Red-light-activatable ruthenium phthalocyanine catalysts

Yuta Ishikawa¹, Tatsuya Kameyama²,³, Tsukasa Torimoto², Hajime Maeda¹,
Masahito Segi¹ and Taniyuki Furuyama*¹,³

¹Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa,
920-1192, Japan

²Graduate School of Engineering, Nagoya University, Nagoya, 464-8603, Japan

³Japan Science and Technology Agency (JST)-PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama, 332-0012,
Japan

Supporting information

Table of Contents

General Comments S–1
Additional Experimental Results S–3
Full Experimental Procedures S–9
Copies of the NMR Spectra of Studied Compounds S–21
References S–50
General Comments

Instrumentation

Photoreactions were carried out in a reaction vessel wherein the reaction mixtures were irradiated using red ($\lambda_{\text{max}} = 634$ nm) or blue ($\lambda_{\text{max}} = 470$ nm) LED light. LDL2-119X16RD2 (nominal wavelength: 634 nm, fwhm: 15.0 nm) and ALDKIT001 (nominal wavelength: 470 nm, fwhm: 24.7 nm) were purchased from CCS Inc. and Aldrich Inc., respectively (Fig. S10). The output power was 12 W, and the LED light was placed 5.0 cm from the reaction vessel. NMR spectra were obtained using JEOL ECA-500 or Bruker AVANCE 400 spectrometer. Chemical shifts are expressed in $\delta$ (ppm) values, and coupling constants are expressed in hertz (Hz). $^1$H and $^{13}$C NMR spectra were referenced to the tetramethylsilane (TMS) or the residual solvent as an internal standard. $^{19}$F NMR spectra were referenced to the trifluoroacetic acid ($\delta = -79.0$ ppm) as an internal standard. The following abbreviations are used: s = singlet, d = doublet, m = multiplet, and brs = broad singlet. High-resolution mass spectra (HRMS) were recorded using a Bruker Daltonics solariX spectrometer (MALDI). Electronic absorption spectra were recorded on a JASCO V-770 spectrophotometer. A photonic multichannel analyzer (Hamamatsu, PMA-12) was used for the measurement of phosphorescence spectra under N2 atmosphere, in which the wavelength of excitation light was 632 nm. Cyclic voltammetry (CV) measurements were recorded using a Hokuto Denko HZ5000 potentiostat under a nitrogen atmosphere with 0.1 M of tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. Measurements were made using a glassy carbon electrode (area = 0.07 cm$^2$), an Ag/AgCl reference electrode, and a Pt wire counter electrode. The concentration of the solution was fixed at 0.5 mM, and the sweep rate was set to 100 mV/s. The ferrocenium/ferrocene (Fc$^+/Fc$) couple was used as an internal standard.

Materials

Unless otherwise noted, materials were purchased from Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers and were used after appropriate purification (distillation or recrystallization). ZnPc,$^1$ Ru(py):TAP,$^2$ 2a,$^3$ 2c,$^4$ 2d,$^5$ 2e,$^6$ 2f,$^7$ 2g,$^8$ 2j,$^9$ and 2n$^{10}$ were synthesized according to published procedures.
Crystallographic data collection

Data collection for 1b was carried out on a Bruker APEXIII CCD diffractometer with Bruker Helios multilayered confocal mirror monochromatized CuKα radiation (λ = 1.54178 Å) at −183°C. The structures were solved by a direct method (SIR2004)\textsuperscript{11} and refined using a full-matrix least square technique (SHELXL-2014).\textsuperscript{12} Yadokari-XG 2009 software was used as a GUI for SHELXL-2014.\textsuperscript{13} All non-hydrogen atoms were refined anisotropically. Positions of all hydrogen atoms were calculated geometrically, and refined by applying riding models. Some large electron peaks due to a solvent molecule(s) were found in the unit cell. As we failed to model them properly, the rest molecules were refined without the effect of the solvent molecule(s) by the Platon squeeze technique.\textsuperscript{14} CCDC-2108084 contains the supplementary crystallographic data. Their data can be obtained free of charge from Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
Additional Experimental Results

Fig. S1 Molecular structure of 1b with thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity and only selected atoms have been labeled.
Table S1 Crystal data and structure refinement for 1b.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{44}H_{24}F_{6}N_{10}Ru</td>
</tr>
<tr>
<td>Formula weight</td>
<td>907.80</td>
</tr>
<tr>
<td>Temperature</td>
<td>90(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54178 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>Cc</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>( a = 20.1094(18) ) Å, ( a = 90^\circ )</td>
</tr>
<tr>
<td></td>
<td>( b = 22.559(2) ) Å, ( \beta = 108.370(2)^\circ )</td>
</tr>
<tr>
<td></td>
<td>( c = 10.5878(10) ) Å, ( \gamma = 90^\circ )</td>
</tr>
<tr>
<td>Volume</td>
<td>4558.4(7) Å³</td>
</tr>
<tr>
<td>Density (Calcd.)</td>
<td>1.323 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>3.351 mm⁻¹</td>
</tr>
<tr>
<td>( F(000) )</td>
<td>1824</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.200 × 0.200 × 0.100 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>5.920 to 66.497°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-23 \leq h \leq 23, -26 \leq k \leq 25, -12 \leq l \leq 12</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>14260</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>6274 \ [R(int) = 0.0395]</td>
</tr>
<tr>
<td>Completeness to theta = 66.497°</td>
<td>98.1%</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on ( F^2 )</td>
</tr>
<tr>
<td>Data / restraints /parameters</td>
<td>6274 / 2 / 550</td>
</tr>
<tr>
<td>Goodness-of-fit on ( F^2 )</td>
<td>1.042</td>
</tr>
<tr>
<td>Final ( R ) indices \ ([I &gt; 2\sigma(I)] )</td>
<td>( R_1 = 0.0431, wR_2 = 0.1125 )</td>
</tr>
<tr>
<td>( R ) indices (all data)</td>
<td>( R_1 = 0.0435, wR_2 = 0.1133 )</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>1.635 and -0.861 e.Å⁻³</td>
</tr>
<tr>
<td>CCDC No.</td>
<td>2108084</td>
</tr>
</tbody>
</table>
Fig. S2 Absorption spectra of RuPcs 1a-d in CHCl₃.

Fig. S3 Structures of H₂Pc, ZnPc, and Ru(py)₂TAP.

Fig. S4 Reaction setup for the shielded condition. The photo shows the reaction vessel immersed in a
methanol solution of methyl red (Fig. 3a, entry 2). The entire reaction system was shielded from natural light during the photoreaction.

![Fig. S5 Absorption spectra of (a) 1b, 4, and [Ru(phen)]Cl2 and (b) 1a and 6. The emission spectra of the LEDs overlapped.](image)

![Fig. S6 Plausible reaction mechanism.](image)
Fig. S7 Cyclic voltammograms of RuPcs 1a-d recorded using 0.5 mM solutions of the analytes in ["Bu4N]ClO4/DMF. Ferrocene was used as the internal standard and the Fc/Fc+ couple was set to 0 V.

Fig. S8 Phosphorescence spectra of RuPcs 1a-d (2 µM) in acetone under an N2 atmosphere (λex = 632 nm).

