<u>Supporting Information</u>

Ferrocenyl Naphthalenes: Substituent- and Substitution Pattern-depending

Charge Transfer Studies

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Content:

Table SI1. Crystallographic data for **3a–c** and **3e**.

Compound	3a	3b	3c	3e
Empiric formula	$C_{20}H_{16}Fe$	$C_{21}H_{18}FeO$	$C_{21}H_{18}Fe$	$C_{21}H_{16}FeO$
M_r, g/mol	312.18	342.20	326.20	340.19
λ, Å	0.71073	0.71073	1.54184	1.54184
Crystal system	orthorhombic	monoclinic	monoclinic	orthorhombic
Space group	$Pbca$	$P2_1/c$	$P2_1/c$	$Pna2_1$
a, Å	20.2076(13)	15.3517(15)	9.662(5)	8.707(10)
b, Å	6.0150(4)	7.3645(7)	10.031(5)	9.473(3)
c, Å	22.725(2)	14.7940(14)	15.390(5)	36.37(3)
α, deg	90	90	90	90
β, deg	90	115.885(3)	94.773(5)	90
γ, deg	90	90	90	90
V, Å^3	2762.2(4)	1504.8(3)	1486.4(12)	3000.0(5)
ρ_{calcd} mg m^{-3}	1.501	1.511	1.458	1.506
Z	8	4	4	8
μ, mm^{-1}	1.080	1.004	8.046	8.054
T, K	114.7(4)	100	100	121(1)
Θ range, deg	3.516 – 24.995	3.761 – 25.000	5.217 – 65.987	4.824 – 64.990
Measured reflections	18663	12544	17497	8386
Independent reflections	2411	2638	2589	4410
R_{int}	0.0836	0.0518	0.0360	0.0595
R_1	0.0367	0.0321	0.0270	0.0720
wR_2, ($I > 2\sigma(I)$)	0.0784	0.0847	0.0682	0.1836
CCDC no.	1897600	1897601	1897602	1897603

Table SI2. Crystallographic data for **4** and **6b–d**.

Compound	4	6b	6c	6d
Empiric formula	$C_{30}H_{22}Fe$	$C_{20}H_{15}BrFe$	$C_{20}H_{15}BrFe$	$C_{20}H_{15}BrFe$
M_r, g/mol	438.32	391.08	391.07	391.08
λ, Å	0.71073	0.71073	1.54184	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$C2/c$	$P2_1/c$	$P2_1/c$	$Pbca$
a, Å	12.8866(8)	12.3825(5)	13.8326(7)	10.3319(10)
b, Å	7.5244(4)	7.7378(4)	11.0072(7)	7.7884(7)
c, Å	21.0448(17)	15.7332(7)	10.0041(5)	37.581(4)
α, deg	90	90	90	90
β, deg	101.335(7)	93.903(3)	96.575(4)	90
γ, deg	90	90	90	90

V, Å^3	2000.8(2)	1503.95(12)	1513.19(14)	3024.1(5)
ρ_{calcd} mg m^{-3}	1.455	1.727	1.717	1.718
Z	4	4	4	8
μ, mm^{-1}	0.769	3.652	10.999	3.632
T, K	130.00(14)	130.00(10)	119(4)	125(10)
Θ range, deg	3.151 – 25.495	2.979 – 26.000	5.148 – 62.489	2.930 – 24.998
Measured reflections	6221	10528	4355	8085
Independent reflections	6221	2950	2364	2658
R_{int}	0.0538	0.0268	0.0391	0.0648
R_1	0.0751	0.0236	0.0407	0.0475
wR_2, ($I > 2\sigma(I)$)	0.1498	0.0555	0.1050	0.0781
CCDC no.	1897604	1897605	1897606	1897607

Table SI3. Crystallographic data for **7a–d**.

Compound	**7a**	**7b**	**7c**	**7d**
Empiric formula	$C_{30}H_{24}Fe_2$	$C_{30}H_{24}Fe_2$	$C_{30}H_{24}Fe_2$	$C_{30}H_{24}Fe_2$
M_r, g/mol	496.19	496.19	496.19	496.19
λ, Å	0.71073	1.54184	0.71073	0.71073
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	$Pna2_1$	$P2_1/n$	$P2_1/c$	$P2_1/n$
a, Å	12.1550(4)	9.6644(16)	17.0392(7)	13.6264(18)
b, Å	12.9938(3)	10.7292(16)	10.0481(5)	9.7347(13)
c, Å	13.7119(4)	10.9942(18)	12.2011(5)	8.1052(11)
α, deg	90	90	90	90
β, deg	90	110.625(18)	92.020(3)	95.977(4)
γ, deg	90	90	90	90
V, Å^3	2165.65(11)	1066.9(3)	2087.67(16)	1069.3(2)
ρ_{calcd} mg m^{-3}	1.522	1.545	1.579	1.541
Z	4	2	4	2
μ, mm^{-1}	1.356	11.006	1.406	1.373
T, K	129.95(10)	117(10)	125(10)	100
Θ range, deg	2.971 – 25.999	5.252 – 64.967	3.342 – 24.997	3.498 – 24.991
Measured reflections	8109	3123	10121	9787
Independent reflections	3646	1782	3653	1869
R_{int}	0.0269	0.0690	0.0225	0.0744
R_1	0.0319	0.0732	0.0259	0.0470
wR_2, ($I > 2\sigma(I)$)	0.0689	0.1985	0.0599	0.1081
CCDC no.	1897608	1897609	1897610	1897611

Table SI4. Selected D-Fe bond lengths, angles and torsion angles of **3a**–**c** and **3e**.

	3a	3b	3c	3e
D1–Fe1 (Å)		1.6459(3)	1.6493(7)	1.646(13)
D2–Fe1 (Å)		1.6489(3)	1.6524(7)	1.645(15)
D3–Fe2 (Å)				1.645(13)
D4–Fe2 (Å)				1.649(15)
D1–Fe1–D2 (°)	179.72(3)	178.16(2)	177.35(2)	177(3)
D3–Fe2–D4 (°)				178(3)
C_5H_4(D1)–C_6(C11) (°)	9.34(12)	46.98(9)	39.97(7)	45.2(5)
C_5H_4(D3)–C_6(C32) (°)				45.2(5)
C1–D1–D2–C6 (°)		–3.87(15)	0.93(11)	–0.2(8)
C1–D1–D2–C10 (°)	5.4 (2)			
C22–D3–D4–C27 (°)				0.6(8)

D1 = centroid of C1-C5; D2 = centroid of C6-C10.

**Table SI5.** Selected D-Fe bond lengths, angles and torsion angles of **4** and **6b**–**d**.

	4	6b	6c	6d
D1–Fe1 (Å)	1.6576(1)	1.6452(3)	1.6595(6)	1.6480(6)
D2–Fe1 (Å)		1.6450(3)	1.6550(6)	1.6510(5)
D1–Fe1–D2 (°)		177.30(2)	177.48(4)	179.53(5)
C_5H_4(D1)–C_6(C11) (°)		39.06(7)	58.26(16)	14.9(2)
C_5H_4(D1)–C_6(C6) (°)	77.59(19)			
C1–D1–D2–C6 (°)		2.91(14)	–10.3(3)	–11.3(3)

D1 = centroid of C1-C5; D2 = centroid of C6-C10; D3 = centroid of C22-C26; D4 = centroid of C27-C31.

Table SI6. Selected D–Fe bond lengths, angles and torsion angles, and plane intersections (°/Å) of **7a**–**d**.

	7a	7b	7c	7d
D1–Fe1 (Å)	1.643(6)	1.6433(8)	1.6537(3)	1.6434(5)
D2–Fe1 (Å)	1.644(8)	1.6469(8)	1.6507(3)	1.6457(5)
D3–Fe2 (Å)	1.644(9)		1.6521(3)	
D4–Fe2 (Å)	1.650(8)		1.6512(3)	
D1–Fe1–D2 (°)	173.2(10)	179.26(6)	178.70(2)	178.64(4)
D3–Fe2–D4 (°)	176.6(10)		178.82(2)	
C_5H_4(D1)–C_6(C11) (°)		46.6(3)	40.02(7)	6.1(2)
C_5H_4(D1)–C_6(C21) (°)	52.57(15)		37.42(7)	
C_5H_4(D3)–C_6(C24) (°)	41.62(18)			
C1–D1–D2–C6 (°)	–19(10)	6.6(4)	–15.22(13)	2.2(3)
C11–D3–D4–C16 (°)	3.9(3)		3.15(12)	
$C_5H_4^A$···$C_5H_4^B$	180.0(4)	151.37(6)	88.82(17)	180.0(3)

D1 = centroid of C1-C5; D2 = centroid of C6-C10; D3 = centroid of C11–C15; D4 = centroid of C16–C20.
A, B = planes of cyclopentadienyls, according to an ascending labeling. The plane intersection is given while considering the orientation of the attached $Fe(C_5H_5)$ fragment.
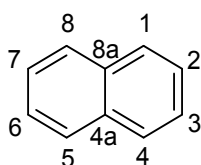
Scheme SI1. Numbering scheme of naphthalene core.

Table SI7. Bond lengths of the naphthalene substituents of **3a**–**c** and **3e**.

	3a	3b	3c	3e (1)	3e (2)
C1–C2 (Å)	1.374(4)	1.387(3)	1.391(3)	1.397(18)	1.396(17)
C2–C3 (Å)	1.418(3)	1.409(3)	1.422(3)	1.42(2)	1.411(18)
C3–C4 (Å)	1.356(4)	1.361(3)	1.355(3)	1.34(2)	1.351(19)
C4–C4a (Å)	1.417(4)	1.408(3)	1.412(3)	1.427(19)	1.422(18)
C4a–C5 (Å)	1.414(4)	1.417(3)	1.413(3)	1.397(19)	1.422(19)
C4a–C8a (Å)	1.420(4)	1.427(3)	1.430(2)	1.430(19)	1.433(18)
C5–C6 (Å)	1.360(4)	1.364(3)	1.365(3)	1.381(19)	1.36(2)
C6–C7 (Å)	1.409(4)	1.404(3)	1.409(3)	1.41(2)	1.40(2)
C7–C8 (Å)	1.361(4)	1.369(3)	1.377(3)	1.36(2)	1.380(19)
C8–C8a (Å)	1.412(4)	1.419(3)	1.417(3)	1.430(18)	1.424(17)
C8a–C1 (Å)	1.419(4)	1.430(3)	1.448(3)	1.430(18)	1.431(18)

(1) = the first molecule in the asymmetric unit of **3e**; (2) = the second molecule in the asymmetric unit of **3e**.

Table SI8. Bond lengths of the naphthalene substituents of **4** and **6b**–**d**.

	4	6b	6c	6d
C1–C2 (Å)	1.369(8)	1.374(3)	1.379(6)	1.381(5)
C2–C3 (Å)	1.408(8)	1.411(3)	1.421(6)	1.426(5)
C3–C4 (Å)	1.355(8)	1.357(3)	1.342(6)	1.361(6)
C4–C4a (Å)	1.414(8)	1.419(3)	1.412(7)	1.415(6)
C4a–C5 (Å)	1.420(8)	1.418(3)	1.423(7)	1.418(6)
C4a–C8a (Å)	1.432(8)	1.433(3)	1.441(6)	1.427(5)
C5–C6 (Å)	1.352(9)	1.359(3)	1.349(8)	1.365(6)
C6–C7 (Å)	1.414(8)	1.416(3)	1.400(7)	1.404(5)
C7–C8 (Å)	1.369(8)	1.356(3)	1.384(7)	1.363(6)
C8–C8a (Å)	1.401(8)	1.422(3)	1.425(6)	1.409(6)
C8a–C1 (Å)	1.440(8)	1.429(3)	1.433(6)	1.411(6)

Table SI9. Bond lengths of the naphthalene substituents of **7a**–**d**.

|	7a	7b	7c	7d
C1–C2 (Å)	1.369(5)	1.377(8)	1.376(3)	1.385(5)
C2–C3 (Å)	1.395(6)	1.414(8)	1.402(3)	1.411(5)
C3–C4 (Å)	1.373(6)	1.356(9)	1.355(3)	1.362(5)
C4–C4a (Å)	1.447(5)		1.410(3)	
C4a–C5 (Å)	1.419(6)		1.412(3)	
C4a–C8a (Å)	1.420(6)		1.434(3)	
C5–C6 (Å)	1.361(5)		1.363(3)	
C6–C7 (Å)	1.393(6)		1.402(3)	
C7–C8 (Å)	1.361(6)		1.374(3)	
C8–C8a (Å)	1.418(5)		1.437(3)	
C8a–C1 (Å)	1.437(5)	1.422(8)	1.435(2)	1.417(5)

Table SI10. Bond lengths of the naphthalenes substituent of **7c**[1], 1,8-Bis(cobaltocenyl)naphthalene[2] (**8**) and 1,8-Bis[(η^5-pentamethylcyclopentadienyl)(η^5-cyclopentadiendiyl)-nickel(II)]naphthalene[3] (**9**).

	7c[1]	**8**[2]	**9**[3]
C1–C2 (Å)	1.380	1.389	1.382
C2–C3 (Å)	1.406	1.409	1.407
C3–C4 (Å)	1.341	1.368	1.357
C4–C4a (Å)	1.422	1.419	1.420
C4a–C5 (Å)	1.411	1.422	1.420
C4a–C8a (Å)	1.429	1.431	1.427
C5–C6 (Å)	1.353	1.367	1.360
C6–C7 (Å)	1.394	1.411	1.399
C7–C8 (Å)	1.380	1.390	1.379
C8–C8a (Å)	1.437	1.446	1.443
C8a–C1 (Å)	1.443	1.443	1.444

Table SI11. RMS (root mean square) deviations of the naphthalene planes of compounds **3a–e**, **6b–d** and **7a–d** and the atom showing the highest displacement (d_{max} / Å).*)

Compd.	RMS	d_{max}	Compd.	RMS	d_{max}
3a	0.0185	0.034(2) C11	**6c**	0.0893	0.150(3) C11
3b	0.0466	0.0861(16) C11	C11–14	0.0160	Angle: 10.9(4)°
C11–14	0.0137	Angle: 7.23(19)°	C16–19	0.0169	0.320(7) Br1[a]
C16–19	0.0078		**6d**	0.0242	0.037(3) C2
3c	0.0138	0.0257(14) C14	**7a**	0.0156	0.026(3) C23
3e	0.0321	0.065(10) C11	**7b**	0.0182	0.020(4) C11
	0.0290	0.067(10) C32	**7c**	0.1136	0.1894(14) C1
4	0.0125	0.021(5) C6	C1–4	0.0163	Angle: 15.54(14)
6b	0.0247	0.0349(18) C18	C6–9	0.0191	0.007(3) C14
			7d	0.0350	

*) The values were calculated by using WinGX. a) Deviation towards the C16–C19 plane.
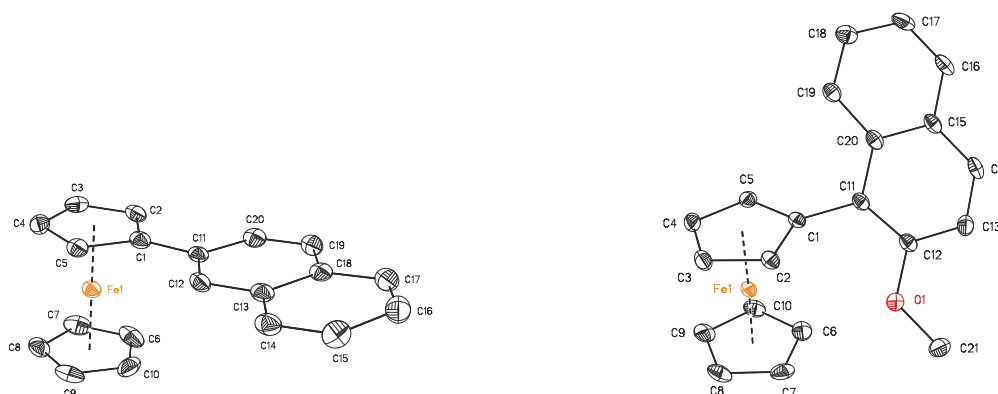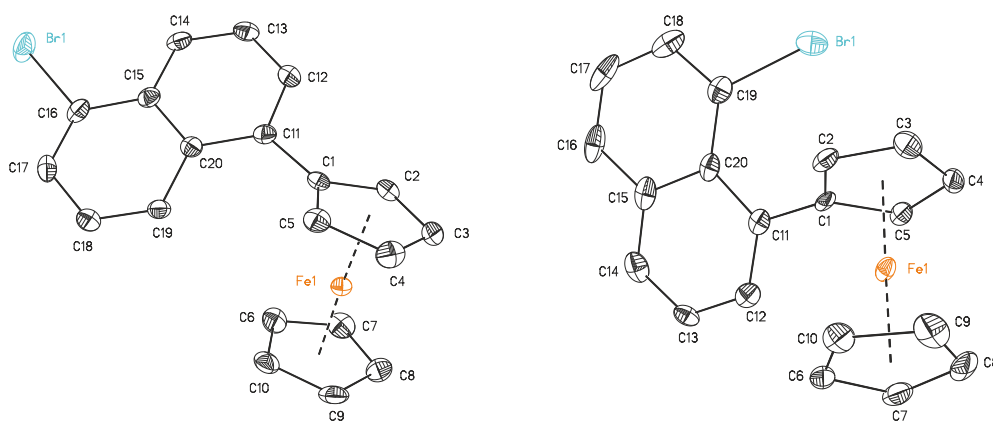

