

Electronic Supplementary Information

Efficient Hydrogenation of Ketones over Diaminophosphino Manganese Complex

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I. General information

Unless otherwise specified, all operations were conducted under a dry Ar or N₂ atmosphere by using glovebox techniques and standard Schlenk manipulations. Organic solvents including toluene, *n*-hexane and tetrahydrofuran (THF) were dried by refluxing with sodium/potassium benzophenone under N₂ prior to use. Ethanol, methanol, isopropanol, *n*-propanol and CH₂Cl₂ were distilled from CaH₂ and kept in the glovebox for use. Aminophosphine ligands were synthesized according to the procedure reported in the literatures^[1-2]. ¹H (400 MHz), ¹³C{¹H} (100 MHz), and ³¹P{¹H} (160 MHz) NMR spectra were measured on a Bruker AVIII-400 spectrometer. Infrared (IR) spectra were recorded using a Nicolet FT-IR 330 spectrometer. Elemental analysis was performed on a Thermo Quest Italia SPA EA 1110 instrument. HRMS (ESI) were measured on a Thermo scientific Q EXACTIVE mass spectrometry system. Crystallographic data for complex **1** was collected at 150 K on a STOE STADIVARI detector. EPR spectra were measured on CIQTEK EPR200M with continues-wave X band frequency.

II. General procedure for the catalytic hydrogenation

In the glovebox, the ketone substrate, manganese complex, KOMe, ethanol solvent, and dodecane (internal standard) were measured into a 25 mL quartz-lined stainless-steel autoclave (Anhui Kemi Machinery Technology Co., Ltd). After transferring the autoclave out of the glovebox, it was carefully pressurized and vented with hydrogen (5 bar) three times. Then, it was pressurized with hydrogen (20 bar) and heated at 100 °C for 6 hours. Afterwards, the autoclave was cooled to approximately 5 °C using an ice bath and slowly depressurized. The reaction solution was passed through a short silica column and then analyzed by gas chromatography (GC, SHANGHAI INSTRUMENT, 9310-VI) equipped with a KB-Wax column (30 m × 0.32 mm × 0.33 μm) and a flame ionization detector (FID), N₂ as carrier gas (0.7 bar). The injector and detector temperature were 200 °C and 250 °C, respectively. Program used: 80 °C for 5 minutes and then ramped to 200 °C at 10 °C/min, and maintained for 10 minutes. The conversion of ketone substrates and the yield of alcohols were calculated using dodecane as the internal standard.

III. Synthetic details

Synthesis of manganese complex 1

In the glovebox, 0.14 g of $\text{Mn}(\text{CO})_5\text{Br}$ (0.5 mmol) and 0.30 g of ethylidene-bridged PNNP ligand (0.5 mmol) were weighed into a 100 mL Schlenk flask containing approximately 40 mL of toluene. The flask was heated at 80 °C for 1 day under an inert atmosphere, during which a yellow precipitate gradually formed. After the reaction was complete and the flask was cooled to room temperature, the yellow solid of complex 1 was collected by filtration, washed with *n*-hexane (3×2 mL), and dried *in vacuo*. Yield: 0.33 g, 83%.

^1H NMR (400 MHz, CD_2Cl_2 , 298 K, ppm): δ = 2.01 (t, $^2J_{\text{HH}}=9.8$ Hz, 2 H), 2.55 (br, 2 H), 3.38 (br, 2 H), 4.11 (d, $^2J_{\text{HH}}=14.6$ Hz, 2 H), 4.54 (d, $^2J_{\text{HH}}=14.9$ Hz, 2 H), 7.31 (br), 7.36-7.45 (m), 7.52 (d, $^2J_{\text{HH}}=7.3$ Hz), 7.56 (d, $^2J_{\text{HH}}=7.9$ Hz), 7.63 (d, $^2J_{\text{HH}}=5.2$ Hz), 7.72 (d, $^2J_{\text{HH}}=7.4$ Hz) (28 H, C_6H_4 and *Ph*).

$^{31}\text{P}\{^1\text{H}\}$ NMR (160 MHz, CD_2Cl_2 , 298 K, ppm): δ = 59.76 (br).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2 , 298 K, ppm): δ = 50.70 (s, CH_2), 56.31 (s, CH_2), 125.35 (t, $J_{\text{PC}} = 9.5$ Hz), 128.89 (s), 129.25 (s), 130.04 (t, $J_{\text{PC}} = 9.0$ Hz), 130.56 (s), 131.11 (s), 131.89 (s), 132.51 (br), 132.66 (s), 133.38 (s), 135.29 (t, $J_{\text{PC}} = 16.7$ Hz), 136.40 (s), 140.58 (br) (C_6H_4 and *Ph*), 225.60 (br) (CO).

IR (Nujol mull, KBr, cm^{-1}): ν = 1935, 1860.

Anal. Calcd (%) for $\text{MnC}_{42}\text{H}_{38}\text{N}_2\text{P}_2\text{O}_2\text{Br}$ ($M_r = 799.6$): C 63.09, N 3.50, H 4.79; found: C 63.15, N 3.46, H 4.83.

HRMS (ESI) calcd for $\text{MnC}_{42}\text{H}_{38}\text{N}_2\text{P}_2\text{O}_2^+$: 719.1789, found 719.1823.

Synthesis of manganese complex **2**

In the glovebox, 0.14 g of $\text{Mn}(\text{CO})_5\text{Br}$ (0.5 mmol) and 0.33 g of cyclohexylidene-bridged PNNP ligand (0.5 mmol) were weighed into a 100 mL Schlenk flask containing approximately 40 mL of toluene. The flask was heated at 80 °C for 1 day under an inert atmosphere, during which a yellow precipitate gradually formed. After the reaction was complete and the flask was cooled to room temperature, the light-yellow solid of complex **2** was collected by filtration, washed with *n*-hexane (3 × 2 mL), and dried *in vacuo*. Yield: 0.37 g, 87%.

^1H NMR (400 MHz, CD_2Cl_2 , 298 K, ppm): δ = -0.25 (br, 2 H), 0.56 (br, 2 H), 1.46 (br, 2 H), 1.56 (br, 2 H), 1.86 (br, 2 H), 2.37 (br, 2 H), 4.00 (br, 2 H), 4.53 (br, 2 H), 7.12-7.18 (m), 7.24 (t, $^2J_{\text{HH}} = 1.4$ Hz), 7.40 (br), 7.43 (br), 7.54 (br), 7.75 (br) (28 H, C_6H_4 and *Ph*).

$^{31}\text{P}\{^1\text{H}\}$ NMR (160 MHz, CD_2Cl_2 , 298 K, ppm): δ = 62.14 (br).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2 , 298 K, ppm): δ = 13.88 (s), 23.93 (s), 30.83 (s), 60.67 (s) (CH and CH_2), 125.56 (t, $J_{\text{PC}} = 14.0$ Hz), 128.92 (t, $J_{\text{PC}} = 4.0$ Hz), 129.68 (s), 130.11 (t, $J_{\text{PC}} = 13.8$ Hz), 130.70 (s), 131.36 (s), 132.42 (t, $J_{\text{PC}} = 9.4$ Hz), 132.62 (s), 133.20 (s), 133.41 (s), 134.60 (t, $J_{\text{PC}} = 19.5$ Hz), 136.57 (s), 139.18 (t, $J_{\text{PC}} = 7.5$ Hz) (C_6H_4 and *Ph*), 226.54 (br) (CO).
IR (Nujol mull, KBr, cm^{-1}): ν = 1935, 1860.

