Supplementary Materials: Manganese(I)-Based CORMs with 5-Substituted 3-(2-Pyridyl)Pyrazole Ligands

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General Procedure for the Preparation of the Ligands

Carboxylate ester and NaH in a 1:1.2 ratio were suspended in toluene. After the mixture was cooled to 0 °C, an equimolar amount of the ketone was added. The reaction was warmed to ambient temperature and an exothermic reaction took place. The reaction mixture was stirred for additional 12 h at room temp. and afterwards heated for 4 h at 80 °C in order to get a higher conversion. Thereafter, all volatiles were removed in vacuo and the residue was quenched with a 1:1 mixture of water and acetic acid. The precipitate was recrystallized from hot ethanol. The received 1,3-substituted-propane-1,3-diones were dissolved in ethanol and hydrazine hydrate (1:1 ratio) was added. The mixture was refluxed for 4 h. All volatiles were removed in vacuo and the residue was recrystallized from hot toluene yielding a pure product of **1**.

R = p-Br (1e)

Yield: 58% as colorless crystals.

^{1}H-NMR (600.130 MHz, [D$_6$]DMSO): δ = 13.70 (s, 1H, NH), 8.62 (d, $^{3}J_{H,H}$ = 5.2 Hz, 1H), 7.94–7.90 (m, 1H), 7.88 (t, $^{3}J_{H,H}$ = 7.0 Hz, $^{3}J_{H,H}$ = 7.3 Hz, 1H), 7.81 (d, $^{3}J_{H,H}$ = 8.5 Hz, 2H), 7.63 (d, $^{3}J_{H,H}$ = 8.4 Hz, 2H), 7.36 (s, 1H), 7.35–7.32 (m, 1H).

^{13}C{^{1}H}-NMR (150.902 MHz, [D$_6$]DMSO): δ = 149.3 (s), 148.0 (s), 137.1 (s), 136.1 (s), 131.7 (s), 127.1 (s), 123.3 (s), 122.9 (s), 120.7 (s), 119.7 (s), 101.1(s).

MS (DEI): *m*/*z* (%) = 301 [M$^+$ + 2] (100), 299 [M$^+$] (92), 272 (5), 270 (6), 191 (28), 165 (2).

IR (solid): 3207 (b), 1593 (w), 1560 (w), 1505 (w), 1469 (w), 1449 (m), 1420 (w), 1372 (m), 1304 (w), 1292 (w), 1267 (w), 1228 (w), 1176 (m), 1146 (w), 1106 (m), 1090 (w), 1071 (m), 1045 (m), 1005 (m), 995 (m), 973 (m), 954 (m), 884 (w), 831 (m), 802 (m), 774 (s), 739 (m), 700 (m), 661 (m), 619 (w), 522 (m), 511 (w), 491 (m), 469 (m).

Elemental Analysis (C$_{14}$H$_{10}$BrN$_3$, 300.15):

calc.: C 56.02 %, H 3.36%, N 14.00%

found: C 55.39 %, H 3.28%, N 13.63%.

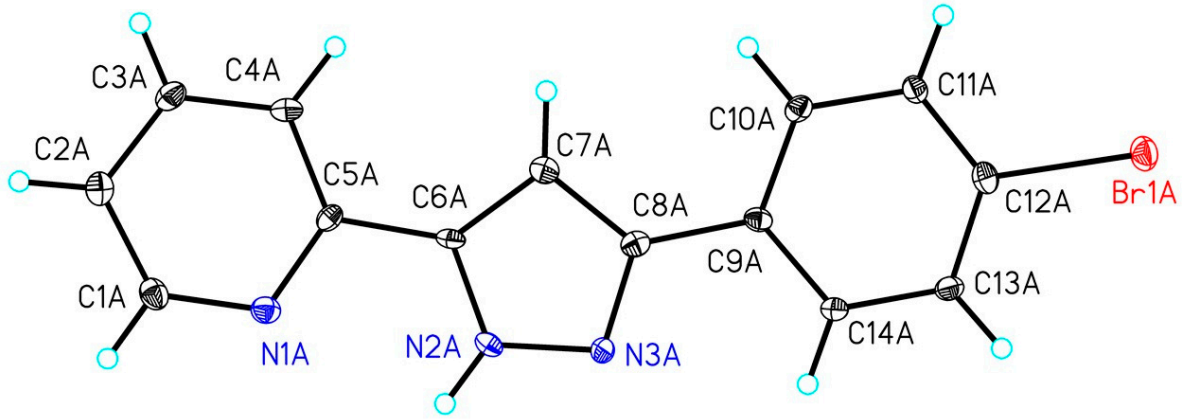


Figure S1. Molecular structure and numbering scheme of **1e**. The ellipsoids represent a probability of 30%, H atoms are shown with arbitrary radii.

R = m-Br (1f)

Yield: 42%, colorless crystals.
^{1}H-NMR (600.130 MHz, [D$_6$]DMSO): δ = 13.71 (s, 1H, NH), 8.63 (d, $^3J_{H,H}$ = 4.8 Hz, 1H), 8.08–8.06 (m, 1H), 7.96–7.84 (m, 3H), 7.53 (d, $^3J_{H,H}$ = 7.8 Hz, 1H), 7.45–7.39 (m, 2H), 7.37–7.35 (m, 1H).
^{13}C{^{1}H}-NMR (100.599 MHz, [D$_6$]DMSO): δ = 149.6 (s), 137.2 (s), 131.0 (s), 130.4 (s), 127.5 (s), 124.1 (s), 123.0 (s), 122.2 (s), 119.8 (s), 101.4 (s).
MS (DEI): *m*/*z* (%) = 301 [M$^+$ + 2] (95), 299 [M$^+$] (100), 272 (5), 270 (2), 220 [M$^+$ − Br] (9), 191 (40), 165 (5), 95 (2), 78 (2).
IR (solid): 3138 (b), 3050 (w), 3012 (w), 2904 (w), 1597 (w), 1567 (w), 1480 (w), 1459 (m), 1445 (w), 1380 (w), 1307 (w), 1222 (w), 1184 (w), 1164 (w), 1114 (w), 1071 (w), 1053 (w), 996 (w), 970 (w), 960 (w), 884 (w), 833 (w), 767 (m), 744 (m), 703 (w), 693 (w), 673 (w), 657 (w), 623 (w), 543 (w), 519 (w), 501 (w), 431 (w), 417 (w).
Elemental analysis (C$_{14}$H$_{10}$BrN$_3$, 300.15):

calc.:	C 56.02%, H 3.36%, N 14.00%
found:	C 55.55%, H 3.52%, N 13.96%.

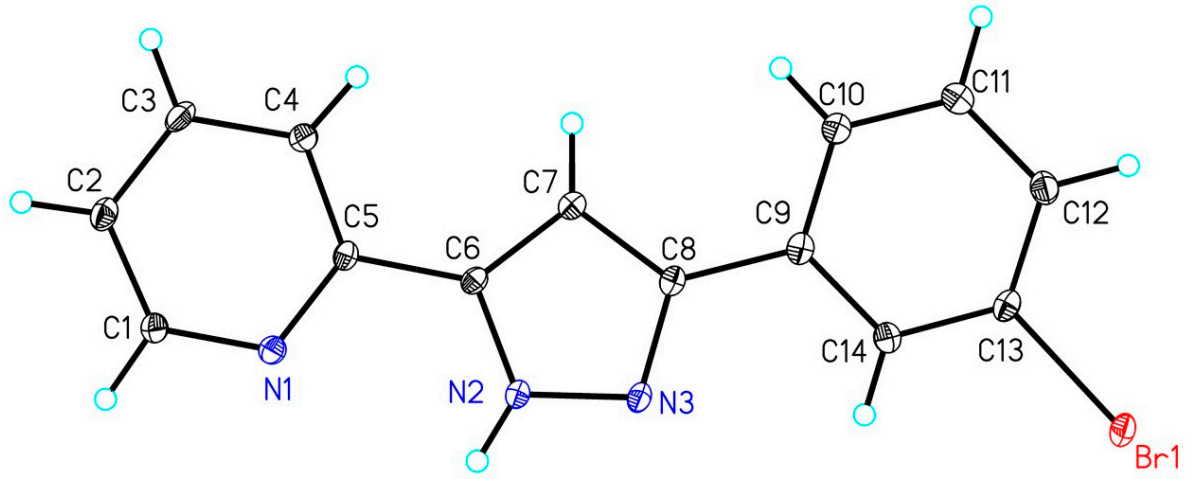


Figure S2. Molecular structure and numbering scheme of **1f**. The ellipsoids represent a probability of 30%, H atoms are shown with arbitrary radii.

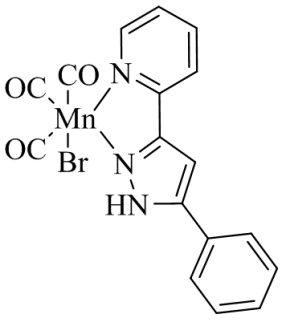
R = Fc (1k)

Yield: 32%, orange crystals.
^{1}H-NMR (600.130 MHz, [D$_6$]DMSO): δ = 13.21 (s, 1H, NH), 8.58–8.56 (m, 1H,), 7.97 (d, $^3J_{H,H}$ = 7.3 Hz, 1H), 7.82–7.80 (m, 1H), 7.30–7.26 (m, 1H), 6.90 (s, 1H), 4.81 (s, 2H), 4.33 (s, 2H), 4.06 (s, 5H).
^{13}C{^{1}H}-NMR (150.902 MHz, [D$_6$]DMSO): δ = 152.3 (s), 151.6 (s), 149.1 (s), 142.5 (s), 136.6 (s), 122.3 (s), 119.1 (s), 100.1 (s), 74.0 (s), 69.4 (s), 68.6 (s), 66.2 (s).
MS (DEI): *m*/*z* (%) = 329 [M$^+$] (100).
IR (solid): 3225 (b), 3094 (b), 1601 (w), 1570 (w), 1543 (w), 1485 (w), 1454 (w), 1411 (w), 1304 (w), 1281 (w), 1169 (w), 1153 (w), 1138 (w), 1103 (w), 1072 (w), 1022 (w), 999 (w), 972 (w), 872 (w), 813 (m), 779 (m), 729 (m), 710 (m), 656 (w), 625 (w).
Elemental analysis (C$_{18}$H$_{15}$FeN$_3$, 329.18):

calc.:	C 65.68%, H 4.59%, N 12.77%
found:	C 65.52%, H 4.56%, N 12.94%.

