Supporting Information

Chelated Fischer carbene complexes of annulated thiophenes: synthesis, structure and electrochemistry

Zandria Lamprecht,[a] Frederick P. Malan,[a] Israel Fernández,[b] Simon Lotz,[a] and Daniela I. Bezuidenhout*[c]

[a] *Department of Chemistry, University of Pretoria, Private Bag X20, Hatfield 0028, Pretoria, South Africa*
[b] *Departamento de Química Orgánica I and Centro de Innovación en Química Avanzada (ORFEO-CINQA), Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040, Madrid, Spain*
[c] *Laboratory of Inorganic Chemistry, Environmental and Chemical Engineering, University of Oulu, P. O. Box 3000, 90014 Oulu, Finland*
*Email: daniela.bezuidenhout@oulu.fi

Table of Contents

S1. Complex synthesis details

By-products and unreacted starting materials not isolated, were quantified based on yields estimated from the NMR spectra of the reaction mixtures.

Table S1. Yields and colours of complex products obtained from the reaction of chromium carbonyl

Compound	Name	Mass (g)	Yield (%)	Colour
***trans*-TT**	$C_6H_4S_2$		< 3	White
Butyl carbene[1]	$[Cr(CO)_5\{C(OEt)C_4H_9\}]$		< 3	Yellow
1	$[Cr(CO)_4\{C(OEt)\}_2\text{-}5,4\text{-}C_6H_2S_2]$	0.25	24	Blue
2	$[Cr(CO)_4\{C(OEt)\}_2\text{-}5,4\text{-}C_6S_2\text{-}5'\text{-}C_4H_9\text{-}4'\text{-}Br]$	0.25	18	Blue
3	$[\{Cr(CO)_4[C(OEt)]_2\}_2\text{-}5,4,5',4'\text{-}C_6S_2]$	0.48	28	Green
4	$[Cr(CO)_4\{C(OEt)\}_2\text{-}5,4\text{-}C_6HS_2\text{-}5'\text{-}C(OEt)Cr(CO)_5]$	0.03	2	Green

Table S2. Yields and colours of complex products obtained from the reaction of tungsten carbonyl

Compound	Name	Mass (g)	Yield (%)	Colour
Butyl carbene[2]	$[W(CO)_5\{C(OEt)C_4H_9\}]$	0.28	13	Yellow
5	$[W(CO)_4\{C(OEt)\}_2\text{-}5,4\text{-}C_6H_2S_2]$	0.36	26	Blue
6	$[W(CO)_4\{C(OEt)\}_2\text{-}5,4\text{-}C_6H_{0/1}S_2\text{-}5'\text{-}C_4H_9\text{-}4'\text{-}H/Br]$	0.22/0.25	15	Blue
7	$[W(CO)_4\{C(OEt)\}_2\text{-}5,4\text{-}C_6S_2\text{-}5'\text{-}OEt\text{-}4'\text{-}C\{CH_2CH_3\}_2C(OEt)\{W(CO)_5\}]$	0.22	8	Green
8	$[\{W(CO)_4[C(OEt)]_2\}_2\text{-}5,4,5',4'\text{-}C_6S_2]$	0.36	15	Green

Table S3: Yields and colours of complex products obtained from the reaction of chromium carbonyl

Compound	Name	Mass (g)	Yield (%)	Colour
Butyl carbene[1]	$[Cr(CO)_5\{C(OEt)C_4H_9\}]$	0.32	21	Yellow
9	$[Cr(CO)_4\{C(OEt)\}_2\text{-}5,4\text{-}C_8H_2S_3]$	0.04	3	Blue
10[3]	$[\{Cr(CO)_5C(OEt)\}_2\text{-}5,5'\text{-}C_8H_2S_3]$	0.03	2	Purple
11	$[\{Cr(CO)_4[C(OEt)]_2\}_2\text{-}5,4,5',4'\text{-}C_8S_3]$	0.80	43	Green

Table S4: Yields and colours of complex products obtained from the two reactions tungsten carbonyl.

Compound	Name	Mass (g)	Yield (%)	Colour
Butyl carbene[2]	$[W(CO)_5\{C(OEt)C_4H_9\}]$	0.35	16	Yellow
***trans*-DTT**	$C_8H_4S_3$		< 3	White
12	$[W(CO)_4\{C(OEt)\}_2\text{-}5,4\text{-}C_8H_2S_3]$	0.03	2	Turquoise
13[3]	$[\{W(CO)_5C(OEt)\}_2\text{-}5,5'\text{-}C_8H_2S_3]$	0.10	4	Purple
14	$[W(CO)_4\{C(OEt)\}_2\text{-}5,4\text{-}C_8H_{0/1}S_3\text{-}5'\text{-}C_4H_9\text{-}4'\text{-}H/Br]$	0.02/0.02	1	Blue

15	$[W(CO)_4\{C(OEt)\}_2$-5,4-$C_8H_1S_3$-5'-$C(OEt)W(CO)_5]$	0.10	4	Purple
16	$[\{W(CO)_4[C(OEt)]_2\}_2$-5,4,5',4'-$C_8S_3]$	1.29	51	Green

Table S5. Yields and colours of complex products obtained from the reaction of tungsten carbonyl.

Compound	Name	Mass (g)	Yield (%)	Colour
Butyl carbene[2]	$[W(CO)_5\{C(OEt)C_4H_9\}]$		< 3	Yellow
17	$[\{W(CO)_4[C(OEt)]_2\}_2$-5,4,5',4'-$C_8S_3]$	0.33	13	Blue

S2. ^{1}H and ^{13}C NMR spectra

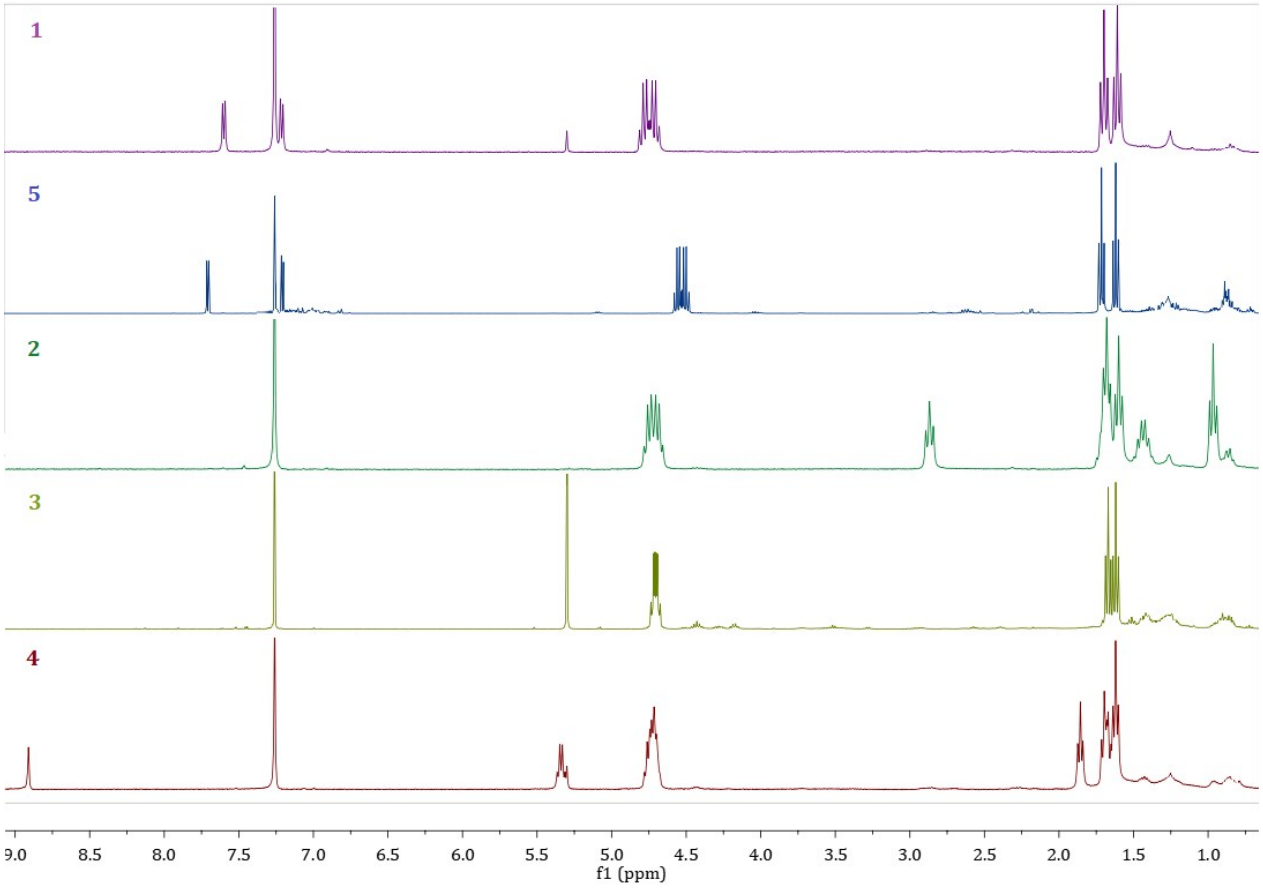

Figure S1. ^{1}H NMR spectra of **1–5** in $CDCl_3$

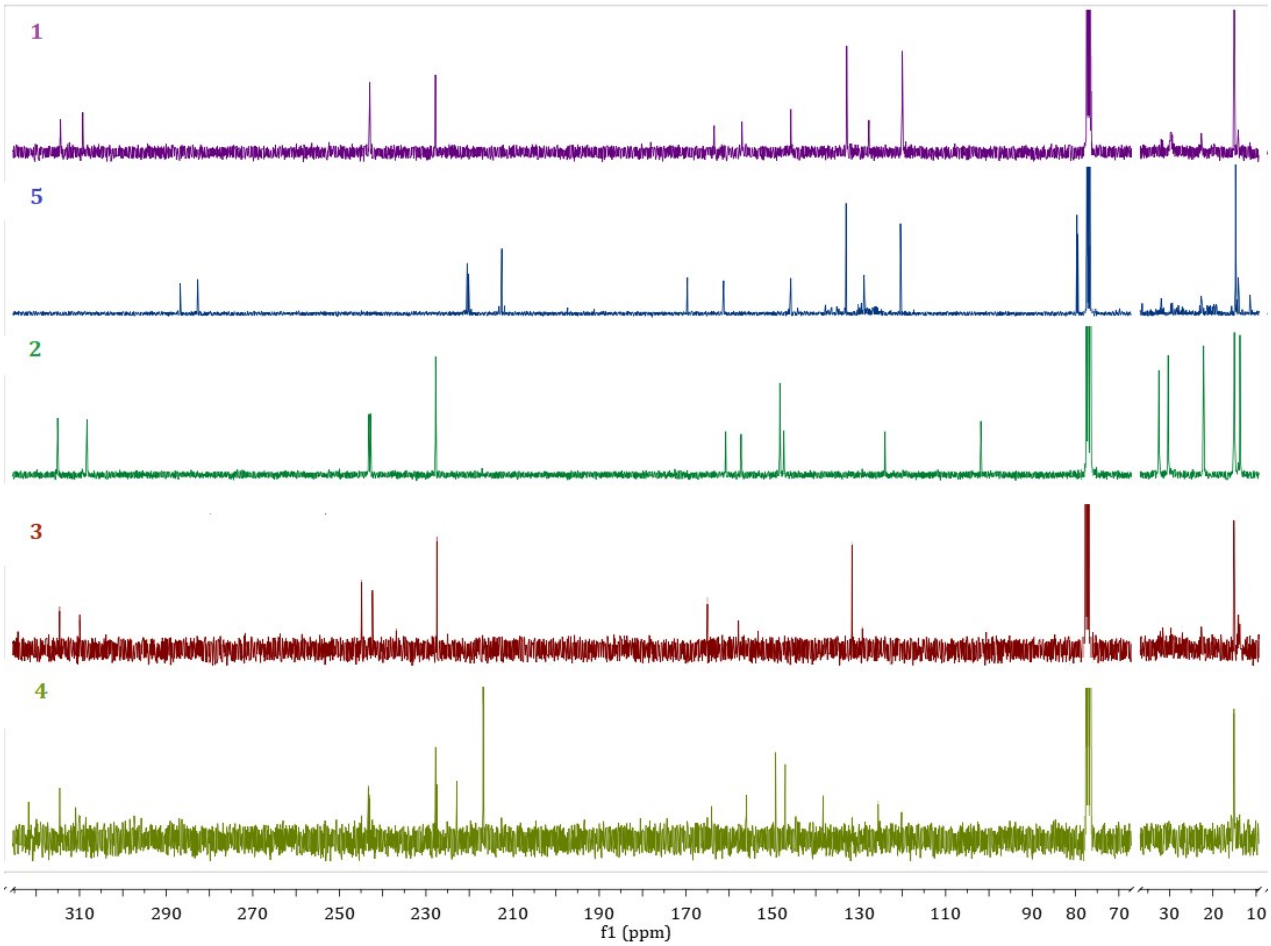

Figure S2. ^{13}C NMR spectra showing chemical shift patterns for **1–5** in $CDCl_3$

