Supplementary information for

Synthesis and Characterisation of Dewar Benzene-Ferrocene Conjugates

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Contents

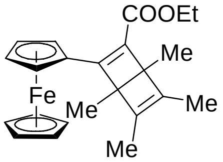
I. General comments

$AlCl_3$, 2-butyne, and 3-hexyne were purchased from Sigma-Aldrich. Dichloromethane was distilled from calcium hydride under argon atmosphere prior to the use. ^{1}H NMR (400 or 300 MHz) and ^{13}C NMR (100 or 75 MHz) spectra were recorded on a Varian Unity Inova 400 or Varian 300 spectrometers. Infrared spectra were recorded with a PE-640 Perkin-Elmer spectrometer. Mass spectra were obtained on a ZAB-EQ VG Analytical spectrometer. Elemental analyses were obtained on a Perkin-Elmer 2400 elemental analyser. TLC was performed on Merck Silica Gel 60 F_{254} aluminium sheets. Preparative TLC chromatography was carried out on Merck Silica Gel 60 F_{254} while conventional column chromatography was performed on Fluka Silica Gel 60.

II. Syntheses

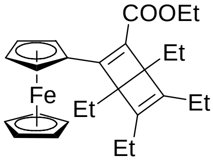
Ethyl 3-ferrocenylpropynoate (1) and (propyn-1-yl)ferrocene (5). Ester **1** and alkyne **5** were prepared as previously described by lithiation of ferrocenylethyne with *n*-BuLi followed by reaction with ethyl chloroformate and methyl iodide, respectively.[1]

General procedure for the preparation of Dewar benzenes. A solution of alkyne (1.2 mmol) in CH_2Cl_2 (3 mL) was added to a stirred suspension of powdered anhydrous $AlCl_3$ (84 mg, 0.55 mmol) in dry dichloromethane (3 mL) at -15 °C. Then, the ferrocene derivative **1** or **5** (0.5 mmol) was added to the reaction mixture at -15 °C. After stirring for 2 h at the same temperature DMSO (230 μL) was added, the mixture was poured onto crushed ice, extracted with diethyl ether (3 × 5 mL), and the combined organic layers were dried over $MgSO_4$. The volatiles were removed under reduced pressure and the residue was purified by column chromatography.

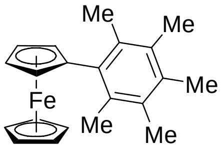


Ethyl 2-ferrocenyl-1,4,5,6-tetramethylbicyclo[2.2.0]hexa-2,5-diene-2-carboxylate (3a). Ethyl 3-ferrocenylpropynoate (**1**; 165mg, 0.59 mmol) and 2-butyne were used in this reaction. Column chromatography on silica gel (9/1 hexane/EtOAc) afforded 120 mg (31%) of the title compound as a red solid: mp 107 °C (methanol); ^{1}H NMR (400 MHz, C_6D_6) δ 1.05 (t, *J* = 7.2 Hz, 3H), 1.29

(s, 3H), 1.44 (s, 3H), 1.63 (bs, 3H), 1.70 (bs, 3H), 4.04 (s, 5H), 4.10-4.14 (m, 2H), 4.18-4.22 (m, 2H), 5.05-5.5.12 (m, 2H); ^{13}C NMR (100 MHz, C_6D_6) δ 11.60, 11.76, 12.06, 12.51, 15.23, 55.70, 56.19, 59.95, 70.33, 70.77, 71.30, 71.53, 72.31, 77.44, 133.62, 142.47, 145.83, 164.72, 167.60; IR (KBr) ν 3118, 3109, 3097, 2981, 2969, 2946, 2914, 2856, 1687, 1614, 1481, 1452, 1440, 1362, 1298, 1271, 1240, 1213, 1181, 1097, 1033, 1001, 960, 821, 794 cm^{-1}; EI-MS m/z (%) 390 (M$^+$, 56), 281 (100), 249 (7), 195 (16), 179 (10), 165 (20), 121 (10), 56 (7) ; HRMS calc. for $C_{23}H_{26}FeO_2$ 390.12822, found 390.12771. R_f (9/1 hexane/EtOAc) = 0.62.

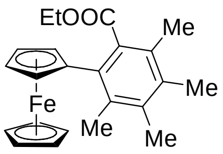


Ethyl 2-ferrocenyl-1,4,5,6-tetraethylbicyclo[2.2.0]hexa-2,5-diene-2-carboxylate (3b). Ethyl 3-ferrocenylpropynoate (**1**, 165 mg, 0.59 mmol) and 3-hexyne were used in this reaction. Column chromatography on silica gel (7/1 hexane/EtOAc) afforded 70 mg (17%) of the title compound as a red oil: ^{1}H NMR (400 MHz, C_6D_6) δ 0.99 (t, J = 7.6 Hz, 3H), 1.06-1.15 (m, 12H), 2.01-2.32 (m, 8H), 4.09 (s, 5H), 4.10-4.23 (m, 4H), 4.95 (bs, 1H), 5.30 (bs, 1H) ; ^{13}C NMR (100 MHz, C_6D_6) δ 11.65, 12.02, 13.33, 13.91, 15.20, 21.65, 22.10, 22.17, 22.83, 59.91, 61.40, 62.47, 70.62, 70.93, 70.98, 71.45, 72.57, 77.69, 132.60, 146.56, 150.25, 164.63, 167.67; IR (ATR, Ge) ν 3100, 2965, 2932, 2875, 2851, 1694, 1616, 1455, 1377, 1296, 1231, 1189, 1153, 1105, 1075, 1024, 1003 cm^{-1}; EI-MS m/z (%) 446 (M$^+$ 98), 400 (5), 351 (7), 337 (100), 233 (7), 205 (18), 193 (8), 179 (10), 149 (9), 121 (9), 91 (6), 57 (17), 41 (9); HRMS calc. for $C_{27}H_{31}FeO_2$ 446.19082, found 446.19016. R_f (9/1 hexane/EtOAc) = 0.65.

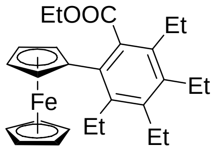


Pentamethylphenylferrocene (6). 1-Propynylferrocene (112 mg, 0.5 mmol) and 3-butyne were used in this reaction. Chromatography on a preparative TLC plate (90/10 hexane/EtOAc) afforded 25 mg (15%) of the title compound as a orange solid: mp 131-133 °C (methanol); ^{1}H NMR (400 MHz, C_6D_6) δ 2.14 (bs, 9H), 2.50 (s, 6H), 4.03 (s, 5H), 4.13-4.14 (m, 2H), 4.17-4.17 (m, 2H); ^{13}C NMR (100 MHz, C_6D_6) δ 17.75, 17.87, 20.99, 67.90, 70.72, 73.62, 90.32, 133.53, 133.88, 133.96, 134.21; IR (KBr) ν 3103, 3092, 2984, 2923, 2854, 1449, 1412, 1383, 1171, 1104, 1052, 1029, 1000 cm^{-1}; EI-MS m/z (%) 332 (M$^+$ 100), 317 (47), 302 (8), 264 (11), 211 (25), 196 (30), 181 (46), 165 (49), 152 (17), 141 (12), 128 (12), 121 (90), 115 (12), 91 (10), 77 (8), 56 (40), 41 (17); HRMS calc. for $C_{21}H_{24}Fe$ 332.12274, found 332.12366. R_f (9/1 hexane/EtOAc) = 0.82.

General procedure for the conversion of Dewar benzenes to arylferrocenes. Dewar benzene **3** (0.05 mmol) was dissolved in THF (3 mL) together with 1-butyl-2,3-dimethylimidazolinium tetrafluoroborate (100 µL) and the reaction mixture was irradiated in a microwave reactor for 6 hours (Biotage initiator, 300 W; temperature reached 170 °C, pressure 16 bar). Column chromatography on silica gel afforded the arylferrocene derivatives.



Ethyl 2-ferrocenyl-3,4,5,6-tetramethylbenzoate (4a). Starting with **3a** (25 mg, 0.064 mmol), the general procedure gave, after column chromatography on silica gel (9/1 hexane/EtOAc), 20 mg (80%) of the title compound as a yellow solid: mp 156-158 °C (methanol); ^{1}H NMR (400 MHz, C_6D_6) δ 0.93 (t, *J* = 7.6 Hz, 3H), 1.95 (s, 3H), 2.07 (s, 3H), 2.26 (s, 3H), 2.70 (s, 3H), 3.96 (s, 5H), 4.02-4.08 (m, 4H), 4.43 (bs, 2H); IR (KBr) ν 3092, 2972, 2917, 2891, 2848, 1718, 1471, 1439, 1384, 1305, 1279, 1183, 1102, 1044, 1027, 829, 809 cm^{-1}. R_f (9/1 hexane/EtOAc) = 0.45. Spectral characteristics were in agreement with the previously published data.[2]



Ethyl 2-ferrocenyl-3,4,5,6-tetraethylbenzoate (4b). Starting with **3b** (25 mg, 0.056 mmol), the general procedure and column chromatography on silica gel (9/1 hexane/EtOAc) afforded 19 mg (76%) of the title compound as a yellow solid mp. 175-177 °C (methanol); ^{1}H NMR (400 MHz, C_6D_6) δ 0.90 (t, *J* = 7.6 Hz, 3H), 1.07 (t, *J* = 7.6 Hz, 3H), 1.14 (t, *J* = 7.6 Hz, 3H), 1.20 (t, *J* = 7.6 Hz, 3H), 1.37 (t, *J* = 7.6 Hz, 3H), 2.61 (q, *J* = 7.6 Hz, 2H), 2.71-2.77 (m, 4H), 3.10-3.60 (bm, 2H); 3.88 (s, 5H), 4.01 (*J* = 7.2 Hz, 2H), 4.04-4.07 (m, 2H), 4.53 (bs, 2 H); ^{13}C NMR (100 MHz, C_6D_6) δ 14.79, 16.55, 17.20, 17.25, 18.26, 22.89, 23.55, 25.20, 61.16, 68.57, 70.65, 71.50, 89.37, 132.65, 137.16, 137.61, 140.11, 140.63, 142.82, 172.33; IR (KBr) ν 3091, 2967, 2923, 2869, 1723, 1451, 1371, 1295, 1188, 1175, 1027, 1001, 820 cm^{-1}; EI-MS m/z (%) 446 (M^+ 100), 351 (9), 337 (31), 297 (8), 279 (9), 221 (5), 207 (8), 193 (12), 179 (16), 165 (19), 152 (10), 121 (47), 97 (7), 83 (9), 69 (20), 55 (34); HRMS calc. for $C_{27}H_{34}FeO_2$ 446.19082, found 446.18962. R_f (9/1 hexane/EtOAc) = 0.47.