Anal. Calcd (%) for $\text{MnC}_{46}\text{H}_{44}\text{N}_2\text{P}_2\text{O}_2\text{Br}$ ($M_r = 853.6$): C 64.72, N 3.28, H 5.20; found: C 64.86, N 3.34, H 5.08.

HRMS (ESI) calcd for $\text{MnC}_{46}\text{H}_{44}\text{N}_2\text{P}_2\text{O}_2^+$: 773.2259, found 773.2230.

Synthesis of manganese complex **3**

In the glovebox, 0.14 g of $\text{Mn}(\text{CO})_5\text{Br}$ (0.5 mmol) and 0.29 g of *o*- $\text{PPh}_2\text{C}_6\text{H}_4\text{CH}_2\text{NH}_2$ ligand (1.0 mmol) were weighed into a 100 mL Schlenk flask containing approximately 40 mL of toluene. The flask was heated at 80 °C for 1 day under an inert atmosphere, during which a yellow precipitate gradually formed. After the reaction was complete and the flask was cooled to room temperature, the yellow solid of complex **3** was collected by filtration, washed with *n*-hexane (3×2 mL), and dried *in vacuo*. Yield: 0.33 g, 86%.

^1H NMR (400 MHz, CD_2Cl_2 , 298 K, ppm): δ = 1.80 (br, 2 H), 3.63 (br, 2 H), 4.11 (br, 2 H), 4.84 (br, 2 H), 7.04 (br), 7.17 (br), 7.24 (br), 7.36 (br), 7.48 (br), 7.54 (br), 7.65 (br) (28 H, C_6H_4 and *Ph*).

$^{31}\text{P}\{^1\text{H}\}$ NMR (160 MHz, CD_2Cl_2 , 298 K, ppm): δ = 59.47 (br).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2 , 298 K, ppm): δ = 50.07 (t, J_{PC} = 6.0 Hz, CH_2), 128.03 (t, J_{PC} = 14.3 Hz), 129.02 (t, J_{PC} = 4.9 Hz), 129.18 (s), 130.07 (t, J_{PC} = 4.0 Hz), 130.30 (d, J_{PC} = 13.3 Hz), 130.87 (d, J_{PC} = 15.4 Hz), 131.43 (t, J_{PC} = 3.1 Hz), 131.81 (s), 133.07 (t, J_{PC} = 4.5 Hz), 133.77 (d, J_{PC} = 23.7 Hz), 134.03 (t, J_{PC} = 4.4 Hz), 134.21 (s), 143.39 (t, J_{PC} = 7.9 Hz) (C_6H_4 and *Ph*), CO not observed.

IR (Nujol mull, KBr, cm^{-1}): ν = 1932, 1857.

Anal. Calcd (%) for $\text{MnC}_{40}\text{H}_{36}\text{N}_2\text{P}_2\text{O}_2\text{Br}$ (M_r = 773.5): C 62.11, N 3.62, H 4.69; found: C 62.33, N 3.69, H 4.53.

HRMS (ESI) calcd for $\text{MnC}_{40}\text{H}_{36}\text{N}_2\text{P}_2\text{O}_2^+$: 693.1633, found 693.1636.

IV. X-ray crystallographic analysis

X-ray crystallographic analysis of complex 1: Crystallographic data for **1** was collected at 150 K on an Agilent Super Nova system using graphite-monochromated Cu- K_{α} radiation ($\lambda = 1.54186 \text{ \AA}$). Intensity measurements were performed on a rapidly cooled crystal with dimensions of $0.15 \times 0.1 \times 0.08 \text{ mm}^3$ in the range $7.218^{\circ} < 2\theta < 125^{\circ}$. The data completeness collected was 98.8%. Absorption correction was applied using the spherical harmonic program (multi-scan type). The structure was solved by direct method (SHELXS-96)^[3] and refined against F^2 using SHELXL-97 program^[4]. In general, non-hydrogen atoms were located from different Fourier synthesis and refined anisotropically, and hydrogen atoms were included using a riding mode with U_{iso} tied to the U_{iso} of the parent atom unless otherwise specified. Crystal data for **1**: $\text{C}_{42}\text{H}_{38}\text{BrMnN}_2\text{O}_2\text{P}_2$, $M_r = 799.53$, triclinic, space group $P-1$, $a = 11.757(2)$, $b = 17.831(3)$, $c = 18.477(3) \text{ \AA}$, $\alpha = 92.962(11)^{\circ}$, $\beta = 105.097(13)^{\circ}$, $\gamma = 90.746(13)^{\circ}$, $V = 3733.4(10) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.422 \text{ g}\cdot\text{cm}^{-3}$, $\mu(\text{Cu}_{K\alpha}) = 5.241 \text{ mm}^{-1}$, $F(000) = 1640$; 228733 measured reflections, 11783 independent ($R_{\text{int}} = 0.0812$). The final refinements converged at $R_1 = 0.0756$ and $wR_2 = 0.1906$ for $I > 2\sigma(I)$ and $R_1 = 0.1294$ and $wR_2 = 0.2572$ for all data. The goodness of fit (GOF) is 1.037. Fourier synthesis gave a min/max residual electron density $1.44/-0.80 \text{ e \AA}^{-3}$. CCDC-2375965 contains the supplementary crystallographic data. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

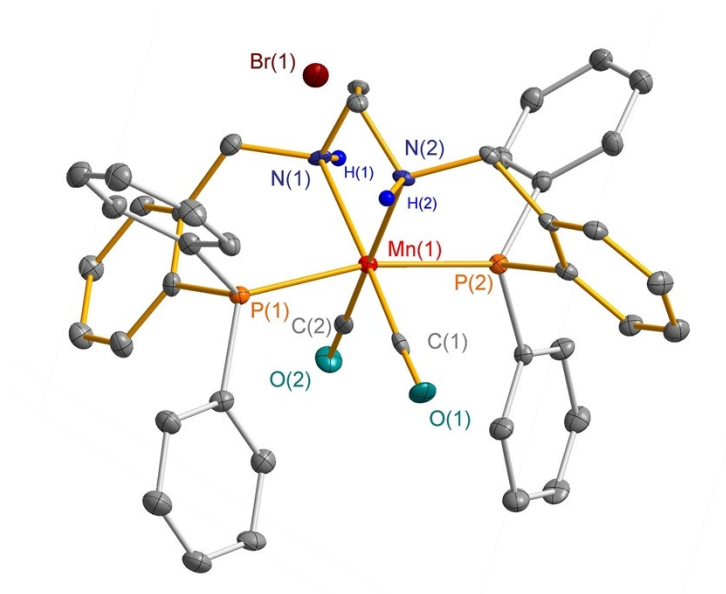


Figure S1 X-ray crystal structure of **1** with thermal ellipsoids at 30% probability level. Hydrogen atoms except H(1) and H(2) are omitted for clarity. Selected bond lengths [Å] and angles [°] for **1**: Mn(1)-P(1) 2.308(2), Mn(1)-P(2) 2.323(2), Mn(1)-N(1) 2.160(6), Mn(1)-N(2) 2.144(6), Mn(1)-C(1) 1.774(9), Mn(1)-C(2) 1.793(10), P(1)-Mn(1)-P(2) 166.96(9), N(1)-Mn(1)-N(2) 81.6(2), P(1)-Mn(1)-N(1) 88.63(18), N(2)-Mn(1)-P(1) 101.37(19), N(2)-Mn(1)-P(2) 89.01(19), C(2)-Mn(1)-P(1) 86.4(2), C(2)-Mn(1)-P(2) 85.6(3), C(2)-Mn(1)-N(1) 169.4(3), C(2)-Mn(1)-N(2) 90.0(3), C(1)-Mn(1)-P(1) 84.7(3), C(1)-Mn(1)-P(2) 86.1(3), C(1)-Mn(1)-N(1) 168.9(3), C(1)-Mn(1)-N(2) 89.9(3), C(1)-Mn(1)-C(2) 97.4(4).

