Synthesis of naphthalene-fused imidazo[1,2-*a*]pyridinium salts showing green luminescence with high quantum yields and large Stokes shift

Sota Abe,[a] Tetsuro Katayama,*[b] Akihiro Furube,[b] Atsushi Tabata,[c] Yasushi Yoshida,[d] Shoko Ueta,[a] Yukihiro Arakawa,[a] Keiji Minagawa,[a] Yasushi Imada [a] and Fumitoshi Yagishita [a,c,*]

[a] *Department of Applied Chemistry, Tokushima University, 2-1 Minamijosanjima, Tokushima 770-8506, Japan*

[b] *Institute of Post-LED Photonics, Tokushima University, 2-1 Minamijosanjima, Tokushima 770-8506, Japan*

[c] *Department of Bioscience and Bioindustry, Tokushima University, 2-1 Minamijosanjima, Tokushima 770-8513, Japan*

[d] *Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan*

*Corresponding author. Tel.: +81-88-656-7401; E-mail: yagishitaf@tokushima-u.ac.jp (FY)
Tel.: +81-88-656-7538; E-mail: tetsuro@tokushima-u.ac.jp (TK)

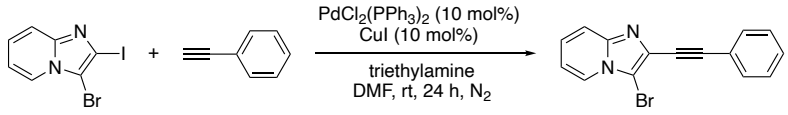
Table of Contents

General Information

NMR spectra were recorded on a JEOL resonance JNM-ECZ-400 operating 400 MHz for ^{1}H- and 100 MHz for ^{13}C-NMR spectroscopy, respectively, in $CDCl_3$ or DMSO-d_6 solutions. Chemical shifts are reported in parts per million (ppm) relative to TMS or residual solvent peaks as an internal standard. Melting points were measured on a AS ONE ATM-01 and uncorrected. High-resolution mass spectra (HRMS) were recorded on a ThermoFisher Exactive. X-ray single crystallographic analysis was conducted using a Rigaku R-AXIS RAPID II. UV/vis spectra were recorded on a Shimadzu UV-1600. PL spectra were recorded on a Shimadzu RF-1500. Absolute PL quantum yields were recorded on a Hamamatsu Photonics Quantaurus-QY Plus C13534-21. Fluorescence lifetimes were recorded on a Horiba DeltaFlex.

Experimental Procedures and Characterization

Preparation of 3-bromo-2-(phenylethynyl)imidazo[1,2-*a*]pyridine:

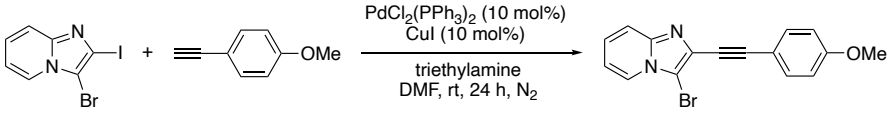


To a 25 mL of DMF solution containing 3-bromo-2-iodoimidazo[1,2-*a*]pyridine (2.0 g, 6.2 mmol) were added ethynylbenzene (6.8 mmol), $PdCl_2(PPh_3)_2$ (0.62 mmol), CuI (0.62 mmol) and triethylamine (3.4 mL), and the mixture was stirred for 24 hours at room temperature under nitrogen atmosphere. After the reaction mixture was poured into water and extracted with dichloromethane, the organic layer was washed with brine, dried over $MgSO_4$ and concentrated in *vacuo*. The residual mixture was subjected to chromatography on silica gel using mixtures of ethyl acetate and hexane as eluents, and 3-bromo-2-(phenylethynyl)imidazo[1,2-*a*]pyridine was isolated in 99% yield.

^{1}H NMR ($CDCl_3$) δ: 2.86 (s, 2H), 3.78 (s, 12H), 6.84 (d, *J* = 9.1 Hz, 8H), 7.44 (d, *J* = 9.1 Hz, 1H).

This compound is known: P.-O. Delaye, M. Pénichon, H. Allouchi, C. Enguehard-Gueiffier and A. Gueiffier, *Org*. *Biomol*. *Chem*. 2017, **15**, 4199.

Preparation of 3-bromo-2-((4-methoxyphenyl)ethynyl)imidazo[1,2-*a*]pyridine:

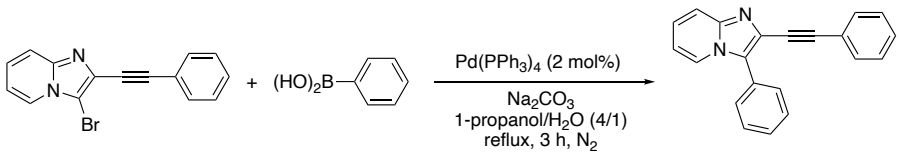


To a 20 mL of DMF solution containing 3-bromo-2-iodoimidazo[1,2-*a*]pyridine (1.0 g, 3.1 mmol) were added 4-ethynylanisole (3.4 mmol), $PdCl_2(PPh_3)_2$ (0.31 mmol), CuI (0.31 mmol) and triethylamine (1.7 mL), and the mixture was stirred for 24 hours at room temperature under nitrogen atmosphere. After the reaction mixture was poured into water and extracted with dichloromethane, the organic layer was washed with brine, dried over $MgSO_4$ and concentrated in *vacuo*. The residual mixture was subjected to chromatography on silica gel using mixtures of ethyl acetate and hexane as eluents, and 3-bromo-2-((4-methoxyphenyl)ethynyl)imidazo[1,2-*a*]pyridine was isolated in

86% yield.

Brown solid; mp 130.0–134.0 °C; ^{1}H NMR ($CDCl_3$) δ: 3.84 (s, 3H), 6.90 (d, *J* = 8.9 Hz, 2H), 6.95 (t, *J* = 6.9 Hz, 1H), 7.27 (dd, *J* = 8.9, 6.6 Hz, 1H), 7.56–7.58 (m, 3H), 8.07 (d, *J* = 6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ: 55.3, 80.1, 94.1, 98.7, 113.6, 114.0, 114.6, 117.7, 123.8, 125.5, 129.1, 133.4, 145.3, 160.0; HRMS (ESI) *m*/*z* calcd for $C_{16}H_{11}ON_2Br$+H 327.0128, found 327.0124.

Preparation of 3-phenyl-2-(phenylethynyl)imidazo[1,2-*a*]pyridine (1a):

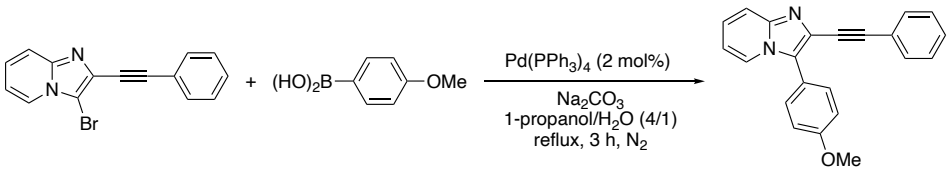


To a 12.5 mL of mixed solution of 1-propanol and water (4 : 1) containing 3-bromo-2-(phenylethynyl)imidazo[1,2-*a*]pyridine (0.15 g, 0.5 mmol) were added 4-methoxyphenylboronic acid (0.55 mmol), $Pd(PPh_3)_4$ (0.0.01 mmol) and sodium carbonate (4.0 mmol), and the mixture was stirred for 3 hours under reflux and nitrogen atmosphere. After the reaction mixture was poured into water and extracted with chloroform, the organic layer was washed with brine, dried over $MgSO_4$ and concentrated in *vacuo*. The residual mixture was subjected to chromatography on silica gel using mixtures of ethyl acetate and hexane as eluents, and 3-(4-methoxyphenyl)-2-(phenylethynyl)imidazo[1,2-*a*]pyridine (**1a**) was isolated in 97% yield.

^{1}H NMR ($CDCl_3$) δ: 6.83 (t, *J* = 6.8 Hz, 1H), 7.25 (dd, *J* = 9.1, 6.8 Hz, 1H), 7.30–7.31 (m, 3H), 7.45–7.49 (m, 3H), 7.57 (t, *J* = 7.5 Hz, 2H), 7.68 (d, *J* = 9.3 Hz, 1H), 7.73–7.75 (m, 2H), 8.28 (d, *J* = 9.0 Hz, 1H).

This compound is known: Y. Gao, M. Yin, W. Wu, H. Huang and H. Jiang, *Adv*. *Synth*. *Catal*. 2013, **355**, 2263.

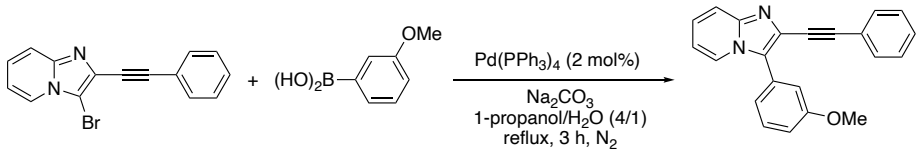
Preparation of 3-(4-methoxyphenyl)-2-(phenylethynyl)imidazo[1,2-*a*]pyridine (1b):



To a 12.5 mL of mixed solution of 1-propanol and water (4 : 1) containing 3-bromo-2-(phenylethynyl)imidazo[1,2-*a*]pyridine (0.15 g, 0.5 mmol) were added 4-methoxyphenylboronic acid (0.55 mmol), $Pd(PPh_3)_4$ (0.001 mmol) and sodium carbonate (4.0 mmol), and the mixture was stirred for 3 hours under reflux and nitrogen atmosphere. After the reaction mixture was poured into water and extracted with chloroform, the organic layer was washed with brine, dried over $MgSO_4$ and concentrated in *vacuo*. The residual mixture was subjected to chromatography on silica gel using mixtures of ethyl acetate and hexane as eluents, and 3-(4-methoxyphenyl)-2-(phenylethynyl)imidazo[1,2-*a*]pyridine (**1b**) was isolated in 96% yield.

Brown solid; mp 118.0–119.0 °C; ^{1}H NMR ($CDCl_3$) δ: 3.91 (s, 3H), 6.81 (t, *J* = 6.8 Hz, 1H), 7.11 (d, *J* = 7.9 Hz, 2H), 7.20–7.24 (m, 1H), 7.31–7.32 (m, 3H), 7.49–7.51 (m, 2H), 7.61 (d, *J* = 9.1 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 2H), 8.22 (d, *J* = 6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ: 55.4, 83.7, 91.7, 112.9, 114.5, 117.9, 120.4, 123.0, 123.2, 125.2, 126.2, 127.7, 128.2, 130.2, 131.6, 144.7, 159.8; HRMS (ESI) *m*/*z* calcd for $C_{22}H_{16}ON_2$+H 325.1335, found 325.1337.

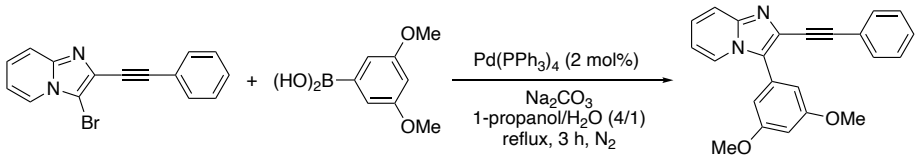
Preparation of 3-(3-methoxyphenyl)-2-(phenylethynyl)imidazo[1,2-*a*]pyridine (1c):



To a 12.5 mL of mixed solution of 1-propanol and water (4 : 1) containing 3-bromo-2-(phenylethynyl)imidazo[1,2-*a*]pyridine (0.15 g, 0.5 mmol) were added 3-methoxyphenylboronic acid (0.55 mmol), $Pd(PPh_3)_4$ (0.001 mmol) and sodium carbonate (4.0 mmol), and the mixture was stirred for 3 hours under reflux and nitrogen atmosphere. After the reaction mixture was poured into water and extracted with chloroform, the organic layer was washed with brine, dried over $MgSO_4$ and concentrated in *vacuo*. The residual mixture was subjected to chromatography on silica gel using mixtures of ethyl acetate and hexane as eluents, and 3-(3-methoxyphenyl)-2-(phenylethynyl)imidazo[1,2-*a*]pyridine (**1c**) was isolated in 79% yield.

Brown solid; mp 95.0–96.0 °C; ^{1}H NMR ($CDCl_3$) δ: 3.87 (s, 3H), 6.83 (t, *J* = 6.9 Hz, 1H), 7.01 (dd, *J* = 8.3, 2.6 Hz, 1H), 7.24 (dd, *J* = 9.2, 6.6 Hz, 1H), 7.31–7.33 (m, 5H), 7.47–7.50 (m, 3H), 7.64 (d, *J* = 9.2 Hz, 1H), 8.32 (d, *J* = 6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ: 55.4, 83.5, 92.1, 113.1, 114.2, 114.5, 118.0, 120.8, 122.9, 123.5, 125.5, 126.7, 127.6, 128.3, 128.4, 129.4, 130.1, 131.6, 145.0, 160.1; HRMS (ESI) *m*/*z* calcd for $C_{22}H_{16}ON_2$+H 325.1335, found 325.1336.

