Supporting Information for

Energy transfer-driven regioselective synthesis of functionalized phenanthridines by visible-light Ir photocatalysis

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Materials and Methods

Photocatalysts

$[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$,[1a] *fac*-$[Ir(ppy)_3]$,[1b] $[Ir(ppy)_2(dtbbpy)]PF_6$,[1c] $[Ru(bpy)_3](PF_6)_2$,[1d] and $[Ir\{dF(CF_3)ppy\}_2(bpy)]PF_6$[1e] were prepared according to the reported procedures.

Reagents

Aldehydes were prepared according to the reported procedures. [2]

(*E*)-3'-methoxybiphenyl-2-carbaldehyde *O*-4-(trifluoromethyl)benzoyl oxime (**3b**) was prepared according to the reported procedures. [3]

1-Aminopyridinum iodide, biphenyl-2-carboxaldehyde, and phenylboronic acid were purchased from Aldrich.

2-Bromobenzaldehyde, 3-methylphenylboronic acid, 3-methoxyphenylboronic acid, 3-isopropylphenylboronic acid, 2-naphthaleneboronic acid, 3-fluorophenylboronic acid, 3-chlorophenylboronic acid, 1-brom-3-iodobenzene, 3-(trifluoromethyl)phenylboronic acid, 3-nitrophenylboronic acid, 2-methoxypyridine-5-boronic acid, 3,4-(methylenedioxy)phenylboronic acid, 3-acetamidophenylboronic acid, 2-formylphenylboronic acid, 6-bromopiperonal, 3-biphenylboronic acid, 3-thienylboronic acid, 2,6-lutidine, and $Pd(PPh_3)_4$ were purchased from TCI.

K_2CO_3, Na_2CO_3, Cs_2CO_3, HBF_4, NaOH, Na_2SO_4, PPh_3 and activated charcoal powder (Wako Special Grade) were purchased from Wako.

Me_2SO_2, and MS3A were purchased from KANTO CHEMICAL CO., INC.

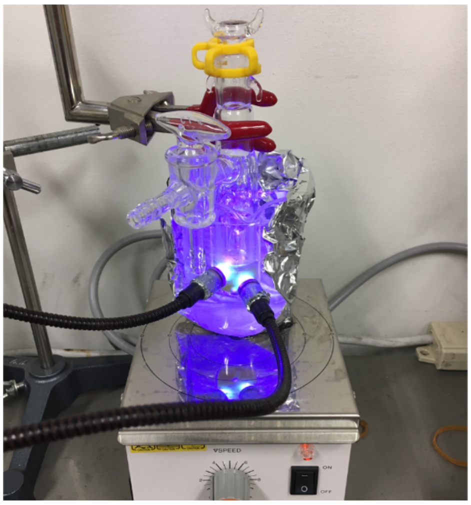
$Pd(OAc)_2$ was purchased from KOJIMA CHEMICALS CO., LTD.

Method

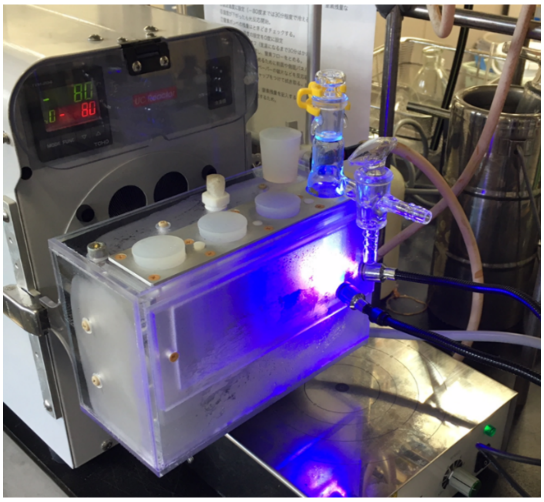
Catalytic reactions were performed under an atmosphere of nitrogen using standard Schlenk techniques unless otherwise noted. Solvents (dehydrated solvent purchased from KANTO CHEMICAL CO., INC.) were degassed with an ultrasonic bath, and stored under N_2 atmosphere. Thin-layer chromatography was performed on silica gel TLC plates (60 F_{254}, Merck). Preparative thin-layer chromatography (PTLC) was performed on silica gel PLC plates (60 F_{254}, Merck). Column chromatography was performed on silica gel 60N from Aldrich. Automated column chromatography was performed using silica gel cartridges (Biotage SNAP Ultra, particle size 25 μm) on a Biotage Isolera One. Recycled gel permeation chromatography (GPC) was performed by LC-9225 on Japan Analytical Industry Co. Ltd (columns: JAIGEL-1H and JAIGEL-2H). Visible light irradiation was performed with Relyon LED lamps (3 W × 2: λ_{max} = 425 nm ± 15 nm). NMR spectra were acquired on Bruker AVANCE-400 (400 MHz) and Bruker AVANCE-HD500 (500 MHz). NMR chemical shifts were referenced to residual protio impurities in the deuterated solvents. ^{19}F NMR chemical shifts were referenced to external trifluoroacetic acid (–76.55 ppm). Electrochemical measurements were recorded on a Hokutodenkou Hz-5000 analyzer (observed in 0.002 M CH_3CN; $[^n\mathrm{Bu}_4\mathrm{N}](\mathrm{PF}_6)$ = 0.1 M; $Ag/AgNO_3$ = electrode; reported with respect to the $[\mathrm{FeCp}_2]/[\mathrm{FeCp}_2]^+$ couple). UV-vis spectra were recorded at room temperature by JASCO V-670DS. Emission spectra were recorded at room temperature by HITACHI F-7000. HRMS (ESI-TOF Mass) spectra were obtained with a Bruker microTOF II spectrometer. Single-crystal X-ray measurement was made on a Rigaku XtaLAB Synergy R, DW system. GC-MS(EI) spectra were acquired on a SHIMADZU GC-2010 (column: Rxi$^{®}$-5ms, 30 m × 0.25 mmI.D.) with a SHIMADZU PARVUM2. DFT calculation was performed with Gaussian09(D01) program package.

Reaction Apparatus

Schlenck-scale experiments at rt.



Schlenck-scale experiments at –80 °C.



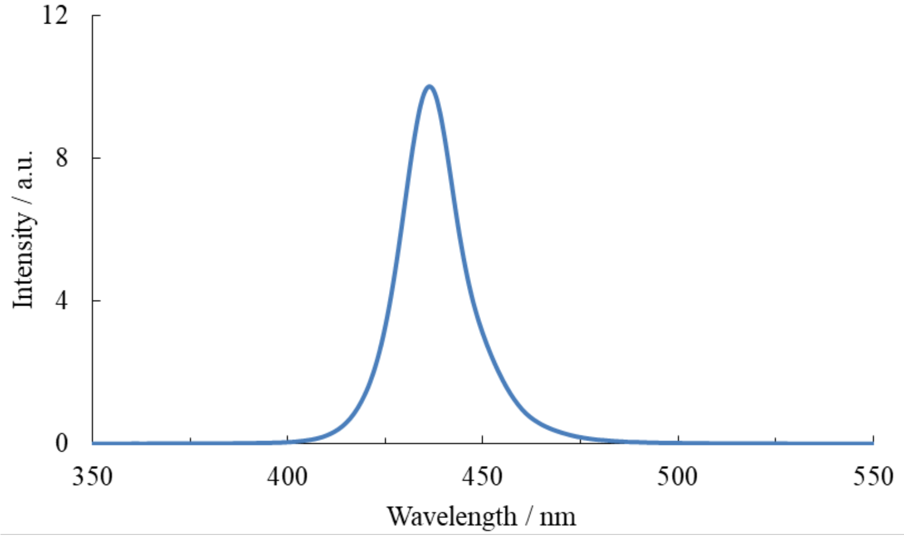
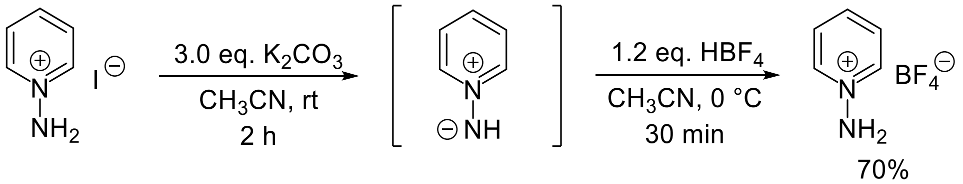


Figure S1 Output spectrum of a Relyon LED lamp (λ = 425 nm).

Preparation of 1-Aminopyridinum Tetrafluoroborate Salt



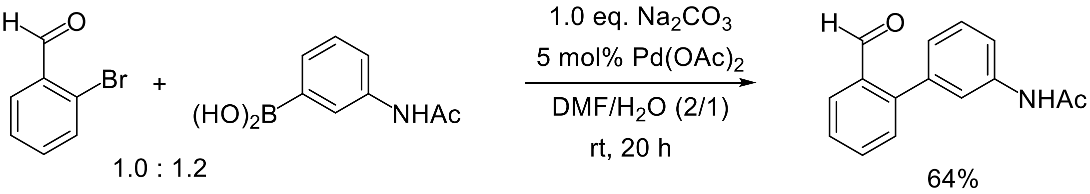
1-Aminopyridinium tetrafluoroborate was prepared according to the literature procedures. [4a] To a mixture of 1-aminopyridinium iodide (3.34 g, 15.0 mmol) and CH_3CN (200 mL) was added K_2CO_3 (6.25 g, 45.2 mmol) at rt. The reaction mixture was vigorously stirred at rt for 2 h (solution color changed from light yellow to violet). The excess salts in the mixture was removed through filtration. To the violet solution was added 42 wt% HBF_4 (4.13 g, 19.7 mmol) at 0 °C (brown solution). After stirring for 30 min, volatiles were removed under reduced pressure, then water was poured into the residue. The mixture was filtered and concentrated *in* vacuo. The crude product was purified by recrystallization (EtOH, 100 ˚C → rt). The obtained beige crystals were dissolved in CH_3CN. The solution was passed through activate carbon and concentrated *in vacuo* to afford 1-aminopyridinum tetrafluoroborate as a white solid (1.90 g, 10.5 mmol, 70% yield).

^{1}H NMR (400 MHz, CD_3CN, rt) δ 8.60 (d, $^3J_{HH}$ = 6.0 Hz, 2H; $C_5H_2H_2HN$), 8.29 (t, $^3J_{HH}$ = 8.0 Hz, 1H; $C_5H_2H_2HN$), 7.93 (dd, $^3J_{HH}$ = 7.2, 7.2 Hz, 2H; $C_5H_2H_2HN$), 7.15 (br s, 2H; $-NH_2$).

^{19}F NMR (376 MHz, CD_3CN, rt) δ –152.55, –152.61 (each s, 4F; BF_4).

Spectral data are in accordance with those reported in the literature. [4b]

Synthesis and Characterization of 3’-Acetoamid-[1,1’]-biphenyl-2-carbaldehyde



3’-Acetoamid-[1,1’]-biphenyl-2-carbaldehyde was prepared according to the literature procedures[2a] from the reaction of 3-acetamidophenylboronic acid with 2-bromobenzaldehyde. To a degassed DMF and H_2O solution of 3-acetamidophenylboronic acid (1.18 g, 6.58 mmol) and Na_2CO_3 (0.596 g, 5.62 mmol) in a 100 mL two-necked flask was added 2-bromobenzaldehyde (1.05 g, 5.66 mmol) at rt under N_2. After stirring for 2 min, to the reaction mixture was added 5 mol% $Pd(OAc)_2$ (0.0636 g, 0.283 mmol). The mixture was stirred at rt for 20 h and filtered through celite pad. The solution was extracted by ether and the combined organic layer was washed by brine, dried by Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*n*-hexane:AcOEt = 3:7) to afford 3’-acetoamid-[1,1’]-biphenyl-2-carbaldehyde (0.867 g, 3.62 mmol, 64% yield) as a white solid.

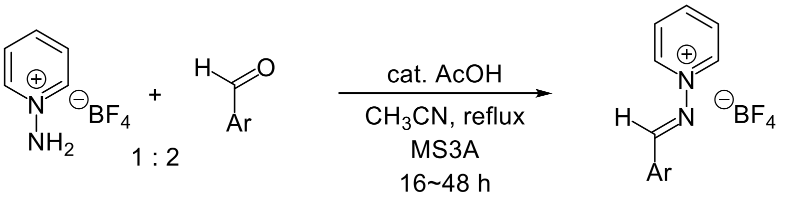
^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 9.96 (s, 1H; -CO*H*), 7.99 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 7.75 (br s, 1H; -N*H*COMe), 7.63–7.56 (3H; Ar*H*), 7.48 (dd, $^3J_{HH}$ = 7.6, 7.6 Hz, 1H; Ar*H*) 7.42–7.35 (2H; Ar*H*), 7.08 (d, $^3J_{HH}$ = 7.2 Hz, 1H; Ar*H*), 2.18 (s, 3H; -NHCOC*H*$_3$).

^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 192.4, 168.7, 145.4, 138.5, 138.1, 133.6 (2C), 130.7, 129.0, 127.9, 127.5, 126.0, 121.2, 119.4, 24.6.

HRMS (ESI-TOF) Calcd. for $C_{15}H_{13}NO_2$ $[M+Na]^+$ requires 262.0838, found 262.0839.

Elemental analysis Calcd. for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85; O, 13.37. Found: C, 75.19; H, 5.44; N, 5.79; O, 13.15.

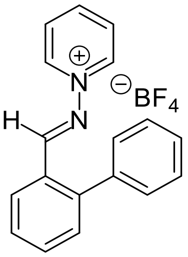
Synthesis and Characterization of *N*-Iminylpyridinium Salts (1)



1

Iminylpyridinium salts were prepared according to literature procedures[5] from the reaction of 1-aminopyridinium tetrafluoroborate with aldehyde. To a mixture of 1-aminopyridinium tetrafluoroborate, CH_3CN, AcOH (5 drops) and MS3A in two-necked flask was added aldehyde at rt under N_2. The mixture solution was refluxed overnight. The solution was concentrated *in vacuo*. The crude product was purified by reprecipitation to afford iminylpyridinium salt **1**.

(*E*)-[1,1’]-Biphenyl-2-iminylpyridinium Tetrafluoroborate (1a)



According to the general procedures, biphenyl-2-carboxaldehyde (2.00 g, 11.0 mmol), 1-aminopyridinum tetrafluoroborate (0.996 g, 5.47 mmol), and CH_3CN (50 mL) afforded **1a** (1.27 g, 3.68 mmol, 67% yield, reaction time = 18 h) as a white solid after purification with reprecipitation (CH_3CN/Et_2O). Recrystallization from EtOH afforded crystals, which are suitable for single-crystal X-ray structure analysis (CCDC 1978371).

^{1}H NMR (400 MHz, CD_3CN, rt) δ 8.73 (d, $^3J_{HH}$ = 6.0 Hz, 2H; pyridinium), 8.72 (s, 1H; -N=C*H*-), 8.50 (t, $^3J_{HH}$ = 8.0 Hz, 1H; pyridinium), 8.30 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 8,07 (dd, $^3J_{HH}$ = 7.2, 7.2 Hz, 2H; pyridinium), 7.80 (dd, $^3J_{HH}$ = 7.6, 6.8 Hz, 1H; Ar*H*), 7.65 (dd, $^3J_{HH}$ = 8.0, 8.0 Hz, 1H; Ar*H*), 7.61

(d, $^3J_{HH}$ = 7.6 Hz, 1H; Ar*H*), 7.52–7.44 (3H; Ar*H*).

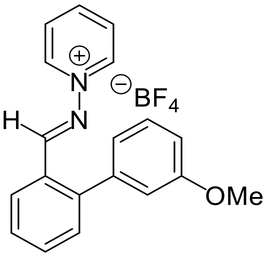
^{13}C NMR (126 MHz, CD_3CN, rt) δ 170.0, 147.4, 146.2, 140.4, 138.9, 135.4, 132.1, 131.1, 129.8, 129.7, 129.44, 129.41, 129.0, 128.8.

^{19}F NMR (376 MHz, CD_3CN, rt) δ –152.74, –152.80 (each s, 4F; B*F*$_4$).

HRMS (ESI-TOF) Calcd. for $C_{18}H_{15}N_2$ $[M]^+$ requires 259.1230, found 259.1232.

Elemental analysis Calcd. for $C_{18}H_{15}BF_4N_2$: C, 62.46; H, 4.37; N, 8.09. Found: C, 62.46; H, 4.36; N, 8.03.

(*E*)-3'-Methoxy-[1,1']-biphenyl-2-iminylpyridinium Tetrafluoroborate (1b)



According to the general procedures, 3'-methoxy-[1,1']-biphenyl-2-carbaldehyde (0.907 g, 4.28 mmol), 1-aminopyridinum tetrafluoroborate (0.398 g, 2.19 mmol), and CH_3CN (65 mL) afforded **1b** (0.547 g, 1.45 mmol, 66% yield, reaction time = 24 h) as a yellow solid after purification with reprecipitation (CH_3CN/Et_2O).

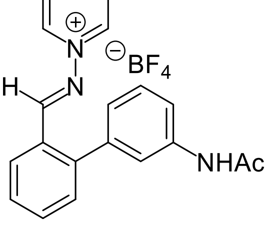
^{1}H NMR (400 MHz, CD_3CN, rt) δ 8.75 (s, 1H; -N=C*H*-), 8.73 (d, $^3J_{HH}$ = 5.6 Hz, 2H; pyridinium), 8.50 (t, $^3J_{HH}$ = 8.0 Hz, 1H; pyridinium), 8.29 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 8.07 (dd, $^3J_{HH}$ = 7.2, 7.2 Hz, 2H; pyridinium), 7.79 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz, 1H; Ar*H*), 7.64 (dd, $^3J_{HH}$ = 8.0, 7.6 Hz, 1H; Ar*H*), 7.60 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 7.41 (dd, $^3J_{HH}$ = 8.0, 7.6 Hz, 1H; Ar*H*), 7.03–6.97 (3H; Ar*H*), 3.82 (s, 3H; -OC*H*$_3$).

^{13}C NMR (126 MHz, CD_3CN, rt) δ 169.9, 160.7, 147.1, 146.0, 140.3, 140.2, 135.2, 131.9, 130.8, 129.6, 129.3, 128.8, 128.7, 123.5, 116.2, 114.8, 56.01.

^{19}F NMR (376 MHz, CD_3CN, rt) δ –152.71, –152.76 (each s, 4F; B*F*$_4$).

HRMS (ESI-TOF) Calcd. for $C_{19}H_{17}N_2O$ $[M]^+$ requires 289.1335, found 289.1337.

(*E*)-3'-Acetamid-[1,1']-biphenyl-2-iminylpyridinium Tetrafluoroborate (1c)



According to the general procedures, 3'-acetoamid-[1,1']-biphenyl-2-carbaldehyde (0.807 g, 3.37 mmol), 1-aminopyridinum tetrafluoroborate (0.366 g, 2.01 mmol), and CH$_3$CN (30 mL) afforded **1c** (0.664 g, 1.65 mmol, 82% yield, reaction time = 16 h) as a white solid after purification with reprecipitation (CH$_3$CN/Et$_2$O).

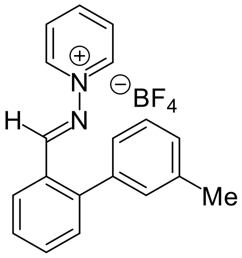
^{1}H NMR (400 MHz, CD$_3$CN, rt) δ 8.91 (d, $^3J_{\mathrm{HH}}$ = 5.6 Hz, 1H; pyridinium) 8.87 (s, 1H; -N=C*H*-), 8.54 (br s, 1H; -N*H*COCH$_3$), 8.50 (t, $^3J_{\mathrm{HH}}$ = 8.0 Hz, 1H; pyridinium), 8.30 (d, $^3J_{\mathrm{HH}}$ = 8.0 Hz, 1H; Ar*H*), 8.07 (dd, $^3J_{\mathrm{HH}}$ = 7.6, 6.8 Hz, 1H; pyridinium), 7.82–7.78 (2H; Ar*H*), 7.66–7.62 (2H; Ar*H*), 7.45 (dd, $^3J_{\mathrm{HH}}$ = 8.0, 7.6 Hz, 1H; Ar*H*), 7.40 (d, $^3J_{\mathrm{HH}}$ = 8.4 Hz, 1H; Ar*H*), 7.21 (d, $^3J_{\mathrm{HH}}$ = 7.6 Hz, 1H; Ar*H*), 2.08 (s, 3H; -NHCOC*H*$_3$).

^{13}C NMR (126 MHz, CD$_3$CN, rt) δ 170.4, 170.3, 146.8, 146.1, 140.6, 140.0, 139.3, 135.3, 131.8, 130.6, 129.6, 129.5, 129.1, 128.8, 125.9, 123.1, 120.4, 24.32.

^{19}F NMR (376 MHz, CD$_3$CN, rt) δ –152.65, –152.70 (each s, 4F; B*F*$_4$).

HRMS (ESI-TOF) Calcd. for C$_{20}$H$_{18}$N$_3$O [M]$^+$ requires 316.1444, found 316.1444.

(*E*)-3'-Methyl-[1,1']-biphenyl-2-iminylpyridinium Tetrafluoroborate (1d)



According to the general procedures, 3'-methyl-[1,1']-biphenyl-2-carbaldehyde (0.900 g, 4.59 mmol), 1-aminopyridinum tetrafluoroborate (0.419 g, 2.30 mmol), and CH$_3$CN (50 mL) afforded **1d** (0.443 g, 1.23 mmol, 54% yield, reaction time = 22 h) as a white solid after purification with reprecipitation (CH$_3$CN/Et$_2$O).

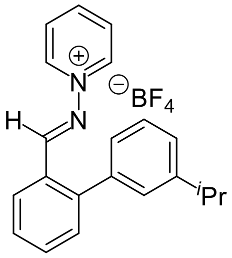
^{1}H NMR (400 MHz, CD$_3$CN, rt) δ 8.74 (d, $^3J_{\mathrm{HH}}$ = 6.4 Hz, 2H; pyridinium), 8.73 (s, 1H; -N=C*H*-), 8.50 (t, $^3J_{\mathrm{HH}}$ = 8.0 Hz, 1H; pyridinium), 8.29 (d, $^3J_{\mathrm{HH}}$ = 8.0 Hz, 1H; Ar*H*), 8.08 (dd, $^3J_{\mathrm{HH}}$ = 7.2, 7.2 Hz, 2H; pyridinium), 7.79 (dd, $^3J_{\mathrm{HH}}$ = 7.6, 7.6 Hz, 1H; Ar*H*), 7.63 (dd, $^3J_{\mathrm{HH}}$ = 8.0, 8.0 Hz, 1H; Ar*H*), 7.59 (d, $^3J_{\mathrm{HH}}$ = 8.0 Hz, 1H; Ar*H*), 7.39 (dd, $^3J_{\mathrm{HH}}$ = 7.6, 7.6 Hz, 1H; Ar*H*), 7.31–7.28 (2H; Ar*H*), 7.22 (d, $^3J_{\mathrm{HH}}$ = 7.6 Hz, 1H; Ar*H*), 2.40 (s, 3H; -C*H*$_3$).

^{13}C NMR (126 MHz, CD$_3$CN, rt) δ170.0, 147.5, 146.1, 140.3, 139.7, 138.8, 135.3, 132.0, 131.5, 130.1, 129.68, 129.66, 129.3, 128.9, 128.7, 128.2, 21.38.

^{19}F NMR (376 MHz, CD$_3$CN, rt) δ –152.79, –152.84 (each s, 4F; B*F*$_4$).

HRMS (ESI-TOF) Calcd. for C$_{19}$H$_{17}$N$_2$ [M]$^+$ requires 273.1386, found 273.1388.

(*E*)-3'-Isopropyl-[1,1']-biphenyl-2-iminylpyridinium Tetrafluoroborate (1e)



According to the general procedures, 3'-isopropyl-[1,1']-biphenyl-2-carbaldehyde (1.35g, 6.01 mmol), 1-aminopyridinum tetrafluoroborate (0.545 g, 3.00 mmol), and CH_3CN (100 mL) afforded **1e** (0.795 g, 2.05 mmol, 68% yield, reaction time = 24 h) as a pale yellow solid after purification with reprecipitation (acetone/*n*-hexane).

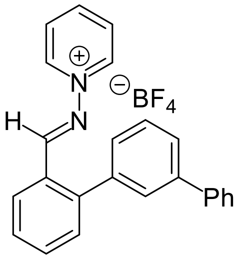
^{1}H NMR (400 MHz, CD_3CN, rt) δ 8.74 (d, $^3J_{HH}$ = 8.4 Hz, 2H; pyridinium), 8.73 (s, 1H; -N=C*H*-), 8.50 (t, $^3J_{HH}$ = 8.0 Hz, 1H; pyridinium), 8.30 (d, $^3J_{HH}$ = 7.6 Hz, 1H; Ar*H*), 8.08 (dd, $^3J_{HH}$ = 7.2, 7.2 Hz, 2H; pyridinium), 7.80 (dd, $^3J_{HH}$ = 7.6, 7.6 Hz, 1H; Ar*H*), 7.66–7.60 (2H; Ar*H*), 7.42 (dd, $^3J_{HH}$ = 7.6, 7.6 Hz, 1H; Ar*H*), 7.36 (d, $^3J_{HH}$ = 7.6 Hz, 1H; Ar*H*), 7.32 (s, 1H; Ar*H*), 7.24 (d, $^3J_{HH}$ = 7.6 Hz, 1H; Ar*H*), 2.98 (sep, $^3J_{HH}$ = 6.8 Hz, 1H; -C*H*(CH_3)$_2$), 1.25 (d, $^3J_{HH}$ = 6.8 Hz, 6H; -CH(C*H*$_3$)$_2$).

^{13}C NMR (126 MHz, CD_3CN, rt) δ 170.2, 150.5, 147.5, 146.1, 140.2, 138.8, 135.2, 132.0, 129.7, 129.6, 129.2, 129.0, 128.9, 128.64, 128.57, 127.4, 34.69, 24.08.

^{19}F NMR (376 MHz, CD_3CN, rt) δ –152.76, –152.81 (each s, 4F; B*F*$_4$).

HRMS (ESI-TOF) Calcd. for $C_{21}H_{21}N_2$ $[M]^+$ requires 301.1699, found 301.1699.

(*E*)-[1.1':3',1"-Terphenyl-2-iminylpyridinium Tetrafluoroborate (1f)



According to the general procedures, 1,1':3',1"-terphenyl-2-carbaldehyde (2.29 g, 8.88 mmol), 1-aminopyridinum tetrafluoroborate (0.812 g, 4.46 mmol), and CH_3CN (30 mL) afforded **1f** (1.26 g, 2.97 mmol, 67% yield, reaction time = 48 h) as a white solid after purification with reprecipitation (CH_3CN/Et_2O).

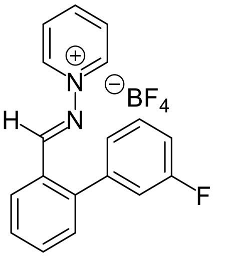
^{1}H NMR (400 MHz, CD_3CN, rt) δ 8.79 (s, 1H; -N=C*H*-), 8.74 (d, $^3J_{HH}$ = 6.0 Hz, 2H; pyridinium), 8.49 (t, $^3J_{HH}$ = 8.0 Hz, 1H; pyridinium), 8.32 (d, $^3J_{HH}$ = 7.2 Hz, 1H; Ar*H*), 8.06 (dd, $^3J_{HH}$ = 7.6, 7.2 Hz, 2H; pyridinium), 7.82 (dd, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.2 Hz, 1H; Ar*H*), 7.76-7.65 (6H; Ar*H*), 7.58 (t, $^3J_{HH}$ = 7.6 Hz, 1H; Ar*H*), 7.47 (dd, $^3J_{HH}$ = 7.6, 7.6 Hz, 2H; Ar*H*), 7.42–7.37 (2H; Ar*H*).

^{13}C NMR (126 MHz, CD_3CN, rt) δ 170.0, 147.2, 146.1, 142.3, 141.0, 140.3, 139.6, 135.3, 132.2, 130.25, 130.19, 129.9, 129.7, 129.5, 129.2, 128.92, 128.90, 128.8, 128.1, 127.9.

^{19}F NMR (376 MHz, CD_3CN, rt) δ −152.69, −152.74 (each s, 4F; B*F*$_4$).

HRMS (ESI-TOF) Calcd. for $C_{24}H_{19}N_2$ $[M]^+$ requires 335.1543, found 335.1542.

(*E*)-3'-Fluoro-[1,1']-biphenyl-2-iminylpyridinium Tetrafluoroborate (1g)



According to the general procedures, 3'-fluoro-[1,1']-biphenyl-2-carbaldehyde (0.488 g, 2.44 mmol), 1-aminopyridinum tetrafluoroborate (0.239 g, 1.31 mmol), and CH_3CN (30 mL) afforded **1g** (0.234 g, 0.643 mmol, 49% yield, reaction time = 17 h) as a white solid after purification with reprecipitation (CH_3CN/Et_2O).

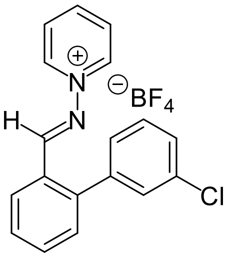
^{1}H NMR (400 MHz, CD_3CN, rt) δ 8.77 (d, $^3J_{HH}$ = 6.0 Hz, 2H; pyridinium), 8.74 (s, 1H; -N=C*H*-), 8.52 (t, $^3J_{HH}$ = 7.6 Hz, 1H; pyridinium), 8.31 (d, $^3J_{HH}$ = 7.6 Hz, 1H; Ar*H*), 8.09 (dd, $^3J_{HH}$ = 7.2, 7.2 Hz, 2H; pyridinium), 7.80 (dd, $^3J_{HH}$ = 7.6, 7.6 Hz, 1H; Ar*H*), 7.67 (dd, $^3J_{HH}$ = 7.6, 7.6 Hz, 1H; Ar*H*), 7.59 (d, $^3J_{HH}$ = 7.6 Hz, 1H; Ar*H*), 7.52 (dd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HF}$ = 14.4 Hz, 1H; Ar*H*), 7.27–7.21 (3H; Ar*H*).

^{13}C NMR (126 MHz, CD_3CN, rt) δ 169.7, 163.6 (d, $^1J_{CF}$ = 245.8 Hz), 146.2, 145.8 (d, $^4J_{CF}$ = 1.6 Hz), 141.2 (d, $^3J_{CF}$ = 8.1 Hz), 140.4, 135.3, 132.0, 131.6 (d, $^3J_{CF}$ = 8.6 Hz), 129.8, 129.6, 129.0, 128.8, 127.2 (d, $^4J_{CF}$ = 2.7 Hz), 117.7 (d, $^2J_{CF}$ = 22.4 Hz), 116.0 (d, $^2J_{CF}$ = 21.2 Hz).

^{19}F NMR (376 MHz, CD_3CN, rt) δ –115.1 (m, 1F; Ar*F*), –152.63, –152.68 (each s, 4F; B*F*$_4$).

HRMS (ESI-TOF) Calcd. for $C_{18}H_{14}FN_2$ $[M]^+$ requires 277.1136, found 277.1137.

(*E*)-3'-Chloro-[1,1']-biphenyl-2-iminylpyridinium Tetrafluoroborate (1h)



According to the general procedures, 3'-chloro-[1,1']-biphenyl-2-carbaldehyde (0.689 g, 3.18 mmol), 1-aminopyridinum tetrafluoroborate (0.392 g, 2.15 mmol), and CH_3CN (20 mL) afforded **1h** (0.394 g, 1.04 mmol, 48% yield, reaction time = 18 h) as a white solid after purification with reprecipitation

(CH_3CN/Et_2O, AcOEt).

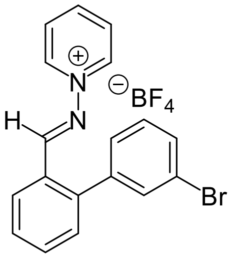
^{1}H NMR (400 MHz, CD_3CN, rt) δ 8.74 (d, $^3J_{HH}$ = 6.0 Hz, 2H; pyridinium), 8.71 (s, 1H; -N=C*H*-), 8.51 (t, $^3J_{HH}$ = 7.6 Hz, 1H; pyridinium), 8.31 (d, $^3J_{HH}$ = 7.6 Hz, 1H; Ar*H*), 8.08 (dd, $^3J_{HH}$ = 7.2, 7.2 Hz, 2H; pyridinium), 7.81 (dd, $^3J_{HH}$ = 7.6, 7.6 Hz, 1H; Ar*H*), 7.67 (dd, $^3J_{HH}$ = 7.6, 7.6 Hz, 1H; Ar*H*), 7.58 (d, $^3J_{HH}$ = 7.6 Hz, 1H; Ar*H*), 7.50–7.45 (3H; Ar*H*), 7.36 (m, 1H; Ar*H*).

^{13}C NMR (126 MHz, CD_3CN, rt) δ 169.6, 146.1, 145.6, 140.9, 140.3, 135.3, 135.1, 132.0, 131.2, 130.5, 129.8, 129.65, 129.57, 129.3, 129.0, 128.8.

^{19}F NMR (376 MHz, CD_3CN, rt) δ –152.73, –152.79 (each s, 4F; B*F*$_4$).

HRMS (ESI-TOF) Calcd. for $C_{18}H_{14}ClN_2$ $[M]^+$ requires 293.0840, found 293.0842.

(*E*)-3'-Bromo-[1,1']-biphenyl-2-iminylpyridinium Tetrafluoroborate (1i)



According to the general procedures, 3'-bromo-[1,1']-biphenyl-2-carbaldehyde (1.10 g, 4.23 mmol), 1-aminopyridinum tetrafluoroborate (0.398 g, 2.19 mmol), and CH_3CN (20 mL) afforded **1i** (0.683 g, 1.61 mmol, 74% yield, reaction time = 16 h) as a white solid after purification with reprecipitation (CH_3CN/cool Et_2O).

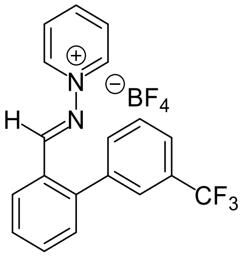
^{1}H NMR (400 MHz, CD_3CN, rt) δ 8.74 (d, $^3J_{HH}$ = 6.0 Hz, 2H; pyridinium), 8.71 (s, 1H; -N=C*H*-), 8.52 (t, $^3J_{HH}$ = 8.0 Hz, 1H; pyridinium), 8.30 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 8.09 (dd, $^3J_{HH}$ = 7.2, 7.2 Hz, 2H; pyridinium), 7.80 (dd, $^3J_{HH}$ = 7.2, 7.2 Hz, 1H; Ar*H*), 7.68–7.63 (3H; Ar*H*), 7.57 (d, $^3J_{HH}$ = 7.6 Hz, 1H; Ar*H*), 7.42–7.40 (2H; Ar*H*).

^{13}C NMR (126 MHz, CD_3CN, rt) δ 169.6, 146.1, 145.5, 141.1, 140.3, 135.3, 133.3, 132.2, 132.0, 131.4, 130.1, 129.8, 129.6, 129.0, 128.8, 123.2.

^{19}F NMR (376 MHz, CD_3CN, rt) δ –152.68, –152.73 (each s, 4F; B*F*$_4$).

HRMS (ESI-TOF) Calcd. for $C_{18}H_{14}BrN_2$ $[M]^+$ requires 337.0335, found 337.0333.

(E)-3’-Trifluoromethyl-[1,1’]-biphenyl-2-iminylpyridinium Tetrafluoroborate (1j)



According to the general procedures, 3’-trifluoromethyl-[1,1’]-biphenyl-2-carbaldehyde (1.44 g, 5.74 mmol), 1-aminopyridinum tetrafluoroborate (0.566 g, 3.11 mmol), and CH_3CN (50 mL) afforded **1j** (0.674 g, 1.63 mmol, 52% yield, reaction time = 24 h) as a white solid after purification with reprecipitation (CH_3CN/Et_2O).

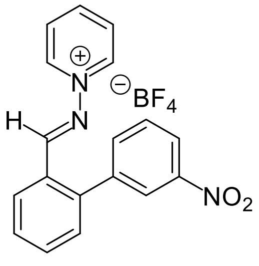
^{1}H NMR (400 MHz, CD_3CN, rt) δ 8.73 (d, $^3J_{HH}$ = 6.4 Hz, 2H; pyridinium), 8.68 (s, 1H; -N=C*H*-), 8.51 (t, $^3J_{HH}$ = 7.6 Hz, 1H; pyridinium), 8.32 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 8.08 (dd, $^3J_{HH}$ = 7.2, 7.2 Hz, 2H; pyridinium), 7.84–7.78 (3H; Ar*H*), 7.71–7.68 (3H; Ar*H*), 7.61 (d, $^3J_{HH}$ = 7.6 Hz, 1H; Ar*H*).

^{13}C NMR (126 MHz, CD_3CN, rt) δ 169.8, 146.2, 145.5, 140.3, 140.0, 135.4, 134.9, 132.2, 131.3 (q, $^2J_{CF}$ = 32.5 Hz), 130.6, 130.0, 129.6, 129.2, 128.9, 127.3 (q, $^3J_{CF}$ = 3.91 Hz), 126.0 (q, $^3J_{CF}$ = 3.78 Hz), 125.2 (q, $^1J_{CF}$ = 271.7 Hz).

^{19}F NMR (376 MHz, CD_3CN, rt) δ –63.95 (s, 3F; C*F*$_3$), –152.76, –152.81 (each s, 4F; B*F*$_4$).

HRMS (ESI-TOF) Calcd. for $C_{19}H_{14}F_3N_2$ $[M]^+$ requires 327.1104, found 327.1104.

(E)-3’-Nitro-[1,1’]-biphenyl-2-iminylpyridinium Tetrafluoroborate (1k)



According to the general procedures, 3’-nitro-[1,1’]-biphenyl-2-carbaldehyde (0.565 g, 2.48 mmol), 1-aminopyridinum tetrafluoroborate (0.235 g, 1.29 mmol), and CH_3CN (30 mL) afforded **1k** (0.192 g, 0.491 mmol, 38% yield, reaction time = 24 h) as a white solid after purification with reprecipitation (CH_3CN/Et_2O).

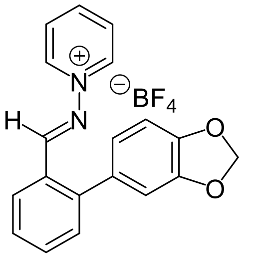
^{1}H NMR (400 MHz, CD_3CN, rt) δ 8.72 (d, $^3J_{HH}$ = 6.4 Hz, 2H; pyridinium), 8.66 (s, 1H; -N=C*H*-), 8.50 (t, $^3J_{HH}$ = 8.0 Hz, 1H; pyridinium), 8.33–8.26 (3H; Ar*H*), 8.07 (dd, $^3J_{HH}$ = 7.2, 7.2 Hz, 2H; pyridinium), 7.86–7.82 (2H; Ar*H*), 7.75–7.70 (2H; Ar*H*), 7.62 (d, $^3J_{HH}$ = 7.6 Hz, 1H; Ar*H*).

^{13}C NMR (126 MHz, CD_3CN, rt) δ 169.6, 149.4, 146.2, 144.6, 140.6, 140.3, 137.1, 135.5, 132.2, 131.1, 130.3, 129.6, 129.4, 129.0, 125.6, 124.1.

^{19}F NMR (376 MHz, CD_3CN, rt) δ –152.83, –152.88 (each s, 4F; B*F*$_4$).

HRMS (ESI-TOF) Calcd. for $C_{18}H_{14}N_3O_2$ $[M]^+$ requires 304.1081, found 304.1082.

(*E*)- 2-(Benzo[d][1,3]dioxol-5-yl)iminylpyridinium Tetrafluoroborate (1l)



According to the general procedures, 2-(benzo[d][1,3]dioxol-5-yl)benzaldehyde (1.93 g, 8.52 mmol), 1-aminopyridinum tetrafluoroborate (0.778 g, 4.27 mmol), and CH_3CN (50 mL) afforded **1l** (1.13 g, 2.89 mmol, 68% yield, reaction time = 17 h) as a yellow solid after purification with reprecipitation (CH_3CN/Et_2O).

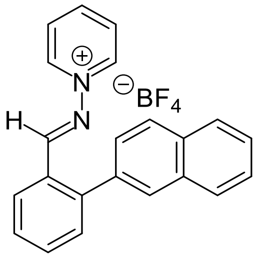
^{1}H NMR (400 MHz, CD_3CN, rt) δ 8.78 (d, $^3J_{HH}$ = 8.0 Hz, 2H; pyridinium) 8.77 (s, 1H; -N=C*H*-), 8.52 (t, $^3J_{HH}$ = 8.0 Hz, 1H; pyridinium), 8.26 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 8.10 (dd, $^3J_{HH}$ = 7.2, 7.2 Hz, 2H; pyridinium), 7.76 (dd, $^3J_{HH}$ = 7.2, 7.2 Hz, 1H; Ar*H*), 7.60 (dd, $^3J_{HH}$ = 7.6, 7.6 Hz, 1H; Ar*H*), 7.57 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 6.97–6.95 (2H; Ar*H*), 6.86 (dd, $^3J_{HH}$ = 8.0, 1.2 Hz, 1H; Ar*H*), 6.02 (s, 2H; -OC*H*$_2$O-).

^{13}C NMR (126 MHz, CD_3CN, rt) δ 169.9, 149.1, 149.0, 146.9, 146.1, 140.4, 135.2, 132.7, 131.9, 129.6, 129.1, 128.94, 128.88, 125.3, 111.0, 109.3, 102.8.

^{19}F NMR (376 MHz, CD_3CN, rt) δ –152.64, –152.69 (each s, 4F; B*F*$_4$).

HRMS (ESI-TOF) Calcd. for $C_{19}H_{15}N_2O_2$ $[M]^+$ requires 303.1128, found 303.1129.

(*E*)- 2-(Naphthalen-2’-yl)iminylpyridinium Tetrafluoroborate (1m)



According to the general procedures, 2-(naphthalene-2’-yl)benzaldehyde (2.04 g, 8.77 mmol), 1-aminopyridinum tetrafluoroborate (0.798 g, 4.39 mmol), and CH_3CN (50 mL) afforded **1m** (0.791 g, 2.00 mmol, 45% yield, reaction time = 48 h) as a yellow solid after purification with reprecipitation (acetone/*n*-hexane).

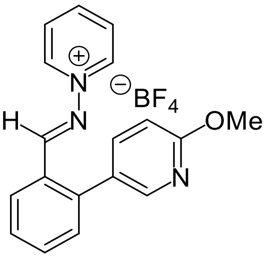
^{1}H NMR (400 MHz, CD_3CN, rt) δ 8.80 (s, 1H; -N=C*H*-), 8.73 (d, $^3J_{HH}$ = 6.0 Hz, 2H; pyridinium), 8.45 (t, $^3J_{HH}$ = 8.0 Hz, 1H; pyridinium), 8.34 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 8.05–8.01 (3H; pyridinium (2H), Ar*H* (1H)), 7.98–7.95 (2H; Ar*H*), 7.93 (s, 1H; Ar*H*), 7.84 (dd, $^3J_{HH}$ = 8.0, 7.6 Hz, 1H; Ar*H*), 7.72–7.66 (2H; Ar*H*), 7.61–7.57 (3H; Ar*H*).

^{13}C NMR (126 MHz, CD_3CN, rt) δ 169.9, 147.2, 146.0, 140.3, 136.4, 135.2, 134.0, 133.7, 132.3, 130.4, 129.5, 129.40, 129.35, 129.2, 129.0, 128.9, 128.6 (2C), 127.78, 127.76.

^{19}F NMR (376 MHz, CD_3CN, rt) δ –152.43, –152.49 (each s, 4F; B*F*$_4$).

HRMS (ESI-TOF) Calcd. for $C_{22}H_{17}N_2$ $[M]^+$ requires 309.1386, found 309.1385.

(*E*)-2'-Methoxypyridine-[1,5']- yl-2-iminylpyridinium Tetrafluoroborate (1n)



According to the general procedures, 2'-methokypyridine-[1,5']-yl-2-carbaldehyde (0.934 g, 4.38 mmol), 1-aminopyridinum tetrafluoroborate (0.402 g, 2.21 mmol), and CH_3CN (20 mL) afforded **1n** (0.597 g, 1.58 mmol, 72% yield, reaction time = 20 h) as a pale yellow solid after purification with reprecipitation (CH_3CN/Et_2O).

