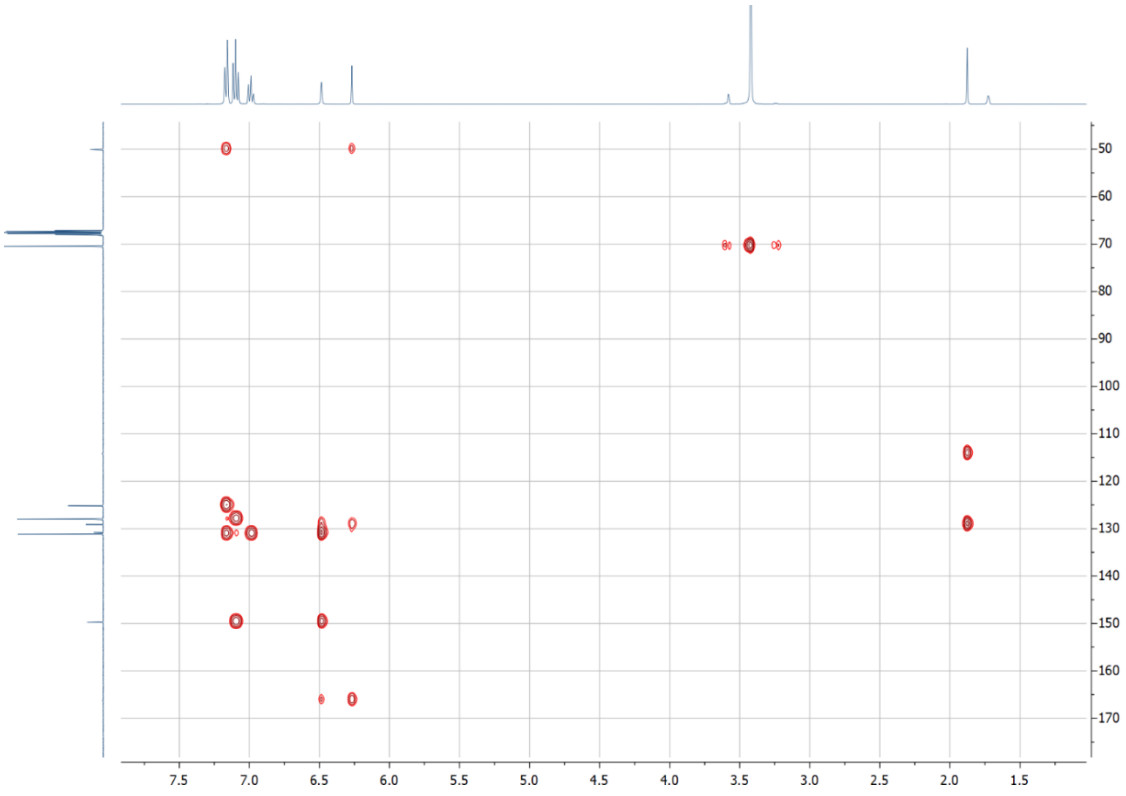


Figure S49. ^{1}H-^{13}C HMBC NMR spectrum of **Na6** recorded in THF-d_8.

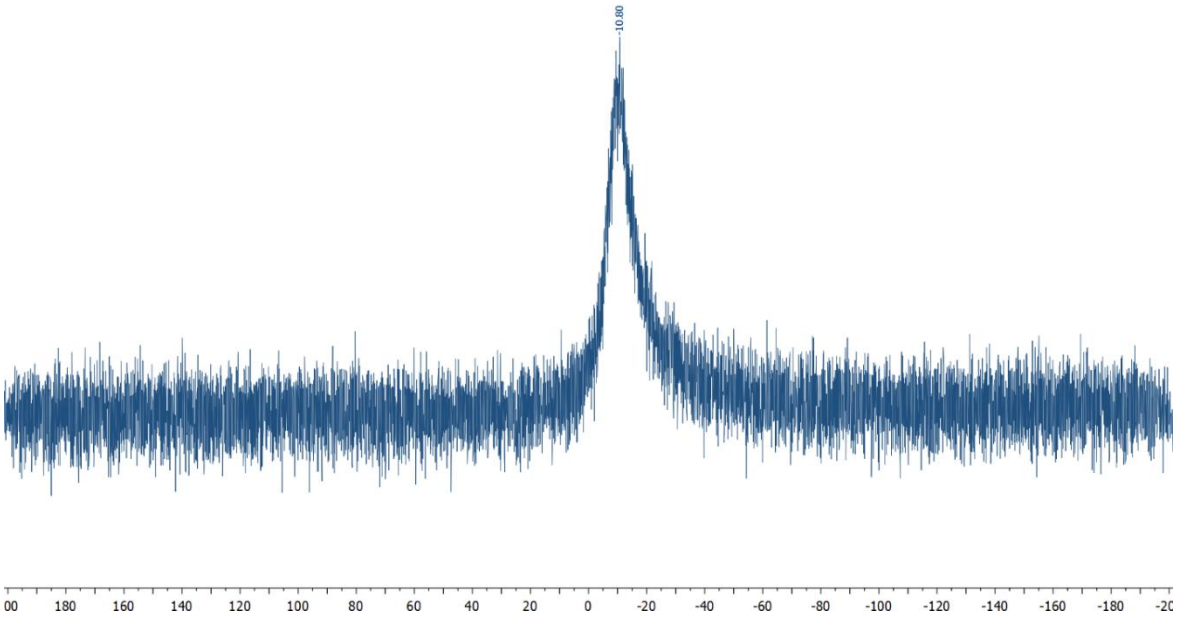


Figure S50. ^{23}Na NMR spectrum of **Na6** recorded in THF-d_8.

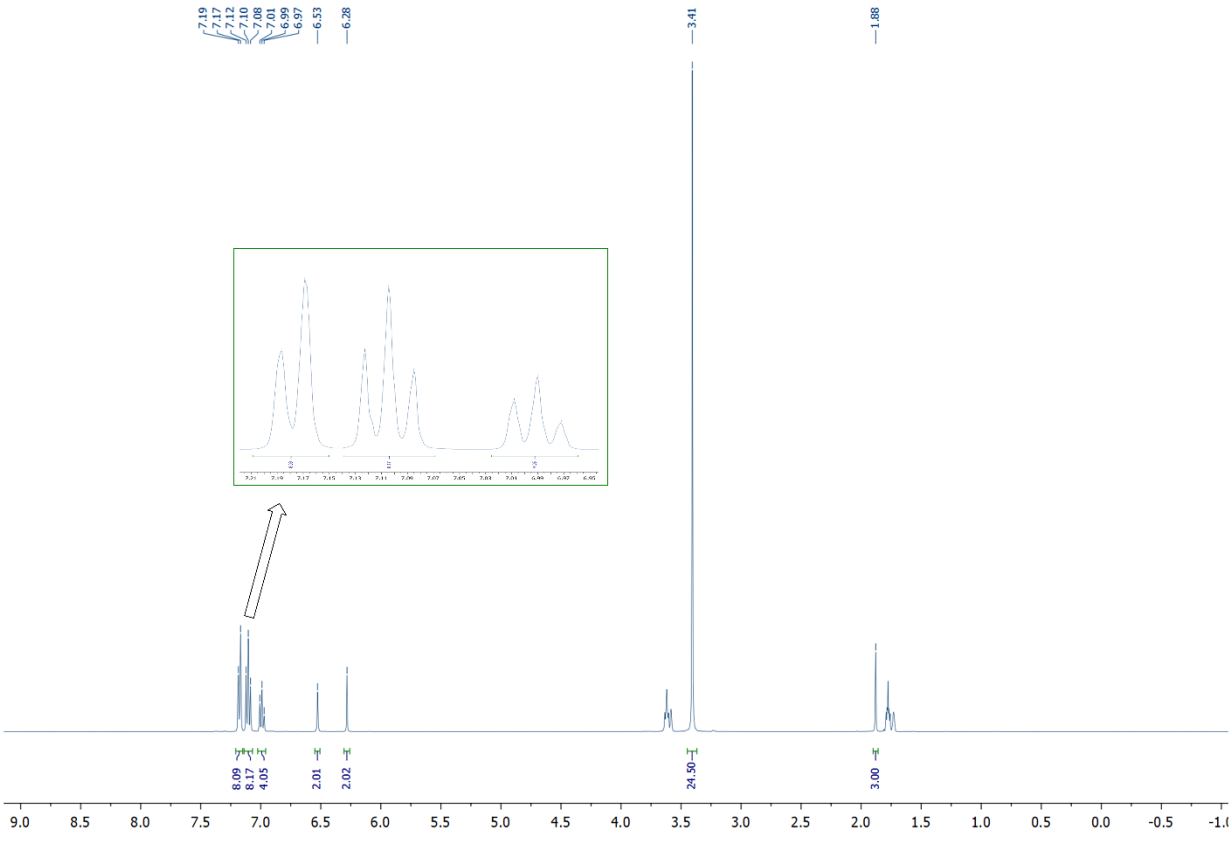


Figure S51. ^{1}H NMR spectrum of **K6** recorded in THF-d_8.

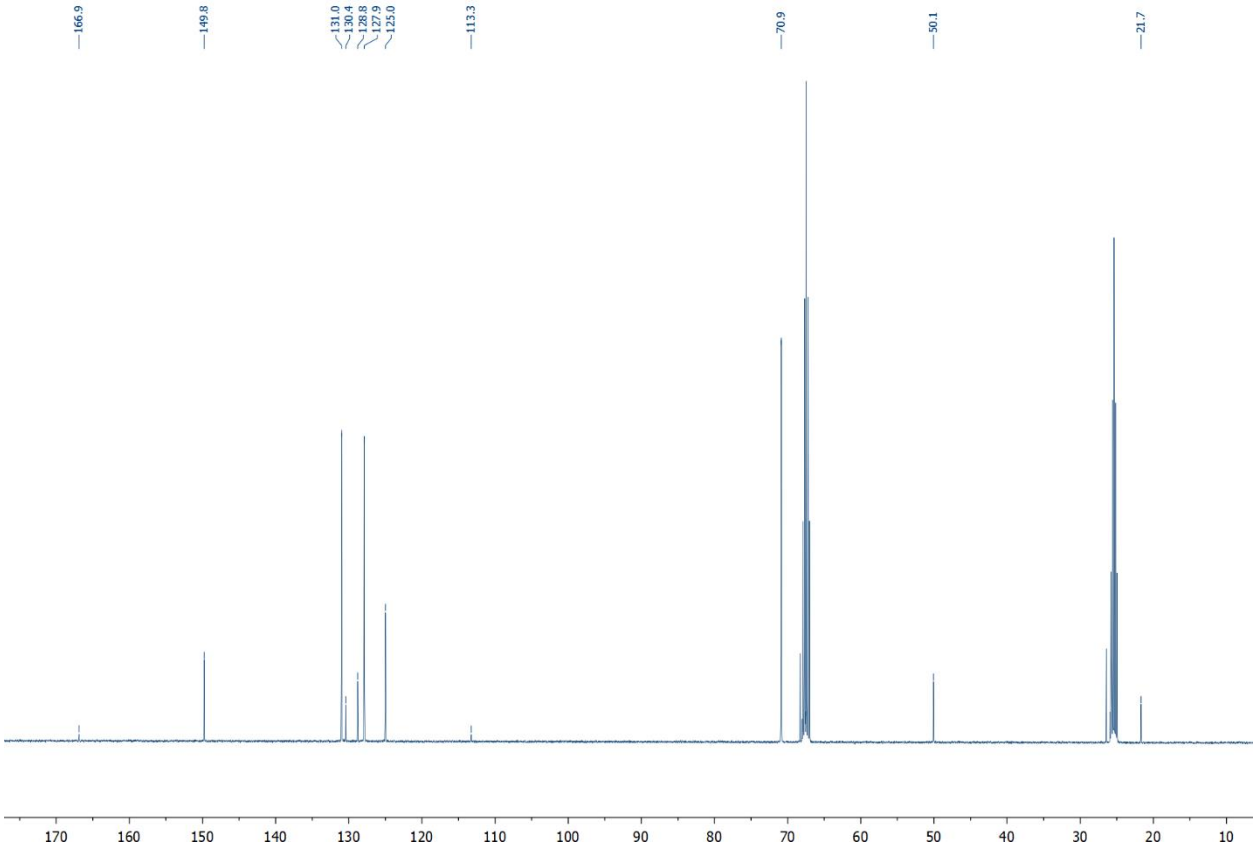


Figure S52. ^{13}C NMR spectrum of **K6** recorded in THF-d_8.

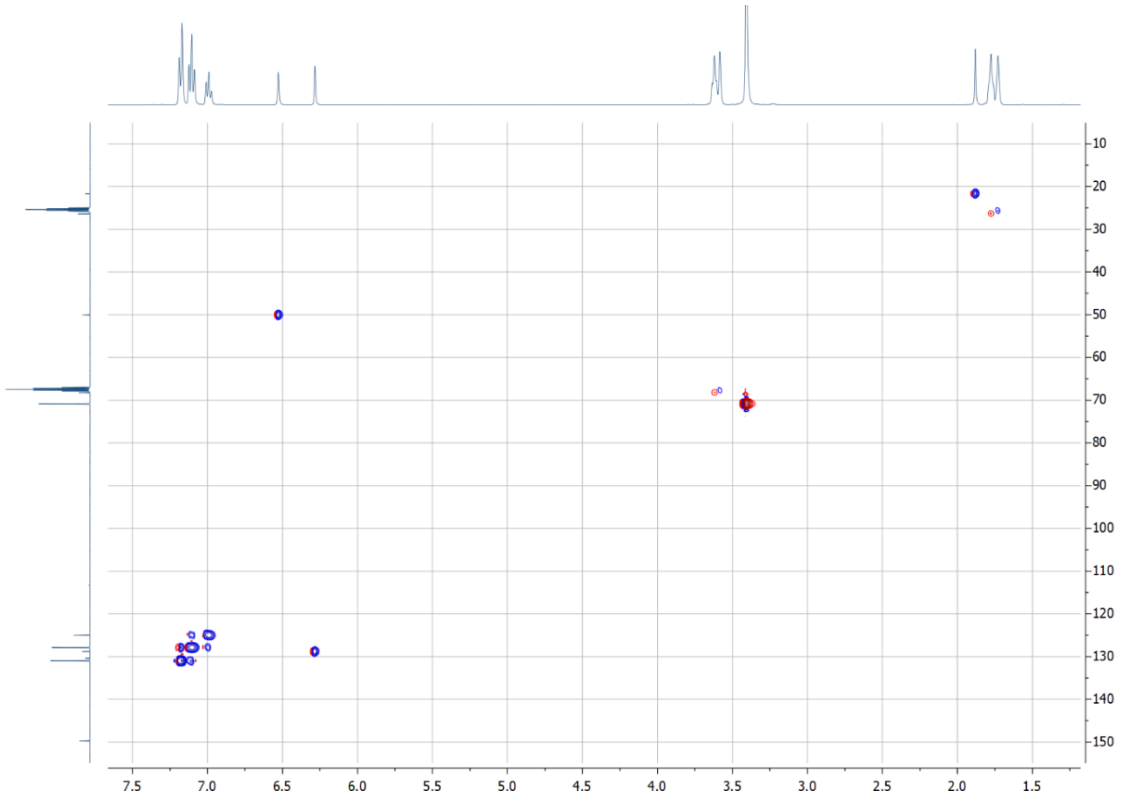


Figure S53. ^{1}H-^{13}C HSQC NMR spectrum of **K6** recorded in THF-d_8.

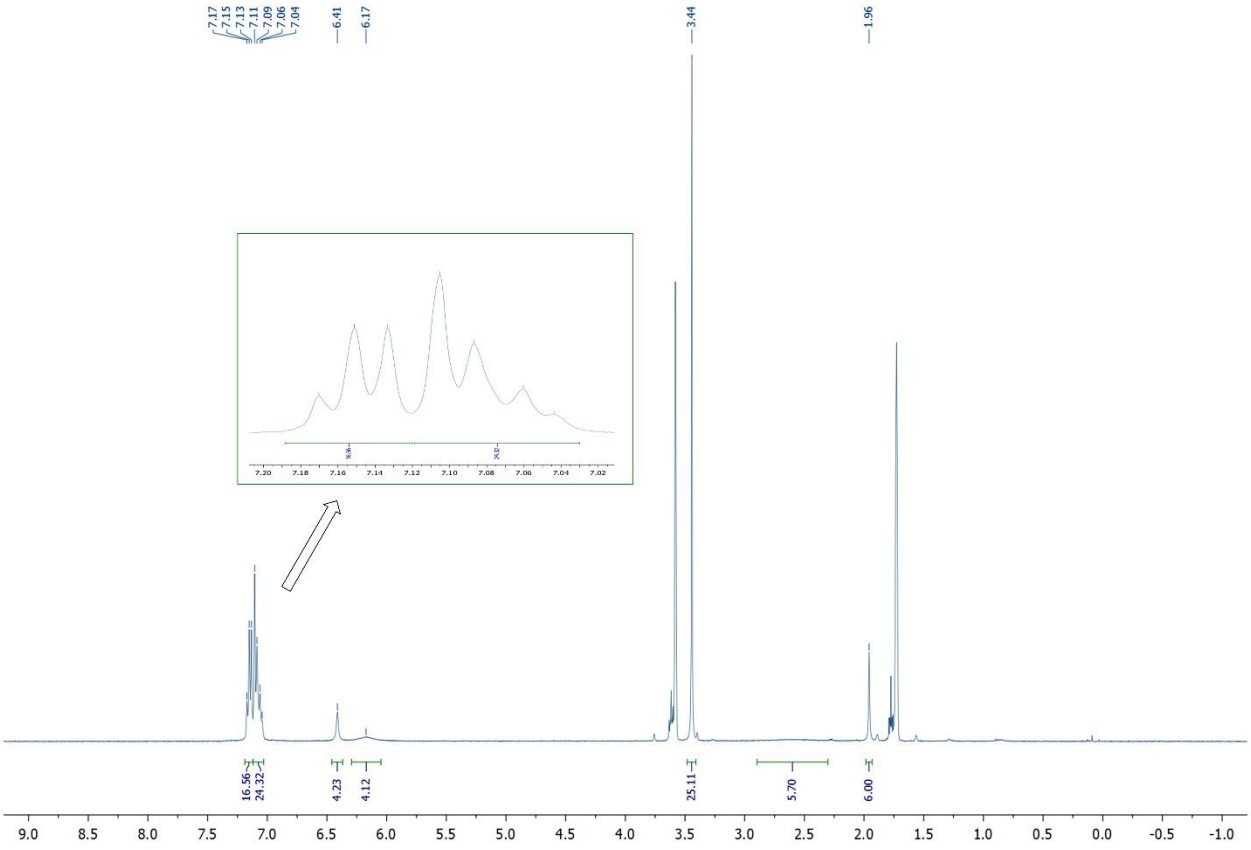


Figure S54. ^{1}H NMR spectrum of **K7** recorded in THF-d_8.

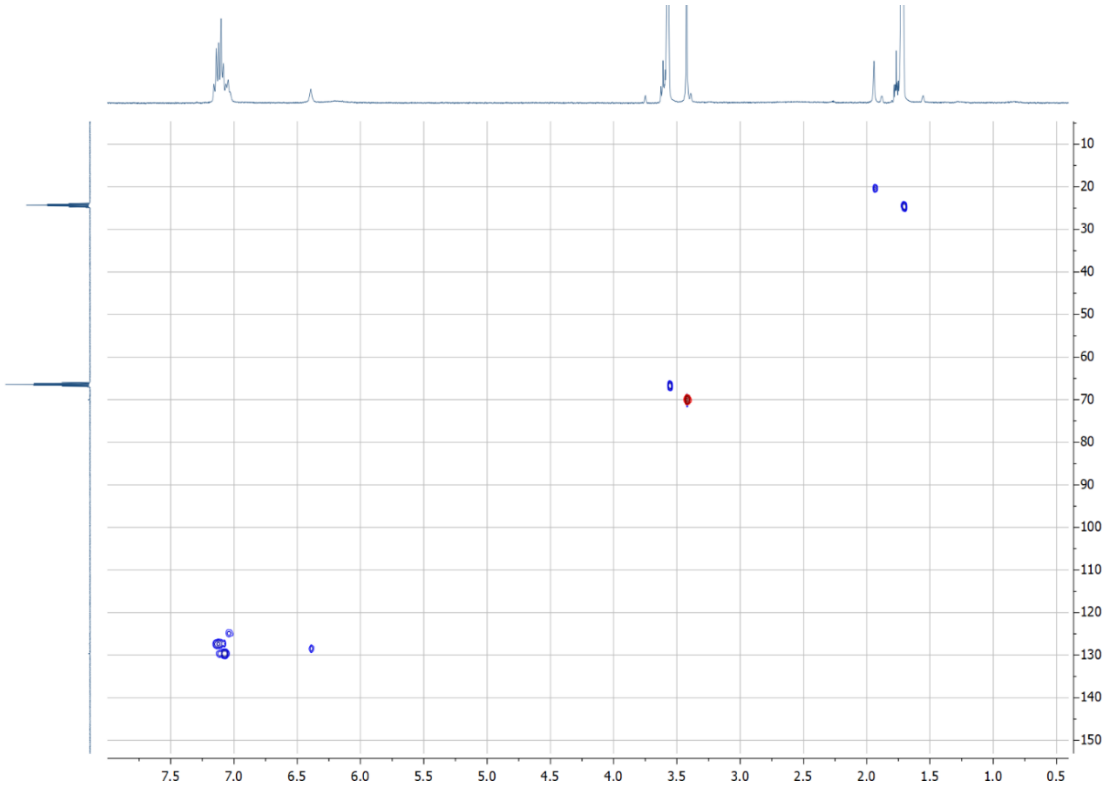


Figure S55. ^{1}H-^{13}C HSQC NMR spectrum of **K7** recorded in THF-d_8.

Additional Photophysical Data

Luminescence decay curves and fitting

Experimental data indicate that nearly all compounds display complex decay kinetics, which are accurately fitted using a bi-exponential function. For example, compounds such as **Na1** and **Na2** exhibit both fast (t_1 ~ 7–34 ns) and slow (t_2 ~ 40–129 ns) components, with the relative amplitudes suggesting multiple emissive states or relaxation channels. The fitting parameters yielded coefficients of determination (R^2) above 0.995, confirming the statistical significance of the bi-exponential model. The resulting decay times are listed in Table S1.

Table S1. Photoluminescence decay times.

Compound	t_1, ns	t_2,ns
K1	4.6	-
K2	8.2	-
K6	3.4	-
K7	2.5	6.0
Li1	3.4	17.0
Li2	2.6	14.9
Li3	2.8	8.9
Na1	33.5	128.6
Na2	7.4	40.1
Na4	3.2	10.0
Na5	3.5	-
Na6	3.0	-

Analysis of these data shows that all decay times lie in the nanosecond range, indicating the fluorescent nature of the emission and the singlet character of the transitions, including charge-transfer (CT) states. The presence of two decay components in some compounds suggests multiple relaxation pathways or different types of excited states.

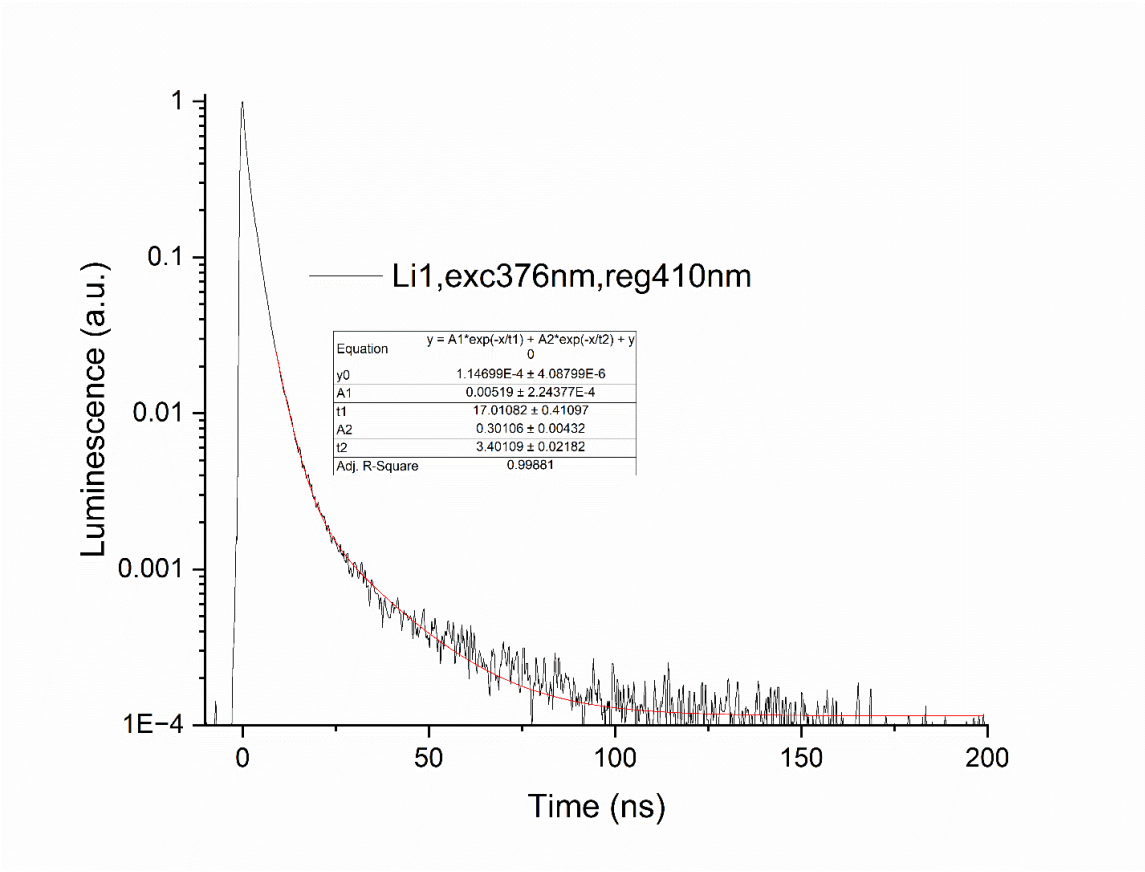


Figure S56. Luminescence decay of **Li1** recorded at 410 nm at room temperature.

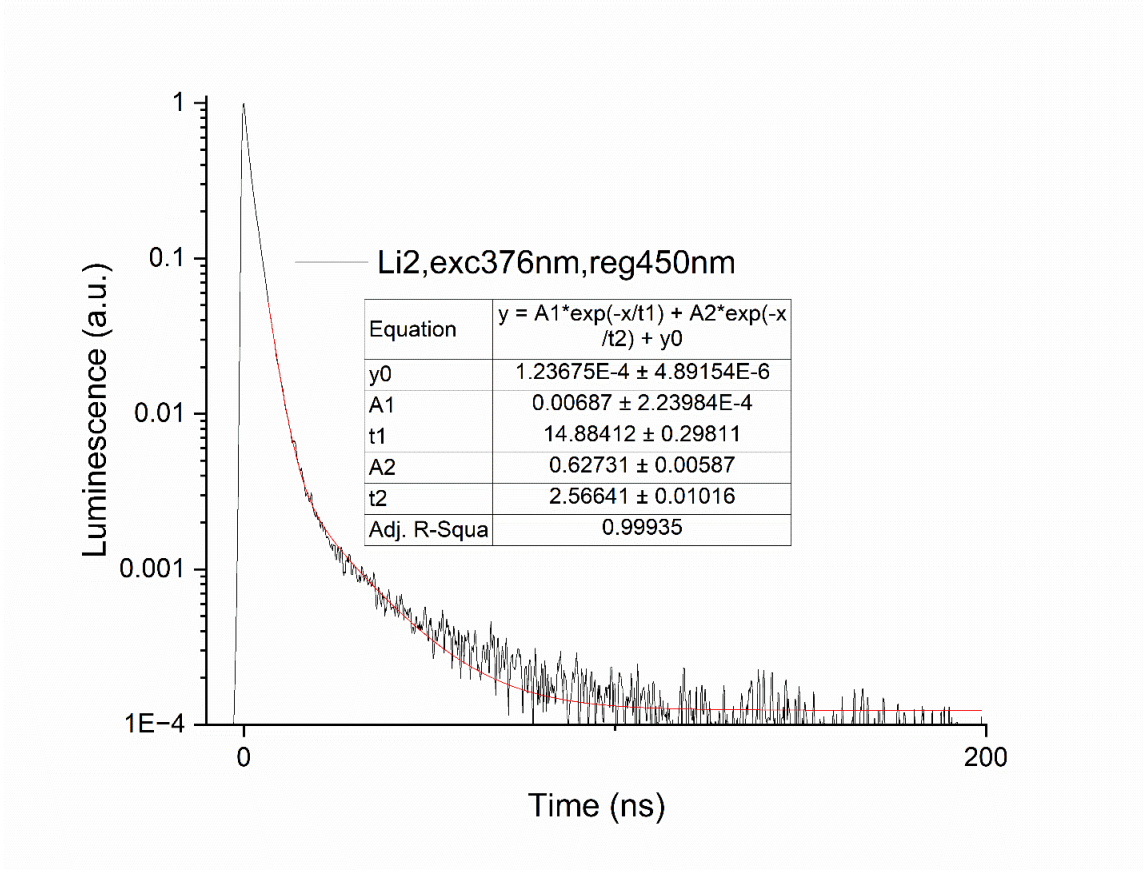


Figure S57. Luminescence decay of **Li2** recorded at 450 nm at room temperature.

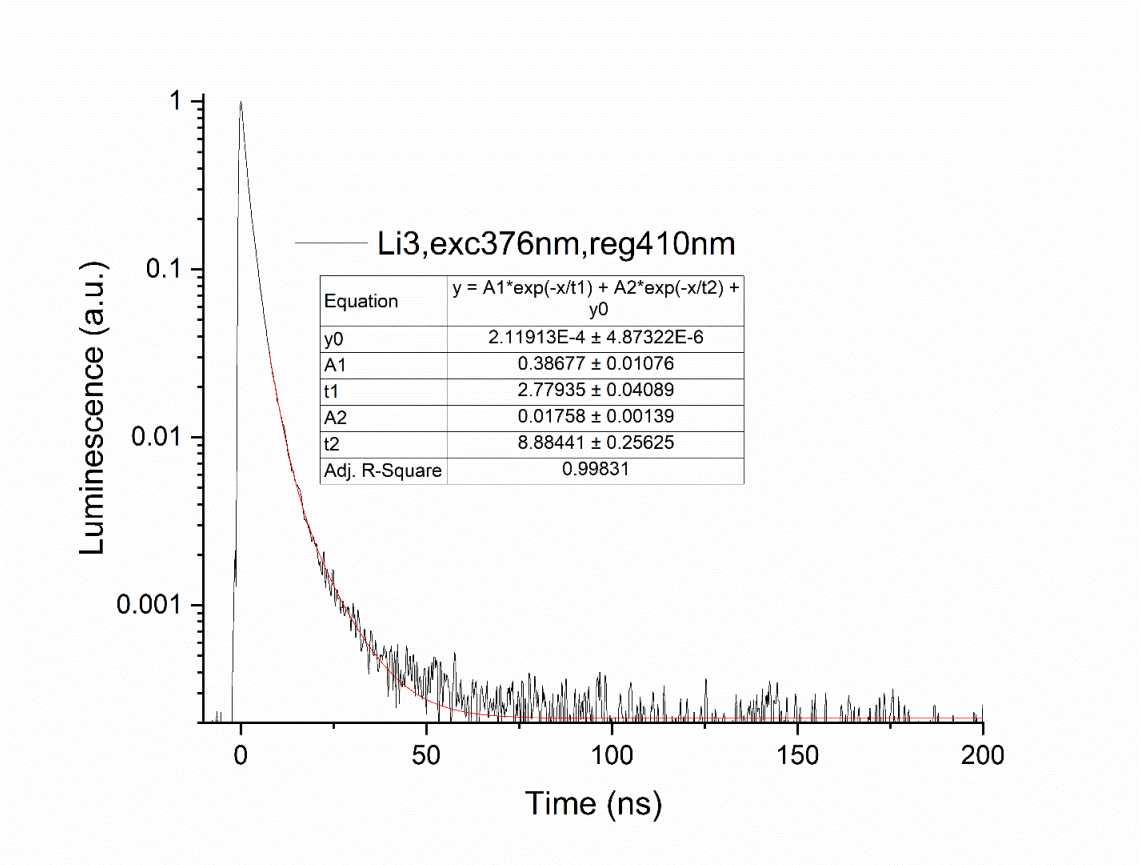


Figure S58. Luminescence decay of **Li3** recorded at 410 nm at room temperature.

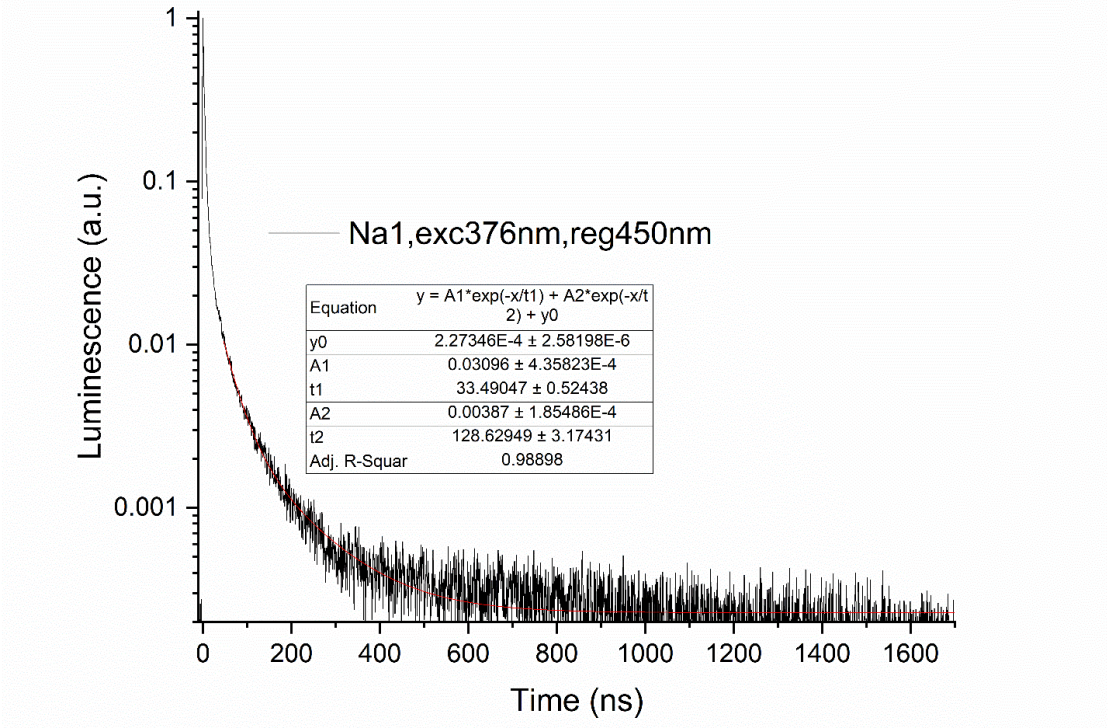


Figure S59. Luminescence decay of **Na1** recorded at 450 nm at room temperature.

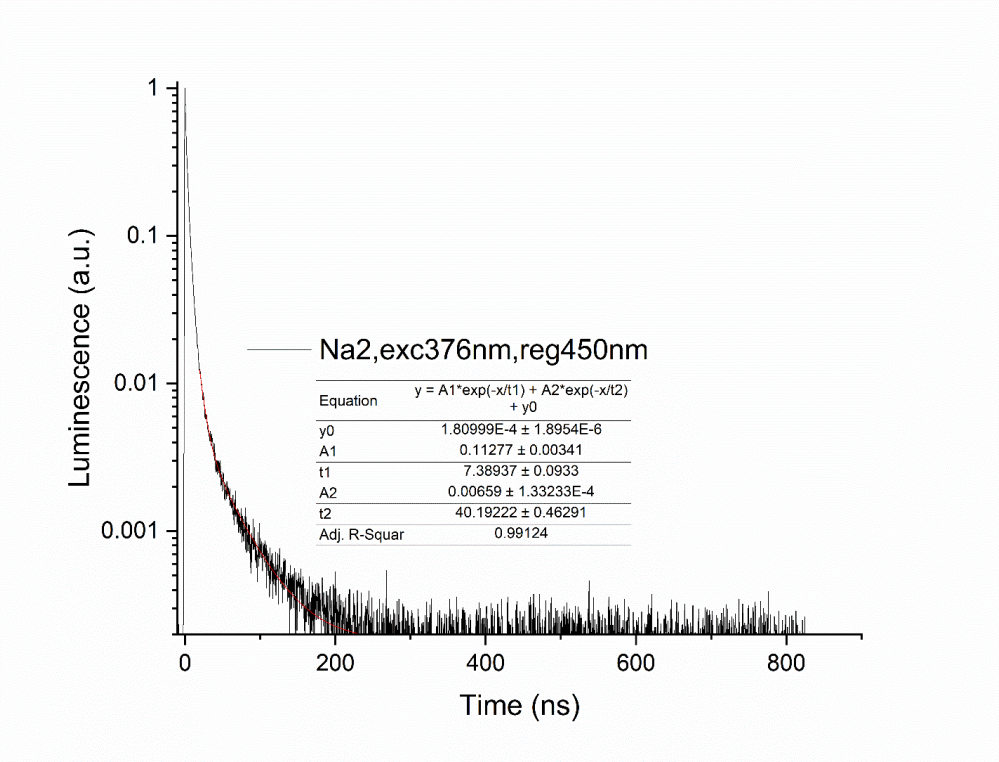


Figure S60. Luminescence decay of **Na2** recorded at 450 nm at room temperature.

