Supplementary Information

Molecular engineering enabling reversible transformation between helical and planar conformations by cyclization of alkynes

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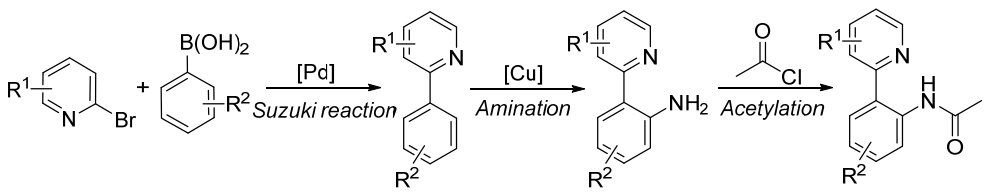
I. General Remarks

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Diarylacetylene were synthesized by literature procedures.[1]

NMR spectra were obtained on an Agilent 400-MR DD2 or a Bruker AV II-400 MHz spectrometer. ^{1}H NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$ or DMSO-d_6 as the internal reference ($CDCl_3$: δ = 7.26 ppm; DMSO-d_6: δ = 2.50 ppm). ^{13}C NMR (100 MHz) chemical shifts were measured relative to $CDCl_3$ or DMSO-d_6 as the internal reference ($CDCl_3$: δ = 77.16 ppm; DMSO-d_6: δ = 39.52 ppm). High-resolution mass spectra (HRMS) were obtained with a Shimadzu LCMS-IT-TOF (ESI) spectrometer. X-ray single crystal diffraction data were collected on an Agilent Gemini Plus single crystal diffractometer. Absorption and fluorescence spectra were obtained using a HITACHI U-2910 spectrometer and a Horiba Fluorolog-3 fluorescence spectrometer, respectively. Absolute quantum yields were collected with a calibrated integrating sphere system. Confocal fluorescence imaging measurements were conducted on a LSM 780 (Zeiss) confocal fluorescent microscope. Cytotoxicity experiments were carried out by CellTiler 96® AQueous One Solution Cell Proliferation Assay.

II. Synthesis of *N*-acetyl-2-(pyridin-2-yl)aniline derivatives



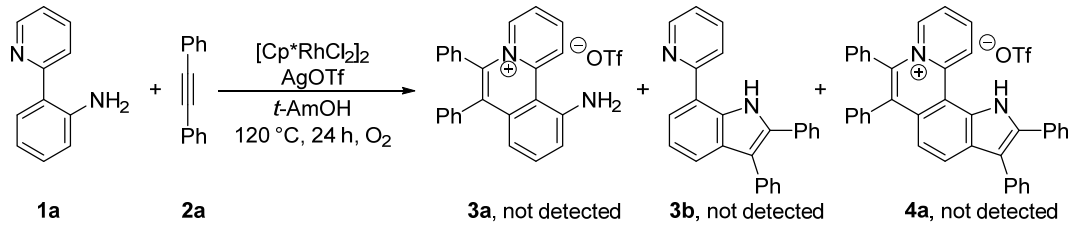
***Suzuki reaction*:** A mixture of 2-bromopyridine derivative (5 mmol), arylboronic acid (7 mmol), $Pd(PPh_3)_4$ (0.25 mmol), Na_2CO_3 (25 mmol), ethanol (6 mL), toluene (30 mL) and water (30 mL) was stirred at 100 °C overnight under N_2. Then, the mixture was poured into brine and extracted with ethyl acetate three times. The organic phase was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The

residue was purified by column chromatography on silica gel to give the 2-arylpyridine derivative.

***Amination*:**[2] A mixture of 2-arylpyridine derivative (2 mmol), trimethylsilyl azide (4 mmol), copper trifluoroacetate (2 mmol), trifluoroacetic acid (2 mmol) and anhydrous 1,2-dichlorobenzene (20 mL) was stirred at 115 °C for 24 h under N_2. After the mixture was cooled to room temperature, 1 mL of ammonia was added and stirred for another 10 min. Then, the mixture was diluted in ethyl acetate (50 mL), and washed with saline three times. The organic phase was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the 2-(pyridin-2-yl)aniline derivative.

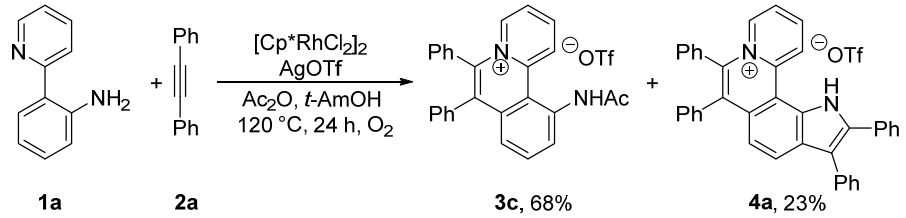
***Acetylation*:** Acetyl chloride (1.5 mmol) was added to a solution of 2-(pyridin-2-yl)aniline derivative (1 mmol), K_2CO_3 (3 mmol), ethyl acetate (10 mL) and water (5 mL). The resulting mixture was stirred at room temperature for 2 h. Then, the mixture was diluted in ethyl acetate (50 mL), and washed with saline three times. The organic phase was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the *N*-acetyl-2-(pyridin-2-yl)aniline derivative.

III. Rh-catalyzed C–H activation/cyclization of 2-(pyridin-2-yl)aniline with diphenylacetylene



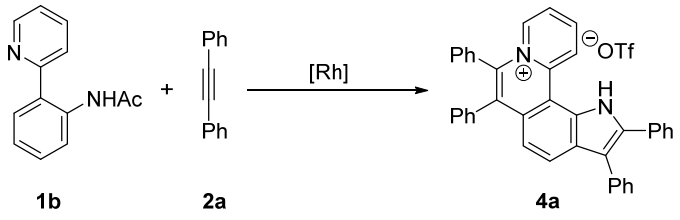
A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with 2-(pyridin-2-yl)aniline **1a** (17.0 mg, 0.1 mmol), diphenylacetylene **2a** (35.6 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 5 mol%), AgOTf (30.8 mg, 0.12 mmol) and 2-methylbutan-2-ol (*t*-AmOH, 1.5 mL) under O_2. The resulting mixture was stirred at

120 °C for 24 h and then diluted with 10 mL of dichloromethane. The results of detection by thin-layer chromatography (TLC) indicated that this reaction delivered no annulated product **3a**, **3b** and **4a**.



A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with 2-(pyridin-2-yl)aniline **1a** (17.0 mg, 0.1 mmol), diphenylacetylene **2a** (35.6 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 5 mol%), AgOTf (30.8 mg, 0.12 mmol), acetic anhydride (47 μL, 0.5 mmol) and 2-methylbutan-2-ol (*t*-AmOH, 1.5 mL) under O_2. The resulting mixture was stirred at 120 °C for 24 h and then diluted with 10 mL of dichloromethane. The mixture was filtered through a celite pad and washed with 20 mL of dichloromethane. Then the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give **3c** as a grayish-white solid (dichloromethane/methanol = 10/1, v/v, 36.7 mg, 68% yield) and **4a** as a yellow solid (dichloromethane/methanol = 30/1, v/v, 15.5 mg, 23% yield).

IV. Optimization of Rh-catalyzed dual C–H activation/cyclization of *N*-acetyl-2-(pyridin-2-yl)aniline with diphenylacetylene



A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with *N*-acetyl-2-(pyridin-2-yl)aniline **1b** (21.2 mg, 0.1 mmol), diphenylacetylene **2a** (35.6 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$, silver salt, oxidant, additive and 2-methylbutan-2-ol (*t*-AmOH) under N_2. The resulting mixture was stirred at 120-140 °C for 24 h and then

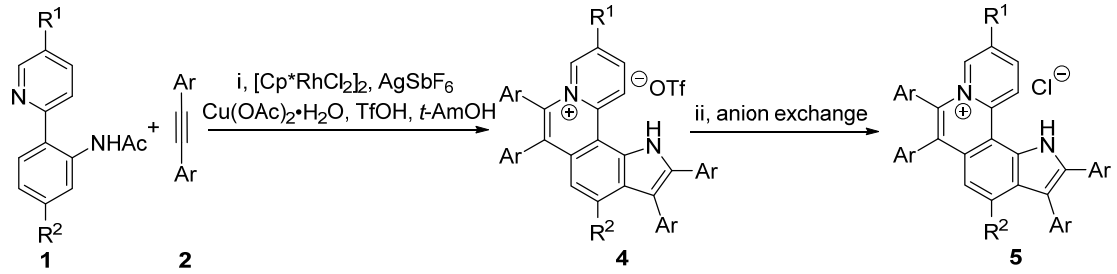
diluted with 10 mL of dichloromethane. The mixture was filtered through a celite pad and washed with 20 mL of dichloromethane. Then the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (dichloromethane/methanol = 30/1, v/v) to give the isolated yield of **4a**.

Table S1. Optimization of reaction conditions.[a]

Entry	[Rh]	[Ag]	Oxidant	Additive	Solvent	Yield (%)[b]
1[c]	$[Cp^*RhCl_2]_2$	AgOTf	Oxygen (1 atm)	—	*t*-AmOH	27
2	$[Cp^*RhCl_2]_2$	AgOTf	Oxygen (1 atm)	TfOH	*t*-AmOH	N.D.
3	$[Cp^*RhCl_2]_2$	AgOTf	$Cu(OAc)_2·H_2O$	TfOH	*t*-AmOH	39
4	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2·H_2O$	TfOH	*t*-AmOH	46
5[d]	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2·H_2O$	TfOH	*t*-AmOH	57
6[e]	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2·H_2O$	TfOH	*t*-AmOH	60
7[f]	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2·H_2O$	TfOH	*t*-AmOH	69
8[g]	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2·H_2O$	TfOH	*t*-AmOH	82
9[h]	$[Cp^*Co(CO)I_2]$	$AgSbF_6$	$Cu(OAc)_2·H_2O$	TfOH	*t*-AmOH	N.D.

[a]Reactions were carried out by using **1b** (0.1 mmol), **2a** (0.2 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), [Ag] (20 mol%), oxidant (0.2 mmol) and additive (0.1 mmol) in 2-methylbutan-2-ol (*t*-AmOH, 1.5 mL) at 120 °C for 24 h under an N_2 atmosphere. [b]Isolated yields. [c]AgOTf (0.12 mmol). [d]$Cu(OAc)_2·H_2O$ (0.3 mmol). [e]$Cu(OAc)_2·H_2O$ (0.3 mmol), TfOH (0.15 mmol). [f]**2a** (0.3 mmol), $Cu(OAc)_2·H_2O$ (0.3 mmol), TfOH (0.15 mmol). [g]**2a** (0.3 mmol), $Cu(OAc)_2·H_2O$ (0.3 mmol), TfOH (0.15 mmol), 140 °C. [h]**2a** (0.3 mmol), $[Cp^*Co(CO)I_2]$ (10 mol%), $Cu(OAc)_2·H_2O$ (0.3 mmol), TfOH (0.15 mmol), 140 °C. AgOTf = silver trifluoromethanesulfonate. TfOH = trifluoromethanesulfonic acid. N.D. = not detected.

V. General procedure for Rh-catalyzed dual C–H activation/cyclization and the subsequent anion exchange reaction

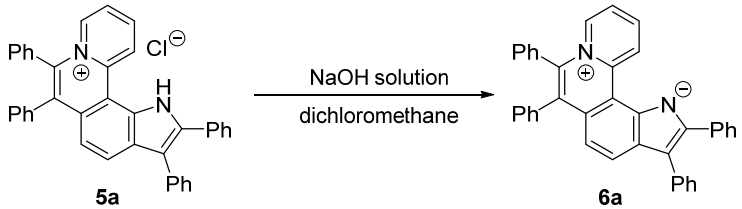


A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with *N*-acetyl-2-(pyridin-2-yl)aniline derivative **1** (0.1 mmol), diarylacetylene **2** (0.3 mmol),

$[Cp^*RhCl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), $Cu(OAc)_2 \cdot H_2O$ (0.3 mmol), trifluoromethanesulfonic acid (0.15 mmol) and 2-methylbutan-2-ol (*t*-AmOH) under an N_2 atmosphere. The resulting mixture was stirred at 140 °C for 24 h and then diluted with 10 mL of dichloromethane. The mixture was filtered through a celite pad and washed with 20 mL of dichloromethane. Then the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (dichloromethane/methanol = 30/1, v/v) to give the trifluoromethanesulfonate product **4**.

Compound **4** was dissolved in ethanol and water (3:1, v/v), and eluted *via* column chromatography on chlorine-ion exchange resin. The resulting solution was concentrated under reduced pressure. The residue was dissolved in dichloromethane, washed with diluted hydrochloric acid, dried over Na_2SO_4, filtered. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (dichloromethane/methanol = 20/1, v/v) to give the desired product **5**.

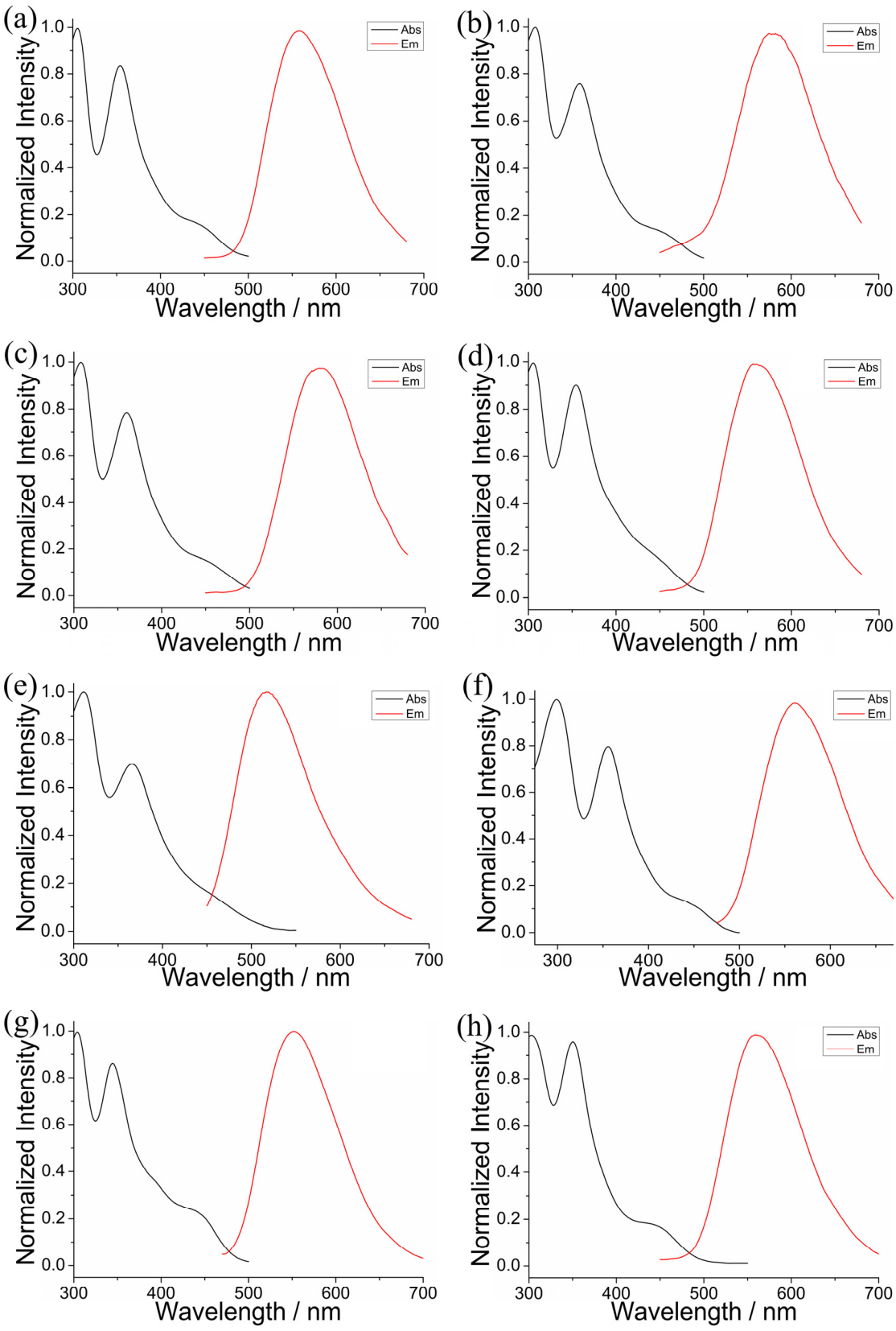
VI. Synthesis of 6a



2 M of NaOH solution (1 mL) was added to the dichloromethane solution (5 mL) of compound **5a** (50.0 mg, 89 μmol). After stirred at room temperature for 5 min, the resulting mixture was stratified and separated. The organic phase was dried over Na_2SO_4, and filtered. Dichloromethane was removed under reduced pressure to give product **6a** as a dark red solid in nearly 100% yield (46.4 mg).

VII. Photophysical properties and calculation of pK_a values of 5

7.1 Absorption and emission spectra of 5 in dichloromethane


(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
Abs
Em
Normalized Intensity
Wavelength / nm
0.0
0.2
0.4
0.6
0.8
1.0
300
400
500
600
700

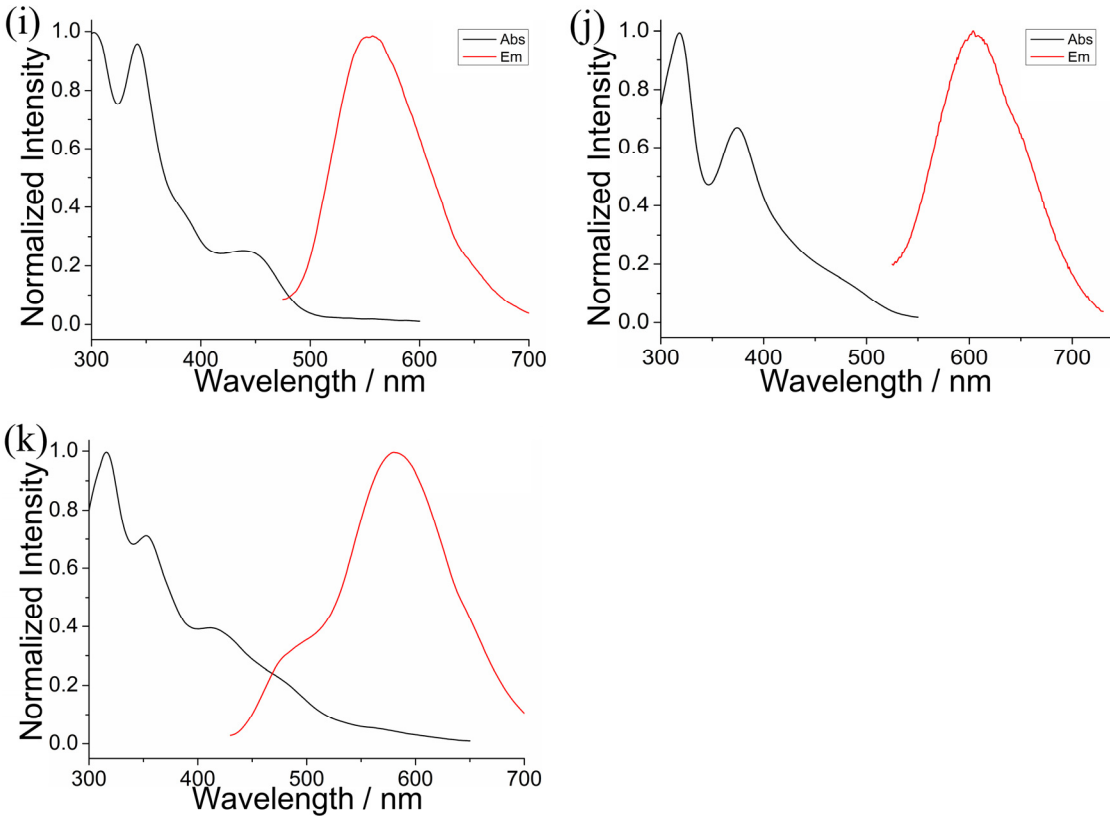
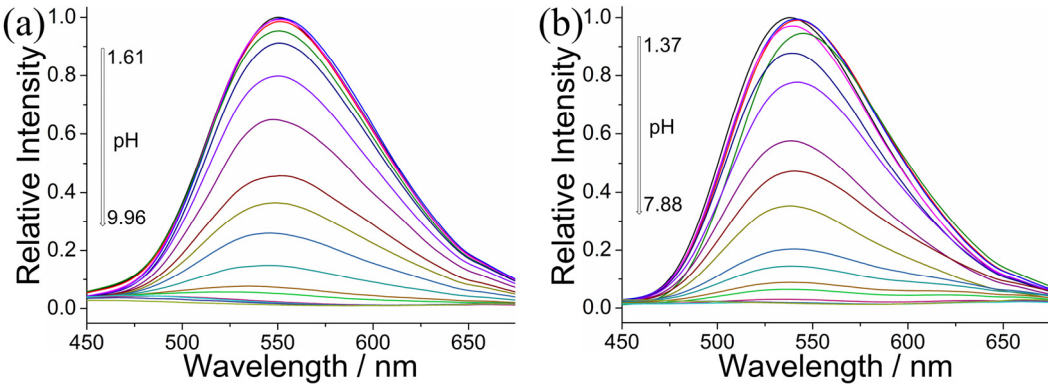


Fig. S1 Absorption and emission spectra of **5** in dichloromethane (1×10^{-5} M). (a) **5a**, 9%; (b) **5b**, 4%; (c) **5c**, 4%; (d) **5d**, 6%; (e) **5e**, 3%; (f) **5f**, 9%; (g) **5g**, 27%; (h) **5h**, 8%; (i) **5i**, 16%; (j) **5j**, 1%; (k) **5k**, 2%. The absolute quantum yields of **5a**-**5k** in CH_2Cl_2 (1×10^{-5} M), which are collected with an integrating sphere system, are shown after the identifiers of corresponding compounds.

7.2 Fluorescence spectra of 5 in phosphate-buffered saline with different pH values



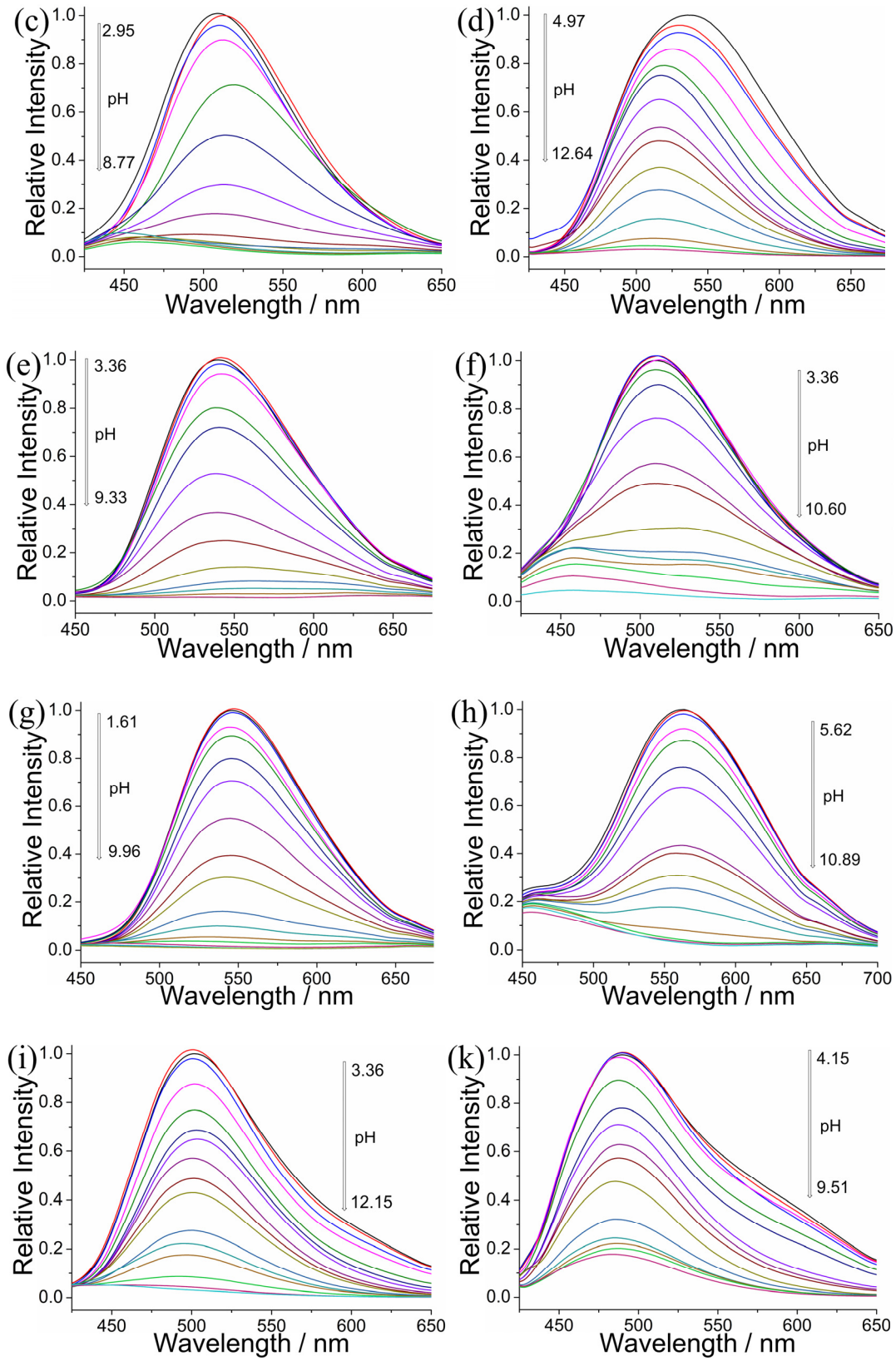


Fig. S2 Fluorescence spectra of **5** in phosphate-buffered saline with different pH values (2×10^{-5} M). (a) **5b**, DMSO/H_2O = 1:9, v/v; (b) **5c**, DMSO/H_2O = 1:9, v/v; (c) **5d**, DMSO/H_2O = 1:9, v/v; (d) **5e**, DMSO/H_2O = 1:9, v/v; (e) **5f**, DMSO/H_2O = 1:9, v/v; (f) **5g**, DMSO/H_2O = 1:9, v/v; (g) **5h**, DMSO/H_2O = 1:9, v/v; (h) **5i**, DMSO/H_2O = 1:1, v/v; (i) **5j**, DMSO/H_2O = 1:9, v/v; (j) **5k**, DMSO/H_2O

= 1:9, v/v.

