Supporting Information

for

Total Synthesis of Indolocarbazole Alkaloid ZHD-0501 and its Seven Isomers

Liping Wang,[a,b,d†] Yapeng Zhang,[a†] Zhihong Xu,[a] Jing Li[a] and Weiming Zhu[*a,b,c]

[a] Key Laboratory of Marine Drugs, Chinese Ministry of Education, School of Medicine and Pharmacy, Ocean University of China, Qingdao 266003, China.

[b] State Key Laboratory of Functions and Applications of Medicinal Plants, Guizhou Medical University, Guiyang 550014, China.

[c] Laboratory for Marine Drugs and Bioproducts, Pilot National Laboratory for Marine Science and Technology (Qingdao), Qingdao 266237, China.

[d] Key Laboratory of Chemistry for Natural Products of Guizhou Province, Chinese Academy of Sciences, Guiyang 550014, China

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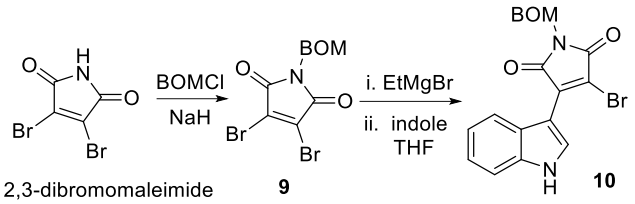
[*] To whom correspondence should be addressed. E-mail: weimingzhu@ouc.edu.cn

[†] These authors contributed equally to this work.

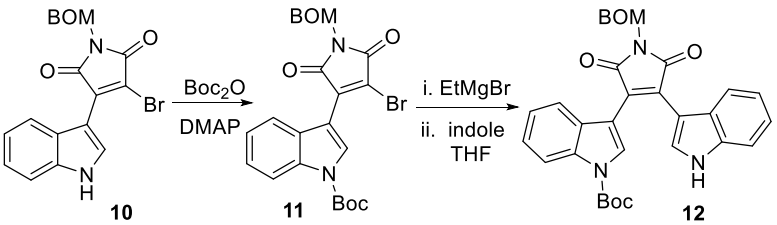
Protocols for synthesis of compounds

Synthesis of *N*-benzyloxymethyl-2-bromo-3-(indol-3-yl)-maleimide (10)



To a solution of 2.55 g (10.0 mmol) of 2,3-dibromomaleimide in 30 mL of DMF was added 480 mg (12 mmol, 60% dispersion) of NaH at 0℃. After stirring for 1h, 2.08 mL (15 mmol) of BOMCl was added dropwise and the reaction was continuously stirring for 2h at room temperature (rt). The reaction was then quenched by the addition of 20 mL of saturated NH_4Cl and diluted with EtOAc (200 mL). The resulting EtOAc solution was washed with H_2O (200 mL) and brine (200 mL) in order, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The obtained reaction gum was purified by a silica gel flash chromatography eluting with petroleum ether (PE)-EtOAc (50:1 EtOAc) to yield *N*-benzyloxymethyl-2,3-dibromomaleimide (**9**) as a colorless crystal (3.55 g, 94% yield). R_f 0.35 (EtOAc-PE, 1:10); ESIMS *m/z* 395.4/397.5/399.4 $[M+Na]^+$. A solution of ethylmagnesium bromide (EtMgBr) in 4 mL of THF was prepared from 432 mg (18.0 mmol) of magnesium turnings and 1.35 mL (18.0 mmol) of freshly distilled bromoethane under anhydrous conditions at 20 ℃. The solution was warmed up to 40℃ and 2.11 g (18.0 mmol) of indole in 10 mL of THF was added. After stirring for 30 min at 40 ℃, the mixture was cooled to 20 ℃ and a solution of 3.29 g (8.9 mmol) of compound **9** was added dropwise via a cannula over 30 min. The mixture was stirred for 4h at rt. The reaction was then quenched by adding 20 mL of saturated NH_4Cl and diluted with EtOAc (100 mL). The resulting EtOAc solution was washed with H_2O (100 mL) and brine (100 mL) in order, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The obtained reaction gum was purified by a silica gel flash chromatography eluting with EtOAc-PE (1:4) to provide *N*-benzyloxymethyl-2-bromo-3-(indol-3- yl)-maleimide (**10**) as an orange crystal (3.46 g, 94% yield). R_f 0.20 (1:4 EtOAc-PE); ^{1}H-NMR (600 MHz, DMSO-d_6) δ 8.93 (brs, 1H, NH), 8.03 (t, J = 7.8 Hz, 1H, ArH), 7.99 (t, J = 7.8 Hz, 1H, ArH), 7.44 (d, J = 7.8 Hz, 1H, ArH), 7.37 (s, 1H, ArH), 7.27-7.36 (m, 5H, ArH), 7.25 (d, J = 7.8 Hz, 1H, ArH), 5.17 (s, 2H, $PhCH_2O\underline{CH_2}N$), 4.67 (s, 2H, $Ph\underline{CH_2}OCH_2N$); ^{13}C NMR (150 MHz, DMSO-d_6) δ 168.8, 166.2, 137.8, 137.8, 136.6, 131.5, 128.2×2, 127.6, 127.5×2, 124.5, 122.6, 122.4, 120.6, 114.1, 112.4, 103.7, 70.5, 67.5; ESIMS *m/z* 433.0/435.1 $[M + Na]^+$.

Synthesis of *N*-benzyloxymethyl-2-(1-*tert*-butoxycarbonylindol-3-yl)-3-(indol-3-yl)-maleimide (12)



To an orange solution of 3.15 g (8.39 mmol) of compound **10** were added 3.82 mL (16.8 mmol) of di-*tert*-butyl

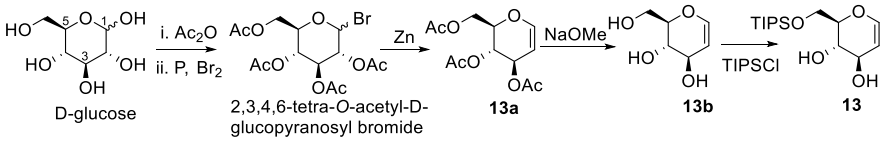
decarbonate (*tert*-butoxycarbonyl anhydride, Boc_2O) and catalytic amounts of 4-dimethylaminopyridine (DMAP) in 50 mL of THF and stirred for 4h at rt. After removing the solvent, the residue was purified by a silica gel flash chromatography eluting with EtOAc-PE (1:20) to provide compound **11** as a yellow crystal (3.9 g, 91% yield).

A solution of EtMgBr in 4 mL of THF was prepared from 367 mg (15.3 mmol) of magnesium turnings and 1.15 mL (15.3 mmol) of freshly distilled bromoethane under anhydrous conditions at 20 ℃. The solution was warmed up to 40 ℃ and 1.8 g (15.3 mmol) of indole in 15 mL of THF was added. After stirring for 30 min at 40 ℃, the mixture was cooled to 20 ℃ and a solution of 3.9 g (7.6 mmol) of compound **11** in 15 mL THF was added dropwise via cannula over 30 min. The mixture was stirred for 4 h at rt. The reaction was then quenched by the addition of 20 mL of saturated NH_4Cl and was diluted with EtOAc (100 mL). The resulting EtOAc solution was washed with H_2O (100 mL) and brine (100 mL) in order, dried over Na_2SO_4, and concentrated *in vacuo*. The obtained reaction gum was purified by a silica gel flash chromatography eluting with EtOAc-PE (1:4, v/v) to provide compound **12** as an orange crystal (3.98 g, 95% yield).

Compound 11: R_f 0.75 (1:4 EtOAc-PE); ^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.23 (d, 1H, J = 8.2 Hz, ArH), 8.18 (s, 1H, ArH), 7.79 (d, J = 7.8 Hz, 1H, ArH), 7.39-7.43 (m, 1H, ArH), 7.31-7.37 (m, 5H, ArH), 7.25-7.28 (m, 1H, ArH), 5.18 (s, 2H, $PhCH_2O\underline{CH_2}N$), 4.68 (s, 2H, $Ph\underline{CH_2}OCH_2N$), 1.71 (s, 9H, $-C(CH_3)_3$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.2, 165.6, 148.9, 137.4, 136.7, 135.4, 130.0, 128.5×2, 127.9, 127.6×2, 126.8, 125.4, 123.3, 122.5, 120.9, 115.4, 108.4, 85.2, 71.9, 67.8, 28.1×3; HR-ESIMS *m/z* 509.0735 $[M-H]^-$ (calcd for $C_{25}H_{22}N_2O_5Br^{79}$, 509.0712).

Compound 12: R_f 0.20 (1:4 EtOAc-PE); ^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.71 (brs, 1H, NH), 8.14 (d, J = 7.8 Hz, 1H, ArH), 8.08 (s, 1H, ArH), 7.78 (d, J = 2.0 Hz, 1H, ArH), 7.40 (d, J = 7.5, 1H, ArH), 7.29-7.33(m, 3H, ArH), 7.24 (t, J = 7.5 Hz, 1H, ArH), 7.15-7.18 (m, 1H, ArH), 7.08 (t, J = 8.2 Hz, 1H, ArH), 7.04 (d, J = 7.8, 1H, ArH), 6.78-6.84 (m, 3H, ArH), 5.24 (s, 2H, $PhCH_2O\underline{CH_2}N$), 4.72 (s, 2H, $Ph\underline{CH_2}OCH_2N$), 1.68 (s, 9H, $-C(CH_3)_3$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.4, 171.2, 149.2, 137.6, 136.0, 135.0, 131.6, 129.9, 128.6, 128.4×2, 128.0, 127.8, 127.7×2, 125.3, 124.6, 124.4, 122.7, 122.6, 121.7, 121.6, 120.7, 115.0, 111.6, 110.7, 106.4, 84.5, 71.7, 67.3, 28.1×3; HR-ESIMS *m/z* 546.2045 $[M-H]^-$ (calcd for $C_{33}H_{28}N_3O_5$, 546.2029).

Synthesis of 6-*O*-triisopropylsilyl-D-glucal (13)

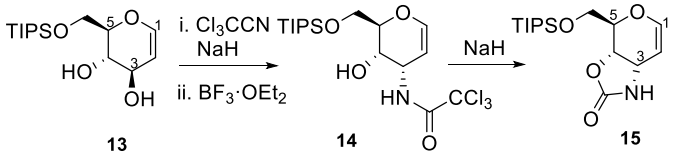


Perchloric acid (70% cont., 0.206 mL) was added dropwise to acetic anhydride (40 mL) at 40 ℃ and stirred for 30 min. The reaction flask was then cooled to 30 ℃, and D-glucose (10 g, 0.0556 mol) was slowly added and stirred for 30 min. The reaction was then cooled to 10 ℃, phosphorus (3.1 g), bromine (5.8 mL) and water (3.6 mL) were slowly added to the reaction solution to control the reaction temperature less than 20 ℃. The reaction was slowly warmed to rt and stirred for 2h, quenched with ice water (50 mL) and extracted with ethyl acetate. The organic layers were washed with saturated $NaHCO_3$ (100 mL×3), dried over Na_2SO_4, and concentrated under reduced pressure to give 2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyl bromide that was directly applied to the next reaction. The resulting residue

was dissolved in EtOAc (50 mL) and cooled to 0 ℃. Then, a suspension of Zn dust (16.1 g), $CuSO_4 \cdot 5H_2O$ (212.0 mg) and NaOAc (1.06 g) in 60% AcOH-H_2O (130 mL) was added and the reaction solution was stirred at 0℃ for 1 h and rt for another 1 h. After the reaction was complete, the suspension was filtered through a pad of Celite. The resulting filtrate was extracted EtOAc (150 mL), and the EtOAc solution was washed with aqueous $NaHCO_3$ (150 mL) and H_2O (150 mL) in order, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by a silica gel flash chromatography eluting with EtOAc-PE (v/v 1:3) to provide compound **13a** as a colorless oil (10.4 g, 68% yield, 2 steps). R_f 0.25 (1:4 EtOAc-PE); ESIMS *m/z* 273.2 $[M+H]^+$. Compound **13a** (5.2 g, 19.1 mmol) was dissolved in MeOH (100 mL), and NaOMe (50%, 300 mg) was added and stirred at rt for 1 h. The reaction mixture was neutralized with Dowex 50×8 (H^+) resin until pH 7, and then was filtered. The filtrates were concentrated *in vacuo* and purified by a silica gel flash chromatography eluting with EtOAc to provide compound **13b** as a colorless oil (2.5 g, 90% yield). R_f 0.10 (EtOAc), ESIMS *m/z* 147.1 $[M+H]^+$. Compound **13b** (5.6 g, 38.4 mmol) was dissolved in pyridine (100 mL) and cooled to 0 ℃. Then, triisopropylsilyl (TIPS) chloride (11.34 mL, 54.22 mmol) and imidazole (15.6 g, 230.4 mmol) were added. The reaction mixture was stirred at rt for 2 h and then quenched by the addition of 50 mL of cooled water and diluted with EtOAc (150 mL). The resulting EtOAc solution was washed with H_2O (100 mL) and brine (100 mL) in order, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by a silica gel flash chromatography eluting with EtOAc-PE (v/v 1:5) to provide 6-*O*-triisopropylsilyl-D-glucal (**13**) as a colorless oil (5.2 g, 46% yield).

Compound 13: R_f 0.35 (1:4 EtOAc-PE); ^{1}H-NMR (600 MHz, $CDCl_3$) δ 6.30 (d, J = 6.0, 1H, H-1), 4.72-4.74 (m, 1H, H-2), 4.27-4.29 (m, 1H, H-4), 4.09 (dd, J = 12.0, 4.8 Hz, 1H, H-6a), 3.98 (dd, J = 12.0, 4.8 Hz, 1H, H-6b), 3.85 (dd, J = 6.0, 3.6 Hz, 1H, H-3), 3.81-3.84 (1H, m, H-5), 3.35 (brs, 1H, OH), 2.35 (brs, 1H, OH), 1.14 (hep, J = 6.0 Hz, 3H, -Si(C<u>H</u>$(CH_3)_2)_3$), 1.08 (d, J = 6.0 Hz, 18H, -Si(CH(C<u>H</u>$_3)_2)_3$); ESIMS *m/z* 303.2 $[M+H]^+$.

Synthesis of 6-*O*-triisopropylsilyl-3,4-dideoxy-(2-oxooxazolo[3,4-*d*])-D-glucal (15)



To a clear, colorless solution of compound **13** (1.43 g, 4.7 mmol) in 100 mL of CH_2Cl_2 at 0 ℃ was added 0.751 g (18.7 mmol, 60% dispersion) of NaH. The reaction was bubbled and stirred at 0 ℃ for 2 h. Then, 5.59 mL (56.4 mmol) of trichloroacetonitrile was added. The reaction mixture was slowly warmed to rt and stirred overnight. The resulting brown solution was cooled to –78 ℃ and then 17.3 mL (141 mmol) of $BF_3 \cdot OEt_2$ was added. After stirring for 6 h at –78 ℃, the reaction was quenched with 20 mL of saturated $NaHCO_3$ at –78 ℃ and then slowly warmed to rt. The crude products were washed with H_2O (100 mL) and brine (100 mL) in order, dried over Na_2SO_4, and concentrated *in vacuo*. The resulting residue was purified by a silica gel flash chromatography eluting with EtOAc-PE (1:20) to yield the glycal **14** as a colorless oil (1.1 g, 60 % yield).

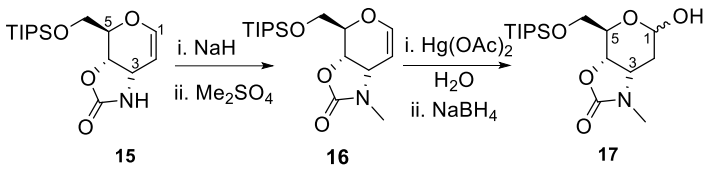
To a clear, colorless solution of 1.1 g (2.4 mmol) of glycal **14** in 30 mL of CH_2Cl_2 at 0 ℃ was added 0.244 g (10.2 mmol, 60% dispersion) of NaH. The reaction was bubbled, warmed slowly to rt and stirred for 3 h. The reaction was

then quenched with H_2O (20 mL) and extracted with CH_2Cl_2 (30 mL). The combined CH_2Cl_2 extracts were washed with brine (30 mL), dried over Na_2SO_4, and concentration *in* v*acuo*. The residue was purified by a silica gel flash chromatography eluting with EtOAc-PE (1:4) to provide 6-*O*-triisopropylsilyl-3,4-dideoxy-(2-oxooxazolo [3,4-*d*])-D-glucal (**15**) as a white solid (0.595 g, 75% yield).

Compound 14: R_f 0.45 (1:9 EtOAc-PE); $[\alpha]_D^{20}$ +121° (*c* 2.02, CH_2Cl_2). ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.02 (brs, 1H, NH), 6.45 (d, *J* = 4.8, 1H, H-1), 4.92-4.94 (m, 1H, H-2), 4.46-4.48 (m, 1H, H-4), 4.16-4.18 (m, 1H, H-3), 4.06 (dd, *J* = 12.0, 5.4 Hz, 1H, H-6a), 3.96 (dd, *J* = 12.0, 5.4 Hz, 1H, H-6b), 3.84-3.86 (m, 1H, H-5), 3.17 (brs, 1H, HO-4), 1.14 (hep, *J* = 6.0 Hz, 3H, -Si(C<u>H</u>$(CH_3)_2)_3$), 1.08 (d, *J* = 6.0 Hz, 18H, -Si(CH(C<u>H</u>$_3)_2)_3$); ^{13}C-NMR (150 MHz, $CDCl_3$): δ 162.3, 145.8, 97.3, 92.6, 74.5, 67.1, 63.4, 45.8, 17.8×3, 11.7×6; ESIMS *m/z* 444.0[M – H]$^-$.

Compound 15: R_f 0.20 (1:4 EtOAc-PE); $[a]_D^{20}$ +108° (*c* 3.00, CH_2Cl_2); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.58 (d, *J* = 7.2, 1H, H-1), 5.96 (brs, 1H, NH), 4.85-4.87 (m, 2H, H-2 and H-4), 4.34 (1H, dd, *J* = 7.2, 4.2 Hz, H-3), 4.06 (dd, *J* = 10.2, 3.6 Hz, 1H, H-6a), 3.96 (dd, *J* = 10.2, 3.6 Hz, 1H, H-6b), 3.80-3.82 (m, 1H, H-5), 1.14 (hep, *J* = 6.0 Hz, 3H, -Si(C<u>H</u>$(CH_3)_2)_3$), 1.08 (d, *J* = 6.0 Hz, 18H, -Si(CH(C<u>H</u>$_3)_2)_3$); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 158.7, 147.2, 98.5, 74.0, 71.0, 61.7, 46.1, 17.9×3, 11.9×6; ESIMS *m/z* 326.0 [M – H]$^-$.

Synthesis of 6-*O*-triisopropylsilyl-2,3,4-trideoxy-(3-methyl-2-oxooxazolo[3,4-*d*])-D-glucose (17)



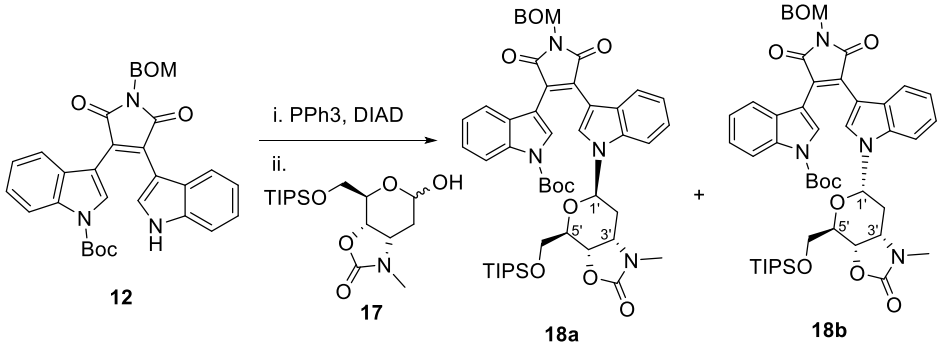
To a clear, colorless solution of 0.595 g (1.8 mmol) of glycal **15** in 20 mL of CH_2Cl_2 was added 0.218 g (9.1 mmol, 60% dispersion) of NaH at 0 ℃. The reaction was bubbled, warmed slowly to rt and stirred for 2 h. Then, the reaction mixture was cooled to 0 ℃, treated with dimethyl sulphate (0.87 mL, 9.1 mmol) and warmed slowly to rt. The reaction was stirred overnight and quenched with 10 mL water at 0 ℃. The reaction mixture was extracted with CH_2Cl_2 (20 mL), and the combined organic layers were washed with brine (20 mL) and dried over Na_2SO_4. After filtration and concentration *in* v*acuo*, the residue was purified by a silica gel flash chromatography eluting with EtOAc-PE (1:6) to provide 6-*O*-triisopropylsilyl-3,4-dideoxy-(3-methyl-2-oxooxazolo[3,4-*d*])-D-glucal (**16**) as a colorless oil (0.6 g, 97% yield).

To a clear, colorless solution of 415 mg (1.22 mmol) of glycal **16** in 20 mL of THF was cooled to 0 ℃ and treated with $Hg(OAc)_2$ (781 mg, 2.44 mmol) that was previously dissolved in water (20 mL). The mixture was diluted with 60 mL of water to the ratio of 4:1 H_2O-THF at 0 ℃. $NaBH_4$ (371 mg, 9.76 mmol) was added and stirred for 10 min, the reaction mixture was then bubbled by CO_2 until pH=7. The suspension was extracted with EtOAc (80 mL×4). The combined EtOAc extracts were washed with brine (100 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The obtained residue was purified by a silica gel flash chromatography eluting with EtOAc-PE (1:2) to yield 6-*O*-triisopropylsilyl-2,3,4-trideoxy-(3-methyl-2-oxooxazolo[3,4-*d*])-D-glucose (**17**) (a pair of 1-epimeric mixture) as a colorless oil (337 mg, 77 % yield).

Compound 16: R_f 0.50 (1:3 EtOAc-PE); $[a]_D^{20}$ +75° (*c* 1.00, CH_2Cl_2); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.68 (d, *J* = 7.2 Hz, 1H, H-1), 4.93 (1H, dd, *J* = 7.2, 4.8 Hz, H-2), 4.74-4.76 (m, 1H, H-4), 4.07-4.10 (m, 1H, H-3, H-6a), 3.98 (dd, *J* = 13.2, 3.6 Hz, 1H, H-6b), 3.61-3.63 (m, 1H, H-5), 2.84 (s, 3H, N-CH_3), 1.14 (hep, *J* = 6.0 Hz, 3H, -Si(C<u>H</u>$(CH_3)_2)_3$), 1.08 (d, *J* = 6.0 Hz, 18H, -Si(CH(C<u>H</u>$_3)_2)_3$); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 157.3, 148.5, 96.0, 74.4, 67.7, 61.6, 51.0, 28.8, 17.9 × 3, 11.9 × 6; HR-ESIMS *m/z* 342.2110 $[M + H]^+$ (calcd for $C_{17}H_{32}NO_4Si$, 342.2101).

Compound 17: R_f 0.15 (1:2 EtOAc-PE); ^{1}H-NMR (600 MHz, $CDCl_3$) δ 5.30-5.33 (m, 1H, H-1)/5.15 (dd, *J* = 6.0, 4.8 Hz, 1H, H-1), 4.63 (t, *J* = 8.4 Hz, 1H, H-4)/ 4.57 (t, *J* = 8.4 Hz, 1H, H-4), 3.97-4.03 (m, 2H, H-6a), 3.91-3.94 (m, 2H, H-6b), 3.86-3.90 (m, 2H, H-3), 3.78-3.81 (m, 1H, H-5)/3.58-3.61 (m, 1H, H-5), 2.86 (s, 3H, N-CH_3)/2.83 (s, 3H, N-CH_3), 2.22-2.26 (m, 1H, H-2a)/2.04-2.08 (m, 1H, H-2a), 1.96-2.01 (m, 1H, H-2b)/1.81 (ddd, *J* = 13.2, 8.4, 6.0 Hz, 1H, H-2b), 1.10 (m, 6H, 2 × -Si(C<u>H</u>$(CH_3)_2)_3$), 1.05 (d, *J* = 7.2 Hz, 36H, 2 × -Si(CH(C<u>H</u>$_3)_2)_3$); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 158.4/158.0, 91.7/90.6, 74.7/69.0, 68.8/68.1, 63.2/63.1, 53.9/52.9, 31.2/29.9, 29.2/28.9, 18.0×3/17.8×3, 12.4×6/12.0×6; HR-ESIMS *m/z* 360.2214 $[M + H]^+$ (calcd for $C_{17}H_{34}NO_5Si$, 360.2206).

Synthesis of 3-(*N*-benzyloxymethyl-3-(1-*tert*-butoxycarbonylindol-3-yl)maleimide-2-yl)indol-1-yl *N*-D-(6-*O*-triisopropylsilyl-2,3,4-trideoxy-(3-methyl-2-oxooxazolo[3,4-*d*]))glucopyranoside (18)



To a solution of compound **12** (712 mg, 1.253 mmol) in THF (20 mL) were added triphenylphosphine (655 mg, 2.515 mmol). The reaction mixture was cooled to –78 ℃, and then diisopropyl azodicarboxylate (DIAD) (0.5 mL, 2.515 mmol) was added dropwise and stirred at –78 ℃ for 1h. Then, a solution of compound **17** (300 mg, 0.835 mmol) in THF (10 mL) was added to the mixture dropwise. After stirring at –78 ℃ for 2h, the reaction mixture was warmed to rt and stirred overnight. The reaction mixture was quenched with water (20 mL), extracted with EtOAc (100 mL) and the combined organic phase was dried over Na_2SO_4. After removal of the solvent *in vacuo*, the residue was purified through a silica gel flash chromatography eluting with EtOAc-PE (1:4) to give 3-(*N*-benzyl oxymethyl-3-(1-*tert*-butoxycarbonylindol-3-yl)maleimide-2-yl)indol-1-yl *N*-β-D-(6-*O*-triisopropylsilyl-2,3,4-trideoxy-(3-methyl-2-oxooxazolo[3,4-*d*]))glucopyranoside (**18a**) (202 mg, 27% yield) and 3-(*N*-benzyloxymethyl-3-(1-*tert*-butoxy carbonylindol-3-yl)maleimide-2-yl)indol-1-yl *N*-α-D-(6-*O*-triisopropylsilyl-2,3,4-trideoxy-(3-methyl-2-oxooxazolo [3,4-*d*]))glucopyranoside (**18b**) (210 mg, 28% yield) as orange solid.

Compound 18a: $[a]_D^{20}$ +14.1° (*c* 0.59, CH_2Cl_2); R_f 0.25 (1:2 EtOAc-PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.8 Hz, 1H, ArH), 8.11 (s, 1H, ArH), 7.77 (s, 1H, ArH), 7.40-7.10 (m, 9H, ArH), 6.86 (t, *J* = 7.8 Hz, 1H, ArH), 6.80-6.77 (m, 2H, ArH), 5.72 (dd, *J* = 10.8, 1.8 Hz, 1H, H-1'), 5.24 (d, *J* = 11.0 Hz, 1H, $PhCH_2OC\underline{H}_2N$), 5.23 (d, *J* =

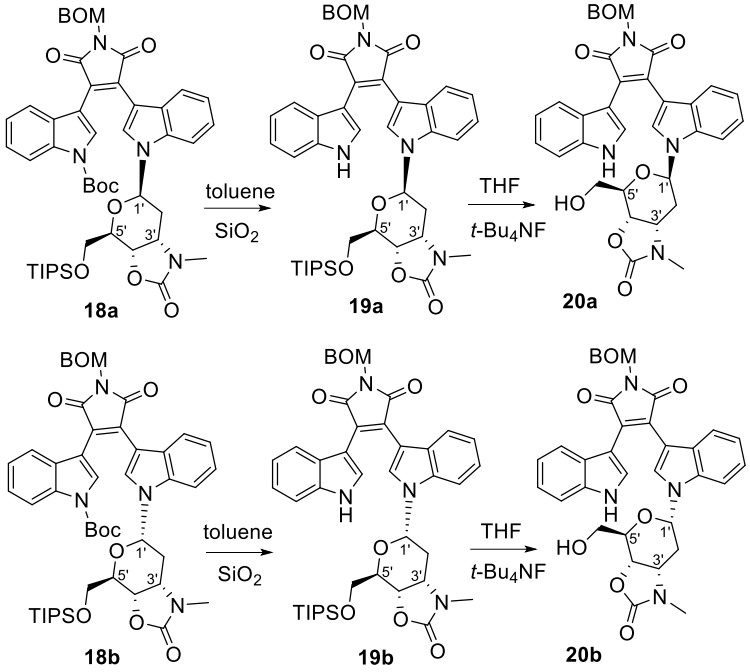
11.0 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 4.72 (s, 2H, $PhC\underline{H_2}OCH_2N$), 4.69 (dd, *J* = 9.0, 7.2 Hz, 1H, H-4'), 4.06-4.08 (m, 1H, H-3'), 4.01 (dd, *J* = 12.0, 2.4 Hz, 1H, H-6'a), 3.95 (dd, *J* = 12.0, 2.4 Hz, 1H, H-6'b), 3.82-3.84 (m,1H, H-5'), 2.87 (s, 3H, $N\text{-}CH_3$), 2.39-2.41 (m, 1H, H-2'a), 2.27-2.30 (m, 1H, H-2'b), 1.69 (s, 9H, $-C(C\underline{H_3})_3$), 1.07 (hep, *J* = 6.0 Hz, 3H, $-Si(C\underline{H}(CH_3)_2)_3$), 1.02 (d, *J* = 6.0 Hz, 18H, $-Si(CH(C\underline{H_3})_2)_3$); ^{13}C NMR(150 MHz, $CDCl_3$) δ 171.1, 171.0, 158.5, 149.1, 137.6, 135.7, 135.1, 130.5, 129.0, 128.6, 128.3×2, 127.7×2, 127.6×2, 126.5, 125.7, 124.6, 123.2, 122.4×2, 121.7, 121.5, 115.1, 110.6, 110.4, 107.0, 84.6, 79.4, 78.3, 71.7, 67.3, 67.0, 62.9, 55.7, 29.5, 29.3, 28.1×3, 17.8×3, 11.8×6; HR-ESIMS *m/z* 911.4044 $[M + Na]^+$ (calcd for $C_{50}H_{60}N_4O_9NaSi$, 911.4027).

