Electronic Supplementary Information for Dalton Transactions

Electronic Supporting Information

First example of an enantiopure planar chiral ligand built on a (η^5-cyclohexadienyl)$Mn(CO)_3$ scaffold.

Derya Cetiner,[a,b] Béatrice Jacques,[a,b] Elina Payet,[a,b] Murielle Chavarot-Kerlidou,*[a,b] Françoise Rose-Munch,*[a,b] Eric Rose,[a,b] Jean-Philippe Tranchier[a,b] and Patrick Herson.[c,d]

[a] UPMC Univ Paris 06, UMR 7611, Laboratoire de Chimie Organique, Institut de Chimie Moléculaire (FR 2769), Case 181, 4 place Jussieu, F-75252 Paris Cedex 05, France.

Fax: (+33) (0)1-44-27-55-04

E-mail: murielle.chavarot-kerlidou@upmc.fr, francoise.rose@upmc.fr

[b] CNRS, UMR 7611, Laboratoire de Chimie Organique, F-75005, Paris, France.

[c] UPMC Univ Paris 06, UMR 7071, Laboratoire de Chimie Inorganique et Matériaux Moléculaires, F-75005, Paris, France.

[d] CNRS, UMR 7071, Laboratoire de Chimie Inorganique et Matériaux Moléculaires, F-75005, Paris, France.

General comments. All reactions and manipulations were routinely performed under a dry nitrogen atmosphere using standard Schlenk techniques. Tetrahydrofurane (THF) was dried over sodium benzophenone ketyl and distilled. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) was distilled over potassium hydroxide (KOH) and stored under nitrogen over 4Å molecular sieves. Ph_2PCl, $Ph_2(O)PCl$ and the palladium complex $[(\eta^3\text{-allyl})PdCl]_2$ were purchased from ACROS and $[H_2C{=}NMe_2][I]$, $(CH_2)_2I_2$ from ALDRICH. NMR spectra were recorded on a Bruker ARX 200 MHz or Avance 400 MHz spectrometer. ^1H and ^{13}C signals of NMR solvent $CDCl_3$ were used as internal standards respectively at δ = 7.26 ppm and δ = 77.36 ppm. The $Mn(CO)_3$ carbonyl signal is known to be difficult to observe, specially when only low quantities of complex are available. Infrared spectra were measured on a Bruker Tensor 27 spectrometer. Elemental analyses were performed by the Service Central d'Analyse du CNRS. Mass spectra were performed for MALDI-TOF by the Plate-Forme Spectrométrie de Masse et Protéomique (IFR83, UPMC), for ES-MS by the Groupe de Spectrométrie de Masse (UMR 7613, UPMC) and for the EI-MS by the Service de Spectrométrie de Masse de l'ENS (Chemistry Dpt, Paris).

Complexes **1**[10] and (*S*)-**8**[17] were synthesized according to procedures previously described in the literature.

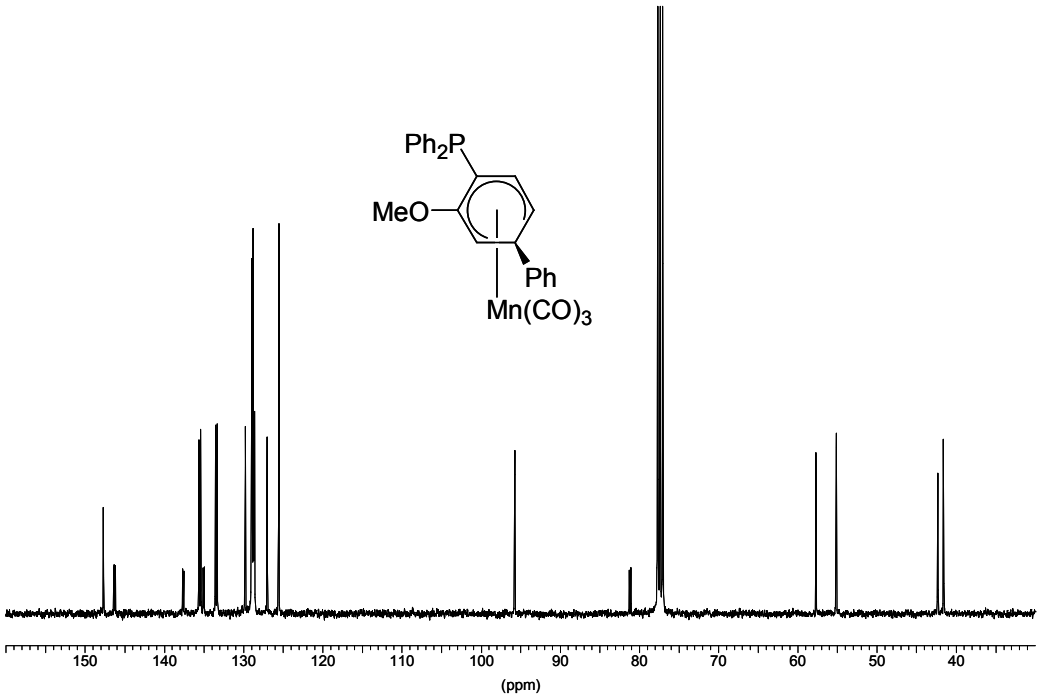
[10] Y. K. Chung, P. G. Williard, D. A. Sweigart, *Organometallics* 1982, **1**, 1053.

