Supporting Information

Efficient Dehydrogenation of 2-Pyridyl Methanols by an Iron Complex

Masahiro Kamitani, Masaki Ito, Masumi Itazaki, and Hiroshi Nakazawa*

Department of Chemistry, Graduate School of Science, Osaka City University,
Sugimoto 3-3-138, Sumiyoshi-ku, Osaka 558-8585, Japan

Table of contents

Experimental procedures (S2)
General procedures for the synthesis of 2-pyridylmethanol derivatives (S2)
General procedures for dehydrogenation of 2-pyridylmethanol derivatives (S3)
Characterization of compounds (S3)
Preparation of CpFe(CO)(Py)(Ph) (8) (S9)
Preparation of (η⁵-C₅Me₅)Fe(CO)(PyCH₂S) (10) (S10)
Dehydrogenation of 2-pyridylbenzylalcohol promoted by 8 (S10)
Dehydrogenation of 2-pyridylbenzylalcohol promoted by 10 (S11)
X-ray diffraction study of 8 (S11)
Spectroscopic Data of New Compounds (S12)
References (S29)
Experimental procedures: All manipulations were carried out using standard Schlenk techniques under a dry argon and nitrogen atmosphere. Methyl iron complexes CpFe(CO)₂(Cl),¹ CpFe(CO)₂(Ph),² Cp*Fe(CO)(Py)(Me)³, 2-picolylthiol⁴ and 2-pyridylmethanols⁵⁻¹¹ were prepared according to the literature methods. Tetrahydrofuran (THF), hexane and toluene was degassed by purging with nitrogen and then dried with a solvent purification system containing activated alumina. Ether and CH₂Cl₂ were distilled from sodium and benzophenone (or CaH₂) prior to use and stored under nitrogen. The other chemicals used were purchased. NMR spectra (¹H, ¹³C{¹H} and ¹⁹F{¹H}) were recorded on a JNM AL−400 spectrometer. ¹H and ¹³C{¹H} NMR data were referred to residual peaks of solvent as an internal standard. Peak positions of the ¹⁹F{¹H} NMR spectra was referenced to an external C₆F₅Br (δ = −132.7 ppm). Elemental analysis data were obtained on a Perkin−Elmer 2400 CHN elemental analyzer.

General procedures for the synthesis of 2-pyridylmethanol derivatives: A solution of bromo compounds (67 mmol) in ether (20 mL) was added dropwise to a suspension of magnesium (73 mmol, 1.78 g) in ether (20 mL) at 0 °C under nitrogen atmosphere. Once the reaction mixture was heated at 50 °C for 30 min and cooled to 0 °C with ice bath. The solution having the Grignard reagent was slowly added to a solution of 2-picolylcarbonate (63 mmol, 6.0 mL) in THF (50 mL) at 0 °C and then was allowed to warm to room temperature gradually. The reaction mixture was quenched by saturated NH₄Cl aqueous solution. The organic layer was removed and the aqueous layer was washed with CH₂Cl₂ (ca. 20 mL, twice). The organic layer and CH₂Cl₂ were combined, washed with saturated NaCl aqueous solution and dried over MgSO₄. After filtration, the filtrate was collected and dried in vacuo to give 2-pyridylmethanol derivative.
General procedures for dehydrogenation of 2-pyridylmethanol derivatives: The mixture of 1 (2.1 mg, 0.010 mmol, corresponding to 1 mol% based on alcohols), NaH (0.49 mg, 0.020 mmol, corresponding to 2 mol% based on alcohols) and 2-pyridylmethanol (1.0 mmol) in toluene (20 mL) was treated under the reflux conditions. After 20 h, the reaction mixture was cooled to ambient temperature and filtered off. The volatile materials were removed under reduced pressure to give the corresponding ketone/aldehyde without further purification. When the mixture of ketone/aldehyde and alcohol was obtained, the residue was passed through alumina column with CH$_2$Cl$_2$/Hexane eluent (the former fraction is ketone) to isolate the product.