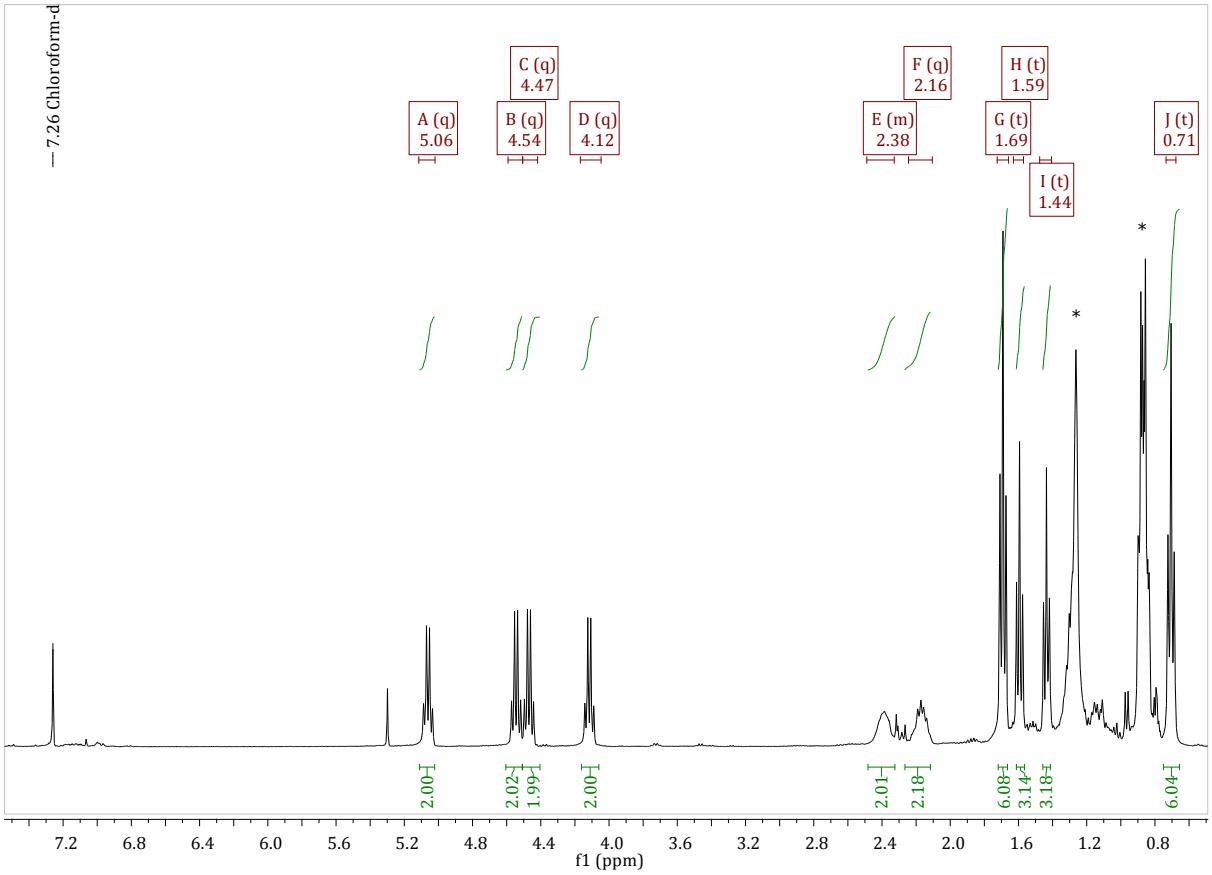

Figure S3. ^{1}H NMR spectrum of **7** in $CDCl_3$. *Residual hexane

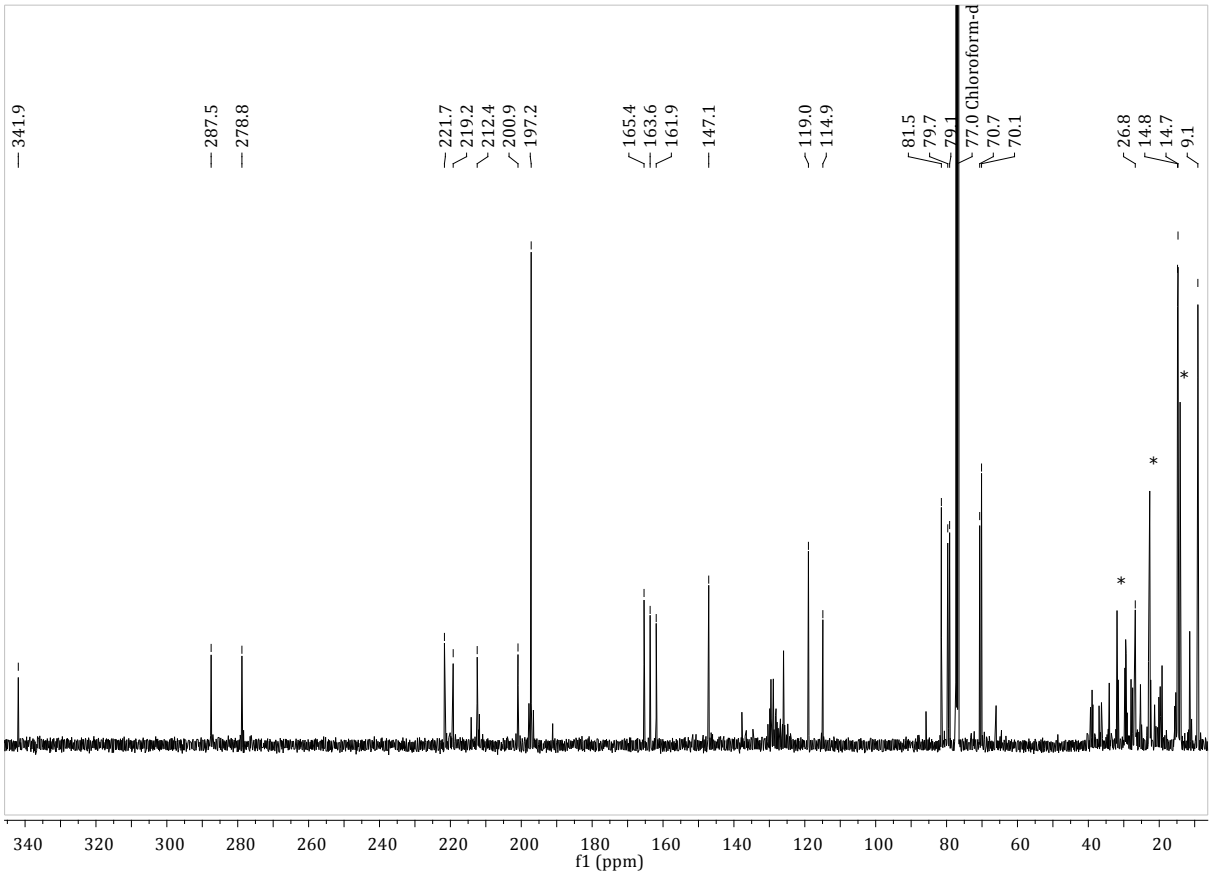

Figure S4. ^{13}C NMR spectrum of **7** in $CDCl_3$. *Residual hexane

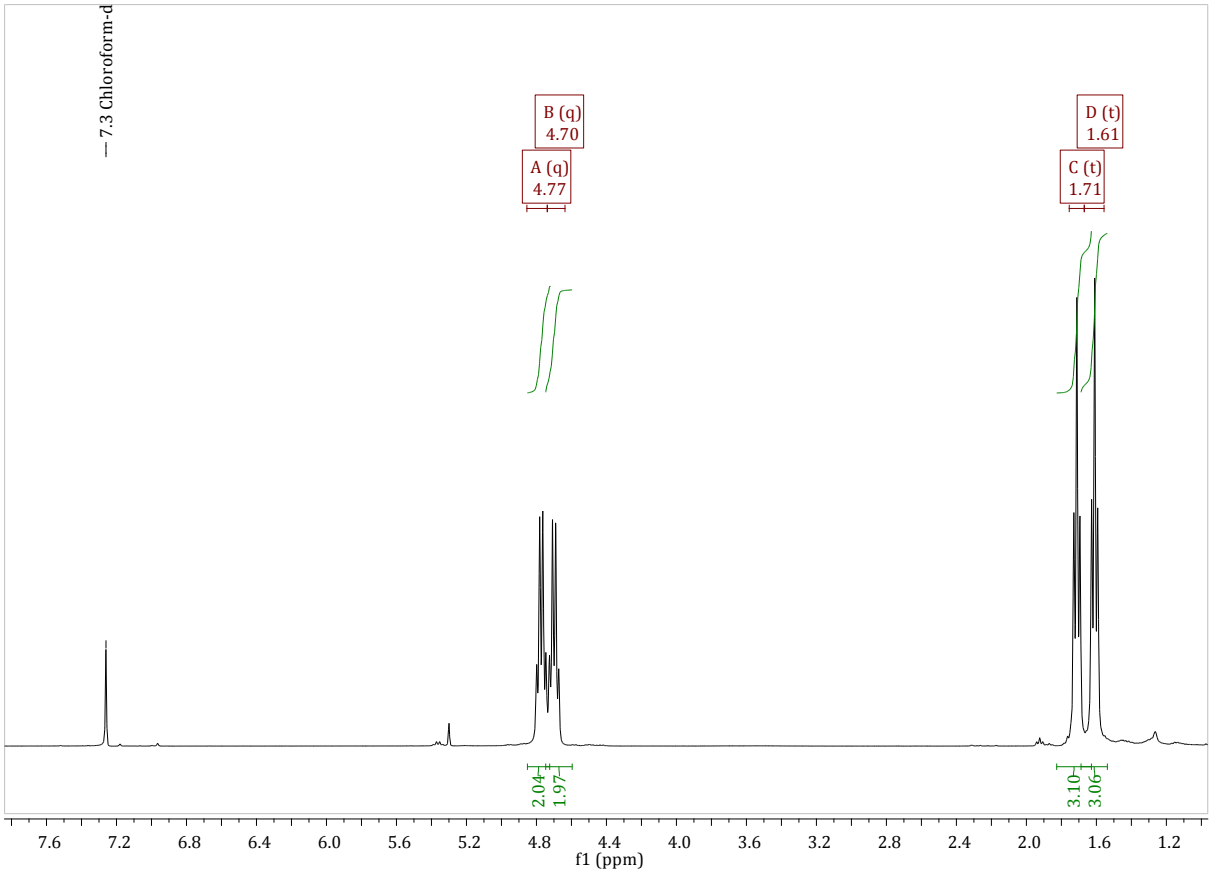

Figure S5. ^{1}H NMR spectrum of **11** in CD_2Cl_2

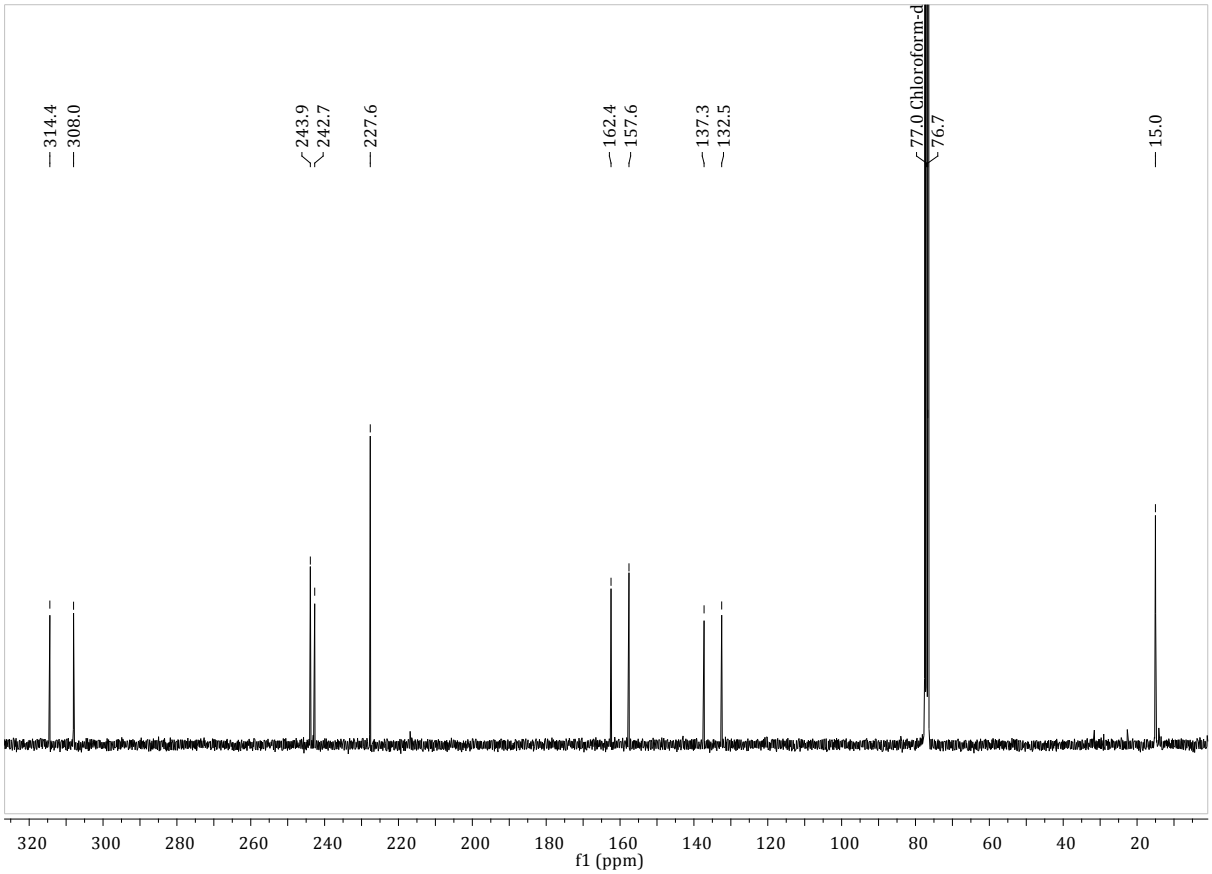

Figure S6. ^{13}C NMR spectrum of **11** in CD_2Cl_2

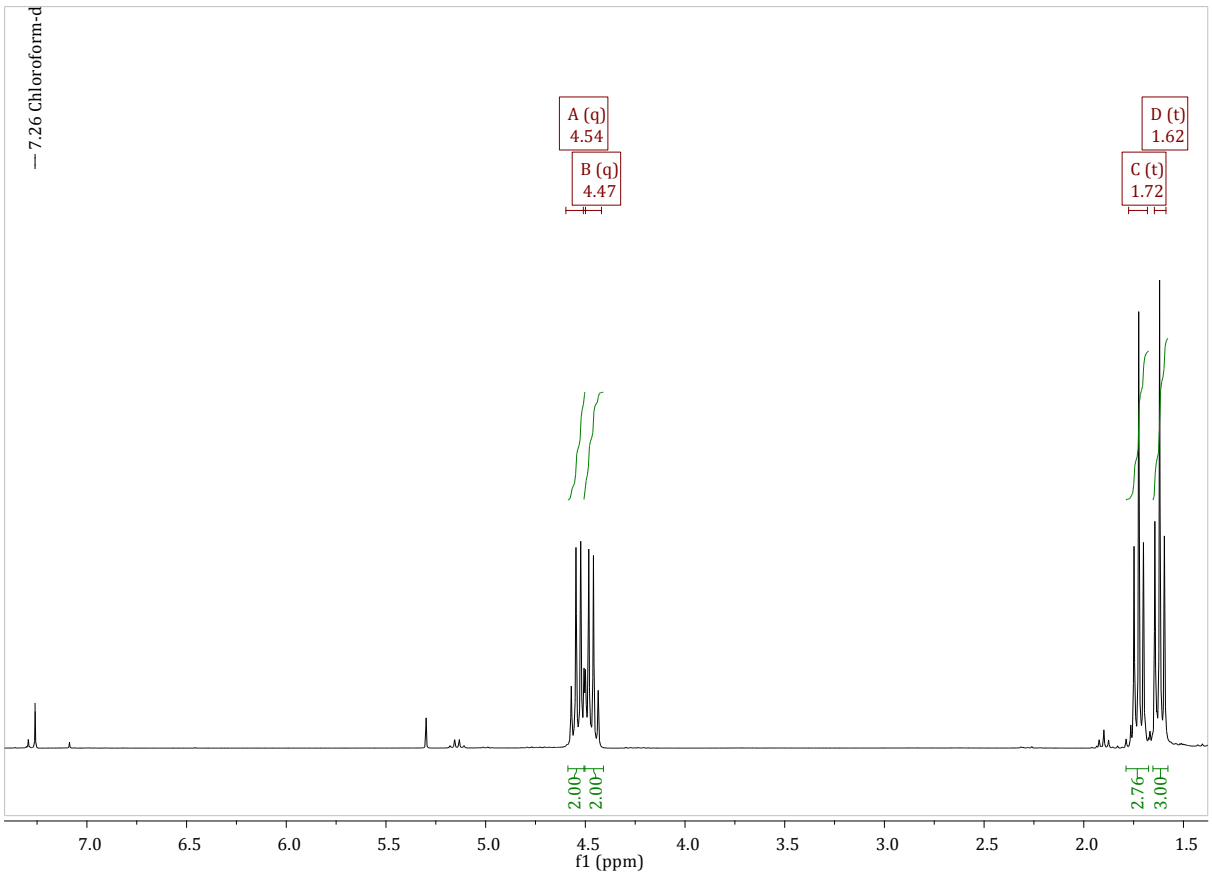

Figure S7. ^{1}H NMR spectrum of **16** in CD_2Cl_2

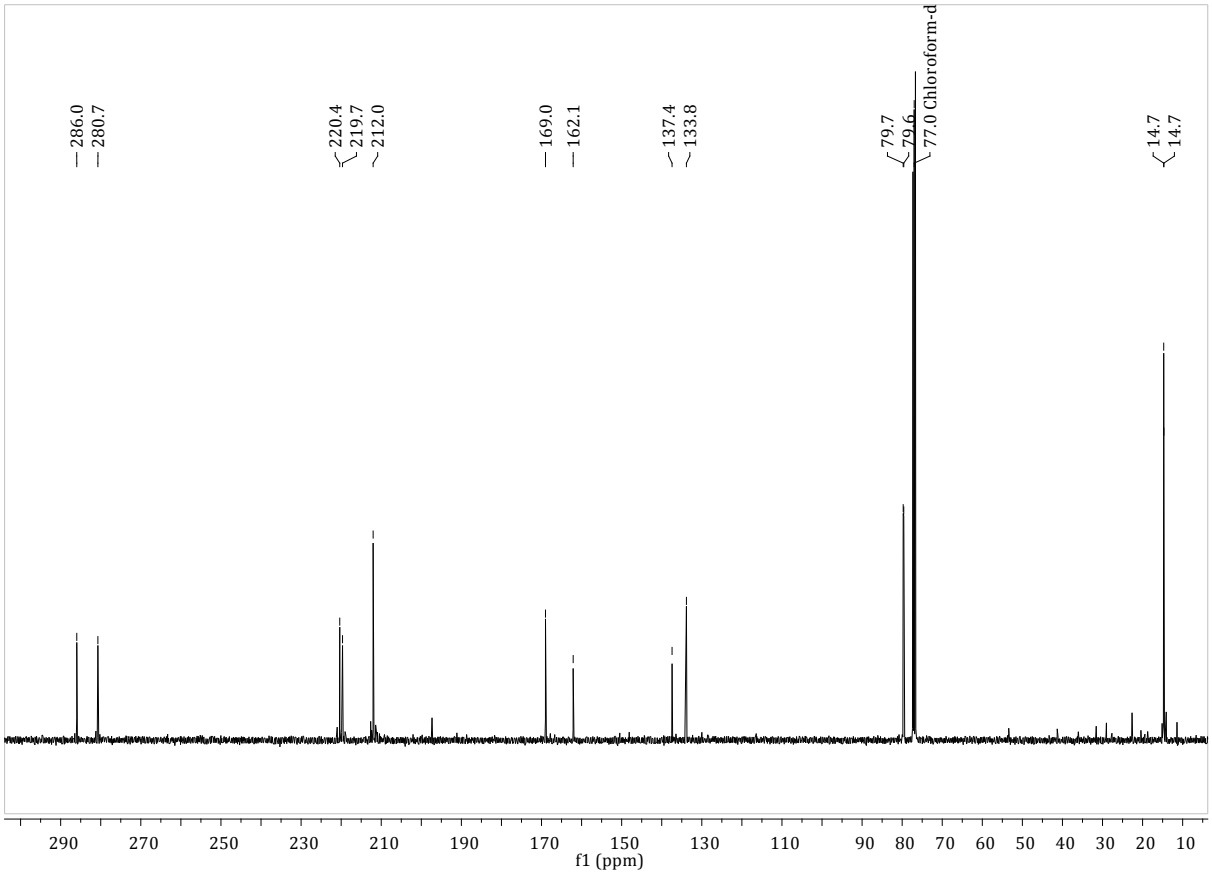

Figure S8. ^{13}C NMR spectrum of **16** in CD_2Cl_2

S3. 2D NMR spectroscopy

Compounds **2** and **7** are chosen as examples for the elucidation of the NMR resonance assignments of chelated carbene complexes, by considering their 2D NMR spectra. The composition of these two multifaceted molecular structures are clarified by 2D NMR spectra and confirmed by XRD studies (*vide infra*). Assignments of proton resonances could not be made by taking into account coupling constants of chemical shifts, as the majority of *J*-values are around 7 Hz.

The typical coupling of methylene and methyl proton resonances, of the ethoxy fragments on the metallacyclic biscarbene component (C7Et and C6Et), is presented in the [^{1}H, ^{1}H] COSY NMR spectrum of **2** (Figure S9(a)). Coupling of the most downfield methylene and methyl resonances occur, along with the coupling of the most upfield methylene and methyl signals. These assignments extrapolate to all the compounds in this chapter. The sequence of proton resonances for the C5'Bu fragment of **2** could also be determined with COSY NMR spectrum. The Bu resonances are labelled as $C(1)H_2C(2)H_2C(3)H_2C(4)H_3$ and resonate in the same sequence from most downfield (green, Figure S9(a)).

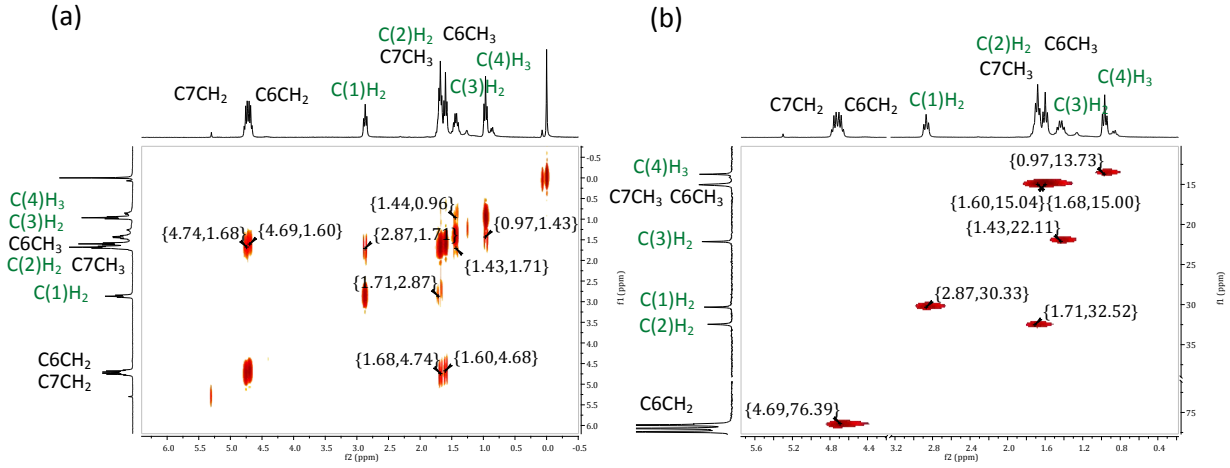

