

## Supporting Information

for

STEREODGENIC

**Diastereoselective *ortho*-Metalation of ~~Scalemie~~ Ferrocenylphosphine Oxides.  
Asymmetric Synthesis of the First Enantiopure Phosphorus-Chiral  
2,2'-Bis(diarylphosphino)-1,1'-biferrocenyls.**

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**(*R<sub>P</sub>*,*R<sub>m</sub>*)-1-Iodo-2-(1-naphthylphenylphosphinoxy)ferrocene, 5a (Minor isomer).**

<sup>1</sup>H-NMR (400.13 MHz): δ 4.08 (m, 1H); 4.28 (s, 5H); 4.33 (m, 1H); 4.78 (m, 1H); 7.35-7.52 (m, 6H); 7.66-7.74 (m, 2H); 7.79-7.89 (m, 2H); 8.03 (d, 1H, *J* = 8.3Hz); 8.68 (d, 1H, *J* = 8.2Hz) ppm.

<sup>13</sup>C-NMR (100.62 MHz): δ 41.51 (d, C, *J<sub>CP</sub>* = 11.3Hz); 71.78 (d, CH, *J<sub>CP</sub>* = 9.9Hz); 72.71 (5CH); 74.71 (d, CH, *J<sub>CP</sub>* = 14.3Hz); 75.31 (d, C, *J<sub>CP</sub>* = 117.2Hz); 79.85 (d, CH, *J<sub>CP</sub>* = 8.7Hz); 124.21 (d, CH, *J<sub>CP</sub>* = 14.1Hz); 136.03 (CH); 126.52 (CH); 127.24 (d, CH, *J<sub>CP</sub>* = 4.0Hz); 128.08 (d, CH, *J<sub>CP</sub>* = 12.1Hz); 128.58 (br, CH); 129.06 (d, C, *J<sub>CP</sub>* = 103.6Hz); 131.45 (d, CH, *J<sub>CP</sub>* = 3.0Hz); 132.31 (d, CH, *J<sub>CP</sub>* = 11.1Hz); 132.76 (d, CH, *J<sub>CP</sub>* = 3.0Hz); 133.44 (d, C, *J<sub>CP</sub>* = 10.1Hz); 133.52 (d, C, *J<sub>CP</sub>* = 9.0Hz); 133.76 (d, CH, *J<sub>CP</sub>* = 10.1Hz); 133.92 (d, C, *J<sub>CP</sub>* = 107.4Hz) ppm.

<sup>31</sup>P-NMR (121.50 MHz): δ 31.54 (s) ppm.

HRMS (FAB<sup>+</sup>): *m/z* calcd. for C<sub>26</sub>H<sub>21</sub>FeIOP: 562.9724; obsd.: 562.9720.

**(*R<sub>P</sub>*,*R<sub>m</sub>*,*S<sub>m</sub>*,*S<sub>P</sub>*)-2,2'-Bis(2-biphenylphenylphosphinoxy)-1,1'-biferrocenyl, meso-6b.**

<sup>1</sup>H-NMR (400.13 MHz; CD<sub>2</sub>Cl<sub>2</sub>): δ 3.71 (s, 10H); 3.87 (m, 2H); 4.36 (m, 2H); 5.93 (m, 2H); 6.97-7.01 (m, 4H); 7.11-7.16 (m, 4H); 7.19-7.24 (m, 2H); 7.28 (ddd, 2H, *J* = 1.2; 4.0; 7.5Hz); 7.35-7.41 (m, 4H); 7.42-7.57 (m, 10H); 7.70 (ddd, 2H, *J* = 1.0; 7.5; 14.0Hz) ppm.

<sup>13</sup>C-NMR (100.62 MHz; CD<sub>2</sub>Cl<sub>2</sub>): δ 70.46 (d, C, *J<sub>CP</sub>* = 114.7Hz); 70.95 (5CH); 71.18 (d, CH, *J<sub>CP</sub>* = 11.5Hz); 75.25 (d, CH, *J<sub>CP</sub>* = 15.3Hz); 77.70 (d, CH, *J<sub>CP</sub>* = 9.2Hz); 87.58 (d, C, *J<sub>CP</sub>* = 9.2Hz); 126.73 (d, CH, *J<sub>CP</sub>* = 12.2Hz); 127.02 (CH); 127.07 (CH); 127.89 (d, CH, *J<sub>CP</sub>* = 12.2Hz); 130.10 (CH); 131.08 (d, CH, *J<sub>CP</sub>* = 2.3Hz); 131.56 (d, CH, *J<sub>CP</sub>* = 2.3Hz); 132.05 (d, CH, *J<sub>CP</sub>* = 9.2Hz); 132.51 (d, CH, *J<sub>CP</sub>* = 9.9Hz); 134.31 (d, C, *J<sub>CP</sub>* = 100.2Hz); 134.35 (d, CH, *J<sub>CP</sub>* = 12.2Hz); 136.47 (d, C, *J<sub>CP</sub>* = 106.3Hz); 141.58 (d, C, *J<sub>CP</sub>* = 3.8Hz); 147.52 (d, C, *J<sub>CP</sub>* = 7.6Hz) ppm.

<sup>31</sup>P-NMR (161.98 MHz; CD<sub>2</sub>Cl<sub>2</sub>): δ 32.53 (s) ppm.

HRMS (FAB<sup>+</sup>): *m/z* calcd. for C<sub>56</sub>H<sub>45</sub>Fe<sub>2</sub>O<sub>2</sub>P<sub>2</sub> (MH<sup>+</sup>): 923.1594; obsd.: 923.1601.

Table S1. Crystal data and structure refinement for  $(R_P, R_m, R_m, R_P)$ -(-)-2,2'-Bis(2-biphenylphenylphosphinoxy)-1,1'-biferrocenyl bisdichloromethane solvate,  $(R_P, R_m, R_m, R_P)$ -**6b**·2CH<sub>2</sub>Cl<sub>2</sub>, C<sub>56</sub>H<sub>44</sub>Fe<sub>2</sub>O<sub>2</sub>P<sub>2</sub>·2CH<sub>2</sub>Cl<sub>2</sub>.

|                                   |                                                                                                                                              |
|-----------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------|
| Identification code               | widkj3fr                                                                                                                                     |
| Empirical formula                 | C <sub>56</sub> H <sub>48</sub> Cl <sub>4</sub> Fe <sub>2</sub> O <sub>2</sub> P <sub>2</sub> (idealized, including solvent)                 |
| Formula weight                    | 1092.40                                                                                                                                      |
| Temperature                       | 213(2) K                                                                                                                                     |
| Wavelength                        | 0.71073 Å                                                                                                                                    |
| Crystal system, space group       | orthorhombic, P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>                                                                                  |
| Unit cell dimensions              | a = 9.620(4) Å      α = 90°<br>b = 12.430(5) Å      β = 90°<br>c = 43.31(2) Å      γ = 90°                                                   |
| Volume                            | 5179(4) Å <sup>3</sup>                                                                                                                       |
| Z, Calculated density             | 4, 1.401 Mg/m <sup>3</sup>                                                                                                                   |
| Absorption coefficient            | 0.871 mm <sup>-1</sup>                                                                                                                       |
| F(000)                            | 2248                                                                                                                                         |
| Crystal size                      | 0.70 x 0.65 x 0.45 mm, orange block                                                                                                          |
| Diffractionmeter                  | Siemens SMART 3-circle with CCD area detector<br>(sealed X-ray tube, Mo Kα radiation, graphite monochr., det.dist. 44.50 mm, 512x512 pixels) |
| Scan type / width / speed         | ω-scan frames / Δω = 0.3° / 8 sec. per frame<br>full sphere, 4 x 606 frames                                                                  |
| Theta range for data collection   | 1.89° to 27.00°                                                                                                                              |
| Index ranges                      | -12 ≤ h ≤ 12, -15 ≤ h ≤ 15, -55 ≤ h ≤ 55                                                                                                     |
| Reflections collected / unique    | 62021 / 11206 [R(int) = 0.036, R(sigma) = 0.025]                                                                                             |
| Completeness to theta = 27.00     | 99.3%                                                                                                                                        |
| Absorption correction             | Empirical (program SADABS; Sheldrick, 1996)                                                                                                  |
| Transmission factors              | 0.746 - 0.626                                                                                                                                |
| Structure solution                | Direct methods (program SHELXS97)                                                                                                            |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup> (prg SHELXL97)                                                                                   |
| Data / restraints / parameters    | 11206 / 0 / 649                                                                                                                              |
| Goodness-of-fit on F <sup>2</sup> | 1.185                                                                                                                                        |
| Final R indices [I > 2σ(I)]       | R1 = 0.0414, wR2 = 0.0846 (10846 data)                                                                                                       |
| R indices (all data)              | R1 = 0.0434, wR2 = 0.0854 (11206 data)                                                                                                       |
| Absolute structure parameter      | 0.019(12)                                                                                                                                    |
| Extinction coefficient            | 0.00047(9)                                                                                                                                   |
| Largest diff. peak and hole       | 0.427 and -0.405 e Å <sup>-3</sup>                                                                                                           |

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|, \quad wR2 = [\Sigma (w(F_o^2 - F_c^2)^2) / \Sigma (w(F_o^2)^2)]^{1/2}$$

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup> x 10<sup>3</sup>) of  $(R_P, R_m, R_m, R_P)$ -(-)-2,2'-Bis(2-biphenylphenylphosphinoxy)-1,1'-biferrocenyl bisdichloromethane solvate,  $(R_P, R_m, R_m, R_P)$ -**6b**·2CH<sub>2</sub>Cl<sub>2</sub>, C<sub>56</sub>H<sub>44</sub>Fe<sub>2</sub>O<sub>2</sub>P<sub>2</sub>·2CH<sub>2</sub>Cl<sub>2</sub>. U<sub>eq</sub> is defined as one third of the trace of the orthogonalized U<sub>ij</sub> tensor.

|       | x          | y           | z          | U <sub>eq</sub> |
|-------|------------|-------------|------------|-----------------|
| Fe(1) | 0.46244(4) | 0.42405(3)  | 0.12143(1) | 26(1)           |
| Fe(2) | 0.46865(5) | 0.71626(3)  | 0.05969(1) | 29(1)           |
| P(1)  | 0.26792(7) | 0.58838(6)  | 0.16970(2) | 23(1)           |
| P(2)  | 0.63469(7) | 0.84085(6)  | 0.11938(2) | 23(1)           |
| O(1)  | 0.1785(2)  | 0.65276(17) | 0.14875(5) | 30(1)           |
| O(2)  | 0.7291(2)  | 0.75602(16) | 0.13172(5) | 33(1)           |
| C(1)  | 0.3770(4)  | 0.3826(3)   | 0.07970(8) | 42(1)           |
| C(2)  | 0.2786(4)  | 0.3665(3)   | 0.10344(8) | 40(1)           |
| C(3)  | 0.3353(4)  | 0.2912(3)   | 0.12470(9) | 43(1)           |
| C(4)  | 0.4690(4)  | 0.2609(2)   | 0.11384(9) | 48(1)           |
| C(5)  | 0.4941(4)  | 0.3177(3)   | 0.08602(9) | 48(1)           |
| C(6)  | 0.4897(3)  | 0.5890(2)   | 0.12422(6) | 24(1)           |
| C(7)  | 0.4285(3)  | 0.5457(2)   | 0.15215(6) | 24(1)           |
| C(8)  | 0.5242(3)  | 0.4682(2)   | 0.16459(7) | 32(1)           |
| C(9)  | 0.6415(3)  | 0.4636(3)   | 0.14463(8) | 36(1)           |

|         |              |             |             |        |
|---------|--------------|-------------|-------------|--------|
| C(10)   | 0.6207(3)    | 0.5366(2)   | 0.12012(8)  | 30(1)  |
| C(11)   | 0.1859(3)    | 0.4654(2)   | 0.18282(7)  | 27(1)  |
| C(12)   | 0.2398(3)    | 0.4010(3)   | 0.20625(7)  | 37(1)  |
| C(13)   | 0.1800(4)    | 0.3017(3)   | 0.21299(8)  | 45(1)  |
| C(14)   | 0.0649(4)    | 0.2669(3)   | 0.19596(9)  | 47(1)  |
| C(15)   | 0.0061(3)    | 0.3331(3)   | 0.17411(9)  | 42(1)  |
| C(16)   | 0.0663(3)    | 0.4327(2)   | 0.16715(7)  | 32(1)  |
| C(17)   | 0.3202(3)    | 0.6647(2)   | 0.20372(6)  | 26(1)  |
| C(18)   | 0.4548(3)    | 0.7079(2)   | 0.20450(7)  | 34(1)  |
| C(19)   | 0.4948(3)    | 0.7757(3)   | 0.22881(8)  | 40(1)  |
| C(20)   | 0.4013(4)    | 0.7999(3)   | 0.25188(8)  | 43(1)  |
| C(21)   | 0.2682(4)    | 0.7569(3)   | 0.25160(7)  | 37(1)  |
| C(22)   | 0.2248(3)    | 0.6892(2)   | 0.22729(6)  | 28(1)  |
| C(23)   | 0.0789(3)    | 0.6464(2)   | 0.22746(7)  | 32(1)  |
| C(24)   | 0.0383(4)    | 0.5699(3)   | 0.24914(7)  | 41(1)  |
| C(25)   | -0.0969(4)   | 0.5293(3)   | 0.24871(9)  | 52(1)  |
| C(26)   | -0.1909(4)   | 0.5639(4)   | 0.22687(10) | 57(1)  |
| C(27)   | -0.1524(4)   | 0.6397(3)   | 0.20532(10) | 50(1)  |
| C(28)   | -0.0184(3)   | 0.6808(3)   | 0.20575(8)  | 39(1)  |
| C(29)   | 0.5798(4)    | 0.5952(3)   | 0.03891(8)  | 45(1)  |
| C(30)   | 0.6644(4)    | 0.6878(3)   | 0.04251(7)  | 39(1)  |
| C(31)   | 0.6008(4)    | 0.7739(3)   | 0.02615(7)  | 45(1)  |
| C(32)   | 0.4765(5)    | 0.7340(4)   | 0.01248(7)  | 56(1)  |
| C(33)   | 0.4635(5)    | 0.6230(3)   | 0.02060(8)  | 56(1)  |
| C(34)   | 0.4297(3)    | 0.6759(2)   | 0.10487(6)  | 24(1)  |
| C(35)   | 0.4794(3)    | 0.7864(2)   | 0.10228(6)  | 25(1)  |
| C(36)   | 0.3827(3)    | 0.8432(3)   | 0.08293(7)  | 33(1)  |
| C(37)   | 0.2765(3)    | 0.7709(3)   | 0.07391(8)  | 36(1)  |
| C(38)   | 0.3046(3)    | 0.6693(3)   | 0.08725(7)  | 31(1)  |
| C(39)   | 0.7138(3)    | 0.9249(2)   | 0.08979(6)  | 27(1)  |
| C(40)   | 0.6467(3)    | 1.0171(2)   | 0.07894(7)  | 32(1)  |
| C(41)   | 0.7071(4)    | 1.0784(3)   | 0.05548(8)  | 45(1)  |
| C(42)   | 0.8339(4)    | 1.0484(3)   | 0.04391(8)  | 49(1)  |
| C(43)   | 0.9028(4)    | 0.9589(3)   | 0.05463(8)  | 45(1)  |
| C(44)   | 0.8434(3)    | 0.8961(3)   | 0.07806(7)  | 33(1)  |
| C(45)   | 0.5776(3)    | 0.9361(2)   | 0.14872(7)  | 28(1)  |
| C(46)   | 0.4399(3)    | 0.9352(3)   | 0.15881(7)  | 37(1)  |
| C(47)   | 0.3931(4)    | 1.0075(3)   | 0.18124(9)  | 50(1)  |
| C(48)   | 0.4846(4)    | 1.0816(4)   | 0.19349(9)  | 59(1)  |
| C(49)   | 0.6222(4)    | 1.0852(3)   | 0.18316(9)  | 50(1)  |
| C(50)   | 0.6716(3)    | 1.0124(3)   | 0.16136(7)  | 33(1)  |
| C(51)   | 0.8202(3)    | 1.0183(3)   | 0.15150(8)  | 36(1)  |
| C(52)   | 0.8693(4)    | 1.1067(3)   | 0.13487(8)  | 40(1)  |
| C(53)   | 1.0059(4)    | 1.1100(3)   | 0.12454(9)  | 48(1)  |
| C(54)   | 1.0956(4)    | 1.0256(3)   | 0.13067(10) | 53(1)  |
| C(55)   | 1.0496(4)    | 0.9376(3)   | 0.14741(10) | 51(1)  |
| C(56)   | 0.9121(3)    | 0.9347(3)   | 0.15804(9)  | 41(1)  |
| C(1S) * | -0.0697(5)   | 0.4728(4)   | 0.05144(11) | 65(2)  |
| Cl(1S)  | 0.08213(15)  | 0.48052(12) | 0.02922(4)  | 81(1)  |
| Cl(2S)  | -0.09223(14) | 0.34510(12) | 0.06837(4)  | 85(1)  |
| C(2SA)  | 0.7056(12)   | 0.3167(9)   | -0.0326(2)  | 128(6) |
| C(2SB)  | 0.705(7)     | 0.291(3)    | -0.0080(15) | 420(3) |
| Cl(3S)  | 0.61587(19)  | 0.31560(14) | 0.00370(3)  | 66(1)  |
| Cl(4S)  | 0.8261(12)   | 0.4120(7)   | -0.0344(2)  | 106(3) |
| Cl(4T)  | 0.7776(12)   | 0.4562(12)  | -0.0310(3)  | 97(4)  |
| Cl(4U)  | 0.7567(13)   | 0.3984(8)   | -0.0541(3)  | 105(5) |

\* Subsequent atoms belonging to two partly disordered CH<sub>2</sub>Cl<sub>2</sub> solvent molecules. Refined site occupation factors: C(1S) 0.99(1), Cl(1S) 0.936(5), Cl(2S) 0.962(5), C(2SA) 0.95(4), C(2SB) 0.82(6), Cl(3S) 0.81(1), Cl(4S) 0.50(2), Cl(4T) 0.25(1), Cl(4U) 0.25(1).

Table 3. Hydrogen coordinates and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  
 $(R_P, R_m, R_m, R_P)$ -(-)-2,2'-Bis(2-biphenylphenylphosphinoxy)-1,1'-biferrocenyl  
 bisdichloromethane solvate,  $(R_P, R_m, R_m, R_P)$ -**6b**·2CH<sub>2</sub>Cl<sub>2</sub>, C<sub>56</sub>H<sub>44</sub>Fe<sub>2</sub>O<sub>2</sub>P<sub>2</sub>·2CH<sub>2</sub>Cl<sub>2</sub>.

|        | x       | y      | z      | U <sub>iso</sub> |
|--------|---------|--------|--------|------------------|
| H(1)   | 0.3664  | 0.4285 | 0.0626 | 50               |
| H(2)   | 0.1911  | 0.3998 | 0.1049 | 48               |
| H(3)   | 0.2920  | 0.2658 | 0.1427 | 51               |
| H(4)   | 0.5299  | 0.2121 | 0.1234 | 57               |
| H(5)   | 0.5748  | 0.3130 | 0.0739 | 58               |
| H(8)   | 0.5115  | 0.4277 | 0.1827 | 39               |
| H(9)   | 0.7197  | 0.4194 | 0.1473 | 44               |
| H(10)  | 0.6829  | 0.5488 | 0.1038 | 36               |
| H(12)  | 0.3173  | 0.4247 | 0.2176 | 44               |
| H(13)  | 0.2166  | 0.2585 | 0.2288 | 54               |
| H(14)  | 0.0276  | 0.1980 | 0.1995 | 57               |
| H(15)  | -0.0751 | 0.3113 | 0.1638 | 50               |
| H(16)  | 0.0265  | 0.4773 | 0.1520 | 39               |
| H(18)  | 0.5183  | 0.6913 | 0.1887 | 41               |
| H(19)  | 0.5851  | 0.8046 | 0.2293 | 47               |
| H(20)  | 0.4280  | 0.8461 | 0.2680 | 52               |
| H(21)  | 0.2063  | 0.7730 | 0.2678 | 45               |
| H(24)  | 0.1019  | 0.5457 | 0.2641 | 49               |
| H(25)  | -0.1241 | 0.4779 | 0.2634 | 63               |
| H(26)  | -0.2816 | 0.5357 | 0.2267 | 68               |
| H(27)  | -0.2165 | 0.6634 | 0.1904 | 59               |
| H(28)  | 0.0074  | 0.7329 | 0.1911 | 47               |
| H(29)  | 0.5980  | 0.5268 | 0.0473 | 54               |
| H(30)  | 0.7479  | 0.6916 | 0.0537 | 47               |
| H(31)  | 0.6349  | 0.8446 | 0.0246 | 53               |
| H(32)  | 0.4140  | 0.7737 | 0.0003 | 67               |
| H(33)  | 0.3907  | 0.5767 | 0.0148 | 67               |
| H(36)  | 0.3889  | 0.9160 | 0.0772 | 40               |
| H(37)  | 0.2002  | 0.7876 | 0.0612 | 43               |
| H(38)  | 0.2497  | 0.6073 | 0.0849 | 37               |
| H(40)  | 0.5609  | 1.0379 | 0.0874 | 39               |
| H(41)  | 0.6613  | 1.1394 | 0.0477 | 54               |
| H(42)  | 0.8749  | 1.0901 | 0.0282 | 59               |
| H(43)  | 0.9895  | 0.9398 | 0.0463 | 54               |
| H(44)  | 0.8904  | 0.8354 | 0.0857 | 39               |
| H(46)  | 0.3774  | 0.8851 | 0.1504 | 44               |
| H(47)  | 0.3001  | 1.0056 | 0.1879 | 60               |
| H(48)  | 0.4543  | 1.1297 | 0.2088 | 71               |
| H(49)  | 0.6826  | 1.1378 | 0.1911 | 60               |
| H(52)  | 0.8093  | 1.1645 | 0.1306 | 48               |
| H(53)  | 1.0376  | 1.1699 | 0.1133 | 57               |
| H(54)  | 1.1877  | 1.0280 | 0.1235 | 63               |
| H(55)  | 1.1102  | 0.8802 | 0.1516 | 62               |
| H(56)  | 0.8814  | 0.8756 | 0.1697 | 50               |
| H(1SA) | -0.1500 | 0.4889 | 0.0383 | 78               |
| H(1SB) | -0.0659 | 0.5274 | 0.0678 | 78               |

Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded. All hydrogen atoms had  $U_{iso} = U_{eq} \times 1.2$  of their carrier atoms.

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $(R_P, R_m, R_m, R_P)-(-)-2,2'$ -Bis(2-biphenylphenylphosphinoxy)-1,1'-biferrocenyl bisdichloromethanesolvate,  $(R_P, R_m, R_m, R_P)$ -**6b**·2CH<sub>2</sub>Cl<sub>2</sub>, C<sub>56</sub>H<sub>44</sub>Fe<sub>2</sub>O<sub>2</sub>P<sub>2</sub>·2CH<sub>2</sub>Cl<sub>2</sub>. The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2hk a^* b^* U_{12}]$

|       | U <sub>11</sub> | U <sub>22</sub> | U <sub>33</sub> | U <sub>23</sub> | U <sub>13</sub> | U <sub>12</sub> |
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Fe(1) | 24(1)           | 24(1)           | 32(1)           | -3(1)           | 2(1)            | 1(1)            |
| Fe(2) | 30(1)           | 35(1)           | 21(1)           | 0(1)            | -2(1)           | -5(1)           |
| P(1)  | 21(1)           | 25(1)           | 23(1)           | 0(1)            | 0(1)            | -1(1)           |
| P(2)  | 20(1)           | 24(1)           | 26(1)           | -1(1)           | 0(1)            | 0(1)            |
| O(1)  | 25(1)           | 36(1)           | 29(1)           | 3(1)            | 0(1)            | 3(1)            |
| O(2)  | 26(1)           | 28(1)           | 45(1)           | 2(1)            | -5(1)           | 1(1)            |
| C(1)  | 54(2)           | 39(2)           | 32(2)           | -10(1)          | -3(2)           | -14(2)          |
| C(2)  | 33(2)           | 36(2)           | 51(2)           | -11(2)          | -6(2)           | -9(1)           |
| C(3)  | 51(2)           | 31(2)           | 47(2)           | -4(2)           | 7(2)            | -12(1)          |
| C(4)  | 55(2)           | 23(1)           | 65(2)           | -9(1)           | -3(2)           | 7(2)            |
| C(5)  | 51(2)           | 39(2)           | 55(2)           | -20(2)          | 17(2)           | -6(2)           |
| C(6)  | 21(1)           | 23(1)           | 29(1)           | -4(1)           | -4(1)           | -3(1)           |
| C(7)  | 20(1)           | 26(1)           | 24(1)           | -4(1)           | -2(1)           | 1(1)            |
| C(8)  | 30(1)           | 33(1)           | 34(2)           | 3(1)            | -7(1)           | 2(1)            |
| C(9)  | 23(1)           | 37(2)           | 49(2)           | 3(2)            | -7(1)           | 6(1)            |
| C(10) | 19(1)           | 31(1)           | 40(2)           | -3(1)           | 3(1)            | -2(1)           |
| C(11) | 24(1)           | 29(1)           | 28(1)           | -3(1)           | 7(1)            | -1(1)           |
| C(12) | 37(2)           | 41(2)           | 32(2)           | 3(1)            | 3(1)            | -2(1)           |
| C(13) | 55(2)           | 39(2)           | 42(2)           | 13(2)           | 10(2)           | 4(2)            |
| C(14) | 48(2)           | 31(2)           | 63(2)           | 1(2)            | 21(2)           | -8(2)           |
| C(15) | 28(2)           | 36(2)           | 62(2)           | -4(2)           | 5(1)            | -5(1)           |
| C(16) | 25(1)           | 30(1)           | 41(2)           | 1(1)            | 2(1)            | 0(1)            |
| C(17) | 29(1)           | 26(1)           | 24(1)           | 0(1)            | 1(1)            | -1(1)           |
| C(18) | 30(2)           | 38(2)           | 35(2)           | -3(1)           | -3(1)           | -2(1)           |
| C(19) | 32(2)           | 45(2)           | 42(2)           | -7(2)           | -7(1)           | -10(1)          |
| C(20) | 51(2)           | 42(2)           | 38(2)           | -13(2)          | -15(2)          | -2(2)           |
| C(21) | 45(2)           | 38(2)           | 29(2)           | -5(1)           | 4(1)            | 7(1)            |
| C(22) | 30(1)           | 26(1)           | 27(1)           | 1(1)            | 0(1)            | 4(1)            |
| C(23) | 31(2)           | 31(2)           | 34(2)           | -5(1)           | 10(1)           | 2(1)            |
| C(24) | 51(2)           | 38(2)           | 34(2)           | -4(1)           | 11(2)           | -1(2)           |
| C(25) | 62(2)           | 40(2)           | 54(2)           | -5(2)           | 27(2)           | -14(2)          |
| C(26) | 36(2)           | 62(3)           | 73(3)           | -22(2)          | 12(2)           | -11(2)          |
| C(27) | 33(2)           | 54(2)           | 62(2)           | -12(2)          | 5(2)            | 3(2)            |
| C(28) | 32(2)           | 42(2)           | 45(2)           | -2(1)           | 8(1)            | 7(1)            |
| C(29) | 59(2)           | 40(2)           | 37(2)           | -16(2)          | 17(2)           | -8(2)           |
| C(30) | 39(2)           | 47(2)           | 30(2)           | -5(1)           | 9(1)            | -6(2)           |
| C(31) | 56(2)           | 52(2)           | 26(2)           | 2(2)            | 7(2)            | -13(2)          |
| C(32) | 64(2)           | 83(3)           | 21(1)           | 3(2)            | -4(2)           | -9(2)           |
| C(33) | 61(2)           | 76(3)           | 30(2)           | -22(2)          | 7(2)            | -31(2)          |
| C(34) | 20(1)           | 28(1)           | 22(1)           | -2(1)           | 3(1)            | -1(1)           |
| C(35) | 24(1)           | 25(1)           | 25(1)           | -2(1)           | -2(1)           | -1(1)           |
| C(36) | 31(2)           | 30(2)           | 39(2)           | 5(1)            | -4(1)           | 2(1)            |
| C(37) | 23(1)           | 44(2)           | 42(2)           | 4(1)            | -8(1)           | 0(1)            |
| C(38) | 24(1)           | 37(2)           | 31(2)           | 0(1)            | -1(1)           | -5(1)           |
| C(39) | 29(1)           | 24(1)           | 29(1)           | -4(1)           | 1(1)            | -5(1)           |
| C(40) | 37(2)           | 28(2)           | 32(2)           | -4(1)           | 0(1)            | 1(1)            |
| C(41) | 64(2)           | 30(2)           | 41(2)           | 6(2)            | -1(2)           | -3(2)           |
| C(42) | 68(2)           | 46(2)           | 33(2)           | 3(2)            | 12(2)           | -17(2)          |
| C(43) | 39(2)           | 52(2)           | 43(2)           | -8(2)           | 16(2)           | -12(2)          |
| C(44) | 31(2)           | 32(2)           | 36(2)           | -6(1)           | 4(1)            | -5(1)           |
| C(45) | 28(1)           | 29(2)           | 26(1)           | -3(1)           | -2(1)           | 2(1)            |
| C(46) | 29(2)           | 48(2)           | 33(2)           | -7(1)           | 2(1)            | 1(1)            |
| C(47) | 34(2)           | 72(3)           | 45(2)           | -9(2)           | 5(2)            | 7(2)            |
| C(48) | 54(2)           | 72(3)           | 51(2)           | -31(2)          | 3(2)            | 9(2)            |
| C(49) | 45(2)           | 54(2)           | 51(2)           | -25(2)          | -10(2)          | 2(2)            |
| C(50) | 31(2)           | 37(2)           | 32(2)           | -2(1)           | -6(1)           | 1(1)            |
| C(51) | 30(2)           | 38(2)           | 40(2)           | -11(1)          | -10(1)          | -6(1)           |
| C(52) | 38(2)           | 32(2)           | 49(2)           | -8(1)           | -11(2)          | -2(1)           |
| C(53) | 41(2)           | 43(2)           | 58(2)           | 2(2)            | -5(2)           | -12(1)          |
| C(54) | 28(2)           | 67(3)           | 62(3)           | -4(2)           | -2(2)           | -6(2)           |

|        |         |        |        |        |         |        |
|--------|---------|--------|--------|--------|---------|--------|
| C(55)  | 29(2)   | 51(2)  | 75(3)  | 4(2)   | -14(2)  | 1(2)   |
| C(56)  | 31(2)   | 42(2)  | 51(2)  | 4(2)   | -12(1)  | -4(1)  |
| C(1S)  | 63(3)   | 61(3)  | 71(3)  | -14(2) | -21(2)  | 17(2)  |
| Cl(1S) | 70(1)   | 82(1)  | 90(1)  | 19(1)  | 2(1)    | -2(1)  |
| Cl(2S) | 66(1)   | 79(1)  | 109(1) | 17(1)  | -2(1)   | -11(1) |
| C(2SA) | 166(10) | 122(8) | 97(7)  | -31(5) | 71(6)   | -35(6) |
| C(2SB) | 560(7)  | 270(3) | 440(6) | 130(3) | -160(5) | -20(4) |
| Cl(3S) | 85(1)   | 66(1)  | 46(1)  | 11(1)  | 2(1)    | 7(1)   |
| Cl(4S) | 102(5)  | 113(5) | 104(4) | 11(3)  | 19(4)   | -41(3) |
| Cl(4T) | 75(5)   | 123(8) | 93(7)  | 63(7)  | 4(4)    | -5(5)  |
| Cl(4U) | 116(8)  | 101(6) | 100(8) | 39(5)  | 38(6)   | 9(5)   |

Table 5. Complete bond lengths [Å] and angles [deg] for (*R<sub>P</sub>*,*R<sub>m</sub>*,*R<sub>m</sub>*,*R<sub>P</sub>*)-(-)-2,2'-Bis(2-biphenylphenylphosphinoxy)-1,1'-biferrocenyl bisdichloromethane solvate, (*R<sub>P</sub>*,*R<sub>m</sub>*,*R<sub>m</sub>*,*R<sub>P</sub>*)-**6b**·2CH<sub>2</sub>Cl<sub>2</sub>, C<sub>56</sub>H<sub>44</sub>Fe<sub>2</sub>O<sub>2</sub>P<sub>2</sub>·2CH<sub>2</sub>Cl<sub>2</sub>).