Procedures for the preparation of the complexes

R = Ph (2a)



370 mg of **1a** (1.67 mmol) were suspended in 5 mL of MeOH. In another flask 460 mg of $Mn(CO)_5Br$ (1.76 mmol) were dissolved in 20 mL of MeOH and transferred at once to the suspension of **1a**. Then the reaction was refluxed for 4 h whereby a yellow precipitate formed. The reaction mixture was cooled to room temperature. The solid was collected, washed with 2 mL of MeOH and dried in vacuo.

Yield: 526 mg (1.19 mmol), 71%.

^{1}H-NMR (400.130 MHz, [D$_8$]THF): δ = 13.64 (s, 1H, NH), 9.09 (s, 1H), 7.90 (s, 2H), 7.79 (s, 1H), 7.72–7.74 (m, 2H), 7.45–7.30 (m, 4H).

^{13}C{^{1}H}-NMR (100.613 MHz, [D$_8$]THF): δ = 223.5 (s, $C_{Carbonyl}$), 223.9 (s, $C_{Carbonyl}$), 154.3 (s), 153.5 (s), 152.8 (s), 149.6 (s), 139.2 (s), 130.2 (s), 129.9 (s), 129.2 (s), 126.9(s), 125.2 (s), 122.5 (s), 102.5 (s).

MS (DEI): *m*/*z* (%) = 357 [M^+ + 2–3CO] (12), 355 [M^+ − 3 CO] (12), 281 (49), 221 [L] (13), 207 (10), 192 (6), 84 (6), 80 (47), 78 (47), 48 (100), 46 (47), 30 (33).

IR (solid): 3351 (w), 3105 (w), 3006 (w), 2969 (w), 2942 (w), 2021 (m), 1895 (s), 1612 (w), 1585 (w), 1572 (w), 1533 (w), 1494 (w), 1463 (w), 1448 (m), 1324 (w), 1301 (w), 1276 (w), 1257 (w), 1219 (w), 1157 (w), 1129 (w), 1100 (w), 1075 (w), 1012 (m), 991 (w), 902 (w), 834 (w), 781 (w), 762 (m), 726 (w), 683 (m), 645 (w), 627 (m), 552 (w), 531 (m), 517 (m), 508 (m), 488 (m), 471 (m), 459 (m), 426 (w).

Elemental analysis ($C_{17}H_{11}BrMnN_3O_3$, 440.14):

calc.:	C 46.39%, H 2.52%, N 9.55%
found:	C 46.08%, H 2.78%, N 9.30%.

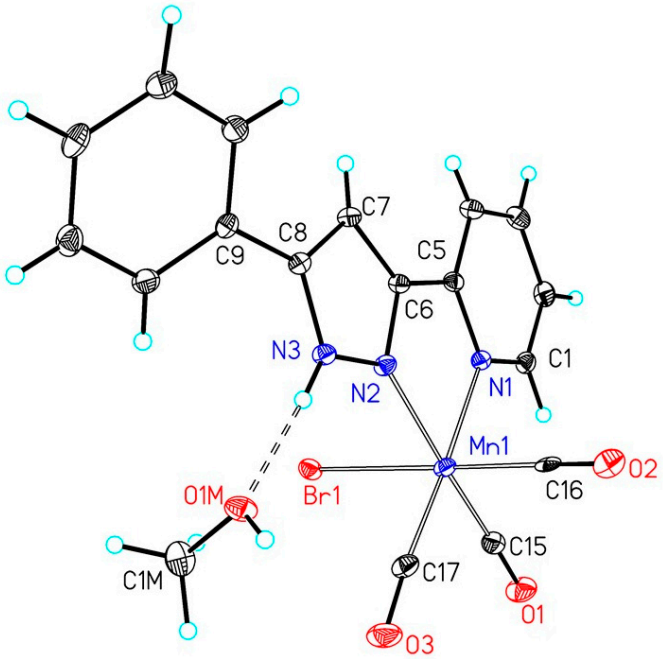


Figure S3. Molecular structure and numbering scheme of **2a**·MeOH. The ellipsoids represent a probability of 30%, H atoms are shown with arbitrary radii. Selected bond lengths are summarized in Table 2.

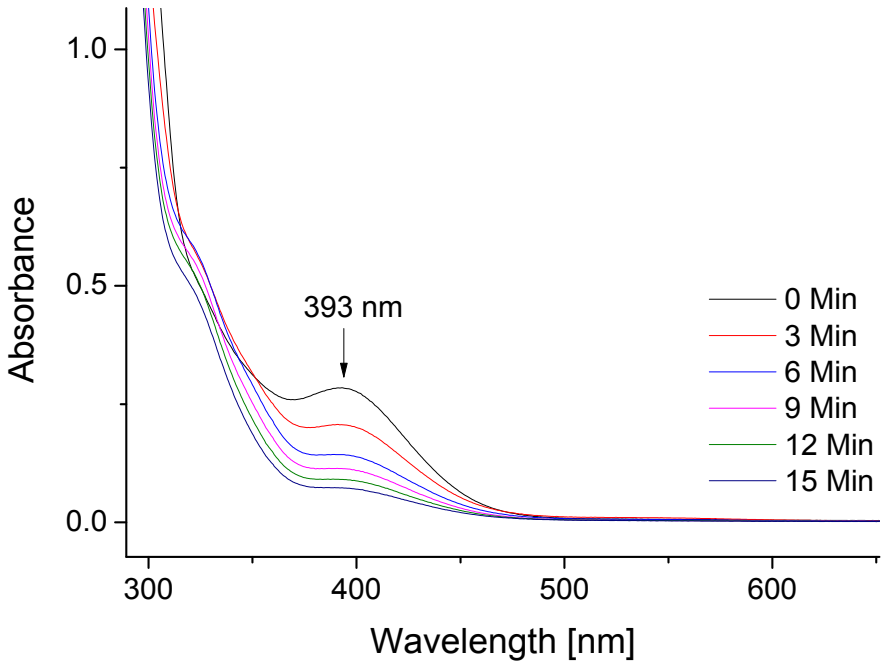
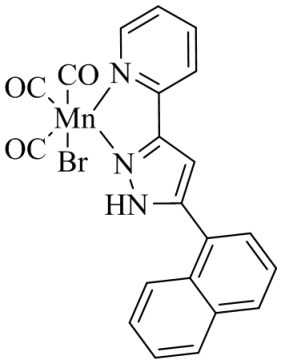


Figure S4. UV–Vis spectra during irradiation of 2a at 480 nm (c = 99 μM) in methanol.

R = Naph (2b)



A similar procedure as described for compound **2a**, using 625 mg (2.27 mmol) of $Mn(CO)_5Br$, 617 mg (2.27 mmol) of **1b** and 24 mL of MeOH, gave compound **2b** as a yellow solid.

Yield: 955 mg (1.95 mmol), 86%.

^{1}H-NMR (400.130 MHz, [D$_8$]THF): δ = 13.87 (s, 1H, NH), 9.16 (s, 1H), 8.06–7.98 (m, 5H), 7.73 (s, 1H), 7.57 (s, 3H), 7.46 (s, 1H), 7.31 (s, 1H).

^{13}C{^{1}H}-NMR (100.613 MHz, [D$_8$]THF): δ = 223.8 (s, $C_{Carbonyl}$), 223.3 (s, $C_{Carbonyl}$), 221.5 (s, $C_{Carbonyl}$), 154.5 (s), 153.2 (s), 153.0 (s), 148.0 (s), 139.4 (s), 134.8 (s), 132.4 (s), 131.0 (s), 129.4 (s), 128.9 (s), 128.1 (s), 127.4 (s), 127.3 (s), 126.0 (s), 125.9 (s), 125.2 (s), 122.6 (s), 106.0 (s).

MS (Micro-ESI neg. in THF + Methanol): *m*/*z* (%) = 587.9 [M − H$^+$].

IR (solid): 3372 (w), 3110 (w), 3051 (w), 2939 (w), 2835 (w), 2026 (m), 1948 (s), 1912 (s), 1612 (w), 1582 (w), 1566 (w), 1450 (w), 1428 (w), 1385 (w), 1368 (w), 1303 (w), 1263 (w), 1160 (w), 1116 (w), 1017 (m), 988 (m), 905 (w), 887 (w), 860 (w), 800 (w), 783 (w), 773 (m), 759 (m), 732 (m), 721 (w), 680 (w), 657 (w), 646 (w), 633 (m), 575 (w), 541 (w), 530 (w), 497 (w), 467 (w), 447 (w), 434 (w), 420 (w).

Elemental analysis ($C_{21}H_{13}BrMnN_3O_3$, 490.19):

calc.:	C 51.45%, H 2.67%, N 8.57%
found:	C 51.33%, H 2.86%, N 8.39%.

