The structural diversity of heterocycle-fused potassium cyclopentadienides

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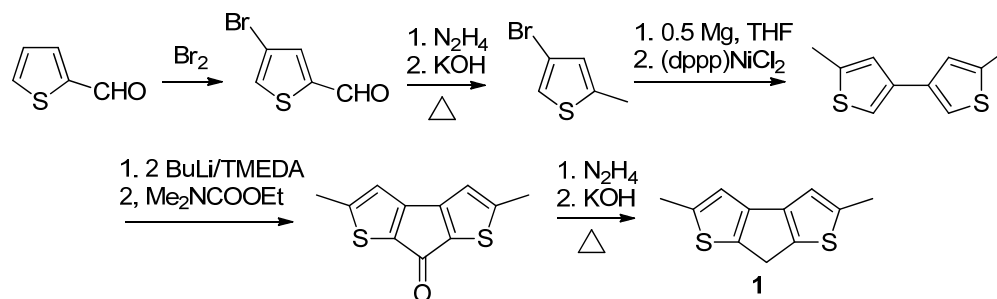
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Supporting Information

S1. Synthesis and NMR spectra of ligands and potassium salts

S1.1. Preparation of 2,5-dimethyl-7H-cyclopenta[1,2-b:4,3-b']dithiophene **1**

4-Bromothiophene-2-carbaldehyde. $AlCl_3$ powder (668 g, 5 mol) was suspended in $CHCl_3$ (1 L). The mixture was cooled to 0 °C, and thiophene-2-carbaldehyde (224 g, 2 mol) was added within 1 h. The suspension was allowed to warm to the room temperature, stirred for 1 h, and cooled to 0 °C. Br_2 (114 mL, 2.2 mol) was added dropwise within 1.5 h. After 15 h of stirring at room temperature, the mixture was poured with stirring into 1 kg of ice and 200 mL of conc. HCl. The organic phase was separated, washed by water and 5% aqueous $NaHCO_3$, dried over $MgSO_4$, and evaporated. The product was used without further purification. The yield was 84-86%. ^{1}H NMR ($CDCl_3$, 20 °C, 400 MHz) δ: 9.88 (d, 1H); 7.69 (d, 1H); 7.66 (t, 1H).

4-Bromo-2-methylthiophene. 4-Bromo-2-thiophenecarboxaldehyde (191 g, 1 mol), diethylene glycol (500 mL) and hydrazine hydrate (146 mL, 3 mol) were refluxed for 1 h with stirring. The mixture was cooled to room temperature, treated with a solution of KOH (342 g, 6 mol) in water (400 mL), and carefully heated to reflux. After the completion of hydrogen evolution, the product was distilled with water steam. CH_2Cl_2 (200 mL) was added to the resulting two-phase mixture, organic layer was isolated, washed with water, dried over $MgSO_4$, evaporated and distilled at 60-64 °C (10 torr). The overall yield starting from 2-thiophenecarboxaldehyde was ~70%. ^{1}H NMR ($CDCl_3$, 20 °C, 400 MHz) δ: 7.02 (d, 1H); 6.73 (q, 1H); 2.52 (d, 3H). [13]C ($CDCl_3$, 20 °C, 101 MHz) δ: 141.0; 127.7; 120.2; 108.9; 15.2.

5,5'-Dimethyl-3,3'-bithiophene. A suspension of Mg (21.4 g, 0.53 mol) in THF (50 mL) was treated with 1,2-dibromoethane (4 mL, 45 mmol). After the completion of ethylene evolution, the mixture was treated with the solution of 4-bromo-2-methylthiophene (253 g, 1.43 mol) and 1,2-dibromoethane (9.5 mL, 110 mmol) in THF (400 mL). After the formation of clear solution, the reaction mixture was cooled to room temperature, treated with THF (700 mL). Then, $(dppp)NiCl_2$ (3.8 g, 14.3 mmol) was added, the mixture was stirred overnight, 10% aq. NH_4Cl (2 L) was added with stirring, the aqueous phase was separated, and the organic phase was treated by 10% aq. NH_4Cl (2 L). After 10 min of stirring, the mixture was filtered, and the product was washed with water (2×200 mL) and treated with hexane (600 mL). The suspension of the product in hexane was filtered, the precititate was washed by hexane (100 mL) and dried *in vacuo*. The mother liquor was

shaked with combined aqueous phase, separated and evaporated under reduced pressure. The residue was recrystallized from ethanol (1 L). Both portions were combined, the total yield was 106 g (77%). ^{1}H NMR (CDCl₃, 20 °C, 400 MHz) δ: 7.08 (d, 1H); 6.98 (quintet, 1H); 2.52 (d, 3H). ^{13}C NMR (CDCl₃, 20 °C, 101 MHz) δ: 140.1; 137.1; 124.4; 117.1; 15.3.

2,5-Dimethyl-7H-cyclopenta[1,2-b:4,3-b']dithiophen-7-one. A mixture of 2,2'-dimethyl-4,4'-dithienyl (48.6 g, 250 mmol), ether (400 mL) and TMEDA (83 mL, 550 mmol) was cooled to –20 °C and treated with 2.2M BuLi in hexane (250 mL, 550 mmol). The mixture was allowed to warm to room temperature, stirred for 3 h and treated with (EtO)C(O)NMe₂ (29.3 g, 250 mmol) in ether (600 mL). After 40 h of stirring, the mixture was poured into 2 L of saturated aqueous solution of NH₄Cl. Organic phase was isolated, washed with 1 L of water, treated with 100 mL of hexane and then filtered. The precipitate was washed with water, hexane (2×100 mL) and dried. Filtrate was evaporated to residual volume of 200 mL, filtered, washed with hot hexane and dried. The total yield was 45 g (82%). ^{1}H NMR (CDCl₃, 20 °C, 400 MHz) δ: 6.58 (q, 1H); 2.50 (d, 6H); ^{13}C NMR (CDCl₃, 20 °C, 101 MHz) δ: 178.8; 152.6; 152.2; 133.0; 118.6; 16.1.

2,5-Dimethyl-7H-cyclopenta[1,2-b:4,3-b']dithiophene **1**. A mixture of 2,5-dimethyl-7H-cyclopenta[1,2-*b*:4,3-*b*']dithiophen-7-one (45 g, 205 mmol), diethylene glycol (600 mL) and hydrazine hydrate (70 mL) was warmed to 80 °C, stirred for 1 h, heated to reflux, and cooled to the room temperature. The solution of KOH (70 g) in 230 mL of water was added, the resulting mixture was carefully heated to rexlux. After 2 h, the mixture was cooled to 70 °C, and poured into 3 L of water. The precipitate was filtered off, washed with water (5×200 mL) and dried. The yield was 32 g (78%). ^{1}H NMR (CDCl₃, 20 °C, 400 MHz) δ : 6.81 (q, 2H); 3.72 (s, 2H); 2.58 (d, 6H). ^{13}C NMR (CDCl₃, 20 °C, 101 MHz) δ: 143.6; 142.1; 140.1; 116.4; 33.1; 15.9.

S1.2. Preparation of 5-methyl-5,6-dihydroindeno[2,1-b]indole **2**
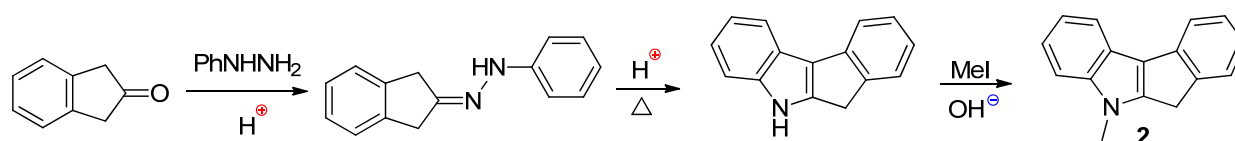
5,6-Dihydroindeno[2,1-b]indole

A mixture of 2-indanone (30.0 g, 0.23 mol), PhNHNH₂ (22.3 mL, 0.23 mol), isopropanol (300 mL) and *p*-TsOH (1 g) was refluxed for 1 h, and cooled. The solution of H₂SO₄ (16 mL) in isopropanol (50 mL) was added, the mixture was refluxed for 40 min, cooled and poured into 2.5% aq. NaOH (800 mL). The precipitate was filtered off, washed by water and by isopropanol (2×100 mL), and dried. The yield was 37.8 g (80%). M.p. 205-206 °C. ^{1}H NMR (DMSO-d₆, 20 °C, 400 MHz) δ: 11.59 (bs, 1H); 7.59 (d, 1H); 7.55 (t, 2H); 7.46 (d, 1H); 7.35 (t, 1H); 7.20 (t, 1H); 7.10 (t,

1H); 7.04 (t, 1H); 3.68 (bs, 2H). ^{13}C NMR (DMSO-d$_6$, 20 °C, 101 MHz) δ: 147.42; 143.58; 140.70; 135.09; 126.62; 125.45; 124.58; 124.11; 120.98; 119.85; 119.28; 118.59; 117.72; 112.41; 29.83.

5-Methyl-5,6-dihydroindeno[2,1-b]indole **2**

A mixture of 5,6-dihydroindeno[2,1-*b*]indole (5.0 g, 22 mmol), methyl iodide (1.6 mL, 25 mmol), 40% NaOH (60 mL), benzene (80 mL) and trimethylcetylammonium bromide (0.2 g) was stirred 8 h at 40 °C. Organic phase was separated, washed by water, dried over Na$_2$SO$_4$ and evaporated under reduced pressure. The residue was recrystallized from 1:2 benzene/hexane mixture. The yield was 3.4 g (71%), colorless crystals. M.p. 172 °C. ^{1}H NMR (CDCl$_3$, 20 °C, 400 MHz) δ: 7.89 (dd, 1H); 7.67 (d, 1H); 7.45 (d, 1H); 7.40–7.35 (m, 2H); 7.27 (m, 2H); 7.12 (t, 1H); 3.78 (s, 3H); 3.66 (s, 2H).

S1.3. Preparation of 5-methyl-5,10-dihydroindeno[1,2-b]indole **3**
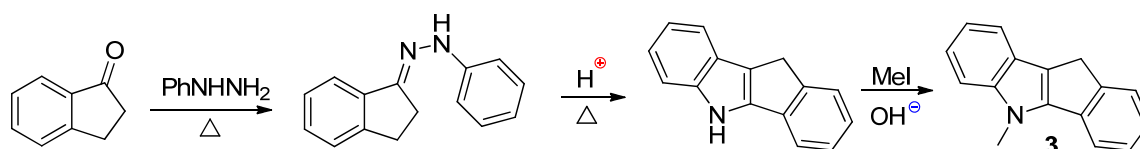
5,10-Dihydroindeno[1,2-b]indole

A mixture of 1-indanone (5.0 g, 38 mmol), PhNHNH$_2$ (3.76 mL, 38 mmol), isopropanol (50 mL) and *p*-TsOH (0.3 g) was refluxed for 40 min, and cooled. The precipitate was filtered off, washed by isopropanol (2×20 mL), and dried. The yield of hydrazone was 7.38 g (88%). M.p. 126 °C. Hydrazone (8.4 g, 38.1 mmol) was suspended in isopropanol (60 mL), and H$_2$SO$_4$ (4 mL) was added. The mixture was refluxed for 10 h, and poured into the solution of KOH (4 g) in 200 mL of water. The residue was recrystallized from benzene. The yield was 5.2 g (67%). M.p. 245 °C. ^{1}H NMR (CDCl$_3$, 20 °C, 400 MHz) δ: 8.33 (bs, 1H, NH); 7.64 (dd, 1H); 7.54 (d, 1H); 7.47 (d, 1H); 7.44 (dd, 1H); 7.33 (t, 1H); 7.22 (t, 1H); 7.18 (m, 1H); 3.74 (s, 2H).

5-Methyl-5,10-dihydroindeno[1,2-b]indole **3**

A mixture of 5,10-dihydroindeno[1,2-*b*]indole (21.9 g, 0.1 mol), methyl iodide (6.23 mL, 0.1 mol), 50% NaOH (300 g), benzene (150 mL) and trimethylcetylammonium bromide (1 g, 2.5 mmol) was stirred 2 h. Organic phase was separated, washed by water, dried over Na$_2$SO$_4$ and evaporated under reduced pressure. The residue was recrystallized from hexane. The yield was 17.3 g (81%), colorless crystals. M.p. 153–154 °C. ^{1}H NMR (CDCl$_3$, 20 °C, 400 MHz) δ: 7.67 (m, 2H); 7.57 (d, 2H); 7.39 (t, 2H); 7.30–7.20 (m, 3H); 4.02 (s, 3H); 3.71 (s, 2H).
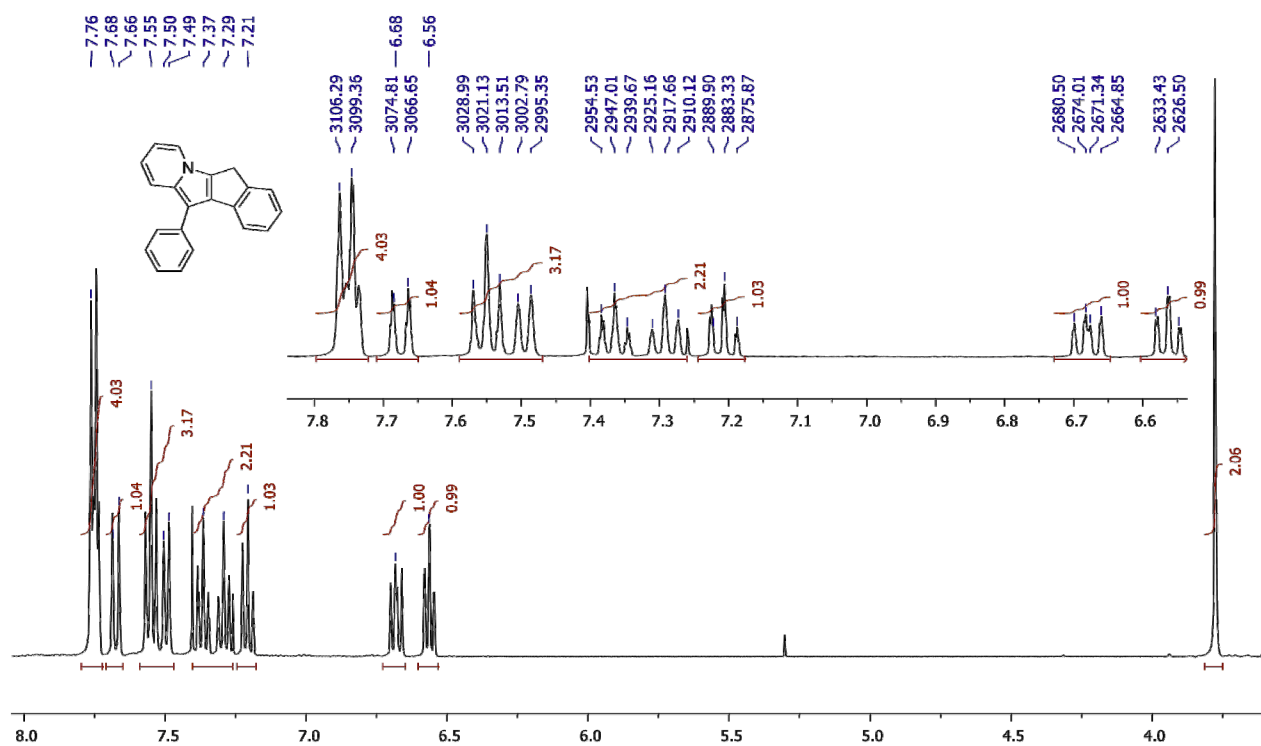
Figure S1. ^{1}H NMR spectrum of **4** (CDCl$_3$, 20 °C, 400 MHz)
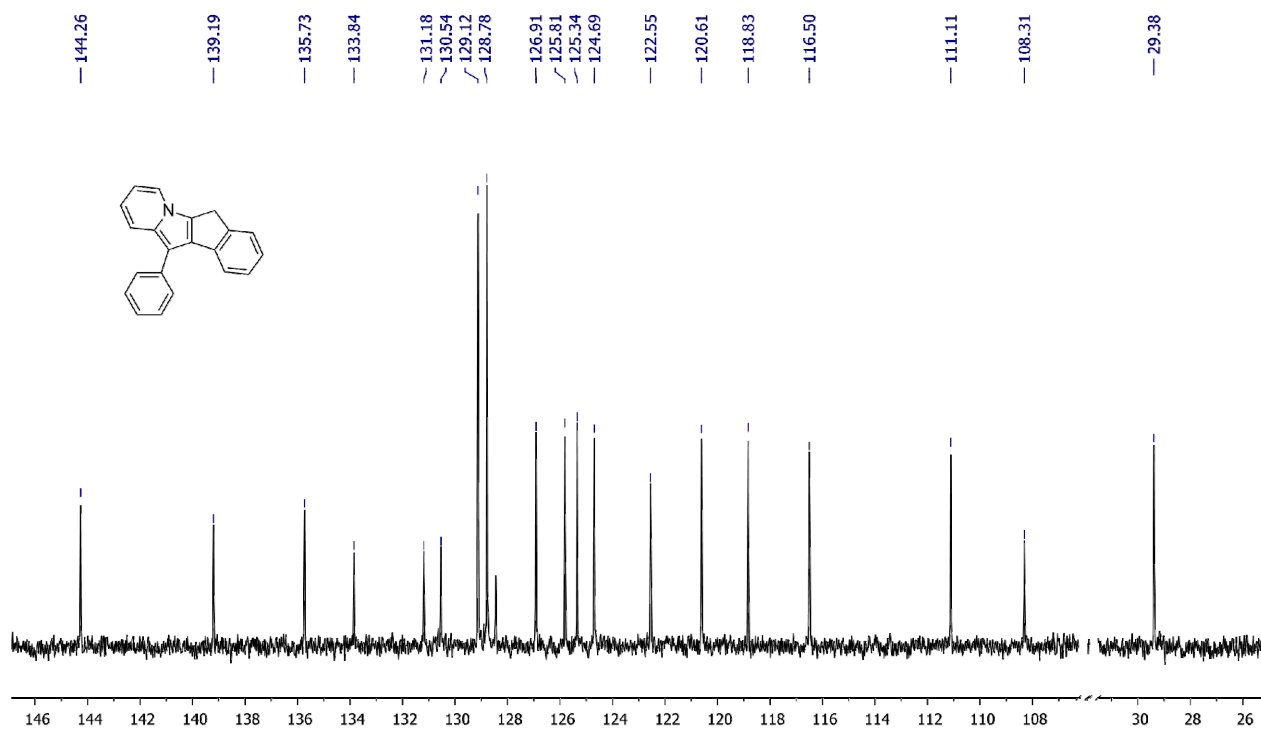
Figure S2. ^{13}C{^{1}H} NMR spectrum of **4** (CDCl$_3$, 20 °C, 101 MHz)

Figure S3. ^{1}H NMR spectrum of **5** (THF-d$_8$, 30 °C, 600 MHz)