7.3 Calculation of pK_a values of 5

The analysis on fluorescence intensities of compound **5** with different pH values by using Henderson-Hasselbach equation

$$\text{LOG}\,[(I_{max} - I)/(I - I_{min})] = pK_a - pH$$

where I represents the fluorescence intensity at a certain wavelength, I_{max} and I_{min} are corresponding maximum and minimum limiting values of I, respectively.[3]

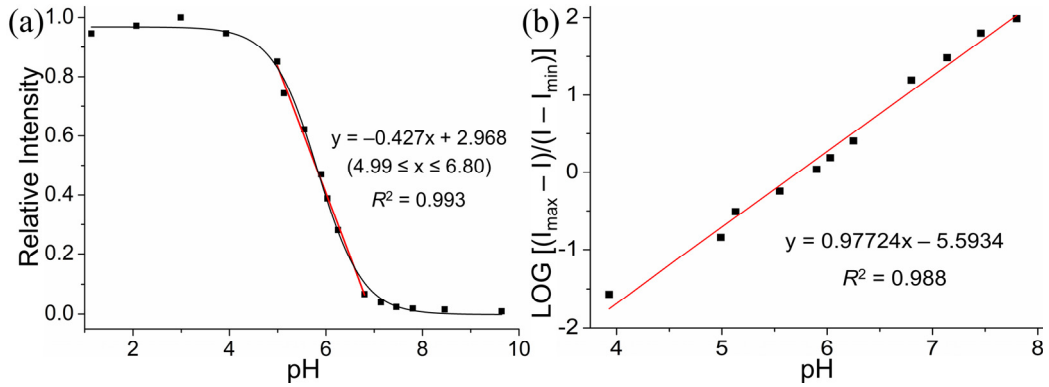


Fig. S3 (a) Relative fluorescence intensities of **5a** at 538 nm in phosphate-buffered saline with different pH values (2 × 10^{-5} M, pH = 1.14-9.64, DMSO/H_2O = 1:9, v/v). Inset: The linear relationship between relative fluorescence intensity of **5a** at 538 nm and pH value ranging from 4.99 to 6.80. (b) Linear relationship between LOG [(I_{max}–I)/(I–I_{min})] and pH values. Based on the pH titration results, the pK_a value of **5a** was calculated to be 5.72 in DMSO–water buffer system.

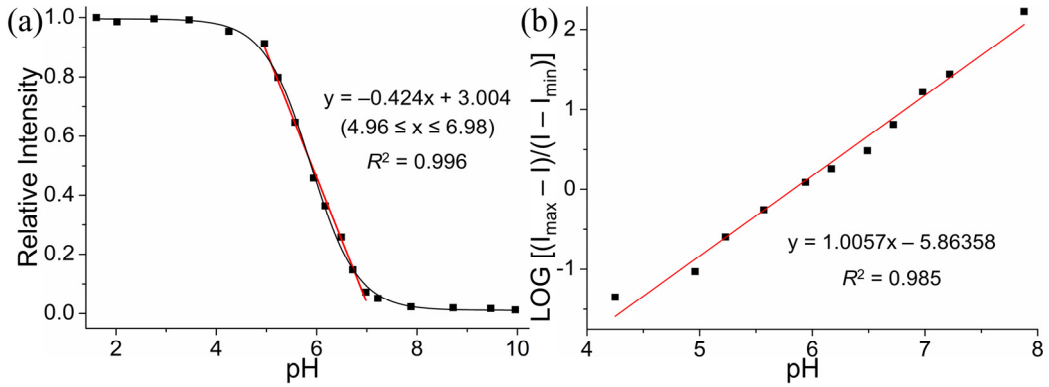


Fig. S4 (a) Relative fluorescence intensities of **5b** at 551 nm in phosphate-buffered saline with different pH values (2 × 10^{-5} M, pH = 1.61-9.96, DMSO/H_2O = 1:9, v/v). Inset: The linear relationship between relative fluorescence intensity of **5b** at 551 nm and pH value ranging from 4.96 to 6.98. (b) Linear relationship between LOG [(I_{max}–I)/(I–I_{min})] and pH values. Based on the pH titration results, the pK_a value of **5b** was calculated to be 5.83 in DMSO–water buffer system.

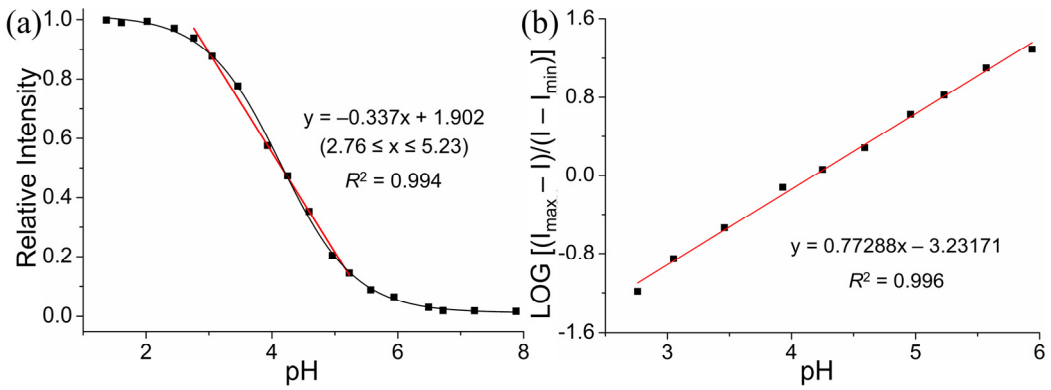


Fig. S5 (a) Relative fluorescence intensities of **5c** at 540 nm in phosphate-buffered saline with different pH values (2 × 10^{-5} M, pH = 1.37-7.88, DMSO/H_2O = 1:9, v/v). Inset: The linear relationship between relative fluorescence intensity of **5c** at 540 nm and pH value ranging from 2.76 to 5.23. (b) Linear relationship between LOG [(I_{max}–I)/(I–I_{min})] and pH values. Based on the pH titration results, the pK_a value of **5c** was calculated to be 4.18 in DMSO–water buffer system.

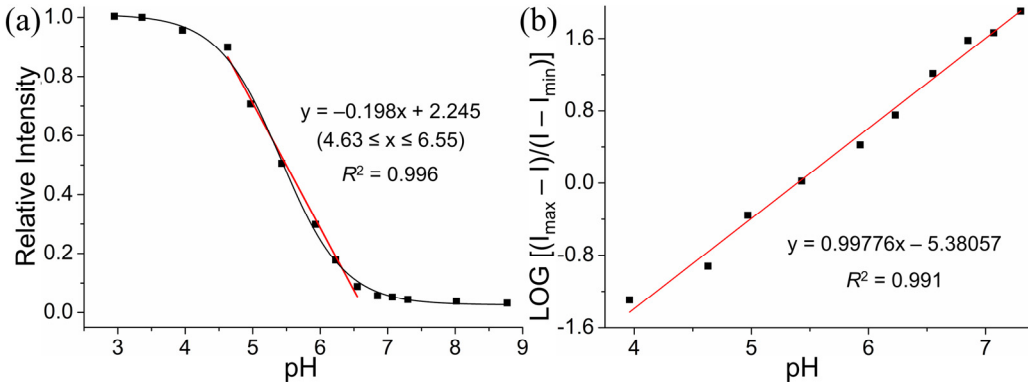


Fig. S6 (a) Relative fluorescence intensities of **5d** at 513 nm in phosphate-buffered saline with different pH values (2 × 10^{-5} M, pH = 2.95-8.77, DMSO/H_2O = 1:9, v/v). Inset: The linear relationship between relative fluorescence intensity of **5d** at 513 nm and pH value ranging from 4.63 to 6.55. (b) Linear relationship between LOG [(I_{max}–I)/(I–I_{min})] and pH values. Based on the pH titration results, the pK_a value of **5d** was calculated to be 5.39 in DMSO–water buffer system.

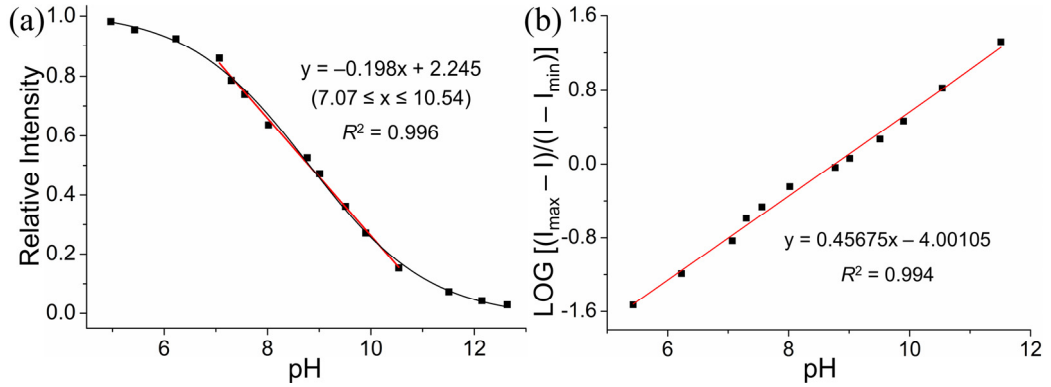


Fig. S7 (a) Relative fluorescence intensities of **5e** at 525 nm in phosphate-buffered saline with different pH values (2 × 10^{-5} M, pH = 4.97-12.64, DMSO/H_2O = 1:9, v/v). Inset: The linear

relationship between relative fluorescence intensity of **5e** at 525 nm and pH value ranging from 7.07 to 10.54. (b) Linear relationship between LOG [(I_{max}–I)/(I–I_{min})] and pH values. Based on the pH titration results, the pK_a value of **5e** was calculated to be 8.76 in DMSO–water buffer system.

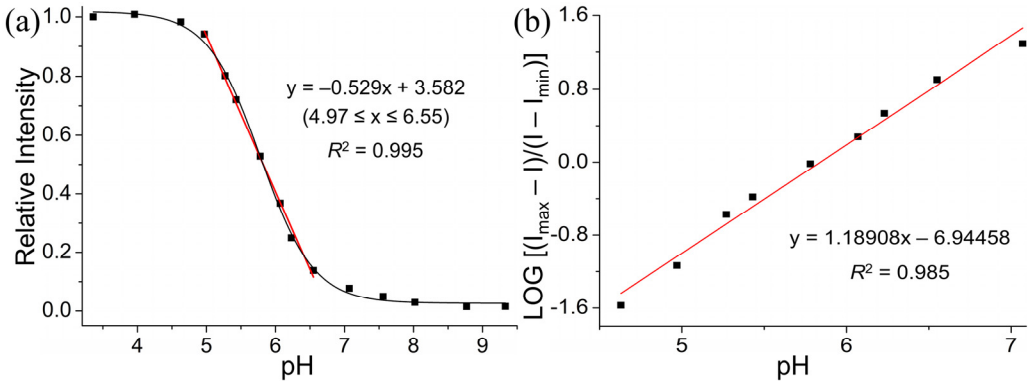


Fig. S8 (a) Relative fluorescence intensities of **5f** at 540 nm in phosphate-buffered saline with different pH values (2 × 10^{-5} M, pH = 3.36-9.33, DMSO/H_2O = 1:9, v/v). Inset: The linear relationship between relative fluorescence intensity of **5f** at 540 nm and pH value ranging from 4.97 to 6.55. (b) Linear relationship between LOG [(I_{max}–I)/(I–I_{min})] and pH values. Based on the pH titration results, the pK_a value of **5f** was calculated to be 5.84 in DMSO–water buffer system.

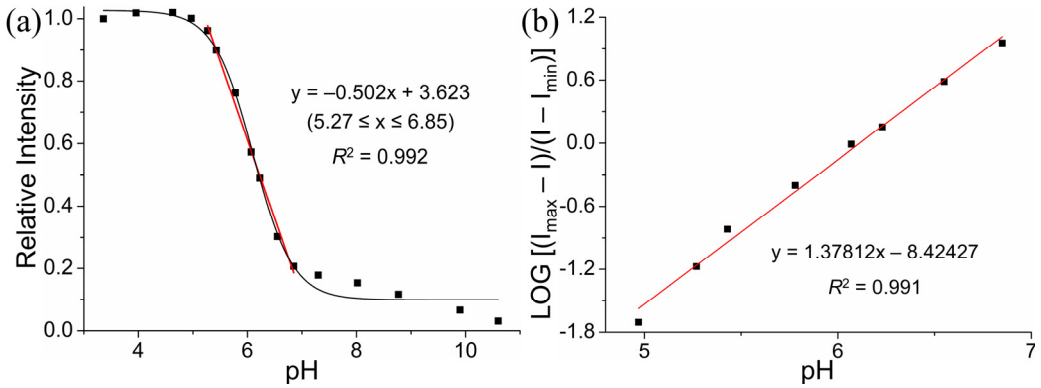


Fig. S9 (a) Relative fluorescence intensities of **5g** at 510 nm in phosphate-buffered saline with different pH values (2 × 10^{-5} M, pH = 3.36-10.60, DMSO/H_2O = 1:9, v/v). Inset: The linear relationship between relative fluorescence intensity of **5g** at 510 nm and pH value ranging from 5.27 to 6.85. (b) Linear relationship between LOG [(I_{max}–I)/(I–I_{min})] and pH values. Based on the pH titration results, the pK_a value of **5g** was calculated to be 6.11 in DMSO–water buffer system.

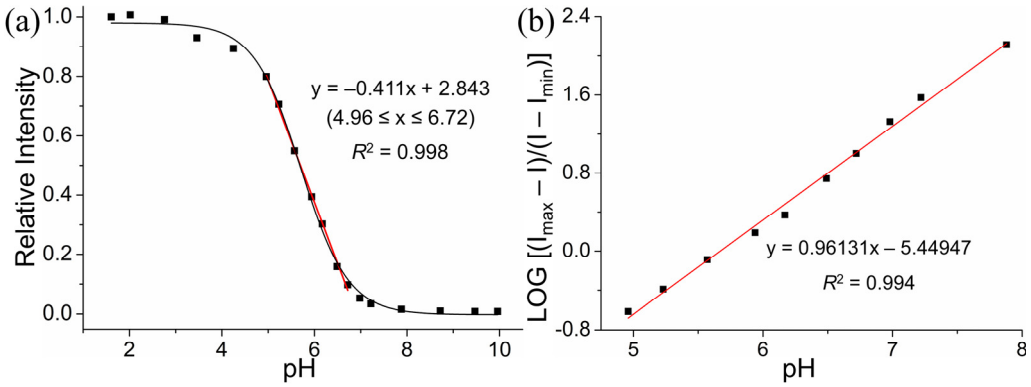


Fig. S10 (a) Relative fluorescence intensities of **5h** at 546 nm in phosphate-buffered saline with different pH values (2 × 10^{-5} M, pH = 1.61-9.96, DMSO/H_2O = 1:9, v/v). Inset: The linear relationship between relative fluorescence intensity of **5h** at 546 nm and pH value ranging from 4.96 to 6.72. (b) Linear relationship between LOG [(I_{max}–I)/(I–I_{min})] and pH values. Based on the pH titration results, the pK_a value of **5h** was calculated to be 5.67 in DMSO–water buffer system.

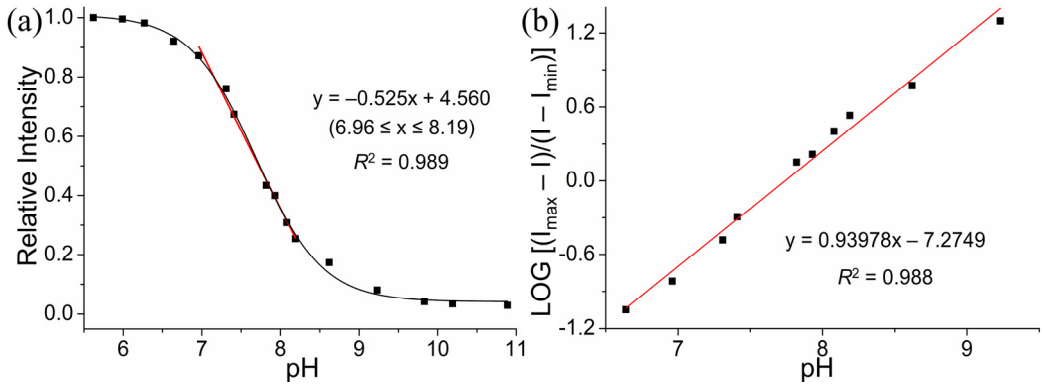


Fig. S11 (a) Relative fluorescence intensities of **5i** at 563 nm in phosphate-buffered saline with different pH values (2 × 10^{-5} M, pH = 5.62-10.89, DMSO/H_2O = 1:1, v/v). Inset: The linear relationship between relative fluorescence intensity of **5i** at 563 nm and pH value ranging from 6.96 to 8.19. (b) Linear relationship between LOG [(I_{max}–I)/(I–I_{min})] and pH values. Based on the pH titration results, the pK_a value of **5i** was calculated to be 7.74 in DMSO–water buffer system.

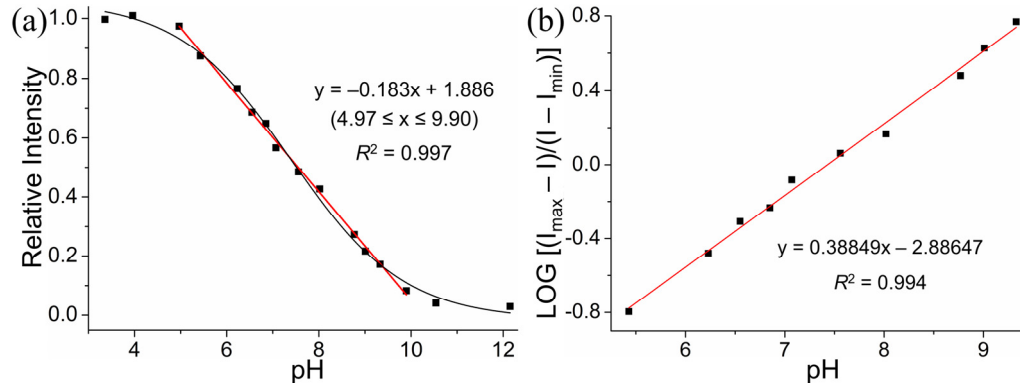


Fig. S12 (a) Relative fluorescence intensities of **5j** at 505 nm in phosphate-buffered saline with different pH values (2 × 10^{-5} M, pH = 3.36-12.15, DMSO/H_2O = 1:9, v/v). Inset: The linear

relationship between relative fluorescence intensity of **5j** at 505 nm and pH value ranging from 4.97 to 9.90. (b) Linear relationship between LOG [(I_{max}–I)/(I–I_{min})] and pH values. Based on the pH titration results, the pK_a value of **5j** was calculated to be 7.43 in DMSO–water buffer system.

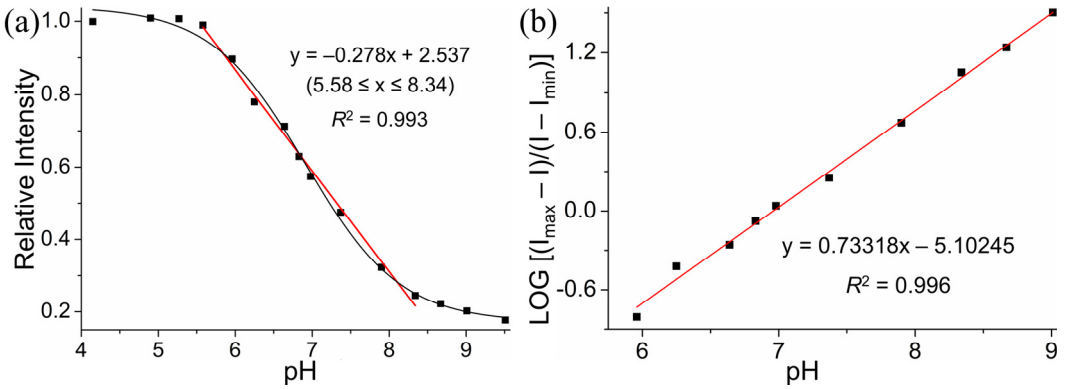


Fig. S13 (a) Relative fluorescence intensities of **5k** at 488 nm in phosphate-buffered saline with different pH values (2 × 10^{-5} M, pH = 4.15-9.51, DMSO/H_2O = 1:9, v/v). Inset: The linear relationship between relative fluorescence intensity of **5k** at 488 nm and pH value ranging from 5.58 to 8.34. (b) Linear relationship between LOG [(I_{max}–I)/(I–I_{min})] and pH values. Based on the pH titration results, the pK_a value of **5k** was calculated to be 6.96 in DMSO–water buffer system.

VIII. Fluorescence spectra of 5a and 6a in solid state

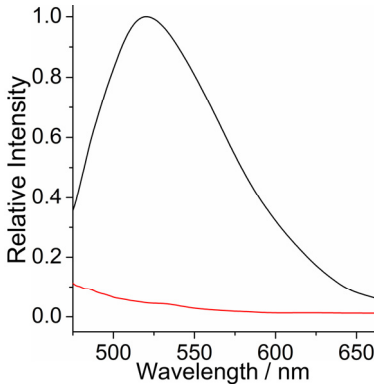


Fig. S14 Fluorescence spectra of **5a** (black) and **6a** (red) in solid state.

IX. Cell experiments

9.1 Cell culture

HepG2 cells were incubated in Dublecco's Modified Eagle's Medium (DMEM) supplemented with 10% (v/v) fetal bovine serum (FBS), 100 mg/mL of streptomycin and 100 units/mL of penicillin at 37 °C in humidified atmosphere containing 5% CO_2.

9.2 Confocal fluorescent imaging experiments

Confocal fluorescent imaging experiments incubated with 5: HepG2 cells were incubated with **5** (2 μM) in DMEM containing 1‰ DMSO for 20 min at 37 °C. Then, HepG2 cells were washed twice with phosphate buffered saline (PBS solution, 1 mL × 2), and covered with 1 mL of DMEM before imaging. The cells were observed with a Zeiss LSM 780 confocal fluorescent microscope.

Confocal fluorescent imaging experiments incubated with 5c and treated with acetic acid: HepG2 cells were incubated with **5c** (2 μM) in DMEM containing 1‰ DMSO for 20 min at 37 °C. Then, HepG2 cells were washed twice with phosphate buffered saline (PBS solution, 1 mL × 2), covered with 1 mL of DMEM, and treated with acetic acid (20 μL) for 30 min before imaging. The cells were observed with a Zeiss LSM 780 confocal fluorescent microscope.

Co-staining experiments: HepG2 cells were incubated with compound **5** or **6a** (2 μM) in DMEM containing 1‰ DMSO for 20 min at 37 °C. After washed twice with phosphate buffered saline (PBS solution, 1 mL × 2), LysoTracker^{TM} Deep Red (50 nM) was added to incubate for another 20 min. Finally, HepG2 cells were washed twice with PBS solution (1 mL × 2) and covered with 1 mL of DMEM before imaging. The cells were observed with a Zeiss LSM 780 confocal fluorescent microscope. In order to show effective contrasts, appropriate colors were chose to the labeled images of organelles, thus giving pseudo colors.

Confocal fluorescent imaging experiments incubated with 5a and treated with hydroxychloroquine sulfate: Two groups of comparative experiments were carried out simultaneously. HepG2 cells were incubated with **5a** (2 μM) only, or incubated with **5a** (2 μM) and hydroxychloroquine sulfate (150 μM), in DMEM containing 1‰ DMSO for 60 min at 37 °C. Then, HepG2 cells were washed twice with phosphate buffered saline (PBS solution, 1 mL × 2), and covered with 1 mL of DMEM before imaging. The cells were observed with a Zeiss LSM 780 confocal fluorescent microscope.

Confocal fluorescent imaging experiments incubated with 5a and treated with

acetic acid: Two groups of comparative experiments were carried out simultaneously. On the one hand, HepG2 cells were incubated with **5a** (2 μM) in DMEM containing 1‰ DMSO for 30 min at 37 °C. Then, HepG2 cells were washed twice with phosphate buffered saline (PBS solution, 1 mL × 2), and covered with 1 mL of DMEM before imaging. On the other hand, HepG2 cells were incubated with **5a** (2 μM) in DMEM containing 1‰ DMSO for 20 min at 37 °C. Then, HepG2 cells were washed twice with phosphate buffered saline (PBS solution, 1 mL × 2), covered with 1 mL of DMEM, and treated with acetic acid (10 μL) for 10 min before imaging. The cells were observed with a Zeiss LSM 780 confocal fluorescent microscope.

Confocal fluorescent imaging experiments incubated with 6a and treated with acetic acid: HepG2 cells were incubated with **6a** (2 μM) in DMEM containing 1‰ DMSO for 20 min at 37 °C. Then, HepG2 cells were washed twice with phosphate buffered saline (PBS solution, 1 mL × 2), covered with 1 mL of DMEM, and treated with acetic acid (10 μL) for 10 min before imaging. The cells were observed with a Zeiss LSM 780 confocal fluorescent microscope.

Confocal fluorescent imaging experiments incubated with 5a, and followed by the treatment with alkaline buffer solution: Two groups of comparative experiments were carried out simultaneously. On the one hand, HepG2 cells were incubated with **5a** (2 μM) in DMEM containing 1‰ DMSO for 20 min at 37 °C, then washed twice with phosphate buffered saline (PBS solution, 1 mL × 2), and covered with 1 mL of PBS solution before imaging. On the other hand, HepG2 cells were incubated with **5a** (2 μM) in DMEM containing 1‰ DMSO for 20 min at 37 °C, then washed twice with phosphate buffered saline (PBS solution, 1 mL × 2), covered with the mixture solution containing 1 mL of PBS solution and 2 μL of NaOH solution (1 M) for 30 min before imaging. The cells were observed with a Zeiss LSM 780 confocal fluorescent microscope.