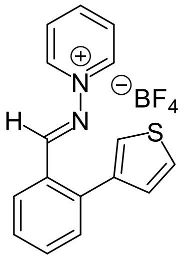
^{1}H NMR (400 MHz, CD_3CN, rt) δ 8.76 (d, $^3J_{HH}$ = 6.0 Hz, 2H; pyridinium), 8.73 (s, 1H; -N=C*H*-), 8.52 (t, $^3J_{HH}$ = 8.0 Hz, 1H; pyridinium), 8.30 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 8.19 (d, $^4J_{HH}$ = 2.0 Hz, 1H; pyridine), 8.09 (dd, $^3J_{HH}$ = 7.2, 7.2 Hz, 2H; pyridinium), 7.80 (dd, $^3J_{HH}$ = 7.6, 7.6 Hz, 1H; Ar*H*), 7.73 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 2.4 Hz, 1H; pyridine), 7.65 (dd, $^3J_{HH}$ = 7.6, 7.6 Hz, 1H; Ar*H*), 7.58 (d, $^3J_{HH}$ = 7.6 Hz, 1H; Ar*H*), 6.89 (d, $^3J_{HH}$ = 8.4 Hz, 1H; pyridine), 3.93 (s, 3H; -OC*H*$_3$).

^{13}C NMR (126 MHz, CD_3CN, rt) δ 169.6, 165.1, 148.4, 146.2, 143.7, 141.2, 140.4, 135.4, 132.3, 129.61, 129.58, 129.2, 129.1, 128.1, 111.5, 54.18.

^{19}F NMR (376 MHz, CD_3CN, rt) δ –152.71, –152.76 (each s, 4F; B*F*$_4$).

HRMS (ESI-TOF) Calcd. for $C_{18}H_{16}N_3O$ $[M]^+$ requires 290.1288, found 290.1290.

(*E*)-Thiophene-[1,3']-yl-2-iminopyridinium Tetrafluoroborate (1o)



According to the general procedures, 2-(thien-3-yl)benzaldehyde (1.26 g, 6.70 mmol), 1-aminopyridinum tetrafluoroborate (0.606 g, 3.33 mmol), and CH_3CN (30 mL) afforded **1o** (0.962 g, 2.73 mmol, 82% yield, reaction time = 22 h) as a white solid after purification with reprecipitation (CH_3CN/Et_2O).

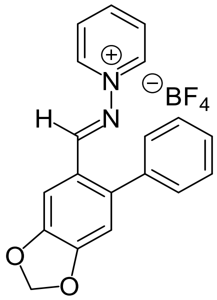
^{1}H NMR (400 MHz, CD_3CN, rt) δ 8.89 (s, 1H; -N=C*H*-), 8.80 (d, $^3J_{HH}$ = 6.0 Hz, 2H; pyridinium), 8.53 (t, $^3J_{HH}$ = 8.0 Hz, 1H; pyridinium), 8.27 (d, $^3J_{HH}$ = 7.6 Hz, 1H; Ar*H*), 8.11 (dd, $^3J_{HH}$ = 7.6, 7.2 Hz, 2H; pyridinium), 7.77 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.2 Hz, 1H; Ar*H*), 7.66-7.58 (3H; Ar*H*), 7.50 (m, 1H; Ar*H*), 7.30 (dd, $^3J_{HH}$ = 5.2 Hz, $^4J_{HH}$ = 1.2 Hz, 1H; Ar*H*).

^{13}C NMR (126 MHz, CD_3CN, rt) δ 169.9, 146.1, 141.8, 140.4, 139.3, 135.3, 131.7, 130.0, 129.7, 129.2, 129.0, 128.9, 128.3, 127.3.

^{19}F NMR (376 MHz, CD_3CN, rt) δ −152.63, −152.68 (each s, 4F; B*F*$_4$).

HRMS (ESI-TOF) Calcd. for $C_{16}H_{13}N_2S$ $[M]^+$ requires 265.0794, found 265.0796.

(*E*)- 2-(Benzo[d][1,3]dioxol-5-yl)iminylpyridinium Tetrafluoroborate (1p)



According to the general procedures, 6-phenylbenzo[d][1,3]dioxole-5-carbaldehyde (0.986 g, 4.36 mmol), 1-aminopyridinum tetrafluoroborate (0.405 g, 2.23 mmol), and CH_3CN (15 mL) afforded **1p** (0.577 g, 1.48 mmol, 66% yield, reaction time = 16 h) as a yellow solid after purification with reprecipitation (CH_3CN/Et_2O).

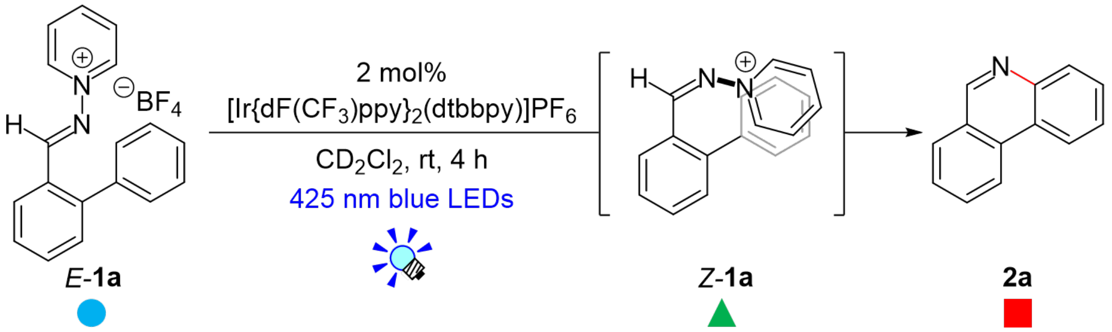
^{1}H NMR (400 MHz, CD_3CN, rt) δ 8.69 (d, $^3J_{HH}$ = 6.0 Hz, 2H; pyridinium), 8.53 (s, 1H; -N=C*H*-), 8.46 (t, $^3J_{HH}$ = 8.0 Hz, 1H; pyridinium), 8.04 (dd, $^3J_{HH}$ = 7.2, 7.2 Hz, 2H; pyridinium), 7.71 (s, 1H; Ar*H*), 7.49–7.39 (5H; Ar*H*), 7.04 (s, 1H; Ar*H*), 6.19 (s, 2H; -OC*H*$_2$O-).

^{13}C NMR (126 MHz, CD_3CN, rt) δ 168.7, 154.3, 149.3, 145.7, 145.4, 140.3, 138.6, 131.1, 129.7, 129.6, 129.4, 122.6, 111.4, 106.6, 104.2.

^{19}F NMR (376 MHz, CD_3CN, rt) δ –152.75, –152.81 (each s, 4F; B*F*$_4$).

HRMS (ESI-TOF) Calcd. for $C_{19}H_{15}N_2O_2$ $[M]^+$ requires 303.1128, found 303.1129.

Typical Procedures for NMR Experiment



Under N_2, an NMR tube was charged with **1a** (50.0 μmol), CD_2Cl_2 (0.5 mL), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (1.00 μmol) and dimethylsulfone (an internal standard). The mixture was degassed by three freeze-pump-thaw cycles. The reaction was carried out at rt (water bath) under irradiation of visible light (placed at a distance of 2–3 cm from the blue LED lamps: hν = 425 nm ± 15 nm). Then, the reaction was followed by ^{1}H NMR spectroscopy.

^{1}H NMR (400 MHz, CD_2Cl_2, rt)

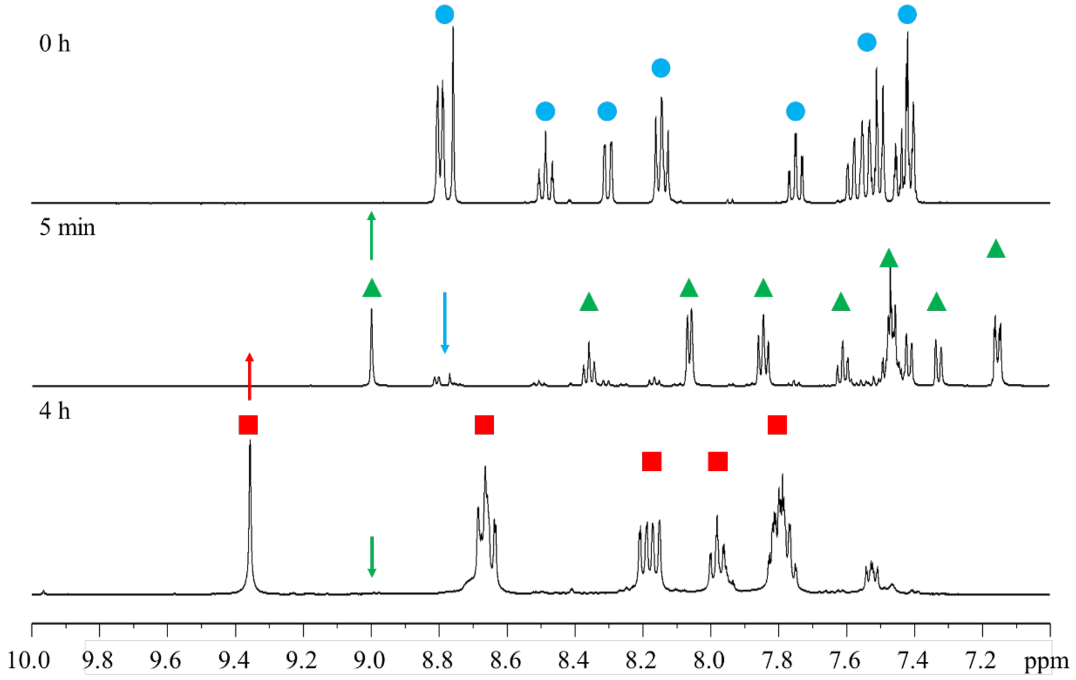
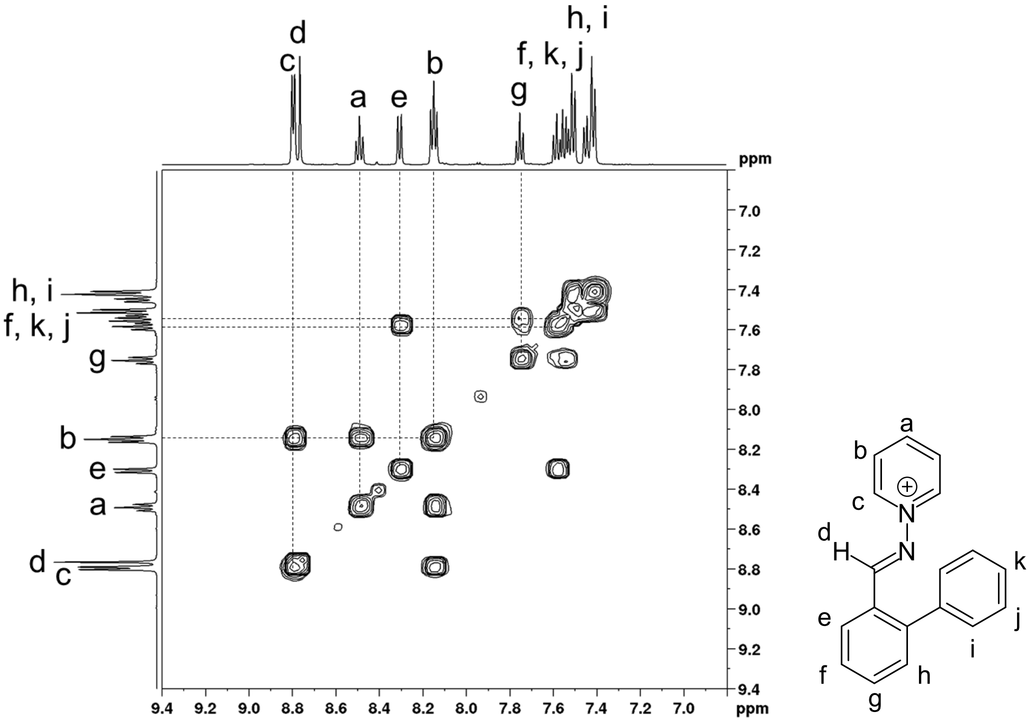


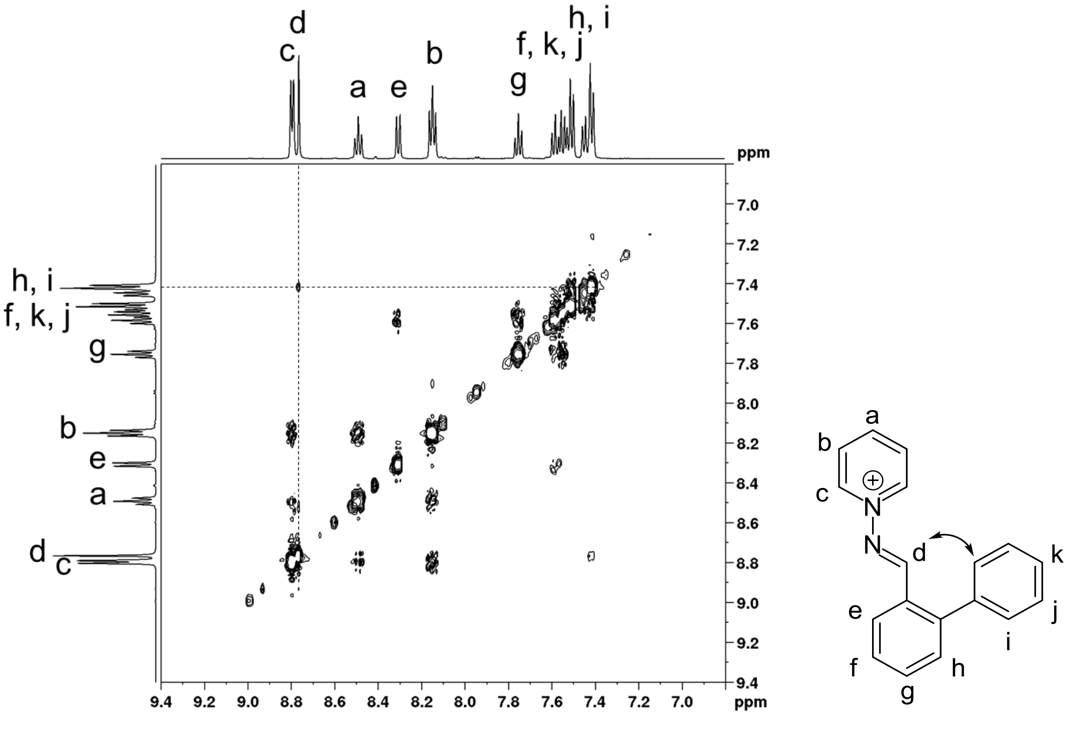
Figure S2 ^{1}H NMR spectra for the reaction of **1a**.

Determination of Stereochemistry of *E*- and *Z*-1a

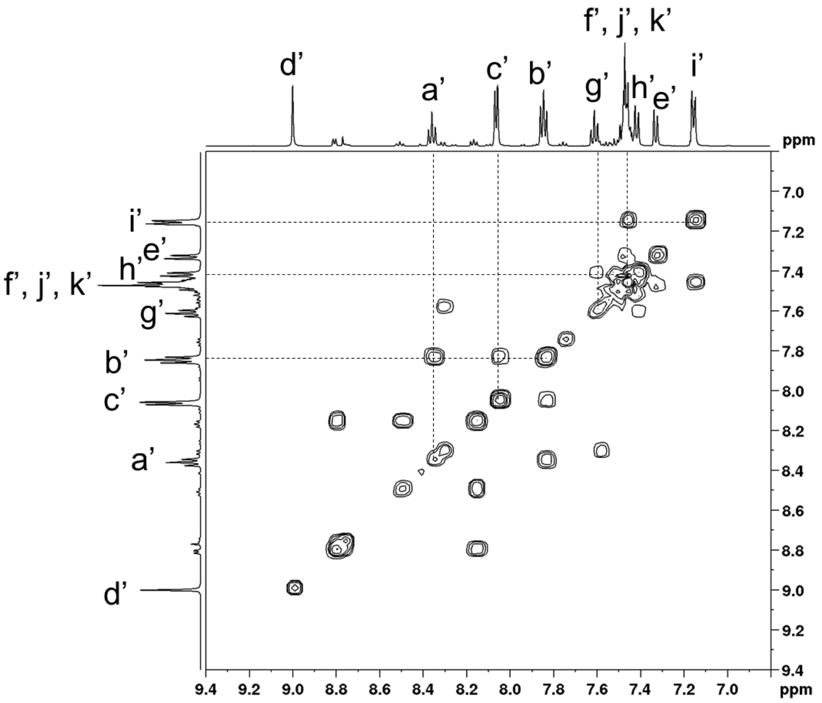
・**COSY NMR of *E*-1a**

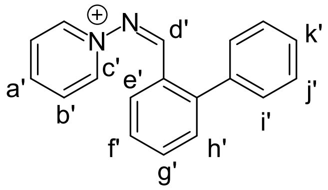


・**NOESY NMR of *E*-1a**

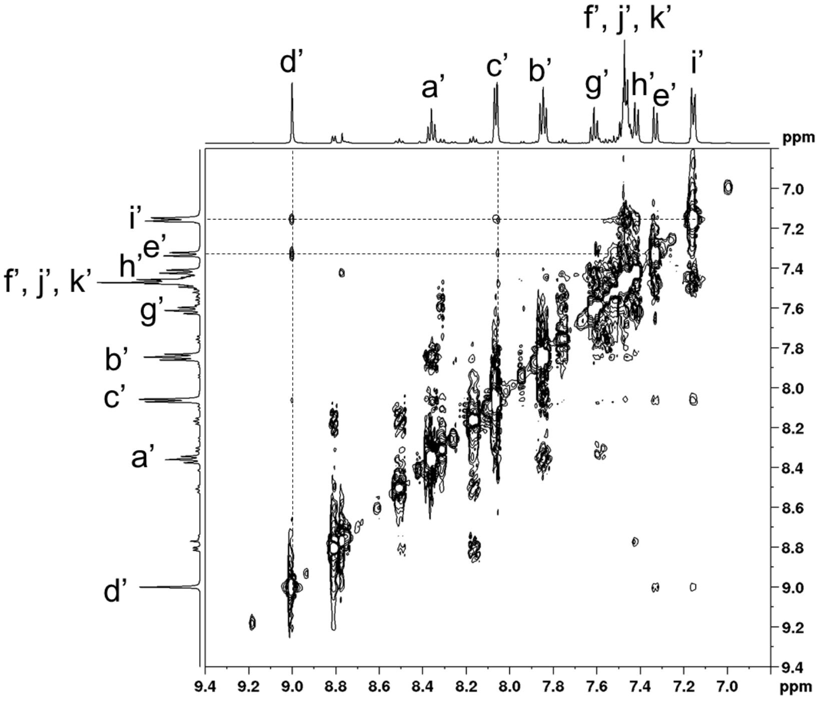


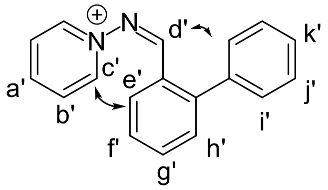
・COSY NMR of *Z*-1a

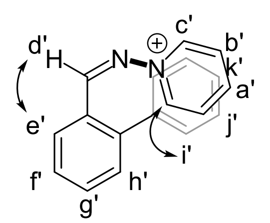




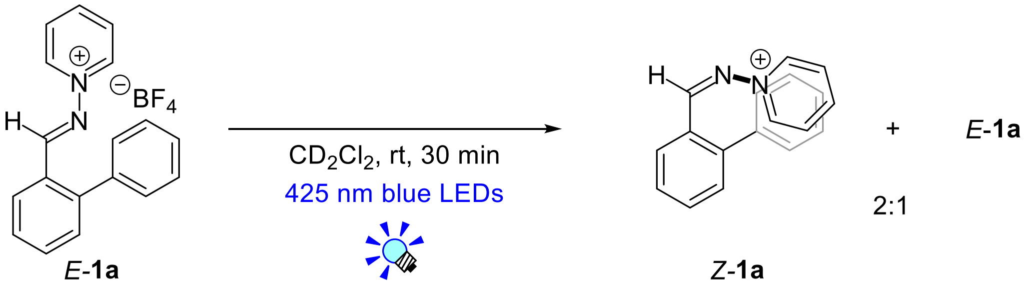
・NOESY NMR of *Z*-1a







Absorption Spectra for a Mixture of *E*- and *Z*-1a



Under N_2, an NMR tube was charged with **1a** (1.7 mg, 4.91 µmol) and CD_2Cl_2 (0.5 mL). The mixture was degassed by three freeze-pump-thaw cycles. The reaction was carried out at rt (water bath) under irradiation of visible light (placed at a distance of 2–3 cm from the blue LED lamps: hν = 425 nm ± 15 nm). After 30 min, formation of ***Z*-1a** was observed by ^{1}H NMR spectroscopy (***E*-1a**:***Z*-1a** = 1:2). The reaction solution was adjusted to 5 mL with a volumetric flask using CH_2Cl_2. Absorption spectra were obtained using HITACHI F-7000.

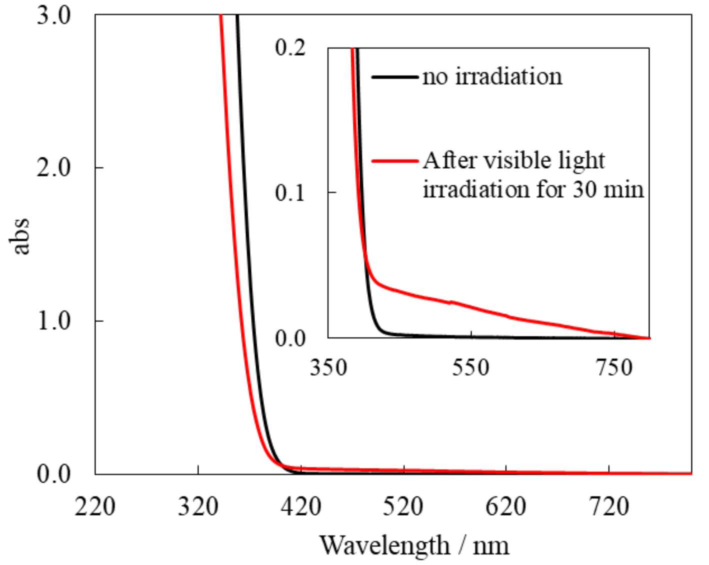
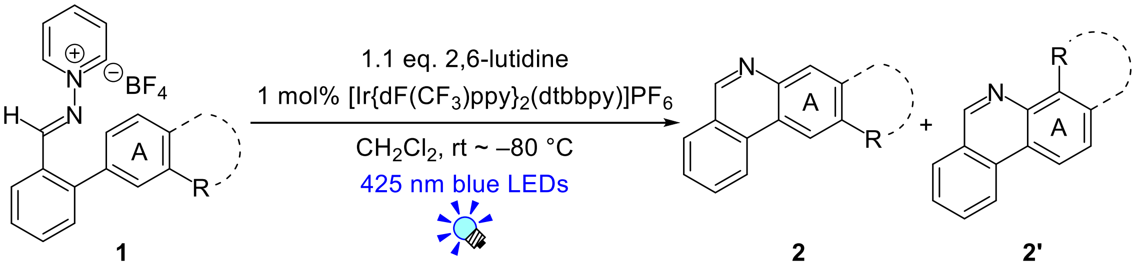


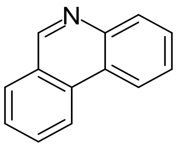
Figure S3 Absorption spectra of 1 mM **1a** in CH_2Cl_2 (no irradiation and after visible light irradiation for 30 min).

General Procedures for the Photocatalytic Synthesis of Phenanthridines and Characterization



Under N_2, to iminylpyridinium salts **1** (0.50 mmol) dissolved in a mixture of CH_2Cl_2 (5.0 mL) in a 20 mL-Schlenk tube, 2,6-lutidine (0.55 mmol) and [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (0.005 mmol) were added. The mixture was degassed by three freeze-pump-thaw cycles. The reaction was carried out at rt (water bath) or 0 ~–80 ˚C (cooling system) under irradiation of visible light (placed at a distance of 2–3 cm from the blue LED lamps: $h\nu = 425 \pm 15$ nm). Then, the reaction mixture was concentrated *in vacuo* to remove the volatile compounds. The crude product was purified by automated column chromatography on silica gel to give phenanthridine (**2** and **2'**). Isomer ratios (**2**;**2'**) were determined by ^{1}H NMR spectra of the crude product.

Phenanthridine (2a)

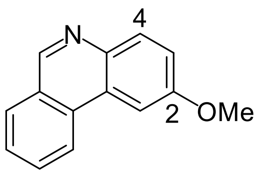


According to the general procedures, **1a** (173.8 mg, 0.502 mmol), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (5.6 mg, 0.0051 mmol) and CH_2Cl_2 (5.0 mL) afforded **2a** (68.8 mg, 0.0384 mmol, 76% yield, reaction time = 8 h, rt) as a white solid after purification with automated column chromatography on silica gel (*n*-hexane:AcOEt = 7:3).

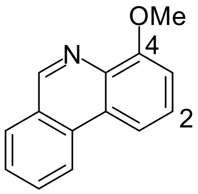
^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 9.30 (s, 1H; -N=C*H*-), 8.63 (d, $^3J_{HH}$ = 8.4 Hz, 1H; Ar*H*), 8.59 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 8.20 (d, $^3J_{HH}$ = 8.4 Hz, 1H; Ar*H*), 8.06 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 7.87 (dd, $^3J_{HH}$ = 8.4, 7.2 Hz, 1H; Ar*H*), 7.78–7.68 (3H; Ar*H*).

Spectral data are in accordance with those reported in the literature. [6a]

2-Methoxyphenanthridine (2b) and 4-methoxyphenanthridine (2b')



2b 2-isomer



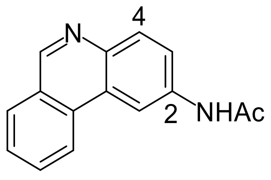
2b' 4-isomer

According to the general procedures, **1b** (189.0 mg, 0.502 mmol), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (6.0 mg, 0.0053 mmol), 2,6-lutidine (59.7 mg, 0.557 mmol), and CH_2Cl_2 (5.0 mL) afforded **2b** and **2b’** (reaction time = 24 h, –80 ˚C, **2b**:**2b’** = 6:1). After photoreaction, the reaction mixture was concentrated *in vacuo* and 10 mL NaOH aq. was added. The aqueous layer was extracted with ether (3 × 10 mL). The combined organic layer was dried over Na_2SO_4 and filtered. The filtrate was concentrated *in vacuo*. The crude product was purified by automated column chromatography on silica gel (*n*-Hexane:AcOEt = 3:2).

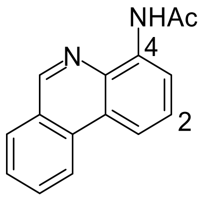
2-Isomer (**2b**) (white solid, 58.5 mg, 0.280 mmol, 56% yield) was obtained.
^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 9.16 (s, 1H; -N=C*H*-), 8.53 (d, $^3J_{HH}$ = 8.4 Hz, 1H; Ar*H*), 8.11 (d, $^3J_{HH}$ = 8.8 Hz, 1H; Ar*H*), 8.03 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 7.91 (d, $^4J_{HH}$ = 2.8 Hz, 1H; Ar*H*), 7.84 (dd, $^3J_{HH}$ = 7.2, 7.2 Hz, 1H; Ar*H*), 7.70 (dd, $^3J_{HH}$ = 7.6, 7.2 Hz, 1H; Ar*H*), 7.38 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 2.8 Hz, 1H; Ar*H*), 4.02 (s, 3H; -OCH_3).
Spectral data are in accordance with those reported in the literature. [3]

4-Isomer (**2b’**) (white solid, 7.5 mg, 0.0358 mmol, 7% yield) was obtained.
^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 9.32 (s, 1H; -N=C*H*-), 8.58 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 8.15 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 8.06 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 7.85 (dd, $^3J_{HH}$ = 7.6, 7.6 Hz, 1H; Ar*H*), 7.71 (dd, $^3J_{HH}$ = 7.6, 7.2 Hz, 1H; Ar*H*), 7.61 (dd, $^3J_{HH}$ = 8.0, 8.0 Hz, 1H; Ar*H*), 7.17 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 4.13 (s, 3H; -OCH_3).
Spectral data are in accordance with those reported in the literature. [3]

2-Acetoamidphenanthridine (2c) and 4-acetoamidphenanthridine (2c’)



2c 2-isomer



2c' 4-isomer

According to the general procedures, **1c** (201.6 mg, 0.500 mmol), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (5.6 mg, 0.0050 mmol), 2,6-lutidine (60.9 mg, 0.568 mmol), and CH_3CN (5.0 mL) afforded **2c** and **2c’** (reaction time = 48 h, 0 ˚C, **2c**:**2c’** = 5:1). After photoreaction, the reaction mixture was concentrated *in vacuo* and 10 mL NaOH aq. was added. The aqueous layer was extracted with AcOEt (3 × 10 mL). The combined organic layer was dried over Na_2SO_4 and filtered. The filtrate was concentrated *in vacuo*. The crude product was purified by automated column chromatography on silica gel (AcOEt).

2-Isomer (**2c**) (white solid, 61.8 mg, 0.262 mmol, 52% yield) was obtained.

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 9.18 (s, 1H; -N=C*H*-), 9.08 (s, 1H; Ar*H*), 8.54 (d, $^3J_{HH}$ = 8.4 Hz, 1H; Ar*H*), 8.10 (d, $^3J_{HH}$ = 8.8 Hz, 1H; Ar*H*), 8.01 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 7.89 (br s, 1H; -N*H*$COCH_3$), 7.81 (dd, $^3J_{HH}$ = 8.0, 7.6 Hz, 1H; Ar*H*), 7.69 (dd, $^3J_{HH}$ = 7.6, 7.2 Hz, 1H; Ar*H*), 7.63 (d, $^3J_{HH}$ = 8.8 Hz, 1H; Ar*H*), 2.29 (s, 3H; -NHCOCH_3).

^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 168.8, 152.6, 141.4, 137.0, 132.5, 131.1, 130.7, 128.8, 127.9, 126.7, 125.0, 122.4, 121.4, 112.1, 24.96.

HRMS (ESI-TOF) Calcd. for $C_{15}H_{12}N_2O$ $[M+Na]^+$ requires 259.0842, found 259.0840.

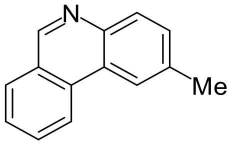
4-Isomer (**2c'**) (white solid, 6.0 mg, 0.025 mmol, 5% yield) was obtained. Recrystallization from $CHCl_3$ afforded crystals, which are suitable for single-crystal X-ray structure analysis (CCDC 1978373).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 9.96 (br s, 1H; -N*H*$COCH_3$), 9.18 (s, 1H; -N=C*H*-), 8.84 (d, $^3J_{HH}$ = 7.6 Hz, 1H; Ar*H*), 8.61 (d, $^3J_{HH}$ = 8.4 Hz, 1H; Ar*H*), 8.25 (d, $^3J_{HH}$ = 8.4 Hz, 1H; Ar*H*), 8.08 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 7.89 (dd, $^3J_{HH}$ = 8.4, 7.2 Hz, 1H; Ar*H*), 7.74 (dd, $^3J_{HH}$ = 8.0, 7.2 Hz, 1H; Ar*H*), 7.67 (dd, $^3J_{HH}$ = 8.0, 8.0 Hz, 1H; Ar*H*), 2.38 (s, 3H; -NHCOCH_3).

^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 168.9, 151.3, 135.5, 133.5, 132.8, 131.6, 129.1, 128.0, 127.8, 126.6, 124.0, 122.4, 116.9, 116.3, 25.40.

HRMS (ESI-TOF) Calcd. for $C_{15}H_{12}N_2O$ $[M+Na]^+$ requires 259.0842, found 259.0841.

2-Methylphenanthridine (2d)

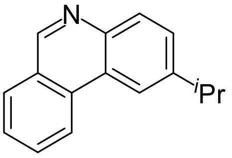


According to the general procedures, **1d** (181 mg, 0.503 mmol), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (5.8 mg, 0.0052 mmol), 2,6-lutidine (59.7 mg, 0.557 mmol), and CH_2Cl_2 (5.0 mL) afforded **2d** (64.5 mg, 0.0334 mmol, 66% yield, reaction time = 24 h, rt) as a white solid after purification with automated column chromatography on silica gel (*n*-hexane:AcOEt = 1:1). Recrystallization from *n*-hexane/AcOEt afforded crystals, which are suitable for single-crystal X-ray structure analysis (CCDC 1978372).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 9.23 (s, 1H; -C*H*=N-), 8.61 (d, $^3J_{HH}$ = 8.4 Hz, 1H; Ar*H*), 8.37 (s, 1H; Ar*H*), 8.10 (d, $^3J_{HH}$ = 8.4 Hz, 1H; Ar*H*), 8.04 (d, $^3J_{HH}$ = 7.6 Hz, 1H; Ar*H*),7.86 (dd, $^3J_{HH}$ = 7.2, 7.2 Hz, 1H; Ar*H*), 7.71 (dd, $^3J_{HH}$ = 7.6, 7.2 Hz, 1H; Ar*H*), 7.58 (dd, $^3J_{HH}$ = 8.4, 1.6 Hz, 1H; Ar*H*), 2.64 (s, 3H; -CH_3).

Spectral data are in accordance with those reported in the literature. [6b]

2-Isopropylphenanthridine (2e)



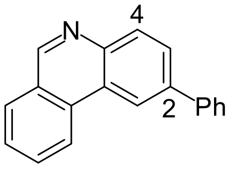
According to the general procedures, **1e** (194.6 mg, 0.501 mmol), [Ir{dF(CF$_3$)ppy}$_2$(dtbbpy)]PF$_6$ (5.7 mg, 0.0051 mmol), 2,6-lutidine (59.2 mg, 0.552 mmol) and CH$_2$Cl$_2$ (5.0 mL) afforded **2e** (90.9 mg, 0.411 mmol, 82% yield, reaction time = 24 h, –80 ˚C) as yellow oil after purification with automated column chromatography on silica gel (*n*-hexane:AcOEt = 1:1).

^{1}H NMR (400 MHz, CDCl$_3$, rt) δ 9.22 (s, 1H; -N=C*H*-), 8.61 (d, $^3J_{\mathrm{HH}}$ = 8.4 Hz, 1H; Ar*H*), 8.38 (s, 1H; Ar*H*), 8.14 (d, $^3J_{\mathrm{HH}}$ = 8.4 Hz, 1H; Ar*H*), 7.99 (d, $^3J_{\mathrm{HH}}$ = 7.6 Hz, 1H; Ar*H*), 7.82 (dd, $^3J_{\mathrm{HH}}$ = 7.2 Hz, 1H; Ar*H*), 7.67–7.63 (2H; Ar*H*), 3.19 (sep, $^3J_{\mathrm{HH}}$ = 6.8 Hz, 1H; -C*H*(CH$_3$)$_2$), 1.41 (d, $^3J_{\mathrm{HH}}$ = 6.8 Hz, 6H; -CH(C*H*$_3$)$_2$).

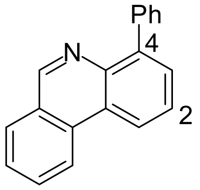
^{13}C NMR (126 MHz, CDCl$_3$, rt) δ 152.7, 147.9, 143.1, 132.6, 130.8, 130.1, 128.8, 127.9, 127.3, 126.5, 124.0, 121.9, 119.2, 34.64, 24.27.

HRMS (ESI-TOF) calculated for C$_{16}$H$_{11}$N [M+Na]$^+$ requires 244.1097, found 244.1099.

2-Phenylphenanthridine (2f) and 4-phenylphenanthridine (2f’)



2f 2-isomer



2f' 4-isomer

According to the general procedures, **1f** (213.0 mg, 0.504 mmol), [Ir{dF(CF$_3$)ppy}$_2$(dtbbpy)]PF$_6$ (5.8 mg, 0.0052 mmol), 2,6-lutidine (64.6 mg, 0.603 mmol), and CH$_2$Cl$_2$ (5.0 mL) afforded **2f** and **2f’** (reaction time = 48 h, –80 ˚C, **2f**:**2f’** = 3:1). After photoreaction, 10 mL NaOH aq. was added in reaction mixture. The aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 10 mL). The combined organic layer was dried over Na$_2$SO$_4$ and filtered. The filtrate was concentration *in vacuo*. The crude product was purified by automated column chromatography on silica gel (n-hexane:AcOEt = 7:3).

2-Isomer (**2f**) (white solid, 35.0 mg, 0.137 mmol, 27% yield) was obtained.

^{1}H NMR (400 MHz, CDCl$_3$, rt) δ 9.27 (s, 1H; -N=C*H*-), 8.72 (d, $^4J_{\mathrm{HH}}$ = 1.6 Hz, 1H; Ar*H*), 8.64 (d, $^3J_{\mathrm{HH}}$ = 8.4 Hz, 1H; Ar*H*), 8.25 (d, $^3J_{\mathrm{HH}}$ = 8.4 Hz, 1H; Ar*H*), 8.03 (d, $^3J_{\mathrm{HH}}$ = 7.6 Hz, 1H; Ar*H*), 7.97 (dd, $^3J_{\mathrm{HH}}$ = 8.8, $^4J_{\mathrm{HH}}$ = 2.0 Hz, 1H; Ar*H*), 7.84 (dd, $^3J_{\mathrm{HH}}$ = 8.0, 7.6 Hz, 1H; Ar*H*), 7.77 (d, $^3J_{\mathrm{HH}}$ = 7.2 Hz, 2H; Ar*H*), 7.69 (dd, $^3J_{\mathrm{HH}}$ = 8.0, 6.8 Hz, 1H; Ar*H*), 7.53 (dd, $^3J_{\mathrm{HH}}$ = 8.0, 7.2 Hz, 2H; Ar*H*), 7.43 (t, $^3J_{\mathrm{HH}}$ = 7.6 Hz, 1H; Ar*H*).

^{13}C NMR (126 MHz, CDCl$_3$, rt) δ 153.4, 143.7, 140.8, 139.8, 132.5, 131.0, 130.4, 128.9, 128.8, 128.0, 127.6, 127.5 (3C), 126.5, 124.2, 121.8, 120.4.

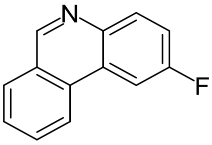
HRMS (ESI-TOF) Calcd. for C$_{19}$H$_{13}$N [M]$^+$ requires 278.0940, found 278.0941.

4-Isomer (**2f'**) (colorless oil, 11.8 mg, 0.046 mmol, 9% yield) was obtained.

^{1}H NMR (400 MHz, CDCl$_3$, rt) δ 9.32 (s, 1H; -N=C*H*-), 8.68 (d, $^3J_{HH}$ = 8.4 Hz, 1H; Ar*H*), 8.63 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 2.0 Hz, 1H; Ar*H*), 8.05 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 7.89 (dd, $^3J_{HH}$ = 8.0, 7.6 Hz, 1H; Ar*H*), 7.79-7.71 (5H; Ar*H*), 7.53 (dd, $^3J_{HH}$ = 8.0, 7.2 Hz, 2H; Ar*H*), 7.44 (t, $^3J_{HH}$ = 7.6 Hz, 1H; Ar*H*).

Spectral data are in accordance with those reported in the literature. [6c]

2-Fluorophenanthridine (2g) (NMR scale)

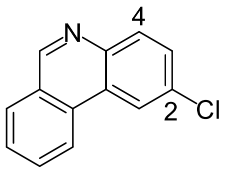


According to the general procedures, **1g** (18.4 mg, 0.0505 mmol), [Ir{dF(CF$_3$)ppy}$_2$(dtbbpy)]PF$_6$ (1.2 mg, 0.0011 mmol), 2,6-lutidine (5.9 mg, 0.0551 mmol), and CD$_2$Cl$_2$ (0.5 mL) afforded **2g** (7.4 mg, 0.0375 mmol, 74% yield, reaction time = 96 h, –80 ˚C) as a white solid after purification with preparative thin layer chromatography on silica gel (*n*-hexane:AcOEt = 1:1).

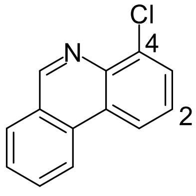
^{1}H NMR (400 MHz, CDCl$_3$, rt) δ 9.24 (s, 1H; -N=C*H*-), 8.49 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 8.20–8.16 (2H; Ar*H*), 8.07 (dd, $^3J_{HH}$ = 8.0, 0.4 Hz, 1H; Ar*H*), 7.88 (m, 1H; Ar*H*), 7.75 (m, 1H; Ar*H*), 7.48 (m, 1H; Ar*H*).

Spectral data are in accordance with those reported in the literature. [6b]

2-Chlorophenanthridine (2h) and 4-chlorophenanthridine (2h')



2h 2-isomer



2h' 4-isomer

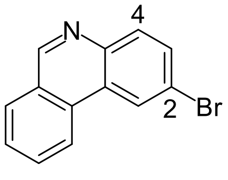
According to the general procedures, **1h** (191.9 mg, 0.504 mmol), [Ir{dF(CF$_3$)ppy}$_2$(dtbbpy)]PF$_6$ (5.7 mg, 0.0051 mmol), 2,6-lutidine (61.0 mg, 0.569 mmol), and CH$_2$Cl$_2$ (5.0 mL) afforded **2h** and **2h'** (reaction time = 48 h, 0 °C, **2h**:**2h'** = 2:1).

2-Isomer (**2h**) (white solid, 52.3 mg, 0.245 mmol, 49% yield) was obtained after purification with

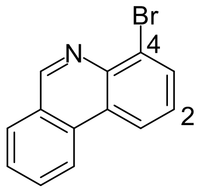
automated column chromatography on silica gel (*n*-hexane:AcOEt = 1:1).
^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 9.21 (s, 1H; -N=C*H*-), 8.45–8.43 (2H; Ar*H*), 8.08 (d, $^3J_{HH}$ = 8.8 Hz, 1H; Ar*H*), 8.01 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 7.83 (dd, $^3J_{HH}$ = 8.0, 7.2 Hz, 1H; Ar*H*), 7.71 (dd, $^3J_{HH}$ = 7.6, 7.6 Hz, 1H; Ar*H*), 7.64 (dd, $^3J_{HH}$ = 8.4, $^4J_{HH}$ = 2.0 Hz, 1H; Ar*H*).
Spectral data are in accordance with those reported in the literature. [6b]

4-Isomer (**2h'**) (white solid, 26.2 mg, 0.123 mmol, 24% yield) was obtained after purification with automated column chromatography on silica gel (*n*-hexane:AcOEt = 1:1).
^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 9.38 (s, 1H; -N=C*H*-), 8.57 (d, $^3J_{HH}$ = 8.4 Hz, 1H; Ar*H*), 8.48 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 8.07 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 7.89–7.83 (2H; Ar*H*), 7.74 (dd, $^3J_{HH}$ = 7.6, 7.6 Hz, 1H; Ar*H*), 7.57 (dd, $^3J_{HH}$ = 8.0, 8.0 Hz, 1H; Ar*H*).
Spectral data are in accordance with those reported in the literature. [6d]

2-Bromophenanthridine (2i) and 4-bromophenanthridine (2i')



2i 2-isomer



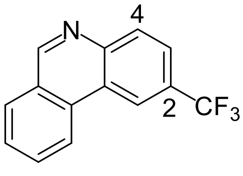
2i' 4-isomer

According to the general procedures, **1i** (210.5 mg, 0.495 mmol), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (5.9 mg, 0.0053 mmol), 2,6-lutidine (60.0 mg, 0.560 mmol), and CH_2Cl_2 (5.0 mL) afforded **2i** and **2i'** (reaction time = 48 h, 0 °C, **2i**:**2i'** = 3:1).

