Electronic Supplementary Information

Figures

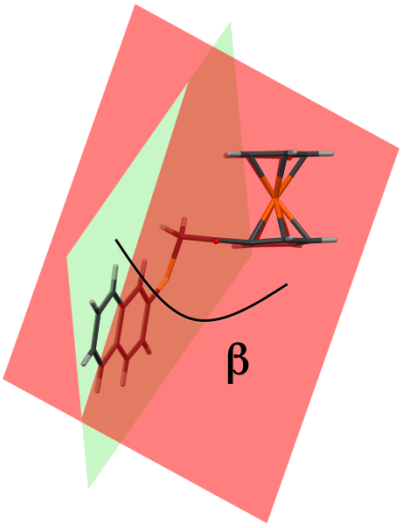

Figure S1. Angle β between the plane of the aryl ring and the plane bisecting the ferrocenyl moiety (containing atoms C(1), Fe(1) and C(6).

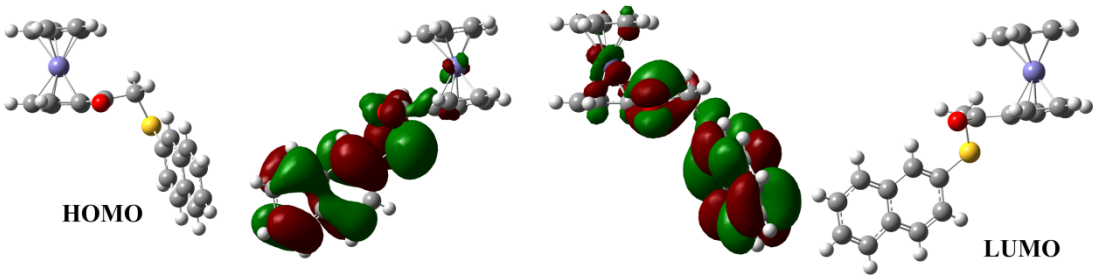

Figure S2. Evidence for HOMO-LUMO charge transfer in the C-H···π interactions in **II** (type 1 molecules are on the left and type 2 molecules on the right).

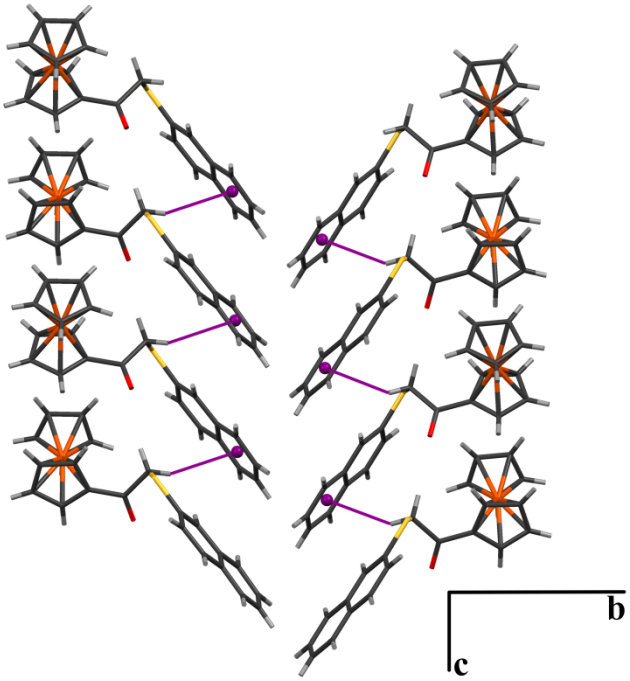

Figure S3. Herring bone structure of compound **II** formed by C-H···π contacts between molecules in linear chains (purple); notice that each molecule in this figure stands for an entire linear chain.

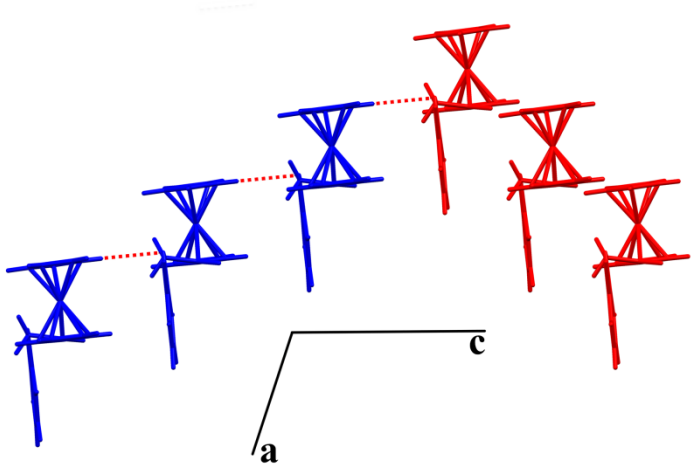

Figure S4. Interaction between planar arrangements of **VII** at an angle of 108.1º by means of C(2)-H(2)···S(1) contacts (in red).

