Trifluoromethyl Substituted Benzocyclobutenone and Benzocyclobutenedione: The Structure Anomaly of (Benzocyclobutenedione)tricarbonylchromium Complexes

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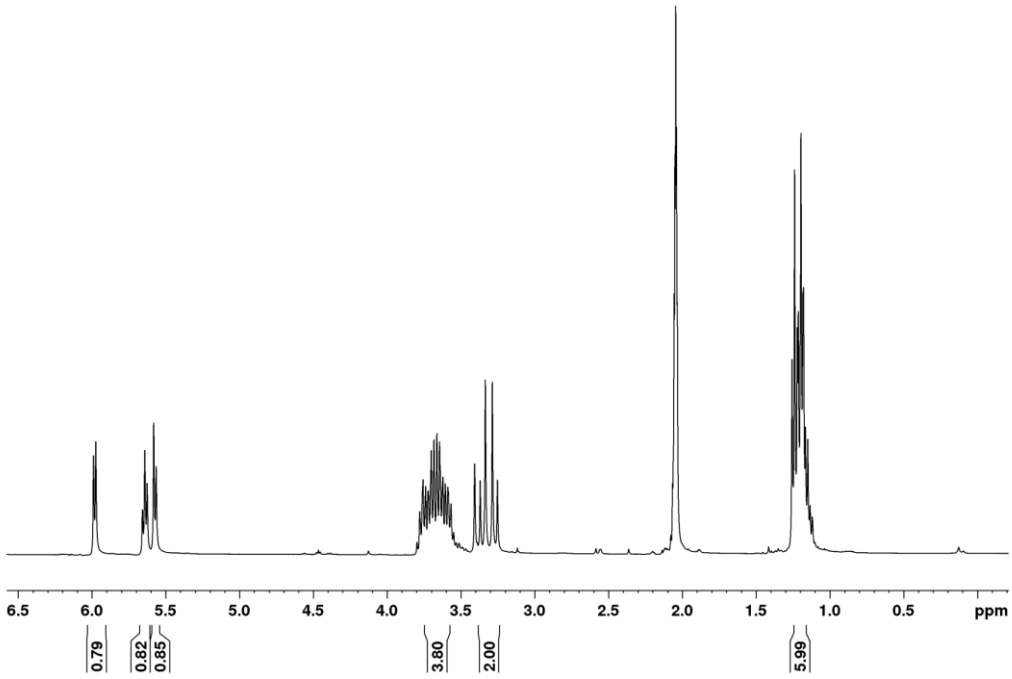
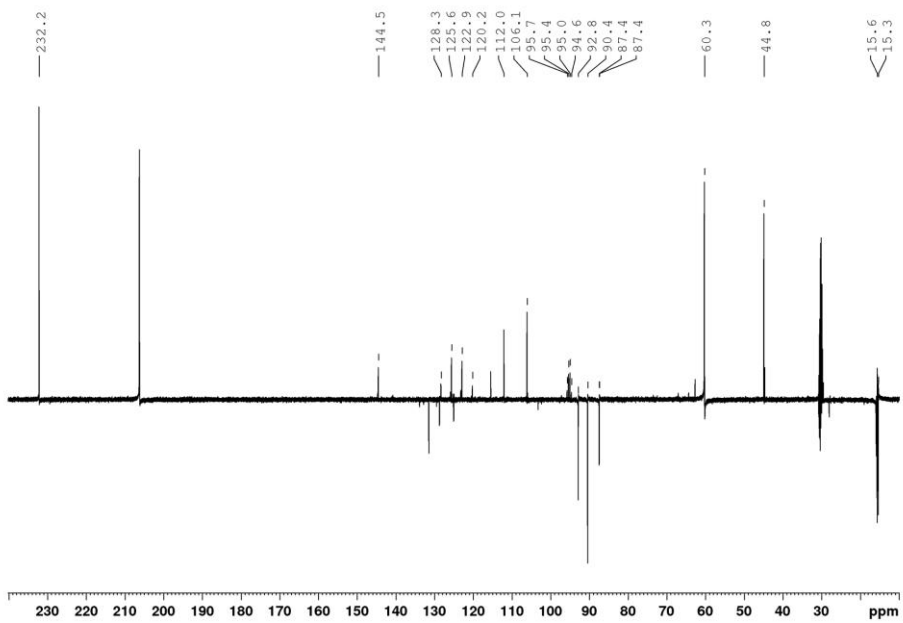
Supporting Information

***rac*-Tricarbonyl[{η^6-[1,1-diethoxy-6-(trifluoromethyl)benzocyclobutene]}-chromium(0) (*rac*-6):**

^{1}H NMR:

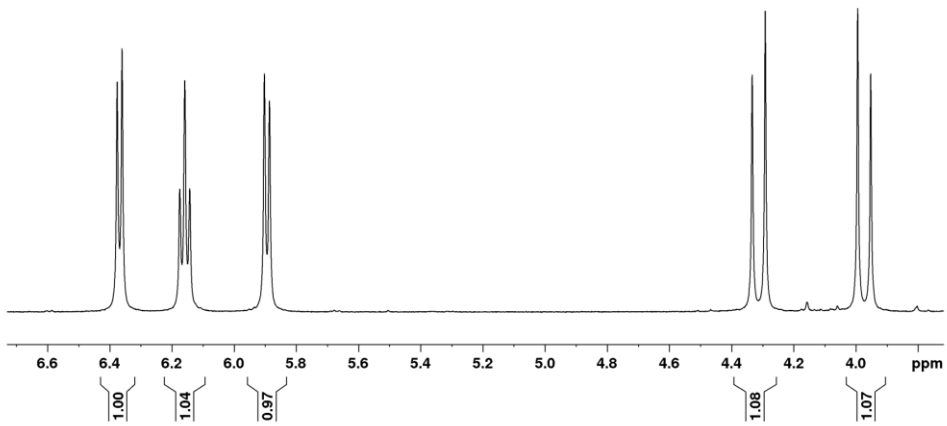


^{13}C NMR:

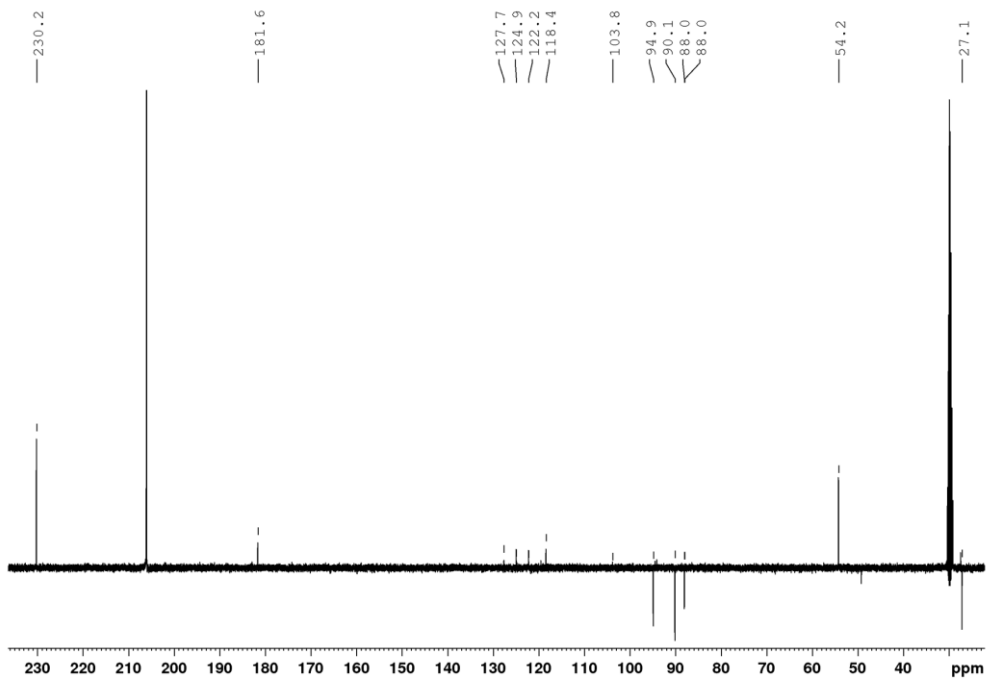


***rac*-Tricarbonyl{η^6-[6-(trifluoromethyl)benzocyclobutenone]chromium(0) (7):**

^{1}H NMR:

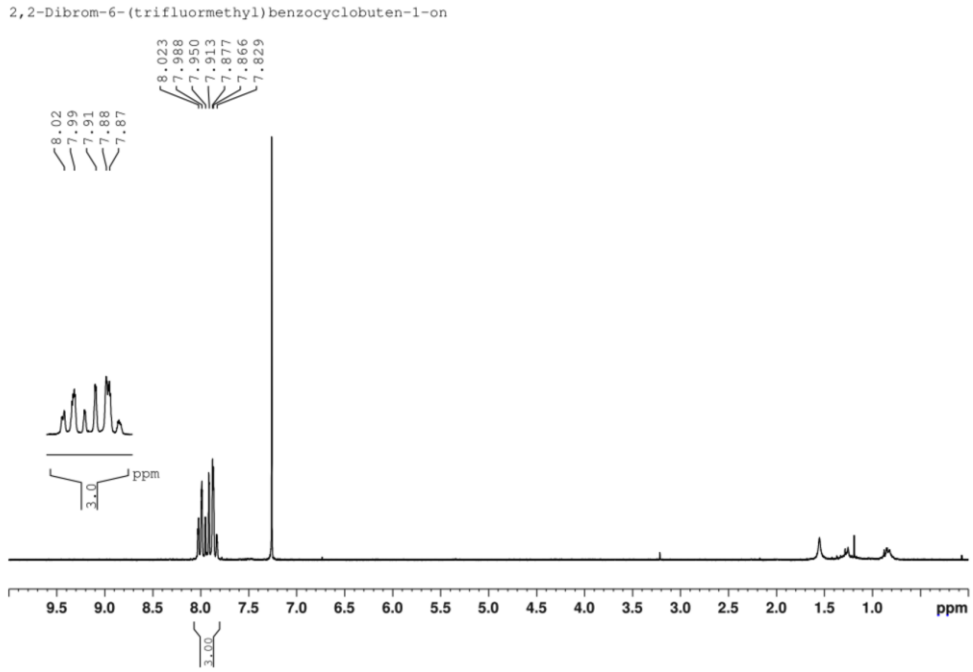


^{13}C NMR:

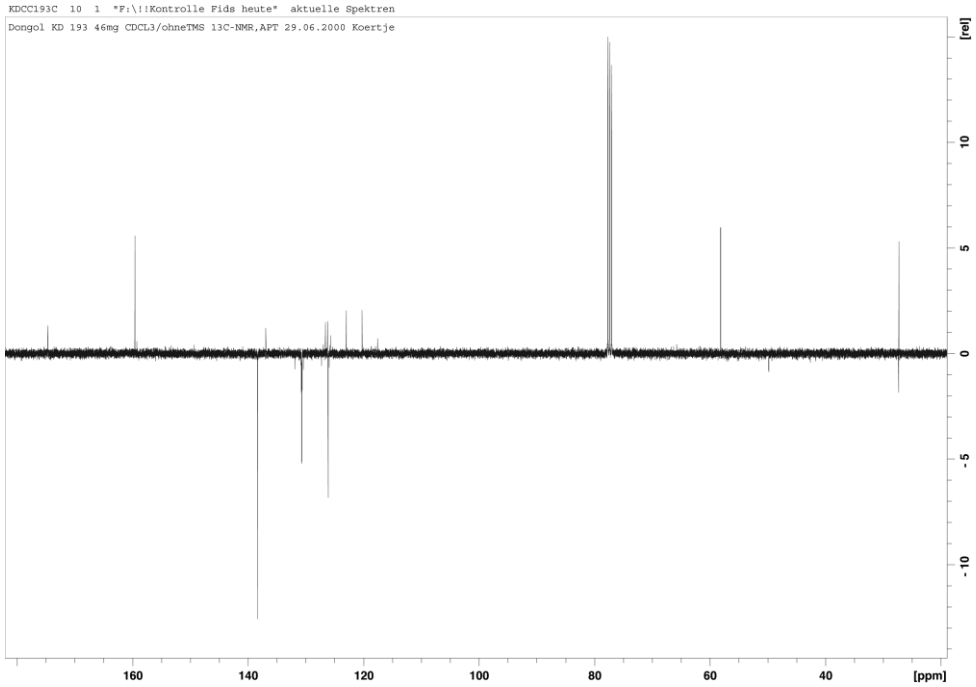


2,2-Dibromo-6-(trifluoromethyl)benzocyclobutenone (9):

^{1}H NMR:

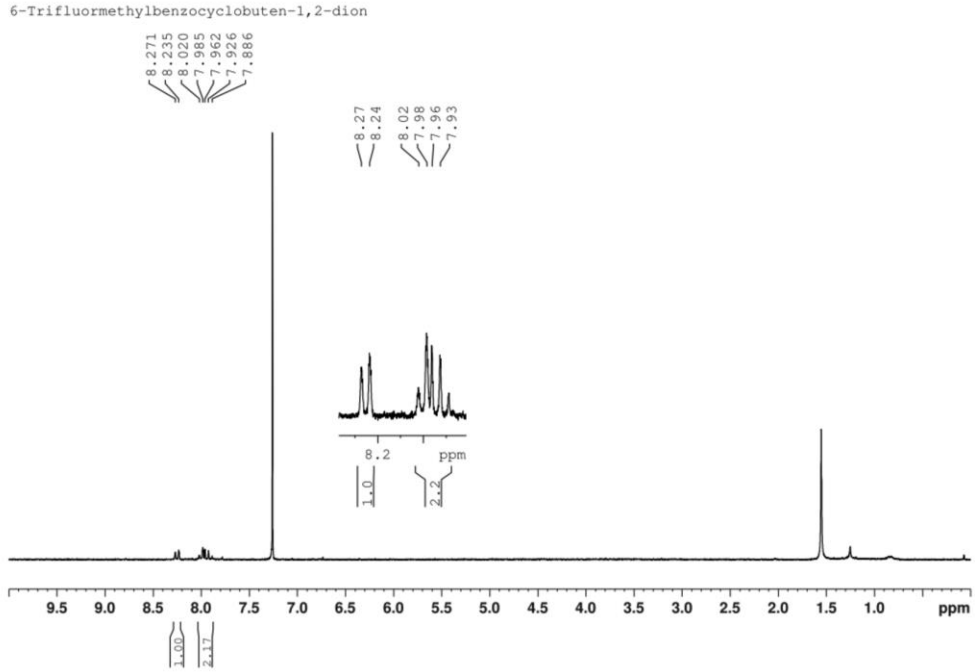


^{13}C NMR:

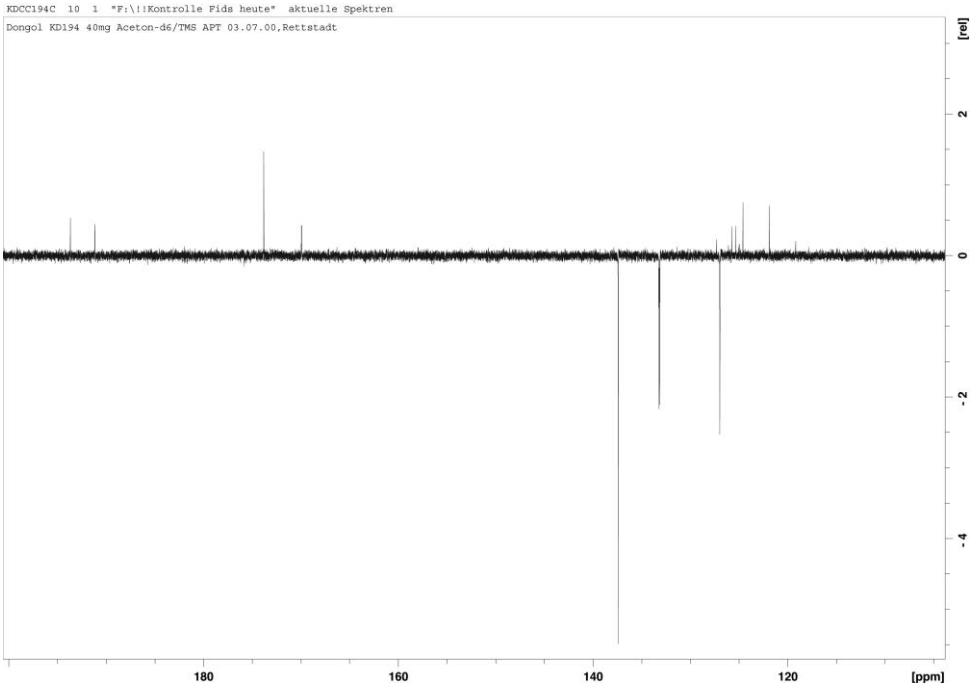


3-(Trifluoromethyl)benzocyclobutenedione (10):

^{1}H NMR:

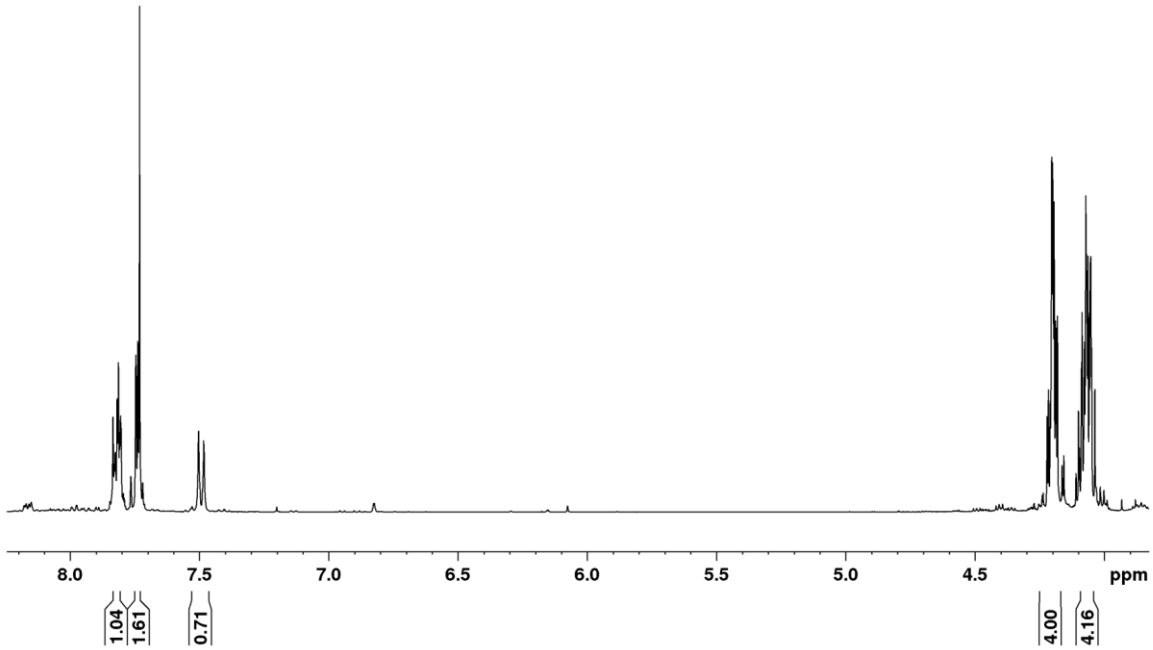


^{13}C NMR

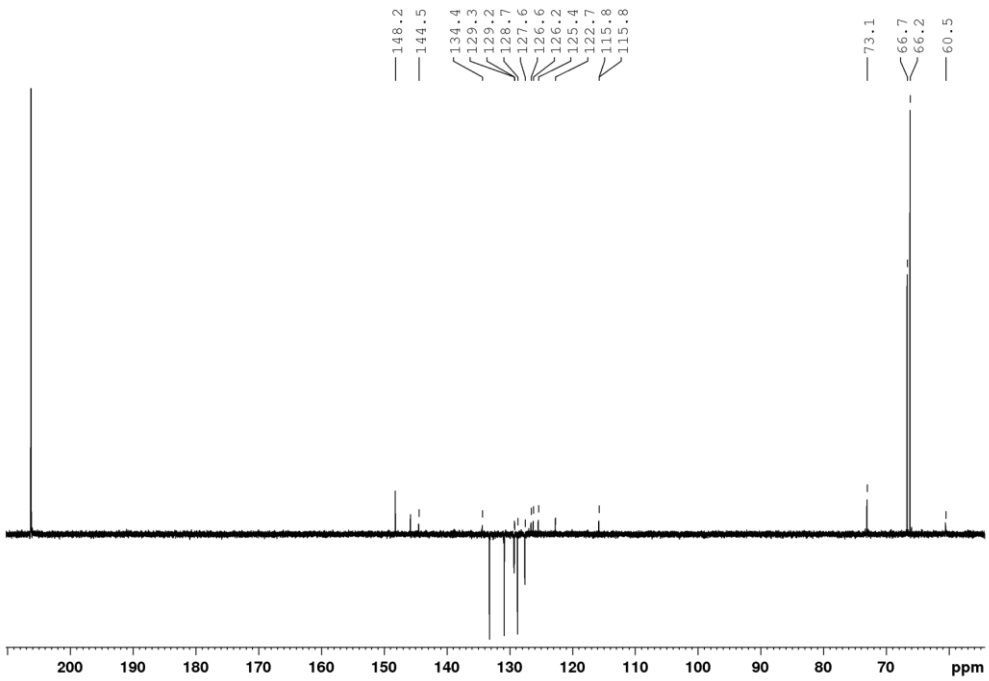


1,2-Bis(ethylenedioxy)-3-(trifluoromethyl)benzocyclobutene (11):

^{1}H NMR:

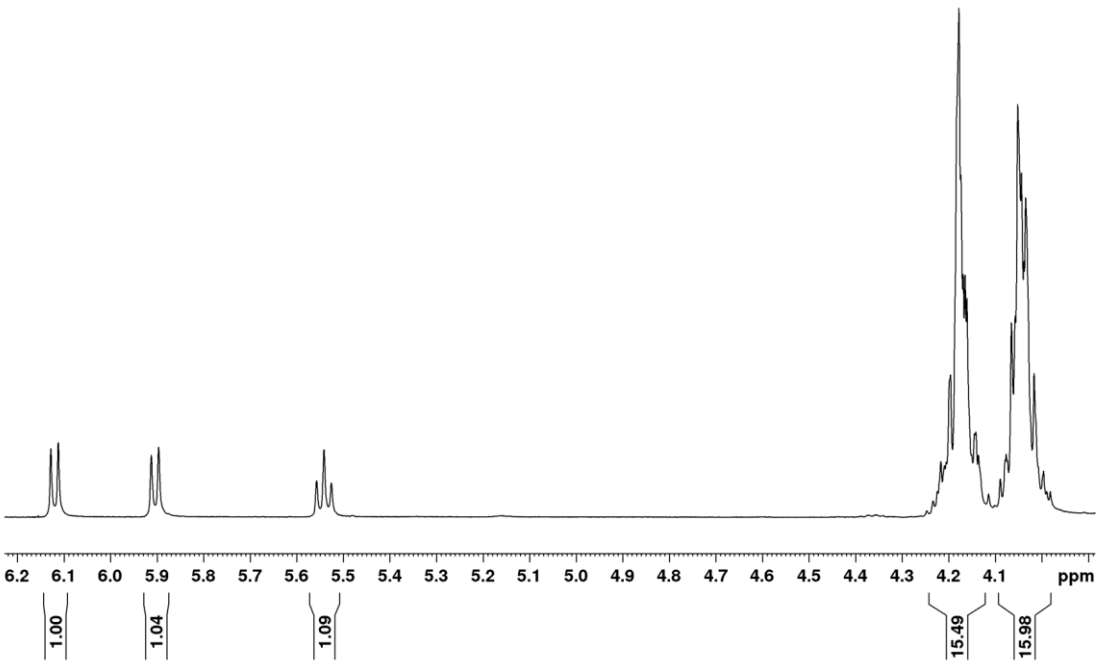


^{13}C NMR

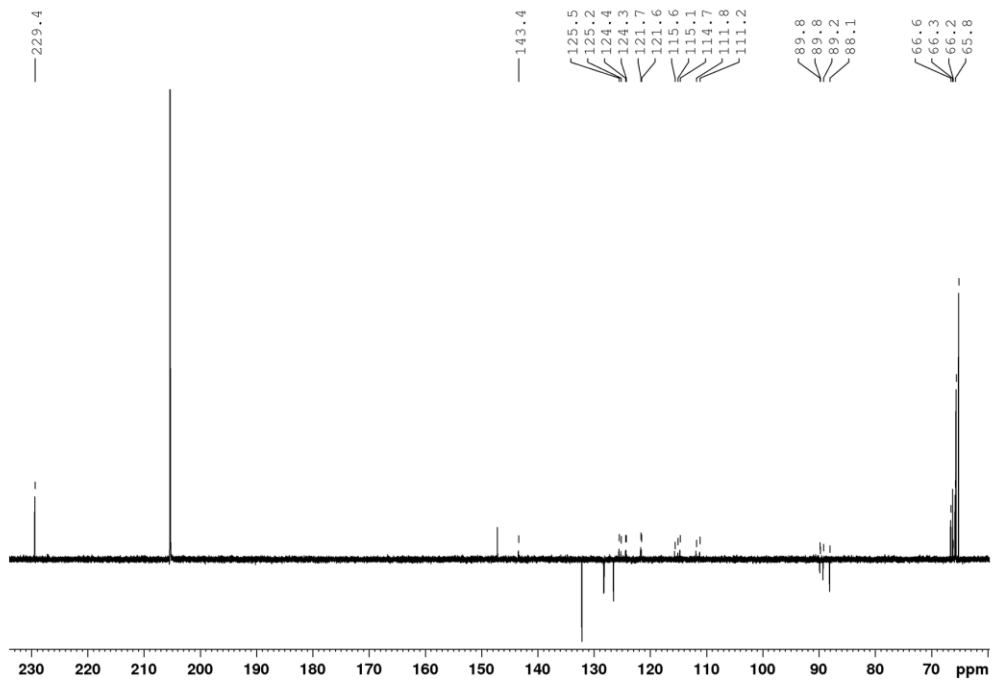


***rac*-{η^6-[1,2-Bis(ethylendioxy)-3-(trifluoromethyl)benzocyclobutene]}tricarbonylchromium(0) (12):**

^{1}H NMR:

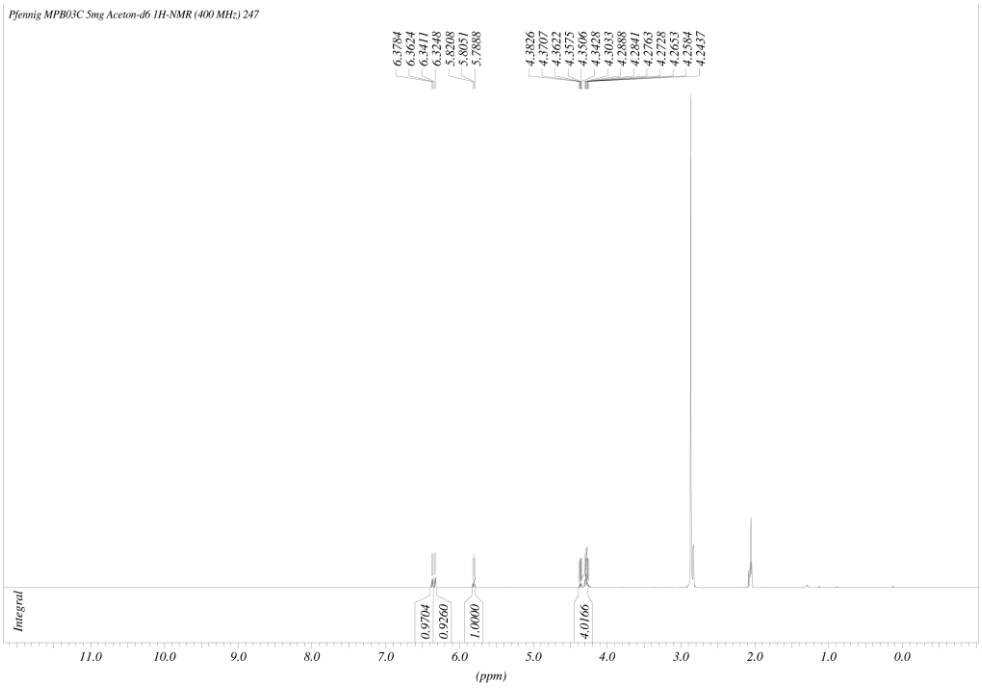


^{13}C NMR

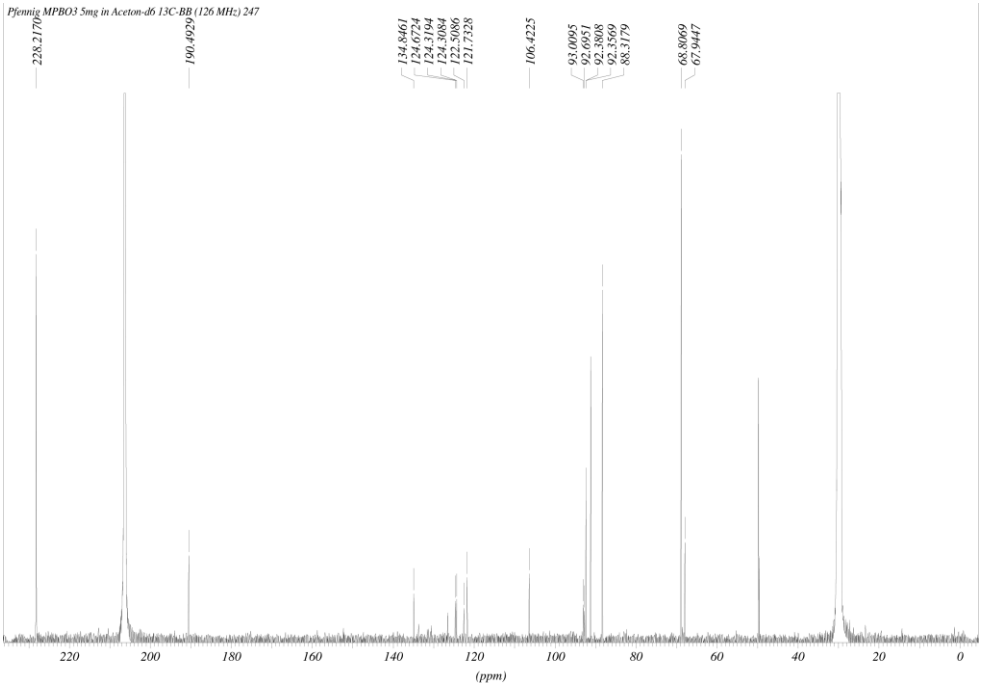


{η^6-[2-(Ethylendioxy)-3-(trifluoromethyl)benzocyclobutenone]}tricarbonyl-chromium(0) (*rac*-14):

^{1}H NMR:

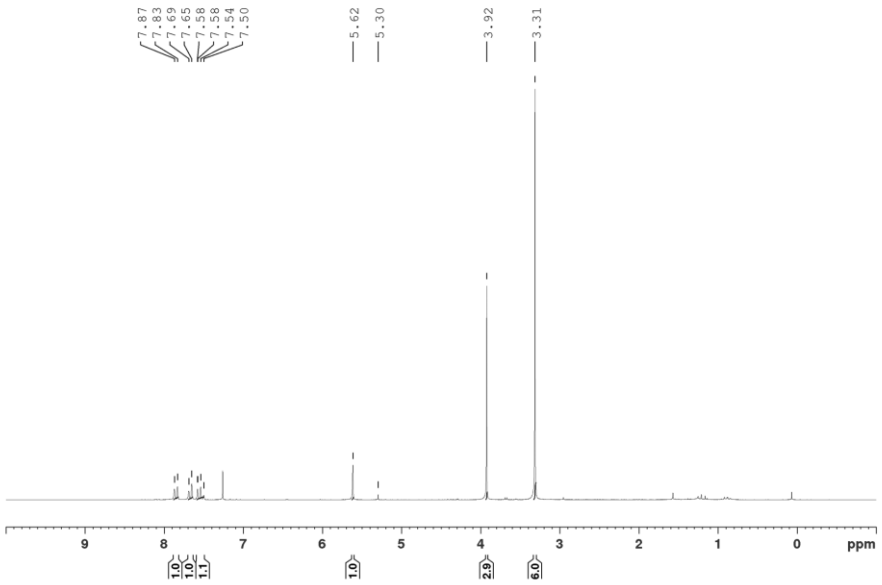


^{13}C NMR:

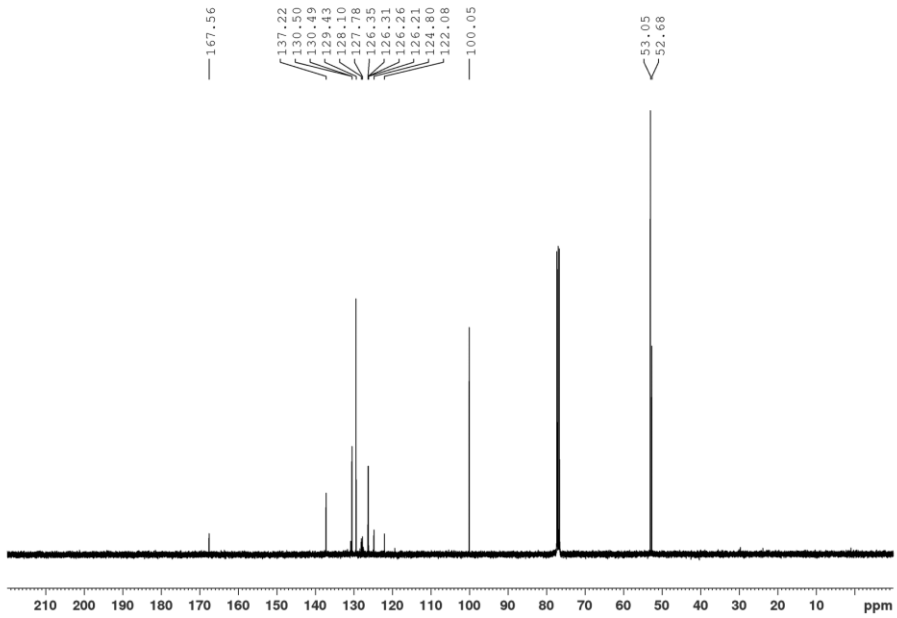


Methyl 2-(dimethoxymethyl)-6-(trifluoromethyl)benzoate (28):