Figure S9. 2D [^{1}H, ^{1}H] COSY (a) and 2D [^{1}H, ^{13}C] HSQC NMR spectra (b) of **2**

Carbon signal assignments are done using [^{1}H, ^{13}C] HSQC (Figure S9 (b)) and [^{1}H, ^{13}C] HMBC NMR spectra (Figure S10). Only one signal is observed for the methylene resonances of the ethoxy fragments of **2**, as the second methylene resonance overlap with the solvent peak. The two methyl resonances, of the ethoxy fragments, resonate so close together that they have the same carbon chemical shifts. This tendency of the methylene and methyl signals is recurrent in chelated carbene complexes. The order of Bu carbon resonances is determined as $C(2)H_2 > C(1)H_2 > C(3)H_2 > C(4)H_3$ from most downfield (green, Figure S9 (b) and Figure S10). The quaternary carbons, C4' and C5', of **2** could be assigned using a HMBC NMR spectrum (Figure S10).

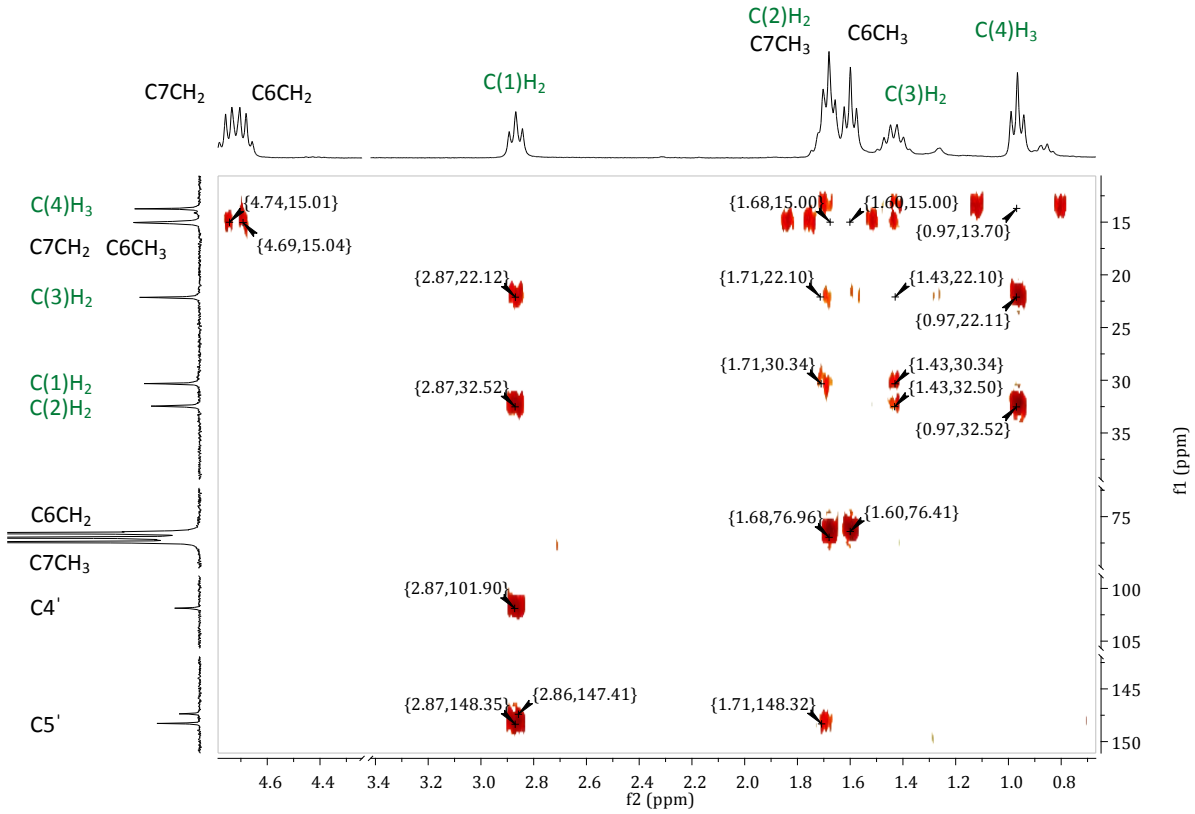

Figure S10. 2D [^{1}H, ^{13}C] HMBC NMR spectrum of **2**

Compound **7** has four ethoxy groups (C6'OEt, C7OEt, C6OEt and C5'OEt) and two ethyl fragments (C4'CEt_2) present in the molecule. Concerning the C6' fragment of **7**, the most downfield methylene and methyl proton signals coupling in the COSY NMR spectrum (Figure S11), belong to C6'OEt. The carbon methylene signal is most downfield of the ethoxy signals (Figure S12). The HSQC NMR spectrum shows the four ethoxy fragments to resonate as two methyl carbon resonances, with two fragments' signals overlapping in each resonance. In the case of C6'OEt, the methyl signal resonates as the more upfield chemical shift of the two methyl signals. From the HMBC NMR spectrum (Figure S13) the C6' carbene carbon is determined as the most downfield resonance in the ^{13}C NMR spectrum. The coupling of the C6' methylene signal to C4'*C*$(Et)_2$ confirms the connectivity of the fragment present at the C4' position as: C4'$C(Et)_2$C6'$(W(CO)_5)$OEt.