[17] a) K. Tani, L. D. Brown, J. Ahmed, J. A. Ibers, M. Yokota, A. Nakamura, S. Otsuka, *J. Am. Chem. Soc*., 1977, **99**, 7876. b) N. K. Roberts, S. B. Wild, *J. Am. Chem. Soc*., 1979, **101**, 6254. c) T. Mino, Y. Tanaka, Y. Hattori, T. Yabusaki, H. Saotome, M. Sakamoto, T. Fujita, *J. Org. Chem*., 2006, **71**, 7346.

Typical procedure for the synthesis of complexes 2, 3, 4, 5 and 6. A solution of complex **1** (for **2**, **3** and **4**) or complex **4** (for **5** and **6**) (1 mmol) and freshly distilled TMEDA (1.6 eq) in 10 mL of THF was cooled to -78°C. A solution of *n*BuLi (1.6M in hexanes, 1.6 eq) was slowly added. The mixture was stirred for 1 hour at -78°C before the addition of the electrophile (Ph_2PCl, $Ph_2(O)PCl$, $[H_2C{=}NMe_2][I]$ or $(CH_2)_2I_2$; 2 eq). The mixture was stirred for another hour at -78°C before warming to room temperature and quenching by addition of H_2O. After extraction of the mixture by Et_2O, the combined organic layers were washed with a saturated aqueous sodium chloride solution and dried over magnesium sulfate. After concentration *in vacuo*, the crude mixture was purified by flash chromatography on silica gel to afford the pure functionalized η^5-cyclohexadienyl complex **2, 3, 4, 5** or **6**.

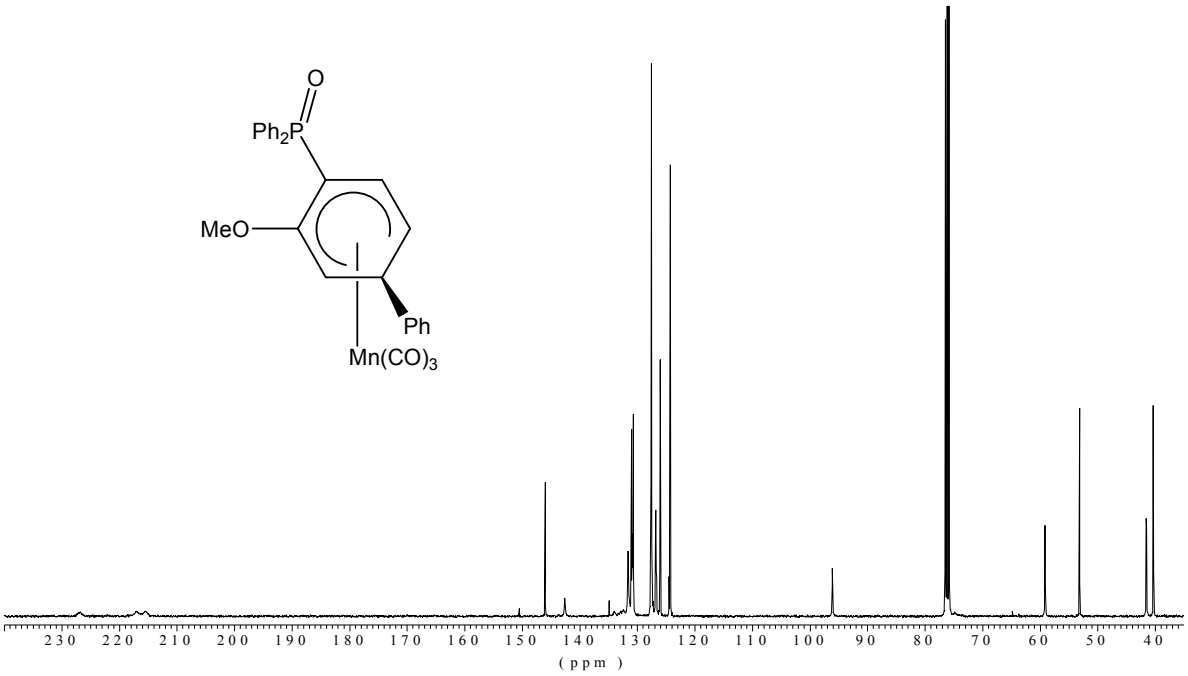
2 (83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.35 (m, 1H, H^5), 3.43 (s, 3H, OMe), 3.56 (m, 1H, H^1), 4.02 (t_{app}, ^{3}J = 6.0 Hz, 1H, H^6), 4.39 (d, ^{3}J = 7.4 Hz, 1H, H^4), 6.98 (d, ^{3}J = 7.0 Hz, 2H, H^{Ar}), 7.22-7.37 (m, 9H, H^{Ar}), 7.44-7.47 (m, 4H, H^{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 41.6 (C^6), 42.3 (C^1), 55.1 (OMe), 57.7 (C^5), 81.2 (d, $^{1}J^{CP}$ = 20 Hz, C^3), 95.7 (C^4), 125.5 (CH^{Ar}), 127.0 (CH^{Ar}), 128.6 (d, $^{3}J^{CP}$ = 7 Hz, CH^{Ar}), 128.8 (CH^{Ar}), 128.9 (d, $^{3}J^{CP}$ = 7 Hz, CH^{Ar}), 128.9 (CH^{Ar}), 129.8 (CH^{Ar}), 133.4 (d, $^{2}J^{CP}$ = 20 Hz, CH^{Ar}), 135.0 (d, $^{1}J^{CP}$ = 12 Hz, C^{Ar}), 135.1 (d, $^{2}J^{CP}$ = 20 Hz, CH^{Ar}), 137.6 (d, $^{1}J^{CP}$ = 12 Hz, C^{Ar}), 146.2 (d, $^{2}J^{CP}$ = 14 Hz, C^2), 147.7 (C^{Ar}). ^{31}P NMR (161 MHz, $CDCl_3$): δ -17.2 (PPh_2). IR (neat): 1917 ($Mn(CO)_3$), 2009 ($Mn(CO)_3$). HRMS (MALDI TOF, positive mode): 509.0266 ($M+H^+$, calcd for $C_{28}H_{23}MnO_4P$: 509.0714). Anal. Calcd for $C_{28}H_{22}MnO_4P$: C, 66.15 ; H, 4.36. Found: C, 66.06 ; H, 4.07.