Figure S4. ^{13}C{^{1}H} NMR spectrum of **5** (THF-d$_8$, 30 °C, 151 MHz)
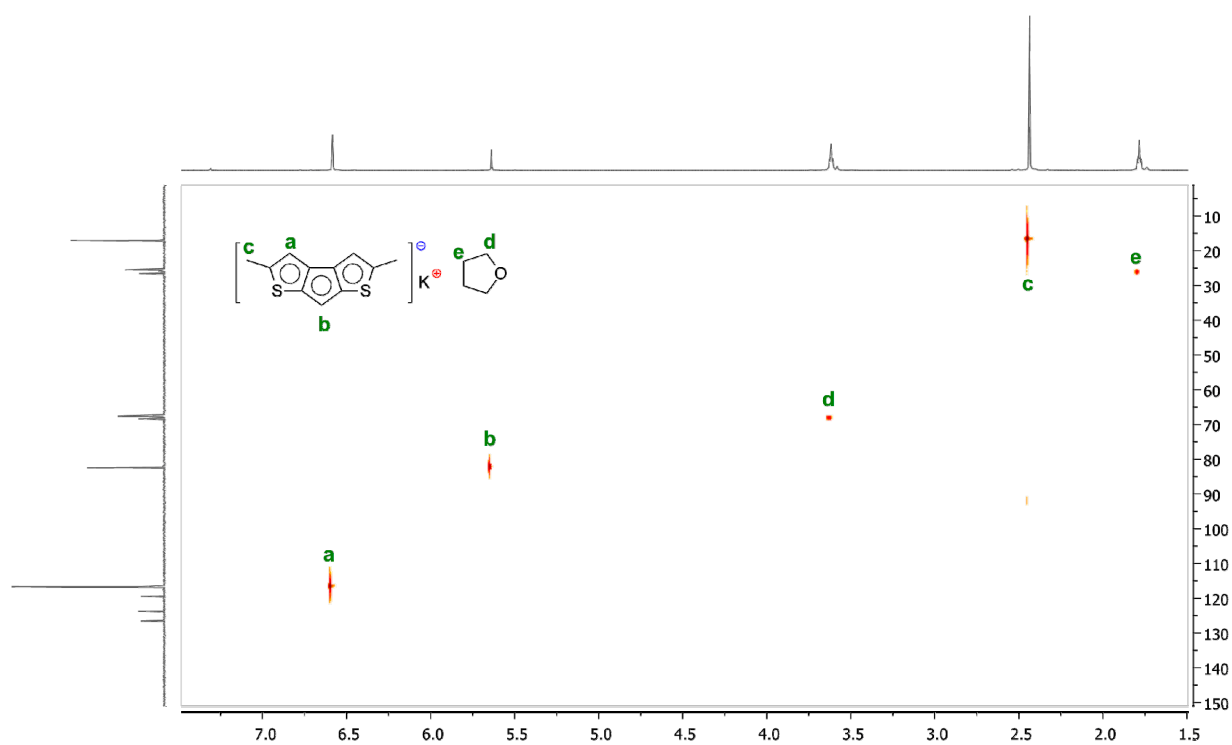
Figure S5. ^{1}H-^{13}C HSQC NMR spectrum of **5**
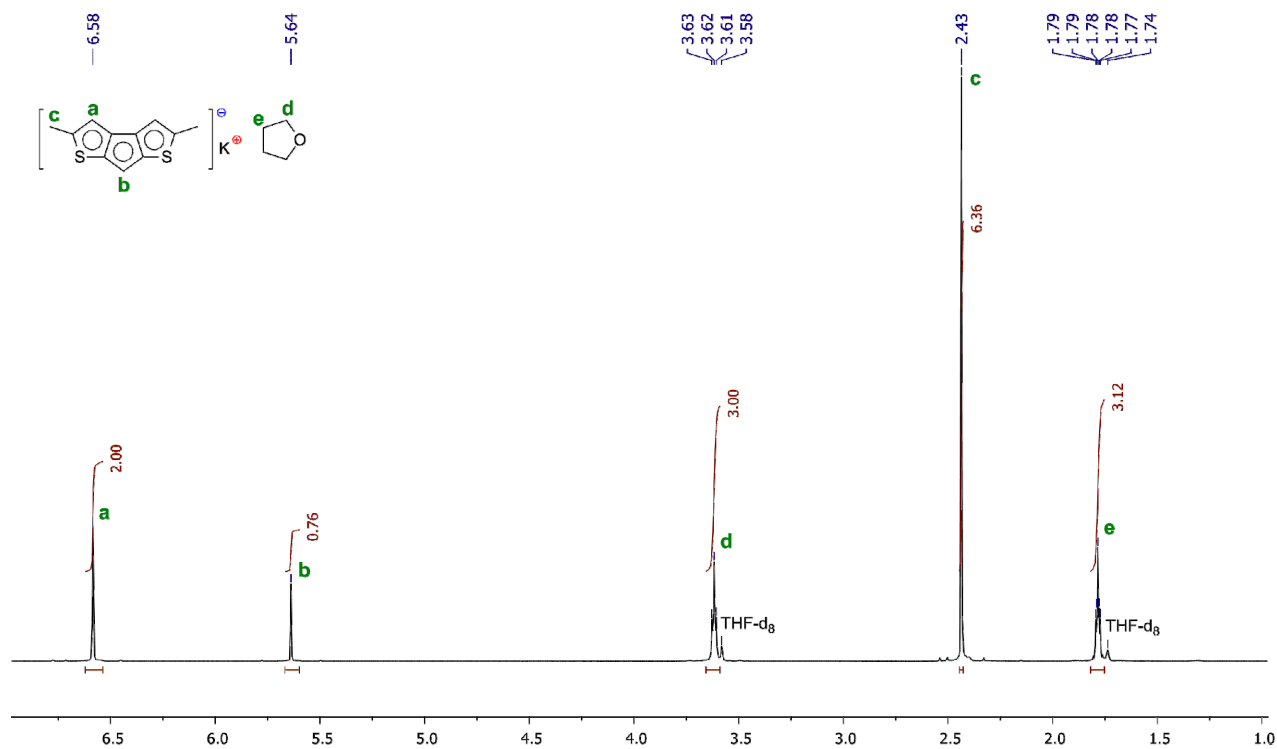

Figure S6. Two enlarged regions of the ^{1}H-^{13}C HMBC NMR spectrum of **5**

Figure S7. ^{1}H NMR spectrum of **6** (THF-d8, 30 °C, 600 MHz). Solvent admixtures are marked with asterisks

Figure S8. Enlarged aromatic region of the ^{1}H-^{1}H COSY NMR spectrum of **6**
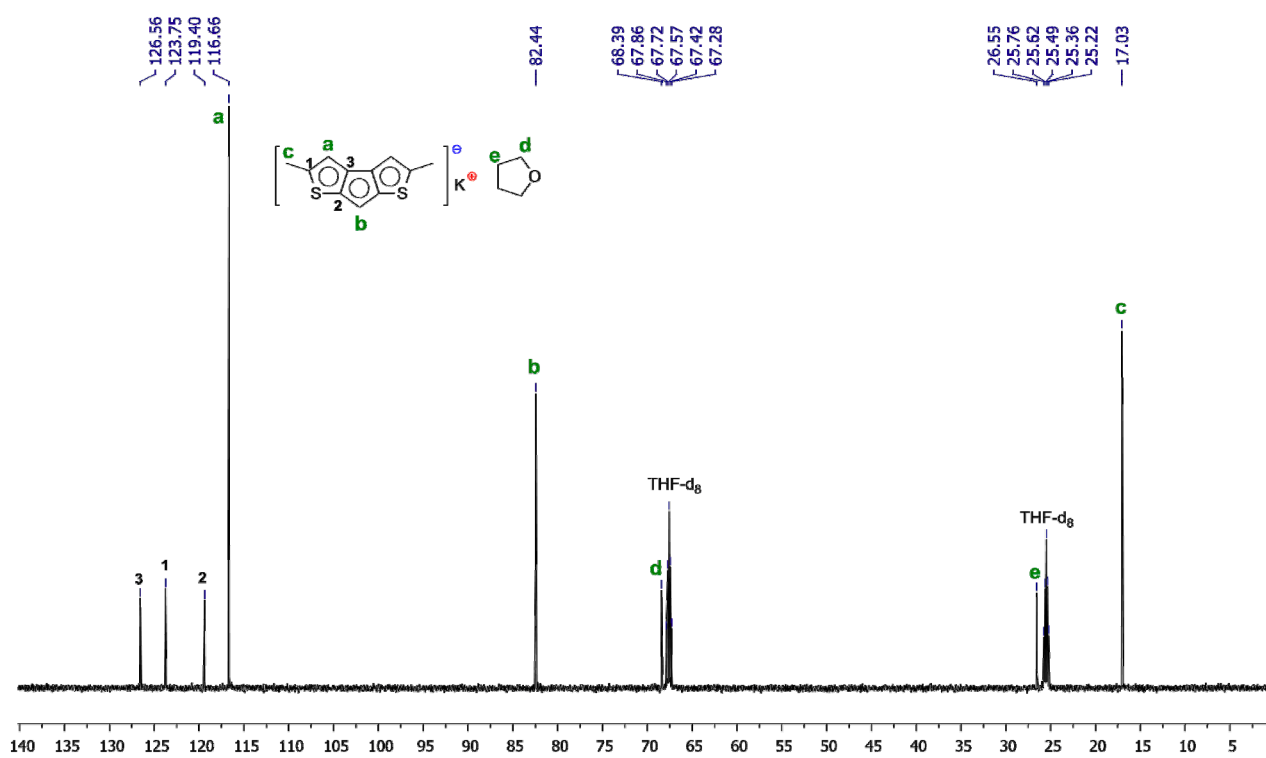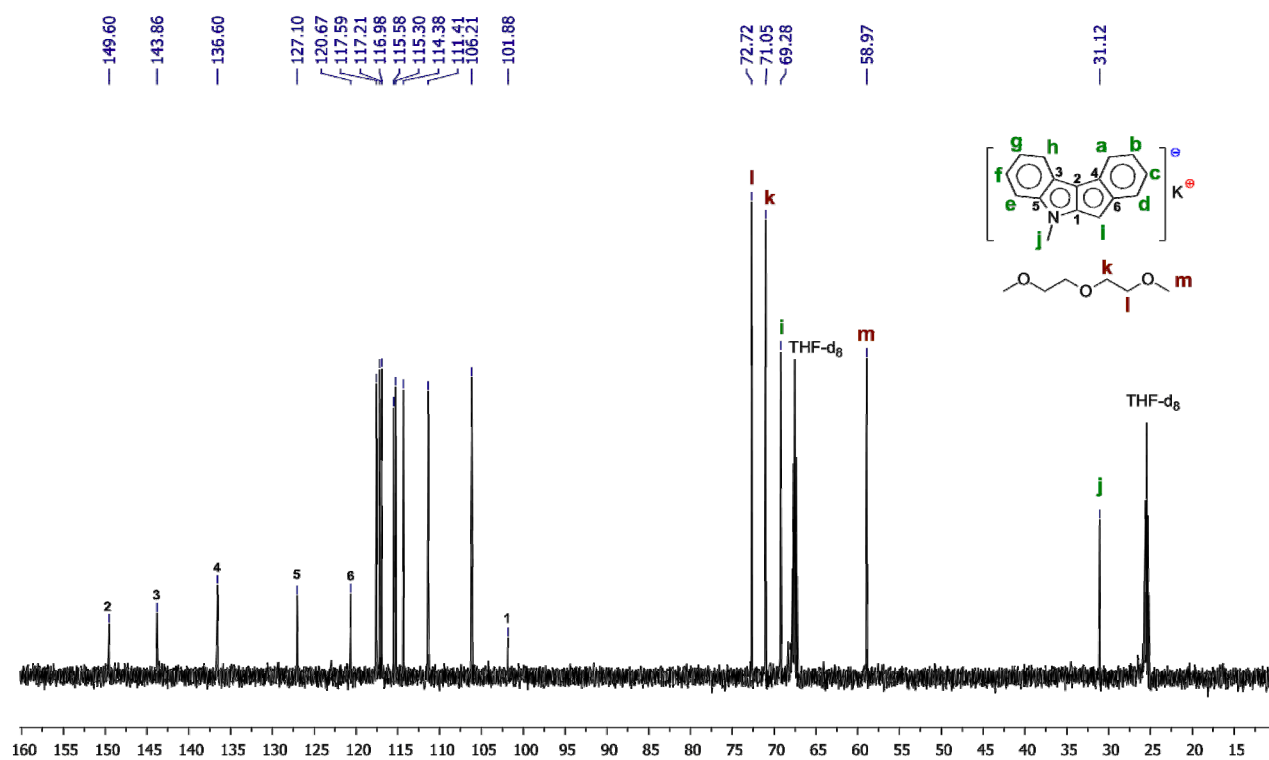
Figure S9. ^{13}C {^1H} NMR spectrum of **6** (THF-d$_8$, 30 °C, 151 MHz)
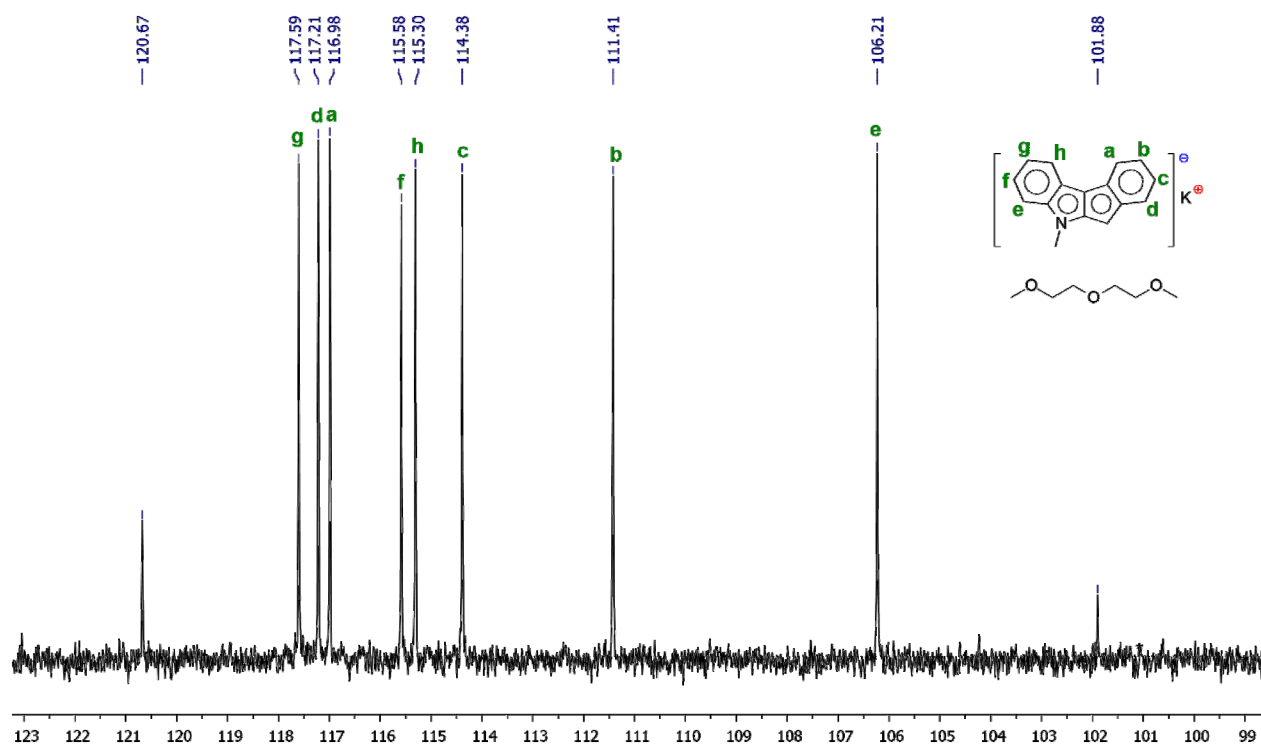
Figure S10. Enlarged aromatic region of the ^{13}C{^1H} NMR spectrum of **6**
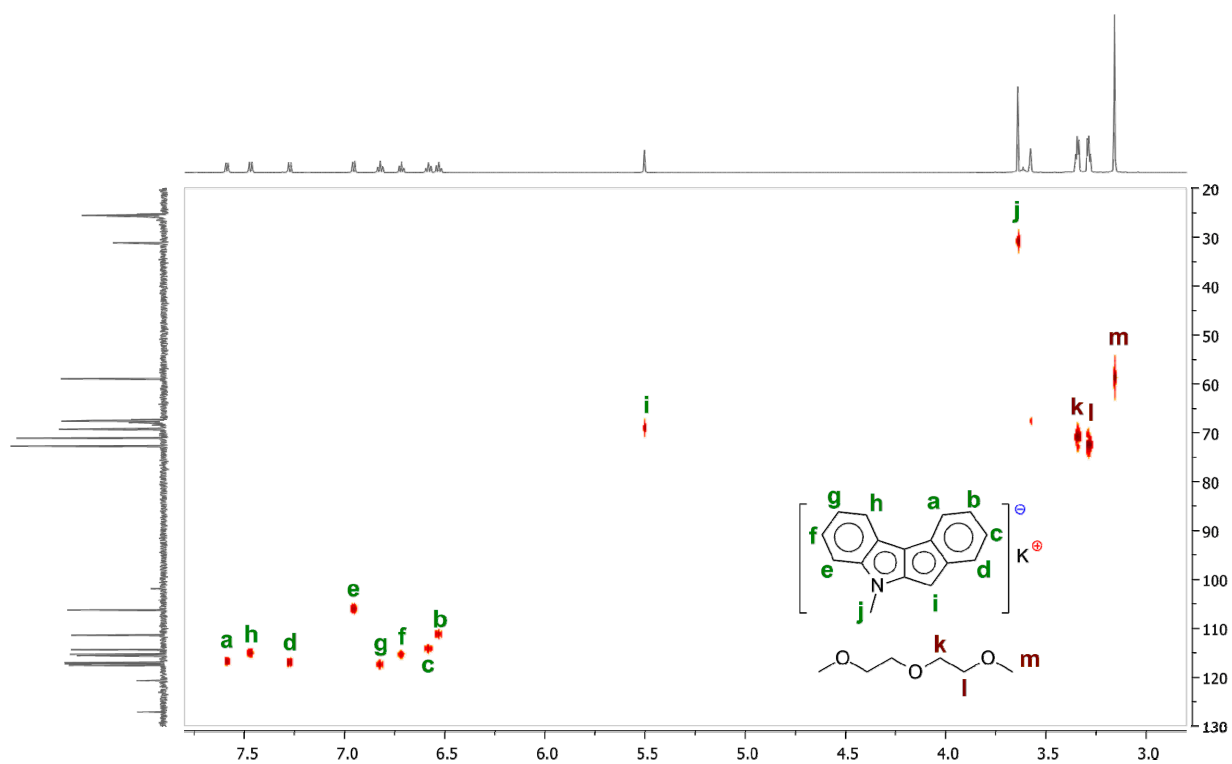
Figure S11. ^{1}H-^{13}C HSQC NMR spectrum of **6**
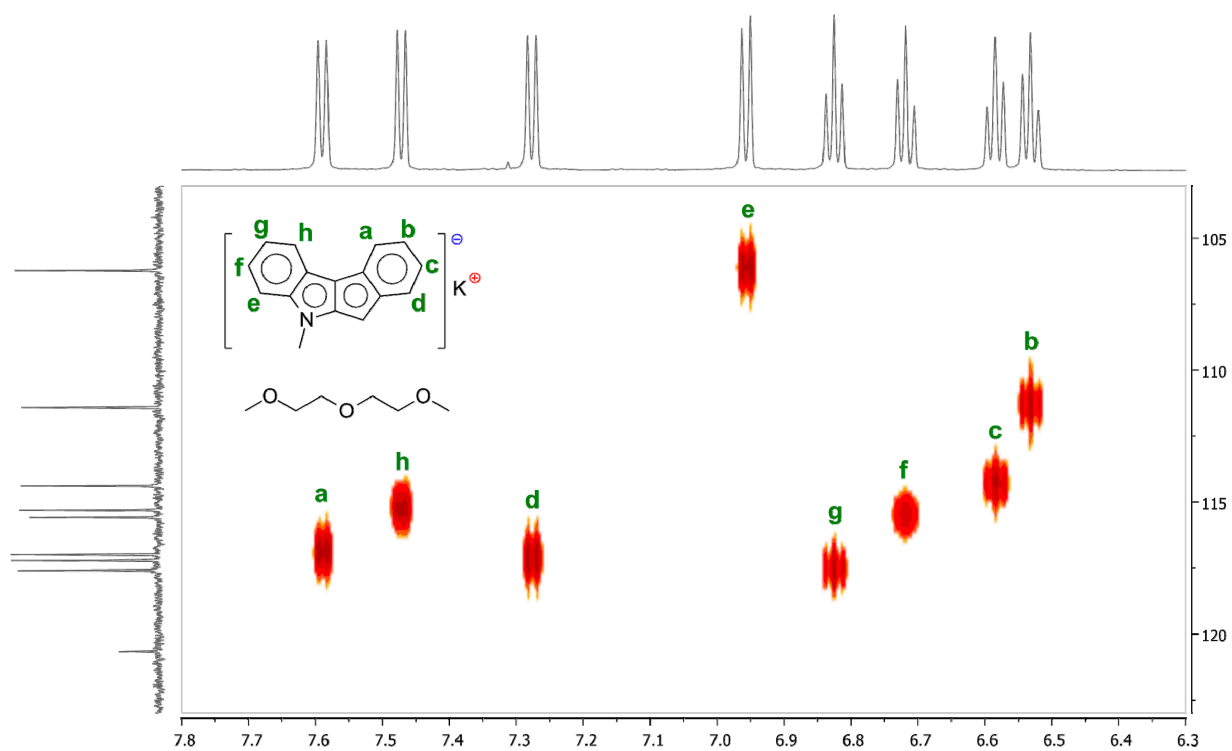
Figure S12. Enlarged aromatic region of the ^{1}H-^{13}C HSQC NMR spectrum of **6**
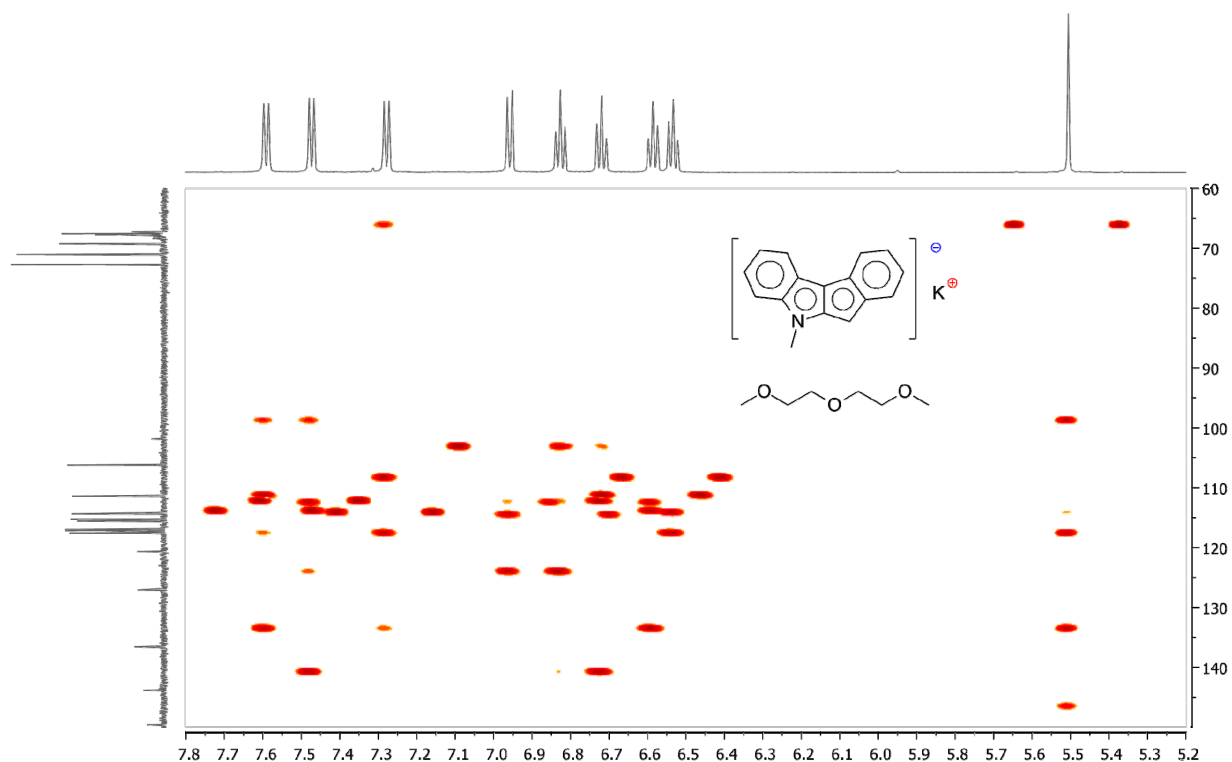
Figure S13. ^{1}H-^{13}C HMBC NMR spectrum of **6**

