Supporting Information

Photoredox-Catalyzed C-Heteroaryl Glycosylation of Biphenyl Isocyanides with Glycosyl Bromides

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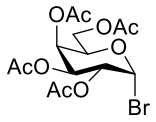
1. General Information

Commercial reagents were purchased from Aldrich Chemical, 3A, Alfa Aesar, TCI, Strem, Acros, Energy Chemical, J&K Chemical, Innochem and were used as received. All catalytic reactions were run in dried glassware. Thin layer chromatography (TLC) was performed on EMD precoated plates (silica gel 60 F254, Art 5715) and visualized by fluorescence quenching under UV light and by staining with phosphomolybdic acid or potassium permanganate, respectively. Column chromatography was performed on EMD Silica Gel 60 (300–400 Mesh) using a forced flow of 0.5–1.0 bar. ^{1}H NMR (400 MHz),^{13}C NMR (100 MHz) and ^{19}F (376 MHz) were measured on a Bruker AVANCE III–400 spectrometer. Chemical shifts are expressed in parts per million (ppm) with respect to the residual solvent peak. Coupling constants are reported as Hertz (Hz), signal shapes and splitting patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. High Resolution Mass spectra were performed on Agilent 1260 Series (ESI Source). High-pressure liquid chromatography (HPLC) was performed on Agilent 1260 Series chromatographs using chiral columns as noted for each compound. Optical rotations were measured on an automatic polarimeter with $[\alpha]_D^{20}$ values; concentration (c) is in g/100 mL. The synthesis of glycosyl bromides **1a-1m** and isocyanides **2a-2l** was according to literature procedures.[1-7]

2. Numbering and Structure of All Substrates



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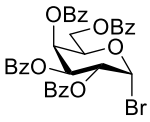

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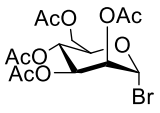

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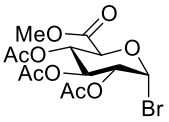

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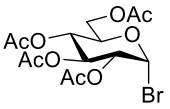

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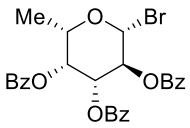

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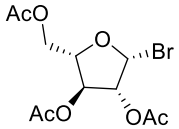

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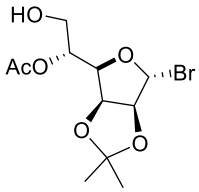

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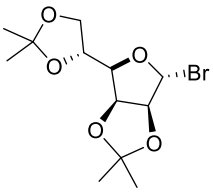

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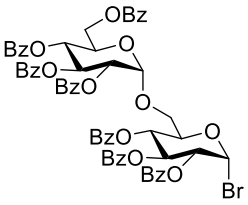

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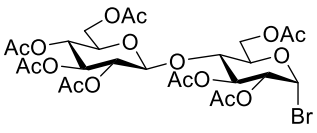

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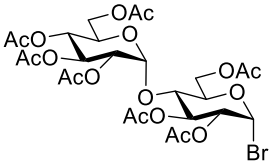

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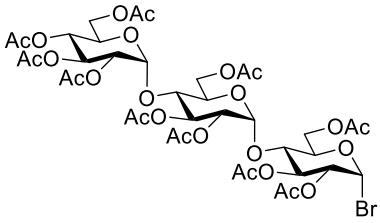

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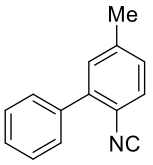

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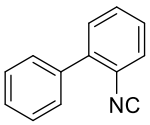

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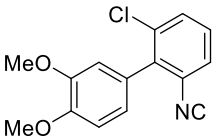

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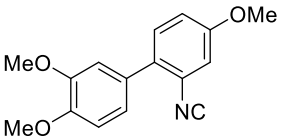

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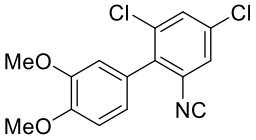

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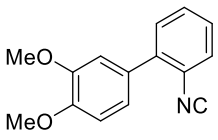

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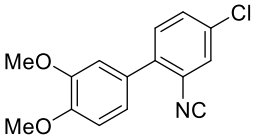

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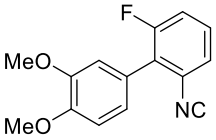

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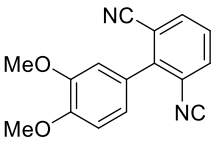

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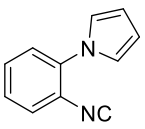

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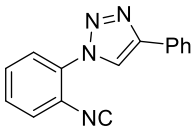

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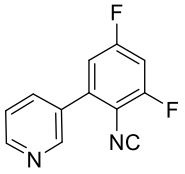

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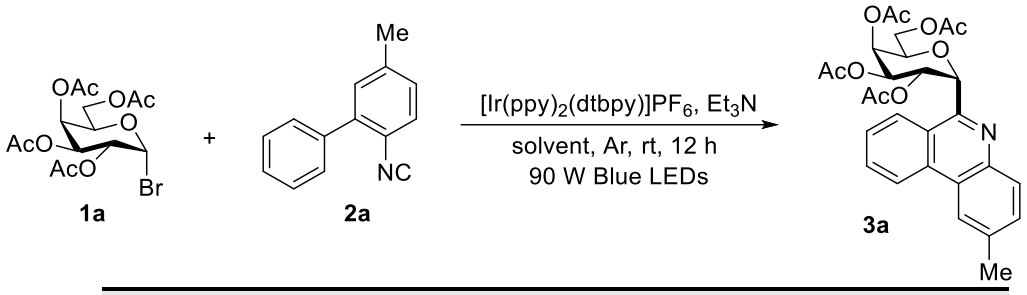
3. Optimization of Conditions

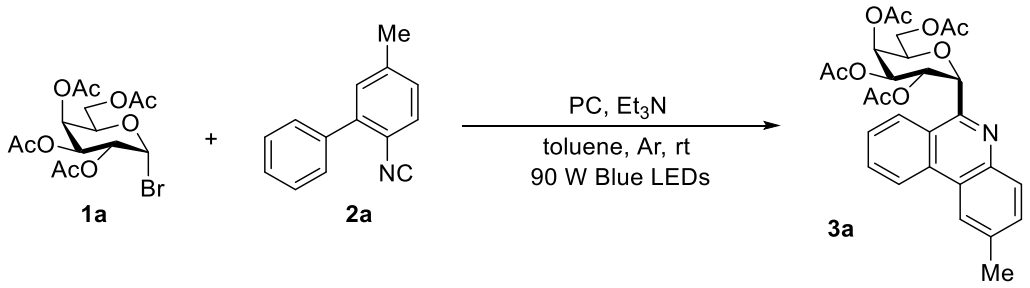
Table S1. The screening of solvent[a]



Entry	Solvent	yield/%[b]
1	PhCl	69 (58[c])
2	MeCN	N.D.
3	DCM	65
4	DCE	49
5	EA	53
6	Et_2O	trace
7	THF	50
8	dioxane	53
9	toluene	72
10	$PhCF_3$	64
11	PhEt	74
12	Xylene	70
13	DMSO	N. D.

[a]Reaction conditions: A solution of **1a** (0.1 mmol), **2a** (0.2 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (2 mol%) and Et_3N (0.2 mmol) in solvent (1 mL) was irradiated by 90 W blue LEDs for 12 hours. [b]Yield was determined by ^1H NMR using dimethyl terephthalate as internal standard. N. D. = No Detection. [c]Isolated yield.

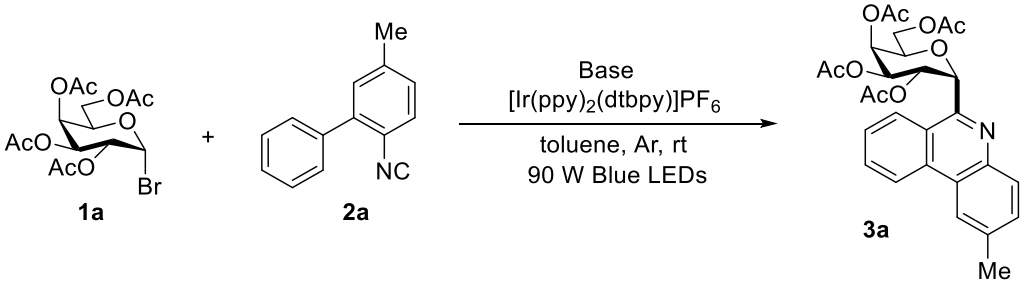
Table S2. The screening of photocatalysis[a]



Entry	PC	yield/%[b]
1	$[Ir(ppy)_2(dtbbpy)]PF_6$	73
2	$Ir(ppy)_3$	N. D.
3	$[Ru(bpy)_3](PF_6)_2$	N. D.
4	$[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$	61
5	4CzIPN	49
6	Eosin Y	N. D.
7	10-phenyl-10H-phenothiazine	N. D.
8	9,10-Dicyanoanthracen	N. D.

[a]Reaction conditions: A solution of **1a** (0.1 mmol), **2a** (0.2 mmol), PC (2 mol%) and Et_3N (0.2 mmol) in toluene (1 mL) was irradiated by 90 W blue LEDs for 12 hours. [b]Yield was determined by ^1H NMR using dimethyl terephthalate as internal standard. N. D. = No Detection.

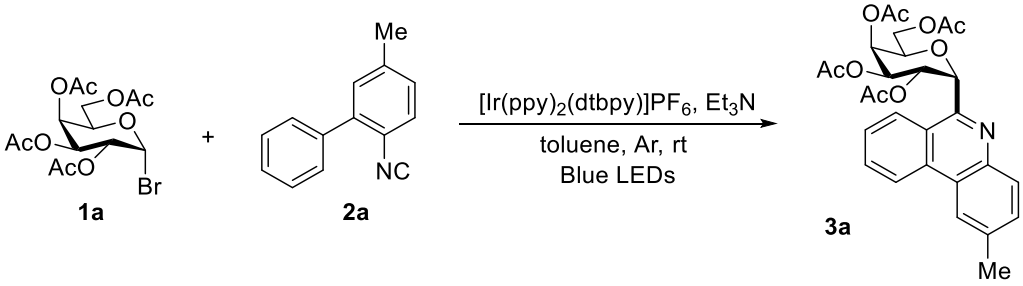
Table S3. The screening of base[a]



Entry	Base	yield/%[b]
1	Et_3N	75
2	DIPEA	59
3	n-Bu_3N	71
4	quinuclidine	N. D.

[a]Reaction conditions: A solution of **1a** (0.1 mmol), **2a** (0.2 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (2 mol%) and base (0.2 mmol) in toluene (1 mL) was irradiated by 90 W blue LEDs for 12 hours. [b]Yield was determined by ^1H NMR using dimethyl terephthalate as internal standard. N. D. = No Detection.

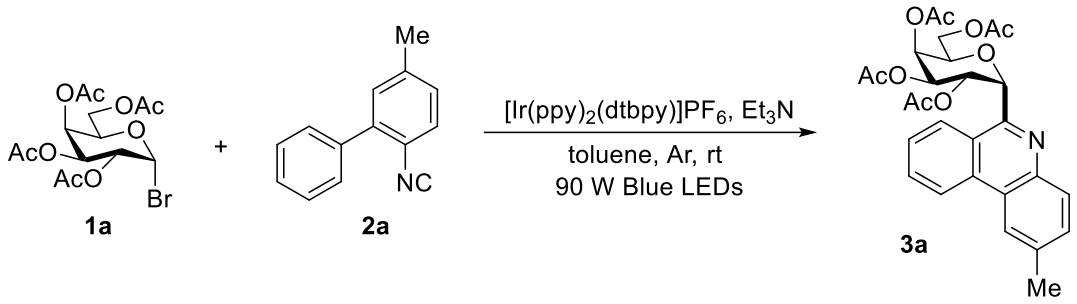
Table S4. The screening of light source[a]



Entry	Light source	yield/%[b]
1	90 W Blue LEDs	76
2	390 nm LEDs	60
3	427 nm LEDs	71
4	440 nm LEDs	68
5	456 nm LEDs	59
6	467 nm LEDs	66
7	90 W White LEDs	69

[a]Reaction conditions: A solution of **1a** (0.1 mmol), **2a** (0.2 mmol), PC (2 mol%) and Et_3N (0.2 mmol) in toluene (1 mL) was irradiated by blue LEDs for 12 hours. [b]Yield was determined by ^1H NMR using dimethyl terephthalate as internal standard. N. D. = No Detection.

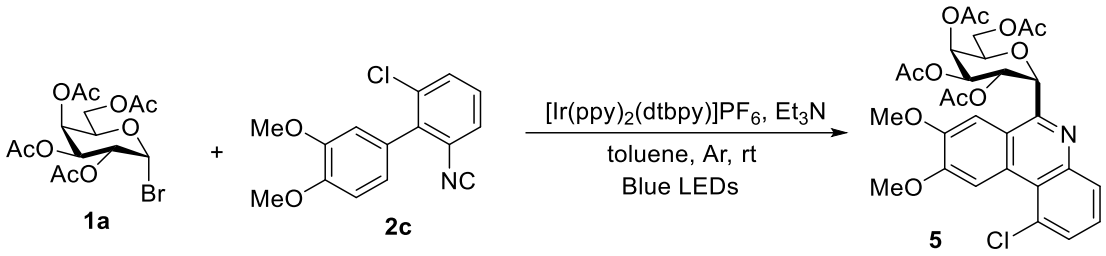
Table S5. The screening of other conditions[a]



Entry	Variations	yield/%[b]
1	none	75
2	24h	72
3	**1a** : **2a** = 1 : 1	57
4	**1a** : **2a** = 1 : 1.5	**92 (85[c])**
5	**1a** : **2a** = 1.5 : 1	71
6	1 mol% PC	67
7	5 mol% PC	64
8	0.1 mmol Et_3N	62
9	0.4 mmol Et_3N	67
10	w/o light	N. D.
11	w/o PC	N. D.
12	K_2CO_3 instead of Et_3N	N. D.

[a]Reaction conditions: A solution of **1a** (0.1 mmol), **2a** (0.2 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (2 mol%) and Et_3N (0.2 mmol) in toluene (1 mL) was irradiated by 90 W blue LEDs for 12 hours. [b]Yield was determined by ^1H NMR using dimethyl terephthalate as internal standard. N. D. = No Detection. [c]Isolated yield.

Table S5. The screening of light source for **1a** and **2c**[a]



Entry	Light source	Reaction time needed	yield/%[b]
1	90 W Blue LEDs	72 h (not complete)	63
2	390 nm LEDs	36 h	trace
3	427 nm LEDs	24 h	67
4	440 nm LEDs	24 h	**85 (75[c])**
5	456 nm LEDs	36 h	77
6	467 nm LEDs	36 h	77

[a]Reaction conditions: A solution of **1a** (0.1 mmol), **2c** (0.15 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (2 mol%) and Et_3N (0.2 mmol) in toluene (1 mL) was irradiated by blue LEDs under TLC monitoring. [b]Yield was determined by ^1H NMR using dimethyl terephthalate as internal standard. N. D. = No Detection. [c]Isolated yield.

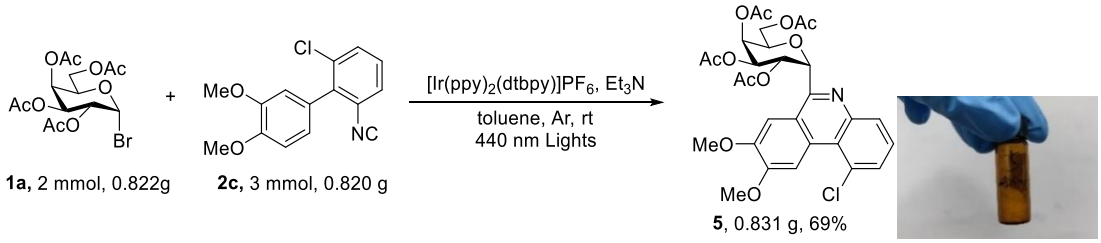
4. Reaction Setup

Medium-sized screw-cap test tubes (8 mL) were used for all 0.1 mmol scale reactions: Fisher13 x 100 mm tubes (Cat. No. 14-959-35C). Cap with Septa: Thermo Scientific ASM PHN CAP w/PTFE/SIL (Cat. No. 03378316)

Light source: Kessil® A360W E-SERIES TUNA BLUE. The distance between the tube and the lamp was about 10 cm (two fans was added)

Figure S1. The reaction setup

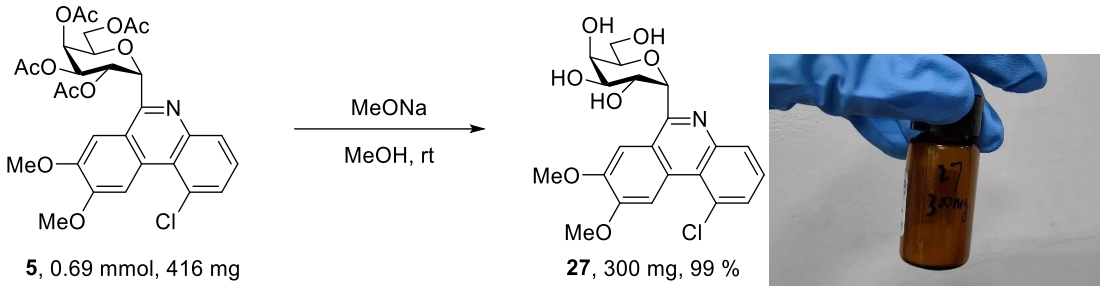
5. Gram-Scale Preparation and Hydrolysis of 5



1a, 2 mmol, 0.822g **2c,** 3 mmol, 0.820 g **5**, 0.831 g, 69%

To a dry 50mL schlenk flask was added stirring bar, galactose bromide **1a** (0.822 g, 2 mmol), isocyanide **2a** (0.820 g, 3 mmol) and $[Ir(ppy)_2(dtbbpy)]PF_6$ (2 mol%, 36.7 mg), and was replaced by argon for three times. Then, Et_3N (555 μL) and toluene (20

mL) are injected into flask. The mixture were stirred and irradiated by 90 W blue LEDs at room temperature for 24h. After TLC completion, it was extracted with EA, washed with water, brine and dried. The organic phase was concentrated and purified by flash chromatography (petroleum ether: ethyl acetate = 3:1, Rf = 0.4) to give **5** (0.831 g, 69%) as a white solid.



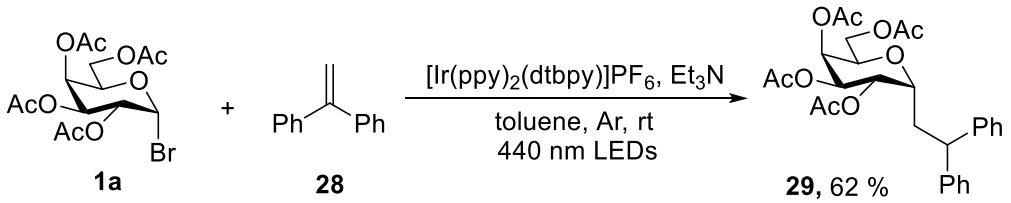
5, 0.69 mmol, 416 mg

27, 300 mg, 99 %

A magnetic stirring bar, **5** (416 mg, 0.69 mmol) and MeONa (37 mg, 0.69 mmol) were added to a 50 mL flask. 6 mL methanol was added, and the suspension was stirred at rt overnight. The emulsion was filtered to give hydrolysis product **27** (300 mg) quantitively as white solid. $[\alpha]_D^{20}$ = + 94.2 (c 0.24, DMSO), ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.24 (s, 1H), 8.18 (s, 1H), 8.05 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.83 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.69 (t, *J* = 7.9 Hz, 1H), 5.72 (d, *J* = 3.8 Hz, 1H), 5.43 (d, *J* = 5.5 Hz, 1H), 5.05 (s, 1H), 4.68 (s, 1H), 4.46 (s, 1H), 4.28 – 4.16 (m, 2H), 4.02 (s, 3H), 4.01 (s, 3H), 3.99 – 3.95 (m, 1H), 3.82 – 3.77 (m, 1H), 3.62 (d, *J* = 2.6 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.33, 151.26, 148.91, 143.01, 130.65, 129.67, 128.61, 127.67, 127.19, 121.79, 120.53, 107.80, 106.28, 76.86, 71.11, 70.58, 70.27, 66.99, 58.96, 55.66, 55.62. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{22}ClNO_7$ 436.1158; Found 436.1160.

6. Mechanism Study

6.1 Radical Trap Experiment



In a 8 mL screw-cap tube equipped with a magnetic stirring bar was added glycosyl bromide **1a** (0.1 mmol, 41 mg), 1,1-Diphenylethylene **28** (0.5 mmol, 90 mg) and $[Ir(ppy)_2(dtbbpy)]PF_6$ (2 mol%, 1.8 mg). The tube was changed with Argon for three times, in which Et_3N was injected, and then 440 nm LEDs was applied to the tube at rt overnight. After TLC completion, it was extracted with EA, washed with H_2O, brine and dried. Concentration and flash chromatography giving radical trapping product 29 (32 mg, 62%) as colorless oil. $[\alpha]_D^{20}$ = + 61.9 (c 1.7, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 6H), 7.24 – 7.16 (m, 4H), 5.40 (dd, *J* = 3.2, 2.1 Hz, 1H), 5.25 (dd, *J* = 9.4, 5.1 Hz, 1H), 5.19 (dd, *J* = 9.4, 3.2 Hz, 1H), 4.16 – 4.00 (m, 4H), 2.39 (ddd, *J* = 14.5, 11.4, 4.5 Hz, 1H), 2.21 (ddd, *J* = 14.5, 11.3, 3.2 Hz, 1H), 2.11 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 2.05 – 2.01 (m, 1H), 1.98 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.61, 170.22, 170.11, 169.79, 144.65, 143.01, 128.83, 128.74, 128.12, 127.70, 126.82, 126.59, 70.23, 68.53, 68.40, 68.29, 67.74, 61.79, 46.67, 31.78, 20.93, 20.79, 20.76. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{32}O_9$ 513.2119; Found 513.2119.

6.2 Stern-Volmer Fluorescence Quenching Experiment

A Hitachi F-7000 fluoresence spectrometer was used to record the emission intensities. All $[Ir(ppy)_2(dtbbpy)]PF_6$ solutions were excited at 376 nm and the emission intensity at 573 nm was observed. Some CH_3CN was degassed with a stream of Ar for 30 min. In a typical experiment, the emission spectrum of a 5 × 10-4 M solution of eosin Y in $[Ir(ppy)_2(dtbbpy)]PF_6$ was collected. Then, appropriate amount of triethylamine was added to the measured solution in a quartz cuvette and the emission

spectrum of the sample was collected. I_0 and I represent the intensities of the emission in the absence and presence of the quencher at 573 nm.

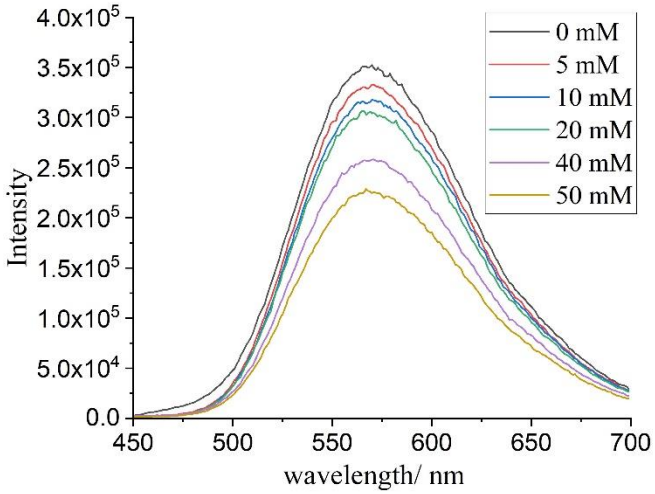


Figure S3. Emission spectra of 5×10^{-4} mol/L $[Ir(ppy)_2(dtbbpy)]PF_6$ at λex = 376 nm

Quenching experiment: Et_3N + 5×10^{-4} mol/L $[Ir(ppy)_2(dtbbpy)]PF_6$

Concentration (mM)	Intensity (573 nm)	I_0/I
0	349830	1
5	331350	1.06
10	315530	1.10
20	301010	1.16
40	256200	1.36
50	224570	1.56

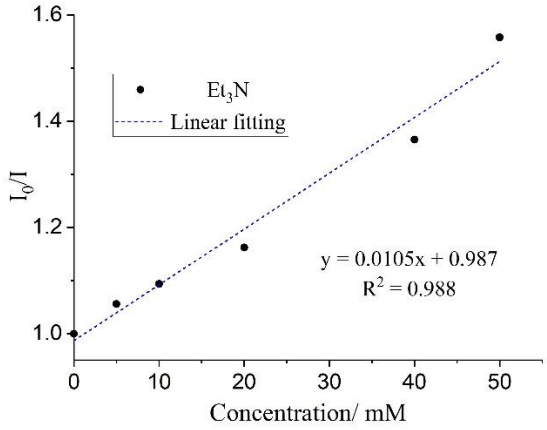
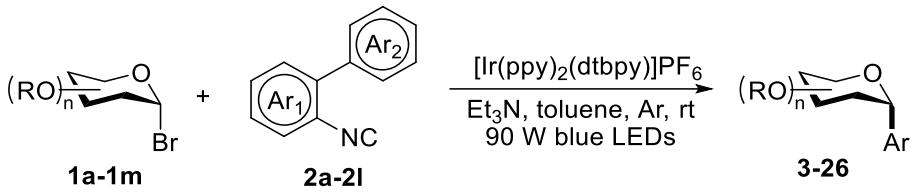


Figure S4. The linear relationship over the increasing concentration of Et_3N

7. General Procedure for the Synthesis of Products

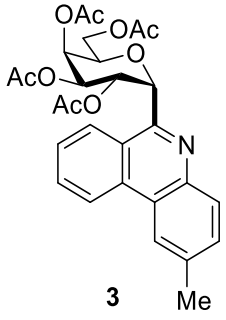


1a-1m 2a-2l 3-26

In an 8 mL screw-cap tube equipped with a magnetic stirring bar was added sugar bromide **1a-1m** (0.1 mmol, 1 equiv), isocyanide **2a-2l** (0.15 mmol, 1.5 equiv) and $[Ir(ppy)_2(dtbbpy)]PF_6$ (2 mol%, 1.8 mg). The tube was changed with Argon for three times, then Et_3N was injected, and 440 nm LEDs was applied to the tube at rt for 12-36 h. After TLC completion, it was extracted with EA, washed with H_2O, brine and dried. The residue was concentrated and purified with flash chromatography to afford product **3-26**.

8. Product Characterization

(2R,3S,4R,5S,6R)-2-(acetoxymethyl)-6-(2-methylphenanthridin-6-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate

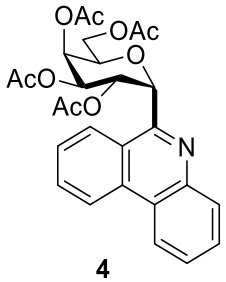


3

According to the general procedure from **1a** (0.1 mmol, 41 mg) and **2a** (0.15 mmol, 29 mg), **3** (44 mg, 85%) was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 3:1 - 2:1, reaction time = 12 h. $[\alpha]_D^{20}$ = + 86.1 (c 0.27, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.66 (dd, *J* = 8.3, 1.3 Hz, 1H), 8.40 – 8.35 (m, 1H), 8.31 (dd, *J* = 8.4, 1.4 Hz, 1H), 8.17 (d, *J* = 8.3 Hz, 1H), 7.83 (ddd, *J* = 8.4, 7.0, 1.3 Hz, 1H), 7.68 (ddd, *J* = 8.3, 7.0, 1.3 Hz, 1H), 7.59 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.90 (dd, *J* = 10.5, 3.7 Hz, 1H), 6.34 (d, *J* = 6.4 Hz, 1H), 5.78 (dd, *J* = 10.5, 6.3 Hz, 1H), 5.62

(dd, *J* = 3.7, 1.6 Hz, 1H), 4.39 (td, *J* = 6.7, 1.6 Hz, 1H), 4.03 (dd, *J* = 6.6, 1.8 Hz, 2H), 2.65 (s, 3H), 2.22 (s, 3H), 2.07 (s, 3H), 1.79 (s, 3H), 1.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.14, 170.47, 170.40, 170.29, 153.30, 151.38, 149.36, 144.13, 131.15, 131.10, 129.61, 128.64, 127.35, 122.04, 121.59, 107.54, 105.39, 71.84, 70.09, 68.84, 68.55, 68.17, 62.00, 56.31, 56.14, 20.98, 20.94, 20.88, 20.63. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{29}NO_9$ 524.1915; Found 524.1919.