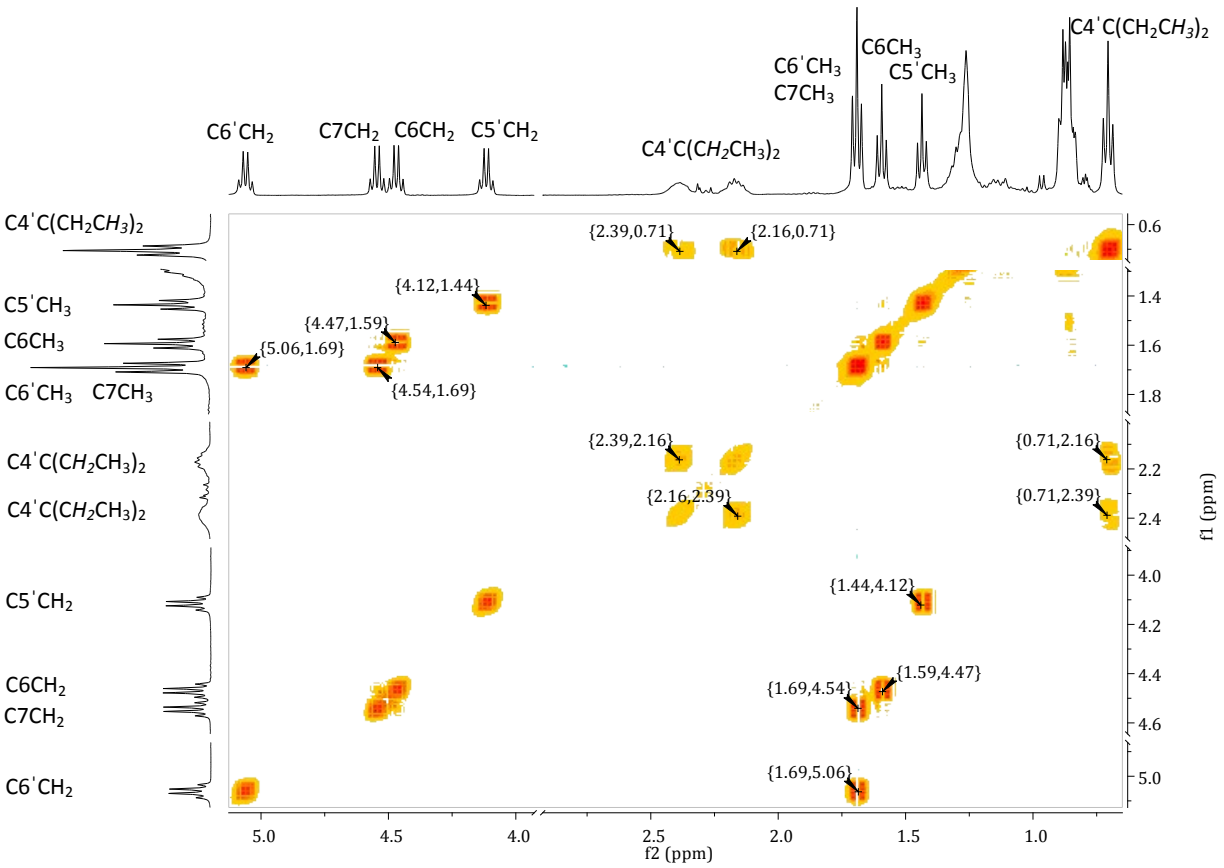

Figure S11. 2D [^{1}H, ^{1}H] COSY NMR spectrum of **7**

Concerning the C4'CEt$_2$ fragment of **7**, the methylene proton signals resonate as two broad resonances upfield from all the methylene signals and couple to the most upfield methyl signal (single signal representing both methyl groups, Figure S11). The carbon signals for the two ethyl groups are determined as a single methylene (broad) and methyl peak (HSQC NMR spectrum, Figure S12), upfield from the other methylene and methyl signals. Coupling of the more upfield methylene proton signal and the methyl signal to C4'*C*(Et)$_2$, along with the coupling of the former with the carbene carbon C6', endorse the fragment at C4' as C4'C(Et)$_2$C6'(W(CO)$_5$)OEt (HMBC NMR spectrum Figure S13).

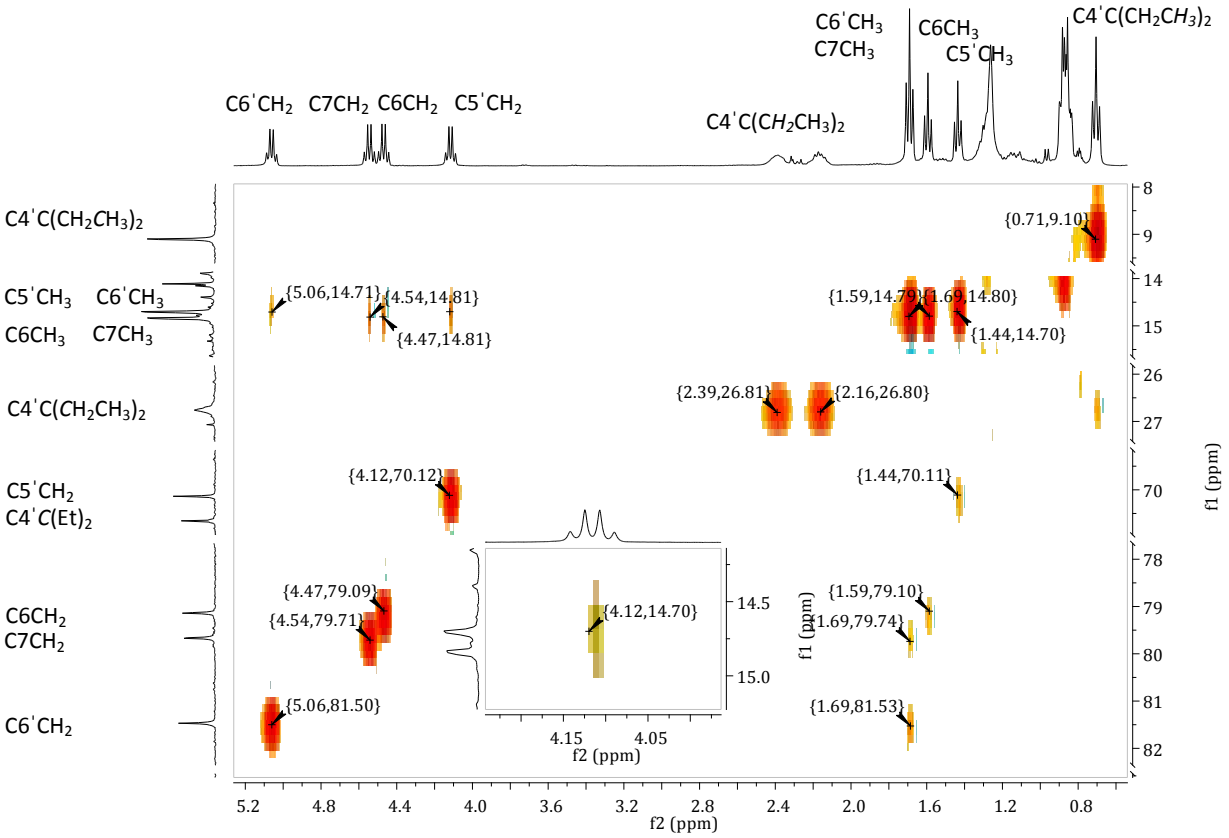

Figure S12. 2D [^{1}H, ^{13}C] HSQC NMR spectrum of **7**

Ethoxy fragments on the metallacyclic biscarbene component (C7Et and C6Et) of **7**, couple by means of the more downfield methylene proton resonance with the more downfield methyl shift (C7Et). The C7 and C6' methyl proton signals overlap (COSY NMR spectrum, Figure S11). The more upfield methylene and methyl proton shifts couple, representing the C6Et fragment. From the HSQC NMR spectrum (Figure S12), it is clear that the C7 methylene carbon signal is more downfield compared to the C6 methylene resonance. The C7 and C6 methyl carbon resonances resonate so close together that they appear as one signal. The carbon chemical shifts of the quaternary carbons, C4, C5, C6 and C7 of **7**, could be assigned using the HMBC NMR spectrum (Figure S13). From their assignment it is clear that the resonance of the carbene carbon C7 > C6 and the quaternary aromatic carbon C5 > C4. Coupling of the C7 methylene proton resonance to C4 and C7 leads to the observation that the C7 ethoxy fragment is on the C4 position, remote from the sulphur atom in *trans*-TT. The C6 ethoxy fragment is on the C5 position (next to the sulphur atom in *trans*-TT), as concluded from the coupling of the C6 methylene proton resonance to C5 and C6.

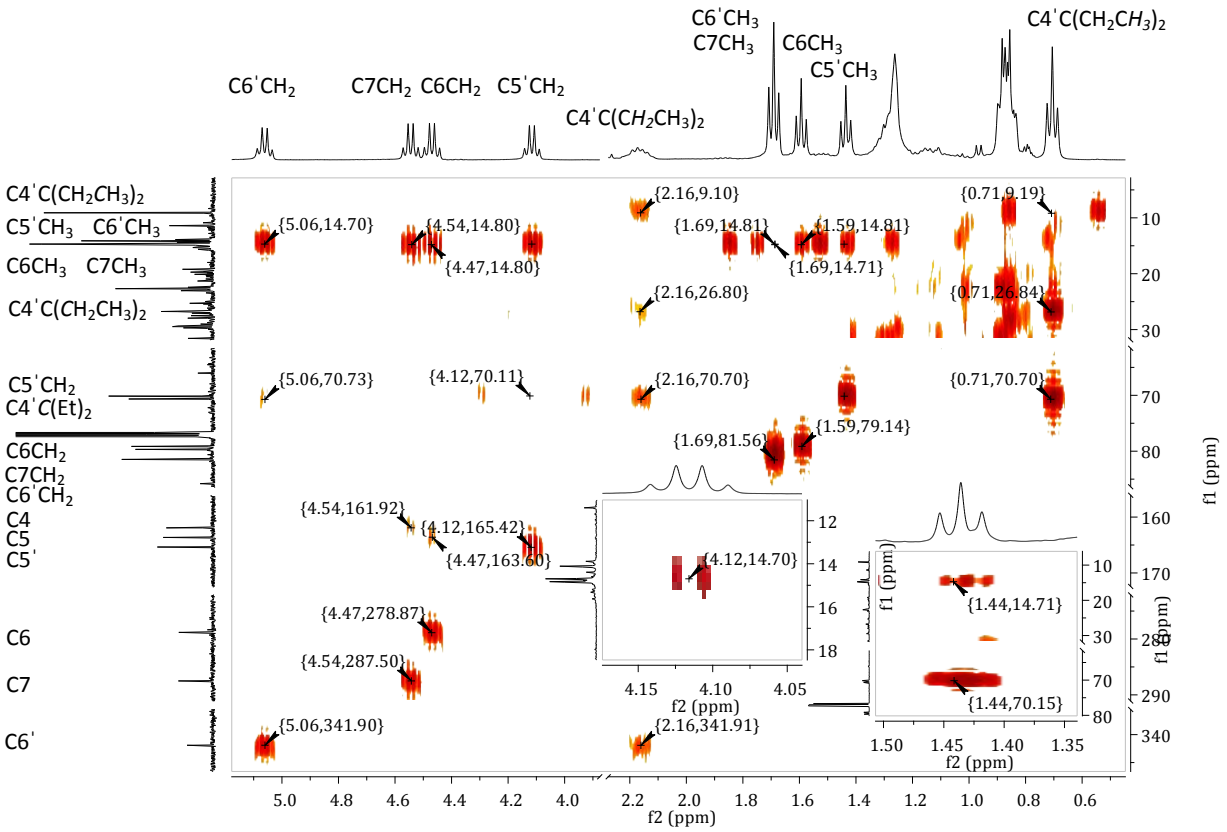

Figure S13. 2D [^{1}H, ^{13}C] HMBC NMR spectrum of **7**

Concerning the C5'OEt fragment of **7**, the methylene and methyl proton signals resonate the most upfield of the ethoxy signals (COSY NMR spectrum, Figure S11). The carbon signals for the C5'OEt groups are determined as a methylene and methyl peak, upfield compare to the other ethoxy groups' signals (HSQC NMR spectrum, Figure S12). The C5' and C6' methyl carbon signals overlap. Coupling of the C5' methylene proton signal to C5', assisted with assigning the most downfield quaternary aromatic carbon as C5' (HMBC NMR spectrum Figure S13).

S4. FT-IR spectroscopy

Table S6. IR data of compounds measured in hexane

Compound	ν_{CO} $M(CO)_4$, cm^{-1}				ν_{CO} $M(CO)_5$, cm^{-1}		
	$A_1^{(1)}$ (*m*)	B_1 (*s*)	$A_1^{(2)}$ (*m*)	B_2 (*m*)	$A_1^{(1)}$ (*m*)	B_1 (*vw*)	E and $A_1^{(2)}$ (*s*)
1	2017	1962	1947	1895			
2	2018	1962	1947	1896			
3	2018	1962	1947	1895			
3[a]	2010	1959	1938	1884			
5	2026	1955	1942	1889			
7	2024	1950	1940 (*s*)[b]	1884	2066	1983, 1976	1940[b]
7[a]	2019	1938	1927 (*s*)[b]	1862	2064	1972	1927[b]
11	2015	1968	1949	1901			
16	2023	1961	1946	1894			

[a] Sample measured in DCM. [b] Overlapping bands.