^{13}C NMR spectrum (100 MHz, $CDCl_3$) of complex **2**.



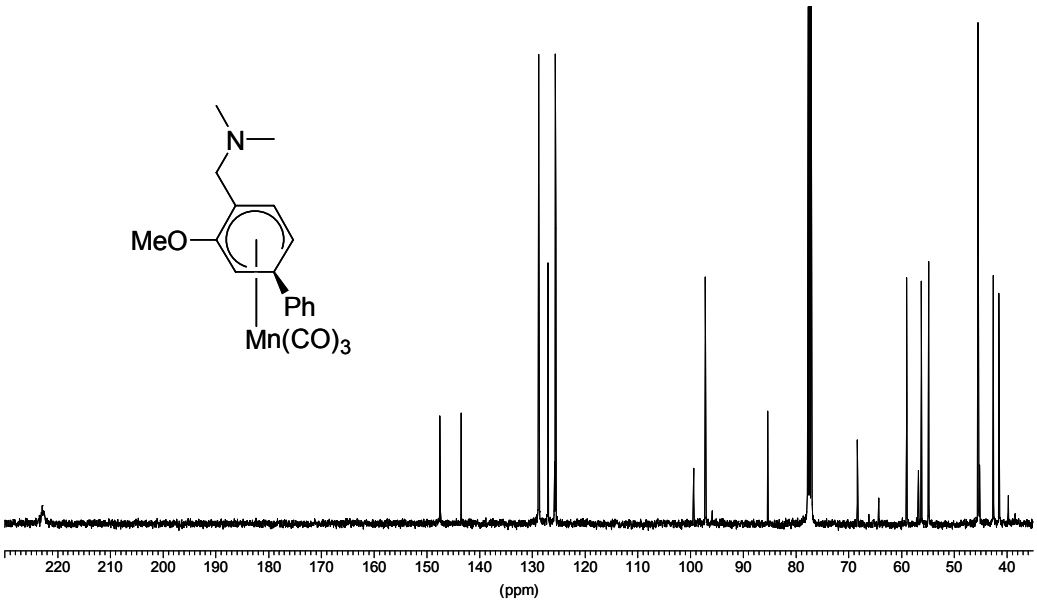
3 (70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.14 (s, 3H, OMe), 3.42 (t_{app}, ^{3}J = 6.0 Hz, 1H, H^1), 3.63 (t_{app}, ^{3}J = 6.0 Hz, 1H, H^5), 4.02 (t, ^{3}J = 6.0 Hz, 1H, H^6), 5.74 (t, ^{3}J = 7.0 Hz, 1H, H^4), 6.97 (d, ^{3}J = 7.0 Hz, 2H, H^8), 7.22-7.29 (m, 5H, H^{Ar}), 7.42-7.56 (m, 4H, H^{Ar}), 7.75-7.89 (m, 4H, H^{Ar}) .^{13}C NMR (100 MHz, $CDCl_3$): δ 41.5 (C6), 42.7 (C1), 54.3 (OMe), 60.3 (C5), 97.3 (C^4), 125.5 (CH^{Ar}), 127.2 (CH^{Ar}), 127.9 (d, $^{2}J^{CP}$ = 12 Hz, CH^{Ar}), 128.6 (d, $^{2}J^{CP}$ = 12 Hz, CH^{Ar}), 128.7 (CH^{Ar}), 131.9 (CH^{Ar}), 132.1 (d, $^{3}J^{CP}$ = 10 Hz, CH^{Ar}), 132.8 (CH^{Ar}), 147.2 (C^2), 216.6 ($Mn(CO)_3$). ^{31}P NMR ($CDCl_3$): δ 30.3. IR (neat): 1952 ($Mn(CO)_3$), 2015($Mn(CO)_3$). HRMS (ESI, positive mode): 525.0658 ($M+H^+$, calcd for $C_{28}H_{23}O_5MnP$: 525.0664).

^{13}C NMR spectrum (100 MHz, $CDCl_3$) of complex **3**.



