

Ligand-Controlled Direct Hydroformylation of Tri-substituted Olefins

Taeil Shin, Hyungsoo Kim, Sungmin Kim, Ansoo Lee, Min-Seob Seo, Jonghoon Choi,
Hyungjun Kim, and Hyunwoo Kim*

*Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141,
Republic of Korea*

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1. General information

Commercially available compounds were used without further purification or drying. $[\text{Rh}(\text{acac})(\text{CO})_2]$ was used as received from Alfa Aesar and was stored under argon. Syngas ($\text{CO}:\text{H}_2 = 1:1$) was purchased from Jong-Ang Industry Gas Company, Korea. Flash column chromatography was performed using silica gel (60-Å pore size, 40-63 μm , 4-6% H_2O content, Merck). Analytical thin-layer chromatography (TLC) was performed using glass plates pre-coated with 0.25 mm silica gel impregnated with fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light, an aqueous solution of phosphomolybdic acid (PMA). ^1H NMR(400 MHz), $^{13}\text{C}\{^1\text{H}\}$ NMR(100 MHz) and $^{31}\text{P}\{^1\text{H}\}$ NMR(162 MHz) spectra were recorded on a Bruker Ascend 400 or a Bruker Avance III HD spectrometer. All coupling constants (J values) were reported in Hertz (Hz). The high-resolution mass spectra (HRMS) were obtained using SYNAPT G2 (Waters, U.K.) spectrometer at the Division of Bioconvergence analysis / Biomedical Omics Center in KBSI.

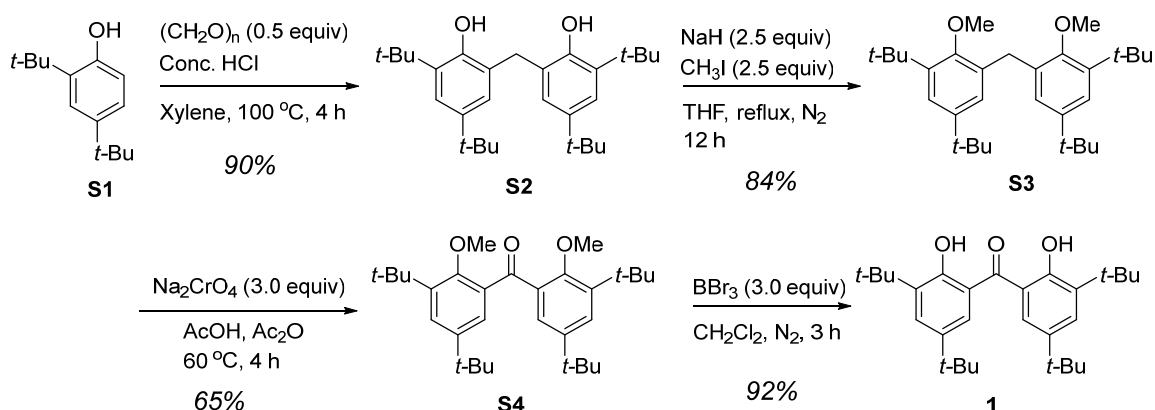
Computational details. Molecular structures were optimized using density functional theory (DFT) by employing the Minnesota 2006 functional (M06)¹ as implemented in the Jaguar 8.4 software package.² For computationally effective and accurate calculations, the Rh atom was described with a LANL2DZ effective core basis set,³ the first coordination atoms of P and N of briphos ligands were described using a standard Pople basis set 6-31G**+, and the other atoms were described using MIDIX basis set.⁴

The exact cone angle of the optimized geometry was calculated by the method defined in the previous work of Allen and co-workers⁵ using the FindConeAngle package of Mathematica 8.0 software [Mathematica 8.0; Wolfram Research, Inc.: Champaign, IL, 2010.].

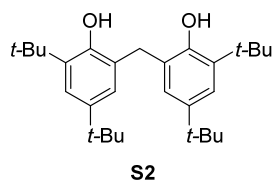
Percent buried volume ($\%V_{\text{bur}}$) was calculated using SambVca 2.0 calculation. For $\%V_{\text{bur}}$ calculation, (1) 3.50 Å was selected as the value for the sphere radius, (2) both 2.28 Å was considered as M-P bond distance, (3) crystallography hydrogen atoms were omitted, (4) scaled Bondi radii were used as recommended by Cavallo.

X-ray Crystallography. The diffraction data of $\text{Rh}(\text{CO})(\text{acac})(\text{L4})$ were collected on a Bruker SMART 1000. A suitable size and quality of crystal was coated with Paratone-N oil and mounted on a MiTeGen MicroLoop. The data were collected with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 120 K. Cell parameters were determined and refined by SMART program.⁶ Data reduction was performed using SAINT software.⁷ An empirical absorption correction was applied using the SADABS program.⁸ The structures were solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 by using the SHELXTL/PC package.⁹ Unless otherwise noted, hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. Full crystallographic details can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif [CCDC 1897350 for $\text{Rh}(\text{CO})(\text{acac})(\text{L4})$].

2. Preparation of briphos ligands L1-L4



A solution of 2,4-di-*tert*-butylphenol (10.0 g, 48.4 mmol) and paraformaldehyde (0.73 g, 24.2 mmol) in xylene (6.0 mL) was added conc. HCl (0.8 mL) and the resulting solution was stirred for 4 h at 100 °C. All volatiles were removed under reduced pressure and the red-brown residue was suspended in diethyl ether (50 mL). H_2O (50 mL) was poured into the flask and the mixture was extracted with diethyl ether (3×50 mL). The combined organic layers were dried over anhydrous MgSO_4 , filtered, and concentrated under reduced pressure to give light gray solid. The solid was suspended in *n*-hexane and stirred overnight. The white solid was filtered off and washed with *n*-hexane to afford 6,6'-methylene bis(2,4-di-*tert*-butyl phenol) (**S2**).

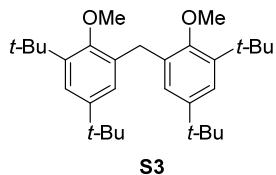


White solid (9.2 g, 21.7 mmol, 90% yield, mp 149-150 °C).

¹H NMR (400 MHz, CDCl_3): δ ppm 1.33 (s, 18H), 1.46 (s, 18H), 3.98 (s, 2H), 5.93 (s, 2H), 7.20 (d, $J = 2.4$ Hz, 2H), 7.24 (d, $J = 2.4$ Hz, 2H). ¹³C{¹H} NMR (100 MHz, CDCl_3): δ ppm 150.0, 143.1, 135.7, 126.2, 125.3, 122.7, 34.8, 34.4, 32.7, 31.7, 30.2.

HRMS (ESI) calculated for $\text{C}_{29}\text{H}_{44}\text{O}_2[\text{M}+\text{Na}]^+$: 447.3239, Found: 447.3228

A solution of 6,6'-methylene bis(2,4-di-*tert*-butyl phenol) (**S2**, 4.3 g, 10.0 mmol) in anhydrous THF (4 mL) was added a cooled suspension (0 °C) of NaH (0.6 g, 25.0 mmol) in anhydrous THF (2 mL) under N_2 atmosphere. The mixture was stirred for an additional 10 min at 0 °C. Iodomethane (1.6 mL, 25.0 mmol) was added into the flask. The mixture was allowed to ambient temperature and then refluxed for 12 h. The reaction was quenched with addition of H_2O (30 mL) and the aqueous phase was extracted with diethyl ether (3×30 mL). The combined organic layers were dried over anhydrous MgSO_4 , filtered, and concentrated in vacuo to give white solid [2,2'-methylene bis(4,6-di-*tert*-butyl anisole) (**S3**)].



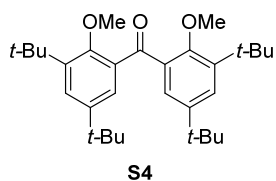
White solid (3.8 g, 8.4 mmol, 84% yield, mp 94-95 °C).

¹H NMR (400 MHz, CDCl₃): δ ppm 1.22 (s, 18H), 1.43 (s, 18H), 3.74 (s, 6H), 4.12 (s, 2H), 6.90 (d, *J* = 2.5 Hz, 2H), 7.21 (d, *J* = 2.5 Hz, 2H). **¹³C{¹H} NMR** (100 MHz, CDCl₃): δ ppm 156.1, 145.3, 141.6, 133.4, 126.6, 122.0, 61.5, 35.4, 34.6, 31.6, 31.3,

31.1.

HRMS (ESI) calculated for C₃₁H₄₈O₂[M+Na]⁺: 475.3552, Found: 475.3555

To a solution of 2,2'-methylene bis(4,6-di-*tert*-butyl anisole) (**S3**, 3.7 g, 8.2 mmol), acetic acid (16 mL), and acetic anhydride (8.8 mL) was added Na₂CrO₄ (4.0 g, 24.6 mmol) and the resulting mixture was stirred for 4.5 h at 60 °C. After cooling to room temperature, H₂O (50 mL) and ethyl acetate (50 mL) were added. The solution was washed with H₂O (3×50 mL) and the organic layer was dried over anhydrous MgSO₄. Removal of volatiles in vacuo provided the crude product as yellow solid. The solid was suspended in EtOH (30 mL) and stirred overnight. The white solid was filtered off and washed with EtOH (10 mL) to afford bis[3,5-bis(*tert*-butyl)-2-methoxyphenyl]methanone (**S4**).

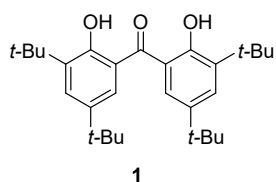


White solid (2.5 g, 5.3 mmol, 65% yield, mp 182-183 °C).

¹H NMR (400 MHz, CDCl₃): δ ppm 1.29 (s, 18H), 1.38 (s, 18H), 3.52 (s, 6H), 7.42 (d, *J* = 2.6 Hz, 2H), 7.49 (d, *J* = 2.6 Hz, 2H). **¹³C{¹H} NMR** (100 MHz, CDCl₃): δ ppm 197.8, 158.2, 144.6, 142.1, 132.4, 127.6, 127.0, 62.9, 35.5, 34.7, 31.6, 30.9. **HRMS**

(ESI) calculated for C₃₁H₄₆O₃[M+Na]⁺: 467.3525, Found: 467.3522

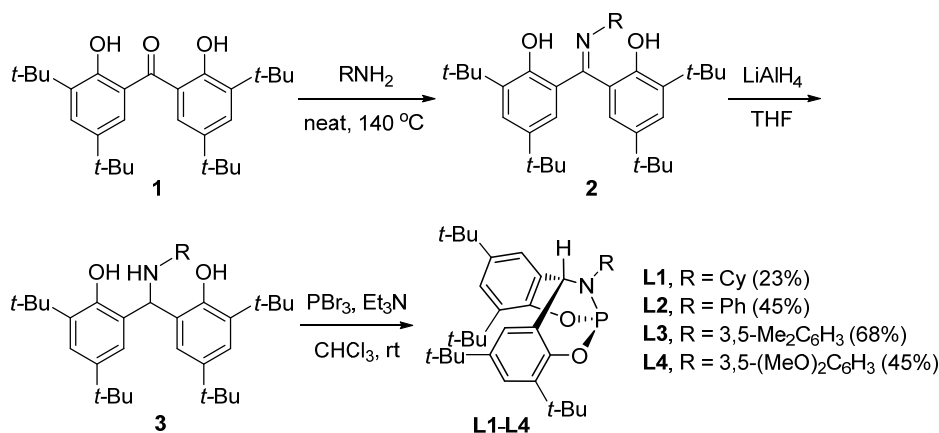
A cooled solution of bis[3,5-bis(*tert*-butyl)-2-methoxyphenyl]methanone (**S4**, 2.4 g, 5.1 mmol) in anhydrous CH₂Cl₂ (20 mL) was added BBr₃ (31 mmol) in CH₂Cl₂ (31 mL) dropwise over 1 h under N₂. The mixture was allowed to ambient temperature and stirred for 3 h. The reaction was quenched with addition of MeOH (100 mL). The aqueous phase was extracted with ethyl acetate (50 mL). The combined organic layer was washed with H₂O (3×50 mL), dried over anhydrous MgSO₄, filtered, and concentrated to give yellow solid product (**1**).



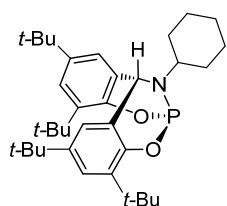
Yellow solid (2.1 g, 4.8 mmol, 92% yield, mp 201-202 °C).

¹H NMR (400 MHz, CDCl₃): δ ppm 1.28 (s, 18H), 1.48 (s, 18H), 7.38 (d, *J* = 2.4 Hz, 2H), 7.57 (d, *J* = 2.4 Hz, 2H), 11.19 (d, *J* = 0.5 Hz, 2H). **¹³C{¹H} NMR** (100 MHz, CDCl₃): δ ppm 204.9, 150.9, 140.0, 138.0, 130.7, 127.7, 119.8, 35.4, 34.5, 31.6, 29.6.

HRMS (ESI) calculated for C₂₉H₄₂O₃[M+H]⁺: 439.3212, Found: 439.3210



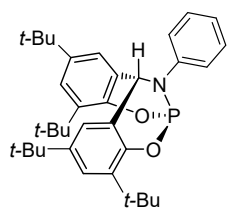
A mixture of 950 mg (2.17 mmol) of **1** and (10.8 mmol) of 3,5-dimethylaniline was stirred for 12 h at 140 °C. The clean formation of imine product **2** was confirmed by ¹H NMR spectra of crude mixtures or thin-layer chromatography (TLC, ethyl acetate : n-hexane = 1:20, R_f: 0.5(UV)). After cooling to ambient temperature, the mixture, dark brown oil loaded on a pad of silica-gel (10 cm) was eluted with ethyl acetate/n-hexane (1/20) to afford yellow solid **2**. The yellow solid **2** was transferred to a round bottom flask charged with THF (20.0 mL). After cooling the mixture at 0 °C, a solution of LiAlH₄ (6.51 mmol) in THF (2.8 mL) was added dropwise under N₂. The mixture was stirred for 4 h and then ethyl acetate (20 mL) was added. The crude mixture was washed with H₂O (3×30 mL), and the organic layer was dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The crude product dissolved in 20 mL of chloroform was mixed with 0.2 mL (2.17 mmol) of phosphorous tribromide and 0.91 mL (6.51 mmol) of Et₃N under N₂ atmosphere. The resulting solution was then stirred at ambient temperature for 4 h. The solution was filtered over a pad of silica-gel (10 cm) with ethyl acetate and concentrated under reduced pressure. The crude product dissolved in 25 mL of ethanol to induce precipitation. The precipitate was filtered and washed with ethanol to afford analytically pure biphenos ligand **L3**.



L1 (23% yield, white solid)

¹H NMR (400 MHz, CDCl₃): δ ppm 7.15 (d, *J* = 2.4 Hz, 2H), 7.00 (d, *J* = 2.4 Hz, 2H), 4.92 (d, *J* = 5.1 Hz, 1H), 3.07 (qt, *J* = 11.4, 3.6 Hz, 1H), 1.83-1.67 (m, 4H), 1.57 (d, *J* = 15.9 Hz, 2H), 1.46-1.41 (m, 1H), 1.38 (s, 18H), 1.28 (s, 18H), 1.21 (dt, *J* = 13.1, 2.9 Hz, 2H), 1.17–

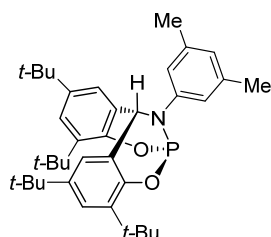
1.01(m, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ ppm 146.3, 143.6, 137.9, 128.4, 122.8, 122.1, 59.9, 59.7, 54.3, 35.1, 34.5, 34.1, 34.0, 31.7, 29.9, 26.1, 25.7. ³¹P{¹H} NMR (162 MHz, CDCl₃): δ ppm 94.9. HRMS (ESI) calculated for C₃₅H₅₂NO₂P[M+H]⁺: 550.3816, Found: 550.3868



L2 (45% yield, white solid)

^1H NMR (400 MHz, CDCl_3): δ ppm 7.26 (d, $J = 1.6$ Hz, 2H), 7.20 (d, $J = 2.4$ Hz, 2H), 7.13 (dt, $J = 2.2, 1.2$ Hz, 1H), 7.11 (q, $J = 1.0$ Hz, 1H), 7.09 (d, $J = 2.4$ Hz, 2H), 7.00 (tt, $J = 7.4, 1.0$ Hz, 1H), 5.5 (d, $J = 4.1$ Hz, 1H), 1.39 (s, 18H), 1.29 (s, 18H). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (100 MHz, CDCl_3): δ ppm 145.9, 144.5, 138.2, 129.5, 127.24, 127.17, 123.3, 122.9, 122.3, 120.8, 120.7,

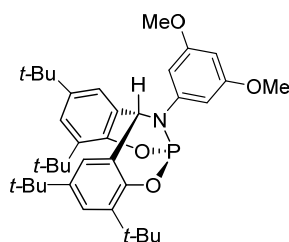
55.3, 35.1, 34.6, 31.7, 29.9. **$^{31}\text{P}\{^1\text{H}\}$ NMR** (162 MHz, CDCl_3): δ ppm 87.1. **HRMS** (ESI) calculated for $\text{C}_{35}\text{H}_{46}\text{NO}_2\text{P}[\text{M}+\text{H}]^+$: 544.3346, Found: 544.3330



L3 (68% yield, white solid)

^1H NMR (400 MHz, CDCl_3): δ ppm 7.21 (d, $J = 2.5$ Hz, 2H), 7.12 (d, $J = 2.4$ Hz, 2H), 6.76 (dq, $J = 1.6, 0.8$ Hz, 2H), 6.66 (tt, $J = 1.5, 0.7$ Hz, 1H), 5.55 (d, $J = 4.1$ Hz, 1H), 2.26 (q, $J = 0.6$ Hz, 6H), 1.42 (s, 18H), 1.31 (s, 18H). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (100 MHz, CDCl_3): δ ppm 146.0, 145.9, 144.7, 144.4, 139.1, 138.1, 127.4, 127.3, 124.7, 123.2, 122.3, 118.6,

118.5, 56.4, 35.1, 34.6, 31.7, 29.9, 21.6. **$^{31}\text{P}\{^1\text{H}\}$ NMR** (162 MHz, CDCl_3): δ ppm 87.1. **HRMS** (ESI) calculated for $\text{C}_{37}\text{H}_{50}\text{NO}_2\text{P}[\text{M}+\text{H}]^+$: 572.3659, Found: 572.3604.



L4 (45% yield, white solid)

^1H NMR (400 MHz, CDCl_3): δ ppm 7.21 (d, $J = 2.4$ Hz, 2H), 7.11 (d, $J = 2.4$ Hz, 2H), 6.31 (dd, $J = 2.2, 1.1$ Hz, 2H), 6.13 (t, $J = 2.2$ Hz, 1H), 5.55 (d, $J = 4.1$ Hz, 1H), 3.74 (s, 3H), 1.41 (s, 18H), 1.30 (s, 18H). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (100 MHz, CDCl_3): δ ppm 161.5, 146.7, 146.5, 145.9, 145.8, 144.6, 138.24, 138.22, 127.13, 127.07, 123.3, 122.3, 100.1,

99.1, 99.0, 95.0, 56.2, 55.4, 35.1, 34.6, 31.7, 29.9. **$^{31}\text{P}\{^1\text{H}\}$ NMR** (162 MHz, CDCl_3): δ ppm 86.9. **HRMS** (ESI) calculated for $\text{C}_{37}\text{H}_{50}\text{NO}_4\text{P}[\text{M}+\text{H}]^+$: 604.3557, Found: 604.3532

3. ^1H NMR spectra of rhodium complexes

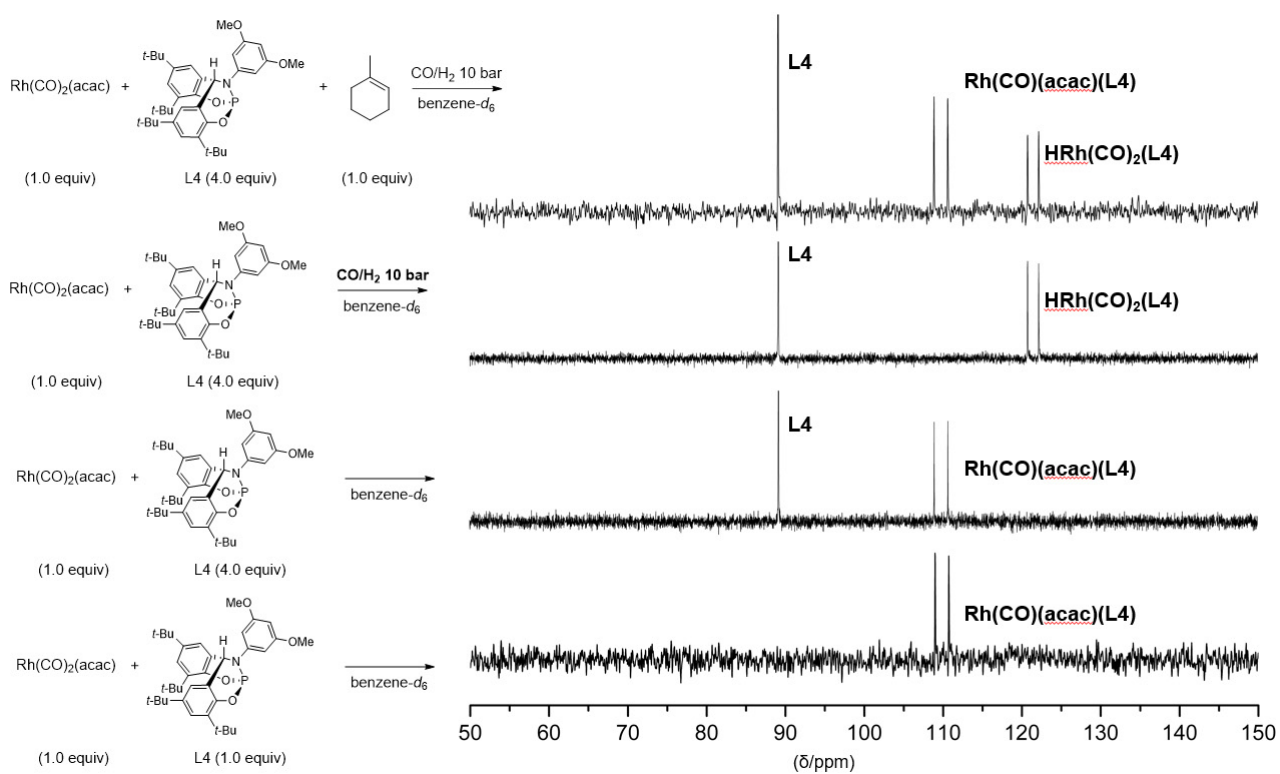


Figure S1. Stacked $^{31}\text{P}\{^1\text{H}\}$ NMR spectra showing ligation of **L4** with $\text{Rh}(\text{CO})_2(\text{acac})$.