V. Activity tests

Table S1 Hydrogenation of acetophenone into 1-phenylethanol by **1** and base.

Entry	Base	Conv. / %	Yield / %
1	NaOMe	78	78
2	KOMe	99	99
3	NaOEt	83	83
4	KOEt	90	90
5	<i>t</i> -BuONa	70	70
6	<i>t</i> -BuOK	85	85
7	KH	71	71

Reaction conditions: 2.0 mmol acetophenone (1.0 mmol/mL EtOH solution), 0.1 mol% **1**, 10.0 mol% base, 20 bar H₂, 100 °C, 6 h. The conversion of acetophenone and the yield of 1-phenylethanol were analyzed by GC.

Table S2 Hydrogenation of acetophenone into 1-phenylethanol by **1** in different solvent.

Entry	Solvent	Conv. / %	Yield / %
1	MeOH	13	13
2	EtOH	99	99
3	<i>n</i> -PrOH	68	68
4	<i>i</i> -PrOH	94	94
5	THF	9	9
6	2-Me-THF	5	5
7	Toluene	10	10
8	CH ₂ Cl ₂	1	1

Reaction conditions: 2.0 mmol acetophenone, 2 mL solvent, 0.1 mol% **1**, 10.0 mol% KOMe, 20 bar H₂, 100 °C, 6 h. The conversion of acetophenone and the yield of 1-phenylethanol were analyzed by GC.

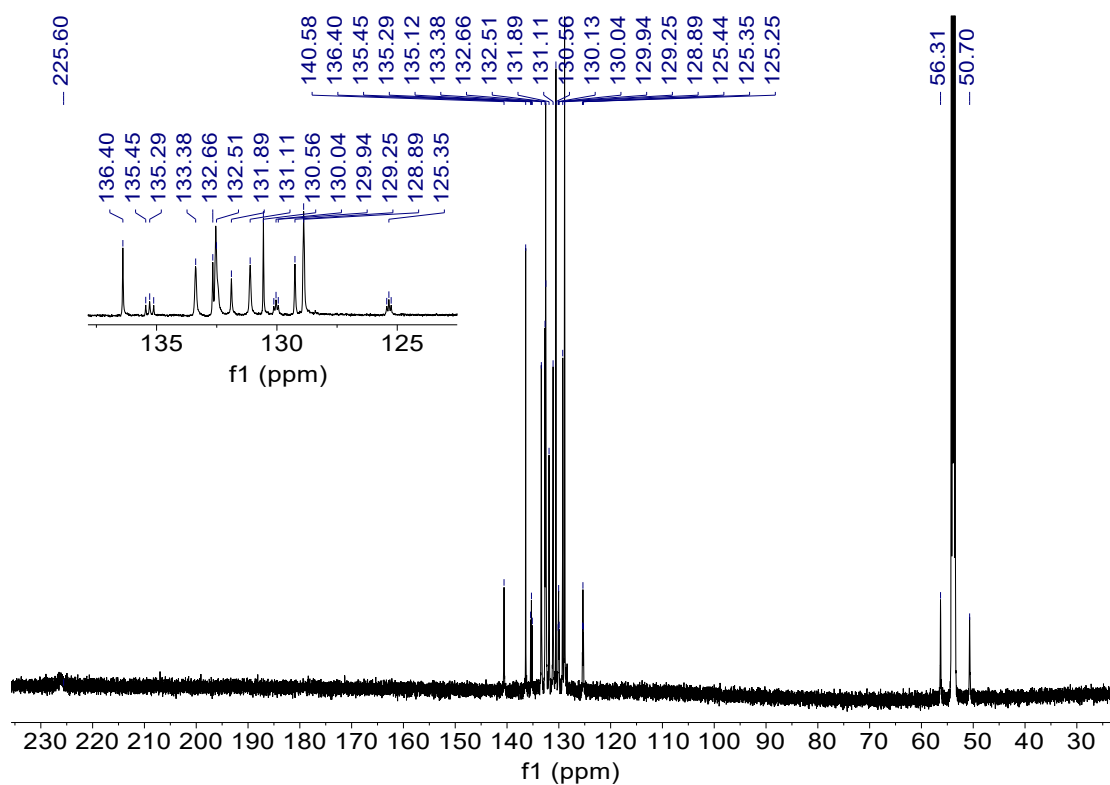


Figure S4 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** measured in CD_2Cl_2 .

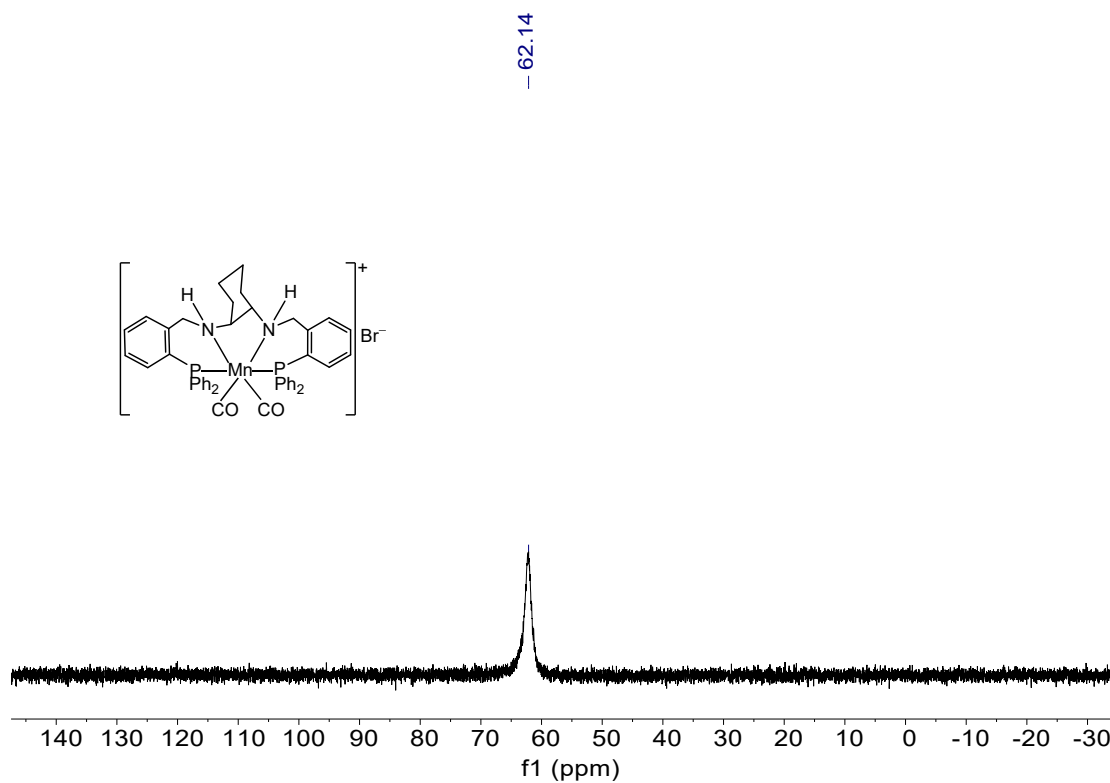


Figure S5 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** measured in CD_2Cl_2 .