Compound 18b: $[a]_D^{20}$ –9.1° (*c* 0.10, CH_2Cl_2); R_f 0.20 (1:2 EtOAc-PE). ^1H NMR(600 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.2 Hz, 1H, ArH), 8.13 (s, 1H, ArH), 7.64 (s, 1H, ArH), 7.39-7.42 (m, 3H, ArH), 7.28-7.32 (m, 3H, ArH), 7.22-7.25 (m, 1H, ArH), 7.15-7.19 (m, 2H, ArH), 6.94-6.96 (m, 1H, ArH), 6.77-6.80 (m, 1H, ArH), 6.71 (d, *J* = 7.8 Hz, 1H, ArH), 6.11 (dd, *J* = 10.7, 4.5 Hz, 1H, H-1'), 5.24 (d, *J* = 11.0 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 5.23 (d, *J* = 11.0 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 4.75 (t, *J* = 7.8 Hz, 1H, H-4'), 4.72 (s, 2H, $Ph\underline{CH_2}OCH_2N$), 3.99-4.03 (m, 1H, H-3'), 3.85-3.93 (m, 2H, H-6'), 3.80-3.83 (m, 1H, H-5'), 2.87 (s, 3H, $N\text{-}CH_3$), 2.40-2.44 (m, 1H, H-2'a), 2.04-2.11 (m, 1H, H-2'b), 1.69 (s, 9H, $-C(C\underline{H_3})_3$), 1.09 (hep, *J* = 6.0 Hz, 3H, $-Si(C\underline{H}(CH_3)_2)_3$), 1.02 (d, *J* = 6.0 Hz, 18H, $-Si(CH(C\underline{H_3})_2)_3$); ^{13}C NMR(150 MHz, $CDCl_3$) δ 171.2, 171.0, 157.4, 149.2, 137.8, 136.0, 135.4, 130.8, 129.4, 128.5×3, 127.9, 127.8×2, 127.3, 126.7, 126.0, 124.7, 123.3, 122.5×2, 122.0, 121.7, 115.4, 110.6, 110.4, 107.1, 84.8, 78.6, 72.5, 71.8, 68.9, 67.4, 63.6, 53.7, 29.8, 29.3, 28.2×3, 18.0×3, 11.9×6; HR-ESIMS *m/z* 911.4036 $[M + Na]^+$ (calcd for $C_{50}H_{60}N_4O_9NaSi$, 911.4027).

In this reaction, we preliminarily optimized the reaction conditions. The experimental results showed that the addition of PPh_3 and DIAD had a great effect on the yield, while heating up or prolonging the reaction time had little effect. Considering that compound **17** was not easy to be prepared, we finally selected the entry 5 to synthesize compounds **18a** and **18b**.

Entry	Solvents	**12** : **17** eq.	PPh_3 : DIAD eq.	Temperature	Time	**18a**:**18b**
1	THF	1 : 1.5	1.5 : 1.5	-78℃ to r.t	12 h	11%:15%
2	THF	1 : 1.5	3 : 3	-78℃ to r.t	12 h	26%:28%
3	THF	1 : 1.5	3 : 3	-78℃ to 50 ℃	12 h	25%:24%
4	THF	1 : 1.5	3 : 3	-78℃ to r.t	24h	25%:25%
5	THF	1.5 :1	3 : 3	-78℃ to r.t	12 h	27%:28%

Synthesis of 3-(*N*-benzyloxymethyl-3-(indol-3-yl)maleimide-2-yl)indol-1-yl *N*-D-(2,3,4-trideoxy-(3-methyl-2-oxooxazolo[3,4-*d*]))glucopyranoside (20)



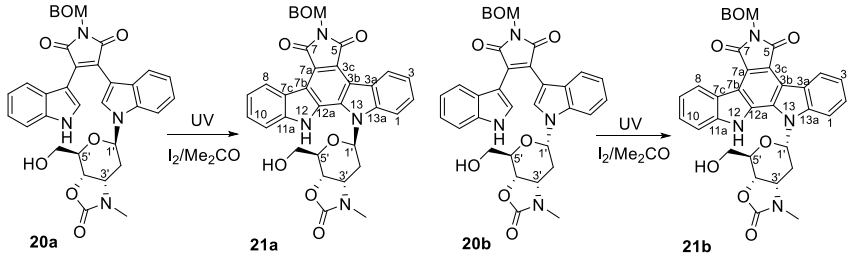
To a solution of **18a** (311 mg, 0.35 mmol) in toluene (40 mL) were added silica gel (3.0 g) and refluxed for 5 h. The mixture was filtered through a pad of Celite and washed by EtOAc to give compound **19a** as orange powder (262 mg, 95% yield). HR-ESIMS *m/z* 787.3530 $[M–H]^-$ (calcd for $C_{45}H_{51}N_4O_7Si$, 787.3527). **19b** (180 mg, 96% yield) was prepared from **18b** (210 mg, 0.236 mmol) by the same method. HR-ESIMS *m/z* 787.3556 $[M–H]^-$ (calcd for $C_{45}H_{51}N_4O_7Si$, 787.3527). To a solution of 262 mg (0.333 mmol) of **19a** in 30 mL of THF at 0 ℃ was added 1.0 mL of *t*-Bu_4NF (1.0 mmol, 1.0 M solution in THF). Over 1 h the reaction turned from orange to darken blue and was complete. The crude reaction mixture was diluted with EtOAc (100 mL) and the combine organic layers were washed with water (50 mL). The organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by a silica gel flash chromatography eluting with EtOAc-PE (2:1, v/v) to provide 3-(*N*-benzyloxymethyl-3-(indol-3-yl)maleimide-2-yl)indol-1-yl *N*-β-D-(2,3,4-trideoxy-(3-methyl-2-oxooxazolo[3,4-*d*]))glucopyranoside (**20a**) as an orange solid (179 mg, 85% yield). By the same procedure, 3-(*N*-benzyloxymethyl-3-(indol-3-yl)maleimide-2-yl)indol-1-yl *N*-α-D-(2,3,4-trideoxy-(3-methyl-2-oxooxazolo[3,4-*d*]))glucopyranoside (**20b**) (179 mg, 0.227 mmol) and purified as an orange solid (136 mg, 95% yield) by a silica gel flash chromatography (3:1 EtOAc-PE).

Compound 20a: $[\alpha]_D^{20}$ –2.5° (*c* 0.01, CH_2Cl_2); R_f 0.30 (2:1 EtOAc-PE); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.40 (s, 1H, NH), 7.68 (d, *J* = 3.0 Hz, 1H, ArH), 7.59 (s, 1H, ArH), 7.36-7.37 (m, 2H, ArH), 7.27-7.32 (m, 4H, ArH), 7.22-7.24 (m, 1H, ArH), 7.14-7.17 (m, 2H, ArH), 7.03-7.06 (m, 1H, ArH), 6.87-6.90 (m, 2H, ArH), 6.76 (t, *J* = 7.8 Hz, 1H, ArH), 5.67 (dd, *J* = 10.2, 1.2 Hz, 1H, H-1'), 5.14 (brs, 2H, $PhCH_2O\underline{CH_2}N$), 4.67 (s, 2H, $Ph\underline{CH_2}OCH_2N$), 4.43 (t, *J* = 7.8 Hz, 1H, H-4'), 3.86-3.87 (m, 1H, H-3'), 3.82 (dd, *J* = 12.0, 2.4 Hz, 1H, H-6'a), 3.72-3.75 (m, 1H, H-5'), 3.64 (dd, *J* = 12.0, 2.4 Hz, 1H, H-6'b), 2.77 (s, 3H, N-CH_3), 2.24-2.29 (m, 1H, H-2'a), 2.12-2.15 (m, 1H, H-2'b); ^{13}C NMR

(150 MHz, $CDCl_3$): δ 171.7×2, 158.6, 137.7, 136.3, 136.0, 129.2, 128.8, 128.5×2, 127.9, 127.8×2, 127.7, 126.6, 126.5, 124.9, 123.3, 122.9, 122.6, 122.2, 121.5, 120.4, 111.8, 110.1, 107.6, 106.5, 78.9, 77.7, 71.7, 67.3, 62.1, 60.5, 55.7, 29.6, 28.8; HR-ESIMS *m/z* 631.2198 $[M–H]^-$ (calcd for $C_{36}H_{31}N_4O_7$, 631.2193).

Compound 20b: $[\alpha]_D^{20}$ –10° (*c* 0.10, CH_2Cl_2); R_f 0.30 (3:1 EtOAc-PE); ^1H NMR (600 MHz, $CDCl_3$) δ 8.89 (s,1H, NH), 7.80 (d, *J* = 3.0 Hz, 1H, ArH), 7.45-7.46 (m, 2H, ArH), 7.38-7.40 (m, 3H, ArH), 7.34-7.36 (m, 1H, ArH), 7.29-7.32 (m, 2H, ArH), 7.20-7.25 (m, 2H, ArH), 7.07-7.10 (m, 1H, ArH), 7.01 (t, *J* = 7.2 Hz, 1H, ArH), 6.72-6.74 (m, 2H, ArH), 6.05 (dd, *J* = 10.4, 5.4 Hz, 1H, H-1'), 5.21 (d, *J* = 11.0 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 5.20 (d, *J* = 11.0 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 4.72 (s, 2H, $Ph\underline{CH_2}OCH_2N$), 4.60 (t, *J* = 8.4 Hz, 1H, H-4'), 3.92-3.97 (m, 1H, H-3'), 3.70 (dd, *J* = 12.0, 2.4 Hz, 1H, H-6'a), 3.60 (dd, *J* = 12.0, 4.2 Hz, 1H, H-6'b), 3.52-3.54 (m, 1H, H-5'), 2.80 (s, 3H, $N\text{-}CH_3$), 2.39-2.43 (m, 1H, H-2'a), 1.99-2.03 (m, 1H, H-2'b); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.7×2, 157.3, 137.8, 136.4, 135.8, 129.7, 129.1, 128.5×2, 127.9, 127.8×2, 127.7, 127.0, 126.8, 124.3, 123.3, 123.0, 122.7, 122.3, 121.6, 120.4, 112.0, 110.1, 107.6, 106.5, 78.4, 71.8, 71.5, 68.9, 67.3, 62.1, 53.2, 29.8, 28.9; HR-ESIMS *m/z* 631.2192 $[M–H]^-$ (calcd for $C_{36}H_{31}N_4O_7$ 631.2193).

Synthesis of 6-benzyloxymethyl-5,7-dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-13-yl *N*-D-(2,3,4-trideoxy-(3-methyl-2-oxooxazolo[3,4-*d*]))glucopyranoside (21)



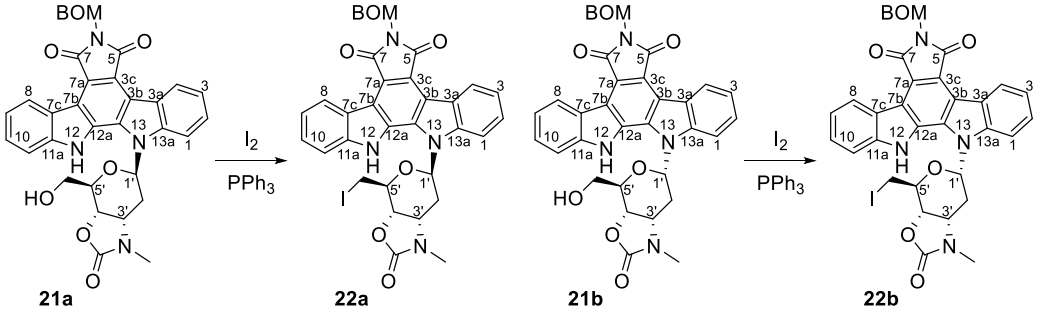
An orange solution of **20a** (30 mg, 0.047 mmol) in 1750 mL of acetone was treated with 3 mg of iodine. The reaction mixture was irradiated with a medium mercury UV lamp (250 W) and stirred vigorously for 12 h, in which acetone was added to the reaction each hour to keep the solvent volume constant. The reaction turned from orange to bright yellow and was complete. The saturated $Na_2S_2O_3$ (5 mL) was added to remove the excess I_2, and the acetone was then evaporated off *in vacuo*. The concentrated solution was extracted by EtOAc (10 mL) and the organic layer was rinsed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by a silica gel flash chromatography eluting with EtOAc-PE (v/v 1:1) to provide 6-benzyloxymethyl-5,7-dioxoindolo [2,3-*a*]pyrrolo[3,4-*c*]carbazole-13-yl *N*-β-D-(2,3,4-trideoxy-(3-methyl-2-oxooxazolo[3,4-*d*]))glucopyranoside (**21a**) as a yellow solid (17 mg, 57% yield). 6-Benzyloxymethyl-5,7-dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-13-yl *N*-α-D-(2,3,4-trideoxy-(3-methyl-2-oxooxazolo[3,4-*d*]))glucopyranoside (**21b**) was prepared from compound **20b** (130 mg, 0.206 mmol) by the same method and purified as a yellow solid (70 mg, 51% yield) by a silica gel flash chromatography eluting with EtOAc-PE (v/v 3:1).

Compound 21a: $[\alpha]_D^{20}$ +71.7° (*c* 0.05, CH_2Cl_2); R_f 0.40 (1:1 EtOAc-PE); ^1H NMR (600 MHz, $CDCl_3$) δ 10.95 (s, 1H, NH), 9.23 (d, *J* = 7.8 Hz, 1H, ArH), 8.77 (d, *J* = 7.8 Hz, 1H, ArH), 7.54-7.57 (m, 1H, ArH), 7.46-7.48 (m, 2H, ArH), 7.39-7.41 (m, 2H, ArH), 7.35-7.38 (m, 2H, ArH), 7.28-7.31 (m, 3H, ArH), 6.97 (d, *J* = 8.4 Hz, 1H, ArH), 6.16

(dd, *J* = 9.0, 1.8 Hz, 1H, H-1'), 5.18 (t, *J* = 7.8 Hz, 1H, H-4'), 5.16 (d, *J* = 11.0 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 5.14 (d, *J* = 11.0 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 4.80 (s, 2H, $Ph\underline{CH_2}OCH_2N$), 4.40 (d, *J* = 12.0 Hz, 1H, H-3'), 4.10-4.16 (m, 3H, H-5', H-6'), 2.91 (s, 3H, N-CH_3), 2.29-2.34 (m, 1H, H-2'a), 1.98-2.01 (m, 1H, H-2'b); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.5, 169.1, 158.7, 140.8, 139.7, 137.5, 129.7, 128.6×2, 128.3, 128.1×2, 128.0, 127.6, 127.2, 126.2, 125.0, 122.7, 121.7×2, 120.7, 120.5, 119.5, 118.4, 118.1, 111.2, 108.6, 79.3, 78.3, 71.9, 66.8, 66.2, 60.9, 56.2, 29.7, 29.0; HR-ESIMS *m/z* 629.2056 $[M–H]^-$ (calcd for $C_{36}H_{29}N_4O_7$, 629.2036).

Compound 21b: $[\alpha]_D^{20}$ –25.7° (*c* 0.16, CH_2Cl_2); R_f 0.20 (3:1 EtOAc-PE); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.38 (s, 1H, NH), 9.22 (d, *J* = 7.8 Hz, 1H, ArH), 9.10 (d, *J* = 7.8 Hz, 1H, ArH), 7.95 (d, *J* = 8.4 Hz, 1H, ArH), 7.79 (d, *J* = 8.4 Hz, 1H, ArH), 7.73-7.74 (m, 1H, ArH), 7.67-7.68 (m, 1H, ArH), 7.61-7.64 (m, 2H, ArH), 7.46 (t, *J* = 7.8 Hz, 1H, ArH), 7.40 (t, *J* = 7.2 Hz, 1H, ArH), 7.32 (d, *J* = 7.2 Hz, 1H, ArH), 7.31 (t, *J* = 7.8 Hz, 1H, ArH), 7.24 (t, *J* = 7.2 Hz, 1H, ArH), 6.94 (dd, *J* = 11.4, 4.8 Hz, 1H, H-1'), 5.45 (t, *J* = 5.4 Hz, 1H, H-4'), 5.20 (brs, 2H, $PhCH_2O\underline{CH_2}N$), 4.83-4.85 (m, 1H, H-3'), 4.69 (s, 2H, $Ph\underline{CH_2}OCH_2N$), 4.44-4.48 (m, 1H, H-5'), 3.90-3.96 (m, 2H, H-6'), 2.68 (s, 3H, N-CH_3), 2.67-2.68 (m, 1H, H-2'a), 2.48-2.52 (m, 1H, H-2'b); ^{13}C NMR (150 MHz, DMSO-d_6) δ 169.6×2, 157.2, 141.2, 140.0, 138.4, 132.3, 132.1, 129.3×2, 129.1, 128.8×2, 128.1×3, 128.0, 125.3, 124.9, 122.6, 122.0, 121.6 121.4, 120.3, 118.8, 118.2, 112.8, 79.5, 75.1, 70.1, 67.3, 65.6, 61.4, 53.4, 29.6, 29.0; HR-ESIMS *m/z* 629.2014 $[M–H]^-$ (calcd for $C_{36}H_{29}N_4O_7$, 629.2036).

Synthesis of 6-benzyloxymethyl-5,7-dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-13-yl *N*-D-(2,3,4,6-tetradeoxy-6-iodo-(3-methyl-2-oxooxazolo[3,4-*d*]))glucopyranoside (22)

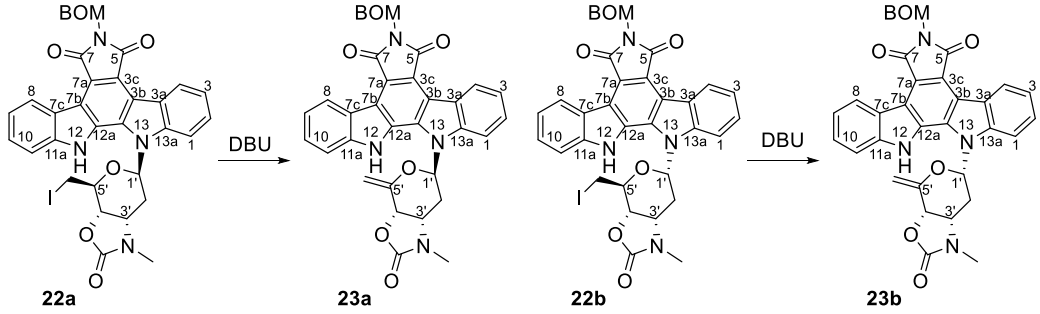


To a solution of 307 mg (1.171 mmol) of triphenylphosphine and 159 mg (2.342 mmol) of imidazole in 20 mL of CH_2Cl_2 at 0 ℃ was added 297 mg (2.342 mmol) of iodine. The reaction turned from colorless to bright yellow over 1 h. A green solution of 123 mg (0.195 mmol) of **21a** in 20 mL of CH_2Cl_2 was then added dropwise via cannula. The reaction slowly warmed to rt and stirred for 6 h. The crude products were diluted with CH_2Cl_2 (20 mL) and the organic layer was washed with H_2O (20 mL) and brine (20 mL) in order, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by a silica gel flash chromatography eluting with EtOAc-PE (v/v 1:2) to provide 6-benzyloxymethyl-5,7-dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-13-yl *N*-β-D-(2,3,4,6-tetradeoxy-6-iodo-(3-methyl-2-oxooxazolo[3,4-*d*]))glucopyranoside (**22a**) as a yellow crystal (80 mg, 56% yield). 6-Benzyloxymethyl-5,7-dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-13-yl *N*-α-D-(2,3,4,6-tetradeoxy-6-iodo-(3-methyl-2-oxooxazolo [3,4-*d*]))glucopyranoside (**22b**) was prepared from **21b** (70 mg) by the same method and purified as a yellow solid (54 mg,65%) by a silica gel flash chromatography (v/v 1:1 EtOAc-PE).

Compound 22a: mp 216 ℃; $[\alpha]_D^{20}$ +68.0° (*c* 0.44, CH_2Cl_2); R_f 0.35 (1:2 EtOAc-PE); ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.24 (s,1H, NH), 9.30 (d, *J* = 8.4 Hz, 1H, ArH), 9.23 (d, *J* = 8.4 Hz, 1H, ArH), 7.73 (d, *J* = 7.8 Hz, 1H, ArH), 7.61 (dt, *J* = 8.4, 1.2 Hz, 1H, ArH), 7.54 (dt, *J* = 8.4, 1.2 Hz, 1H, ArH), 7.49 (d, *J* = 8.4 Hz, 1H, ArH), 7.44-7.39 (m, 4H, ArH), 7.31 (t, *J* = 7.2 Hz, 2H, ArH), 7.23 (t, *J* = 7.2 Hz, 1H, ArH), 6.37 (dd, *J* = 11.4, 2.4 Hz, 1H, H-1'), 5.31(brs, 2H, $PhCH_2O\underline{CH_2}N$), 4.93 (dd, *J* = 8.8, 7.0 Hz, 1H, H-4'), 4.77(s, 2H, $Ph\underline{CH_2}OCH_2N$), 4.16-4.18 (m, 1H, H-5'), 3.89-3.91 (m, 1H, H-3'), 3.85-3.87 (m, 2H, H-6), 2.90 (s, 3H, N-CH_3), 2.67-2.72 (m, 1H, H-2'a), 2.09-2.11 (1H, m, H-2'b); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.4, 169.3, 158.1, 141.0, 140.5, 137.8, 129.9, 128.5×2, 128.3, 127.9×3, 127.8, 126.5, 125.9, 122.9, 122.6, 122.4, 121.7, 121.3, 120.1, 119.2×2, 111.9×2, 108.8, 80.7, 77.2, 71.7, 71.5, 67.0, 56.3, 29.9, 29.4, 8.8; HR-ESIMS *m/z* 739.1045 $[M–H]^-$ (calcd for $C_{36}H_{28}N_4O_6I$, 739.1054).

Compound 22b: $[\alpha]_D^{20}$ –15.5° (*c* 0.1, CH_2Cl_2); R_f 0.30 (1:1 EtOAc-PE); ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.72 (s, 1H, NH), 9.14 (d, *J* = 7.8 Hz, 1H, ArH), 9.03 (d, *J* = 7.8 Hz, 1H, ArH), 7.60-7.65 (m, 2H, ArH), 7.48-7.55 (m, 2H, ArH), 7.43-7.47 (m, 2H, ArH), 7.39-7.40 (m, 2H, ArH), 7.29-7.34 (m, 2H, ArH), 7.22-7.24 (m, 1H, ArH), 6.33 (dd, *J* = 12.0, 3.0 Hz, 1H, H-1'), 5.09 (d, *J* = 11.0 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 5.07 (d, *J* = 11.0 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 4.82-4.85 (m, 1H, H-4'), 4.71-4.73 (m, 1H, H-5') 4.70 (s, 2H, $Ph\underline{CH_2}OCH_2$), 4.15-4.18 (m, 1H, H-3'), 3.66-3.69 (m, 2H, H-6'), 2.73 (s, 3H, N-CH_3), 2.31-2.38 (m, 2H, H-2'); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.1×2, 156.5, 140.8, 139.8, 137.7, 129.4, 128.8, 128.7, 128.5×2, 128.0×2, 127.8, 127.4, 126.2, 125.2, 122.7, 122.0, 121.9, 121.4, 120.6, 119.1, 118.8, 118.6, 112.0, 109.3, 76.1, 73.8, 71.6, 70.9, 66.7, 53.1, 31.5, 29.1, 14.3; HR-ESIMS *m/z* 739.1068 $[M–H]^-$ (calcd for $C_{36}H_{28}N_4O_6I$, 739.1054).

Synthesis of 6-benzyloxymethyl-5,7-dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-13-yl *N*-D-(2,3,4-trideoxy-5,6-dehydro-(3-methyl-2-oxooxazolo[3,4-*d*]))glucopyranoside (23)



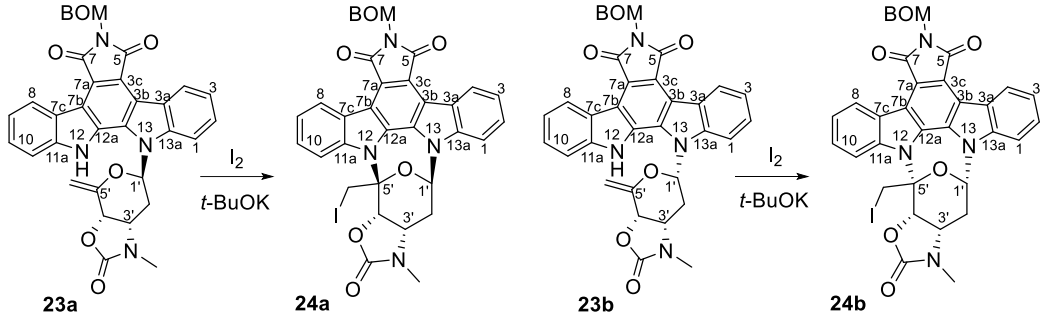
To a green solution of **22a** (30 mg, 0.041 mmol) in 10 mL of THF at 0 ℃ was added 0.4 mL (2.67 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The reaction turned from green to red and stirred at 0 ℃ for 1 h, then at 40 ℃ for 1 h. The reaction mixture was diluted with EtOAc (20 mL) and treated with H_2O (20 mL). The organic layer was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The obtained residue was purified by a silica gel flash chromatography eluting with EtOAc-PE (v/v 1:1) to provide 6-benzyloxymethyl-5,7-dioxoindolo[2,3-*a*] pyrrolo[3,4-*c*]carbazole-13-yl *N*-β-D-(2,3,4-trideoxy-5,6-dehydro-(3-methyl-2-oxooxazolo[3,4-*d*]))glucopyrano side (**23a**) as a yellow solid (22 mg, 89% yield). 6-Benzyloxymethyl-5,7-dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*] carbazole-13-yl *N*-β-D-(2,3,4-trideoxy-5,6-dehydro-(3-methyl-2-oxooxazolo[3,4-*d*]))glucopyranoside (**23b**) was prepared from **22b** (54 mg) by the same procedure and purified as a yellow solid (40 mg, 90% yield) by a silica gel flash

chromatography eluting with 3:1 EtOAc-PE.

Compound 23a: $[\alpha]_D^{20}$ +101.1° (*c* 0.5, CH_2Cl_2); R_f 0.35 (1:1 EtOAc-PE); ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.16 (s, 1H, NH), 9.22 (d, *J* = 7.8 Hz, 1H, ArH), 9.08 (d, *J* = 8.4 Hz, 1H, ArH), 7.86 (d, *J* = 8.4 Hz, 1H, ArH), 7.72 (d, *J* = 8.4 Hz, 1H, ArH), 7.60-7.63 (m, 2H, ArH), 7.47 (d, *J* = 7.2 Hz, 1H, ArH), 7.41-7.36 (m, 3H, ArH), 7.31 (t, *J* = 7.2 Hz, 2H, ArH), 7.24 (t, *J* = 7.2 Hz, 1H, ArH), 7.20 (dd, *J* = 12.0, 2.4 Hz, 1H, H-1'), 5.40 (d, *J* = 9.6, 1H, H-4'), 5.18 (d, *J* = 11.0 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 5.16 (d, *J* = 11.0 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 5.08 (d, *J* = 1.1 Hz, 1H, H-6'a), 5.07 (d, *J* = 1.1 Hz, 1H, H-6'b), 4.67 (s, 2H, $Ph\underline{CH_2}OCH_2N$), 4.33-4.36 (m, 1H, H-3'), 2.70 (s, 3H, N-CH_3), 2.47-2.49 (m, 1H, H-2'a), 2.10-2.14 (m, 1H, H-2'b); ^{13}C NMR (150 MHz, DMSO-d_6) δ 169.6, 169.5, 157.1, 152.9, 142.3, 140.6, 138.4, 129.9, 129.4, 128.8×2, 128.3, 128.1×3, 128.0, 125.6, 124.9, 123.7, 122.5, 121.8, 121.5, 120.5, 119.2, 118.8, 118.4, 113.8, 112.9, 101.2, 81.0, 71.4, 71.0, 67.3, 53.1, 28.9, 28.0; HR-ESIMS *m/z* 611.1921 $[M-H]^-$ (calcd for $C_{36}H_{27}N_4O_6$ 611.1931).

Compound 23b: $[\alpha]_D^{20}$ –21.4° (*c* 0.7, CH_2Cl_2); R_f 0.40 (3:1 EtOAc-PE); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.62 (s, 1H, NH), 9.27 (d, *J* = 7.8 Hz, 1H, ArH), 9.10 (d, *J* = 8.4 Hz, 1H, ArH), 7.64 (d, *J* = 8.2 Hz, 1H, ArH), 7.53-7.56 (m, 2H, ArH), 7.40-7.46 (m, 4H, ArH), 7.29-7.37 (m, 3H, ArH), 7.21-7.24 (m, 1H, ArH), 6.27 (dd, *J* = 11.4, 2.4 Hz, 1H, H-1′), 5.44 (d, *J* = 2.0 Hz, 1H, H-6′a), 5.30 (d, *J* = 2.0 Hz, 1H, H-6′b), 5.21 (d, *J* = 11.0 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 5.17 (d, *J* = 11.0 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 5.07 (d, 1H, *J* = 7.2 Hz, H-4′), 4.73 (s, 2H, $Ph\underline{CH_2}OCH_2N$), 4.14-4.18 (m, 1H, H-3′), 2.77 (s, 3H, N-CH_3), 2.47-2.53 (m, 1H, H-2′a), 2.38-2.42 (m, 1H, H-2′b); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.4, 169.2, 156.7, 151.3, 140.8, 139.7, 137.7, 129.3, 128.5×2, 128.2, 128.0×3, 127.8, 127.6, 126.3, 125.3, 122.6, 122.2, 121.9, 121.6, 121.0, 119.5, 119.3, 118.8, 111.9, 108.8, 100.0, 81.9, 71.6, 70.1, 66.8, 54.4, 32.8, 29.2; HR-ESIMS *m/z* 611.1911 $[M-H]^-$ (calcd for $C_{36}H_{27}N_4O_6$ 611.1931).