Table S1. Selected bond lengths and angles for compounds **I-VIII.**

	I	II 1	II 2	III	IV	V 1	V2	VI	VII	VIII 1	VIII 2
Fe(1)-Centroid Cp(C1-5)	1.6498(13)	1.639(5)	1.635(5)	1.6541(12)	1.6493(2)	1.657(4)	1.650(4)	1.645(3)	1.648(2)	1.662(6)	1.630(7)
Fe(1)-Centroid Cp(C6-C10)	1.6482(13)	1.661(5)	1.640(5)	1.6500(11)	1.6396(3)	1.640(4)	1.642(4)	1.638(3)	1.646(2)	1.642(4)	1.648(4)
Average C-C Cp's	1.4206(13)	1.3815(80)	1.3751(79)	1.4142(13)	1.4164(13)	1.4068(45	1.4154(49	1.4160(42	1.4162(31	1.4455(95	1.3631(86)
	1.4244(13)	1.4151(67)	1.4147(68)	1.4242(9)	1.4232(13)	1.4094(47	1.4153(45	1.4284(36	1.4173(26	1.4146(58	1.4230(58)
Average C-C 6 membered rings	1.3884(14)	1.3979(54)	b	1.3894(10)	1.3884(13)	1.4066(39)	1.3835(40)	1.3865(34	1.3847(26)	1.3815(45	1.3844(43)
C(6)-C(11)	1.470(3)	1.483(13)	1.466(13)	1.465(2)	1.467(3)	1.501(10)	1.486(9)	1.433(7)	1.462(6)	1.462(11)	1.467(12)
C(11)-O(1)	1.220(3)	1.222(10)	1.226(10)	1.2182(19)	1.226(3)	1.225(7)	1.251(7)	1.233(6)	1.216(5)	1.229(10)	1.212(10)
C(11)-C(12)	1.517(3)	1.505(13)	1.513(13)	1.522(2)	1.507(3)	1.542(9)	1.515(9)	1.518(7)	1.528(5)	1.517(12)	1.510(11)
C(12)-S(1)	1.812(2)	1.778(11)	1.777(11)	1.8066(16)	1.820(2)	1.788(8)	1.818(7)	1.809(5)	1.787(5)	1.788(8)	1.791(8)
S(1)-C(13)	1.778(2)	1.761(10)	1.766(6)	1.7721(17)	1.776(2)	1.747(6)	1.753(7)	1.762(6)	1.764(4)	1.741(8)	1.750(8)
C(16)-N(1)	---	--	--	---	---	---	---	---	---	1.452(11)	1.482(11)
N(1)-O(2)	---	--	--	---	---	---	---	---	---	1.224(8)	1.213(9)
N(1)-O(3)	---	--	--	---	---	---	---	---	---	1.212(8)	1.206(9)
C(16)-O(2)	---	---	---	1.360(2)	---	---	---	---	---	---	---
C(15)-O(2)	---	--	--	---	1.368(3)	---	---	---	---	---	---
O(2)-C(19)	---	--	---	1.423(3)	1.426(3)	---	---	---	---	---	---
C(16)-Cl(1)	---	--	--	---	---	1.717(7)	1.729(7)	---	---	---	---
C(15)-Cl(1)	---	--	--	---	---	---	---	1.738(5)	---	---	---
C(14)-Cl(1)	---	--	--	---	---	---	---	---	1.742(4)	---	---

Cg(1)--Fe(1)--Cg(2)	178.59(5)	178.0(3)	178.4(3)	178.01(4)	178.06(5)	178.32(19)	178.87(19)	177.82(14)	179.41(11)	178.9(3)	179.2(3)
C(7)-C(6)-C(11)	124.63(19)	126.2(10)	124.1(9)	124.55(13)	125.54(19)	123.8(6)	125.4(6)	124.0(5)	124.6(4)	127.6(9)	123.5(8)
C(10)-C(6)-C(11)	127.90(18)	127.0(9)	127.9(9)	127.57(13)	126.62(18)	127.1(6)	124.8(6)	129.1(5)	127.9(4)	124.6(8)	130.3(9)
C(6)-C(11)-C(12)	115.52(17)	118.1(8)	117.6(8)	117.69(13)	117.57(19)	115.5(6)	117.5(6)	118.2(5)	116.3(4)	118.7(8)	116.1(8)
C(11)-C(12)-S(1)	115.40(15)	111.6(6)	112.1(7)	112.99(10)	111.16(14)	113.7(5)	111.7(5)	109.1(3)	114.9(3)	108.9(6)	109.0(6)
C(12)-S(1)-C(13)	101.14(10)	106.1(5)	106.0(4)	102.69(8)	105.05(10)	105.8(3)	105.3(4)	105.1(3)	104.0(2)	102.5(4)	102.9(4)
C(15)-C(16)-N(1)	---	---	---	---	---	---	---	---	---	118.9(7)	118.2(8)
C(17)-C(16)-N(1)	---	---	---	---	---	---	---	---	---	119.0(8)	120.3(9)
C(16)-N(1)-O(2)	---	---	---	---	---	---	---	---	---	119.3(7)	116.1(9)
C(16)-N(1)-O(3)	---	---	---	---	---	---	---	---	---	118.7(7)	118.0(9)
O(2)-N(1)-O(3)	---	---	---	--	---	---	---	---	---	122.0(8)	125.8(8)
C(16)-O(2)-C(19)	---	---	---	117.98(19)	---	---	---	---	---	---	---
C(15)-O(2)-C(19)	---	---	---	--	117.0(2)	---	---	---	---	---	---
C(7)-C(6)-C(11)-C(12)	-179.38(18)	-4.1(14)	-167.2(8)	157.44(13)	165.09(18)	167.3(7)	-165.6(6)	178.5(5)	-164.7(4)	-171.4(8)	173.2(7)
C(10)-C(6)-C(11)-C(12)	7.0(3)	168.8(8)	7.5(14)	-17.8(2)	-9.0(3)	-4.6(9)	5.3(9)	-4.1(8)	9.4(6)	-1.3(13)	1.9(13)
C(11)-C(12)-S(1)-C(13)	74.00(17)	76.7(8)	-76.8(7)	-71.04(12)	73.92(17)	85.3(5)	-82.9(6)	-74.0(4)	78.9(3)	177.8(6)	-174.8(6)
C(15)-C(16)-N(1)-O(3)	---	---	---	---	---	---	---	---	---	0.4(13)	3.0(10)
C(17)-C(16)-N(1)-O(2)	---	---	---	---	---	---	---	---	---	-0.8(13)	10.9(11)
C(15)-C(16)-O(2)-C(19)	---	---	---	-1.2(2)	---	---	---	---	---		