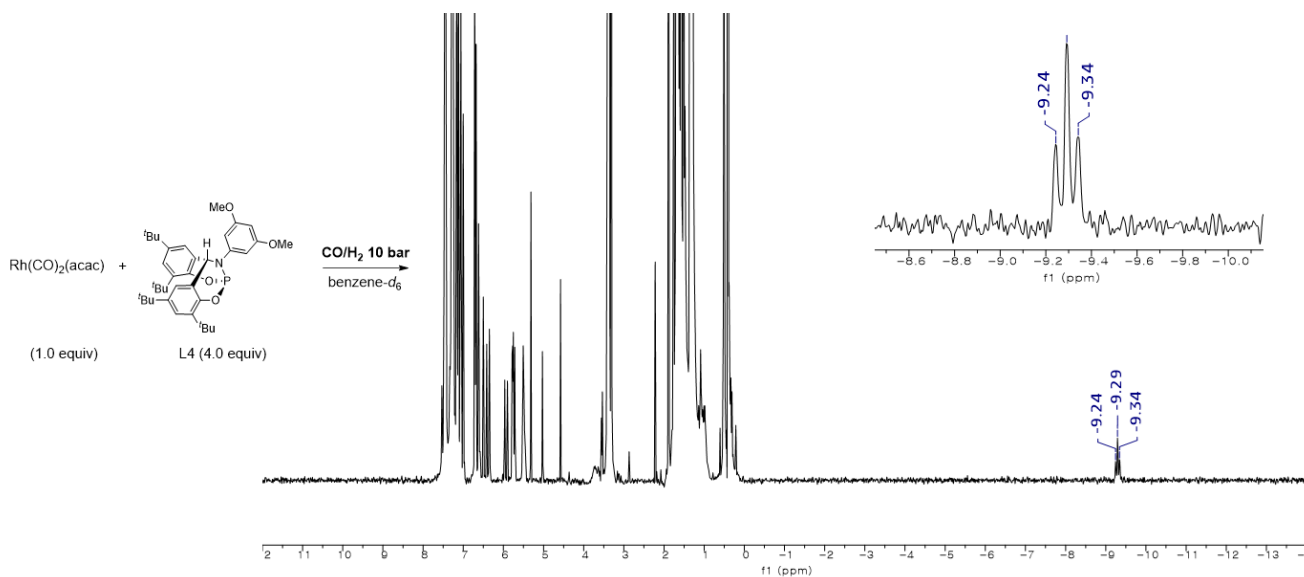


Figure S2. ^1H NMR spectra of $\text{HRh}(\text{CO})_2(\text{L4})$

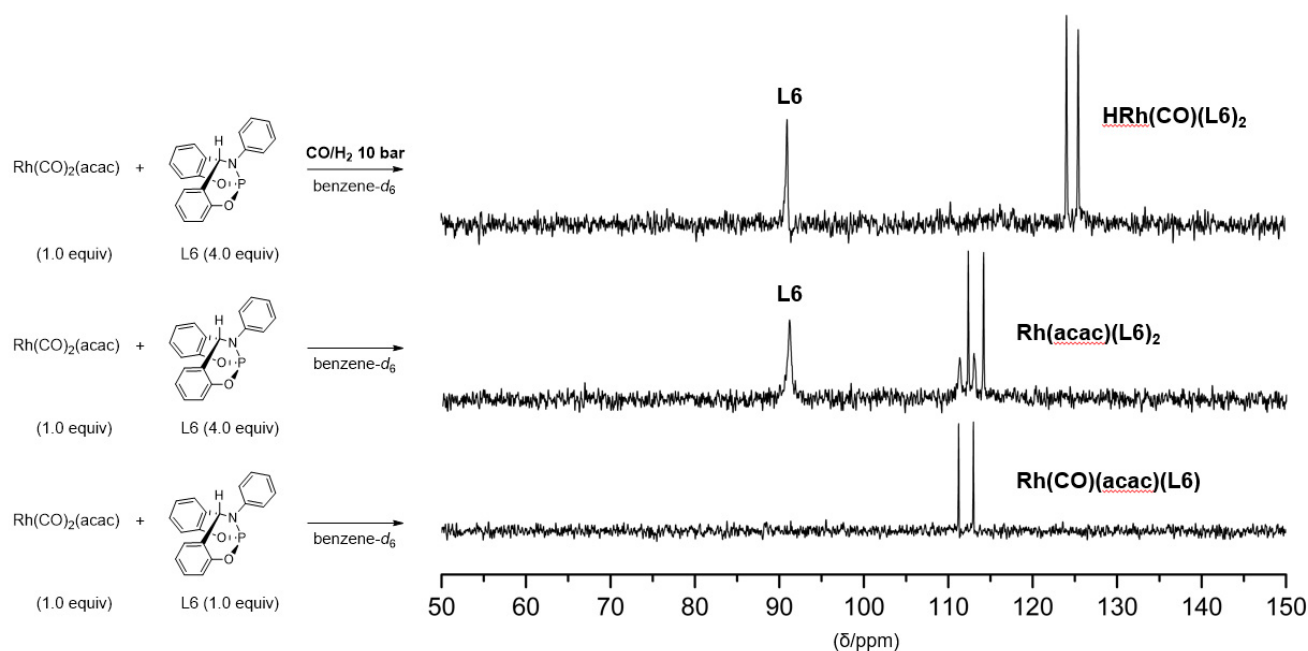
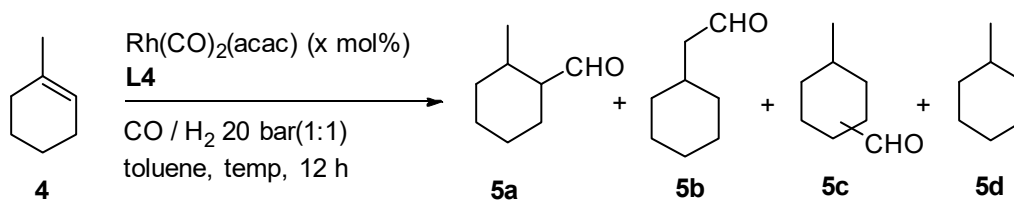


Figure S3. Stacked $^{31}\text{P}\{^1\text{H}\}$ NMR spectra showing ligation of **L6** with $\text{Rh}(\text{CO})_2(\text{acac})$.

4. General procedure for hydroformylation

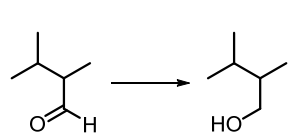
In a glovebox filled with argon, a 5 mL vial equipped with a magnetic bar was added $\text{Rh}(\text{acac})(\text{CO})_2$ (0.01 mmol in 0.5 mL toluene) and ligand (0.02 mmol). After stirring for 30 min, 1-methyl-1-cyclohexene (1.0 mmol) and additional toluene was charged to bring the total volume of 2.0 mL. The vial was transferred into an autoclave and taken out of the glovebox then 20 bar of syngas ($\text{CO}:\text{H}_2 = 1:1$) was charged. The reaction mixture was stirred at 100 °C for 12 h. After the reaction, autoclave reactor was cooled to ambient temperature and the pressure was carefully released in a well-ventilated fume hood. The conversion of 1-methyl-1-cyclohexene was determined by ^1H NMR spectra of the crude reaction mixture. The ratio of isomers (**5a** to **5d**) was determined by GC-MS analysis of the crude reaction mixture. The conversion and selectivity of other substrates were determined by GC-MS spectra with mesitylene as internal standard. Isolated yields were determined after purifying the crude product by silica-gel column chromatography (ethyl acetate : *n*-hexane = 1:10). For volatile aldehyde products, reduction with NaBH_4 was performed and the resulting alcohols were characterized.

- **Optimization of Rh/L4-catalyzed hydroformylation**



Entry	Catalyst	L/Rh	Pressure	Temperature	Conversion	5a/5b
1	0.1 mol%	2	20 bar	100 °C	30%	2.5
2	0.5 mol%	2	20 bar	100 °C	83%	3.3
3	1.0 mol%	2	20 bar	100 °C	83%	4.0
4	4.0 mol%	2	20 bar	100 °C	>99%	4.0
5	1.0 mol%	2	20 bar	80 °C	17%	2.3
6	1.0 mol%	2	20 bar	120 °C	48%	3.8
7	1.0 mol%	10	20 bar	100 °C	54%	3.8
8	1.0 mol%	5	20 bar	100 °C	70%	4.0
9	1.0 mol%	1	20 bar	100 °C	33%	4.0
10	1.0 mol%	2	10 bar	100 °C	68%	4.0
11	1.0 mol%	2	40 bar	100 °C	63%	3.9
12	1.0 mol%	2	CO 20 bar H ₂ 10 bar	100 °C	10%	2.3
13	1.0 mol%	2	CO 10 bar H ₂ 20 bar	100 °C	7%	4.7

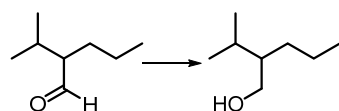
- **Product characterization**



2,3-Dimethylbutan-1-ol (6): colorless oil. ^1H NMR (400 MHz, CDCl_3): δ ppm 3.59

(dd, $J = 10.6, 5.9$ Hz, 1H), 3.44 (dd, $J = 10.6, 7.0$ Hz, 1H), 1.74-1.66 (m, 1H), 1.53-1.47 (m, 1H), 0.91 (d, $J = 6.9$ Hz, 3H), 0.86 (d, $J = 6.9$ Hz, 3H), 0.83 (d, $J = 6.8$ Hz,

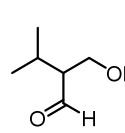
3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ ppm 66.8, 41.6, 29.0, 20.8, 18.2, 12.7. **HRMS** (ESI) calculated for $\text{C}_6\text{H}_{14}\text{O}[\text{M-H}]^+$: 101.0966, Found: 101.0968

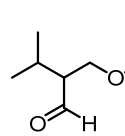


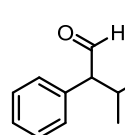
2-Isopropylpentan-1-ol (7): colorless oil. ^1H NMR (400 MHz, CDCl_3): δ ppm

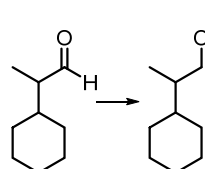
3.50 (dd, $J = 10.5, 5.8$ Hz, 1H), 3.41 (dd, $J = 10.5, 6.6$ Hz, 1H), 1.67-1.42 (m, 2H), 1.35-1.26 (m, 1H), 1.26-1.04 (m, 3H), 0.96-0.86 (m, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz,

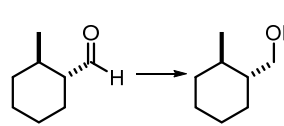
CDCl_3): δ ppm 68.6, 36.4, 36.2, 31.0, 28.4, 22.9, 22.6, 16.7. **HRMS** (ESI) calculated for $\text{C}_8\text{H}_{18}\text{O}[\text{M-H}]^+$: 129.1279, Found: 129.1275

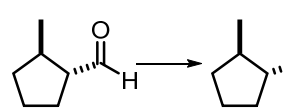
 **2-(Hydroxymethyl)-3-methylbutanal (8):** colorless oil. ^1H NMR (400 MHz, CDCl_3): δ ppm 9.81 (d, $J = 1.3$ Hz, 1H), 3.96 (dd, $J = 11.2, 8.1$ Hz, 1H), 3.75 (dd, $J = 11.2, 3.6$ Hz, 1H), 2.40 (m, 1H), 2.17 (m, 1H), 1.03 (d, $J = 6.7$ Hz, 3H), 1.00 (d, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ ppm 206.3, 60.0, 59.7, 26.5, 20.7, 20.2. **HRMS** (ESI) calculated for $\text{C}_6\text{H}_{12}\text{O}_2[\text{M}+\text{H}]^+$: 117.0916, Found: 117.0912.

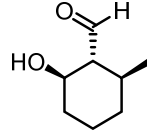
 **2-Formyl-3-methylbutyl acetate (9):** pale-yellow oil. ^1H NMR (400 MHz, CDCl_3): δ ppm 9.71 (d, $J = 2.6$ Hz, 1H), 4.38 (dd, $J = 11.4, 8.3$ Hz, 1H), 4.27 (dd, $J = 11.4, 4.5$ Hz, 1H), 2.47 (dddd, $J = 8.3, 6.4, 4.5, 2.6$ Hz, 1H), 2.13 (dq, $J = 13.6, 6.8$ Hz, 1H), 2.03 (s, 3H), 1.02 (d, $J = 3.5$ Hz, 3H), 0.93 (d, $J = 3.6$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ ppm 202.7, 170.8, 61.0, 56.8, 26.3, 20.7, 20.3, 19.7. **HRMS** (ESI) calculated for $\text{C}_8\text{H}_{14}\text{O}_3[\text{M}+\text{Na}]^+$: 181.0841, Found: 181.0842.

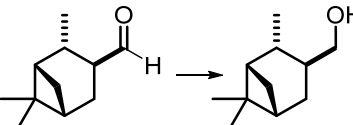
 **3-Methyl-2-phenylbutanal (10):** pale-yellow oil. ^1H NMR (400 MHz, CDCl_3): δ ppm 9.67 (d, $J = 3.3$ Hz, 1H), 7.35-7.25 (m, 3H), 7.18-7.16 (m, 2H), 3.17 (dd, $J = 9.5, 3.3$ Hz, 1H), 2.40 (dp, $J = 9.5, 6.7$ Hz, 1H), 1.03 (d, $J = 6.6$ Hz, 3H), 0.75 (d, $J = 6.7$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ ppm 201.1, 135.5, 129.3, 128.9, 127.5, 66.8, 28.8, 21.2, 20.0. **HRMS** (ESI) calculated for $\text{C}_{11}\text{H}_{14}\text{O}[\text{M}+\text{H}]^+$: 163.1123, Found: 163.1128.

 **2-Cyclohexylpropan-1-ol (11):** colorless oil. ^1H NMR (400 MHz, CDCl_3): δ ppm 3.59 (dd, $J = 10.5, 5.7$ Hz, 1H), 3.43 (dd, $J = 10.5, 6.9$ Hz, 1H), 1.71 (m, 2H), 1.62 (m, 3H), 1.47 (tt, $J = 6.9$ Hz, 5.4 Hz, 1H), 1.38-1.27 (m, 1H), 1.25-1.05 (m, 4H), 1.01-0.91 (m, 1H), 0.86 (d, $J = 6.9$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ ppm 66.4, 41.0, 39.5, 31.1, 28.9, 26.9, 26.8, 26.7, 13.5. **HRMS** (ESI) calculated for $\text{C}_9\text{H}_{18}\text{O}[\text{M}-\text{H}]^+$: 141.1279, Found: 141.1281.

 ***trans*-2-(Methylcyclohexyl)methanol (5a):** colorless oil. ^1H NMR (400 MHz, CDCl_3): δ ppm 3.71 (dd, $J = 10.7, 2.7$ Hz, 1H), 3.52 (dd, $J = 10.7, 5.8$ Hz, 1H), 1.82-1.73 (m, 2H), 1.69-1.64 (m, 2H), 1.33 (s, 1H), 1.28-1.20 (m, 3H), 1.11-1.07 (m, 2H), 0.92 (d, $J = 6.2$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ ppm 66.2, 46.7, 35.8, 33.8, 29.7, 26.5, 26.4, 20.3. **HRMS** (ESI) calculated for $\text{C}_8\text{H}_{16}\text{O}[\text{M}+\text{Na}]^+$: 151.1099, Found: 151.1088

 ***trans*-2-(Methylcyclopentyl)methanol (12):** colorless oil. ^1H NMR (400 MHz, CDCl_3): δ ppm 3.65 (dd, $J = 10.5, 5.0$ Hz, 1H), 3.47 (dd, $J = 10.5, 7.0$ Hz, 1H), 1.87-1.76 (m, 2H), 1.65-1.49 (m, 4H), 1.39-1.32 (m, 1H), 1.22-1.15 (m, 1H), 1.01 (d, $J = 6.4$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ ppm 66.7, 49.9, 37.1, 35.2, 29.6, 24.1, 20.2. **HRMS** (ESI) calculated for $\text{C}_7\text{H}_{14}\text{O}[\text{M}-\text{H}]^+$: 113.0966, Found: 113.0964.


(1*R*,2*R*,6*S*)-2-Hydroxy-6-methylcyclohexane-1-carbaldehyde (13): pale-yellow oil. **¹H NMR** (400 MHz, CDCl₃): δ ppm 9.76 (d, *J* = 3.6 Hz, 1H), 3.87-3.81 (td, *J* = 10.3, 4.5 Hz, 1H), 2.04 (dd, *J* = 11.9, 3.1 Hz, 1H), 1.93 (td, *J* = 10.4, 10.0, 3.6 Hz, 1H), 1.81-1.63 (m, 3H), 1.40-1.24 (m, 3H), 1.01 (d, *J* = 6.4 Hz, 3H). **¹³C{¹H} NMR** (100 MHz, CDCl₃): δ ppm 205.6, 69.6, 64.6, 34.0, 33.7, 31.8, 23.3, 19.7. **HRMS** (ESI) calculated for C₈H₁₄O₂[M+H]⁺: 143.1072, Found: 143.1082.


((1*S*,2*S*,3*S*,5*R*)-2,6,6-Trimethyl bicyclo[3.1.1]heptan-3-yl)methanol (14): colorless oil. **¹H NMR** (400 MHz, CDCl₃): δ ppm 3.58 (dd, *J* = 10.2, 5.7 Hz, 1H), 3.45 (dd, *J* = 10.2, 7.5 Hz, 1H), 2.31-2.25 (dtd, *J* = 9.6, 6.2, 2.1 Hz, 1H), 2.16-2.09 (dddd, *J* = 13.5, 10.1, 3.4, 2.1 Hz, 1H), 1.94-1.86 (m, 2H), 1.78-1.75 (m, 1H), 1.72-1.68 (m, 1H), 1.55 (ddd, *J* = 13.5, 5.8, 2.7 Hz, 1H), 1.19 (s, 3H), 1.07 (d, *J* = 7.2 Hz, 3H), 1.01 (s, 3H), 0.73 (d, *J* = 9.6 Hz, 1H). **¹³C{¹H} NMR** (100 MHz, CDCl₃): δ ppm 70.1, 47.9, 41.5, 39.5, 39.1, 39.0, 33.6, 31.3, 28.1, 23.0, 22.2. **HRMS** (ESI) calculated for C₁₁H₂₀O[M-H]⁺: 167.1436, Found: 167.1432

5. Determination of aldehyde structures

For substrate No. 9

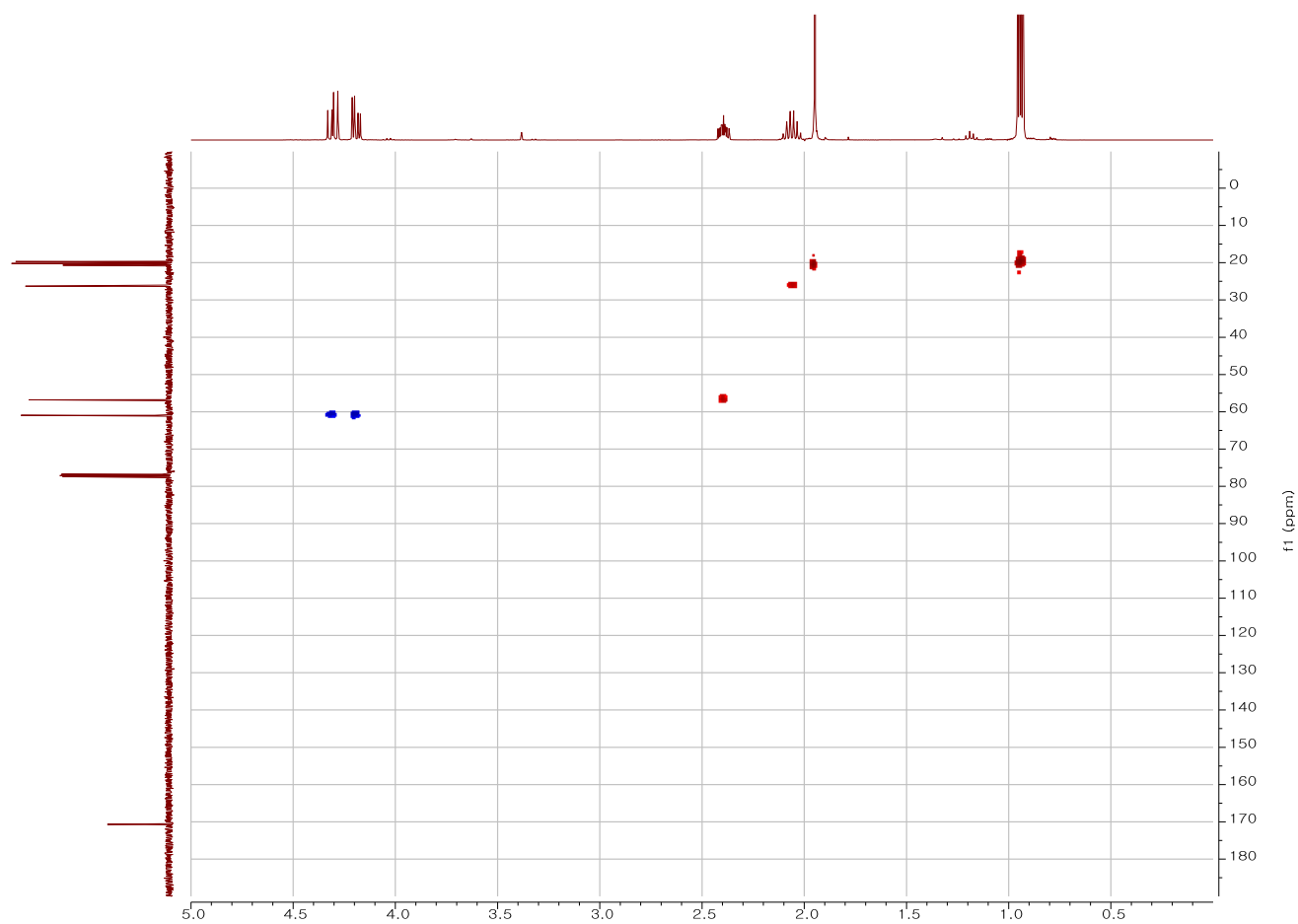
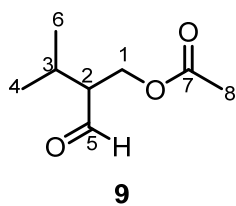


Figure S4. HSQC spectrum of 9 in CDCl₃.