Table S2 Summary of optical and redox parameters for the photocatalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$E_{\text{ox}}$ [V]</th>
<th>$E_{\text{red}}$ [V]</th>
<th>$\lambda_{\text{phos, max}}$ [nm]</th>
<th>$E_{0,0}$ [eV]</th>
<th>$E_{\text{ox}*}$ [V]</th>
<th>$E_{\text{red}*}$ [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(cat/cat+)</td>
<td>(cat/cat+)</td>
<td>[nm]</td>
<td></td>
<td>(cat*/cat+)</td>
<td>(cat*/cat+)</td>
</tr>
<tr>
<td>1a</td>
<td>+0.30</td>
<td>−1.25</td>
<td>863</td>
<td>1.55</td>
<td>−1.25</td>
<td>+0.30</td>
</tr>
<tr>
<td>1b</td>
<td>+0.29</td>
<td>−1.34</td>
<td>863</td>
<td>1.53</td>
<td>−1.24</td>
<td>+0.19</td>
</tr>
<tr>
<td>1c</td>
<td>+0.18</td>
<td>−1.30</td>
<td>N.D. b</td>
<td>N.D. b</td>
<td>N.D. b</td>
<td>N.D. b</td>
</tr>
<tr>
<td>1d</td>
<td>+0.04</td>
<td>−2.00</td>
<td>868</td>
<td>1.57</td>
<td>−1.53</td>
<td>−0.43</td>
</tr>
<tr>
<td>Ru(phen)Cl2 c</td>
<td>+0.88</td>
<td>−1.74</td>
<td>610</td>
<td>2.15</td>
<td>−1.25</td>
<td>+0.44</td>
</tr>
</tbody>
</table>

a vs Fc/Fc+. b Not determined. c The data was taken from ref. 15.
Fig. S9 (a) Phosphorescence spectra of 1a (16 μM, in acetone) with CF$_3$SO$_2$Cl (0–60 mM). (b) The Stern-Volmer plot for 1a/CF$_3$SO$_2$Cl, 2a, and K$_2$HPO$_4$. When the lifetime $\tau_0$ of 1a was 135 ns (in CH$_2$Cl$_2$)$_{16}$, the quencher rate coefficient $k_q$ of CF$_3$SO$_2$Cl was calculated as $5.8 \times 10^8$ M$^{-1}$s$^{-1}$.

Fig. S10 Emission spectra of the NIR and blue LEDs.
Full Experimental Procedures

Preparation of catalysts

Bis(pyridyl) ruthenium(II) phthalocyanine (1a)

\[
\begin{array}{c}
\text{HC} = \text{CN} \quad \text{pyridine, RuCl}_3 \cdot n\text{H}_2\text{O} \\
\text{DBU, 1-pentanol, reflux, 3 d}
\end{array}
\]

A mixture of phthalonitrile (201 mg, 1.6 mmol), pyridine (0.15 mL, 1.9 mmol), and DBU (0.05 mL, 0.33 mmol) in 1-pentanol (4.0 mL) was refluxed. At the same time, RuCl₃·nH₂O (108 mg, 521 µmol) was boiled in 1-pentanol (2.0 mL) until a blue color formed. The RuCl₃ blue solution was added over 5 min to the phthalonitrile/pyridine/DBU mixture, and resulting solution was refluxed for 3 d. After the 1-pentanol was removed by evaporation, the crude product was purified by silica gel column chromatography (CHCl₃). The blue band was collected and concentrated. Then, MeOH was added to the residue, and precipitate was collected by filtration. The desired complex was obtained as a blue solid (61.9 mg, 20%).

400 MHz \(^1\text{H NMR (CDCl₃) δ (ppm):} 9.16-9.14 (m, 8H, Pc-H), 7.90-7.88 (m, 8H, Pc-H), 6.04 (t, \(J = 7.6\) Hz, 2H, py), 5.23 (dd, \(J = 7.6, 6.8\) Hz, 4H, py), 2.45 (d, \(J = 5.2\) Hz, 4H, py).

UV-vis(CHCl₃) (\(ε \times 10^4\)) \(λ_{\text{max}}\) nm: 315(9.4), 378(2.3), 626(6.2).

Bis(4-trifluoromethylpyridyl) ruthenium(II) phthalocyanine (1b)

\[
\begin{align*}
\text{CF}_3
\end{align*}
\]

Synthesized according to the procedure for 1a. Blue solid. (14%)

500 MHz $^1$H NMR (CDCl$_3$) $\delta$ (ppm): 9.21-9.17 (m, 8H, Pc-H), 7.96-7.92 (m, 8H, Pc-H), 5.47 (d, $J = 7.4$ Hz, 4H, 4-CF$_3$-py), 2.53 (d, $J = 6.4$ Hz, 4H, 4-CF$_3$-py).

470MHz $^{19}$F-NMR (CDCl$_3$) $\delta$ (ppm): -67 (s, CF$_3$).

UV-vis(CHCl$_3$) ($\varepsilon \times 10^4$) $\lambda_{\text{max}}$ nm: 312(9.3), 418(0.95), 628(5.4).


Bis(N, N-dimethyl-4-aminopyridyl) ruthenium(II) phthalocyanine (1c)

\[
\begin{align*}
\text{N} & \text{N} \\
\text{N} & \text{N}
\end{align*}
\]

Synthesized according to the procedure for 1a. Blue solid. (7%)

400 MHz $^1$H NMR (CDCl$_3$) $\delta$ (ppm): 9.09-9.07 (m, 8H, Pc-H), 7.83-7.81 (m, 8H, Pc-H), 4.37 (d, $J = 7.6$ Hz, 4H, DMAP), 2.21 (d, $J = 7.6$ Hz, 4H, DMAP), 2.01 (s, 12H, DMAP).

UV-vis(CHCl$_3$) ($\varepsilon \times 10^4$) $\lambda_{\text{max}}$ nm: 318(7.8), 383(1.9), 571(2.0), 624(6.3).

HR-MALDI-FT-ICR-MS calcd for C$_{46}$H$_{36}$N$_{12}$Ru [M]$^+$: 858.2236. Found: 858.2239.
β-tetrakis('Bu) bis(pyridyl) ruthenium(II) phthalocyanine (1d)

A mixture of 6-'Bu-1,3-diminoindoline (500 mg, 2.5 mmol), pyridine (1.3 mL, 17 mmol), RuCl₃·nH₂O (150 mg, 750 µmol), and DBU (1.0 mL, 6.70 mmol) in 2-ethoxyethanol (5.0 mL) was refluxed for 20 h under Ar atmosphere. After the reaction mixture was cooled, MeOH was added. Then, the precipitate was collected by filtration. After the residue was dried under reduced pressure, the product was purified by silica gel column chromatography (CHCl₃). The desired complex was obtained as a blue solid. (5.1 mg, 8%)

400 MHz ¹H NMR(CDCl₃) δ(ppm): 9.21-9.16 (m, 4H, Pc-H), 9.09-9.03 (m, 4H, Pc-H), 7.97-7.26 (m, 4H, Pc-H), 6.01 (t, J = 7.8 Hz, 2H, py), 5.21 (dd, J = 7.52, 6.64 Hz, 4H, py), 2.47 (d, J = 5.2 Hz, 4H, py), 1.74-1.23 (m, 36H, 'Bu)

UV-vis(CHCl₃) (ε×10⁴) λ_max nm: 317(6.6), 379(1.4), 632(3.8).


Preparation of substrates

Compound 2i

To a solution of 4-butylphenol (316 mg, 2.1 mmol) and K₂CO₃ (733 mg, 5.3 mmol) in 20 mL of MeCN, 4-bromo-1-butene (549 mg, 4.1 mmol) was added, and the mixture was refluxed for 23 h. The reaction was quenched with water, extracted with EtOAc and washed with water and brine. The organic layer was dried over Na₂SO₄ and concentrated in vacuo. The product was purified by silica gel column chromatography (hexane : EtOAc = 9 : 1). The desired compound was obtained as colorless oil. (165 mg,
38%)

400 MHz $^1$H NMR (CDCl$_3$) $\delta$(ppm): 7.08 (d, $J = 8.7$ Hz, 2H, Ar), 6.82 (d, $J = 8.7$ Hz, 2H, Ar), 5.94-5.87 (m, 1H, CH), 5.19-5.08 (m, 2H, CH$_2$), 3.99 (t, $J = 6.7$ Hz, 2H, CH$_2$), 2.56-2.51 (m, 4H, CH$_2 \times 2$), 1.59-1.52 (m, 2H, CH$_2$), 1.37-1.31 (m, 2H, CH$_2$), 0.92 (t, $J = 7.3$ Hz, 3H, CH$_3$).

100 MHz $^{13}$C NMR(CDCl$_3$) $\delta$(ppm): 157.05, 135.19, 134.73, 129.36, 117.01, 114.51, 67.38, 34.87, 34.04, 33.87, 22.44, 14.10.


**Compound 2k**

![Chemical structure diagram]

To a solution of 8-hydroxyquinoline (218 mg, 1.5 mmol) and K$_2$CO$_3$ (525 mg, 3.8 mmol) in 5 mL of MeCN, 6-bromo-1-hexene (294 mg, 1.8 mmol) was added, and the mixture was refluxed overnight.