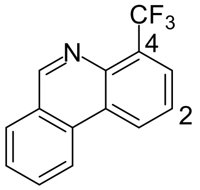
2-Isomer (**2i**) (white solid, 45.4 mg, 0.176 mmol, 36% yield) was obtained after purification with automated column chromatography on silica gel (*n*-hexane:AcOEt = 1:1).
^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 9.29 (s, 1H; -N=C*H*-), 8.71 (d, $^4J_{HH}$ = 2.0 Hz, 1H; Ar*H*), 8.55 (d, $^3J_{HH}$ = 8.4 Hz, 1H; Ar*H*), 8.08–8.06 (2H; Ar*H*), 7.90 (dd, $^3J_{HH}$ = 6.8, 6.8 Hz, 1H; Ar*H*), 7.83 (dd, $^3J_{HH}$ = 8.8, $^4J_{HH}$ = 2.0 Hz, 1H; Ar*H*), 7.76 (dd, $^3J_{HH}$ =8.0, 7.2 Hz, 1H; Ar*H*).
Spectral data are in accordance with those reported in the literature. [6b]

4-Isomer (**2i'**) (white solid, 15.8 mg, 0.0612 mmol, 12% yield) was obtained after purification with automated column chromatography on silica gel (*n*-hexane:AcOEt = 1:1).
^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 9.38 (s, 1H; -N=C*H*-), 8.58 (d, $^3J_{HH}$ = 8.4 Hz, 1H; Ar*H*), 8.53 (d, $^3J_{HH}$ = 8.4 Hz, 1H; Ar*H*), 8.09–8.04 (2H; Ar*H*), 7.88 (dd, $^3J_{HH}$ = 8.0, 7.6 Hz, 1H; Ar*H*), 7.74 (dd, $^3J_{HH}$ = 8.0, 8.0 Hz, 1H; Ar*H*), 7.51 (dd, $^3J_{HH}$ = 8.0, 7.6 Hz, 1H; Ar*H*).
Spectral data are in accordance with those reported in the literature. [6e]

2-(Trifluoromethyl)phenanthridine (2j) and 4-(trifluoromethyl)phenanthridine (2j')



2j 2-isomer



2j' 4-isomer

According to the general procedures, **1j** (204.3 mg, 0.493 mmol), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (5.6 mg, 0.0051 mmol), 2,6-lutidine (59.9 mg, 0.559 mmol), and CH_2Cl_2 (5.0 mL) following the general procedures afforded **2j** and **2j'**(reaction time = 96 h, 0 °C, **2j**:**2j'** = 3:1).

2-Isomer (**2j**) (white solid, 36.5 mg, 0.148 mmol, 30% yield) after purification with automated column chromatography on silica gel (*n*-hexane:AcOEt = 4:1).

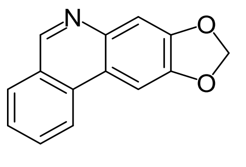
^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 9.32 (s, 1H; -N=C*H*-), 8.78 (s, 1H; Ar*H*), 8.57 (d, $^3J_{HH}$ = 8.4 Hz, 1H; Ar*H*), 8.25 (d, $^3J_{HH}$ = 8.4 Hz, 1H; Ar*H*), 8.05 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 7.92–7.87 (2H; Ar*H*), 7.75 (dd, $^3J_{HH}$ = 7.6, 7.2 Hz, 1H; Ar*H*).

Spectral data are in accordance with those reported in the literature. [6f]

4-Isomer (**2j'**); 12% yield (was determined by ^{1}H and ^{19}F NMR).

Spectral data are in accordance with those reported in the literature. [6d]

[1,3]Dioxolo[4,5-c]phenanthridine (2l)

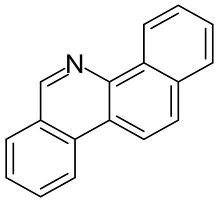


According to the general procedures, **1l** (197.4 mg, 0.506 mmol), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (5.8 mg, 0.0052 mmol), 2,6-lutidine (60.0 mg, 0.560 mmol), and CH_2Cl_2 (10 mL) afforded **2l** (79.0 mg, 0.354 mmol, 70% yield, reaction time = 24 h, rt) as a white solid. After photoreaction, the reaction mixture was concentrated *in vacuo* and 10 mL NaOH aq. was added. The aqueous layer was extracted with AcOEt (3 × 10 mL). The combined organic layer was dried over Na_2SO_4 and filtered. The filtrate was concentrated *in vacuo*. The crude product was purified by automated column chromatography on silica gel (*n*-hexane:AcOEt = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 9.11 (s, 1H; -N=C*H*-), 8.31 (d, $^3J_{HH}$ = 8.4 Hz, 1H; Ar*H*), 7.95 (d, $^3J_{HH}$ = 8.4 Hz, 1H; Ar*H*), 7.78 (s, 1H; Ar*H*), 7.74 (dd, $^3J_{HH}$ = 7.6, 7.2 Hz, 1H; Ar*H*), 7.59 (dd, $^3J_{HH}$ = 7.6, 7.2 Hz, 1H; Ar*H*), 7.50 (s, 1H; Ar*H*), 6.11 (s, 2H; -OC*H*$_2$O-).

Spectral data are in accordance with those reported in the literature. [6g]

Benzo[c]phenanthridine (2m)

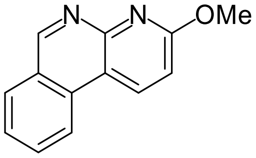


According to the general procedures, **1m** (197.0 mg, 0.497 mmol), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (5.9 mg, 0.0053 mmol), 2,6-lutidine (60.5 mg, 0.565 mmol), and CH_2Cl_2 (5.0 mL) afforded **2m** (84.3 mg, 0.368 mmol, 74% yield, reaction time = 24 h, –80 °C) as a white solid after purification with automated column chromatography on silica gel (*n*-hexane:AcOEt = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 9.50 (s, 1H; N=C*H*), 9.42 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 8.71 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 8.58 (d, $^3J_{HH}$ = 8.8 Hz, 1H; Ar*H*), 8.17 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 8.06 (d, $^3J_{HH}$ = 8.8 Hz, 1H; Ar*H*), 8.00 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 7.92 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.2 Hz, 1H; Ar*H*), 7.80–7.69 (3H; Ar*H*).

Spectral data are in accordance with those reported in the literature. [6h]

2-Methoxybenzo[c][1,8]naphthyridine (2n)



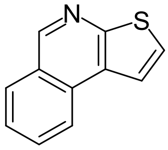
According to the general procedures, **1n** (189.1 mg, 0.501 mmol), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (5.6 mg, 0.0050 mmol), 2,6-lutidine (59.1 mg, 0.552 mmol), and CH_2Cl_2 (5.0 mL) afforded **2n** (52.1 mg, 0.228 mmol, 50% yield, reaction time = 24 h, rt) as an orange solid. After photoreaction, the reaction mixture was concentrated *in vacuo* and 10 mL NaOH aq. was added. The aqueous layer was extracted with AcOEt (3 × 10 mL). The combined organic layer was dried over Na_2SO_4 and filtered. The filtrate was concentrated *in vacuo*. The crude product was purified by automated column chromatography on silica gel (*n*-hexane:AcOEt = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 9.34 (s, 1H; -N=C*H*-), 8.62 (d, $^3J_{HH}$ = 8.8 Hz, 1H; Ar*H*), 8.32 (d, $^3J_{HH}$ = 8.4 Hz, 1H; Ar*H*), 7.97 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 7.75 (dd, $^3J_{HH}$ = 7.6, 7.6 Hz, 1H; Ar*H*), 7.58 (dd, $^3J_{HH}$ = 7.6, 7.6 Hz, 1H; Ar*H*), 7.02 (d, $^3J_{HH}$ = 8.8 Hz, 1H; Ar*H*), 4.14 (s, 3H; -OC*H*$_3$).

^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 164.1, 156.1, 152.6, 133.7, 132.9, 131.2, 128.7, 126.6, 125.5, 121.1, 113.5, 112.8, 53.9.

HRMS (ESI-TOF) Calcd. for $C_{13}H_{10}N_2O$ $[M+Na]^+$ requires 233.0685, found 233.0686.

Thieno[2,3-c]isoquinoline (2o)

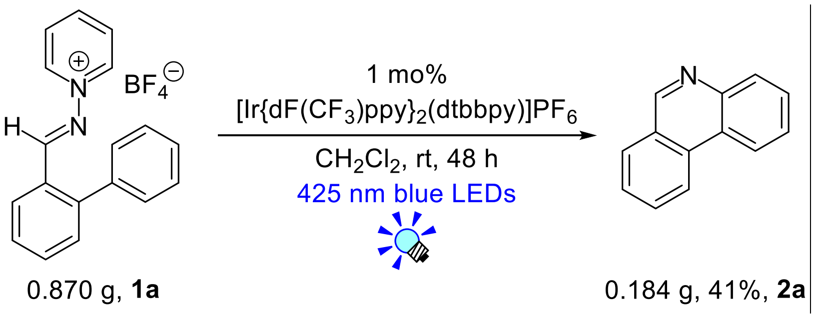


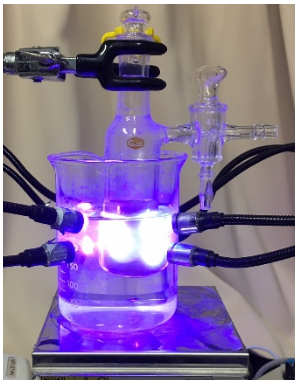
According to the general procedures, **1o** (176.6 mg, 0.501 mmol), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (5.8 mg, 0.0052 mmol), 2,6-lutidine (60.1 mg, 0.561 mmol), and CH_2Cl_2 (5.0 mL) afforded **2o** (57.4 mg, 0.310 mmol, 62% yield, reaction time = 24 h, –80 ˚C) as white solid after purification with automated column chromatography on silica gel (*n*-pentane:ether = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 9.09 (s, 1H; -N=C*H*-), 8.18 (d, $^3J_{HH}$ = 8.4 Hz, 1H; Ar*H*), 8.02 (d, 1H; Ar*H*), 7.79 (d, $^3J_{HH}$ = 5.6 Hz, 1H; Ar*H*), 7.75 (d, $^3J_{HH}$ = 8.0, 7.2 Hz, 1H; Ar*H*), 7.61-7.57 (2H; Ar*H*).

Spectral data are in accordance with those reported in the literature. [6i]

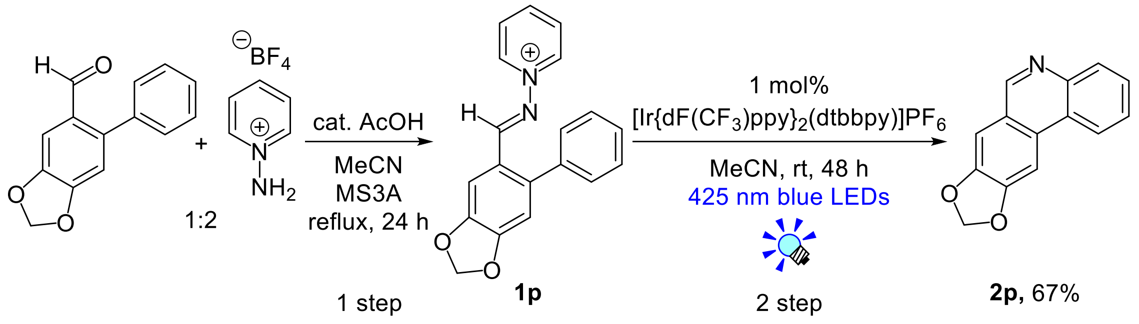
A Large-scale Reaction of 1a

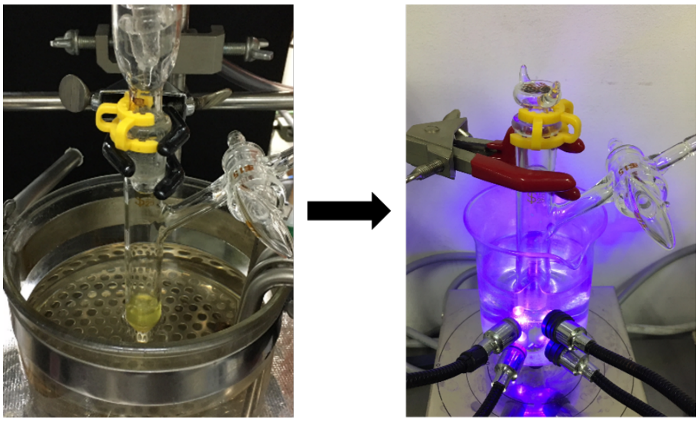




Under N_2, to 1a (0.870 g, 2.51 mmol) dissolved in a mixture of CH_2Cl_2 (5.0 mL) in a 50 mL-Schlenk tube and [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (0.005 mmol) were added. The mixture was degassed by three freeze-pump-thaw cycles. The reaction was carried out at rt (water bath) under irradiation of visible light (placed at a distance of 2–3 cm from the blue LED lamps: *hv* = 425 ± 15 nm). Then, the reaction mixture was concentrated *in vacuo* to remove the volatile compounds. The crude product was purified by automated column chromatography on silica gel (*n*-hexane:AcOEt = 7:3) to give **2a** (0.184 g, 1.03 mmol, 41% yield, reaction time = 48 h, rt).

One-pot Synthesis of Trisphaeridine (2p)



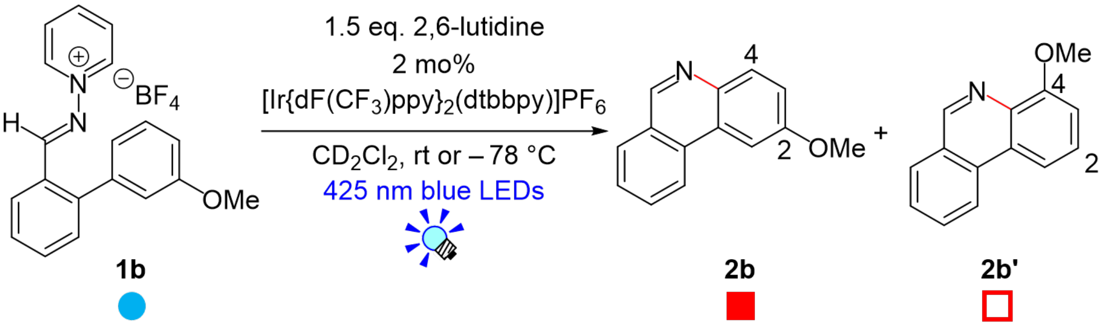


One-pot synthesis of Trisphaeridine (**2p**) was performed with 6-phenylbenzo[d][1,3]dioxole-5-carbaldehyde. To a mixture of 1-aminopyridinium tetrafluoroborate (161.6 mg, 0.888 mmol), CH_3CN (5 mL), AcOH (5 drops) and MS3A in Schlenk tube (10 mL) was added 6-phenylbenzo[d][1,3]dioxole-5-carbaldehyde (102.0 mg, 0.451 mmol) at rt under N_2. The mixture solution was stirred at reflux temperature. After 24 h, the solution was cooled at rt and $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (5.2 mg, 0.0046 mmol) was added. Then, the mixture was degassed by three freeze-pump-thaw cycles. The photocatalytic reaction was carried out at rt (water bath) under irradiation of visible light (placed at a distance of 2–3 cm from the blue LED lamps: $h\nu = 425 \pm 15$ nm). Then, the reaction mixture was concentrated *in vacuo* to remove the volatile compounds and 10 mL NaOH aq. was added. The aqueous layer was extracted with AcOEt (3 × 10 mL). The combined organic layer was dried over Na_2SO_4 and filtered. The filtrate was concentrated *in vacuo*. The crude product was purified by automated column chromatography on silica gel (n-hexane:AcOEt = 1:1) to give Trisphaeridine (**2p**, 67.2 mg, 0.301 mmol, 67% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 9.22 (s, 1H; -N=C*H*-), 8.49 (d, $^3J_{HH}$ = 8.0 Hz, 1H; Ar*H*), 8.31 (d, $^3J_{HH}$ = 8.4 Hz, 1H; Ar*H*), 8.00 (s, 1H; Ar*H*), 8.85 (dd, $^3J_{HH}$ = 8.0, 8.0 Hz, 1H; Ar*H*), 7.77 (dd, $^3J_{HH}$ = 7.2, 7.2 Hz, 1H; Ar*H*), 7.44 (s, 1H; ArH), 6.29 (s, 2H; -OCH_2O-).

Spectral data are in accordance with those reported in the literature. [3]

NMR Experiment with (*E*)-3’-Methoxy-[1,1’]-biphenyl-2-iminylpyridinium Tetrafluoroborate (1b)



rt : 93% yield (**2b**:**2b'**/1.4:1.0), 2 h
– 78 °C: 96% yield (**2b**:**2b'**/8:1), 2 h

Under N_2, an NMR tube was charged with **1b** (50.0 µmol), CD_2Cl_2 (0.5 mL), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (1.00 µmol), 2,6-lutidine (75.0 µmol) and dimethylsulfone (an internal standard). The mixture was degassed by three freeze-pump-thaw cycles. The reaction was carried out at rt (water bath) or –78 ˚C (dryice MeOH) under irradiation of visible light (placed at a distance of 2–3 cm from the blue LED lamps: hν = 425 nm ± 15 nm). Then, the reaction was followed by ^{1}H NMR spectroscopy.

^{1}H NMR (400 MHz, CD_2Cl_2, rt), –78 °C

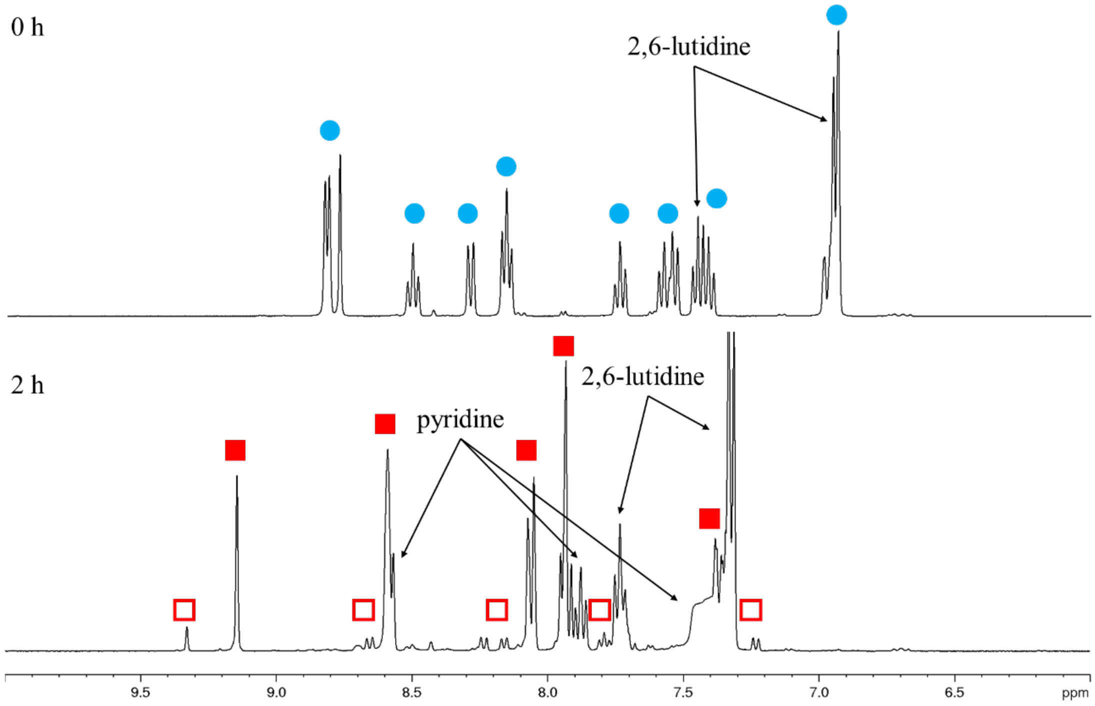
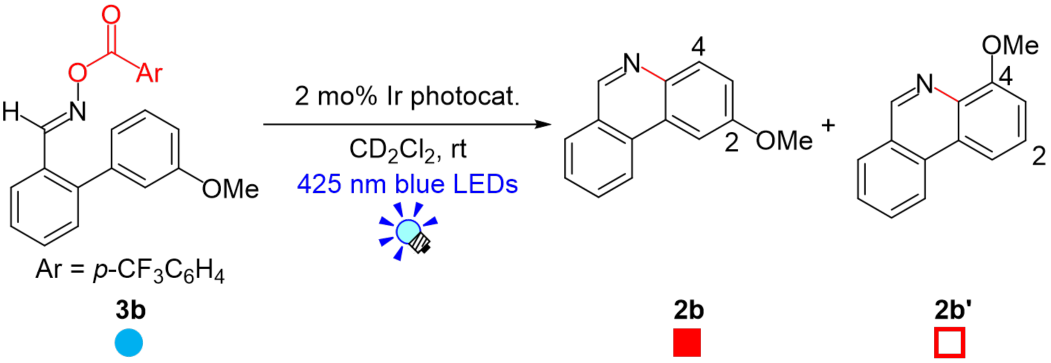


Figure S4 ^{1}H NMR spectra for the reaction of **1b**.

NMR Experiment with (*E*)-3’-Methoxybiphenyl-2-carbaldehyde *O*-4-(trifluoromethyl)benzoyl Oxime (3b)



Ir-1: 96% yield (**2b**:**2b'**/1:4), 8 h
Ir-3: 67% yield (**2b**:**2b'**/1:3), 1 h

Under N_2, an NMR tube was charged with **3b** (50.0 μmol), CD_2Cl_2 (0.5 mL), Ir photocat. (1.00 μmol, **Ir-1**: *fac*-[Ir(ppy)$_3$], **Ir-3**: [Ir{dF(CF$_3$)ppy}$_2$(dtbbpy)]PF$_6$) and dimethylsulfone (an internal standard). The mixture was degassed by three freeze-pump-thaw cycles. The reaction was carried out at rt (water bath) under irradiation of visible light (placed at a distance of 2–3 cm from the blue LED lamps: hν = 425 nm ± 15 nm). Then, the reaction was followed by ^{1}H NMR spectroscopy.

^{1}H NMR (400 MHz, CD_2Cl_2, rt, **Ir-3**)

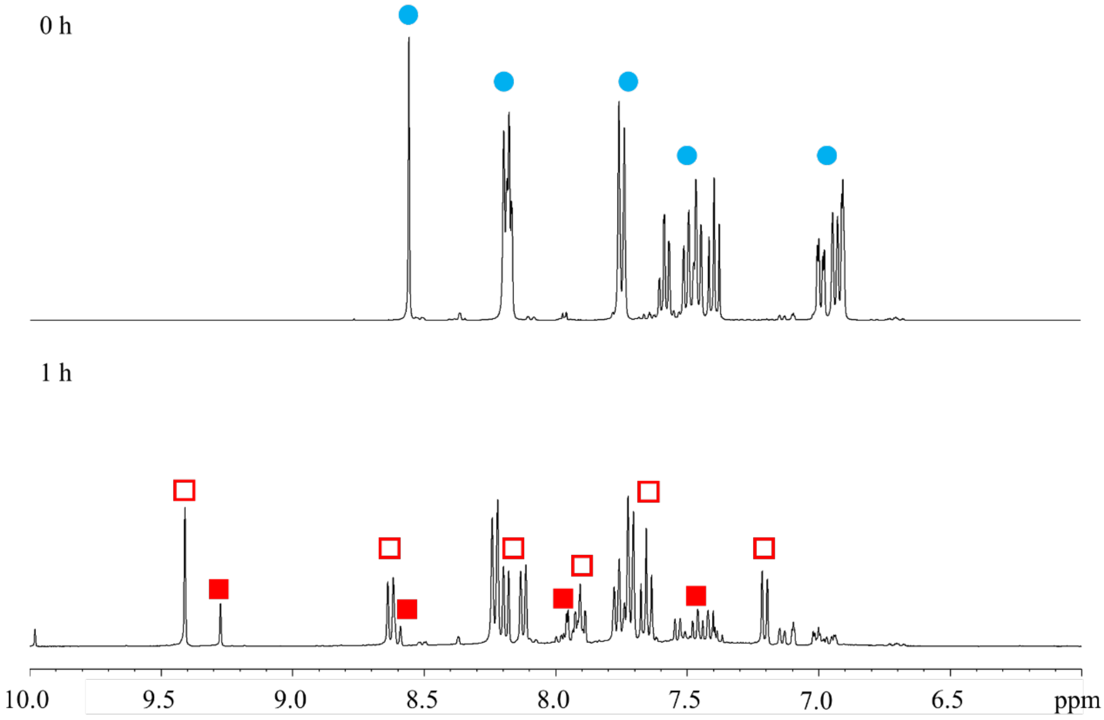


Figure S5 ^{1}H NMR spectra for the reaction of **3b**.

Cyclic Voltammograms for Iminylpyridinium Salts

Cyclic voltammetry was performed using Hokutodenkyoku HZ-5000 analyzer under N_2 at rt (observed in 2.0 mM CH_2Cl_2; [^{n}Bu$_4$N](PF$_6$) = 0.1 M; Ag/AgNO$_3$ = electrode; reported with respect to the [FeCp$_2$]/[FeCp$_2$]+ couple).

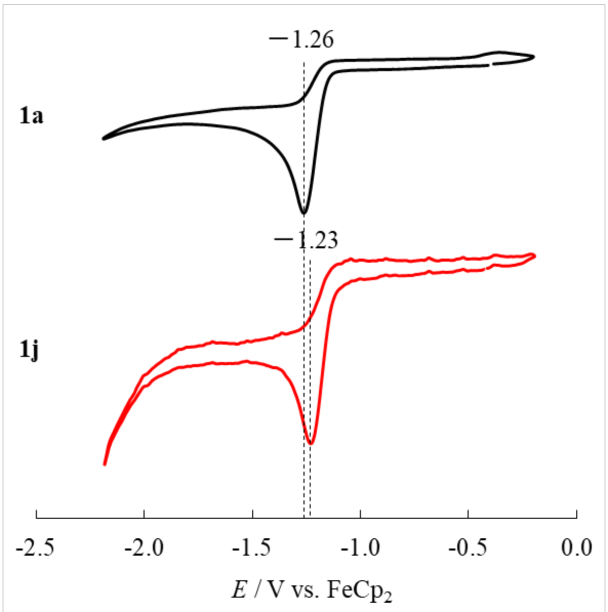


Figure S6 Reduction potentials of **1a** (R = H), **1j** (R = CF_3).

Luminescence Spectra of Photocatalysts

Luminescence spectra was obtained using HITACHI F-7000 under N_2 (observed in 0.1 mM CH_2Cl_2, **Ir-1**; *fac*-[Ir(ppy)$_3$], **Ir-2**; [Ir(ppy)$_2$(dtbbpy)]PF$_6$, **Ir-3**; [Ir{dF(CF$_3$)ppy}$_2$(dtbbpy)]PF$_6$, **Ir-4**; [Ir{dF(CF$_3$)ppy}$_2$(bpy)]PF$_6$, **Ru**; [Ru(bpy)$_3$](PF$_6$)$_2$).

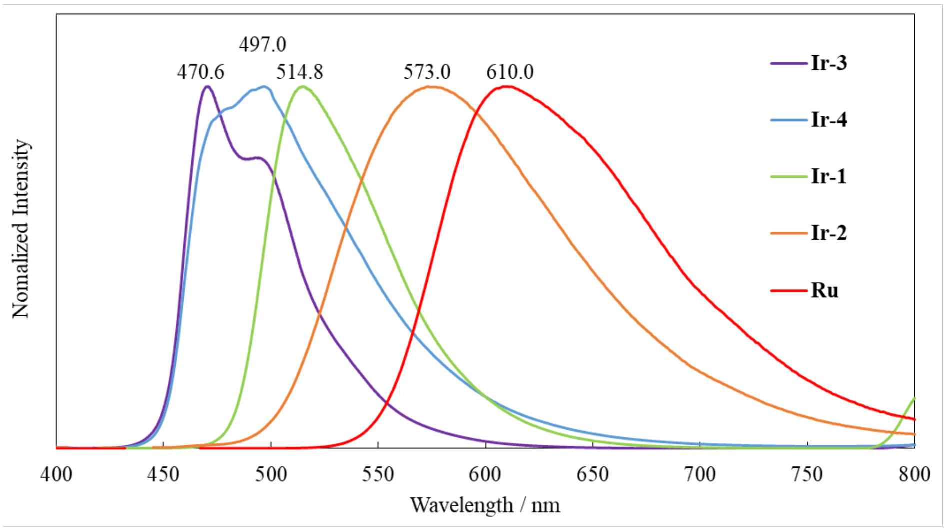


Figure S7 Luminescence spectra and maximum emission wavelength of photocatalysts.

Luminescence Quenching Experiments

A CH_2Cl_2 solution of the [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (3×10^{-5} M in CH_2Cl_2) was prepared as to show the absorbance = 0.1 at excitation wavelength (425nm) and degassed by three freeze-pump-thaw cycles in a 1 cm quartz cell equipped with an sphere moiety for freeze. The solution of quencher (**1a**) was added to the solution of the Ir catalyst before measurement of emission intensities (469 nm).

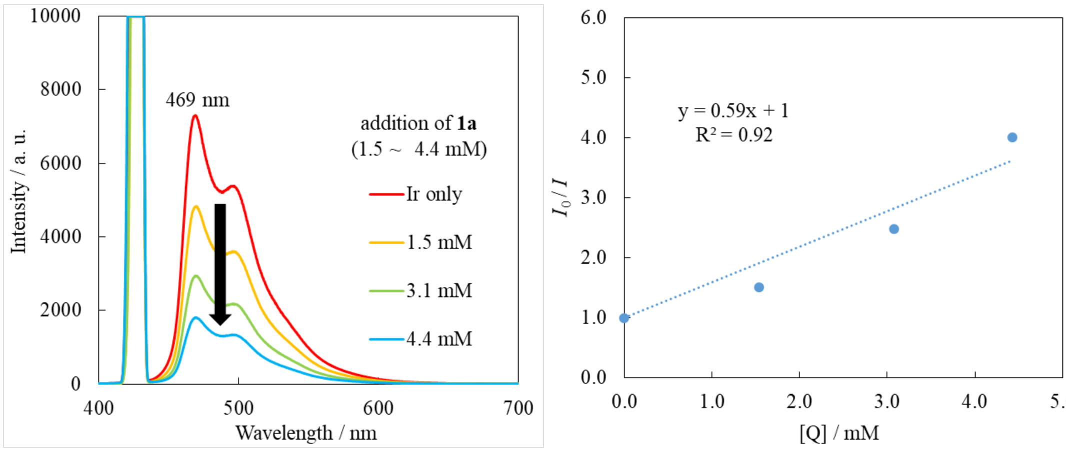
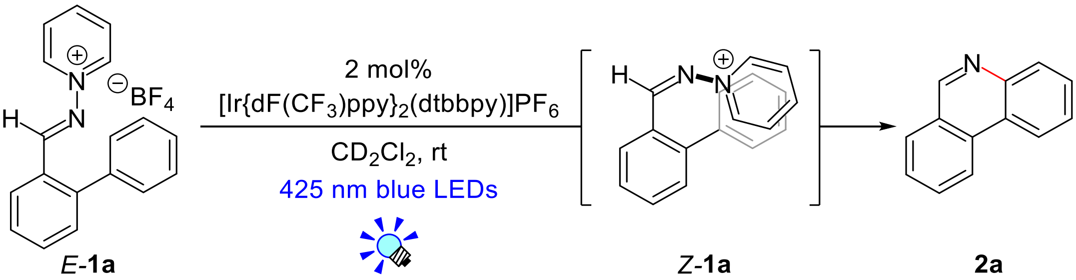


Figure S8 Stern-Volmer studies for [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 photocatalyst.

Time Profile of Photocatalytic Reaction of (*E*)-[1,1']-Biphenyl-2-iminylpyridinium Tetrafluoroborate (1a)

The photocatalytic reaction of **1a** was performed with/without visible light irradiation. The time profile is shown in **Figure S9**. As a result, continuous irradiation of visible light is necessary for efficient reaction. This result suggests that radical chain mechanism is not a main component in this reaction. In addition, it was found that photoisomerization of **1a** is reversible.



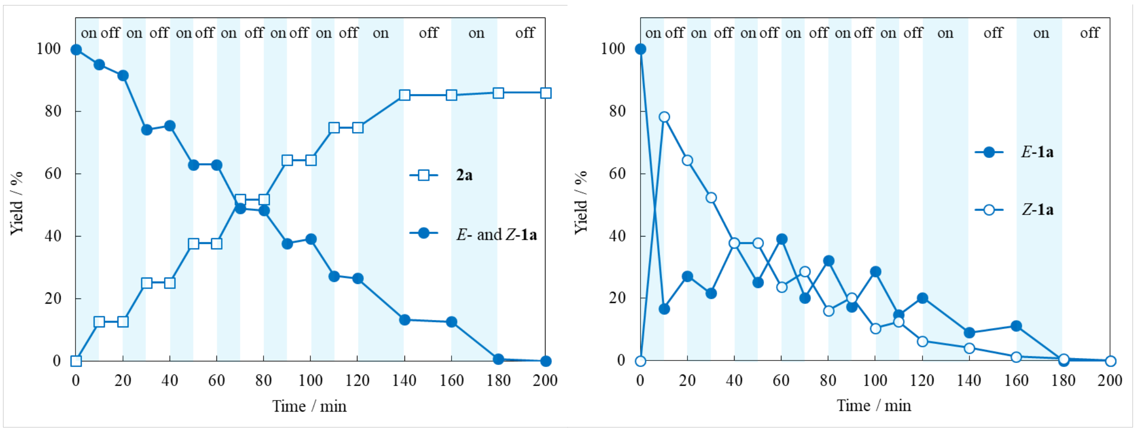


Figure S9 Time profile of photocatalytic reaction of **1a**.

DFT Calculation

Theoretical calculations were performed by using Gaussian 09(D01) program package. [7] Ground state and triplet excited state geometries of *E*- and *Z*-**1a** were optimized with the B3LYP/6-311G+(2d, p)/CPCM-dichloromethane level of theory. Vibration frequency analysis at the same level was carried out and no imaginary frequencies were found.

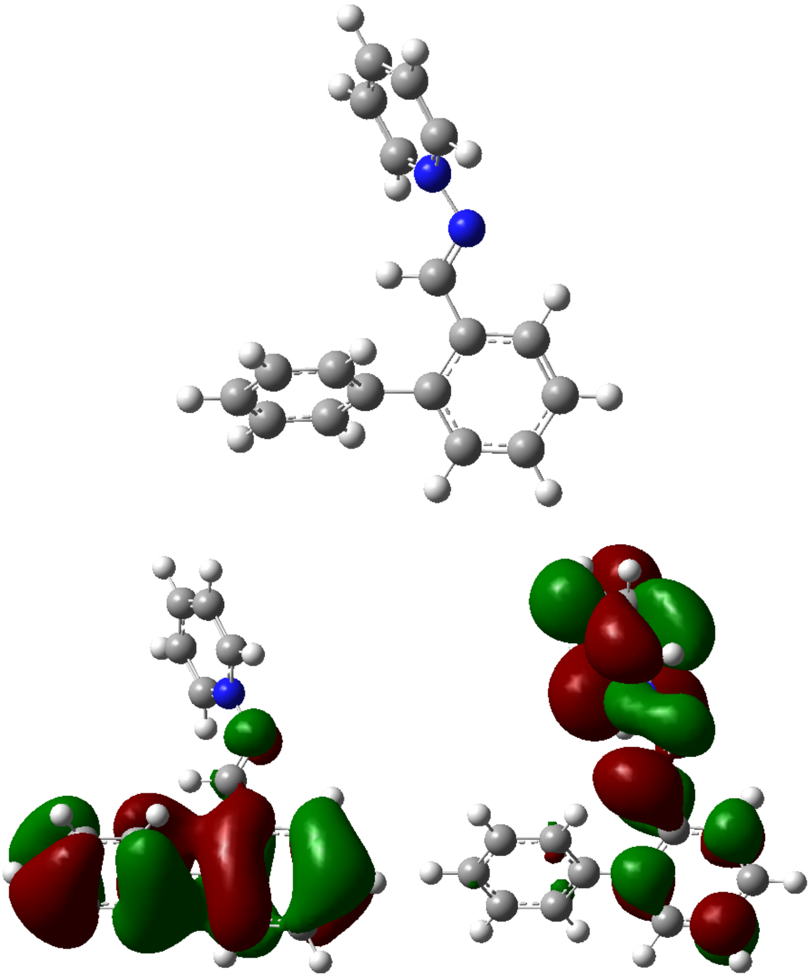
Table S1 Calculation of triplet energy E_T.

	E / hartree		E_T / kJ·mol^{-1}
	singlet	triplet	
E-**1a**	–804.47390473	–804.38488403	234
Z-**1a**	–804.46269996	–804.38421454	206

DFT level; UB3LYP/6-311G + (2d, p)/CPCM-dichloromethane.

E_T = (E (triplet) – E (singlet)) × 2625.5 kJ·mol^{-1}

E-**1a** (charge +1, singlet; –804.47390473 hartree)



HOMO LUMO

Figure S10 Grand state geometries and frontier orbital of *E*-**1a** by DFT calculations.

Table S2 Cartesian coordinates of *E*-**1a**, singlet.

C	-2.0654	0.6916	-0.0030
C	-0.8458	1.4091	0.0124
C	-0.8576	2.8141	0.0521
C	-2.0509	3.5093	0.0891
C	-3.2559	2.8060	0.0969
C	-3.2584	1.4189	0.0532
C	-2.1305	-0.7902	-0.1032
C	-1.5276	-1.4730	-1.1670
C	-1.6279	-2.8568	-1.2698
C	-2.3287	-3.5803	-0.3102

C	-2.9361	-2.9117	0.7496
C	-2.8430	-1.5285	0.8496
H	0.0848	3.3451	0.0778
H	-2.0491	4.5912	0.1238
H	-4.1963	3.3424	0.1309
H	-4.1999	0.8846	0.0355
H	-1.0043	-0.9163	-1.9358
H	-1.1655	-3.3674	-2.1059
H	-2.4062	-4.6577	-0.3900
H	-3.4830	-3.4683	1.5010
H	-3.3143	-1.0157	1.6796
C	0.4193	0.6949	0.0661
H	0.3860	-0.3682	0.2989
N	1.5384	1.2908	-0.1486
C	2.8839	-0.2553	1.1372
C	3.6223	0.5836	-0.9407
C	4.0543	-0.9690	1.2861
H	2.1049	-0.2311	1.8838
C	4.8009	-0.1192	-0.8300
H	3.3716	1.2272	-1.7702
C	5.0252	-0.9083	0.2936
H	4.1979	-1.5538	2.1835
H	5.5335	-0.0384	-1.6202
H	5.9506	-1.4583	0.3995
N	2.6844	0.4892	0.0265

E-**1a** (charge +1, triplet; -804.38488403 hartree)

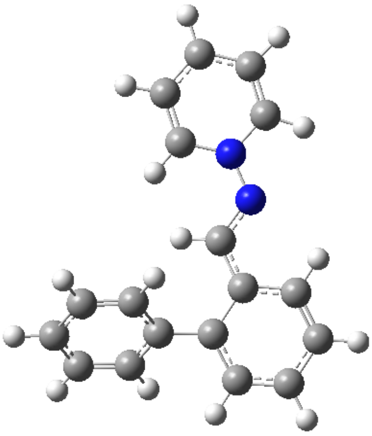


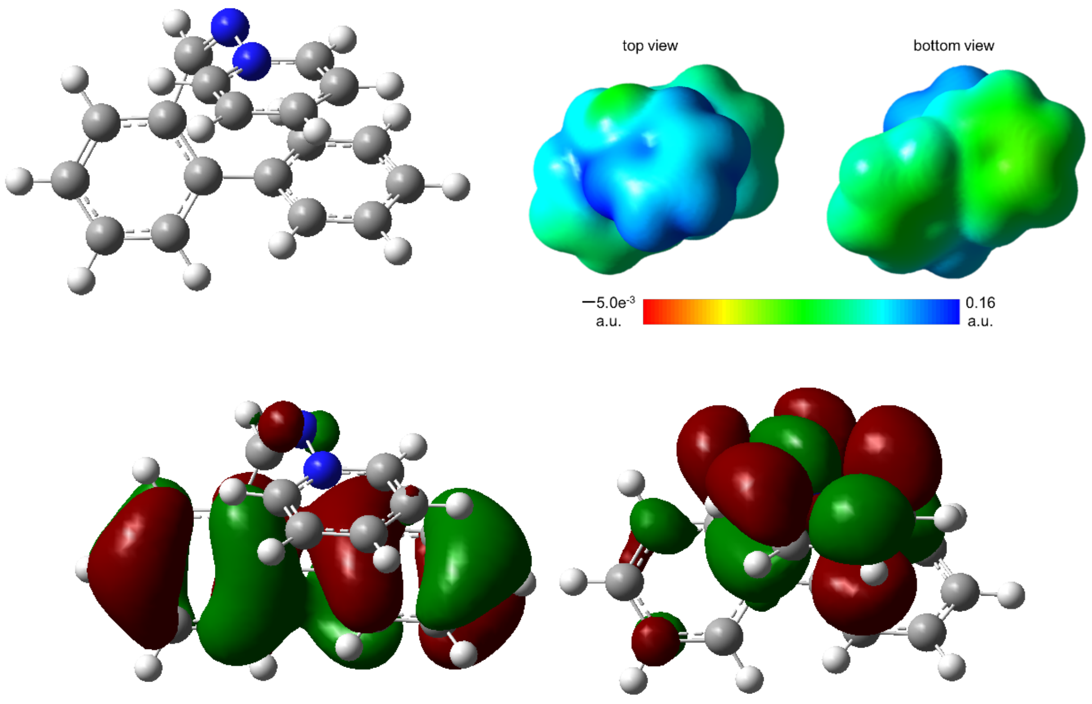
Figure S11 Triplet state geometries of *E*-**1a** by DFT calculations.

Table S3 Cartesian coordinates of *E*-**1a**, triplet.

C	-2.0949	-0.5959	0.0073
C	-0.7900	-1.2481	0.1615
C	-0.7647	-2.6587	0.4164
C	-1.9139	-3.3926	0.3995
C	-3.1642	-2.7704	0.1506
C	-3.2323	-1.3990	-0.0431
C	-2.2388	0.8609	-0.0914
C	-1.5728	1.7306	0.7953
C	-1.7811	3.0993	0.7339
C	-2.6371	3.6367	-0.2263
C	-3.2993	2.7911	-1.1156
C	-3.1144	1.4201	-1.0419
H	0.1914	-3.1348	0.5748
H	-1.8748	-4.4622	0.5636
H	-4.0698	-3.3628	0.1473
H	-4.1995	-0.9305	-0.1697
H	-0.9265	1.3240	1.5627
H	-1.2811	3.7503	1.4404
H	-2.7895	4.7076	-0.2795
H	-3.9592	3.2045	-1.8682
H	-3.6247	0.7718	-1.7429
C	0.4011	-0.5265	-0.0304

H	0.3502	0.5083	-0.3313
N	1.5731	-1.1924	0.0973
C	2.8743	0.8393	-0.1087
C	3.8566	-1.3369	0.0952
C	4.1271	1.3913	-0.1831
H	1.9802	1.4348	-0.1361
C	5.1045	-0.7962	0.0223
H	3.6455	-2.3890	0.2031
C	5.2683	0.5909	-0.1235
H	4.2053	2.4651	-0.2860
H	5.9575	-1.4581	0.0780
H	6.2546	1.0282	-0.1860
N	2.7250	-0.5346	0.0259

Z-**1a** (charge +1, singlet; -804.46169996 hartree)



HOMO LUMO

Figure S12 Grand state geometries, electrostatic potential and frontier orbital of *Z*-**1a** by DFT calculations.

Table S4 Cartesian coordinates of *Z*-**1a**, singlet.

C	-1.3390	0.7539	-0.1979
C	-1.8447	-0.2053	0.7057
C	-3.1667	-0.6576	0.5852
C	-3.9676	-0.2433	-0.4671
C	-3.4609	0.6643	-1.3917
C	-2.1737	1.1630	-1.2446
C	-0.0162	1.4108	-0.0394
C	0.3906	1.9250	1.1983
C	1.6063	2.5873	1.3282
C	2.4357	2.7515	0.2226
C	2.0384	2.2540	-1.0153
C	0.8226	1.5935	-1.1464
H	-3.5544	-1.3625	1.3114
H	-4.9794	-0.6169	-0.5577
H	-4.0789	1.0093	-2.2113
H	-1.8142	1.9166	-1.9339
H	-0.2605	1.8376	2.0599
H	1.8982	2.9875	2.2916
H	3.3809	3.2708	0.3234
H	2.6764	2.3800	-1.8816
H	0.5278	1.2023	-2.1126
C	-1.0903	-0.8036	1.8265
C	2.0581	-1.2100	0.7162
C	0.2574	-2.3153	-0.3343
C	2.8847	-1.4980	-0.3477
H	2.3712	-0.6810	1.6030
C	1.0554	-2.6295	-1.4130
H	-0.7714	-2.6261	-0.2427
C	2.3832	-2.2162	-1.4271
H	3.9129	-1.1679	-0.3153
H	0.6327	-3.2045	-2.2244
H	3.0224	-2.4626	-2.2643
N	0.0329	-1.4146	1.8939
N	0.7683	-1.6028	0.6930
H	-1.5932	-0.7967	2.7924

Z-**1a’** (charge +1, triplet; -804.38421454 hartree)

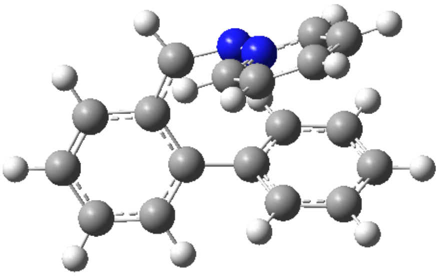


Figure S13 Triplet state geometries of *Z*-**1a** by DFT calculations.

