Supplementary Information

Aerobic Oxygenation of α-Methylene Ketones under Visible-light Catalysed by a $CeNi_3$ Complex with a Macrocyclic Tris(salen)-Ligand

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Contents:

1. General information

All the manipulations were carried out under the protection of argon using standard Schlenk or glovebox techniques when we treated air and moisture sensitive compound. All the reagents were purchased from commercial sources and directly used without further purification. All solvents, such as acetonitrile, THF, Et_2O, hexane, and CH_2Cl_2, were dried and deoxygenated using a Grubbs column (Glass Counter Solvent Dispending System, Nikko Hansen & Co, Ltd.). MeOH, benzonitrile, DMSO, DMF were used as purchased. NMR spectra were recorded on Bruker Avance III-400 spectrometers. All ^{1}H NMR chemical shifts are reported in ppm (δ) relative to tetramethylsilane at δ 0.00 or referenced to the chemical shifts of residual solvent resonances. All $^{13}C\{^1H\}$ NMR chemical shifts are reported in ppm (δ) relative to carbon resonances of $CDCl_3$ or methanol-d_4. All $^{19}F\{^1H\}$ NMR chemical shifts are reported in ppm (δ) relative to fluorine resonances in external standard of α,α,α-trifluorotoluene at δ -63.90. All melting points were recorded on a BUCHI Melting Point M-565. Flash column chromatography was performed using silica gel 60 (0.040-0.063 nm, 230-400 mesh ASTM). The elemental analyses were recorded by using Perkin Elmer 2400 at the Faculty of Engineering Science, Osaka University. GC analyses were recorded on a Shimadzu GC-2014 gas chromatograph with SH-Rtx-50 column. ESI-MS spectrometric data was obtained using BRUKER microTOF-II spectrometer. UV-Vis spectra were recorded using an Agilent 8453 UV/Vis spectroscopy system. IR spectrum was recorded on JASCO FT/IR4000 spectrometer. High resolution mass spectra (HRMS) were recorded by JEOL JMS-700.

Optimization of reaction conditions for visible-light-induced aerobic oxygenation of benzyl phenyl ketone (2a)

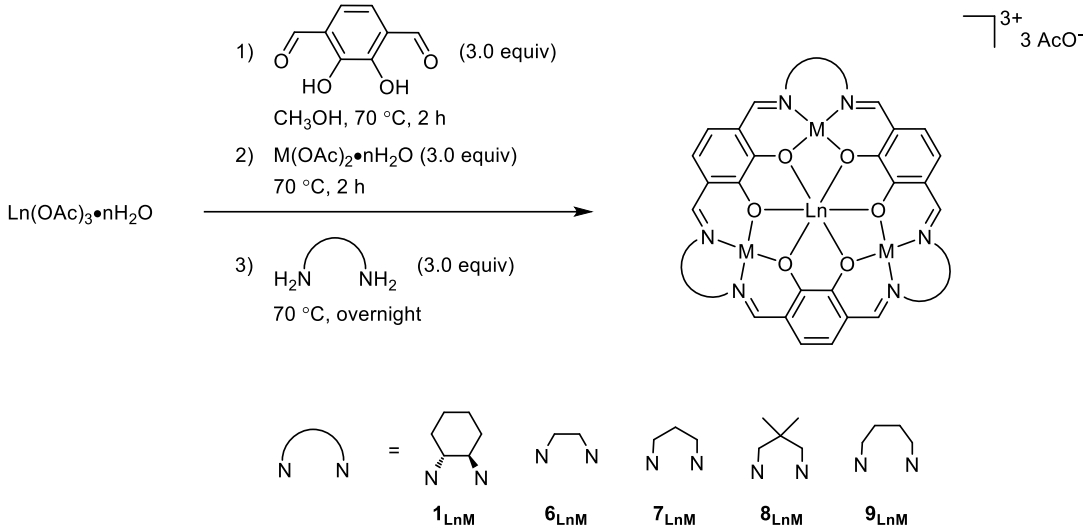
All manipulations were conducted under aerobic condition. To a macrocyclic complex (5.0 μmol) and **2a** (0.50 mmol) placed in a test tube (size: φ 15 mm × 130 mm), was added acetonitrile (1.5 mL) as solvent. The reaction mixture was irradiated with 40 W blue LEDs with stirring at room temperature under air. The yield was determined by GC analysis with triphenylmethane as an internal standard.

General procedure for visible-light-induced aerobic oxygenation of 2

All manipulations were conducted under aerobic condition. To $\mathbf{1}_{\mathbf{CeNi}}$ (5.0 μmol) and **2** (0.50 mmol) placed in a test tube (size: φ 15 mm × 130 mm), was added acetonitrile (1.5 mL) as solvent. The reaction mixture was irradiated with 40 W blue LEDs with stirring at room temperature under air. After a predetermined reaction period, 1 M HCl aq. (15 mL) was added to the reaction mixture, and the organic moieties were extracted with EtOAc. To the organic layer, was added sat. $Na_2S_2O_3$ aq. (5 mL) to quench peroxides which was possibly formed during the oxygenation reaction. The quenched organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography, then all volatiles were removed under reduced pressure to obtain α-diketone with small amount of substrate. The conversion of **2** and yield of **3** were determined by their weight and ^{1}H NMR analysis.

2. Preparation and characterisation of complexes and substrates

2-1. Preparation of complexes $\mathbf{1}_{LnM}$ and $\mathbf{6}_{LnM}$—$\mathbf{9}_{LnM}$



General: Methanol was added to a mixture of $Ln(OAc)_3•nH_2O$ (1.0 equiv) and 2,3-dihydroxybenzene-1,4-dicarbaldehyde (3.0 equiv). After stirring at 70 °C for 2 hours, a solution of $M(OAc)_2•nH_2O$ (3.0 equiv) in methanol was added, and the resulting mixture was stirred for 2 hours at 70 °C. To the reaction mixture, a solution of a corresponding diamine (3.0 equiv) in methanol was added and stirred overnight at 70 °C. Corresponding products was obtained by reprecipitation in Et_2O or Et_2O/hexane.

Complex $\mathbf{1}_{CeNi}$

Brown powder (298 mg, 244 μmol, 81% yield): MS (ESI^+) *m/z*: 1160.1 ($[CeNi_3L(OAc)_2]^+$); Anal. Calcd for $C_{48}H_{51}N_6O_{12}CeNi_3 + 6H_2O$: C, 43.41; H, 4.78; N, 6.33. Found: C, 43.32; H, 4.84; N, 6.23; ^1H NMR (400 MHz, methanol-d_4, 30 °C): δ 8.22 (s, 6H, imine), 7.24 (s, 6H, Ar), 3.47 (br s, 6H, =NC*H*–), 2.76 (d, *J* = 10.4 Hz, 6H, =NCHC*H*H–), 2.34 (br s, 9H, $OCOCH_3$), 2.01 (d, *J* = 7.2 Hz, 6H, =NCHCH$_2$C*H*H–), 1.59 (m, 6H, =NCHCH*H*–), 1.50-1.48 (m, 6H, =NCHCH$_2$CH*H*–). $^{13}C\{^1H\}$ NMR (100 MHz, methanol-d_4, 30 °C): δ 161.6, 152.0, 126.5, 122.0, 73.0, 29.9, 25.5. m.p. > 300 °C.

Complex $\mathbf{1}_{LaNi}$

Brown powder (54.8 mg, 45.0 μmol, 90% yield): MS (ESI^+) *m/z*: 1159.1 ($[LaNi_3L(OAc)_2]^+$); Anal. Calcd for $C_{48}H_{51}N_6O_{12}LaNi_3 + 8H_2O$: C, 42.30; H, 4.95; N, 6.17. Found: C, 42.61; H, 4.56; N, 6.01; ^1H NMR (400 MHz, methanol-d_4, 30 °C): δ 7.88 (s, 6H, imine), 6.90 (s, 6H, Ar), 3.25 (br s, 6H, =NC*H*–), 2.61 (d, *J* = 8.8 Hz, 6H, =NCHC*H*H–), 1.93 (d, *J* = 6.8 Hz, 6H, =NCHCH$_2$C*H*H–), 1.40 (m, 12H, =NCHCH*H*CH*H*–). $^{13}C\{^1H\}$ NMR (100 MHz, methanol-d_4, 30 °C): δ 161.1, 152.3, 121.8, 121.4, 72.6, 29.7, 25.4. m.p. > 300 °C.

Complex $\mathbf{1}_{NdNi}$

Dark purple powder (96.5 mg, 78.8 μmol, 79% yield): MS (ESI^+) *m/z*: 1200.1 ($[NdNi_3L(OAc)_2(H_2O)_2]^+$); Anal. Calcd for $C_{48}H_{51}N_6O_{12}NdNi_3 + 7H_2O$: C, 42.69; H, 4.85; N, 6.22. Found: C, 42.74; H, 4.80; N, 5.74. m.p. > 300 °C.

Complex $\mathbf{1}_{\mathbf{SmNi}}$

Dark purple powder (99.3 mg, 80.7 μmol, 81% yield): MS (ESI^+) *m/z*: 1236.1 ($[SmNi_3L(OAc)_2(CH_3OH)_2]^+$); Anal. Calcd for $C_{48}H_{51}N_6O_{12}SmNi_3 + 9H_2O$: C, 41.40; H, 4.99; N, 6.04. Found: C, 41.72; H, 4.67; N, 5.71. m.p. > 300 °C.

Complex $\mathbf{1}_{\mathbf{EuNi}}$

Dark purple powder (99.9 mg, 81.1 μmol, 81% yield): MS (ESI^+) *m/z*: 1235.1 ($[EuNi_3L(OAc)_2(CH_3OH)_2]^+$); Anal. Calcd for $C_{48}H_{51}N_6O_{12}EuNi_3 + 8H_2O$: C, 41.89; H, 4.91; N, 6.11. Found: C, 41.86; H, 4.56; N, 5.87. m.p. > 300 °C.

Complex $\mathbf{1}_{\mathbf{YbNi}}$

Dark purple powder (79.6 mg, 63.5 μmol, 64% yield): MS (ESI^+) *m/z*: 553.5 ($[YbNi_3L(OCH_3)]^{2+}$); Anal. Calcd for $C_{48}H_{51}N_6O_{12}YbNi_3 + 5H_2O$: C, 42.92; H, 4.58; N, 6.26. Found: C, 42.73; H, 4.25; N, 6.16. m.p. > 300 °C.

Complex $\mathbf{1}_{\mathbf{CeCu}}$

Brown powder (43.4 mg, 35.1 μmol, 81% yield): MS (ESI^+) *m/z*: 1175.1 ($[CeCu_3L(OAc)_2]^+$); Anal. Calcd for $C_{48}H_{51}N_6O_{12}CeCu_3 + 6H_2O$: C, 42.93; H, 4.73; N, 5.96. Found: C, 42.91; H, 4.90; N, 5.93. m.p. > 300 °C.

Complex $\mathbf{1}_{\mathbf{CeZn}}$

Yellowish brown powder (119 mg, 95.6 μmol, 96% yield): MS (ESI^+) *m/z*: 1180.0 ($[CeZn_3L(OAc)_2]^+$); Anal. Calcd for $C_{48}H_{51}N_6O_{12}CeZn_3 + 2CH_3OH + 2H_2O$: C, 44.81; H, 4.74; N, 6.27. Found: C, 45.14; H, 4.27; N, 5.80. m.p. > 300 °C.

Complex $\mathbf{6}_{\mathbf{CeNi}}$

Reddish brown powder (103 mg, 97.6 μmol, 98% yield): MS (ESI^+) *m/z*: 998.0 ($[CeNi_3L(OAc)_2]^+$); Anal. Calcd for $C_{36}H_{33}N_6O_{12}CeNi_3 + 5H_2O$: C, 37.31; H, 3.78; N, 7.32. Found: C, 37.49; H, 3.20; N, 7.79; ^1H NMR (400 MHz, methanol-d_4, 30 °C): δ 8.26 (s, 6H, imine), 7.15 (s, 6H, Ar), 3.78 (s, 12H, $–CH_2–$), 2.50 (br s, 9H, $OCOCH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, methanol-d_4, 30 °C): δ 165.7, 151.6, 126.5, 121.6, 60.3. m.p. > 300 °C.

Complex $\mathbf{7}_{\mathbf{CeNi}}$

Orange powder (73.8 mg, 67.1 μmol, 67% yield): MS (ESI^+) *m/z*: 490.5 ($[CeNi_3L(OAc)]^{2+}$); Anal. Calcd for $C_{39}H_{39}N_6O_{12}CeNi_3 + 6H_2O$: C, 38.78; H, 4.26; N, 6.96. Found: C, 38.66; H, 3.74; N, 7.44. m.p. > 300 °C.

Complex $\mathbf{8}_{\mathbf{CeNi}}$

Reddish purple powder (112 mg, 94.7 μmol, 95% yield): MS (ESI^+) *m/z*: 518.5 ($[CeNi_3L(OCH_3)]^{2+}$); Anal. Calcd for $C_{45}H_{51}N_6O_{12}CeNi_3 + 4H_2O$: C, 43.03; H, 4.73; N, 6.69. Found: C, 43.06; H, 4.69; N, 6.66. m.p. > 300 °C.

Complex $\mathbf{9}_{\mathbf{CeNi}}$

Reddish brown powder (84.3 mg, 73.8 μmol, 74% yield): MS (ESI^+) *m/z*: 1118.0

([$CeNi_3L(OAc)_2(H2O)_2$]$^+$); Anal. Calcd for $C_{42}H_{45}N_6O_{12}CeNi_3$ + 11H_2O: C, 37.64; H, 5.04; N, 6.27. Found: C, 37.20; H, 4.58; N, 6.04. m.p. > 300 °C.

Complex $\mathbf{1}_{\mathbf{CeCo}}$

Brown solid (56.0 mg, 45.9 μmol, 51% yield): MS (ESI$^+$) *m/z*: 1160.6 ([$CeCo_3L(OAc)_2$]$^+$); Anal. Calcd for $C_{48}H_{51}N_6O_{12}CeCo_3$: C, 47.22; H, 4.21; N, 6.88. Found: C, 46.94; H, 4.56; N, 6.56. m.p. > 300 °C.

Complex $\mathbf{1}_{\mathbf{CeFe}}$

Black solid (124 mg, 102 μmol, 102% yield): MS (ESI$^+$) *m/z*: 1290.6 ([$(CeFe_3L)_2(CH_3O)_4(H_2O)$]$^{2+}$); Anal. Calcd for $C_{48}H_{51}N_6O_{12}CeFe_3$ + H_2O: C, 46.89; H, 4.34; N, 6.83. Found: C, 47.11; H, 4.60; N, 6.39. m.p. > 300 °C.

Complex $\mathbf{1}_{\mathbf{CeMn}}$

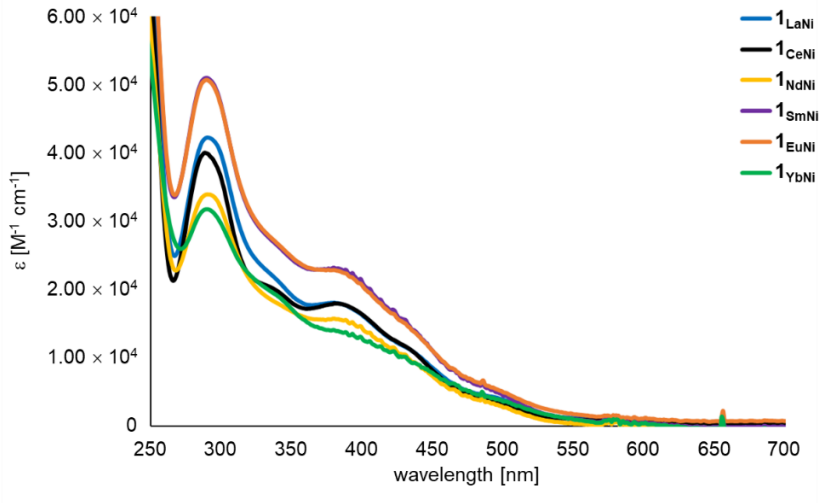
Dark brown solid (42.6 mg, 35.2 μmol, 70% yield): MS (ESI$^+$) *m/z*: 1167.6 ([$CeMn_3L(OAc)_2(H_2O)$]$^+$); Anal. Calcd for $C_{48}H_{51}N_6O_{12}CeMn_3$ + 3CH_3OH + H_2O: C, 46.30; H, 4.95; N, 6.35. Found: C, 46.12; H, 5.01; N, 6.03. m.p. > 300 °C.

Complex $\mathbf{1}_{\mathbf{CeCr}}$

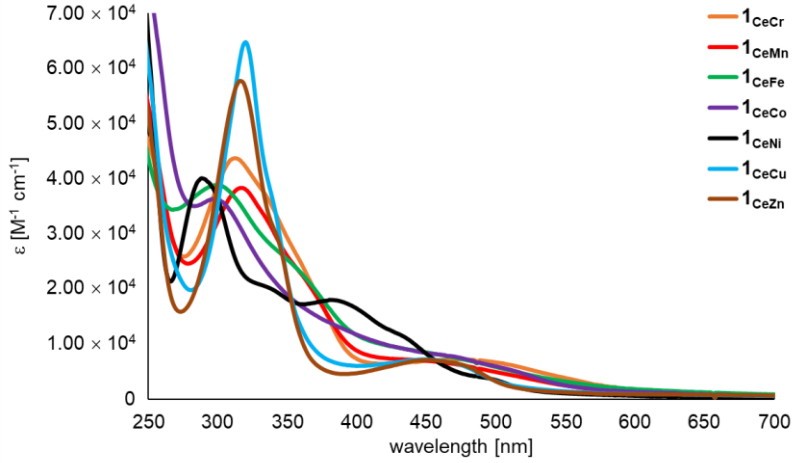
Dark purple solid (139 mg, 115 μmol, 115% yield): MS (ESI$^+$) *m/z*: 1290.6 ([$CeCr_3L(OAc)_2(CH_3OH)_3(H_2O)_3$]$^+$); Anal. Calcd for $C_{48}H_{51}N_6O_{12}CeCr_3$ + 6CH_3OH: C, 46.58; H, 5.43; N, 6.04. Found: C, 46.86; H, 5.54; N, 5.68. m.p. > 300 °C.

2-2. UV-Vis spectra of $\mathbf{1}_{LnM}$ and $\mathbf{6}_{CeNi}$-$\mathbf{9}_{CeNi}$

(a) UV-Vis spectra of $\mathbf{1}_{LnNi}$



(b) UV-Vis spectra of $\mathbf{1}_{CeM}$



(c) UV-Vis spectra of $\mathbf{6}_{CeNi}$—$\mathbf{9}_{CeNi}$

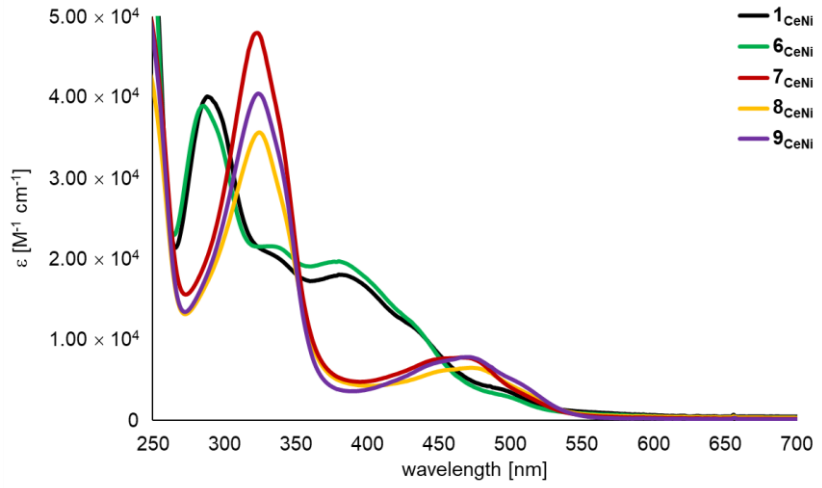
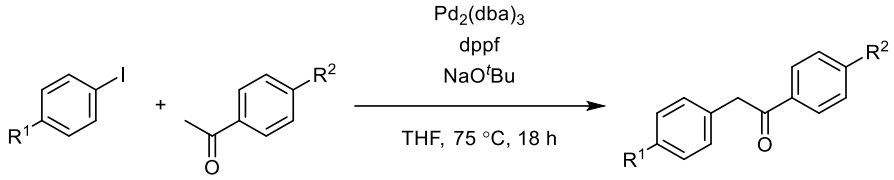


Figure S1. UV-Vis spectra of $\mathbf{1}_{LnM}$ and $\mathbf{6}_{CeNi}$—$\mathbf{9}_{CeNi}$; (a) $\mathbf{1}_{LnNi}$, (b) $\mathbf{1}_{CeM}$, (c) $\mathbf{6}_{CeNi}$—$\mathbf{9}_{CeNi}$.

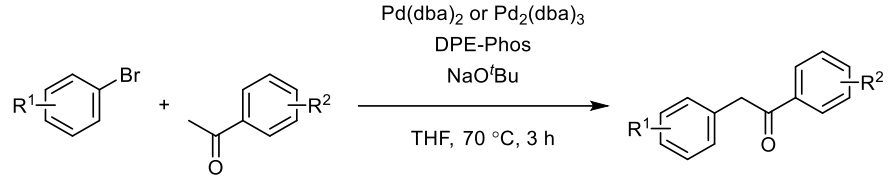
2-3. Preparation of benzyl phenyl ketone derivatives 2

Method A[S1]



An oven-dried flask containing a stir bar was charged with $Pd_2(dba)_3$ (0.46 g, 0.50 mmol, 2.5 mol%) and dppf (0.67 g, 1.2 mmol, 6.0 mol%). To the flask, THF (104 mL) was added and allowed to stir for 50 minutes before the addition of NaO^{t}Bu (4.2 g, 44 mmol). Then, iodobenzene derivative (20 mmol) was added to the reaction mixture, followed by acetophenone derivative (20 mmol). The resulting mixture was heated at 75 °C for 18 h under Ar atmosphere and cooled to room temperature. The crude product was purified by silica gel flash chromatography.

Method B[S2]



An oven-dried flask containing a stir bar was charged with $Pd_2(dba)_3$ (0.070 g, 0.076 mmol, 1.5 mol %) or $Pd(dba)_2$ (0.088 g, 0.15 mmol, 3.0 mol%), and DPE-Phos (0.10 g, 0.19 mmol, 3.7 mol %), and NaO^{t}Bu (0.63 g, 6.5 mmol) under Ar atmosphere. THF (5 mL) was added followed by bromobenzene derivative (5.0 mmol) and acetophenone derivative (5.6 mmol). The resulting mixture was heated at 70 °C for 3 h under Ar atmosphere and cooled to room temperature. Water (20 mL) was then added, and the mixture was extracted with diethyl ether. The organic layer was combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography, then vaporable solvent was removed to obtain benzyl phenyl ketone derivative.

4-Fluorobenzyl phenyl ketone (**2b**)[S3a]

Method A: White crystal (0.992 g, 4.63 mmol, 23% yield): ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 8.00 (d, *J* = 7.6 Hz, 2H, Ar), 7.56 (t, *J* = 7.6 Hz, 1H, Ar), 7.46 (t, *J* = 7.6 Hz, 2H, Ar), 7.22 (dd, *J* = 8.4 Hz, *J* = 5.6 Hz, 2H, Ar), 7.01 (t, *J* = 8.8 Hz, 2H, Ar), 4.25 (s, 2H, –CH_2–). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 197.2, 161.7 (d, *J* = 244 Hz), 136.3, 133.1, 130.9 (d, *J* = 8 Hz), 130.0 (d, *J* = 4 Hz), 128.5, 128.3, 115.3 (d, *J* = 22 Hz), 44.3. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 30 °C): δ -117.1; HRMS (EI$^+$) *m/z* calcd. for $C_{14}H_{11}OF$ $[M]^+$ 214.0794, found 214.0789.

4-(Trifluoromethyl)benzyl phenyl ketone (**2d**)[S3b]

Method A: White solid (1.64 g, 6.21 mmol, 33% yield): ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 8.01 (d, *J* = 8.0 Hz, 2H, Ar), 7.59-7.58 (m, 3H, Ar), 7.48 (t, *J* = 7.6 Hz, 2H, Ar), 7.38 (d, *J* = 8.0 Hz, 2H, Ar), 4.35 (s, 2H, –CH_2–). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 196.8, 138.7, 136.5, 133.6, 130.1, 129.5 (q, *J* = 32 Hz), 128.9, 128.6, 125.7 (q, *J* = 4 Hz), 124.3 (q, *J* = 270 Hz), 45.2. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 30 °C): δ -63.6; HRMS (EI$^+$) *m/z* calcd. for $C_{15}H_{11}OF_3$ $[M]^+$ 264.0762,

found 264.0767.