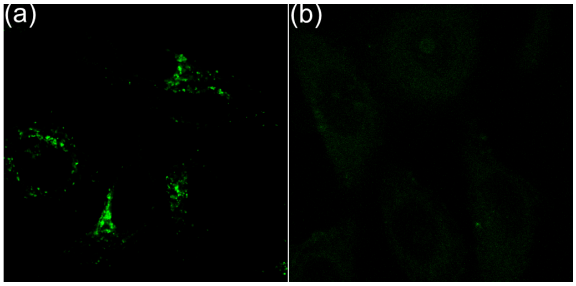


Fig. S15 Fluorescence images of HepG2 cells. (a) Incubated with **5a** for 20 min. (b) Incubated with **5a** for 20 min, and followed by the treatment with alkaline phosphate buffer solution for 30 min.

9.3 Cytotoxicity assay

The cytotoxicity experiments were investigated by CellTiler 96® AQueous One Solution Cell Proliferation Assay. HepG2 cells were seeded in 96-well culture plates and incubated for 24 h in stationary cultures. Then, the culture medium was replaced with a fresh complete medium containing compound **5** at concentrations of 0, 0.625, 1.25, 2.5, 5, 8, and 10 μM, respectively (0 μM for the control experiment). After another 24 h of incubation, 20 μL of CellTiler 96® AQueous One Solution was added to each well, and incubated for further one hour. Afterwards, the absorbance of each well was recorded on the ELISA plate reader (model 680, BioRad) at a wavelength of 490 nm. The cell viability was calculated by the following formula:

(Mean optical density in the treated well / Mean optical density in the control well) × 100%

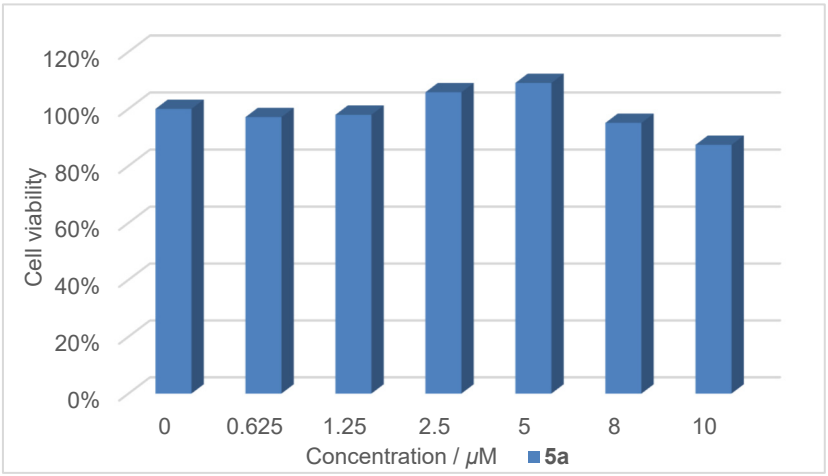


Fig. S16 Cell viability values (%) estimated by CellTiler 96® AQueous One Solution Cell Proliferation Assay, employing HepG2 cells stained with 0–10 μM of **5a** at 37 °C for 24 h.

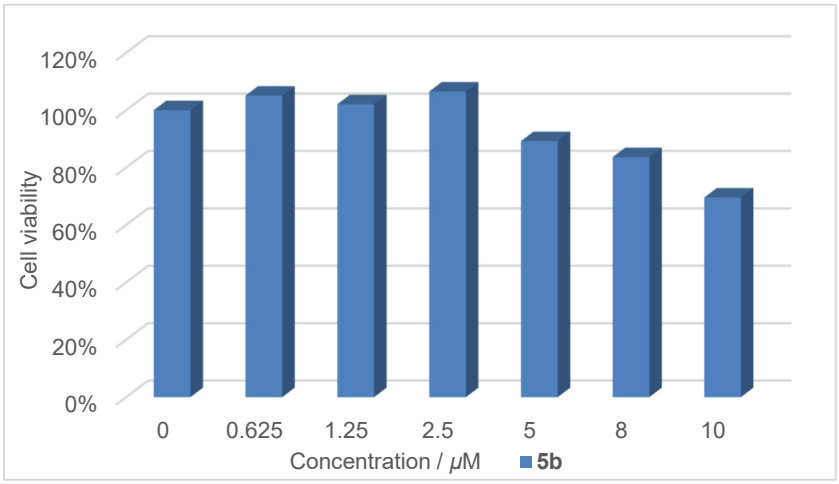


Fig. S17 Cell viability values (%) estimated by CellTiler 96® AQueous One Solution Cell Proliferation Assay, employing HepG2 cells stained with 0−10 μM of **5b** at 37 °C for 24 h.

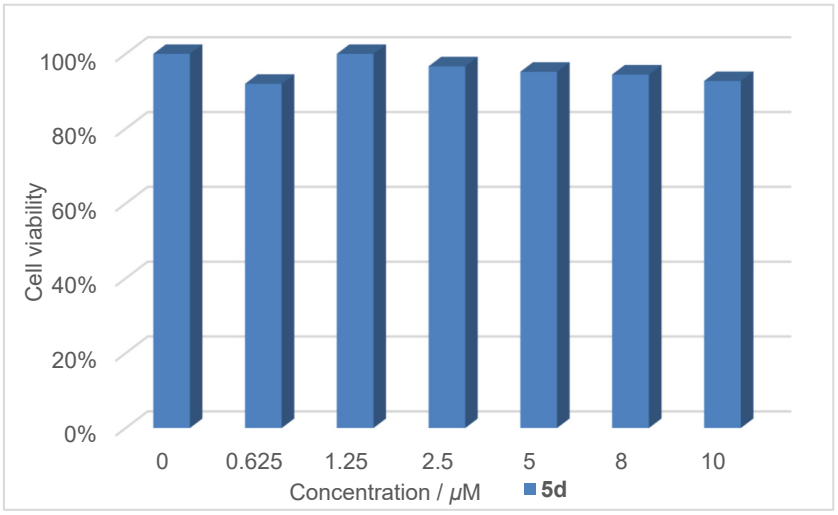


Fig. S18 Cell viability values (%) estimated by CellTiler 96® AQueous One Solution Cell Proliferation Assay, employing HepG2 cells stained with 0−10 μM of **5d** at 37 °C for 24 h.

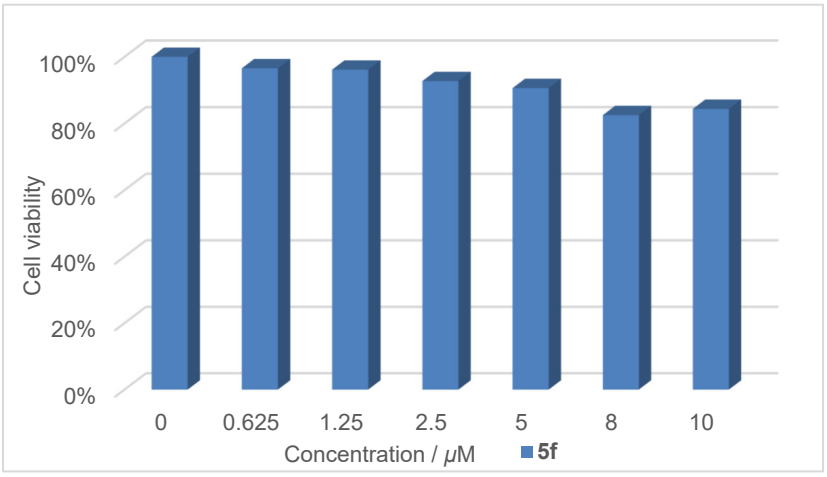


Fig. S19 Cell viability values (%) estimated by CellTiler 96® AQueous One Solution Cell

Proliferation Assay, employing HepG2 cells stained with 0–10 μM of **5f** at 37 °C for 24 h.

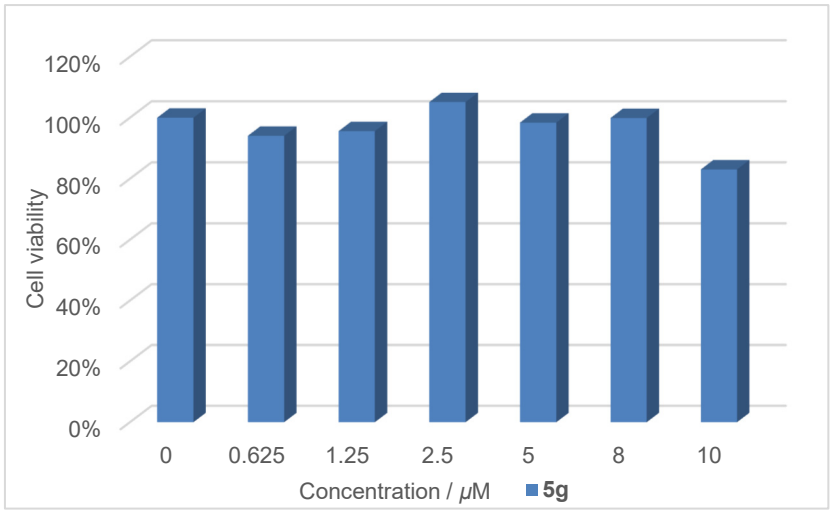


Fig. S20 Cell viability values (%) estimated by CellTiler 96® AQueous One Solution Cell Proliferation Assay, employing HepG2 cells stained with 0–10 μM of **5g** at 37 °C for 24 h.

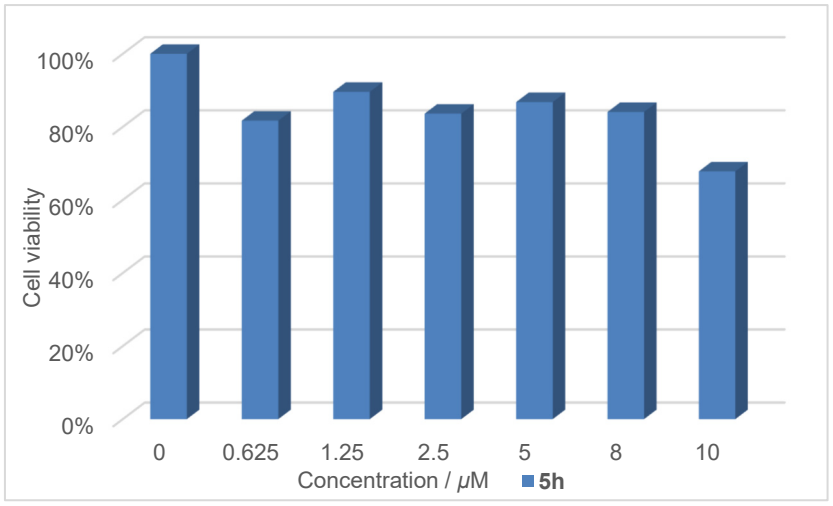


Fig. S21 Cell viability values (%) estimated by CellTiler 96® AQueous One Solution Cell Proliferation Assay, employing HepG2 cells stained with 0–10 μM of **5h** at 37 °C for 24 h.

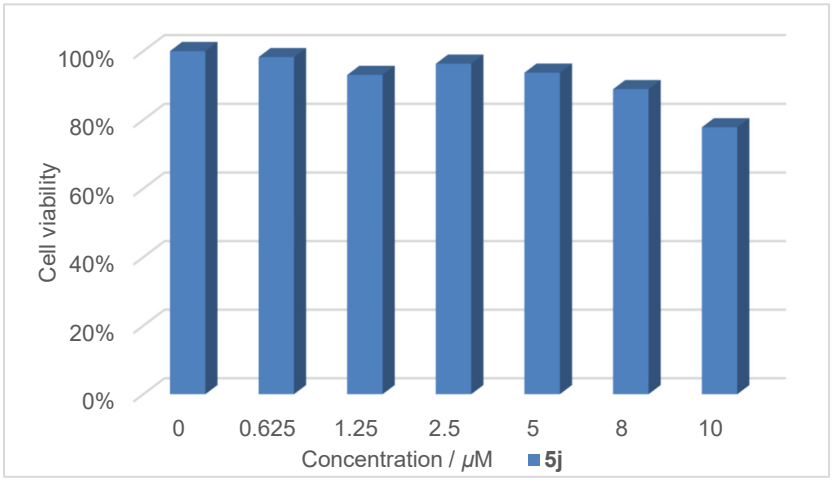


Fig. S22 Cell viability values (%) estimated by CellTiler 96® AQueous One Solution Cell Proliferation Assay, employing HepG2 cells stained with 0−10 μM of **5j** at 37 °C for 24 h.

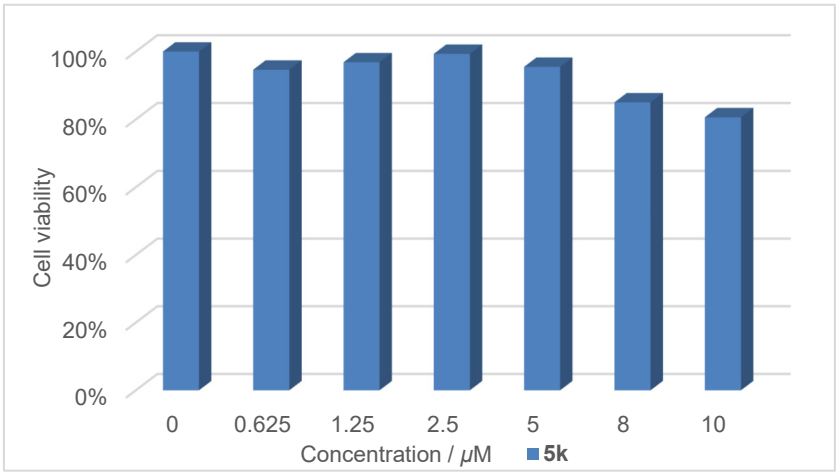
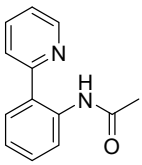


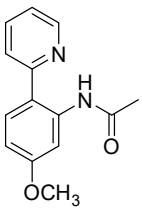
Fig. S23 Cell viability values (%) estimated by CellTiler 96® AQueous One Solution Cell Proliferation Assay, employing HepG2 cells stained with 0−10 μM of **5k** at 37 °C for 24 h.

X. Preparation and characterization of the described compounds



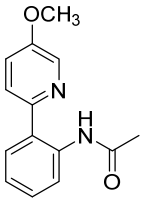
N-Acetyl-(2-pyridin-2-yl)aniline (1b)

Following general procedures for the synthesis of *N*-acetyl-2-(pyridin-2-yl)aniline derivatives, compound **1b** was obtained as a deep-yellow liquid (197.4 mg) in a total yield of 61%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.18 (s, 3H), 7.16 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.27-7.30 (m, 1H), 7.39-7.43 (m, 1H), 7.64 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.85 (td, *J* = 7.6 Hz, 2.0 Hz, 1H), 8.52 (d, *J* = 8.4 Hz, 1H), 8.64-8.66 (m, 1H), 12.07 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.4, 122.0, 122.1, 123.3, 123.6, 125.7, 129.0, 130.2, 137.7, 137.9, 147.5, 158.5, 168.7 ppm. ESI-HRMS: calcd for $C_{13}H_{12}N_2ONa$ $[M+Na]^+$ 235.0842, found 235.0842.



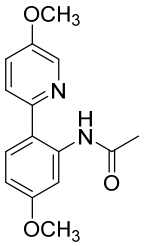
***N*-Acetyl-5-methoxy-(2-pyridin-2-yl)aniline (1c)**

Following general procedures for the synthesis of *N*-acetyl-2-(pyridin-2-yl)aniline derivatives, compound **1c** was obtained as a pale-yellow solid (220.8 mg) in a total yield of 49%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.20 (s, 3H), 3.88 (s, 3H), 6.71 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 7.20-7.23 (m, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.77-7.82 (m, 1H), 8.30 (d, *J* = 2.4 Hz, 1H), 8.58-8.60 (m, 1H), 12.59 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.6, 55.6, 105.9, 110.4, 117.7, 121.2, 122.3, 129.8, 137.7, 139.6, 147.3, 158.4, 161.1, 169.0 ppm. ESI-HRMS: calcd for $C_{14}H_{15}N_2O_2$ $[M+H]^+$ 243.1128, found 243.1133.



***N*-Acetyl-[2-(5-methoxypyridin-2-yl)]aniline (1d)**

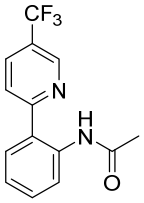
Following general procedures for the synthesis of *N*-acetyl-2-(pyridin-2-yl)aniline derivatives, compound **1d** was obtained as a pale-yellow solid (229.7 mg) in a total yield of 59%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.17 (s, 3H), 3.93 (s, 3H), 7.14 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.34-7.38 (m, 2H), 7.57 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 8.33 (dd, *J* = 2.8 Hz, 0.4 Hz, 1H), 8.49 (d, *J* = 8.4 Hz, 1H), 11.88 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.4, 55.9, 122.0, 122.6, 123.6, 123.9, 125.7, 128.5, 129.4, 134.8, 137.1, 150.8, 154.5, 168.7 ppm. ESI-HRMS: calcd for $C_{14}H_{15}N_2O_2$ $[M+H]^+$ 243.1128, found 243.1124.



***N*-Acetyl-5-methoxy-[2-(5-methoxypyridin-2-yl)]aniline (1e)**

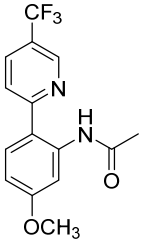
Following general procedures for the synthesis of *N*-acetyl-2-(pyridin-2-yl)aniline

derivatives, compound **1e** was obtained as a pale-yellow solid (255.1 mg) in a total yield of 56%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.19 (s, 3H), 3.86 (s, 3H), 3.92 (s, 3H), 6.69 (dd, *J* = 8.8 Hz, 2.8 Hz, 1H), 7.34 (dd, *J* = 8.8 Hz, 2.8 Hz, 1H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 1H), 8.25 (d, *J* = 2.8 Hz, 1H), 8.28 (dd, *J* = 2.8 Hz, 0.4 Hz, 1H), 12.30 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.6, 55.6, 55.9, 105.9, 110.3, 117.9, 122.9, 123.0, 129.3, 134.3, 138.8, 150.9, 154.0, 160.4, 168.9 ppm. ESI-HRMS: calcd for $C_{15}H_{17}N_2O_3$ $[M+H]^+$ 273.1234, found 273.1236.



***N*-Acetyl-2-[5-(trifluoromethyl)pyridin-2-yl]aniline (1f)**

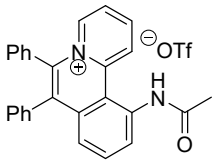
Following general procedures for the synthesis of *N*-acetyl-2-(pyridin-2-yl)aniline derivatives, compound **1f** was obtained as a pale-yellow solid (257.8 mg) in a total yield of 44%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.19 (s, 3H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 8.53 (d, *J* = 8.0 Hz, 1H), 8.92 (s, 1H), 11.70 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.4, 122.5, 123.0, 123.5 (q, *J* = 270.3 Hz), 123.9, 124.6, 129.4, 131.3, 134.9 (q, *J* = 3.3 Hz), 137.9, 144.7 (q, *J* = 4.0 Hz), 161.8, 168.8 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -62.37 ppm. ESI-HRMS: calcd for $C_{14}H_{11}F_3N_2ONa$ $[M+Na]^+$ 303.0716, found 303.0712.



***N*-Acetyl-5-methoxy-2-[5-(trifluoromethyl)pyridin-2-yl]aniline (1g)**

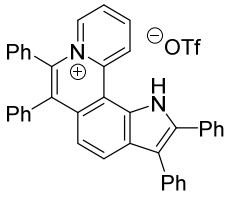
Following general procedures for the synthesis of *N*-acetyl-2-(pyridin-2-yl)aniline derivatives, compound **1g** was obtained as a pale-yellow solid (285.5 mg) in a total

yield of 46%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.21 (s, 3H), 3.88 (s, 3H), 6.72 (dd, *J* = 9.2 Hz, 2.8 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.99-8.02 (m, 1H), 8.30 (d, *J* = 2.4 Hz, 1H), 8.85 (dd, *J* = 1.2 Hz, 0.8 Hz, 1H), 12.29 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.6, 55.6, 106.0, 110.7, 121.9, 123.6 (q, *J* = 270.4 Hz), 123.8 (q, *J* = 33.4 Hz), 130.3, 134.6 (q, *J* = 3.2 Hz), 140.1, 144.4 (q, *J* = 4.0 Hz), 161.6, 162.0, 169.0 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -62.32 ppm. ESI-HRMS: calcd for $C_{15}H_{13}F_3N_2O_2Na$ $[M+Na]^+$ 333.0821, found 333.0826.



11-Acetamido-6,7-diphenylphenanthridizin-5-ium trifluoromethanesulfonate (3c)

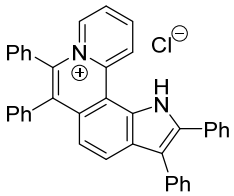
Compound **3c** was obtained as a grayish-white solid (36.7 mg) in 68% yield *via* Rh-catalyzed C–H activation/cyclization of 2-(pyridin-2-yl)aniline **1a** with diphenylacetylene **2a**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.42 (s, 3H), 7.13-7.15 (m, 2H), 7.30-7.33 (m, 5H), 7.39 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.43-7.44 (m, 3H), 7.75 (td, *J* = 7.2 Hz, 1.6 Hz, 1H), 7.85 (t, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 7.2 Hz, 1H), 8.35-8.40 (m, 1H), 8.67 (d, *J* = 6.8 Hz, 1H), 9.82 (d, *J* = 9.2 Hz, 1H), 10.47 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.2, 120.1, 123.6, 125.0, 126.7, 128.7, 128.8, 130.0, 130.1, 130.3, 130.6, 130.7, 130.9, 133.6, 134.0, 134.3, 135.4, 137.1, 137.2, 137.4, 138.4, 144.4, 170.8 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -78.43 ppm. ESI-HRMS: calcd for $C_{27}H_{21}N_2O$ $[M]^+$ 389.1648, found 389.1644.



2,3,6,7-Tetraphenyl-1*H*-pyrrolo[3,2-*k*]phenanthridizin-8-ium trifluoromethanesulfonate (4a)

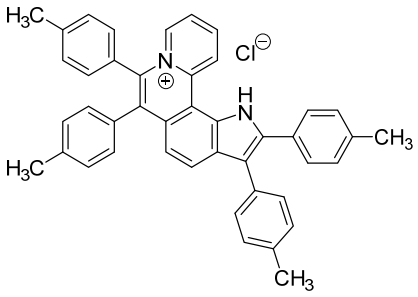
Compound **4a** was obtained as a yellow solid (55.2 mg) in 82% yield *via* Rh-catalyzed dual C–H activation/cyclization of *N*-acetyl-2-(pyridin-2-yl)aniline **1b** with

diphenylacetylene **2a**. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.24 (d, J = 8.8 Hz, 1H), 7.28-7.53 (m, 16H), 7.55-7.57 (m, 2H), 7.69-7.71 (m, 2H), 8.10 (td, J = 6.8 Hz, 1.2 Hz, 1H), 8.20 (d, J = 8.8 Hz, 1H), 8.73 (td, J = 8.4 Hz, 1.2 Hz, 1H), 8.83 (d, J = 6.8 Hz, 1H), 9.86 (d, J = 8.8 Hz, 1H), 12.81 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 109.6, 113.0, 116.4, 119.0, 123.6, 126.7, 126.8, 127.1, 128.2, 128.3, 128.6, 128.7, 129.0, 129.3, 129.5, 129.8, 129.96, 130.04, 130.11, 130.15, 131.19, 131.21, 131.7, 133.3, 135.5, 136.0, 136.1, 136.3, 138.7, 139.4, 140.3 ppm. ^{19}F NMR (376 MHz, DMSO-d_6): δ = -77.74 ppm. ESI-HRMS: calcd for $C_{39}H_{27}N_2$ $[M]^+$ 523.2169, found 523.2162.



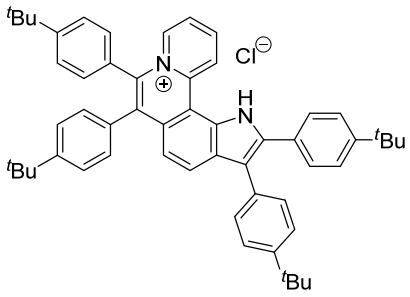
2,3,6,7-Tetraphenyl-1*H*-pyrrolo[3,2-*k*]phenanthridizin-8-ium chloride (5a)

Following the general procedure for Rh-catalyzed dual C–H activation/cyclization and the subsequent anion exchange reaction, compound **5a** was obtained as a yellow solid (42.5 mg) in a total yield of 76%. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.23 (d, J = 8.4 Hz, 1H), 7.28-7.51 (m, 16H), 7.55-7.57 (m, 2H), 7.70-7.72 (m, 2H), 8.11 (td, J = 7.2 Hz, 1.2 Hz, 1H), 8.20 (d, J = 8.4 Hz, 1H), 8.73 (td, J = 7.2 Hz, 1.2 Hz, 1H), 8.82 (d, J = 7.2 Hz, 1H), 9.88 (d, J = 8.8 Hz, 1H), 12.88 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 109.6, 113.0, 116.4, 118.9, 123.6, 126.67, 127.1, 128.1, 128.2, 128.5, 128.6, 128.9 , 129.3, 129.4, 129.8, 129.9, 130.00, 130.02, 130.11, 130.13, 130.15, 131.2, 131.6, 133.3, 135.5, 135.9, 136.1, 136.2, 138.7, 139.4, 140.2 ppm. ESI-HRMS: calcd for $C_{39}H_{27}N_2$ $[M]^+$ 523.2169, found 523.2168.