Preparation of 3-(3,5-dimethoxyphenyl)-2-(phenylethynyl)imidazo[1,2-*a*]pyridine (1d):

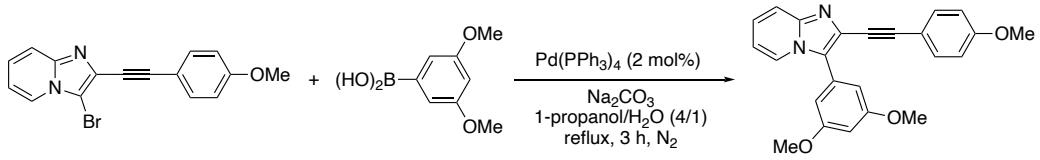


To a 75 mL of mixed solution of 1-propanol and water (4 : 1) containing 3-bromo-2-(phenylethynyl)imidazo[1,2-*a*]pyridine (1.0 g, 3.37 mmol) were added 3,5-dimethoxyphenylboronic acid (3.7 mmol), $Pd(PPh_3)_4$ (0.0674 mmol) and sodium carbonate (27.0 mmol), and the mixture was stirred for 3 hours under reflux and nitrogen atmosphere. After the reaction mixture was poured into water and extracted with chloroform, the organic layer was washed with brine, dried over $MgSO_4$ and concentrated in *vacuo*. The residual mixture was subjected to chromatography on silica gel using mixtures of ethyl acetate and hexane as eluents, and 3-(4-methoxyphenyl)-2-(phenylethynyl)imidazo[1,2-*a*]pyridine (**1d**) was isolated in 92% yield.

White solid; mp 164.0–165.0 °C; ^{1}H NMR ($CDCl_3$) δ: 3.86 (s, 6H), 6.57 (t, *J* = 2.3 Hz, 1H), 6.83 (t, *J* = 6.8 Hz, 1H),

6.91 (d, *J* = 2.3 Hz, 2H), 7.22–7.26 (m, 1H), 7.32–7.33 (m, 3H), 7.50–7.52 (m, 2H), 7.62 (d, *J* = 9.1 Hz, 1H), 8.36 (d, *J* = 6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ: 55.5, 83.6, 92.2, 100.8, 106.7, 113.1, 117.9, 123.0, 123.6, 125.4, 126.8, 127.6, 128.3, 128.4, 129.9, 131.6, 145.0, 161.2; HRMS (ESI) *m*/*z* calcd for $C_{23}H_{18}O_2N_2$+H 355.1441, found 355.1434.

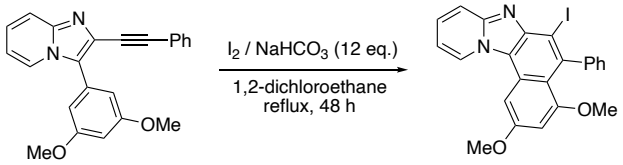
Preparation of 3-(3,5-dimethoxyphenyl)-2-((4-methoxyphenyl)ethynyl)imidazo[1,2-*a*]pyridine (1e):



To a 62.5 mL of mixed solution of 1-propanol and water (4 : 1) containing 3-bromo-2-(4-methoxyphenyl)ethynyl)imidazo[1,2-*a*]pyridine (0.8 g, 2.5 mmol) were added 3,5-dimethoxyphenylboronic acid (2.7 mmol), $Pd(PPh_3)_4$ (0.05 mmol) and sodium carbonate (20.0 mmol), and the mixture was stirred for 3 hours under reflux and nitrogen atmosphere. After the reaction mixture was poured into water and extracted with chloroform, the organic layer was washed with brine, dried over $MgSO_4$ and concentrated in *vacuo*. The residual mixture was subjected to chromatography on silica gel using mixtures of ethyl acetate and hexane as eluents, and 3-(3,5-dimethoxyphenyl)-2-((4-methoxyphenyl)ethynyl)imidazo[1,2-*a*]pyridine (**1e**) was isolated in 87% yield.

brown solid; mp 167.0–168.0 °C; ^{1}H NMR ($CDCl_3$) δ: 3.82 (s, 3H), 3.85 (s, 6H), 6.56 (t, *J* = 2.3 Hz, 1H), 6.82 (t, *J* = 6.8 Hz, 1H), 6.86 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 2.3 Hz, 2H), 7.23 (dd, *J* = 9.1, 6.7 Hz, 1H), 7.45 (d, *J* = 8.9 Hz, 2H), 7.60 (d, *J* = 9.1 Hz, 1H), 8.35 (d, *J* = 7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ: 55.3, 55.5, 82.3, 92.3, 100.8, 106.6, 112.9, 114.0, 115.1, 117.9, 123.6, 125.3, 127.1, 130.0, 133.1, 145.0, 159.7, 161.2; HRMS (ESI) *m*/*z* calcd for $C_{24}H_{20}O_3N_2$+H 385.1547, found 385.1538.

Preparation of 6-iodo-2,4-dimethoxy-5-phenylnaphtho[2',1':4,5]imidazo[1,2-*a*]pyridine (2d):



1d **2d**

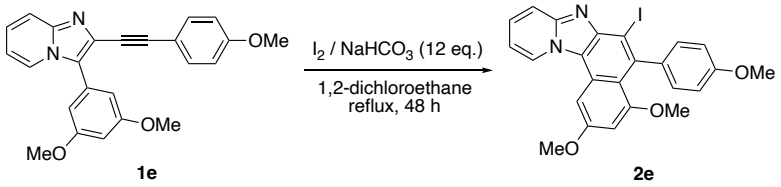
To a 10 mL of 1,2-dichloroethane solution containing **1d** (0.3 mmol) were added iodine (3.6 mmol) and sodium hydrogen carbonate (3.6 mmol), and the mixture was stirred for 48 hours under reflux. Then, the reaction was quenched by addition of saturated $Na_2S_2O_3$ aqueous solution. After the mixture was extracted with dichloromethane, the organic layer was washed with brine, dried over $MgSO_4$ and concentrated in *vacuo*. The residual mixture was subjected to chromatography on silica gel using mixtures of ethyl acetate and hexane as eluents, and 6-iodo-2,4-dimethoxy-5-phenylnaphtho[2',1':4,5]imidazo[1,2-*a*]pyridine (**2d**) was isolated in 86% yield.

Yellow solid; mp 186.0–187.0 °C; ^{1}H NMR ($CDCl_3$) δ: 3.37 (s, 3H), 4.06 (s, 3H), 6.52 (d, *J* = 2.3 Hz, 1H), 7.10 (t, *J* =

6.9 Hz,1H), 7.18–7.20 (m, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.48 (d, *J* = 2.3 Hz, 1H), 7.51 (dd, *J* = 9.2, 6.6 Hz, 1H), 8.02 (d, *J* = 9.2 Hz, 1H), 9.10 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ: 55.5, 55.6, 93.2, 93.8, 96.8, 112.2, 116.7, 118.6, 119.5, 125.3, 126.1, 126.95, 127.04, 127.3, 128.7, 141.9, 144.5, 147.5, 148.8, 158.5, 159.7; HRMS (ESI) *m*/*z* calcd for $C_{23}H_{17}O_2N_2I$+H 481.0407, found 481.0408.

Crystal data of **2d**: $C_{34}H_{28}O_4$, *Mr* = 500.56, monoclinic space group $P2_1/c$, *a* = 6.82330(10) Å, *b* = 13.6419(3) Å, *c* = 21.6469(4) Å, *β* = 90.365(6)°, *V* = 2014.91(6) Å^3, *Z* = 4, *ρ* = 1.583 Mg/m^3, in the final least-squares refinement cycles on F^2, the model converged at R_1 = 0.0456, *wR2* = 0.1091, and GOF = 1.064 for 3684 reflections CCDC2428944.

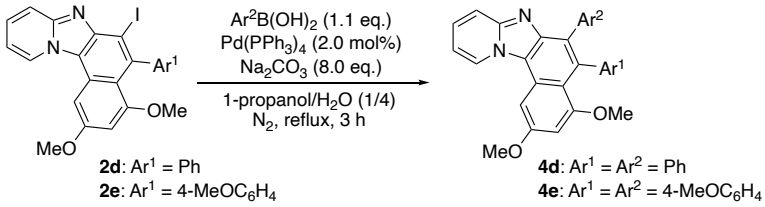
Preparation of 6-iodo-2,4-dimethoxy-5-(4-methoxyphenyl)naphtho[2',1':4,5]imidazo[1,2-*a*]pyridine (2e):



To a 10 mL of 1,2-dichloroethane solution containing **1e** (0.3 mmol) were added iodine (3.6 mmol) and sodium hydrogen carbonate (3.6 mmol), and the mixture was stirred for 48 hours under reflux. Then, the reaction was quenched by addition of saturated $Na_2S_2O_3$ aqueous solution. After the mixture was extracted with dichloromethane, the organic layer was washed with brine, dried over $MgSO_4$ and concentrated in *vacuo*. The residual mixture was subjected to chromatography on silica gel using mixtures of ethyl acetate and hexane as eluents, and 6-iodo-2,4-dimethoxy-5-phenylnaptho[2',1':4,5]imidazo[1,2-*a*]pyridine (**2e**) was isolated in 94% yield.

Brown solid; mp 239.0–240.0 °C; ^{1}H NMR ($CDCl_3$) δ: 3.42 (s, 3H), 3.92 (s, 3H), 4.05 (s, 3H), 6.53 (d, *J* = 2.3 Hz, 1H), 6.98 (t, *J* = 8.8 Hz, 2H), 7.07–7.11 (m, 3H), 7.47 (d, *J* = 2.3 Hz, 1H), 7.50 (dd, *J* = 9.1, 6.6 Hz, 1H), 8.01 (d, *J* = 9.1 Hz, 1H), 9.09 (d, *J* = 7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ: 55.3, 55.5, 55.9, 93.4, 94.9, 97.0, 112.2, 112.5, 117.2, 118.9, 119.6, 125.5, 127.0, 127.2, 129.8, 141.6, 141.7, 144.8, 147.7, 158.1, 158.8, 159.7; HRMS (ESI) *m*/*z* calcd for $C_{24}H_{19}O_3N_2I$+H 511.0513, found 511.0501.

General procedure for Suzuki–Miyaura cross-coupling reaction of 2:



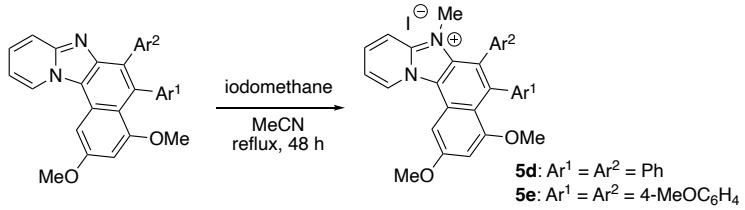
To a 37.5 mL of mixed solution of 1-propanol and water (4 : 1) solution containing **2e** (1.04 mmol) were added phenylboronic acid (1.14 mmol), $Pd(PPh_3)_4$ (0.0208 mmol) and sodium carbonate (8.32 mmol), and the mixture was stirred for 3 hours under reflux and nitrogen atmosphere. After the reaction mixture was poured into water and

extracted with chloroform, the organic layer was washed with brine, dried over $MgSO_4$ and concentrated in *vacuo*. The residual mixture was subjected to chromatography on silica gel using mixtures of ethyl acetate and hexane as eluents, and compound **4d** was isolated in 94% yield. Similarly, compound **4e** was obtained in 64% isolated yield by reaction of **2e** with 4-methoxyphenyl boronic acid.

4d: white solid; mp 221.0–222.0 °C; ^{1}H NMR ($CDCl_3$) δ: 3.38 (s, 3H), 4.10 (s, 3H), 6.58 (d, *J* = 2.3 Hz, 1H), 7.05–7.24 (m, 11H), 7.43 (dd, *J* = 9.1, 6.7 Hz, 1H), 7.60 (d, *J* = 2.3 Hz, 1H), 7.88 (d, *J* = 9.1 Hz, 1H), 9.19 (d, *J* = 7.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ: 55.55, 55.60, 93.4, 97.1, 111.7, 115.9, 118.8, 121.1, 124.9, 125.2, 126.1, 126.2, 126.6, 126.7, 127.3, 129.9, 130.9, 131.2, 135.6, 138.0, 143.4, 143.5, 148.4, 159.3, 160.0; HRMS (ESI) *m*/*z* calcd for $C_{29}H_{22}O_2N_2$+H 431.1754, found 431.1749.

4e: Red solid; mp 282.0–283.0 °C; ^{1}H NMR ($CDCl_3$)) δ: 3.43 (s, 3H), 3.78 (s, 3H), 3.79 (s, 3H), 4.09 (s, 3H), 6.58 (d, *J* = 2.3 Hz, 1H), 6.70 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 7.04 (t, *J* = 6.9 Hz, 1H), 7.12 (d, *J* = 8.8 Hz, 2H), 7.41 (dd, *J* = 9.2, 6.7 Hz, 1H), 7.59 (d, *J* = 2.3 Hz, 1H), 7.88 (d, *J* = 9.1 Hz, 1H), 9.17 (d, *J* = 7.1 Hz, 1H); ^{13}C NMR (DMSO-d_6) δ: 54.86, 54.88, 55.6, 55.8, 93.5, 97.5, 111.6, 112.1, 112.4, 115.2, 117.3, 120.4, 124.7, 127.7, 128.4, 130.0, 130.4, 130.6, 132.3, 134.6, 135.6, 147.6, 156.6, 157.2, 159.2, 159.3; HRMS (ESI) *m*/*z* calcd for $C_{31}H_{26}O_2N_2$+H 491.1965, found 491.1954.