Table S5 Cartesian coordinates of *Z*-**1a**, triplet.

C	-1.6256	0.9865	-0.2301
C	-2.0389	-0.1366	0.5541
C	-3.4160	-0.4936	0.5532
C	-4.3329	0.1849	-0.2198
C	-3.9143	1.2502	-1.0209
C	-2.5756	1.6367	-1.0127
C	-0.2329	1.5025	-0.2151
C	0.3387	1.9909	0.9701
C	1.6244	2.5234	0.9720
C	2.3614	2.5726	-0.2060
C	1.8029	2.0944	-1.3912
C	0.5160	1.5699	-1.3967
H	-3.7349	-1.3316	1.1614
H	-5.3739	-0.1133	-0.2086
H	-4.6266	1.7871	-1.6345
H	-2.2642	2.4865	-1.6082
H	-0.2385	1.9784	1.8861
H	2.0438	2.9086	1.8936
H	3.3618	2.9883	-0.2060
H	2.3711	2.1337	-2.3128
H	0.0877	1.2019	-2.3215
C	-1.1638	-0.9656	1.2954
C	2.3818	-1.3321	0.9698
C	0.6531	-2.2582	-0.3705
C	3.3326	-1.9913	0.2318

H	2.5893	-0.6865	1.8092
C	1.5818	-2.9338	-1.1239
H	-0.4123	-2.3072	-0.5362
C	2.9377	-2.8062	-0.8275
H	4.3745	-1.8672	0.4904
H	1.2400	-3.5560	-1.9390
H	3.6764	-3.3359	-1.4139
N	0.1989	-0.7809	1.4928
N	1.0604	-1.4727	0.6659
H	-1.5814	-1.7654	1.9049

Crystallographic Data

(*E*)-[1,1’]-Biphenyl-2-iminylpyridinium Tetrafluoroborate (1a)

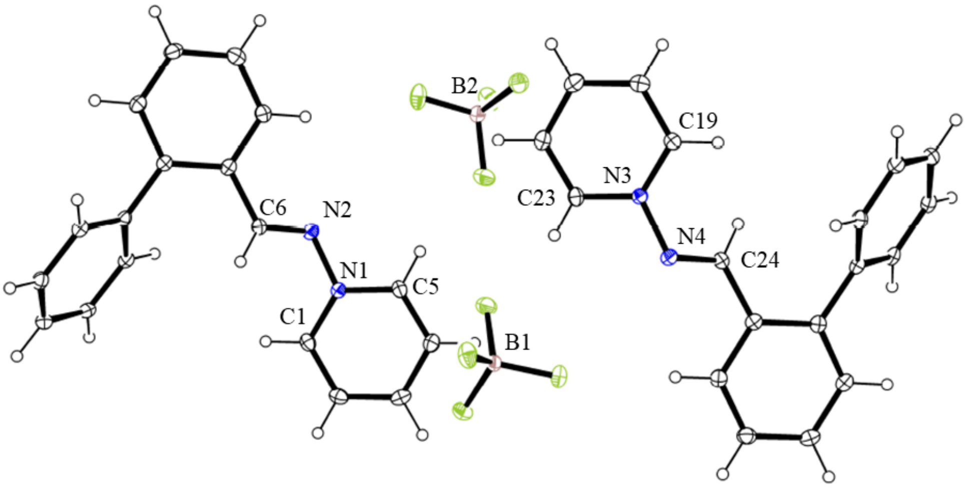


Figure S14 Crystal structure of **1a**.

Table S6 Data collection and structure refinement for **1a**.

Empirical formula	$C_{36}H_{30}B_2F_8N_4$	
Formula weight	692.26	
Temperature	93.15 K	
Crystal system	orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.2138(3) Å	α = 90°
	b = 18.7396(6) Å	β = 90°
	c = 19.0243(6) Å	γ = 90°
Volume	3284.79(18) $Å^3$	
Z	4	
Density (calculated)	1.400 g/cm^3	
Absorption coefficient	0.976 mm^{-1}	
F(000)	1424.0	
Crystal size	0.46 × 0.055 × 0.021 mm^3	
Radiation	CuKα (λ = 1.54184)	
2Θ range for data collection	6.62 ° to 151.742 °	
Index ranges	$-5 \leq h \leq 11$, $-22 \leq k \leq 23$, $-23 \leq l \leq 23$	
Reflections collected	13665	
Independent reflections	6054 [R_{int} = 0.0291, R_{sigma} = 0.0360]	
Data/restraints/parameters	6054/0/451	

Goodness-of-fit on F2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0340, wR_2 = 0.0853
Final R indexes [all data]	R_1 = 0.0376, wR_2 = 0.0872
Largest diff. peak/hole	0.44/-0.30 e $Å^{-3}$
Flack parameter	0.48(5)

Table S7 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **1a**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
F1	7745.4(15)	3068.3(8)	499.9(8)	26.9(3)
F2	9858.5(15)	3436.5(7)	1008.8(9)	29.5(3)
F3	9411.6(16)	2250.3(8)	878.2(10)	34.2(4)
F4	8119.7(16)	2902.6(9)	1673.2(8)	31.9(3)
N1	3489(2)	2589.1(10)	1828.9(10)	17.2(4)
N2	3061(2)	2150.7(10)	2403.1(11)	20.5(4)
C1	2771(3)	2604.9(13)	1210.0(13)	21.3(5)
C2	3228(3)	3066.7(13)	694.3(13)	24.4(5)
C3	4401(3)	3511.1(14)	815.9(14)	25.7(5)
C4	5087(3)	3496.5(13)	1465.3(14)	23.9(5)
C5	4613(2)	3029.7(12)	1970.7(14)	21.2(5)
C6	2797(2)	1497.6(12)	2243.7(12)	18.7(5)
C7	2448(2)	988.5(12)	2800.4(13)	19.1(5)
C8	2885(3)	1126.4(13)	3492.1(13)	23.5(5)
C9	2690(3)	622.4(14)	4013.2(14)	26.7(5)
C10	2081(3)	-38.9(14)	3846.8(14)	26.1(5)
C11	1629(2)	-178.7(13)	3162.5(14)	22.5(5)
C12	1775(2)	333.2(12)	2632.8(13)	17.8(4)
C13	1146(2)	195.5(12)	1927.2(13)	19.0(5)
C14	1427(2)	-448.8(12)	1575.4(13)	20.7(5)
C15	797(3)	-586.6(13)	922.7(14)	22.7(5)
C16	-134(3)	-90.4(13)	618.5(13)	23.8(5)
C17	-427(3)	546.0(13)	963.5(14)	22.6(5)
C18	211(2)	688.5(13)	1612.9(13)	20.4(5)
B1	8786(3)	2912.3(14)	1007.9(15)	21.3(5)
F5	7140.0(16)	3039.3(9)	4426.0(9)	34.8(4)
F6	4924.5(18)	3574.5(9)	4512.3(10)	38.6(4)

F7	5098.8(17)	2445.0(8)	4109.9(10)	35.8(4)
F8	5895(2)	3371.5(12)	3438.0(9)	52.7(5)
B2	5783(3)	3099.1(16)	4117.4(16)	25.8(6)
N3	11323(2)	3379.2(10)	3061.3(11)	17.4(4)
N4	11747(2)	3820.8(10)	2490.7(11)	20.1(4)
C19	12120(3)	3321.2(12)	3655.2(13)	20.7(5)
C20	11698(3)	2844.4(13)	4167.1(13)	24.8(5)
C21	10474(3)	2430.4(14)	4065.7(15)	27.4(5)
C22	9691(3)	2498.2(13)	3446.9(14)	26.2(5)
C23	10138(2)	2972.6(12)	2942.0(13)	21.9(5)
C24	12081(2)	4462.3(12)	2663.3(12)	18.1(4)
C25	12460(2)	4979.9(13)	2116.2(13)	19.7(5)
C26	11936(3)	4876.5(13)	1429.1(13)	21.9(5)
C27	12150(3)	5392.2(14)	918.7(14)	25.7(5)
C28	12897(3)	6017.2(14)	1088.1(13)	25.6(5)
C29	13429(3)	6118.3(13)	1762.6(14)	22.7(5)
C30	13234(2)	5605.7(12)	2285.8(13)	19.3(5)
C31	13853(2)	5723.3(12)	3001.3(13)	20.0(5)
C32	14655(2)	5194.0(12)	3342.3(14)	21.7(5)
C33	15211(3)	5307.1(13)	4013.8(14)	24.5(5)
C34	14990(3)	5962.3(14)	4347.1(14)	25.9(5)
C35	14209(2)	6493.8(13)	4008.2(14)	23.5(5)
C36	13651(2)	6376.9(12)	3339.1(13)	21.4(5)

Table S8 Anisotropic Displacement Parameters ($Å^2\times10^3$) for **1a**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}
F1	25.6(7)	31.5(7)	23.6(7)	0.7(6)
F2	26.7(7)	23.4(7)	38.2(9)	-2.3(7)
F3	33.5(8)	20.0(7)	49.2(10)	-5.5(7)
F4	30.6(7)	43.0(9)	22.1(7)	2.5(7)
N1	17.9(9)	15.1(8)	18.6(9)	-1.6(8)
N2	21.1(9)	19.2(9)	21.1(9)	0.3(8)
C1	21.1(10)	19.0(11)	23.8(12)	-3.9(10)
C2	29.3(12)	24.2(12)	19.8(11)	-0.3(10)
C3	28.7(12)	24.3(12)	24.0(12)	6.3(11)

C4	20.6(11)	22.4(11)	28.7(13)	0.9(11)
C5	20.4(10)	19.6(11)	23.6(12)	-2.4(10)
C6	16.7(10)	18.6(10)	20.9(11)	-1.4(9)
C7	18.0(10)	17.9(10)	21.3(11)	-0.6(9)
C8	24.7(11)	22.4(11)	23.4(12)	-2.2(10)
C9	27.0(12)	31.5(12)	21.5(12)	-1.8(11)
C10	27.8(12)	26.6(12)	24.0(12)	7.4(10)
C11	20.5(10)	21.8(11)	25.1(13)	2.1(10)
C12	15.3(10)	18.4(10)	19.7(11)	0.2(9)
C13	17.7(10)	18.9(10)	20.4(11)	1.3(10)
C14	19.3(10)	18.3(11)	24.4(12)	1.4(10)
C15	25.3(11)	20.4(11)	22.5(12)	-2.1(10)
C16	27.3(11)	24.5(12)	19.5(11)	0.6(10)
C17	23.9(11)	23.0(12)	20.8(12)	5.6(10)
C18	22.4(10)	17.2(10)	21.5(12)	1.2(9)
B1	22.6(12)	18.9(12)	22.5(13)	1.5(11)
F5	24.1(7)	45.0(9)	35.4(8)	7.8(8)
F6	45.0(9)	26.5(8)	44.3(10)	-8.2(7)
F7	32.1(8)	22.1(7)	53.1(11)	-7.9(7)
F8	56.4(11)	77.0(14)	24.8(9)	10.9(9)
B2	26.7(13)	25.1(14)	25.6(14)	3.5(12)
N3	19.2(9)	16.2(8)	16.9(9)	-0.8(8)
N4	21.6(9)	18.7(9)	20.0(10)	0.9(8)
C19	20.9(10)	19.9(11)	21.3(11)	-1.5(9)
C20	28.0(11)	25.2(12)	21.2(12)	0.0(10)
C21	32.2(13)	22.6(12)	27.4(13)	3.2(11)
C22	26.4(12)	21.7(12)	30.6(13)	-0.5(11)
C23	21.6(10)	19.0(11)	25.1(12)	-3.6(10)
C24	16.1(10)	19.3(10)	19.0(10)	-2.0(9)
C25	19.8(10)	19.0(10)	20.4(11)	-0.4(10)
C26	20.9(10)	22.0(11)	22.7(12)	-3.4(10)
C27	25.9(11)	30.6(13)	20.6(12)	1.7(11)
C28	28.5(11)	25.0(12)	23.3(12)	6.0(10)
C29	22.6(11)	19.7(11)	25.9(13)	1.2(10)
C30	16.5(10)	19.4(11)	22.0(12)	-1.7(10)
C31	17.9(10)	18.6(10)	23.6(12)	1.2(10)

C32	20.6(10)	18.5(11)	26.0(12)	-2.4(10)
C33	24.5(11)	23.3(12)	25.5(13)	3.4(10)
C34	27.0(12)	29.7(13)	20.9(12)	-1.5(11)
C35	23.0(11)	21.1(11)	26.3(12)	-5.2(10)
C36	20.7(10)	16.9(10)	26.5(12)	0.6(10)

Table S9 Bond Lengths for **1a**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	B1	1.392(3)	F5	B2	1.386(3)
F2	B1	1.394(3)	F6	B2	1.408(4)
F3	B1	1.390(3)	F7	B2	1.378(3)
F4	B1	1.407(3)	F8	B2	1.393(3)
N1	N2	1.423(3)	N3	N4	1.420(3)
N1	C1	1.351(3)	N3	C19	1.352(3)
N1	C5	1.351(3)	N3	C23	1.351(3)
N2	C6	1.284(3)	N4	C24	1.284(3)
C1	C2	1.374(4)	C19	C20	1.378(4)
C2	C3	1.384(4)	C20	C21	1.383(4)
C3	C4	1.388(4)	C21	C22	1.387(4)
C4	C5	1.372(4)	C22	C23	1.372(4)
C6	C7	1.461(3)	C24	C25	1.465(3)
C7	C8	1.400(3)	C25	C26	1.407(3)
C7	C12	1.412(3)	C25	C30	1.410(3)
C8	C9	1.381(4)	C26	C27	1.384(4)
C9	C10	1.396(4)	C27	C28	1.396(4)
C10	C11	1.392(4)	C28	C29	1.387(4)
C11	C12	1.398(3)	C29	C30	1.395(3)
C12	C13	1.484(3)	C30	C31	1.492(3)
C13	C14	1.405(3)	C31	C32	1.396(3)
C13	C18	1.398(3)	C31	C36	1.396(3)
C14	C15	1.395(4)	C32	C33	1.393(4)
C15	C16	1.391(4)	C33	C34	1.397(4)
C16	C17	1.388(4)	C34	C35	1.387(4)
C17	C18	1.394(4)	C35	C36	1.390(4)

Table S10 Bond Angles for **1a**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	N1	N2	123.08(19)	F5	B2	F6	109.4(2)
C1	N1	C5	122.4(2)	F5	B2	F8	110.8(2)
C5	N1	N2	114.33(19)	F7	B2	F5	110.2(2)
C6	N2	N1	114.93(19)	F7	B2	F6	108.2(2)
N1	C1	C2	119.1(2)	F7	B2	F8	110.5(2)
C1	C2	C3	119.9(2)	F8	B2	F6	107.7(2)
C2	C3	C4	119.5(2)	C19	N3	N4	122.46(19)
C5	C4	C3	119.4(2)	C23	N3	N4	114.98(19)
N1	C5	C4	119.6(2)	C23	N3	C19	122.3(2)
N2	C6	C7	119.5(2)	C24	N4	N3	114.6(2)
C8	C7	C6	119.8(2)	N3	C19	C20	119.3(2)
C8	C7	C12	119.9(2)	C19	C20	C21	119.7(2)
C12	C7	C6	120.0(2)	C20	C21	C22	119.4(2)
C9	C8	C7	120.7(2)	C23	C22	C21	119.8(2)
C8	C9	C10	119.8(2)	N3	C23	C22	119.4(2)
C11	C10	C9	120.0(2)	N4	C24	C25	119.7(2)
C10	C11	C12	121.1(2)	C26	C25	C24	119.2(2)
C7	C12	C13	121.8(2)	C26	C25	C30	120.0(2)
C11	C12	C7	118.4(2)	C30	C25	C24	120.6(2)
C11	C12	C13	119.7(2)	C27	C26	C25	120.5(2)
C14	C13	C12	120.6(2)	C26	C27	C28	119.6(2)
C18	C13	C12	120.8(2)	C29	C28	C27	120.2(2)
C18	C13	C14	118.5(2)	C28	C29	C30	121.4(2)
C15	C14	C13	120.4(2)	C25	C30	C31	121.7(2)
C16	C15	C14	120.2(2)	C29	C30	C25	118.3(2)
C17	C16	C15	119.8(2)	C29	C30	C31	120.0(2)
C16	C17	C18	120.1(2)	C32	C31	C30	121.4(2)
C17	C18	C13	120.8(2)	C36	C31	C30	119.9(2)
F1	B1	F2	109.9(2)	C36	C31	C32	118.7(2)
F1	B1	F4	109.1(2)	C33	C32	C31	120.8(2)
F2	B1	F4	108.5(2)	C32	C33	C34	119.8(2)
F3	B1	F1	110.5(2)	C35	C34	C33	119.7(2)
F3	B1	F2	109.6(2)	C34	C35	C36	120.3(2)
F3	B1	F4	109.2(2)	C35	C36	C31	120.7(2)

Table S11 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **1a**.

Atom	x	y	z	U(eq)
H1	1961.05	2301.17	1132.47	26
H2	2738.99	3080.88	254.82	29
H3	4734.72	3823.75	457.55	31
H4	5878.75	3807.2	1558.85	29
H5	5070.88	3016.13	2417.82	25
H6	2828.69	1346.48	1767.29	22
H8	3321.39	1571.51	3604.14	28
H9	2967.83	725.19	4483.25	32
H10	1976.11	-393.04	4200.41	31
H11	1214.7	-629.57	3053.63	27
H14	2050.64	-793.04	1783.24	25
H15	1003.51	-1020.72	685.2	27
H16	-568.82	-186.96	175.7	29
H17	-1062.73	885.25	756.76	27
H18	8.15	1126.26	1844.71	24
H19	12962.54	3606.41	3718.92	25
H20	12246.33	2800.16	4587.82	30
H21	10171.7	2102.34	4417.14	33
H22	8846.89	2216.9	3372.78	31
H23	9618.57	3014.73	2512.57	26
H24	12082.71	4600.69	3143.72	22
H26	11432.73	4449.61	1314.58	26
H27	11789.87	5321.33	455.92	31
H28	13040.44	6374.13	740.37	31
H29	13936.8	6545.59	1870.63	27
H32	14822.45	4751.12	3113.27	26
H33	15738.49	4939.88	4244.46	29
H34	15371.97	6043.63	4803.84	31
H35	14055.87	6939.48	4234.28	28
H36	13125.37	6745.69	3109.47	26

2-Methylphenanthridine (2d)

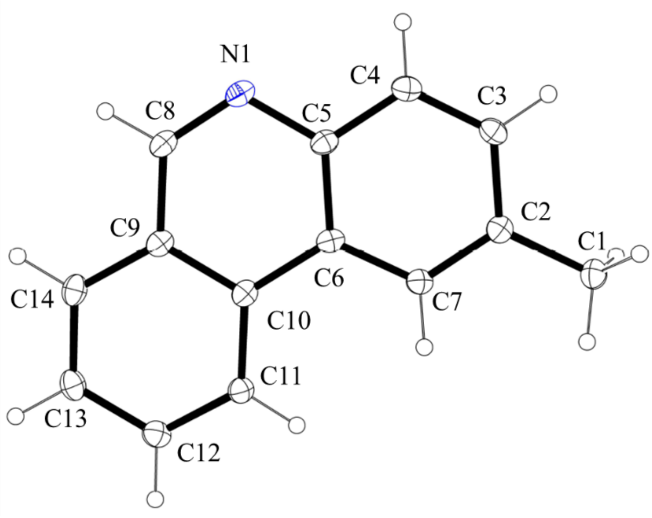


Figure S15 Crystal structure of **2d**.

Table S12 Data collection and structure refinement for **2d**.

Empirical formula	$C_{14}H_{11}N$	
Formula weight	193.24	
Temperature	93.0 K	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 3.9998(3) Å	α = 90°
	b = 17.7191(12) Å	β = 91.352(6)°
	c = 13.7434(8) Å	γ = 90°
Volume	973.76(11) Å^3	
Z	4	
Density (calculated)	1.318 g/cm^3	
Absorption coefficient	0.591 mm^{-1}	
F(000)	408.0	
Crystal size/mm^3	0.327 × 0.048 × 0.026	
Radiation	CuKα (λ = 1.54184)	
2Θ range for data collection/°	8.144 to 152.02	
Index ranges	$-4 \leq h \leq 3$, $-21 \leq k \leq 21$, $-17 \leq l \leq 17$	
Reflections collected	5832	
Independent reflections	1929 [R_{int} = 0.0295, R_{sigma} = 0.0345]	
Data/restraints/parameters	1929/0/137	
Goodness-of-fit on F2	1.028	

Final R indexes [I>=2σ (I)]	$R_1 = 0.0518$, $wR_2 = 0.1413$
Final R indexes [all data]	$R_1 = 0.0611$, $wR_2 = 0.1488$
Largest diff. peak/hole / e Å^{-3}	0.27/-0.22

Table S13 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$) for **2d**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
C10	8930(3)	1750.4(8)	1654.8(10)	22.0(3)
C7	6137(3)	2990.0(8)	1267.9(10)	22.6(3)
N1	7385(3)	2011.8(7)	3655.0(8)	26.4(3)
C5	6460(4)	2525.7(8)	2933.4(10)	23.9(4)
C9	9827(4)	1231.8(8)	2399.9(10)	23.8(4)
C3	3739(4)	3714.5(9)	2558.1(11)	25.9(4)
C6	7180(3)	2427.3(8)	1936.0(10)	22.1(4)
C2	4457(3)	3624.6(8)	1562.4(10)	24.2(4)
C8	8978(4)	1408.5(9)	3379.8(10)	26.1(4)
C11	9772(4)	1576.6(8)	689.8(10)	23.7(3)
C4	4730(4)	3171.6(9)	3227.0(10)	26.7(4)
C13	12238(4)	393.5(9)	1221.6(11)	28.0(4)
C14	11487(4)	559.1(9)	2173.6(11)	26.6(4)
C12	11366(4)	907.8(9)	485.0(11)	27.0(4)
C1	3334(4)	4216.5(9)	837.7(11)	28.4(4)

Table S14 Anisotropic Displacement Parameters (Å$^2 \times 10^3$) for **2d**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C10	22.1(7)	20.2(7)	23.8(7)	1.2(5)	-1.8(5)	-6.2(5)
C7	23.5(7)	21.5(8)	22.8(6)	-2.2(5)	1.1(5)	-4.6(5)
N1	30.4(7)	29.3(7)	19.4(6)	2.6(5)	-1.4(5)	-4.3(5)
C5	25.4(7)	25.5(8)	20.8(7)	0.6(6)	-0.8(5)	-4.9(6)
C9	24.6(7)	23.1(8)	23.6(7)	1.4(6)	-1.3(5)	-5.9(5)
C3	26.2(7)	23.5(8)	28.0(7)	-5.7(6)	2.0(6)	-1.5(6)
C6	22.5(7)	23.9(8)	19.9(7)	-1.3(5)	0.1(5)	-7.0(5)
C2	23.9(7)	22.7(8)	25.9(7)	-0.6(6)	-1.6(5)	-4.0(5)
C8	30.0(8)	26.4(8)	21.7(7)	4.3(6)	-3.0(5)	-3.9(6)
C11	27.1(7)	20.4(7)	23.6(7)	-0.3(5)	0.8(5)	-2.9(6)

C4	28.6(8)	29.1(8)	22.4(7)	-4.4(6)	2.3(5)	-3.2(6)
C13	27.3(8)	20.0(7)	36.7(8)	-1.8(6)	0.3(6)	-0.3(6)
C14	26.0(8)	21.1(8)	32.5(8)	4.5(6)	-4.1(6)	-3.1(6)
C12	28.3(8)	24.7(8)	28.1(7)	-2.6(6)	3.7(6)	-3.0(6)
C1	30.4(8)	24.1(8)	30.7(7)	1.1(6)	-1.8(6)	-0.4(6)

Table S15 Bond Lengths for **2d**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C10	C9	1.416(2)	C9	C8	1.431(2)
C10	C6	1.446(2)	C9	C14	1.403(2)
C10	C11	1.410(2)	C3	C2	1.414(2)
C7	C6	1.412(2)	C3	C4	1.382(2)
C7	C2	1.376(2)	C2	C1	1.507(2)
N1	C5	1.3901(19)	C11	C12	1.378(2)
N1	C8	1.305(2)	C13	C14	1.381(2)
C5	C6	1.4182(19)	C13	C12	1.400(2)
C5	C4	1.402(2)			

Table S16 Bond Angles for **2d**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	C10	C6	117.47(13)	C7	C6	C10	123.34(12)
C11	C10	C9	118.45(14)	C7	C6	C5	118.56(13)
C11	C10	C6	124.08(13)	C5	C6	C10	118.10(13)
C2	C7	C6	121.66(13)	C7	C2	C3	119.25(14)
C8	N1	C5	116.97(12)	C7	C2	C1	120.95(13)
N1	C5	C6	123.52(14)	C3	C2	C1	119.80(14)
N1	C5	C4	117.03(13)	N1	C8	C9	125.46(14)
C4	C5	C6	119.45(14)	C12	C11	C10	120.12(14)
C10	C9	C8	118.48(14)	C3	C4	C5	120.83(13)
C14	C9	C10	120.29(13)	C14	C13	C12	119.39(14)
C14	C9	C8	121.23(14)	C13	C14	C9	120.35(14)
C4	C3	C2	120.25(14)	C11	C12	C13	121.37(13)

Table S17 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **2d**.

Atom	x	y	z	U(eq)
H7	6606.34	2928.9	598.09	27
H3	2571.91	4149.78	2768.2	31
H8	9628.96	1057.24	3870.95	31
H11	9238.94	1921.25	179.83	28
H4	4231.95	3237.02	3894.22	32
H13	13336.11	-65.19	1067.88	34
H14	12097.25	215.66	2678.03	32
H12	11884.6	793.24	-169.69	32
H1A	4210.9	4094.66	196.72	43
H1B	4175.59	4711.26	1047.26	43
H1C	884.77	4228.22	798.16	43

4-Acetoamidphenanthridine (2c')

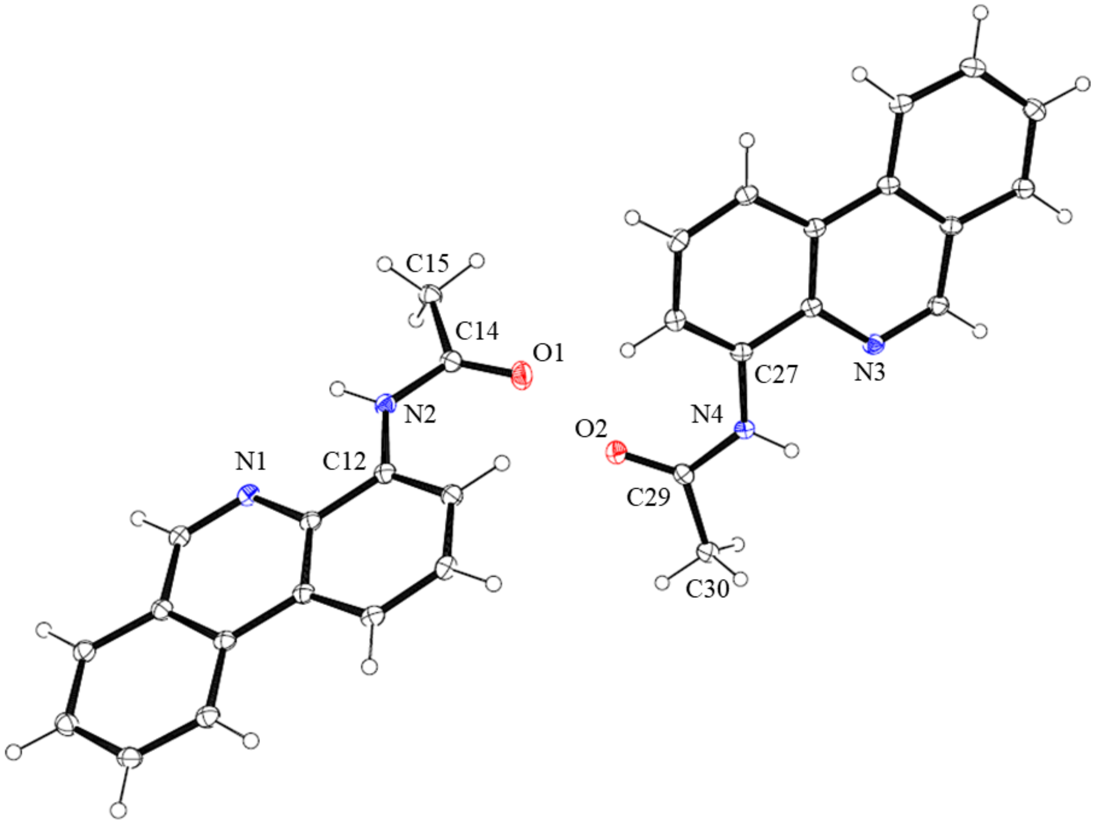


Figure S16 Crystal structure of **2c'** (4-isomer).

Table S18 Data collection and structure refinement for **2c'** (4-isomer).

Empirical formula	$C_{30}H_{24}N_4O_2$	
Formula weight	472.53	
Temperature	90.0 K	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 5.6047(3) Å	α = 90°
	b = 32.8239(15) Å	β = 100.303(4)°
	c = 12.3602(5) Å	γ = 90°
Volume	2237.22(18) $Å^3$	
Z	4	
Density (calculated)	1.403 g/cm^3	
Absorption coefficient	0.717 mm^{-1}	
F(000)	992.0	
Crystal size/mm^3	0.202 × 0.063 × 0.051	
Radiation	CuKα (λ = 1.54184)	
2Θ range for data collection/°	7.752 to 152.934	
Index ranges	$-6 \leq h \leq 4$, $-39 \leq k \leq 40$, $-15 \leq l \leq 15$	
Reflections collected	14884	
Independent reflections	4453 [R_{int} = 0.0447, R_{sigma} = 0.0410]	
Data/restraints/parameters	4453/0/328	
Goodness-of-fit on F2	1.077	
Final R indexes [I>=2σ (I)]	R_1 = 0.0466, wR_2 = 0.1210	
Final R indexes [all data]	R_1 = 0.0557, wR_2 = 0.1262	
Largest diff. peak/hole / e $Å^{-3}$	0.25/-0.20	

Table S19 Fractional Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2\times10^3$) for **2c'** (4-isomer). U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
O1	1688(2)	6610.8(4)	6155.8(10)	28.4(3)
O2	4049(2)	5520.5(4)	5445.2(11)	31.6(3)
N1	-1580(3)	7091.2(4)	2535.2(12)	21.3(3)
N3	6991(2)	4836.0(4)	8917.0(12)	20.3(3)
N2	-718(3)	6739.2(4)	4501.2(11)	20.3(3)
N4	6134(3)	5191.0(4)	6940.2(12)	21.1(3)

C7	1215(3)	6930.9(5)	866.0(13)	19.1(3)
C23	3190(3)	4442.4(5)	8517.5(13)	18.6(3)
C8	1811(3)	6732.3(5)	1928.5(13)	18.3(3)
C13	357(3)	6822.6(5)	2722.8(14)	18.5(3)
C28	4857(3)	4726.5(5)	8225.9(13)	18.5(3)
C27	4378(3)	4916.6(5)	7171.7(14)	19.3(3)
C14	-244(3)	6722.5(5)	5628.1(14)	20.5(3)
C22	3770(3)	4253.4(5)	9595.3(13)	18.7(3)
C11	2730(3)	6359.9(5)	4024.9(14)	21.2(4)
C24	1079(3)	4350.0(5)	7754.2(14)	20.5(3)
C16	7491(3)	4659.6(5)	9875.1(14)	20.7(4)
C17	5980(3)	4362.1(5)	10270.4(14)	20.0(3)
C25	656(3)	4535.5(5)	6739.0(14)	21.4(4)
C9	3736(3)	6453.5(5)	2209.2(14)	21.4(4)
C21	2277(3)	3967.5(5)	10003.0(14)	21.9(4)
C29	5902(3)	5474.3(5)	6119.4(14)	21.7(4)
C26	2290(3)	4817.7(5)	6438.1(14)	20.9(4)
C12	848(3)	6635.2(5)	3772.4(13)	19.1(3)
C18	6667(3)	4181.9(5)	11315.5(14)	22.6(4)
C2	-805(3)	7195.3(5)	687.8(14)	20.0(3)
C1	-2105(3)	7261.4(5)	1572.7(14)	21.5(4)
C3	-1488(3)	7396.7(5)	-325.6(14)	22.2(4)
C10	4150(3)	6271.4(5)	3226.8(14)	22.2(4)
C20	2980(3)	3795.2(5)	11026.9(14)	23.6(4)
C6	2516(3)	6876.2(5)	-3.1(14)	22.8(4)
C19	5198(3)	3899.7(6)	11693.3(14)	24.5(4)
C30	8122(3)	5732.5(5)	6118.6(15)	24.2(4)
C4	-160(3)	7343.4(6)	-1149.4(15)	24.8(4)
C15	-2319(3)	6863.9(6)	6157.5(14)	24.9(4)
C5	1843(3)	7079.3(6)	-980.7(15)	26.0(4)

Table S20 Anisotropic Displacement Parameters (Å^2×10^3) for **2c'** (4-isomer). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	25.0(7)	37.2(7)	22.3(6)	1.8(5)	2.3(5)	3.2(5)
O2	27.7(7)	30.4(7)	33.9(7)	12.1(6)	-1.9(6)	-1.2(5)

N1	22.2(7)	19.6(7)	23.3(7)	0.5(6)	7.0(6)	2.7(6)
N3	18.1(7)	19.6(7)	23.2(7)	-1.4(6)	4.0(6)	0.5(5)
N2	18.7(7)	23.2(7)	19.5(7)	1.1(5)	4.8(5)	1.3(6)
N4	18.3(7)	20.5(7)	24.1(7)	2.0(6)	2.9(5)	-0.5(5)
C7	19.7(8)	16.4(8)	22.1(8)	-2.3(6)	6.4(6)	-2.6(6)
C23	19.4(8)	16.1(8)	21.2(8)	-2.2(6)	6.2(6)	3.0(6)
C8	18.0(8)	15.6(8)	21.6(8)	-2.8(6)	4.7(6)	-3.2(6)
C13	18.8(8)	14.8(7)	22.6(8)	-1.3(6)	5.1(6)	-1.4(6)
C28	18.3(8)	16.9(8)	21.1(8)	-2.1(6)	5.9(6)	2.6(6)
C27	20.0(8)	15.4(8)	23.2(8)	-0.3(6)	6.0(6)	1.7(6)
C14	24.7(9)	16.2(8)	20.4(8)	1.0(6)	3.9(6)	-2.6(6)
C22	19.0(8)	17.0(8)	21.2(8)	-2.4(6)	7.2(6)	2.8(6)
C11	22.7(9)	18.7(8)	21.3(8)	-0.7(6)	1.8(6)	-1.5(6)
C24	19.2(8)	17.2(8)	26.0(8)	-1.2(6)	6.6(7)	-0.3(6)
C16	18.2(8)	21.4(8)	22.1(8)	-0.9(6)	2.7(6)	0.7(6)
C17	21.3(8)	18.6(8)	21.1(8)	-1.0(6)	6.0(6)	2.7(6)
C25	19.4(8)	20.7(8)	23.1(8)	-2.5(6)	1.4(6)	1.7(6)
C9	19.7(8)	19.8(8)	25.5(8)	-2.8(7)	6.5(7)	0.4(6)
C21	21.4(9)	19.4(8)	25.8(9)	-1.0(7)	6.4(7)	0.7(6)
C29	24.2(9)	18.5(8)	23.1(8)	0.5(6)	6.2(7)	2.6(7)
C26	21.5(8)	19.8(8)	21.7(8)	0.3(6)	4.8(6)	2.4(6)
C12	19.4(8)	17.4(8)	21.2(8)	-2.3(6)	5.4(6)	-3.3(6)
C18	20.9(9)	24.3(9)	22.8(8)	-0.3(7)	4.7(7)	3.3(7)
C2	21.3(8)	18.3(8)	21.7(8)	-0.3(6)	7.1(6)	-2.9(6)
C1	21.7(9)	19.3(8)	24.1(8)	1.8(6)	6.2(7)	3.5(6)
C3	23.6(9)	19.8(8)	24.1(9)	1.0(7)	6.6(7)	0.7(7)
C10	20.3(8)	17.7(8)	27.8(9)	-3.2(7)	2.6(7)	1.6(6)
C20	24.9(9)	21.6(9)	26.6(9)	2.0(7)	11.0(7)	1.4(7)
C6	20.8(9)	23.0(9)	26.3(9)	-1.5(7)	9.1(7)	0.8(7)
C19	28.1(9)	24.0(9)	22.8(9)	2.1(7)	8.0(7)	4.5(7)
C30	26.3(9)	21.8(9)	25.1(9)	2.4(7)	6.5(7)	-1.1(7)
C4	30.0(10)	23.9(9)	21.2(8)	3.0(7)	6.0(7)	-2.9(7)
C15	26.1(9)	26.7(9)	22.6(8)	0.3(7)	6.6(7)	-0.3(7)
C5	27.7(10)	28.9(9)	24.0(9)	-1.6(7)	11.6(7)	-2.9(7)

Table S21 Bond Lengths for **2c'** (4-isomer).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C14	1.217(2)	C27	C26	1.385(2)
O2	C29	1.219(2)	C14	C15	1.506(2)
N1	C13	1.385(2)	C22	C17	1.410(2)
N1	C1	1.299(2)	C22	C21	1.409(2)
N3	C28	1.387(2)	C11	C12	1.382(2)
N3	C16	1.303(2)	C11	C10	1.404(2)
N2	C14	1.372(2)	C24	C25	1.377(2)
N2	C12	1.408(2)	C16	C17	1.434(2)
N4	C27	1.401(2)	C17	C18	1.410(2)
N4	C29	1.365(2)	C25	C26	1.399(2)
C7	C8	1.451(2)	C9	C10	1.374(2)
C7	C2	1.412(2)	C21	C20	1.378(2)
C7	C6	1.414(2)	C29	C30	1.505(2)
C23	C28	1.412(2)	C18	C19	1.375(3)
C23	C22	1.453(2)	C2	C1	1.435(2)
C23	C24	1.408(2)	C2	C3	1.407(2)
C8	C13	1.415(2)	C3	C4	1.376(2)
C8	C9	1.410(2)	C20	C19	1.406(3)
C13	C12	1.418(2)	C6	C5	1.373(3)
C28	C27	1.426(2)	C4	C5	1.404(3)

Table S22 Bond Angles for **2c'** (4-isomer).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	N1	C13	117.99(14)	C12	C11	C10	118.84(16)
C16	N3	C28	117.77(14)	C25	C24	C23	120.17(16)
C14	N2	C12	127.62(15)	N3	C16	C17	124.63(16)
C29	N4	C27	127.78(15)	C22	C17	C16	118.71(15)
C2	C7	C8	117.77(14)	C22	C17	C18	120.19(16)
C2	C7	C6	117.89(15)	C18	C17	C16	121.10(16)
C6	C7	C8	124.34(15)	C24	C25	C26	121.40(16)
C28	C23	C22	117.79(15)	C10	C9	C8	120.26(16)
C24	C23	C28	119.11(15)	C20	C21	C22	120.76(16)
C24	C23	C22	123.09(15)	O2	C29	N4	123.30(16)
C13	C8	C7	117.77(15)	O2	C29	C30	122.17(16)

C9	C8	C7	123.83(15)	N4	C29	C30	114.53(15)
C9	C8	C13	118.40(15)	C27	C26	C25	119.86(16)
N1	C13	C8	123.26(15)	N2	C12	C13	116.06(15)
N1	C13	C12	116.57(14)	C11	C12	N2	123.54(15)
C8	C13	C12	120.17(15)	C11	C12	C13	120.38(15)
N3	C28	C23	123.45(15)	C19	C18	C17	120.77(16)
N3	C28	C27	116.74(15)	C7	C2	C1	118.43(15)
C23	C28	C27	119.81(15)	C3	C2	C7	120.68(15)
N4	C27	C28	116.33(15)	C3	C2	C1	120.87(16)
C26	C27	N4	124.01(15)	N1	C1	C2	124.75(16)
C26	C27	C28	119.64(15)	C4	C3	C2	120.14(16)
O1	C14	N2	123.27(16)	C9	C10	C11	121.93(16)
O1	C14	C15	122.86(15)	C21	C20	C19	121.04(16)
N2	C14	C15	113.86(15)	C5	C6	C7	120.61(16)
C17	C22	C23	117.61(15)	C18	C19	C20	119.07(16)
C21	C22	C23	124.23(15)	C3	C4	C5	119.51(16)
C21	C22	C17	118.16(15)	C6	C5	C4	121.15(16)

Table S23 Torsion Angles for **2c’** (4-isomer).

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
N1	C13	C12	N2	0.9(2)	C22	C23	C24	C25	-178.96(15)
N1	C13	C12	C11	179.30(15)	C22	C17	C18	C19	-0.2(3)
N3	C28	C27	N4	0.8(2)	C22	C21	C20	C19	0.1(3)
N3	C28	C27	C26	179.37(15)	C24	C23	C28	N3	-179.66(15)
N3	C16	C17	C22	-1.1(3)	C24	C23	C28	C27	0.4(2)
N3	C16	C17	C18	179.29(16)	C24	C23	C22	C17	177.95(15)
N4	C27	C26	C25	179.09(15)	C24	C23	C22	C21	-1.6(3)
C7	C8	C13	N1	-0.4(2)	C24	C25	C26	C27	-0.3(3)
C7	C8	C13	C12	179.59(15)	C16	N3	C28	C23	1.5(2)
C7	C8	C9	C10	-178.58(15)	C16	N3	C28	C27	-178.57(15)
C7	C2	C1	N1	-0.8(3)	C16	C17	C18	C19	179.38(16)
C7	C2	C3	C4	-1.2(3)	C17	C22	C21	C20	-0.9(2)
C7	C6	C5	C4	-0.5(3)	C17	C18	C19	C20	-0.6(3)
C23	C28	C27	N4	-179.25(14)	C9	C8	C13	N1	-179.93(15)
C23	C28	C27	C26	-0.7(2)	C9	C8	C13	C12	0.0(2)
C23	C22	C17	C16	1.8(2)	C21	C22	C17	C16	-178.62(15)

C23	C22	C17	C18	-178.60(15)	C21	C22	C17	C18	1.0(2)
C23	C22	C21	C20	178.63(15)	C21	C20	C19	C18	0.7(3)
C23	C24	C25	C26	0.0(3)	C29	N4	C27	C28	-164.50(16)
C8	C7	C2	C1	1.8(2)	C29	N4	C27	C26	17.0(3)
C8	C7	C2	C3	-179.79(15)	C12	N2	C14	O1	0.2(3)
C8	C7	C6	C5	-179.37(16)	C12	N2	C14	C15	178.92(15)
C8	C13	C12	N2	-179.05(14)	C12	C11	C10	C9	0.7(3)
C8	C13	C12	C11	-0.7(2)	C2	C7	C8	C13	-1.2(2)
C8	C9	C10	C11	-1.3(3)	C2	C7	C8	C9	178.33(15)
C13	N1	C1	C2	-0.8(3)	C2	C7	C6	C5	0.9(3)
C13	C8	C9	C10	0.9(2)	C2	C3	C4	C5	1.5(3)
C28	N3	C16	C17	-0.5(2)	C1	N1	C13	C8	1.4(2)
C28	C23	C22	C17	-1.0(2)	C1	N1	C13	C12	-178.61(15)
C28	C23	C22	C21	179.51(15)	C1	C2	C3	C4	177.23(16)
C28	C23	C24	C25	-0.1(2)	C3	C2	C1	N1	-179.27(17)
C28	C27	C26	C25	0.6(2)	C3	C4	C5	C6	-0.7(3)
C27	N4	C29	O2	-1.1(3)	C10	C11	C12	N2	178.58(15)
C27	N4	C29	C30	178.04(15)	C10	C11	C12	C13	0.3(2)
C14	N2	C12	C13	-155.84(16)	C6	C7	C8	C13	179.05(16)
C14	N2	C12	C11	25.8(3)	C6	C7	C8	C9	-1.4(3)
C22	C23	C28	N3	-0.7(2)	C6	C7	C2	C1	-178.47(15)
C22	C23	C28	C27	179.33(14)	C6	C7	C2	C3	0.0(2)

Table S24 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **2c’** (4-isomer).