The reaction was quenched with water, extracted with EtOAc and washed with water. The organic layer was dried by Na$_2$SO$_4$ and concentrated in vacuo. The product was purified by silica gel column chromatography (hexane : EtOAc = 9 : 1). The desired compound was obtained as colorless oil. (332 mg, 99%)

400 MHz $^1$H NMR (CDCl$_3$) $\delta$(ppm): 8.95 (dd, $J = 4.2$, 1.8 Hz, 1H, Ar), 8.12 (dd, $J = 8.3$, 1.7 Hz, 1H, Ar), 7.46-7.36 (m, 3H, Ar), 7.06 (dd, $J = 7.7$, 1.3 Hz, 1H, Ar), 5.85-5.81 (m, 1H, CH), 5.06-4.95 (m, 2H, CH$_2$), 4.25 (t, $J = 7.0$ Hz, 2H, CH$_2$), 2.18-2.14 (m, 2H, CH$_2$), 2.07-2.03 (m, 2H, CH$_2$), 1.67-1.63 (m, 2H, CH$_2$).

100 MHz $^{13}$C NMR(CDCl$_3$) $\delta$(ppm): 154.92, 149.37, 140.50, 138.58, 135.94, 129.58, 126.74, 121.59, 119.47, 114.87, 108.68, 68.84, 33.59, 28.53, 25.46.

HR-MALDI-FT-ICR-MS calcd for C$_{15}$H$_{17}$NO [M]$^+$: 228.1383. Found: 228.1384.
Compound 4

A mixture of Coumarin 343 (77 mg, 0.20 mmol), 5-hexen-1-ol (64 mg, 0.64 mmol), N, N-dimethylaminopyridine (DMAP) (25 mg, 0.20 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI) (78 mg, 0.41 mmol), in 20 mL of CH₂Cl₂ was refluxed overnight. The reaction was quenched with water, extracted with CH₂Cl₂ and washed with 1N HCl (∗2), sat. NaHCO₃aq and brine. The organic layer was dried over Na₂SO₄ and concentrated in vacuo. The product was purified by silica gel column chromatography (CHCl₃ : MeOH = 30 : 1). The desired compound was obtained as a yellow solid. (64 mg, 87%).

400 MHz ¹H NMR (CDCl₃) δ(ppm): 8.30 (s, 1H, Ar), 6.94 (s, 1H, Ar), 5.91–5.73 (m, 1H, CH), 5.10–4.90 (m, 2H, CH₂), 4.29 (t, J = 6.7 Hz, 2H, CH₂), 3.33 (q, J = 6.5 Hz, 4H, CH₂×2), 2.87 (t, J = 6.4 Hz 2H, CH₂), 2.75 (t, J = 6.2 Hz 2H, CH₂), 2.19–2.04 (m, 2H, CH₂), 2.01–1.93 (m, 4H, CH₂×2), 1.84–1.71 (m, 2H, CH₂), 1.64–1.46 (m, 2H, CH₂)

100 MHz ¹³C NMR (CDCl₃) δ(ppm): 164.76, 158.74, 153.61, 149.20, 148.58, 138.65, 127.06, 119.23, 114.90, 107.81, 107.66, 105.93, 65.00, 50.39, 50.01, 33.49, 28.33, 27.56, 25.41, 21.32, 20.34, 20.22.

UV-vis(CHCl₃) (ε×10⁴) λ₅ₙₐₓ nm: 437(1.7).


Compound 6¹⁹

To a flask, rhodamine B (479 mg, 1.0 mmol), allyl bromide (658 mg, 5.4 mmol), and Cs₂CO₃ (990 mg, 3.0 mmol) were dissolved in 10 mL of dry DMF and the mixture was heated at 80°C for 2 days. Then, the solvent was removed in vacuo. The product was purified by silica gel column chromatography (CHCl₃ : MeOH = 100 : 1). The desired compound was obtained as a gold solid. (352 mg, 68%).
500 MHz $^1$H NMR (CDCl$_3$) δ(ppm): 8.30 (dd, $J = 7.9, 0.9$ Hz, 1H, Ar), 7.82 (td, $J = 7.5, 1.3$ Hz, 1H, Ar), 7.73 (td, $J = 7.7, 1.3$ Hz, 1H, Ar), 7.31 (dd, $J = 7.6, 0.9$ Hz, 1H, Ar), 7.06 (d, $J = 9.5$ Hz, 2H, Ar), 6.91 (dd, $J = 9.5, 2.5$ Hz, 2H, Ar), 6.80 (d, $J = 2.5$ Hz, 2H, Ar), 5.71-5.66 (m, 1H, CH), 5.21-5.10 (m, 2H, CH$_2$), 4.50 (dt, $J = 5.9, 1.3$ Hz, 2H, CH$_2$), 3.65 (q, $J = 7.2$ Hz, 8H, CH$_2$×4), 1.32 (t, $J = 7.1$ Hz, 12H, CH$_3$×4).

100 MHz $^{13}$C-NMR(CDCl$_3$) δ(ppm): 164.86, 158.83, 157.91, 155.69, 133.80, 133.35, 131.46, 131.40, 131.25, 130.53, 130.47, 130.05, 119.24, 114.48, 113.73, 96.57, 66.26, 46.37, 12.85.

UV-vis(CHCl$_3$) (ε×10$^4$) $\lambda_{max}$ nm: 260(2.6), 352(0.64), 557(8.8).

**General procedure for the red-light-mediated chlorotrifluoromethylation of alkenes: Compound 3a**

In a 4 mL glass-vial, 1a (3.9 mg, 5 µmol), K$_2$HPO$_4$ (174.1 mg, 1 mmol), and 2a (59 mg, 0.5 mmol) were suspended in acetone (3 mL) and the solution was degassed by argon. After CF$_3$SO$_2$Cl (169.0 mg, 1 mmol) was added, the reaction mixture was stirred for 20 h and irradiation with 634 nm red-LED light, then the reaction was quenched with water. The mixture was extracted with ethyl acetate, and then washed with water and brine. The organic layer was dried over Na$_2$SO$_4$. The solvent was removed and purified using flash column chromatography on silica gel (hexane:ethyl acetate = 9:1 v/v). Compound 3a$^{20}$ was obtained (155 mg, 94%) as a white solid.

500 MHz $^1$H NMR (CDCl$_3$) δ(ppm): 7.75 (d, $J = 8.3$ Hz, 2H, Ar), 7.33 (d, $J = 8.0$ Hz, 2H, Ar), 4.61 (br t, $J = 6.5$ Hz, 1H, NH), 4.18-4.16 (m, 1H, CH), 3.23-3.12 (m, 2H, CH$_2$), 2.67-2.57 (m, 1H, CH$_2$), 2.54-2.46 (m, 1H, CH$_2$), 2.44 (s, 3H, CH$_3$), 2.13-2.07 (m, 1H, CH$_2$), 1.87-1.80 (m, 1H, CH$_2$).

100 MHz $^{13}$C NMR(CDCl$_3$) δ(ppm): 143.95, 136.65, 130.00, 127.21 (q, $J_{C,F} = 277.7$ Hz), 51.32 (q, $J_{C,F} = 3.3$ Hz), 42.44 (q, $J_{C,F} = 28.7$ Hz), 40.11, 37.88, 21.63.

470 MHz $^{19}$F NMR (CDCl$_3$) δ(ppm): -67 (t, $J_{C,F} = 9.7$ Hz, CF$_3$).

**Compound 3b$^{21}$**

![Compound 3b](image-url)
400 MHz $^1$H NMR (CDCl$_3$) δ(ppm): 6.77 (d, $J = 7.9$ Hz, 1H, Ar), 6.71 (d, $J = 1.5$ Hz, 1H, Ar), 6.66 (dd, $J = 7.9$, 1.7 Hz, 1H, Ar), 5.96 (s, 2H, CH$_2$), 4.28-4.21 (m, 1H, CH), 3.02 (d, $J = 6.9$ Hz, 2H, CH$_2$), 2.62-2.49 (m, 2H, CH$_2$).

100 MHz $^{13}$C NMR(CDCl$_3$) δ(ppm): 148.00, 147.01, 130.03, 125.48 (q, $J_{C,F} = 277.5$ Hz), 122.75, 109.81, 108.53, 101.25, 54.32 (q, $J_{C,F} = 3.0$ Hz), 44.25, 41.34 (q, $J_{C,F} = 28.7$ Hz).