|              |          |             |          |
|--------------|----------|-------------|----------|
| Bond lengths |          | C(9)-C(10)  | 1.410(4) |
|              |          | C(9)-H(9)   | 0.94     |
| Fe(1)-C(8)   | 2.037(3) | C(10)-H(10) | 0.94     |
| Fe(1)-C(7)   | 2.041(3) | C(11)-C(12) | 1.393(4) |
| Fe(1)-C(5)   | 2.047(3) | C(11)-C(16) | 1.396(4) |
| Fe(1)-C(1)   | 2.051(3) | C(12)-C(13) | 1.392(5) |
| Fe(1)-C(9)   | 2.054(3) | C(12)-H(12) | 0.94     |
| Fe(1)-C(4)   | 2.055(3) | C(13)-C(14) | 1.399(5) |
| Fe(1)-C(3)   | 2.060(3) | C(13)-H(13) | 0.94     |
| Fe(1)-C(2)   | 2.061(3) | C(14)-C(15) | 1.376(5) |
| Fe(1)-C(10)  | 2.068(3) | C(14)-H(14) | 0.94     |
| Fe(1)-C(6)   | 2.071(3) | C(15)-C(16) | 1.399(4) |
|              |          | C(15)-H(15) | 0.94     |
| Fe(2)-C(35)  | 2.043(3) | C(16)-H(16) | 0.94     |
| Fe(2)-C(36)  | 2.046(3) | C(17)-C(18) | 1.402(4) |
| Fe(2)-C(33)  | 2.053(3) | C(17)-C(22) | 1.406(4) |
| Fe(2)-C(29)  | 2.054(3) | C(18)-C(19) | 1.403(4) |
| Fe(2)-C(34)  | 2.054(3) | C(18)-H(18) | 0.94     |
| Fe(2)-C(30)  | 2.055(3) | C(19)-C(20) | 1.377(5) |
| Fe(2)-C(32)  | 2.058(3) | C(19)-H(19) | 0.94     |
| Fe(2)-C(31)  | 2.059(3) | C(20)-C(21) | 1.388(5) |
| Fe(2)-C(38)  | 2.063(3) | C(20)-H(20) | 0.94     |
| Fe(2)-C(37)  | 2.063(3) | C(21)-C(22) | 1.411(4) |
|              |          | C(21)-H(21) | 0.94     |
| P(1)-O(1)    | 1.484(2) | C(22)-C(23) | 1.501(4) |
| P(1)-C(7)    | 1.801(3) | C(23)-C(24) | 1.392(4) |
| P(1)-C(11)   | 1.812(3) | C(23)-C(28) | 1.394(5) |
| P(1)-C(17)   | 1.824(3) | C(24)-C(25) | 1.396(5) |
| P(2)-O(2)    | 1.491(2) | C(24)-H(24) | 0.94     |
| P(2)-C(35)   | 1.799(3) | C(25)-C(26) | 1.377(6) |
| P(2)-C(39)   | 1.820(3) | C(25)-H(25) | 0.94     |
| P(2)-C(45)   | 1.821(3) | C(26)-C(27) | 1.377(6) |
|              |          | C(26)-H(26) | 0.94     |
| C(1)-C(5)    | 1.412(5) | C(27)-C(28) | 1.387(5) |
| C(1)-C(2)    | 1.412(5) | C(27)-H(27) | 0.94     |
| C(1)-H(1)    | 0.94     | C(28)-H(28) | 0.94     |
| C(2)-C(3)    | 1.422(5) |             |          |
| C(2)-H(2)    | 0.94     | C(29)-C(33) | 1.414(6) |
| C(3)-C(4)    | 1.420(5) | C(29)-C(30) | 1.419(5) |
| C(3)-H(3)    | 0.94     | C(29)-H(29) | 0.94     |
| C(4)-C(5)    | 1.417(5) | C(30)-C(31) | 1.422(5) |
| C(4)-H(4)    | 0.94     | C(30)-H(30) | 0.94     |
| C(5)-H(5)    | 0.94     | C(31)-C(32) | 1.424(5) |
| C(6)-C(10)   | 1.430(4) | C(31)-H(31) | 0.94     |
| C(6)-C(7)    | 1.449(4) | C(32)-C(33) | 1.430(6) |
| C(6)-C(34)   | 1.484(4) | C(32)-H(32) | 0.94     |
| C(7)-C(8)    | 1.437(4) | C(33)-H(33) | 0.94     |
| C(8)-C(9)    | 1.422(5) | C(34)-C(38) | 1.427(4) |
| C(8)-H(8)    | 0.94     | C(34)-C(35) | 1.458(4) |

|                    |            |                   |            |
|--------------------|------------|-------------------|------------|
| C(35)-C(36)        | 1.438(4)   | C(1)-Fe(1)-C(9)   | 145.82(14) |
| C(36)-C(37)        | 1.416(4)   | C(8)-Fe(1)-C(4)   | 113.81(14) |
| C(36)-H(36)        | 0.94       | C(7)-Fe(1)-C(4)   | 147.19(14) |
| C(37)-C(38)        | 1.415(4)   | C(5)-Fe(1)-C(4)   | 40.41(15)  |
| C(37)-H(37)        | 0.94       | C(1)-Fe(1)-C(4)   | 67.88(15)  |
| C(38)-H(38)        | 0.94       | C(9)-Fe(1)-C(4)   | 106.79(15) |
| C(39)-C(44)        | 1.393(4)   | C(8)-Fe(1)-C(3)   | 109.03(14) |
| C(39)-C(40)        | 1.398(4)   | C(7)-Fe(1)-C(3)   | 117.03(13) |
| C(40)-C(41)        | 1.396(5)   | C(5)-Fe(1)-C(3)   | 67.79(14)  |
| C(40)-H(40)        | 0.94       | C(1)-Fe(1)-C(3)   | 67.74(14)  |
| C(41)-C(42)        | 1.371(5)   | C(9)-Fe(1)-C(3)   | 131.02(14) |
| C(41)-H(41)        | 0.94       | C(4)-Fe(1)-C(3)   | 40.37(15)  |
| C(42)-C(43)        | 1.376(5)   | C(8)-Fe(1)-C(2)   | 133.69(14) |
| C(42)-H(42)        | 0.94       | C(7)-Fe(1)-C(2)   | 111.49(12) |
| C(43)-C(44)        | 1.402(5)   | C(5)-Fe(1)-C(2)   | 67.69(15)  |
| C(43)-H(43)        | 0.94       | C(1)-Fe(1)-C(2)   | 40.16(14)  |
| C(44)-H(44)        | 0.94       | C(9)-Fe(1)-C(2)   | 171.06(14) |
| C(45)-C(46)        | 1.395(4)   | C(4)-Fe(1)-C(2)   | 67.89(15)  |
| C(45)-C(50)        | 1.420(4)   | C(3)-Fe(1)-C(2)   | 40.39(14)  |
| C(46)-C(47)        | 1.397(5)   | C(8)-Fe(1)-C(10)  | 68.17(13)  |
| C(46)-H(46)        | 0.94       | C(7)-Fe(1)-C(10)  | 68.55(11)  |
| C(47)-C(48)        | 1.381(6)   | C(5)-Fe(1)-C(10)  | 107.87(13) |
| C(47)-H(47)        | 0.94       | C(1)-Fe(1)-C(10)  | 116.15(14) |
| C(48)-C(49)        | 1.398(5)   | C(9)-Fe(1)-C(10)  | 40.01(13)  |
| C(48)-H(48)        | 0.94       | C(4)-Fe(1)-C(10)  | 129.82(14) |
| C(49)-C(50)        | 1.391(5)   | C(3)-Fe(1)-C(10)  | 168.85(13) |
| C(49)-H(49)        | 0.94       | C(2)-Fe(1)-C(10)  | 148.88(14) |
| C(50)-C(51)        | 1.495(4)   | C(8)-Fe(1)-C(6)   | 69.06(11)  |
| C(51)-C(56)        | 1.393(5)   | C(7)-Fe(1)-C(6)   | 41.26(11)  |
| C(51)-C(52)        | 1.395(5)   | C(5)-Fe(1)-C(6)   | 131.62(13) |
| C(52)-C(53)        | 1.389(5)   | C(1)-Fe(1)-C(6)   | 110.55(13) |
| C(52)-H(52)        | 0.94       | C(9)-Fe(1)-C(6)   | 68.16(11)  |
| C(53)-C(54)        | 1.384(5)   | C(4)-Fe(1)-C(6)   | 169.25(13) |
| C(53)-H(53)        | 0.94       | C(3)-Fe(1)-C(6)   | 149.90(12) |
| C(54)-C(55)        | 1.384(6)   | C(2)-Fe(1)-C(6)   | 118.31(12) |
| C(54)-H(54)        | 0.94       | C(10)-Fe(1)-C(6)  | 40.42(10)  |
| C(55)-C(56)        | 1.401(5)   |                   |            |
| C(55)-H(55)        | 0.94       | C(35)-Fe(2)-C(36) | 41.16(11)  |
| C(56)-H(56)        | 0.94       | C(35)-Fe(2)-C(33) | 170.77(15) |
|                    |            | C(36)-Fe(2)-C(33) | 146.27(17) |
| C(1S)-Cl(1S)       | 1.751(5)   | C(35)-Fe(2)-C(29) | 133.01(14) |
| C(1S)-Cl(2S)       | 1.762(5)   | C(36)-Fe(2)-C(29) | 172.33(14) |
| C(1S)-H(1SA)       | 0.98       | C(33)-Fe(2)-C(29) | 40.28(17)  |
| C(1S)-H(1SB)       | 0.98       | C(35)-Fe(2)-C(34) | 41.70(11)  |
|                    |            | C(36)-Fe(2)-C(34) | 69.26(12)  |
| C(2SA)-C(2SB)      | 1.11(5)    | C(33)-Fe(2)-C(34) | 130.03(14) |
| C(2SA)-Cl(4U)      | 1.462(12)  | C(29)-Fe(2)-C(34) | 109.48(13) |
| C(2SA)-Cl(4S)      | 1.659(11)  | C(35)-Fe(2)-C(30) | 110.73(12) |
| C(2SA)-Cl(3S)      | 1.796(8)   | C(36)-Fe(2)-C(30) | 132.93(13) |
| C(2SA)-Cl(4T)      | 1.869(17)  | C(33)-Fe(2)-C(30) | 68.06(16)  |
| C(2SB)-Cl(3S)      | 1.04(8)    | C(29)-Fe(2)-C(30) | 40.38(13)  |
| C(2SB)-Cl(4S)      | 2.21(6)    | C(34)-Fe(2)-C(30) | 118.03(12) |
| Cl(4S)-Cl(4T)      | 0.737(10)  | C(35)-Fe(2)-C(32) | 148.15(15) |
| Cl(4S)-Cl(4U)      | 1.096(11)  | C(36)-Fe(2)-C(32) | 114.89(16) |
| Cl(4T)-Cl(4U)      | 1.25(3)    | C(33)-Fe(2)-C(32) | 40.72(17)  |
|                    |            | C(29)-Fe(2)-C(32) | 67.92(17)  |
|                    |            | C(34)-Fe(2)-C(32) | 168.29(15) |
|                    |            | C(30)-Fe(2)-C(32) | 67.99(16)  |
|                    |            | C(35)-Fe(2)-C(31) | 117.21(13) |
|                    |            | C(36)-Fe(2)-C(31) | 109.16(14) |
|                    |            | C(33)-Fe(2)-C(31) | 68.27(15)  |
|                    |            | C(29)-Fe(2)-C(31) | 67.94(15)  |
|                    |            | C(34)-Fe(2)-C(31) | 150.39(13) |
|                    |            | C(30)-Fe(2)-C(31) | 40.43(14)  |
|                    |            | C(32)-Fe(2)-C(31) | 40.46(15)  |
|                    |            | C(35)-Fe(2)-C(38) | 68.74(12)  |
|                    |            | C(36)-Fe(2)-C(38) | 67.96(13)  |
|                    |            | C(33)-Fe(2)-C(38) | 107.37(14) |
| Bond angles [deg.] |            |                   |            |
| C(8)-Fe(1)-C(7)    | 41.28(11)  |                   |            |
| C(8)-Fe(1)-C(5)    | 144.89(14) |                   |            |
| C(7)-Fe(1)-C(5)    | 172.17(14) |                   |            |
| C(8)-Fe(1)-C(1)    | 173.33(14) |                   |            |
| C(7)-Fe(1)-C(1)    | 134.16(13) |                   |            |
| C(5)-Fe(1)-C(1)    | 40.30(15)  |                   |            |
| C(8)-Fe(1)-C(9)    | 40.69(13)  |                   |            |
| C(7)-Fe(1)-C(9)    | 68.74(12)  |                   |            |
| C(5)-Fe(1)-C(9)    | 113.37(15) |                   |            |

|                   |            |                   |            |
|-------------------|------------|-------------------|------------|
| C(29)-Fe(2)-C(38) | 116.37(14) | C(6)-C(7)-Fe(1)   | 70.48(15)  |
| C(34)-Fe(2)-C(38) | 40.57(11)  | P(1)-C(7)-Fe(1)   | 129.07(14) |
| C(30)-Fe(2)-C(38) | 149.48(13) | C(9)-C(8)-C(7)    | 107.9(3)   |
| C(32)-Fe(2)-C(38) | 129.28(15) | C(9)-C(8)-Fe(1)   | 70.30(18)  |
| C(31)-Fe(2)-C(38) | 168.23(13) | C(7)-C(8)-Fe(1)   | 69.51(16)  |
| C(35)-Fe(2)-C(37) | 68.61(12)  | C(9)-C(8)-H(8)    | 126.1      |
| C(36)-Fe(2)-C(37) | 40.30(12)  | C(7)-C(8)-H(8)    | 126.1      |
| C(33)-Fe(2)-C(37) | 114.24(16) | Fe(1)-C(8)-H(8)   | 125.7      |
| C(29)-Fe(2)-C(37) | 146.97(14) | C(10)-C(9)-C(8)   | 108.6(3)   |
| C(34)-Fe(2)-C(37) | 68.44(12)  | C(10)-C(9)-Fe(1)  | 70.56(17)  |
| C(30)-Fe(2)-C(37) | 170.22(14) | C(8)-C(9)-Fe(1)   | 69.01(17)  |
| C(32)-Fe(2)-C(37) | 107.11(16) | C(10)-C(9)-H(9)   | 125.7      |
| C(31)-Fe(2)-C(37) | 130.49(15) | C(8)-C(9)-H(9)    | 125.7      |
| C(38)-Fe(2)-C(37) | 40.11(12)  | Fe(1)-C(9)-H(9)   | 126.3      |
| O(1)-P(1)-C(7)    | 113.46(13) | C(9)-C(10)-C(6)   | 108.9(3)   |
| O(1)-P(1)-C(11)   | 113.20(13) | C(9)-C(10)-Fe(1)  | 69.43(17)  |
| C(7)-P(1)-C(11)   | 104.92(13) | C(6)-C(10)-Fe(1)  | 69.88(15)  |
| O(1)-P(1)-C(17)   | 111.92(13) | C(9)-C(10)-H(10)  | 125.5      |
| C(7)-P(1)-C(17)   | 104.91(13) | C(6)-C(10)-H(10)  | 125.5      |
| C(11)-P(1)-C(17)  | 107.80(13) | Fe(1)-C(10)-H(10) | 126.7      |
| O(2)-P(2)-C(35)   | 112.79(13) | C(12)-C(11)-C(16) | 119.6(3)   |
| O(2)-P(2)-C(39)   | 113.78(13) | C(12)-C(11)-P(1)  | 123.4(2)   |
| C(35)-P(2)-C(39)  | 105.86(13) | C(16)-C(11)-P(1)  | 116.9(2)   |
| O(2)-P(2)-C(45)   | 113.15(13) | C(13)-C(12)-C(11) | 120.5(3)   |
| C(35)-P(2)-C(45)  | 106.35(13) | C(13)-C(12)-H(12) | 119.7      |
| C(39)-P(2)-C(45)  | 104.15(14) | C(11)-C(12)-H(12) | 119.7      |
| C(5)-C(1)-C(2)    | 108.2(3)   | C(12)-C(13)-C(14) | 119.4(3)   |
| C(5)-C(1)-Fe(1)   | 69.7(2)    | C(12)-C(13)-H(13) | 120.3      |
| C(2)-C(1)-Fe(1)   | 70.28(19)  | C(14)-C(13)-H(13) | 120.3      |
| C(5)-C(1)-H(1)    | 125.9      | C(15)-C(14)-C(13) | 120.2(3)   |
| C(2)-C(1)-H(1)    | 125.9      | C(15)-C(14)-H(14) | 119.9      |
| Fe(1)-C(1)-H(1)   | 125.7      | C(13)-C(14)-H(14) | 119.9      |
| C(1)-C(2)-C(3)    | 107.9(3)   | C(14)-C(15)-C(16) | 120.5(3)   |
| C(1)-C(2)-Fe(1)   | 69.56(19)  | C(14)-C(15)-H(15) | 119.8      |
| C(3)-C(2)-Fe(1)   | 69.79(19)  | C(16)-C(15)-H(15) | 119.8      |
| C(1)-C(2)-H(2)    | 126.1      | C(11)-C(16)-C(15) | 119.6(3)   |
| C(3)-C(2)-H(2)    | 126.1      | C(11)-C(16)-H(16) | 120.2      |
| Fe(1)-C(2)-H(2)   | 126.2      | C(15)-C(16)-H(16) | 120.2      |
| C(4)-C(3)-C(2)    | 107.9(3)   | C(18)-C(17)-C(22) | 120.2(3)   |
| C(4)-C(3)-Fe(1)   | 69.61(19)  | C(18)-C(17)-P(1)  | 118.3(2)   |
| C(2)-C(3)-Fe(1)   | 69.82(18)  | C(22)-C(17)-P(1)  | 121.3(2)   |
| C(4)-C(3)-H(3)    | 126.1      | C(17)-C(18)-C(19) | 120.1(3)   |
| C(2)-C(3)-H(3)    | 126.1      | C(17)-C(18)-H(18) | 120.0      |
| Fe(1)-C(3)-H(3)   | 126.1      | C(19)-C(18)-H(18) | 120.0      |
| C(5)-C(4)-C(3)    | 107.7(3)   | C(20)-C(19)-C(18) | 119.8(3)   |
| C(5)-C(4)-Fe(1)   | 69.52(18)  | C(20)-C(19)-H(19) | 120.1      |
| C(3)-C(4)-Fe(1)   | 70.02(18)  | C(18)-C(19)-H(19) | 120.1      |
| C(5)-C(4)-H(4)    | 126.1      | C(19)-C(20)-C(21) | 120.8(3)   |
| C(3)-C(4)-H(4)    | 126.1      | C(19)-C(20)-H(20) | 119.6      |
| Fe(1)-C(4)-H(4)   | 125.9      | C(21)-C(20)-H(20) | 119.6      |
| C(1)-C(5)-C(4)    | 108.3(3)   | C(20)-C(21)-C(22) | 120.6(3)   |
| C(1)-C(5)-Fe(1)   | 69.99(18)  | C(20)-C(21)-H(21) | 119.7      |
| C(4)-C(5)-Fe(1)   | 70.07(19)  | C(22)-C(21)-H(21) | 119.7      |
| C(1)-C(5)-H(5)    | 125.9      | C(17)-C(22)-C(21) | 118.5(3)   |
| C(4)-C(5)-H(5)    | 125.9      | C(17)-C(22)-C(23) | 122.5(3)   |
| Fe(1)-C(5)-H(5)   | 125.7      | C(21)-C(22)-C(23) | 118.9(3)   |
| C(10)-C(6)-C(7)   | 107.0(2)   | C(24)-C(23)-C(28) | 118.4(3)   |
| C(10)-C(6)-C(34)  | 127.2(2)   | C(24)-C(23)-C(22) | 120.5(3)   |
| C(7)-C(6)-C(34)   | 125.7(2)   | C(28)-C(23)-C(22) | 121.1(3)   |
| C(10)-C(6)-Fe(1)  | 69.70(15)  | C(23)-C(24)-C(25) | 120.0(4)   |
| C(7)-C(6)-Fe(1)   | 68.25(15)  | C(23)-C(24)-H(24) | 120.0      |
| C(34)-C(6)-Fe(1)  | 129.69(18) | C(25)-C(24)-H(24) | 120.0      |
| C(8)-C(7)-C(6)    | 107.6(2)   | C(26)-C(25)-C(24) | 120.5(4)   |
| C(8)-C(7)-P(1)    | 126.1(2)   | C(26)-C(25)-H(25) | 119.7      |
| C(6)-C(7)-P(1)    | 126.2(2)   | C(24)-C(25)-H(25) | 119.7      |
| C(8)-C(7)-Fe(1)   | 69.21(16)  | C(27)-C(26)-C(25) | 120.2(4)   |
|                   |            | C(27)-C(26)-H(26) | 119.9      |
|                   |            | C(25)-C(26)-H(26) | 119.9      |

|                   |            |                      |          |
|-------------------|------------|----------------------|----------|
| C(26)-C(27)-C(28) | 119.5(4)   | C(44)-C(39)-P(2)     | 118.9(2) |
| C(26)-C(27)-H(27) | 120.2      | C(40)-C(39)-P(2)     | 120.9(2) |
| C(28)-C(27)-H(27) | 120.2      | C(41)-C(40)-C(39)    | 120.0(3) |
| C(27)-C(28)-C(23) | 121.4(3)   | C(41)-C(40)-H(40)    | 120.0    |
| C(27)-C(28)-H(28) | 119.3      | C(39)-C(40)-H(40)    | 120.0    |
| C(23)-C(28)-H(28) | 119.3      | C(42)-C(41)-C(40)    | 119.3(3) |
|                   |            | C(42)-C(41)-H(41)    | 120.4    |
| C(33)-C(29)-C(30) | 108.5(3)   | C(40)-C(41)-H(41)    | 120.4    |
| C(33)-C(29)-Fe(2) | 69.8(2)    | C(41)-C(42)-C(43)    | 121.7(3) |
| C(30)-C(29)-Fe(2) | 69.86(19)  | C(41)-C(42)-H(42)    | 119.2    |
| C(33)-C(29)-H(29) | 125.7      | C(43)-C(42)-H(42)    | 119.2    |
| C(30)-C(29)-H(29) | 125.7      | C(42)-C(43)-C(44)    | 119.9(3) |
| Fe(2)-C(29)-H(29) | 126.2      | C(42)-C(43)-H(43)    | 120.1    |
| C(29)-C(30)-C(31) | 108.0(3)   | C(44)-C(43)-H(43)    | 120.1    |
| C(29)-C(30)-Fe(2) | 69.76(19)  | C(39)-C(44)-C(43)    | 119.0(3) |
| C(31)-C(30)-Fe(2) | 69.9(2)    | C(39)-C(44)-H(44)    | 120.5    |
| C(29)-C(30)-H(30) | 126.0      | C(43)-C(44)-H(44)    | 120.5    |
| C(31)-C(30)-H(30) | 126.0      | C(46)-C(45)-C(50)    | 119.2(3) |
| Fe(2)-C(30)-H(30) | 125.9      | C(46)-C(45)-P(2)     | 120.0(2) |
| C(30)-C(31)-C(32) | 107.8(3)   | C(50)-C(45)-P(2)     | 120.8(2) |
| C(30)-C(31)-Fe(2) | 69.64(19)  | C(45)-C(46)-C(47)    | 121.3(3) |
| C(32)-C(31)-Fe(2) | 69.7(2)    | C(45)-C(46)-H(46)    | 119.4    |
| C(30)-C(31)-H(31) | 126.1      | C(47)-C(46)-H(46)    | 119.4    |
| C(32)-C(31)-H(31) | 126.1      | C(48)-C(47)-C(46)    | 119.3(3) |
| Fe(2)-C(31)-H(31) | 126.1      | C(48)-C(47)-H(47)    | 120.3    |
| C(31)-C(32)-C(33) | 107.9(4)   | C(46)-C(47)-H(47)    | 120.3    |
| C(31)-C(32)-Fe(2) | 69.83(18)  | C(47)-C(48)-C(49)    | 120.2(3) |
| C(33)-C(32)-Fe(2) | 69.44(19)  | C(47)-C(48)-H(48)    | 119.9    |
| C(31)-C(32)-H(32) | 126.1      | C(49)-C(48)-H(48)    | 119.9    |
| C(33)-C(32)-H(32) | 126.1      | C(50)-C(49)-C(48)    | 121.3(4) |
| Fe(2)-C(32)-H(32) | 126.3      | C(50)-C(49)-H(49)    | 119.4    |
| C(29)-C(33)-C(32) | 107.7(3)   | C(48)-C(49)-H(49)    | 119.4    |
| C(29)-C(33)-Fe(2) | 69.92(19)  | C(49)-C(50)-C(45)    | 118.6(3) |
| C(32)-C(33)-Fe(2) | 69.8(2)    | C(49)-C(50)-C(51)    | 119.3(3) |
| C(29)-C(33)-H(33) | 126.1      | C(45)-C(50)-C(51)    | 122.1(3) |
| C(32)-C(33)-H(33) | 126.1      | C(56)-C(51)-C(52)    | 118.5(3) |
| Fe(2)-C(33)-H(33) | 125.7      | C(56)-C(51)-C(50)    | 120.8(3) |
| C(38)-C(34)-C(35) | 106.9(2)   | C(52)-C(51)-C(50)    | 120.7(3) |
| C(38)-C(34)-C(6)  | 126.0(2)   | C(53)-C(52)-C(51)    | 120.7(3) |
| C(35)-C(34)-C(6)  | 127.0(2)   | C(53)-C(52)-H(52)    | 119.7    |
| C(38)-C(34)-Fe(2) | 70.05(16)  | C(51)-C(52)-H(52)    | 119.7    |
| C(35)-C(34)-Fe(2) | 68.73(15)  | C(54)-C(53)-C(52)    | 120.3(3) |
| C(6)-C(34)-Fe(2)  | 130.13(19) | C(54)-C(53)-H(53)    | 119.8    |
| C(36)-C(35)-C(34) | 107.2(2)   | C(52)-C(53)-H(53)    | 119.8    |
| C(36)-C(35)-P(2)  | 126.3(2)   | C(53)-C(54)-C(55)    | 120.0(3) |
| C(34)-C(35)-P(2)  | 126.5(2)   | C(53)-C(54)-H(54)    | 120.0    |
| C(36)-C(35)-Fe(2) | 69.54(17)  | C(55)-C(54)-H(54)    | 120.0    |
| C(34)-C(35)-Fe(2) | 69.56(15)  | C(54)-C(55)-C(56)    | 119.6(4) |
| P(2)-C(35)-Fe(2)  | 125.05(15) | C(54)-C(55)-H(55)    | 120.2    |
| C(37)-C(36)-C(35) | 108.4(3)   | C(56)-C(55)-H(55)    | 120.2    |
| C(37)-C(36)-Fe(2) | 70.51(19)  | C(51)-C(56)-C(55)    | 120.8(4) |
| C(35)-C(36)-Fe(2) | 69.30(16)  | C(51)-C(56)-H(56)    | 119.6    |
| C(37)-C(36)-H(36) | 125.8      | C(55)-C(56)-H(56)    | 119.6    |
| C(35)-C(36)-H(36) | 125.8      |                      |          |
| Fe(2)-C(36)-H(36) | 126.0      | Cl(1S)-C(1S)-Cl(2S)  | 112.4(2) |
| C(38)-C(37)-C(36) | 108.5(3)   | Cl(1S)-C(1S)-H(1SA)  | 109.1    |
| C(38)-C(37)-Fe(2) | 69.94(18)  | Cl(2S)-C(1S)-H(1SA)  | 109.1    |
| C(36)-C(37)-Fe(2) | 69.20(18)  | Cl(1S)-C(1S)-H(1SB)  | 109.1    |
| C(38)-C(37)-H(37) | 125.8      | Cl(2S)-C(1S)-H(1SB)  | 109.1    |
| C(36)-C(37)-H(37) | 125.8      | H(1SA)-C(1S)-H(1SB)  | 107.9    |
| Fe(2)-C(37)-H(37) | 126.7      |                      |          |
| C(37)-C(38)-C(34) | 109.1(3)   | Cl(3S)-C(2SA)-Cl(4S) | 112.4(5) |
| C(37)-C(38)-Fe(2) | 69.95(18)  | Cl(3S)-C(2SA)-Cl(4T) | 98.7(6)  |
| C(34)-C(38)-Fe(2) | 69.38(16)  | Cl(3S)-C(2SA)-Cl(4U) | 136.4(8) |
| C(37)-C(38)-H(38) | 125.5      | Cl(4S)-C(2SA)-Cl(4T) | 23.1(3)  |
| C(34)-C(38)-H(38) | 125.5      | Cl(4S)-C(2SA)-Cl(4U) | 40.5(5)  |
| Fe(2)-C(38)-H(38) | 126.8      | Cl(4T)-C(2SA)-Cl(4U) | 41.9(9)  |
| C(44)-C(39)-C(40) | 120.1(3)   |                      |          |

## Torsion angles [deg]

|               |              |                |              |
|---------------|--------------|----------------|--------------|
| C8-Fe1-C1-C5  | -143.7 (11)  | C8-Fe1-C4-C3   | 91.8 (2)     |
| C7-Fe1-C1-C5  | 171.9 (2)    | C7-Fe1-C4-C3   | 58.0 (3)     |
| C9-Fe1-C1-C5  | 49.8 (3)     | C5-Fe1-C4-C3   | -118.8 (3)   |
| C4-Fe1-C1-C5  | -37.7 (2)    | C1-Fe1-C4-C3   | -81.2 (2)    |
| C3-Fe1-C1-C5  | -81.4 (2)    | C9-Fe1-C4-C3   | 134.7 (2)    |
| C2-Fe1-C1-C5  | -119.2 (3)   | C2-Fe1-C4-C3   | -37.7 (2)    |
| C10-Fe1-C1-C5 | 87.1 (2)     | C10-Fe1-C4-C3  | 172.5 (2)    |
| C6-Fe1-C1-C5  | 130.9 (2)    | C6-Fe1-C4-C3   | -164.9 (7)   |
| C8-Fe1-C1-C2  | -24.5 (12)   | C2-C1-C5-C4    | -0.1 (4)     |
| C7-Fe1-C1-C2  | -69.0 (3)    | Fe1-C1-C5-C4   | 59.9 (2)     |
| C5-Fe1-C1-C2  | 119.2 (3)    | C2-C1-C5-Fe1   | -60.0 (2)    |
| C9-Fe1-C1-C2  | 169.0 (2)    | C3-C4-C5-C1    | 0.0 (4)      |
| C4-Fe1-C1-C2  | 81.5 (2)     | Fe1-C4-C5-C1   | -59.8 (2)    |
| C3-Fe1-C1-C2  | 37.7 (2)     | C3-C4-C5-Fe1   | 59.9 (2)     |
| C10-Fe1-C1-C2 | -153.75 (19) | C8-Fe1-C5-C1   | 173.1 (2)    |
| C6-Fe1-C1-C2  | -109.9 (2)   | C7-Fe1-C5-C1   | -48.1 (10)   |
| C5-C1-C2-C3   | 0.1 (4)      | C9-Fe1-C5-C1   | -152.1 (2)   |
| Fe1-C1-C2-C3  | -59.5 (2)    | C4-Fe1-C5-C1   | 119.1 (3)    |
| C5-C1-C2-Fe1  | 59.6 (2)     | C3-Fe1-C5-C1   | 81.3 (2)     |
| C8-Fe1-C2-C1  | 176.2 (2)    | C2-Fe1-C5-C1   | 37.5 (2)     |
| C7-Fe1-C2-C1  | 134.0 (2)    | C10-Fe1-C5-C1  | -109.6 (2)   |
| C5-Fe1-C2-C1  | -37.6 (2)    | C6-Fe1-C5-C1   | -71.2 (3)    |
| C9-Fe1-C2-C1  | -136.3 (8)   | C8-Fe1-C5-C4   | 54.0 (3)     |
| C4-Fe1-C2-C1  | -81.4 (2)    | C7-Fe1-C5-C4   | -167.2 (9)   |
| C3-Fe1-C2-C1  | -119.1 (3)   | C1-Fe1-C5-C4   | -119.1 (3)   |
| C10-Fe1-C2-C1 | 50.2 (3)     | C9-Fe1-C5-C4   | 88.7 (2)     |
| C6-Fe1-C2-C1  | 88.8 (2)     | C3-Fe1-C5-C4   | -37.8 (2)    |
| C8-Fe1-C2-C3  | -64.7 (3)    | C2-Fe1-C5-C4   | -81.6 (2)    |
| C7-Fe1-C2-C3  | -106.9 (2)   | C10-Fe1-C5-C4  | 131.2 (2)    |
| C5-Fe1-C2-C3  | 81.5 (2)     | C6-Fe1-C5-C4   | 169.6 (2)    |
| C1-Fe1-C2-C3  | 119.1 (3)    | C8-Fe1-C6-C10  | 80.52 (19)   |
| C9-Fe1-C2-C3  | -17.2 (10)   | C7-Fe1-C6-C10  | 118.9 (2)    |
| C4-Fe1-C2-C3  | 37.7 (2)     | C5-Fe1-C6-C10  | -65.8 (2)    |
| C10-Fe1-C2-C3 | 169.3 (2)    | C1-Fe1-C6-C10  | -106.6 (2)   |
| C6-Fe1-C2-C3  | -152.05 (19) | C9-Fe1-C6-C10  | 36.68 (19)   |
| C1-C2-C3-C4   | -0.1 (4)     | C4-Fe1-C6-C10  | -27.1 (8)    |
| Fe1-C2-C3-C4  | -59.4 (2)    | C3-Fe1-C6-C10  | 172.6 (3)    |
| C1-C2-C3-Fe1  | 59.3 (2)     | C2-Fe1-C6-C10  | -150.13 (19) |
| C8-Fe1-C3-C4  | -104.7 (2)   | C8-Fe1-C6-C7   | -38.37 (16)  |
| C7-Fe1-C3-C4  | -148.9 (2)   | C5-Fe1-C6-C7   | 175.34 (19)  |
| C5-Fe1-C3-C4  | 37.9 (2)     | C1-Fe1-C6-C7   | 134.50 (17)  |
| C1-Fe1-C3-C4  | 81.6 (2)     | C9-Fe1-C6-C7   | -82.22 (17)  |
| C9-Fe1-C3-C4  | -64.4 (3)    | C4-Fe1-C6-C7   | -146.0 (7)   |
| C2-Fe1-C3-C4  | 119.1 (3)    | C3-Fe1-C6-C7   | 53.7 (3)     |
| C10-Fe1-C3-C4 | -31.2 (8)    | C2-Fe1-C6-C7   | 90.97 (19)   |
| C6-Fe1-C3-C4  | 174.4 (2)    | C10-Fe1-C6-C7  | -118.9 (2)   |
| C8-Fe1-C3-C2  | 136.2 (2)    | C8-Fe1-C6-C34  | -157.4 (3)   |
| C7-Fe1-C3-C2  | 92.0 (2)     | C7-Fe1-C6-C34  | -119.1 (3)   |
| C5-Fe1-C3-C2  | -81.2 (2)    | C5-Fe1-C6-C34  | 56.3 (3)     |
| C1-Fe1-C3-C2  | -37.5 (2)    | C1-Fe1-C6-C34  | 15.4 (3)     |
| C9-Fe1-C3-C2  | 176.5 (2)    | C9-Fe1-C6-C34  | 158.7 (3)    |
| C4-Fe1-C3-C2  | -119.1 (3)   | C4-Fe1-C6-C34  | 95.0 (8)     |
| C10-Fe1-C3-C2 | -150.2 (7)   | C3-Fe1-C6-C34  | -65.4 (4)    |
| C6-Fe1-C3-C2  | 55.4 (3)     | C2-Fe1-C6-C34  | -28.1 (3)    |
| C2-C3-C4-C5   | 0.0 (4)      | C10-Fe1-C6-C34 | 122.0 (3)    |
| Fe1-C3-C4-C5  | -59.5 (2)    | C10-C6-C7-C8   | 0.4 (3)      |
| C2-C3-C4-Fe1  | 59.6 (2)     | C34-C6-C7-C8   | -176.4 (2)   |
| C8-Fe1-C4-C5  | -149.4 (2)   | Fe1-C6-C7-C8   | 59.52 (19)   |
| C7-Fe1-C4-C5  | 176.8 (2)    | C10-C6-C7-P1   | 176.1 (2)    |
| C1-Fe1-C4-C5  | 37.6 (2)     | C34-C6-C7-P1   | -0.6 (4)     |
| C9-Fe1-C4-C5  | -106.5 (2)   | Fe1-C6-C7-P1   | -124.7 (2)   |
| C3-Fe1-C4-C5  | 118.8 (3)    | C10-C6-C7-Fe1  | -59.17 (18)  |
| C2-Fe1-C4-C5  | 81.1 (2)     | C34-C6-C7-Fe1  | 124.1 (3)    |
| C10-Fe1-C4-C5 | -68.7 (3)    | O1-P1-C7-C8    | -168.7 (2)   |
| C6-Fe1-C4-C5  | -46.1 (8)    | C11-P1-C7-C8   | -44.6 (3)    |
|               |              | C17-P1-C7-C8   | 68.8 (3)     |
|               |              | O1-P1-C7-C6    | 16.3 (3)     |
|               |              | C11-P1-C7-C6   | 140.3 (2)    |