S5. Crystal data collection and structure refinement parameters

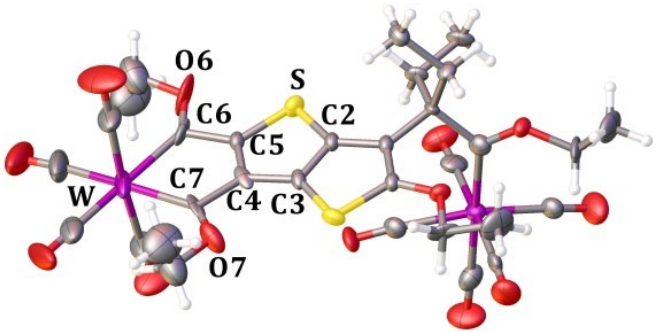

Figure S14. The molecular structure of **7** with atomic displacement ellipsoids shown at the 50% probability level.

Compound **11** has two molecules in the unit cell, with disorder of one of the C7OEt groups in each molecule, along with two benzene molecules (see CIF file). In the case of **16** the molecule is accompanied by one and a half benzene molecules in the unit cell.

Compound 1: $C_{16}H_{12}CrO_6S_2$ (*M* =416.38 g/mol): triclinic, space group P-1 (no. 2), *a* = 7.4276(4) Å, *b* = 10.7016(6) Å, *c* = 12.2391(6) Å, *α* = 74.238(2)°, *β* = 75.469(2)°, *γ* = 71.410(2)°, *V* = 872.91(8) Å^3, *Z* = 2, *T* = 150(2) K, μ(MoKα) = 0.923 mm^{-1}, *Dcalc* = 1.584 g/cm^3, 25511 reflections measured (4.816° ≤ 2Θ ≤ 52.744°), 3567 unique (R_{int} = 0.0311, R_{sigma} = 0.0202) which were used in all calculations. The final R_1 was 0.0235 (I > 2σ(I)) and wR_2 was 0.0608 (all data). CCDC 2032755

Compound 2: $C_{20}H_{19}BrCrO_6S_2$ (*M* =551.38 g/mol): triclinic, space group P-1 (no. 2), *a* = 7.5092(2) Å, *b* = 10.8694(3) Å, *c* = 15.5717(3) Å, *α* = 100.253(2)°, *β* = 102.100(2)°, *γ* = 108.802(3)°, *V* = 1134.26(5) Å^3, *Z* = 2, *T* = 293(2) K, μ(CuKα) = 8.230 mm^{-1}, *Dcalc* = 1.614 g/cm^3, 22103 reflections measured (6.02° ≤ 2Θ ≤ 144.202°), 4462 unique (R_{int} = 0.1044, R_{sigma} = 0.0588) which were used in all calculations. The final R_1 was 0.0710 (I > 2σ(I)) and wR_2 was 0.1867 (all data). CCDC 2032754

Compound 3: $C_{26}H_{20}Cr_2O_{12}S_2$ (*M* =692.54 g/mol): triclinic, space group P-1 (no. 2), *a* = 7.1185(6) Å, *b* = 9.6691(8) Å, *c* = 10.7876(9) Å, *α* = 92.975(3)°, *β* = 96.209(3)°, *γ* = 103.001(3)°, *V* = 717.00(10) Å^3, *Z* = 1, *T* = 150(2) K, μ(MoKα) = 0.966 mm^{-1}, *Dcalc* = 1.604 g/cm^3, 23044 reflections measured (4.336° ≤ 2Θ ≤ 52.744°), 2926 unique (R_{int} = 0.0818, R_{sigma} = 0.0459) which were used in all calculations. The final R_1 was 0.0278 (I > 2σ(I)) and wR_2 was 0.0667 (all data). CCDC 2032756

Compound 5: $C_{16}H_{12}O_6S_2W$ (*M* =548.23 g/mol): triclinic, space group P-1 (no. 2), *a* = 7.4467(4) Å, *b* = 10.7958(5) Å, *c* = 12.3241(6) Å, *α* = 75.9140(10)°, *β* = 75.794(2)°, *γ* = 70.5600(10)°, *V* = 891.44(8) Å^3, *Z* = 2, *T* = 150(2) K, μ(MoKα) = 6.742 mm^{-1}, *Dcalc* = 2.042 g/cm^3, 25438 reflections measured (4.852° ≤ 2Θ ≤ 52.742°), 3650 unique (R_{int} = 0.0588, R_{sigma} = 0.0342) which were used in all calculations. The final R_1 was 0.0205 (I > 2σ(I)) and wR_2 was 0.0524 (all data). CCDC 2032757

Compound 7: $C_{31}H_{30}O_{13}S_2W_2$ (*M* =1012.26 g/mol): monoclinic, space group C2/c (no. 15), *a* = 16.9578(18) Å, *b* = 28.884(4) Å, *c* = 15.272(3) Å, *β* = 102.558(4)°, *V* = 7301.6(17) Å^3, *Z* = 8, *T* = 150(2) K, μ(MoKα) = 6.470 mm^{-1}, *Dcalc* = 1.842 g/cm^3, 16614 reflections measured (4.294° ≤ 2Θ ≤ 45.93°), 4808 unique (R_{int} = 0.0963, R_{sigma} = 0.0859) which were used in all calculations. The final R_1 was 0.0708 (I > 2σ(I)) and wR_2 was 0.1686 (all data).

Compound 11: $C_{30.85}H_{22.85}Cr_2O_{12}S_3$ (*M* =785.75 g/mol): triclinic, space group P-1 (no. 2), *a* = 10.7421(13) Å, *b* = 16.0557(18) Å, *c* = 21.988(3) Å, *α* = 101.964(4)°, *β* = 99.888(4)°, *γ* = 103.629(4)°, *V* = 3507.1(7) Å^3, *Z* = 4, *T* = 150(2) K, μ(MoKα) = 0.857 mm^{-1}, *Dcalc* = 1.488 g/cm^3, 108937 reflections measured (4.492° ≤ 2Θ ≤ 52.744°), 14354 unique (R_{int} = 0.0664, R_{sigma} = 0.0438) which were used in all calculations. The final R_1 was 0.0706 (I > 2σ(I)) and wR_2 was 0.1778 (all data). CCDC 2032759

Compound 16: $C_{18.5}H_{14.5}O_6S_{1.5}W$ (*M* =564.74 g/mol): triclinic, space group P-1 (no. 2), *a* = 11.0377(11) Å, *b* = 12.0180(11) Å, *c* = 16.5239(16) Å, *α* = 69.060(3)°, *β* = 74.437(3)°, *γ* = 77.654(3)°, *V* = 1955.1(3) Å^3, *Z* = 4, *T* = 150(2) K, μ(MoKα) = 6.100 mm^{-1}, *Dcalc* = 1.919 g/cm^3, 46500 reflections measured (4.222° ≤ 2Θ ≤ 52.04°), 7708 unique (R_{int} = 0.0601, R_{sigma} = 0.0389) which were used in all calculations. The final R_1 was 0.0289 (I > 2σ(I)) and wR_2 was 0.0780 (all data). CCDC 2032758

S6. Crystal Packing

Stacking and columnar crystal packing is observed for **1**. The packing patterns consist of molecules that pack as dimers and fit on top of each other, down the column, in a parallel fashion (Figure S15). Because each pair of dimers is antiparallel and non-planar, the columns can interlock while packing in a planar and parallel fashion. Each column is enclosed by eight other columns. When viewed along the a- and b- crystallographic axes, grid networks form, where the interlocked columns result in overlapping, parallel regions of alternating metal carbonyls and thienylenes (Figure S15). In the case of the *a*-axis, the overlapping parallel regions are horizontal and in the *b*-axis vertical. Columns consisting of molecules that pack with small π-π interaction distances are present when viewed down the crystallographic *a*-axis of **1**, with distances measures at 7.428 Å. Packed molecules with longer π-π separation distances, 10.702 Å., called layers of columns is observed when viewed down the crystallographic *b*-axis. Partial overlap of the *trans*-TT spacers, results in true π-π stacking where the π-π interaction distance is measured as 3.667 Å. Compound **2** and **5** display similar solid-state packing as **1**, but with larger π-π interaction distances. The true π-π stacking distance of **2** and **5** are measured as 3.516 and 3.622 Å, respectively. Instead of forming grid networks consisting of multiple parallel rows of compounds, a singular row of compounds packed horizontally in the *a*-axis and vertically in the *b*-axis of **2**.

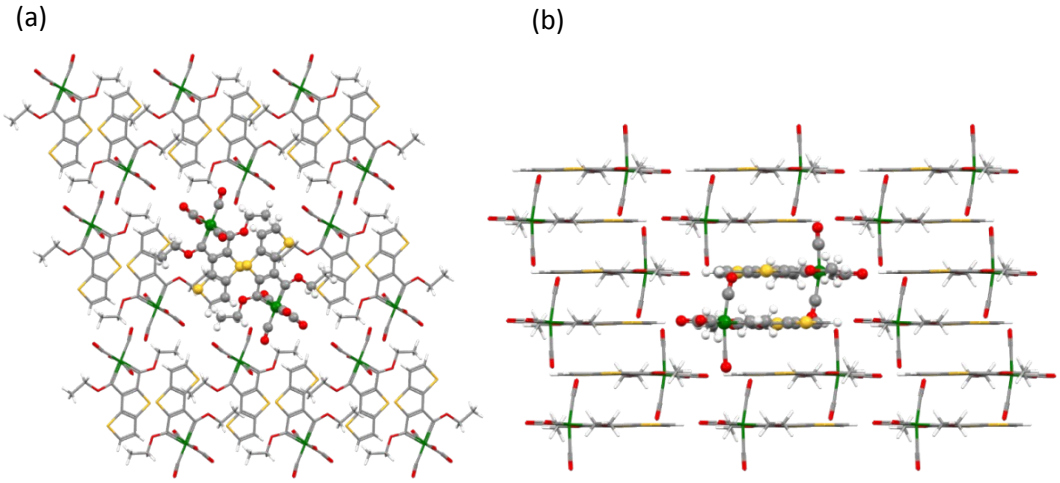

Figure S15. Crystal packing of **1** viewed down the crystallographic a-axis (a) and b-axis (b)

Considering the packing of **11**, π-π stacking occurs through a benzene molecule flanked by two molecules of the compound. The two molecules of compound fit precisely on top of each other (Figure S16(a)). The π-π separation distances are between 3.3-3.9 Å (Figure S16(b)). The next set of two molecules of compound flanking benzene, are displaced and continues in this fashion to form a pattern. The distance between two sets is 3.746 Å, with partial overlap of the aromatic regions (Figure S16(c)). The packing leads to a network of displaced "cages" when viewed along the crystallographic *a*-axis (Figure S16(b)). When viewed down the crystallographic *a*-axis, each cage traps two sets of benzene molecules with different orientations (the second set of benzene molecules are omitted because they do not take part in π-π stacking). The crystal packing of **16** is very similar to **11**. In the case of **16**, the two molecules flanking benzene are now in opposite directions. The π-π separation distances are between 3.4-3.9 Å and the distance between two sets of molecules flanking benzene is 3.810 Å. Each "cage" now confines three sets of benzene molecules with different orientations.

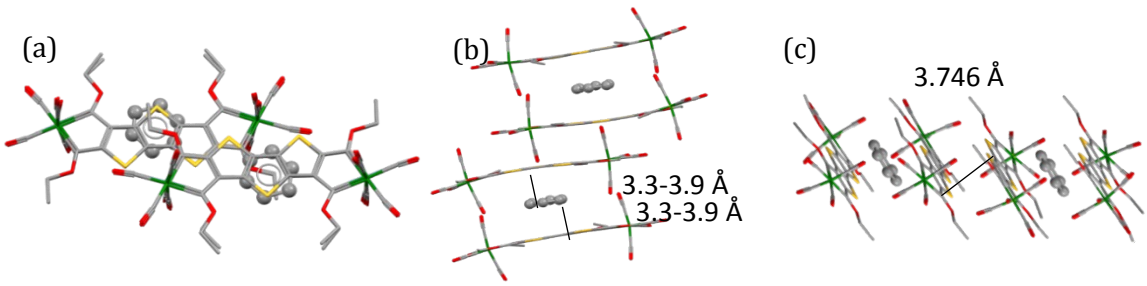

Figure S16. Crystal packing of **11** (a), viewed down the crystallographic a-axis (b) and b-axis (c), hydrogens omitted for clarity

The crystal packing of **16** is very similar to **11**. In the case of **16**, the two molecules flanking benzene are now in opposite directions. The π-π separation distances are between 3.4-3.9 Å and the distance between two sets of molecules flanking benzene is 3.810 Å. Each "cage" now confines three sets of benzene molecules with different orientations (see CIF file).

S7. Cyclic voltammetry data

Table S7 CV data (potentials (V)) for oxidation processes observed for selected compounds

Compound	Oxidation (O)			
	O1	**O2**	**O3**	**O4**
1	E_{pa}=0.01, E_{pc}=-0.07 $E°'$=-0.03, ΔE_p=0.08	E_{pa}=0.88[a]	E_{pa}=1.28[a]	E_{pa}=1.70[a]
3	E_{pa}=0.07[b]	E_{pa}=0.20[b]		
11	E_{pa}=0.12[ab]	E_{pa}=0.64[b]		
16	E_{pa}=0.54[ab]	E_{pa}=1.41		
18	E_{pa}=0.61, E_{pc}=0.53 $E°'$=0.57, ΔE_p=0.08	E_{pa}=0.97[b]	E_{pa}=1.10[b]	
19	E_{pa}=-0.03[b]	E_{pa}=0.08[b]	E_{pa}=1.14[a]	E_{pa}=1.39[a]
20	E_{pa}=0.60, E_{pc}=0.52 $E°'$=0.56, ΔE_p=0.08	E_{pa}=0.98[b]	E_{pa}=1.05[b]	
21	E_{pa}=0.74, E_{pc}=0.45 $E°'$=0.59, ΔE_p=0.29	E_{pa}=1.13[ab]	E_{pa}=1.62	

Only unambiguously identifiable waves are reported.