III. X-ray crystallography

Single crystals suitable for X-ray diffraction analysis were grown by recrystallisation from methanol (**3a**: red prism, 0.08 × 0.18 × 0.37 mm^3; **6**: orange plate, 0.10 × 0.45 × 0.80 mm^3) and from heptane (**4a**: orange plate, 0.05 × 0.10 × 0.55 mm^3).

Full-set diffraction data ($\pm h \pm k \pm l$, $2\theta \leq 55.0$-$55.2°$) were collected with a Nonius KappaCCD diffractometer equipped with a Cryostream Cooler (Oxford Cryosystems) using graphite monochromatised MoKα radiation ($\lambda = 0.71073$ Å). The data were analyzed with the HKL program package.[3] No absorption correction was applied. The crystal of **4a** was a non-merohedral twin. Correction for the contribution of the second part was applied and included into the refinement (volume ratio 0.472:0.528).

The phase problems were solved by direct methods (SIR97)[4] and the structure were refined by full-matrix least-squares procedure based on F^2 (SHELXL97).[5] The non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in their calculated positions and refined as riding atoms with $U_{\mathrm{iso}}(\mathrm{H})$ assigned to a multiple of $U_{\mathrm{eq}}(\mathrm{C})$ of their bonding carbon atom. Relevant crystallographic data and structure refinement parameters are given in Table S4. Geometric parameters and structural drawings were obtained with a recent version of the PLATON program.[6]

CCDC 718552-718554 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via the Internet at www.ccdc.cam.ac.uk/data_request/cif.

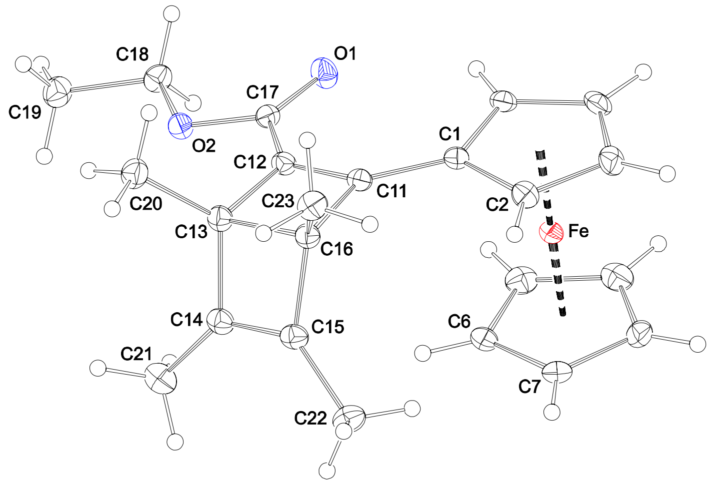


Figure S1. View of the molecular structure of **3a**. Displacement ellipsoids enclose the 30% probability level. The dihedral angle of the C(1-5) Cp(1) and C(11,12,13,16) planes is 6.7(1)°.

Table S1. Selected distances and angles for **3a** (in Å and deg).[a]

Distances		Angles	
Fe-Cg1[b]	1.6440(9) [1.654]	∠Cp1,Cp2[b]	0.8(1) [2]
Fe-Cg2[b]	1.652(1) [1.655]	C1-C11-C12	137.2(2) [137.1]
C1-C11	1.454(2) [1.447]	C1-C11-C16	129.3(2) [129.7]
C11-C12	1.351(2) [1.364]	C16-C11-C12	93.5(1) [93.2]
C12-C13	1.532(3) [1.531]	C11-C12-C13	94.8(1) [94.9]
C13-C14	1.523(3) [1.536]	C12-C13-C14	114.9(2) [115.0]
C13-C16	1.574(3) [1.581]	C13-C16-C11	86.1(1) [86.2]
C14-C15	1.342(3) [1.346]	C12-C13-C16	85.6(1) [85.6]
C15-C16	1.528(3) [1.539]	C13-C14-C15	94.5(2) [94.4]
C16-C11	1.540(2) [1.543]	C14-C15-C16	94.3(2) [94.4]
C-CH$_3$[c]	1.484(3)-1.528(3) [1.492-1.520]	C15-C16-C11	114.6(1) [115.1]
C12-C17	1.461(2) [1.460]	C-C-CH$_3$[d]	118.5(1)-131.0(2) [118.8-135.4]
C17-O1	1.212(2) [1.223]	C11-C12-C17	133.4(2) [133.4]
C17-O2	1.346(2) [1.362]	C13-C12-C17	131.7(2) [131.4]
O2-C18	1.457(2) [1.442]	O1-C17-O2	123.2(2) [122.3]
C18-C19	1.501(3) [1.518]	C17-O2-C18	114.9(1) [115.8]

[a] Values in square brackets have been calculated by DFT calculations. [b] Definition of the ring planes: Cp1 = C(1-5), Cp2 = C(6-10). Cg1 and Cg2 stand for the respective ring centroids. [c] The range of C13-C20, C14-C21, C15-C22, and C16-C23 bond lengths. [d] The range of C12/C14-C13-C20, C13/C15-C14-C21, C14/C16-C15-C22 and C11/C15-C16-C23 angles.

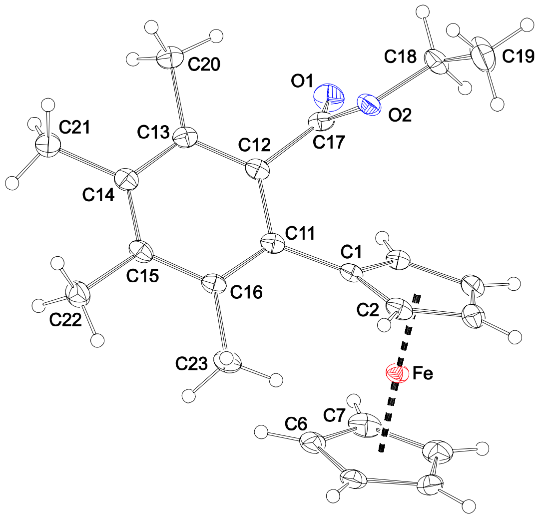


Figure S2. View of the molecular structure of **4a**. Displacement ellipsoids enclose the 30% probability level. The dihedral angle of the C(1-5) (Cp1) and C(11-16) planes is 42.4(1)°.

Table S2. Selected distances and angles for **4a** (in Å and deg).[a]

Distances		Angles	
Fe-Cg1[b]	1.652(1) [1.664]	∠Cp1,Cp2[b]	4.7(2) [6]
Fe-Cg2[b]	1.647(1) [1.663]	C1-C11-C12	117.0(2) [117.9]
C1-C11	1.497(3) [1.492]	C1-C11-C16	124.4(2) [123.9]
C11-C12	1.412(4) [1.417]	C12-C11-C16	118.6(2) [118.2]
C12-C13	1.397(4) [1.405]	C11-C12-C13	121.7(2) [122.0]
C13-C14	1.405(4) [1.409]	C12-C13-C14	119.0(2) [118.9]
C14-C15	1.395(4) [1.406]	C13-C14-C15	120.1(2) [119.7]
C15-C16	1.410(4) [1.411]	C14-C15-C16	120.7(2) [120.9]
C16-C11	1.408(3) [1.411]	C11-C16-C15	119.8(2) [119.9]
C-CH_3[c]	1.509(4)-1.516(4) [1.512-1.517]	C-C-CH_3[d]	118.9(2)-121.2(2) [118.6-121.5]
C12-C17	1.493(4) [1.505]	C11-C12-C17	119.3(2) [120.1]
C17-O1	1.209(3) [1.216]	C13-C12-C17	118.8(2) [117.9]
C17-O2	1.343(3) [1.349]	O1-C17-O2	123.2(2) [123.2]
O2-C18	1.453(3) [1.446]	C17-O2-C18	116.6(2) [116.0]
C18-C19	1.502(5) [1.517]	O2-C18-C19	106.6(2) [107.4]

[a] Values in square brackets have been calculated by DFT calculations. [b] Definition of the ring planes: Cp1 = C(1-5), Cp2 = C(6-10). Cg1 and Cg2 denote the respective ring centroids. [c] The range of C13-C20, C14-C21, C15-C22 and C16-C23 bond lengths. [d] The range of C12/C14-C13-C20, C13/C15-C14-C21, C14/C16-C15-C22 and C11/C15-C16-C23 angles.