*S1.7. NMR spectra of [K(diglyme)(C$_{16}$H$_{12}$N)] **7***
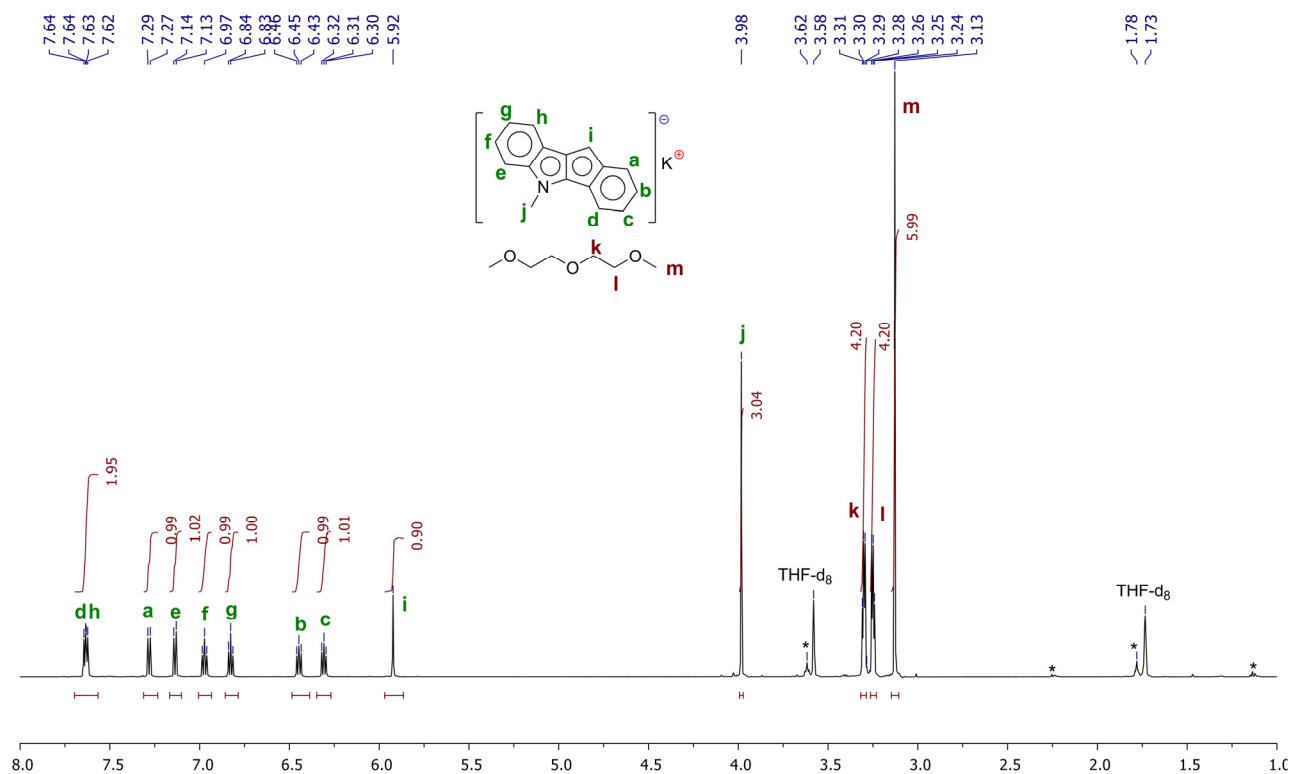
Figure S14. ^{1}H NMR spectrum of **7** (THF-d$_8$, 30 °C, 600 MHz). Solvent admixtures are marked with asterisks.
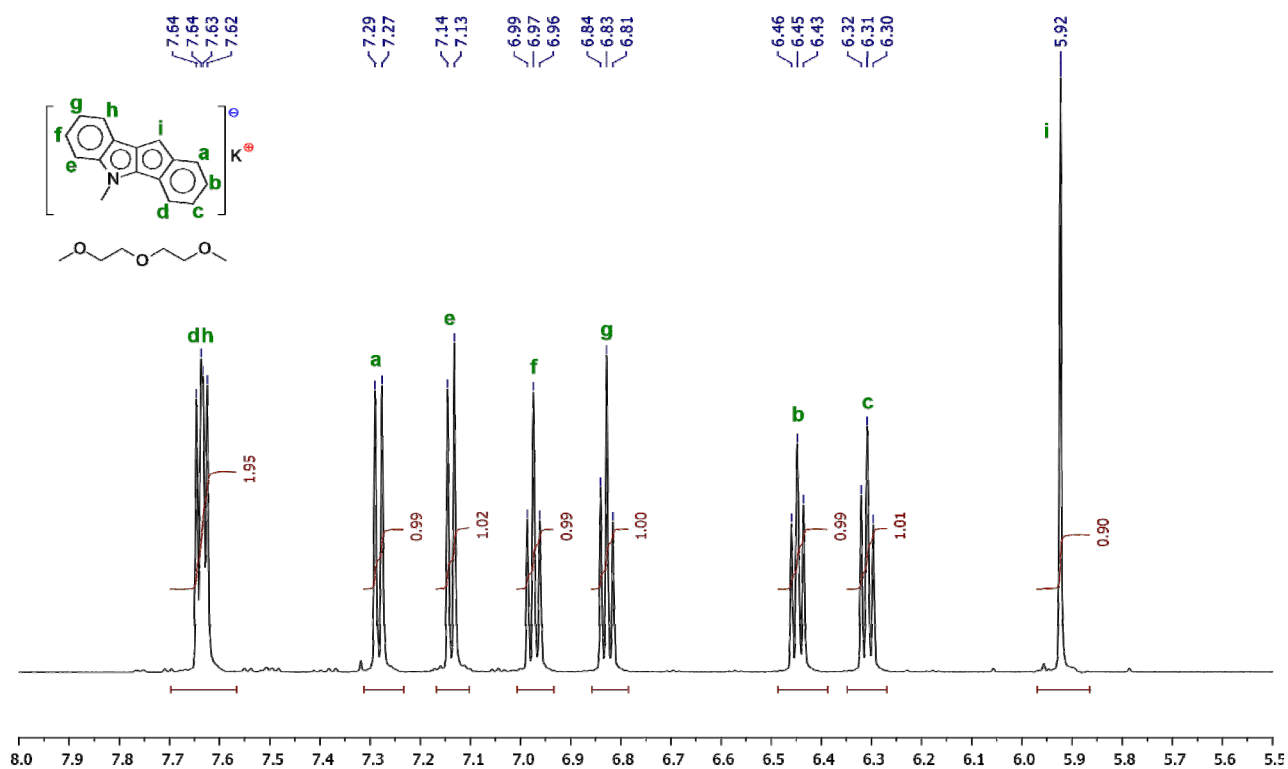
Figure S15. Enlarged aromatic regions of the ^{1}H NMR spectrum of **7**
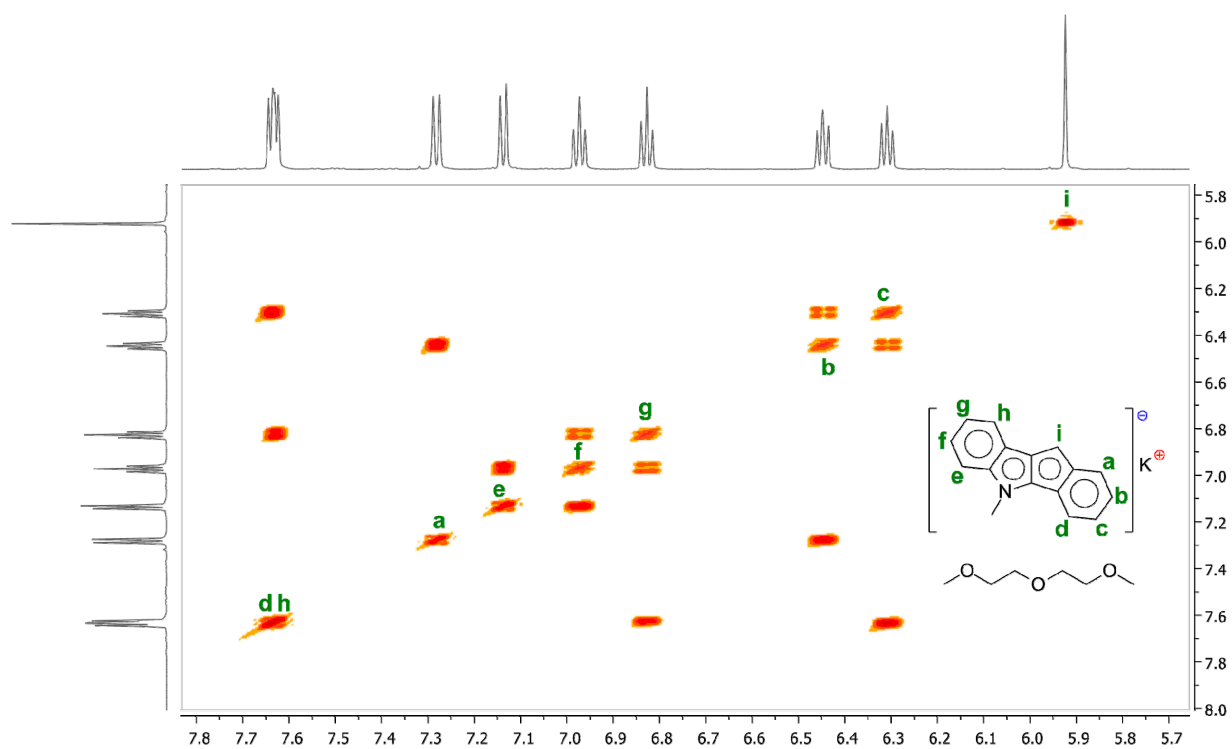
Figure S16. Enlarged aromatic region of the ^{1}H-^{1}H COSY NMR spectrum of **7**
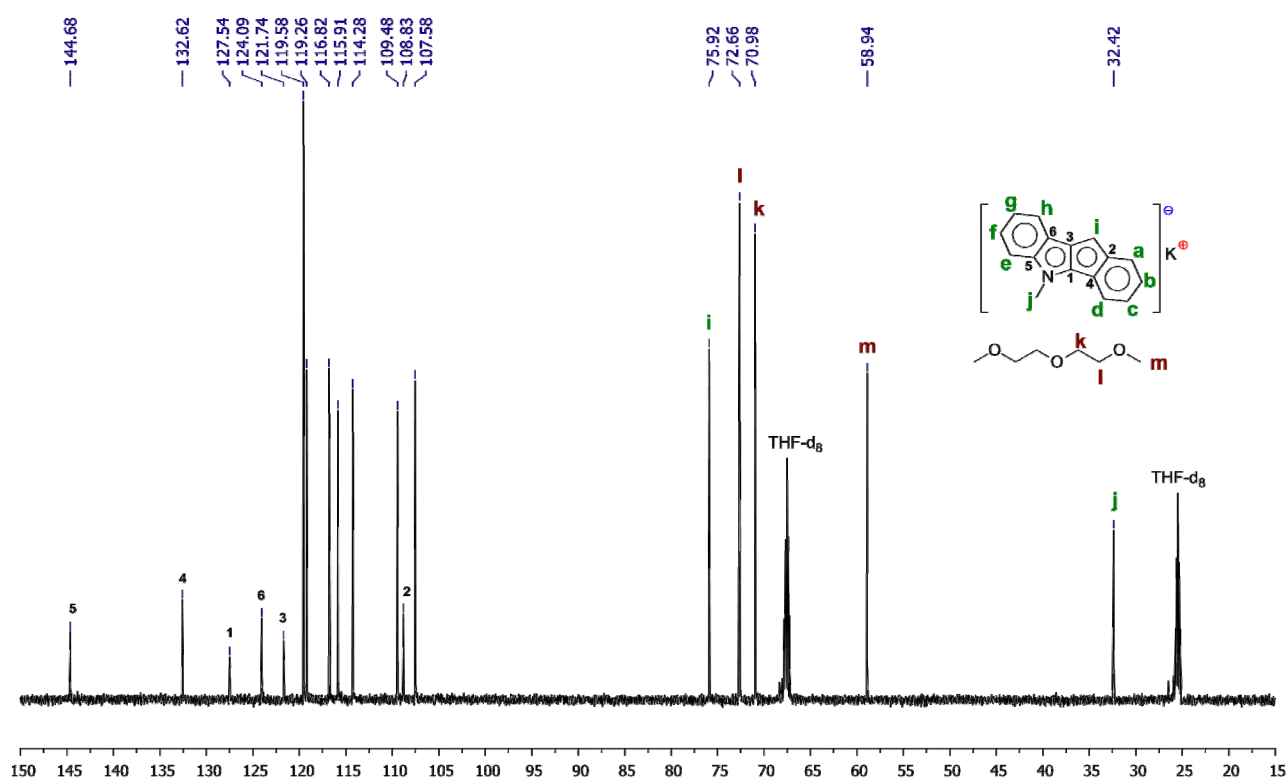
Figure S17. $^{13}C\{^1H\}$ NMR spectrum of **7** (THF-d$_8$, 30 °C, 151 MHz)
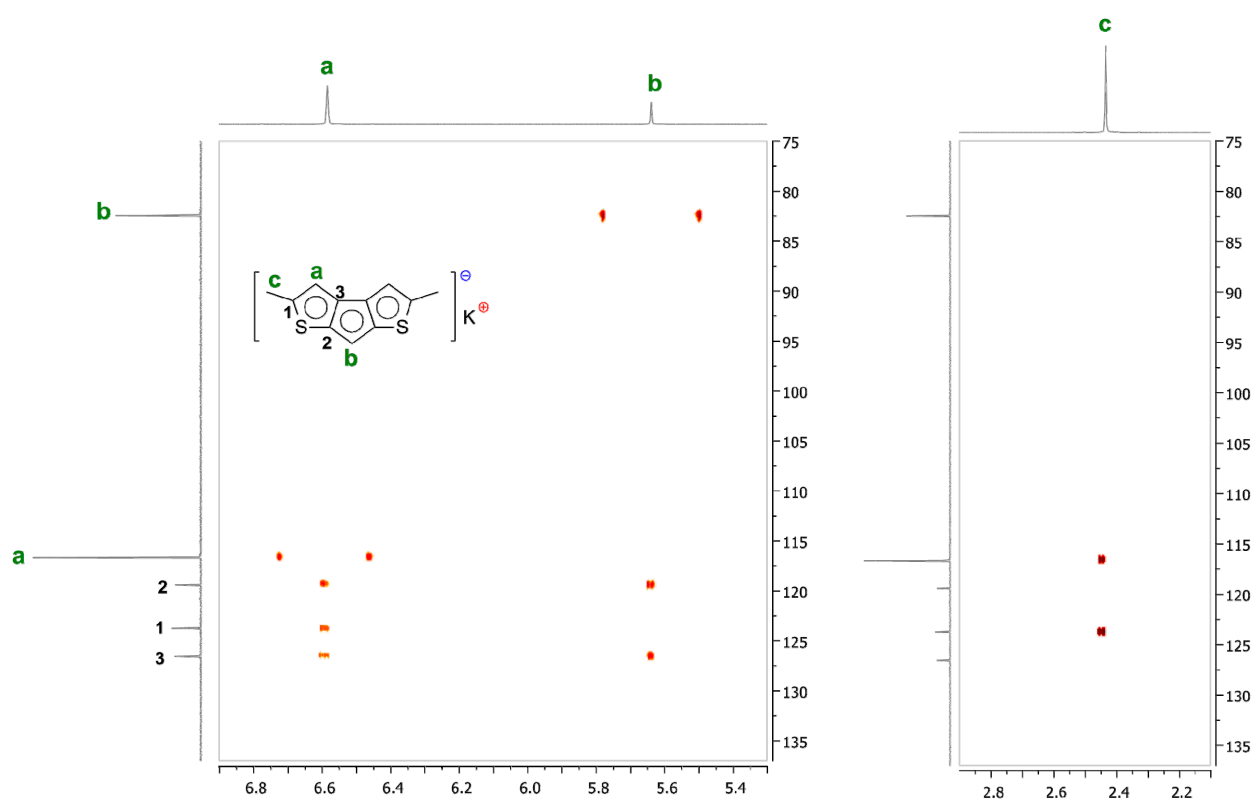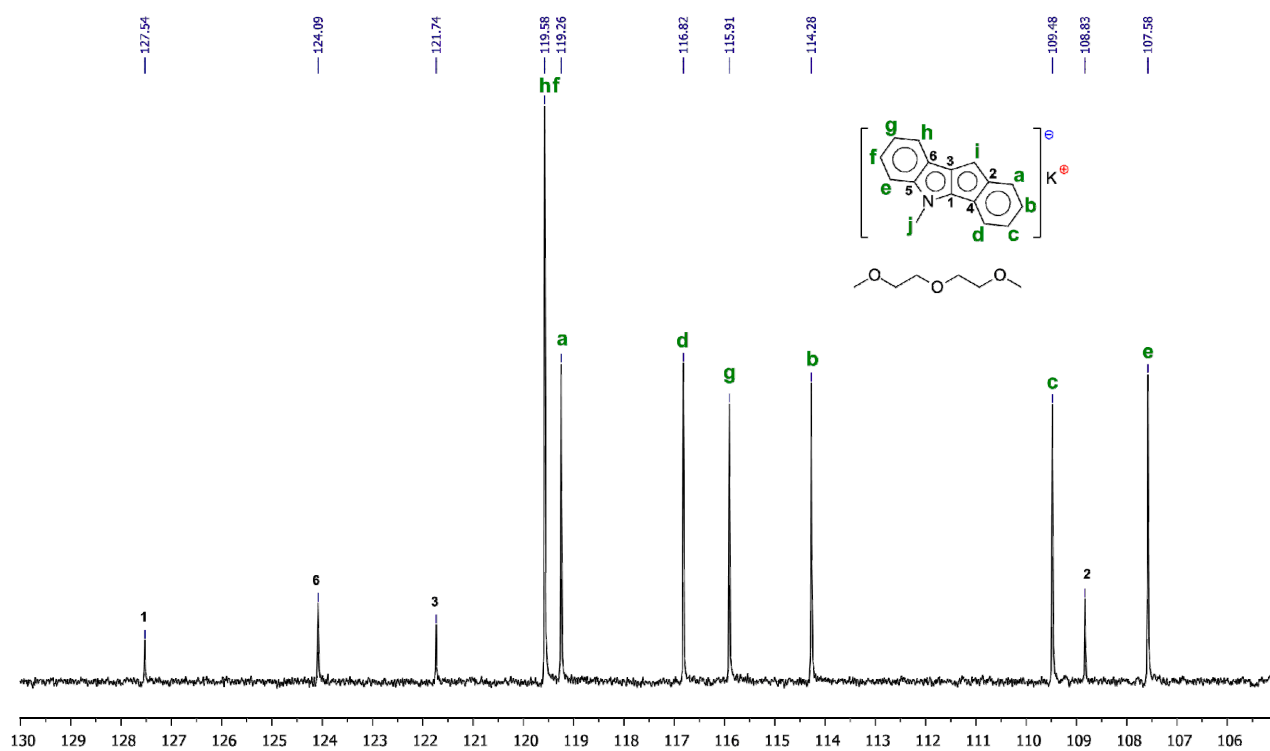

