Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

The Reductive Aromatization of Tridecacyclene

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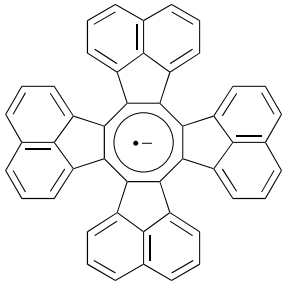
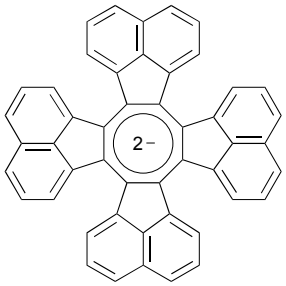
General Procedures: Unless otherwise noted, all reagents were used as received and all reactions were carried out under a N_2 atmosphere in a glove box using solvents freshly dried over potassium metal. UV-visible absorption spectra were recorded on a Shimadzu 2450 UV-visible Spectrometer with UV Probe 2.33 software. ^{1}H (500 Mhz) and ^{13}C (125 Mhz) NMR spectra were recorded on a Bruker Ascend 500 Mhz Spectrometer at room temperature. Tridecacyclene was prepared through a previously published procedure.[1]

Syntheses:



Tridecacyclene radical anion (**2**): In a glove box under nitrogen atmosphere freshly cut potassium metal (excess) was added to tridecacyclene (10 mg, 0.016 mmol) dissolved in 0.5 mL THF in a scintillation vial with vigorous stirring. Reduction to the radical anion was observed as the solution adopted a dark green color, quickly followed by reduction to the dianion indicated by a dark purple color. Excess potassium metal was removed through filtration and tridecacyclene (10mg, 0.016 mmol) in 0.5 mL THF was added to the reaction mixture to produce the dark green solution of the radical anion. ^{1}H showed no identifiable peaks, consistent of a species with an unpaired electron.



Tridecacyclene dianion (**3**): In a glove box under nitrogen atmosphere freshly cut potassium metal (excess) was added to tridecacyclene (20mg, 0.03 mmol) dissolved in 1 mL THF in a scintillation vial with vigorous stirring. Reduction to the dianion was observed as the reaction mixture adopted a dark purple color. Excess potassium metal was removed through filtration to yield the tridecacyclene dianion. ^{1}H NMR (500 Mhz, d_8-THF, ppm) δ 8.21 (t, 2H, *J* = 5 Hz) 6.65 (d, 1H, *J* = 5 Hz) ^{13}C NMR (125 Mhz, d_8-THF, ppm) δ 143.7, 133.9, 131.5, 126.7, 120.8, 118.3, 113.4 Crystals suitable for X-Ray diffraction were grown by layering hexanes onto the THF solution and standing overnight.