^{1}H NMR:

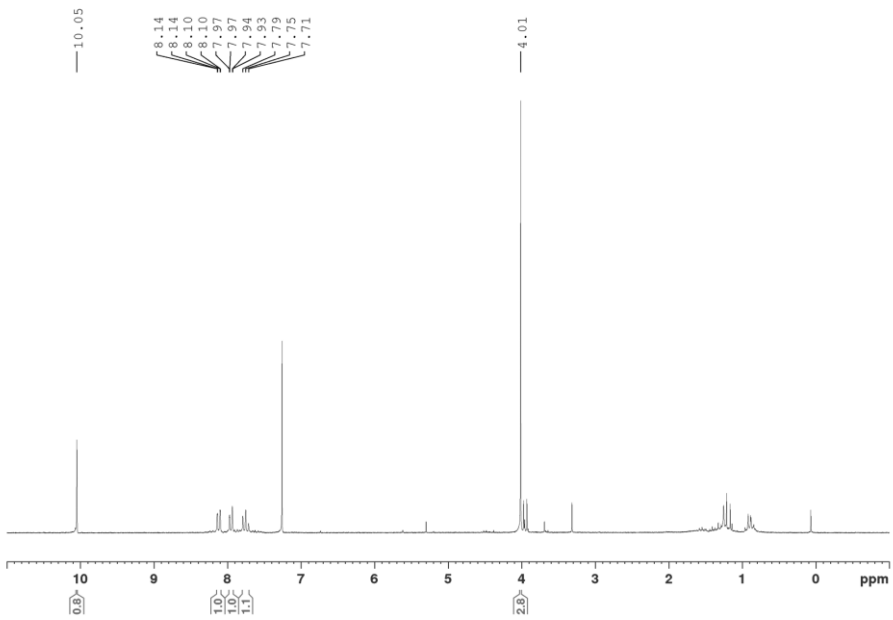


^{13}C NMR:

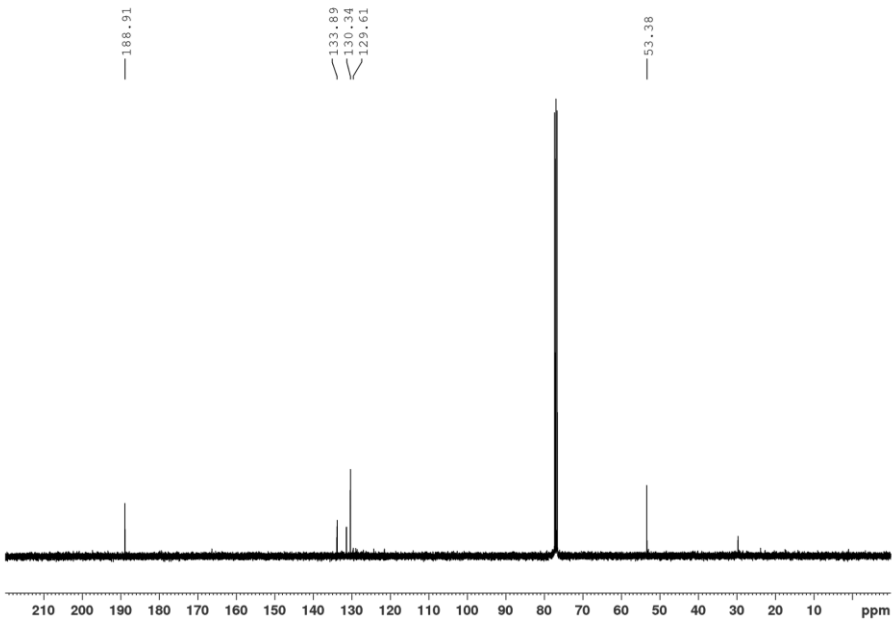


2-(Methoxycarbonyl)-3-(trifluoromethyl)benzic acid (29):

^{1}H NMR:

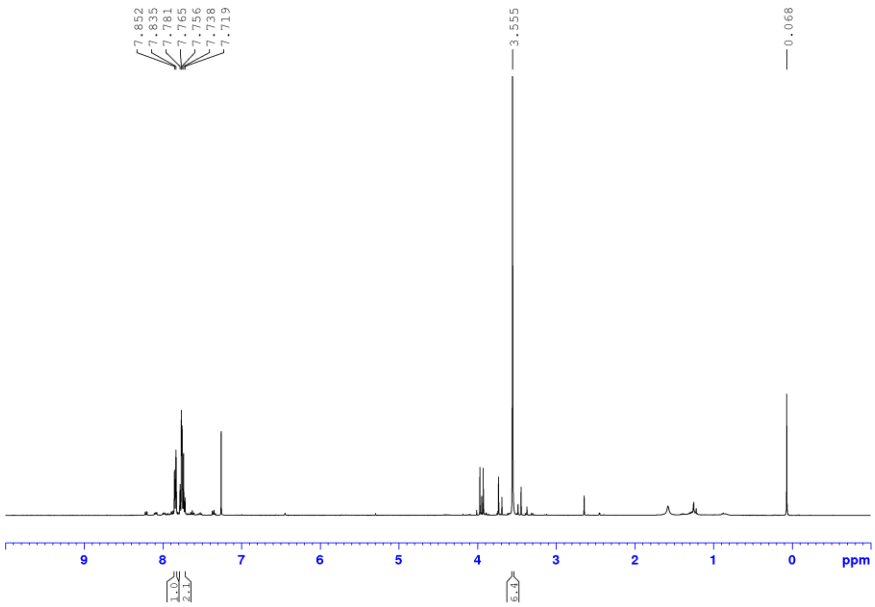


^{13}C NMR:

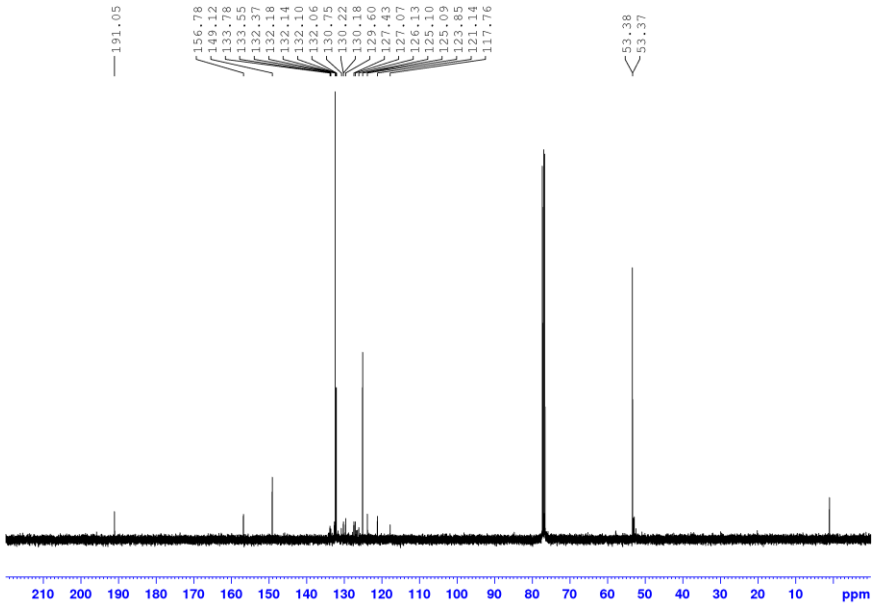


2,2-Dimethoxy-3-(trifluoromethyl)benzocyclobuten-1-one (30):

^{1}H NMR:

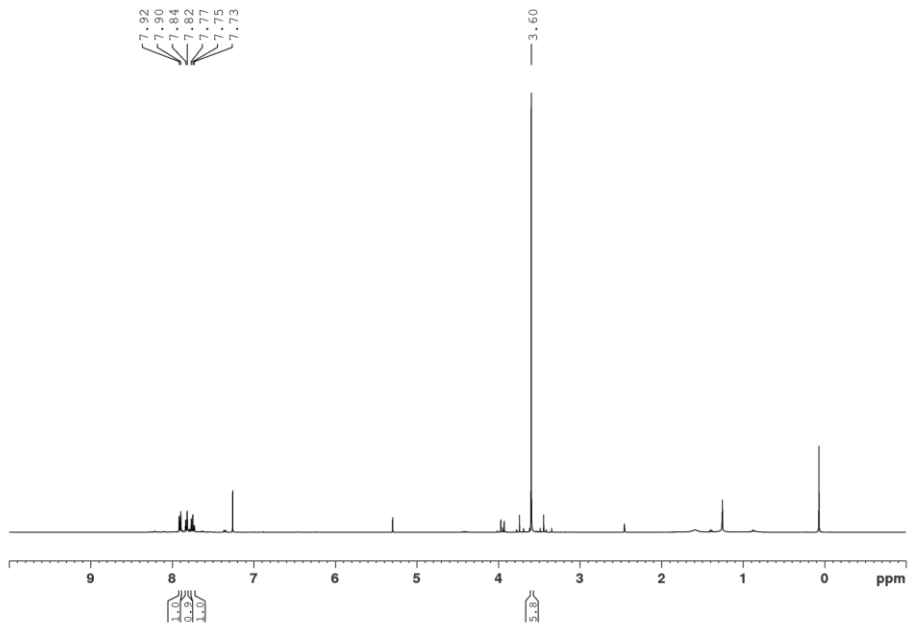


^{13}C NMR:

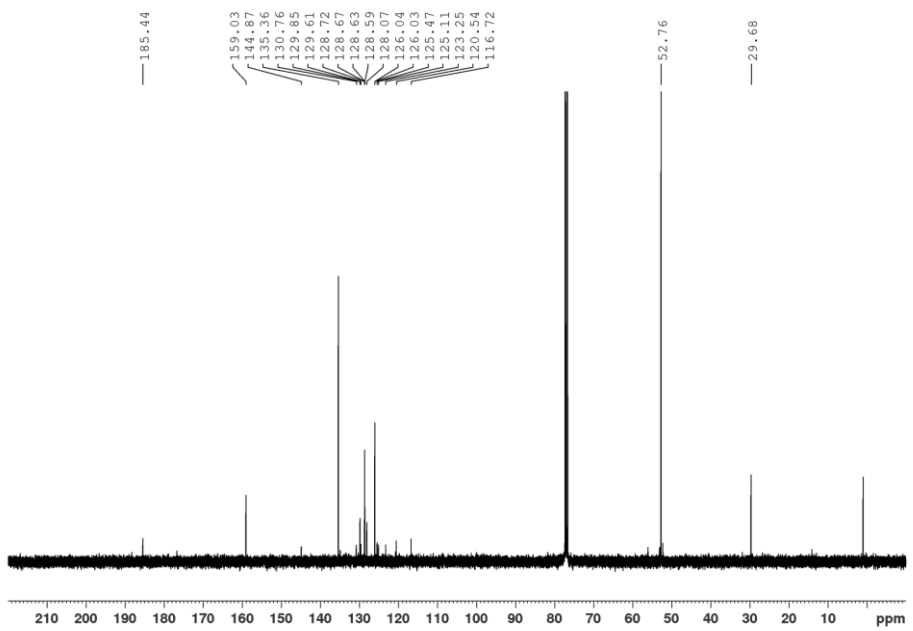


2,2-Dimethoxy-6-(trifluoromethyl)benzocyclobuten-1-one (31):