4-Methoxybenzyl phenyl ketone (**2e**)[S3a]

Method A: White crystal (0.937 g, 4.14 mmol, 14% yield): ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 8.00 (d, *J* = 7.2 Hz, 2H, Ar), 7.54 (t, *J* = 7.2 Hz, 1H, Ar), 7.44 (t, *J* = 7.2 Hz, 2H, Ar), 7.17 (d, *J* = 8.4 Hz, 2H, Ar), 6.86 (d, *J* = 8.4 Hz, 2H, Ar), 4.21 (s, 2H, –CH_2–), 3.77 (s, 3H, OMe). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 198.0, 158.7, 136.8, 133.2, 130.6, 128.7$_4$, 128.7$_2$, 126.7, 114.3, 55.4, 44.8; HRMS (EI$^+$) *m/z* calcd. for $C_{15}H_{14}O_2$ [M]$^+$ 226.0994, found 226.0993.

3-Methylbenzyl phenyl ketone (**2g**)[S3a]

Method B: Pale yellow liquid (0.834 g, 3.97 mmol, 79% yield): ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 8.01 (d, *J* = 7.2 Hz, 2H, Ar), 7.54 (t, *J* = 7.2 Hz, 1H, Ar), 7.45 (t, *J* = 7.2 Hz, 2H, Ar), 7.20 (t, *J* = 7.6 Hz, 1H, Ar), 7.08-7.05 (m, 3H, Ar), 4.24 (s, 2H, –CH_2–), 2.32 (s, 3H, Me). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 198.2, 138.8, 137.2, 134.9, 133.6, 130.6, 129.1$_0$, 129.0$_8$, 129.0, 128.1, 126.9, 45.9, 21.8; HRMS (EI$^+$) *m/z* calcd. for $C_{15}H_{14}O$ [M]$^+$ 210.1045, found 210.1048.

2-Methylbenzyl phenyl ketone (**2h**)[S3a]

Method B: White crystal (0.390 g, 1.85 mmol, 37% yield): ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 8.02 (d, *J* = 7.2 Hz, 2H, Ar), 7.57 (t, *J* = 7.2 Hz, 1H, Ar), 7.47 (t, *J* = 7.6 Hz, 2H, Ar), 7.21-7.11 (m, 4H, Ar), 4.30 (s, 2H, –CH_2–), 2.26 (s, 3H, Me). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 197.6, 137.1, 137.0, 133.6, 133.3, 130.5, 130.4, 128.8, 128.5, 127.4, 126.3, 43.6, 19.9; HRMS (EI$^+$) *m/z* calcd. for $C_{15}H_{14}O$ [M]$^+$ 210.1045, found 210.1045.

Benzyl 4-(trifluoromethyl)phenyl ketone (**2k**)[S3c]

Method B: White crystal (0.305 g, 1.15 mmol, 23% yield): ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 8.09 (d, *J* = 8.4 Hz, 2H, Ar), 7.71 (d, *J* = 8.0 Hz, 2H, Ar), 7.33 (t, *J* = 7.6 Hz, 2H, Ar), 7.28-7.24 (m, 3H, Ar), 4.30 (s, 2H, –CH_2–). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 196.7, 139.4, 134.6 (q, *J* = 33 Hz), 129.5, 129.1, 129.0, 127.3, 125.9 (q, *J* = 4 Hz), 123.7 (q, *J* = 270 Hz), 46.0. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 30 °C): δ -63.9; HRMS (EI$^+$) *m/z* calcd. for $C_{15}H_{11}OF_3$ [M]$^+$ 264.0762, found 264.0759.

Benzyl 4-methoxyphenyl ketone (**2l**)[S3a]

Method B: White crystal (0.623 g, 2.75 mmol, 54% yield): ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.99 (d, *J* = 8.8 Hz, 2H, Ar), 7.32-7.21 (m, 5H, Ar), 6.92 (d, *J* = 8.8 Hz, 2H, Ar), 4.22 (s, 2H, –CH_2–), 3.85 (s, 3H, OMe). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 196.3, 163.7, 135.2, 131.1, 129.9, 129.5, 128.8, 126.9, 114.0, 55.6, 45.4; HRMS (EI$^+$) *m/z* calcd. for $C_{15}H_{14}O_2$ [M]$^+$ 226.0994, found 226.0993.

Benzyl 4-methylphenyl ketone (**2m**)[S3a]

Method B: White crystal (0.623 g, 2.96 mmol, 59% yield): ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.91 (d, *J* = 8.0 Hz, 2H, Ar), 7.33-7.22 (m, 7H, Ar), 4.25 (s, 2H, –CH_2–), 2.40 (s, 3H, Me). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 197.4, 144.1, 135.0, 134.3, 129.6, 129.5, 128.9, 128.8, 127.0, 45.6, 21.8; HRMS (EI$^+$) *m/z* calcd. for $C_{15}H_{14}O$ [M]$^+$ 210.1045, found 210.1049.

Benzyl 3-methylphenyl ketone (**2n**)[S3a]

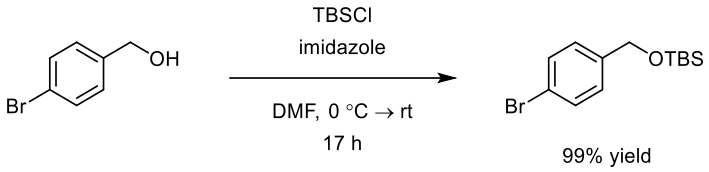
Method B: Pale yellow liquid (0.835 g, 3.97 mmol, 79% yield): ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.80 (d, *J* = 9.2 Hz, 2H, Ar), 7.37-7.30 (m, 4H, Ar), 7.27-7.22 (m, 3H, Ar), 4.26 (s, 2H, –CH_2–), 2.40 (s, 3H, Me). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 197.9, 138.6, 136.9, 134.8, 134.0, 129.6, 129.2, 128.8, 128.6, 127.0, 126.0, 45.7, 21.5; HRMS (EI$^+$) *m/z* calcd. for $C_{15}H_{14}O$ [M]$^+$ 210.1045, found 210.1045.

Benzyl 2-methylphenyl ketone (**2o**)[S3a]

Method B: Pale yellow liquid (0.813 g, 3.87 mmol, 77% yield): ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.70 (d, *J* = 7.6 Hz, 1H, Ar), 7.35 (t, *J* = 7.2 Hz, 1H, Ar), 7.31 (t, *J* = 7.6 Hz, 2H, Ar), 7.21-7.25 (m, 5H, Ar), 4.20 (s, 2H, –CH_2–), 2.43 (s, 3H, Me). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 201.6, 138.6, 137.9, 134.6, 132.1, 131.4, 129.7, 128.8, 128.7, 127.0, 125.7, 48.6, 21.4; HRMS (EI$^+$) *m/z* calcd. for $C_{15}H_{14}O$ [M]$^+$ 210.1045, found 210.1049.

Preparation of 4-(hydroxymethyl)benzyl phenyl ketone (2p)

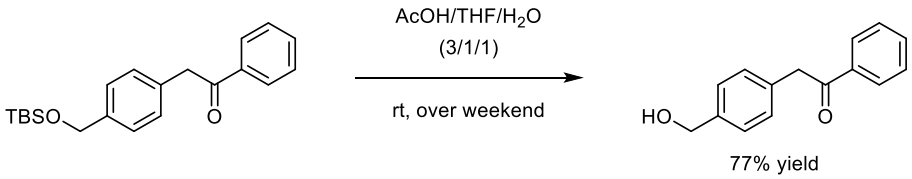
Preparation of 4-(*tert*-butyldimethylsilyloxymethyl)bromobenzene



To a solution of 4-bromobenzyl alcohol (2.54 g, 13.6 mmol) in DMF (90 mL), imidazole (3.88 g, 57.0 mmol) and TBSCl (4.11 g, 27.3 mmol) were added at 0 °C. The reaction mixture was stirred at room temperature for 17 hours, then the reaction mixture was quenched by water (150 mL). The product was extracted with EtOAc (2 × 50 mL), and the organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (hexane/EtOAc = 4/1), then all volatiles were removed to obtain colorless liquid (4.05 g, 13.4 mmol, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.45 (d, *J* = 8.4 Hz, 2H, Ar), 7.20 (d, *J* = 8.0 Hz, 2H, Ar), 4.69 (s, 2H, –CH_2–), 0.94 (s, 9H, –Si^t*Bu*Me_2), 0.10 (s, 6H, –Si^{t}Bu*Me*$_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 140.6, 131.4, 127.9, 120.7, 64.5, 26.1, 18.5, -5.1.

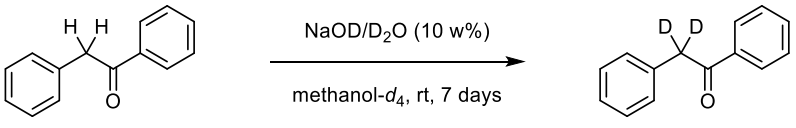
4-(*tert*-Butyldimethylsilyloxymethyl)benzyl pheny ketone

Method B: Pale yellow solid (1.04 g, 3.05 mmol, 61% yield): ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 8.00 (d, *J* = 6.8 Hz, 2H, Ar), 7.54 (t, *J* = 7.2 Hz, 1H, Ar), 7.44 (t, *J* = 7.6 Hz, 2H, Ar), 7.28 (d, *J* = 8.0 Hz, 2H, Ar), 7.22 (d, *J* = 8.0 Hz, 2H, Ar), 4.71 (s, 2H, –CH_2–), 4.27 (s, 2H, –CH_2–), 0.93 (s, 9H, –Si^t*Bu*Me_2), 0.08 (s, 6H, –Si^{t}Bu*Me*$_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 197.8, 140.3, 136.8, 133.2, 129.4, 129.1, 128.8$_0$, 128.7$_7$, 126.6, 64.9, 45.4, 26.1, 18.6, -5.1.



4-(*tert*-Butyldimethylsilyloxymethyl)benzyl pheny ketone (463 mg, 1.36 mmol) was dissolved in AcOH/THF/H_2O (3/1/1, 15 mL). After the mixture was stirred for over weekend at room temperature, the reaction mixture was quenched by sat. $NaHCO_3$ aq. The product was extracted with EtOAc (6 × 50 mL), and the organic layer was dried over Na_2SO_4, the organic layer was concentrated under reduced pressure. The residues were purified by silica gel flash column chromatography (hexane/EtOAc = 1/1), then all volatiles were removed to obtain white powder (237 mg, 1.05 mmol, 77% yield). IR (neat KBr, ν/cm^{-1}) 3360 br m, 3057 w, 2908 w, 2865 w, 1686 s, 1597 w, 1579 w, 1518 w, 1447 m, 1413 w, 1385 w, 1335 m, 1220 m, 1203 m, 1107 w, 1075 w, 1035 m, 1017 m, 1000 m, 906 w, 867 w, 784 w, 751 m, 688 s, 663 w, 569 w; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 8.01 (d, *J* = 7.2 Hz, 2H, Ar), 7.56 (t, *J* = 7.2 Hz, 1H, Ar), 7.45 (t, *J* = 7.2 Hz, 2H, Ar), 7.33 (d, *J* = 8.0 Hz, 2H, Ar), 7.26 (d, *J* = 8.4 Hz, 2H, Ar), 4.67 (s, 2H, –CH_2–), 4.28 (s, 2H, –CH_2–), 1.66 (br s, 1H, OH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 197.7, 139.7, 136.8, 134.1, 133.3, 129.9, 128.8, 128.7, 127.5, 65.3, 45.4; HRMS (EI$^+$) *m/z* calcd. for $C_{15}H_{14}O_2$ $[M]^+$ 226.0994, found 227.0996.

Preparation of benzyl phenyl ketone-d_2 (2a-d_2)



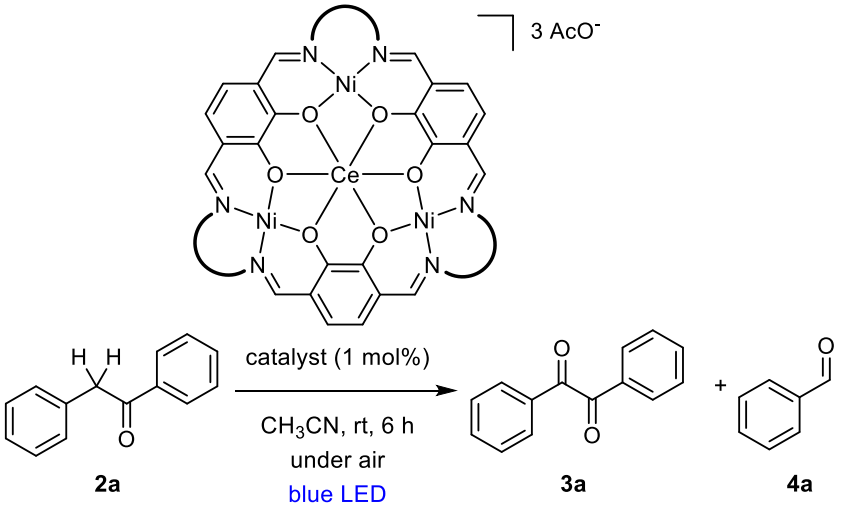
75% yield
>95%D

To a solution of benzyl phenyl ketone (981 mg, 5.00 mmol) in methanol-d_4 (25 mL), NaOD/D_2O (10 w%, 1.00 mL) was added. The reaction mixture was stirred at room temperature for 7 days, then DCl/D_2O (35 w%) was added until the solution became the solution neutral. The reaction mixture was dried over Na_2SO_4, and the deuterated product was purified by silica gel flash column chromatography (hexane/EtOAc = 15/1) to obtain white solid (0.741 g, 3.74 mmol, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 8.01 (d, *J* = 7.2 Hz, 2H, Ar), 7.54 (t, *J* = 7.2 Hz, 1H, Ar), 7.44 (t, *J* = 7.2 Hz, 2H, Ar), 7.32 (t, *J* = 7.2 Hz, 2H, Ar), 7.27-7.22 (m, 3H, Ar). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 197.8, 136.7, 134.6, 133.3, 129.6, 128.8$_0$, 128.7$_6$, 128.7$_5$, 127.0, 45.0 (quint., *J* = 19 Hz); HRMS (EI$^+$) *m/z* calcd. for $C_{14}H_{10}D_2O$ $[M]^+$ 198.1014, found 198.1011.

3. Screening of Catalyst $\mathbf{1}_{CeNi}$ and $\mathbf{6}_{CeNi}$—$\mathbf{9}_{CeNi}$

In addition to the complex $\mathbf{1}_{CeNi}$, a catalytic performance of complexes $\mathbf{6}_{CeNi}$—$\mathbf{9}_{CeNi}$ was examined by the oxygenation of benzyl phenyl ketone (**2a**) in CH_3CN at room temperature for 6 hours under air and blue LED irradiation, and results are summarized in Table S1. Among tested complexes, $\mathbf{1}_{CeNi}$ exhibited the highest catalytic activity to afford diketone **2a** in 80% yield (entry 1). Complexes $\mathbf{6}_{CeNi}$ and $\mathbf{7}_{CeNi}$ exhibited lower catalytic activity than that of $\mathbf{1}_{CeNi}$ (entries 2 and 3). Complex $\mathbf{8}_{CeNi}$ showed the second highest catalytic activity (entry 4). The catalytic activity of $\mathbf{9}_{CeNi}$ was very low to give **3a** in 53% yield (entry 5). Accordingly, we selected the complex $\mathbf{1}_{CeNi}$ as the best catalyst.

Table S1. Screening of catalysts.



entry	catalyst	N N	yield [%][a] 3a	4a
1	$\mathbf{1}_{CeNi}$		80	2
2	$\mathbf{6}_{CeNi}$		64	trace
3	$\mathbf{7}_{CeNi}$		50	2
4	$\mathbf{8}_{CeNi}$		72	3
5	$\mathbf{9}_{CeNi}$		53	1

[a] Determined by GC analysis with triphenylmethane as an internal standard.

4. Mechanistic studies

Kinetic study

All manipulations were conducted under aerobic conditions. A solution of an internal standard, 1,3,5-trimethoxybenzen, in acetonitrile-d_3 (1.5 mL) was added to a mixture of complex $\mathbf{1}_{\mathbf{CeNi}}$ (5.0 μmol) and **2a** or **2a-*d*$_2$** (0.50 mmol) in a test tube (size: φ 15 mm × 130 mm). The reaction mixture was irradiated with 40 W blue LEDs with stirring at room temperature under air. The conversion of **2a** or **2a-*d*$_2$** and yield of **3a** were determined by ^{1}H NMR analysis at a predetermined reaction time, 0 min, 10 min, 20 min, 30 min, 1 h, 2 h, 3 h, 4 h, 6 h, and 21 h.

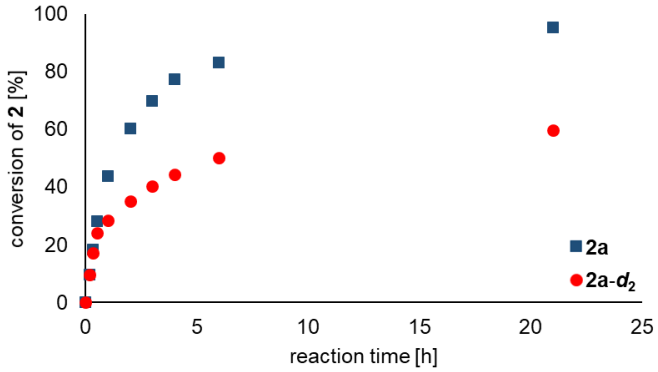


Figure S2. Time course for visible-light-induced aerobic oxygenation of **2a** or catalyzed by $\mathbf{1}_{\mathbf{CeNi}}$.

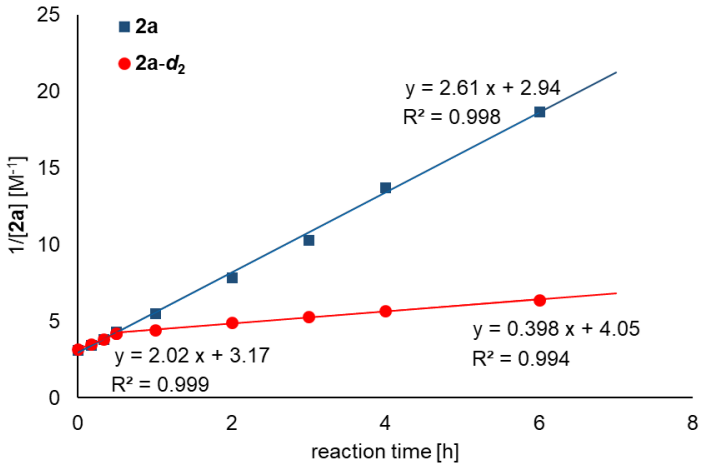


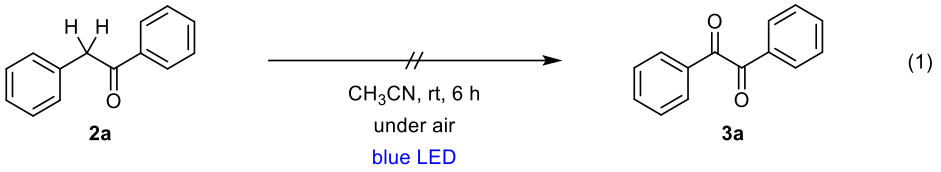
Figure S3. Second-order plots for visible-light-induced aerobic oxygenation of **2a** catalyzed by $\mathbf{1}_{\mathbf{CeNi}}$.

Deuteration of 2a in the presence of $\mathbf{1}_{CeNi}$ and D_2O

All manipulations were conducted under argon. To a mixture of $\mathbf{1}_{CeNi}$ (1.0 μmol) and **2a** (0.10 mmol) placed in a J-young tube, was added acetonitrile-d_3 (0.5 mL) and D_2O (1.0 mmol). The reaction mixture was irradiated with/without 40 W blue LEDs with stirring at room temperature for 3 hours. The **2a** to **2a**-d_1 ratio was determined by the ^{1}H NMR integral ratio of two peaks of δ 8.02 and δ 4.34-4.31.

Oxygenation of 2a in the absence of $\mathbf{1}_{CeNi}$

No reaction was observed when an aerobic oxygenation of **2a** was conducted in the absence of $\mathbf{1}_{CeNi}$.



(1)

5. X-ray crystallographic analyses

Crystals of $\mathbf{1}_{\mathbf{CeNi}}$, $\mathbf{1}_{\mathbf{CeZn}}$, and $\mathbf{6}_{\mathbf{CeNi}}$ were handled similarly. The crystals were mounted on the CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 113(2) K. Measurements were made on Rigaku XtaLAB P200 system with graphite-monochromated Mo–Kα (0.71075 Å) radiation. The structures of compounds $\mathbf{1}_{\mathbf{CeNi}}$ and $\mathbf{1}_{\mathbf{CeZn}}$ were solved by direct methods (SHELXT2015)[4] in the CrystalClear program,[5] and the structures of compounds $\mathbf{6}_{\mathbf{CeNi}}$ was solved by olex2.solve 1.3 in OLEX2 programs.[6] The structures were refined on F^2 by full-matrix least-squares method, using SHELXL-2013.[4] H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\Sigma w(F_o^2 - F_c^2)^2]$ ($w = 1 / [\sigma^2 (F_o^2) + (aP)^2 + bP]$), where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2) / 3$ with $\sigma^2(F_o^2)$ from counting statistics. The function $R1$ and $wR2$ were $(\Sigma||F_o| - |F_c||) / \Sigma|F_o|$ and $[\Sigma w(F_o^2 - F_c^2)^2 / \Sigma(wF_o^4)]^{1/2}$, respectively. Crystal data and structure refinement parameters are listed below. The ORTEP-3 program was used to draw the molecule.[7]

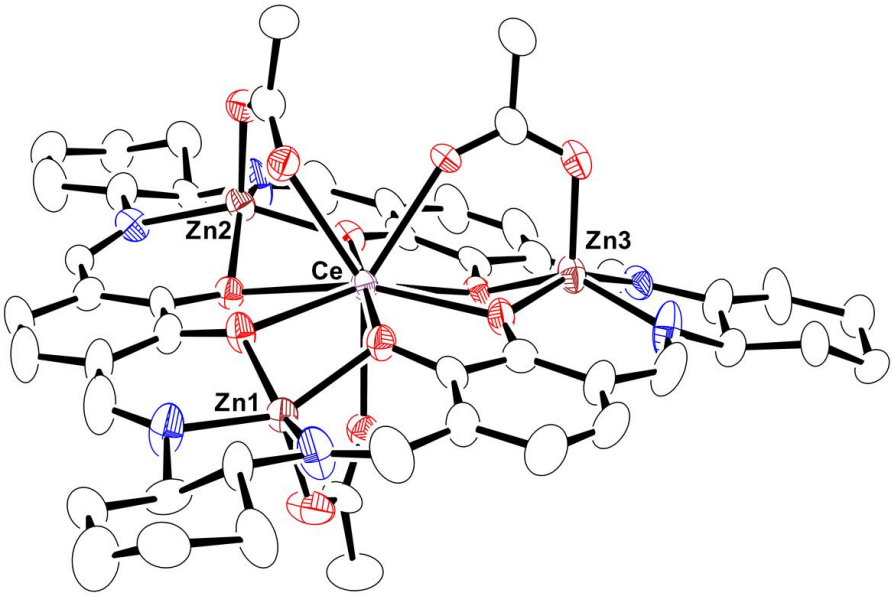


Figure S4. Molecular structure of $\mathbf{1}_{CeZn}$: all hydrogen atoms, acetate anion, and solvent molecules are omitted for clarity.

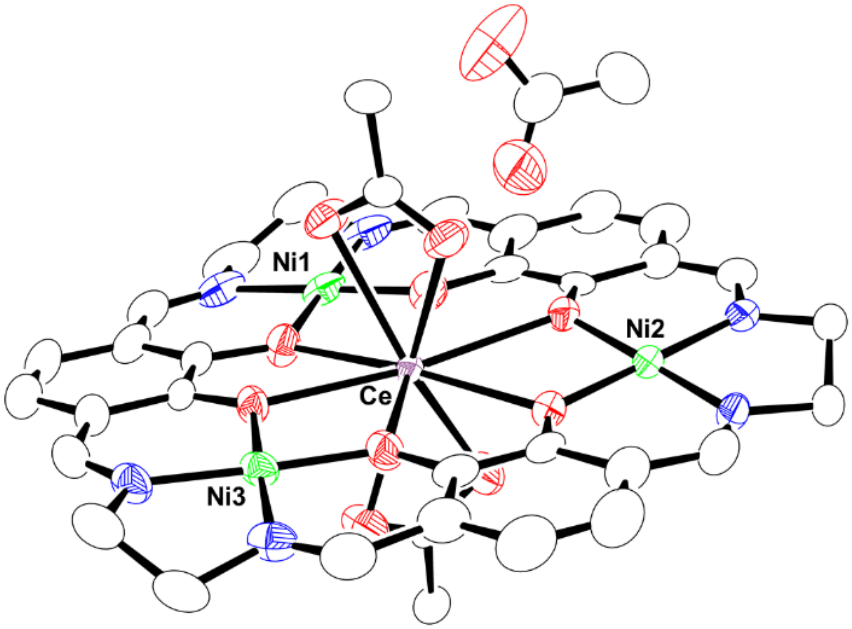


Figure S5. Molecular structure of $\mathbf{6}_{CeNi}$: all hydrogen atoms, acetate anion, and solvent molecules are omitted for clarity.