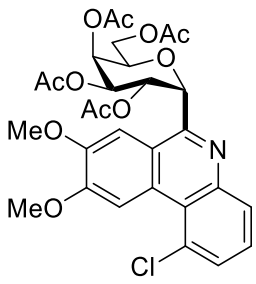
(2R,3S,4R,5S,6R)-2-(acetoxymethyl)-6-(phenanthridin-6-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate



4

According to the general procedure from **1a** (0.1 mmol, 41 mg) and **2b** (0.15 mmol, 27 mg), **3** (35 mg, 69%) was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 3:1 - 2:1, reaction time = 12 h. $[\alpha]_D^{20}$ = + 67.4 (c 0.27, $CHCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (dt, *J* = 8.3, 0.7 Hz, 1H), 8.63 – 8.56 (m, 1H), 8.37 – 8.31 (m, 1H), 8.31 – 8.25 (m, 1H), 7.86 (ddd, *J* = 8.3, 7.0, 1.3 Hz, 1H), 7.81 – 7.73 (m, 1H), 7.76 – 7.66 (m, 2H), 6.90 (dd, *J* = 10.4, 3.6 Hz, 1H), 6.37 (d, *J* = 6.4 Hz, 1H), 5.79 (dd, *J* = 10.5, 6.3 Hz, 1H), 5.62 (dd, *J* = 3.7, 1.6 Hz, 1H), 4.41 (td, *J* = 6.6, 1.6 Hz, 1H), 4.10 – 3.98 (m, 2H), 2.22 (s, 3H), 2.07 (s, 3H), 1.80 (s, 3H), 1.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.97, 170.52, 170.43, 170.29, 154.35, 142.31, 133.44, 131.20, 130.73, 128.93, 127.94, 127.67, 126.03, 125.49, 124.07, 122.64, 122.00, 71.33, 69.75, 68.70, 68.48, 68.37, 61.84, 21.01, 20.88, 20.66. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{27}NO_9$ 510.1759; Found 510.1756.

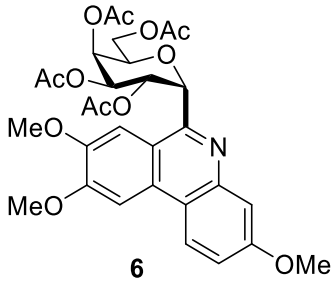
(2R,3S,4R,5S,6R)-2-(acetoxymethyl)-6-(1-chloro-8,9-dimethoxyphenanthridin-6-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate



5

According to the general procedure from **1a** (0.1 mmol, 41 mg) and **2c** (0.15 mmol, 41 mg), **5** (45 mg, 75%) was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 3:1 - 2:1, reaction time = 24 h. $[\alpha]_D^{20}$ = + 82.4 (c 0.3, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 8.20 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.74 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.68 (s, 1H), 7.58 (t, *J* = 7.9 Hz, 1H), 6.90 (dd, *J* = 10.7, 3.7 Hz, 1H), 6.29 (d, *J* = 6.4 Hz, 1H), 5.75 (dd, *J* = 10.7, 6.4 Hz, 1H), 5.59 (dd, *J* = 3.7, 1.5 Hz, 1H), 4.31 (ddd, *J* = 7.1, 6.1, 1.4 Hz, 1H), 4.12 (s, 3H), 4.06 (s, 4H), 4.11 – 3.97 (m, 2H), 2.21 (s, 3H), 2.07 (s, 3H), 1.79 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.14, 170.47, 170.40, 170.29, 153.30, 151.38, 149.36, 144.13, 131.15, 131.10, 129.61, 128.64, 127.35, 122.04, 121.59, 107.54, 105.39, 71.84, 70.09, 68.84, 68.55, 68.17, 62.00, 56.31, 56.14, 20.98, 20.94, 20.88, 20.63. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{30}ClNO_{11}$ 604.1580; Found 604.1579.

(2R,3S,4R,5S,6R)-2-(acetoxymethyl)-6-(3,8,9-trimethoxyphenanthridin-6-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate

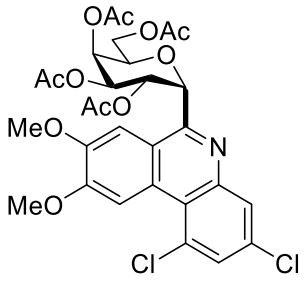


6

According to the general procedure from **1a** (0.1 mmol, 41 mg) and **2d** (0.15 mmol, 41 mg), **6** (49 mg, 81%) was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 3:1 - 2:1, reaction time = 12 h. $[\alpha]_D^{20}$ = + 85.3 (c 0.33, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 9.2 Hz, 1H), 7.82 (s, 1H), 7.56 (d,

J = 2.8 Hz, 2H), 7.30 (dd, *J* = 9.0, 2.8 Hz, 1H), 6.85 (dd, *J* = 10.6, 3.7 Hz, 1H), 6.29 (d, *J* = 6.5 Hz, 1H), 5.75 (dd, *J* = 10.5, 6.5 Hz, 1H), 5.64 (dd, *J* = 3.8, 1.5 Hz, 1H), 4.54 – 4.46 (m, 1H), 4.12 (s, 3H), 4.09 – 3.99 (m, 2H), 4.03 (s, 3H), 4.02 (s, 3H), 2.21 (s, 3H), 2.06 (s, 3H), 1.81 (s, 3H), 1.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.16, 170.52, 170.45, 170.30, 159.68, 153.30, 152.61, 148.98, 143.69, 129.65, 122.74, 119.93, 118.89, 117.99, 110.30, 105.35, 101.75, 71.58, 69.87, 68.84, 68.65, 68.33, 62.02, 56.17, 55.82, 21.02, 20.95, 20.88, 20.67. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{33}NO_{12}$ 600.2076; Found 600.2077.

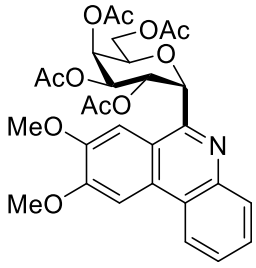
(2R,3S,4R,5S,6R)-2-(acetoxymethyl)-6-(1,3-dichloro-8,9-dimethoxyphenanthridin-6-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate



7

According to the general procedure from **1a** (0.1 mmol, 41 mg) and **2e** (0.15 mmol, 46 mg), **7** (32 mg, 50%) was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 3:1 - 2:1, reaction time = 24 h. $[\alpha]_D^{20}$ = + 72.3 (c 0.26, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 2.2 Hz, 1H), 7.83 – 7.78 (m, 2H), 7.59 (s, 1H), 6.89 (dd, *J* = 10.8, 3.6 Hz, 1H), 6.36 (d, *J* = 6.7 Hz, 1H), 5.73 (dd, *J* = 10.7, 6.7 Hz, 1H), 5.68 (dd, *J* = 3.7, 1.5 Hz, 1H), 4.78 (td, *J* = 6.5, 1.5 Hz, 1H), 4.16 (s, 3H), 4.06 (s, 3H), 4.09 – 3.99 (m, 2H), 2.21 (s, 3H), 2.03 (s, 3H), 1.85 (s, 3H), 1.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.32, 170.52, 170.50, 170.03, 154.01, 153.10, 150.79, 137.34, 136.71, 132.71, 128.63, 128.25, 125.80, 121.41, 120.03, 105.26, 102.59, 71.19, 70.07, 69.02, 68.53, 68.26, 62.30, 56.46, 56.35, 20.94, 20.89, 20.73. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{29}Cl_2NO_{11}$ 638.1190; Found 638.1192.

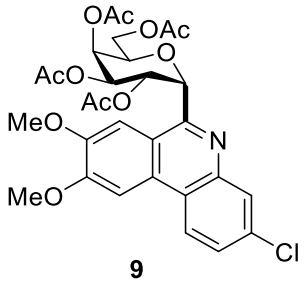
(2R,3S,4R,5S,6R)-2-(acetoxymethyl)-6-(8,9-dimethoxyphenanthridin-6-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate



8

According to the general procedure from **1a** (0.1 mmol, 41 mg) and **2f** (0.15 mmol, 36 mg), **8** (50 mg, 87%) was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 3:1 - 2:1, reaction time = 12 h. $[\alpha]_D^{20}$ = + 91.2 (c 0.35, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.48 – 8.42 (m, 1H), 8.27 – 8.21 (m, 1H), 7.94 (s, 1H), 7.69 (td, *J* = 7.2, 1.6 Hz, 2H), 7.62 (s, 1H), 6.92 (dd, *J* = 10.7, 3.6 Hz, 1H), 6.31 (d, *J* = 6.5 Hz, 1H), 5.76 (dd, *J* = 10.7, 6.4 Hz, 1H), 5.62 (dd, *J* = 3.8, 1.5 Hz, 1H), 4.41 (td, *J* = 6.5, 1.5 Hz, 1H), 4.14 (s, 3H), 4.05 (s, 3H), 4.12 – 3.96 (m, 2H), 2.21 (s, 3H), 2.07 (s, 3H), 1.80 (s, 3H), 1.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.20, 170.50, 170.44, 170.27, 152.73, 152.48, 149.73, 142.06, 131.26, 129.30, 128.01, 127.40, 123.79, 121.51, 120.89, 105.50, 102.31, 71.75, 69.92, 68.90, 68.65, 68.30, 62.01, 56.24, 21.00, 20.96, 20.90, 20.66. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{31}NO_{11}$ 570.1970; Found 570.1978.

(2R,3S,4R,5S,6R)-2-(acetoxymethyl)-6-(3-chloro-8,9-dimethoxyphenanthridin-6-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate

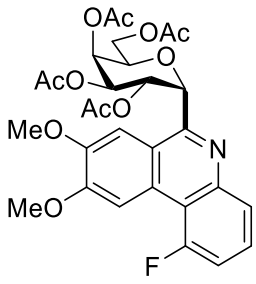


9

According to the general procedure from **1a** (0.1 mmol, 41 mg) and **2g** (0.15 mmol, 41 mg), **9** (44 mg, 72%) was obtained as white solid. Flash column chromatography eluent,

Petroleum ether: ethyl acetate = 3:1 - 2:1, reaction time = 12 h. $[\alpha]_D^{20}$ = + 91.2 (c 0.35, $CHCl_3$). $[\alpha]_D^{20}$ = + 107.4 (c 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.9 Hz, 1H), 8.23 (d, *J* = 2.2 Hz, 1H), 7.86 (s, 1H), 7.65 – 7.56 (m, 2H), 6.82 (dd, *J* = 10.6, 3.7 Hz, 1H), 6.29 (d, *J* = 6.6 Hz, 1H), 5.75 (dd, *J* = 10.7, 6.4 Hz, 1H), 5.62 (dd, *J* = 3.7, 1.5 Hz, 1H), 4.35 (td, *J* = 6.5, 1.5 Hz, 1H), 4.14 (s, 3H), 4.11 – 3.97 (m, 2H), 4.05 (s, 3H), 2.21 (s, 3H), 2.07 (s, 3H), 1.81 (s, 3H), 1.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.18, 170.47, 170.42, 170.29, 154.06, 152.87, 149.98, 142.69, 133.70, 130.10, 129.05, 127.99, 122.99, 122.30, 120.87, 105.62, 102.20, 71.72, 69.99, 68.77, 68.53, 68.25, 61.92, 56.31, 56.28, 20.99, 20.95, 20.88, 20.65. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{30}ClNO_{11}$ 604.1580; Found 604.1581.

(2R,3S,4R,5S,6R)-2-(acetoxymethyl)-6-(1-fluoro-8,9-dimethoxyphenanthridin-6-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate

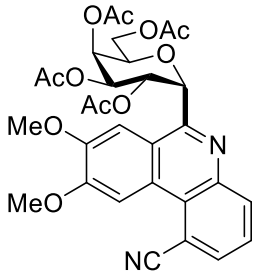


10

According to the general procedure from **1a** (0.1 mmol, 41 mg) and **2h** (0.15 mmol, 39 mg), **10** (48 mg, 82%) was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 3:1 - 2:1, reaction time = 12 h. $[\alpha]_D^{20}$ = + 91.2 (c 0.35, $CHCl_3$). $[\alpha]_D^{20}$ = + 89.9 (c 0.27, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 5.3 Hz, 1H), 8.07 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.67 (s, 1H), 7.62 (td, *J* = 8.1, 5.5 Hz, 1H), 7.38 (ddd, *J* = 13.4, 7.9, 1.3 Hz, 1H), 6.88 (dd, *J* = 10.6, 3.7 Hz, 1H), 6.30 (d, *J* = 6.4 Hz, 1H), 5.76 (dd, *J* = 10.6, 6.4 Hz, 1H), 5.60 (dd, *J* = 3.7, 1.5 Hz, 1H), 4.35 (ddd, *J* = 7.2, 6.2, 1.5 Hz, 1H), 4.12 (s, 3H), 4.06 (s, 3H), 4.09 – 3.98 (m, 2H), 2.21 (s, 3H), 2.07 (s, 3H), 1.79 (s, 3H), 1.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.16, 170.48, 170.42, 170.28, 159.88 (d, J_1 = 253.4 Hz), 153.69, 152.39, 149.54, 149.52, 144.00 (d, J_4 = 2.7 Hz), 127.39, 127.32, 127.28, 127.24, 127.21, 121.44, 113.90 (d, J_3

= 8.6 Hz), 113.54 (d, J_2= 24.1 Hz), 107.49 (d, J_2 = 23.6 Hz), 105.42, 71.79, 70.07, 68.85, 68.57, 68.21, 62.01, 56.21, 56.15, 20.99, 20.94, 20.89, 20.64. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{30}FNO_{11}$ 588.1876; Found 588.1872.

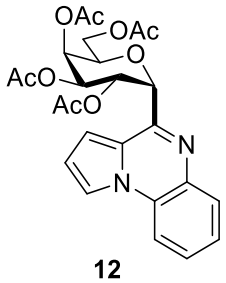
(2R,3S,4R,5S,6R)-2-(acetoxymethyl)-6-(1-cyano-8,9-dimethoxyphenanthridin-6-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate



11

According to the general procedure from **1a** (0.1 mmol, 41 mg) and **2i** (0.15 mmol, 40 mg), **11** (33 mg, 56%) was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 3:1 - 2:1, reaction time = 24 h. $[\alpha]_D^{20}$ = + 91.2 (c 0.35, $CHCl_3$). $[\alpha]_D^{20}$ = + 112.0 (c 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 8.48 (dd, *J* = 8.2, 1.5 Hz, 1H), 8.08 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.73 (dd, *J* = 8.3, 7.3 Hz, 1H), 7.69 (s, 1H), 6.84 (dd, *J* = 10.8, 3.7 Hz, 1H), 6.30 (d, *J* = 6.4 Hz, 1H), 5.75 (dd, *J* = 10.6, 6.4 Hz, 1H), 5.59 (dd, *J* = 3.7, 1.5 Hz, 1H), 4.30 (ddd, *J* = 7.2, 6.1, 1.5 Hz, 1H), 4.17 (s, 3H), 4.08 (s, 3H), 4.11 – 3.95 (m, 2H), 2.21 (s, 3H), 2.07 (s, 3H), 1.79 (s, 3H), 1.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.07, 170.45, 170.39, 170.33, 154.51, 152.76, 150.52, 142.37, 137.07, 136.40, 127.73, 127.10, 124.13, 122.04, 121.39, 106.13, 105.61, 104.98, 71.78, 70.20, 68.72, 68.45, 68.08, 61.96, 56.79, 56.28, 20.96, 20.91, 20.86, 20.62. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{30}N_2O_{11}$ 595.1922; Found 595.1923.

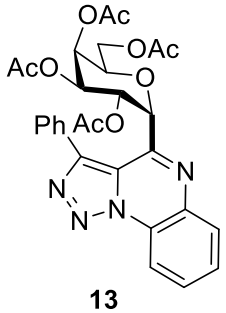
(2R,3S,4R,5S,6R)-2-(acetoxymethyl)-6-(pyrrolo[1,2-a]quinoxalin-4-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate



12

According to the general procedure from **1a** (0.1 mmol, 41 mg) and **2j** (0.15 mmol, 25 mg), **12** (30 mg, 60%) was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 3:1 - 2:1, reaction time = 24 h. $[\alpha]_D^{20}$ = + 91.2 (c 0.35, $CHCl_3$). $[\alpha]_D^{20}$ = + 107.7 (c 0.27, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.94 (dd, *J* = 2.7, 1.3 Hz, 1H), 7.85 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.55 (ddd, *J* = 8.3, 7.2, 1.6 Hz, 1H), 7.47 (ddd, *J* = 8.6, 7.2, 1.3 Hz, 1H), 6.92 (dd, *J* = 4.1, 1.3 Hz, 1H), 6.86 (dd, *J* = 4.2, 2.7 Hz, 1H), 6.45 (dd, *J* = 10.2, 3.5 Hz, 1H), 5.81 (d, *J* = 6.5 Hz, 1H), 5.73 – 5.64 (m, 2H), 5.10 (td, *J* = 6.6, 1.8 Hz, 1H), 4.18 – 4.05 (m, 2H), 2.19 (s, 3H), 2.03 (s, 3H), 1.95 (s, 3H), 1.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.79, 170.63, 170.48, 170.16, 151.39, 134.95, 131.05, 128.38, 127.46, 126.14, 125.43, 114.83, 114.08, 113.80, 106.72, 71.44, 70.44, 68.58, 68.21, 61.91, 20.95, 20.87, 20.85, 20.80. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{26}N_2O_9$ 499.1711; Found 499.1706.

(2R,3S,4R,5S,6R)-2-(acetoxymethyl)-6-(3-phenyl-[1,2,3]triazolo[1,5-a]quinoxalin-4-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate

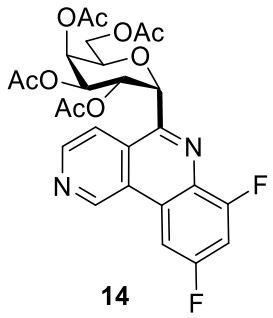


13

According to the general procedure from **1a** (0.1 mmol, 41 mg) and **2k** (0.15 mmol, 37 mg), **13** (27 mg, 47%) was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 3:1 - 2:1, reaction time = 48 h. $[\alpha]_D^{20}$ = + 91.2

(c 0.35, $CHCl_3$). $[\alpha]_D^{20}$ = + 57.0 (c 0.33, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.77 (dd, *J* = 8.3, 1.5 Hz, 1H), 8.29 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.85 (ddd, *J* = 8.3, 7.3, 1.5 Hz, 1H), 7.79 (ddd, *J* = 8.8, 7.3, 1.5 Hz, 1H), 7.74 – 7.65 (m, 2H), 7.56 (dd, *J* = 4.9, 2.0 Hz, 3H), 6.57 (dd, *J* = 10.2, 3.6 Hz, 1H), 5.75 (d, *J* = 6.6 Hz, 1H), 5.62 (dd, *J* = 3.6, 1.8 Hz, 1H), 5.46 (dd, *J* = 10.2, 6.5 Hz, 1H), 4.61 (td, *J* = 6.7, 1.8 Hz, 1H), 4.06 (d, *J* = 6.7 Hz, 2H), 2.15 (s, 3H), 1.99 (s, 3H), 1.95 (s, 3H), 1.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.55, 170.41, 170.24, 169.95, 149.77, 143.53, 135.19, 131.16, 130.76, 130.53, 130.07, 129.76, 129.23, 129.05, 125.78, 123.85, 115.88, 70.33, 69.86, 68.46, 68.00, 67.42, 61.57, 20.91, 20.84, 20.82, 20.74. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{28}N_4O_9$ 577.1929; Found 577.1923.

(2R,3S,4R,5S,6R)-2-(acetoxymethyl)-6-(7,9-difluorobenzo[c][2,6]naphthyridin-5-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate

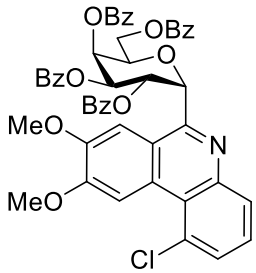


14

According to the general procedure from **1a** (0.1 mmol, 41 mg) and **2l** (0.15 mmol, 33 mg), **14** (36 mg, 66%) was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 3:1 - 2:1, reaction time = 24 h. $[\alpha]_D^{20}$ = + 91.2 (c 0.35, $CHCl_3$). $[\alpha]_D^{20}$ = + 102.7 (c 0.33, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 9.09 (dd, *J* = 4.3, 1.6 Hz, 1H), 8.79 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.94 (ddd, *J* = 9.4, 2.6, 1.6 Hz, 1H), 7.80 (dd, *J* = 8.4, 4.3 Hz, 1H), 7.33 (ddd, *J* = 9.3, 8.6, 2.6 Hz, 1H), 7.09 (d, *J* = 6.8 Hz, 1H), 6.38 (dd, *J* = 10.4, 3.4 Hz, 1H), 5.93 (dd, *J* = 10.4, 6.8 Hz, 1H), 5.75 (dd, *J* = 3.4, 1.8 Hz, 1H), 5.44 (td, *J* = 6.6, 2.0 Hz, 1H), 4.20 (dd, *J* = 11.2, 6.5 Hz, 1H), 4.10 (dd, *J* = 11.3, 6.7 Hz, 1H), 2.22 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H), 1.55 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.71, 170.59, 170.22, 170.07, 161.52 (dd, J_1 = 250.6, J_3 = 12.1 Hz), 159.60 (dd, J_1 = 261.3, J_3 = 13.3)158.23, 151.39, 141.55, 131.05, 129.64,

129.61, 129.53, 127.09, 127.05, 127.01, 126.14, 126.12, 126.04, 126.02, 125.61, 105.37 (dd, J_2 = 28.2, J_2 = 22.7 Hz), 102.98 (dd, J_2 = 23.2, J_4 = 5.0 Hz), 70.33, 68.92, 68.29, 67.60, 62.34, 20.92, 20.91, 20.86, 20.68. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{24}F_2N_2O_9$ 547.1523; Found 547.1527.

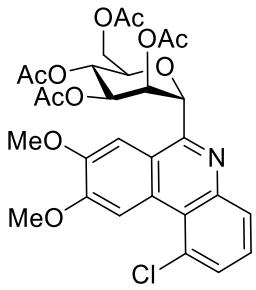
(2R,3S,4R,5S,6R)-2-((benzoyloxy)methyl)-6-(1-chloro-8,9-dimethoxyphenanthridin-6-yl)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate



15

According to the general procedure from **1b** (0.1 mmol, 66 mg) and **2c** (0.15 mmol, 41 mg), **15** (72 mg, 85%) was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 3:1 - 2:1, reaction time = 24 h. $[\alpha]_D^{20}$ = + 91.2 (c 0.35, $CHCl_3$). $[\alpha]_D^{20}$ = + 90.0 (c 0.3, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (s, 1H), 8.44 (dd, J = 8.0, 1.5 Hz, 1H), 8.24 – 8.16 (m, 2H), 7.92 – 7.81 (m, 4H), 7.81 – 7.74 (m, 2H), 7.70 – 7.61 (m, 3H), 7.62 – 7.51 (m, 4H), 7.50 – 7.41 (m, 2H), 7.41 – 7.32 (m, 1H), 7.31 – 7.17 (m, 6H), 6.53 (d, J = 6.4 Hz, 1H), 6.35 (dd, J = 10.5, 6.2 Hz, 1H), 6.07 (dd, J = 3.9, 1.2 Hz, 1H), 4.56 (dd, J = 11.4, 7.9 Hz, 1H), 4.32 (ddd, J = 7.9, 4.3, 1.2 Hz, 1H), 4.25 (dd, J = 11.4, 4.4 Hz, 1H), 4.10 (s, 3H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.50, 165.98, 165.93, 152.91, 151.36, 149.37, 144.23, 133.68, 133.25, 133.19, 133.15, 131.24, 131.22, 130.20, 129.88, 129.84, 129.70, 129.65, 129.56, 129.47, 129.45, 129.35, 128.81, 128.69, 128.41, 128.30, 127.49, 122.02, 121.76, 107.43, 105.63, 73.04, 70.88, 69.97, 69.41, 69.07, 63.26, 56.20, 55.95. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{49}H_{38}ClNO_{11}$ 852.2206; Found 852.2208.

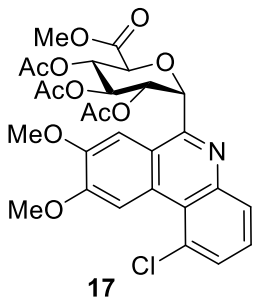
(2R,3R,4R,5R,6R)-2-(acetoxymethyl)-6-(1-chloro-8,9-dimethoxyphenanthridin-6-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate



16

According to the general procedure from **1c** (0.1 mmol, 41 mg) and **2c** (0.15 mmol, 41 mg), **16** (46 mg, 77%) was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 3:1 - 2:1, reaction time = 24 h. $[\alpha]_D^{20}$ = + 91.2 (c 0.35, $CHCl_3$). $[\alpha]_D^{20}$ = + 81.3 (c 0.27, $CHCl_3$).^{1}H NMR (400 MHz, $CDCl_3$) δ 9.41 (d, *J* = 1.3 Hz, 1H), 8.26 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.91 (s, 1H), 7.74 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.59 (t, *J* = 7.9 Hz, 1H), 6.44 – 6.36 (m, 2H), 5.82 (d, *J* = 1.5 Hz, 1H), 5.43 (ddd, *J* = 11.5, 10.2, 1.6 Hz, 1H), 4.21 (dd, *J* = 12.3, 5.8 Hz, 1H), 4.12 (s, 3H), 4.08 (s, 3H), 3.94 (dd, *J* = 12.3, 2.1 Hz, 1H), 3.42 (ddd, *J* = 10.2, 5.8, 2.1 Hz, 1H), 2.29 (s, 3H), 2.09 (s, 3H), 1.96 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.73, 170.62, 170.22, 170.00, 153.18, 151.54, 149.25, 144.37, 131.36, 131.17, 129.56, 128.77, 127.55, 121.77, 121.05, 107.53, 106.08, 78.23, 72.26, 71.00, 70.32, 67.35, 62.69, 56.31, 21.38, 20.96, 20.83, 20.71. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{30}ClNO_{11}$ 604.1580; Found 604.1572.

(2R,3S,4R,5S,6S)-2-(1-chloro-8,9-dimethoxyphenanthridin-6-yl)-6-(methoxycarbonyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate

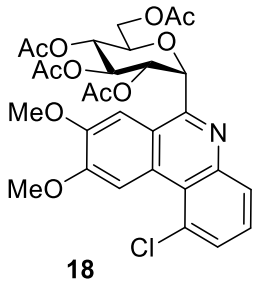


17

According to the general procedure from **1d** (0.1 mmol, 40 mg) and **2c** (0.15 mmol, 41 mg), **17** (41 mg, 70%) was obtained as white solid. Flash column chromatography

eluent, Petroleum ether: ethyl acetate = 3:1 - 2:1, reaction time = 24 h. $[\alpha]_D^{20}$ = + 91.2 (c 0.35, $CHCl_3$). $[\alpha]_D^{20}$ = + 18.8 (c 0.29, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (s, 1H), 8.37 (s, 1H), 8.07 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.71 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.55 (t, *J* = 7.9 Hz, 1H), 6.24 (d, *J* = 3.7 Hz, 1H), 6.04 (t, *J* = 6.0 Hz, 1H), 5.74 (dd, *J* = 6.2, 3.7 Hz, 1H), 5.42 (t, *J* = 5.3 Hz, 1H), 4.80 (d, *J* = 5.0 Hz, 1H), 4.12 (s, 3H), 4.08 (s, 3H), 3.79 (s, 3H), 2.10 (s, 3H), 2.09 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.41, 169.84, 169.13, 169.05, 153.41, 151.34, 149.33, 144.37, 130.97, 130.65, 129.57, 128.71, 127.21, 122.22, 121.69, 107.24, 106.97, 77.36, 73.54, 71.85, 68.64, 68.30, 67.83, 56.49, 56.23, 52.79, 21.05, 20.95, 20.86. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{28}ClNO_{11}$ 590.1424; Found 590.1430.

