Stereochemical requirements of oxidative cyclisations in extended iterative organoiron-mediated routes to alkaloids

G. Richard Stephenson,* Caroline Roe, Christopher E. Anson,

School of Chemistry, University of East Anglia, Norwich, UK

Supporting Information

Contents:

1. General: Chemicals were reagent grade and used as supplied unless otherwise stated. All reactions were carried out in oven or flame dried glassware, under dry, oxygen-free nitrogen. Diethyl ether and THF were dried by distillation from sodium and benzophenone; dichloromethane was dried by distillation from calcium hydride. Reaction temperatures: –78 °C refers to acetone/dry ice; 0 °C refers to ice/ water cooling. Filtration refers to filtration under water-pump suction. TLC was visualized by UV irradiation (254 nm) or exposure to alkaline potassium permanganate solution followed by heating. IR spectra were recorded as a thin film or in solution in the specified solvent. HRMS measurements were performed on a high resolution double focussing (BE) mass spectrometer.

2. Use of 2D NMR spectra to obtain reliable assignments of ^{1}H and ^{13}C NMR spectra:

Assigning the ^{1}H NMR spectrum of alcohol **21** Illustrates the methods used to establish the assignments presented in Table S1. The benzylic CH_2 is a characteristic pair of doublets at ~4.5 ppm which are confirmed to be coupled by cross peaks in the COSY spectrum (geminal coupling ^{2}J = 12.2 Hz). The COSY spectrum also shows that there is a coupling (vicinal coupling ^{3}J = 6.7 Hz) between the inner diene proton 3-H doublet of doublets at 5.27 ppm and the 4-H doublet at 2.70 ppm. Similarly, couplings (^{3}J = 7.9 and 6.6 Hz) between the 5-H doublet of doublets at 3.02 ppm and

the two 6-H doublet of doublet of doublets at 2.42 and 1.66 ppm are apparent in the COSY spectrum. The *endo* 6β-H in tricarbonyliron complexes is further downfield than *exo* 6a-H. This is consistently the case in all the examples presented in table S1. There is also a large (^2J = 14.8 Hz) geminal coupling between the two 6-H peaks. On further expansion of the COSY, cross peaks for small couplings (^3J = 3.1 and 2.7 Hz) can also be identified between the two 6-H peaks and the 1-H doublet of doublet of doublets at 3.57 ppm and a tiny coupling (long-range ^4J = 2.0 Hz) is observed between 1-H and 3-H. The alcohol proton is a singlet at 1.58 ppm. The two aromatic proton peaks can be distinguished because of the cross peaks in the NOESY spectrum between the higher field aromatic peak at 6.87 ppm and the benzylic CH_2 protons at 4.61 and 4.52 ppm and also a cross peak between the lower field aromatic peak at 7.14 ppm and 4-H at 2.70 ppm, as shown by the two doubly boxed peaks in the NOESY spectrum (Figure S1). The NOSEY spectrum also allows the three methoxy groups to be unambiguously assigned. The 2-OMe is the furthest upfield at 3.67 ppm and can be identified because of the cross peak with 3-H at 5.27 ppm in the NOESY spectrum. The next methoxy peak is at 3.87 ppm and shows a cross peak with 6.87 ppm. The one remaining tall singlet at 3.95 ppm is confirmed by the cross peak with 7.14 ppm. These significant nOe effects are shown by the three singly boxed peaks in the NOESY spectrum (Figure S.1). In summary, the key to full assignment of the structure is to use NOESY data to differentiate the aromatic hydrogens by the proximity to the benzylic protons and then use this information to distinguish the OMe groups on the arene by further pairs of cross peaks. The OMe in the diene complex is typically upfield of Ar-OMe signals and so is easily identified in all the examples in Table S1.

With the ^{1}H NMR assignments complete, the HSQC spectra showed all the correlations between the ^{1}H and ^{13}C NMR spectra, so that all the carbons could be accurately assigned, except for the five quaternary carbons. For these, however, chemical shift positions give a good guide, as the two at the lowest field (148.3 and 146.8 ppm) which are aromatic are shifted downfield because they carry the oxygens of OMe groups. The diene carbon 2-C bearing an oxygen and is identified at 140.5 ppm consistently in all the structures with C-2 OMe groups, leaving the other two aromatic carbons (the point of attachment between the arene and the diene, and the position bearing the benzylic CH_2OH) at higher field at 135.7 and 130.1 ppm. This

general quaternary carbon assignment offers a useful guide for most of the compounds found in Table S2.

Similar methods have been used to complete the assignments shown in Tables S1 (^{1}H NMR) and S2 (^{13}C NMR). The full details of the 2D NRM spectra and presented in Section 2.

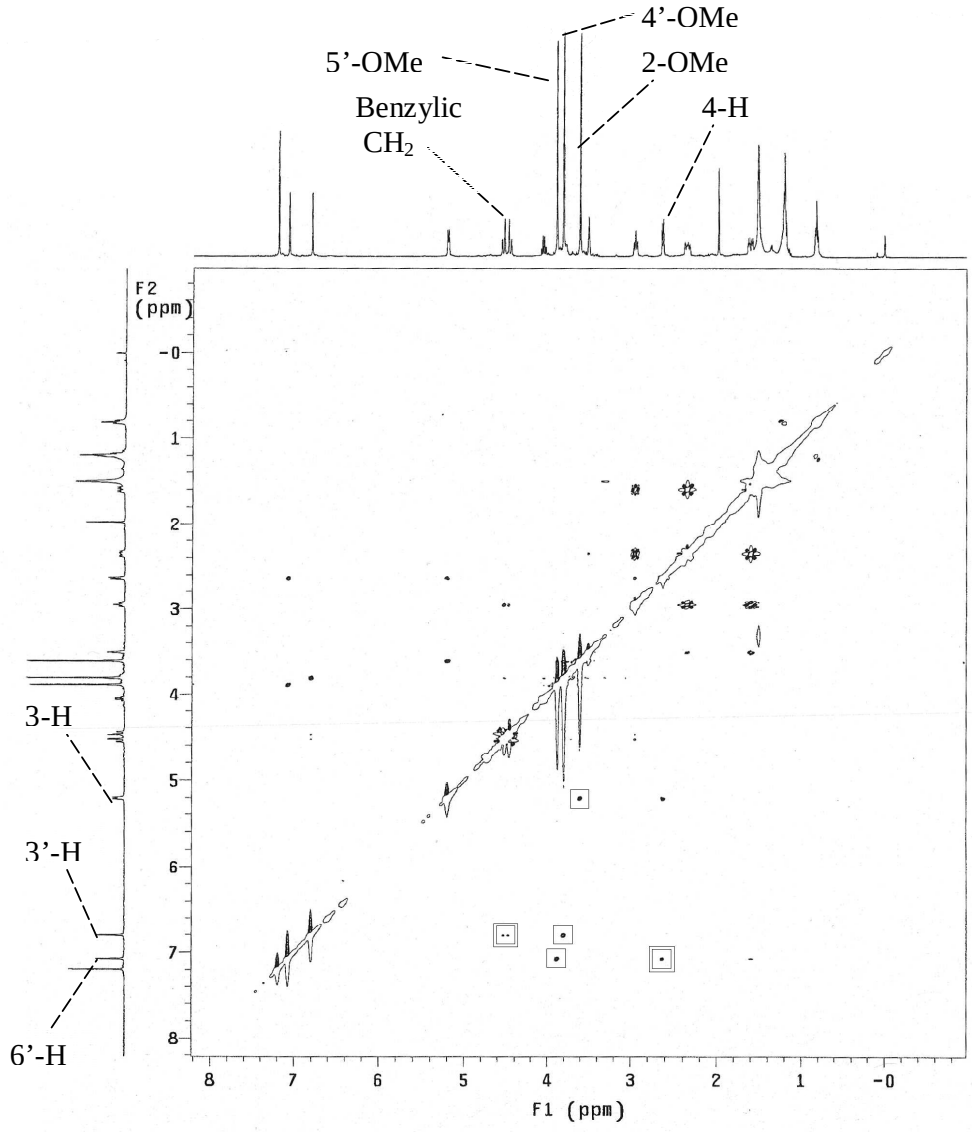
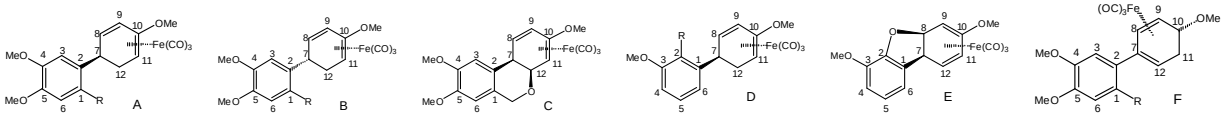


Figure S1. Example of the use of NOESY cross-peaks to distinguish 3'-H and 6'-H and the three OMe groups.

Table S1. Assignments for ^{1}H NMR spectra

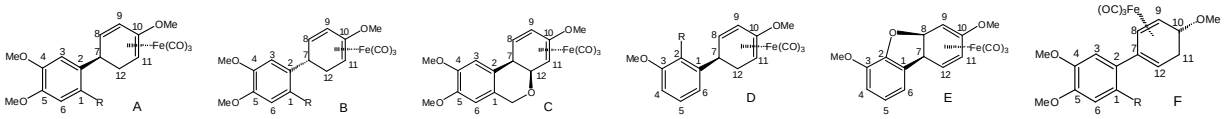


Number (structure type)	**11 (A)**	**8 (A)**	**9 (A)**	**21 (B)**	**18b (B)**	**18c (B)**	**10 (C)**	**13 (D)**	**14 (D)**	**15 (E)**	**19a (F)**	**19b (F)**	**19c (F)**
R	CHO	CH_2OMe	CH_2OH	CH_2OH	CH_2O-TBDPS	CH_2O-TIPS	-	OSEM	OH	-	CH_2O-Me	CH_2O-TBDPS	CH_2O-TIPS
δ_H	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]
1-H (11[a])	3.48 dd	3.50-3.42 m	3.51-3.45 m	3.57 ddd	3.47 m	3.55 m	3.33 dd[b]	3.48 dt	3.46 dt	3.60 dd[b]	3.45-3.38 m	3.17-3.10 m	3.40 d
3-H (9[a]) (8[c])	5.22 dd	5.19 dd	5.19 dd	5.27 dd	5.13 dd	5.25 d	5.01 dd[d]	5.16 dd	5.18 dd	5.17 dd[d]	5.41 d	5.27 dd	5.36 d[e]
4-H (8[a]) (9[c])	2.72 dd	2.74 dd	2.73 dd	2.70 d	2.61 d	2.72 d	2.88 dd[f]	2.83 dd	2.79 dd	2.97 dd[f]	3.26 dd[g]	3.17-3.10 m[g]	3.26 d[g]
5-H (7[a])	4.17 ddd[h]	3.50-3.42 m	3.51-3.45 m	3.02 dd	2.69 dd	2.82 dd	3.12 dd[i]	3.71 m	3.61 dt	3.80 dd[j]	3.45-3.38	3.17-3.10	3.30 m
6β-H (12[a])	2.48 ddd	2.37 ddd	2.39 ddd	2.42 ddd	2.11 ddd	2.35 ddd	4.56 dd[k,l]	2.39 ddd	2.40 ddd	5.31 dd[k]	2.16 ddd	1.61 dd	2.12 dd
6α-H (12[a])	1.73 dd	1.66 dd	1.68 d	1.66 ddd	1.50 ddd	1.60 dd	-	1.68 ddd	1.76 ddd	-	1.76 ddd	1.47 d	1.74 d
3'-H (6[a])	7.28	6.66[a]	6.68[a]	6.87	7.04	7.13	6.52[m]	-	-	-	6.90	7.01	7.17
4'-H (4[a])	-	-	-	-	-	-	-	6.72 d	6.82-6.68	6.66 dd[o]	-	-	-
5'-H (5[a])	-	-	-	-	-	-	-	6.99 t	6.82-6.68	6.77 dd[n]	-	-	-
6'-H (3[a])	6.76	6.75[a]	6.80[a]	7.14	7.07	7.09	6.69[p]	6.72 d	6.82-6.68	6.70 dd[q]	6.95	6.88	6.90
2-OMe (10-OMe)	3.71	3.70	3.71	3.67	3.63	3.68	3.64[r]	3.70	3.69	3.61[r]	-	-	
5β-OMe (10-OMe)											3.45-3.38	3.23	3.22
3'-OMe (3-OMe)	-	-	-	-	-		-	3.80	3.87	3.83[s]			

4'-OMe (5-OMe)	3.90	3.85[a]	3.85[a]	3.87	3.83	3.86	3.84[t]	-	-	-	3.91	3.85	3.90
5'-OMe (4-OMe)	3.96	3.87[a]	3.88[a]	3.95	3.95	3.94	3.87[u]	-	-	-	3.87	3.88	3.87
R CH_nO	10.19[v]	4.33	4.63	4.61 d, 4.52 d	4.67 d, 4,57 d	4.74 d, 4.62 d	-	5.09	5.71		4.48	4.81 d, 4.71 d	4.97 d, 4.81
R OP	-	3.39	1.60	1.58[w]	7.67 dt, 7.48-7.34 m, 1.07	1.21-1.05 m, 1.08 d	-	3.99-3.78	5.71[x]		3.41	7.67 dd, 7.63 dd, 7.48-7.33, 1.08	1.21-1.08 m, 1.09

[a] numbering used in images of spectra to aid comparison; [b] position 4 in C & E; [c] numbering for (8) and (9) is reversed in F; [d] position 2 in C & E; [e] unusual δ because next to Ar; [f] 1 in C & E; [g] unusual δ because next to 5β-OMe; [h] unusual δ because next to formyl Ar; [i] position 10b in C; [j] position 9b in E; [k] position 4a in C & E; [l] unusual δ because next to O; [m] position 7 in C; [n] position 8 in E; [o] position 7 in E; [p] position 10 in C; [q] position 9 in E; [r] 3-OMe in C & E; [s] 6-OMe in E; [t] 8-OMe in C; [u] 9-OMe in C; [v] unusual δ because formyl CHO; [w] OH; [x] phenolic OH.

