Supplementary information for:

"Oxidative purification of halogenated ferrocenes"

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Contents

Electrochemistry

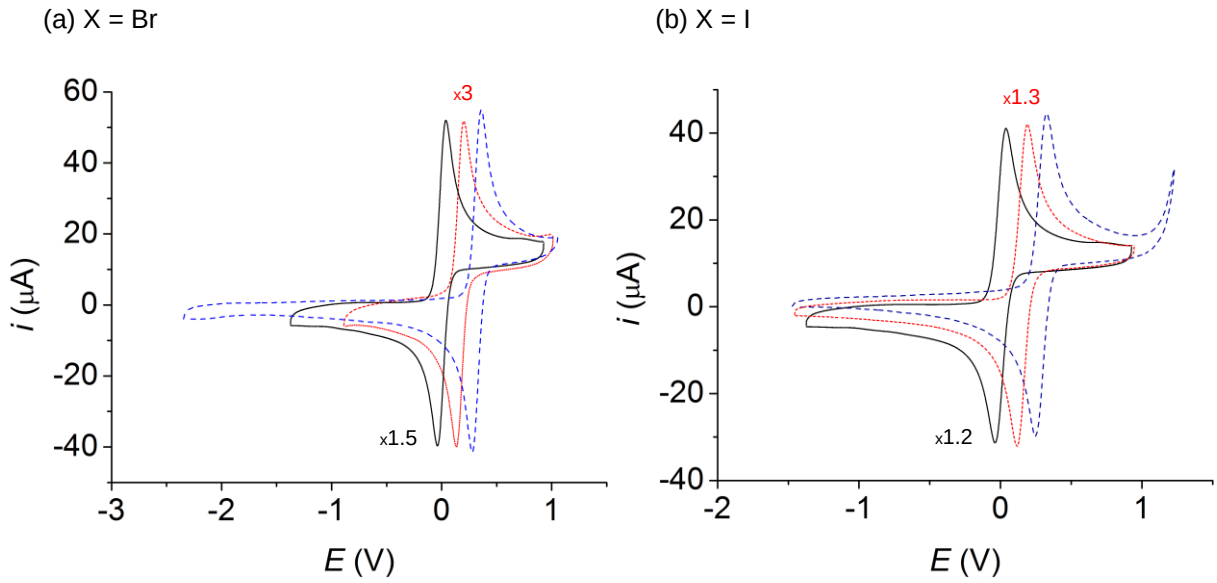


Figure S1. Cyclic voltammograms of FcH (black solid line), pure FcX (red dotted line) and fcX_2 (blue dashed line) (potentials reported versus $[FcH]^+/[FcH]$) – current scaled for clarity.

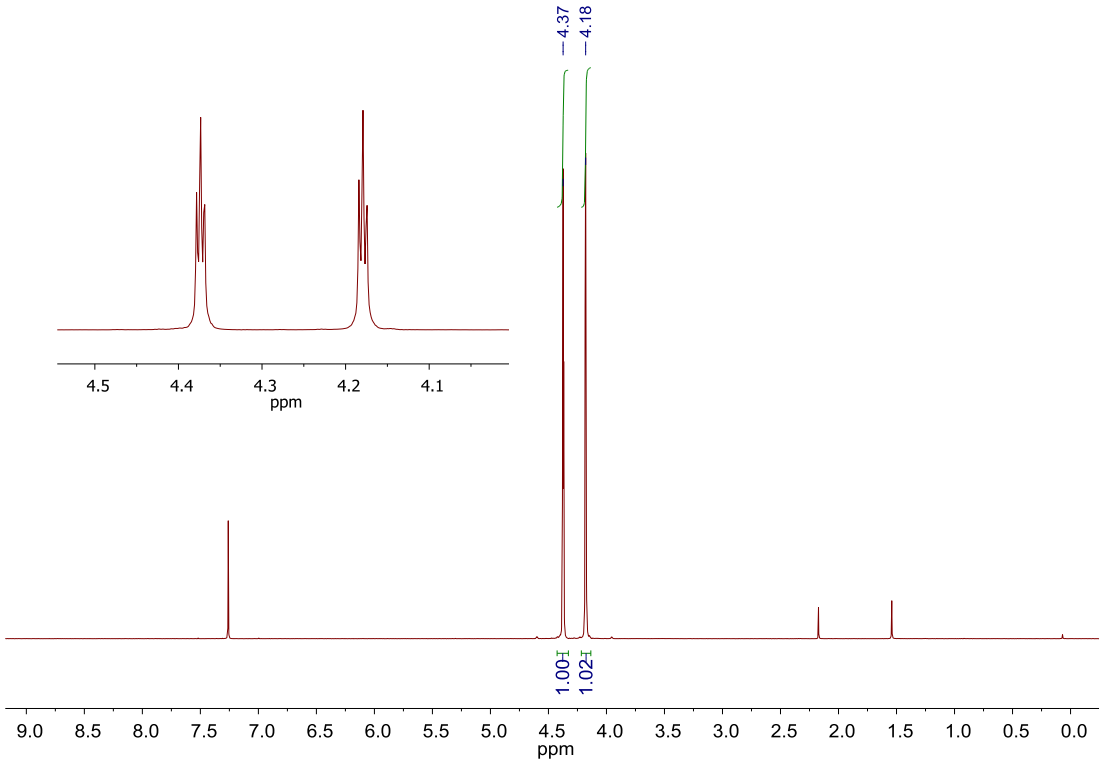
Table S1. Electrochemical data for the haloferrocenes.[a]