Table S2. Crystal data and data collection parameters.

	$\mathbf{1}_{CeNi}$	$\mathbf{1}_{CeZn}$
CCDC Reference No.	2103374	2103375
empirical formula	$C_{46}H_{47.9}CeN_6Ni_3O_{11}$	$C_{49}H_{55}CeCl_3N_6O_{13}Zn_3$
formula weight	1177.05	1312.07
crystal system	*triclinic*	*monoclinic*
space group	$P\bar{1}$ (#2)	$P2_1/n$ (#14)
a, Å	8.5388(15)	12.2210(16)
b, Å	17.266(3)	15.1088(19)
c, Å	18.085(2)	32.186(4)
α, deg.	63.591(8)	-
β, deg.	80.604(13)	95.719(3)
γ, deg.	87.018(14)	-
V, Å^3	2355.4(7)	5913.4(12)
Z	2	4
*D*calcd, g/cm^3	1.660	1.474
μ [Mo-*K*α], mm^{-1}	2.194	2.033
T, K	113(2)	113(2)
crystal size, mm	0.09 × 0.03 ×0.01	0.12 × 0.06 × 0.01
θ range for data collection (deg.)	3.053 to 27.542	4.049 to 27.536
no. of reflections measured	99729	95190
unique data (*R*int)	10809 (0.1765)	13546 (0.1091)
data / restraints / parameters	10809/0/654	13546/0/745
*R*1 ($I > 2.0\sigma(I)$)	0.0570	0.0738
*wR*2 ($I > 2.0\sigma(I)$)	0.1379	0.1517
*R*1 (all data)	0.0907	0.1187
*wR*2 (all data)	0.1460	0.1685
GOF on F^2	1.013	1.162
Δρ, e Å^{-3}	1.86, -1.09	0.96, -1.22

a) $R1 = (\Sigma||Fo| - |Fc||)/(\Sigma|Fo|)$ b) $wR2 = [\{\Sigma w(Fo^2\text{-}Fc^2)^2\}/\{\Sigma w(Fo^4)\}]^{1/2}$

	6$_{CeNi}$
CCDC Reference No.	2103376
empirical formula	$C_{36}H_{33}CeN_6Ni_3O_{12}$
formula weight	1057.93
crystal system	*triclinic*
space group	$P\bar{1}$ (#2)
a, Å	8.3694(5)
b, Å	17.4057(11)
c, Å	18.0006(13)
α, deg.	62.578(3)
β, deg.	75.394(4)
γ, deg.	77.110(4)
V, Å^3	2234.9(3)
Z	2
*D*calcd, g/cm^3	1.572
μ [Mo-*K*α], mm^{-1}	2.305
T, K	113(2)
crystal size, mm	0.2 × 0.15 ×0.04
θ range for data collection (deg.)	3.005 to 27.485
no. of reflections measured	82021
unique data (*R*int)	10221 (0.1211)
data / restraints / parameters	10221/0/544
*R*1 ($I > 2.0\sigma(I)$)	0.0434
*wR*2 ($I > 2.0\sigma(I)$)	0.1204
*R*1 (all data)	0.0534
*wR*2 (all data)	0.1248
GOF on F^2	1.046
Δρ, e Å^{-3}	2.30, -1.14

a) $R1 = (\Sigma||Fo| - |Fc||)/(\Sigma|Fo|)$ b) $wR2 = [\{\Sigma w(Fo^2\text{-}Fc^2)^2\}/\{\Sigma w(Fo^4)\}]^{1/2}$

7. NMR data of products

3a[S3d]

Yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.98 (d, *J* = 7.2 Hz, 4H, Ar), 7.66 (t, *J* = 7.2 Hz, 2H, Ar), 7.51 (t, *J* = 7.6 Hz, 4H, Ar). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 194.7, 135.0, 133.2, 130.0, 129.2; HRMS (EI$^+$) *m/z* calcd. for $C_{14}H_{10}O_2$ $[M]^+$ 210.0681, found 210.0679.

3b (**3i**)[S3d]

Yellow liquid: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 8.02 (dd, *J* = 8.8 Hz, *J* = 5.6 Hz, 2H, Ar), 7.97 (d, *J* = 7.6 Hz, 2H, Ar), 7.67 (t, *J* = 7.6 Hz, 1H, Ar), 7.52 (t, *J* = 7.6 Hz, 2H, Ar), 7.19 (t, *J* = 8.4 Hz, 2H, Ar). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 194.2, 192.9, 166.9 (d, *J* = 257 Hz), 135.1, 133.1, 132.9 (d, *J* = 10 Hz), 130.1, 129.7 (d, *J* = 3 Hz), 129.2, 116.5 (d, *J* = 22 Hz). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 30 °C): δ = -102.4; HRMS (EI$^+$) *m/z* calcd. for $C_{14}H_9O_2F$ $[M]^+$ 228.0587, found 228.0589.

3c (**3j**)[S3d]

Yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.96 (d, *J* = 7.2 Hz, 2H, Ar), 7.92 (d, *J* = 8.4 Hz, 2H, Ar), 7.67 (t, *J* = 7.6 Hz, 1H, Ar), 7.52 (t, *J* = 8.0 Hz, 2H, Ar), 7.49 (d, *J* = 8.4 Hz, 2H, Ar). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 194.0, 193.2, 141.7, 135.2, 133.0, 131.5, 131.4, 130.1, 130.0, 129.2; HRMS (EI$^+$) *m/z* calcd. for $C_{14}H_9O_2Cl$ $[M]^+$ 244.0291, found 244.0290.

3d (**3k**)[S3d]

Yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 8.11 (d, *J* = 8.0 Hz, 2H, Ar), 7.98 (d, *J* = 7.2 Hz, 2H, Ar), 7.78 (d, *J* = 8.4 Hz, 2H, Ar), 7.69 (t, *J* = 7.2 Hz, 1H, Ar), 7.54 (t, *J* = 7.6 Hz, 2H, Ar). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 193.6, 193.2, 136.0 (q, *J* = 32 Hz), 135.8, 135.4, 132.8, 130.4, 130.1, 129.3, 126.2 (q, *J* = 4 Hz), 123.5 (q, *J* = 271 Hz). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 30 °C): δ = -64.5; HRMS (EI$^+$) *m/z* calcd. for $C_{15}H_9O_2F_3$ $[M]^+$ 278.0555, found 278.0558.

3e (**3l**)[S3d]

Yellow liquid: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.98-7.94 (m, 4H, Ar), 7.64 (t, *J* = 7.2 Hz, 1H, Ar), 7.50 (t, *J* = 7.6 Hz, 2H, Ar), 6.98 (d, *J* = 9.2 Hz, 2H, Ar), 3.88 (s, 3H, OMe). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 195.0, 193.3, 165.2, 134.8, 133.4, 132.5, 130.1, 129.1, 126.3, 114.5, 55.8; HRMS (EI$^+$) *m/z* calcd. for $C_{15}H_{12}O_3$ $[M]^+$ 240.0786, found 240.0788.

3f (**3m**)[S3d]

Yellow liquid: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.97 (d, *J* = 7.6 Hz, 2H, Ar), 7.87 (d, *J* = 8.0 Hz, 2H, Ar), 7.65 (t, *J* = 7.6 Hz, 1H, Ar), 7.50 (t, *J* = 7.6 Hz, 2H, Ar), 7.31 (d, *J* = 8.0 Hz, 2H, Ar), 2.43 (s, 3H, Me). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 194.9, 194.4, 146.3, 134.9, 133.3, 130.8, 130.2, 130.0, 129.9, 129.1, 22.1; HRMS (EI$^+$) *m/z* calcd. for $C_{15}H_{12}O_2$ $[M]^+$ 224.0837, found 224.0839.

3g (**3n**)[S3d]

Yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.97 (d, *J* = 7.6 Hz, 2H, Ar), 7.78-7.76 (m, 2H, Ar), 7.65 (t, *J* = 7.6 Hz, 1H, Ar), 7.51 (t, *J* = 7.6 Hz, 2H, Ar), 7.47 (d, *J* = 7.6 Hz, 1H, Ar), 7.39 (t, *J* = 7.6 Hz, 1H, Ar), 2.41 (s, 3H, Me). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 195.0, 194.8, 139.2,

135.9, 135.0, 133.2, 130.4, 130.1, 129.2, 129.1, 129.1, 127.4, 21.4; HRMS (EI^+) *m/z* calcd. for $C_{15}H_{12}O_2$ $[M]^+$ 224.0837, found 224.0838.

3h (3o)[S3e]

Yellow liquid: ^1H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.97 (d, *J* = 7.6 Hz, 2H, Ar), 7.65 (t, *J* = 7.6 Hz, 2H, Ar), 7.51 (t, *J* = 7.6 Hz, 2H, Ar), 7.47 (d, *J* = 7.6 Hz, 1H, Ar), 7.34 (d, *J* = 8.0 Hz, 1H, Ar), 7.26 (t, *J* = 7.6 Hz, 1H, Ar), 2.41 (s, 3H, Me). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 30 °C): δ 196.9, 195.0, 141.5, 134.8, 133.9, 133.3, 133.2, 132.7, 132.0, 130.1, 129.2, 126.2, 22.0; HRMS (EI^+) *m/z* calcd. for $C_{15}H_{12}O_2$ $[M]^+$ 224.0837, found 224.0837.

3p[S3f]

Yellow oil: ^1H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.98-7.96 (m, 4H, Ar), 7.66 (t, *J* = 7.6 Hz, 1H, Ar), 7.53-7.50 (m, 4H, Ar), 4.80 (d, *J* = 4.4 Hz, 2H, $–CH_2–$), 2.01 (t, *J* = 5.6 Hz, 1H, –OH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 30 °C): δ 194.7, 194.4, 148.5, 135.0, 133.2, 132.4, 130.3, 130.1, 129.2, 127.0, 64.6; HRMS (CI^+) *m/z* calcd. for $C_{15}H_{13}O_3$ $[M+H]^+$ 241.0865, found 241.0864.

8. References

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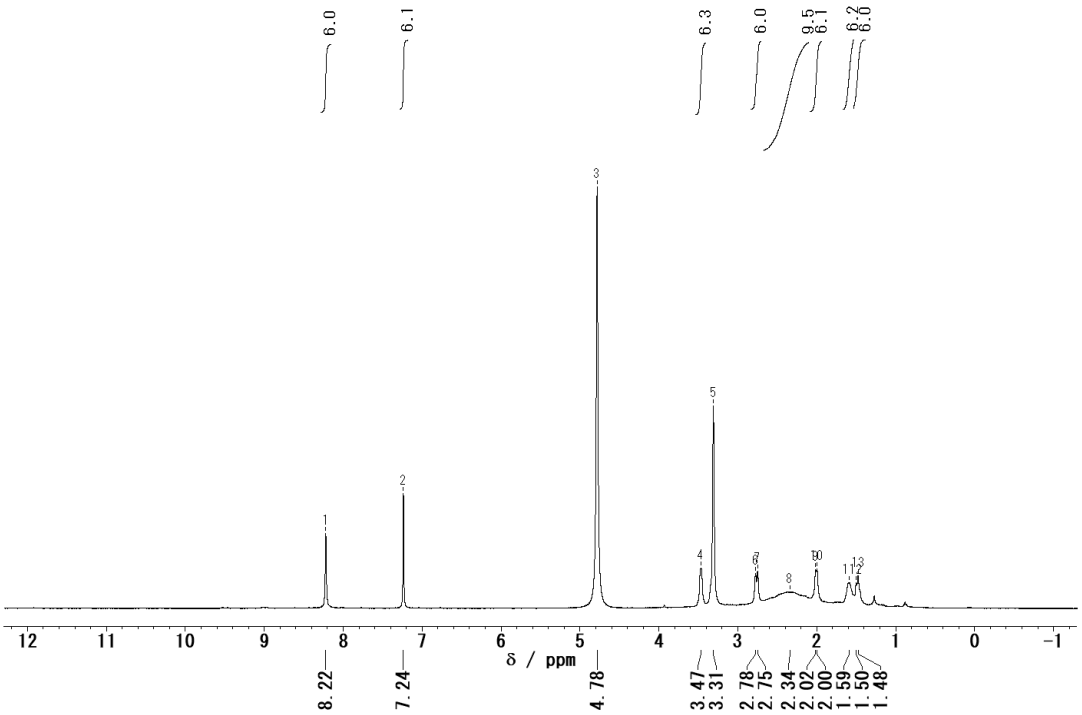
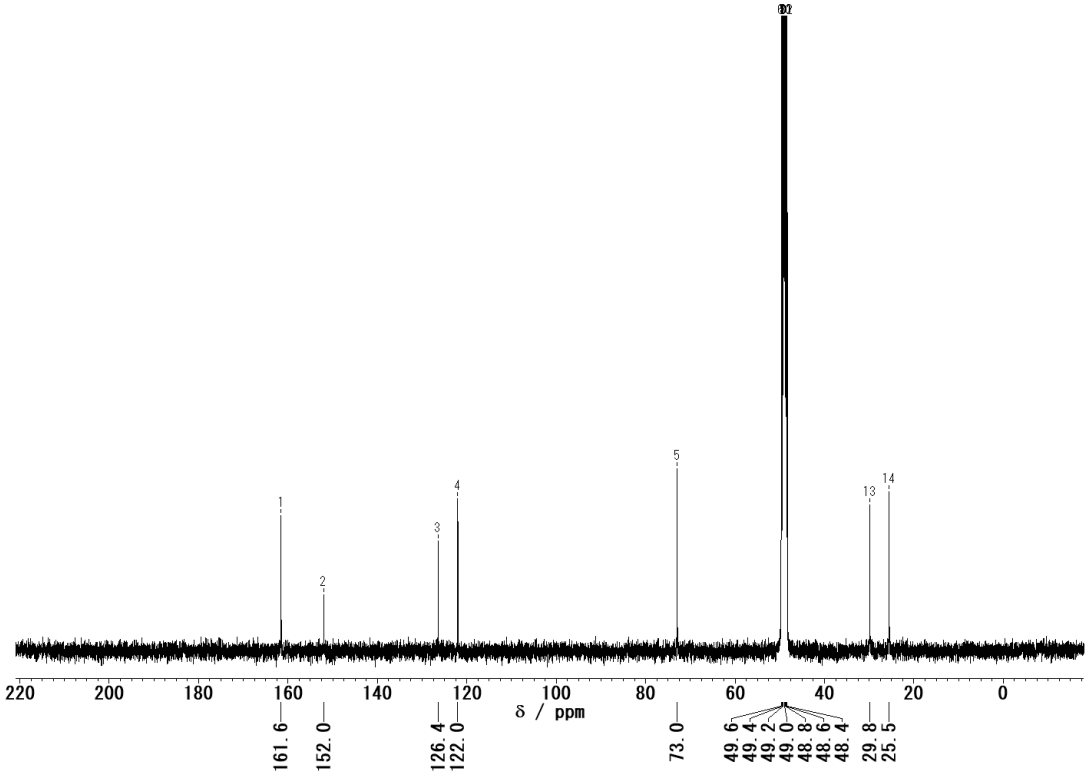
9. NMR chart

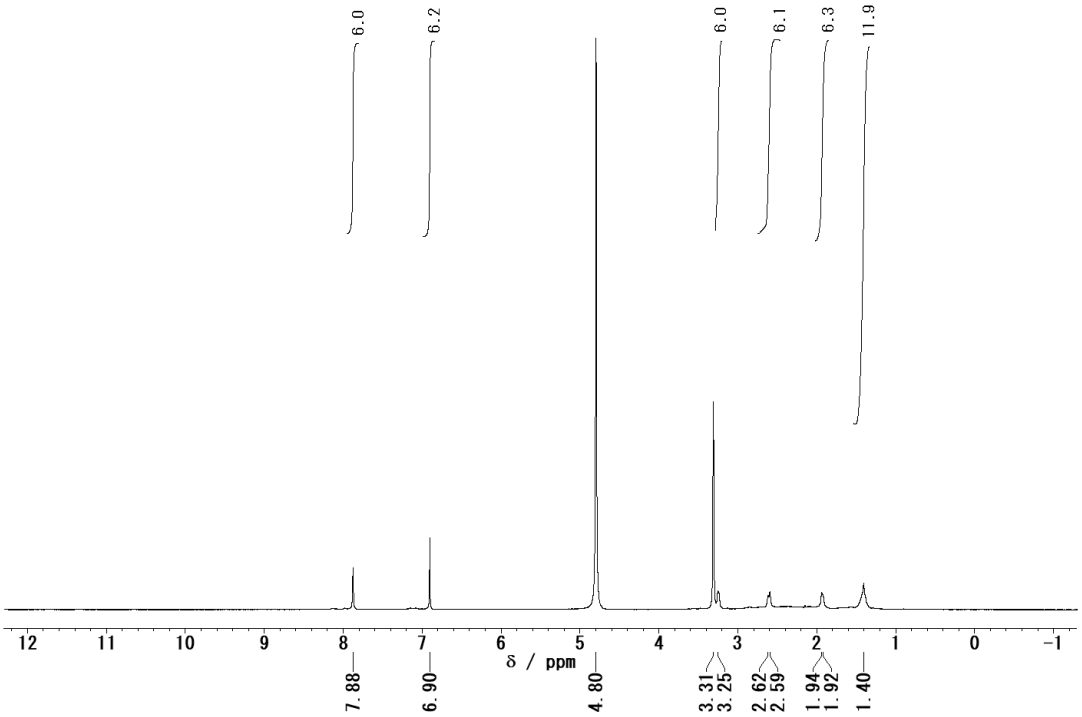
^{1}H NMR of **1**$_{\mathbf{CeNi}}$



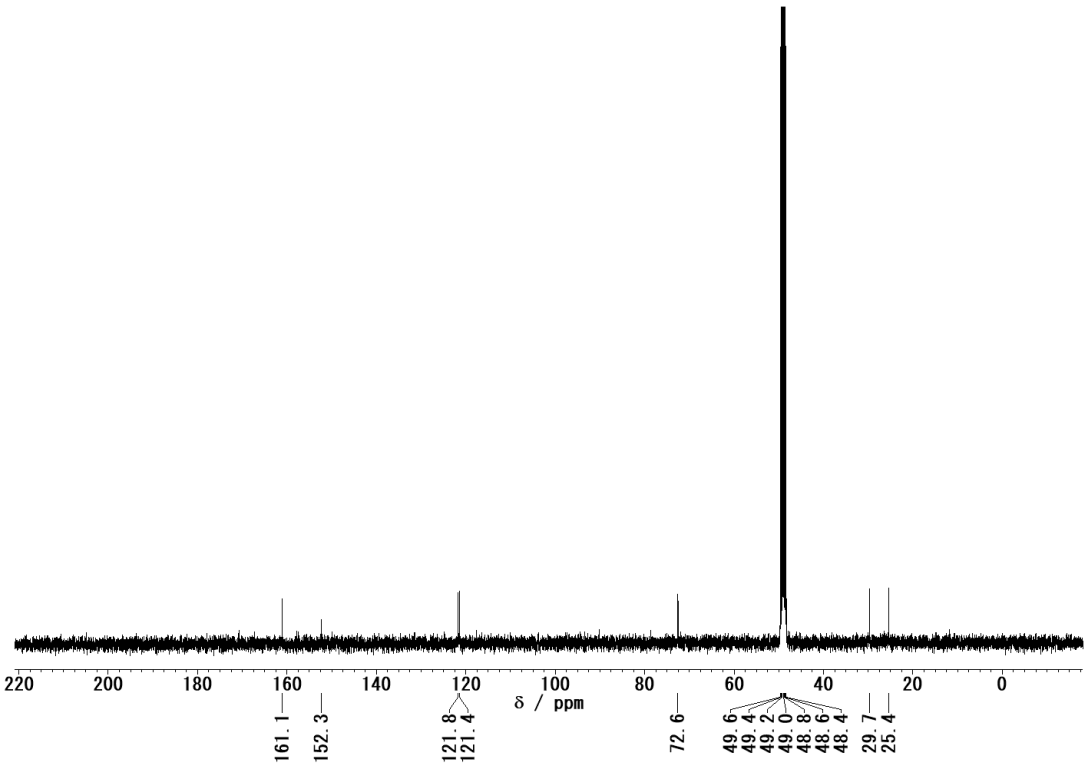
^{13}C{^{1}H} NMR of **1**$_{\mathbf{CeNi}}$



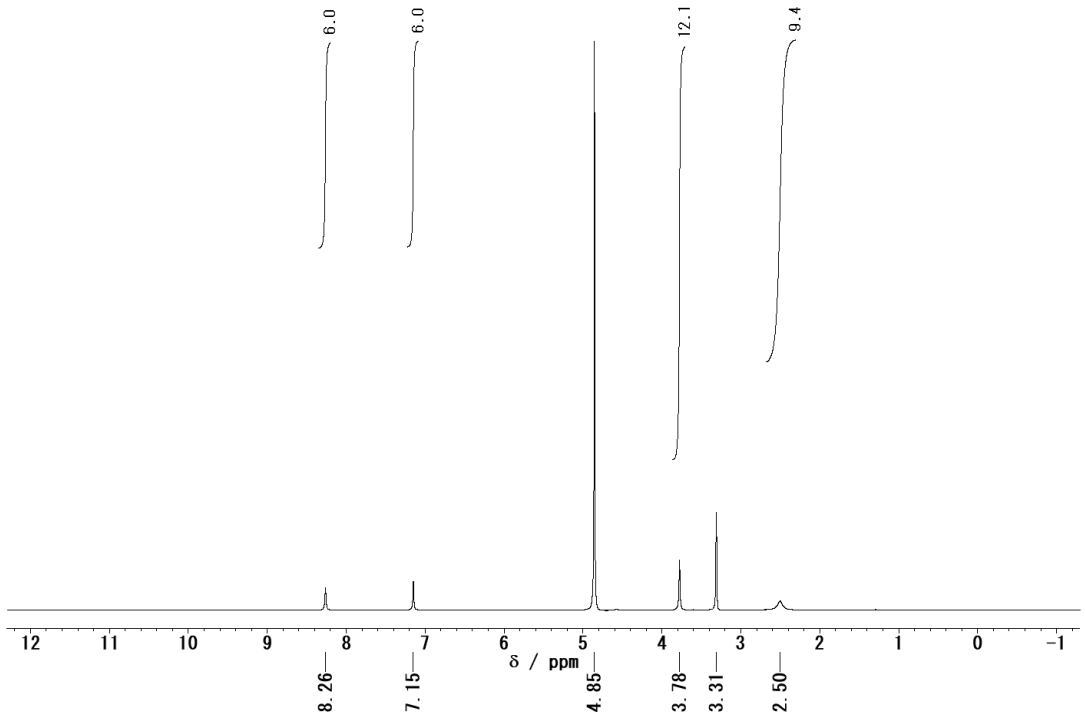
^{1}H NMR of $\mathbf{1}_{\mathbf{LaNi}}$