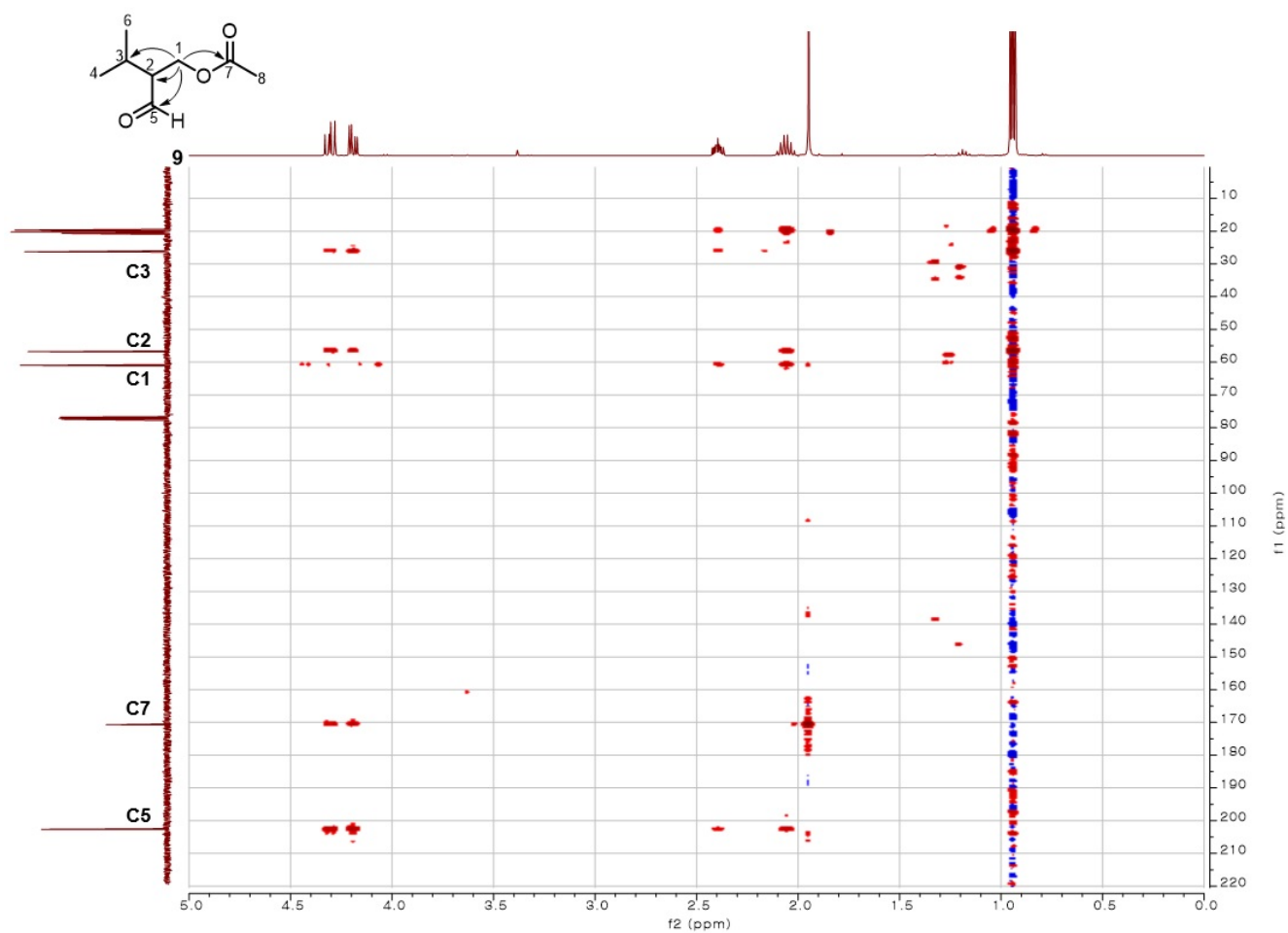
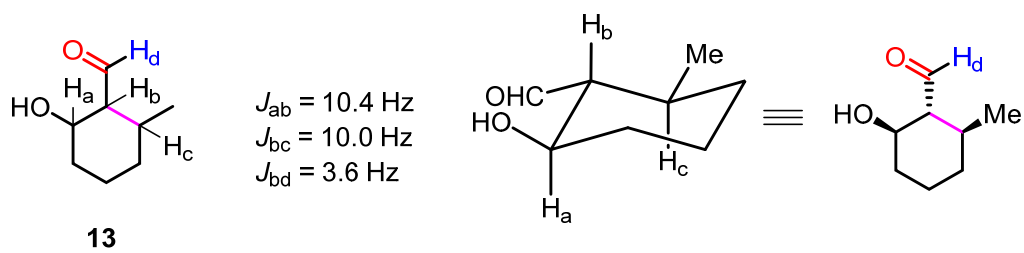


Figure S5. HMBC spectrum of **9** in CDCl_3

For substrate No. **13**



For substrate No. **14**

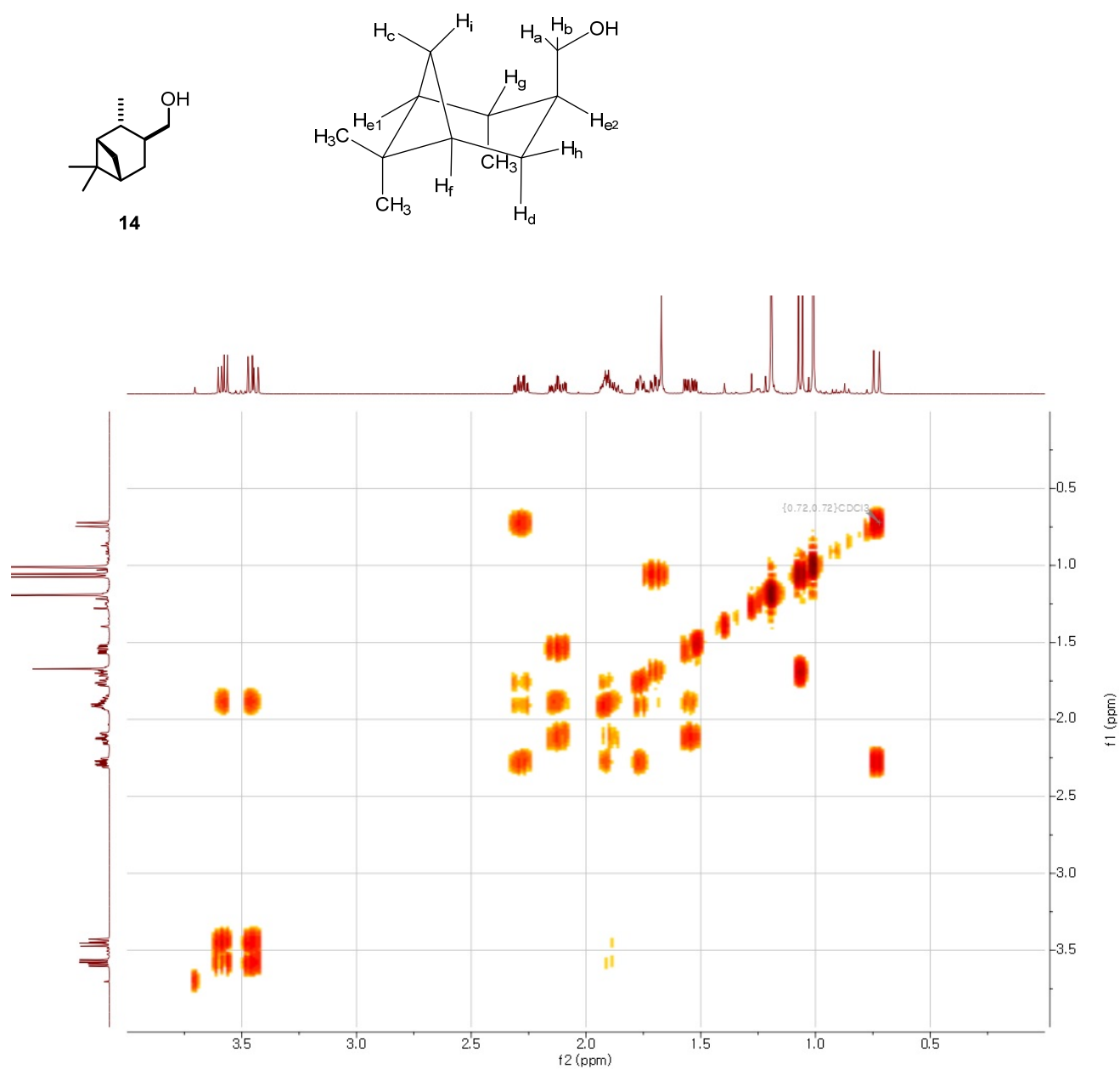


Figure S6. COSY spectrum of **14** in CDCl₃.

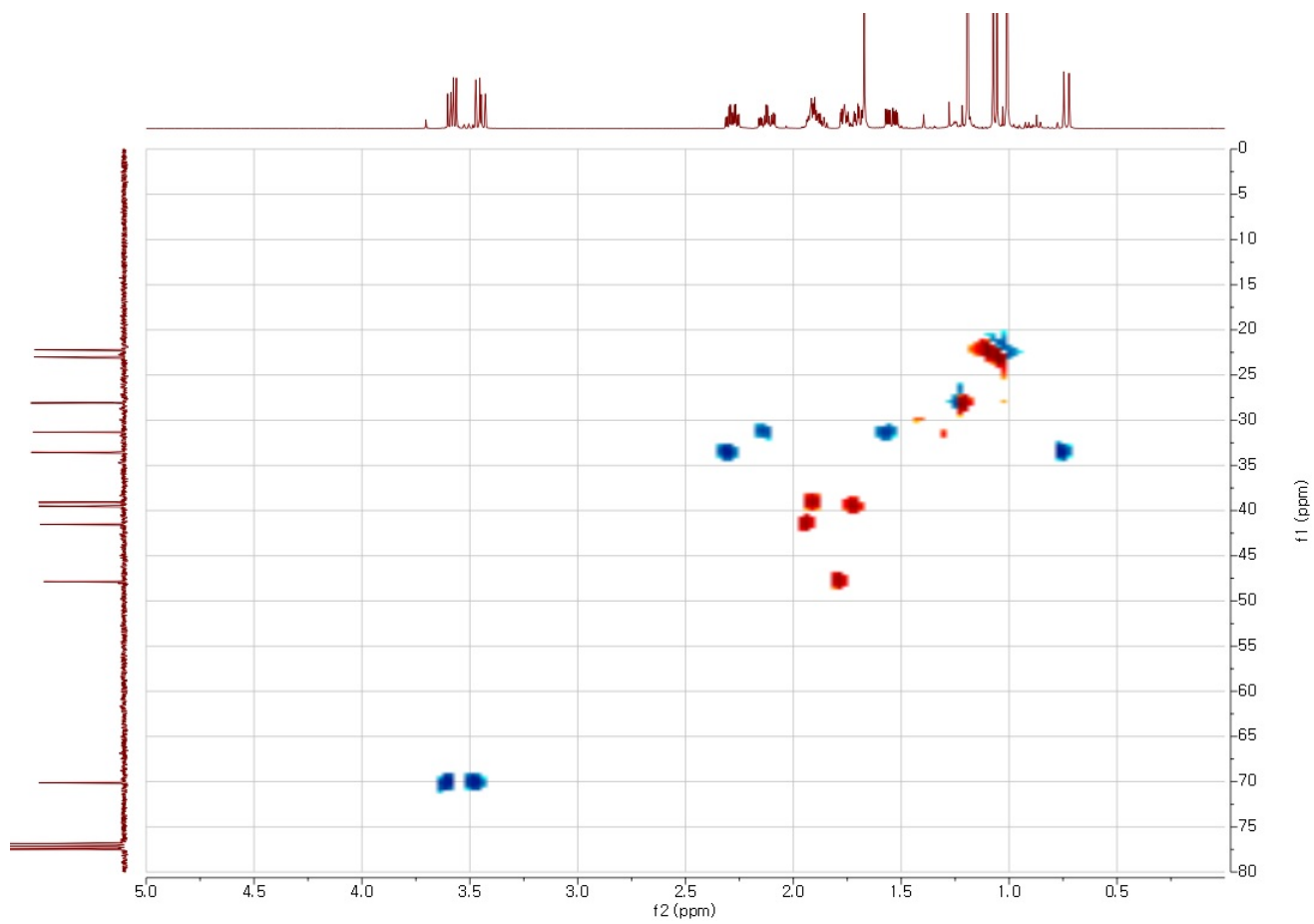


Figure S7. HSQC spectrum of **14** in CDCl_3 .

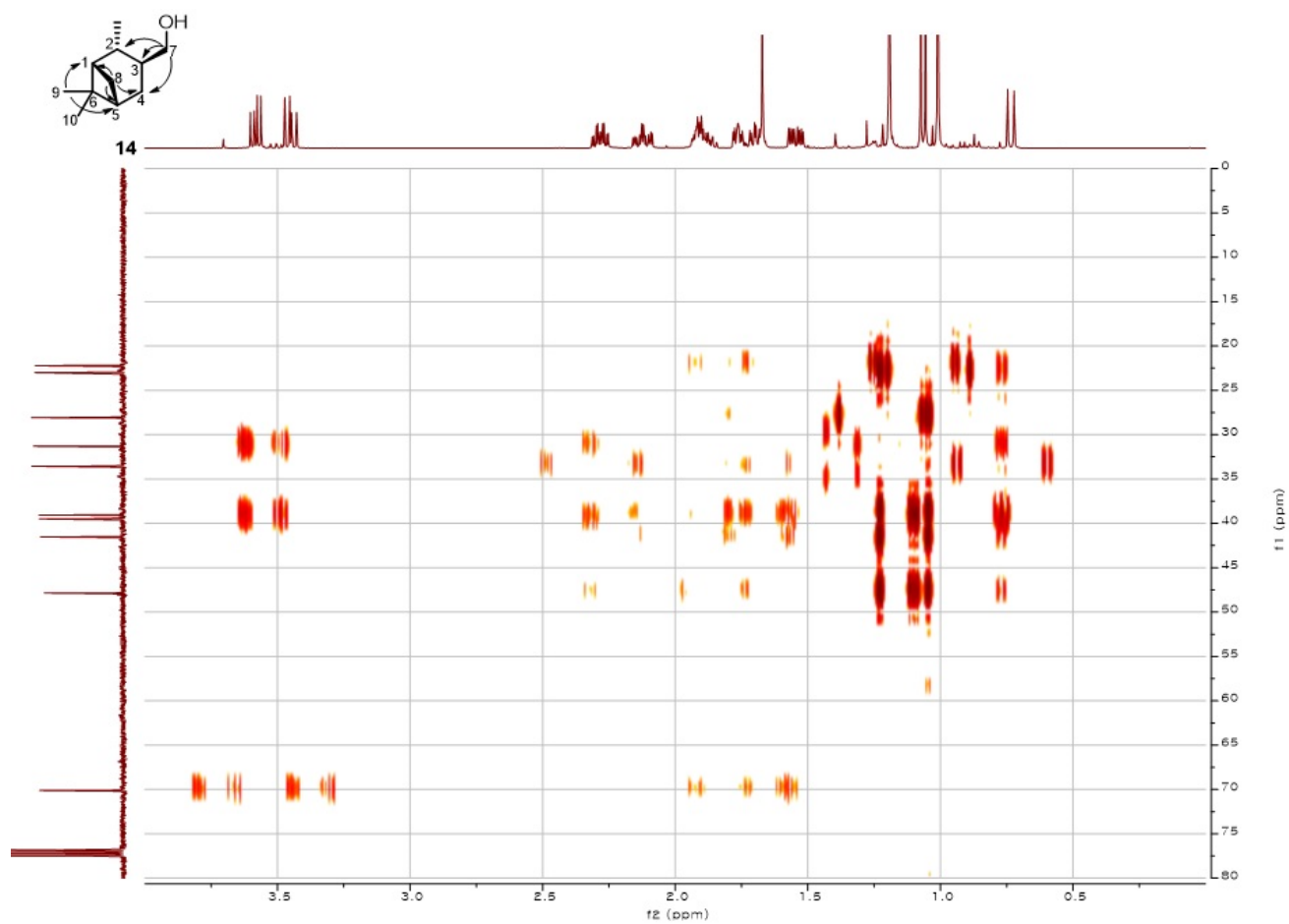


Figure S8. HMBC spectrum of **14** in CDCl_3 .

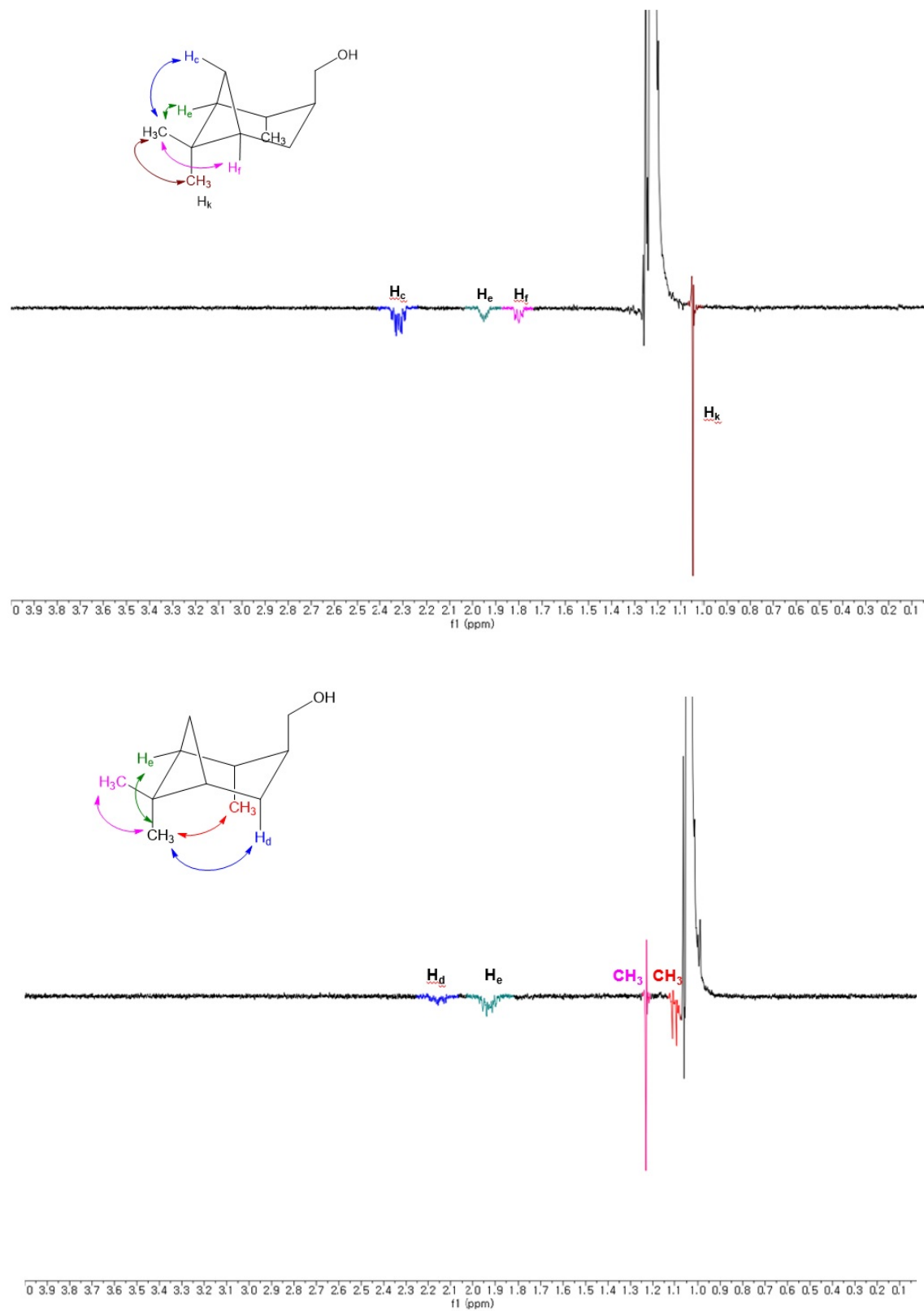
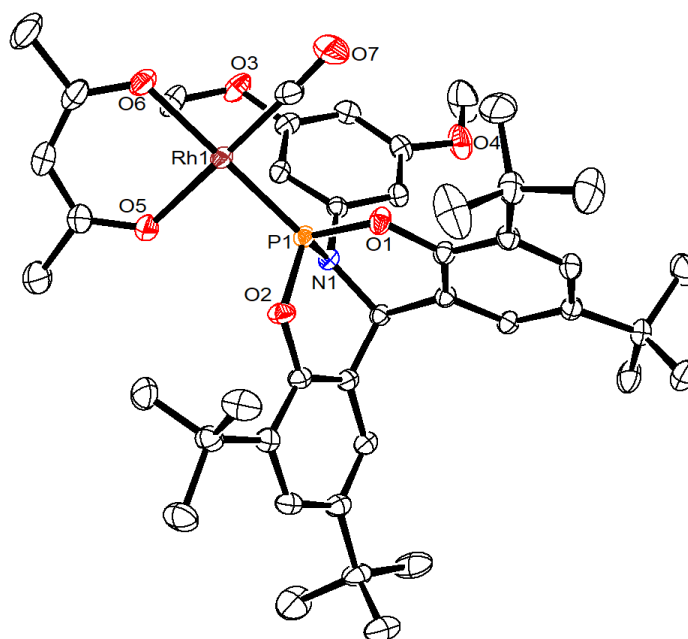


Figure S9. NOE spectrum of **14** in CDCl_3 .

6. Crystal data



ORTEP representation (50% probability) of the crystal structure of Rh(CO)(acac)(L4)

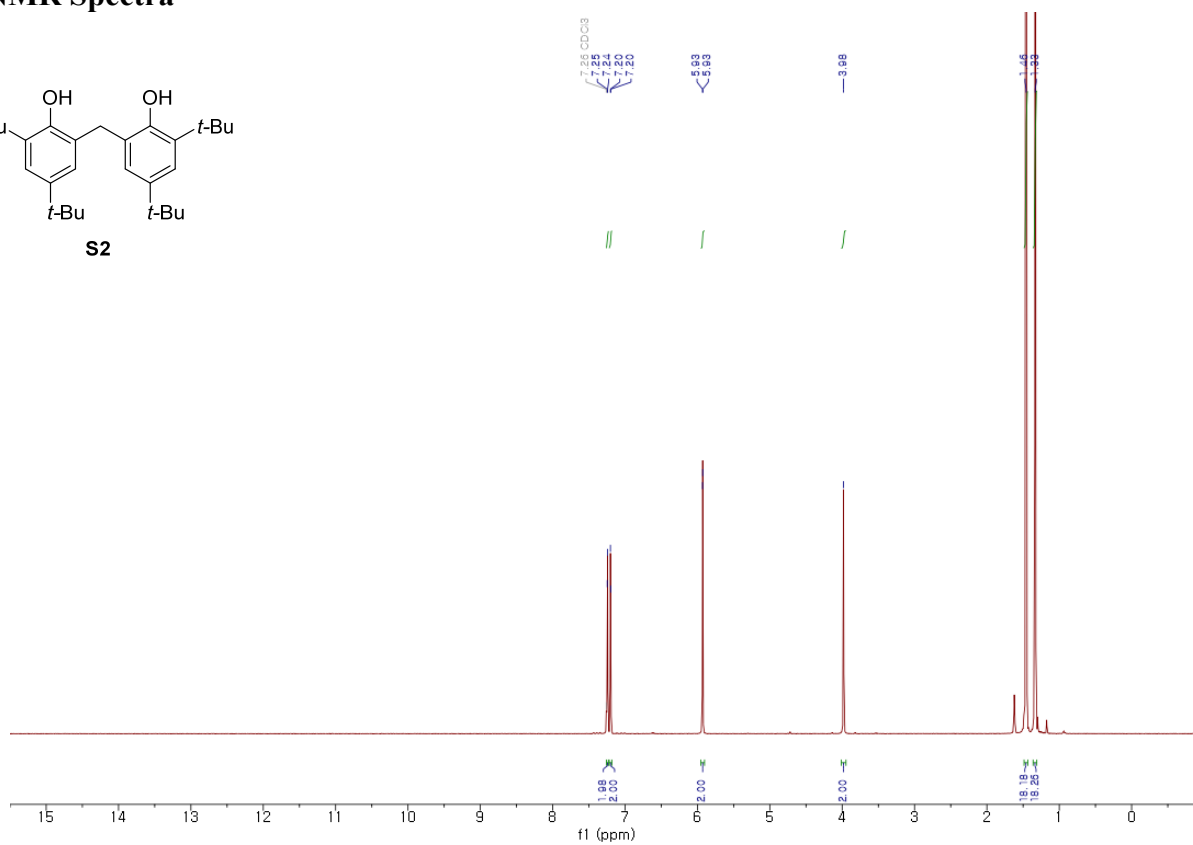
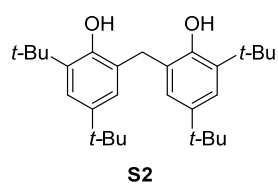
Identification code	0521B-1_a	
Empirical formula	C ₄₃ H ₅₇ N O ₇ P Rh	
Formula weight	833.77	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2 ₁ /c	
Unit cell dimensions	a = 16.1403(6) Å	$\alpha = 90^\circ$.
	b = 12.6980(5) Å	$\beta = 92.570(2)^\circ$.
	c = 20.9045(7) Å	$\gamma = 90^\circ$.
Volume	4280.1(3) Å ³	
Z	4	
Density (calculated)	1.294 Mg/m ³	
Absorption coefficient	0.484 mm ⁻¹	
F(000)	1752	