General procedure for *N*-methylation of 4 using iodomethane:



To a 10 mL of acetonitrile solution containing **4e** (0.23 mmol) was added methyl iodide (20 mL), and the mixture was stirred for 48 hours under reflux. After the reaction mixture was concentrated in *vacuo*, the residual mixture was subjected to chromatography on silica gel using mixtures of ethyl acetate and hexane as eluents. As a result, salt **5d** was isolated in quantitative yield. Similarly, salt **5e** was also obtained in quantitative isolated yield by the reaction of **4e** with methyl iodide.

5d: yellow solid; mp 245.0–246.0 °C; ^{1}H NMR ($CDCl_3$) δ: 3.33 (s, 3H), 3.60 (s, 3H), 4.22 (s, 3H), 6.60 (d, *J* = 2.1 Hz, 1H), 6.94 (d, *J* = 6.6 Hz, 2H), 7.06–7.12 (m, 3H), 7.14–7.16 (m, 2H), 7.23–7.25 (m, 3H), 7.64 (d, *J* = 2.1 Hz, 1H), 8.18 (t, *J* = 7.0 Hz, 1H), 8.25 (dd, *J* = 9.1, 7.1 Hz, 1H), 8.59 (d, *J* = 9.1 Hz, 1H), 9.96 (d, *J* = 7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ: 34.8, 55.6, 57.5, 93.1, 99.9, 112.3, 117.1, 119.7, 119.8, 123.3, 124.3, 125.7, 126.4, 127.9, 128.2, 128.8, 130.1, 130.7, 131.6, 134.7, 136.0, 141.1, 142.1, 142.6, 159.7, 161.7; HRMS (ESI) *m*/*z* calcd for $C_{30}H_{25}O_2N_2I$–I 445.1911, found 445.1905.

5e: yellow solid; mp 143.0–144.0 °C; ^{1}H NMR ($CDCl_3$) δ: 3.36 (s, 3H), 3.57 (s, 3H), 3.77 (s, 3H), 3.80 (s, 3H), 4.16 (s, 3H), 6.57 (d, *J* = 1.7 Hz, 1H), 6.66 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.3 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 1.7 Hz, 1H), 8.05–8.09 (m, 1H), 8.36–8.38 (m, 2H), 9.71 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ: 33.3, 55.0, 55.1, 56.1, 56.2, 94.0, 99.4, 111.4, 111.9, 113.1, 116.5, 117.9, 119.4, 123.6, 123.8, 127.1, 129.9, 130.7, 131.0, 132.8, 133.8, 136.0, 141.2, 142.6, 157.0, 158.6, 159.4, 161.0; HRMS (ESI) *m*/*z* calcd for $C_{32}H_{29}O_4N_2I$–I 505.2122, found 505.2113.

Photophysical properties of 4 and 5

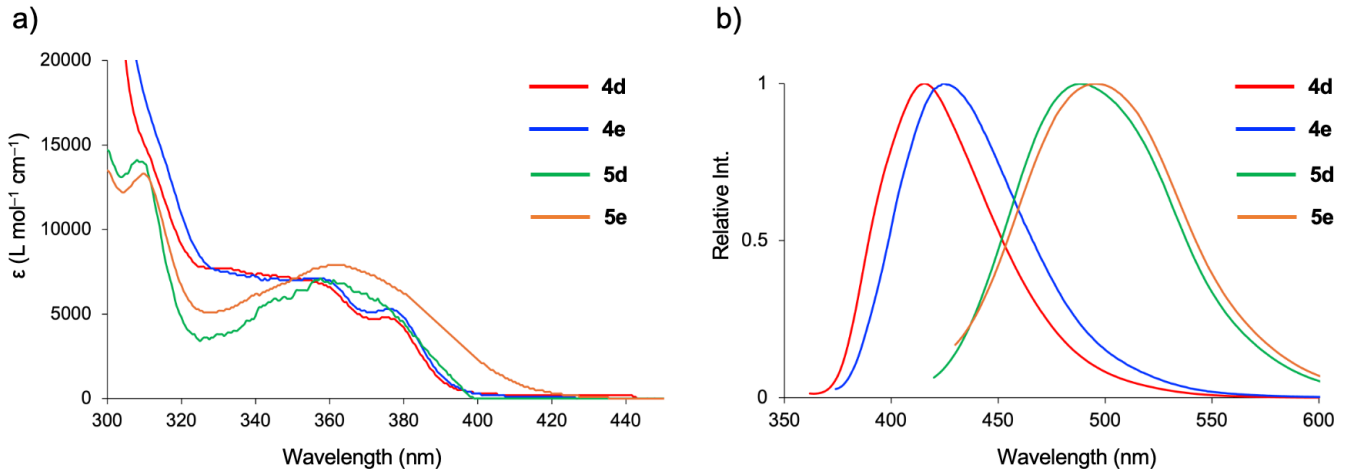


Fig. S1. Absorption and PL spectra of **4** and **5** in DMSO.

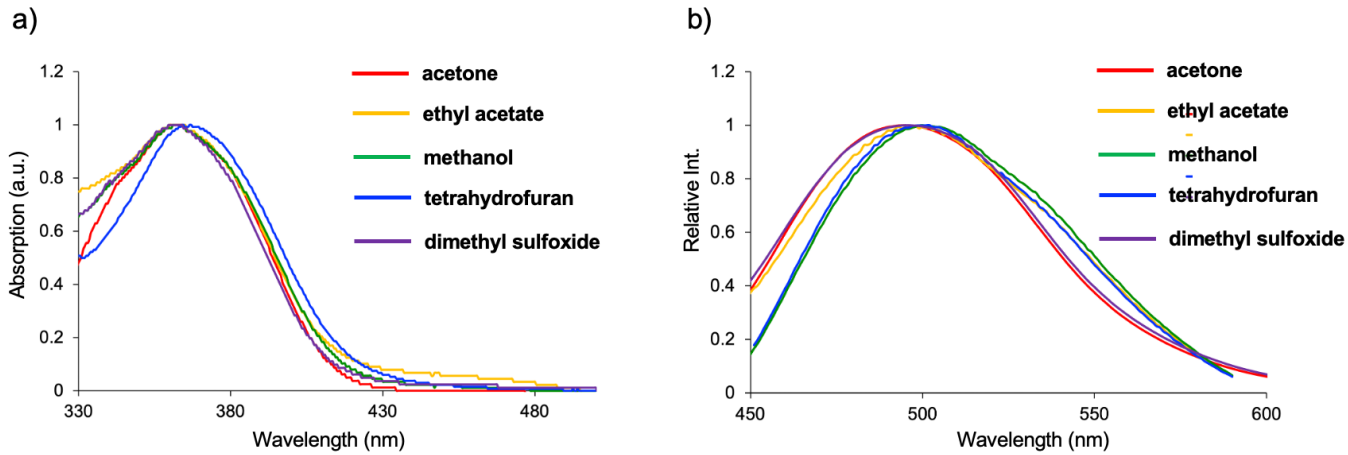


Fig. S2. Absorption and PL spectra of **5e** in various organic solvents.

Table S1. Photophysical properties of **5e** in various organic solvents.

solvent	λ_{abs} (nm)	λ_{em} (nm)	Stokes shift (nm)
acetone	362	495	133
ethyl acetate	363	496	133
methanol	363	500	137
tetrahydrofuran	367	502	135
dimethyl sulfoxide	361	496	135

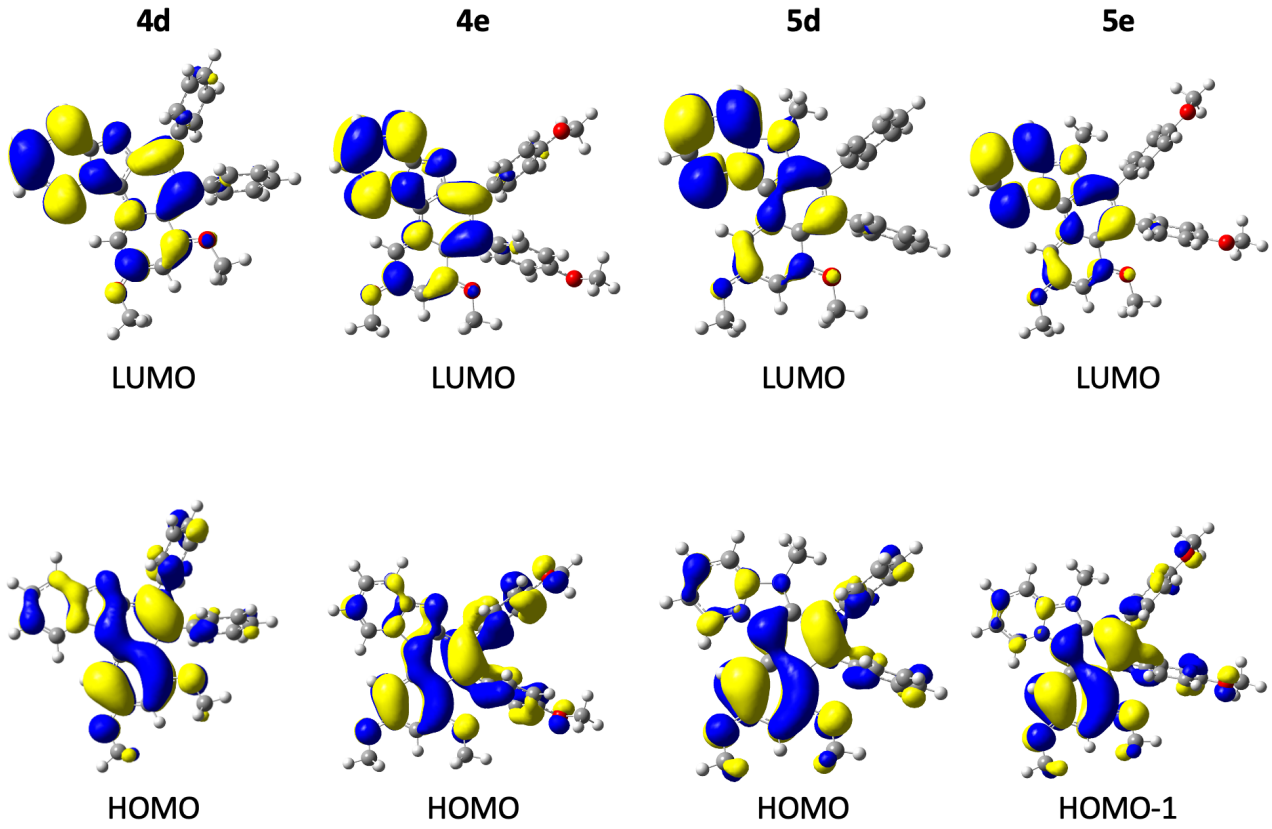


Fig. S3. HOMOs and LUMOs of **4** and **5** estimated by TD-DFT calculations at B3LYP/6-31G+(d) level.

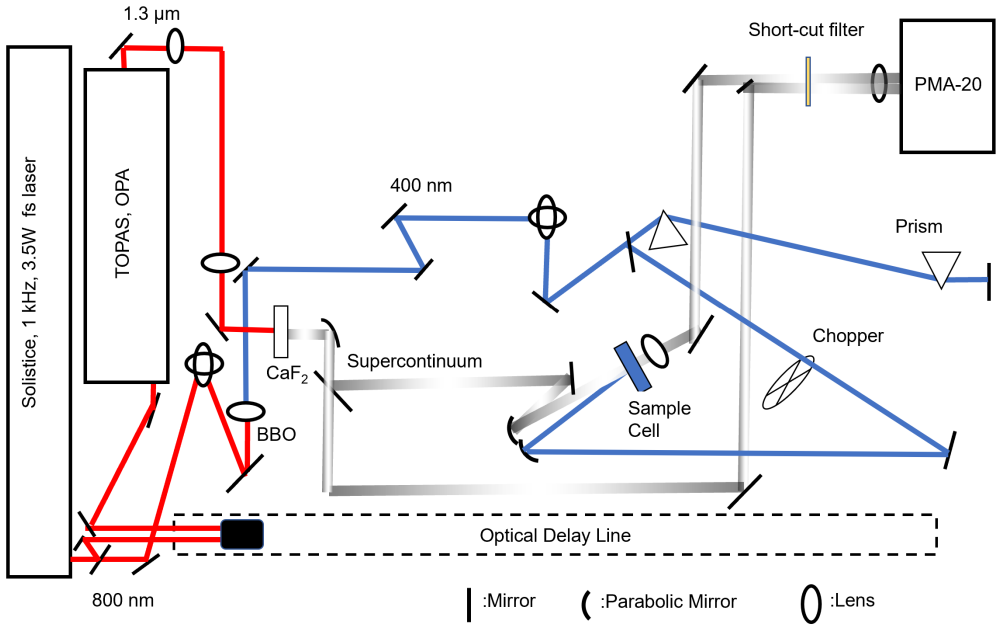


Fig. S4. Experimental setup for femtosecond transient absorption spectra.