(2R,3R,4R,5S,6R)-2-(acetoxymethyl)-6-(1-chloro-8,9-dimethoxyphenanthridin-6-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate

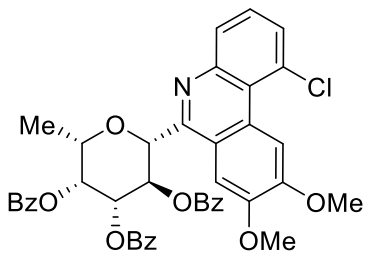


18

According to the general procedure from **1e** (0.1 mmol, 41 mg) and **2c** (0.15 mmol, 41 mg), **18** (40 mg, 66%) was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 3:1 - 2:1, reaction time = 24 h. $[\alpha]_D^{20}$ = + 91.2 (c 0.35, $CHCl_3$). $[\alpha]_D^{20}$ = + 46.3 (c 0.15, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 8.28 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.76 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.70 (s, 1H), 7.60 (t, *J* = 7.9 Hz, 1H), 7.03 (dd, *J* = 10.1, 9.0 Hz, 1H), 6.21 (d, *J* = 6.2 Hz, 1H), 5.48 (dd, *J* = 10.1, 6.3 Hz, 1H), 5.22 (dd, *J* = 10.1, 8.9 Hz, 1H), 4.19 (dd, *J* = 12.3, 4.8 Hz, 1H), 4.13 (s, 3H), 4.08 (s, 3H), 3.94 (ddd, *J* = 10.1, 4.8, 2.2 Hz, 1H), 3.89 (dd, *J* = 12.2, 2.3 Hz, 1H), 2.09 (s, 3H), 2.02 (s, 3H), 1.94 (s, 3H), 1.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.94, 170.68, 170.54, 170.00, 152.84, 151.46, 149.45, 144.18, 131.28, 131.22, 129.60, 128.69, 127.39, 121.99, 121.60, 107.56, 105.38, 71.92, 71.20, 71.16,

70.80, 69.79, 62.24, 56.32, 56.24, 21.05, 20.87, 20.77. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{30}ClNO_{11}$ 604.1580; Found 604.1582.

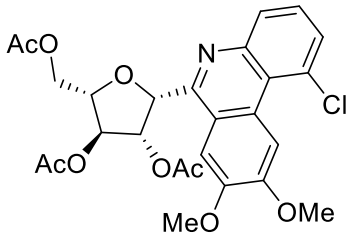
(2R,3R,4R,5R,6S)-2-(1-chloro-8,9-dimethoxyphenanthridin-6-yl)-6-methyltetrahydro-2H-pyran-3,4,5-triyl tribenzoate



19

According to the general procedure from **1f** (0.1 mmol, 54 mg) and **2c** (0.15 mmol, 41 mg), **19** (62 mg, 84%) was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 3:1 - 2:1, reaction time = 24 h. $[\alpha]_D^{20}$ = + 91.2 (c 0.35, $CHCl_3$). $[\alpha]_D^{20}$ = + 17.2 (c 0.27, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (s, 1H), 8.34 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.19 – 8.12 (m, 2H), 7.95 (s, 1H), 7.82 (ddt, *J* = 14.6, 6.8, 1.4 Hz, 4H), 7.69 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.61 – 7.50 (m, 2H), 7.45 (tt, *J* = 6.6, 1.5 Hz, 2H), 7.40 – 7.30 (m, 2H), 7.26 – 7.15 (m, 4H), 6.76 (dd, *J* = 10.3, 3.7 Hz, 1H), 6.69 (dd, *J* = 3.7, 1.6 Hz, 1H), 5.91 (d, *J* = 1.8 Hz, 1H), 5.76 (t, *J* = 10.0 Hz, 1H), 4.05 (s, 3H), 3.98 (s, 3H), 3.54 (dq, *J* = 9.8, 6.1 Hz, 1H), 1.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.25, 166.11, 165.81, 154.23, 151.53, 149.36, 144.59, 133.48, 133.32, 133.07, 131.36, 131.22, 130.20, 130.18, 129.90, 129.86, 129.83, 129.60, 129.50, 128.76, 128.74, 128.47, 128.41, 127.56, 121.87, 121.41, 107.57, 106.30, 77.99, 73.25, 72.58, 71.09, 70.31, 56.33, 56.30, 18.35. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{42}H_{34}ClNO_9$ 732.1995; Found 732.1998.

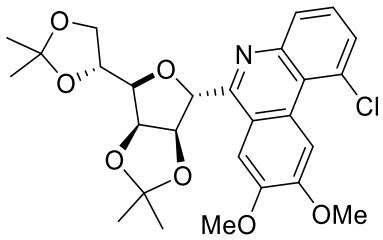
(2S,3S,4S,5R)-2-(acetoxymethyl)-5-(1-chloro-8,9-dimethoxyphenanthridin-6-yl)tetrahydrofuran-3,4-diyl diacetate



20

According to the general procedure from **1g** (0.1 mmol, 34 mg) and **2c** (0.15 mmol, 41 mg), **20** (39 mg, 73%) was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 3:1 - 2:1, reaction time = 24 h. $[\alpha]_D^{20}$ = + 91.2 (c 0.35, $CHCl_3$). $[\alpha]_D^{20}$ = + 26.9 (c 0.26, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 0.24H, **β-isomer**), 9.40 (s, 1H), 8.08 (dd, *J* = 8.2, 1.5 Hz, 1H), 8.09 – 8.05 (m, 0.25H, **β-isomer**), 7.94 (s, 0.25H, **β-isomer**), 7.91 (s, 1H), 7.70 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.70 (dd, *J* = 7.7, 1.3 Hz, 0.25H, **β-isomer**), 7.54 (t, *J* = 7.9 Hz, 1H), 7.54 (t, *J* = 7.9 Hz, 0.25H, **β-isomer**), 6.22 (t, *J* = 9.9 Hz, 0.25H, **β-isomer**), 5.97 – 5.92 (m, 1H), 5.76 (d, *J* = 2.8 Hz, 1H), 5.71 (dd, *J* = 5.8, 2.8 Hz, 1H), 5.58 – 5.52 (m, 0.25H, **β-isomer**), 5.49 (ddd, *J* = 7.9, 4.4, 3.3 Hz, 1H), 5.39 (dd, *J* = 10.0, 3.7 Hz, 0.25H, **β-isomer**), 5.11 (d, *J* = 9.8 Hz, 0.25H, **β-isomer**), 4.28 (dd, *J* = 13.1, 2.1 Hz, 0.25H, **β-isomer**), 4.22 – 4.13 (m, 1H), 4.12 (s, 1.5H), 4.12 (s, 3H), 4.08 (s, 3H), 4.03 (dd, *J* = 13.1, 1.3 Hz, 0.25H, **β-isomer**), 3.96 (dd, *J* = 11.4, 8.7 Hz, 1H), 2.21 (s, 3H), 2.20 (s, 0.75H), 2.11 (s, 3H), 2.06 (s, 0.75H), 1.83 (s, 3H), 1.69 (s, 0.75H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.53, 170.06, 169.83, 169.56, 169.26, 153.73, 153.16, 151.44, 151.29, 149.19, 148.98, 144.90, 144.73, 130.99, 130.90, 130.53, 130.51, 129.68, 129.65, 129.00, 128.84, 127.29, 121.83, 121.60, 121.54, 107.61, 107.50, 106.21, 106.02, 81.93, 76.44, 72.32, 69.72, 69.04, 67.89, 67.45, 66.58, 64.68, 56.25, 56.02, 55.88, 21.17, 21.05, 20.98, 20.93, 20.91, 20.71. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{26}ClNO_9$ 532.1369; Found 532.1370.

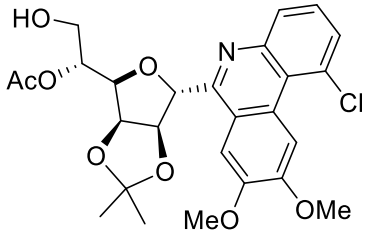
1-chloro-6-((3aR,4R,6R,6aS)-6-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)-8,9-dimethoxyphenanthridine



21

According to the general procedure from **1h** (0.1 mmol, 32 mg) and **2c** (0.15 mmol, 41 mg), **21** (36 mg, 69%) was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 3:1 - 2:1, reaction time = 24 h. $[\alpha]_D^{20}$ = + 91.2 (c 0.35, $CHCl_3$). $[\alpha]_D^{20}$ = + 40.0 (c 0.24, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (s, 1H), 8.03 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.76 (s, 1H), 7.69 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.53 (t, *J* = 7.9 Hz, 1H), 5.89 (d, *J* = 6.0 Hz, 1H), 5.82 (s, 1H), 5.06 (dd, *J* = 6.1, 3.9 Hz, 1H), 4.46 (ddd, *J* = 7.6, 6.4, 4.8 Hz, 1H), 4.12 (s, 3H), 4.11 – 4.08 (m, 1H), 4.07 (s, 3H), 3.93 (dd, *J* = 8.6, 4.8 Hz, 1H), 3.80 (dd, *J* = 7.5, 3.9 Hz, 1H), 1.65 (s, 3H), 1.49 (s, 3H), 1.33 (s, 3H), 1.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.26, 151.42, 149.29, 144.54, 130.71, 130.53, 129.72, 128.56, 127.09, 121.81, 121.37, 112.30, 109.19, 107.56, 106.08, 83.76, 83.18, 81.78, 81.42, 73.59, 67.05, 56.28, 26.88, 26.29, 25.36, 24.67. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{30}ClNO_7$ 516.1784; Found 516.1789.

(R)-1-((3aS,4R,6R,6aR)-6-(1-chloro-8,9-dimethoxyphenanthridin-6-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)-2-hydroxyethyl acetate

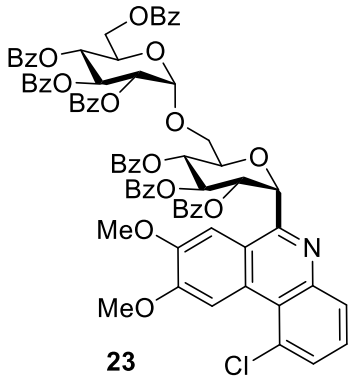


22

According to the general procedure from **1i** (0.1 mmol, 32 mg) and **2c** (0.15 mmol, 41 mg), **22** (23 mg, 45%) was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 3:1 - 2:1, reaction time = 24 h. $[\alpha]_D^{20}$ = + 91.2 (c 0.35, $CHCl_3$). $[\alpha]_D^{20}$ = + 29.3 (c 0.27 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (s, 1H), 8.06 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.74 (s, 1H), 7.69 (d, *J* = 1.5 Hz, 1H), 7.54 (t, *J* =

7.9 Hz, 1H), 5.84 (s, 1H), 5.76 (d, *J* = 5.9 Hz, 1H), 5.31 (ddd, *J* = 7.7, 4.5, 2.8 Hz, 1H), 4.98 (dd, *J* = 6.0, 3.9 Hz, 1H), 4.18 (dd, *J* = 8.1, 3.9 Hz, 1H), 4.12 (s, 3H), 4.10 (s, 3H), 3.86 (dd, *J* = 11.3, 2.9 Hz, 1H), 3.68 (dd, *J* = 11.4, 4.5 Hz, 1H), 2.08 (s, 3H), 1.62 (s, 3H), 1.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.78, 155.10, 151.47, 149.32, 144.62, 130.77, 130.63, 129.74, 128.50, 127.13, 121.78, 121.06, 112.64, 107.60, 105.89, 84.00, 83.29, 81.09, 80.21, 69.95, 56.28, 33.62, 26.40, 24.99, 21.12. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{28}ClNO_8$ 518.1576; Found 518.1584.

(2R,3R,4S,5R,6S)-2-((benzoyloxy)methyl)-6-(((2R,3R,4R,5S,6R)-3,4,5-tris(benzoyloxy)-6-(1-chloro-8,9-dimethoxyphenanthridin-6-yl)tetrahydro-2H-pyran-2-yl)methoxy)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate

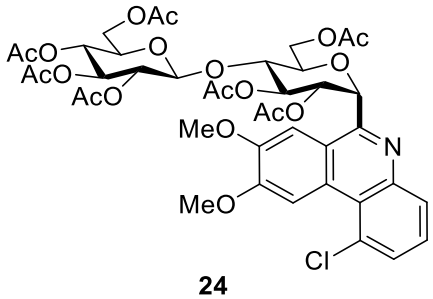


23

According to the general procedure from **1j** (0.1 mmol, 114 mg) and **2c** (0.15 mmol, 41 mg), **23** (58 mg, 44%) was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 3:1 - 2:1, reaction time = 48 h. $[\alpha]_D^{20}$ = + 91.2 (c 0.35, $CHCl_3$). $[\alpha]_D^{20}$ = + 80.0 (c 0.25, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (s, 1H), 8.49 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.17 (dd, *J* = 7.4, 2.4 Hz, 2H), 8.07 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.99 – 7.89 (m, 4H), 7.81 (dddd, *J* = 26.7, 11.7, 8.0, 1.4 Hz, 7H), 7.72 – 7.63 (m, 1H), 7.60 (d, *J* = 18.2 Hz, 3H), 7.57 – 7.50 (m, 3H), 7.51 – 7.41 (m, 5H), 7.40 – 7.31 (m, 5H), 7.30 – 7.24 (m, 2H), 7.20 (td, *J* = 7.9, 7.5, 3.5 Hz, 4H), 6.26 (d, *J* = 6.5 Hz, 1H), 6.05 (dd, *J* = 3.5, 1.3 Hz, 1H), 6.00 (dd, *J* = 10.6, 3.5 Hz, 1H), 5.85 (t, *J* = 9.8 Hz, 1H), 5.68 (dd, *J* = 10.6, 3.7 Hz, 1H), 5.58 (dd, *J* = 10.0, 6.3 Hz, 1H), 5.46 (d, *J* = 3.8 Hz, 1H), 4.70 – 4.62 (m, 1H), 4.32 (d, *J* = 6.5 Hz, 2H), 4.11 (t, *J* = 2.4 Hz, 1H), 4.06

(s, 3H), 3.87 (s, 1H), 3.84 (s, 3H), 3.47 (dd, *J* = 11.6, 2.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.48, 166.33, 166.04, 165.92, 165.73, 165.40, 153.13, 151.54, 149.55, 144.33, 133.62, 133.40, 133.16, 133.11, 133.07, 131.27, 131.11, 130.16, 130.09, 129.94, 129.89, 129.86, 129.80, 129.77, 129.70, 129.64, 129.56, 129.42, 129.17, 128.77, 128.74, 128.67, 128.51, 128.49, 128.44, 128.37, 128.35, 127.43, 122.00, 121.70, 107.60, 105.51, 97.27, 72.19, 72.12, 71.88, 71.59, 69.79, 69.51, 69.43, 68.58, 67.21, 66.74, 62.84, 56.22, 56.09. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{76}H_{60}ClNO_{19}$ 1326.3521; Found 1326.3532.

(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-(((2R,3R,4S,5S,6R)-4,5-diacetoxy-2-(acetoxymethyl)-6-(1-chloro-8,9-dimethoxyphenanthridin-6-yl)tetrahydro-2H-pyran-3-yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate

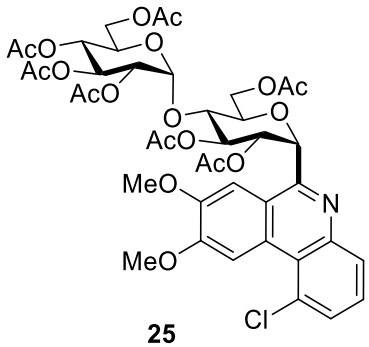


24

According to the general procedure from **1k** (0.1 mmol, 70 mg) and **2c** (0.15 mmol, 41 mg), **24** (36 mg, 40%) was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 3:1 - 2:1, reaction time = 48 h. $[\alpha]_D^{20}$ = + 91.2 (c 0.35, $CHCl_3$). $[\alpha]_D^{20}$ = + 53.6 (c 0.28, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.41 (s, 1H), 8.28 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.75 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.71 (s, 1H), 7.62 (t, *J* = 7.9 Hz, 1H), 6.99 (dd, *J* = 9.9, 8.6 Hz, 1H), 6.06 (d, *J* = 6.2 Hz, 1H), 5.38 (dd, *J* = 9.8, 6.1 Hz, 1H), 5.13 (t, *J* = 9.3 Hz, 1H), 5.05 (t, *J* = 9.7 Hz, 1H), 4.91 (dd, *J* = 9.3, 7.9 Hz, 1H), 4.61 (d, *J* = 7.9 Hz, 1H), 4.28 (ddd, *J* = 12.5, 5.1, 3.3 Hz, 2H), 4.12 (s, 3H), 4.09 (d, *J* = 7.0 Hz, 1H), 4.07 (s, 3H), 3.94 (dd, *J* = 12.3, 2.4 Hz, 1H), 3.87 (dd, *J* = 10.0, 8.6 Hz, 1H), 3.78 (ddd, *J* = 9.9, 5.0, 2.1 Hz, 1H), 3.60 (ddd, *J* = 9.8, 4.3, 2.4 Hz, 1H), 2.11 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.96 (d, *J* = 1.0 Hz, 6H), 1.91 (s, 3H), 1.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.08, 170.62, 170.42, 170.39, 169.93, 169.42,

169.10, 152.83, 151.39, 149.34, 144.20, 131.43, 131.22, 129.53, 128.68, 127.52, 121.91, 121.54, 107.53, 105.52, 100.69, 78.06, 73.27, 72.20, 71.99, 71.94, 71.79, 71.38, 70.21, 68.02, 62.10, 61.73, 56.31, 56.21, 29.83, 20.96, 20.93, 20.91, 20.69, 20.67. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{41}H_{46}ClNO_{19}$ 914.2245; Found 914.2250.

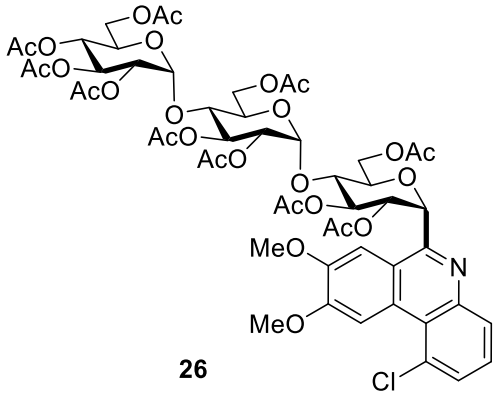
(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(((2R,3R,4S,5S,6R)-4,5-diacetoxy-2-(acetoxymethyl)-6-(1-chloro-8,9-dimethoxyphenanthridin-6-yl)tetrahydro-2H-pyran-3-yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate



25

According to the general procedure from **1l** (0.1 mmol, 70 mg) and **2c** (0.15 mmol, 41 mg), **25** (63 mg, 69%) was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 3:1 - 2:1, reaction time = 48 h. $[\alpha]_D^{20}$ = + 91.2 (c 0.35, $CHCl_3$). $[\alpha]_D^{20}$ = + 112.1 (c 0.45, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 8.26 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.76 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.72 (s, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 6.96 (dd, *J* = 9.7, 8.0 Hz, 1H), 6.06 (d, *J* = 6.0 Hz, 1H), 5.49 (d, *J* = 4.0 Hz, 1H), 5.39 – 5.33 (m, 1H), 5.35 – 5.29 (m, 1H), 5.05 (t, *J* = 9.9 Hz, 1H), 4.90 (dd, *J* = 10.5, 4.1 Hz, 1H), 4.34 (dd, *J* = 12.1, 2.6 Hz, 1H), 4.25 (dd, *J* = 12.4, 3.8 Hz, 1H), 4.18 – 4.11 (m, 1H), 4.14 (s, 3H), 4.09 (s, 3H), 4.08 – 4.05 (m, 1H), 4.07 – 4.00 (m, 1H), 3.98 – 3.87 (m, 2H), 2.13 (s, 3H), 2.11 (s, 3H), 2.10 (s, 3H), 2.01 (s, 3H), 1.98 (s, 6H), 1.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.90, 170.59, 170.42, 170.05, 169.90, 169.46, 152.73, 151.28, 149.24, 144.19, 131.03, 130.99, 129.51, 128.58, 127.29, 121.75, 121.51, 107.46, 105.27, 95.55, 73.89, 73.15, 71.99, 71.45, 71.40, 69.98, 69.51, 68.35, 68.08, 62.76, 61.51, 56.16, 56.07, 21.11, 20.78, 20.72, 20.68, 20.61, 20.56. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{41}H_{46}ClNO_{19}$ 914.2245; Found 914.2249.

(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(((2R,3R,4S,5R,6R)-4,5-diacetoxy-2-(acetoxymethyl)-6-(((2R,3R,4S,5S,6R)-4,5-diacetoxy-2-(acetoxymethyl)-6-(1-chloro-8,9-dimethoxyphenanthridin-6-yl)tetrahydro-2H-pyran-3-yl)oxy)tetrahydro-2H-pyran-3-yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate



26

According to the general procedure from **1m** (0.1 mmol, 99 mg) and **2c** (0.15 mmol, 41 mg), **26** (43 mg, 36%) was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 3:1 - 2:1, reaction time = 48 h. $[\alpha]_D^{20}$ = + 91.2 (c 0.35, $CHCl_3$). $[\alpha]_D^{20}$ = + 94.4 (c 0.27, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.75 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.71 (s, 1H), 7.61 (t, *J* = 7.9 Hz, 1H), 6.91 (dd, *J* = 9.5, 7.9 Hz, 1H), 6.04 (d, *J* = 6.0 Hz, 1H), 5.39 – 5.36 (m, 3H), 5.35 – 5.33 (m, 1H), 5.30 (dd, *J* = 10.6, 9.5 Hz, 1H), 5.04 (t, *J* = 9.8 Hz, 1H), 4.80 (ddd, *J* = 19.8, 10.4, 4.1 Hz, 2H), 4.47 (dd, *J* = 12.2, 2.0 Hz, 1H), 4.35 (dd, *J* = 12.1, 2.7 Hz, 1H), 4.27 – 4.20 (m, 2H), 4.20 – 4.12 (m, 1H), 4.13 (s, 3H), 4.08 (d, *J* = 2.6 Hz, 3H), 4.07 – 4.04 (m, 1H), 4.03 (dd, *J* = 10.6, 1.8 Hz, 1H), 3.97 – 3.94 (m, 1H), 3.95 – 3.90 (m, 2H), 3.89 – 3.87 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.01, 170.84, 170.72, 170.67, 170.58, 170.54, 170.12, 169.97, 169.78, 169.58, 152.86, 151.40, 149.40, 144.36, 131.24, 131.13, 129.60, 128.70, 127.47, 121.90, 121.64, 107.62, 105.38, 95.74, 74.76, 73.32, 72.60, 72.12, 72.04, 71.64, 71.53, 70.57, 70.15, 69.53, 68.94, 68.57, 68.06, 62.98, 62.47, 61.51, 56.30, 56.22, 21.23, 21.05, 20.98, 20.96, 20.85, 20.80, 20.77, 20.70. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{53}H_{62}ClNO_{27}$ 1202.3090; Found 1202.3092.

9. References

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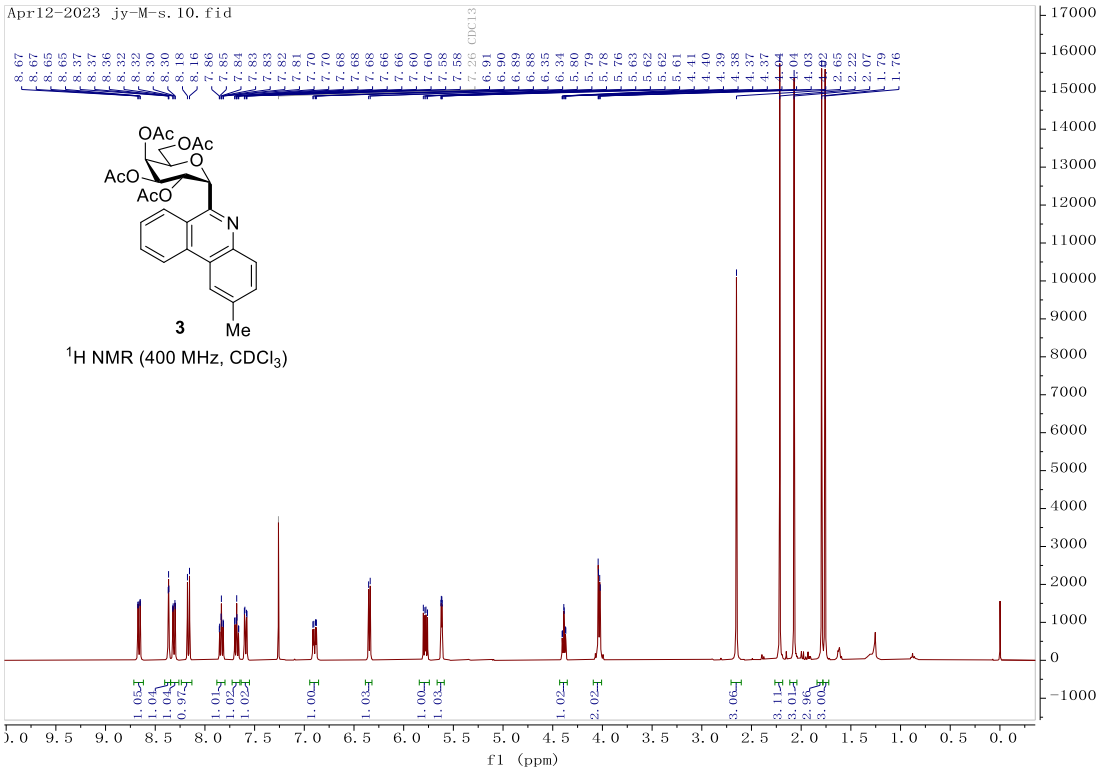
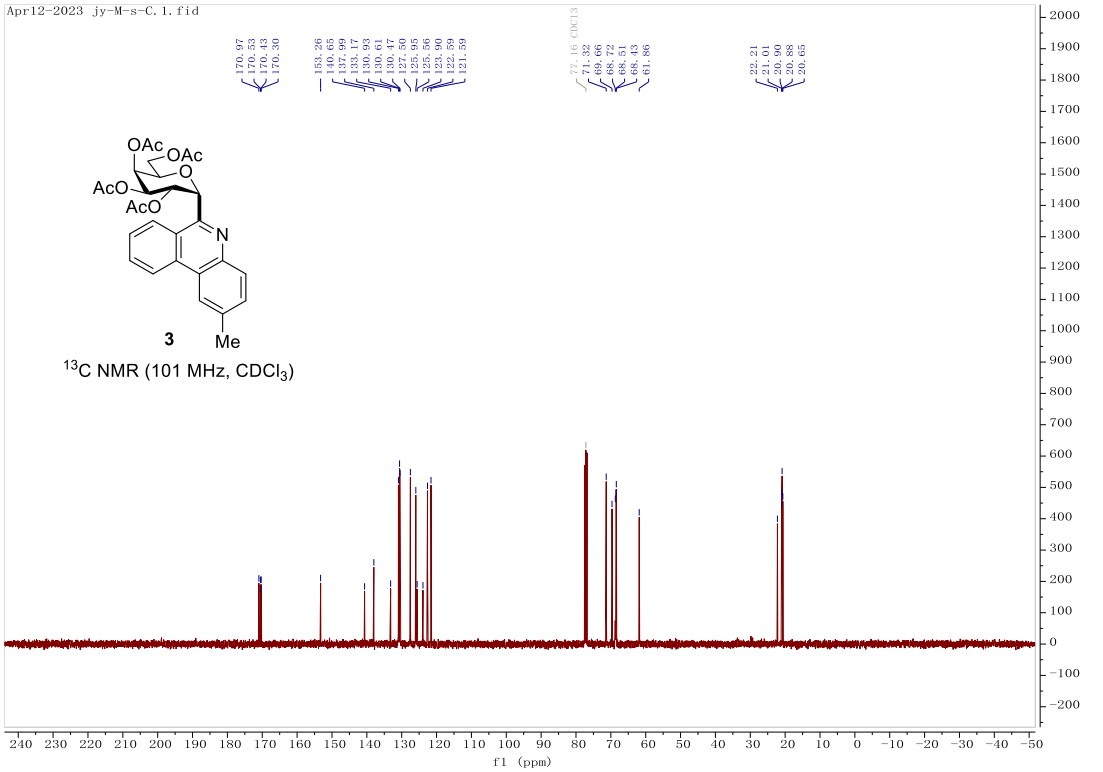
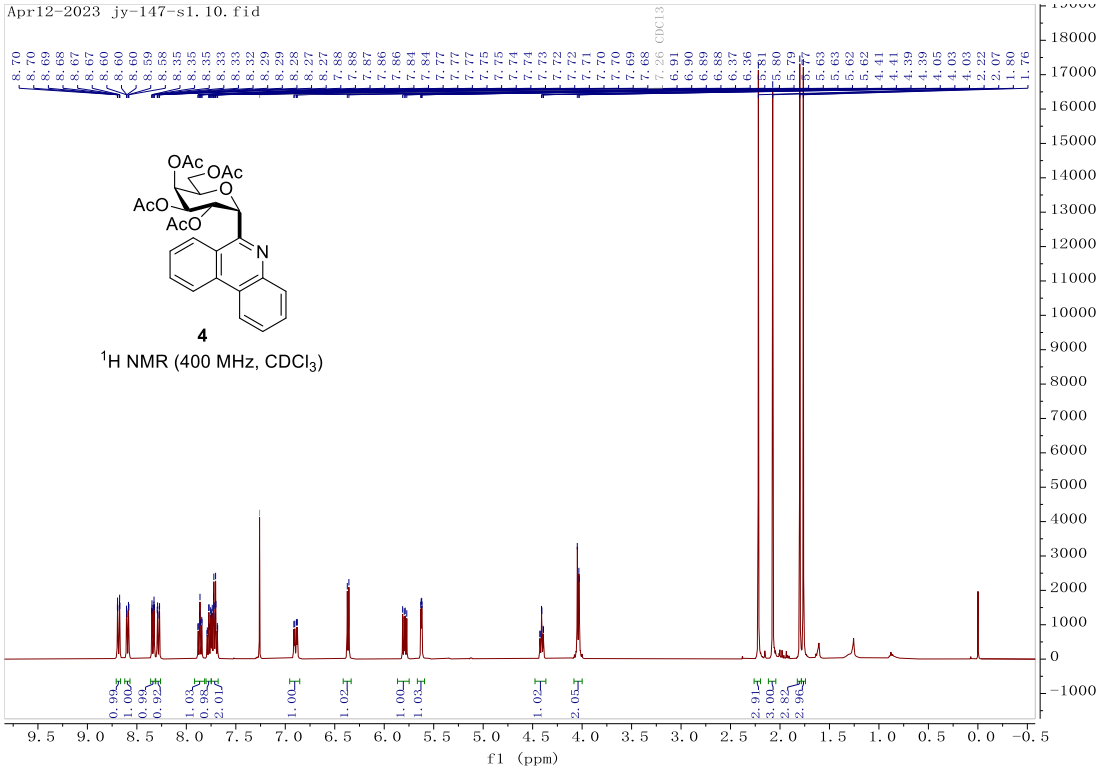
10. NMR Spectra Data for the Products



