Supporting Information

Monometalated Tribenzotriquinacene: *Exo* and *Endo* Coordination of Sodium and Potassium by a Rigid Bowl-Shaped Hydrocarbon Anion

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General Methods.

n-Hexane and tetrahydropyran (THP) were distilled from potassium-benzophenone. All synthetic work was carried out under an inert argon atmosphere using standard Schlenk and glove-box techniques. $NaCH_2SiMe_3$,[1] KCH_2SiMe_3,[1] and tribenzotriquinacene[2] were prepared following literature procedures.

^1H, COSY, HSQC and ^{13}C NMR spectra were recorded on a Bruker AV 300 spectrometer, variable temperature ^1H and HMBC spectra were recorded on a Bruker AV 400 spectrometer and were referenced to the resonances of the deuterated [D_8]THF used.

Single-crystal structural analysis: Single crystals were mounted in inert oil under protective atmosphere by applying the X-Temp2 device.[3] Data for X-ray crystal structure determination were obtained with a Bruker SMART 6000 diffractometer using Cu-K_α radiation ($\lambda = 1.54188$ Å) with a rotating anode. All structures were refined to convergence against F^2 using programs from the SHELX family.[4]

Elemental analysis was carried out on an Elementar 4.1 vario EL 3.

Synthesis of [(THP)$_3$NaC$_4$H$_3$(C$_6$H$_4$)$_3$], 2: A suspension of tribenzotriquinacene (0.12 g, 0.43 mmol) and NaCH$_2$SiMe$_3$ (0.13 g, 1.2 mmol) in *n*-hexane (10 mL) was stirred for 2 h, then THP (1 mL) was added and stirred for 1 h. All the solvent was removed in vacuum and the solid dissolved in THP (10 mL) to produce a yellow solution. After filtration, most of the solvent was removed in vacuum and storing the filtrate at -21°C for 3 d afforded orange crystals suitable for X-ray diffractometry. Transferring the crystals to the glove-box led to the loss of 1.5 equivalents of solvent [(THP)$_{1.5}$NaC$_4$H$_3$(C$_6$H$_4$)$_3$], (0.11 g, 60.5 %). ^{1}H NMR (300 MHz, 298 K, [D$_8$]THF, TMS): δ=7.14 (m, 2H; H13/14), 6.95 (d, ^3J(H,H)=6.9 Hz, 2H; H9/18), 6.90 (m, 2H; H12/15), 6.54 (td, ^3J(H,H)=7.4 Hz, 2H; H7/20), 6.15 (d, ^3J(H,H)=7.3 Hz, 2H; H6/21), 5.81 (td, ^3J(H,H)=7.2 Hz, 2H; H8/19), 4.41 (t, ^3J(H,H)=7.7 Hz, 1H; H1), 4.03 (d, ^3J(H,H)=7.7 Hz, 2H; H3/4), 3.54 (m, 6H, α-THP), 1.61 (m, 3H, γ-THP), 1.50 ppm (m, 6H, β-THP). ^{13}C NMR (75 MHz, 298 K, [D$_8$]THF, TMS): δ=151.1 (C11/16), 150.4 (C5/22), 148.5 (C10/17), 128.1 (C7/20), 126.4 (C12/15), 125.1 (C13/14), 122.98 (C9/18), 110.7 (C6/21), 110.0 (C8/19), 80.3 (C2), 69.1 (α-THP), 58.0 (C1), 55.5 (C3/4), 27.8 (β-THP), 24.7 ppm (γ-THP). Elemental analysis (%) calcd. for C$_{59}$H$_{60}$O$_3$Na$_2$ (M = 431.54 g/mol): C, 82.1; H, 7.00; found: C, 82.0; H, 6.24.

Synthesis of [(THP)$_3$KC$_4$H$_3$(C$_6$H$_4$)$_3$], 3: A suspension of tribenzotriquinacene (0.15 g, 0.54 mmol) and KH (0.20 g, 5.0 mmol) in THP (20 mL) was stirred at 100°C for 3 h. The warm solution was filtered, storing the filtrate at -21°C for 3 d afforded orange crystals suitable for X-ray diffractometry. Transferring the crystals to the glove-box led to the loss of most solvent, (0.08 g, 46.3 %). ^{1}H NMR (300 MHz, 298 K, [D$_8$]THF, TMS): δ=7.22 (m, 2H; H13/14), 7.02 (m, 2H; H12/15), 6.96 (d, ^3J(H,H)=6.8 Hz, 2H; H9/18), 6.55 (td, ^3J(H,H)=7.4 Hz, 2H; H7/20), 5.92 (d, ^3J(H,H)=7.5 Hz, 2H; H6/21), 5.71 (td, ^3J(H,H)=7.3 Hz, 2H; H8/19), 4.38 (t, ^3J(H,H)=7.7 Hz, 1H; H1), 3.89 (d, ^3J(H,H)=7.7 Hz, 2H; H3/4). ^{13}C NMR (75 MHz, 298 K, [D$_8$]THF, TMS): δ=150.9 (C11/16), 149.9 (C5/22), 146.0 (C10/17), 129.1 (C7/20), 127.1 (C12/15), 124.9 (C13/14), 123.1 (C9/18), 108.4 (C6/21), 107.9 (C8/19), 89.8 (C2), 58.4 (C1), 54.2 (C3/4). Elemental analysis was inconclusive due to solvent loss and decomposition.

Table 1: Crystallographic data and refinement for compounds **2** and **3**.

Compound	$[(THP)_3NaC_4H_3(C_6H_4)_3]$, **2**	$[(THP)_3KC_4H_3(C_6H_4)_3]$, **3**
Formula	$C_{37}H_{45}NaO_3$	$C_{37}H_{45}KO_3$
M_r [g mol^{-1}]	560.72	576.83
Crystal system	triclinic	monoclinic
Space group	*P*	*C*c
a [Å]	10.364(2)	16.783(2)
b [Å]	18.028(2)	12.416(2)
c [Å]	33.590(3)	15.368(2)
α [°]	90.01(2)	90
β [°]	90.01(2)	102.75(2)
γ [°]	93.40(2)	90
V [Å^3]	6265.0(15)	3123.4(8)
Z	8	4
ρ_{calcd} [g cm^{-3}]	1.189	1.227
μ(Mo/Cu$_{K\alpha}$) [mm^{-1}]	0.691	1.750
T [K]	100(2)	100(2)
measured refl.	197816	27313
independent refl.	22618	4682
R(int)	0.0289	0.0196
refined parameters	1514	379
*R*1 (*R*1 all data)	0.0305 (0.0312)	0.0201 (0.0202)
*wR*2 (*wR*2 all data)	0.0830 (0.0838)	0.0485 (0.0486)
max, min peaks [eÅ^{-3}]	0.225, -0.272	0.163, -0.093

Figure 1: ^{1}H NMR of $[(THP)_3NaC_4H_3(C_6H_4)_3]$, **2** in $[D_8]THF$:

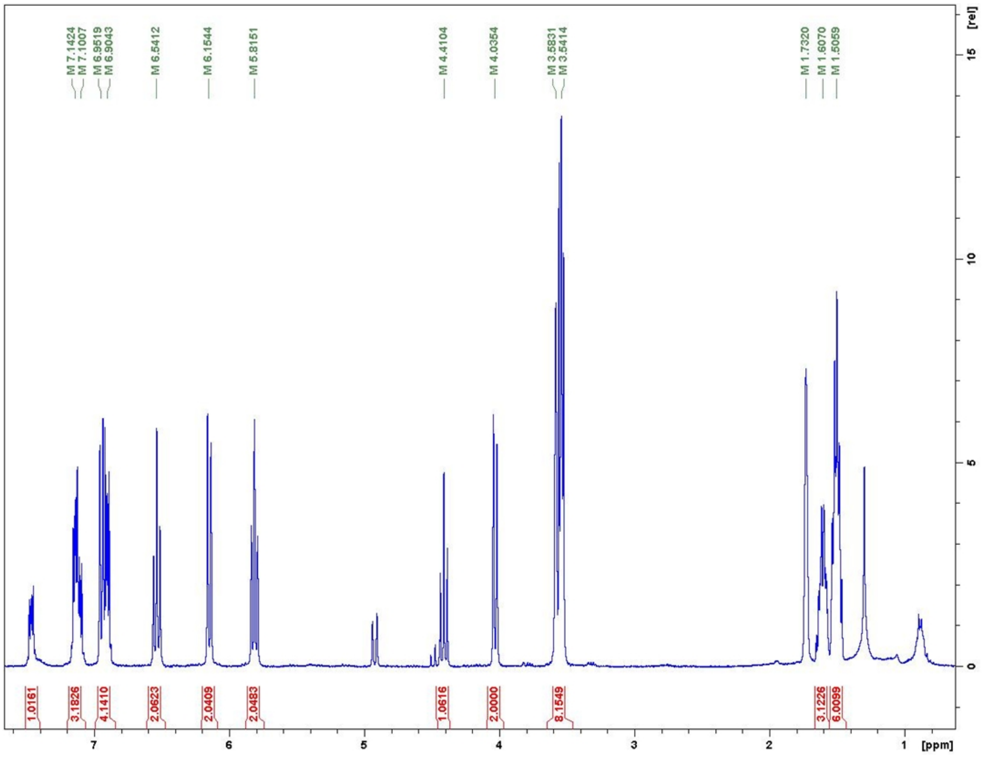


Figure 2: ^{13}C NMR of $[(THP)_3NaC_4H_3(C_6H_4)_3]$, **2** in $[D_8]THF$:

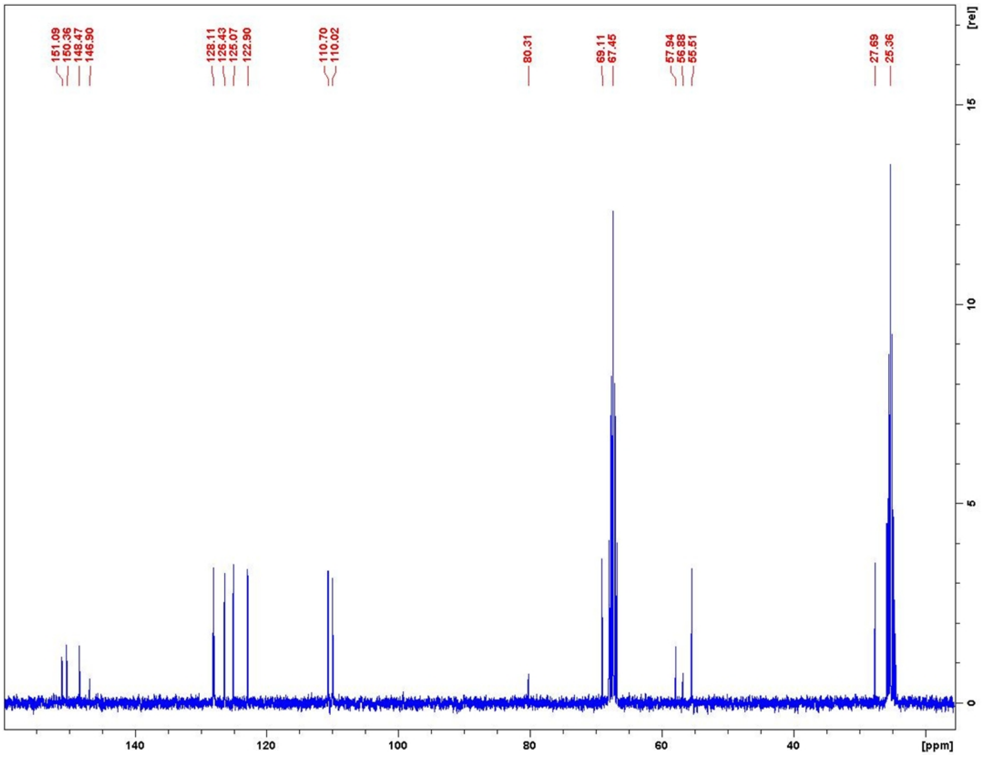


Figure 3: $^1H/^1H$ COSY NMR of $[(THP)_3NaC_4H_3(C_6H_4)_3]$, **2** in $[D_8]$THF:

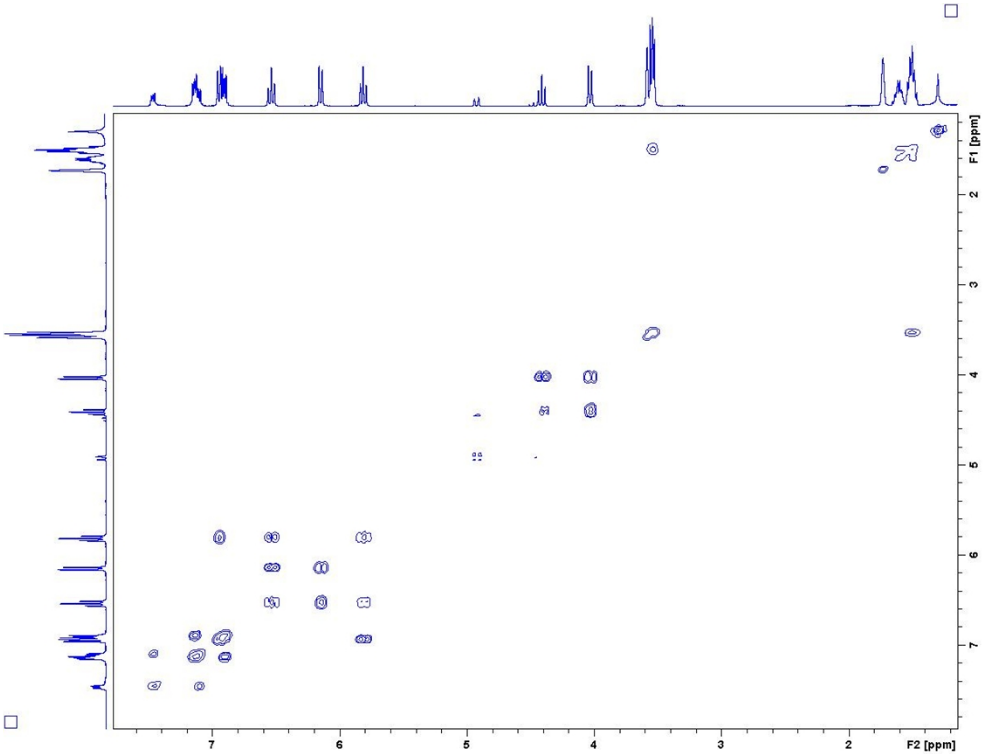


Figure 4: $^1H/^{13}C$ HSQC NMR of $[(THP)_3NaC_4H_3(C_6H_4)_3]$, **2** in $[D_8]$THF:

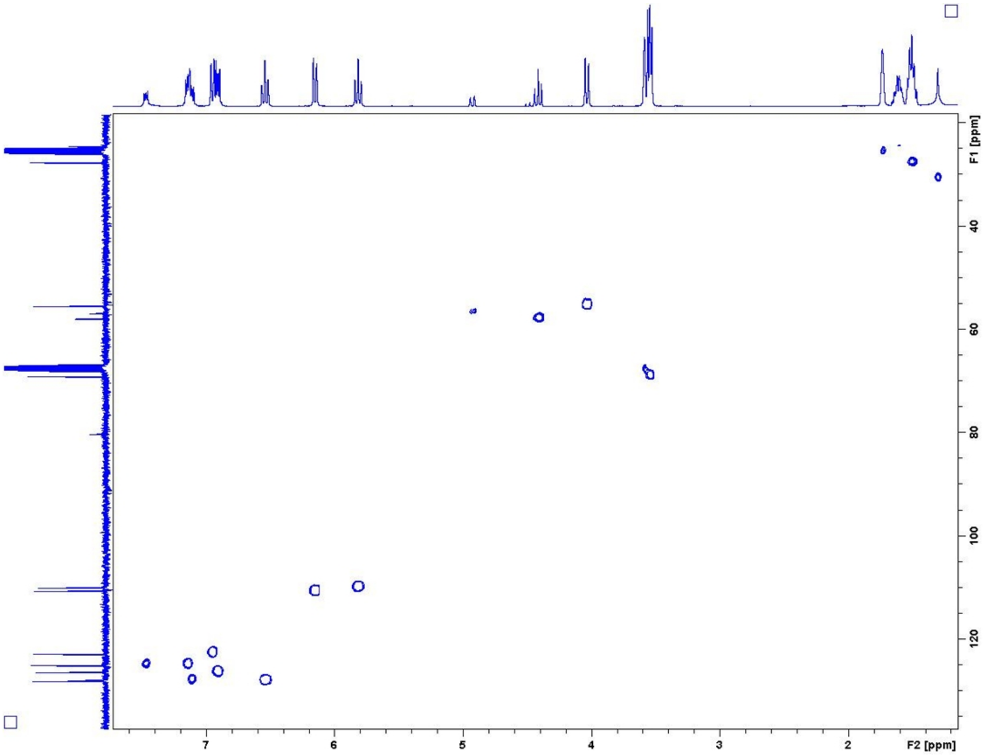


Figure 5: ^{1}H NMR of $[(THP)_3KC_4H_3(C_6H_4)_3]$, **3** in $[D_8]$THF:

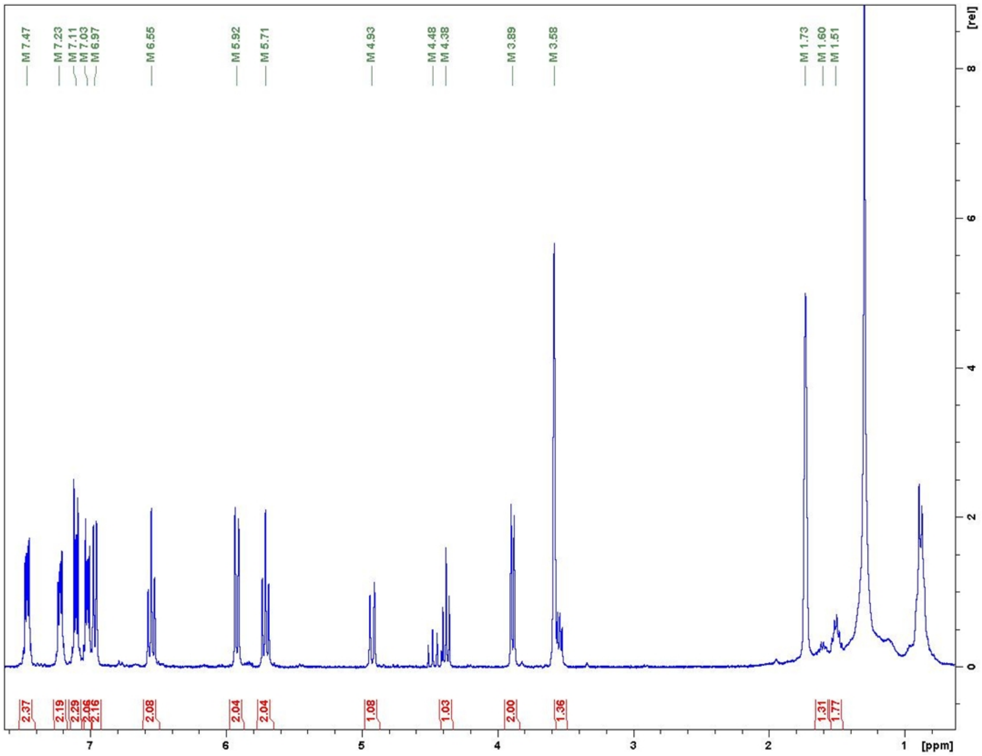


Figure 6: ^{13}C NMR of $[(THP)_3KC_4H_3(C_6H_4)_3]$, **3** in $[D_8]$THF:

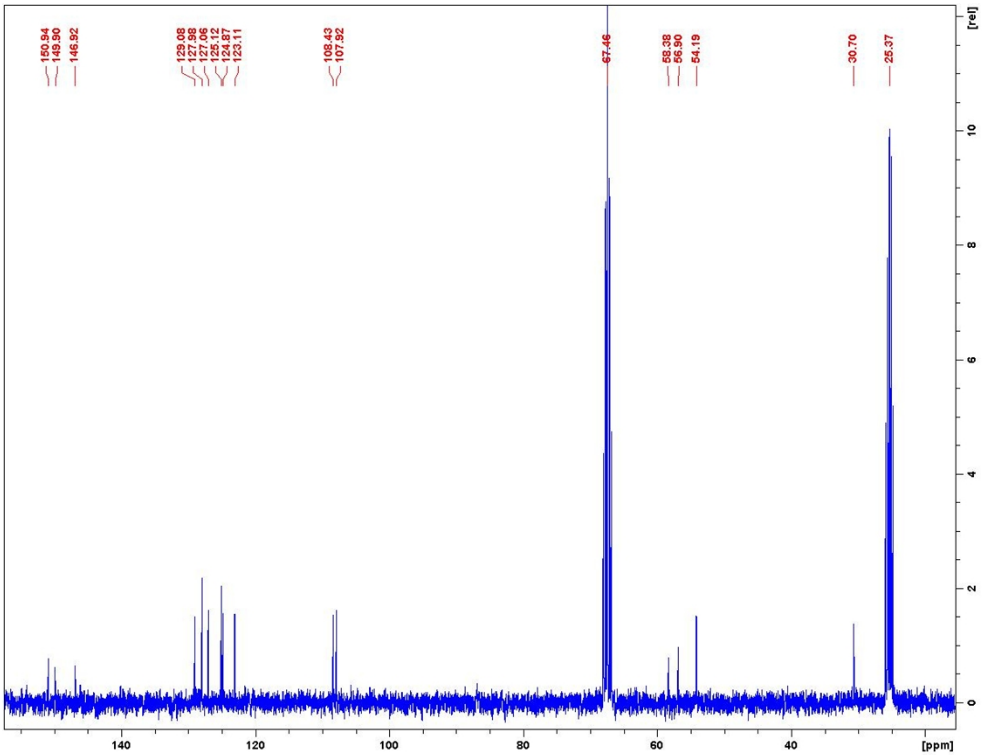


Figure 7: $^1H/^1H$ COSY NMR of $[(THP)_3KC_4H_3(C_6H_4)_3]$, **3** in $[D_8]THF$:

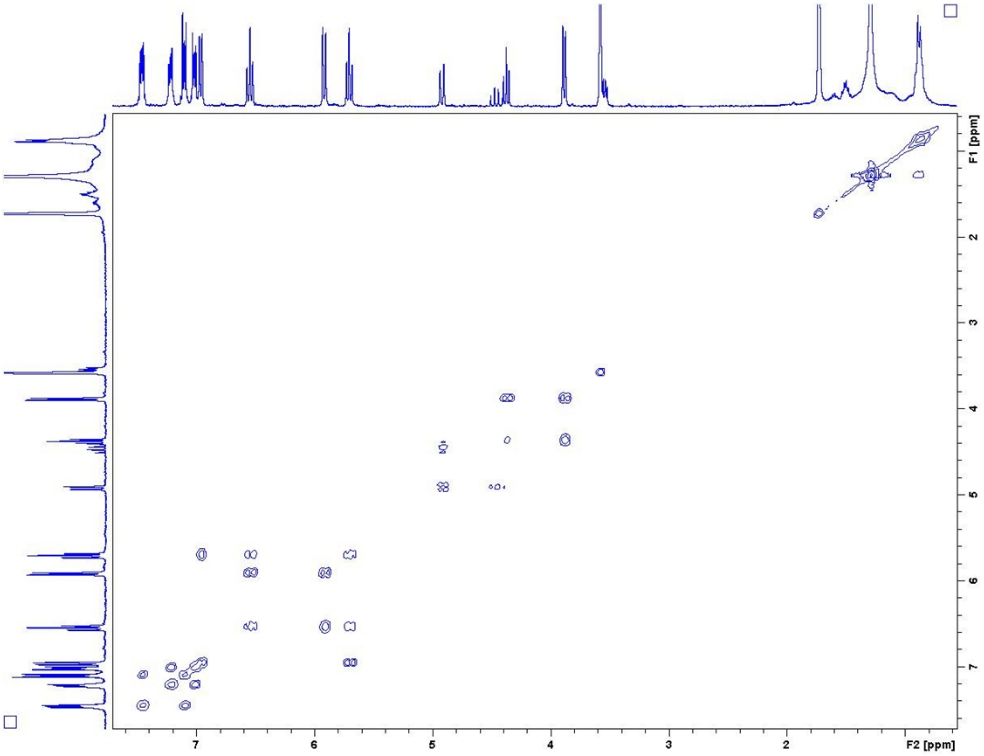


Figure 8: $^1H/^{13}C$ HSQC NMR of $[(THP)_3KC_4H_3(C_6H_4)_3]$, **3** in $[D_8]THF$:

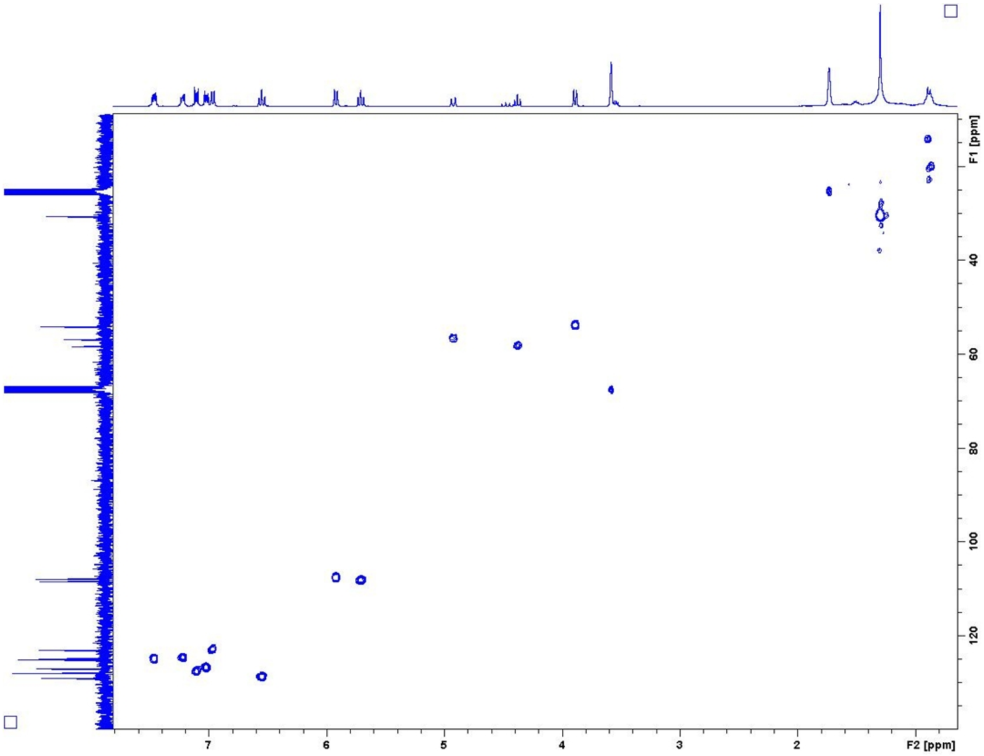


Figure 9: Numbering scheme for monometalated tribenzotriquinacene in compounds **2** and **3**:

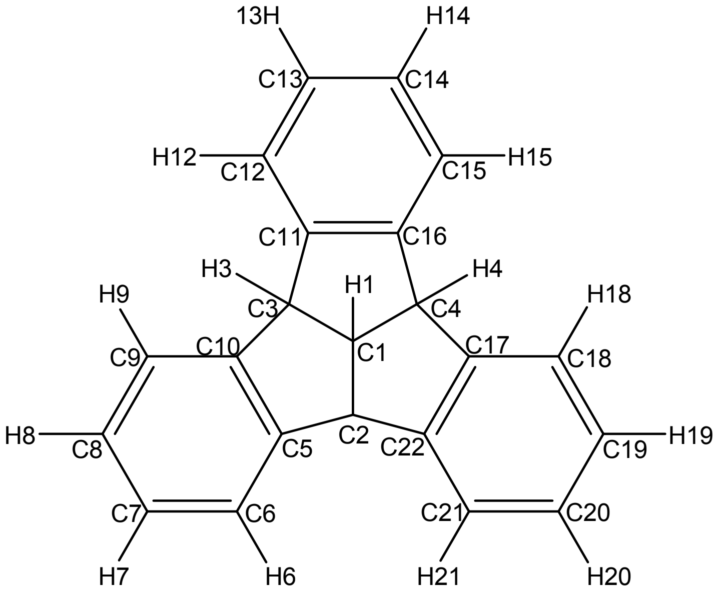


Table 2: NMR spectroscopic data for compounds **2** and **3** at 25°C in [D_8]THF [ppm].

[D_8]THF	[$(THP)_3NaC_4H_3(C_6H_4)_3$], **2**		[$(THP)_3KC_4H_3(C_6H_4)_3$], **3**	
Atom	**^{1}H**	**^{13}C**	**^{1}H**	**^{13}C**
C(1)-H	4.41, t, 7.7Hz, 1H	58.1	4.38, t, 6.9Hz, 1H	58.5
C(2)	-	80.4	-	89.8
C(3,4)-H	4.03, d, 7.7Hz, 2H	55.6	3.89, d, 6.9Hz	54.3
C(5,22)	-	150.5	-	150.0
C(6,21)-H	6.15, d, 7.3Hz, 2H	110.8	5.92, d, 7.5Hz,2H	108.0
C(7,20)-H	6.54, td, 7.4Hz,1.2Hz,2H	128.2	6.55, td, 7.4Hz, 1.2Hz, 2H	129.2
C(8,19)-H	5.81,td, 7.2Hz, 1.0Hz, 2H	110.1	5.71, td, 7.3Hz, 1.2Hz, 2H	108.5
C(9,18)-H	6.95, d, 6.9Hz,2H	123.0	6.96, d, 6.8Hz	123.2
C(10,17)	-	148.6	-	146.4
C(11,16)	-	151.2	-	151.0
C(12,15)-H	6.90, m, 2H	126.6	7.02, m, 2H	127.2
C(13,14)-H	7.14, m, 2H	125.2	7.22, m, 2H	125.0
C-H (α-THP)	3.54, m, 6H	69.2	3.54, m, 2H	-
C-H (β-THP)	1.50, m, 6H	27.8	1.50, m, 2H	-
C-H (γ-THP)	1.61, m, 3H	24.7	1.60, m, 1H	-

Figure 10: $^{1}H/^{13}C$ HMBC NMR of $[(THP)_3NaC_4H_3(C_6H_4)_3]$, **2** in $[D_8]THF$ in a temperature range from 65°C to -75°C (detail):

Figure 11:$^{1}H/^{13}C$ HMBC NMR of $[(THP)_3KC_4H_3(C_6H_4)_3]$, **3** in $[D_8]THF$ in a temperature range from 65°C to -75°C (detail):

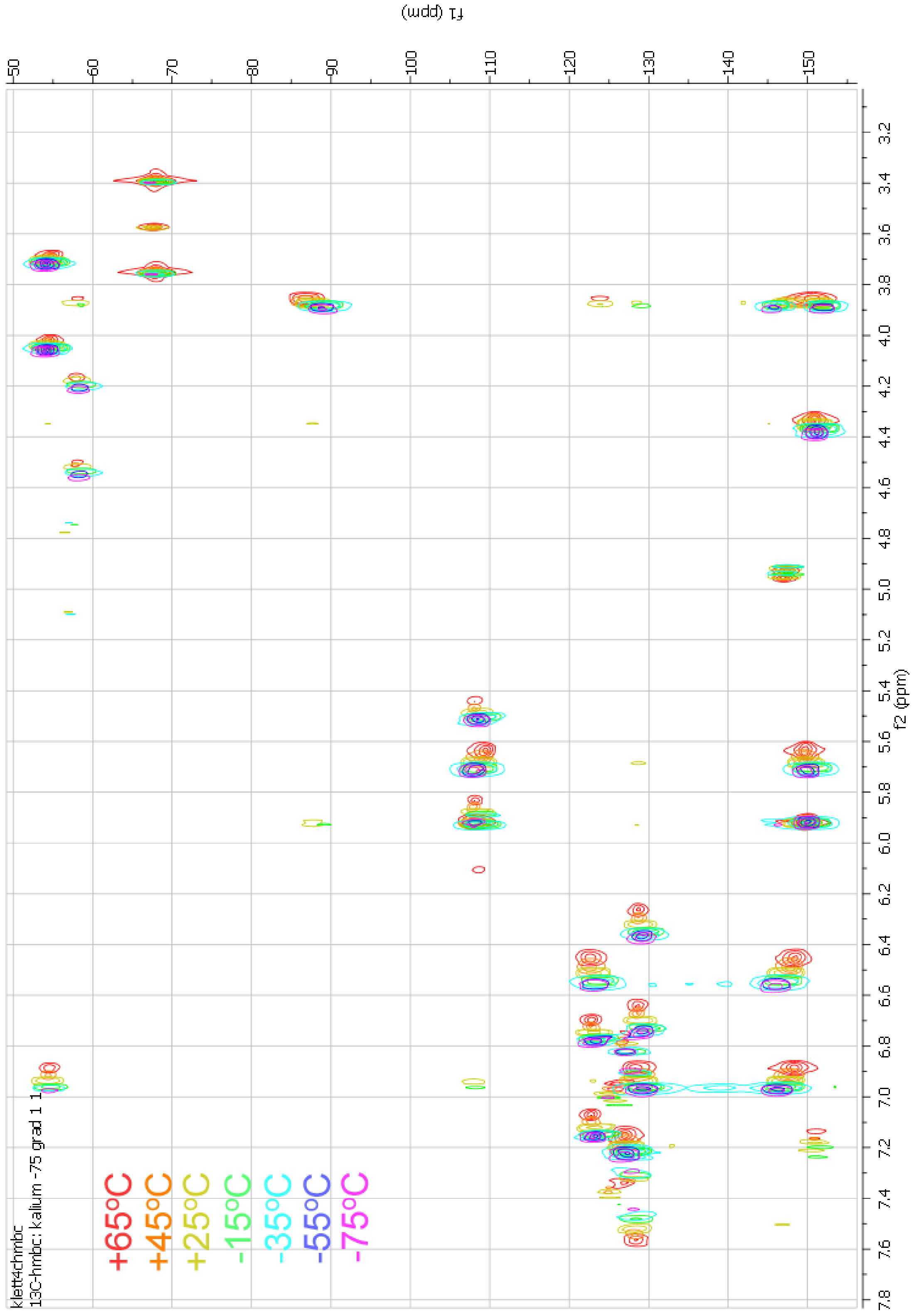


Table 3: ^{1}H NMR spectroscopic data for compound **2** in a temperature range from 65°C to -75°C in [D_8]THF [ppm].