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|---------------|-------------|-----------------|------------|
| C17-P1-C7-C6  | -106.2(2)   | C6-Fe1-C9-C8    | 82.86(18)  |
| O1-P1-C7-Fe1  | -77.3(2)    | C8-C9-C10-C6    | 0.2(3)     |
| C11-P1-C7-Fe1 | 46.8(2)     | Fe1-C9-C10-C6   | 58.9(2)    |
| C17-P1-C7-Fe1 | 160.29(17)  | C8-C9-C10-Fe1   | -58.7(2)   |
| C5-Fe1-C7-C8  | -145.0(9)   | C7-C6-C10-C9    | -0.3(3)    |
| C1-Fe1-C7-C8  | 172.9(2)    | C34-C6-C10-C9   | 176.4(3)   |
| C9-Fe1-C7-C8  | -37.81(18)  | Fe1-C6-C10-C9   | -58.6(2)   |
| C4-Fe1-C7-C8  | 50.4(3)     | C7-C6-C10-Fe1   | 58.25(18)  |
| C3-Fe1-C7-C8  | 88.5(2)     | C34-C6-C10-Fe1  | -125.0(3)  |
| C2-Fe1-C7-C8  | 132.60(19)  | C8-Fe1-C10-C9   | 37.51(19)  |
| C10-Fe1-C7-C8 | -80.91(19)  | C7-Fe1-C10-C9   | 82.1(2)    |
| C6-Fe1-C7-C8  | -118.5(2)   | C5-Fe1-C10-C9   | -105.3(2)  |
| C8-Fe1-C7-C6  | 118.5(2)    | C1-Fe1-C10-C9   | -148.1(2)  |
| C5-Fe1-C7-C6  | -26.5(10)   | C4-Fe1-C10-C9   | -65.9(3)   |
| C1-Fe1-C7-C6  | -68.6(2)    | C3-Fe1-C10-C9   | -40.0(8)   |
| C9-Fe1-C7-C6  | 80.68(17)   | C2-Fe1-C10-C9   | 178.4(2)   |
| C4-Fe1-C7-C6  | 168.9(2)    | C6-Fe1-C10-C9   | 120.4(3)   |
| C3-Fe1-C7-C6  | -153.01(17) | C8-Fe1-C10-C6   | -82.91(18) |
| C2-Fe1-C7-C6  | -108.91(17) | C7-Fe1-C10-C6   | -38.35(17) |
| C10-Fe1-C7-C6 | 37.58(15)   | C5-Fe1-C10-C6   | 134.26(19) |
| C8-Fe1-C7-P1  | -120.2(3)   | C1-Fe1-C10-C6   | 91.5(2)    |
| C5-Fe1-C7-P1  | 94.9(10)    | C9-Fe1-C10-C6   | -120.4(3)  |
| C1-Fe1-C7-P1  | 52.7(3)     | C4-Fe1-C10-C6   | 173.65(19) |
| C9-Fe1-C7-P1  | -158.0(2)   | C3-Fe1-C10-C6   | -160.5(7)  |
| C4-Fe1-C7-P1  | -69.8(3)    | C2-Fe1-C10-C6   | 58.0(3)    |
| C3-Fe1-C7-P1  | -31.7(2)    | O1-P1-C11-C12   | -169.4(2)  |
| C2-Fe1-C7-P1  | 12.4(2)     | C7-P1-C11-C12   | 66.4(3)    |
| C10-Fe1-C7-P1 | 158.9(2)    | C17-P1-C11-C12  | -45.1(3)   |
| C6-Fe1-C7-P1  | 121.3(3)    | O1-P1-C11-C16   | 13.9(3)    |
| C6-C7-C8-C9   | -0.2(3)     | C7-P1-C11-C16   | -110.3(2)  |
| P1-C7-C8-C9   | -176.0(2)   | C17-P1-C11-C16  | 138.2(2)   |
| Fe1-C7-C8-C9  | 60.1(2)     | C16-C11-C12-C13 | 3.5(5)     |
| C6-C7-C8-Fe1  | -60.33(18)  | P1-C11-C12-C13  | -173.1(2)  |
| P1-C7-C8-Fe1  | 123.9(2)    | C11-C12-C13-C14 | 0.1(5)     |
| C7-Fe1-C8-C9  | -118.8(2)   | C12-C13-C14-C15 | -4.1(5)    |
| C5-Fe1-C8-C9  | 53.4(3)     | C13-C14-C15-C16 | 4.5(5)     |
| C1-Fe1-C8-C9  | -168.4(11)  | C12-C11-C16-C15 | -3.2(4)    |
| C4-Fe1-C8-C9  | 88.3(2)     | P1-C11-C16-C15  | 173.6(2)   |
| C3-Fe1-C8-C9  | 131.57(19)  | C14-C15-C16-C11 | -0.8(5)    |
| C2-Fe1-C8-C9  | 169.9(2)    | O1-P1-C17-C18   | -101.8(2)  |
| C10-Fe1-C8-C9 | -36.90(18)  | C7-P1-C17-C18   | 21.7(3)    |
| C6-Fe1-C8-C9  | -80.45(19)  | C11-P1-C17-C18  | 133.1(2)   |
| C5-Fe1-C8-C7  | 172.2(2)    | O1-P1-C17-C22   | 72.0(3)    |
| C1-Fe1-C8-C7  | -49.6(12)   | C7-P1-C17-C22   | -164.6(2)  |
| C9-Fe1-C8-C7  | 118.8(2)    | C11-P1-C17-C22  | -53.1(3)   |
| C4-Fe1-C8-C7  | -152.84(18) | C22-C17-C18-C19 | 0.0(5)     |
| C3-Fe1-C8-C7  | -109.62(18) | P1-C17-C18-C19  | 173.8(2)   |
| C2-Fe1-C8-C7  | -71.3(2)    | C17-C18-C19-C20 | -0.1(5)    |
| C10-Fe1-C8-C7 | 81.90(18)   | C18-C19-C20-C21 | 0.7(5)     |
| C6-Fe1-C8-C7  | 38.36(16)   | C19-C20-C21-C22 | -1.3(5)    |
| C7-C8-C9-C10  | 0.0(3)      | C18-C17-C22-C21 | -0.5(4)    |
| Fe1-C8-C9-C10 | 59.6(2)     | P1-C17-C22-C21  | -174.2(2)  |
| C7-C8-C9-Fe1  | -59.6(2)    | C18-C17-C22-C23 | 179.2(3)   |
| C8-Fe1-C9-C10 | -119.9(3)   | P1-C17-C22-C23  | 5.6(4)     |
| C7-Fe1-C9-C10 | -81.55(19)  | C20-C21-C22-C17 | 1.2(5)     |
| C5-Fe1-C9-C10 | 90.3(2)     | C20-C21-C22-C23 | -178.6(3)  |
| C1-Fe1-C9-C10 | 57.7(3)     | C17-C22-C23-C24 | 110.3(3)   |
| C4-Fe1-C9-C10 | 132.9(2)    | C21-C22-C23-C24 | -69.9(4)   |
| C3-Fe1-C9-C10 | 170.51(19)  | C17-C22-C23-C28 | -68.7(4)   |
| C2-Fe1-C9-C10 | -174.8(8)   | C21-C22-C23-C28 | 111.1(3)   |
| C6-Fe1-C9-C10 | -37.03(17)  | C28-C23-C24-C25 | 0.2(5)     |
| C7-Fe1-C9-C8  | 38.34(17)   | C22-C23-C24-C25 | -178.8(3)  |
| C5-Fe1-C9-C8  | -149.81(19) | C23-C24-C25-C26 | 0.3(5)     |
| C1-Fe1-C9-C8  | 177.6(2)    | C24-C25-C26-C27 | -0.4(6)    |
| C4-Fe1-C9-C8  | -107.2(2)   | C25-C26-C27-C28 | 0.0(6)     |
| C3-Fe1-C9-C8  | -69.6(2)    | C26-C27-C28-C23 | 0.5(5)     |
| C2-Fe1-C9-C8  | -54.9(9)    | C24-C23-C28-C27 | -0.6(5)    |
| C10-Fe1-C9-C8 | 119.9(3)    | C22-C23-C28-C27 | 178.4(3)   |

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|-----------------|-------------|-----------------|-------------|
| C35-Fe2-C29-C33 | 170.8(2)    | C34-Fe2-C32-C33 | -41.7(9)    |
| C36-Fe2-C29-C33 | -151.1(10)  | C30-Fe2-C32-C33 | 81.5(3)     |
| C34-Fe2-C29-C33 | 129.6(2)    | C31-Fe2-C32-C33 | 119.2(4)    |
| C30-Fe2-C29-C33 | -119.7(3)   | C38-Fe2-C32-C33 | -69.0(3)    |
| C32-Fe2-C29-C33 | -38.2(2)    | C37-Fe2-C32-C33 | -107.5(3)   |
| C31-Fe2-C29-C33 | -82.0(2)    | C30-C29-C33-C32 | 0.5(4)      |
| C38-Fe2-C29-C33 | 86.0(2)     | Fe2-C29-C33-C32 | 59.9(3)     |
| C37-Fe2-C29-C33 | 49.5(4)     | C30-C29-C33-Fe2 | -59.3(2)    |
| C35-Fe2-C29-C30 | -69.5(3)    | C31-C32-C33-C29 | -0.4(4)     |
| C36-Fe2-C29-C30 | -31.5(11)   | Fe2-C32-C33-C29 | -59.9(2)    |
| C33-Fe2-C29-C30 | 119.7(3)    | C31-C32-C33-Fe2 | 59.5(2)     |
| C34-Fe2-C29-C30 | -110.7(2)   | C35-Fe2-C33-C29 | -46.9(10)   |
| C32-Fe2-C29-C30 | 81.5(2)     | C36-Fe2-C33-C29 | 173.3(2)    |
| C31-Fe2-C29-C30 | 37.7(2)     | C34-Fe2-C33-C29 | -71.5(3)    |
| C38-Fe2-C29-C30 | -154.31(19) | C30-Fe2-C33-C29 | 37.4(2)     |
| C37-Fe2-C29-C30 | 169.2(2)    | C32-Fe2-C33-C29 | 118.7(4)    |
| C33-C29-C30-C31 | -0.4(4)     | C31-Fe2-C33-C29 | 81.1(2)     |
| Fe2-C29-C30-C31 | -59.7(2)    | C38-Fe2-C33-C29 | -110.5(2)   |
| C33-C29-C30-Fe2 | 59.3(2)     | C37-Fe2-C33-C29 | -153.0(2)   |
| C35-Fe2-C30-C29 | 132.9(2)    | C35-Fe2-C33-C32 | -165.6(8)   |
| C36-Fe2-C30-C29 | 174.5(2)    | C36-Fe2-C33-C32 | 54.7(4)     |
| C33-Fe2-C30-C29 | -37.3(2)    | C29-Fe2-C33-C32 | -118.7(4)   |
| C34-Fe2-C30-C29 | 87.6(2)     | C34-Fe2-C33-C32 | 169.8(2)    |
| C32-Fe2-C30-C29 | -81.3(2)    | C30-Fe2-C33-C32 | -81.3(3)    |
| C31-Fe2-C30-C29 | -119.1(3)   | C31-Fe2-C33-C32 | -37.6(3)    |
| C38-Fe2-C30-C29 | 49.9(3)     | C38-Fe2-C33-C32 | 130.8(3)    |
| C37-Fe2-C30-C29 | -142.8(7)   | C37-Fe2-C33-C32 | 88.4(3)     |
| C35-Fe2-C30-C31 | -108.0(2)   | C10-C6-C34-C38  | 117.3(3)    |
| C36-Fe2-C30-C31 | -66.4(3)    | C7-C6-C34-C38   | -66.6(4)    |
| C33-Fe2-C30-C31 | 81.8(2)     | Fe1-C6-C34-C38  | 23.6(4)     |
| C29-Fe2-C30-C31 | 119.1(3)    | C10-C6-C34-C35  | -68.5(4)    |
| C34-Fe2-C30-C31 | -153.38(19) | C7-C6-C34-C35   | 107.6(3)    |
| C32-Fe2-C30-C31 | 37.7(2)     | Fe1-C6-C34-C35  | -162.2(2)   |
| C38-Fe2-C30-C31 | 169.0(2)    | C10-C6-C34-Fe2  | 23.8(4)     |
| C37-Fe2-C30-C31 | -23.8(9)    | C7-C6-C34-Fe2   | -160.1(2)   |
| C29-C30-C31-C32 | 0.1(4)      | Fe1-C6-C34-Fe2  | -69.9(3)    |
| Fe2-C30-C31-C32 | -59.5(2)    | C35-Fe2-C34-C38 | 118.2(2)    |
| C29-C30-C31-Fe2 | 59.6(2)     | C36-Fe2-C34-C38 | 79.93(19)   |
| C35-Fe2-C31-C30 | 90.6(2)     | C33-Fe2-C34-C38 | -67.6(3)    |
| C36-Fe2-C31-C30 | 134.7(2)    | C29-Fe2-C34-C38 | -108.1(2)   |
| C33-Fe2-C31-C30 | -81.2(2)    | C30-Fe2-C34-C38 | -151.50(18) |
| C29-Fe2-C31-C30 | -37.7(2)    | C32-Fe2-C34-C38 | -33.0(8)    |
| C34-Fe2-C31-C30 | 53.2(4)     | C31-Fe2-C34-C38 | 172.5(3)    |
| C32-Fe2-C31-C30 | -119.1(3)   | C37-Fe2-C34-C38 | 36.59(18)   |
| C38-Fe2-C31-C30 | -151.5(6)   | C36-Fe2-C34-C35 | -38.27(16)  |
| C37-Fe2-C31-C30 | 174.83(19)  | C33-Fe2-C34-C35 | 174.2(2)    |
| C35-Fe2-C31-C32 | -150.4(2)   | C29-Fe2-C34-C35 | 133.67(17)  |
| C36-Fe2-C31-C32 | -106.2(3)   | C30-Fe2-C34-C35 | 90.30(18)   |
| C33-Fe2-C31-C32 | 37.8(3)     | C32-Fe2-C34-C35 | -151.2(7)   |
| C29-Fe2-C31-C32 | 81.4(3)     | C31-Fe2-C34-C35 | 54.3(3)     |
| C34-Fe2-C31-C32 | 172.3(3)    | C38-Fe2-C34-C35 | -118.2(2)   |
| C30-Fe2-C31-C32 | 119.1(3)    | C37-Fe2-C34-C35 | -81.61(17)  |
| C38-Fe2-C31-C32 | -32.4(8)    | C35-Fe2-C34-C6  | -121.0(3)   |
| C37-Fe2-C31-C32 | -66.1(3)    | C36-Fe2-C34-C6  | -159.3(3)   |
| C30-C31-C32-C33 | 0.2(4)      | C33-Fe2-C34-C6  | 53.2(3)     |
| Fe2-C31-C32-C33 | -59.2(3)    | C29-Fe2-C34-C6  | 12.6(3)     |
| C30-C31-C32-Fe2 | 59.4(2)     | C30-Fe2-C34-C6  | -30.7(3)    |
| C35-Fe2-C32-C31 | 56.5(4)     | C32-Fe2-C34-C6  | 87.7(8)     |
| C36-Fe2-C32-C31 | 90.8(3)     | C31-Fe2-C34-C6  | -66.8(4)    |
| C33-Fe2-C32-C31 | -119.2(4)   | C38-Fe2-C34-C6  | 120.8(3)    |
| C29-Fe2-C32-C31 | -81.4(3)    | C37-Fe2-C34-C6  | 157.4(3)    |
| C34-Fe2-C32-C31 | -160.9(7)   | C38-C34-C35-C36 | -0.3(3)     |
| C30-Fe2-C32-C31 | -37.7(2)    | C6-C34-C35-C36  | -175.4(3)   |
| C38-Fe2-C32-C31 | 171.9(2)    | Fe2-C34-C35-C36 | 59.64(19)   |
| C37-Fe2-C32-C31 | 133.3(2)    | C38-C34-C35-P2  | -179.1(2)   |
| C35-Fe2-C32-C33 | 175.7(3)    | C6-C34-C35-P2   | 5.8(4)      |
| C36-Fe2-C32-C33 | -150.0(3)   | Fe2-C34-C35-P2  | -119.1(2)   |
| C29-Fe2-C32-C33 | 37.8(3)     | C38-C34-C35-Fe2 | -59.96(19)  |

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| C6-C34-C35-Fe2  | 124.9(3)    | C33-Fe2-C37-C36 | -151.6(2)  |
| O2-P2-C35-C36   | -166.2(2)   | C29-Fe2-C37-C36 | 175.8(2)   |
| C39-P2-C35-C36  | -41.1(3)    | C34-Fe2-C37-C36 | 82.95(19)  |
| C45-P2-C35-C36  | 69.2(3)     | C30-Fe2-C37-C36 | -50.1(8)   |
| O2-P2-C35-C34   | 12.3(3)     | C32-Fe2-C37-C36 | -108.5(2)  |
| C39-P2-C35-C34  | 137.4(2)    | C31-Fe2-C37-C36 | -70.2(2)   |
| C45-P2-C35-C34  | -112.3(2)   | C38-Fe2-C37-C36 | 119.9(3)   |
| O2-P2-C35-Fe2   | -77.0(2)    | C36-C37-C38-C34 | -0.2(4)    |
| C39-P2-C35-Fe2  | 48.0(2)     | Fe2-C37-C38-C34 | 58.5(2)    |
| C45-P2-C35-Fe2  | 158.41(16)  | C36-C37-C38-Fe2 | -58.6(2)   |
| C33-Fe2-C35-C36 | -147.0(9)   | C35-C34-C38-C37 | 0.3(3)     |
| C29-Fe2-C35-C36 | 172.81(19)  | C6-C34-C38-C37  | 175.5(3)   |
| C34-Fe2-C35-C36 | -118.4(2)   | Fe2-C34-C38-C37 | -58.8(2)   |
| C30-Fe2-C35-C36 | 132.34(19)  | C35-C34-C38-Fe2 | 59.12(18)  |
| C32-Fe2-C35-C36 | 51.0(3)     | C6-C34-C38-Fe2  | -125.7(3)  |
| C31-Fe2-C35-C36 | 88.4(2)     | C35-Fe2-C38-C37 | 81.64(19)  |
| C38-Fe2-C35-C36 | -80.40(19)  | C36-Fe2-C38-C37 | 37.20(18)  |
| C37-Fe2-C35-C36 | -37.20(18)  | C33-Fe2-C38-C37 | -107.2(2)  |
| C36-Fe2-C35-C34 | 118.4(2)    | C29-Fe2-C38-C37 | -149.8(2)  |
| C33-Fe2-C35-C34 | -28.6(10)   | C34-Fe2-C38-C37 | 120.6(3)   |
| C29-Fe2-C35-C34 | -68.8(2)    | C30-Fe2-C38-C37 | 176.7(2)   |
| C30-Fe2-C35-C34 | -109.30(17) | C32-Fe2-C38-C37 | -67.6(3)   |
| C32-Fe2-C35-C34 | 169.3(3)    | C31-Fe2-C38-C37 | -40.9(7)   |
| C31-Fe2-C35-C34 | -153.20(18) | C35-Fe2-C38-C34 | -38.99(16) |
| C38-Fe2-C35-C34 | 37.95(16)   | C36-Fe2-C38-C34 | -83.43(18) |
| C37-Fe2-C35-C34 | 81.16(17)   | C33-Fe2-C38-C34 | 132.1(2)   |
| C36-Fe2-C35-P2  | -120.7(3)   | C29-Fe2-C38-C34 | 89.6(2)    |
| C33-Fe2-C35-P2  | 92.3(9)     | C30-Fe2-C38-C34 | 56.0(3)    |
| C29-Fe2-C35-P2  | 52.1(3)     | C32-Fe2-C38-C34 | 171.8(2)   |
| C34-Fe2-C35-P2  | 120.9(2)    | C31-Fe2-C38-C34 | -161.5(6)  |
| C30-Fe2-C35-P2  | 11.6(2)     | C37-Fe2-C38-C34 | -120.6(3)  |
| C32-Fe2-C35-P2  | -69.7(3)    | O2-P2-C39-C44   | 8.8(3)     |
| C31-Fe2-C35-P2  | -32.3(2)    | C35-P2-C39-C44  | -115.6(2)  |
| C38-Fe2-C35-P2  | 158.9(2)    | C45-P2-C39-C44  | 132.5(2)   |
| C37-Fe2-C35-P2  | -157.9(2)   | O2-P2-C39-C40   | -171.0(2)  |
| C34-C35-C36-C37 | 0.2(3)      | C35-P2-C39-C40  | 64.6(3)    |
| P2-C35-C36-C37  | 179.0(2)    | C45-P2-C39-C40  | -47.3(3)   |
| Fe2-C35-C36-C37 | 59.9(2)     | C44-C39-C40-C41 | 2.4(4)     |
| C34-C35-C36-Fe2 | -59.65(18)  | P2-C39-C40-C41  | -177.8(2)  |
| P2-C35-C36-Fe2  | 119.1(2)    | C39-C40-C41-C42 | -1.7(5)    |
| C35-Fe2-C36-C37 | -119.5(3)   | C40-C41-C42-C43 | 0.6(6)     |
| C33-Fe2-C36-C37 | 51.5(3)     | C41-C42-C43-C44 | -0.3(6)    |
| C29-Fe2-C36-C37 | -162.7(10)  | C40-C39-C44-C43 | -2.0(4)    |
| C34-Fe2-C36-C37 | -80.73(19)  | P2-C39-C44-C43  | 178.2(2)   |
| C30-Fe2-C36-C37 | 169.8(2)    | C42-C43-C44-C39 | 1.0(5)     |
| C32-Fe2-C36-C37 | 87.4(2)     | O2-P2-C45-C46   | -109.4(3)  |
| C31-Fe2-C36-C37 | 130.8(2)    | C35-P2-C45-C46  | 15.0(3)    |
| C38-Fe2-C36-C37 | -37.04(18)  | C39-P2-C45-C46  | 126.5(3)   |
| C33-Fe2-C36-C35 | 170.9(2)    | O2-P2-C45-C50   | 71.2(3)    |
| C29-Fe2-C36-C35 | -43.3(11)   | C35-P2-C45-C50  | -164.4(2)  |
| C34-Fe2-C36-C35 | 38.76(16)   | C39-P2-C45-C50  | -52.8(3)   |
| C30-Fe2-C36-C35 | -70.8(2)    | C50-C45-C46-C47 | -0.5(5)    |
| C32-Fe2-C36-C35 | -153.13(19) | P2-C45-C46-C47  | -179.9(3)  |
| C31-Fe2-C36-C35 | -109.74(19) | C45-C46-C47-C48 | 0.5(6)     |
| C38-Fe2-C36-C35 | 82.45(18)   | C46-C47-C48-C49 | 1.0(7)     |
| C37-Fe2-C36-C35 | 119.5(3)    | C47-C48-C49-C50 | -2.4(7)    |
| C35-C36-C37-C38 | 0.0(4)      | C48-C49-C50-C45 | 2.4(6)     |
| Fe2-C36-C37-C38 | 59.1(2)     | C48-C49-C50-C51 | -178.9(4)  |
| C35-C36-C37-Fe2 | -59.1(2)    | C46-C45-C50-C49 | -0.9(5)    |
| C35-Fe2-C37-C38 | -81.97(18)  | P2-C45-C50-C49  | 178.4(3)   |
| C36-Fe2-C37-C38 | -119.9(3)   | C46-C45-C50-C51 | -179.6(3)  |
| C33-Fe2-C37-C38 | 88.5(2)     | P2-C45-C50-C51  | -0.3(4)    |
| C29-Fe2-C37-C38 | 55.9(3)     | C49-C50-C51-C56 | 114.7(4)   |
| C34-Fe2-C37-C38 | -36.99(17)  | C45-C50-C51-C56 | -66.6(4)   |
| C30-Fe2-C37-C38 | -170.0(7)   | C49-C50-C51-C52 | -66.9(4)   |
| C32-Fe2-C37-C38 | 131.5(2)    | C45-C50-C51-C52 | 111.8(4)   |
| C31-Fe2-C37-C38 | 169.89(19)  | C56-C51-C52-C53 | 1.3(5)     |
| C35-Fe2-C37-C36 | 37.98(18)   | C50-C51-C52-C53 | -177.2(3)  |

|                 |         |                 |          |
|-----------------|---------|-----------------|----------|
| C51-C52-C53-C54 | -0.1(5) | C52-C51-C56-C55 | -1.8(5)  |
| C52-C53-C54-C55 | -0.5(6) | C50-C51-C56-C55 | 176.6(3) |
| C53-C54-C55-C56 | 0.0(6)  | C54-C55-C56-C51 | 1.2(6)   |

Table S6. Crystal data and structure refinement for ( $R_p, R_m, S_m, S_p$ )-2,2'-Bis(2-biphenylphenylphosphinoxy)-1,1'-biferrocenyl, meso-**6b**,  $C_{56}H_{44}Fe_2O_2P_2$ .

|                                       |                                                                                                                                                      |
|---------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------|
| Identification code                   | widlj3fr                                                                                                                                             |
| Empirical formula                     | $C_{56}H_{44}Fe_2O_2P_2$                                                                                                                             |
| Formula weight                        | 922.55                                                                                                                                               |
| Temperature                           | 296(2) K                                                                                                                                             |
| Wavelength                            | 0.71073 Å                                                                                                                                            |
| Crystal system, space group           | triclinic, $P\bar{1}$ (No. 2)                                                                                                                        |
| Unit cell dimensions                  | $a = 8.289(4)$ Å $\alpha = 108.55(1)^\circ$<br>$b = 9.607(5)$ Å $\beta = 90.84(1)^\circ$<br>$c = 14.485(7)$ Å $\gamma = 96.99(1)^\circ$              |
| Volume                                | $1083.7(9)$ Å <sup>3</sup>                                                                                                                           |
| Z, Calculated density                 | 1, 1.414 Mg/m <sup>3</sup>                                                                                                                           |
| Absorption coefficient                | $0.788$ mm <sup>-1</sup>                                                                                                                             |
| F(000)                                | 478                                                                                                                                                  |
| Crystal size                          | 0.22 × 0.10 × 0.07 mm, orange prism                                                                                                                  |
| Diffractometer                        | Siemens SMART 3-circle with CCD area detector<br>(sealed X-ray tube, Mo K $\alpha$ radiation, graphite monochr., det.dist. 44.50 mm, 512x512 pixels) |
| Scan type / width / speed             | $\omega$ -scan frames / $\Delta\omega = 0.3^\circ$ / 30 sec. per frame<br>full sphere, 4 × 606 frames                                                |
| Theta range for data collection       | $2.26^\circ$ to $25.00^\circ$                                                                                                                        |
| Index ranges                          | $-9 \leq h \leq 9$ , $-11 \leq k \leq 10$ , $0 \leq l \leq 17$                                                                                       |
| Reflections collected / unique        | 11063 / 3801 [R(int) = 0.094, R(sigma) = 0.081]                                                                                                      |
| Completeness to theta = $25.00^\circ$ | 99.7%                                                                                                                                                |
| Absorption correction                 | Empirical (program XABS2)                                                                                                                            |
| Correction factors                    | 0.78 - 1.37 (reflection profile anisotropy!)                                                                                                         |
| Structure solution                    | Patterson method (program SHELXS97)                                                                                                                  |
| Refinement method                     | Full-matrix least-squares on $F^2$ (prg SHELXL97)                                                                                                    |
| Data / restraints / parameters        | 3801 / 0 / 280                                                                                                                                       |
| Goodness-of-fit on $F^2$              | 1.092                                                                                                                                                |
| Final R indices [I > 2sigma(I)]       | R1 = 0.0499, wR2 = 0.0906 (2654 data)                                                                                                                |
| R indices (all data)                  | R1 = 0.0889, wR2 = 0.1077 (3801 data)                                                                                                                |
| Largest diff. peak and hole           | 0.351 and -0.326 e Å <sup>-3</sup>                                                                                                                   |

$$R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|, \quad wR2 = [\Sigma(w(F_o^2 - F_c^2)^2) / \Sigma(w(F_o^2)^2)]^{1/2}$$