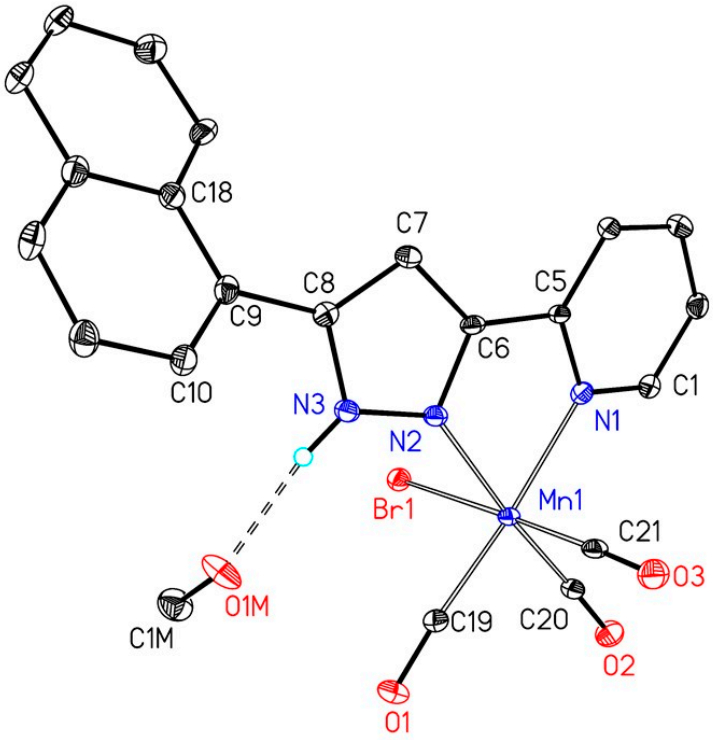
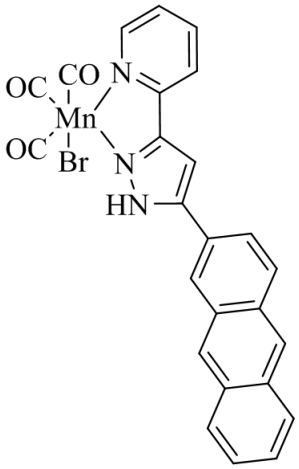


Figure S5. Molecular structure and numbering scheme of **2b**·MeOH. The ellipsoids represent a probability of 30%, H atoms are omitted. Selected bond lengths are summarized in Table 2.

R = Anth (2c)



A similar procedure as described for compound **2a**, using 850 mg (3.09 mmol) of $Mn(CO)_5Br$, 994 mg (3.09 mmol) of **1c** and 25 mL of MeOH, yielded compound **2c** as a yellow solid.

Yield: 1585 mg (2.93 mmol), 95%.

^{1}H-NMR (400.130 MHz, [D$_8$]THF): δ = 13.66 (s, 1H, NH), 9.14 (d, $^3J_{H,H}$ = 4.6 Hz, 1H), 8.01–7.94 (m, 4H), 7.88–7.81 (m, 2H), 7.57 (d, $^3J_{H,H}$ = 7.2 Hz, 1H), 7.42– 7.30 (m, 6H).

^{13}C{^{1}H}-NMR (100.613 MHz, [D$_8$]THF): δ = 154.6 (s), 153.7 (s), 153.1 (s), 150.2 (s), 145.2 (s), 144.9 (s), 144.1 (s), 142.0 (s), 139.3 (s), 129.2 (s), 129.1 (s), 128.3 (s), 127.9 (s), 127.6 (s), 126.0 (s), 126.0 (s), 125.3 (s), 123.7 (s), 122.5 (s), 121.3 (s), 121.2 (s), 102.3 (s).

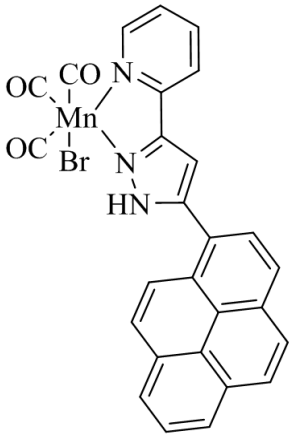
MS (Micro-ESI pos. in THF + Methanol): *m*/*z* (%) = 539.2 [M + H$^+$].

IR (solid): 3102 (w), 2023 (s), 1931 (m), 1904 (s), 1653 (w), 1613 (w), 1574 (w), 1540 (w), 1487 (w), 1449 (m), 1401 (w), 1301 (w), 1260 (w), 1243 (w), 1198 (w), 1159 (w), 1124 (w), 1098 (w), 1059 (w), 994 (w), 972 (w), 955 (w), 926 (w), 899 (w), 877 (w), 823 (w), 780 (m), 768 (m), 732 (m), 684 (m), 647 (w), 624 (m), 555 (w), 528 (m), 484 (w), 416 (w).

Elemental analysis ($C_{25}H_{15}BrMnN_3O_3$, 540.26):

calc.:	C 55.58%, H 2.80%, N 7.78%
found:	C 55.35%, H 2.95%, N 7.94%.

R = Pyrenyl (2d)



A similar procedure as described for compound **2a**, using 302 mg (1.10 mmol) of $Mn(CO)_5Br$, 361 mg (1.04 mmol) of **1d** and 14 mL of MeOH, yielded compound **2d** as a yellow solid.

Yield: 545 mg (0.97 mmol), 93%.

^{1}H-NMR (400.130 MHz, [D$_8$]THF): δ = 14.02 (s, 1H, NH), 9.20 (d, $^3J_{H,H}$ = 5.2 Hz, 1H), 8.40–8.04 (m, 11H), 7.52–7.48 (m, 2H).

^{13}C{^{1}H}-NMR (100.613 MHz, [D$_8$]THF): δ = 154.7 (s), 153.5 (s), 153.3 (s), 148.7 (s), 139.3 (s), 133.4 (s), 132.6 (s), 132.0 (s), 130.4 (s), 129.9 (s), 129.7 (s), 129.2 (s), 128.6 (s), 128.2 (s), 127.5 (s), 127.0 (s), 126.8 (s), 125.8 (s), 125.6 (s), 125.3 (s), 125.1 (s), 124.4 (s), 122.7 (s), 106.5 (s).

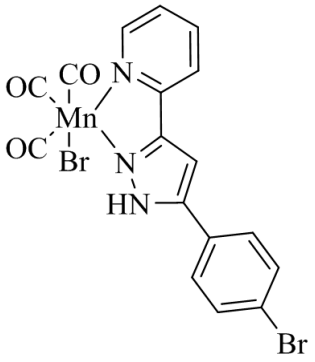
MS (Micro-ESI neg. in THF + Methanol): *m*/*z* (%) = 562.0 [M − H$^+$].

IR (solid): 3142 (w), 2027 (s), 1930 (m), 1898 (s), 1864 (m), 1615 (w), 1603 (w), 1571 (w), 1561 (w), 1529 (w), 1502 (w), 1462 (w), 1445 (m), 1412 (w), 1299 (w), 1252 (w), 1203 (w), 1159 (w), 1114 (w), 957 (w), 862 (m), 841 (w), 834 (m), 825 (m), 813 (w), 799 (m), 774 (m), 752 (m), 716 (w), 697 (m), 682 (w), 660 (w), 647 (m), 627 (w), 580 (w), 530 (m), 507 (m), 472 (w), 426 (w).

Elemental analysis ($C_{27}H_{15}BrMnN_3O_3$, 564.28):

calc.:	C 57.47%, H 2.68%, N 7.45%
found:	C 56.91%, H 2.67%, N 7.09%.

R = p-Br-Phenyl (2e)



A similar procedure as described for compound **2a**, using 381 mg (1.39 mmol) of $Mn(CO)_5Br$, 416 mg (1.39 mmol) of **1e** and 20 mL of MeOH, yielded compound **2e** as a yellow solid.

Yield: 448 mg (0.86 mmol), 62%.

^{1}H-NMR (400.130 MHz, [D$_8$]THF): δ = 13.76 (s, 1H, NH), 9.13 (d, $^3J_{H,H}$ = 5.4 Hz, 1H), 8.01–7.94 (m, 2H), 7.77–7.66 (m, 4H), 7.48–7.40 (m, 2H).

^{13}C{^{1}H}-NMR (100.613 MHz, [D$_8$]THF): δ = 228.5 (s, $C_{Carbonyl}$), 226.3 (s, $C_{Carbonyl}$), 154.6 (s), 153.8 (s), 152.8 (s), 148.6 (s), 139.4 (s), 133.3 (s), 128.8 (s), 128.5 (s), 125.4 (s), 124.3 (s), 122.5 (s), 102.7 (s).

MS (Micro-ESI pos. in Methanol): *m*/*z* (%) = 517.8 [M + H$^+$].

IR (solid): 3152 (m), 2020 (s), 1940 (s), 1906 (s), 1886 (s), 1614 (m), 1600 (m), 1530 (w), 1486 (m), 1458 (m), 1447 (s), 1388 (w), 1299 (m), 1260 (m), 1211 (w), 1154 (m), 1129 (w), 1105 (m), 1071 (w), 1056 (m), 1007 (m), 992 (m), 838 (m), 825 (s), 808 (s), 776 (m), 750 (m), 702 (s), 682 (m), 647 (s), 625 (m), 552 (s), 522 (s), 497 (m), 482 (w), 473 (m), 460 (w), 427 (m).

Elemental analysis ($C_{17}H_{10}Br_2MnN_3O_3$, 519.03):

calc.:	C 39.34%, H 1.94%, N 8.10%
found:	C 39.40%, H 1.94%, N 8.04%.