^{13}C{^{1}H} NMR of $\mathbf{1}_{\mathbf{LaNi}}$



^{1}H NMR of **6$_{CeNi}$**



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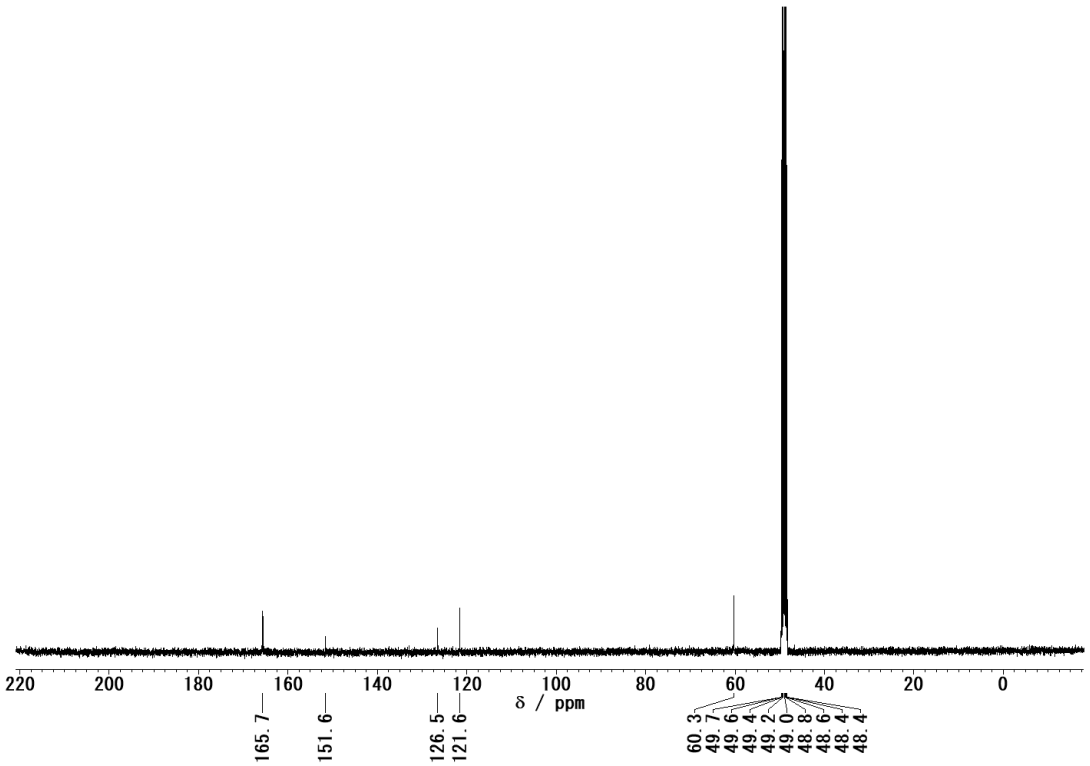
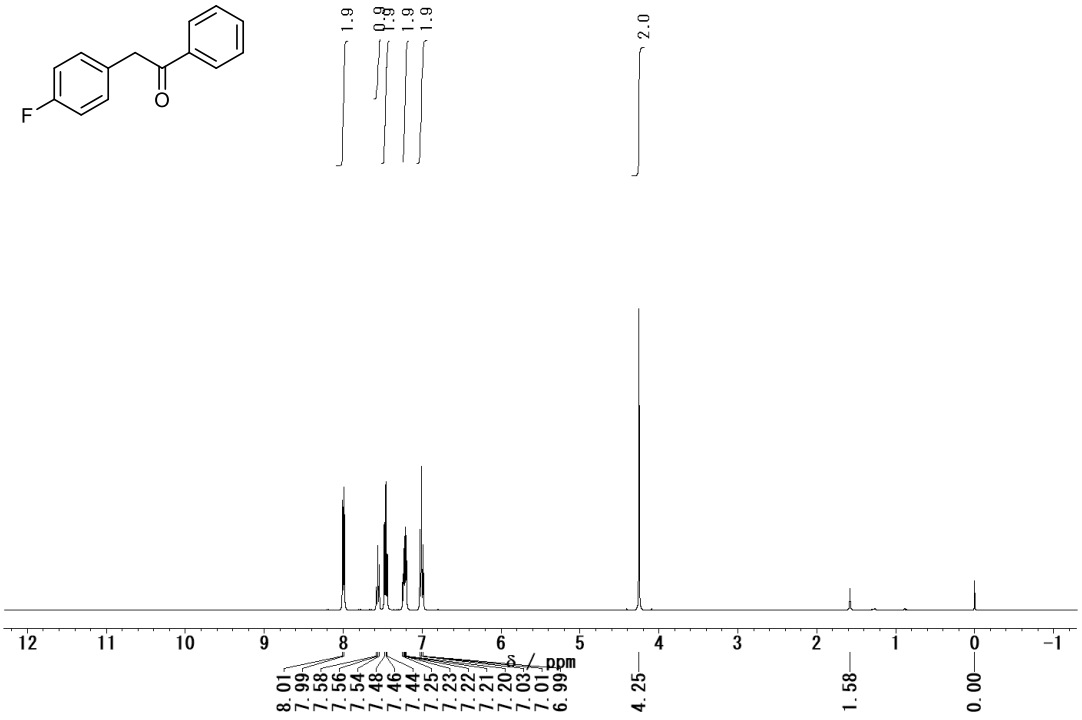
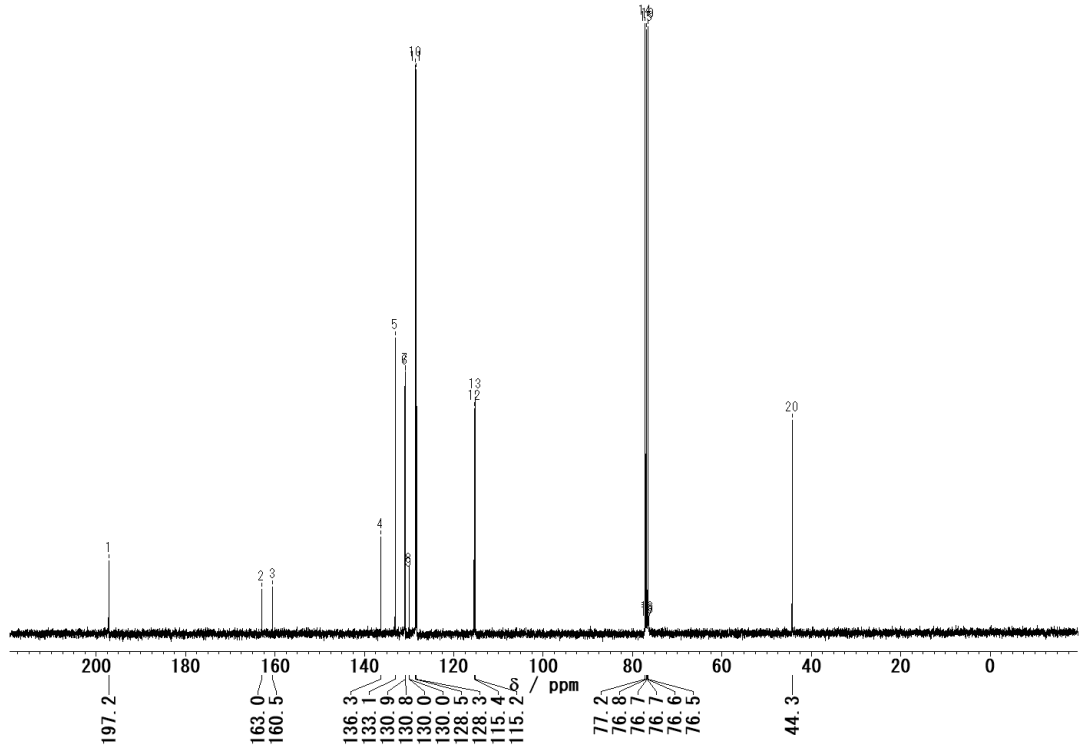


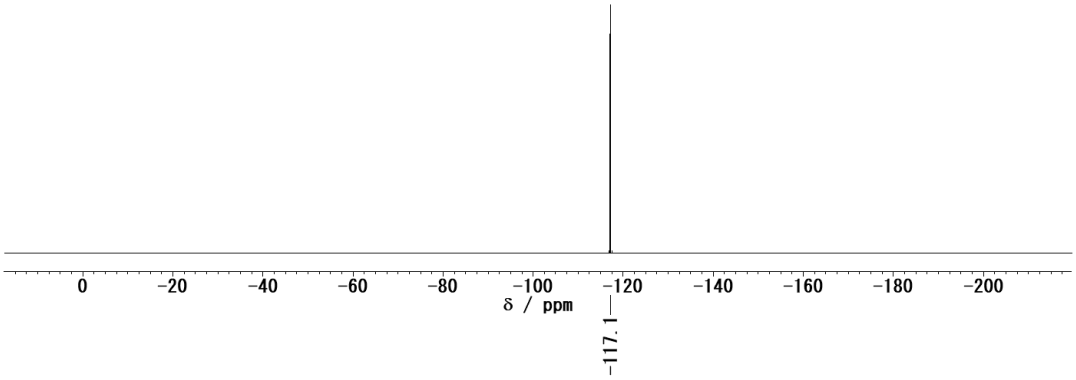
^{1}H NMR of **2b**



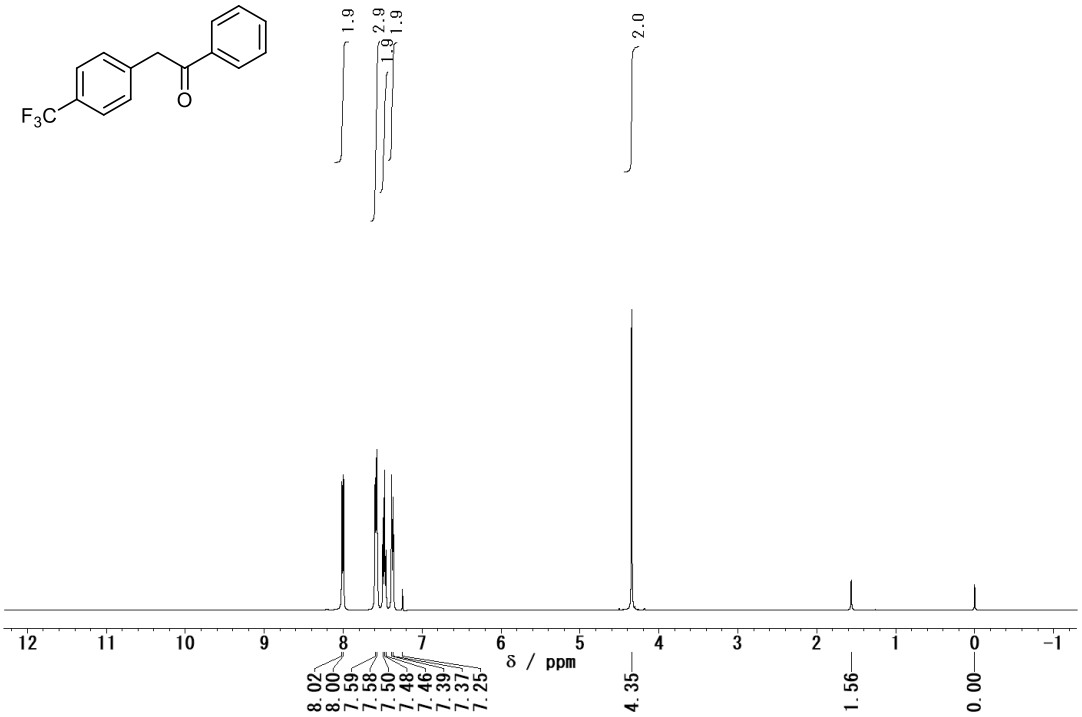
^{13}C{^{1}H} NMR of **2b**



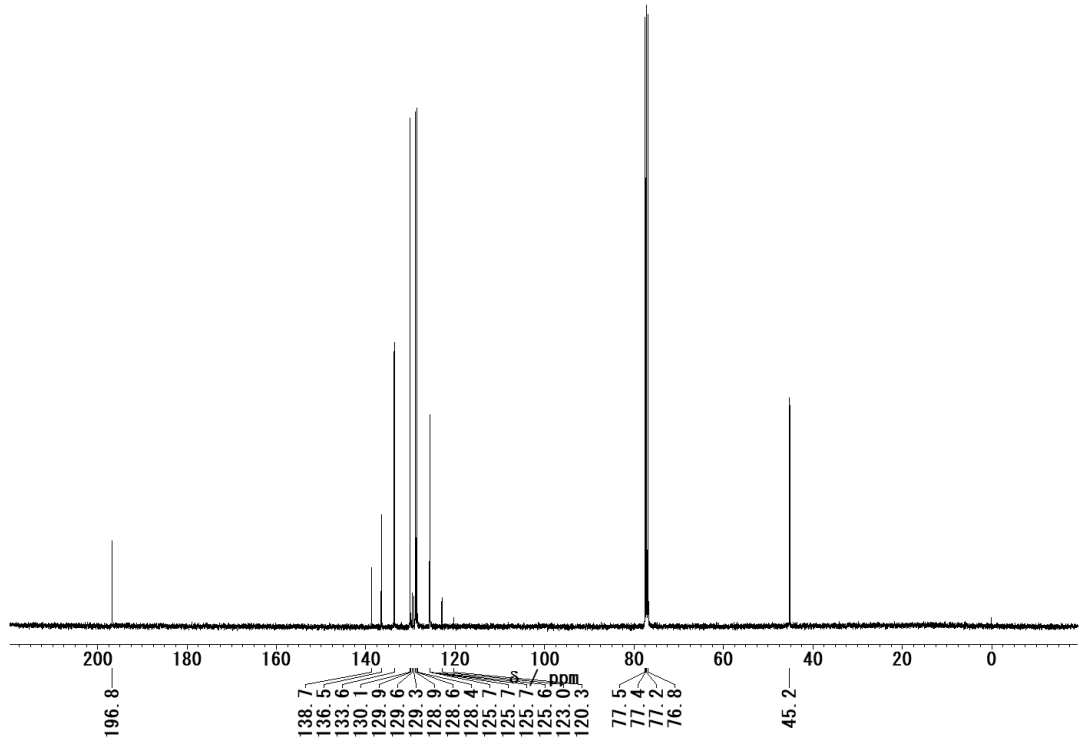
$^{19}F\{^{1}H\}$ NMR of **2b**



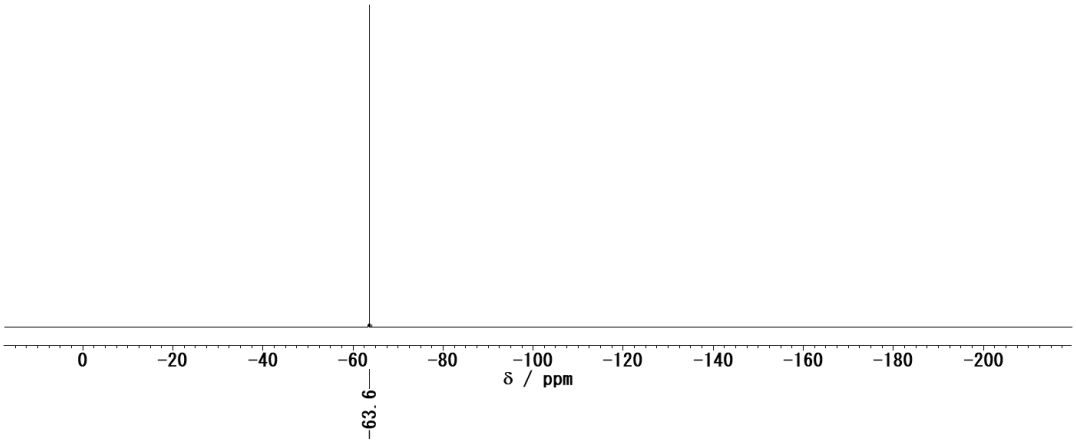
^{1}H NMR of **2d**



^{13}C{^{1}H} NMR of **2d**



$^{19}F\{^{1}H\}$ NMR pf **2d**



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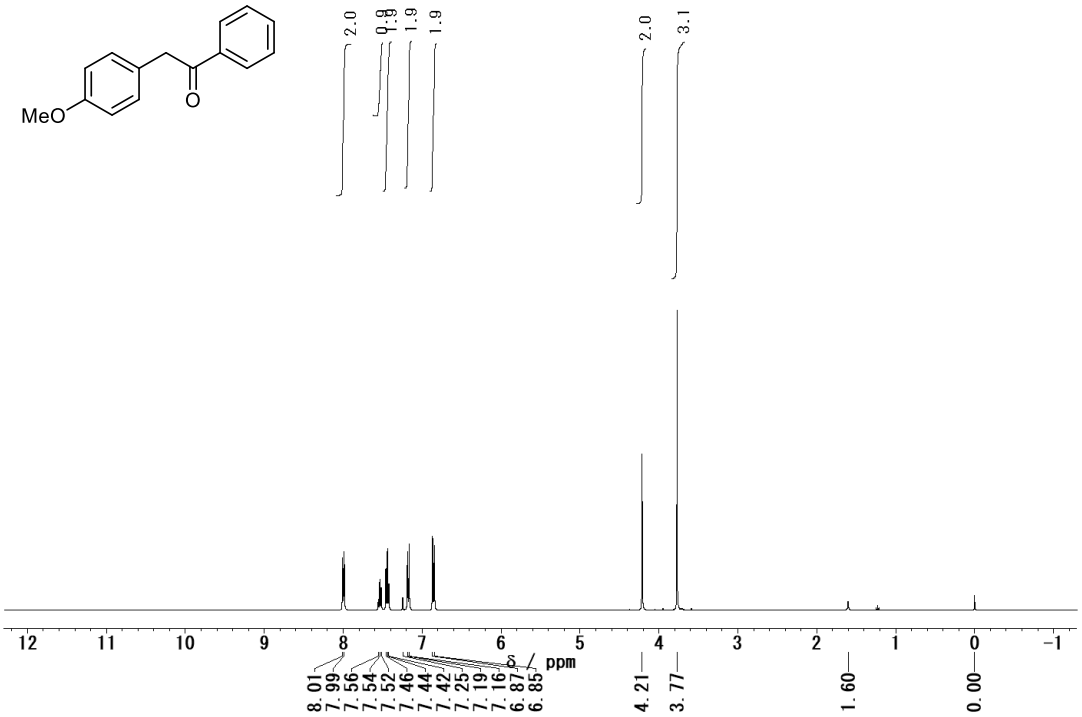
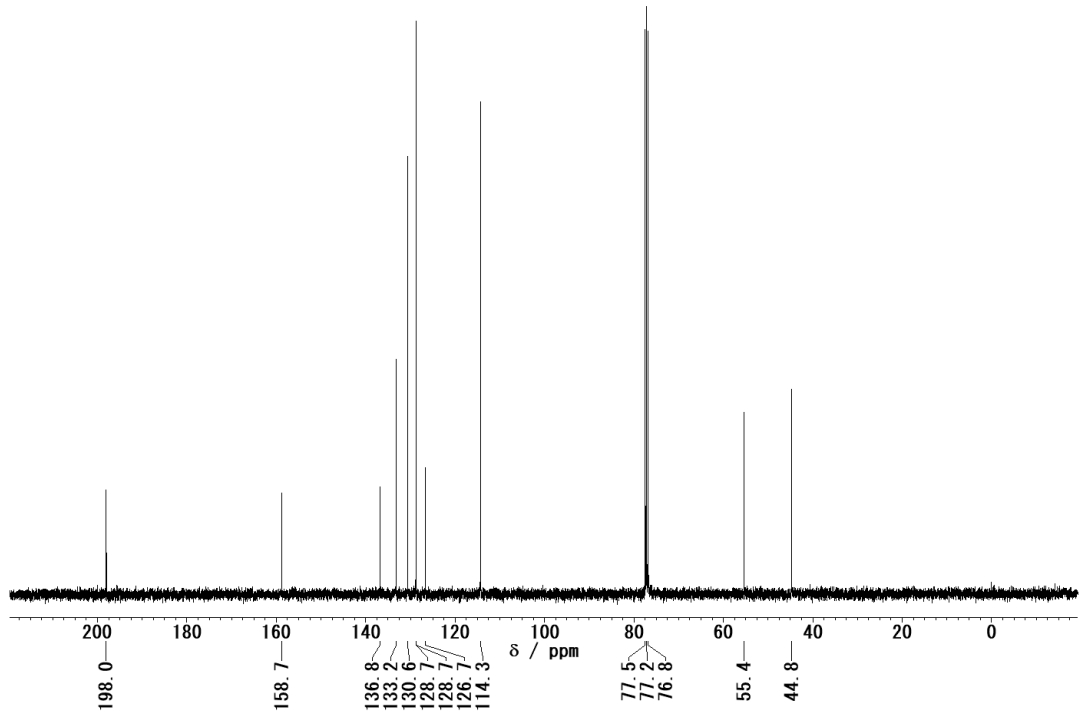
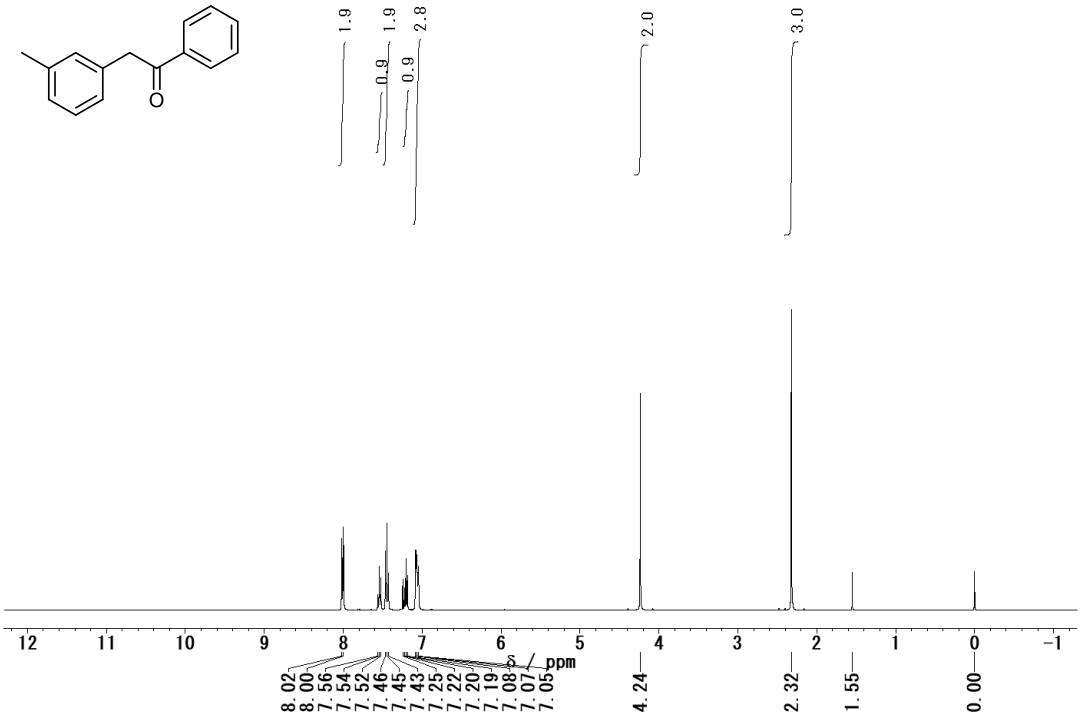


