Supplementary Materials: Hydrosilylation of Aldehydes by a Manganese α-Diimine Complex

Veeranna Yempally, Azal Shahbaz, Wai Yip Fan, Sherzod T. Madrahimov and Ashfaq A. Bengali

Table S1. Crystal data and structure refinement for ***fac*-Mn(Br)(CO)$_3$(MePh-DAB), 2a**.

Identification code	**J418**	
Empirical formula	$C_{21}H_{20}BrMnN_2O_3$	
Formula weight	483.24	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 19.8860(6) Å	α= 90°.
	b = 7.1917(2) Å	β= 96.2120(10)°.
	c = 14.1124(4) Å	γ = 90°.
Volume	2006.42(10) Å3	
Z	4	
Density (calculated)	1.600 Mg/m^3	
Absorption coefficient	2.674 mm^{-1}	
F(000)	976	
Crystal size	0.319 x 0.302 x 0.052 mm^3	
Theta range for data collection	3.014 to 29.587°.	
Index ranges	-27<=h<=27, -9<=k<=9, -19<=l<=16	
Reflections collected	32697	
Independent reflections	5606 [R(int) = 0.0519]	
Completeness to theta = 25.242°	99.80%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7459 and 0.5725	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5606 / 40 / 285	
Goodness-of-fit on F2	1.273	
Final R indices [I>2sigma(I)]	R1 = 0.0561, wR2 = 0.1271	
R indices (all data)	R1 = 0.0630, wR2 = 0.1299	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.549 and -0.898 e.Å^{-3}	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for ***fac*-Mn(Br)(CO)$_3$(MePh-DAB), 2a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	3364(1)	6824(2)	5318(1)	21(1)
O(3)	1576(4)	2767(13)	7127(6)	23(1)
C(3)	1948(6)	3516(16)	6644(8)	22(1)
Br(1A)	1712(1)	3179(1)	6843(1)	19(1)
O(3A)	3521(3)	7410(9)	5173(5)	23(1)
C(3A)	3140(4)	6372(11)	5457(6)	20(1)
Mn(1)	2545(1)	4824(1)	5983(1)	15(1)
O(1)	3310(1)	5536(4)	7861(2)	24(1)
O(2)	1652(2)	8061(4)	6201(2)	29(1)
N(1)	2012(1)	3944(4)	4730(2)	15(1)
N(2)	3102(1)	2541(4)	5653(2)	15(1)
C(1)	3025(2)	5267(5)	7129(2)	17(1)
C(2)	1998(2)	6828(5)	6114(2)	20(1)
C(4)	2246(2)	2453(5)	4386(3)	24(1)
C(5)	2863(2)	1714(5)	4874(3)	24(1)
C(6)	1363(2)	4585(5)	4281(2)	19(1)
C(7)	1333(2)	6304(6)	3808(2)	23(1)
C(8)	711(2)	6899(7)	3364(3)	38(1)
C(9)	146(2)	5877(9)	3387(4)	51(2)
C(10)	172(2)	4181(9)	3861(4)	48(2)
C(11)	782(2)	3463(7)	4309(3)	31(1)
C(12)	1950(2)	7476(6)	3736(3)	30(1)
C(13)	788(3)	1598(7)	4770(4)	46(1)
C(14)	3746(2)	1868(4)	6092(2)	15(1)
C(15)	3768(2)	918(5)	6960(2)	17(1)
C(16)	4391(2)	244(5)	7360(3)	24(1)
C(17)	4969(2)	505(6)	6926(3)	29(1)
C(18)	4938(2)	1425(6)	6065(3)	27(1)
C(19)	4327(2)	2113(5)	5621(3)	20(1)
C(21)	4317(2)	3038(6)	4662(3)	29(1)
C(20)	3148(2)	518(5)	7446(3)	23(1)

Table S3. Bond lengths [Å] and angles [°] for *fac*-Mn(Br)(CO)$_3$(MePh-DAB), 2a.

Br(1)-Mn(1)	2.4349(15)
O(3)-C(3)	1.187(12)
C(3)-Mn(1)	1.846(11)
Br(1A)-Mn(1)	2.4608(10)
O(3A)-C(3A)	1.165(9)
C(3A)-Mn(1)	1.838(8)
Mn(1)-C(1)	1.815(3)
Mn(1)-C(2)	1.828(4)
Mn(1)-N(1)	2.061(3)
Mn(1)-N(2)	2.061(3)
O(1)-C(1)	1.140(4)
O(2)-C(2)	1.137(4)
N(1)-C(4)	1.284(5)
N(1)-C(6)	1.450(4)
N(2)-C(5)	1.294(4)
N(2)-C(14)	1.445(4)
C(4)-C(5)	1.442(5)
C(4)-H(4)	0.95
C(5)-H(5)	0.95
C(6)-C(7)	1.403(5)
C(6)-C(11)	1.412(5)
C(7)-C(8)	1.391(5)
C(7)-C(12)	1.502(6)
C(8)-C(9)	1.347(8)
C(8)-H(8)	0.95
C(9)-C(10)	1.389(9)
C(9)-H(9)	0.95
C(10)-C(11)	1.405(6)
C(10)-H(10)	0.95
C(11)-C(13)	1.490(7)
C(12)-H(12A)	0.98
C(12)-H(12B)	0.98
C(12)-H(12C)	0.98
C(13)-H(13A)	0.98
C(13)-H(13B)	0.98
C(13)-H(13C)	0.98
C(14)-C(15)	1.399(5)
C(14)-C(19)	1.405(5)
C(15)-C(16)	1.392(5)
C(15)-C(20)	1.502(5)
C(16)-C(17)	1.372(6)
C(16)-H(16)	0.95
C(17)-C(18)	1.379(6)
C(17)-H(17)	0.95
C(18)-C(19)	1.396(5)
C(18)-H(18)	0.95
C(19)-C(21)	1.507(5)
C(21)-H(21A)	0.98
C(21)-H(21B)	0.98
C(21)-H(21C)	0.98
C(20)-H(20A)	0.98
C(20)-H(20B)	0.98
C(20)-H(20C)	0.98
O(3)-C(3)-Mn(1)	174.9(11)
O(3A)-C(3A)-Mn(1)	176.1(9)
C(1)-Mn(1)-C(2)	91.87(15)
C(1)-Mn(1)-C(3A)	87.4(3)
C(2)-Mn(1)-C(3A)	88.8(3)
C(1)-Mn(1)-C(3)	86.8(3)