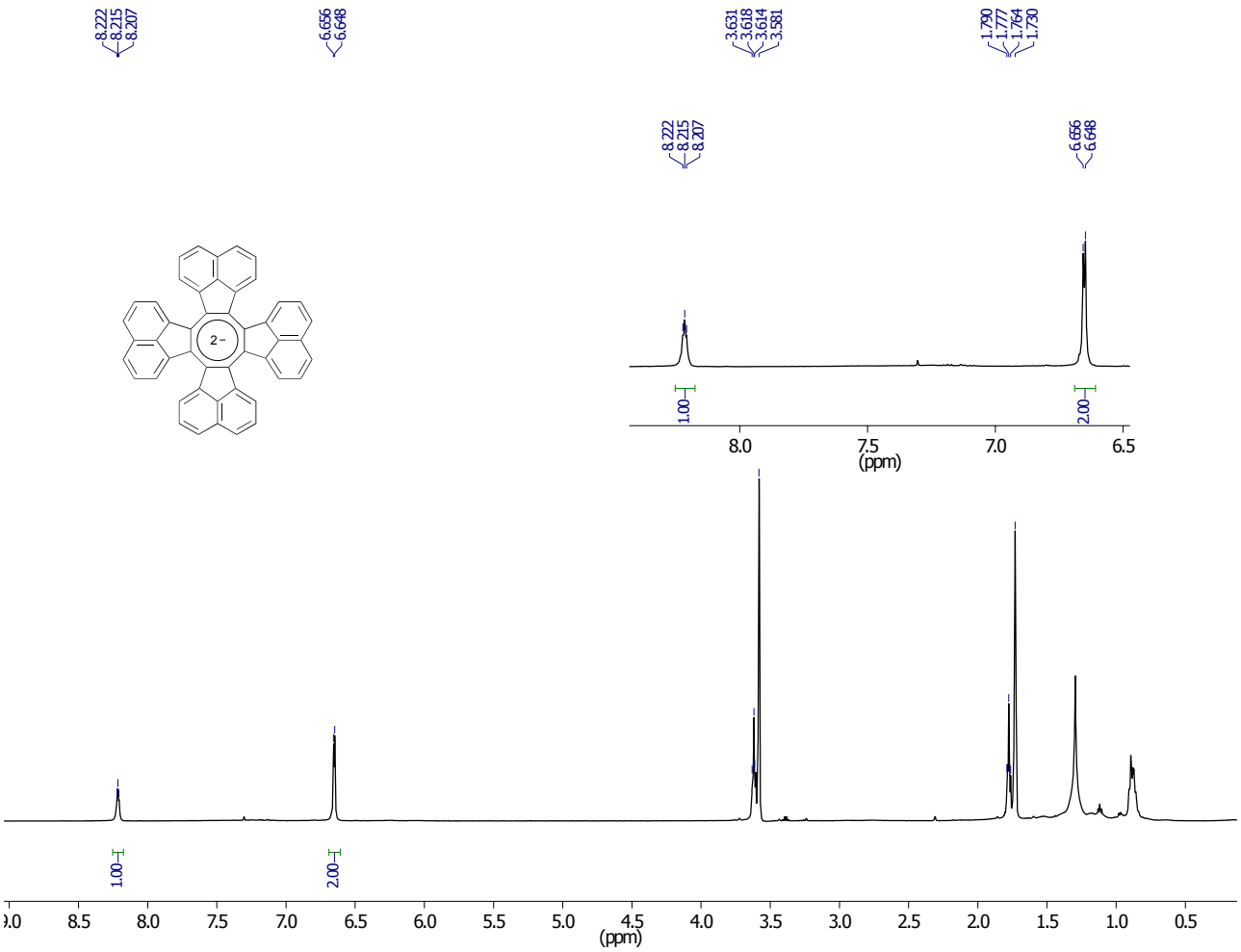


Figure S1: ^{1}H NMR of (**3**) in d_8-THF

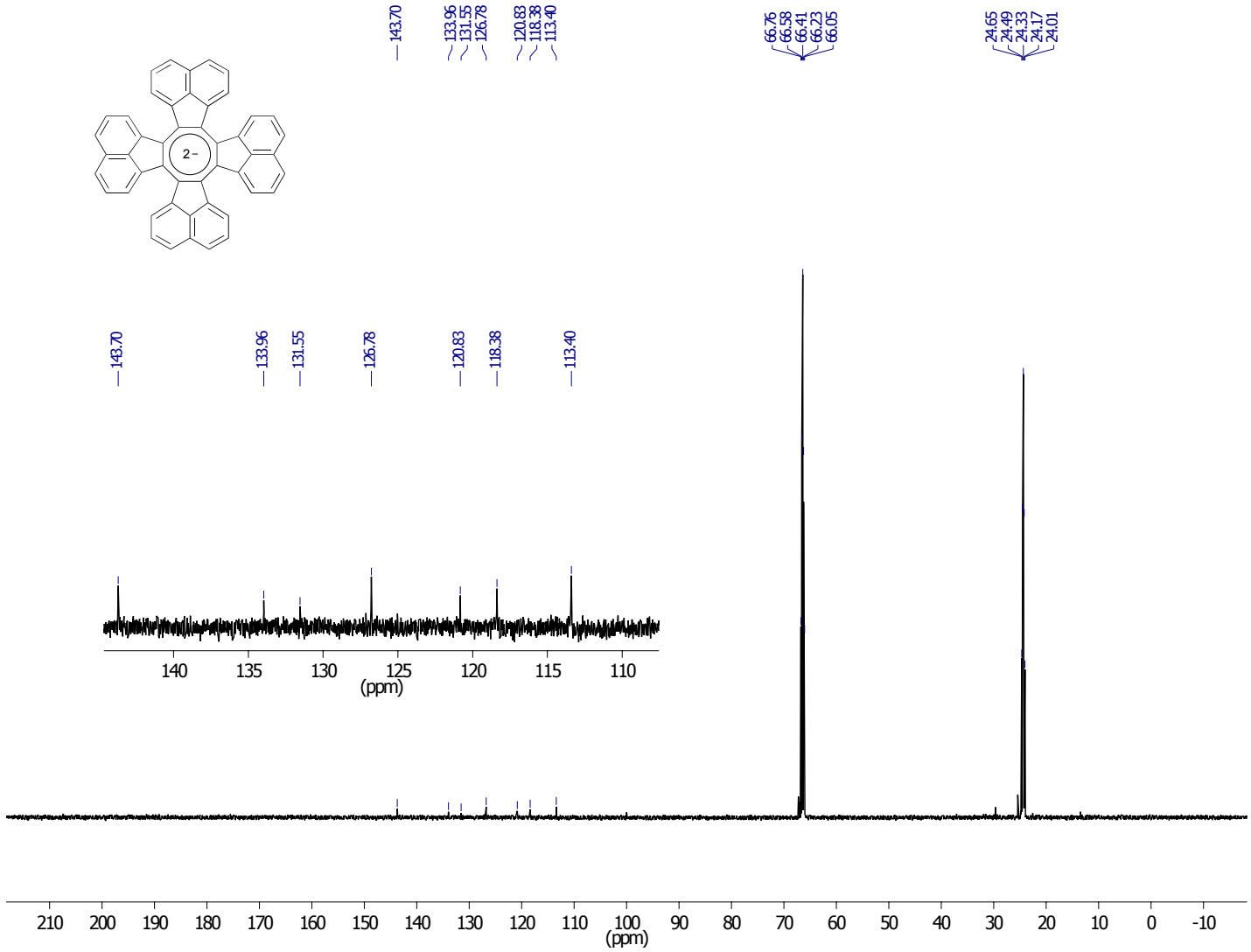


Figure S2: ^{13}C NMR of (**3**) in d_8-THF

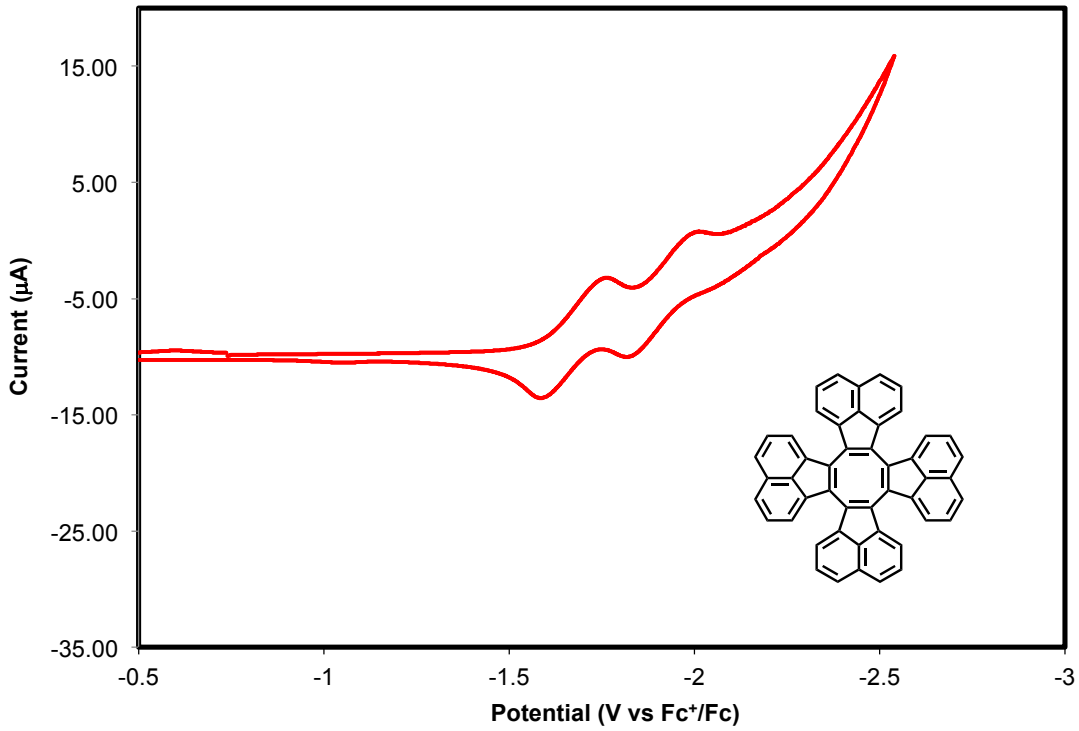


Figure S3: Cyclic voltammetry of **1** in 0.05 M tetrabutylammonium hexafluorophosphate in MeCN with a Pt working electrode, Pt counter electrode, and Ag/AgCl reference electrode. Scan rate: 50 mV s^{-1}. Ferrocene was added as an internal standard and referenced to 0 V.