Table S2. Assignments for [13]C NMR spectra.



Number (structure type)	**11 (A)**	**8 (A)**	**9 (A)**	**21 (B)**	**18b (B)**	**18c (B)**	**10 (C)**	**13 (D)**	**14 (D)**	**15 (E)**	**19a (F)**	**19b (F)**	**19c (F)**
R	CHO	CH_2O Me	CH_2OH	CH_2OH	CH_2O-TBDPS	CH_2O-TIPS	-	OSEM	OH	-	CH_2O-Me	CH_2O-TBDPS	CH_2O-TIPS
δ_C	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]
1-C (11[a])	53.0	53.4	53.3	55.7	55.7	55.7	52.0[b]	53.7	53.6	53.2[b]	75.4[c]	75.4[c]	75.4[c]
2-C (10[a])	140.3	140.2	140.2	140.5	140.4	140.4	141.1[d]	140.8/ 140.3	140.1	140.1[d]	106.5[e]	106.2[e]	106.5[e]
3-C (9[a])	66.1	66.5	66.2	65.5	65.5	65.6	75.0[e]	66.6	66.6	67.7[f]	86.3[c]	86.2[c]	82.3[c]
4-C (8[a])	54.4	55.8	55.6	55.7	55.7	55.5	51.7[g]	55.7	54.6	49.4[g]	61.2	61.0	60.9
5-C (7[a])	36.7	38.5	38.2	33.1	32.8	32.9	35.4[h]	35.7	36.1	45.6[i]	62.1[j]	62.2[j]	62.1[j]
6-C (12[a])	34.6	34.3	34.5	38.2	37.1	37.1	65.8[k]	34.0	33.0	86.9[k]	34.6	34.2	34.5

1'-C (2[a])	144.2	137.7	137.2	135.7/ 130.1	134.3/ 130.5	133.4/ 131.0	131.7[l]	140.8/ 140.3	132.1	136.1[m]	130.0/ 129.2	133.3 / 133.0	133.7 / 126.6
2'-C (1[a])	126.4	127.6	130.1	135.7/ 130.1	134.3/ 130.5	133.4/ 131.0	126.8[n]	152.0	146.1 / 142.8	147.2 / 144.4[o]	130.0/ 129.2	133.3 / 133.0	133.7 / 126.6
3'-C (6[a])	111.1	109.5	109.6	111.9	111.0	109.9	108.0[p]	144.1	146.1 / 142.8	147.2 / 144.4[q]	112.3	110.4	109.6
4'-C (5[a])	147.5	148.7/ 146.9	148.6/ 147.0	148.3/ 146.8	147.8/ 146.9	147.2/ 146.8	148.5/ 147.1[r]	109.9	108.2	115.7[s]	149.1/ 148.3	148.9 / 147.5	149.0 / 147.2
5'-C (4[a])	153.8	148.7/ 146.9	148.6/ 147.0	148.3/ 146.8	147.8/ 146.9	147.2/ 146.8	148.5/ 147.1[t]	124.5	119.3 / 119.1	120.8[u]	149.1/ 148.3	148.9 / 147.5	149.0 / 147.2
6'-C (3[a])	108.7	112.5	111.7	110.0	109.8	109.6	111.2[v]	118.7	119.3 / 119.1	111.0[w]	114.0	113.5	113.5
2-OMe (10-OMe)	54.5	54.4	54.4	54.5	54.3	54.5	54.7[x]	54.3	54.3	54.8[x]	-	-	-
5β-OMe (10-OMe)	-	-	-	-	-	-	-	-	-	-	55.9	55.1	55.3
4'-OMe (5-OMe)	56.0	55.9	55.8	55.9	55.7	55.7	55.9	-	-	-	55.9	55.8	55.8
5'-OMe (4-OMe) (3-OMe)[y]	56.0	56.0	55.9	55.8	55.7	55.8	56.0	55.6	56.0	55.8[z]	55.9	56.0	56.0
R CH_nO	189.4[aa]	72.6	62.7	62.8	63.0	62.2	62.7	97.4	-	-	72.4	63.7	62.9
R OP	-	58.1	-	-	135.7, 133.6, 129.8, 127.8, 26.7, 19.2	18.1, 12.0	-	64.7 18.1 –1.6	-	-	55.2	135.6, 129.9, 129.8, 127.8, 127.7, 127.3, 26.8, 19.3	18.0, 12.0
Fe-CO	n.o.[ab]	212.7	211.2	211.5	211.5	n.o.[ab]	210.7	211.5	211.3	n.o.[ab]	211.0	210.7	210.7

[a] numbering used in images of spectra to aid comparison; [b] position 4 in C & E; [c] unusual δ because next to Ar; [d] position 3 in C & E; [e] unusual δ because C-Ar; [f] position 2 in C & E; [f] unusual δ because next to Ar; [g] position 1 in C & E; [h] position 10b in C; [i] position 9b in E; [j] unusual δ because C-O; [k] position 4a in C & E; [l] position 10a in C; [m] position 9a in E; [n] position 6a in C; [o] position 5a in E; [p] position 7 in C; [q] position 6 in E; [r] position 8 in C; [s] position 7 in E; [t] position 9 in C; [u] position 8 in E; [v] position 10 in C; [w] position 9 in E; [x] 3-OMe in C & D; [y] (numbered in scans as 3-OMe in D & E) [z] 6-OMe in E; [aa] CHO; [ab] not observed.

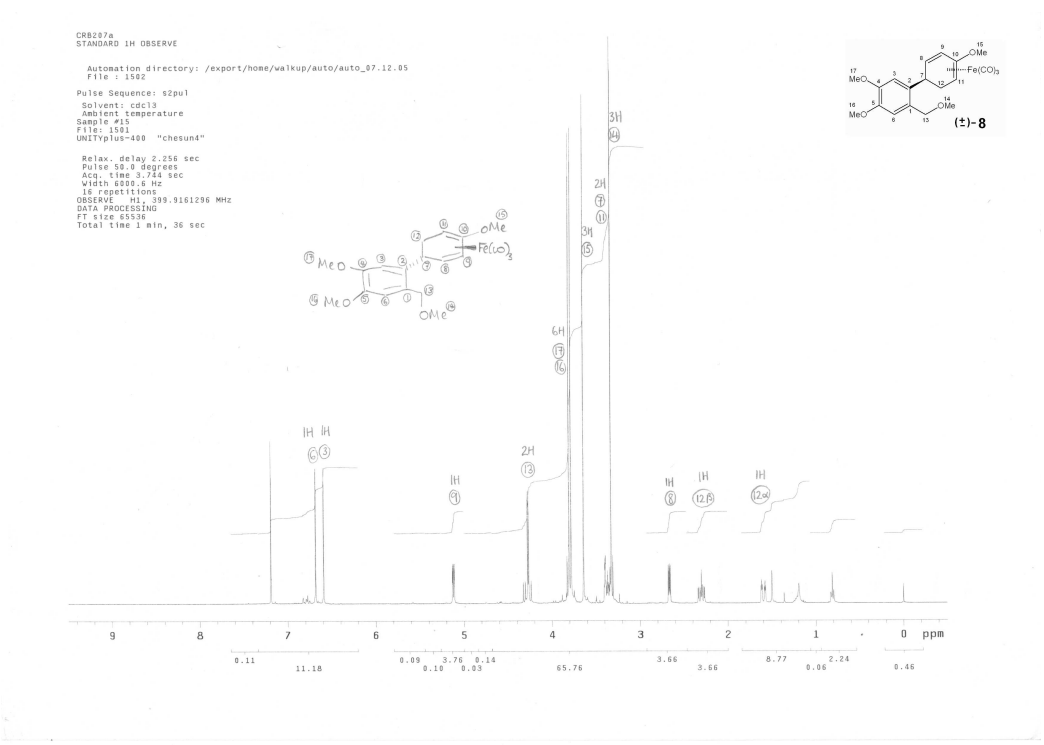
The similarities in chemical shift positions in tables S1 and S2 add further confirmation to the assignments. In many cases (see footnotes) the structural causes for exceptions to the general pattern are apparent. For a few examples, additional

information about the interpretation of 2D NMR data is needed to support the assignments. For structure **10** (the cyclised product with a 6-membered ring containing OCH_2), the resonance at 6.69 ppm shows NOESY cross-peak with the signal at 2.88 ppm which corresponds to a hydrogen on the dieneiron complex, and 6.52 shows NOESY cross-peak with 4.30 which is one of the Hs of the OCH_2 in the oxacyclic ring. The OMe group at 3.84 ppm shows a NOESY cross-peak with the signal at 6.52 ppm, and the OMe at 3.87 ppm shows a NOESY cross-peak with 6.69. For structure **11** (which has a formyl group on Ar), the aromatic hydrogens are much more widely separated (7.28 and 6.76 ppm) with the signal at 7.28 showing a NOESY cross-peak with the formyl hydrogen at 10.19 ppm. The resonance for the aromatic hydrogen at 7.28 ppm is moved substantially because of the formyl group and is now the more down-field of the two aromatic hydrogens. The other aromatic hydrogen at 6.76 ppm shows a NOESY cross-peak with 6a-H at 1.73 ppm and so is beside the point of attachment of the cyclohexadienyliron group. The OMe group at 3.96 ppm shows a NOESY cross-peak with 6.76, and the OMe group at 3.90 ppm shows a NOESY cross-peak with the signal at 7.28 ppm. For structure **18b**, aromatic hydrogens at 7.04.and 7.07 ppm are distinguished by the nOe between 7.07 and 4-H at 2.61 which shows that the signal at 7.04 ppm must be beside the benzylic position, so order of Ar Hs is reversed compared to **18c**. So for **18b** 7.07 is near to 4-H and is also beside OMe at 3.95 (NOESY cross peak) and 7.04 is next to OMe at 3.83. (see expansion NOESY). For structure **18c**, the aromatic hydrogens are at 7.13.and 7.09 ppm. In this case, NOESY cross peak with the benzylic hydrogens was not observed. The nOe between 7.09 and 4-H at 2.72, however, shows that the hydrogen with the resonance at 7.13 ppm must be beside the benzylic position, so order of Ar Hs is reversed compared to **18b**. For rearranged 2-aryldiene structure **19a**, the signal at 6.90 ppm shows a NOESY cross-peak with the benzylic CH_2 at 4.48. The other aromatic hydrogen shows a NOESY cross-peak with the inner hydrogen (3-H) of the rearranged diene (the CH beside the Ar group) at 5.41 (this cross-peak for the inner H on the diene is a signature for the rearranged structure). The aromatic hydrogens are reversed in order in **19a**, compared to **19b** and **19c**. The 7.17 signal shows NOESY cross-peak with the OMe group at 3.90 and the ArH at 6.90 shows NOESY cross-peak with the OMe group at 3.87, so distinguishing the two OMe groups. For **19b**, the aromatic hydrogen at 7.01 ppm shows a NOESY cross-peak with the benzylic CHs at 4.81 and 4.71. The other aromatic hydrogen at 6.88 ppm shows a NOESY cross-peak