376 MHz $^{19}$F NMR (CDCl$_3$) δ(ppm): -66 (t, $J_{F,H} = 10.1$ Hz, CF$_3$).

**Compound 3c**

![Structure](image)

400 MHz $^1$H NMR (CDCl$_3$) δ(ppm): 7.87-7.84 (m, 2H, Ar), 7.76-7.71 (m, 2H, Ar), 4.18-4.15 (m, 1H, CH), 3.96-3.85 (m, 2H, CH$_2$), 2.69-2.59 (m, 2H, CH$_2$), 2.17-2.11 (m, 1H, CH$_2$).

100 MHz $^{13}$C-NMR(CDCl$_3$) δ(ppm): 168.29, 134.29, 132.11, 123.78 (q, $J_{C,F} = 277.7$ Hz), 123.56, 51.49 (q, $J_{C,F} = 3.3$ Hz), 42.40 (q, $J_{C,F} = 28.9$ Hz), 36.59, 35.18.

376 MHz $^{19}$F- NMR (CDCl$_3$) δ(ppm): -67 (t, $J_{F,H} = 10.2$ Hz, CF$_3$).


**Compound 3d**

![Structure](image)

500 MHz $^1$H NMR (CDCl$_3$) δ(ppm): 7.30-7.26 (m, 1H, Ar), 7.15 (d, $J = 7.3$ Hz, 1H, Ar), 6.92 (tt, $J = 7.5$, 1.4 Hz, 1H, Ar), 6.88 (d, $J = 8.1$ Hz, 1H, Ar), 4.45 (p, $J = 6.6$ Hz, 1H, CH), 3.84 (d, $J = 1.6$ Hz, 3H, CH$_3$), 3.15 (dd, $J = 13.6$, 6.5 Hz, 1H, CH$_2$), 3.07 (dd, $J = 13.6$, 6.5 Hz, 1H, CH$_2$), 2.59-2.52 (m, 2H, CH$_2$).

100 MHz $^{13}$C NMR(CDCl$_3$) δ(ppm): 157.64, 131.66, 128.93, 125.66 (q, $J_{C,F} = 277.5$ Hz), 124.96, 120.66, 110.61, 55.37, 53.07 (q, $J_{C,F} = 3.1$ Hz), 41.65 (q, $J_{C,F} = 28.6$ Hz), 40.13.

470 MHz $^{19}$F NMR (CDCl$_3$) δ(ppm): -67 (t, $J_{F,H} = 10.2$ Hz, CF$_3$).

**Compound 3e**

![Structure](image)
400 MHz $^1$H NMR (CDCl$_3$) $\delta$(ppm): 7.58 (d, $J = 8.9$ Hz, 2H, Ar), 6.93 (d, $J = 8.9$ Hz, 2H, Ar), 4.16-4.14 (m, 1H, CH), 4.02 (t, $J = 6.1$ Hz, 2H, CH$_2$), 2.66-2.53 (m, 2H, CH$_2$), 1.94-1.64 (m, 6H, CH$_2$$\times$3).

100 MHz $^{13}$C-NMR(CDCl$_3$) $\delta$(ppm): 162.32, 134.10, 125.32 (q, $J_{C,F} = 277.6$ Hz), 119.34, 115.26, 104.01, 67.99, 54.01 (q, $J_{C,F} = 3.2$ Hz), 42.53 (q, $J_{C,F} = 28.5$ Hz), 37.70, 28.36, 22.76.

376 MHz $^{19}$F NMR (CDCl$_3$) $\delta$(ppm): -67 (t, $J_{F,H} = 10.3$ Hz, CF$_3$).


**Compound 3f**

400 MHz $^1$H NMR (CDCl$_3$) $\delta$(ppm): 8.20 (d, $J = 9.3$ Hz, 2H, Ar), 6.94 (d, $J = 9.3$ Hz, 2H, Ar), 4.16-4.14 (m, 1H, CH), 4.08 (t, $J = 6.1$ Hz, 2H, CH$_2$), 2.67-2.54 (m, 2H, CH$_2$), 1.95-1.65 (m, 6H, CH$_2$$\times$3).

100 MHz $^{13}$C-NMR(CDCl$_3$) $\delta$(ppm): 164.10, 141.60, 126.05, 125.34 (q, $J_{C,F} = 277.6$ Hz), 114.51, 68.48, 54.02 (q, $J_{C,F} = 3.3$ Hz), 42.56 (q, $J_{C,F} = 28.5$ Hz), 37.71, 28.39, 22.77.

376 MHz $^{19}$F-NMR (CDCl$_3$) $\delta$(ppm): -67 (t, $J_{F,H} = 10.1$ Hz, CF$_3$).


**Compound 3g**

400 MHz $^1$H NMR (CDCl$_3$) $\delta$(ppm): 7.40 (d, $J = 2.5$ Hz, 1H, Ar), 7.22 (dd, $J = 8.8, 2.5$ Hz, 1H, Ar), 6.89 (d, $J = 8.8$ Hz, 1H, Ar) 4.70-4.42 (m, 1H, CH), 4.37-4.07 (m, 2H, CH$_2$), 2.97-2.62 (m, 2H, CH$_2$), 2.56-2.36 (m, 1H, CH$_2$), 2.29-2.00 (m, 1H, CH$_3$).

100 MHz $^{13}$C-NMR(CDCl$_3$) $\delta$(ppm): 153.01, 130.23, 127.79, 126.45, 125.30 (q, $J_{C,F} = 277.6$ Hz), 124.05, 114.36, 65.60, 50.98 (q, $J_{C,F} = 28.7$ Hz), 37.52.

376 MHz $^{19}$F-NMR (CDCl$_3$) $\delta$(ppm): -67 (t, $J_{F,H} = 10.2$ Hz, CF$_3$).

S-16

**Compound 3h**

\[
\begin{align*}
\text{Cl} & \quad \text{CF}_3 \\
\end{align*}
\]

400 MHz \( ^1\text{H} \) NMR (CDCl₃) \( \delta \) (ppm): 7.37-7.21 (m, 5H, Ar), 4.36-4.30 (m, 1H, CH), 3.11 (d, 2H, CH₂), 2.62-2.53 (m, 2H, CH₂).

100 MHz \( ^{13}\text{C} \)-NMR (CDCl₃) \( \delta \) (ppm): 136.40, 129.55, 128.83, 127.50, 125.47 (q, \( J_{C,F} = 278.76 \) Hz), 54.16 (q, \( J_{C,F} = 3.03 \) Hz), 44.58, 41.49 (q, \( J_{C,F} = 28.28 \) Hz).

376 MHz \( ^{19}\text{F} \)-NMR (CDCl₃) \( \delta \) (ppm): -67 (t, \( J_{F,H} = 11.3 \) Hz, CF₃).

**Compound 3i**

\[
\begin{align*}
\text{O} & \quad \text{Cl} & \quad \text{CF}_3 \\
\end{align*}
\]

400 MHz \( ^1\text{H} \) NMR (CDCl₃) \( \delta \) (ppm): 7.10 (d, \( J = 8.7 \) Hz, 2H, Ar), 6.82 (d, \( J = 8.6 \) Hz, 2H, Ar), 4.45-4.43 (m, 1H, CH), 4.18-4.12 (m, 2H, CH₂), 2.72-2.63 (m, 2H, CH₂), 2.55 (t, \( J = 7.7 \) Hz, 2H, CH₂), 2.37-2.34 (m, 1H, CH₂), 2.15-2.12 (m, 1H, CH₂), 1.60-1.53 (m, 2H, CH₂), 1.37-1.32 (m, 2H, CH₂), 0.92 (t, \( J = 7.3 \) Hz, 3H, CH₃).

100 MHz \( ^{13}\text{C} \)-NMR (CDCl₃) \( \delta \) (ppm): 156.63, 135.72, 129.49, 126.74 (q, \( J_{C,F} = 277.7 \) Hz), 114.48, 64.05, 51.16 (q, \( J_{C,F} = 3.3 \) Hz), 42.69 (q, \( J_{C,F} = 28.6 \) Hz), 37.88, 34.88, 34.03, 22.44, 14.10.