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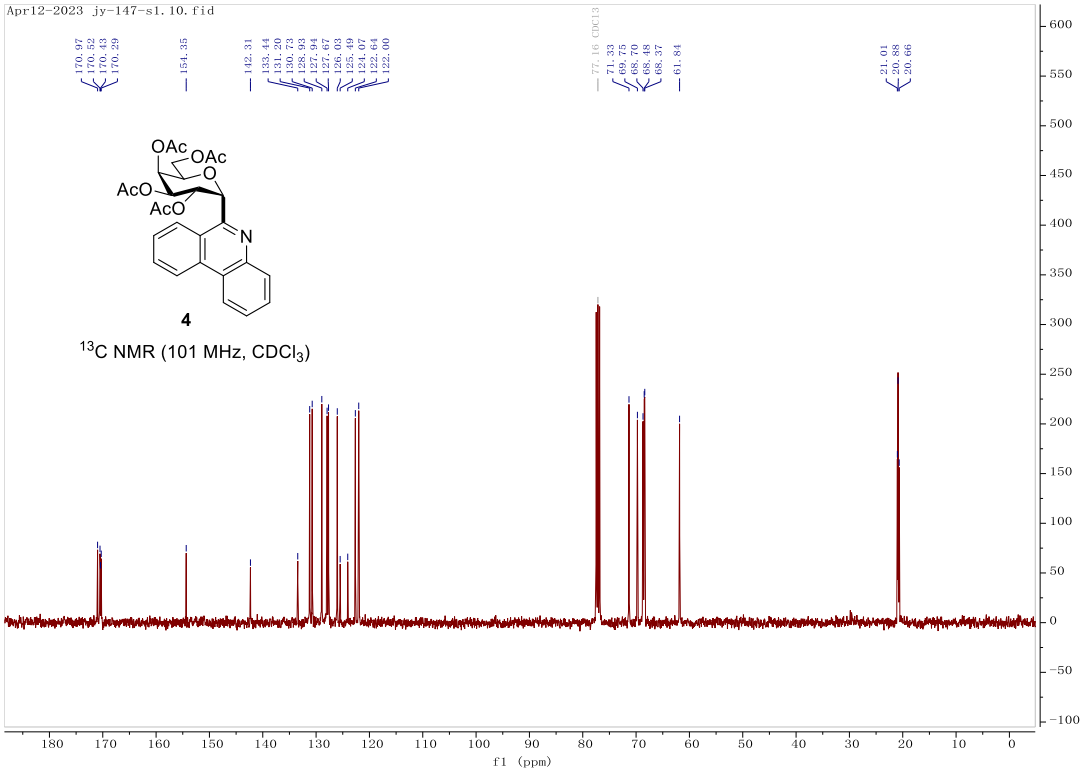
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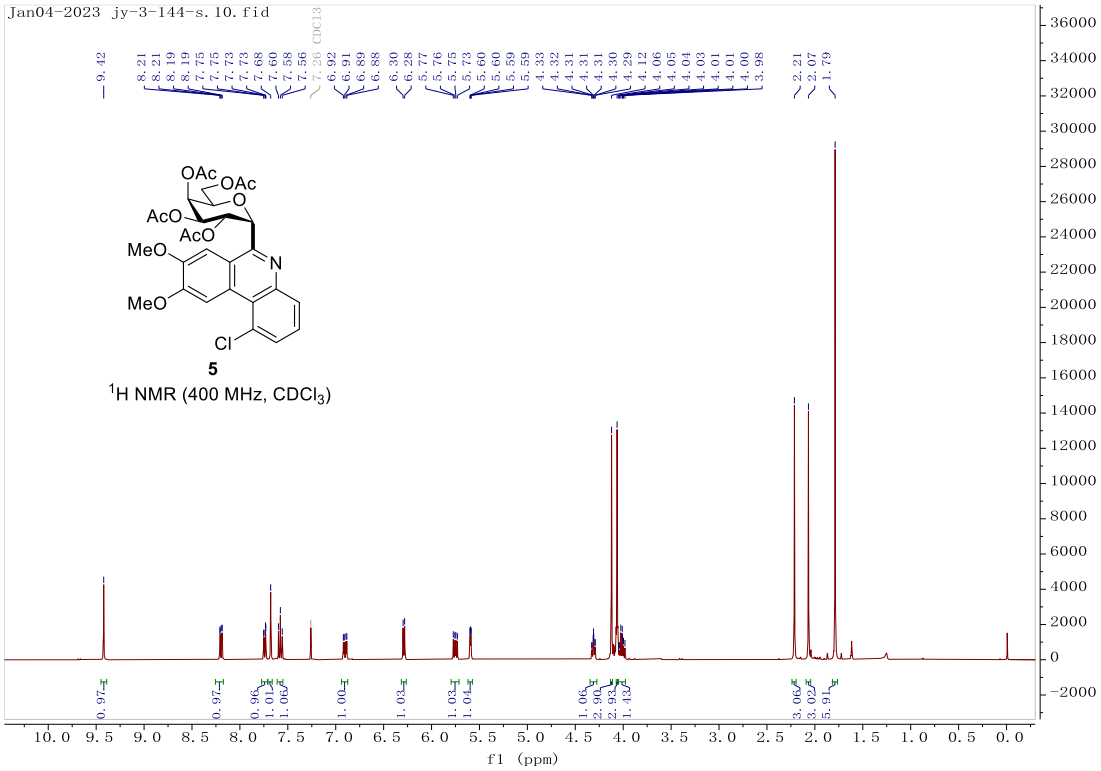
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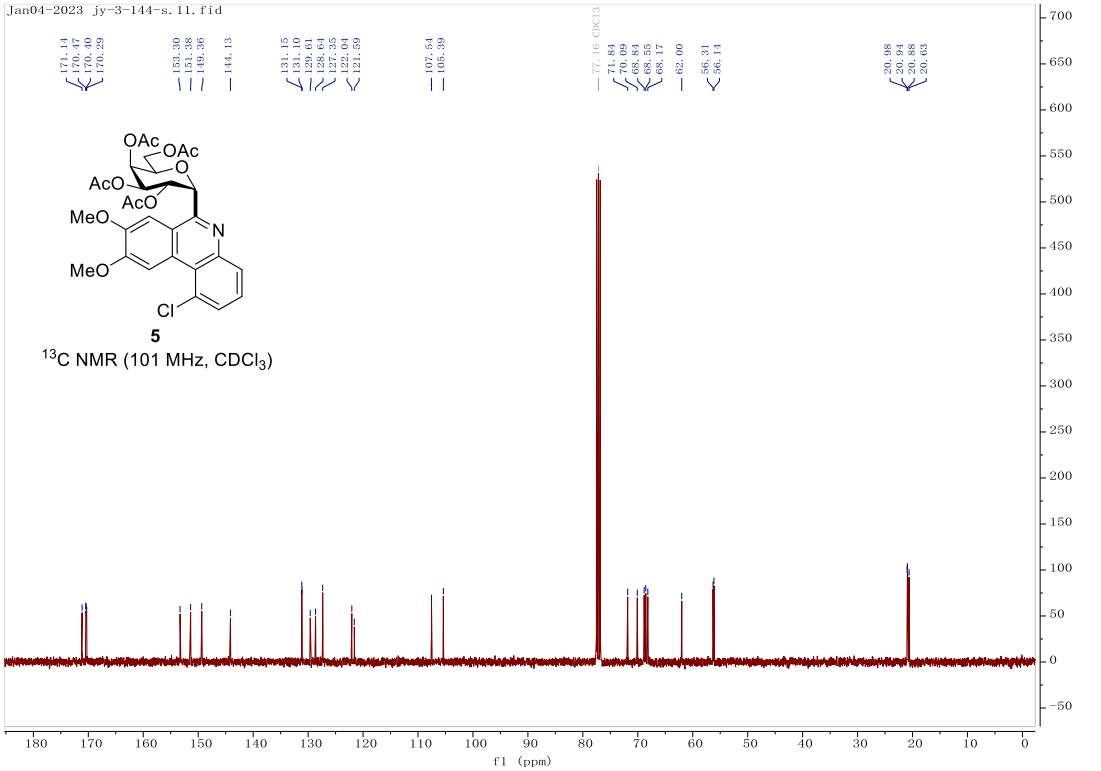
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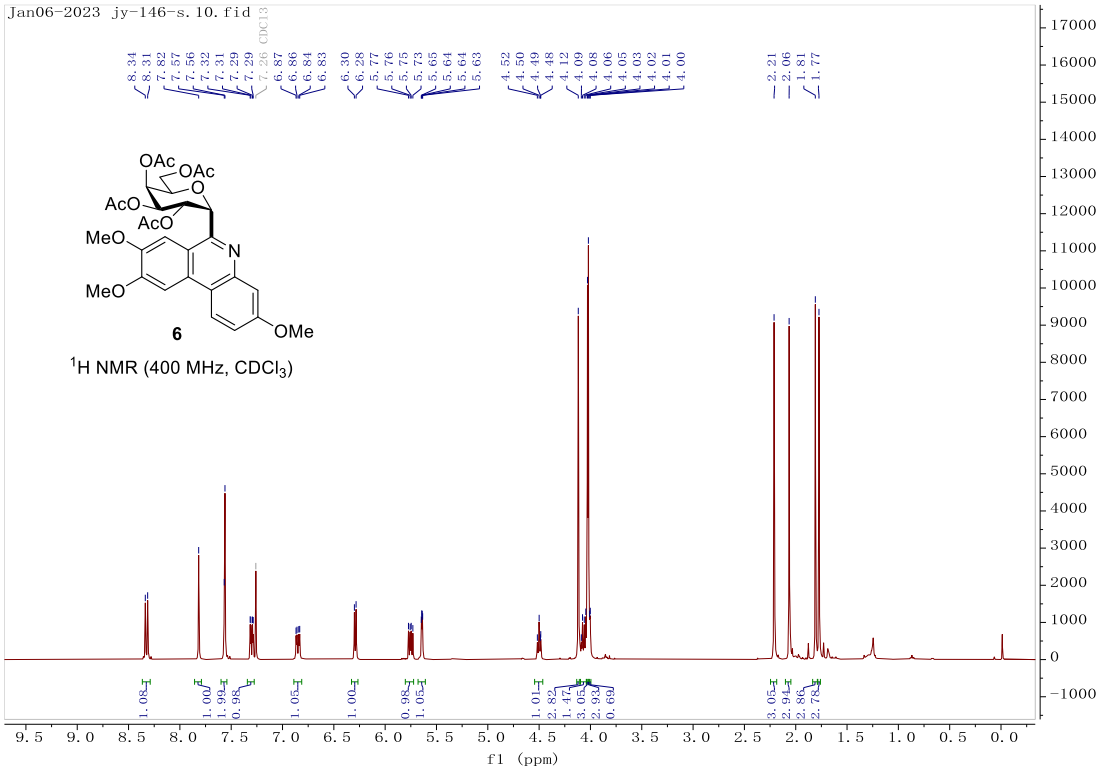
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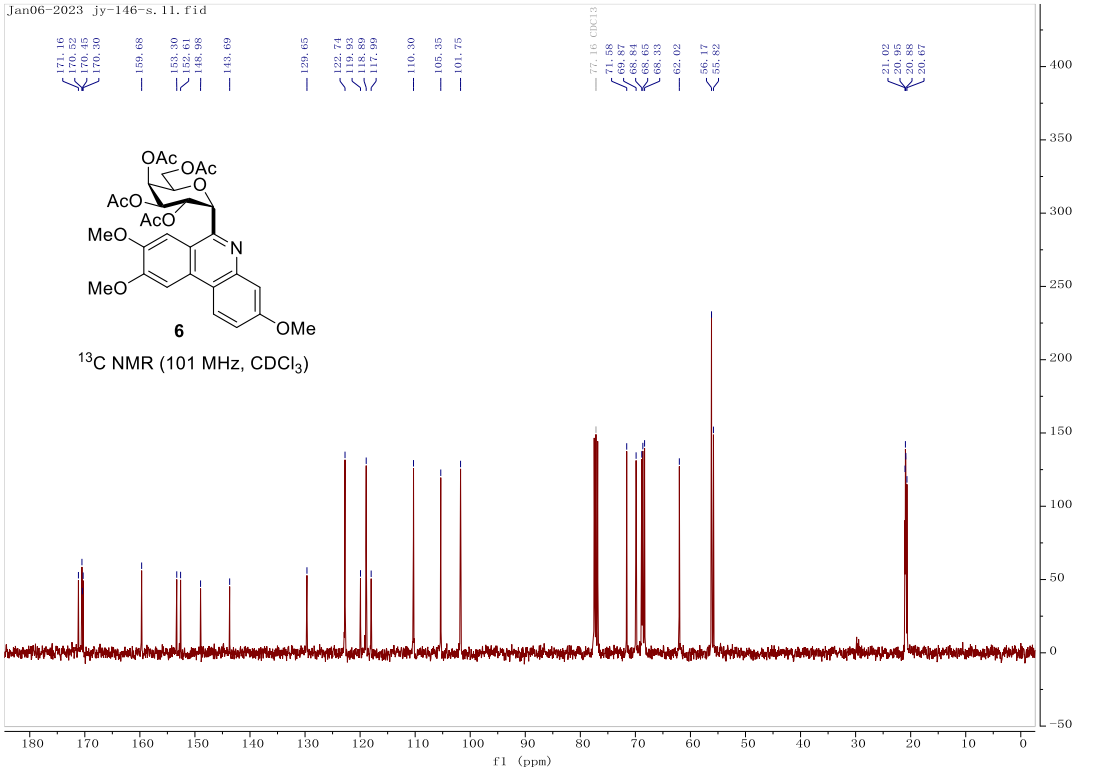
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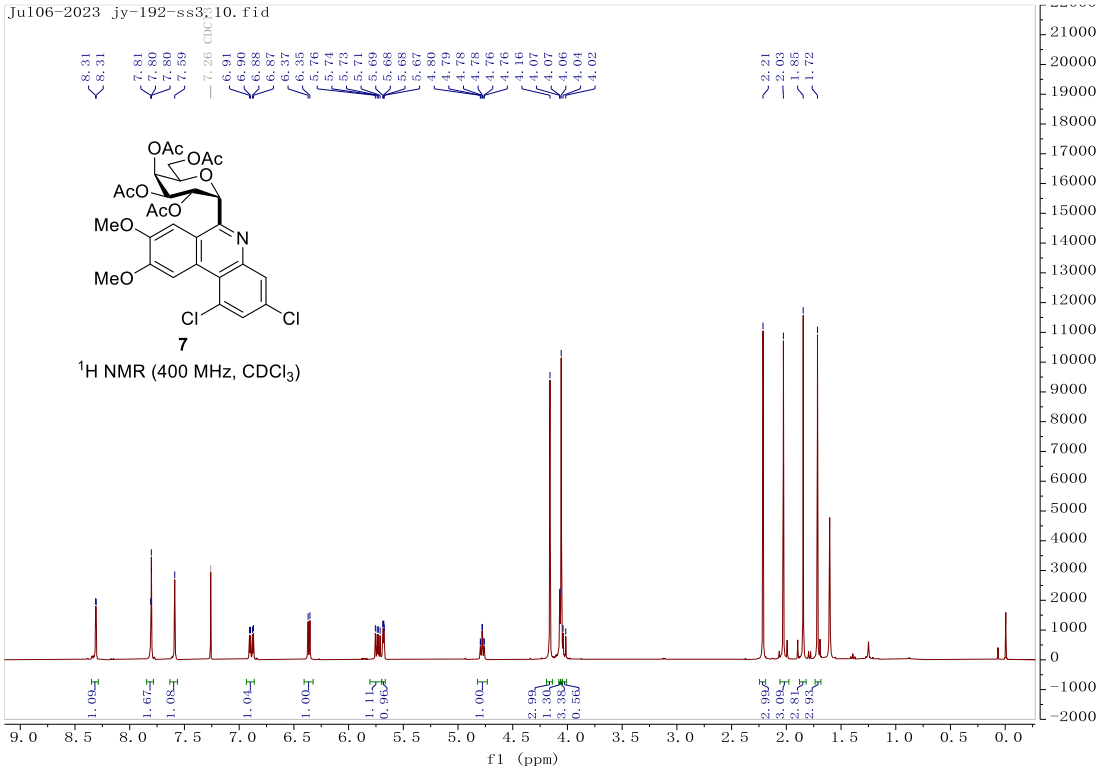
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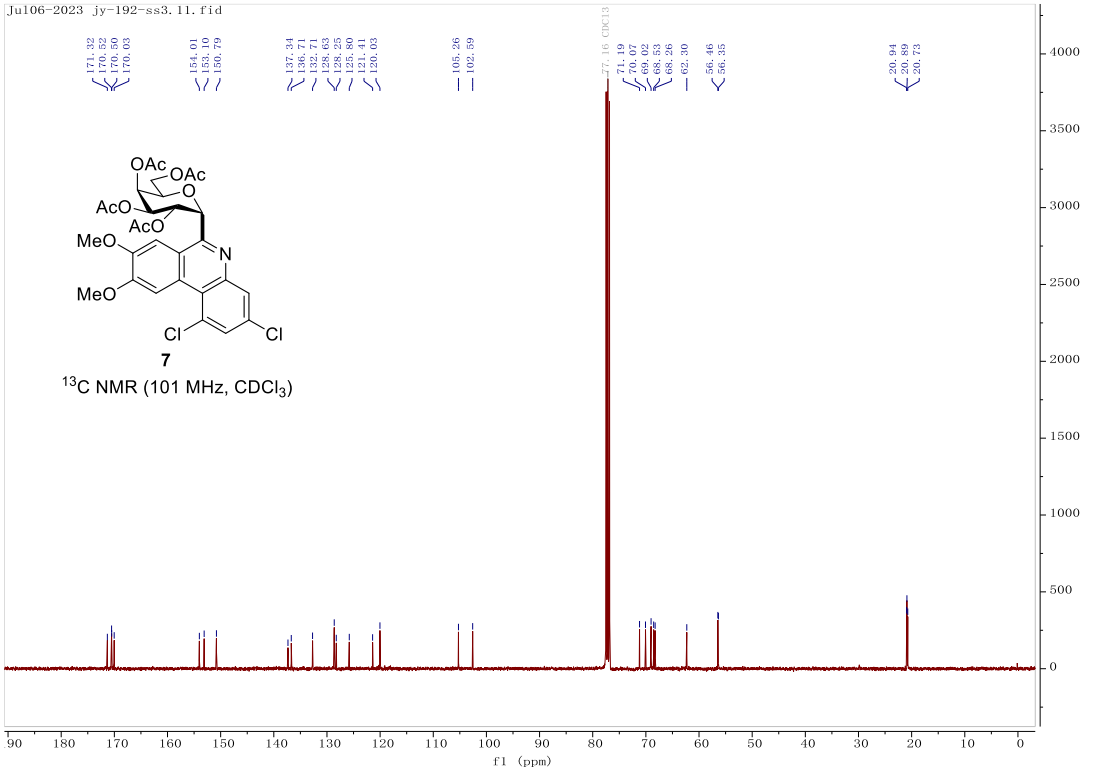
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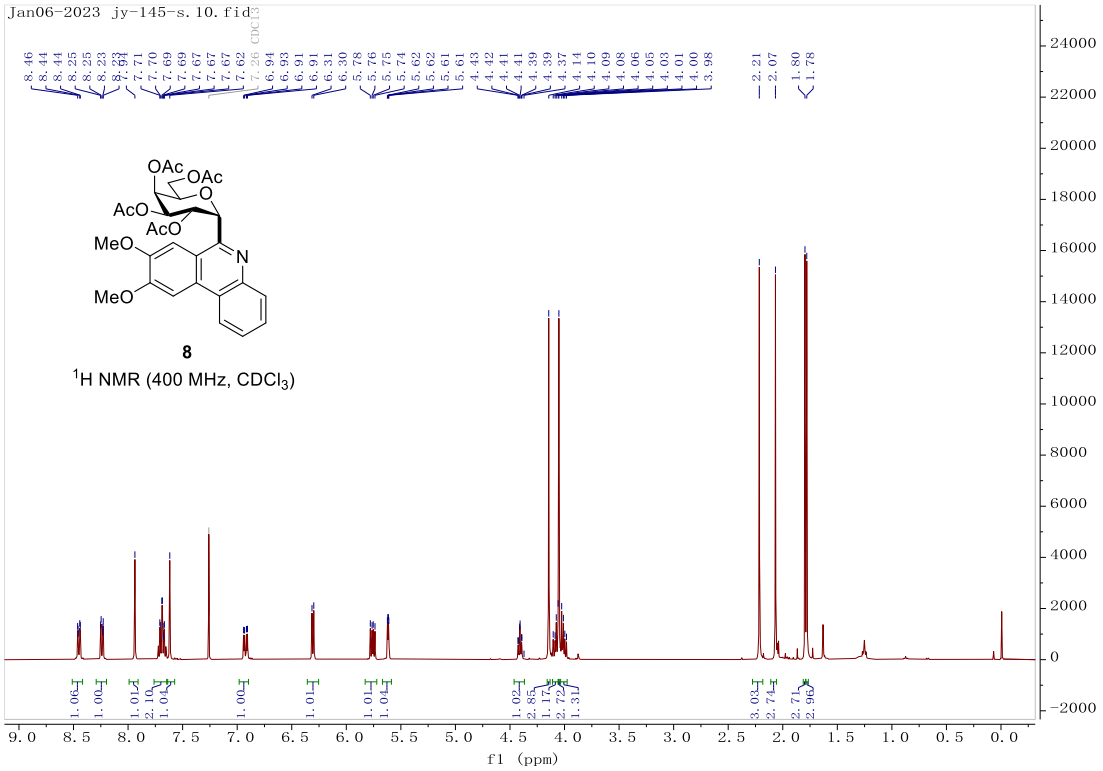
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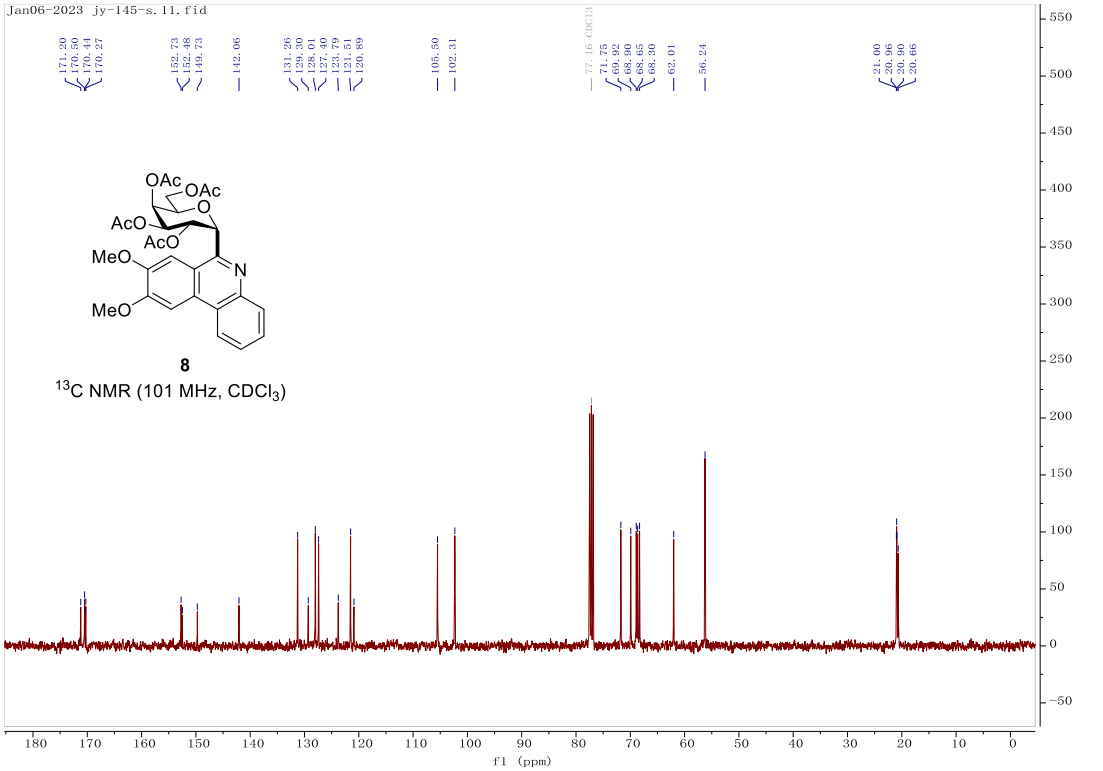
OAc
O
AcO
AcO
MeO
MeO
N
8
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Jan06-2023 jy-145-s.11.fid
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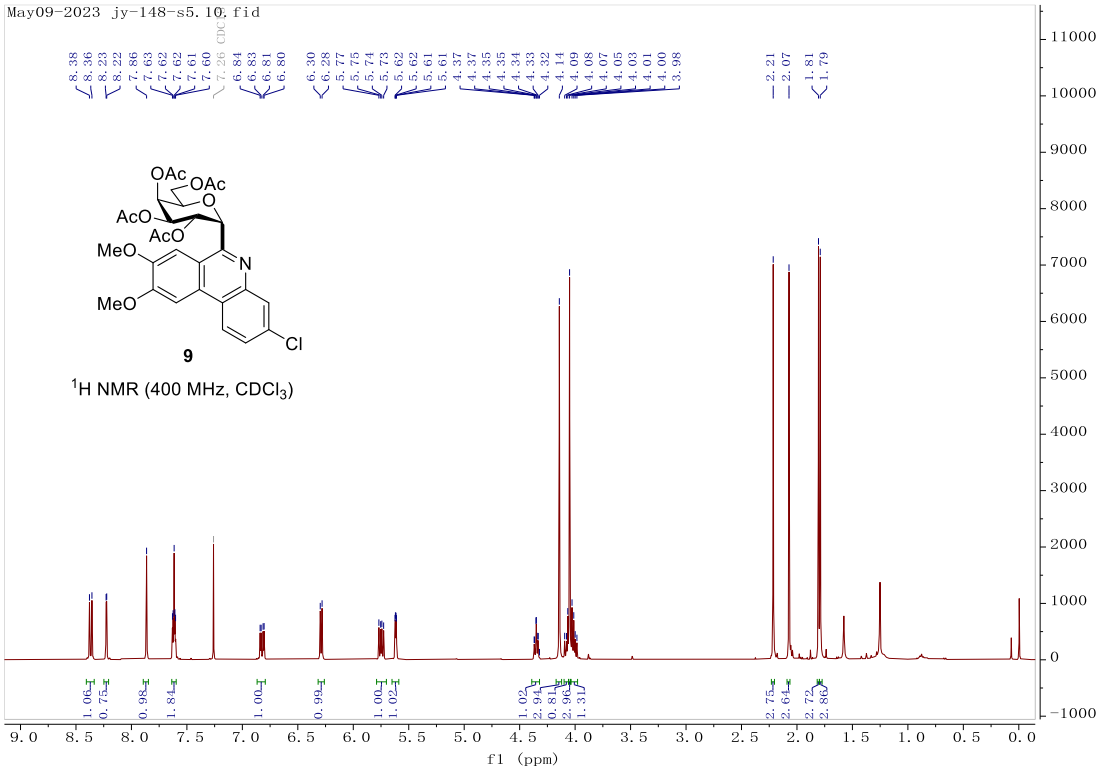
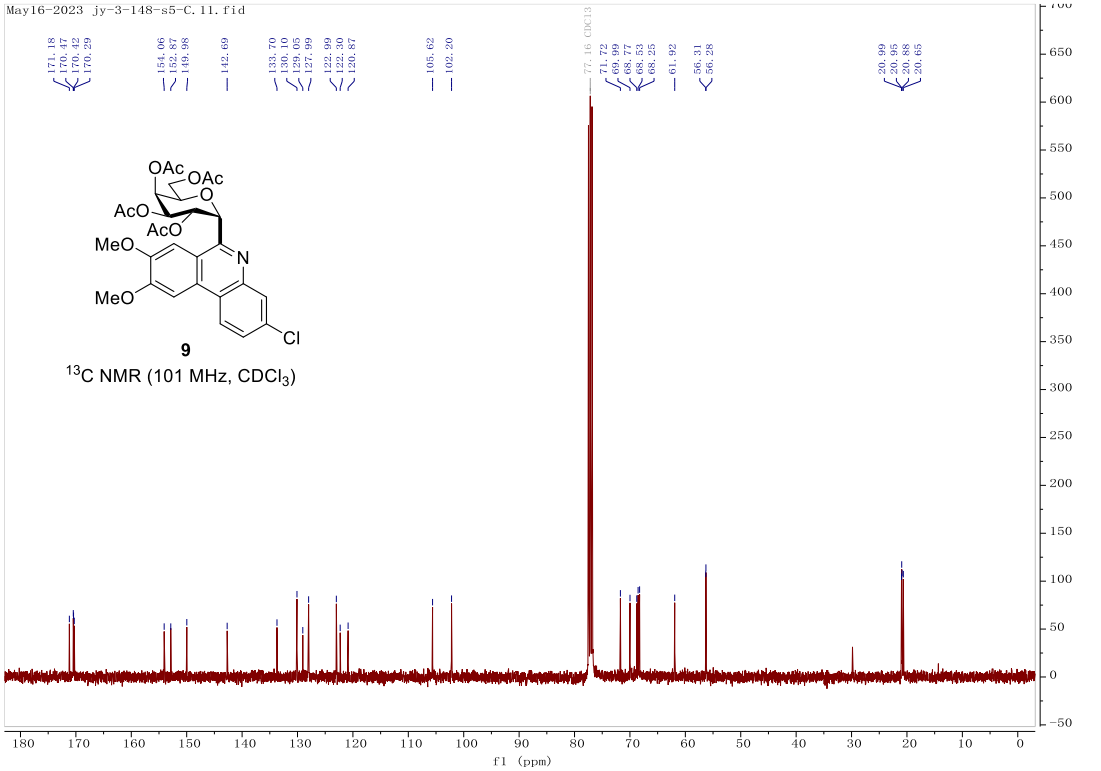
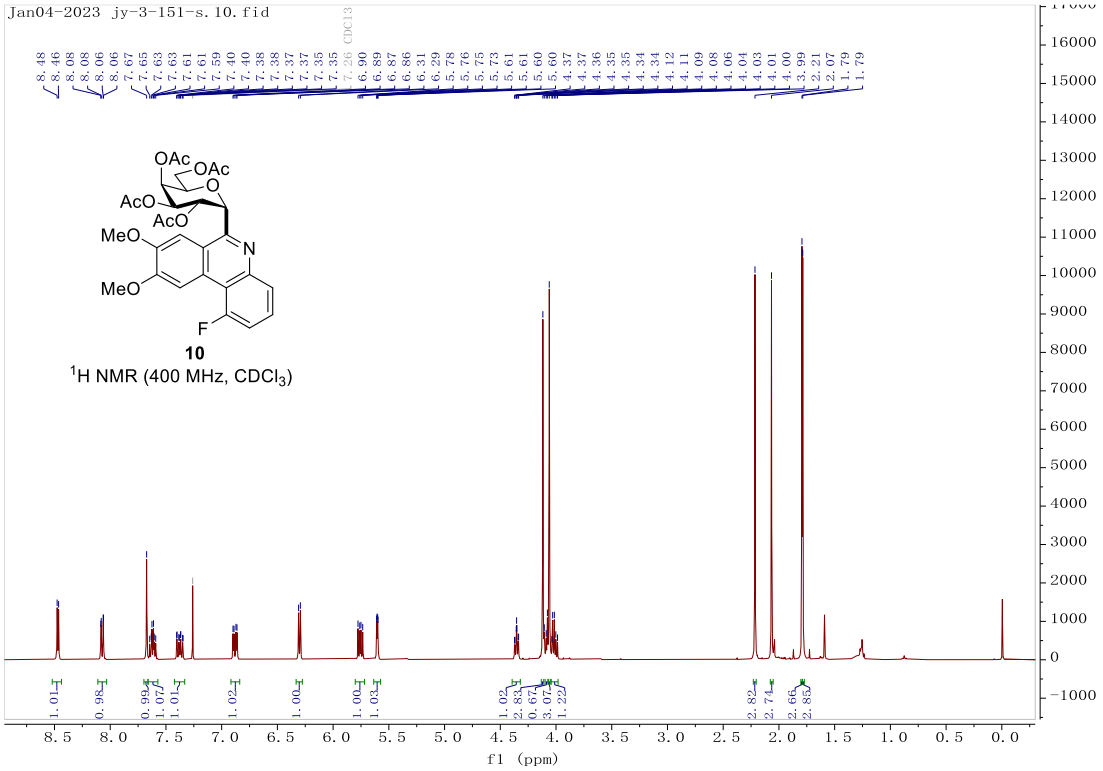
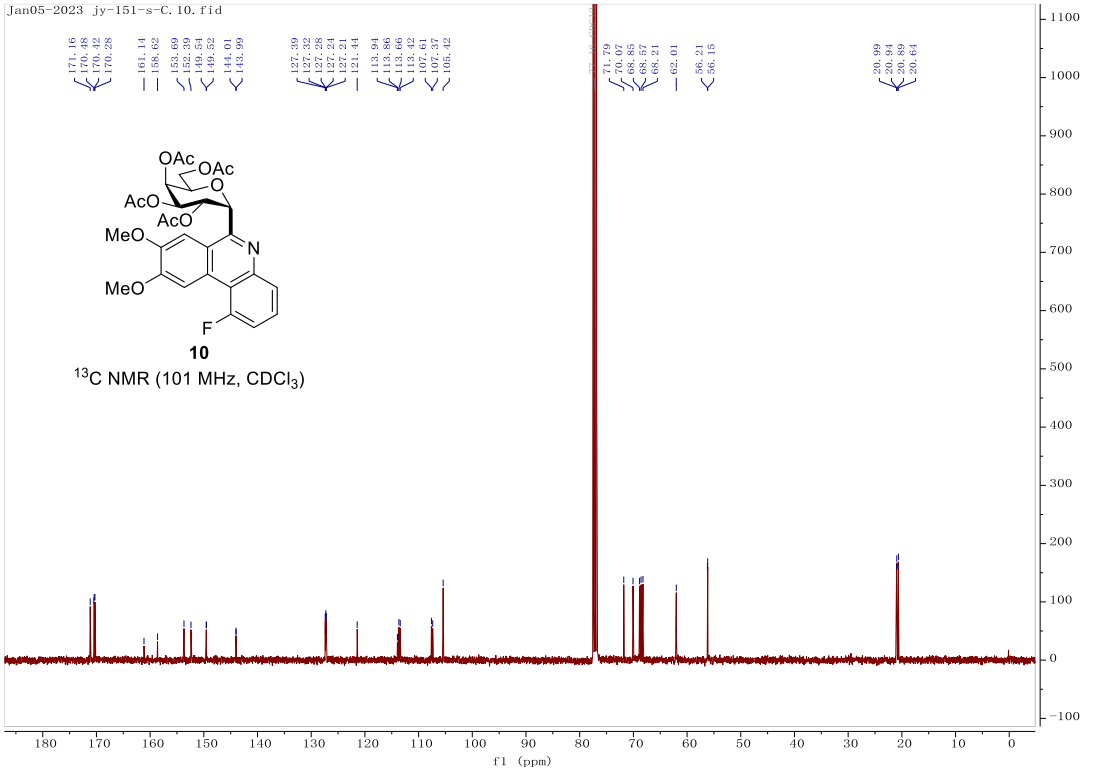
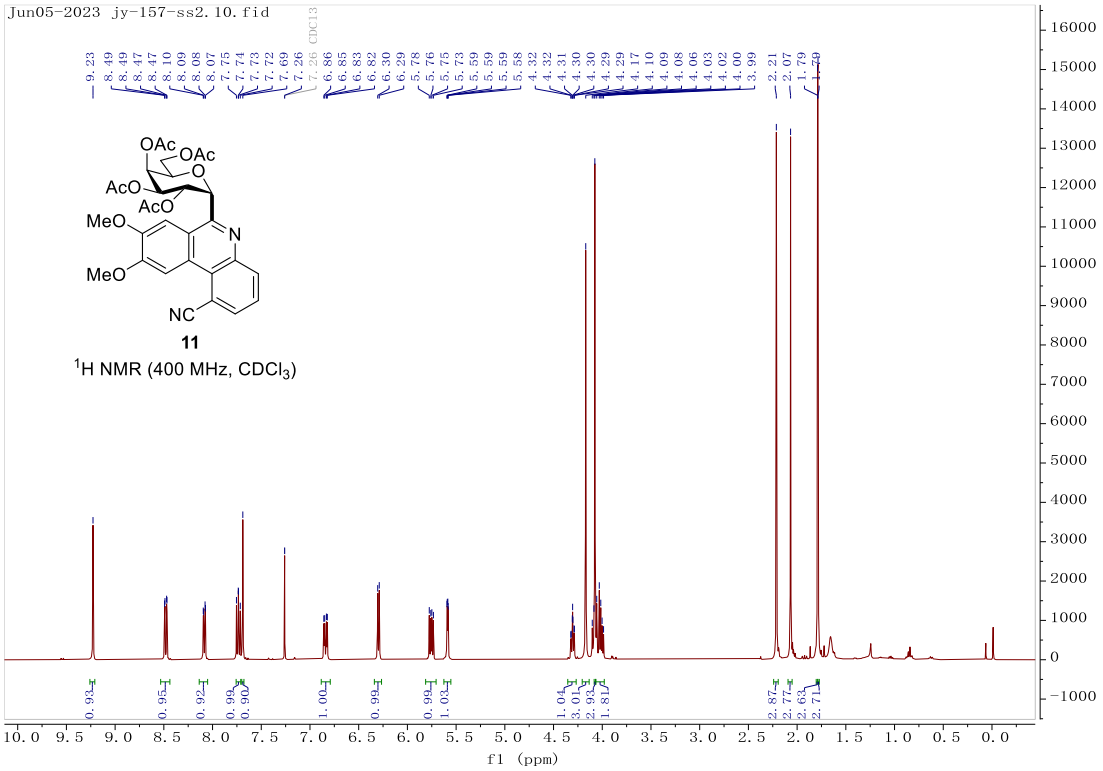
OAc
O
AcO
AcO
MeO
MeO
N
8
13C NMR (101 MHz, CDCl3)
f1 (ppm)