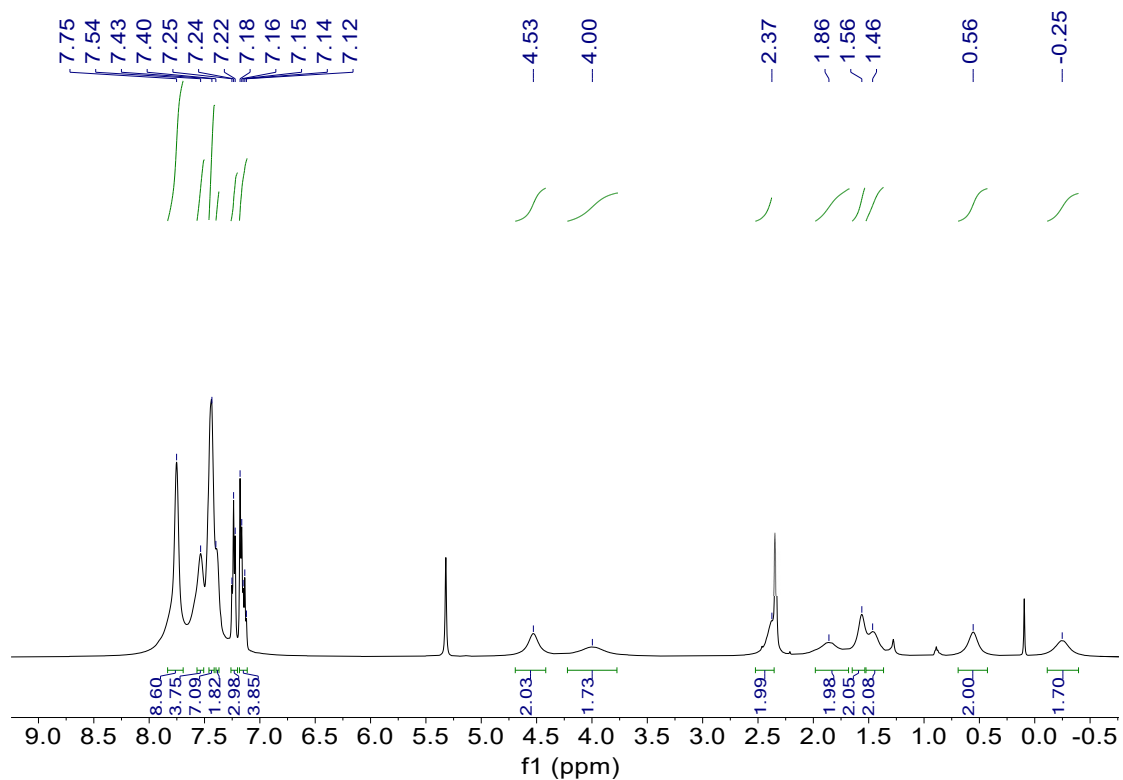


Figure S6 ^1H NMR spectrum of **2** measured in CD_2Cl_2 .

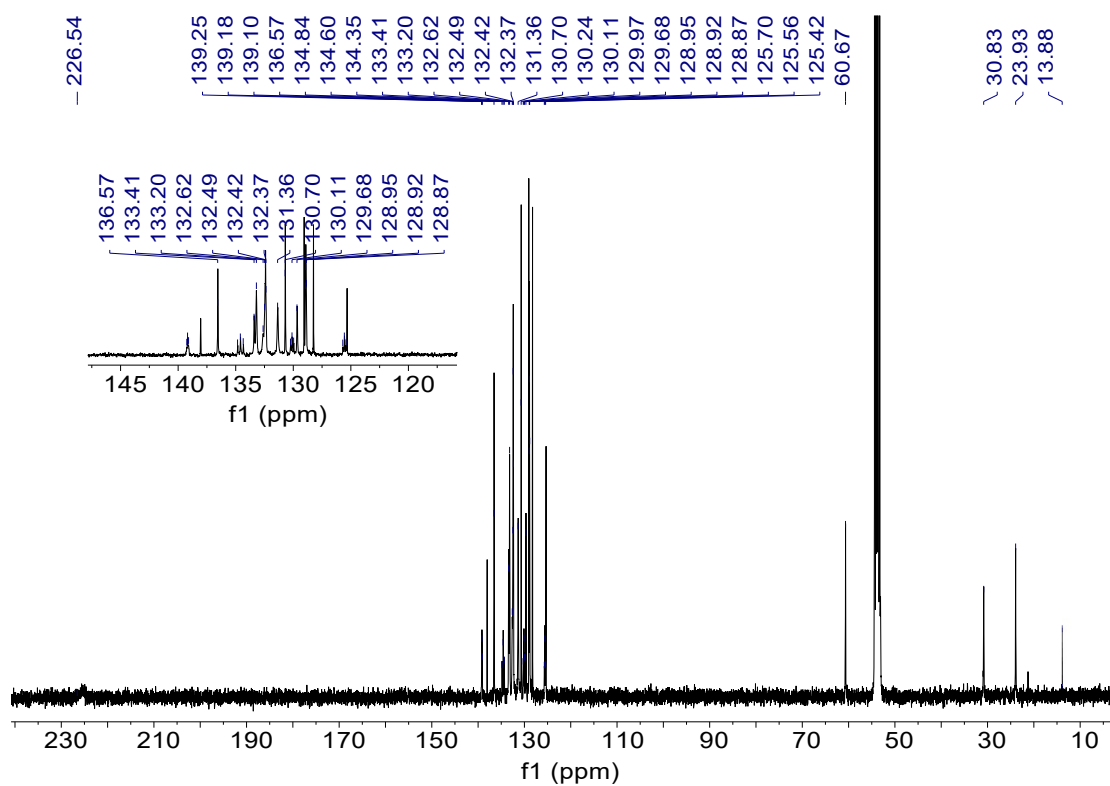


Figure S7 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2** measured in CD_2Cl_2 .

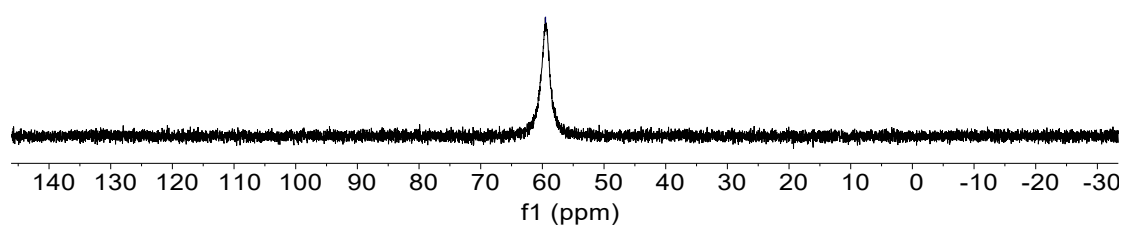
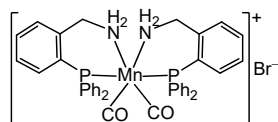


Figure S8 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3** measured in CD_2Cl_2 .