Bioassay

Cytotoxicity against HeLa cells:

HeLa cells were cultured in EMEM supplemented with 10%(v/v) of heat-inactivated fetal bovine serum (FBS) and antibiotics (penicillin G and streptomycin) at 37 °C under a 5% CO_2 atmosphere in 96-well flat bottom plate. After overnight cultivation, HeLa cells were incubated with a dilution series of **5e** for 1 hour or overnight. The viability was evaluated using CCK-8 (Dojindo). The absorbance at 450 nm (A_{450}) was measured by a microplate reader (TECAN Infinite M200). The A_{450} from independent 3 wells was used to calculate the percentage of cell viability according to the formula below and show with standard deviation. This result is shown in **Fig. S5**.

Percentage of cell viability = A_{450} of treated cells / A_{450} of untreated cells × 100

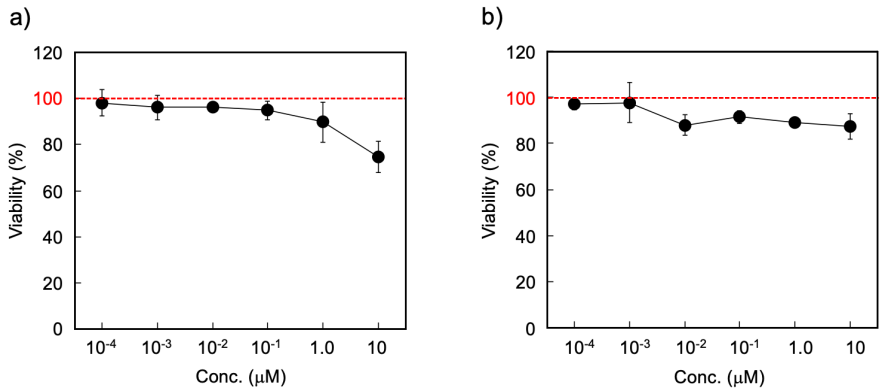


Fig. S5. The viabilities of HeLa cells incubated with various concentrations of **5e** after 1 hour for acute toxicity assay (a) and overnight for subacute toxicity assay (b).

Staining experiment of HeLa cells using 5e:

HeLa cells were incubated with **5e** (final concentration: 1.0 × 10^{-5} mol/L) at 37 °C for 1 hour under a 5% CO_2 atmosphere. The fluorescence images were observed through the WU filter for the detection of green fluorescence signals indicating **5e** using an OLYMPUS IX71 inverted microscope. This result is shown in **Fig. 4a**.

Co-staining experiment of HeLa cells using 5e and mitochondrial marker:

HeLa cells were incubated with **5e** (final concentration: 1.0 × 10^{-5} mol/L) and a mitochondrial marker (MitoTracker Red®, ThermoFisher Scientific) at 37 °C for 1 hour under a 5% CO_2 atmosphere. The fluorescence images were observed through the WU filter for the detection of green fluorescence signals indicating **5e** and the WIY filter for the detection of red fluorescence signals indicating the mitochondrial marker using an OLYMPUS IX71 inverted microscope. The bright image was also observed in the same field. This result is shown in **Fig. S6**.

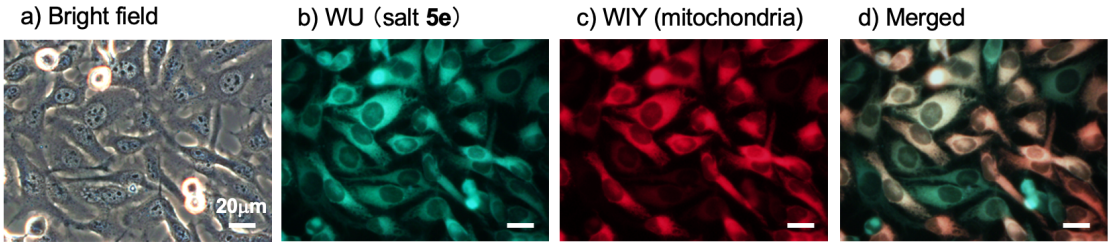


Fig. S6. Observed images focused on mitochondria in HeLa cells with **5e** and a mitochondrial marker: Bright field image (a), green fluorescence of **5e** through a WU filter (b), red fluorescence of mitochondrial marker through a WIY filter (c) and their merged image (d).

Co-staining experiment of HeLa cells using 5e and Hoechst33342:

HeLa cells were incubated with **5e** (final concentration: 1.0×10^{-5} mol/L) and Hoechst33342 (Dojindo) at 37 °C for 1 hour under a 5% CO_2 atmosphere. The fluorescence image was observed through the WU filter using an OLYMPUS IX71 inverted microscope. The bright image was also observed in the same field. This result is shown in **Fig. 4b** and **Fig. S7**.

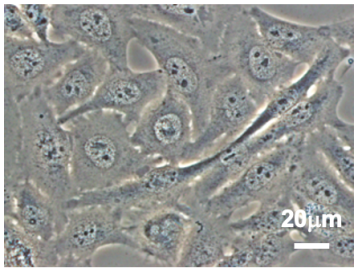
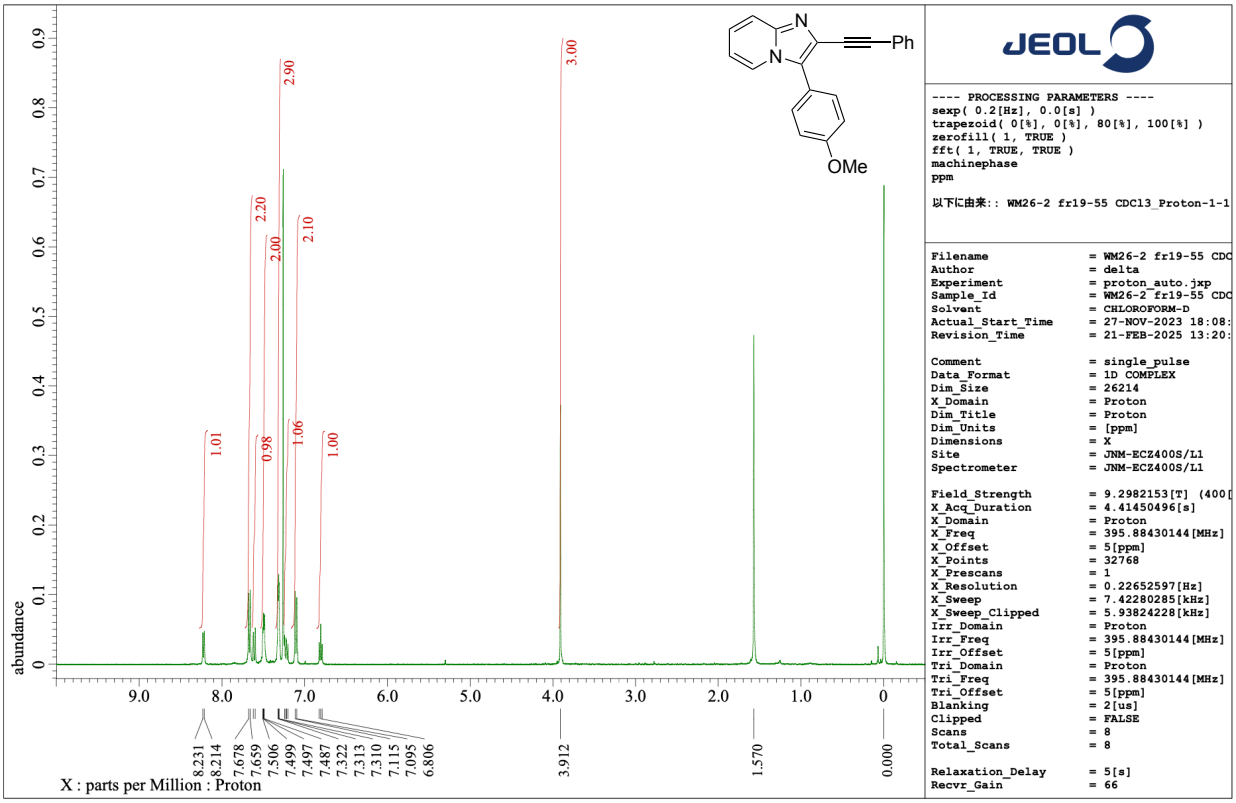
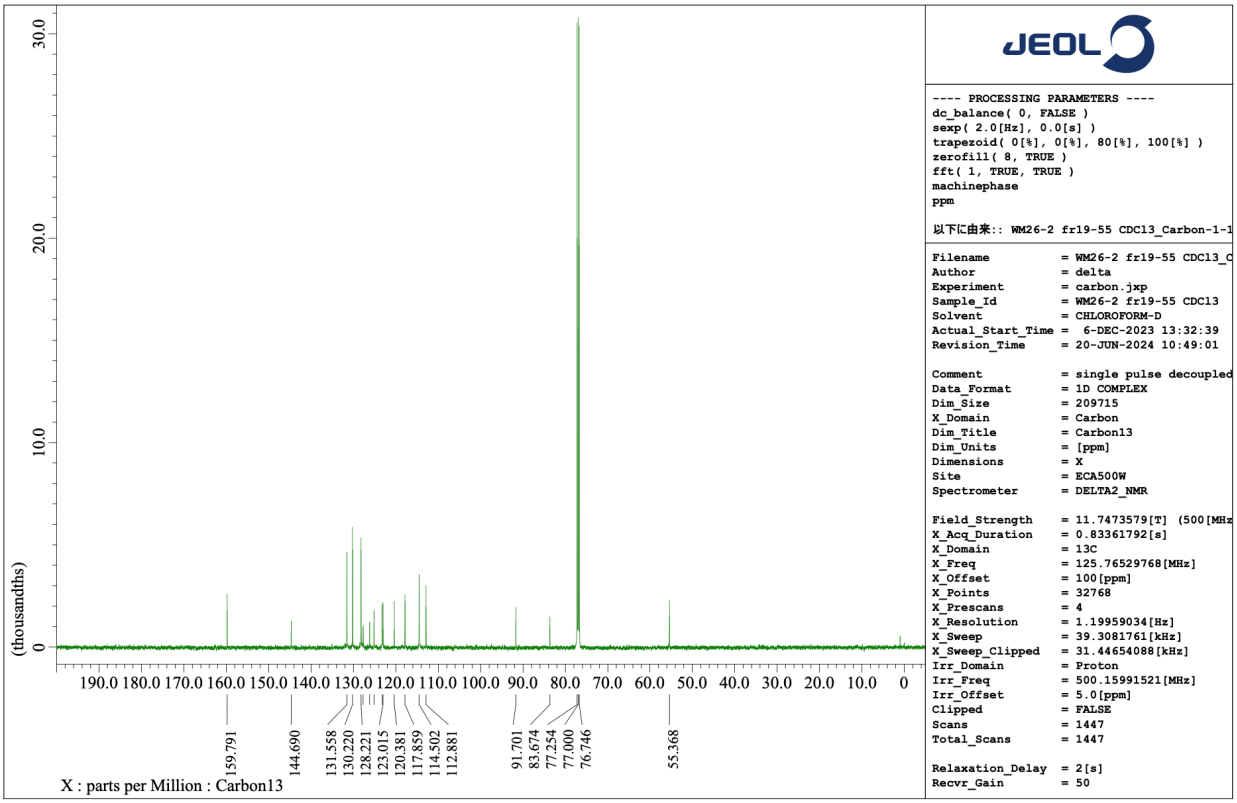


Fig. S7. The bright image of HeLa cells incubated with **5e** and Hoechst 33342.