Figure SI1. ORTEP (50 % probability level) of the molecular structures of **3a** (left) and **3b** (right) with the atom-numbering scheme. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å), angles (deg), and torsion angles (deg): **3a**, C1–C11 = 1.471(4), C2–C1–C11 = 126.6(2), C5–C1–C11 = 126.6(2), C11–C1–C2–C3 = -175.1(2), C11–C1–C5–C4 = 174.9(2), C2–C1–C11–C12 = 178.0(2), C5–C1–C11–C12 = 2.9(4), C1–C11–C12–C13 = −173.7(2), C5–C1–C11–C20 = −173.0(2), C2–C1–C11–C20 = 2.1(4); **3b**, C1–C11 = 1.477(3), C12–O1 = 1.367(3), C21–O1 = 1.426(3), C2–C1–C11 = 128.02(19), C5–C1–C11 = 125.43(19), C12–O1–C21 = 118.33(17), C11–C1–C2–C3 = 174.39(19), C11–C1–C5–C4 = −174.71(19), C2–C1–C11–C12 = 48.7(3), C5–C1–C11–C12 = −135.9(2), C1–C11–C12–C13 = 172.24(19), C5–C1–C11–C20 = 45.5(3), C2–C1–C11–C20 = −129.9(2), C11–C12–O1–C21 = −10.2(3).
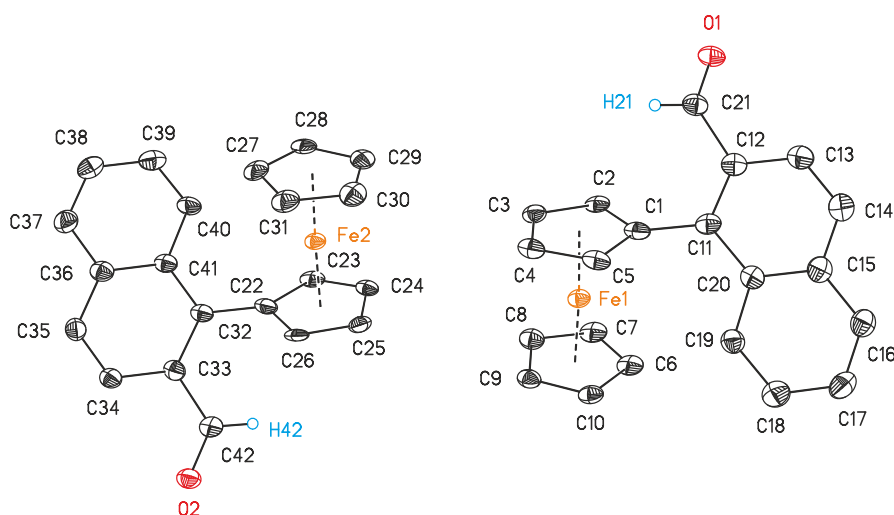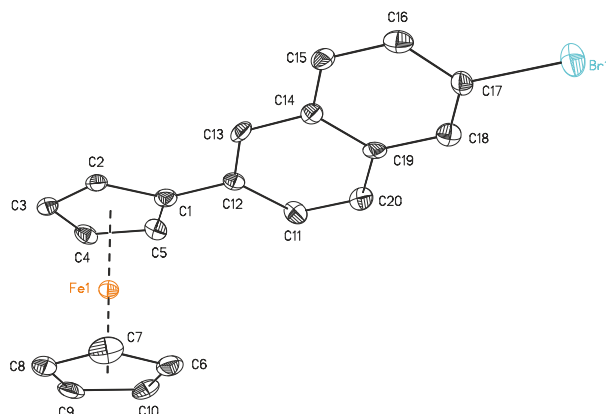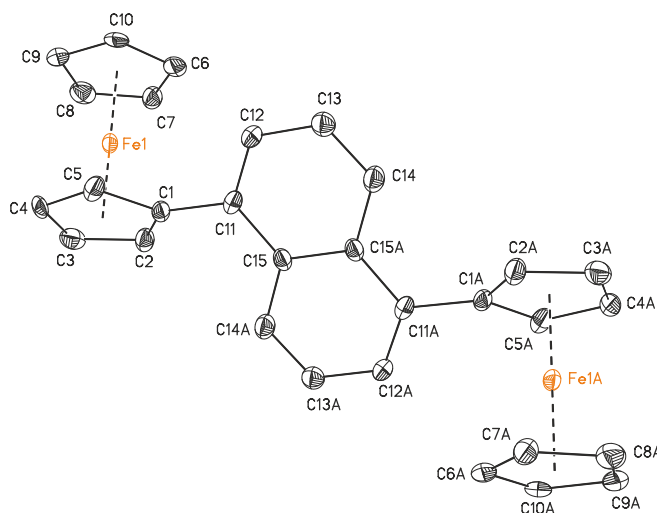
Figure SI2. ORTEP (50 % probability level) of the molecular structure of **3e** with the atom-numbering scheme. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å), angles (deg), and torsion angles (deg): C1–C11 = 1.480(18), C22–C32 = 1.458(18), C21–O1 = 1.214(16), C21–H21 = 0.9300, C42–O2 = 1.234(15), C42–H42 = 0.9300, C5–C1–C11 = 129.2(12), C2–C1–C11 = 123.5(11), O1–C21–C12 = 124.7(13), O1–C21–H21 = 117.7, C12–C21–H21 = 117.7, C23–C22–C32 = 131.1(12), C26–C22–C32 = 123.2(11), O2–C42–C33 = 123.4(11), O2–C42–H42 = 118.3, C33–C42–H42 = 118.3, C11–C1–C2–C3 = −174.3(11), C11–C1–C5–C4 = 173.9(12), C2–C1–C11–C12 = 40.9(18), C5–C1–C11–C12 = −133.9(13), C1–C11–C12–C13 = −170.7(12), C5–C1–C11–C20 = 50.4(19), C2–C1–C11–C20 = −134.8(13), C32–C22–C23–C24 = −175.8(12), C32–C22–C26–C25 = 174.8(11), C23–C22–C32–C33 = 131.6(13), C26–C22–C32–C33 = −41.6(17), C22–C32–C33–C34 = 170.6(11), C26–C22–C32–C41 = 135.7(12), C23–C22–C32–C41 = −51.1(19), C11–C12–C21–O1 = −168.1(12), C13–C12–C21–O1 = 17.6(19), C32–C33–C42–O2 = 168.9(12), C34–C33–C42–O2 = −15.1(18).
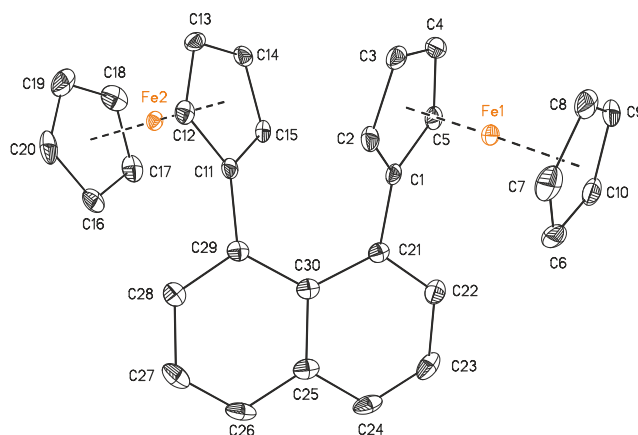

Figure SI3. ORTEP (50 % probability level) of the molecular structures of **6b** (left) and **6c** (right) with the atom-numbering scheme. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å), angles (deg), and torsion angles (deg): **6b**, C1–C11 = 1.488(3), C16–Br1 = 1.911(2), C2–C1–C11 = 124.02(18), C5–C1–C11 = 129.04(18), C17–C16–Br1 = 117.84(16), C15–C16–Br1 = 118.71(15), C11–C1–C2–C3 = 172.64(18), C11–C1–C5–C4 = −172.22(19), C2–C1–C11–C12 = −34.8(3), C5–C1–C11–C12 = 136.6(2), C1–C11–C12–C13 = −178.1(2), C5–C1–C11–C20 = −40.8(3), C2–C1–C11–C20 = 147.8(2), C14–C15–C16–Br1 = −4.3(3), C20–C15–C16–Br1 = 177.33(14), Br1–C16–C17–C18 = −178.85(16); **6c**, C1–C11 = 1.490(5), C19–Br1 = 1.908(4), C2–C1–C11 = 126.1(3), C5–C1–C11 = 126.1(3), C18–C19–Br1 = 113.8(3), C20–C19–Br1 = 122.9(3), C11–C1–C2–C3 = −176.6(4), C11–C1–C5–C4 = 177.0(4), C2–C1–C11–C12 = −120.5(4), C5–C1–C11–C12 = 62.3(5), C1–C11–C12–C13 = 173.2(3), C5–C1–C11–C20 = −119.8(4), C2–C1–C11–C20 = 57.4(5), C17–C18–C19–Br1 = 171.3(3), Br1–C19–C20–C15 = −163.8(3), Br1–C19–C20–C11 = 13.6(6).
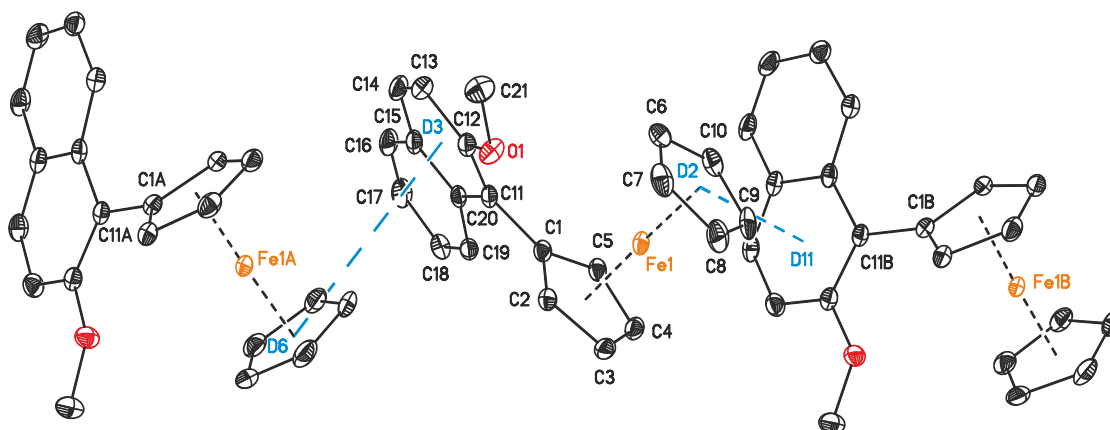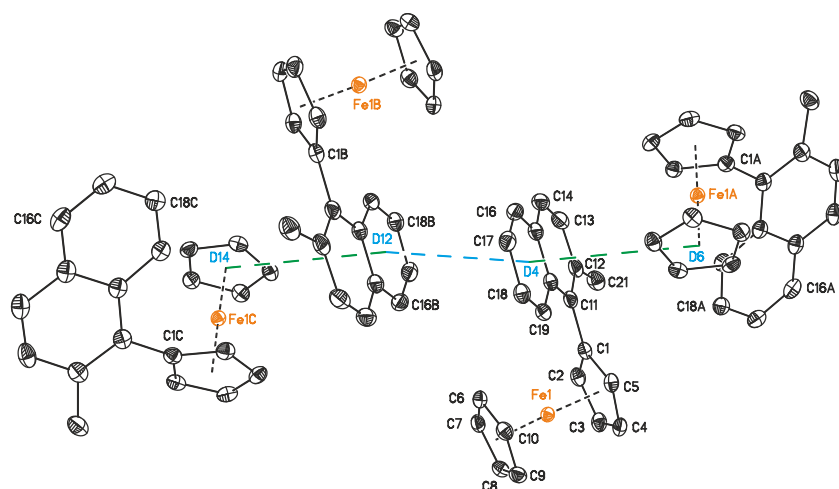
Figure SI4. ORTEP (50 % probability level) of the molecular structure of **6d** with the atom-numbering scheme. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å), angles (deg), and torsion angles (deg): **6d**, C1–C12 = 1.469(6), C17–Br1 = 1.902(4), C2–C1–C11 = 125.9(4), C5–C1–C11 = 127.1(4), C18–C17–Br1 = 118.6(3), C16–C17–Br1 = 119.1(3), C12–C1–C2–C3 = 179.9(4), C12–C1–C5–C4 = 179.9(4), C11–C12–C1–C2 = –15.1(6), C11–C12–C1–C5 = 164.9(4), C13–C12–C1–C5 = –14.7(6), C13–C12–C1–C2 = 165.4(4), C20–C11–C12–C1 = 178.7(4), C1–C11–C12–C13 = –178.1(2), C15–C16–C17–Br1 = 179.0(3), Br1–C17–C18–C19 = –179.5(3).

Figure SI5. ORTEP (50 % probability level) of the molecular structure of **7b** with the atom-numbering scheme. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): C1–C11 = 1.495(8), C2–C1–C11 = 128.6(5), C5–C1–C11 = 123.8(5), C12–C11–C1 = 119.3(5), C15–C11–C1 = 120.9(5), C11–C1–C2–C3 = 178.7(6), C11–C1–C5–C4 = –179.3(5), C2–C1–C11–C12 = 133.5(6), C5–C1–C11–C12 = –45.7(8), C1–C11–C12–C13 = 179.4(3), C5–C1–C11–C15 = 132.7(6), C2–C1–C11–C15 = –48.1(8). (Symmetry generated atoms are indicated by the suffix A; symmetry code: –x, –y, –z+1.).

Figure SI6. ORTEP (50 % probability level) of the molecular structure of **7c** with the atom-numbering scheme. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): C1–C21 = 1.483(3), C11–C29 = 1.481(3), C2–C1–C21 = 126.49(16), C5–C1–C21 = 126.69(16), C30–C21–C1 = 121.86(16), C22–C21–C1 = 119.02(16), C15–C11–C29 = 127.51(16), C12–C11–C29 = 125.46(16), C28–C29–C11 = 119.18(17), C30–C29–C11 = 121.68(16), C21–C1–C2–C3 = −179.72(17), C21–C1–C5–C4 = 179.59(17), C2–C1–C21–C22 = −132.96(19), C5–C1–C21–C22 = 45.7(3), C1–C21–C22–C23 = 169.75(17), C5–C1–C21–C30 = −139.50(18), C2–C1–C21–C30 = 41.9(3), C1–C21–C30–C29 = 19.0(3), C(11)–C(29)–C(30)–C(25) = −161.93(16), C(11)–C(29)–C(30)–C(21) = 17.9(3), C(28)–C(29)–C(11)–C(12) = 43.1(3), C(30)–C(29)–C(11)–C(12) = −141.67(18), C(28)–C(29)–C(11)–C(15) = −135.72(19), C(30)–C(29)–C(11)–C(15) = 39.5(3), C(29)–C(11)–C(15)–C(14) = −179.29(16), C(29)–C(11)–C(12)–C(13) = 179.46(17).