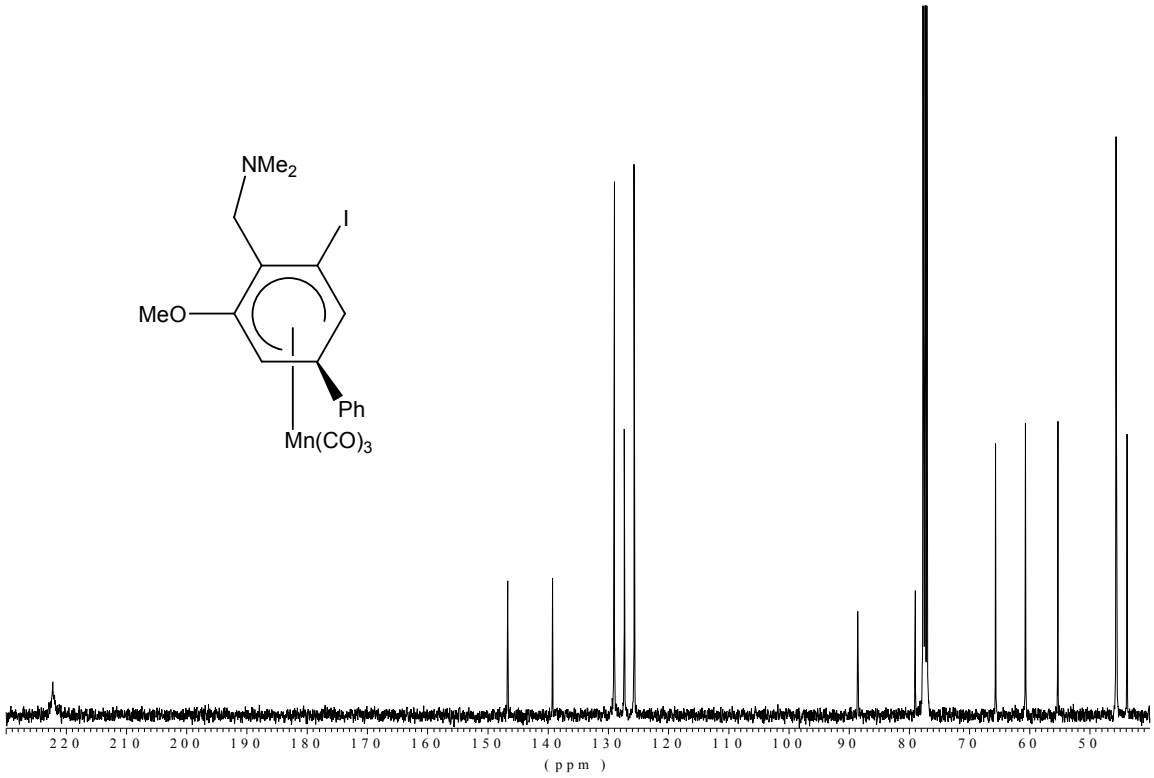
4 (73%). ^1H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 6H, NMe_2), 3.06 (d, ^2J = 12.5 Hz, 1H, H^{11}), 3.31 (ddd, ^3J = 7.3 Hz, ^3J = 6.2 Hz, ^4J = 1.6 Hz, 1H, H^5), 3.40 (dd, ^3J = 6.2 Hz, ^4J = 1.6 Hz, 1H, H^1), 3.42 (s, 3H, OMe), 3.91 (t_{app}, ^3J = 6.2 Hz, 1H, H^6), 4.21 (d, ^2J = 12.5 Hz, 1H, H^{11}), 5.05 (d, ^3J = 7.3 Hz, 1H, H^4), 6.94 (d, ^3J = 7.3 Hz, 2H, H^{Ar}), 7.13 (t, ^3J = 7.3 Hz, 1H, H^{Ar}), 7.21 (t_{app}, ^3J = 7.3 Hz, 2H, H^{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 41.5 (C^1), 42.6 (C^6), 45.5 (NMe_2), 54.8 (OMe), 56.2 (C^5), 59.0 (C^{11}), 85.3 (C^3), 97.2 (C^4), 125.6 (CH^{Ar}), 127.0 (CH^{Ar}), 128.8 (CH^{Ar}), 143.4 (C^2 or C^{Ar}), 147.5 (C^2 or C^{Ar}), 222.9 ($Mn(CO)_3$). IR (neat): 1909 ($Mn(CO)_3$), 2006 ($Mn(CO)_3$). HRMS (MALDI TOF, positive mode): 382.0798 ($M+H^+$, calcd for $C_{19}H_{21}O_4MnN$: 382.0851).

^{13}C NMR spectrum (100 MHz, $CDCl_3$) of complex **4**.