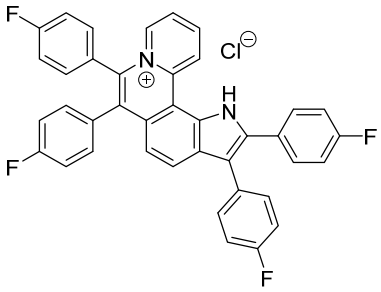
2,3,6,7-Tetra(4-tolyl)-1*H*-pyrrolo[3,2-*k*]phenanthridizin-8-ium chloride (5b)

Following the general procedure for Rh-catalyzed dual C–H activation/cyclization and the subsequent anion exchange reaction, compound **5b** was obtained as a yellow solid (46.6 mg) in a total yield of 76%. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.30 (s, 3H), 2.34 (s, 3H), ,2.36 (s, 3H), 2.38 (s, 3H), 7.16-7.21 (m, 5H), 7.24-7.32 (m, 8H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 8.07 (t, *J* = 7.2 Hz, 1H), 8.15 (d, *J* = 8.8 Hz, 1H), 8.69 (t, *J* = 8.4 Hz, 1H), 8.76 (d, *J* = 6.8 Hz, 1H), 9.83 (d, *J* = 8.4 Hz, 1H), 12.69 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4, 21.5, 21.6, 113.0, 116.7, 119.1, 122.6, 127.2, 127.7, 128.0, 128.4, 129.2, 129.3, 129.5, 129.6, 130.0, 130.3, 130.68, 130.75, 130.8, 131.0, 132.1, 132.3, 134.3, 135.2, 136.7, 137.9, 138.2, 138.6, 139.4, 140.6, 140.7, 141.5 ppm. ESI-HRMS: calcd for $C_{43}H_{35}N_2$ $[M]^+$ 579.2795, found 579.2792.



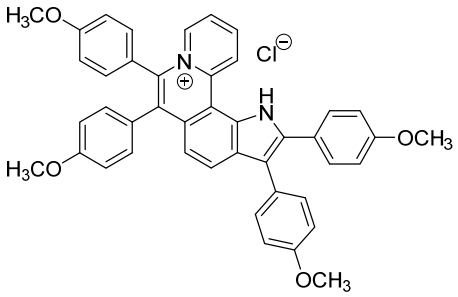
2,3,6,7-Tetra[4-(*tert*-butyl)phenyl]-1*H*-pyrrolo[3,2-*k*]phenanthridizin-8-ium chloride (5c)

Following the general procedure for Rh-catalyzed dual C–H activation/cyclization and the subsequent anion exchange reaction, compound **5c** was obtained as a yellow solid (56.2 mg) in a total yield of 72%. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.22 (s, 9H), 1.24 (s, 9H), 1.33 (s, 9H), 1.34 (s, 9H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.31-7.54 (m, 13H), 7.65 (d, *J* = 8.4 Hz, 2H), 8.11 (t, *J* = 6.8 Hz, 1H), 8.20 (d, *J* = 8.8 Hz, 1H), 8.69 (t, *J* = 7.6 Hz, 1H), 8.95 (d, *J* = 6.8 Hz, 1H), 9.82 (br, 1H), 12.67 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.2, 31.3, 31.4, 31.6, 34.71, 34.74, 34.8, 35.0, 113.3, 116.7, 118.9, 122.6, 125.1, 125.6, 125.7, 126.6, 127.7, 128.2, 128.3, 128.6, 129.3, 129.9, 130.2, 130.8, 131.0, 131.3, 132.4, 132.6, 133.9, 135.0, 138.1, 138.6, 141.0, 141.3, 149.8, 151.2, 151.3, 153.5 ppm. ESI-HRMS: calcd for $C_{55}H_{59}N_2$ $[M]^+$ 747.4673, found 747.4672.



2,3,6,7-Tetra(4-fluorophenyl)-1*H*-pyrrolo[3,2-*k*]phenanthridizin-8-ium chloride (5d)

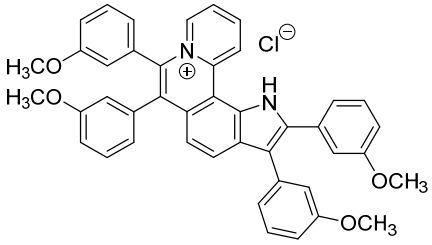
Following the general procedure for Rh-catalyzed dual C–H activation/addition/cyclization and the subsequent anion exchange reaction, compound **5d** was obtained as a yellow solid (41.7 mg) in a total yield of 66%. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.21-7.40 (m, 11H), 7.42-7.46 (m, 2H), 7.62-7.65 (m, 2H), 7.73-7.76 (m, 2H), 8.10 (td, *J* = 7.2 Hz, 1.2 Hz, 1H), 8.18 (d, *J* = 8.8 Hz, 1H), 8.74 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 8.88 (d, *J* = 6.8 Hz, 1H), 9.92 (d, *J* = 7.6 Hz, 1H), 12.94 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 109.6, 113.0, 115.3, 115.4 (d, *J* = 21.7 Hz), 115.6 (d, *J* = 21.5 Hz), 116.0 (d, *J* = 21.3 Hz), 116.5 (d, *J* = 21.9 Hz), 118.8, 123.6, 126.6 (d, *J* = 5.0 Hz), 127.5, 128.0 (d, *J* = 3.4 Hz), 128.2, 129.3, 129.5 (d, *J* = 2.1 Hz), 130.1, 130.2, 130.9, 131.8 (d, *J* = 3.3 Hz), 131.9 (d, *J* = 8.2 Hz), 132.2 (d, *J* = 8.2 Hz), 133.8 (d, *J* = 8.7 Hz), 135.6 (d, *J* = 8.2 Hz), 136.3, 138.7, 138.9, 140.3, 161.3 (d, *J* = 243.0 Hz), 161.6 (d, *J* = 244.3 Hz), 162.2 (d, *J* = 245.3 Hz), 162.6 (d, *J* = 246.7 Hz) ppm. ^{19}F NMR (376 MHz, DMSO-d_6): δ = -110.57, -112.56, -113.30, -115.12 ppm. ESI-HRMS: calcd for $C_{39}H_{23}F_4N_2$ $[M]^+$ 595.1792, found 595.1787.



2,3,6,7-Tetra(4-methoxyphenyl)-1*H*-pyrrolo[3,2-*k*]phenanthridizin-8-ium chloride (5e)

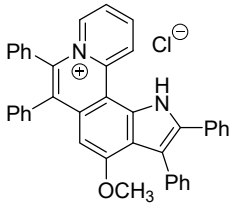
Following the general procedure for Rh-catalyzed dual C–H activation/cyclization and

the subsequent anion exchange reaction, compound **5e** was obtained as a yellow solid (53.1 mg) in a total yield of 78%. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.76 (s, 3H), 3.79 (s, 3H), 3.80 (s, 3H), 3.82 (s, 3H), 6.94 (d, *J* = 8.8 Hz, 2H), 7.02-7.07 (m, 6H), 7.19-7.24 (m, 3H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 8.08 (t, *J* = 6.8 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 8.69 (t, *J* = 8.4 Hz, 1H), 8.83 (d, *J* = 6.8 Hz, 1H), 9.83 (d, *J* = 8.8 Hz, 1H), 12.66 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 55.07, 55.09, 55.2, 55.3, 109.6, 112.7, 113.7, 114.0, 114.4, 114.8, 115.3, 118.7, 123.3, 123.6, 123.8, 125.5, 126.4, 126.6, 127.8, 129.6, 129.9, 130.5, 130.9, 131.1, 131.3, 132.6, 135.8, 136.3, 138.4, 139.1, 140.2, 158.2, 158.6, 159.5, 159.8 ppm. ESI-HRMS: calcd for $C_{43}H_{35}N_2O_4$ $[M]^+$ 643.2591, found 643.2584.



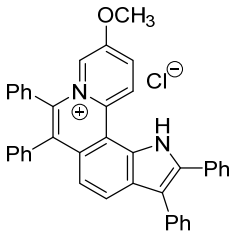
2,3,6,7-Tetra(3-methoxyphenyl)-1*H*-pyrrolo[3,2-*k*]phenanthridizin-8-ium chloride (5f)

Following the general procedure for Rh-catalyzed dual C–H activation/cyclization and the subsequent anion exchange reaction, compound **5f** was obtained as a yellow solid (39.5 mg) in a total yield of 58%. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.69 (d, *J* = 3.2 Hz, 3H), 3.72 (d, *J* = 7.2 Hz, 3H), 3.74 (s, 3H), 3.76 (s, 3H), 6.86-7.44 (m, 17H), 8.10 (t, *J* = 7.2 Hz, 1H), 8.24 (d, *J* = 8.8 Hz, 1H), 8.73 (t, *J* = 8.4 Hz, 1H), 8.86 (d, *J* = 7.2 Hz, 1H), 9.86 (d, *J* = 8.4 Hz, 1H), 12.80 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 55.06, 55.14 (d, *J* = 3.2 Hz), 55.2, 55.3 (d, *J* = 5.1 Hz), 109.6, 112.7, 112.9, 113.5, 113.7, 113.9, 115.47, 115.52, 115.8, 115.9, 116.1, 116.4, 116.7, 116.8, 119.0, 122.1, 122.4, 123.16, 123.23, 123.6, 126.7, 126.9, 129.3, 129.5, 129.7, 130.0, 130.1, 130.63, 130.64, 132.4, 132.8, 134.7, 135.7, 135.9, 136.0, 136.7, 138.8, 139.2, 140.2, 158.8, 159.1, 159.5, 159.6 ppm. ESI-HRMS: calcd for $C_{43}H_{35}N_2O_4$ $[M]^+$ 643.2591, found 643.2592.



4-Methoxy-2,3,6,7-tetraphenyl-1*H*-pyrrolo[3,2-*k*]phenanthridizin-8-ium chloride (5g)

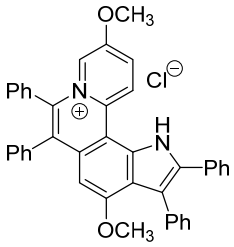
Following the general procedure for Rh-catalyzed dual C–H activation/cyclization and the subsequent anion exchange reaction, compound **5g** was obtained as a yellow solid (38.1 mg) in a total yield of 65%. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.50 (s, 3H), 6.49 (s, 1H), 7.30-7.50 (m, 16H), 7.54-7.57 (m, 4H), 7.94 (td, *J* = 7.2 Hz, 1.2 Hz, 1H), 8.58 (td, *J* = 8.4 Hz, 1.2 Hz, 1H), 8.69 (d, *J* = 6.8 Hz, 1H), 9.70 (d, *J* = 8.8 Hz, 1H), 12.80 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 55.2, 97.7, 108.6, 116.4, 120.4, 122.0, 125.7, 126.6, 127.5, 128.2, 128.26, 128.30, 128.7, 129.3, 129.7, 129.87, 129.93, 131.1, 131.2, 131.3, 131.6, 131.8, 132.3, 134.5, 135.1, 135.3, 135.4, 136.7, 137.6, 138.8, 139.6, 159.0 ppm. ESI-HRMS: calcd for $C_{40}H_{29}N_2O$ $[M]^+$ 553.2274, found 553.2273.



10-Methoxy-2,3,6,7-tetraphenyl-1*H*-pyrrolo[3,2-*k*]phenanthridizin-8-ium chloride (5h)

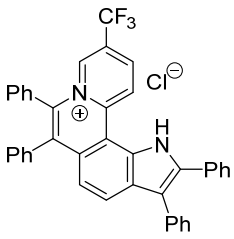
Following the general procedure for Rh-catalyzed dual C–H activation/cyclization and the subsequent anion exchange reaction, compound **5h** was obtained as a yellow solid (35.8 mg) in a total yield of 61%. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.86 (s, 3H), 7.20 (d, *J* = 8.8 Hz, 1H), 7.29-7.52 (m, 16H), 7.57 (dd, *J* = 7.6 Hz, 1.2 Hz, 2H), 7.69 (dd, *J* = 8.0 Hz, 1.2 Hz, 2H), 8.12-8.15 (m, 2H), 8.53 (dd, *J* = 9.6 Hz, 2.4 Hz, 1H), 9.88 (d, *J* = 9.6 Hz, 1H), 12.79 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 57.3, 113.5, 117.1, 118.9, 119.3, 121.1, 122.1, 126.5, 127.1, 128.32, 128.35, 128.46, 128.48, 128.52,

128.7, 128.9, 129.5, 130.1, 130.2, 130.50, 130.53, 130.7, 131.0, 131.5, 131.9, 134.0, 134.5, 135.3, 136.0, 138.2, 140.6, 155.2 ppm. ESI-HRMS: calcd for $C_{40}H_{29}N_2O$ $[M]^+$ 553.2274, found 553.2272.



4,10-Dimethoxy-2,3,6,7-tetraphenyl-1*H*-pyrrolo[3,2-*k*]phenanthridizin-8-ium chloride (5i)

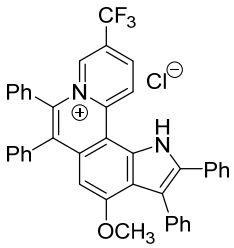
Following the general procedure for Rh-catalyzed dual C–H activation/cyclization and the subsequent anion exchange reaction, compound **5i** was obtained as a yellow solid (34.7 mg) in a total yield of 56%. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.48 (s, 3H), 3.81 (s, 3H), 6.46 (s, 1H), 7.32-7.58 (m, 20H), 8.00 (d, J = 2.8 Hz, 1H), 8.42 (dd, J = 10.0 Hz, 2.8 Hz, 1H), 9.68 (d, J = 10.0 Hz, 1H), 12.84 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 55.2, 56.6, 97.5, 109.0, 116.5, 118.6, 120.6, 126.7, 127.1, 127.5, 128.20, 128.22, 128.25, 128.31, 128.4, 128.6, 129.5, 129.7, 129.9, 130.1, 131.0, 131.1, 131.2, 131.3, 131.8, 134.6, 135.1, 135.5, 135.8, 136.2, 138.9, 153.1, 158.3 ppm. ESI-HRMS: calcd for $C_{41}H_{31}N_2O_2$ $[M]^+$ 583.2380, found 583.2383.



2,3,6,7-Tetraphenyl-10-trifluoromethyl-1*H*-pyrrolo[3,2-*k*]phenanthridizin-8-ium chloride (5j)

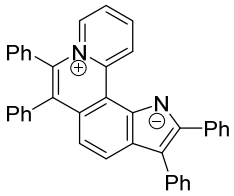
Following the general procedure for Rh-catalyzed dual C–H activation/cyclization and the subsequent anion exchange reaction, compound **5j** was obtained as a yellow solid (39.6 mg) in a total yield of 63%. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.28-7.54 (m, 17H), 7.58-7.60 (m, 2H), 7.70-7.72 (m, 2H), 8.33 (d, J = 8.8 Hz, 1H), 8.86 (s, 1H), 9.05

(dd, *J* = 9.2 Hz, 1.6 Hz, 1H), 10.03 (d, *J* = 9.2 Hz, 1H), 13.10 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 112.7, 116.7, 119.0, 120.6, 123.2 (q, *J* = 34.0 Hz), 127.3, 128.45, 128.50, 128.6, 128.8, 129.0, 129.4, 129.8, 129.9, 130.0, 130.2, 130.4, 130.6, 130.7, 131.0, 131.3, 133.0, 133.1, 135.0, 137.1, 137.3, 139.9, 141.9 ppm. ^{19}F NMR (376 MHz, DMSO-d_6): δ = -62.11 ppm. ESI-HRMS: calcd for $C_{40}H_{26}F_3N_2$ $[M]^+$ 591.2043, found 591.2040.



4-Methoxy-2,3,6,7-tetraphenyl-10-trifluoromethyl-1*H*-pyrrolo[3,2-*k*]phenanthridizin-8-ium chloride (5k)

Following the general procedure for Rh-catalyzed dual C–H activation/cyclization and the subsequent anion exchange reaction, compound **5k** was obtained as a yellow solid (38.8 mg) in a total yield of 59%. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.55 (s, 3H), 6.56 (s, 1H), 7.31-7.45 (m, 13H), 7.49-7.53 (m, 3H), 7.57-7.61 (m, 4H), 8.74 (s, 1H), 8.86 (d, *J* = 9.6 Hz, 1H), 9.83 (d, *J* = 9.2 Hz, 1H), 13.08 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.6, 98.5, 109.4, 117.5, 121.8 (q, *J* = 271.4 Hz), 122.5, 124.2 (q, *J* = 35.6 Hz), 126.8, 127.7, 128.3, 128.4, 128.8, 129.0, 129.8, 129.9, 130.2, 130.7, 130.79, 130.85, 131.0, 131.1, 131.5, 132.2, 132.5, 133.6, 134.95, 135.01, 136.2, 137.4, 141.0, 141.4, 161.7 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -63.15 ppm. ESI-HRMS: calcd for $C_{41}H_{28}F_3N_2O$ $[M]^+$ 621.2148, found 621.2143.



2,3,6,7-Tetraphenylpyrrolo[3,2-*k*]phenanthridizin-8-ium-1-ide (6a)

Compound **6a** was obtained as a dark red solid (46.4 mg) in nearly 100% yield *via* the

reaction of pyrrolo[3,2-*k*]phenanthridizinium **5a** with NaOH solution. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.73 (d, *J* = 8.4 Hz, 1H), 7.18-7.42 (m, 16H), 7.47 (dd, *J* = 7.2 Hz, 1.2 Hz, 2H), 7.76 (td, *J* = 7.2 Hz, 1.2 Hz, 1H), 7.87 (d, *J* = 7.2 Hz, 2H), 7.98 (d, *J* = 8.4 Hz, 1H), 8.51 (t, *J* = 6.8 Hz, 2H), 12.29 (d, *J* = 8.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 112.5, 114.0, 114.4, 120.7, 124.8, 125.7, 125.8, 127.2, 127.5, 127.8, 128.0, 128.4, 128.5, 128.7, 129.1, 129.4, 129.9, 130.1, 131.5, 132.5, 132.7, 132.8, 133.6, 135.6, 136.5, 136.8, 138.3, 139.2, 141.5, 141.6, 148.6 ppm. ESI-HRMS: calcd for $C_{39}H_{27}N_2$ $[M+H]^+$ 523.2169, found 523.2170.

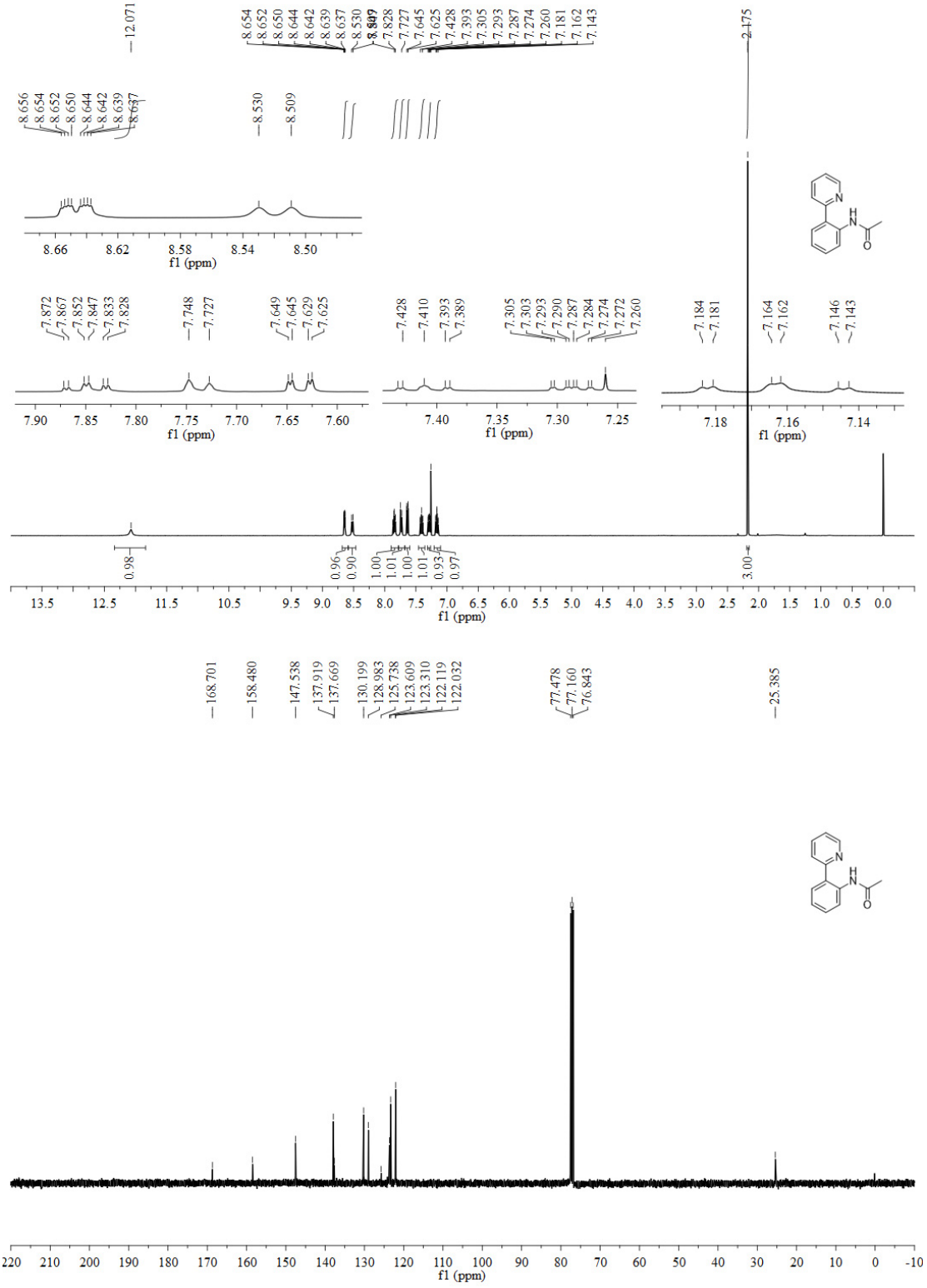
XI. References

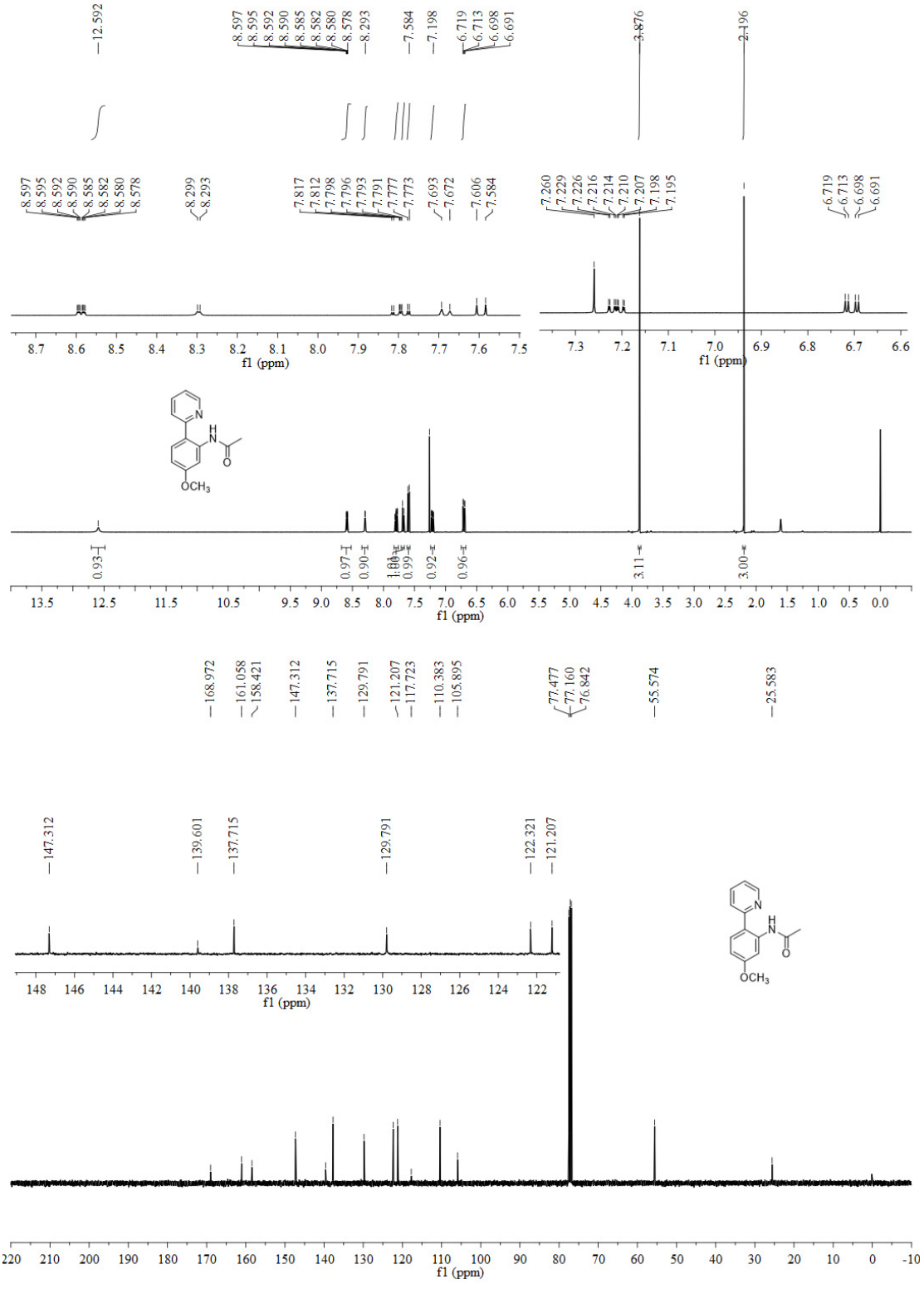
1 K. Park, G. Bae, J. Moon, J. Choe, K. H. Song and S. Lee, *J. Org. Chem.*, 2010, **75**, 6244–6251.