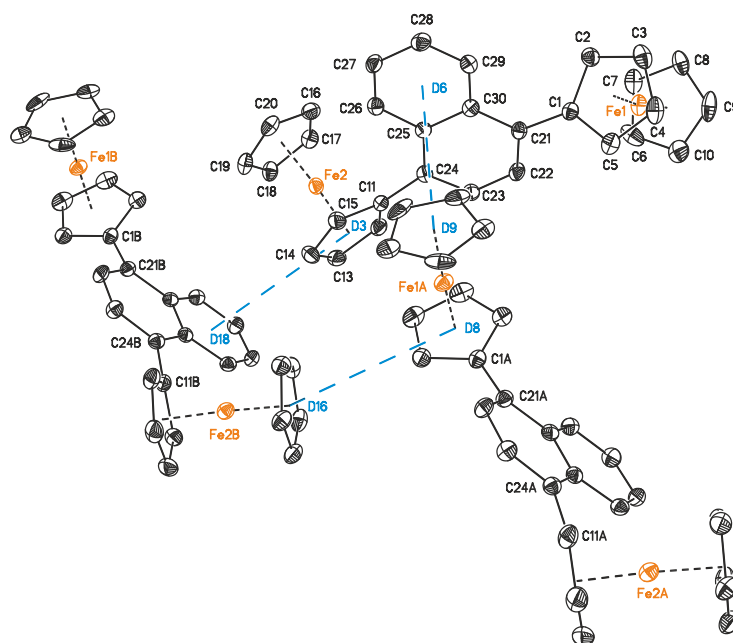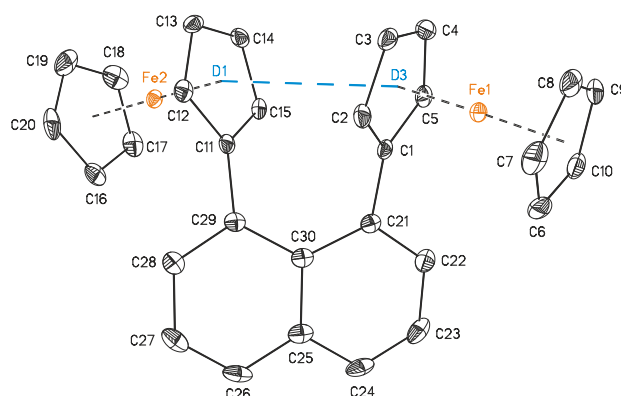|	d (Å)	α (°)
Ct ⋯ D	4.721(16)	85.79(12)

Figure SI7. ORTEP (50 % probability level) of the molecular structure of **3b** with selected atom-numbering scheme, showing the intermolecular *T*-shaped π-interaction (blue dashed lines) between the C_5H_5 unit and the C_6H_4 moiety (including C11 to C20). Only a section of different π-π interaction pattern is shown and all hydrogen atoms have been omitted for clarity. (Symmetry code for generating-equivalent atoms; A: x, 3/2–y, −1/2+z; B: x, 3/2–y, 1/2+z).

	d (Å)	α (°)
Ct ⋯ D	4.576(3)	88.28(9)
D ⋯ D	3.860(2)	0
C16 ⋯ C18	3.399(3)	

Figure SI8. ORTEP (50 % probability level) of the molecular structure of **3c** with selected atom-numbering scheme, showing the intermolecular *T*-shaped π-interaction (green dashed lines) between the C_5H_5 unit and the C_6H_4 moiety (including C16 and C18) and parallel displaced pattern (blue dashed lines) between the C_6H_4 moieties (including C16 and C18). Only a section of different π-π interaction pattern is shown and all hydrogen atoms have been omitted for clarity. (Symmetry code for generating-equivalent atoms; A: –1/2+x, 1/2+y, 3/2–z; B: –1+x, –y, 1–z; C: –1/2+x, 1/2–y, –1/2+z).
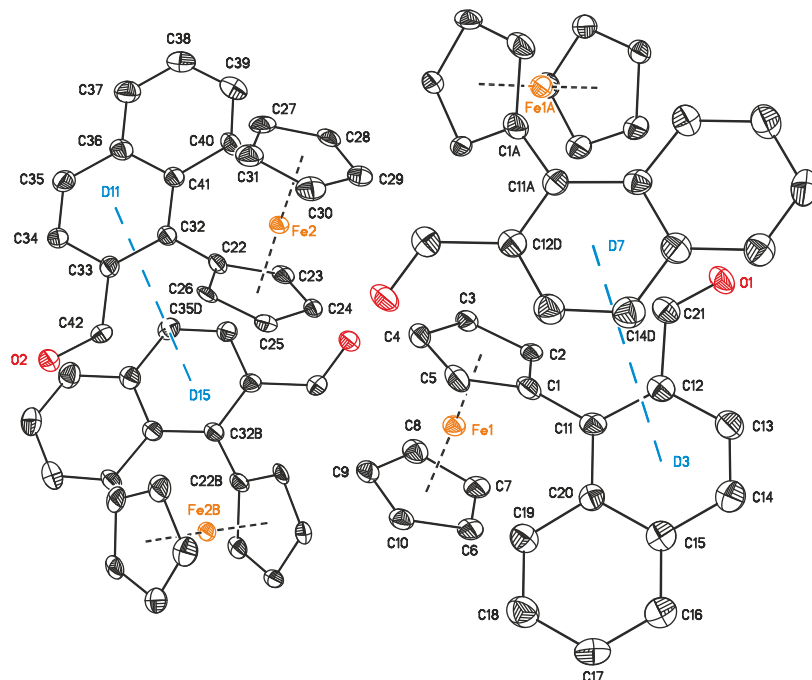
|	d (Å)	α (°)
D ⋯ D	4.488(9)	2
D ⋯ D	4.475(9)	1
C12 ⋯ C14	3.486(18)	
C32 ⋯ C35	3.660(18)	

Figure SI9. ORTEP (50 % probability level) of the molecular structure of **3e** with selected atom-numbering scheme, showing the intermolecular parallel displaced π-interaction (blue dashed lines)

between the naphthalene moieties (including C11 to C20 and C32 to C41) forming dimers. All hydrogen atoms have been omitted for clarity. (Symmetry code for generating-equivalent atoms; A: x+1/2, 3/2–y, z; B: x+1/2, 3/2–y, z).

	d (Å)	α (°)
D3 ⋯ D10	4.6688(13)	78.12(12)
D4 ⋯ D10	4.9217(14)	79.47(12)
D3 ⋯ D8	3.8925(13)	0
D3 ⋯ D7	4.5528(12)	2.52(10)
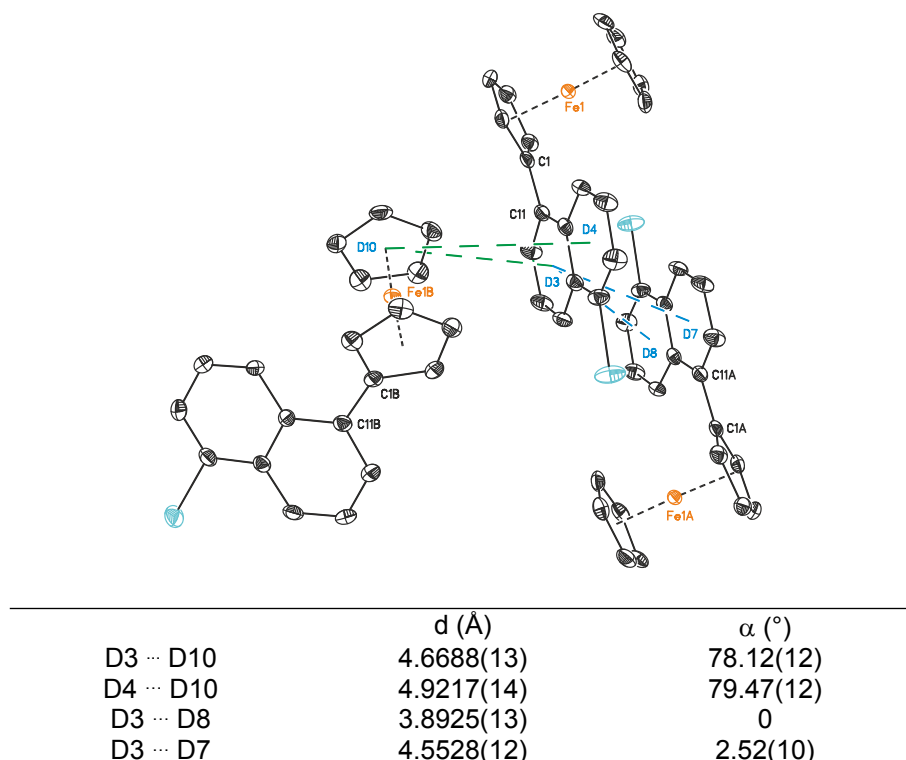
Figure SI10. ORTEP (50 % probability level) of the molecular structure of **6b** with selected atom-numbering scheme, showing the intermolecular *T*-shaped π-interaction (green dashed lines) between the C₅H₅ unit and the C₆H₄ moiety (including C11 to C20) and parallel displaced pattern (blue dashed lines) between the C₆H₄ moieties (including C11 to C20 and C15 to C20). Only a section of different π-π interaction pattern is shown and all hydrogen atoms have been omitted for clarity. (Symmetry code for generating-equivalent atoms; A: 2–x, 1–y, 2–z; B: x, 3/2–y, 1/2–z).

	d (Å)	α (°)
D2 ⋯ D6	4.975(3)	89
D1 ⋯ D9	4.648(3)	90
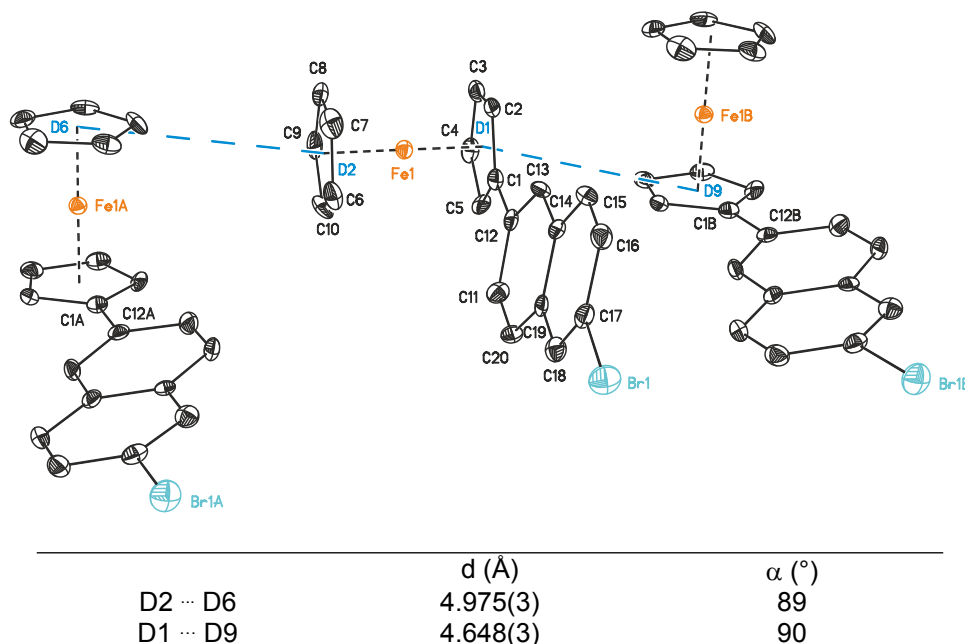
Figure SI11. ORTEP (50 % probability level) of the molecular structure of **6d** with selected atom-numbering scheme, showing the intermolecular *T*-shaped π-interaction (blue dashed lines) between the

C_5H_5 units and C_4H_5 units. All hydrogen atoms and further interactions have been omitted for clarity. (Symmetry code for generating-equivalent atoms; A: 5/2–x, –1/2+y, z; B: 5/2–x, 1/2+y, z).

	d (Å)	α (°)
D8 ⋯ D16	4.606(3)	88.7(3)
D9 ⋯ D6	4.758(7)	87.5(6)
D3 ⋯ D18	4.820(3)	83.7(2)

Figure SI12. ORTEP (50 % probability level) of the molecular structure of **7a** with selected atom-numbering scheme, showing the intermolecular *T*-shaped π-interaction (blue dashed lines) between the C_5H_5 unit and the C_6H_4 moiety (including C25 to C30). All hydrogen atoms and further interactions have been omitted for clarity. (Symmetry code for generating-equivalent atoms; A: –x, –y, z–1/2; B: 1–x, –y, z–1/2).

	d (Å)	α (°)
D ⋯ D	3.860(2)	28.62(11)