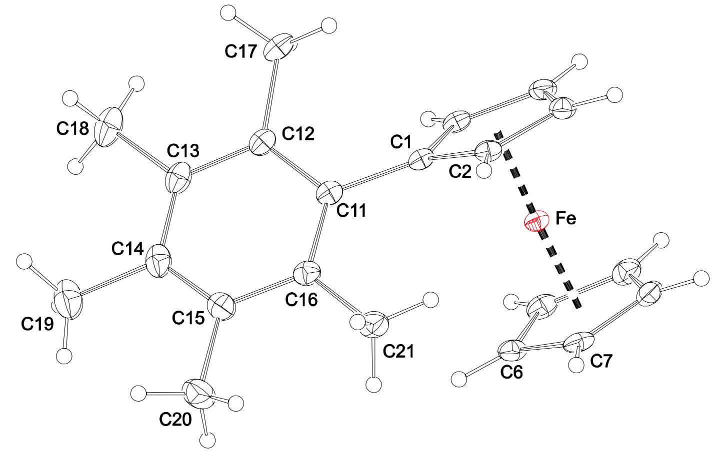


Figure S3. View of the molecular structure of **6**. Displacement ellipsoids enclose the 30% probability level. The dihedral angle of the C(1-5) (Cp1) and C(11-16) planes is 43.69(9)°.

Table S3. Selected distances and angles for **6** (in Å and deg).[a]

Distances		Angles	
Fe-Cg1[b]	1.6491(7) [1.666]	∠Cp1,Cp2[b]	4.6(1) [6]
Fe-Cg2[b]	1.6482(8) [1.664]	C1-C11-C12	117.2(2) [117.9]
C1-C11	1.492(2) [1.500]	C1-C11-C16	123.5(2) [123.2]
C11-C12	1.415(2) [1.419]	C16-C11-C12	119.2(2) [118.9]
C12-C13	1.399(3) [1.408]	C11-C12-C13	119.8(2) [120.1]
C13-C14	1.401(3) [1.407]	C12-C13-C14	120.3(2) [120.4]
C14-C15	1.399(3) [1.408]	C13-C14-C15	119.7(2) [119.5]
C15-C16	1.405(3) [1.410]	C14-C15-C16	120.4(2) [120.3]
C16-C11	1.409(2) [1.416]	C15-C16-C11	119.8(2) [120.2]
C-CH_3[c]	1.514(3)-1.523(3) [1.515-1.520]	C-C-CH_3[d]	118.7(2)-121.6(2) [117.7-122.2]

[a] Values in square brackets have been calculated by DFT calculations. [b] The ring planes are defined as follows: Cp1 = C(1-5), Cp2 = C(6-10). Cg1 and Cg2 denote the respective ring centroids. [c] The range of C12-C17, C13-C18, C14-C19, C15-C20 and C16-C21 bond lengths. [d] The range of C11/C13-C12-C17, C12/C14-C13-C18, C13/C15-C14-C19, C14/C16-C15-C20 and C11/C15-C16-C21 angles.

Table S4. Crystallographic data, data collection and structure refinement parameters[a]

Compound	**3a**	**4a**	**6**
Formula	$C_{23}H_{26}FeO_2$	$C_{23}H_{26}FeO_2$	$C_{21}H_{24}Fe$
M/g mol^{-1}	390.29	390.29	332.25
Crystal system	triclinic	monoclinic	monoclinic
Space group	P–1 (no. 2)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a/Å	7.3695(2)	14.9261(5)	20.1331(2)
b/Å	10.1814(5)	7.3837(2)	9.1392(2)
c/Å	13.4315(6)	18.0000(6)	8.9108(4)
α/°	89.394(2)		
β/°	86.159(3)	107.659(1)	102.700(1)
γ/°	75.385(3)		
V/Å^3	972.97(7)	1890.3(1)	1599.48(8)
Z	2	4	4
D_{calc}/g mL^{-1}	1.332	1.371	1.38
μ(MoKα)/mm^{-1}	0.788	0.812	0.937
Diffractions total	14778	26499	22400
R_{int}[b]/%	3.6	4.0	4.2
Unique/observed[c] diffractions	4282/3653	3694/3349	3665/3133
R (obsd diffrns)[c,d]/%	3.43	3.20	3.01
R, wR (all diffrns)[d]/%	4.48, 8.00	3.75, 7.40	3.92, 8.10
$\Delta\rho$/e Å^{-3}	0.47, –0.43	0.37, –0.49	0.33, –0.37
CCDC entry	718552	718553	718554

[a] Common details: T = 150(2) K. [b] $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma F_o^2$, where F_o^2(mean) is the average intensity for symmetry-equivalent diffractions. [c] Diffractions with $I_o > 2\sigma(I_o)$.

[d] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR = [\Sigma\{w(F_o^2 - F_c^2)_2\}/\Sigma\ w(F_o^2)^2]^{1/2}$.

IV. Electrochemistry

Table S5. Summary of the electrochemical data.[a]

Compound	$E^{\circ\prime}$ (mV)[a]
3a	+0.08
3b	+0.09
4a	+0.05
4b	+0.08
6	–0.02

[a] $E^{\circ\prime}$ is an average of the peak potentials from cyclic voltammetry: $E^{\circ\prime} = \frac{1}{2}(E_{pa} + E_{pc})$, and is given relative to the ferrocene/ferrocenium reference (for details, see below).

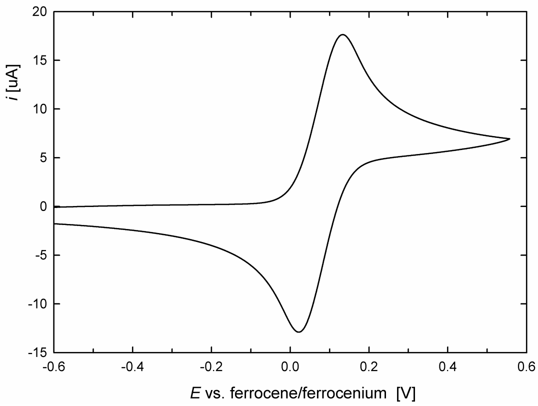


Figure S4. Representative cyclic voltammogram of **3a**. Conditions: Pt disc electrode, scan rate 100 mV s^{-1}; dichloromethane solution: $c \approx 1$ mM, 0.1 M $Bu_4N[PF_6]$.

Electrochemical measurements were carried out with a computer-controlled multipurpose polarograph μAUTOLAB III (Eco Chemie, Netherlands) at 22 °C using a standard three-electrode cell with rotating platinum disc electrode (AUTOLAB RDE, 3 mm diameter) as the working electrode, platinum sheet auxiliary electrode, and Ag/AgCl (3 M KCl) reference electrode. The compounds were dissolved in dichloromethane (Fluka, absolute, declared H_2O content ≤0.005%) to give a solution containing ca. 1×10^{-3} M of the analyte and 0.1 M $Bu_4N[PF_6]$ (Fluka, purissimum for electrochemistry) as the supporting electrolyte. The solutions were deaerated with argon prior to the measurement and then kept under an argon blanket. The redox potentials are given relative to the ferrocene/ferrocenium reference.

V. Computational details

The molecules of **3a**, **a** and **6** were also studied theoretically using density functional theory (DFT), in particular the Becke three parameter hybrid functional B3LYP[7] that is known to be both reliable and accurate,[8] and standard 6-31G* basis set. The geometry was optimized starting from the experimental geometry using analytic gradients as implemented in the Gaussian 03 program package.[9] The resulting stationary points were checked to be true minima using the eigenvalues of the Hessian matrix. The calculated bond lengths and angles are given in Tables S1-3 for a comparison.

Figure S5. Selected molecular orbitals for **3a** (0.05 a.u. isosurface plots).