C(2)-Mn(1)-C(3)	85.8(4)
C(1)-Mn(1)-N(1)	172.21(14)
C(2)-Mn(1)-N(1)	94.15(13)
C(3A)-Mn(1)-N(1)	97.7(3)
C(3)-Mn(1)-N(1)	88.7(3)
C(1)-Mn(1)-N(2)	95.60(13)
C(2)-Mn(1)-N(2)	172.44(13)
C(3A)-Mn(1)-N(2)	90.4(3)
C(3)-Mn(1)-N(2)	95.7(4)
N(1)-Mn(1)-N(2)	78.51(11)
C(1)-Mn(1)-Br(1)	86.03(11)
C(2)-Mn(1)-Br(1)	90.19(12)
C(3)-Mn(1)-Br(1)	171.7(3)
N(1)-Mn(1)-Br(1)	98.87(8)
N(2)-Mn(1)-Br(1)	89.20(8)
C(1)-Mn(1)-Br(1A)	87.81(11)
C(2)-Mn(1)-Br(1A)	83.61(12)
C(3A)-Mn(1)-Br(1A)	170.9(2)
N(1)-Mn(1)-Br(1A)	87.96(8)
N(2)-Mn(1)-Br(1A)	97.78(8)
C(4)-N(1)-C(6)	116.3(3)
C(4)-N(1)-Mn(1)	114.0(2)
C(6)-N(1)-Mn(1)	128.9(2)
C(5)-N(2)-C(14)	116.0(3)
C(5)-N(2)-Mn(1)	113.6(2)
C(14)-N(2)-Mn(1)	130.0(2)
O(1)-C(1)-Mn(1)	178.0(3)
O(2)-C(2)-Mn(1)	179.1(4)
N(1)-C(4)-C(5)	116.9(3)
N(1)-C(4)-H(4)	121.6
C(5)-C(4)-H(4)	121.6
N(2)-C(5)-C(4)	116.8(3)
N(2)-C(5)-H(5)	121.6
C(4)-C(5)-H(5)	121.6
C(7)-C(6)-C(11)	121.6(4)
C(7)-C(6)-N(1)	118.5(3)
C(11)-C(6)-N(1)	119.8(3)
C(8)-C(7)-C(6)	118.4(4)
C(8)-C(7)-C(12)	119.3(4)
C(6)-C(7)-C(12)	122.3(3)
C(9)-C(8)-C(7)	121.7(5)
C(9)-C(8)-H(8)	119.2
C(7)-C(8)-H(8)	119.2
C(8)-C(9)-C(10)	120.1(4)
C(8)-C(9)-H(9)	119.9
C(10)-C(9)-H(9)	119.9
C(9)-C(10)-C(11)	121.7(5)
C(9)-C(10)-H(10)	119.1
C(11)-C(10)-H(10)	119.1
C(10)-C(11)-C(6)	116.5(5)
C(10)-C(11)-C(13)	119.5(4)
C(6)-C(11)-C(13)	124.0(4)
C(7)-C(12)-H(12A)	109.5
C(7)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(7)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(11)-C(13)-H(13A)	109.5
C(11)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5

C(11)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(15)-C(14)-C(19)	121.8(3)
C(15)-C(14)-N(2)	118.8(3)
C(19)-C(14)-N(2)	119.4(3)
C(16)-C(15)-C(14)	117.8(3)
C(16)-C(15)-C(20)	119.1(3)
C(14)-C(15)-C(20)	123.0(3)
C(17)-C(16)-C(15)	121.6(4)
C(17)-C(16)-H(16)	119.2
C(15)-C(16)-H(16)	119.2
C(16)-C(17)-C(18)	119.9(4)
C(16)-C(17)-H(17)	120
C(18)-C(17)-H(17)	120
C(17)-C(18)-C(19)	121.3(4)
C(17)-C(18)-H(18)	119.4
C(19)-C(18)-H(18)	119.4
C(18)-C(19)-C(14)	117.6(3)
C(18)-C(19)-C(21)	119.0(3)
C(14)-C(19)-C(21)	123.3(3)
C(19)-C(21)-H(21A)	109.5
C(19)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(19)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(15)-C(20)-H(20A)	109.5
C(15)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(15)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S4. Crystal data and structure refinement for *fac*-[$Mn(CO)_3$(MePh-DAB)(CH_3CN)]PF_6 (2b).