C(17)-C(16)-O(2)-C(19)	---	---	---	179.36(15)	---	---	---	---	---	---	---
C(16)-C(15)-O(2)-C(19)	---	---	---	---	-170.8(2)	---	---	---	---	---	---
C(14)-C(15)-O(2)-C(19)	---	---	---	---	8.9(3)	---	---	---	---	---	---
Tilt angle c	3.52	6.68	-5.65	1.45	9.41	-2.03	0.97	3.50	-0.81	10.44	-6.64
C(1)-Fe(1)-C(6) /Aromatic ring	50.70(9)	35.49(37)	32.94(31)	46.83(7)	24.32(8)	64.94(27)	62.76(30)	37.91(20)	2.63(16)	79.88(35)	c

Table S2 – Atomic point charges in molecules **I-VIII**

		I	II 1	II 2	III	IV	V 1	V 2	VI	VII	VIII 1	VIII 2
	Fe1	9.4	3.8	3.8	4.3	6.1	3.2	4.8	5.5	4.3	3.7	8.0
Ciclopentadienyl	C1	-5.3	-8.3	-8.4	-10.2	-9.7	-6.8	-10.2	-8.2	-15.2	-6.8	-1.1
	C2	-13.6	-10.4	-7.1	-8.7	-7.4	-8.7	-7.7	-8.5	-9.2	-10.3	-11.3
	C3	-7.2	-9.6	-10.8	-12.2	-13.4	-9.7	-10.4	-12.4	-7.2	-10.8	-13.3
	C4	-10.3	-4.3	-6.2	-7.3	-6.5	-9.9	-8.6	-6.8	-11.9	-5.9	-6.6
	C5	-1.8	-13.1	-10.6	-10.2	-13.5	-12.3	-11.8	-13.1	-6.4	-6.4	-18.8
	H1	9.3	8.8	8.1	8.8	9.7	8.4	10.3	9.5	15.1	7.7	6.8
	H2	11.4	10.2	9.6	10.5	9.8	10.4	10.0	11.0	10.3	11.1	11.9
	H3	9.3	9.8	9.2	10.9	11.1	10.3	10.2	10.9	9.5	10.4	11.3
	H4	9.6	7.5	8.7	9.5	9.1	10.4	10.0	9.6	10.7	7.8	10.8
	H5	15.3	10.6	9.5	9.7	10.8	10.2	9.8	10.1	8.0	8.9	11.6
Substituted Ciclopentadienyl	C6	-14.4	-4.2	-0.1	-4.7	-3.6	-5.0	-3.6	-3.7	-15.3	-16.0	-22.0
	C7	0.1	-2.1	-6.2	-6.8	-5.9	-8.0	-7.4	-6.1	-2.8	1.5	-2.6
	C8	-17.5	-13.8	-10.8	-11.6	-12.1	-10.2	-9.4	-9.3	-11.8	-14.0	-10.0
	C9	-1.5	-1.7	-2.1	-3.4	-3.2	-1.1	-4.3	-4.9	-6.6	-7.0	-7.0
	C10	-17.8	-25.0	-27.1	-23.9	-24.5	-22.2	-22.4	-21.1	-11.0	-13.3	-6.9
	H7	8.7	8.1	9.4	10.3	9.7	10.4	9.8	9.6	9.0	7.4	8.1
	H8	12	10.8	9.2	10.9	10.9	10.3	10.1	10.1	10.8	12.0	10.7
	H9	8.3	8.3	8.1	8.9	8.7	7.5	8.9	9.3	9.5	10.5	9.2
	H10	11.3	17.2	18.7	17.7	10.7	17.7	17.4	18.4	9.4	10.2	8.5
	C11	49.8	44.2	40.2	48.5	45.0	48.3	48.7	43.2	56.2	51.3	61.0
	O1	-51.0	-49.1	-48.3	-50.4	-49.7	-49.2	-49.7	-48.9	-50.0	-44.6	-47.3
	C12	15.8	14.0	15.2	2.8	6.6	-0.3	-5.8	10.6	4.4	8.5	-1.5
	H12A	4.9	5.0	-1.1	-3.2	6.8	10.0	4.5	1.3	9.2	3.0	3.9
	H12B	-3.9	-1.2	4.9	12.8	0.8	2.3	11.4	4.8	-2.0	2.1	3.6
	S1	-31.2	-32.5	-35.0	-30.8	-31.6	-31.1	-28.5	-29.6	-25.3	-23.6	-20.6
	C13	19.3	19.6	26.4	17.0	27.4	22.0	20.2	17.4	11.3	15.2	12.3
	C14	-5.0	-25.7	-33.5	-5.8	-40.2	-16.1	-14.0	-10.5	8.3	-15.2	-8.6
	C15	-11.4	10.3	16.1	-32.0	43.3	-10.8	-9.6	7.4	-10.6	-8.4	-12.7
	C16	-11.2	20.7	16.9	39.4	-29.3	9.0	6.2	-7.9	-7.7	2.1	3.1
	C17	-3.2	-23.6	-24.4	-24.6	-1.9	-6.9	-3.2	-11.0	-16.0	-9.6	-12.5
	C18	-18.7	-13.4	-15.4	-16.1	-23.5	-21.6	-21.0	-15.4	-6.2	-14.5	-12.6
	C19	---	-17.9	-19.0	---	---	---	---	---	---	---	---
	C20	---	-3.1	-8.2	---	---	---	---	---	---	---	---
	C21	---	-10.1	-7.5	---	---	---	---	---	---	---	---
	C22	---	-27.0	-21.6	---	---	---	---	---	---	---	---
	H14	9.1	16.9	19.0	11.3	21.3	14.9	13.2	12.3	---	16.3	12.2
	H15	10.3	---	---	16.6	---	12.7	12.0	---	9.9	10.3	12.1
	H16	9.3	---	---	---	14.3	---	---	9.9	9.7	---	---
	H17	7.1	12.0	14.0	14.0	9.2	9.7	8.4	10.9	11.4	11.0	11.7
	H18	10.5	14.2	14.1	13.4	13.7	17.2	16.0	13.7	9.3	12.2	13.2
	H19	---	11.2	11.3	---	---	---	---	---	---	---	---
	H20	---	10.0	9.1	---	---	---	---	---	---	---	---
	H21	---	7.1	8.7	---	---	---	---	---	---	---	---
	H22	---	14.9	12.2	---	---	---	---	---	---	---	---
	O2	---	---	---	-40.9	-40.3	---	---	---	---	-40.3	-39.4
	C19met	---	---	---	27.9	25.2	---	---	---	---	---	---
	H19A	---	---	---	1.9	2.4	---	---	---	---	---	---
	H19B	---	---	---	-1.5	-3.6	---	---	---	---	---	---
	H19C	---	---	---	-2.9	0.0	---	---	---	---	---	---
	Cl1	---	---	---	---	---	-15.0	-14.3	-14.1	-11.2	---	---
	N1	---	---	---	---	---	---	---	---	---	62.5	63.4
	O3	---	---	---	---	---	---	---	---	---	-39.1	-38.8