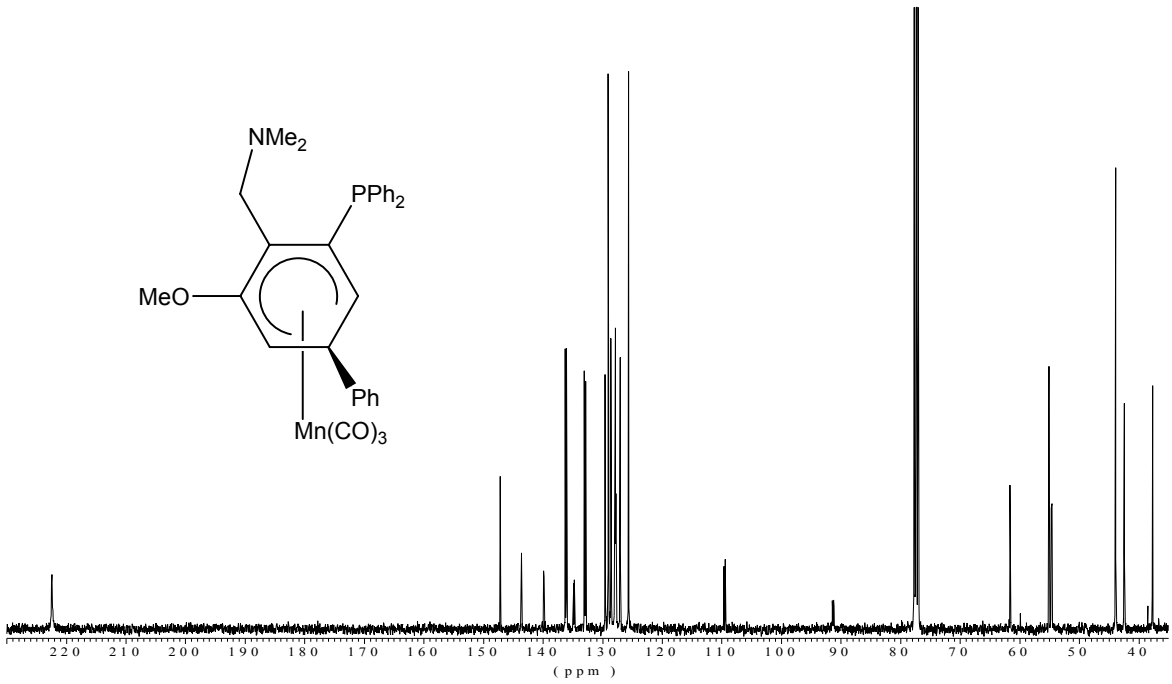
5 (94%). ^1H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, 6H, NMe_2), 3.39 (s, 3H, OMe), 3.49 (d, ^3J = 6.1 Hz, 1H, H^1), 3.59 (d, ^2J = 12.8 Hz, 1H, H^{11}), 3.84 (m, 2H, H^5 and H^6), 4.14 (d, ^2J = 12.8 Hz, 1H, H^{11}), 6.92 (d, ^3J = 7.5 Hz, 2H, H^{Ar}), 7.15 (t, ^3J = 7.3 Hz, 1H, H^{Ar}), 7.23 (t, ^3J = 7.7 Hz, 2H, H^{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.8 (C^1), 45.5 (C^6), 45.6 (NMe_2), 55.3 (OMe), 60.7 (C^{11}), 65.6 (C^5), 78.9 (C^3 or C^4), 88.5 (C^3 or C^4), 125.6 (CH^{Ar}), 127.3 (CH^{Ar}), 128.9 (CH^{Ar}), 139.2 (C^{Ar}), 146.9 (C^2). IR (neat): 1910 ($Mn(CO)_3$), 2022 ($Mn(CO)_3$). HRMS (ESI, positive mode): 507.9812 ($M+H^+$, calcd for $C_{19}H_{20}IMnNO_4$: 507.9818).

^{13}C NMR spectrum (100 MHz, $CDCl_3$) of complex **5**.



6 (76%). ^1H NMR (400 MHz, $CDCl_3$): δ 1.92 (s, 6H, NMe_2), 3.19 (d, ^3J = 6.1 Hz, 1H, H^5), 3.28 (dd, ^3J = 5.0 Hz, ^4J = 1.3 Hz, 1H, H^1), 3.61 (s, 3H, OMe), 3.83 (d, ^2J = 12.7 Hz, 1H, H^{11}), 3.97 (t, ^3J = 6.0 Hz, 1H, H^6), 4.14 (dd, ^2J = 12.7 Hz, J = 4.1 Hz, 1H, H^{11}), 6.81 (t, ^3J = 7.6 Hz, 2H, H^{Ar}), 6.89 (t, ^3J = 7.1 Hz, 2H, H^{Ar}), 6.95 (d, ^3J = 7.2 Hz, 2H, H^{Ar}), 7.10 (t, ^3J = 7.1 Hz, 1H, H^{Ar}), 7.20-7.37 (m, 8H, H^{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.7 (C^1), 42.4 (C^6), 43.9 (NMe_2), 54.6 (d, $^3J^{CP}$ = 13.7 Hz, C^{11}), 55.0 (OMe), 61.5 (d, $^2J^{CP}$ = 5 Hz, C^5), 91.3 (d, J^{CP} = 21 Hz, C^3 or C^4), 109.5 (d, J^{CP} = 23 Hz, C^3 or C^4), 125.6 (CH^{Ar}), 127.0 (CH^{Ar}), 127.7 (d, $^3J^{CP}$ = 8 Hz, CH^{Ar}), 127.9 (CH^{Ar}), 128.6 (d, $^3J^{CP}$ = 12 Hz, CH^{Ar}), 129.0 (CH^{Ar}), 129.5 (CH^{Ar}), 132.9 (d, $^2J^{CP}$ = 16 Hz, CH^{Ar}), 134.8 (C^{Ar}), 136.1 (d, $^2J^{CP}$ = 20 Hz, C^{Ar}), 143.6 (d, $^3J^{CP}$ = 5 Hz, C^2), 147.1 (C^{Ar}), 222.4 ($Mn(CO)_3$). ^{31}P NMR (161 MHz, $CDCl_3$): δ -9.2 (PPh_2). IR (neat): 1925 ($Mn(CO)_3$), 2010 ($Mn(CO)_3$). HRMS (ESI, positive mode): 566.1287 ($M+H^+$, calcd for $C_{31}H_{30}O_4MnNP$: 566.1293).

^{13}C NMR spectrum (100 MHz, $CDCl_3$) of complex **6**.