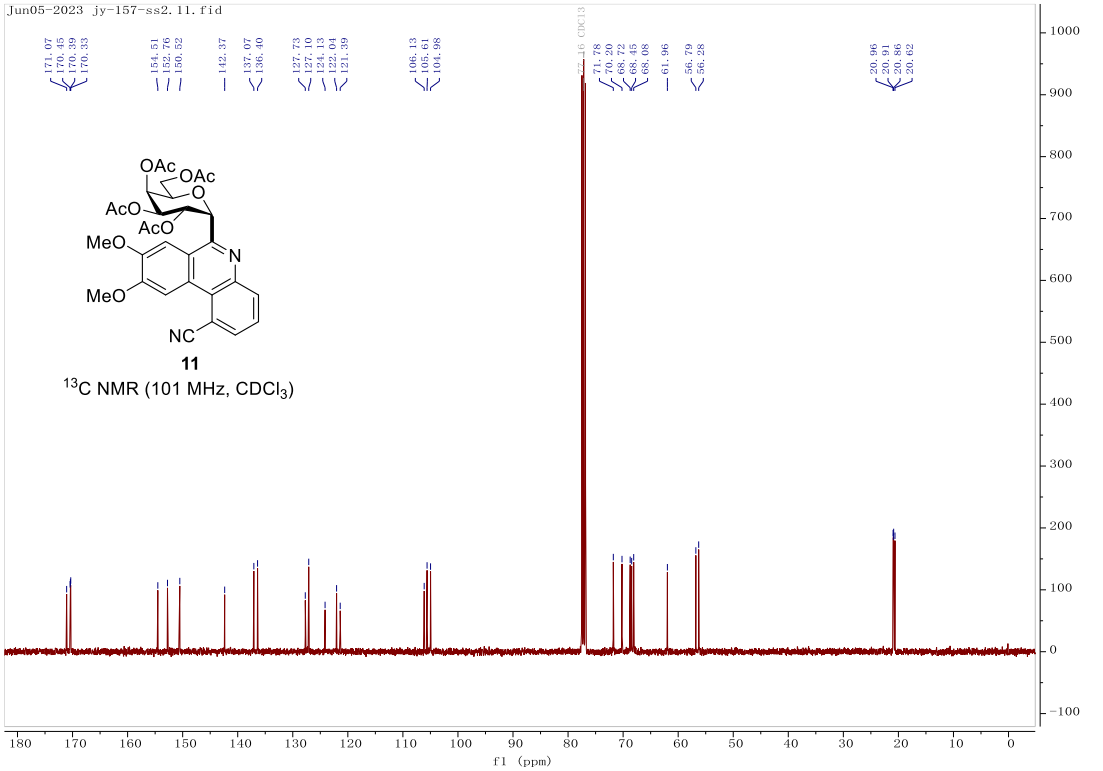

May09-2023 jy-148-s5.10.fid
OAc
OAc
O
AcO
AcO
MeO
MeO
N
Cl
9
1H NMR (400 MHz, CDCl3)
f1 (ppm)

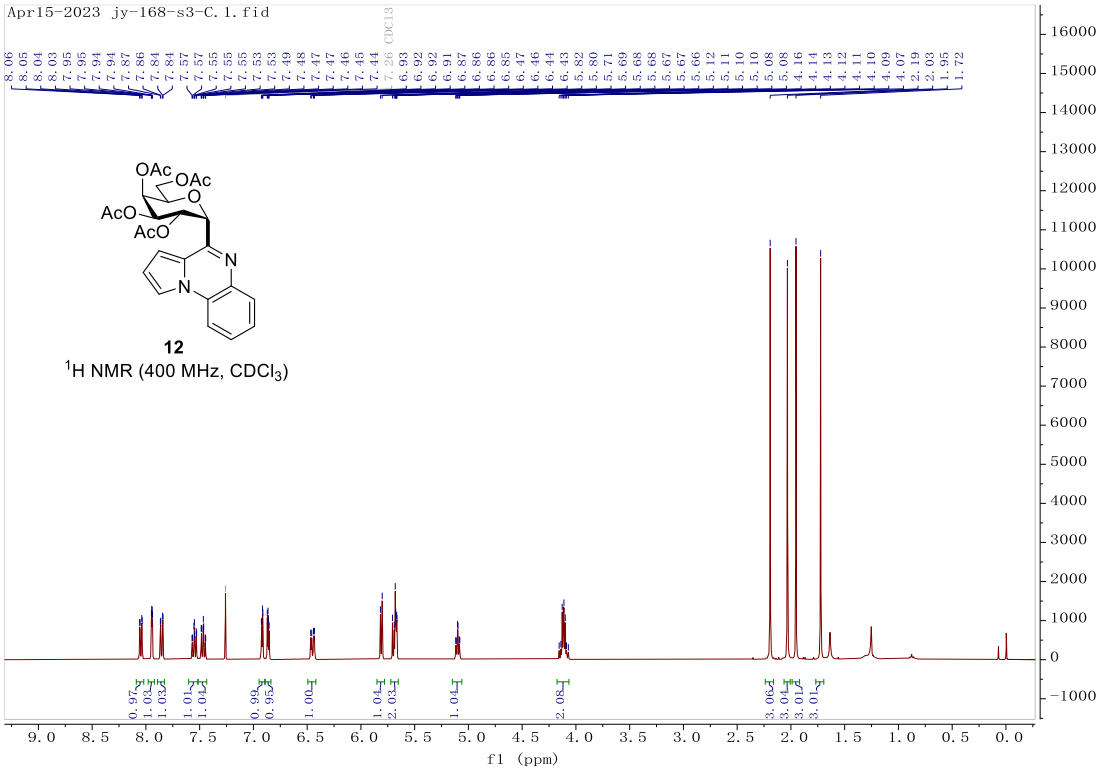

May16-2023 jy-3-148-s5-C.11.fid
OAc
OAc
O
AcO
AcO
MeO
MeO
N
Cl
9
13C NMR (101 MHz, CDCl3)
f1 (ppm)

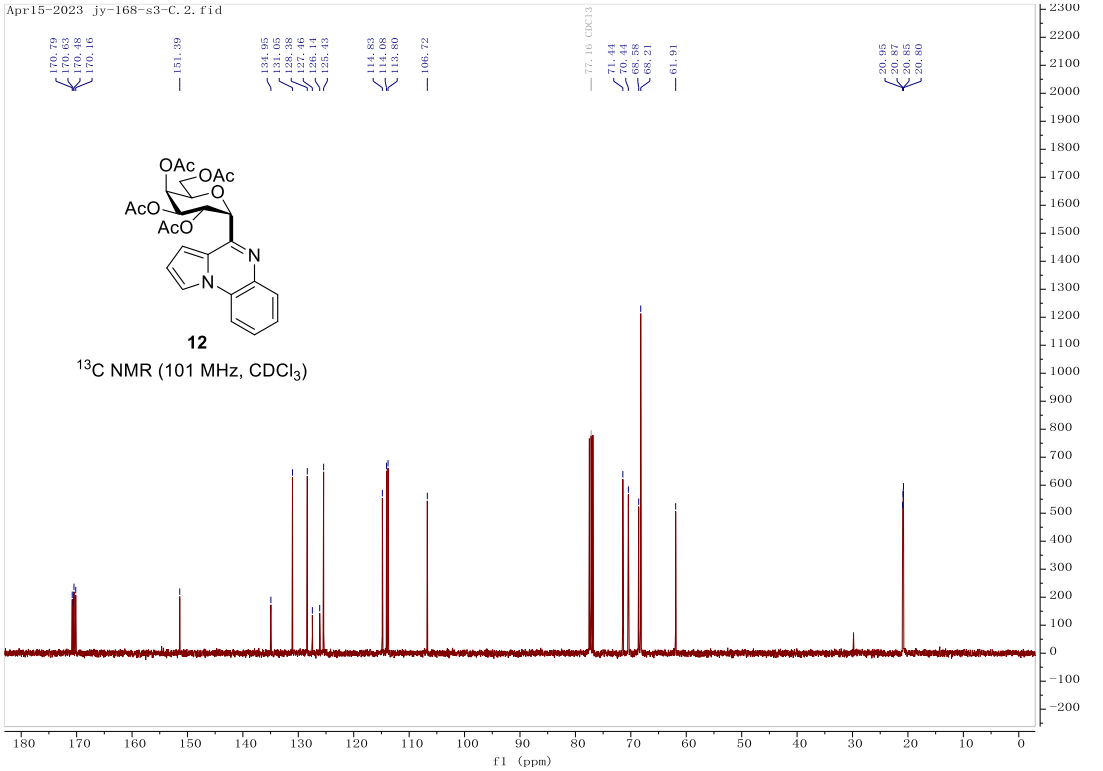

Jan04-2023 jy-3-151-s.10.fid
OAc
OAc
O
AcO
AcO
MeO
MeO
N
F
10
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

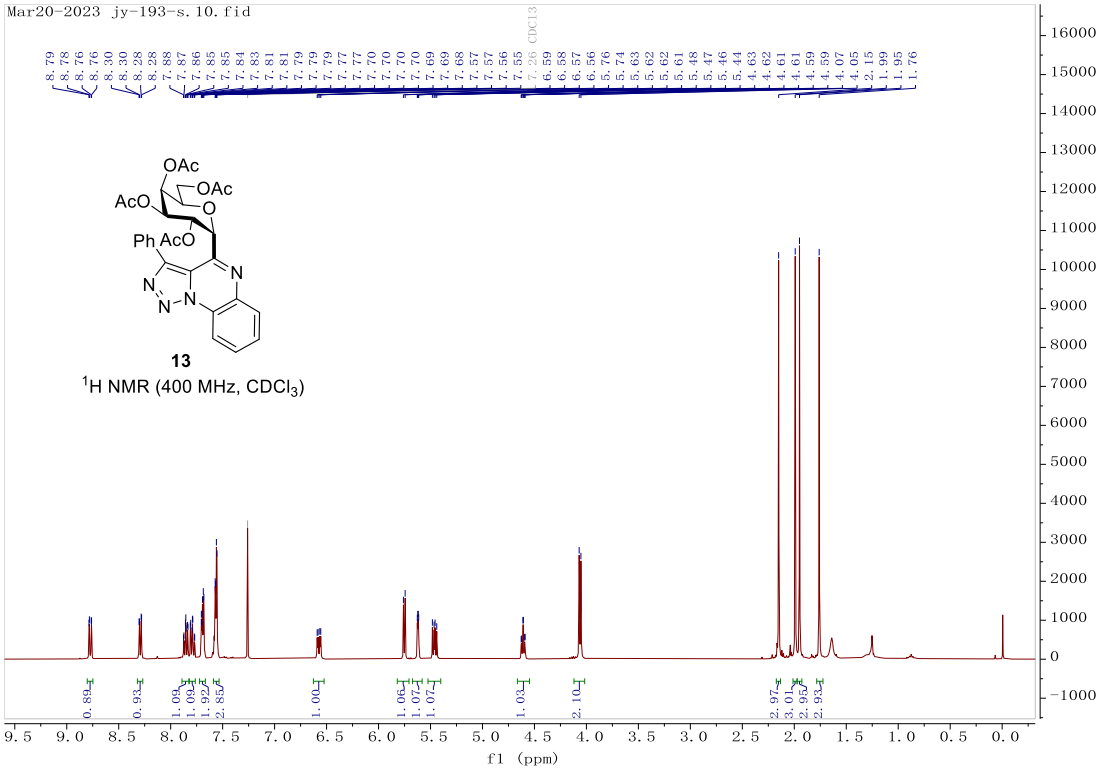

Jan05-2023 jy-151-s-C.10.fid
OAc
OAc
O
AcO
AcO
MeO
MeO
N
F
10
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)


Jun05-2023 jy-157-ss2.10.fid
OAc
OAc
AcO
AcO
MeO
MeO
N
NC
11
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Jun05-2023 jy-157-ss2.11.fid
OAc
OAc
AcO
AcO
MeO
MeO
N
NC
11
13C NMR (101 MHz, CDCl3)
f1 (ppm)


Apr15-2023 jy-168-s3-C.1.fid
OAc
OAc
AcO
AcO
O
N
N
12
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Apr15-2023 jy-168-s3-C.2.fid
OAc
OAc
AcO
AcO
O
N
N
12
13C NMR (101 MHz, CDCl3)
f1 (ppm)