Table S7. Atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) of ( $R_p, R_m, S_m, S_p$ )-2,2'-Bis(2-biphenylphenylphosphinoxy)-1,1'-biferrocenyl, meso-**6b**,  $C_{56}H_{44}Fe_2O_2P_2$ .  $U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

|       | x           | y           | z          | $U_{eq}$ |
|-------|-------------|-------------|------------|----------|
| Fe    | 0.63956(7)  | 0.22775(6)  | 0.46204(4) | 37(1)    |
| P     | 0.59089(12) | 0.26950(11) | 0.70494(7) | 33(1)    |
| O     | 0.7297(3)   | 0.1983(3)   | 0.7247(2)  | 41(1)    |
| C(1)  | 0.8509(5)   | 0.1395(5)   | 0.4232(3)  | 52(1)    |
| C(2)  | 0.8830(5)   | 0.2737(5)   | 0.5015(3)  | 56(1)    |
| C(3)  | 0.8313(5)   | 0.3877(5)   | 0.4726(4)  | 58(1)    |
| C(4)  | 0.7698(6)   | 0.3239(5)   | 0.3748(4)  | 61(1)    |
| C(5)  | 0.7795(6)   | 0.1709(5)   | 0.3447(3)  | 57(1)    |
| C(6)  | 0.4845(4)   | 0.0744(4)   | 0.5004(3)  | 31(1)    |
| C(7)  | 0.5161(4)   | 0.2168(4)   | 0.5793(3)  | 31(1)    |
| C(8)  | 0.4620(5)   | 0.3258(4)   | 0.5424(3)  | 38(1)    |
| C(9)  | 0.4010(5)   | 0.2564(4)   | 0.4451(3)  | 41(1)    |
| C(10) | 0.4146(5)   | 0.1052(4)   | 0.4193(3)  | 35(1)    |

|       |           |           |           |       |
|-------|-----------|-----------|-----------|-------|
| C(11) | 0.6416(5) | 0.4704(4) | 0.7419(3) | 35(1) |
| C(12) | 0.5297(5) | 0.5670(5) | 0.7814(3) | 46(1) |
| C(13) | 0.5756(6) | 0.7187(5) | 0.8071(3) | 57(1) |
| C(14) | 0.7302(6) | 0.7749(5) | 0.7958(3) | 58(1) |
| C(15) | 0.8432(6) | 0.6820(5) | 0.7581(3) | 54(1) |
| C(16) | 0.7993(5) | 0.5299(5) | 0.7326(3) | 47(1) |
| C(17) | 0.4111(4) | 0.2385(4) | 0.7697(3) | 34(1) |
| C(18) | 0.2570(5) | 0.2234(4) | 0.7243(3) | 45(1) |
| C(19) | 0.1153(5) | 0.1941(5) | 0.7676(4) | 56(1) |
| C(20) | 0.1263(6) | 0.1758(5) | 0.8581(4) | 60(1) |
| C(21) | 0.2763(6) | 0.1925(5) | 0.9049(3) | 55(1) |
| C(22) | 0.4202(5) | 0.2261(4) | 0.8641(3) | 40(1) |
| C(23) | 0.5753(5) | 0.2515(4) | 0.9243(3) | 38(1) |
| C(24) | 0.6644(5) | 0.3905(5) | 0.9596(3) | 48(1) |
| C(25) | 0.7996(6) | 0.4164(6) | 1.0227(3) | 59(1) |
| C(26) | 0.8476(6) | 0.3039(6) | 1.0514(3) | 65(1) |
| C(27) | 0.7604(7) | 0.1661(6) | 1.0170(4) | 67(1) |
| C(28) | 0.6244(6) | 0.1389(5) | 0.9544(3) | 54(1) |

Table S8. Hydrogen coordinates and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $(R_P, R_m, S_m, S_P)$ -2,2'-Bis(2-biphenylphenylphosphinoxy)-1,1'-biferrocenyl, meso-**6b**,  $C_{56}H_{44}Fe_2O_2P_2$ .

|       | x      | y      | z      | $U_{iso}$ |
|-------|--------|--------|--------|-----------|
| H(1)  | 0.8730 | 0.0471 | 0.4236 | 62        |
| H(2)  | 0.9306 | 0.2846 | 0.5624 | 67        |
| H(3)  | 0.8365 | 0.4867 | 0.5106 | 69        |
| H(4)  | 0.7294 | 0.3748 | 0.3365 | 73        |
| H(5)  | 0.7451 | 0.1029 | 0.2839 | 68        |
| H(8)  | 0.4664 | 0.4261 | 0.5770 | 45        |
| H(9)  | 0.3589 | 0.3033 | 0.4048 | 49        |
| H(10) | 0.3830 | 0.0353 | 0.3587 | 43        |
| H(12) | 0.4244 | 0.5298 | 0.7905 | 55        |
| H(13) | 0.4999 | 0.7829 | 0.8323 | 68        |
| H(14) | 0.7593 | 0.8770 | 0.8137 | 70        |
| H(15) | 0.9483 | 0.7206 | 0.7497 | 64        |
| H(16) | 0.8768 | 0.4670 | 0.7089 | 57        |
| H(18) | 0.2497 | 0.2334 | 0.6626 | 54        |
| H(19) | 0.0143 | 0.1869 | 0.7363 | 67        |
| H(20) | 0.0323 | 0.1521 | 0.8873 | 71        |
| H(21) | 0.2816 | 0.1810 | 0.9662 | 66        |
| H(24) | 0.6332 | 0.4676 | 0.9407 | 58        |
| H(25) | 0.8584 | 0.5107 | 1.0459 | 71        |
| H(26) | 0.9387 | 0.3215 | 1.0938 | 78        |
| H(27) | 0.7930 | 0.0894 | 1.0359 | 81        |
| H(28) | 0.5653 | 0.0447 | 0.9324 | 65        |

Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded. All hydrogen atoms had  $U_{iso} = U_{eq} \times 1.2$  of their carrier atoms.

Table S9. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $(R_P, R_m, S_m, S_P)$ -2,2'-Bis(2-biphenylphenylphosphinoxy)-1,1'-biferrocenyl, meso-**6b**,  $C_{56}H_{44}Fe_2O_2P_2$ . The anisotropic displacement factor exponent takes the form:  $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

|      | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|------|----------|----------|----------|----------|----------|----------|
| Fe   | 39(1)    | 36(1)    | 33(1)    | 10(1)    | 7(1)     | 1(1)     |
| P    | 30(1)    | 39(1)    | 27(1)    | 6(1)     | 2(1)     | 2(1)     |
| O    | 33(2)    | 52(2)    | 32(2)    | 6(1)     | -4(1)    | 10(1)    |
| C(1) | 45(3)    | 54(3)    | 58(3)    | 18(2)    | 16(2)    | 7(2)     |
| C(2) | 37(2)    | 69(3)    | 54(3)    | 13(3)    | 4(2)     | -3(2)    |

|       |       |       |       |       |       |        |
|-------|-------|-------|-------|-------|-------|--------|
| C(3)  | 50(3) | 42(3) | 74(4) | 12(3) | 18(2) | -5(2)  |
| C(4)  | 59(3) | 63(3) | 73(4) | 40(3) | 28(3) | 7(3)   |
| C(5)  | 60(3) | 64(3) | 42(3) | 12(2) | 21(2) | 4(2)   |
| C(6)  | 27(2) | 36(2) | 30(2) | 10(2) | 3(2)  | 0(2)   |
| C(7)  | 29(2) | 35(2) | 28(2) | 11(2) | 2(2)  | 3(2)   |
| C(8)  | 44(2) | 37(2) | 31(2) | 10(2) | 4(2)  | 4(2)   |
| C(9)  | 43(2) | 45(2) | 37(2) | 18(2) | 0(2)  | 4(2)   |
| C(10) | 42(2) | 37(2) | 26(2) | 9(2)  | 0(2)  | 3(2)   |
| C(11) | 37(2) | 39(2) | 25(2) | 7(2)  | 4(2)  | -2(2)  |
| C(12) | 51(3) | 48(3) | 34(2) | 7(2)  | 10(2) | 5(2)   |
| C(13) | 70(3) | 45(3) | 48(3) | 2(2)  | 14(2) | 10(2)  |
| C(14) | 80(4) | 46(3) | 37(3) | 1(2)  | 4(2)  | -4(3)  |
| C(15) | 56(3) | 56(3) | 39(3) | 8(2)  | 1(2)  | -13(2) |
| C(16) | 42(2) | 49(3) | 42(2) | 5(2)  | 2(2)  | 1(2)   |
| C(17) | 33(2) | 31(2) | 33(2) | 3(2)  | 4(2)  | 3(2)   |
| C(18) | 33(2) | 52(3) | 45(3) | 10(2) | 4(2)  | 4(2)   |
| C(19) | 32(2) | 60(3) | 62(3) | 1(2)  | 6(2)  | 5(2)   |
| C(20) | 48(3) | 59(3) | 57(3) | 2(2)  | 23(2) | -7(2)  |
| C(21) | 60(3) | 57(3) | 40(3) | 10(2) | 18(2) | -4(2)  |
| C(22) | 46(2) | 33(2) | 31(2) | 1(2)  | 11(2) | 1(2)   |
| C(23) | 46(2) | 43(2) | 22(2) | 7(2)  | 10(2) | 4(2)   |
| C(24) | 53(3) | 44(3) | 44(3) | 12(2) | -2(2) | 1(2)   |
| C(25) | 55(3) | 63(3) | 47(3) | 7(2)  | -6(2) | -2(2)  |
| C(26) | 62(3) | 92(4) | 40(3) | 16(3) | -1(2) | 20(3)  |
| C(27) | 81(4) | 74(4) | 58(3) | 31(3) | 4(3)  | 29(3)  |
| C(28) | 72(3) | 46(3) | 48(3) | 19(2) | 15(2) | 8(2)   |

Table S10. Complete bond lengths [Å] and angles [deg] for (*R<sub>P</sub>*,*R<sub>m</sub>*,*S<sub>m</sub>*,*S<sub>P</sub>*)-2,2'-Bis(2-biphenylphenylphosphinoxy)-1,1'-biferrocenyl, meso-**6b**, C<sub>56</sub>H<sub>44</sub>Fe<sub>2</sub>O<sub>2</sub>P<sub>2</sub>.

|              |          |             |          |
|--------------|----------|-------------|----------|
| Bond lengths |          | C(9)-H(9)   | 0.93     |
|              |          | C(10)-H(10) | 0.93     |
| Fe-C(7)      | 2.020(4) | C(11)-C(16) | 1.388(5) |
| Fe-C(8)      | 2.025(4) | C(11)-C(12) | 1.391(5) |
| Fe-C(4)      | 2.038(4) | C(12)-C(13) | 1.388(6) |
| Fe-C(5)      | 2.039(4) | C(12)-H(12) | 0.93     |
| Fe-C(3)      | 2.040(4) | C(13)-C(14) | 1.362(6) |
| Fe-C(2)      | 2.045(4) | C(13)-H(13) | 0.93     |
| Fe-C(1)      | 2.047(4) | C(14)-C(15) | 1.371(6) |
| Fe-C(9)      | 2.051(4) | C(14)-H(14) | 0.93     |
| Fe-C(6)      | 2.052(4) | C(15)-C(16) | 1.388(6) |
| Fe-C(10)     | 2.053(4) | C(15)-H(15) | 0.93     |
| P-O          | 1.477(3) | C(16)-H(16) | 0.93     |
| P-C(7)       | 1.805(4) | C(17)-C(18) | 1.398(5) |
| P-C(17)      | 1.816(4) | C(17)-C(22) | 1.411(5) |
| P-C(11)      | 1.824(4) | C(18)-C(19) | 1.381(6) |
| C(1)-C(5)    | 1.406(6) | C(18)-H(18) | 0.93     |
| C(1)-C(2)    | 1.413(6) | C(19)-C(20) | 1.380(6) |
| C(1)-H(1)    | 0.93     | C(19)-H(19) | 0.93     |
| C(2)-C(3)    | 1.400(6) | C(20)-C(21) | 1.375(6) |
| C(2)-H(2)    | 0.93     | C(20)-H(20) | 0.93     |
| C(3)-C(4)    | 1.411(6) | C(21)-C(22) | 1.387(6) |
| C(3)-H(3)    | 0.93     | C(21)-H(21) | 0.93     |
| C(4)-C(5)    | 1.407(6) | C(22)-C(23) | 1.493(6) |
| C(4)-H(4)    | 0.93     | C(23)-C(24) | 1.380(6) |
| C(5)-H(5)    | 0.93     | C(23)-C(28) | 1.389(5) |
| C(6)-C(10)   | 1.430(5) | C(24)-C(25) | 1.382(6) |
| C(6)-C(7)    | 1.468(5) | C(24)-H(24) | 0.93     |
| C(6)-C(6)#1  | 1.480(7) | C(25)-C(26) | 1.372(6) |
| C(7)-C(8)    | 1.430(5) | C(25)-H(25) | 0.93     |
| C(8)-C(9)    | 1.409(5) | C(26)-C(27) | 1.364(7) |
| C(8)-H(8)    | 0.93     | C(26)-H(26) | 0.93     |
| C(9)-C(10)   | 1.400(5) | C(27)-C(28) | 1.381(7) |
|              |          | C(27)-H(27) | 0.93     |

|                |            |                   |            |
|----------------|------------|-------------------|------------|
| C(28)-H(28)    | 0.93       | C(2)-C(3)-Fe      | 70.2(3)    |
|                |            | C(4)-C(3)-Fe      | 69.7(3)    |
| C(7)-Fe-C(8)   | 41.41(14)  | C(2)-C(3)-H(3)    | 126.5      |
| C(7)-Fe-C(4)   | 157.54(17) | C(4)-C(3)-H(3)    | 126.5      |
| C(8)-Fe-C(4)   | 121.50(18) | Fe-C(3)-H(3)      | 125.2      |
| C(7)-Fe-C(5)   | 160.69(17) | C(5)-C(4)-C(3)    | 108.9(4)   |
| C(8)-Fe-C(5)   | 156.22(17) | C(5)-C(4)-Fe      | 69.8(2)    |
| C(4)-Fe-C(5)   | 40.39(18)  | C(3)-C(4)-Fe      | 69.8(3)    |
| C(7)-Fe-C(3)   | 121.93(18) | C(5)-C(4)-H(4)    | 125.5      |
| C(8)-Fe-C(3)   | 107.75(18) | C(3)-C(4)-H(4)    | 125.5      |
| C(4)-Fe-C(3)   | 40.49(19)  | Fe-C(4)-H(4)      | 126.4      |
| C(5)-Fe-C(3)   | 68.44(19)  | C(1)-C(5)-C(4)    | 107.5(4)   |
| C(7)-Fe-C(2)   | 108.64(17) | C(1)-C(5)-Fe      | 70.2(2)    |
| C(8)-Fe-C(2)   | 125.37(17) | C(4)-C(5)-Fe      | 69.8(2)    |
| C(4)-Fe-C(2)   | 67.2(2)    | C(1)-C(5)-H(5)    | 126.2      |
| C(5)-Fe-C(2)   | 67.76(19)  | C(4)-C(5)-H(5)    | 126.2      |
| C(3)-Fe-C(2)   | 40.09(18)  | Fe-C(5)-H(5)      | 125.4      |
| C(7)-Fe-C(1)   | 124.71(16) |                   |            |
| C(8)-Fe-C(1)   | 162.09(17) | C(10)-C(6)-C(7)   | 106.2(3)   |
| C(4)-Fe-C(1)   | 67.48(19)  | C(10)-C(6)-C(6)#1 | 124.4(4)   |
| C(5)-Fe-C(1)   | 40.26(17)  | C(7)-C(6)-C(6)#1  | 129.4(4)   |
| C(3)-Fe-C(1)   | 68.11(19)  | C(10)-C(6)-Fe     | 69.6(2)    |
| C(2)-Fe-C(1)   | 40.41(17)  | C(7)-C(6)-Fe      | 67.7(2)    |
| C(7)-Fe-C(9)   | 69.13(15)  | C(6)#1-C(6)-Fe    | 127.2(3)   |
| C(8)-Fe-C(9)   | 40.45(15)  | C(8)-C(7)-C(6)    | 106.8(3)   |
| C(4)-Fe-C(9)   | 107.16(18) | C(8)-C(7)-P       | 119.6(3)   |
| C(5)-Fe-C(9)   | 120.73(18) | C(6)-C(7)-P       | 133.4(3)   |
| C(3)-Fe-C(9)   | 123.73(18) | C(8)-C(7)-Fe      | 69.5(2)    |
| C(2)-Fe-C(9)   | 160.80(17) | C(6)-C(7)-Fe      | 70.05(19)  |
| C(1)-Fe-C(9)   | 156.45(17) | P-C(7)-Fe         | 128.57(19) |
| C(7)-Fe-C(6)   | 42.25(14)  | C(9)-C(8)-C(7)    | 108.9(3)   |
| C(8)-Fe-C(6)   | 69.62(15)  | C(9)-C(8)-Fe      | 70.8(2)    |
| C(4)-Fe-C(6)   | 158.81(18) | C(7)-C(8)-Fe      | 69.1(2)    |
| C(5)-Fe-C(6)   | 122.54(17) | C(9)-C(8)-H(8)    | 125.6      |
| C(3)-Fe-C(6)   | 158.96(18) | C(7)-C(8)-H(8)    | 125.6      |
| C(2)-Fe-C(6)   | 123.42(17) | Fe-C(8)-H(8)      | 126.1      |
| C(1)-Fe-C(6)   | 107.63(16) | C(10)-C(9)-C(8)   | 108.5(3)   |
| C(9)-Fe-C(6)   | 68.60(15)  | C(10)-C(9)-Fe     | 70.1(2)    |
| C(7)-Fe-C(10)  | 69.33(15)  | C(8)-C(9)-Fe      | 68.8(2)    |
| C(8)-Fe-C(10)  | 68.00(15)  | C(10)-C(9)-H(9)   | 125.7      |
| C(4)-Fe-C(10)  | 122.87(19) | C(8)-C(9)-H(9)    | 125.7      |
| C(5)-Fe-C(10)  | 106.75(18) | Fe-C(9)-H(9)      | 126.9      |
| C(3)-Fe-C(10)  | 159.15(17) | C(9)-C(10)-C(6)   | 109.6(3)   |
| C(2)-Fe-C(10)  | 158.71(17) | C(9)-C(10)-Fe     | 70.0(2)    |
| C(1)-Fe-C(10)  | 122.19(17) | C(6)-C(10)-Fe     | 69.6(2)    |
| C(9)-Fe-C(10)  | 39.89(14)  | C(9)-C(10)-H(10)  | 125.2      |
| C(6)-Fe-C(10)  | 40.76(14)  | C(6)-C(10)-H(10)  | 125.2      |
|                |            | Fe-C(10)-H(10)    | 126.8      |
| O-P-C(7)       | 116.42(16) |                   |            |
| O-P-C(17)      | 114.28(17) | C(16)-C(11)-C(12) | 118.4(4)   |
| C(7)-P-C(17)   | 104.12(17) | C(16)-C(11)-P     | 118.9(3)   |
| O-P-C(11)      | 111.52(17) | C(12)-C(11)-P     | 122.7(3)   |
| C(7)-P-C(11)   | 104.40(17) | C(13)-C(12)-C(11) | 119.9(4)   |
| C(17)-P-C(11)  | 104.95(17) | C(13)-C(12)-H(12) | 120.1      |
|                |            | C(11)-C(12)-H(12) | 120.1      |
| C(5)-C(1)-C(2) | 107.7(4)   | C(14)-C(13)-C(12) | 120.8(4)   |
| C(5)-C(1)-Fe   | 69.6(2)    | C(14)-C(13)-H(13) | 119.6      |
| C(2)-C(1)-Fe   | 69.7(2)    | C(12)-C(13)-H(13) | 119.6      |
| C(5)-C(1)-H(1) | 126.1      | C(13)-C(14)-C(15) | 120.4(4)   |
| C(2)-C(1)-H(1) | 126.1      | C(13)-C(14)-H(14) | 119.8      |
| Fe-C(1)-H(1)   | 126.1      | C(15)-C(14)-H(14) | 119.8      |
| C(3)-C(2)-C(1) | 108.9(4)   | C(14)-C(15)-C(16) | 119.5(4)   |
| C(3)-C(2)-Fe   | 69.8(3)    | C(14)-C(15)-H(15) | 120.3      |
| C(1)-C(2)-Fe   | 69.9(2)    | C(16)-C(15)-H(15) | 120.3      |
| C(3)-C(2)-H(2) | 125.6      | C(11)-C(16)-C(15) | 121.0(4)   |
| C(1)-C(2)-H(2) | 125.6      | C(11)-C(16)-H(16) | 119.5      |
| Fe-C(2)-H(2)   | 126.4      | C(15)-C(16)-H(16) | 119.5      |
| C(2)-C(3)-C(4) | 107.0(4)   |                   |            |

|                   |          |                 |           |
|-------------------|----------|-----------------|-----------|
| C(18)-C(17)-C(22) | 118.1(4) | O-P-C7-C6       | 42.7(4)   |
| C(18)-C(17)-P     | 119.2(3) | C17-P-C7-C6     | -84.1(4)  |
| C(22)-C(17)-P     | 122.6(3) | C11-P-C7-C6     | 166.1(3)  |
| C(19)-C(18)-C(17) | 122.4(4) | O-P-C7-Fe       | -56.1(3)  |
| C(19)-C(18)-H(18) | 118.8    | C17-P-C7-Fe     | 177.1(2)  |
| C(17)-C(18)-H(18) | 118.8    | C11-P-C7-Fe     | 67.3(3)   |
| C(20)-C(19)-C(18) | 118.8(4) | C6-C7-C8-C9     | -0.6(4)   |
| C(20)-C(19)-H(19) | 120.6    | P-C7-C8-C9      | -176.6(3) |
| C(18)-C(19)-H(19) | 120.6    | Fe-C7-C8-C9     | 59.8(3)   |
| C(21)-C(20)-C(19) | 119.9(4) | C6-C7-C8-Fe     | -60.4(2)  |
| C(21)-C(20)-H(20) | 120.1    | P-C7-C8-Fe      | 123.6(3)  |
| C(19)-C(20)-H(20) | 120.1    | C7-C8-C9-C10    | 0.2(4)    |
| C(20)-C(21)-C(22) | 122.4(4) | Fe-C8-C9-C10    | 59.0(3)   |
| C(20)-C(21)-H(21) | 118.8    | C7-C8-C9-Fe     | -58.8(3)  |
| C(22)-C(21)-H(21) | 118.8    | C8-C9-C10-C6    | 0.2(4)    |
| C(21)-C(22)-C(17) | 118.3(4) | Fe-C9-C10-C6    | 58.4(3)   |
| C(21)-C(22)-C(23) | 117.7(4) | C8-C9-C10-Fe    | -58.2(3)  |
| C(17)-C(22)-C(23) | 124.0(3) | C7-C6-C10-C9    | -0.6(4)   |
| C(24)-C(23)-C(28) | 118.2(4) | C6#1-C6-C10-C9  | 179.5(4)  |
| C(24)-C(23)-C(22) | 121.0(4) | Fe-C6-C10-C9    | -58.7(3)  |
| C(28)-C(23)-C(22) | 120.4(4) | C7-C6-C10-Fe    | 58.1(2)   |
| C(23)-C(24)-C(25) | 120.8(4) | C6#1-C6-C10-Fe  | -121.8(4) |
| C(23)-C(24)-H(24) | 119.6    |                 |           |
| C(25)-C(24)-H(24) | 119.6    | O-P-C11-C16     | 34.2(4)   |
| C(26)-C(25)-C(24) | 120.4(5) | C7-P-C11-C16    | -92.4(3)  |
| C(26)-C(25)-H(25) | 119.8    | C17-P-C11-C16   | 158.4(3)  |
| C(24)-C(25)-H(25) | 119.8    | O-P-C11-C12     | -144.2(3) |
| C(27)-C(26)-C(25) | 119.3(5) | C7-P-C11-C12    | 89.3(3)   |
| C(27)-C(26)-H(26) | 120.4    | C17-P-C11-C12   | -19.9(4)  |
| C(25)-C(26)-H(26) | 120.4    | C16-C11-C12-C13 | 2.3(6)    |
| C(26)-C(27)-C(28) | 120.9(5) | P-C11-C12-C13   | -179.4(3) |
| C(26)-C(27)-H(27) | 119.6    | C11-C12-C13-C14 | -1.2(7)   |
| C(28)-C(27)-H(27) | 119.6    | C12-C13-C14-C15 | 0.4(7)    |
| C(27)-C(28)-C(23) | 120.4(5) | C13-C14-C15-C16 | -0.8(7)   |
| C(27)-C(28)-H(28) | 119.8    | C12-C11-C16-C15 | -2.7(6)   |
| C(23)-C(28)-H(28) | 119.8    | P-C11-C16-C15   | 178.9(3)  |
|                   |          | C14-C15-C16-C11 | 2.0(6)    |
|                   |          | O-P-C17-C18     | -144.9(3) |
|                   |          | C7-P-C17-C18    | -16.8(3)  |
|                   |          | C11-P-C17-C18   | 92.6(3)   |
|                   |          | O-P-C17-C22     | 33.9(4)   |
|                   |          | C7-P-C17-C22    | 162.0(3)  |
|                   |          | C11-P-C17-C22   | -88.6(3)  |
|                   |          | C22-C17-C18-C19 | -1.3(6)   |
|                   |          | P-C17-C18-C19   | 177.5(3)  |
|                   |          | C17-C18-C19-C20 | -1.5(7)   |
|                   |          | C18-C19-C20-C21 | 2.5(7)    |
|                   |          | C19-C20-C21-C22 | -0.7(7)   |
|                   |          | C20-C21-C22-C17 | -2.1(6)   |
|                   |          | C20-C21-C22-C23 | 176.1(4)  |
|                   |          | C18-C17-C22-C21 | 3.1(5)    |
|                   |          | P-C17-C22-C21   | -175.7(3) |
|                   |          | C18-C17-C22-C23 | -175.0(4) |
|                   |          | P-C17-C22-C23   | 6.2(5)    |
|                   |          | C21-C22-C23-C24 | -111.2(4) |
|                   |          | C17-C22-C23-C24 | 66.9(5)   |
|                   |          | C21-C22-C23-C28 | 62.2(5)   |
|                   |          | C17-C22-C23-C28 | -119.7(4) |
|                   |          | C28-C23-C24-C25 | 0.4(6)    |
|                   |          | C22-C23-C24-C25 | 174.0(4)  |
|                   |          | C23-C24-C25-C26 | 0.0(7)    |
|                   |          | C24-C25-C26-C27 | 0.0(7)    |
|                   |          | C25-C26-C27-C28 | -0.4(7)   |
|                   |          | C26-C27-C28-C23 | 0.9(7)    |
|                   |          | C24-C23-C28-C27 | -0.9(6)   |
|                   |          | C22-C23-C28-C27 | -174.5(4) |

## Selected torsion angles

|               |           |  |  |
|---------------|-----------|--|--|
| C5-C1-C2-C3   | 0.4(5)    |  |  |
| Fe-C1-C2-C3   | -59.0(3)  |  |  |
| C5-C1-C2-Fe   | 59.4(3)   |  |  |
| C1-C2-C3-C4   | -1.2(5)   |  |  |
| Fe-C2-C3-C4   | -60.3(3)  |  |  |
| C1-C2-C3-Fe   | 59.1(3)   |  |  |
| C2-C3-C4-C5   | 1.6(5)    |  |  |
| Fe-C3-C4-C5   | -59.0(3)  |  |  |
| C2-C3-C4-Fe   | 60.6(3)   |  |  |
| C2-C1-C5-C4   | 0.6(5)    |  |  |
| Fe-C1-C5-C4   | 60.1(3)   |  |  |
| C2-C1-C5-Fe   | -59.5(3)  |  |  |
| C3-C4-C5-C1   | -1.3(5)   |  |  |
| Fe-C4-C5-C1   | -60.3(3)  |  |  |
| C3-C4-C5-Fe   | 59.0(3)   |  |  |
| C10-C6-C7-C8  | 0.7(4)    |  |  |
| C6#1-C6-C7-C8 | -179.4(4) |  |  |
| Fe-C6-C7-C8   | 60.0(2)   |  |  |
| C10-C6-C7-P   | 176.0(3)  |  |  |
| C6#1-C6-C7-P  | -4.1(7)   |  |  |
| Fe-C6-C7-P    | -124.7(3) |  |  |
| C10-C6-C7-Fe  | -59.3(2)  |  |  |
| C6#1-C6-C7-Fe | 120.6(5)  |  |  |
| O-P-C7-C8     | -142.5(3) |  |  |
| C17-P-C7-C8   | 90.7(3)   |  |  |
| C11-P-C7-C8   | -19.1(3)  |  |  |

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z+1

Table S11. Crystal data and structure refinement for (±)-2,2'-Bis(1-naphthylphenylphosphinoxy)-1,1'-biferrocenyl, (±)-**6a**, C<sub>52</sub>H<sub>40</sub>Fe<sub>2</sub>O<sub>2</sub>P<sub>2</sub>.

|                                   |                                                                                                                                              |
|-----------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------|
| Identification code               | widhj3fr                                                                                                                                     |
| Empirical formula                 | C <sub>52</sub> H <sub>40</sub> Fe <sub>2</sub> O <sub>2</sub> P <sub>2</sub>                                                                |
| Formula weight                    | 870.48                                                                                                                                       |
| Temperature                       | 299(2) K                                                                                                                                     |
| Wavelength                        | 0.71073 Å                                                                                                                                    |
| Crystal system, space group       | monoclinic, P2 <sub>1</sub> /c (No. 14)                                                                                                      |
| Unit cell dimensions              | a = 14.861(3) Å    α = 90°<br>b = 16.076(4) Å    β = 90.17(1)°<br>c = 17.451(5) Å    γ = 90°.                                                |
| Volume                            | 4169.1(18) Å <sup>3</sup>                                                                                                                    |
| Z, Calculated density             | 4, 1.387 Mg/m <sup>3</sup>                                                                                                                   |
| Absorption coefficient            | 0.814 mm <sup>-1</sup>                                                                                                                       |
| F(000)                            | 1800                                                                                                                                         |
| Crystal size                      | 0.7 x 0.14 x 0.14 mm, orange prism from CH <sub>3</sub> NO <sub>2</sub>                                                                      |
| Diffractometer                    | Siemens SMART 3-circle with CCD area detector<br>(sealed X-ray tube, Mo Kα radiation, graphite monochr., det.dist. 44.50 mm, 512x512 pixels) |
| Scan type / width / speed         | ω-scan frames / Δω = 0.3° / 25 sec. per frame<br>full sphere, 4 x 606 frames                                                                 |
| Theta range for data collection   | 2.20° to 25.00°                                                                                                                              |
| Index ranges                      | -17 ≤ h ≤ 17, -19 ≤ k ≤ 19, -20 ≤ l ≤ 20                                                                                                     |
| Reflections collected / unique    | 41082 / 7301 [R(int) = 0.042, R(sigma) = 0.029]                                                                                              |
| Completeness to theta = 25.00     | 95.9%                                                                                                                                        |
| Absorption correction             | Empirical (program SADABS; Sheldrick, 1996)                                                                                                  |
| Transmission factors              | 0.96 - 0.75                                                                                                                                  |
| Structure solution                | Direct methods (program SHELXS97)                                                                                                            |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup> (prg SHELXL97)                                                                                   |
| Data / restraints / parameters    | 7301 / 0 / 524                                                                                                                               |
| Goodness-of-fit on F <sup>2</sup> | 1.059                                                                                                                                        |
| Final R indices [I > 2σ(I)]       | R1 = 0.0312, wR2 = 0.0684 (5868 data)                                                                                                        |
| R indices (all data)              | R1 = 0.0468, wR2 = 0.0771 (7301 data)                                                                                                        |
| Extinction coefficient            | 0.00025(8)                                                                                                                                   |
| Largest diff. peak and hole       | 0.298 and -0.258 e Å <sup>-3</sup>                                                                                                           |

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|, \quad wR2 = [\Sigma (w(F_o^2 - F_c^2)^2) / \Sigma (w(F_o^2)^2)]^{1/2}$$

Table S12. Atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup> x 10<sup>3</sup>) for (±)-2,2'-Bis(1-naphthylphenylphosphinoxy)-1,1'-biferrocenyl, (±)-**6a**, C<sub>52</sub>H<sub>40</sub>Fe<sub>2</sub>O<sub>2</sub>P<sub>2</sub>. U<sub>eq</sub> is defined as one third of the trace of the orthogonalized U<sub>ij</sub> tensor.