Synthesis of 6-benzyloxymethyl-5,7-dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-12,13-diyl *N*-D-(2,3,4,6-tetra deoxy-6-iodo-(3-methyl-2-oxooxazolo[3,4-*d*]))-1,5-glucopyranoside (24)



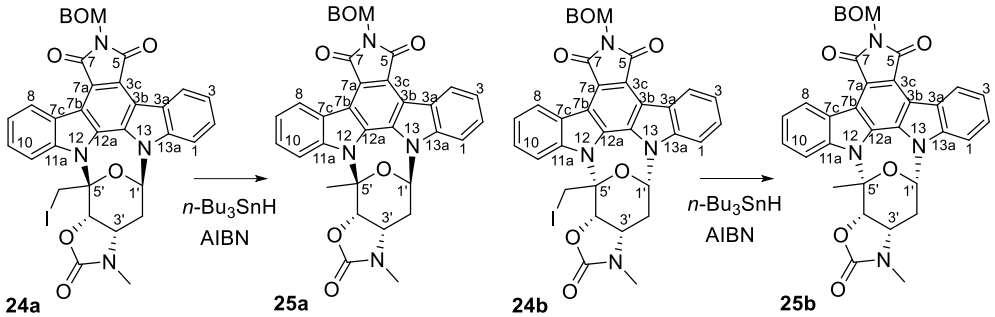
To a green solution of **23a** (30 mg, 0.05 mmol) in 10 mL of THF and 1 mL of MeOH was added 22 mg (0.2 mmol) of *t*-BuOK and stirred for 2 h at rt. The reaction turned red and was treated by 38 mg (0.15 mmol) of iodine for 12 h. The reaction was diluted with EtOAc (20 mL) and saturated $Na_2S_2O_3$ (10 mL) was added to remove the excess I_2. The EtOAc layer was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The obtained residue was purified by a silica gel flash chromatography eluting with EtOAc-PE (v/v 1:2) to provide 6-benzyloxymethyl-5,7-dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-12,13-diyl *N*-D-(2,3,4,6-tetradeoxy-6-iodo-(3-methyl-2-oxooxazolo [3,4-*d*]))-1β,5β-glucopyranoside (**24a**) as a yellow solid (20 mg, 54% yield). By the same procedure, 6-benzyloxy

methyl-5,7-dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-12,13-diyl *N*-D-(2,3,4,6-tetradeoxy-6-iodo-(3-methyl-2-oxooxazolo [3,4-*d*]))-1α,5α-glucopyranoside (**24b**) was prepared from **23b** (40 mg) and purified as a yellow crystal (20 mg, 42% yield) by a silica gel flash chromatography eluting with EtOAc-PE (3:1).

Compound 24a: $[\alpha]_D^{20}$ +45.9° (*c* 0.05, CH_2Cl_2); R_f 0.30 (1:1 EtOAc-PE); ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.28 (d, *J* = 7.8 Hz, 1H, ArH), 9.04 (d, *J* = 7.8 Hz, 1H, ArH), 8.12 (d, *J* = 9.0 Hz, 1H, ArH), 8.07 (d, *J* = 8.4 Hz, 1H, ArH), 7.66-7.70 (m, 2H, ArH), 7.56 (t, *J* = 7.2 Hz, 1H, ArH), 7.48 (t, *J* = 7.2 Hz, 1H, ArH), 7.37-7.40 (m, 2H, ArH), 7.32 (t, *J* = 7.2 Hz, 2H, ArH), 7.24 (t, *J* = 7.2 Hz, 1H, ArH), 7.08 (dd, *J* = 9.6, 7.2 Hz, 1H, H-1'), 5.91 (d, *J* = 9.0 Hz, 1H, H-4'), 5.26 (brs, 2H, $PhCH_2O\underline{CH_2}$), 4.71 (s, 2H, $Ph\underline{CH_2}OCH_2$), 4.63 (1H, d, *J* = 12.6 Hz, H-6′a), 4.48-4.51 (m, 1H, H-3′), 3.79 (1H, d, *J* = 12.6 Hz, H-6′b), 3.00 (s, 3H, N-CH_3), 2.86-2.90 (m, 1H, H-2′a), 2.51-2.54 (m, 1H, H-2′b); ^{13}C NMR(150 MHz, $CDCl_3$) 169.4, 169.0, 156.8, 139.5, 138.6, 138.1, 137.5, 131.0, 128.9, 128.5×2, 128.0, 127.8×2, 127.6, 126.2, 126.0, 125.5, 122.7, 122.1, 121.8, 121.4, 121.3, 117.9, 116.7, 112.6, 107.9, 93.5, 77.8, 71.9, 70.3, 67.0, 53.2, 29.8, 27.8, 9.5; HR-ESIMS *m/z* 739.1033 $[M+H]^+$ (calcd for $C_{36}H_{28}N_4O_6I$, 739.1054).

Compound 24b: mp174 °C; $[\alpha]_D^{20}$ –73.4° (*c* 0.21, CH_2Cl_2); R_f 0.25 (3:1 EtOAc-PE); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.41 (d, *J* = 8.4 Hz, 1H, ArH), 9.23 (d, *J* = 8.4 Hz, 1H, ArH), 8.05 (d, *J* = 8.4 Hz, 1H, ArH), 7.61 (t, *J* = 7.2 Hz, 2H, ArH), 7.49 (t, *J* = 7.2 Hz, 1H, ArH), 7.43-7.46 (m, 4H, ArH), 7.30 (t, *J* = 7.2 Hz, 2H, ArH), 7.22 (t, *J* = 7.2 Hz, 1H, ArH), 6.63 (dd, *J* = 10.8, 6.0 Hz, 1H, H-1′), 5.34 (brs, 2H, $PhCH_2O\underline{CH_2}$), 5.31 (d, *J* = 9.0 Hz, 1H, H-4′), 4.77 (s, 2H, $Ph\underline{CH_2}OCH_2$), 4.52 (d, *J* = 11.4 Hz, 1H, H-6′a), 4.27-4.32 (m, 1H, H-3′), 3.96 (1H, d, *J* = 11.4 Hz, H-6′b), 2.84-2.89 (m, 1H, H-2′a), 2.80 (s, 3H, N-CH_3), 2.41-2.48 (m, 1H, H-2′b); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.4, 169.2, 155.4, 141.7, 137.8×2, 131.8, 128.7, 128.4×2, 128.0, 127.9×2, 127.8, 127.6, 126.6, 126.1, 125.1, 122.8, 122.3, 121.7, 121.3, 119.7×2, 115.0, 114.2, 107.6, 92.2, 79.5, 73.5, 71.6, 67.0, 53.4, 29.5, 29.0, 14.2; HR-ESIMS *m/z* 739.1038 $[M+H]^+$ (calcd for $C_{36}H_{28}N_4O_6I$, 739.1054).

Synthesis of 6-benzyloxymethyl-5,7-dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-12,13-diyl *N*-D-(2,3,4,6-tetra deoxy-(3-methyl-2-oxooxazolo[3,4-*d*]))-1,5-glucopyranoside (25)



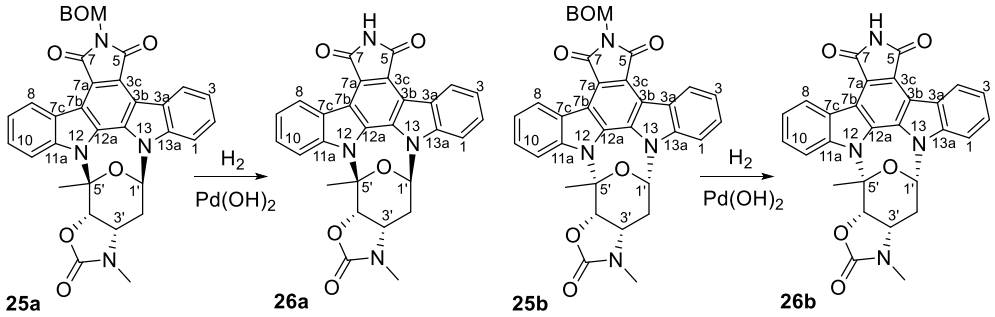
To a degassed green solution of **24a** (25 mg, 0.034 mmol) in 20 mL of benzene was added 0.1 mL of *n*-Bu_3SnH and 3 mg of 2,2'-azobisisobutyronitrile (AIBN). The reaction mixture was stirred for 1 h at refluxing. After cooling to rt, the reaction was concentrated *in vacuo*. The obtained residue was purified by a silica gel flash chromatography eluting with EtOAc-PE (v/v 2:1) to provide 6-benzyloxymethyl-5,7-dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-12,13-diyl *N*-D-(2,3,4,6-tetradeoxy-(3-methyl-2-oxooxazolo[3,4-*d*]))-1β,5β-glucopyranoside (**25a**) as a yellow solid (17 mg, 80% yield). By the same procedure, 6-benzyloxymethyl-5,7-dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*] carbazole-12,13-diyl *N*-D-

(2,3,4,6-tetradeoxy-(3-methyl-2-oxooxazolo[3,4-*d*]))-1α,5α-glucopyranoside (**25b**) was prepared from **24b** (20 mg) and purified as a yellow solid (15mg, 96% yield) by a silica gel flash chromatography eluting with EtOAc-PE (2:1).

Compound 25a: $[\alpha]_D^{20}$ +87.3° (*c* 0.29, CH_2Cl_2); R_f 0.28 (1:1 EtOAc-PE); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.35 (d, *J* = 7.2 Hz, 1H, ArH), 9.10 (d, *J* = 7.8 Hz, 1H, ArH), 7.64-7.57 (m, 3H, ArH), 7.47-7.42 (m, 4H, ArH), 7.30-7.37 (m, 3H, ArH), 7.23 (t, *J* = 7.2 Hz, 1H, ArH), 6.49 (dd, *J* = 9.6, 7.2 Hz, 1H, H-1'), 5.63 (d, *J* = 9.6 Hz, 1H, H-4'), 5.32 (d, *J* = 11.0 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 5.27 (d, *J* = 11.0 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 4.76 (s, 2H, $Ph\underline{CH_2}OCH_2$), 4.32-4.35 (m, 1H, H-3'), 3.10 (s, 3H, N-CH_3), 2.69-2.73 (m, 1H, H-2'a), 2.36-2.40 (m, 1H, H-2'b), 1.94 (s, 3H, H_3-6'); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.5, 169.2, 157.3, 140.1, 138.1, 137.7, 130.1, 129.0, 128.5×2, 128.0×2, 127.8, 127.6, 127.5, 126.7, 126.3, 124.7, 122.2, 122.1, 121.5, 121.1, 119.6, 118.5, 117.5, 112.4, 107.9, 94.0, 77.2, 71.7, 71.4, 66.9, 52.7, 29.6, 26.2, 24.6; HR-ESIMS *m/z* 635.1935 $[M+Na]^+$ (calcd for $C_{36}H_{28}N_4O_6Na$, 635.1907).

Compound 25b: $[\alpha]_D^{20}$ –24.0° (*c* 0.19, CH_2Cl_2); R_f 0.20 (3:1 EtOAc-PE); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.38 (d, *J* = 7.8 Hz, 1H, ArH), 9.21 (d, *J* = 7.8 Hz, 1H, ArH), 8.07 (d, *J* = 7.8 Hz, 1H, ArH), 7.56-7.59 (m, 2H, ArH), 7.41-7.45 (m, 5H, ArH), 7.29 (t, *J* = 7.8 Hz, 2H, ArH), 7.21 (t, *J* = 7.2 Hz, 1H, ArH), 6.56 (dd, *J* = 9.6, 6.6 Hz, 1H, H-1'), 5.37 (brs, 2H, $PhCH_2O\underline{CH_2}$), 5.08 (d, *J* = 8.4 Hz, 1H, H-4'), 4.75 (s, 2H, $Ph\underline{CH_2}OCH_2$), 4.23-4.29 (m, 1H, H-3'), 2.78-2.82 (m, 1H, H-2'a), 2.75 (s, 3H, N-CH_3), 2.39-2.45 (m, 1H, H-2'b), 2.05 (s, 3H, H_3-6'); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.5, 169.3, 155.8, 142.2, 137.8×2, 131.0, 130.6, 128.9, 128.7, 128.4×2, 128.0×2, 127.8, 127.6, 127.5, 126.6, 125.8, 124.6, 122.3×2, 121.6, 119.7, 119.5, 116.4, 107.5, 93.3, 79.0, 76.2, 71.6, 67.0, 53.0, 30.0, 29.7, 29.5; HR-ESIMS *m/z* 635.1912 $[M+Na]^+$ (calcd for $C_{36}H_{28}N_4O_6Na$, 635.1907).

Synthesis of 5,7-dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-12,13-diyl *N*-D-(2,3,4,6-tetradeoxy-(3-methyl-2-oxooxazolo[3,4-*d*]))-1,5-glucopyranoside (26)

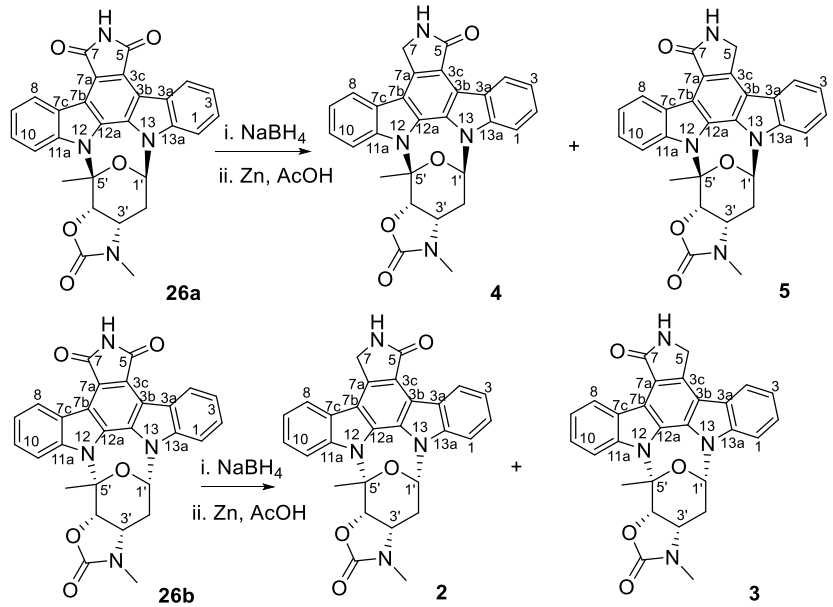


To a green solution of **25a** (10 mg, 0.016 mmol) in 10 mL of EtOAc and 10 mL of MeOH was added 1 mg of $Pd(OH)_2$ (20% on carbon). The reaction was then placed on a H_2 atmosphere by several evacuation/refill with H_2 cycles. The reaction was stirred vigorously overnight under the H_2 atmosphere. The reaction was then filtered through a pad of Celite and eluted with EtOAc and MeOH. The filtrate was concentrated *in vacuo* and then purified by HPLC eluting with 90% MeOH/H_2O to give 5,7-dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-12,13-diyl *N*-D-(2,3,4,6-tetradeoxy-(3-methyl-2-oxooxazolo[3,4-*d*]))-1β,5β-glucopyranoside (**26a**) as a green solid (7 mg, 89% yield, t_R 5.1 min). 5,7-Dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-12,13-diyl *N*-D-(2,3,4,6-tetradeoxy-(3-methyl-2-oxooxazolo[3,4-*d*]))-1α,5α-glucopyranoside (**26b**) was prepared from **25b** (15 mg) by the same method and purified as a green solid (11.3 mg, 96% yield) by a RP-18 flash chromatography eluting with 70% MeOH/H_2O.

Compound 26a: $[\alpha]_D^{20}$ +63.1° (*c* 0.1, CH_2Cl_2); R_f 0.45 (RP-18 TLC, 95% MeOH/H_2O); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.19 (s, 1H, NH), 9.22 (d, *J* = 7.8 Hz, 1H, ArH), 8.99 (d, *J* = 7.8 Hz, 1H, ArH), 8.08 (d, *J* = 7.8 Hz, 1H, ArH), 7.95 (d, *J* = 7.8 Hz, 1H, ArH), 7.65 (t, *J* = 7.8 Hz, 1H, ArH), 7.63 (t, *J* = 7.2 Hz, 1H, ArH), 7.48 (t, *J* = 7.8 Hz, 1H, ArH), 7.41 (t, *J* = 7.8 Hz, 1H, ArH), 6.99 (dd, *J* = 9.8, 6.9 Hz, 1H, H-1'), 5.77 (d, *J* = 9.6 Hz, 1H, H-4'), 4.45 (dt, *J* = 9.6, 3.0 Hz, 1H, H-3'), 2.99 (s, 3H, N-CH_3), 2.81 (ddd, *J* = 16.0, 6.9, 3.0 Hz, 1H, H-2'a), 2.18 (ddd, *J* = 16.0, 9.8, 3.0 Hz, 1H, H-2'b), 1.80 (s, 3H, H_3-6'); ^{13}C NMR(150 MHz, DMSO-d_6) δ 171.5, 171.2, 157.4, 140.5, 138.6, 130.3, 129.1, 127.8×2, 125.8, 125.4, 124.3, 122.1, 122.0, 121.6, 121.5, 120.7, 117.6, 116.5, 114.3, 110.7, 94.2, 78.0, 71.5, 52.5, 29.5, 25.5, 25.0; HR-ESIMS *m/z* 491.1358 $[M-H]^-$ (calcd for $C_{28}H_{19}N_4O_5$ 491.1355).

Compound 26b: $[\alpha]_D^{20}$ –89.2° (*c* 0.2, CH_2Cl_2); R_f 0.35 (RP-18 TLC, 95% MeOH/H_2O); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.19 (s, 1H, NH), 9.24 (d, *J* = 8.0 Hz, 1H, ArH), 9.04 (d, *J* = 8.0 Hz, 1H, ArH), 8.10 (d, *J* = 8.6 Hz, 1H, ArH), 7.88 (d, *J* = 8.6 Hz, 1H, ArH), 7.66 (d, *J* = 8.0 Hz, 1H, ArH), 7.60 (d, *J* = 8.0 Hz, 1H, ArH), 7.42-7.45 (m, 2H, ArH), 7.01 (dd, *J* = 9.6, 6.4 Hz, 1H, H-1'), 5.33 (d, *J* = 8.5 Hz, 1H, H-4'), 4.32-4.36 (m, 1H, H-3'), 2.94-2.99 (m, 1H, H-2'a), 2.58 (s, 3H, N-CH_3), 2.06-2.12 (m, 1H, H-2'b), 2.06 (s, 3H, H_3-6'); ^{13}C NMR (150 MHz, DMSO-d_6) δ 170.9, 170.6, 155.7, 141.4, 137.7, 130.0, 128.2, 127.2, 126.6, 125.0, 124.6, 123.5, 121.3, 121.2, 121.1, 120.9, 119.9, 117.5, 116.7, 115.8, 109.4, 92.7, 79.1, 75.4, 52.1, 29.8, 28.3×2; HR-ESIMS *m/z* 491.1366 $[M-H]^-$ (calcd for $C_{28}H_{19}N_4O_5$ 491.1355).

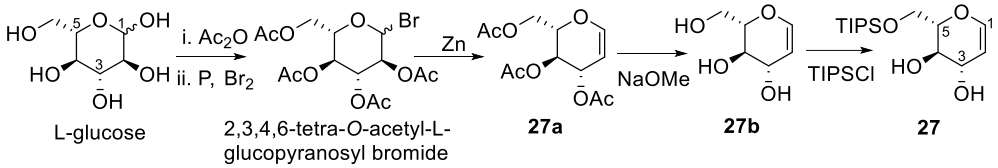
Synthesis of *ent*-ZHD-0501 (2), 5-deoxo-7-oxo-*ent*-ZHD-0501 (3), 3',4'-di*epi*-ZHD-0501 (4) and 3',4'-di*epi*-5-deoxo-7-oxo-ZHD-0501 (5)



To a green solution of **26a** (15 mg, 0.03 mmol) in 10 mL of MeOH was added 7.6 mg (0.2 mmol) of $NaBH_4$ at 0 °C. Over 2.0 h the reaction had turned slowly clear and was complete by TLC detection. The crude products were diluted with EtOAc (30 mL), washed with saturated NH_4Cl (20 mL) and brine (20 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude products were re-dissolved in 5 mL of AcOH and were treated with 20 mg (0.32 mmol) of Zn dust. After stirring at 40 °C for 1.5 h, the reaction was cooled to rt and diluted with EtOAc (20 mL) and then neutralized with saturated $NaHCO_3$ (20 mL). The organic layer was washed with brine, dried over Na_2SO_4, and

concentrated *in vacuo*. The obtained residue was purified by HPLC (40% MeCN/H_2O) to give 3',4'-di*epi*- ZHD-0501 (**4**) (5.2 mg, 36% yield, t_R 22.0 min) and 3',4'-di*epi*-5-deoxo-7-oxo-ZHD-0501 (**5**) (5.2 mg, 36% yield, t_R 24.0 min) as the light-yellow solid. *ent*-ZHD-0501 (**2**) (4.0 mg, 38% yield, t_R 23.3 min) and 5-deoxo-7-oxo-*ent*- ZHD-0501 (**3**) (4.0 mg, 38% yield, t_R 24.9 min) were prepared from **26b** (11 mg, 0.022 mmol) and purified by the same procedures.

Synthesis of 6-*O*-triisopropylsilyl-L-glucal (27)



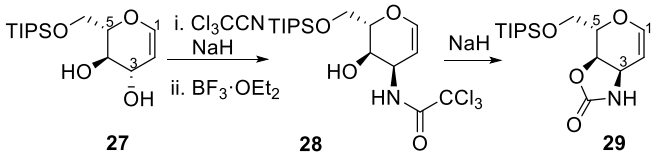
Perchloric acid (0.041 mL 70% cont.) was added dropwise to acetic anhydride (8 mL) at 40 ℃ and stirred for 30 min. The flask was then cooled to 30 ℃, and L-glucose (2 g) was slowly added and stirred for 30 min. The reaction was cooled to 10℃, and was slowly added phosphorus (0.62 g), bromine (1.16 mL) and water (0.72 mL) to control the reaction temperature less than 20 ℃. The reaction mixture was then slowly warmed to rt and stirred for 2 h. The reaction was quenched with ice water (10 mL) and then extracted with EtOAc (20 mL×3). The combined organic layers were washed with saturated $NaHCO_3$ (20 mL×3), dried over Na_2SO_4, and concentrated *in vacuo* to give the crude 2,3,4,6-tetra-*O*-acetyl-L-glucopyranosyl bromide. This crude intermediate was re-dissolved in 50 mL of EtOAc and cooled to 0 ℃. A suspension of Zn dust (3.22 g), $CuSO_4 \cdot 5H_2O$ (42.4 mg) and AcONa (212 mg) in 60% AcOH-H_2O (30 mL) was added to the EtOAc solution and the mixture was stirred at 0 ℃ for 1 h and then at rt for 3 h. After the reaction was complete, the suspension was filtered through a pad of Celite and eluted with EtOAc. The filtrate was washed with aqueous $NaHCO_3$ and H_2O in order, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified on a silica gel column eluting with EtOAc-PE (v/v 1:3) to provide 3,4,6-*O*-triacetyl-L- glucal (**27a**) as a colorless oil (2.50 g, 82% yield, 2 steps). R_f 0.25 (1:4 EtOAc-PE); ESIMS *m/z* 273.3 $[M+H]^+$.

Compound **27a** (2.5 g, 9.19 mmol) was dissolved in MeOH (100 mL), and then MeONa (60 mg) was added and stirred at rt for 1 h. The reaction mixture was neutralized by a H^+ Dowex (50×8) resin till pH 7, which was removed by filtration. After concentrated *in vacuo*, the filtrate was purified on a silica gel column using EtOAc as the eluent to provide L- glucal (**27b**) (1.3 g, 97% yield) as a colorless oil; ESIMS *m/z* 147.2 $[M+H]^+$.

Compound **27b** (1.3 g, 8.9 mmol) was dissolved in pyridine (30 mL) and cooled to 0 ℃ and then triisopropylsilyl (TIPS) chloride (3.78 mL, 17.8 mmol) and imidazole (3.61 g, 53.4 mmol) were added. The reaction mixture was stirred at rt for 2 h and then quenched by the addition of 50 mL of cooled water and diluted with EtOAc (150 mL). The resulting EtOAc solution was washed with H_2O (100 mL) and brine (100 mL) in order, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by a silica gel column eluting with EtOAc-PE (v/v 1:4) to provide 6-*O*-triisopropylsilyl-L-glucal (**27**) (1.41 g, 52% yield) as a colorless oil. $[\alpha]_D^{20}$ –4.10° (*c* 2.53, CH_2Cl_2); R_f 0.35 (1:4 EtOAc-PE); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.27 (dd, *J* = 6.0 Hz, 1.7, 1H, H-1), 4.69 (dd, *J* = 6.0 Hz, 2.2, 1H, H-2), 4.26 (brs, 1H, H-4), 4.04 (dd, *J* = 12.0, 4.8 Hz, 1H, H-6a), 3.98 (dd, *J* = 12.0, 4.8 Hz, 1H, H-6b), 3.79-3.82 (m, 2H, H-3 and H-5), 1.13 (hep, *J* = 6.0 Hz, 3H, $((CH_3)_2C\underline{H})_3Si$-), 1.06 (d, *J* = 6.0 Hz, 18H, $((C\underline{H}_3)_2CH)_3Si$-). ^{13}C-NMR (125

MHz, $CDCl_3$) δ 143.9, 102.5, 76.5, 72.5, 69.4, 64.4, 17.8×3, 11.8×6; ESIMS *m/z* 325.1 $[M + Na]^+$.

Synthesis of 6-*O*-triisopropylsilyl-3,4-dideoxy-(2-oxooxazolo[3,4-*d*])-L-glucal (29)



27 **28** **29**

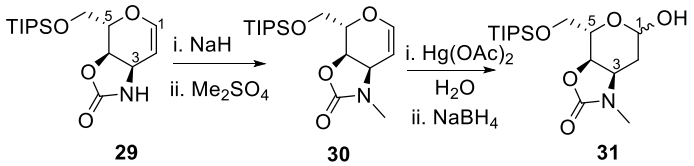
To a clear, colorless solution of 1.41 g (4.7 mmol) of glycal **27** in 20 mL of CH_2Cl_2 at -5 ℃ was added 0.74 g (18.5 mmol, 60% dispersion) of NaH. The reaction was air bubbled and stirred at 0 ℃ for 20 min, and then was warmed to rt for 1.5 h. Cl_3CCN (5.51 mL, 55.6 mmol) was added to the reaction mixture at -5 ℃ and then was slowly warmed to rt and stirred overnight. The resulting brown solution was cooled to -78 ℃ and 17.0 mL (139 mmol) of $BF_3{\cdot}OEt_2$ was added. After stirring for 6 h at -78 ℃, the reaction was quenched at -78℃ with 20 mL of saturated $NaHCO_3$. The reaction was then slowly warmed to rt, diluted with H_2O and extracted with CH_2Cl_2 (20 mL×3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The resulting residue was purified by a silica gel flash chromatography eluting with EtOAc-PE (v/v 1:40) to yield 3- trichloroacetylamino glucal **28** as a colorless oil (880 mg, 42% yield).

To a clear, colorless solution of 880 mg (1.98 mmol) of glycal **28** in 20 mL of CH_2Cl_2 at 0 ℃ was added 194 mg (4.95 mmol, 60% dispersion) of NaH. The reaction was warmed slowly to rt and was stirred for 3h. The reaction was quenched with H_2O (20 mL) and extracted with CH_2Cl_2 (20 mL×3). The combined CH_2Cl_2 layer was washed with brine, and then dried over Na_2SO_4. After filtration and concentration *in vacuo*, the EtOAc extracts were purified by flash chromatography on a silica gel column eluting with EtOAc-PE (v/v 1:4) to provide 6-*O*-triisopropylsilyl-3,4-dideoxy-(2-oxooxazolo[3,4-*d*])-L-glucal (**29**) as a white solid (537 mg, 84% yield).

Compound 28: $[\alpha]_D^{20}$-71.6° (*c* 0.90, CH_2Cl_2); R_f 0.45 (1:9 EtOAc-PE). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.02 (brs, 1H, NH), 6.45 (d, *J* = 6.0, 1H, H-1), 4.93 (dd, *J* = 6.0, 5.0 Hz, 1H, H-2), 4.46-4.49 (m, 1H, H-4), 4.16-4.18 (m, 1H, H-3), 4.06 (dd, *J* = 12.0, 5.4 Hz, 1H, H-6a), 3.96 (dd, *J* = 12.0, 5.4 Hz, 1H, H-6b), 3.82-3.86 (m, 1H, H-5), 1.14 (hep, *J* = 6.0 Hz, 3H, $((CH_3)_2C\underline{H})_3Si$-), 1.07 (d, *J* = 6.0 Hz, 18H, $((C\underline{H}_3)_2CH)_3Si$-); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 162.4, 145.8, 97.3, 92.6, 74.6, 67.3, 63.5, 45.9, 17.9×3, 11.8×6; ESIMS *m/z* 446.1 $[M + H]^+$.

Compound 29: $[\alpha]_D^{20}$ –86.0° (*c* 0.50, CH_2Cl_2); R_f 0.20 (1:4 EtOAc-PE). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.59 (d, *J* = 6.0, 1H, H-1), 5.87 (brs, 1H, NH), 4.85-4.88 (m, 2H, H-2 and H-4), 4.34 (dd, *J* = 7.5, 4.0 Hz, 1H, H-3), 4.04 (dd, *J* = 11.0, 3.0 Hz, 1H, H-6a), 3.99 (dd, *J* = 11.0, 3.60 Hz, 1H, H-6b), 3.82-3.84 (m, 1H, H-5), 1.13 (hep, *J* = 6.0 Hz, 3H, $((CH_3)_2C\underline{H})_3Si$-), 1.06 (d, *J* = 6.0 Hz, 18H, $((C\underline{H}_3)_2CH)_3Si$-); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 158.5, 147.2, 98.5, 74.1, 71.1, 61.8, 46.1, 17.9×3, 11.9×6; ESIMS *m/z* 326.1 $[M - H]^-$.