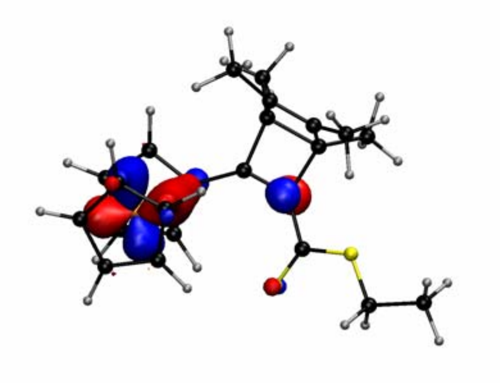
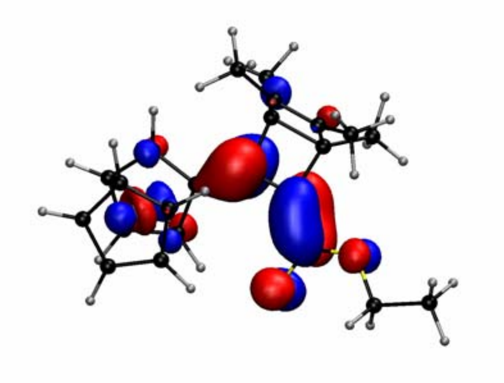
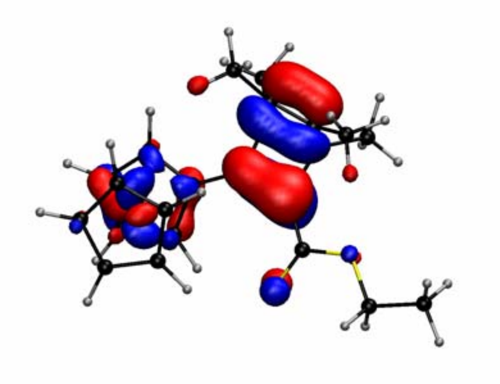
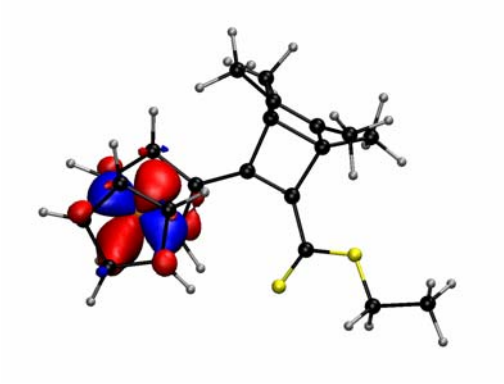
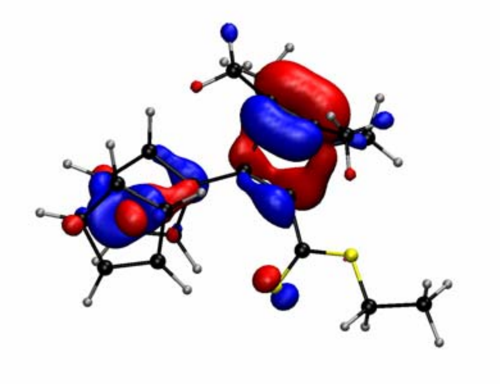
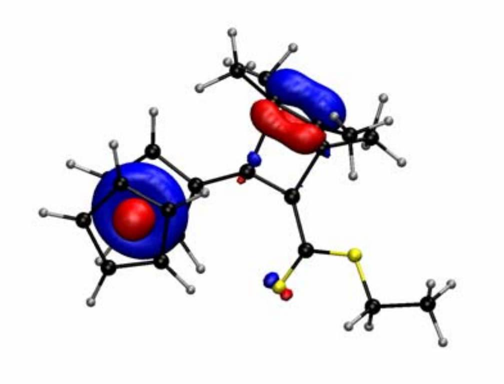
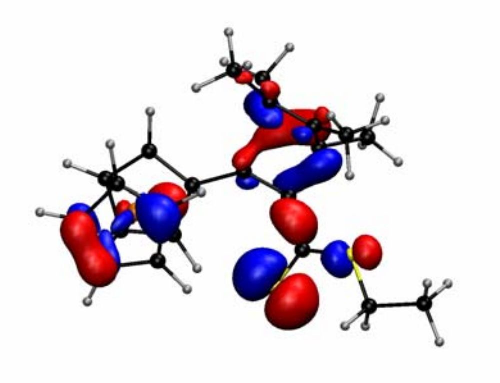
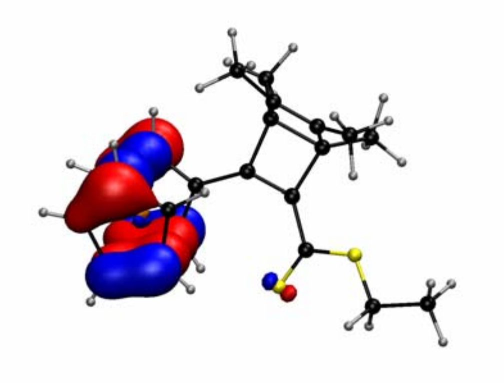
 orbital 103 (HOMO), *E* = –0.19021 a.u.	 orbital 104 (LUMO), *E* = –0.04828 a.u.
 orbital 101, *E* = –0.21391 a.u.	 orbital 102, *E* = –0.19306 a.u.
 orbital 99, *E* = –0.22765 a.u.	 orbital 100, *E* = –0.22266 a.u.
 orbital 97, *E* = –0.25377 a.u.	 orbital 98, *E* = –0.24582 a.u.

Figure S5 (continued).

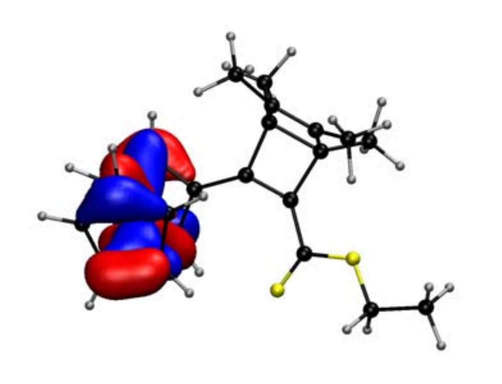
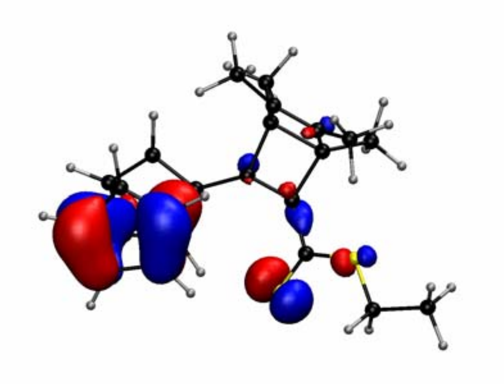
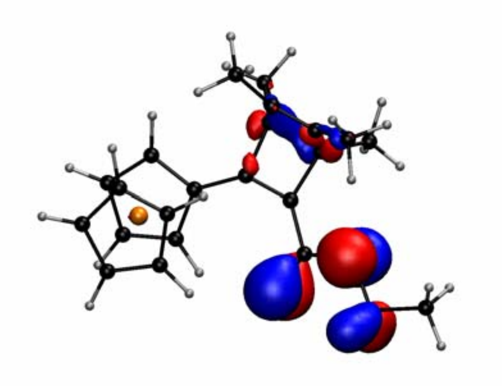
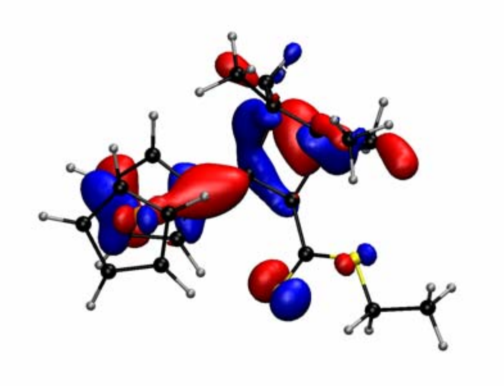
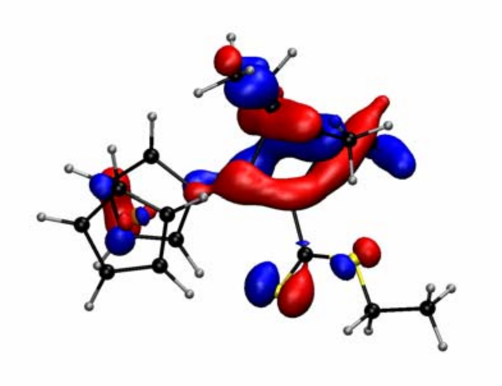
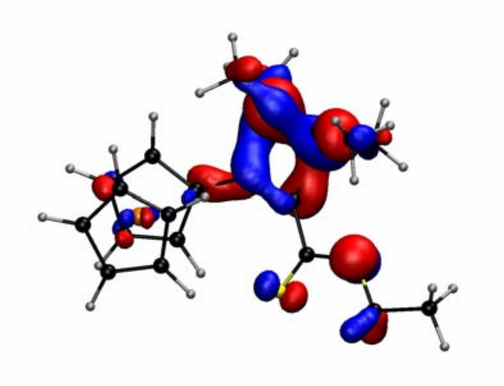
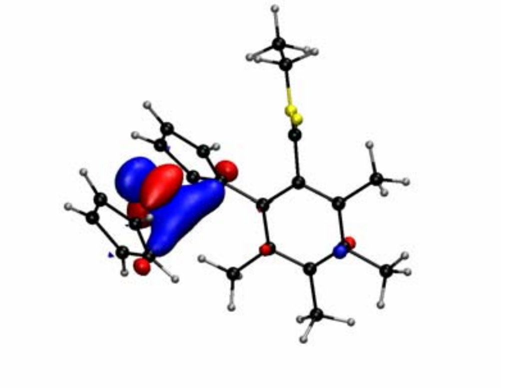
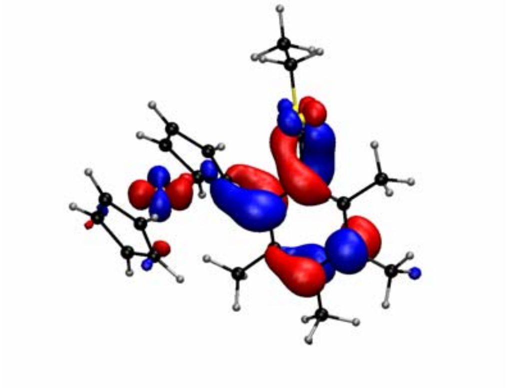
 orbital 95, $E = -0.26507$ a.u.	 orbital 96, $E = -0.26002$ a.u.
 orbital 93, $E = -0.29019$ a.u.	 orbital 94, $E = -0.27496$ a.u.
 orbital 91, $E = -0.29821$ a.u.	 orbital 92, $E = -0.29106$ a.u.

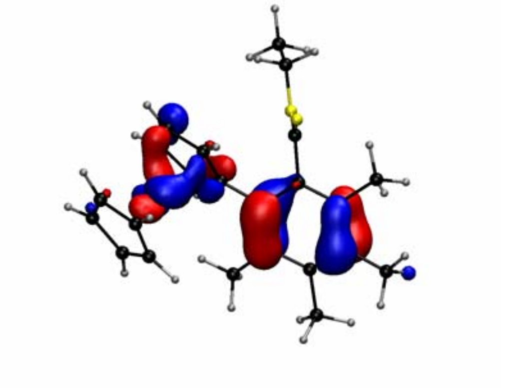
Figure S6. Selected molecular orbitals for **4a** (0.05 a.u. isosurface plots).