|       | x           | y          | z          | U <sub>iso</sub> |
|-------|-------------|------------|------------|------------------|
| Fe(1) | 0.33431(2)  | 0.26639(2) | 0.54306(2) | 36(1)            |
| Fe(2) | 0.09118(2)  | 0.25482(2) | 0.39831(2) | 40(1)            |
| P(1)  | 0.45240(4)  | 0.32956(3) | 0.38083(3) | 32(1)            |
| P(2)  | 0.12399(4)  | 0.46378(3) | 0.36576(3) | 34(1)            |
| O(1)  | 0.43124(10) | 0.26060(9) | 0.32758(9) | 43(1)            |
| O(2)  | 0.13256(11) | 0.49461(9) | 0.44543(8) | 45(1)            |
| C(1)  | 0.2850(2)   | 0.1476(2)  | 0.5416(2)  | 55(1)            |
| C(2)  | 0.3772(2)   | 0.1471(2)  | 0.5250(2)  | 56(1)            |
| C(3)  | 0.4234(2)   | 0.1820(2)  | 0.5880(2)  | 57(1)            |
| C(4)  | 0.3592(2)   | 0.2044(2)  | 0.6437(1)  | 58(1)            |
| C(5)  | 0.2735(2)   | 0.1835(2)  | 0.6149(2)  | 56(1)            |
| C(6)  | 0.2761(1)   | 0.3353(1)  | 0.4568(1)  | 32(1)            |

|       |            |           |           |       |
|-------|------------|-----------|-----------|-------|
| C(7)  | 0.3733(1)  | 0.3440(1) | 0.4568(1) | 32(1) |
| C(8)  | 0.3988(2)  | 0.3767(1) | 0.5299(1) | 38(1) |
| C(9)  | 0.3206(2)  | 0.3884(1) | 0.5740(1) | 42(1) |
| C(10) | 0.2460(2)  | 0.3632(1) | 0.5296(1) | 37(1) |
| C(11) | 0.5593(1)  | 0.3153(1) | 0.4295(1) | 37(1) |
| C(12) | 0.5846(2)  | 0.2351(2) | 0.4490(1) | 49(1) |
| C(13) | 0.6643(2)  | 0.2205(2) | 0.4882(2) | 66(1) |
| C(14) | 0.7194(2)  | 0.2858(2) | 0.5073(2) | 71(1) |
| C(15) | 0.6961(2)  | 0.3655(2) | 0.4882(2) | 66(1) |
| C(16) | 0.6160(2)  | 0.3805(2) | 0.4493(1) | 50(1) |
| C(17) | 0.4628(1)  | 0.4318(1) | 0.3369(1) | 36(1) |
| C(18) | 0.4169(2)  | 0.4982(1) | 0.3668(1) | 41(1) |
| C(19) | 0.4281(2)  | 0.5795(2) | 0.3383(1) | 49(1) |
| C(20) | 0.4853(2)  | 0.5939(2) | 0.2799(2) | 53(1) |
| C(21) | 0.5337(2)  | 0.5283(2) | 0.2459(1) | 47(1) |
| C(22) | 0.5918(2)  | 0.5427(2) | 0.1834(2) | 61(1) |
| C(23) | 0.6376(2)  | 0.4794(2) | 0.1510(2) | 68(1) |
| C(24) | 0.6293(2)  | 0.3982(2) | 0.1789(2) | 61(1) |
| C(25) | 0.5734(2)  | 0.3813(2) | 0.2392(1) | 48(1) |
| C(26) | 0.5232(2)  | 0.4452(1) | 0.2742(1) | 39(1) |
| C(27) | 0.0591(2)  | 0.2245(2) | 0.5092(2) | 64(1) |
| C(28) | 0.0053(2)  | 0.2909(2) | 0.4833(2) | 62(1) |
| C(29) | -0.0439(2) | 0.2644(2) | 0.4194(2) | 64(1) |
| C(30) | -0.0211(2) | 0.1814(2) | 0.4048(2) | 71(1) |
| C(31) | 0.0428(2)  | 0.1564(2) | 0.4602(2) | 72(1) |
| C(32) | 0.2179(1)  | 0.3069(1) | 0.3928(1) | 32(1) |
| C(33) | 0.1512(1)  | 0.3564(1) | 0.3527(1) | 34(1) |
| C(34) | 0.1134(2)  | 0.3048(1) | 0.2935(1) | 42(1) |
| C(35) | 0.1550(2)  | 0.2263(1) | 0.2972(1) | 46(1) |
| C(36) | 0.2182(2)  | 0.2276(1) | 0.3576(1) | 39(1) |
| C(37) | 0.0109(2)  | 0.4761(1) | 0.3283(1) | 40(1) |
| C(38) | -0.0593(2) | 0.4792(1) | 0.3796(2) | 50(1) |
| C(39) | -0.1464(2) | 0.4900(2) | 0.3547(2) | 63(1) |
| C(40) | -0.1640(2) | 0.4996(2) | 0.2784(2) | 69(1) |
| C(41) | -0.0955(2) | 0.4974(2) | 0.2264(2) | 64(1) |
| C(42) | -0.0070(2) | 0.4853(2) | 0.2504(1) | 52(1) |
| C(43) | 0.1919(2)  | 0.5182(1) | 0.2959(1) | 37(1) |
| C(44) | 0.2480(2)  | 0.4748(2) | 0.2482(1) | 44(1) |
| C(45) | 0.2971(2)  | 0.5143(2) | 0.1904(2) | 55(1) |
| C(46) | 0.2896(2)  | 0.5977(2) | 0.1816(2) | 60(1) |
| C(47) | 0.2335(2)  | 0.6459(2) | 0.2287(1) | 51(1) |
| C(48) | 0.2251(2)  | 0.7330(2) | 0.2197(2) | 70(1) |
| C(49) | 0.1697(2)  | 0.7774(2) | 0.2643(2) | 77(1) |
| C(50) | 0.1190(2)  | 0.7392(2) | 0.3221(2) | 68(1) |
| C(51) | 0.1260(2)  | 0.6554(2) | 0.3339(2) | 52(1) |
| C(52) | 0.1831(2)  | 0.6064(1) | 0.2876(1) | 41(1) |

Table S13. Hydrogen coordinates and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for ( $\pm$ )-2,2'-Bis(1-naphthylphenylphosphinoxy)-1,1'-biferrocenyl, ( $\pm$ )-**6a**,  $\text{C}_{52}\text{H}_{40}\text{Fe}_2\text{O}_2\text{P}_2$ .

|       | x      | y      | z      | $U_{\text{iso}}$ |
|-------|--------|--------|--------|------------------|
| H(1)  | 0.2393 | 0.1278 | 0.5100 | 66               |
| H(2)  | 0.4034 | 0.1272 | 0.4803 | 67               |
| H(3)  | 0.4854 | 0.1890 | 0.5921 | 68               |
| H(4)  | 0.3714 | 0.2286 | 0.6910 | 70               |
| H(5)  | 0.2190 | 0.1918 | 0.6398 | 67               |
| H(8)  | 0.4573 | 0.3883 | 0.5457 | 45               |
| H(9)  | 0.3185 | 0.4091 | 0.6237 | 50               |
| H(10) | 0.1864 | 0.3647 | 0.5456 | 45               |
| H(12) | 0.5477 | 0.1906 | 0.4357 | 58               |
| H(13) | 0.6804 | 0.1665 | 0.5016 | 79               |
| H(14) | 0.7729 | 0.2759 | 0.5334 | 85               |
| H(15) | 0.7338 | 0.4095 | 0.5011 | 79               |
| H(16) | 0.6002 | 0.4347 | 0.4365 | 60               |
| H(18) | 0.3773 | 0.4894 | 0.4071 | 50               |

|       |         |        |        |    |
|-------|---------|--------|--------|----|
| H(19) | 0.3961  | 0.6233 | 0.3598 | 59 |
| H(20) | 0.4928  | 0.6478 | 0.2617 | 63 |
| H(22) | 0.5985  | 0.5964 | 0.1644 | 73 |
| H(23) | 0.6752  | 0.4899 | 0.1095 | 81 |
| H(24) | 0.6620  | 0.3554 | 0.1564 | 73 |
| H(25) | 0.5685  | 0.3270 | 0.2572 | 57 |
| H(27) | 0.0981  | 0.2254 | 0.5509 | 77 |
| H(28) | 0.0029  | 0.3437 | 0.5051 | 75 |
| H(29) | -0.0846 | 0.2963 | 0.3915 | 76 |
| H(30) | -0.0440 | 0.1485 | 0.3655 | 85 |
| H(31) | 0.0695  | 0.1042 | 0.4638 | 86 |
| H(34) | 0.0689  | 0.3205 | 0.2588 | 50 |
| H(35) | 0.1430  | 0.1814 | 0.2652 | 55 |
| H(36) | 0.2545  | 0.1831 | 0.3721 | 47 |
| H(38) | -0.0476 | 0.4740 | 0.4318 | 59 |
| H(39) | -0.1933 | 0.4907 | 0.3899 | 75 |
| H(40) | -0.2228 | 0.5076 | 0.2617 | 82 |
| H(41) | -0.1080 | 0.5041 | 0.1746 | 77 |
| H(42) | 0.0395  | 0.4835 | 0.2149 | 62 |
| H(44) | 0.2534  | 0.4175 | 0.2543 | 52 |
| H(45) | 0.3345  | 0.4837 | 0.1584 | 67 |
| H(46) | 0.3225  | 0.6238 | 0.1433 | 72 |
| H(48) | 0.2586  | 0.7599 | 0.1822 | 84 |
| H(49) | 0.1647  | 0.8345 | 0.2567 | 92 |
| H(50) | 0.0806  | 0.7709 | 0.3524 | 81 |
| H(51) | 0.0930  | 0.6304 | 0.3728 | 62 |

Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded. All hydrogen atoms had  $U_{\text{iso}} = U_{\text{eq}} \times 1.2$  of their carrier atoms.

Table S14. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $(\pm)$ -2,2'-Bis(1-naphthylphenylphosphinoxy)-1,1'-biferrocenyl,  $(\pm)$ -**6a**,  $\text{C}_{52}\text{H}_{40}\text{Fe}_2\text{O}_2\text{P}_2$ . The anisotropic displacement factor exponent takes the form:  $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

|       | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|-------|----------|----------|----------|----------|----------|----------|
| Fe(1) | 40(1)    | 40(1)    | 28(1)    | 4(1)     | -1(1)    | 4(1)     |
| Fe(2) | 36(1)    | 37(1)    | 48(1)    | 2(1)     | -3(1)    | -6(1)    |
| P(1)  | 34(1)    | 33(1)    | 29(1)    | -1(1)    | -1(1)    | -1(1)    |
| P(2)  | 37(1)    | 33(1)    | 33(1)    | 0(1)     | -4(1)    | 1(1)     |
| O(1)  | 49(1)    | 41(1)    | 38(1)    | -9(1)    | -1(1)    | -4(1)    |
| O(2)  | 55(1)    | 45(1)    | 35(1)    | -5(1)    | -5(1)    | 3(1)     |
| C(1)  | 70(2)    | 42(1)    | 52(2)    | 14(1)    | -8(1)    | -6(1)    |
| C(2)  | 74(2)    | 46(1)    | 47(2)    | 8(1)     | 4(1)     | 15(1)    |
| C(3)  | 54(2)    | 61(2)    | 55(2)    | 19(1)    | -7(1)    | 12(1)    |
| C(4)  | 79(2)    | 62(2)    | 34(1)    | 14(1)    | -11(1)   | 5(1)     |
| C(5)  | 63(2)    | 58(2)    | 48(2)    | 21(1)    | 9(1)     | 4(1)     |
| C(6)  | 36(1)    | 29(1)    | 32(1)    | 4(1)     | -2(1)    | 2(1)     |
| C(7)  | 34(1)    | 31(1)    | 31(1)    | 2(1)     | -3(1)    | 0(1)     |
| C(8)  | 37(1)    | 42(1)    | 35(1)    | -3(1)    | -7(1)    | -1(1)    |
| C(9)  | 49(1)    | 44(1)    | 32(1)    | -8(1)    | -2(1)    | 6(1)     |
| C(10) | 37(1)    | 40(1)    | 35(1)    | -1(1)    | 1(1)     | 6(1)     |
| C(11) | 35(1)    | 47(1)    | 31(1)    | -1(1)    | 2(1)     | 4(1)     |
| C(12) | 48(1)    | 54(2)    | 44(1)    | -1(1)    | 1(1)     | 11(1)    |
| C(13) | 66(2)    | 80(2)    | 50(2)    | 5(1)     | -4(1)    | 32(2)    |
| C(14) | 49(2)    | 116(3)   | 48(2)    | -11(2)   | -11(1)   | 22(2)    |
| C(15) | 45(2)    | 97(2)    | 55(2)    | -15(2)   | -7(1)    | -8(2)    |
| C(16) | 44(1)    | 59(2)    | 47(1)    | -3(1)    | -5(1)    | -5(1)    |
| C(17) | 39(1)    | 38(1)    | 32(1)    | 2(1)     | -6(1)    | -5(1)    |
| C(18) | 47(1)    | 40(1)    | 37(1)    | 1(1)     | -5(1)    | -1(1)    |
| C(19) | 60(2)    | 39(1)    | 49(2)    | 2(1)     | -13(1)   | 2(1)     |
| C(20) | 63(2)    | 41(1)    | 55(2)    | 11(1)    | -19(1)   | -9(1)    |
| C(21) | 46(1)    | 56(2)    | 40(1)    | 14(1)    | -12(1)   | -15(1)   |
| C(22) | 58(2)    | 74(2)    | 51(2)    | 20(1)    | -2(1)    | -15(2)   |
| C(23) | 56(2)    | 101(2)   | 47(2)    | 22(2)    | 5(1)     | -20(2)   |

|       |        |       |        |        |        |        |
|-------|--------|-------|--------|--------|--------|--------|
| C(24) | 51(2)  | 89(2) | 43(2)  | -6(1)  | 4(1)   | -3(1)  |
| C(25) | 46(1)  | 59(2) | 38(1)  | 1(1)   | -1(1)  | -6(1)  |
| C(26) | 38(1)  | 48(1) | 32(1)  | 2(1)   | -8(1)  | -7(1)  |
| C(27) | 53(2)  | 84(2) | 56(2)  | 22(2)  | 4(1)   | -11(2) |
| C(28) | 53(2)  | 69(2) | 65(2)  | 1(2)   | 16(1)  | -7(1)  |
| C(29) | 36(1)  | 73(2) | 83(2)  | 11(2)  | 2(1)   | -4(1)  |
| C(30) | 53(2)  | 65(2) | 95(2)  | 1(2)   | -3(2)  | -26(2) |
| C(31) | 61(2)  | 51(2) | 103(3) | 25(2)  | 11(2)  | -13(1) |
| C(32) | 31(1)  | 33(1) | 32(1)  | 2(1)   | -1(1)  | -3(1)  |
| C(33) | 36(1)  | 33(1) | 34(1)  | 1(1)   | -3(1)  | -4(1)  |
| C(34) | 47(1)  | 42(1) | 37(1)  | -1(1)  | -12(1) | -4(1)  |
| C(35) | 54(1)  | 37(1) | 47(1)  | -10(1) | -4(1)  | -5(1)  |
| C(36) | 41(1)  | 33(1) | 44(1)  | -2(1)  | 0(1)   | 2(1)   |
| C(37) | 40(1)  | 32(1) | 47(1)  | 0(1)   | -6(1)  | 1(1)   |
| C(38) | 47(1)  | 42(1) | 59(2)  | -8(1)  | -1(1)  | 7(1)   |
| C(39) | 45(2)  | 49(2) | 93(2)  | -16(2) | 0(2)   | 9(1)   |
| C(40) | 47(2)  | 44(2) | 116(3) | -10(2) | -27(2) | 7(1)   |
| C(41) | 73(2)  | 51(2) | 70(2)  | 6(1)   | -32(2) | 0(1)   |
| C(42) | 55(2)  | 49(1) | 51(2)  | 7(1)   | -14(1) | -3(1)  |
| C(43) | 41(1)  | 36(1) | 35(1)  | 1(1)   | -7(1)  | -3(1)  |
| C(44) | 48(1)  | 41(1) | 42(1)  | -3(1)  | -1(1)  | -6(1)  |
| C(45) | 59(2)  | 61(2) | 46(2)  | -3(1)  | 6(1)   | -10(1) |
| C(46) | 63(2)  | 71(2) | 45(2)  | 10(1)  | 4(1)   | -18(1) |
| C(47) | 57(2)  | 47(1) | 49(2)  | 10(1)  | -16(1) | -13(1) |
| C(48) | 88(2)  | 49(2) | 74(2)  | 21(2)  | -14(2) | -15(2) |
| C(49) | 100(3) | 35(2) | 94(3)  | 16(2)  | -23(2) | -2(2)  |
| C(50) | 82(2)  | 39(2) | 82(2)  | -4(1)  | -19(2) | 11(1)  |
| C(51) | 60(2)  | 39(1) | 56(2)  | 2(1)   | -10(1) | 2(1)   |
| C(52) | 45(1)  | 35(1) | 42(1)  | 3(1)   | -13(1) | -5(1)  |

Table S15. Complete bond lengths [Å] and angles [deg] for (±)-2,2'-Bis(1-naphthylphenylphosphinoxy)-1,1'-biferrocenyl, (±)-**6a**, C<sub>52</sub>H<sub>40</sub>Fe<sub>2</sub>O<sub>2</sub>P<sub>2</sub>.

| Bond lengths |            |             |          |
|--------------|------------|-------------|----------|
| Fe(1)-C(8)   | 2.029(2)   | C(1)-C(2)   | 1.402(4) |
| Fe(1)-C(7)   | 2.041(2)   | C(1)-C(5)   | 1.414(4) |
| Fe(1)-C(5)   | 2.043(2)   | C(1)-H(1)   | 0.93     |
| Fe(1)-C(9)   | 2.044(2)   | C(2)-C(3)   | 1.411(4) |
| Fe(1)-C(1)   | 2.046(3)   | C(2)-H(2)   | 0.93     |
| Fe(1)-C(2)   | 2.046(3)   | C(3)-C(4)   | 1.410(4) |
| Fe(1)-C(10)  | 2.049(2)   | C(3)-H(3)   | 0.93     |
| Fe(1)-C(3)   | 2.051(2)   | C(4)-C(5)   | 1.408(4) |
| Fe(1)-C(4)   | 2.052(2)   | C(4)-H(4)   | 0.93     |
| Fe(1)-C(6)   | 2.057(2)   | C(5)-H(5)   | 0.93     |
| Fe(2)-C(33)  | 2.025(2)   | C(6)-C(10)  | 1.422(3) |
| Fe(2)-C(34)  | 2.026(2)   | C(6)-C(7)   | 1.451(3) |
| Fe(2)-C(28)  | 2.044(3)   | C(6)-C(32)  | 1.484(3) |
| Fe(2)-C(31)  | 2.047(3)   | C(7)-C(8)   | 1.429(3) |
| Fe(2)-C(30)  | 2.047(3)   | C(8)-C(9)   | 1.408(3) |
| Fe(2)-C(29)  | 2.048(3)   | C(8)-H(8)   | 0.93     |
| Fe(2)-C(27)  | 2.053(3)   | C(9)-C(10)  | 1.409(3) |
| Fe(2)-C(35)  | 2.058(2)   | C(9)-H(9)   | 0.93     |
| Fe(2)-C(32)  | 2.063(2)   | C(10)-H(10) | 0.93     |
| Fe(2)-C(36)  | 2.066(2)   | C(11)-C(12) | 1.384(3) |
| P(1)-O(1)    | 1.4798(15) | C(11)-C(16) | 1.389(3) |
| P(1)-C(7)    | 1.789(2)   | C(12)-C(13) | 1.386(4) |
| P(1)-C(11)   | 1.814(2)   | C(12)-H(12) | 0.93     |
| P(1)-C(17)   | 1.820(2)   | C(13)-C(14) | 1.372(4) |
| P(2)-O(2)    | 1.4811(16) | C(13)-H(13) | 0.93     |
| P(2)-C(33)   | 1.788(2)   | C(14)-C(15) | 1.368(4) |
| P(2)-C(43)   | 1.810(2)   | C(14)-H(14) | 0.93     |
| P(2)-C(37)   | 1.812(2)   | C(15)-C(16) | 1.389(4) |
|              |            | C(15)-H(15) | 0.93     |
|              |            | C(16)-H(16) | 0.93     |

|             |          |
|-------------|----------|
| C(17)-C(18) | 1.371(3) |
| C(17)-C(26) | 1.435(3) |
| C(18)-C(19) | 1.408(3) |
| C(18)-H(18) | 0.93     |
| C(19)-C(20) | 1.350(4) |
| C(19)-H(19) | 0.93     |
| C(20)-C(21) | 1.407(4) |
| C(20)-H(20) | 0.93     |
| C(21)-C(22) | 1.412(4) |
| C(21)-C(26) | 1.433(3) |
| C(22)-C(23) | 1.351(4) |
| C(22)-H(22) | 0.93     |
| C(23)-C(24) | 1.399(4) |
| C(23)-H(23) | 0.93     |
| C(24)-C(25) | 1.369(3) |
| C(24)-H(24) | 0.93     |
| C(25)-C(26) | 1.410(3) |
| C(25)-H(25) | 0.93     |
|             |          |
| C(27)-C(28) | 1.407(4) |
| C(27)-C(31) | 1.409(4) |
| C(27)-H(27) | 0.93     |
| C(28)-C(29) | 1.399(4) |
| C(28)-H(28) | 0.93     |
| C(29)-C(30) | 1.401(4) |
| C(29)-H(29) | 0.93     |
| C(30)-C(31) | 1.412(4) |
| C(30)-H(30) | 0.93     |
| C(31)-H(31) | 0.93     |
|             |          |
| C(32)-C(36) | 1.415(3) |
| C(32)-C(33) | 1.450(3) |
| C(33)-C(34) | 1.439(3) |
| C(34)-C(35) | 1.406(3) |
| C(34)-H(34) | 0.93     |
| C(35)-C(36) | 1.410(3) |
| C(35)-H(35) | 0.93     |
| C(36)-H(36) | 0.93     |
|             |          |
| C(37)-C(38) | 1.378(3) |
| C(37)-C(42) | 1.392(3) |
| C(38)-C(39) | 1.375(4) |
| C(38)-H(38) | 0.93     |
| C(39)-C(40) | 1.366(4) |
| C(39)-H(39) | 0.93     |
| C(40)-C(41) | 1.366(4) |
| C(40)-H(40) | 0.93     |
| C(41)-C(42) | 1.393(4) |
| C(41)-H(41) | 0.93     |
| C(42)-H(42) | 0.93     |
|             |          |
| C(43)-C(44) | 1.372(3) |
| C(43)-C(52) | 1.431(3) |
| C(44)-C(45) | 1.399(3) |
| C(44)-H(44) | 0.93     |
| C(45)-C(46) | 1.353(4) |
| C(45)-H(45) | 0.93     |
| C(46)-C(47) | 1.405(4) |
| C(46)-H(46) | 0.93     |
| C(47)-C(48) | 1.414(4) |
| C(47)-C(52) | 1.423(3) |
| C(48)-C(49) | 1.341(5) |
| C(48)-H(48) | 0.93     |
| C(49)-C(50) | 1.403(5) |
| C(49)-H(49) | 0.93     |
| C(50)-C(51) | 1.367(3) |
| C(50)-H(50) | 0.93     |

|             |          |
|-------------|----------|
| C(51)-C(52) | 1.414(3) |
| C(51)-H(51) | 0.93     |

## Bond angles

|                   |            |
|-------------------|------------|
| C(8)-Fe(1)-C(7)   | 41.10(8)   |
| C(8)-Fe(1)-C(5)   | 148.20(10) |
| C(7)-Fe(1)-C(5)   | 168.25(10) |
| C(8)-Fe(1)-C(9)   | 40.46(9)   |
| C(7)-Fe(1)-C(9)   | 68.68(9)   |
| C(5)-Fe(1)-C(9)   | 114.80(10) |
| C(8)-Fe(1)-C(1)   | 169.65(10) |
| C(7)-Fe(1)-C(1)   | 131.64(9)  |
| C(5)-Fe(1)-C(1)   | 40.47(10)  |
| C(9)-Fe(1)-C(1)   | 149.64(10) |
| C(8)-Fe(1)-C(2)   | 130.85(10) |
| C(7)-Fe(1)-C(2)   | 111.75(9)  |
| C(5)-Fe(1)-C(2)   | 67.76(11)  |
| C(9)-Fe(1)-C(2)   | 166.25(10) |
| C(1)-Fe(1)-C(2)   | 40.07(11)  |
| C(8)-Fe(1)-C(10)  | 68.02(9)   |
| C(7)-Fe(1)-C(10)  | 68.54(8)   |
| C(5)-Fe(1)-C(10)  | 106.36(10) |
| C(9)-Fe(1)-C(10)  | 40.26(9)   |
| C(1)-Fe(1)-C(10)  | 118.59(10) |
| C(2)-Fe(1)-C(10)  | 153.44(10) |
| C(8)-Fe(1)-C(3)   | 108.48(10) |
| C(7)-Fe(1)-C(3)   | 120.16(10) |
| C(5)-Fe(1)-C(3)   | 67.64(11)  |
| C(9)-Fe(1)-C(3)   | 126.79(11) |
| C(1)-Fe(1)-C(3)   | 67.53(11)  |
| C(2)-Fe(1)-C(3)   | 40.29(11)  |
| C(10)-Fe(1)-C(3)  | 163.58(10) |
| C(8)-Fe(1)-C(4)   | 115.96(10) |
| C(7)-Fe(1)-C(4)   | 151.33(10) |
| C(5)-Fe(1)-C(4)   | 40.24(11)  |
| C(9)-Fe(1)-C(4)   | 104.98(10) |
| C(1)-Fe(1)-C(4)   | 67.70(11)  |
| C(2)-Fe(1)-C(4)   | 67.70(11)  |
| C(10)-Fe(1)-C(4)  | 125.52(10) |
| C(3)-Fe(1)-C(4)   | 40.21(10)  |
| C(8)-Fe(1)-C(6)   | 69.14(8)   |
| C(7)-Fe(1)-C(6)   | 41.46(8)   |
| C(5)-Fe(1)-C(6)   | 127.95(10) |
| C(9)-Fe(1)-C(6)   | 68.55(8)   |
| C(1)-Fe(1)-C(6)   | 110.12(9)  |
| C(2)-Fe(1)-C(6)   | 121.51(9)  |
| C(10)-Fe(1)-C(6)  | 40.51(8)   |
| C(3)-Fe(1)-C(6)   | 154.92(10) |
| C(4)-Fe(1)-C(6)   | 164.19(10) |
|                   |            |
| C(33)-Fe(2)-C(34) | 41.60(8)   |
| C(33)-Fe(2)-C(28) | 109.47(10) |
| C(34)-Fe(2)-C(28) | 130.29(11) |
| C(33)-Fe(2)-C(31) | 170.56(12) |
| C(34)-Fe(2)-C(31) | 147.25(12) |
| C(28)-Fe(2)-C(31) | 67.39(12)  |
| C(33)-Fe(2)-C(30) | 147.85(11) |
| C(34)-Fe(2)-C(30) | 114.40(12) |
| C(28)-Fe(2)-C(30) | 67.24(13)  |
| C(31)-Fe(2)-C(30) | 40.34(12)  |
| C(33)-Fe(2)-C(29) | 116.31(10) |
| C(34)-Fe(2)-C(29) | 107.15(11) |
| C(28)-Fe(2)-C(29) | 39.97(12)  |
| C(31)-Fe(2)-C(29) | 67.51(12)  |
| C(30)-Fe(2)-C(29) | 40.01(12)  |
| C(33)-Fe(2)-C(27) | 131.77(11) |

|                   |            |                   |            |
|-------------------|------------|-------------------|------------|
| C(34)-Fe(2)-C(27) | 169.79(11) | C(4)-C(5)-C(1)    | 107.9(2)   |
| C(28)-Fe(2)-C(27) | 40.16(11)  | C(4)-C(5)-Fe(1)   | 70.23(14)  |
| C(31)-Fe(2)-C(27) | 40.21(12)  | C(1)-C(5)-Fe(1)   | 69.90(14)  |
| C(30)-Fe(2)-C(27) | 67.63(13)  | C(4)-C(5)-H(5)    | 126.0      |
| C(29)-Fe(2)-C(27) | 67.51(12)  | C(1)-C(5)-H(5)    | 126.0      |
| C(33)-Fe(2)-C(35) | 68.73(9)   | Fe(1)-C(5)-H(5)   | 125.4      |
| C(34)-Fe(2)-C(35) | 40.27(9)   |                   |            |
| C(28)-Fe(2)-C(35) | 167.48(11) | C(10)-C(6)-C(7)   | 106.61(18) |
| C(31)-Fe(2)-C(35) | 116.36(12) | C(10)-C(6)-C(32)  | 125.85(19) |
| C(30)-Fe(2)-C(35) | 107.27(12) | C(7)-C(6)-C(32)   | 127.48(18) |
| C(29)-Fe(2)-C(35) | 128.74(12) | C(10)-C(6)-Fe(1)  | 69.44(12)  |
| C(27)-Fe(2)-C(35) | 149.83(11) | C(7)-C(6)-Fe(1)   | 68.67(11)  |
| C(33)-Fe(2)-C(32) | 41.52(8)   | C(32)-C(6)-Fe(1)  | 128.91(14) |
| C(34)-Fe(2)-C(32) | 69.28(9)   | C(8)-C(7)-C(6)    | 107.26(18) |
| C(28)-Fe(2)-C(32) | 119.37(10) | C(8)-C(7)-P(1)    | 122.39(16) |
| C(31)-Fe(2)-C(32) | 131.30(11) | C(6)-C(7)-P(1)    | 130.05(15) |
| C(30)-Fe(2)-C(32) | 168.69(11) | C(8)-C(7)-Fe(1)   | 69.00(12)  |
| C(29)-Fe(2)-C(32) | 150.83(10) | C(6)-C(7)-Fe(1)   | 69.87(11)  |
| C(27)-Fe(2)-C(32) | 110.80(10) | P(1)-C(7)-Fe(1)   | 130.95(11) |
| C(35)-Fe(2)-C(32) | 68.09(9)   | C(9)-C(8)-C(7)    | 108.63(19) |
| C(33)-Fe(2)-C(36) | 68.40(8)   | C(9)-C(8)-Fe(1)   | 70.35(13)  |
| C(34)-Fe(2)-C(36) | 67.81(9)   | C(7)-C(8)-Fe(1)   | 69.90(12)  |
| C(28)-Fe(2)-C(36) | 151.98(11) | C(9)-C(8)-H(8)    | 125.7      |
| C(31)-Fe(2)-C(36) | 109.88(11) | C(7)-C(8)-H(8)    | 125.7      |
| C(30)-Fe(2)-C(36) | 129.96(11) | Fe(1)-C(8)-H(8)   | 125.6      |
| C(29)-Fe(2)-C(36) | 167.17(11) | C(10)-C(9)-C(8)   | 108.12(19) |
| C(27)-Fe(2)-C(36) | 119.27(11) | C(10)-C(9)-Fe(1)  | 70.06(12)  |
| C(35)-Fe(2)-C(36) | 39.98(9)   | C(8)-C(9)-Fe(1)   | 69.19(12)  |
| C(32)-Fe(2)-C(36) | 40.09(8)   | C(10)-C(9)-H(9)   | 125.9      |
|                   |            | C(8)-C(9)-H(9)    | 125.9      |
| O(1)-P(1)-C(7)    | 115.08(9)  | Fe(1)-C(9)-H(9)   | 126.4      |
| O(1)-P(1)-C(11)   | 112.52(10) | C(9)-C(10)-C(6)   | 109.38(19) |
| C(7)-P(1)-C(11)   | 104.26(10) | C(9)-C(10)-Fe(1)  | 69.68(13)  |
| O(1)-P(1)-C(17)   | 115.47(10) | C(6)-C(10)-Fe(1)  | 70.05(12)  |
| C(7)-P(1)-C(17)   | 104.54(10) | C(9)-C(10)-H(10)  | 125.3      |
| C(11)-P(1)-C(17)  | 103.69(10) | C(6)-C(10)-H(10)  | 125.3      |
|                   |            | Fe(1)-C(10)-H(10) | 126.6      |
| O(2)-P(2)-C(33)   | 115.10(9)  |                   |            |
| O(2)-P(2)-C(43)   | 115.07(10) | C(12)-C(11)-C(16) | 118.6(2)   |
| C(33)-P(2)-C(43)  | 104.70(10) | C(12)-C(11)-P(1)  | 118.01(18) |
| O(2)-P(2)-C(37)   | 112.27(10) | C(16)-C(11)-P(1)  | 123.42(18) |
| C(33)-P(2)-C(37)  | 105.63(10) | C(11)-C(12)-C(13) | 120.6(3)   |
| C(43)-P(2)-C(37)  | 102.87(10) | C(11)-C(12)-H(12) | 119.7      |
|                   |            | C(13)-C(12)-H(12) | 119.7      |
| C(2)-C(1)-C(5)    | 108.0(2)   | C(14)-C(13)-C(12) | 119.9(3)   |
| C(2)-C(1)-Fe(1)   | 69.97(15)  | C(14)-C(13)-H(13) | 120.0      |
| C(5)-C(1)-Fe(1)   | 69.63(15)  | C(12)-C(13)-H(13) | 120.0      |
| C(2)-C(1)-H(1)    | 126.0      | C(15)-C(14)-C(13) | 120.5(3)   |
| C(5)-C(1)-H(1)    | 126.0      | C(15)-C(14)-H(14) | 119.8      |
| Fe(1)-C(1)-H(1)   | 126.0      | C(13)-C(14)-H(14) | 119.8      |
| C(1)-C(2)-C(3)    | 108.1(2)   | C(14)-C(15)-C(16) | 119.8(3)   |
| C(1)-C(2)-Fe(1)   | 69.96(14)  | C(14)-C(15)-H(15) | 120.1      |
| C(3)-C(2)-Fe(1)   | 70.02(15)  | C(16)-C(15)-H(15) | 120.1      |
| C(1)-C(2)-H(2)    | 126.0      | C(11)-C(16)-C(15) | 120.6(3)   |
| C(3)-C(2)-H(2)    | 126.0      | C(11)-C(16)-H(16) | 119.7      |
| Fe(1)-C(2)-H(2)   | 125.6      | C(15)-C(16)-H(16) | 119.7      |
| C(4)-C(3)-C(2)    | 108.0(2)   |                   |            |
| C(4)-C(3)-Fe(1)   | 69.94(14)  | C(18)-C(17)-C(26) | 119.1(2)   |
| C(2)-C(3)-Fe(1)   | 69.69(14)  | C(18)-C(17)-P(1)  | 120.04(17) |
| C(4)-C(3)-H(3)    | 126.0      | C(26)-C(17)-P(1)  | 120.71(16) |
| C(2)-C(3)-H(3)    | 126.0      | C(17)-C(18)-C(19) | 122.0(2)   |
| Fe(1)-C(3)-H(3)   | 126.0      | C(17)-C(18)-H(18) | 119.0      |
| C(5)-C(4)-C(3)    | 107.9(2)   | C(19)-C(18)-H(18) | 119.0      |
| C(5)-C(4)-Fe(1)   | 69.53(14)  | C(20)-C(19)-C(18) | 120.0(2)   |
| C(3)-C(4)-Fe(1)   | 69.85(14)  | C(20)-C(19)-H(19) | 120.0      |
| C(5)-C(4)-H(4)    | 126.1      | C(18)-C(19)-H(19) | 120.0      |
| C(3)-C(4)-H(4)    | 126.1      | C(19)-C(20)-C(21) | 120.9(2)   |
| Fe(1)-C(4)-H(4)   | 126.1      | C(19)-C(20)-H(20) | 119.5      |