Synthesis of 6-*O*-triisopropylsilyl-2,3,4-trideoxy-(3-methyl-2-oxooxazolo[3,4-*d*])-L-glucose (31)



29 **30** **31**

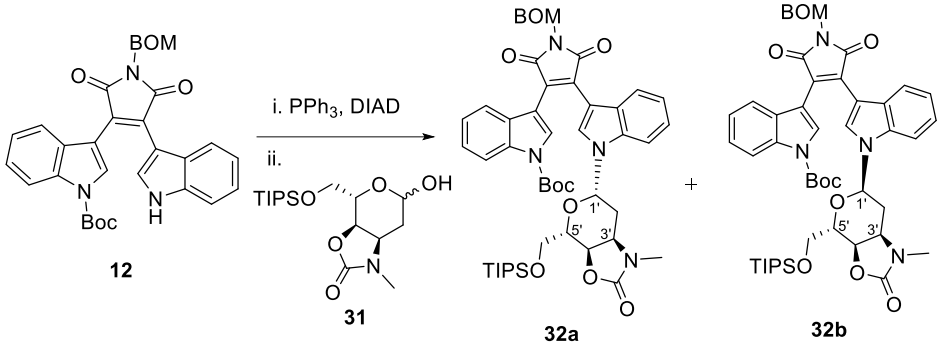
To a clear, colorless solution of 537 mg (1.64 mmol) of the glycal **29** in 20 mL of CH_2Cl_2 was added 197 mg (4.92 mmol, 60% dispersion) of NaH at 0 ℃. The reaction was bubbled and warmed slowly to rt and then stirred for 2h. After cooling to 0 ℃, the reaction mixture was treated with dimethyl sulphate (0.79 mL, 8.21 mmol) and warmed slowly to rt. The reaction mixture was stirred overnight at rt, quenched with 10 mL water at 0 ℃, and then was extracted with CH_2Cl_2 (20 mL×3). The combined CH_2Cl_2 layer was washed with brine and dried over Na_2SO_4. After filtration and concentration *in vacuo*, the EtOAc extracts were purified by flash chromatography on a silica gel column eluting with EtOAc-PE (v/v 1:8) to provide 6-*O*-triisopropylsilyl-3,4-dideoxy-(3-methyl-2-oxooxazolo[3,4-*d*])-L-glucal (**30**) as a colorless oil (467 mg, 83% yield).

To a clear, colorless solution of 467 mg (1.37 mmol) of the glycal **30** in 20 mL of THF was cooled to 0 ℃ and treated with $Hg(OAc)_2$ (876 mg, 2.74 mmol) dissolved in water (20 mL). After stirred for 2 h at 30-40 ℃ till the glycal **30** was consumed up by TLC detection, the reaction mixture was diluted with 60 mL of water. Then, $NaBH_4$ (416.5 mg, 11.0 mmol) was added at 0 ℃ in 1 min, and the reaction mixture was bubbled by CO_2 till pH 7. The suspension was extracted with EtOAc (50 mL×4). The combined EtOAc layer was washed with brine and dried over anhydrous Na_2SO_4. After filtration and concentration *in vacuo*, the EtOAc extracts were purified by flash chromatography on a silica gel column eluting with EtOAc-PE (v/v 1:3) to yield 6-*O*-triisopropylsilyl-3,4-dideoxy-(3-methyl-2-oxooxazolo[3,4-*d*])-L-glucal (**31**) as a 1-epimeric mixture (400 mg, 81% yield).

Compound 30: $[\alpha]_D^{20}$ –77.0° (*c* 1.0, CH_2Cl_2); R_f 0.50 (1:3 EtOAc-PE). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.67 (d, *J* = 6.0 Hz, 1H, H-1), 4.93 (dd, *J* = 6.0, 4.0 Hz, 1H, H-2), 4.74 (1H, dd, *J* = 9.0, 7.5 Hz, H-4), 4.05-4.07 (m, 1H, H-3), 4.04 (dd, *J* = 12.0, 2.5 Hz, 1H, H-6a), 4.00 (dd, *J* = 12.0, 2.5 Hz, 1H, H-6b), 3.60-3.63 (1H, m, H-5), 2.84 (s, 3H, N-CH_3) 1.12 (hep, *J* = 6.0 Hz, 3H, $((CH_3)_2C\underline{H})_3Si$-), 1.06 (d, *J* = 6.0 Hz, 18H, $((C\underline{H}_3)_2CH)_3Si$-); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 157.3, 148.4, 96.0, 74.5, 67.8, 61.7, 51.0, 28.6, 17.9×3, 11.9×6; HR-ESIMS *m/z* 342.2096 $[M + H]^+$ (calcd for $C_{17}H_{32}NO_4Si$, 342.2101).

Compound 31: colorless oil; R_f 0.15 (1:2 EtOAc-PE); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.31 (ddd, *J* = 5.6, 3.7, 3.7 Hz, 1H, H-1)/ 5.17 (ddd, *J* = 6.6, 4.1, 2.6 Hz, 1H, H-1), 4.64-4.68 (m, 1H, H-4)/4.56-4.60 (m, 1H, H-4), 3.87-3.96 (m, 4H, H-6), 3.77-3.82 (m, 1H, H-5)/3.60-3.63 (m, 1H, H-5), 2.87 (s, 3H, N-CH_3)/2.84 (s, 3H, N-CH_3), 2.22-2.27 (m, 1H, H-2a)/2.05-2.09 (m, 1H, H-2a), 1.97-2.02 (m, 1H, H-2b)/1.79-1.85 (m, 1H, H-2b), 1.13 (hep, *J* = 7.2 Hz, 6H, 2×$((CH_3)_2C\underline{H})_3Si$-), 1.07 (d, *J* = 7.2 Hz, 36H, 2×$((C\underline{H}_3)_2CH)_3Si$-). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 158.2/157.8, 91.6/90.6, 74.5/69.0, 68.7/68.1, 63.2/63.0, 53.7/52.8, 31.1/29.9, 29.1/28.8, 17.9×6, 12.0×12; HR-ESIMS *m/z* 360.2220 $[M + H]^+$ (calcd for $C_{17}H_{34}NO_5Si$, 360.2206).

Synthesis of 3-(*N*-benzyloxymethyl-3-(1-*tert*-butoxycarbonylindol-3-yl)maleimide-2-yl)indol-1-yl *N*-L-(6-*O*-triisopropylsilyl-2,3,4-trideoxy-(3-methyl-2-oxooxazolo[3,4-*d*]))glucopyranoside (32)



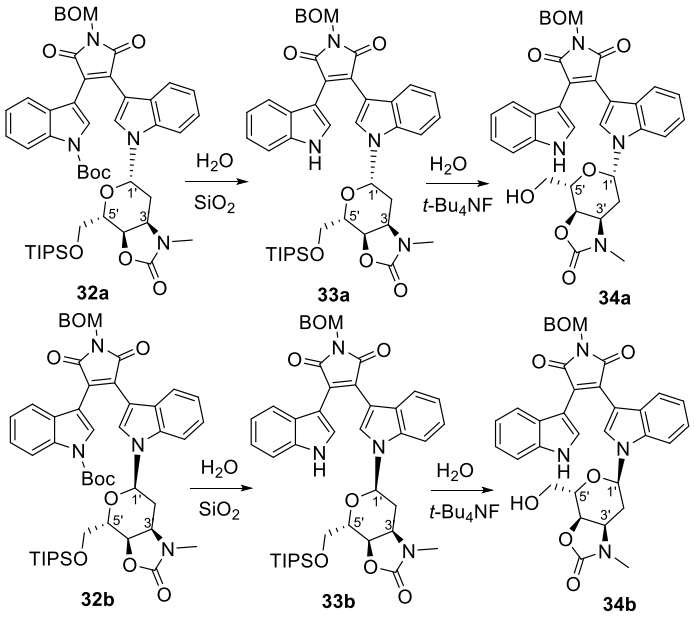
To a solution of **12** (870 mg, 1.59 mmol) in THF (20 mL) were added triphenylphosphine (833 mg, 3.18 mmol). The mixture was cooled to -78 ℃, and then DIAD (0.62 mL, 3.18 mmol) was added dropwise and stirred at -78 ℃ for 1h. Then, a solution of **31** (380 mg, 1.06 mmol) was added to the mixture dropwise. After stirring for 2 h at -78℃, the mixture was warmed to rt and stirred overnight. The crude reaction mixture was quenched with water (30 mL), extracted with EtOAc (50 ×3 mL) and the combined organic phase was dried over anhydrous Na_2SO_4. After removal of the solvent, and the residue was purified through a silica gel column eluting with EtOAc-PE (v/v 1:3) to give 3-(*N*-benzyloxymethyl-3-(1-*tert*-butoxycarbonylindol-3-yl)maleimide-2-yl)indol-1-yl *N*-β-L-(6-*O*-triisopropylsilyl-2,3,4-trideoxy-(3-methyl-2-oxooxazolo[3,4-*d*]))glucopyranoside (**32a**) (226 m, 24% yield) and 3-(*N*-benzyloxy methyl-3-(1-*tert*-butoxycarbonylindol-3-yl)maleimide-2-yl)indol-1-yl *N*-α-L-(6-*O*-triisopropyl silyl-2,3,4-trideoxy-(3-methyl-2-oxooxazolo[3,4-*d*]))glucopyranoside (**32b**) (230 mg, 2 25% yield) as orange powder.

Compound 32a: $[a]_D^{20}$ −14.2° (*c* 1.0, CH_2Cl_2); R_f 0.25 (1:2 EtOAc-PE). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.8 Hz, 1H, ArH), 8.11 (s, 1H, ArH), 7.77 (s, 1H, ArH), 7.36-7.40 (m, 3H, ArH), 7.29-7.32 (m, 2H, ArH), 7.23-7.25 (m, 1H, ArH), 7.15-7.18 (m, 1H, ArH), 7.10-7.12 (m, 2H, ArH), 6.86 (t, *J* = 7.8 Hz, 1H, ArH), 6.77-6.81 (m, 2H, ArH), 5.71 (dd, *J* = 10.5, 2.0 Hz, 1H, H-1'), 5.23 (d, *J* = 11.0 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 5.21 (d, *J* = 11.0 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 4.71 (s, 2H, $PhC\underline{H_2}OCH_2N$), 4.69 (dd, *J* = 9.0, 7.5 Hz, 1H, H-4'), 4.05-4.09 (1H, m, H-3'), 4.00 (dd, *J* = 12.0, 2.0 Hz, 1H, H-6'a), 3.95 (dd, *J* = 12.0, 2.0 Hz, 1H, H-6'b), 3.82-3.85 (1H, m, H-5'), 2.88 (s, 3H, N-CH_3), 2.39-2.44 (m, 1H, H-2'a), 2.27-2.30 (m, 1H, H-2'b), 1.69 (s, 9H, $(C\underline{H_3})_3CO$-), 1.08 (hep, *J* = 6.0 Hz, 3H, $((CH_3)_2C\underline{H})_3Si$-), 1.02 (d, *J* = 6.0 Hz, 18H, $((C\underline{H_3})_2CH)_3Si$-).^{13}C NMR (125 MHz, $CDCl_3$) δ 171.1, 171.0, 158.5, 149.2, 137.7, 135.8, 135.2, 130.6, 129.0, 128.6, 128.4×2, 127.7×2, 127.6×2, 126.6, 125.8, 124.6, 123.2, 122.5, 122.2, 121.8, 121.6, 115.1, 110.6, 110.5, 107.1, 84.6, 79.5, 78.4, 71.7, 67.4, 67.1, 63.0, 55.8, 29.6, 29.4, 28.2×3, 17.9×3, 11.9×6; HR-ESIMS *m/z* 911.4015 $[M + Na]^+$ (calcd for $C_{50}H_{60}N_4O_9NaSi$, 911.4027).

Compound 32b: $[a]_D^{20}$ +9.3° (*c* 0.40, CH_2Cl_2); R_f 0.20 (1:2 EtOAc-PE). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.2 Hz, 1H, ArH), 8.13 (s, 1H, ArH), 7.64 (s, 1H, ArH), 7.39-7.42 (m, 3H, ArH), 7.28-7.33 (m, 3H, ArH), 7.22-7.25 (m, 1H, ArH), 7.15-7.20 (m, 2H, ArH), 6.95 (t, *J* = 7.0 Hz, 1H, ArH), 6.78 (t, *J* = 8.0 Hz, 1H, ArH), 6.72 (d, *J* = 8.0 Hz, 1H, ArH), 6.10 (dd, *J* = 10.0, 6.0 Hz, 1H, H-1'), 5.24 (d, *J* = 11.0 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 5.22 (d, *J* = 11.0 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 4.76 (t, *J* = 7.8 Hz, 1H, H-4'), 4.72 (s, 2H, $PhC\underline{H_2}OCH_2N$), 3.99-4.04 (m, 1H, H-3'), 3.85-3.94

(m, 2H, H-6'), 3.80-3.83 (m, 1H, H-5'), 2.87 (s, 3H, N-CH_3), 2.39-2.45 (m, 1H, H-2'a), 2.05-2.13 (m, 1H, H-2'b), 1.69 (s, 9H, ($C\underline{H}_3$)$_3$CO-), 1.07 (hep, J = 6.0 Hz, 3H, ((CH_3)$_2$C$\underline{H}$)$_3$Si-), 1.02 (d, J = 6.0 Hz, 18H, (($C\underline{H}_3$)$_2$CH)$_3$Si-).^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 170.9, 157.2, 149.2, 137.8, 136.0, 135.4, 130.8, 129.3, 128.4×3, 127.7, 127.6×2, 127.3, 126.7, 126.0, 124.6, 123.2, 122.4×2, 121.9, 121.6, 115.3, 110.5, 110.3, 107.1, 84.7, 78.6, 72.4, 71.8, 68.8, 67.4, 63.5, 53.6, 29.7, 29.2, 28.2×3, 17.9×3, 11.9×6; HR-ESIMS *m/z* 911.4038 $[M + Na]^+$ (calcd for $C_{50}H_{60}N_4O_9NaSi$, 911.4027).

Synthesis of 3-(*N*-benzyloxymethyl-3-(indol-3-yl)maleimide-2-yl)indol-1-yl *N*-L-(2,3,4-trideoxy-(3-methyl-2-oxooxazolo[3,4-*d*]))glucopyranoside (34)



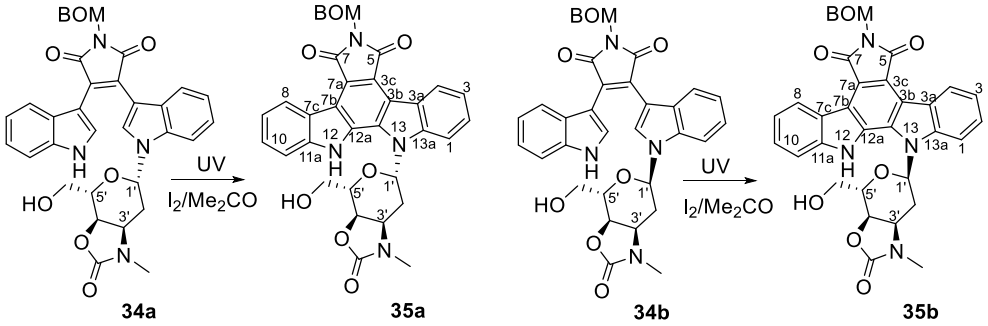
To a solution of **32a** (226 mg, 0.254 mmol) in toluene (40 mL) were added silica gel (3.0 g) and refluxed for 5h. The mixture was filtered through a pad of Celite and washed with EtOAc to give 3-(*N*-benzyloxymethyl-3-(indol-3-yl) maleimide-2-yl)indol-1-yl *N*-β-L-(6-*O*-triisopropylsilyl-2,3,4-trideoxy-(3-methyl-2-oxooxazolo[3,4-*d*]))gluco pyranoside (**33a**) as orange powder (200 mg, 100% yield), R_f 0.30 (1:1 EtOAc-PE), HR-ESIMS *m/z* 787.3556 $[M–H]^–$ (calcd for $C_{45}H_{51}N_4O_7Si$, 787.3527). 3-(*N*-Benzyloxymethyl-3-(indol-3-yl)maleimide-2-yl)indol-1-yl *N*-α-L-(6-*O*-triisopropylsilyl-2,3,4-trideoxy-(3-methyl-2-oxooxazolo [3,4-*d*]))glucopyranoside (**33b**) (201mg, 100% yield) was achieved by the same method from **32b** (226 mg, 0.254 mmol), R_f 0.15 (1:1 EtOAc-PE), HR-ESIMS *m/z* 787.3525 $[M–H]^–$ (calcd for $C_{45}H_{51}N_4O_7Si$, 787.3527). To a solution of 200 mg (0.253mmol) of **33a** in 30 mL of THF at 0 ℃ was added 1.0 mL of *t*-Bu_4NF (1.0 mmol, 1.0 *M* solution in THF). Over 1 h the reaction turned from orange to darken blue and was complete. The crude reaction mixture was diluted with EtOAc (100 mL) and the combine organic layers were washed with water (50 mL). After dried over anhydrous Na_2SO_4, the EtOAc layer was concentrated *in vacuo* and then was purified by flash chromatography on silica gel eluting with EtOAc-PE (2:1, v/v) to provide 3-(*N*-benzyloxymethyl-3-(indol- 3-yl)maleimide-2-yl)indol-1-yl *N*-β-L-(2,3,4-trideoxy-(3-methyl-2-oxo oxazolo[3,4-*d*]))glucopyranoside (**34a**) as an orange powder (158 mg, 98% yield). By the same method, 3-(*N*-benzyloxymethyl-3-(indol-3-yl)maleimide-2-yl)indol-1-yl *N*-α-L-(2,3,4-trideoxy-(3-methyl-2-oxooxazolo[3,4-*d*]))

glucopyranoside (**34b**) was achieved from **33b** (201 mg) and purified as an orange powder (151.7 mg, 94% yield, 0.24mmol) by a silica gel flash chromatography eluting with EtOAc-PE (3:1, v/v).

Compound 34a: $[a]_D^{20}$ +11.6° (*c* 0.55, CH_2Cl_2); R_f 0.30 (2:1 EtOAc-PE); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (brs, 1H, NH), 7.69 (d, *J* = 3.0 Hz, 1H, ArH), 7.62 (s, 1H, ArH), 7.37-7.38 (m, 2H, ArH), 7.28-7.33 (m, 4H, ArH), 7.23-7.26 (m, 1H, ArH), 7.15-7.19 (m, 1H, ArH), 7.14 (d, *J* = 7.5 Hz, 1H, ArH), 7.07-7.10 (m, 1H, ArH), 6.87-6.92 (m, 2H, ArH), 6.77-6.80 (m, 1H, ArH), 5.71 (dd, *J* = 10.5, 2.0 Hz, 1H, H-1'), 5.17 (brs, 2H, $PhCH_2O\underline{CH_2}N$), 4.68 (s, 2H, $Ph\underline{CH_2}OCH_2N$), 4.46 (1H, dd, *J* = 9.0, 7.0 Hz, H-4'), 3.92-3.95 (m, 1H, H-3'), 3.85-3.87 (m, 1H, H-6'a), 3.76-3.79 (m, 1H, H-5'), 3.66-3.69 (m, 1H, H-6'b), 2.82 (s, 3H, N-CH_3), 2.30-2.36 (m, 1H, H-2'a), 2.20-2.23 (m, 1H, H-2'b).^{13}C NMR (125 MHz, $CDCl_3$) δ 171.6, 171.5, 158.4, 137.7, 136.1, 136.0, 129.2, 129.0, 128.4×2, 127.8, 127.7 ×2, 127.6, 126.8, 126.5, 124.8, 123.2, 122.8, 122.7, 122.2, 121.4, 120.4, 111.5, 109.8, 107.6, 106.7, 78.8, 77.6, 71.6, 67.2, 62.1, 60.5, 55.7, 29.5, 28.9; HR-ESIMS *m/z* 631.2185 $[M - H]^-$ (calcd for $C_{36}H_{31}N_4O_7$ 631.2193).

Compound 34b: $[a]_D^{20}$ +19.3° (*c* 0.25, CH_2Cl_2); R_f 0.30 (3:1 EtOAc-PE); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.80 (s, 1H, NH), 7.83 (d, *J* = 3.0 Hz, 1H, ArH), 7.47 (s, 1H, ArH), 7.45 (d, *J* = 7.5 Hz, 1H, ArH), 7.38-7.41 (m, 3H, ArH), 7.36 (d, *J* = 8.0 Hz, 1H, ArH), 7.29-7.32 (m, 2H, ArH), 7.20-7.25 (m, 2H, ArH), 7.08-7.11 (m, 1H, ArH), 7.00-7.03 (m, 1H, ArH), 6.73-6.76 (m, 2H, ArH), 6.06 (dd, *J* = 10.0, 5.0 Hz, 1H, H-1'), 5.23 (d, *J* = 11.0 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 5.21 (d, *J* = 11.0 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 4.72 (s, 2H, $Ph\underline{CH_2}OCH_2N$), 4.62 (t, *J* = 9.5 Hz, 1H, H-4'), 3.94-3.99 (m, 1H, H-3'), 3.71-3.73 (m, 1H, H-6'a), 3.61-3.63 (m, 1H, H-6'b), 3.54-3.57 (m, 1H, H-5'), 2.81 (s, 3H, N-CH_3), 2.42-2.47 (m, 1H, H-2'a), 2.01-2.08 (m, 1H, H-2'b); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.5×2, 157.0, 137.8, 136.2, 135.8, 129.3, 129.0, 128.4×2, 127.7×3, 127.4, 127.2, 126.8, 124.3, 123.2, 122.8, 122.7, 122.2, 121.5, 120.4, 111.6, 109.8, 107.7, 106.7, 78.3, 71.7, 71.3, 68.6, 67.3, 62.1, 53.2, 29.7, 28.7; HR-ESIMS *m/z* 631.2180 $[M - H]^-$ (calcd for $C_{36}H_{31}N_4O_7$ 631.2193).

Synthesis of 6-benzyloxymethyl-5,7-dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-13-yl *N*-L-(2,3,4-trideoxy-(3-methyl-2-oxooxazolo[3,4-*d*]))glucopyranoside (35)



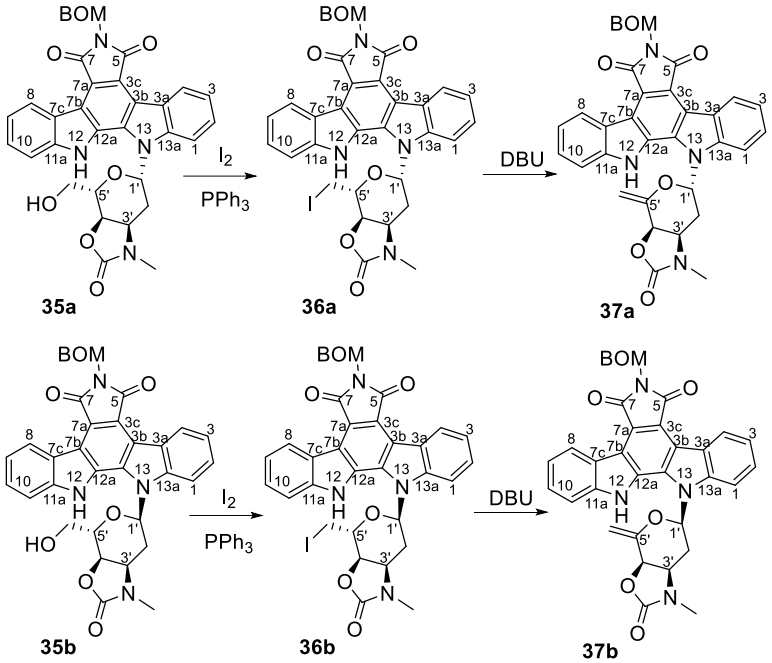
An orange solution of 10 mg (0.016 mmol) of **34a** in 1000 mL of acetone was treated with 1 mg of iodine. The reaction mixture was irradiated with a medium mercury lamp (125 W) and stirring vigorously for 12 h. Acetone was added to the reaction each hour to keep the solvent volume constant. The reaction turned from orange to bright yellow and was complete. The saturated $Na_2S_2O_3$ (10 mL) was added to remove the excess I_2, and the acetone was then evaporated off *in vacuo*. The concentrated solution was extracted by EtOAc (20 mL) and the organic layer was rinsed

with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The crude products were purified by flash chromatography on a silica gel column eluting with EtOAc-PE (1:1, v/v) to provide 6-benzyloxymethyl-5,7-dioxoindolo[2,3-*a*] pyrrolo[3,4-*c*]carbazole-13-yl *N*-β-L-(2,3,4-trideoxy-(3-methyl-2-oxooxazolo[3,4-*d*]))glucopyranoside (**35a**) as a yellow solid (6.1 mg, 61% yield). 6-Benzyloxymethyl-5,7-dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*] carbazole-13-yl *N*-α-L-(2,3,4-trideoxy-(3-methyl-2-oxooxazolo[3,4-*d*]))glucopyranoside (**35b**) was prepared from **34b** (10 mg) by the same method and purified as a yellow solid (5.3 mg, 53% yield) by a silica gel flash chromatography eluting with EtOAc-PE (v/v 3:1).

Compound 35a: $[a]_D^{20}$ −51.7° (*c* 0.07, CH_2Cl_2); R_f 0.4 (1:1 EtOAc-PE). ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.98 (s, 1H, NH), 9.06 (d, *J* = 7.8 Hz, 1H, ArH), 8.64 (d, *J* = 7.8 Hz, 1H, ArH), 7.47 (t, *J* = 7.7 Hz, 1H, ArH), 7.39 (d, *J* = 7.5 Hz, 2H, ArH), 7.38 (d, *J* = 7.7 Hz, 1H, ArH), 7.31 (t, *J* = 7.8 Hz, 2H, ArH), 7.23-7.26 (m, 3H, ArH), 7.19 (t, *J* = 7.8 Hz, 1H, ArH), 6.85 (t, *J* = 8.4 Hz, 1H, ArH), 6.11 (dd, *J* = 11.0, 2.0 Hz, 1H, H-1'), 5.15 (t, *J* = 7.8 Hz, 1H, H-4'), 4.95 (brs, 2H, $PhCH_2O\underline{CH_2}N$), 4.70 (s, 2H, $Ph\underline{CH_2}OCH_2N$), 4.28 (d, *J* = 10.3 Hz, 1H, H-3'), 4.04-4.08 (m, 3H, H-5', H-6'), 2.88 (s, 3H, N-CH_3), 2.21-2.26 (m, 1H, H-2'a), 1.97-2.00 (m, 1H, H-2'b); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.2, 168.9, 158.8, 140.7, 139.6, 137.5, 129.6, 128.5 × 2, 128.1, 127.9×3, 127.4, 126.9, 125.9, 124.7, 122.4, 121.5, 121.4, 120.4, 120.2, 119.2, 118.1, 117.8, 111.3, 108.6, 79.1, 78.3, 71.6, 66.5, 66.3, 60.5, 56.1, 29.6, 28.9; HR-ESIMS *m/z* 629.2045 $[M–H]^-$ (calcd for $C_{36}H_{29}N_4O_7$, 629.2036).

Compound 35b: $[a]_D^{20}$ +32.6° (*c* 0.11, CH_2Cl_2); R_f 0.2 (3:1 EtOAc-PE). ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.78 (s, 1H, NH), 8.91-8.94 (m, 2H, ArH), 7.47 (d, *J* = 8.2 Hz, 1H, ArH), 7.39-7.41 (m, 3H, ArH), 7.34 (t, *J* = 7.5 Hz, 1H, ArH), 7.31 (t, *J* = 7.8 Hz, 2H, ArH), 7.27 (d, *J* = 8.2 Hz, 1H, ArH), 7.23-7.26 (m, 1H, ArH), 7.21 (t, *J* = 7.8 Hz, 1H, ArH), 7.16 (t, *J* = 7.8 Hz, 1H, ArH), 6.63 (dd, *J* = 10.70, 2.0 Hz, 1H, H-1'), 5.07 (d, *J* = 11.2 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 5.01 (d, *J* = 11.2 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 4.70 (s, 2H, $Ph\underline{CH_2}OCH_2N$), 4.68 (brs, 1H, H-4'), 4.49-4.50 (m, 1H, H-3'), 4.31-4.33 (m, 1H, H-5'), 4.04-4.09 (m, 2H, H-6'), 2.59 (s, 3H, N-CH_3), 2.07-2.11 (m, 1H, H-2'a), 1.97-2.03 (m, 1H, H-2'b); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.2, 169.0, 157.0, 140.6, 139.7, 137.6, 129.1, 128.6×2, 128.1×2, 128.0×2, 127.7, 127.1, 125.8, 124.9, 122.2, 121.6 × 2, 121.0 , 123.1, 118.7, 118.3, 118.1, 111.9, 109.0, 77.6, 75.3, 70.9, 66.8, 64.6, 60.5, 54.6, 29.8, 28.8; HR-ESIMS *m/z* 629.2023 $[M–H]^-$ (calcd for $C_{36}H_{29}N_4O_7$, 629.2036).

Synthesis of 6-benzyloxymethyl-5,7-dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-13-yl *N*-L-(2,3,4-trideoxy-5,6-dehydro-(3-methyl-2-oxooxazolo[3,4-*d*]))glucopyranoside (37)



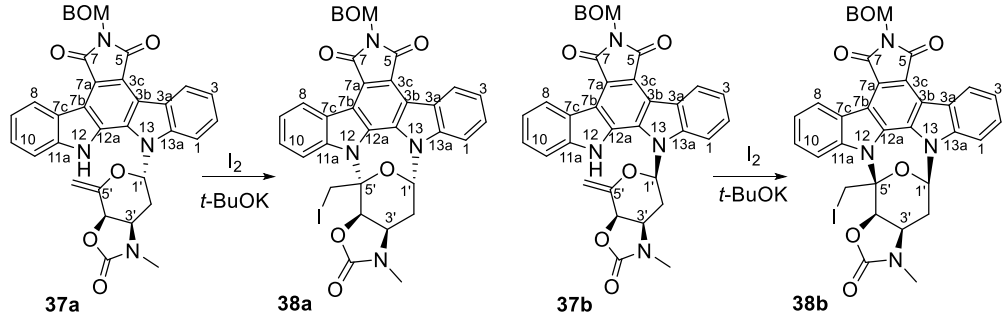
To a solution of 242 mg (0.92 mmol) of triphenylphosphine (Ph_3P) and 126 mg (1.85 mmol) of imidazole in 20 mL of CH_2Cl_2 at 0 ℃ was added 234 mg (1.85 mmol) of iodine. The reaction turned to clear and bright yellow solution over 1 h. Then, a green solution of 97 mg (0.15 mmol) of **35a** in 20 mL of CH_2Cl_2 was added dropwise via cannula. The reaction slowly warmed to rt and stirred for 6 h. The reaction mixture was diluted with CH_2Cl_2 (20 mL) and H_2O (20 mL). The organic layer was rinsed with brine (20 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude products were purified by a silica gel flash chromatography eluting with EtOAc-PE (v/v 1:2) to provide 6-benzyloxymethyl-5,7-dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-13-yl *N*-β-L-(2,3,4,6-tetradeoxy-6-iodo-(3-methyl-2-oxooxazolo[3,4-*d*]))glucopyranoside (**36a**) as a yellow solid (105 mg, 77% yield). R_f 0.40 (1:1 EtOAc-PE); HR-ESIMS *m/z* 739.1055 $[M–H]^-$ (calcd for $C_{36}H_{28}N_4O_6I$, 739.1054). 6-Benzyloxymethyl-5,7-dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-13-yl *N*-α-L-(2,3,4,6-tetradeoxy-6-iodo-(3-methyl-2-oxooxazolo[3,4-*d*]))glucopyranoside (**36b**) was prepared from **35b** (80 mg) by the same method and purified as a yellow solid (90 mg, 95% yield) by silica gel flash chromatography eluting with EtOAc-PE (v/v 1:1). R_f 0.30 (1:1 EtOAc-PE); HR-ESIMS *m/z* 739.1079 $[M–H]^-$ (calcd for $C_{36}H_{28}N_4O_6I$, 739.1054). To a green solution of 105 mg (0.142 mmol) of **36a** in 20 mL of THF at 0 ℃ was added 0.4 mL (2.67 mmol) of DBU. The reaction turned from green to red and was stirred for 1 h at 0 ℃ and then 1 h at 40 ℃. The mixture was diluted with EtOAc (20 mL) and H_2O (20 mL). The organic layer was rinsed with brine (20 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude products were purified by a silica gel flash chromatography eluting with EtOAc-PE (v/v 1:1) to provide 6-benzyloxymethyl-5,7-dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-13-yl *N*-β-L-(2,3,4-trideoxy-5,6-dehydro-(3-methyl-2-oxooxazolo[3,4-*d*]))glucopyranoside (**37a**) as a yellow solid (80 mg, 92% yield). 6-Benzyloxymethyl-5,7-dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-13-yl *N*-α-L-(2,3,4-trideoxy-5,6-dehydro-(3-methyl-2-oxooxazolo[3,4-*d*]))glucopyranoside (**37b**) was prepared from **36b** (90 mg)

by the same method and purified as a yellow solid (67 mg, 90% yield) by a silica gel flash chromatography eluting with EtOAc-PE (v/v 3:1).