Table S3 – Molecular interactions parameters.

Compound I		
Hydrogen bonds		
C(18)···O(1)	H(18)···O(1)	C(18)-H(18)···O(1)
3.411(3) Å	2.51 Å	158 º
C-H···π interactions		
H(1)-Cg(13-18)	C(1)-Pln(13-18)	H(1)-Pln(13-18)
2.81	3.463(2) Å [a]	2.752(1) Å [a]
D_{pln} = 2.7516(2) Å [b]	D_{cp} =0.558 Å[b]	α = 138.5º [b]
S···C(π)=O	S(1)···C(11)	
	3.467(3) Å	
π-π interactions		
centroid-centroid	off-set angle[d]	slippage[e]
3.618(2) Å	24.9º	1.525 Å

Compound II		
Hydrogen bonds		
C(18)···O(1)	H(18)···O(1)	C(18)-H(18)···O(1)
3.591(15) Å	2.67 Å	163º
C(18A)···O(1A)	H(18A)···O(1A)	C(18A)-H(18A)···O(1A)
3.480(11) Å	2.68 Å	142º
C-H···π interactions		
H(20)···Cg(15A,16A,19A-22A)	C(20)-Pln(15A,16A,19A-22A)	H(20)-Pln(15A,16A,19A-22A)
2.96 Å	3.648 Å [c]	2.855 Å [c]
D_{pln} = 2.855 Å[b]	D_{cp} = 0.796 Å[b]	α = 141.2º [b]
H(12B)-Cg(15,16,19-22)	C(12)-Pln(15,16,19-22)	H(12B)-Pln(15,16,19-22)
2.90 Å	2.714 Å[c]	2.895 Å [c]
D_{pln} = 2.895 Å[b]	D_{cp} = 0.170 Å[b]	α = 100.5º [b]
H(12C)-Cg(15A,16A,19A-22A)	C(12A)-Pln(15A,16A,19A-22A)	H(12C)-Pln(15A,16A,19A-22A)
2.88 Å	3.429 Å[c]	2.774 Å[c]
D_{pln} = 2.774 Å[b]	D_{cp} = 0,774 Å[b]	α = 131.4º[b]

Compound III		
Hydrogen bonds		
C(18)···O(1)	H(18)···O(1)	C(18)-H(18)···O(1)
3.488(3) Å	2.55 Å	171º
C(10)···O(1)	H(10)···O(1)	C(10)-H(10)···O(1)
3.555(3) Å	2.69 Å	152º
C(12)···O(1)	H(12B)···O(1)	C(12)-H(12B)···O(1)
3.371(3) Å	2.73 Å	130º
C(5)···S(1)	H(5)···S(1)	C(5)-H(5)···S(1)
3.663(3) Å	2.92 Å	136º
C(4)···O(2)	H(4)···O(2)	C(4)-H(4)···O(2)
3.325(3) Å	2.67 Å	126º
C-H···π interactions		
H(19A)-Cg(1-5)	C(19)-Pln(1-5)	H(19A)-Pln(1-5)
2.95(3) Å	3.325 Å[c]	2.713 Å[c]
D_{pln} = 2.713 Å[b]	D_{cp} = 1.342 Å[b]	α = 129.1º [b]