|                   |            |                   |            |
|-------------------|------------|-------------------|------------|
| C(21)-C(20)-H(20) | 119.5      | Fe(2)-C(34)-H(34) | 125.4      |
| C(20)-C(21)-C(22) | 121.1(2)   | C(34)-C(35)-C(36) | 108.30(19) |
| C(20)-C(21)-C(26) | 119.8(2)   | C(34)-C(35)-Fe(2) | 68.62(13)  |
| C(22)-C(21)-C(26) | 119.1(2)   | C(36)-C(35)-Fe(2) | 70.29(13)  |
| C(23)-C(22)-C(21) | 120.7(3)   | C(34)-C(35)-H(35) | 125.9      |
| C(23)-C(22)-H(22) | 119.6      | C(36)-C(35)-H(35) | 125.9      |
| C(21)-C(22)-H(22) | 119.6      | Fe(2)-C(35)-H(35) | 126.8      |
| C(22)-C(23)-C(24) | 120.8(3)   | C(35)-C(36)-C(32) | 109.51(19) |
| C(22)-C(23)-H(23) | 119.6      | C(35)-C(36)-Fe(2) | 69.72(13)  |
| C(24)-C(23)-H(23) | 119.6      | C(32)-C(36)-Fe(2) | 69.84(12)  |
| C(25)-C(24)-C(23) | 120.5(3)   | C(35)-C(36)-H(36) | 125.2      |
| C(25)-C(24)-H(24) | 119.7      | C(32)-C(36)-H(36) | 125.2      |
| C(23)-C(24)-H(24) | 119.7      | Fe(2)-C(36)-H(36) | 126.8      |
| C(24)-C(25)-C(26) | 120.7(2)   |                   |            |
| C(24)-C(25)-H(25) | 119.6      | C(38)-C(37)-C(42) | 119.2(2)   |
| C(26)-C(25)-H(25) | 119.6      | C(38)-C(37)-P(2)  | 118.20(18) |
| C(25)-C(26)-C(21) | 118.2(2)   | C(42)-C(37)-P(2)  | 122.53(18) |
| C(25)-C(26)-C(17) | 123.7(2)   | C(39)-C(38)-C(37) | 120.9(3)   |
| C(21)-C(26)-C(17) | 118.1(2)   | C(39)-C(38)-H(38) | 119.6      |
|                   |            | C(37)-C(38)-H(38) | 119.6      |
| C(28)-C(27)-C(31) | 107.4(3)   | C(40)-C(39)-C(38) | 120.0(3)   |
| C(28)-C(27)-Fe(2) | 69.58(16)  | C(40)-C(39)-H(39) | 120.0      |
| C(31)-C(27)-Fe(2) | 69.68(17)  | C(38)-C(39)-H(39) | 120.0      |
| C(28)-C(27)-H(27) | 126.3      | C(39)-C(40)-C(41) | 120.3(3)   |
| C(31)-C(27)-H(27) | 126.3      | C(39)-C(40)-H(40) | 119.9      |
| Fe(2)-C(27)-H(27) | 126.0      | C(41)-C(40)-H(40) | 119.9      |
| C(29)-C(28)-C(27) | 108.6(3)   | C(40)-C(41)-C(42) | 120.6(3)   |
| C(29)-C(28)-Fe(2) | 70.17(16)  | C(40)-C(41)-H(41) | 119.7      |
| C(27)-C(28)-Fe(2) | 70.26(16)  | C(42)-C(41)-H(41) | 119.7      |
| C(29)-C(28)-H(28) | 125.7      | C(37)-C(42)-C(41) | 119.1(3)   |
| C(27)-C(28)-H(28) | 125.7      | C(37)-C(42)-H(42) | 120.5      |
| Fe(2)-C(28)-H(28) | 125.5      | C(41)-C(42)-H(42) | 120.5      |
| C(30)-C(29)-C(28) | 108.0(3)   |                   |            |
| C(30)-C(29)-Fe(2) | 69.98(15)  | C(44)-C(43)-C(52) | 119.8(2)   |
| C(28)-C(29)-Fe(2) | 69.86(15)  | C(44)-C(43)-P(2)  | 120.28(17) |
| C(30)-C(29)-H(29) | 126.0      | C(52)-C(43)-P(2)  | 119.77(17) |
| C(28)-C(29)-H(29) | 126.0      | C(43)-C(44)-C(45) | 121.7(2)   |
| Fe(2)-C(29)-H(29) | 125.8      | C(43)-C(44)-H(44) | 119.1      |
| C(29)-C(30)-C(31) | 108.0(3)   | C(45)-C(44)-H(44) | 119.1      |
| C(29)-C(30)-Fe(2) | 70.01(15)  | C(46)-C(45)-C(44) | 119.3(2)   |
| C(31)-C(30)-Fe(2) | 69.81(15)  | C(46)-C(45)-H(45) | 120.4      |
| C(29)-C(30)-H(30) | 126.0      | C(44)-C(45)-H(45) | 120.4      |
| C(31)-C(30)-H(30) | 126.0      | C(45)-C(46)-C(47) | 121.9(2)   |
| Fe(2)-C(30)-H(30) | 125.7      | C(45)-C(46)-H(46) | 119.0      |
| C(27)-C(31)-C(30) | 108.0(3)   | C(47)-C(46)-H(46) | 119.0      |
| C(27)-C(31)-Fe(2) | 70.12(15)  | C(46)-C(47)-C(48) | 122.3(3)   |
| C(30)-C(31)-Fe(2) | 69.85(16)  | C(46)-C(47)-C(52) | 119.3(2)   |
| C(27)-C(31)-H(31) | 126.0      | C(48)-C(47)-C(52) | 118.4(3)   |
| C(30)-C(31)-H(31) | 126.0      | C(49)-C(48)-C(47) | 121.1(3)   |
| Fe(2)-C(31)-H(31) | 125.6      | C(49)-C(48)-H(48) | 119.4      |
|                   |            | C(47)-C(48)-H(48) | 119.4      |
| C(36)-C(32)-C(33) | 106.77(18) | C(48)-C(49)-C(50) | 121.1(3)   |
| C(36)-C(32)-C(6)  | 126.97(19) | C(48)-C(49)-H(49) | 119.5      |
| C(33)-C(32)-C(6)  | 126.24(18) | C(50)-C(49)-H(49) | 119.5      |
| C(36)-C(32)-Fe(2) | 70.06(12)  | C(51)-C(50)-C(49) | 120.0(3)   |
| C(33)-C(32)-Fe(2) | 67.85(11)  | C(51)-C(50)-H(50) | 120.0      |
| C(6)-C(32)-Fe(2)  | 128.36(14) | C(49)-C(50)-H(50) | 120.0      |
| C(34)-C(33)-C(32) | 107.15(18) | C(50)-C(51)-C(52) | 120.6(3)   |
| C(34)-C(33)-P(2)  | 124.13(16) | C(50)-C(51)-H(51) | 119.7      |
| C(32)-C(33)-P(2)  | 128.55(15) | C(52)-C(51)-H(51) | 119.7      |
| C(34)-C(33)-Fe(2) | 69.21(12)  | C(51)-C(52)-C(47) | 118.8(2)   |
| C(32)-C(33)-Fe(2) | 70.62(11)  | C(51)-C(52)-C(43) | 123.3(2)   |
| P(2)-C(33)-Fe(2)  | 128.92(12) | C(47)-C(52)-C(43) | 117.9(2)   |
| C(35)-C(34)-C(33) | 108.26(19) |                   |            |
| C(35)-C(34)-Fe(2) | 71.11(14)  |                   |            |
| C(33)-C(34)-Fe(2) | 69.19(12)  |                   |            |
| C(35)-C(34)-H(34) | 125.9      |                   |            |
| C(33)-C(34)-H(34) | 125.9      |                   |            |

## Selected torsion angles

C8-Fe1-C1-C2 31.4(6)

|               |              |                |              |
|---------------|--------------|----------------|--------------|
| C7-Fe1-C1-C2  | 73.34 (19)   | C1-Fe1-C4-C3   | 81.10 (18)   |
| C5-Fe1-C1-C2  | -119.2 (2)   | C2-Fe1-C4-C3   | 37.63 (17)   |
| C9-Fe1-C1-C2  | -162.93 (18) | C10-Fe1-C4-C3  | -168.85 (16) |
| C10-Fe1-C1-C2 | 159.16 (14)  | C6-Fe1-C4-C3   | 166.3 (3)    |
| C3-Fe1-C1-C2  | -37.75 (15)  | C3-C4-C5-C1    | 0.4 (3)      |
| C4-Fe1-C1-C2  | -81.39 (17)  | Fe1-C4-C5-C1   | 59.98 (17)   |
| C6-Fe1-C1-C2  | 115.42 (15)  | C3-C4-C5-Fe1   | -59.55 (18)  |
| C8-Fe1-C1-C5  | 150.6 (5)    | C2-C1-C5-C4    | -0.5 (3)     |
| C7-Fe1-C1-C5  | -167.51 (14) | Fe1-C1-C5-C4   | -60.19 (17)  |
| C9-Fe1-C1-C5  | -43.8 (3)    | C2-C1-C5-Fe1   | 59.65 (17)   |
| C2-Fe1-C1-C5  | 119.2 (2)    | C8-Fe1-C5-C4   | -51.7 (3)    |
| C10-Fe1-C1-C5 | -81.69 (17)  | C7-Fe1-C5-C4   | 171.3 (4)    |
| C3-Fe1-C1-C5  | 81.40 (17)   | C9-Fe1-C5-C4   | -83.96 (18)  |
| C4-Fe1-C1-C5  | 37.76 (16)   | C1-Fe1-C5-C4   | 118.7 (2)    |
| C6-Fe1-C1-C5  | -125.43 (16) | C2-Fe1-C5-C4   | 81.29 (18)   |
| C5-C1-C2-C3   | 0.4 (3)      | C10-Fe1-C5-C4  | -126.19 (16) |
| Fe1-C1-C2-C3  | 59.88 (17)   | C3-Fe1-C5-C4   | 37.59 (17)   |
| C5-C1-C2-Fe1  | -59.44 (17)  | C6-Fe1-C5-C4   | -165.31 (15) |
| C8-Fe1-C2-C1  | -172.88 (14) | C8-Fe1-C5-C1   | -170.37 (17) |
| C7-Fe1-C2-C1  | -129.57 (15) | C7-Fe1-C5-C1   | 52.6 (5)     |
| C5-Fe1-C2-C1  | 37.77 (15)   | C9-Fe1-C5-C1   | 157.34 (15)  |
| C9-Fe1-C2-C1  | 141.4 (4)    | C2-Fe1-C5-C1   | -37.41 (16)  |
| C10-Fe1-C2-C1 | -44.3 (3)    | C10-Fe1-C5-C1  | 115.11 (16)  |
| C3-Fe1-C2-C1  | 119.0 (2)    | C3-Fe1-C5-C1   | -81.11 (17)  |
| C4-Fe1-C2-C1  | 81.41 (17)   | C4-Fe1-C5-C1   | -118.7 (2)   |
| C6-Fe1-C2-C1  | -84.15 (17)  | C6-Fe1-C5-C1   | 75.99 (18)   |
| C8-Fe1-C2-C3  | 68.15 (19)   | C8-Fe1-C6-C10  | -80.17 (13)  |
| C7-Fe1-C2-C3  | 111.47 (16)  | C7-Fe1-C6-C10  | -118.30 (17) |
| C5-Fe1-C2-C3  | -81.20 (17)  | C5-Fe1-C6-C10  | 68.72 (17)   |
| C9-Fe1-C2-C3  | 22.4 (5)     | C9-Fe1-C6-C10  | -36.65 (13)  |
| C1-Fe1-C2-C3  | -119.0 (2)   | C1-Fe1-C6-C10  | 110.85 (14)  |
| C10-Fe1-C2-C3 | -163.29 (19) | C2-Fe1-C6-C10  | 153.85 (14)  |
| C4-Fe1-C2-C3  | -37.56 (16)  | C3-Fe1-C6-C10  | -169.4 (2)   |
| C6-Fe1-C2-C3  | 156.89 (14)  | C4-Fe1-C6-C10  | 31.8 (4)     |
| C1-C2-C3-C4   | -0.2 (3)     | C8-Fe1-C6-C7   | 38.13 (12)   |
| Fe1-C2-C3-C4  | 59.66 (18)   | C5-Fe1-C6-C7   | -172.97 (14) |
| C1-C2-C3-Fe1  | -59.84 (17)  | C9-Fe1-C6-C7   | 81.65 (13)   |
| C8-Fe1-C3-C4  | 108.63 (17)  | C1-Fe1-C6-C7   | -130.85 (13) |
| C7-Fe1-C3-C4  | 152.19 (16)  | C2-Fe1-C6-C7   | -87.85 (15)  |
| C5-Fe1-C3-C4  | -37.62 (17)  | C10-Fe1-C6-C7  | 118.30 (17)  |
| C9-Fe1-C3-C4  | 67.4 (2)     | C3-Fe1-C6-C7   | -51.1 (3)    |
| C1-Fe1-C3-C4  | -81.56 (18)  | C4-Fe1-C6-C7   | 150.1 (3)    |
| C2-Fe1-C3-C4  | -119.1 (2)   | C8-Fe1-C6-C32  | 159.8 (2)    |
| C10-Fe1-C3-C4 | 33.8 (4)     | C7-Fe1-C6-C32  | 121.6 (2)    |
| C6-Fe1-C3-C4  | -171.3 (2)   | C5-Fe1-C6-C32  | -51.3 (2)    |
| C8-Fe1-C3-C2  | -132.25 (16) | C9-Fe1-C6-C32  | -156.7 (2)   |
| C7-Fe1-C3-C2  | -88.69 (17)  | C1-Fe1-C6-C32  | -9.2 (2)     |
| C5-Fe1-C3-C2  | 81.50 (17)   | C2-Fe1-C6-C32  | 33.8 (2)     |
| C9-Fe1-C3-C2  | -173.50 (15) | C10-Fe1-C6-C32 | -120.1 (2)   |
| C1-Fe1-C3-C2  | 37.56 (15)   | C3-Fe1-C6-C32  | 70.6 (3)     |
| C10-Fe1-C3-C2 | 152.9 (3)    | C4-Fe1-C6-C32  | -88.3 (4)    |
| C4-Fe1-C3-C2  | 119.1 (2)    | C10-C6-C7-C8   | 0.3 (2)      |
| C6-Fe1-C3-C2  | -52.1 (3)    | C32-C6-C7-C8   | 177.52 (19)  |
| C2-C3-C4-C5   | -0.2 (3)     | Fe1-C6-C7-C8   | -59.09 (14)  |
| Fe1-C3-C4-C5  | 59.35 (18)   | C10-C6-C7-P1   | -173.51 (16) |
| C2-C3-C4-Fe1  | -59.51 (17)  | C32-C6-C7-P1   | 3.8 (3)      |
| C8-Fe1-C4-C5  | 152.63 (15)  | Fe1-C6-C7-P1   | 127.15 (18)  |
| C7-Fe1-C4-C5  | -176.30 (18) | C10-C6-C7-Fe1  | 59.35 (14)   |
| C9-Fe1-C4-C5  | 110.85 (16)  | C32-C6-C7-Fe1  | -123.4 (2)   |
| C1-Fe1-C4-C5  | -37.98 (16)  | O1-P1-C7-C8    | 150.20 (16)  |
| C2-Fe1-C4-C5  | -81.45 (18)  | C11-P1-C7-C8   | 26.5 (2)     |
| C10-Fe1-C4-C5 | 72.07 (19)   | C17-P1-C7-C8   | -82.07 (18)  |
| C3-Fe1-C4-C5  | -119.1 (2)   | O1-P1-C7-C6    | -36.9 (2)    |
| C6-Fe1-C4-C5  | 47.2 (4)     | C11-P1-C7-C6   | -160.58 (19) |
| C8-Fe1-C4-C3  | -88.29 (18)  | C17-P1-C7-C6   | 90.9 (2)     |
| C7-Fe1-C4-C3  | -57.2 (3)    | O1-P1-C7-Fe1   | 60.86 (17)   |
| C5-Fe1-C4-C3  | 119.1 (2)    | C11-P1-C7-Fe1  | -62.86 (16)  |
| C9-Fe1-C4-C3  | -130.07 (17) | C17-P1-C7-Fe1  | -171.41 (13) |

|               |             |                 |             |
|---------------|-------------|-----------------|-------------|
| C5-Fe1-C7-C8  | 146.9(5)    | C7-C6-C10-C9    | -0.1(2)     |
| C9-Fe1-C7-C8  | 37.34(12)   | C32-C6-C10-C9   | -177.46(19) |
| C1-Fe1-C7-C8  | -169.49(14) | Fe1-C6-C10-C9   | 58.71(15)   |
| C2-Fe1-C7-C8  | -127.88(14) | C7-C6-C10-Fe1   | -58.85(13)  |
| C10-Fe1-C7-C8 | 80.72(13)   | C32-C6-C10-Fe1  | 123.8(2)    |
| C3-Fe1-C7-C8  | -83.78(16)  | C8-Fe1-C10-C9   | -37.54(13)  |
| C4-Fe1-C7-C8  | -44.9(2)    | C7-Fe1-C10-C9   | -81.94(14)  |
| C6-Fe1-C7-C8  | 118.64(17)  | C5-Fe1-C10-C9   | 109.26(15)  |
| C8-Fe1-C7-C6  | -118.64(17) | C1-Fe1-C10-C9   | 151.28(14)  |
| C5-Fe1-C7-C6  | 28.3(5)     | C2-Fe1-C10-C9   | -177.9(2)   |
| C9-Fe1-C7-C6  | -81.30(13)  | C3-Fe1-C10-C9   | 43.2(4)     |
| C1-Fe1-C7-C6  | 71.87(16)   | C4-Fe1-C10-C9   | 69.43(17)   |
| C2-Fe1-C7-C6  | 113.48(13)  | C6-Fe1-C10-C9   | -120.72(18) |
| C10-Fe1-C7-C6 | -37.92(12)  | C8-Fe1-C10-C6   | 83.18(13)   |
| C3-Fe1-C7-C6  | 157.58(13)  | C7-Fe1-C10-C6   | 38.78(12)   |
| C4-Fe1-C7-C6  | -163.54(19) | C5-Fe1-C10-C6   | -130.02(14) |
| C8-Fe1-C7-P1  | 115.3(2)    | C9-Fe1-C10-C6   | 120.72(18)  |
| C5-Fe1-C7-P1  | -97.8(5)    | C1-Fe1-C10-C6   | -88.00(15)  |
| C9-Fe1-C7-P1  | 152.59(17)  | C2-Fe1-C10-C6   | -57.2(3)    |
| C1-Fe1-C7-P1  | -54.2(2)    | C3-Fe1-C10-C6   | 163.9(3)    |
| C2-Fe1-C7-P1  | -12.63(18)  | C4-Fe1-C10-C6   | -169.85(14) |
| C10-Fe1-C7-P1 | -164.03(17) | O1-P1-C11-C12   | -35.3(2)    |
| C3-Fe1-C7-P1  | 31.47(19)   | C7-P1-C11-C12   | 90.06(18)   |
| C4-Fe1-C7-P1  | 70.4(3)     | C17-P1-C11-C12  | -160.76(17) |
| C6-Fe1-C7-P1  | -126.1(2)   | O1-P1-C11-C16   | 146.01(18)  |
| C6-C7-C8-C9   | -0.3(2)     | C7-P1-C11-C16   | -88.6(2)    |
| P1-C7-C8-C9   | 174.07(15)  | C17-P1-C11-C16  | 20.5(2)     |
| Fe1-C7-C8-C9  | -59.92(15)  | C16-C11-C12-C13 | 0.6(3)      |
| C6-C7-C8-Fe1  | 59.65(13)   | P1-C11-C12-C13  | -178.11(19) |
| P1-C7-C8-Fe1  | -126.01(15) | C11-C12-C13-C14 | -0.7(4)     |
| C7-Fe1-C8-C9  | 119.46(18)  | C12-C13-C14-C15 | 0.3(4)      |
| C5-Fe1-C8-C9  | -48.4(2)    | C13-C14-C15-C16 | 0.1(4)      |
| C1-Fe1-C8-C9  | 168.8(5)    | C12-C11-C16-C15 | -0.2(3)     |
| C2-Fe1-C8-C9  | -164.79(14) | P1-C11-C16-C15  | 178.47(19)  |
| C10-Fe1-C8-C9 | 37.36(13)   | C14-C15-C16-C11 | -0.2(4)     |
| C3-Fe1-C8-C9  | -125.54(14) | O1-P1-C17-C18   | 130.04(17)  |
| C4-Fe1-C8-C9  | -82.67(16)  | C7-P1-C17-C18   | 2.6(2)      |
| C6-Fe1-C8-C9  | 81.01(13)   | C11-P1-C17-C18  | -106.42(18) |
| C5-Fe1-C8-C7  | -167.82(17) | O1-P1-C17-C26   | -54.2(2)    |
| C9-Fe1-C8-C7  | -119.46(18) | C7-P1-C17-C26   | 178.30(17)  |
| C1-Fe1-C8-C7  | 49.4(6)     | C11-P1-C17-C26  | 69.34(19)   |
| C2-Fe1-C8-C7  | 75.75(17)   | C26-C17-C18-C19 | -0.7(3)     |
| C10-Fe1-C8-C7 | -82.10(13)  | P1-C17-C18-C19  | 175.15(17)  |
| C3-Fe1-C8-C7  | 115.00(14)  | C17-C18-C19-C20 | 0.0(4)      |
| C4-Fe1-C8-C7  | 157.87(13)  | C18-C19-C20-C21 | 0.7(4)      |
| C6-Fe1-C8-C7  | -38.45(12)  | C19-C20-C21-C22 | 178.3(2)    |
| C7-C8-C9-C10  | 0.2(3)      | C19-C20-C21-C26 | -0.8(4)     |
| Fe1-C8-C9-C10 | -59.45(16)  | C20-C21-C22-C23 | -179.7(3)   |
| C7-C8-C9-Fe1  | 59.64(15)   | C26-C21-C22-C23 | -0.6(4)     |
| C8-Fe1-C9-C10 | 119.47(18)  | C21-C22-C23-C24 | -0.6(4)     |
| C7-Fe1-C9-C10 | 81.55(13)   | C22-C23-C24-C25 | 1.0(4)      |
| C5-Fe1-C9-C10 | -86.25(15)  | C23-C24-C25-C26 | 0.0(4)      |
| C1-Fe1-C9-C10 | -56.6(2)    | C24-C25-C26-C21 | -1.1(3)     |
| C2-Fe1-C9-C10 | 176.1(4)    | C24-C25-C26-C17 | 179.3(2)    |
| C3-Fe1-C9-C10 | -166.01(14) | C20-C21-C26-C25 | -179.5(2)   |
| C4-Fe1-C9-C10 | -127.93(14) | C22-C21-C26-C25 | 1.4(3)      |
| C6-Fe1-C9-C10 | 36.87(12)   | C20-C21-C26-C17 | 0.1(3)      |
| C7-Fe1-C9-C8  | -37.91(12)  | C22-C21-C26-C17 | -179.0(2)   |
| C5-Fe1-C9-C8  | 154.29(14)  | C18-C17-C26-C25 | -179.9(2)   |
| C1-Fe1-C9-C8  | -176.06(18) | P1-C17-C26-C25  | 4.3(3)      |
| C2-Fe1-C9-C8  | 56.6(4)     | C18-C17-C26-C21 | 0.6(3)      |
| C10-Fe1-C9-C8 | -119.47(18) | P1-C17-C26-C21  | -175.20(16) |
| C3-Fe1-C9-C8  | 74.52(17)   | C33-Fe2-C27-C28 | 68.6(2)     |
| C4-Fe1-C9-C8  | 112.61(14)  | C34-Fe2-C27-C28 | 22.8(7)     |
| C6-Fe1-C9-C8  | -82.59(13)  | C31-Fe2-C27-C28 | -118.6(3)   |
| C8-C9-C10-C6  | 0.0(3)      | C30-Fe2-C27-C28 | -80.75(19)  |
| Fe1-C9-C10-C6 | -58.94(15)  | C29-Fe2-C27-C28 | -37.30(17)  |
| C8-C9-C10-Fe1 | 58.91(16)   | C35-Fe2-C27-C28 | -166.77(19) |

|                 |             |                 |             |
|-----------------|-------------|-----------------|-------------|
| C32-Fe2-C27-C28 | 111.30(17)  | Fe2-C27-C31-C30 | -59.8(2)    |
| C36-Fe2-C27-C28 | 154.82(16)  | C28-C27-C31-Fe2 | 59.59(18)   |
| C33-Fe2-C27-C31 | -172.85(16) | C29-C30-C31-C27 | 0.2(3)      |
| C34-Fe2-C27-C31 | 141.4(6)    | Fe2-C30-C31-C27 | 60.01(19)   |
| C28-Fe2-C27-C31 | 118.6(3)    | C29-C30-C31-Fe2 | -59.9(2)    |
| C30-Fe2-C27-C31 | 37.84(18)   | C33-Fe2-C31-C27 | 34.5(7)     |
| C29-Fe2-C27-C31 | 81.28(19)   | C34-Fe2-C31-C27 | -168.20(18) |
| C35-Fe2-C27-C31 | -48.2(3)    | C28-Fe2-C31-C27 | -37.84(18)  |
| C32-Fe2-C27-C31 | -130.11(17) | C30-Fe2-C31-C27 | -118.8(3)   |
| C36-Fe2-C27-C31 | -86.60(19)  | C29-Fe2-C31-C27 | -81.3(2)    |
| C31-C27-C28-C29 | 0.3(3)      | C35-Fe2-C31-C27 | 155.29(17)  |
| Fe2-C27-C28-C29 | 59.91(19)   | C32-Fe2-C31-C27 | 72.1(2)     |
| C31-C27-C28-Fe2 | -59.66(19)  | C36-Fe2-C31-C27 | 112.19(18)  |
| C33-Fe2-C28-C29 | 108.07(17)  | C33-Fe2-C31-C30 | 153.3(6)    |
| C34-Fe2-C28-C29 | 65.8(2)     | C34-Fe2-C31-C30 | -49.4(3)    |
| C31-Fe2-C28-C29 | -81.47(19)  | C28-Fe2-C31-C30 | 81.0(2)     |
| C30-Fe2-C28-C29 | -37.58(18)  | C29-Fe2-C31-C30 | 37.52(19)   |
| C27-Fe2-C28-C29 | -119.4(3)   | C27-Fe2-C31-C30 | 118.8(3)    |
| C35-Fe2-C28-C29 | 28.6(6)     | C35-Fe2-C31-C30 | -85.9(2)    |
| C32-Fe2-C28-C29 | 152.65(16)  | C32-Fe2-C31-C30 | -169.07(17) |
| C36-Fe2-C28-C29 | -171.55(19) | C36-Fe2-C31-C30 | -129.00(19) |
| C33-Fe2-C28-C27 | -132.58(17) | C10-C6-C32-C36  | -119.8(2)   |
| C34-Fe2-C28-C27 | -174.83(16) | C7-C6-C32-C36   | 63.4(3)     |
| C31-Fe2-C28-C27 | 37.89(18)   | Fe1-C6-C32-C36  | -28.3(3)    |
| C30-Fe2-C28-C27 | 81.8(2)     | C10-C6-C32-C33  | 62.2(3)     |
| C29-Fe2-C28-C27 | 119.4(3)    | C7-C6-C32-C33   | -114.5(2)   |
| C35-Fe2-C28-C27 | 148.0(4)    | Fe1-C6-C32-C33  | 153.76(16)  |
| C32-Fe2-C28-C27 | -87.99(19)  | C10-C6-C32-Fe2  | -26.8(3)    |
| C36-Fe2-C28-C27 | -52.2(3)    | C7-C6-C32-Fe2   | 156.39(16)  |
| C27-C28-C29-C30 | -0.2(3)     | Fe1-C6-C32-Fe2  | 64.7(2)     |
| Fe2-C28-C29-C30 | 59.81(19)   | C33-Fe2-C32-C36 | -118.62(18) |
| C27-C28-C29-Fe2 | -59.97(18)  | C34-Fe2-C32-C36 | -79.77(14)  |
| C33-Fe2-C29-C30 | 151.65(18)  | C28-Fe2-C32-C36 | 154.75(15)  |
| C34-Fe2-C29-C30 | 107.74(19)  | C31-Fe2-C32-C36 | 70.07(19)   |
| C28-Fe2-C29-C30 | -119.0(3)   | C30-Fe2-C32-C36 | 31.3(6)     |
| C31-Fe2-C29-C30 | -37.8(2)    | C29-Fe2-C32-C36 | -168.0(2)   |
| C27-Fe2-C29-C30 | -81.5(2)    | C27-Fe2-C32-C36 | 111.16(15)  |
| C35-Fe2-C29-C30 | 68.7(2)     | C35-Fe2-C32-C36 | -36.42(13)  |
| C32-Fe2-C29-C30 | -174.2(2)   | C34-Fe2-C32-C33 | 38.86(12)   |
| C36-Fe2-C29-C30 | 42.9(6)     | C28-Fe2-C32-C33 | -86.63(15)  |
| C33-Fe2-C29-C28 | -89.36(19)  | C31-Fe2-C32-C33 | -171.31(16) |
| C34-Fe2-C29-C28 | -133.27(17) | C30-Fe2-C32-C33 | 150.0(6)    |
| C31-Fe2-C29-C28 | 81.2(2)     | C29-Fe2-C32-C33 | -49.4(3)    |
| C30-Fe2-C29-C28 | 119.0(3)    | C27-Fe2-C32-C33 | -130.22(14) |
| C27-Fe2-C29-C28 | 37.47(18)   | C35-Fe2-C32-C33 | 82.21(13)   |
| C35-Fe2-C29-C28 | -172.35(16) | C36-Fe2-C32-C33 | 118.62(18)  |
| C32-Fe2-C29-C28 | -55.2(3)    | C33-Fe2-C32-C6  | 119.5(2)    |
| C36-Fe2-C29-C28 | 161.9(4)    | C34-Fe2-C32-C6  | 158.3(2)    |
| C28-C29-C30-C31 | 0.0(3)      | C28-Fe2-C32-C6  | 32.8(2)     |
| Fe2-C29-C30-C31 | 59.73(19)   | C31-Fe2-C32-C6  | -51.9(2)    |
| C28-C29-C30-Fe2 | -59.73(19)  | C30-Fe2-C32-C6  | -90.6(6)    |
| C33-Fe2-C30-C29 | -53.1(3)    | C29-Fe2-C32-C6  | 70.1(3)     |
| C34-Fe2-C30-C29 | -87.9(2)    | C27-Fe2-C32-C6  | -10.8(2)    |
| C28-Fe2-C30-C29 | 37.55(19)   | C35-Fe2-C32-C6  | -158.3(2)   |
| C31-Fe2-C30-C29 | 118.9(3)    | C36-Fe2-C32-C6  | -121.9(2)   |
| C27-Fe2-C30-C29 | 81.2(2)     | C36-C32-C33-C34 | -0.3(2)     |
| C35-Fe2-C30-C29 | -130.46(19) | C6-C32-C33-C34  | 177.99(19)  |
| C32-Fe2-C30-C29 | 165.5(5)    | Fe2-C32-C33-C34 | -59.84(14)  |
| C36-Fe2-C30-C29 | -168.62(17) | C36-C32-C33-P2  | -175.64(16) |
| C33-Fe2-C30-C31 | -172.04(19) | C6-C32-C33-P2   | 2.7(3)      |
| C34-Fe2-C30-C31 | 153.20(19)  | Fe2-C32-C33-P2  | 124.83(18)  |
| C28-Fe2-C30-C31 | -81.4(2)    | C36-C32-C33-Fe2 | 59.52(14)   |
| C29-Fe2-C30-C31 | -118.9(3)   | C6-C32-C33-Fe2  | -122.2(2)   |
| C27-Fe2-C30-C31 | -37.71(19)  | O2-P2-C33-C34   | 151.92(18)  |
| C35-Fe2-C30-C31 | 110.6(2)    | C43-P2-C33-C34  | -80.7(2)    |
| C32-Fe2-C30-C31 | 46.6(7)     | C37-P2-C33-C34  | 27.5(2)     |
| C36-Fe2-C30-C31 | 72.5(2)     | O2-P2-C33-C32   | -33.5(2)    |
| C28-C27-C31-C30 | -0.3(3)     | C43-P2-C33-C32  | 93.9(2)     |