Compound 37a: $[\alpha]_D^{20}$ –96.0° (*c* 0.55, CH_2Cl_2); R_f 0.4 (2:1 EtOAc-PE). ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.21 (s, 1H, NH), 9.22 (d, *J* = 7.8 Hz, 1H, ArH), 9.08 (d, *J* = 8.4 Hz, 1H, ArH), 7.88 (d, *J* = 8.4 Hz, 1H, ArH), 7.75 (d, *J* = 8.4 Hz, 1H, ArH), 7.63-7.65 (m, 2H, ArH), 7.49 (d, *J* = 7.2 Hz, 1H, ArH), 7.34-7.43(m, 5H, ArH), 7.28-7.30 (m, 1H, ArH), 7.24 (dd, *J* = 11.0, 2.6 Hz, 1H, H-1'), 5.46 (d, *J* = 8.5 Hz, 1H, H-4'), 5.13 (brs, 2H, H-6'), 5.12 (d, *J* = 11.2 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 5.07 (d, *J* = 11.2 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 4.67 (s, 2H, $Ph\underline{CH_2}OCH_2N$), 4.40-4.41 (m, 1H, H-3'), 2.77 (3H, s, N-CH_3), 2.50-2.54 (m, 1H, H-2'a), 2.17-2.20 (m, 1H, H-2'b); ^{13}C NMR (150 MHz, DMSO-d_6) δ 169.4, 169.3, 157.1, 152.9, 142.1, 140.5, 138.3, 129.6, 129.2, 128.8×2, 128.2, 128.1×3, 127.9, 125.5, 124.8, 123.6, 122.4, 121.7, 121.4, 120.3, 119.2, 118.6, 118.4, 113.6, 112.8, 101.2, 81.0, 71.4, 70.9, 67.0, 53.0, 28.8, 27.9; HR-ESIMS *m/z* 611.1938 $[M - H]^-$ (calcd for $C_{36}H_{27}N_4O_6$ 611.1931).

Compound 37b: $[\alpha]_D^{20}$+12.4° (*c* 0.20, CH_2Cl_2); R_f 0.4 (3:1 EtOAc-PE); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.62 (s, 1H, NH), 9.28 (d, *J* = 8.2 Hz, 1H, ArH), 9.10 (d, *J* = 8.2 Hz, 1H, ArH), 7.66 (d, *J* = 8.2 Hz, 1H, ArH), 7.55-7.59 (m, 2H, ArH), 7.42-7.47 (m, 4H, ArH), 7.36-7.41 (m, 3H, ArH), 7.30 (t, *J* = 7.8 Hz, 1H, ArH), 6.30 (dd, *J* = 11.4, 2.4 Hz, 1H, H-1′), 5.52 (d, *J* = 2.0 Hz, 1H, H-6′a), 5.36 (d, *J* = 2.0 Hz, 1H, H-6′b), 5.17 (d, *J* = 11.2 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 5.11 (d, 1H, *J* = 7.2 Hz, H-4′),5.10 (d, *J* = 11.2 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 4.67 (s, 2H, $Ph\underline{CH_2}OCH_2N$), 4.18-4.21 (m, 1H, H-3′), 2.83 (s, 3H,N-CH_3), 2.51-2.57 (m, 1H, H-2′a), 2.43-2.47 (m, 1H, H-2′b); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.3, 169.2, 156.9, 151.6, 140.9, 139.9, 138.0, 129.4, 128.6×2, 128.3, 128.1×2, 128.0, 127.9, 127.7, 126.4, 125.4, 122.7, 122.4, 121.9, 121.7, 121.0, 119.5, 119.3, 118.9, 112.0, 108.9, 100.2, 82.0, 71.7, 70.3, 66.9, 54.6, 33.0, 29.3; HR-ESIMS *m/z* 611.1925 $[M - H]^-$ (calcd for $C_{36}H_{27}N_4O_6$ 611.1931).

Synthesis of 6-benzyloxymethyl-5,7-dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-12,13-diyl *N*-L-(2,3,4,6-tetra deoxy-6-iodo-(3-methyl-2-oxooxazolo[3,4-*d*]))-1,5-glucopyranoside (38)

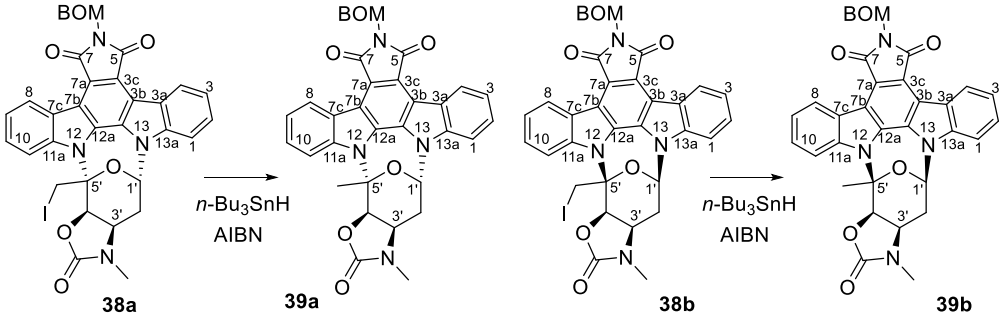


To a green solution of 80 mg (0.13 mmol) **37a** in 10 mL of THF and 1 mL of MeOH was added 59 mg (0.2 mmol) of *t*-BuOK and the mixture was stirred for 1h at rt. The reaction turned red and was treated with 133 mg (0.15 mmol) of iodine. The reaction was stirred at rt overnight and then diluted with EtOAc (30 mL). After washed by saturated $Na_2S_2O_3$ (30 mL) and brine (30 mL) in order, the organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification of the crude products by flash chromatography on silica gel eluting with EtOAc-PE (1:2, v/v) provided 6-benzyloxymethyl-5,7-dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-12,13-diyl *N*-β-L-(2,3,4,6-tetradeoxy-6-iodo-(3-methyl-2-oxooxazolo[3,4-*d*]))-1,5-glucopyranoside (**38a**) as a yellow solid (60 mg, 62% yield). 6-

Benzyloxymethyl-5,7-dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-12,13-diyl *N*-α-L-(2,3,4,6-tetradeoxy-6-iodo-(3-methyl-2-oxooxazolo[3,4-*d*]))-1,5-glucopyranoside (**38b**) was prepared from **37b** (40 mg) by the same method and purified as a yellow solid (25 mg, 52% yield) by a silica gel flash chromatography eluting with EtOAc-PE (3:1, v/v). **Compound 38a**: $[a]_D^{20}$ −40.2° (*c* 0.06, CH_2Cl_2); R_f 0.30 (1:1 EtOAc-PE). ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.22 (d, *J* = 7.8 Hz, 1H, ArH), 9.00 (d, *J* = 7.8 Hz, 1H, ArH), 8.10 (d, *J* = 8.4 Hz, 1H, ArH), 8.05 (d, *J* = 8.4 Hz, 1H, ArH), 7.63-7.67 (m, 2H, ArH), 7.49-7.54 (m, 1H, ArH), 7.43 (t, *J* = 7.2 Hz, 1H, ArH), 7.37-7.38 (m, 2H, ArH), 7.29-7.32 (m, 2H, ArH), 7.23 (t, *J* = 7.2 Hz, 1H, ArH), 7.09 (dd, *J* = 9.6, 7.2 Hz, 1H, H-1'), 5.92 (d, *J* = 9.0 Hz, 1H, H-4'), 5.20 (brs, 2H, $PhCH_2O\underline{CH_2}$), 4.69 (s, 2H, $Ph\underline{CH_2}OCH_2$), 4.61 (1H, d, *J* = 12.6 Hz, H-6′a), 4.51-4.53 (m, 1H, H-3′), 3.80 (1H, d, *J* = 12.6 Hz, H-6′b), 3.01 (s, 3H, N-CH_3), 2.86-2.90 (m, 1H, H-2′a), 2.51-2.55 (m, 1H, H-2′b); ^{13}C NMR (150 MHz, DMSO-d_6) δ 169.4, 169.1, 156.8, 139.8, 138.5, 138.2, 137.4, 132.0, 129.1, 128.6 × 2, 128.1, 127.9 × 3, 125.5, 125.0, 124.4, 122.3, 121.5, 121.2, 120.5, 119.2, 117.5, 116.8, 113.0, 110.6, 93.3, 78.2, 70.8, 70.3, 65.4, 52.7, 29.3, 28.4, 11.6; HR-ESIMS *m/z* 739.1045 $[M+H]^+$ (calcd for $C_{36}H_{28}N_4O_6I$, 739.1054).

Compound 38b: $[a]_D^{20}$ +51.3° (*c* 0.12, CH_2Cl_2); R_f 0.25 (3:1 EtOAc-PE); ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.25 (d, *J* = 8.2 Hz, 1H, ArH), 9.03 (d, *J* = 8.2 Hz, 1H, ArH), 8.17 (d, *J* = 8.2 Hz, 1H, ArH), 7.90 (d, *J* = 8.2 Hz, 1H, ArH), 7.65-7.68 (m, 1H, ArH), 7.60-7.63 (m, 1H, ArH), 7.44-7.50 (m, 2H, ArH),7.36 (d, *J* = 8.2 Hz, 2H, ArH), 7.30 (t, *J* = 7.2 Hz, 2H, ArH), 7.23 (t, *J* = 7.2 Hz, 1H, ArH), 7.06 (dd, *J* = 10.6, 6.0 Hz, 1H, H-1′), 5.49 (d, *J* = 9.0 Hz, 1H, H-4′), 5.17 (d, *J* = 11.2 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 5.14 (d, *J* = 11.2 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 4.93 (d, *J* = 11.4 Hz, 1H, H-6′a), 4.67 (s, 2H, $Ph\underline{CH_2}OCH_2$), 4.34-4.38 (m, 1H, H-3′), 3.96 (1H, d, *J* = 11.4 Hz, H-6′b), 2.99-3.03 (m, 1H, H-2′a), 2.65 (s, 3H, N-CH_3), 2.51-2.55 (m, 1H, H-2′b); ^{13}C NMR (150 MHz, DMSO-d_6) δ 169.6, 169.3, 155.9, 141.6, 138.4, 138.3, 132.2, 132.1, 128.9, 128.8×2, 128.1×4, 125.4, 125.1, 124.4, 122.3, 121.8, 121.5, 120.5, 119.2, 118.2, 116.7, 116.1, 110.2, 92.6, 80.1, 73.6, 71.0, 65.6, 53.1, 30.6, 29.0, 14.2; HR-ESIMS *m/z* 739.1025 $[M+H]^+$ (calcd for $C_{36}H_{28}N_4O_6I$, 739.1054).

Synthesis of 6-benzyloxymethyl-5,7-dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-12,13-diyl *N*-L-(2,3,4,6-tetra deoxy-(3-methyl-2-oxooxazolo[3,4-*d*]))-1,5-glucopyranoside (39)



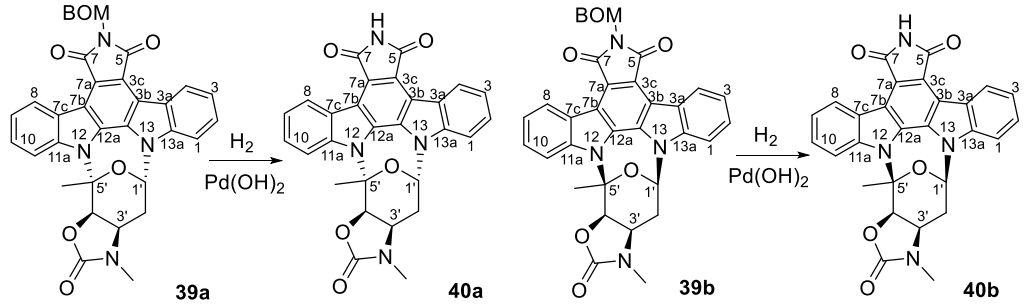
To a degassed green solution of 60 mg (0.08 mmol) of **38a** in 20 mL of benzene were added 0.2 mL of *n*-Bu_3SnH and 10 mg of AIBN, and then the reaction was heated to reflux for 1h. After cooling to rt, the reaction was concentrated *in vacuo*. Purification of the crude products by flash chromatography on silica gel eluting with EtOAc-PE (v/v, 1:2) provided 6-benzyloxymethyl-5,7-dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-12,13-diyl *N*-β-L-(2,3,4,6-tetradeoxy-(3-methyl-2-oxooxazolo[3,4-*d*]))-1,5-glucopyranoside (**39a**) as a yellow solid (42 mg, 85%

yield). 6-Benzyloxymethyl-5,7-dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-12,13-diyl *N*-α-L-(2,3,4,6-tetradeoxy-(3-methyl-2-oxooxazolo[3,4-*d*]))-1,5-glucopyranoside (**39b**) was achieved from **38b** (25 mg) by the same method and purified as a yellow solid (20 mg, 96% yield) by a silica gel flash chromatography eluting with EtOAc-PE (v/v, 2:1).

Compound 39a: $[a]_D^{20}$ −63.5° (*c* 0.09, CH_2Cl_2); R_f 0.28 (1:1 EtOAc-PE); ^{1}H NMR (600MHz, $CDCl_3$) *δ* 9.30 (d, *J* = 7.2 Hz, 1H, ArH), 9.10 (d, *J* = 7.8 Hz, 1H, ArH), 7.68-7.61 (m, 3H, ArH), 7.51–7.43 (m, 4H, ArH), 7.37 (t, *J* = 7.2 Hz, 3H, ArH), 7.30 (t, *J* = 7.8 Hz, 1H, ArH), 6.55 (dd, *J* = 9.6, 7.2 Hz, 1H, H-1'), 5.71 (d, *J* = 9.6 Hz, 1H, H-4'), 5.21 (d, *J* = 11.0 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 5.19 (d, *J* = 11.0 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 4.81(s, 2H, $Ph\underline{CH_2}OCH_2$), 4.44-4.46 (m, 1H, H-3'), 3.18 (s, 3H, N-CH_3), 2.76-2.81 (m, 1H, H-2'a), 2.46-2.51 (m, 1H, H-2'b), 1.99 (s, 3H, H_3-6'); ^{13}C NMR (150 MHz, $CDCl_3$) *δ* 169.3, 169.1, 157.3, 140.1, 138.1, 137.7, 130.1, 128.9, 128.5×2, 127.9×2, 127.8, 127.6, 127.4, 126.5, 126.2, 124.6, 122.1, 122.0, 121.4, 120.9, 119.4, 118.4, 117.4, 112.3, 107.8, 94.0, 77.2, 71.7, 71.4, 66.8, 52.7, 29.6, 26.2, 24.6; HR-ESIMS *m/z* 635.1918 $[M+Na]^+$ (calcd for $C_{36}H_{28}N_4O_6Na$, 635.1907).

Compound 39b: $[a]_D^{20}$ +33.1° (*c* 0.13, CH_2Cl_2); R_f 0.20 (3:1 EtOAc-PE, v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.38 (d, *J* = 8.0 Hz, 1H, ArH), 9.21 (d, *J* = 7.9 Hz, 1H, ArH), 8.08 (d, *J* = 8.6 Hz, 1H, ArH), 7.57-5.60 (m, 2H, ArH), 7.41-7.46 (m, 5H, ArH), 7.31 (t, *J* = 7.6 Hz, 2H, ArH), 7.23 (t, *J* = 7.4 Hz, 1H, ArH), 6.58 (dd, *J* = 10.3, 6.4 Hz, 1H, H-1'), 5.34 (d, *J* = 11.0 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 5.31 (d, *J* = 11.0 Hz, 1H, $PhCH_2O\underline{CH_2}N$), 5.09 (d, *J* = 8.9 Hz, 1H, H-4'), 4.76 (s, 2H, $Ph\underline{CH_2}OCH_2$), 4.24-4.28 (m, 1H, H-3'), 2.80-2.84 (m, 1H, H-2'a), 2.76 (s, 3H, 3'-NCH_3), 2.41-2.47 (m, 1H, H-2'b), 2.07 (s, 3H, H_3-6'); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.5, 169.3, 155.9, 142.2, 137.9, 137.8, 131.1, 130.7, 129.0, 128.7, 128.5×2, 128.0×2, 127.8, 127.6, 127.5, 126.5, 125.8, 124.6, 122.3×2, 121.6, 119.7, 119.5, 116.4, 107.5, 93.3, 79.0, 76.2, 71.6, 67.0, 53.1, 30.0, 29.8, 29.7; HR-ESIMS *m/z* 635.1923 $[M+Na]^+$ (calcd for $C_{36}H_{28}N_4O_6Na$, 635.1907).

Synthesis of 5,7-dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-12,13-diyl *N*-L-(2,3,4,6-tetradeoxy-(3-methyl-2-oxooxazolo[3,4-*d*]))-1,5-glucopyranoside (40)



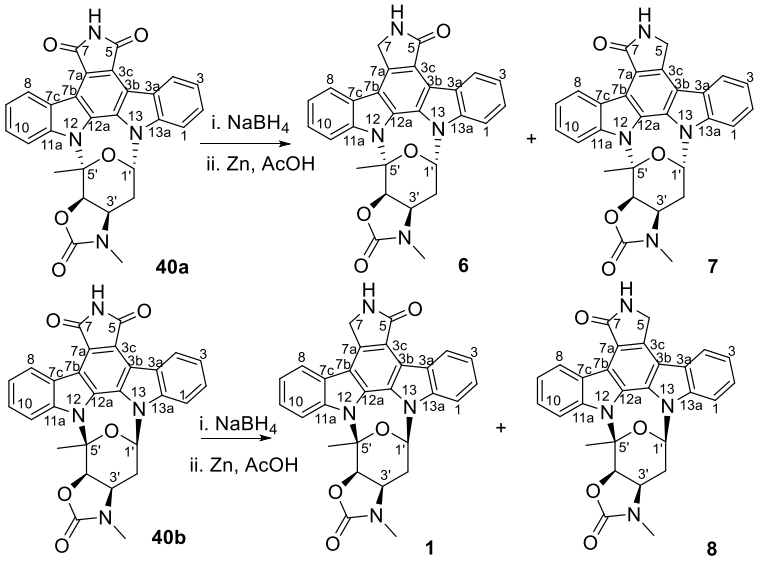
To a green solution of 40 mg (0.065 mmol) of **39a** in 10 mL of EtOAc and 10 mL of MeOH was added 20 mg of $Pd(OH)_2$ (20% on carbon). The reaction was then placed on a H_2 atmosphere by several evacuation/refill with H_2 cycles at rt. The reaction stirred vigorously overnight. The reaction mixture was then filtered through a pad of Celite and washed with EtOAc (20 mL) and MeOH (20 mL) in order. The filtrates were concentrated *in vacuo* and purified by RP-18 flash chromatography eluting with 70% MeOH/H_2O to give 5,7-dioxo-indolo[2,3-*a*]pyrrolo[3,4-*c*] carbazole-12,13-diyl *N*-β-L-(2,3,4,6-tetradeoxy-(3-methyl-2-oxooxazolo[3,4-*d*]))-1,5-glucopyranoside (**40a**) as a green solid (28 mg, 89% yield). 5,7-Dioxoindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-12,13-diyl *N*-α-L-(2,3,4,6-

tetradeoxy-(3-methyl-2-oxooxazolo[3,4-*d*]))-1,5-glucopyranoside (**40b**) (15 mg, 96% yield) was achieved by the same method from **39b** (20 mg) and purified as a green solid by RP-18 flash chromatography eluting with 70% MeOH/H_2O.

Compound 40a: $[\alpha]_D^{20}$ −69.5° (*c* 2.0, CH_2Cl_2); R_f 0.45 (RP-18 TLC, 95% MeOH/H_2O); ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.20 (s, 1H, NH), 9.21 (d, *J* = 7.8 Hz, 1H, ArH), 8.98 (d, *J* = 7.8 Hz, 1H, ArH), 8.07 (d, *J* = 7.8 Hz, 1H, ArH), 7.94 (d, *J* = 8.4 Hz, 1H, ArH), 7.61-7.67 (m, 2H, ArH), 7.48 (t, *J* = 7.8 Hz, 1H, ArH), 7.41 (t, *J* = 7.8 Hz, 1H, ArH), 6.99 (dd, *J* = 10.0, 6.8 Hz, 1H, H-1'), 5.76 (d, *J* = 10.4 Hz, 1H, H-4'), 4.44-4.46 (m, 1H, H-3'), 2.99 (s, 3H, N-CH_3), 2.79-2.83 (m, 1H, H-2'a), 2.15-2.20 (m, 1H, H-2'b), 1.80 (s, 3H, H_3-6'); ^{13}C NMR (125 MHz, DMSO-d_6) δ 171.5, 171.2, 157.4, 140.5, 138.6, 130.2, 129.1, 127.8, 127.7, 125.8, 125.3, 124.3, 122.1, 122.0, 121.5, 121.4, 120.7, 117.6, 116.5, 114.3, 110.7, 94.1, 77.9, 71.4, 52.4, 29.5, 25.4, 24.9; HR-ESIMS *m/z* 491.1348 $[M - H]^-$ (calcd for $C_{28}H_{19}N_4O_5$ 491.1355).

Compound 40b: $[\alpha]_D^{20}$ +112.9° (*c* 0.1, CH_2Cl_2); R_f 0.35 (RP-18 TLC, 95% MeOH/H_2O); ^{1}H NMR (500MHz, DMSO-d_6) δ 11.19 (s, 1H, NH), 9.23 (d, *J* = 9.0 Hz, 1H, ArH), 9.04 (d, *J* = 9.0 Hz, 1H, ArH), 8.09 (d, *J* = 9.5 Hz, 1H, ArH), 7.88 (d, *J* = 9.5 Hz, 1H, ArH), 7.65 (t, *J* = 9.0 Hz, 1H, ArH), 7.58 (t, *J* = 9.5 Hz, 1H, ArH), 7.43 (t, *J* = 9.0 Hz, 2H, ArH), 7.01 (dd, *J* = 10.0, 8.5 Hz, 1H, H-1'), 5.33 (d, *J* = 8.5 Hz, 1H, H-4'), 4.31-4.36 (m, 1H, H-3'), 2.93-2.98 (m, 1H, H-2'a), 2.57 (s, 3H, N-CH_3), 2.04-2.11 (m, 1H, H-2'b), 2.05 (3H, s, H_3-6'); ^{13}C NMR (125 MHz, DMSO-d_6) δ 170.8, 170.5, 155.5, 141.3, 137.6, 129.8, 128.0, 127.0, 126.5, 124.8, 124.5, 123.5, 121.2, 121.0 × 2, 120.8, 119.8, 117.4, 116.5, 115.7, 109.3, 92.6, 79.0, 75.3, 52.0, 29.6, 28.2×2; HR-ESIMS *m/z* 491.1365 $[M - H]^-$ (calcd for $C_{28}H_{19}N_4O_5$ 491.1355).

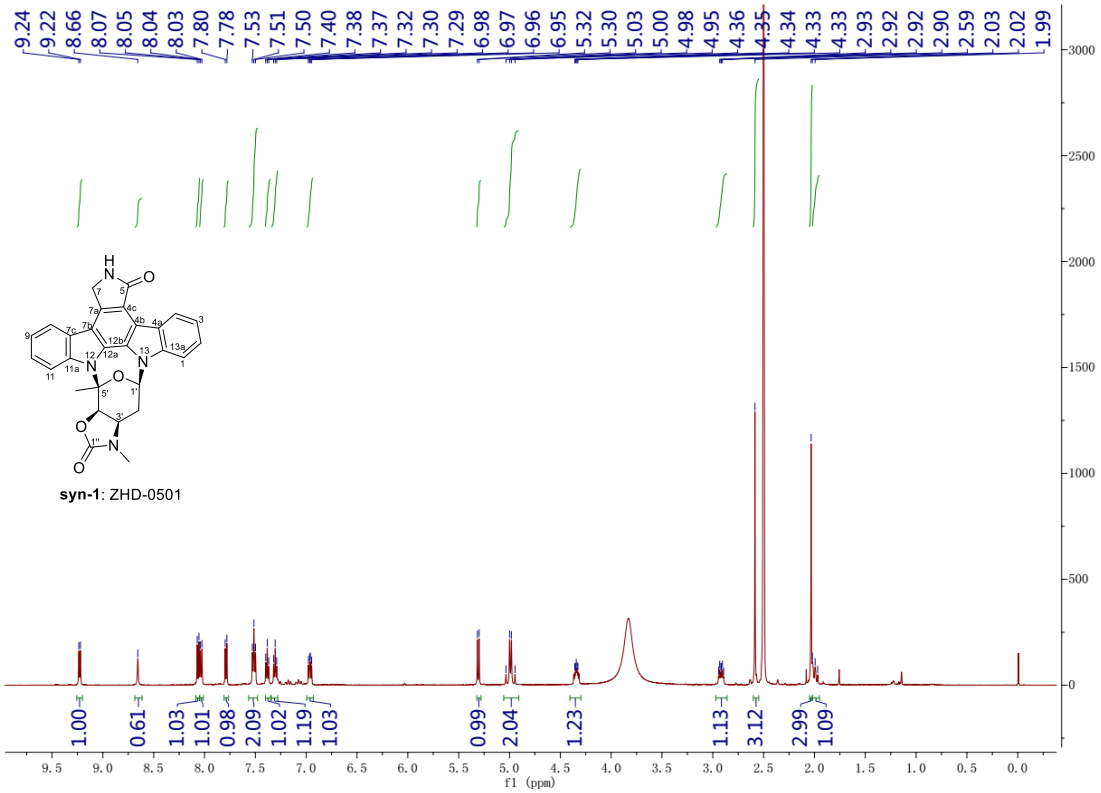
Synthesis of ZHD-0501 (1), 1',5'-di*epi*-ZHD-0501 (6), 1',5'-di*epi*-5-deoxo-7-oxo-ZHD-0501 (7) and 5-deoxo-7-oxo-ZHD-0501 (8)



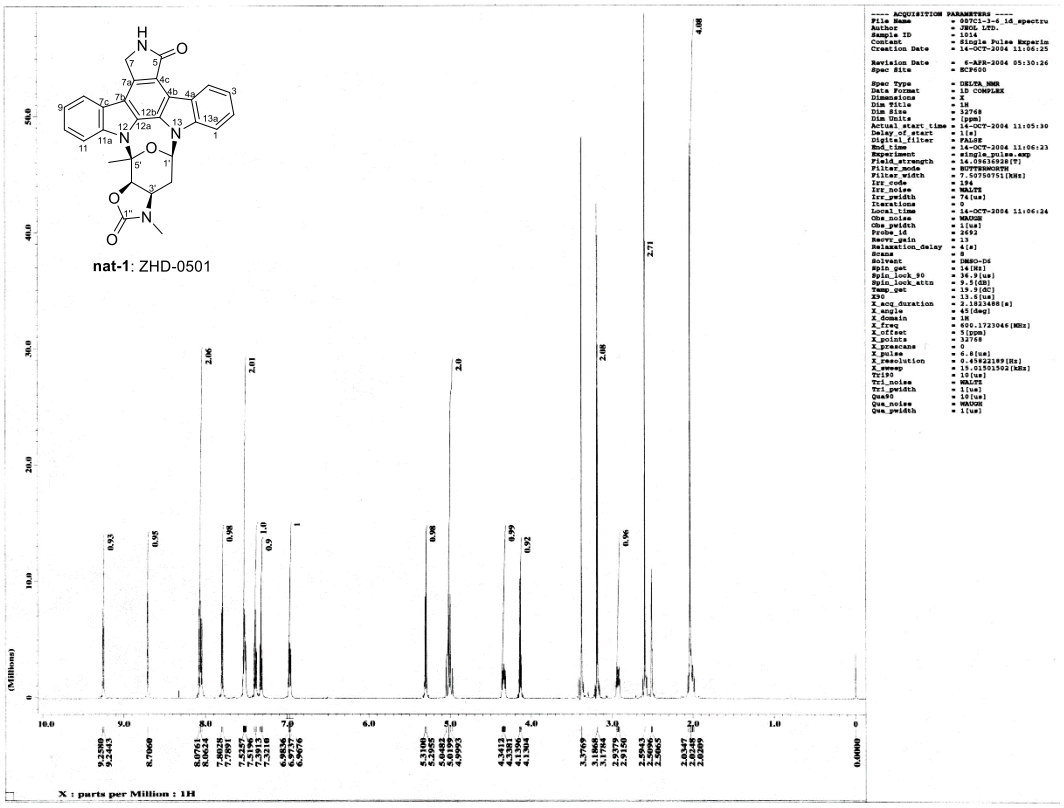
To a green solution of 10 mg (0.020 mmol) of **40a** in 10 mL of MeOH was added 7.6 mg (0.2 mmol) of $NaBH_4$ at 0 ℃. Over 2 h the reaction slowly turned to clear and was complete by TLC detection. The reaction mixture was

diluted with EtOAc (50 mL) and the organic layer was washed with saturated NH_4Cl, $NaHCO_3$, and brine in sequence. After dried over Na_2SO_4 and concentrated *in vacuo*, the obtained crude products were dissolved in 5 mL of AcOH and then 15 mg (0.23 mmol) Zn dust was added and stirring for 1.5 h at 40 ℃. The reaction mixture was then cooled to rt and diluted with EtOAc (50 mL). After washed with saturated $NaHCO_3$ and brine in sequence, the organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to give the crude products, which was purified by HPLC eluting with 35% MeCN/H_2O to give 1',5'-di*epi*-ZHD-0501 (**6**) (3.2 mg, t_R 26.0 min, 35% yield) and 1',5'-di*epi*-5-deoxo-7-oxo-ZHD-0501 (**7**) (3.2 mg, t_R 27.5 min, 35% yield) as a light-yellow solid. By the same procedures, ZHD-0501 (**1**) (2.7 mg, t_R 27.3 min, 28% yield) and 5-deoxo-7-oxo-ZHD-0501 (**8**) (2.7 mg, t_R 28.5 min, 28% yield) were prepared from **40b** (10 mg) and purified as the light-yellow solids by HPLC (35% MeCN/H_2O).