Atom	x	y	z	U(eq)
H2	-2172.32	6825.06	4198.24	24
H4A	7557.84	5179.25	7376.04	25
H11	3057.87	6232.72	4726.2	25
H24	-56.89	4159.16	7940.26	25
H16	8959.79	4733.19	10345.13	25
H25	-776.04	4470.41	6231.9	26
H9	4750.85	6391.25	1692.88	26
H21	769.13	3892.6	9566.81	26
H26	1968.01	4941.29	5731.9	25
H18	8161.77	4256.31	11763.8	27

H1	-3447.51	7442.7	1445.7	26
H3	-2868.12	7569.87	-440.96	27
H10	5434.12	6080.02	3395.21	27
H20	1948.2	3602.81	11286.63	28
H6	3869.55	6697.23	90.42	27
H19	5676.26	3777.06	12394.84	29
H30A	7957.38	5881.3	5421.81	36
H30B	9559.68	5557.43	6204.17	36
H30C	8293.24	5926.93	6729.38	36
H4	-595.23	7484.2	-1827.53	30
H15A	-1945.42	6808.84	6949.04	37
H15B	-3798.53	6717.79	5832.1	37
H15C	-2562.26	7157.17	6035.91	37
H5	2747.63	7040.58	-1553.2	31

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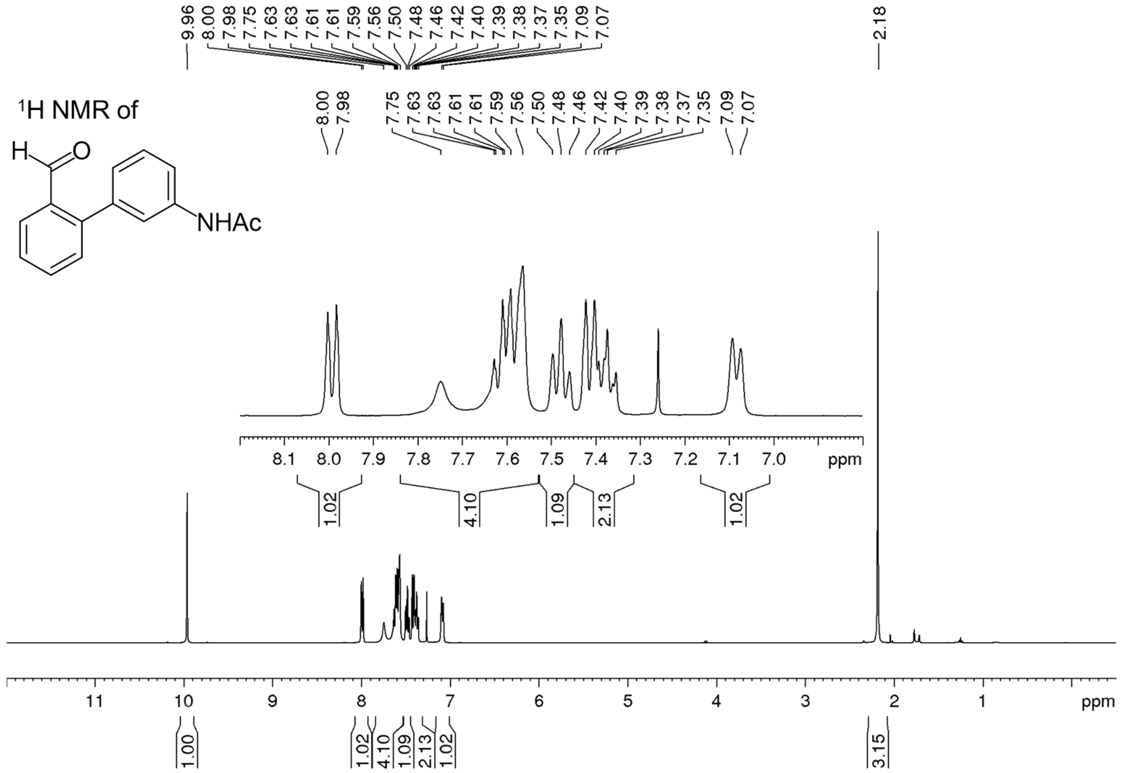
NMR spectra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7.07
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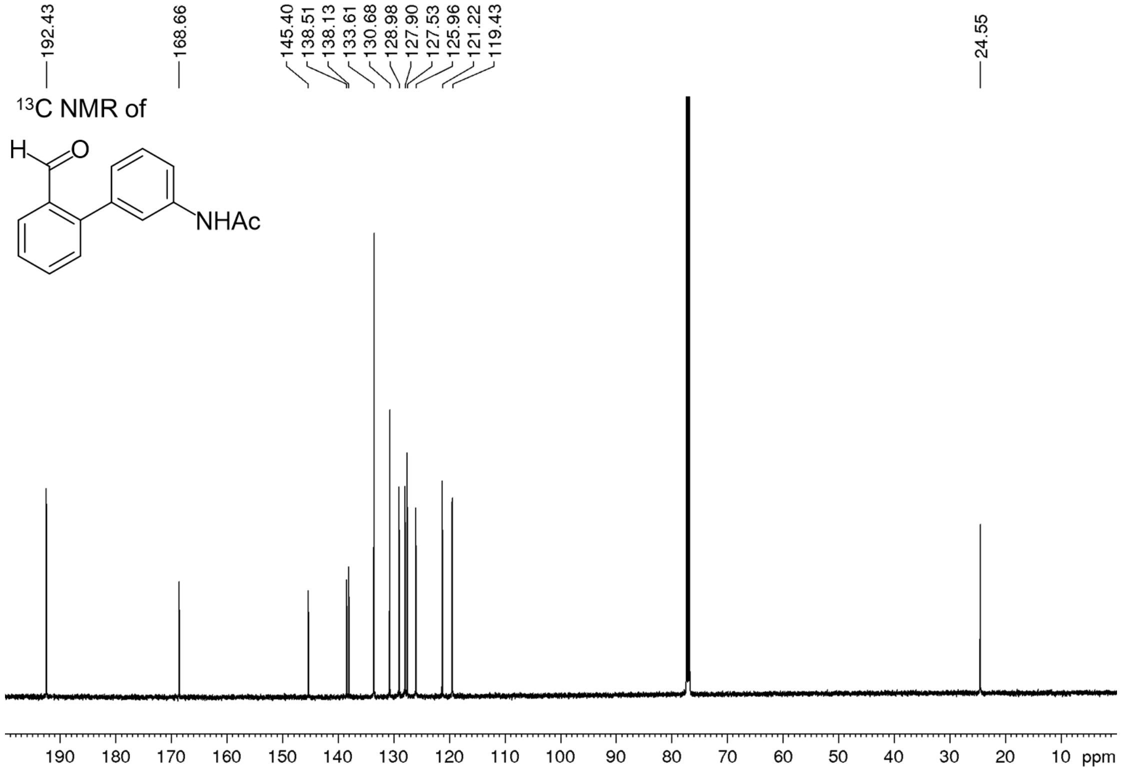
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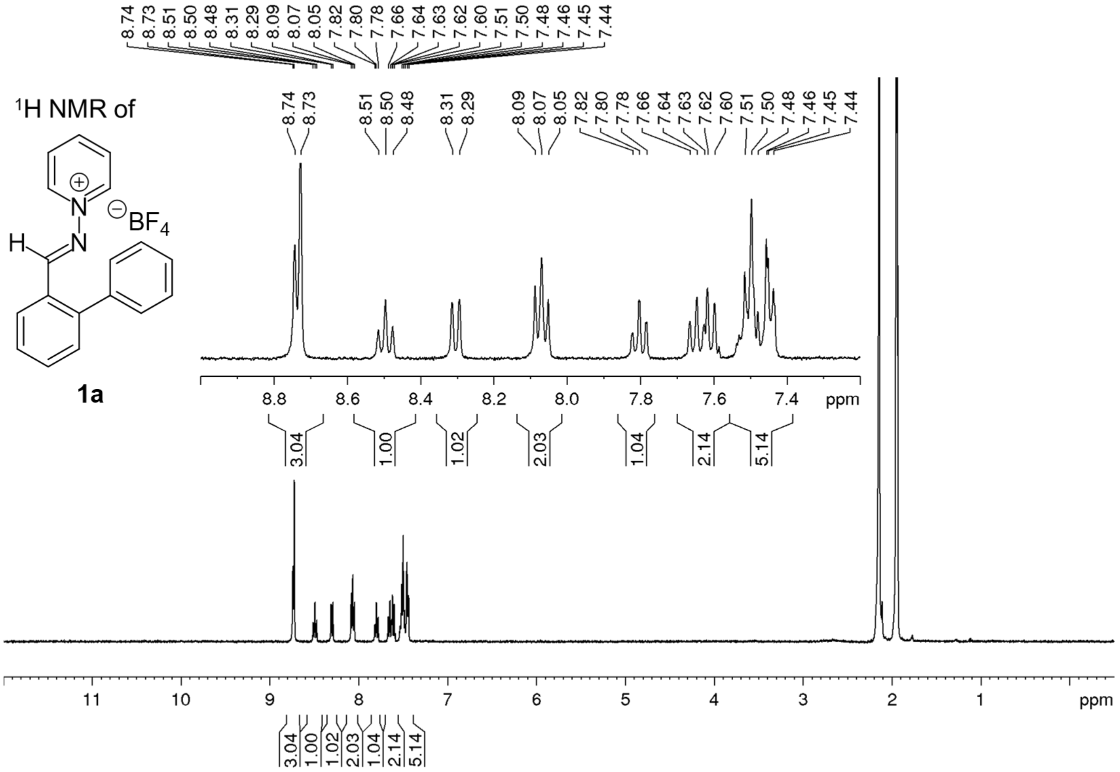

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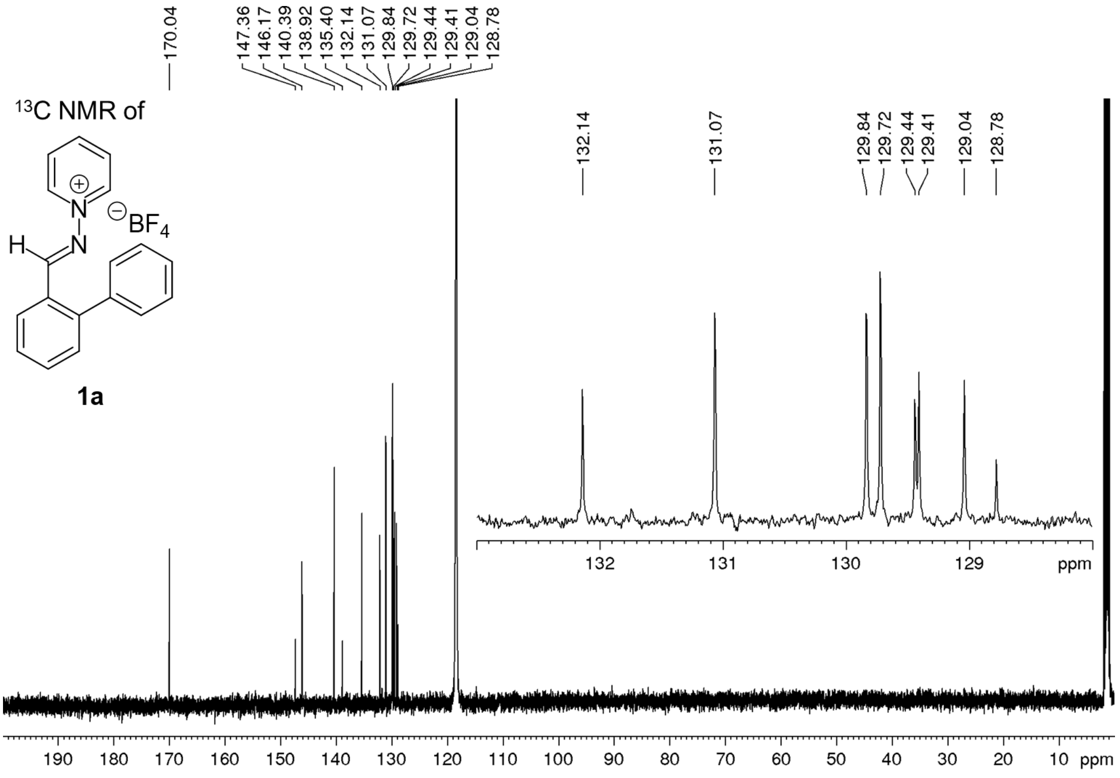

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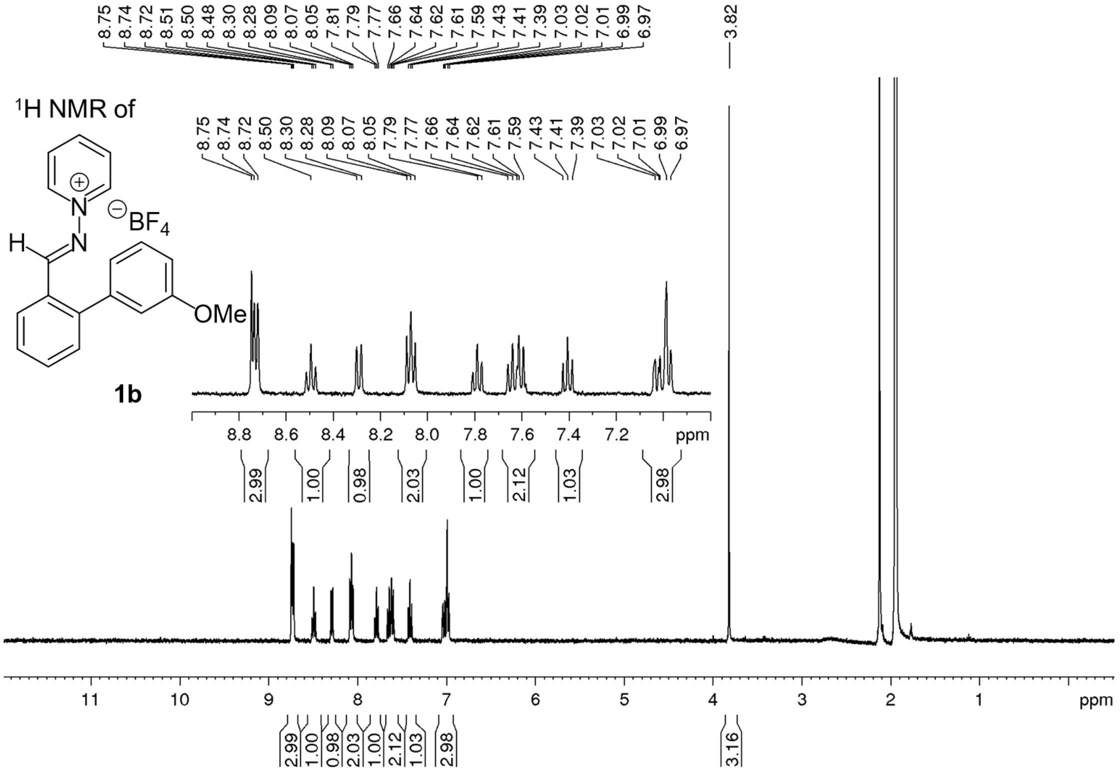
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OMe
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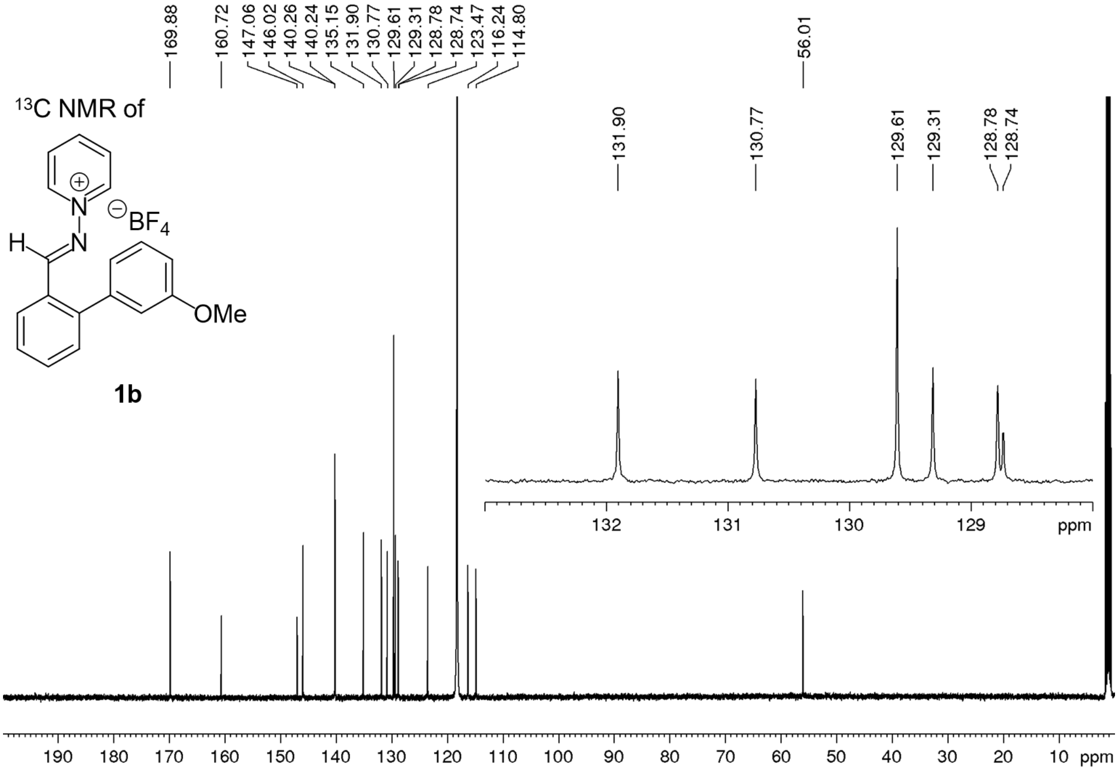
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N
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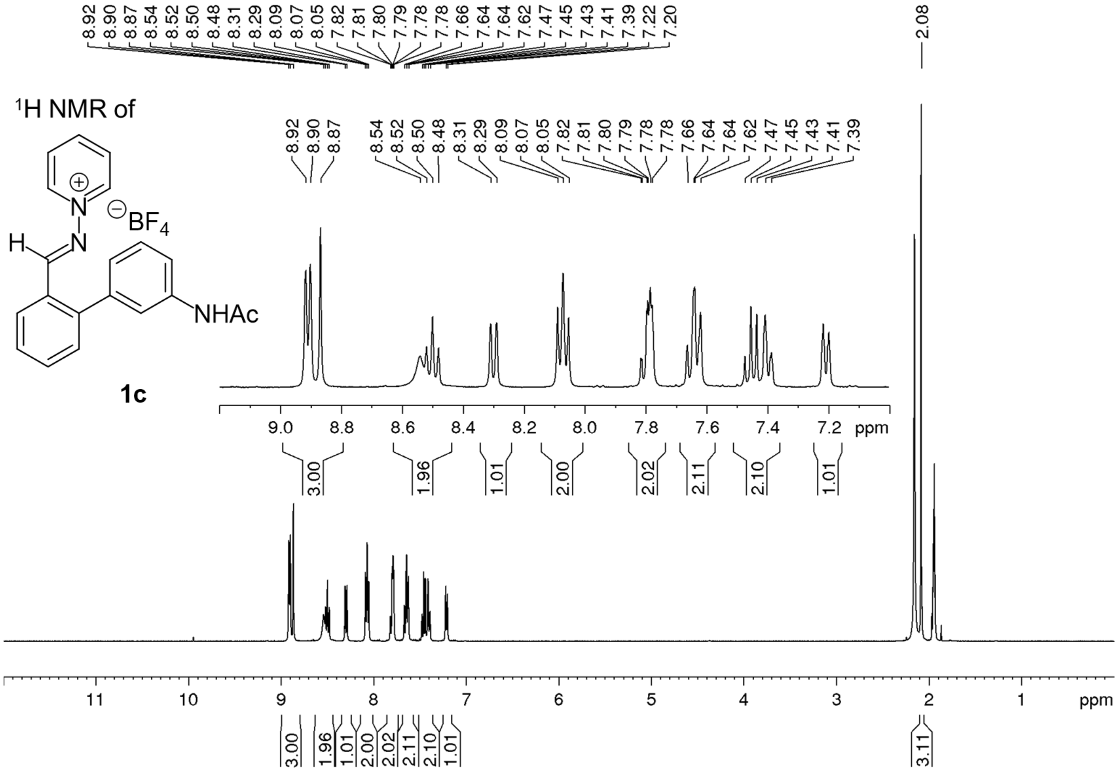

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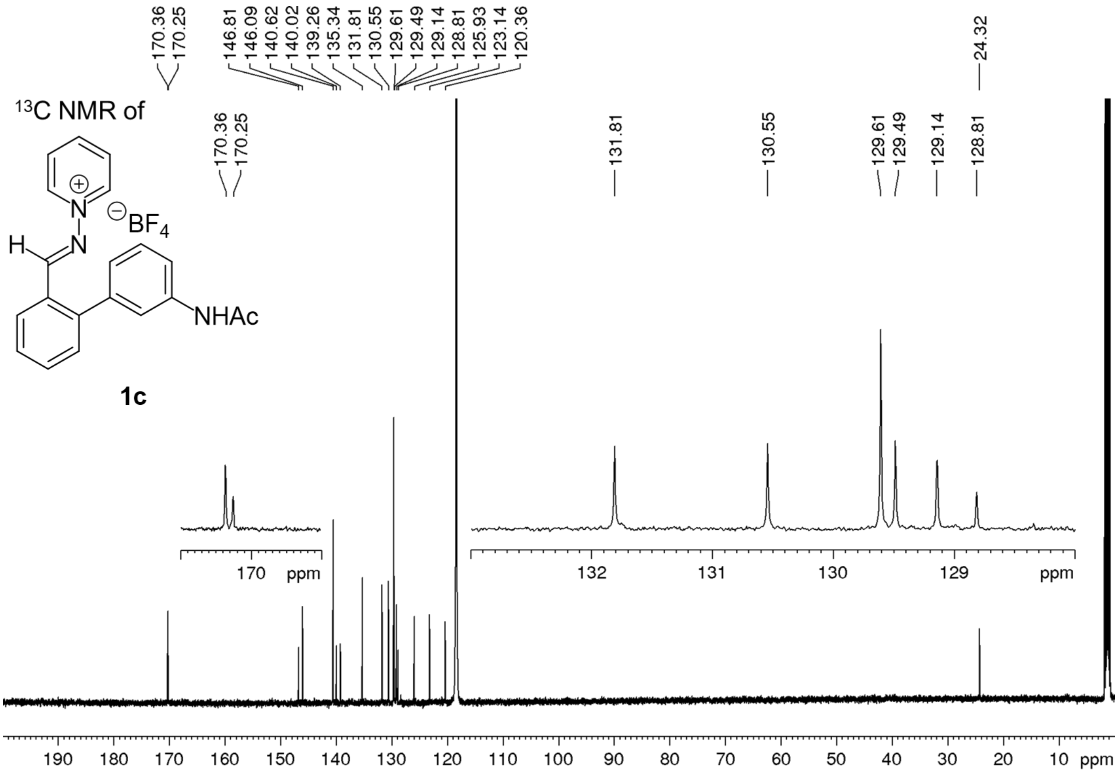

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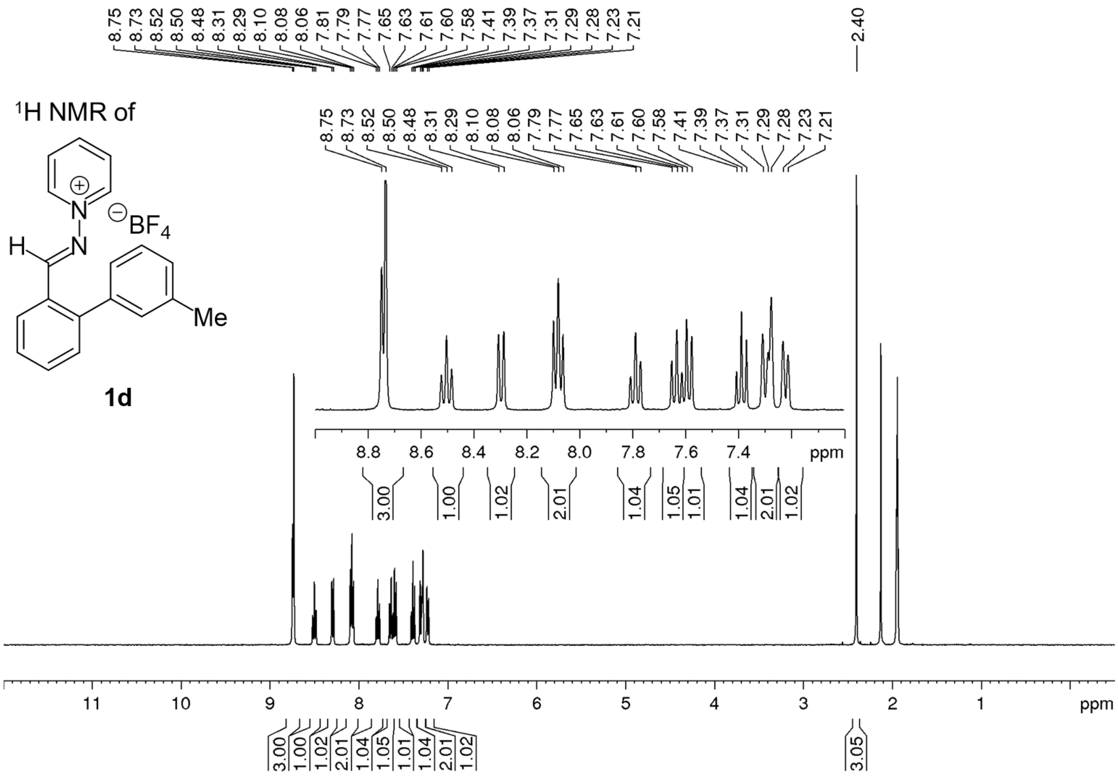
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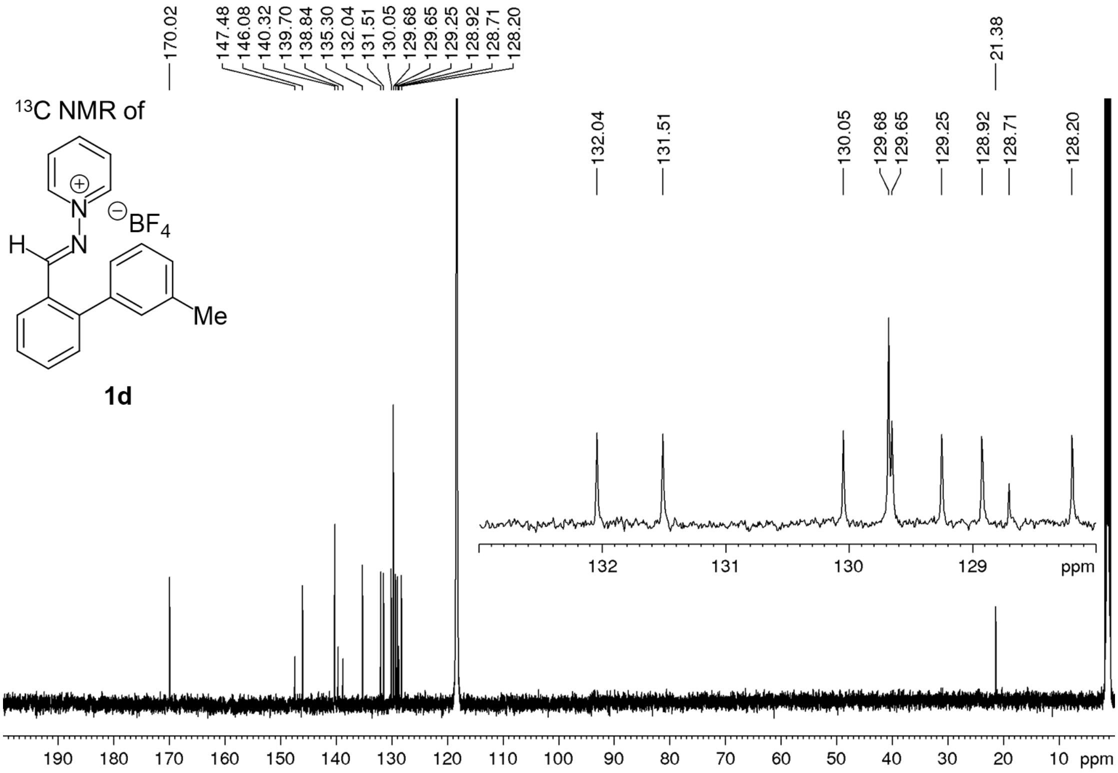
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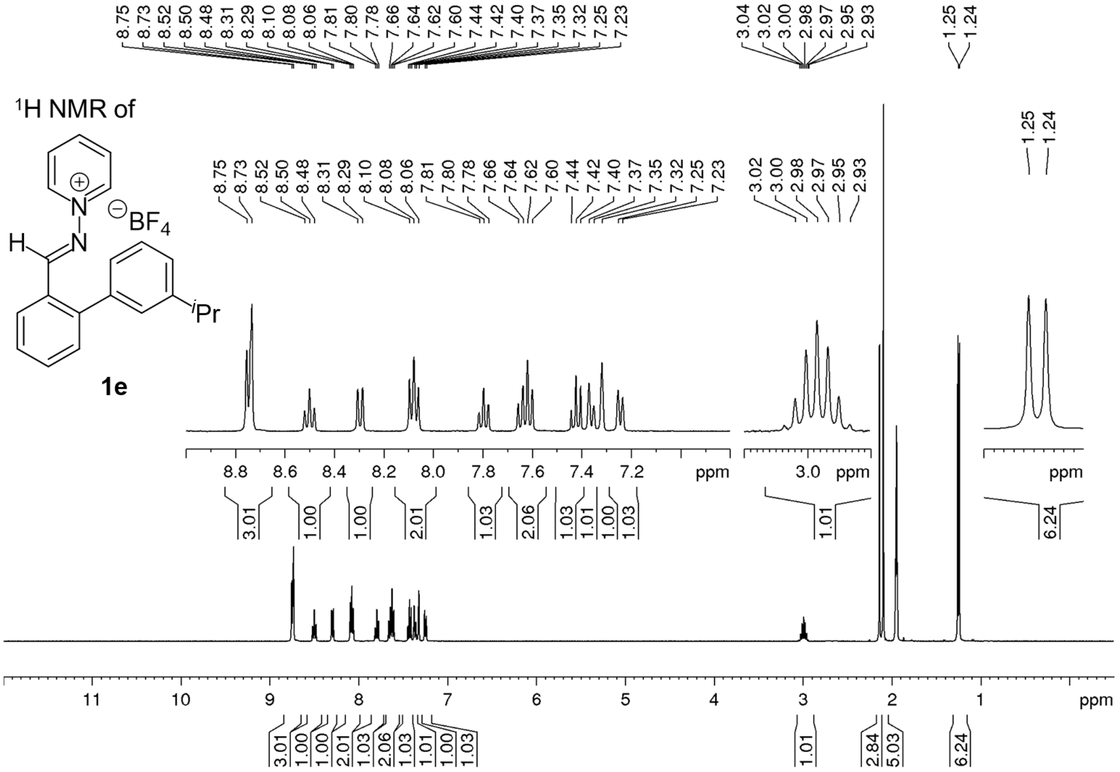

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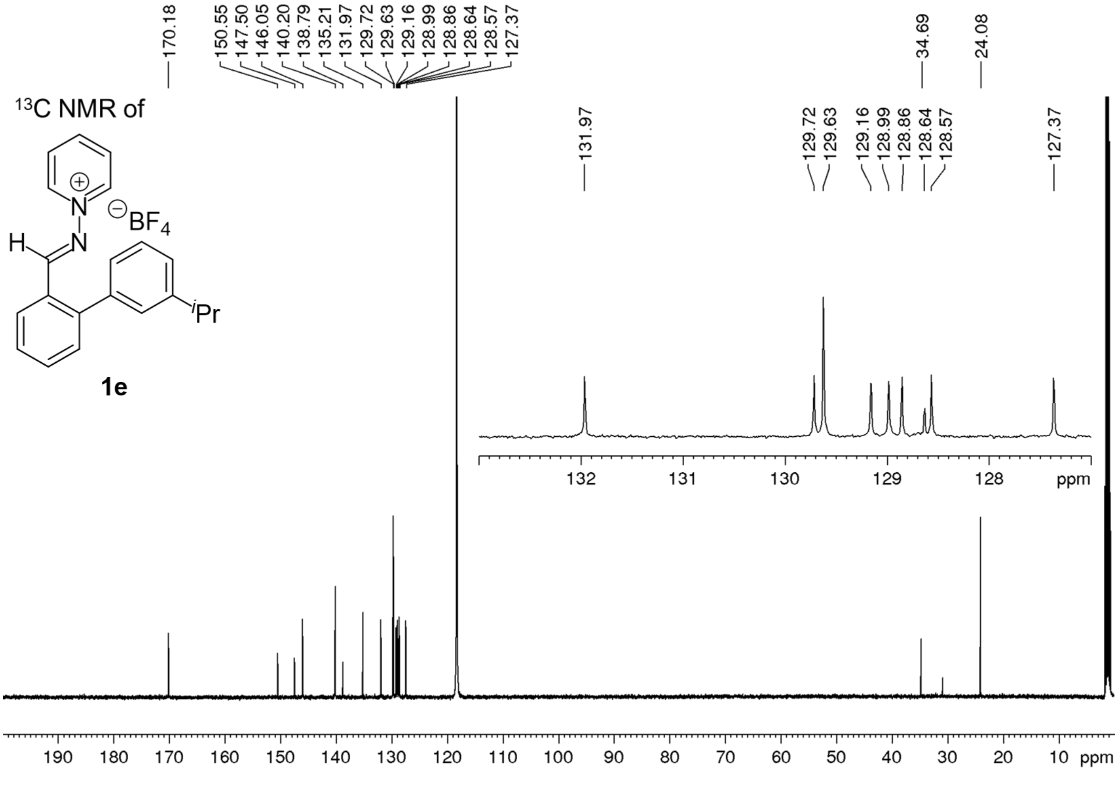

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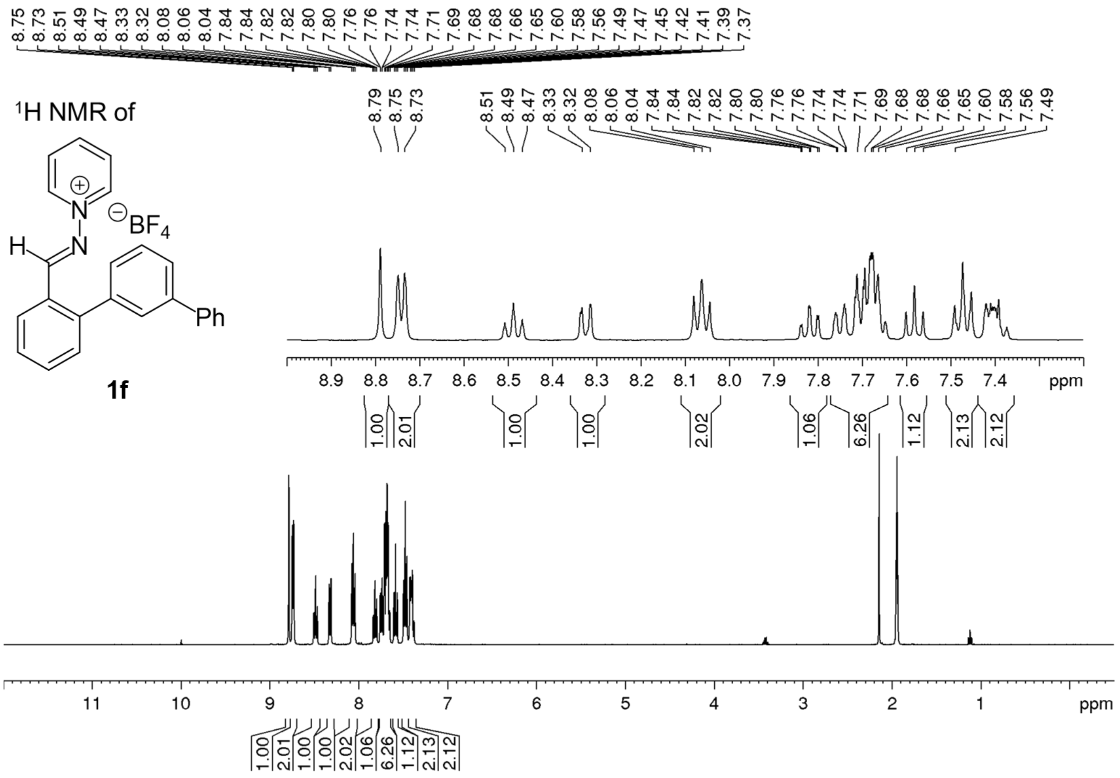
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H
N
N
⊕
⊖BF$_4$
Ph
1f
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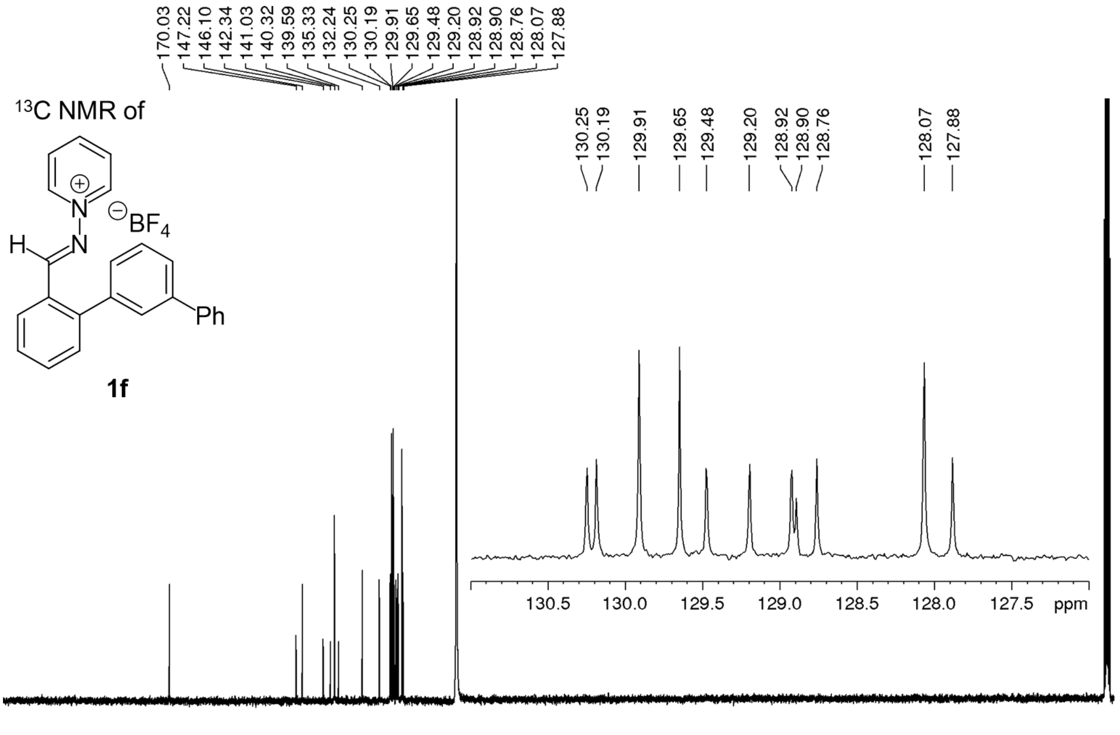
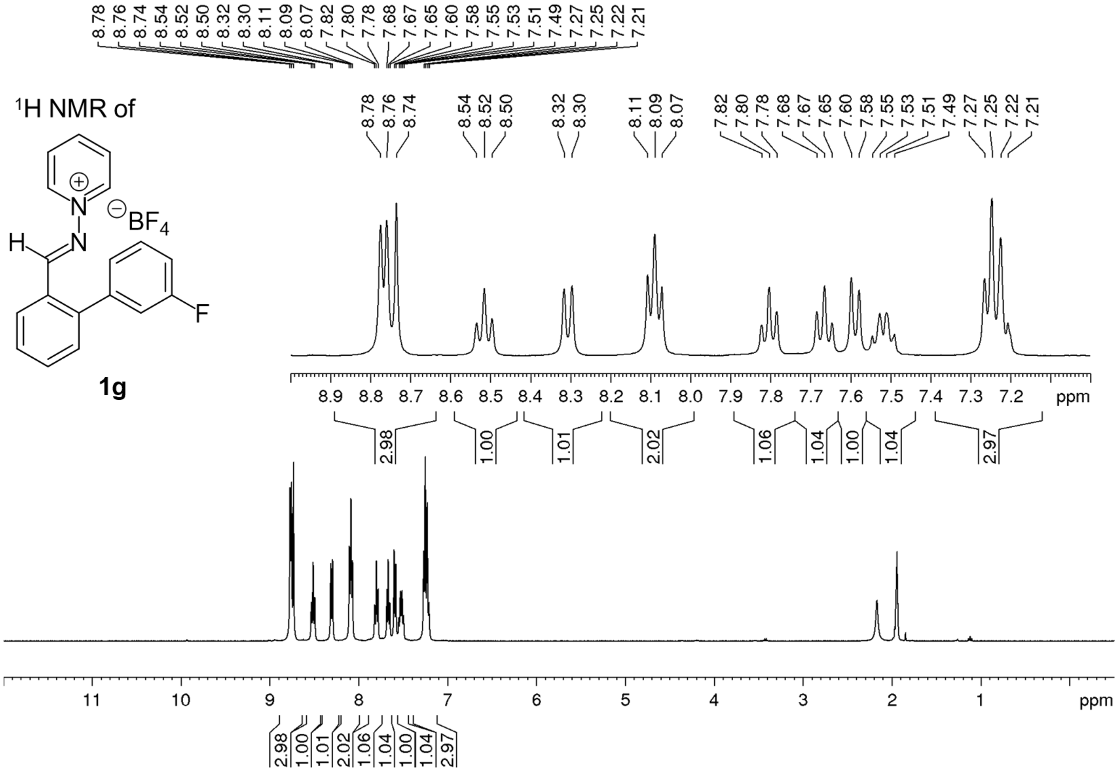
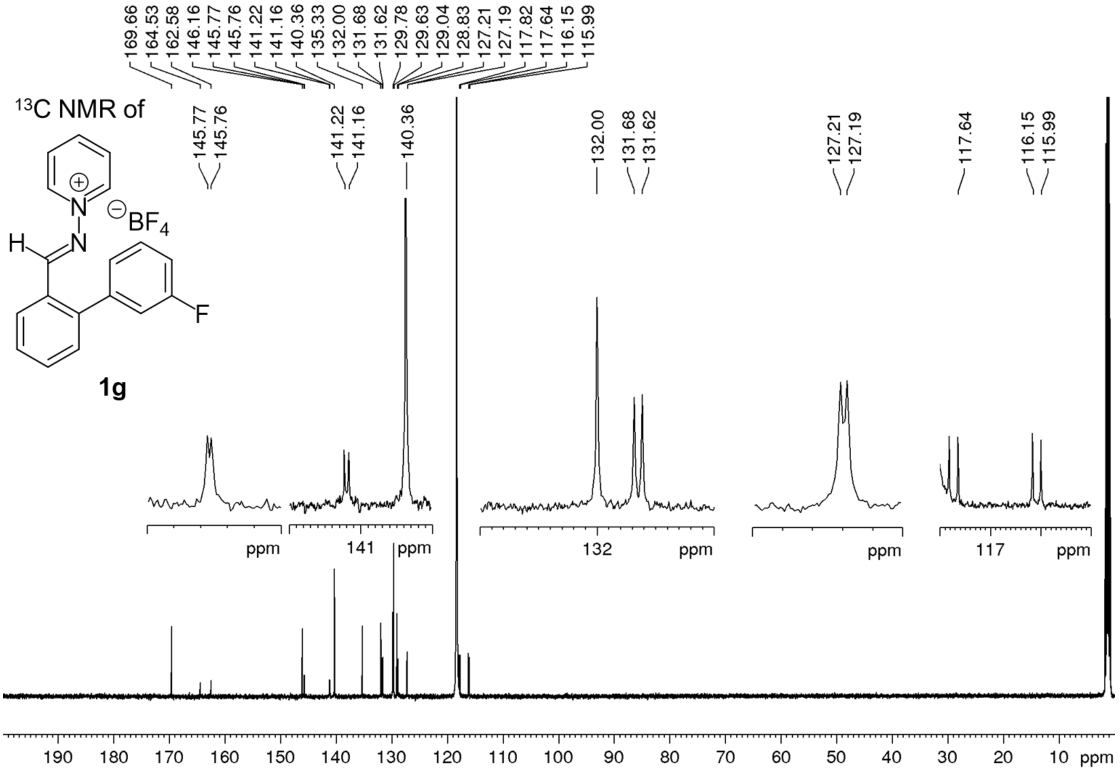