compound	E_{pa} (V)	E_{pc} (V)	ΔE (V)[b]	i_p^a/i_p^c	$E_{1/2}$ (V)[c]
FcI	0.116	0.194	0.078	1.00	0.155
FcBr	0.133	0.201	0.068	1.00	0.167
fcI_2	0.250	0.323	0.073	1.04	0.287
$fcBr_2$	0.279	0.359	0.080	1.03	0.319

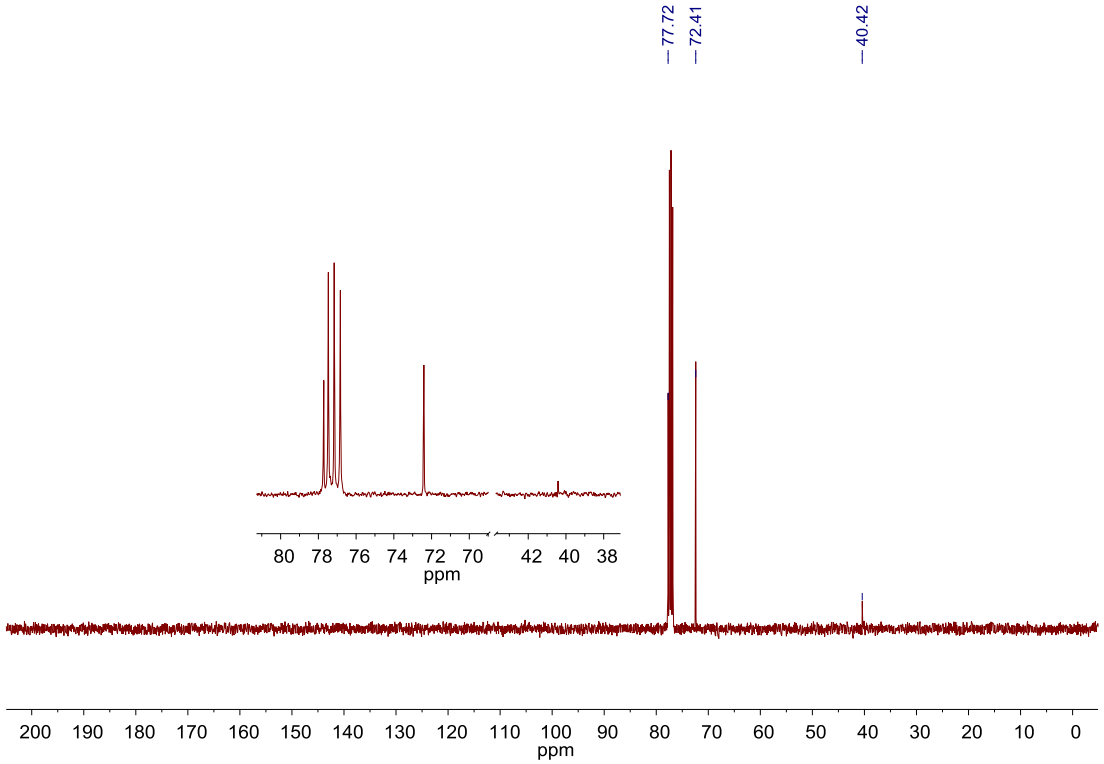
[a] For scan rate = 0.1 Vs^{-1}. $Bu_4N^+PF_6^-$ (0.1 M) in MeCN; WE: glassy carbon; RE, CE: Pt. All potentials (error = ±0.02 V) assigned to the Fe(II)/Fe(III) redox couple and reported relative to an internal $[FcH]^+/[FcH]$ reference. [b] $\Delta E > 0.060$ V due to a small uncompensated solution resistance effect. [c] $E_{1/2} = ½(E_{pa} + E_{pc})$.