^{1}H NMR:

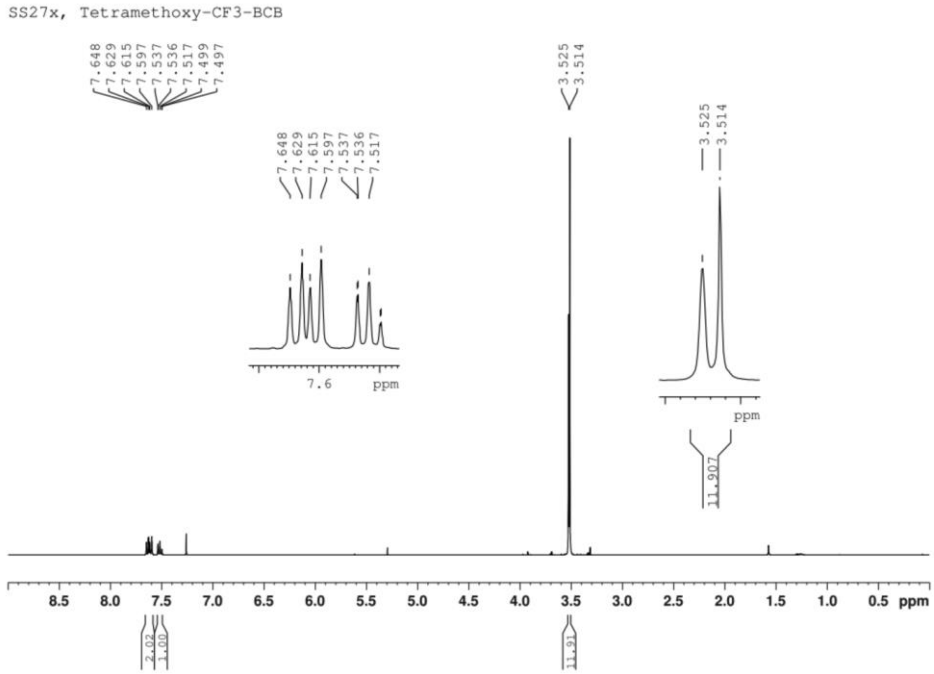


^{13}C NMR:

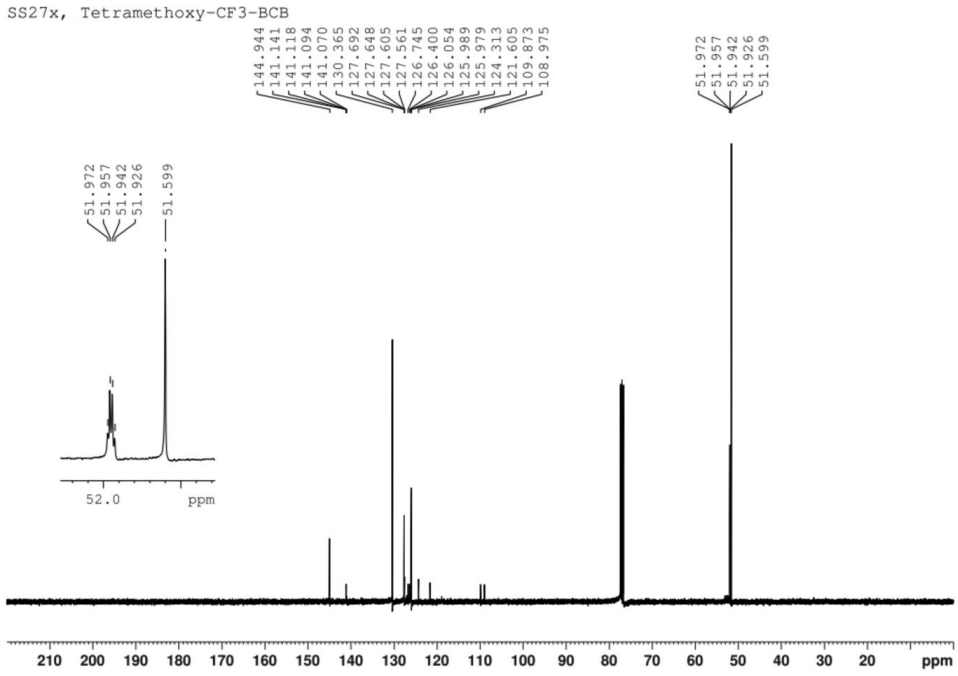


1,1,2,2-Tetramethoxy-3-(trifluoromethyl)benzocyclobutene (32):

^{1}H NMR:

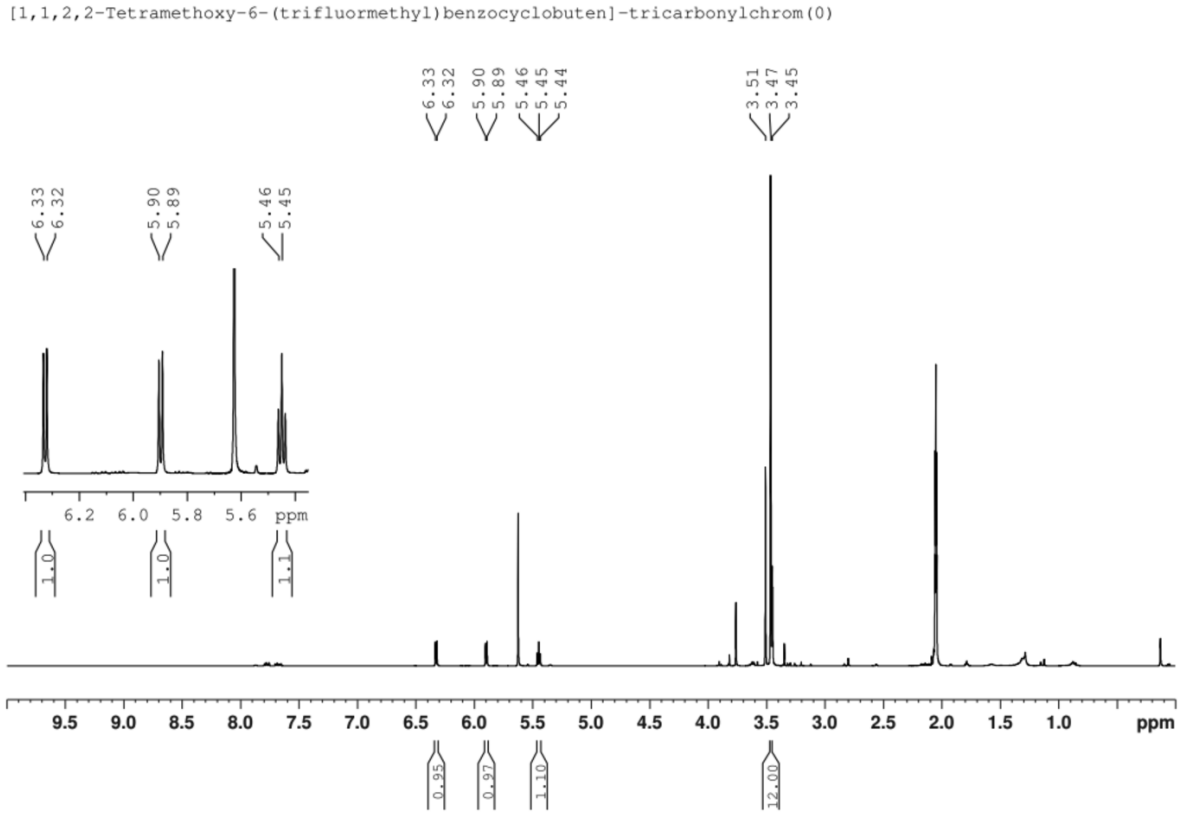


^{13}C NMR:

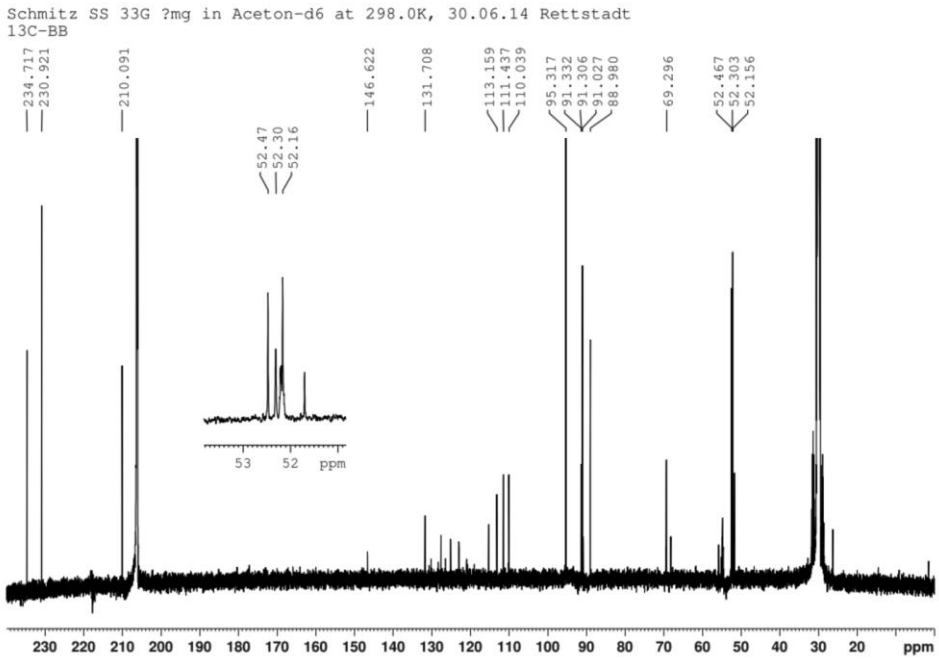


***rac*-Tricarbonyl[1,1,2,2-tetramethoxy-3-(trifluoromethyl)benzocyclobutene]-chromium(0) (*rac*-33):**

^{1}H NMR:

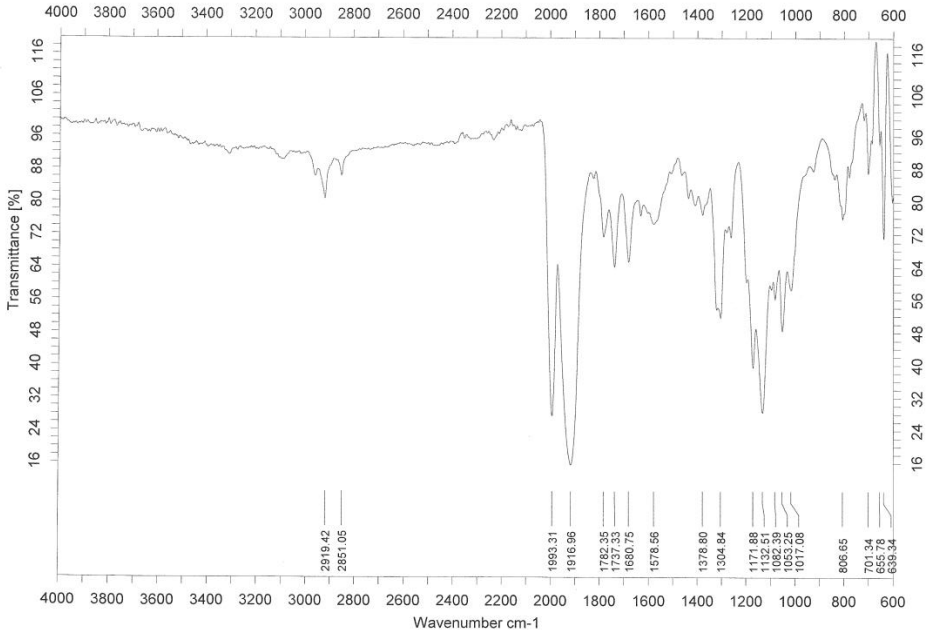


^{13}C NMR:

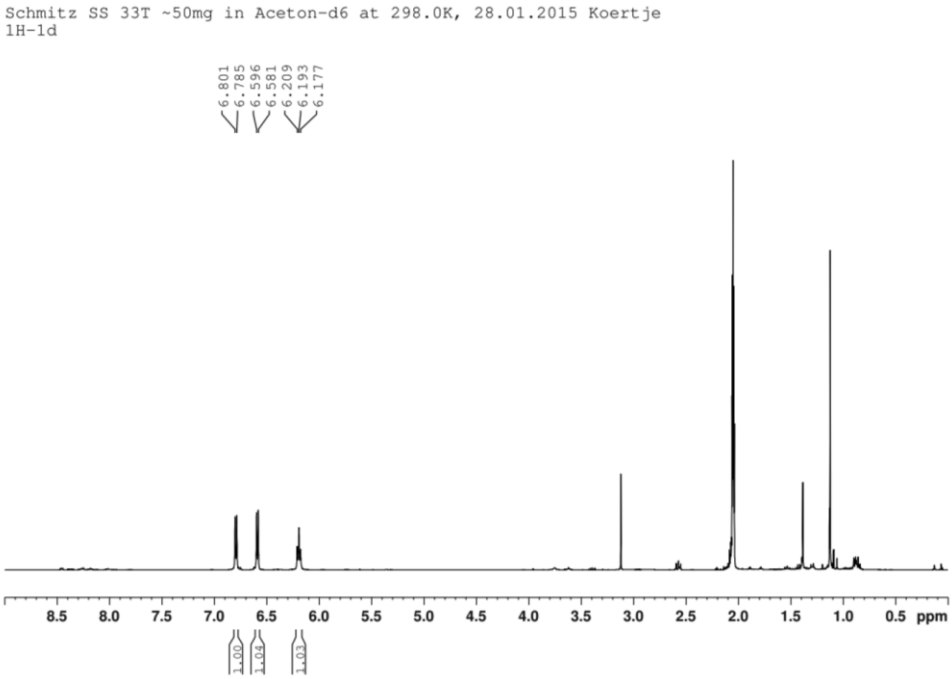


***rac*-Tricarbonyl[(3-trifluormethyl)benzocyclobutenedione]chromium(0) (*rac*-13):**

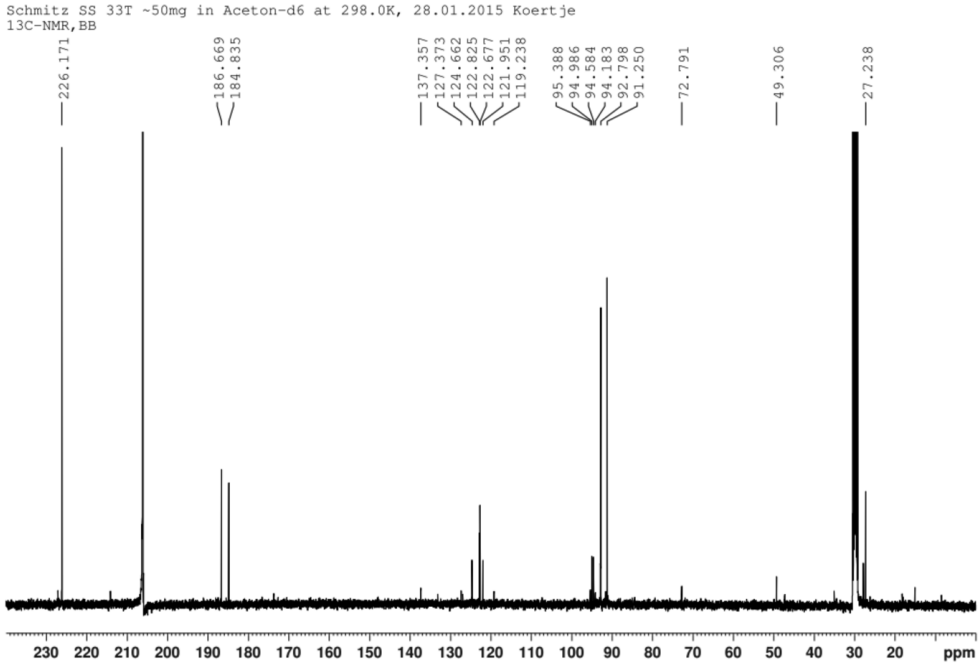
IR:



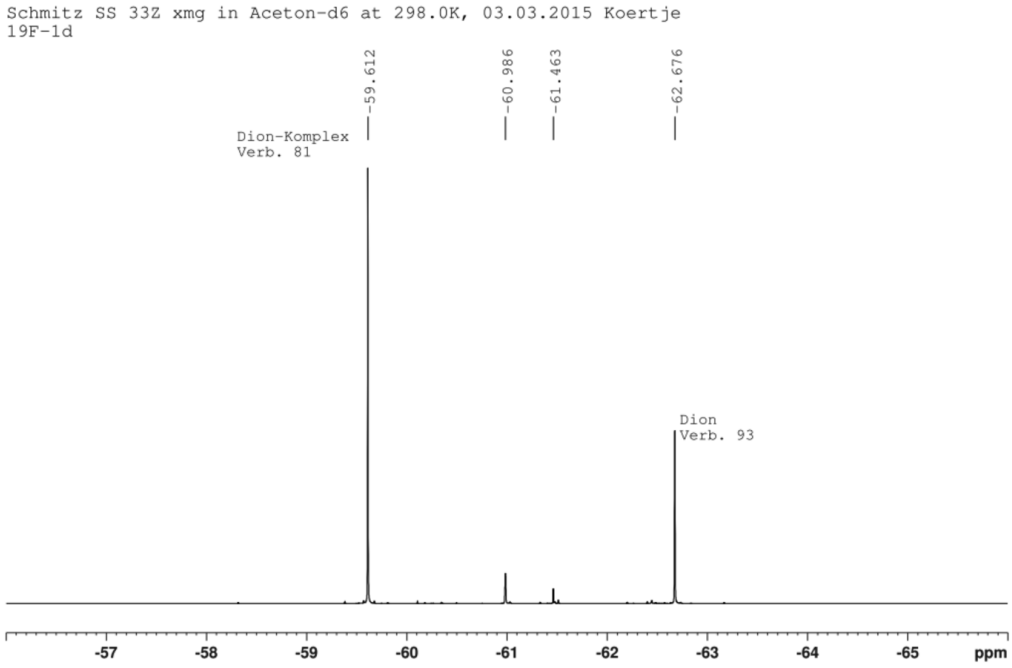
^{1}H NMR:



^{13}C-NMR:



^{19}F NMR:



Crystal structure analysis of *rac*-tricarbonyl-[η^6-(benzocyclobutenone)-chromium(0) (*rac*-1):[47]

$C_{11}H_6CrO_4$, molecular weight 254.16, crystal system monoclinic, space group P 21/c (no. 14), a = 7.960(1), b = 20.393(4), c = 12.927(2) Å, α =90, β = 100.62(2), γ = 90°, V = 2062.5(6) Å^3, Z = 8, d_{calc} = 1.637 gcm^{-3}, F(000) = 1024, μ = 0.11 cm^{-1}, crystal: red fragment, size 0.30 x 0.24 x 0.18 mm, Stoe IPDS (Imaging Plate) diffractometer, T = 300K, λ (MoK$_\alpha$) = 0.71073 A, $2\theta_{min}$ = 3.7°, $2\theta_{max}$ = 45°, 160 exposures, $\Delta\Phi$ = 1.2°, 9511 measured reflections, $-8 \leq h \leq 8$, $-21 \leq k \leq 21$, $-13 \leq l \leq 13$, 2625 unique reflections, R_{int} = 0.12, 1080 observed reflections ($I > 2\sigma(I)$), completeness of data 97.5 %, no absorption correction, no extinction correction, structure solution with direct methods with SHELXS-86, refinement with SHELXL-93, hydrogen atoms in geometrically calculated positions, N_{par} = 289, R = 0.08, wR_2 = 0.16, S = 1.04, minimal and maximal residual electron density -0.48, 0.86 e/Å^3. There are two molecules in the asymmetric unit, which differ in the atomic distances.

We do not interpret these differences, because the crystal was of bad quality.

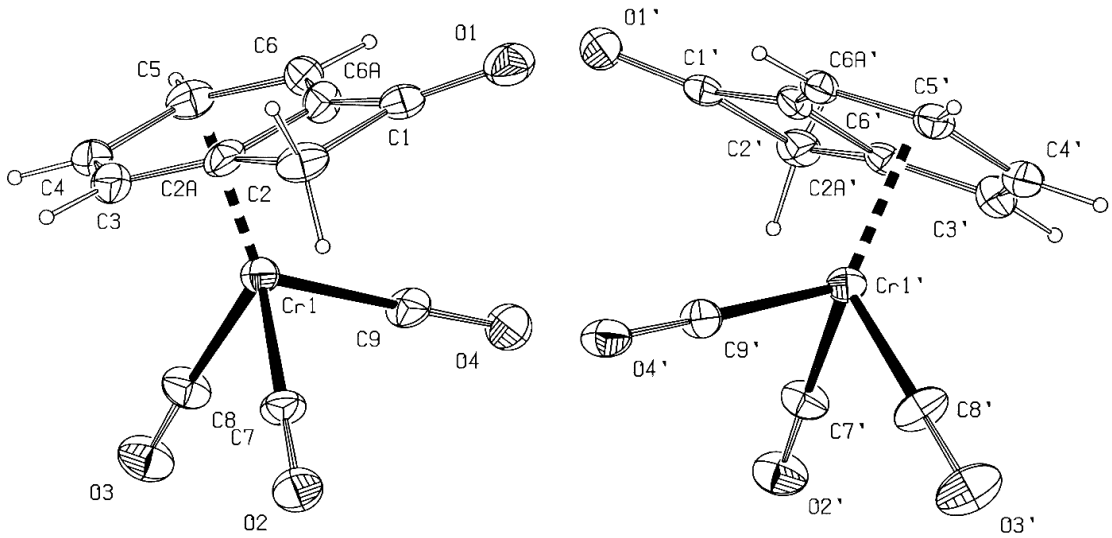


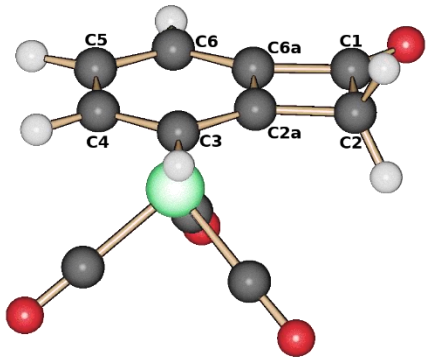
Figure S1. Structure of *rac*-**1** in the crystal.

Table S1. Bond lengths and torsional angles in *rac*-**1**.