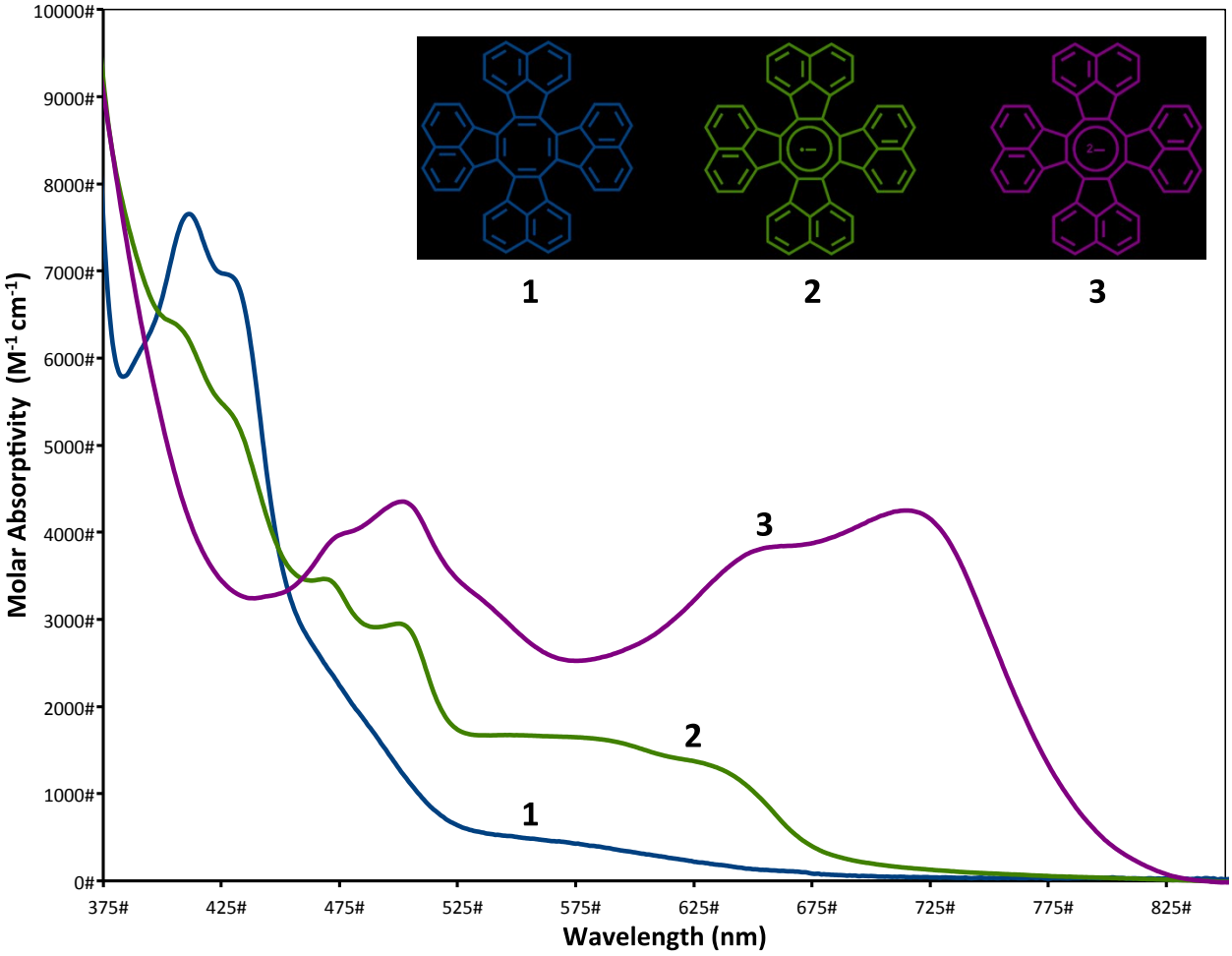


Figure S4: UV-vis spectra of **1, 2** ,and **3** in THF.