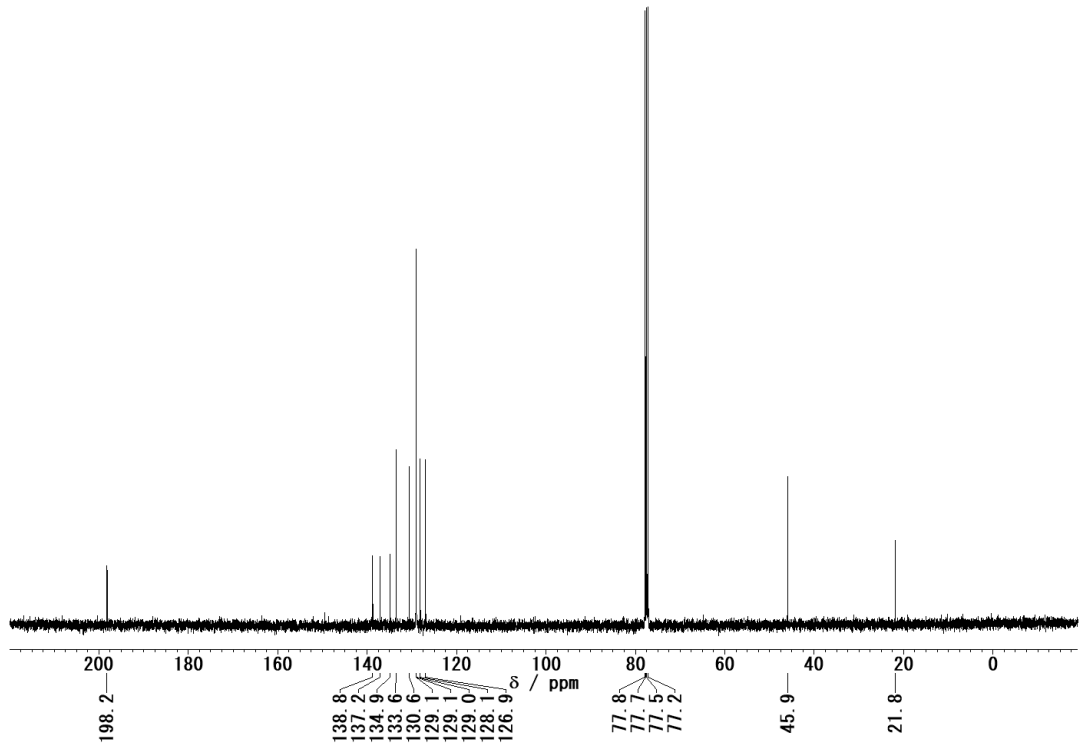
^{13}C{^{1}H} NMR of **2e**



^{1}H NMR of **2g**



^{13}C{^{1}H} NMR of **2g**



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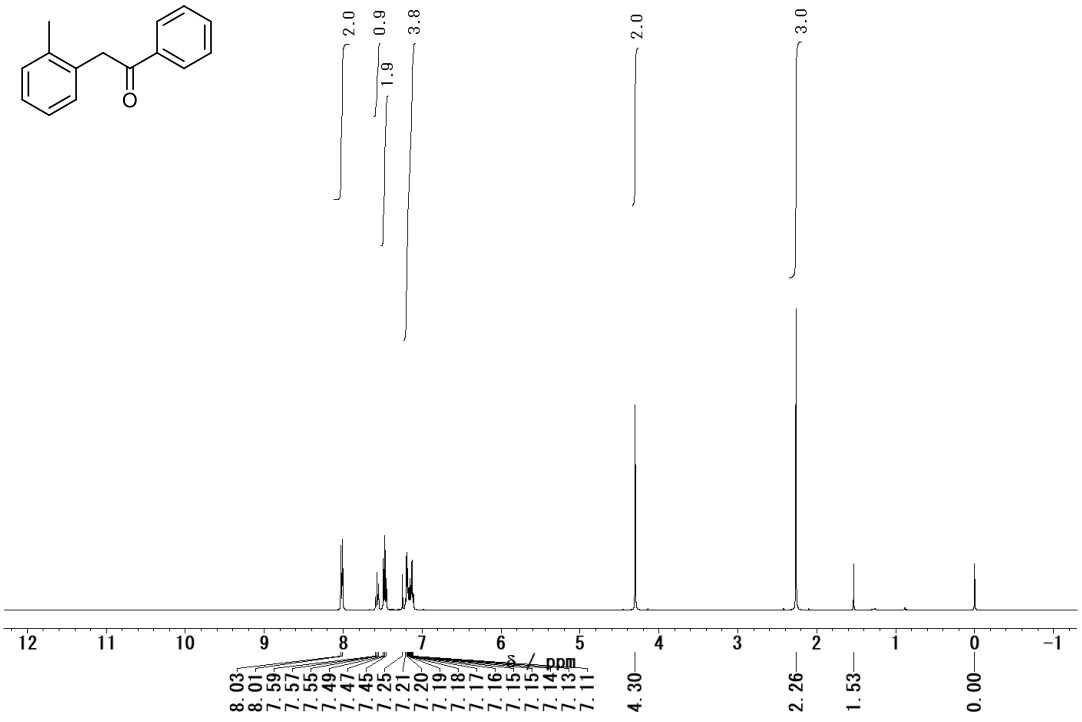

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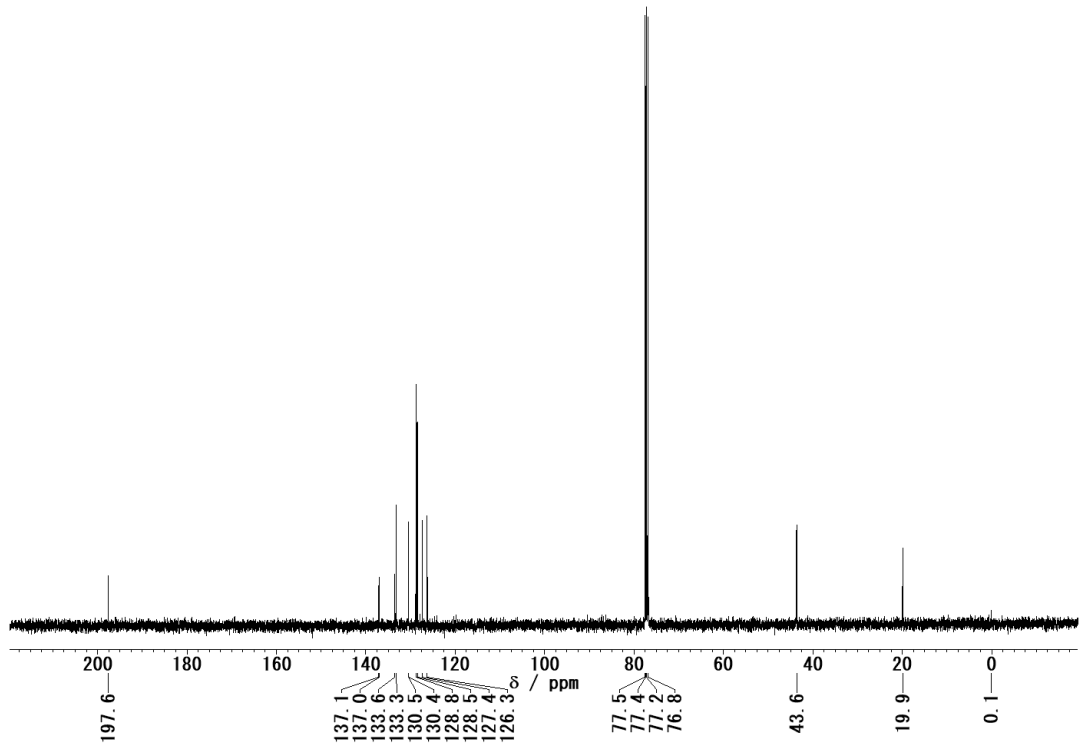

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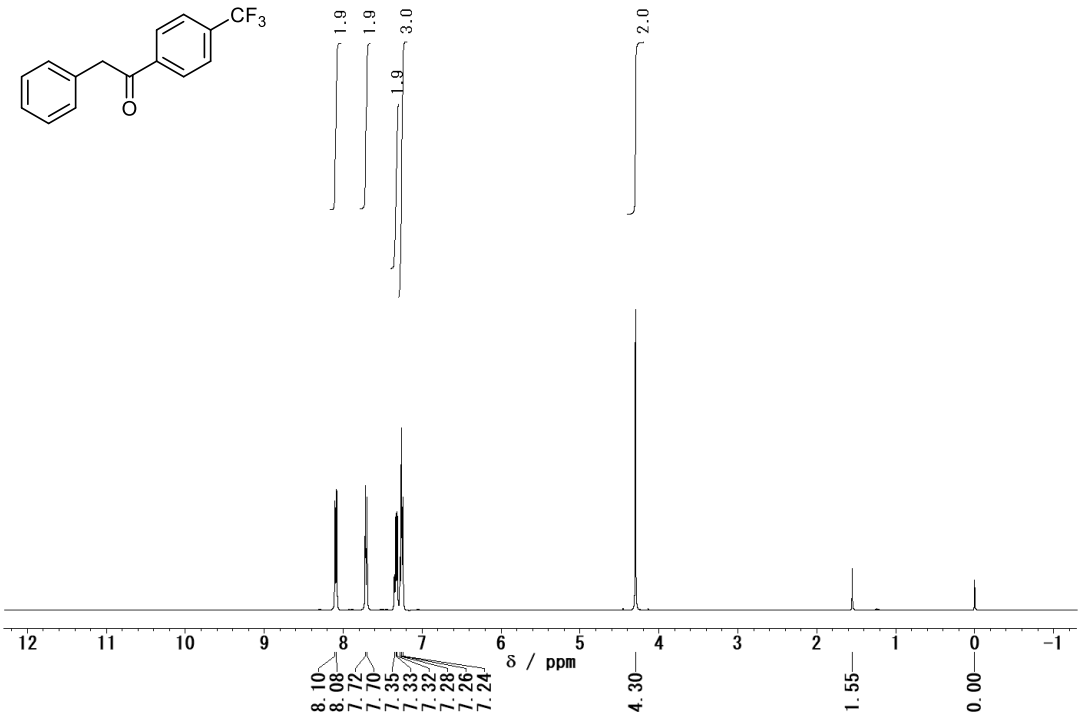

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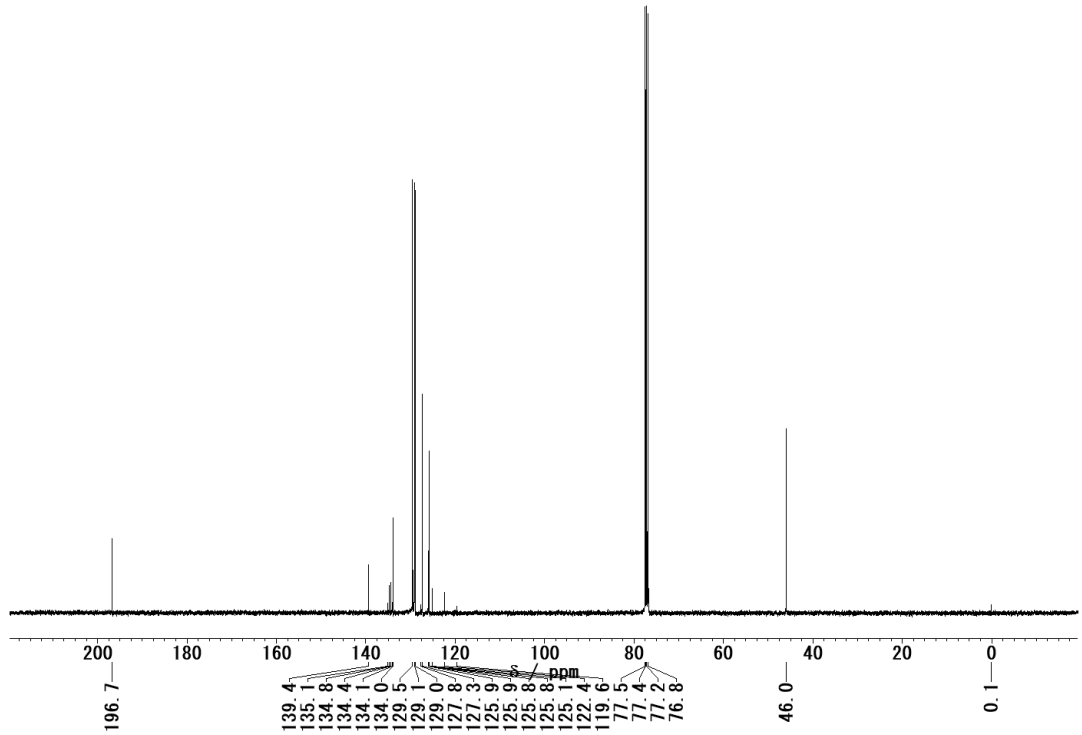
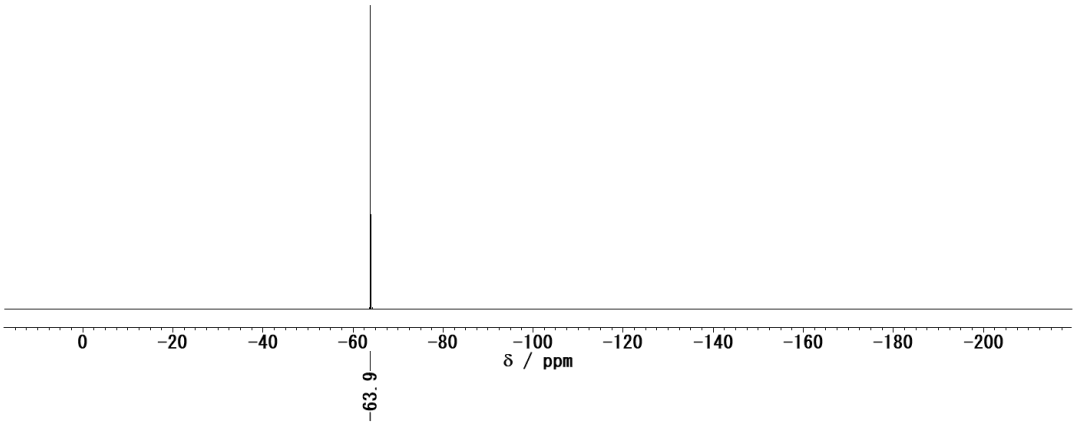


$^{19}F\{^{1}H\}$ NMR of **2k**



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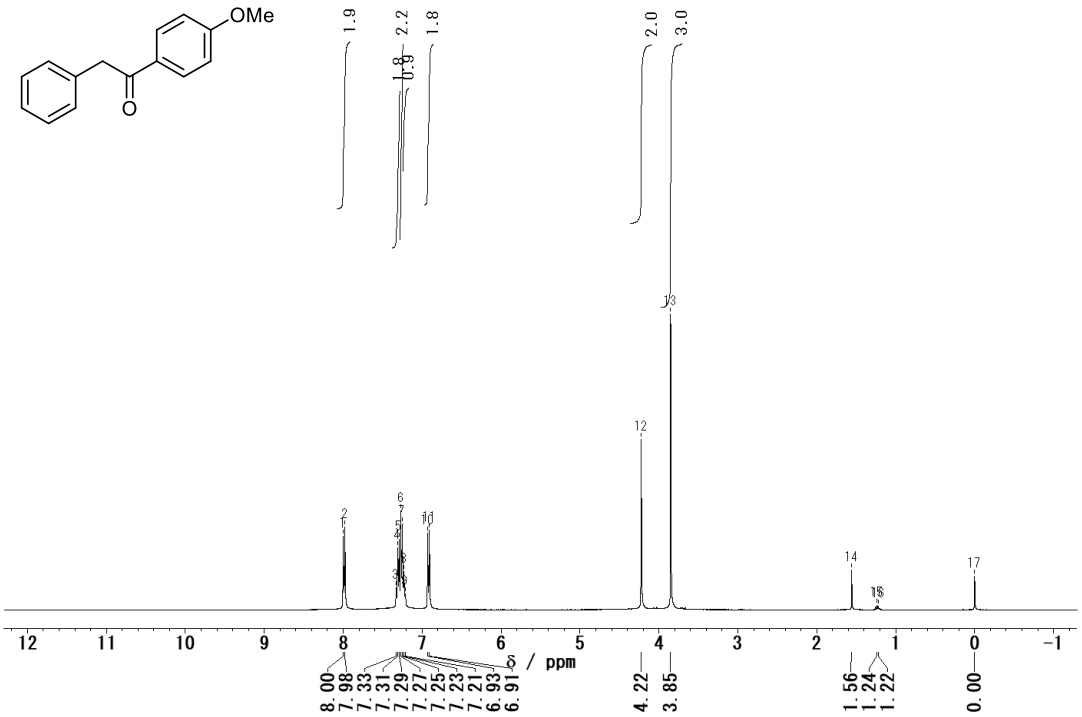

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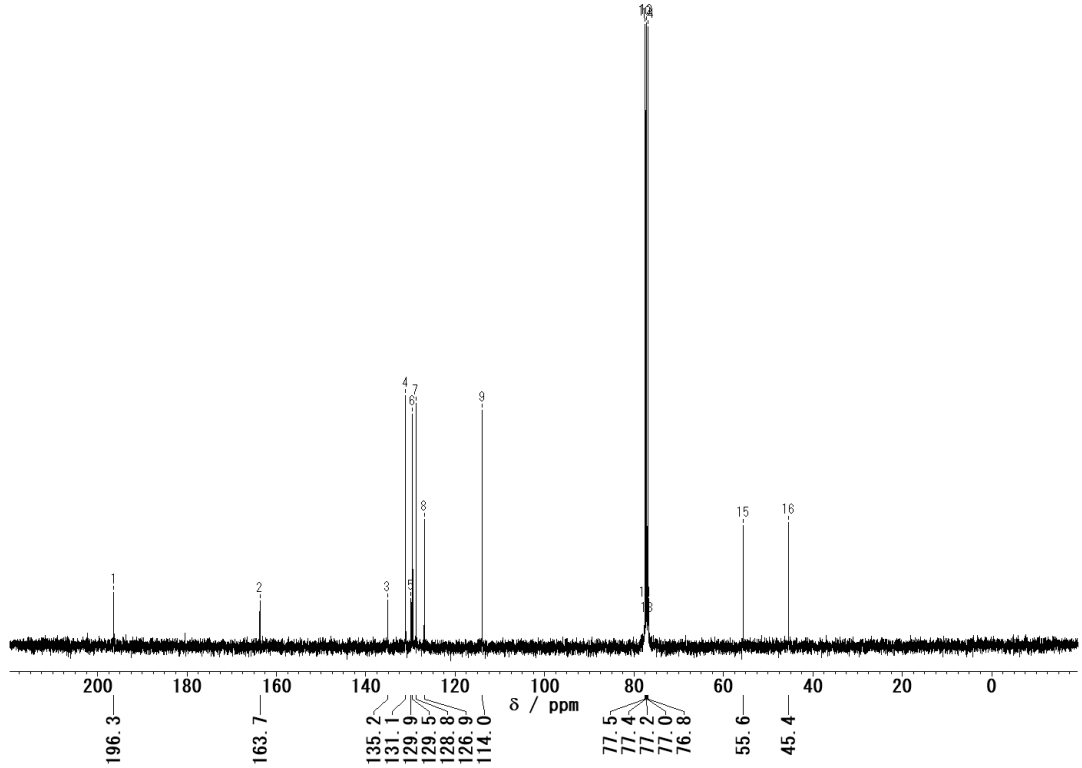
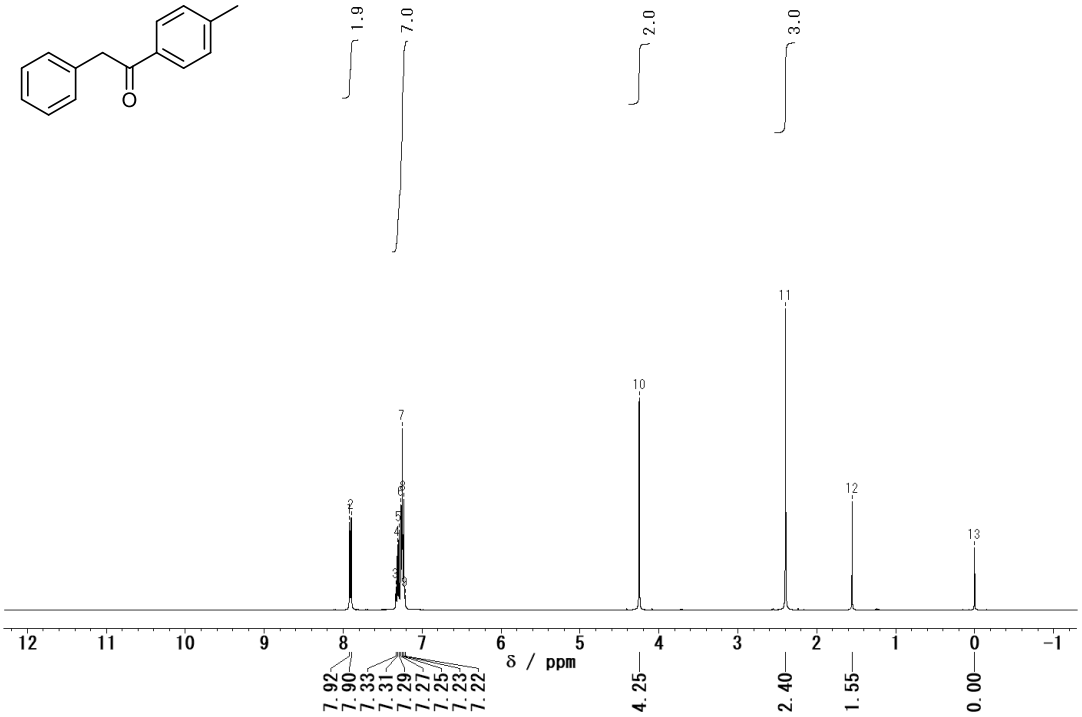
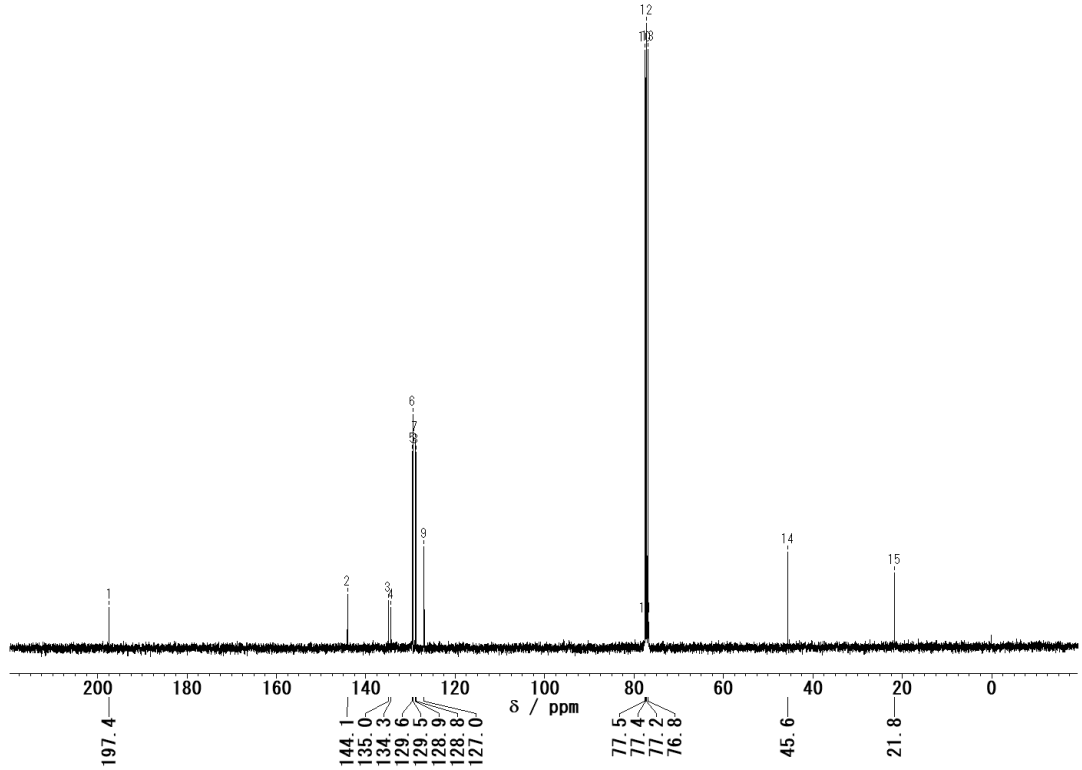