Figure SI13. ORTEP (50 % probability level) of the molecular structure of **7c** with selected atom-numbering scheme, showing the intramolecular π-π interaction between the C_5H_5 unit of the ferrocene moietys. All hydrogen atoms have been omitted for clarity.
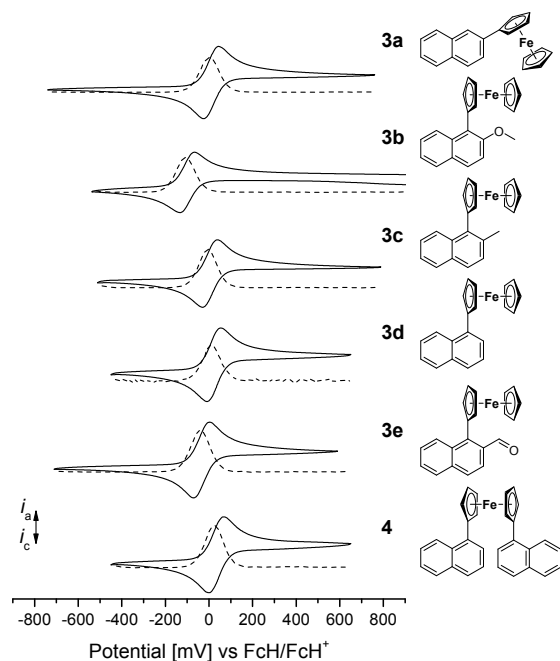
Figure SI14. Cyclic and square wave voltammograms (CV: potential area -1000 to 1000 mV; SW: potential area -1000 to 750 mV) of **3a–3e** and **4**. Conditions: scan rate 100 mV s^{-1} (CV), 2.5 mV s^{-1} (SW) in dichloromethane solutions (1.0 mmol L^{-1}), supporting electrolyte 0.1 mol L^{-1} [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$], working electrode glassy carbon.
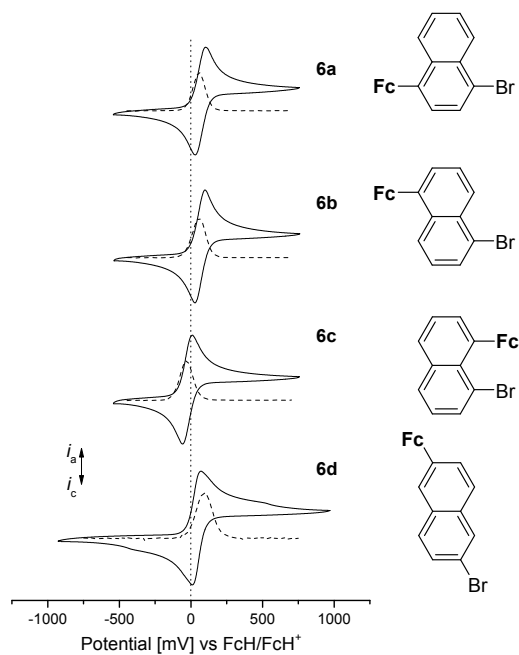
Figure SI15. Cyclic and square wave voltammograms (CV: potential area -1000 to 1000 mV; SW: potential area -1000 to 750 mV) of **6a–d**. Conditions: scan rate 100 mV s^{-1} (CV), 2.5 mV s^{-1} (SW) in dichloromethane solutions (1.0 mmol L^{-1}), supporting electrolyte 0.1 mol L^{-1} [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$], working electrode glassy carbon.
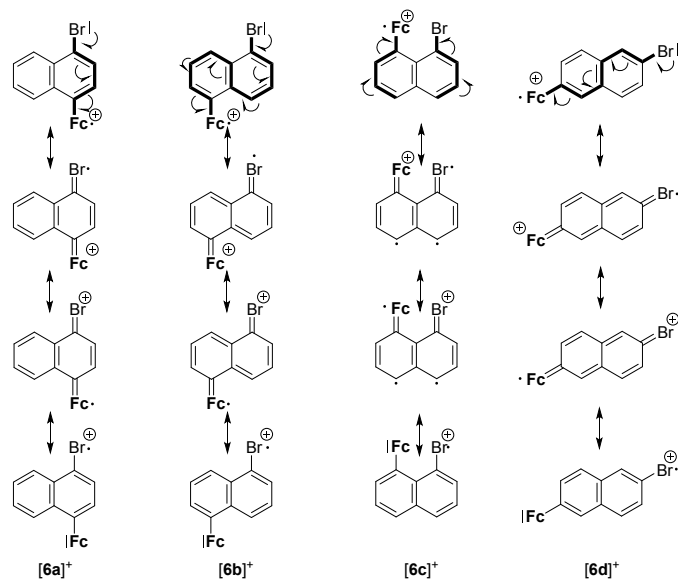
Scheme SI2. Resonance structures illustrating the through-bond charge transfer pathways in [**6a**]+, [**6b**]+, [**6c**]+ and [**6d**]+.
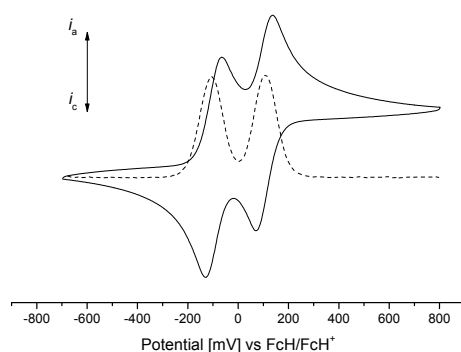
Figure SI16. Cyclic and square wave voltammograms (CV: potential area -500 to 1000 mV; SW: potential area -500 to 750 mV) of **7c**. Conditions: scan rate 100 mV s^{-1} (CV), 2.5 mV s^{-1} (SW) in dichloromethane solutions (1.0 mmol L^{-1}), supporting electrolyte 0.1 mol L^{-1} [N^{n}Bu$_4$][PF$_6$], working electrode glassy carbon.
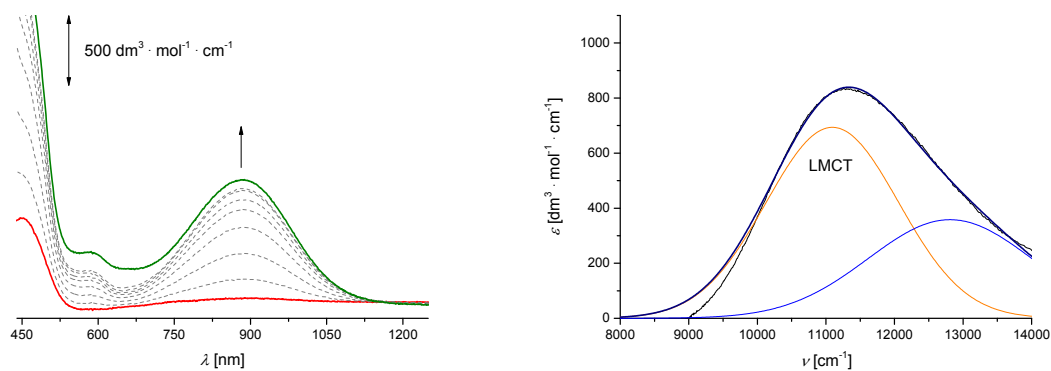
Figure SI17. Left: vis/NIR spectra of **3a** at 25 °C in dichloromethane (2.00 mmol · L^{-1}) at rising potentials (-200 to 1100 mV *vs* Ag/Ag+); supporting electrolyte [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$]; arrows indicate the increasing absorptions. Right: Deconvolution of the NIR absorption of [**3a**]+ using two Gaussian shaped bands.
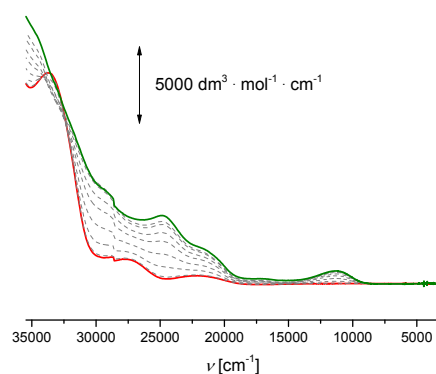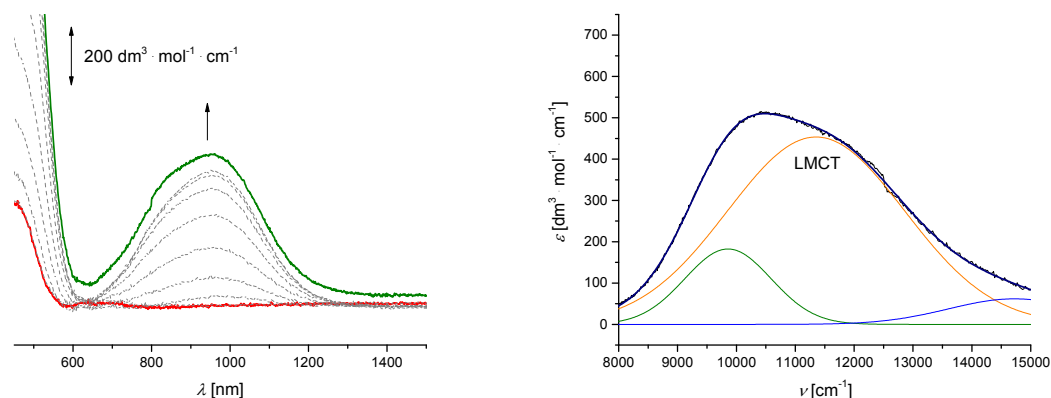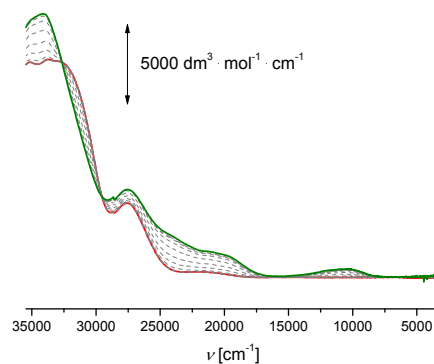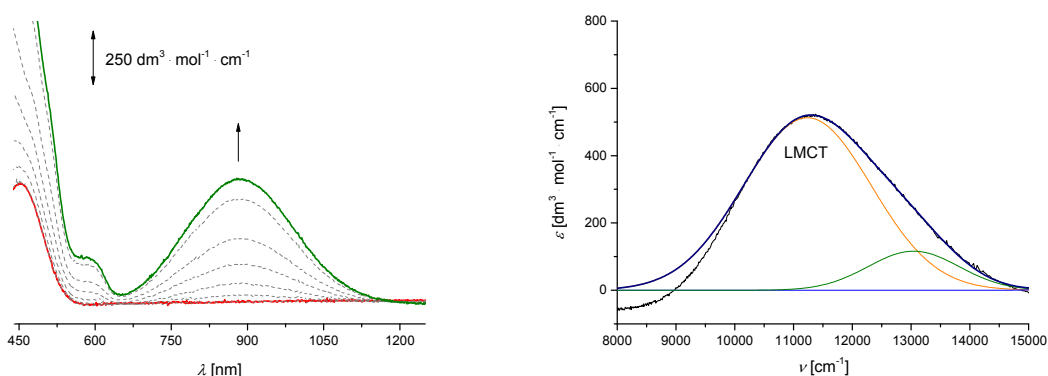
Figure SI18. UV/vis/NIR spectra of **3a** at 25 °C in dichloromethane (2.00 mmol $\cdot$ L^{-1}) at rising potentials (-200 to 1100 mV *vs* Ag/Ag$^+$); supporting electrolyte [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$].
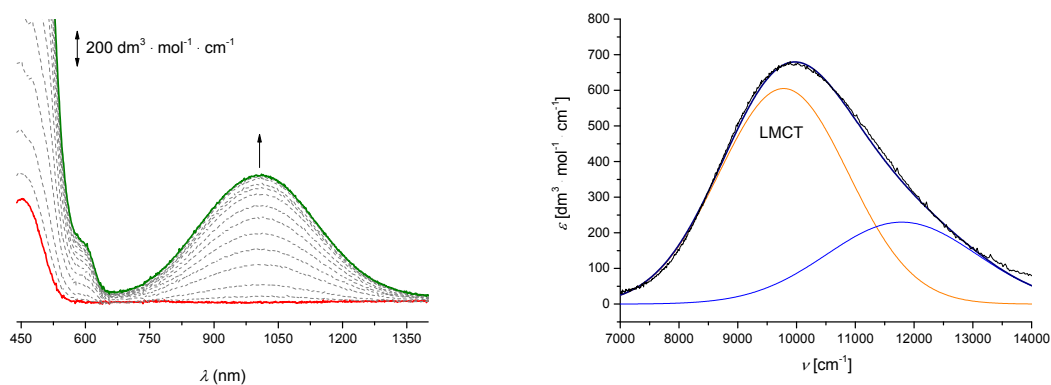
Figure SI19. Left: vis/NIR spectra of **3b** at 25 °C in dichloromethane (2.00 mmol $\cdot$ L^{-1}) at rising potentials (-200 to 1000 mV *vs* Ag/Ag$^+$); supporting electrolyte [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$]; arrows indicate the increasing absorptions. Right: Deconvolution of the NIR absorption of [**3b**]$^+$ using two Gaussian shaped bands.
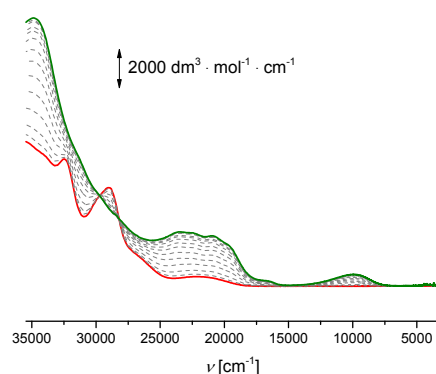
Figure SI20. UV/vis/NIR spectra of **3b** at 25 °C in dichloromethane (2.00 mmol $\cdot$ L^{-1}) at rising potentials (-200 to 1000 mV *vs* Ag/Ag$^+$); supporting electrolyte [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$].
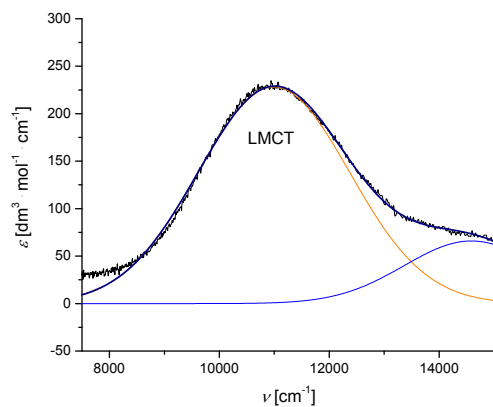
Figure SI21. Deconvolution of the NIR absorption of [**3c**]+ using two Gaussian shaped bands.
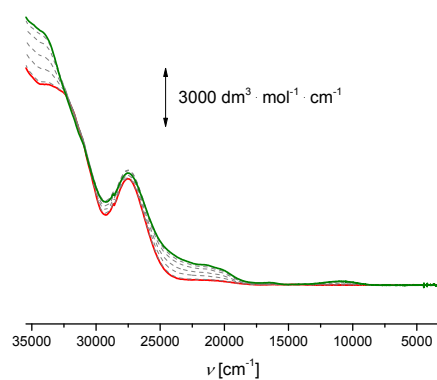
Figure SI22. UV/vis/NIR spectra of **3c** at 25 °C in dichloromethane (2.00 mmol · L⁻¹) at rising potentials (-200 to 250 mV *vs* Ag/Ag+); supporting electrolyte [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$].
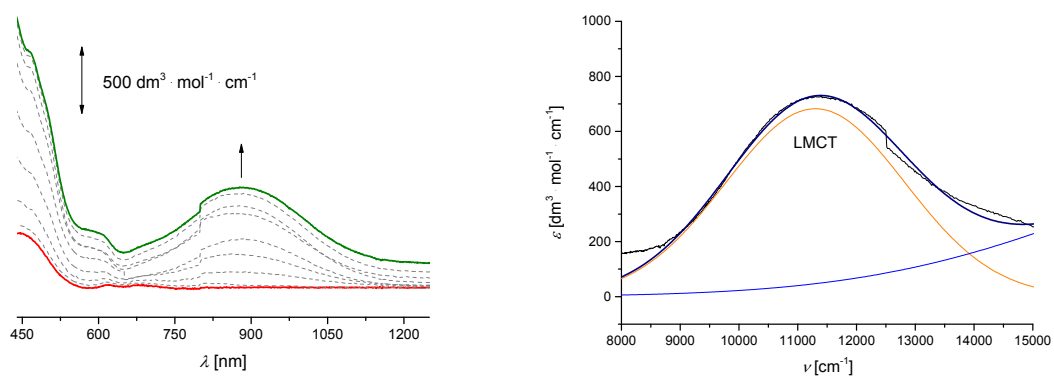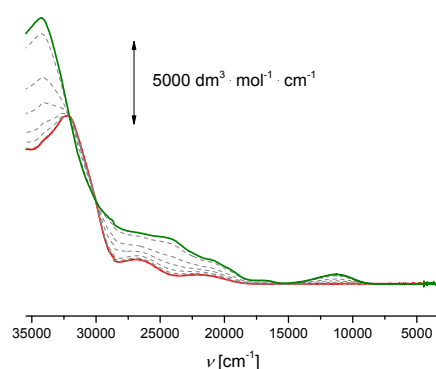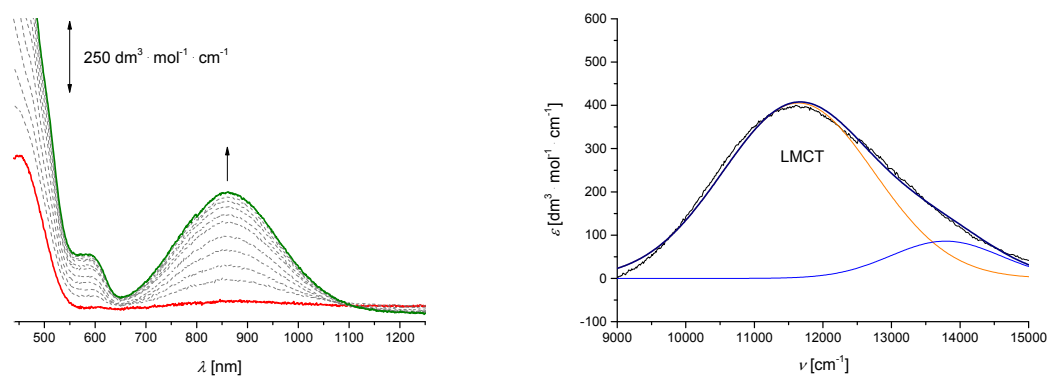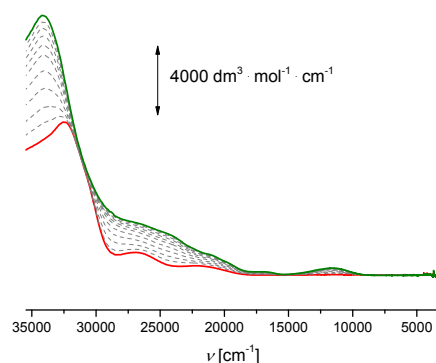

Figure SI23. Left: vis/NIR spectra of **3d** at 25 °C in dichloromethane (2.00 mmol · L⁻¹) at rising potentials (-200 to 400 mV *vs* Ag/Ag+); supporting electrolyte [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$]; arrows indicate the increasing absorptions. Right: Deconvolution of the NIR absorption of [**3d**]+ using two Gaussian shaped bands.
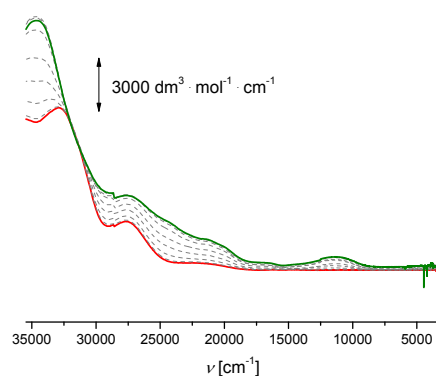
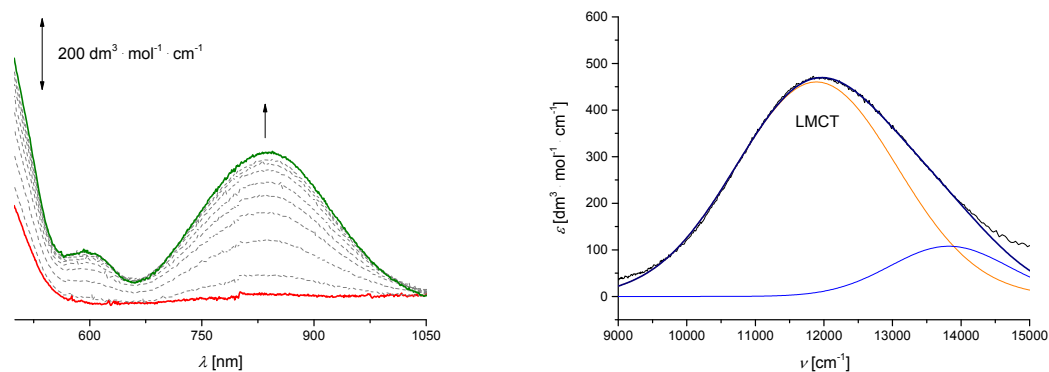**Figure SI24**. UV/vis/NIR spectra of **3d** at 25 °C in dichloromethane (2.00 mmol · L^{-1}) at rising potentials (-200 to 400 mV *vs* Ag/Ag$^+$); supporting electrolyte [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$].
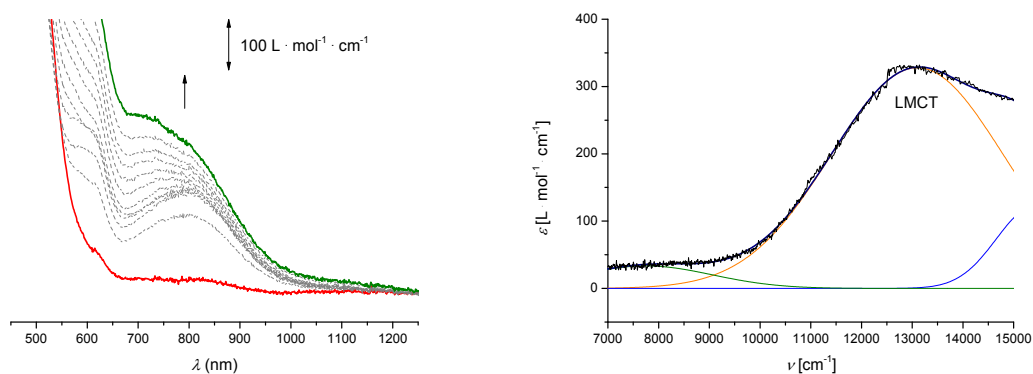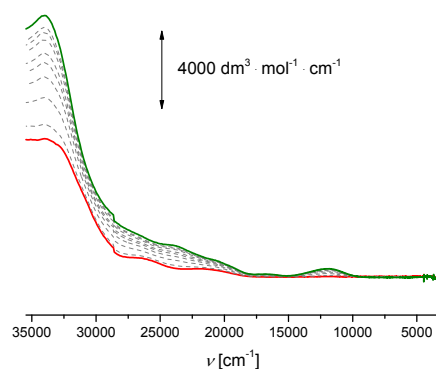

Figure SI25. Left: vis/NIR spectra of **3e** at 25 °C in dichloromethane (2.00 mmol · L^{-1}) at rising potentials (-200 to 950 mV *vs* Ag/Ag$^+$); supporting electrolyte [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$]; arrows indicate the increasing absorptions. Right: Deconvolution of the NIR absorption of [**3e**]$^+$ using three Gaussian shaped bands.
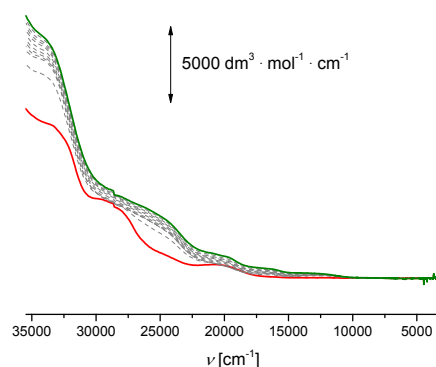
Figure SI26. UV/vis/NIR spectra of **3e** at 25 °C in dichloromethane (2.00 mmol · L^{-1}) at rising potentials (-200 to 950 mV *vs* Ag/Ag$^+$); supporting electrolyte [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$].
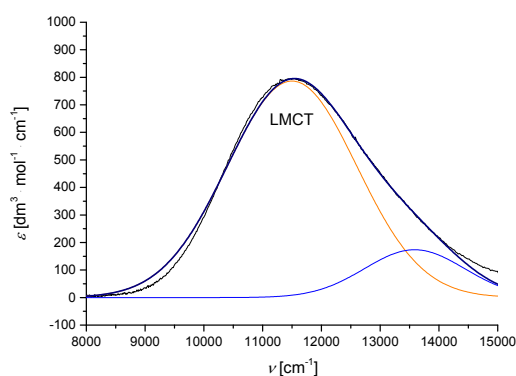
Figure SI27. Left: vis/NIR spectra of **4** at 25 °C in dichloromethane (2.00 mmol · L⁻¹) at rising potentials (-200 to 400 mV *vs* Ag/Ag⁺); supporting electrolyte [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$]; arrows indicate the increasing absorptions. Right: Deconvolution of the NIR absorption of [**4**]⁺ using three Gaussian shaped bands.