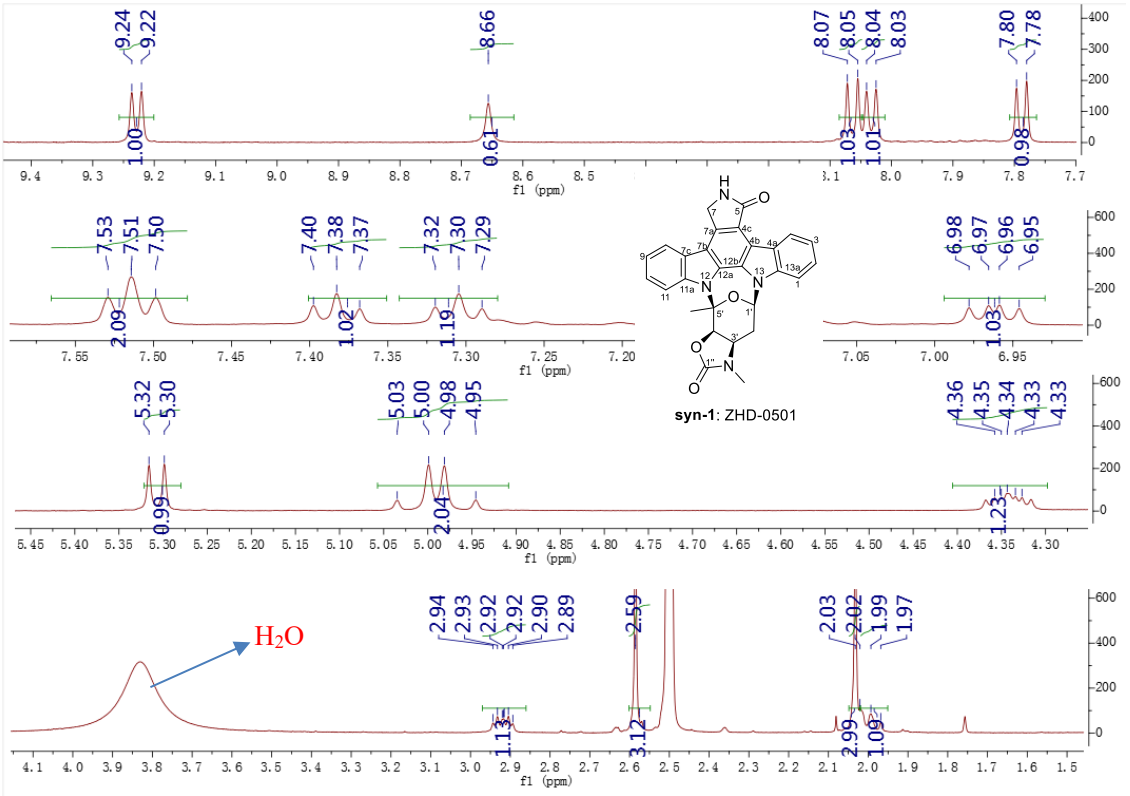
NMR Spectra



syn-1: ZHD-0501



nat-1: ZHD-0501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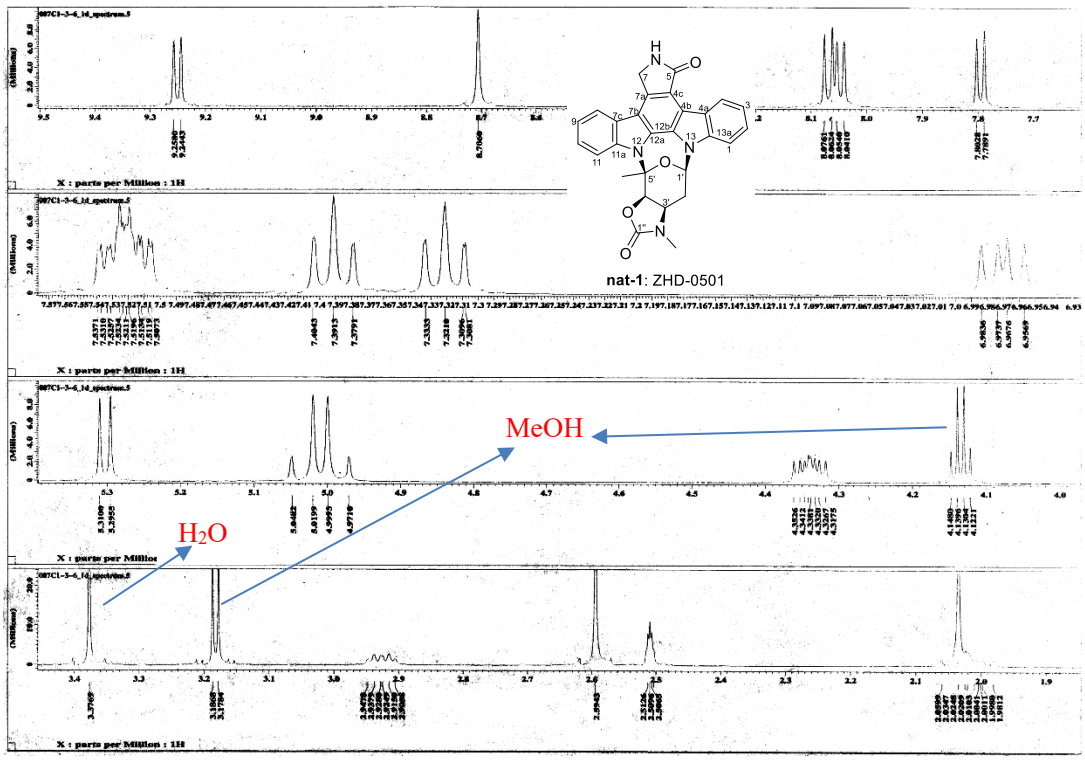
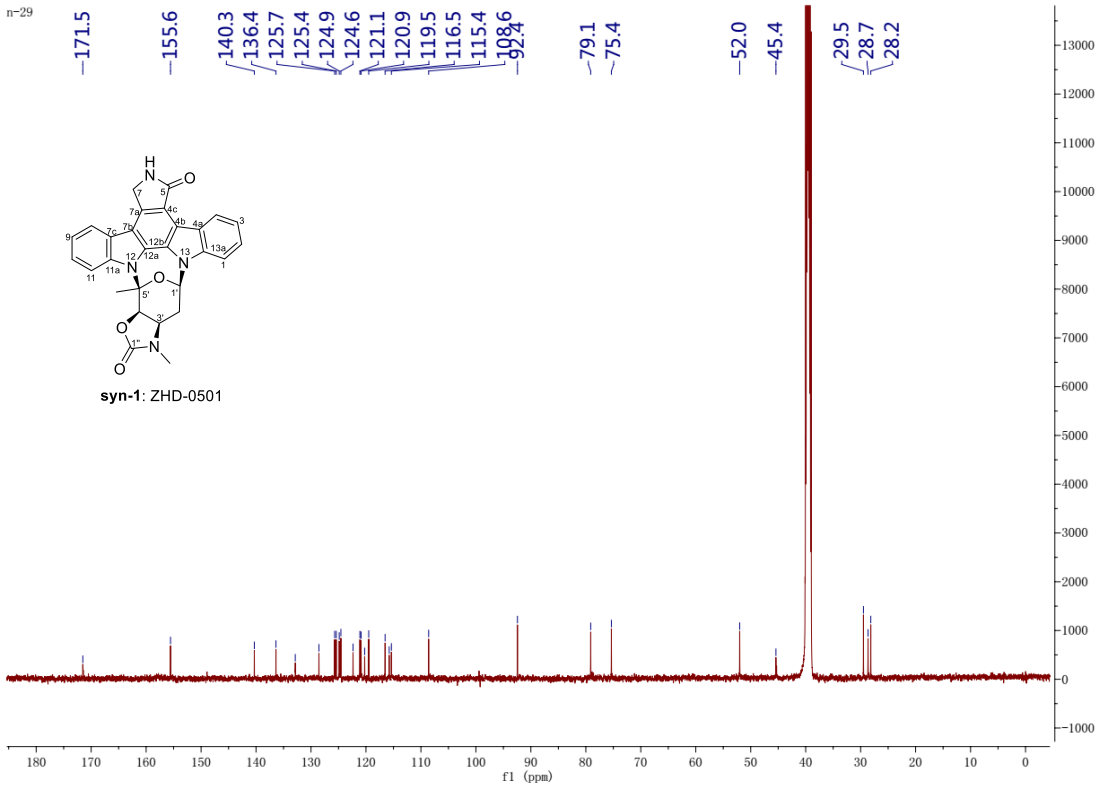
9.22
8.66
8.07
8.05
8.04
8.03
7.80
7.78
1.00
0.61
1.03
1.01
0.98
f1 (ppm)
7.53
7.51
7.50
7.40
7.38
7.37
7.32
7.30
7.29
6.98
6.97
6.96
6.95
2.09
1.02
1.19
1.03
5.32
5.30
5.03
5.00
4.98
4.95
4.36
4.35
4.34
4.33
4.33
0.99
2.04
1.23
syn-1: ZHD-0501
2.94
2.93
2.92
2.92
2.90
2.89
2.59
2.03
2.02
1.99
1.97
H2O
1.13
3.12
2.99
1.09


nat-1: ZHD-0501
MeOH
H2O
X : parts per Million : 1H



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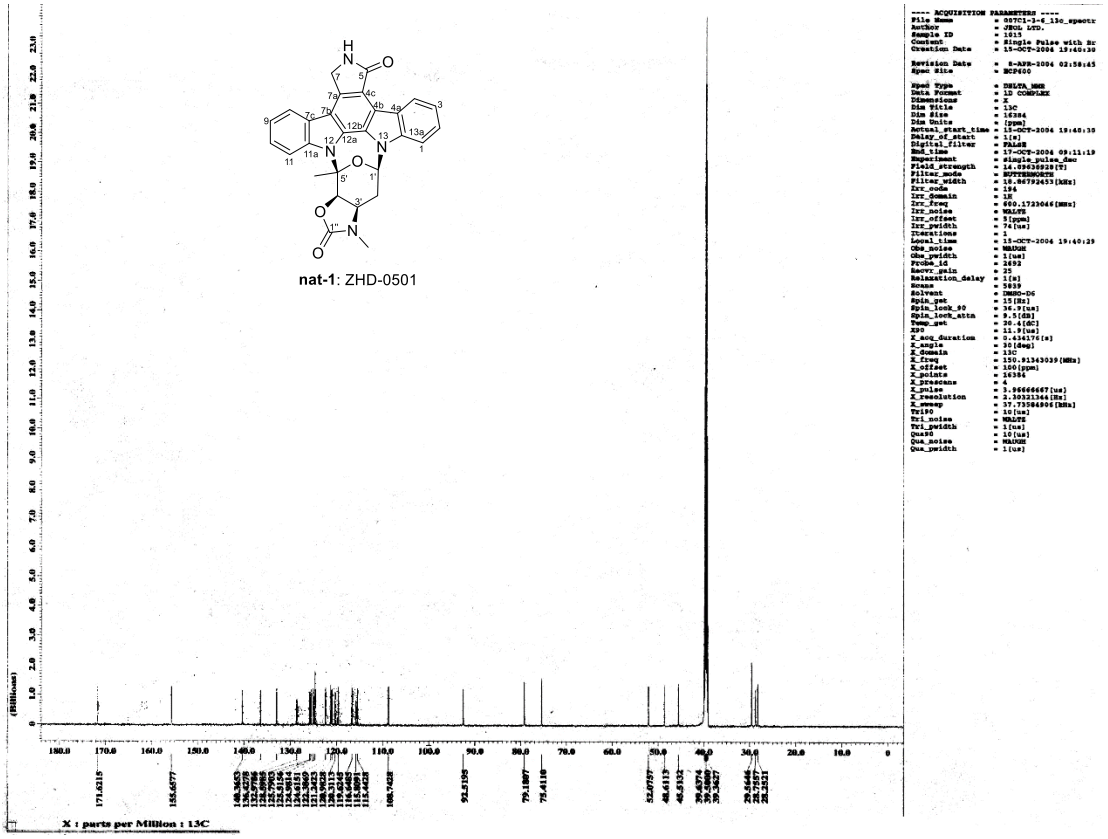
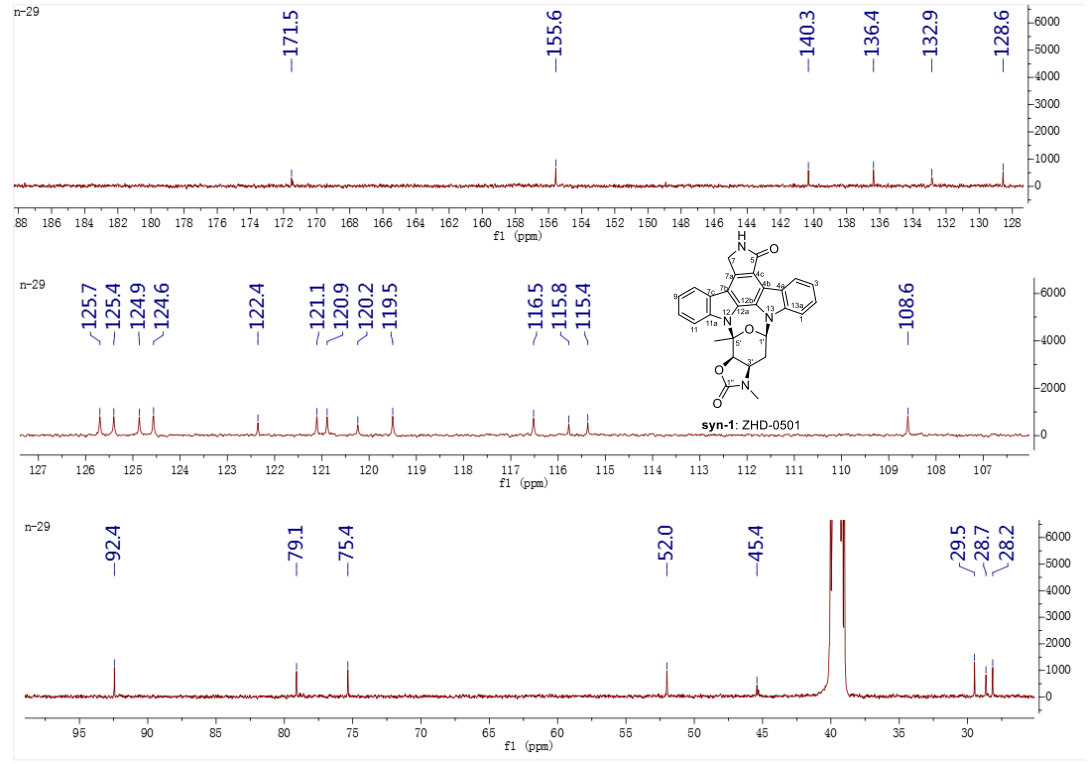


nat-1: ZHD-0501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140.3
136.4
132.9
128.6
f1 (ppm)
n-29
125.7
125.4
124.9
124.6
122.4
121.1
120.9
120.2
119.5
116.5
115.8
115.4
108.6
syn-1: ZHD-0501
f1 (ppm)
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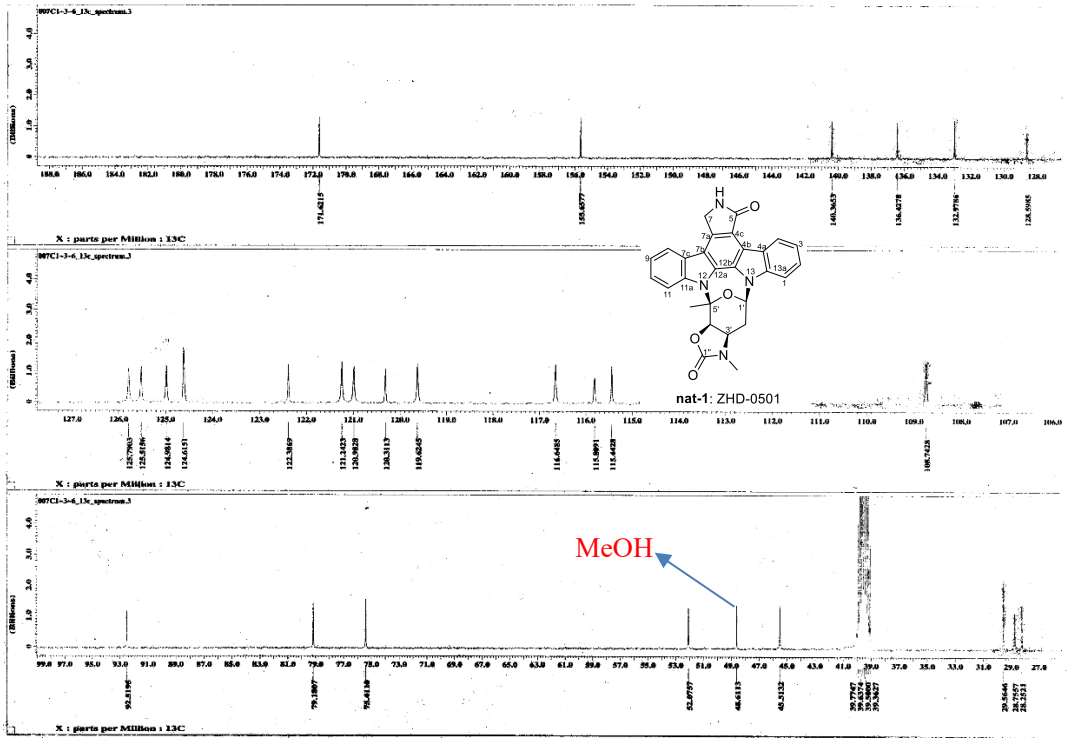
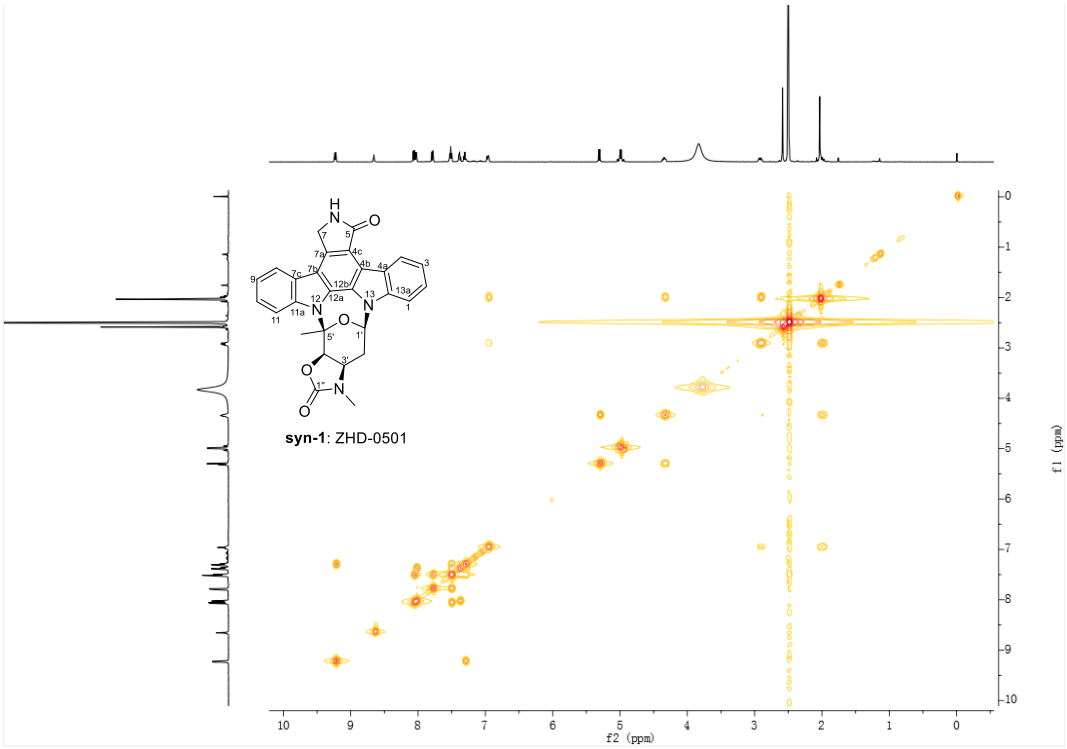
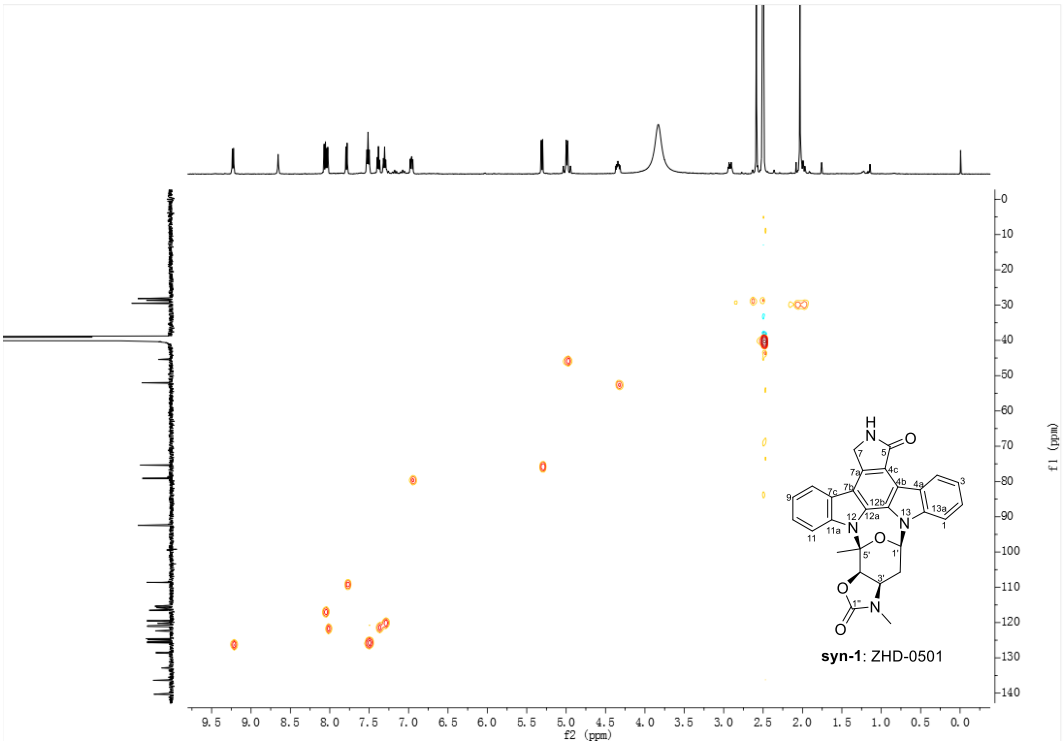
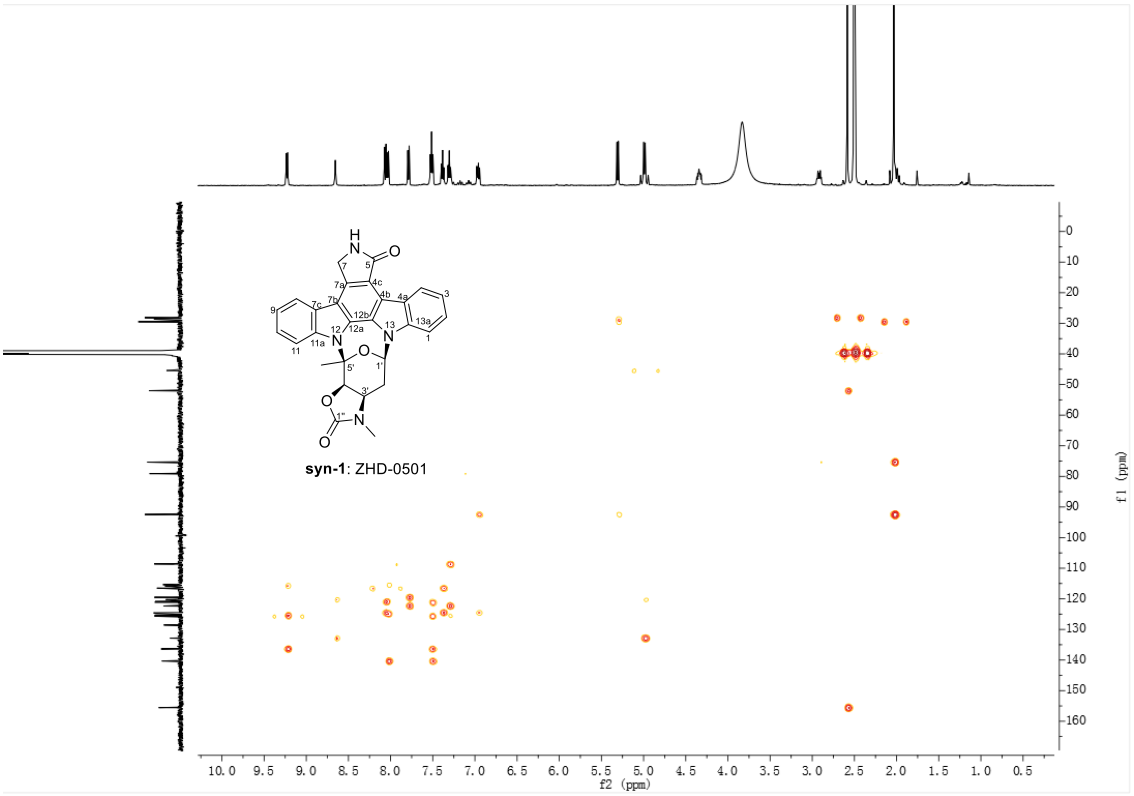
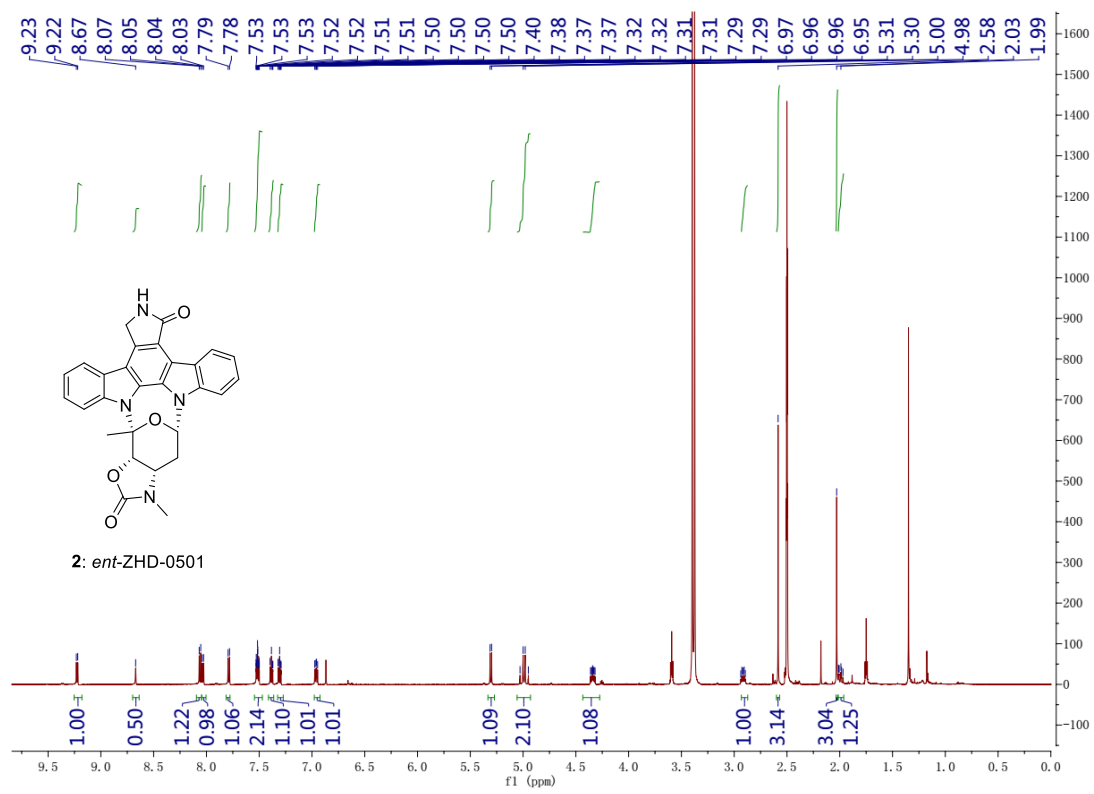
79.1
75.4
52.0
45.4
29.5
28.7
28.2
f1 (ppm)