$^{1}H/^{13}C$ NMR spectroscopy

^{1}H NMR spectrum for fcI_2 in $CDCl_3$



^{13}C NMR spectrum for fcI_2 in $CDCl_3$



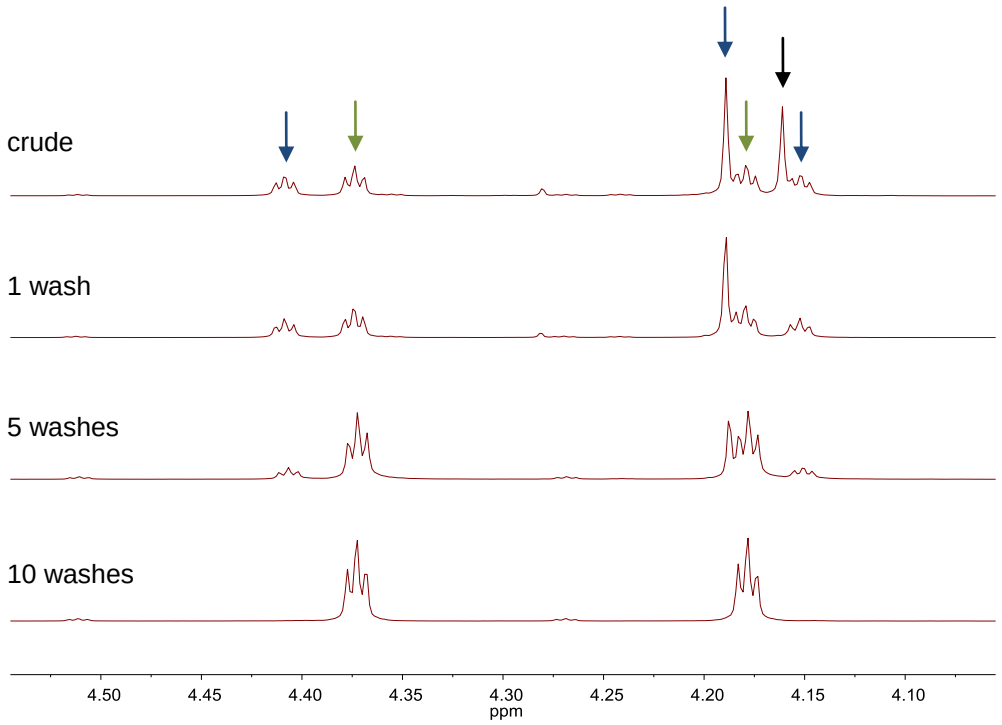
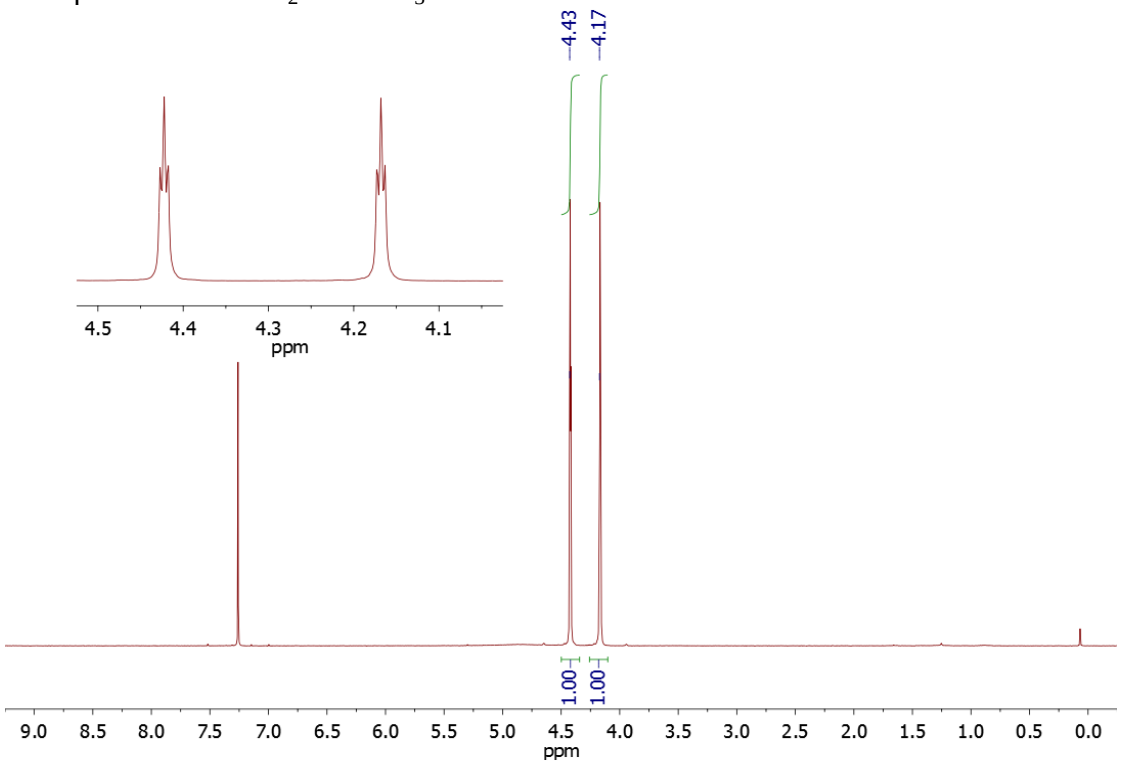
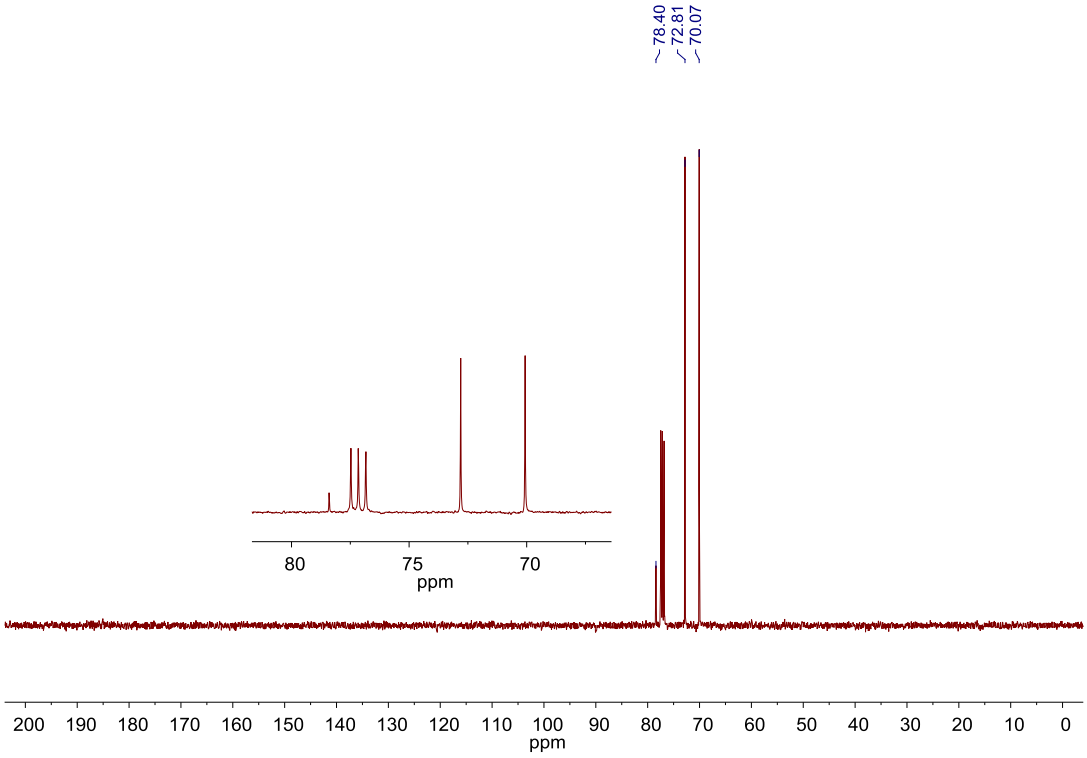