Crystal size	0.230 x 0.130 x 0.110 mm ³
Theta range for data collection	2.238 to 33.802°.
Index ranges	-25≤h≤25, -19≤k≤19, -32≤l≤32
Reflections collected	148484
Independent reflections	17093 [R(int) = 0.0519]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	17093 / 0 / 494
Goodness-of-fit on F ²	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0312, wR2 = 0.0776
R indices (all data)	R1 = 0.0444, wR2 = 0.0847
Extinction coefficient	n/a
Largest diff. peak and hole	0.552 and -0.400 e.Å ⁻³

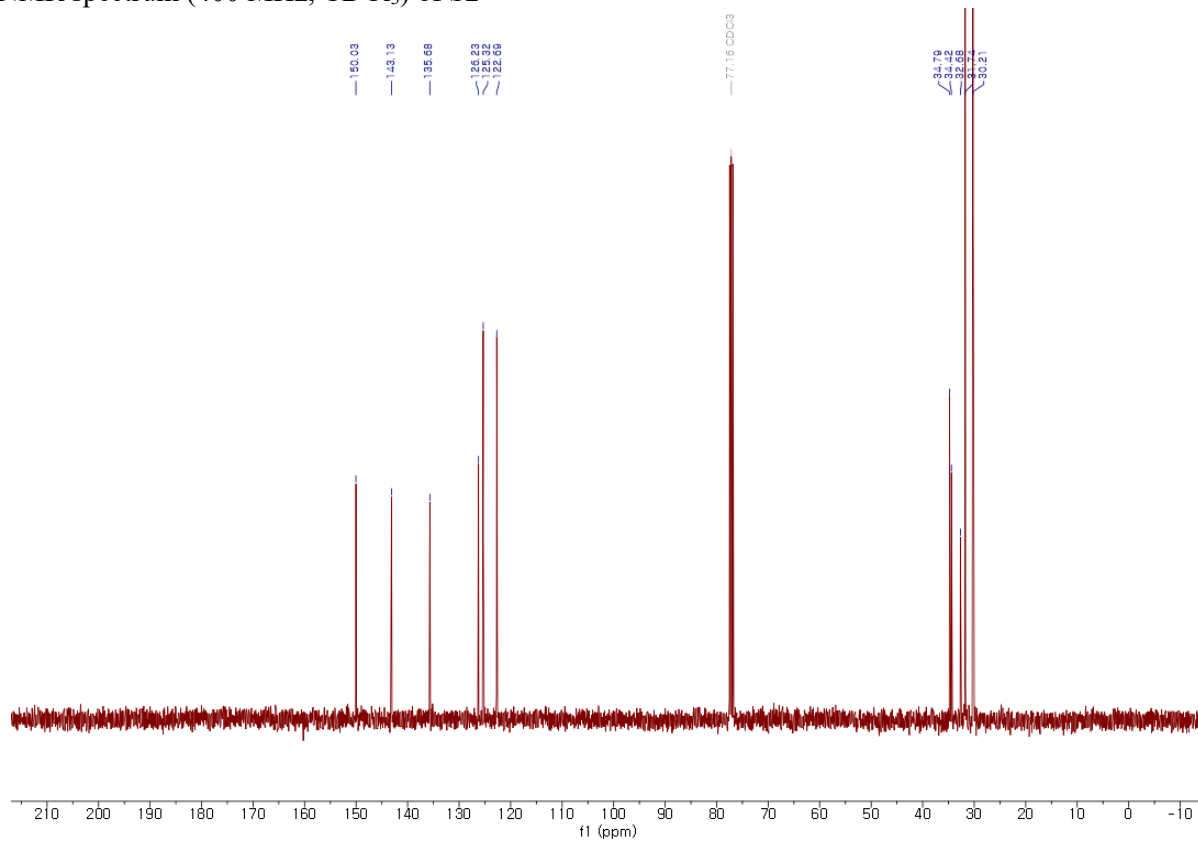
7. Reference

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8. G. M. Sheldrick, SADABS: program for absorption correction with the Bruker SMART system; Universität Göttingen, Germany, 1996.
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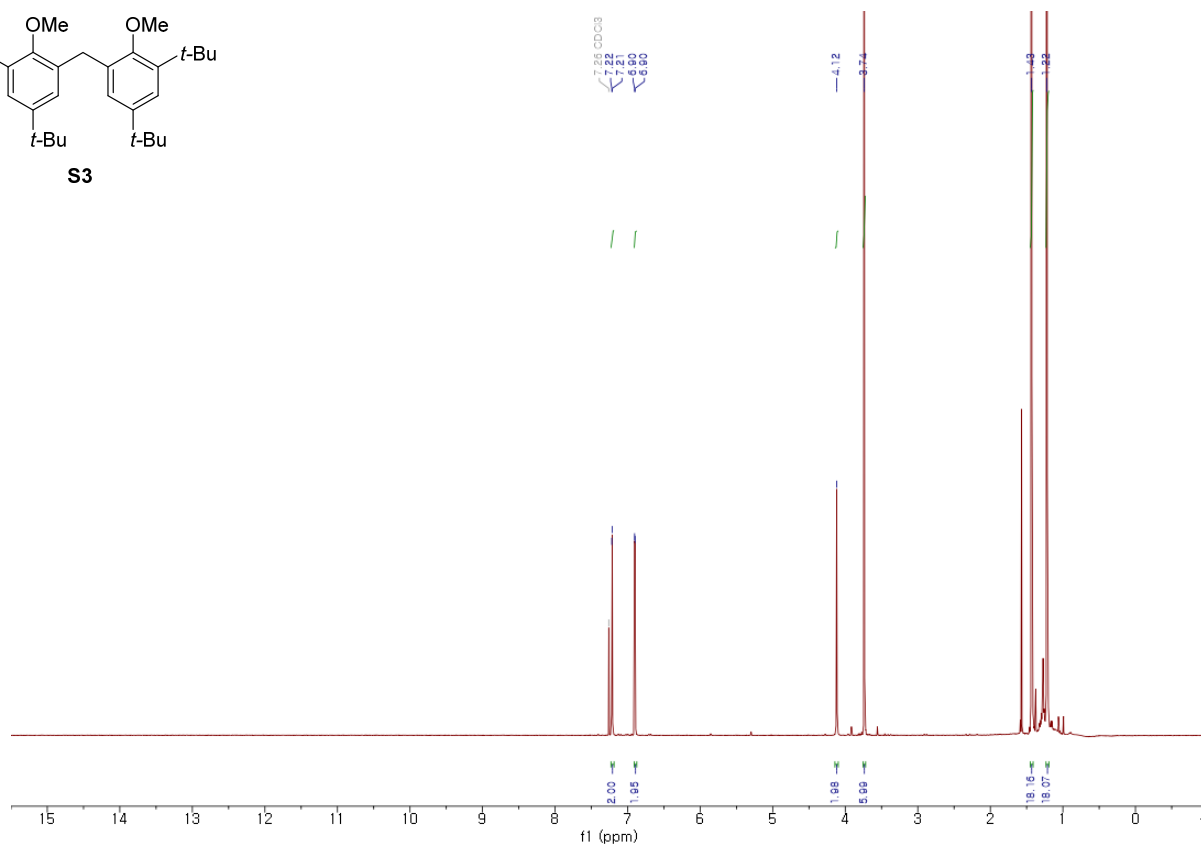
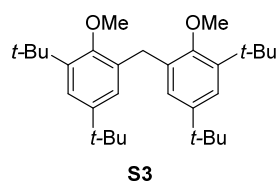
8. NMR Spectra



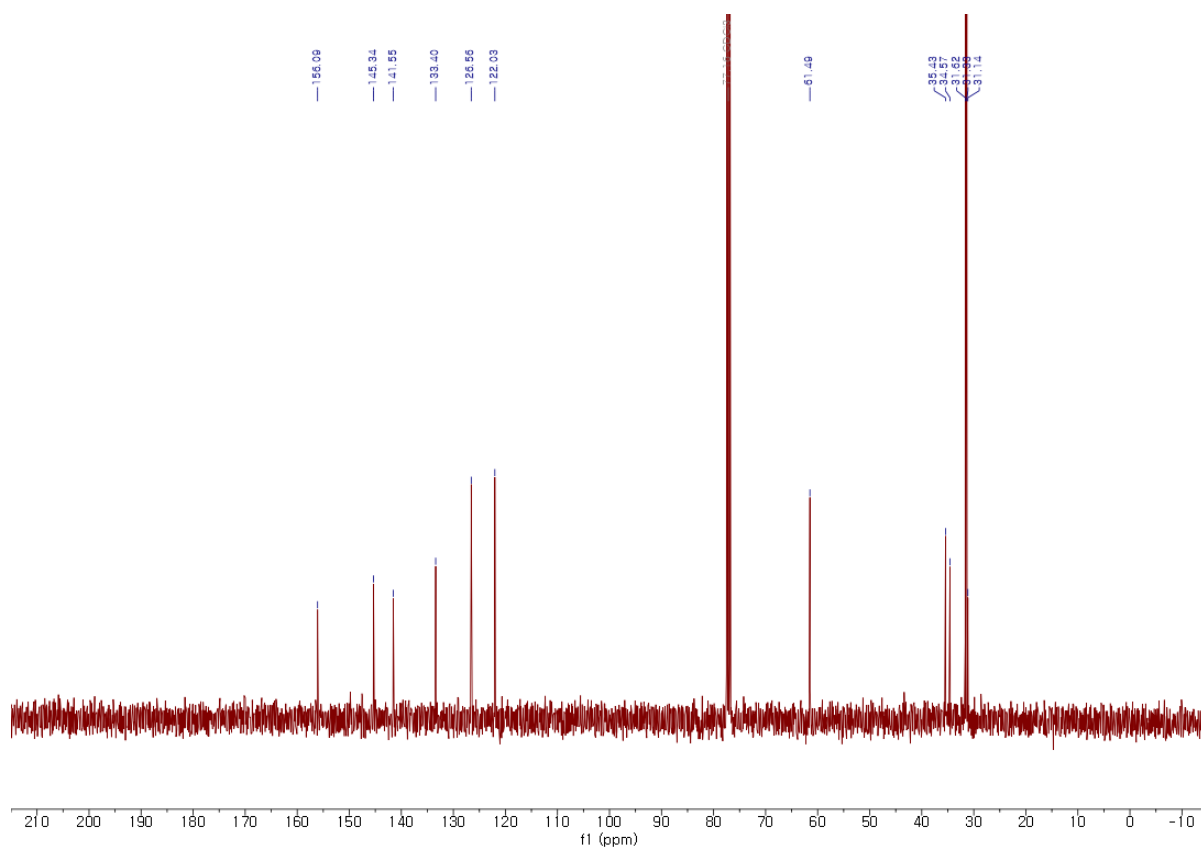
^1H NMR spectrum (400 MHz, CDCl_3) of **S2**



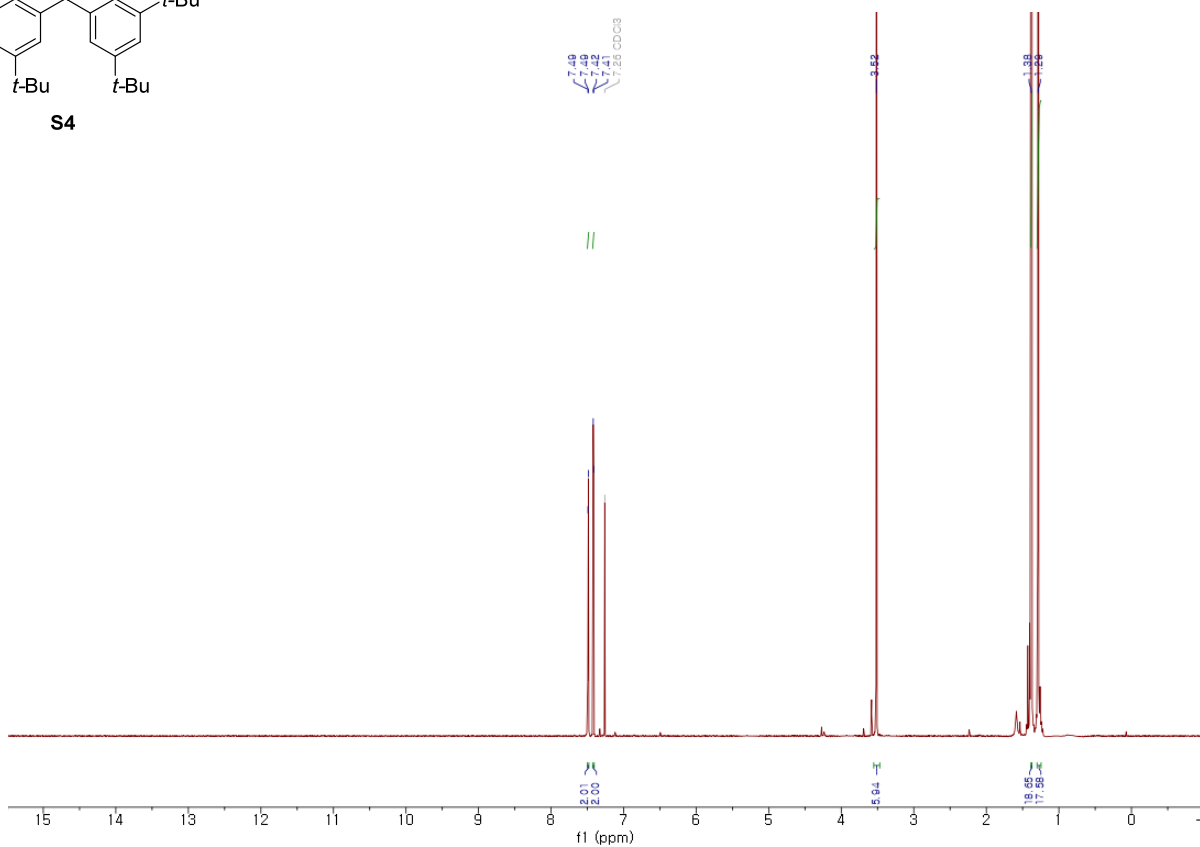
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, CDCl_3) of **S2**



¹H NMR spectrum (400 MHz, CDCl₃) of **S3**



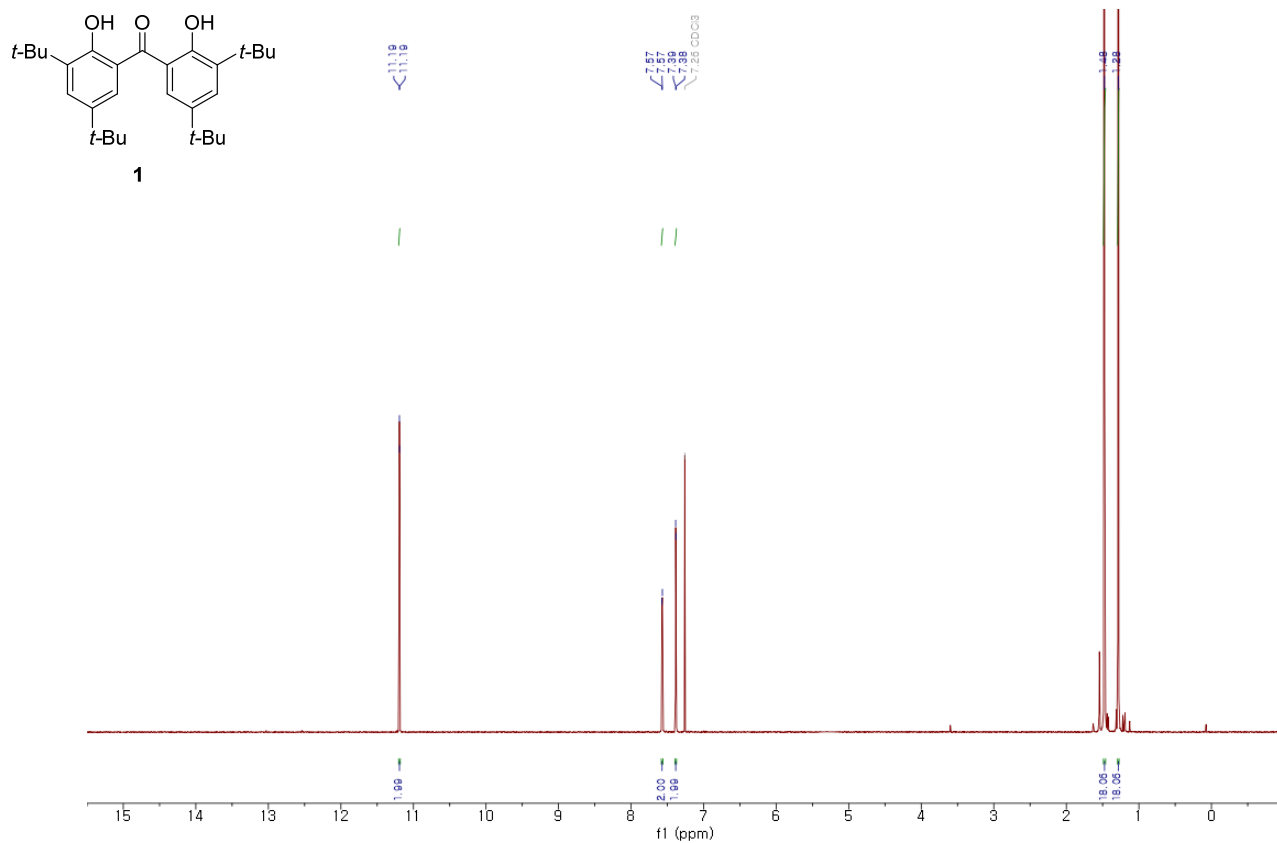
¹³C{¹H} NMR spectrum (100 MHz, CDCl₃) of **S3**



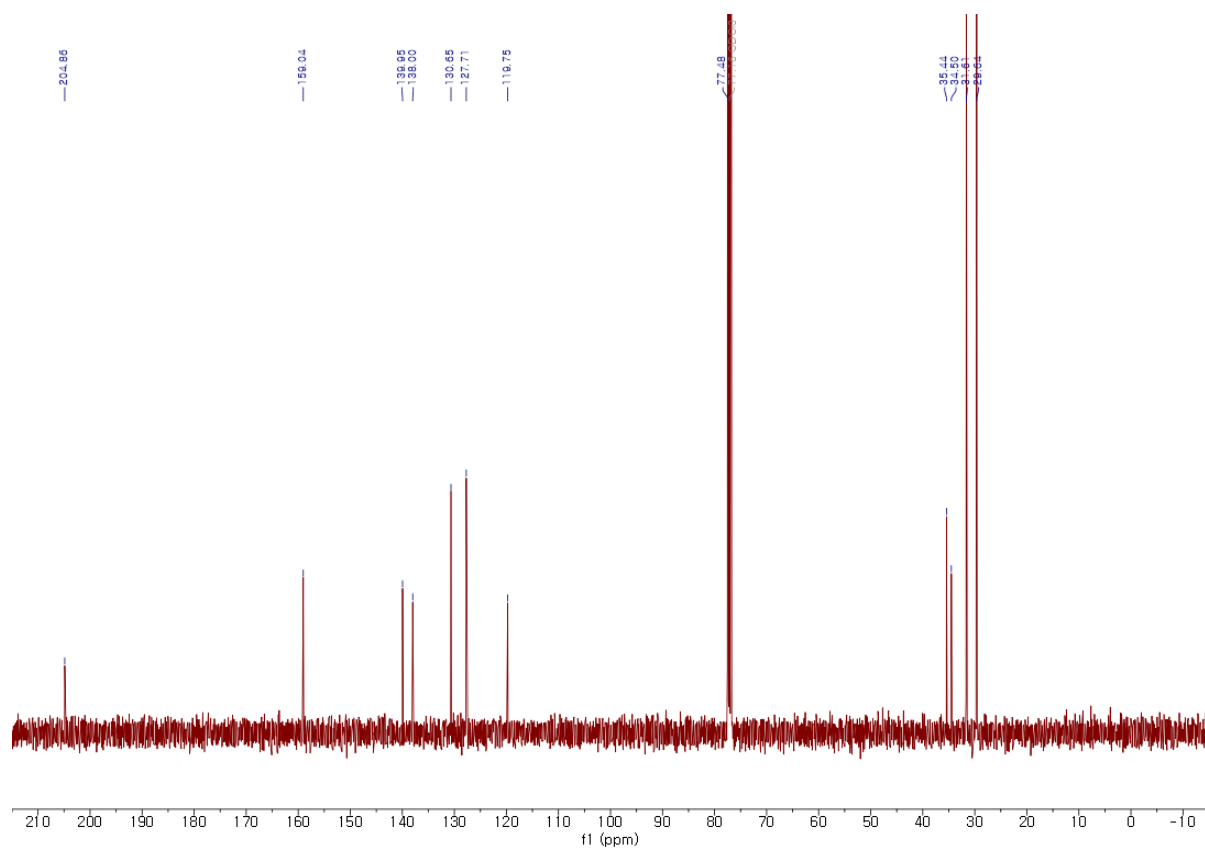
¹³C NMR spectrum (100 MHz, CDCl₃) of 5a. The spectrum shows several peaks in the aromatic and carbonyl region (127-198 ppm) and aliphatic region (31-63 ppm). The solvent peak for CDCl₃ is present at 77.0 ppm.