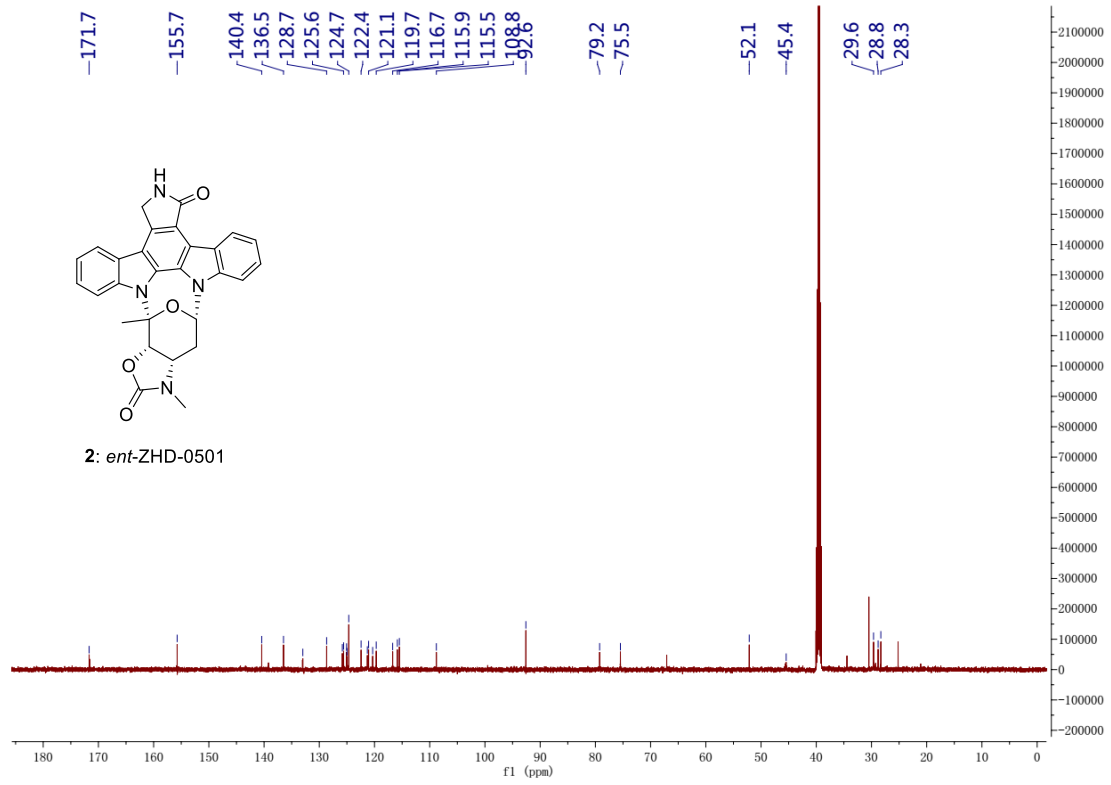

X : parts per Million : 13C
nat-1: ZHD-0501
X : parts per Million : 13C
MeOH
X : parts per Million : 13C


syn-1: ZHD-0501
f2 (ppm)
f1 (ppm)

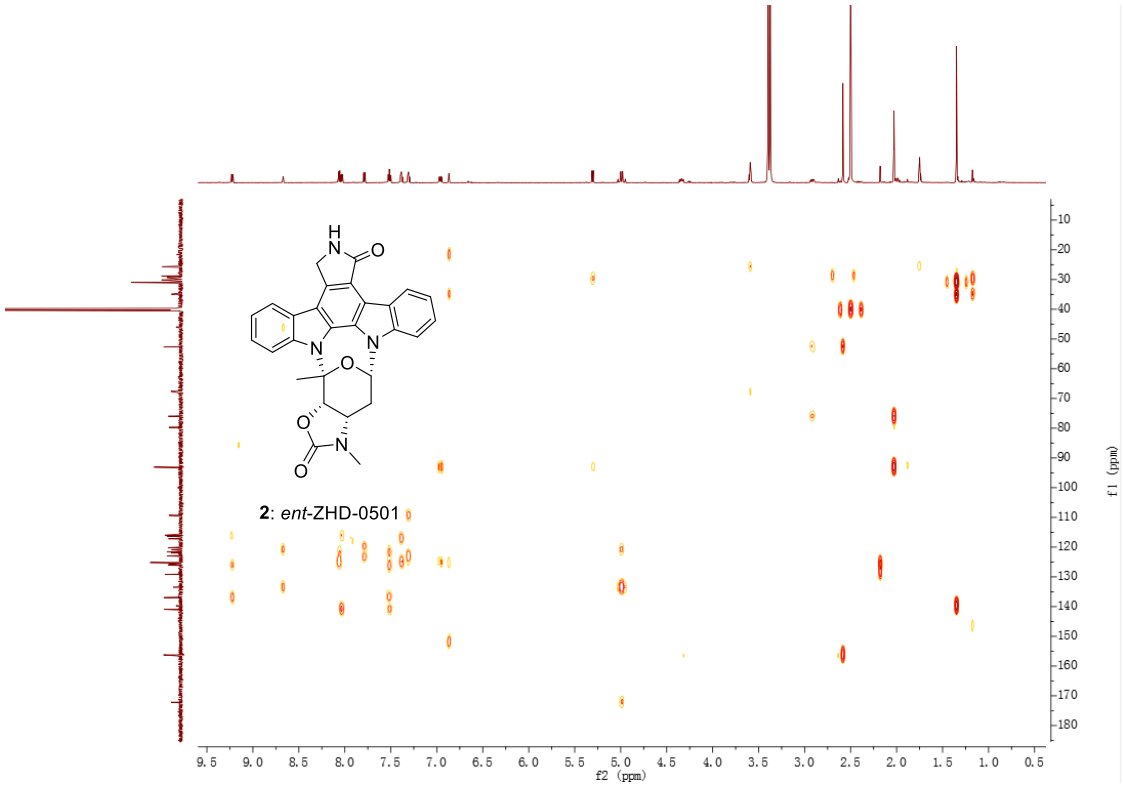

syn-1: ZHD-0501
f2 (ppm)
f1 (ppm)


syn-1: ZHD-0501
f2 (ppm)
f1 (ppm)


9.23 9.22 8.67 8.07 8.05 8.04 8.03 7.79 7.78 7.53 7.53 7.53 7.52 7.52 7.51 7.51 7.50 7.50 7.50 7.50 7.40 7.38 7.37 7.37 7.32 7.32 7.31 7.31 7.29 7.29 6.97 6.96 6.96 6.95 5.31 5.30 5.00 4.98 2.58 2.03 1.99
1.00 0.50 1.22 0.98 1.06 2.14 1.10 1.01 1.01 1.09 2.10 1.08 1.00 3.14 3.04 1.25
2: ent-ZHD-0501
f1 (ppm)



2: *ent*-ZHD-0501



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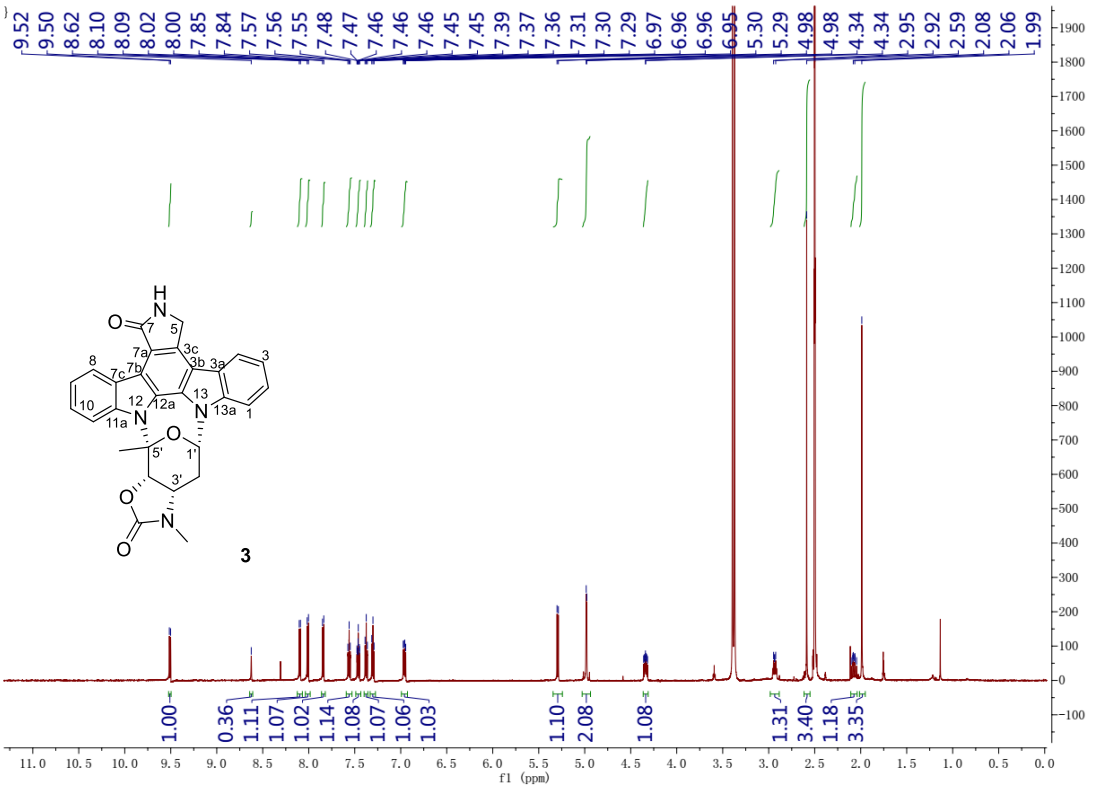
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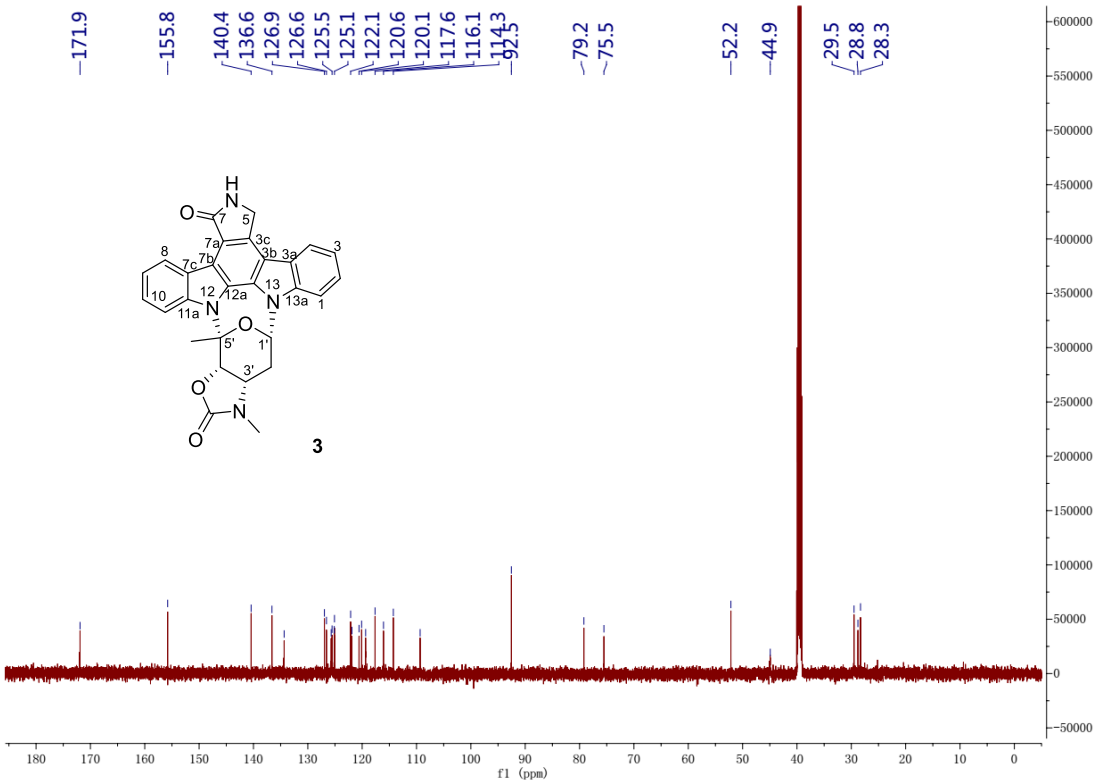
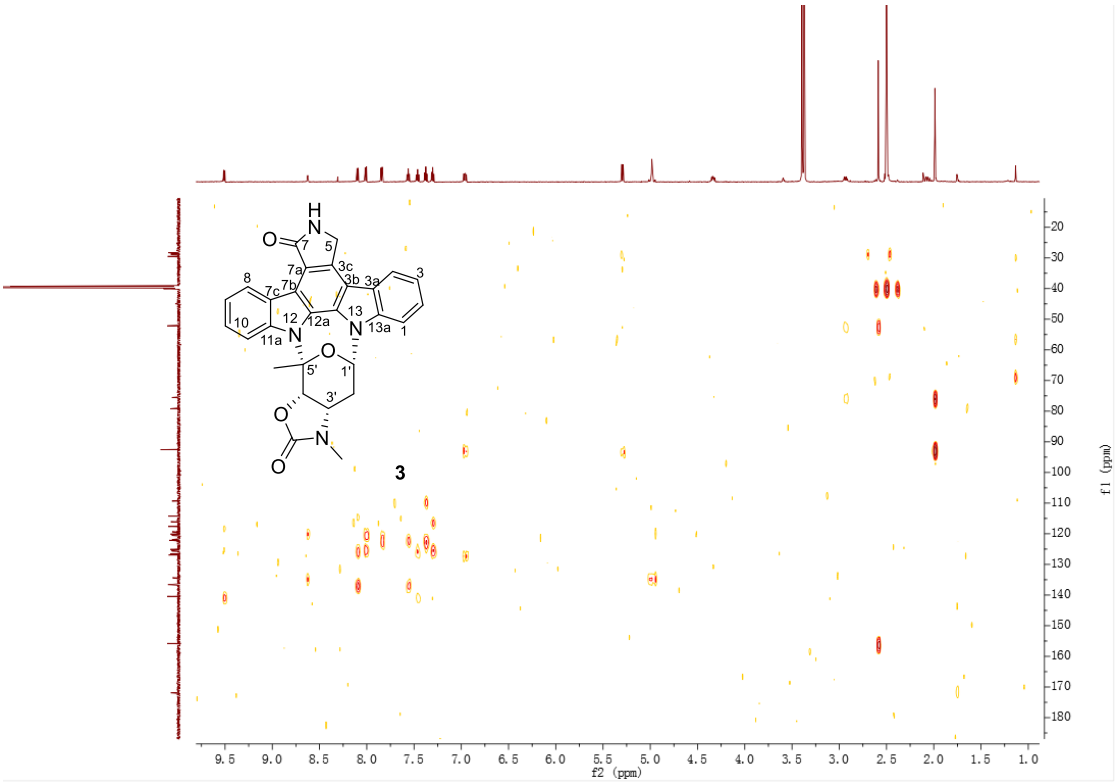
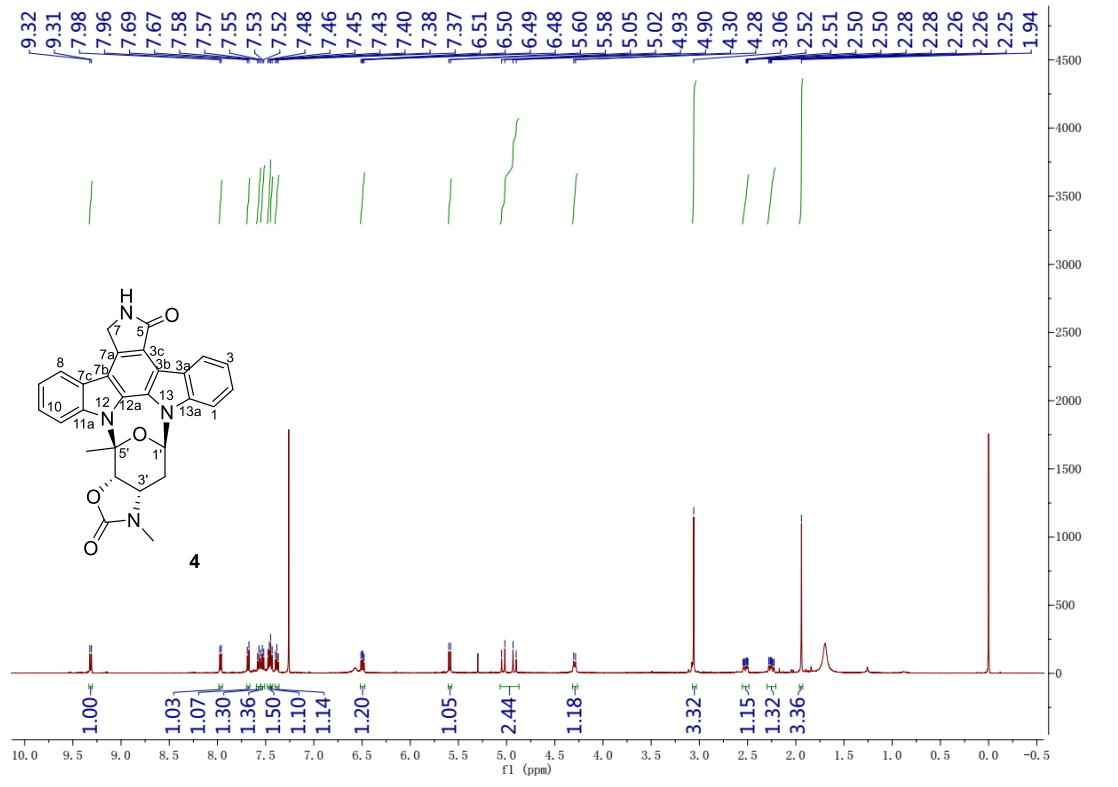
1.00 0.36 1.11 1.07 1.02 1.14 1.08 1.07 1.06 1.03 1.10 2.08 1.08 1.31 3.40 1.18 3.35
f1 (ppm)
3


171.9 155.8 140.4 136.6 126.9 126.6 125.5 125.1 122.1 120.6 120.1 117.6 116.1 114.3 92.5 79.2 75.5 52.2 44.9 29.5 28.8 28.3
f1 (ppm)
3