Identification code	**J419**	
Empirical formula	$C_{26.50}H_{27}F_6MnN_3O_3P$	
Formula weight	635.42	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.5180(7) Å	α= 66.565(2)°.
	b = 12.1665(8) Å	β= 82.219(3)°.
	c = 12.9112(8) Å	γ = 71.681(2)°.
Volume	1439.00(16) $Å^3$	
Z	2	
Density (calculated)	1.466 Mg/m^3	
Absorption coefficient	0.586 mm^{-1}	
F(000)	650	
Crystal size	0.195 x 0.164 x 0.132 mm^3	
Theta range for data collection	3.165 to 28.281°.	
Index ranges	-13<=h<=14, -16<=k<=16, -17<=l<=17	
Reflections collected	31470	
Independent reflections	7113 [R(int) = 0.0941]	
Completeness to theta = 25.242°	99.80%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7459 and 0.6331	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7113 / 312 / 457	
Goodness-of-fit on F2	0.948	
Final R indices [I>2sigma(I)]	R1 = 0.0677, wR2 = 0.1537	
R indices (all data)	R1 = 0.1019, wR2 = 0.1773	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.622 and -0.618 $e.Å^{-3}$	

Table S5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for ***fac*-[Mn(CO)$_3$(MePh-DAB)(CH$_3$CN)]PF$_6$ (2b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Mn(1)	6344(1)	4054(1)	2220(1)	39(1)
N(1)	8044(3)	3462(3)	3132(2)	36(1)
N(2)	6179(3)	2401(3)	3441(2)	40(1)
N(3)	7387(3)	3065(3)	1295(2)	42(1)
O(1)	6961(3)	6337(3)	517(2)	59(1)
O(2)	4587(3)	5672(3)	3368(2)	53(1)
O(3)	3830(3)	4768(3)	1012(2)	62(1)
C(1)	6736(3)	5454(4)	1176(3)	44(1)
C(2)	5309(3)	5008(4)	2983(3)	42(1)
C(3)	4811(4)	4446(4)	1477(3)	48(1)
C(4)	8289(3)	2351(3)	3872(3)	40(1)
C(5)	7215(3)	1743(3)	4053(3)	40(1)
C(6)	8943(3)	4207(3)	3027(3)	41(1)
C(7)	8720(3)	4837(3)	3763(3)	44(1)
C(8)	9492(4)	5643(4)	3601(3)	51(1)
C(9)	10454(4)	5786(4)	2760(4)	60(1)
C(10)	10680(4)	5126(4)	2074(3)	57(1)
C(11)	9926(3)	4313(4)	2179(3)	48(1)
C(12)	7734(4)	4636(4)	4738(3)	48(1)
C(13)	10211(4)	3590(4)	1426(3)	55(1)
C(14)	4971(3)	1977(3)	3740(3)	41(1)
C(15)	4515(3)	1581(4)	3021(3)	46(1)
C(16)	3267(4)	1336(4)	3282(3)	50(1)
C(17)	2532(4)	1470(4)	4218(3)	52(1)
C(18)	3037(3)	1814(3)	4942(3)	48(1)
C(19)	4284(3)	2060(3)	4731(3)	44(1)
C(20)	4822(4)	2389(4)	5562(3)	49(1)
C(21)	5311(4)	1373(4)	2018(4)	57(1)
C(22)	7924(4)	2515(4)	748(3)	48(1)
C(23)	8571(5)	1819(4)	32(3)	64(1)
P(1)	10420(1)	-660(1)	2954(1)	52(1)
F(1)	10170(6)	-88(4)	3973(3)	72(2)
F(2)	11935(3)	-1297(4)	3377(4)	73(2)
F(3)	10644(6)	-1201(4)	2051(3)	72(2)
F(4)	8870(4)	10(6)	2679(5)	71(2)
F(5)	10033(6)	-1861(5)	3898(4)	47(2)
F(6)	10776(5)	578(4)	2129(4)	65(2)
F(1A)	11192(11)	-414(9)	3617(7)	84(4)
F(2A)	11771(8)	-1726(7)	2693(8)	83(4)
F(3A)	9690(12)	-1005(8)	2017(7)	74(3)
F(4A)	9101(10)	312(10)	2905(10)	75(3)
F(5A)	9991(12)	-1746(11)	3918(9)	67(5)
F(6A)	10869(11)	356(9)	1749(8)	71(3)
C(24)	7557(14)	8340(14)	1069(15)	129(5)
C(25)	6373(17)	9130(20)	540(18)	78(3)
C(26)	6310(16)	10071(15)	-460(15)	72(3)
C(27)	5080(17)	10852(17)	-926(18)	86(3)
C(28)	3911(17)	10620(20)	-322(19)	85(3)
C(29)	4052(17)	9552(17)	669(18)	88(4)
C(30)	5311(16)	8791(17)	1071(18)	81(3)

Table S6. Bond lengths [Å] and angles [°] for *fac*-[Mn(CO)$_3$(MePh-DAB)(CH$_3$CN)]PF$_6$ (2b).