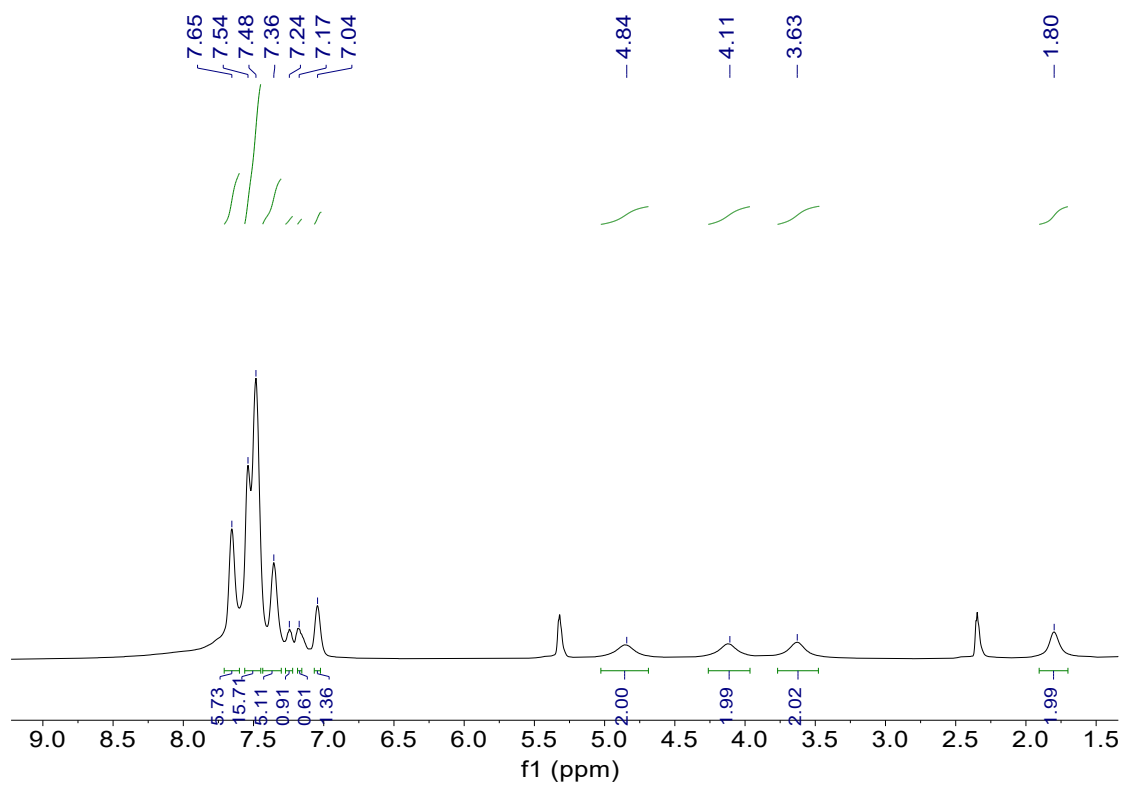


Figure S9 ^1H NMR spectrum of **3** measured in CD_2Cl_2 .

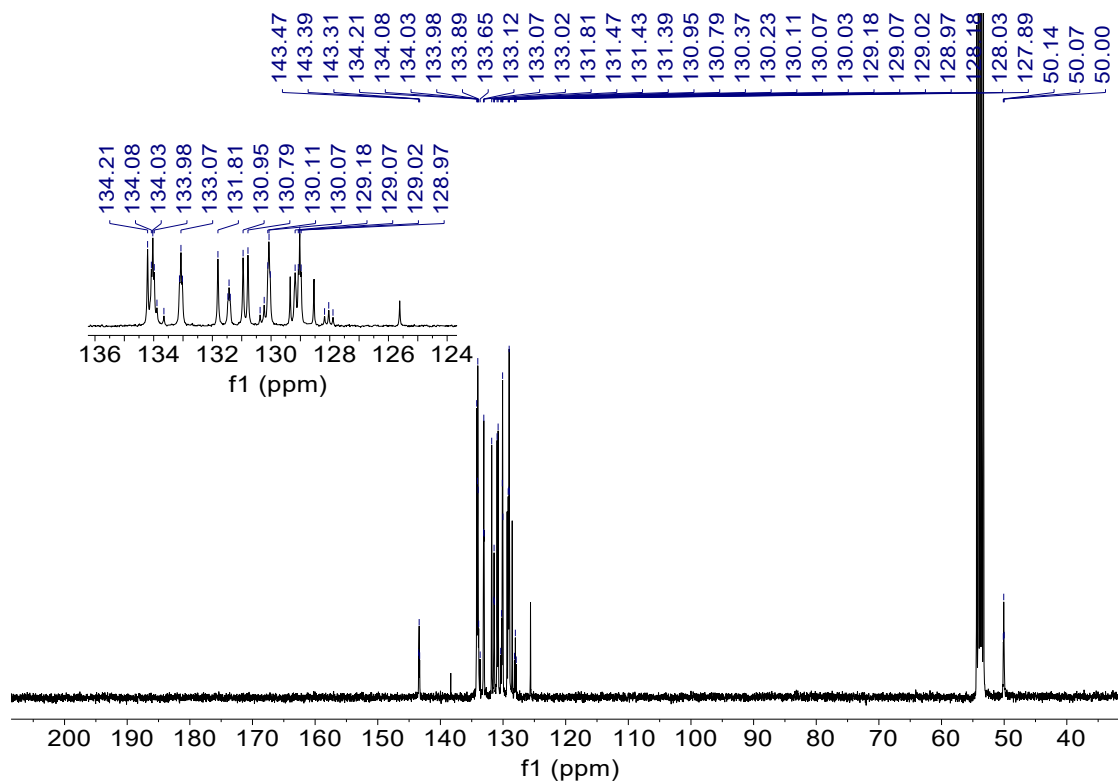


Figure S10 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3** measured in CD_2Cl_2 .

VII. IR Spectra

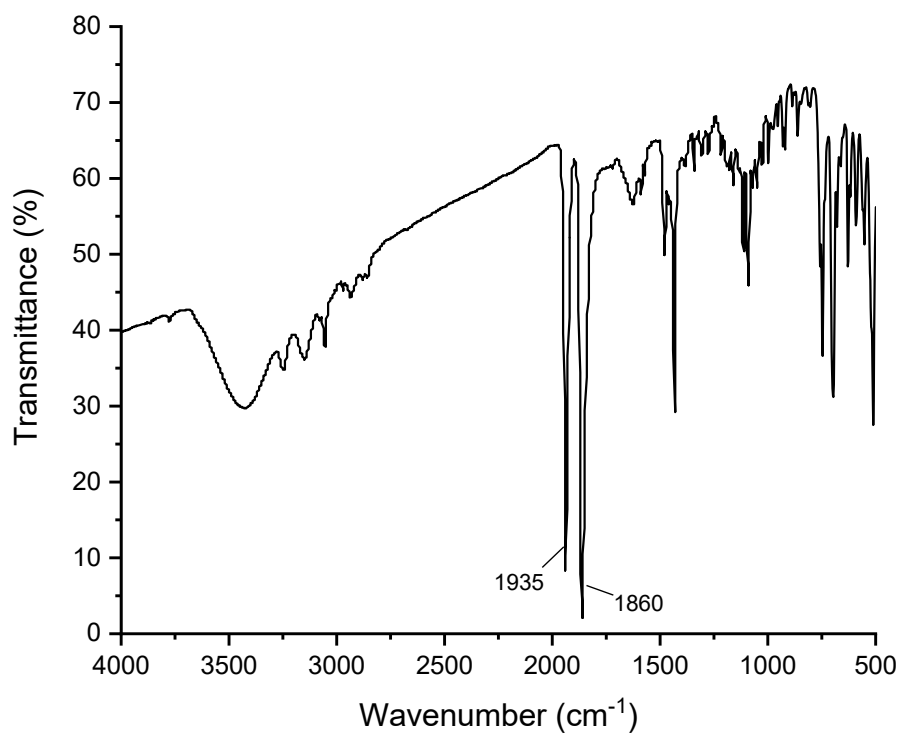


Figure S11 IR spectrum of complex 1.