	Temperature [°C]							
Atom	**65**	**45**	**25**	**5**	**-15**	**-35**	**-55**	**-75**
H(1)	4.41	4.41	4.41	4.40	4.37	4.34	4.32	4.31
H(3,4)	4.06	4.05	4.03	3.97	3.89	3.80	3.76	3.75
H(6,21)	6.18	6.17	6.15	6.08	5.98	5.88	5.83	5.82
H(7,20)	6.56	6.55	6.54	6.49	6.43	6.38	6.35	6.35
H(8,19)	5.85	5.84	5.81	5.74	5.64	5.55	5.51	5.50
H(9,18)	6.97	6.96	6.95	6.91	6.86	6.81	6.80	6.79
H(12,15)	6.90	6.90	6.90	6.90	6.89	6.88	6.89	6.90
H(13,14)	7.14	7.14	7.14	7.13	7.12	7.11	7.10	7.11
α-THP	3.54	3.54	3.54	3.54	3.54	3.54	3.31	3.28, 3.81
β-THP	1.50	1.50	1.50	1.50	1.50	1.50	1.49	1.48
γ-THP	1.61	1.61	1.61	1.61	1.61	1.61	-	-

Table 4: ^{1}H NMR spectroscopic data for compound **3** in a temperature range from 65°C to -75°C in [D_8]THF [ppm].

	Temperature [°C]							
Atom	**65**	**45**	**25**	**5**	**-15**	**-35**	**-55**	**-75**
H(1)	4.39	4.38	4.38	4.37	4.36	4.36	4.35	4.34
H(3,4)	3.90	3.89	3.89	3.88	3.88	3.88	3.87	3.86
H(6,21)	5.92	5.92	5.92	5.92	5.92	5.93	5.93	5.92
H(7,20)	6.56	6.55	6.55	6.54	6.53	6.52	6.49	6.46
H(8,19)	5.71	5.71	5.71	5.70	5.70	5.69	5.67	5.64
H(9,18)	6.97	6.97	6.96	6.96	6.95	6.94	6.92	6.89
H(12,15)	7.02	7.02	7.02	7.02	7.02	7.01	6.99	6.97
H(13,14)	7.23	7.22	7.22	7.22	7.21	7.20	7.18	7.16
α-THP	3.54	3.54	3.54	3.54	3.54	-	-	3.28, 3.80
β-THP	1.50	1.50	1.50	1.50	1.50	1.50	1.49	1.50
γ-THP	1.61	1.61	1.60	1.60	1.60	1.60	-	1.59

Table 5: ^{13}C NMR spectroscopic data for compound **2** in a temperature range from 65°C to -75°C in [D_8]THF [ppm] (taken from $^{1}H/^{13}C$ HMBC NMR).

	Temperature [°C]							
Atom	**65**	**45**	**25**	**5**	**-15**	**-35**	**-55**	**-75**
C(1)	57.2	58.1	58.1	58.2	58.2	58.6	58.4	58.3
C(2)	79.3	80.1	80.7	82.3	85.1	87.9	88.9	89.0
C(3,4)	55.7	55.7	55.5	55.5	54.9	54.6	54.2	54.4
C(5,22)	148.9	148.9	149.0	149.1	149.2	149.5	149.5	149.8
C(6,21)	110.6	110.8	110.9	110.6	109.9	109.5	109.5	109.3
C(7,20)	128.3	128.6	128.4	128.3	128.1	128.1	128.0	128.1
C(8,19)	110.9	110.3	110.1	109.6	108.1	107.1	106.2	106.6
C(9,18)	124.1	123.3	123.1	123.1	122.5	122.1	122.0	121.9
C(10,17)	151.8	151.4	151.2	150.9	149.6	148.7	148.3	148.0
C(11,16)	149.8	150.5	150.7	151.0	151.1	151.0	151.2	151.1

Table 6: ^{13}C NMR spectroscopic data for compound **3** in a temperature range from 65°C to -75°C in [D_8]THF [ppm] (taken from $^{1}H/^{13}C$ HMBC NMR).

	Temperature [°C]							
Atom	**65**	**45**	**25**	**5**	**-15**	**-35**	**-55**	**-75**
C(1)	58.3	58.3	59.0	58.5	58.5	58.1	57.8	58.0
C(2)	88.9	88.8	89.1	89.1	88.9	87.7	86.9	86.8
C(3,4)	53.9	54.3	54.7	54.6	54.5	54.3	54.3	54.7
C(5,22)	149.8	150.0	150.5	150.5	149.9	149.7	149.5	149.6
C(6,21)	108.4	108.5	108.8	109.0	108.8	108.5	108.8	109.5
C(7,20)	129.2	129.3	129.4	129.6	129.2	128.8	128.7	128.7
C(8,19)	107.8	108.1	108.6	109.0	108.8	108.4	108.1	108.0
C(9,18)	123.0	123.4	123.7	123.8	123.6	123.1	122.6	122.7
C(10,17)	146.1	146.1	146.1	147.0	147.1	147.2	147.7	148.3
C(11,16)	151.0	151.1	151.6	151.6	151.1	150.9	150.8	150.7

Figure 12: ^{1}H NMR spectroscopic data for compound **2** in a temperature range from 65°C to -75°C in [D_8]THF [ppm].

