Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

for

Ferrocenylmethylation reactions with a phosphinoferrocene betaine

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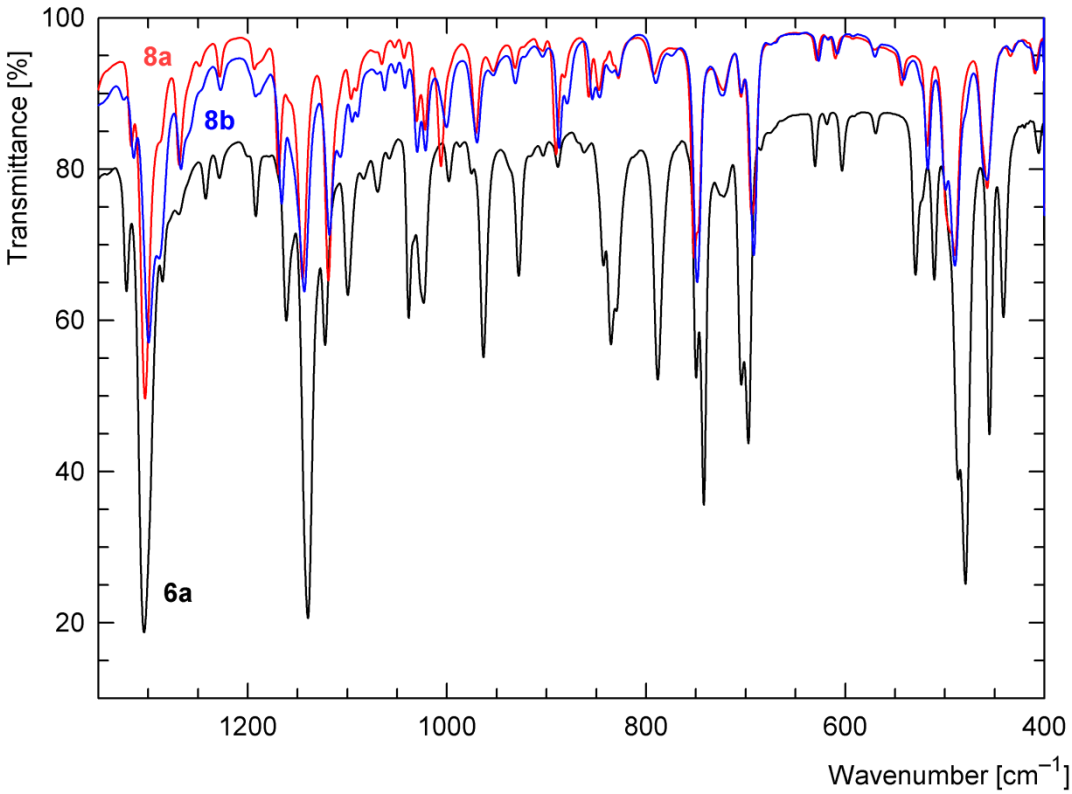

Figure S1. IR spectra of sulfone **6a** (black) and its Zn-Na complexes **8a** (red) and **8b** (blue).