Compound IV		
Hydrogen bonds		
C(18)···O(1)	H(18)···O(1)	C(18)-H(18)···O(1)
3. 677(3) Å	2.78 Å	157º
C(16)···O(2)	H(16)···O(2)	C(16)-H(16)···O(2)
3.460(3) Å	2.69 Å	139º

Compound V			
Hydrogen bonds			
C(10)···O(1)	H(10)···O(1)	C(10)-H(10)···O(1)	
3.632 (12) Å	2.79 Å	151º	
C(10A)···O(1)	H(10A)···O(1)	C(10A)-H(10A)···O(1)	
3.672 (3) Å	2.81 Å	154º	
C(5A)···Cl(1)	H(5A)···Cl(1)	C(5A)-H(5A)···Cl(1)	H(5A)…Cl(1)-C(16)
3.696 (11) Å	3.00 Å	133º	104º
C(5)···Cl(1A)	H(5)···Cl(1A)	C(5)-H(5)···Cl(1A)	H(5)…Cl(1A)-C(16A)
3. 686 (11) Å	3.00 Å	131º	101º
C-H···π interactions			
H(12A)-Cg(13A-18A)	C(12)···Pln(13A-18A)	H(12A)···Pln(13A-18A)	
3.00 Å	3.542 Å[c]	2.855 Å[c]	
D_{pln} = 2.855 Å[b]	D_{cp} = 0.663 Å[b]	α = 133.9º [b]	
H(12D)-Cg(13-18)	C(12A)···Pln(13-18)	H(12D)···Pln(13-18)	
2.99 Å	3.568 Å[c]	2.879 Å[c]	
D_{pln} = 2.879 Å[b]	D_{cp} = 0.780 Å[b]	α = 134.1º [b]	
Halogen Bonds			
Cl1···Cl1A	C16-Cl1-Cl1A	C16A-Cl1A-Cl1	
3.474(4) Å	136.4(4)º	144.4(4)º	

Compound VI			
Hydrogen bonds			
C(1)···O(1)	H(1)···O(1)	C(1)-H(1)···O(1)	
3.492 (8) Å	2.68 Å	144º	
C(9)···Cl(1)	H(9)···Cl(1)	C(9)-H(9)···Cl(1)	H(9)···Cl(1)-C(15)
3.643(6) Å	2.98 Å	139º	98º
C(16)···Cl(1)	H(16)···Cl(1)	C(16)-H(16)···Cl(1)	H(16)···Cl(1)-C(15)
3.703 (6) Å	3.00 Å	131º	86º
C-H···π interactions			
H(12)-Cg(7-10)	C(12A)-Pln(7-10)	H(12A)···Pln(7-10)	
2.39 Å	3.376 Å[c]	2.612 Å[c]	
D_{pln} = 2.612 Å[b]	D_{cp} = 1.184 Å[b]	α = 140.5º [b]	
H(14)-Cg(7-10)	C(14)···Pln(7-10)	H(14)···Pln(7-10)	
2.71 Å	3.645 Å[c]	2.817 Å[c]	
D_{pln} = 2.817 Å[b]	D_{cp} = 1.171 Å[b]	α = 150.6º [b]	

Compound VII			
Hydrogen bonds			
C(1)···O(1)	H(1)···O(1)	C(1)-H(1)···O(1)	
3.226(6) Å	2.65 Å	120º	
C(12)···O(1)	H(12A)···O(1)	C(12)-H(12A)···O(1)	
3.423(5) Å	2.61 Å	140º	
C(9)···Cl(1)	H(9)···Cl(1)	C(9)-H(9)···Cl(1)	C(14)-Cl(1)…H(9)
3.824(4) Å	2.95 Å	153º	95º
C(2)···S(1)	H(2)···S(1)	C(2)-H(2)···S(1)	
3.825(5) Å	2.88 Å	176º	
C-H···π interactions			
H(7)-Cg(13-18)	C(7)···Pln(13-18)	H(7)···Pln(13-18)	
2. 71 Å	3.544 Å[c]	2.684 Å[c]	
D_{pln} = 2.684 Å[b]	D_{cp} = 0.402 Å[b]	α = 154.9º [b]	

Compound VIII		
Hydrogen bonds		
C(10)···O(1)	H(10)···O(1)	C(10)-H(10)···O(1)
3.407(15) Å	2.66 Å	136º
C(10A)···O(1A)	H(10A)···O(1A)	C(10A)-H(10A)···O(1A)
3.375(15) Å	2.53 Å	148º
C(4)···O(1)	H(4)···O(1)	C(4)-H(4)···O(1)
3.384(17) Å	2.57 Å	144º
C(4A)···O(1A)	H(4A)···O(1A)	C(4A)-H(4A)···O(1A)
3.33(2) Å	2.65 Å	130º
C(5A)···O(3)	H(5A)···O(3)	C(5A)-H(5A)···O(3)
3.51 (2) Å	2.60 Å	161º
C(5)···O(3A)	H(5)···O(3A)	C(5)-H(5)···O(3A)
3.614(20) Å	2.81 Å	143º

Cg(X-Y) – centroid of the ring formed by atom X to Y.