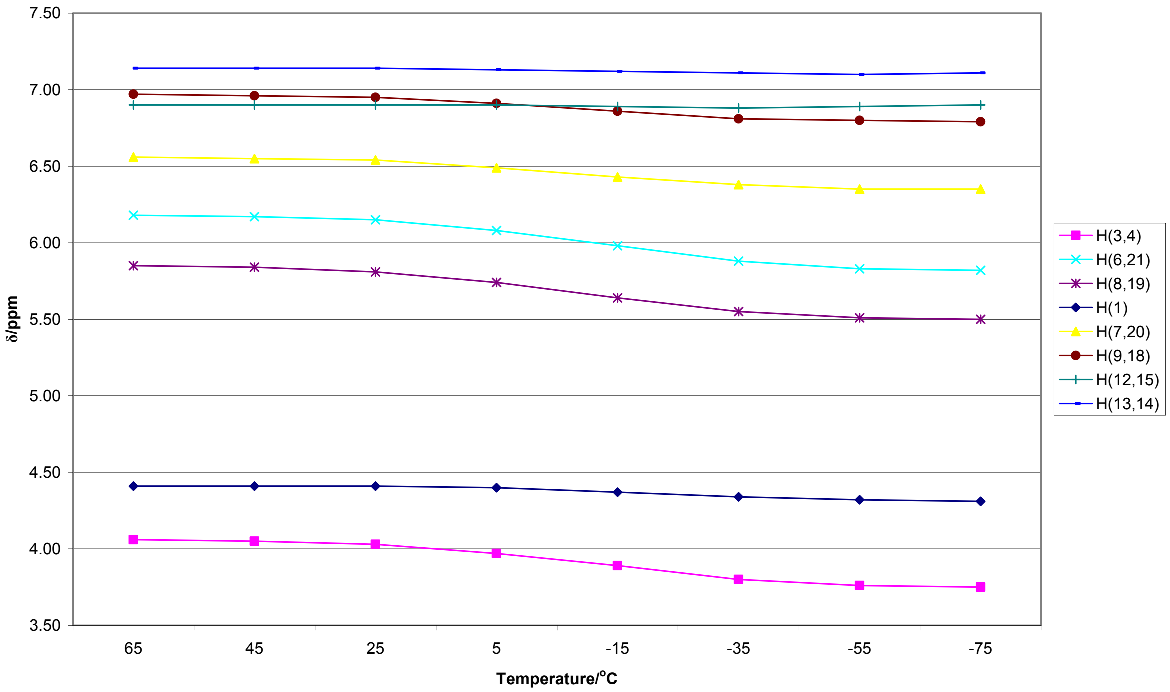


Figure 13: ^{1}H NMR spectroscopic data for compound **3** in a temperature range from 65°C to -75°C in [D_8]THF [ppm].

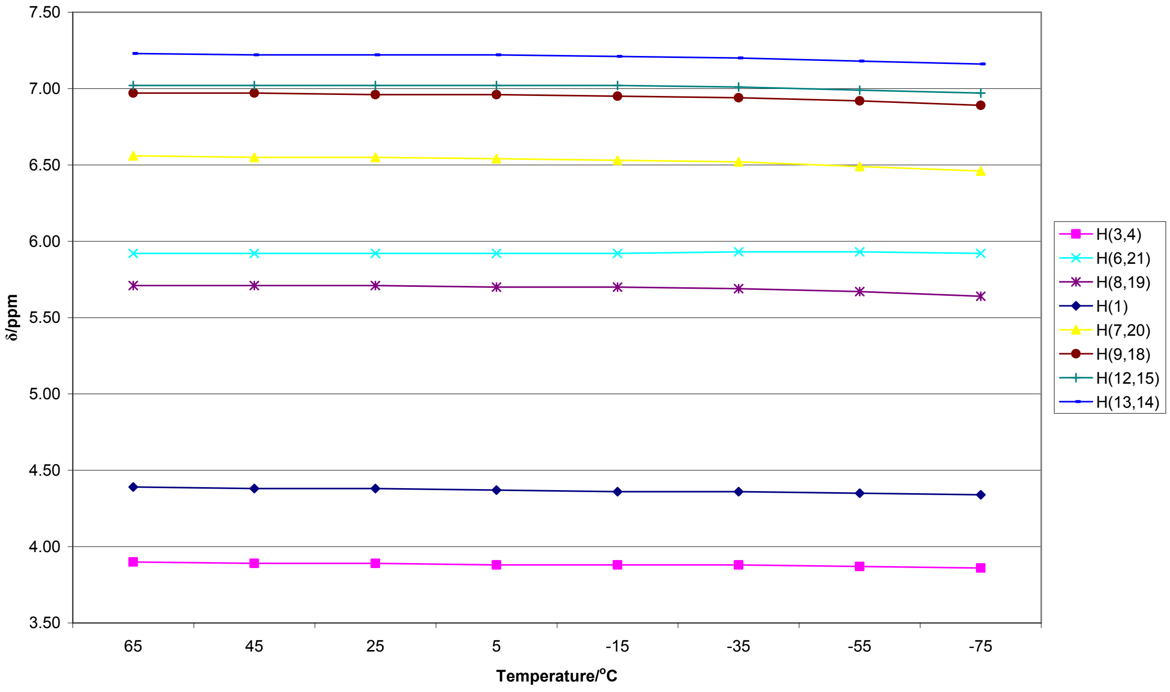


Figure 14: ^{13}C NMR spectroscopic data for compound **2** in a temperature range from 65°C to -75°C in [D$_8$]THF [ppm] (taken from ^{1}H/^{13}C HMBC NMR).