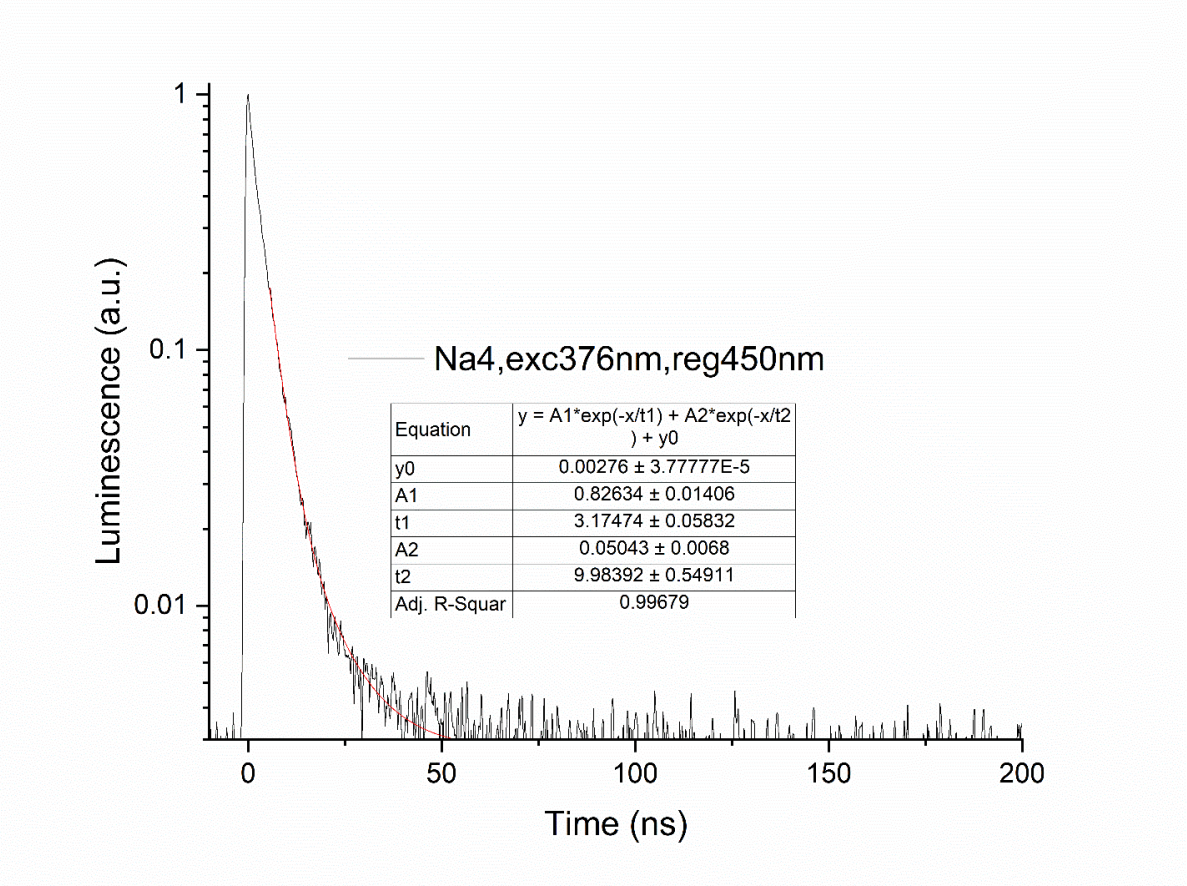


Figure S61. Luminescence decay of **Na4** recorded at 450 nm at room temperature.

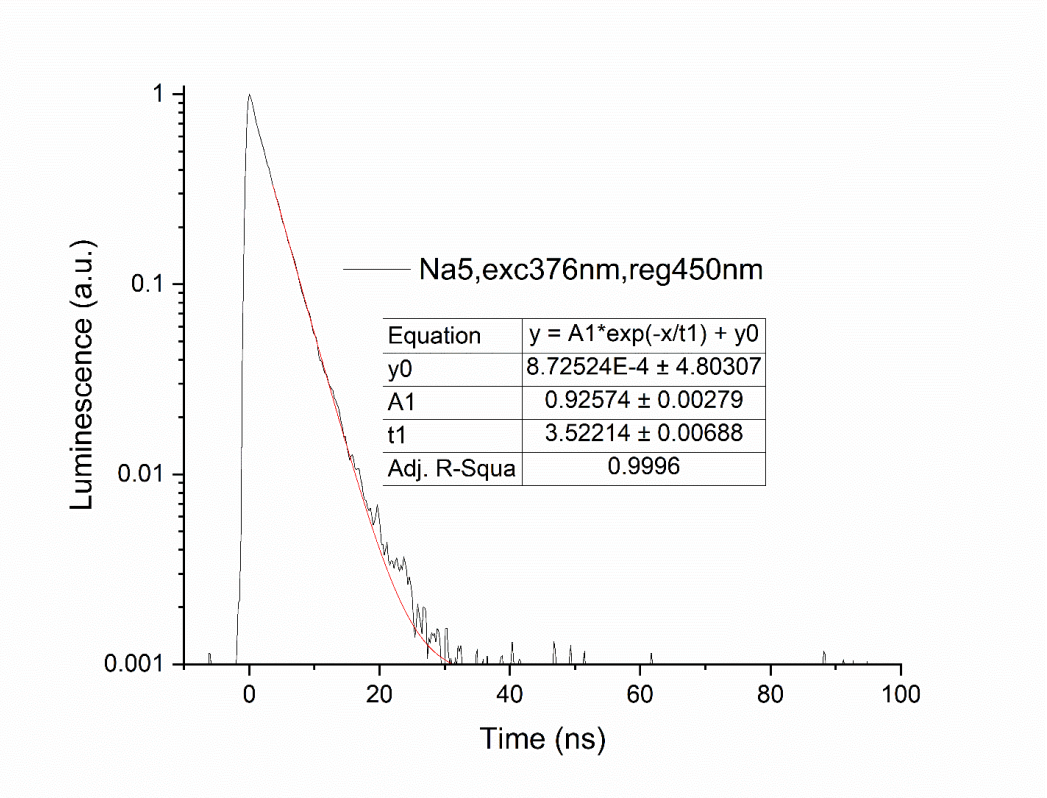


Figure S62. Luminescence decay of **Na5** recorded at 450 nm at room temperature.

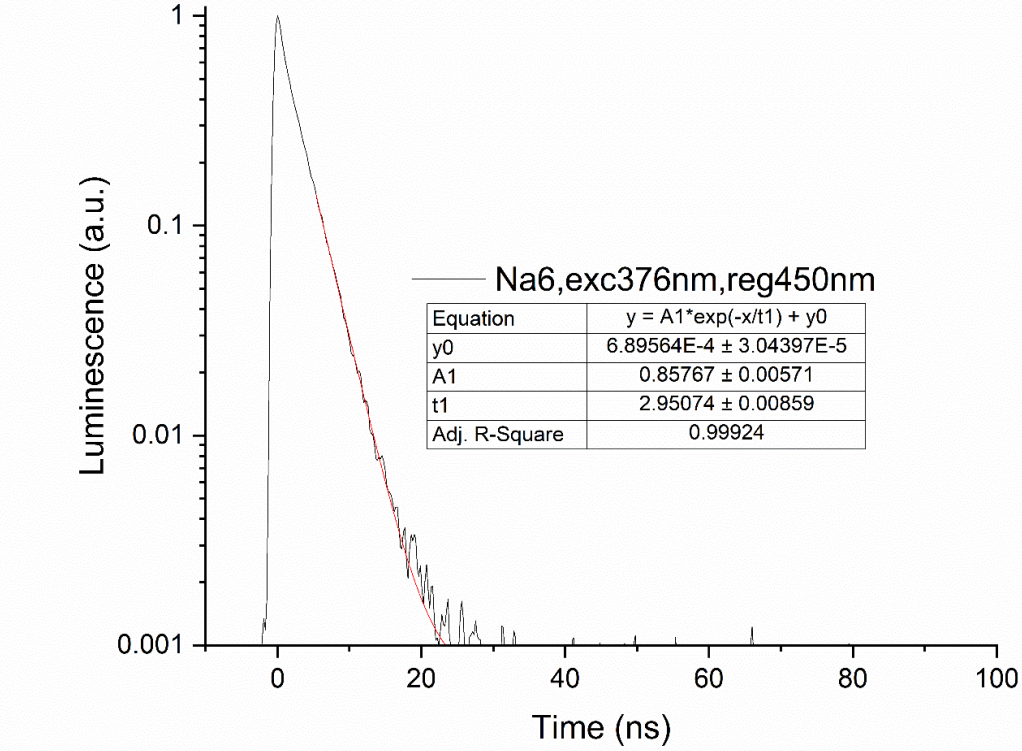


Figure S63. Luminescence decay of **Na6** recorded at 450 nm at room temperature.

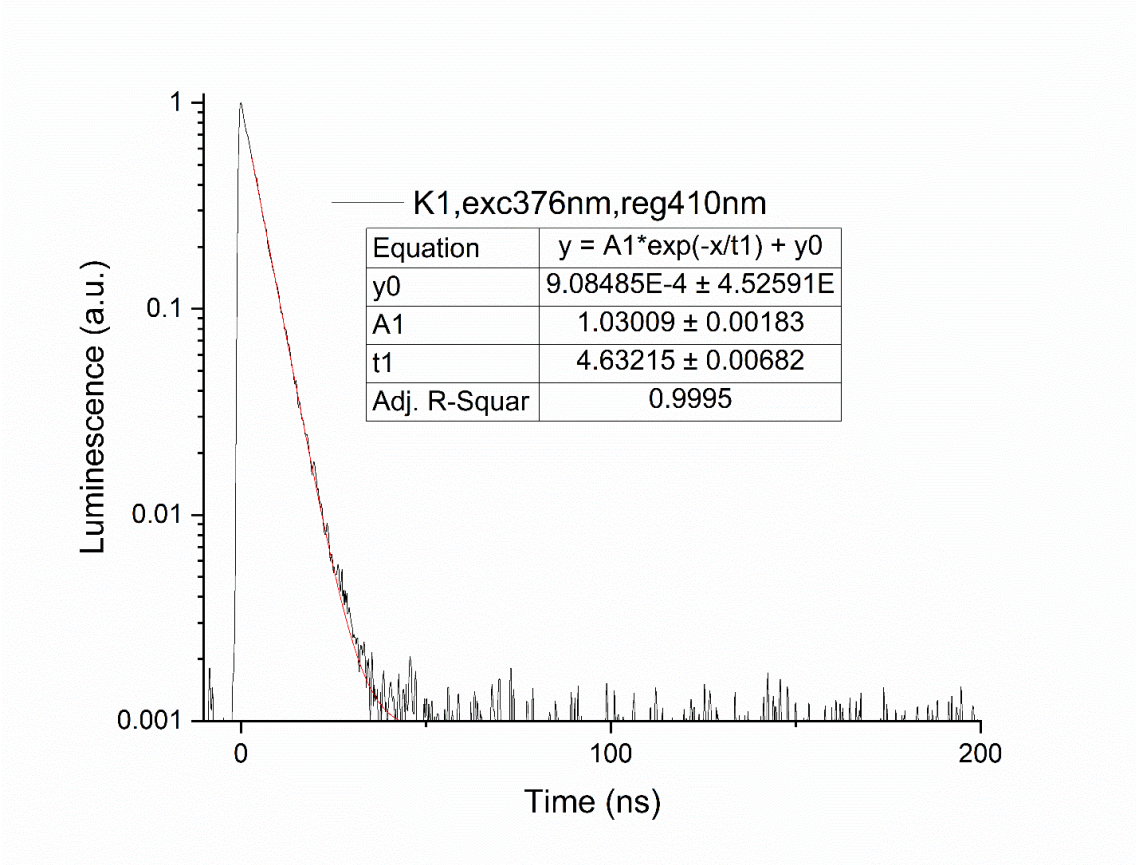


Figure S64. Luminescence decay of **K1** recorded at 410 nm at room temperature.

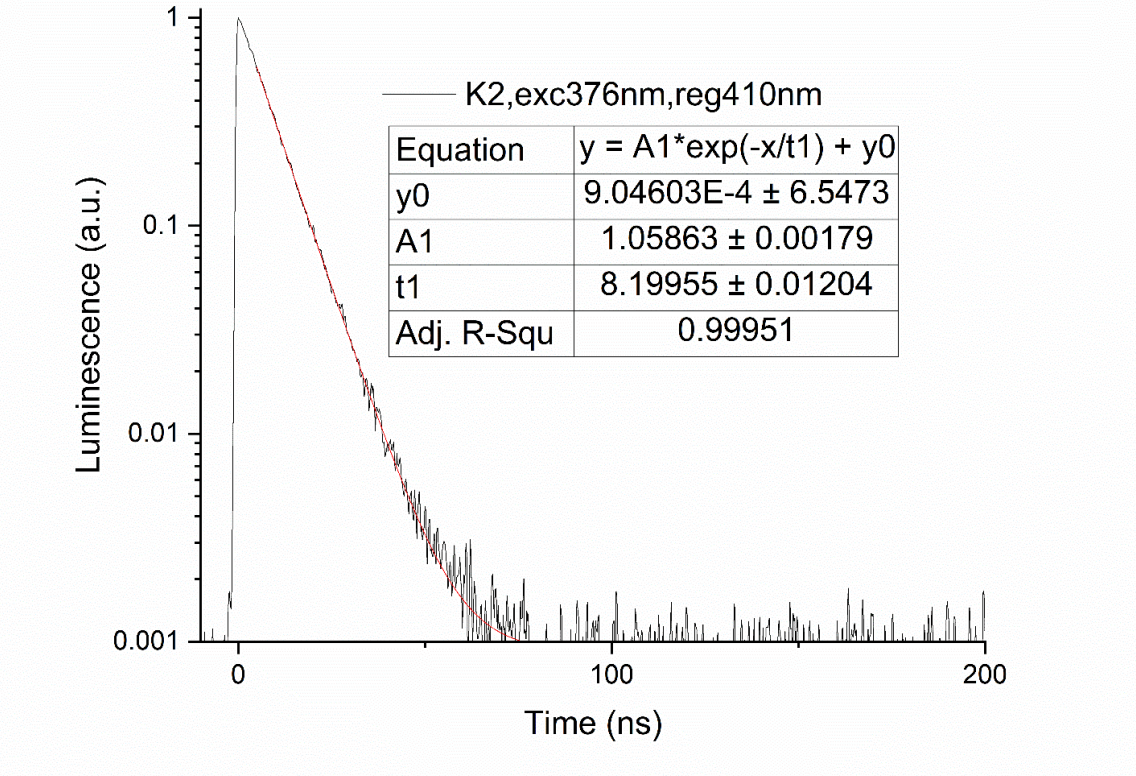


Figure S65. Luminescence decay of **K2** recorded at 410 nm at room temperature.

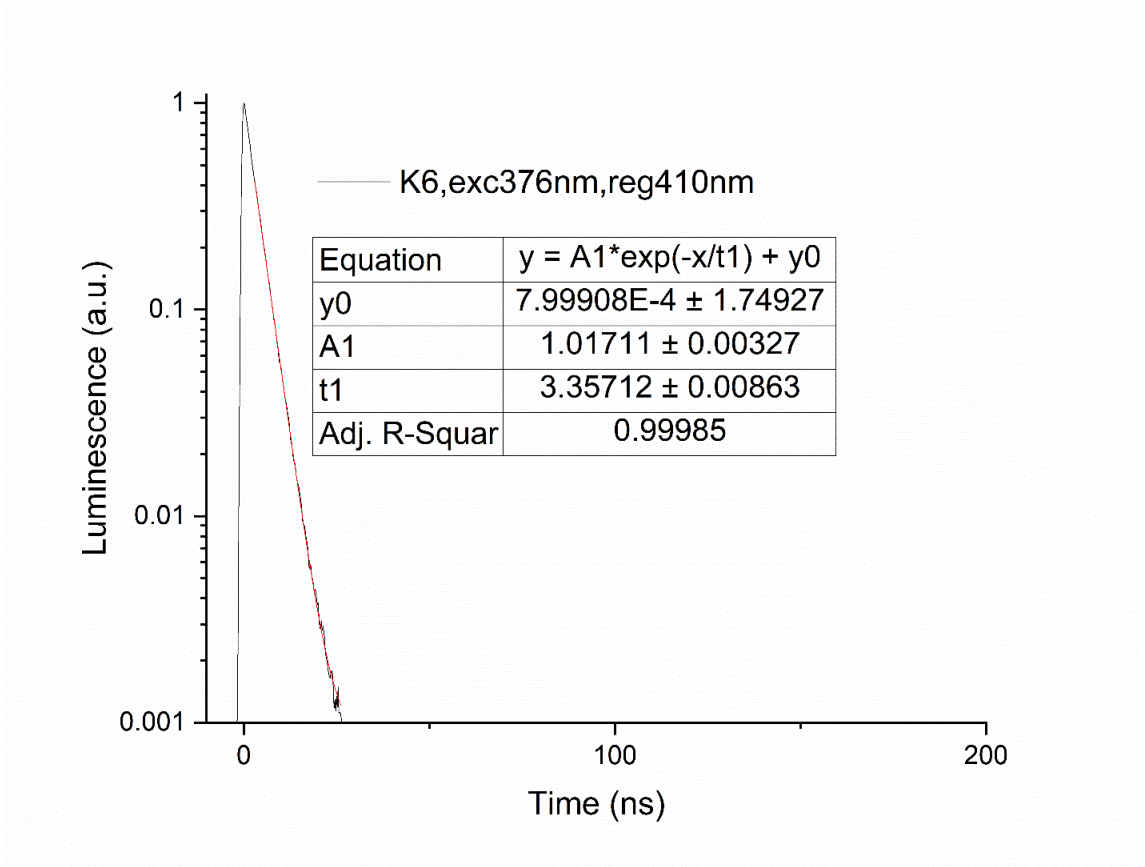


Figure S66. Luminescence decay of **K6** recorded at 410 nm at room temperature.

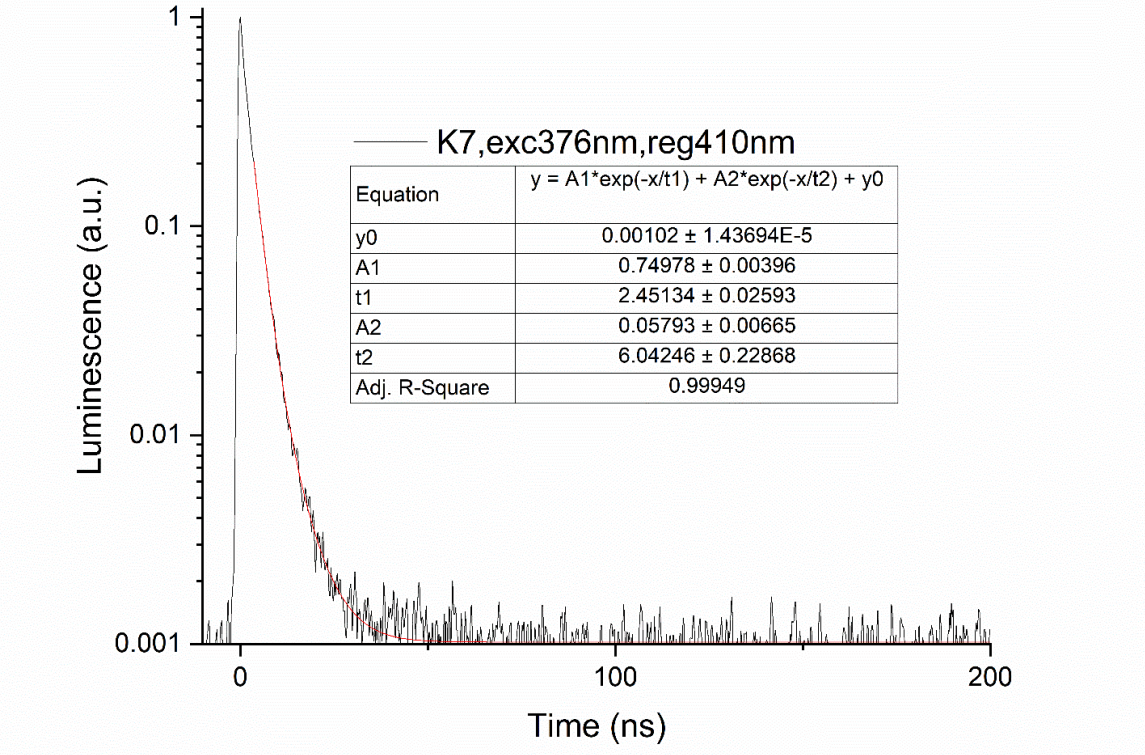


Figure S67. Luminescence decay of **K7** recorded at 410 nm at room temperature.

Luminescence decay curves at various emission wavelengths

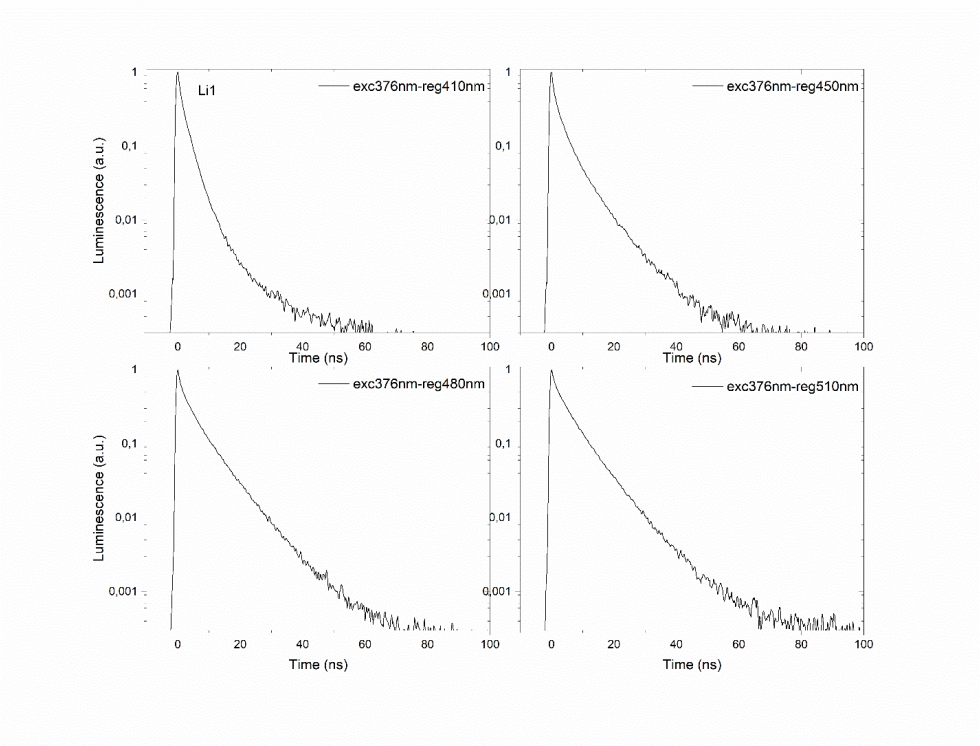


Figure S68. Luminescence decays of **Li1** at various emission wavelengths recorded at room temperature.

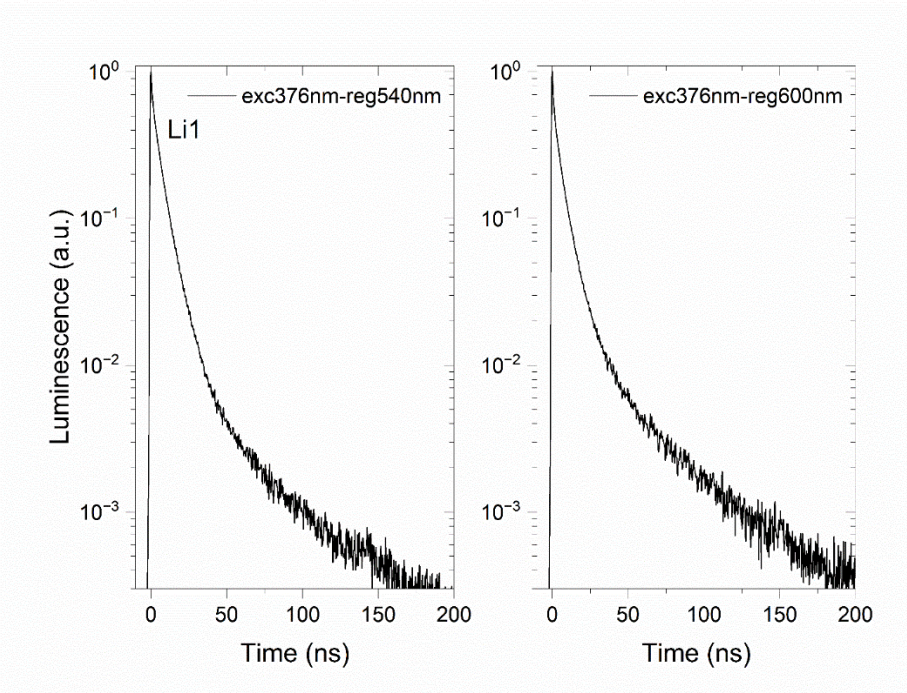


Figure S69. Luminescence decays of **Li1** at various emission wavelengths recorded at room temperature.

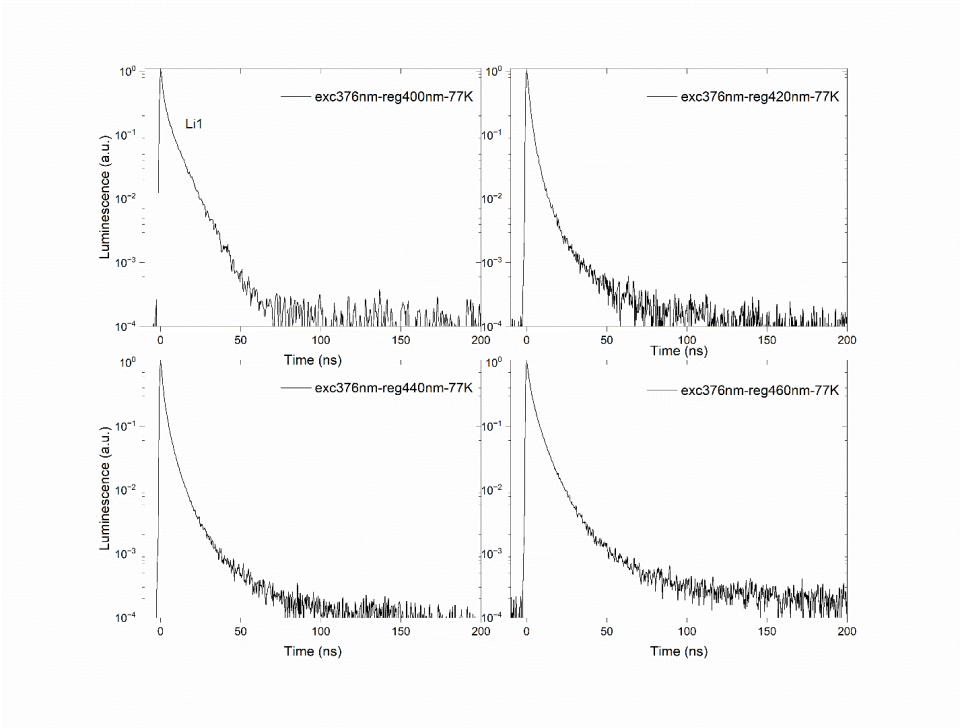


Figure S70. Luminescence decays of **Li1** at various emission wavelengths recorded at 77 K.

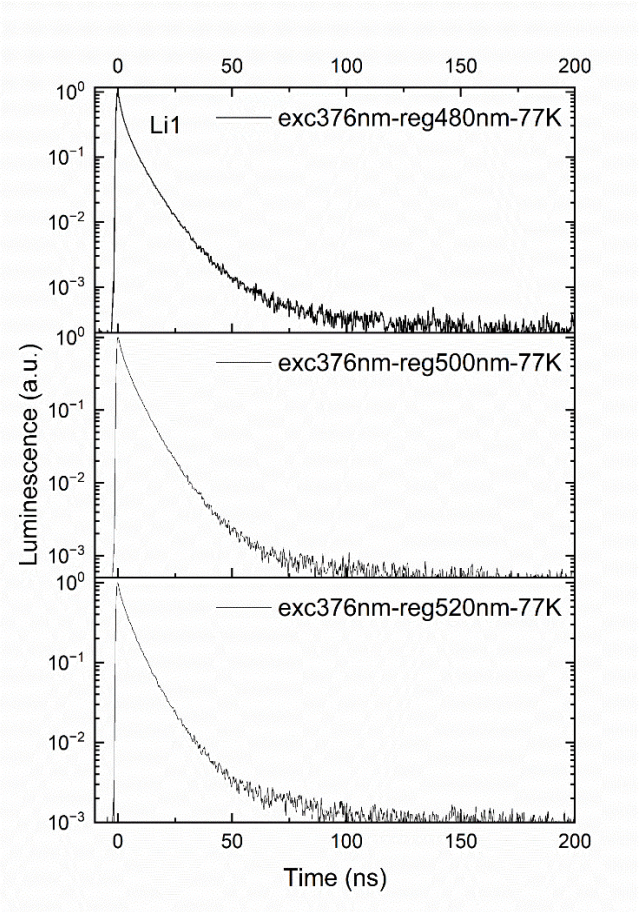


Figure S71. Luminescence decays of **Li1** at various emission wavelengths recorded at 77 K.

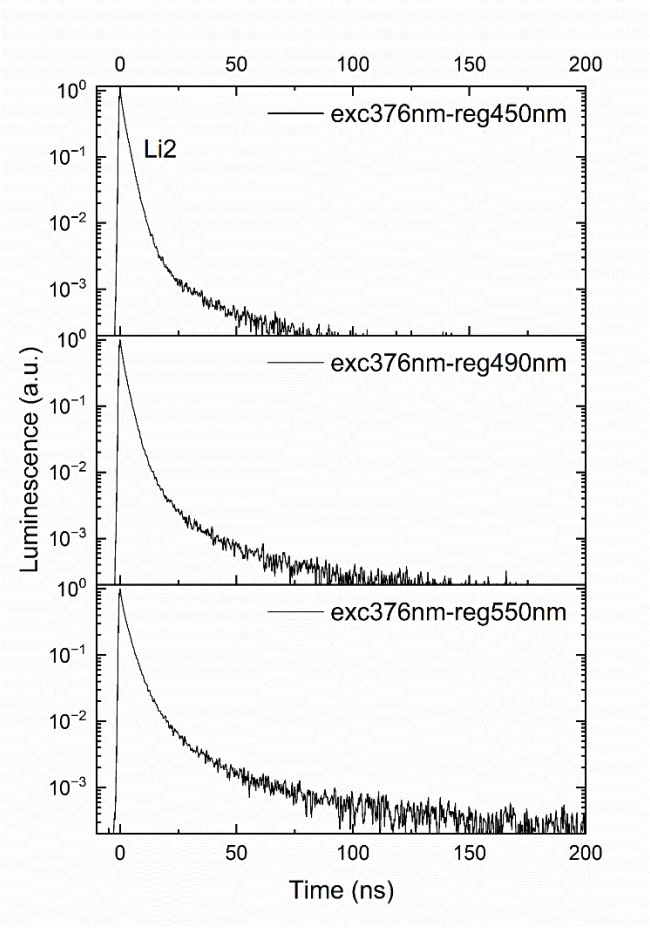


Figure S72. Luminescence decays of **Li2** at various emission wavelengths recorded at room temperature.

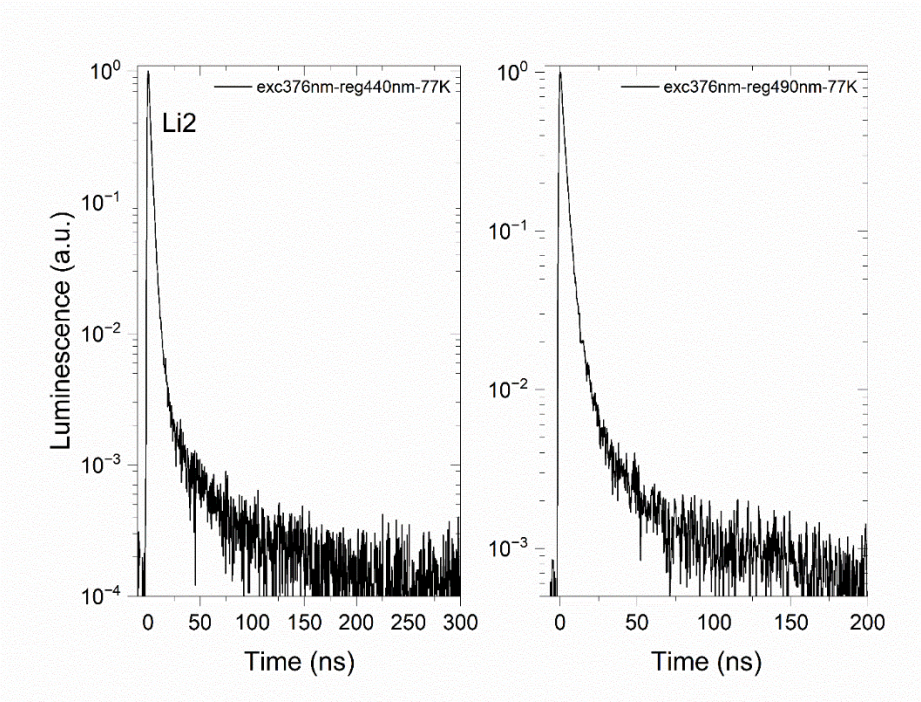


Figure S73. Luminescence decays of **Li2** at various emission wavelengths recorded at 77 K.

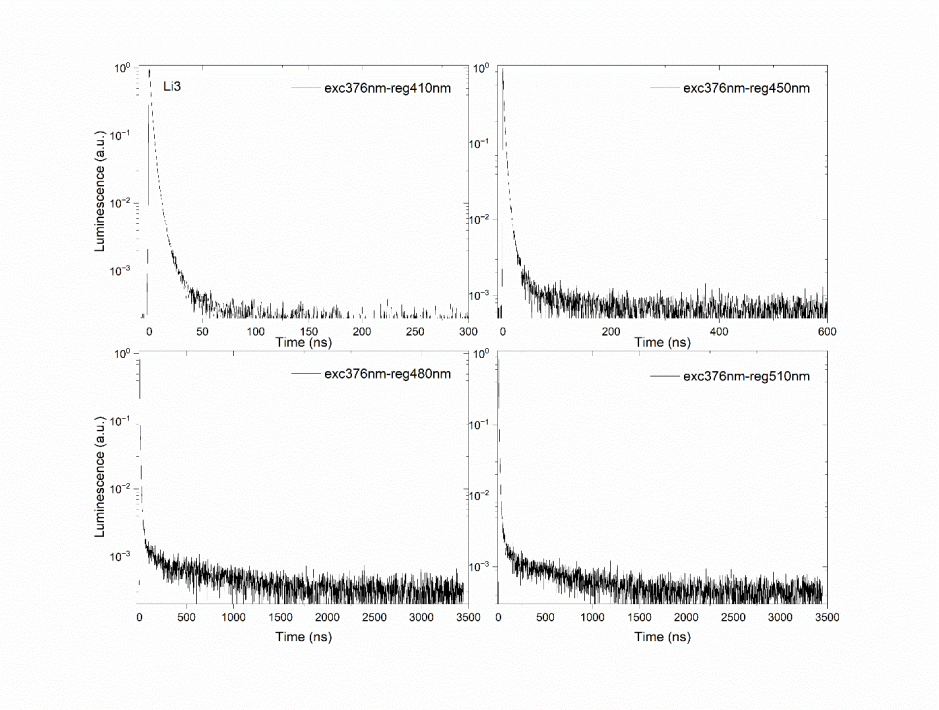


Figure S74. Luminescence decays of **Li3** at various emission wavelengths recorded at room temperature.

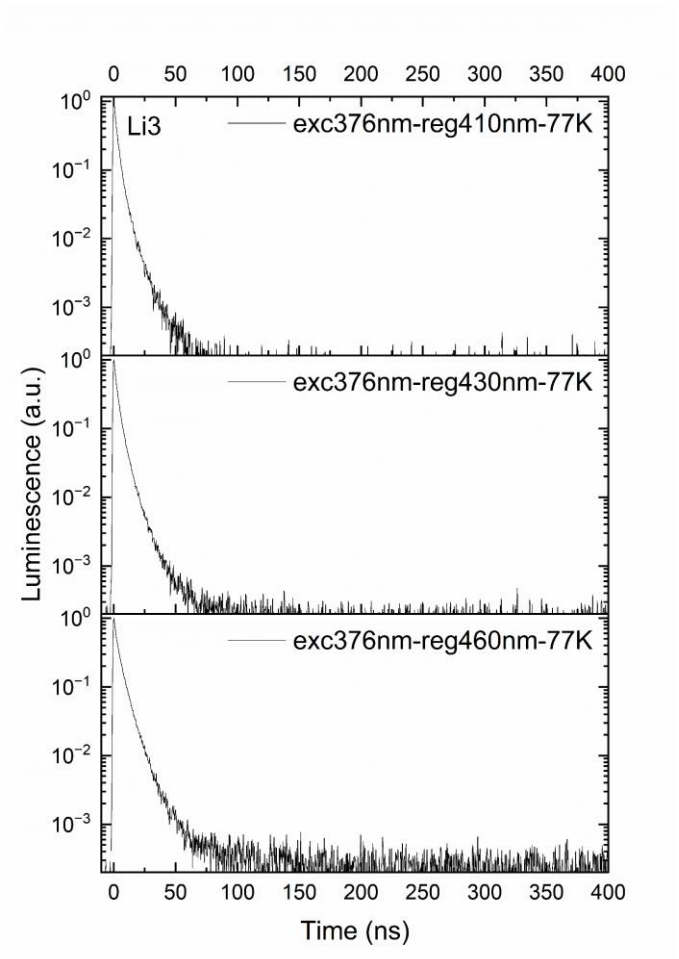


Figure S75. Luminescence decays of **Li3** at various emission wavelengths recorded at 77 K.