Pln(X-Y) – Plane formed by atoms X to Y.

a – calculated using Parst

b - criteria developed by Nishio and co-workers (see ref [8]) to describe C-H···π interactions:

D_{pln} – distance from the H atom to the plane of the π ring system

D_{cp} – distance between the projection of the hydrogen atom on the ring plane and the π system centroid

α – angle between the C-H bond and the projection of the hydrogen atom on the ring plane

c – measured using Mercury

d - off-set angle: angle between the line that connects both centroids in a π-π interaction and the perpendicular to one of the rings with the origin at is centroid (see ref [9]).

e - distance between Cg(I) and Perpendicular Projection of Cg(J) on Ring I.

Experimental section

General considerations

All commercially available reagents were acquired from Sigma-Aldrich Química, S.A. (Madrid, Spain). Melting temperatures were measured with a Leica Galen III hot stage apparatus and are uncorrected. Infrared (IR) spectra were obtained in KBr pellets on a Shimadzu FTIR-8400S instrument. Group frequencies are reported in cm^{-1}; the symbols *s*, *m*, and *w* represent strong, medium, and week bands, respectively. ^{1}H NMR spectra were recorded in acetone-d_6, unless indicated otherwise, on a Bruker Avance III 400 spectrometer, operating at 400 MHz. ^{13}C NMR spectra were recorded on the same instrument, operating at 100.62 MHz. Chemical shifts are reported in ppm downfield from tetramethylsilane, and coupling constants (*J*) are reported in Hz; the subscripts *ortho* and *meta* refer to *ortho* and *meta* couplings, respectively. The abbreviations used to assign specific protons and carbons include Fc (ferrocenyl) and Ar (aryl). Resonance assignments were based on the analysis of coupling patterns, including the ^{13}C-^{1}H coupling profiles obtained in heteronuclear bidimensional HSQC and HMBC experiments, performed with standard pulse programs. Mass spectra (MS) were recorded on a Varian 500-MS LC ion trap mass spectrometer, operated in the electrospray ionization (ESI) mode; the spray voltage was set at ±5 kV and the capillary voltage was set at 10 V. The assignments are indicated in square brackets. High resolution electron ionization mass spectra (HRMS) were obtained in a Finnigan FT/MS 2001 DT FTICR mass spectrometer operated at 70 eV.

Spectral characterization data for 1-(ferrocenyl)-2-(aryl)thioethanones

1-Ferrocenyl-2-(phenyl)thioethanone (I). η 80%. **Mp** 75-77 °C. **IR** 1659 (*s*, C=O), 1447(*m*), 1439 (*m*), 1375 (*m*), 1232 (*m*), 1071 (*m*), 821(*m*), 744 (*m*) cm^{-1}. **^{1}H NMR** δ 7.44 (2H, d, *J* 7.6, Ar-**H2**,**6**), 7.31 (2H, t, *J* 7.6, Ar-**H3**,**5**), 7.20 (1H, t, *J* 7.6, Ar-**H4**), 4.86 (2H, t, *J* 1.8, Fc-**H2**,**5**/Fc-**H3**,**4**), 4.58 (2H, t, *J* 1.8, Fc-**H2**,**5**/Fc-**H3**,**4**), 4.24 (2H, s, C**H$_2$**S), 4.23 (5H, s, Fc-**H1'-H5'**). **^{13}C NMR** δ 197.9 (**C**O), 138.0 (Ar-**C1**), 130.1 (Ar-**C2,6**/Ar-**C3,5**), 129.9 (Ar-**C2,6**/Ar-**C3,5**), 127.2 (Ar-**C4**), 79.8 (Fc-**C1**), 73.4 (Fc-**C2**,**5**/Fc-**C3,4**), 70.9 (Fc-**C1'-C5'**), 70.6 (Fc-**C2**,**5**/Fc-**C3,4**), 42.1 (**C**H$_2$S). **MS (ESI$^+$)**

m/z 337 [MH^+], 229 [$(MH_2\text{-}C_6H_5SH)^+$], 228 [$(MH\text{-}C_6H_5SH)^+$]. **HRMS Calcd. for $C_{18}H_{16}FeOS$:** 336.02713. **Found:** 336.02558.