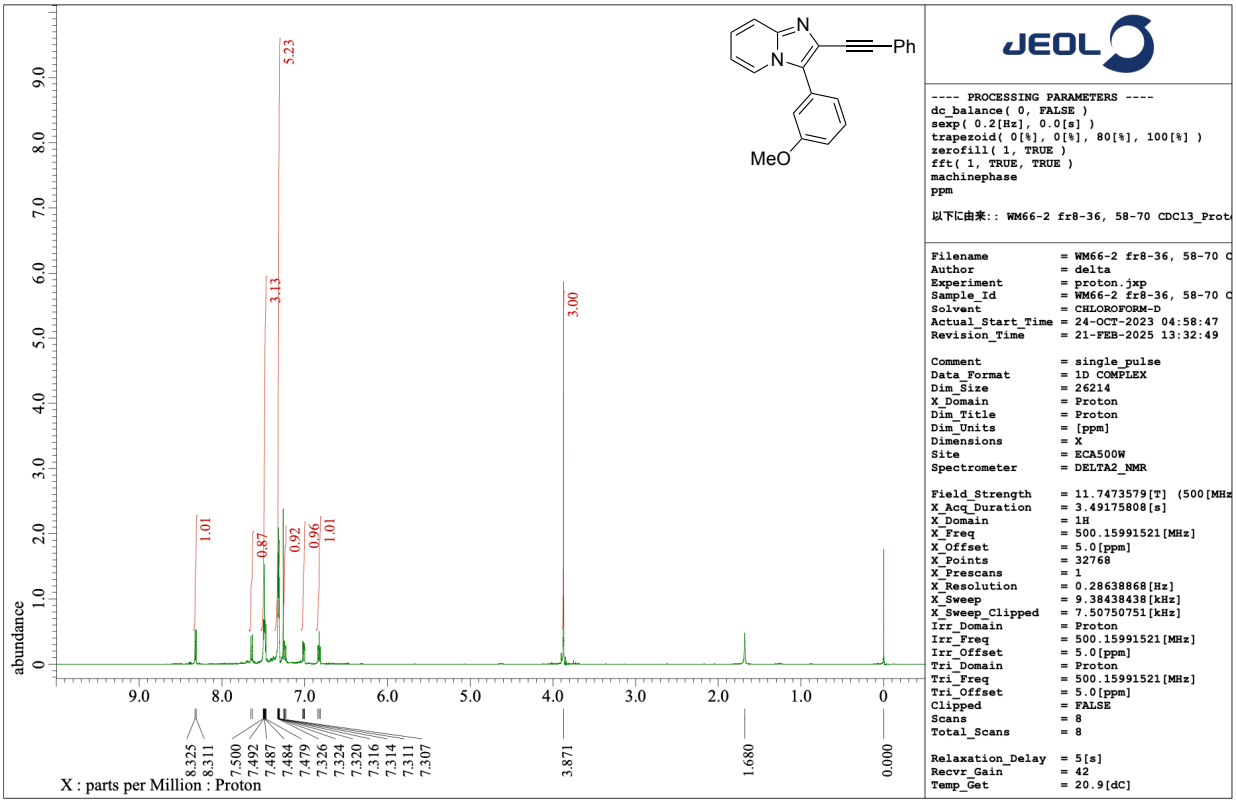
^{1}H NMR spectrum of 1b



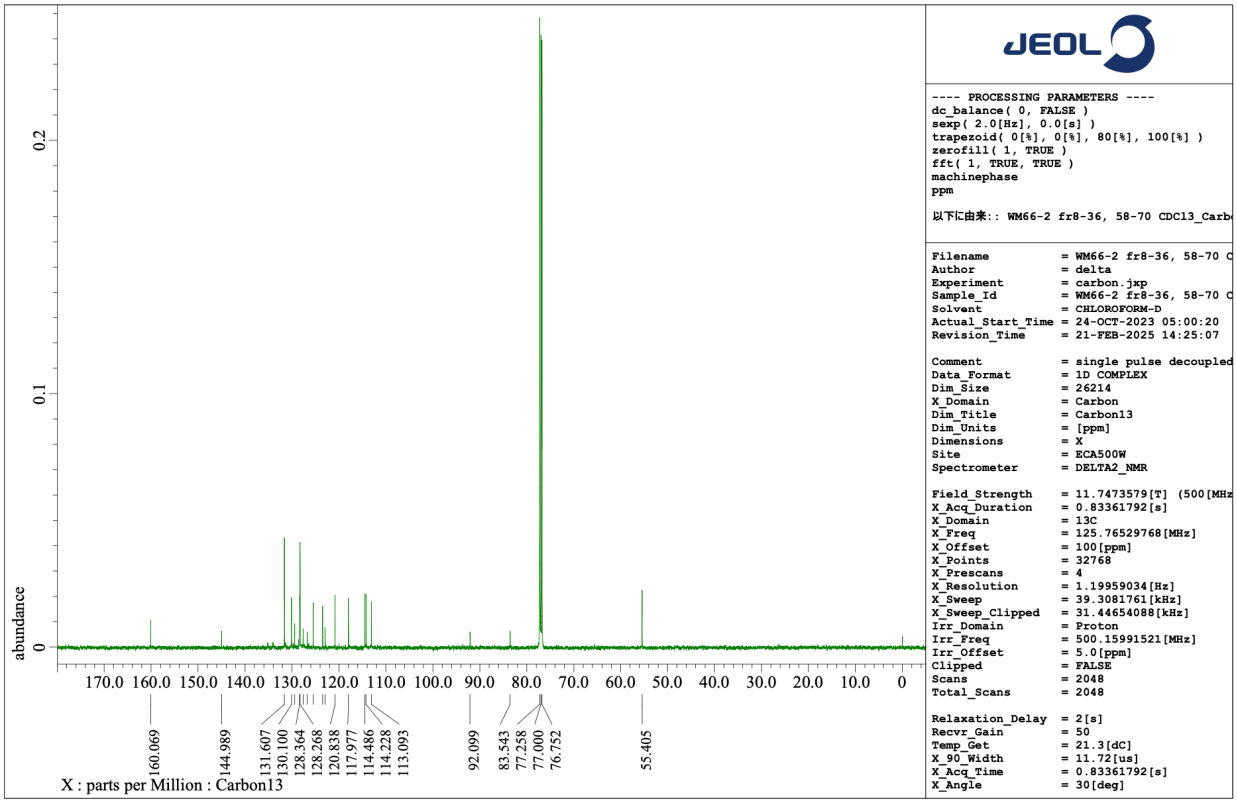
^{13}C NMR spectrum of 1b



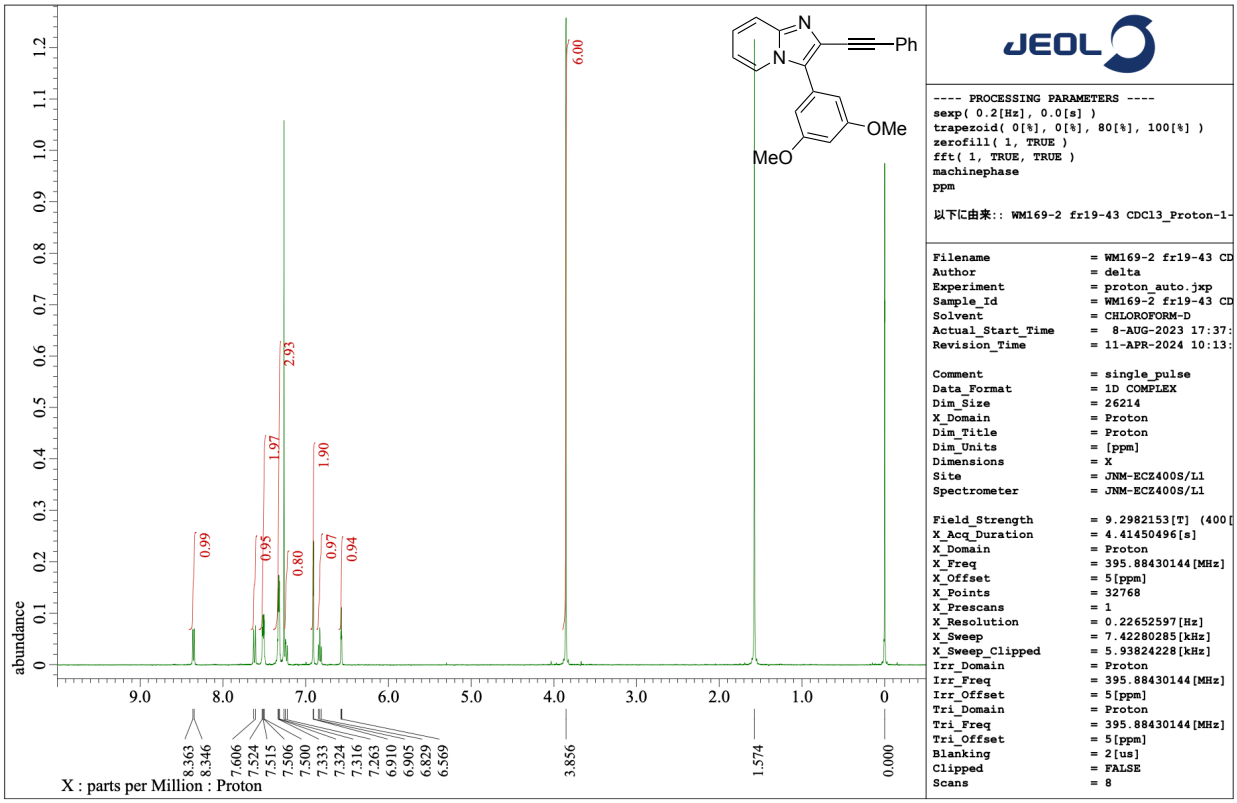
^{1}H NMR spectrum of 1c



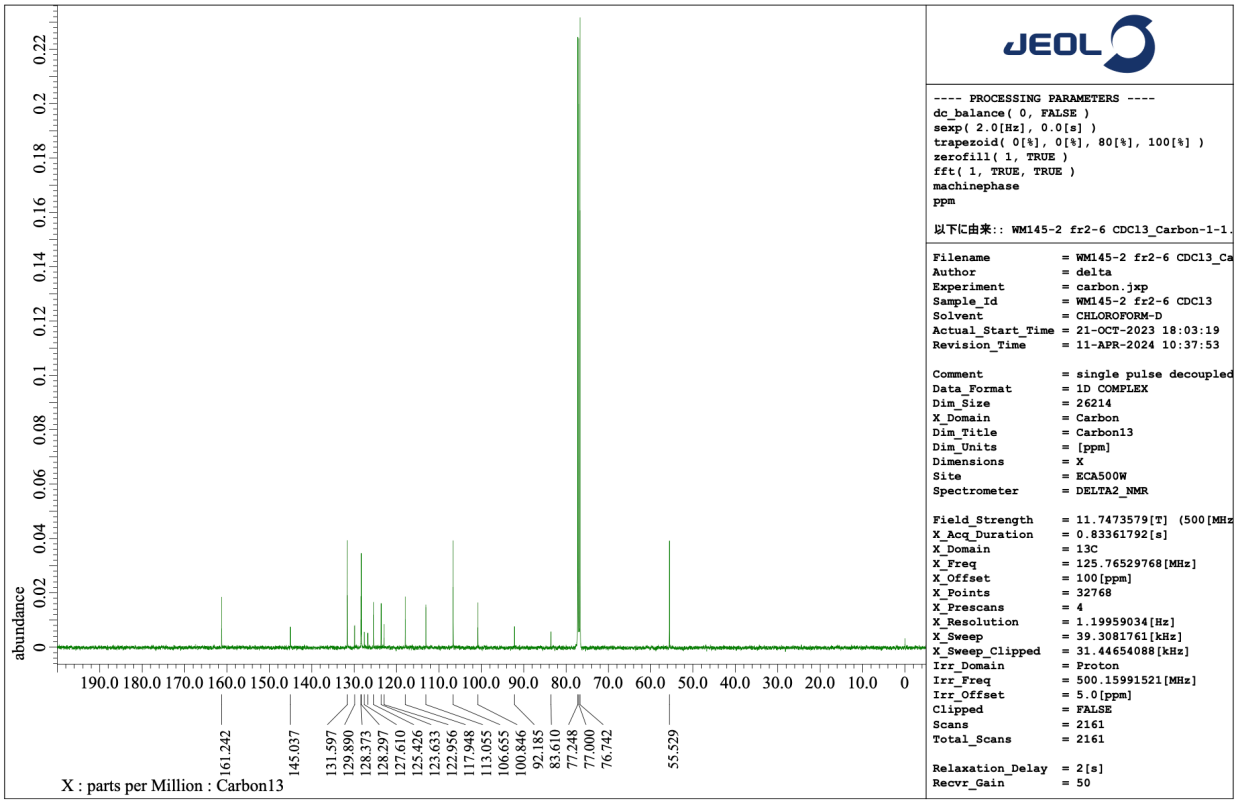
^{13}C NMR spectrum of 1c



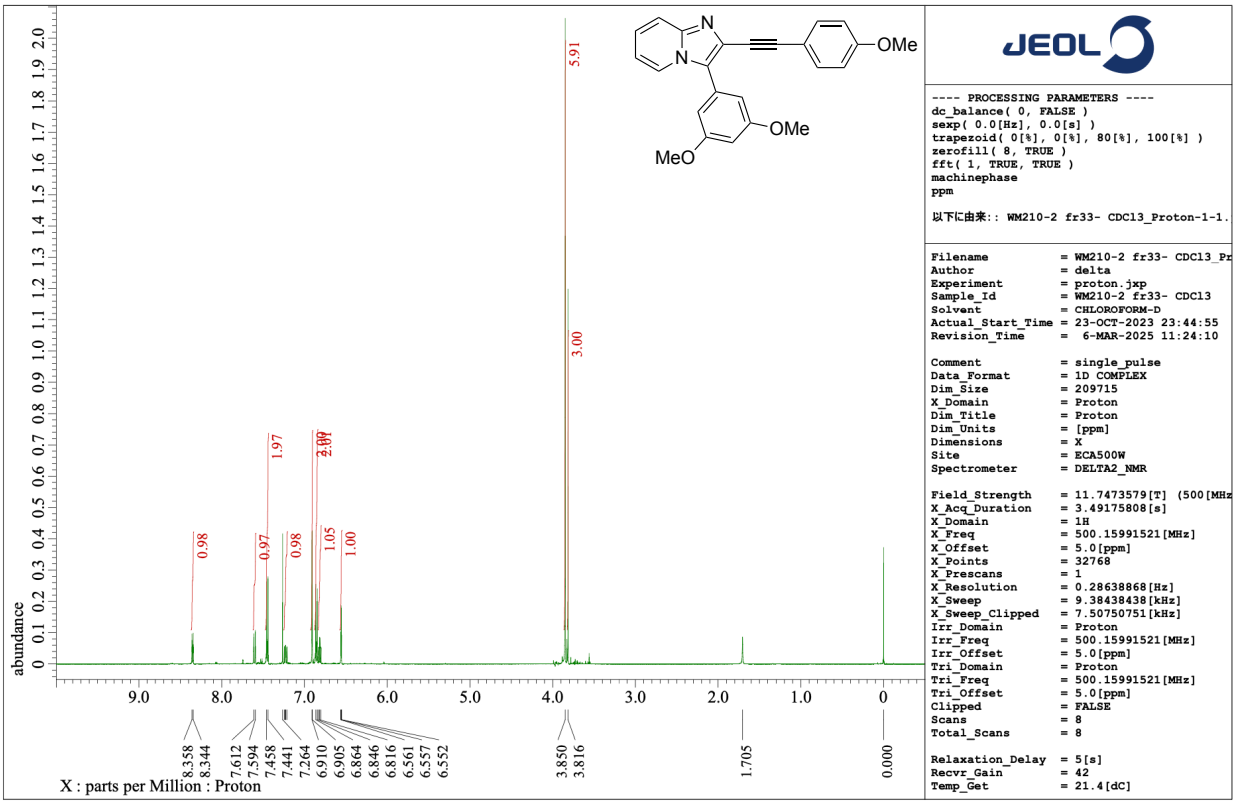