Figure S2. Selected ^{1}H NMR spectra in $CDCl_3$ showing the elimination of FcH (black arrow, after 1 wash with 0.5 M aqueous $FeCl_3$) and FcI (blue arrows, after 10 washings) from their mixture with fcI_2 (green arrows).

^{1}H NMR spectrum for $fcBr_2$ in $CDCl_3$



^{13}C NMR spectrum for $fcBr_2$ in $CDCl_3$



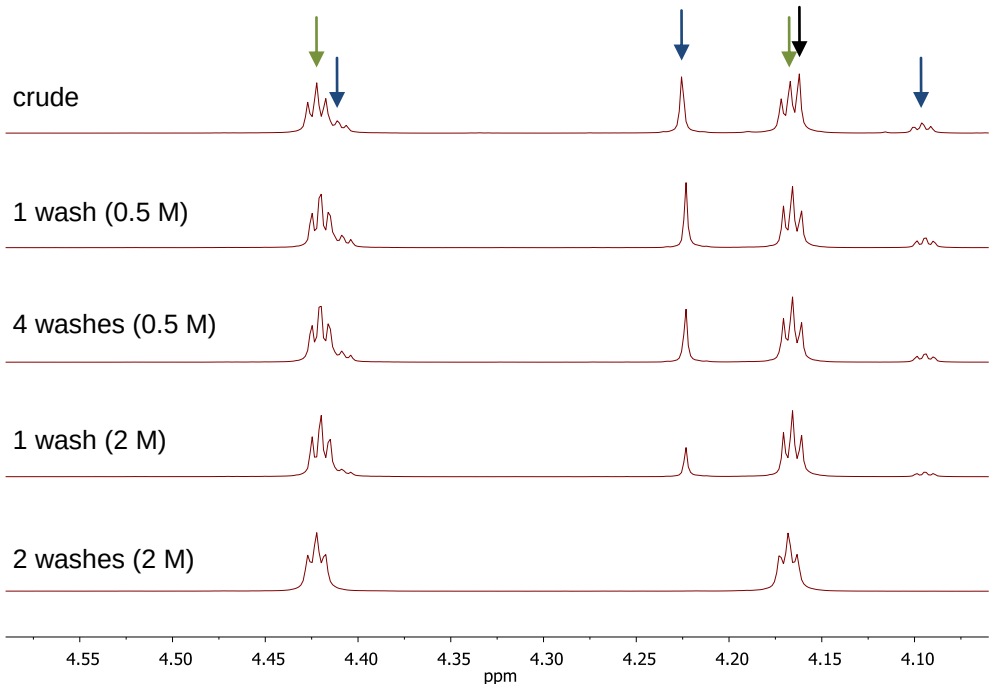
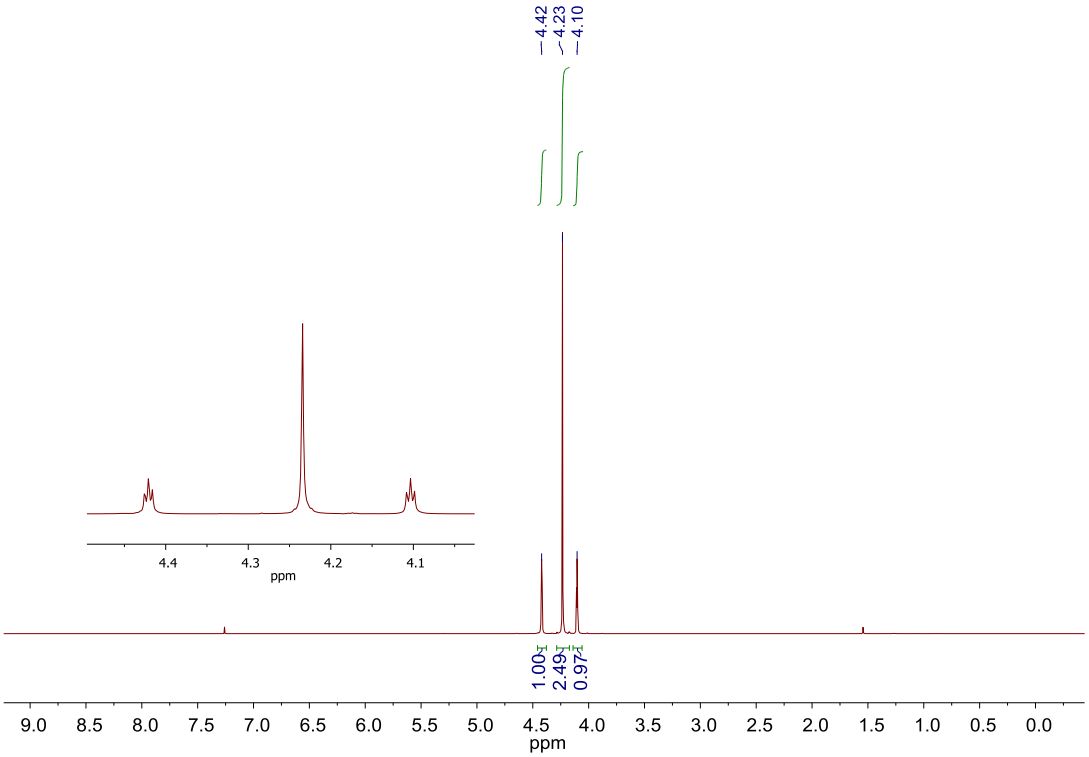
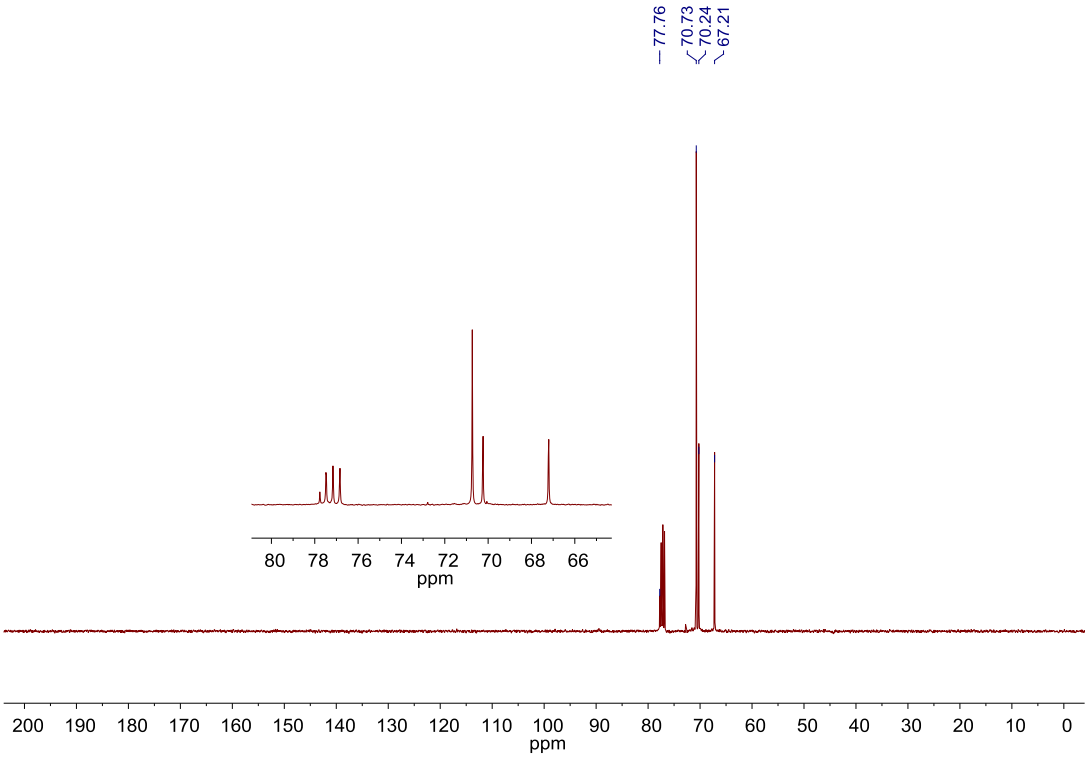