1-Ferrocenyl-2-[(naphthalen-2-yl)thio]ethanone (II). η 70%. **Mp** 110-112 ºC. **IR** 1658 (*s*, C=O), 1454 (*w*), 1283 (*w*), 1074 (*w*), 847 (*m*), 818 (*m*) cm^{-1}. **^{1}H NMR** δ 7.97 (1H, J_{meta} 1.9, Ar-**H1**), 7.88 (1H, d, *J* 7.8, Ar-**H5**/Ar-**H8**), 7.87 (1H, d, *J* 8.6, Ar-**H4**), 7.84 (1H, d, *J* 7.8, Ar-**H5/Ar-H8**), 7.57 (1H, dd, J_{ortho} 8.6, J_{meta} 1.9, Ar-**H3**), 7.52 (1H, m, Ar-**H6**/Ar-**H7**), 7.47 (1H, m, Ar-**H6**/Ar-**H7**), 4.92 (2H, t, *J* 1.9, Fc-**H2**,**5**/Fc-**H3**,**4**), 4.60 (2H, t, *J* 1.8, Fc-**H2**,**5**/Fc-**H3**,**4**), 4.41 (2H, s, C**H$_2$**S), 4.26 (5H, s, Fc- **H1'-H5'**). **^{13}C NMR** δ 198.7 (**C**O), 135.6 (Ar-**C2/C4a/C8a**), 135.5 (Ar-**C2/C4a/C8a**), 133.5 (Ar-**C2/C4a/C8a**), 129.9 (Ar-**C4**), 129.3 (Ar-**C5/C8**), 128.7 (Ar-**C3/C5/C8**), 128.6 (Ar-**C3/C5/C8**), 128.2 (Ar-**C1** + Ar-**C6/C7**), 127.3 (Ar-**C6/C7**), 79.6 (Fc-**C1**), 74.1 (Fc-**C2**,**5**/Fc-**C3,4**), 71.4 (Fc-**H1'-H5'**), 71.2 (Fc-**C2**,**5**/Fc-**C3,4**), 42.5 (C**H$_2$**S). **MS (ESI)** *m/z* 794 [2M+Na]$^+$, 409 [M+Na]$^+$, 387 [MH]$^+$. **HRMS Calcd. for $C_{22}H_{18}FeOS$:** 386.04278. **Found:** 386.04140.

1-Ferrocenyl-2-[4-(methoxyphenyl)thio]ethanone (III). η 95%. **Mp** 76-78 °C. **IR** 1651 (*s*, C=O), 1591 (*m*), 1496 (*m*), 1457 (*m*), 1292 (*m*), 1248 (*m*), 1032 (*m*), 839 (*m*) cm^{-1}. **^{1}H NMR** δ 7.42 (2H, d, *J* 8.8, Ar-**H2**,**6**), 6.89 (2H, d, *J* 8.8, Ar-**H3**,**5**), 4.80 (2H, t, *J* 2.0, Fc-**H2**,**5**/Fc-**H3**,**4**), 4.56 (2H, t, *J* 2.0, Fc-**H2**,**5**/Fc-**H3**,**4**), 4.19 (5H, s, Fc- **H1'-H5'**), 4.08 (2H, s, C**H$_2$**S), 3.77 (3H, s, C**H$_3$**O). **^{13}C NMR** δ 197.1 (**C**O), 159.5 (Ar-**C4**), 133.4 (Ar-**C2,6**), 126.1 (Ar-**C1**), 114.6 (Ar-**C3,5**), 78.2 (Fc-**C1**), 72.3 (Fc-**C2**,**5**/Fc-**C3,4**), 69.7 (Fc-**C1'-C5'**), 69.6 (Fc-**C2**,**5**/Fc-**C3,4**), 54.8 (**C**H_3O), 43.0 (**C**H_2S). **MS (ESI$^+$)** *m/z* 367 [MH^+], 366 [M^+], 229 [$(MH_2\text{-}C_6H_4(OCH_3)SH)^+$]. **HRMS. Calcd. for $C_{19}H_{18}FeO_2S$:** 366.03769. **Found:** 366.03731.

1-Ferrocenyl-2-[4-(chlorophenyl)thio]ethanone (V). η 85%. **Mp** 94-96 ºC. **IR** 1652 (*s*, C=O), 1478 (*m*), 1454 (*m*), 1285 (*m*), 1094 (*m*), 1073 (*m*), 810 (*m*) cm^{-1}. **^{1}H NMR** δ ($CDCl_3$) 7.39 (2H, d, *J* 8.8, Ar-**H2**,**6**/Ar-**H3,5**), 7.27 (2H, d, *J* 8.8, Ar-**H2**,**6**/Ar-**H3,5**), 4.80 (2H, t, *J* 1.8, Fc-**H2**,**5**/Fc-**H3**,**4**), 4.56 (2H, t, *J* 1.8, Fc-**H2**,**5**/Fc-**H3**,**4**), 4.20 (5H, s, Fc-**H1'-H5'**), 4.01 (2H, s, C**H$_2$**S). **^{13}C NMR** δ ($CDCl_3$) 197.7 (**C**O), 133.7 (Ar-**C1**), 132.7 (Ar-**C4**), 131.2 (Ar-**C2,6**/Ar-**C3,5**), 128.8 (Ar-**C2,6**/Ar-**C3,5**), *ca.* 77.0 (Fc-**C1**, obscured by the solvent resonance), 72.5 (Fc-**C2**,**5**/Fc-**C3,4**), 69.7 (Fc- **H1'-H5'**), 69.4 (Fc-**C2**,**5**/Fc-**C3,4**), 41.7 (**C**H_2S). **MS (ESI)** *m/z* 395 [M(^{37}Cl)+Na]$^+$, 393

[M(^{35}Cl)+Na]$^+$, 373 [M(^{37}Cl)H]$^+$, 371 [M(^{35}Cl)H]$^+$. **HRMS Calcd. for $C_{18}H_{15}{}^{35}ClFeOS$:** 369.98815. **Found:** 369.98842.