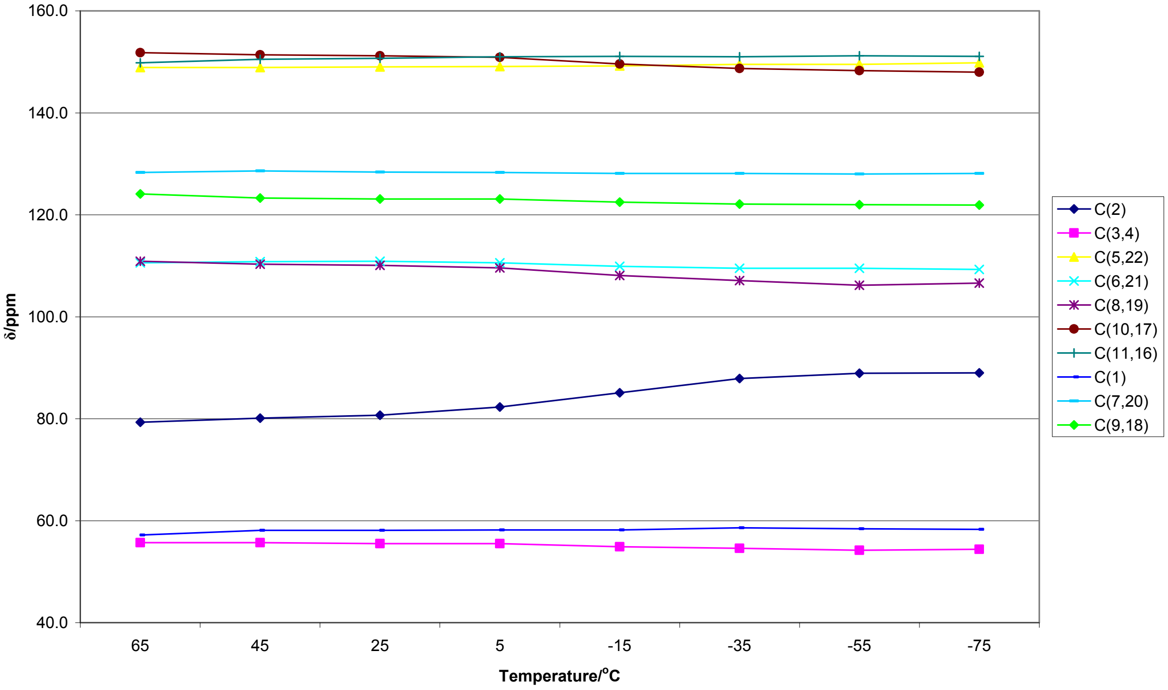
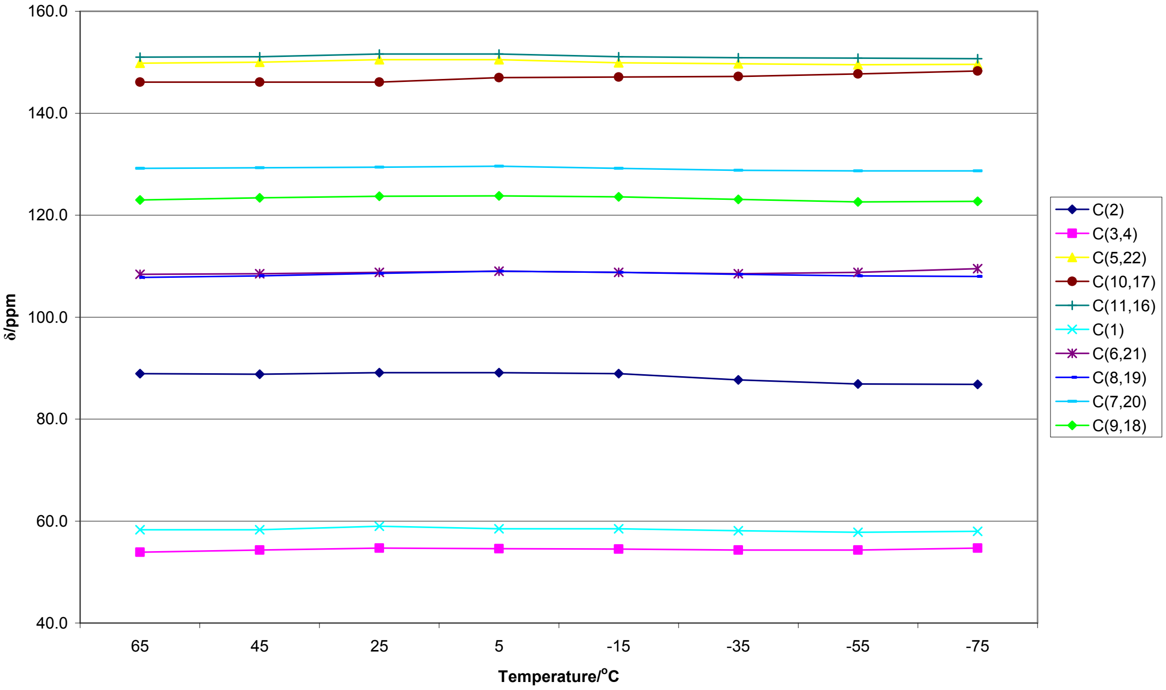


Figure 15: ^{13}C NMR spectroscopic data for compound **3** in a temperature range from 65°C to -75°C in [D$_8$]THF [ppm] (taken from ^{1}H/^{13}C HMBC NMR).



Computational Details

All structures were optimised at the B3LYP level of theory, the basis set used was 6-31G*. Geometry optimizations without constraints were carried out with standard procedures based on analytical energy gradients. Frequency calculations were performed to characterise the optimized structures as minima. All calculations were performed within the Gaussian 03 package.[5] The models were based on the observed structures of **2** and **3**, and the corresponding metal atom was placed in the original position, respectively. Energies are used with zero-point corrections.

Figure 16: Electronic Energies for Optimized Structures

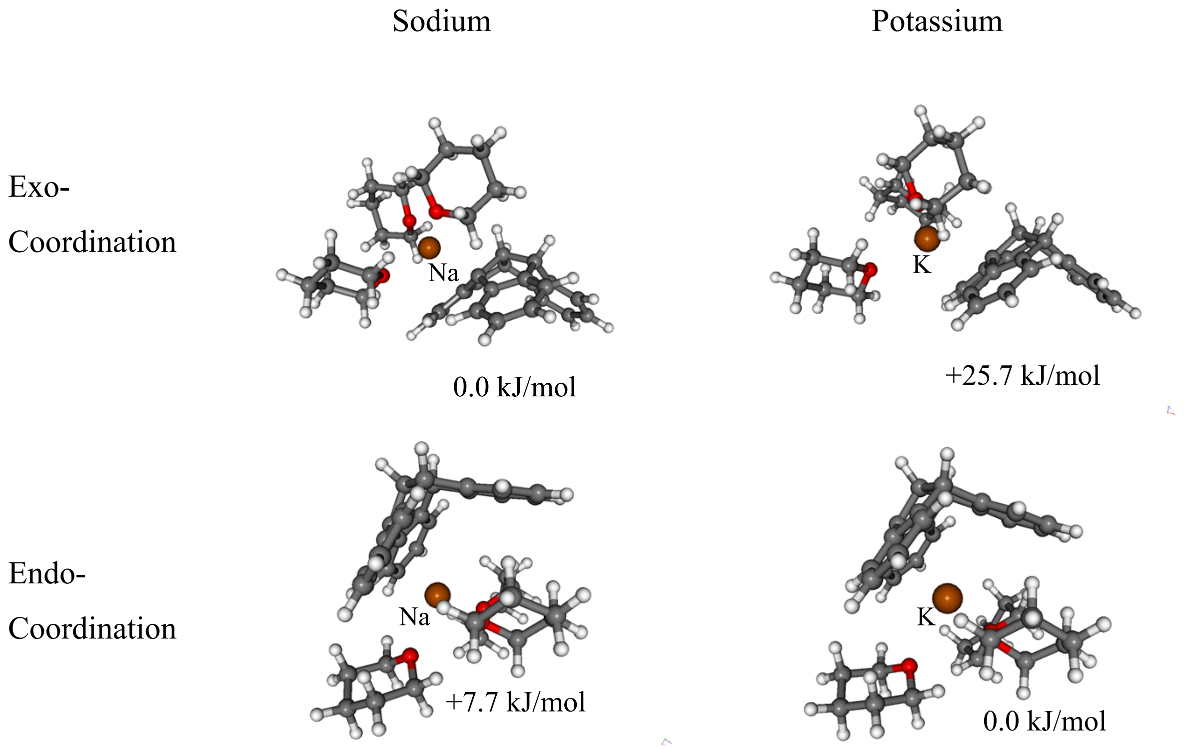


Table 7: Absolute and relative energies for exo- or endo-coordinated of sodium or potassium tribenzotriquinacene.

Coordination	absolute energy (zero-point) [Hartree/Particle]	relative energy [Hartree/Particle]	relative energy [kcal/mol]	relative energy [kJ/mol]
Na-Exo	-1824.302829	0.0000000	0.00	0.00
Na-Endo	-1824.299915	+0.0029140	+1.83	+7.65
K-Exo	-2261.906346	+0.0097810	+6.14	+25.68
Na-Endo	-2261.916127	0.0000000	0.00	0.00

References

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