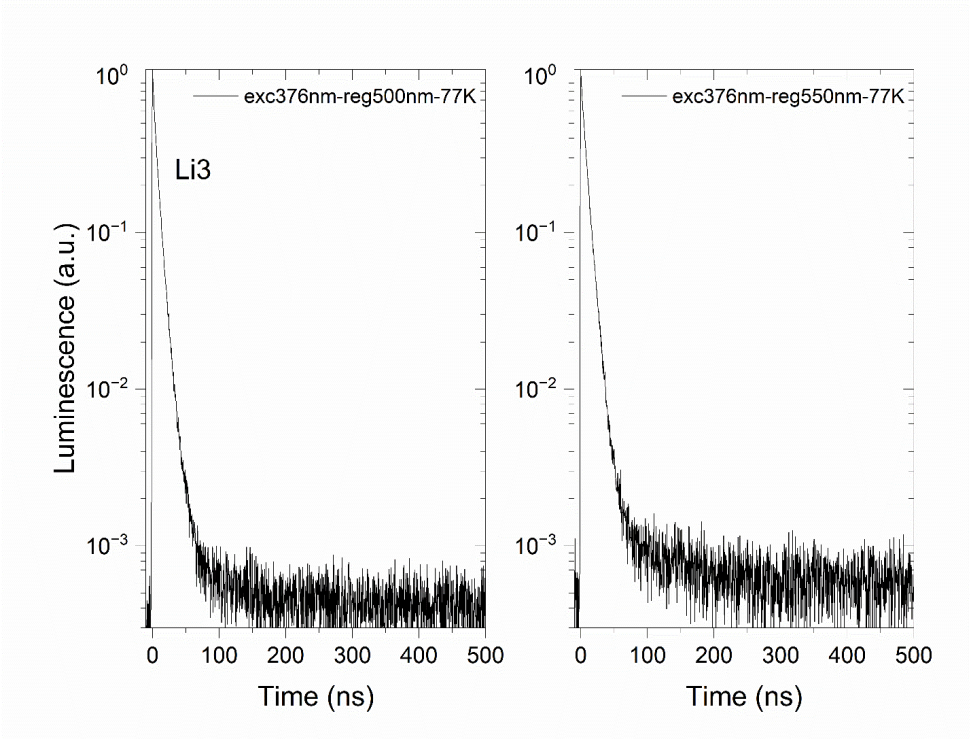


Figure S76. Luminescence decays of **Li3** at various emission wavelengths recorded at 77 K.

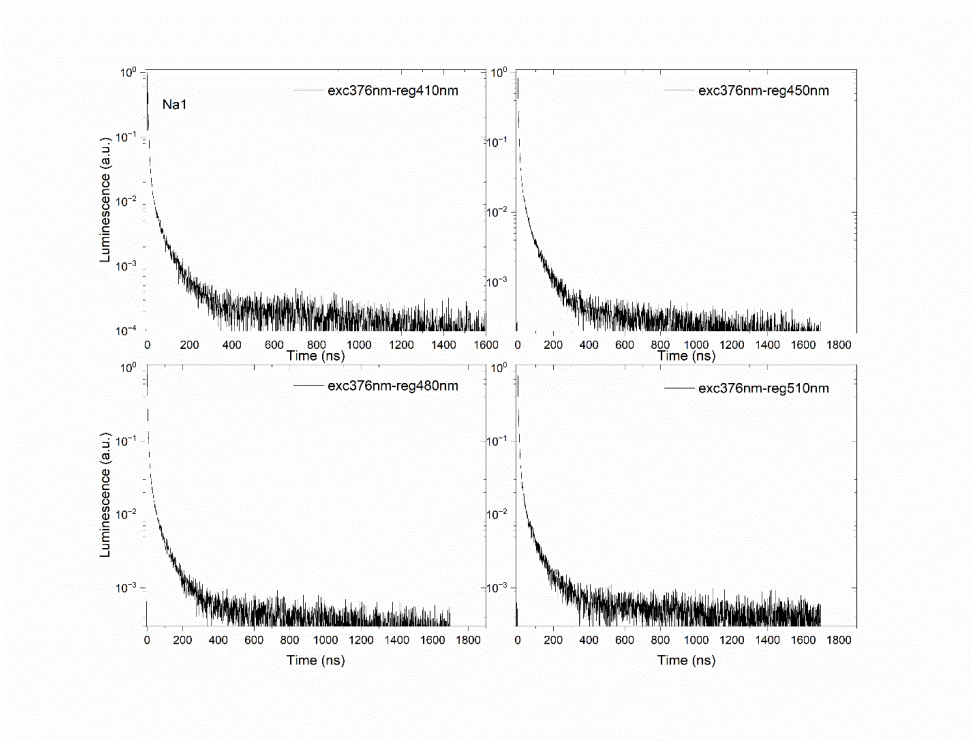


Figure S77. Luminescence decays of **Na1** at various emission wavelengths recorded at room temperature.

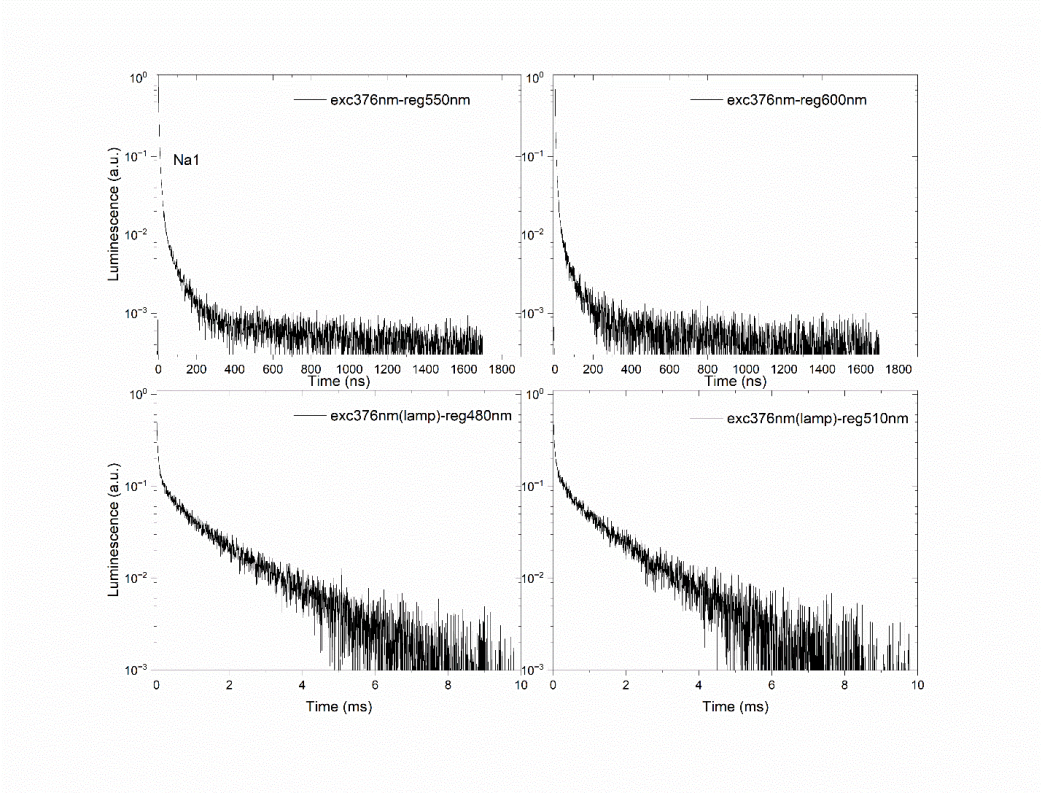


Figure S78. Luminescence decays of **Na1** at various emission wavelengths recorded at room temperature.

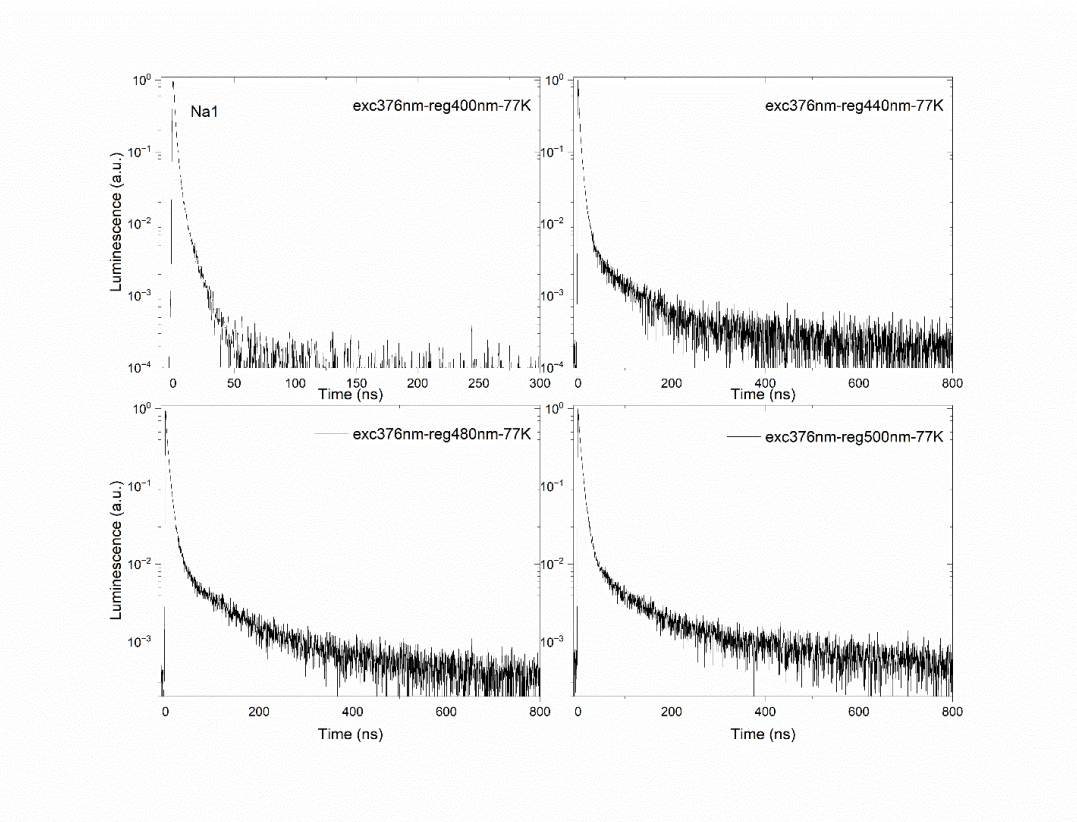


Figure S79. Luminescence decays of **Na1** at various emission wavelengths recorded at 77 K.

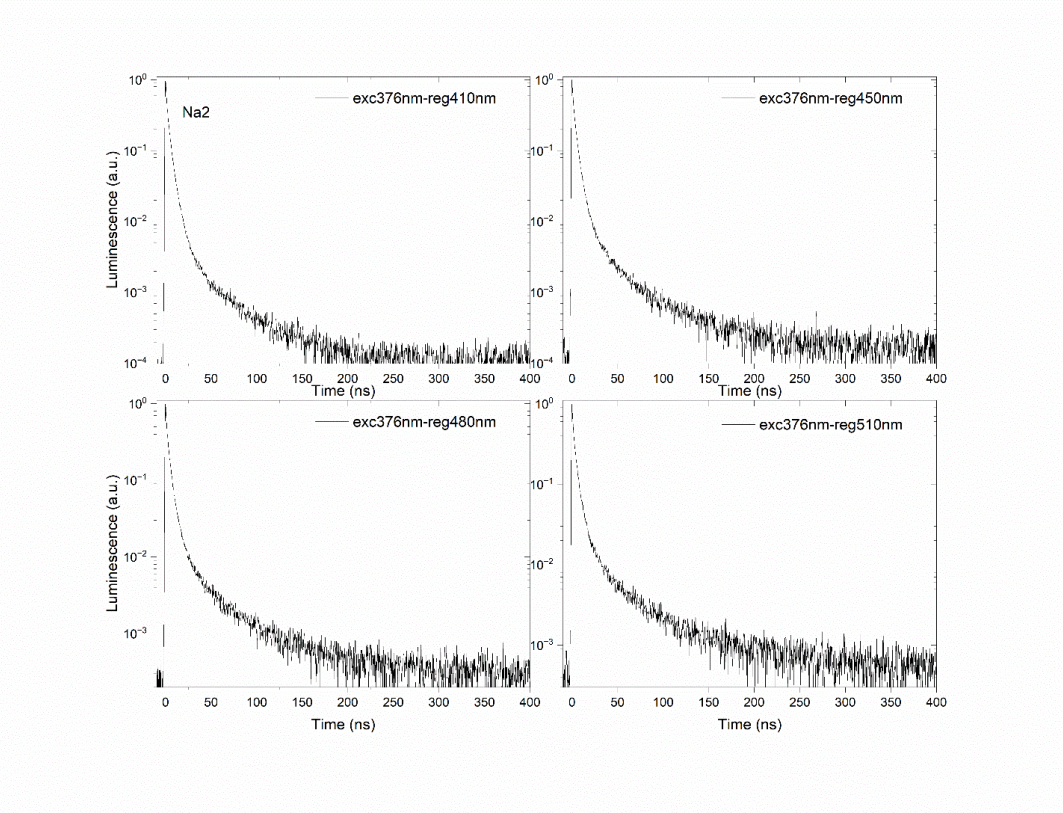


Figure S80. Luminescence decays of **Na2** at various emission wavelengths recorded at room temperature.

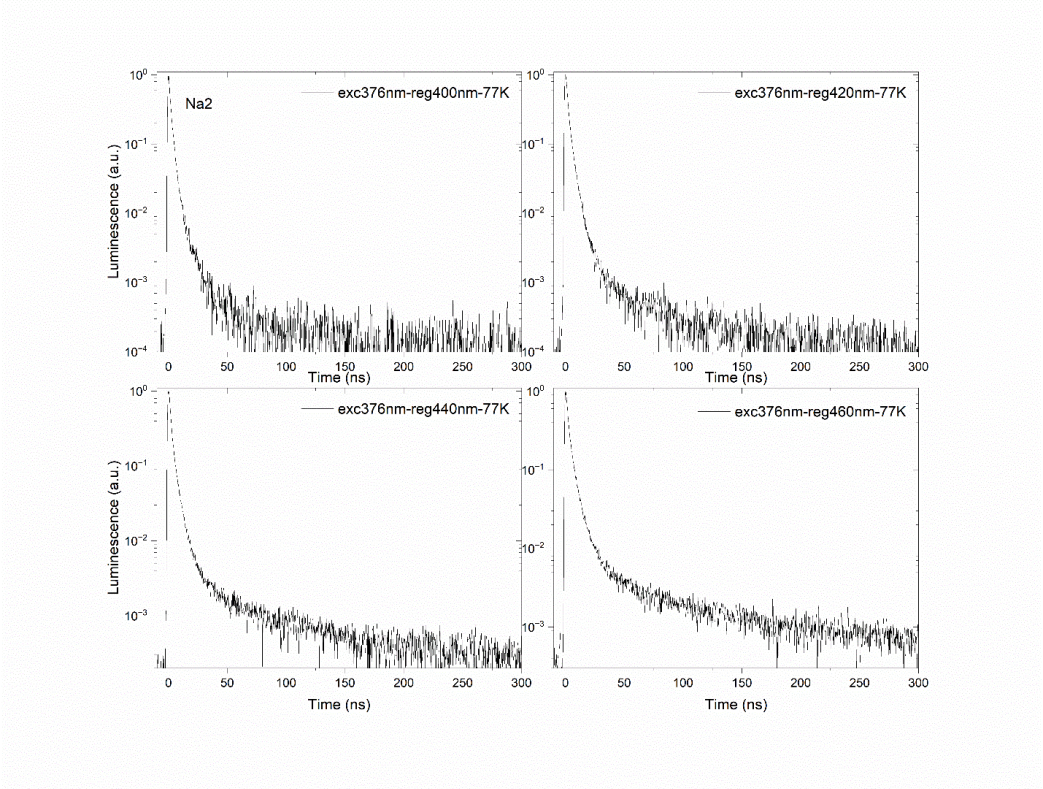


Figure S81. Luminescence decays of **Na2** at various emission wavelengths recorded at 77 K.

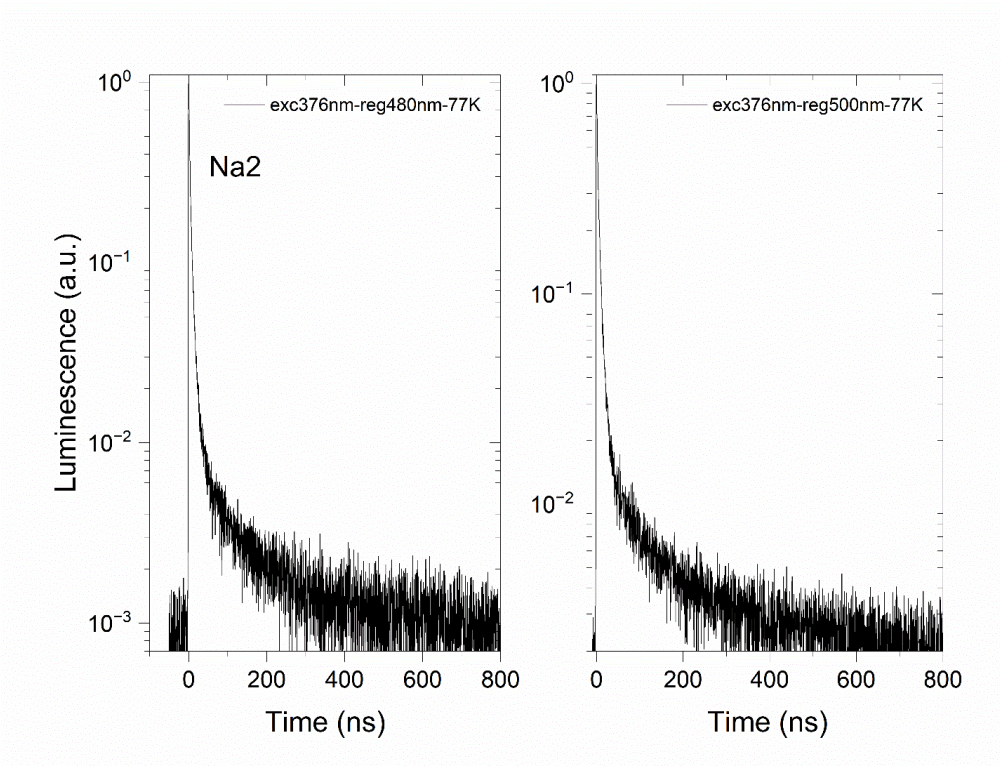


Figure S82. Luminescence decays of **Na2** at various emission wavelengths recorded at 77 K.

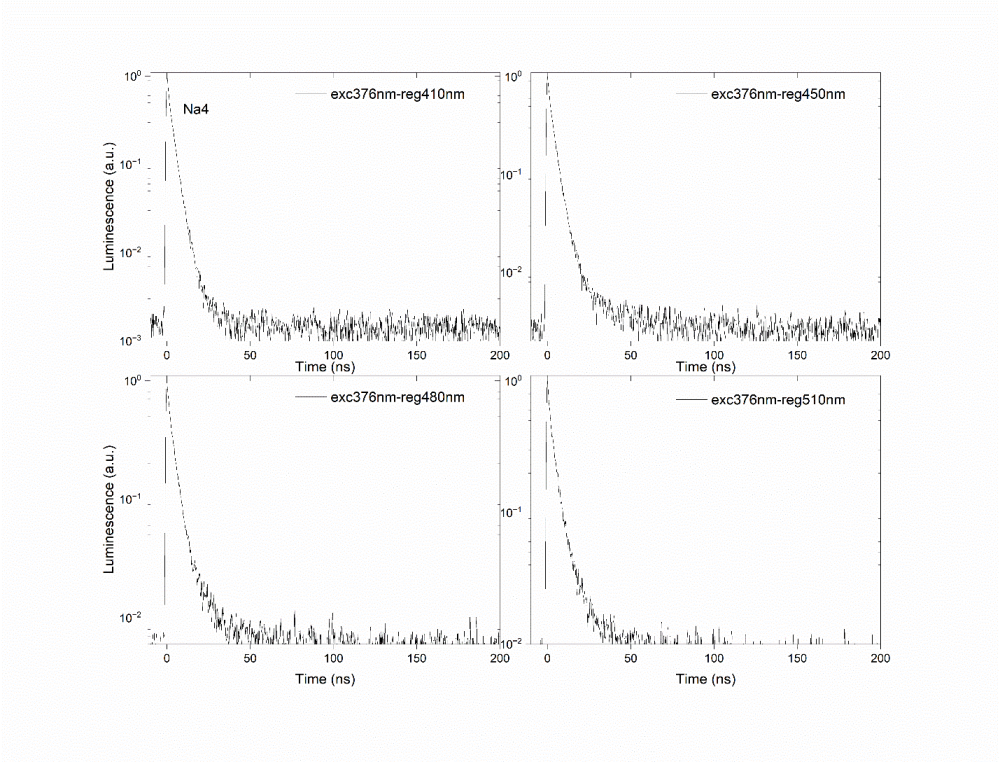


Figure S83. Luminescence decays of **Na4** at various emission wavelengths recorded at room temperature.

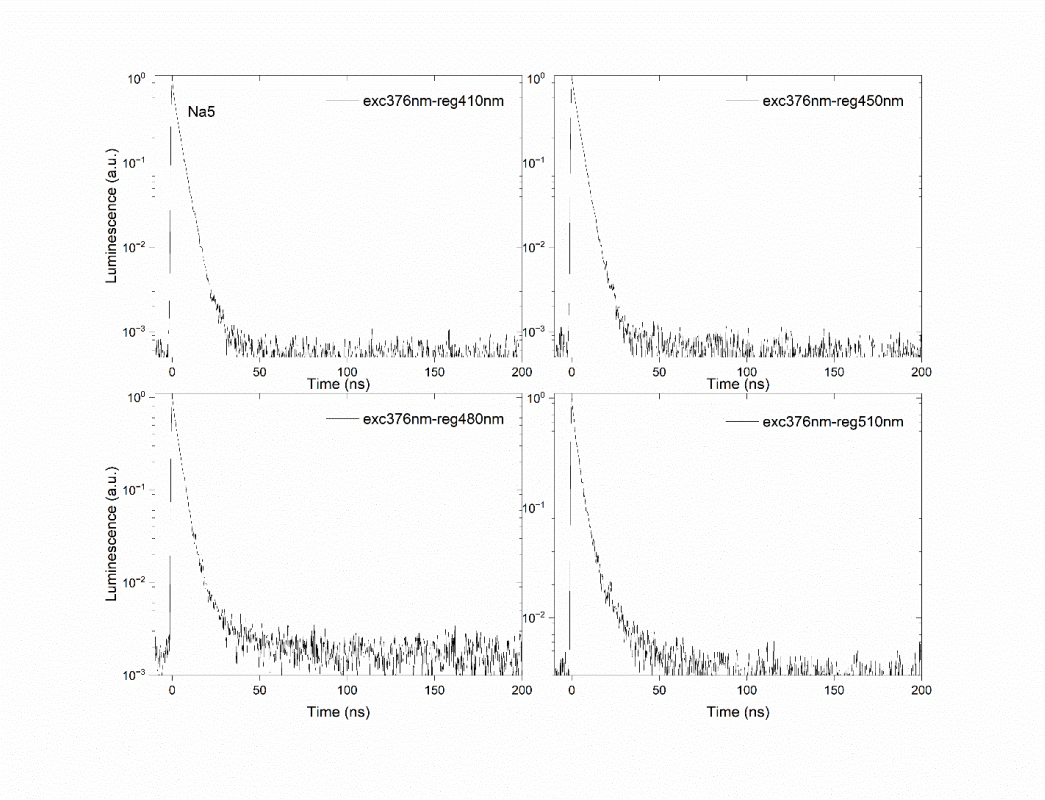


Figure S84. Luminescence decays of **Na5** at various emission wavelengths recorded at room temperature.

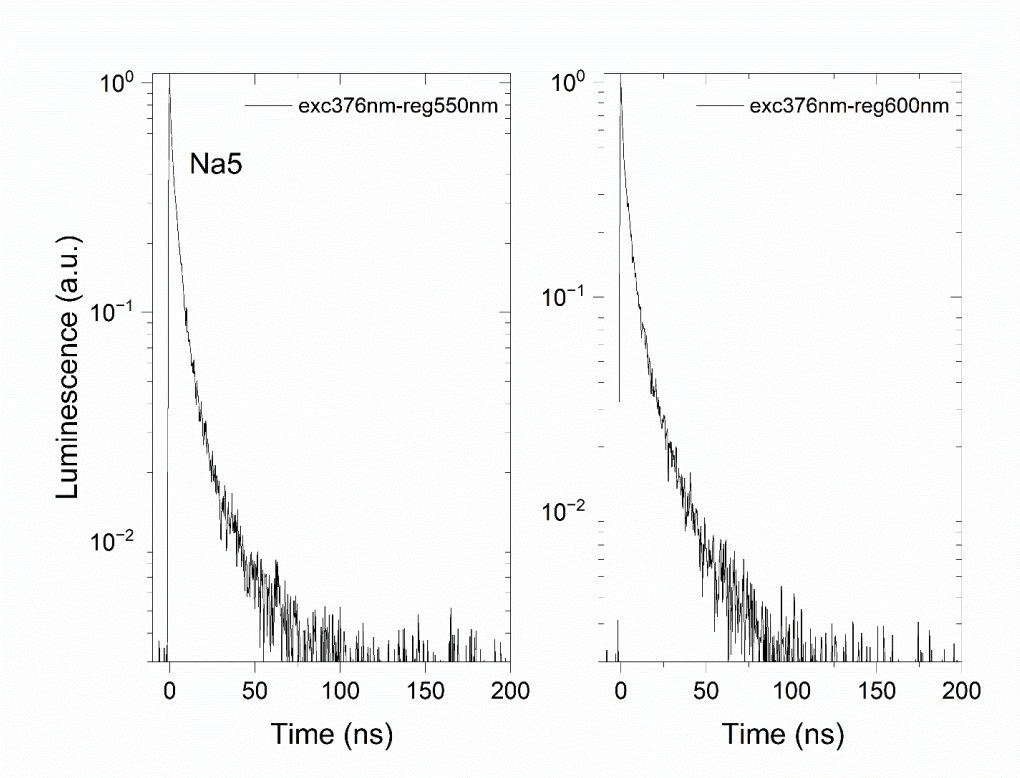


Figure S85. Luminescence decays of **Na5** at various emission wavelengths recorded at room temperature.

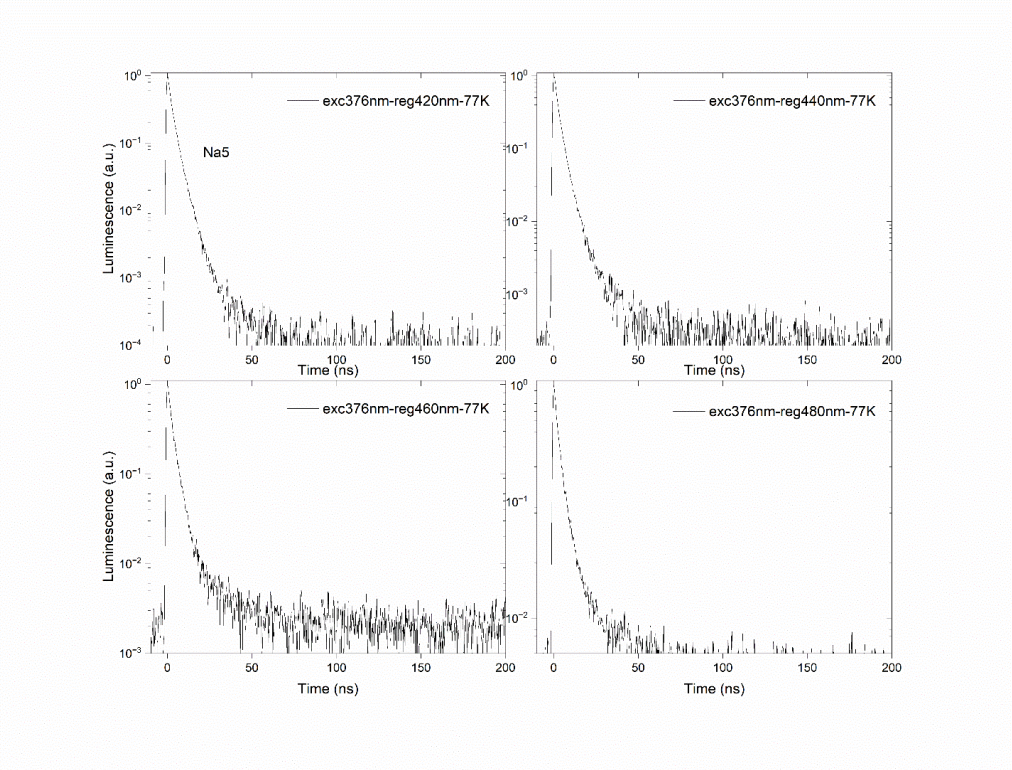


Figure S86. Luminescence decays of **Na5** at various emission wavelengths recorded at 77 K.

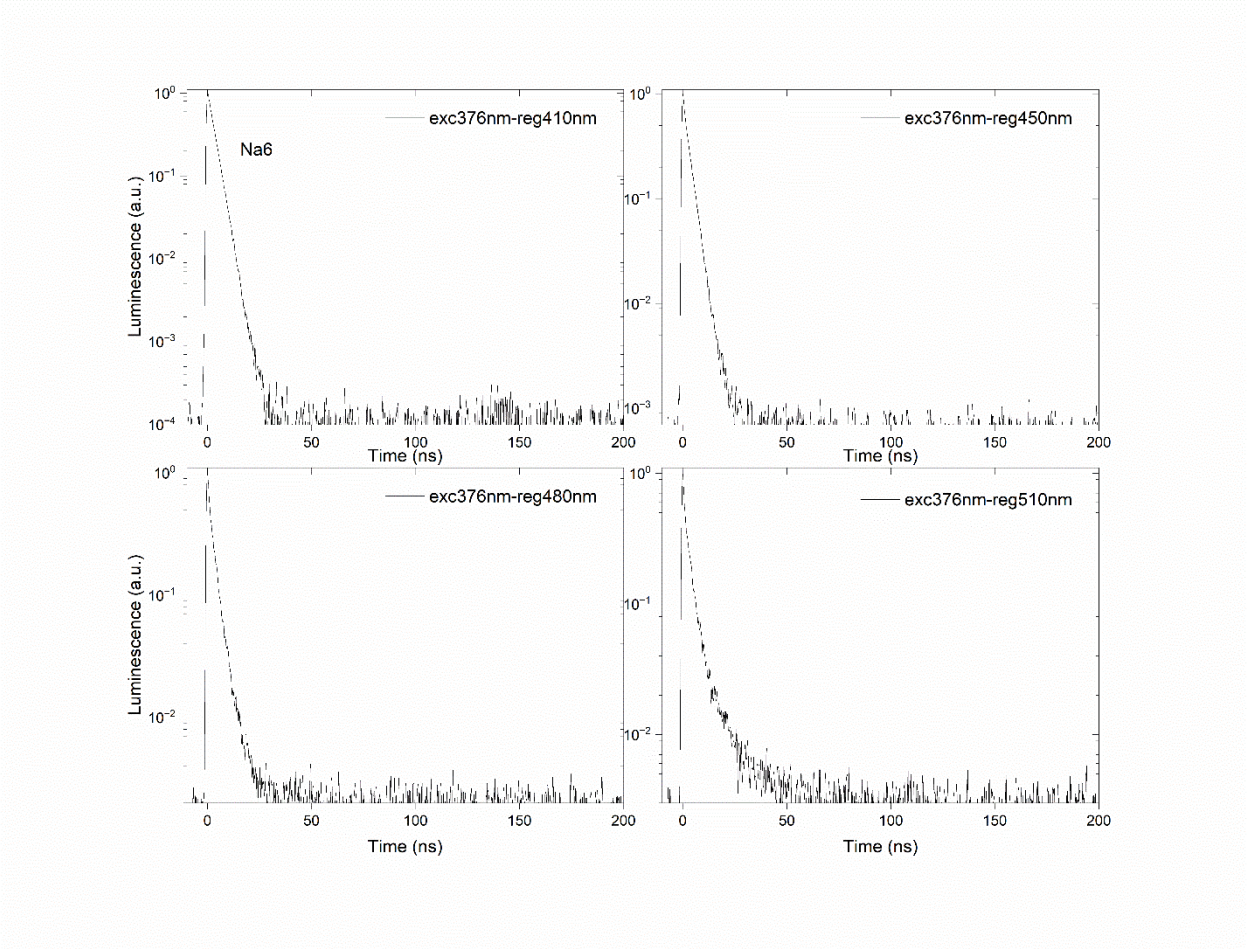


Figure S87. Luminescence decays of **Na6** at various emission wavelengths recorded at room temperature.

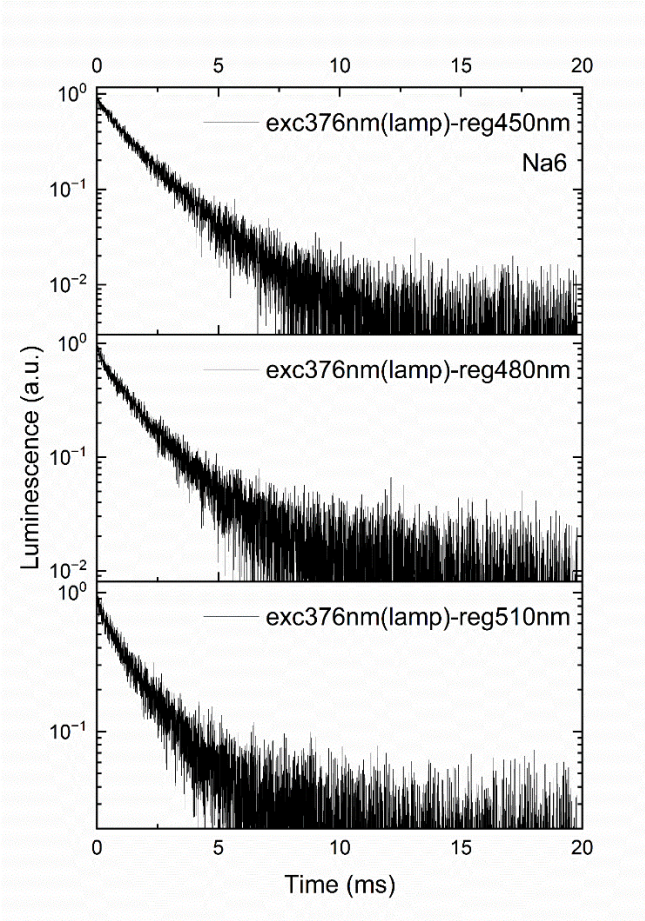


Figure S88. Luminescence decays of **Na6** at various emission wavelengths recorded at room temperature.

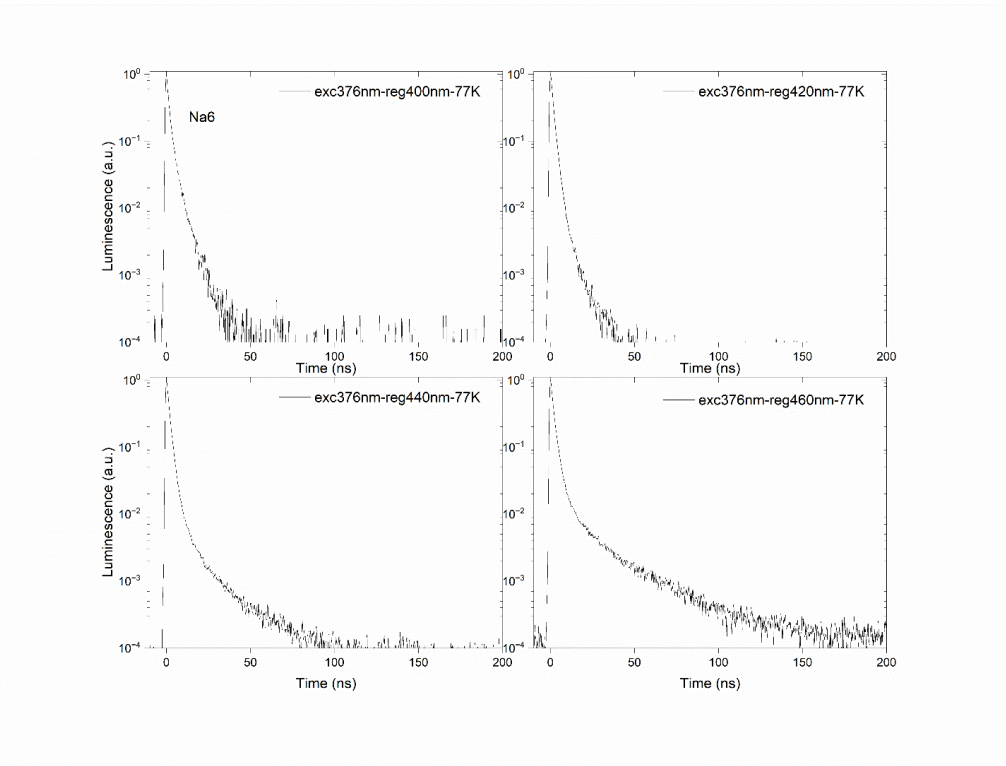


Figure S89. Luminescence decays of **Na6** at various emission wavelengths recorded at 77 K.