Mn(1)-C(3)	1.822(4)
Mn(1)-C(2)	1.824(4)
Mn(1)-C(1)	1.832(4)
Mn(1)-N(3)	2.009(3)
Mn(1)-N(2)	2.045(3)
Mn(1)-N(1)	2.046(3)
N(1)-C(4)	1.275(4)
N(1)-C(6)	1.464(4)
N(2)-C(5)	1.278(4)
N(2)-C(14)	1.466(4)
N(3)-C(22)	1.139(5)
O(1)-C(1)	1.145(4)
O(2)-C(2)	1.143(4)
O(3)-C(3)	1.143(4)
C(4)-C(5)	1.481(4)
C(4)-H(4)	0.95
C(5)-H(5)	0.95
C(6)-C(11)	1.397(5)
C(6)-C(7)	1.397(5)
C(7)-C(8)	1.398(5)
C(7)-C(12)	1.510(5)
C(8)-C(9)	1.377(6)
C(8)-H(8)	0.95
C(9)-C(10)	1.368(6)
C(9)-H(9)	0.95
C(10)-C(11)	1.409(5)
C(10)-H(10)	0.95
C(11)-C(13)	1.498(5)
C(12)-H(12A)	0.98
C(12)-H(12B)	0.98
C(12)-H(12C)	0.98
C(13)-H(13A)	0.98
C(13)-H(13B)	0.98
C(13)-H(13C)	0.98
C(14)-C(15)	1.395(5)
C(14)-C(19)	1.406(5)
C(15)-C(16)	1.405(5)
C(15)-C(21)	1.508(5)
C(16)-C(17)	1.381(6)
C(16)-H(16)	0.95
C(17)-C(18)	1.385(5)
C(17)-H(17)	0.95
C(18)-C(19)	1.404(5)
C(18)-H(18)	0.95
C(19)-C(20)	1.510(5)
C(20)-H(20A)	0.98
C(20)-H(20B)	0.98
C(20)-H(20C)	0.98
C(21)-H(21A)	0.98
C(21)-H(21B)	0.98
C(21)-H(21C)	0.98
C(22)-C(23)	1.457(6)
C(23)-H(23A)	0.98
C(23)-H(23B)	0.98
C(23)-H(23C)	0.98
P(1)-F(1A)	1.424(6)
P(1)-F(4A)	1.503(8)
P(1)-F(3)	1.512(3)

P(1)-F(5A)	1.553(8)
P(1)-F(6)	1.586(4)
P(1)-F(4)	1.593(4)
P(1)-F(2)	1.601(3)
P(1)-F(5)	1.615(4)
P(1)-F(1)	1.674(3)
P(1)-F(6A)	1.677(8)
P(1)-F(2A)	1.695(7)
P(1)-F(3A)	1.757(7)
C(24)-C(25)	1.377(18)
C(24)-H(24A)	0.98
C(24)-H(24B)	0.98
C(24)-H(24C)	0.98
C(25)-C(30)	1.320(11)
C(25)-C(26)	1.335(11)
C(26)-C(27)	1.386(11)
C(26)-H(26)	0.95
C(27)-C(28)	1.407(12)
C(27)-H(27)	0.95
C(28)-C(29)	1.400(12)
C(28)-H(28)	0.95
C(29)-C(30)	1.383(11)
C(29)-H(29)	0.95
C(30)-H(30)	0.95
C(3)-Mn(1)-C(2)	85.11(16)
C(3)-Mn(1)-C(1)	90.42(16)
C(2)-Mn(1)-C(1)	88.88(15)
C(3)-Mn(1)-N(3)	91.12(14)
C(2)-Mn(1)-N(3)	175.99(13)
C(1)-Mn(1)-N(3)	89.77(14)
C(3)-Mn(1)-N(2)	97.00(14)
C(2)-Mn(1)-N(2)	94.37(13)
C(1)-Mn(1)-N(2)	172.12(13)
N(3)-Mn(1)-N(2)	87.45(11)
C(3)-Mn(1)-N(1)	174.99(15)
C(2)-Mn(1)-N(1)	96.16(13)
C(1)-Mn(1)-N(1)	94.45(13)
N(3)-Mn(1)-N(1)	87.71(11)
N(2)-Mn(1)-N(1)	78.08(11)
C(4)-N(1)-C(6)	119.0(3)
C(4)-N(1)-Mn(1)	115.1(2)
C(6)-N(1)-Mn(1)	125.9(2)
C(5)-N(2)-C(14)	118.2(3)
C(5)-N(2)-Mn(1)	114.9(2)
C(14)-N(2)-Mn(1)	126.5(2)
C(22)-N(3)-Mn(1)	176.8(3)
O(1)-C(1)-Mn(1)	179.0(3)
O(2)-C(2)-Mn(1)	173.3(3)
O(3)-C(3)-Mn(1)	175.6(4)
N(1)-C(4)-C(5)	115.3(3)
N(1)-C(4)-H(4)	122.4
C(5)-C(4)-H(4)	122.4
N(2)-C(5)-C(4)	115.5(3)
N(2)-C(5)-H(5)	122.2
C(4)-C(5)-H(5)	122.2
C(11)-C(6)-C(7)	123.0(3)
C(11)-C(6)-N(1)	119.7(3)
C(7)-C(6)-N(1)	117.2(3)
C(6)-C(7)-C(8)	117.6(3)
C(6)-C(7)-C(12)	122.6(3)

C(8)-C(7)-C(12)	119.8(3)
C(9)-C(8)-C(7)	120.9(4)
C(9)-C(8)-H(8)	119.6
C(7)-C(8)-H(8)	119.6
C(10)-C(9)-C(8)	120.3(3)
C(10)-C(9)-H(9)	119.9
C(8)-C(9)-H(9)	119.9
C(9)-C(10)-C(11)	121.8(4)
C(9)-C(10)-H(10)	119.1
C(11)-C(10)-H(10)	119.1
C(6)-C(11)-C(10)	116.4(4)
C(6)-C(11)-C(13)	123.0(3)
C(10)-C(11)-C(13)	120.6(3)
C(7)-C(12)-H(12A)	109.5
C(7)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(7)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(11)-C(13)-H(13A)	109.5
C(11)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(11)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(15)-C(14)-C(19)	123.1(3)
C(15)-C(14)-N(2)	119.9(3)
C(19)-C(14)-N(2)	116.9(3)
C(14)-C(15)-C(16)	117.1(3)
C(14)-C(15)-C(21)	123.3(3)
C(16)-C(15)-C(21)	119.6(3)
C(17)-C(16)-C(15)	121.3(3)
C(17)-C(16)-H(16)	119.3
C(15)-C(16)-H(16)	119.3
C(16)-C(17)-C(18)	120.2(3)
C(16)-C(17)-H(17)	119.9
C(18)-C(17)-H(17)	119.9
C(17)-C(18)-C(19)	121.1(3)
C(17)-C(18)-H(18)	119.5
C(19)-C(18)-H(18)	119.5
C(18)-C(19)-C(14)	117.1(3)
C(18)-C(19)-C(20)	119.5(3)
C(14)-C(19)-C(20)	123.5(3)
C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(15)-C(21)-H(21A)	109.5
C(15)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(15)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
N(3)-C(22)-C(23)	178.2(4)
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5