Chemical Shift (ppm)
197.83
158.15
144.60
142.10
132.38
127.61
127.09
62.85
33.49
31.65
30.95
30.87

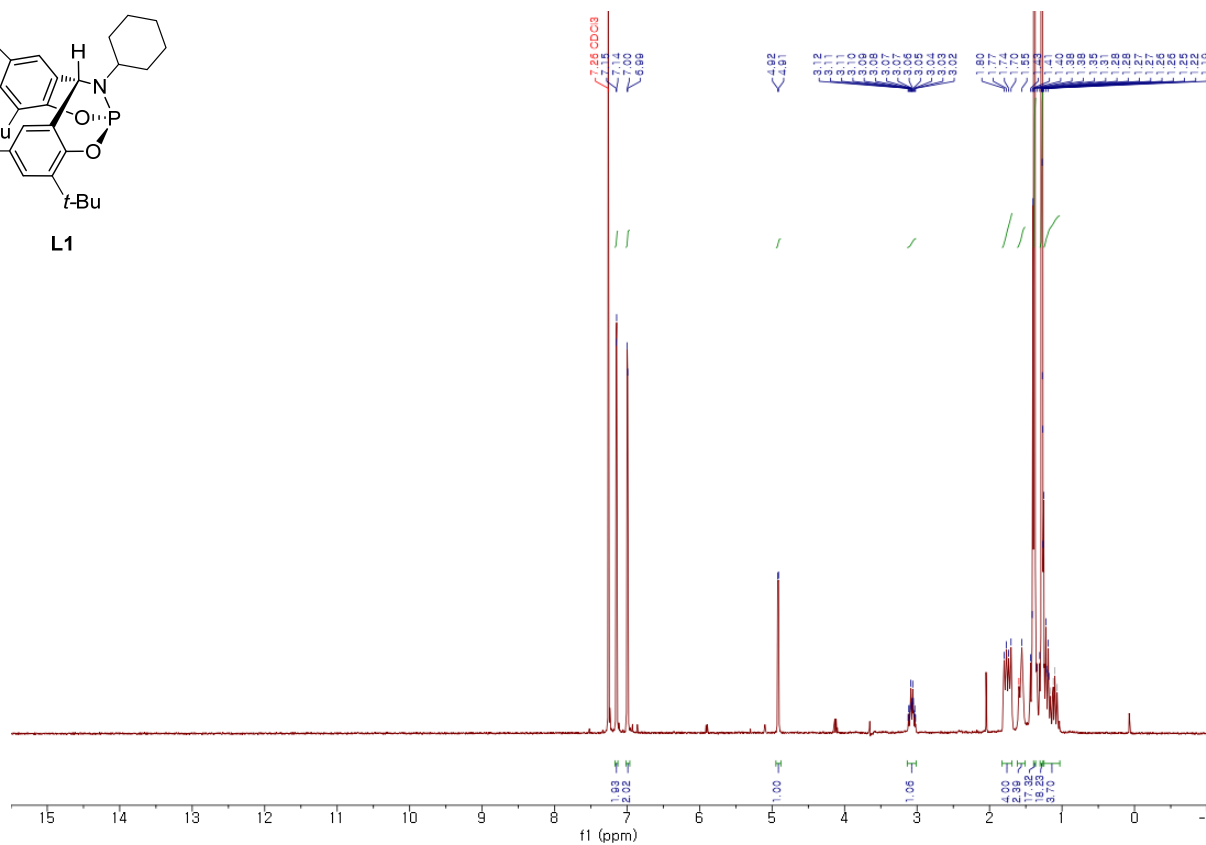
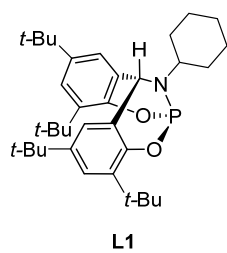
S22



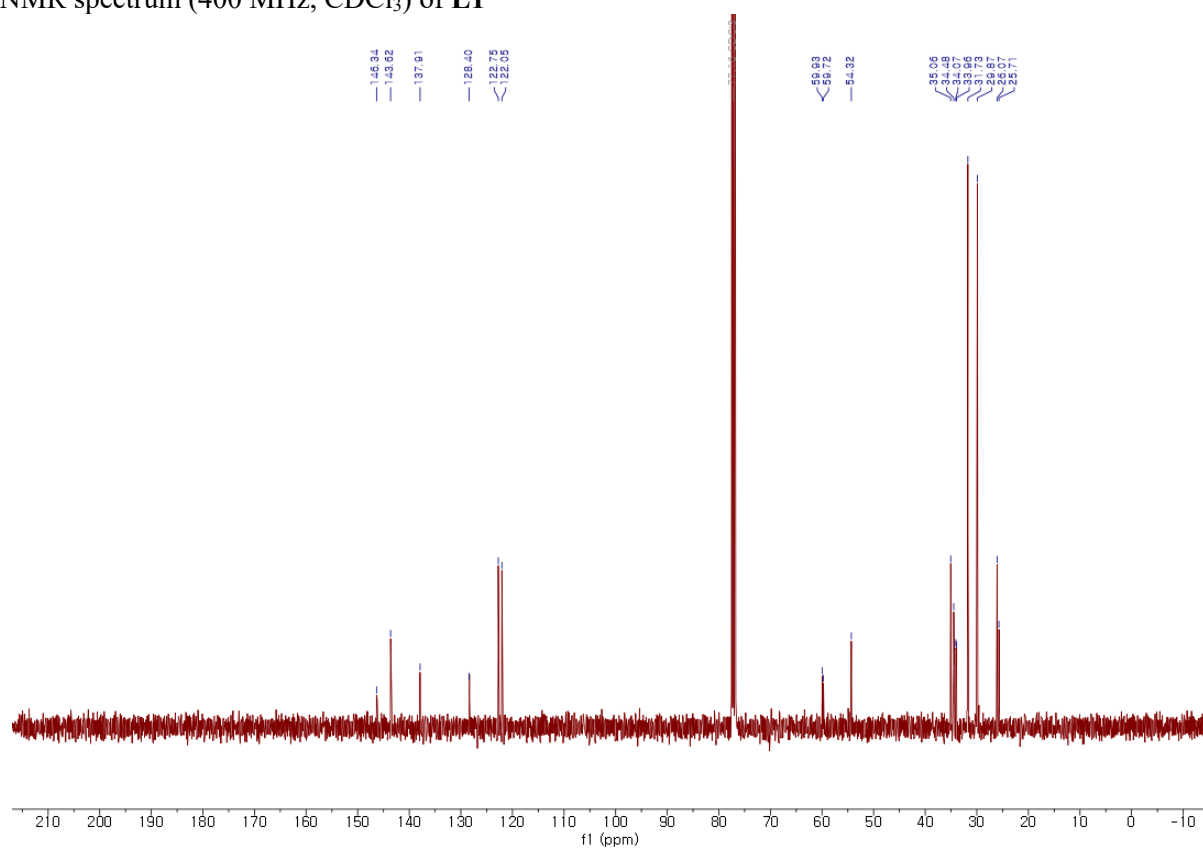
^1H NMR spectrum (400 MHz, CDCl_3) of **1**



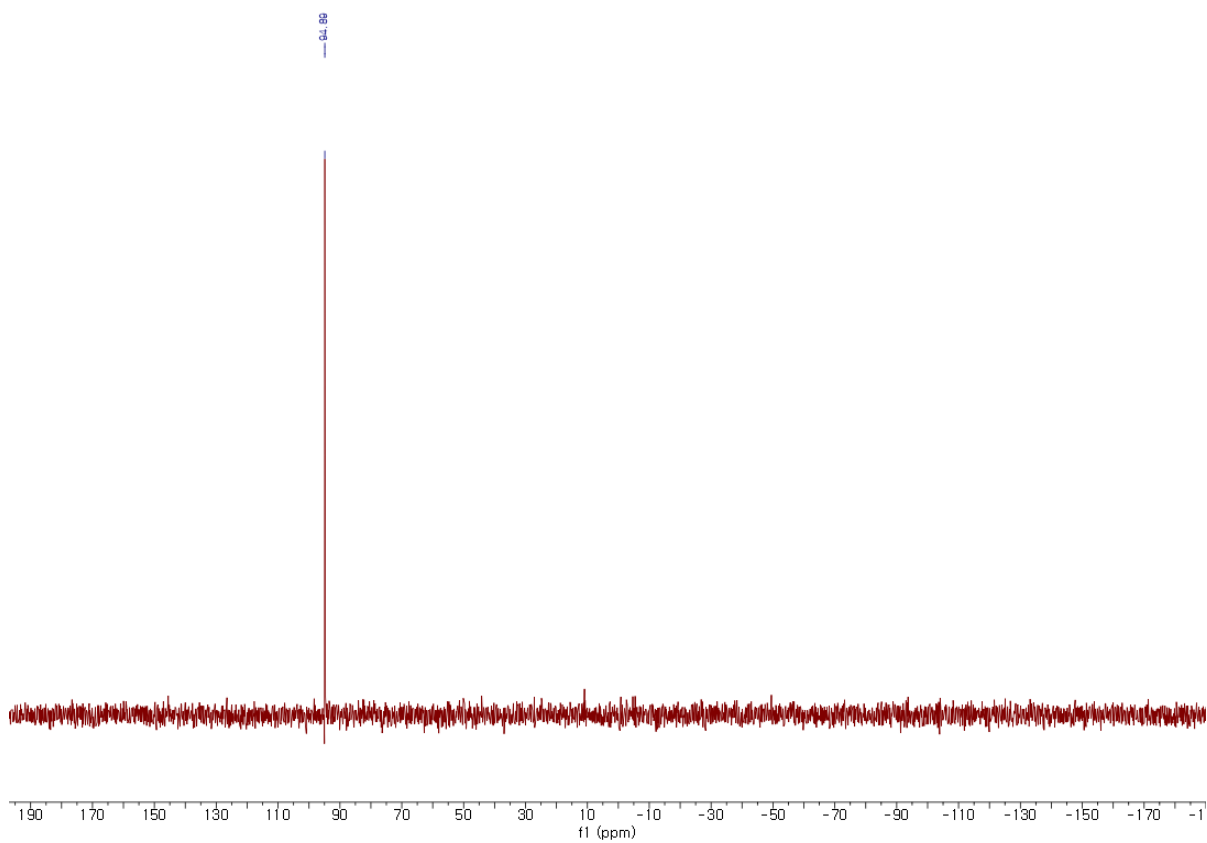
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, CDCl_3) of **1**



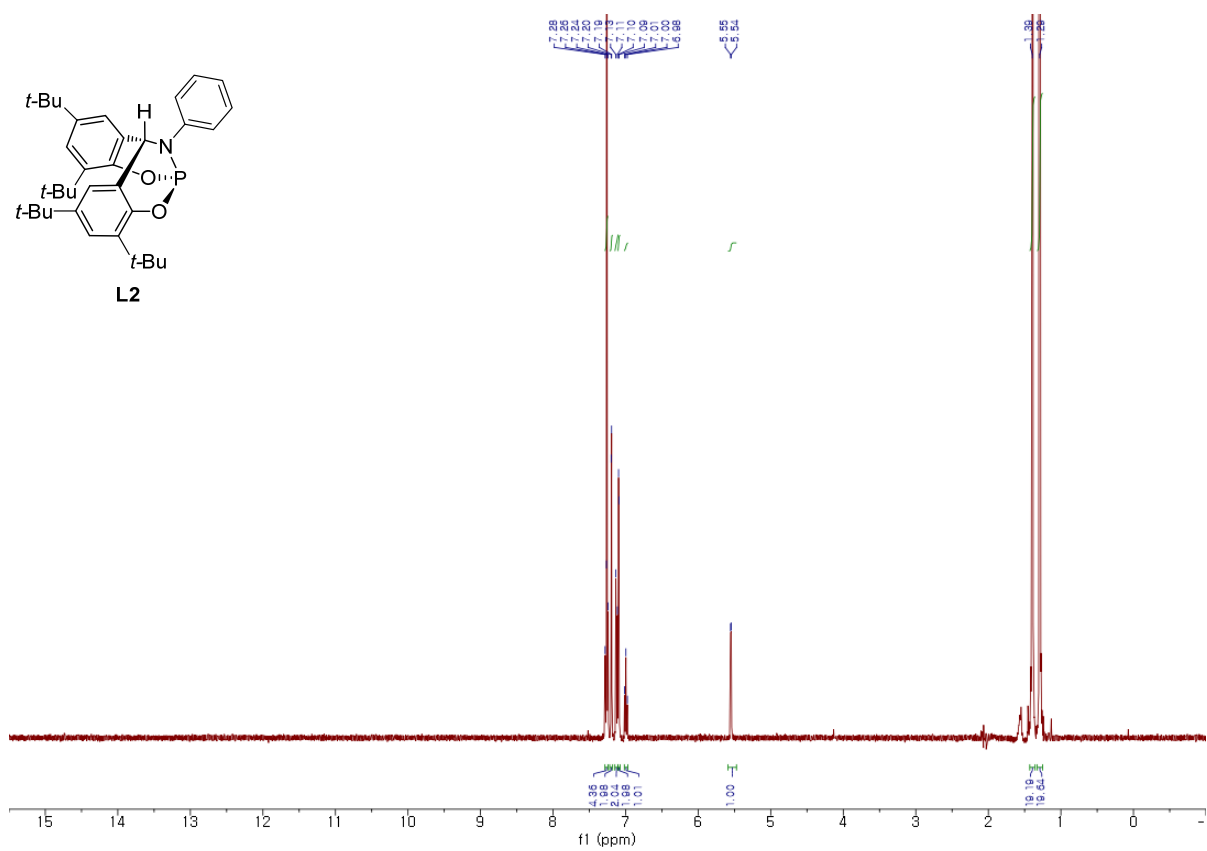
¹H NMR spectrum (400 MHz, CDCl₃) of **L1**



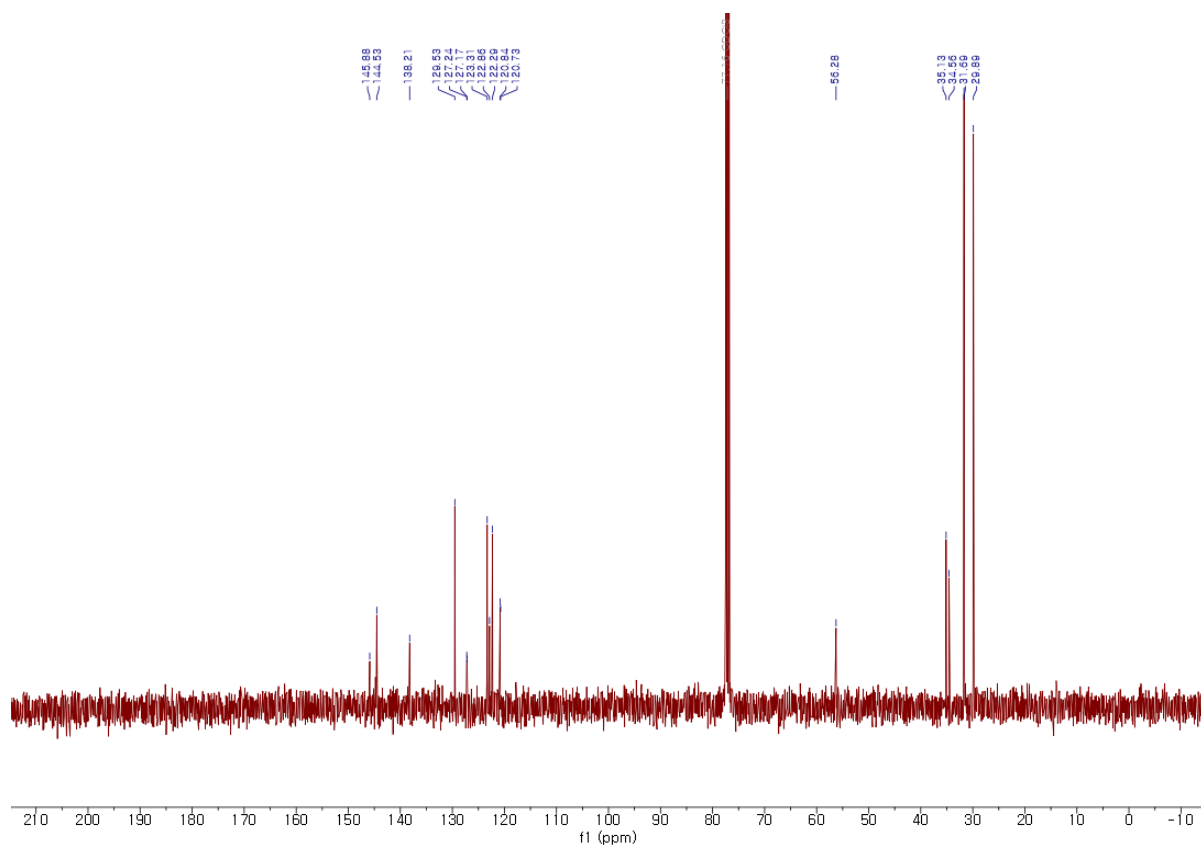
¹³C {¹H} NMR spectrum (100 MHz, CDCl₃) of **L1**



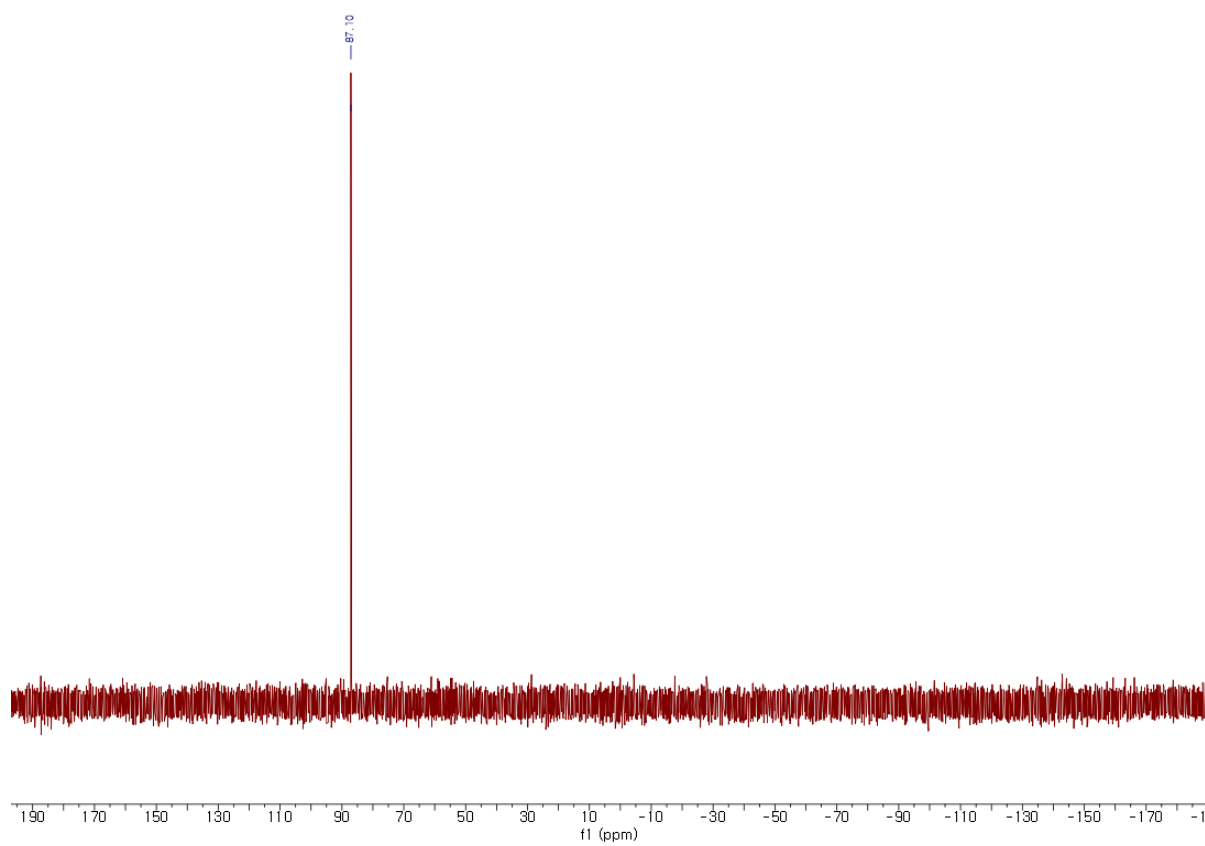
$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, CDCl_3) of **L1**



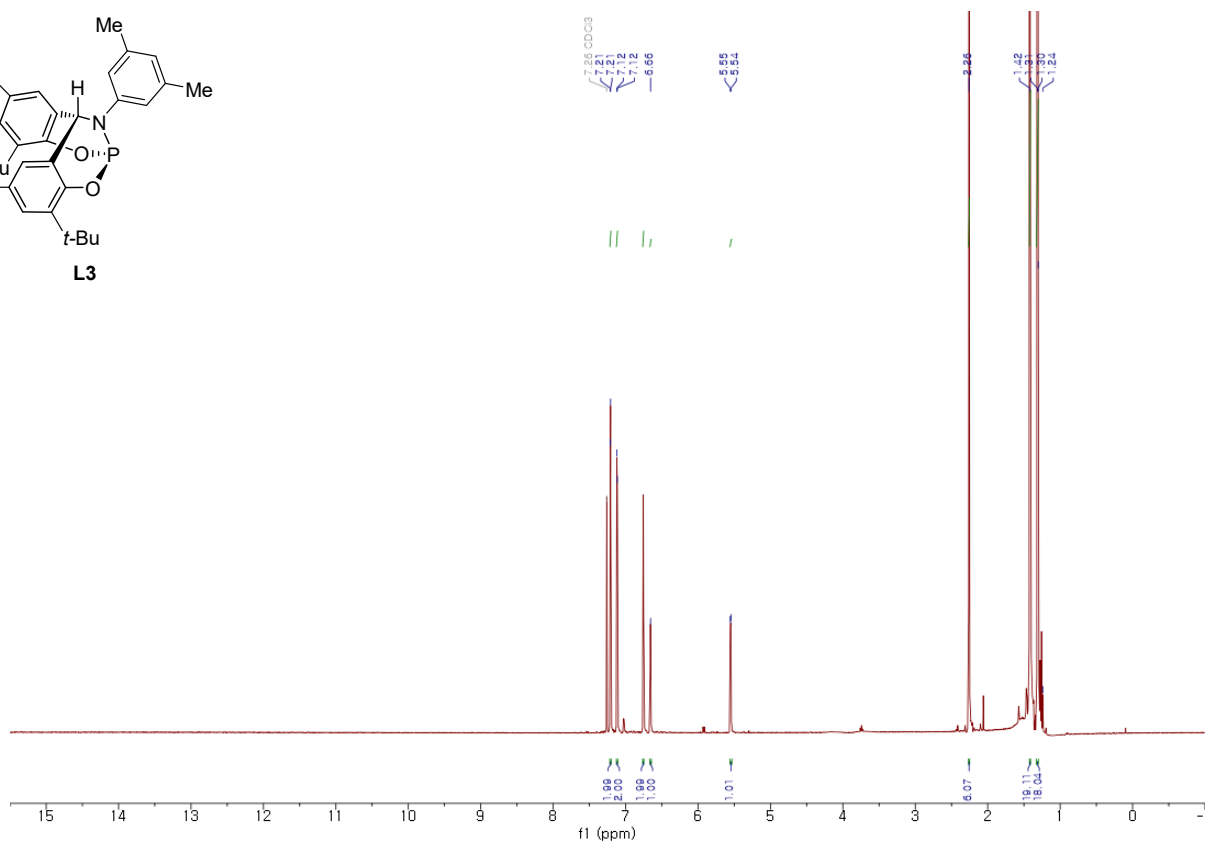
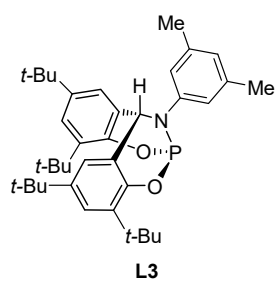
^1H NMR spectrum (400 MHz, CDCl_3) of **L2**