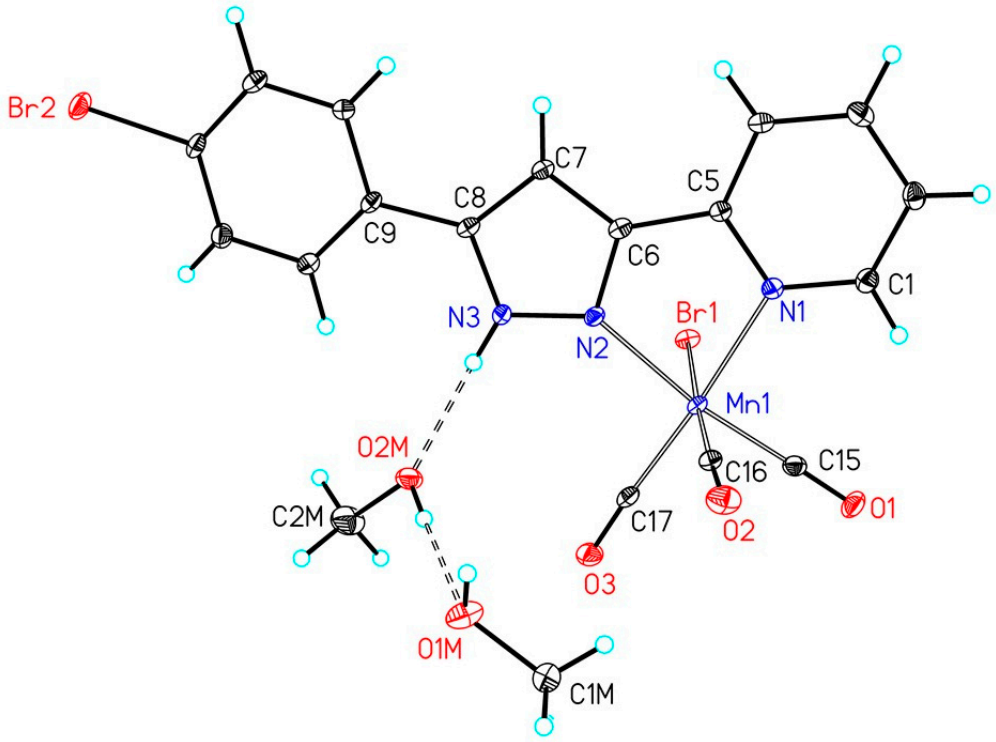
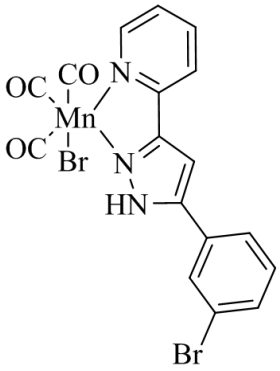


Figure S6. Molecular structure and numbering scheme of **2e**·2MeOH. The ellipsoids represent a probability of 30%, H atoms are shown with arbitrary radii. Selected bond lengths are summarized in Table 2.

R = m-Br-Phenyl (2f)



A similar procedure as described for compound **2a**, using 372 mg (1.35 mmol) of $Mn(CO)_5Br$, 405 mg (1.35 mmol) of **1f** and 20 mL of MeOH, yielded compound **2f** as a yellow solid.

Yield: 613 mg (1.18 mmol), 87%.

^{1}H-NMR (400.130 MHz, [D$_8$]THF): δ = 13.71 (s, 1H, NH), 9.08 (d, $^3J_{H,H}$ = 5.3 Hz, 1H), 8.01 (s, 1H), 7.93–7.88 (m, 2H), 7.71 (d, $^3J_{H,H}$ = 7.5 Hz, 1H), 7.57–7.52 (m, 1H), 7.44–7.35 (m, 3H)

^{13}C{^{1}H}-NMR (100.613 MHz, [D$_8$]THF): δ = 223.2 (s, $C_{Carbonyl}$), 221.5 (s, $C_{Carbonyl}$), 154.5 (s), 153.7 (s), 152.8 (s), 148.0 (s), 139.4 (s), 133.1 (s), 131.8 (s), 131.3 (s), 129.8 (s), 125.9 (s), 125.4 (s), 123.9 (s), 122.5 (s), 103.0 (s).

MS (Micro-ESI pos. in Methanol): *m*/*z* (%) = 517.8 [M + H$^+$].

IR (solid): 3354 (w), 3088 (w), 2829 (w), 2024 (s), 1914 (s), 1862 (m), 1838 (m), 1819 (w), 1786 (w), 1612 (m), 1579 (m), 1451 (m), 1402 (w), 1390 (w), 1380 (w), 1304 (m), 1255 (w), 1221 (w), 1160 (m), 1105 (w), 1076 (w), 1019 (s), 994 (m), 965 (w), 899 (w), 891 (w), 834 (s), 773 (m), 751 (s), 708 (s), 680 (w), 646 (s), 627 (w), 555 (s), 538 (w), 528 (m), 510 (m), 488 (s), 473 (m), 462 (m), 424 (s).

Elemental analysis ($C_{17}H_{10}Br_2MnN_3O_3$, 519.03):

calc.:	C 39.34%, H 1.94%, N 8.10%
found:	C 39.57%, H 2.50%, N 7.70%.

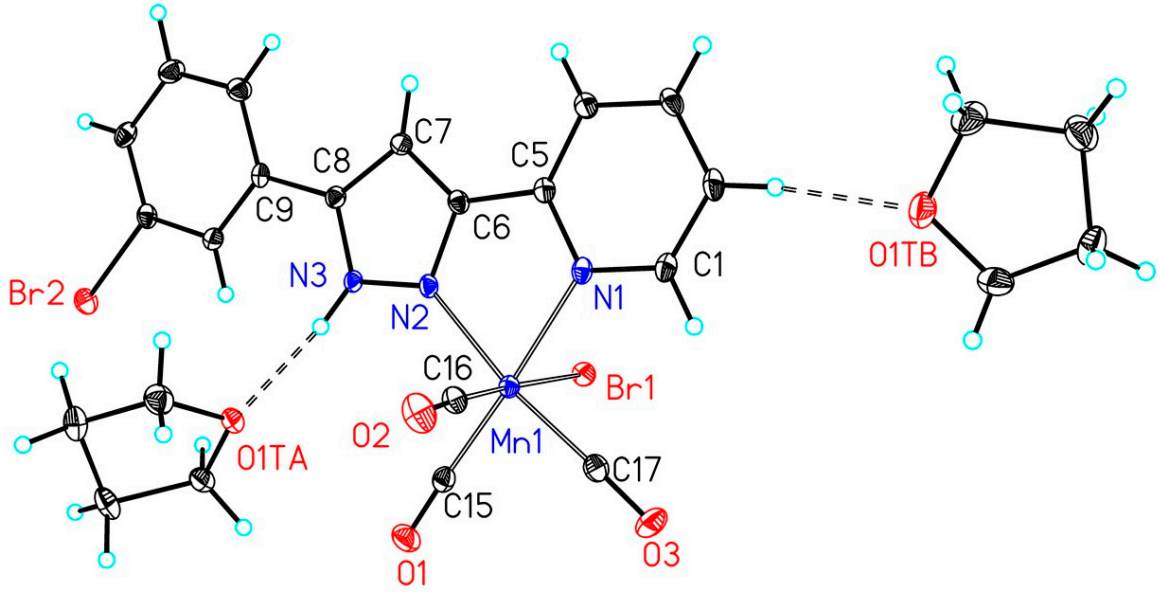
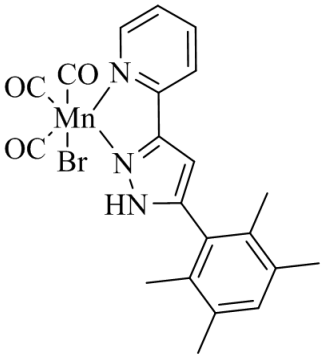


Figure S7. Molecular structure and numbering scheme of **2f**·2THF. The ellipsoids represent a probability of 30%, H atoms are drawn with arbitrary radii. Selected bond lengths are summarized in Table 2.

R = Duryl (2g)



A similar procedure as described for compound **2a**, using 408 mg (1.48 mmol) of $Mn(CO)_5Br$, 413 mg (1.48 mmol) of **1g** and 15 mL of MeOH, yielded compound **2g** as a yellow solid.

Yield: 478 mg (0.96 mmol), 65%.

^{1}H-NMR (400.130 MHz, [D$_8$]THF): δ = 13.37 (s, 1H, NH), 9.14 (d, $^3J_{H,H}$ = 5.3 Hz, 1H), 8.02–7.94 (m, 2H), 7.47–7.42 (m, 1H), 7.10 (s, 1H), 6.93–6.89 (m, 1H,), 2.26 (s, 6H), 2.03 (s, 6H).

^{13}C{^{1}H}-NMR (100.613 MHz, [D$_8$]THF): δ = 222.9 (s, $C_{Carbonyl}$), 220.6 (s, $C_{Carbonyl}$), 153.4 (s), 152.2 (s), 148.0 (s), 138.1 (s), 133.7 (s), 132.4 (s), 128.7 (s), 128.0 (s), 123.9 (s), 121.4 (s), 104.3 (s), 19.0 (s), 16.2 (s).

MS (DEI): *m*/*z* (%) = 494 [M$^+$ − H] (4), 429 (2), 410 [M$^+$ − H − 3CO] (20), 382 (24), 354 (10), 326 (12), 298 (24), 270 (42), 215 (6), 191 (8), 162 (4), 136 (6), 134 (10), 91 (6), 74 (54), 59 (68), 31 (100).

IR (solid): 3188 (w), 2969 (w), 2861 (w), 2022 (s), 1940 (s), 1902 (s), 1641 (w), 1613 (w), 1500(w), 1492 (m), 1412 (w), 1389 (w), 1300 (w), 1248 (w), 1212 (w), 1159 (w), 1114 (w), 1082 (w), 1057 (w), 1009 (w), 776 (m), 752 (w), 685 (m), 621 (m), 525 (m), 498 (w), 466 (w), 424 (w).