Characterization of alcohols and ketones

\[
\text{(78\%)}
\]

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 1.51$ (d, $J_{HH} = 6.7$ Hz, 3H, CH$_3$), 3.83 (br, 1H, OH), 4.92 (q, $J_{HH} = 6.1$ Hz, 1H, CH), 7.23 (m, 1H, Py), 7.31 (d, $J_{HH} = 6.9$ Hz, 1H, Py), 7.72 (t, $J_{HH} = 6.9$ Hz, 1H, Py), 8.55 (d, $J_{HH} = 4.1$ Hz, 1H, Py). Exhibited spectral data in accordance with previous report.$^5$

\[
\text{(93\%)}
\]

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 4.82$ (br, 1H, OH), 5.77 (s, 1H, CH), 7.16 (d, $J_{HH} = 7.8$ Hz, 1H, aromatic), 7.21 (t, $J_{HH} = 6.1$ Hz, 1H, aromatic), 7.27 (m, 1H, aromatic), 7.34 (t, $J_{HH} = 7.8$ Hz, 2H, aromatic), 7.39 (m, 2H, aromatic), 7.63 (t, $J_{HH} = 6.7$ Hz, 1H, aromatic), 8.57 (d, $J_{HH} = 4.9$
Hz, 1H, aromatic). Exhibited spectral data in accordance with previous report.6

\[
\begin{align*}
\text{N} & \quad \text{OH} \\
\text{N} & \quad \text{NMe}_2 \\
\text{PICI} & \quad \text{4H NMR (400 MHz, CDCl}_3\text{): } \delta = 2.33 (s, 3H, CH}_3\text{), 4.80 (br, 1H, OH), 5.75 (s, 1H, CH), 7.15 (d, } J_{HH} = 6.7 \text{ Hz, 1H, aromatic), 7.18 (d, } J_{HH} = 6.1 \text{ Hz, 2H, aromatic), 7.20 (t, } J_{HH} = 6.1 \text{ Hz, 1H, aromatic), 7.27 (d, } J_{HH} = 6.7 \text{ Hz, 2H, aromatic), 7.63 (m,1H, aromatic), 8.56 (d, } J_{HH} = 4.1 \text{ Hz, 1H, aromatic). Exhibited spectral data in accordance with previous report.6
\end{align*}
\]

\[
\begin{align*}
\text{N} & \quad \text{OH} \\
\text{N} & \quad \text{NMe}_2 \\
\text{PICI} & \quad \text{4H NMR (400 MHz, CDCl}_3\text{): } \delta = 2.92 (s, 6H, NCH}_3\text{), 4.80 (br, 1H, OH), 5.69 (s, 1H, CH), 6.69 (d, } J_{HH} = 7.8 \text{ Hz, 2H, aromatic), 7.16 (d, } J_{HH} = 7.8 \text{ Hz, 2H, aromatic), 7.23 (m, 2H, aromatic), 7.60 (t, } J_{HH} = 6.7 \text{ Hz, 1H, aromatic), 8.54 (d, } J_{HH} = 4.9 \text{ Hz, 1H, aromatic). Exhibited spectral data in accordance with previous report.6}
\end{align*}
\]