Figure S18. Enlarged aromatic region of the $^{13}C\{^1H\}$ NMR spectrum of **7** (THF-d$_8$, 30 °C, 151 MHz)
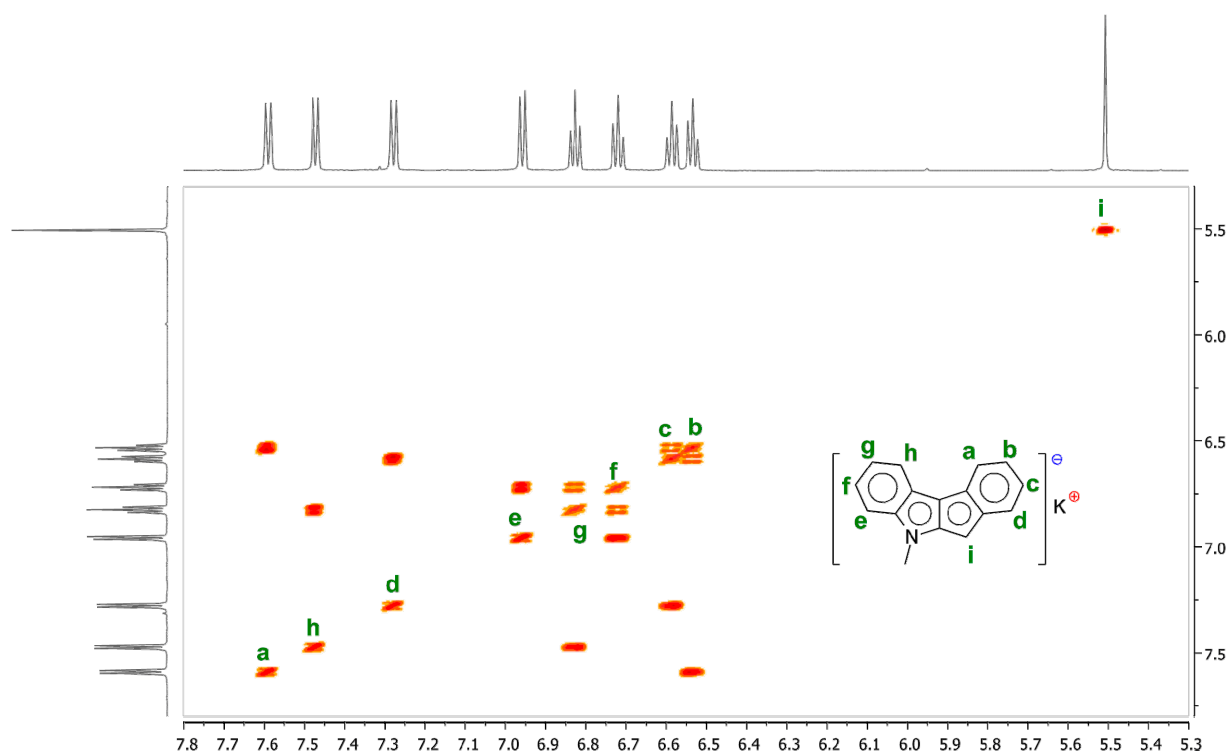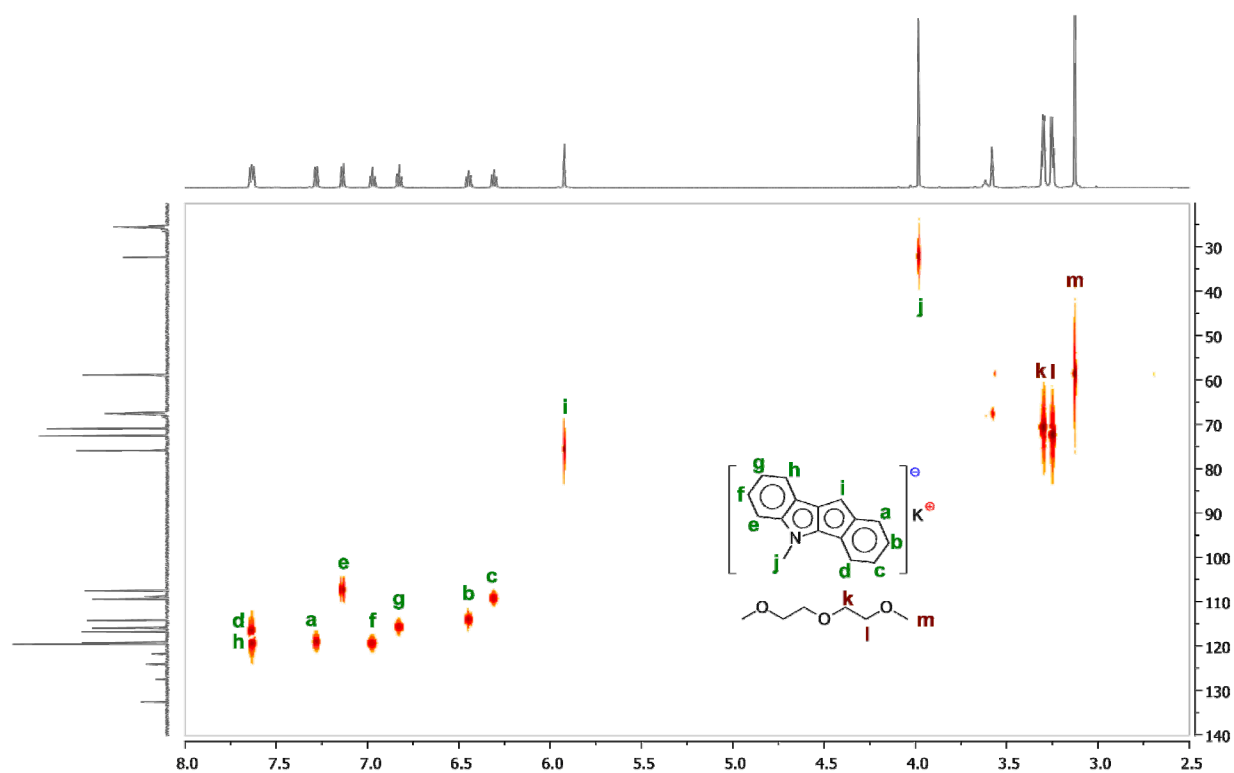
Figure S19. ^{1}H-^{13}C HSQC NMR spectrum of **7** (protons are marked)
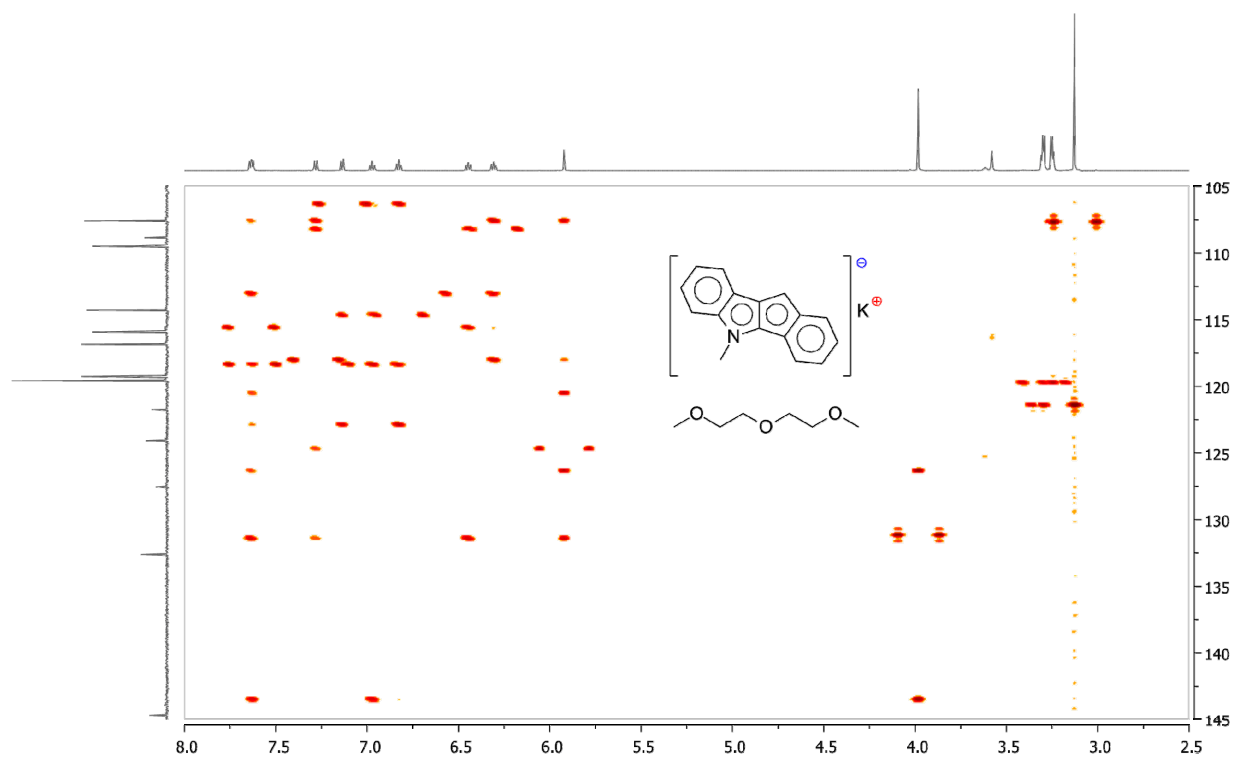
Figure S20. The ^{1}H-^{13}C HMBC NMR spectrum of **7**
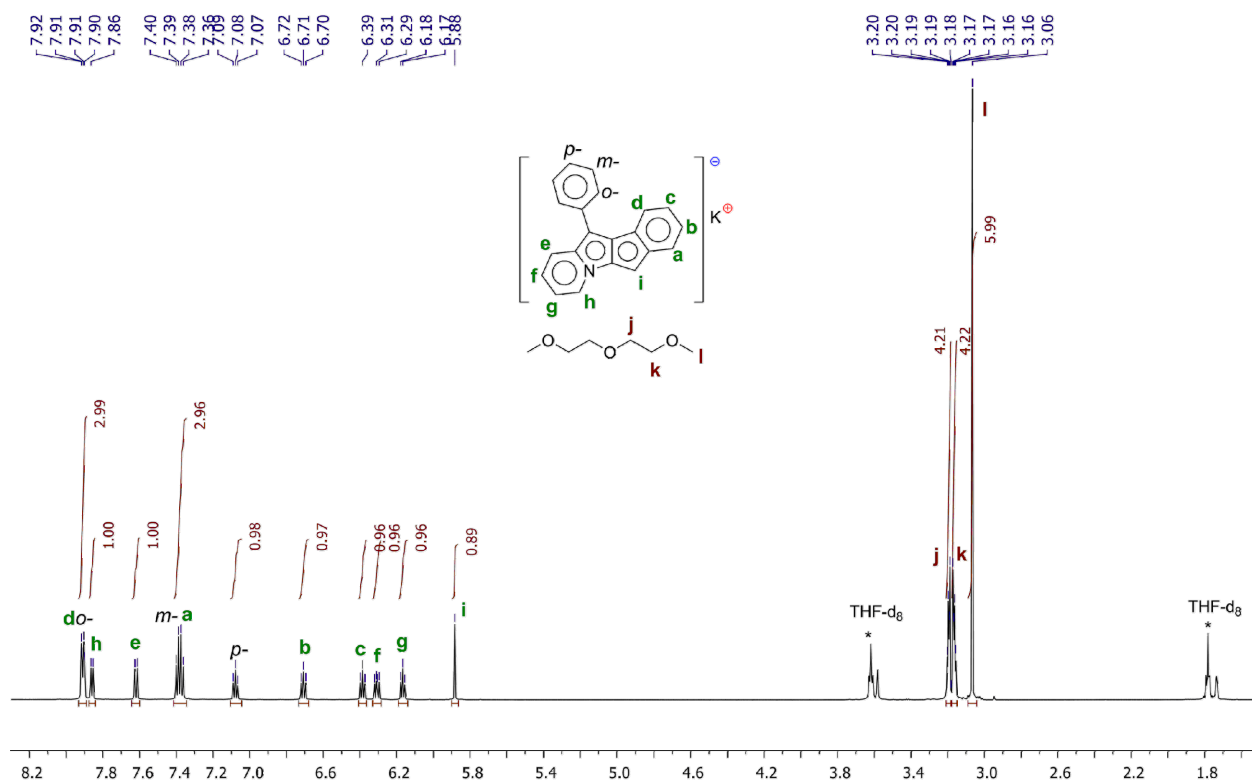
Figure S21. ^{1}H NMR spectrum of **8** (THF-d$_8$, 30 °C, 600 MHz)
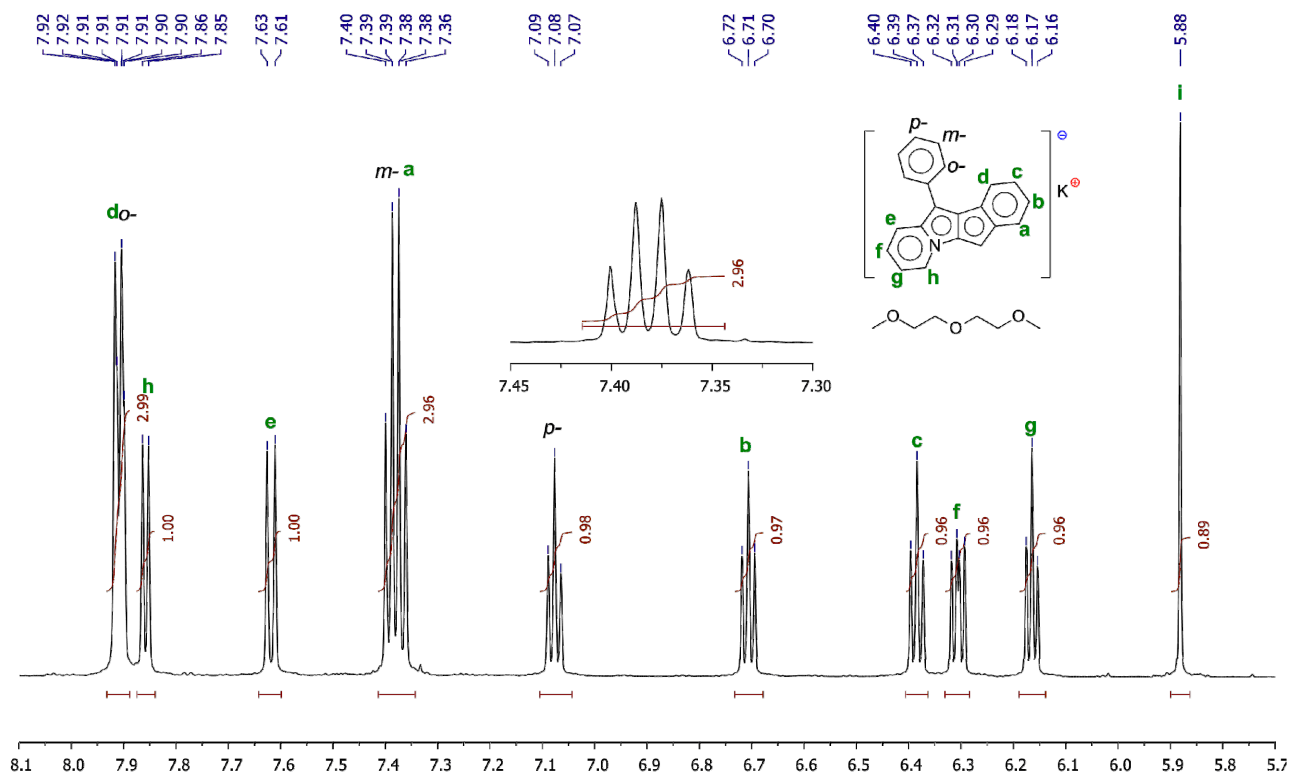
Figure S22. Enlarged aromatic regions of the ^{1}H NMR spectra of **8** at 600MHz and 303K