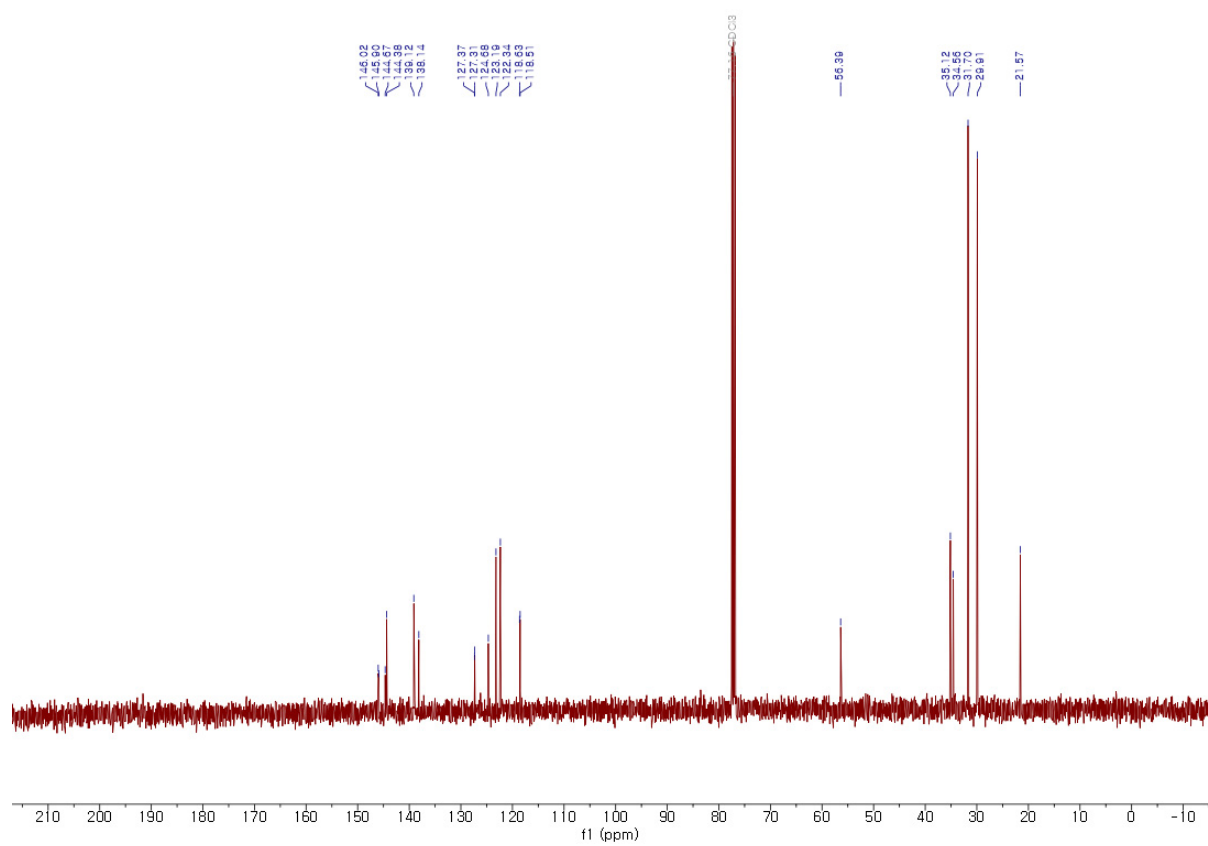
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, CDCl_3) of **L2**



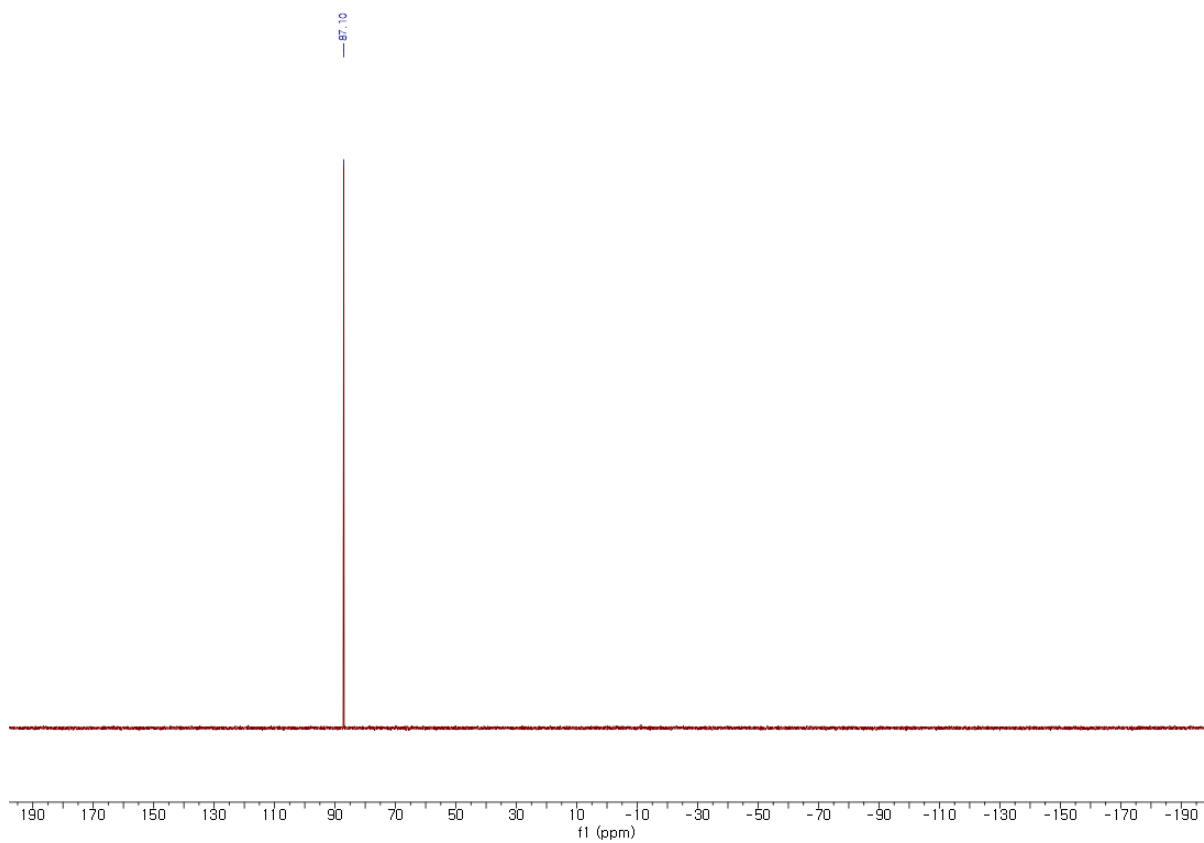
$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, CDCl_3) of **L2**



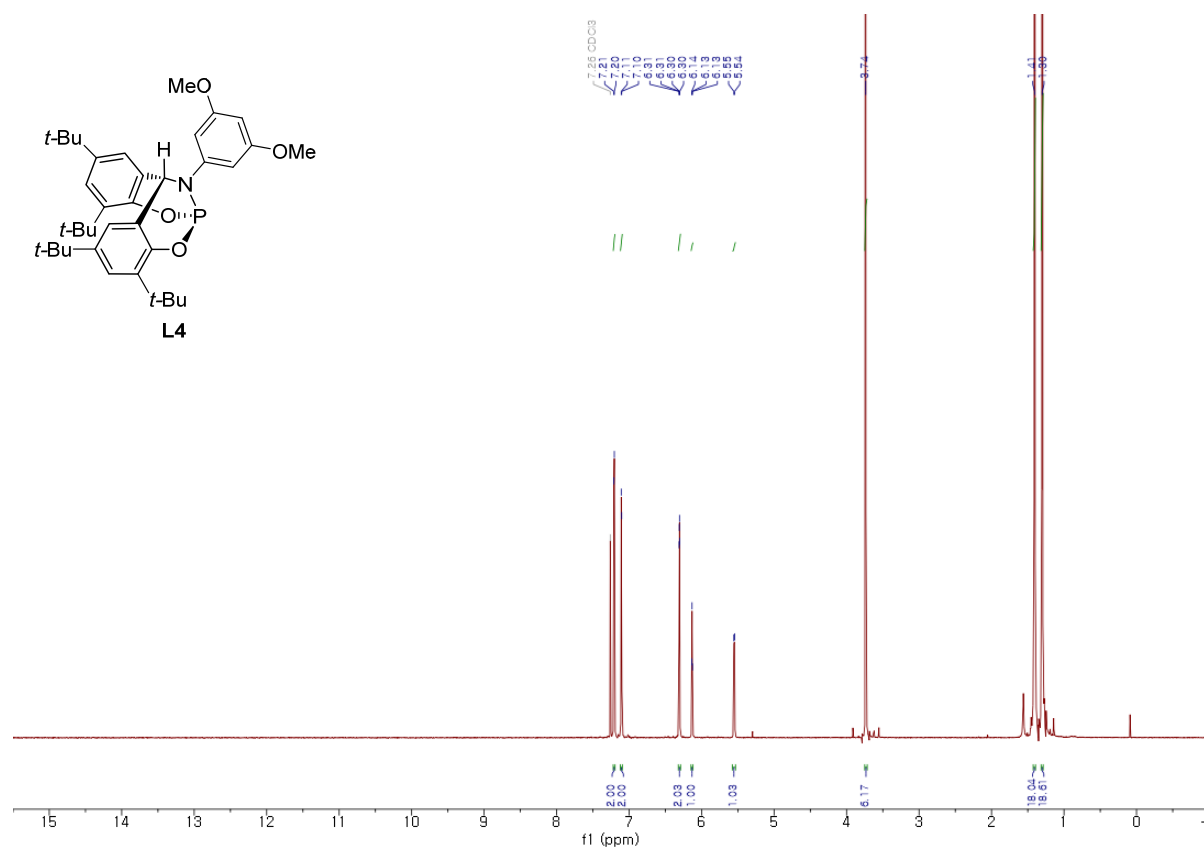
¹H NMR spectrum (400 MHz, CDCl₃) of **L3**



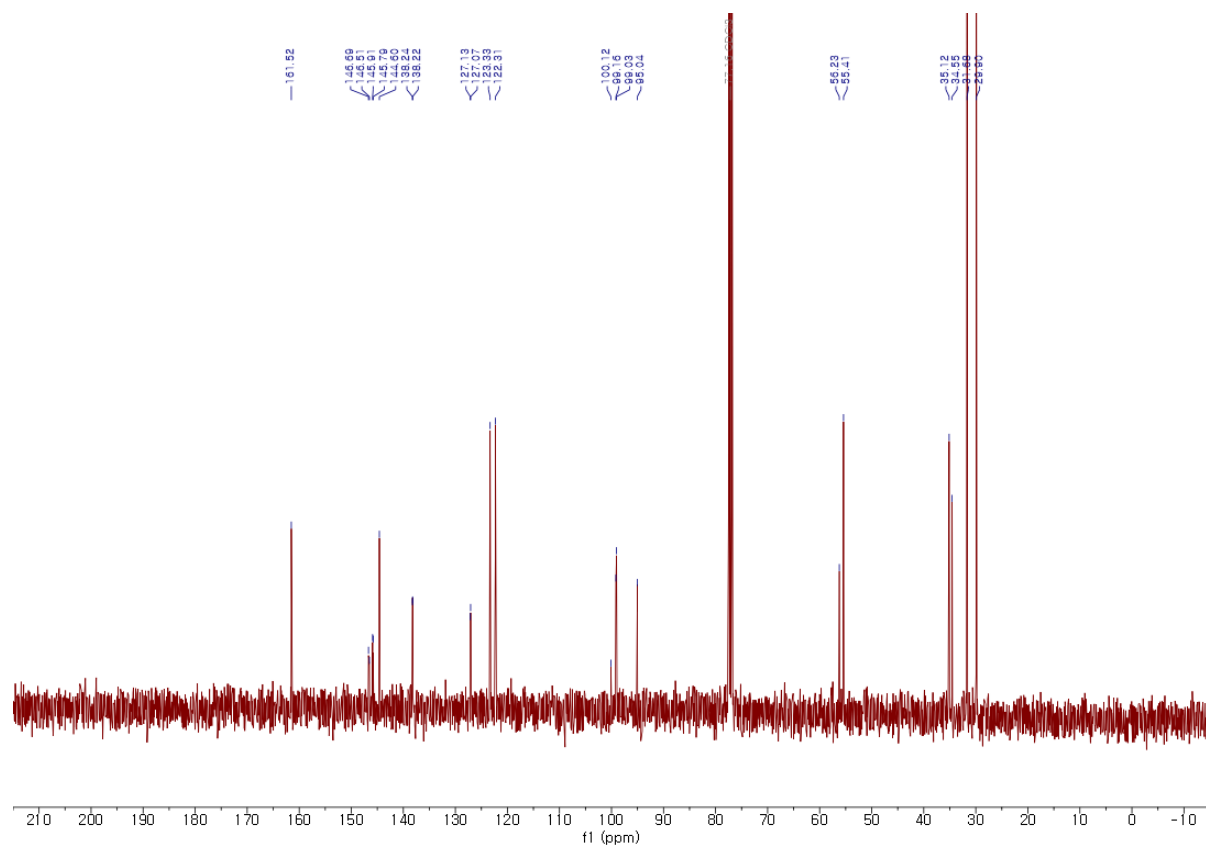
¹³C{¹H} NMR spectrum (100 MHz, CDCl₃) of **L3**



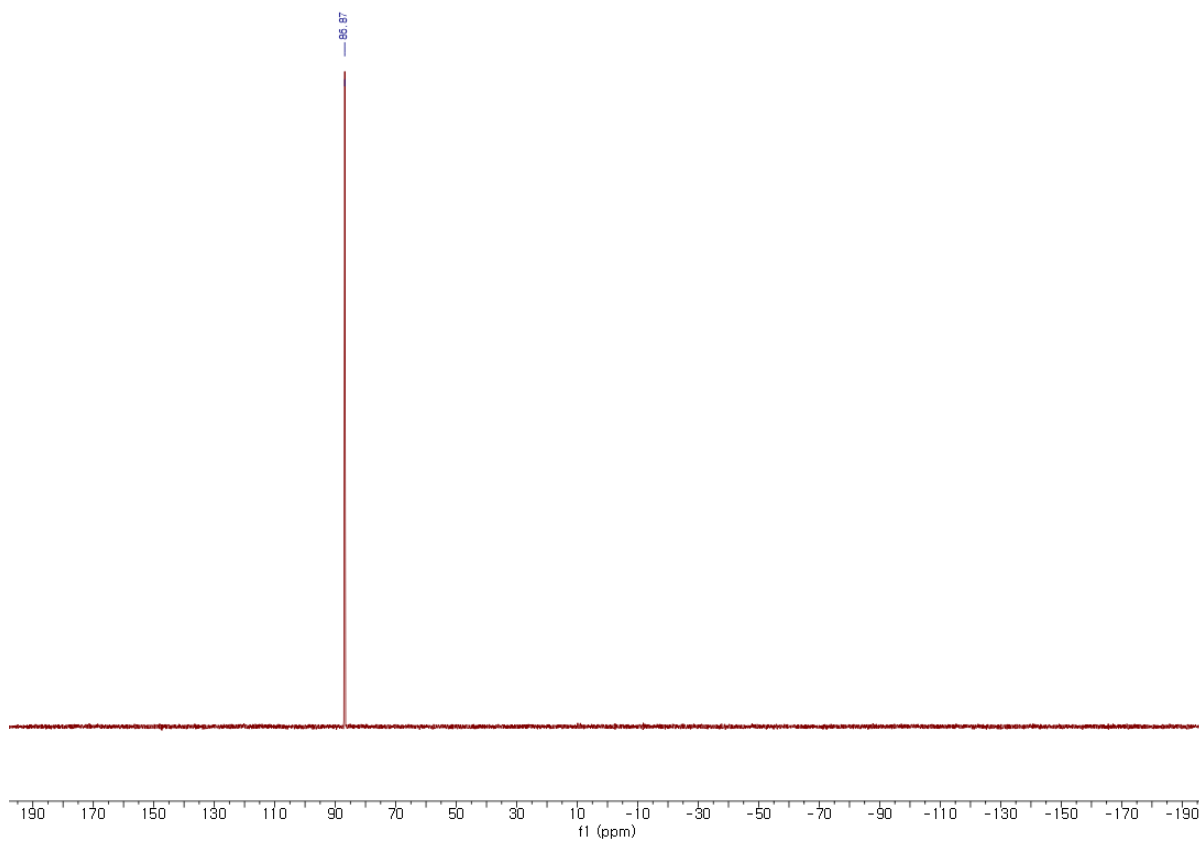
$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, CDCl_3) of **L3**



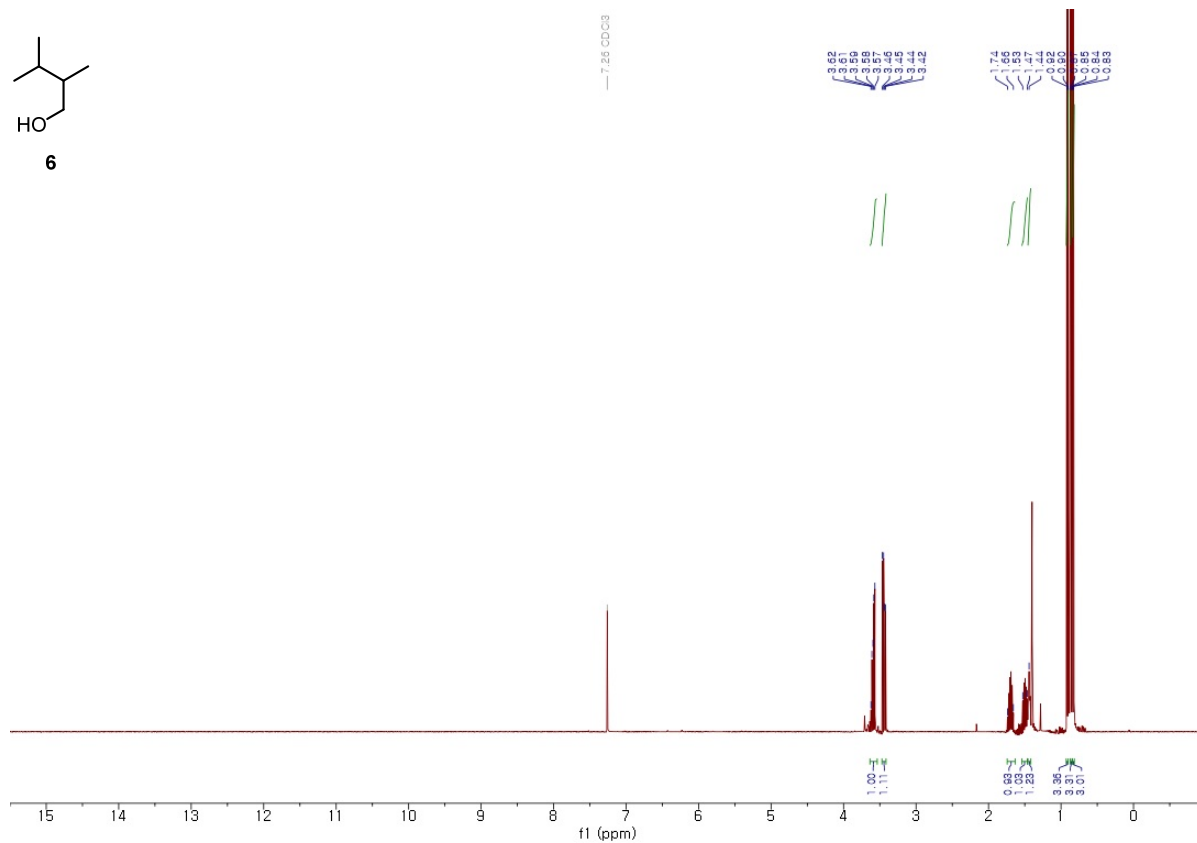
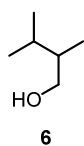
^1H NMR spectrum (400 MHz, CDCl_3) of **L4**



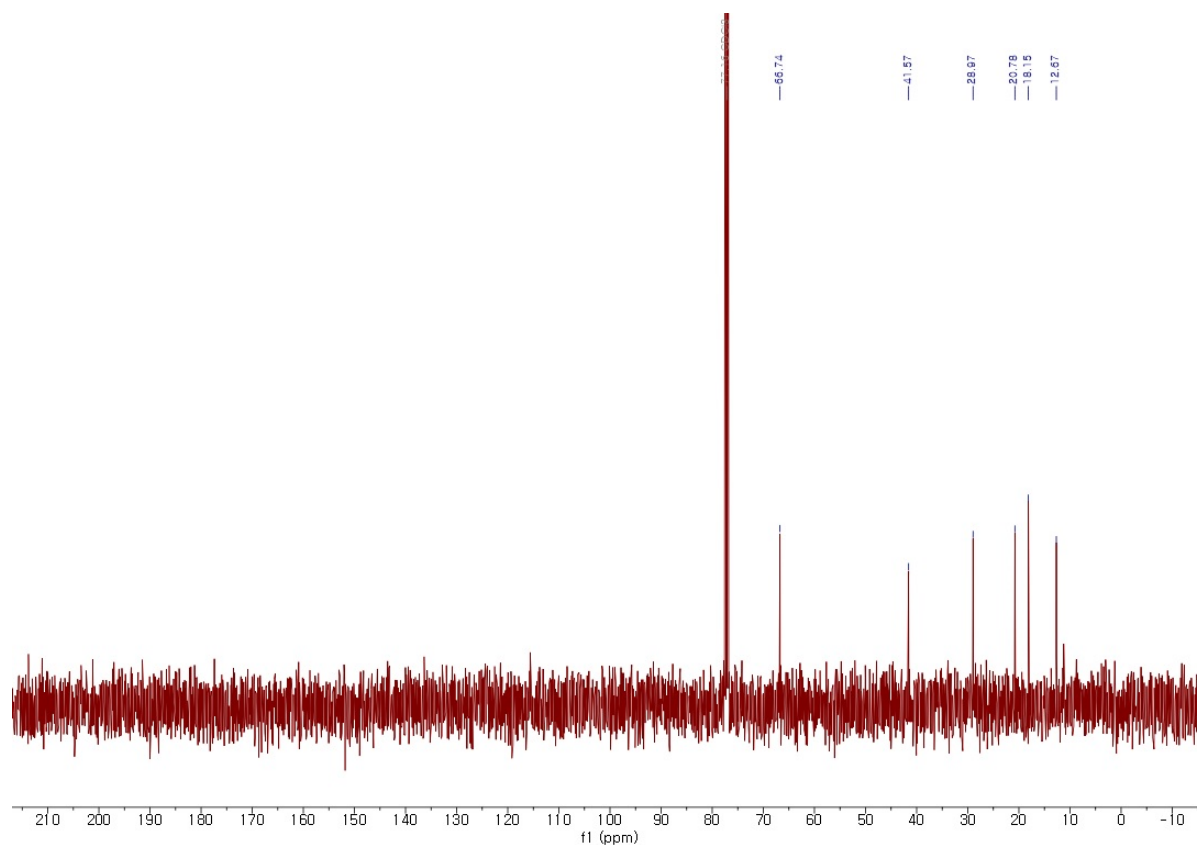
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, CDCl_3) of **L4**