376 MHz \( ^{19}\text{F} \)-NMR (CDCl₃) \( \delta \) (ppm): -67 (t, \( J_{F,H} = 10.1 \) Hz, CF₃).

HR-MALDI-FT-ICR-MS calcd for \( \text{C}_{15}\text{H}_{20}\text{Cl}_{5}\text{F}_{3}\text{O} \) [M]^+ : 308.1149. Found: 308.1151.

**Compound 3j**

\[
\begin{align*}
\text{O} & \quad \text{Ph} & \quad \text{Cl} & \quad \text{CF}_3 \\
\end{align*}
\]

500 MHz \( ^1\text{H} \) NMR (CDCl₃) \( \delta \) (ppm): 8.21-8.19 (m, 2H, Ar), 7.69-7.66 (m, 1H, Ar), 7.56-7.53 (m, 1H, Ar), 7.40-7.34 (m, 2H, Ar), 7.30-7.26 (m, 1H, Ar), 7.23-7.21 (m, 1H, Ar), 4.41-4.35 (m, 1H, CH), 3.16 (dd, \( J = 14.4, 5.9 \) Hz, 1H, CH₂), 3.04 (dd, \( J = 14.3, 8.3 \) Hz, 1H, CH₂), 2.60-2.56 (m, 2H, CH₂).

S-17
100 MHz $^{13}$C NMR(CDCl$_3$) δ(ppm): 164.95, 149.49, 133.98, 131.57, 130.16, 128.99, 128.84, 128.80, 128.79, 126.34, 125.20 (q, $J_{C,F} = 277.6$ Hz), 122.94, 53.10 (q, $J_{C,F} = 3.1$ Hz), 41.86 (q, $J_{C,F} = 28.7$ Hz), 39.38.

470 MHz $^{19}$F NMR (CDCl$_3$) δ(ppm): -67 (t, $J_{F,H} = 9.5$ Hz, CF$_3$).

HR-MALDI-FT-ICR-MS calcd for C$_{17}$H$_{14}$ClF$_3$O$_2$ [M]$^+$: 343.0707. Found: 343.0711.

**Compound 3k**

\[ \text{Structure Image} \]

400 MHz $^1$H NMR (CDCl$_3$) δ(ppm): 8.95 (dd, $J = 4.2$, 1.8 Hz, 1H, Ar), 8.13 (dd, $J = 8.3$, 1.8 Hz, 1H, Ar), 7.50-7.36 (m, 3H, Ar), 7.06 (dd, $J = 7.6$, 1.4 Hz, 1H, Ar), 4.27 (t, $J = 6.7$ Hz, 2H, CH$_2$), 4.22-4.11 (m, 1H, CH), 2.71-2.49 (m, 2H, CH$_2$), 2.17-1.66 (m, 6H, CH$_2$×3).

100 MHz $^{13}$C NMR(CDCl$_3$) δ(ppm): 154.75, 149.40, 140.39, 136.11, 129.64, 126.79, 125.40 (q, $J_{C,F} = 277.7$ Hz), 121.70, 119.76, 108.87, 68.66, 54.09 (q, $J_{C,F} = 3.3$ Hz), 42.53 (q, $J_{C,F} = 28.4$ Hz), 37.93, 28.33, 22.98.

376 MHz $^{19}$F NMR (CDCl$_3$) δ(ppm): -67 (t, $J_{F,H} = 10.4$ Hz, CF$_3$).

Compound 3f

400 MHz $^1$H NMR (CDCl$_3$) $\delta$(ppm): 4.14-4.08 (m, 1H, CH), 2.62-2.53 (m, 2H, CH$_2$), 1.83-1.73 (m, 2H, CH$_2$), 1.55-1.42 (m, 8H, CH$_2$×4) 0.91-0.88 (m, 3H, CH$_3$).

376 MHz $^{19}$F-NMR (CDCl$_3$) $\delta$(ppm): -67 (t, $J_{F,H}$ = 10.2 Hz, CF$_3$).

Compound 3m

(dr 1 : 1.7)

400 MHz $^1$H NMR (CDCl$_3$) $\delta$(ppm): 4.24-4.14 (m, 1H), 2.62-2.46 (m, 0.40H), 2.42-2.27 (m, 0.67H), 1.89-1.32 (m, 8H), 0.98-0.92 (m, 6H).

100 MHz $^{13}$C NMR(CDCl$_3$) $\delta$(ppm): 127.30 (q, $J_{C,F}$ = 281.5 Hz), 125.68 (q, $J_{C,F}$ = 281.7 Hz), 59.87 (q, $J_{C,F}$ = 3.0 Hz), 59.08 (q, $J_{C,F}$ = 3.3 Hz), 49.46 (q, $J_{C,F}$ = 24.2 Hz), 48.45 (q, $J_{C,F}$ = 24.7 Hz), 38.59, 36.14 (d, $J_{C,F}$ = 1.6 Hz), 26.79 (q, $J_{C,F}$ = 1.8 Hz), 26.54 (q, $J_{C,F}$ = 2.0 Hz), 21.37, 21.10, 20.52, 20.25, 14.21, 14.05, 13.45, 13.44.

376 MHz $^{19}$F NMR (CDCl$_3$) $\delta$(ppm): -69 (d, $J_{F,H}$ = 9.6 Hz, CF$_3$), -70 (d, $J_{F,H}$ = 9.1 Hz, CF$_3$).


Compound 3n

500 MHz $^1$H NMR (CDCl$_3$) $\delta$(ppm): 4.20 (m, $J$ = 7.2 Hz, 2H, CH$_2$×2), 3.57-3.38 (m, 2H, CH$_2$×2), 2.72-2.42 (m, 4H, CH$_2$×2), 2.41-1.95 (m, 1H, CH$_3$+CH×2), 1.25 (t, $J$ = 7.1 Hz, 3H, CH$_3$), 1.25 (t, $J$ = 7.1 Hz, 3H, CH$_3$).

100 MHz $^{13}$C-NMR(CDCl$_3$) $\delta$(ppm): 172.20, 172.11, 126.94 (q, $J_{C,F}$ = 277.1 Hz), 61.96, 61.92, 58.62, 44.43, 43.98, 38.61, 37.08, 35.56 (q, $J_{C,F}$ = 2.5 Hz), 33.37 (q, $J_{C,F}$ = 28.7 Hz), 14.10.
470 MHz $^{19}$F-NMR (CDCl$_3$) δ(ppm): -67 ($J_{F,H} = 10.5$ Hz, CF$_3$).

**Compound 5**

![Chemical Structure](image)

400 MHz $^1$H NMR (CDCl$_3$) δ(ppm): 8.31 (s, 1H, Ar), 6.93 (s, 1H, Ar), 4.31 (t, $J = 6.3$ Hz, 2H, CH$_2$), 4.19-4.08 (m, 1H, CH), 3.33 (q, $J = 6.3$ Hz, 4H, CH$_2$×2), 2.87 (t, $J = 6.4$ Hz, 2H, CH$_2$), 2.81-2.71 (m, 2H, CH$_2$), 2.70-2.50 (m, 2H, CH$_2$), 2.02-1.92 (m, 4H, CH$_2$×2), 1.88-1.69 (m, 4H, CH$_2$×2), 1.67-1.51 (m, 2H, CH$_2$).

100 MHz $^{13}$C NMR (CDCl$_3$) δ(ppm): 164.77, 158.72, 153.61, 149.32, 148.69, 127.08, 125.40 (q, $J_{C,F} = 277.6$ Hz), 119.31, 107.62, 107.36, 105.84, 64.53, 54.11 (q, $J_{C,F} = 3.2$ Hz), 50.37, 49.98, 42.49 (q, $J_{C,F} = 28.4$ Hz), 37.73, 28.07, 27.52, 22.73, 21.25, 20.27, 20.17.

470 MHz $^{19}$F NMR (CDCl$_3$) δ(ppm): -67 ($t, J_{F,H} = 10.3$ Hz, CF$_3$).

UV-vis(CHCl$_3$) (ε×10$^4$) $\lambda_{max}$ nm: 438(3.8).

Copies of the NMR Spectra of Studied Compounds

1a $^1{H}$ NMR in CDCl$_3$

1b $^1{H}$ NMR in CDCl$_3$
1d $^1$H NMR in CDCl$_3$ (a mixture of isomers)

2i $^1$H NMR in CDCl$_3$
$^{13}$C NMR (101 MHz, Chloroform-d$_3$) δ 125.11 (q, $J = 277.7$ Hz), 51.32 (q, $J = 3.3$ Hz), 42.44 (q, $J = 28.7$ Hz).