Figure SI28. UV/vis/NIR spectra of **4** at 25 °C in dichloromethane (2.00 mmol · L⁻¹) at rising potentials (-200 to 400 mV *vs* Ag/Ag⁺); supporting electrolyte [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$].

Figure S29. Left: vis/NIR spectra of **6a** at 25 °C in dichloromethane (2.00 mmol · L⁻¹) at rising potentials (-200 to 950 mV *vs* Ag/Ag⁺); supporting electrolyte [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$]; arrows indicate the increasing absorptions. Right: Deconvolution of the NIR absorption of [**6a**]⁺ using three Gaussian shaped bands.

Figure S30. UV/vis/NIR spectra of **6a** at 25 °C in dichloromethane (2.00 mmol · L^{-1}) at rising potentials (-200 to 950 mV *vs* Ag/Ag$^+$); supporting electrolyte [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$].
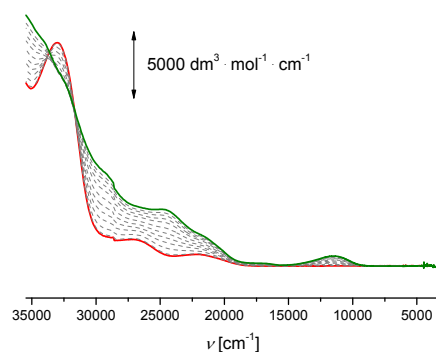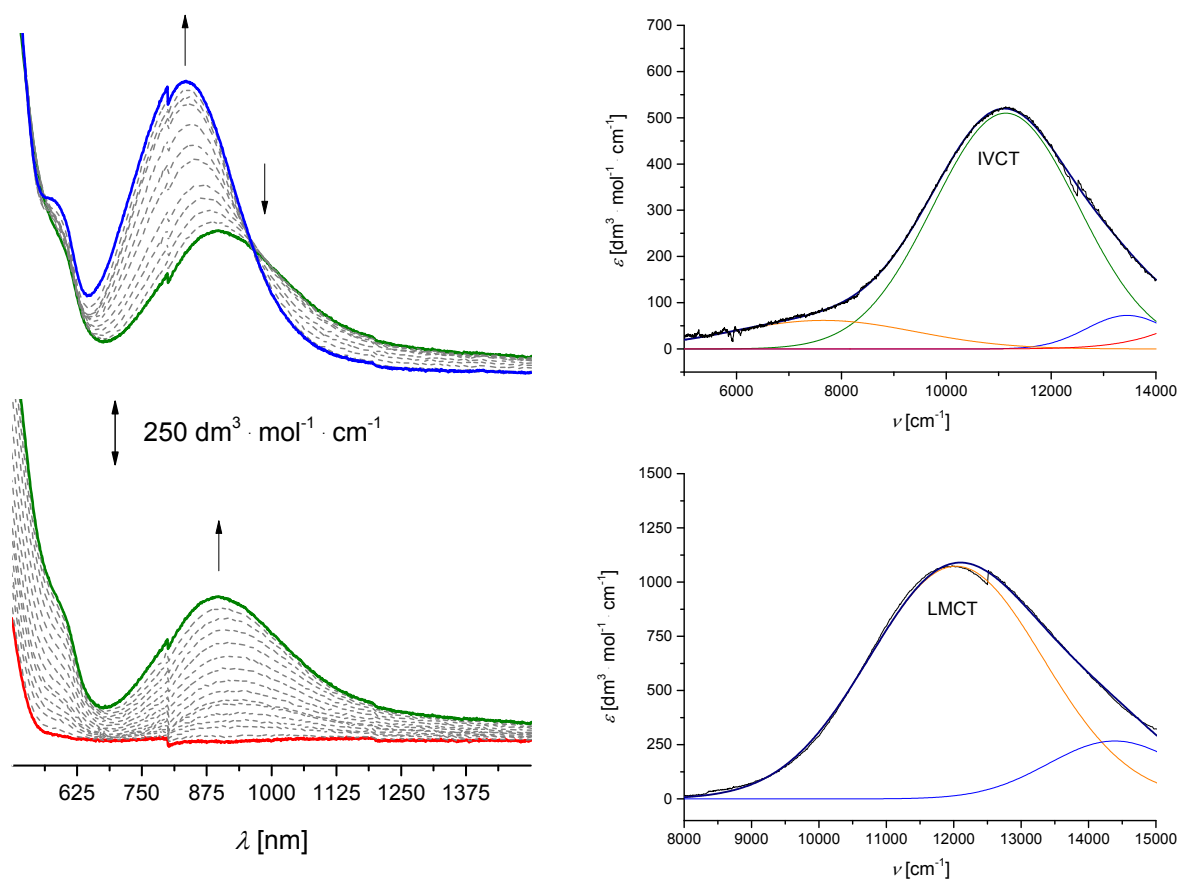

Figure SI31. Left: vis/NIR spectra of **6b** at 25 °C in dichloromethane (2.00 mmol · L^{-1}) at rising potentials (-200 to 1100 mV *vs* Ag/Ag$^+$); supporting electrolyte [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$]; arrows indicate the increasing absorptions. Right: Deconvolution of the NIR absorption of [**6b**]$^+$ using two Gaussian shaped bands.

Figure SI32. Left: UV/vis/NIR spectra of **6b** at 25 °C in dichloromethane (2.00 mmol · L^{-1}) at rising potentials (-200 to 1100 mV *vs* Ag/Ag$^+$); supporting electrolyte [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$].

Figure SI33. Left: vis/NIR spectra of **6c** at 25 °C in dichloromethane (2.00 mmol · L^{-1}) at rising potentials (-200 to 800 mV *vs* Ag/Ag$^+$); supporting electrolyte [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$]; arrows indicate the increasing absorptions. Right: Deconvolution of the NIR absorption of [**6c**]$^+$ using two Gaussian shaped bands.

Figure SI34. UV/vis/NIR spectra of **6c** at 25 °C in dichloromethane (2.00 mmol · L^{-1}) at rising potentials (-200 to 800 mV *vs* Ag/Ag$^+$); supporting electrolyte [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$].

Figure SI35. Deconvolution of the NIR absorption of [**6d**]$^+$ using two Gaussian shaped bands.

Figure SI36. UV/vis/NIR spectra of **6d** at 25 °C in dichloromethane (2.00 mmol · L^{-1}) at rising potentials (-200 to 900 mV *vs* Ag/Ag$^+$); supporting electrolyte [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$].
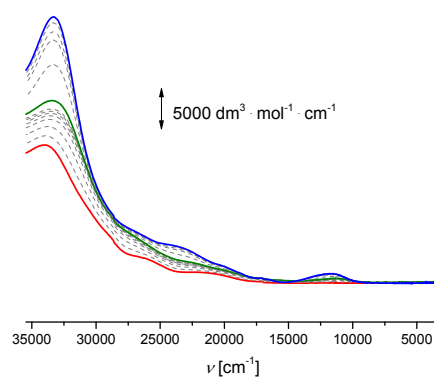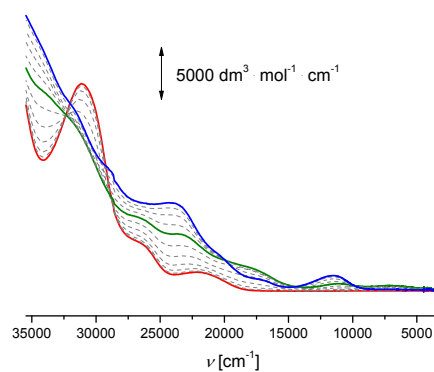

Figure SI37. Left: vis/NIR spectra of 1,5-diferrocenylnaphthalene (**7b**) at 25 °C in dichloromethane (2.00 mmol · L^{-1}) at rising potentials (-200 to 555 mV; top: 555 to 1100 mV *vs* Ag/Ag$^+$); supporting electrolyte [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$]; arrows indicate the increasing and decreasing absorptions. Right, top: Deconvolution of the NIR absorption of [**7b**]$^+$ using three Gaussian shaped bands. Right, bottom: Deconvolution of NIR absorption of [**7b**]$^{2+}$ using two Gaussian shaped bands.
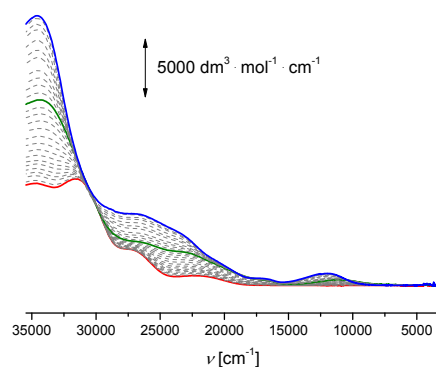
Figure SI38. UV/vis/NIR spectra of 1,5-diferrocenylnaphthalene (**7b**) at 25 °C in dichloromethane (2.00 mmol · L⁻¹) at rising potentials (-200 to 1100 mV *vs* Ag/Ag⁺); supporting electrolyte [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$].
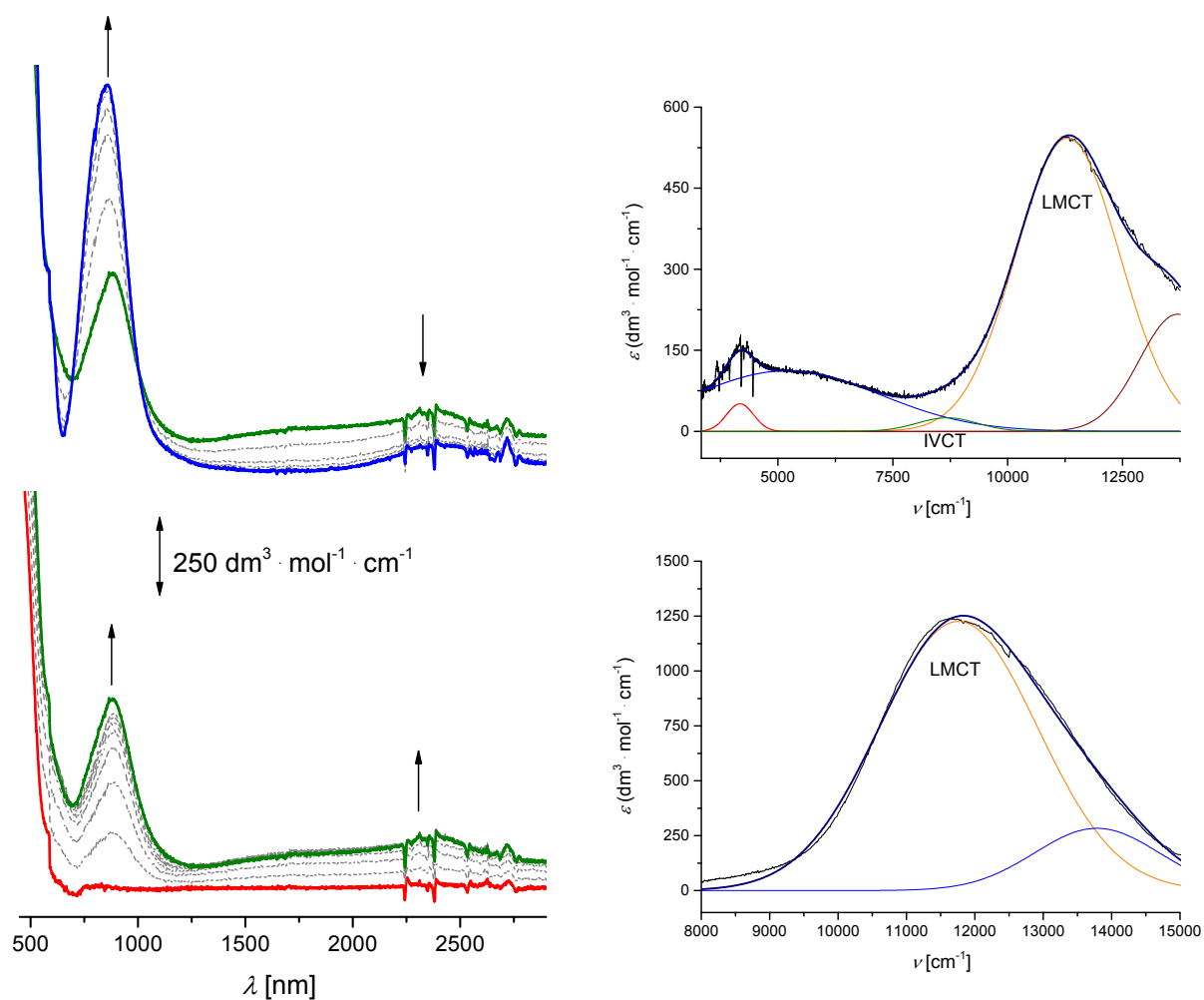
Figure SI39. Left: vis/NIR spectra of 1,8-diferrocenylnaphthalene (**7c**) at 25 °C in dichloromethane (2.00 mmol · L⁻¹) at rising potentials (bottom: -200 to 525 mV; top: 525 to 700 mV *vs* Ag/Ag⁺); supporting electrolyte [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$]; arrows indicate the increasing and decreasing absorptions. Right, top: Deconvolution of the NIR absorption of [**7c**]⁺ using three Gaussian shaped bands. Right, bottom: Deconvolution of NIR absorption of [**7c**]²⁺ using two Gaussian shaped bands.

5000 dm³ · mol⁻¹ · cm⁻¹

Figure SI40. UV/vis/NIR spectra of 1,8-diferrocenylnaphthalene (**7c**) at 25 °C in dichloromethane (2.00 mmol · L⁻¹) at rising potentials (bottom: -200 to 700 mV *vs* Ag/Ag⁺); supporting electrolyte [N*n*Bu₄][B(C₆F₅)₄].