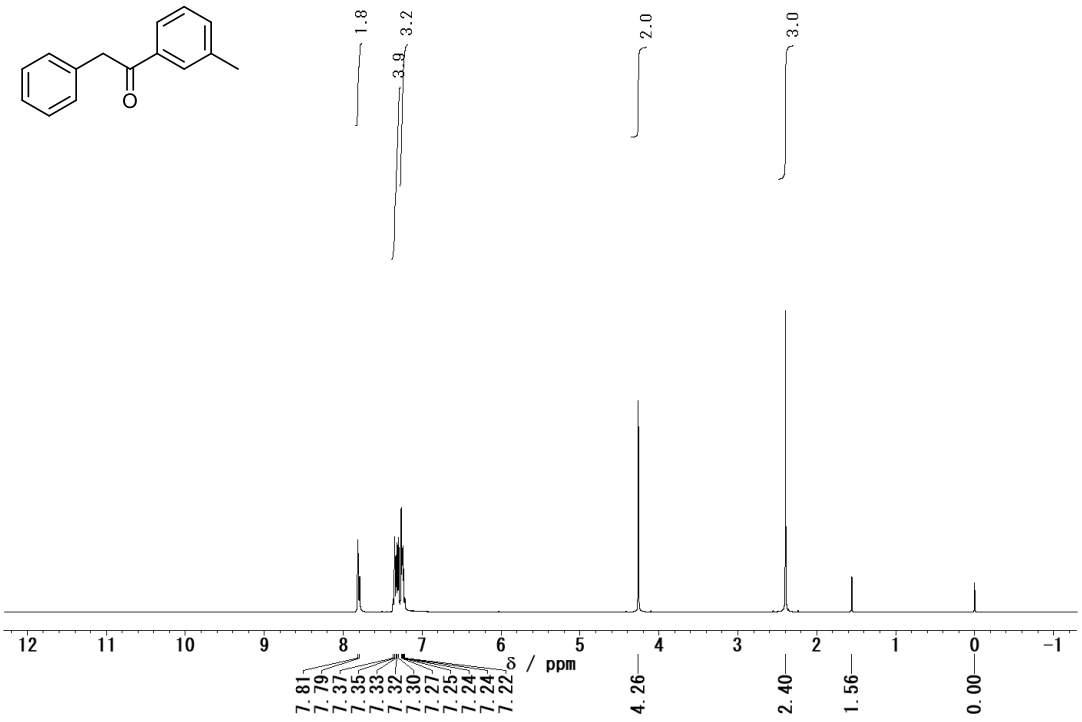
^{1}H NMR of **2m**



^{13}C{^{1}H} NMR of **2m**



^{1}H NMR of **2n**



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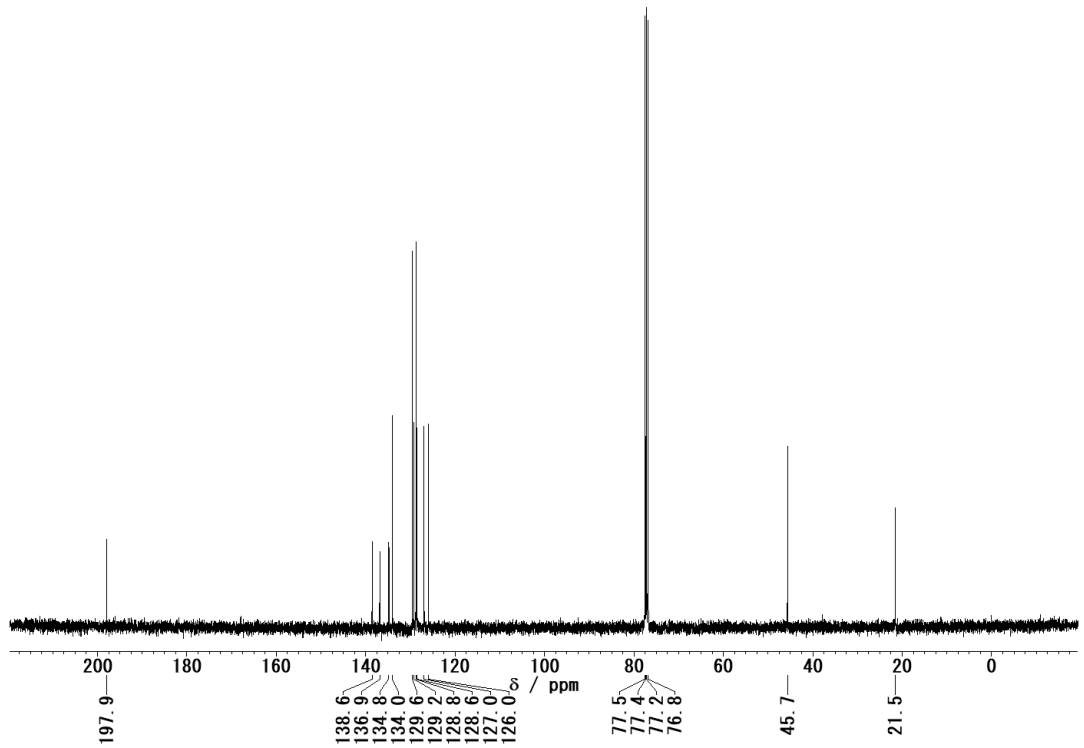
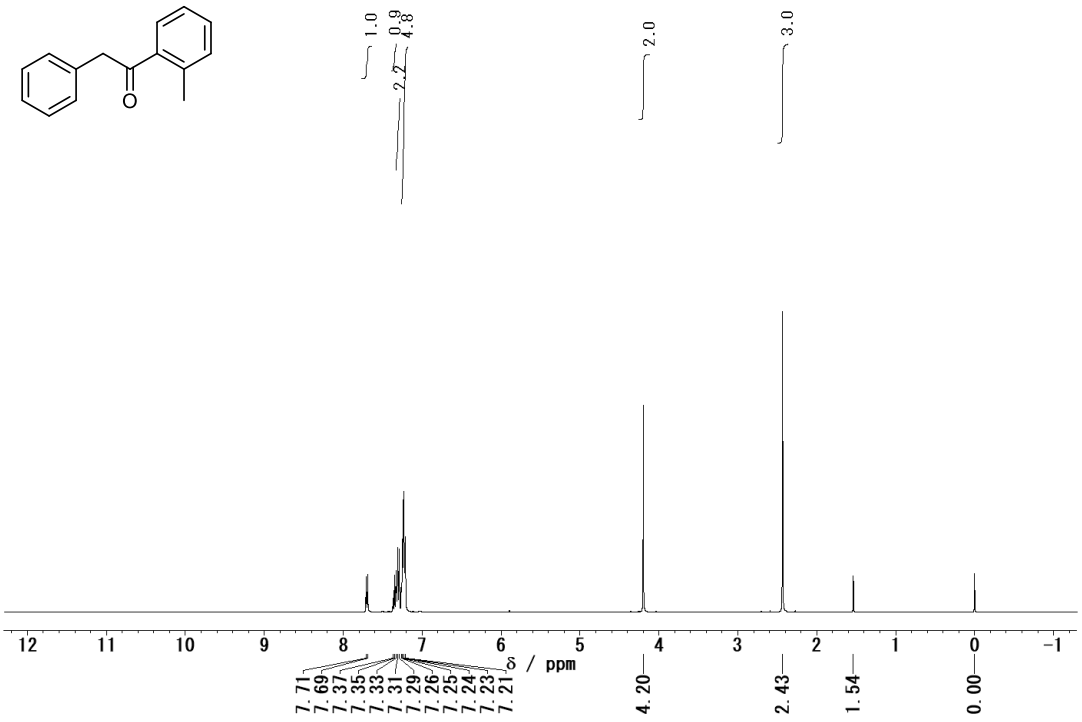


^{1}H NMR of **2o**



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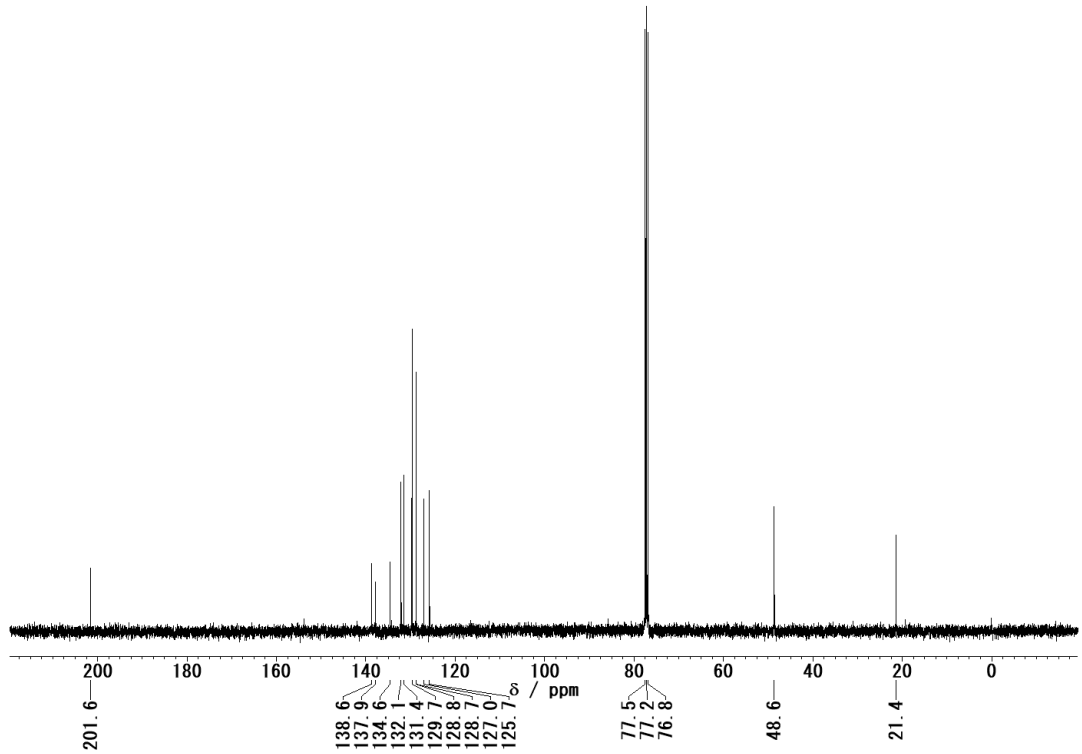
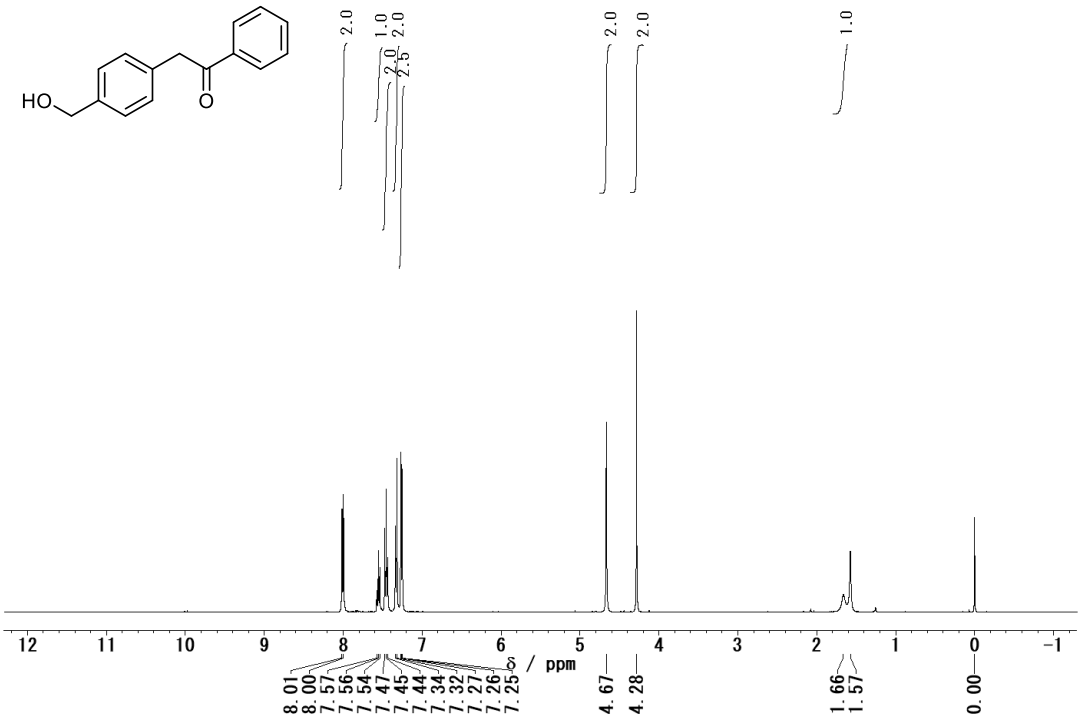


^{1}H NMR of **2p**



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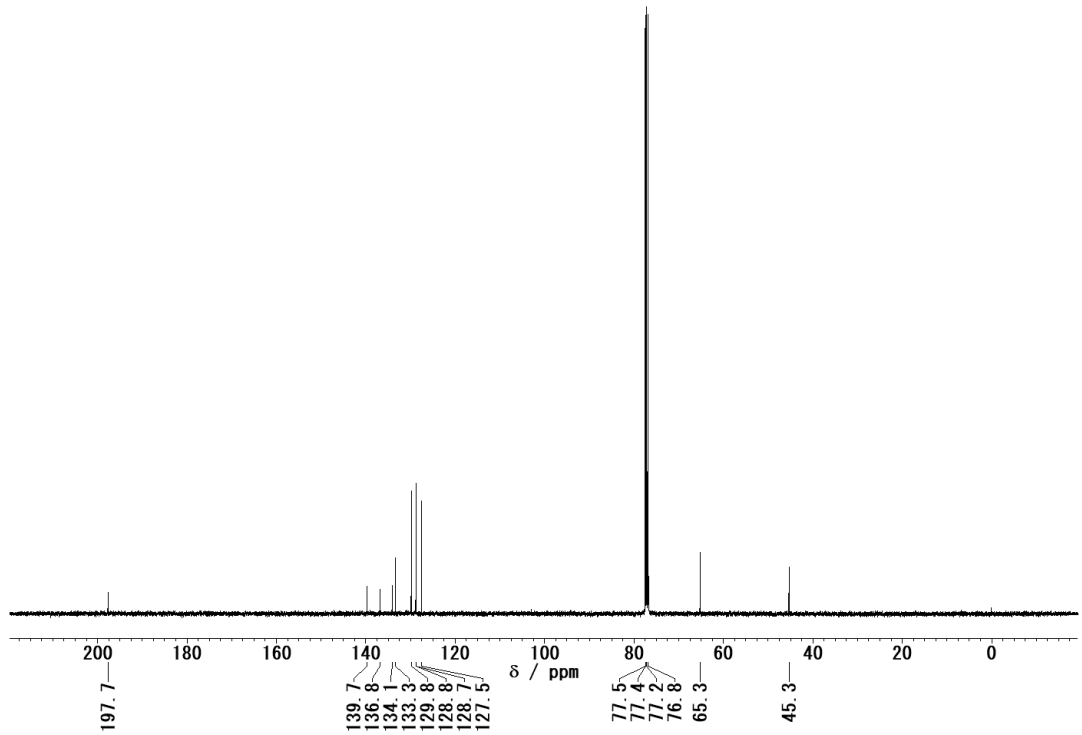
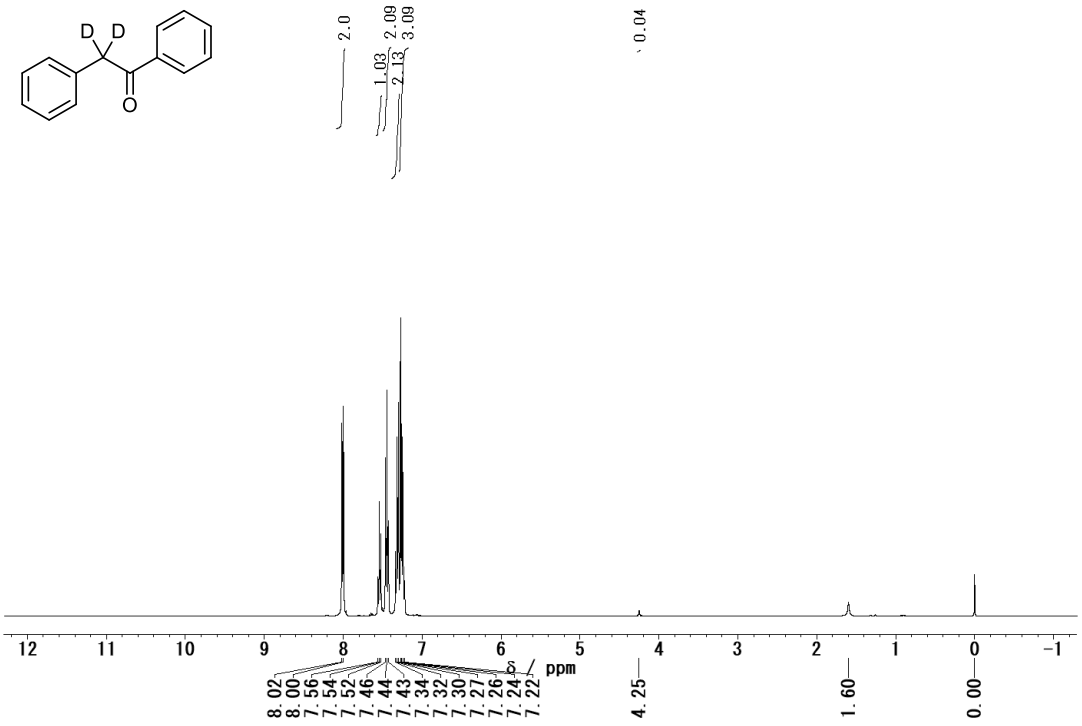
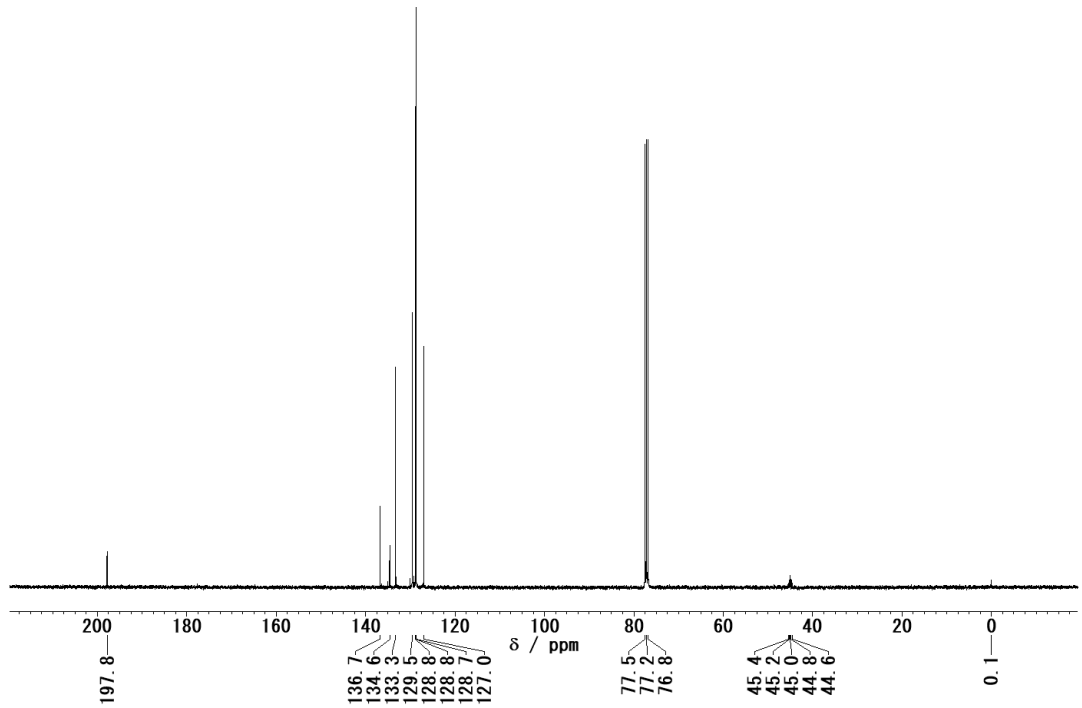


^{1}H NMR of **2a-*d*$_2$**



^{13}C{^{1}H} NMR of **2a-*d*$_2$**



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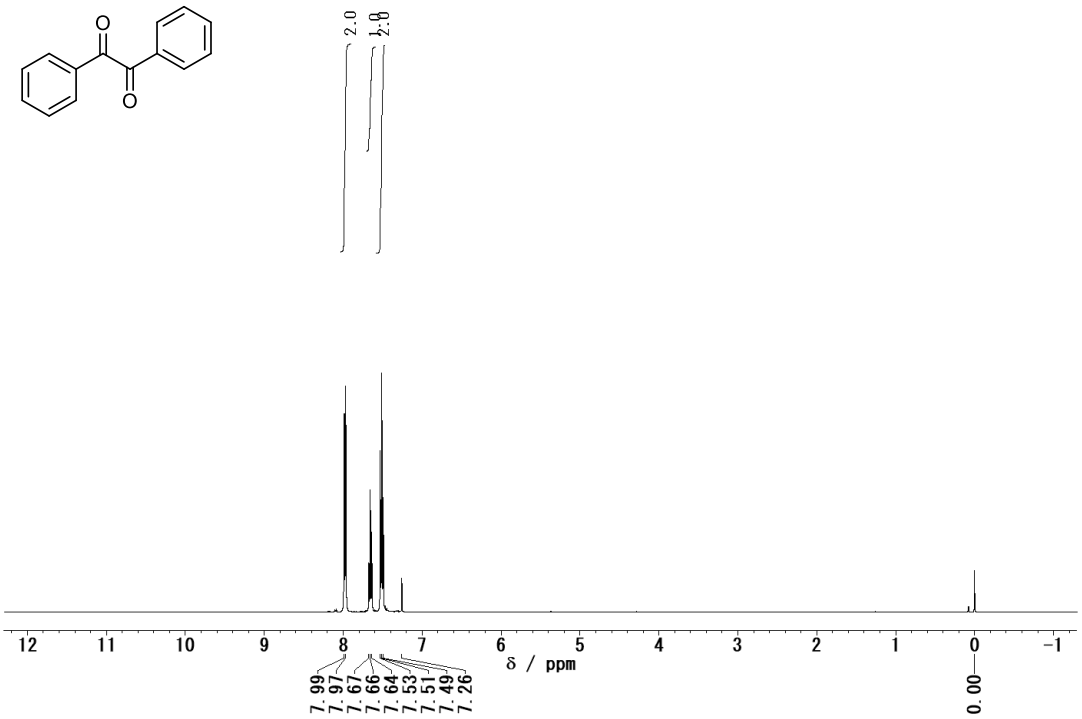
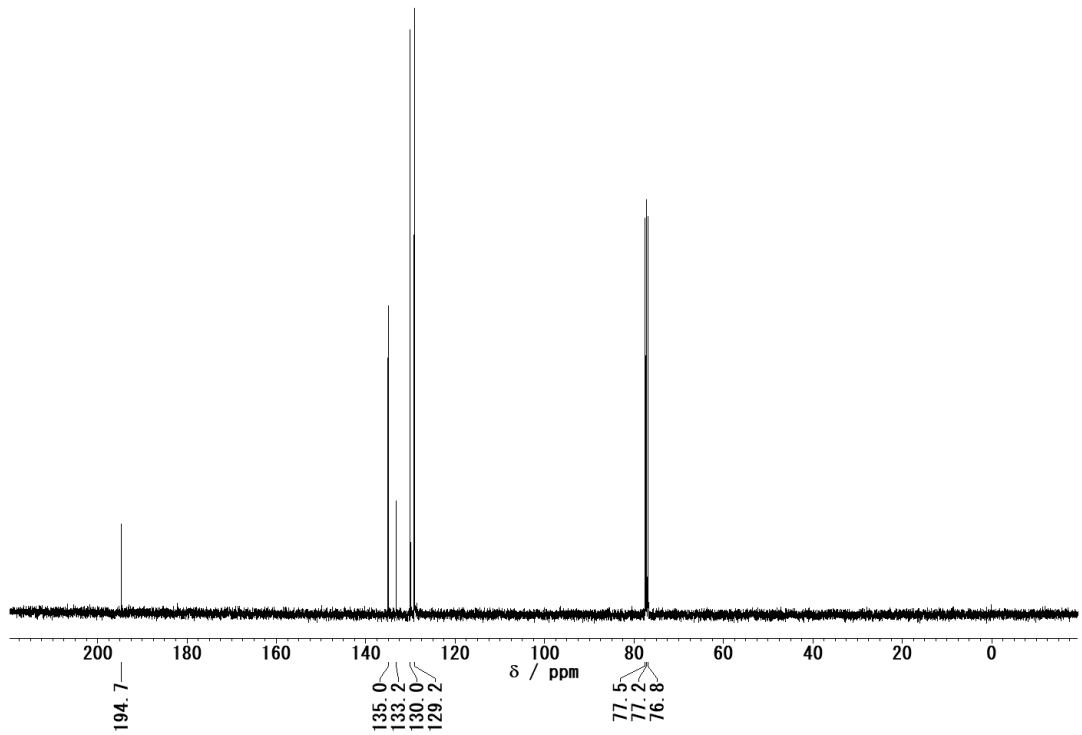


^{13}C{^{1}H} NMR of **3a**



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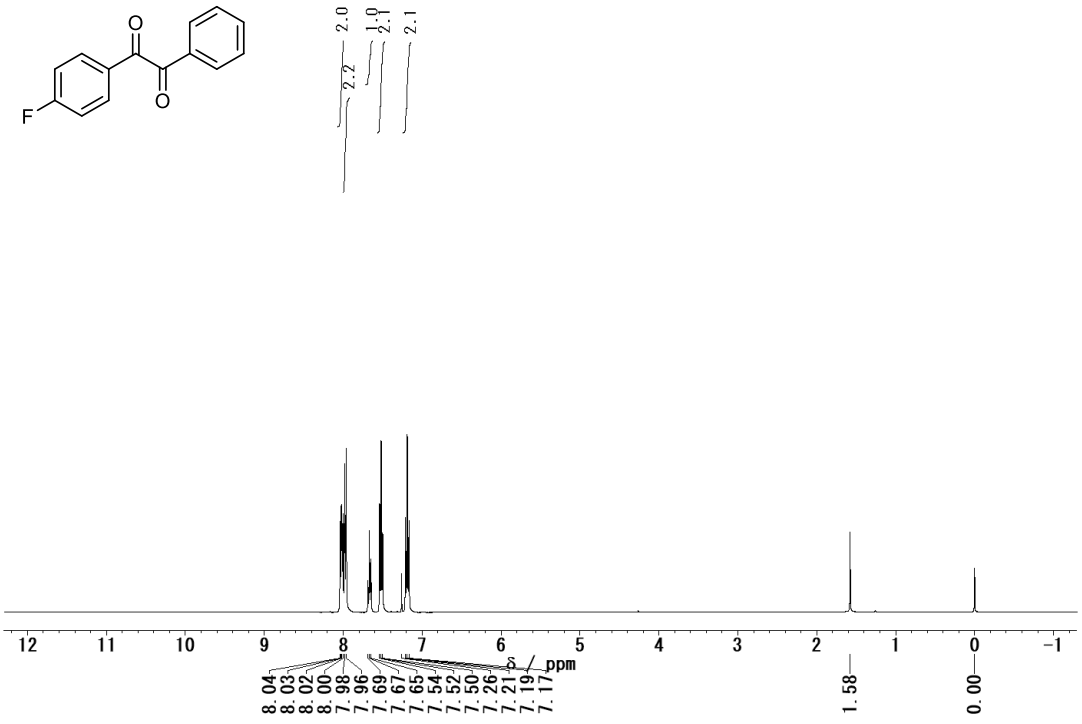