^{1}H NMR spectrum of 1d



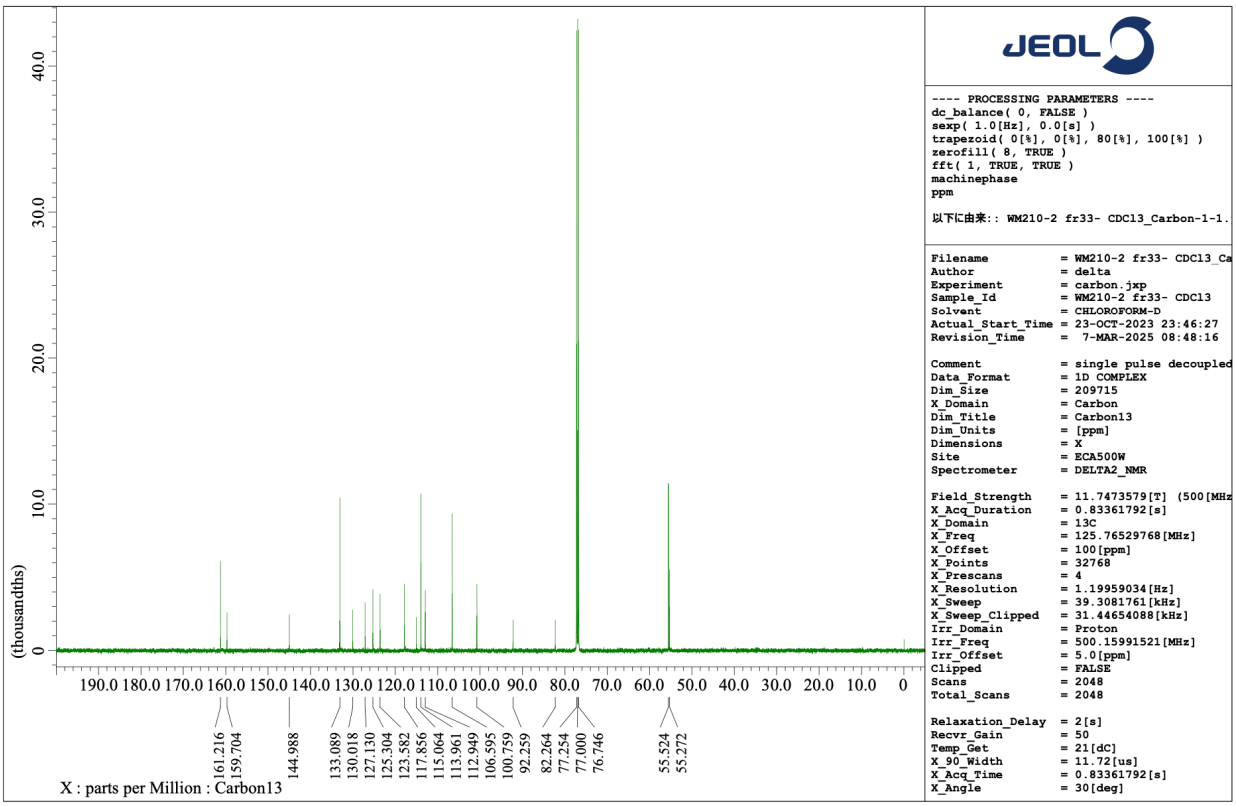
^{13}C NMR spectrum of 1d



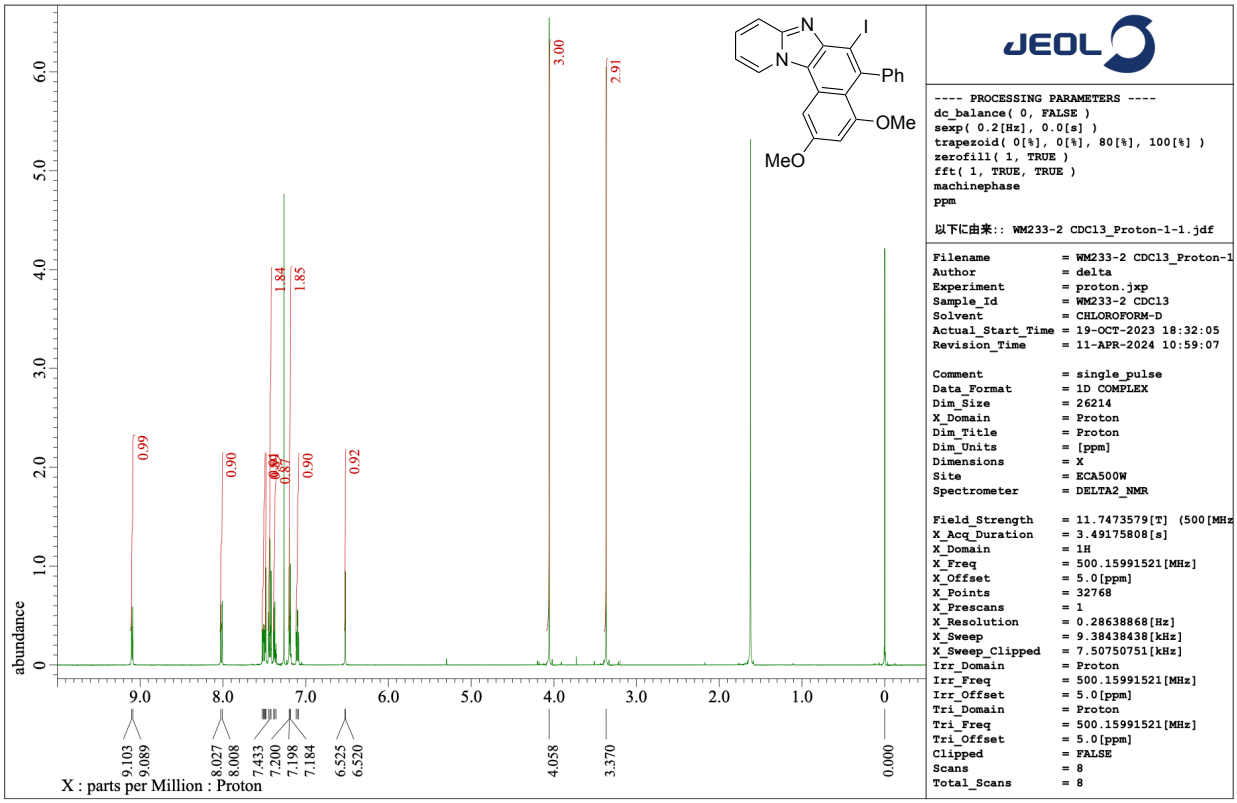
^{1}H NMR spectrum of 1e



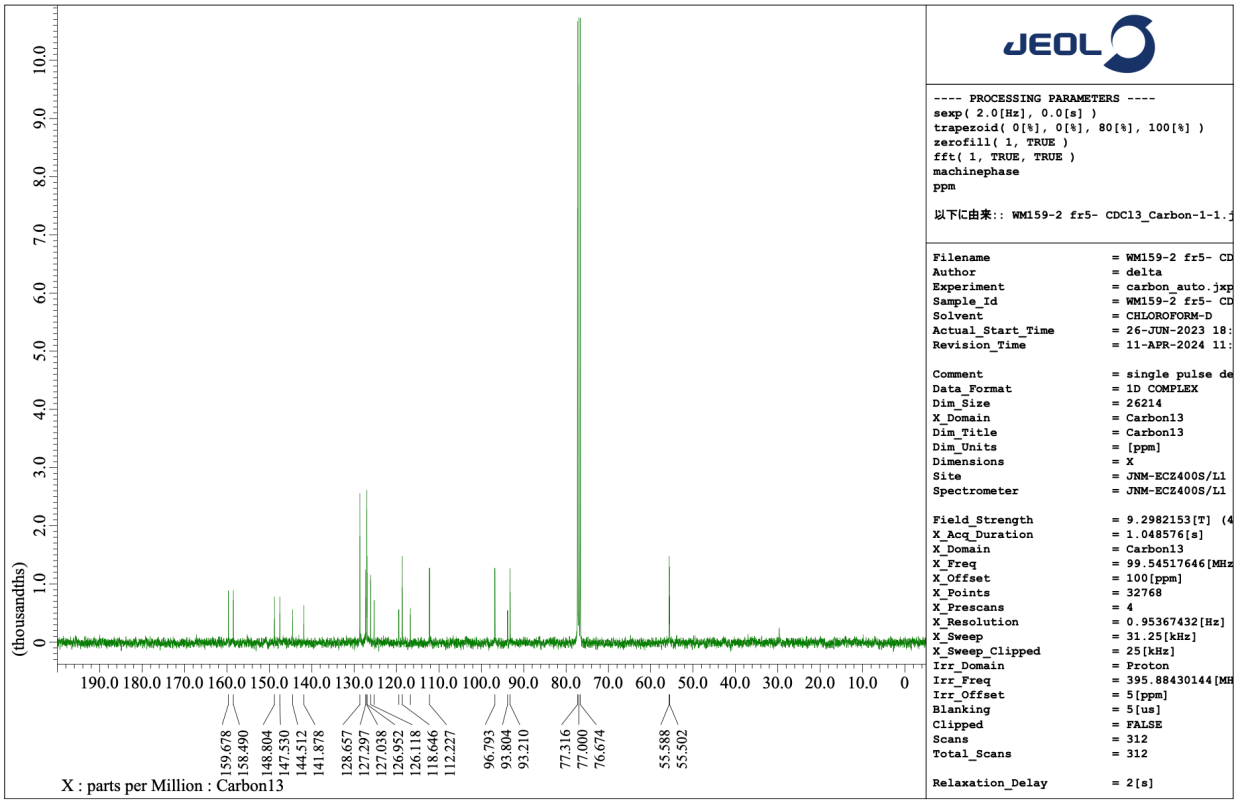
^{13}C NMR spectrum of 1e



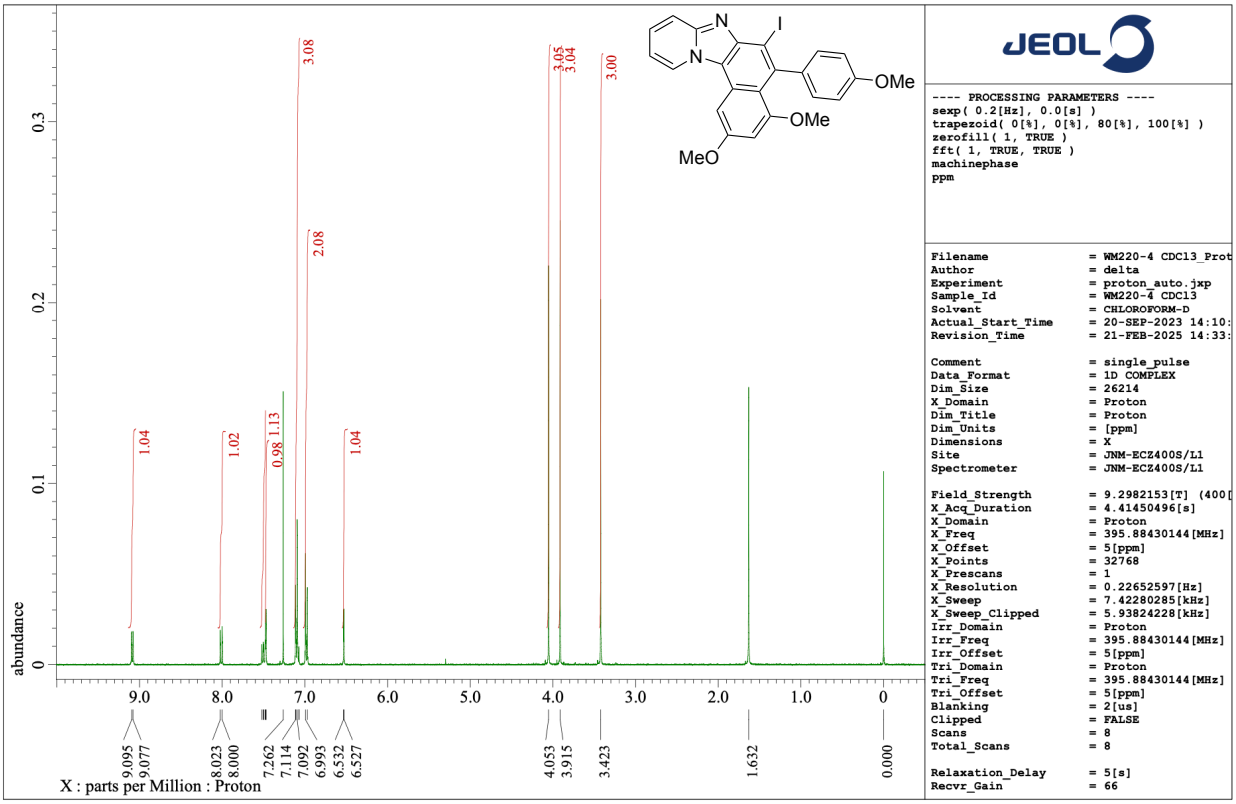
^{1}H NMR spectrum of 2d