|                 |              |                 |              |
|-----------------|--------------|-----------------|--------------|
| C37-P2-C33-C32  | -157.92 (19) | C32-Fe2-C35-C36 | 36.52 (12)   |
| O2-P2-C33-Fe2   | 62.15 (17)   | C34-C35-C36-C32 | -0.4 (3)     |
| C43-P2-C33-Fe2  | -170.50 (13) | Fe2-C35-C36-C32 | -58.63 (15)  |
| C37-P2-C33-Fe2  | -62.30 (16)  | C34-C35-C36-Fe2 | 58.24 (16)   |
| C28-Fe2-C33-C34 | -129.42 (15) | C33-C32-C36-C35 | 0.4 (2)      |
| C31-Fe2-C33-C34 | 161.7 (6)    | C6-C32-C36-C35  | -177.9 (2)   |
| C30-Fe2-C33-C34 | -51.5 (3)    | Fe2-C32-C36-C35 | 58.55 (16)   |
| C29-Fe2-C33-C34 | -86.47 (16)  | C33-C32-C36-Fe2 | -58.12 (14)  |
| C27-Fe2-C33-C34 | -168.97 (15) | C6-C32-C36-Fe2  | 123.6 (2)    |
| C35-Fe2-C33-C34 | 37.36 (13)   | C33-Fe2-C36-C35 | -82.25 (14)  |
| C32-Fe2-C33-C34 | 117.90 (18)  | C34-Fe2-C36-C35 | -37.24 (13)  |
| C36-Fe2-C33-C34 | 80.45 (14)   | C28-Fe2-C36-C35 | -173.3 (2)   |
| C34-Fe2-C33-C32 | -117.90 (18) | C31-Fe2-C36-C35 | 107.68 (16)  |
| C28-Fe2-C33-C32 | 112.68 (14)  | C30-Fe2-C36-C35 | 66.65 (19)   |
| C31-Fe2-C33-C32 | 43.8 (7)     | C29-Fe2-C36-C35 | 31.8 (5)     |
| C30-Fe2-C33-C32 | -169.4 (2)   | C27-Fe2-C36-C35 | 150.93 (15)  |
| C29-Fe2-C33-C32 | 155.63 (14)  | C32-Fe2-C36-C35 | -120.99 (18) |
| C27-Fe2-C33-C32 | 73.13 (17)   | C33-Fe2-C36-C32 | 38.75 (12)   |
| C35-Fe2-C33-C32 | -80.54 (13)  | C34-Fe2-C36-C32 | 83.75 (14)   |
| C36-Fe2-C33-C32 | -37.45 (12)  | C28-Fe2-C36-C32 | -52.3 (3)    |
| C34-Fe2-C33-P2  | 117.7 (2)    | C31-Fe2-C36-C32 | -131.33 (15) |
| C28-Fe2-C33-P2  | -11.73 (18)  | C30-Fe2-C36-C32 | -172.35 (16) |
| C31-Fe2-C33-P2  | -80.6 (7)    | C29-Fe2-C36-C32 | 152.8 (4)    |
| C30-Fe2-C33-P2  | 66.2 (3)     | C27-Fe2-C36-C32 | -88.07 (16)  |
| C29-Fe2-C33-P2  | 31.22 (19)   | C35-Fe2-C36-C32 | 120.99 (18)  |
| C27-Fe2-C33-P2  | -51.3 (2)    | O2-P2-C37-C38   | -25.1 (2)    |
| C35-Fe2-C33-P2  | 155.05 (17)  | C33-P2-C37-C38  | 101.06 (19)  |
| C32-Fe2-C33-P2  | -124.4 (2)   | C43-P2-C37-C38  | -149.42 (18) |
| C36-Fe2-C33-P2  | -161.85 (17) | O2-P2-C37-C42   | 152.59 (18)  |
| C32-C33-C34-C35 | 0.1 (2)      | C33-P2-C37-C42  | -81.2 (2)    |
| P2-C33-C34-C35  | 175.68 (16)  | C43-P2-C37-C42  | 28.3 (2)     |
| Fe2-C33-C34-C35 | -60.66 (16)  | C42-C37-C38-C39 | 1.0 (3)      |
| C32-C33-C34-Fe2 | 60.75 (14)   | P2-C37-C38-C39  | 178.82 (18)  |
| P2-C33-C34-Fe2  | -123.67 (16) | C37-C38-C39-C40 | -1.4 (4)     |
| C33-Fe2-C34-C35 | 118.97 (19)  | C38-C39-C40-C41 | 0.8 (4)      |
| C28-Fe2-C34-C35 | -168.30 (15) | C39-C40-C41-C42 | 0.1 (4)      |
| C31-Fe2-C34-C35 | -55.6 (2)    | C38-C37-C42-C41 | 0.0 (3)      |
| C30-Fe2-C34-C35 | -88.22 (17)  | P2-C37-C42-C41  | -177.76 (18) |
| C29-Fe2-C34-C35 | -130.47 (15) | C40-C41-C42-C37 | -0.5 (4)     |
| C27-Fe2-C34-C35 | 172.6 (6)    | O2-P2-C43-C44   | 127.55 (18)  |
| C32-Fe2-C34-C35 | 80.18 (14)   | C33-P2-C43-C44  | 0.2 (2)      |
| C36-Fe2-C34-C35 | 36.99 (13)   | C37-P2-C43-C44  | -110.04 (19) |
| C28-Fe2-C34-C33 | 72.73 (18)   | O2-P2-C43-C52   | -56.1 (2)    |
| C31-Fe2-C34-C33 | -174.54 (19) | C33-P2-C43-C52  | 176.51 (17)  |
| C30-Fe2-C34-C33 | 152.81 (15)  | C37-P2-C43-C52  | 66.29 (19)   |
| C29-Fe2-C34-C33 | 110.56 (15)  | C52-C43-C44-C45 | -0.3 (3)     |
| C27-Fe2-C34-C33 | 53.6 (6)     | P2-C43-C44-C45  | 175.98 (19)  |
| C35-Fe2-C34-C33 | -118.97 (19) | C43-C44-C45-C46 | 0.3 (4)      |
| C32-Fe2-C34-C33 | -38.79 (12)  | C44-C45-C46-C47 | -0.1 (4)     |
| C36-Fe2-C34-C33 | -81.98 (13)  | C45-C46-C47-C48 | -179.8 (3)   |
| C33-C34-C35-C36 | 0.2 (3)      | C45-C46-C47-C52 | 0.0 (4)      |
| Fe2-C34-C35-C36 | -59.28 (17)  | C46-C47-C48-C49 | 178.5 (3)    |
| C33-C34-C35-Fe2 | 59.45 (15)   | C52-C47-C48-C49 | -1.4 (4)     |
| C33-Fe2-C35-C34 | -38.56 (13)  | C47-C48-C49-C50 | 0.9 (5)      |
| C28-Fe2-C35-C34 | 45.5 (5)     | C48-C49-C50-C51 | 0.2 (5)      |
| C31-Fe2-C35-C34 | 150.13 (15)  | C49-C50-C51-C52 | -0.9 (4)     |
| C30-Fe2-C35-C34 | 107.58 (16)  | C50-C51-C52-C47 | 0.5 (4)      |
| C29-Fe2-C35-C34 | 68.75 (18)   | C50-C51-C52-C43 | -178.6 (2)   |
| C27-Fe2-C35-C34 | -177.4 (2)   | C46-C47-C52-C51 | -179.2 (2)   |
| C32-Fe2-C35-C34 | -83.37 (14)  | C48-C47-C52-C51 | 0.7 (3)      |
| C36-Fe2-C35-C34 | -119.89 (19) | C46-C47-C52-C43 | -0.1 (3)     |
| C33-Fe2-C35-C36 | 81.33 (13)   | C48-C47-C52-C43 | 179.8 (2)    |
| C34-Fe2-C35-C36 | 119.89 (19)  | C44-C43-C52-C51 | 179.3 (2)    |
| C28-Fe2-C35-C36 | 165.4 (4)    | P2-C43-C52-C51  | 3.0 (3)      |
| C31-Fe2-C35-C36 | -89.98 (16)  | C44-C43-C52-C47 | 0.2 (3)      |
| C30-Fe2-C35-C36 | -132.52 (15) | P2-C43-C52-C47  | -176.12 (16) |
| C29-Fe2-C35-C36 | -171.36 (14) |                 |              |
| C27-Fe2-C35-C36 | -57.5 (3)    |                 |              |

|                       |           |                 |          |
|-----------------------|-----------|-----------------|----------|
| Non-bonding distances |           | 5.3420 (0.0012) | P1 - P2  |
|                       |           | 6.1757 (0.0023) | O1 - O2  |
| 4.4063 (0.0009)       | Fe1 - Fe2 | 3.4419 (0.0010) | Fe2 - P2 |
| 3.4865 (0.0009)       | Fe1 - P1  | 3.9889 (0.0018) | Fe2 - O2 |
| 4.0319 (0.0019)       | Fe1 - O1  |                 |          |

Table S16. Crystal data and structure refinement for ( $\pm$ )-2,2'-Bis(1-naphthylphenylphosphino)-1,1'-biferrocenyl bisdichloromethane solvate, ( $\pm$ )-**1a**·2CH<sub>2</sub>Cl<sub>2</sub>, C<sub>52</sub>H<sub>40</sub>Fe<sub>2</sub>P<sub>2</sub>·2CH<sub>2</sub>Cl<sub>2</sub>.

|                                   |                                                                                                                                                      |
|-----------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------|
| Identification code               | widij4fr                                                                                                                                             |
| Empirical formula                 | C <sub>54</sub> H <sub>40</sub> Cl <sub>4</sub> Fe <sub>2</sub> P <sub>2</sub> (with 2 solvent CH <sub>2</sub> Cl <sub>2</sub> )                     |
| Formula weight                    | 1004.30                                                                                                                                              |
| Temperature                       | 213(2) K                                                                                                                                             |
| Wavelength                        | 0.71073 Å                                                                                                                                            |
| Crystal system, space group       | orthorhombic, Pbcn (No. 60)                                                                                                                          |
| Unit cell dimensions              | a = 16.392(8) Å $\alpha$ = 90°<br>b = 17.161(8) Å $\beta$ = 90°<br>c = 16.522(8) Å $\gamma$ = 90°                                                    |
| Volume                            | 4648(4) Å <sup>3</sup>                                                                                                                               |
| Z, Calculated density             | 4, 1.435 Mg/m <sup>3</sup>                                                                                                                           |
| Absorption coefficient            | 0.960 mm <sup>-1</sup>                                                                                                                               |
| F(000)                            | 2056                                                                                                                                                 |
| Crystal size                      | 0.3 x 0.3 x 0.2 mm, orange fragment from CD <sub>2</sub> Cl <sub>2</sub>                                                                             |
| Diffractionmeter                  | Siemens SMART 3-circle with CCD area detector<br>(sealed X-ray tube, Mo K $\alpha$ radiation, graphite monochr., det.dist. 44.50 mm, 512x512 pixels) |
| Scan type / width / speed         | $\omega$ -scan frames / $\Delta\omega$ = 0.3° / 30 sec. per frame<br>full sphere, 4 x 606 frames                                                     |
| Theta range for data collection   | 2.11° to 27.00°                                                                                                                                      |
| Index ranges                      | -20 ≤ h ≤ 20, -21 ≤ k ≤ 21, -21 ≤ l ≤ 21                                                                                                             |
| Reflections collected / unique    | 51546 / 5008 [R(int) = 0.041, R(sigma) = 0.018]                                                                                                      |
| Completeness to theta = 27.00     | 89.5%                                                                                                                                                |
| Absorption correction             | Empirical (program SADABS; Sheldrick, 1996)                                                                                                          |
| Transmission factors              | 0.862 - 0.685                                                                                                                                        |
| Structure solution                | Direct methods (program SHELXS97)                                                                                                                    |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup> (prg SHELXL97)                                                                                           |
| Data / restraints / parameters    | 5008 / 0 / 334                                                                                                                                       |
| Goodness-of-fit on F <sup>2</sup> | 1.121                                                                                                                                                |
| Final R indices [I > 2sigma(I)]   | R1 = 0.0363, wR2 = 0.0813 (4463 data)                                                                                                                |
| R indices (all data)              | R1 = 0.0429, wR2 = 0.0847 (5008 data)                                                                                                                |
| Extinction coefficient            | 0.00049(8)                                                                                                                                           |
| Largest diff. peak and hole       | 0.280 and -0.253 e Å <sup>-3</sup>                                                                                                                   |

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad wR2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2)^2)]^{1/2}$$

Table S17. Atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup> x 10<sup>3</sup> for ( $\pm$ )-2,2'-Bis(1-naphthylphenylphosphino)-1,1'-biferrocenyl bisdichloromethane solvate, ( $\pm$ )-**1a**·2CH<sub>2</sub>Cl<sub>2</sub>, C<sub>52</sub>H<sub>40</sub>Fe<sub>2</sub>P<sub>2</sub>·2CH<sub>2</sub>Cl<sub>2</sub>. U<sub>eq</sub> is defined as one third of the trace of the orthogonalized U<sub>ij</sub> tensor.

|      | x           | y           | z           | U <sub>eq</sub> |
|------|-------------|-------------|-------------|-----------------|
| Fe   | 0.43932(2)  | 0.81435(2)  | 0.87375(2)  | 26(1)           |
| P    | 0.64433(3)  | 0.78753(3)  | 0.86142(3)  | 28(1)           |
| C(1) | 0.41433(13) | 0.91701(12) | 0.81583(12) | 34(1)           |
| C(2) | 0.47130(13) | 0.92964(12) | 0.87912(13) | 35(1)           |
| C(3) | 0.43470(14) | 0.90622(13) | 0.95298(13) | 39(1)           |
| C(4) | 0.35503(13) | 0.87923(13) | 0.93514(13) | 40(1)           |
| C(5) | 0.34238(13) | 0.88582(12) | 0.85053(14) | 38(1)           |
| C(6) | 0.48892(11) | 0.73508(10) | 0.79347(11) | 25(1)           |

|        |               |             |             |         |
|--------|---------------|-------------|-------------|---------|
| C(7)   | 0.54201(11)   | 0.74653(11) | 0.86318(11) | 27(1)   |
| C(8)   | 0.49626(12)   | 0.72574(11) | 0.93398(11) | 31(1)   |
| C(9)   | 0.41661(13)   | 0.70274(12) | 0.90998(12) | 33(1)   |
| C(10)  | 0.41194(12)   | 0.70828(11) | 0.82425(12) | 29(1)   |
| C(11)  | 0.66094(11)   | 0.81154(12) | 0.96926(11) | 30(1)   |
| C(12)  | 0.66398(15)   | 0.88949(13) | 0.99134(14) | 43(1)   |
| C(13)  | 0.67869(17)   | 0.91106(15) | 1.07134(16) | 54(1)   |
| C(14)  | 0.69180(15)   | 0.85490(16) | 1.12926(14) | 48(1)   |
| C(15)  | 0.68909(13)   | 0.77782(15) | 1.10827(13) | 42(1)   |
| C(16)  | 0.67381(12)   | 0.75568(13) | 1.02902(12) | 35(1)   |
| C(17)  | 0.70880(13)   | 0.69935(14) | 0.85558(12) | 37(1)   |
| C(18)  | 0.67756(17)   | 0.62607(14) | 0.85149(14) | 47(1)   |
| C(19)  | 0.72910(20)   | 0.55987(18) | 0.84342(17) | 72(1)   |
| C(20)  | 0.81060(20)   | 0.56890(20) | 0.83973(16) | 79(1)   |
| C(21)  | 0.84649(18)   | 0.64270(30) | 0.84384(14) | 71(1)   |
| C(22)  | 0.93290(20)   | 0.65480(40) | 0.84047(19) | 104(2)  |
| C(23)  | 0.96640(20)   | 0.72600(40) | 0.84510(20) | 114(2)  |
| C(24)  | 0.91690(18)   | 0.79110(30) | 0.85304(19) | 92(1)   |
| C(25)  | 0.83326(15)   | 0.78400(20) | 0.85557(16) | 64(1)   |
| C(26)  | 0.79605(14)   | 0.71035(18) | 0.85165(12) | 49(1)   |
| C(27S) | \$ 0.3855(6)  | 0.5044(4)   | 0.8704(6)   | 208(6)  |
| Cl(1A) | \$ 0.3991(10) | 0.4272(7)   | 0.8072(12)  | 129(5)  |
| Cl(1B) | \$ 0.4594(6)  | 0.4969(6)   | 0.7917(5)   | 195(6)  |
| Cl(1C) | \$ 0.3828(11) | 0.4231(9)   | 0.8540(40)  | 260(20) |
| Cl(1D) | \$ 0.3845(12) | 0.4308(15)  | 0.8161(14)  | 116(7)  |
| Cl(2A) | \$ 0.3947(14) | 0.4773(15)  | 0.9705(17)  | 393(19) |
| Cl(2B) | \$ 0.3617(5)  | 0.4758(3)   | 0.9709(4)   | 106(3)  |
| Cl(2C) | \$ 0.4521(17) | 0.4787(12)  | 0.9590(14)  | 278(12) |

\$ CH<sub>2</sub>Cl<sub>2</sub> solvent molecule with disordered Cl sites. Refined site occupancies C(27S) 1.15(2), Cl(1A) 0.30(3), Cl(1B) 0.28(1), Cl(1C) 0.22(2), Cl(1D) 0.19(3), Cl(2A) 0.42(2), Cl(2B) 0.31(1), Cl(2C) 0.24(1).

Table S18. Hydrogen coordinates and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for ( $\pm$ )-2,2'-Bis(1-naphthylphenylphosphino)-1,1'-biferrocenyl bisdichloromethane solvate, ( $\pm$ )-1a·2CH<sub>2</sub>Cl<sub>2</sub>, C<sub>52</sub>H<sub>40</sub>Fe<sub>2</sub>P<sub>2</sub>·2CH<sub>2</sub>Cl<sub>2</sub>.

|       | x      | y      | z      | U <sub>iso</sub> |
|-------|--------|--------|--------|------------------|
| H(1)  | 0.4228 | 0.9275 | 0.7606 | 41               |
| H(2)  | 0.5242 | 0.9500 | 0.8731 | 42               |
| H(3)  | 0.4589 | 0.9082 | 1.0045 | 46               |
| H(4)  | 0.3171 | 0.8602 | 0.9729 | 48               |
| H(5)  | 0.2947 | 0.8719 | 0.8224 | 45               |
| H(8)  | 0.5158 | 0.7271 | 0.9875 | 37               |
| H(9)  | 0.3744 | 0.6867 | 0.9447 | 40               |
| H(10) | 0.3658 | 0.6963 | 0.7928 | 35               |
| H(12) | 0.6560 | 0.9282 | 0.9519 | 52               |
| H(13) | 0.6797 | 0.9640 | 1.0857 | 65               |
| H(14) | 0.7026 | 0.8694 | 1.1831 | 57               |
| H(15) | 0.6977 | 0.7395 | 1.1480 | 50               |
| H(16) | 0.6721 | 0.7025 | 1.0155 | 42               |
| H(18) | 0.6208 | 0.6190 | 0.8541 | 56               |
| H(19) | 0.7062 | 0.5097 | 0.8407 | 87               |
| H(20) | 0.8441 | 0.5247 | 0.8343 | 95               |
| H(22) | 0.9674 | 0.6113 | 0.8348 | 124              |
| H(23) | 1.0234 | 0.7318 | 0.8430 | 137              |
| H(24) | 0.9408 | 0.8408 | 0.8567 | 111              |
| H(25) | 0.8007 | 0.8289 | 0.8600 | 77               |

Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded. All hydrogen atoms had U<sub>iso</sub> = U<sub>eq</sub> × 1.2 of their carrier atoms.

Table S19. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $(\pm)$ -2,2'-Bis(1-naphthylphenylphosphino)-1,1'-biferrocenyl bisdichloromethane solvate,  $(\pm)$ -**1a**·2CH<sub>2</sub>Cl<sub>2</sub>, C<sub>52</sub>H<sub>40</sub>Fe<sub>2</sub>P<sub>2</sub>·2CH<sub>2</sub>Cl<sub>2</sub>. The anisotropic displacement factor exponent takes the form:  $-\frac{1}{2} \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

|         | U <sub>11</sub> | U <sub>22</sub> | U <sub>33</sub> | U <sub>23</sub> | U <sub>13</sub> | U <sub>12</sub> |
|---------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Fe      | 25 (1)          | 29 (1)          | 24 (1)          | 1 (1)           | 1 (1)           | 1 (1)           |
| P       | 26 (1)          | 33 (1)          | 26 (1)          | 2 (1)           | -4 (1)          | 2 (1)           |
| C (1)   | 39 (1)          | 31 (1)          | 33 (1)          | 4 (1)           | 2 (1)           | 9 (1)           |
| C (2)   | 35 (1)          | 29 (1)          | 42 (1)          | -4 (1)          | 3 (1)           | 0 (1)           |
| C (3)   | 48 (1)          | 37 (1)          | 30 (1)          | -7 (1)          | 1 (1)           | 6 (1)           |
| C (4)   | 37 (1)          | 43 (1)          | 41 (1)          | -1 (1)          | 14 (1)          | 7 (1)           |
| C (5)   | 29 (1)          | 37 (1)          | 46 (1)          | -2 (1)          | 0 (1)           | 8 (1)           |
| C (6)   | 26 (1)          | 23 (1)          | 27 (1)          | 1 (1)           | -3 (1)          | 1 (1)           |
| C (7)   | 29 (1)          | 26 (1)          | 25 (1)          | 1 (1)           | -2 (1)          | 4 (1)           |
| C (8)   | 35 (1)          | 32 (1)          | 26 (1)          | 4 (1)           | -2 (1)          | 3 (1)           |
| C (9)   | 36 (1)          | 34 (1)          | 31 (1)          | 7 (1)           | 3 (1)           | -3 (1)          |
| C (10)  | 30 (1)          | 27 (1)          | 31 (1)          | 2 (1)           | -2 (1)          | -3 (1)          |
| C (11)  | 24 (1)          | 36 (1)          | 29 (1)          | -2 (1)          | -4 (1)          | 2 (1)           |
| C (12)  | 50 (1)          | 35 (1)          | 44 (1)          | -2 (1)          | -13 (1)         | 4 (1)           |
| C (13)  | 66 (2)          | 41 (1)          | 54 (2)          | -17 (1)         | -14 (1)         | 8 (1)           |
| C (14)  | 45 (1)          | 66 (2)          | 33 (1)          | -15 (1)         | -7 (1)          | 10 (1)          |
| C (15)  | 39 (1)          | 57 (1)          | 30 (1)          | 4 (1)           | -5 (1)          | 10 (1)          |
| C (16)  | 34 (1)          | 39 (1)          | 33 (1)          | 1 (1)           | -6 (1)          | 5 (1)           |
| C (17)  | 36 (1)          | 52 (1)          | 23 (1)          | 1 (1)           | -3 (1)          | 15 (1)          |
| C (18)  | 59 (2)          | 43 (1)          | 38 (1)          | 2 (1)           | -1 (1)          | 19 (1)          |
| C (19)  | 116 (3)         | 56 (2)          | 45 (1)          | 6 (1)           | 8 (2)           | 44 (2)          |
| C (20)  | 96 (3)          | 101 (3)         | 39 (1)          | 17 (2)          | 14 (2)          | 70 (2)          |
| C (21)  | 56 (2)          | 135 (3)         | 22 (1)          | 15 (1)          | 7 (1)           | 55 (2)          |
| C (22)  | 54 (2)          | 221 (6)         | 36 (2)          | 25 (2)          | 11 (2)          | 75 (3)          |
| C (23)  | 31 (2)          | 268 (7)         | 44 (2)          | 12 (3)          | 4 (1)           | 30 (3)          |
| C (24)  | 36 (2)          | 190 (4)         | 51 (2)          | 0 (2)           | 0 (1)           | -19 (2)         |
| C (25)  | 32 (1)          | 120 (3)         | 41 (1)          | -4 (2)          | -1 (1)          | -4 (2)          |
| C (26)  | 34 (1)          | 91 (2)          | 22 (1)          | 1 (1)           | -1 (1)          | 22 (1)          |
| C (27S) | 257 (10)        | 96 (5)          | 270 (11)        | 20 (5)          | 103 (8)         | 30 (5)          |
| Cl (1A) | 109 (7)         | 103 (7)         | 177 (9)         | -41 (7)         | 9 (5)           | 53 (7)          |
| Cl (1B) | 233 (11)        | 171 (9)         | 181 (7)         | -14 (5)         | 8 (6)           | 91 (8)          |
| Cl (1C) | 90 (7)          | 67 (7)          | 620 (60)        | 75 (17)         | 30 (20)         | -18 (5)         |
| Cl (1D) | 60 (7)          | 144 (17)        | 143 (14)        | 33 (11)         | 4 (5)           | -33 (8)         |
| Cl (2A) | 208 (14)        | 420 (30)        | 550 (40)        | 350 (30)        | 141 (14)        | 38 (13)         |
| Cl (2B) | 107 (4)         | 97 (4)          | 115 (5)         | 22 (3)          | 21 (3)          | -15 (2)         |
| Cl (2C) | 250 (20)        | 309 (19)        | 275 (19)        | -62 (14)        | -82 (14)        | 84 (14)         |

§ CH<sub>2</sub>Cl<sub>2</sub> solvent molecule with disordered Cl sites, see Table 2.

Table S20. Complete bond lengths [ $\text{\AA}$ ] and angles [deg] for  $(\pm)$ -2,2'-Bis(1-naphthylphenylphosphino)-1,1'-biferrocenyl bisdichloromethane solvate,  $(\pm)$ -**1a**·2CH<sub>2</sub>Cl<sub>2</sub>, C<sub>52</sub>H<sub>40</sub>Fe<sub>2</sub>P<sub>2</sub>·2CH<sub>2</sub>Cl<sub>2</sub>.

| Bond lengths |           |              |           |
|--------------|-----------|--------------|-----------|
|              |           | P-C (17)     | 1.848 (2) |
|              |           | P-C (11)     | 1.849 (2) |
| Fe-C (9)     | 2.041 (2) | C (1)-C (5)  | 1.416 (3) |
| Fe-C (8)     | 2.043 (2) | C (1)-C (2)  | 1.419 (3) |
| Fe-C (5)     | 2.044 (2) | C (1)-H (1)  | 0.94      |
| Fe-C (4)     | 2.044 (2) | C (2)-C (3)  | 1.418 (3) |
| Fe-C (10)    | 2.045 (2) | C (2)-H (2)  | 0.94      |
| Fe-C (1)     | 2.046 (2) | C (3)-C (4)  | 1.417 (3) |
| Fe-C (2)     | 2.049 (2) | C (3)-H (3)  | 0.94      |
| Fe-C (3)     | 2.051 (2) | C (4)-C (5)  | 1.418 (3) |
| Fe-C (7)     | 2.054 (2) | C (4)-H (4)  | 0.94      |
| Fe-C (6)     | 2.067 (2) | C (5)-H (5)  | 0.94      |
| P-C (7)      | 1.819 (2) | C (6)-C (10) | 1.436 (3) |

|               |           |
|---------------|-----------|
| C(6)-C(7)     | 1.457(2)  |
| C(6)-C(6)#1   | 1.482(4)  |
| C(7)-C(8)     | 1.435(3)  |
| C(8)-C(9)     | 1.420(3)  |
| C(8)-H(8)     | 0.94      |
| C(9)-C(10)    | 1.422(3)  |
| C(9)-H(9)     | 0.94      |
| C(10)-H(10)   | 0.94      |
| C(11)-C(12)   | 1.387(3)  |
| C(11)-C(16)   | 1.392(3)  |
| C(12)-C(13)   | 1.394(3)  |
| C(12)-H(12)   | 0.94      |
| C(13)-C(14)   | 1.375(4)  |
| C(13)-H(13)   | 0.94      |
| C(14)-C(15)   | 1.368(4)  |
| C(14)-H(14)   | 0.94      |
| C(15)-C(16)   | 1.386(3)  |
| C(15)-H(15)   | 0.94      |
| C(16)-H(16)   | 0.94      |
| C(17)-C(18)   | 1.360(3)  |
| C(17)-C(26)   | 1.444(3)  |
| C(18)-C(19)   | 1.422(3)  |
| C(18)-H(18)   | 0.94      |
| C(19)-C(20)   | 1.347(5)  |
| C(19)-H(19)   | 0.94      |
| C(20)-C(21)   | 1.397(5)  |
| C(20)-H(20)   | 0.94      |
| C(21)-C(26)   | 1.432(4)  |
| C(21)-C(22)   | 1.433(5)  |
| C(22)-C(23)   | 1.342(7)  |
| C(22)-H(22)   | 0.94      |
| C(23)-C(24)   | 1.386(7)  |
| C(23)-H(23)   | 0.94      |
| C(24)-C(25)   | 1.377(4)  |
| C(24)-H(24)   | 0.94      |
| C(25)-C(26)   | 1.405(4)  |
| C(25)-H(25)   | 0.94      |
| C(27S)-Cl(1C) | 1.42(2)   |
| C(27S)-Cl(1D) | 1.55(3)   |
| C(27S)-Cl(1A) | 1.701(12) |
| C(27S)-Cl(2A) | 1.72(3)   |
| C(27S)-Cl(2B) | 1.776(11) |
| C(27S)-Cl(1B) | 1.781(10) |
| C(27S)-Cl(2C) | 1.878(16) |