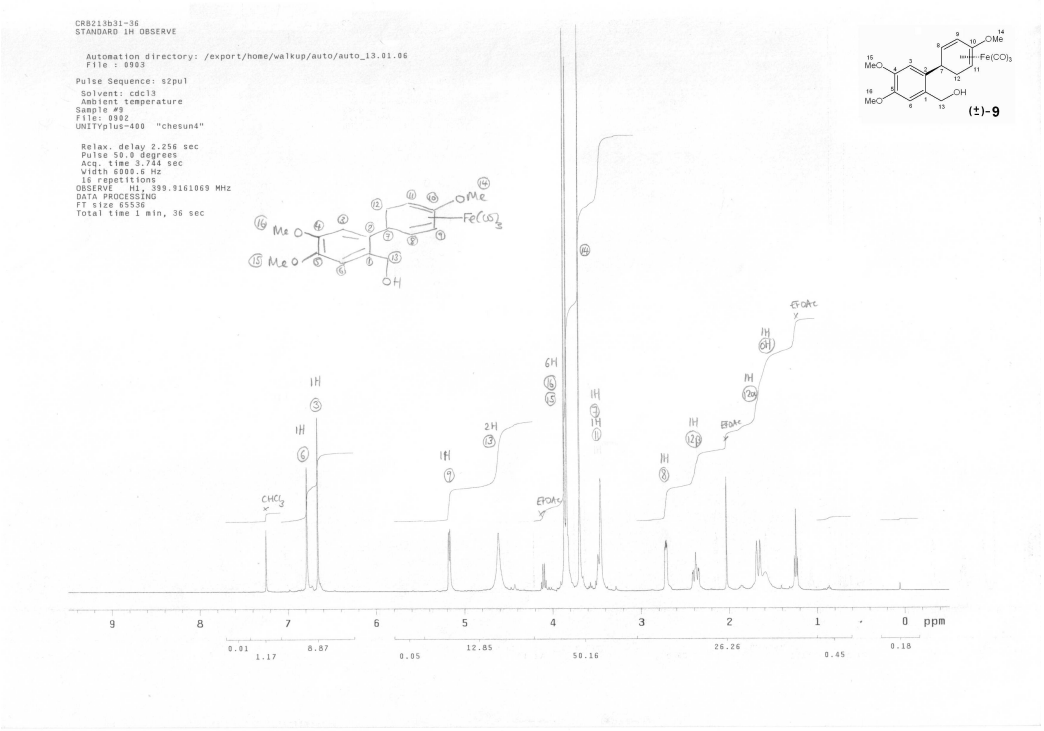
with the inner of the rearranged diene (CH beside the Ar group) at 5.27 (again, note that this cross-peak for the inner H on the diene is a signature for the rearranged structure). The 7.01 signal shows a NOESY cross-peak with the OMe group at 3.85 ppm, and the aromatic hydrogens at 6.88 ppm shows a NOESY cross-peak with the OMe group at 3.88 ppm, so distinguishing the two OMe groups. For **19c**, the aromatic hydrogen at 7.17 ppm shows a NOESY cross-peak with the benzylic CHs at 4.97 and 4.81 ppm. The other aromatic hydrogen shows a NOESY cross-peak with the inner of the rearranged diene (CH beside the Ar group) at 5.36 (the signature for the rearranged structure). The 7.17 ppm signal shows a NOESY cross-peak with the OMe group at 3.90 ppm, and the aromatic hydrogen at 6.90 ppm shows a NOESY cross-peak with the OMe group at 3.87 ppm, so distinguishing the two OMe groups. In the three unexpected rearranged structures (**19a**, **19b**, **19c**), the new nOe effect between the inner H on the diene and the aromatic hydrogen confirms that the 2-aryldiene structure confirmed by X-ray crystallography for **19a** is present in all three examples.

3. Spectroscopic and Mass Spectrometric Data:

(±)-Tricarbonyl[(1,2,3,4-η)-5α-(4',5'-dimethoxy-2'-methoxymethyl-phenyl)-2-methoxy-1,3-cyclohexadiene]iron(0) **8**

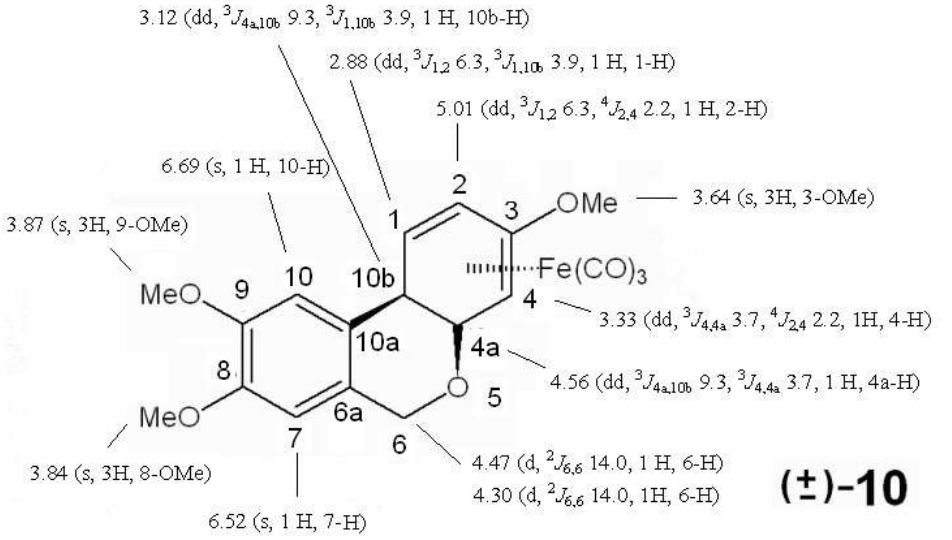


(±)-Tricarbonyl[(1,2,3,4-η)-5α-(4',5'-dimethoxy-2'-hydroxymethyl-phenyl)-2-methoxy-1,3-cyclohexadiene]iron(0) **9**

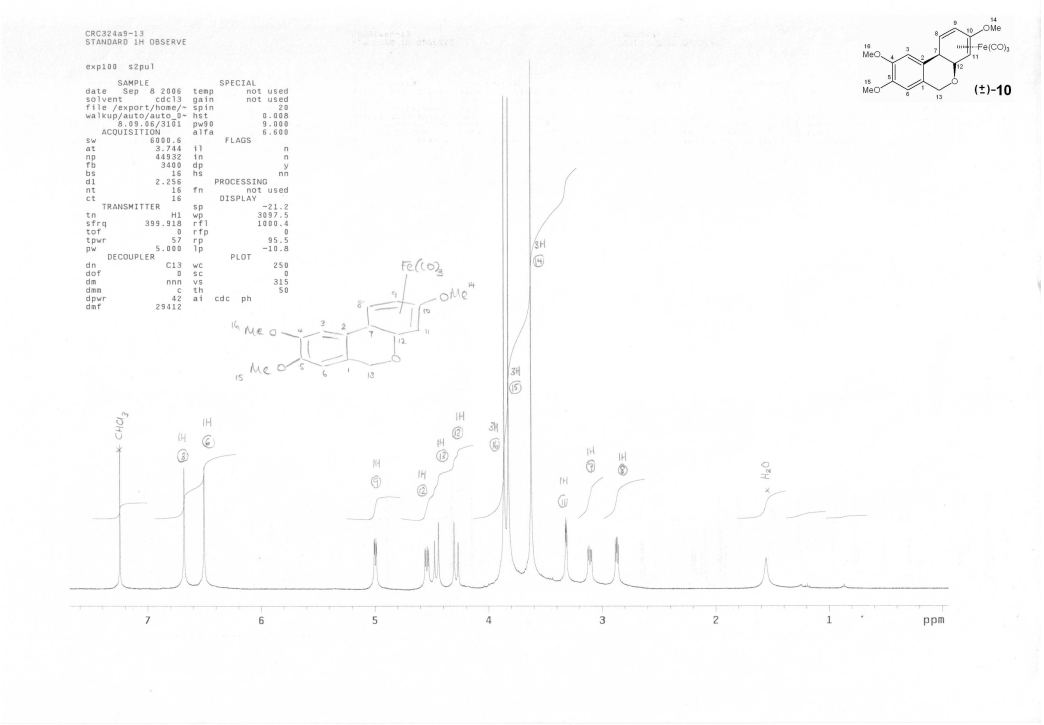


(±)-Tricarbonyl[(1,2,3,4-η)-(4a,10b-dihydro-3,8,9-trimethoxy-6*H*-dibenzo[*b*,*d*]pyran)]iron(0)

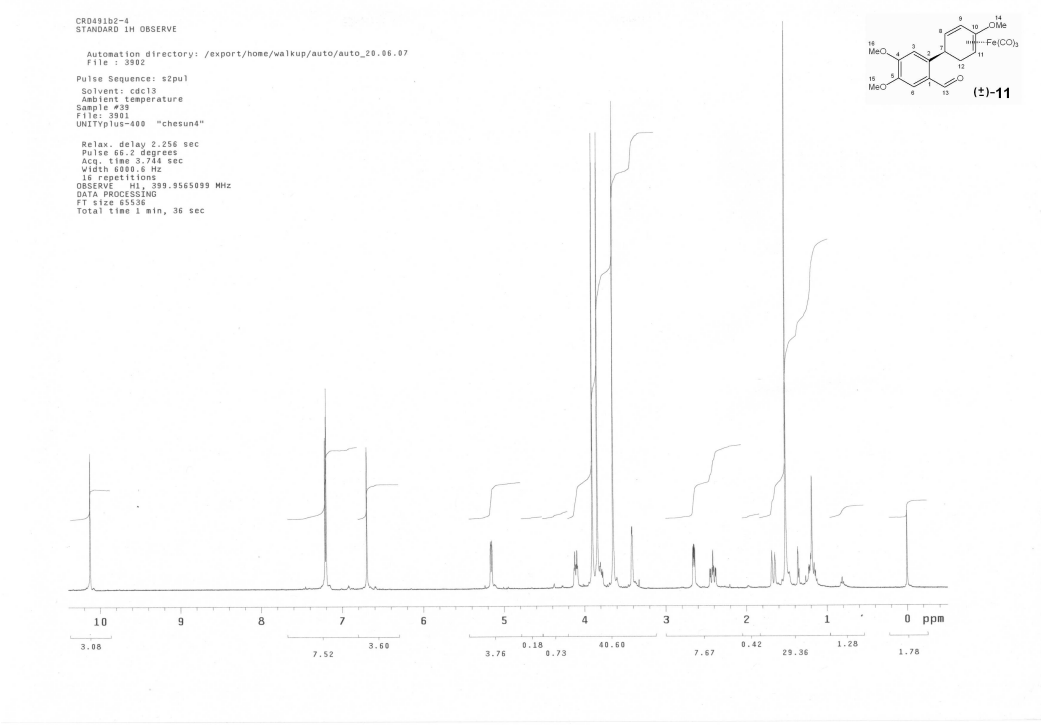
10



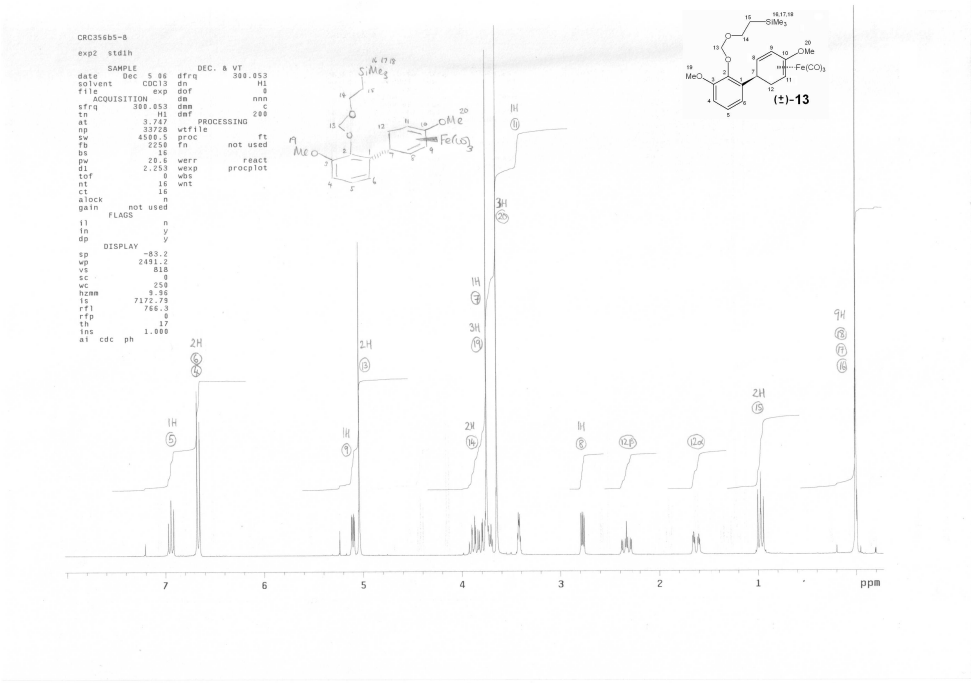
(±)-Tricarbonyl[(1,2,3,4-η)-(4a,10b-dihydro-3,8,9-trimethoxy-6*H*-dibenzo[*b*,*d*]pyran)]iron(0) 10



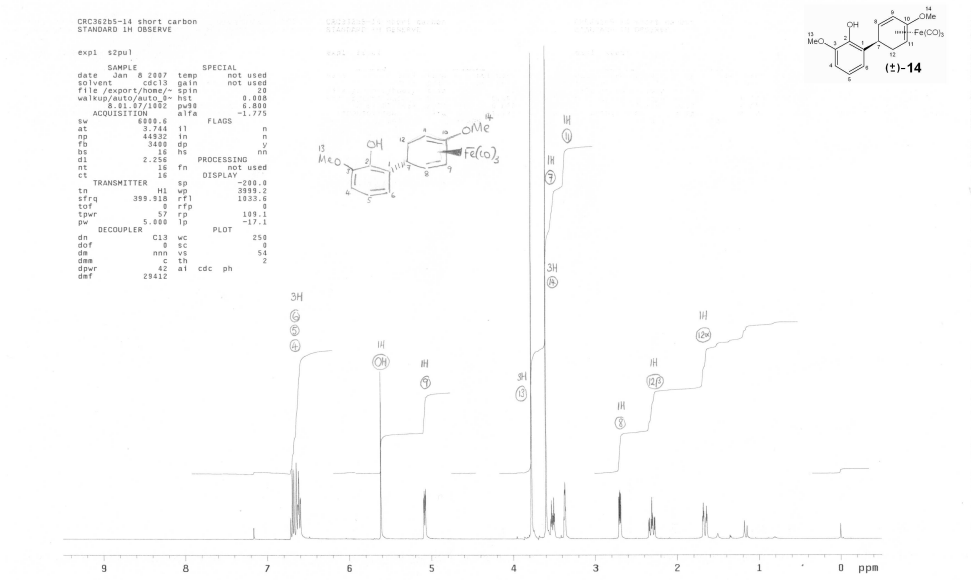
(±)-Tricarbonyl[(1,2,3,4-η)-5α-(2’-formyl-4’,5’-dimethoxyphenyl)-2-methoxy-1,3-cyclohexadiene]iron(0) **11**