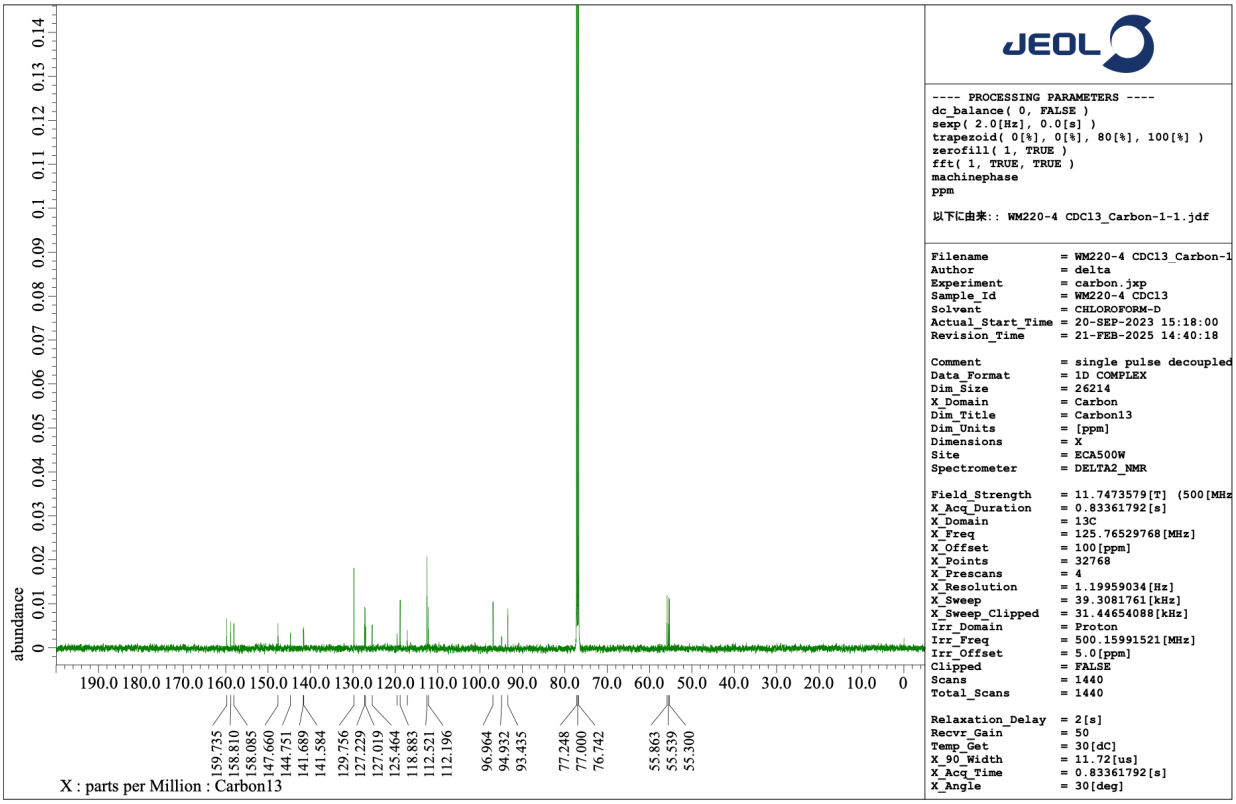
^{13}C NMR spectrum of 2d



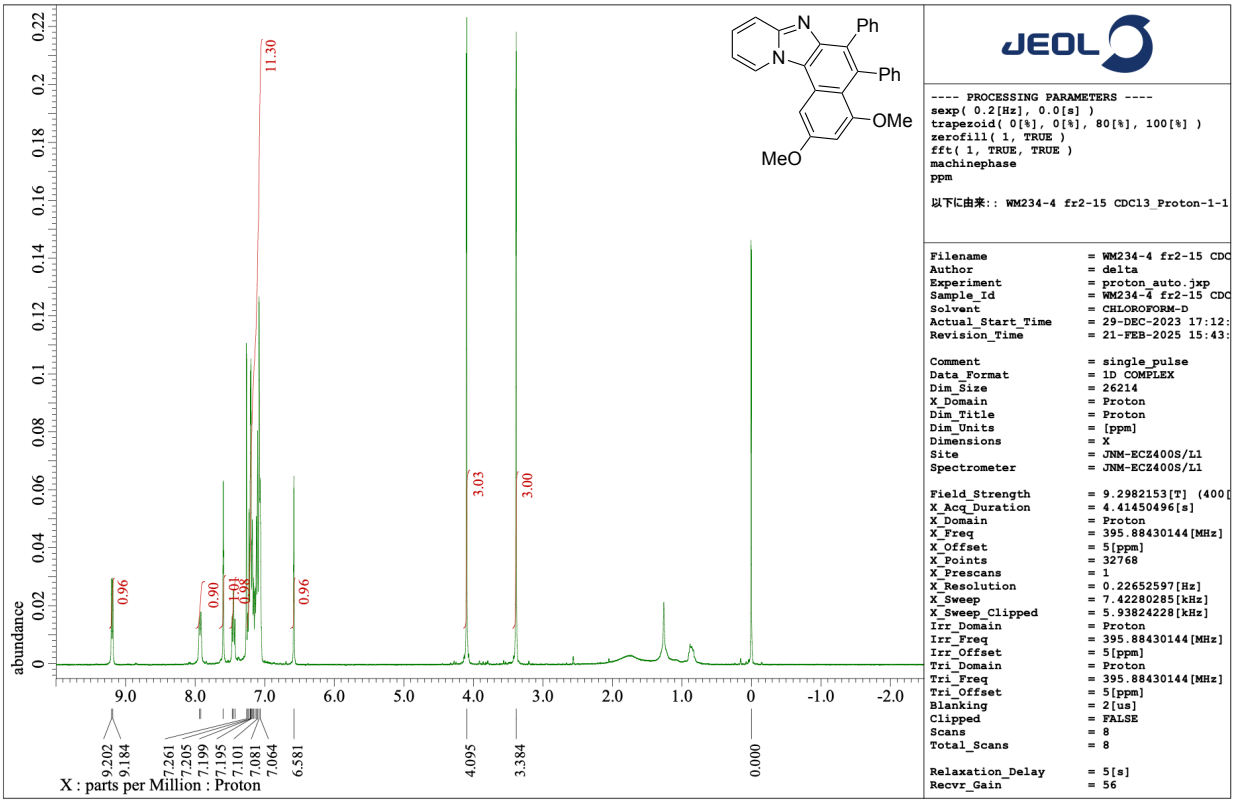
^{1}H NMR spectrum of 2e



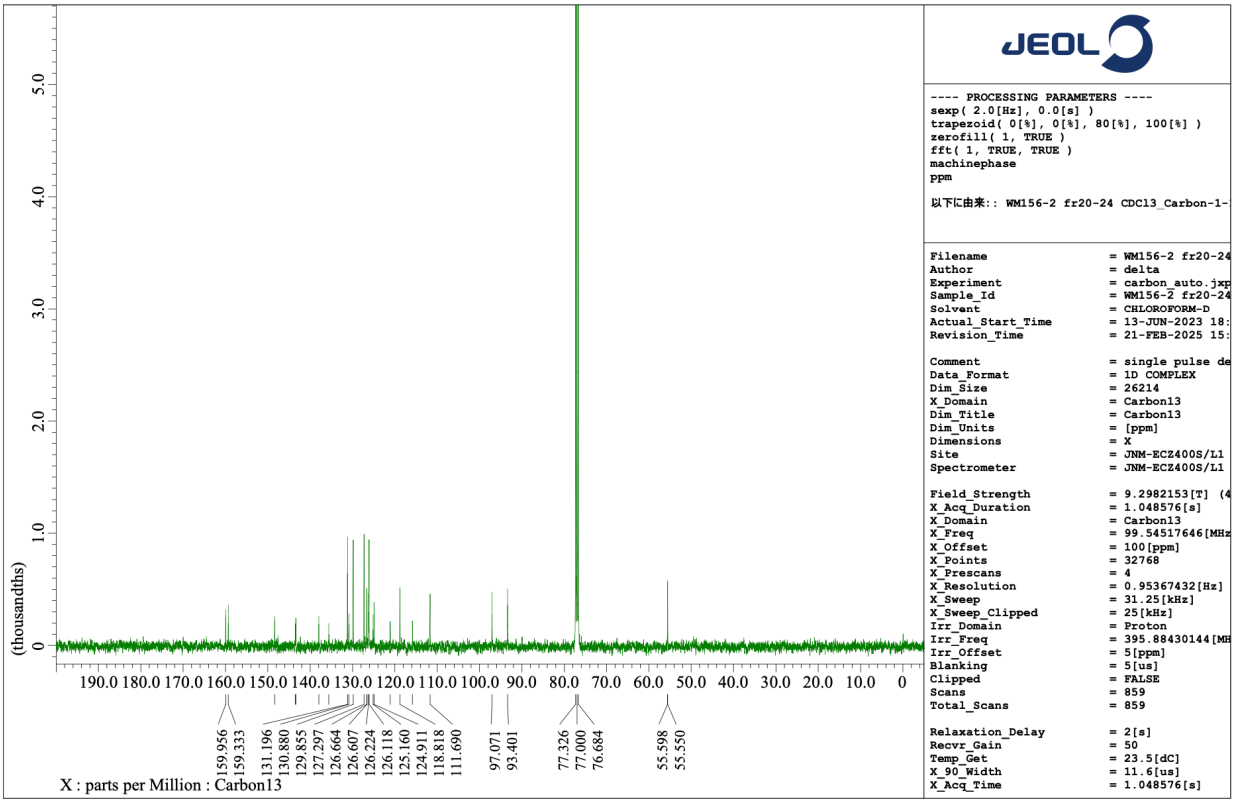
^{13}C NMR spectrum of 2e



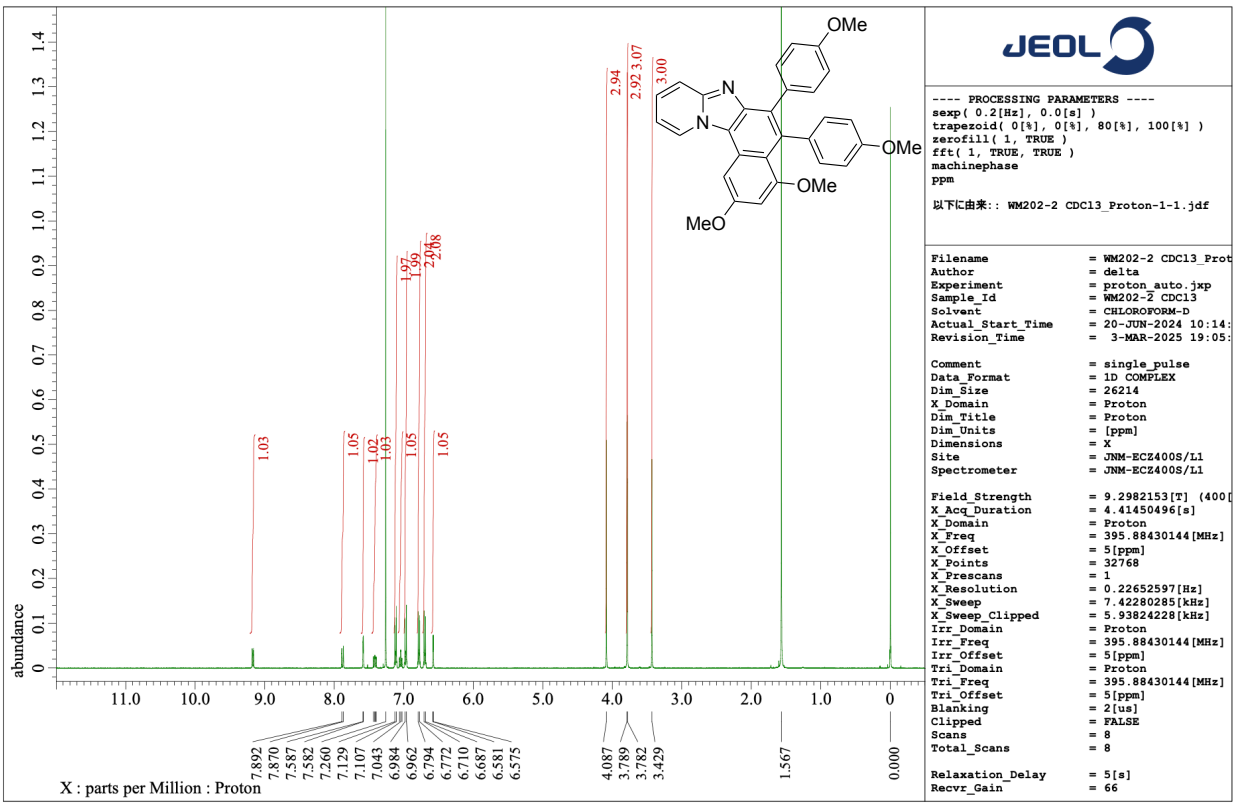
^{1}H NMR spectrum of 4d



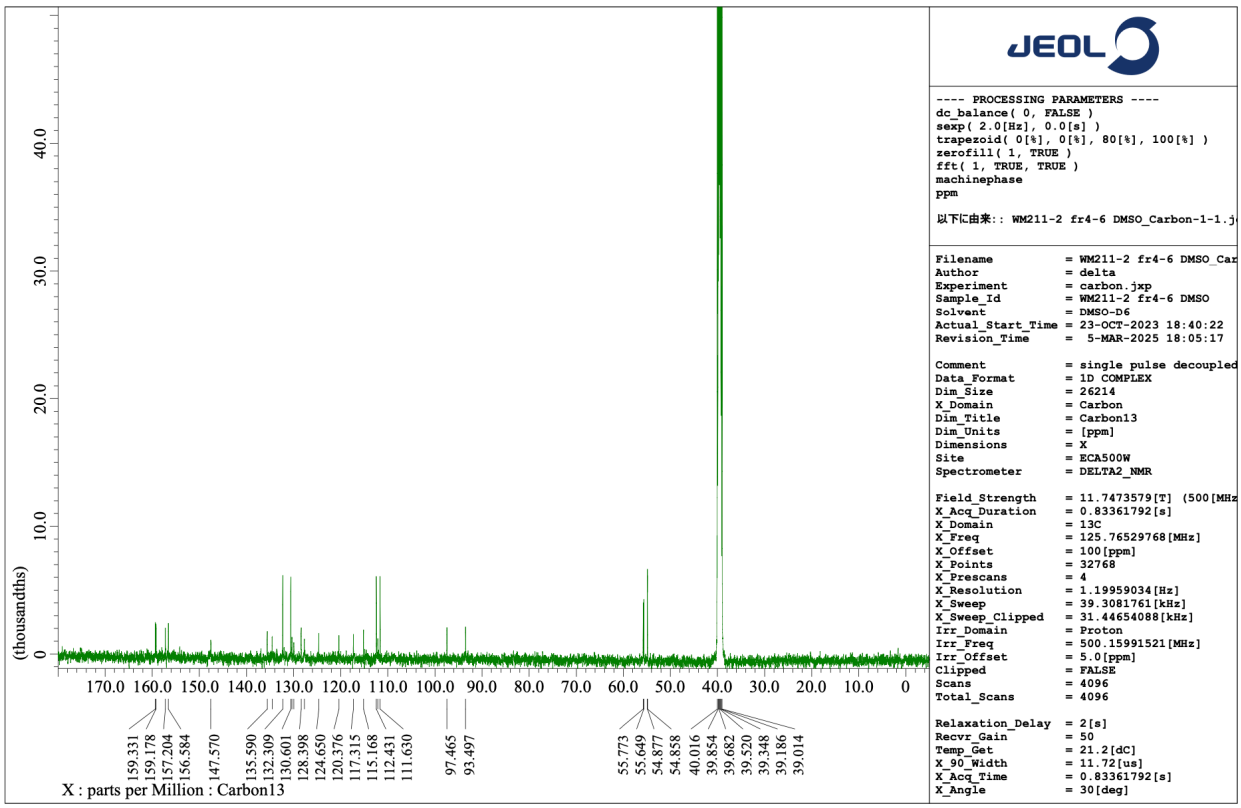