5000 dm³ · mol⁻¹ · cm⁻¹

Figure SI41. UV/vis/NIR spectra of 2,6-diferrocenylnaphthalene (**7d**) at 25 °C in dichloromethane (2.00 mmol · L⁻¹) at rising potentials (bottom: -200 to 700 mV *vs* Ag/Ag⁺); supporting electrolyte [N*n*Bu₄][B(C₆F₅)₄].
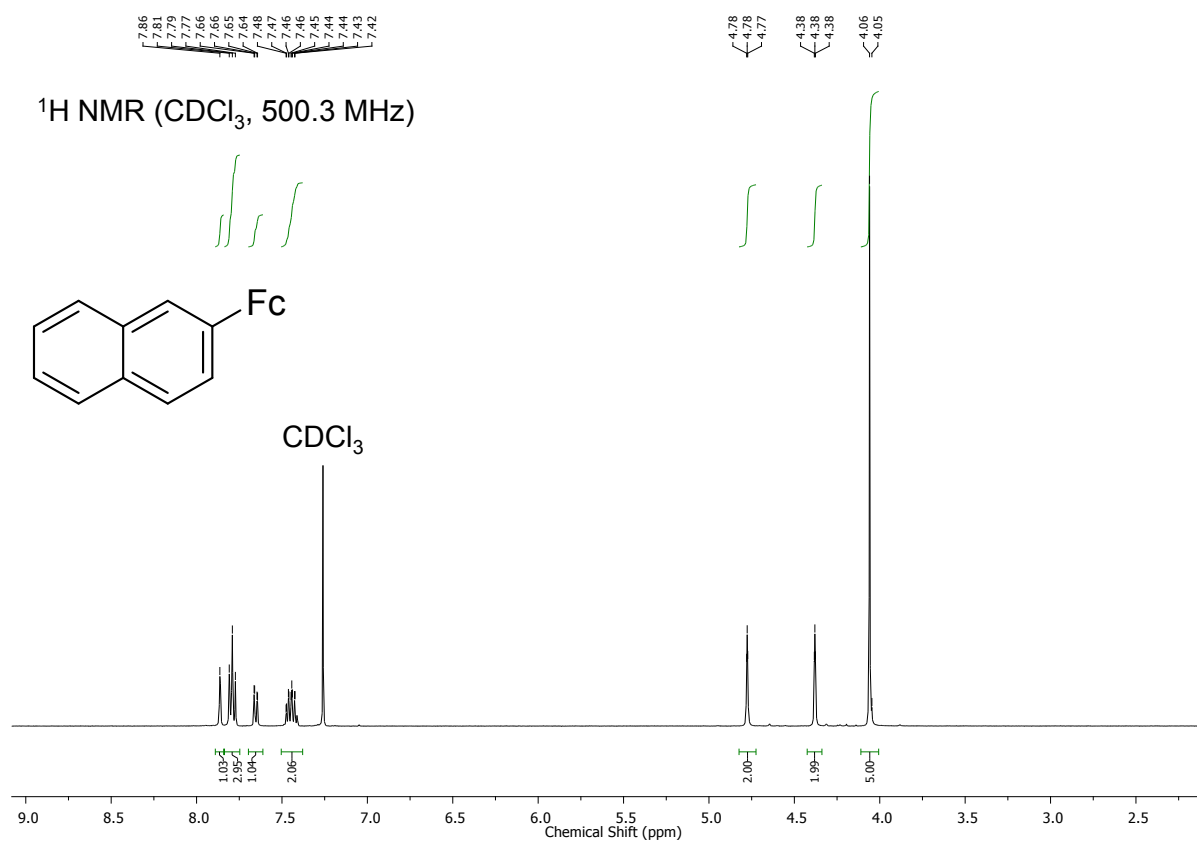
Figure SI42. ^1H NMR spectrum of **3a** in CDCl$_3$.
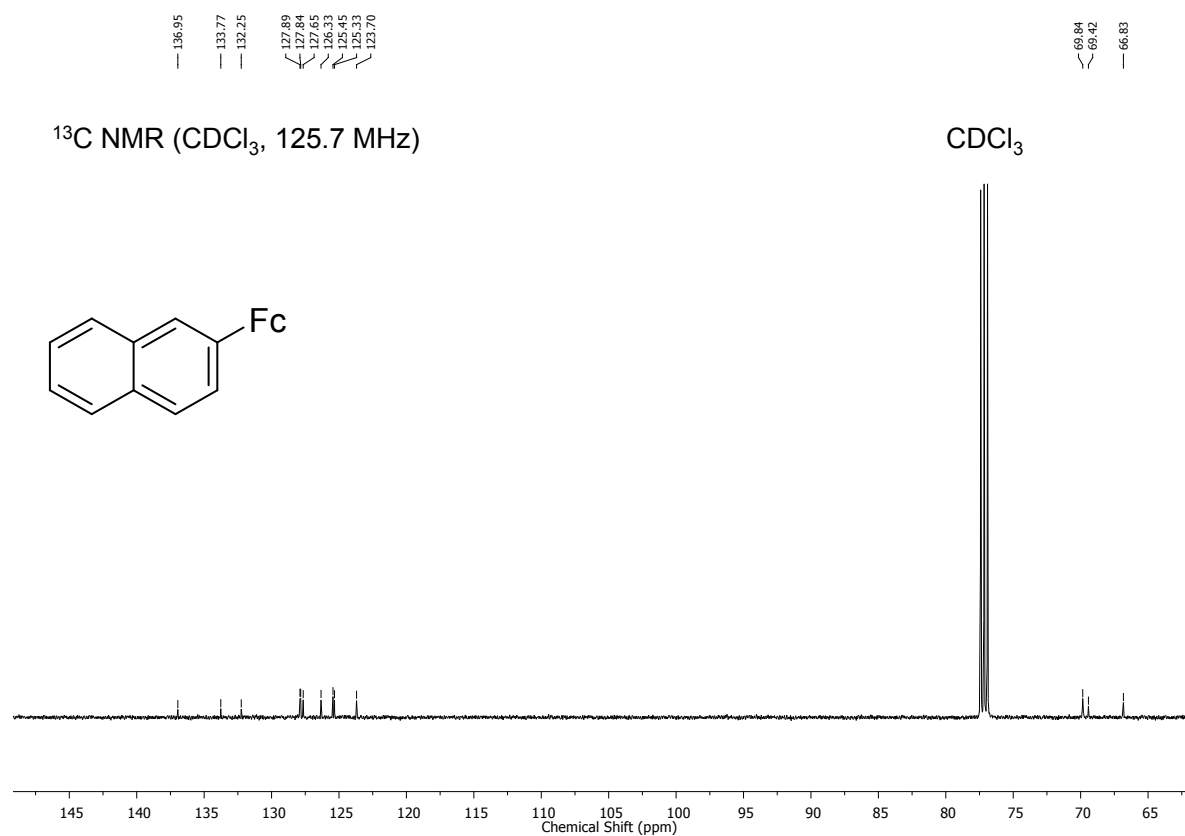
Figure SI43. ^{13}C NMR spectrum of **3a** in CDCl$_3$.
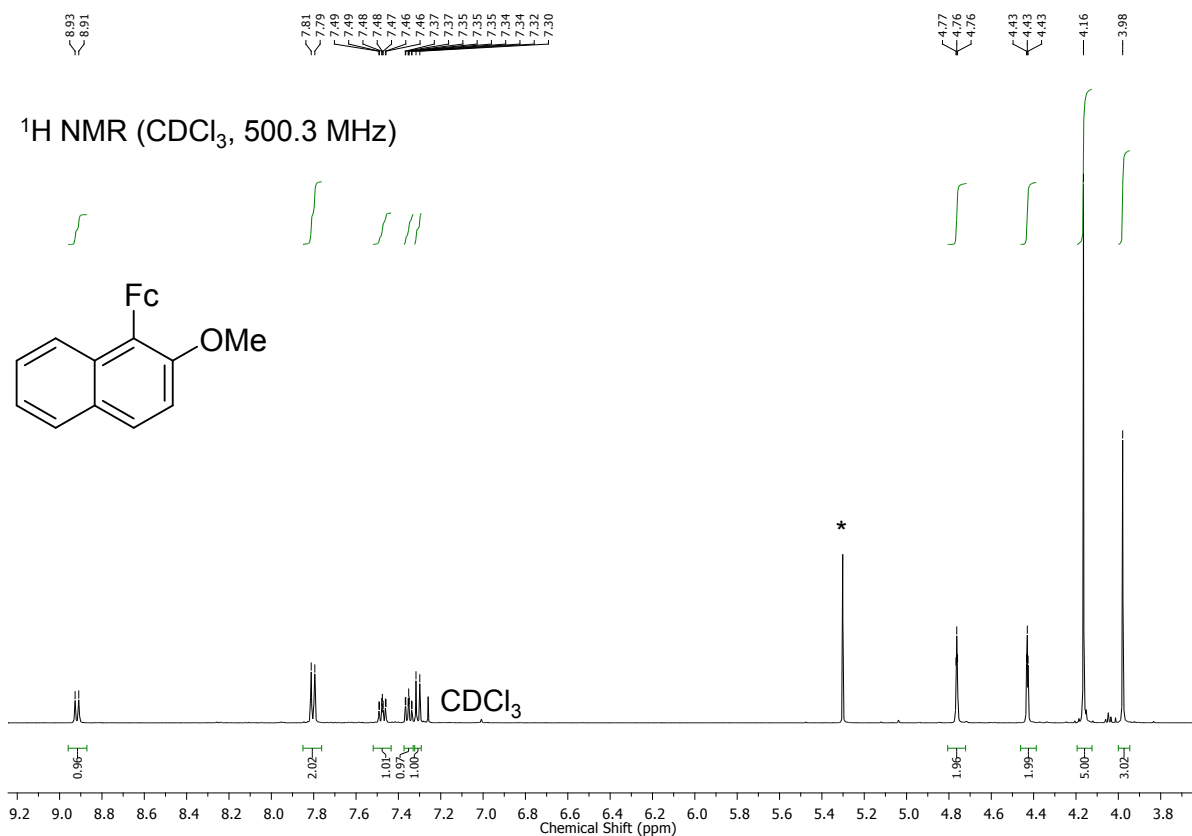
Figure SI44. ^{1}H NMR spectrum of **3b** in CDCl$_3$, *CH$_2$Cl$_2$.

Figure SI45. ^{13}C NMR spectrum of **3b** in CDCl$_3$.

¹H NMR (CDCl₃, 500.3 MHz)
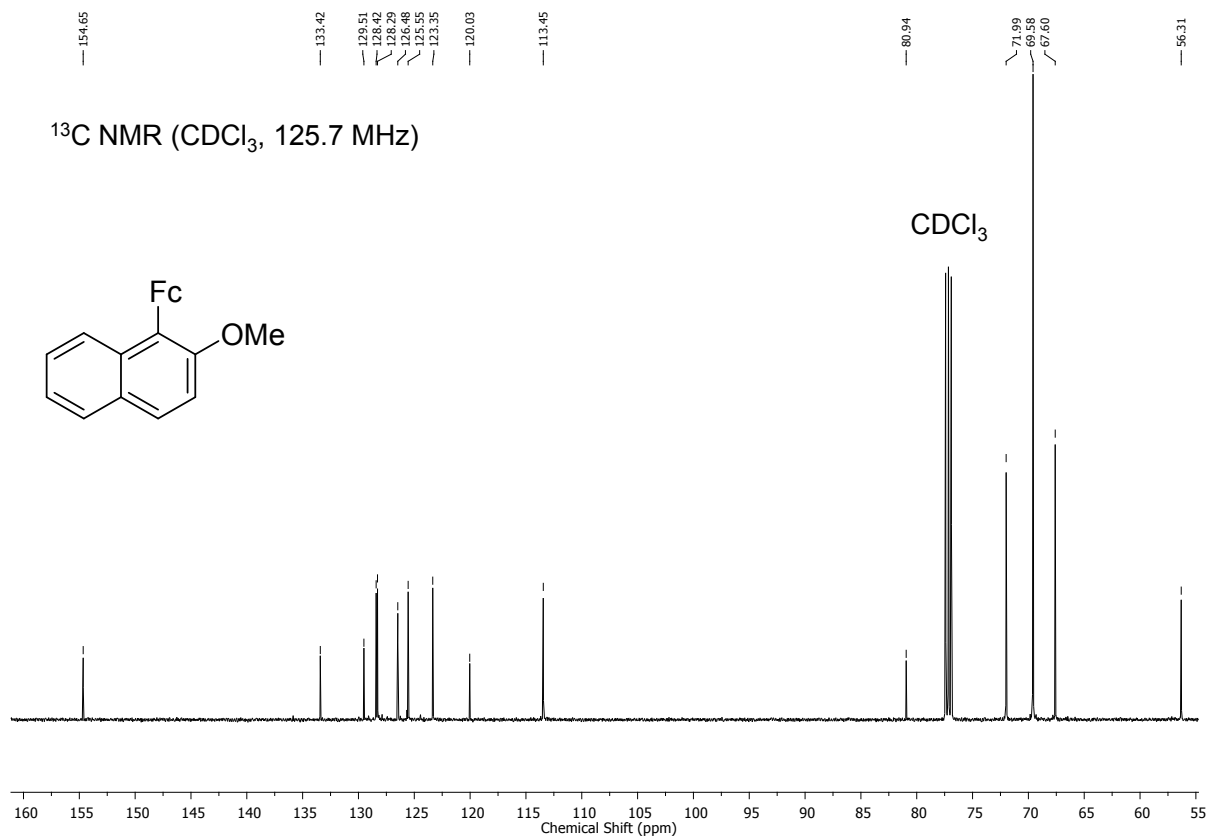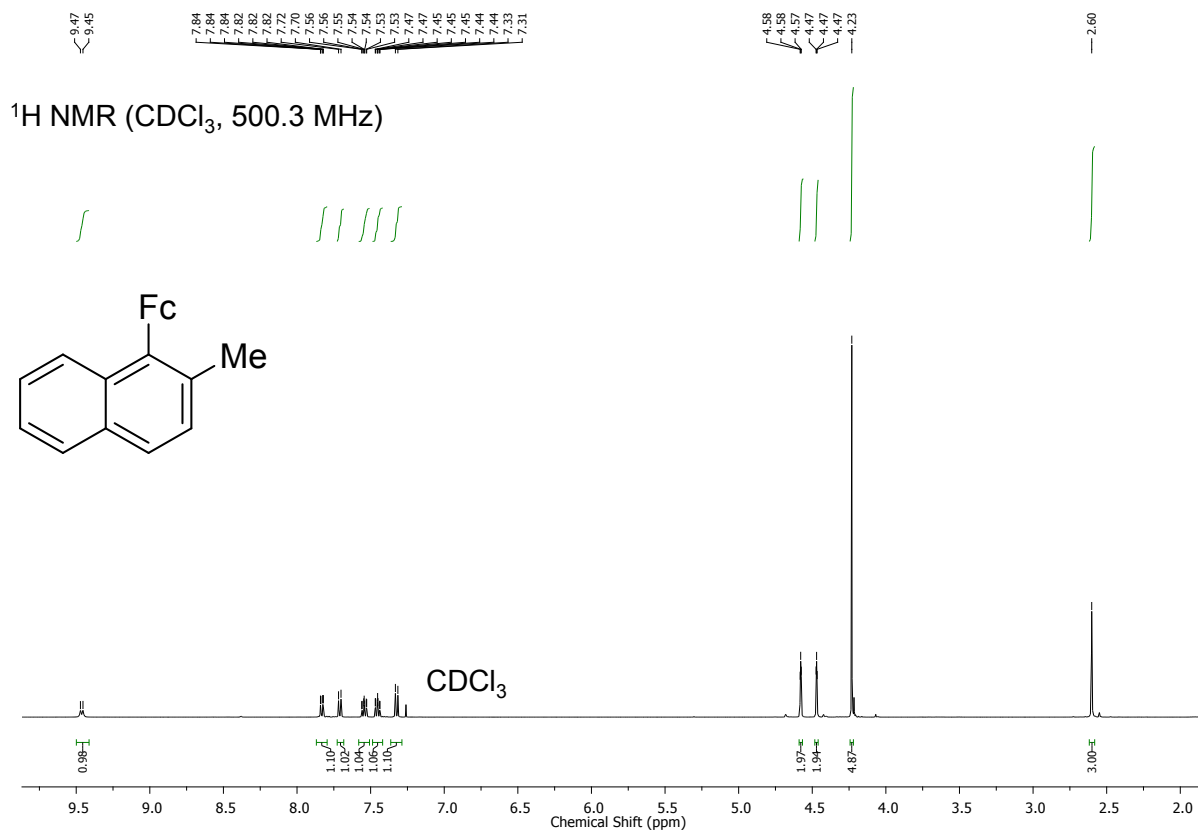
Figure SI46. ¹H NMR spectrum of **3c** in CDCl₃.