2 J. Peng, M. Chen, Z. Xie, S. Luo and Q. Zhu, *Org. Chem. Front.*, 2014, **1**, 777–781.

3 C. N. Baki and E. U. Akkaya, *J. Org. Chem.*, 2001, **66**, 1512–1513.

XII. Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra

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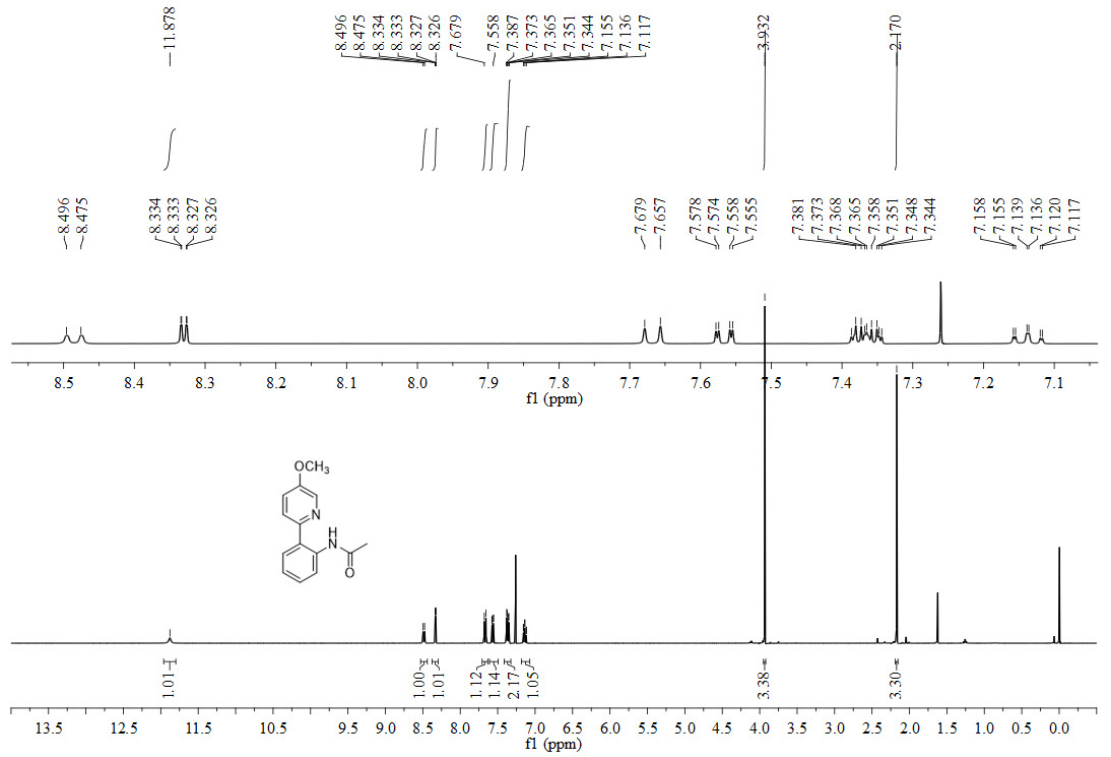
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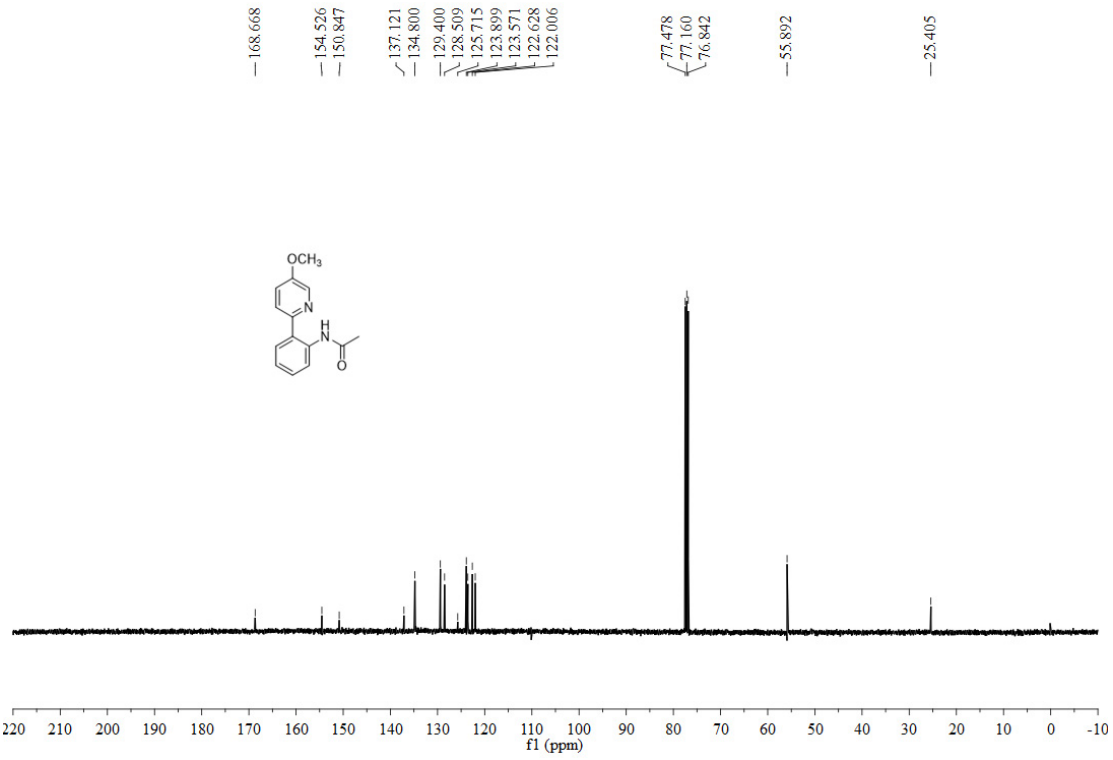
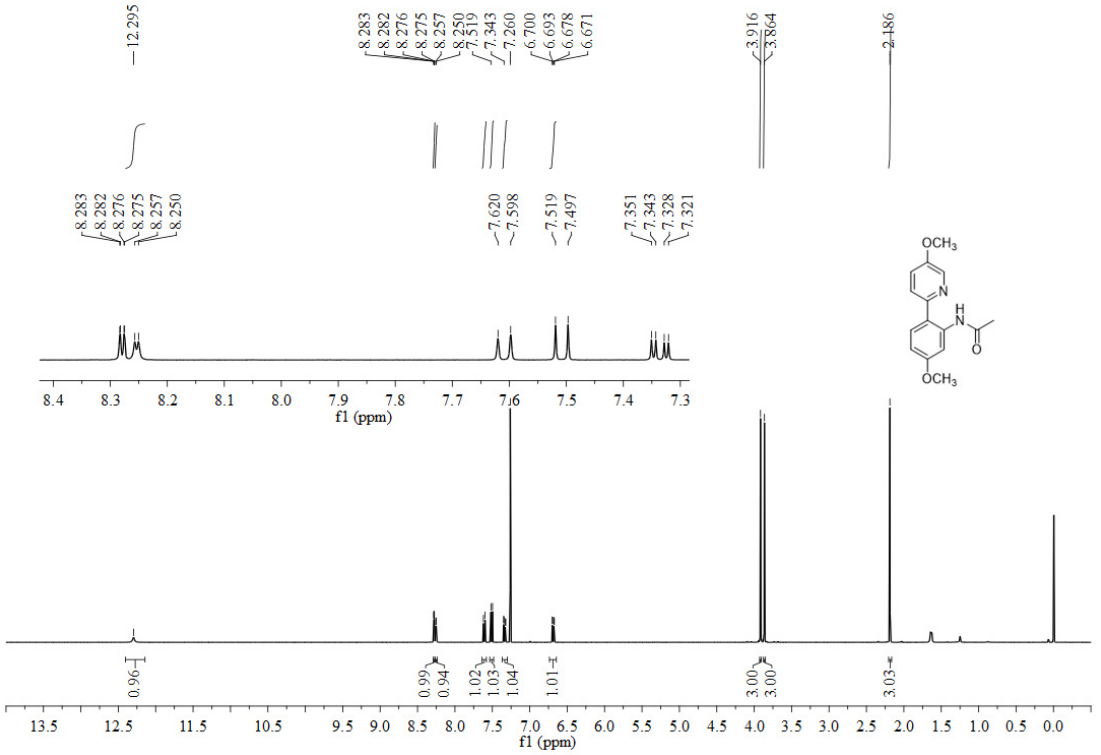
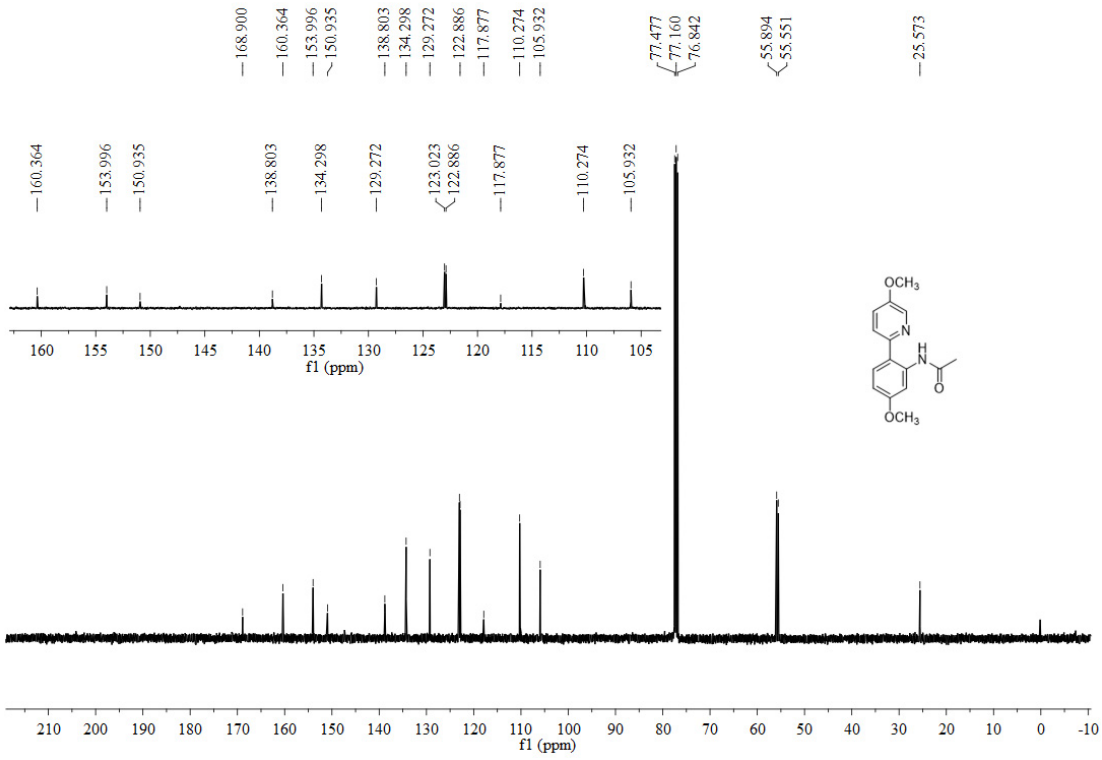
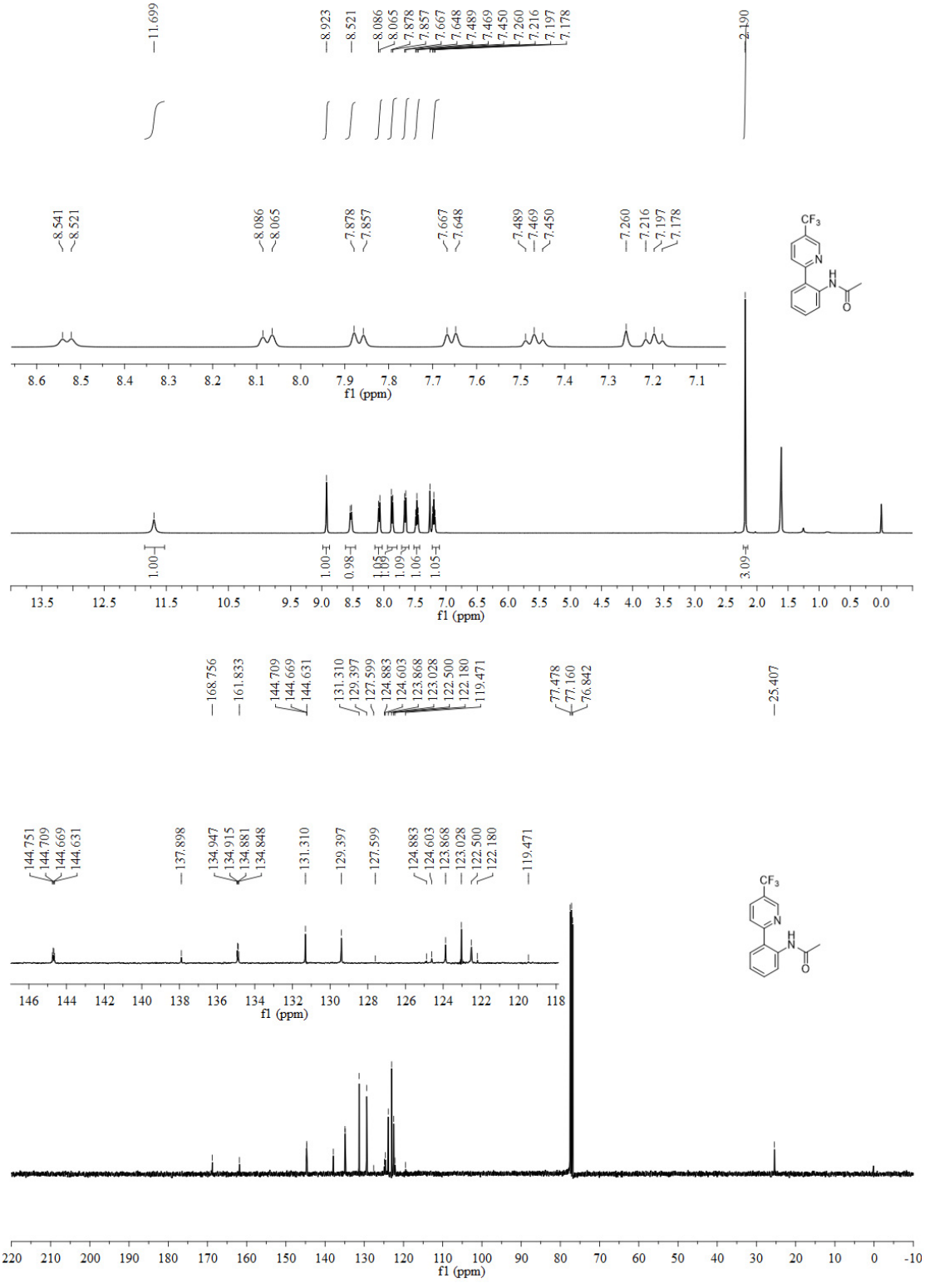
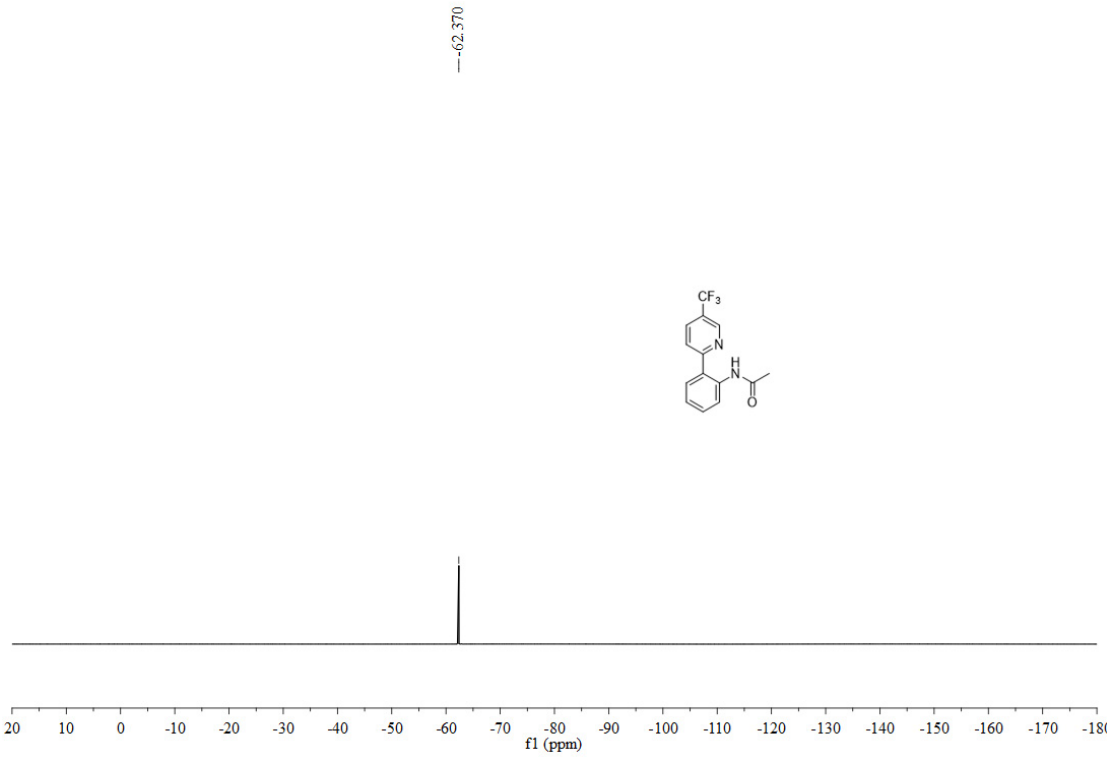
8.496
8.475
8.334
8.333
8.327
8.326
7.679
7.558
7.387
7.373
7.365
7.351
7.344
7.155
7.136
7.117
3.932
2.170
7.657
7.578
7.574
7.558
7.555
7.381
7.373
7.368
7.365
7.358
7.351
7.348
7.344
7.158
7.155
7.139
7.136
7.120
7.117
f1 (ppm)
OCH3
1.01
1.00
1.01
1.12
1.14
2.17
1.05
3.38
3.30
f1 (ppm)

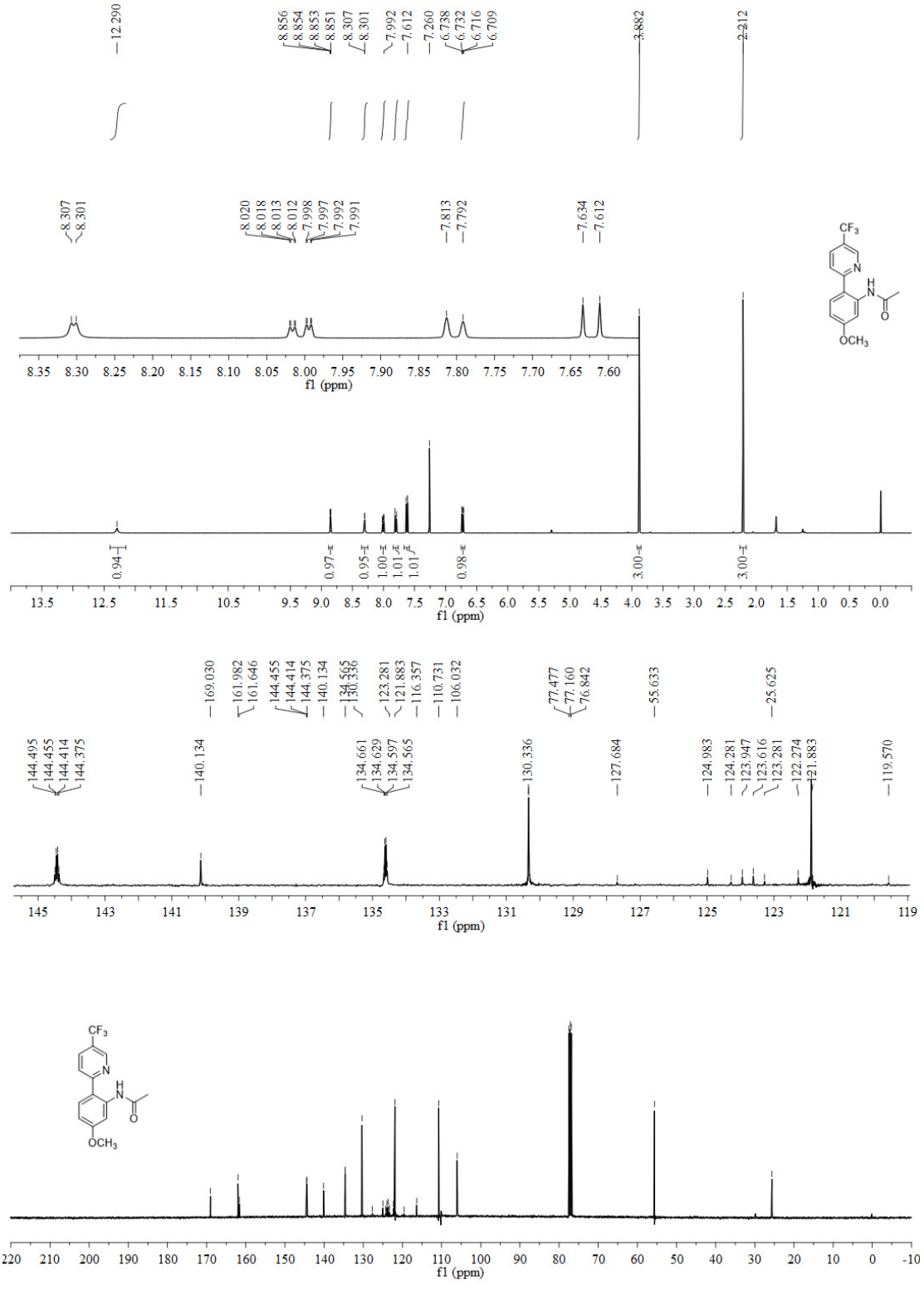

168.668
154.526
150.847
137.121
134.800
129.400
128.509
125.715
123.899
123.571
122.628
122.006
77.478
77.160
76.842
55.892
25.405
OCH3
f1 (ppm)

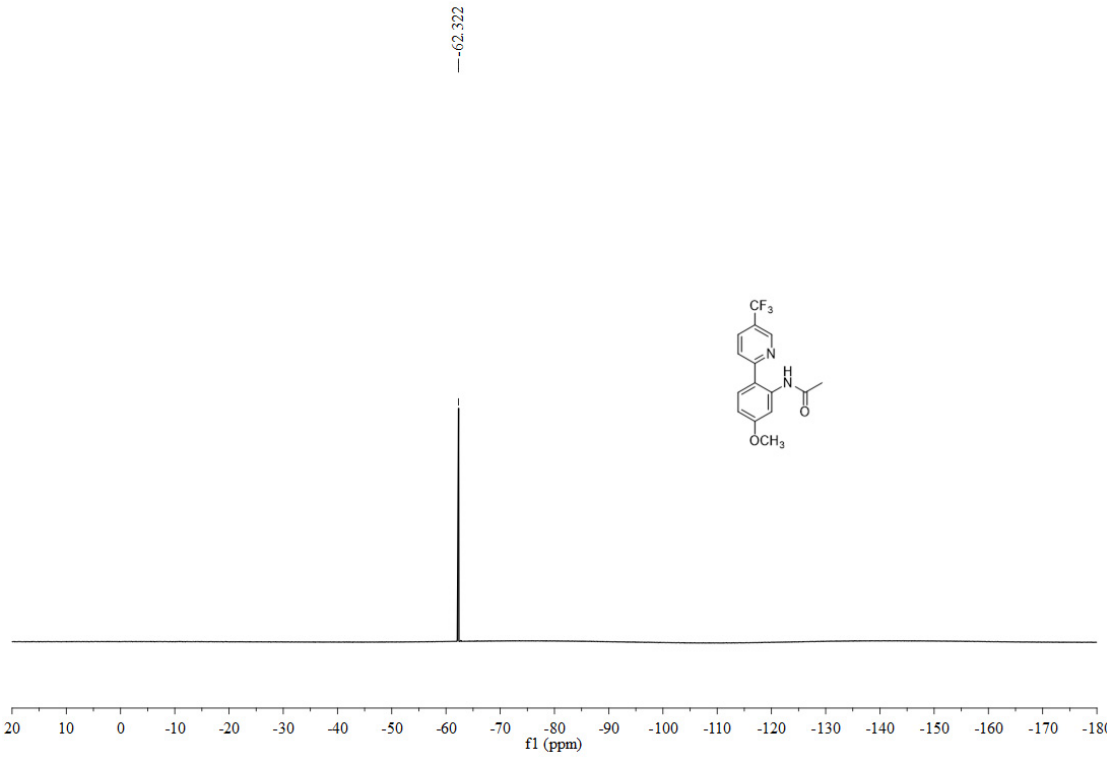

12.295
8.283
8.282
8.276
8.275
8.257
8.250
7.519
7.343
7.260
6.700
6.693
6.678
6.671
3.916
3.864
2.486
7.620
7.598
7.519
7.497
7.351
7.343
7.328
7.321
OCH3
N
H
N
O
OCH3
f1 (ppm)
0.96
0.99
0.94
1.02
1.03
1.04
1.01
3.00
3.00
3.03

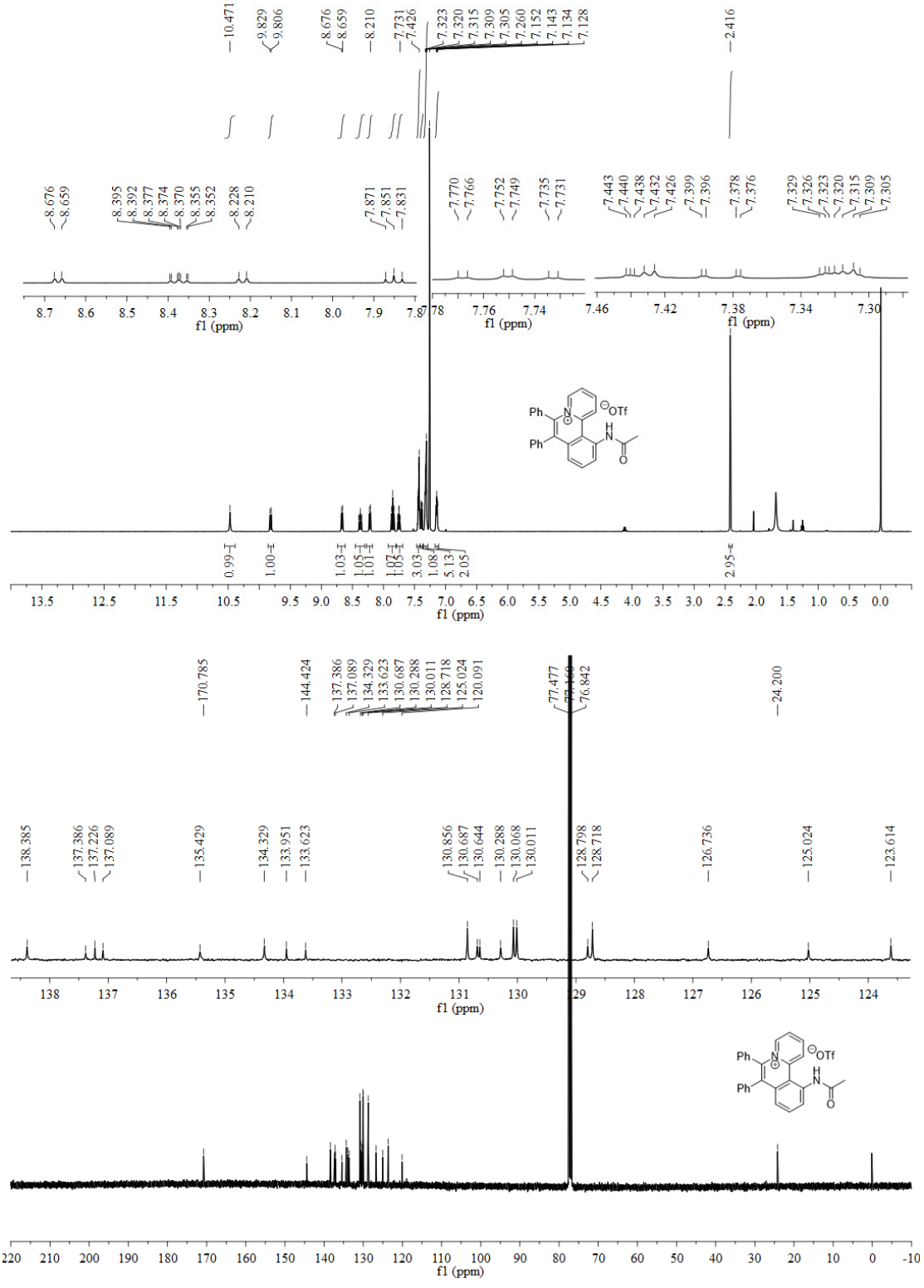

168.900
160.364
153.996
150.935
138.803
134.298
129.272
122.886
117.877
110.274
105.932
77.477
77.160
76.842
55.894
55.551
25.573
123.023
OCH3
N
H
N
O
OCH3
f1 (ppm)