$^{19}$F NMR (471 MHz, Chloroform-d$_3$) δ -66.39 (t, $J = 9.7$ Hz).
**$^1$H NMR in CDCl$_3$**

$^1$H NMR (400 MHz, Chloroform-d) δ 7.67 (d, J = 7.9 Hz, 1H), 6.77 (d, J = 1.5 Hz, 1H), 6.64 (dd, J = 7.9, 1.7 Hz, 1H), 5.90 (s, 2H), 4.58 – 3.72 (m, 5H), 3.02 (d, J = 6.9 Hz, 2H), 2.77 – 2.37 (m, 2H).

**$^{13}$C NMR in CDCl$_3$**

$^{13}$C NMR (101 MHz, Chloroform-d) δ 125.48 (q, J = 277.5 Hz), 54.32 (q, J = 3.0 Hz), 41.34 (q, J = 28.7 Hz).
$^{19}$F NMR (376 MHz, Chloroform-d$_3$, J = 10.1 Hz).

$^{1}$H NMR in CDCl$_3$. 

Parameter | Value
---|---
1 Data File Name | C:/ Users/ hayama/ Documents/ Personal data/ Ishikawa/Ryuta/ NMR/ data/ 2009011_exCF3r_CDCl3_2 Rd
2 Title | 2009011_exCF3r_CDCl3_2 RM
3 Comment | 
4 Origin | Bruker BioSpin GmbH
5 Owner | rrmssu
6 Site | 
7 Instrument | Avance
8 Author | 
9 Solvent | CDCl$_3$
10 Temperature | 298.1
11 Pulse Sequence | zg
12 Experiment | 1D
13 Probe | Z16098_0842_0PA BDU-4001_1D-F-05 2 SP
14 Number of Scans | 16
15 Receiver Gain | 101.0
16 Relaxation Delay | 1.0000
17 Pulse Width | 18.0000
18 Presaturation Frequency | 
19 Acquisition Time | 0.7209
20 Acquisition Date | 2020-09-1T00:4
21 Modification Date | 2020-09-1T00:3
$^{13}$C NMR (100 MHz, Chloroform-d$_2$) δ 51.49 (q, $J = 3.5$ Hz), 42.40 (q, $J = 28.9$ Hz).

$^{19}$F NMR (376 MHz, Chloroform-d$_2$) δ -66.70 (s), $J = 10.2$ Hz.)
$^1$H NMR (500 MHz, Chloroform-d) δ 7.33 – 7.23 (m, 1H), 7.15 (d, J = 7.5 Hz, 1H), 6.92 (t, J = 5.1 Hz, 2H), 6.88 (d, J = 8.1 Hz, 1H), 4.45 (q, J = 6.6 Hz, 1H), 3.94 (d, J = 5.0 Hz, 1H), 3.15 (dd, J = 13.6, 6.5 Hz, 1H), 2.87 (dd, J = 13.6, 7.6 Hz, 1H), 2.45 – 2.48 (m, 1H).

$^{13}$C NMR (125 MHz, Chloroform-d) δ 128.0 (s), 127.0 (s), 125.1 (s), 121.9 (s), 115.1 (s), 110.5 (s), 108.3 (s), 53.8 (s), 41.9 (s), 28.6 (s).
$^{31}$P NMR (471 MHz, Chloroform-$d_3$ $d_{-66.6}$, $J = 19.2$ Hz).

$^3$H NMR (400 MHz, Chloroform-$d_3$ $d_{7.58}$, d, $J = 8.9$ Hz, 2H), 6.95 (d, $J = 8.9$ Hz, 2H), 4.20 – 4.09 (m, 1H), 4.02 (t, $J = 6.1$ Hz, 2H), 2.7 – 2.47 (m, 2H), 2.01 – 1.55 (m, 4H).
$^{13}$C NMR (100 MHz, Chloroform-d$_3$) δ 62.32, 134.10, 125.52 (q, $J$ = 277.6 Hz), 119.34, 115.26, 104.01, 67.99, 54.01 (q, $J$ = 3.7 Hz), 42.53 (q, $J$ = 28.5 Hz), 37.01, 25.36, 22.76.

$^{19}$F NMR (376 MHz, Chloroform-d$_3$) δ -66.67 (t, $J$ = 10.3 Hz).

Parameter | Value
--- | ---
1 Data File Name | C:/Users/sonyama/Documents/PersonalData/ishikawa/Data/NMR:/data/200916_ex277_CD(CD3)_1.txt
2 Title | 200916_ex277_CD(CD3)_1.txt
3 Comment | 
4 Origin | Bruker Biospin GmbH
5 Owner | rmiyu
6 Site | 
7 Instrument | Avance
8 Author | 
9 Solvent | CDCl$_3$
10 Temperature | 298.1
11 Pulse Sequence | zgpg3d
12 Experiment | 10
13 Probe | Z116098_0842 (90,000,000; BBF):H-D-0-95 Z SP
14 Number of Scans | 16
15 Receiver Gain | 34.9
16 Relaxation Delay | 2.0000
17 Pulse Width | 10.0000
18 Presaturation Frequency | 
19 Acquisition Time | 1.7763
20 Acquisition Date | 2020-09-17T13:35:44
$^{35}$Cl NMR in CDCl$_3$

$^{19}$F NMR in CDCl$_3$

$^{39}$F NMR (176 MHz, Chloroform-d) $\delta$ -66.58 (t, $J = 10.2$ Hz).

Parameter | Value
--- | ---
1. Data File Name | C:/ Users/ [user]/ Documents/ PersonalData/ IshikawaVita/ NMR/ data/ 201212_ex289_C DC03_3.gd
2. Title | 201212_ex289_C DC03_3.d
3. Comment | 
4. Origin | Bruker BioSpin GmbH
5. Owner | retsu
6. Site | 
7. Instrument | Avance
8. Author | 
9. Solvent | CDCl$_3$
10. Temperature | 298.1
11. Pulse Sequence | zg
12. Experiment | 10
13. Probe | Z116098_0842 (FA BBO-0051 BFO-H-0-05 Z SP)
14. Number of Scans | 8
15. Receiver Gain | 20.4
16. Relaxation Delay | 0.0000
17. Pulse Width | 10.0000
19. Acquisition Time | 0.709 2020-10-09T14:3
20. Acquisition Date | 
21. Modification Date | 

$^{35}$Cl NMR (100 MHz, Chloroform-d) $\delta$ 153.01, 130.23, 127.79, 126.45, 125.90 (q, $J = 277.7$ Hz), 124.05, 114.36, 65.60, 54.98 (q, $J = 5.4$ Hz), 42.69 (q, 28.7 Hz), 37.52.

Parameter | Value
--- | ---
1. Data File Name | C:/ Users/ [user]/ Documents/ PersonalData/ IshikawaVita/ NMR/ data/ 201009_ex289_CD CJI_2.gd
2. Title | 201009_ex289_CD CJI_2.d
3. Comment | 
4. Origin | Bruker BioSpin GmbH
5. Owner | retsu
6. Site | 
7. Instrument | Avance
8. Author | 
9. Solvent | CDCl$_3$
10. Temperature | 298.1
11. Pulse Sequence | zg
12. Experiment | 10
13. Probe | Z116098_0842 (FA BBO-0051 BFO-H-0-05 Z SP)
14. Number of Scans | 16
15. Receiver Gain | 20.4
16. Relaxation Delay | 1.0000
17. Pulse Width | 18.0000
18. Preparation Frequency | 0.7209 2020-10-09T14:3
19. Acquisition Time | 6.28
20. Acquisition Date | 
21. Modification Date | 

$^{39}$F NMR (176 MHz, Chloroform-d) $\delta$ -66.58 (t, $J = 10.2$ Hz).
$^{3} \text{H} \text{NMR in CDCl}_3$