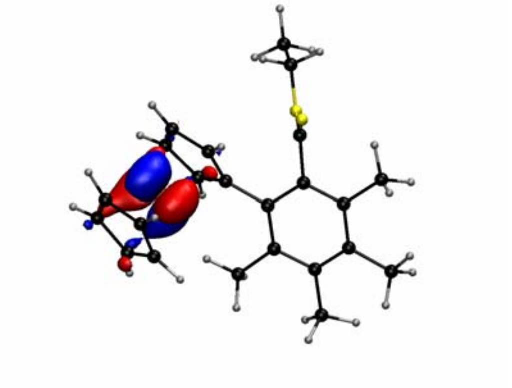
orbital 103 (HOMO), *E* = –0.19058 a.u.



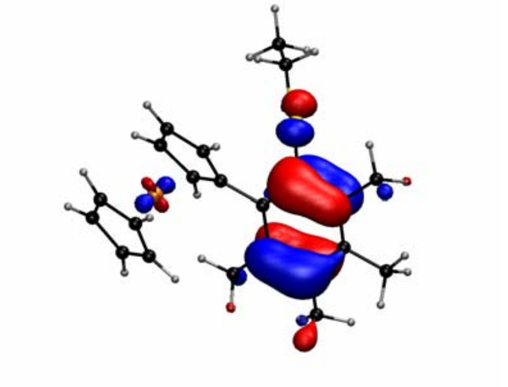
orbital 104 (LUMO), *E* = –0.01805 a.u.



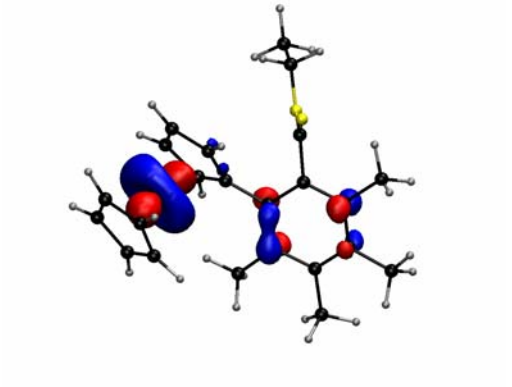
orbital 101, *E* = –0.21659 a.u.



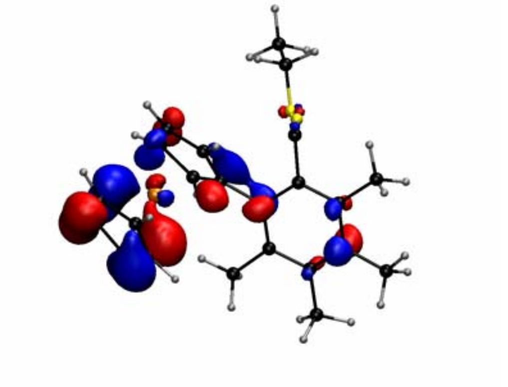
orbital 102, *E* = –0.19312 a.u.



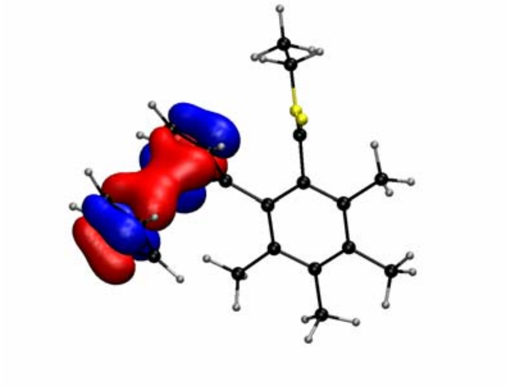
orbital 99, *E* = –0.22537 a.u.



orbital 100, *E* = –0.22453 a.u.

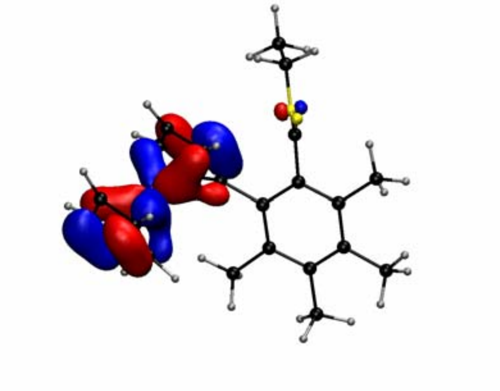


orbital 97, *E* = –0.25204 a.u.

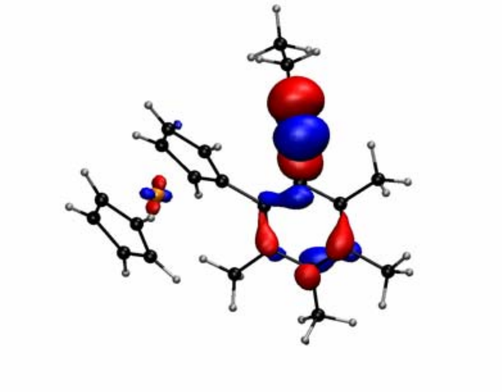


orbital 98, *E* = –0.24632 a.u.

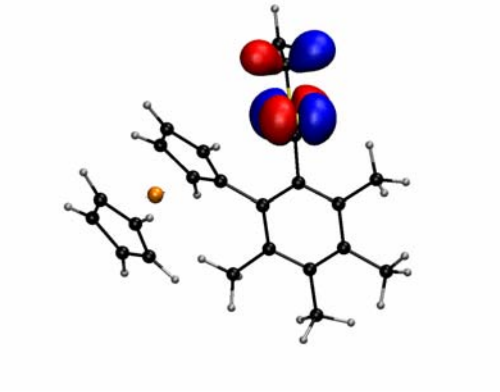
Figure S6 (continued).



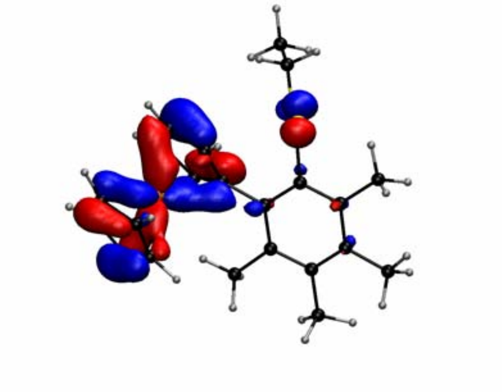
orbital 95, $E = -0.26436$ a.u.



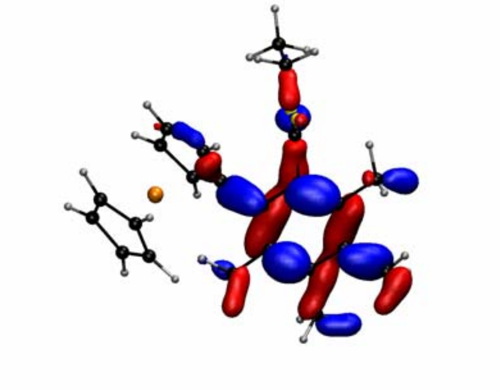
orbital 96, $E = -0.26313$ a.u.



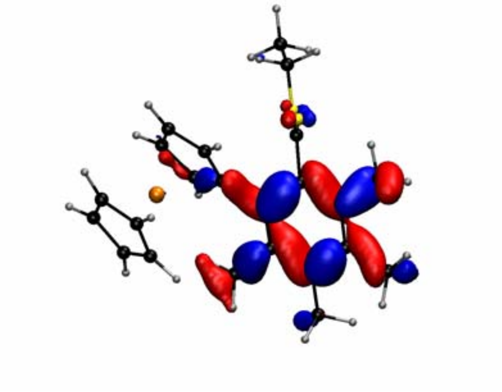
orbital 93, $E = -0.29026$ a.u.



orbital 94, $E = -0.26676$ a.u.



orbital 91, $E = -0.32860$ a.u.



orbital 92, $E = -0.32129$ a.u.

Figure S7. (a) DFT optimised geometry of hypothetic ferrocenyl-pentamethyl Dewar benzene. (b) Predicted bonds lengths for this species (in Å).