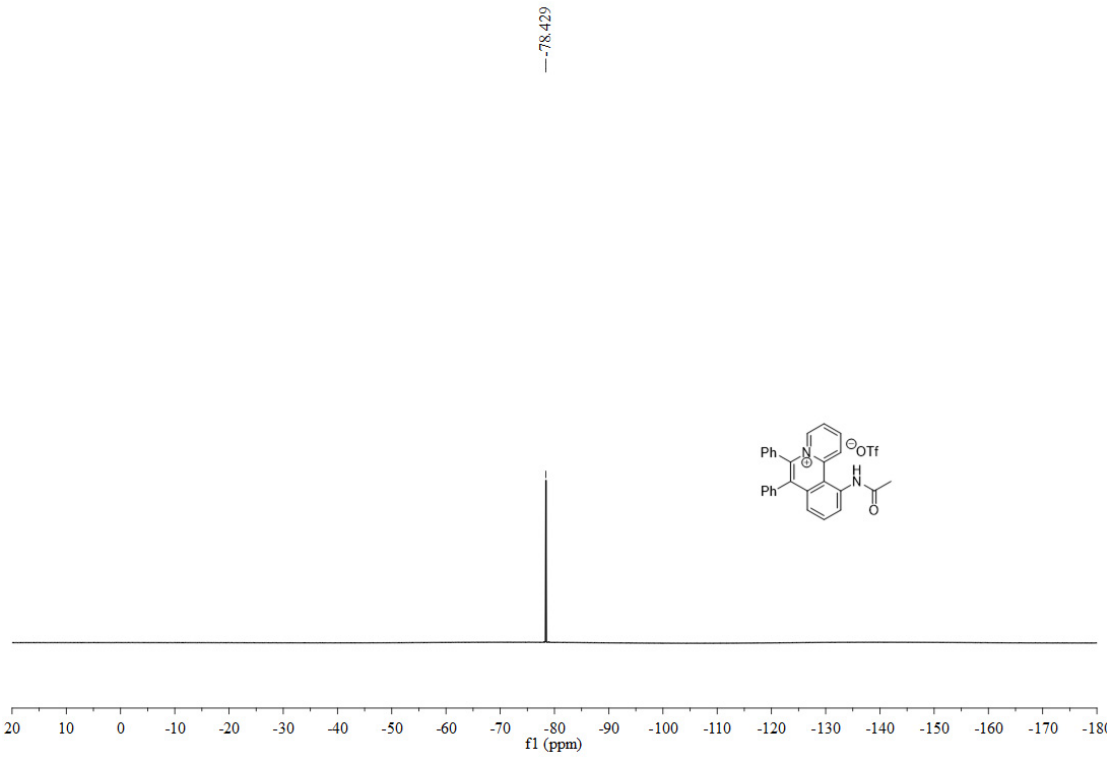

11.699
8.923
8.521
8.086
8.065
7.878
7.857
7.667
7.648
7.489
7.469
7.450
7.260
7.216
7.197
7.178
2.190
CF3
f1 (ppm)
168.756
161.833
144.709
144.669
144.631
131.310
129.397
127.599
124.883
124.603
123.868
123.028
122.500
122.180
119.471
77.478
77.160
76.842
25.407

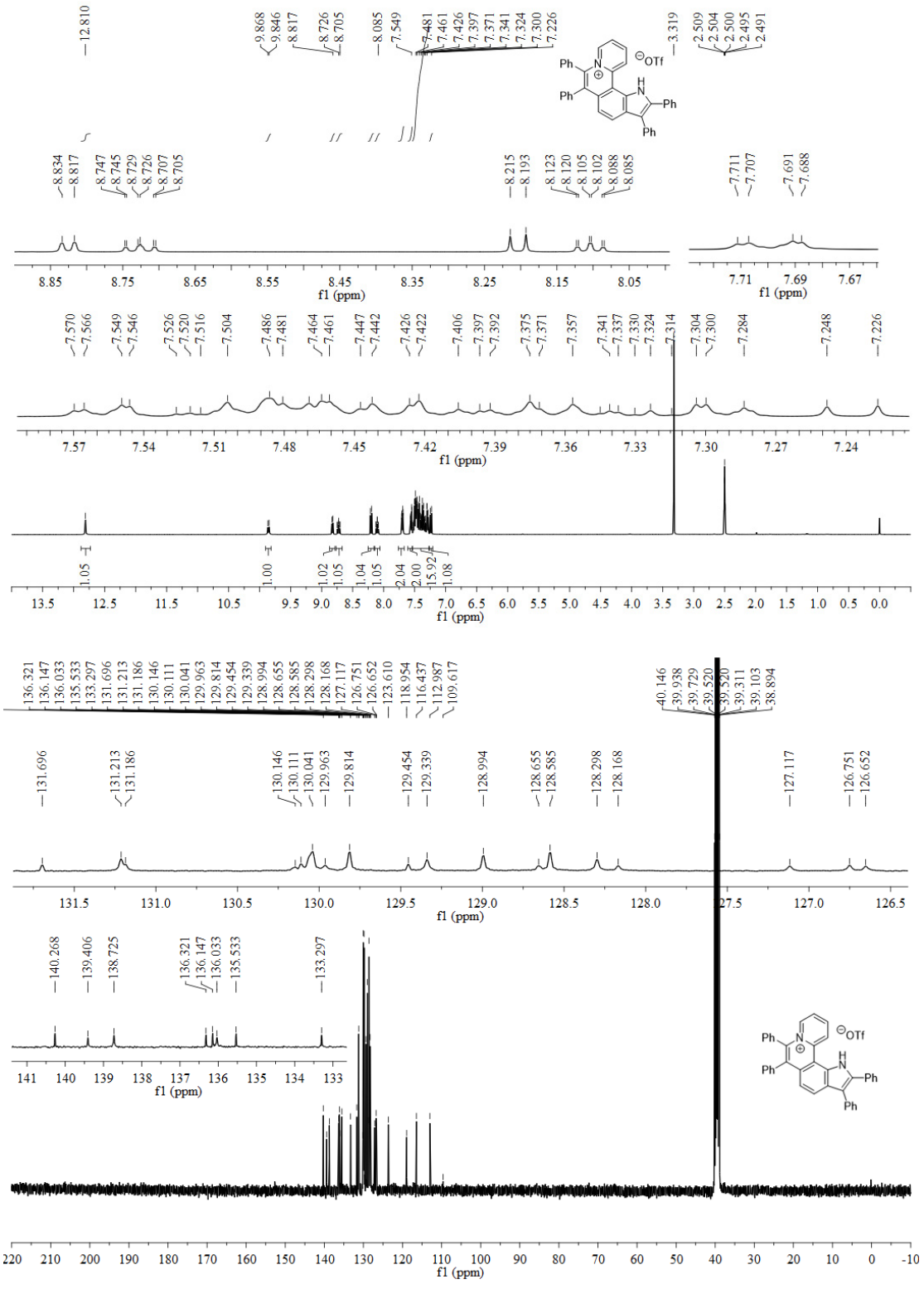

-62.370
CF3
N
H
N
O
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

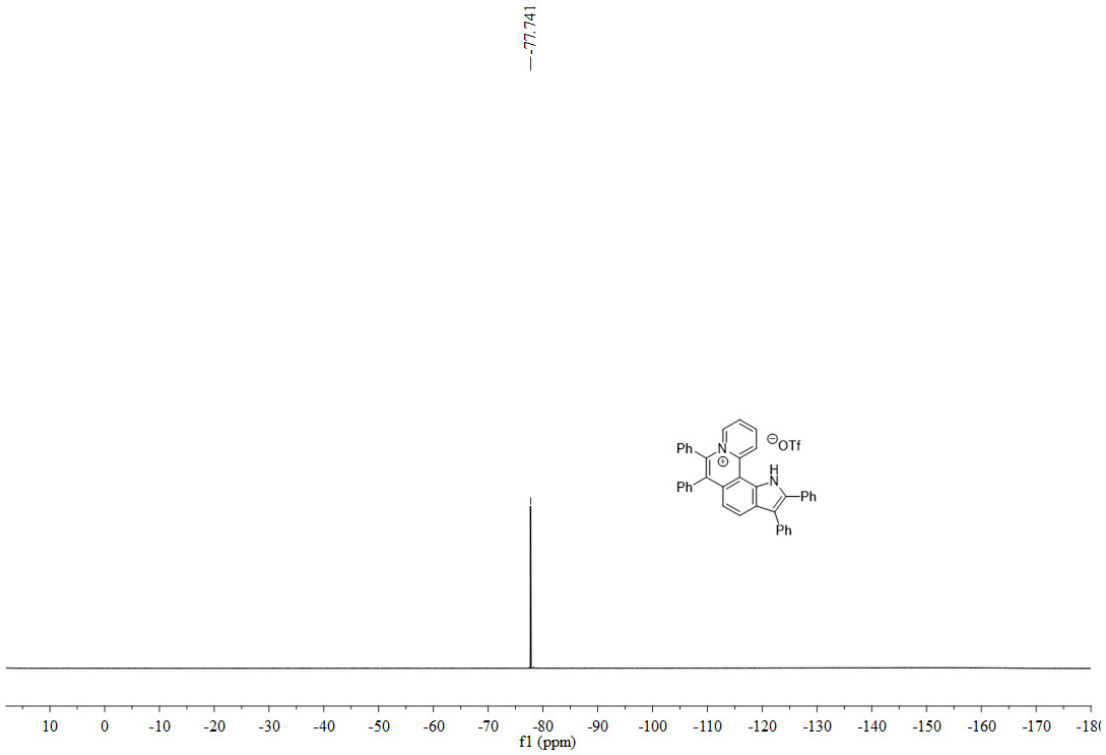

12.290
8.856
8.854
8.853
8.851
8.307
8.301
7.992
7.612
7.260
6.738
6.732
6.716
6.709
3.882
2.212
f1 (ppm)
CF3
OCH3
169.030
161.982
161.646
144.455
144.414
144.375
140.134
134.565
130.336
123.281
121.883
116.357
110.731
106.032
77.477
77.160
76.842
55.633
25.625
134.661
134.629
134.597
134.565
130.336
127.684
124.983
124.281
123.947
123.616
123.281
122.274
121.883
119.570

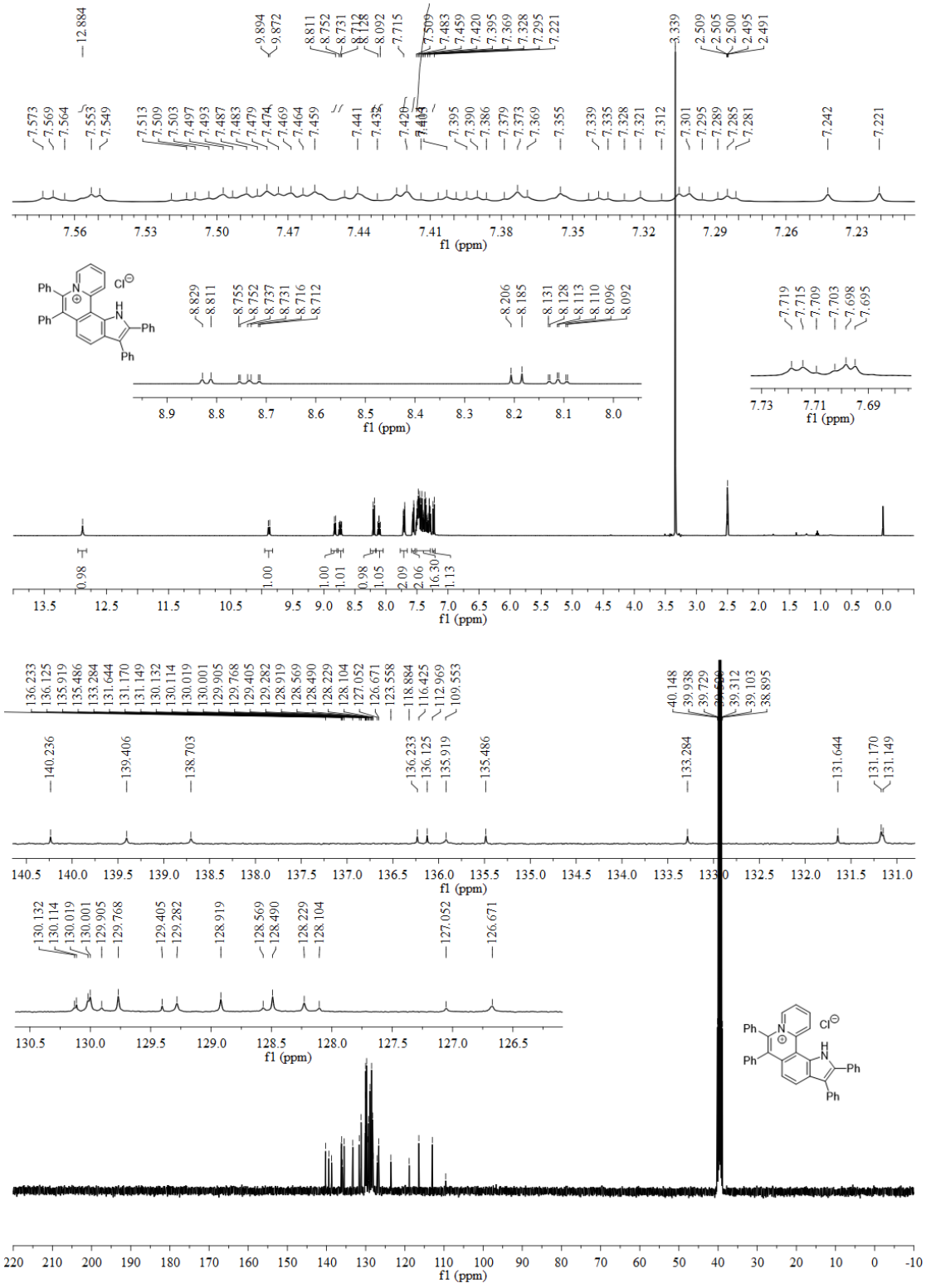

-62.322
CF3
N
H
N
O
OCH3
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

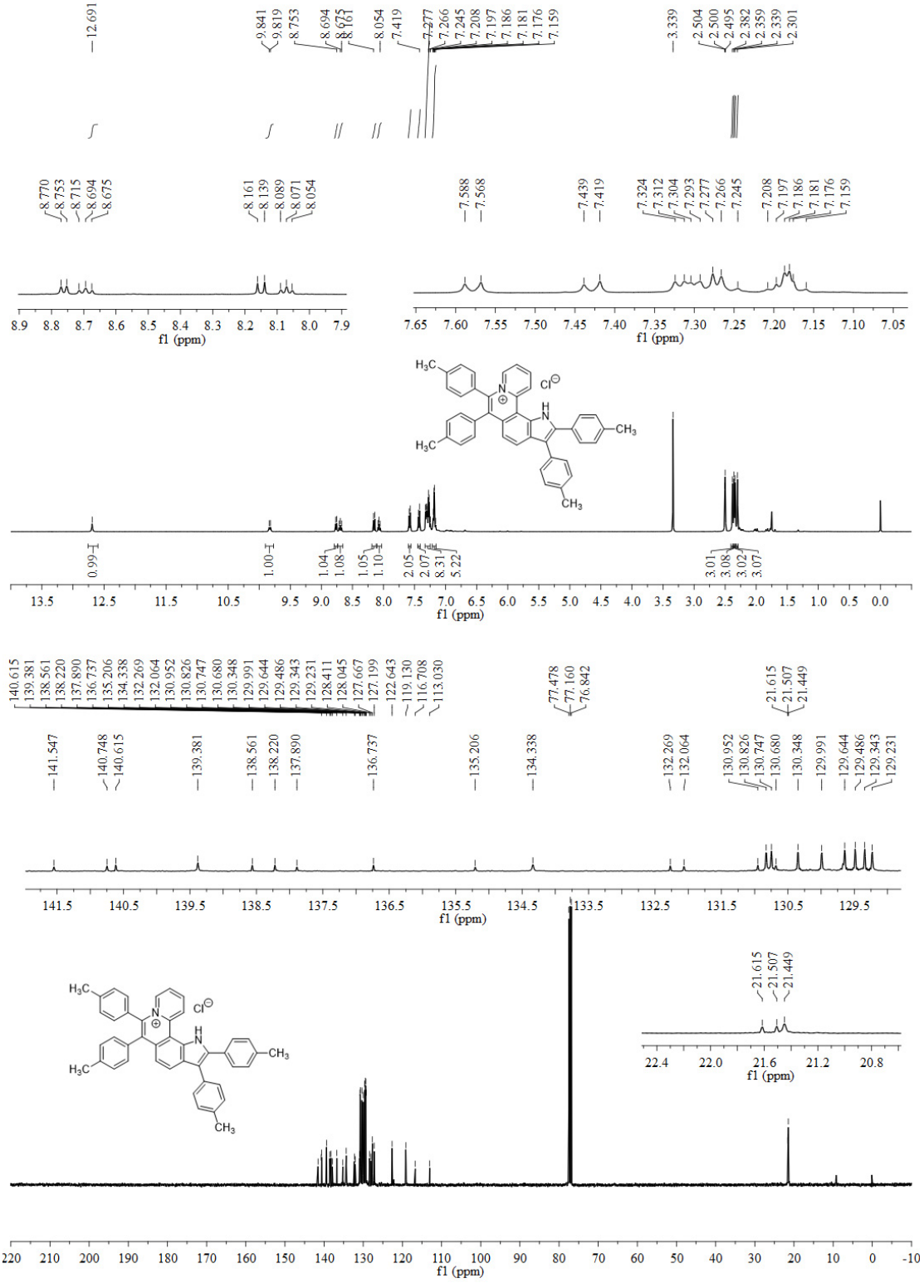

10.471
9.829
9.806
8.676
8.659
8.210
7.731
7.426
7.323
7.320
7.315
7.309
7.305
7.260
7.152
7.143
7.134
7.128
2.416
f1 (ppm)
Ph
Ph
OTf
N
H
O
0.99
1.00
1.03
1.05
1.01
1.02
1.05
3.03
1.08
5.13
2.05
2.95
170.785
144.424
137.386
137.089
134.329
133.623
130.687
130.288
130.011
128.718
125.024
120.091
77.477
76.842
24.200
138.385
137.386
137.226
137.089
135.429
134.329
133.951
133.623
130.856
130.687
130.644
130.288
130.068
130.011
128.798
128.718
126.736
125.024
123.614

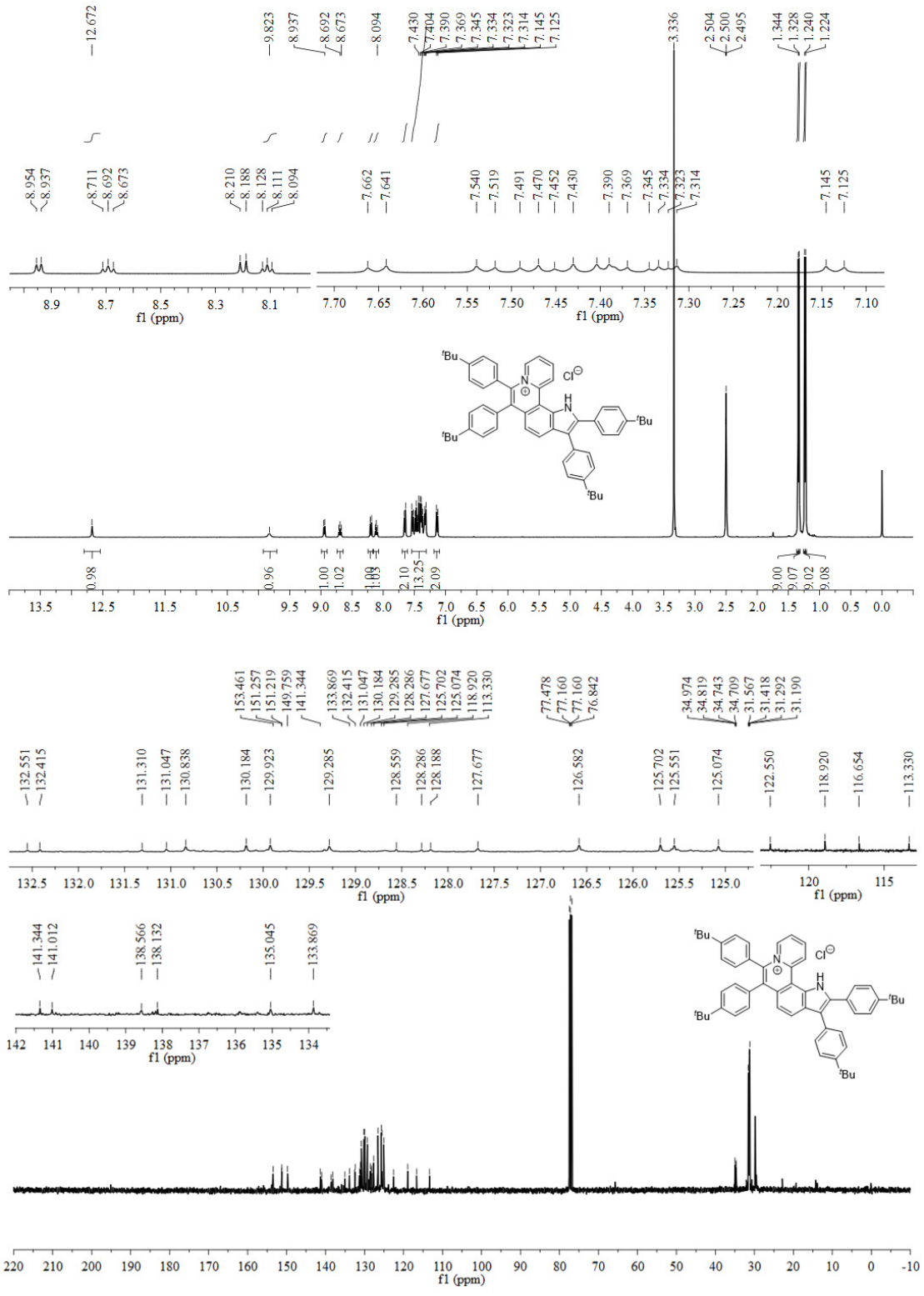

-78.429
Ph
Ph
OTf
H
N
O
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)


12.810
9.868
9.846
8.817
8.726
8.705
8.085
7.549
7.481
7.461
7.426
7.397
7.371
7.341
7.324
7.300
7.226
3.319
2.509
2.504
2.500
2.495
2.491
OTf
Ph
Ph
Ph
Ph
8.834
8.817
8.747
8.745
8.729
8.726
8.707
8.705
8.215
8.193
8.123
8.120
8.105
8.102
8.088
8.085
7.711
7.707
7.691
7.688
f1 (ppm)
7.570
7.566
7.549
7.546
7.526
7.520
7.516
7.504
7.486
7.481
7.464
7.461
7.447
7.442
7.426
7.422
7.406
7.397
7.392
7.375
7.371
7.357
7.341
7.337
7.330
7.324
7.314
7.304
7.300
7.284
7.248
7.226
1.05
1.00
1.02
1.05
1.04
1.05
2.04
2.00
15.92
1.08
f1 (ppm)
136.321
136.147
136.033
135.533
133.297
131.696
131.213
131.186
130.146
130.111
130.041
129.963
129.814
129.454
129.339
128.994
128.655
128.585
128.298
128.168
127.117
126.751
126.652
123.610
118.954
116.437
112.987
109.617
40.146
39.938
39.729
39.520
39.311
39.103
38.894
f1 (ppm)
140.268
139.406
138.725
136.321
136.147
136.033
135.533
133.297
f1 (ppm)
f1 (ppm)


-77.741
Ph
Ph
N
OTf
H
N
Ph
Ph
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)


12.884
9.894
9.872
8.811
8.752
8.731
8.712
8.128
8.092
7.715
7.509
7.483
7.459
7.420
7.395
7.369
7.328
7.295
7.221
3.339
2.509
2.505
2.500
2.495
2.491
7.573
7.569
7.564
7.553
7.549
7.513
7.509
7.503
7.497
7.493
7.487
7.483
7.479
7.474
7.469
7.464
7.459
7.441
7.432
7.420
7.403
7.395
7.390
7.386
7.379
7.373
7.369
7.355
7.339
7.335
7.328
7.321
7.312
7.301
7.295
7.289
7.285
7.281
7.242
7.221
f1 (ppm)
8.829
8.811
8.755
8.752
8.737
8.731
8.716
8.712
8.206
8.185
8.131
8.128
8.113
8.110
8.096
8.092
7.719
7.715
7.709
7.703
7.698
7.695
0.98
1.00
1.00
1.01
0.98
1.05
2.09
2.06
16.30
1.13
136.233
136.125
135.919
135.486
133.284
131.644
131.170
131.149
130.132
130.114
130.019
130.001
129.905
129.768
129.405
129.282
128.919
128.569
128.490
128.229
128.104
127.052
126.671
123.558
118.884
116.425
112.969
109.553
40.148
39.938
39.729
39.312
39.103
38.895
140.236
139.406
138.703
136.233
136.125
135.919
135.486
133.284
131.644
131.170
131.149
130.132
130.114
130.019
130.001
129.905
129.768
129.405
129.282
128.919
128.569
128.490
128.229
128.104
127.052
126.671
Ph
Ph
Ph
Ph
Cl
N
H