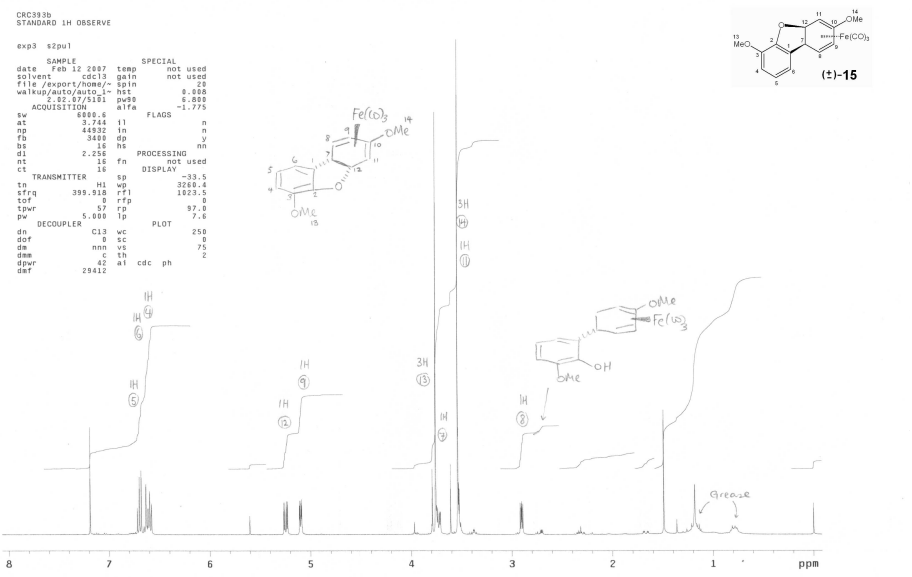
(±)-Tricarbonyl[(1,2,3,4-η)-2-methoxy-5α-(3’-methoxy-2’-(2’’-trimethylsilanyl-ethoxymethoxy)-phenyl)-1,3-cyclohexadiene]iron(0) **13**



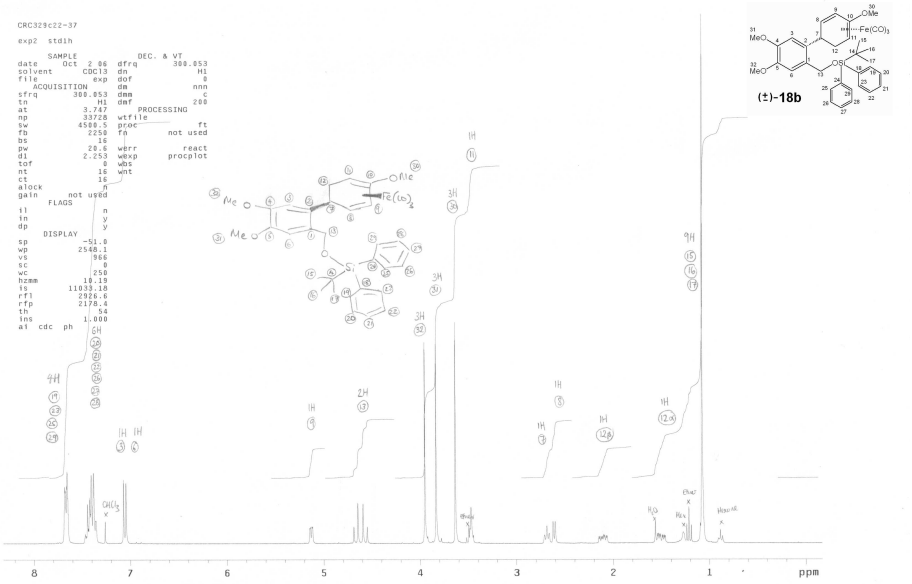
(±)-Tricarbonyl[(1,2,3,4-η)-5α-(2’-hydroxy-3’-methoxy-phenyl)-2-methoxy-1,3-cyclohexadiene]iron(0) **14**



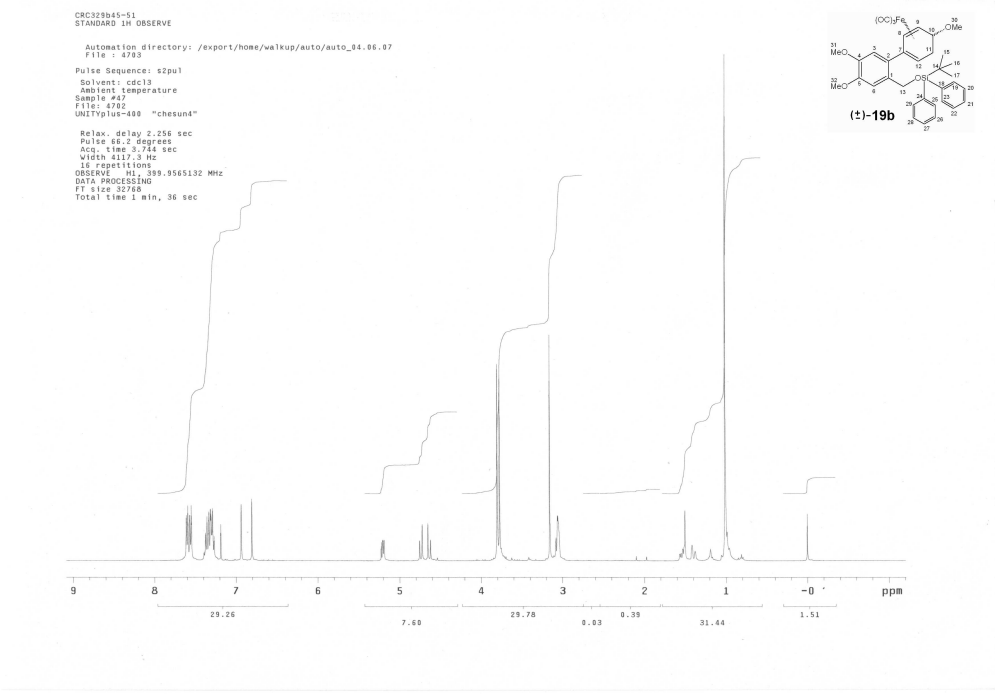
(±)-Tricarbonyl[(1,2,3,4-η)-(3,6-dimethoxy-4a,9b-dihydrodibenzofuran)]iron(0) **15**



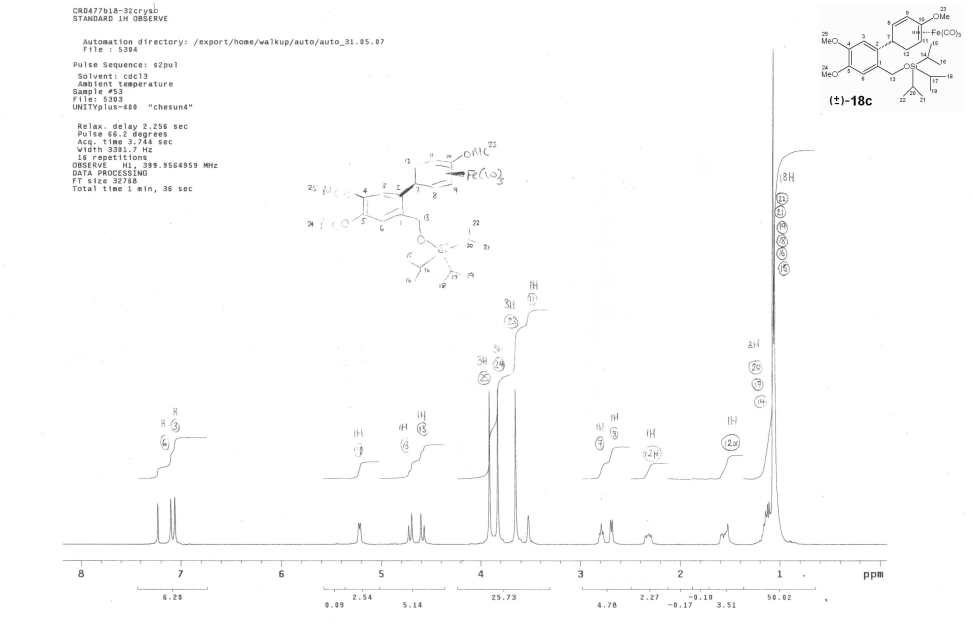
(±)-Tricarbonyl[(1,2,3,4-η)-5β-(2'-(*tert*-butyl-diphenyl-silanyloxymethyl)-4',5'-dimethoxyphenyl)-2-methoxy-1,3-cyclohexadiene]iron(0) **18b**



(±)-Tricarbonyl[(1,2,3,4-η)-2-(2'-(*tert*-butyl-diphenyl-silanyloxymethyl)-4',5'-dimethoxyphenyl)-5β-methoxy-1,3-cyclohexadiene]iron(0) **19b**

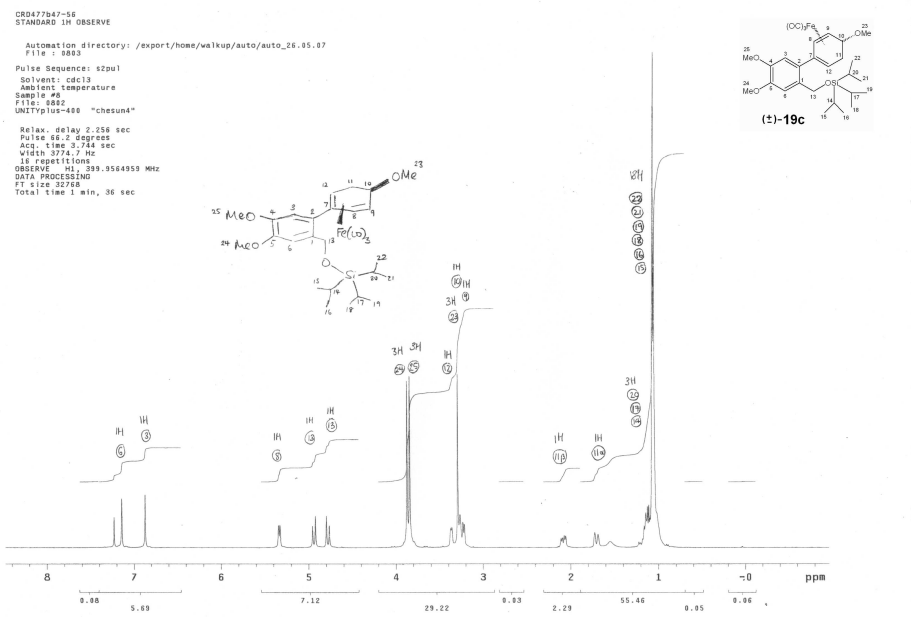


(±)-Tricarbonyl[(1,2,3,4-η)-5β-(4',5'-dimethoxy-2'-triisopropylsilanyloxymethyl-phenyl)-2-methoxy-1,3-cyclohexadiene]iron(0) **18c**

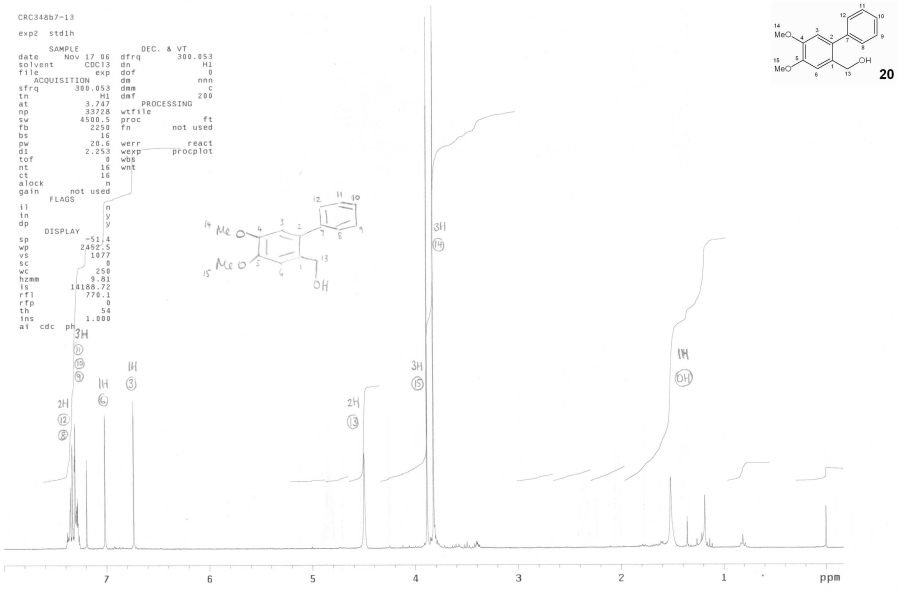


For **18c**: Ar Hs at 7.13.and 7.09. NoE between 7.09 and 2.72 shows that 7.13 must be beside the benzylic one (NOESY cross peak missing), so order of Ar Hs is reversed compared to **18b**