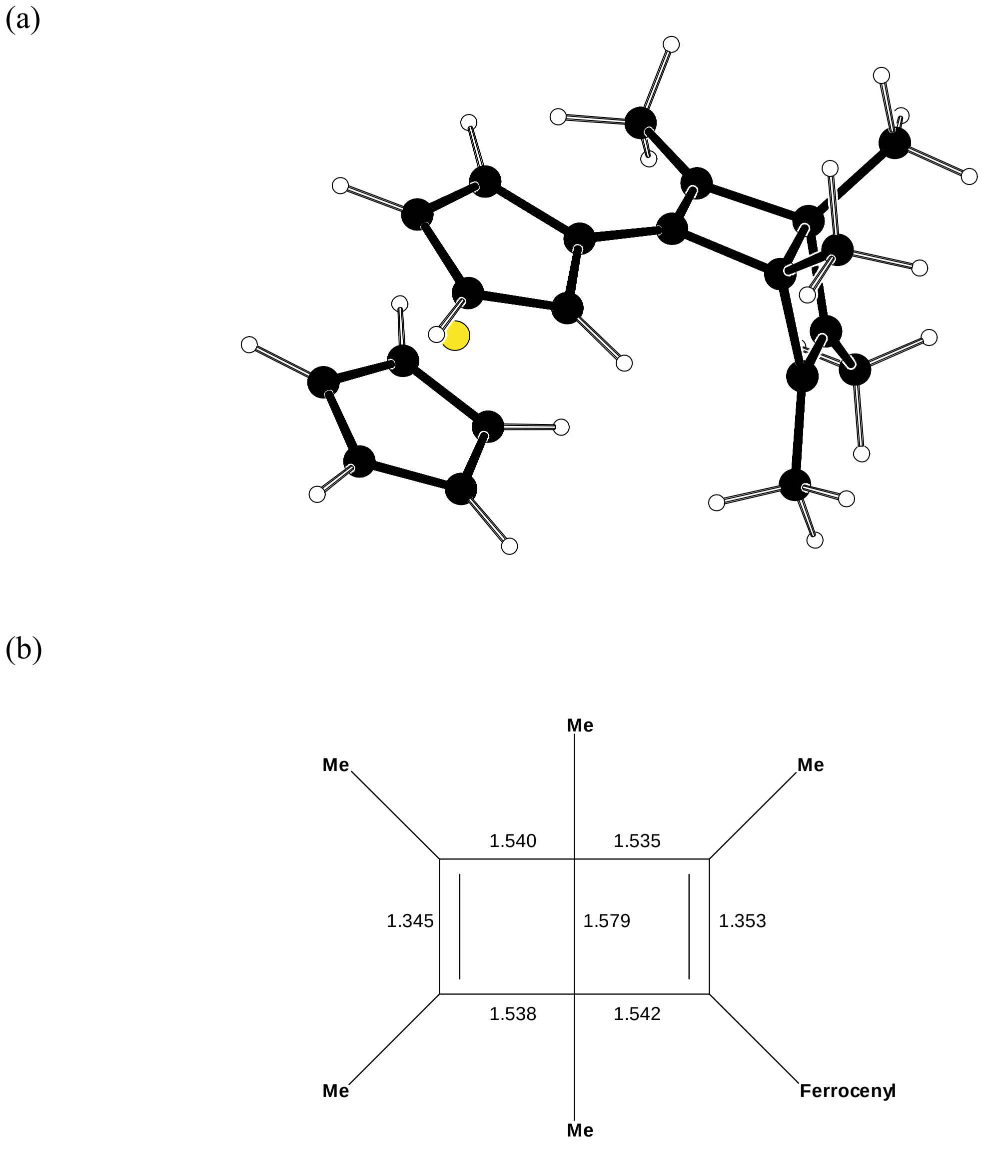
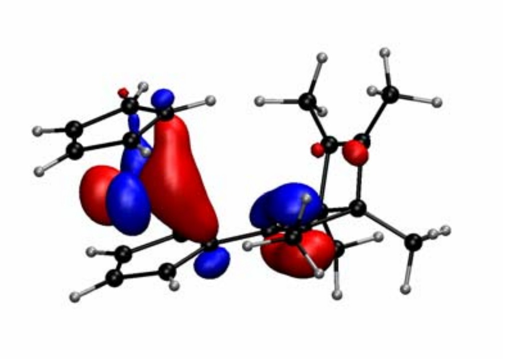
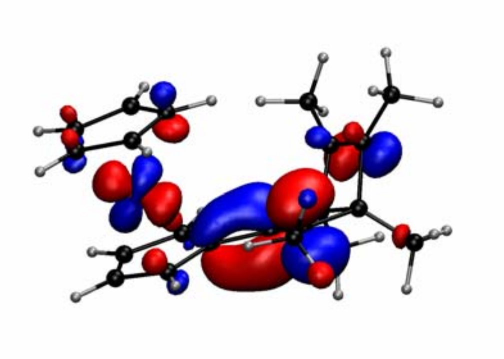


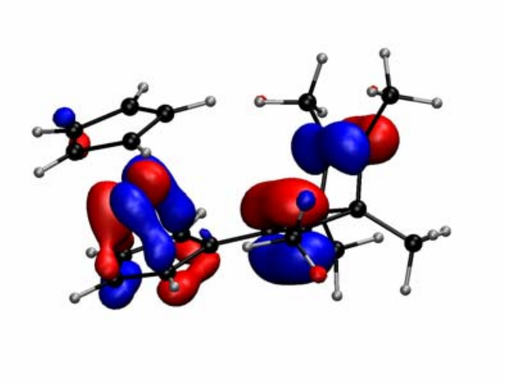
Figure S8. Selected molecular orbitals for Me_5Fc-Dewar benzene (0.05 a.u. isosurface plots).



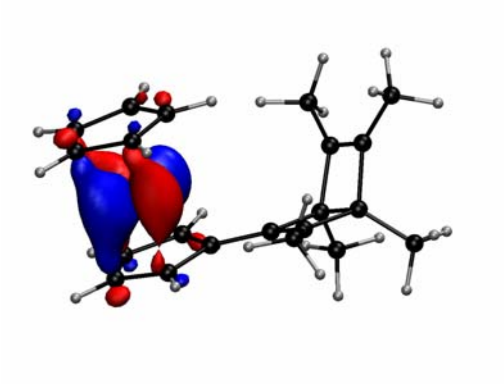
orbital 88 (HOMO), *E* = –0.18348 a.u.



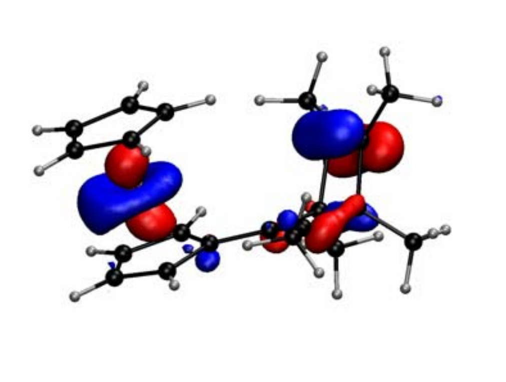
orbital 89 (LUMO), *E* = –0.01030 a.u.



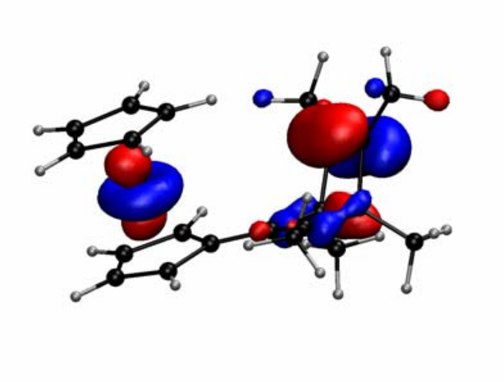
orbital 86, *E* = –0.20291 a.u.



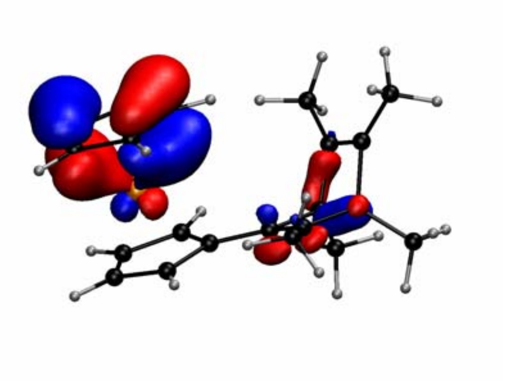
orbital 87, *E* = –0.18885 a.u.



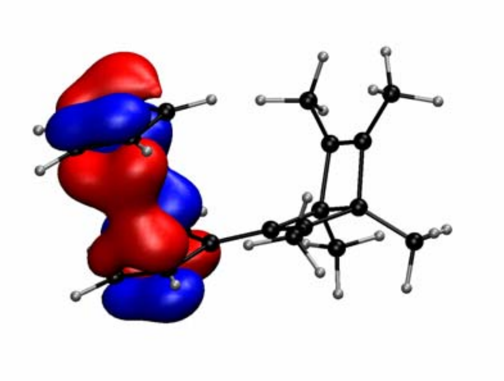
orbital 84, *E* = –0.22194 a.u.



orbital 85, *E* = –0.21795 a.u.



orbital 82, *E* = –0.25406 a.u.



orbital 83, *E* = –0.24396 a.u.

Figure S8 (continued).