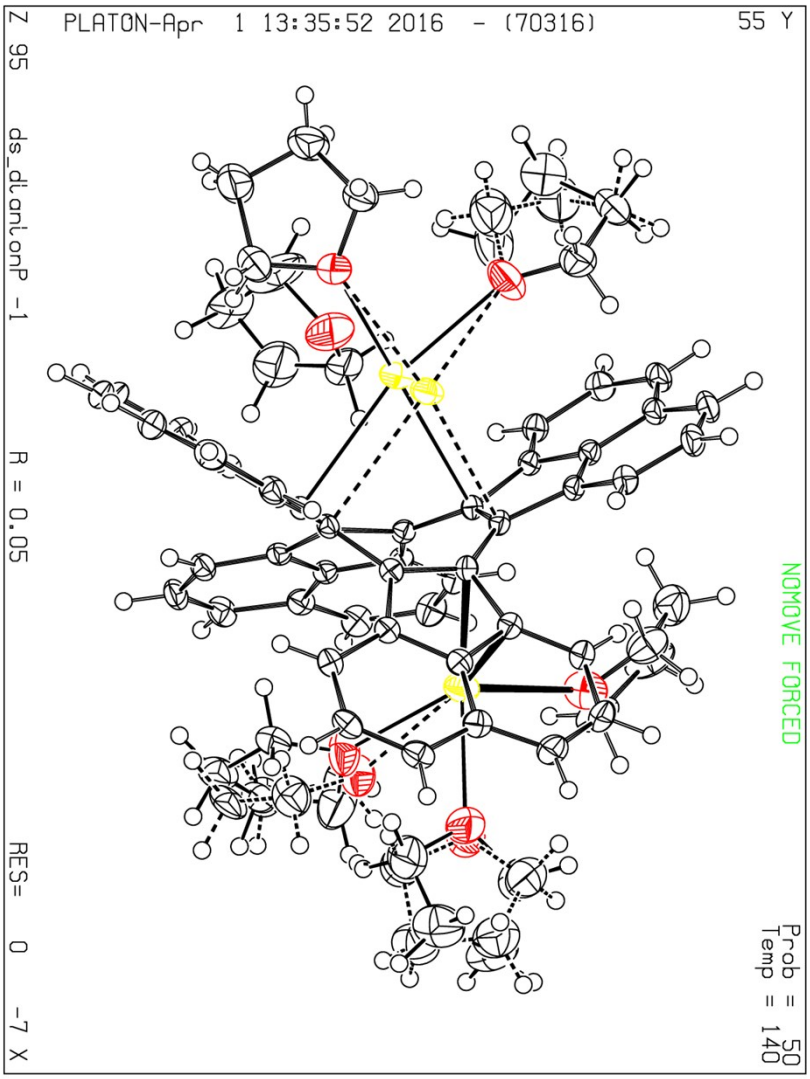
Crystal Structure and Refinement of 3

X-Ray quality crystals were obtained from a freshly prepared solution of **3** in THF with hexanes layered on top. X-Ray diffraction data was collected at 140K on a Bruker APEX 2 CCD platform diffractometer (MoKα, λ = 0.71073 Å). Crystals were mounted under Paratone-N cryoprotectant oil onto a nylon loop. A structural model consisting of host, 5.5 THF solvent ligands, and 2 K atoms was developed. One potassium atom occupies two positions with a 50:50 ratio.H atoms were included as riding idealized contributors. H atom U values were assigned as 1.2 times the carrier U~eq~. Three of the THF molecules had significantly larger thermal parameters; thus, these moieties were modeled as disordered over two discrete positions. Rigid-bond restraints (s.u. 0.01) were imposed on displacement parameters for all disordered sites and similar displacement amplitudes (s.u. 0.01) were imposed on disordered sites overlapping by less than the sum of van der Waals radii. The C-C bonds and C-O bonds for disordered positions were restrained to be similar (s.u. 0.01); the 1,4-distances were also restrained to be similar (s.u. 0.04).The displacement parameters of C60A and C60B were constrained to be equivalent. One THF molecule sits on an inversion center. The occupancies of the atoms of this molecule were set to 0.5 as befitting the special position. Bond lengths were fixed to idealized values. The C-C bonds for C71-C72 and C70-C69 were fixed at 1.535 Å, for C71-C70, 1.539 Å, for O6-C69 and O6-C72, 1.443 Å. In addition, Rigid-bond restraints (s.u. 0.01) and similar displacement amplitudes (s.u. 0.01) were imposed for these atoms.

Table S1: Crystallographic details for **3**.

formula	$C_{140}H_{136}K_4O_{11}$