Preparation of complex 7 ((2)Pd(allyl)Cl). In a glove box, the dimeric complex $[(allyl)PdCl]_2$ (0,20 mmol, 1eq) was introduced in a Schlenck tube. Then, under N_2, complex **2** (0,42 mmol, 2,1 eq) was added. At -78°C, Et_2O (5 mL) was added and the mixture was stirred for 30 minutes at -78°C before warming slowly to room temperature. After concentration *in vacuo*, the crude mixture was washed with pentane and filtered. The palladium complex **7** was isolated in 63% yield as a cream powder.

^1H NMR (400MHz, $CDCl_3$): δ 2.78 (d, J = 12.1 Hz, 1H, allyl), 3.02 (s, 3H, OMe), 3.05 (m, 1H), 3.07 (s, 3H, OMe), 3.16 (m, 1H), 3.35 (m, 1H), 3.47 (m, 2H), 3.56-3.76 (m, 4H), 4.01 (m, 2H), 4.72 (m, 2H), 5.56 (m, 2H), 6.06 (m, 1H), 6.24 (m, 1H), 7.00-7.06 (m, 4H, H^{Ar}), 7.20-7.43 (m, 18H, H^{Ar}), 7.65-7.77 (m, 8H, H^{Ar}). ^{31}P NMR (161 MHz, $CDCl_3$): δ 24.6, 25.4. IR (neat): 1926 ($Mn(CO)_3$), 2015 ($Mn(CO)_3$). HRMS (MALDI TOF, positive mode): 655.0125 ($M\text{-}Cl^-$, calcd for $C_{31}H_{27}MnO_4PPd$: 655.0062).

Resolution procedure of racemic complex (±)-2:

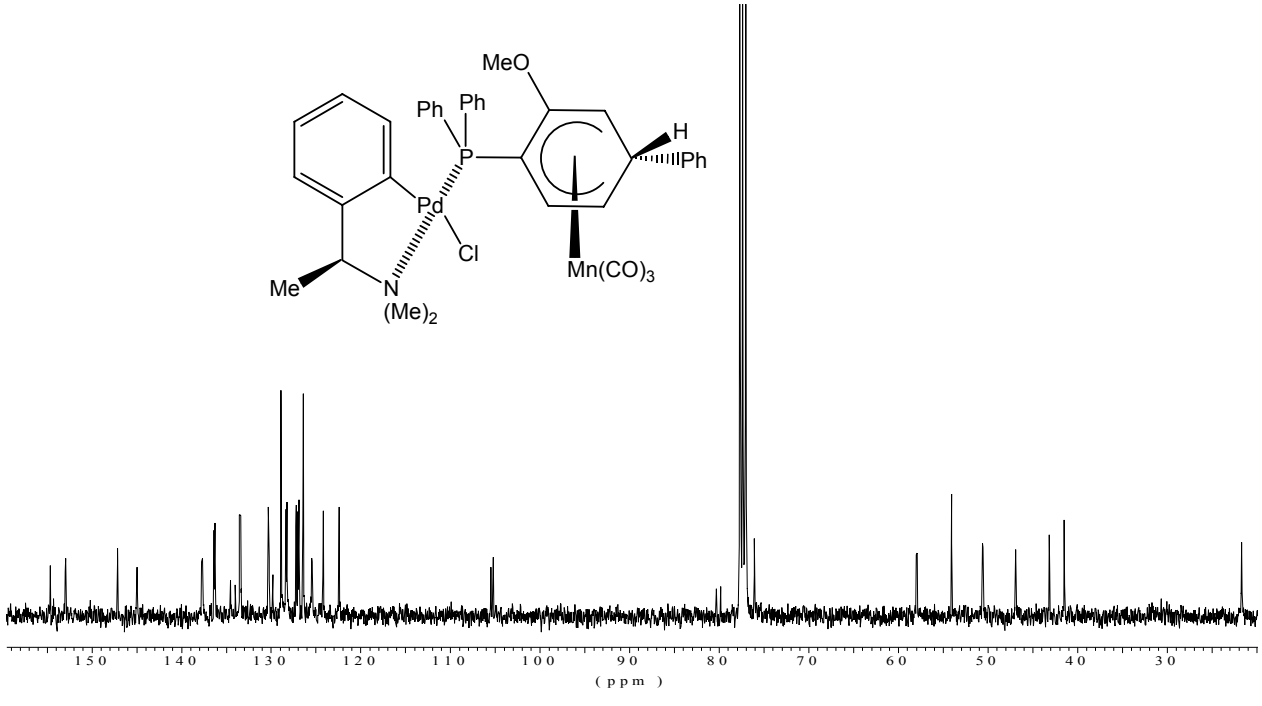
Synthesis and separation of diastereoisomeric complexes (*S,6R,3pR*)-8 and (*S,6S,3pS*)-8:

A mixture of (±)-**2** (0.200 g, 0.4 mmol) and (S)-(+)-di-μ-chlorobis[2-[(dimethylamino)ethyl]phenyl-C^2,N]dipalladium(II) (0.116 g, 0.2 mmol) in toluene (3.0 mL)

was stirred at room temperature for 1h. After concentration *in vacuo*, the crude mixture was purified by flash chromatography on silica gel to separate the diastereoisomeric mixture of (*S,6R,3pR*)-**8** and (*S,6S,3pS*)-**8**.