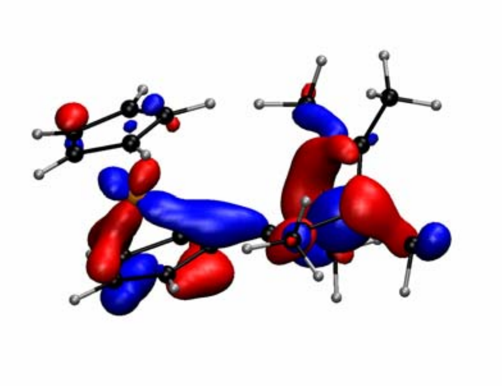
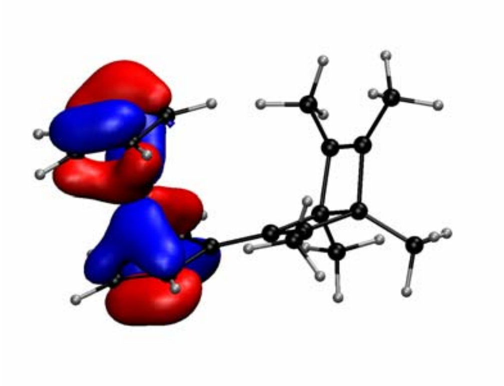
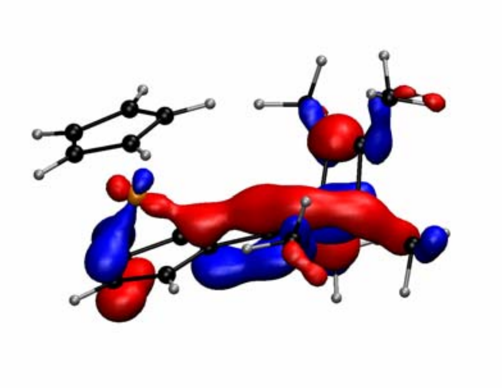
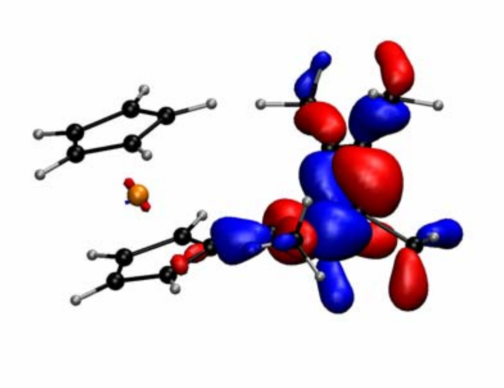
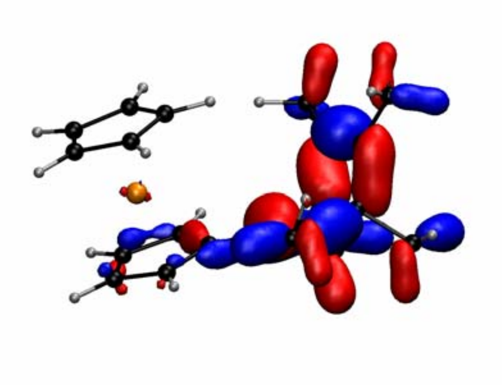
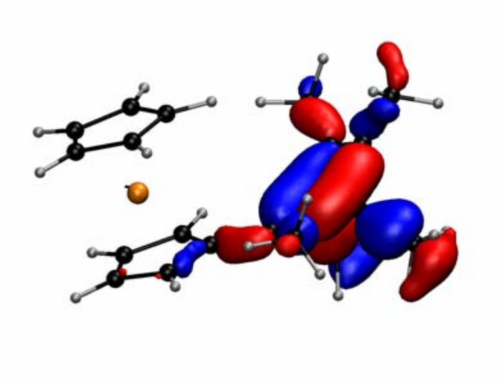
 orbital 80, *E* = –0.26519 a.u.	 orbital 81, *E* = –0.26171 a.u.
 orbital 78, *E* = –0.28518 a.u.	 orbital 79, *E* = –0.27810 a.u.
 orbital 76, *E* = –0.32021 a.u.	 orbital 77, *E* = –0.31216 a.u.

Figure S9. Selected molecular orbitals for **6** (0.05 a.u. isosurface plots).

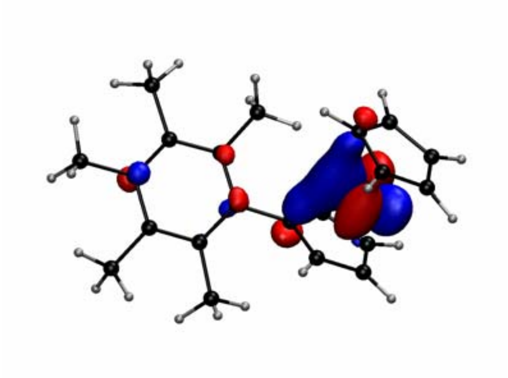
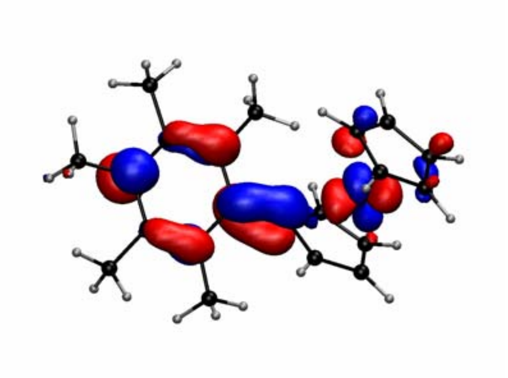
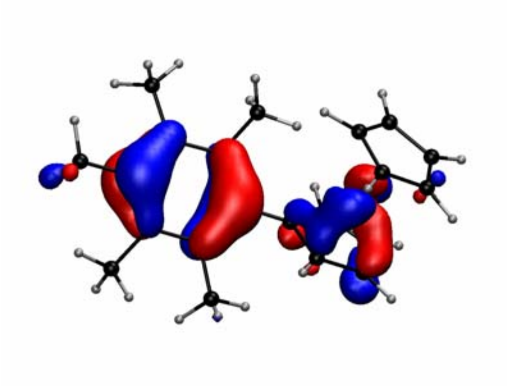
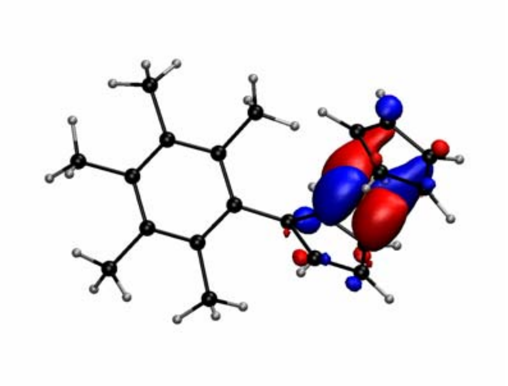
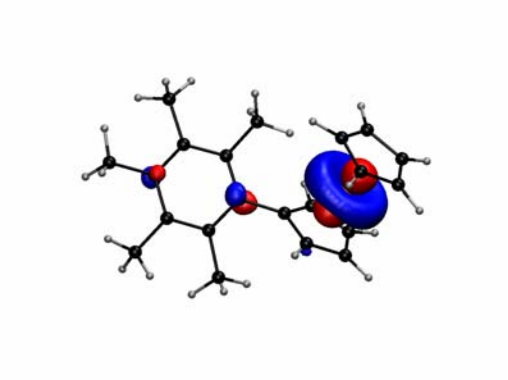
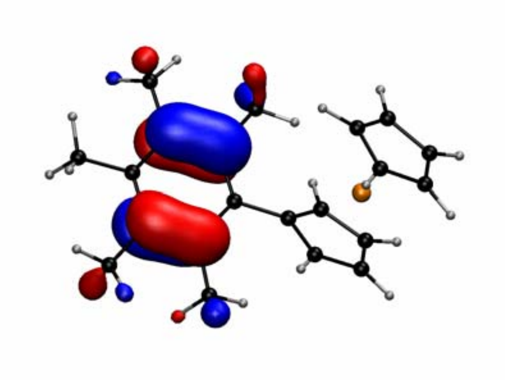
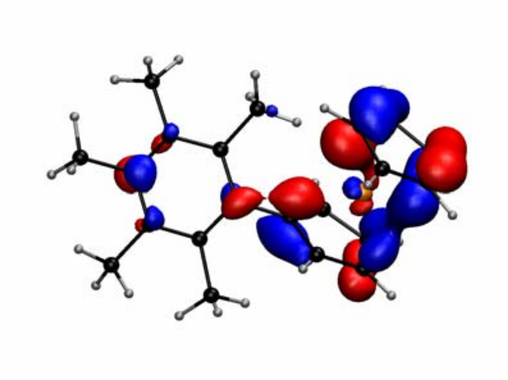
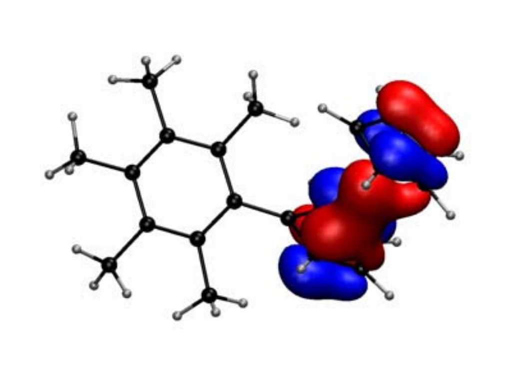
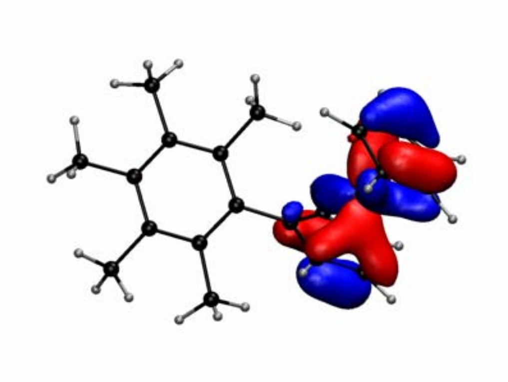
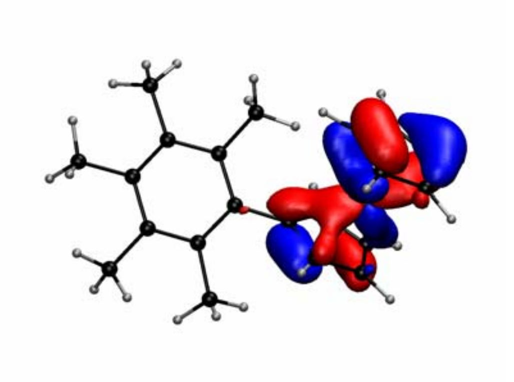
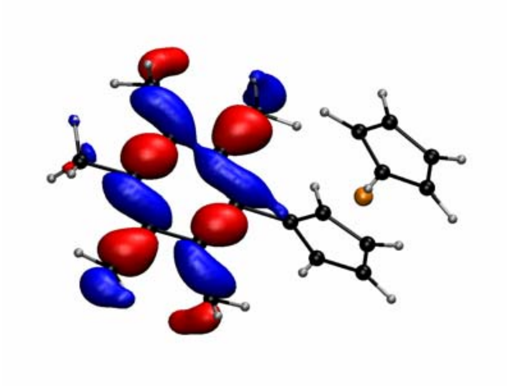
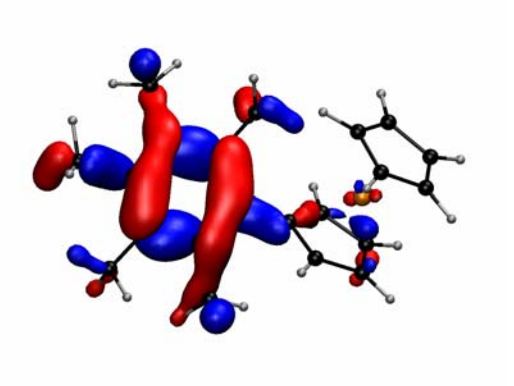
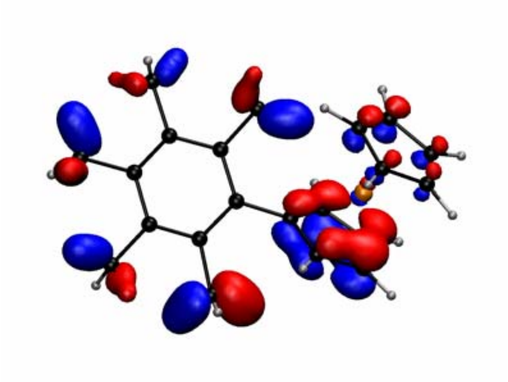
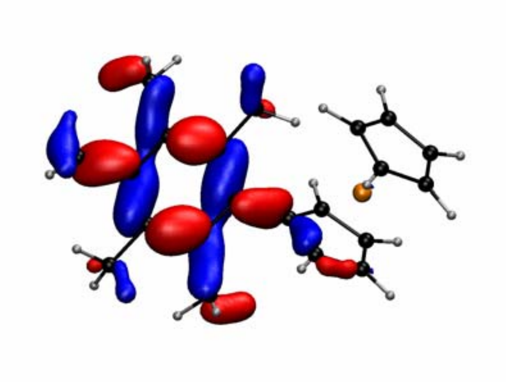
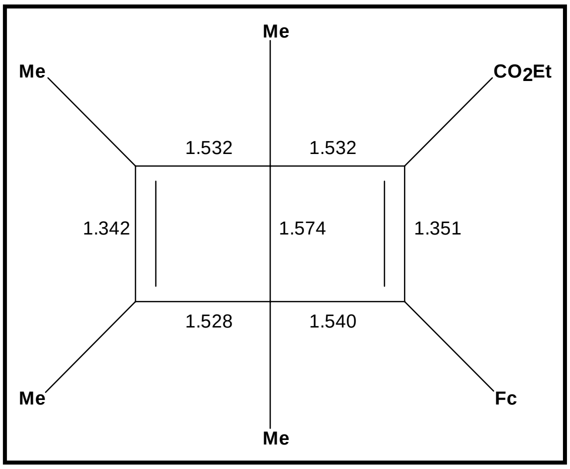
 orbital 88 (HOMO), *E* = –0.18775 a.u.	 orbital 89 (LUMO), *E* = –0.00701 a.u.
 orbital 86, *E* = –0.21090 a.u.	 orbital 87, *E* = –0.19074 a.u.
 orbital 84, *E* = –0.22165 a.u.	 orbital 85, *E* = –0.21238 a.u.
 orbital 82, *E* = –0.24759 a.u.	 orbital 83, *E* = –0.24413 a.u.