Bond / Torsional Angle	**Molecule 1** **Bond Length [pm]** **Torsional Angle [°]**	**Molecule 2** **Bond Length [pm]** **Torsional Angle [°]**
Cr-C9	178.1(14)	180.9(13)
Cr-C7	179.7(13)	180.4(14)
Cr-C8	182.9(14)	179.9(12)
Cr-C2a	215.8(12)	217.3(10)
Cr-C6a	217.5(13)	216.7(10)
Cr-C4	218.7(12)	218.9(13)
Cr-C6	219.7(12)	218.4(11)
Cr-C3	221.0(12)	218.4(13)
Cr-C5	221.6(12)	220.6(12)
O1-C1	123.3(16)	118.7(13)
O2-C7	116.5(11)	115.8(12)
O3-C8	114.5(12)	115.1(12)
O4-C9	117.5(13)	116.3(12)
C1-C6a	140.5(19)	150.6(17)
C1-C2	154.9(18)	152.3(16)
C1-C2a	201(2)	207(2)
C2-C2a	154.0(17)	153.5(16)
C2a-C3	134.1(17)	135.4(15)
C3-C4	137.7(16)	135.1(16)
C4-C5	144.5(17)	142.3(16)
C5-C6	136.0(16)	135.8(15)
C6-C6a	137.4(16)	135.6(14)
C1-C6a-C2a-C3	178.6(13	–179.0(9)
C2-C2a-C6a-C6	179.4(12)	179.6(9)

Table S2. Comparison of VWN, PBE and PBE0 optimized structure parameters of compound *rac*-**1** with experimental crystal structure data.

Bond [pm]	VWN	PBE	PBE0	Experiment
C1-C2	155.8	158.0	156.2	152.3(16)
C1-C6a	149.2	150.5	149.6	150.6(17)
C2-C2a	150.8	152.6	151.8	153.5(16)
C2a-C3	139.5	140.7	139.8	135.4(15)
C2a-C6a	141.9	142.8	141.3	142.4(14)
C3-C4	141.5	142.5	141.4	135.1(16)
C4-C5	141.5	142.8	141.8	142.3(16)
C5-C6	140.9	141.9	140.6	135.8(15)
C6-C6a	140.5	141.9	140.9	135.6(14)
C1-O1	119.6	120.5	119.1	118.7(13)
C2a-Cr	214.7	220.8	218.5	217.3(10)
C3-Cr	218.9	224.4	221.9	218.4(13)
C4-Cr	213.8	219.0	216.8	218.9(13)
C5-Cr	216.5	221.8	219.7	220.6(12)
C6-Cr	215.5	221.3	219.3	218.4(11)
C6a-Cr	214.9	220.7	218.2	216.7(10)
C1-Cr	317.9	326.3	323.2	322.1(14)
C2-Cr	323.8	332.4	329.3	328.6(13)
O1-Cr	414.9	424.0	419.7	418.8(10)
Dihedral [°]				
C1-C6a-C2a-C3	–176.6	–178.2	–177.8	–179.0(09)
C2-C2a-C6a-C6	175.8	178.0	177.9	179.6(09)



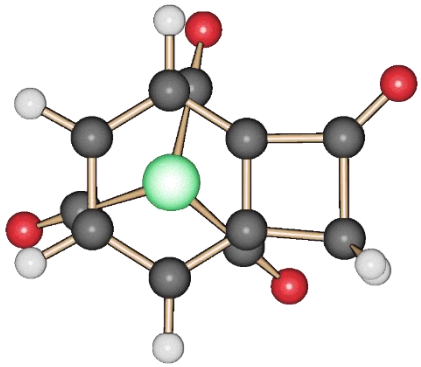
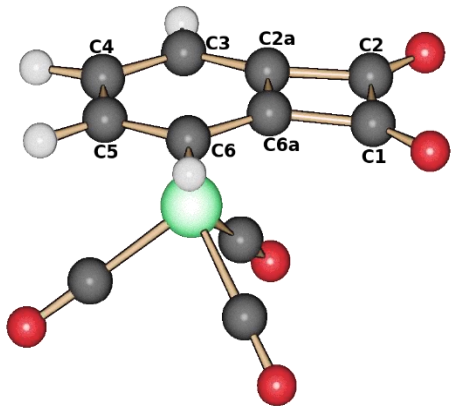


Table S3. Comparison of VWN, PBE and PBE0 optimized structure parameters of compound **2** with experimental crystal structure data.

Bond [pm]	VWN	PBE	PBE0	Experiment
C1-C2	158.4	160.2	158.3	156.6(7)
C1-C6a	150.6	152.0	150.7	150.7(6)
C2-C2a	150.6	152.0	150.7	150.4(6)
C2a-C3	140.3	141.5	140.6	140.7(3)
C2a-C6a	142.2	143.1	141.7	141.8(3)
C3-C4	140.6	141.7	140.6	139.9(4)
C4-C5	142.0	143.2	142.2	141.0(4)
C5-C6	140.6	141.7	140.6	139.9(4)
C6-C6a	140.3	141.5	140.6	140.7(3)
C1-O1	119.2	120.1	118.7	118.9(8)
C2-O2	119.2	120.1	118.7	118.9(8)
C2a-Cr	211.9	217.9	215.6	215.2(23)
C3-Cr	217.6	223.1	220.5	222.1(4)
C4-Cr	215.8	221.0	218.7	220.8(8)
C5-Cr	215.8	221.1	218.7	220.5(14)
C6-Cr	217.6	223.1	220.5	222.2(2)
C6a-Cr	211.8	217.8	215.6	215.9(16)
C1...Cr	305.9	317.6	314.9	312.7(23)
C2...Cr	305.9	317.6	314.9	312.7(23)
O1…Cr	400.6	414.0	410.1	408(6)
O2…Cr	400.6	414.0	410.1	408(6)
Dihedral [°]				
C1-C6a-C2a-C3	168.9	172.7	172.6	171.2(2)
C2-C2a-C6a-C6	–168.9	–172.8	–172.7	–174.6(2)



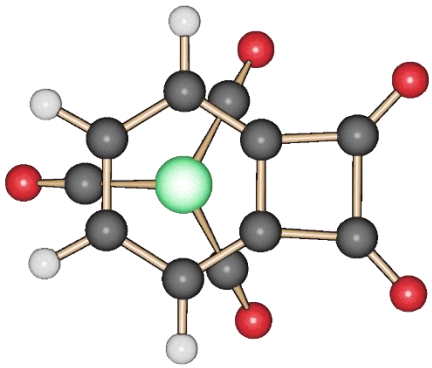


Table S4. Comparison of VWN, PBE and PBE0 optimized structure parameters of compound *rac*-**3** with experimental crystal structure data.

Bond [pm]	VWN	PBE	PBE0	Experiment
C1-C2	154.7	156.8	155.3	155.6(4)
C1-C6a	149.3	150.8	150.0	150.2(3)
C2-C2a	150.8	152.4	151.6	152.3(3)
C2a-C3	139.0	140.0	138.9	138.9(4)
C2a-C6a	142.7	143.8	142.5	142.8(3)
C3-C4	141.7	142.8	141.7	141.1(3)
C4-C5	140.9	142.0	141.0	141.5(3)
C5-C6	141.5	142.7	141.5	141.0(3)
C6-C6a	141.3	142.6	141.4	141.7(3)
C1-O1	119.9	120.8	119.3	118.8(3)
C6-OCH_3	132.1	133.9	132.6	133.8(3)
C2a-Cr	213.0	218.9	216.9	218.1(2)
C3-Cr	218.4	223.9	222.0	223.4(2)
C4-Cr	213.3	218.3	216.1	217.3(2)
C5-Cr	218.0	223.9	221.6	222.1(2)
C6-Cr	223.6	231.3	228.5	231.1(2)
C6a-Cr	217.3	224.0	221.3	222.5(2)
C1-Cr	321.4	329.7	326.0	327.6(2)
C2-Cr	322.8	330.9	328.0	329.6(2)
O1-Cr	421.6	430.0	424.4	425.6(2)
Dihedral [°]				
C1-C6a-C2a-C3	–179.4	–179.3	–179.9	–179.5(2)
C2-C2a-C6a-C6	179.0	178.6	178.9	177.7(2)

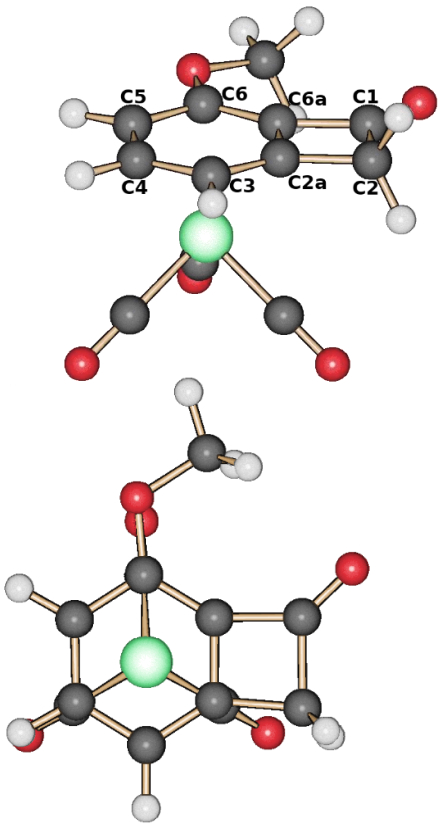
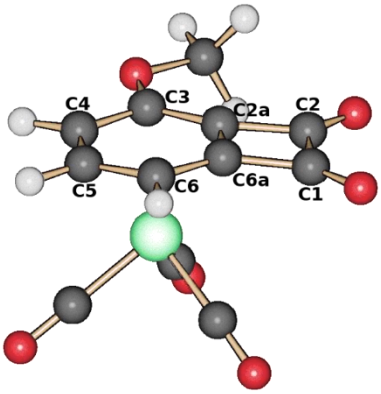


Table S5. Comparison of VWN, PBE and PBE0 optimized structure parameters of compound *rac*-**4** with experimental crystal structure data.

Bond [pm]	VWN	PBE	PBE0	Experiment
C1-C2	157.3	159.0	157.5	156.1(4)
C1-C6a	150.4	151.7	150.5	149.8(4)
C2-C2a	151.2	152.7	151.1	151.0(4)
C2a-C3	141.4	142.6	141.6	141.2(3)
C2a-C6a	143.0	144.1	142.7	143.1(4)
C3-C4	141.1	142.3	141.0	139.8(4)
C4-C5	141.3	142.6	141.7	140.9(4)
C5-C6	140.8	141.8	140.6	140.3(4)
C6-C6a	139.7	140.9	139.9	139.3(4)
C1-O1	119.2	120.1	118.7	119.4(4)
C2-O2	119.4	120.3	118.8	118.8(4)
C3-OCH_3	132.1	134.0	132.7	133.7(3)
C2a-Cr	214.2	220.2	217.8	217.7(3)
C3-Cr	225.4	232.8	229.1	231.1(3)
C4-Cr	219.1	225.0	222.3	223.9(3)
C5-Cr	215.0	220.3	218.0	219.6(3)
C6-Cr	217.9	223.3	221.1	221.5(3)
C6a-Cr	209.9	215.6	213.3	212.2(3)
C1…Cr	302.1	312.7	311.1	303.2(3)
C2…Cr	306.0	316.5	314.4	309.6(3)
O1…Cr	395.9	408.2	405.7	395.8(2)
O2…Cr	403.2	414.5	411.2	406.7(2)
Dihedral [°]				
C1-C6a-C2a-C3	170.7	174.9	174.9	172.2(2)
C2-C2a-C6a-C6	–169.5	–172.7	–173.2	–171.8(3)



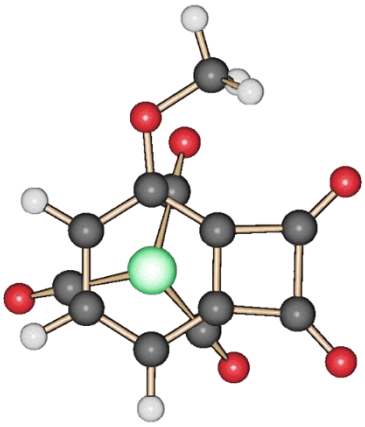
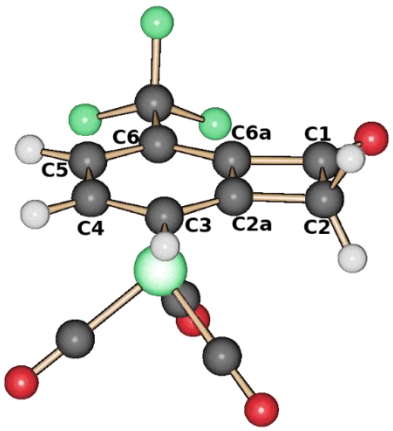


Table S6. Comparison of VWN, PBE and PBE0 optimized structure parameters of compound *rac*-**7** with experimental crystal structure data.