[a] Large (more than one-electron) irreversible oxidation peak, no E_{pc} detected.

[b] Overlapping irreversible oxidation peak. No E_{pc} detected.

For a redox process to be electrochemically and chemically reversible, $\Delta E_p = E_{pa} - E_{pc}$ = 59 mV and i_{pc}/i_{pa} = 1.[4] For the monocarbene complexes (**18**, **20** and **21**) O1 is a reversible one-electron process, around 0.58 V, assigned as the $Cr^{0/I}$ couple. In the case of **18** and **20**, O2 and O3 are two one-electron irreversible oxidations that are overlapping. Compound **21** has a large irreversible O2 that seems to consist of more than one peak that's overlapping and an irreversible one-electron O3.

The chromium chelated carbene complexes (**1**, **3**, **11** and **19**) display O1 potentials ranging around -0.03–0.12 V (Table S7), *ca.* 0.50 V less positive than the monocarbene complexes. This is anticipated as the metallacyclic ring in the chelated carbene complexes allows more electron density to be donated to the carbene ligands, from the thienylene spacer, as two attachment points exist. The chelated biscarbene complexes are therefore more easily oxidized, and their potentials correlate to that of chelated monocarbene complexes (E_{pa}=5−20 mV *vs.* $FcH^{0/+1}$ in CH_3CN).[5]

Compound **1** has a quasi-reversible one-electron O1, as the current ratio is approximately 2. O2, O3 and O4 are large irreversible oxidations. Compound **3** shows at least two one-electron overlapping irreversible oxidations. Compound **19** displays two one-electron overlapping irreversible oxidations (O1 and O2), along with two large irreversible oxidations (O3 and O4). Compound **11** has a large irreversible oxidation (O1) that is overlapping with another irreversible oxidation (O2). Compound **16** displays a very large irreversible O1, with E_{pa}=0.54 V, that appears like its overlapping with more oxidations. O2 is a two-electron irreversible oxidation.

S8. Computational details

Cartesian coordinates (in Å) and total energies (in a. u., ZPVE included) of all the stationary points discussed in the text. All calculations have been performed at the B3LYP-D3/def2-SVP level.

18: E= -2829.316134

Cr	1.913907000	-0.643314000	0.001763000
S	-2.210713000	1.838806000	-0.013092000
S	-4.459916000	-1.700303000	0.001938000
O	0.477138000	2.098856000	-0.069333000
O	0.425794000	-2.206654000	2.160270000
O	3.404519000	0.787526000	2.249893000
O	0.483216000	-2.180425000	-2.215029000
O	3.554392000	0.790449000	-2.136218000
O	4.074647000	-2.783247000	0.040033000
C	0.375738000	0.777793000	-0.034702000
C	-1.708401000	-0.744612000	-0.012852000
H	-1.201474000	-1.704844000	-0.019662000
C	-3.544586000	0.738280000	-0.002142000
C	-4.962834000	0.871806000	0.007525000
H	-5.505756000	1.816763000	0.011631000
C	-1.048066000	0.482207000	-0.016347000
C	0.973471000	-1.608897000	1.346192000
C	2.828586000	0.275910000	1.395428000
C	2.914651000	0.280116000	-1.327662000
C	1.017572000	-1.595243000	-1.383372000
C	-3.108185000	-0.597336000	-0.005472000
C	1.687915000	2.867105000	-0.148837000
H	2.111151000	2.742643000	-1.156292000
H	2.414376000	2.490171000	0.582108000
C	-5.572293000	-0.359335000	0.010196000
H	-6.644083000	-0.558459000	0.016674000
C	3.258425000	-1.972755000	0.026602000
C	1.318033000	4.310433000	0.125423000
H	0.577569000	4.669878000	-0.605063000
H	2.214870000	4.944741000	0.055536000
H	0.891841000	4.417725000	1.134412000

18$^{\bullet-}$: E= -2829.379136

Cr	1.982675000	-0.679380000	0.019259000
S	-2.224066000	1.820376000	0.124876000
S	-4.486455000	-1.724167000	-0.125424000
O	0.486824000	2.112247000	0.210088000
O	0.470444000	-2.165411000	2.215537000
O	3.264567000	1.058084000	2.166861000
O	0.593398000	-2.258002000	-2.189882000
O	3.501060000	0.773320000	-2.183679000
O	4.216256000	-2.702143000	0.186807000
C	0.331502000	0.750060000	0.010520000
C	-1.731408000	-0.786259000	-0.060660000
H	-1.226990000	-1.745830000	-0.126797000
C	-3.574907000	0.709876000	0.043247000
C	-4.987010000	0.836562000	0.054986000
H	-5.523192000	1.785089000	0.122483000
C	-1.037549000	0.450540000	0.016921000
C	1.023136000	-1.595869000	1.379278000

C	2.774957000	0.400454000	1.352632000
C	2.906450000	0.248427000	-1.340971000
C	1.099579000	-1.655755000	-1.345846000
C	-3.124114000	-0.621706000	-0.049653000
C	1.521792000	2.845463000	-0.403623000
H	1.523496000	2.670743000	-1.495596000
H	2.510946000	2.534799000	-0.024366000
C	-5.621708000	-0.386077000	-0.029818000
H	-6.692895000	-0.583620000	-0.042245000
C	3.355366000	-1.924003000	0.118887000
C	1.278917000	4.313438000	-0.095142000
H	0.297774000	4.629888000	-0.482769000
H	2.062444000	4.942178000	-0.548726000
H	1.282155000	4.476876000	0.994198000

1: E= -2907.786264

Cr	-1.573670000	0.666510000	0.000020000
C	-3.423490000	0.309910000	-0.000130000
O	-4.571990000	0.181430000	-0.000160000
S	1.527010000	-2.814130000	-0.000180000
S	4.066040000	0.540840000	0.000290000
C	-1.446050000	0.590140000	-1.908340000
O	-1.332420000	0.524210000	-3.050650000
O	-1.333380000	0.523490000	3.050730000
C	-1.446600000	0.589690000	1.908400000
O	-2.553710000	3.537760000	0.000320000
C	-2.130740000	2.461850000	0.000190000
O	1.251240000	2.061690000	0.000140000
C	0.442950000	1.019440000	0.000170000
O	-1.477100000	-2.496750000	-0.000220000
C	0.756100000	3.412260000	-0.000090000
H	0.124820000	3.554490000	0.890260000
H	0.124660000	3.554120000	-0.890390000
C	1.236630000	-0.197970000	0.000160000
C	1.955450000	4.336080000	-0.000390000
H	2.577370000	4.167910000	0.892080000
H	1.620630000	5.384540000	-0.000630000
H	2.577260000	4.167460000	-0.892850000
C	0.507570000	-1.387280000	0.000000000
C	-0.930690000	-1.296510000	-0.000090000
C	-2.903420000	-2.679580000	-0.000240000
H	-3.321020000	-2.184960000	-0.890590000
H	-3.321080000	-2.184860000	0.890020000
C	-3.173480000	-4.169020000	-0.000160000
H	-2.739460000	-4.645090000	-0.892720000
H	-4.258830000	-4.351910000	-0.000160000
H	-2.739480000	-4.644980000	0.892470000
C	2.636600000	-0.442460000	0.000120000
C	2.957070000	-1.807490000	-0.000020000
C	4.359360000	-2.062940000	0.000030000
H	4.819220000	-3.051050000	-0.000060000
C	5.069410000	-0.887120000	0.000180000
H	6.153920000	-0.777740000	0.000240000

1$^{\bullet-}$: E= -2907.857123

Cr	-1.597464000	0.703741000	-0.000031000
C	-3.414789000	0.341501000	-0.000087000
O	-4.572536000	0.191260000	-0.000125000
S	1.524684000	-2.857894000	0.000060000

S	4.071008000	0.510854000	0.000113000
C	-1.471454000	0.615266000	-1.886382000
O	-1.375518000	0.549369000	-3.038220000
O	-1.375689000	0.549225000	3.038163000
C	-1.471558000	0.615183000	1.886323000
O	-2.483146000	3.584853000	0.000023000
C	-2.097375000	2.482010000	0.000000000
O	1.325870000	2.070358000	0.000015000
C	0.496426000	1.005769000	0.000015000
O	-1.499659000	-2.556851000	-0.000041000
C	0.810007000	3.392506000	-0.000039000
H	0.172613000	3.545675000	0.886355000
H	0.172621000	3.545603000	-0.886452000
C	1.234606000	-0.195270000	0.000045000
C	1.994920000	4.341509000	-0.000073000
H	2.622303000	4.176171000	0.890220000
H	1.650612000	5.388165000	-0.000116000
H	2.622309000	4.176098000	-0.890348000
C	0.476602000	-1.406544000	0.000026000
C	-0.914359000	-1.336691000	-0.000024000
C	-2.912465000	-2.665708000	-0.000102000
H	-3.329906000	-2.158924000	-0.886435000
H	-3.329982000	-2.158946000	0.886208000
C	-3.258908000	-4.143919000	-0.000134000
H	-2.840733000	-4.639719000	-0.890806000
H	-4.351960000	-4.283265000	-0.000181000
H	-2.840807000	-4.639741000	0.890560000
C	2.637452000	-0.471935000	0.000081000
C	2.960355000	-1.830019000	0.000095000
C	4.362115000	-2.082786000	0.000132000
H	4.814777000	-3.075750000	0.000147000
C	5.088234000	-0.912825000	0.000145000
H	6.172798000	-0.806519000	0.000172000

1^{-2}: E= -2907.787253

Cr	1.617090000	0.751828000	0.000037000
C	3.414551000	0.399046000	0.000074000
O	4.583009000	0.241580000	0.000097000
S	-1.528067000	-2.921693000	-0.000061000
S	-4.078873000	0.472075000	-0.000103000
C	1.500723000	0.639434000	1.870450000
O	1.434507000	0.564504000	3.031267000
O	1.434629000	0.564516000	-3.031202000
C	1.500799000	0.639441000	-1.870383000
O	2.392103000	3.653743000	0.000056000
C	2.049933000	2.523605000	0.000049000
O	-1.416500000	2.074160000	-0.000030000
C	-0.554288000	0.991405000	-0.000013000
O	1.552979000	-2.618074000	0.000022000
C	-0.895653000	3.375325000	0.000019000
H	-0.253611000	3.546754000	-0.883408000
H	-0.253661000	3.546707000	0.883491000
C	-1.238552000	-0.203338000	-0.000039000
C	-2.076547000	4.337042000	0.000011000
H	-2.707364000	4.168230000	-0.888548000
H	-1.733428000	5.386134000	0.000049000
H	-2.707414000	4.168182000	0.888525000
C	-0.436635000	-1.436596000	-0.000025000
C	0.911139000	-1.379540000	0.000013000

C	2.949031000	-2.645826000	0.000091000
H	3.364794000	-2.124118000	0.883685000
H	3.364883000	-2.124124000	-0.883464000
C	3.381243000	-4.107182000	0.000117000
H	2.983025000	-4.624607000	0.889326000
H	4.481619000	-4.196474000	0.000169000
H	2.983108000	-4.624613000	-0.889125000
C	-2.637128000	-0.510969000	-0.000075000
C	-2.967210000	-1.868552000	-0.000089000
C	-4.365274000	-2.114544000	-0.000122000
H	-4.811354000	-3.113233000	-0.000137000
C	-5.112411000	-0.948214000	-0.000133000
H	-6.197891000	-0.845487000	-0.000158000

3: E= -4788.620394

Cr	4.707211000	-0.297763000	0.000042000
S	-0.660289000	-2.008518000	-0.000032000
O	4.436358000	-0.242805000	-3.052480000
O	6.563277000	-2.701945000	-0.000306000
O	7.391355000	1.125289000	0.000933000
O	4.435703000	-0.244144000	3.052521000
O	3.603397000	2.663109000	-0.000011000
O	2.481437000	-2.529025000	0.000189000
C	4.564170000	-0.268329000	-1.910677000
C	5.815699000	-1.821428000	-0.000206000
C	6.345444000	0.635336000	0.000558000
C	4.563779000	-0.269181000	1.910739000
C	4.668440000	4.794808000	-0.000388000
H	4.104344000	5.105428000	0.892304000
H	4.104506000	5.105136000	-0.893285000
H	5.636783000	5.317885000	-0.000384000
C	4.894176000	3.298173000	-0.000117000
H	5.448617000	2.964420000	-0.890605000
H	5.448604000	2.964740000	0.890495000
C	3.474104000	1.350928000	0.000146000
C	2.078667000	0.977714000	0.000182000
C	1.770944000	-0.383716000	0.000125000
C	2.912463000	-1.283567000	-0.000041000
C	3.384042000	-3.650624000	-0.000329000
H	4.027043000	-3.581620000	0.890315000
H	4.027003000	-3.580809000	-0.890936000
C	2.544975000	-4.910363000	-0.000870000
H	3.199436000	-5.795193000	-0.001247000
H	1.902244000	-4.951119000	-0.893495000
H	1.902248000	-4.951893000	0.891722000
C	0.366374000	-0.599570000	0.000026000
S	0.660283000	2.008529000	0.000048000
O	-3.603396000	-2.663099000	0.000036000
O	-2.481422000	2.529028000	-0.000200000
C	-4.668435000	-4.794800000	0.000472000
H	-4.104323000	-5.105448000	-0.892201000
H	-4.104515000	-5.105097000	0.893388000
H	-5.636777000	-5.317879000	0.000469000
C	-4.894174000	-3.298165000	0.000148000
H	-5.448627000	-2.964384000	0.890617000
H	-5.448592000	-2.964762000	-0.890482000
C	-3.474108000	-1.350917000	-0.000148000
C	-2.078671000	-0.977703000	-0.000178000
C	-1.770950000	0.383726000	-0.000117000
C	-2.912469000	1.283576000	0.000049000