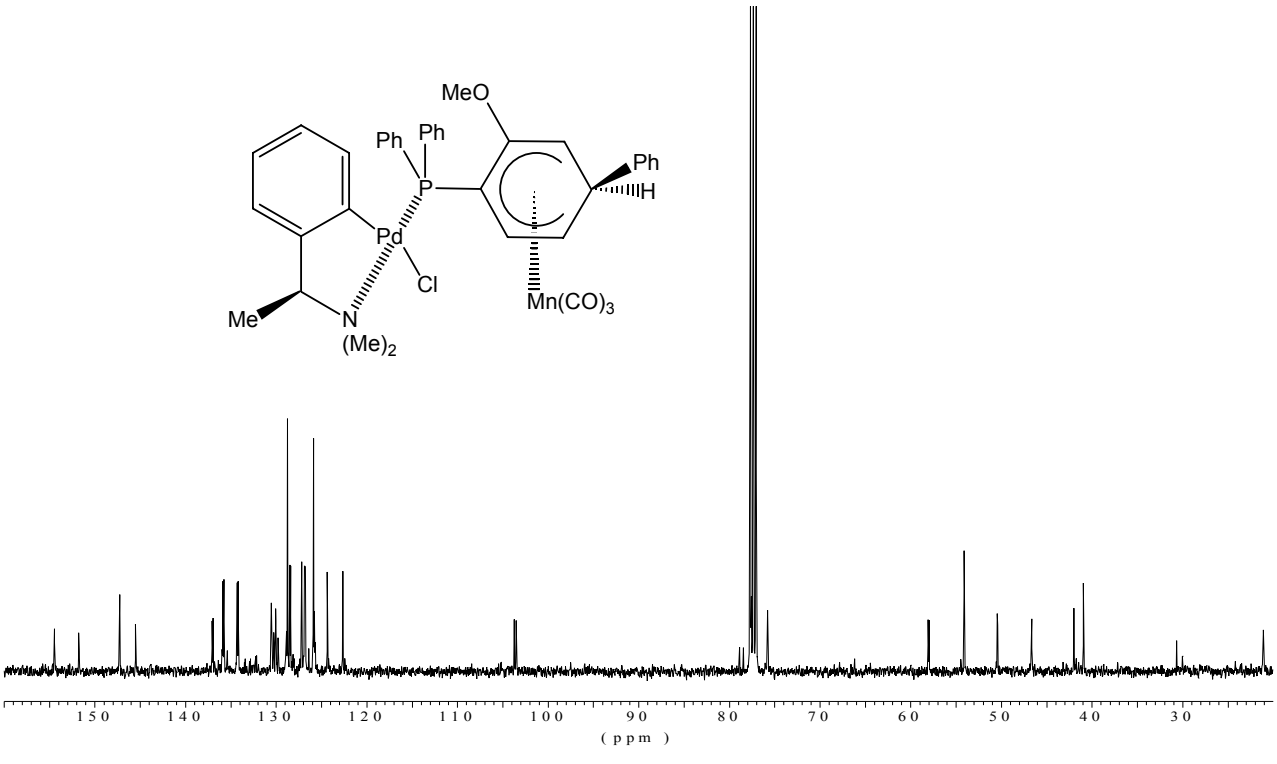
(*S,6R,3pR*)-**8** (34%). de = 95%. R_f = 0.66 (Et_2O). $[\alpha]_D^{20}$ +45 (*c* 0.23, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 1.84 (d, ^3J = 6.6 Hz, 3H, H^{26}), 2.69 (s, 3H, NMe), 2.76 (s, 3H, NMe), 2.89 (s, 3H, OMe), 3.36 (d, ^3J = 6.4 Hz, 1H, H^1), 3.47 (t, ^3J = 7.1 Hz, 1H, H^5), 3.75 (t, ^3J = 5.7 Hz, 1H, H^{25}), 3.95 (t, ^3J = 5.9 Hz, 1H, H^6), 6.39-6.46 (m, 2H, H^{Ar}), 6.52 (t, ^3J = 7.8 Hz, 1H, H^4), 6.84 (t, ^3J = 7.6 Hz, 1H, H^{Ar}), 6.93 (d, ^3J = 7.0 Hz, 1H, H^{Ar}), 7.15-7.43 (m, 11H, H^{Ar}), 7.65 (dd, ^3J = 7.4 Hz, ^3J = 12.0, 2H, H^{Ar}), 7.80 (dd, ^3J = 7.3 Hz, ^3J = 11.9 Hz, 2H, H^{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7 (C^{26}), 41.5 (C^6), 43.1 (C^1), 46.9 (NMe), 50.6 (NMe), 54.0 (OMe), 57.9 (d, $^3J^{CP}$ = 10 Hz, C^5), 76.0 (C^{25}), 80.1 (d, $^1J^{CP}$ = 47 Hz, C^3), 105.3 (d, $^2J^{CP}$ = 22 Hz, C^4), 122.4 (CH^{Ar}), 124.2 (CH^{Ar}), 125.4 (d, $^3J^{CP}$ = 5 Hz, CH^{Ar}), 126.4 (CH^{Ar}), 126.9 (d, $^2J^{CP}$ = 12 Hz, CH^{Ar}), 127.2 (CH^{Ar}), 128.3 (d, $^2J^{CP}$ = 11 Hz, CH^{Ar}), 128.9 (CH^{Ar}), 130.3 (d, $^3J^{CP}$ = 8 Hz, CH^{Ar}), 133.4 (d, $^2J^{CP}$ = 11 Hz, CH^{Ar}), 134.0 (C^{Ar}), 134.5 (C^{Ar}), 136.2 (d, $^2J^{CP}$ = 11 Hz, CH^{Ar}), 137.6 (d, $^3J^{CP}$ = 8 Hz, CH^{Ar}), 144.9 (C^2), 147.1 (C^{Ar}), 152.9 (C^{Ar}), 154.6 (C^{Ar}). ^{31}P NMR (161 MHz, $CDCl_3$): δ 39.0 (PPh_2). IR (neat): 1925 ($Mn(CO)_3$), 2014 ($Mn(CO)_3$). HRMS (ESI, positive mode): 798.0568 ($M+H^+$, Calcd for: $C_{38}H_{37}O_4ClMnNPPd$: 798.0564).