formula weight	2150.88
crystal system	triclinic
space group	P-1
a (Å)	13.3928(13)
b (Å)	15.4263(15)
c (Å)	15.9182(15)
α (deg)	72.759(1)
β (deg)	71.007(1)
γ (deg)	66.158(1)
V ($Å^3$)	2792.2(5)
Z	1

Table S2: Complete list of bond lengths for tridecacyclene dianion



Bond Pair	Length [Å]
K(2) O(4)	2.619(2
K(2) O(5)	2.6153(19)
K(2) O(6)	2.697(5)
K(2) C(1)	3.423(2)
K(2) C(2)	3.360(2)
K(2) C(13)	2.9290(19)
K(2) C(14)	3.1534(19)
K(2) C(17)	3.393(2)
K(2) C(37)	3.0419(19)
K(2) C(38)	3.2193(19)
K(2) C(41)	3.519(2)
K(3) O(4)	2.729(2)
K(3) O(5)	2.7521(18)
K(3) C(13)	3.445(2)
K(3) C(14)	3.0032(19)
K(3) C(15)	3.3863(19)
K(3) C(25)	3.2785(19)
K(3) C(26)	3.2670(19)
K(3) C(37)	3.497(2)
K(3) C(38)	3.0187(19)
K(3) C(39)	3.3825(19)
K(3) C(47)	3.517(2) 2_667
K(1) O(1A)	2.802(14)
K(1) O(1B)	2.741(4)
K(1) O(2A)	2.631(12)
K(1) O(2B)	2.574(3)
K(1) O(3)	2.6821(18)
K(1) C(1)	3.1180(17)
K(1) C(5)	3.4316(17)
K(1) C(26)	2.9610(17)

K(1) C(27)	3.1093(17)
K(1) C(36)	3.4980(19)
K(1) C(37)	3.2435(18)
K(1) C(38)	3.1965(17)
O(1A) C(49A)	1.406(8)
O(1A) C(52A)	1.419(8)
O(1B) C(49B)	1.407(5)
O(1B) C(52B)	1.421(4)
O(2A) C(57A)	1.419(8)
O(2A) C(60A)	1.420(8)
O(2B) C(57B)	1.421(4)
O(2B) C(60B)	1.448(5)
O(3) C(53)	1.415(3)
O(3) C(56)	1.424(3)
O(4) C(65)	1.419(3)
O(4) C(68A)	1.421(5)
O(4) C(68B)	1.436(10)
O(5) C(61)	1.426(3)
O(5) C(64)	1.430(3)
O(6) C(69)	1.428(13)
O(6) C(72)	1.453(8)
C(1) C(2)	1.429(2)
C(1) C(5)	1.478(2)
C(1) C(37)	1.438(2)
C(2) C(3)	1.485(2)
C(2) C(13)	1.432(2)
C(3) C(4)	1.414(2)
C(3) C(12)	1.388(2)
C(4) C(5)	1.414(2)
C(4) C(9)	1.400(2)
C(5) C(6)	1.387(2)
C(6) H(6)	0.95
C(6) C(7)	1.416(3)
C(7) H(7)	0.95
C(7) C(8)	1.377(3)
C(8) H(8)	0.95
C(8) C(9)	1.418(3)
C(9) C(10)	1.428(3)
C(10) H(10)	0.95
C(10) C(11)	1.377(3)
C(11) H(11)	0.95
C(11) C(12)	1.410(3)
C(12) H(12)	0.95