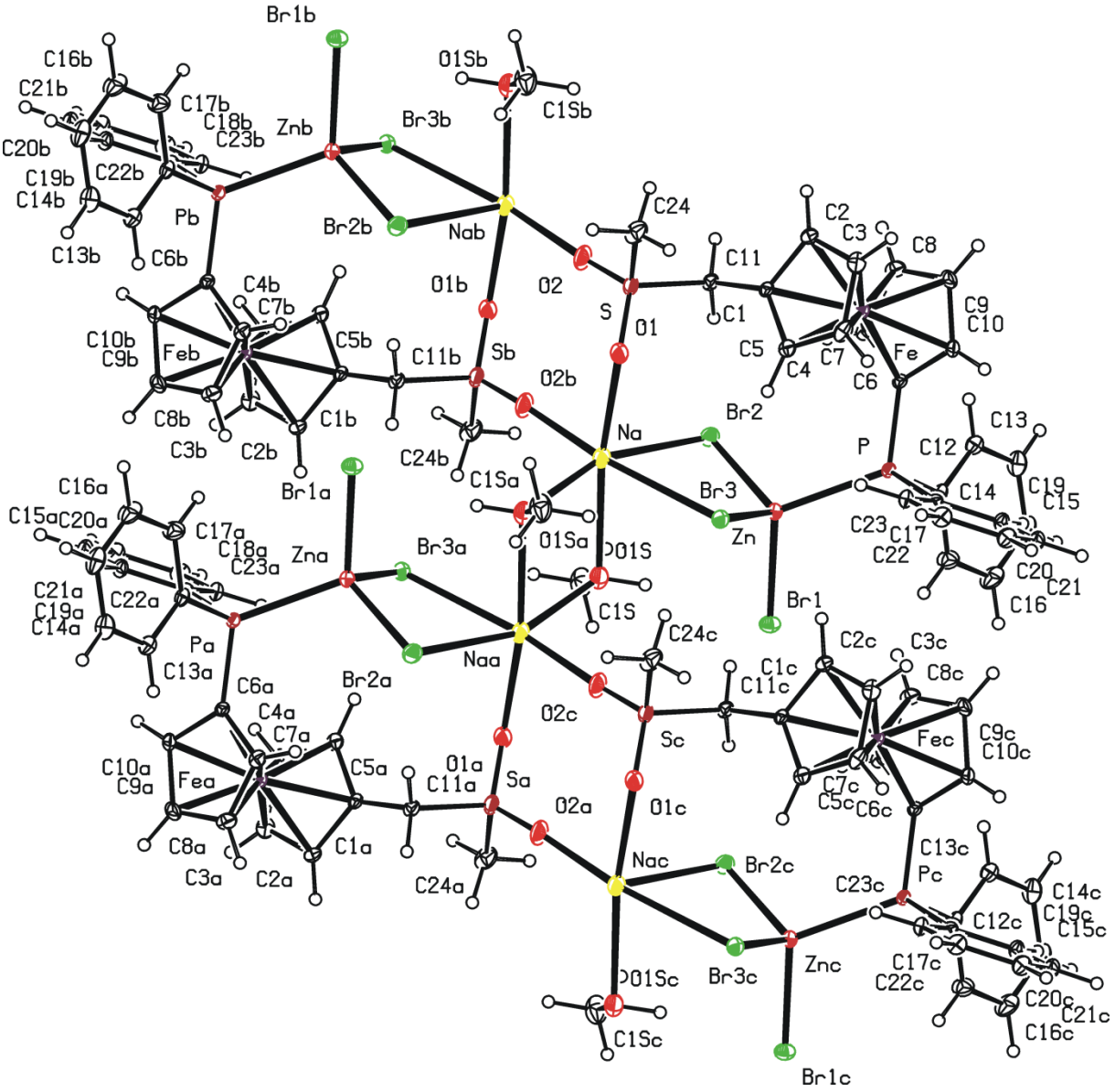

Figure S2. PLATON plot of the structure of **8a** (30% probability ellipsoids).