C	-3.383977000	3.650667000	0.000322000
H	-4.026977000	3.581702000	-0.890326000
H	-4.026943000	3.580877000	0.890925000
C	-2.544854000	4.910368000	0.000874000
H	-3.199275000	5.795227000	0.001247000
H	-1.902129000	4.951093000	0.893505000
H	-1.902116000	4.951870000	-0.891712000
C	-0.366379000	0.599582000	-0.000016000
Cr	-4.707228000	0.297762000	-0.000054000
O	-4.436382000	0.242652000	3.052464000
O	-6.563410000	2.701844000	0.000377000
O	-7.391368000	-1.125297000	-0.001072000
O	-4.435642000	0.244275000	-3.052528000
C	-4.564215000	0.268274000	1.910664000
C	-5.815725000	1.821418000	0.000235000
C	-6.345448000	-0.635363000	-0.000643000
C	-4.563757000	0.269261000	-1.910749000

3•⁻: E= -4788.718028

Cr	-4.725176000	-0.326659000	0.000090000
S	0.641417000	-2.020826000	0.000130000
O	-4.479084000	-0.209208000	3.042673000
O	-6.515274000	-2.756815000	0.000302000
O	-7.405677000	1.081417000	-0.000100000
O	-4.479009000	-0.209811000	-3.042510000
O	-3.611494000	2.702514000	-0.000076000
O	-2.453324000	-2.537111000	0.000240000
C	-4.587551000	-0.261155000	1.894660000
C	-5.785588000	-1.849758000	0.000221000
C	-6.352138000	0.590356000	-0.000027000
C	-4.587506000	-0.261520000	-1.894490000
C	-4.754727000	4.781677000	-0.000101000
H	-4.198777000	5.112792000	-0.891289000
H	-4.198755000	5.112820000	0.891063000
H	-5.741819000	5.270310000	-0.000097000
C	-4.915472000	3.273625000	-0.000073000
H	-5.469272000	2.927514000	0.887883000
H	-5.469290000	2.927483000	-0.888006000
C	-3.445654000	1.373287000	-0.000025000
C	-2.092143000	1.001018000	-0.000031000
C	-1.769383000	-0.381947000	0.000062000
C	-2.890637000	-1.282644000	0.000157000
C	-3.351576000	-3.648728000	0.000363000
H	-3.999857000	-3.588818000	-0.887796000
H	-3.999811000	-3.588655000	0.888544000
C	-2.509490000	-4.909120000	0.000456000
H	-3.158272000	-5.799024000	0.000562000
H	-1.862930000	-4.943699000	0.890967000
H	-1.862987000	-4.943870000	-0.890090000
C	-0.376285000	-0.599976000	0.000050000
S	-0.641420000	2.020818000	-0.000126000
O	3.611481000	-2.702522000	0.000078000
O	2.453295000	2.537093000	-0.000241000
C	4.754741000	-4.781668000	0.000118000
H	4.198795000	-5.112786000	0.891307000
H	4.198775000	-5.112825000	-0.891045000
H	5.741840000	-5.270287000	0.000118000
C	4.915463000	-3.273614000	0.000081000
H	5.469262000	-2.927500000	-0.887875000
H	5.469276000	-2.927458000	0.888012000

C	3.445648000	-1.373293000	0.000025000
C	2.092137000	-1.001024000	0.000030000
C	1.769378000	0.381940000	-0.000063000
C	2.890632000	1.282630000	-0.000159000
C	3.351486000	3.648758000	-0.000365000
H	3.999770000	3.588890000	0.887793000
H	3.999722000	3.588728000	-0.888547000
C	2.509327000	4.909102000	-0.000457000
H	3.158057000	5.799044000	-0.000565000
H	1.862762000	4.943642000	-0.890967000
H	1.862823000	4.943814000	0.890090000
C	0.376280000	0.599971000	-0.000049000
Cr	4.725198000	0.326646000	-0.000093000
O	4.479194000	0.209500000	-3.042700000
O	6.515466000	2.756661000	-0.000311000
O	7.405605000	-1.081596000	0.000101000
O	4.479118000	0.210127000	3.042531000
C	4.587525000	0.261129000	-1.894660000
C	5.785635000	1.849719000	-0.000224000
C	6.352064000	-0.590540000	0.000030000
C	4.587477000	0.261499000	1.894481000

3^{-2}: E= -4788.706385

Cr	-4.768797000	0.339376000	-0.000110000
S	0.636783000	2.027572000	-0.000112000
O	-4.556379000	0.203147000	-3.037014000
O	-6.515664000	2.788975000	-0.000300000
O	-7.427998000	-1.086841000	-0.000037000
O	-4.556450000	0.203573000	3.036817000
O	-3.622156000	-2.740008000	0.000097000
O	-2.439645000	2.555269000	-0.000222000
C	-4.639182000	0.262994000	-1.882009000
C	-5.797019000	1.862174000	-0.000227000
C	-6.373453000	-0.578170000	-0.000062000
C	-4.639226000	0.263256000	1.881801000
C	-4.809012000	-4.784720000	0.000176000
H	-4.256826000	-5.127717000	0.890104000
H	-4.256787000	-5.127806000	-0.889694000
H	-5.806725000	-5.254165000	0.000178000
C	-4.929090000	-3.269536000	0.000097000
H	-5.487716000	-2.919271000	-0.885649000
H	-5.487754000	-2.919181000	0.885783000
C	-3.437950000	-1.389427000	0.000020000
C	-2.111485000	-1.013144000	0.000026000
C	-1.777892000	0.386384000	-0.000057000
C	-2.875173000	1.283628000	-0.000144000
C	-3.347368000	3.644300000	-0.000341000
H	-4.001050000	3.587190000	0.885584000
H	-4.000996000	3.587038000	-0.886296000
C	-2.520542000	4.917970000	-0.000425000
H	-3.176355000	5.804118000	-0.000527000
H	-1.870873000	4.955458000	-0.889063000
H	-1.870935000	4.955618000	0.888251000
C	-0.378175000	0.596589000	-0.000041000
S	-0.636739000	-2.027578000	0.000124000
O	3.622179000	2.740013000	-0.000100000
O	2.439698000	-2.555283000	0.000230000
C	4.808949000	4.784772000	-0.000190000
H	4.256745000	5.127743000	-0.890118000

H	4.256713000	5.127838000	0.889681000
H	5.806643000	5.254260000	-0.000197000
C	4.929089000	3.269593000	-0.000106000
H	5.487734000	2.919358000	0.885639000
H	5.487765000	2.919263000	-0.885795000
C	3.437992000	1.389424000	-0.000020000
C	2.111527000	1.013140000	-0.000020000
C	1.777935000	-0.386391000	0.000066000
C	2.875215000	-1.283635000	0.000149000
C	3.347438000	-3.644294000	0.000344000
H	4.001117000	-3.587171000	-0.885583000
H	4.001069000	-3.587022000	0.886297000
C	2.520634000	-4.917979000	0.000430000
H	3.176461000	-5.804117000	0.000528000
H	1.870968000	-4.955478000	0.889070000
H	1.871023000	-4.955635000	-0.888244000
C	0.378219000	-0.596598000	0.000052000
Cr	4.768855000	-0.339409000	0.000108000
O	4.556298000	-0.203051000	3.036994000
O	6.515294000	-2.789327000	0.000312000
O	7.427853000	1.087214000	0.000017000
O	4.556334000	-0.203452000	-3.036798000
C	4.639243000	-0.263100000	1.882009000
C	5.797021000	-1.862236000	0.000215000
C	6.373496000	0.578154000	0.000054000
C	4.639272000	-0.263362000	-1.881805000

19: E= -4788.611786

Cr	3.884933000	-0.733139000	0.023805000
C	3.967395000	-2.612995000	-0.032096000
O	4.061130000	-3.764535000	-0.049239000
C	5.729051000	-0.801717000	0.422017000
O	6.852225000	-0.919106000	0.664038000
C	4.187850000	-0.564303000	-1.855265000
O	4.340194000	-0.440423000	-2.989158000
C	3.386982000	-0.755244000	1.874873000
O	3.045023000	-0.763620000	2.972434000
C	3.683651000	1.320477000	0.077628000
O	4.470771000	2.374920000	0.125190000
C	1.890927000	-0.596109000	-0.372377000
O	0.972349000	-1.334656000	-0.946768000
Cr	-3.885018000	-0.733142000	-0.023746000
C	-3.968090000	-2.612966000	0.032830000
O	-4.062195000	-3.764462000	0.050548000
C	-5.729234000	-0.801525000	-0.421811000
O	-6.852455000	-0.918663000	-0.663695000
C	-3.386925000	-0.756057000	-1.874812000
O	-3.044733000	-0.765060000	-2.972291000
C	-4.187040000	-0.563889000	1.855419000
O	-4.338532000	-0.439835000	2.989408000
C	-3.683776000	1.320447000	-0.077812000
O	-4.470812000	2.374947000	-0.125609000
C	-1.890997000	-0.596222000	0.372363000
O	-0.972329000	-1.334955000	0.946404000
S	1.592871000	3.333677000	0.079320000
S	-1.593003000	3.333644000	-0.079044000
C	2.291574000	1.713916000	0.055109000
C	1.331188000	0.714272000	-0.044202000
C	-0.000038000	1.230218000	0.000216000
C	-1.331282000	0.714219000	0.044379000

C	-2.291665000	1.713841000	-0.055048000
C	-0.000063000	2.636253000	0.000207000
C	5.904868000	2.241762000	0.128389000
H	6.196199000	1.596600000	-0.714835000
H	6.205445000	1.740116000	1.060615000
C	6.495048000	3.630701000	0.014883000
H	6.176259000	4.115922000	-0.920266000
H	7.593978000	3.570039000	0.019254000
H	6.177902000	4.261227000	0.859567000
C	1.235721000	-2.642813000	-1.483789000
H	1.444931000	-3.329495000	-0.649941000
H	2.137960000	-2.590446000	-2.112593000
C	0.008100000	-3.054517000	-2.269879000
H	-0.881116000	-3.088622000	-1.622470000
H	0.158530000	-4.052367000	-2.708637000
H	-0.194689000	-2.339515000	-3.081176000
C	-5.904913000	2.241876000	-0.129057000
H	-6.196401000	1.596732000	0.714119000
H	-6.205392000	1.740259000	-1.061337000
C	-6.495026000	3.630851000	-0.015599000
H	-6.176279000	4.116025000	0.919588000
H	-7.593958000	3.570258000	-0.020064000
H	-6.177763000	4.261370000	-0.860245000
C	-1.235699000	-2.643165000	1.483243000
H	-1.445310000	-3.329677000	0.649335000
H	-2.137689000	-2.590816000	2.112404000
C	-0.007876000	-3.055221000	2.268845000
H	0.881181000	-3.089066000	1.621216000
H	-0.158212000	-4.053277000	2.707171000
H	0.195122000	-2.340600000	3.080428000

19$^{\bullet-}$: E= -4788.703645

Cr	3.935246000	-0.739112000	-0.016668000
C	4.052705000	-2.586433000	-0.180461000
O	4.183895000	-3.739415000	-0.267206000
C	5.761040000	-0.780572000	0.361424000
O	6.897278000	-0.877630000	0.591262000
C	4.204566000	-0.444947000	-1.869253000
O	4.349196000	-0.249827000	-2.999767000
C	3.453123000	-0.866947000	1.818531000
O	3.126289000	-0.945094000	2.922959000
C	3.675643000	1.351545000	0.150685000
O	4.473574000	2.423639000	0.238412000
C	1.891084000	-0.599179000	-0.369954000
O	0.970703000	-1.377850000	-0.910327000
Cr	-3.935254000	-0.739128000	0.016691000
C	-4.052736000	-2.586446000	0.180510000
O	-4.183917000	-3.739426000	0.267280000
C	-5.761059000	-0.780583000	-0.361349000
O	-6.897304000	-0.877612000	-0.591162000
C	-3.453179000	-0.866981000	-1.818519000
O	-3.126356000	-0.945138000	-2.922950000
C	-4.204519000	-0.444949000	1.869281000
O	-4.349098000	-0.249818000	2.999800000
C	-3.675661000	1.351528000	-0.150685000
O	-4.473597000	2.423617000	-0.238416000
C	-1.891084000	-0.599188000	0.369929000
O	-0.970682000	-1.377841000	0.910292000
S	1.577395000	3.313591000	0.143032000
S	-1.577421000	3.313582000	-0.143089000

C	2.310851000	1.694884000	0.134852000
C	1.334891000	0.678972000	-0.015852000
C	-0.000008000	1.191873000	-0.000020000
C	-1.334904000	0.678965000	0.015818000
C	-2.310870000	1.694872000	-0.134874000
C	-0.000011000	2.604029000	-0.000021000
C	5.890245000	2.271003000	0.215088000
H	6.178534000	1.671982000	-0.664075000
H	6.214634000	1.717031000	1.110598000
C	6.500307000	3.658600000	0.169473000
H	6.170244000	4.198673000	-0.731871000
H	7.599538000	3.591047000	0.155639000
H	6.196603000	4.246451000	1.050073000
C	1.269074000	-2.652787000	-1.479538000
H	1.566362000	-3.350899000	-0.681677000
H	2.127030000	-2.550210000	-2.163681000
C	0.016355000	-3.117499000	-2.197561000
H	-0.826527000	-3.203695000	-1.495789000
H	0.186504000	-4.099236000	-2.666428000
H	-0.277558000	-2.396957000	-2.975726000
C	-5.890267000	2.270976000	-0.215061000
H	-6.178536000	1.671963000	0.664114000
H	-6.214673000	1.716994000	-1.110559000
C	-6.500334000	3.658571000	-0.169448000
H	-6.170252000	4.198655000	0.731884000
H	-7.599564000	3.591015000	-0.155589000
H	-6.196650000	4.246414000	-1.050061000
C	-1.269006000	-2.652780000	1.479523000
H	-1.566405000	-3.350876000	0.681689000
H	-2.126874000	-2.550199000	2.163775000
C	-0.016204000	-3.117525000	2.197377000
H	0.826588000	-3.203715000	1.495496000
H	-0.186307000	-4.099271000	2.666242000
H	0.277815000	-2.397004000	2.975523000