C(13) C(14)	1.427(2)
C(13) C(17)	1.481(2)
C(14) C(15)	1.479(2)
C(14) C(25)	1.437(2)
C(15) C(16)	1.414(2)
C(15) C(24)	1.390(2)
C(16) C(17)	1.417(3)
C(16) C(21)	1.400(2)
C(17) C(18)	1.389(2)
C(18) H(18)	0.95
C(18) C(19)	1.416(3)
C(19) H(19)	0.95
C(19) C(20)	1.373(3)
C(20) H(20)	0.95
C(20) C(21)	1.427(3)
C(21) C(22)	1.423(3)
C(22) H(22)	0.95
C(22) C(23)	1.376(3)
C(23) H(23)	0.95
C(23) C(24)	1.419(3)
C(24) H(24)	0.95
C(25) C(26)	1.432(2)
C(25) C(29)	1.474(2)
C(26) C(27)	1.476(2)
C(26) C(38)	1.437(2)
C(27) C(28)	1.416(2)
C(27) C(36)	1.393(2)
C(28) C(29)	1.420(2)
C(28) C(33)	1.400(2)
C(29) C(30)	1.392(2)
C(30) H(30)	0.95
C(30) C(31)	1.418(3)
C(31) H(31)	0.95
C(31) C(32)	1.381(3)
C(32) H(32)	0.95
C(32) C(33)	1.422(3)
C(33) C(34)	1.421(3)
C(34) H(34)	0.95
C(34) C(35)	1.375(3)
C(35) H(35)	0.95
C(35) C(36)	1.416(3)
C(36) H(36)	0.95
C(37) C(38)	1.429(2)

C(37)	C(41)	1.483(2)
C(38)	C(39)	1.475(2)
C(39)	C(40)	1.413(2)
C(39)	C(48)	1.389(2)
C(40)	C(41)	1.419(2)
C(40)	C(45)	1.402(2)
C(41)	C(42)	1.386(2)
C(42)	H(42)	0.95
C(42)	C(43)	1.416(3)
C(43)	H(43)	0.95
C(43)	C(44)	1.379(3)
C(44)	H(44)	0.95
C(44)	C(45)	1.421(3)
C(45)	C(46)	1.428(3)
C(46)	H(46)	0.95
C(46)	C(47)	1.377(3)
C(47)	K(3)	3.517(2) 2_667
C(47)	H(47)	0.95
C(47)	C(48)	1.421(3)
C(48)	H(48)	0.95
C(49A)	H(49A)	0.99
C(49A)	H(49B)	0.99
C(49A)	C(50A)	1.488(8)
C(49B)	H(49C)	0.99
C(49B)	H(49D)	0.99
C(49B)	C(50B)	1.504(5)
C(50A)	H(50A)	0.99
C(50A)	H(50B)	0.99
C(50A)	C(51A)	1.508(9)
C(50B)	H(50C)	0.99
C(50B)	H(50D)	0.99
C(50B)	C(51B)	1.511(5)
C(51A)	H(51A)	0.99
C(51A)	H(51B)	0.99
C(51A)	C(52A)	1.475(8)
C(51B)	H(51C)	0.99
C(51B)	H(51D)	0.99
C(51B)	C(52B)	1.470(5)
C(52A)	H(52A)	0.99
C(52A)	H(52B)	0.99
C(52B)	H(52C)	0.99
C(52B)	H(52D)	0.99
C(53)	H(53A)	0.99

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References:

[1] D. P. Sumy, C. M. Harrison, A. D. Finke and A. C. Whalley, *Chem. Eur. J.* **2016**, *22*, 14, 4709–4712