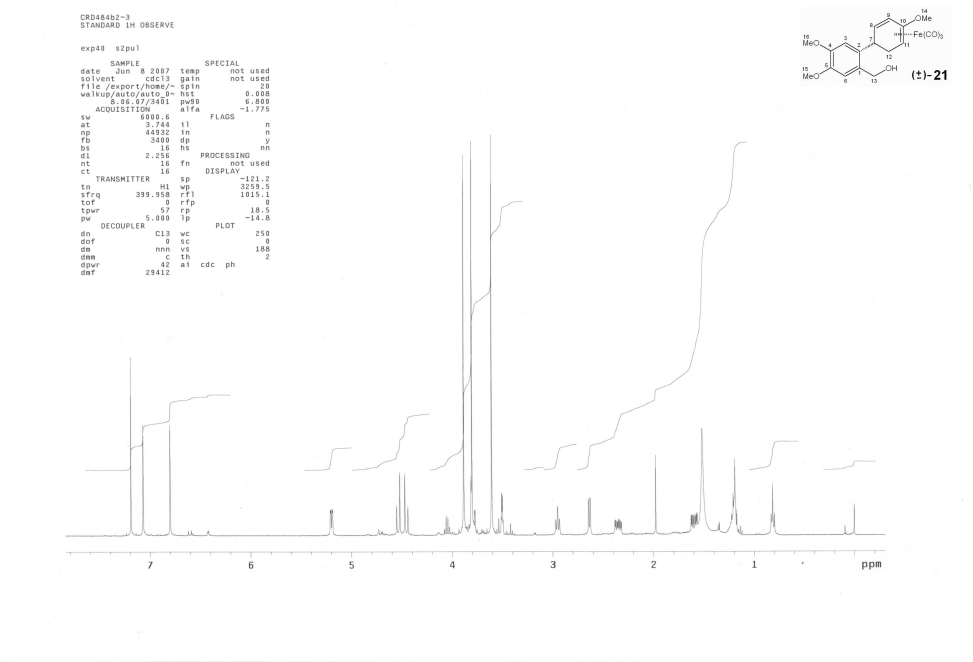
(±)-Tricarbonyl[(1,2,3,4-η)-2-(4',5'-dimethoxy-2'-triisopropylsilanyloxymethyl-phenyl)-5β-methoxy-1,3-cyclohexadiene]iron(0) **19c**



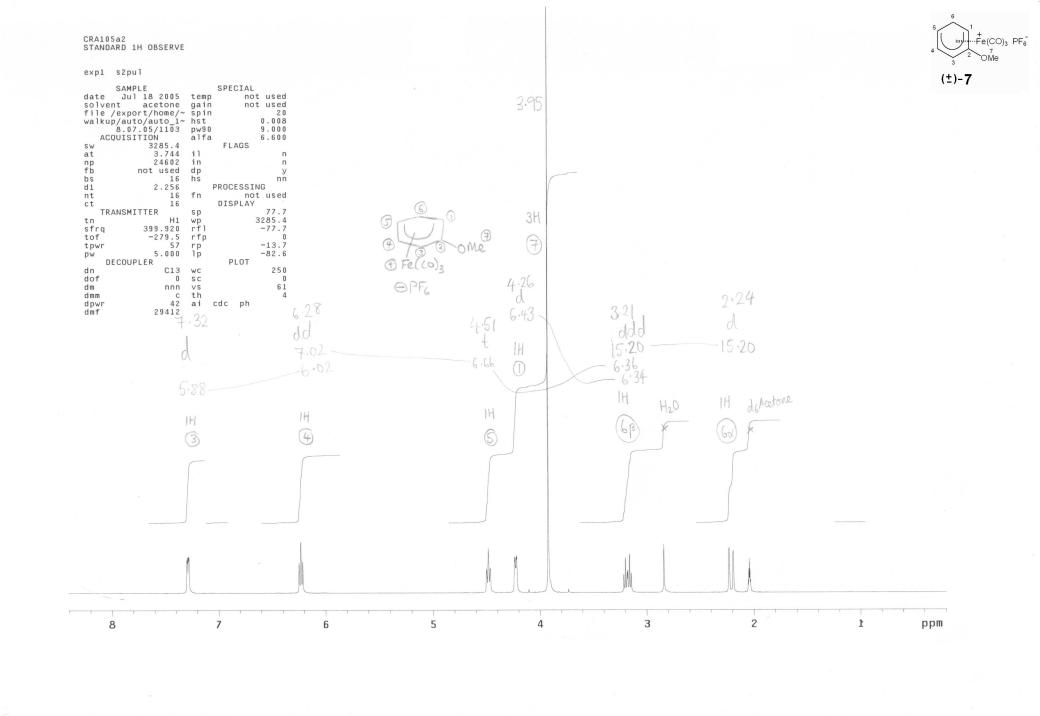
(4,5-Dimethoxy-biphenyl-2-yl)methanol **20**



(±)-Tricarbonyl[(1,2,3,4-η)-5β-(4',5'-dimethoxy-2'-hydroxymethyl-phenyl)-2-methoxy-1,3-cyclohexadiene]iron(0) **21**



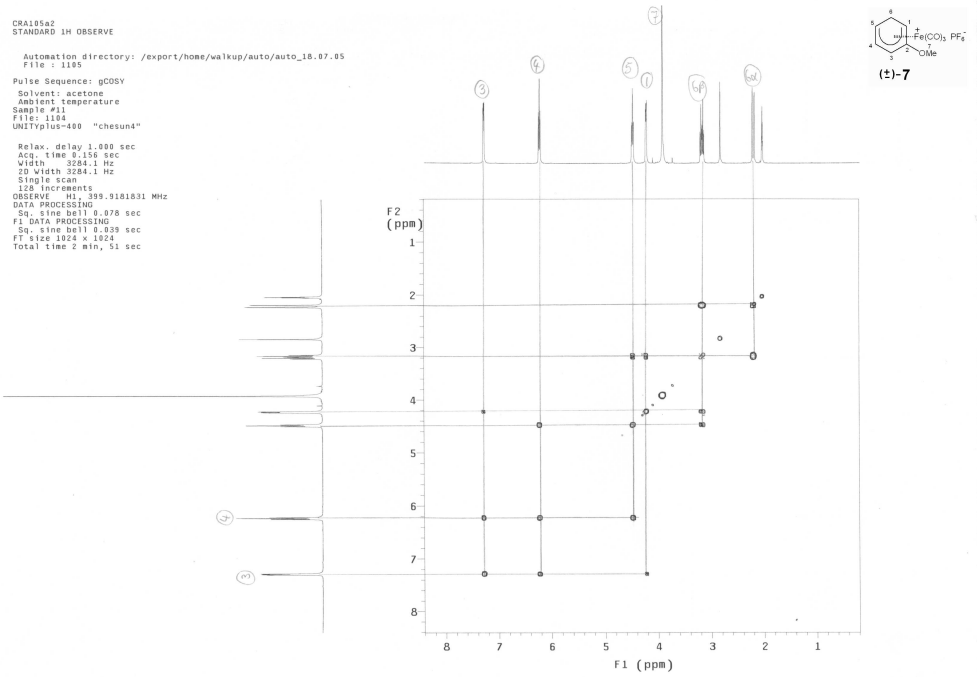
(±)-Tricarbonyl[(1,2,3,4,5-η)-2-methoxycyclohexadienyl]iron(1+) hexafluorophosphate(1–) **7**

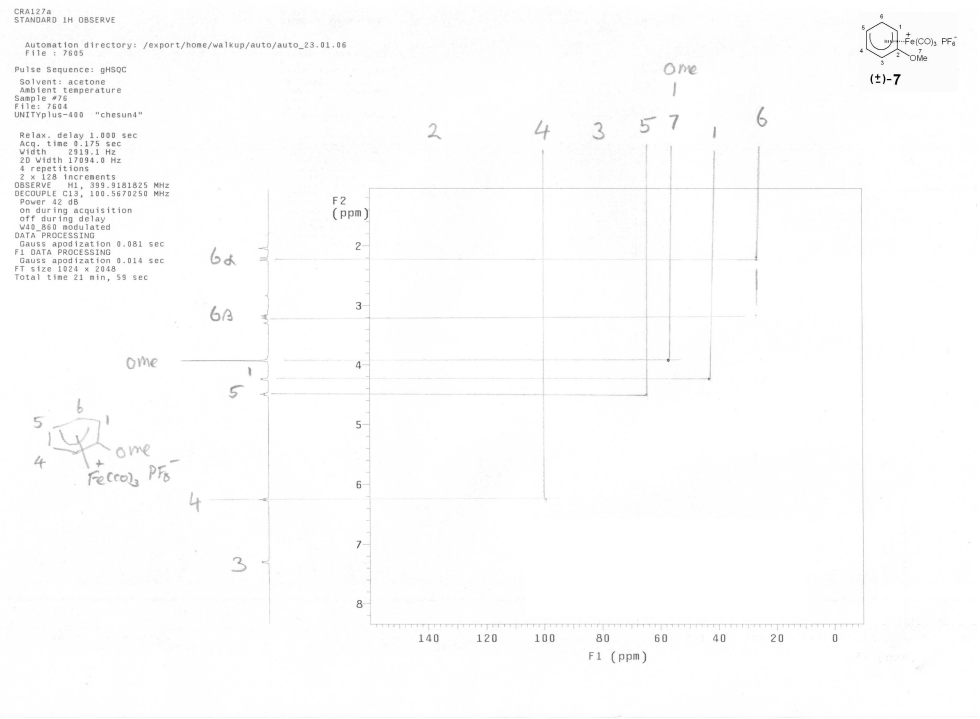


δ_H (400 MHz, d_6-acetone) 7.32 (1H, d, $J_{3,4}$ 6.0, 3-H), 6.28 (1H, dd, $J_{4,5}$ 6.8, $J_{3,4}$ 6.0, 4-H), 4.51 (1H, dd, $J_{4,5}$ 6.8, $J_{5,6\beta}$ 6.5, 5-H), 4.26 (1H, d, $J_{1,6\beta}$ 6.4, 1-H), 3.95 (3H, s, 7-

H_3), 3.21 (1H, ddd, $J_{6\alpha,6\beta}$ 15.2, $J_{5,6\beta}$ 6.5, $J_{1,6\beta}$ 6.4, 6β-H), 2.24 (1H, d, $J_{6\alpha,6\beta}$ 15.2, 6α-H).

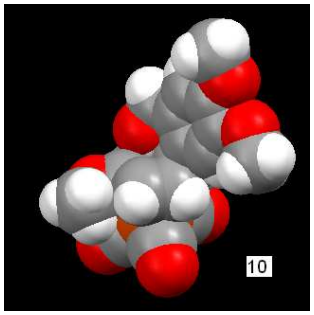
δ_C (75 MHz, d_6-acetone) 123.7 (2-C), 100.1 (4-C), 76.9 (3-C), 65.4 (5-C), 57.7 (7-C), 43.8 (1-C), 27.4 (6-C).

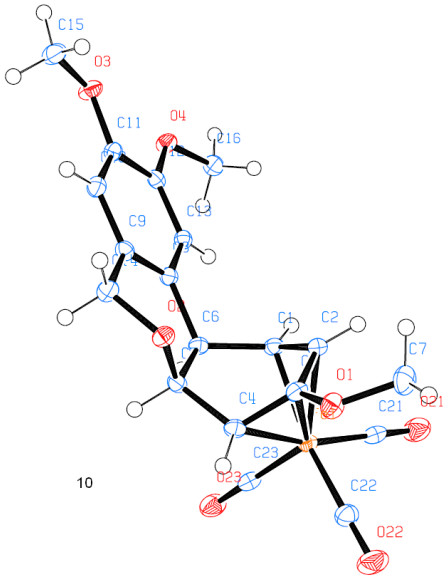




4. Selected bond lengths and angles:

X-ray structure of the cyclisation product **10**.