19^{-2}: E= -4788.687111

Cr	-4.009368000	-0.742473000	0.033636000
C	-4.168010000	-2.561019000	0.273981000
O	-4.338952000	-3.711879000	0.412351000
C	-5.814215000	-0.736692000	-0.349101000
O	-6.960533000	-0.796639000	-0.586533000
C	-4.265080000	-0.372780000	1.861582000
O	-4.418501000	-0.139619000	2.989437000
C	-3.523298000	-0.958063000	-1.780409000
O	-3.204262000	-1.101710000	-2.885381000
C	-3.678229000	1.374357000	-0.207971000
O	-4.476252000	2.474454000	-0.312275000
C	-1.905903000	-0.602547000	0.363621000
O	-0.993519000	-1.428601000	0.880981000
Cr	4.009366000	-0.742476000	-0.033637000
C	4.168004000	-2.561022000	-0.273980000
O	4.338933000	-3.711885000	-0.412350000
C	5.814214000	-0.736699000	0.349096000
O	6.960533000	-0.796641000	0.586526000
C	3.523306000	-0.958058000	1.780412000
O	3.204276000	-1.101696000	2.885387000
C	4.265083000	-0.372780000	-1.861582000
O	4.418509000	-0.139613000	-2.989435000
C	3.678230000	1.374355000	0.207971000

O	4.476254000	2.474450000	0.312274000
C	1.905901000	-0.602548000	-0.363619000
O	0.993516000	-1.428602000	-0.880979000
S	-1.571714000	3.300651000	-0.182708000
S	1.571716000	3.300650000	0.182710000
C	-2.327761000	1.678322000	-0.189728000
C	-1.346042000	0.646006000	-0.002920000
C	0.000000000	1.164340000	0.000001000
C	1.346042000	0.646005000	0.002923000
C	2.327762000	1.678320000	0.189729000
C	0.000001000	2.567008000	0.000001000
C	-5.879029000	2.322241000	-0.261603000
H	-6.169021000	1.754202000	0.639434000
H	-6.235361000	1.741963000	-1.130154000
C	-6.490687000	3.713534000	-0.250300000
H	-6.140602000	4.281934000	0.626638000
H	-7.591182000	3.654086000	-0.217130000
H	-6.195370000	4.273256000	-1.152896000
C	-1.340355000	-2.672260000	1.463757000
H	-1.725138000	-3.361664000	0.694400000
H	-2.152345000	-2.525249000	2.196903000
C	-0.081626000	-3.217466000	2.116902000
H	0.710357000	-3.367505000	1.368231000
H	-0.288589000	-4.179939000	2.613177000
H	0.310028000	-2.505943000	2.860065000
C	5.879030000	2.322236000	0.261598000
H	6.169021000	1.754197000	-0.639439000
H	6.235363000	1.741956000	1.130149000
C	6.490690000	3.713528000	0.250297000
H	6.140604000	4.281930000	-0.626640000
H	7.591186000	3.654079000	0.217125000
H	6.195376000	4.273249000	1.152894000
C	1.340351000	-2.672260000	-1.463756000
H	1.725133000	-3.361665000	-0.694400000
H	2.152341000	-2.525249000	-2.196902000
C	0.081621000	-3.217465000	-2.116901000
H	-0.710361000	-3.367503000	-1.368230000
H	0.288583000	-4.179937000	-2.613178000
H	-0.310033000	-2.505940000	-2.860064000

11: E= -5262.850724

Cr	5.559784000	0.403237000	0.000378000
Cr	-5.559749000	0.403381000	-0.000205000
S	1.962452000	-2.553164000	-0.000359000
S	0.000011000	1.210903000	-0.000095000
S	-1.962481000	-2.553137000	-0.000250000
O	5.298621000	0.301198000	3.052545000
O	8.446345000	-0.547210000	0.001352000
O	6.974895000	3.090092000	0.001205000
O	5.300567000	0.302065000	-3.051979000
O	4.972803000	-2.706252000	-0.000513000
O	2.987669000	2.222944000	-0.000241000
O	-5.300526000	0.300633000	3.052110000
O	-8.446386000	-0.546791000	-0.001012000
O	-5.299023000	0.301127000	-3.052390000
O	-6.974683000	3.090341000	-0.000738000
O	-4.972904000	-2.706124000	0.000356000
O	-2.987539000	2.222998000	0.000111000
C	5.422202000	0.348477000	1.910885000
C	7.333012000	-0.240089000	0.000923000

C	6.390725000	2.093384000	0.000905000
C	5.423431000	0.348996000	-1.910223000
C	4.623464000	-1.434608000	-0.000168000
C	6.352621000	-3.112673000	-0.000749000
H	6.842066000	-2.690333000	0.890156000
H	6.842117000	-2.689083000	-0.891030000
C	6.384686000	-4.625931000	-0.001792000
H	5.881630000	-5.027127000	-0.894835000
H	5.881447000	-5.028344000	0.890599000
H	7.427810000	-4.976905000	-0.001923000
C	3.625416000	1.068906000	-0.000003000
C	3.684204000	3.482062000	-0.000342000
H	4.330085000	3.523570000	-0.890668000
H	4.329506000	3.524025000	0.890381000
C	2.639779000	4.577562000	-0.000959000
H	1.999699000	4.505209000	-0.893585000
H	3.129835000	5.562938000	-0.001026000
H	1.999085000	4.505635000	0.891260000
C	3.188492000	-1.299396000	-0.000130000
C	2.651304000	-0.011409000	-0.000041000
C	1.232422000	-0.030581000	-0.000191000
C	0.709534000	-1.336291000	-0.000337000
C	-0.709553000	-1.336281000	-0.000322000
C	-1.232422000	-0.030565000	-0.000220000
C	-2.651300000	-0.011359000	-0.000155000
C	-3.188516000	-1.299336000	-0.000194000
C	-4.623470000	-1.434512000	0.000024000
C	-3.625371000	1.068999000	0.000023000
C	-3.683972000	3.482166000	0.000416000
H	-4.329388000	3.524243000	-0.890224000
H	-4.329752000	3.523657000	0.890818000
C	-2.639477000	4.577589000	0.001000000
H	-1.999425000	4.506304000	-0.891731000
H	-1.998753000	4.504532000	0.893106000
H	-3.129467000	5.562996000	0.002175000
C	-6.352764000	-3.112426000	0.000943000
H	-6.842387000	-2.690041000	-0.889845000
H	-6.842003000	-2.688784000	0.891341000
C	-6.384963000	-4.625678000	0.002008000
H	-5.882000000	-5.028149000	-0.890513000
H	-7.428119000	-4.976557000	0.002421000
H	-5.881705000	-5.026908000	0.894921000
C	-5.423405000	0.348345000	1.910390000
C	-7.333026000	-0.239753000	-0.000684000
C	-5.422414000	0.348544000	-1.910711000
C	-6.390559000	2.093605000	-0.000482000

11$^{\bullet-}$: E= -5262.948040

Cr	5.562554000	0.437302000	-0.000224000
Cr	-5.562552000	0.437264000	0.000248000
S	1.958198000	-2.594763000	-0.000150000
S	-0.000003000	1.184201000	0.000015000
S	-1.958166000	-2.594781000	0.000048000
O	5.337344000	0.271231000	3.042315000
O	8.449871000	-0.479397000	-0.000304000
O	6.893981000	3.146688000	-0.000127000
O	5.337223000	0.271473000	-3.042767000
O	4.999045000	-2.742375000	-0.000322000
O	2.939169000	2.212292000	-0.000124000
O	-5.337214000	0.271488000	3.042796000

O	-8.449909000	-0.479296000	0.000275000
O	-5.337337000	0.271547000	-3.042311000
O	-6.894309000	3.146467000	0.000298000
O	-4.998979000	-2.742438000	0.000232000
O	-2.939185000	2.212262000	0.000183000
C	5.437920000	0.344839000	1.895037000
C	7.327229000	-0.180311000	-0.000276000
C	6.337512000	2.124673000	-0.000164000
C	5.437844000	0.344991000	-1.895487000
C	4.604185000	-1.462957000	-0.000260000
C	6.383333000	-3.077196000	-0.000427000
H	6.867221000	-2.639276000	0.887658000
H	6.867117000	-2.639145000	-0.888504000
C	6.488637000	-4.589967000	-0.000543000
H	5.999251000	-5.013091000	-0.891777000
H	5.999352000	-5.013221000	0.890683000
H	7.545943000	-4.898311000	-0.000625000
C	3.593537000	1.056045000	-0.000155000
C	3.623359000	3.467473000	-0.000166000
H	4.271731000	3.523341000	-0.888486000
H	4.271739000	3.523395000	0.888146000
C	2.567453000	4.554821000	-0.000193000
H	1.925189000	4.471928000	-0.890701000
H	3.043824000	5.547586000	-0.000217000
H	1.925189000	4.471972000	0.890319000
C	3.207239000	-1.332352000	-0.000182000
C	2.646124000	-0.029601000	-0.000128000
C	1.238928000	-0.057108000	-0.000065000
C	0.702414000	-1.367449000	-0.000064000
C	-0.702393000	-1.367456000	0.000004000
C	-1.238920000	-0.057121000	0.000052000
C	-2.646117000	-0.029627000	0.000119000
C	-3.207221000	-1.332381000	0.000128000
C	-4.604166000	-1.463005000	0.000206000
C	-3.593537000	1.056008000	0.000189000
C	-3.623412000	3.467423000	0.000260000
H	-4.271813000	3.523340000	-0.888037000
H	-4.271770000	3.523257000	0.888592000
C	-2.567539000	4.554804000	0.000284000
H	-1.925290000	4.471990000	-0.890242000
H	-1.925254000	4.471915000	0.890778000
H	-3.043940000	5.547554000	0.000335000
C	-6.383245000	-3.077353000	0.000337000
H	-6.867171000	-2.639446000	-0.887732000
H	-6.867055000	-2.639364000	0.888430000
C	-6.488447000	-4.590131000	0.000413000
H	-5.999139000	-5.013328000	-0.890828000
H	-7.545732000	-4.898547000	0.000494000
H	-5.999026000	-5.013246000	0.891632000
C	-5.437830000	0.344900000	1.895508000
C	-7.327226000	-0.180365000	0.000270000
C	-5.437913000	0.344938000	-1.895019000
C	-6.337496000	2.124639000	0.000281000

11^{-2}: E= -5262.944984

Cr	5.618574000	0.439912000	-0.000278000
Cr	-5.618606000	0.439958000	0.000298000
S	1.956103000	-2.592564000	-0.000145000
S	-0.000013000	1.188635000	0.000016000

S	-1.956165000	-2.592546000	0.000056000
O	5.413869000	0.283790000	3.037405000
O	8.476639000	-0.528748000	-0.000414000
O	6.934110000	3.148447000	-0.000287000
O	5.413603000	0.283892000	-3.037948000
O	5.001933000	-2.778132000	-0.000304000
O	2.946739000	2.239328000	-0.000125000
O	-5.413494000	0.283750000	3.037948000
O	-8.476555000	-0.529096000	0.000417000
O	-5.413794000	0.283874000	-3.037379000
O	-6.933553000	3.148806000	0.000417000
O	-5.002009000	-2.778087000	0.000213000
O	-2.946756000	2.239364000	0.000187000
C	5.495439000	0.351326000	1.883397000
C	7.353763000	-0.199580000	-0.000361000
C	6.380735000	2.116167000	-0.000281000
C	5.495273000	0.351390000	-1.883945000
C	4.604139000	-1.478047000	-0.000263000
C	6.378843000	-3.092041000	-0.000384000
H	6.871156000	-2.654806000	0.885382000
H	6.871063000	-2.654767000	-0.886182000
C	6.503322000	-4.606331000	-0.000424000
H	6.014145000	-5.033848000	-0.890512000
H	6.014240000	-5.033888000	0.889698000
H	7.563566000	-4.908365000	-0.000487000
C	3.593121000	1.058543000	-0.000173000
C	3.658720000	3.465546000	-0.000155000
H	4.312632000	3.517746000	-0.886422000
H	4.312725000	3.517736000	0.886043000
C	2.630358000	4.582398000	-0.000094000
H	1.983619000	4.511510000	-0.888865000
H	3.127753000	5.565967000	-0.000115000
H	1.983715000	4.511500000	0.888746000
C	3.227984000	-1.329069000	-0.000190000
C	2.665266000	-0.011061000	-0.000141000
C	1.244863000	-0.047998000	-0.000069000
C	0.705525000	-1.347287000	-0.000062000
C	-0.705576000	-1.347279000	0.000011000
C	-1.244901000	-0.047985000	0.000060000
C	-2.665303000	-0.011035000	0.000136000
C	-3.228032000	-1.329042000	0.000143000
C	-4.604190000	-1.478007000	0.000213000
C	-3.593145000	1.058580000	0.000204000
C	-3.658725000	3.465585000	0.000247000
H	-4.312738000	3.517799000	-0.885946000
H	-4.312630000	3.517774000	0.886520000
C	-2.630355000	4.582430000	0.000199000
H	-1.983719000	4.511542000	-0.888647000
H	-1.983610000	4.511519000	0.888964000
H	-3.127742000	5.566004000	0.000243000
C	-6.378924000	-3.091961000	0.000289000
H	-6.871232000	-2.654682000	-0.885459000
H	-6.871129000	-2.654703000	0.886106000
C	-6.503443000	-4.606248000	0.000279000
H	-6.014376000	-5.033787000	-0.889860000
H	-7.563694000	-4.908256000	0.000338000
H	-6.014272000	-5.033807000	0.890350000
C	-5.495286000	0.351352000	1.883960000
C	-7.353807000	-0.199491000	0.000370000
C	-5.495473000	0.351428000	-1.883379000
C	-6.380747000	2.116221000	0.000369000

S9. References

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[4] van der Westhuizen, B.; Swarts, P. J.; Strydom, I.; Liles, D. C.; Fernández, I.; Swarts, J. C.; Bezuidenhout, D. I. *Dalton Trans.* **2013**, *42* (15), 5367–5378.

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