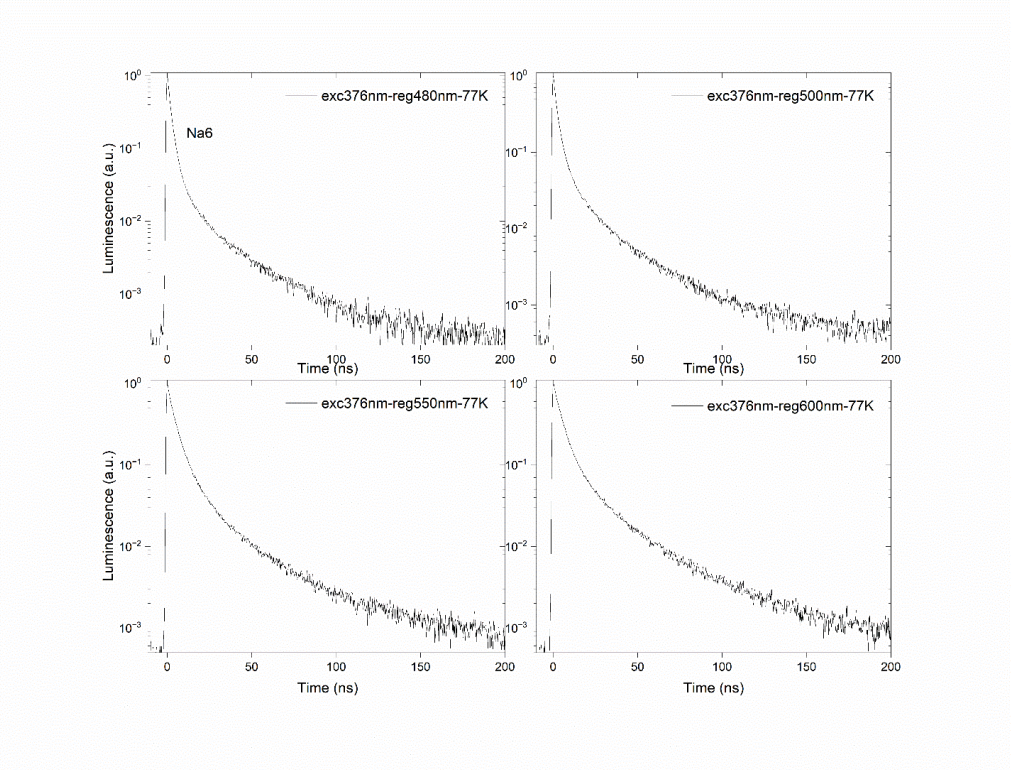


Figure S90. Luminescence decays of **Na6** at various emission wavelengths recorded at 77 K.

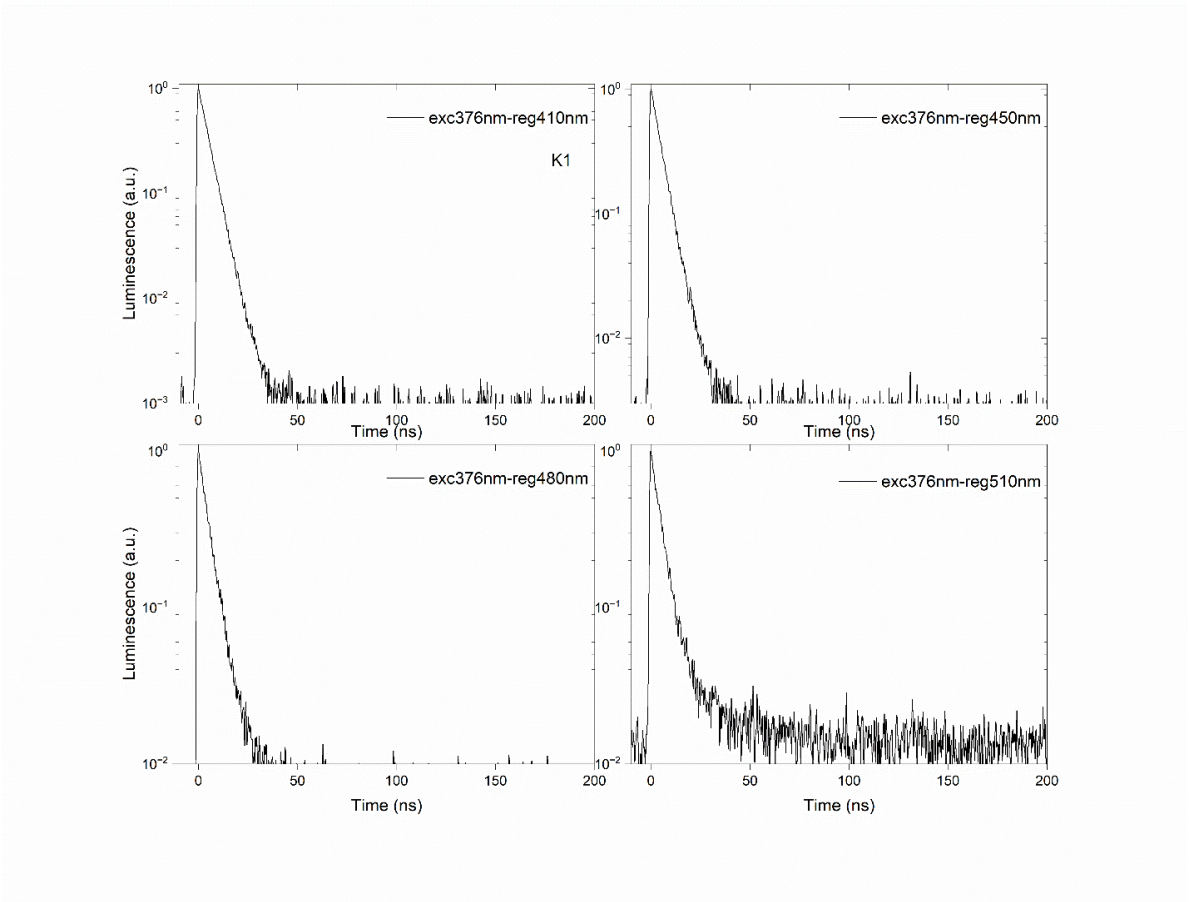


Figure S91. Luminescence decays of **K1** at various emission wavelengths recorded at room temperature.

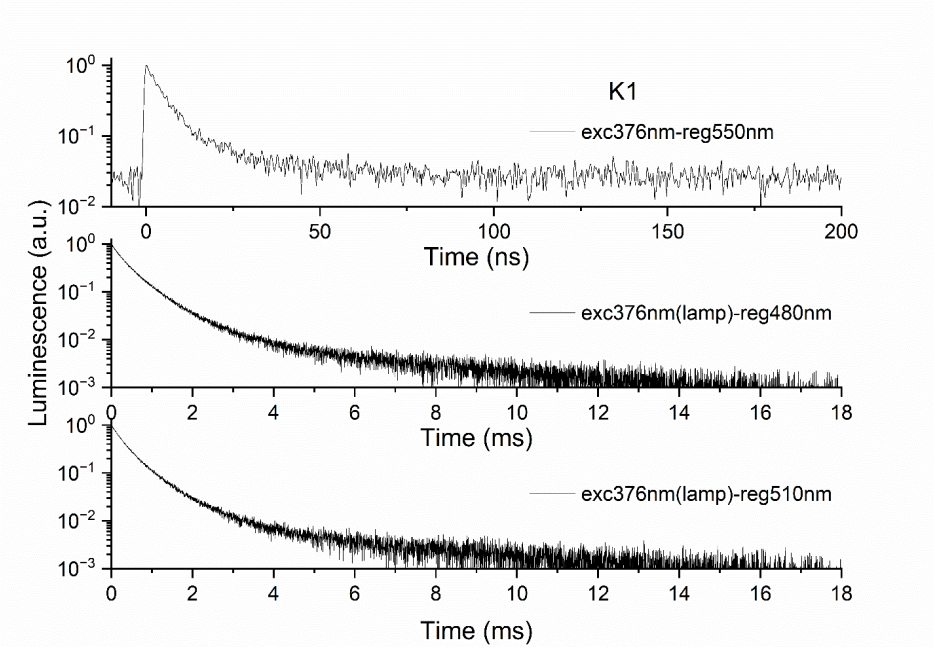


Figure S92. Luminescence decays of **K1** at various emission wavelengths recorded at room temperature.

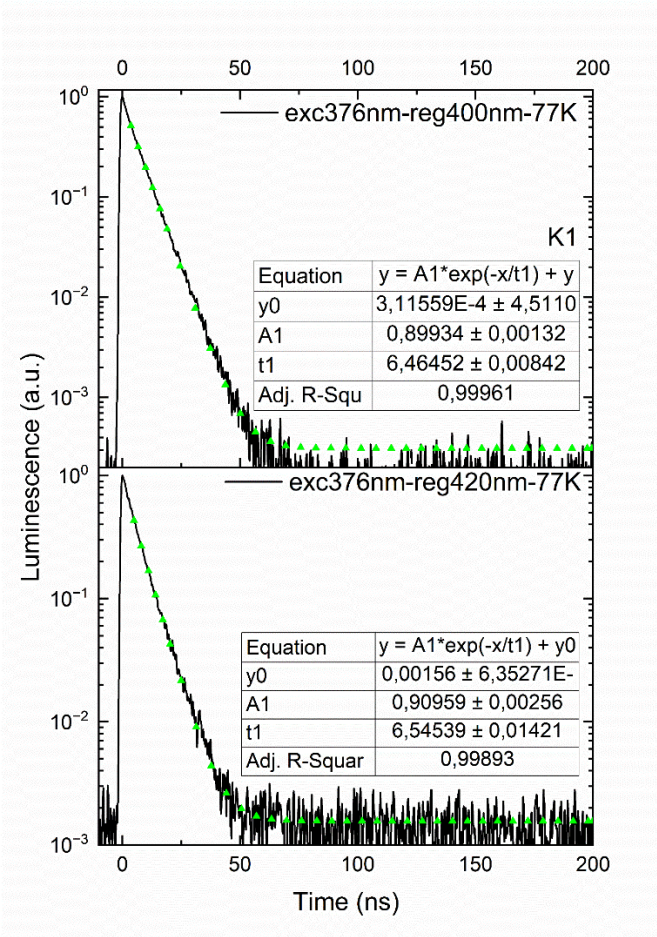


Figure S93. Luminescence decays of **K1** at various emission wavelengths recorded at 77 K.

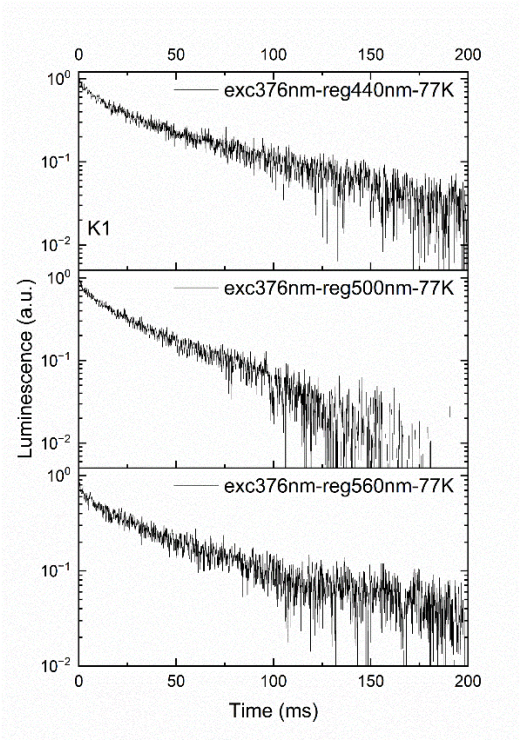


Figure S94. Luminescence decays of **K2** at various emission wavelengths recorded at 77 K.

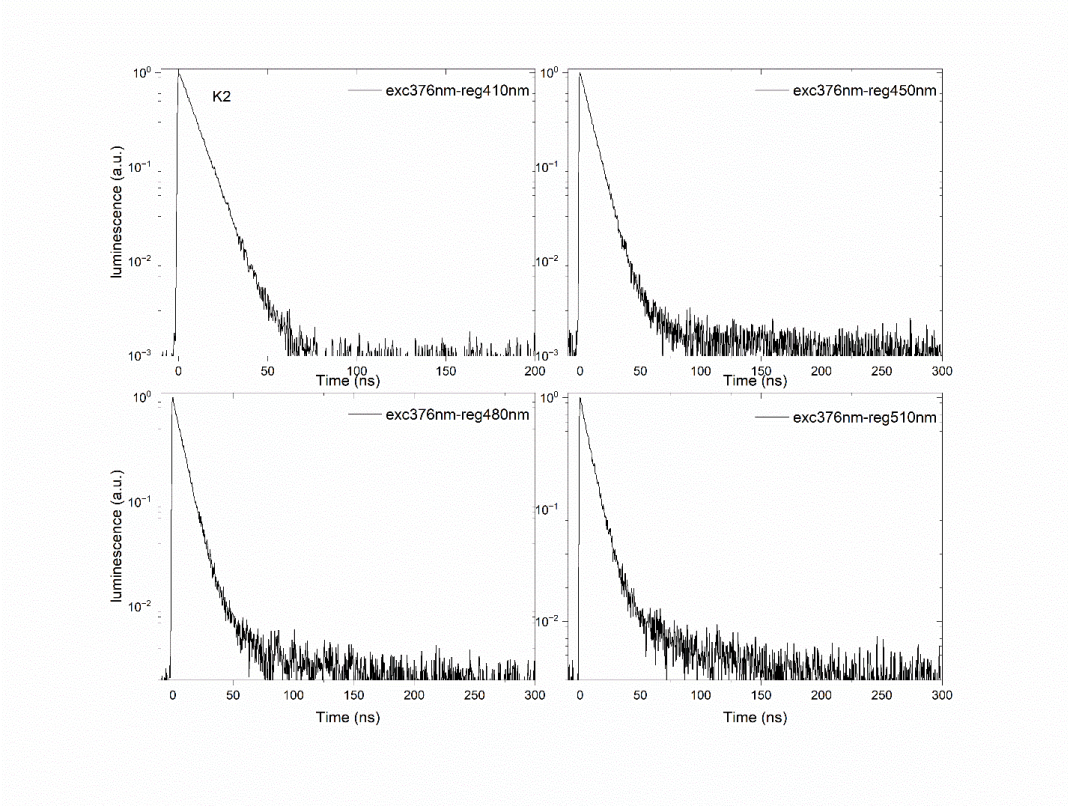


Figure S95. Luminescence decays of **K2** at various emission wavelengths recorded at room temperature.

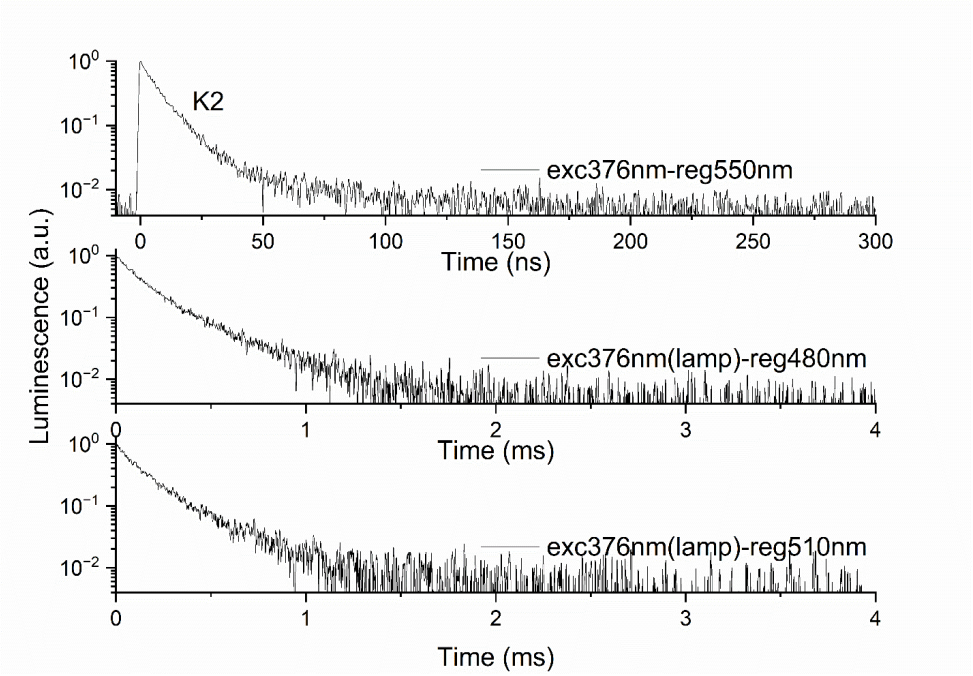


Figure S96. Luminescence decays of **K2** at various emission wavelengths recorded at room temperature.

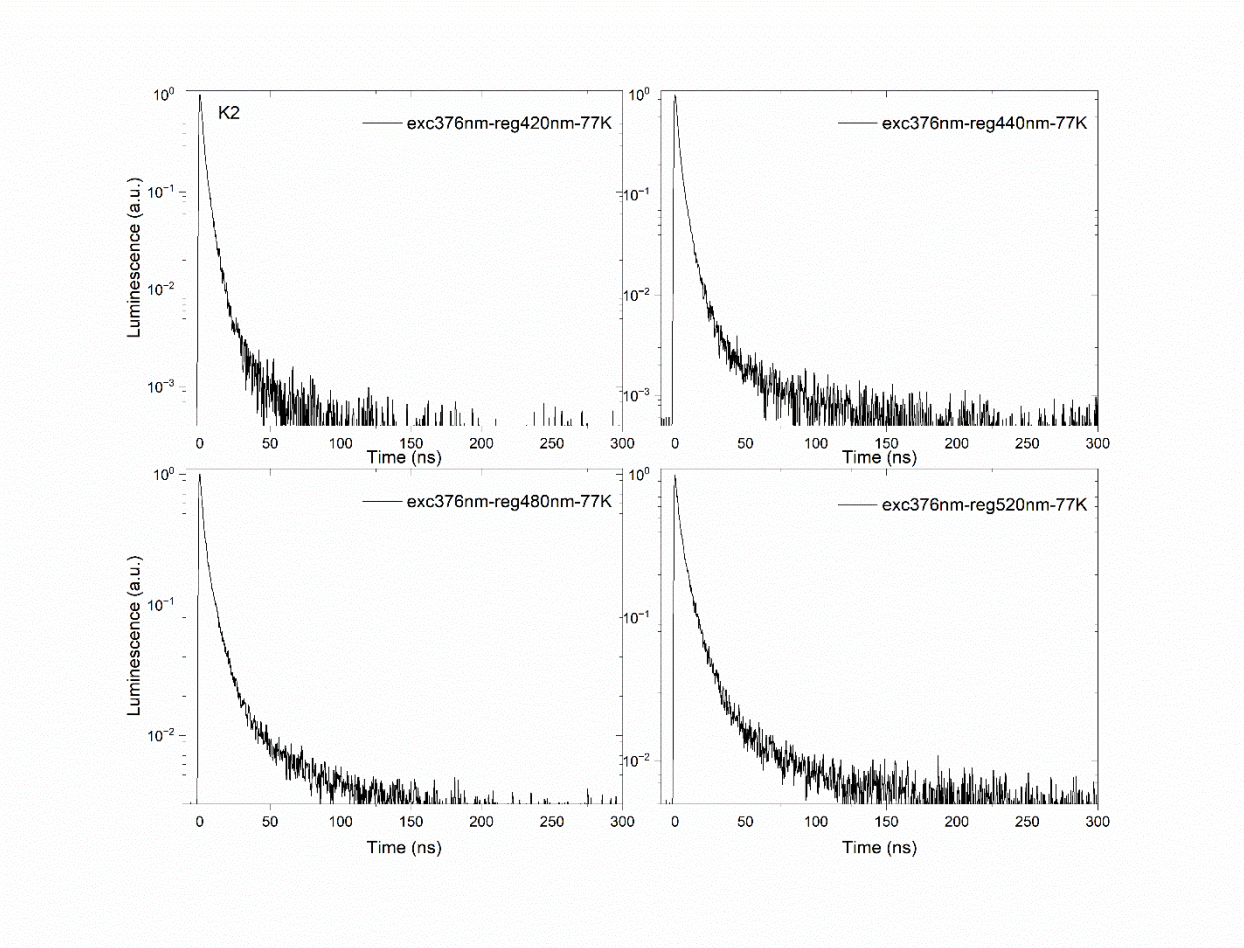


Figure S97. Luminescence decays of **K6** at various emission wavelengths recorded at 77 K.

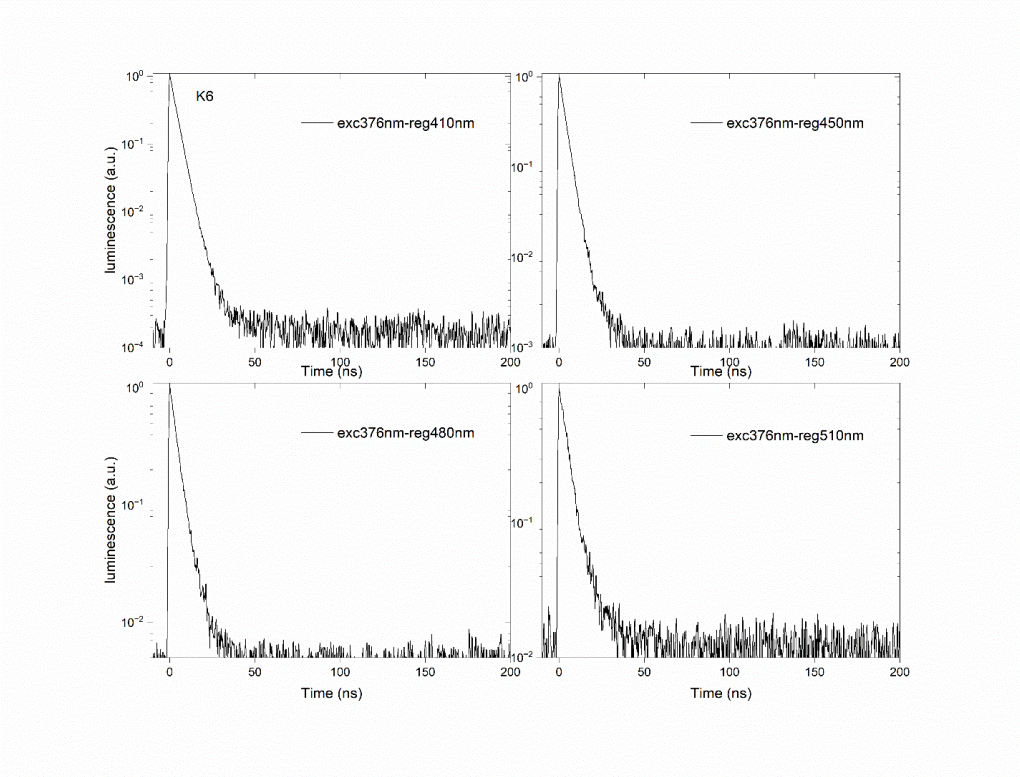


Figure S98. Luminescence decays of **K6** at various emission wavelengths recorded at room temperature.

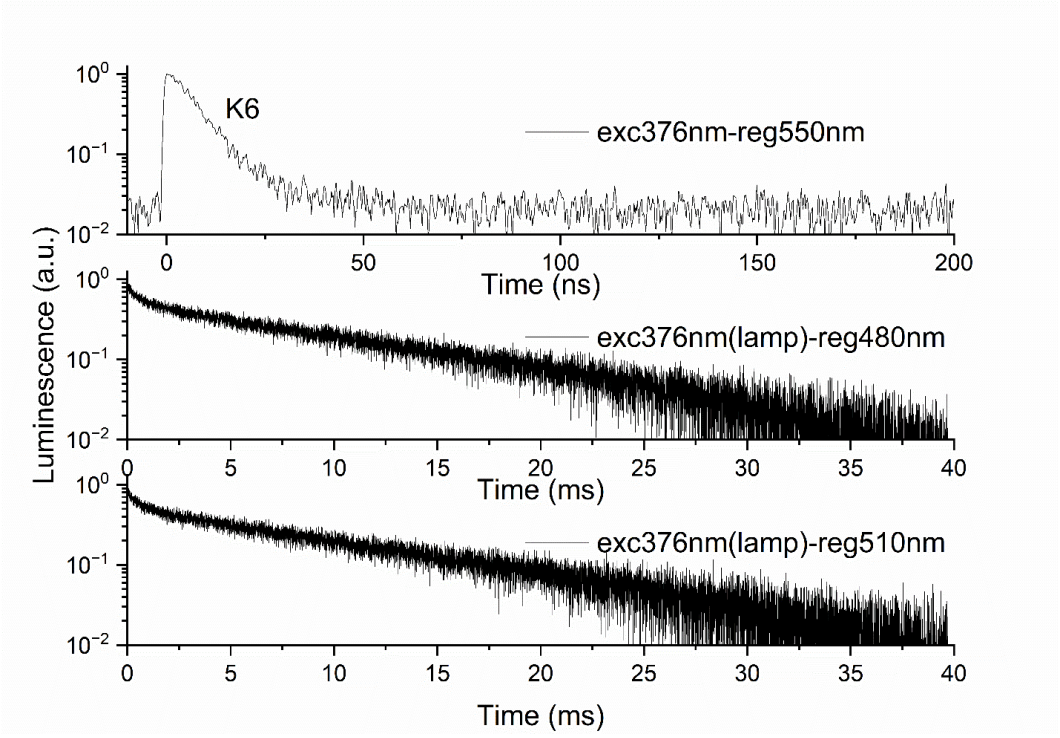


Figure S99. Luminescence decays of **K6** at various emission wavelengths recorded at room temperature.

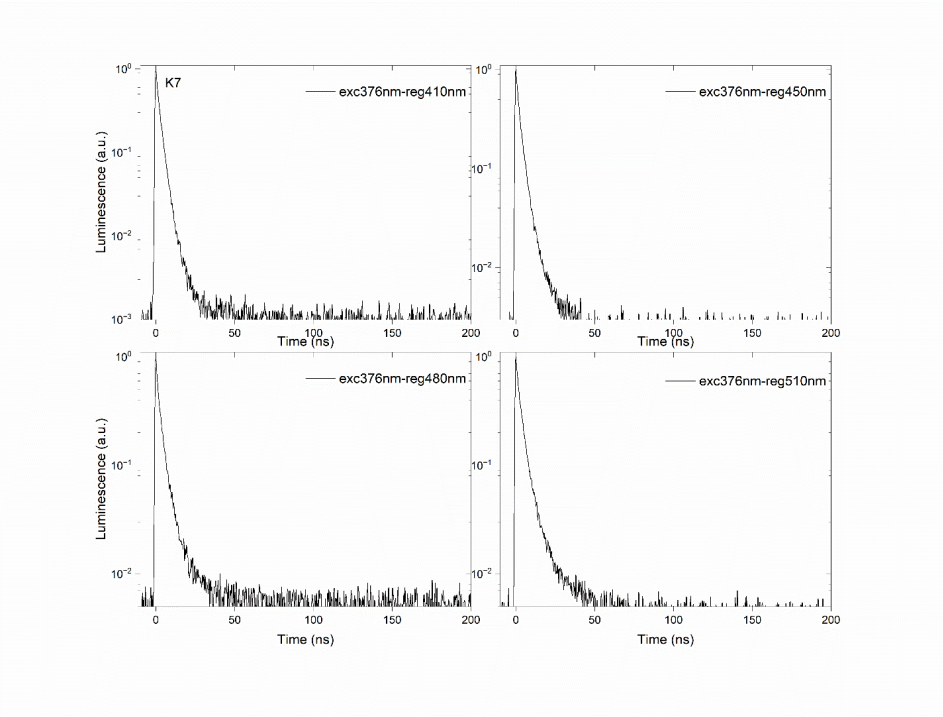


Figure S100. Luminescence decays of **K7** at various emission wavelengths recorded at room temperature.

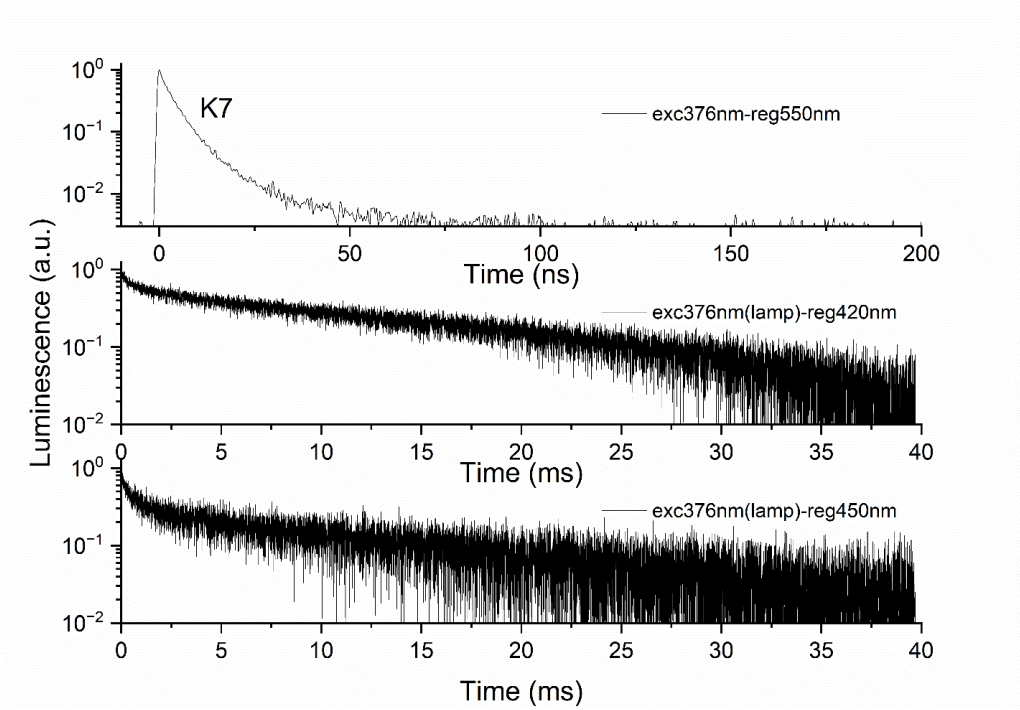


Figure S101. Luminescence decays of **K7** at various emission wavelengths recorded at room temperature.

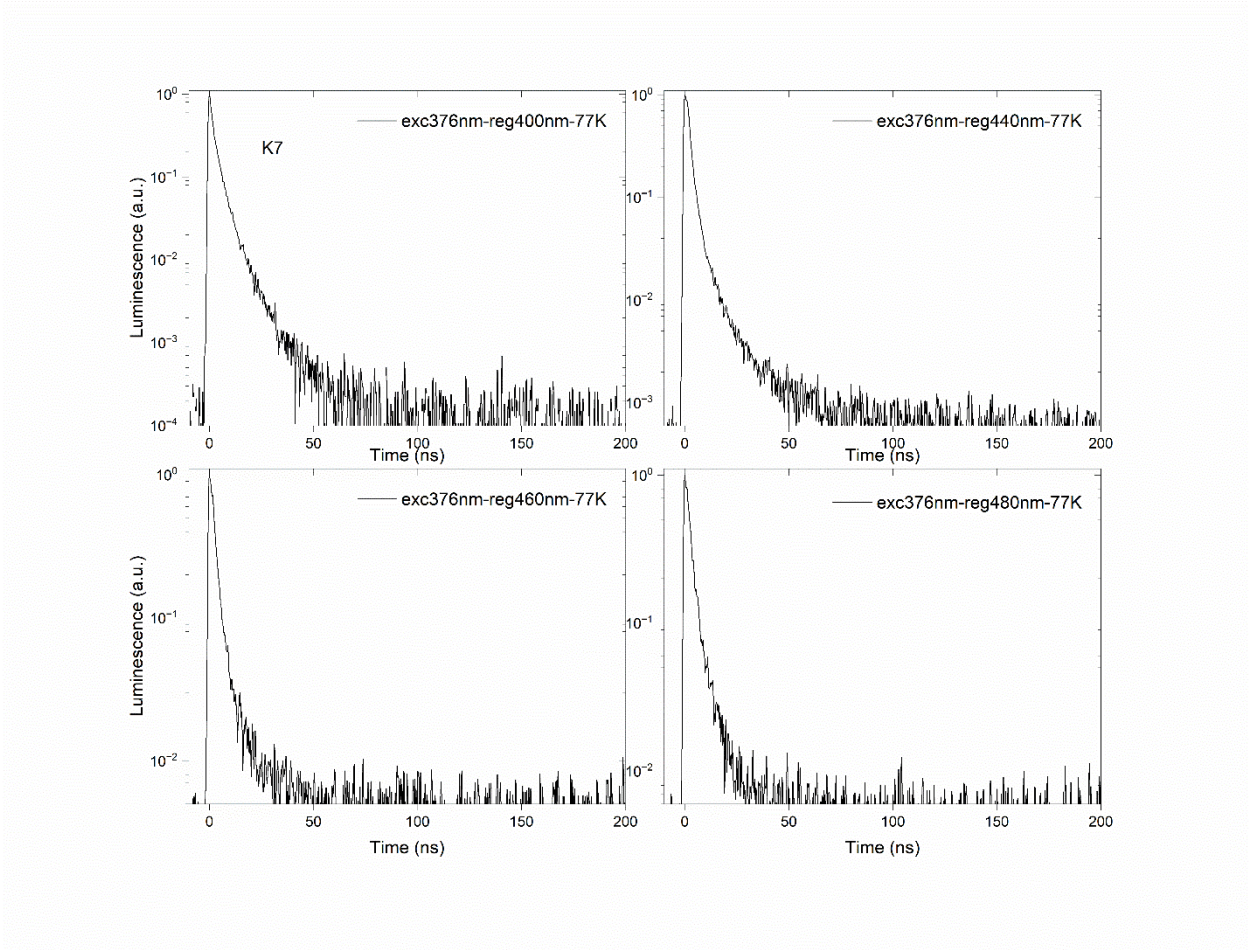


Figure S102. Luminescence decays of **K7** at various emission wavelengths recorded at 77 K.

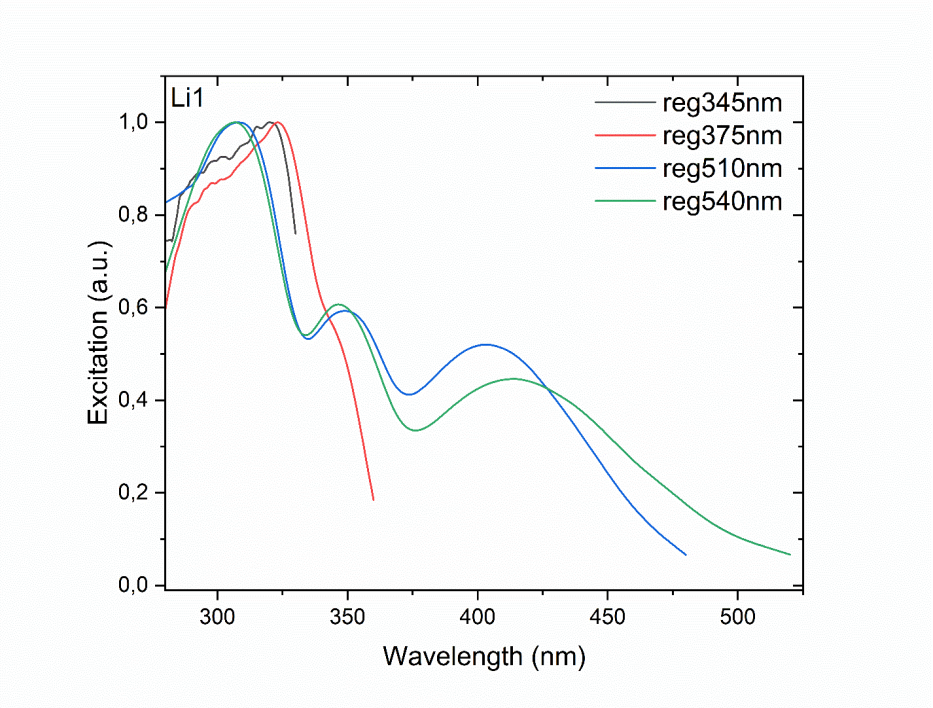


Figure S103. Excitation spectra of **Li1** at various emission wavelengths recorded at room temperature.

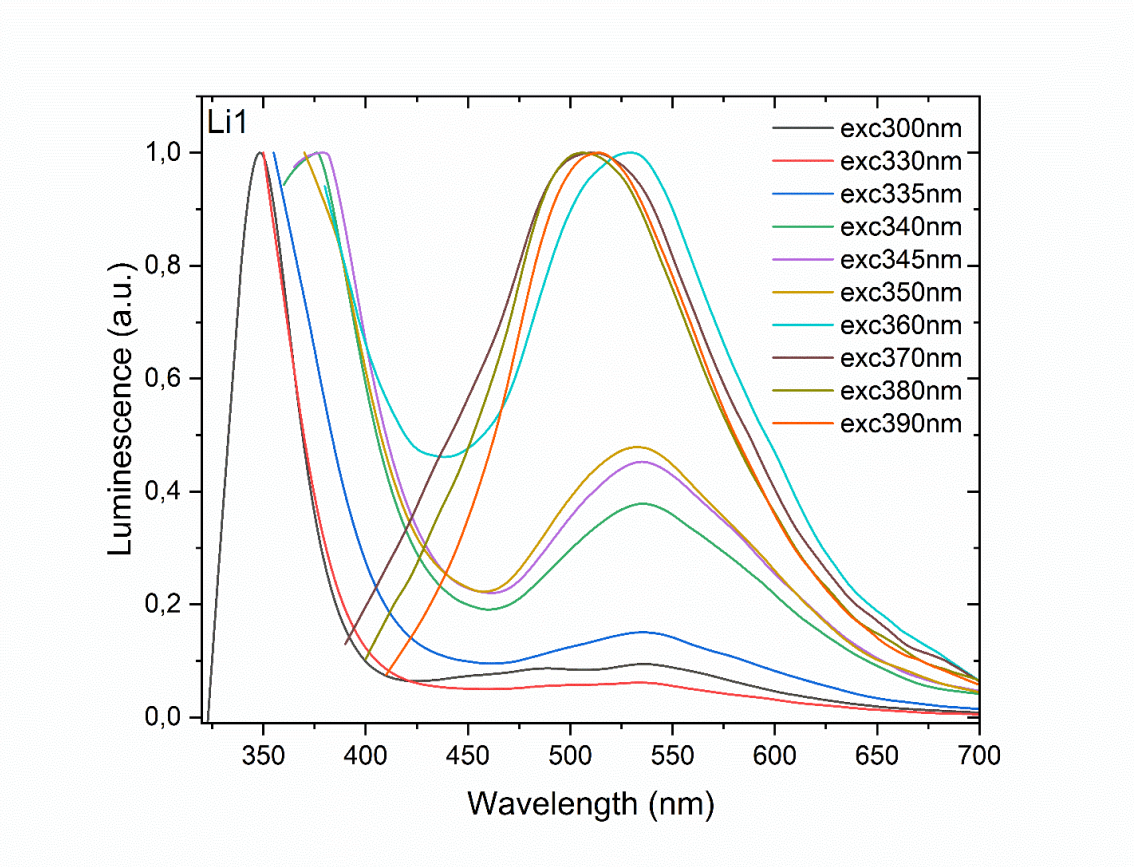


Figure S104. Emission spectra of **Li1** at various excitation wavelengths recorded at room temperature.