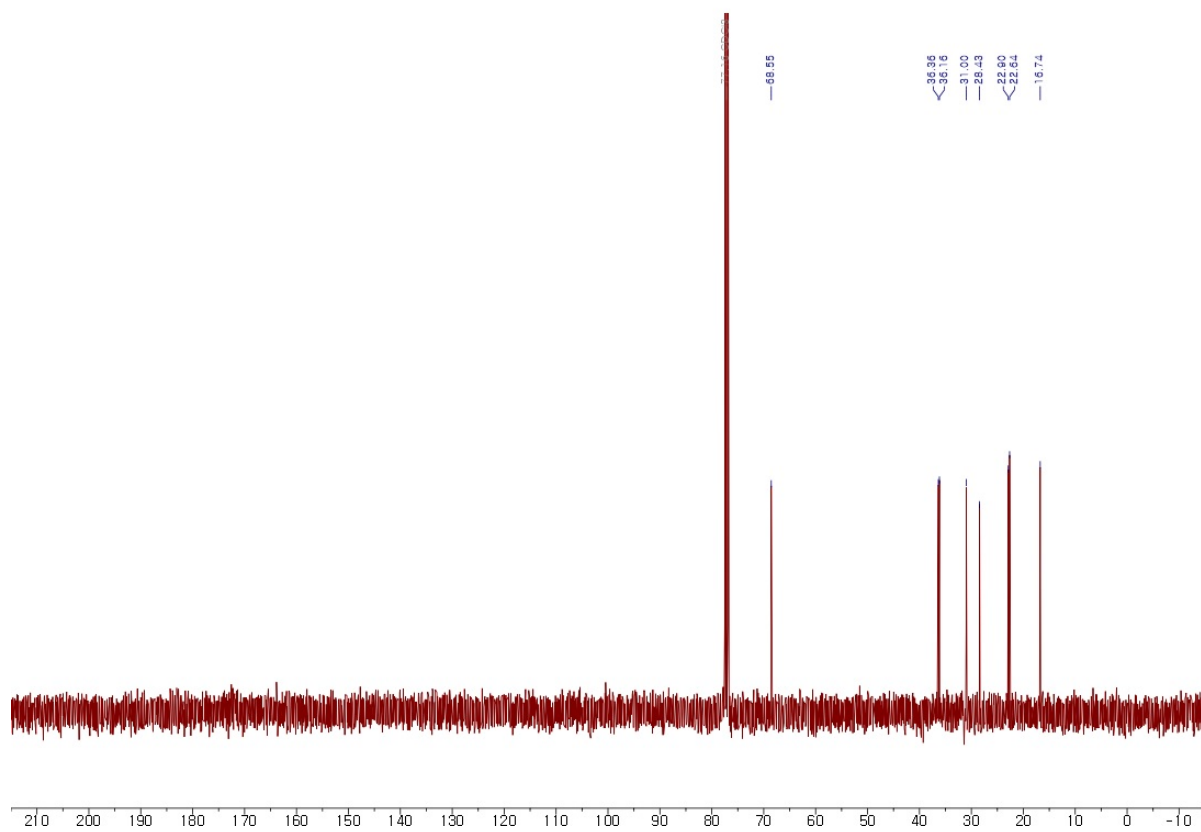
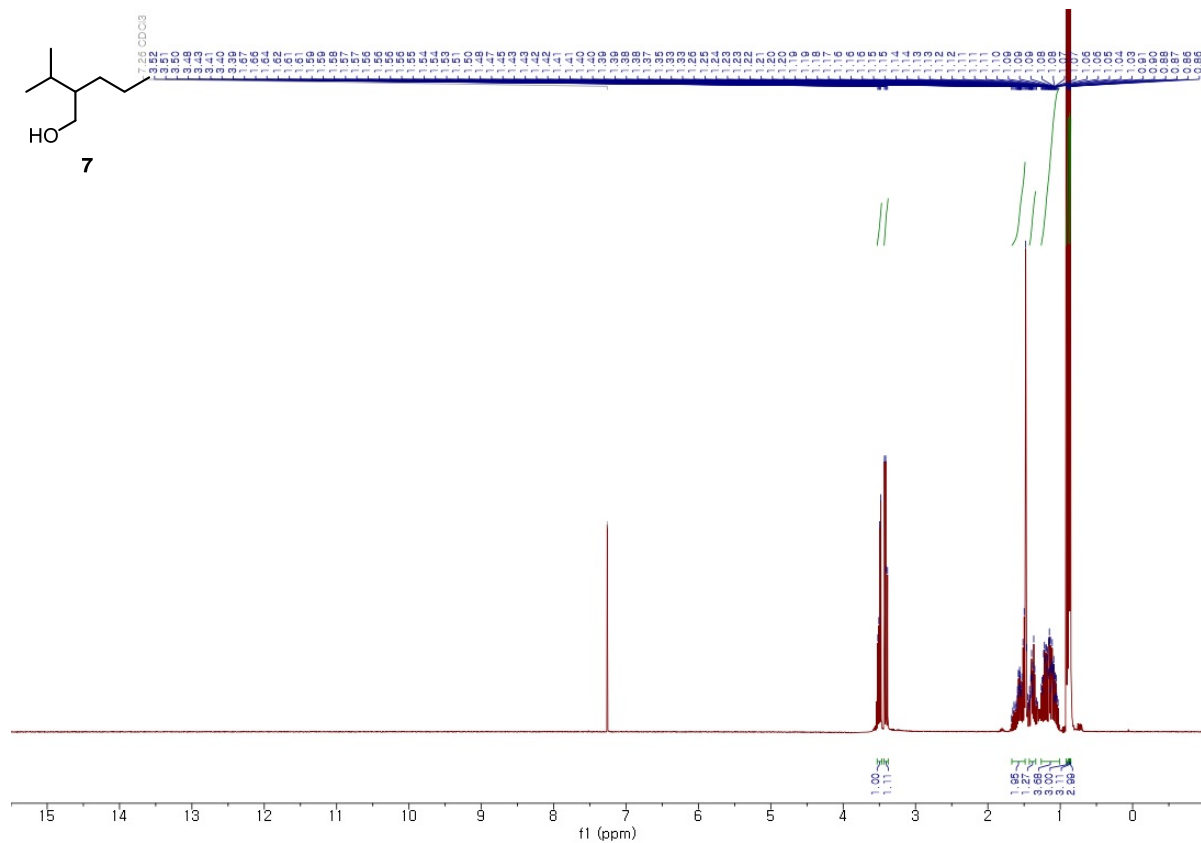
$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, CDCl_3) of **L4**

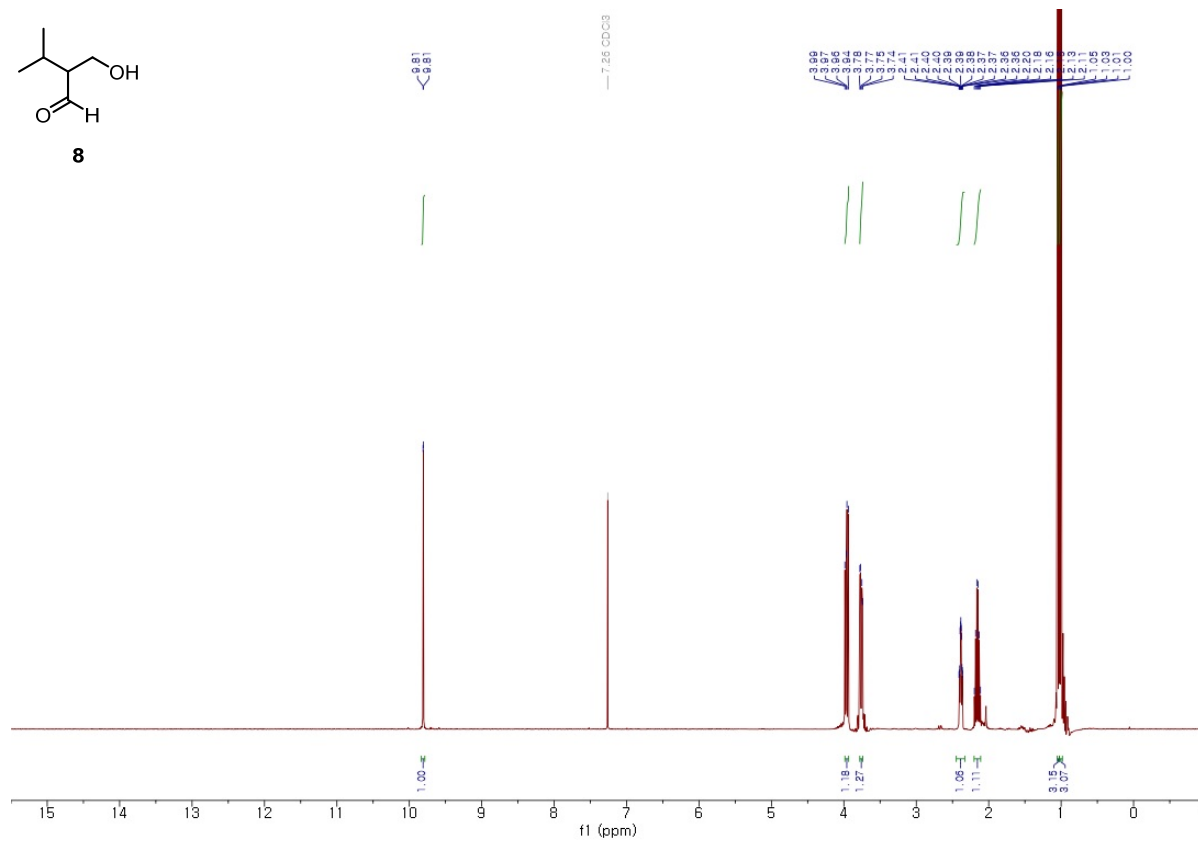
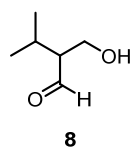


^1H NMR spectrum (400 MHz, CDCl_3) of **6**

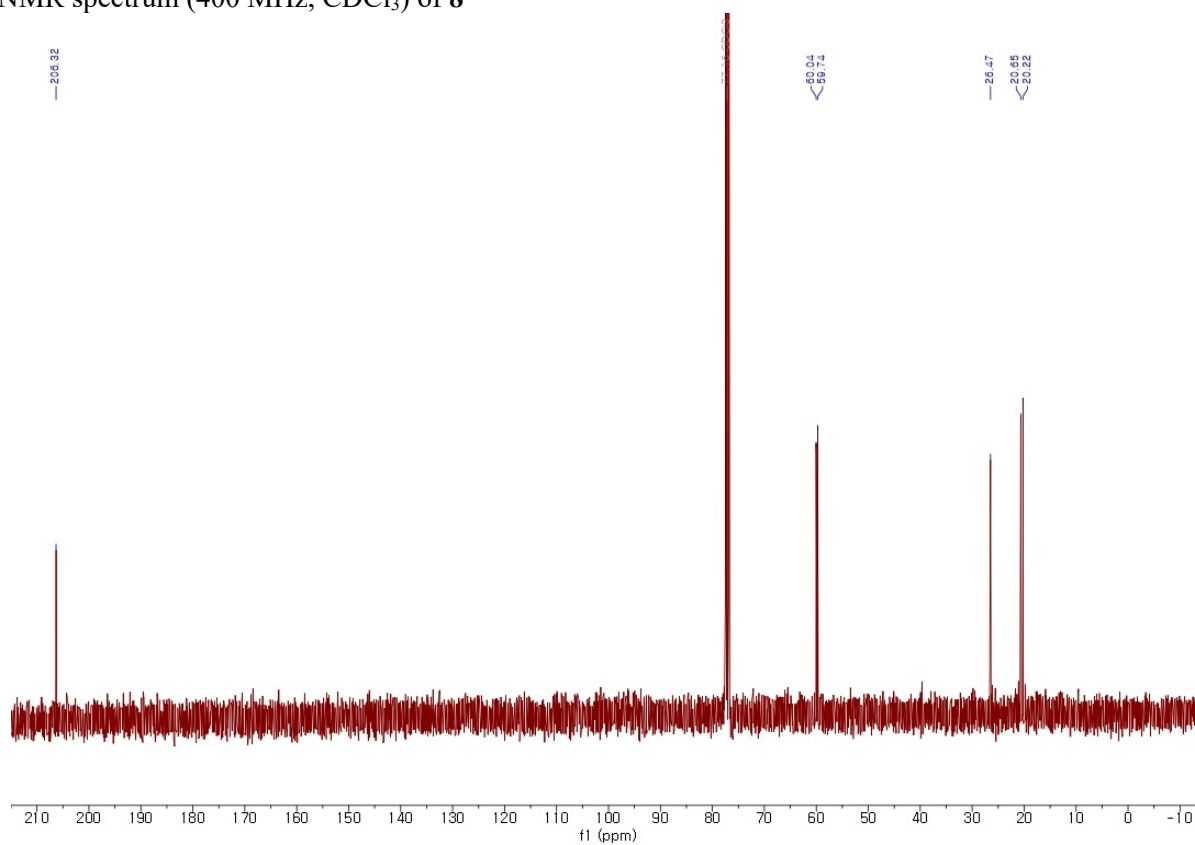


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, CDCl_3) of **6**

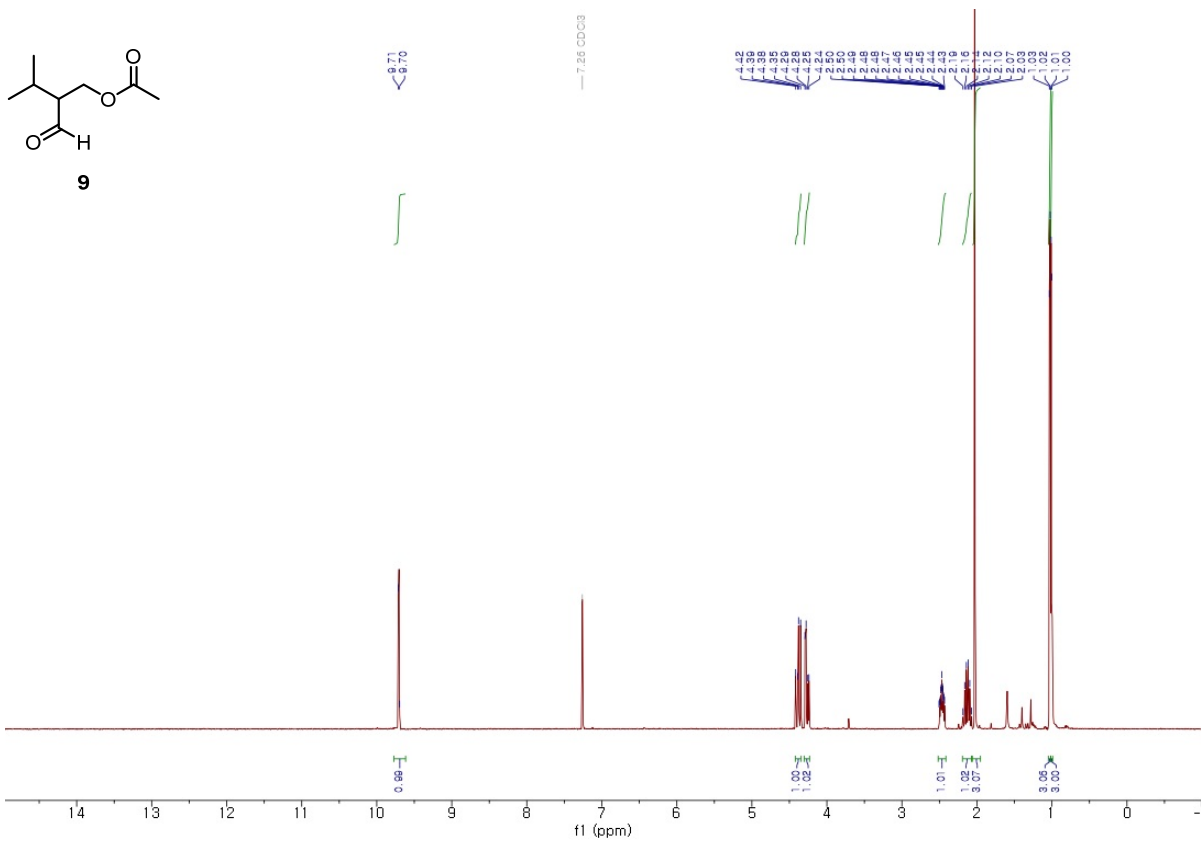




^1H NMR spectrum (400 MHz, CDCl_3) of **8**

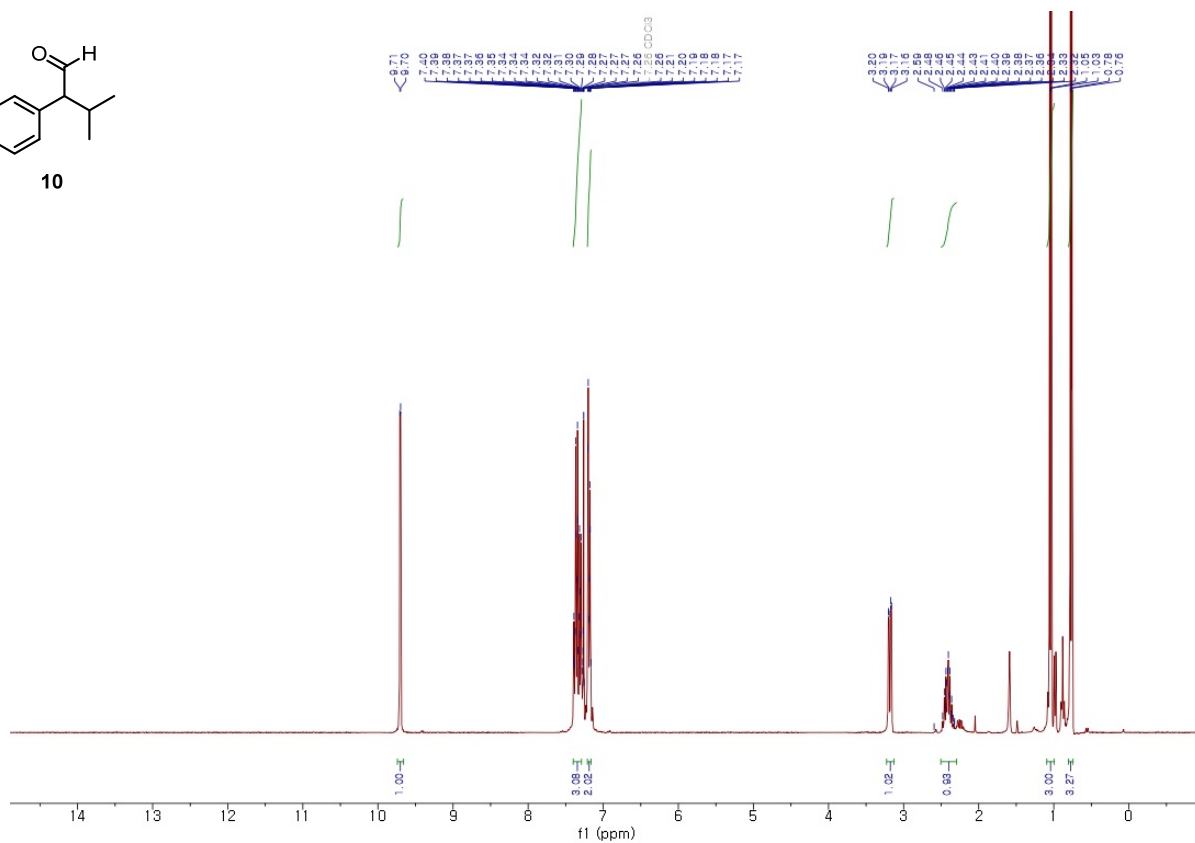
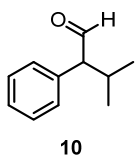


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, CDCl_3) of **8**

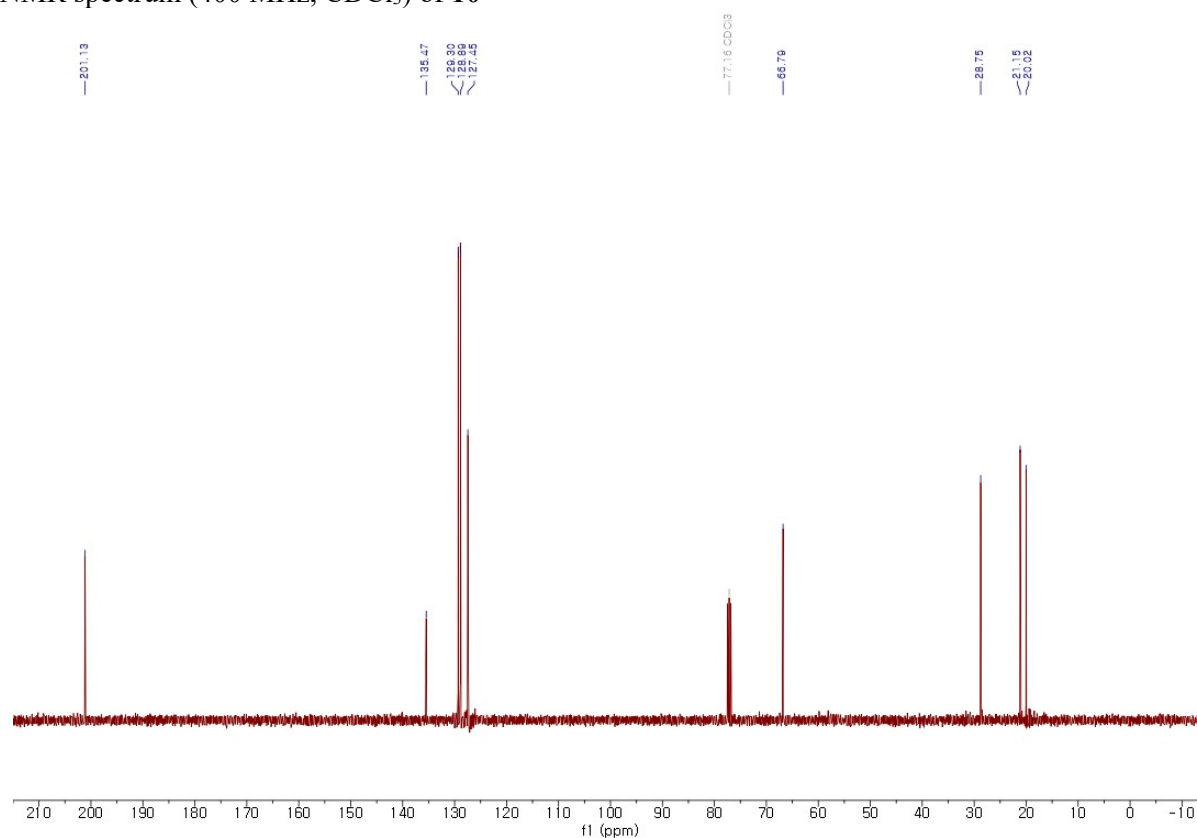


¹³C NMR spectrum of compound 10a in CDCl₃. The x-axis is labeled 'f1 (ppm)' and ranges from -10 to 210. The spectrum shows several sharp peaks. Key peaks are labeled with their chemical shifts: 202.71, 170.75, 77.16 (CDCl₃), 61.00, 56.84, 26.34, 20.73, 20.27, and 19.73. A cluster of peaks is visible between 20 and 30 ppm.