Elemental analysis ($C_{21}H_{19}BrMnN_3O_3$, 496.24):

calc.:	C 50.83%, H 3.86%, N 8.47%
found:	C 50.59%, H 4.11%, N 8.00%.

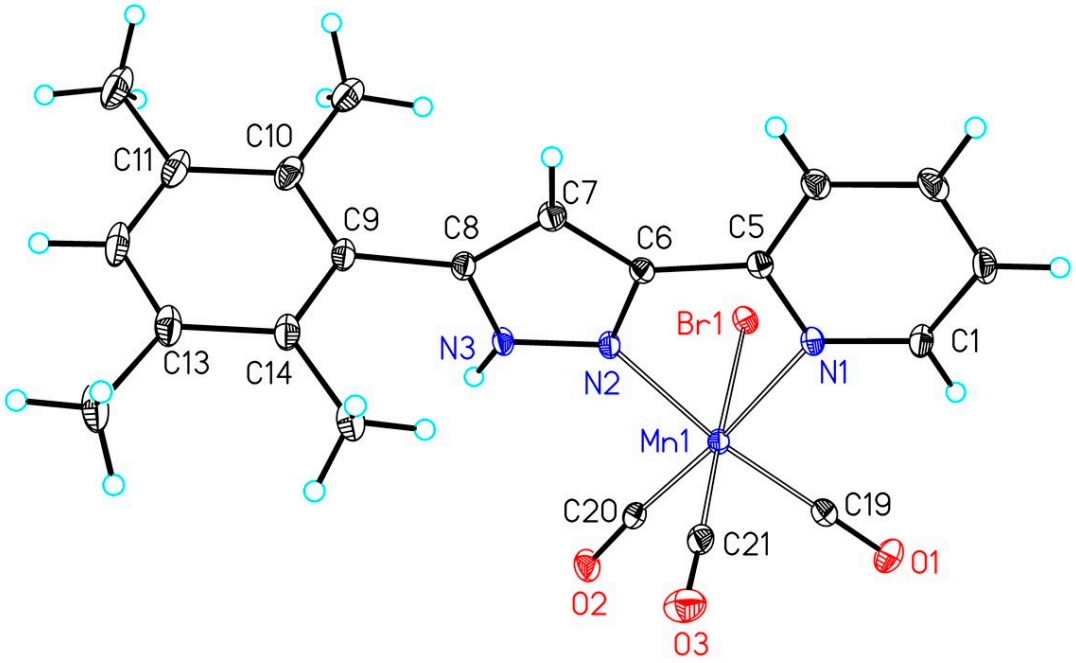
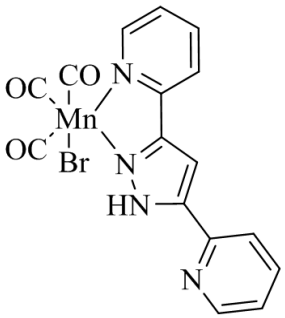


Figure S8. Molecular structure and numbering scheme of **2g**. The ellipsoids represent a probability of 30%, H atoms are shown with arbitrary radii. Selected bond lengths are summarized in Table 2.

R = Pyridyl (2h)



The suspension of 426 mg of $Mn(CO)_5Br$ (1.55 mmol) and 344 mg of **1h** (1.55 mmol) in 17 mL of Et_2O was refluxed for 3 h until gas evolution ceased. During this time, a yellow solid precipitated. Then the reaction mixture was cooled to room temperature. The precipitate was collected, washed with 2 mL of cold Et_2O and dried in vacuo.

Yield: 668 mg (1.51 mmol), 98%.

^{1}H-NMR (400.130 MHz, [D$_6$]DMSO): δ = 9.09 (d, $^3J_{H,H}$ = 5.2 Hz, 1H), 8.74 (d, $^3J_{H,H}$ = 4.6 Hz, 1H), 8.25–8.11 (m, 2H), 8.05–8.01 (m, 2H), 7.89 (s, 1H), 7.61–7.55 (m, 1H), 7.53–7.45 (m, 1H).

^{13}C{^{1}H}-NMR (100.613 MHz, [D$_6$]DMSO): δ = 222.3 (s, $C_{Carbonyl}$), 221.2 (s, $C_{Carbonyl}$), 220.9 (s, $C_{Carbonyl}$), 153.3 (s), 152.0 (s), 151.1 (s), 149.6 (s), 147.5 (s), 146.3 (s), 139.2 (s), 137.7 (s), 124.8 (s), 124.2 (s), 121.7 (s), 120.8 (s), 103.0 (s).

MS (Micro-ESI neg. in Methanol): *m*/*z* (%) = 439.0 [M − H$^+$].

IR (solid): 3129 (w), 3106 (w), 3065 (w), 2024 (s), 1932 (s), 1892 (s), 1612 (m), 1575 (m), 1560 (m), 1530 (m), 1484 (m), 1457 (m), 1446 (m), 1278 (w), 1252 (w), 1230 (w), 1195 (w), 1154 (w), 1135 (w), 815 (w), 777 (s), 732 (m), 719 (m), 623 (s), 510 (m), 489 (w), 473 (w), 461 (w).

Elemental analysis ($C_{16}H_{10}BrMnN_4O_3$, 441.12):

calc.:	C 43.57%, H 2.29%, N 12.70%
found:	C 43.56%, H 2.25%, N 12.53%.

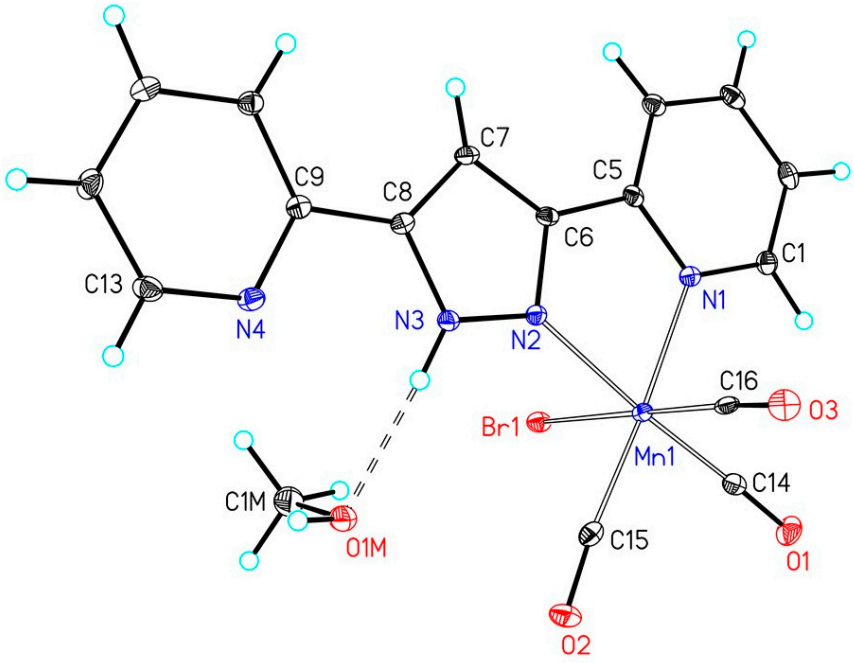
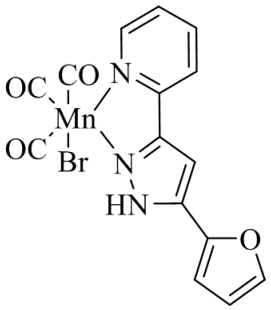


Figure S9. Molecular structure and numbering scheme of **2h**·MeOH. The ellipsoids represent a probability of 30%, H atoms are shown with arbitrary radii. Selected bond lengths are summarized in Table 2.

R = Furanyl (2i)



A similar procedure as described for compound **2h**, using 880 mg (3.20 mmol) of $Mn(CO)_5Br$, 676 mg (3.20 mmol) of **1i** and 20 mL of Et_2O, yielded compound **2i** as a yellow solid.

Yield: 1130 mg (2.63 mmol), 82%.

^{1}H-NMR (400.130 MHz, [D$_8$]THF): δ = 13.91 (s, 1H, NH), 9.12 (d, $^3J_{H,H}$ = 5.2 Hz, 1H), 7.98 (s, 2H), 7.68 (s, 1H), 7.43 (s, 1H), 7.27 (s, 1H), 6.91 (s, 1H), 6.60 (s, 1H).

^{13}C{^{1}H}-NMR (100.613 MHz, [D$_8$]THF): δ = 154.6 (s), 153.5 (s), 152.8 (s), 144.8 (s), 144.7 (s), 140.7 (s), 139.3 (s), 125.4 (s), 122.6 (s), 112.9 (s), 109.5 (s), 101.2 (s).

MS (Micro-ESI neg. in Methanol): *m*/*z* (%) = 428.0 [M − H$^+$].

IR (solid): 3131 (w), 3111 (m), 3083 (w), 2986 (w), 2024 (s), 1933 (s), 1895 (vs), 1635 (w), 1611 (m), 1567 (w), 1545 (w), 1525 (m), 1484 (m), 1466 (w), 1448 (m), 1382 (w), 1297 (w), 1254 (w), 1224 (m), 1155 (w), 1125 (w), 1102 (w), 1075 (w), 1018 (m), 997 (m), 972 (w), 888 (w), 870 (w), 817 (w), 796 (w), 774 (s), 742 (m), 712 (m), 683 (m), 667 (w), 645 (m), 625 (s), 590 (m), 553 (m), 527 (m), 516 (s), 470 (m), 460 (m), 426 (m).

Elemental analysis ($C_{15}H_9BrMnN_3O_4$, 430.10):

calc.:	C 41.89%, H 2.11%, N 9.77%,
found:	C 41.73%, H 2.00%, N 9.57%.