H(23B)-C(23)-H(23C)	109.5
F(1A)-P(1)-F(4A)	101.6(6)
F(1A)-P(1)-F(5A)	97.6(5)
F(4A)-P(1)-F(5A)	95.4(6)
F(3)-P(1)-F(6)	93.4(2)
F(3)-P(1)-F(4)	93.5(2)
F(6)-P(1)-F(4)	90.5(2)
F(3)-P(1)-F(2)	93.7(2)
F(6)-P(1)-F(2)	90.8(2)
F(4)-P(1)-F(2)	172.6(3)
F(3)-P(1)-F(5)	92.8(2)
F(6)-P(1)-F(5)	173.9(3)
F(4)-P(1)-F(5)	89.2(2)
F(2)-P(1)-F(5)	88.8(2)
F(3)-P(1)-F(1)	178.9(2)
F(6)-P(1)-F(1)	87.8(2)
F(4)-P(1)-F(1)	86.6(2)
F(2)-P(1)-F(1)	86.1(2)
F(5)-P(1)-F(1)	86.1(2)
F(1A)-P(1)-F(6A)	92.4(5)
F(4A)-P(1)-F(6A)	88.5(5)
F(5A)-P(1)-F(6A)	168.3(6)
F(1A)-P(1)-F(2A)	91.8(6)
F(4A)-P(1)-F(2A)	165.2(6)
F(5A)-P(1)-F(2A)	89.1(5)
F(6A)-P(1)-F(2A)	84.5(4)
F(1A)-P(1)-F(3A)	171.4(5)
F(4A)-P(1)-F(3A)	85.2(5)
F(5A)-P(1)-F(3A)	86.9(5)
F(6A)-P(1)-F(3A)	82.4(4)
F(2A)-P(1)-F(3A)	80.9(5)
C(25)-C(24)-H(24A)	109.5
C(25)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(25)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(30)-C(25)-C(26)	123.1(10)
C(30)-C(25)-C(24)	113.1(14)
C(26)-C(25)-C(24)	123.6(14)
C(25)-C(26)-C(27)	120.3(10)
C(25)-C(26)-H(26)	119.8
C(27)-C(26)-H(26)	119.8
C(26)-C(27)-C(28)	118.4(10)
C(26)-C(27)-H(27)	120.8
C(28)-C(27)-H(27)	120.8
C(29)-C(28)-C(27)	118.0(9)
C(29)-C(28)-H(28)	121
C(27)-C(28)-H(28)	121
C(30)-C(29)-C(28)	120.4(10)
C(30)-C(29)-H(29)	119.8
C(28)-C(29)-H(29)	119.8
C(25)-C(30)-C(29)	118.9(10)
C(25)-C(30)-H(30)	120.6
C(29)-C(30)-H(30)	120.6

Symmetry transformations used to generate equivalent atoms:

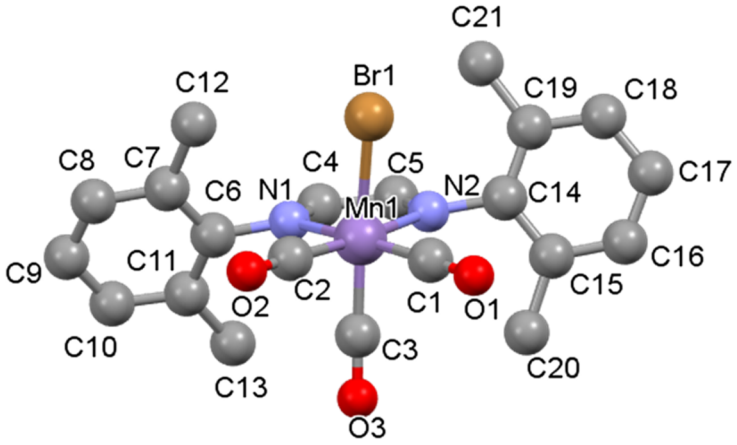
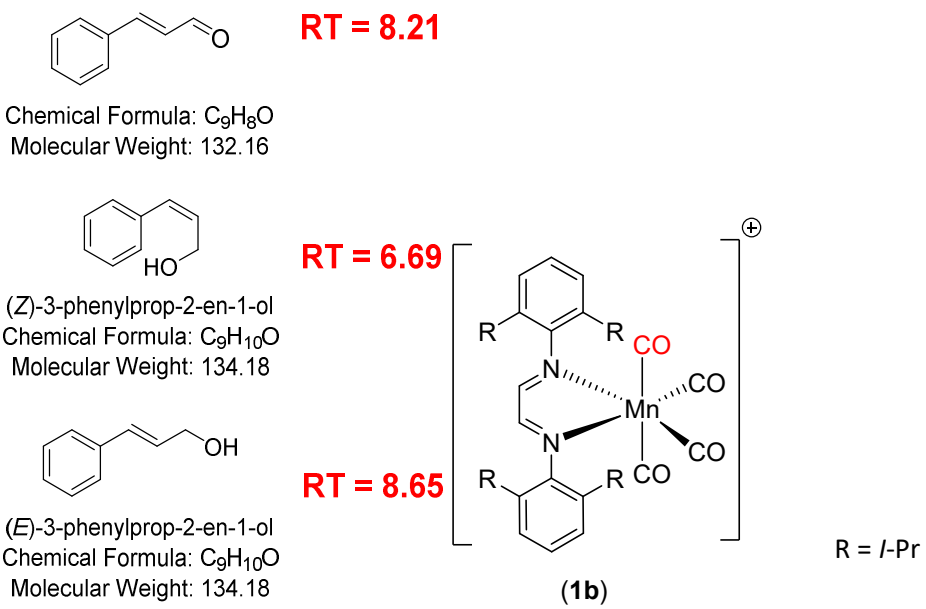