## Bond angles

|               |           |
|---------------|-----------|
| C(9)-Fe-C(8)  | 40.71(8)  |
| C(9)-Fe-C(5)  | 118.45(9) |
| C(8)-Fe-C(5)  | 153.30(8) |
| C(9)-Fe-C(4)  | 104.03(9) |
| C(8)-Fe-C(4)  | 118.20(9) |
| C(5)-Fe-C(4)  | 40.59(9)  |
| C(9)-Fe-C(10) | 40.72(8)  |
| C(8)-Fe-C(10) | 68.45(8)  |
| C(5)-Fe-C(10) | 106.76(9) |
| C(4)-Fe-C(10) | 122.33(9) |
| C(9)-Fe-C(1)  | 155.31(9) |
| C(8)-Fe-C(1)  | 163.76(8) |
| C(5)-Fe-C(1)  | 40.52(8)  |
| C(4)-Fe-C(1)  | 68.15(9)  |
| C(10)-Fe-C(1) | 122.36(9) |
| C(9)-Fe-C(2)  | 160.10(9) |
| C(8)-Fe-C(2)  | 125.51(9) |
| C(5)-Fe-C(2)  | 68.13(9)  |
| C(4)-Fe-C(2)  | 68.00(9)  |
| C(10)-Fe-C(2) | 158.89(8) |

|                   |            |
|-------------------|------------|
| C(1)-Fe-C(2)      | 40.54(9)   |
| C(9)-Fe-C(3)      | 121.85(9)  |
| C(8)-Fe-C(3)      | 106.16(9)  |
| C(5)-Fe-C(3)      | 68.27(9)   |
| C(4)-Fe-C(3)      | 40.49(9)   |
| C(10)-Fe-C(3)     | 158.65(8)  |
| C(1)-Fe-C(3)      | 68.23(9)   |
| C(2)-Fe-C(3)      | 40.47(9)   |
| C(9)-Fe-C(7)      | 69.06(8)   |
| C(8)-Fe-C(7)      | 41.00(7)   |
| C(5)-Fe-C(7)      | 164.01(8)  |
| C(4)-Fe-C(7)      | 154.82(8)  |
| C(10)-Fe-C(7)     | 68.99(8)   |
| C(1)-Fe-C(7)      | 127.74(8)  |
| C(2)-Fe-C(7)      | 109.95(8)  |
| C(3)-Fe-C(7)      | 121.35(8)  |
| C(9)-Fe-C(6)      | 69.04(8)   |
| C(8)-Fe-C(6)      | 69.08(8)   |
| C(5)-Fe-C(6)      | 125.48(8)  |
| C(4)-Fe-C(6)      | 160.56(8)  |
| C(10)-Fe-C(6)     | 40.88(7)   |
| C(1)-Fe-C(6)      | 110.20(8)  |
| C(2)-Fe-C(6)      | 124.25(8)  |
| C(3)-Fe-C(6)      | 158.49(8)  |
| C(7)-Fe-C(6)      | 41.41(7)   |
| C(7)-P-C(17)      | 102.21(10) |
| C(7)-P-C(11)      | 101.92(8)  |
| C(17)-P-C(11)     | 98.54(9)   |
| C(5)-C(1)-C(2)    | 107.91(19) |
| C(5)-C(1)-Fe      | 69.64(12)  |
| C(2)-C(1)-Fe      | 69.82(12)  |
| C(5)-C(1)-H(1)    | 126.0      |
| C(2)-C(1)-H(1)    | 126.0      |
| Fe-C(1)-H(1)      | 126.1      |
| C(3)-C(2)-C(1)    | 108.21(19) |
| C(3)-C(2)-Fe      | 69.84(12)  |
| C(1)-C(2)-Fe      | 69.64(12)  |
| C(3)-C(2)-H(2)    | 125.9      |
| C(1)-C(2)-H(2)    | 125.9      |
| Fe-C(2)-H(2)      | 126.2      |
| C(4)-C(3)-C(2)    | 107.68(19) |
| C(4)-C(3)-Fe      | 69.50(12)  |
| C(2)-C(3)-Fe      | 69.69(12)  |
| C(4)-C(3)-H(3)    | 126.2      |
| C(2)-C(3)-H(3)    | 126.2      |
| Fe-C(3)-H(3)      | 126.2      |
| C(3)-C(4)-C(5)    | 108.29(19) |
| C(3)-C(4)-Fe      | 70.01(12)  |
| C(5)-C(4)-Fe      | 69.70(12)  |
| C(3)-C(4)-H(4)    | 125.9      |
| C(5)-C(4)-H(4)    | 125.9      |
| Fe-C(4)-H(4)      | 126.0      |
| C(1)-C(5)-C(4)    | 107.90(19) |
| C(1)-C(5)-Fe      | 69.84(12)  |
| C(4)-C(5)-Fe      | 69.71(12)  |
| C(1)-C(5)-H(5)    | 126.0      |
| C(4)-C(5)-H(5)    | 126.0      |
| Fe-C(5)-H(5)      | 126.0      |
| C(10)-C(6)-C(7)   | 106.74(16) |
| C(10)-C(6)-C(6)#1 | 123.98(19) |
| C(7)-C(6)-C(6)#1  | 128.3(2)   |
| C(10)-C(6)-Fe     | 68.77(11)  |
| C(7)-C(6)-Fe      | 68.82(10)  |
| C(6)#1-C(6)-Fe    | 135.95(7)  |
| C(8)-C(7)-C(6)    | 107.39(16) |
| C(8)-C(7)-P       | 126.24(14) |
| C(6)-C(7)-P       | 126.18(14) |
| C(8)-C(7)-Fe      | 69.09(11)  |

|                   |            |
|-------------------|------------|
| C(6)-C(7)-Fe      | 69.77(10)  |
| P-C(7)-Fe         | 122.54(10) |
| C(9)-C(8)-C(7)    | 108.77(17) |
| C(9)-C(8)-Fe      | 69.57(11)  |
| C(7)-C(8)-Fe      | 69.91(11)  |
| C(9)-C(8)-H(8)    | 125.6      |
| C(7)-C(8)-H(8)    | 125.6      |
| Fe-C(8)-H(8)      | 126.5      |
| C(8)-C(9)-C(10)   | 108.01(17) |
| C(8)-C(9)-Fe      | 69.72(11)  |
| C(10)-C(9)-Fe     | 69.82(11)  |
| C(8)-C(9)-H(9)    | 126.0      |
| C(10)-C(9)-H(9)   | 126.0      |
| Fe-C(9)-H(9)      | 126.0      |
| C(9)-C(10)-C(6)   | 109.08(17) |
| C(9)-C(10)-Fe     | 69.47(12)  |
| C(6)-C(10)-Fe     | 70.35(11)  |
| C(9)-C(10)-H(10)  | 125.5      |
| C(6)-C(10)-H(10)  | 125.5      |
| Fe-C(10)-H(10)    | 126.3      |
| C(12)-C(11)-C(16) | 118.16(19) |
| C(12)-C(11)-P     | 118.26(16) |
| C(16)-C(11)-P     | 123.53(16) |
| C(11)-C(12)-C(13) | 120.8(2)   |
| C(11)-C(12)-H(12) | 119.6      |
| C(13)-C(12)-H(12) | 119.6      |
| C(14)-C(13)-C(12) | 120.1(2)   |
| C(14)-C(13)-H(13) | 120.0      |
| C(12)-C(13)-H(13) | 120.0      |
| C(15)-C(14)-C(13) | 119.7(2)   |
| C(15)-C(14)-H(14) | 120.1      |
| C(13)-C(14)-H(14) | 120.1      |
| C(14)-C(15)-C(16) | 120.7(2)   |
| C(14)-C(15)-H(15) | 119.7      |
| C(16)-C(15)-H(15) | 119.7      |
| C(15)-C(16)-C(11) | 120.6(2)   |
| C(15)-C(16)-H(16) | 119.7      |
| C(11)-C(16)-H(16) | 119.7      |
| C(18)-C(17)-C(26) | 119.5(2)   |
| C(18)-C(17)-P     | 122.99(18) |
| C(26)-C(17)-P     | 117.49(19) |
| C(17)-C(18)-C(19) | 121.3(3)   |
| C(17)-C(18)-H(18) | 119.3      |
| C(19)-C(18)-H(18) | 119.3      |
| C(20)-C(19)-C(18) | 120.1(3)   |
| C(20)-C(19)-H(19) | 119.9      |
| C(18)-C(19)-H(19) | 119.9      |
| C(19)-C(20)-C(21) | 121.3(3)   |
| C(19)-C(20)-H(20) | 119.4      |
| C(21)-C(20)-H(20) | 119.4      |
| C(20)-C(21)-C(26) | 119.8(3)   |
| C(20)-C(21)-C(22) | 123.0(4)   |
| C(26)-C(21)-C(22) | 117.2(4)   |
| C(23)-C(22)-C(21) | 122.3(4)   |
| C(23)-C(22)-H(22) | 118.9      |
| C(21)-C(22)-H(22) | 118.9      |
| C(22)-C(23)-C(24) | 120.0(3)   |
| C(22)-C(23)-H(23) | 120.0      |
| C(24)-C(23)-H(23) | 120.0      |
| C(25)-C(24)-C(23) | 121.0(4)   |
| C(25)-C(24)-H(24) | 119.5      |
| C(23)-C(24)-H(24) | 119.5      |
| C(24)-C(25)-C(26) | 120.7(4)   |
| C(24)-C(25)-H(25) | 119.7      |
| C(26)-C(25)-H(25) | 119.7      |
| C(25)-C(26)-C(21) | 118.9(3)   |
| C(25)-C(26)-C(17) | 123.0(2)   |
| C(21)-C(26)-C(17) | 118.0(3)   |

|                      |           |
|----------------------|-----------|
| Cl(1C)-C(27S)-Cl(1D) | 24(3)     |
| Cl(1C)-C(27S)-Cl(1A) | 29(3)     |
| Cl(1D)-C(27S)-Cl(1A) | 8.6(8)    |
| Cl(1C)-C(27S)-Cl(2A) | 85(2)     |
| Cl(1D)-C(27S)-Cl(2A) | 109.7(12) |
| Cl(1A)-C(27S)-Cl(2A) | 111.6(13) |
| Cl(1C)-C(27S)-Cl(2B) | 84(3)     |
| Cl(1D)-C(27S)-Cl(2B) | 108.3(8)  |
| Cl(1A)-C(27S)-Cl(2B) | 112.8(9)  |
| Cl(2A)-C(27S)-Cl(2B) | 17.7(7)   |
| Cl(1C)-C(27S)-Cl(1B) | 79(2)     |
| Cl(1D)-C(27S)-Cl(1B) | 61.7(8)   |
| Cl(1A)-C(27S)-Cl(1B) | 53.6(7)   |
| Cl(2A)-C(27S)-Cl(1B) | 128.4(9)  |
| Cl(2B)-C(27S)-Cl(1B) | 144.3(6)  |
| Cl(1C)-C(27S)-Cl(2C) | 86(2)     |
| Cl(1D)-C(27S)-Cl(2C) | 105.4(10) |
| Cl(1A)-C(27S)-Cl(2C) | 102.7(8)  |
| Cl(2A)-C(27S)-Cl(2C) | 30.5(10)  |
| Cl(2B)-C(27S)-Cl(2C) | 48.2(11)  |
| Cl(1B)-C(27S)-Cl(2C) | 99.0(11)  |

## Torsion angles

|              |             |
|--------------|-------------|
| C9-Fe-Cl-C5  | 37.9(3)     |
| C8-Fe-Cl-C5  | -154.2(3)   |
| C4-Fe-Cl-C5  | -37.81(13)  |
| C10-Fe-Cl-C5 | 77.53(15)   |
| C2-Fe-Cl-C5  | -119.07(18) |
| C3-Fe-Cl-C5  | -81.57(14)  |
| C7-Fe-Cl-C5  | 164.89(12)  |
| C6-Fe-Cl-C5  | 121.42(13)  |
| C9-Fe-Cl-C2  | 156.94(18)  |
| C8-Fe-Cl-C2  | -35.1(3)    |
| C5-Fe-Cl-C2  | 119.07(18)  |
| C4-Fe-Cl-C2  | 81.26(14)   |
| C10-Fe-Cl-C2 | -163.40(12) |
| C3-Fe-Cl-C2  | 37.49(13)   |
| C7-Fe-Cl-C2  | -76.05(15)  |
| C6-Fe-Cl-C2  | -119.51(12) |
| C5-Cl-C2-C3  | 0.1(2)      |
| Fe-Cl-C2-C3  | -59.39(14)  |
| C5-Cl-C2-Fe  | 59.45(14)   |
| C9-Fe-C2-C3  | -31.8(3)    |
| C8-Fe-C2-C3  | -71.96(15)  |
| C5-Fe-C2-C3  | 81.70(14)   |
| C4-Fe-C2-C3  | 37.79(13)   |
| C10-Fe-C2-C3 | 161.5(2)    |
| C1-Fe-C2-C3  | 119.43(18)  |
| C7-Fe-C2-C3  | -115.30(13) |
| C6-Fe-C2-C3  | -159.40(12) |
| C9-Fe-C2-C1  | -151.3(2)   |
| C8-Fe-C2-C1  | 168.61(12)  |
| C5-Fe-C2-C1  | -37.73(12)  |
| C4-Fe-C2-C1  | -81.65(14)  |
| C10-Fe-C2-C1 | 42.1(3)     |
| C3-Fe-C2-C1  | -119.43(18) |
| C7-Fe-C2-C1  | 125.27(12)  |
| C6-Fe-C2-C1  | 81.17(14)   |
| C1-C2-C3-C4  | -0.1(2)     |
| Fe-C2-C3-C4  | -59.35(15)  |
| C1-C2-C3-Fe  | 59.27(14)   |
| C9-Fe-C3-C4  | -73.25(15)  |
| C8-Fe-C3-C4  | -114.74(13) |
| C5-Fe-C3-C4  | 37.61(13)   |
| C10-Fe-C3-C4 | -42.8(3)    |
| C1-Fe-C3-C4  | 81.40(14)   |

|              |             |                |             |
|--------------|-------------|----------------|-------------|
| C2-Fe-C3-C4  | 118.95(19)  | C9-Fe-C6-C6#1  | 154.5(3)    |
| C7-Fe-C3-C4  | -156.70(12) | C8-Fe-C6-C6#1  | -161.7(3)   |
| C6-Fe-C3-C4  | 171.44(19)  | C5-Fe-C6-C6#1  | 43.8(3)     |
| C9-Fe-C3-C2  | 167.80(12)  | C4-Fe-C6-C6#1  | 82.3(3)     |
| C8-Fe-C3-C2  | 126.31(13)  | C10-Fe-C6-C6#1 | 117.4(3)    |
| C5-Fe-C3-C2  | -81.34(14)  | C1-Fe-C6-C6#1  | 0.9(3)      |
| C4-Fe-C3-C2  | -118.95(19) | C2-Fe-C6-C6#1  | -42.3(3)    |
| C10-Fe-C3-C2 | -161.7(2)   | C3-Fe-C6-C6#1  | -80.8(3)    |
| C1-Fe-C3-C2  | -37.56(13)  | C7-Fe-C6-C6#1  | -123.8(3)   |
| C7-Fe-C3-C2  | 84.35(14)   | C10-C6-C7-C8   | 0.5(2)      |
| C6-Fe-C3-C2  | 52.5(3)     | C6#1-C6-C7-C8  | -168.38(10) |
| C2-C3-C4-C5  | 0.1(2)      | Fe-C6-C7-C8    | 59.07(13)   |
| Fe-C3-C4-C5  | -59.40(15)  | C10-C6-C7-P    | -174.67(14) |
| C2-C3-C4-Fe  | 59.47(15)   | C6#1-C6-C7-P   | 16.4(2)     |
| C9-Fe-C4-C3  | 123.03(13)  | Fe-C6-C7-P     | -116.14(15) |
| C8-Fe-C4-C3  | 81.84(15)   | C10-C6-C7-Fe   | -58.53(13)  |
| C5-Fe-C4-C3  | -119.38(19) | C6#1-C6-C7-Fe  | 132.55(9)   |
| C10-Fe-C4-C3 | 162.99(12)  | C17-P-C7-C8    | 90.94(18)   |
| C1-Fe-C4-C3  | -81.63(14)  | C11-P-C7-C8    | -10.66(19)  |
| C2-Fe-C4-C3  | -37.77(13)  | C17-P-C7-C6    | -94.73(17)  |
| C7-Fe-C4-C3  | 52.6(3)     | C11-P-C7-C6    | 163.67(16)  |
| C6-Fe-C4-C3  | -170.6(2)   | C17-P-C7-Fe    | 177.66(10)  |
| C9-Fe-C4-C5  | -117.59(14) | C11-P-C7-Fe    | 76.06(12)   |
| C8-Fe-C4-C5  | -158.77(13) | C9-Fe-C7-C8    | -37.15(11)  |
| C10-Fe-C4-C5 | -77.63(15)  | C5-Fe-C7-C8    | -158.3(3)   |
| C1-Fe-C4-C5  | 37.75(13)   | C4-Fe-C7-C8    | 41.1(2)     |
| C2-Fe-C4-C5  | 81.61(14)   | C10-Fe-C7-C8   | -80.90(12)  |
| C3-Fe-C4-C5  | 119.38(19)  | C1-Fe-C7-C8    | 163.77(12)  |
| C7-Fe-C4-C5  | 171.94(17)  | C2-Fe-C7-C8    | 121.62(12)  |
| C6-Fe-C4-C5  | -51.2(3)    | C3-Fe-C7-C8    | 78.21(14)   |
| C2-C1-C5-C4  | 0.0(2)      | C6-Fe-C7-C8    | -118.80(16) |
| Fe-C1-C5-C4  | 59.55(15)   | C9-Fe-C7-C6    | 81.65(12)   |
| C2-C1-C5-Fe  | -59.56(14)  | C8-Fe-C7-C6    | 118.80(16)  |
| C3-C4-C5-C1  | 0.0(2)      | C5-Fe-C7-C6    | -39.5(3)    |
| Fe-C4-C5-C1  | -59.63(15)  | C4-Fe-C7-C6    | 159.89(18)  |
| C3-C4-C5-Fe  | 59.59(15)   | C10-Fe-C7-C6   | 37.90(10)   |
| C9-Fe-C5-C1  | -163.04(12) | C1-Fe-C7-C6    | -77.43(14)  |
| C8-Fe-C5-C1  | 164.25(17)  | C2-Fe-C7-C6    | -119.58(11) |
| C4-Fe-C5-C1  | 119.01(19)  | C3-Fe-C7-C6    | -162.98(11) |
| C10-Fe-C5-C1 | -120.53(13) | C9-Fe-C7-P     | -157.61(13) |
| C2-Fe-C5-C1  | 37.74(13)   | C8-Fe-C7-P     | -120.46(16) |
| C3-Fe-C5-C1  | 81.49(14)   | C5-Fe-C7-P     | 81.3(3)     |
| C7-Fe-C5-C1  | -48.5(4)    | C4-Fe-C7-P     | -79.4(2)    |
| C6-Fe-C5-C1  | -79.56(15)  | C10-Fe-C7-P    | 158.64(13)  |
| C9-Fe-C5-C4  | 77.95(15)   | C1-Fe-C7-P     | 43.31(15)   |
| C8-Fe-C5-C4  | 45.2(2)     | C2-Fe-C7-P     | 1.16(13)    |
| C10-Fe-C5-C4 | 120.46(14)  | C3-Fe-C7-P     | -42.25(14)  |
| C1-Fe-C5-C4  | -119.01(19) | C6-Fe-C7-P     | 120.74(16)  |
| C2-Fe-C5-C4  | -81.26(14)  | C6-C7-C8-C9    | -0.6(2)     |
| C3-Fe-C5-C4  | -37.52(14)  | P-C7-C8-C9     | 174.58(14)  |
| C7-Fe-C5-C4  | -167.5(3)   | Fe-C7-C8-C9    | 58.87(14)   |
| C6-Fe-C5-C4  | 161.44(13)  | C6-C7-C8-Fe    | -59.50(13)  |
| C9-Fe-C6-C10 | 37.10(11)   | P-C7-C8-Fe     | 115.71(15)  |
| C8-Fe-C6-C10 | 80.83(12)   | C5-Fe-C8-C9    | 46.7(2)     |
| C5-Fe-C6-C10 | -73.60(14)  | C4-Fe-C8-C9    | 78.37(14)   |
| C4-Fe-C6-C10 | -35.1(3)    | C10-Fe-C8-C9   | -37.78(12)  |
| C1-Fe-C6-C10 | -116.51(12) | C1-Fe-C8-C9    | -172.3(3)   |
| C2-Fe-C6-C10 | -159.70(11) | C2-Fe-C8-C9    | 160.35(12)  |
| C3-Fe-C6-C10 | 161.8(2)    | C3-Fe-C8-C9    | 120.37(13)  |
| C7-Fe-C6-C10 | 118.81(15)  | C7-Fe-C8-C9    | -120.13(16) |
| C9-Fe-C6-C7  | -81.71(12)  | C6-Fe-C8-C9    | -81.78(12)  |
| C8-Fe-C6-C7  | -37.98(11)  | C9-Fe-C8-C7    | 120.13(16)  |
| C5-Fe-C6-C7  | 167.59(11)  | C5-Fe-C8-C7    | 166.88(17)  |
| C4-Fe-C6-C7  | -153.9(2)   | C4-Fe-C8-C7    | -161.50(12) |
| C10-Fe-C6-C7 | -118.81(15) | C10-Fe-C8-C7   | 82.35(12)   |
| C1-Fe-C6-C7  | 124.68(11)  | C1-Fe-C8-C7    | -52.2(3)    |
| C2-Fe-C6-C7  | 81.49(13)   | C2-Fe-C8-C7    | -79.52(14)  |
| C3-Fe-C6-C7  | 43.0(3)     | C3-Fe-C8-C7    | -119.50(12) |

|                |             |                 |             |
|----------------|-------------|-----------------|-------------|
| C6-Fe-C8-C7    | 38.35(11)   | C2-Fe-C10-C6    | 52.8(3)     |
| C7-C8-C9-C10   | 0.5(2)      | C3-Fe-C10-C6    | -161.6(2)   |
| Fe-C8-C9-C10   | 59.55(14)   | C7-Fe-C10-C6    | -38.38(10)  |
| C7-C8-C9-Fe    | -59.08(13)  | C7-P-C11-C12    | -110.65(18) |
| C5-Fe-C9-C8    | -158.15(12) | C17-P-C11-C12   | 144.86(18)  |
| C4-Fe-C9-C8    | -117.16(13) | C7-P-C11-C16    | 72.00(18)   |
| C10-Fe-C9-C8   | 119.14(17)  | C17-P-C11-C16   | -32.49(19)  |
| C1-Fe-C9-C8    | 174.87(17)  | C16-C11-C12-C13 | -0.6(3)     |
| C2-Fe-C9-C8    | -53.5(3)    | P-C11-C12-C13   | -178.1(2)   |
| C3-Fe-C9-C8    | -77.31(14)  | C11-C12-C13-C14 | 1.1(4)      |
| C7-Fe-C9-C8    | 37.41(11)   | C12-C13-C14-C15 | -1.0(4)     |
| C6-Fe-C9-C8    | 81.90(12)   | C13-C14-C15-C16 | 0.4(4)      |
| C8-Fe-C9-C10   | -119.14(17) | C14-C15-C16-C11 | 0.0(3)      |
| C5-Fe-C9-C10   | 82.71(14)   | C12-C11-C16-C15 | 0.1(3)      |
| C4-Fe-C9-C10   | 123.70(13)  | P-C11-C16-C15   | 177.43(16)  |
| C1-Fe-C9-C10   | 55.7(2)     | C7-P-C17-C18    | 1.7(2)      |
| C2-Fe-C9-C10   | -172.7(2)   | C11-P-C17-C18   | 105.99(19)  |
| C3-Fe-C9-C10   | 163.55(12)  | C7-P-C17-C26    | 178.94(15)  |
| C7-Fe-C9-C10   | -81.73(12)  | C11-P-C17-C26   | -76.81(17)  |
| C6-Fe-C9-C10   | -37.24(12)  | C26-C17-C18-C19 | 0.0(3)      |
| C8-C9-C10-C6   | -0.1(2)     | P-C17-C18-C19   | 177.15(18)  |
| Fe-C9-C10-C6   | 59.37(13)   | C17-C18-C19-C20 | 0.1(4)      |
| C8-C9-C10-Fe   | -59.49(14)  | C18-C19-C20-C21 | 0.1(4)      |
| C7-C6-C10-C9   | -0.3(2)     | C19-C20-C21-C26 | -0.4(4)     |
| C6#1-C6-C10-C9 | 169.26(13)  | C19-C20-C21-C22 | 179.7(3)    |
| Fe-C6-C10-C9   | -58.83(14)  | C20-C21-C22-C23 | -179.5(3)   |
| C7-C6-C10-Fe   | 58.56(12)   | C26-C21-C22-C23 | 0.6(4)      |
| C6#1-C6-C10-Fe | -131.91(12) | C21-C22-C23-C24 | -0.3(6)     |
| C8-Fe-C10-C9   | 37.77(12)   | C22-C23-C24-C25 | -0.6(5)     |
| C5-Fe-C10-C9   | -114.38(13) | C23-C24-C25-C26 | 1.2(4)      |
| C4-Fe-C10-C9   | -72.80(15)  | C24-C25-C26-C21 | -0.8(4)     |
| C1-Fe-C10-C9   | -155.88(12) | C24-C25-C26-C17 | 178.8(2)    |
| C2-Fe-C10-C9   | 173.1(2)    | C20-C21-C26-C25 | -179.9(2)   |
| C3-Fe-C10-C9   | -41.3(3)    | C22-C21-C26-C25 | 0.0(3)      |
| C7-Fe-C10-C9   | 81.92(13)   | C20-C21-C26-C17 | 0.4(3)      |
| C6-Fe-C10-C9   | 120.29(16)  | C22-C21-C26-C17 | -179.7(2)   |
| C9-Fe-C10-C6   | -120.29(16) | C18-C17-C26-C25 | -179.9(2)   |
| C8-Fe-C10-C6   | -82.52(12)  | P-C17-C26-C25   | 2.8(3)      |
| C5-Fe-C10-C6   | 125.32(12)  | C18-C17-C26-C21 | -0.3(3)     |
| C4-Fe-C10-C6   | 166.91(11)  | P-C17-C26-C21   | -177.55(15) |
| C1-Fe-C10-C6   | 83.83(13)   |                 |             |

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Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+1/2

Table 21: Crystal structure refinement data for  $[(S_P, R_m, R_m, S_P)\text{-}2,2'\text{-Bis(1-naphthylphenylphosphino)-1,1'\text{-biferrocenyl]dichloro-platinum(II), 8a}$  (s2156a).

|                                   |                                                                                                                  |
|-----------------------------------|------------------------------------------------------------------------------------------------------------------|
| Identification code               | s2156a                                                                                                           |
| Empirical formula                 | C <sub>52</sub> H <sub>40</sub> Cl <sub>2</sub> Fe <sub>2</sub> P <sub>2</sub> Pt [*]                            |
| Formula weight                    | 1104.47 [*]                                                                                                      |
| Temperature                       | 150(2) K                                                                                                         |
| Wavelength                        | 0.71073 Å                                                                                                        |
| Crystal system, space group       | Orthorhombic, P 21 21 21                                                                                         |
| Unit cell dimensions              | a = 11.8381(3) Å    alpha = 90 deg.<br>b = 19.7931(5) Å    beta = 90 deg.<br>c = 20.8439(5) Å    gamma = 90 deg. |
| Volume                            | 4884.0(2) Å <sup>3</sup>                                                                                         |
| Z, Calculated density             | 4, 1.502 Mg/m <sup>3</sup> [*]                                                                                   |
| Absorption coefficient            | 3.651 mm <sup>-1</sup> [*]                                                                                       |
| F(000)                            | 2184                                                                                                             |
| Crystal size                      | 0.45 x 0.45 x 0.10 mm                                                                                            |
| Theta range for data collection   | 1.42 to 27.50 deg.                                                                                               |
| Limiting indices                  | -15<=h<=15, 0<=k<=25, 0<=l<=27                                                                                   |
| Reflections collected / unique    | 11186 / 11186 [R(int) = 0.0677]                                                                                  |
| Completeness to theta = 27.50     | 99.7 %                                                                                                           |
| Absorption correction             | MULABS as implemented in PLATON                                                                                  |
| Max. and min. transmission        | 0.70 and 0.53                                                                                                    |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup>                                                                      |
| Data / restraints / parameters    | 11186 / 64 / 532                                                                                                 |
| Goodness-of-fit on F <sup>2</sup> | 1.041                                                                                                            |
| Final R indices [I>2sigma(I)]     | R1 = 0.0413, wR2 = 0.1031                                                                                        |
| R indices (all data)              | R1 = 0.0476, wR2 = 0.1063                                                                                        |
| Absolute structure parameter      | -0.020(5)                                                                                                        |
| Largest diff. peak and hole       | 2.446 and -1.120 e.Å <sup>-3</sup>                                                                               |

[\*] Structure contains disordered solvent molecules (339 electrons/unit cell). Their contribution to the structure factors is handled with CALC SQUEEZE as implemented in PLATON. Fw, density and abs.coeff. is calculated without solvent contribution.

Table 22. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for s2156a.

U(eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

|         | x         | y        | z        | U (eq)  |
|---------|-----------|----------|----------|---------|
| Pt (1)  | 6339 (1)  | 5803 (1) | 4107 (1) | 27 (1)  |
| Cl (1)  | 5581 (1)  | 6892 (1) | 3907 (1) | 37 (1)  |
| Cl (1A) | 7518 (1)  | 5937 (1) | 3200 (1) | 38 (1)  |
| Fe (1)  | 5095 (1)  | 4871 (1) | 6504 (1) | 36 (1)  |
| P (1)   | 5191 (1)  | 5698 (1) | 4966 (1) | 28 (1)  |
| C (1)   | 5753 (5)  | 5233 (3) | 5651 (3) | 28 (1)  |
| C (2)   | 5922 (5)  | 4522 (3) | 5695 (3) | 28 (1)  |
| C (3)   | 6565 (5)  | 4393 (3) | 6270 (3) | 35 (1)  |
| C (4)   | 6796 (5)  | 5011 (3) | 6565 (3) | 35 (1)  |
| C (5)   | 6291 (6)  | 5536 (3) | 6204 (3) | 35 (1)  |
| C (6)   | 3555 (7)  | 4421 (4) | 6656 (4) | 56 (2)  |
| C (7)   | 4312 (7)  | 4240 (5) | 7149 (4) | 61 (2)  |
| C (8)   | 4695 (8)  | 4837 (6) | 7461 (4) | 65 (3)  |
| C (9)   | 4159 (7)  | 5385 (5) | 7167 (4) | 56 (2)  |
| C (10)  | 3442 (6)  | 5135 (5) | 6676 (4) | 52 (2)  |
| C (11)  | 4723 (7)  | 6493 (3) | 5340 (2) | 43 (2)  |
| C (12)  | 3585 (8)  | 6564 (4) | 5440 (2) | 55 (2)  |
| C (13)  | 3186 (10) | 7142 (5) | 5775 (3) | 81 (3)  |
| C (14)  | 3944 (13) | 7626 (5) | 5995 (3) | 95 (3)  |
| C (15)  | 5859 (18) | 8053 (5) | 6123 (4) | 111 (4) |
| C (16)  | 6990 (17) | 7989 (5) | 6027 (4) | 112 (4) |
| C (17)  | 7442 (11) | 7428 (4) | 5696 (3) | 78 (3)  |
| C (18)  | 6703 (8)  | 6934 (4) | 5462 (3) | 54 (2)  |
| C (19)  | 5520 (8)  | 6984 (3) | 5561 (3) | 52 (2)  |
| C (20)  | 5075 (11) | 7558 (3) | 5894 (3) | 77 (2)  |
| C (21)  | 3908 (5)  | 5288 (3) | 4662 (3) | 34 (1)  |
| C (22)  | 3598 (6)  | 5418 (3) | 4016 (3) | 41 (1)  |
| C (23)  | 2668 (7)  | 5118 (5) | 3752 (4) | 54 (2)  |
| C (24)  | 2016 (6)  | 4678 (4) | 4104 (5) | 58 (2)  |
| C (25)  | 2296 (7)  | 4547 (4) | 4746 (4) | 53 (2)  |
| C (26)  | 3245 (5)  | 4855 (4) | 5019 (3) | 41 (2)  |
| Fe (1A) | 6192 (1)  | 3148 (1) | 4827 (1) | 34 (1)  |
| P (1A)  | 7070 (1)  | 4769 (1) | 4254 (1) | 30 (1)  |
| C (1A)  | 6075 (5)  | 4135 (3) | 4531 (2) | 27 (1)  |
| C (2A)  | 5610 (5)  | 4071 (3) | 5170 (3) | 27 (1)  |
| C (3A)  | 4730 (5)  | 3584 (3) | 5150 (3) | 36 (1)  |
| C (4A)  | 4602 (6)  | 3360 (4) | 4501 (3) | 42 (2)  |
| C (5A)  | 5415 (5)  | 3693 (3) | 4122 (3) | 33 (1)  |
| C (6A)  | 6436 (8)  | 2316 (3) | 5392 (3) | 55 (2)  |
| C (7A)  | 6227 (9)  | 2132 (3) | 4741 (4) | 57 (2)  |
| C (8A)  | 7119 (8)  | 2415 (4) | 4374 (4) | 57 (2)  |
| C (9A)  | 7809 (7)  | 2788 (4) | 4773 (3) | 48 (2)  |
| C (10A) | 7380 (7)  | 2733 (4) | 5425 (4) | 49 (2)  |
| C (11A) | 7697 (6)  | 4337 (3) | 3550 (3) | 41 (1)  |
| C (12A) | 8693 (7)  | 4029 (3) | 3631 (3) | 53 (2)  |
| C (13A) | 9092 (9)  | 3523 (4) | 3194 (4) | 72 (2)  |
| C (14A) | 8453 (9)  | 3357 (4) | 2691 (4) | 76 (3)  |
| C (15A) | 6716 (11) | 3480 (4) | 2058 (4) | 86 (3)  |
| C (16A) | 5692 (11) | 3777 (5) | 1946 (4) | 84 (3)  |
| C (17A) | 5270 (8)  | 4283 (4) | 2348 (3) | 66 (2)  |
| C (18A) | 5896 (7)  | 4482 (3) | 2871 (3) | 47 (2)  |
| C (19A) | 7000 (6)  | 4169 (3) | 3013 (3) | 45 (1)  |
| C (20A) | 7388 (9)  | 3666 (4) | 2584 (3) | 66 (2)  |