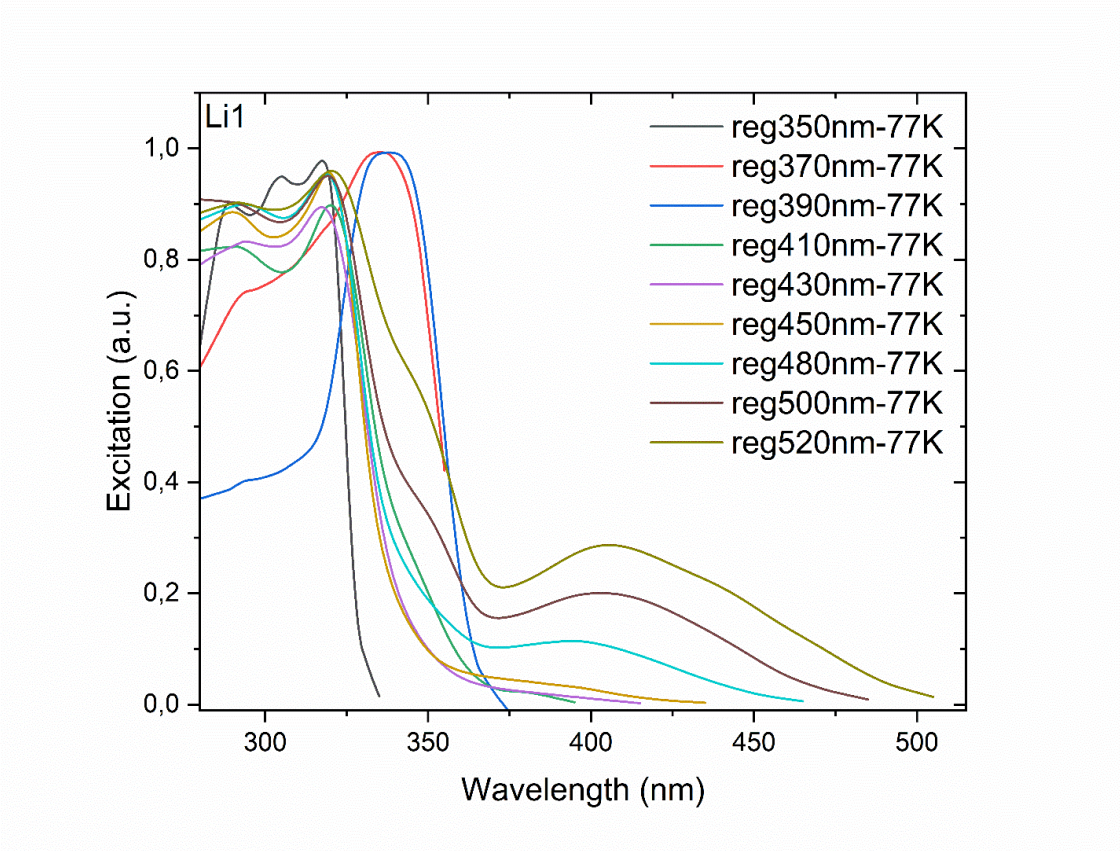


Figure S105. Excitation spectra of **Li1** at various emission wavelengths recorded at 77 K.

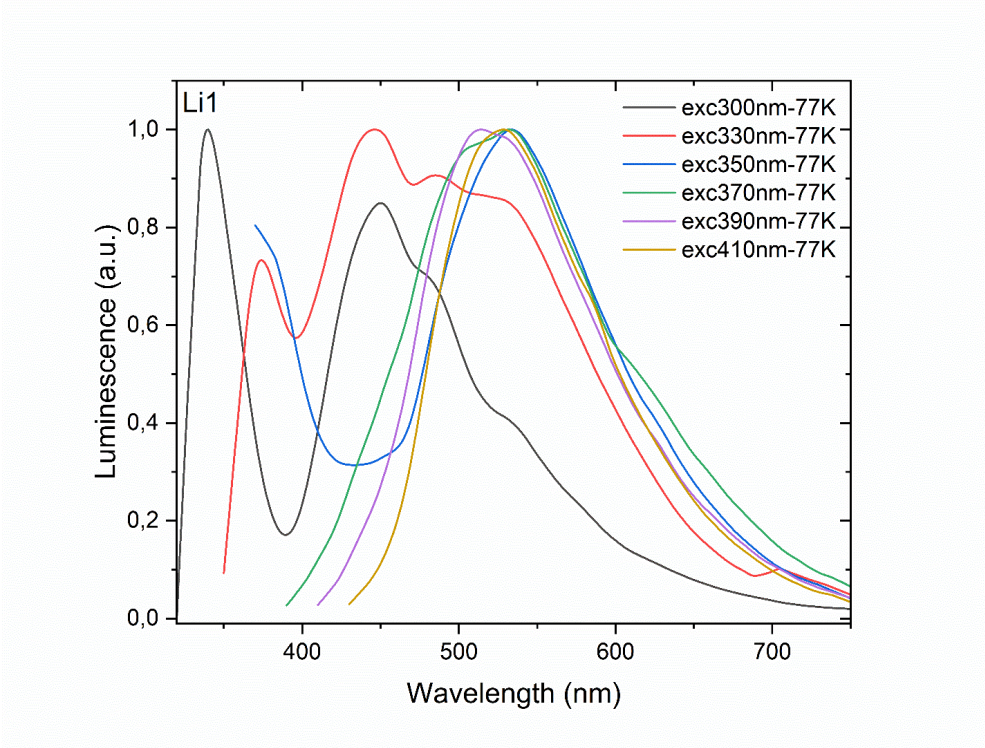


Figure S106. Emission spectra of **Li1** at various excitation wavelengths recorded at 77 K.

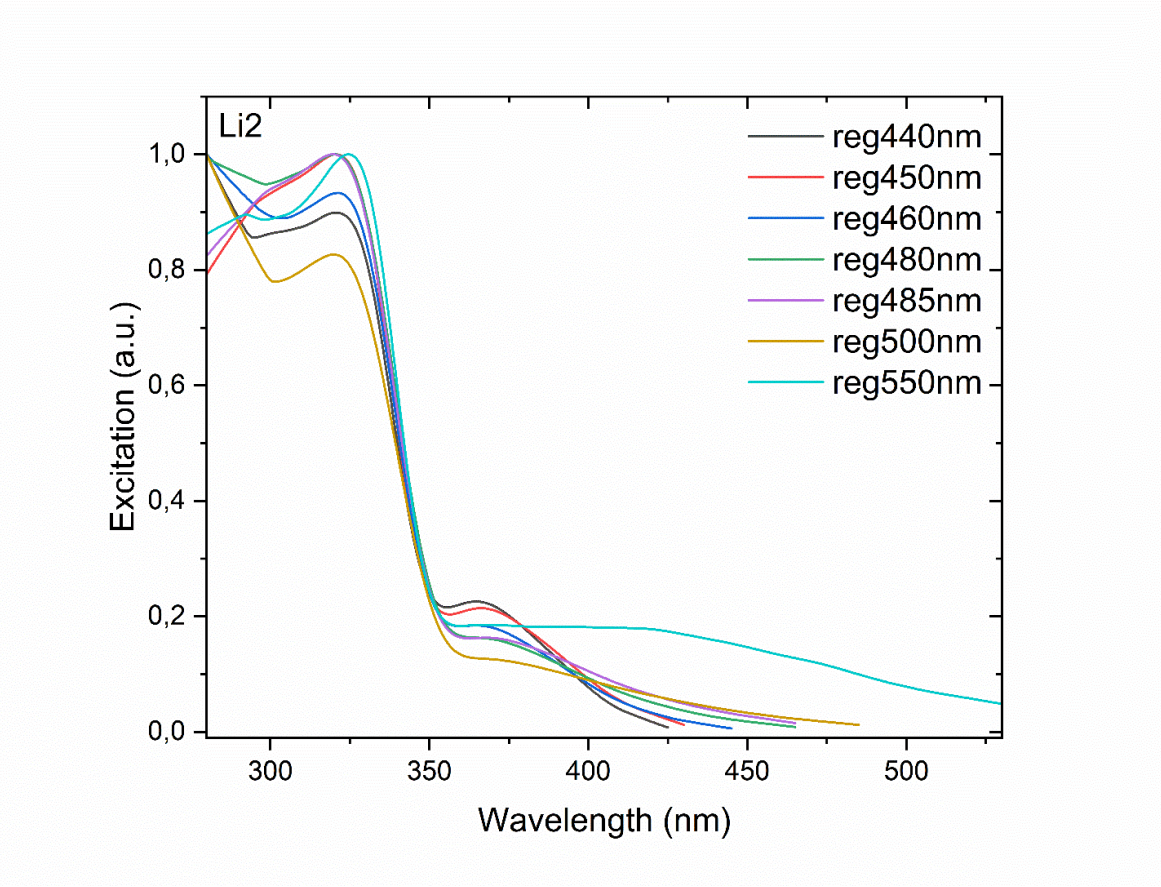


Figure S107. Excitation spectra of **Li2** at various emission wavelengths recorded at room temperature.

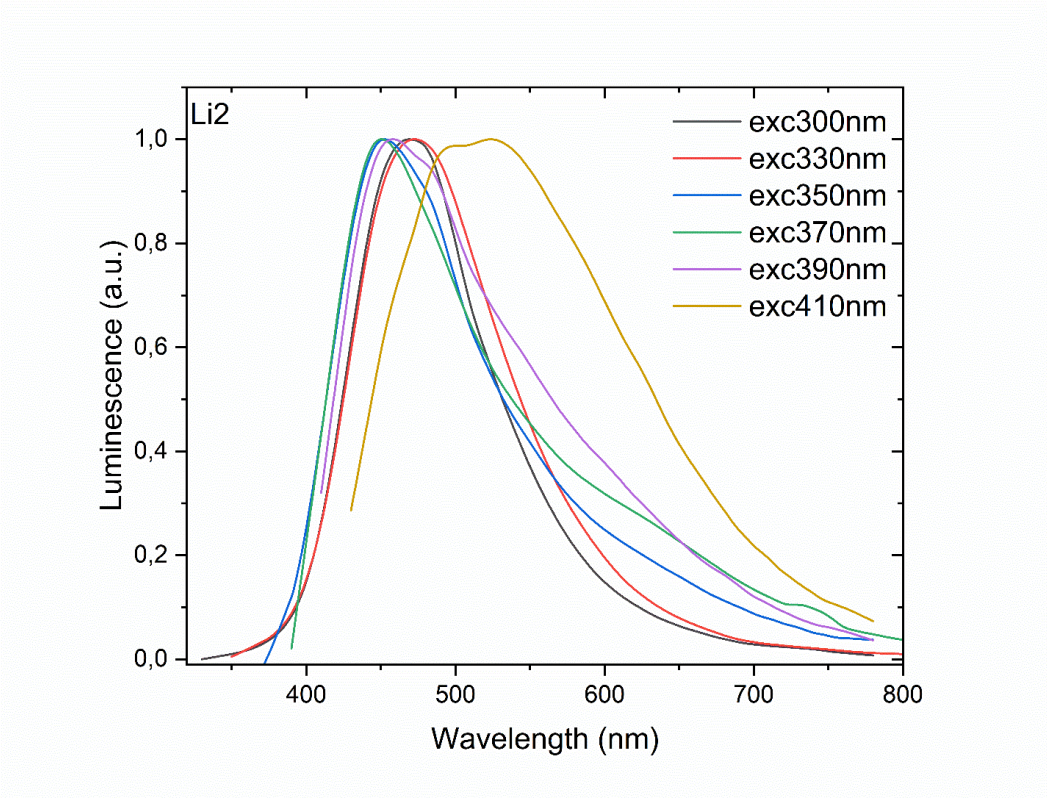


Figure S108. Emission spectra of **Li2** at various excitation wavelengths recorded at room temperature.

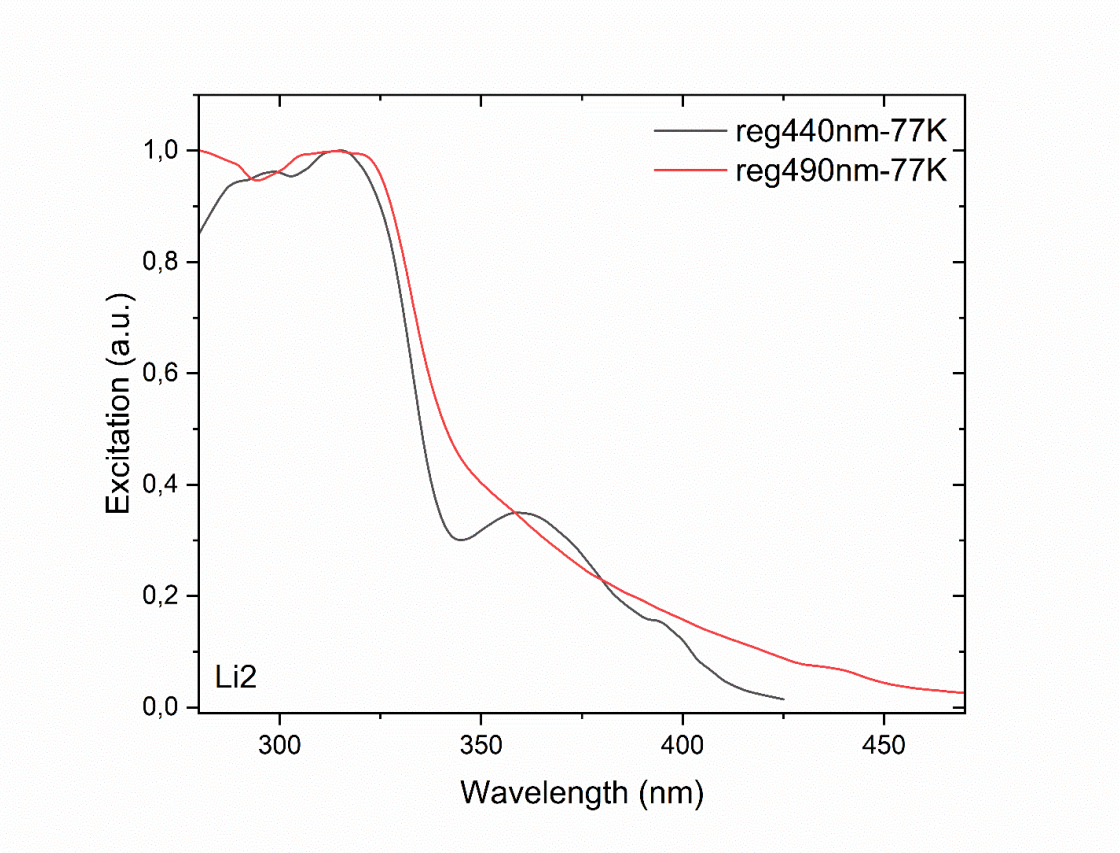


Figure S109. Excitation spectra of **Li2** at various emission wavelengths recorded at 77 K.

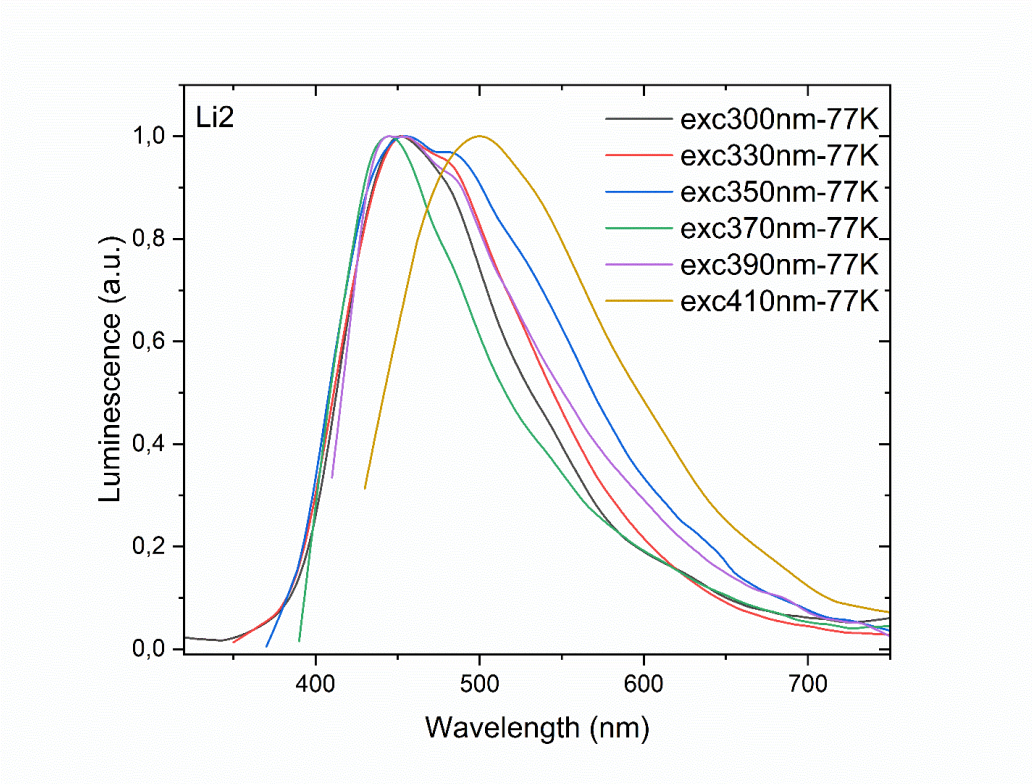


Figure S110. Emission spectra of **Li2** at various excitation wavelengths recorded at 77 K.

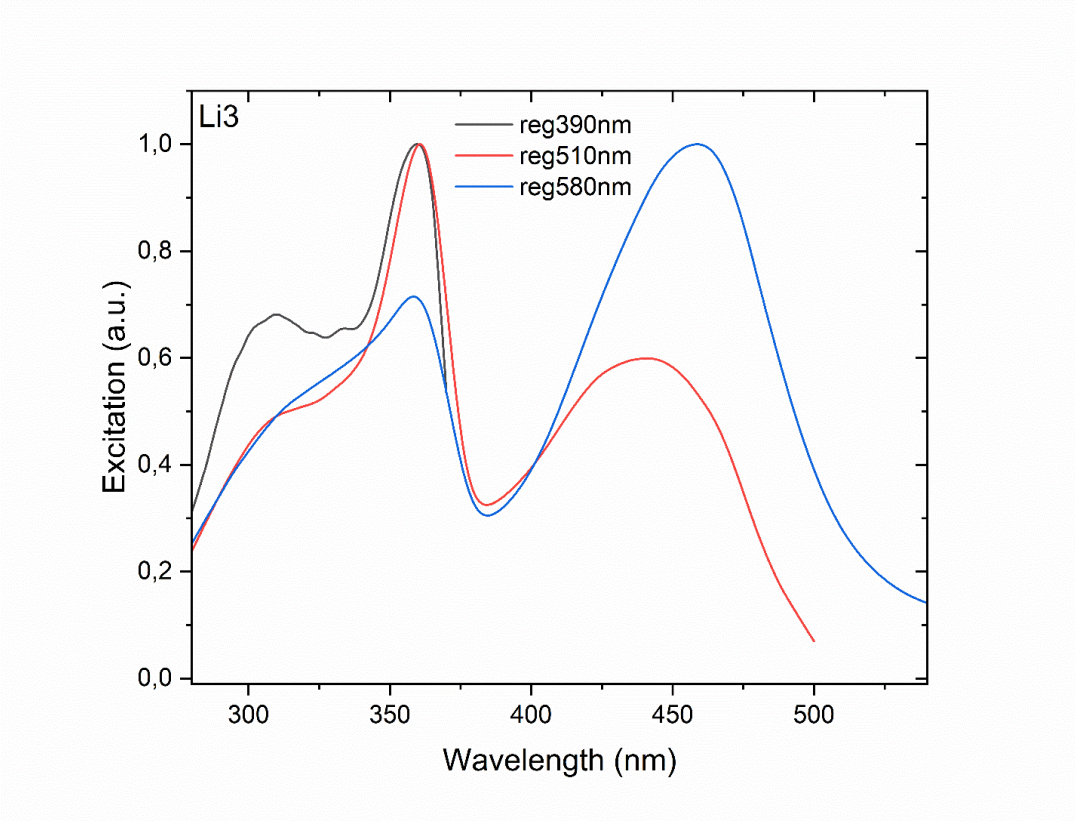


Figure S111. Excitation spectra of **Li3** at various emission wavelengths recorded at room temperature.

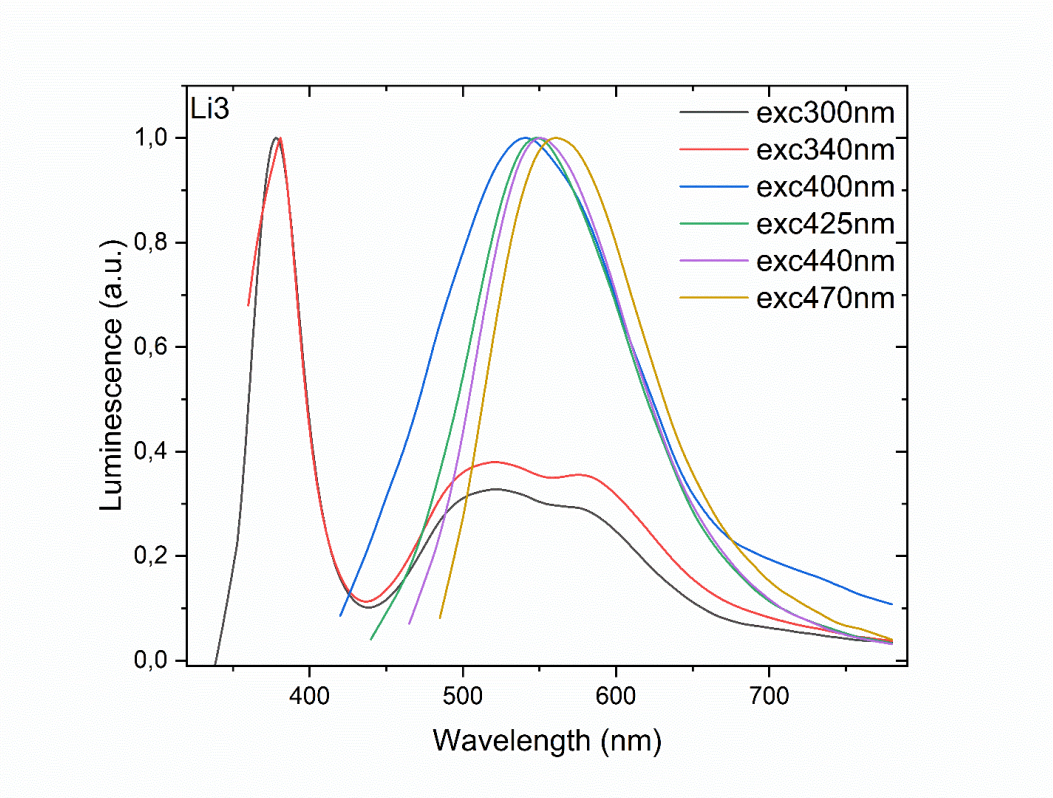


Figure S112. Emission spectra of **Li3** at various excitation wavelengths recorded at room temperature.

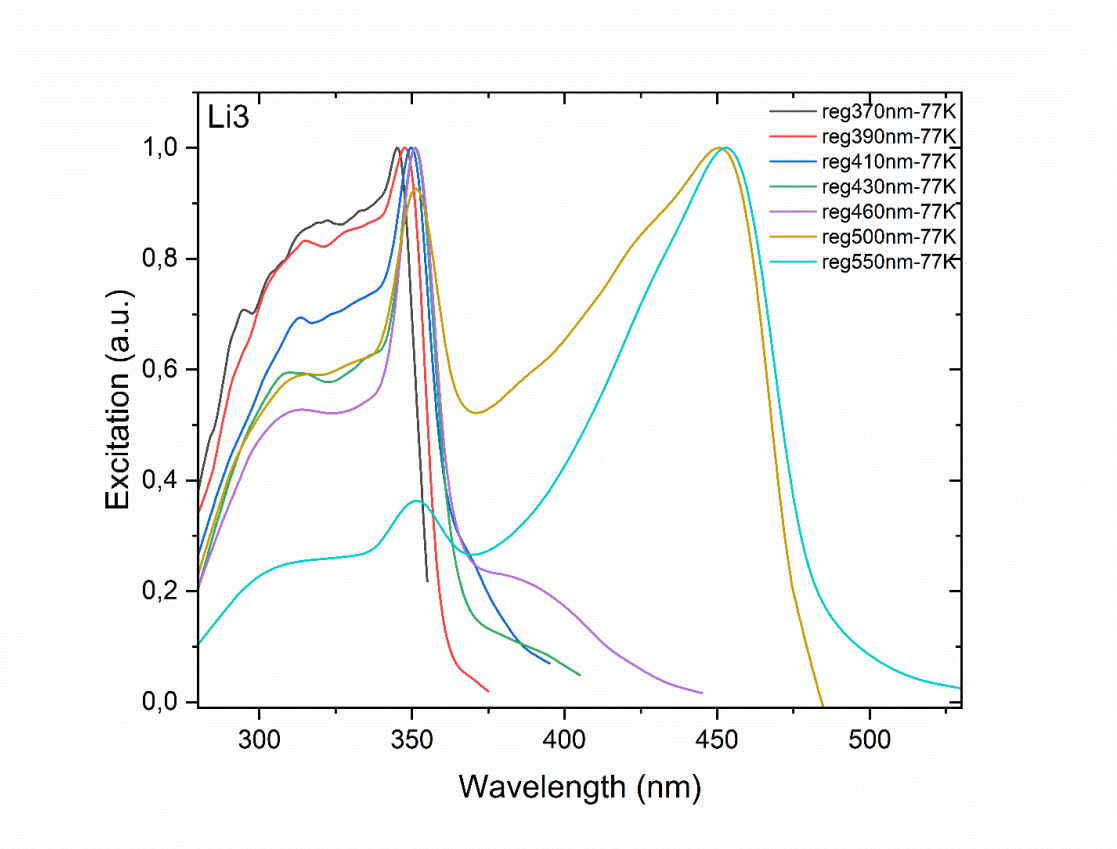


Figure S113. Excitation spectra of **Li3** at various emission wavelengths recorded at 77 K.

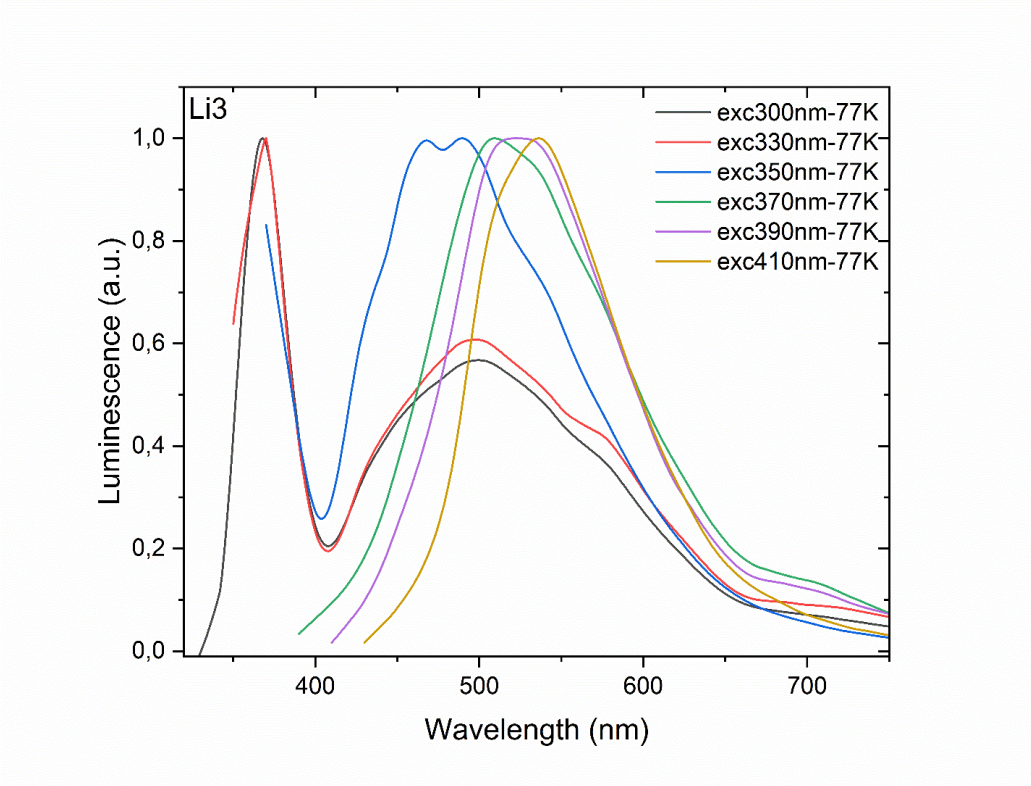


Figure S114. Emission spectra of **Li3** at various excitation wavelengths recorded at 77 K.

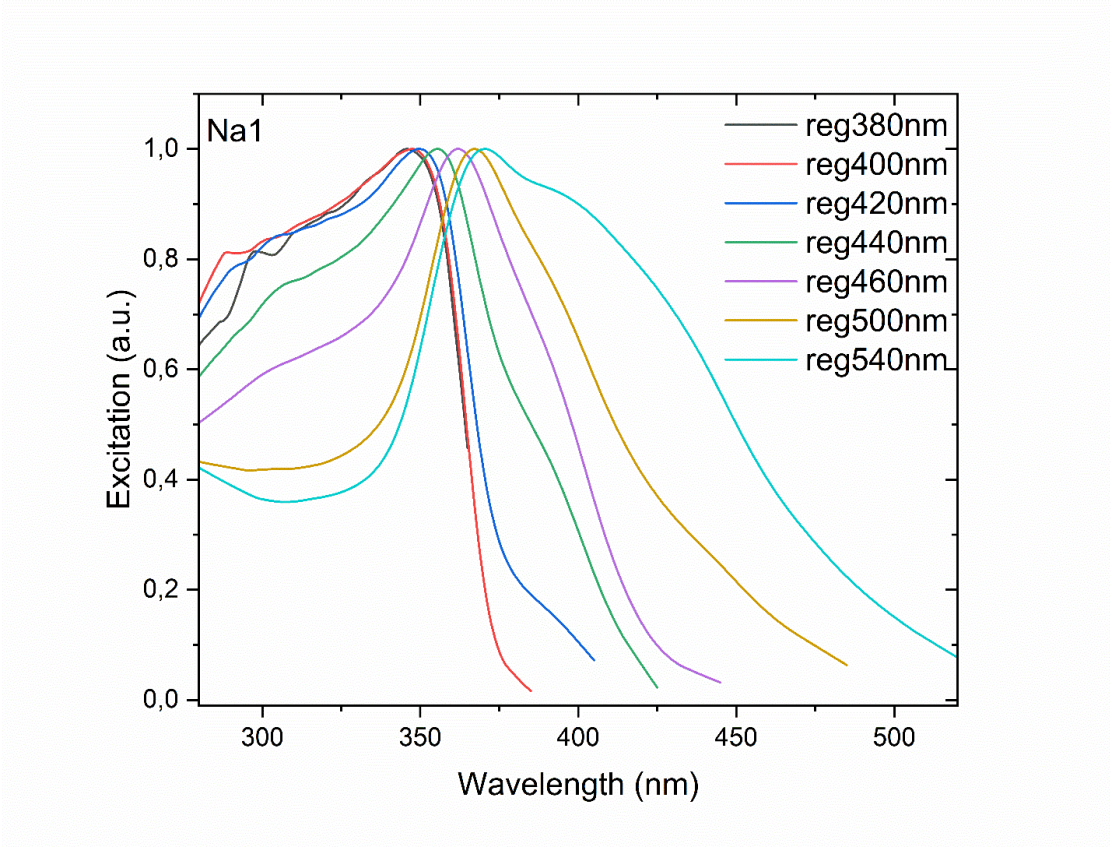


Figure S115. Excitation spectra of **Na1** at various emission wavelengths recorded at room temperature.

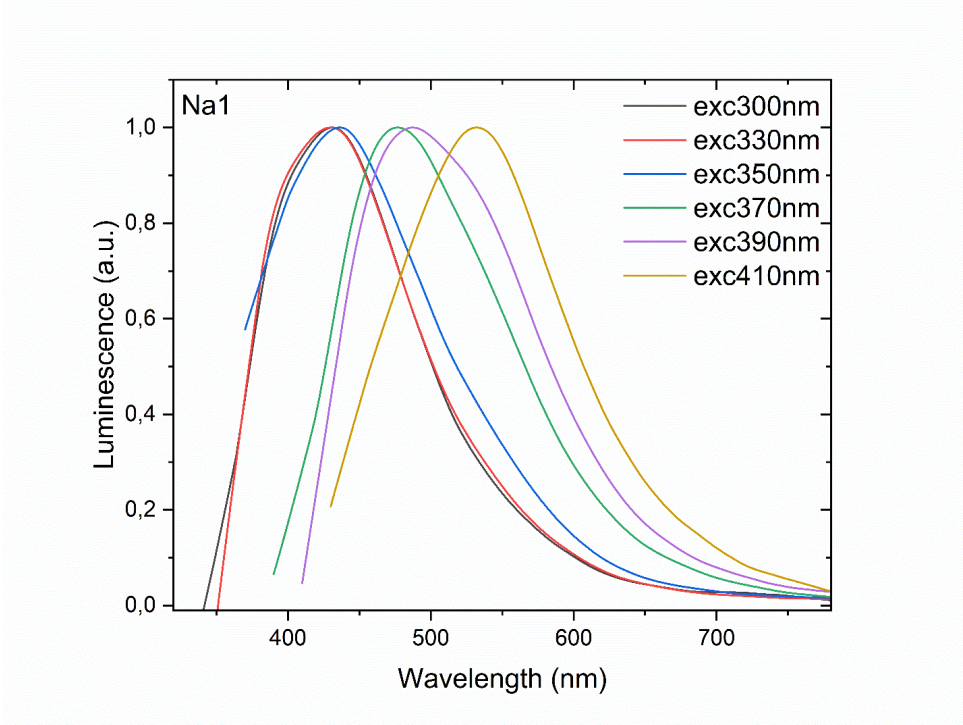


Figure S116. Emission spectra of **Na1** at various excitation wavelengths recorded at room temperature.

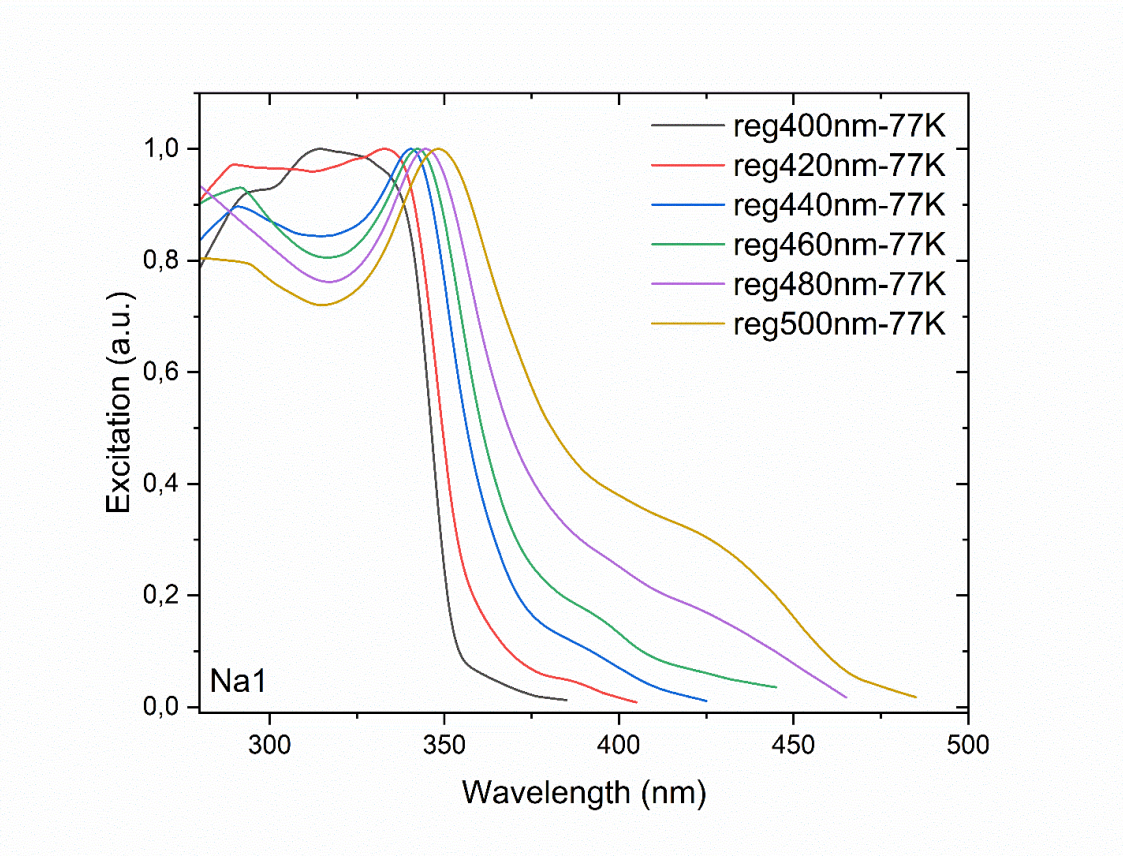


Figure S117. Excitation spectra of **Na1** at various emission wavelengths recorded at 77 K.