Mar20-2023 jy-193-s.10.fid
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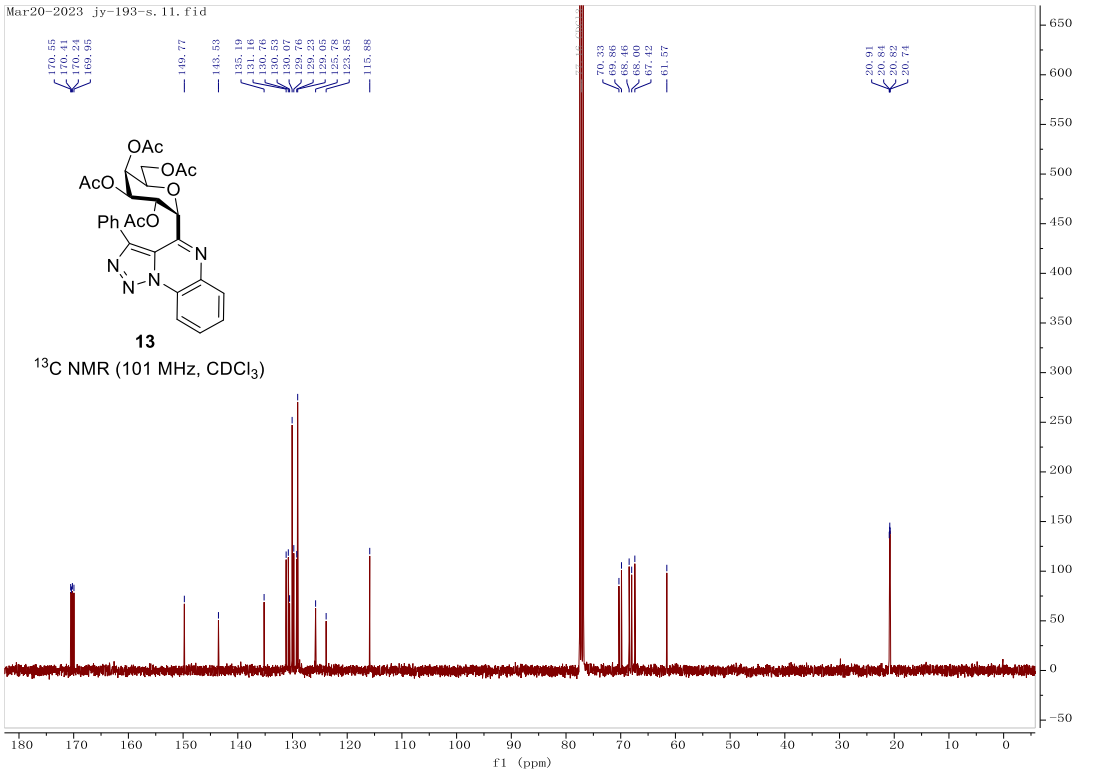
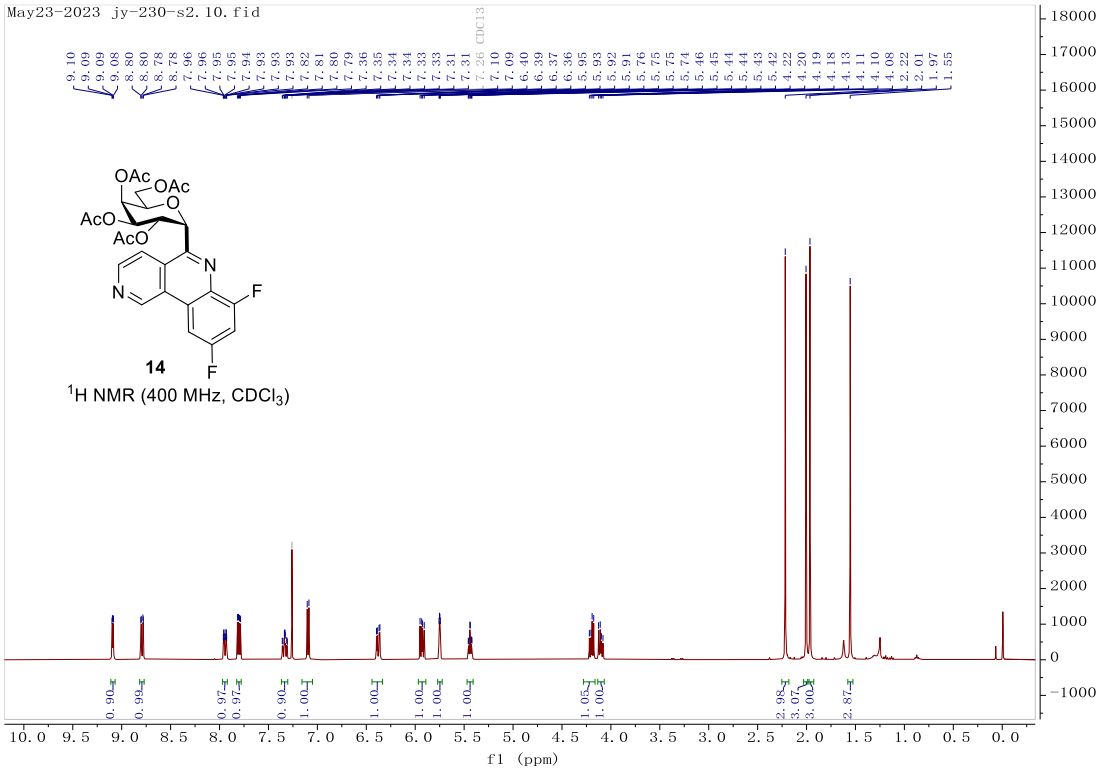
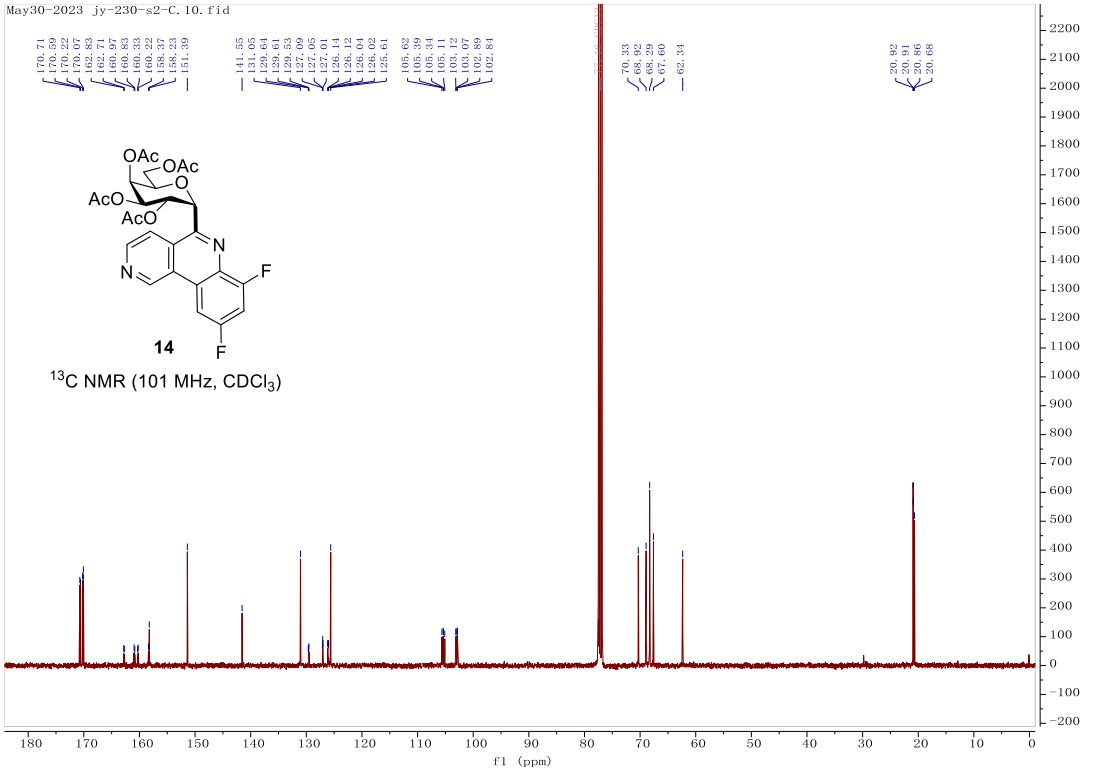
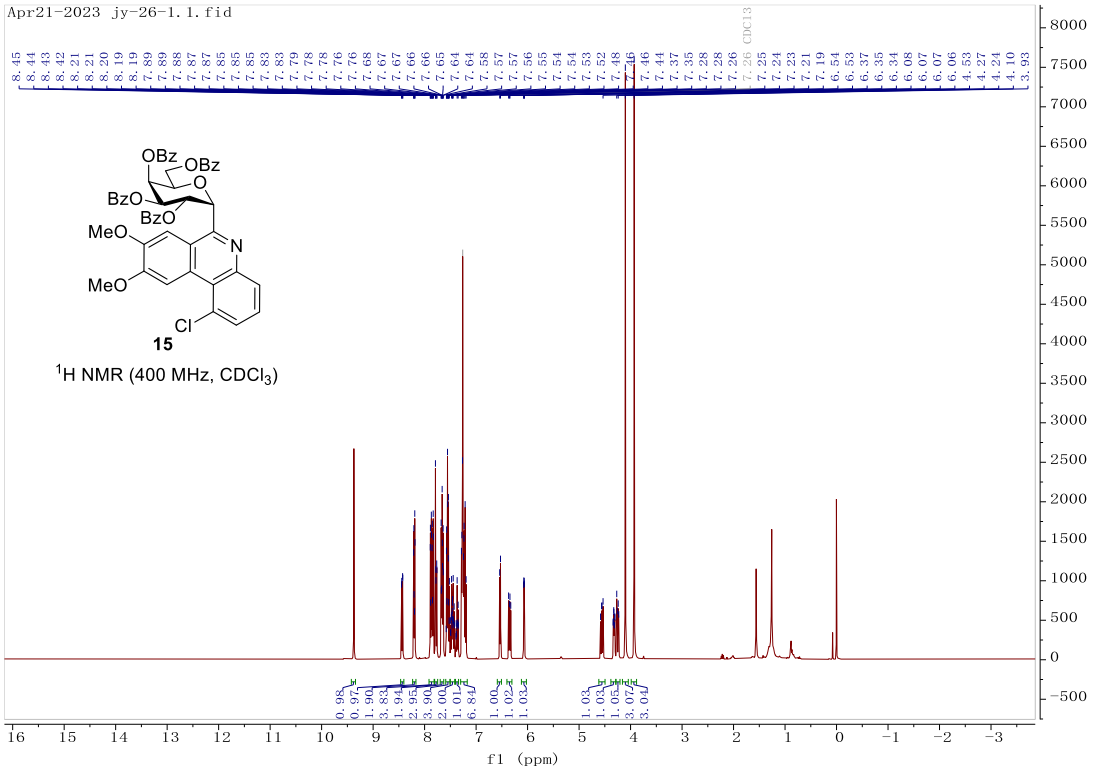
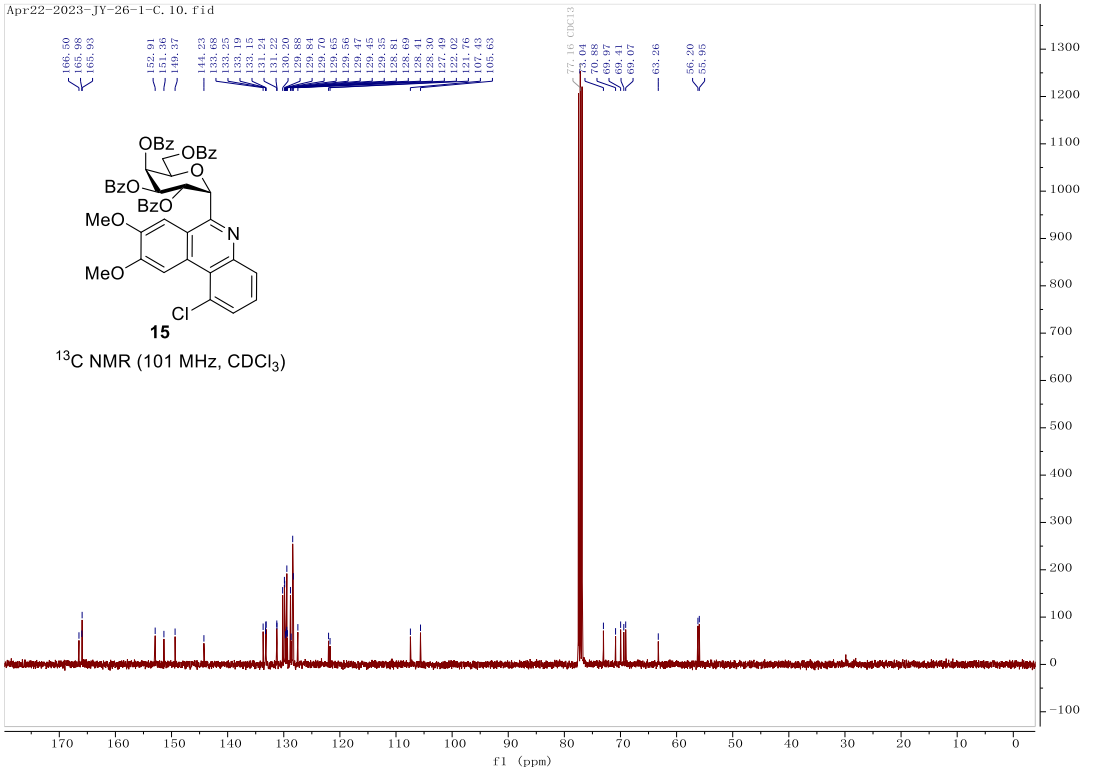
OAc
AcO
O
Ph AcO
N
N
N
13
1H NMR (400 MHz, CDCl3)
f1 (ppm)

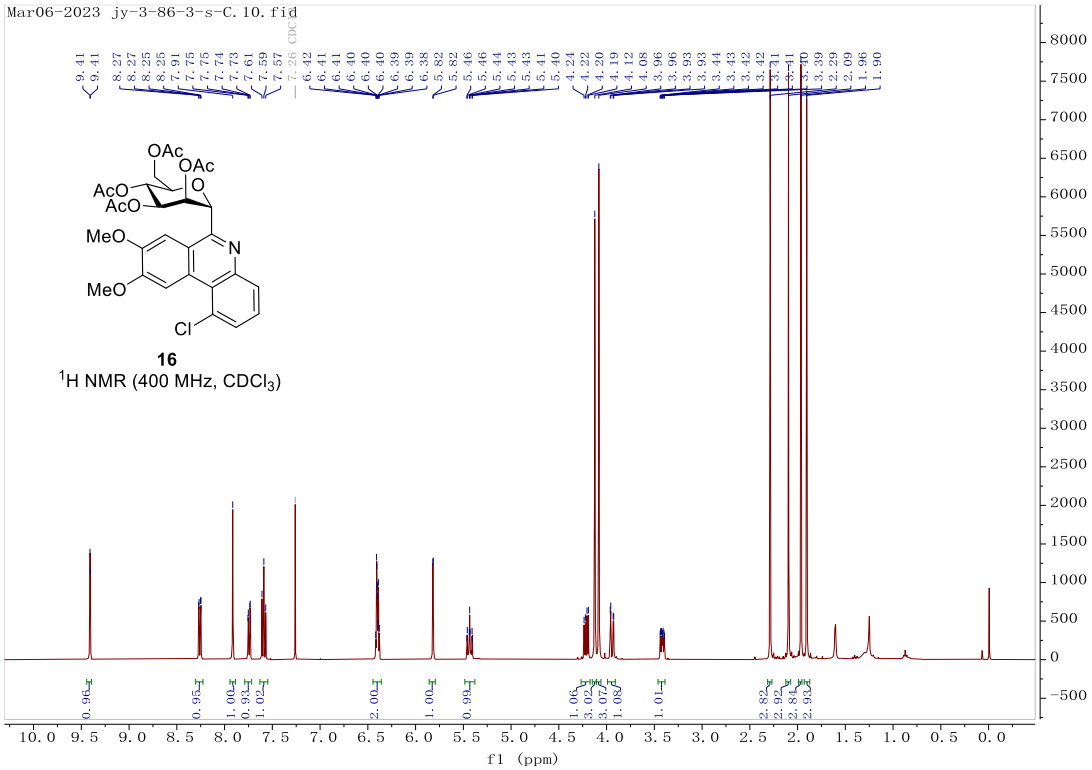

Mar20-2023 jy-193-s.11.fid
OAc
OAc
AcO
O
Ph AcO
N
N
N
13
13C NMR (101 MHz, CDCl3)
f1 (ppm)

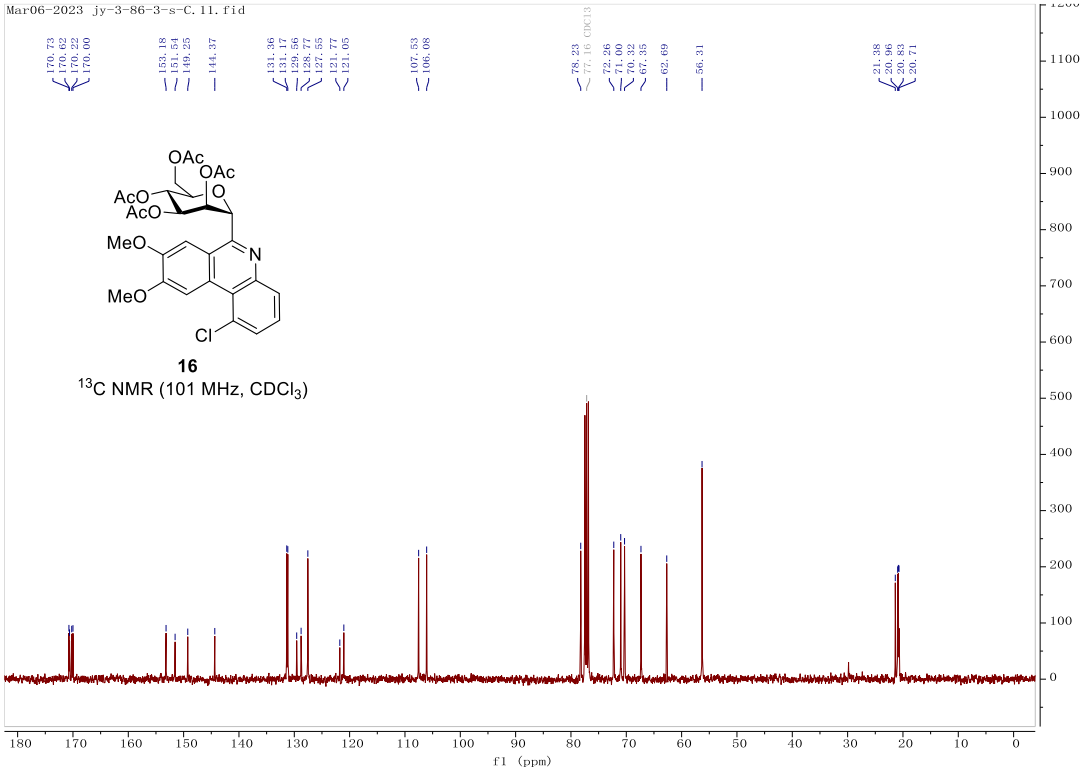

May23-2023 jy-230-s2.10.fid
14
1H NMR (400 MHz, CDCl3)
f1 (ppm)

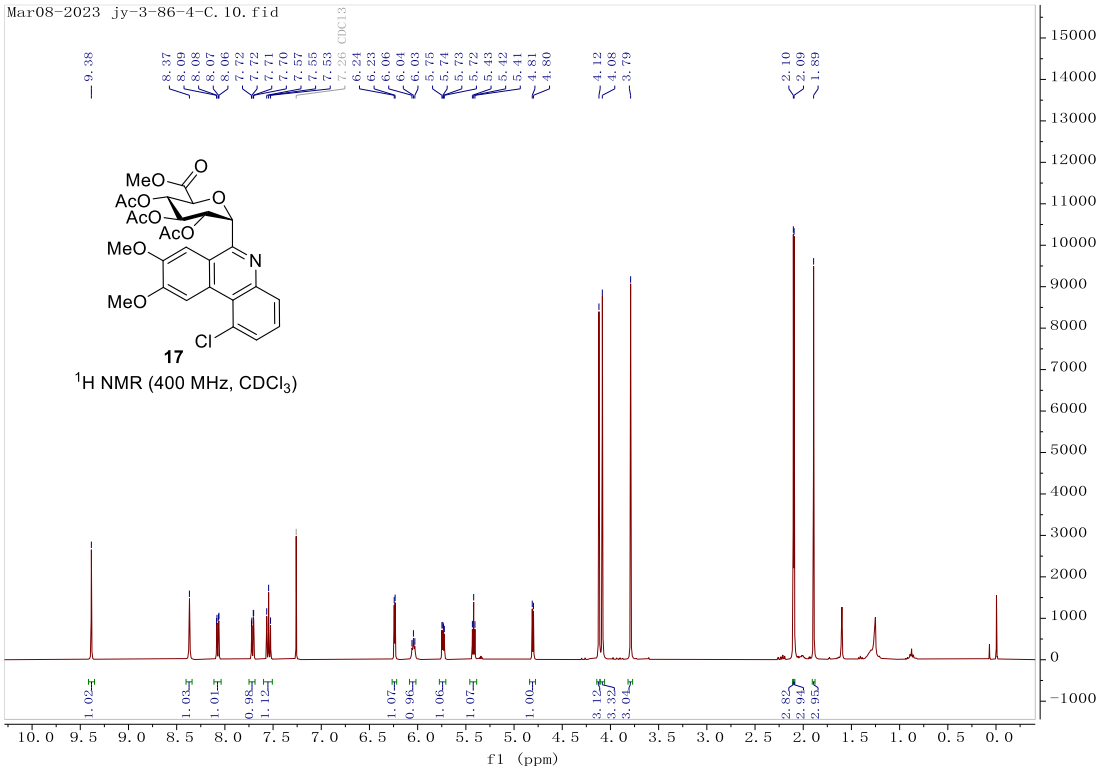

May30-2023 jy-230-s2-C.10.fid
14
13C NMR (101 MHz, CDCl3)
f1 (ppm)


Apr21-2023 jy-26-1.1.fid
OBz
OBz
O
BzO
BzO
MeO
MeO
N
Cl
15
1H NMR (400 MHz, CDCl3)
f1 (ppm)

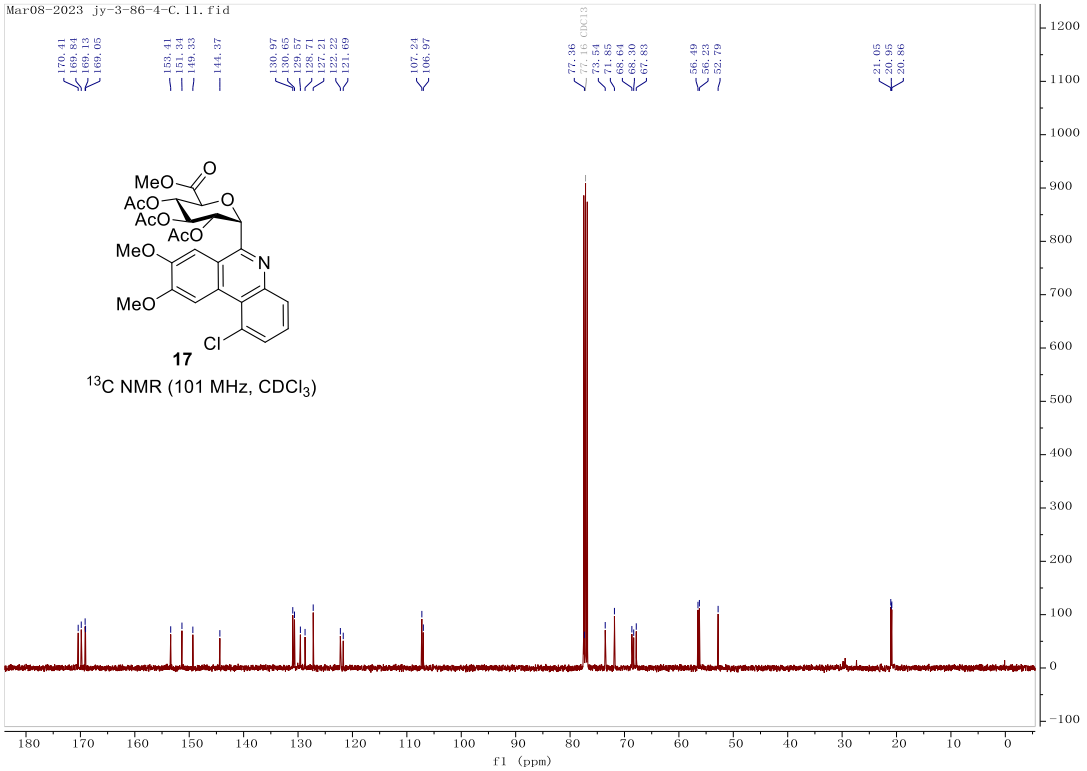

Apr22-2023-JY-26-1-C.10.fid
OBz
OBz
O
BzO
BzO
MeO
MeO
N
Cl
15
13C NMR (101 MHz, CDCl3)
f1 (ppm)


Mar06-2023 jy-3-86-3-s-C. 10. fid
OAc
OAc
AcO
AcO
O
MeO
MeO
N
Cl
16
1H NMR (400 MHz, CDCl3)
f1 (ppm)

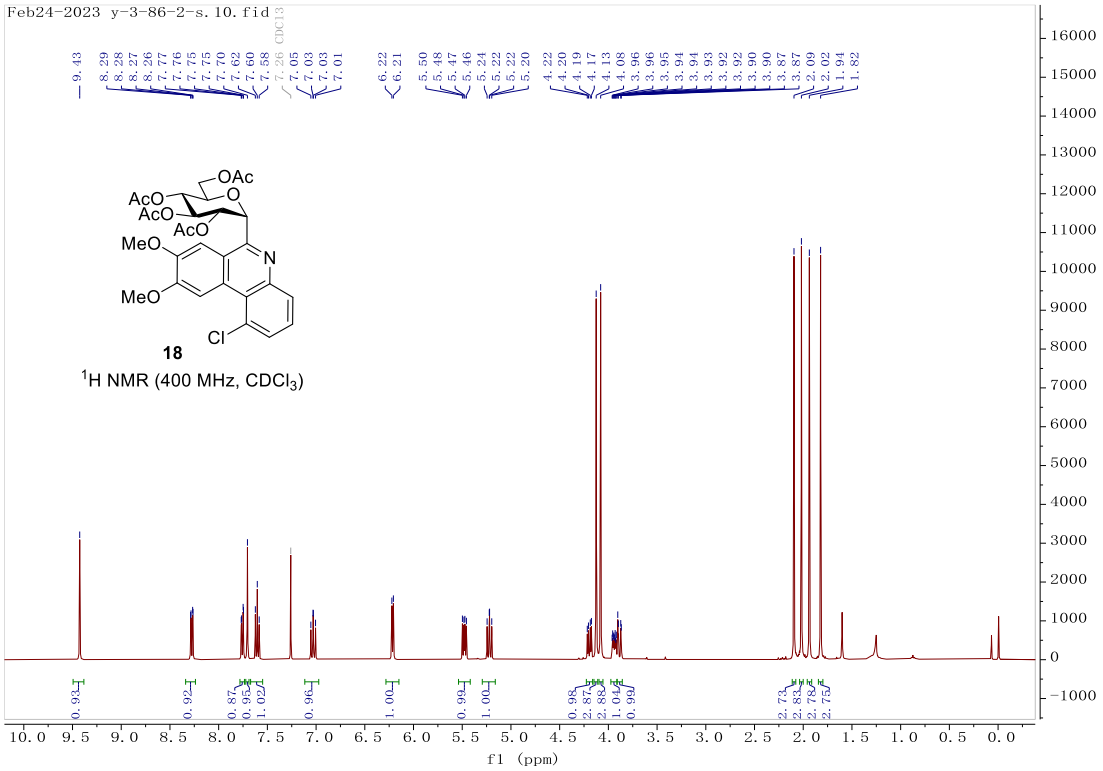

Mar06-2023 jy-3-86-3-s-C. 11. fid
OAc
OAc
AcO
AcO
O
MeO
MeO
N
Cl
16
13C NMR (101 MHz, CDCl3)
f1 (ppm)

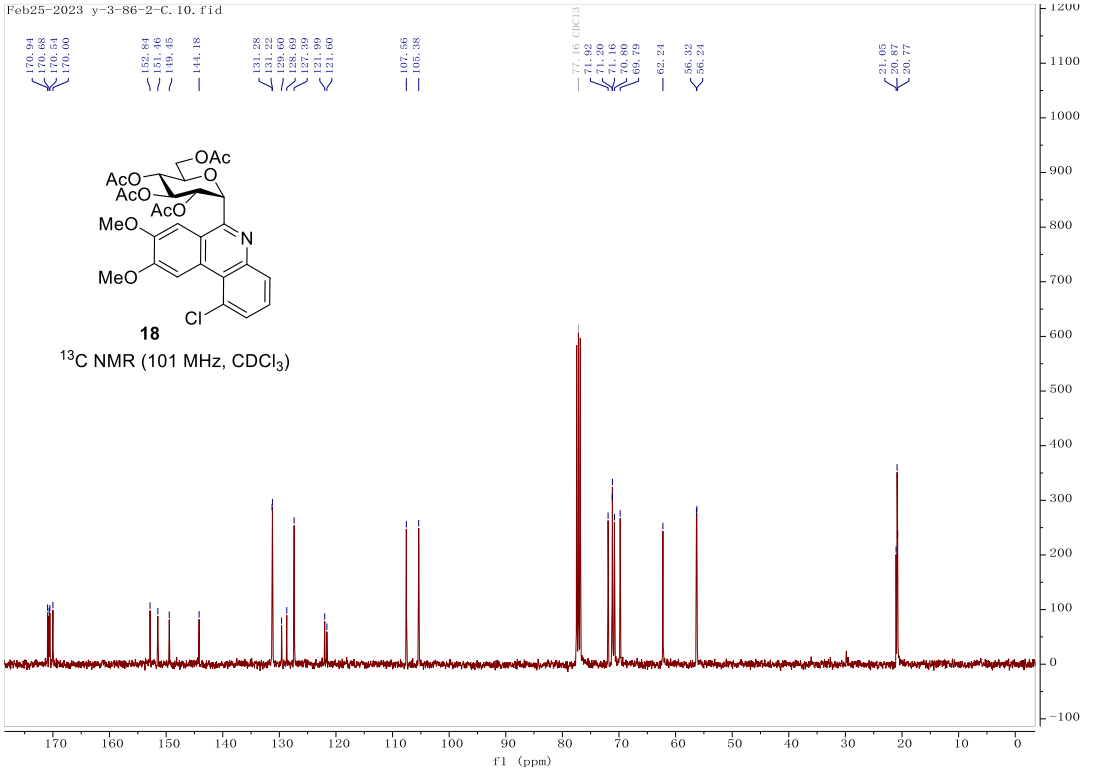


^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)


Feb24-2023 y-3-86-2-s.10.fid
OAc
AcO
AcO
AcO
MeO
MeO
N
Cl
18
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)