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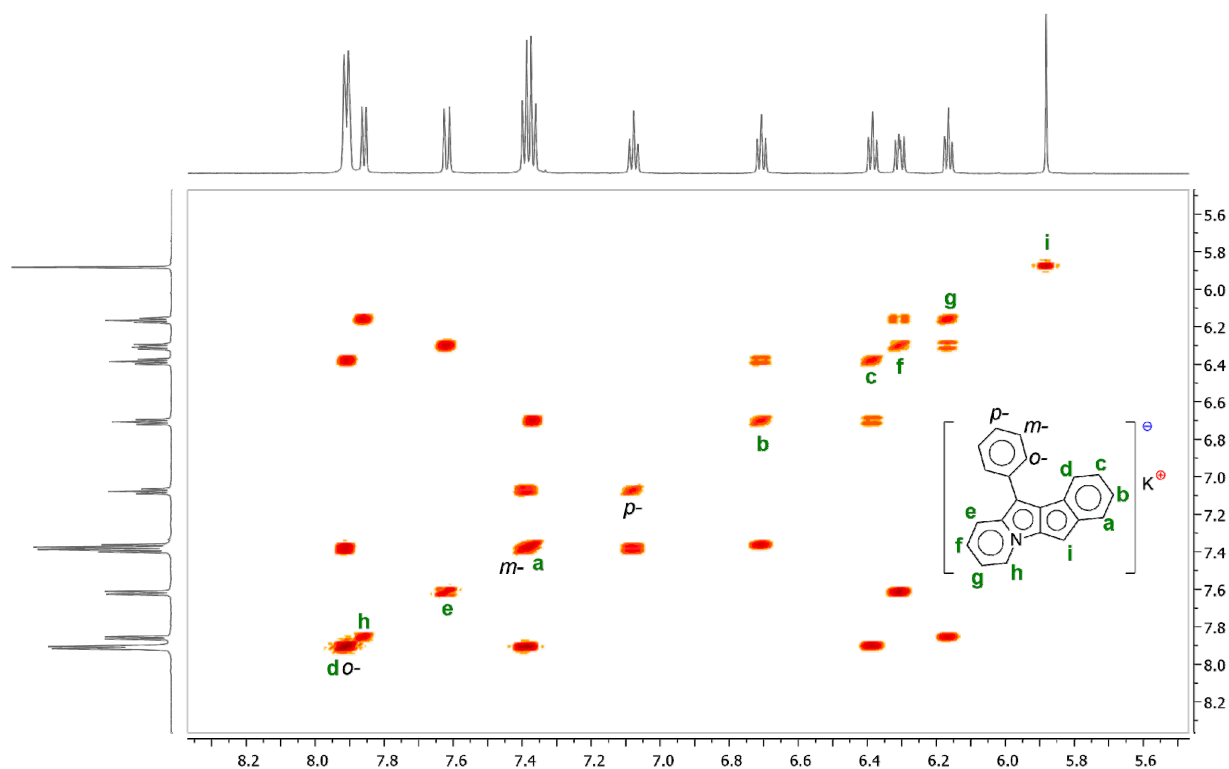
Figure S23. Enlarged aromatic region of the ^{1}H-^{1}H COSY NMR spectrum of **8**
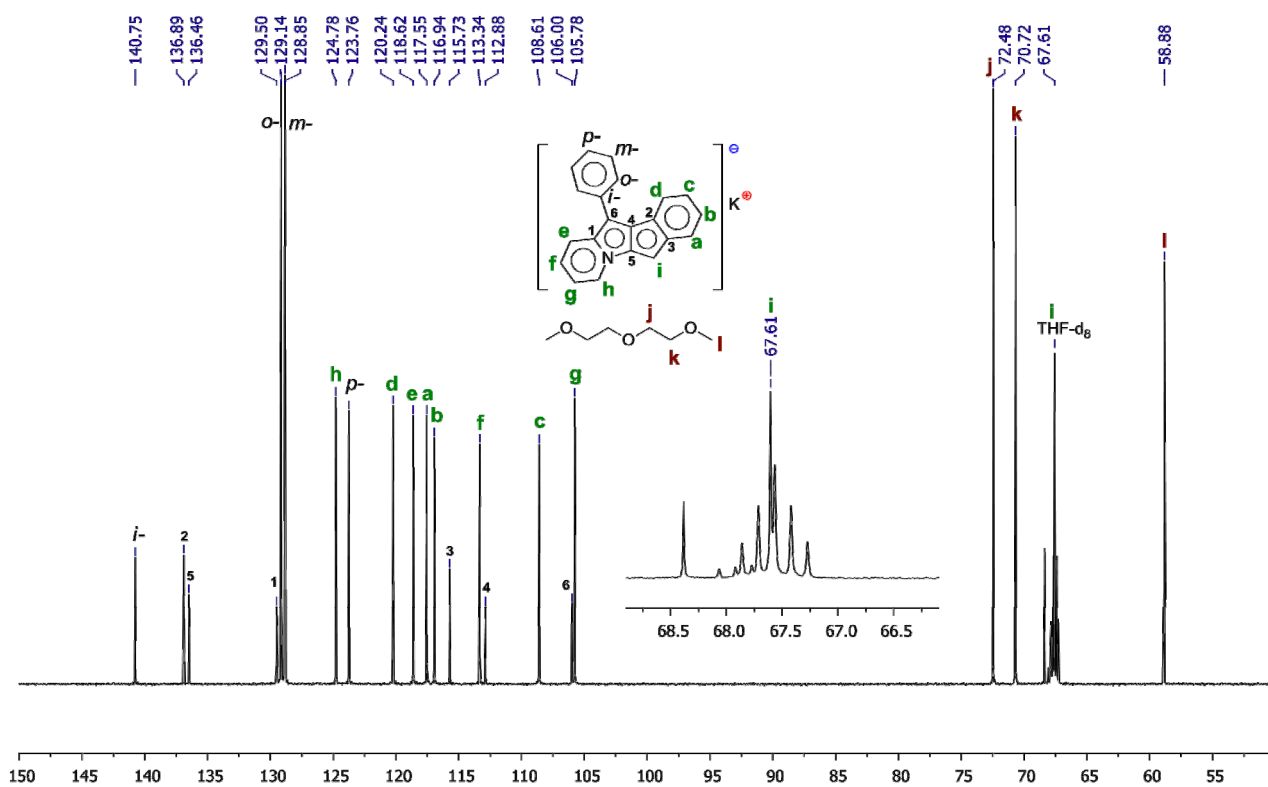
Figure S24. The ^{13}C{^{1}H} NMR spectrum of **8** (THF-d$_8$, 30 °C, 151 MHz)
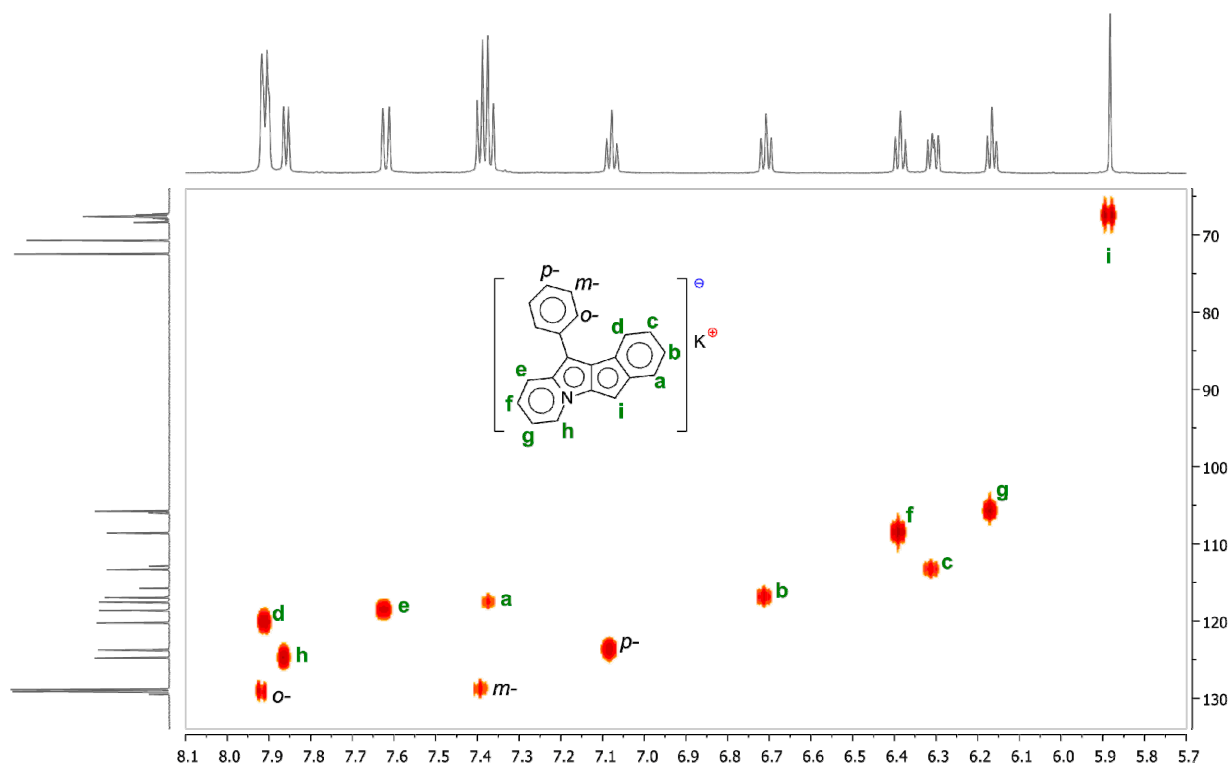
Figure S25. The enlarged aromatic region of the ^{1}H-^{13}C HSQC NMR spectrum of **8**
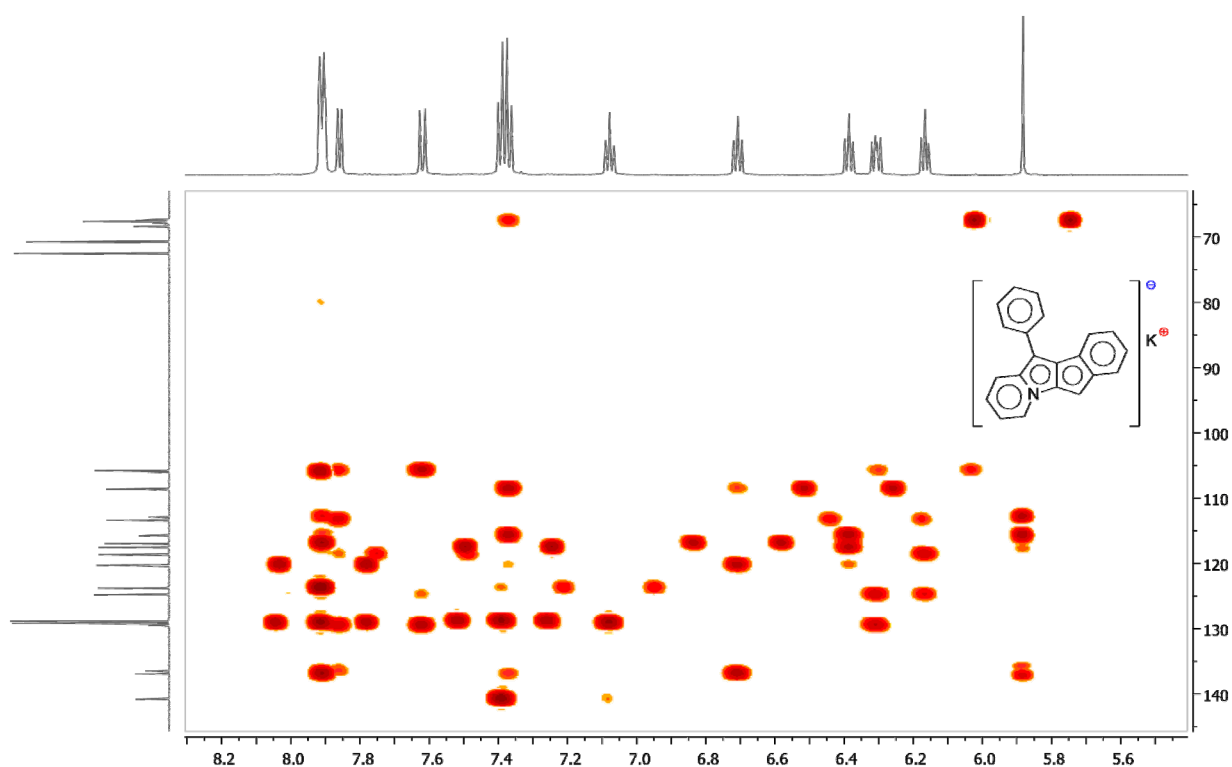
Figure S26. The enlarged aromatic region of the ^{1}H-^{13}C HMBC NMR spectrum of **8**

S2. Crystal structures

S2.1. X-ray Data Collection and Refinement

Experimental intensities of single crystal reflections were measured on a *Bruker SMART APEX II* platform at 120 K, using graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å) in an ω-scan mode. The collected data were integrated with the *SAINT* program.[1] Absorption corrections based on measurements of equivalent reflections were carried out by *SADABS2016* (multi-scan method).[2] The structures were solved by direct methods with the *SHELXS2013* program[3] and refined by full matrix least-squares on F^2 with *SHELXL2017*.[4] Absolute structure parameter (Flack) for **5** was determined using quotients [(I+)-(I-)]/[(I+)+(I-)].[5] Crystal data, data collection and structure refinement details are summarized in Table S1.

Positions of all non-H and atoms were found from electron difference density maps. Non-hydrogen atoms were refined with individual anisotropic displacement parameters. Positions of all hydrogen atoms (with the exception of disordered THF fragments in **5** and **8**) were also found from the difference map but H-atoms were positioned geometrically (C-H distance = 0.950 Å for aromatic and Cp, 0.980 Å for methyl, 0.990 Å for methylene H atoms) and refined as riding atoms with relative isotropic displacement parameters (U_{iso}(H)=1.5 U_{eq}(C) for methyl and 1.2 U_{eq}(C) for other hydrogen atoms). A rotating group model was applied for methyl groups. In **5**, two atoms in each coordinated THF molecules are disordered over two positions: C23A, C24A / C23B, C24B (the disorder ratio is 0.617(5):0.383(5)) and C27A, C28A / C27B, C28B (0.769(6):0.231(6)) (see Fig. S1). In **8**, one oxygen atom in diglyme and the entire THF molecule are disordered over two positions (atoms O27A / O27B, the disorder ratio is 0.807(3):0.193(3), and atoms O32A-C36A / O32B-C36B, 0.686(3):0.314(3)) (see Fig. S14 in SI). All C-C and C-O bond distances in both THF molecules in **5** and in the THF molecule in **8** were restrained to be equal within 0.002Å. Similarity constraints were applied to the anisotropic displacement parameters of the disordered atoms in **5** and **8**. Attempts to refine positions of H atoms and their individual anisotropic displacement parameters did not improve the crystallographic model parameters for **5**–**8**. The *SHELXTL* program suite[6] and the *Mercury* program[7] were used for molecular graphics.

Table S1. Crystal data, data collection and structure refinement details

Compound	5	6	7	8
Formula	$C_{30}H_{34}K_2O_2S_4$	$C_{22}H_{26}KNO_3$	$C_{22}H_{26}KNO_3$	$C_{31}H_{36}KNO_4$
M_r	633.01	391.54	391.54	525.71
Crystal system, space group	Monoclinic, $P2_1$	Monoclinic, $P2_1/c$	Tetragonal, $P4_2/n$	Triclinic, $P\bar{1}$
a (Å)	8.6879 (3)	10.9961 (6)	14.9197 (8)	9.4637 (12)
b (Å)	15.9969 (6)	17.9129 (10)	14.9197 (8)	11.0911 (15)
c (Å)	11.3681 (4)	10.9897 (6)	18.2151 (10)	13.9898 (17)
α (°)	90	90	90	74.333 (3)
β (°)	102.318 (1)	111.9626 (12)	90	89.812 (3)
γ (°)	90	90	90	81.725 (3)
V (Å^3)	1543.56 (10)	2007.57 (19)	4054.6 (5)	1398.2 (3)
Z	2	4	8	2
μ (mm^{-1})	0.60	0.29	0.28	0.23
F(000)	664	832	1664	560
Crystal size (mm)	0.32 × 0.21 × 0.17	0.36 × 0.27 × 0.19	0.42 × 0.24 × 0.18	0.36 × 0.28 × 0.23
T_{min}, T_{max}	0.842, 0.934	0.894, 0.952	0.870, 0.991	0.789, 0.862
Θ range (°)	1.83 to 29.00	2.00 to 29.00	1.76 to 29.00	1.51 to 29.00
Completeness to Θ (%)	100	100	100	99.8
Index ranges	-11≤h≤11	-14≤h≤14	-16≤h≤20	-12≤h≤12
	-21≤k≤21	-24≤k≤24	-20≤k≤19	-15≤k≤15
	-15≤l≤15	-14≤l≤14	-24≤l≤24	-19≤l≤19
Reflections				
Measured	18860	24760	30785	16762
Independent [R_{int}]	8156 [0.023]	5328 [0.035]	5398 [0.054]	7402 [0.026]
Observed [$I > 2\sigma(I)$]	7580	4315	4054	5136
Parameters	363	247	247	346
Restraints	13	0	0	10
R1, wR2 [$I > 2\sigma(I)$]	0.027, 0.060	0.035, 0.087	0.038, 0.085	0.058, 0.136
R1, wR2 (all data)	0.031, 0.062	0.047, 0.094	0.059, 0.096	0.089, 0.157
GooF on F^2	1.03	1.03	1.02	1.03
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.27, −0.25	0.37, −0.25	0.39, −0.24	0.68, −0.59
Absolute structure parameter	0.024 (15)	-	-	-
No. of quotients	3385	-	-	-
CCDC number	1920202	1920203	1920204	1920205

S2.2 Crystal structure and selected bond distances in K(THF)(Me$_2$C$_9$H$_3$S$_2$)]$_\infty$ (5)

The asymmetric unit of the complex [K(THF)(Me$_2$C$_9$H$_3$S$_2$)] (**5**) contains two K$^+$ cations connected *via* two bridging THF molecules, forming the dimeric dication [K$_2$(μ-THF)$_2$]$^{2+}$, and two 2,5-dimethyl-7H-cyclopenta[1,2-b:4,3-b']dithiophenide ligands (Fig. S27). Each K$^+$ cation is coordinated by two symmetrically nonequivalent flat cyclopentadithiophenide anions (Fig. S28) being in two coordination modes: μ-η^5:η^6 and μ-η^5:η^7. The highest deviations from the planes defined by non-hydrogen atoms S1, S2, C1 through C11, and by S3, S4, C12 through C22 are observed for atoms C3 [0.059(2) Å], C11 [0.072(2)Å], S1 [0.079(1)Å] and S4 [0.054(1)Å], C12 [0.061(2)Å], C16 [0.064(2)Å], C21 [0.091(2)Å], correspondingly, indicating that the ligand is not entirely flat. Indeed, folding angles between planes of C$_5$ and C$_4$S rings are 2.34(10)° (planes C1-C5-C6-C7-S1 / C1-C2-C3-C4-C5), 3.29(11)° (C3-C4-C8-C9-S2 / C1-C2-C3-C4-C5) and 4.56(7)° (C12-C16-C17-C18-S3 / C12-C13-C14-C15-C16), 3.33(6)° (C14-C15-C19-C20-S4 / C12-C13-C14-C15-C16).
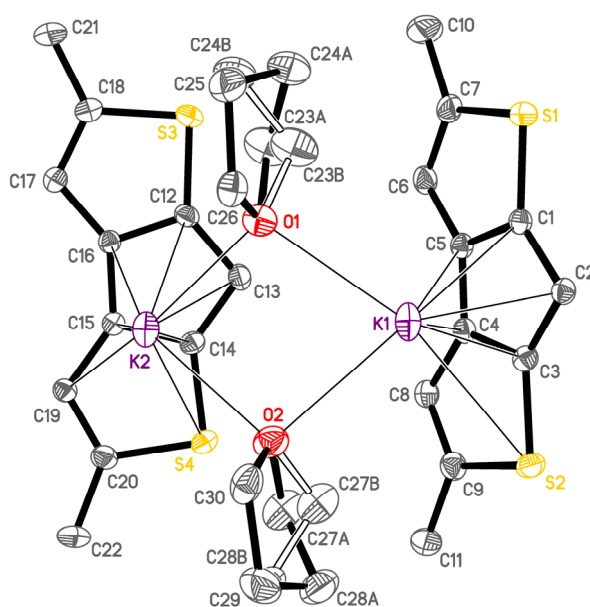
Figure S27. The asymmetric unit [K$_2$(THF)$_2$(Me$_2$C$_9$H$_3$S$_2$)$_2$]. Displacement ellipsoids are drawn at the 50% probability level. The disorder ratios are 0.617(5):0.383(5) for the C23A, C24A / C23B, C24B fragments and 0.769(6):0.231(6) for atoms C27A, C28A / C27B, C28B. Minor components of disorder are shown with open solid lines. All H atoms are omitted for clarity.

The C-C bond lengths within the central C$_5$-rings (Table S2) are ranging from 1.416 (3) Å to 1.432(3)Å with the average values of 1.420(6)Å for C1…C5 and 1.423(6)Å for C12…C16. As expected, the C-C bond distances in the thiophene fragments alternate, resulting in more pronounced double character for the bonds C6-C7, C8-C9 and C17-C18, C19-C20.
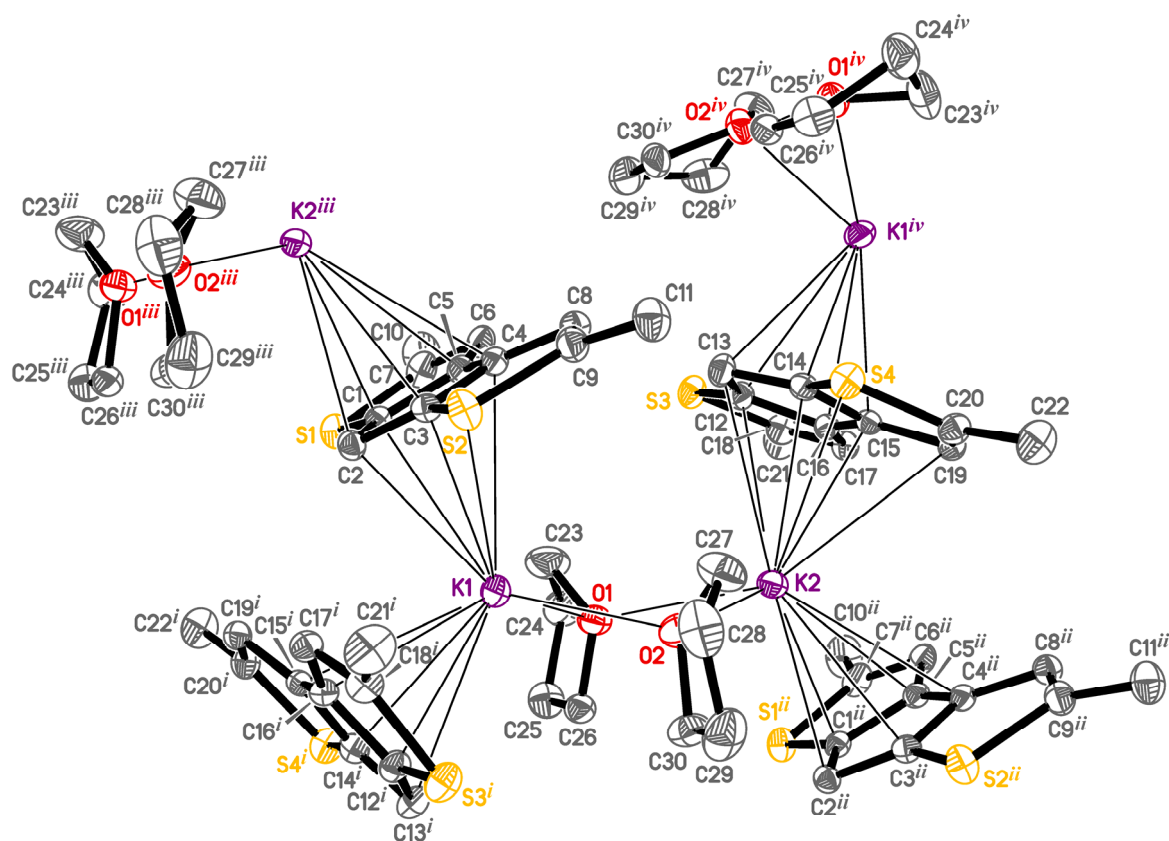
Figure S28. The structure of $[K_2(THF)_2(Me_2C_9H_3S_2)_2]_\infty$, (**1**). Displacement ellipsoids are drawn at the 50% probability level. All H atoms are omitted, and THF disorder is not shown for clarity. [Symmetry codes: (i) -x+1, y-1/2, -z+1; (ii) x+1, y, z; (iii) x-1, y, z; (iv) -x+1, y+1/2, -z+1.]