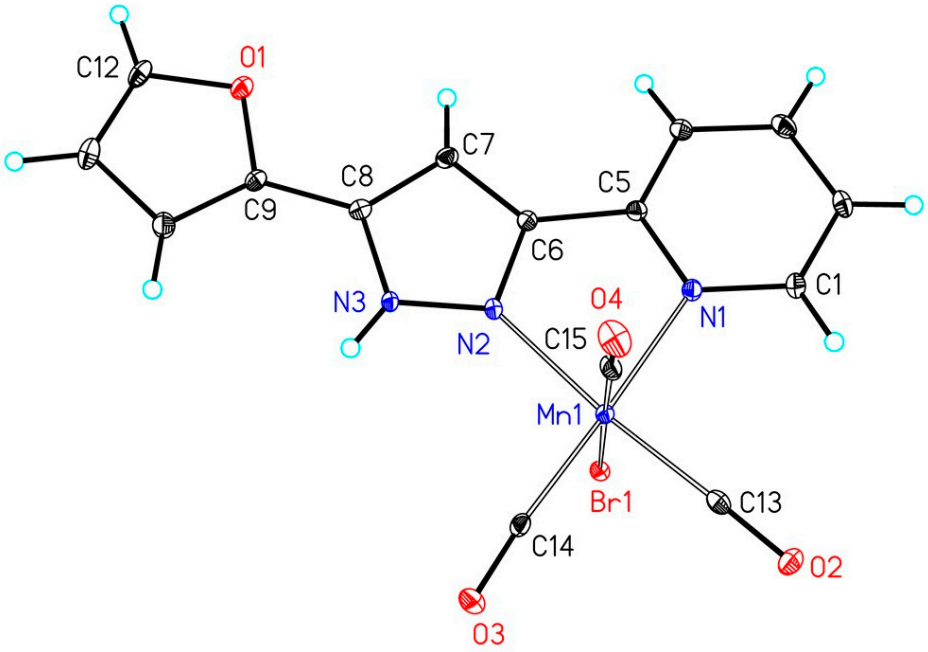
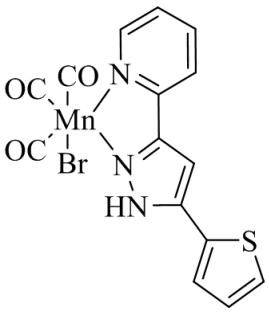


Figure S10. Molecular structure and numbering scheme of **2i**. The ellipsoids represent a probability of 30%, H atoms are shown with arbitrary radii. Selected bond lengths are summarized in Table 2.

R = Thienyl (2j)



A similar procedure as described for compound **2h**, using 480 mg (1.75 mmol) of $Mn(CO)_5Br$, 397 mg (1.75 mmol) of **1j** and 15 mL of Et_2O, yielded compound **2j** as a yellow solid.

Yield: 625 mg (1.19 mmol), 80%.

^{1}H-NMR (400.130 MHz, [D$_8$]THF): δ = 13.83 (s, 1H, NH), 9.15 (d, $^3J_{H,H}$ = 3.9 Hz, 1H), 8.02 (s, 3H), 7.60 (s, 1H), 7.59 (s, 1H), 7.47 (s, 1H), 7.30 (s, 1H), 7.19 (s, 2H).

^{13}C{^{1}H}-NMR (100.613 MHz, [D$_8$]THF): δ = 154.5 (s), 153.5 (s), 152.8 (s), 143.7 (s), 139.3 (s), 131.0 (s), 129.0 (s), 128.0 (s), 127.3 (s), 125.4 (s), 122.6 (s), 102.6 (s).

MS (Micro-ESI neg. in Methanol): *m*/*z* (%) = 444.0 [M − H$^+$].

IR (solid): 3110 (w), 3091 (w), 2994 (w), 2969 (w), 2933 (w), 2896 (w), 2859 (w), 2807 (w), 2020 (m), 1910 (s), 1786 (w), 1764 (w), 1742 (w), 1725 (w), 1709 (w), 1690 (w), 1677 (w), 1658 (w), 1640 (w), 1630 (w), 1613 (w), 1585 (w), 1485 (w), 1442 (m), 1413 (m), 1384 (w), 1351 (w), 1296 (w), 1281 (w), 1263 (w), 1227 (w), 1212 (w), 1153 (m), 1125 (w), 1095 (m), 1038 (m), 988 (w), 966 (w), 935 (w), 843 (m), 774 (m), 749 (m), 710 (m), 682 (m), 645 (w), 627 (m), 546 (w), 529 (m), 510 (m), 486 (w), 466 (w), 426 (w), 412 (w).

Elemental analysis ($C_{15}H_9BrMnN_3O_3S$ x 1 Et_2O, 520.28):

calc.:	C 43.86%, H 3.68%, N 8.08%, S 6.16%
found:	C 43.75%, H 3.50%, N 8.30%, S 6.24%.

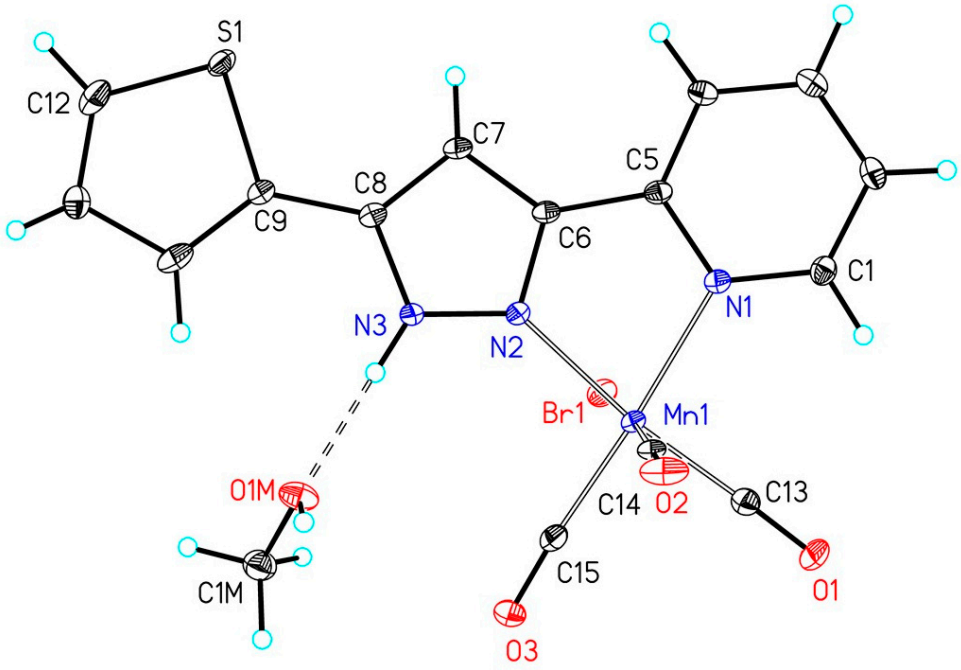
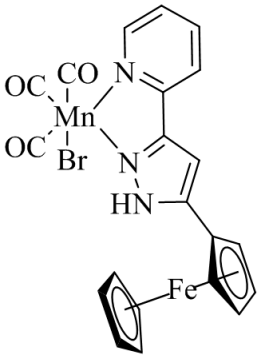


Figure S11. Molecular structure and numbering scheme of **2j**·MeOH. The ellipsoids represent a probability of 30%, H atoms are shown with arbitrary radii. Selected bond lengths are summarized in Table 2.

R = Ferrocenyl (2k)



A similar procedure as described for compound **2h**, using 452 mg (1.64 mmol) of $Mn(CO)_5Br$, 541 mg (1.64 mmol) of **1k** and 20 mL of Et_2O, gave compound **2k** as an orange solid.

Yield: 847 mg (1.64 mmol), 94%.

^{1}H-NMR (400.130 MHz, [D$_8$]THF): δ = 13.28 (s, 1H, NH), 9.12 (d, $^3J_{H,H}$ = 5.1 Hz, 1H), 7.95 (s, 2H), 7.42 (t, $^3J_{H,H}$ = 5.2 Hz, 1H), 7.12 (s, 1H), 4.85 (d, $^3J_{H,H}$ = 13.5 Hz, 2H), 4.40 (s, 2H), 4.13 (s, 5H).

^{13}C{^{1}H}-NMR (100.613 MHz, [D$_8$]THF): δ = 224.1 (s, $C_{Carbonyl}$), 223.5 (s, $C_{Carbonyl}$), 221.9 (s, $C_{Carbonyl}$), 154.5 (s), 153.4 (s), 153.2 (s), 149.6 (s), 139.2 (s), 125.1 (s), 122.4 (s), 101.6 (s), 73.5 (s), 70.9 (s), 70.5 (s), 70.5(s).

MS (Micro-ESI neg. in Methanol): *m*/*z* (%) = 546.0 [M − H$^+$].

IR (solid): 3187 (w), 3157 (w), 3095 (w), 3071 (w), 3023 (w), 2023 (s), 1931 (s), 1911 (vs), 1866 (s), 1613 (w), 1586 m, 1531 (w), 1477 (w), 1448 (m), 1401 (w), 1369 (w), 1303 (w), 1256 (w), 1207 (w), 1160 (w), 1134 (w), 1107 (m), 1079 (w), 1050 (w), 1038 (w), 1030 (w), 996 (w), 968 (w), 873 (w), 819 (m), 777 (m), 756 (m), 694 (w), 682 (m), 645 (m), 632 (m), 600 (m), 549 (m), 531 (m), 509 (m), 498 (m), 483 (m), 454 (m), 421 (m).

Elemental analysis ($C_{21}H_{15}BrMnN_3O_3Fe$, 548.06):

calc.:	C 46.02%, H 2.76%, N 7.67%,
found:	C 45.71%, H 2.76%, N 7.52%.