12.691
9.841
9.819
8.753
8.694
8.675
8.161
8.139
8.089
8.071
8.054
7.419
7.277
7.266
7.245
7.208
7.197
7.186
7.181
7.176
7.159
3.339
2.504
2.500
2.495
2.382
2.359
2.339
2.301
f1 (ppm)
0.99
1.00
1.04
1.08
1.05
1.10
2.05
2.07
8.31
5.22
3.01
3.08
3.02
3.07
140.615
139.381
138.561
138.220
137.890
136.737
135.206
134.338
132.269
132.064
130.952
130.826
130.747
130.680
130.348
129.991
129.644
129.486
129.343
129.231
128.411
128.045
127.667
127.199
122.643
119.130
116.708
113.030
77.478
77.160
76.842
21.615
21.507
21.449
Cl
CH3
H3C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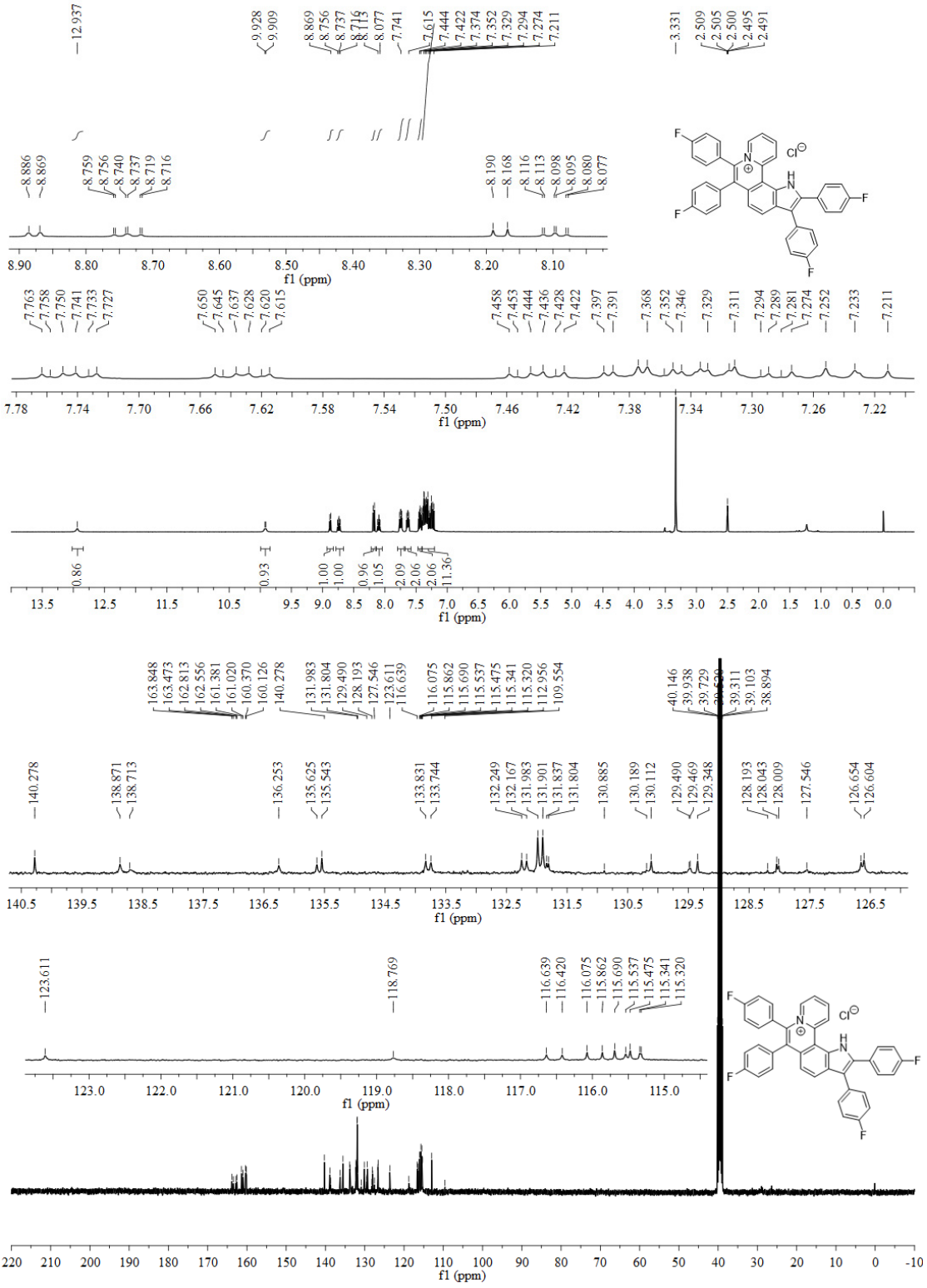
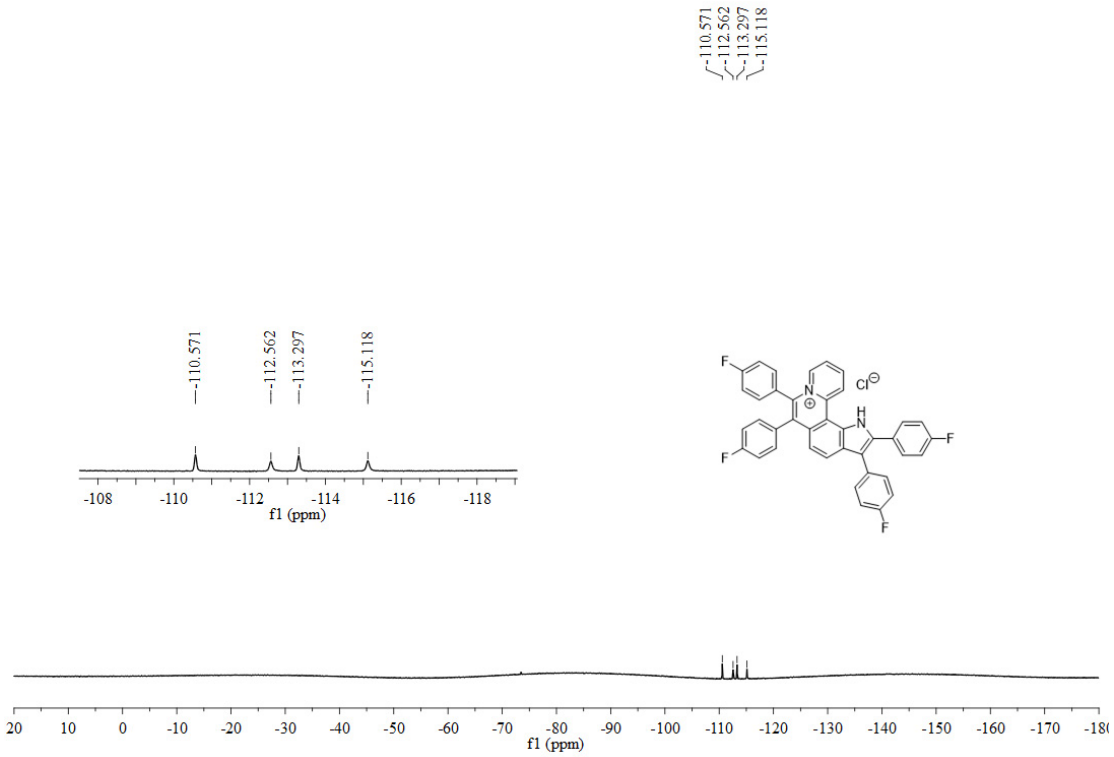
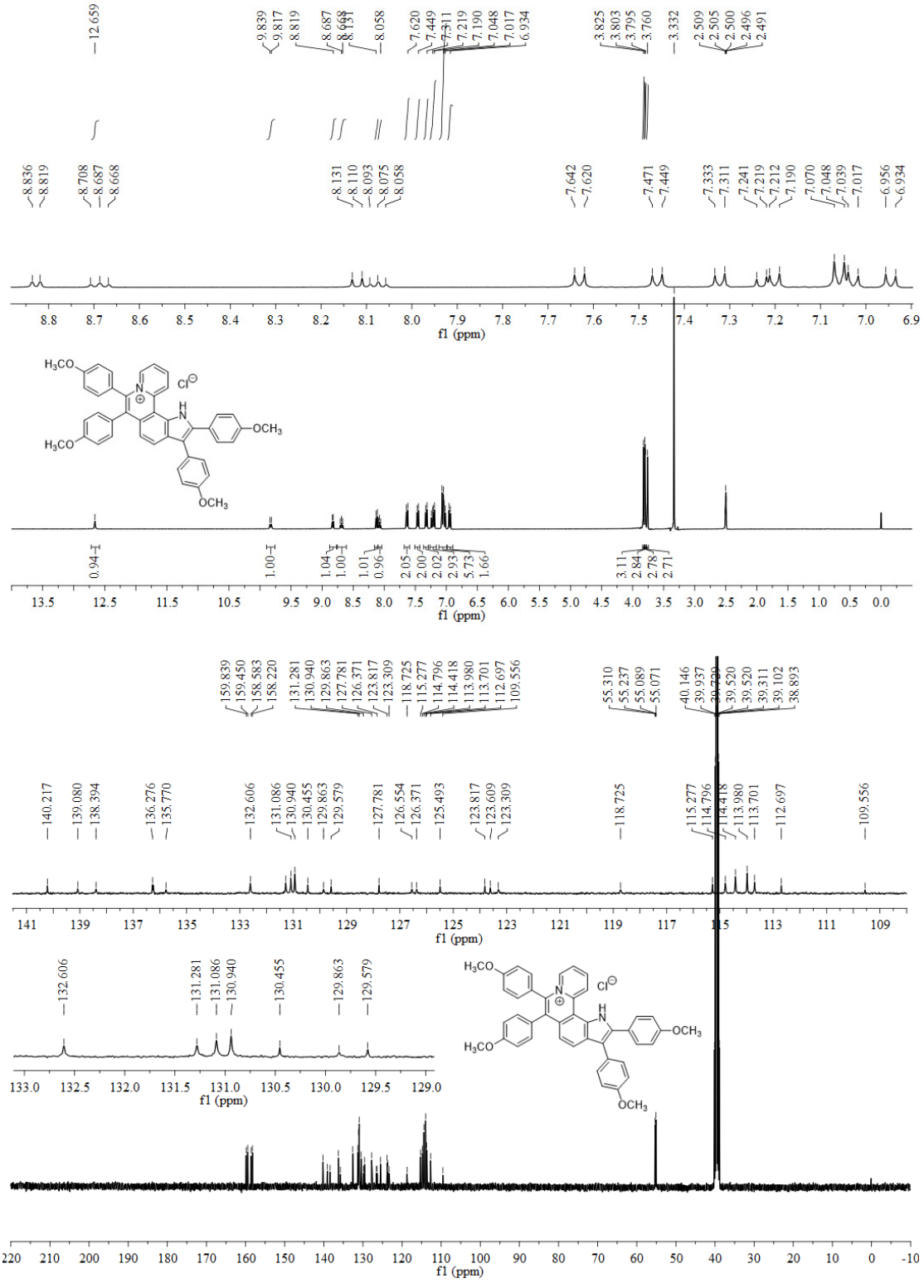
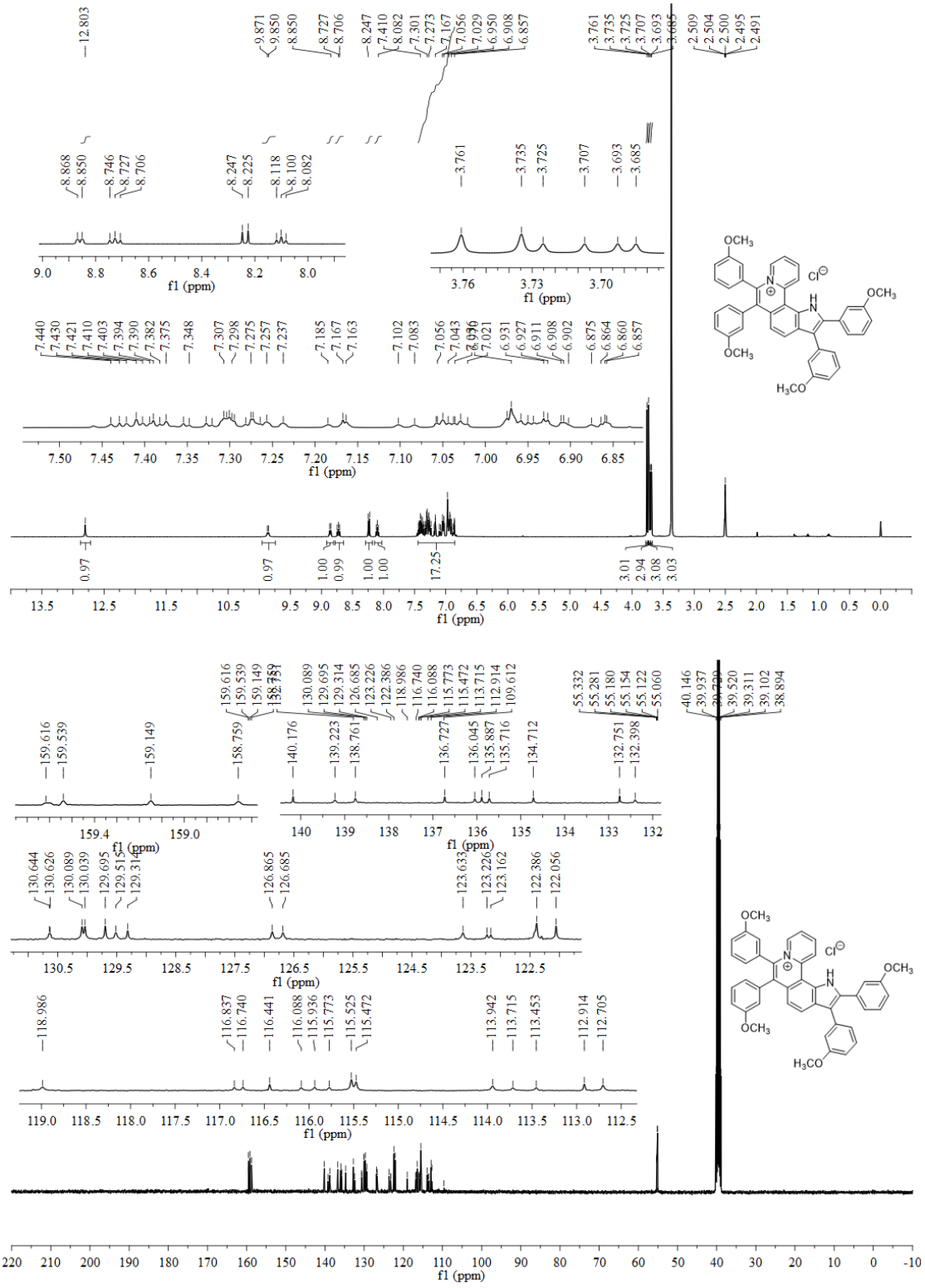
9.823
8.937
8.692
8.673
8.094
7.430
7.404
7.390
7.369
7.345
7.334
7.323
7.314
7.145
7.125
3.336
2.504
2.500
2.495
1.344
1.328
1.240
1.224
8.954
8.937
8.711
8.692
8.673
8.210
8.188
8.128
8.111
8.094
7.662
7.641
7.540
7.519
7.491
7.470
7.452
7.430
7.390
7.369
7.345
7.334
7.323
7.314
7.145
7.125
f1 (ppm)
tBu
Cl
H
N
0.98
0.96
1.00
1.02
1.08
1.03
2.10
13.25
2.09
9.00
9.07
9.02
9.08
153.461
151.257
151.219
149.759
141.344
133.869
132.415
131.047
130.184
129.285
128.286
127.677
125.702
125.074
118.920
113.330
77.478
77.160
77.160
76.842
34.974
34.819
34.743
34.709
31.567
31.418
31.292
31.190
132.551
132.415
131.310
131.047
130.838
130.184
129.923
129.285
128.559
128.286
128.188
127.677
126.582
125.702
125.551
125.074
122.550
118.920
116.654
113.330
141.344
141.012
138.566
138.132
135.045
133.869


f1 (ppm)


-110.571
-112.562
-113.297
-115.118
-108
-110
-112
-114
-116
-118
f1 (ppm)
F
Cl
N
H
F
F
F
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)


12.659
9.839
9.817
8.819
8.687
8.668
8.151
8.058
7.620
7.449
7.311
7.219
7.190
7.048
7.017
6.934
3.825
3.803
3.795
3.760
3.332
2.509
2.505
2.500
2.496
2.491
8.836
8.819
8.708
8.687
8.668
8.131
8.110
8.093
8.075
8.058
7.642
7.620
7.471
7.449
7.333
7.311
7.241
7.219
7.212
7.190
7.070
7.048
7.039
7.017
6.956
6.934
f1 (ppm)
H3CO
Cl⊖
N
H
OCH3
H3CO
OCH3
0.94
1.00
1.04
1.00
1.01
0.96
2.05
2.00
2.02
2.93
5.73
1.66
3.11
2.84
2.78
2.71
f1 (ppm)
159.839
159.450
158.583
158.220
131.281
130.940
129.863
127.781
126.371
123.817
123.309
118.725
115.277
114.796
114.418
113.980
113.701
112.697
109.556
55.310
55.237
55.089
55.071
40.146
39.937
39.729
39.520
39.520
39.311
39.102
38.893
140.217
139.080
138.394
136.276
135.770
132.606
131.086
130.940
130.455
129.863
129.579
127.781
126.554
126.371
125.493
123.817
123.609
123.309
118.725
115.277
114.796
114.418
113.980
113.701
112.697
109.556
f1 (ppm)
132.606
131.281
131.086
130.940
130.455
129.863
129.579
f1 (ppm)
H3CO
Cl⊖
N
H
OCH3
H3CO
OCH3
f1 (ppm)