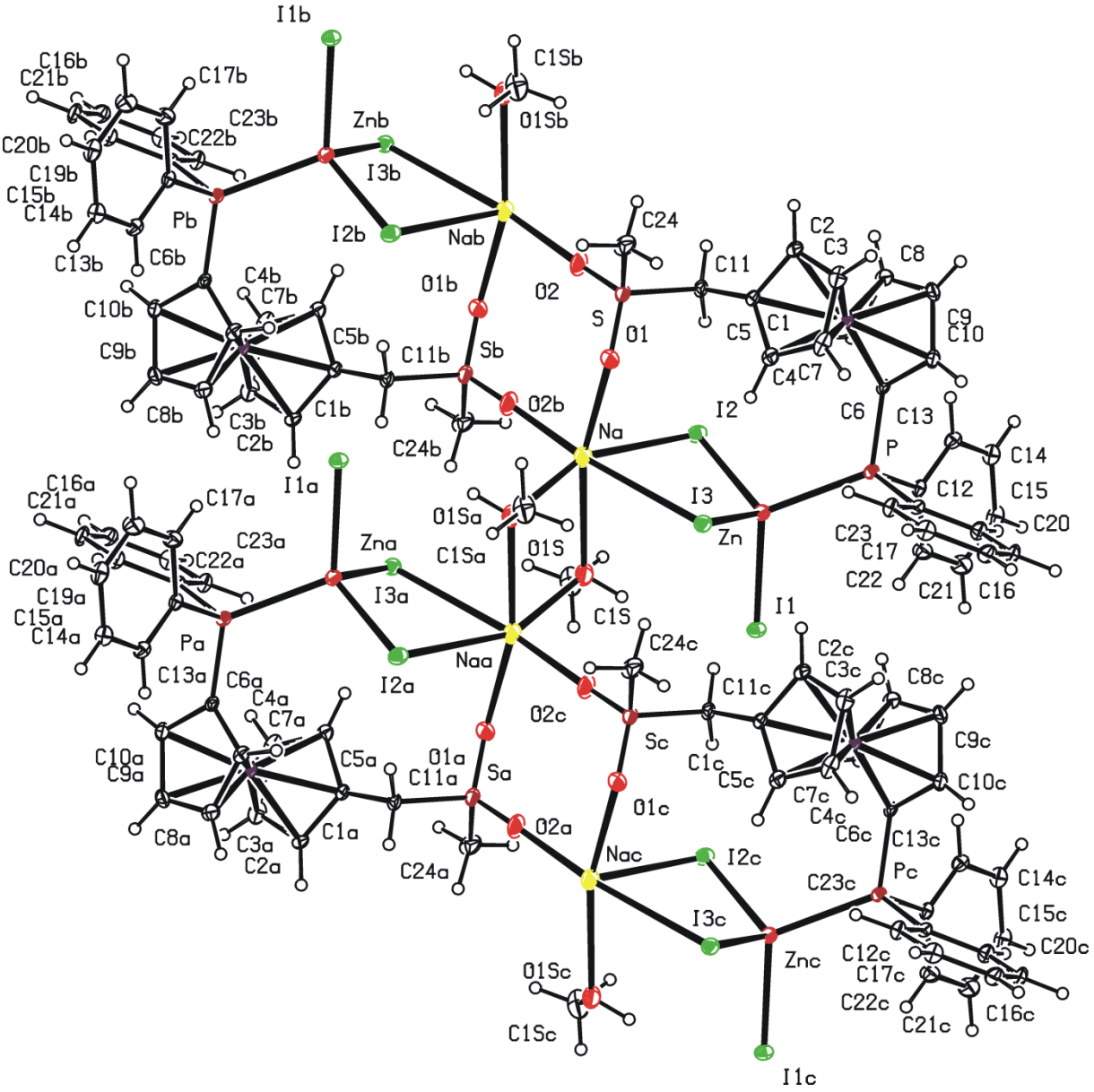

Figure S3. PLATON plot of the structure of **8b** (30% probability ellipsoids).