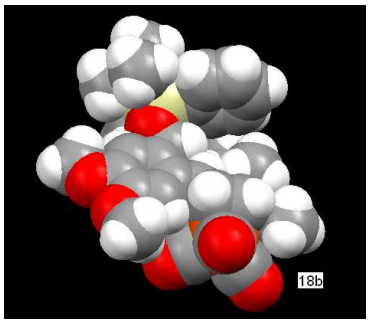
Selected geometric informations for 10

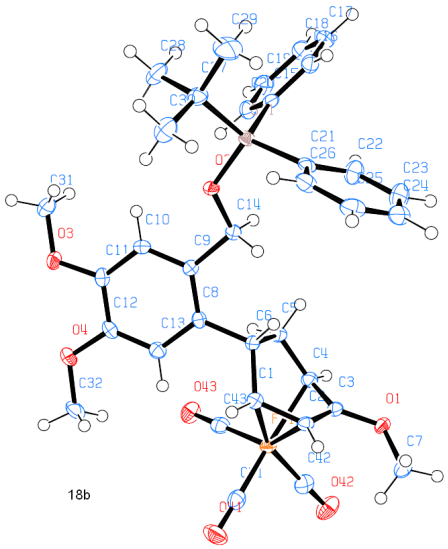
Atoms 1,2	d 1,2 [Å]	Atoms 1,2	d 1,2 [Å]
Fe1—C23	1.7869(19)	C7—H71	0.98(2)
Fe1—C21	1.7902(19)	C7—H72	0.99(2)
Fe1—C22	1.7992(19)	C7—H73	0.96(2)
Fe1—C2	2.0751(17)	C8—C9	1.383(2)
Fe1—C1	2.0873(16)	C8—C13	1.400(2)
Fe1—C3	2.0878(16)	C9—C10	1.403(2)
Fe1—C4	2.0997(17)	C9—C14	1.505(2)
C21—O21	1.143(2)	C10—C11	1.379(2)
C22—O22	1.143(2)	C10—H12	0.93(2)
C23—O23	1.144(2)	C11—O3	1.371(2)
C1—C2	1.428(2)	C11—C12	1.409(2)
C1—C6	1.529(2)	C12—O4	1.366(2)
C1—H1	0.95(2)	C12—C13	1.383(2)
C2—C3	1.412(2)	C13—H13	0.902(19)
C2—H2	0.91(2)	C14—O2	1.423(2)
C3—O1	1.360(2)	C14—H141	0.95(2)
C3—C4	1.425(2)	C14—H142	0.98(2)
C4—C5	1.512(2)	O3—C15	1.425(2)
C4—H4	0.97(2)	C15—H151	0.96(2)
C5—O2	1.445(2)	C15—H152	0.93(2)
C5—C6	1.534(2)	C15—H153	0.98(2)
C5—H5	0.995(19)	O4—C16	1.431(2)
C6—C8	1.528(2)	C16—H161	0.99(2)
C6—H6	0.931(19)	C16—H162	0.98(2)
O1—C7	1.437(2)	C16—H163	0.95(2)

Atoms 1,2,3	Angle 1,2,3 [°]	Atoms 1,2,3	Angle 1,2,3 [°]
C23—Fe1—C21	100.06(8)	C6—C5—H5	111.3(11)
C23—Fe1—C22	102.32(8)	C8—C6—C1	113.59(13)
C21—Fe1—C22	91.85(8)	C8—C6—C5	112.88(13)
C23—Fe1—C2	134.40(7)	C1—C6—C5	108.66(14)
C21—Fe1—C2	94.89(7)	C8—C6—H6	106.1(11)
C22—Fe1—C2	120.07(8)	C1—C6—H6	108.3(11)

C23—Fe1—C1	95.75(7)	C5—C6—H6	106.9(11)
C21—Fe1—C1	93.70(7)	C3—O1—C7	116.33(14)
C22—Fe1—C1	159.86(8)	O1—C7—H71	109.9(13)
C2—Fe1—C1	40.14(7)	O1—C7—H72	111.1(13)
C23—Fe1—C3	132.11(7)	H71—C7—H72	106.9(19)
C21—Fe1—C3	125.43(8)	O1—C7—H73	112.6(13)
C22—Fe1—C3	91.35(7)	H71—C7—H73	110.0(18)
C2—Fe1—C3	39.64(7)	H72—C7—H73	106.1(18)
C1—Fe1—C3	69.72(7)	C9—C8—C13	119.27(15)
C23—Fe1—C4	93.12(7)	C9—C8—C6	121.02(15)
C21—Fe1—C4	164.30(8)	C13—C8—C6	119.67(14)
C22—Fe1—C4	93.64(8)	C8—C9—C10	119.86(15)
C2—Fe1—C4	69.66(7)	C8—C9—C14	120.14(15)
C1—Fe1—C4	76.40(7)	C10—C9—C14	119.97(15)
C3—Fe1—C4	39.79(7)	C11—C10—C9	120.76(15)
O21—C21—Fe1	179.43(18)	C11—C10—H12	122.3(13)
O22—C22—Fe1	179.43(17)	C9—C10—H12	116.9(13)
O23—C23—Fe1	178.41(18)	O3—C11—C10	124.94(15)
C2—C1—C6	121.47(15)	O3—C11—C12	115.44(15)
C2—C1—Fe1	69.47(9)	C10—C11—C12	119.61(15)
C6—C1—Fe1	108.37(11)	O4—C12—C13	125.57(15)
C2—C1—H1	114.8(12)	O4—C12—C11	115.18(14)
C6—C1—H1	116.2(12)	C13—C12—C11	119.24(15)
Fe1—C1—H1	117.6(12)	C12—C13—C8	121.23(15)
C3—C2—C1	114.34(15)	C12—C13—H13	119.1(12)
C3—C2—Fe1	70.66(9)	C8—C13—H13	119.6(12)
C1—C2—Fe1	70.39(9)	O2—C14—C9	110.68(14)
C3—C2—H2	124.1(12)	O2—C14—H141	107.9(13)
C1—C2—H2	121.2(12)	C9—C14—H141	110.7(13)
Fe1—C2—H2	122.4(12)	O2—C14—H142	109.5(13)
O1—C3—C2	126.82(16)	C9—C14—H142	112.2(13)
O1—C3—C4	118.67(15)	H141—C14—H142	105.8(18)
C2—C3—C4	114.42(15)	C14—O2—C5	112.08(13)
O1—C3—Fe1	125.87(11)	C11—O3—C15	116.11(14)
C2—C3—Fe1	69.7(1)	O3—C15—H151	111.7(14)
C4—C3—Fe1	70.56(9)	O3—C15—H152	107.0(13)
C3—C4—C5	113.86(14)	H151—C15—H152	109.0(18)
C3—C4—Fe1	69.65(9)	O3—C15—H153	110.6(12)
C5—C4—Fe1	113.00(11)	H151—C15—H153	109.4(19)
C3—C4—H4	115.2(12)	H152—C15—H153	109.0(17)
C5—C4—H4	116.2(12)	C12—O4—C16	116.36(13)
Fe1—C4—H4	120.6(11)	O4—C16—H161	112.4(12)
O2—C5—C4	103.91(13)	O4—C16—H162	109.9(11)
O2—C5—C6	112.11(13)	H161—C16—H162	109.7(16)
C4—C5—C6	110.38(14)	O4—C16—H163	104.1(12)
O2—C5—H5	106.5(10)	H161—C16—H163	110.6(16)
C4—C5—H5	112.4(11)	H162—C16—H163	110.0(17)

X-ray structure of the 5-*endo*-aryl product **18b**





Selected geometric informations for 18b

Atoms 1,2	d 1,2 [Å]	Atoms 1,2	d 1,2 [Å]
Fe1—C43	1.789(4)	Fe2—C54	2.102(4)
Fe1—C41	1.796(4)	Fe2—C53	2.112(4)
Fe1—C42	1.802(4)	C91—O91	1.145(5)
Fe1—C2	2.048(4)	C92—O92	1.132(5)
Fe1—C1	2.086(4)	C93—O93	1.146(5)
Fe1—C3	2.108(3)	C51—C52	1.437(5)
Fe1—C4	2.110(4)	C51—C56	1.515(5)
C41—O41	1.141(5)	C51—H51	1.01(4)
C42—O42	1.138(5)	C52—C53	1.401(5)
C43—O43	1.147(4)	C52—H52	1.05(4)
C1—C2	1.434(5)	C53—O51	1.360(4)
C1—C6	1.536(5)	C53—C54	1.419(5)
C1—H1	0.96(4)	C54—C55	1.500(5)
C2—C3	1.406(5)	C54—H54	0.92(4)
C2—H2	0.95(4)	C55—C56	1.548(5)
C3—O1	1.361(4)	C55—H55A	0.9900
C3—C4	1.427(5)	C55—H55B	0.9900
C4—C5	1.518(5)	C56—C58	1.535(5)
C4—H4	0.98(4)	C56—H56A	1.0000
C5—C6	1.540(5)	O51—C57	1.434(5)
C5—H5A	0.9900	C57—H57A	0.9800
C5—H5B	0.9900	C57—H57B	0.9800
C6—C8	1.523(5)	C57—H57C	0.9800
C6—H6A	1.0000	C58—C59	1.395(5)
O1—C7	1.428(4)	C58—C63	1.400(5)
C7—H7A	0.9800	C59—C60	1.404(5)
C7—H7B	0.9800	C59—C64	1.504(5)
C7—H7C	0.9800	C60—C61	1.378(5)
C8—C9	1.386(5)	C60—H60A	0.9500
C8—C13	1.409(5)	C61—O53	1.372(4)
C9—C10	1.400(5)	C61—C62	1.399(5)
C9—C14	1.514(5)	C62—O54	1.367(4)
C10—C11	1.387(5)	C62—C63	1.383(5)
C10—H10A	0.9500	C63—H63A	0.9500
C11—O3	1.376(4)	C64—O52	1.443(4)

C11—C12	1.400(5)	C64—H64A	0.9900
C12—O4	1.371(4)	C64—H64B	0.9900
C12—C13	1.378(5)	O52—Si2	1.651(3)
C13—H13A	0.9500	Si2—C71	1.876(4)
C14—O2	1.425(4)	Si2—C65	1.876(4)
C14—H14A	0.9900	Si2—C77	1.889(4)
C14—H14B	0.9900	C65—C66	1.397(5)
O2—Si1	1.648(2)	C65—C70	1.399(5)
Si1—C15	1.869(4)	C66—C67	1.383(6)
Si1—C27	1.885(4)	C66—H66A	0.9500
Si1—C21	1.886(4)	C67—C68	1.372(6)
C15—C16	1.394(5)	C67—H67A	0.9500
C15—C20	1.405(5)	C68—C69	1.383(6)
C16—C17	1.383(5)	C68—H68A	0.9500
C16—H16A	0.9500	C69—C70	1.386(6)
C17—C18	1.396(6)	C69—H69A	0.9500
C17—H17A	0.9500	C70—H70A	0.9500
C18—C19	1.382(5)	C71—C76	1.388(5)
C18—H18A	0.9500	C71—C72	1.406(5)
C19—C20	1.383(5)	C72—C73	1.385(5)
C19—H19A	0.9500	C72—H72A	0.9500
C20—H20A	0.9500	C73—C74	1.377(6)
C21—C22	1.388(5)	C73—H73A	0.9500
C21—C26	1.398(5)	C74—C75	1.395(6)
C22—C23	1.392(5)	C74—H74A	0.9500
C22—H22A	0.9500	C75—C76	1.387(5)
C23—C24	1.379(6)	C75—H75A	0.9500
C23—H23A	0.9500	C76—H76A	0.9500
C24—C25	1.360(6)	C77—C79	1.539(6)
C24—H24A	0.9500	C77—C80	1.538(6)
C25—C26	1.398(5)	C77—C78	1.550(6)
C25—H25A	0.9500	C78—H78A	0.9800
C26—H26A	0.9500	C78—H78B	0.9800
C27—C30	1.530(5)	C78—H78C	0.9800
C27—C28	1.535(5)	C79—H79A	0.9800
C27—C29	1.537(5)	C79—H79B	0.9800
C28—H28A	0.9800	C79—H79C	0.9800
C28—H28B	0.9800	C80—H80A	0.9800
C28—H28C	0.9800	C80—H80B	0.9800
C29—H29A	0.9800	C80—H80C	0.9800
C29—H29B	0.9800	O53—C81	1.428(4)
C29—H29C	0.9800	C81—H81A	0.9800
C30—H30A	0.9800	C81—H81B	0.9800
C30—H30B	0.9800	C81—H81C	0.9800
C30—H30C	0.9800	O54—C82	1.426(4)
O3—C31	1.423(5)	C82—H82A	0.9800
C31—H31A	0.9800	C82—H82B	0.9800
C31—H31B	0.9800	C82—H82C	0.9800
C31—H31C	0.9800	C101—C101^{i}	1.366(11)
O4—C32	1.427(4)	C101—C102	1.513(8)
C32—H32A	0.9800	C101—H10B	0.9900
C32—H32B	0.9800	C101—H10C	0.9900
C32—H32C	0.9800	C102—C103	1.365(9)
Fe2—C93	1.781(4)	C102—H10D	0.9900
Fe2—C91	1.799(5)	C102—H10E	0.9900
Fe2—C92	1.801(4)	C103—H10F	0.9800
Fe2—C52	2.065(4)	C103—H10G	0.9800
Fe2—C51	2.094(4)	C103—H10H	0.9800