Table S2. Selected geometric parameters (Å, °) for **5**.

C1—C2	1.417 (3)	C12—C13	1.416 (3)
C1—C5	1.424 (3)	C12—C16	1.420 (3)
C2—C3	1.420 (3)	C13—C14	1.420 (3)
C3—C4	1.420 (3)	C14—C15	1.416 (3)
C4—C5	1.432 (3)	C15—C16	1.430 (3)
C4—C8	1.438 (3)	C15—C19	1.433 (3)
C5—C6	1.439 (3)	C16—C17	1.436 (3)
C6—C7	1.356 (3)	C17—C18	1.355 (3)
C8—C9	1.350 (3)	C19—C20	1.356 (3)
C7—C10	1.500 (3)	C18—C21	1.499 (3)
C9—C11	1.505 (3)	C20—C22	1.492 (3)
S1—C1	1.745 (2)	S3—C12	1.750 (2)
S1—C7	1.760 (2)	S3—C18	1.759 (2)
S2—C3	1.749 (2)	S4—C14	1.745 (2)

S2—C9	1.758 (2)	S4—C20	1.764 (2)
K1—O1	2.7543 (17)	K2—O1	2.7998 (17)
K1—O2	2.8042 (18)	K2—O2	2.9013 (18)
K1—S2	3.7814 (8)	K2—S4	3.6343 (8)
K1—C1	3.173 (2)	K2—C12	3.434 (2)
K1—C2	2.937 (2)	K2—C13	3.332 (2)
K1—C3	2.989 (2)	K2—C14	2.976 (2)
K1—C4	3.300 (2)	K2—C15	2.907 (2)
K1—C5	3.425 (2)	K2—C16	3.214 (2)
K1—C12^{i}	3.097 (2)	K2—C1^{ii}	3.018 (2)
K1—C13^{i}	3.222 (2)	K2—C2^{ii}	3.001 (2)
K1—C14^{i}	3.162 (2)	K2—C3^{ii}	3.142 (2)
K1—C15^{i}	3.084 (2)	K2—C4^{ii}	3.290 (2)
K1—C16^{i}	3.043 (2)	K2—C5^{ii}	3.197 (2)
		K2—C19	3.353 (2)
K2—K1—K2^{i}	139.35 (1)	K1—K2—K1^{ii}	118.33 (1)
K2—K1—K2^{iii}	118.33 (1)	K1—K2—K1^{iv}	109.98 (1)
K2^{i}—K1—K2^{iii}	99.74 (1)	K1^{ii}—K2—K1^{iv}	131.63 (1)

Symmetry codes: (i) −x+1, y−1/2, −z+1; (ii) x+1, y, z; (iii) x-1, y, z; (iv) -x+1, y+1/2, -z+1.

Cation K1^{+} is coordinated by two ligands *via* the middle ring: atoms C1 to C5 and C12^{i} to C16^{i} [Symmetry code: (i) −x+1, y−1/2, −z+1] (see Table 2 for K1-C distances). The K1-C12^{i}..C16^{i} interaction is almost symmetrical: the value of the normal to the C$_5$ plane [2.8702(12)Å] is nearly identical to the corresponding K1-C$_5$(centroid) distance [2.8790(12)Å]. The K1-C1..C5 interaction is less symmetrical: 2.8526(13)Å for the normal and 2.9301(11) Å for the K1-C$_5$(centroid) distance. The intersection point of the normal and the C$_5$-plane is shifted from the C$_5$-centroid towards atom C2. The difference between last distances (~ 0.078 Å) is likely due to the presence of a relatively long K1-S2 contact (Figs. S1, S2). Coordination of K2 with one ligand *via* η^5-coordinatation by C1^{ii}...C5^{ii} atoms is also close to a symmetrical one (Fig. S28; Table S2) [Symmetry code: (ii) x+1, y, z]. The normal to the C1^{ii}...C5^{ii} plane [2.8614(12)Å] is close to the K2-centroid(C1^{ii}...C5^{ii}) distance [2.8882(11)Å]. However, the interaction with the second ligand is far from symmetrical — cation K2 is coordinated not only by C12...C16, but also by atoms C19 and S4. The normal from K2 to the C12…C16 plane is 2.8415(14)Å, and it intersects the plane close to the middle of the C14-C15 bond. The K2-centroid(C12…C16) and K2-centroid(C13…C16,C19,S4) distances are 2.9405(11)Å, 2.8308(9)Å, correspondingly. Therefore, the anionic ligand displays two coordination

modes: μ-η^5:η^6 (for C1…C11, S1, S2) and μ-η^5:η^7 (for C12…C22, S3, S4). The [K$_2$(μ-THF)$_2$]$^{2+}$ moiety exhibits bonds with four [2,5-Me$_2$C$_9$H$_3$S$_2$]$^-$ anions, thus forming a 2D coordination polymer (Figs. S3-S4). All K$^+$ cations lie nearly in one plane in the 2D sheet with the K-K-K angles ranging from 99.74 (1)° to 139.35 (1)° (Table S2). A simplified scheme of Coulomb interactions between dications [K$_2$(THF)$_2$]$^{2+}$ and anions [Me$_2$C$_9$H$_3$S$_2$]$^-$ within the 2D layer is given in Fig. S31. A few negligible van der Waals interactions between the 2D sheets are limited to only H···H intermolecular contacts along the **c** axis between groups Me···Me (atoms C10 and C22) and Me···CH$_{2(THF)}$ (atoms C21 and C25).
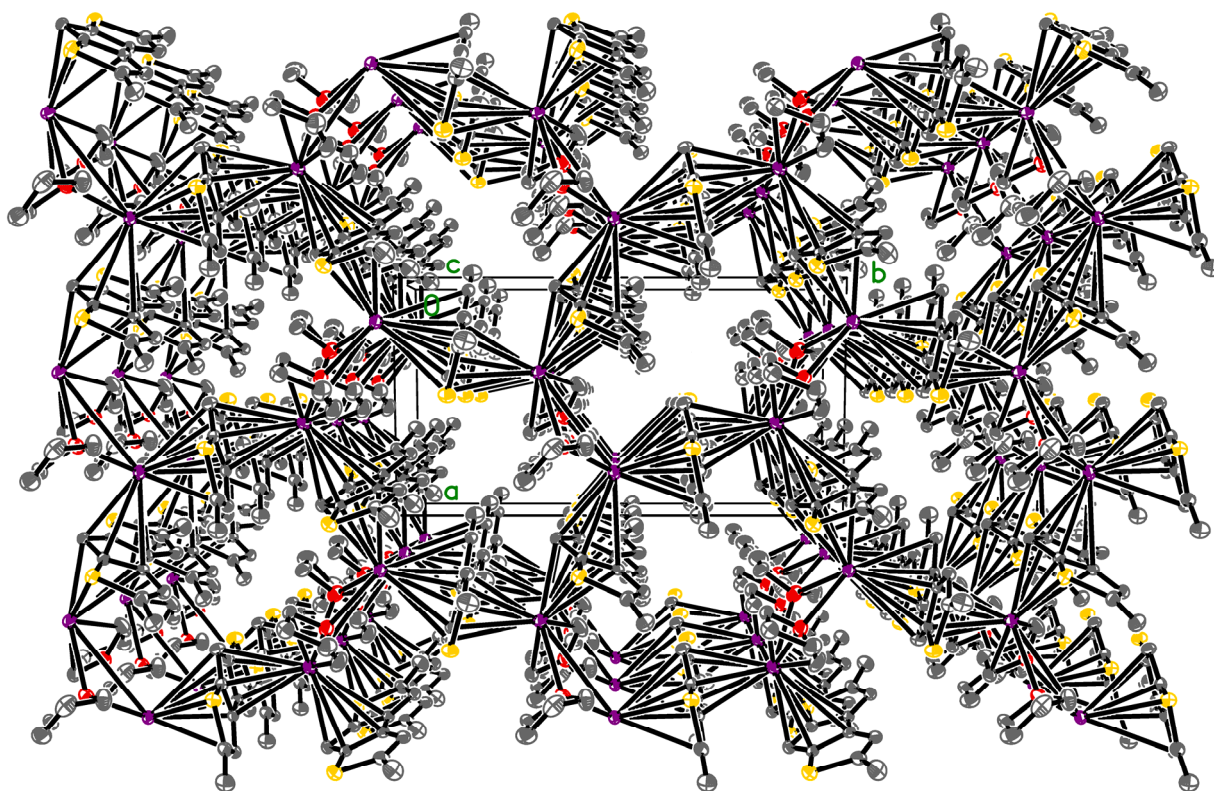
Figure S29. The packing plot of [K$_2$(THF)$_2$(Me$_2$C$_9$H$_3$S$_2$)$_2$]$_\infty$, **5**, parallel to the **ab** plane. Three layers are shown. Displacement ellipsoids are drawn at the 50% probability level.
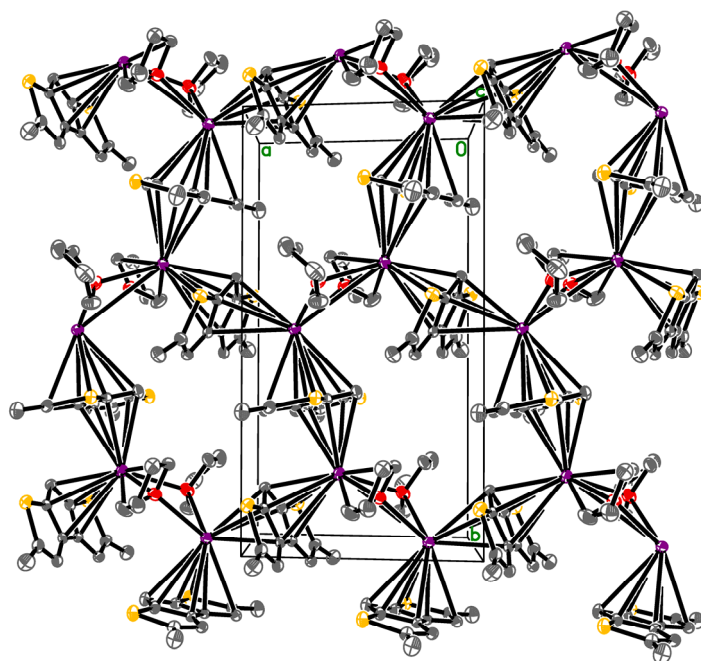
Figure S30. The packing plot of $[K_2(THF)_2(Me_2C_9H_3S_2)_2]_\infty$, **5**, parallel to the ***ab*** plane. One layer is shown. Displacement ellipsoids are drawn at the 50% probability level.
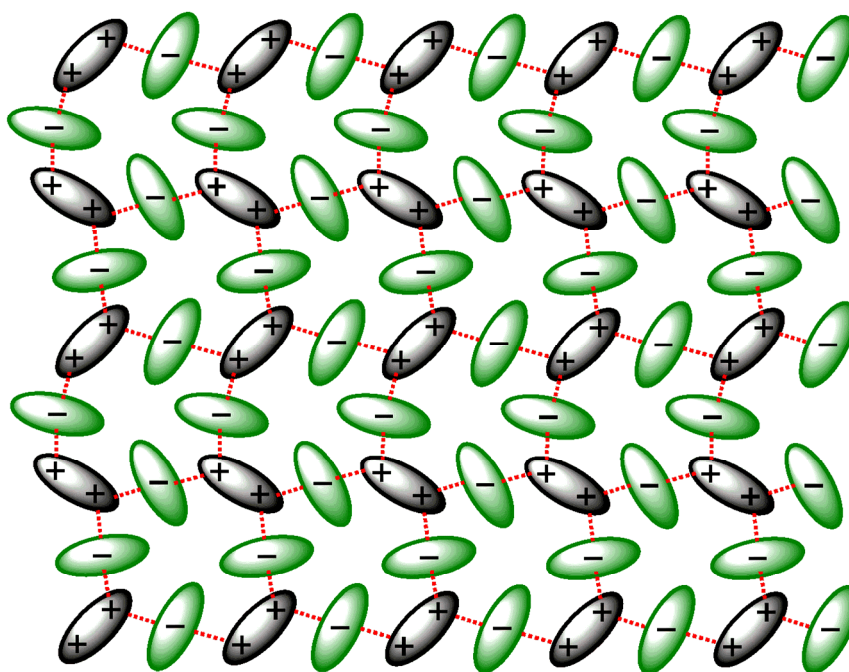

Figure S31. A simplified interactions among dications $[K_2(THF)_2]^{2+}$ and anions $[Me_2C_9H_3S_2]^-$ of $[K_2(THF)_2(Me_2C_9H_3S_2)_2]_\infty$ within the 2D layer parallel to the ***ab*** plane.

S2.3 Crystal structure and selected bond distances in [K(diglyme)(C$_{16}$H$_{12}$N)]$_\infty$ containing 5-methyl-5,6-dihydroindeno[2,1-b]indolide ligand, 6

The colourless salt [K(diglyme)(C$_{16}$H$_{12}$N)] containing 5-methyl-5,6-dihydroindeno[2,1-b]indolyl ligand, (**6**), has one organic anion [C$_{16}$H$_{12}$N]$^-$ and one [K(diglyme-κO,O',O'')]$^+$ cation in its asymmetric unit (Fig. S32). The K$^+$ cation is also coordinated by two μ-η^3:η^3-dihydroindenoindolide anions [atoms C2, C6, C7 and C6^i, C7^i, C8^i; symmetry code: (i) x, -y+1/2 ,z+1/2; see Table 3 for bond distances] (Fig. 33). The second anion additionally exhibits a rather long K1-C12^i contact. More or less equal charge redistribution within the anion is supported by the values of all C-N and C-C distances (Table S3) with the exception of a noticeably longer C7-C8 bond. The dihydroindenoindolide ligand is nearly flat with highest deviation from the plane for atoms C9 [0.0682 (11) Å], C12 [0.0815 (12) Å], C14 [0.0824 (11) Å]. The ligand folding angles are 2.82 (8)° (for planes defined by N1, C2-C5 / C4, C5, C13-C16), 2.62(8)° (N1, C2-C5 / C2, C3, C6-C8) and 2.05 (8)° (C2, C3, C6-C8 / C7-C12). Normals from K1 cation to the ligand planes are 2.9962 (6) Å for the ligand defined by N1,C1-C17 and 2.9841 (5) Å for the N1^i,C1^i-C17^i plane, and intersect the planes close to the positions of centroids defined by atoms C2, C6, C7 and C6^i, C7^i, C8^i, accordingly. Corresponding K$^+$-centroid distances that are 3.0115 (8) Å for K1—centroid(C2,C6,C7) and 3.0071 (7) Å for K1—centroid(C6^i,C7^i,C8^i) are very close to values of the normals. The centroid(C2,C6,C7)—K1—centroid(C6^i,C7^i,C8^i) angle is 118.01(5)°.
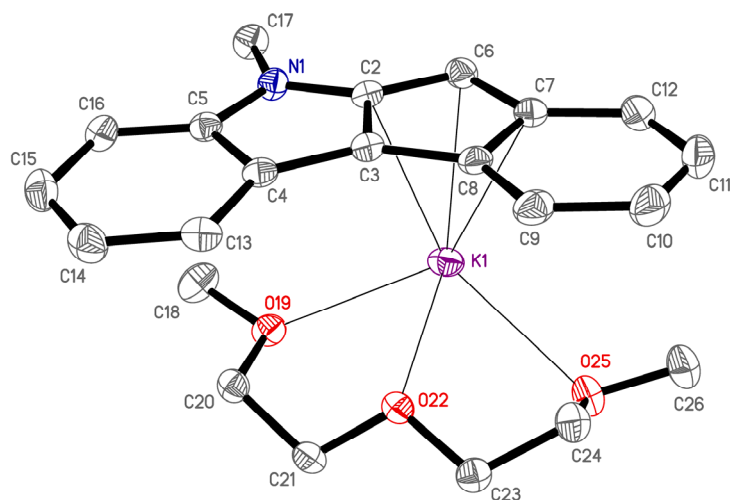
Figure S32. The asymmetric unit of (**6**). Displacement ellipsoids are drawn at the 50% probability level. All H atoms are omitted for clarity.
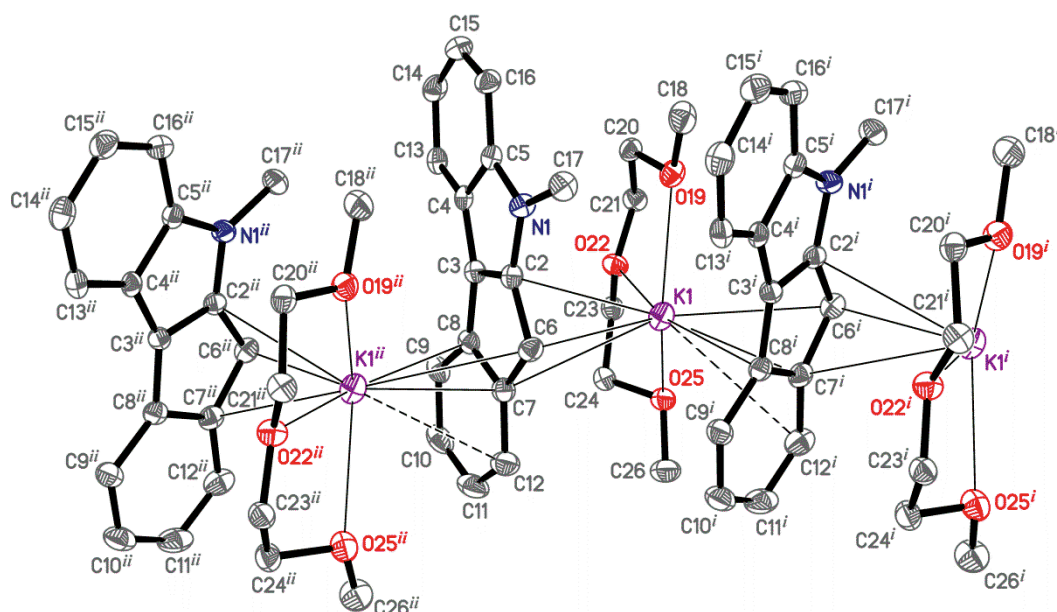
Figure S33. The structure of [K(diglyme)(C$_{16}$H$_{12}$N)]$_\infty$ containing 5-methyl-5,6-dihydroindeno[2,1-b]indolide ligand, **6**. Displacement ellipsoids are drawn at the 50% probability level. All H atoms are omitted for clarity.

Table S3. Bond distances (Å) for **6**.