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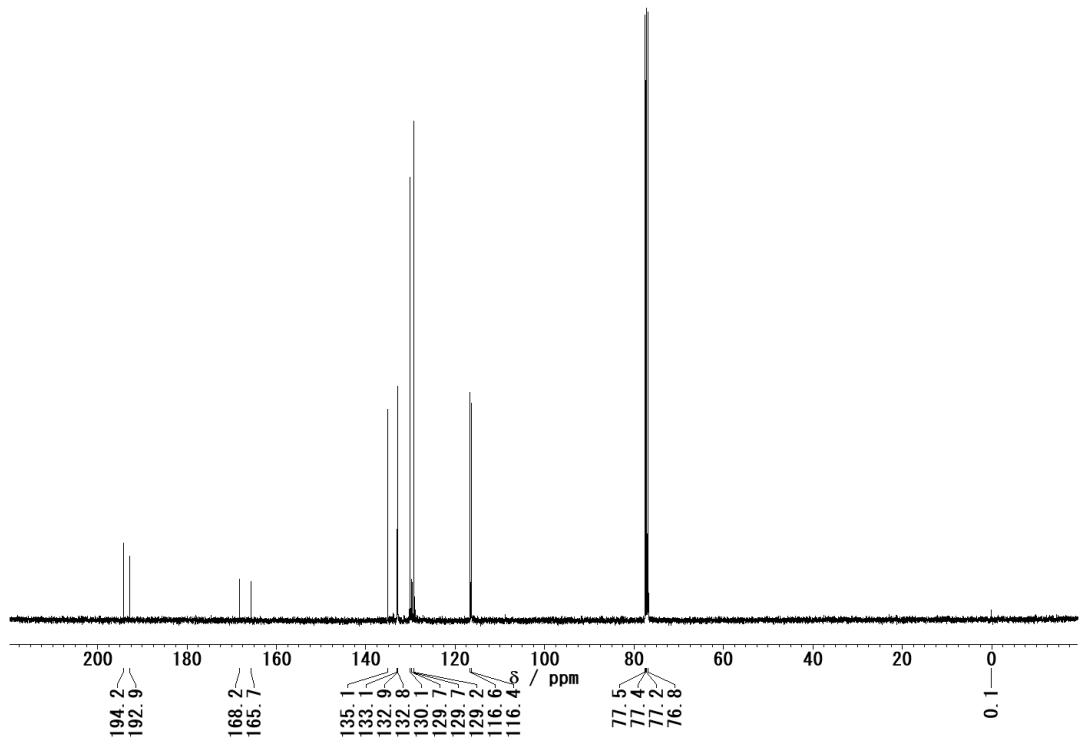
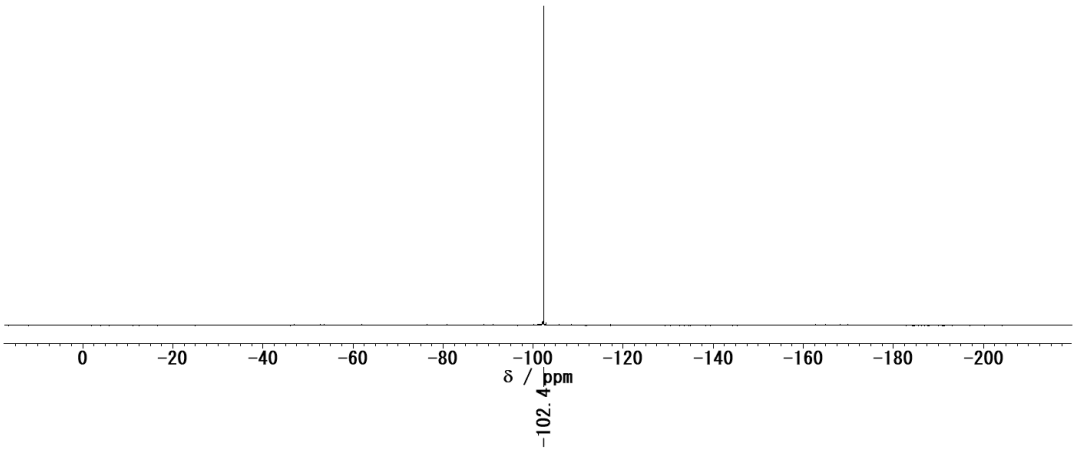
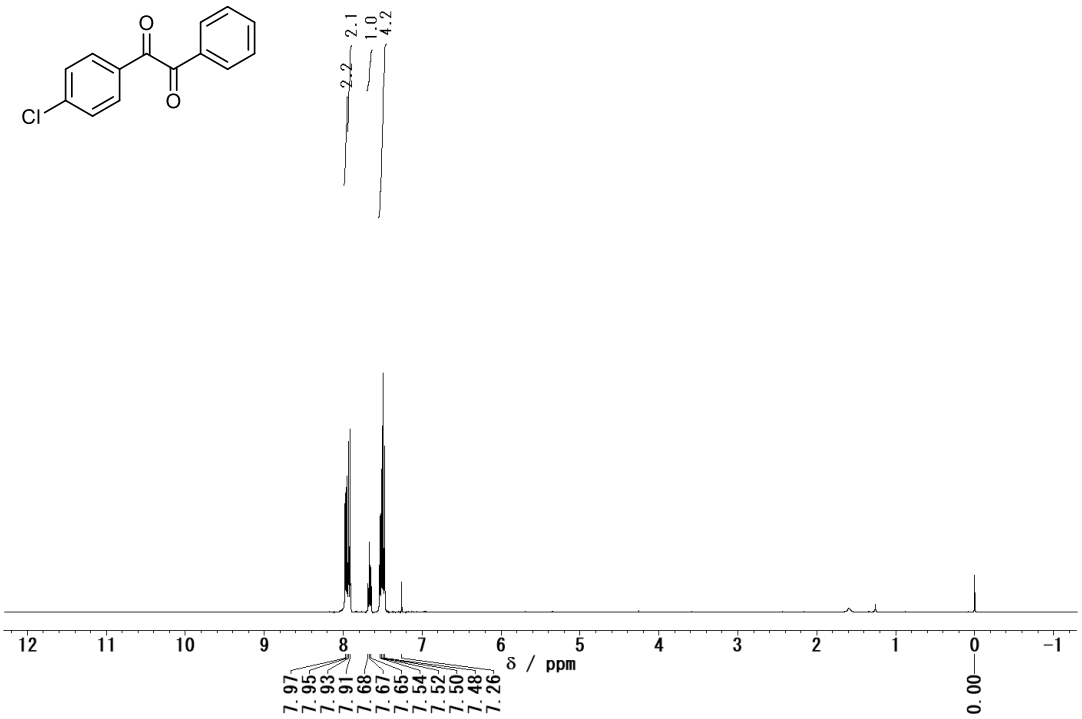


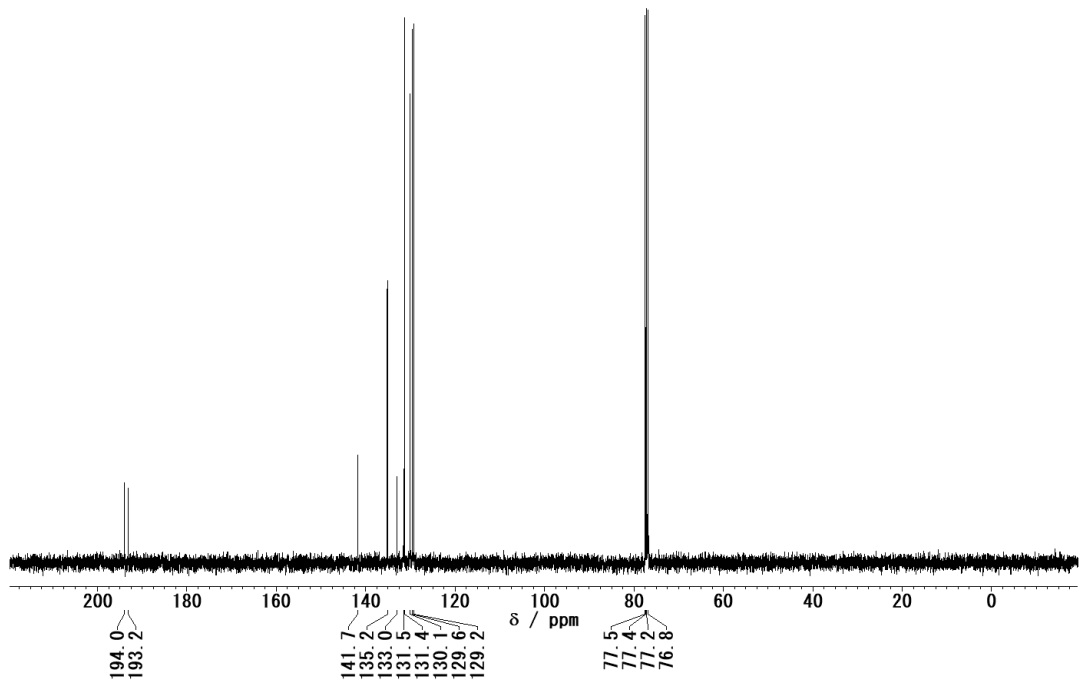
$^{19}F\{^{1}H\}$ NMR of **3b**



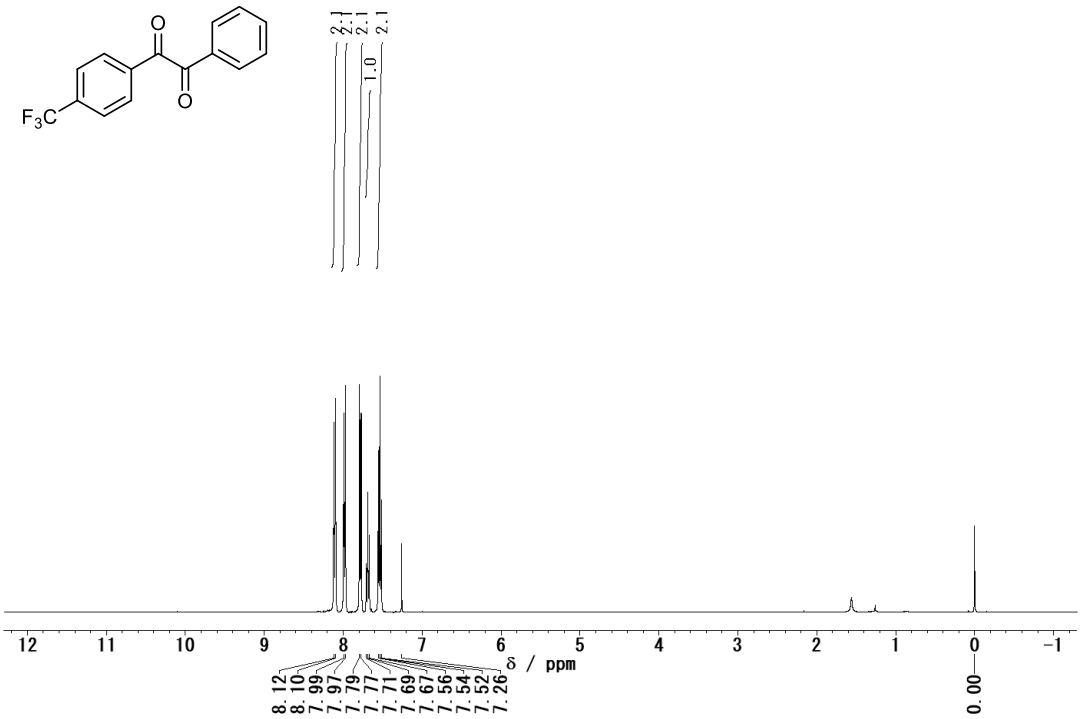
^{1}H NMR of **3c**



^{13}C{^{1}H} NMR of **3c**



^{1}H NMR of **3d**



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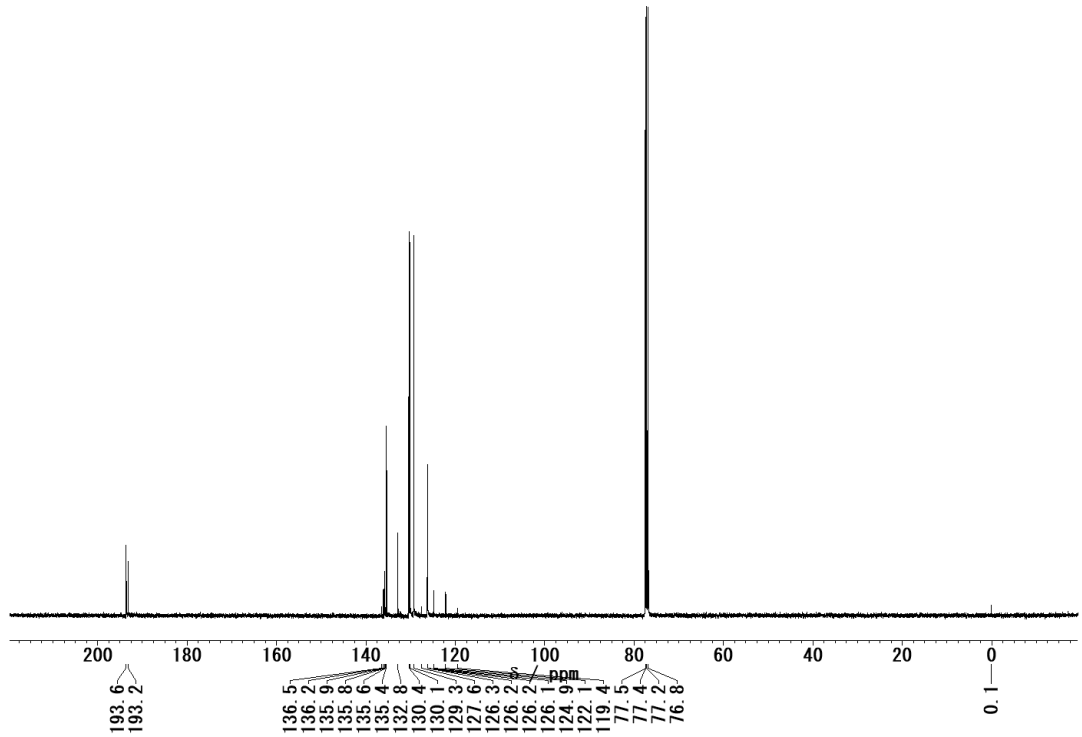

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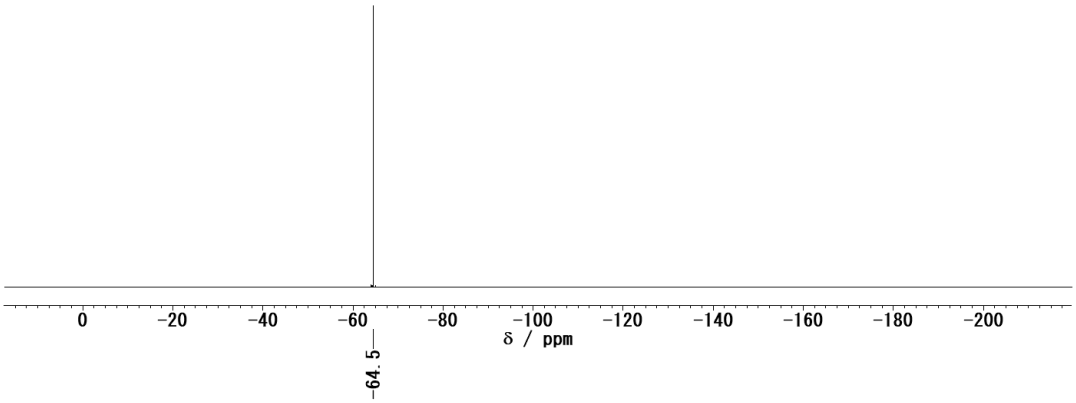

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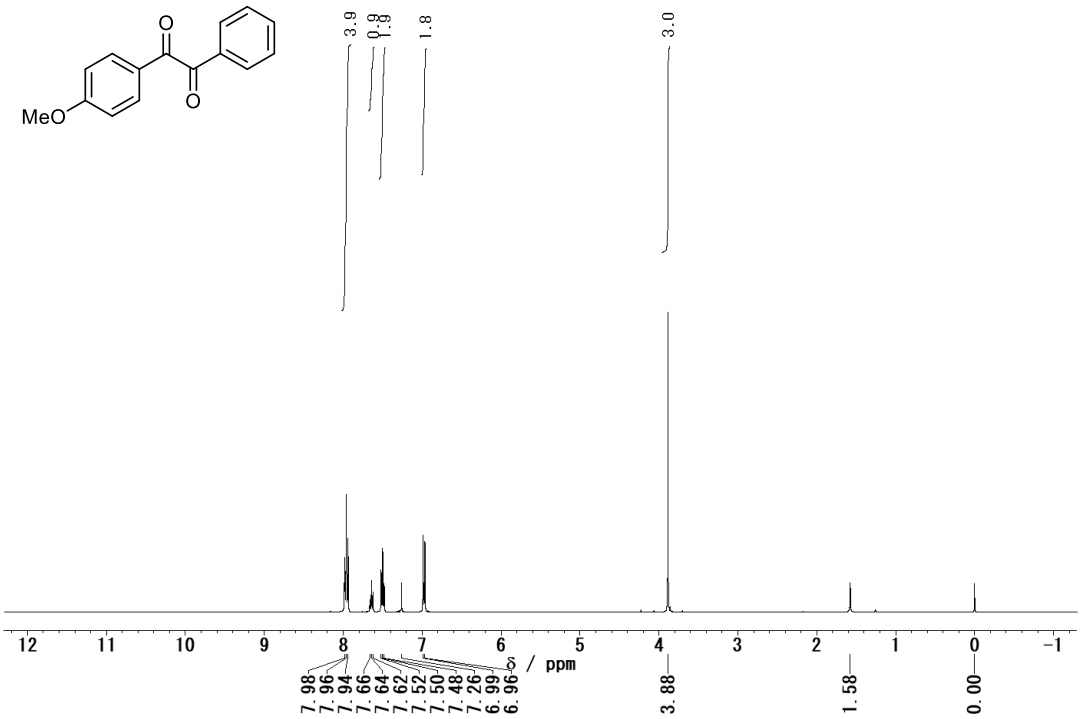

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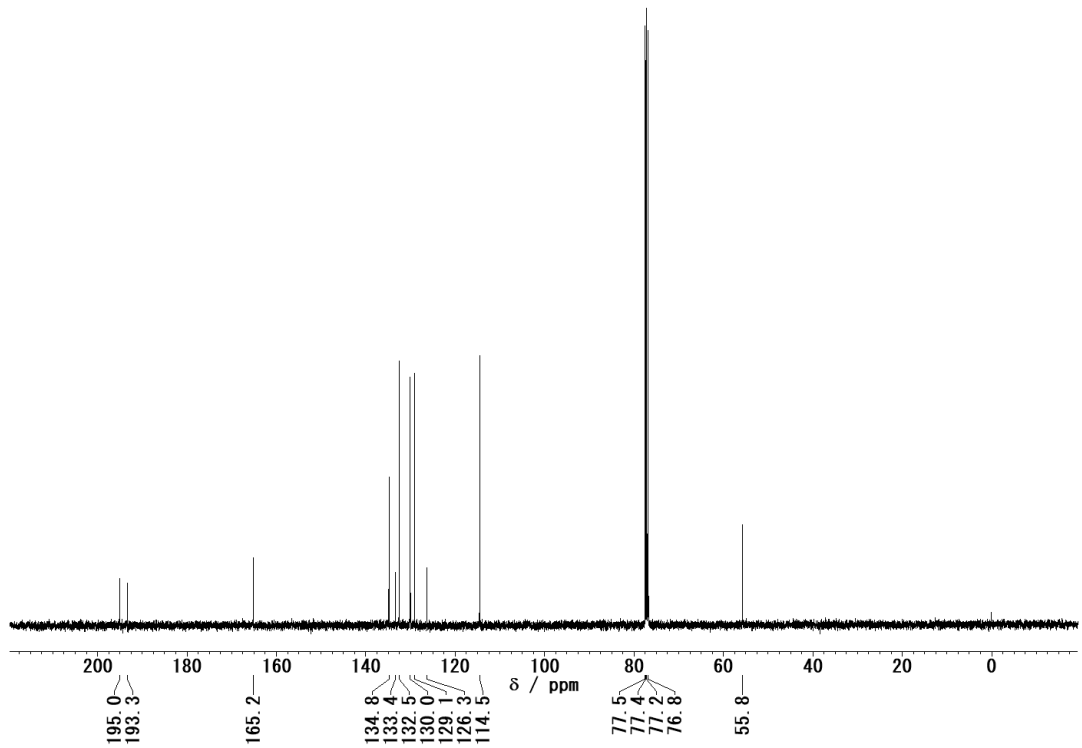

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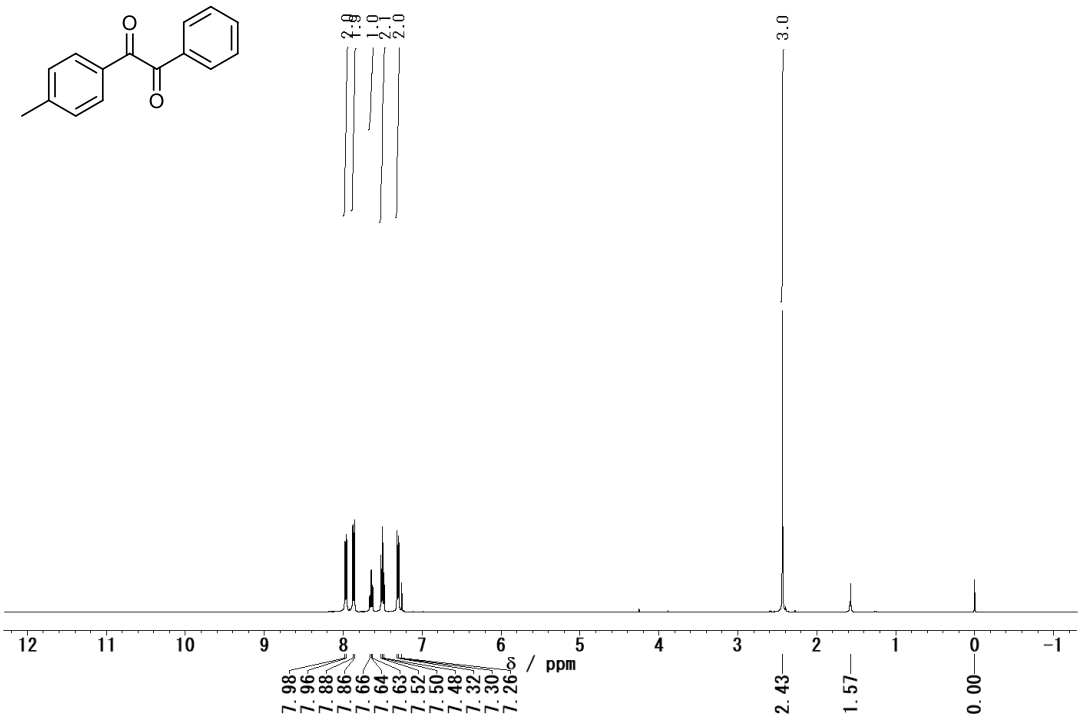