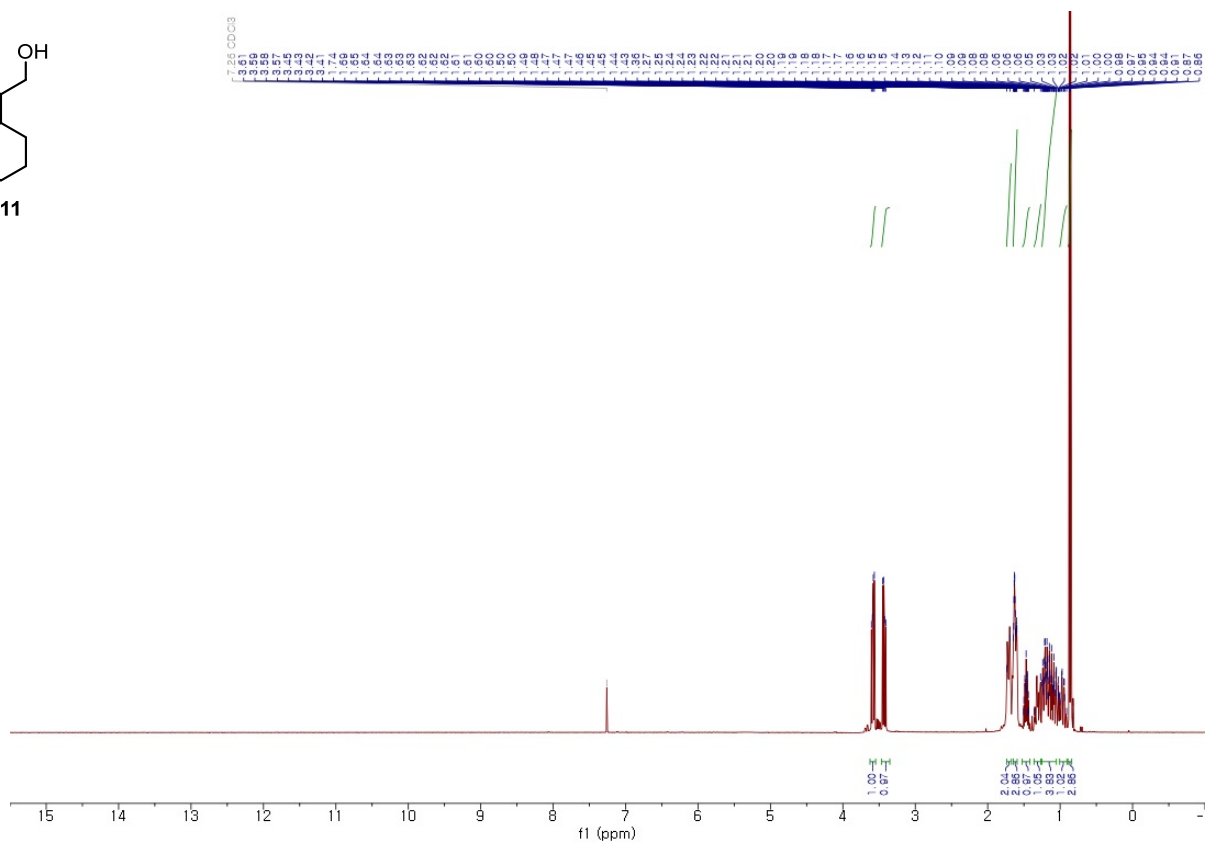
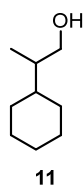
S33



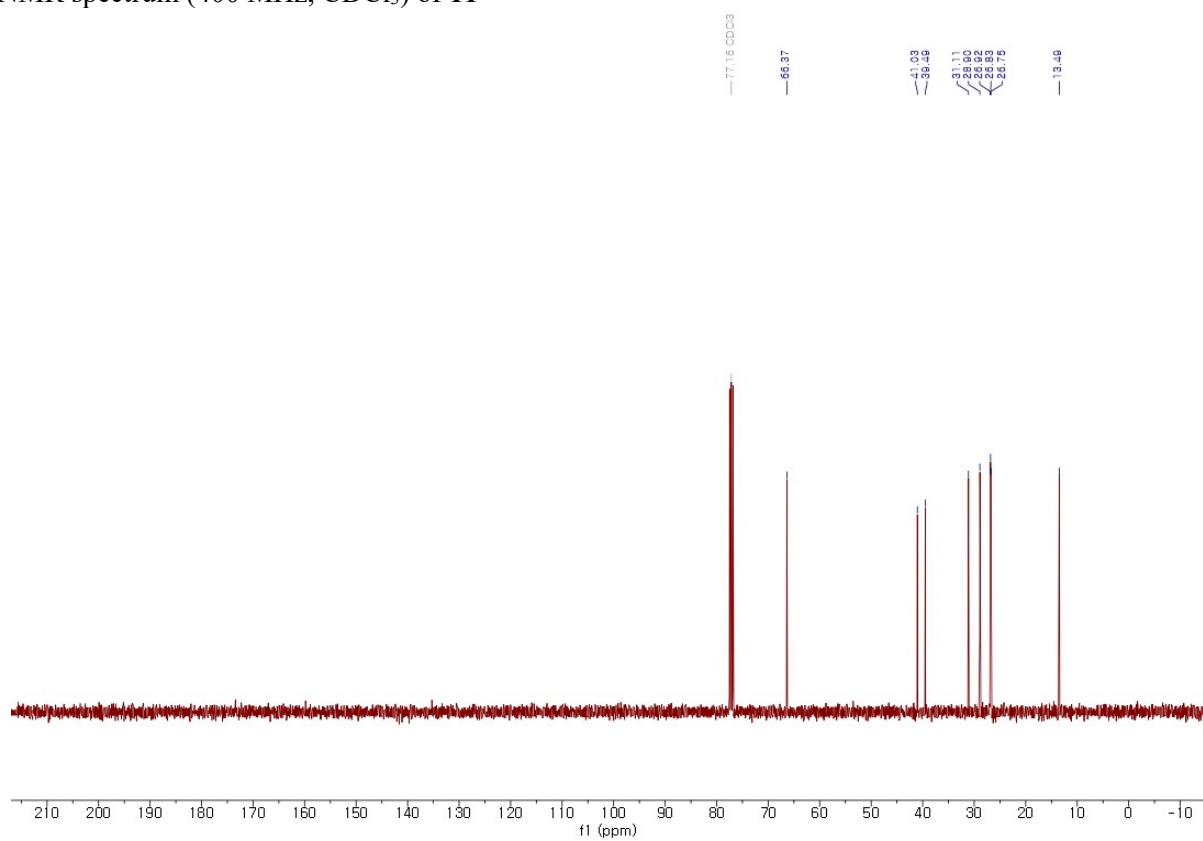
^1H NMR spectrum (400 MHz, CDCl_3) of **10**



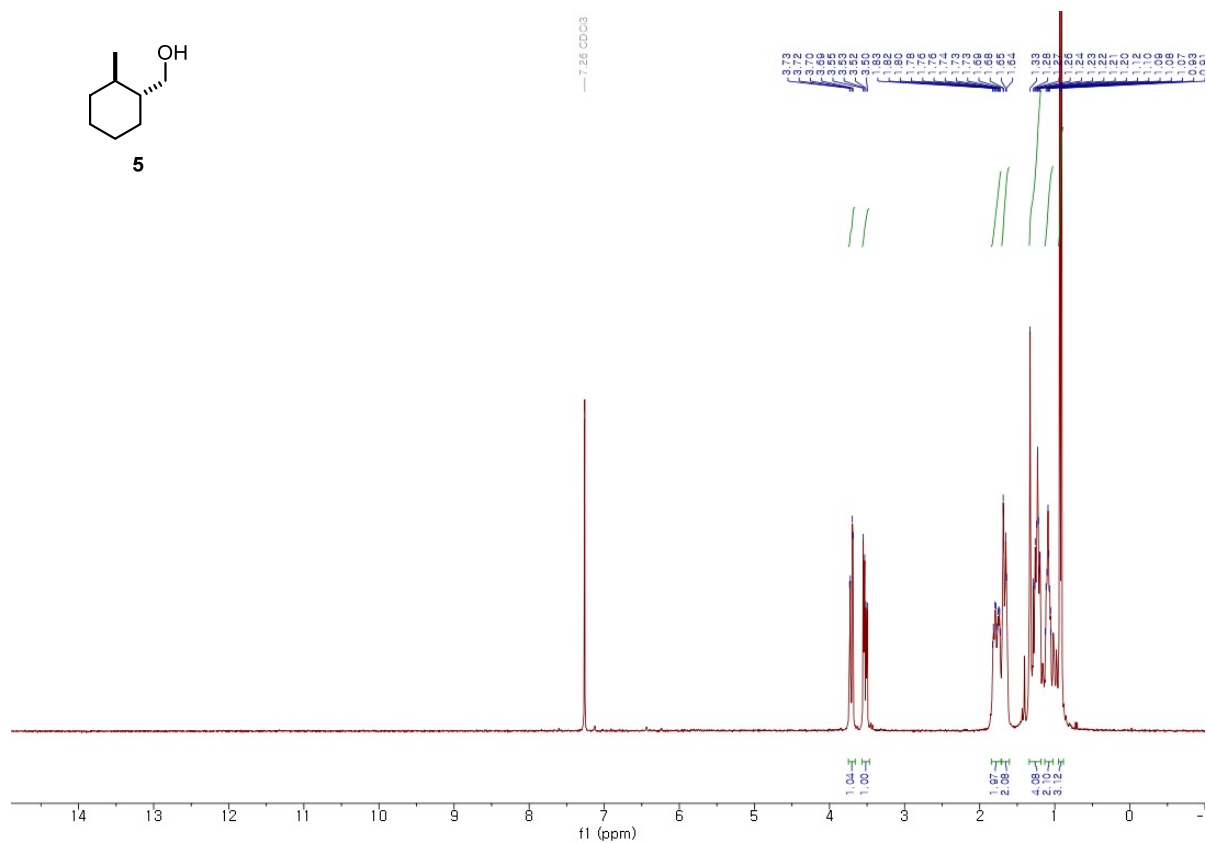
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, CDCl_3) of **10**

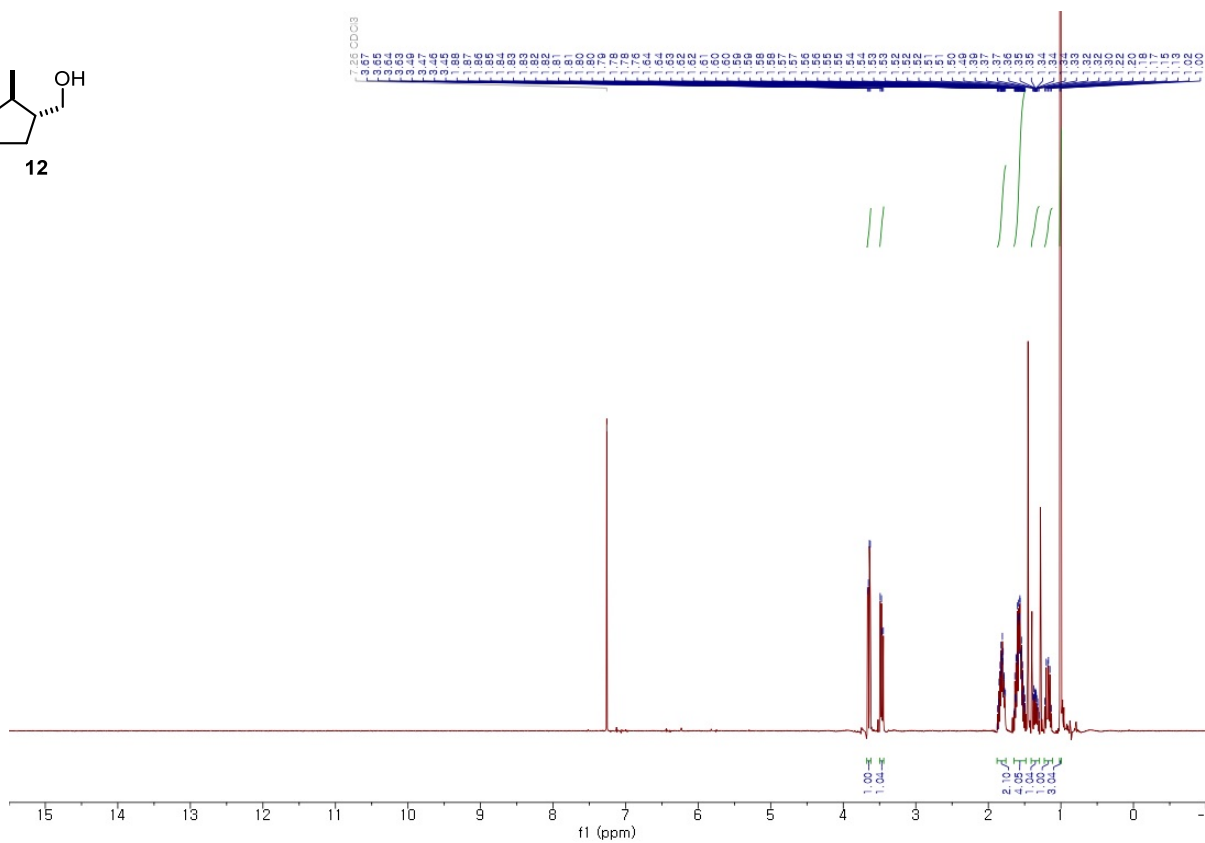
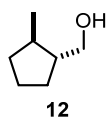


^1H NMR spectrum (400 MHz, CDCl_3) of **11**

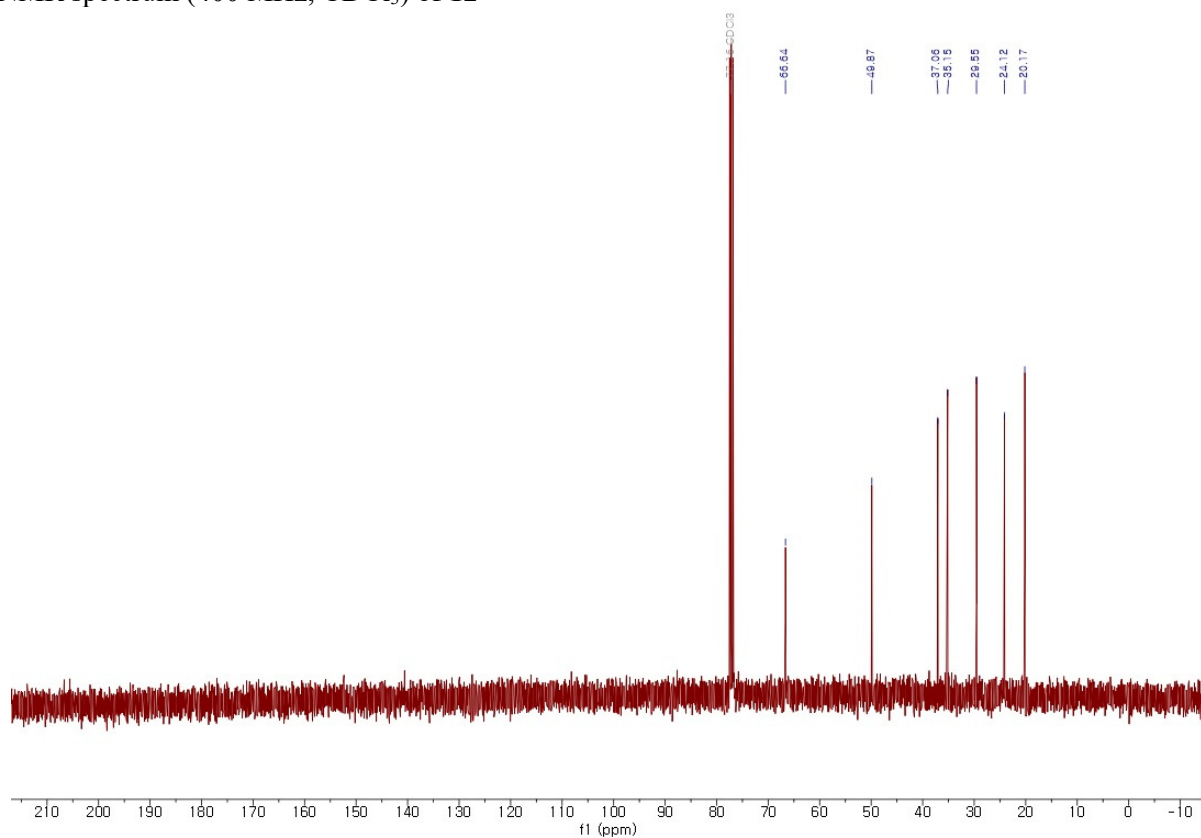


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, CDCl_3) of **11**

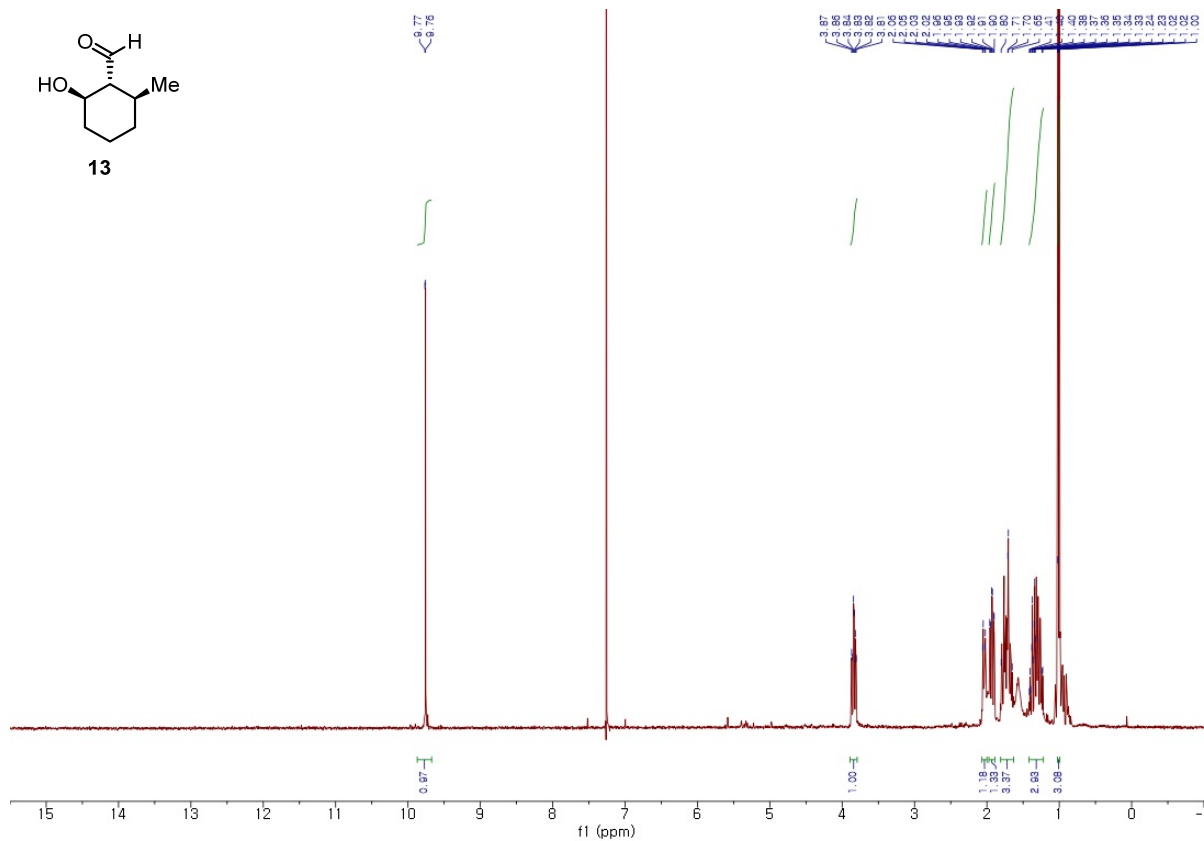
[illegible] $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, CDCl_3) of **5**



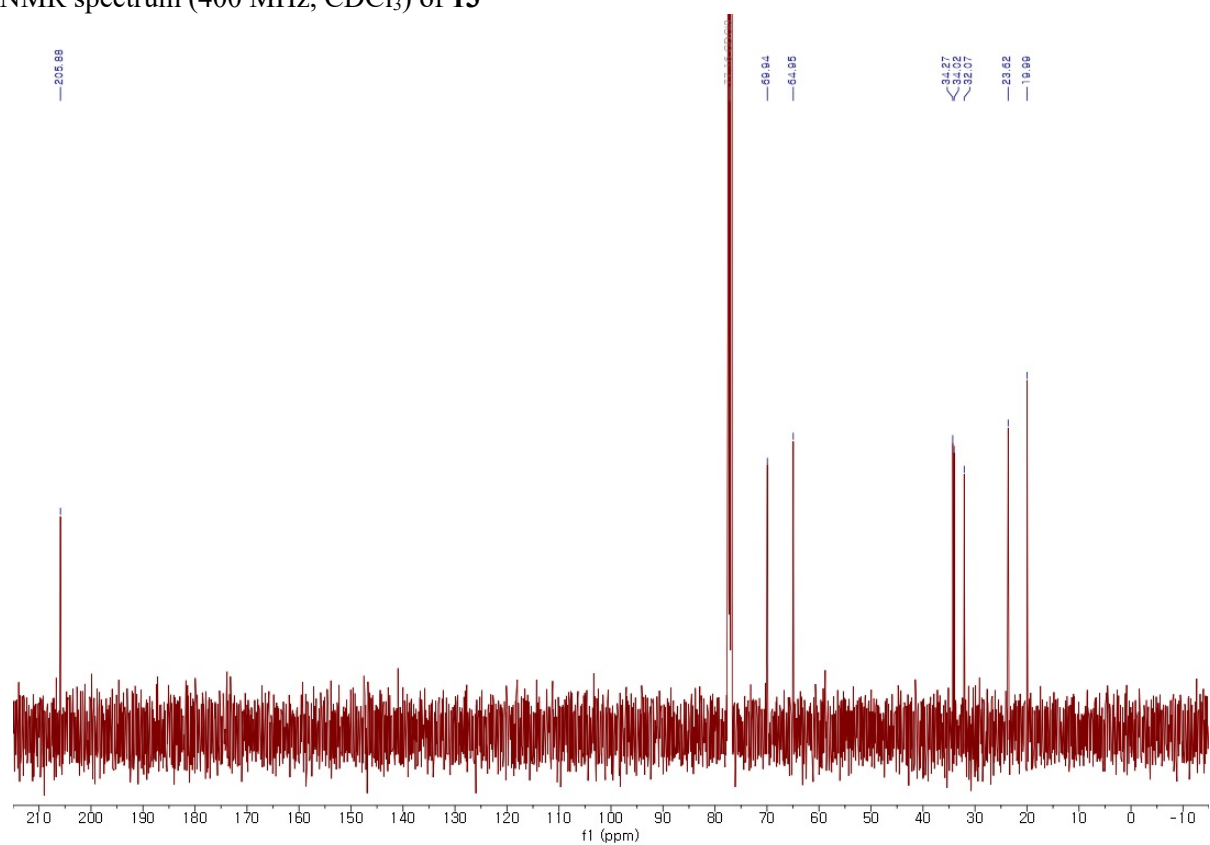
¹H NMR spectrum (400 MHz, CDCl₃) of **12**



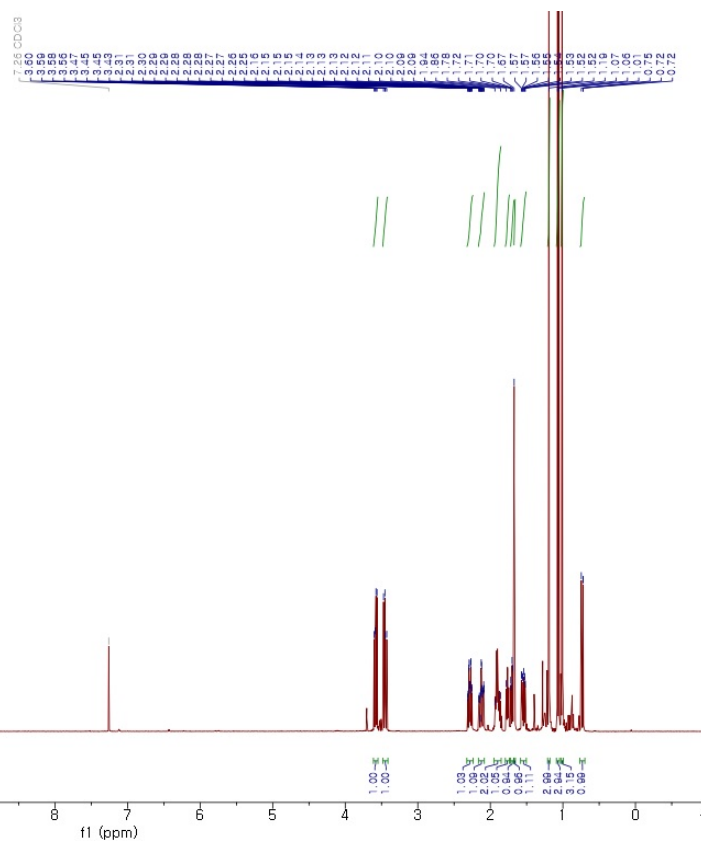
¹³C{¹H} NMR spectrum (100 MHz, CDCl₃) of **12**



^1H NMR spectrum (400 MHz, CDCl_3) of **13**



$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, CDCl_3) of **13**



¹³C NMR spectrum of compound 10 in CDCl₃. The x-axis represents the chemical shift in ppm, ranging from -10 to 210. The spectrum shows a triplet for the CDCl₃ solvent at 77.16 ppm. Several peaks for the compound are observed, with the following chemical shifts labeled: 47.85, 41.82, 38.09, 38.05, 33.55, 31.31, 28.09, 23.00, and 22.21. A peak at 70.12 is also indicated.

 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, CDCl_3) of **14**