Figure S1. X-ray crystal structure for compound ***fac*-Mn(Br)(CO)$_3$(MePh-DAB), (2a)**. Hydrogen atoms omitted for clarity.



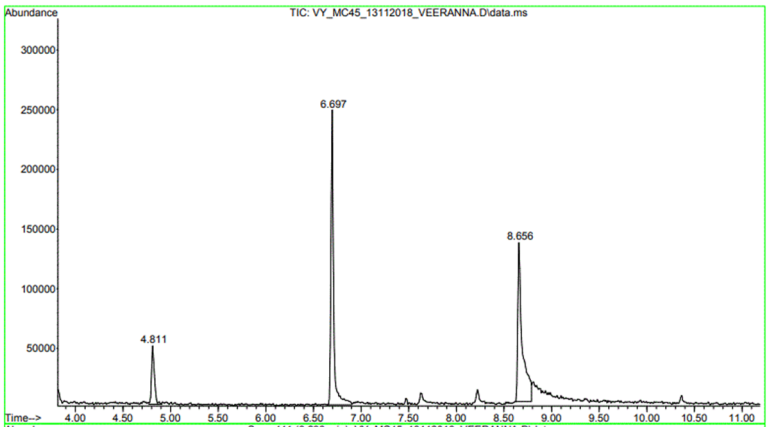
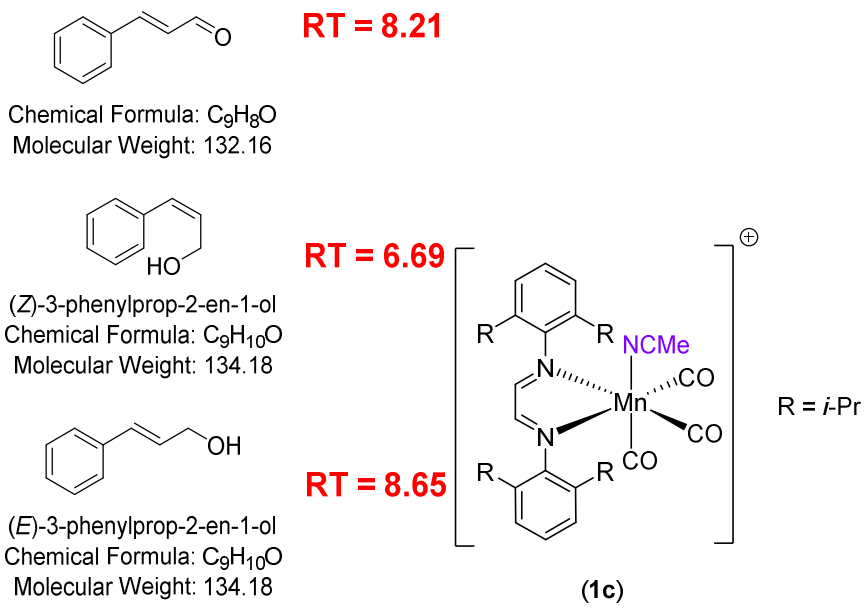


Figure S2. GC-MS data obtained after 10 min for a reaction mixture of Cinnamaldehyde and Phenyl silane ($PhSiH_3$) under neat conditions with 2.50 mol % catalyst **1b** at 80 °C.



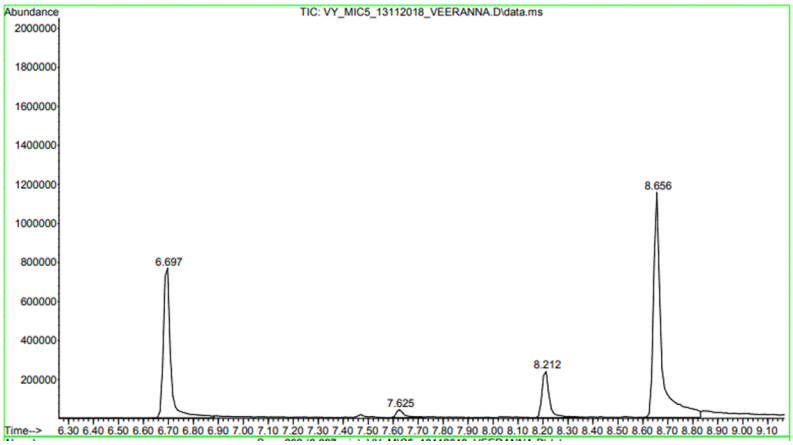


Figure S3. GC-MS data obtained after 10 min for a reaction mixture of Cinnamaldehyde and Phenyl silane ($PhSiH_3$) under neat conditions with 2.50 mol % catalyst **1c** at 80 °C.