\[
\begin{align*}
\text{N} & \quad \text{OH} \\
\text{N} & \quad \text{Cl} \\
\text{PICI} & \quad \text{4H NMR (400 MHz, CDCl}_3\text{): } \delta = 4.92 (br, 1H, OH), 5.74 (s, 1H, CH), 7.13 (d, } J_{HH} = 7.8 \text{ Hz, 1H, aromatic), 7.24 (m, 3H, aromatic), 7.31 (d, } J_{HH} = 7.8 \text{ Hz, 2H, aromatic), 7.64 (t, } J_{HH} = 6.8 \text{ Hz, 1H, aromatic), 8.55 (d, } J_{HH} = 4.9 \text{ Hz, 1H, aromatic). Exhibited spectral data in accordance with previous report.7}
\end{align*}
\]
$\text{H NMR (400 MHz, CDCl}_3$: $\delta = 5.17$ (br, 1H, OH), 5.77 (s, 1H, CH), 6.97–7.06 (m, 2H, aromatic), 7.14 (d, $J_{HH} = 7.8$ Hz, 1H, aromatic), 7.23 (dd, $J_{HH} = 6.8$, 4.9 Hz, 1H, aromatic), 7.31–7.39 (m, 2H, aromatic), 7.66 (t, $J_{HH} = 6.8$ Hz, 1H, aromatic), 8.57 (d, $J_{HH} = 4.9$ Hz, 1H, aromatic). $^{13}$C-$^1$H NMR (100.4 MHz, CDCl$_3$: $\delta = 74.21$ (s, CH), 115.57 (d, $J_{CF} = 21.5$ Hz, aromatic), 122.17 (d, $J_{CF} = 122.7$ Hz, aromatic), 128.88 (d, $J_{CF} = 8.3$ Hz, aromatic), 137.42 (s, aromatic), 138.97 (d, $J_{CF} = 3.1$ Hz, aromatic), 147.62 (s, aromatic), 160.67 (s, aromatic), 161.30 (s, aromatic) 163.75 (s, aromatic). $^{19}$F NMR (375 MHz, CDCl$_3$: $\delta = -112.99$. Elemental analysis; Calcd: C$_{12}$H$_{10}$O$_1$N$_1$F$_1$: C, 70.93; H, 4.96; N, 6.89%; Found: C, 70.93; H, 5.16, N, 6.80%.

$\text{H NMR (400 MHz, CDCl}_3$: $\delta = 4.31$ (br, 1H, OH), 5.86 (s, 1H, CH), 7.18 (d, $J_{HH} = 6.1$ Hz, 1H, aromatic), 7.27 (m, 1H, aromatic), 7.53 (d, $J_{HH} = 7.8$ Hz, 2H, aromatic), 7.63 (d, $J_{HH} = 7.8$ Hz, 2H, aromatic), 7.70 (t, $J_{HH} = 6.1$ Hz, 1H, aromatic), 8.59 (d, $J_{HH} = 5.3$ Hz, 1H, aromatic). $^{19}$F NMR (375 MHz, CDCl$_3$: $\delta = -60.96$. Exhibited spectral data in accordance with previous report.\(^6\)

$\text{H NMR (400 MHz, CDCl}_3$: $\delta = 2.18$ (s, 6H, CH$_3$), 2.26 (s, 3H, CH$_3$), 5.43 (br, 1H, OH), 6.20
(s, 1H, CH), 6.83 (s, 2H, aromatic), 6.91 (d, $J_{HH} = 7.8$ Hz, 1H, aromatic), 7.18~7.25 (m, 1H, aromatic), 7.58 (t, $J_{HH} = 7.8$ Hz, 1H, aromatic), 8.59 (d, $J_{HH} = 4.5$ Hz, 1H, aromatic). $^{13}$C{$^1$H} NMR (100.4 MHz, CDCl$_3$): $\delta = 20.30$ (s, CH$_3$), 20.79 (s, CH$_3$), 70.31 (s, CH), 120.25 (s, aromatic), 121.71 (s, aromatic), 129.86 (s, aromatic), 135.05 (s, aromatic), 136.70 (s, aromatic), 137.11 (s, aromatic), 137.33 (s, aromatic), 147.32 (s, aromatic), 161.31 (s, aromatic). Elemental analysis; Calcd: C$_{15}$H$_{17}$O$_1$N$_1$: C, 79.26; H, 7.54; N, 6.16%; Found: C, 79.15; H, 7.65; N, 6.10%.