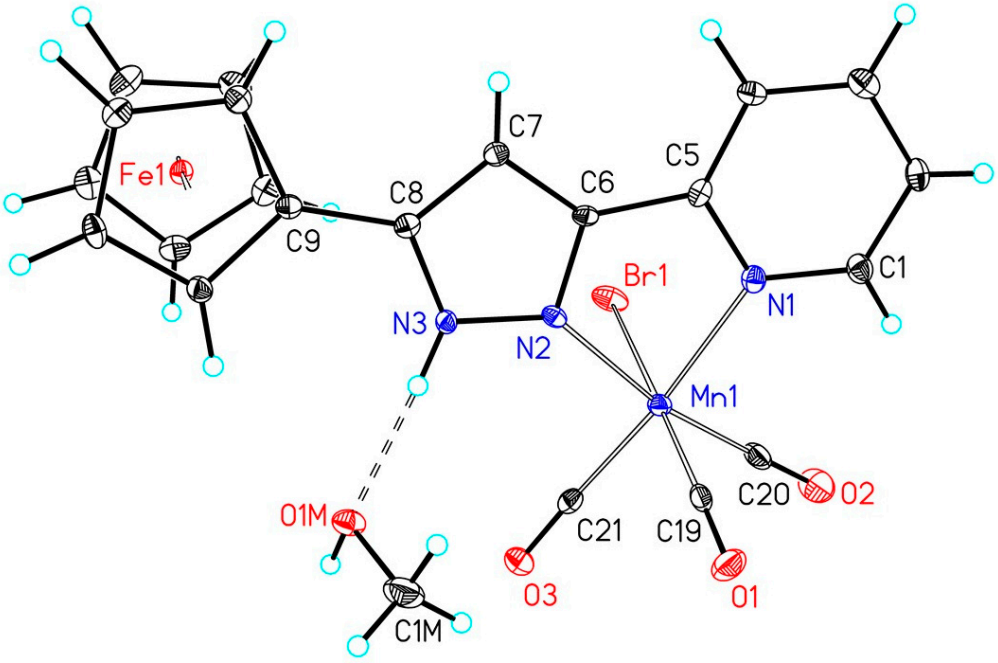


Figure S12. Molecular structure and numbering scheme of **2a**·MeOH. The ellipsoids represent a probability of 30%, H atoms are shown with arbitrary radii. Selected bond lengths are summarized in Table 2.

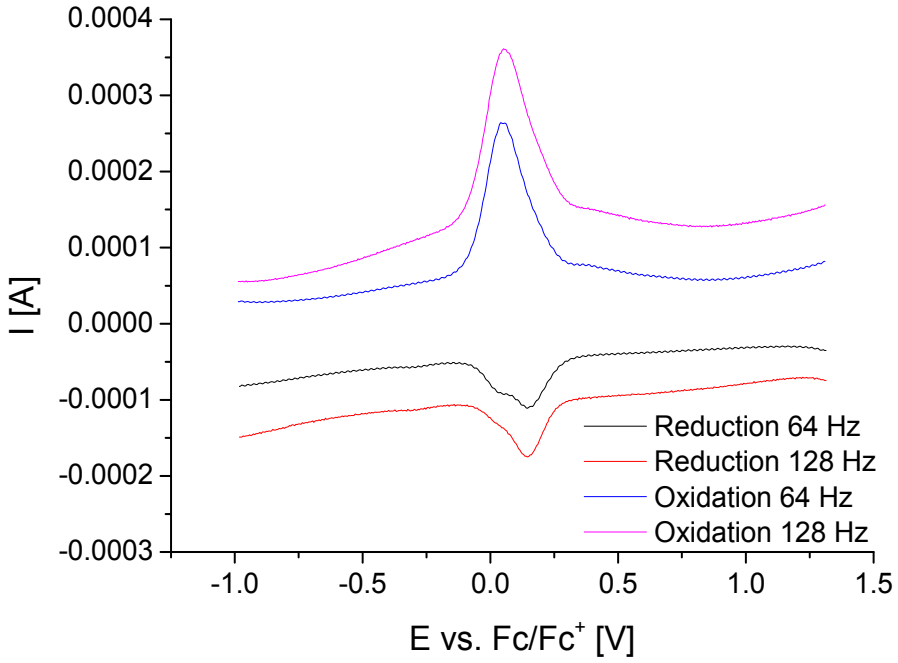


Figure S13. Square-wave voltammogram of **1k** in acetonitrile/$TBABF_4$.

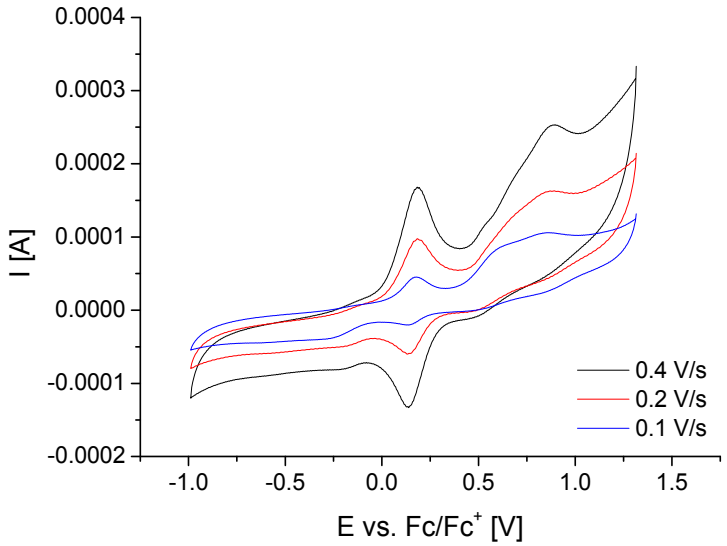


Figure S14. Cyclovoltammogram of **2k** in ACN/$TBABF_4$.

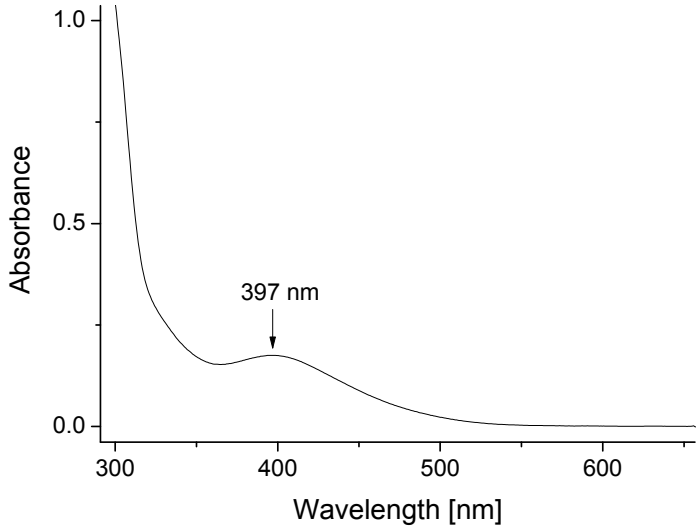
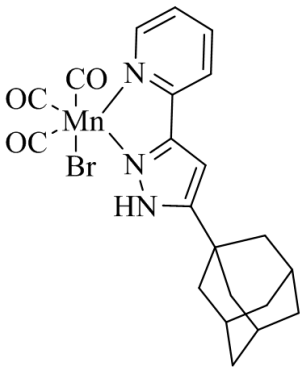


Figure S15. UV–Vis spectrum of **2k** (c = 100 µM) in methanol.

R = Adamantyl (2l)



A similar procedure as described for compound **2h**, using 303 mg (1.10 mmol) of $Mn(CO)_5Br$, 308 mg (1.10 mmol) of **1l** and 12 mL of Et_2O, yielded compound **2l** as a yellow solid.

Yield: 495 mg (0.99 mmol), 90%.

^{1}H-NMR (400.130 MHz, [D$_6$]DMSO): δ = 13.94 (s, 1H, NH), 9.04 (d, $^3J_{H,H}$ = 5.4 Hz, 1H), 8.17–8.05 (m, 2H), 7.54 (t, $^3J_{H,H}$ = 6.1 Hz, 1H), 7.06 (s, 1H), 2.09 (s, 3H), 2.02 (s, 6H), 1.77 (s, 6H).

^{13}C{^{1}H}-NMR (100.613 MHz, [D$_6$]DMSO): δ = 158.9 (s), 153.3 (s), 151.6 (s), 150.7 (s), 139.1 (s), 124.6 (s), 121.6 (s), 100.4 (s), 41.2 (s), 35.9 (s), 33.2 (s), 27.7 (s).

MS (Micro-ESI neg. in DMSO + Methanol): m/z (%) = 496.1 [M − H$^+$].

IR (solid): 3151 (w), 3117 (w), 3065 (w), 2905 (m), 2885 (w), 2849 (w), 2030 (s), 1943 (s), 1913 (s), 1893 (s), 1612 (w), 1586 (w), 1567 (w), 1554 (w), 1524 (w), 1461 (w), 1447 (m), 1407 (w), 1369 (w), 1344 (w), 1315 (w),

1298 (w), 1246 (w), 1226 (w), 1196 (w), 1158 (w), 1122 (w), 1101 (w), 999 (w), 976 (w), 832 (w), 815 (w), 781 (m), 757 (m), 731 (w), 682 (m), 645 (w), 629 (m), 547 (w), 533 (m), 513 (w), 492 (w), 469 (w), 460 (w), 427 (w).

Elemental analysis ($C_{21}H_{21}BrMnN_3O_3$, 498.26):

calc.: C 50.62%, H 4.25%, N 8.43%

found: C 49.19%, H 4.13%, N 8.05%.