$^{13} \text{C} \text{NMR in CDCl}_3$

Parameter | Value
--- | ---
1. Data File Name | C:/ Users/ syuyama/ Documents/ Personaldata/ IshikawaLab/ NMR/ data/ 200703_05cd41.png
2. Title | 200703_05cd41.png
3. Parameter | Value
4. Origin | Bruker BioSpin GmbH
5. Owner | mmsu
6. Site | Ava
7. Instrument | Ava
8. Author | Ava
9. Solvent | CDCl3
10. Temperature | 298.1
11. Pulse Sequence | zg50
12. Experiment | 1D
13. Probe | Z110982842 (PA BRD-005), BIO-H-D-05 Z SP
14. Number of Scans | 16
15. Receiver Gain | 102.4
16. Relaxation Delay | 1.0000
17. Pulse Width | 10.0000
18. Pre-saturation Frequency | 3.9777
19. Acquisition Time | 2.58
20. Acquisition Date | 2020-07-03T14:50
21. Modification Date | 2020-07-03T14:50

Parameter | Value
--- | ---
1. Data File Name | C:/ Users/ syuyama/ Documents/ Personaldata/ IshikawaLab/ NMR/ data/ 200710_chlorotrifluoro_xyleneCDCl3.png
2. Title | 200710_chlorotrifluoro_xyleneCDCl3.png
3. Comment | 
4. Origin | Bruker BioSpin GmbH
5. Owner | mmsu
6. Site | Avance
7. Instrument | Avance
8. Author | Avance
9. Solvent | CDCl3
10. Temperature | 298.1
11. Pulse Sequence | zg50
12. Experiment | 1D
13. Probe | Z110982842 (PA BRD-005), BIO-H-D-05 Z SP
14. Number of Scans | 1024
15. Receiver Gain | 32.6
16. Relaxation Delay | 2.0000
17. Pulse Width | 10.0000
18. Pre-saturation Frequency | 1.3763
19. Acquisition Time | 2.58
$^{31}$C NMR (100 MHz, Chloroform-d$_3$): 5 156.63, 135.72, 129.09, 126.74 ($q$, $J = 27.7$ Hz), 114.48, 64.05, 51.16 ($q$, $J = 3.3$ Hz), 42.69 ($q$, $J = 28.0$
Hz). 17.88, 14.68, 14.01, 37.44, 14.11.

$^{19}$F NMR (270 MHz, Chloroform-d$_3$): -46.31 ($q$, $J = 18.1$ Hz).
$^{1}H$ NMR (500 MHz, Chloroform-d) δ 8.24 (dd, 1H), 7.77 (s, 1H), 7.51 (dd, 1H), 7.29 (d, 1H), 7.64 - 7.35 (m, 1H), 7.33 - 7.27 (m, 1H), 7.23 - 7.18 (m, 1H), 4.48 - 4.28 (m, 1H), 3.16 (dd, J = 14.4, 5.8 Hz, 1H), 3.04 (dd, J = 14.3, 4.5 Hz, 1H), 2.16 - 2.49 (m, 1H).

$^{13}C$ NMR (101 MHz, Chloroform-d) δ 164.95, 149.40, 133.98, 131.57, 130.36, 128.99, 128.84, 128.80, 128.79, 128.34, 125.20 (g, J = 277.6 Hz), 122.94, 53.10 (q, J = 3.1 Hz), 41.86 (q, J = 28.7 Hz), 39.38.

Parameter | Value
--- | ---
1 Data File Name | C:/Users/furuya/Documents/Personaldatas/IshikawaTatsu/NMR/010918_ex279_CDC3_1.pdf
2 Title | S-159812
3 Comment |
4 Origin | JFL
5 Owner |
6 Site |
7 Instrument | ECA 100
8 Author | Mehta
9 Solvent | CDCl3
10 Temperature | 20.8
11 Pulse Sequence | single_pulse.kk2
12 Experiment | 1D
13 Probe | 2756
14 Number of Scans | 8
15 Receiver Gain | 15.0
16 Relaxation Delay | 5.0000
17 Pulse Width | 1.7000
18 Presaturation Frequency | 19 Acquisition Time | 1.7459
20 Acquisition Date | 2020-09-18T14:08:43
21 Modification Date | 2020-09-18T14:27:56
22 Class |
23 Spectrometer |

Parameter | Value
--- | ---
1 Data File Name | C:/Users/furuya/Documents/Personaldatas/IshikawaTatsu/NMR/201215_ex279_CDC3_1.pdf
2 Title | 201215_ex279_CDC3_1.pdf
3 Comment |
4 Origin | Bruker BioSpin GmbH
5 Owner | mrsu
6 Site |
7 Instrument | Avance
8 Author |
9 Solvent | CDCl3
10 Temperature | 298.1
11 Pulse Sequence | 0900007000
12 Experiment | 1D
13 Probe | Z11D
14 Number of Scans | 10000
15 Receiver Gain | 15.0
16 Relaxation Delay | 2.0000
17 Pulse Width | 10.0000
18 Presaturation Frequency | 19 Acquisition Time | 1.3763
20 Acquisition Date | 2020-11-26T05:39:08

S-39
$^{19}$F NMR (471 MHz, Chloroform-d) δ -66.62 (s, J = 8.5 Hz).

$^1$H NMR (400 MHz, Chloroform-d) δ 8.89 (dd, J = 4.2, 1.8 Hz, 1H), 8.33 (dd, J = 8.3, 1.8 Hz, 1H), 7.59 – 7.38 (m, 1H), 7.06 (dd, J = 7.8, 1.4 Hz, 1H), 4.37 (t, J = 6.7 Hz, 2H), 4.22 – 4.11 (m, 1H), 2.71 – 2.49 (m, 2H), 2.17 – 1.64 (m, 6H).
$^{13}$C NMR (101 MHz, Chloroform-d) δ 154.75, 149.40, 140.39, 136.31, 129.64, 126.79, 121.40 (q, J = 277.7 Hz), 121.70, 119.76, 108.87, 68.66, 54.09 (q, J = 3.3 Hz), 42.53 (q, J = 26.4 Hz), 37.95, 28.33, 22.98.

$^{19}$F NMR (376 MHz, Chloroform-d) δ -66.68 (t, J = 10.4 Hz).
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data File Name</td>
<td>C:/Users/leroyar/documents/personaldata/NMR/data/200716_ex247_extracted_CDX3/1/200716_ex247 extracted_CDX3_2.H</td>
</tr>
<tr>
<td>Title</td>
<td>200716_ex247 extracted_CDX3_2.h</td>
</tr>
<tr>
<td>Comment</td>
<td></td>
</tr>
<tr>
<td>Origin</td>
<td>Bruker BioSpin GmbH</td>
</tr>
<tr>
<td>Owner</td>
<td>innsae</td>
</tr>
<tr>
<td>Site</td>
<td></td>
</tr>
<tr>
<td>Instrument</td>
<td>Avance</td>
</tr>
<tr>
<td>Author</td>
<td></td>
</tr>
<tr>
<td>Solvent</td>
<td>CDCl3</td>
</tr>
<tr>
<td>Temperature</td>
<td>298.1</td>
</tr>
<tr>
<td>Pulse Sequence</td>
<td>zg</td>
</tr>
<tr>
<td>Experiment</td>
<td>ID</td>
</tr>
<tr>
<td>Probe</td>
<td>Z116098_2842 (PA 900, 4001, 8/128 Mz(0-32 Z SP))</td>
</tr>
<tr>
<td>Number of Scans</td>
<td>66</td>
</tr>
<tr>
<td>Receiver Gain</td>
<td>100.0</td>
</tr>
<tr>
<td>Relaxation Delay</td>
<td>1.0000</td>
</tr>
<tr>
<td>Pulse Width</td>
<td>10.0000</td>
</tr>
<tr>
<td>Preprocessing Frequency</td>
<td>3.9977</td>
</tr>
<tr>
<td>Acquisition Time</td>
<td>2020-07-18T19:06:24</td>
</tr>
</tbody>
</table>