(90%)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 5.56$ (br, 1H, OH), 6.18 (s, 1H, CH), 7.16 (d, $J_{HH} = 7.8$ Hz, 1H, aromatic), 7.24~7.32 (m, 1H, aromatic), 7.71 (t, $J_{HH} = 7.8$ Hz, 1H, aromatic), 8.61 (d, $J_{HH} = 3.9$ Hz, 1H, aromatic). $^{13}$C{$^1$H} NMR (100.4 MHz, CDCl$_3$): $\delta = 65.77$ (s, CH), 116.80 (t-m, $J_{CF} = 23.3$ Hz, aromatic), 120.41 (s, aromatic), 123.13 (s, aromatic), 137.38 (s, aromatic), 137.61 (d-m, $J_{CF} = 252.8$ Hz, aromatic), 140.04 (d-m, $J_{CF} = 254.4$ Hz, aromatic), 145.32 (d-m, $J_{CF} = 250.4$ Hz, aromatic), 148.05 (s, aromatic), 157.99 (s, aromatic). $^{19}$F NMR (375 MHz, CDCl$_3$): $\delta = -160.67$ ~ $-160.75$ (m), $-153.31$ (t, $J_{FF} = 22.4$ Hz), $-141.87$ (d-d, $J_{FF} = 8.4$, 22.4 Hz). Elemental analysis; Calcd: C$_{12}$H$_6$O$_1$N$_1$F$_5$: C, 52.38; H, 2.20; N, 5.09%; Found: C, 52.29; H, 2.28; N, 5.13%.

(62%)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.70$ (s, 3H, CH$_3$), 7.41~7.47 (m, 1H, Py), 7.76~7.82 (m, 1H, Py), 7.99~8.04 (m, 1H, Py), 8.65 (d, $J_{HH} = 3.3$ Hz, 1H, Py). Exhibited spectral data in accordance with previous report.$^8$
1H NMR (400 MHz, CDCl₃): δ = 7.47~7.53 (m, 3H, aromatic), 7.60 (t, J_HH = 7.8 Hz, 1H, aromatic), 7.88~7.94 (m, 1H, aromatic), 8.03~8.08 (m, 3H, aromatic), 8.73 (d, J_HH = 3.8 Hz, 1H, aromatic). Exhibited spectral data in accordance with previous report.⁸

1H NMR (400 MHz, CDCl₃): δ = 2.43 (s, 3H, CH₃), 7.29 (d, J_HH = 7.8 Hz, 2H, aromatic), 7.18 (d-d, J_HH = 7.8, 4.7 Hz, 1H, aromatic), 7.90 (t, J_HH = 7.8 Hz, 1H, aromatic), 7.97 (d, J_HH = 7.8 Hz, 2H, aromatic), 8.02 (d, J_HH = 7.8 Hz, 1H, aromatic), 8.72 (d, J_HH = 4.7 Hz, 1H, aromatic). Exhibited spectral data in accordance with previous report.⁹

1H NMR (400 MHz, CDCl₃): δ = 3.08 (s, 6H, NCH₃), 6.69 (d, J_HH = 8.7 Hz, 2H, aromatic), 7.40~7.46 (m, 1H, aromatic), 7.85 (t, J_HH = 7.8, 1H, aromatic), 7.92 (d, J_HH = 7.8 Hz, 1H, aromatic), 8.06 (d, J_HH = 8.7 Hz, 2H, aromatic), 8.70 (d, J_HH = 4.1 Hz, 1H, aromatic). Exhibited spectral data in accordance with previous report.⁸

1H NMR (400 MHz, CDCl₃): δ = 7.47 (d, J_HH = 8.7 Hz, 2H, aromatic), 7.49~7.55 (m, 1H,
aromatic), 7.88−7.94 (m, 1H, aromatic), 8.04−8.09 (m, 3H, aromatic), 8.72 (d, $J_{HH} = 5.3$ Hz, 1H, aromatic). Exhibited spectral data in accordance with previous report.\(^{10}\)