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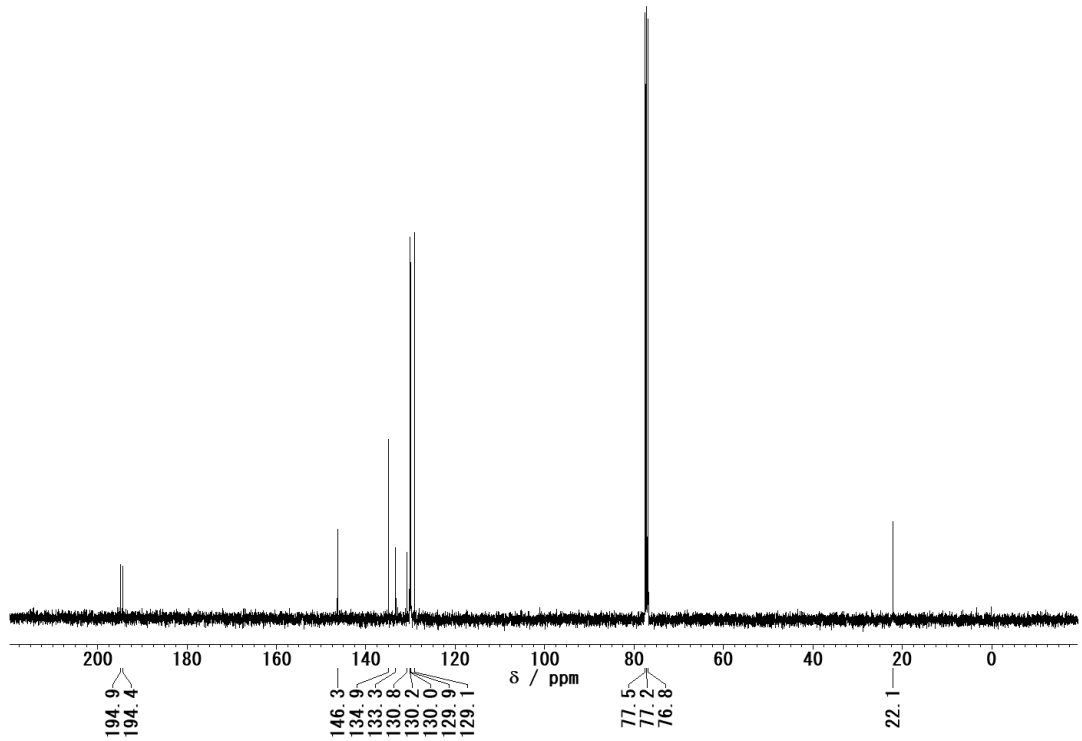
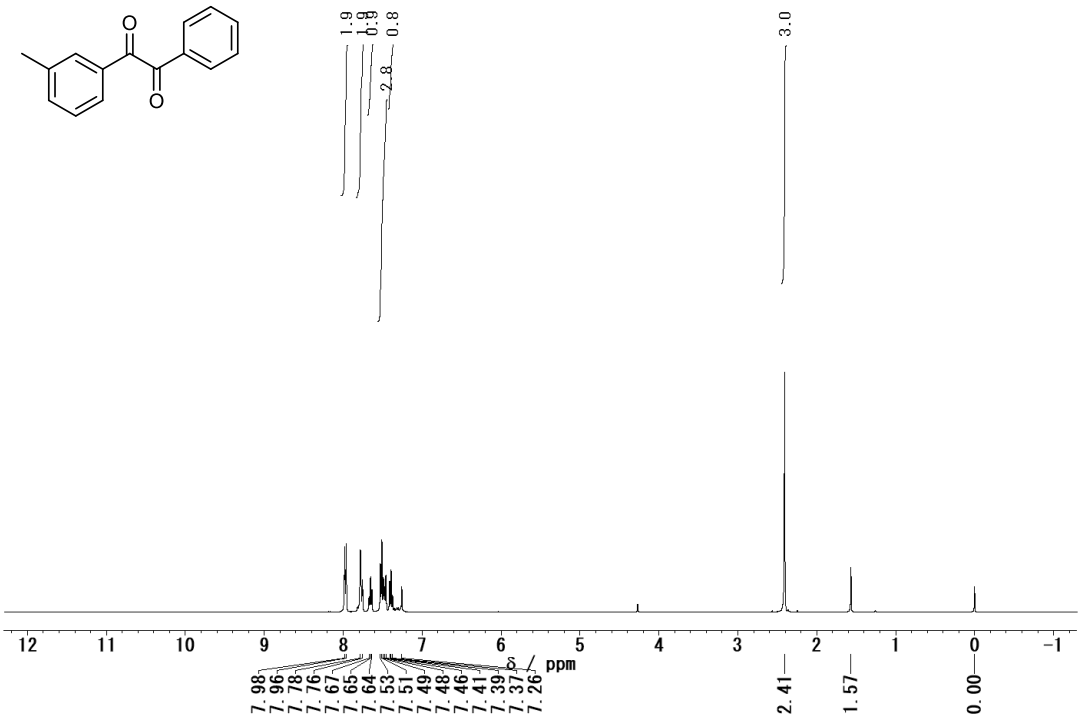
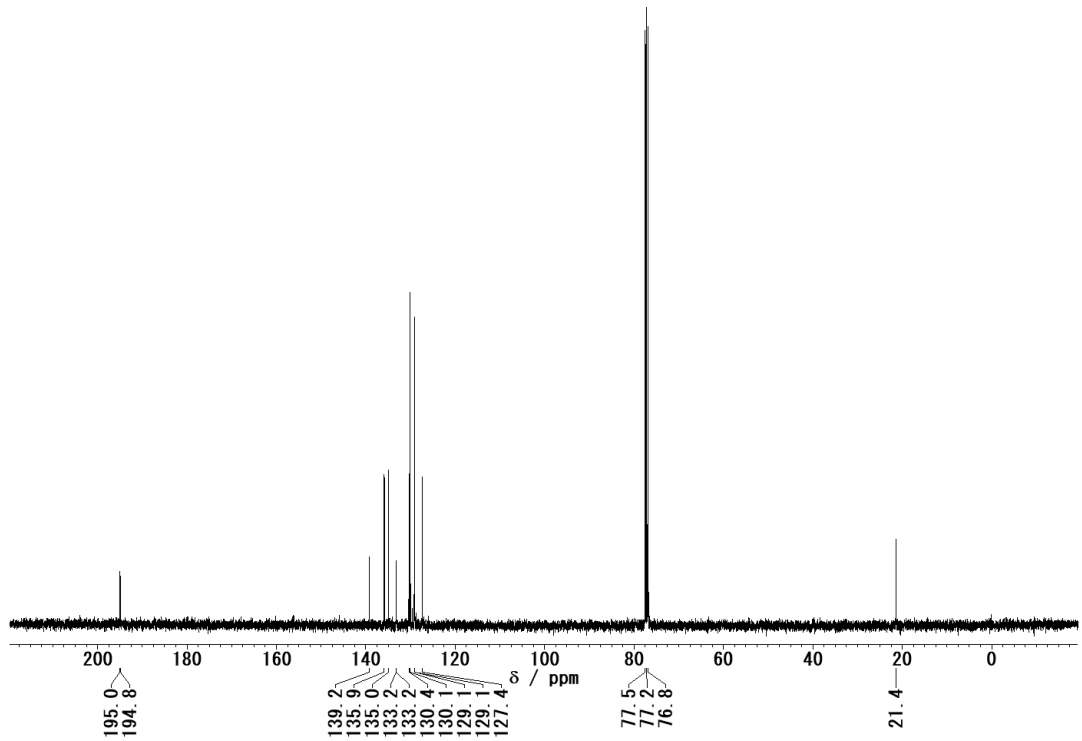


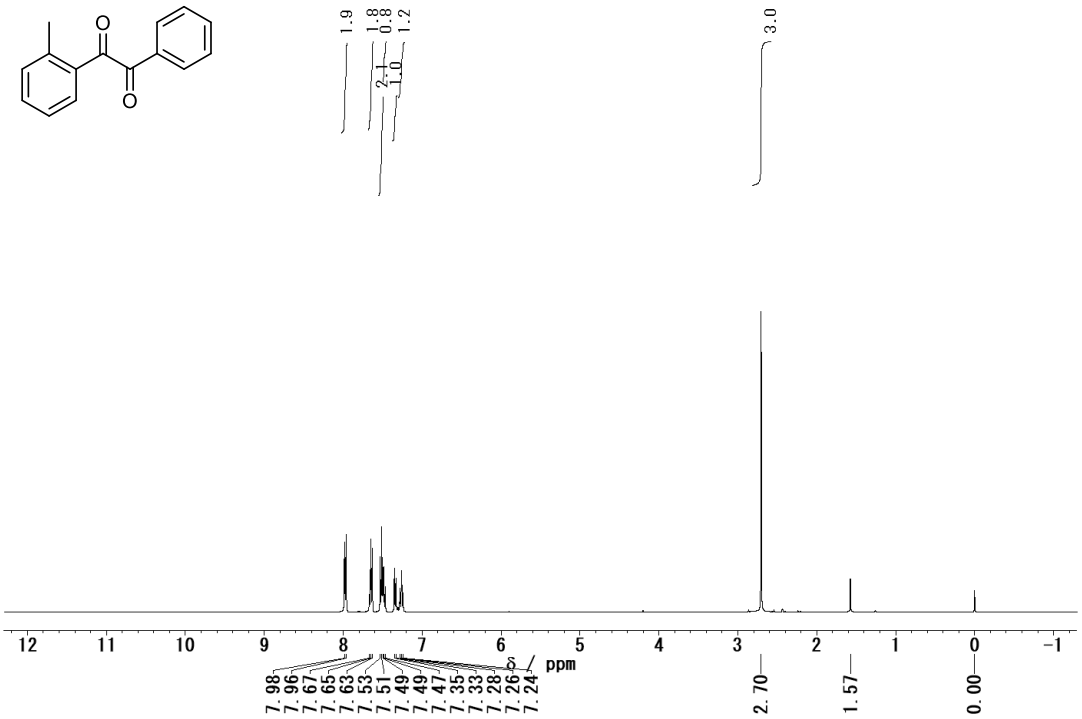
^{1}H NMR of **3g**



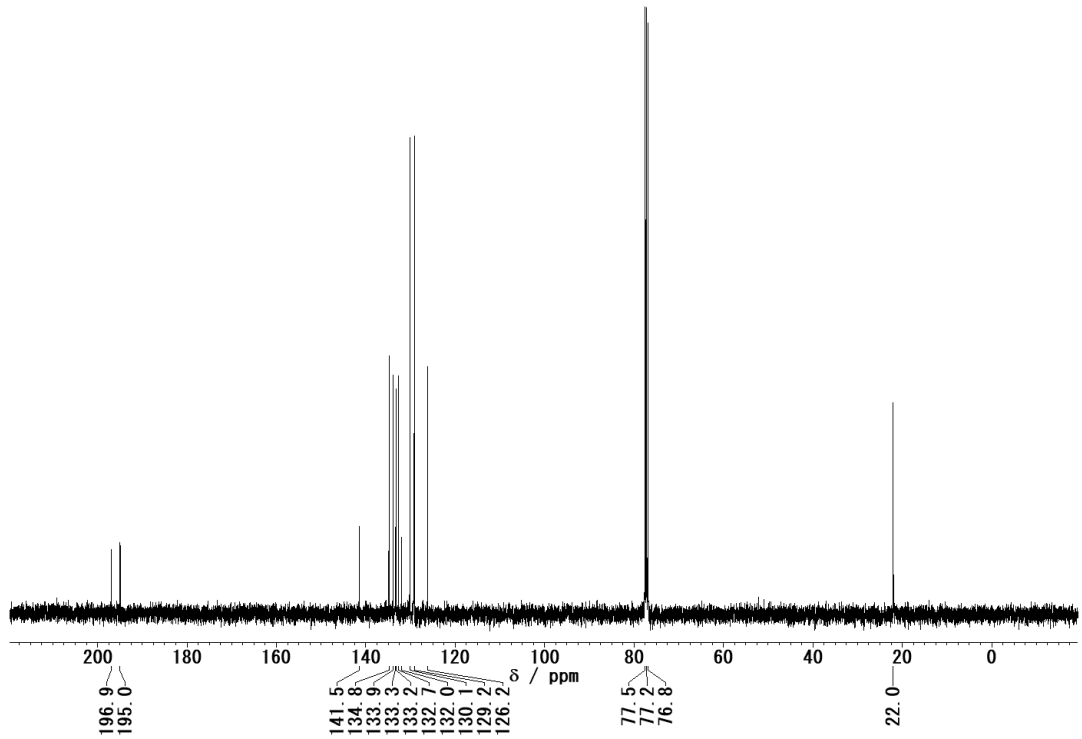
^{13}C{^{1}H} NMR of **3g**



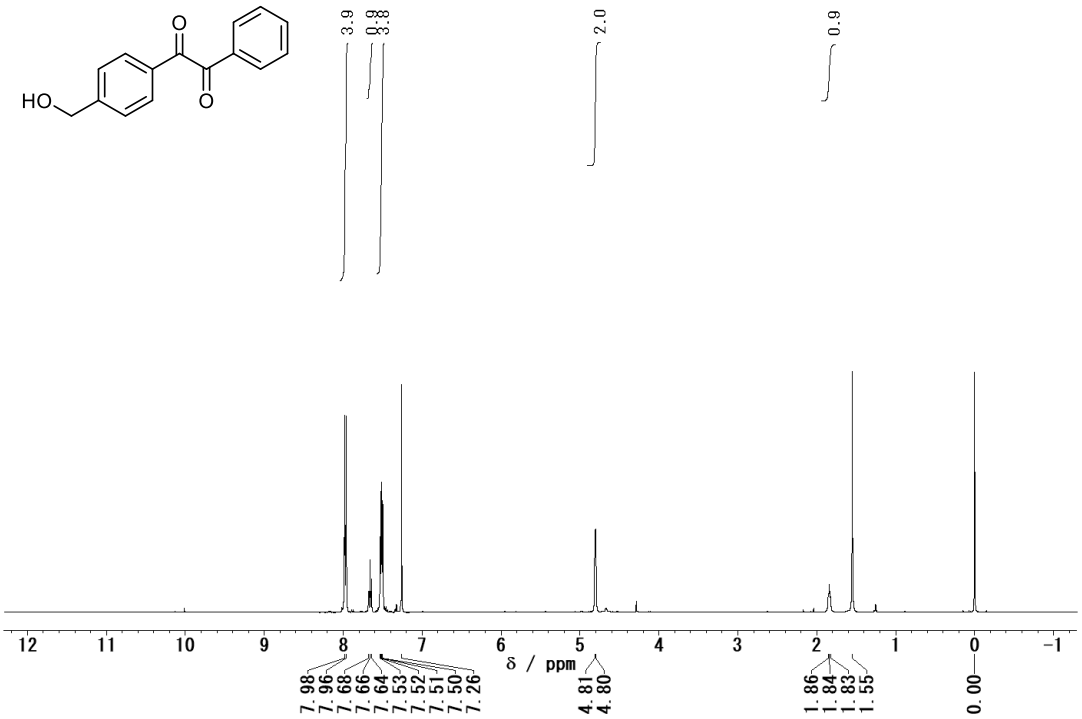
^{1}H NMR of **3h**



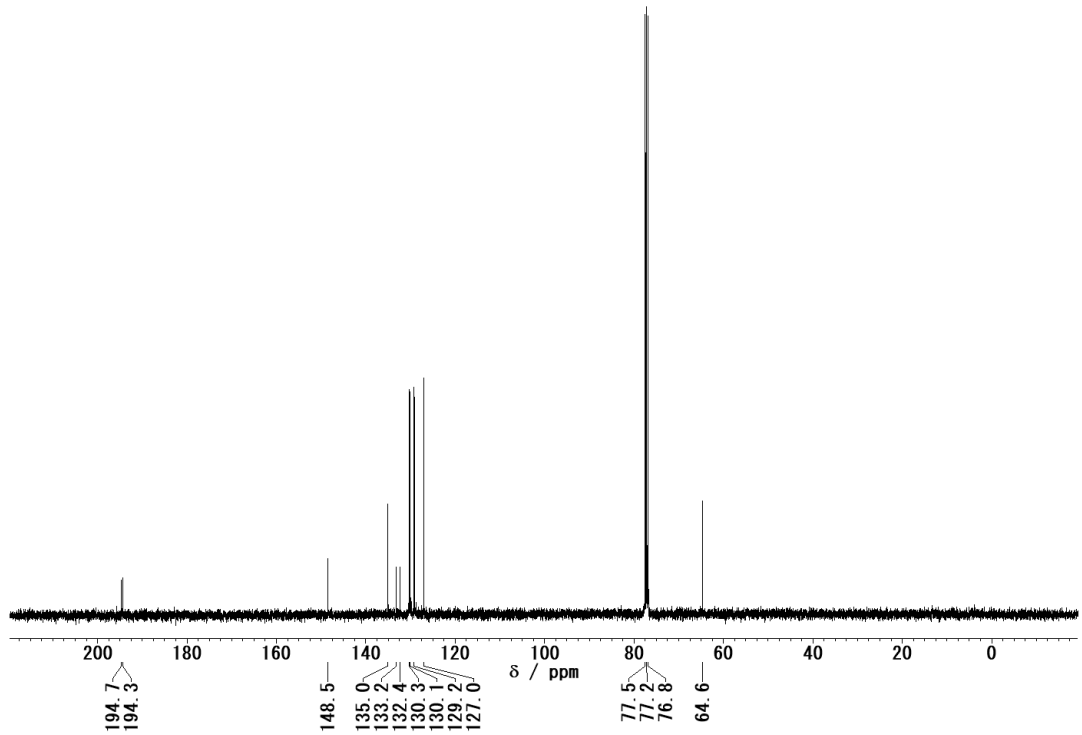
^{13}C{^{1}H} NMR of **3h**



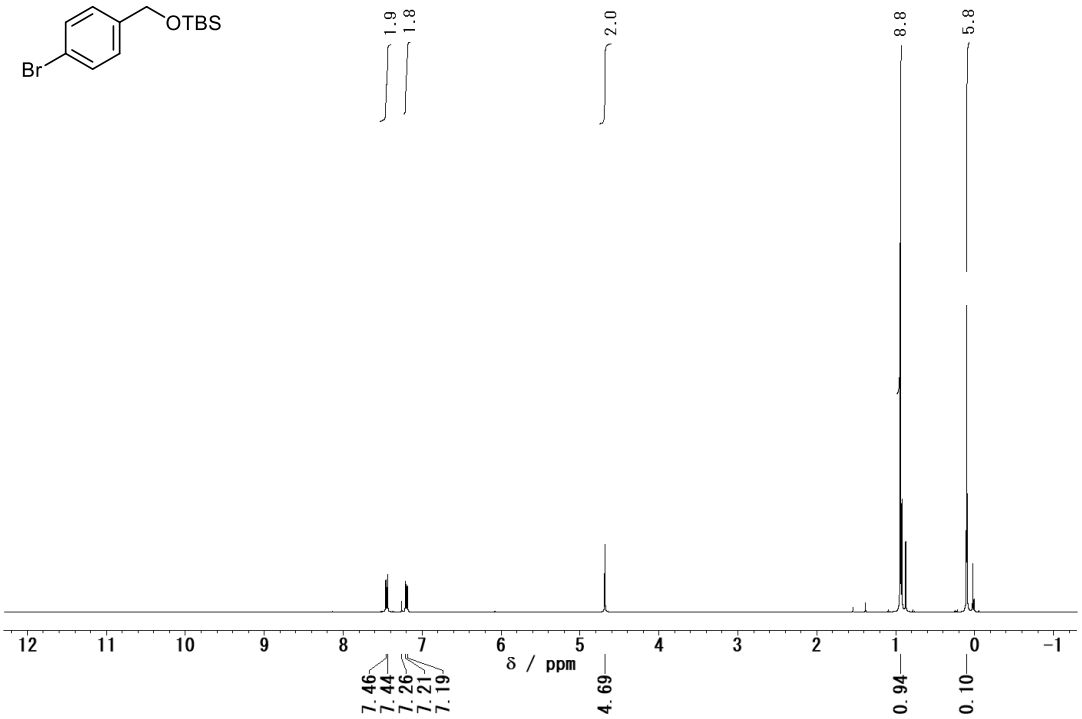
^{1}H NMR of **3p**



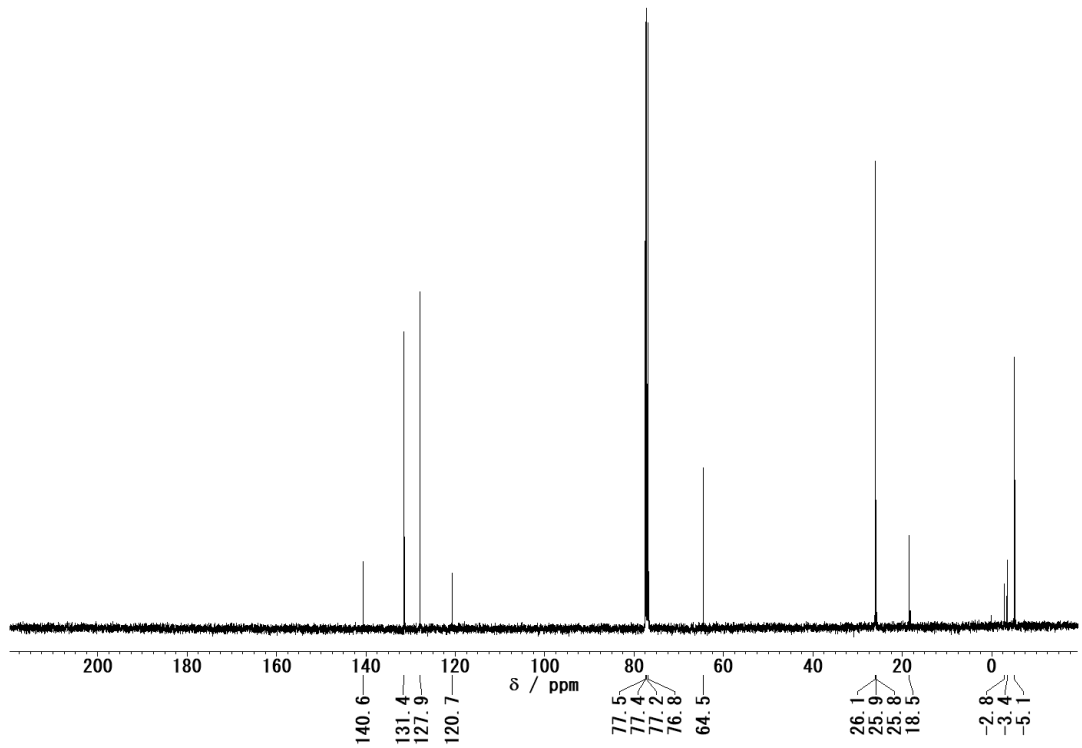
^{13}C{^{1}H} NMR of **3p**



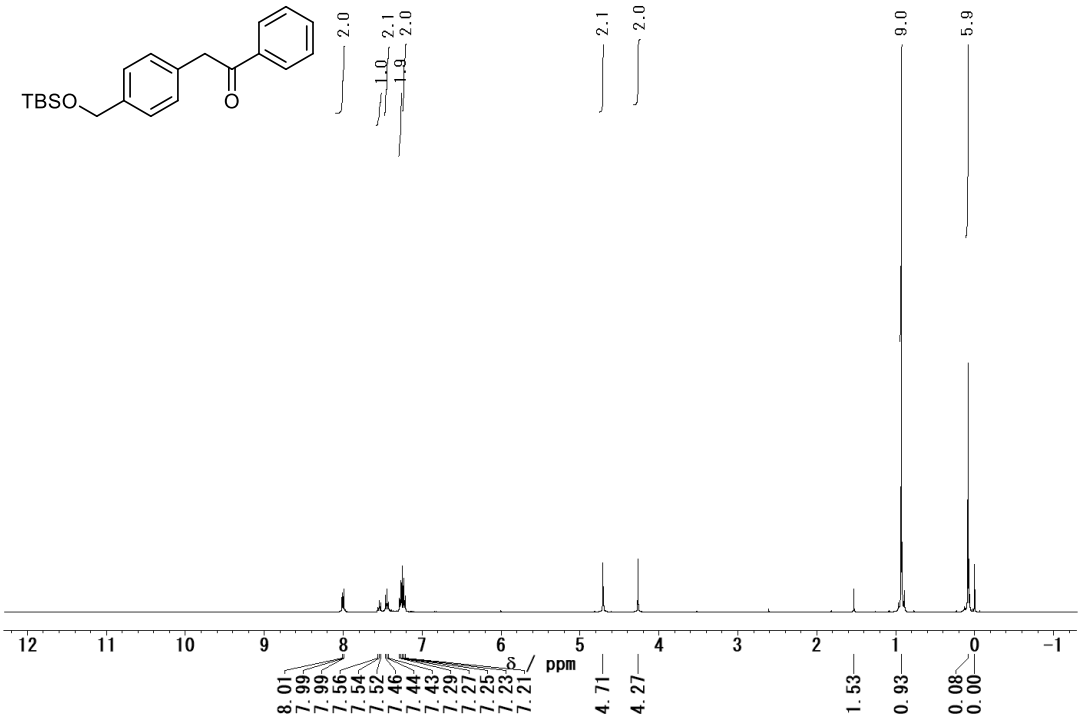
^{1}H NMR of 4-(*tert*-butyldimethylsilyloxymethyl)bromobenzene



^{13}C{^{1}H} NMR of 4-(*tert*-butyldimethylsilyloxymethyl)bromobenzene



^{1}H NMR of 4-(*tert*-Butyldimethylsilyloxymethyl)benzyl pheny ketone



^{13}C{^{1}H} NMR of 4-(*tert*-Butyldimethylsilyloxymethyl)benzyl pheny ketone