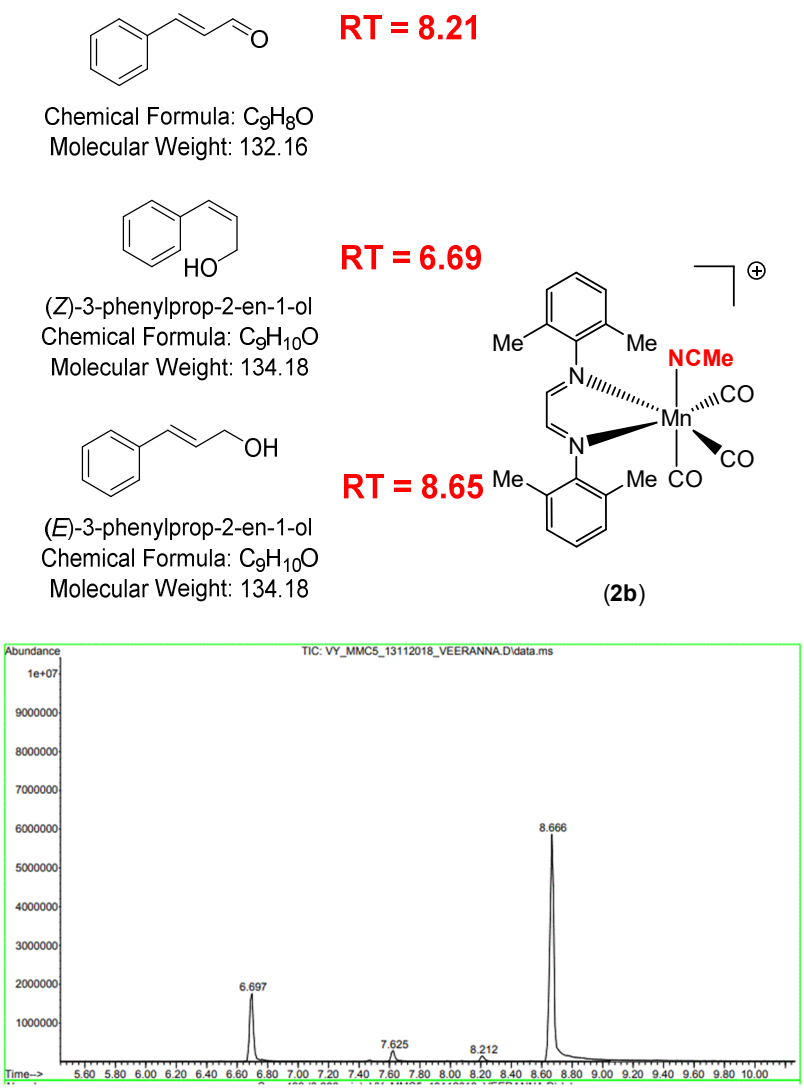


Figure S4. GC-MS data obtained after 10 min for a reaction mixture of Cinnamaldehyde and Phenyl silane ($PhSiH_3$) under neat conditions with 2.50 mol % catalyst **2b** at 80 °C.