¹³C NMR (CDCl₃, 125.7 MHz)
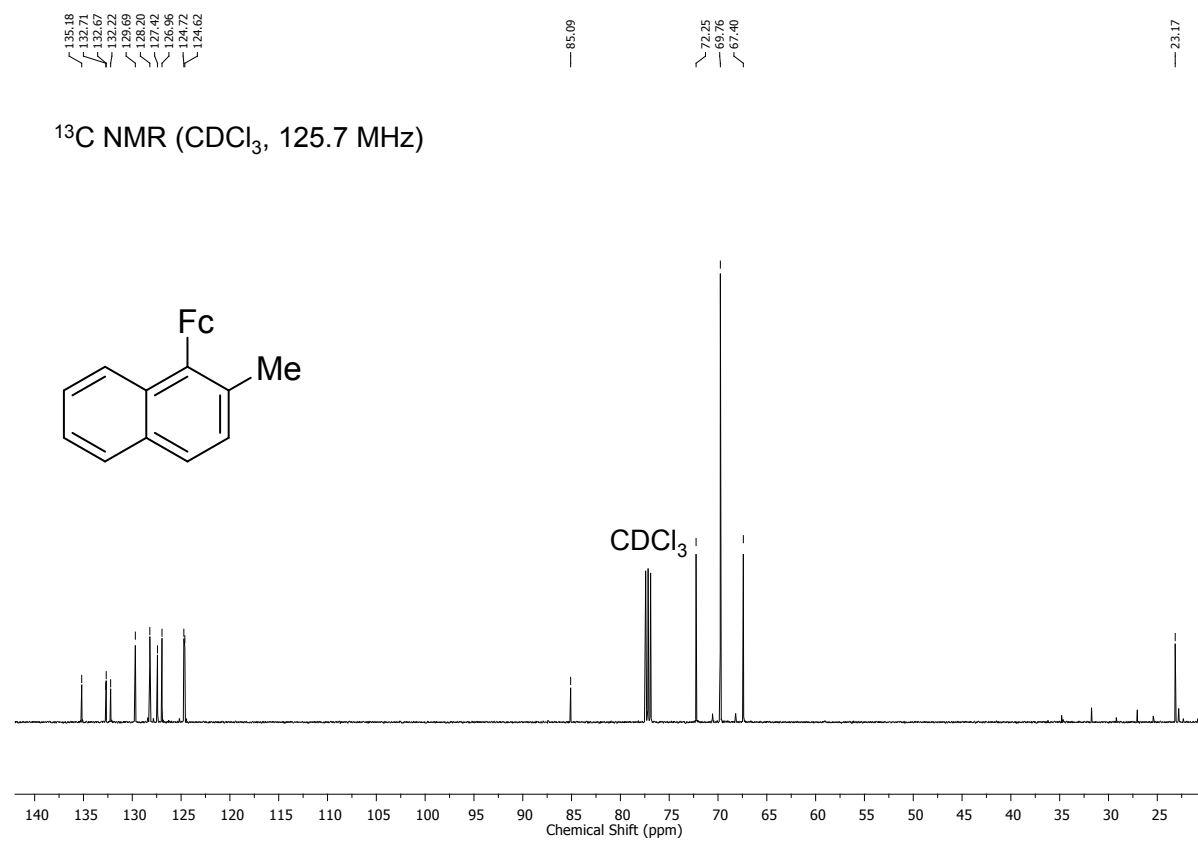
Figure SI47. ¹³C NMR spectrum of **3c** in CDCl₃.
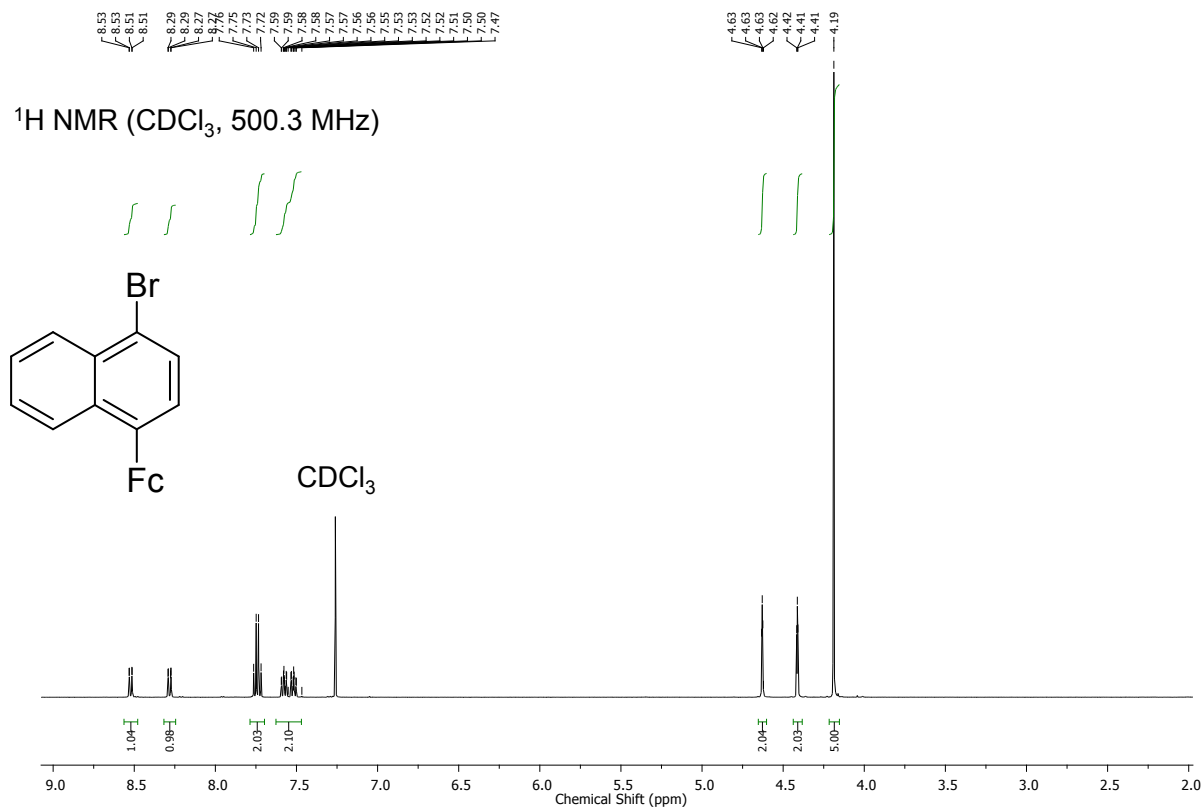
Figure SI48. ^{1}H NMR spectrum of **6a** in CDCl$_3$.
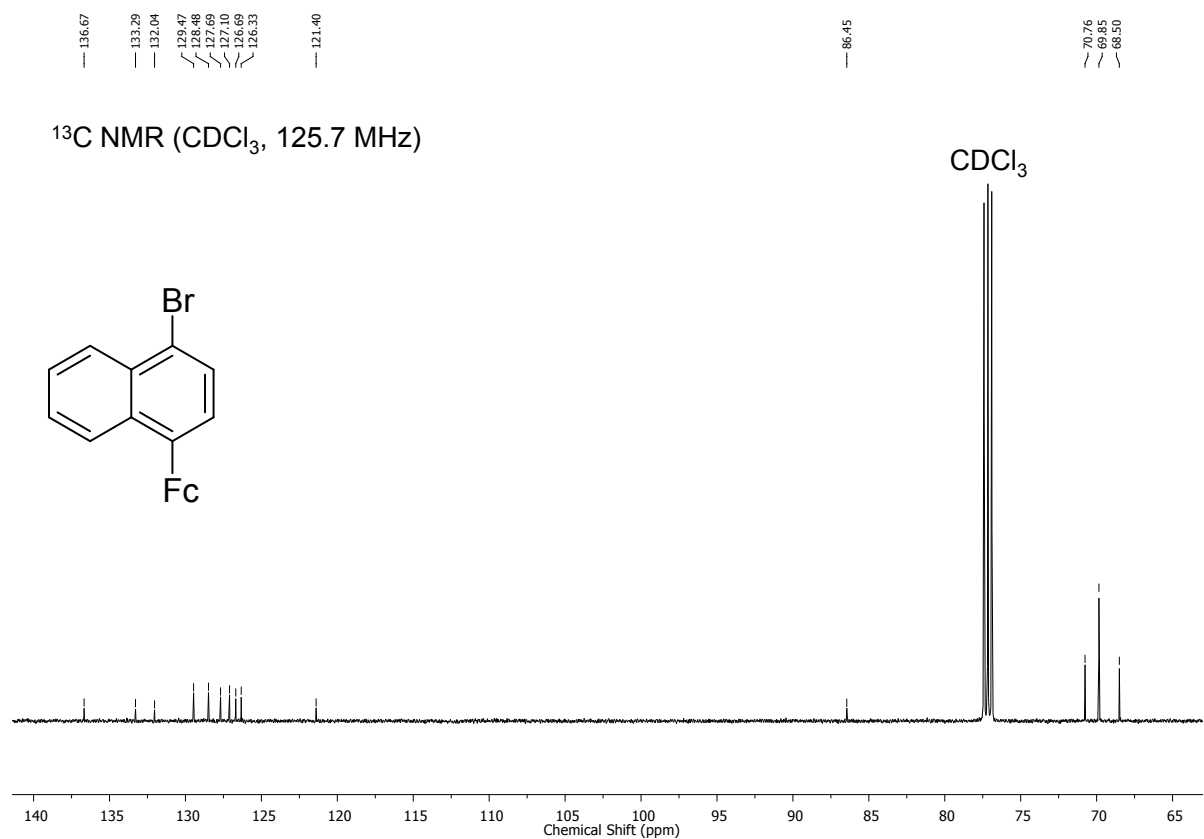
Figure SI49. ^{13}C NMR spectrum of **6a** in CDCl$_3$.
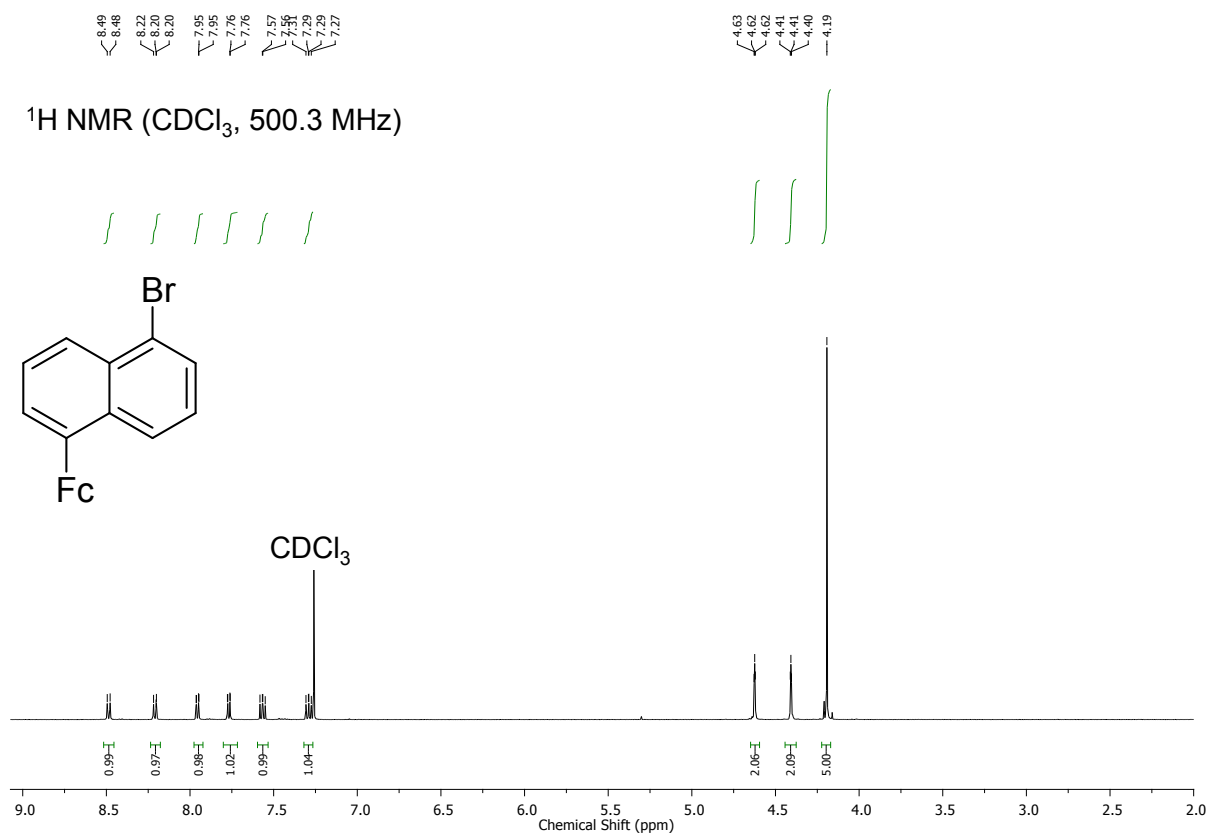
Figure SI50. ^{1}H NMR spectrum of **6b** in CDCl$_3$.
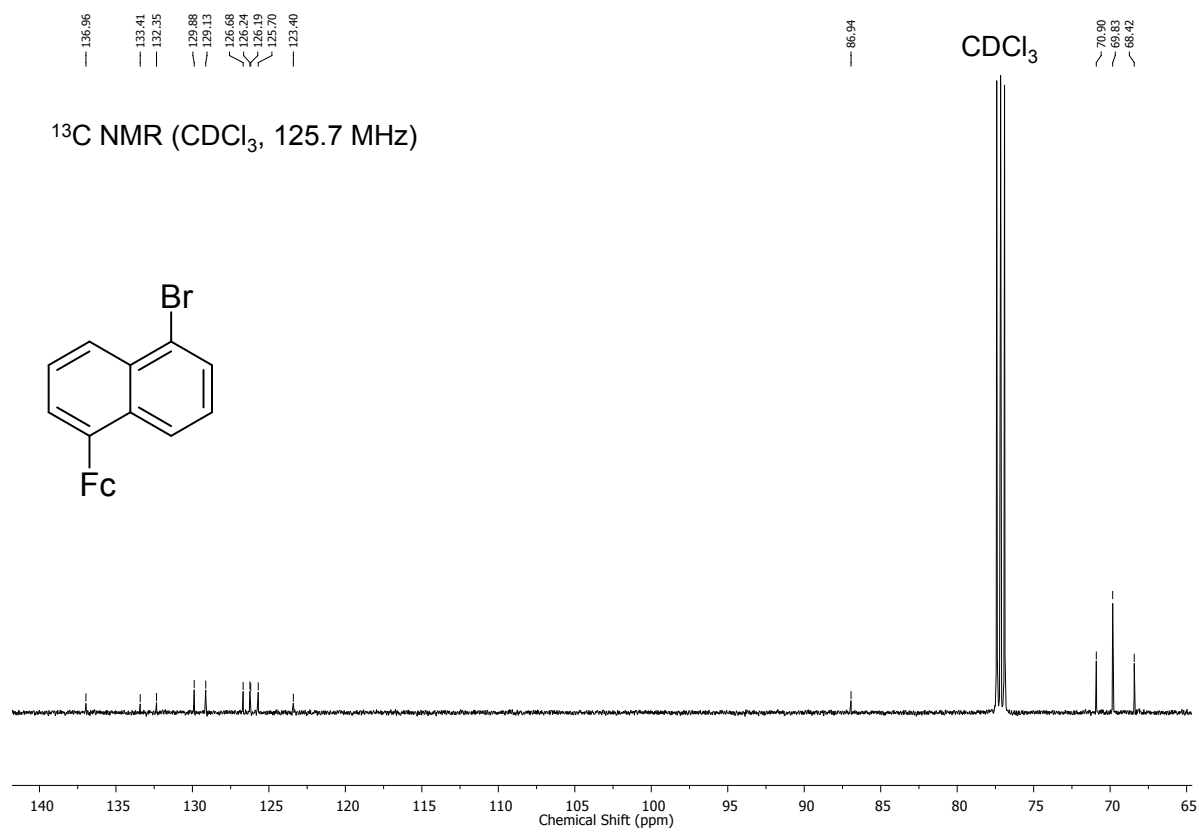
Figure SI51. ^{13}C NMR spectrum of **6b** in CDCl$_3$.
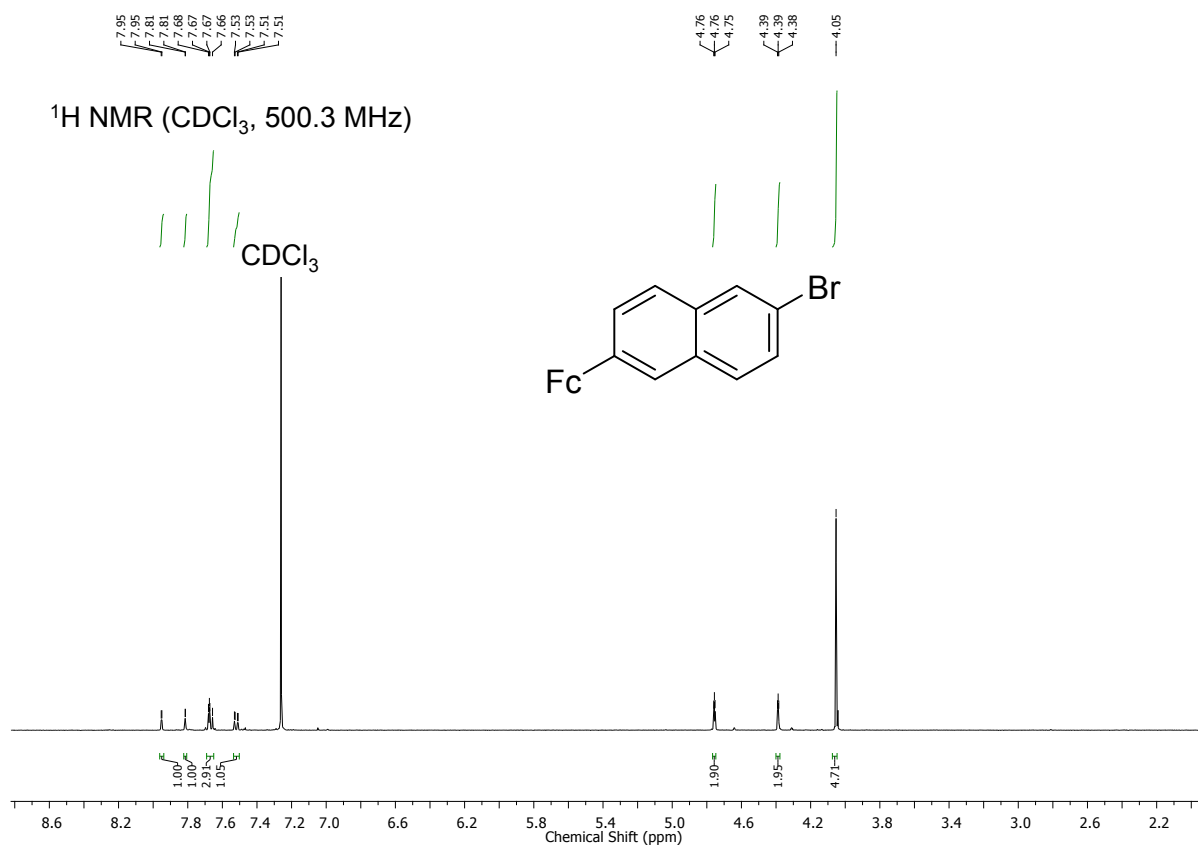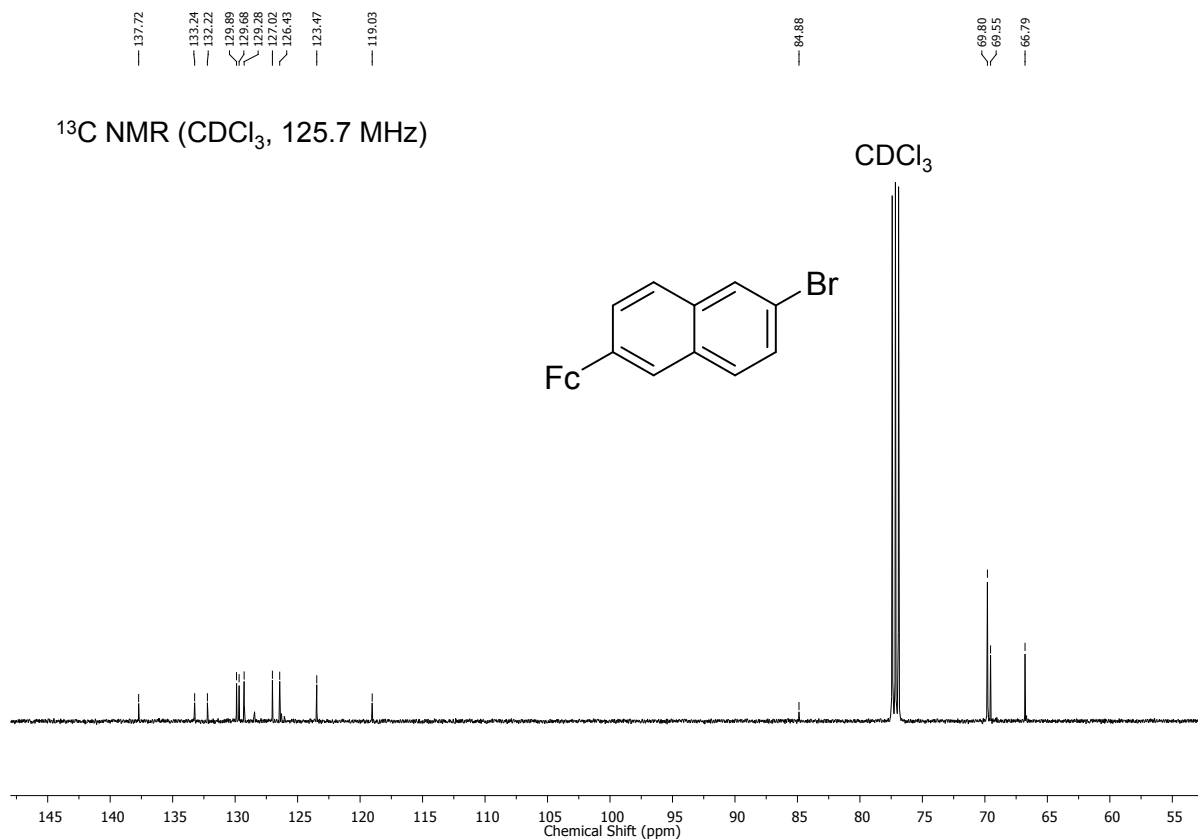
Figure SI52. ¹H NMR spectrum of **6d** in CDCl₃.
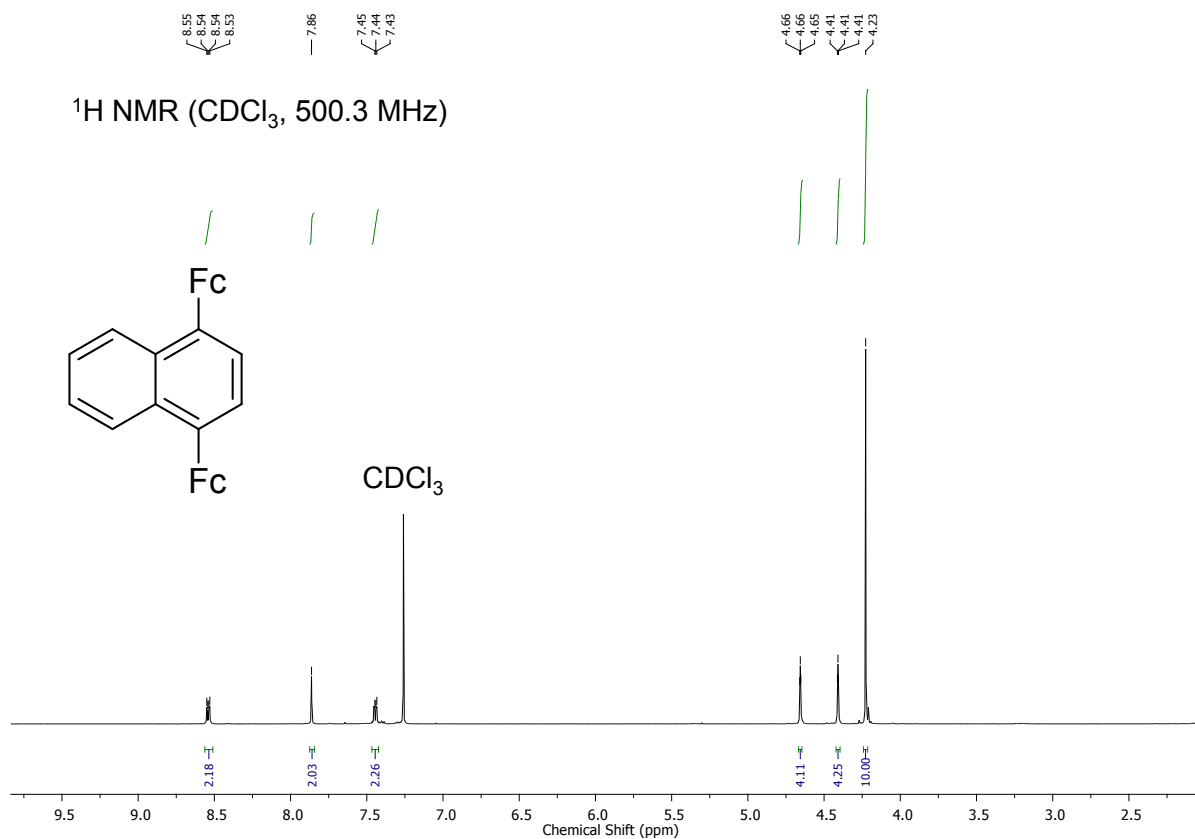