170.03 147.22 146.10 142.34 141.03 140.32 139.59 135.33 132.24 130.25 130.19 129.91 129.65 129.48 129.20 128.92 128.90 128.76 128.07 127.88
^{13}C NMR of
H
N
N
⊕
⊖BF$_4$
Ph
1f
130.25 130.19 129.91 129.65 129.48 129.20 128.92 128.90 128.76 128.07 127.88
130.5 130.0 129.5 129.0 128.5 128.0 127.5 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

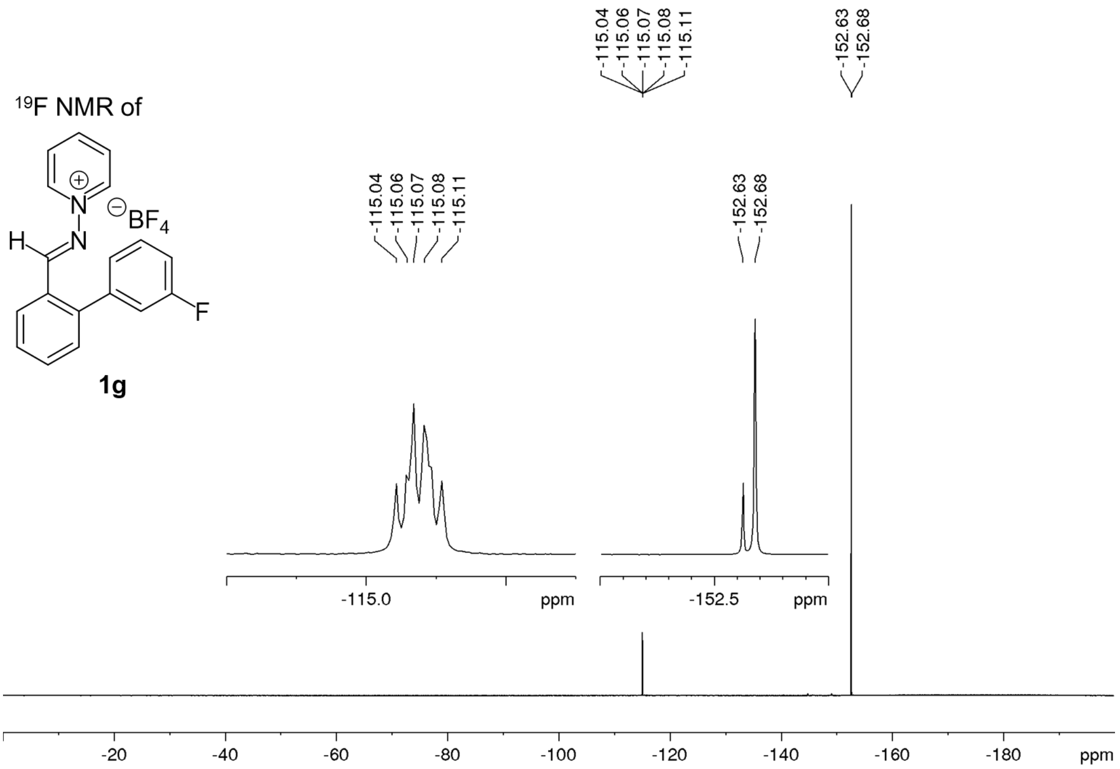


^{1}H NMR of **1g**



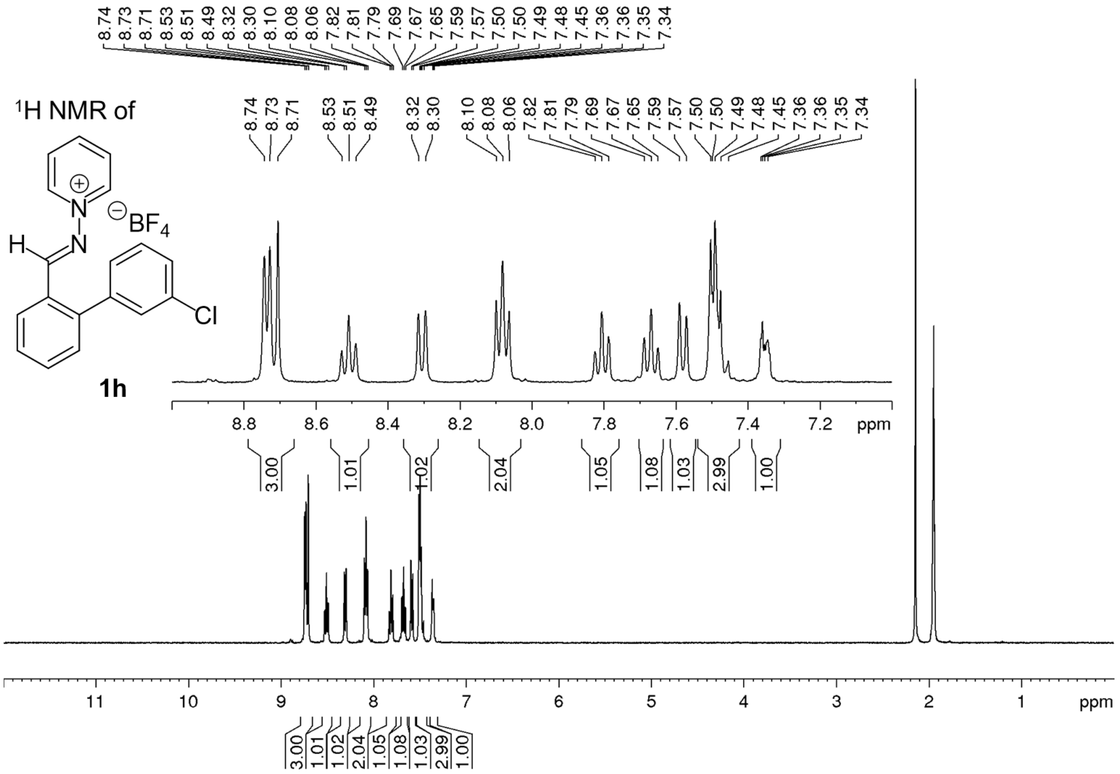
^{13}C NMR of **1g**

^{19}F NMR of



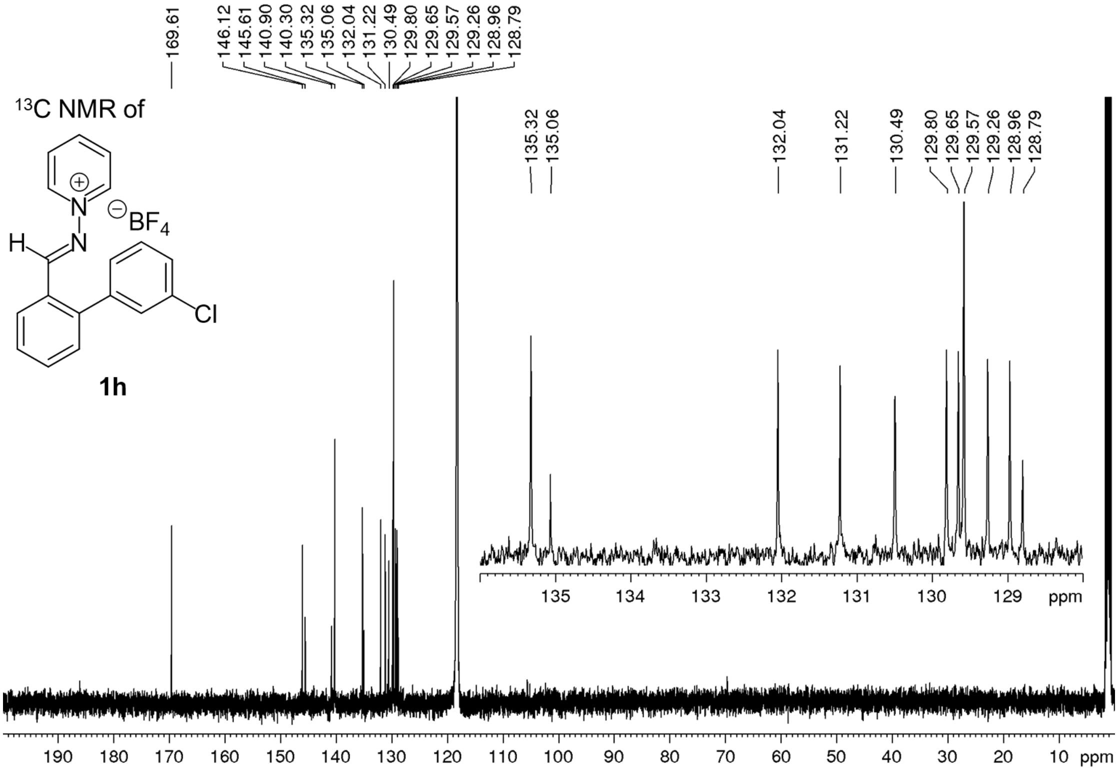
1g

^{1}H NMR of



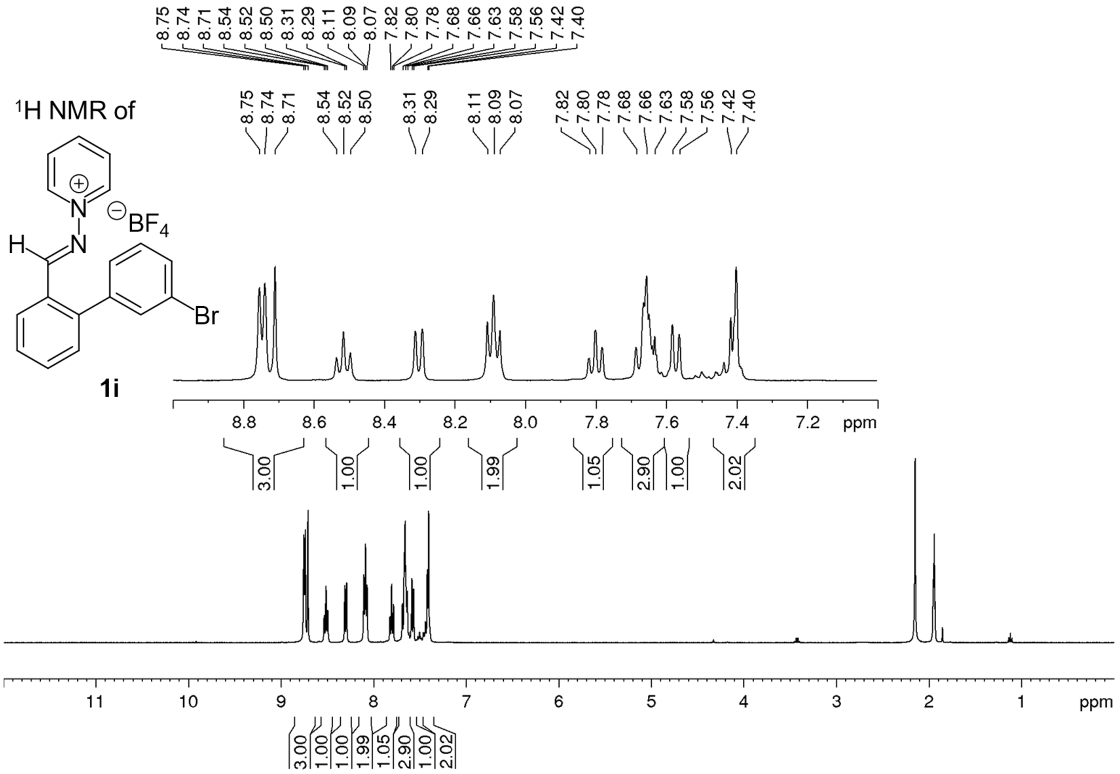
1h

^{13}C NMR of

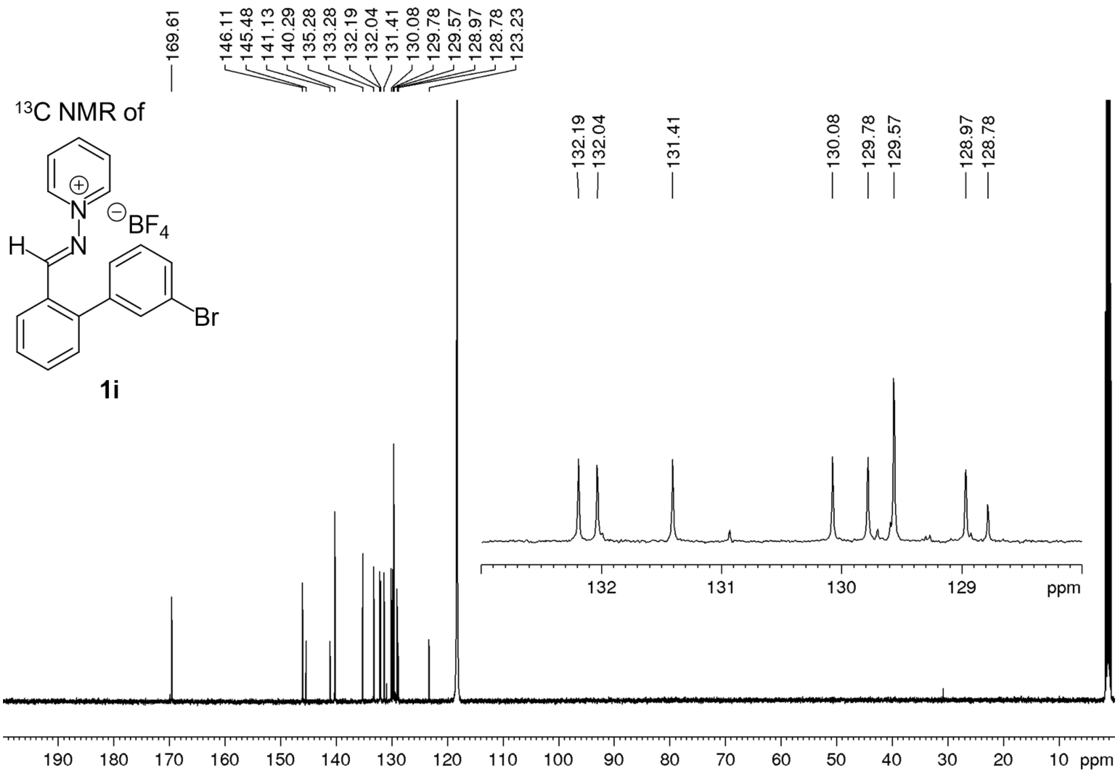


1h

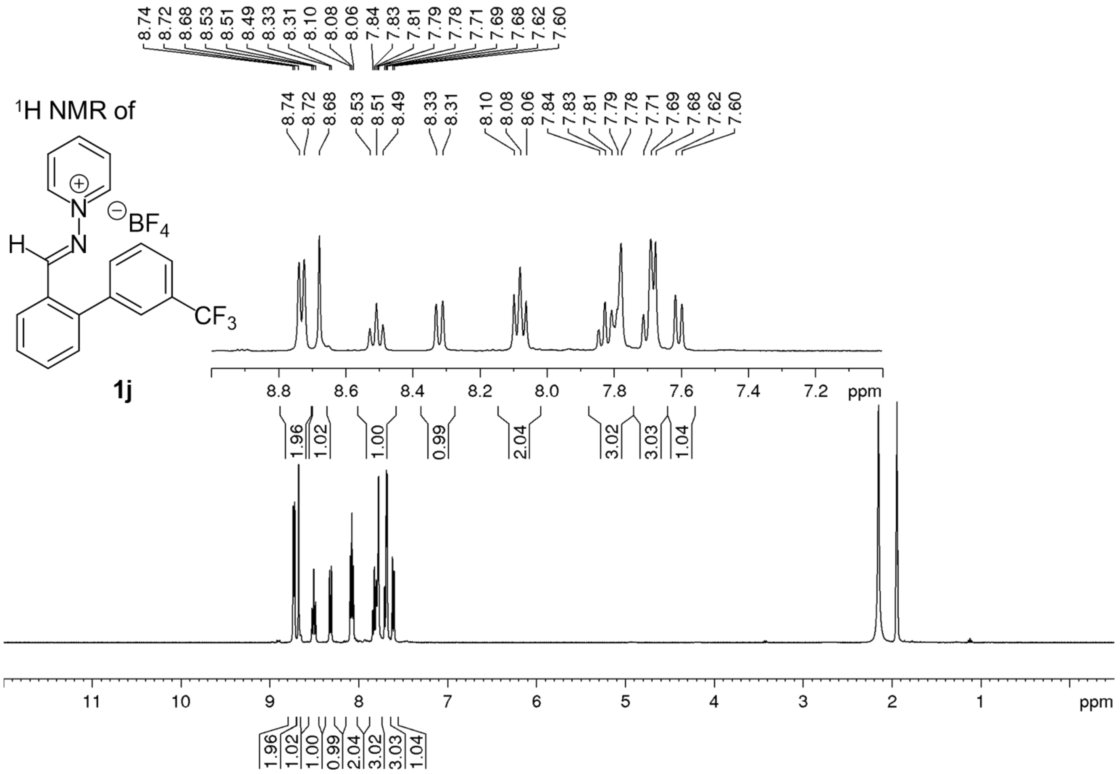
^{1}H NMR of



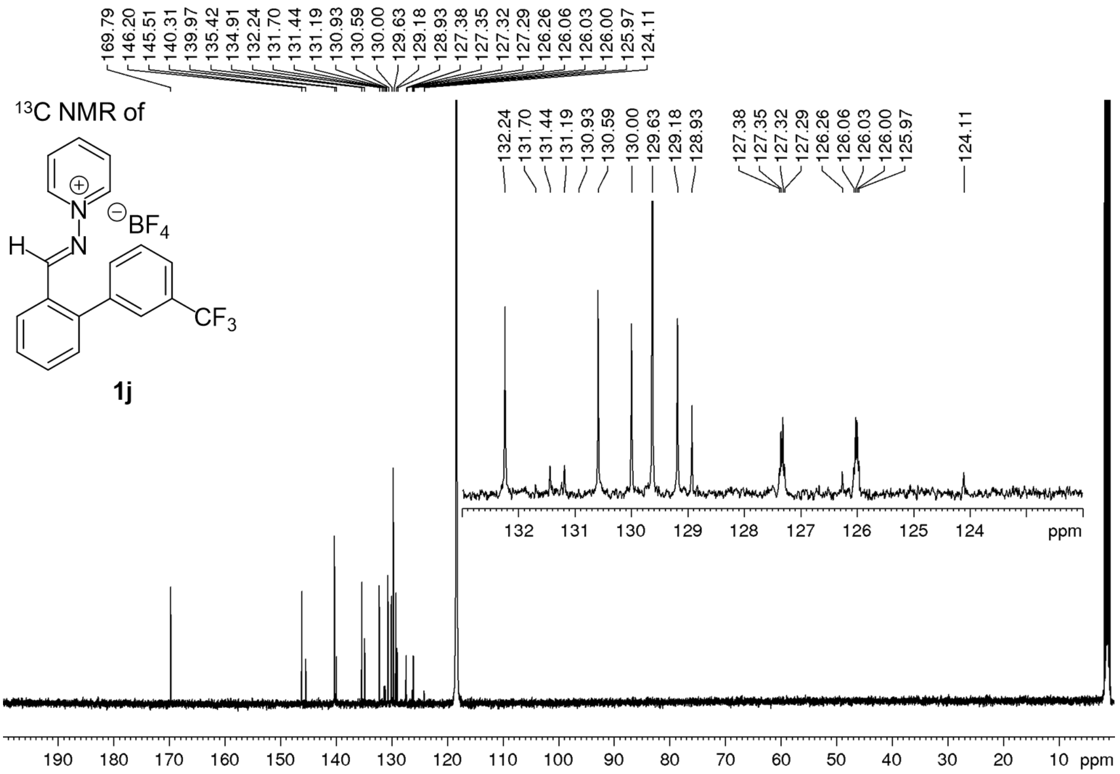
1i

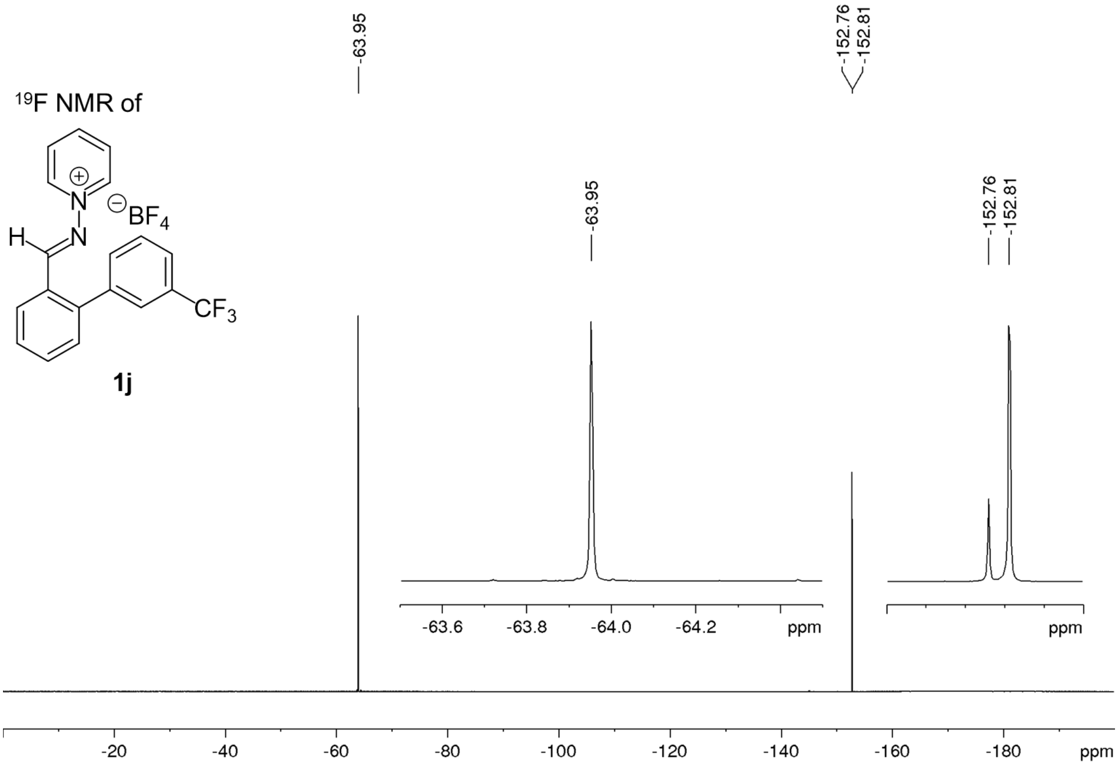


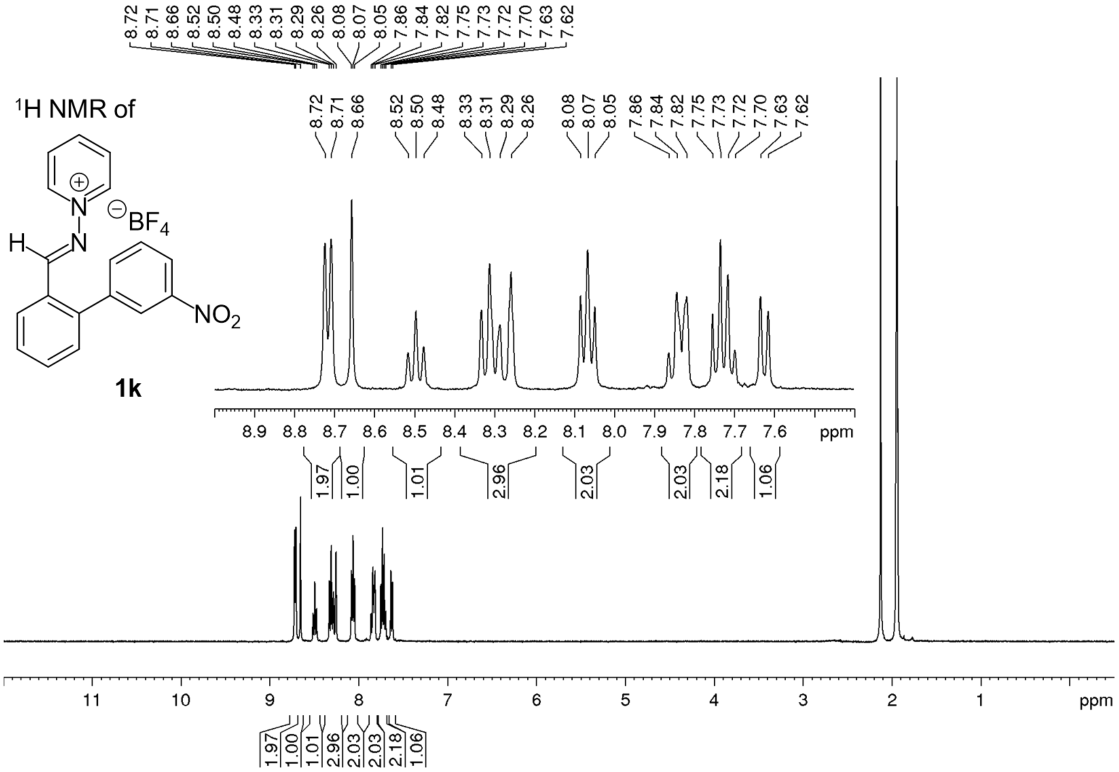
^{13}C NMR of **1i**

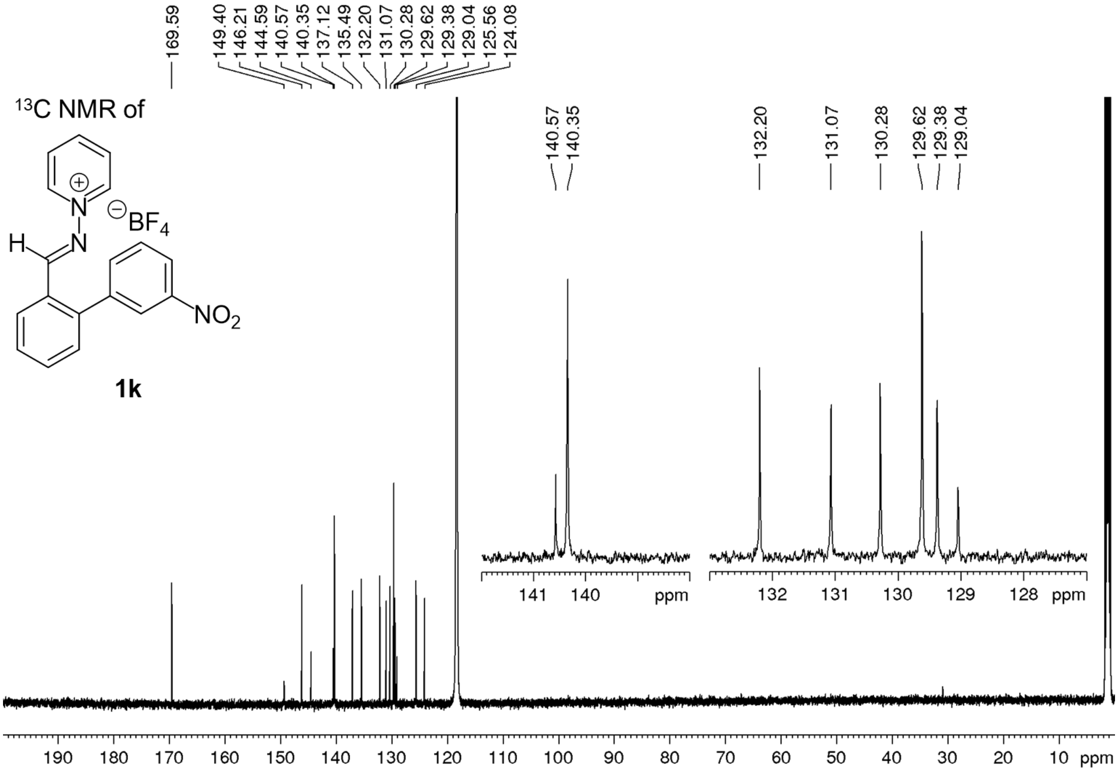


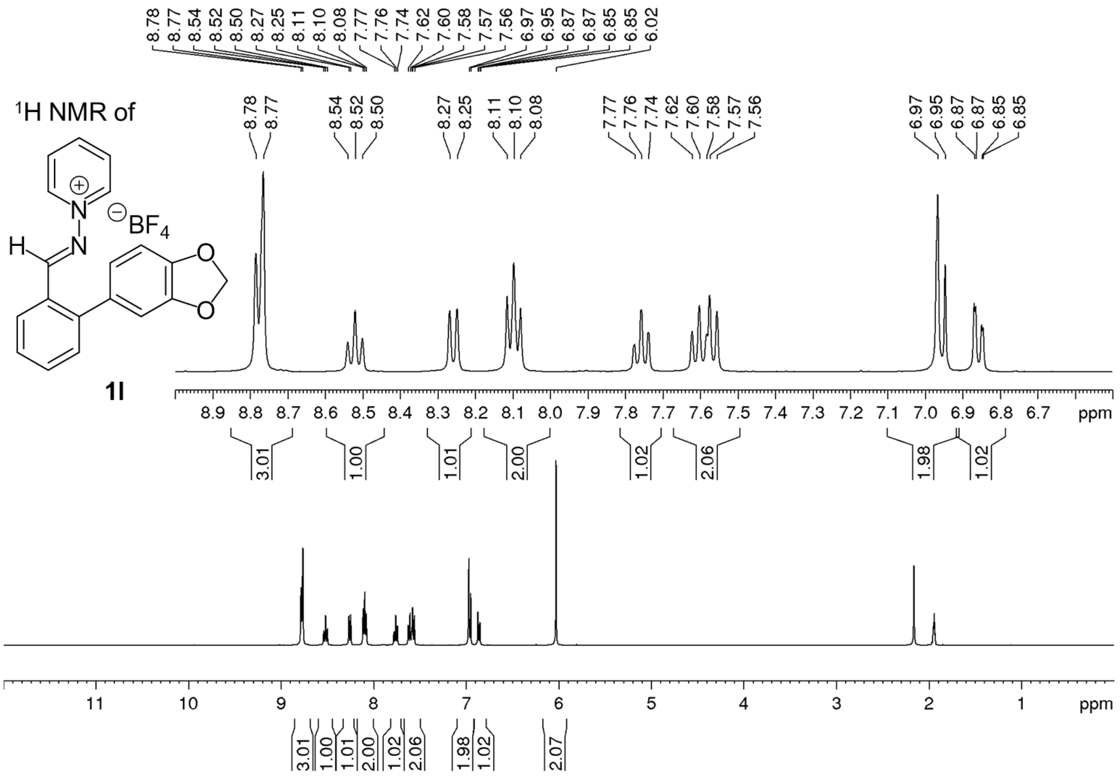
^{1}H NMR of **1j**

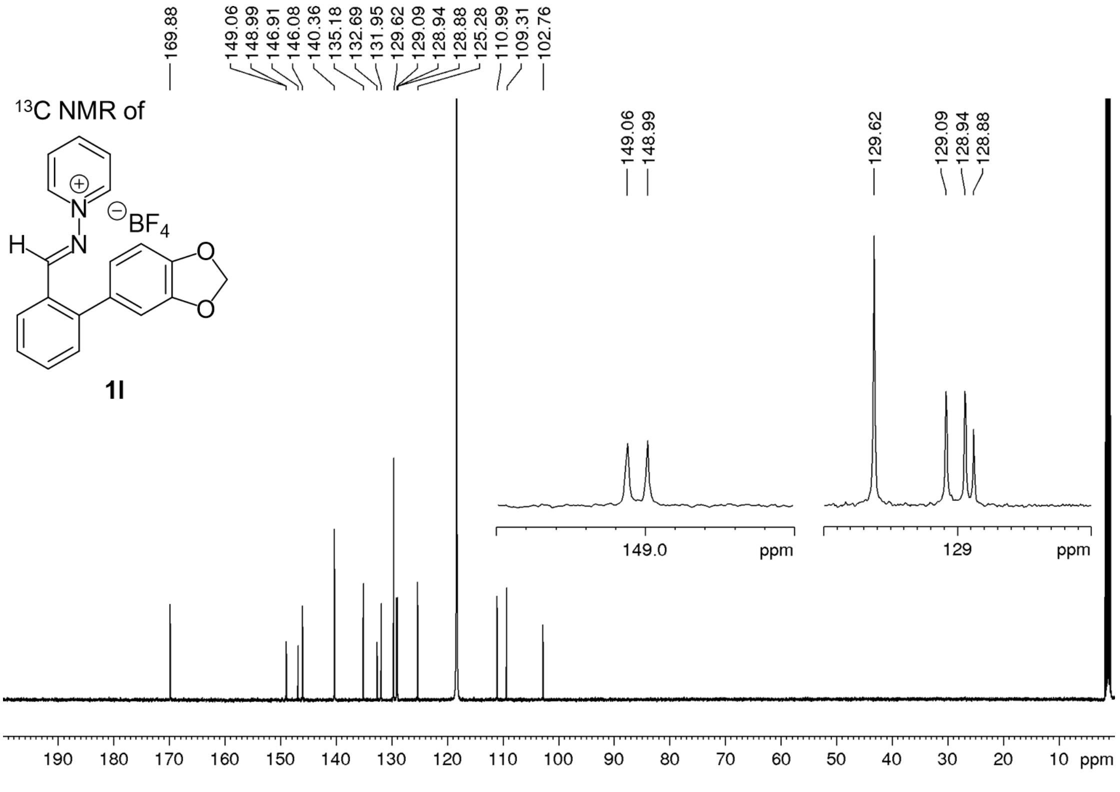

^{13}C NMR of
1j
H
N
N
BF$_4$
CF$_3$
169.79
146.20
145.51
140.31
139.97
135.42
134.91
132.24
131.70
131.44
131.19
130.93
130.59
130.00
129.63
129.18
128.93
127.38
127.35
127.32
127.29
126.26
126.06
126.03
126.00
125.97
124.11
132
131
130
129
128
127
126
125
124
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

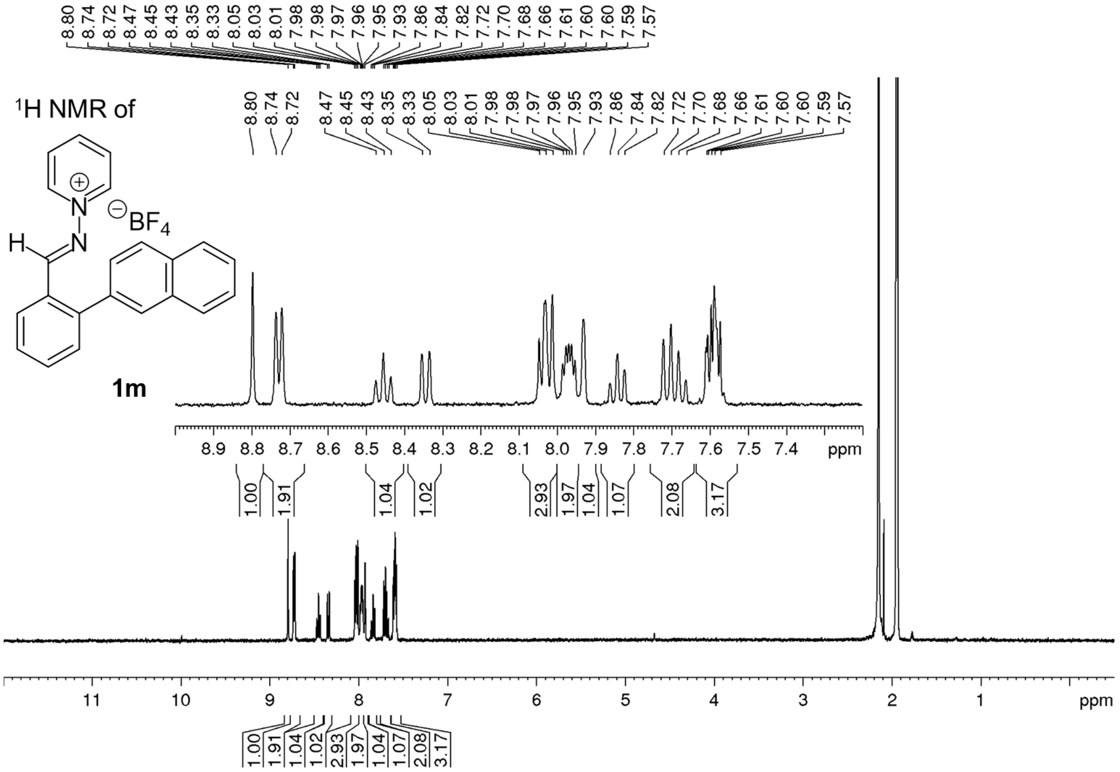

^{19}F NMR of
1j
H
N
N
BF$_4$
CF$_3$
-63.95
-152.76
-152.81
-63.6
-63.8
-64.0
-64.2
ppm
ppm
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm


8.72 8.71 8.66 8.52 8.50 8.48 8.33 8.31 8.29 8.26 8.08 8.07 8.05 7.86 7.84 7.82 7.75 7.73 7.72 7.70 7.63 7.62
^{1}H NMR of
$\oplus$
N
N
H
$^{\ominus}BF_4$
NO_2
1k
8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 ppm
1.97 1.00 1.01 2.96 2.03 2.03 2.18 1.06
11 10 9 8 7 6 5 4 3 2 1 ppm

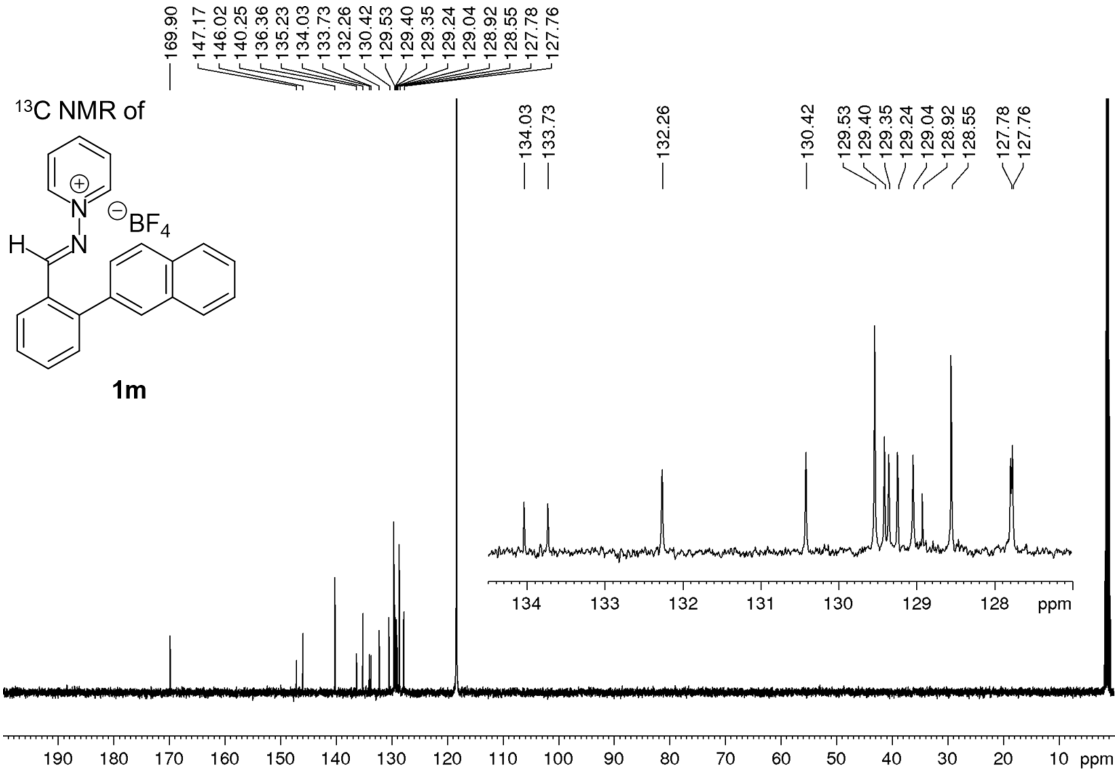

169.59
149.40 146.21 144.59 140.57 140.35 137.12 135.49 132.20 131.07 130.28 129.62 129.38 129.04 125.56 124.08
^{13}C NMR of
$\oplus$
N
N
H
$^{\ominus}BF_4$
NO_2
1k
140.57 140.35
141 140 ppm
132.20 131.07 130.28 129.62 129.38 129.04
132 131 130 129 128 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


1H NMR of
1l
BF4
8.78 8.77 8.54 8.52 8.50 8.27 8.25 8.11 8.10 8.08 7.77 7.76 7.74 7.62 7.60 7.58 7.57 7.56 6.97 6.95 6.87 6.87 6.85 6.85 6.02
8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 ppm
3.01 1.00 1.01 2.00 1.02 2.06 1.98 1.02
11 10 9 8 7 6 5 4 3 2 1 ppm
3.01 1.00 1.01 2.00 1.02 2.06 1.98 1.02 2.07

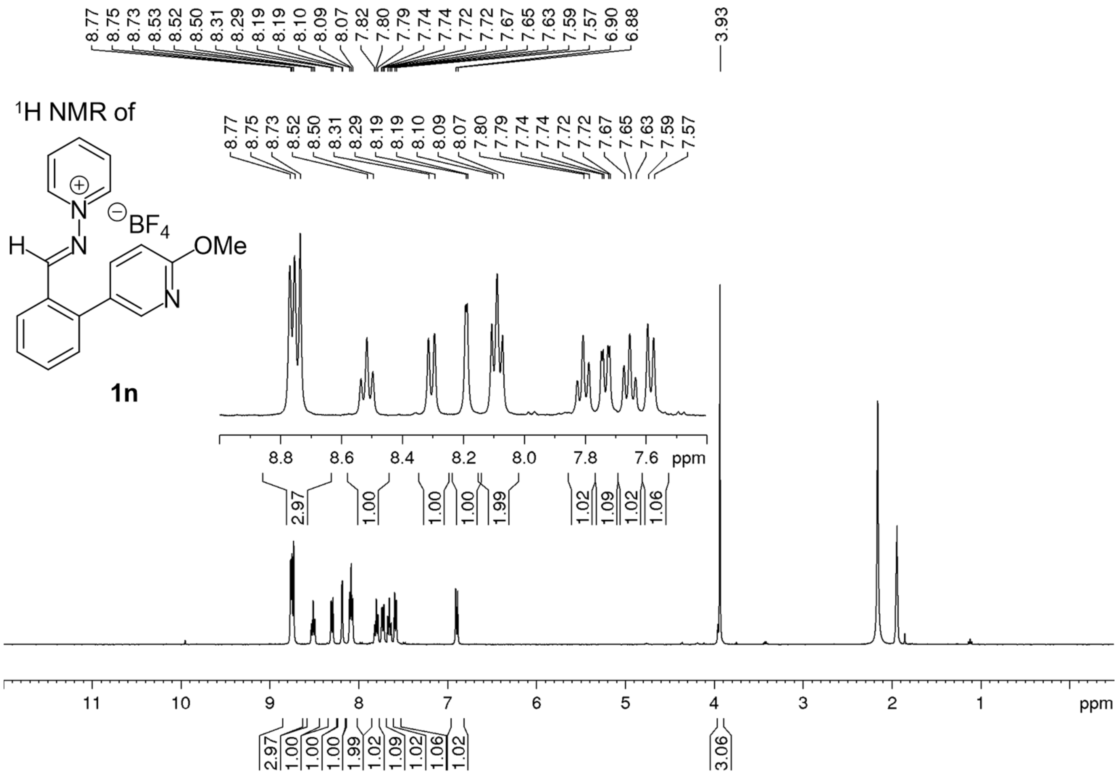

13C NMR of
1l
BF4
169.88
149.06 148.99 146.91 146.08 140.36 135.18 132.69 131.95 129.62 129.09 128.94 128.88 125.28 110.99 109.31 102.76
149.06 148.99
149.0 ppm
129.62 129.09 128.94 128.88
129 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