12.803
9.871
9.850
8.850
8.727
8.706
8.247
7.410
8.082
7.301
7.273
7.167
7.056
7.029
6.950
6.908
6.857
3.761
3.735
3.725
3.707
3.693
3.685
2.509
2.504
2.500
2.495
2.491
f1 (ppm)
OCH3
Cl⊖
H3CO
0.97
1.00
17.25
3.01
2.94
3.08
3.03
159.616
159.539
159.149
158.759
140.176
139.223
138.761
136.727
136.045
135.887
135.716
134.712
132.751
132.398
130.644
130.626
130.089
130.039
129.695
129.515
129.314
126.865
126.685
123.633
123.226
123.162
122.386
122.056
118.986
116.837
116.740
116.441
116.088
115.936
115.773
115.525
115.472
113.942
113.715
113.453
112.914
112.705
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39.520
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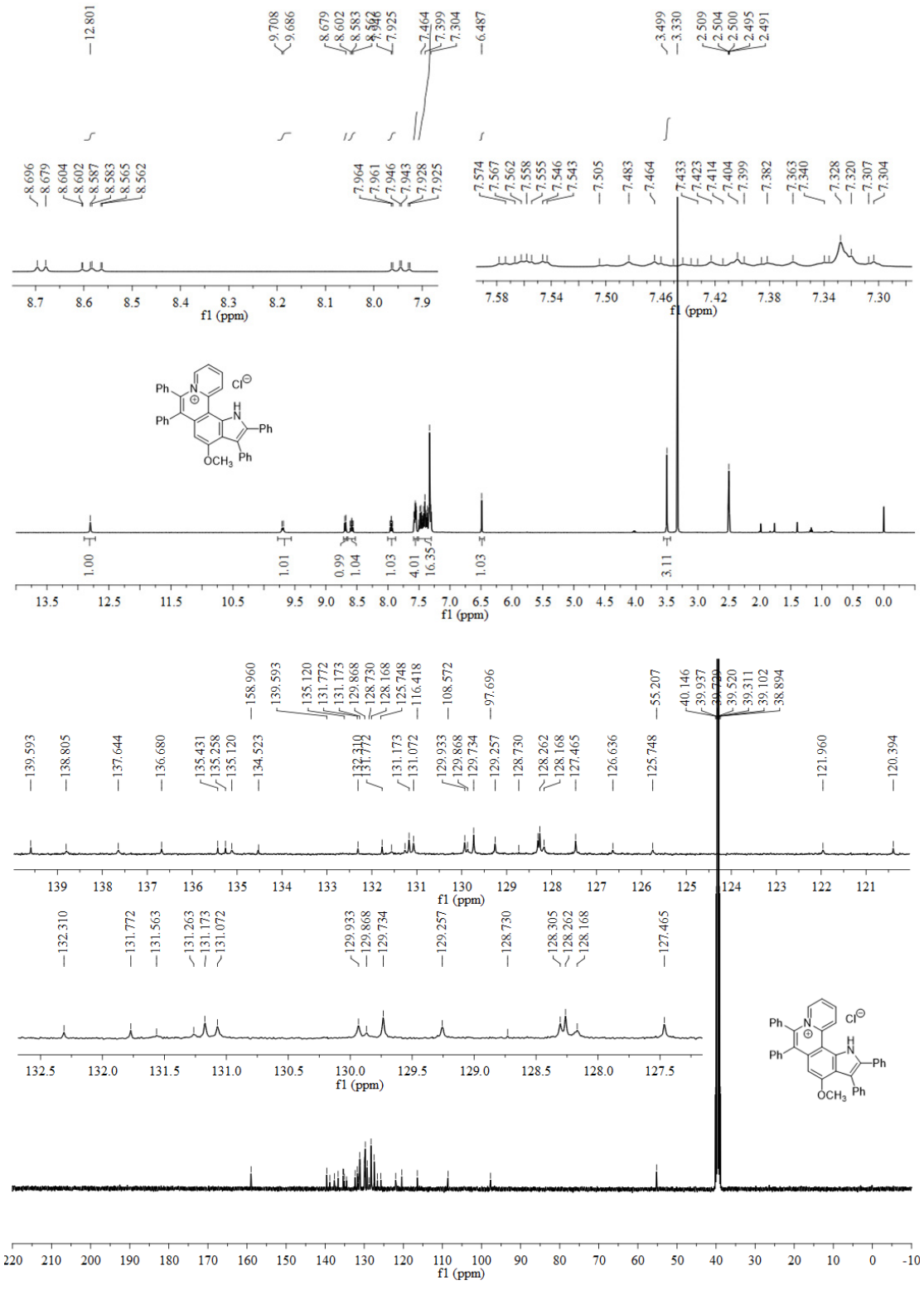
39.102
38.894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7.464
7.399
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3.499
3.330
2.509
2.504
2.500
2.495
2.491
8.696
8.679
8.604
8.602
8.587
8.583
8.565
8.562
7.964
7.961
7.946
7.943
7.928
7.925
7.574
7.567
7.562
7.558
7.555
7.546
7.543
7.505
7.483
7.464
7.433
7.423
7.414
7.404
7.399
7.382
7.363
7.340
7.328
7.320
7.307
7.304
f1 (ppm)
Ph
Cl
Ph
Ph
OCH3
Ph
1.00
1.01
0.99
1.04
1.03
4.01
16.35
1.03
3.11
158.960
139.593
135.120
131.772
131.173
129.868
128.730
128.168
125.748
116.418
108.572
97.696
55.207
40.146
39.937
39.729
39.520
39.311
39.102
38.894
139.593
138.805
137.644
136.680
135.431
135.258
135.120
134.523
132.310
131.772
131.173
131.072
129.933
129.868
129.734
129.257
128.730
128.262
128.168
127.465
126.636
125.748
121.960
120.394
132.310
131.772
131.563
131.263
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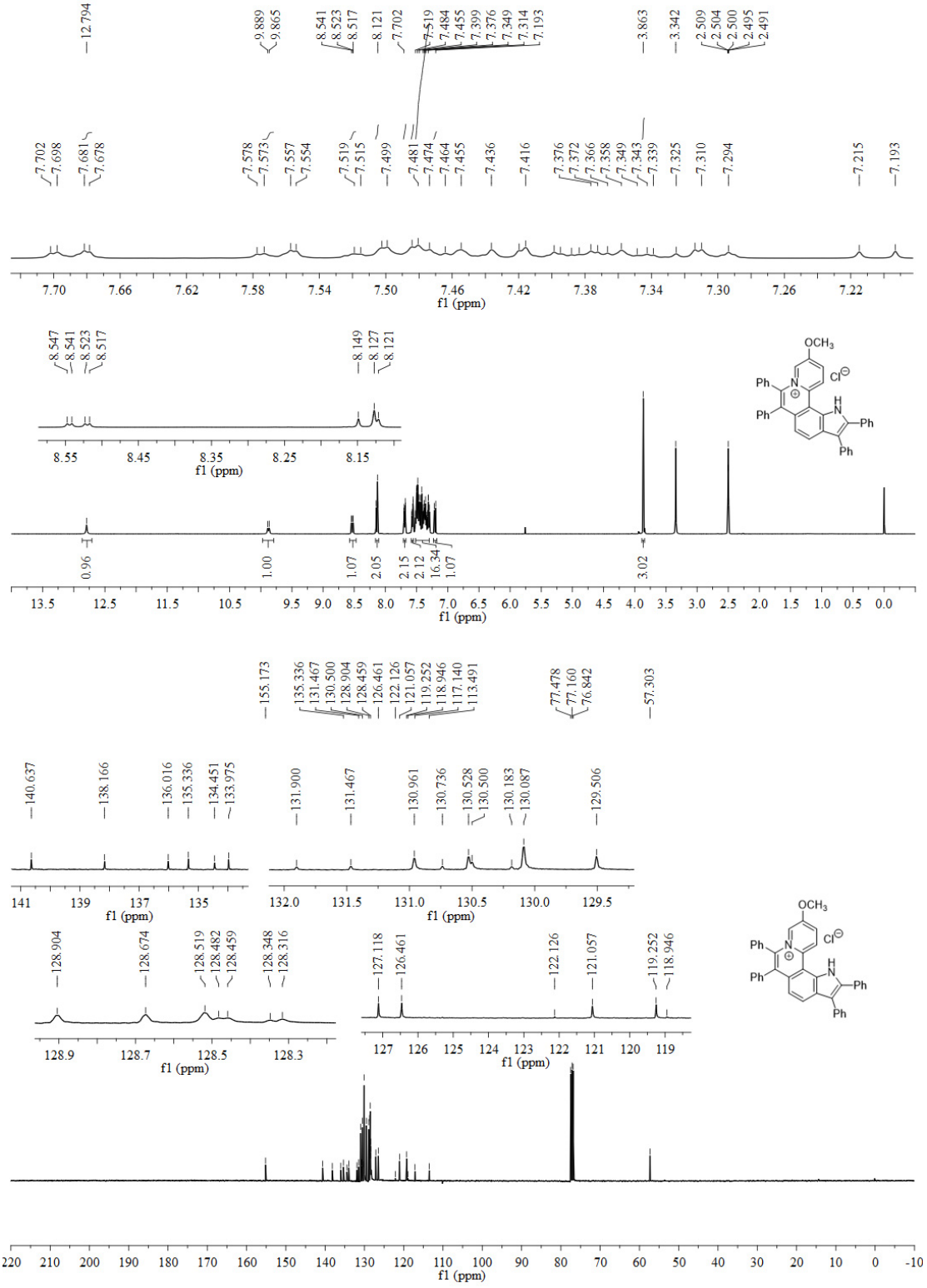
129.868
129.734
129.257
128.730
128.305
128.262
128.168
127.465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7.702
7.519
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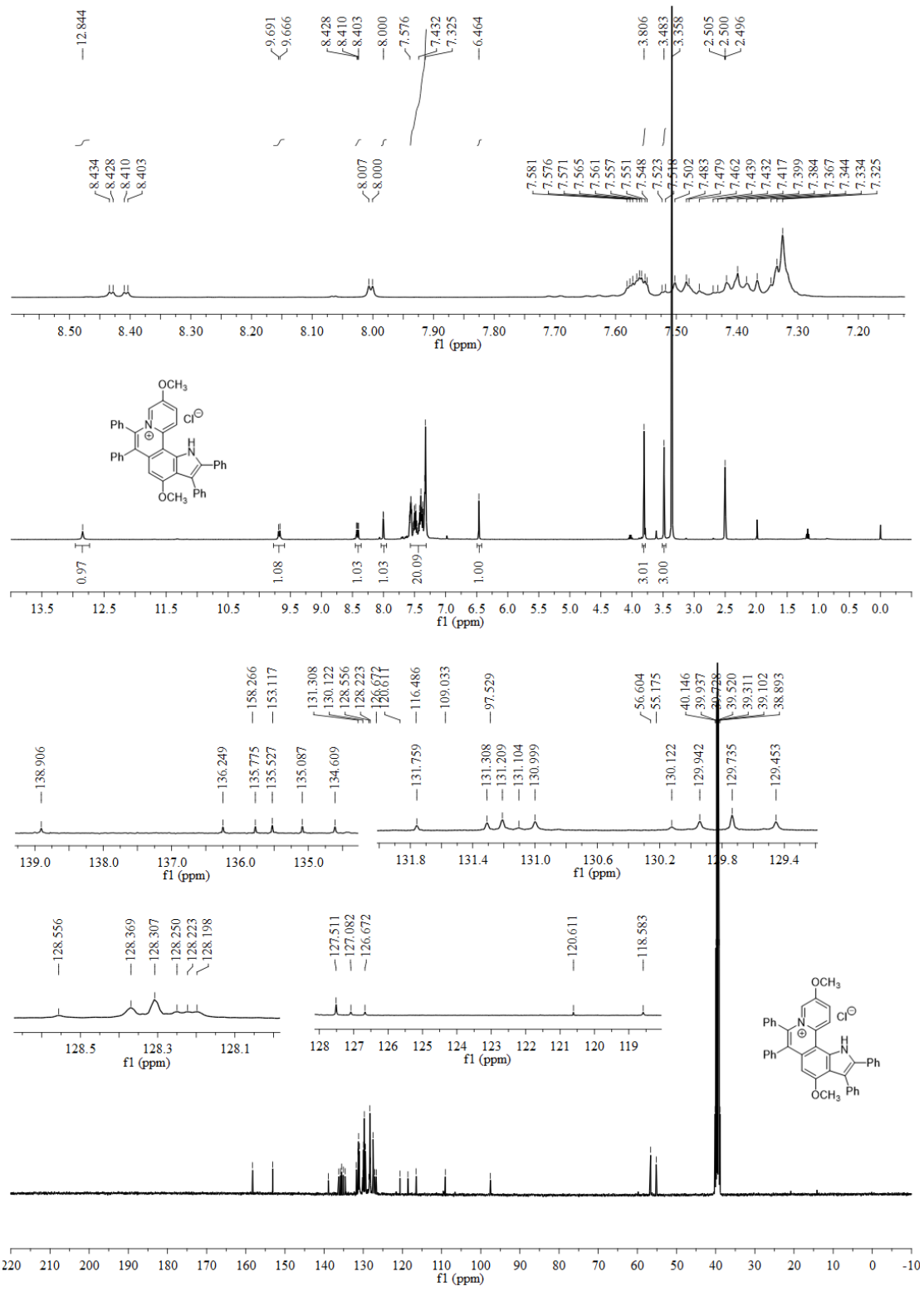
7.399
7.376
7.349
7.314
7.193
3.863
3.342
2.509
2.504
2.500
2.495
2.491
7.702
7.698
7.681
7.678
7.578
7.573
7.557
7.554
7.519
7.515
7.499
7.481
7.474
7.464
7.455
7.436
7.416
7.376
7.372
7.366
7.358
7.349
7.343
7.339
7.325
7.310
7.294
7.215
7.193
f1 (ppm)
8.547
8.541
8.523
8.517
8.149
8.127
8.121
f1 (ppm)
OCH3
Cl
Ph
Ph
H
N
Ph
Ph
0.96
1.00
1.07
2.05
2.15
2.12
16.34
1.07
3.02
f1 (ppm)
155.173
135.336
131.467
130.500
128.904
128.459
126.461
122.126
121.057
119.252
118.946
117.140
113.491
77.478
77.160
76.842
57.303
140.637
138.166
136.016
135.336
134.451
133.975
131.900
131.467
130.961
130.736
130.528
130.500
130.183
130.087
129.506
f1 (ppm)
f1 (ppm)
128.904
128.674
128.519
128.482
128.459
128.348
128.316
127.118
126.461
122.126
121.057
119.252
118.946
f1 (ppm)
f1 (ppm)
f1 (ppm)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9.666
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8.410
8.403
8.000
7.576
7.432
7.325
6.464
3.806
3.483
3.358
2.505
2.500
2.496
f1 (ppm)
OCH3
Cl
Ph
N
H
0.97
1.08
1.03
1.03
20.09
1.00
3.01
3.00
158.266
153.117
131.308
130.122
128.556
128.223
126.672
120.611
116.486
109.033
97.529
56.604
55.175
40.146
39.937
39.728
39.520
39.311
39.102
38.893
138.906
136.249
135.775
135.527
135.087
134.609
131.759
131.308
131.209
131.104
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130.122
129.942
129.735
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127.082
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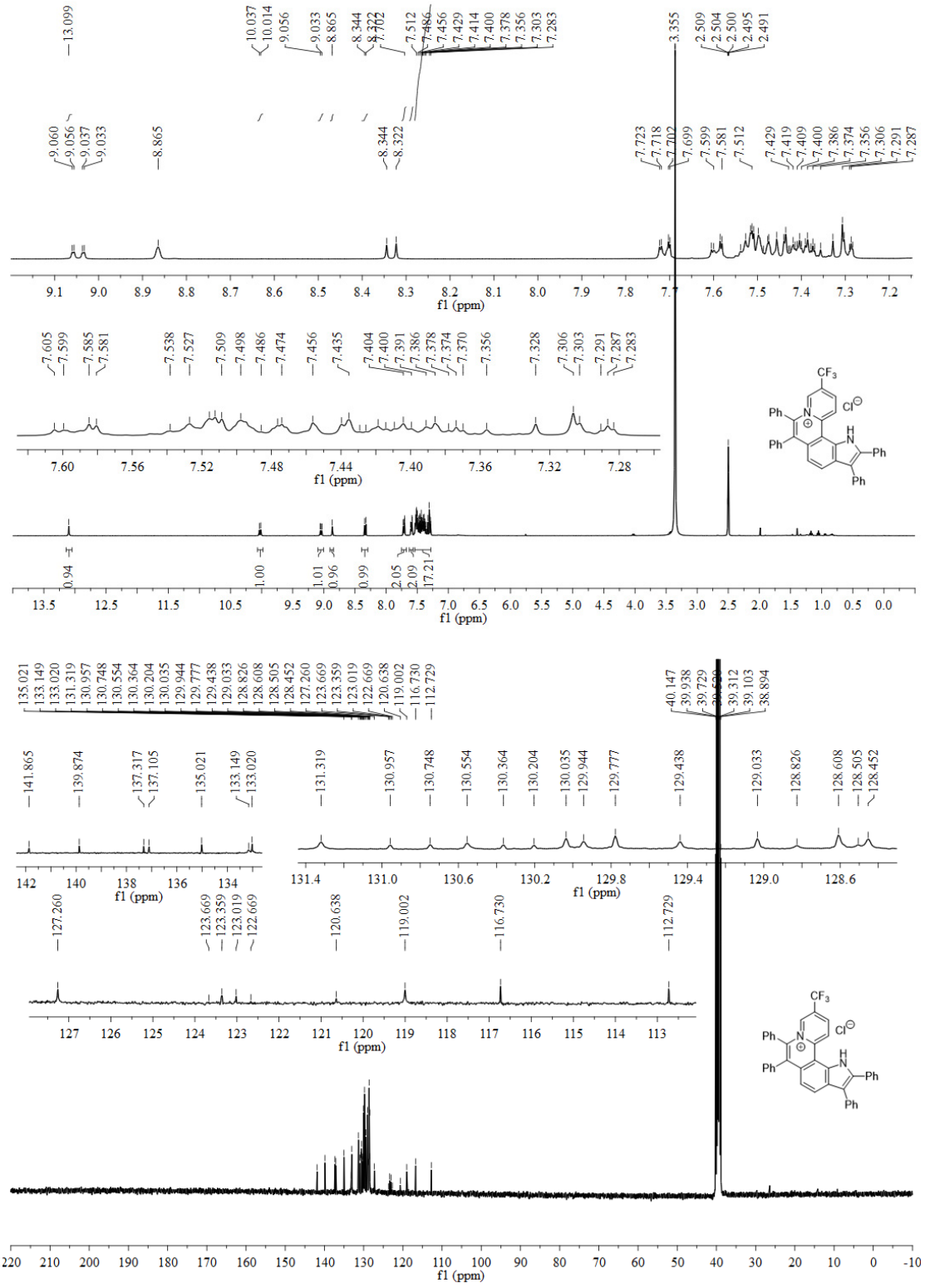
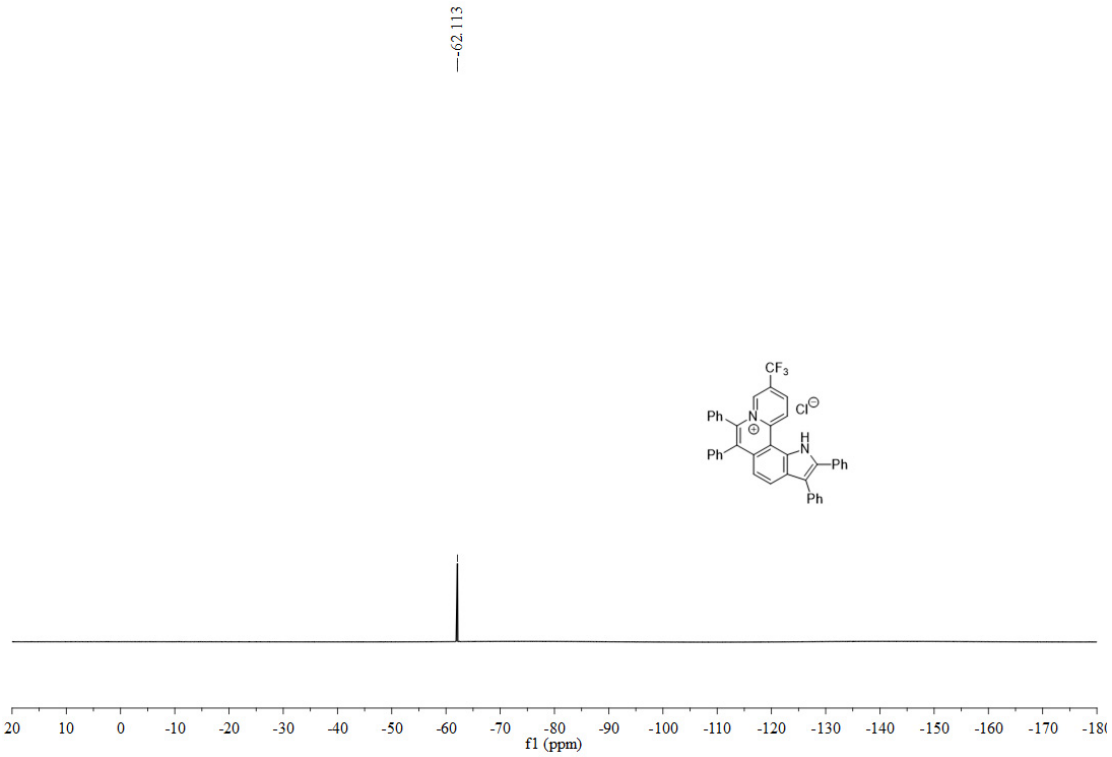
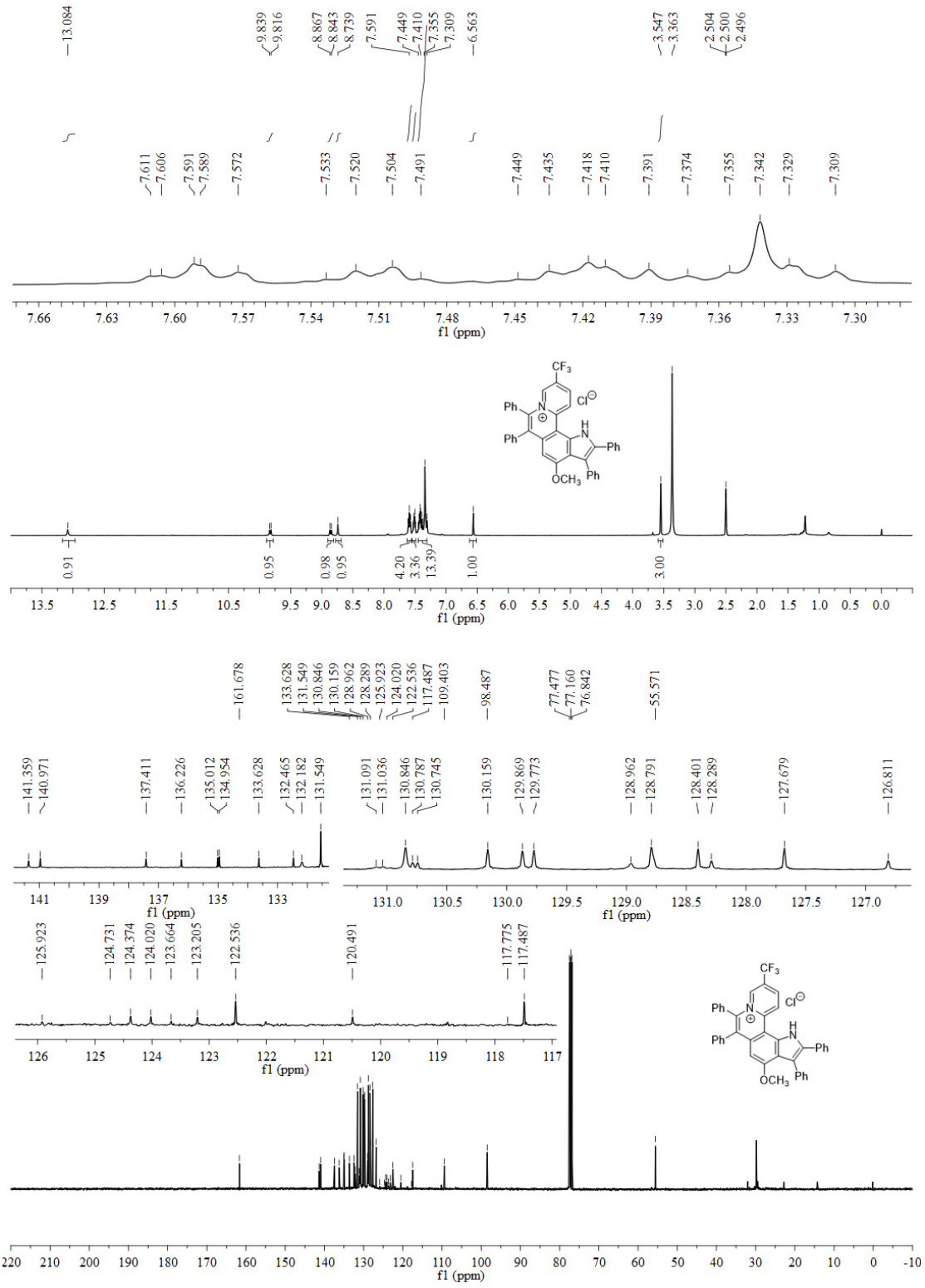
120.611
118.583


f1 (ppm)
CF3
Cl
Ph
N
H


-62.113
CF3
Cl
Ph
Ph
N
H
N
Ph
Ph
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)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9.816
8.867
8.843
8.739
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7.449
7.410
7.355
7.309
6.563
3.547
3.363
2.504
2.500
2.496
7.611
7.606
7.591
7.589
7.572
7.533
7.520
7.504
7.491
7.449
7.435
7.418
7.410
7.391
7.374
7.355
7.342
7.329
7.309
f1 (ppm)
CF3
Cl
Ph
N
H
OCH3
0.91
0.95
0.98
0.95
4.20
3.36
13.39
1.00
3.00
161.678
133.628
131.549
130.846
130.159
128.962
128.289
125.923
124.020
122.536
117.487
109.403
98.487
77.477
77.160
76.842
55.571
141.359
140.971
137.411
136.226
135.012
134.954
133.628
132.465
132.182
131.549
131.091
131.036
130.846
130.787
130.745
130.159
129.869
129.773
128.962
128.791
128.401
128.289
127.679
126.811
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124.731
124.374
124.020
123.664
123.205
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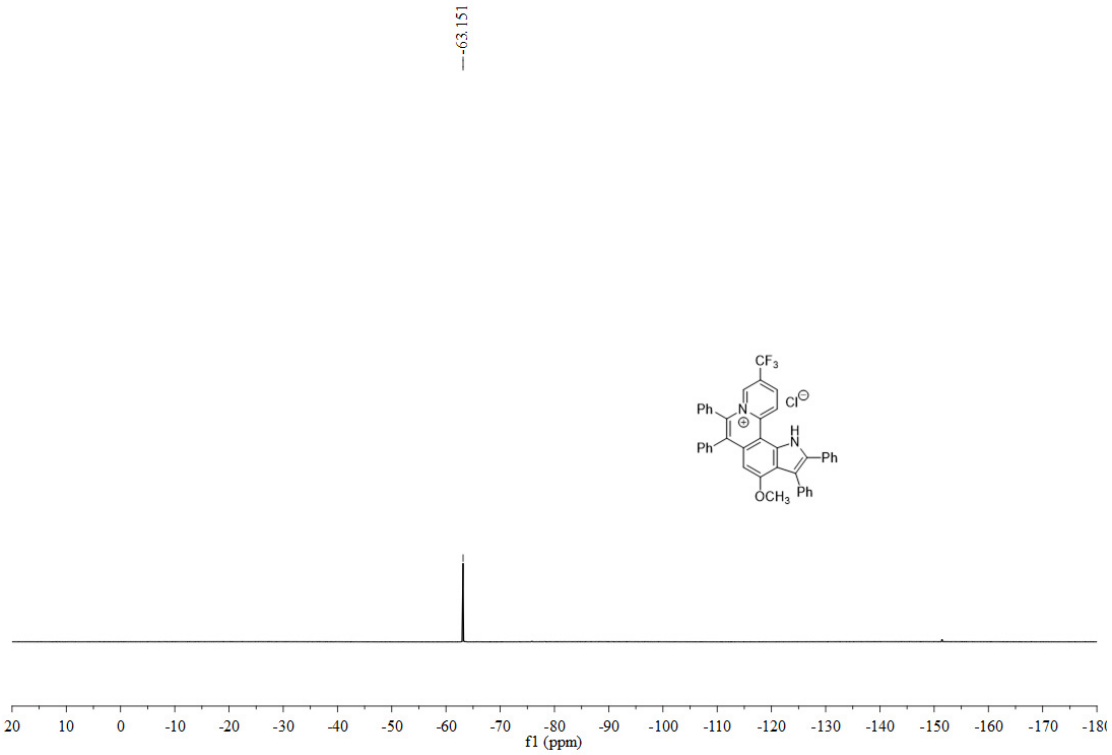
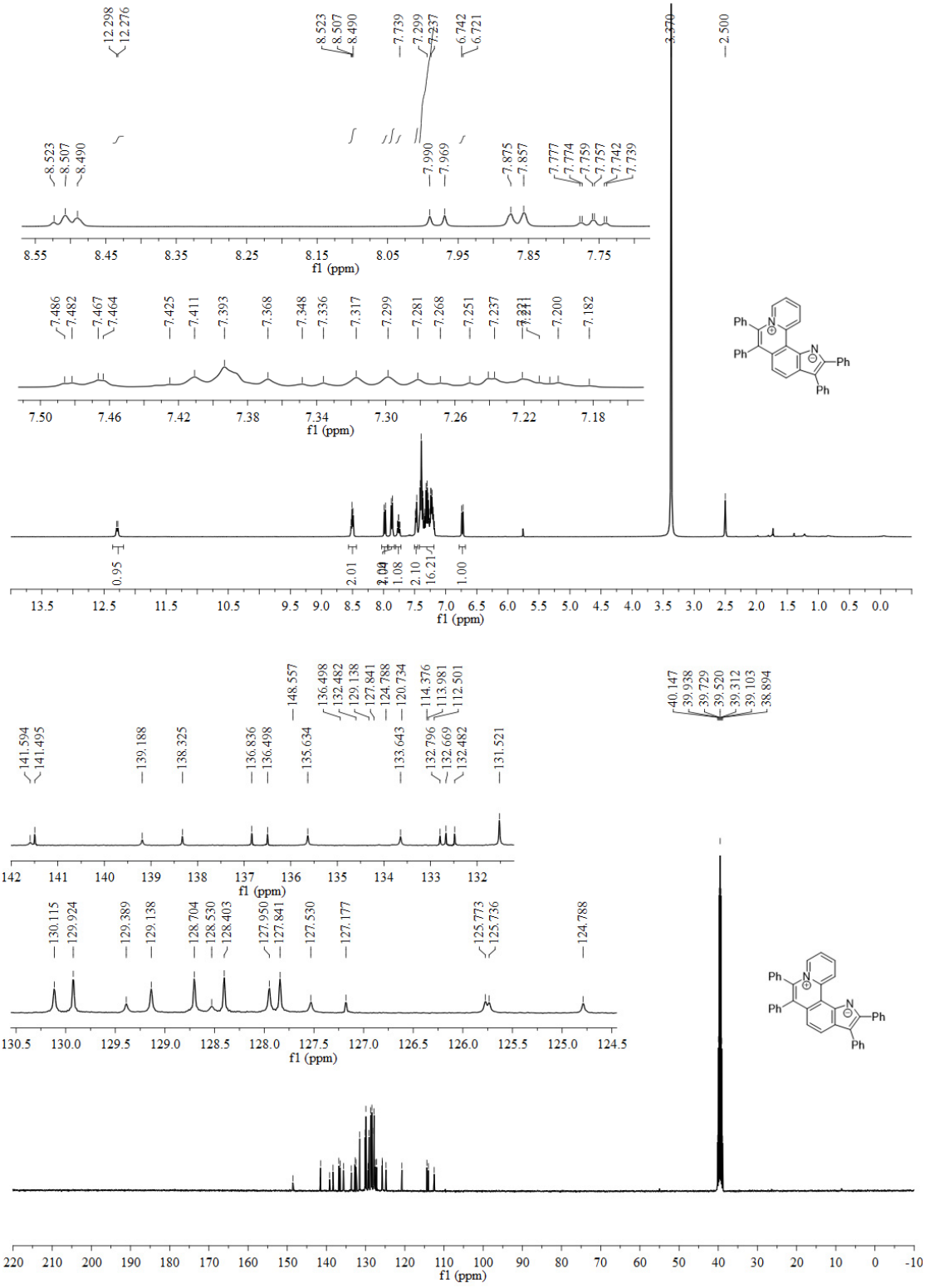
120.491
117.775
117.487


-63.151
CF3
Cl
Ph
Ph
N
H
N
Ph
Ph
OCH3
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)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8.490
7.739
7.299
7.237
6.742
6.721
3.370
2.500
7.990
7.969
7.875
7.857
7.777
7.774
7.759
7.757
7.742
7.739
f1 (ppm)
7.486
7.482
7.467
7.464
7.425
7.411
7.393
7.368
7.348
7.336
7.317
7.299
7.281
7.268
7.251
7.237
7.200
7.182
Ph
Ph
Ph
Ph
0.95
2.01
1.08
2.10
16.21
1.00
148.557
136.498
132.482
129.138
127.841
124.788
120.734
114.376
113.981
112.501
141.594
141.495
139.188
138.325
136.836
136.498
135.634
133.643
132.796
132.669
132.482
131.521
40.147
39.938
39.729
39.520
39.312
39.103
38.894
130.115
129.924
129.389
129.138
128.704
128.530
128.403
127.950
127.841
127.530
127.177
125.773
125.736
124.788