Degradation product R = Ph (3a)

The defined degradation product **3a** can be obtained as pale yellow crystals by dissolving of **2a** in a small amount of MeOH after 7 d at daylight.

MS (DEI): *m*/*z* (%) = 1294 [M^+ + 5 − OMe] (20), 1293 [M^+ + 4 − OMe] (60), 1292 [M^+ + 3 − OMe] (67) 1291 [M^+ + 2 − OMe] (100), 1290 [M^+ + 1 − OMe] (36), 1289 [M^+ − OMe] (41).

IR (solid): 3054 (w), 2927 (w), 2823 (w), 1601 (w), 1566 (w), 1469 (w), 1445 (m), 1392 (w), 1333 (w), 1270 (w), 1250 (w), 1177 (w), 1150 (w), 1100 (w), 1080 (w), 1066 (w), 1049 (w), 993 (m), 967 (w), 913 (w), 800 (w), 782 (w), 755 (m), 724 (m), 692 (m), 678 (m), 635 (w), 545 (w), 491 (w), 440 (m), 422 (m).

Elemental analysis ($C_{58}H_{46}Br_2Mn_4N_{12}O_2$, 1322.65):

calc.: C 52.67%, H 3.51%, N 12.71%

found: C 49.32%, H 3.73%, N 11.35%.

Degradation product R = Naph (3b)

The defined degradation product **3b** can be obtained as red crystals by dissolving of **2b** in a few milliliters of MeOH after 10 d at daylight.

MS (DEI): *m*/*z* (%) = 731 [$Mn_2BrL_2^+$ + 2] (9), 729 [$Mn_2BrL_2^+$] (9), 649 (34), 405 (5), 325 (7), 285 (12), 169 (32), 147 (6), 119 (16), 105 (40), 91 (28), 64 (100), 44 (87), 31 (72).

IR (solid): 3370 (w), 3041 (w), 2917 (w), 2812 (w), 1602 (w), 1568 (w), 1511 (w), 1490 (w), 1445 (w), 1392 (w), 1377 (w), 1342 (w), 1300 (w), 1277 (w), 1253 (w), 1234 (w), 1201 (w), 1184 (w), 1135 (w), 1109 (w), 1084 (w), 1051 (w), 1012 (m), 943 (w), 818 (w), 797 (w), 776 (m), 748 (w), 713 (w), 688 (w), 657 (w), 635 (w), 555 (m), 504 (m), 453 (m), 428 (w), 413 (w).

Elemental analysis ($C_{46}H_{58}Br_2Mn_4N_6O_{10}$, 1234.56):

calc.: C 44.75%, H 4.74%, N 6.81%

found: C 42.44%, H 4.21%, N 6.65%.

Table S1. Crystal data and refinement details for the X-ray structure determinations of the compounds **1e–3b.**

Compound	**1e**	**1f**	**2a**	**2b**	**2e**
formula	$C_{14}H_{10}BrN_3$	$C_{14}H_{10}BrN_3$	$C_{18}H_{15}BrMnN_3O_4$	$C_{22}H_{17}BrMnN_3O_4$	$C_{19}H_{18}Br_2MnN_3O_5$
fw (g·mol^{-1})	300.16	300.16	472.18	522.24	583.12
°C	−140(2)	−140(2)	20(2)	−140(2)	−140(2)
crystal system	orthrhombic	monoclinic	monoclinic	triclinic	triclinic
space group	P c a 2_1	C 2/c	P 2_1/c	P ī	P ī
a/Å	17.4723(4)	16.5402(5)	17.8730(3)	7.7299(2)	7.2675(2)
b/Å	5.6934(1)	7.3312(3)	11.1246(2)	8.2135(3)	11.9274(3)
c/Å	23.9478(6)	19.9475(7)	9.7566(2)	16.7895(5)	13.4161(3)
α/°	90	90	90	88.875(2)	100.095(1)
β/°	90	99.348(2)	102.747(1)	87.358(2)	103.438(2)
γ/°	90	90	90	88.9600(1)	102.674(1)
V/Å^3	2382.25(9)	2386.70(15)	1892.09(6)	1064.46(6)	1071.71(5)
Z	8	8	4	2	2
ρ (g·cm^{-3})	1.674	1.671	1.658	1.629	1.807
μ (cm^{-1})	34.34	34.28	28.38	25.31	43.8
measured data	5082	6826	14714	7551	7091
data with $I > 2\sigma(I)$	4757	2524	3955	4192	4448
unique data (R_{int})	5082/0.0000	2729/0.0193	4322/0.0364	4511/0.0287	4854/0.0222
wR_2 (all data, on F^2) [a]	0.1054	0.0751	0.0786	0.2330	0.0685
R_1 ($I > 2\sigma(I)$) [a]	0.0428	0.0306	0.0348	0.0727	0.0306
s [b]	1.125	1.086	1.115	1.207	1.061
Res. dens./e·Å^{-3}	1.751/−0.657	1.625/−0.287	0.729/−0.594	3.820/−0.999	0.796/−0.696
Flack-parameter	0.503(13)	-	-	-	-
absorpt method	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
absorpt corr $T_{min/max}$	0.5873/0.7456	0.5734/0.7456	0.5709/0.7456	0.6103/0.7456	0.4683/0.7456
CCDC No.	1520243	1520244	1520245	1520246	1520247

Table S1. *Cont.*

Compound	2f	2g	2h	2i	2j
formula	$C_{25}H_{26}Br_2MnN_3O_5$	$C_{21}H_{19}BrMnN_3O_3$ [*]	$C_{17}H_{14}BrMnN_4O_4$	$C_{15}H_9BrMnN_3O_4$	$C_{16}H_{13}BrMnN_3O_4S$
fw ($g \cdot mol^{-1}$)	663.25	496.24 [*]	473.17	430.10	478.20
°C	−140(2)	−140(2)	−140(2)	−140(2)	−140(2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	P $2_1/c$	C 2/c	P $2_1/n$	P $2_1/c$	P $2_1/c$
a/Å	13.2094(3)	17.2476(3)	6.9507(2)	15.4805(5)	10.5153(2)
b/Å	10.7647(2)	13.8976(2)	16.3141(4)	11.0812(3)	13.2486(2)
c/Å	19.2739(4)	18.1003(3)	16.1414(3)	9.0482(2)	13.2768(2)
α/°	90	90	90	90	90
β/°	105.947(1)	95.553(1)	91.911(1)	98.349(2)	100.192(1)
γ/°	90	90	90	90	90
V/$Å^3$	2635.19(9)	4318.29(12)	1829.33(8)	1535.70(7)	1820.44(5)
Z	4	8	4	4	4
ρ ($g \cdot cm^{-3}$)	1.672	1.527 [*]	1.718	1.860	1.745
μ (cm^{-1})	35.74	24.88 [*]	29.37	34.87	30.61
measured data	17110	12296	12655	10151	10969
data with $I > 2\sigma(I)$	5115	4214	3752	3191	3668
unique data (R_{int})	6032/0.0554	4752/0.0263	4166/0.0321	3458/0.0350	4177/0.0305
wR_2 (all data, on F^2) [(a)]	0.0775	0.0614	0.0566	0.0598	0.0646
R_1 ($I > 2\sigma(I)$) [(a)]	0.0319	0.0279	0.0275	0.0276	0.0308
s [(b)]	1.069	1.055	1.050	1.086	1.045
Res. dens./$e \cdot Å^{-3}$	0.494/−0.444	0.334/−0.287	0.398/−0.280	0.390/−0.367	0.491/−0.394
absorpt method	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
absorpt corr $T_{min/max}$	0.5024/0.7456	0.6070/0.7456	0.7033/0.7456	0.6266/0.7456	0.6449/0.7456
CCDC No.	1520248	1520249	1520250	1520251	1520252

[*] derived parameters do not contain the contribution of the disordered solvent.

Table S1. *Cont.*

Compound	2k	3a	3b
formula	$C_{22}H_{19}BrFeMnN_3O_4$	$C_{58}H_{46}Br_2Mn_4N_{12}O_2$	$C_{48}H_{66}Br_2Mn_4N_6O_{12}$
fw ($g \cdot mol^{-1}$)	580.10	1322.65	1298.65
°C	−140(2)	−140(2)	−140(2)
crystal system	monoclinic	triclinic	triclinic
space group	C 2/c	P ī	P ī
a/Å	27.6169(6)	10.073(2)	8.6799(3)
b/Å	11.7315(3)	11.148(2)	12.0118(6)
c/Å	15.6609(4)	12.310(2)	14.4763(7)
α/°	90	91.429(9)	113.405(2)
β/°	120.807(1)	96.848(8)	97.479(3)
γ/°	90	95.679(11)	90.983(3)
V/Å^3	4357.99(18)	1364.8(4)	1369.41(11)
Z	8	1	1
ρ ($g \cdot cm^{-3}$)	1.768	1.609	1.575
μ (cm^{-1})	31.14	24.23	24.23
measured data	13138	15114	9804
data with $I > 2\sigma(I)$	3788	4846	5262
unique data (R_{int})	5008/0.0689	6127/0.0423	6083/0.0294
wR_2 (all data, on F^2) [a]	0.1065	0.1759	0.1267
R_1 ($I > 2\sigma(I)$) [a]	0.0570	0.0663	0.0504
s [b]	1.132	1.094	1.180
Res. dens./$e \cdot Å^{-3}$	0.636/−0.530	1.067/−0.971	1.062/−0.715
absorpt method	multi-scan	multi-scan	multi-scan
absorpt corr $T_{min/max}$	0.6165/0.7456	0.5457/0.7456	0.6468/0.7456
CCDC No.	1520253	1520254	1520255

[a] Definition of the *R* indices: $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = [2F_c^2 + \mathrm{Max}(F_o^2]/3$; [b] $s = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.