Bond [pm]	VWN	PBE	PBE0	Experiment
C1-C2	155.7	157.7	156.1	156.6(12)
C1-C6a	149.7	151.2	150.3	150.6(13)
C2-C2a	150.8	152.4	151.6	152.8(9)
C2a-C3	139.5	140.9	140.0	140.0(11)
C2a-C6a	141.8	142.5	141.0	136.7(12)
C3-C4	141.5	142.2	141.0	137.0(12)
C4-C5	141.2	142.7	141.7	141.7(11)
C5-C6	141.0	141.9	140.6	139.2(12)
C6-C6a	140.8	142.6	141.6	141.9(15)
C1-O1	119.3	120.2	118.8	117.1(11)
C6-CF3	149.3	151.3	150.5	150.1(16)
C2a-Cr	214.9	220.5	218.2	218.3(6)
C3-Cr	219.0	224.1	221.4	222.5(8)
C4-Cr	213.9	219.4	217.1	217.4(8)
C5-Cr	215.9	221.2	218.9	218.4(6)
C6-Cr	213.1	220.2	217.8	217.0(9)
C6a-Cr	214.8	220.4	217.7	217.6(9)
C1-Cr	319.0	327.4	324.1	325.7(9)
C2-Cr	324.2	323.4	329.3	328.6(6)
O1-Cr	416.3	425.5	421.0	416.8(6)
Dihedral [°]				
C1-C6a-C2a-C3	–176.7	–178.4	–177.8	–177.2(6)
C2-C2a-C6a-C6	175.4	178.1	178.0	177.5(8)



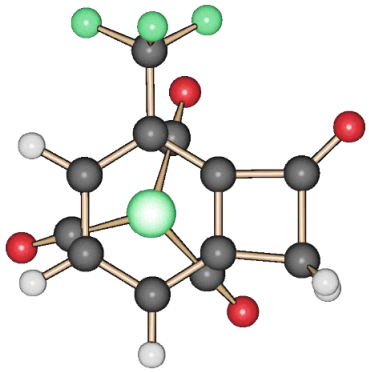
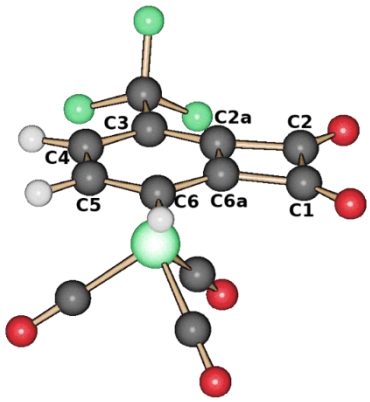


Table S7. Comparison of the VWN, PBE and PBE0 optimized structure parameters of compound *rac*-**13**.

Bond [pm]	**VWN**	**PBE**	**PBE0**
C1-C2	158.4	160.0	158.1
C2-C2a	151.5	153.2	151.7
C1-C6a	150.5	151.8	150.5
C2a-C6a	142.0	143.0	141.6
C2a-C3	140.6	142.0	141.0
C3-C4	140.8	142.1	140.9
C4-C5	141.7	142.8	141.8
C5-C6	140.6	141.6	140.5
C6-C6a	140.3	141.5	140.6
C3-CF3	149.3	151.3	150.5
C1-O1	119.1	120.0	118.6
C2-O2	118.9	119.8	118.4
C2a-Cr	211.6	217.6	215.3
C3-Cr	215.7	222.0	218.9
C4-Cr	214.7	220.0	217.5
C5-Cr	216.3	221.6	219.1
C6-Cr	217.6	222.9	220.2
C6a-Cr	212.3	218.1	215.8
C1…Cr	307.0	318.3	315.8
C2…Cr	307.6	319.2	316.6
O1…Cr	401.8	414.6	410.9
O2…Cr	402.7	416.1	412.3
Dihedral [°]			
C1-C6a-C2a-C3	169.2	173.2	173.0
C2-C2a-C6a-C6	–169.0	–172.7	–172.7



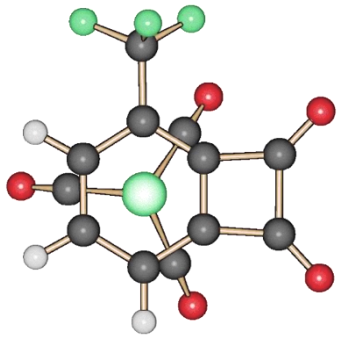
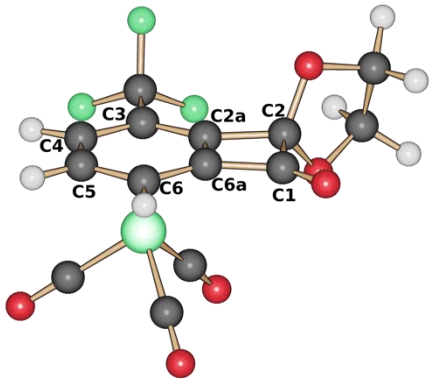


Table S8. Comparison of VWN, PBE and PBE0 optimized structure parameters of compound *rac*-**14** with experimental crystal structure data.

Bond [pm]	VWN	PBE	PBE0	Experiment
C1-C2	158.9	160.9	158.7	157.8(6)
C2-C2a	152.8	155.1	153.7	155.0(5)
C1-C6a	149.3	150.4	149.4	149.2(6)
C6a-C6	140.8	142.0	141.1	141.4(6)
C2a-C6a	141.3	142.3	140.8	139.7(6)
C5-C6	140.6	141.5	140.3	139.1(7)
C4-C5	141.6	142.7	141.7	138.9(7)
C3-C4	141.1	142.4	141.2	143.6(6)
C2a-C3	140.3	141.7	140.7	140.2(5)
C1-O1	119.5	120.4	119.0	119.1(5)
C3-CF3	148.8	150.8	150.0	147.4(7)
C6a-Cr	214.6	220.4	217.8	218.3(3)
C6-Cr	216.3	221.7	219.4	220.7(4)
C5-Cr	216.2	221.4	219.0	222.4(5)
C4-Cr	213.6	218.8	216.4	219.3(5)
C3-Cr	215.6	221.9	218.9	221.0(4)
C2a-Cr	212.6	219.1	216.9	218.1(3)
C2…Cr	322.3	333.3	329.6	331.4(3)
C1…Cr	316.5	326.5	322.9	319.8(4)
O1…Cr	414.1	424.7	419.6	412.6(3)
Dihedral [°]				
C1-C6a-C2a-C3	174.9	178.1	177.0	174.8(3)
C2-C2a-C6a-C6	–175.0	–178.1	–177.7	–179.1(3)



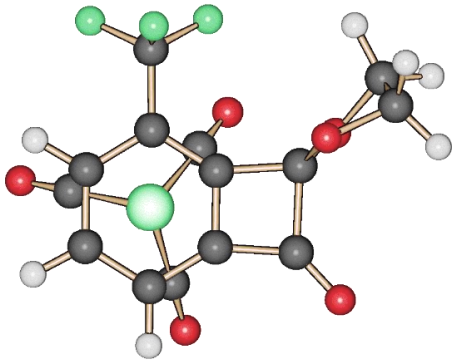
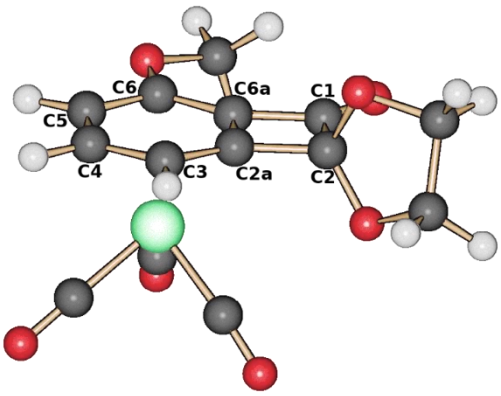
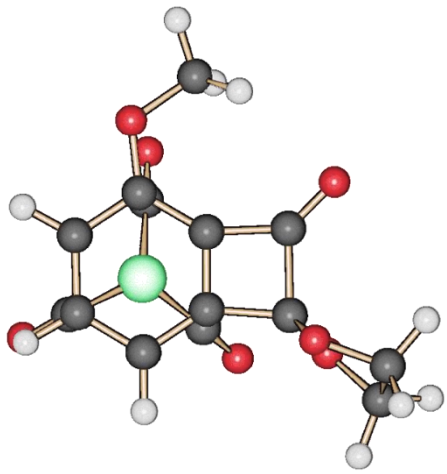


Table S9. Comparison of VWN, PBE and PBE0 optimized structure parameters of compound *rac*-**16** with experimental crystal structure data.

Bond [pm]	VWN	PBE	PBE0	Experiment
C1-C2	158.0	160.2	158.3	158.2(6)
C1-C6a	149.0	150.7	149.7	150.1(7)
C2-C2a	151.4	153.4	152.3	151.7(6)
C2a-C3	139.2	140.3	139.3	138.6(6)
C2a-C6a	142.7	143.6	142.2	143.0(6)
C3-C4	141.3	142.2	141.1	139.7(6)
C4-C5	141.1	142.4	141.4	138.7(6)
C5-C6	141.2	142.3	141.0	140.6(6)
C6-C6a	141.6	143.0	141.9	140.1(9)
C1-O1	120.0	120.8	119.3	117.1(5)
C6-OMe	132.2	134.1	132.8	135.0(6)
C2a-Cr	211.7	217.9	216.0	216.7(5)
C3-Cr	218.5	223.9	221.8	222.2(5)
C4-Cr	213.7	218.9	216.6	217.9(5)
C5-Cr	218.3	224.2	221.8	222.0(5)
C6-Cr	223.7	231.2	228.1	227.3(5)
C6a-Cr	217.2	223.7	220.9	218.6(5)
C1-Cr	319.9	329.4	325.3	313.6(6)
C2-Cr	322.3	332.2	329.0	324.5(5)
O1-Cr	420.0	429.6	423.4	402.1(4)
Dihedral [°]				
C1-C6a-C2a-C3	–178.3	–179.6	–179.3	–171.3(5)
C2-C2a-C6a-C6	179.6	177.3	177.7	177.3(5)