**Fig. S1.** Cyclic voltammograms of [Fe(CH)3Fe]+[BF4]−, 2a, recorded in CH2Cl2/0.1 M [′Bu4N][PF6]− with a scan rate of 50 mV s−1. Both scans show the reversible 2+/2− couple, (a), while the lower scan also shows the 2+/2−, (b), and 2+/2−, (c), processes, as well as decomposition products, (d), at ca. −400 mV. 1+ and 4+ show qualitatively similar voltammograms.
Figure S2. $^1$H NMR spectrum (benzene-$d_6$, 300 MHz) for a mixture of the isomers of 1-ferrocenyl-2-bromothiophene. FeCH=CHBr.
Figure S3. $^{13}$C($^{1}$H) NMR spectrum (benzene-$d_{6}$, 75 MHz) for a mixture of the isomers of 1-ferrocenyl-2-bromoethene, FsCH=CHBr.
Figure S4. $^1$H NMR spectrum (benzene-$d_6$, 300 MHz) for a mixture of the isomers of 1-(2,3,4,5,1',2',3',4'-octamethylferrocen-1-yl)-2-bromoethene, Fe"CH=CHBr.
Figure S5. $^{13}$C($^1$H) NMR spectrum (benzene-$d_6$, 75 MHz) for a mixture of the isomers of 1-(2,3,4,5,1',2',3',4'-octamethylferrocen-1-yl)-2-bromoethene, Fc"CH=CHBr.
Figure S6. $^1$H NMR spectrum (benzene-$d_6$, 300 MHz) for a mixture of the isomers of 1-ruthenocenyl-2-bromoethene, ReCH=CHBr.
Figure S7. $^{13}\text{C}^{\text{\{}^{1}\text{H}}\text{}}$ NMR spectrum (benzene-$d_6$, 75 MHz) for a mixture of the isomers of 1-ruthenocenyl-2-bromoethene, FeCH=CHBr.