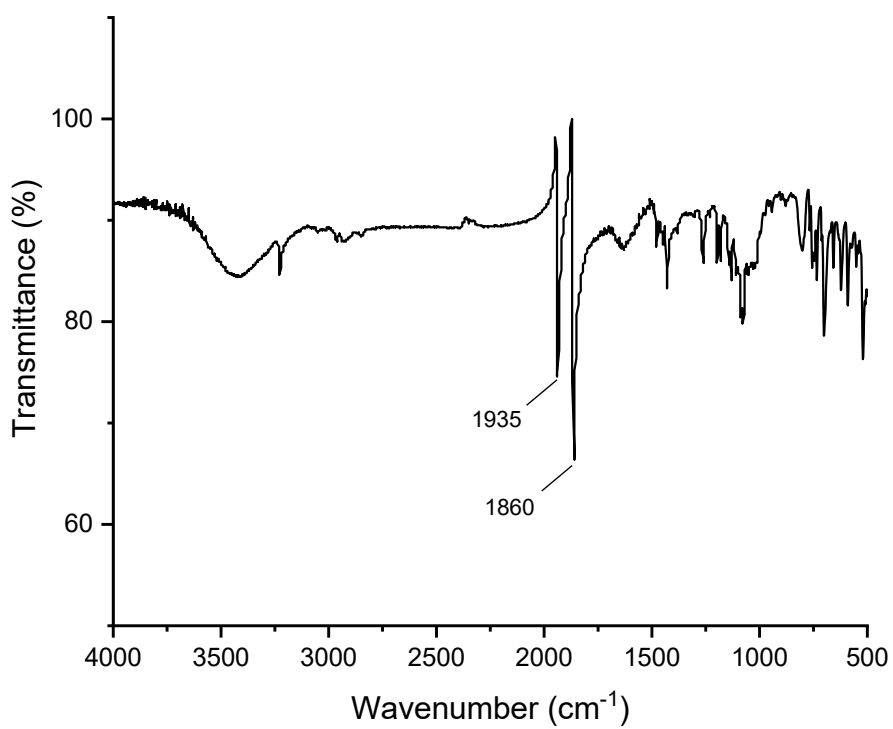


Figure S12 IR spectrum of complex 2.

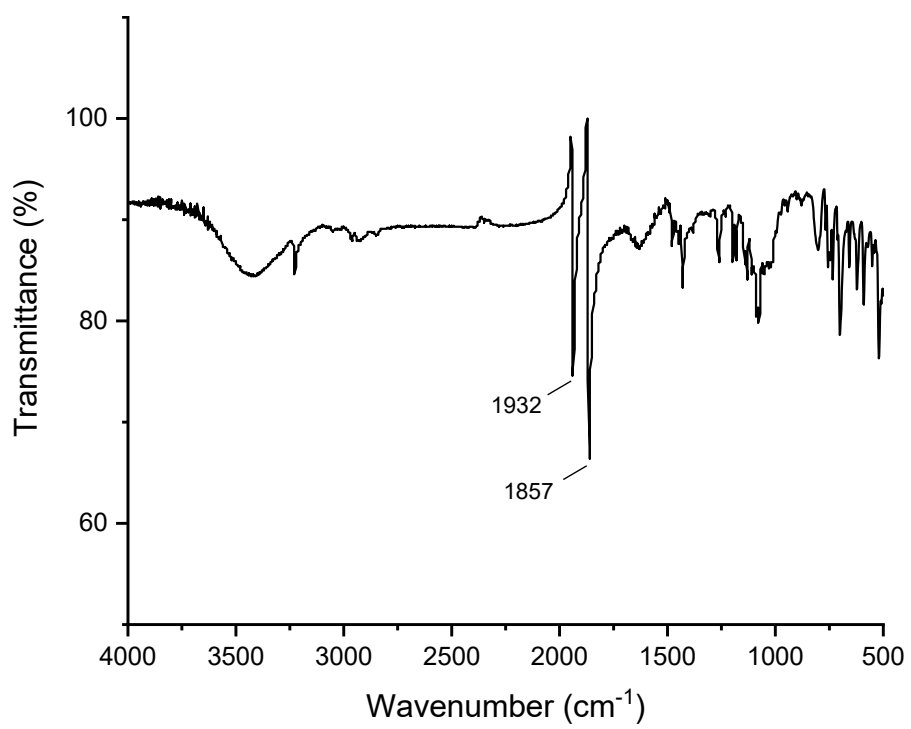


Figure S13 IR spectrum of complex 3.

VIII. EPR Spectra

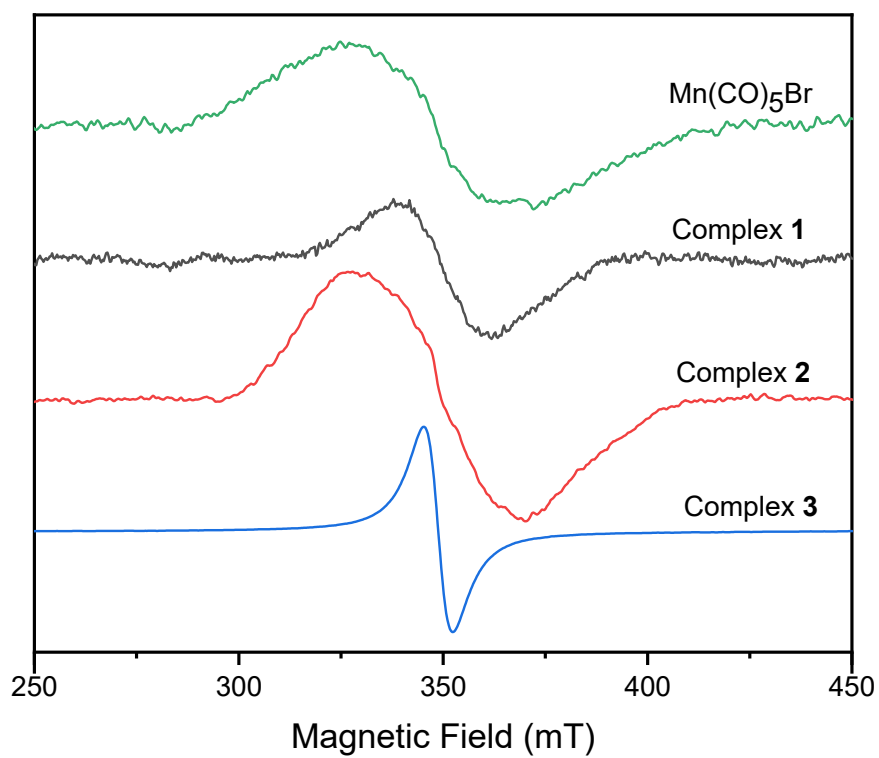


Figure S14 EPR spectra of Mn(CO)₅Br and manganese complexes 1-3.

IX. GC for Hydrogenation Products

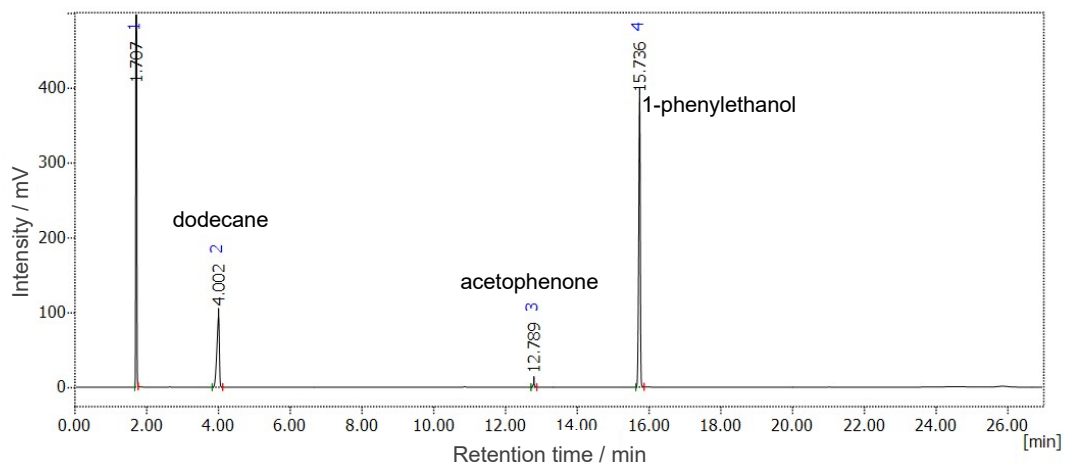


Figure S15 GC analysis result for catalytic hydrogenation of acetophenone by **1** (Entry 1, Table 1).