Figure SI53. ¹³C NMR spectrum of **6d** in CDCl₃.

Figure SI54. ^{1}H NMR spectrum of **7a** in CDCl$_3$.
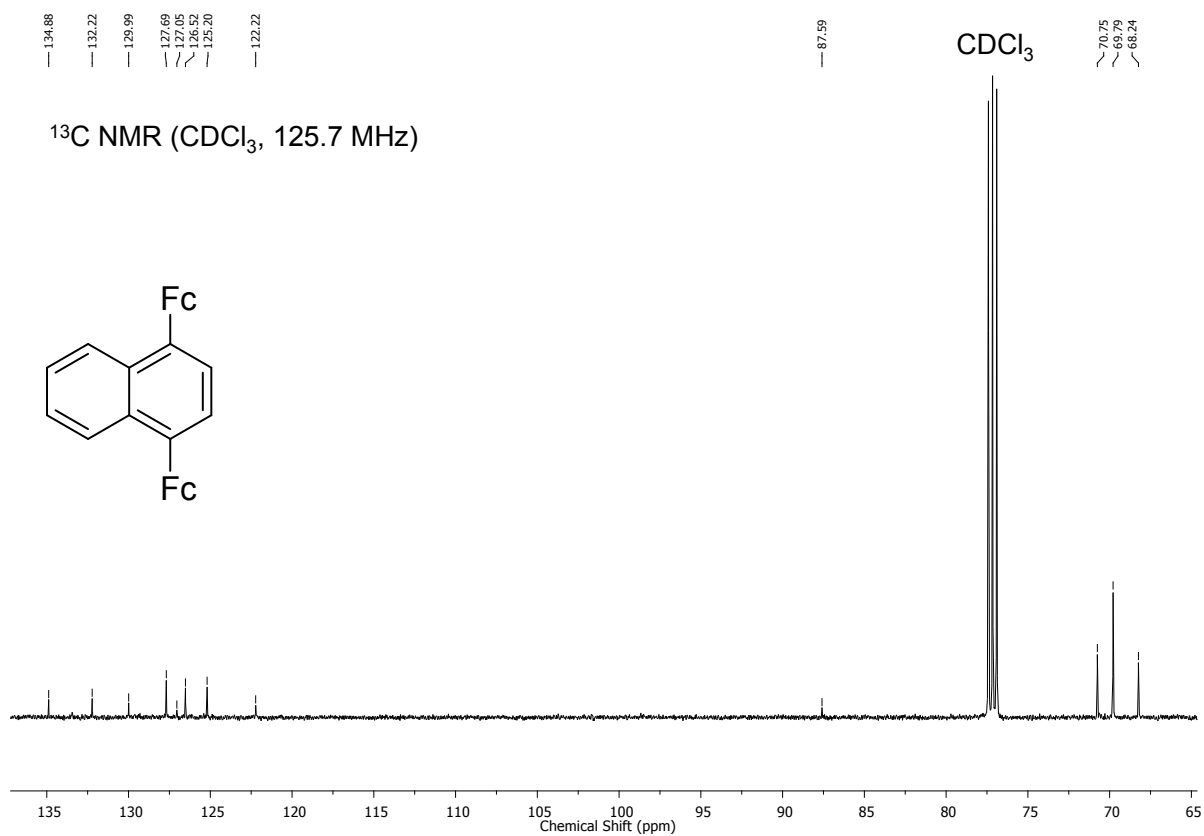
Figure SI55. ^{13}C NMR spectrum of **7a** in CDCl$_3$.
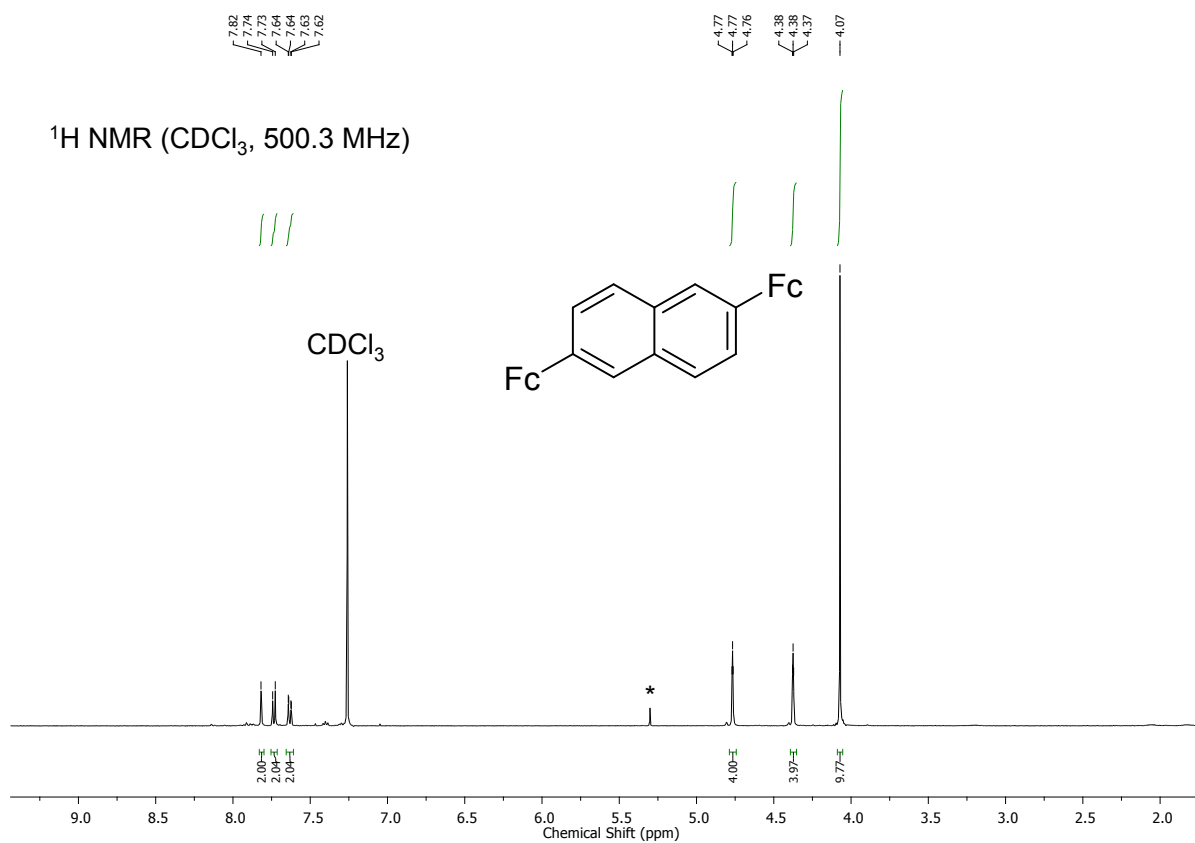
Figure SI56. ^{1}H NMR spectrum of **7d** in CDCl$_3$, *CH$_2$Cl$_2$.
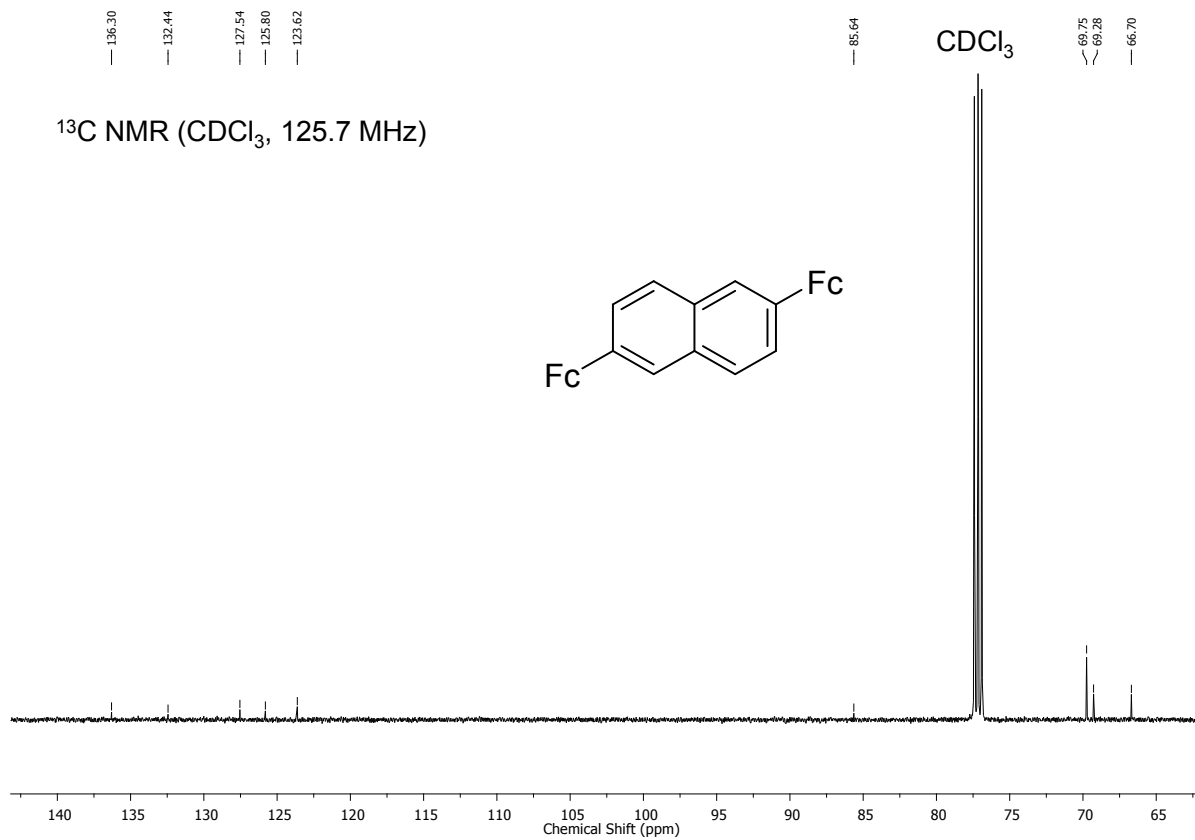
Figure SI57. ^{13}C NMR spectrum of **7d** in CDCl$_3$.

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