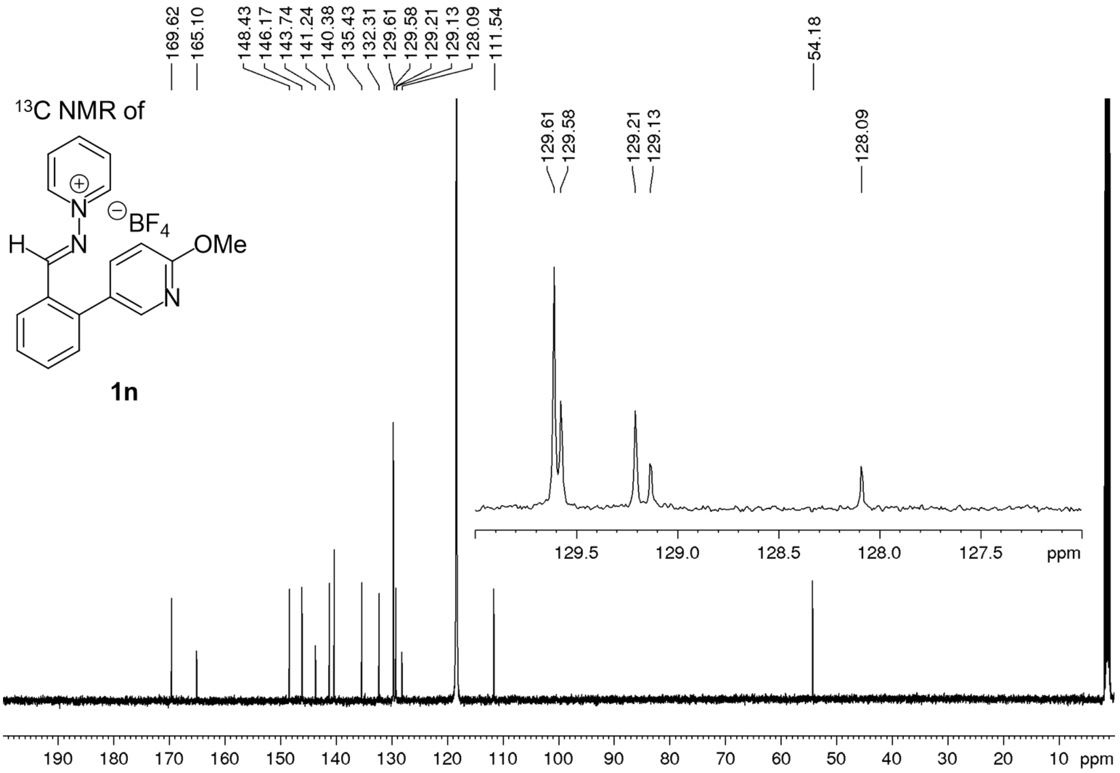


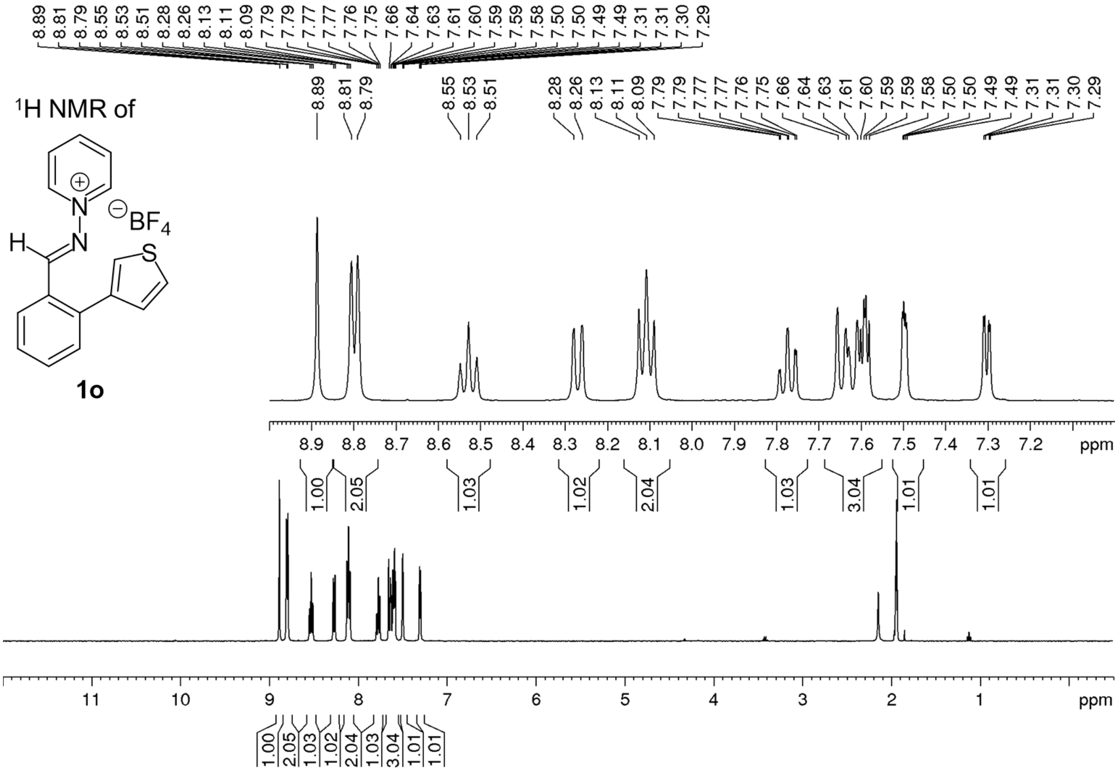
8.80 8.74 8.72 8.47 8.45 8.43 8.35 8.33 8.05 8.03 8.01 7.98 7.98 7.97 7.96 7.95 7.93 7.86 7.84 7.82 7.72 7.70 7.68 7.66 7.61 7.60 7.60 7.59 7.57
^{1}H NMR of
$\oplus$
N
N
H
$^\ominus BF_4$
1m
8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 ppm
1.00 1.91 1.04 1.02 2.93 1.97 1.04 1.07 2.08 3.17
11 10 9 8 7 6 5 4 3 2 1 ppm
1.00 1.91 1.04 1.02 2.93 1.97 1.04 1.07 2.08 3.17



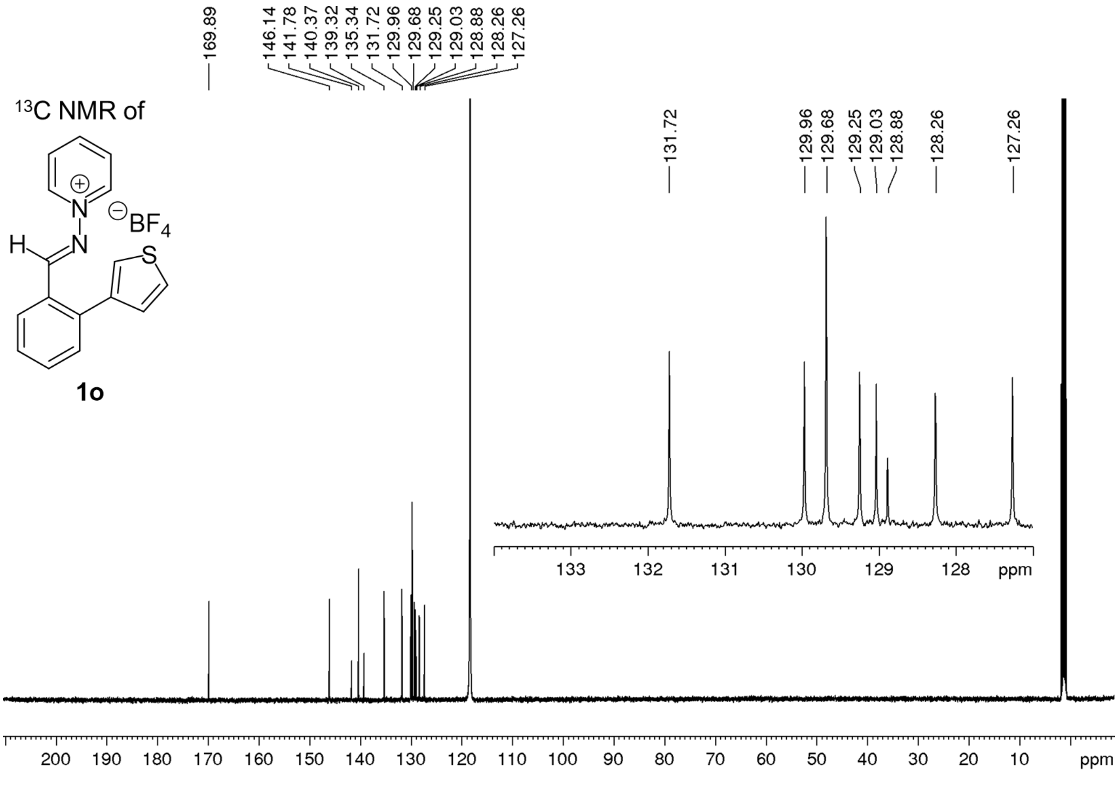
169.90 147.17 146.02 140.25 136.36 135.23 134.03 133.73 132.26 130.42 129.53 129.40 129.35 129.24 129.04 128.92 128.55 127.78 127.76
^{13}C NMR of
$\oplus$
N
N
H
$^\ominus BF_4$
1m
134.03 133.73 132.26 130.42 129.53 129.40 129.35 129.24 129.04 128.92 128.55 127.78 127.76
134 133 132 131 130 129 128 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.77
8.75
8.73
8.53
8.52
8.50
8.31
8.29
8.19
8.19
8.10
8.09
8.07
7.82
7.80
7.79
7.74
7.74
7.72
7.72
7.67
7.65
7.63
7.59
7.57
6.90
6.88
3.93
1H NMR of
OMe
BF4
H
N
1n
8.8
8.6
8.4
8.2
8.0
7.8
7.6
ppm
2.97
1.00
1.00
1.00
1.99
1.02
1.09
1.02
1.06
11
10
9
8
7
6
5
4
3
2
1
ppm
2.97
1.00
1.00
1.00
1.00
1.99
1.02
1.09
1.02
1.06
1.02
3.06

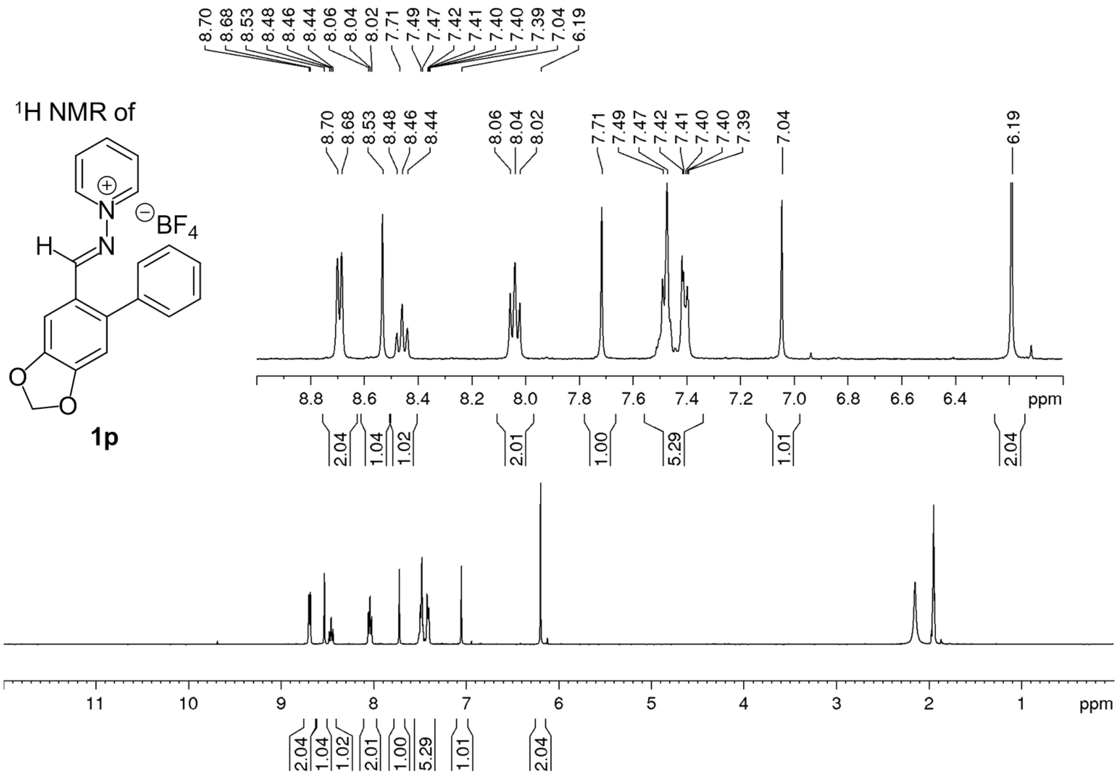

169.62
165.10
148.43
146.17
143.74
141.24
140.38
135.43
132.31
129.61
129.58
129.21
129.13
128.09
111.54
54.18
13C NMR of
OMe
BF4
H
N
1n
129.61
129.58
129.21
129.13
128.09
129.5
129.0
128.5
128.0
127.5
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


^{1}H NMR of

1o

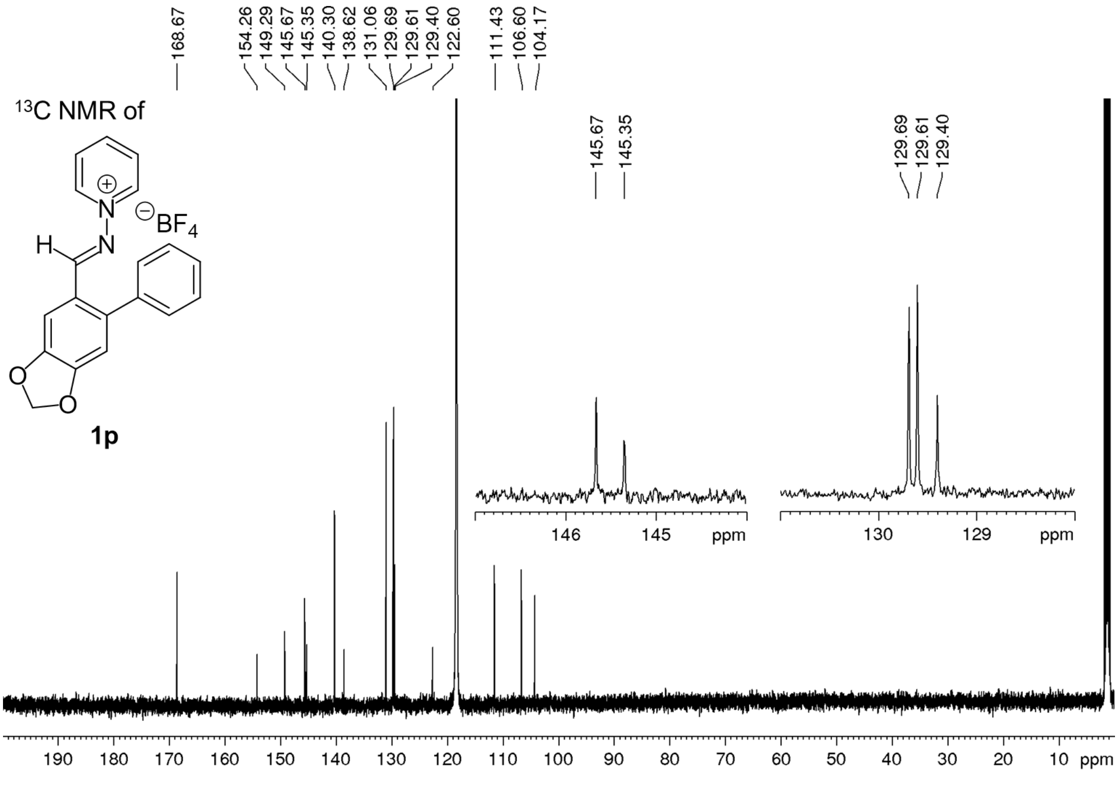

^{13}C NMR of

1o



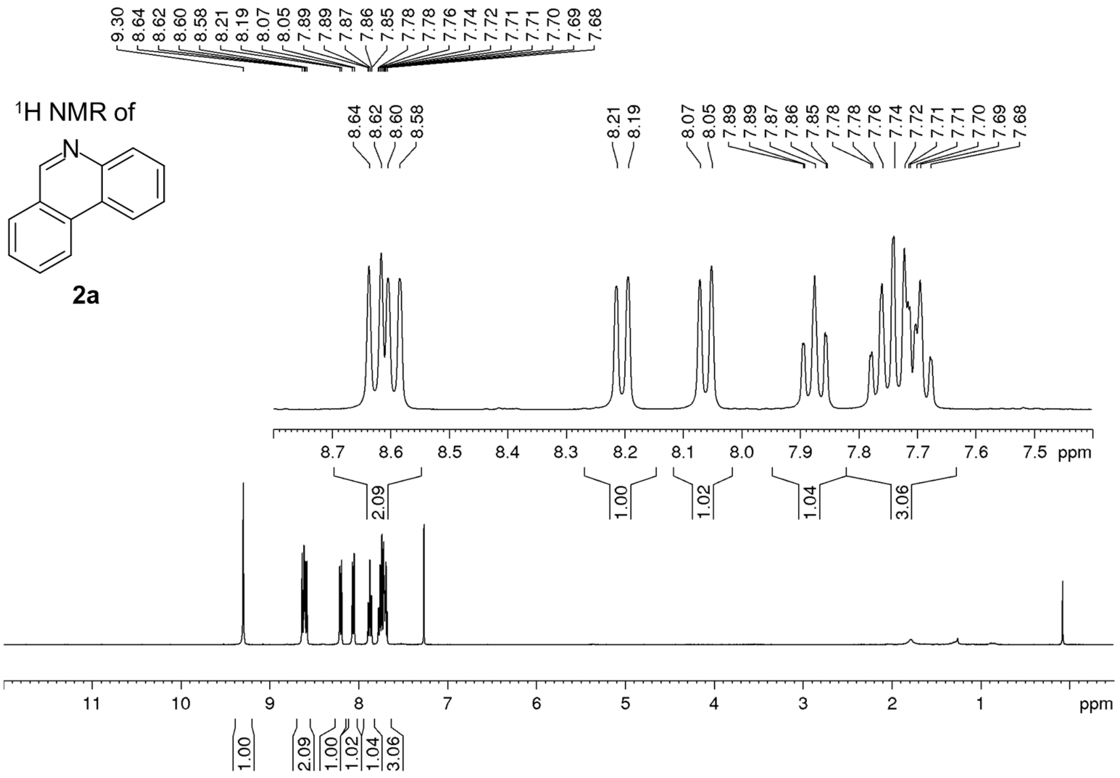
^{1}H NMR of

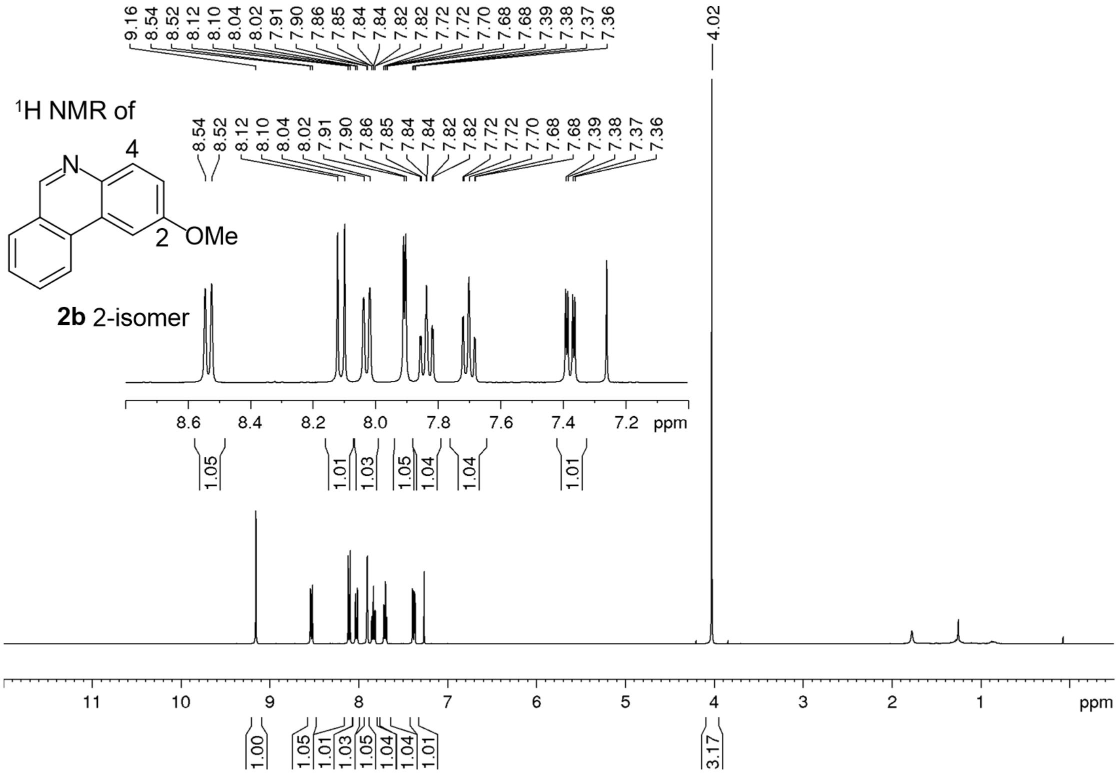
1p

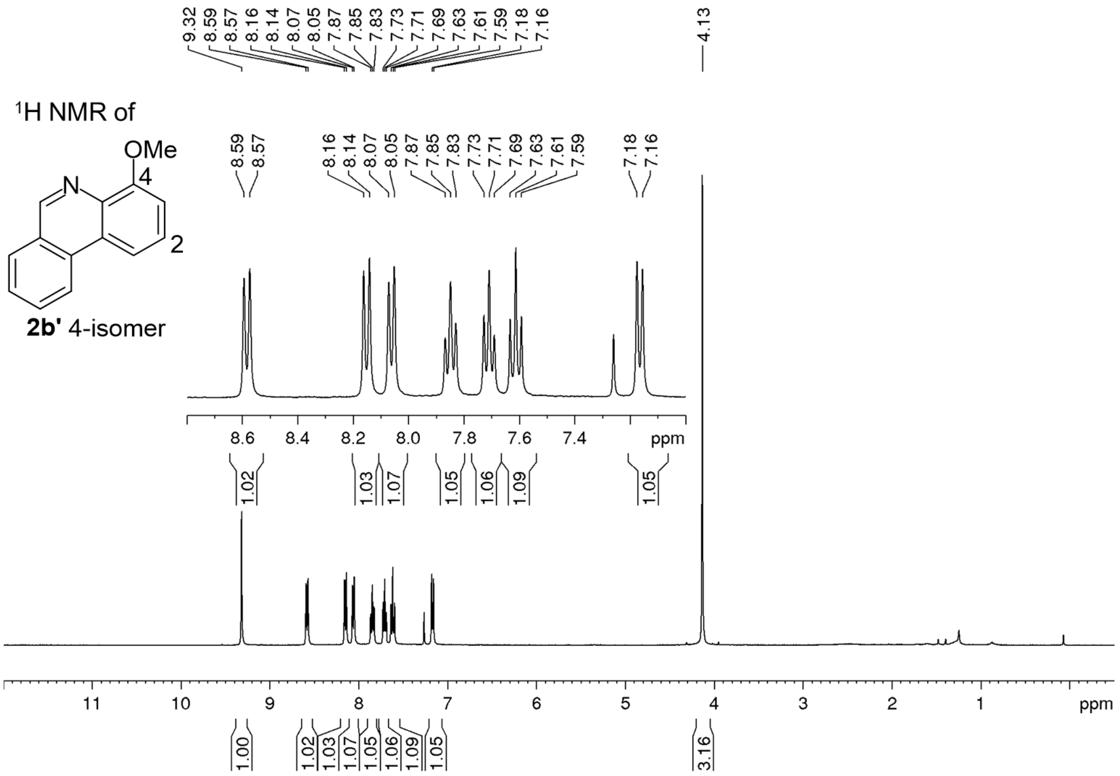


^{13}C NMR of

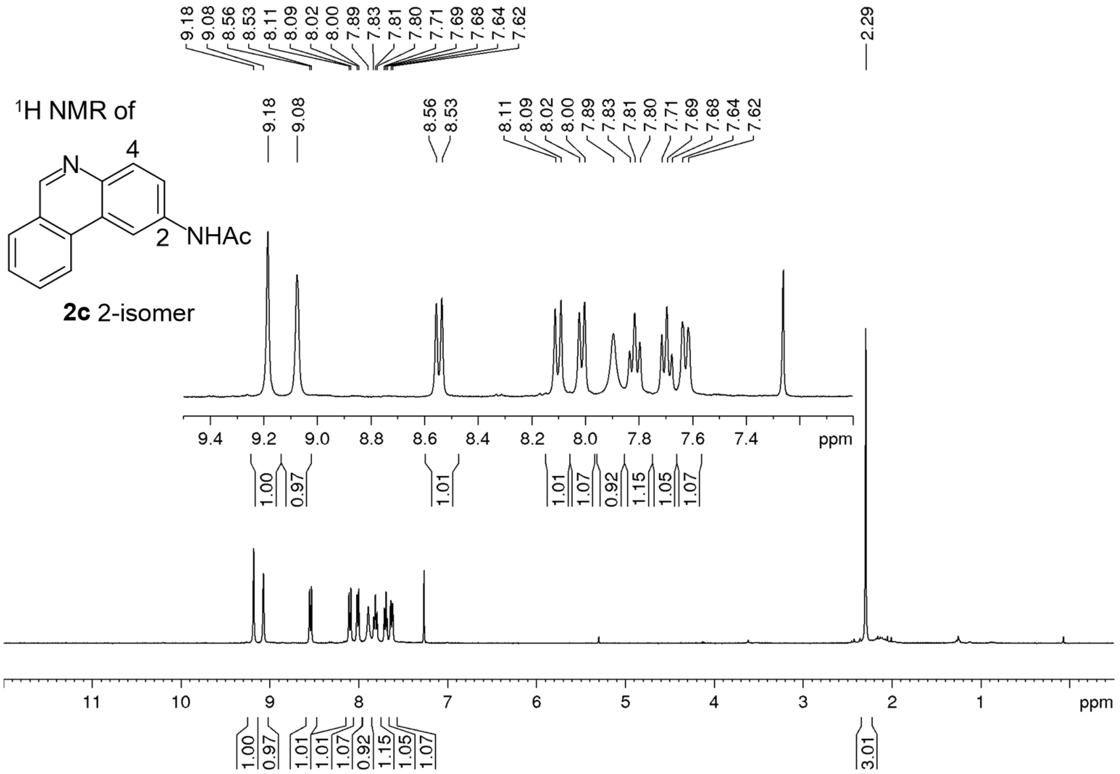
1p


9.30 8.64 8.62 8.60 8.58 8.21 8.19 8.07 8.05 7.89 7.89 7.87 7.86 7.85 7.78 7.78 7.76 7.74 7.72 7.71 7.71 7.70 7.69 7.68
¹H NMR of
N
2a
8.64 8.62 8.60 8.58
8.21 8.19
8.07 8.05 7.89 7.89 7.87 7.86 7.85 7.78 7.78 7.76 7.74 7.72 7.71 7.71 7.70 7.69 7.68
8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 ppm
2.09 1.00 1.02 1.04 3.06
11 10 9 8 7 6 5 4 3 2 1 ppm
1.00 2.09 1.00 1.02 1.04 3.06

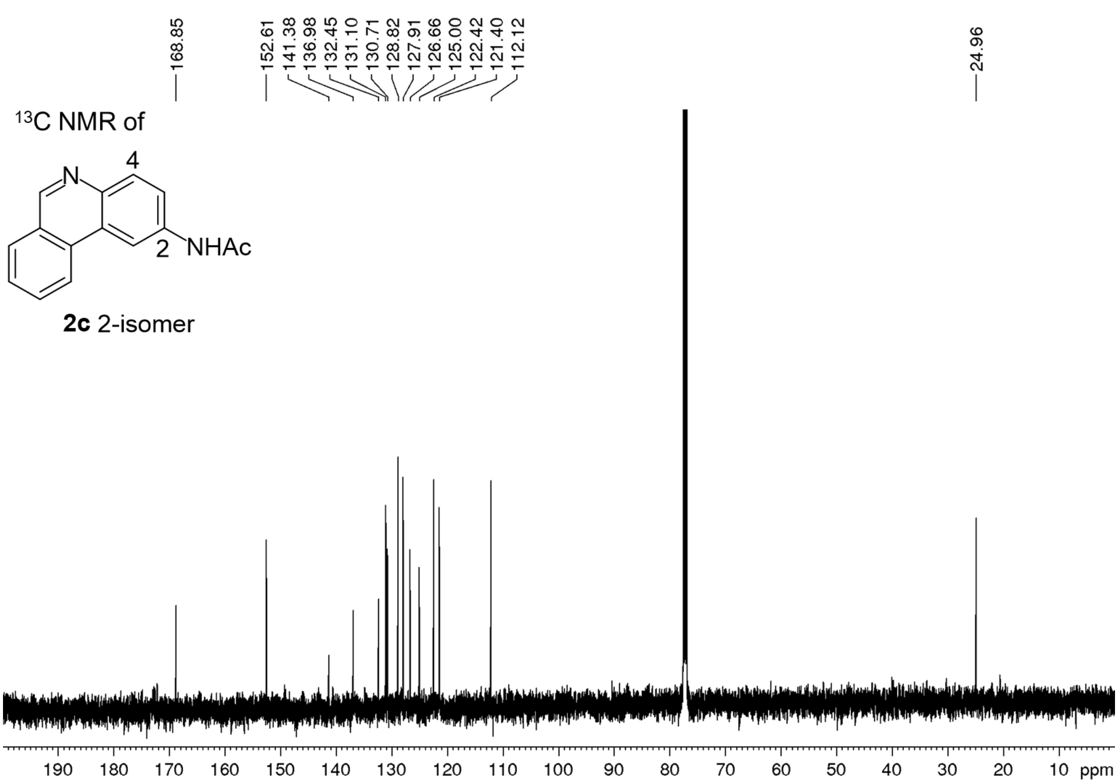

9.16 8.54 8.52 8.12 8.10 8.04 8.02 7.91 7.90 7.86 7.85 7.84 7.84 7.82 7.82 7.72 7.72 7.70 7.68 7.68 7.39 7.38 7.37 7.36
4.02
¹H NMR of
N
4
2
OMe
2b 2-isomer
8.54 8.52 8.12 8.10 8.04 8.02 7.91 7.90 7.86 7.85 7.84 7.84 7.82 7.82 7.72 7.72 7.70 7.68 7.68 7.39 7.38 7.37 7.36
8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 ppm
1.05 1.01 1.03 1.05 1.04 1.04 1.01
11 10 9 8 7 6 5 4 3 2 1 ppm
1.00 1.05 1.01 1.03 1.05 1.04 1.04 1.01 3.17

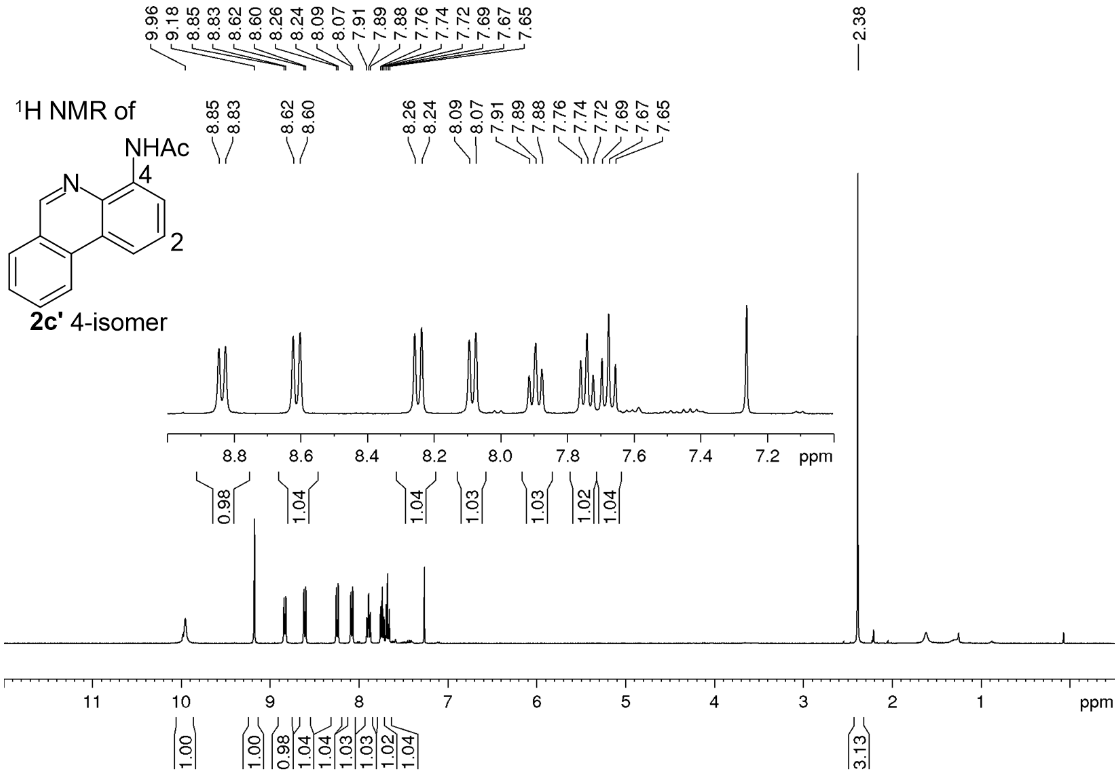


^{1}H NMR of **2b'** 4-isomer

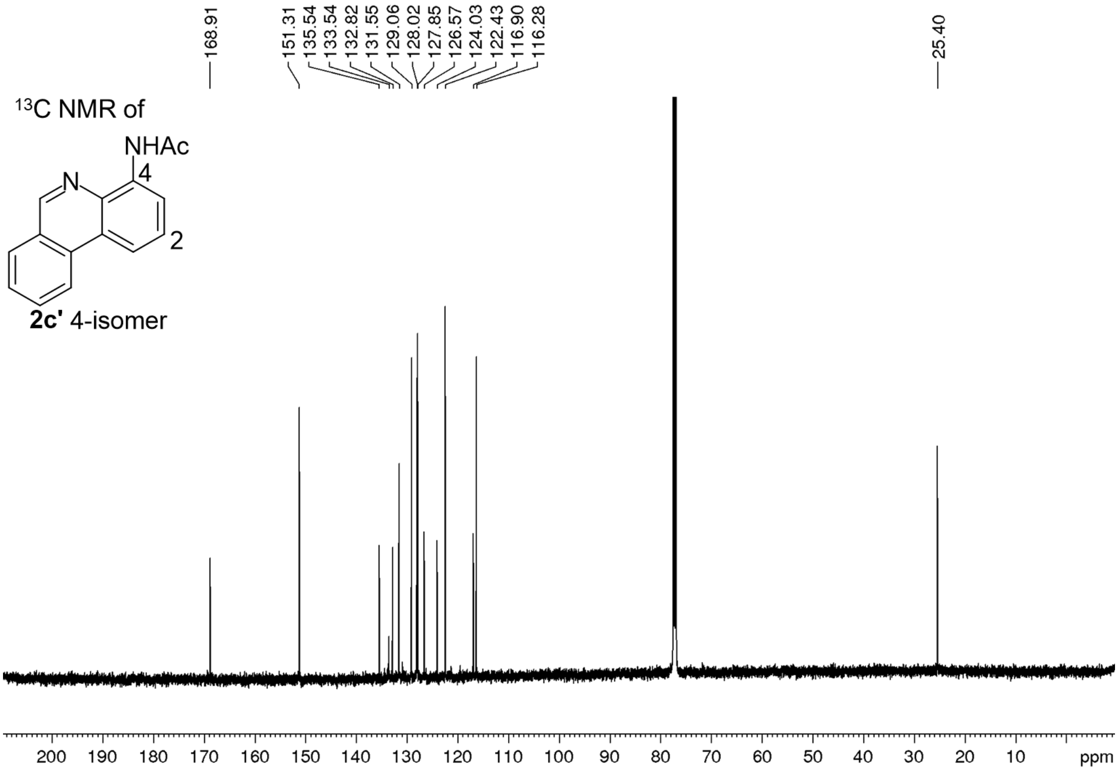


^{1}H NMR of **2c** 2-isomer


168.85
152.61
141.38
136.98
132.45
131.10
130.71
128.82
127.91
126.66
125.00
122.42
121.40
112.12
24.96
^{13}C NMR of
N
4
2
NHAc
2c 2-isomer
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

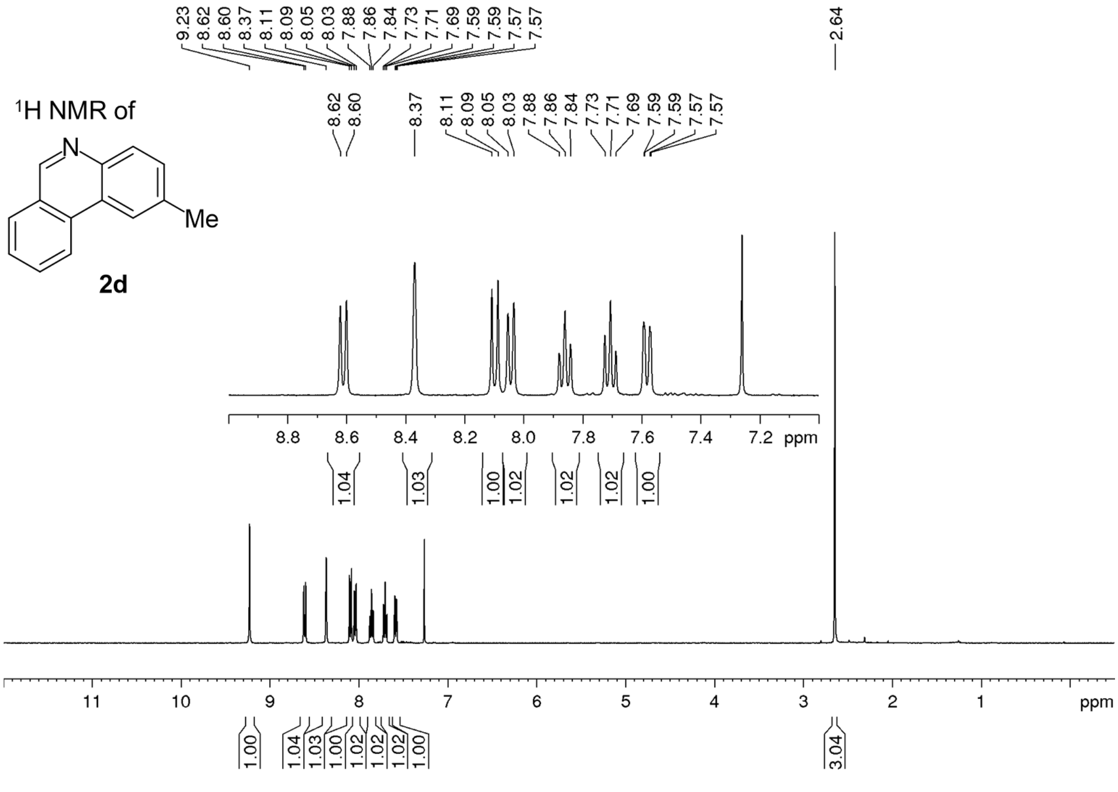

9.96
9.18
8.85
8.83
8.62
8.60
8.26
8.24
8.09
8.07
7.91
7.89
7.88
7.76
7.74
7.72
7.69
7.67
7.65
2.38
^{1}H NMR of
NHAc
N
4
2
2c' 4-isomer
8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 ppm
0.98
1.04
1.04
1.03
1.03
1.02
1.04
11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
1.00
0.98
1.04
1.04
1.03
1.03
1.02
1.04
3.13