**19F NMR (76 MHz, Chloroform-δ 3.66.73, J = 10.3 Hz):**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data File Name</td>
<td>C:/Users/leroyar/documents/personaldata/NMR/data/200716_ex247_extracted_CDX3/1/200716_ex247 extracted_CDX3_2.H</td>
</tr>
<tr>
<td>Title</td>
<td>200716_ex247 extracted_CDX3_2.h</td>
</tr>
<tr>
<td>Comment</td>
<td></td>
</tr>
<tr>
<td>Origin</td>
<td>Bruker BioSpin GmbH</td>
</tr>
<tr>
<td>Owner</td>
<td>innsae</td>
</tr>
<tr>
<td>Site</td>
<td></td>
</tr>
<tr>
<td>Instrument</td>
<td>Avance</td>
</tr>
<tr>
<td>Author</td>
<td></td>
</tr>
<tr>
<td>Solvent</td>
<td>CDCl3</td>
</tr>
<tr>
<td>Temperature</td>
<td>298.1</td>
</tr>
<tr>
<td>Pulse Sequence</td>
<td>zg</td>
</tr>
<tr>
<td>Experiment</td>
<td>ID</td>
</tr>
<tr>
<td>Probe</td>
<td>Z116098_2842 (PA 900, 4001, 8/128 Mz(0-32 Z SP))</td>
</tr>
<tr>
<td>Number of Scans</td>
<td>66</td>
</tr>
<tr>
<td>Receiver Gain</td>
<td>101.0</td>
</tr>
<tr>
<td>Relaxation Delay</td>
<td>1.0000</td>
</tr>
<tr>
<td>Pulse Width</td>
<td>10.0000</td>
</tr>
<tr>
<td>Preprocessing Frequency</td>
<td>3.9977</td>
</tr>
<tr>
<td>Acquisition Time</td>
<td>2020-07-18T19:06:24</td>
</tr>
</tbody>
</table>
$\text{S-43}$

$\text{Cl}$

$\text{CF}_3$

$3\text{m} \ ^1\text{H} \text{NMR in CDCl}_3$

(a mixture of syn/anti isomers)

$\text{Cl}$

$\text{CF}_3$

$3\text{m} \ ^{13}\text{C} \text{NMR in CDCl}_3$

(a mixture of syn/anti isomers)
$\text{Cl} \quad \text{CF}_3$ 

$3\text{m} \quad ^{19}\text{F NMR in CDCl}_3$ 
(a mixture of syn/anti isomers)

$\text{Cl} \quad \text{CF}_3$ 

$3\text{n} \quad ^1\text{H NMR in CDCl}_3$
$^{13}$C NMR (101 MHz, Chloroform-d$_3$) δ 172.28, 172.31, 126.94 (q, J = 27.1 Hz), 64.96, 64.92, 38.62, 44.43, 43.98, 38.61, 37.08, 35.56 (q, J = 2.5 Hz), 88.19, 14.18.

# 1H NMR

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data File Name</td>
<td>C:/Users/yourname/Documents/Personaldata/InskawaData/NMR:/data/201212_ex295_C_D03.1.dfd</td>
</tr>
<tr>
<td>Title</td>
<td>201212_ex295_C_D03.1.dfd</td>
</tr>
<tr>
<td>Comment</td>
<td>Bruker BioSpin GmbH</td>
</tr>
<tr>
<td>Size</td>
<td>nmrsw</td>
</tr>
<tr>
<td>Instrument</td>
<td>Avance</td>
</tr>
<tr>
<td>Solvent</td>
<td>CDCl$_3$</td>
</tr>
<tr>
<td>Temperature</td>
<td>298.15 K</td>
</tr>
<tr>
<td>Pulse Sequence</td>
<td>zg90/30</td>
</tr>
<tr>
<td>Experiment</td>
<td>10</td>
</tr>
<tr>
<td>Probe</td>
<td>Z116098_0482 (Bruker-0051) BRF-II-O-05 Z SP</td>
</tr>
<tr>
<td>Number of Scans</td>
<td>1024</td>
</tr>
<tr>
<td>Receiver Gain</td>
<td>27.1</td>
</tr>
<tr>
<td>Relaxation Delay</td>
<td>2.0000</td>
</tr>
<tr>
<td>Pulse Width</td>
<td>10.0000</td>
</tr>
<tr>
<td>Presaturation Frequency</td>
<td>18.0000</td>
</tr>
<tr>
<td>Acquisition Time</td>
<td>1.7640</td>
</tr>
<tr>
<td>Upload Date</td>
<td>2020-11-25T00:02:48</td>
</tr>
</tbody>
</table>

$^{19}$F NMR (376 MHz, Chloroform-d$_3$) δ -87.24, -87.12.

$^{19}$F NMR (376 MHz, Chloroform-d$_3$) δ -87.24, -87.12.

$^{19}$F NMR (376 MHz, Chloroform-d$_3$) δ -87.24, -87.12.
$^1$H NMR (400 MHz, Chloroform-d) δ 8.31 (s, 1H), 6.93 (s, 1H), 4.31 (q, $J$ = 6.3 Hz, 2H), 4.19 – 4.08 (m, 1H), 3.53 (s, $J$ = 6.1 Hz, 4H), 2.87 (q, $J$ = 6.4 Hz, 2H), 2.81 – 2.71 (m, 2H), 2.70 – 2.50 (m, 2H), 2.02 – 1.92 (m, 4H), 1.88 – 1.49 (m, 4H), 1.67 – 1.51 (m, 2H).

$^{13}$C NMR (101 MHz, Chloroform-d) δ 164.72, 158.72, 153.64, 149.82, 148.69, 127.08, 125.46 (q, $J$ = 277.6 Hz), 119.31, 107.62, 107.36, 105.84, 64.53, 54.11 (q, $J$ = 3.2 Hz), 30.37, 49.98, 42.40 (q, $J$ = 28.4 Hz), 37.73, 33.07, 27.52, 22.73, 21.25, 20.27, 20.17.
$^1$H NMR (300 MHz, Chloroform-d): 8.80 (s, J = 7.6 Hz, 1H), 7.74 (dd, J = 7.6, 7 Hz, 1H), 7.15 (dd, J = 7.6, 1.3 Hz, 1H), 7.06 (dd, J = 7.6, 1.3 Hz, 1H), 6.96 (dd, J = 7.6, 2.5 Hz, 1H), 6.80 (dd, J = 7.6, 2.5 Hz, 1H), 5.94 (dd, J = 7.6, 4.5 Hz, 1H), 5.11 (s, J = 7.6 Hz, 3H), 3.90 (t, J = 7.6 Hz, 2H), 3.85 (s, J = 7.6 Hz, 3H), 3.68 (q, J = 7.6 Hz, 2H), 3.50 (s, J = 7.6 Hz, 2H), 3.22 (s, J = 7.6 Hz, 2H).

$^13$C NMR (75 MHz, Chloroform-d): 86.66 (s, J = 10.5 Hz).

$^15$F NMR (376 MHz, Chloroform-d): 8.66-6.65 (m, J = 10.5 Hz).

Parameter | Value
--- | ---
1. Data File Name | C:/Users/fukuyama/Documents/Personaldaten/ishikawa.shigeo/NMR/6HCDCl3/1D/7A047167.SCDF3
2. Title | 6H NMR in CDCl3
3. Comment |
4. Origin | Bruker Biospin GmbH
5. Owner |
6. Site |
7. Instrument | Avance
8. Author |
9. Solvent | DMSO-D6
10. Temperature | 298.2 K
11. Pulse Sequence | zg
12. Experiment | 1D
13. Probe | Z16098_0842_9A01012_1DF20-1-06-09-01
14. Number of Scans | 16
15. Receiver Gain | 101.0
16. Relaxation Delay | 1.0000
17. Pulse Width | 18.0000
18. Precuration Frequency | 0.729
19. Acquisition Time | 0.729
20. Acquisition Date | 2021-02-04T16:5
21. Modification Date | 2021-02-04T16:5

Parameter | Value
--- | ---
1. Data File Name | C:/Users/fukuyama/Documents/Personaldaten/ishikawa.shigeo/NMR/6HCDCl3/1D/7A047167.SCDF3
2. Title | 6H NMR in CDCl3
3. Comment |
4. Origin | JDSL
5. Owner |
6. Site |
7. Instrument | ECA 100
8. Author |
9. Solvent | CDCl3
10. Temperature | 298.2 K
11. Pulse Sequence | zg
12. Experiment | 1D
13. Probe |
14. Number of Scans | 8
15. Receiver Gain | 46.0
16. Relaxation Delay | 5.0000
17. Pulse Width | 1.7000
18. Precuration Frequency | 0.729
19. Acquisition Time | 2021-11-02T10:5
20. Acquisition Date | 2021-11-02T10:5
21. Modification Date | 2021-11-02T10:5
22. Class |
23. Spectrometer | 500.16

S-48
References