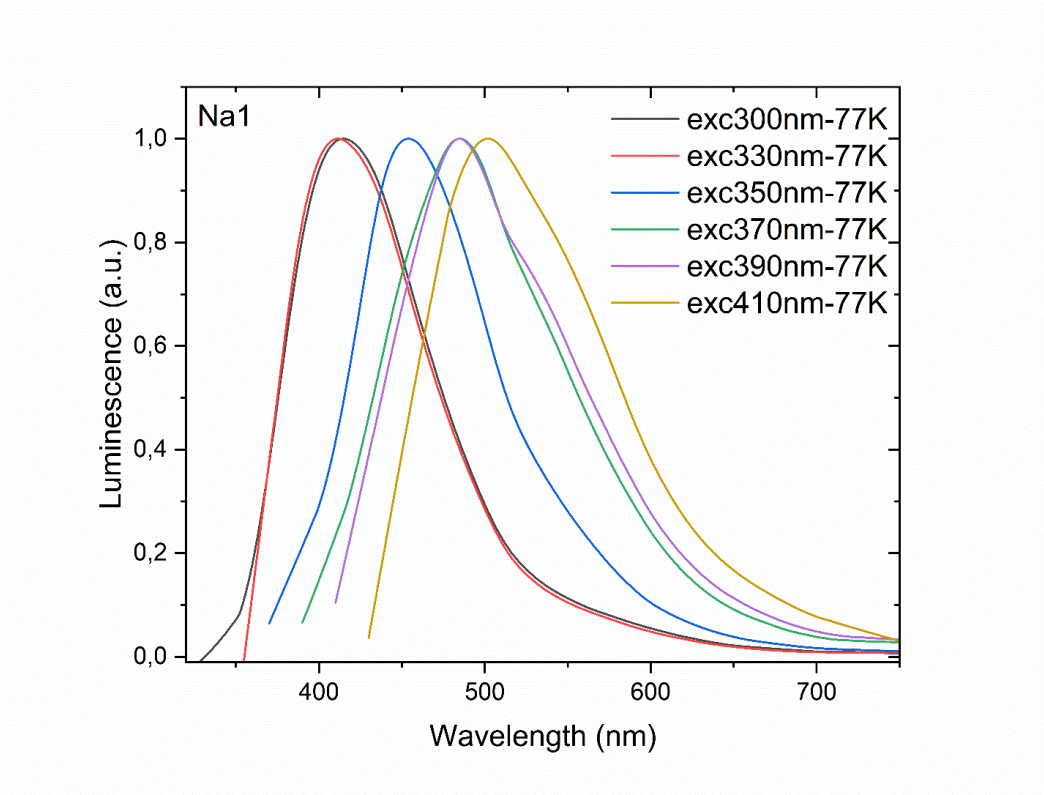


Figure S118. Emission spectra of **Na1** at various excitation wavelengths recorded at 77 K.

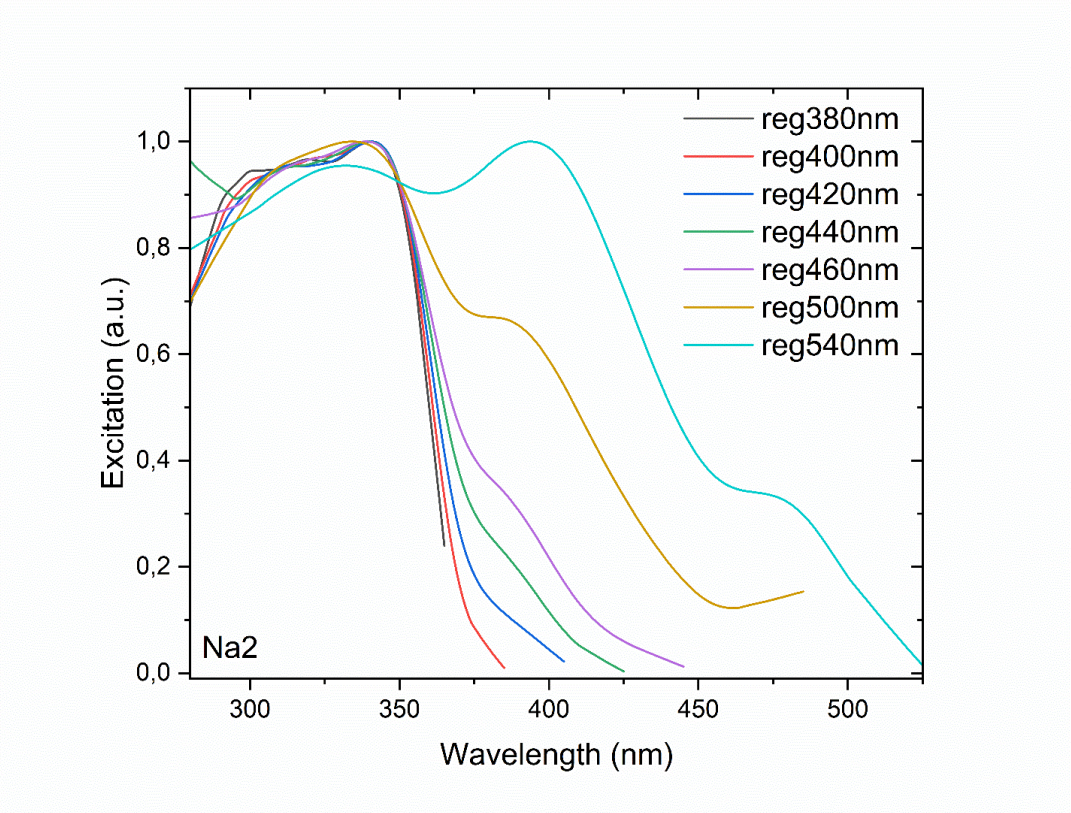


Figure S119. Excitation spectra of **Na2** at various emission wavelengths recorded at room temperature.

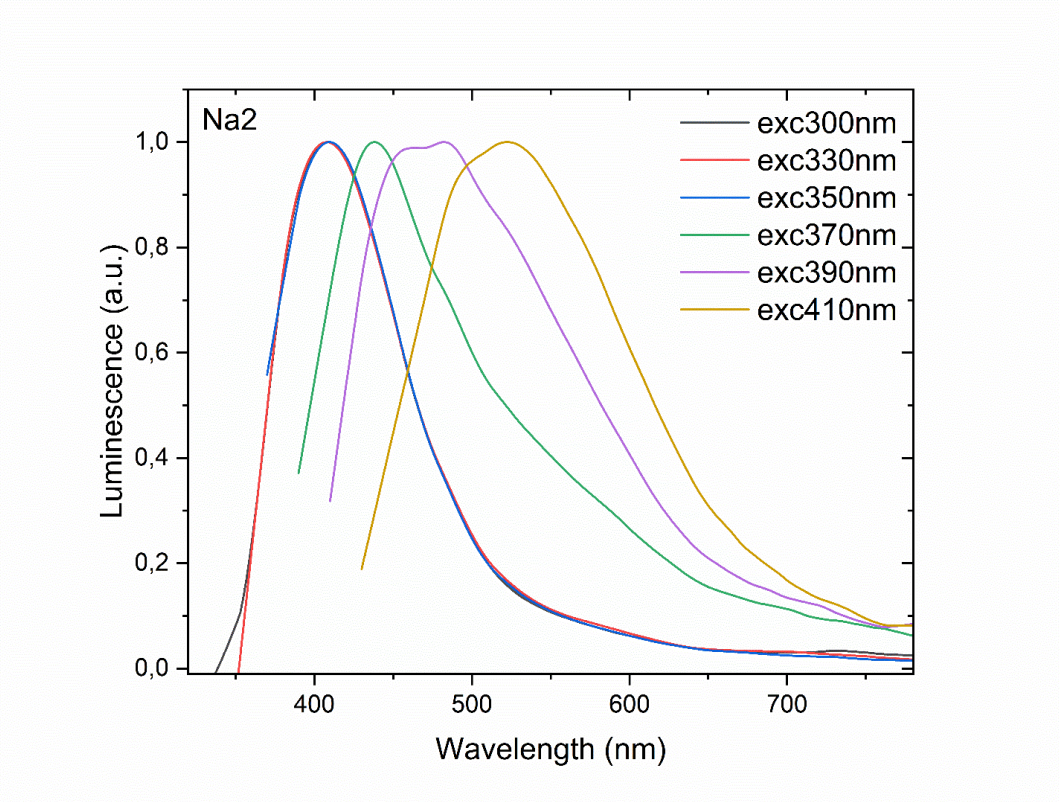


Figure S120. Emission spectra of **Na2** at various excitation wavelengths recorded at room temperature.

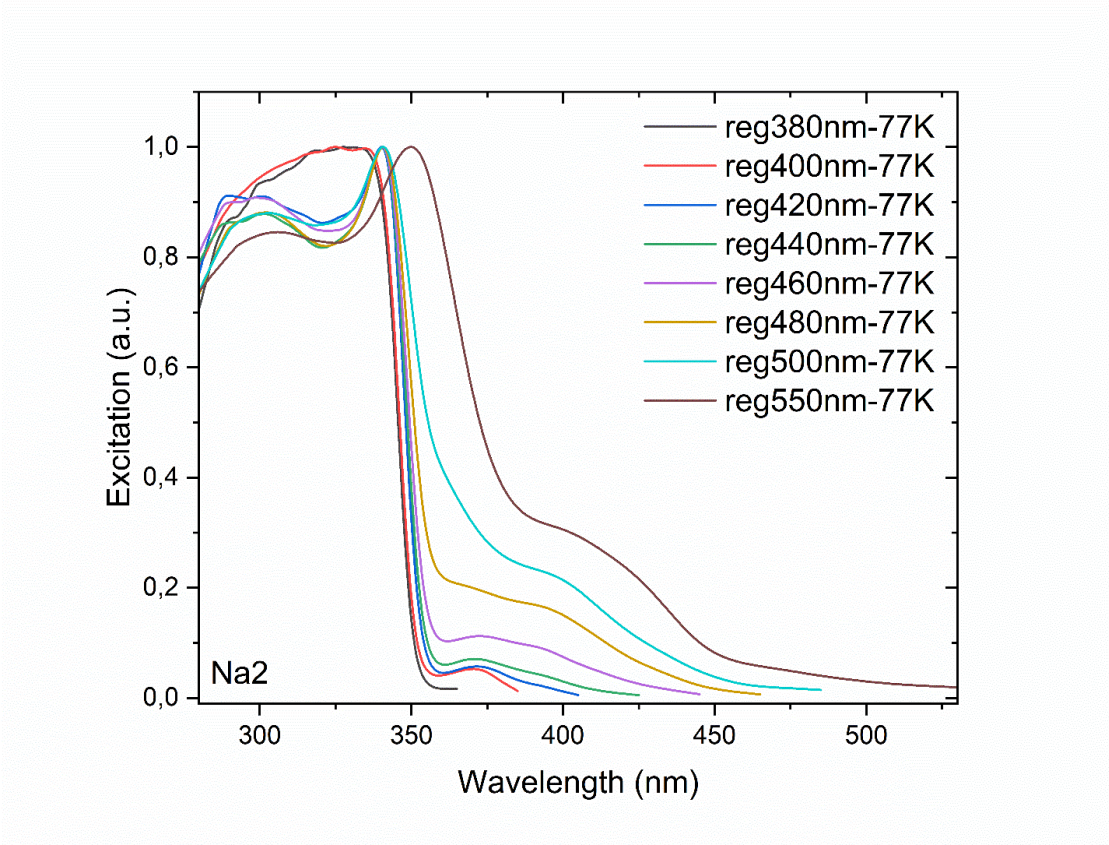


Figure S121. Excitation spectra of **Na2** at various emission wavelengths recorded at 77 K.

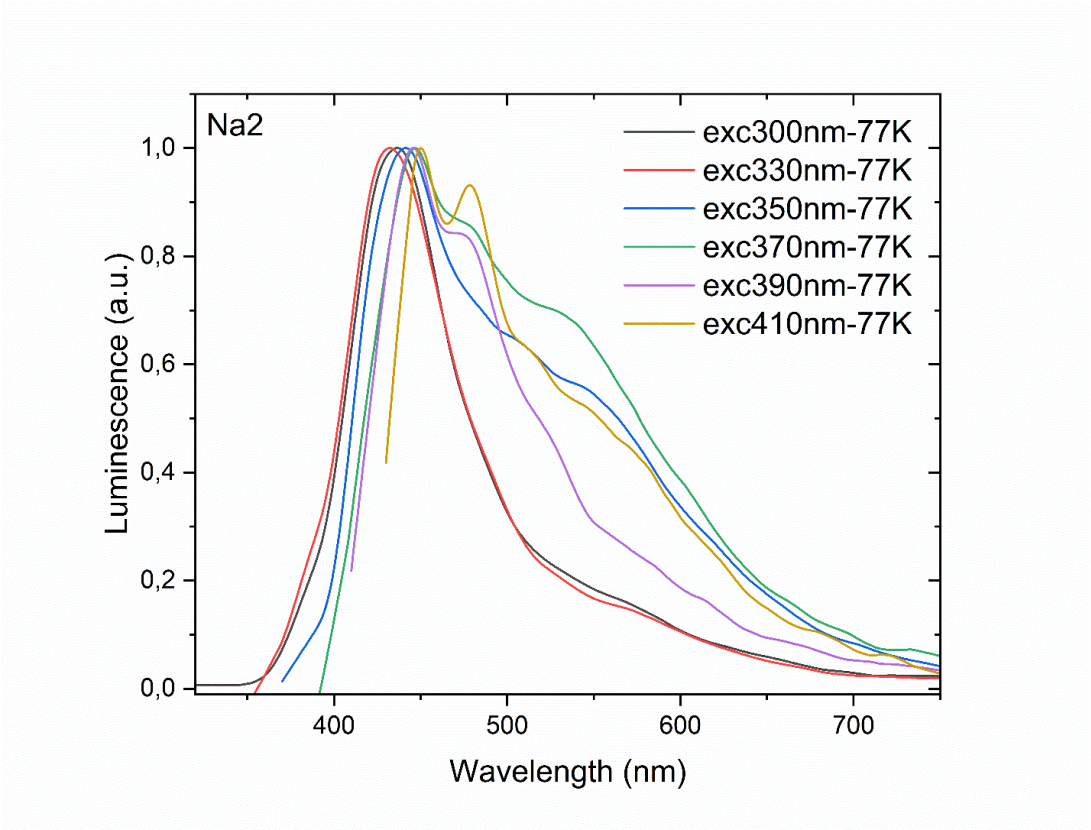


Figure S122. Emission spectra of **Na2** at various excitation wavelengths recorded at 77 K.

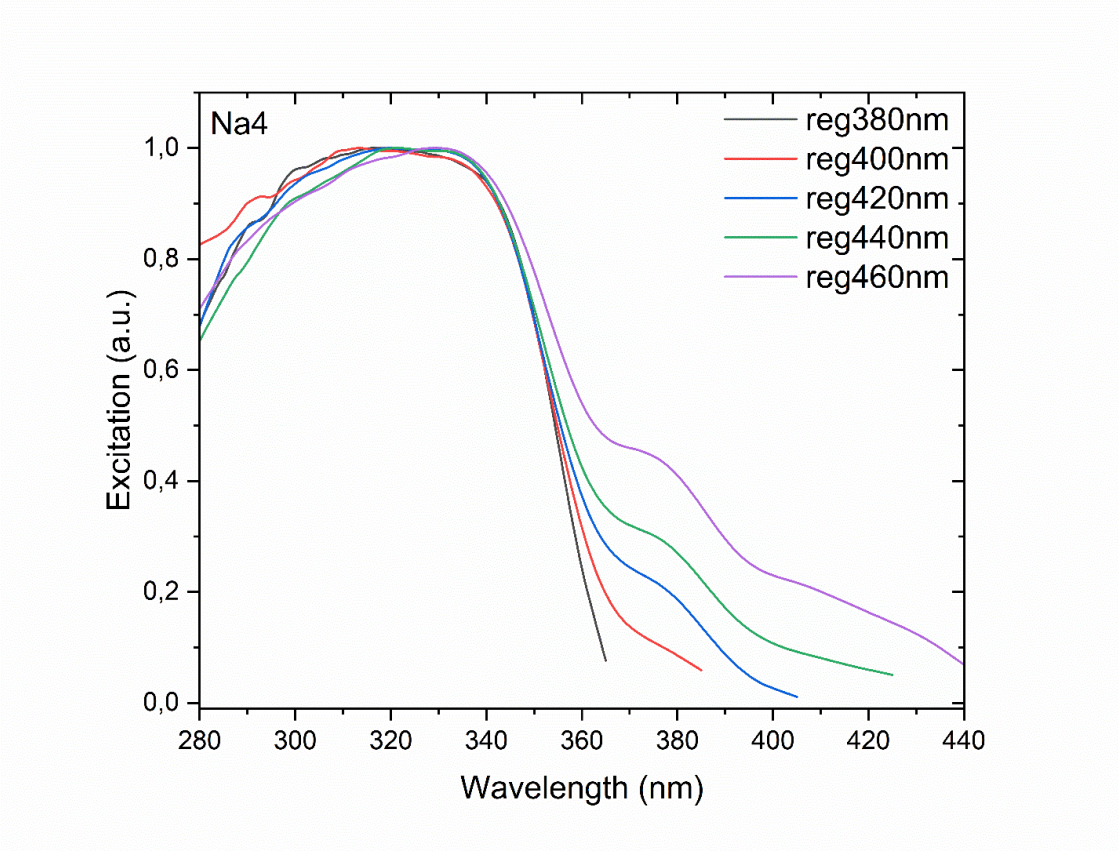


Figure S123. Excitation spectra of **Na4** at various emission wavelengths recorded at room temperature.

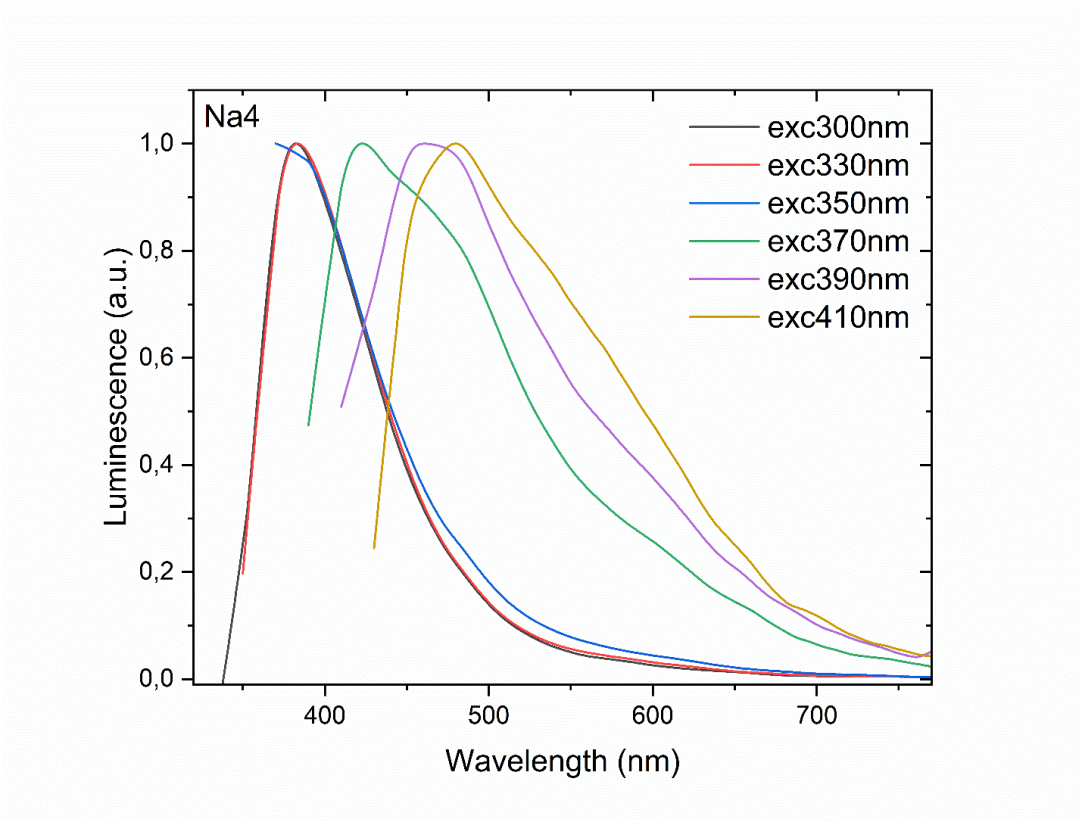


Figure S124. Emission spectra of **Na4** at various excitation wavelengths recorded at room temperature.

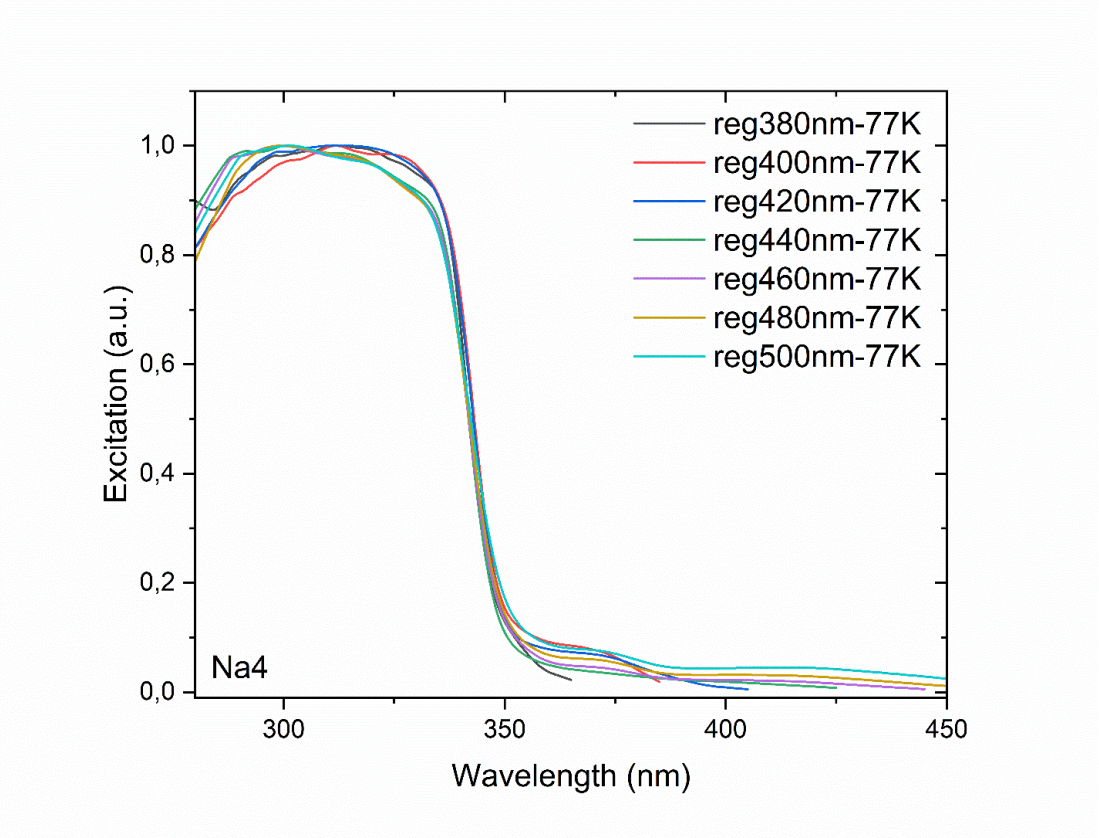


Figure S125. Excitation spectra of **Na4** at various emission wavelengths recorded at 77 K.

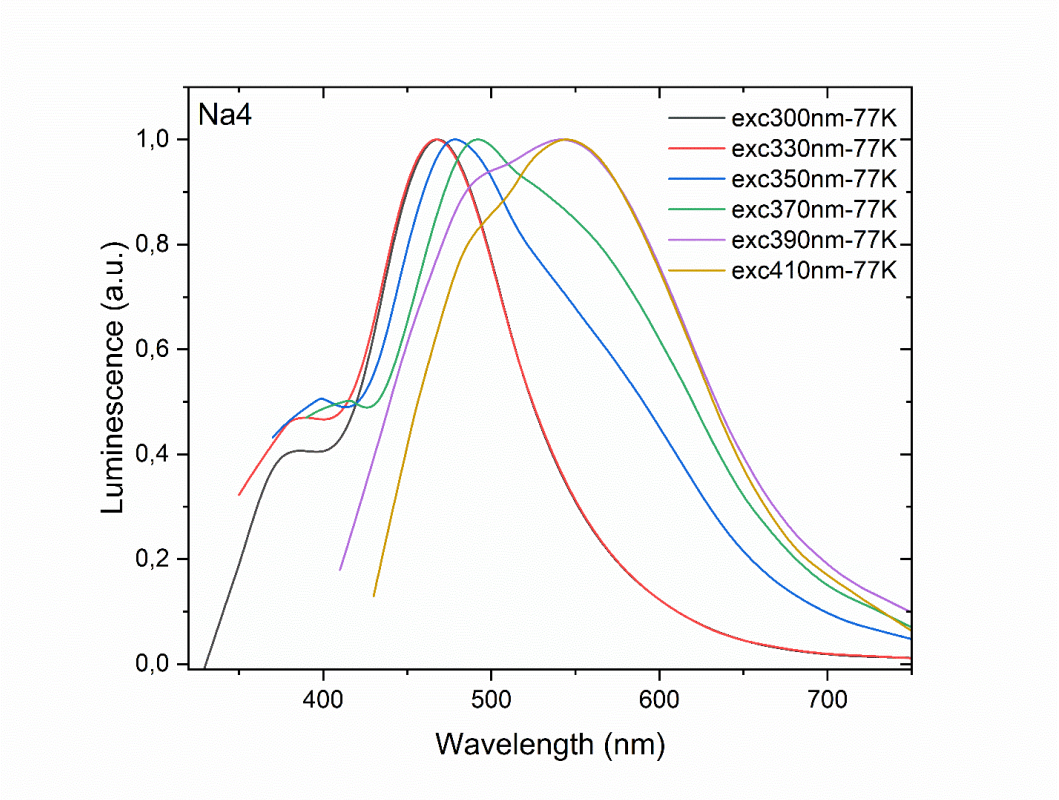


Figure S126. Emission spectra of **Na4** at various excitation wavelengths recorded at 77 K.

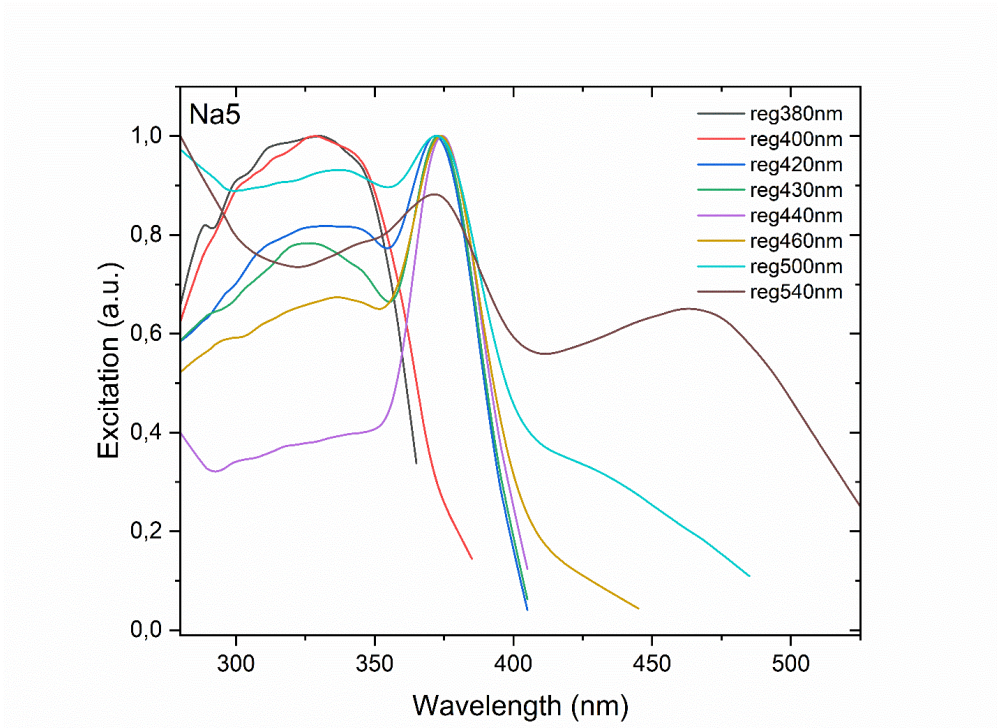


Figure S127. Excitation spectra of **Na5** at various emission wavelengths recorded at room temperature.

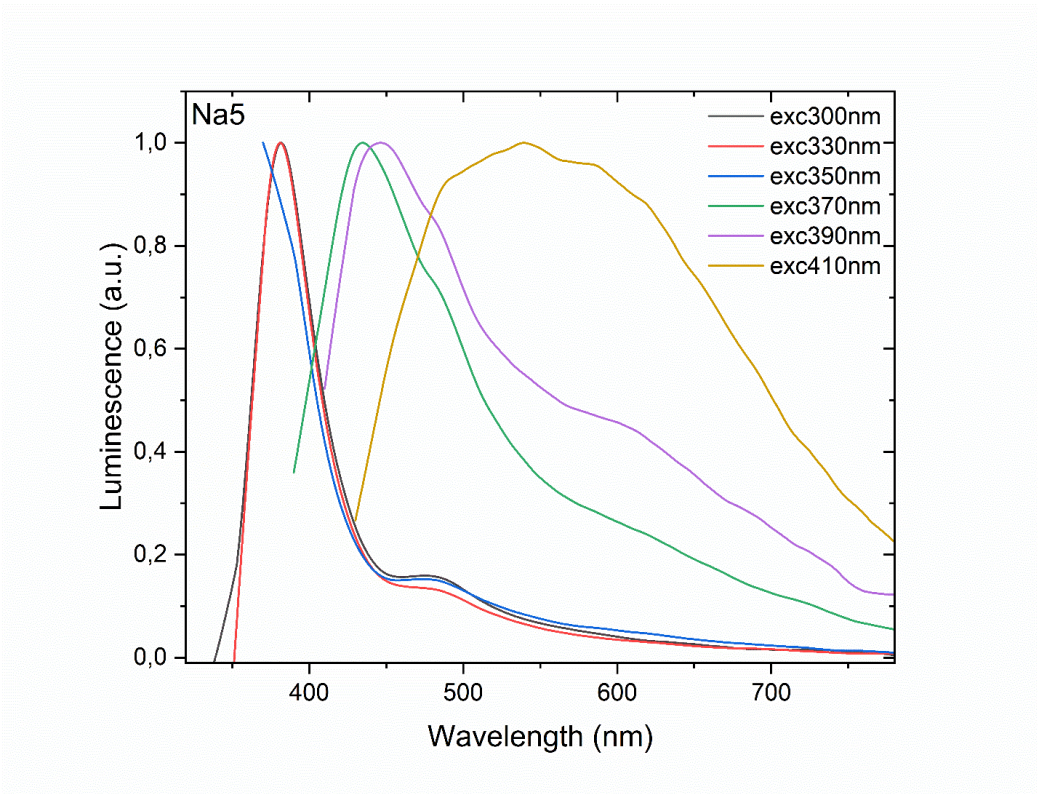


Figure S128. Emission spectra of **Na5** at various excitation wavelengths recorded at room temperature.

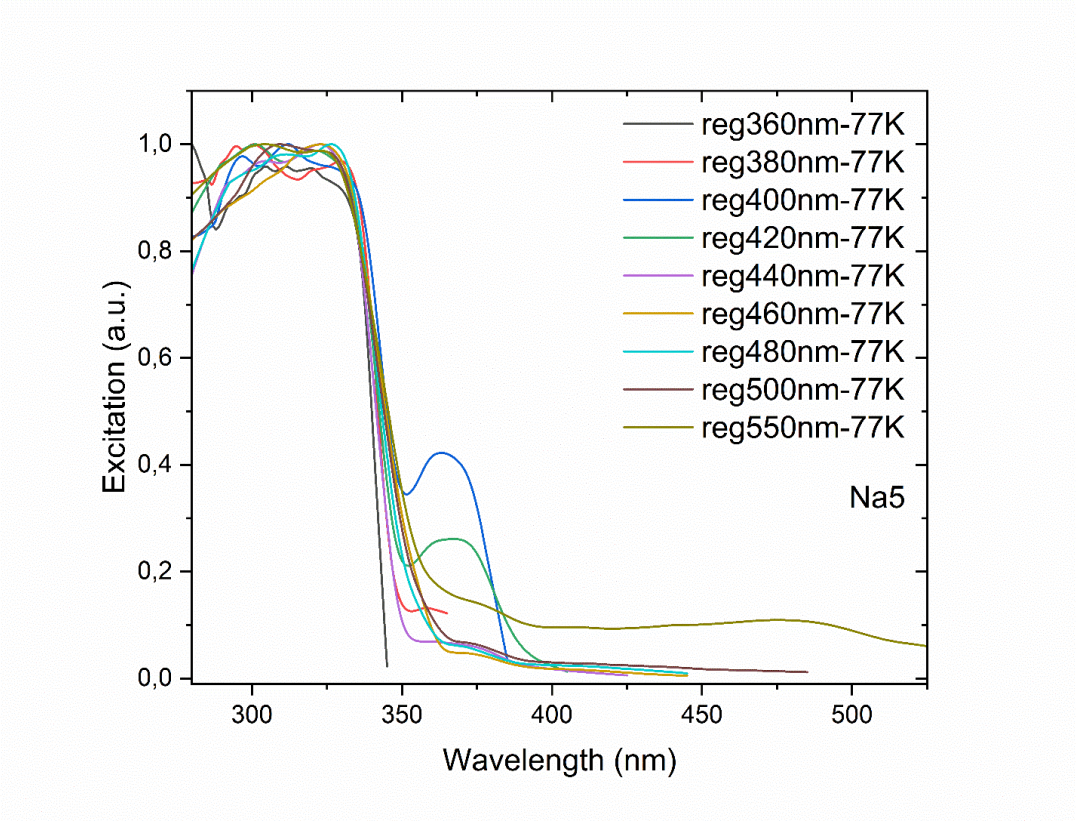


Figure S129. Excitation spectra of **Na5** at various emission wavelengths recorded at 77 K.

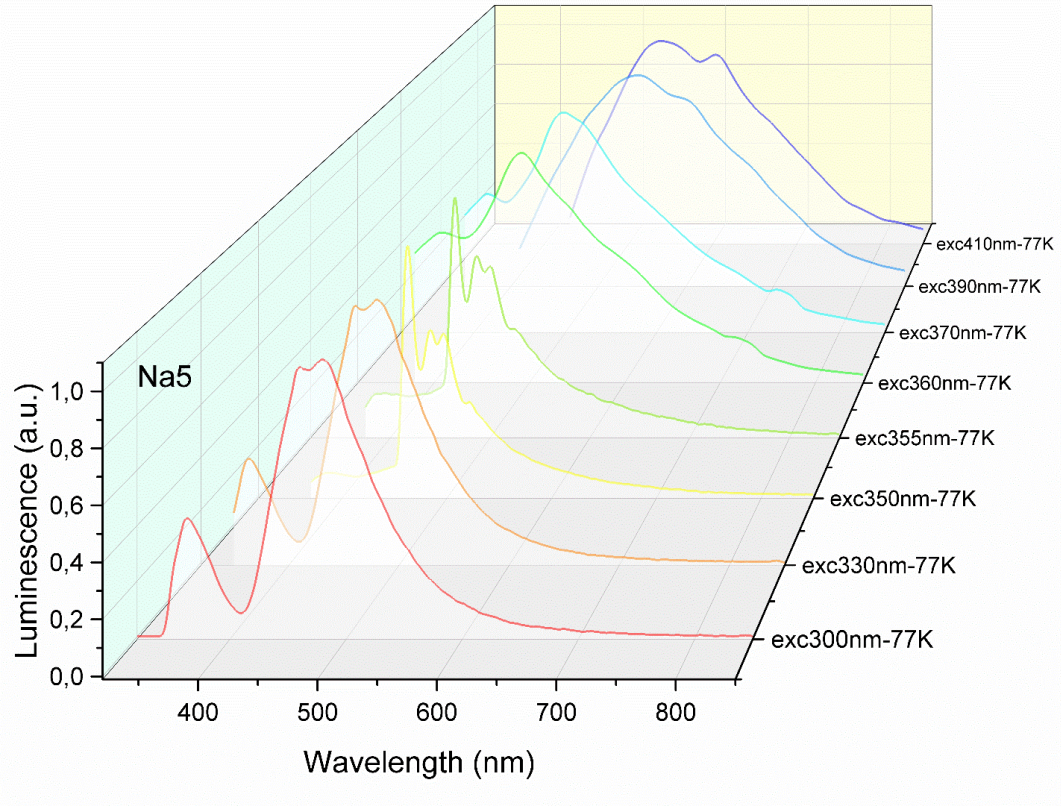


Figure S130. Emission spectra of **Na5** at various excitation wavelengths recorded at 77 K.