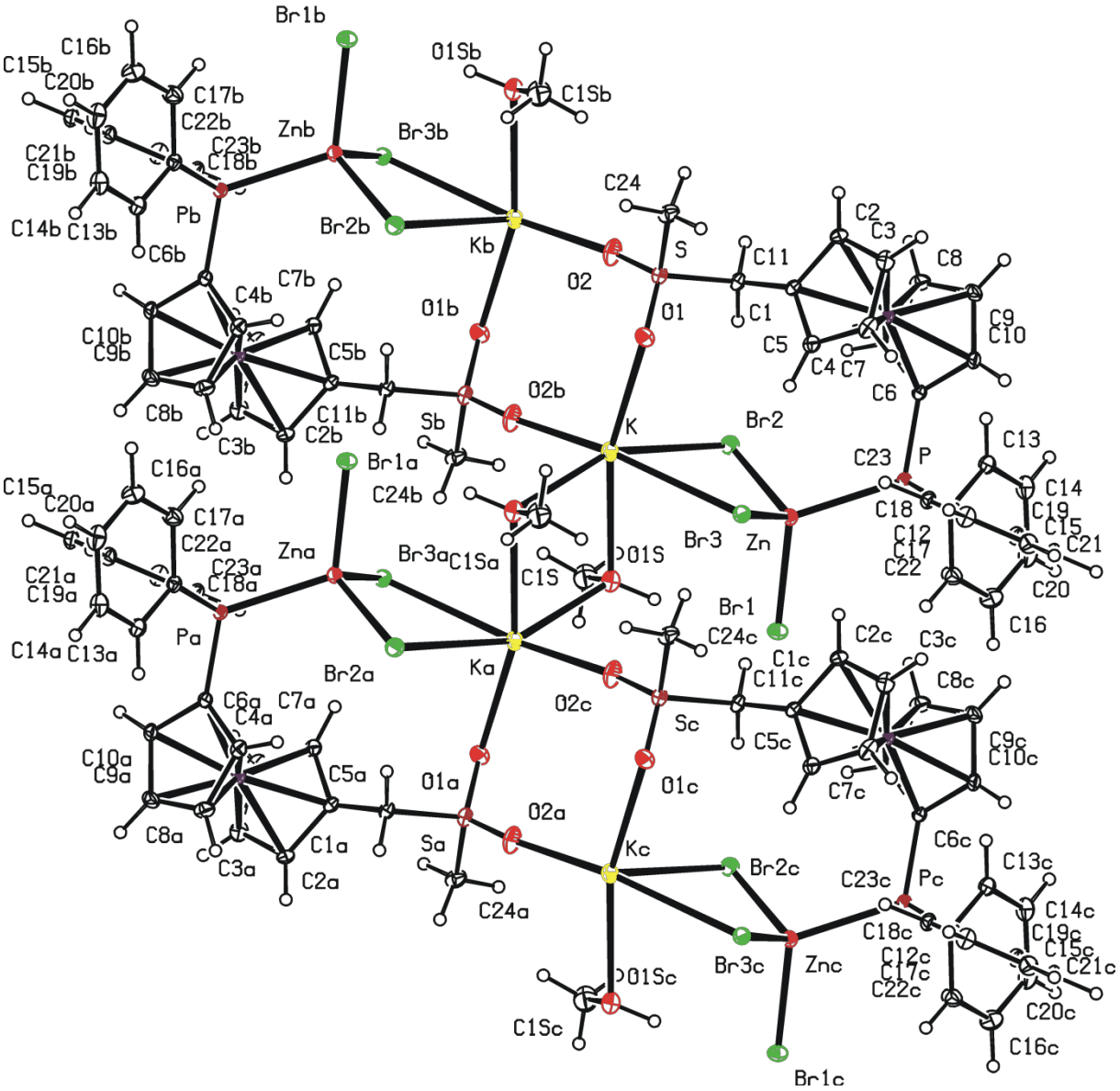

Figure S4. PLATON plot of the structure of **9a** (30% probability ellipsoids).