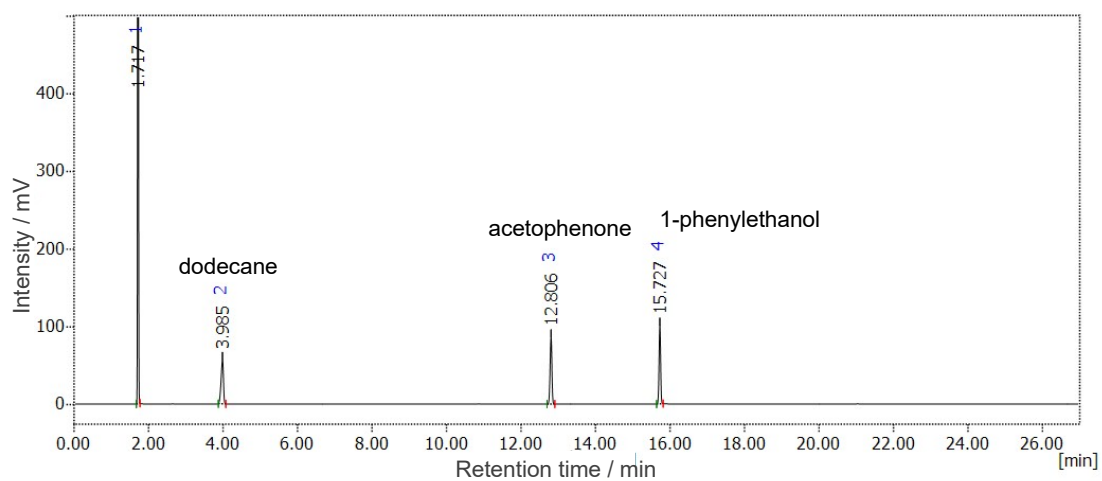


Figure S16 GC analysis result for catalytic hydrogenation of acetophenone by **2** (Entry 2, Table 1).

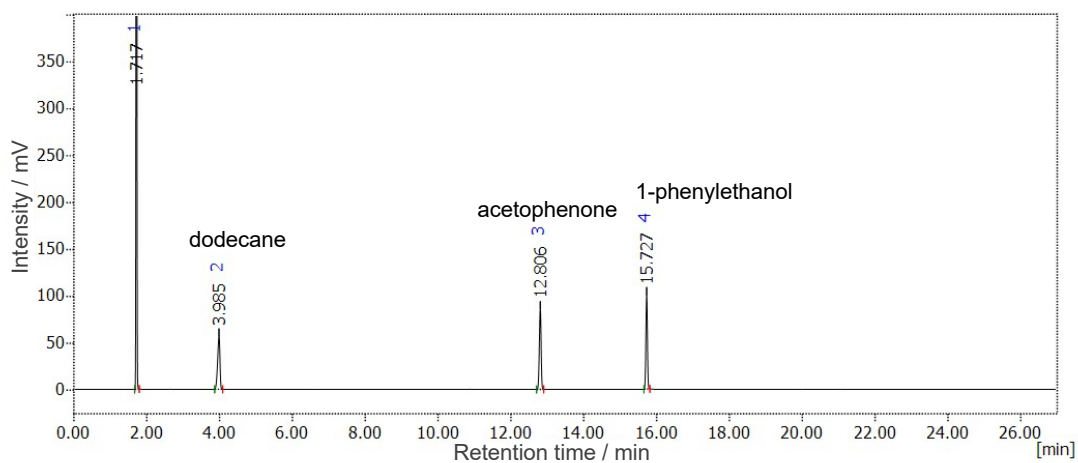


Figure S17 GC analysis result for catalytic hydrogenation of acetophenone by **3** (Entry 3, Table 1).

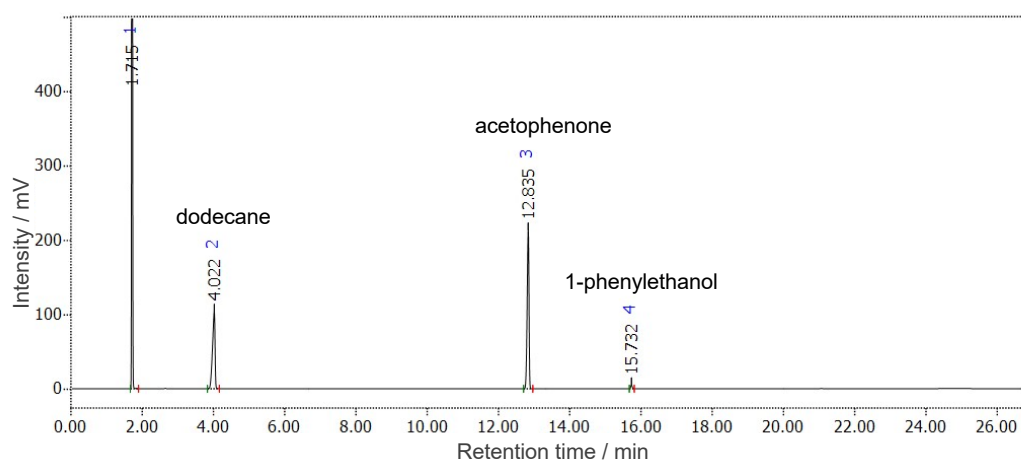


Figure S18 GC analysis result for catalytic hydrogenation of acetophenone by $\text{Mn}(\text{CO})_5\text{Br}$ (Entry 4, Table 1).

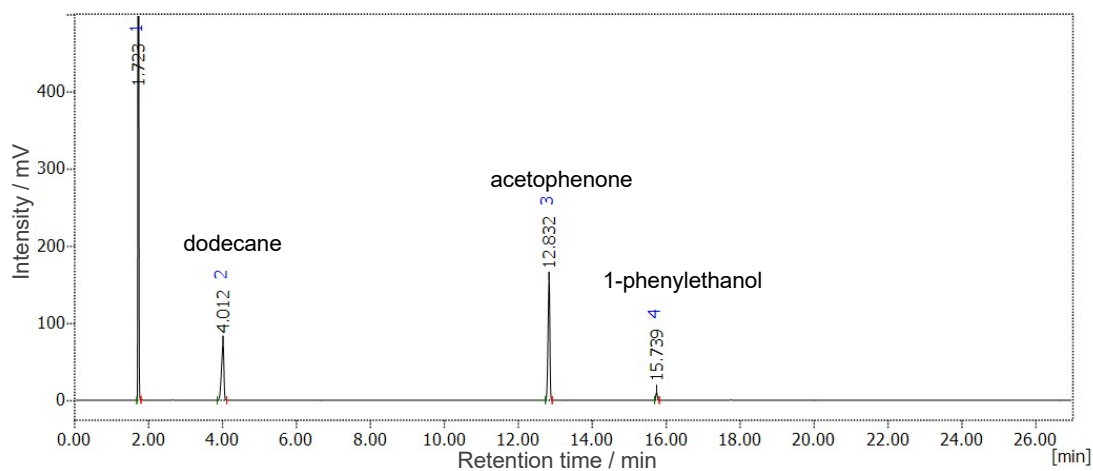


Figure S19 GC analysis result for catalytic hydrogenation of acetophenone by **1** (Entry 6, Table 1).