^{13}C NMR spectrum of 4d



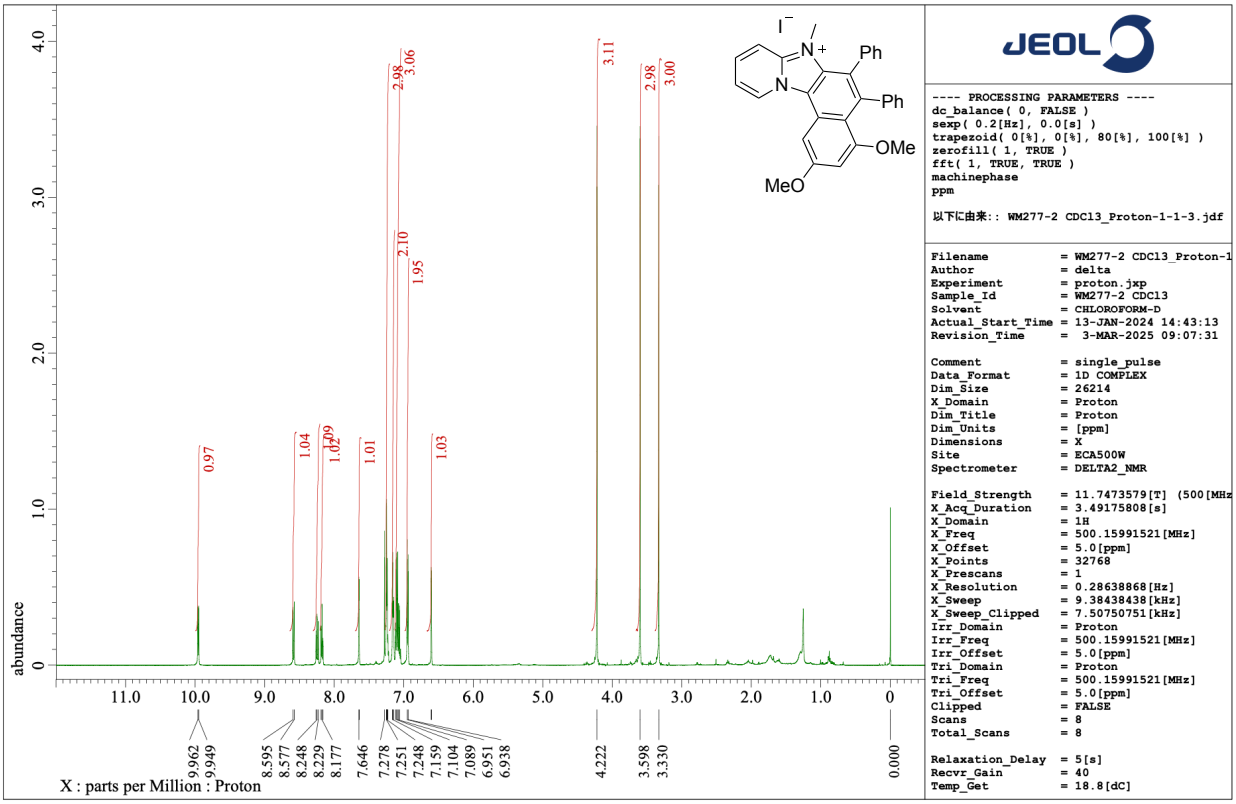
^{1}H NMR spectrum of 4e



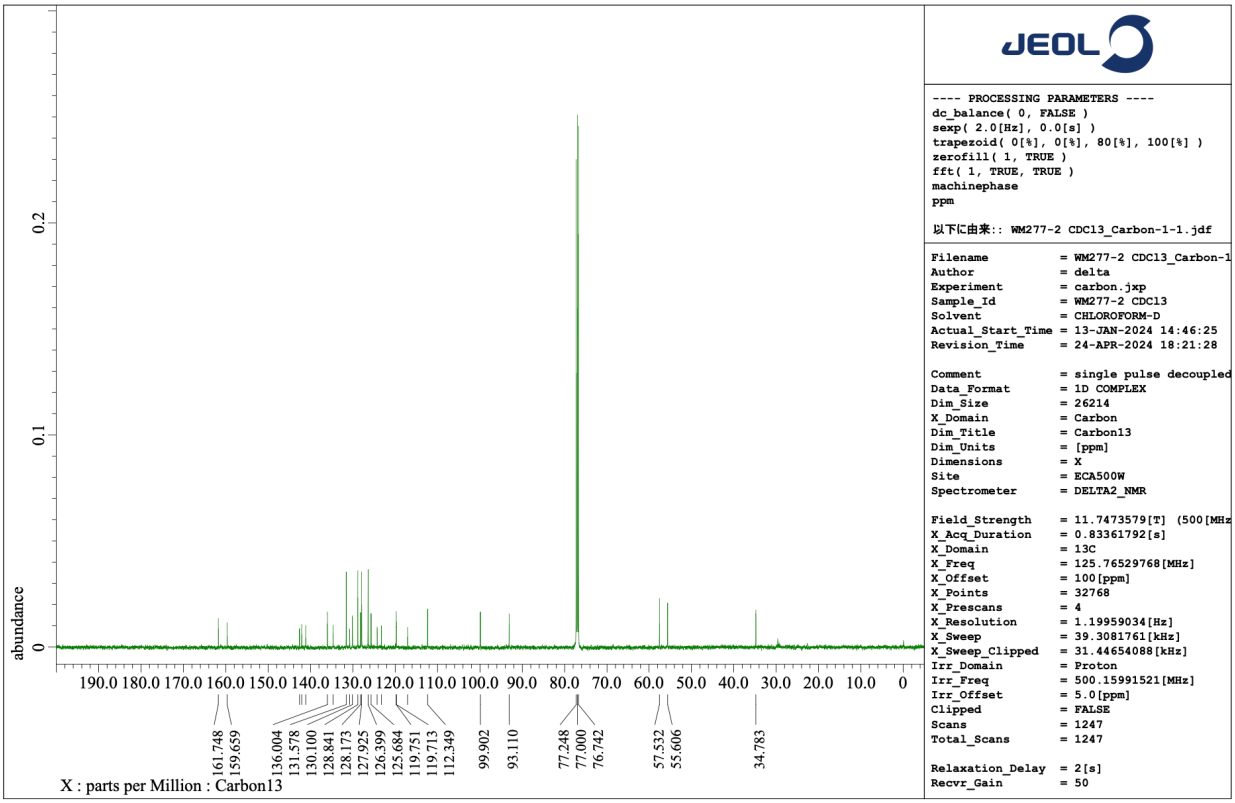
^{13}C NMR spectrum of 4e



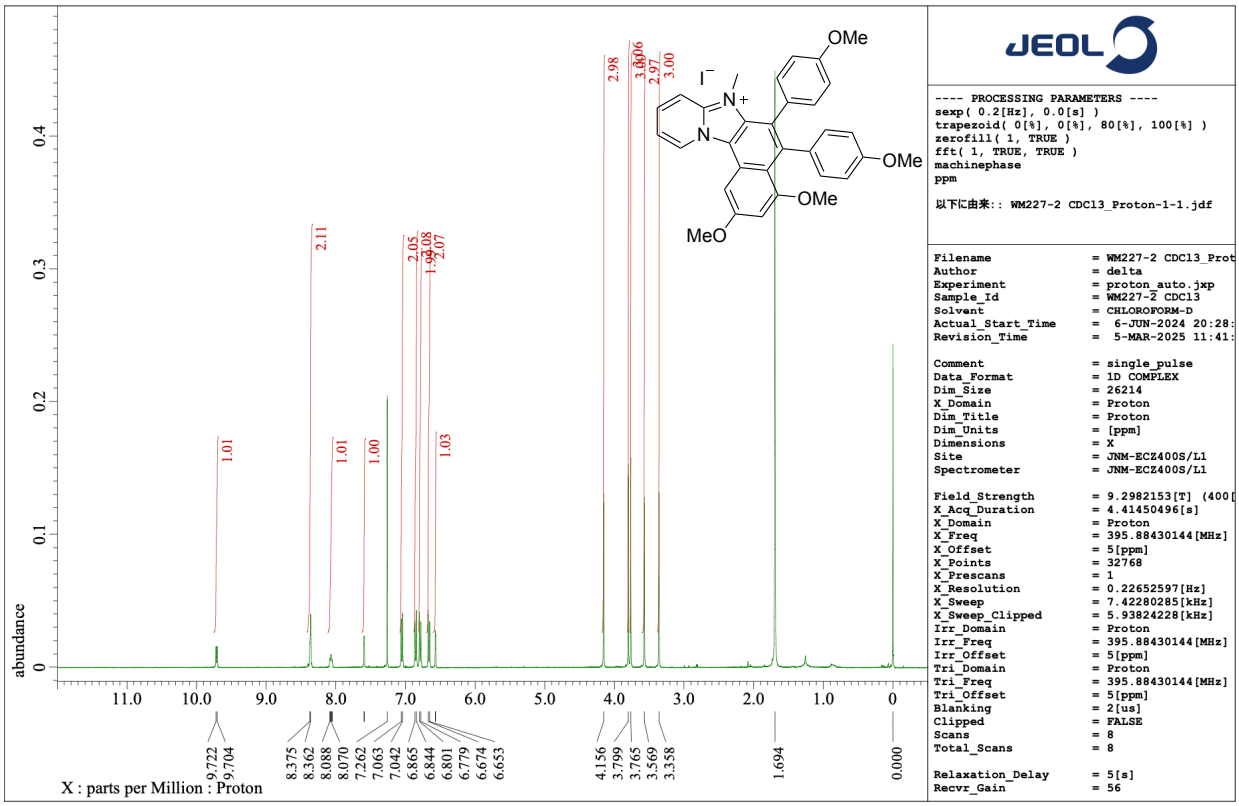
^{1}H NMR spectrum of 5d



^{13}C NMR spectrum of 5d



^{1}H NMR spectrum of 5e



^{13}C NMR spectrum of 5e