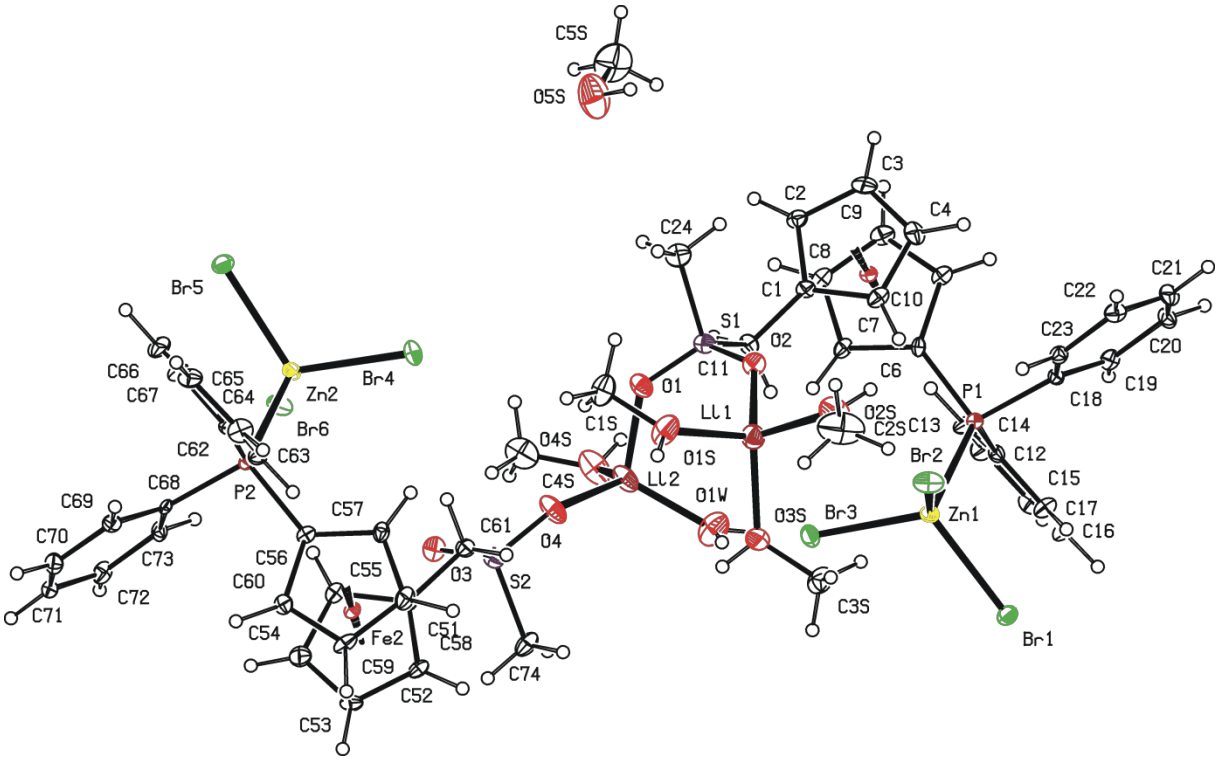

Figure S5. PLATON plot of the structure of **10a**·CH_3OH (30% probability ellipsoids).

Crystallization conditions

Single crystals suitable for X-ray diffraction analysis were obtained by liquid-phase diffusion of diethyl ether *and* tetrahydrofuran into a solution in methanol (**2**·CH_3OH: orange prism, 0.30 × 0.38 × 0.50 mm^3) or similarly from hexane-ethyl acetate (**6a**: orange prism, 0.18 × 0.33 × 0.46 mm^3; **6b**: orange prism, 0.52 × 0.59 × 0.72 mm^3; **6c**: orange prism, 0.27 × 0.39 × 0.53 mm^3) and chloroform-hexane **7** (orange prism, 0.32 × 0.40 × 0.42 mm^3). The crystals of **5** were grown from hot heptane (orange plate, 0.16 × 0.34 × 0.51 mm^3), while crystals of **6a′** separated during an attempted crystallization of a **6a**-$ZnBr_2$ mixture from methanol-diethyl ether (orange plate, 0.12 × 0.32 × 0.47 mm^3). Finally, the crystals of the alkali metal-Zn complexes were selected from the preparative batches (see the main text; **8a**: orange prism, 0.14 × 0.21 × 0.49 mm^3; **8b**: orange prism, 0.11 × 0.13 × 0.20 mm^3; **9a**: orange prism, 0.22 × 0.27 × 0.45 mm^3; **10a**: orange plate, 0.09 × 0.17 × 0.37 mm^3).

Table S1. Summary of relevant crystallographic data and structure refinement parameters.[a]

Compound	**2**·CH_3OH	**5**	**6a**
Formula	$C_{29}H_{36}FeNO_4PS$	$C_{23}H_{21}FeP$	$C_{24}H_{23}FeO_2PS$
M	581.47	384.22	462.30
Crystal system	triclinic	monoclinic	triclinic
Space group	*P*–1 (no. 2)	$P2_1/c$ (no. 14)	*P*–1 (no. 2)
a [Å]	7.0893(3)	8.7389(2)	7.8229(4)
b [Å]	9.9492(3)	16.9638(4)	11.1181(5)
c [Å]	19.5949(7)	13.0688(3)	12.0934(6)
α [°]	95.151(1)		101.649(2)
β [°]	95.806(1)	107.331(1)	94.256(2)
γ [°]	98.625(1)		90.378(2)
V [$Å^3$]	1351.68(9)	1849.43(7)	1027.08(9)
Z	2	4	2
D_{calc} [g cm^{-3}]	1.429	1.380	1.495
μ(MoKα) [mm^{-1}]	0.731	0.904	0.932
Diffrns total	23173	17737	12206
Independent/obsd[b] diffrns	6191/5736	4242/3747	4682/4224
R_{int}[c]	1.69	2.07	1.66
Parameters	337	227	263
R (obsd diffrns) [%][b,c]	2.53	2.73	2.50
R, *wR* (all data) [%][c]	2.80, 6.60	3.30, 7.22	2.91, 6.52
Δρ [e $Å^{-3}$]	0.30, –0.37	0.49, –0.30	0.35, –0.29