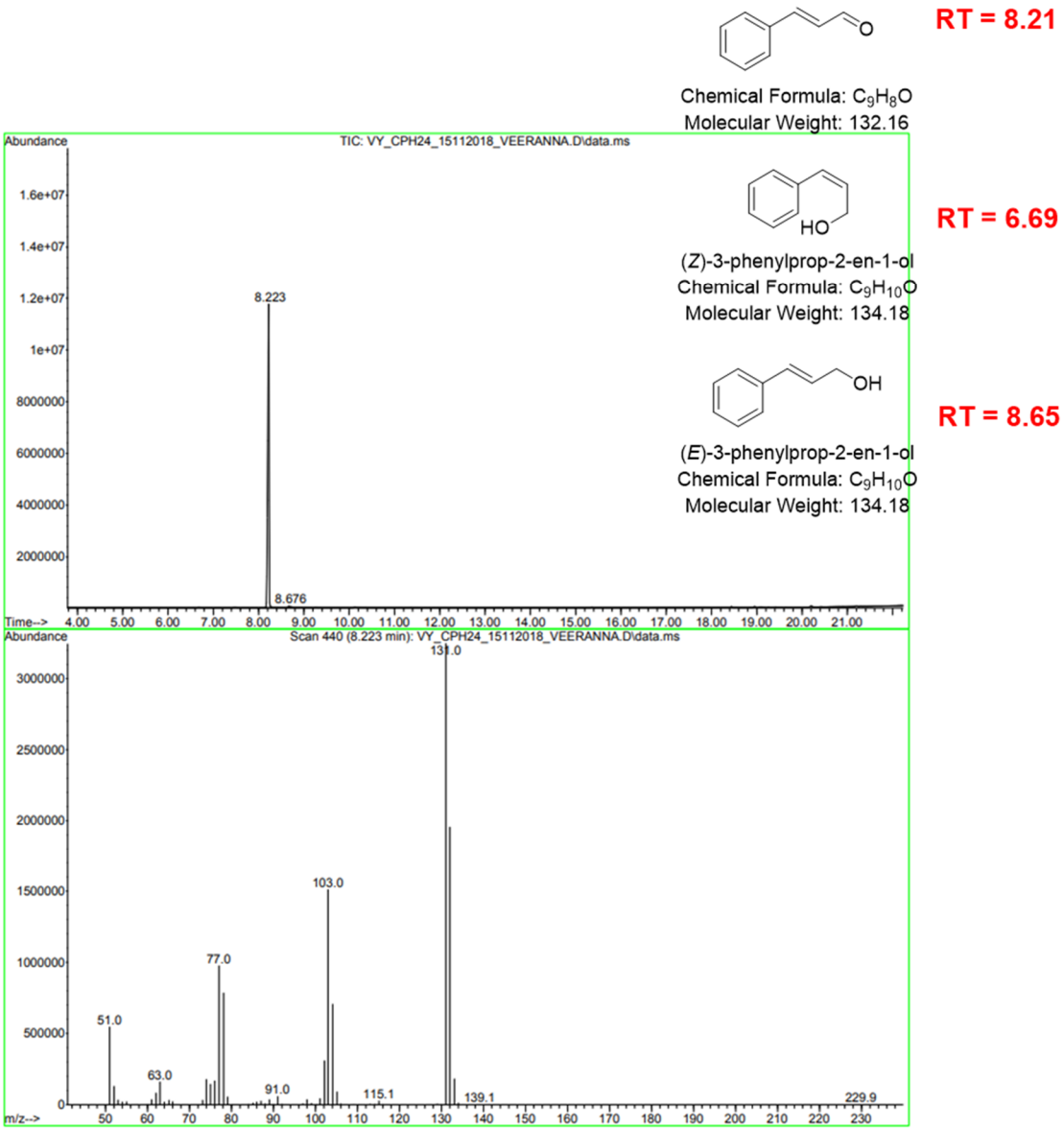


Figure S5. GC-MS data obtained after 24 h for a reaction mixture of Cinnamaldehyde and Phenyl silane ($PhSiH_3$) under neat conditions without any catalyst.

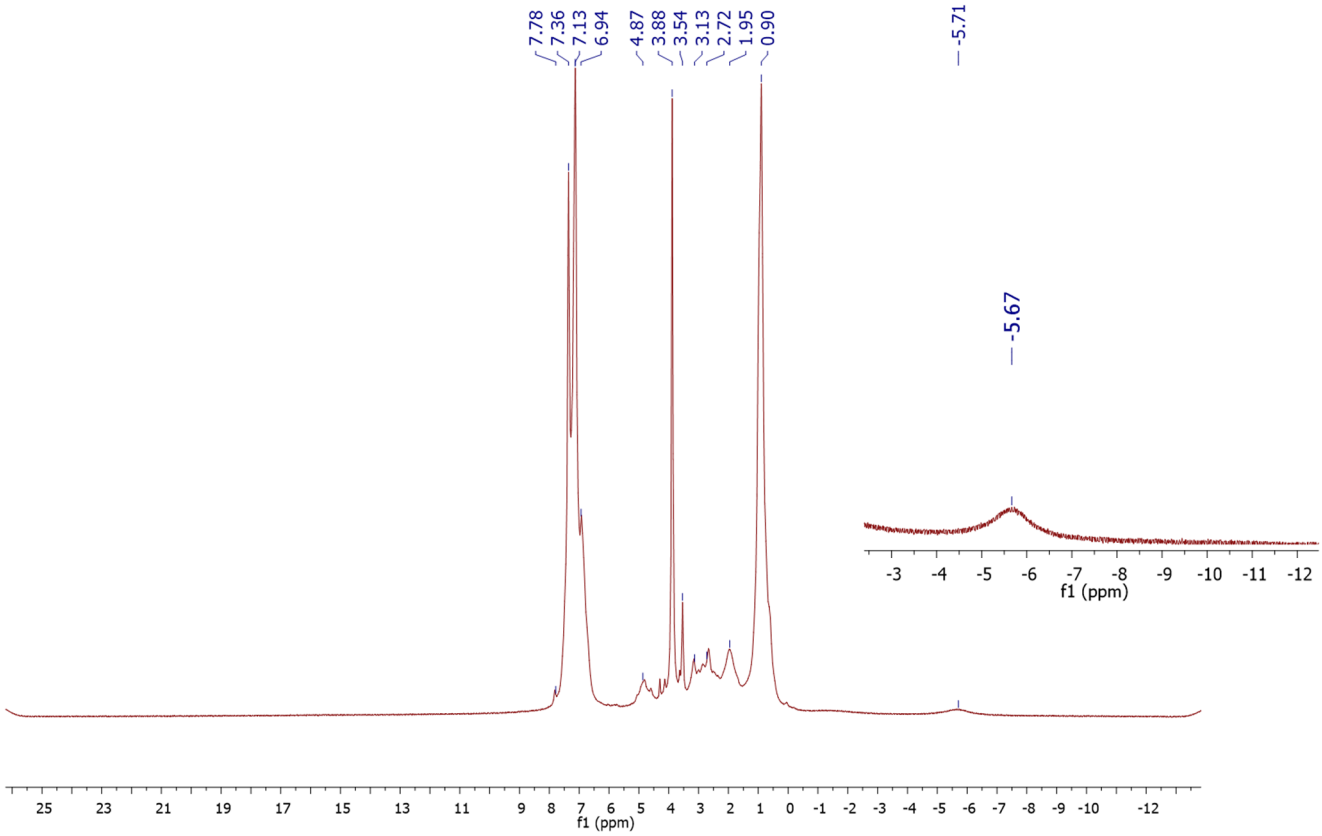


Figure S6. ^{1}H-NMR spectrum of catalyst **1b** with a stoichiometric amount of $PhSiH_3$ in acetonitrile-d_3 at 80 °C after 2 h. The inset shows an expansion of the hydride region.