![Image](image1)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): $\delta = 7.15$ (d-d, $J_{HH} = 8.7$ Hz, $J_{HF} = 8.7$ Hz, 2H, aromatic), 7.49−7.53 (m, 1H, aromatic), 7.89−7.95 (m, 1H, aromatic), 8.06 (d, $J_{HH} = 7.3$ Hz, 1H, aromatic), 8.16 (d-d, $J_{HH} = 8.7$ Hz, $J_{HF} = 5.8$ Hz, 2H, aromatic) (d, $J_{HH} = 4.8$ Hz, aromatic). \(^{19}\)F NMR (375 MHz, CDCl\(_3\)): $\delta = -103.69$. Exhibited spectral data in accordance with previous report.\(^{10}\)

![Image](image2)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): $\delta = 7.54$ (d-d, $J_{HH} = 7.8$, 4.8 Hz, 1H, aromatic), 7.75 (d, $J_{HH} = 7.8$ Hz, 2H, aromatic), 7.95 (t, $J_{HH} = 7.8$ Hz, 1H, aromatic), 8.14 (d, $J_{HH} = 7.8$ Hz, 1H, aromatic), 8.17 (d, $J_{HH} = 7.8$ Hz, 2H, aromatic), 8.73 (d, $J_{HH} = 4.3$ Hz, 1H, aromatic). \(^{19}\)F NMR (375 MHz, CDCl\(_3\)): $\delta = -61.56$. Exhibited spectral data in accordance with previous report.\(^{11}\)

![Image](image3)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): $\delta = 2.09$ (s, 6H, CH\(_3\)), 2.32 (s, 3H, CH\(_3\)), 6.90 (s, 2H, aromatic), 7.44−7.47 (m, 1H, aromatic), 7.89 (t, $J_{HH} = 7.8$ Hz, 1H, aromatic), 8.12 (d, $J_{HH} = 7.8$ Hz, 1H, aromatic), 8.70 (d, $J_{HH} = 4.2$ Hz, 1H, aromatic). \(^{13}\)C\(_{\{1\}H}\) NMR (100.4 MHz, CDCl\(_3\)): $\delta = 19.64$ (s, CH\(_3\)), 21.31 (s, CH\(_3\)), 123.23 (s, aromatic), 127.02 (s, aromatic), 128.46 (s, aromatic), 134.46
(s, aromatic), 136.88 (s, aromatic), 137.10 (s, aromatic), 138.85 (s, aromatic), 150.00 (s, aromatic), 154.32 (s, aromatic), 201.05 (s, C=O). Elemental analysis; Calcd: C<sub>15</sub>H<sub>15</sub>N<sub>1</sub>O<sub>1</sub>: C, 79.97; H, 6.71; N, 6.22%; Found: C, 79.83; H, 6.81; N, 6.11%.

\[
\begin{array}{c}
\text{N} \\
\text{O} \\
\text{F} \\
\text{F} \\
\text{F} \\
\text{F}
\end{array}
\]

(15%)  

\[\delta = 7.55-7.58 (m, 1H, \text{aromatic}), 7.95 (t, J_{HH} = 8.3 \text{ Hz}, 1H, \text{aromatic}), 8.20 (d, J_{HH} = 8.3 \text{ Hz}, 1H, \text{aromatic}), 8.67 (d, J_{HH} = 4.9 \text{ Hz}, 1H, \text{aromatic}). \]