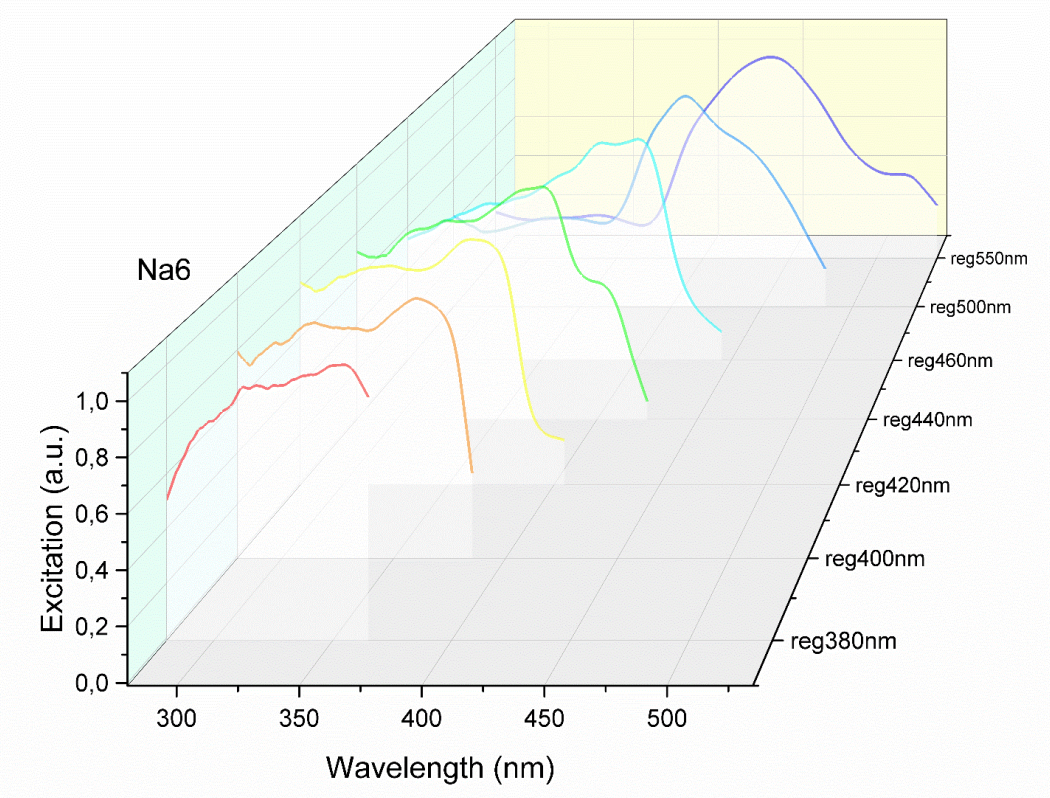


Figure S131. Excitation spectra of **Na6** at various emission wavelengths recorded at room temperature.

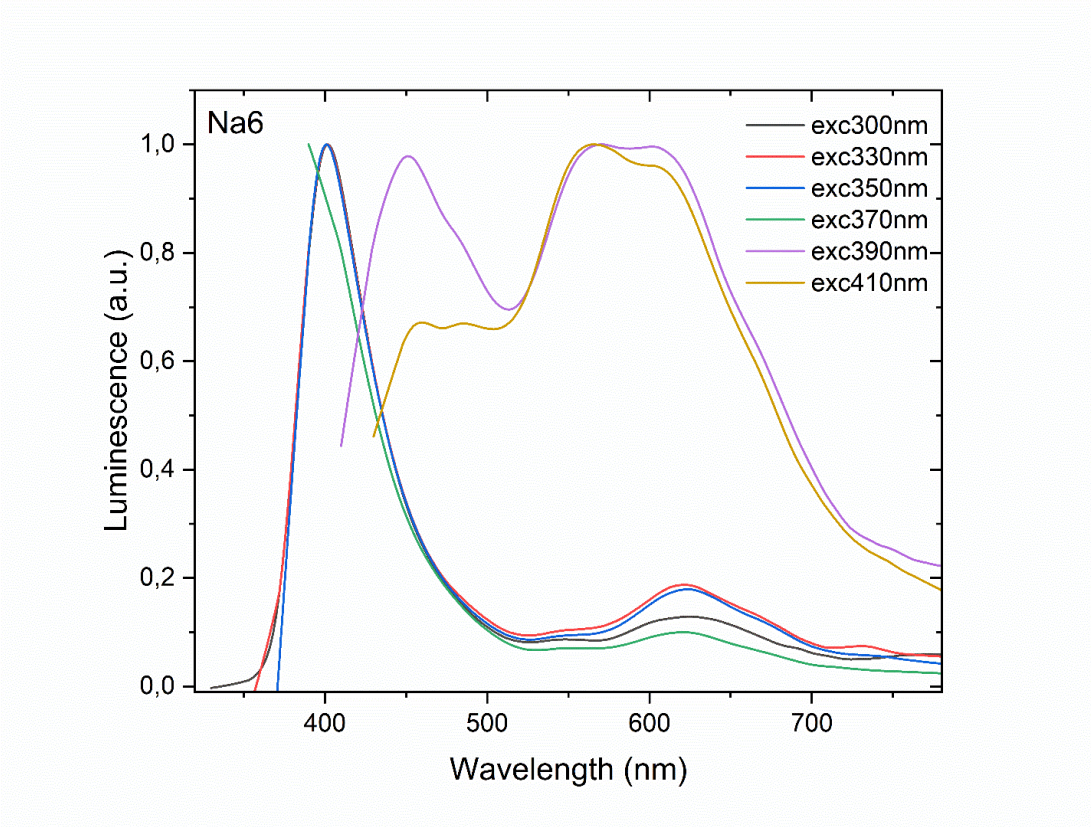


Figure S132. Emission spectra of **Na6** at various excitation wavelengths recorded at room temperature.

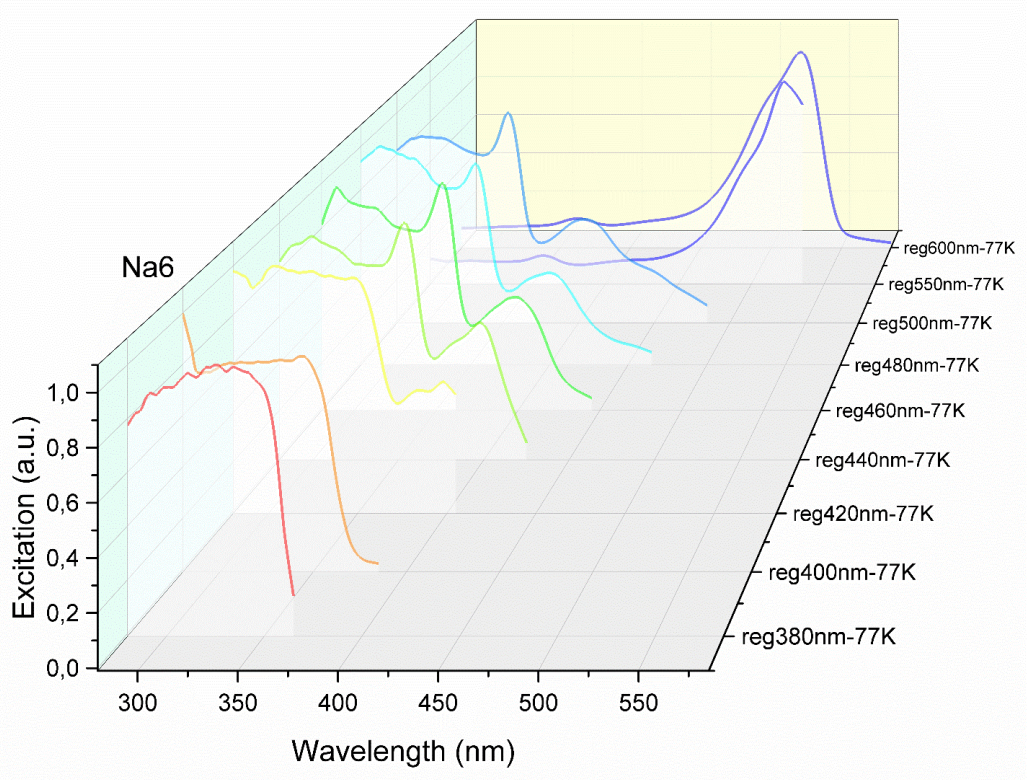


Figure S133. Excitation spectra of **Na6** at various emission wavelengths recorded at 77 K.

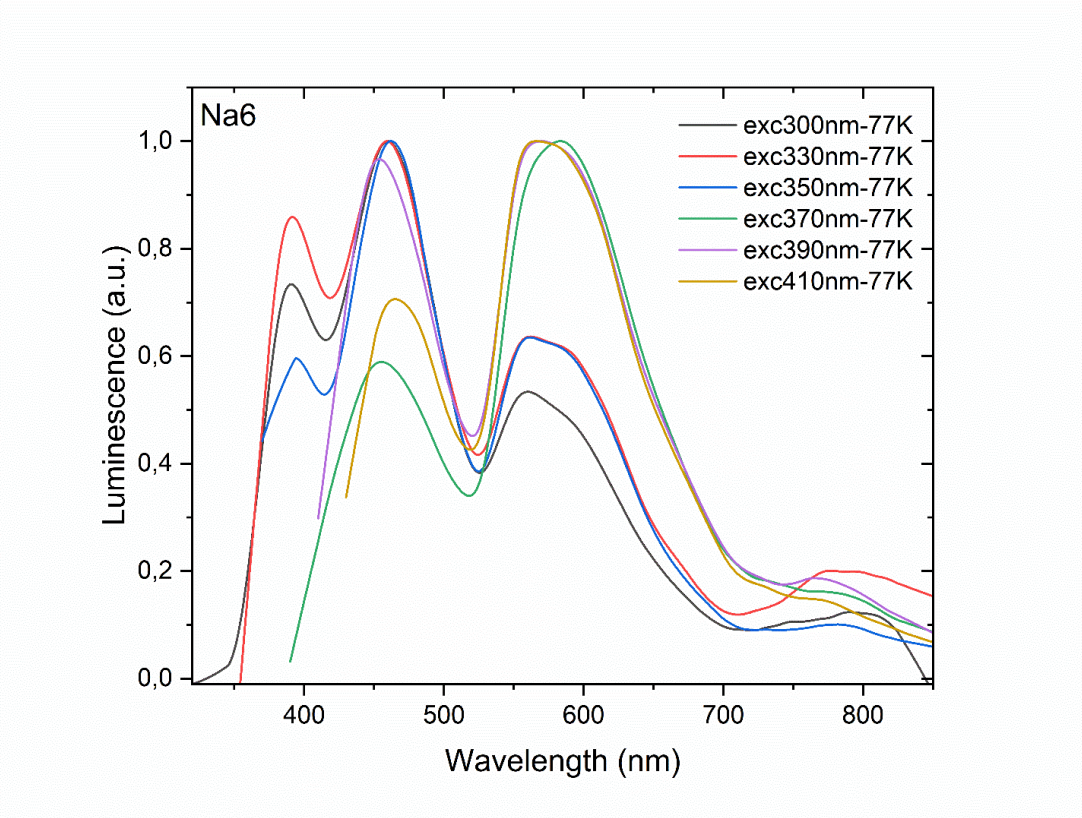


Figure S134. Emission spectra of **Na6** at various excitation wavelengths recorded at 77 K.

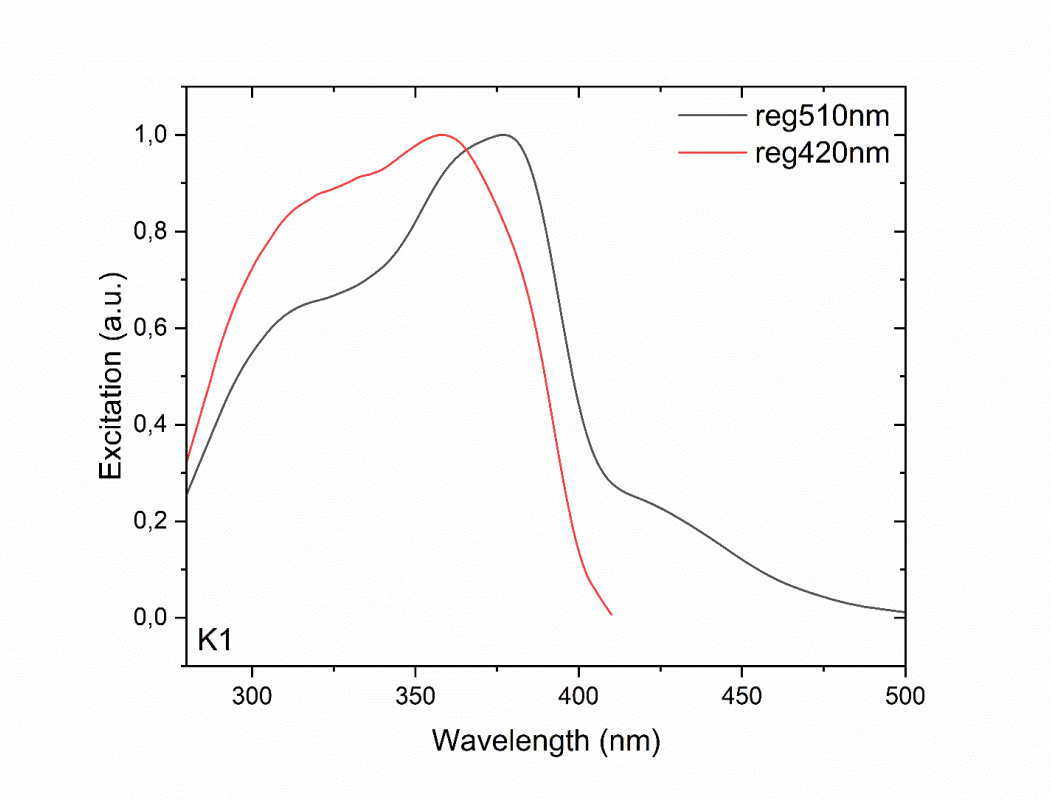


Figure S135. Excitation spectra of **K1** at various emission wavelengths recorded at room temperature.

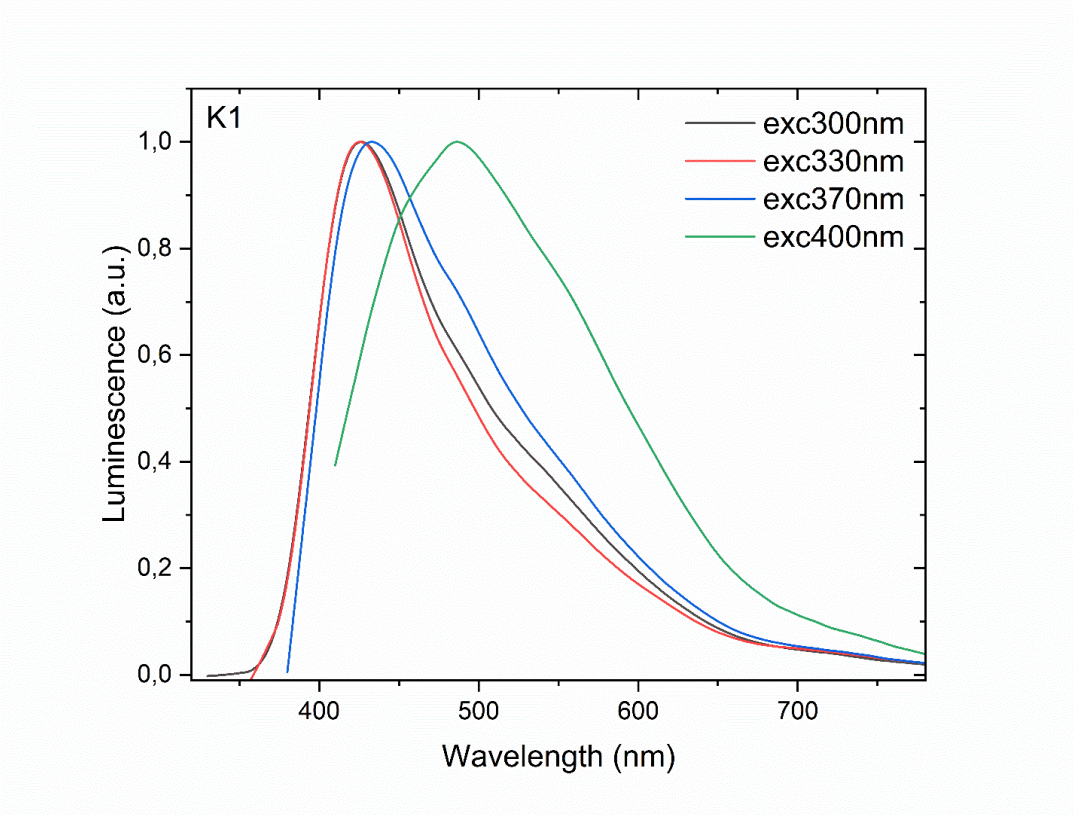


Figure S136. Emission spectra of **K1** at various excitation wavelengths recorded at room temperature.

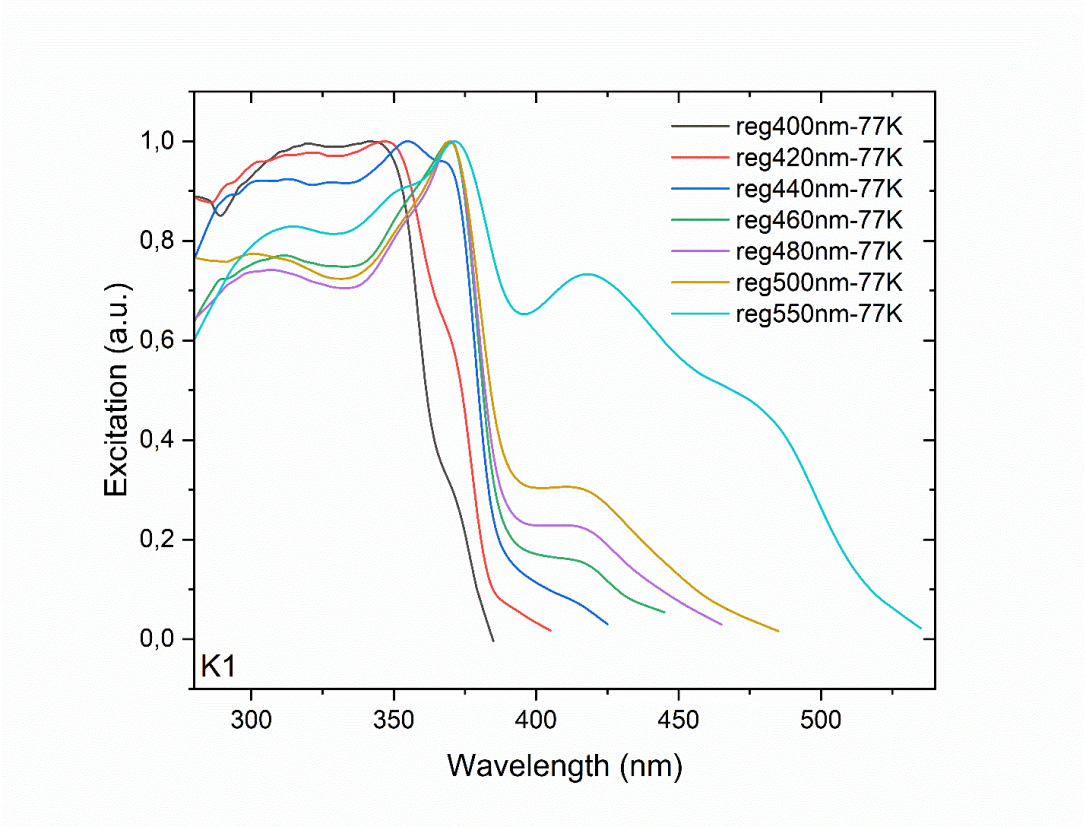


Figure S137. Excitation spectra of **K1** at various emission wavelengths recorded at 77 K.

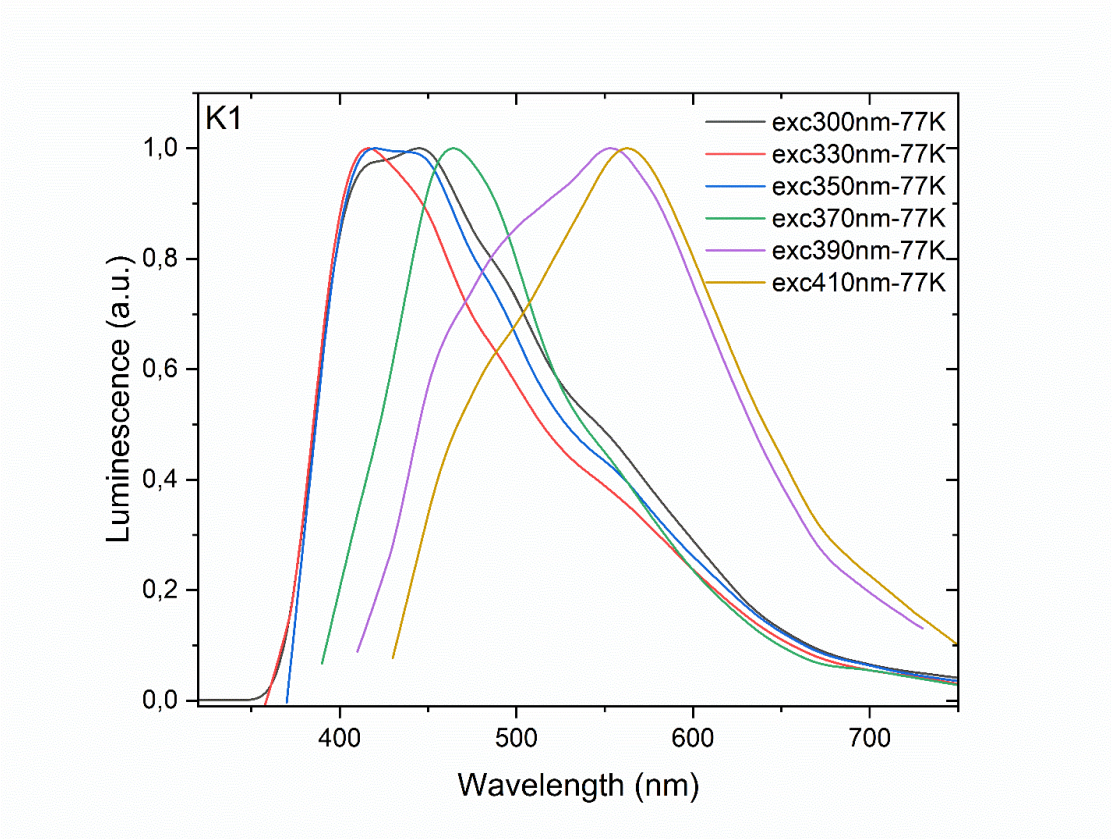


Figure S138. Emission spectra of **K1** at various excitation wavelengths recorded at 77 K.

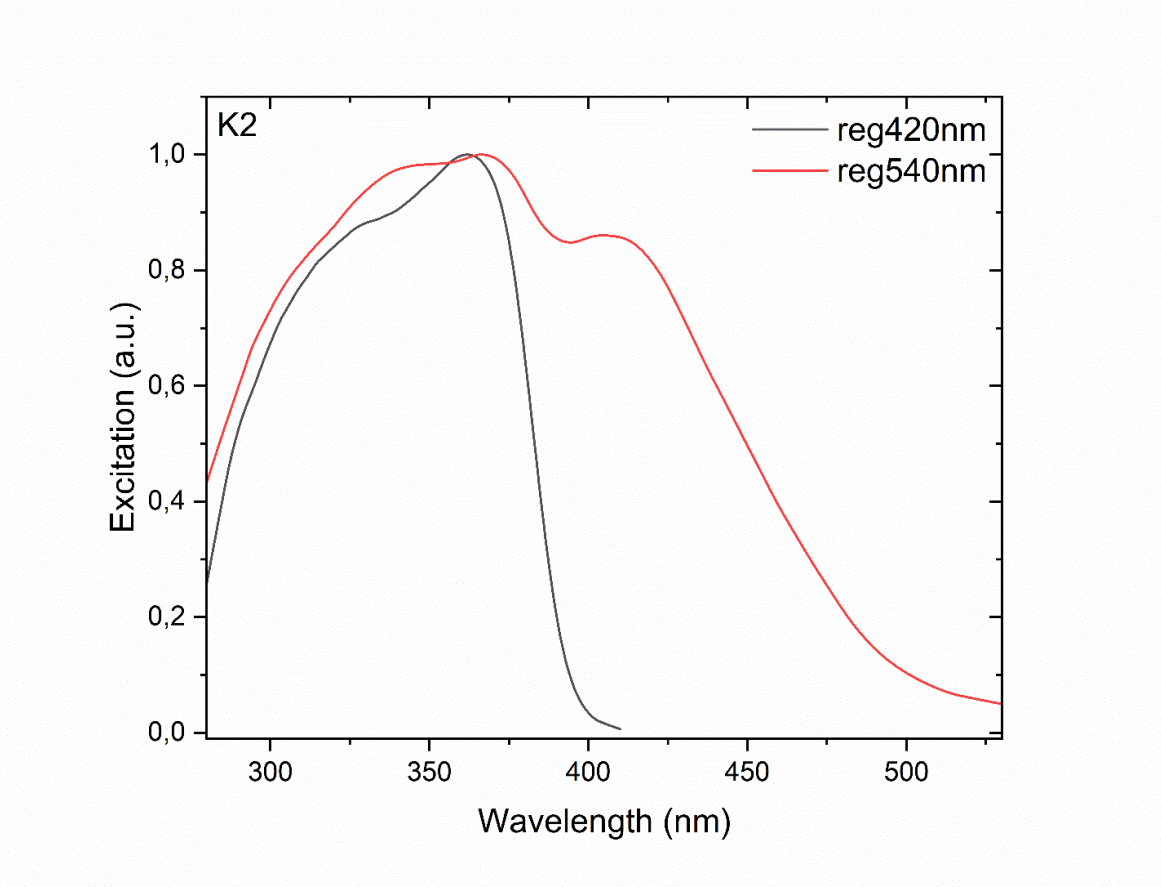


Figure S139. Excitation spectra of **K2** at various emission wavelengths recorded at room temperature.

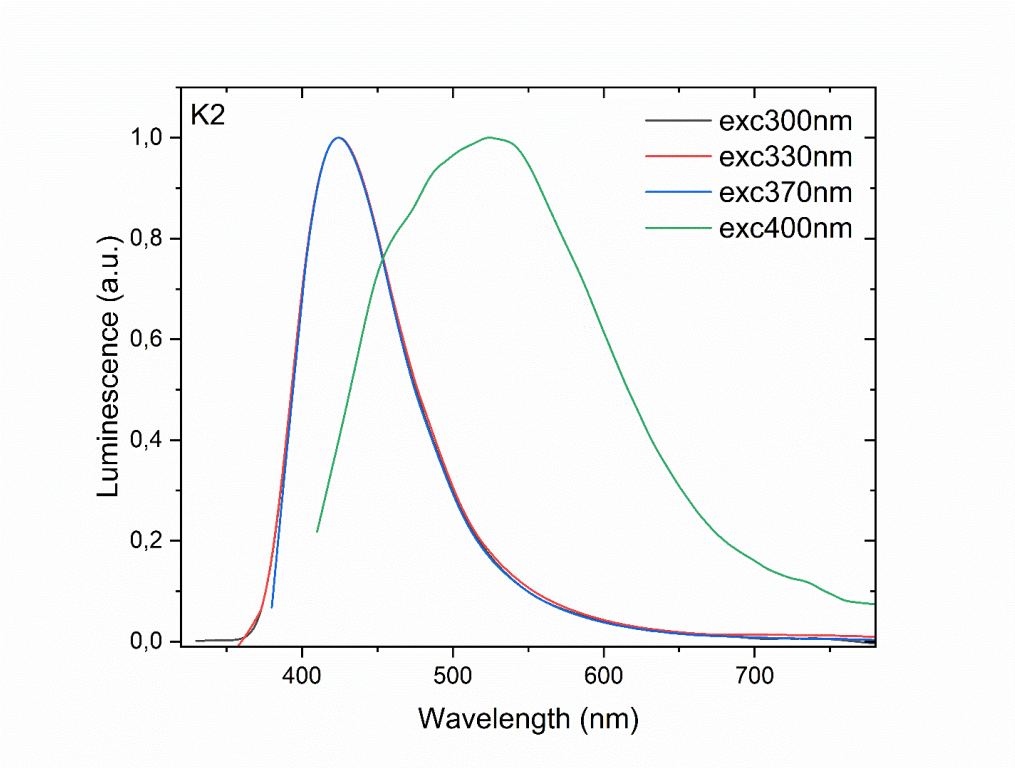


Figure S140. Emission spectra of **K2** at various excitation wavelengths recorded at room temperature.

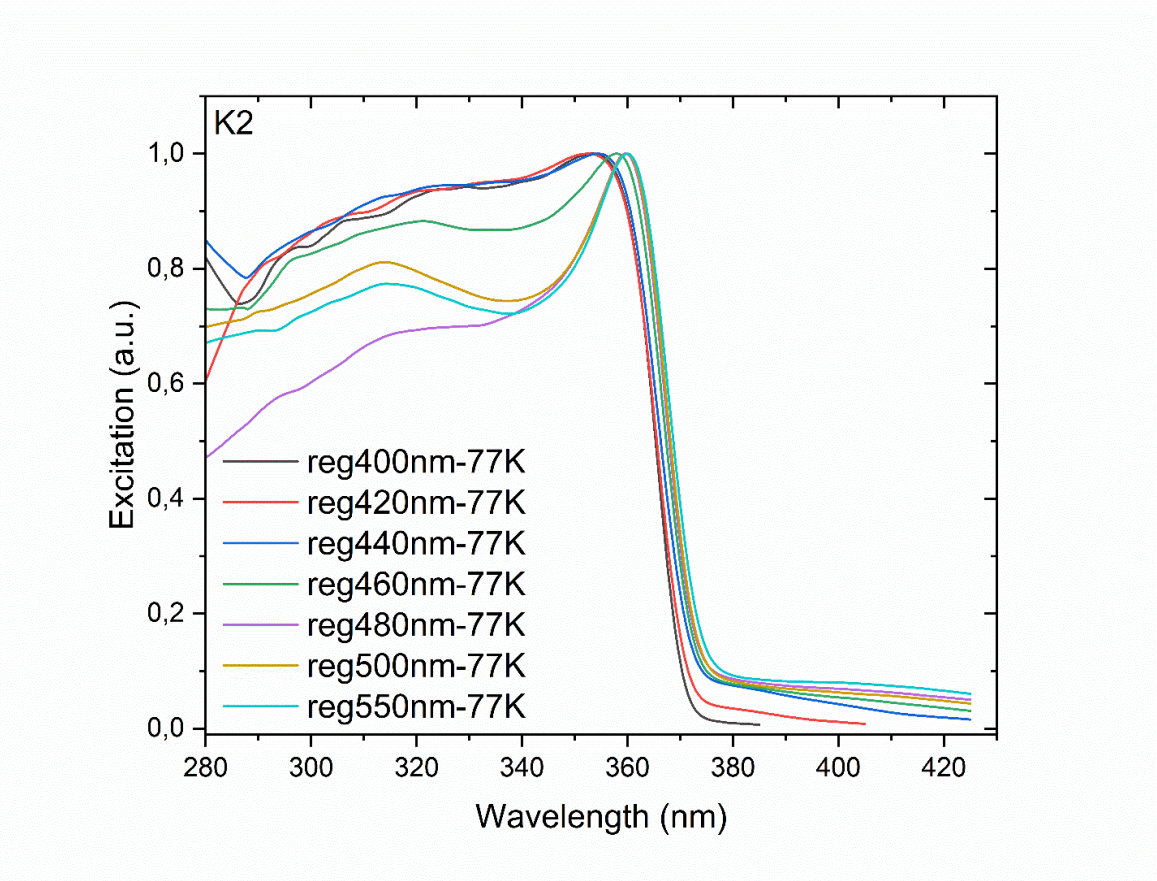


Figure S141. Excitation spectra of **K2** at various emission wavelengths recorded at 77 K.

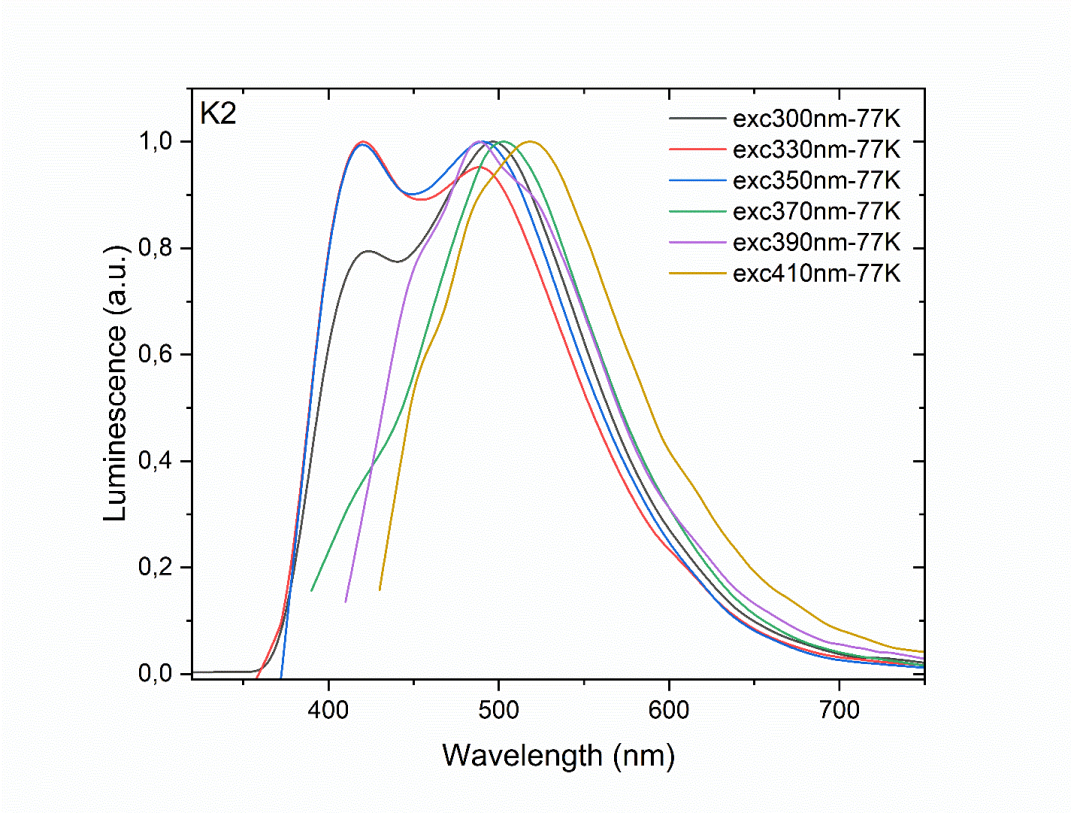


Figure S142. Emission spectra of **K2** at various excitation wavelengths recorded at 77 K.

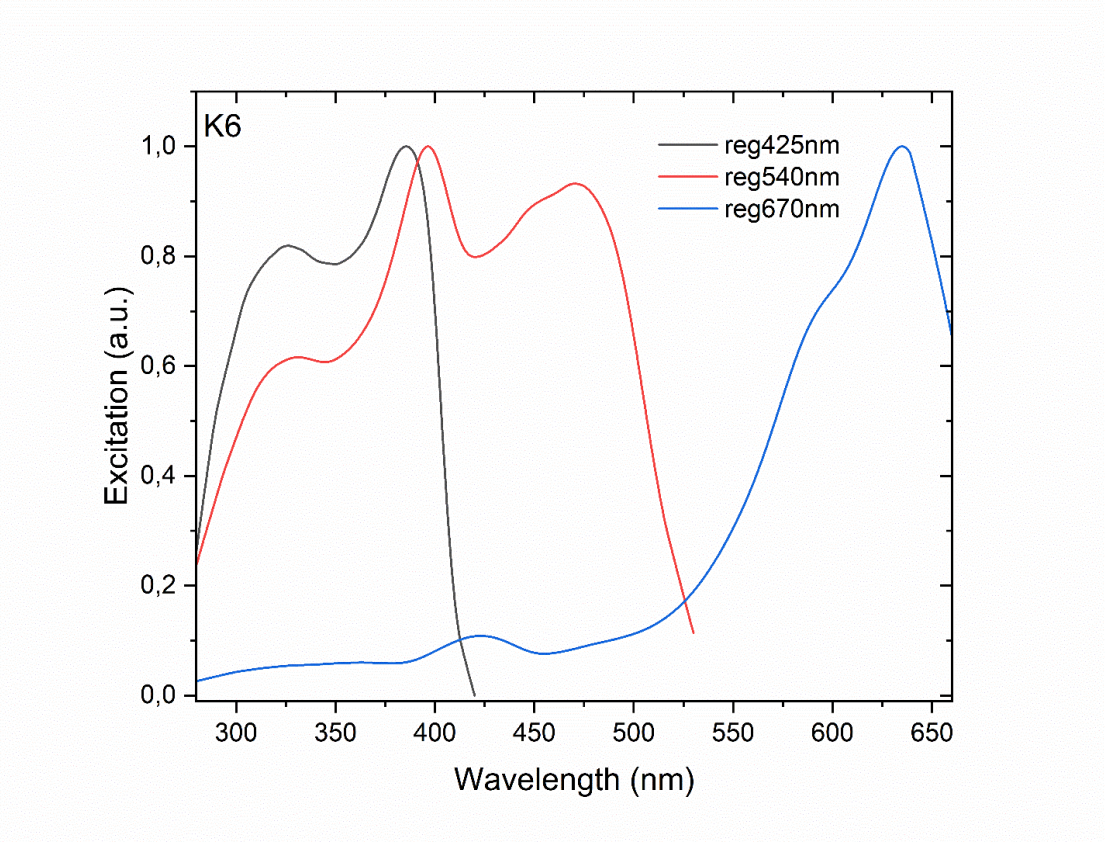


Figure S143. Excitation spectra of **K6** at various emission wavelengths recorded at room temperature.

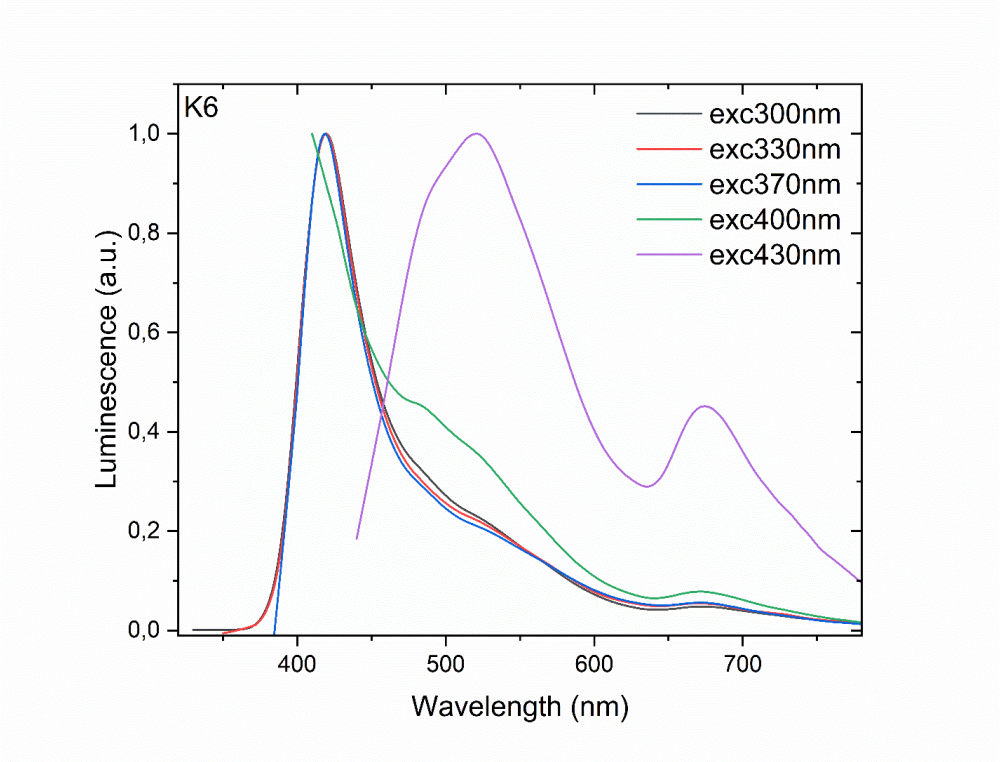


Figure S144. Emission spectra of **K6** at various excitation wavelengths recorded at room temperature.