Feb25-2023 y-3-86-2-C.10.fid
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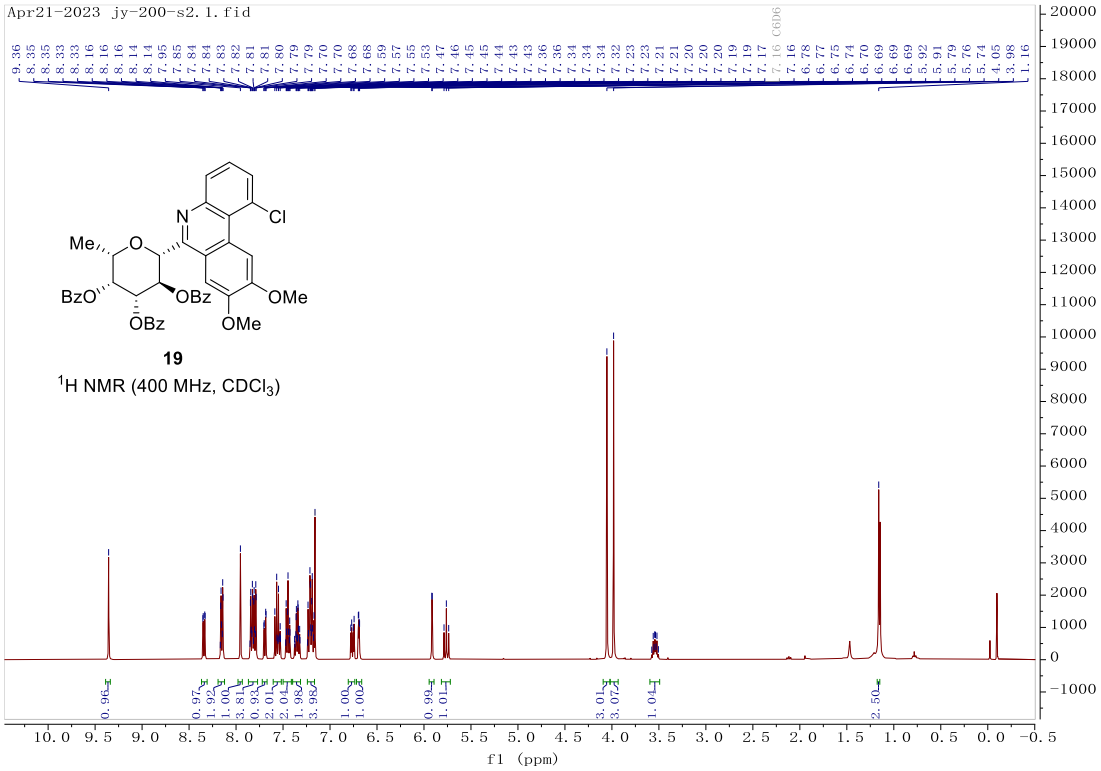
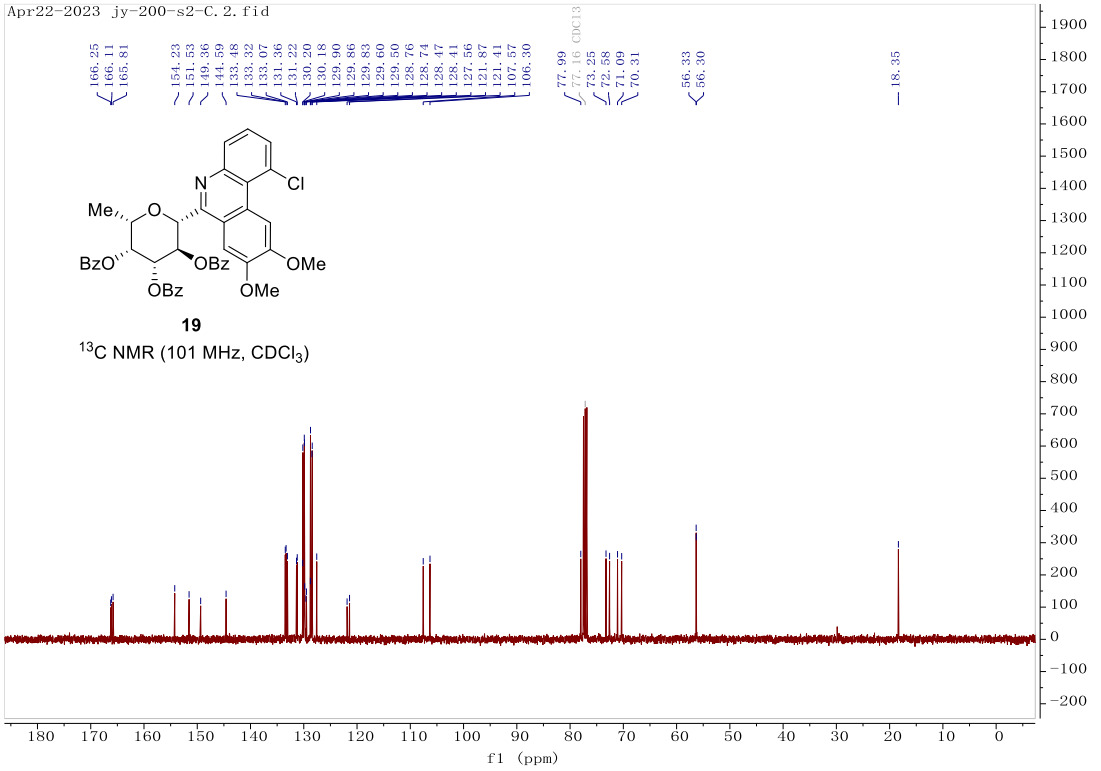
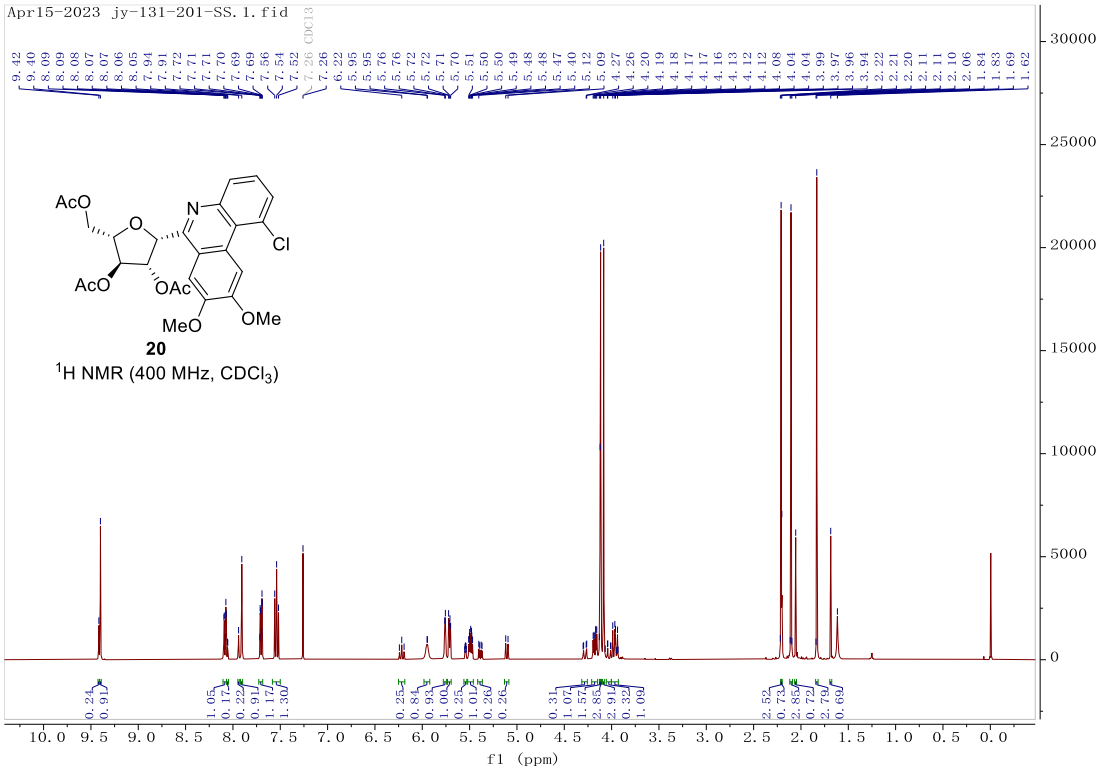
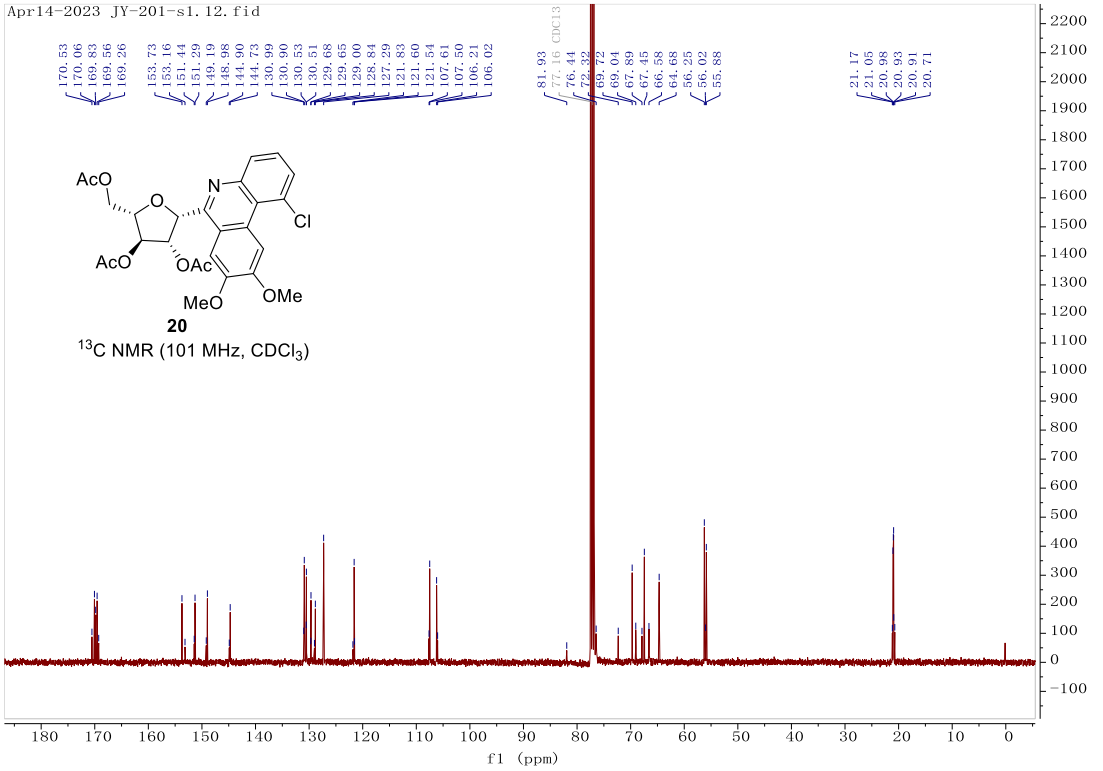
AcO
AcO
AcO
MeO
MeO
N
Cl
18
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)


Apr21-2023 jy-200-s2.1.fid
Me
O
N
Cl
BzO
OBz
OBz
OMe
OMe
19
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Apr22-2023 jy-200-s2-C.2.fid
Me
O
N
Cl
BzO
OBz
OBz
OMe
OMe
19
13C NMR (101 MHz, CDCl3)
f1 (ppm)


Apr15-2023 jy-131-201-SS.1.fid
AcO
AcO
OAc
MeO
OMe
N
O
Cl
20
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Apr14-2023 JY-201-s1.12.fid
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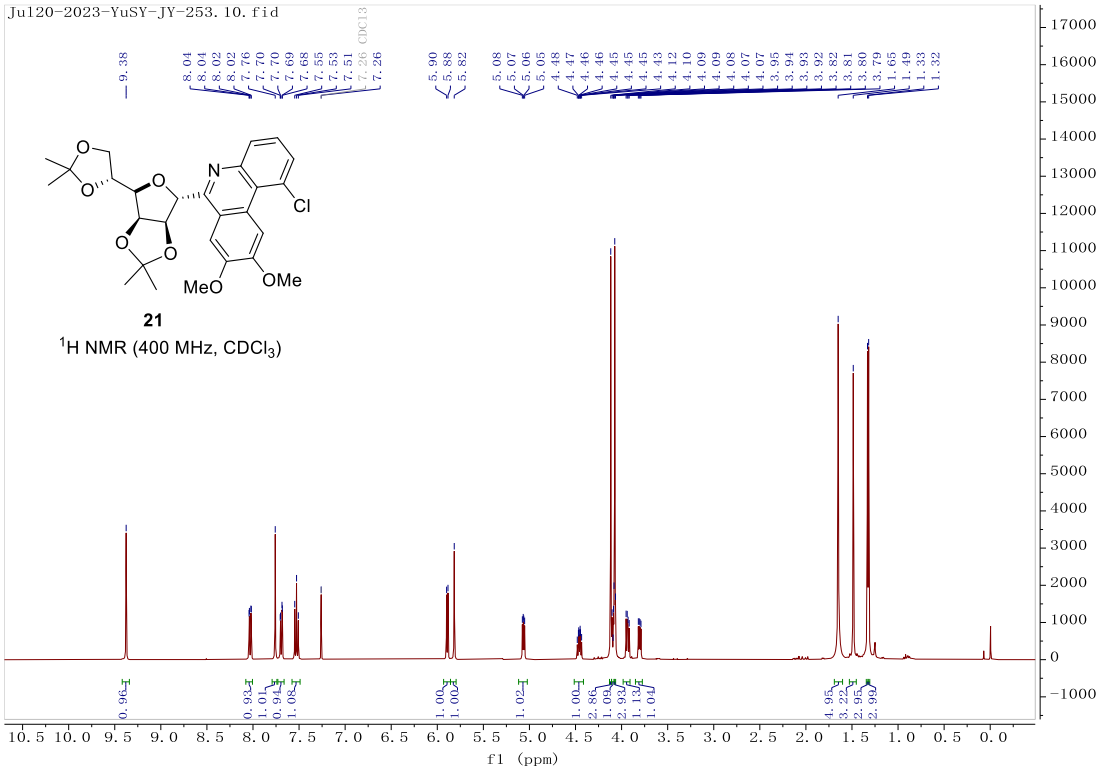
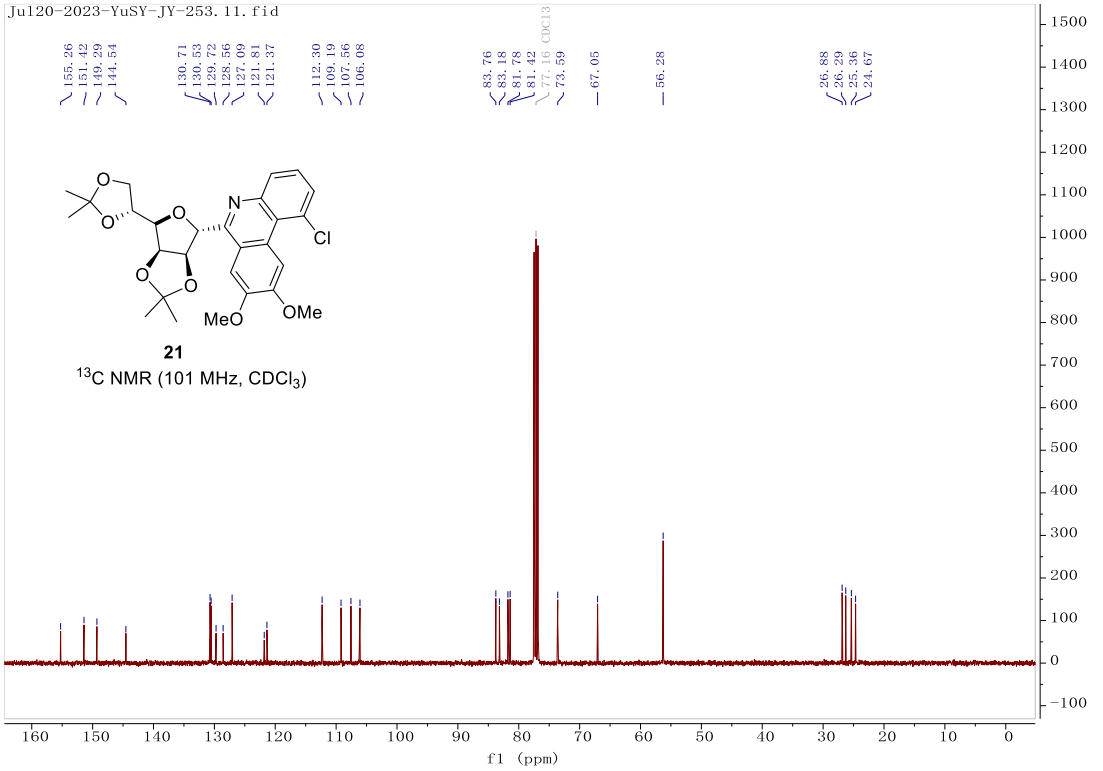
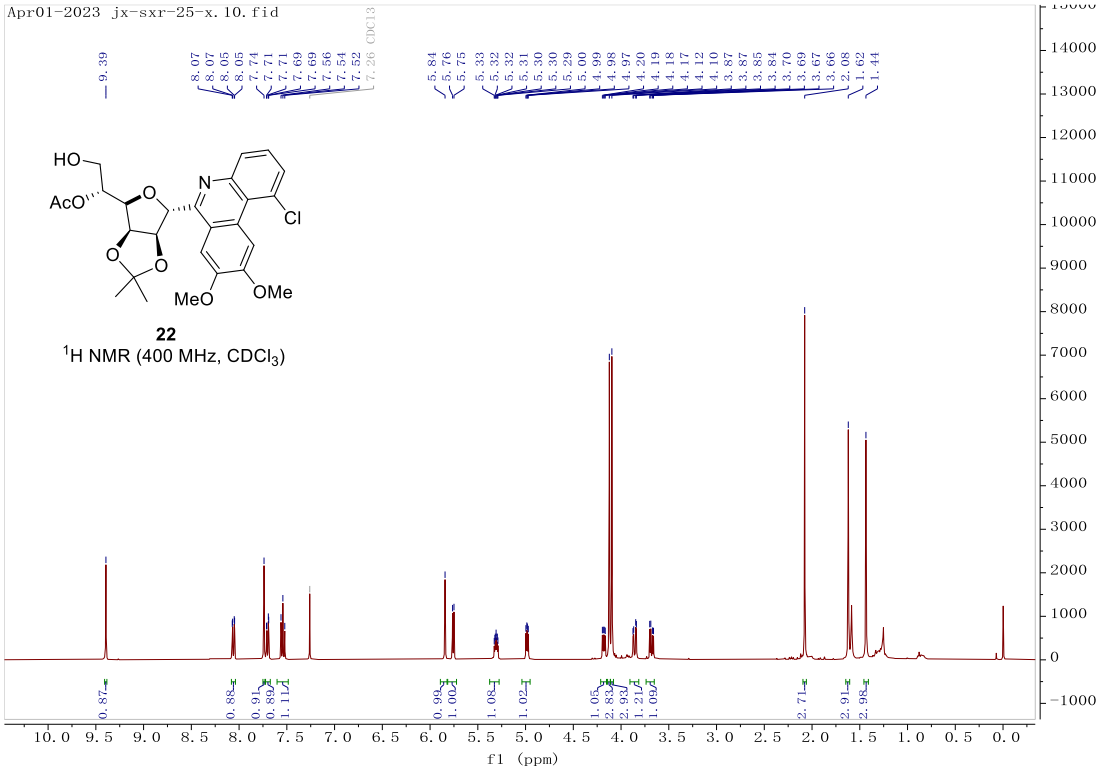
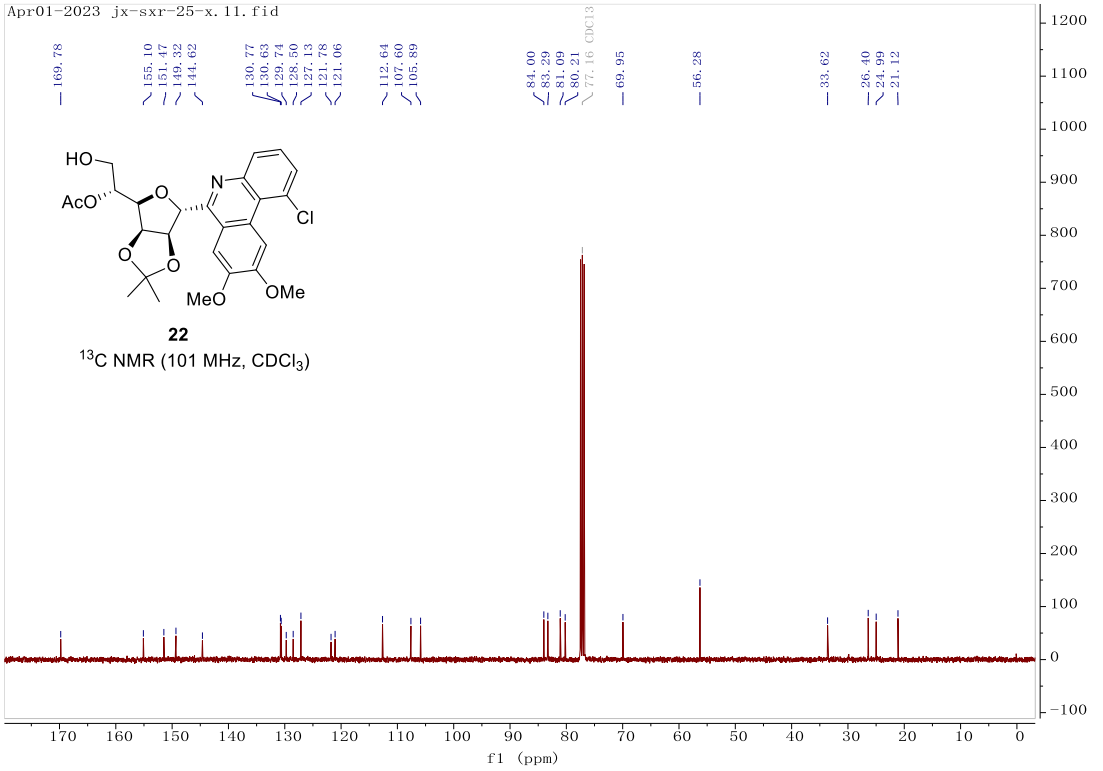
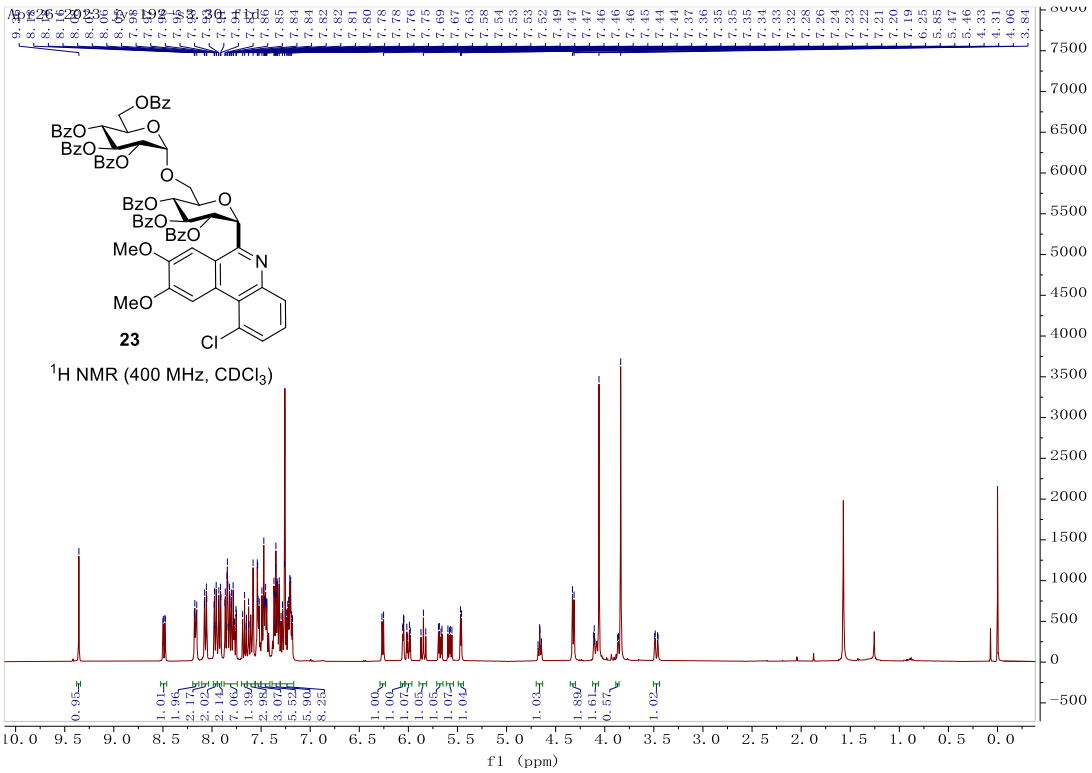
AcO
OAc
MeO
OMe
N
O
Cl
20
13C NMR (101 MHz, CDCl3)
f1 (ppm)

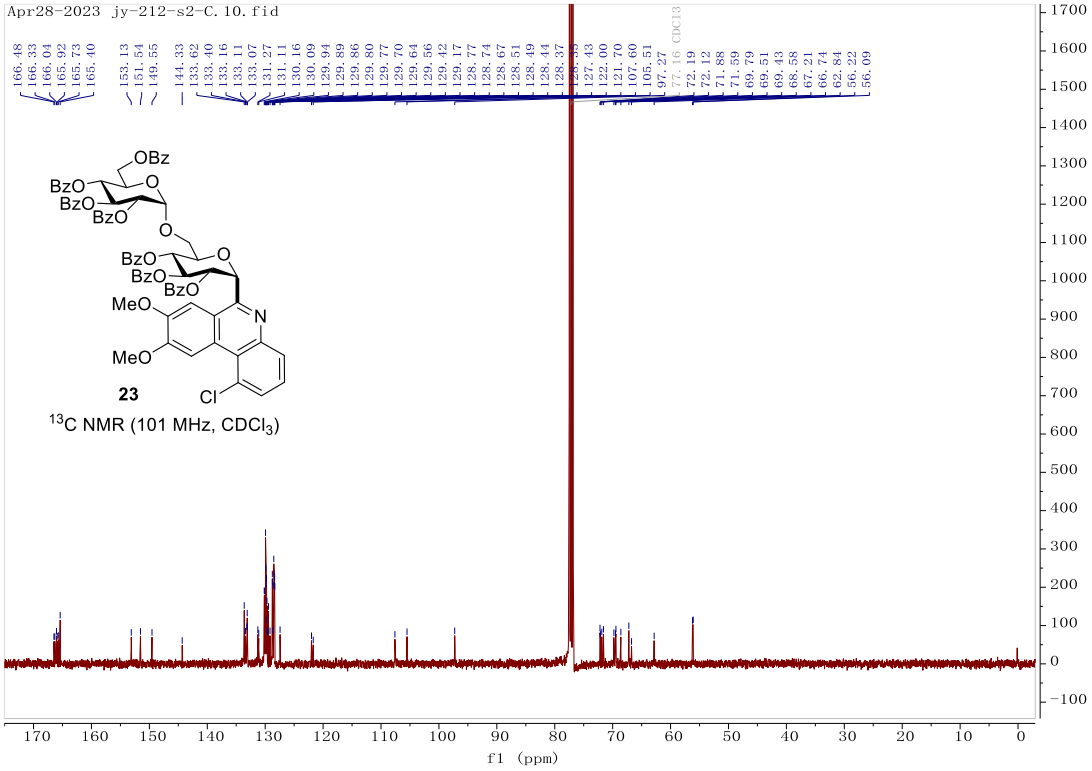

Jul20-2023-YuSY-JY-253.10.fid
21
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