C<sub>15</sub>H<sub>15</sub>N<sub>1</sub>O<sub>1</sub> NMR (100.4 MHz, CDCl<sub>3</sub>): \[\delta = 114.11 \text{ (t-m, } J_{CF} = 27.5 \text{ Hz, aromatic), } 123.33 \text{ (s, aromatic), } 128.37 \text{ (s, aromatic), } 137.36 \text{ (s, aromatic), } 137.83 \text{ (d-m, } J_{CF} = 251.5 \text{ Hz, aromatic), } 142.66 \text{ (d-m, } J_{CF} = 257.5 \text{ Hz, aromatic), } 144.35 \text{ (d-m, } J_{CF} = 251.6 \text{ Hz, aromatic), } 149.74 \text{ (s, aromatic), } 152.33 \text{ (s, aromatic), } 186.77 \text{ (s, C=O).} \]

F NMR (375 MHz, CDCl<sub>3</sub>): \[\delta = -159.34 \text{ ~} -159.44 \text{ (m), } -149.07 \text{ (t, } J_{FF} = 20.0 \text{ Hz), } -137.69 \text{ (d, } J_{FF} = 20.0 \text{ Hz).} \]

Preparation of CpFe(CO)(Py)(Ph) (8): A toluene solution (15 mL) containing CpFe(CO)<sub>2</sub>(Ph)<sub>2</sub> (312 mg, 1.23 mmol) and pyridine (5 mL) was photoirradiated for 12 h at 5 °C. After photoirradiation, the color was changed from yellow to dark red after the reaction. The reaction mixture was allowed to warm to room temperature and was filtered off. The volatile materials were removed from the filtrate under reduced pressure. The residue was washed with hexane (1 ml, twice) and was dried in vacuo to give the title compound as a dark reddish powder (333 mg, 1.09 mmol, 89%). \[\delta = 4.18 \text{ (s, } 5H, \text{ Cp), } 5.87 \text{ (m, } 2H, \text{ aromatic), } 6.40 \text{ (m, } 1H, \text{ aromatic), } 7.08 \text{ (m, } 1H, \text{ aromatic), } 7.19 \text{ (m, } 2H, \text{ aromatic), } 7.21 \text{ (m, } 2H, \text{ aromatic),} \]

S9
8.23 (m, 2H, aromatic). $^{13}$C{¹H} NMR (100 MHz, C₆D₆): $\delta$ = 84.01 (s, Cp), 121.93 (s, aromatic), 123.28 (s, aromatic), 126.88 (s, aromatic), 134.46 (s, aromatic), 144.78 (s, aromatic), 157.85 (s, aromatic), 165.18 (s, aromatic). Elemental analysis; Calcd: C₁₇H₁₅O₁N₁Fe₁: C, 66.91; H, 4.95; N, 4.59%; Found: C, 66.68; H, 4.77; N, 4.49%.

Preparation of (η⁵-C₅Me₅)Fe(CO)(PyCH₂S) (10): A toluene solution (5 mL) containing Cp*Fe(CO)(Py)(Me) (9)³ (156 mg, 0.50 mmol) was added 2-pyridylmethanethiol⁴ (62.4 mg, 0.50 mmol) at room temperature. The color was changed from dark red to dark yellow immediately. After stirred at room temperature for 2 h, the reaction mixture was filtered off. The volatile materials were removed from the filtrate under reduced pressure. The residue was washed with hexane (1 ml, twice) and was dried in vacuo to give the title compound as a green powder (166 mg, 49 mmol, 98%). $^1$H NMR (400 MHz, C₆D₆): $\delta$ = 1.46 (s, 15H, Cp*), 3.42 (d, J_HH = 16.0 Hz, 1H, CHH), 3.86 (d, J_HH = 16.0 Hz, 1H, CHH), 6.04 (t, J_HH = 6.2 Hz, 1H, Py), 6.34 (d, J_HH = 6.2 Hz, 1H, Py), 6.53 (t, J_HH = 6.2 Hz, 1H, aromatic), 8.23 (d, J_HH = 6.2 Hz, 1H, Py). $^{13}$C{¹H} NMR (100 MHz, C₆D₆): $\delta$ = 9.67 (s, CCH₃), 38.78 (s, CH₂), 89.68 (s, CCH₃), 120.02 (s, Py), 120.65 (s, Py), 134.90 (s, Py), 155.06 (s, Py), 172.96 (s, Py), 224.79 (s, CO). Elemental analysis; Calcd: C₁₇H₂₁O₁N₁S₁Fe₁: C, 59.48; H, 6.17; N, 4.08%; Found: C, 59.22.; H, 6.15; N, 4.16%.