^{13}C NMR spectrum (100 MHz, $CDCl_3$) of complex (*S,6R,3pR*)-**8**.



(*S,6S,3pS*)-**8** (36%). de = 95%. R_f = 0.50 (Et_2O). $[\alpha]_D^{20}$ −50 (*c* 0.21, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.79 (d, ^3J = 6.4 Hz, 3H, H^{26}), 2.72 (s, 6H, NMe_2), 2.99 (s, 3H, OMe), 3.29 (t_{app}, ^3J = 6.5 Hz, H^5), 3.37 (d, ^3J = 5.9 Hz, 1H, H^1), 3.79 (t, ^3J = 5.8 Hz, 1H, H^{25}), 3.93 (t, ^3J = 6.0 Hz, 1H, H^6), 5.91 (t, ^3J = 7.8 Hz, 1H, H^4), 6.46 (t, ^3J = 7.2 Hz, 1H, H^{Ar}), 6.59 (t, ^3J = 6.8Hz, 1H, H^{Ar}), 6.84 (t, ^3J = 7.2 Hz, 1H, H^{Ar}), 6.93 (d, ^3J = 6.8 Hz, 1H, H^{Ar}), 7.08 (d, ^3J = 7.2 Hz, 2H, H^{Ar}), 7.22-7.27 (m, 4H, H^{Ar}), 7.32-7.37 (m, 4H, H^{Ar}), 7.44 (d, ^3J = 6.8 Hz, 1H, H^{Ar}), 7.72 (dd, ^3J = 7.0Hz, ^3J = 11.9 Hz, 2H, H^{Ar}), 7.95 (dd, ^3J = 7.4 Hz, ^3J = 11.5 Hz, 2H, H^{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1 (C^{26}), 40.9 (C^6), 41.9 (C^1), 46.6 (NMe), 50.4 (NMe), 54.0 (OMe), 58.0 (d, $^3J^{CP}$ = 10.3 Hz, C^5), 75.7 (C^{25}), 78.6 (d, $^1J^{CP}$ = 46 Hz, C^3), 103.6 (d, $^2J^{CP}$ = 10.3 Hz, C^4), 122.6 (CH^{Ar}), 124.3 (CH^{Ar}), 125.7 (d, $^3J^{CP}$ = 5.1 Hz, CH^{Ar}), 125.9 (CH^{Ar}), 126.8 (d, $^2J^{CP}$ = 12 Hz, CH^{Ar}), 127.2 (CH^{Ar}), 128.4 (d, $^2J^{CP}$ = 10.3 Hz, CH^{Ar}), 128.7 (CH^{Ar}), 128.9 (d, $^3J^{CP}$ = 5.1 Hz, CH^{Ar}), 129.9 (d, $^3J^{CP}$ = 2.6 Hz, CH^{Ar}), 130.4 (d, $^3J^{CP}$ = 2.6 Hz, CH^{Ar}), 134.2 (d, $^2J^{CP}$ = 12 Hz, CH^{Ar}), 135.8 (d, $^2J^{CP}$ = 12 Hz, CH^{Ar}), 137.0 (d, $^2J^{CP}$ = 10.3, CH^{Ar}), 145.5 (C^2), 147.2 (C^{Ar}), 151.7 (C^{Ar}), 154.4 (C^{Ar}). ^{31}P NMR (161 MHz, $CDCl_3$): δ 39.0 (PPh_2). IR (neat): 1920 ($Mn(CO)_3$), 2011 ($Mn(CO)_3$). HRMS (ESI, positive mode): 798.0596 ($M+H^+$, Calcd for: $C_{38}H_{37}O_4ClMnNPPd$: 798.0564).

^{13}C NMR spectrum (100 MHz, $CDCl_3$) of complex (*S,6S,3pS*)-**8**.



Decomplexation of (*S,6S,3pS*)-8 and (*S,6R,3pR*)-8:

To an individual diastereoisomer (*S,6S,3pS*)-**8** and (*S,6R,3pR*)-**8** (0.1 mmol) was added a 0.1 M solution of ethylenediamine in chloroform (2 mL, 0.2 mmol) at room temperatue and the mixture was stirred for 10 min. After concentration *in vacuo*, the crude mixture was purified by flash chromatography on silica gel to afford the enantiopure (6*S,*3*pS*)-**2** or (6*R,*3*pR*)-**2**.

(6*S,*3*pS*)-**2** (77%). $[\alpha]_D^{20}$ = +57 (c 0.21, $CHCl_3$)

(6*R,*3*pR*)-**2** (84%). $[\alpha]_D^{20}$ = -58 (c 0.21, $CHCl_3$)