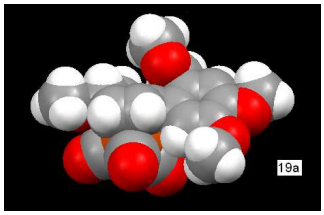
Atoms 1,2,3	Angle 1,2,3 [°]	Atoms 1,2,3	Angle 1,2,3 [°]
C43—Fe1—C41	98.69(17)	C52—Fe2—C51	40.41(15)
C43—Fe1—C42	101.49(16)	C93—Fe2—C54	91.70(17)
C41—Fe1—C42	92.13(17)	C91—Fe2—C54	165.58(18)
C43—Fe1—C2	140.64(15)	C92—Fe2—C54	95.17(17)
C41—Fe1—C2	95.63(16)	C52—Fe2—C54	69.87(16)
C42—Fe1—C2	114.43(15)	C51—Fe2—C54	76.42(15)
C43—Fe1—C1	102.27(15)	C93—Fe2—C53	130.88(16)
C41—Fe1—C1	91.95(16)	C91—Fe2—C53	128.57(17)
C42—Fe1—C1	154.98(15)	C92—Fe2—C53	91.58(16)
C2—Fe1—C1	40.57(13)	C52—Fe2—C53	39.17(15)
C43—Fe1—C3	131.01(16)	C51—Fe2—C53	68.81(15)
C41—Fe1—C3	128.79(16)	C54—Fe2—C53	39.37(15)
C42—Fe1—C3	89.47(15)	O91—C91—Fe2	177.3(4)
C2—Fe1—C3	39.52(14)	O92—C92—Fe2	179.2(4)
C1—Fe1—C3	68.93(14)	O93—C93—Fe2	178.3(4)
C43—Fe1—C4	91.60(16)	C52—C51—C56	119.0(3)
C41—Fe1—C4	165.74(16)	C52—C51—Fe2	68.7(2)
C42—Fe1—C4	95.49(16)	C56—C51—Fe2	111.5(3)
C2—Fe1—C4	70.24(14)	C52—C51—H51	115.(2)
C1—Fe1—C4	76.14(14)	C56—C51—H51	115.(2)
C3—Fe1—C4	39.54(14)	Fe2—C51—H51	121.(2)
O41—C41—Fe1	178.9(3)	C53—C52—C51	113.8(4)
O42—C42—Fe1	177.5(3)	C53—C52—Fe2	72.2(2)
O43—C43—Fe1	179.3(3)	C51—C52—Fe2	70.9(2)
C2—C1—C6	116.5(3)	C53—C52—H52	124.(2)
C2—C1—Fe1	68.3(2)	C51—C52—H52	123.(2)
C6—C1—Fe1	114.1(2)	Fe2—C52—H52	124.(2)
C2—C1—H1	115.(2)	O51—C53—C52	125.9(3)
C6—C1—H1	114.(2)	O51—C53—C54	118.0(3)
Fe1—C1—H1	121.(2)	C52—C53—C54	115.6(3)
C3—C2—C1	113.4(3)	O51—C53—Fe2	124.4(2)
C3—C2—Fe1	72.5(2)	C52—C53—Fe2	68.6(2)
C1—C2—Fe1	71.1(2)	C54—C53—Fe2	69.9(2)
C3—C2—H2	122.(2)	C53—C54—C55	119.8(3)
C1—C2—H2	124.(2)	C53—C54—Fe2	70.7(2)
Fe1—C2—H2	125.(2)	C55—C54—Fe2	107.7(3)
O1—C3—C2	127.0(3)	C53—C54—H54	116.(3)
O1—C3—C4	117.1(3)	C55—C54—H54	113.(3)
C2—C3—C4	115.3(3)	Fe2—C54—H54	123.(3)
O1—C3—Fe1	124.6(2)	C54—C55—C56	111.5(3)
C2—C3—Fe1	68.0(2)	C54—C55—H55A	109.300
C4—C3—Fe1	70.3(2)	C56—C55—H55A	109.300
C3—C4—C5	119.8(3)	C54—C55—H55B	109.300
C3—C4—Fe1	70.1(2)	C56—C55—H55B	109.300
C5—C4—Fe1	108.4(2)	H55A—C55—H55B	108.000
C3—C4—H4	117.(2)	C51—C56—C58	114.1(3)
C5—C4—H4	114.(2)	C51—C56—C55	108.8(3)
Fe1—C4—H4	121.(2)	C58—C56—C55	114.2(3)
C4—C5—C6	110.4(3)	C51—C56—H56A	106.400
C4—C5—H5A	109.600	C58—C56—H56A	106.400
C6—C5—H5A	109.600	C55—C56—H56A	106.400
C4—C5—H5B	109.600	C53—O51—C57	116.5(3)
C6—C5—H5B	109.600	O51—C57—H57A	109.500
H5A—C5—H5B	108.100	O51—C57—H57B	109.500
C8—C6—C1	115.1(3)	H57A—C57—H57B	109.500
C8—C6—C5	111.2(3)	O51—C57—H57C	109.500

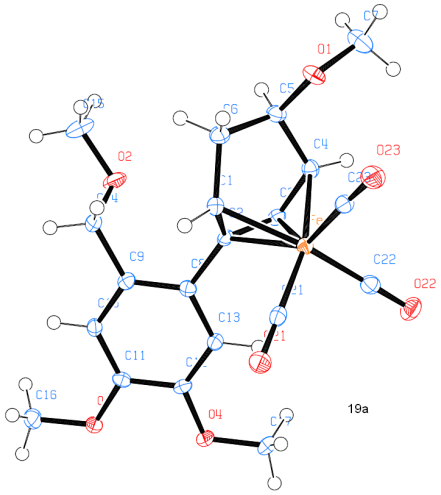
C1—C6—C5	108.5(3)	H57A—C57—H57C	109.500
C8—C6—H6A	107.200	H57B—C57—H57C	109.500
C1—C6—H6A	107.200	C59—C58—C63	118.3(3)
C5—C6—H6A	107.200	C59—C58—C56	120.8(3)
C3—O1—C7	117.7(3)	C63—C58—C56	120.9(3)
O1—C7—H7A	109.500	C58—C59—C60	119.6(3)
O1—C7—H7B	109.500	C58—C59—C64	122.8(3)
H7A—C7—H7B	109.500	C60—C59—C64	117.6(3)
O1—C7—H7C	109.500	C61—C60—C59	121.5(3)
H7A—C7—H7C	109.500	C61—C60—H60A	119.300
H7B—C7—H7C	109.500	C59—C60—H60A	119.300
C9—C8—C13	118.8(3)	O53—C61—C60	125.6(3)
C9—C8—C6	122.0(3)	O53—C61—C62	115.3(3)
C13—C8—C6	119.1(3)	C60—C61—C62	119.1(3)
C8—C9—C10	119.8(3)	O54—C62—C63	125.4(3)
C8—C9—C14	122.0(3)	O54—C62—C61	115.1(3)
C10—C9—C14	118.2(3)	C63—C62—C61	119.5(3)
C11—C10—C9	121.0(3)	C62—C63—C58	121.9(3)
C11—C10—H10A	119.500	C62—C63—H63A	119.000
C9—C10—H10A	119.500	C58—C63—H63A	119.000
O3—C11—C10	125.3(3)	O52—C64—C59	111.6(3)
O3—C11—C12	115.5(3)	O52—C64—H64A	109.300
C10—C11—C12	119.2(3)	C59—C64—H64A	109.300
O4—C12—C13	124.5(3)	O52—C64—H64B	109.300
O4—C12—C11	115.7(3)	C59—C64—H64B	109.300
C13—C12—C11	119.8(3)	H64A—C64—H64B	108.000
C12—C13—C8	121.2(3)	C64—O52—Si2	123.2(2)
C12—C13—H13A	119.400	O52—Si2—C71	107.91(15)
C8—C13—H13A	119.400	O52—Si2—C65	110.32(15)
O2—C14—C9	109.8(3)	C71—Si2—C65	109.57(16)
O2—C14—H14A	109.700	O52—Si2—C77	105.11(16)
C9—C14—H14A	109.700	C71—Si2—C77	109.46(17)
O2—C14—H14B	109.700	C65—Si2—C77	114.22(18)
C9—C14—H14B	109.700	C66—C65—C70	116.3(4)
H14A—C14—H14B	108.200	C66—C65—Si2	123.7(3)
C14—O2—Si1	123.9(2)	C70—C65—Si2	120.0(3)
O2—Si1—C15	107.82(15)	C67—C66—C65	122.1(4)
O2—Si1—C27	104.40(15)	C67—C66—H66A	119.000
C15—Si1—C27	110.66(16)	C65—C66—H66A	119.000
O2—Si1—C21	109.43(14)	C68—C67—C66	120.3(4)
C15—Si1—C21	108.43(16)	C68—C67—H67A	119.800
C27—Si1—C21	115.79(17)	C66—C67—H67A	119.800
C16—C15—C20	117.2(3)	C67—C68—C69	119.4(4)
C16—C15—Si1	123.2(3)	C67—C68—H68A	120.300
C20—C15—Si1	119.5(3)	C69—C68—H68A	120.300
C17—C16—C15	121.5(4)	C68—C69—C70	120.1(4)
C17—C16—H16A	119.200	C68—C69—H69A	119.900
C15—C16—H16A	119.200	C70—C69—H69A	119.900
C16—C17—C18	120.0(3)	C69—C70—C65	121.8(4)
C16—C17—H17A	120.000	C69—C70—H70A	119.100
C18—C17—H17A	120.000	C65—C70—H70A	119.100
C19—C18—C17	119.7(4)	C76—C71—C72	117.1(3)
C19—C18—H18A	120.200	C76—C71—Si2	119.4(3)
C17—C18—H18A	120.200	C72—C71—Si2	123.1(3)
C18—C19—C20	119.9(4)	C73—C72—C71	121.2(4)
C18—C19—H19A	120.100	C73—C72—H72A	119.400
C20—C19—H19A	120.100	C71—C72—H72A	119.400
C19—C20—C15	121.7(3)	C74—C73—C72	120.3(4)

C19—C20—H20A	119.200	C74—C73—H73A	119.800
C15—C20—H20A	119.200	C72—C73—H73A	119.800
C22—C21—C26	117.2(3)	C73—C74—C75	119.7(4)
C22—C21—Si1	119.3(3)	C73—C74—H74A	120.100
C26—C21—Si1	123.4(3)	C75—C74—H74A	120.100
C21—C22—C23	121.2(4)	C76—C75—C74	119.4(4)
C21—C22—H22A	119.400	C76—C75—H75A	120.300
C23—C22—H22A	119.400	C74—C75—H75A	120.300
C24—C23—C22	120.4(4)	C75—C76—C71	122.2(4)
C24—C23—H23A	119.800	C75—C76—H76A	118.900
C22—C23—H23A	119.800	C71—C76—H76A	118.900
C25—C24—C23	119.7(4)	C79—C77—C80	109.8(4)
C25—C24—H24A	120.100	C79—C77—C78	109.6(4)
C23—C24—H24A	120.100	C80—C77—C78	107.9(4)
C24—C25—C26	120.2(4)	C79—C77—Si2	109.5(3)
C24—C25—H25A	119.900	C80—C77—Si2	108.7(3)
C26—C25—H25A	119.900	C78—C77—Si2	111.3(3)
C25—C26—C21	121.3(4)	C77—C78—H78A	109.500
C25—C26—H26A	119.400	C77—C78—H78B	109.500
C21—C26—H26A	119.400	H78A—C78—H78B	109.500
C30—C27—C28	107.6(3)	C77—C78—H78C	109.500
C30—C27—C29	109.8(3)	H78A—C78—H78C	109.500
C28—C27—C29	109.6(3)	H78B—C78—H78C	109.500
C30—C27—Si1	112.4(3)	C77—C79—H79A	109.500
C28—C27—Si1	108.0(3)	C77—C79—H79B	109.500
C29—C27—Si1	109.4(3)	H79A—C79—H79B	109.500
C27—C28—H28A	109.500	C77—C79—H79C	109.500
C27—C28—H28B	109.500	H79A—C79—H79C	109.500
H28A—C28—H28B	109.500	H79B—C79—H79C	109.500
C27—C28—H28C	109.500	C77—C80—H80A	109.500
H28A—C28—H28C	109.500	C77—C80—H80B	109.500
H28B—C28—H28C	109.500	H80A—C80—H80B	109.500
C27—C29—H29A	109.500	C77—C80—H80C	109.500
C27—C29—H29B	109.500	H80A—C80—H80C	109.500
H29A—C29—H29B	109.500	H80B—C80—H80C	109.500
C27—C29—H29C	109.500	C61—O53—C81	117.0(3)
H29A—C29—H29C	109.500	O53—C81—H81A	109.500
H29B—C29—H29C	109.500	O53—C81—H81B	109.500
C27—C30—H30A	109.500	H81A—C81—H81B	109.500
C27—C30—H30B	109.500	O53—C81—H81C	109.500
H30A—C30—H30B	109.500	H81A—C81—H81C	109.500
C27—C30—H30C	109.500	H81B—C81—H81C	109.500
H30A—C30—H30C	109.500	C62—O54—C82	117.6(3)
H30B—C30—H30C	109.500	O54—C82—H82A	109.500
C11—O3—C31	117.5(3)	O54—C82—H82B	109.500
O3—C31—H31A	109.500	H82A—C82—H82B	109.500
O3—C31—H31B	109.500	O54—C82—H82C	109.500
H31A—C31—H31B	109.500	H82A—C82—H82C	109.500
O3—C31—H31C	109.500	H82B—C82—H82C	109.500
H31A—C31—H31C	109.500	C101^{i}—C101—C102	111.1(7)
H31B—C31—H31C	109.500	C101^{i}—C101—H10B	109.400
C12—O4—C32	116.6(3)	C102—C101—H10B	109.400
O4—C32—H32A	109.500	C101^{i}—C101—H10C	109.400
O4—C32—H32B	109.500	C102—C101—H10C	109.400
H32A—C32—H32B	109.500	H10B—C101—H10C	108.000
O4—C32—H32C	109.500	C103—C102—C101	116.8(6)
H32A—C32—H32C	109.500	C103—C102—H10D	108.100
H32B—C32—H32C	109.500	C101—C102—H10D	108.100

C93—Fe2—C91	98.87(18)	C103—C102—H10E	108.100
C93—Fe2—C92	98.74(18)	C101—C102—H10E	108.100
C91—Fe2—C92	92.91(19)	H10D—C102—H10E	107.300
C93—Fe2—C52	139.98(16)	C102—C103—H10F	109.500
C91—Fe2—C52	95.79(18)	C102—C103—H10G	109.500
C92—Fe2—C52	117.51(17)	H10F—C103—H10G	109.500
C93—Fe2—C51	101.91(16)	C102—C103—H10H	109.500
C91—Fe2—C51	91.72(18)	H10F—C103—H10H	109.500
C92—Fe2—C51	157.86(17)	H10G—C103—H10H	109.500