N1—C2	1.3889 (15)	C10—C11	1.408 (2)
N1—C5	1.3948 (15)	C11—C12	1.387 (2)
N1—C17	1.4460 (15)	C13—C14	1.3961 (18)
C2—C3	1.4163 (16)	C14—C15	1.3958 (19)
C2—C6	1.4047 (17)	C15—C16	1.3965 (18)
C3—C4	1.4367 (17)	K1—C2	3.1916 (12)
C3—C8	1.4313 (17)	K1—C6	3.0119 (13)
C4—C5	1.4338 (17)	K1—C7	3.3135 (13)
C4—C13	1.3999 (16)	K1—C6^i	3.2869 (13)
C5—C16	1.3880 (17)	K1—C7^i	3.0399 (12)
C6—C7	1.4338 (18)	K1—C8^i	3.2182 (12)
C7—C8	1.4651 (17)	K1—C12^i	3.5107 (14)
C7—C12	1.4100 (18)	K1—O19	2.7784 (10)
C8—C9	1.4030 (17)	K1—O22	2.7611 (9)
C9—C10	1.3889 (19)	K1—O25	2.8821 (10)

Symmetry code: (i) *x*, −*y*+1/2, *z*+1/2.
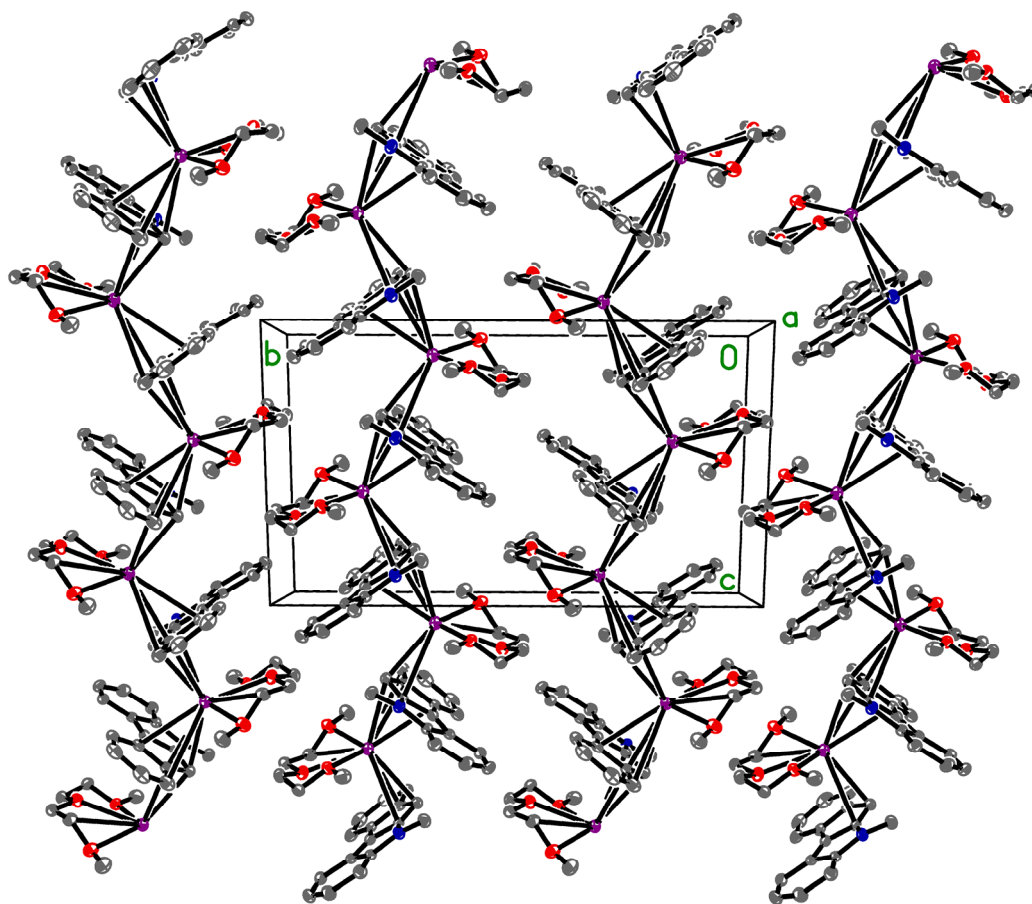
Figure S34. The packing plot of the 1D coordination polymer (**1**) parallel to the **bc** plane. Displacement ellipsoids are drawn at the 50% probability level.
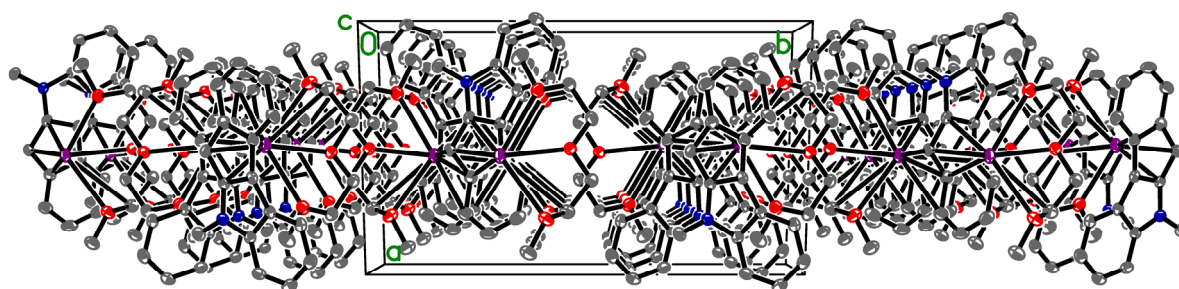
Figure S35. The packing plot of (**1**) parallel to the **ab** plane. Displacement ellipsoids are drawn at the 50% probability level.

The mentioned interionic interactions between the $[K(diglyme)]^+$ and $[C_{16}H_{12}N]^-$ moieties provide formation of a 1D coordination polymer structure $[K(diglyme)(C_{16}H_{12}N)]_\infty$, a part of which is shown on Fig. S33, with the $K1^i$—K1—$K1^{ii}$ angle of 127.65 (1)° [symmetry code: (ii) x, -y+1/2, z-1/2]. The formed polymer chains are aligned along the **c** axis (Fig. S34). There are a few C_{Ph}-

H···H-CH$_{diglyme}$ non-valence interchain interactions (corresponding atoms C15···C20 and C13···C23). Packing plot parallel to the **ab** plane for several chains is shown in Fig S35.

S2.4 Crystal structure and selected bond distances in [K(diglyme)(C$_{16}$H$_{12}$N)]$_4$ containing 5-methyl-5,10-dihydroindeno[1,2-b]indolide ligand, 7

Red compound [K(diglyme)(C$_{16}$H$_{12}$N)] containing 5-methyl-5,10-dihydroindeno[1,2-b]indolyl ligand has a similar asymmetric unit consisting of a [K(diglyme-κO,O',O")]$^+$ cation and a [μ-η^3:η^5-C$_{16}$H$_{12}$N]$^-$ anion (Fig. S36). The C-C and C-N bond distances are given in Table S4. The C-C bond distances are more or less similar, but the C7-C8 bond [1.4711 (19) Å] connecting C$_5$ and C$_6$ rings is significantly elongated as in the case of isomer (**6**) above [1.4651 (17) Å]. This fact is yet to be explained. The anion in (**7**) is even "less flat" than in (**6**): the highest deviations from the N1..C17 plane are 0.1013(13)Å for C9, 0.1206(13)Å for C10, 0.0689(12)Å for C12, and 0.1158(13)Å for C17. However, the ligand folding angles are not high: 2.03(9)° (C2,C3,C13-C16 / N1,C2-C4 planes), 1.00(10)° (N1,C2-C4 / C4-C8), 2.98(9)° (C4-C8 / C7-C12). Atom K1 is coordinated by one η^5 ligand (atoms C4-C8) and by one η^3 ligand (atoms C6^i, C7^i and C12^i) shown in Fig. 4 [symmetry code: (i) y, $-x+3/2$, $-z+1/2$]. The normal from K1 to the plane defined by N1,C2-C17 is 2.9430(5)Å, which is close to the K1-centroid(C4-C8) distance [2.9243(7)Å]. The K1-centroid(C6^i,C7^i,C12^i) is 2.9871(9)Å, whereas the normal to the N1^i,C2^i-C17^i plane cannot be used in this case since it intersects the plane relatively far from the ligand and even from the C6^i,C7^i,C12^i centroid.
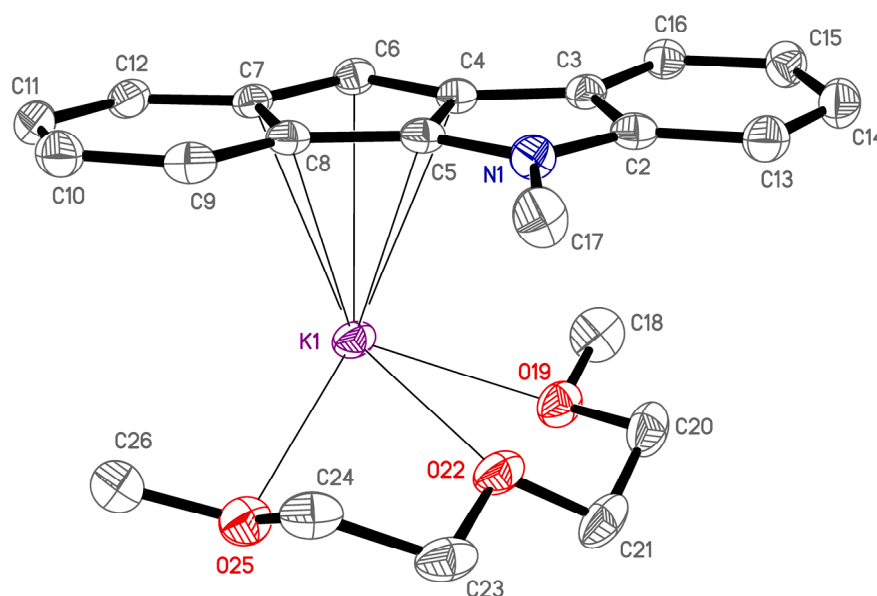
Figure S36. The asymmetric unit of **7**. Displacement ellipsoids are drawn at the 50% probability level. All H atoms are omitted for clarity.

The [K(diglyme)($C_{16}H_{12}N$)] moiety is located near the 4-fold rotoinversion axis, which results in formation of the coordination tetramer [K(diglyme)($C_{16}H_{12}N$)]$_4$ (Fig. S37) displaying the rare S_4 point group in a crystal structure. All four K$^+$ cations are located nearly but not in the same plane with the K1^i—K1—K1^{ii} angle of 89.65(0.00)° [symmetry code: (ii) -y+3/2, x, -z+1/2]. The tetramer forms layers parallel to the **ab** plane (Fig. S38). Packing of two such layers parallel to the **ac** plane is shown in Fig. S39. Non-valence H···H inter- and intralayer intermolecular interactions are following: H21B interacts with five atoms N1,C2-C4, a weak C23-H23B···O25 bonding is present, other C16-H16···H15-C15, C17-H17A···C13, H21A···K1 interactions might be also noted. It seems that first two interactions might give greater contribution into formation of molecular crystal lattice
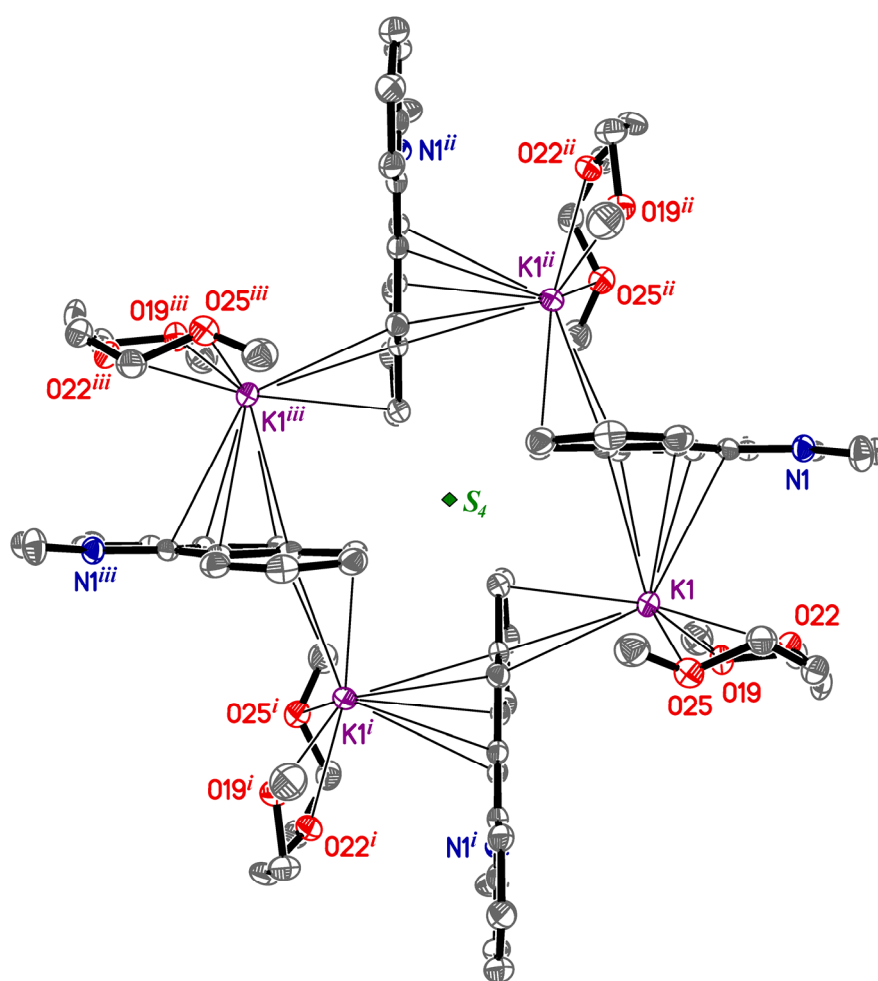
Figure S37. The [K(diglyme)($C_{16}H_{12}N$)]$_4$ tetrameric unit of **7**, demonstrating a 4-fold rotoinversion axis (S_4). Displacement ellipsoids are drawn at the 50% probability level. All H atoms are omitted, C atoms are not labelled for clarity. [Symmetry codes: (i) y, -x+3/2, -z+1/2; (ii) -y+3/2, x, -z+1/2; (iii) -x+3/2, -y+3/2, z.]

Table S4. Selected geometric parameters (Å) for **7**.

N1—C2	1.3833 (18)	C11—C12	1.378 (2)
N1—C5	1.3980 (17)	C13—C14	1.389 (2)
N1—C17	1.4448 (18)	C14—C15	1.399 (2)
C2—C3	1.4313 (19)	C15—C16	1.388 (2)
C2—C13	1.392 (2)	K1—O19	2.7295 (12)
C3—C4	1.4423 (19)	K1—O22	2.7170 (10)
C3—C16	1.4016 (19)	K1—O25	2.8313 (12)
C4—C5	1.4086 (19)	K1—C4	3.1508 (14)
C4—C6	1.4231 (19)	K1—C5	3.2627 (13)
C5—C8	1.4195 (19)	K1—C6	3.0442 (14)
C6—C7	1.421 (2)	K1—C7	3.0866 (13)
C7—C8	1.4711 (19)	K1—C8	3.2825 (14)
C7—C12	1.419 (2)	K1—C6[i]	3.1131 (14)
C8—C9	1.413 (2)	K1—C7[i]	3.1300 (14)
C9—C10	1.382 (2)	K1—C12[i]	3.2972 (15)
C10—C11	1.417 (2)		

Symmetry code: (i) y, $-x+3/2$, $-z+1/2$.
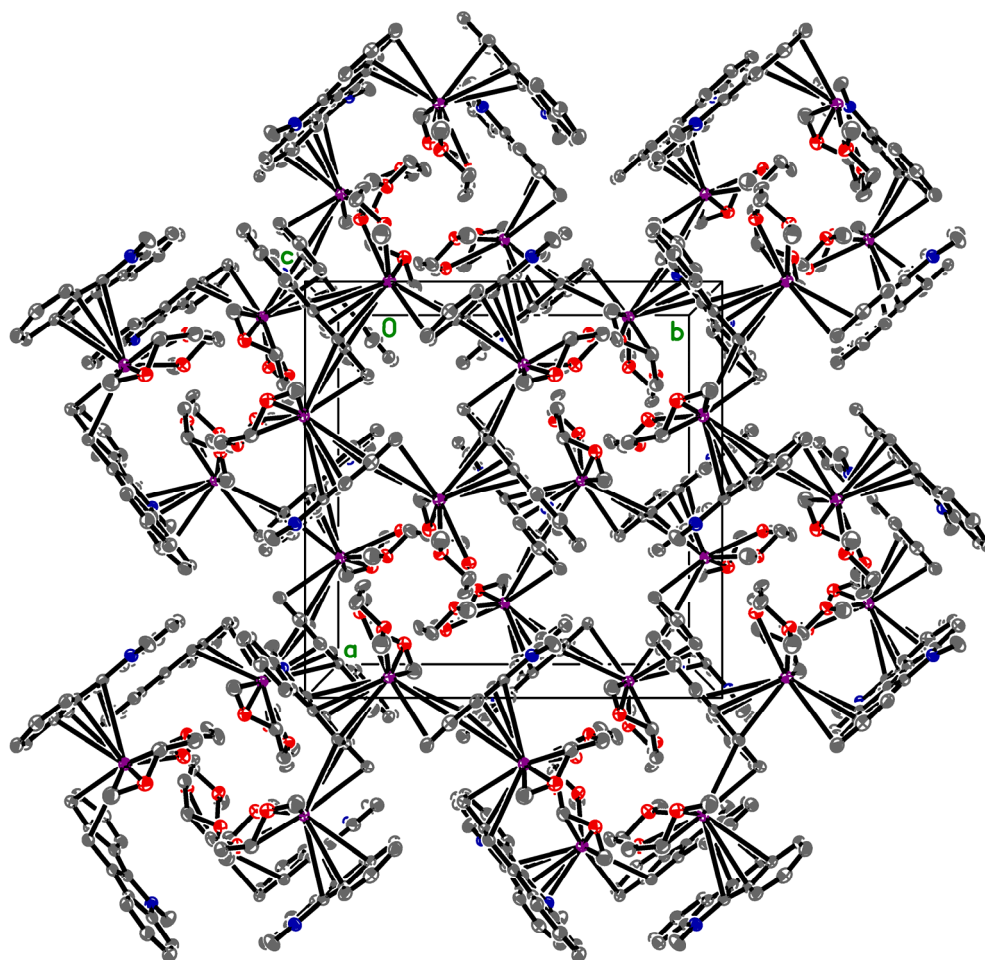
Figure S38. The packing plot of [K(diglyme)(C$_{16}$H$_{12}$N)]$_4$, **7**, parallel to the **ab** plane. One layer is shown. Displacement ellipsoids are drawn at the 50% probability level.
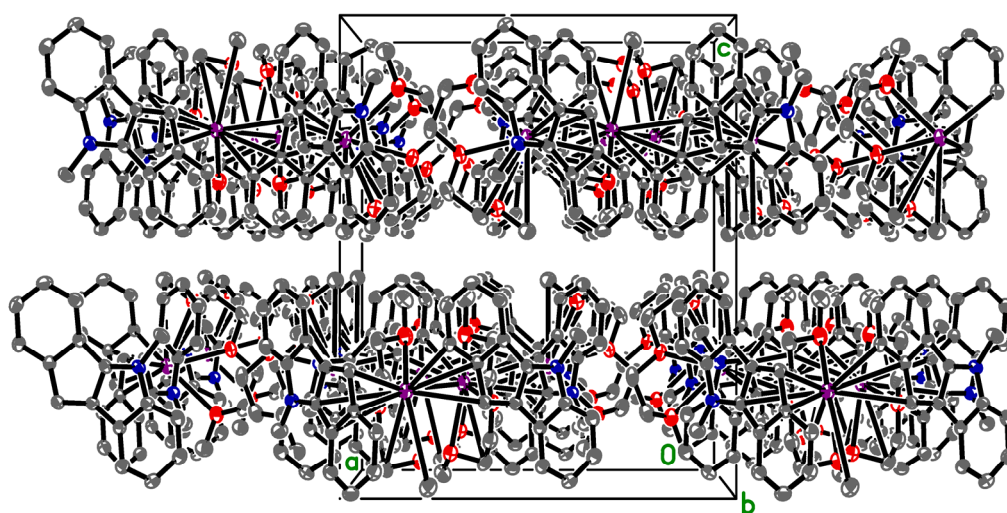
Figure S39 The packing plot of **7** parallel to the **ac** plane. Displacement ellipsoids are drawn at the 50% probability level.
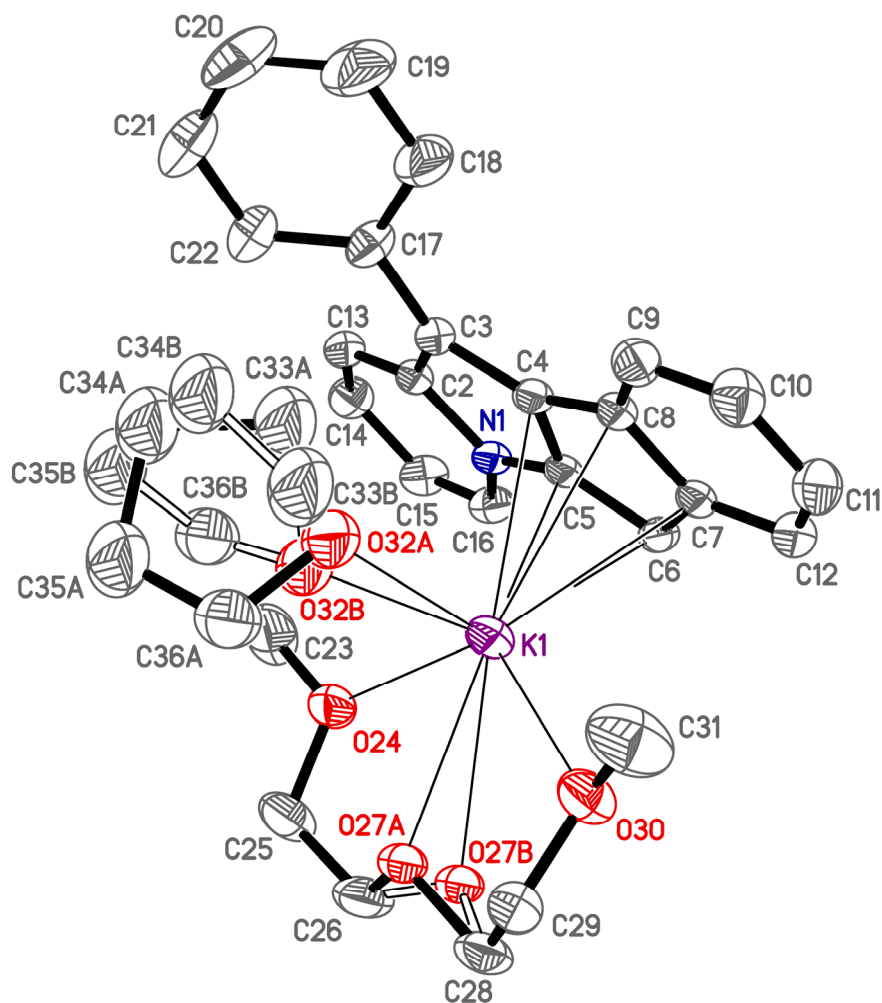
Figure S40. The structure of [K(diglyme)(THF)(C$_{21}$H$_{14}$N)], (**8**). Displacement ellipsoids are drawn at the 50% probability level. Atom O27 in diglyme and the coordinated THF molecule are disordered over two positions with the corresponding disorder ratios of 0.807(3):0.193(3) for O27A / O27B and 0.686(3):0.314(3) for atoms O32A-C36A / O32B-C36B. Minor components of disorder are shown with open solid lines. All H atoms are omitted for clarity.