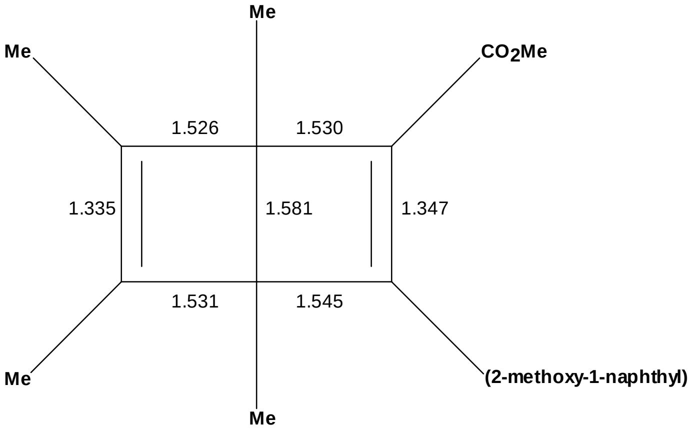
Figure S9 (continued).

 orbital 80, *E* = –0.26369 a.u.	 orbital 81, *E* = –0.26132 a.u.
 orbital 78, *E* = –0.31264 a.u.	 orbital 79, *E* = –0.30908 a.u.
 orbital 76, *E* = –0.34697s a.u.	 orbital 77, *E* = –0.31806 a.u.

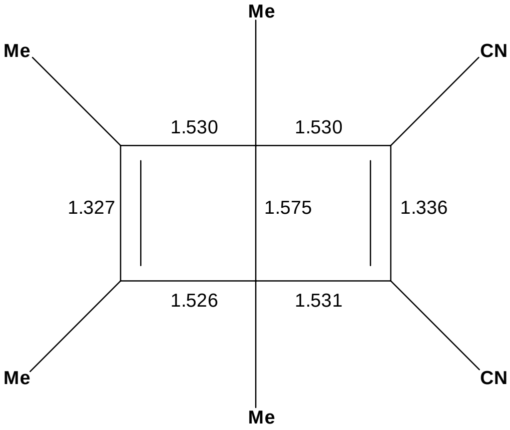
VI. Comparison of bond lengths in structurally characterised Dewar benzenes



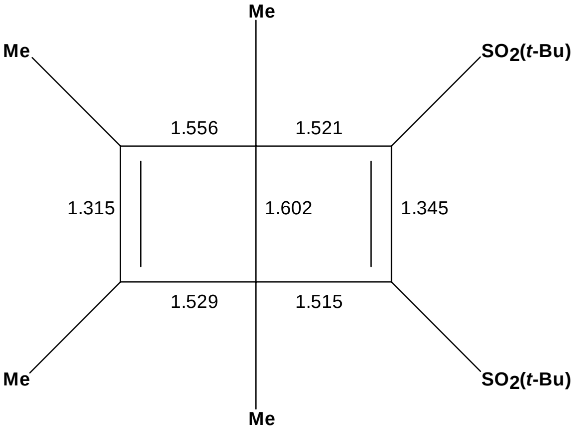
compound **3a**



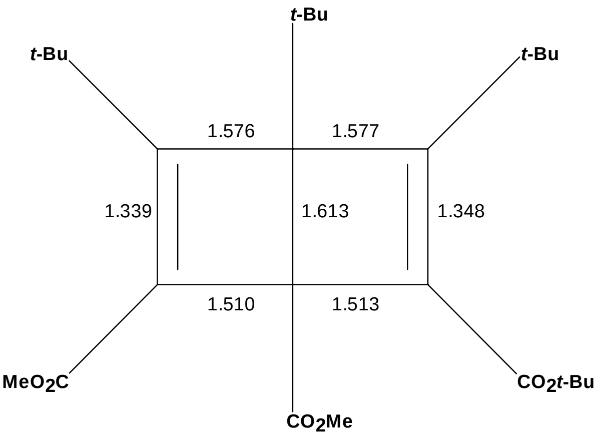
refcode **CITSII**



refcode **JUJYOC**



refcode **NADXEV**



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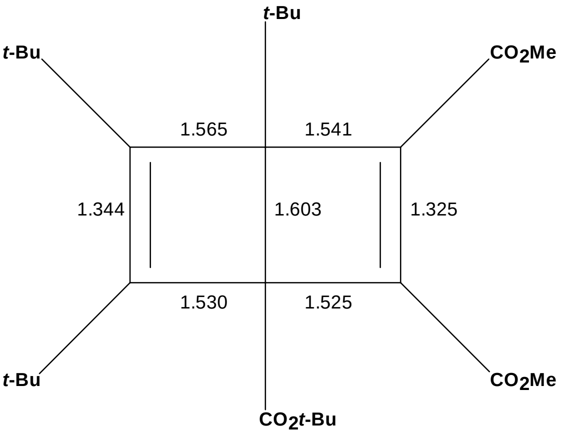

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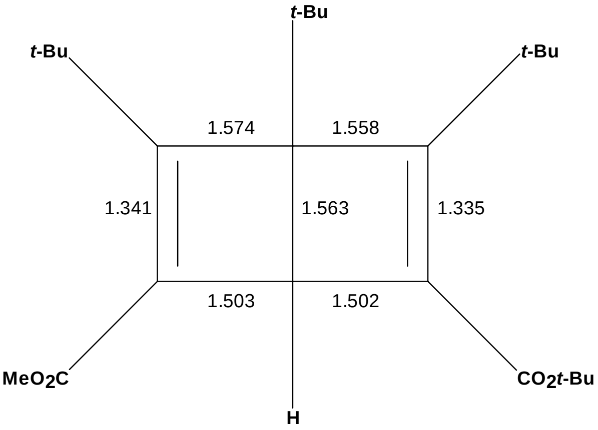

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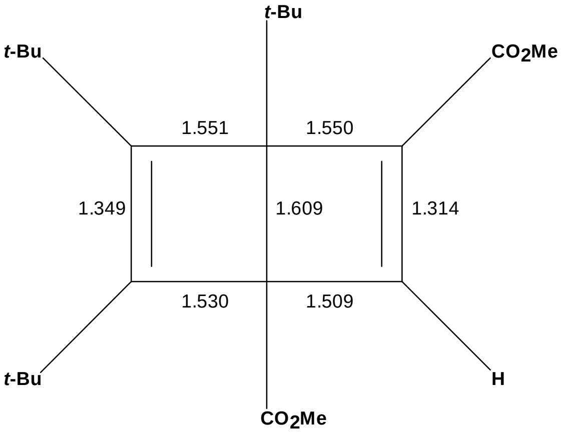

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