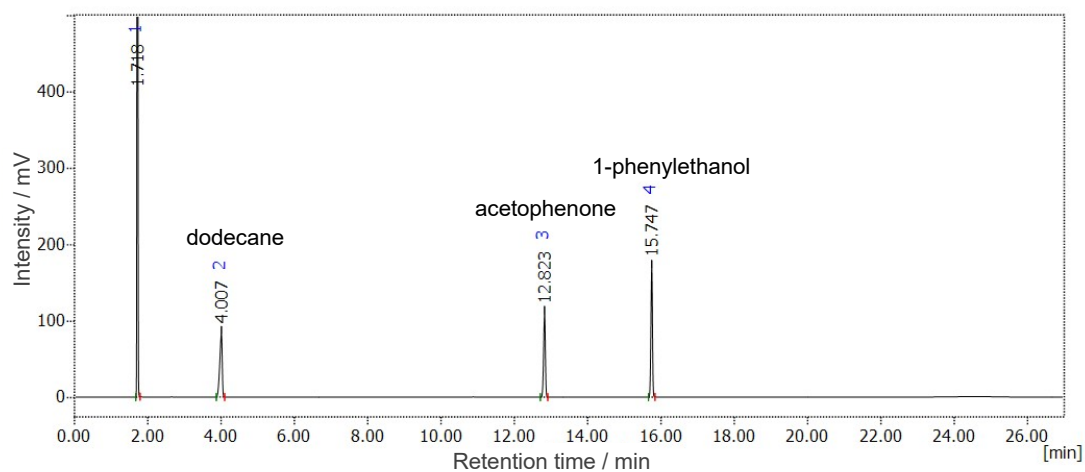


Figure S20 GC analysis result for catalytic hydrogenation of acetophenone by **1** (Entry 7, Table 1).

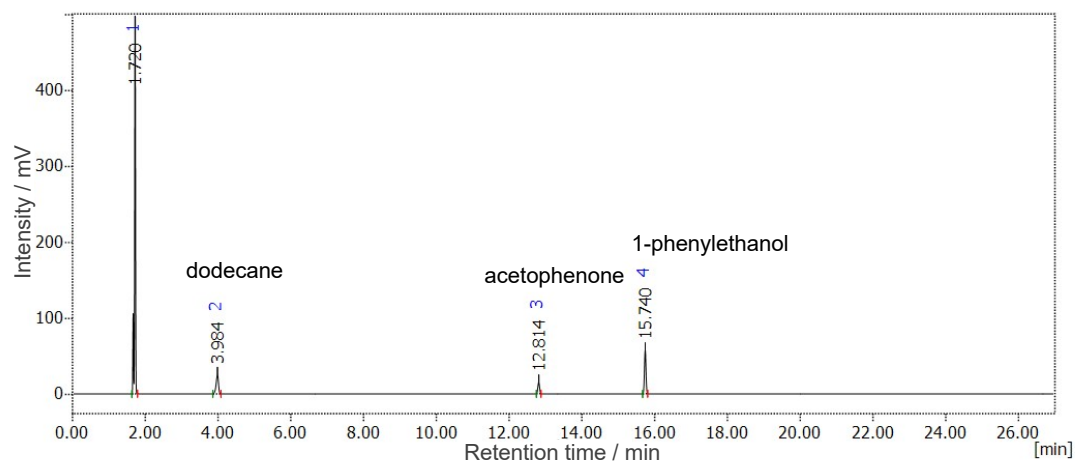


Figure S21 GC analysis result for catalytic hydrogenation of acetophenone by **1** (Entry 8, Table 1).

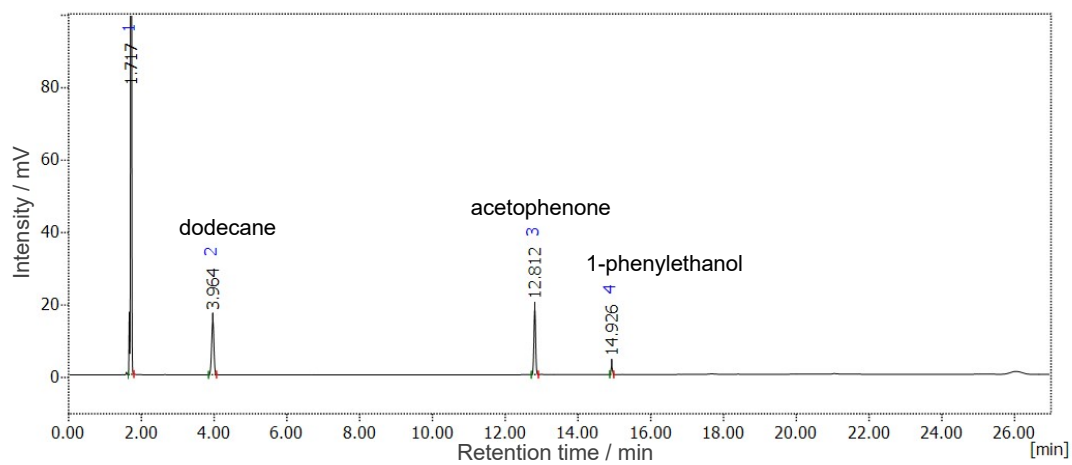


Figure S22 GC analysis result for catalytic hydrogenation of acetophenone by **1** (Entry 9, Table 1).

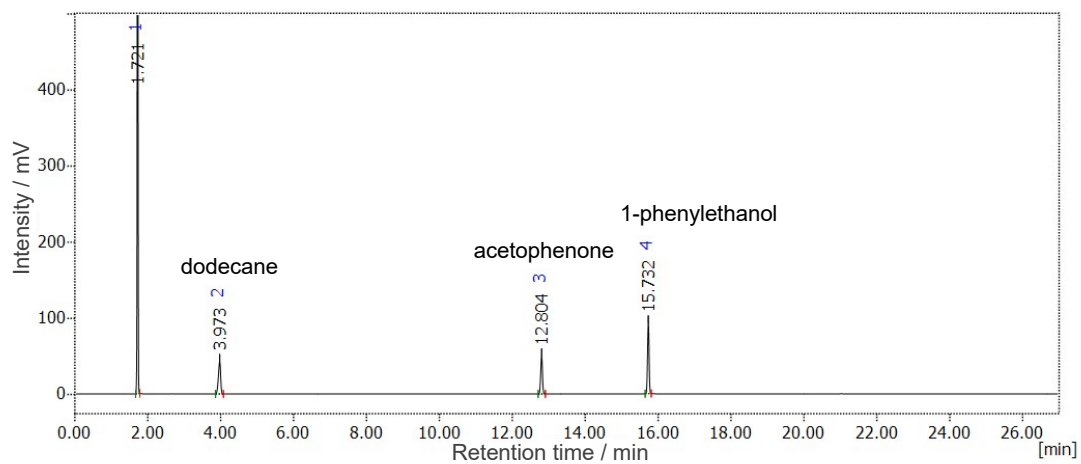


Figure S23 GC analysis result for catalytic hydrogenation of acetophenone by **1** (Entry 12, Table 1).

X. References

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