1-Ferrocenyl-2-[3-(chlorophenyl)thio]ethanone (VI). η 47%. **Mp** 72-74 ºC. **IR** 1663 (*s*, C=O), 1451 (*m*), 1283 (*m*), 1029 (*m*), 822 (*m*), 784 (*s*) cm^{-1}. **^{1}H NMR** δ 7.48 (1H, t, J_{meta} 1.5, Ar-**H2**), 7.37(1H, dt, J_{meta} 1.5, J_{ortho} 7.5, Ar-**H4**/Ar-**H6**), 7.31 (1H, t, J_{ortho} 7.5, Ar-**H5**), 7.21 (1H, ddd, J_{meta} 1.5, J'_{meta} 1.8, J_{ortho} 7.5, Ar-**H4**/Ar-**H6**), 4.90 (2H, t, *J* 2.0, Fc-**H2**,**5**/Fc-**H3**,**4**), 4.60 (2H, t, *J* 2.0, Fc-**H2**,**5**/Fc-**H3**,**4**), 4.35 (2H, s, C**H$_2$**S), 4.25(5H, s, Fc-**H1'-H5'**). **^{13}C NMR** δ 196.9 (**C**O), 139.2 (Ar-**C1**), 134.2 (Ar-**C3**), 130.2 (Ar-**C5**), 127.7 (Ar-**C2**), 126.9 (Ar-**C4**/Ar-**C6**), 125.8 (Ar-**C4**/Ar-**C6**), 77.8 (Fc-**C1**), 72.5 (Fc-**C2**,**5**/Fc-**C3,4**), 69.9 (Fc- **H1'-H5'**), 69.6 (Fc-**C2**,**5**/Fc-**C3,4**), 40.5 (**C**H$_2$S). **MS (ESI)** *m/z* 373 [M(^{37}Cl)H]$^+$, 371 [M(^{35}Cl)H]$^+$. **HRMS Calcd. for $C_{18}H_{15}{}^{35}ClFeOS$:** 369.98815. **Found:** 369.98653.

1-Ferrocenyl-2-[2-(chlorophenyl)thio]ethanone (VII). η 58%. **Mp** 87-89 ºC. **IR** 1668 (*s*, C=O), 1452 (*s*), 748 (*s*) cm^{-1}. **^{1}H NMR** δ 7.53 (1H, dd, J_{ortho} 7.8, J_{meta} 1.5, Ar-**H6**), 7.42 (1H, dd, J_{ortho} 7.8, J_{meta} 1.5, Ar-**H3**), 7.31 (1H, dt, J_{ortho} 7.8, J_{meta} 1.5, Ar-**H5**), 7.20 (1H, dt, J_{ortho} 7.8, J_{meta} 1.5, Ar-**H4**), 4.93 (2H, t, *J* 1.8, Fc-**H2**,**5**/Fc-**H3**,**4**), 4.62 (2H, t, *J* 1.8, Fc-**H2**,**5**/Fc-**H3**,**4**), 4.35 (2H, s, C**H$_2$**S), 4.27 (5H, s, Fc- **H1'-H5'**). **^{13}C NMR** δ 200.8 (**C**O), 139.9 (Ar-**C1**), 136.1 (Ar-**C2**), 133.5 (Ar-**C3**), 132.7 (Ar-**C6**), 131.5 (Ar-**C5**), 130.7 (Ar-**C4**), 81.9 (Fc-**C1**), 76.6 (Fc-**C2**,**5**/Fc-**C3,4**), 73.9 (Fc- **H1'-H5'**), 73.7 (Fc-**C2**,**5**/Fc-**C3,4**), 43.7 (**C**H$_2$S). **MS (ESI)** *m/z* 373 [M(^{37}Cl)H]$^+$, 371 [M(^{35}Cl)H]$^+$. **HRMS Calcd. for $C_{18}H_{15}{}^{35}ClFeOS$:** 369.98815. **Found:** 369.98761.

1-Ferrocenyl-2-[4-(nitrophenyl)thio]ethanone (VIII). η 63%. **Mp** 119-121 °C. **IR** 1655 (*s*, C=O), 1580 (*m*), 1505 (*s*, NO$_2$), 1339 (*s*, NO$_2$), 1220 (*w*), 1097 (*w*), 1067 (*w*), 854 (*m*), 826 (*m*), 724 (*m*). **^{1}H NMR** δ 8.18 (2H, d, *J* 9.2, Ar-**H3,5**), 7.64 (2H, d, *J* 9.2, Ar-**H2,6**), 4.98 (2H, t, *J* 1.8, Fc-**H2,5**/Fc-**H3,4**), 4.67 (2H, t, *J* 1.8, Fc-**H2,5**/Fc-**H3,4**), 4.57 (2H, s, C**H$_2$**S), 4.32 (5H, s, Fc-**H1'-H5'**). **^{13}C NMR** δ 198.1 (**C**O), 148.9 (Ar-**C1**), 146.8 (Ar-**C4**), 128.3 (Ar-**C2,6**), 125.3 (Ar-**C3,5**), 79.2 (Fc-**C1**), 74.3 (Fc-**C2**,**5**/Fc-**C3,4**), 71.6 (Fc-**C1'-C5'**), 71.3 (Fc-**C2**,**5**/Fc-**C3,4**), 41.0 (**C**H$_2$S). **MS (ESI$^+$)** *m/z* 382 [MH$^+$], 381 [M$^+$]; (**ESI$^-$**) 380 [(M-H)$^-$]. **HRMS Calcd. for $C_{18}H_{15}FeNO_3S$**: 381.01221. **Found:** 381.01092.