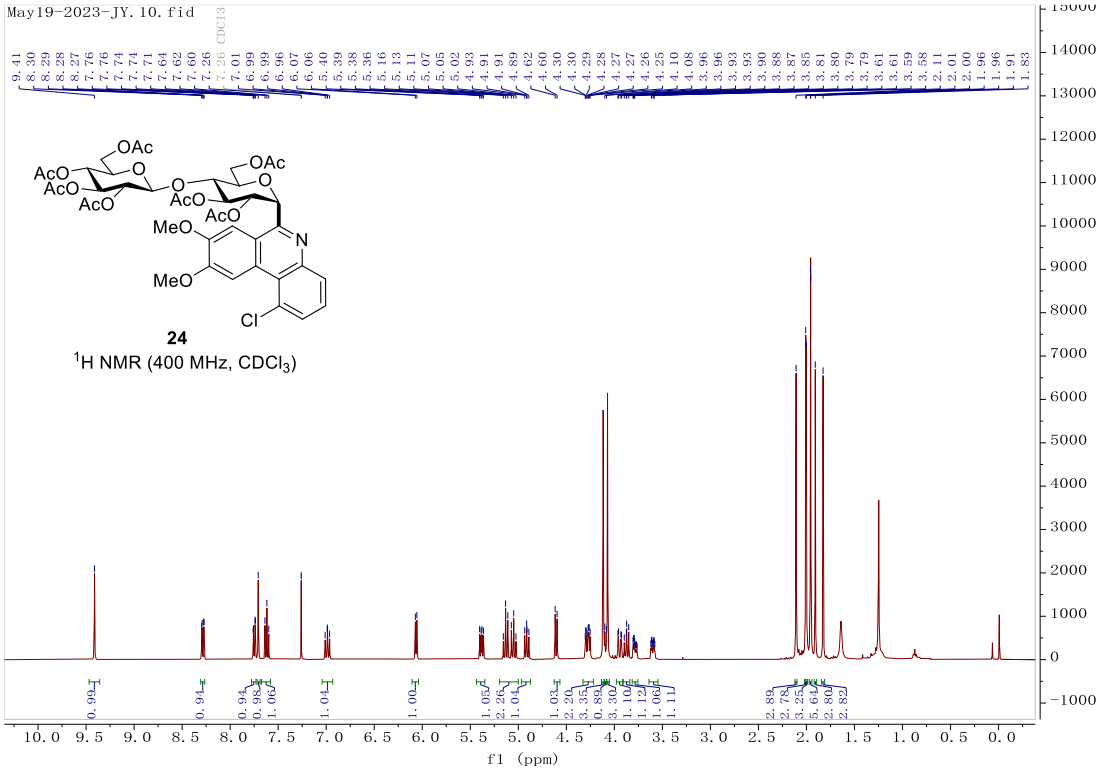

Jul20-2023-YuSY-JY-253.11.fid
21
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)

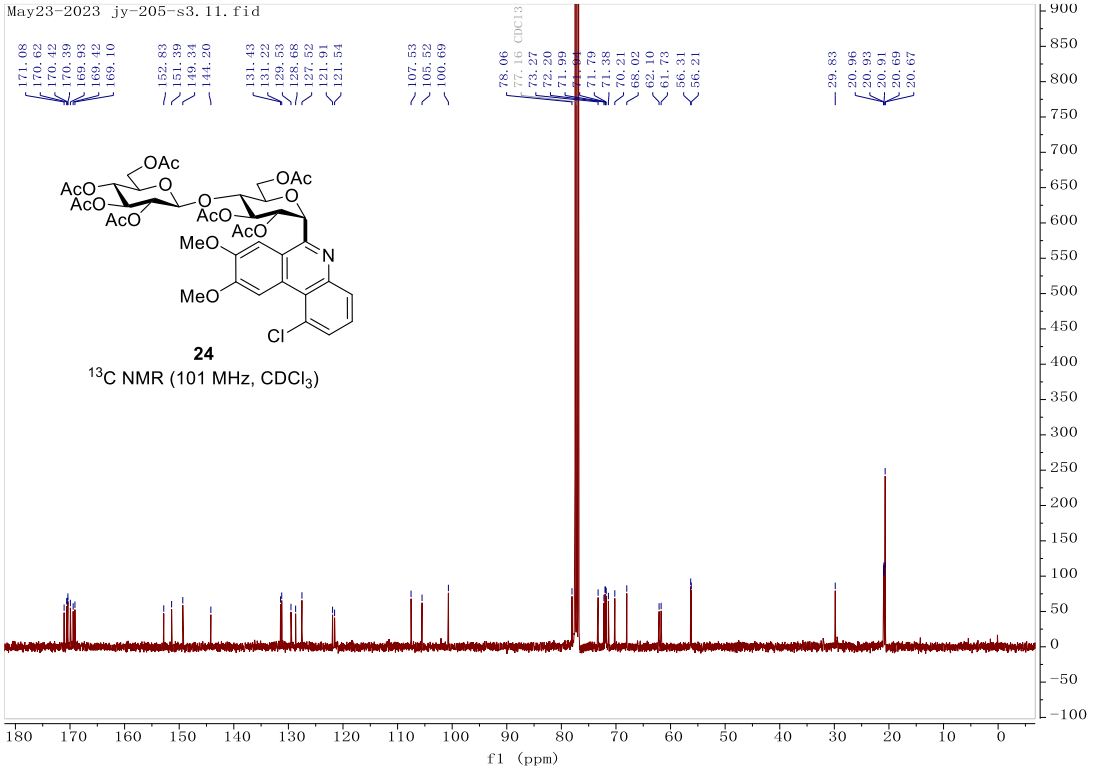

Apr01-2023 jx-sxr-25-x.10.fid
HO
AcO
O
N
Cl
O
O
MeO
OMe
22
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

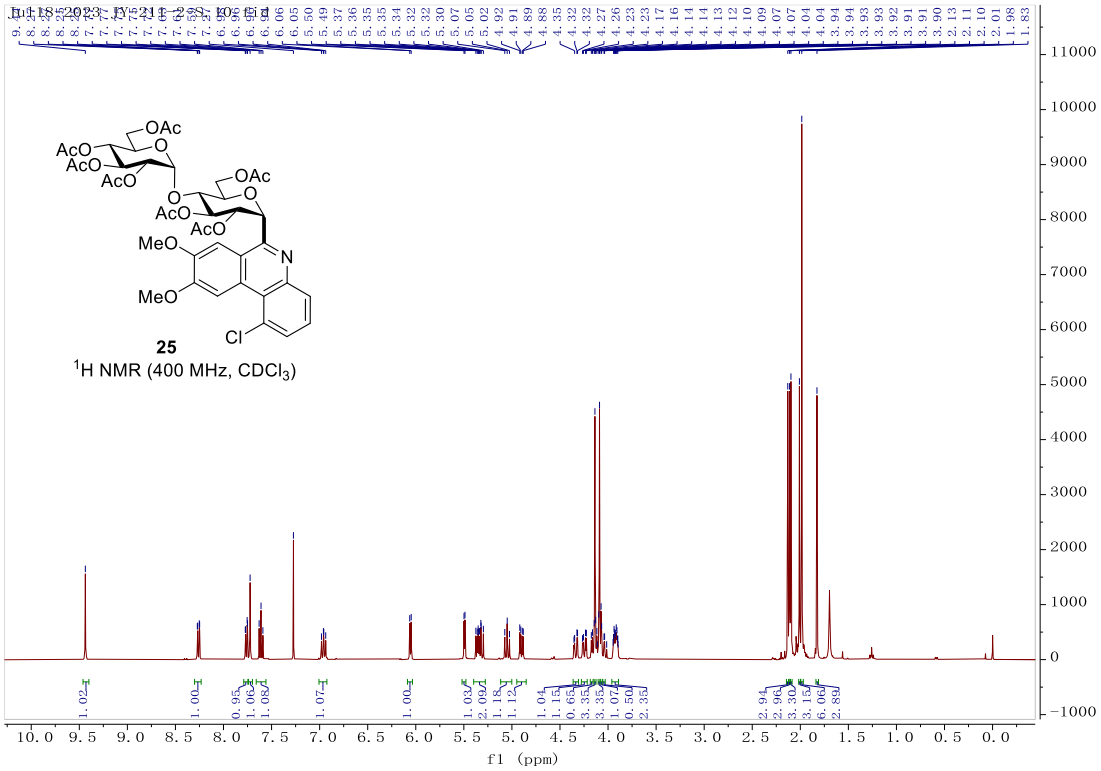

Apr01-2023 jx-sxr-25-x.11.fid
HO
AcO
O
N
Cl
O
O
MeO
OMe
22
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)

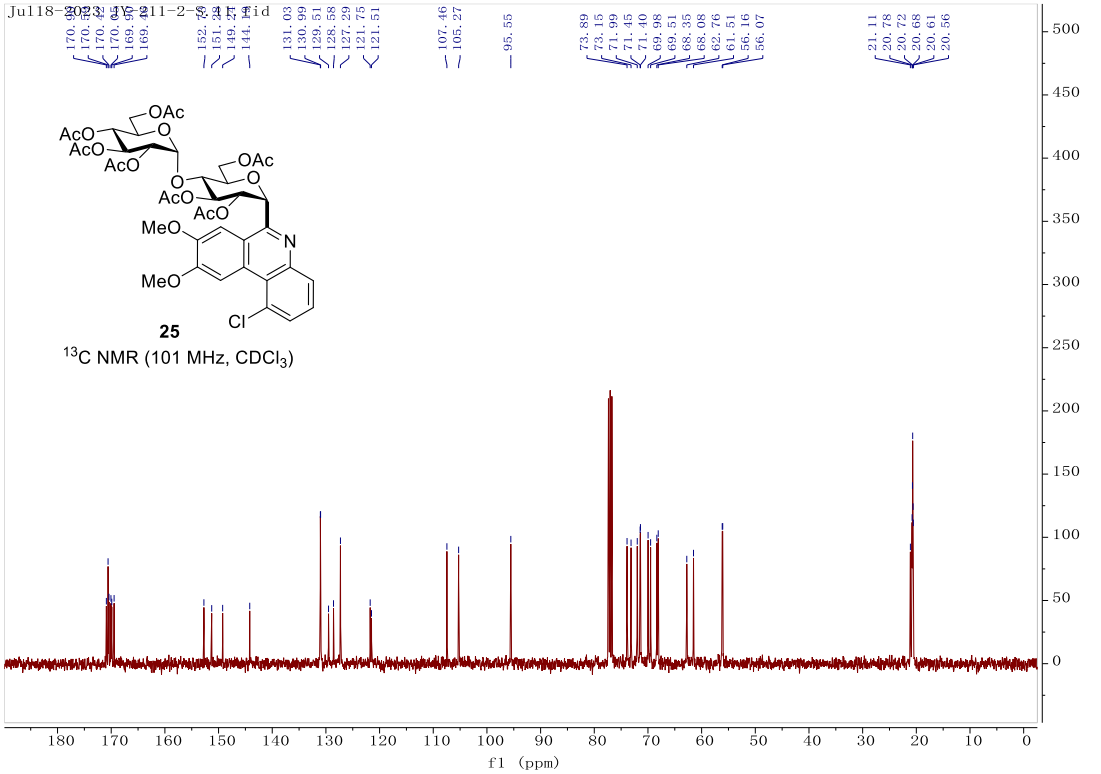

OBz
BzO
BzO
BzO
O
MeO
MeO
N
Cl
23
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

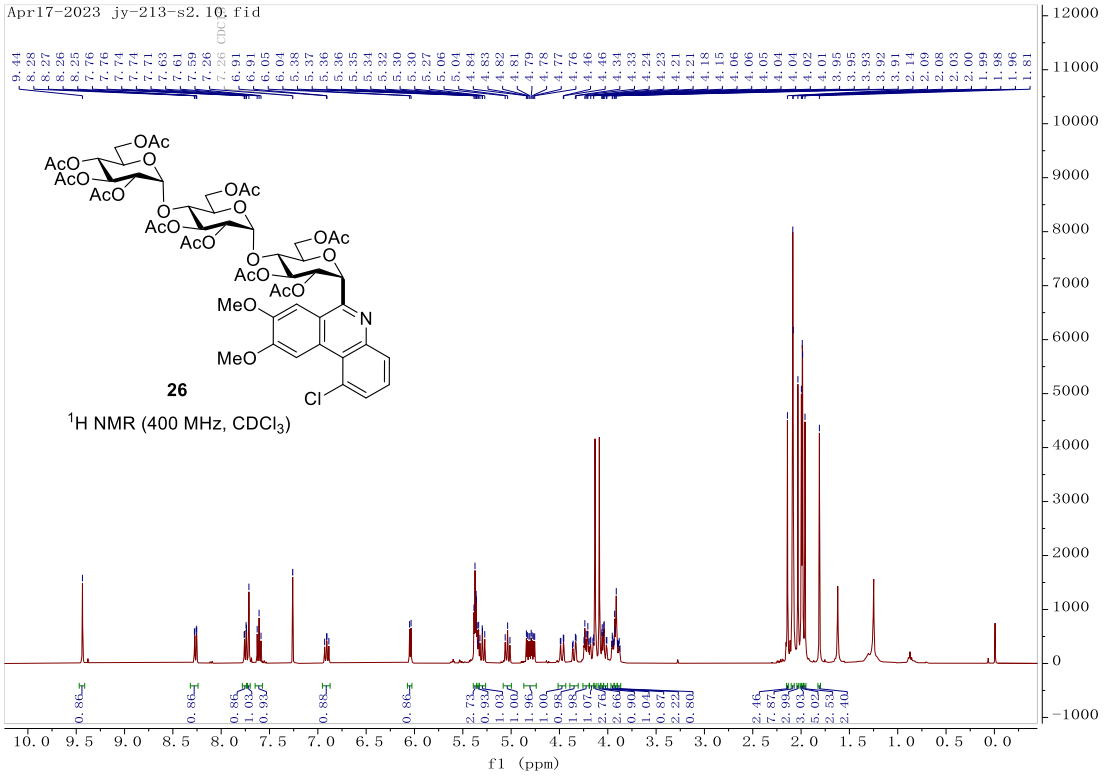

Apr28-2023 jy-212-s2-C.10.fid
OBz
BzO
BzO
BzO
O
MeO
MeO
N
Cl
23
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)

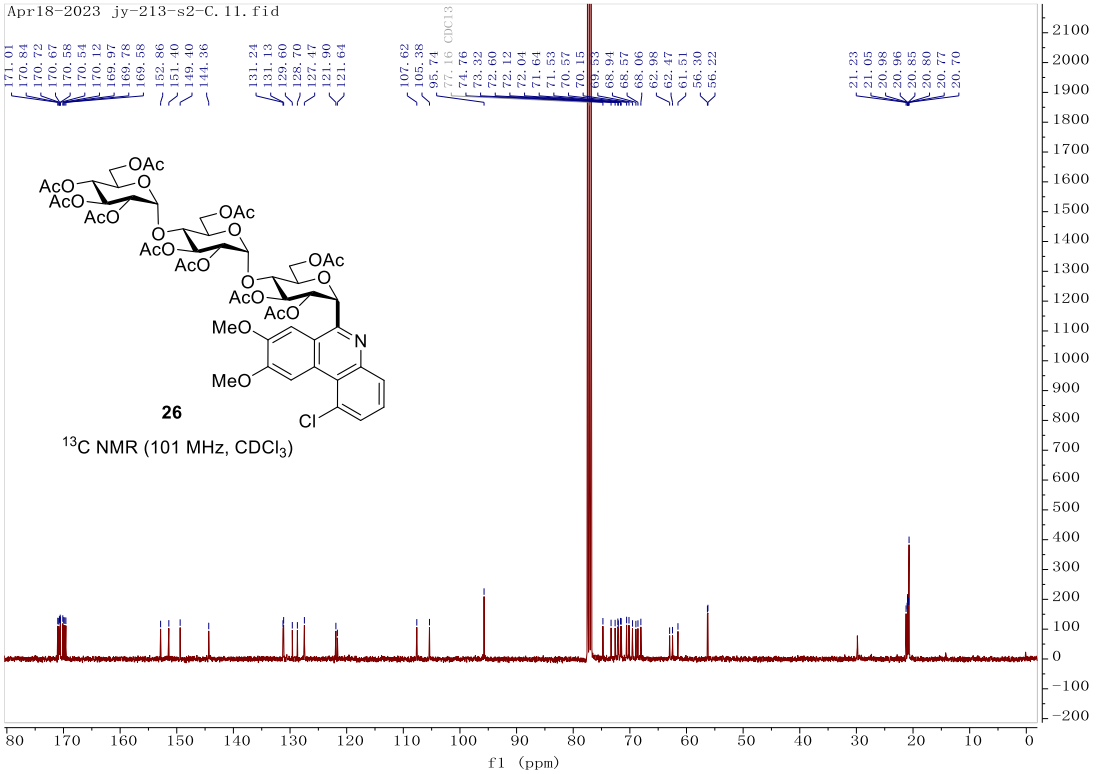

May19-2023-JY.10.fid
24
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

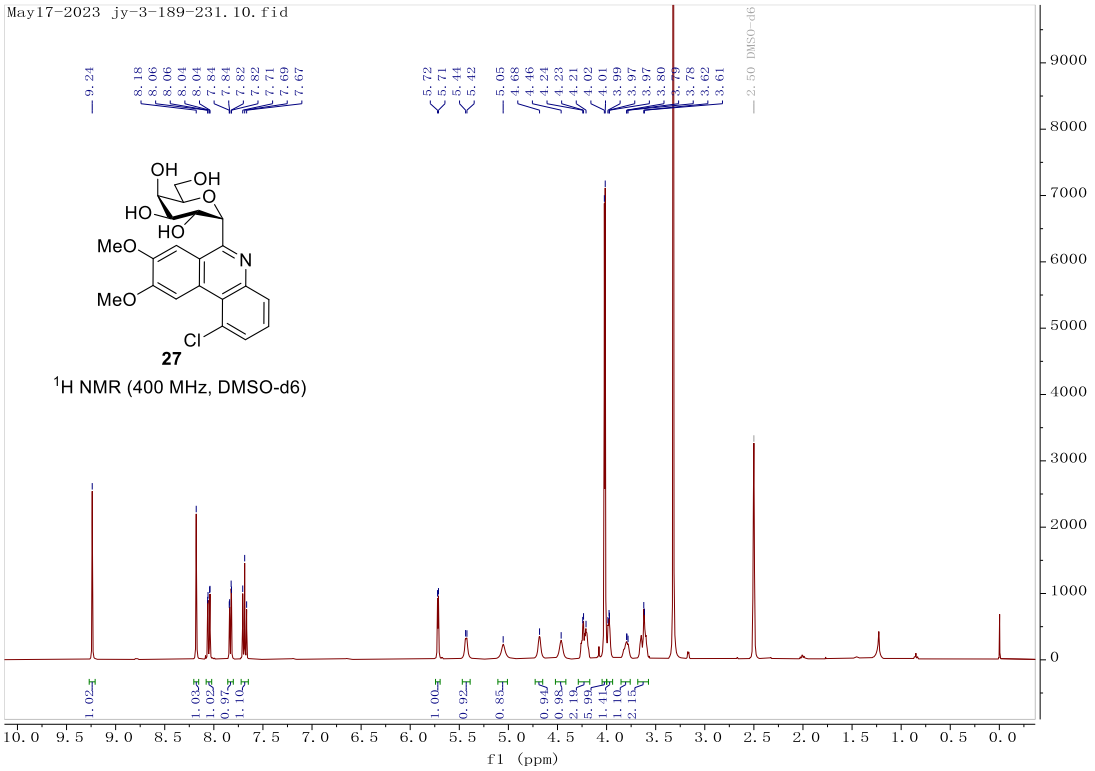

May23-2023 jy-205-s3.11.fid
24
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)

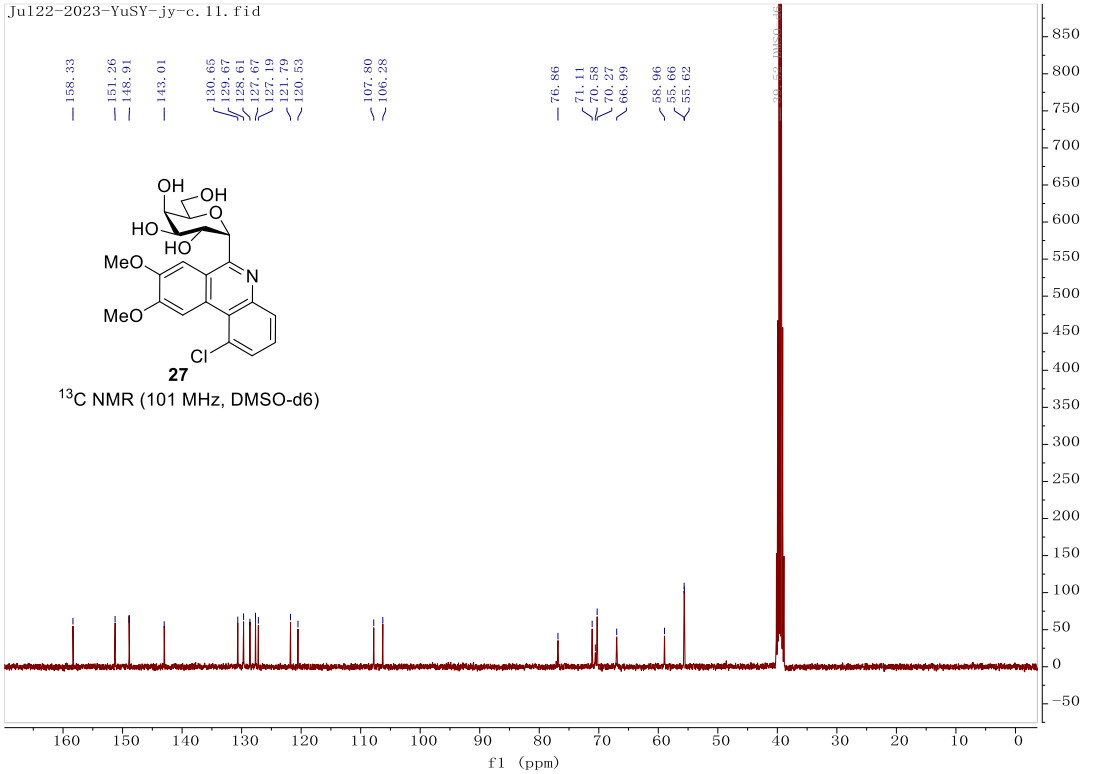

OAc
AcO
AcO
AcO
OAc
O
AcO
AcO
MeO
MeO
N
Cl
25
1H NMR (400 MHz, CDCl3)
f1 (ppm)

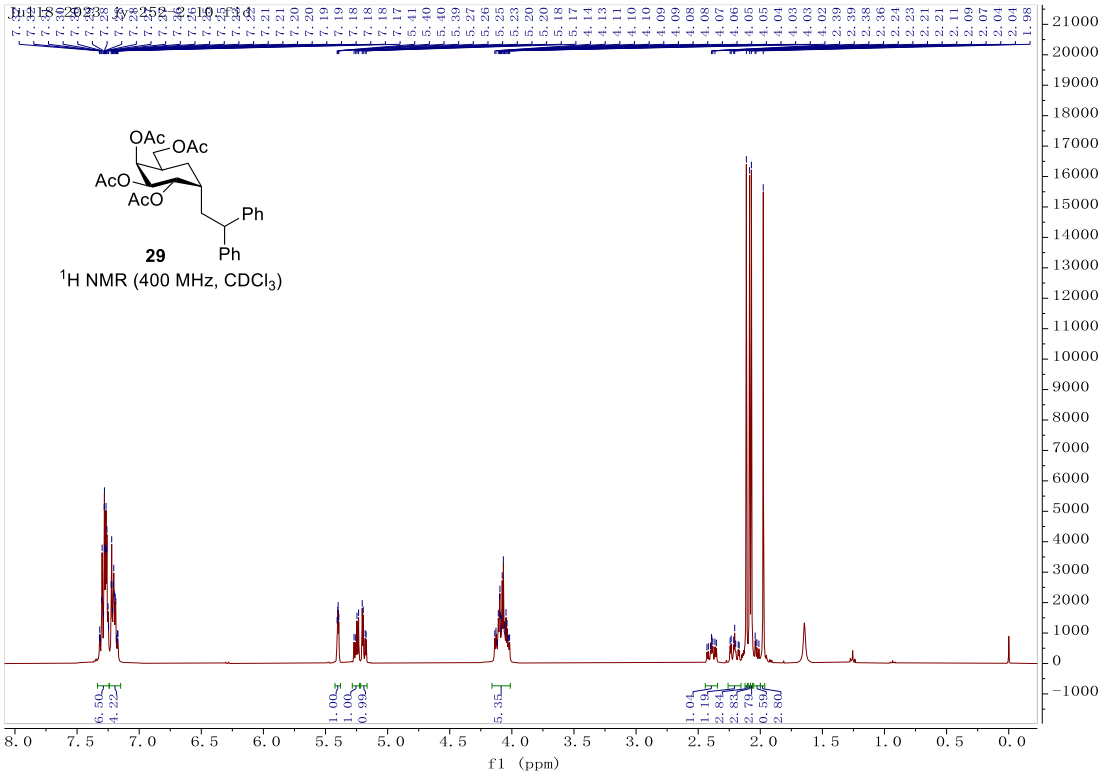

OAc
AcO
AcO
AcO
OAc
O
AcO
AcO
MeO
MeO
N
Cl
25
13C NMR (101 MHz, CDCl3)
f1 (ppm)

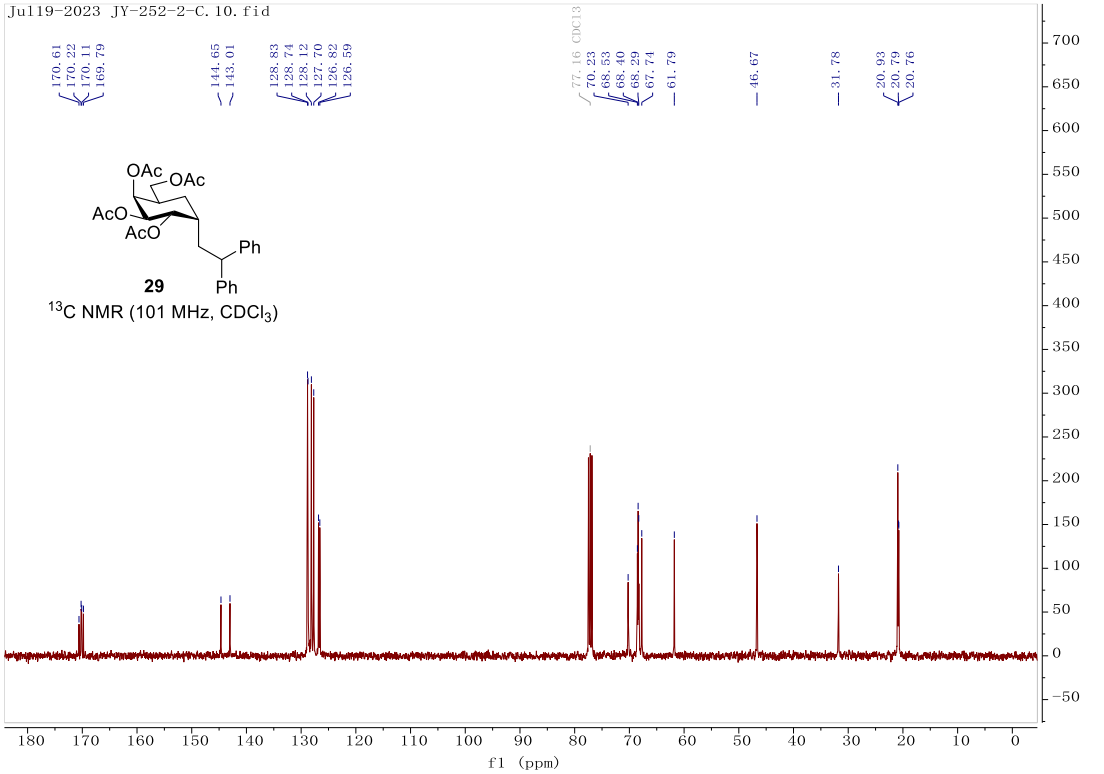

Apr17-2023 jy-213-s2.10.fid
26
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)


Apr18-2023 jy-213-s2-C.11.fid
26
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)


May17-2023 jy-3-189-231.10.fid
9.24
8.18
8.06
8.06
8.04
8.04
7.84
7.84
7.82
7.82
7.71
7.69
7.67
5.72
5.71
5.44
5.42
5.05
4.68
4.46
4.24
4.23
4.21
4.02
4.01
3.99
3.97
3.97
3.80
3.79
3.78
3.62
3.61
2.50 DMSO-d6
OH
OH
O
HO
HO
MeO
MeO
N
Cl
27
1H NMR (400 MHz, DMSO-d6)
f1 (ppm)


Jul22-2023-YuSY-jy-c.11.fid
158.33
151.26
148.91
143.01
130.65
129.67
128.61
127.67
127.19
121.79
120.53
107.80
106.28
76.86
71.11
70.58
70.27
66.99
58.96
55.66
55.62
39.52 DMSO-d6
OH
OH
O
HO
HO
MeO
MeO
N
Cl
27
13C NMR (101 MHz, DMSO-d6)
f1 (ppm)


OAc
OAc
AcO
AcO
Ph
Ph
29
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)


OAc
OAc
AcO
AcO
Ph
Ph
29
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)