Dehydrogenation of 2-Pyridylbenzylalcohol promoted by 8: The mixture of 8 (3.1 mg, 0.010 mmol, corresponding to 1 mol% based on alcohols) and 2-pyridylbenzylalcohol (185 mg, 1.0 mmol) in toluene (20 mL) was treated under the reflux conditions. After 20 h, the reaction mixture was cooled to ambient temperature and filtered off. The volatile materials were removed under reduced pressure to give the corresponding ketone as a white powder (183 mg, 1.0 mmol, 100%).
Dehydrogenation of 2-Pyridylbenzylalcohol promoted by 10: The mixture of 10 (3.4 mg, 0.010 mmol, corresponding to 1 mol% based on alcohols) and 2-pyridylbenzylalcohol (185 mg, 1.0 mmol) in toluene (20 mL) was treated under the reflux conditions. After 20 h, the reaction mixture was cooled to ambient temperature and filtered off. The volatile materials were removed under reduced pressure to give the corresponding ketone as a white powder (66.2 mg, 36.2 mmol, 36%).

X-ray Crystal structure determination of 8: Red crystals of 8 suitable for an X-ray diffraction study were obtained through crystallization from toluene/hexane. The single crystal was mounted in a glass capillary. Data for 8 were collected at 200 K (2) on Rigaku/MSC Mercury CCD area-detector diffractometer equipped with monochromated MoKα radiation. Calculations for 9 were performed with the teXane crystallographic software package of Molecular Structure Corporation. Crystal Data: C₁₇H₁₅FeNO, \( M = 305.16 \), red platelet, \( 0.18 \times 0.13 \times 0.10 \text{ mm}^3 \), monoclinic, space group \( C2/c \) (No. 15), \( a = 15.794(3) \text{ Å} \), \( b = 10.620(2) \text{ Å} \), \( c = 17.360(4) \text{ Å} \), \( \beta = 102.863(4)° \), \( V = 2838.8(10) \text{ Å}^3 \), \( Z = 8 \), \( D \text{calc} = 1.428 \text{ g/cm}^3 \), 3212 reflections collected, 2612 \( (I > 2\sigma I) \) unique reflections were used in all calculations, number of variables = 241, \( R = 0.0379 \), \( R_w = 0.0837 \), and goodness of fit = 1.006. CCDC 934658.
ORTEP drawing of 8.
Spectroscopic Data of New Compounds

\[ ^1H \text{NMR (400 MHz, CDCl}_3 \]
$^{13}\text{C}^{\text{1H}}$ NMR (100.4 MHz, CDCl$_3$)
$^{19}$F NMR (375 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}\text{C}^1\text{H}$ NMR (100.4 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C{$_1^3$H} NMR (100.4 MHz, CDCl$_3$)
$^{19}$F NMR (375 MHz, CDCl$_3$)
^{1}H NMR (400 MHz, CDCl$_3$)
$^{13}\text{C}^{1\text{H}}$ NMR (100.4 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}\text{C}^{1}\text{H)}$ NMR (100.4 MHz, CDCl$_3$)
$^{19}$F NMR (375 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, C$_6$D$_6$)
$^{13}$C\textsubscript{${}^1$H} NMR (100.4 MHz, CDCl$_3$)
$^{1}$H NMR (400 MHz, C$_6$D$_6$)
$^{13}\text{C}\{^1\text{H}\}$ NMR (100.4 MHz, $\text{C}_6\text{D}_6$)
References