The salt [K(diglyme-κ^{3}O,O',O'')(THF-κO)(η^5-C$_{21}$H$_{14}$N)], **8**, demonstrates a molecular structure (Fig. S40), where K$^+$ is coordinated with the 11-phenyl-6H-indeno[1,2-b]indolizinide anion (η^5-mode), diglyme and THF molecules, resulting in potassium coordination number of 7. The K-O, K-N distances and bond lengths within the anion are given in Table S5. Due to steric hindrance, the Ph group is rotated by 35.80(7)° with respect to the nearly flat indenoindolizinide fragment. This indicates that the conjugation between Ph and Cp fragments is lost to a significant extent. The C$_{ipso}$(Ph) atom (C17) lies in the plane of the indenoindolizinide fragment, but the latter is not entirely flat with the highest deviation from the plane of 0.1090(19)Å for C14. To be more precise, the dihedral angles within the indenoindolizinide fragment are 4.12(7)° for the planes formed by atoms N1,C2,C13-C16 and N1,C2-C5, 1.23(7)° for N1,C2-C5 and C4-C8, 1.32(6)° for

32

C4-C8 and C7-C12. The η^5-coordination mode of the anion is a symmetrical one: the K-centroid(C4…C8) distance (2.8539(10)Å) and the normal from K to the C4…C8 plane (2.8287(10)Å) are similar.

The [K(diglyme)(THF)($C_{21}H_{14}N$)] unit is sterically crowded enough not to form coordination polymers, yet the K^+ coordination sphere is insufficiently saturated. Therefore, the anion [$C_{21}H_{14}N$]$^-$ (atoms N1, C16, C5, C6, C13) and the cation [K(diglyme)(THF)]$^+$ of two different units, which are related by an inversion centre (Fig. S41), demonstrate weak electrostatic intermolecular interactions, leading to interatomic distances lying in the range of 3.876(2)Å for C16···K1 to 5.033(2)Å for C5···K1. Packing plots of **8**, demonstrating the molecular lattice, are given in Figs. S42 and S43.
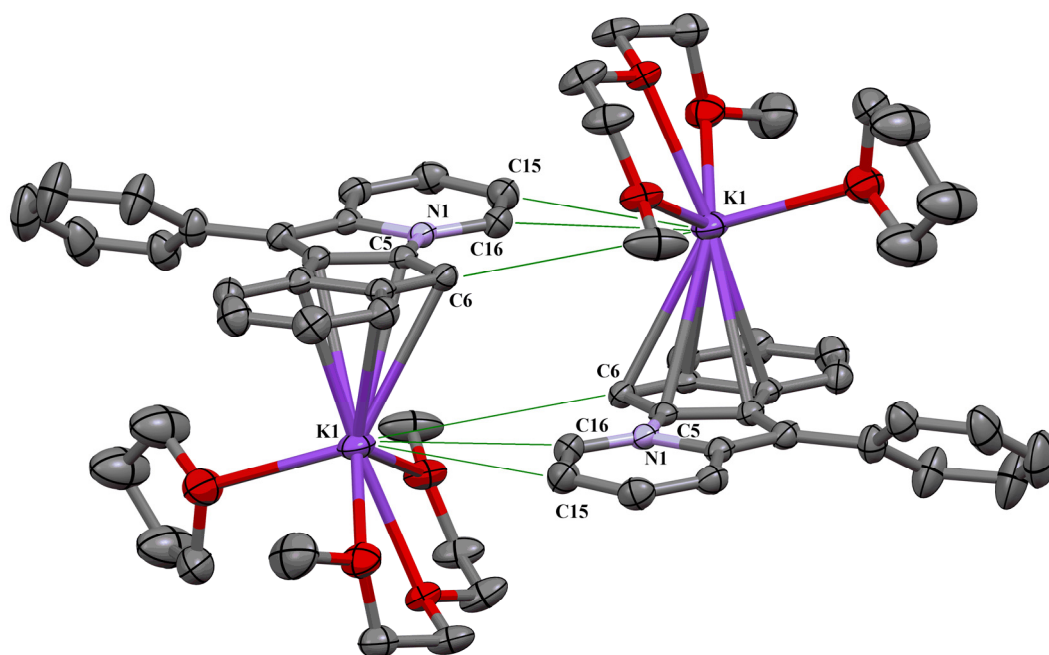
Figure S41. Two [K(diglyme)(THF)($C_{21}H_{14}N$)] units demonstrating Coulomb interactions. Displacement ellipsoids are drawn at the 50% probability level. All H atoms are omitted for clarity. Minor disorder components are not shown. Intermolecular distances are 3.876(2)Å (C16…K1), 4.545(2)Å (C15…K1), 4.609(2)Å (C6…K1), 4.835(2)Å (N1…K1), 5.033(2)Å (C5…K1).

Table S5. Selected bond distances (Å) for **8**.

K1—O24	2.7209 (17)	C2—C13	1.416 (3)
K1—O27A	2.7374 (17)	C4—C5	1.416 (3)
K1—O27B	2.895 (7)	C4—C8	1.437 (3)
K1—O30	2.7342 (18)	C5—C6	1.410 (3)
K1—O32A	2.686 (4)	C6—C7	1.418 (3)
K1—O32B	2.563 (10)	C7—C8	1.471 (3)
K1—C4	3.1598 (19)	C7—C12	1.412 (3)
K1—C5	3.2236 (19)	C8—C9	1.402 (3)

K1—C6	3.156 (2)	C9—C10	1.386 (3)
K1—C7	2.9824 (19)	C10—C11	1.411 (3)
K1—C8	2.9827 (19)	C11—C12	1.376 (3)
N1—C2	1.431 (2)	C13—C14	1.361 (3)
N1—C5	1.379 (3)	C14—C15	1.429 (3)
N1—C16	1.376 (3)	C15—C16	1.347 (3)
C2—C3	1.396 (3)	C3—C17	1.471 (3)
C3—C4	1.445 (3)		
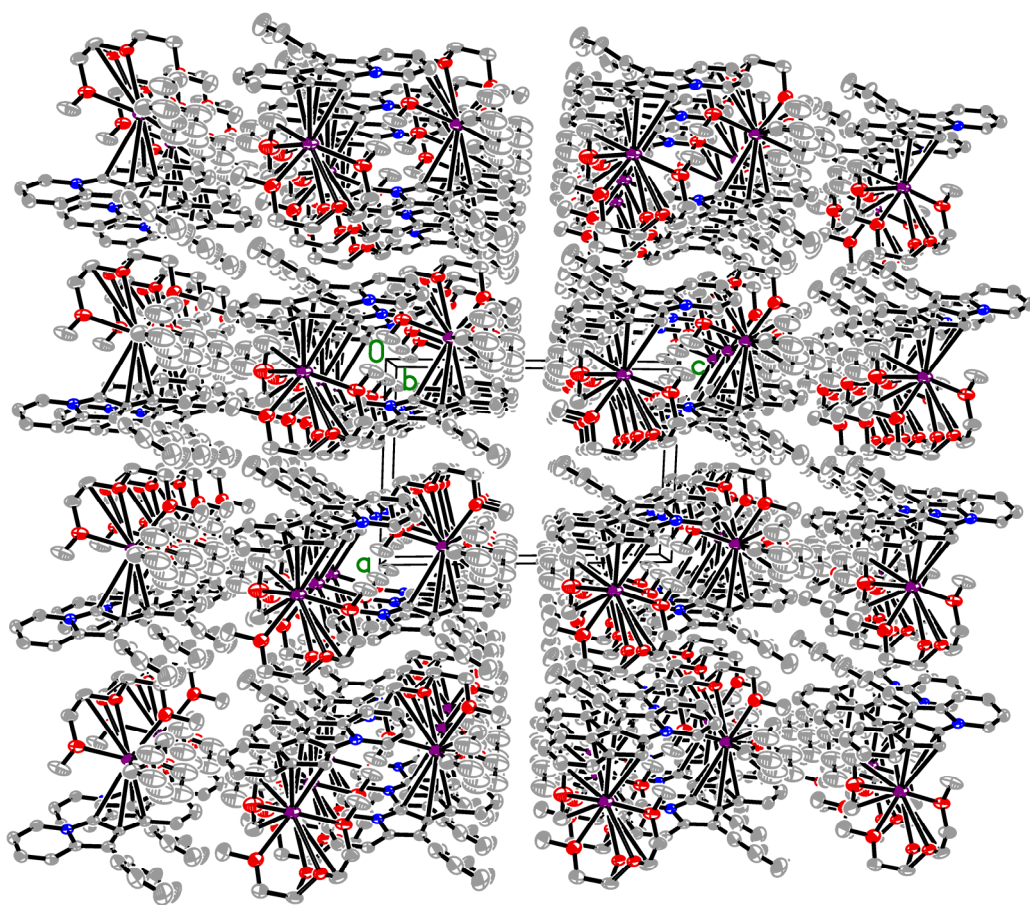
Figure S42. The packing plot of **8** parallel to the **ac** plane. Displacement ellipsoids are drawn at the 50% probability level. Displacement ellipsoids are drawn at the 50% probability level. All H atoms are omitted for clarity
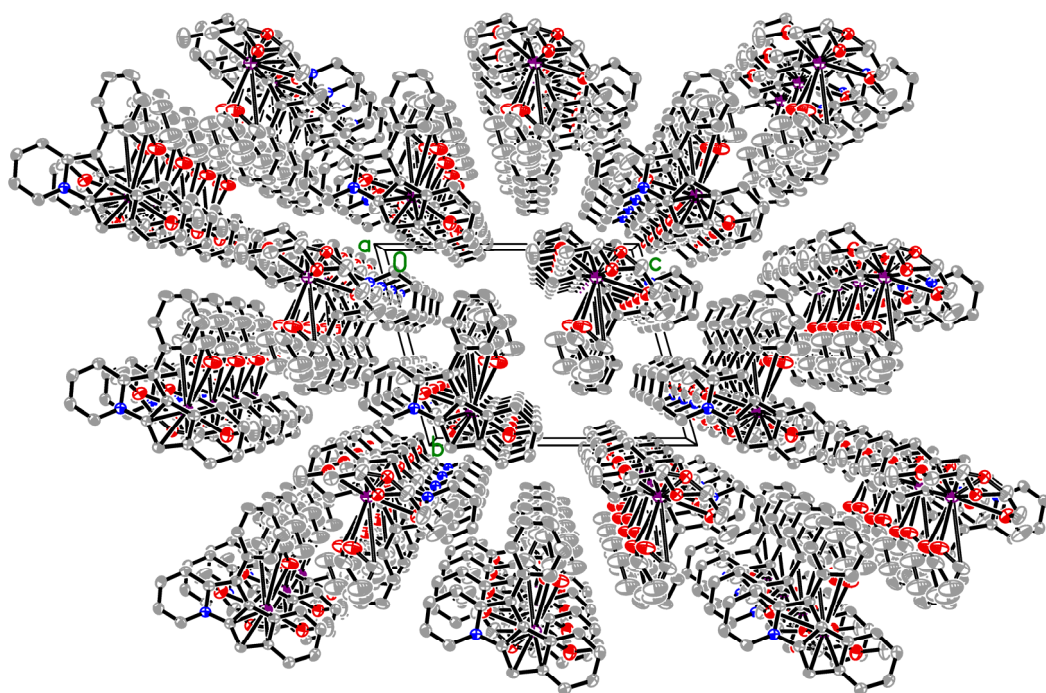
Figure S43. The packing plot of **8** parallel to the **bc** plane. Displacement ellipsoids are drawn at the 50% probability level. Displacement ellipsoids are drawn at the 50% probability level. All H atoms are omitted for clarity

S3. Quantum chemical calculations

Table S6. Partial atomic charges in anions **5–8**. Atom labeling corresponds to calculated geometries provided in corresponding XYZ-files

|	5		6		7		8
S1	0.03	N1	-1.25	N1	-1.25	C1	0.27
C2	-0.22	C2	0.33	C2	0.40	N2	-1.29
S3	0.03	C3	-0.06	C3	-0.02	C3	-0.01
C4	-0.08	C4	-0.01	C4	-0.05	C4	-0.06
H5	0.00	C5	0.37	C5	0.29	C5	0.36
C6	-0.22	C6	-0.13	C6	-0.11	C6	-0.12
C7	-0.03	H7	-0.01	H7	-0.01	H7	0.00
C8	-0.03	C8	-0.03	C8	-0.03	C8	-0.02
C9	-0.04	C9	-0.02	C9	-0.04	C9	-0.03
H10	0.00	C10	-0.06	C10	-0.06	C10	-0.07
C11	-0.20	H11	0.00	H11	-0.02	H11	-0.01
C12	-0.04	C12	-0.08	C12	-0.08	C12	-0.07
H13	0.00	H13	-0.02	H13	-0.02	H13	-0.01
C14	-0.20	C14	-0.08	C14	-0.08	C14	-0.08
C15	0.00	H15	-0.02	H15	-0.02	H15	-0.01
H16	0.00	C16	-0.07	C16	-0.07	C16	-0.06
H17	-0.01	H17	-0.01	H17	-0.01	H17	0.01
H18	-0.01	C18	-0.06	C18	-0.06	C18	0.41
C19	0.00	H19	0.01	H19	0.00	H19	0.05
H20	0.00	C20	-0.07	C20	-0.06	C20	-0.05
H21	-0.01	H21	-0.01	H21	0.00	H21	0.02
H22	-0.01	C22	-0.07	C22	-0.07	C22	-0.07
		H23	-0.01	H23	-0.01	H23	0.01
		C24	-0.07	C24	-0.05	C24	-0.04
		H25	0.00	H25	0.01	H25	0.04
		C26	0.37	C26	0.37	C26	0.01
		H27	0.03	H27	0.01	C27	-0.05
		H28	0.00	H28	0.00	H28	0.06
		H29	0.01	H29	0.03	C29	-0.05
						H30	0.02
						C31	-0.06
						H32	0.01
						C33	-0.06
						H34	0.01
						C35	-0.05
						H36	0.03
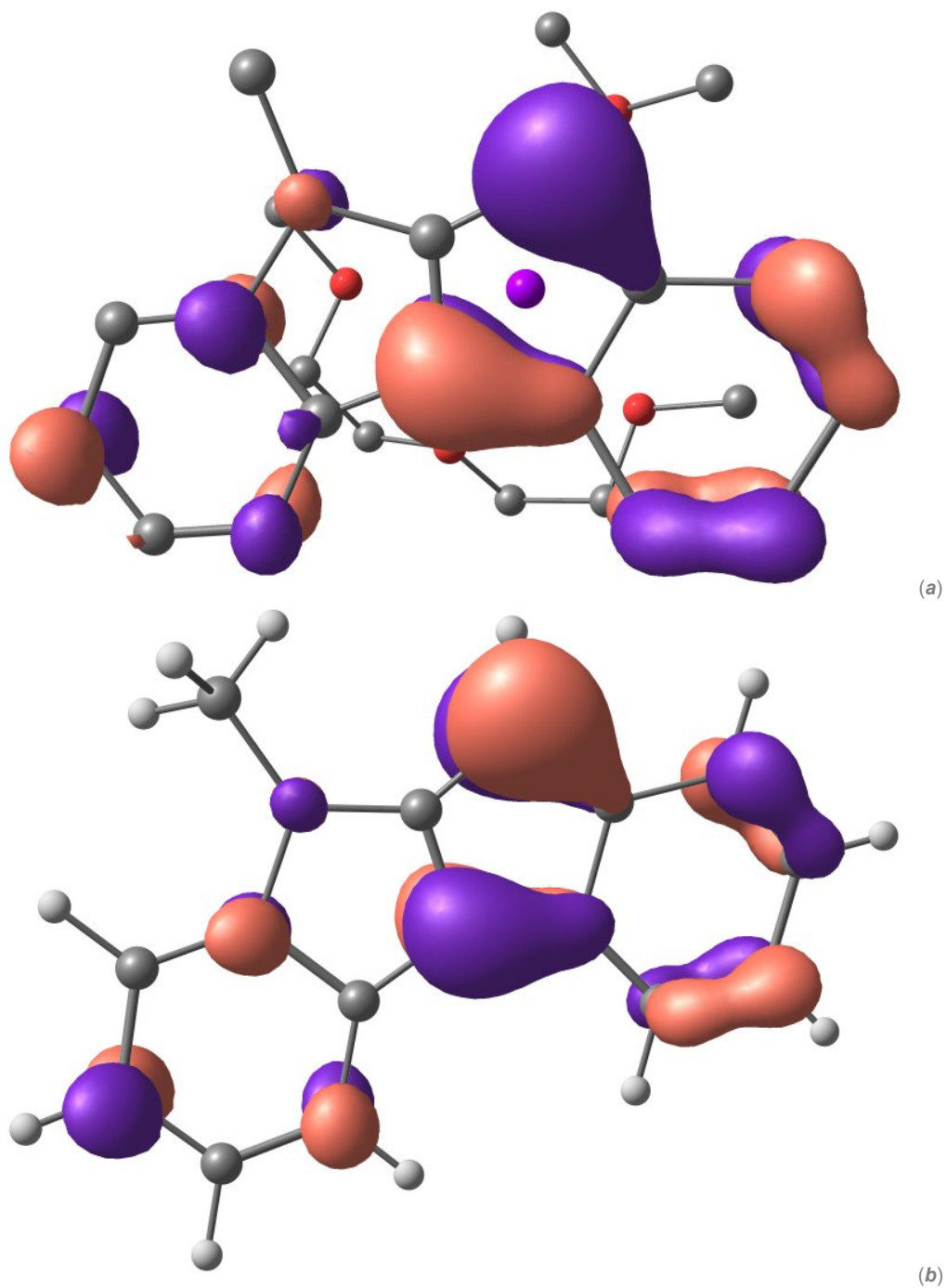
Figure S44. HOMO for hypothetical $[K(Me_2O)(diglyme)]^+[C_{16}H_{12}N]^-$ (**a**) and HOMO for free anion $[C_{16}H_{12}N]^-$ (**b**), where $C_{16}H_{12}N^-$ is the 5-methyl-5,6-dihydroindeno[2,1-b]indolide-anion

S4. References

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