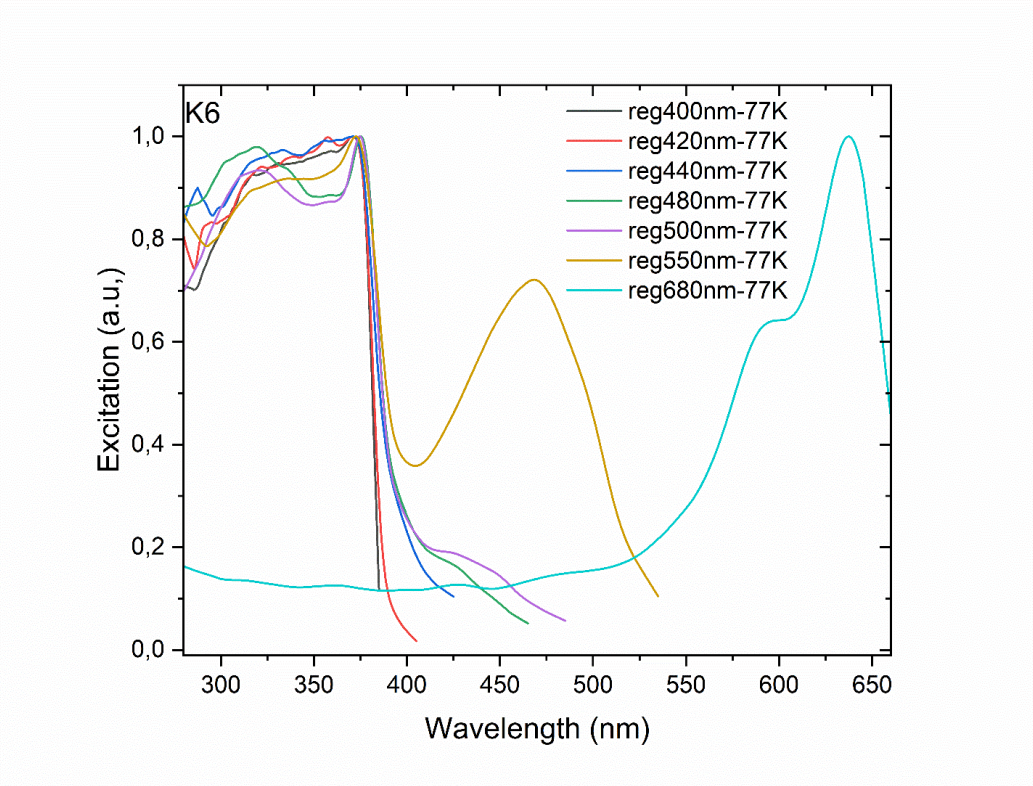


Figure S145. Excitation spectra of **K6** at various emission wavelengths recorded at 77 K.

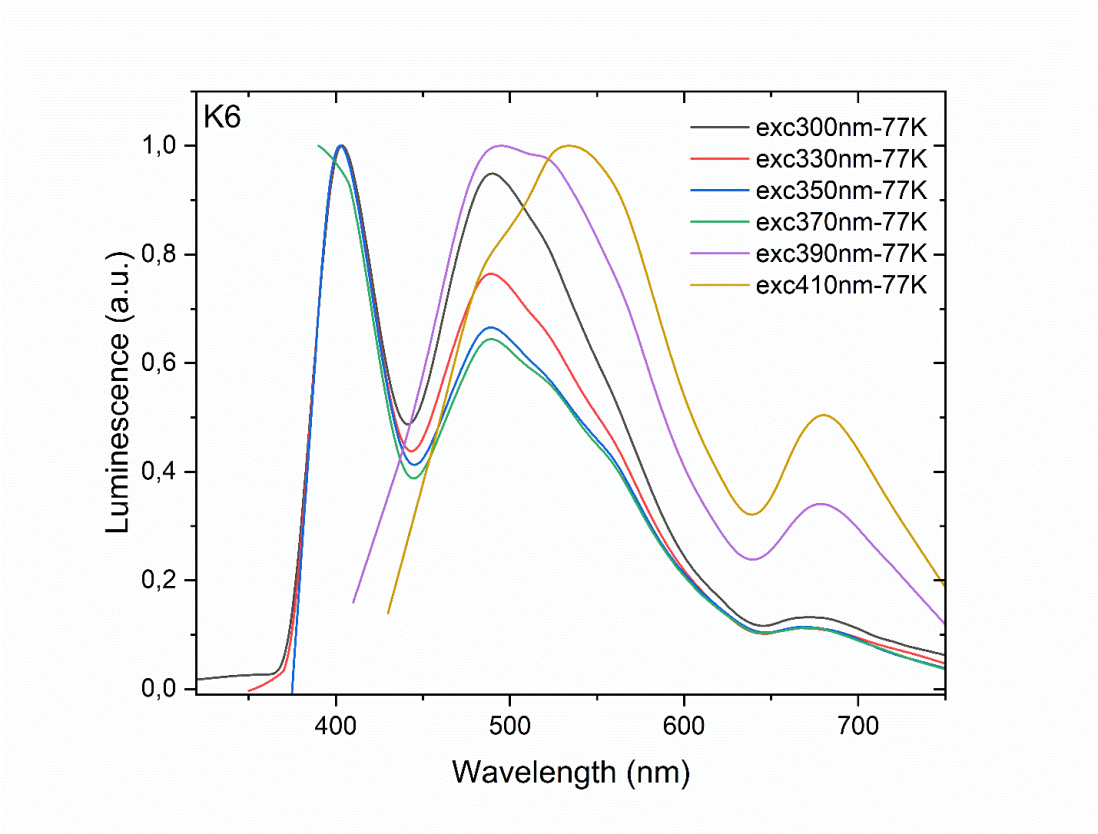


Figure S146. Emission spectra of **K6** at various excitation wavelengths recorded at 77 K.

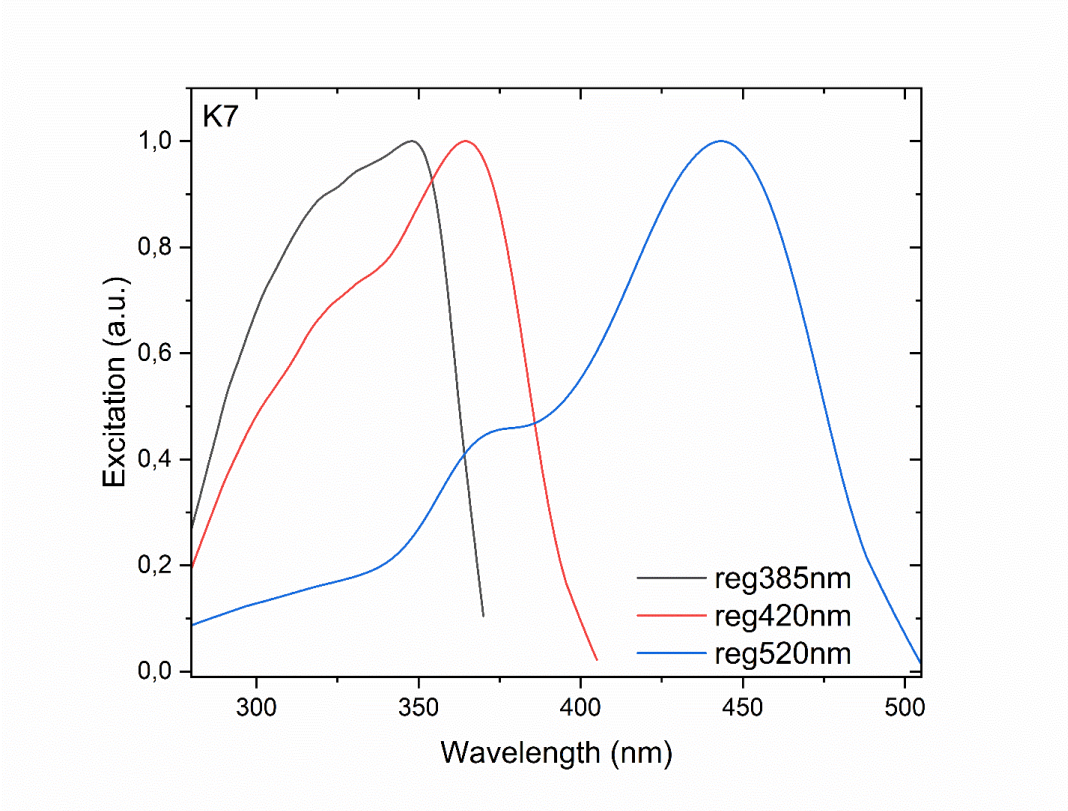


Figure S147. Excitation spectra of **K7** at various emission wavelengths recorded at room temperature.

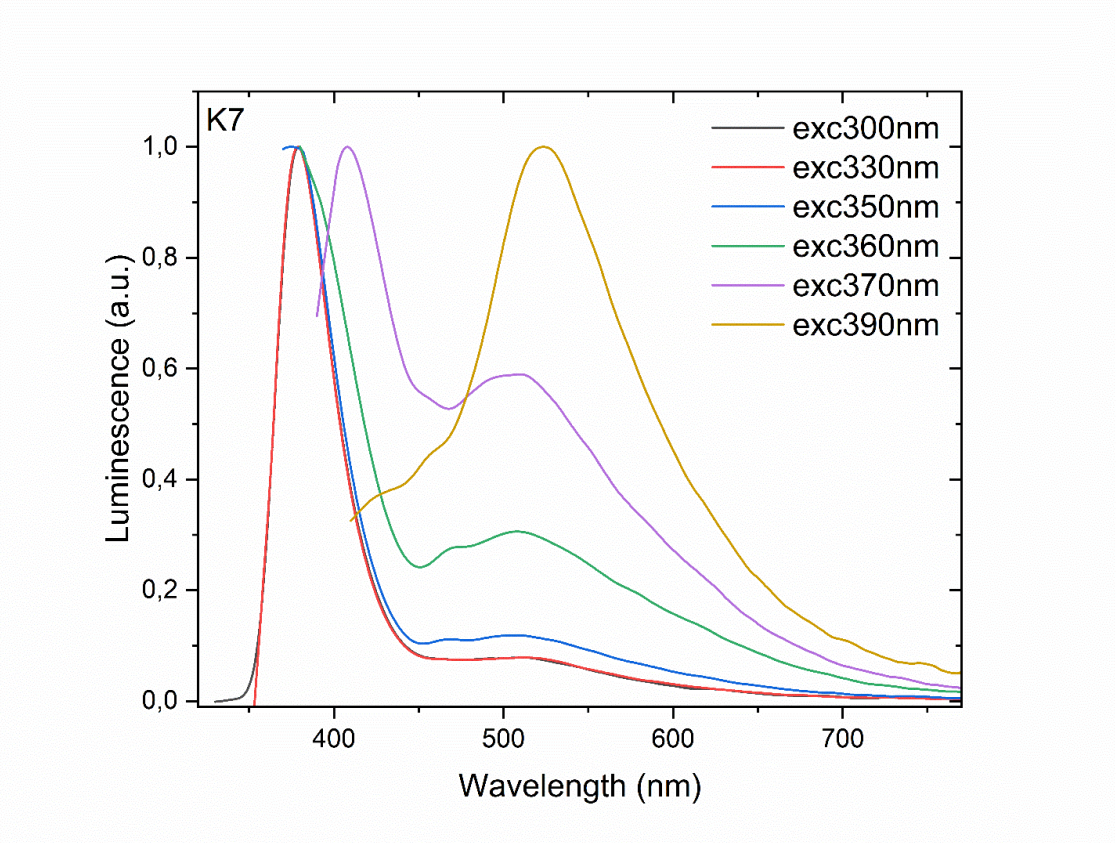


Figure S148. Emission spectra of **K7** at various excitation wavelengths recorded at room temperature.

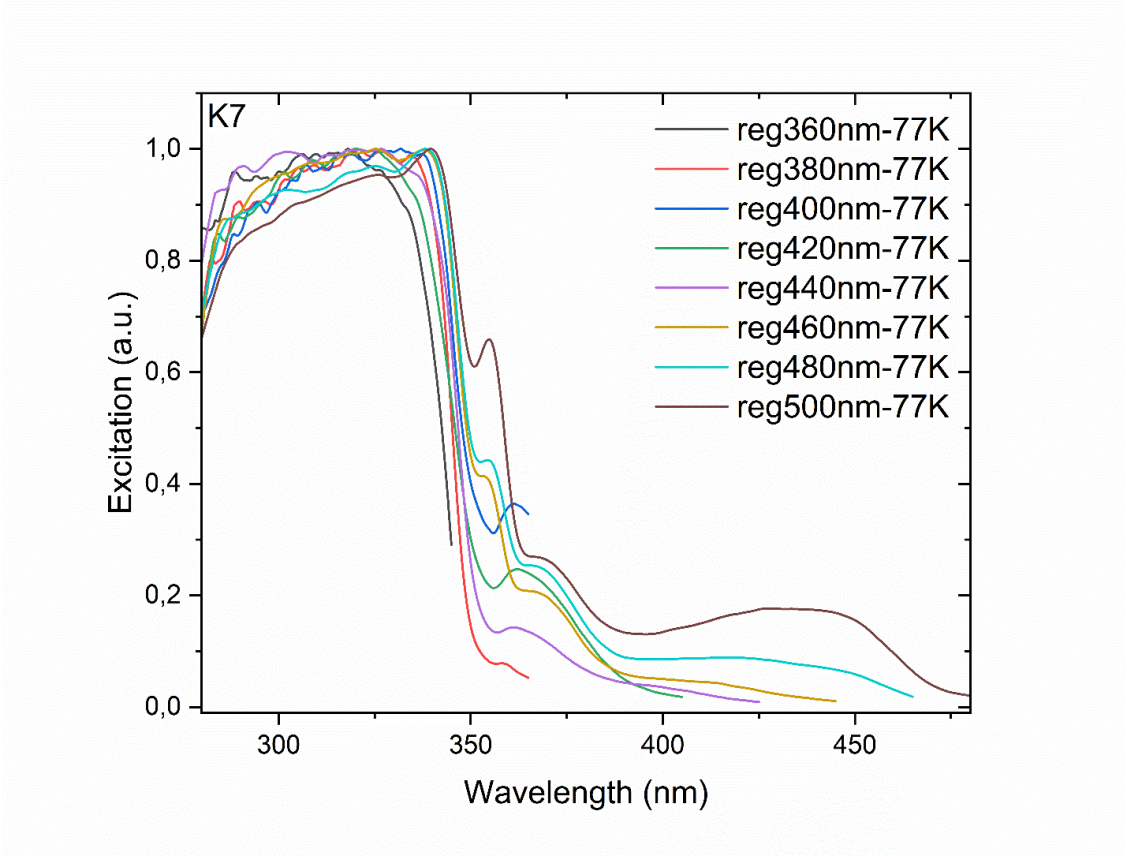


Figure S149. Excitation spectra of **K7** at various emission wavelengths recorded at 77 K.

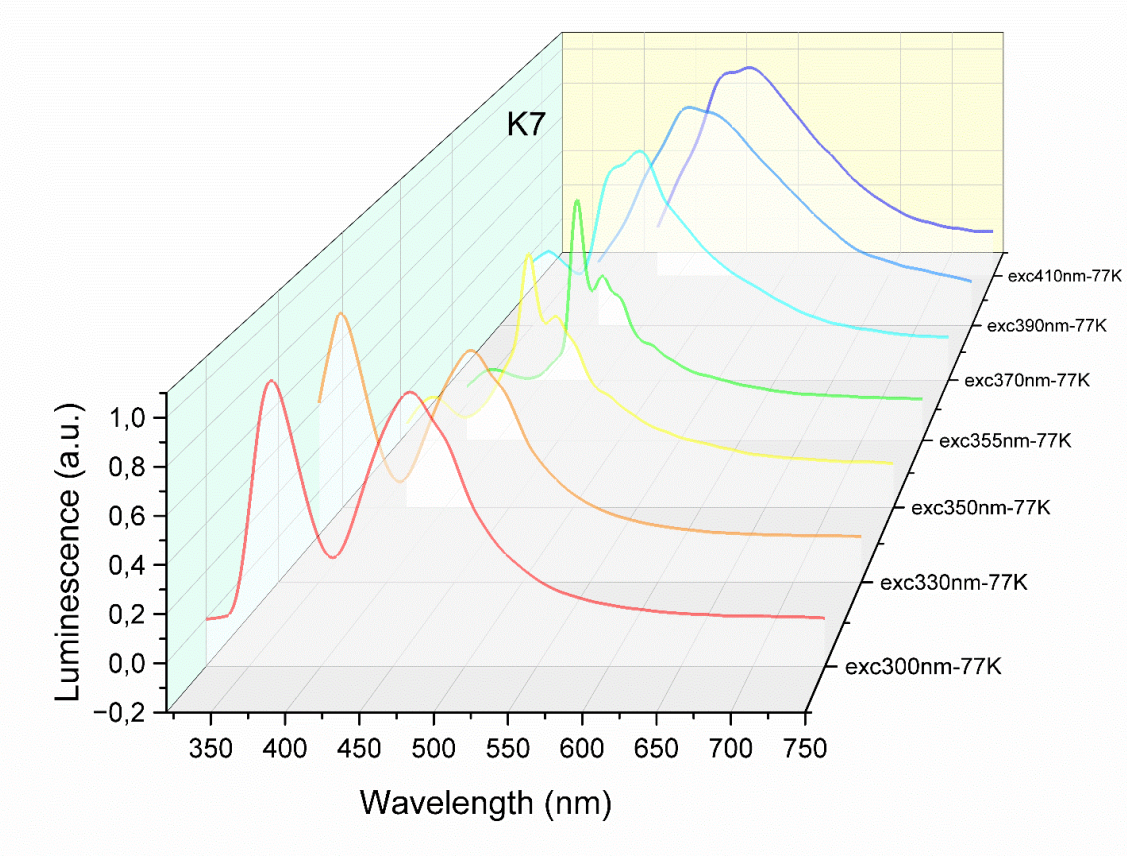


Figure S150. Emission spectra of **K7** at various excitation wavelengths recorded at 77 K.

X-ray diffraction studies.

X-ray diffraction data for **Ar*OH**, **Li1**, **Li1_Tol**, **Li2′**, **Li2**, **Li3**, **Na1**, **Na2**, **Na4**, **Na5**, **Na6**, **K1**, **K1′**, **K2**, **K6**, **K7** were collected at 100K on a four-circle Rigaku XtaLAB Synergy-S diffractometer equipped with a HyPix-6000HE area-detector (kappa geometry, shutterless ω-scan technique), using monochromatized CuK□-radiation. The intensity data were integrated and semi-empirically or analytically corrected for absorption by the CrysAlisPro program.[1] The structures were solved by dual methods using SHELXT-2014/5[2] and refined by the full-matrix least-squares minimization method on F^2 using SHELXL-2018/3[3] within the OLEX2 program (ver. 1.5-ac7).[4] All non-hydrogen atoms were refined with individual anisotropic displacement parameters. A position of H1 in **K7** was located from the electron density-difference map. All other hydrogen atoms were placed in geometrically calculated ideal positions (C-H distance = 0.950 Å for aromatic, 0.980 Å for methyl, 0.990 Å for methylene and 1.000 Å for tertiary hydrogen atoms) and refined as riding atoms with relative isotropic displacement parameters taken as U_{iso}(H)=1.5U_{eq}(C) for methyl groups and U_{iso}(H)=1.2U_{eq}(C) otherwise. A rotating group model was applied for methyl groups. In a few structures, intensities of reflections at lowest 2θ-angles were affected by the beam stop, their (I_{obs}-I_{calcd})/σ(W) values were over 10; therefore, these reflections were omitted from the final stages of the refinement. Any found disorder was modeled in a regular manner by applying similarity constraints on anisotropic displacement parameters on similar atoms and by constraining similar distances to be equal within the deviation of 0.003Å for complexes and 0.02Å for lattice solvent molecules, as well as applying constrains on carbon atoms of phenyl groups to be flat.

The structures and atom connectivity for anions in crystals of **Na5** and in **K6** were accurately determined. However, due to both poor quality of crystal diffraction and relatively high disorder in the Na(12-crown-4) and K(18-crown-6) moieties, in which positions and reasonable atomic displacement parameters of some C and O atoms cannot be determined form the obtained diffraction data. Therefore, we report herein the unit cell parameters only (Table S3).

The crystal of **Ar*OH** was refined as a racemic twin, using the absolute structure parameter to determine the crystal domain ratio. All studied crystals of Ar*OH were of poor diffraction quality likely due to an additional non-merohedral twinning and the presence of many minor crystal domains with irregular twin laws. Attempts to get monocrystals of good X-ray quality failed. The unaccounted non-merohedral twinning led to some deviations of F^2_{obs} versus F^2_{calc} and omitting of some reflections at the final stages of the refinement. Molecules of **Ar*OH** exhibit a rotational disorder of diphenylmethyl groups with the disorder ratios of 0.503(5):0.489(5) for C56A..C68A/C56B..C68B atoms and 0.511(5):0.489(5) for C38A..C50A/C38B..C50B atoms, correspondingly, and the rotational disorder for phenyl group with the ratios of 0.48(4):0.52(4) for C28A..C33A/C28B..C33B atoms.

The molecule of **Li1** (in a crystal of **Li1**) is located at an inversion center (Z'=0.5). It exhibits a conformational disorder of a coordinated THF molecule over three positions; the disorder ratio of atom sets O2A, C34A..C37A / O2B, C34B..C37B / O2C, C34C..C37C is 0.508(3):0.292(2):0.200(3). The disorder ratio for a phenyl group (C14A..C19A / C14B..C19B) is 0.527(7):0.473(7). The site occupancy for a lattice

THF molecule (O3, C38..C41) is 0.763(3). The structure factor corresponding to another highly disordered non-coordinating THF molecule was removed by the Solvent Mask procedure of the Olex2 program.[4] Both crystallographically unique molecules of **Li1** in **Li1_Tol** are located at inversion centers. Both complexes **Li1** display disorders of the $Li(THF)^+$ moiety with the disorder ratios of 0.893(4):0.107(4) (atoms Li1A, O2A, C34A..C37A / Li1B, O2B, C34B..C37B) and 0.924(4):0.076(4) (Li2A, O4A, C71A..C74A / Li2B, O4B, C71B..C74B). **Li1_Tol** displays relatively large R factors due to very poor crystal quality; we suppose that the intensities of reflections might be affected by the presence of unidentified minor crystal domains. Several attempts to reprocess the collected data resulted in even worse models. Complexes **Na1**, **K1**, **K1'** are also located at inversion centers (Z'=0.5). A non-coordinating THF molecule in **K1'** is disordered over three positions (0.639(3):0.166(2):0.195(3) for atoms O2A, C34A..C37A / O2B, C34B..C37B / O2C, C34C..C37C).

Complex **Li2** (in **Li2**), **Li2** in **Li2'**, **Na** and **K2** are also located at an inversion center (Z'=0.5). In **Li2**, two phenyl groups, a coordinated pyridine molecule and one non-coordinating pyridine molecule are all disordered over two positions with the following disorder ratios: 0.520(6):0.480(6) (C8A..C13A / C8B..C13B), 0.637(13):0.363(13) (C14A..C19A / C14B..C19B), 0.728(2):0.272(2) (N1A, C34A..C38A / N1B, C34B..C38B) and 0.7379(15):0.2621(15) (N2A, C40A..C44A / N2B, C40B..C44B). Two additional lattice molecules of pyridine are highly disordered over 2-fold rotation axes and cannot be reasonably modeled in a regular way, therefore their structure factor was removed by the Solvent Mask procedure of the Olex2 program.[4] A non-coordinating pyridine molecule (N2, C39..C43) in **Li2'** is located at an inversion center and, therefore, disordered over two positions (0.5:0.5). A coordinated pyridine molecule in **K2** is disordered over 2 positions: 0.716(18):0.284(18) for atoms N1A, C34A..C38A / N1B, C34B..C38B.

A molecule of 12-crown-4 in **Na4** is disordered over two positions (0.9451(9):0.0549(9) for atoms O2A..O5A, C34A..C41A / O2B..O5B, C34B..C41B); two phenyl groups are also disordered (0.688(19):0.312(19) for C22A..C27A / C22B..C27B and 0.640(17):0.360(17) for C28A..C33A / C28B..C33B)

K7 exhibits disorders of two phenyl group of one Ar^*O^- anion (0.844(3):0.156(3) for atoms C41A..C46A / C41B..C46B and 0.417(9):0.583(9) for C61A..C66A / C61B..C66B), of a diphenylmethyl group of the second Ar^*O^- anion (0.358(12):0.642(12) for atoms C21A..C33A / C21B..C33B), of two coordinated THF molecules in cation $[K(18\text{-crown-6})(THF)_2]^+$ (0.876(3):0.124(3) for O9A, C79A..C82A / O9B, C79B..C82B and 0.926(3):0.074(3) for O10A, C83A..C86A / O10B, C83B..C86B) and of a non-coordinating THF molecule (0.623(2):0.246(3):0.130(3) for atoms O11A, C87A..C90A / O11B, C87B..C90B / O11C, C87C..C90C).

Crystal data, data collection and structure refinement details for **Ar*OH**, **Li1**, **Li1_Tol**, **Li2′**, **Li2**, **Li3**, **Na1**, **Na2**, **Na4**, **Na6**, **K1**, **K1′**, **K2** and **K7** are summarized in Table S2. The structures have been deposited at the Cambridge Crystallographic Data Center with the reference CCDC numbers 2486431-2486444; they also contain the supplementary crystallographic data. These data can be obtained free of charge from the CCDC *via* https://www.ccdc.cam.ac.uk/structures/ . The SHELXTL software suite [5] was used for molecular graphics.

Table S2. Crystal data and structure refinement

	Ar*OH	**Li1**	**Li1_Tol**	**Na1**
Empirical formula	$C_{33}H_{28}O$	$C_{74}H_{70}Li_2O_4$• 3.5(C_4H_8O)	$C_{74}H_{70}Li_2O_4$• 2(C_7H_8)	$C_{74}H_{70}Na_2O_4$
Formula weight	440.55	1293.79	1221.45	1069.28
Temperature (K)	99.9(5)	99.9(4)	99.9(2)	100.0(2)
Wavelength (Å)	1.54184			
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic
Space group	$Cmc2_1$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
Unit cell dimensions				
a (Å)	50.4688(4)	10.7672(1)	10.8054(3)	12.4199(1)
b (Å)	10.73782(9)	27.4493(2)	14.1131(3)	18.3706(1)
c (Å)	17.3477(2)	12.3213(1)	24.2657(2)	13.3175(1)
α (º)	90	90	90.411(1)	90
β (º)	90	93.552(1)	94.438(1)	103.379(1)
γ (º)	90	90	111.613(2)	90
Volume ($Å^3$)	9401.2(1)	3634.59(5)	3427.44(3)	2956.07(4)
Z	16	2	2	2
D_{calcd} (g/cm^3)	1.245	1.182	1.184	1.201
μ (mm^{-1})	0.560	0.567	0.537	0.690
F(000)	3744	1389	1304	1136
Θ Range (º)	3.503 to 67.730	3.220 to 77.809	3.371 to 77.967	4.176 to 77.760
Complentess to Θ_{full} / Θ_{max}	0.999 / 0.999	1.000 / 0.995	0.999 / 0.998	1.000 / 0.995
Index ranges	$-60 \le h \le 60$, $-12 \le k \le 10$, $-20 \le l \le 20$	$-13 \le h \le 11$, $-34 \le k \le 34$, $-15 \le l \le 15$	$-13 \le h \le 12$, $-17 \le k \le 17$, $-30 \le l \le 27$	$-11 \le h \le 15$, $-23 \le k \le 23$, $-16 \le l \le 16$
Reflections collected	55663	98377	83883	41819
Reflections unique (R_{int})	8285 (0.0753)	7731 (0.0400)	14365 (0.0707)	6280 (0.0278)
Reflections with I > 2σ(I)	7987	7389	11605	5884
Variables / restraints	735/159	461/82	912/94	378/6
Goodness-of-fit on F^2	1.097	1.041	1.074	1.057
R_1/wR_2 indices with I>2σ(I)	0.0922 / 0.2435	0.0571, 0.1526	0.0890, 0.2730	0.0365, 0.0929
R_1/wR_2 indices (all data)	0.0952 / 0.2471	0.0583, 0.1536	0.1006, 0.2842	0.0385, 0.0942
Largest difference peak/hole ($e/Å^3$)	0.438 / -0.610	0.471/-0.290	0.642/-0.339	0.323/-0.247
CCDC number	2486431	2486436	2486437	2486441

Table S2. Crystal data and structure refinement (continued)

	K1	**K1′**	**Li2′**	**Li2**
Empirical formula	$C_{74}H_{70}K_2O_4$	$C_{66}H_{54}K_2O_2$• 2(C_4H_8O)	$C_{76}H_{64}Li_2N_2O_2$• C_5H_5N	$C_{76}H_{64}Li_2N_2O_2$• 4(C_5H_5N)
Formula weight	1101.50	1101.50	1130.27	1367.57
Temperature (K)	99.9(2)	99.9(5)	100.0(1)	99.9(5)
Wavelength (Å)	1.54184	1.54184	1.54184	1.54184
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	C2/c
Unit cell dimensions				
a (Å)	12.2267(1)	10.7669(1)	11.1331(3)	27.8573(2)
b (Å)	14.8345(1)	11.3608(2)	11.7087(2)	17.9133(1)
c (Å)	17.1733(1)	12.8692(2)	11.9358(3)	15.5068(1)
α (º)	90	90.457(1)	86.0210(19)	90
β (º)	106.337(1)	99.184(1)	83.123(2)	100.6426(5)
γ (º)	90	111.163(1)	83.042(2)	90
Volume ($Å^3$)	2989.07(4)	1445.50(4)	1530.92(6)	7605.05(7)
Z	2	1	1	4
D_{calcd} (g/cm^3)	1.224	1.265	1.226	1.194
μ (mm^{-1})	1.787	1.848	0.553	0.544
F(000)	1168	584	598	2896
Θ Range (º)	3.767 to 77.868	3.488 to 79.832	3.736 to 79.905	2.948 to 79.550
Complentess to Θ_{full} / Θ_{max}	1.000 / 0.997	0.999 / 0.991	0.998 / 0.978	0.999 / 0.991
Index ranges	$-14 \le h \le 15$, $-18 \le k \le 18$, $-21 \le l \le 21$	$-13 \le h \le 13$, $-14 \le k \le 14$, $-16 \le l \le 16$	$-14 \le h \le 13$, $-14 \le k \le 14$, $-15 \le l \le 15$	$-35 \le h \le 35$, $-15 \le k \le 22$, $-19 \le l \le 19$
Reflections collected	40549	38063	30287	53587
Reflections unique (R_{int})	6373 (0.0265)	6250 (0.0309)	6521 (0.0737)	8178 (0.0239)
Reflections with $I > 2\sigma(I)$	6169	6142	5839	7756
Variables / restraints	362 / 0	395 / 43	395/33	505/97
Goodness-of-fit on F^2	1.086	1.095	1.087	1.034
R_1 / wR_2 indices with $I>2\sigma(I)$	0.0357 / 0.0937	0.0399 / 0.1042	0.0643 / 0.1814	0.0473 / 0.1169
R_1 / wR_2 indices (all data)	0.0365 / 0.0943	0.0403 / 0.1046	0.0680 / 0.1858	0.0487 / 0.1180
Largest difference peak/hole ($e/Å^3$)	0.282 / -0.313	0.413 / -0.500	0.392 / -0.357	0.355 / -0.304
CCDC number	2486433	2486432	2486438	2486439

Table S2. Crystal data and structure refinement (continued)

	Na2	**K2**	**Li3**
Empirical formula	$C_{76}H_{64}Na_2N_2O_2$	$C_{76}H_{64}K_2N_2O_2$	$C_{42}H_{48}LiN_3O$
Formula weight	1083.27	1115.49	617.77
Temperature (K)	100.0(2)	100.0(2)	100.0(3)
Wavelength (Å)	1.54184	1.54184	1.54184
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
Unit cell dimensions			
a (Å)	12.5132(1)	12.3599(1)	8.9421(1)
b (Å)	18.0414(1)	15.1436(2)	11.3380(2)
c (Å)	13.3588(1)	16.7657(2)	18.0220(2)
α (º)	90	90	74.276(1)
β (º)	102.914(1)	104.433(1)	81.494(1)
γ (º)	90	90	78.602(1)
Volume ($Å^3$)	2939.54(4)	3039.05(6)	1715.47(4)
Z	2	2	2
D_{calcd} (g/cm^3)	1.224	1.219	1.196
μ (mm^{-1})	0.688	1.752	0.540
F(000)	1144	1176	664
Θ Range (º)	4.187 to 77.869	3.693 to 77.761	2.560 to 77.709
Complentess to Θ_{full} / Θ_{max}	1.000 / 0.998	1.000 / 0.996	0.999 / 0.991
Index ranges	$-10 \le h \le 15$, $-22 \le k \le 22$, $-16 \le l \le 16$	$-15 \le h \le 14$, $-19 \le k \le 18$, $-16 \le l \le 21$	$-11 \le h \le 11$, $-14 \le k \le 14$, $-22 \le l \le 21$
Reflections collected	39813	42357	43784
Reflections unique (R_{int})	6256 (0.0304)	6459 (0.0337)	7258 (0.0452)
Reflections with $I > 2\sigma(I)$	5885	6112	6915
Variables / restraints	371 / 0	390 / 11	448 / 21
Goodness-of-fit on F^2	1.037	1.043	1.044
R_1 / wR_2 indices with $I>2\sigma(I)$	0.0360 / 0.0919	0.0387 / 0.0999	0.0416 / 0.1088
R_1 / wR_2 indices (all data)	0.0377 / 0.0932	0.0403 / 0.1011	0.0430 / 0.1100
Largest difference peak/hole ($e/Å^3$)	0.231 / -0.249	0.256 / -0.410	0.239 / -0.207
CCDC number	2486442	2486434	2486440

Table S2. Crystal data and structure refinement (continued)

	Na4	**Na6**	**K7**
Empirical formula	$C_{49}H_{59}NaO_9$	$C_{45}H_{51}NaO_7$	$C_{90}H_{103}KO_{11}$
Formula weight	814.95	726.84	1399.82
Temperature (K)	100.0(3)	100.0(2)	99.9(4)
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
Unit cell dimensions			
a (Å)	13.1871(1)	11.0879(2)	14.0182(1)
b (Å)	19.1661(1)	13.4341(2)	23.2391(3)
c (Å)	17.4859(1)	14.7219(2)	23.5570(3)
α (º)	90	80.838(1)	90
β (º)	106.105(1)	68.502(1)	90.153(1)
γ (º)	90	72.663(1)	90
Volume ($Å^3$)	4246.03(5)	1944.57(6)	7674.2(2)
Z	4	2	4
D_{calcd} (g/cm^3)	1.275	1.241	1.212
μ (mm^{-1})	0.784	0.756	1.090
F(000)	1744	776	3000
Θ Range (º)	3.498 to 77.875	3.232 to 77.855	2.671 to 77.854
Complentess to Θ_{full} / Θ_{max}	1.000 / 0.991	0.999 / 0.991	0.955 / 0.914
Index ranges	$-16 \le h \le 16$, $-24 \le k \le 20$, $-21 \le l \le 21$	$-13 \le h \le 14$, $-16 \le k \le 17$, $-18 \le l \le 17$	$-17 \le h \le 14$, $-29 \le k \le 26$, $-29 \le l \le 29$
Reflections collected	60706	51310	54923
Reflections unique (R_{int})	8992 (0.0264)	8226 (0.0301)	14986 (0.0390)
Reflections with $I > 2\sigma(I)$	8553	7885	12199
Variables / restraints	608/46	480 / 0	1072/157
Goodness-of-fit on F^2	1.032	1.031	1.026
R_1 / wR_2 indices with $I>2\sigma(I)$	0.348 / 0.0872	0.0328 / 0.0825	0.0473 / 0.1170
R_1 / wR_2 indices (all data)	0.0362 / 0.0882	0.0338 / 0.0833	0.0600 / 0.1246
Largest difference peak/hole ($e/Å^3$)	0.254 / -0.312	0.305 / -0.206	0.462 / -0.358
CCDC number	2486443	2486444	2486435

Table S3. Unit cell parameters for **Na5** and **K6** .

	Na5	**K6**
Empirical formula	$C_{82}H_{87}NaO_{10}$	$C_{45}H_{51}KO_7$
Formula weight	1255.51	742.95
Temperature (K)	100.0(4)	99.9(2)
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_12_12_1$
Unit cell dimensions		
a (Å)	12.0261(1)	12.6629(1)
b (Å)	13.2833(1)	14.2791(1)
c (Å)	13.4653(1)	21.6293(1)
α (°)	75.839(1)	90
β (°)	68.080(1)	90
γ (°)	73.468(1)	90
Volume ($Å^3$)	1889.72(3)	3910.90(5)
Z	1	4

Lit. Ref.

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