X-ray structure of the rearranged 5-*endo*-methoxy product **19a**





Selected geometric informations for 19a

Atoms 1,2	d 1,2 [Å]	Atoms 1,2	d 1,2 [Å]
Fe1—C23	1.7910(19)	Fe2—C72	1.791(2)
Fe1—C22	1.796(2)	Fe2—C73	1.7913(19)
Fe1—C21	1.8017(19)	Fe2—C71	1.804(2)
Fe1—C3	2.0535(18)	Fe2—C53	2.0573(19)
Fe1—C2	2.0754(17)	Fe2—C52	2.0754(17)
Fe1—C1	2.0944(18)	Fe2—C51	2.0915(19)
Fe1—C4	2.1025(19)	Fe2—C54	2.1074(19)
C21—O21	1.143(2)	C71—O71	1.137(2)
C22—O22	1.145(2)	C72—O72	1.147(2)
C23—O23	1.144(2)	C73—O73	1.149(2)
C1—C2	1.438(2)	C51—C52	1.439(3)
C1—C6	1.519(3)	C51—C56	1.512(3)
C1—H1	0.976(19)	C51—H51	0.95(2)
C2—C3	1.412(2)	C52—C53	1.411(3)
C2—C8	1.492(2)	C52—C58	1.497(2)
C3—C4	1.430(3)	C53—C54	1.432(3)
C3—H3	1.01(2)	C53—H53	0.95(2)
C4—C5	1.521(3)	C54—C55	1.513(3)
C4—H4	0.92(2)	C54—H54	0.95(2)
C5—O1	1.431(2)	C55—O51	1.436(2)
C5—C6	1.528(3)	C55—C56	1.528(3)
C5—H5	0.987(19)	C55—H55	1.01(2)
O1—C7	1.419(2)	O51—C57	1.422(3)
C7—H71	0.98(2)	C57—H571	0.96(2)

C7—H72	0.94(3)	C57—H572	0.94(3)
C7—H73	0.99(3)	C57—H573	1.01(3)
C6—H61	1.00(2)	C56—H561	0.98(2)
C6—H62	0.89(2)	C56—H562	1.02(2)
C8—C9	1.394(2)	C58—C59	1.399(3)
C8—C13	1.407(2)	C58—C63	1.409(3)
C9—C10	1.403(2)	C59—C60	1.404(3)
C9—C14	1.509(3)	C59—C64	1.516(3)
C10—C11	1.390(3)	C60—C61	1.384(3)
C10—H10	0.94(2)	C60—H60	0.94(2)
C11—O3	1.365(2)	C61—O53	1.367(2)
C11—C12	1.407(2)	C61—C62	1.409(3)
C12—O4	1.371(2)	C62—O54	1.369(2)
C12—C13	1.383(2)	C62—C63	1.386(2)
C13—H13	0.98(2)	C63—H63	0.96(2)
C14—O2	1.426(2)	C64—O52	1.426(3)
C14—H141	0.98(2)	C64—H641	0.95(2)
C14—H142	0.95(2)	C64—H642	1.01(2)
O2—C15	1.424(2)	O52—C65	1.419(3)
C15—H151	0.97(3)	C65—H651	0.95(2)
C15—H152	0.97(2)	C65—H652	0.97(3)
C15—H153	1.03(2)	C65—H653	0.99(3)
O3—C16	1.431(2)	O53—C66	1.430(2)
C16—H161	0.96(2)	C66—H661	0.94(2)
C16—H162	0.96(2)	C66—H662	0.99(2)
C16—H163	0.95(3)	C66—H663	0.94(3)
O4—C17	1.427(2)	O54—C67	1.427(2)
C17—H171	0.96(2)	C67—H671	0.97(2)
C17—H172	1.00(2)	C67—H672	0.93(2)
C17—H173	0.99(2)	C67—H673	0.97(2)

Atoms 1,2,3	Angle 1,2,3 [°]	Atoms 1,2,3	Angle 1,2,3 [°]
C23—Fe1—C22	99.31(8)	C72—Fe2—C73	99.41(8)
C23—Fe1—C21	100.02(8)	C72—Fe2—C71	93.24(8)
C22—Fe1—C21	93.28(8)	C73—Fe2—C71	99.54(8)
C23—Fe1—C3	131.30(8)	C72—Fe2—C53	94.29(8)
C22—Fe1—C3	91.86(8)	C73—Fe2—C53	132.64(8)
C21—Fe1—C3	126.64(8)	C71—Fe2—C53	124.80(8)
C23—Fe1—C2	137.88(8)	C72—Fe2—C52	122.31(8)
C22—Fe1—C2	119.44(8)	C73—Fe2—C52	135.86(8)
C21—Fe1—C2	93.96(7)	C71—Fe2—C52	92.36(8)
C3—Fe1—C2	39.98(7)	C53—Fe2—C52	39.94(7)
C23—Fe1—C1	99.59(8)	C72—Fe2—C51	162.54(8)
C22—Fe1—C1	159.69(8)	C73—Fe2—C51	96.81(8)
C21—Fe1—C1	90.72(8)	C71—Fe2—C51	90.40(8)
C3—Fe1—C1	69.96(7)	C53—Fe2—C51	69.78(8)
C2—Fe1—C1	40.33(7)	C52—Fe2—C51	40.39(7)
C23—Fe1—C4	91.32(8)	C72—Fe2—C54	96.08(8)
C22—Fe1—C4	95.61(8)	C73—Fe2—C54	93.10(8)
C21—Fe1—C4	164.28(7)	C71—Fe2—C54	162.86(8)
C3—Fe1—C4	40.23(7)	C53—Fe2—C54	40.19(7)
C2—Fe1—C4	70.37(7)	C52—Fe2—C54	70.50(7)
C1—Fe1—C4	76.57(7)	C51—Fe2—C54	76.56(8)
O21—C21—Fe1	179.07(17)	O71—C71—Fe2	177.97(16)
O22—C22—Fe1	179.61(16)	O72—C72—Fe2	179.8(2)
O23—C23—Fe1	177.49(17)	O73—C73—Fe2	177.77(17)
C2—C1—C6	119.15(16)	C52—C51—C56	119.00(17)
C2—C1—Fe1	69.12(10)	C52—C51—Fe2	69.2(1)

C6—C1—Fe1	110.49(12)	C56—C51—Fe2	110.44(13)
C2—C1—H1	115.8(11)	C52—C51—H51	116.2(12)
C6—C1—H1	116.5(11)	C56—C51—H51	116.1(13)
Fe1—C1—H1	116.9(11)	Fe2—C51—H51	117.2(12)
C3—C2—C1	113.16(16)	C53—C52—C51	112.76(16)
C3—C2—C8	122.29(16)	C53—C52—C58	121.20(17)
C1—C2—C8	124.49(16)	C51—C52—C58	125.94(17)
C3—C2—Fe1	69.18(10)	C53—C52—Fe2	69.34(10)
C1—C2—Fe1	70.55(10)	C51—C52—Fe2	70.41(10)
C8—C2—Fe1	126.27(12)	C58—C52—Fe2	125.44(12)
C2—C3—C4	115.83(17)	C52—C53—C54	116.24(17)
C2—C3—Fe1	70.84(10)	C52—C53—Fe2	70.72(11)
C4—C3—Fe1	71.73(10)	C54—C53—Fe2	71.79(11)
C2—C3—H3	120.9(12)	C52—C53—H53	117.2(12)
C4—C3—H3	122.6(12)	C54—C53—H53	126.5(13)
Fe1—C3—H3	119.4(12)	Fe2—C53—H53	124.0(13)
C3—C4—C5	119.11(16)	C53—C54—C55	119.73(18)
C3—C4—Fe1	68.04(10)	C53—C54—Fe2	68.02(11)
C5—C4—Fe1	110.43(12)	C55—C54—Fe2	109.66(13)
C3—C4—H4	115.3(13)	C53—C54—H54	116.9(13)
C5—C4—H4	115.8(13)	C55—C54—H54	114.7(13)
Fe1—C4—H4	119.7(13)	Fe2—C54—H54	119.6(13)
O1—C5—C4	113.08(15)	O51—C55—C54	112.33(16)
O1—C5—C6	106.68(15)	O51—C55—C56	107.54(15)
C4—C5—C6	110.29(15)	C54—C55—C56	110.12(16)
O1—C5—H5	110.1(11)	O51—C55—H55	108.2(12)
C4—C5—H5	108.5(11)	C54—C55—H55	109.7(12)
C6—C5—H5	108.1(11)	C56—C55—H55	108.9(12)
C7—O1—C5	113.58(15)	C57—O51—C55	113.54(16)
O1—C7—H71	105.7(14)	O51—C57—H571	107.0(14)
O1—C7—H72	111.0(15)	O51—C57—H572	107.2(17)
H71—C7—H72	110.(2)	H571—C57—H572	110.(2)
O1—C7—H73	112.5(14)	O51—C57—H573	112.5(16)
H71—C7—H73	107.7(19)	H571—C57—H573	111.(2)
H72—C7—H73	110.(2)	H572—C57—H573	110.(2)
C1—C6—C5	111.03(16)	C51—C56—C55	111.42(16)
C1—C6—H61	108.6(12)	C51—C56—H561	111.0(13)
C5—C6—H61	112.4(12)	C55—C56—H561	108.1(13)
C1—C6—H62	112.0(13)	C51—C56—H562	109.0(13)
C5—C6—H62	107.2(13)	C55—C56—H562	111.1(13)
H61—C6—H62	105.5(17)	H561—C56—H562	106.2(18)
C9—C8—C13	119.13(16)	C59—C58—C63	119.24(17)
C9—C8—C2	120.85(16)	C59—C58—C52	121.36(16)
C13—C8—C2	119.86(16)	C63—C58—C52	119.20(16)
C8—C9—C10	119.39(17)	C58—C59—C60	118.86(17)
C8—C9—C14	123.02(16)	C58—C59—C64	122.73(17)
C10—C9—C14	117.49(16)	C60—C59—C64	118.34(17)
C11—C10—C9	121.33(17)	C61—C60—C59	121.89(18)
C11—C10—H10	119.6(12)	C61—C60—H60	120.3(12)
C9—C10—H10	119.1(12)	C59—C60—H60	117.8(12)
O3—C11—C10	124.48(16)	O53—C61—C60	125.33(17)
O3—C11—C12	116.39(16)	O53—C61—C62	115.44(16)
C10—C11—C12	119.12(16)	C60—C61—C62	119.22(17)
O4—C12—C13	125.10(16)	O54—C62—C63	125.14(17)
O4—C12—C11	115.20(15)	O54—C62—C61	115.44(16)
C13—C12—C11	119.69(17)	C63—C62—C61	119.42(17)
C12—C13—C8	121.28(17)	C62—C63—C58	121.35(17)
C12—C13—H13	119.4(12)	C62—C63—H63	121.5(12)

C8—C13—H13	119.3(12)	C58—C63—H63	117.1(12)
O2—C14—C9	108.60(15)	O52—C64—C59	113.67(17)
O2—C14—H141	108.3(12)	O52—C64—H641	109.5(13)
C9—C14—H141	111.5(12)	C59—C64—H641	109.7(13)
O2—C14—H142	110.9(12)	O52—C64—H642	105.3(12)
C9—C14—H142	113.0(12)	C59—C64—H642	113.4(12)
H141—C14—H142	104.3(16)	H641—C64—H642	104.8(17)
C15—O2—C14	111.36(16)	C65—O52—C64	112.18(17)
O2—C15—H151	111.1(15)	O52—C65—H651	107.9(14)
O2—C15—H152	111.1(14)	O52—C65—H652	106.5(16)
H151—C15—H152	107.(2)	H651—C65—H652	105.(2)
O2—C15—H153	112.8(13)	O52—C65—H653	112.7(15)
H151—C15—H153	108.(2)	H651—C65—H653	112.(2)
H152—C15—H153	106.5(19)	H652—C65—H653	113.(2)
C11—O3—C16	116.38(15)	C61—O53—C66	116.48(15)
O3—C16—H161	104.2(12)	O53—C66—H661	104.2(14)
O3—C16—H162	110.3(13)	O53—C66—H662	110.7(13)
H161—C16—H162	114.2(18)	H661—C66—H662	110.6(18)
O3—C16—H163	110.6(14)	O53—C66—H663	110.9(15)
H161—C16—H163	111.5(18)	H661—C66—H663	112.(2)
H162—C16—H163	106.1(19)	H662—C66—H663	109.(2)
C12—O4—C17	116.93(14)	C62—O54—C67	117.12(15)
O4—C17—H171	105.9(13)	O54—C67—H671	105.9(13)
O4—C17—H172	108.4(12)	O54—C67—H672	108.1(13)
H171—C17—H172	111.9(17)	H671—C67—H672	110.7(19)
O4—C17—H173	111.3(11)	O54—C67—H673	112.7(13)
H171—C17—H173	109.8(17)	H671—C67—H673	107.3(18)
H172—C17—H173	109.5(16)	H672—C67—H673	111.9(18)