Figure S3. Selected ^{1}H NMR spectra in $CDCl_3$ showing the elimination of FcH (black arrow, after 1 wash with 0.5 M aqueous $FeCl_3$) and FcBr (blue arrows, after 4 washings with 0.5 M aqueous $FeCl_3$ followed by 2 washings with 2 M aqueous $FeCl_3$) from their mixture with $fcBr_2$ (green arrows).

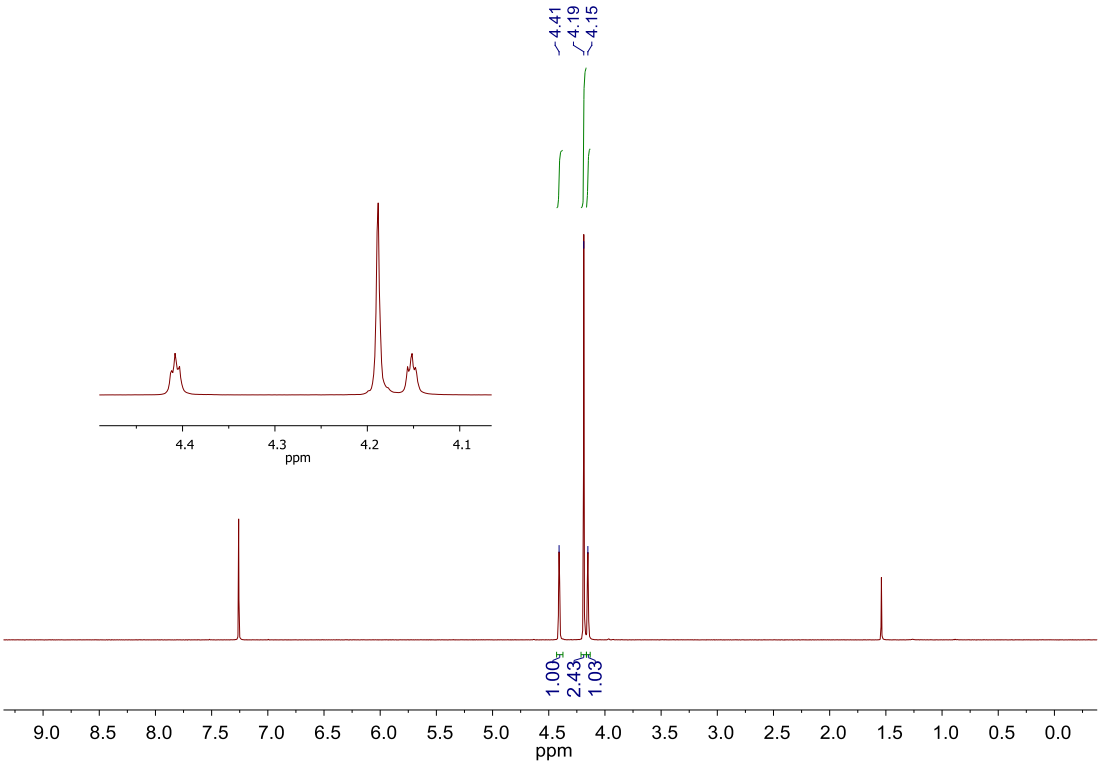
^{1}H NMR spectrum for FcBr in $CDCl_3$



^{13}C NMR spectrum for FcBr in $CDCl_3$



^{1}H NMR spectrum for FcI in $CDCl_3$



^{13}C NMR spectrum for FcI in $CDCl_3$