^{13}C NMR of



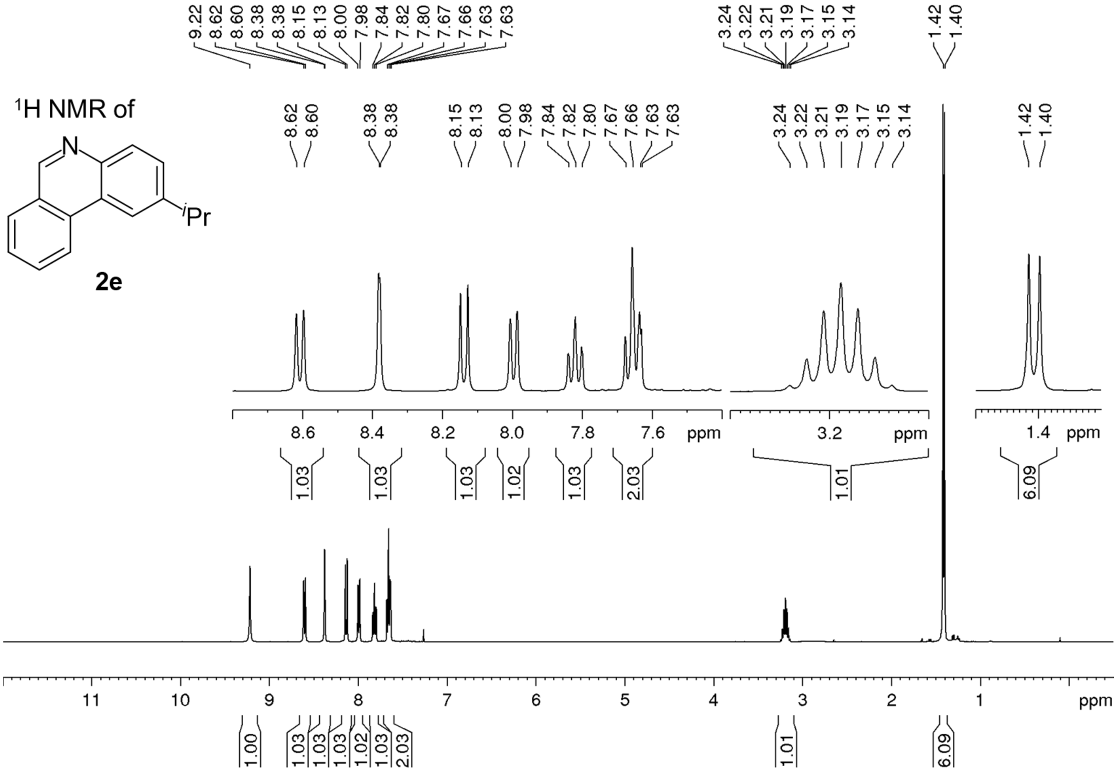
2c' 4-isomer

^{1}H NMR of



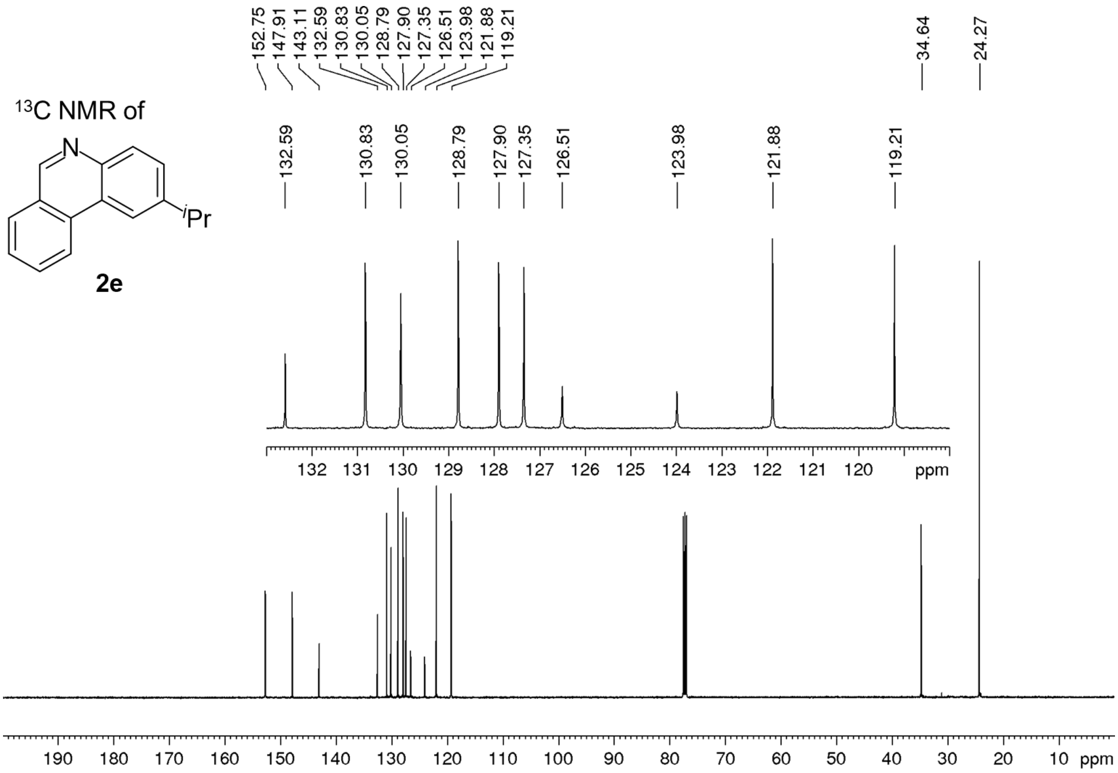
2d

^{1}H NMR of

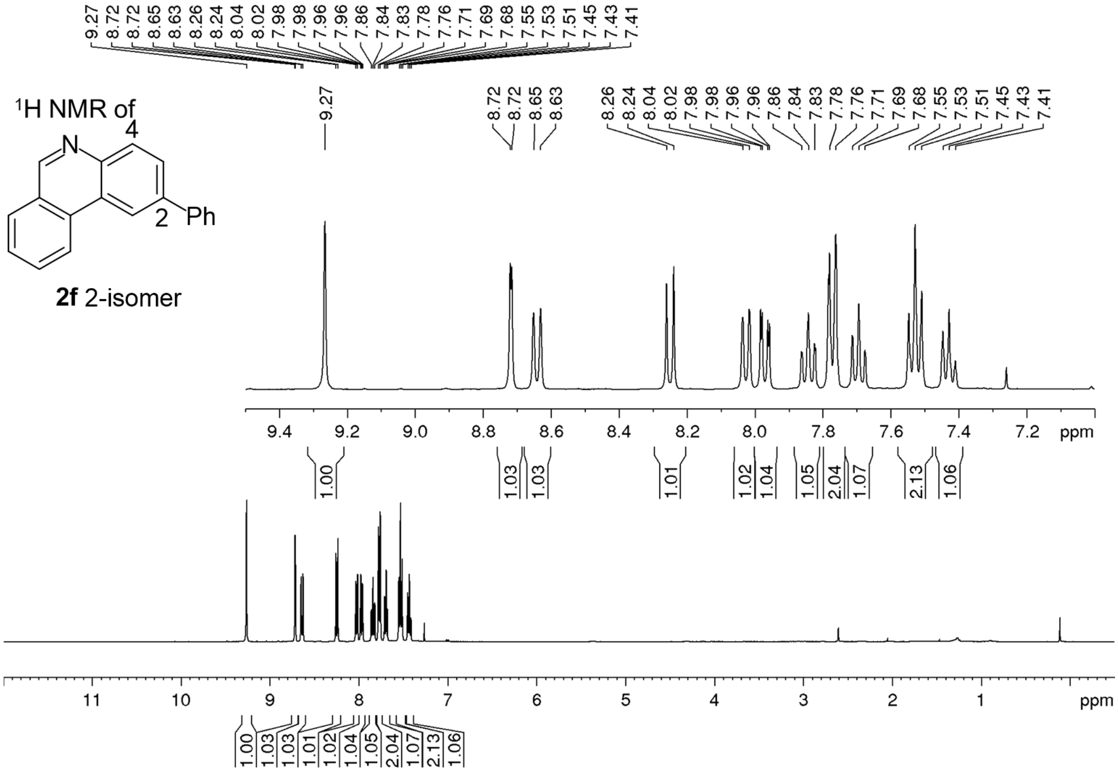


2e

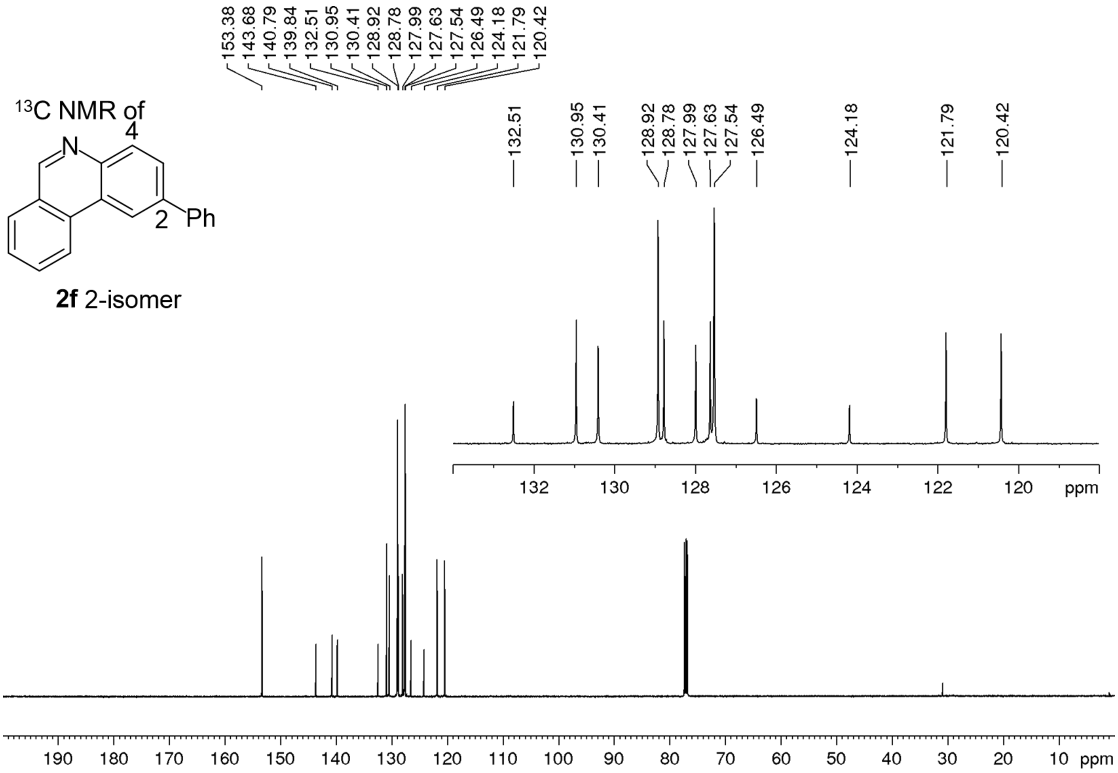
^{13}C NMR of



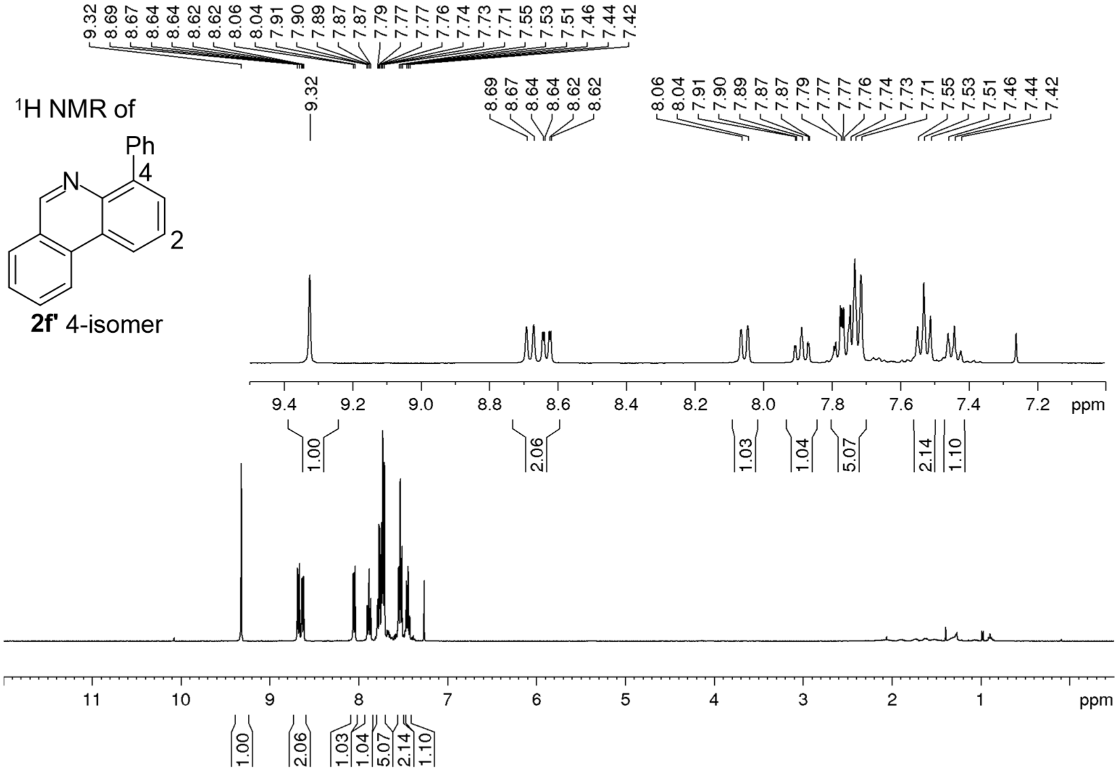
2e


^{1}H NMR of

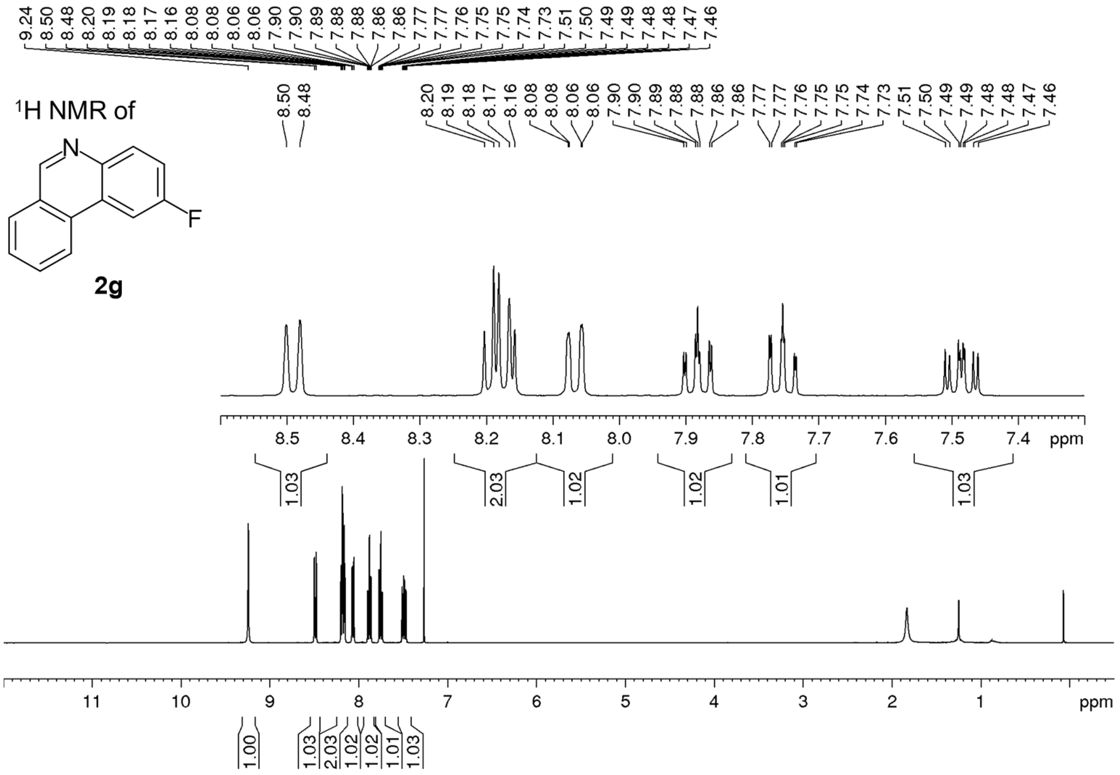
2f 2-isomer

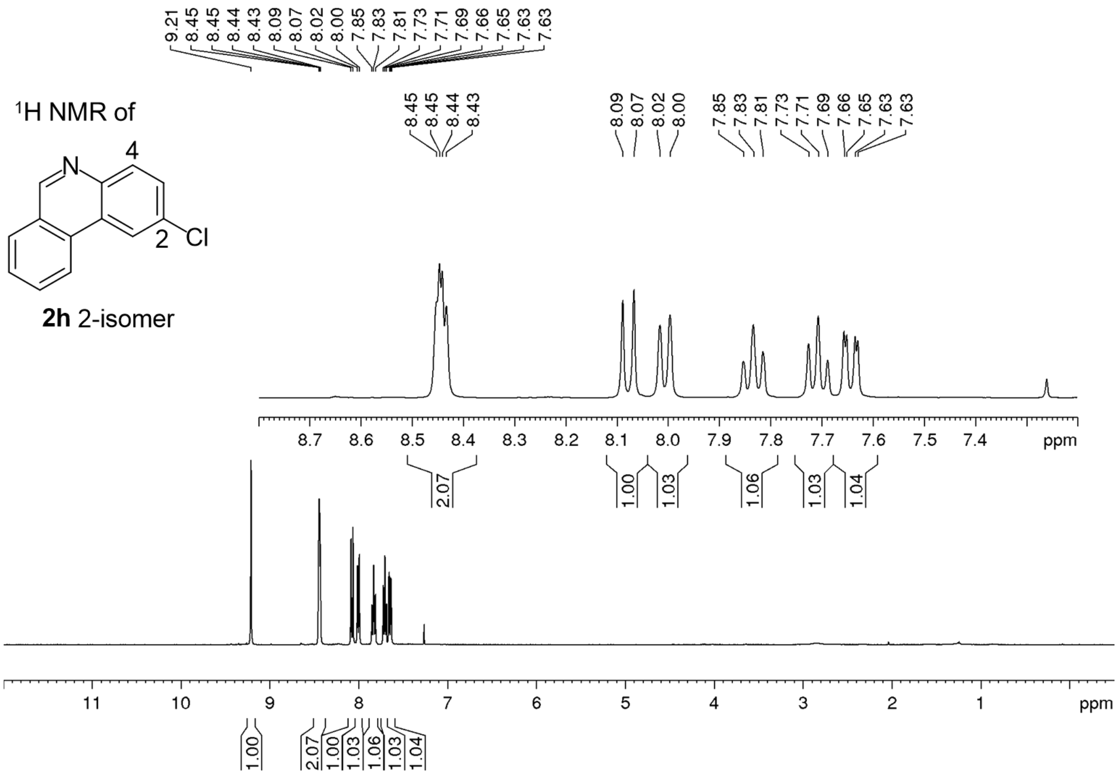

^{13}C NMR of

2f 2-isomer


9.32 8.69 8.67 8.64 8.64 8.62 8.62 8.06 8.04 7.91 7.90 7.89 7.87 7.87 7.79 7.77 7.77 7.76 7.74 7.73 7.71 7.55 7.53 7.51 7.46 7.44 7.42

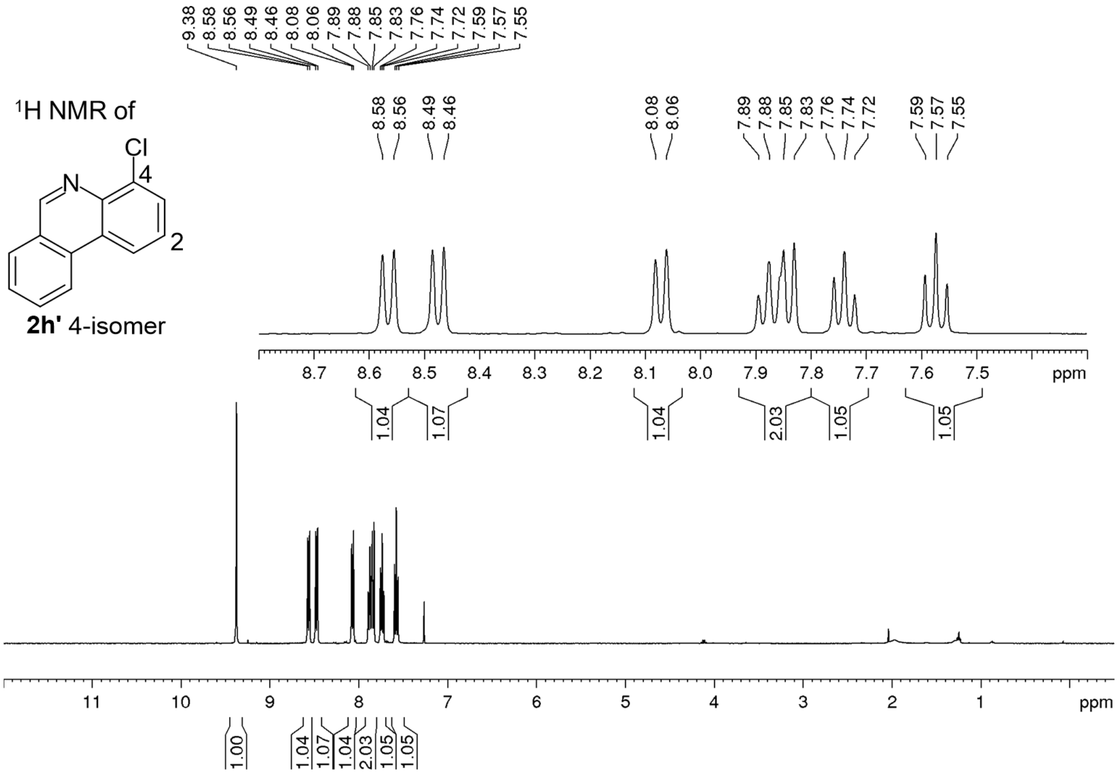
1H NMR of
Ph
4
N
2
2f' 4-isomer
9.32
8.69 8.67 8.64 8.64 8.62 8.62
8.06 8.04 7.91 7.90 7.89 7.87 7.87 7.79 7.77 7.77 7.76 7.74 7.73 7.71 7.55 7.53 7.51 7.46 7.44 7.42
9.4 9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 ppm
1.00 2.06 1.03 1.04 5.07 2.14 1.10
11 10 9 8 7 6 5 4 3 2 1 ppm
1.00 2.06 1.03 1.04 5.07 2.14 1.10


9.24 8.50 8.48 8.20 8.19 8.18 8.17 8.16 8.08 8.08 8.06 8.06 7.90 7.90 7.89 7.88 7.88 7.86 7.86 7.77 7.77 7.76 7.75 7.75 7.74 7.73 7.51 7.50 7.49 7.49 7.48 7.48 7.47 7.46
1H NMR of
N
F
2g
8.50 8.48
8.20 8.19 8.18 8.17 8.16 8.08 8.08 8.06 8.06 7.90 7.90 7.89 7.88 7.88 7.86 7.86 7.77 7.77 7.76 7.75 7.75 7.74 7.73 7.51 7.50 7.49 7.49 7.48 7.48 7.47 7.46
8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 ppm
1.03 2.03 1.02 1.02 1.01 1.03
11 10 9 8 7 6 5 4 3 2 1 ppm
1.00 1.03 2.03 1.02 1.02 1.01 1.03



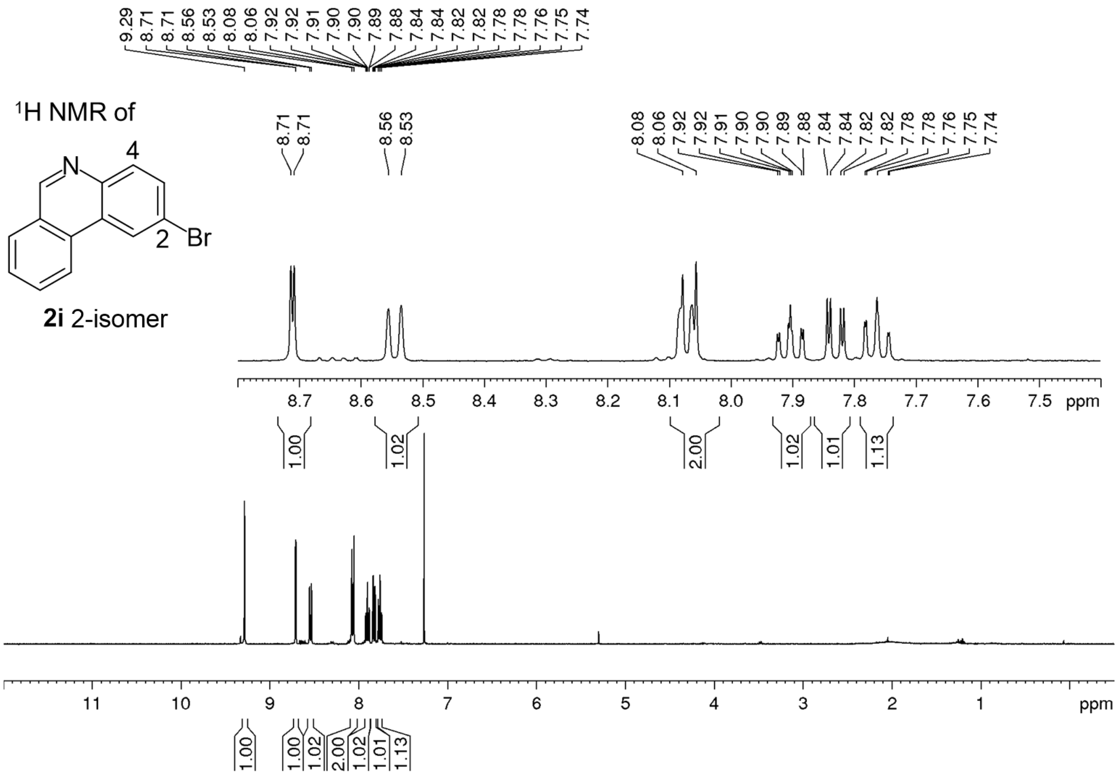
^{1}H NMR of

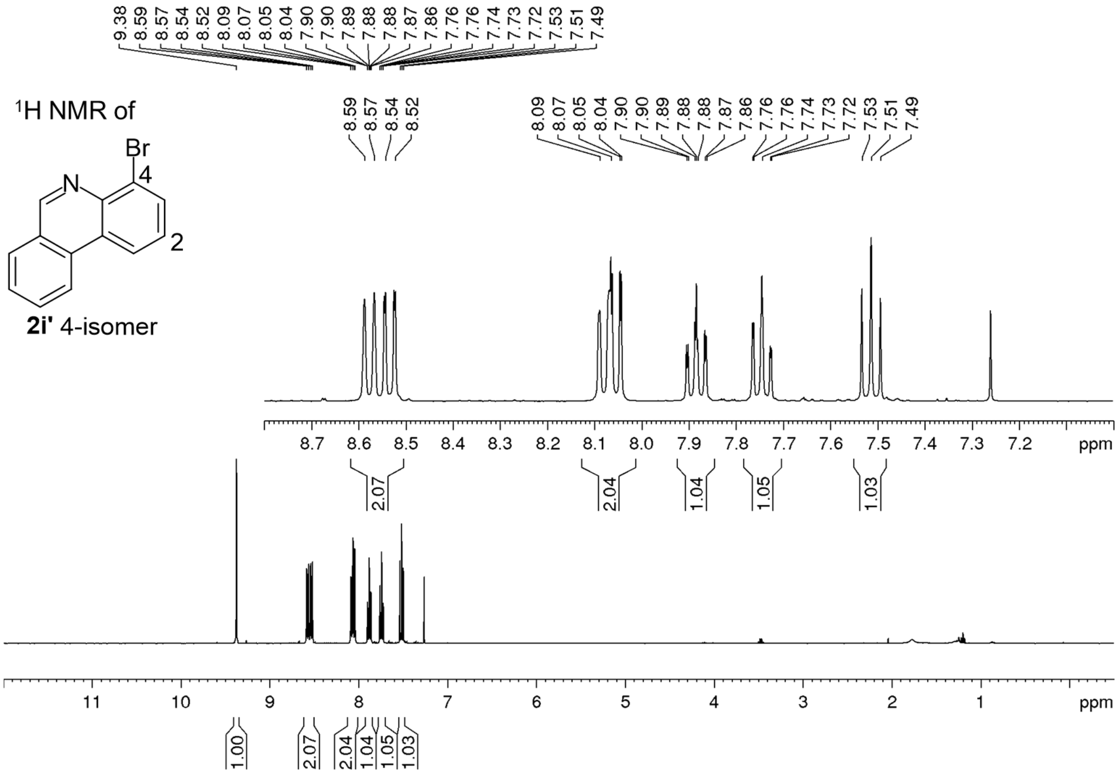
2h 2-isomer

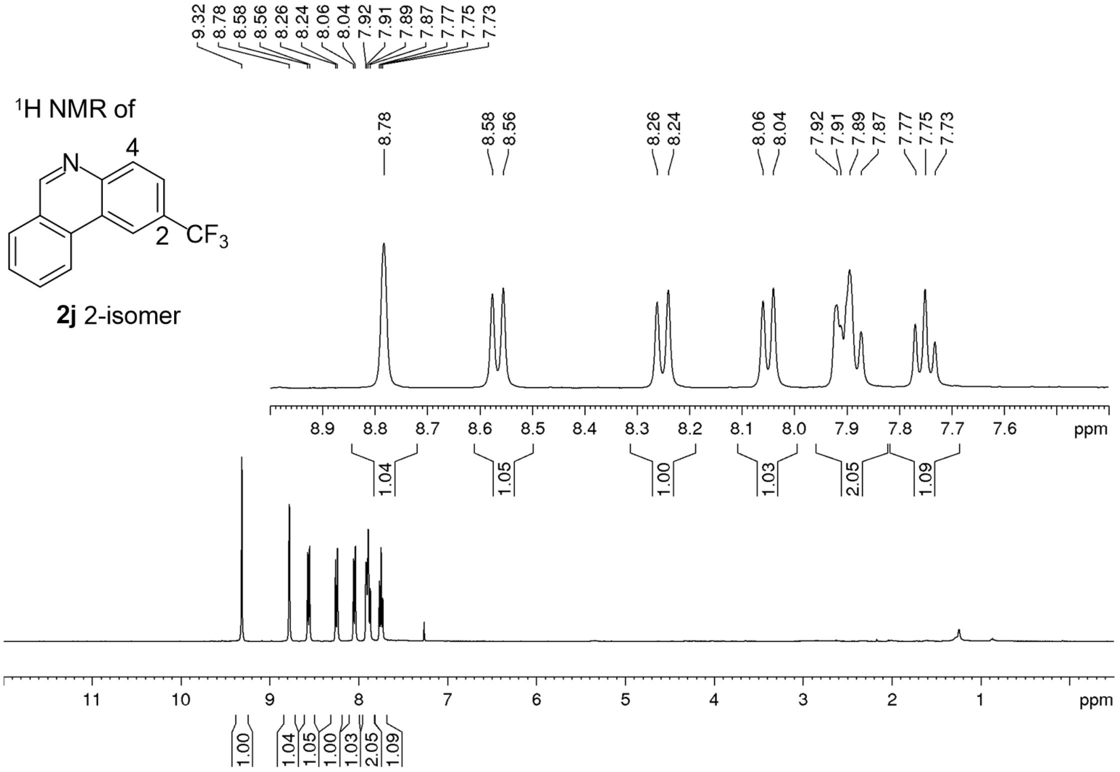


^{1}H NMR of

2h' 4-isomer

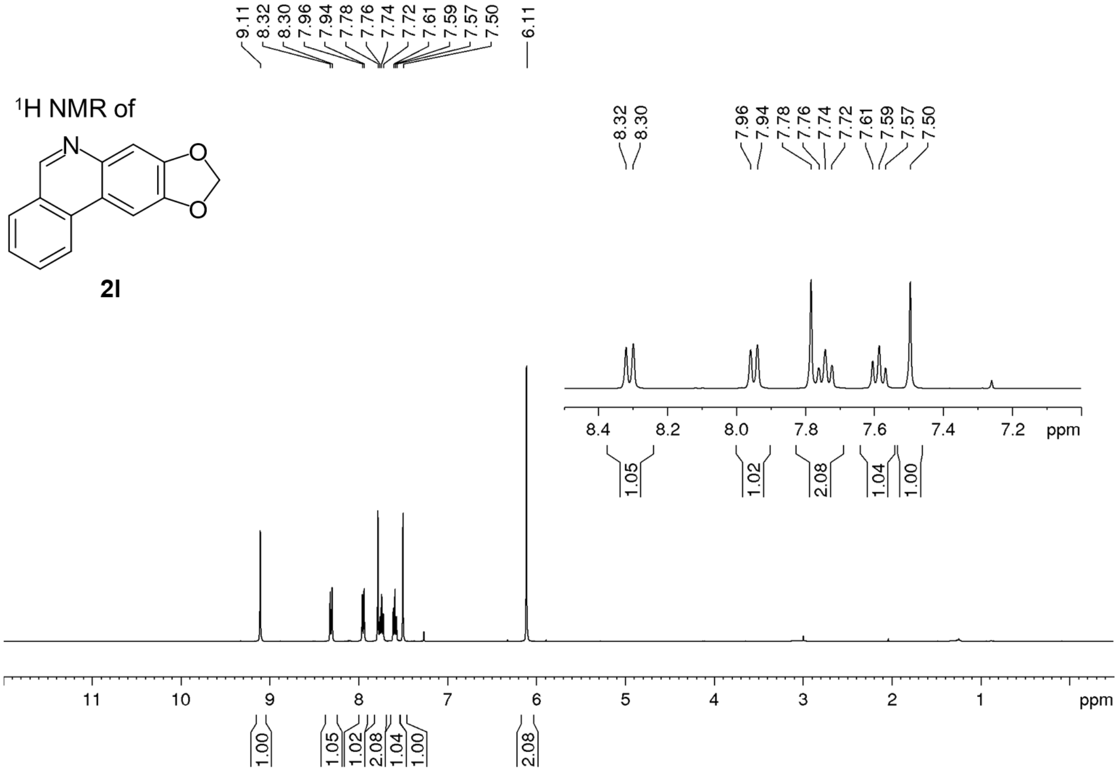

9.29
8.71
8.71
8.56
8.53
8.08
8.06
7.92
7.92
7.91
7.90
7.90
7.89
7.88
7.84
7.84
7.82
7.82
7.78
7.78
7.76
7.75
7.74
¹H NMR of
N
4
2
Br
2i 2-isomer
1.00
1.02
2.00
1.02
1.01
1.13
ppm
1.00
1.00
1.02
2.00
1.02
1.01
1.13
ppm


9.38
8.59
8.57
8.54
8.52
8.09
8.07
8.05
8.04
7.90
7.89
7.88
7.88
7.87
7.86
7.76
7.76
7.74
7.73
7.72
7.53
7.51
7.49
¹H NMR of
Br
4
N
2
2i' 4-isomer
2.07
2.04
1.04
1.05
1.03
ppm
1.00
2.07
2.04
1.04
1.05
1.03
ppm



^{1}H NMR of

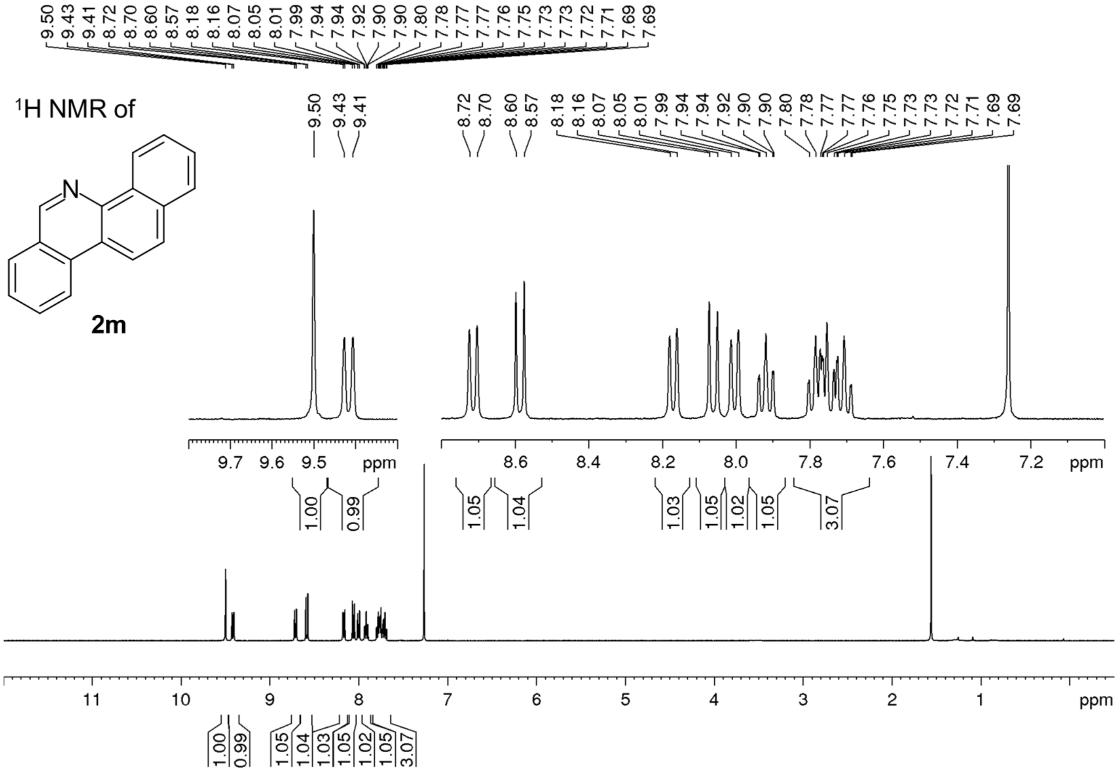
2j 2-isomer



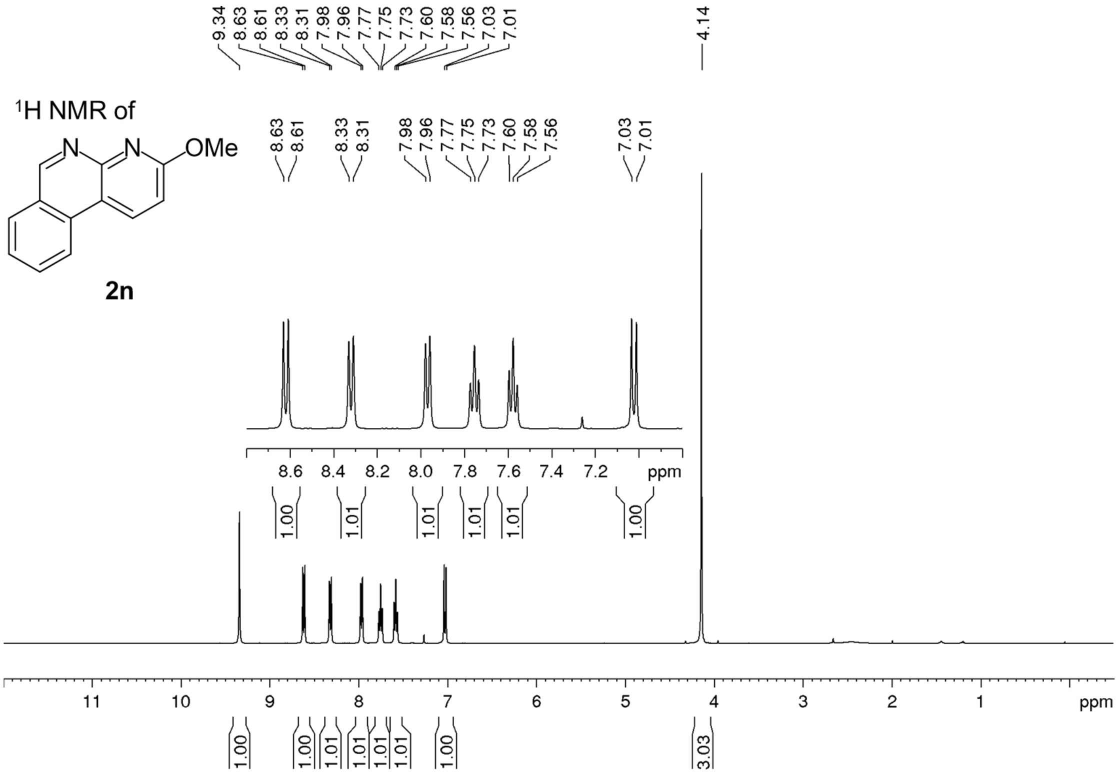
^{1}H NMR of

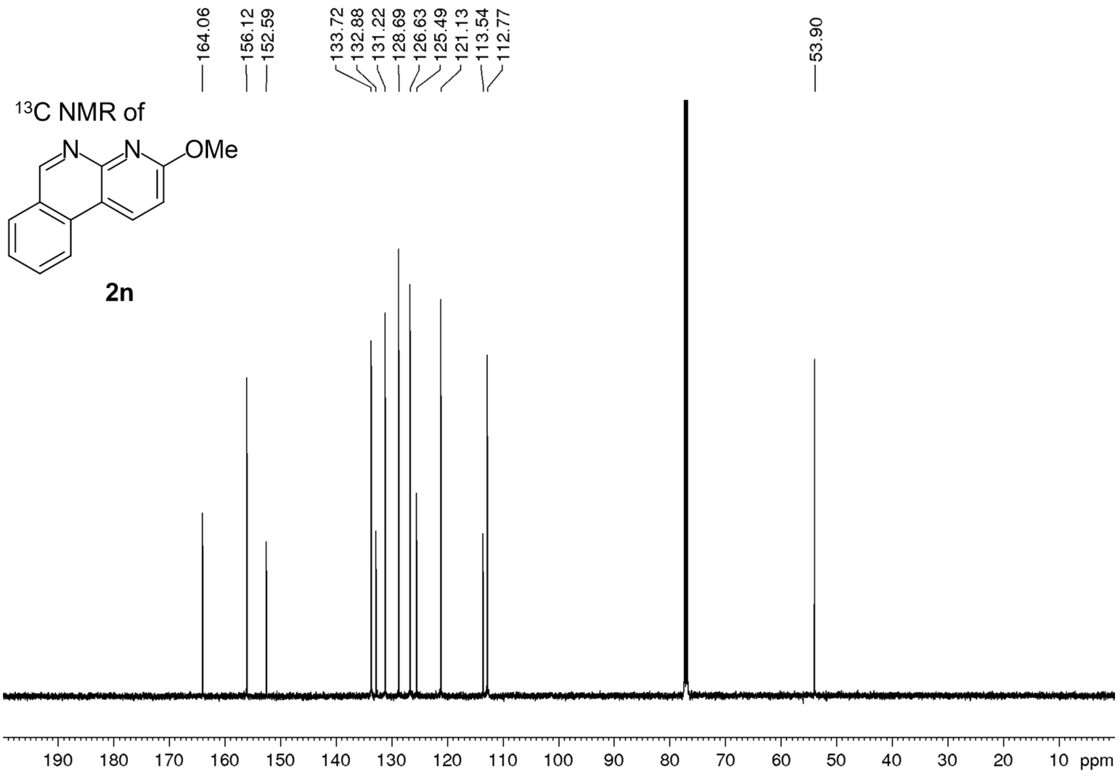
2l

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

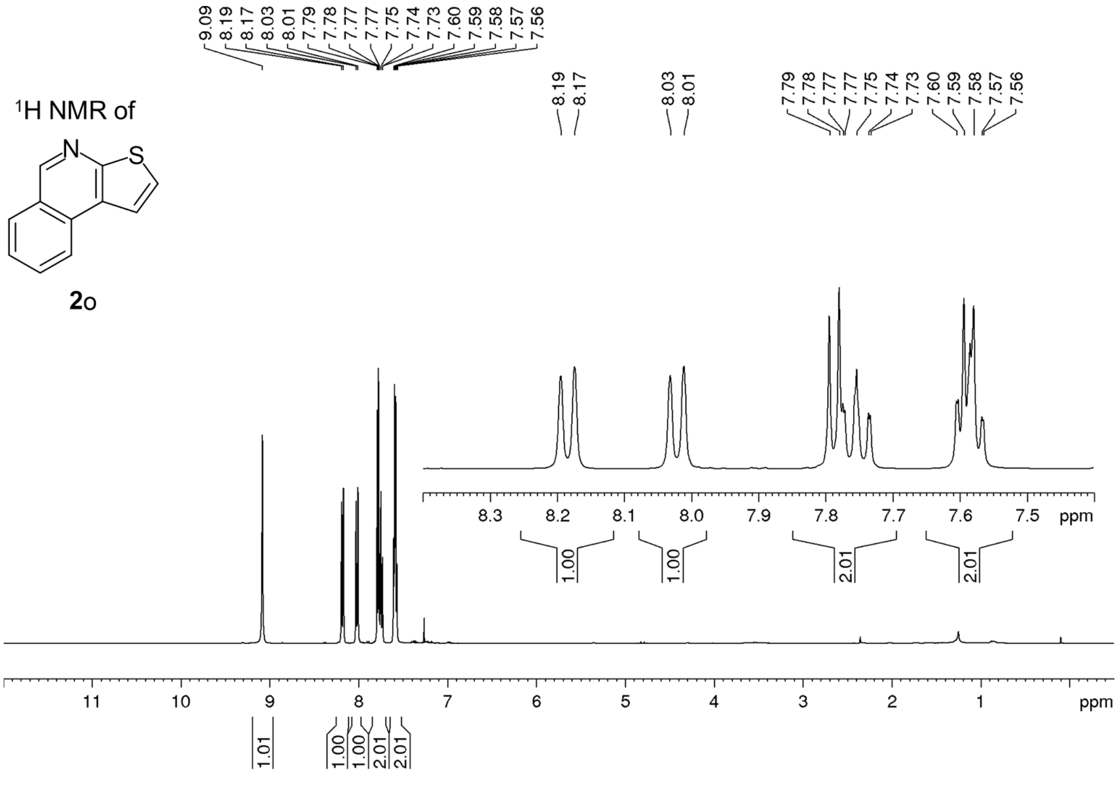


^{1}H NMR of **2n**



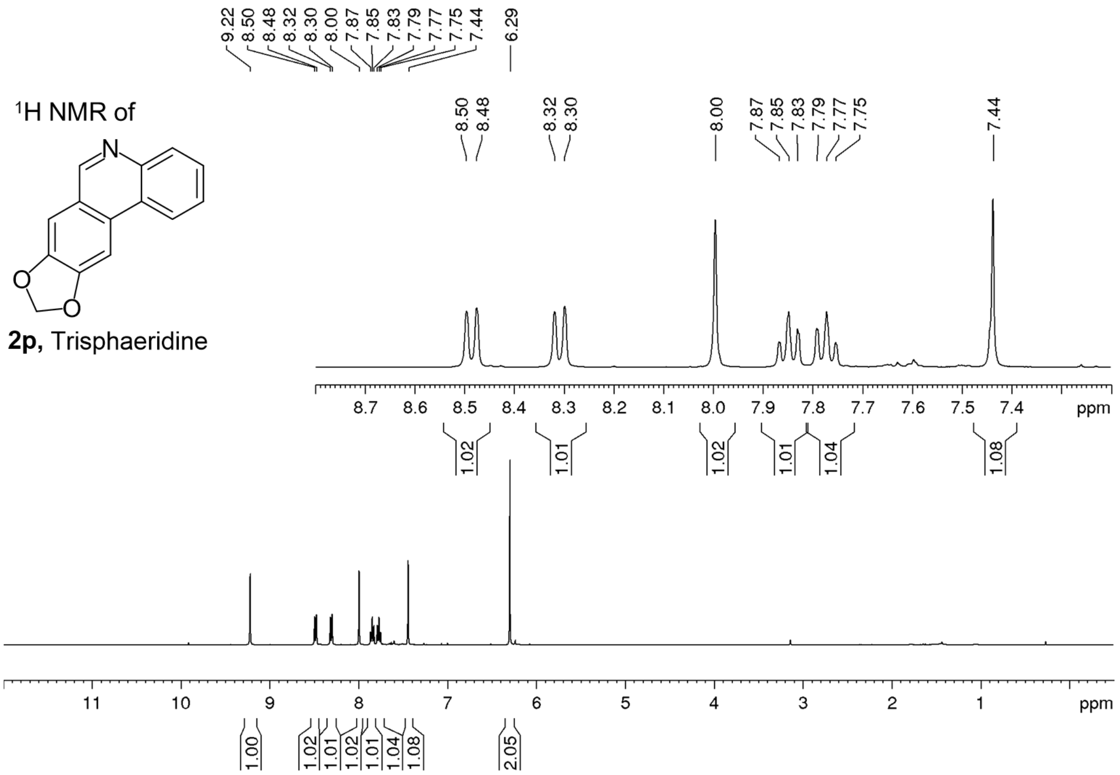


164.06
156.12
152.59
133.72
132.88
131.22
128.69
126.63
125.49
121.13
113.54
112.77
53.90
^{13}C NMR of
N
N
OMe
2n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



9.09
8.19
8.17
8.03
8.01
7.79
7.78
7.77
7.77
7.75
7.74
7.73
7.60
7.59
7.58
7.57
7.56
^{1}H NMR of
N
S
2o
8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 ppm
1.00
1.00
2.01
2.01
11 10 9 8 7 6 5 4 3 2 1 ppm
1.01
1.00
1.00
2.01
2.01

^{1}H NMR of



2p, Trisphaeridine