Table S1 continued

Compound	**6a'**	**6b**	**6c**
Formula	$C_{24}H_{23}FeO_2PS$	$C_{29}H_{25}FeO_2PS$	$C_{30}H_{27}FeO_2PS$
M	462.30	524.37	538.40
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a [Å]	14.1802(9)	16.2612(6)	8.2576(5)
b [Å]	9.4057(5)	18.1098(7)	12.8146(9)
c [Å]	15.804(1)	8.3519(3)	13.7867(9)
α [°]			110.459(2)
β [°]	90.557(3)	96.312(1)	102.564(3)
γ [°]			99.109(2)
V [Å^3]	2107.7(2)	2444.6(2)	1289.6(2)
Z	4	4	2
D_{calc} [g cm^{-3}]	1.457	1.425	1.387
μ(MoKα) [mm^{-1}]	0.909	0.793	0.754
Diffrns total	16500	22343	13745
Independent/obsd[b] diffrns	4836/3929	5615/5161	5908/5235
R_{int}[c]	3.22	1.72	2.93
Parameters	263	307	317
R (obsd diffrns) [%][b,c]	3.31	2.69	3.63
R, *wR* (all data) [%][c]	4.61, 7.84	3.01, 6.97	4.19, 10.3
$\Delta\rho$ [e Å^{-3}]	0.90, –0.33	0.38, –0.36	1.22,[d] –0.45

Table S1 continued

Compound	**7**	**8a**	**8b**
Formula	$C_{40}H_{34}FeP_2$	$C_{25}H_{27}Br_3FeNaO_3PSZn$	$C_{25}H_{27}FeI_3NaO_3PSZn$
M	632.46	822.44	963.41
Crystal system	triclinic	triclinic	triclinic
Space group	*P*–1 (no. 2)	*P*–1 (no. 2)	*P*–1 (no. 2)
a [Å]	9.9555(3)	8.7397(2)	8.9509(2)
b [Å]	11.1437(3)	9.2716(2)	9.5006(2)
c [Å]	15.0607(4)	18.1021(5)	18.2554(4)
α [°]	71.439(1)	91.264(1)	91.0698(9)
β [°]	80.375(1)	100.075(1)	99.5953(8)
γ [°]	86.098(1)	95.088(1)	95.3065(7)
V [Å^3]	1561.45(8)	1437.46(6)	1523.22(6)
Z	2	2	2
D_{calc} [g cm^{-3}]	1.345	1.900	2.101
μ(MoKα) [mm^{-1}]	0.614	5.678	4.464
Diffrns total	23640	21875	19034
Indep/obsd[b] diffrns	7169/6067	6597/5423	6997/6007
R_{int}[c]	2.79	2.39	2.38
Parameters	388	327	327
R (obsd diffrns) [%][b,c]	3.86	2.87	2.70
R, *wR* (all data) [%][c]	4.77, 10.8	4.08, 6.51	3.38, 5.76
$\Delta\rho$ [e Å^{-3}]	0.97,[d] –0.31	0.76, –0.72	1.86,[e] –0.82

Table S1 continued

Compound	**9a**	**10a**·CH_3OH
Formula	$C_{25}H_{27}Br_3FeKO_3PSZn$	$C_{53}H_{68}Br_6Fe_2Li_2O_{10}P_2S_2Zn_2$
M	838.55	1726.91
Crystal system	triclinic	triclinic
Space group	*P*–1 (no. 2)	*P*1 (no. 1)[f]
a [Å]	8.8279(3)	8.5888(7)
b [Å]	9.3796(3)	9.6908(6)
c [Å]	18.2463(5)	19.623(2)
α [°]	88.457(1)	85.139(3)
β [°]	80.307(1)	80.198(3)
γ [°]	85.691(1)	85.628(3)
V [Å^3]	1484.90(8)	1600.5(2)
Z	2	1
D_{calc} [g cm^{-3}]	1.875	1.792
μ(MoKα) [mm^{-1}]	5.622	5.096
Diffrns total	20827	32003
Indep/obsd[b] diffrns	6801/5876	14458/11651
R_{int}[c]	2.27	3.48
Parameters	326	716
R (obsd diffrns) [%][b,c]	2.33	3.53
R, *wR* (all data) [%][c]	3.19, 4.99	5.40, 6.87
$\Delta\rho$ [e Å^{-3}]	0.91, –0.38	0.78, –0.76

[a] Common details: T = 150(2) K. [b] Observed diffractions with $I_o \geq 2\sigma(I_o)$. [c] Definitions: $R_{int} = \Sigma \left| F_o^2 - F_o^2(\text{mean}) \right| / \Sigma F_o^2$, where F_o^2(mean) is the average intensity of symmetry-equivalent diffractions. $R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $wR(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$. [d] Residual electron density attributable to the lone electron pair at the phosphorus atom. [e] Residual electron density in the vicinity of heavy atoms (iodine). [f] Flack's enantiomorph parameter: –0.013(6).