3
f2 (ppm)
f1 (ppm)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2.26
2.25
1.94
4
1.00
1.03
1.07
1.30
1.36
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1.18
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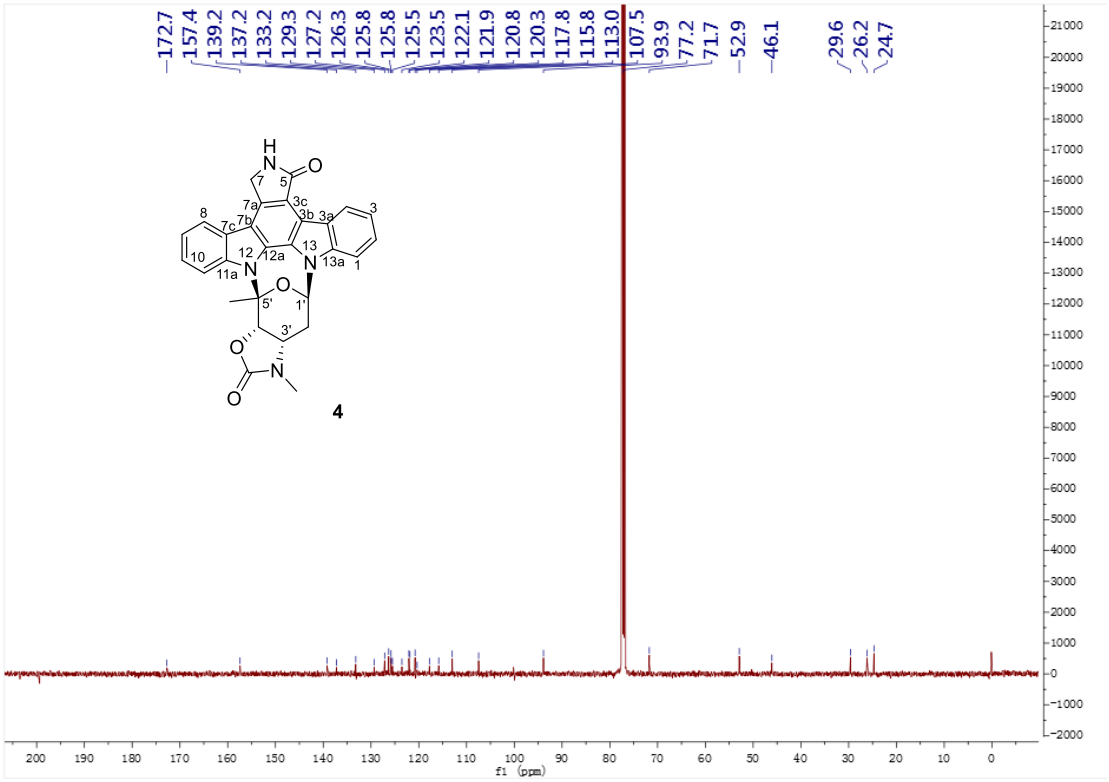
1.15
1.32
3.36
f1 (ppm)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125.5
123.5
122.1
121.9
120.8
120.3
117.8
115.8
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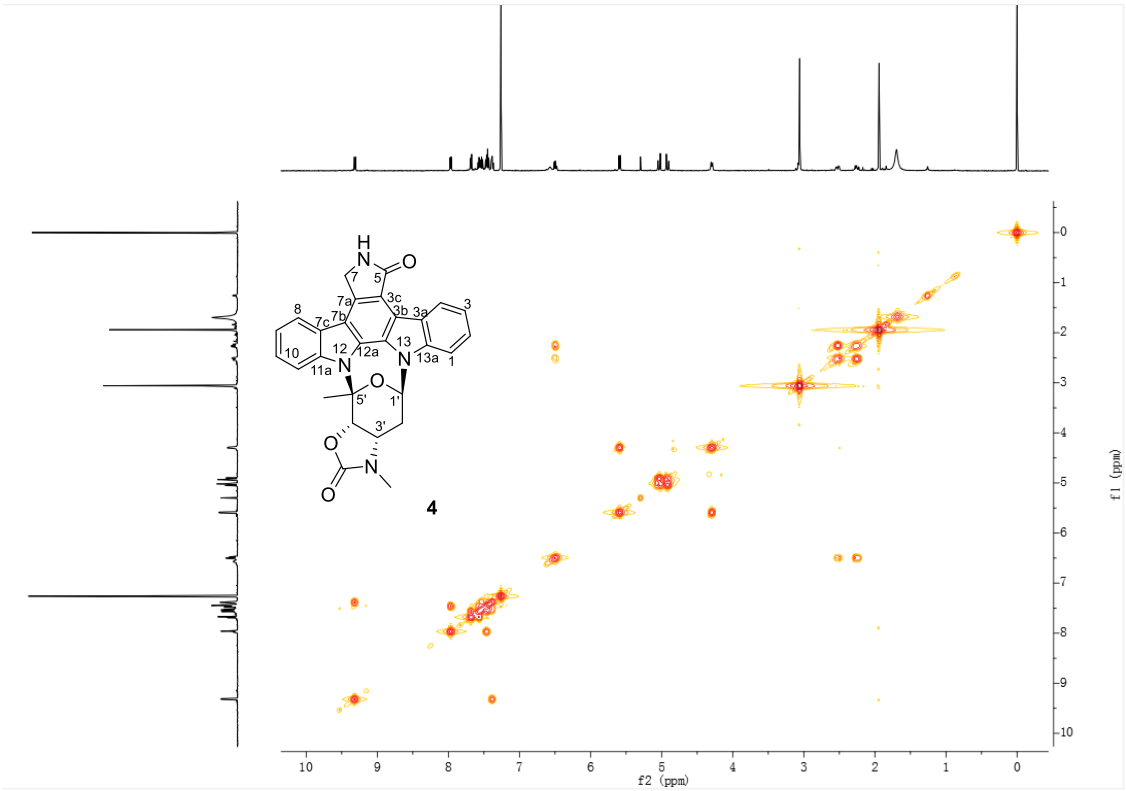
24.7
f1 (ppm)
4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f1 (ppm)
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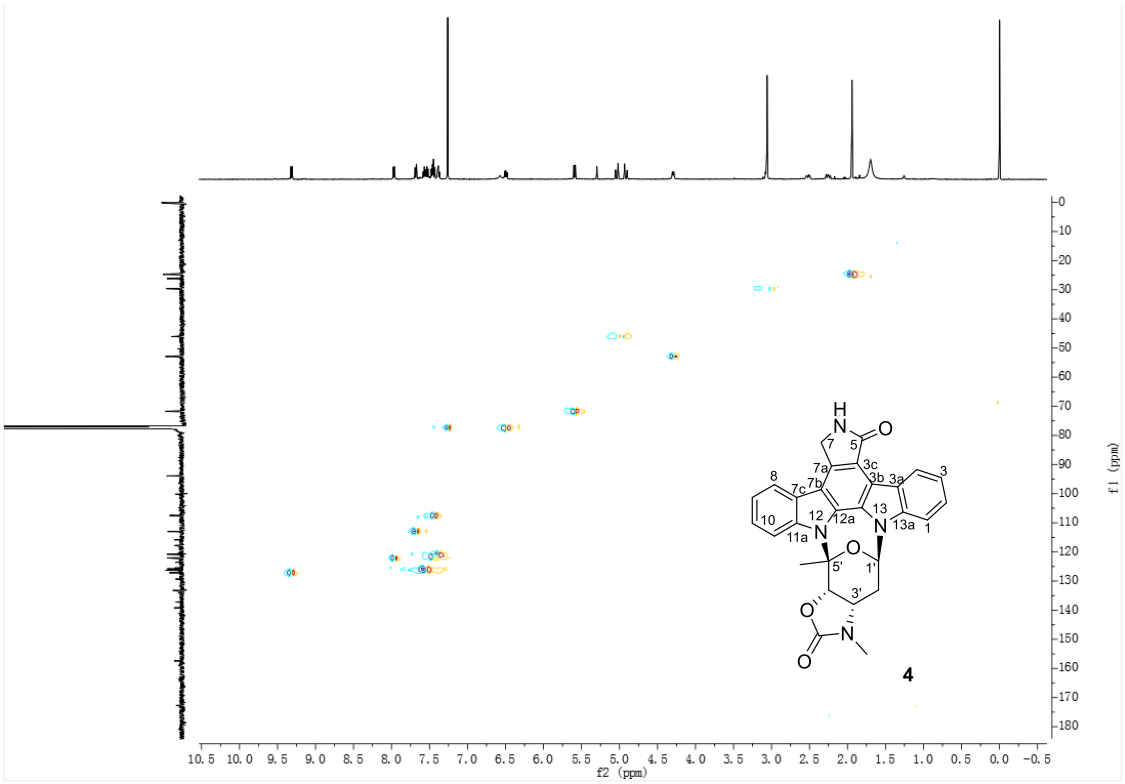
f2 (ppm)
f1 (ppm)
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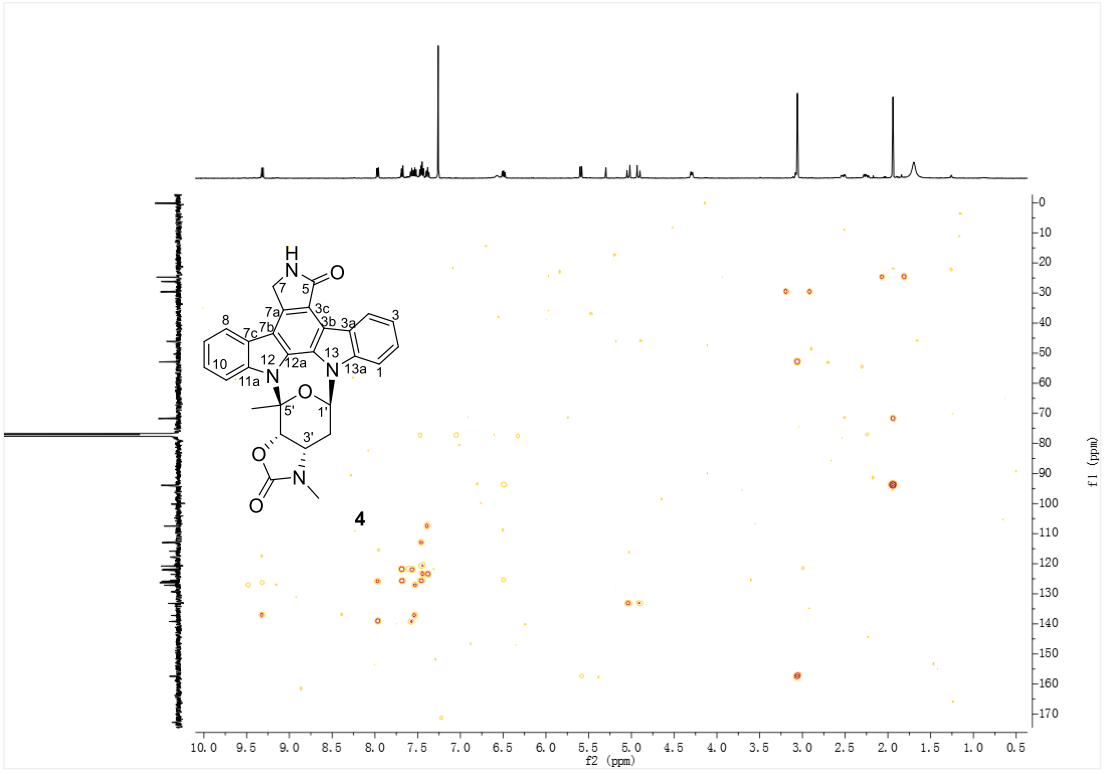
f2 (ppm)
f1 (ppm)
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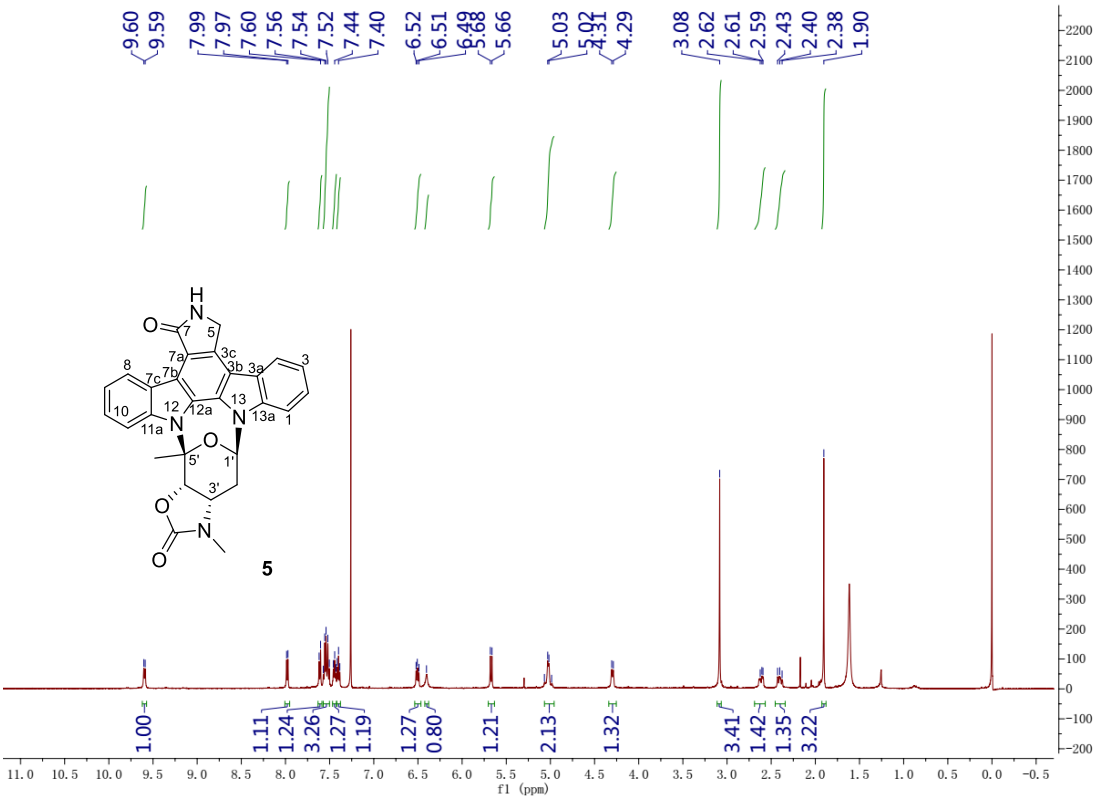
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2.59
2.43
2.40
2.38
1.90
1.00
1.11
1.24
3.26
1.27
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1.32
3.41
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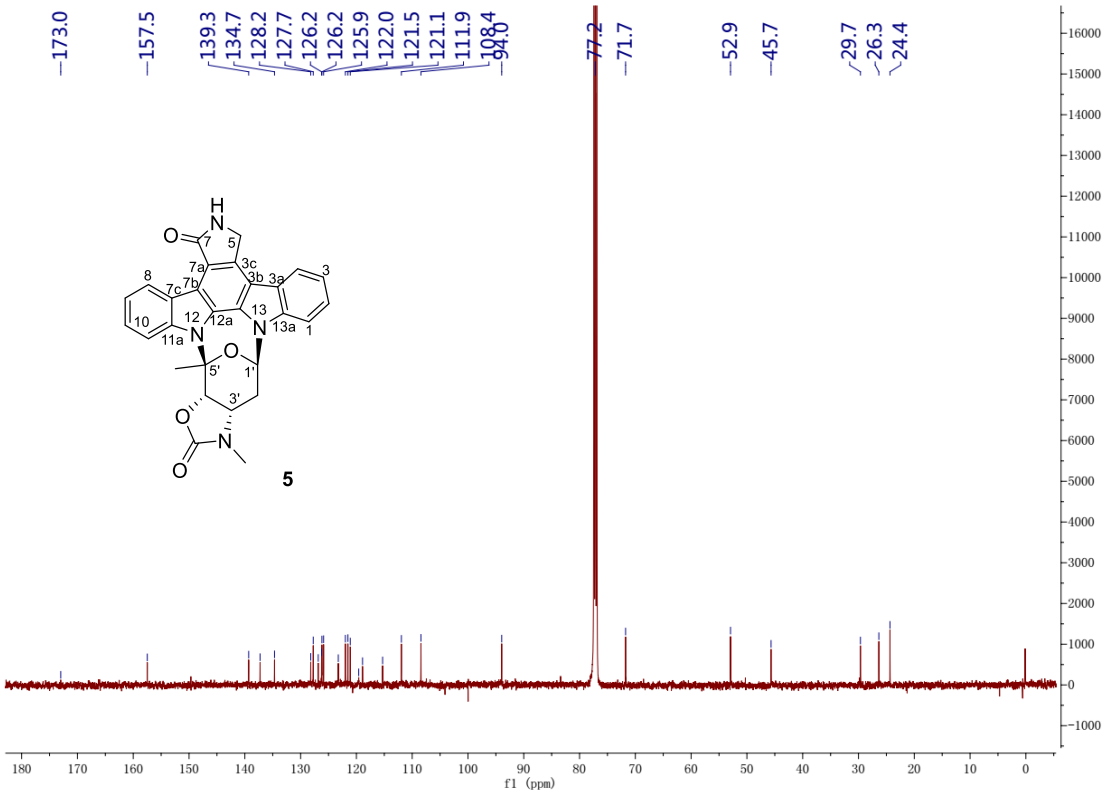
3.22
f1 (ppm)
5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121.5
121.1
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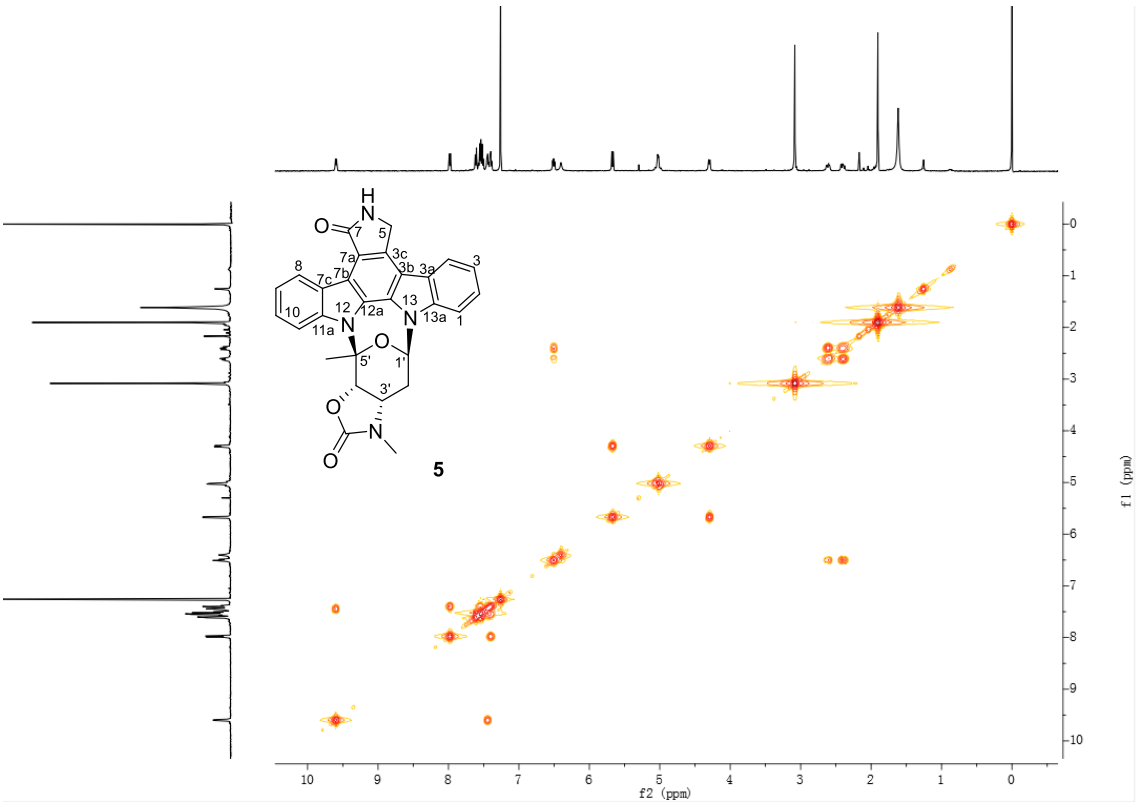
45.7
29.7
26.3
24.4
f1 (ppm)
5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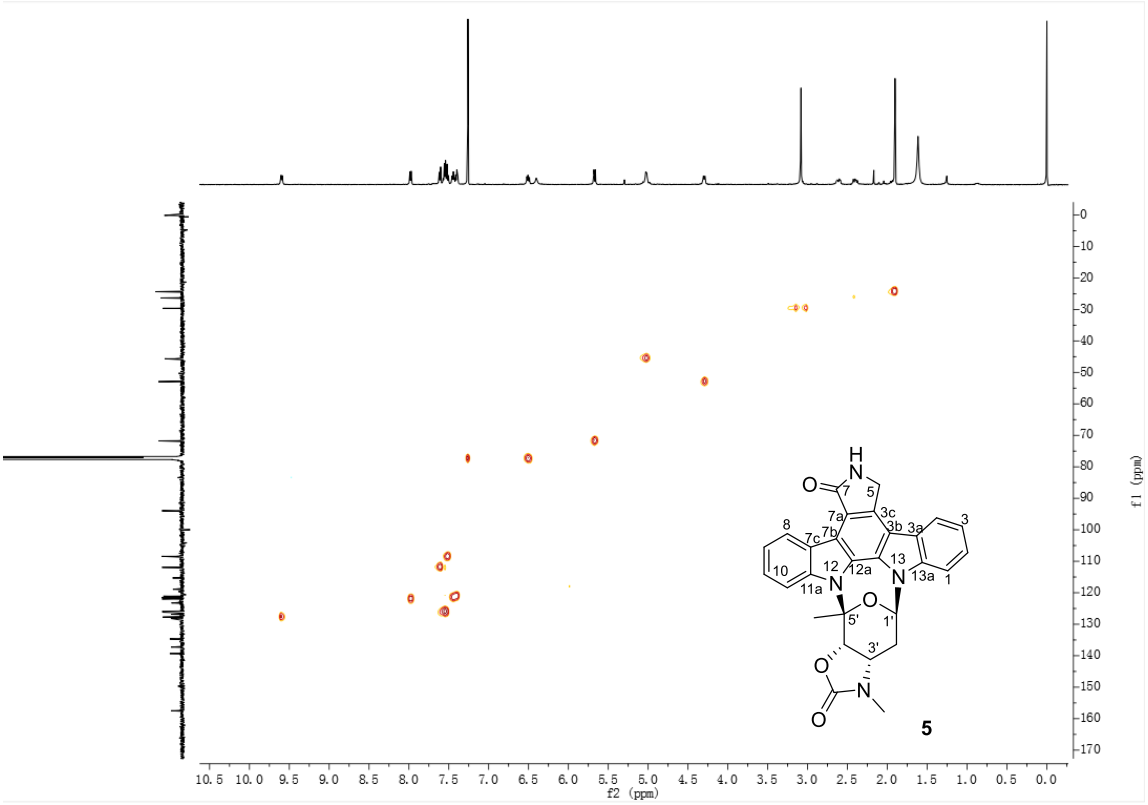
f1 (ppm)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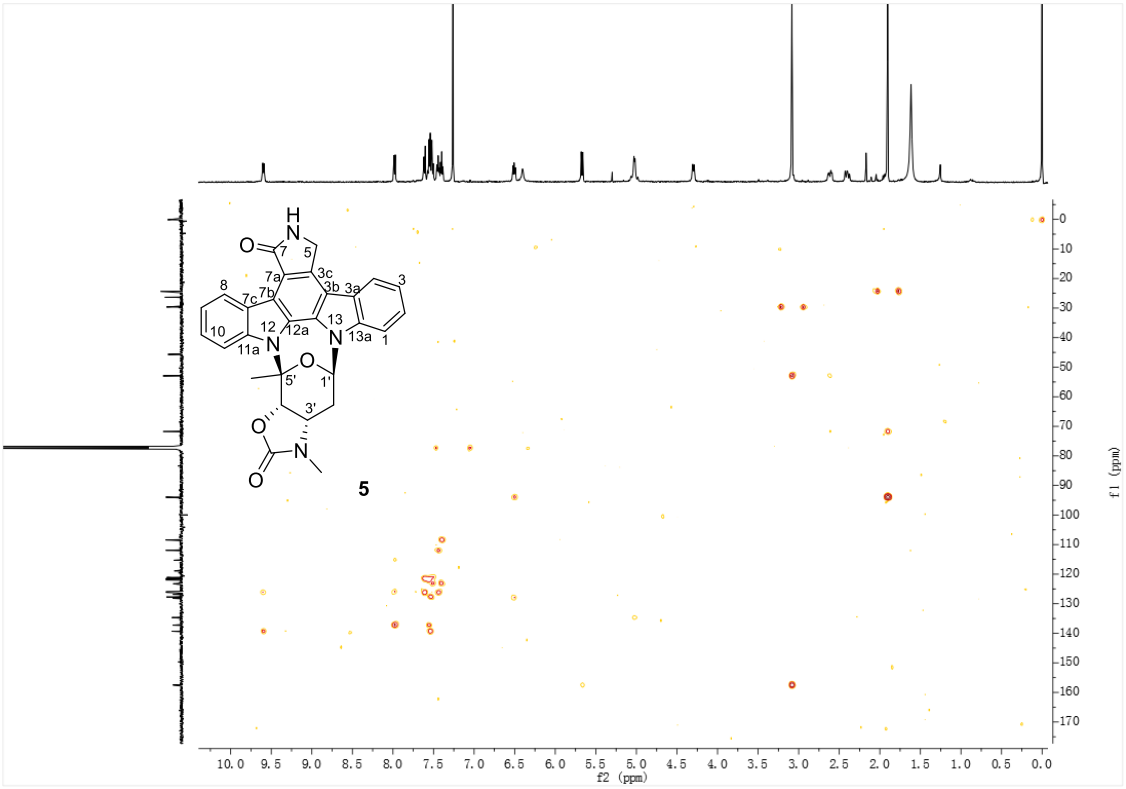
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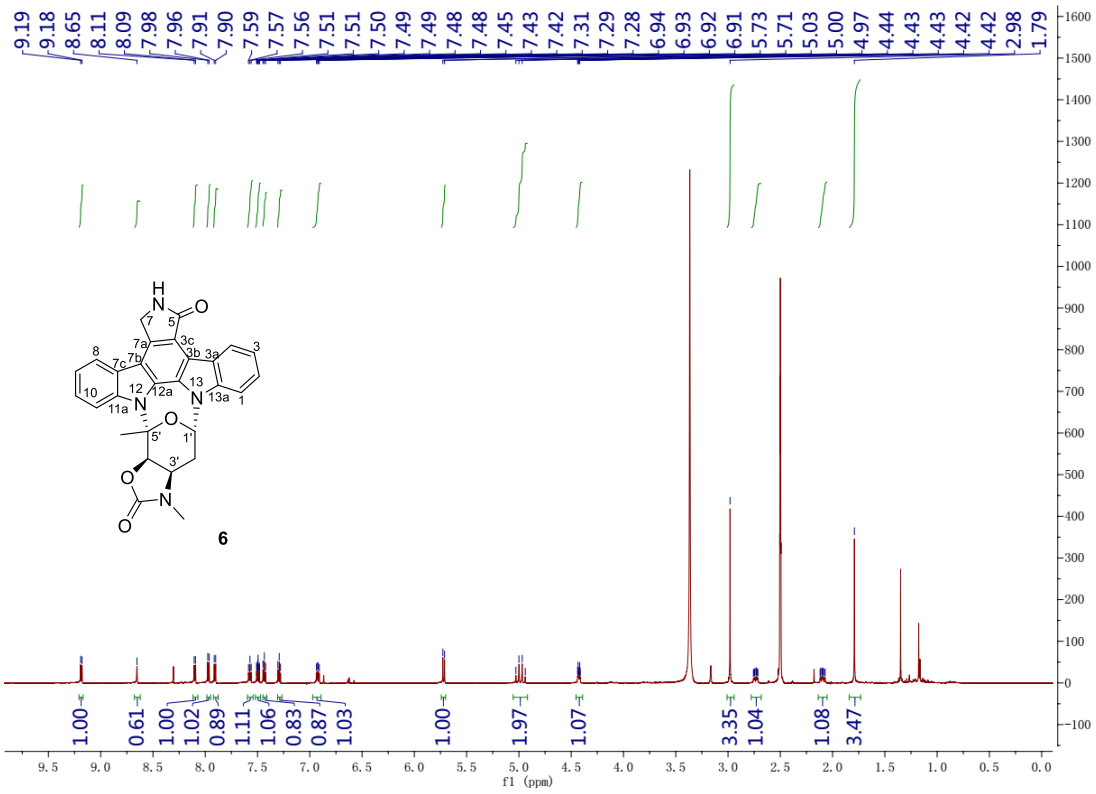
f1 (ppm)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4.43
4.43
4.42
4.42
2.98
1.79
1.00
0.61
1.00
1.02
0.89
1.11
1.06
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1.00
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1.07
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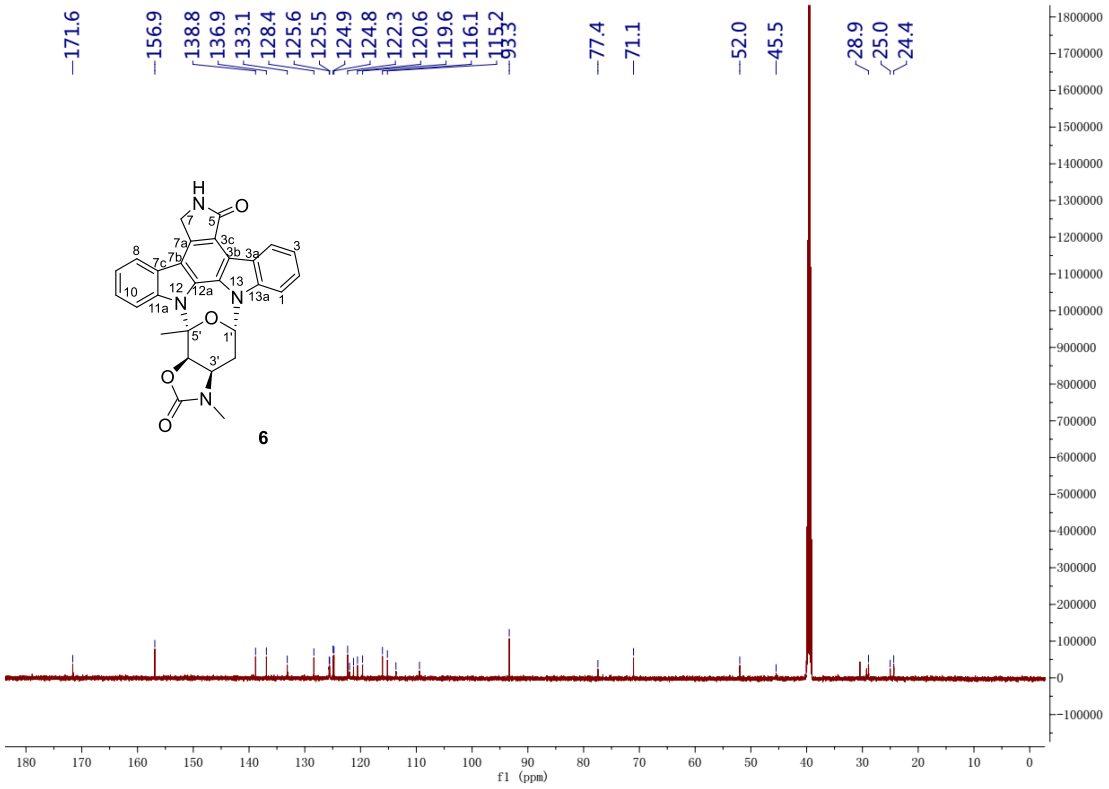
1.04
1.08
3.47
6
f1 (ppm)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124.8
122.3
120.6
119.6
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28.9
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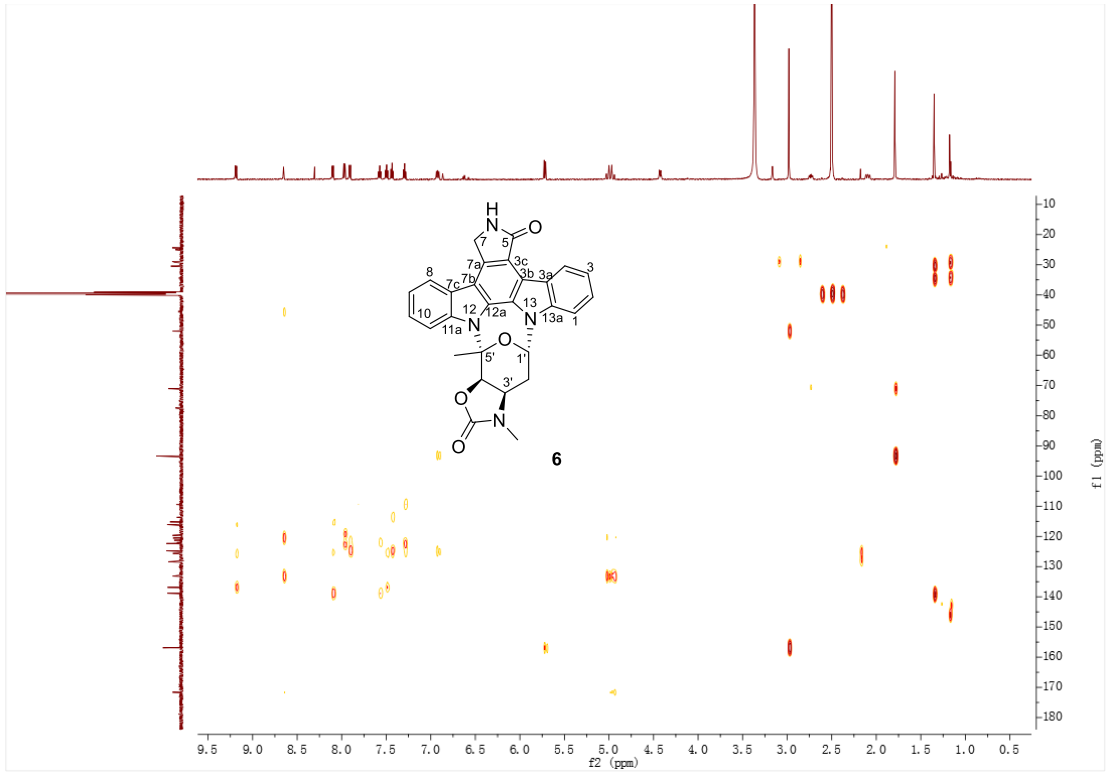
6
f1 (ppm)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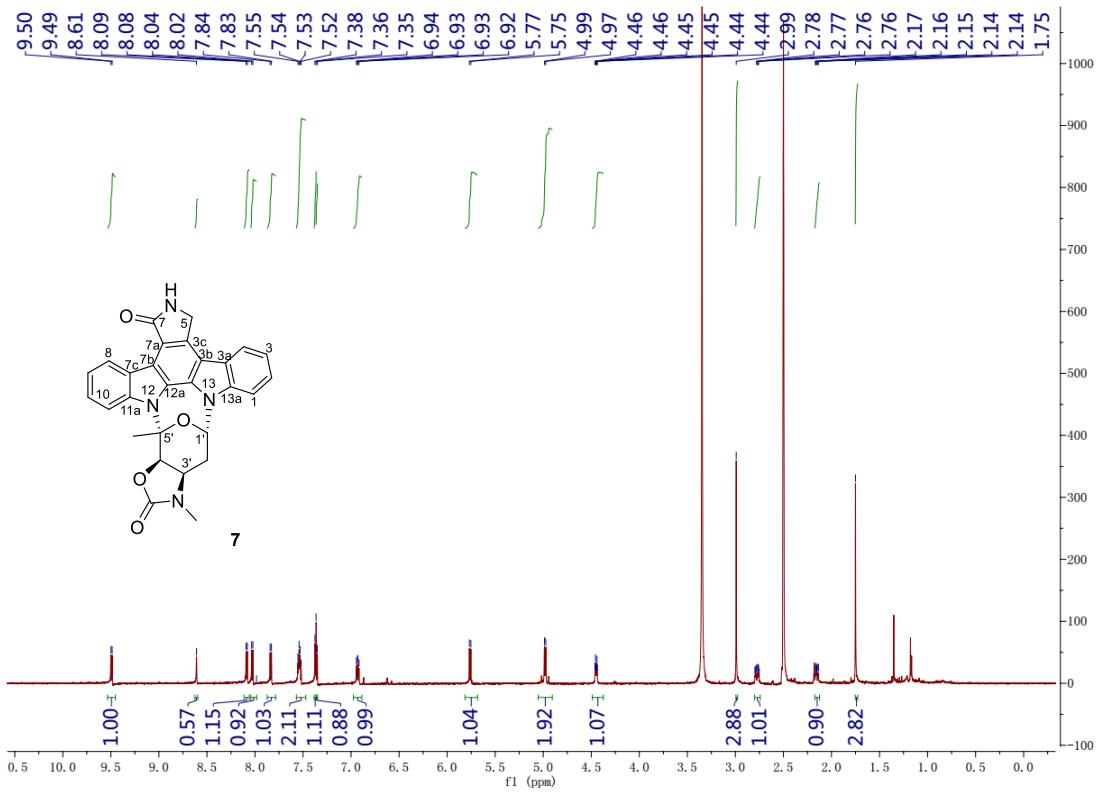
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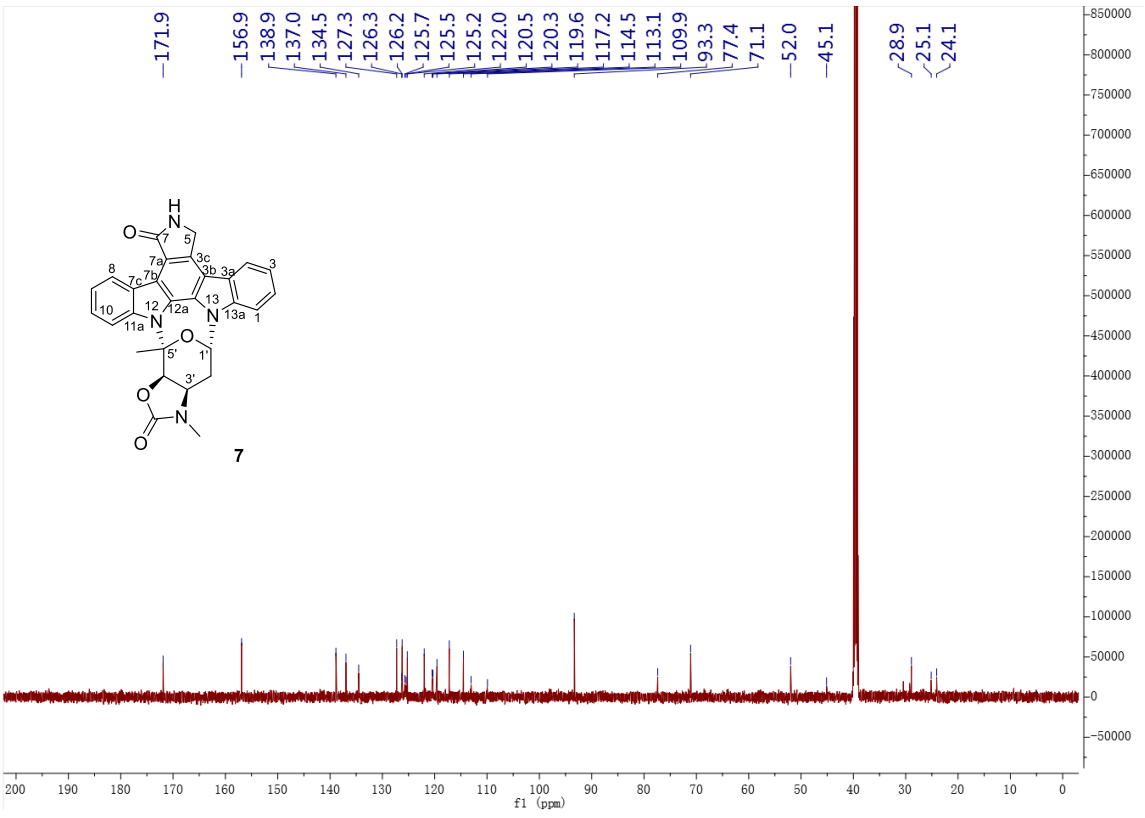
1.00 0.57 1.15 0.92 1.03 2.11 1.11 0.88 0.99 1.04 1.92 1.07 2.88 1.01 0.90 2.82
f1 (ppm)
7


171.9 156.9 138.9 137.0 134.5 127.3 126.3 126.2 125.7 125.5 125.2 122.0 120.5 120.3 119.6 117.2 114.5 113.1 109.9 93.3 77.4 71.1 52.0 45.1 28.9 25.1 24.1
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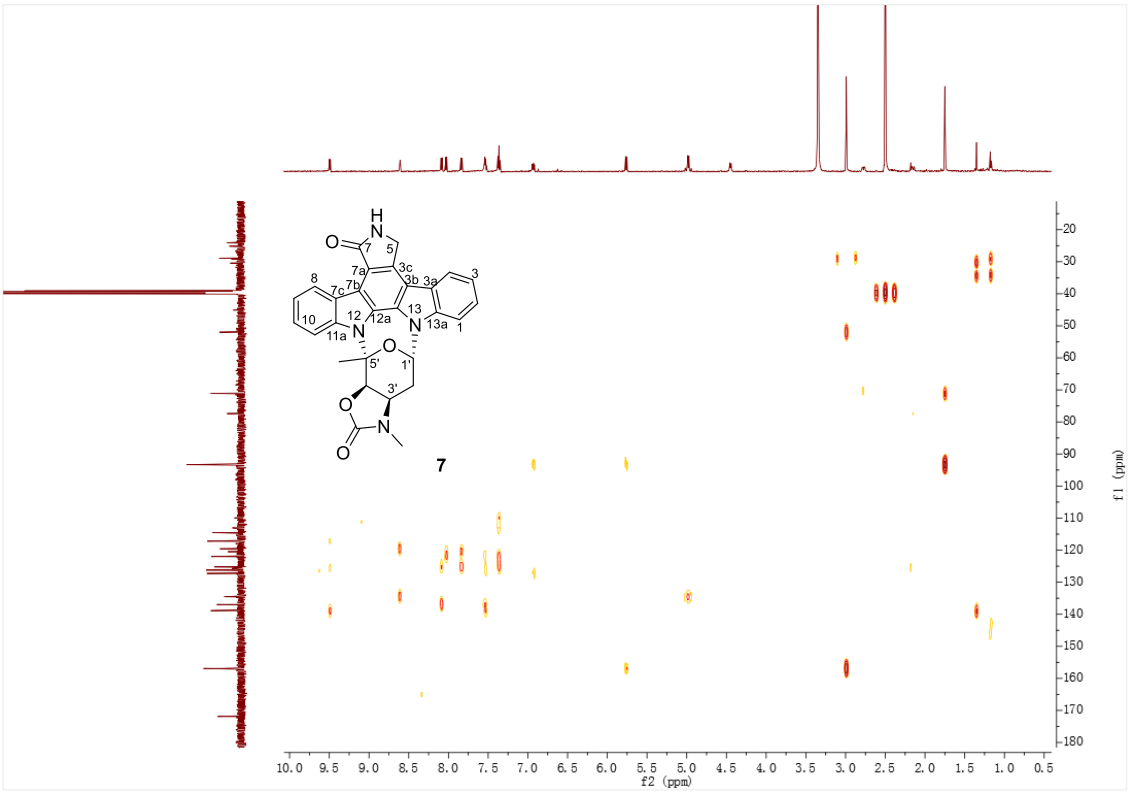
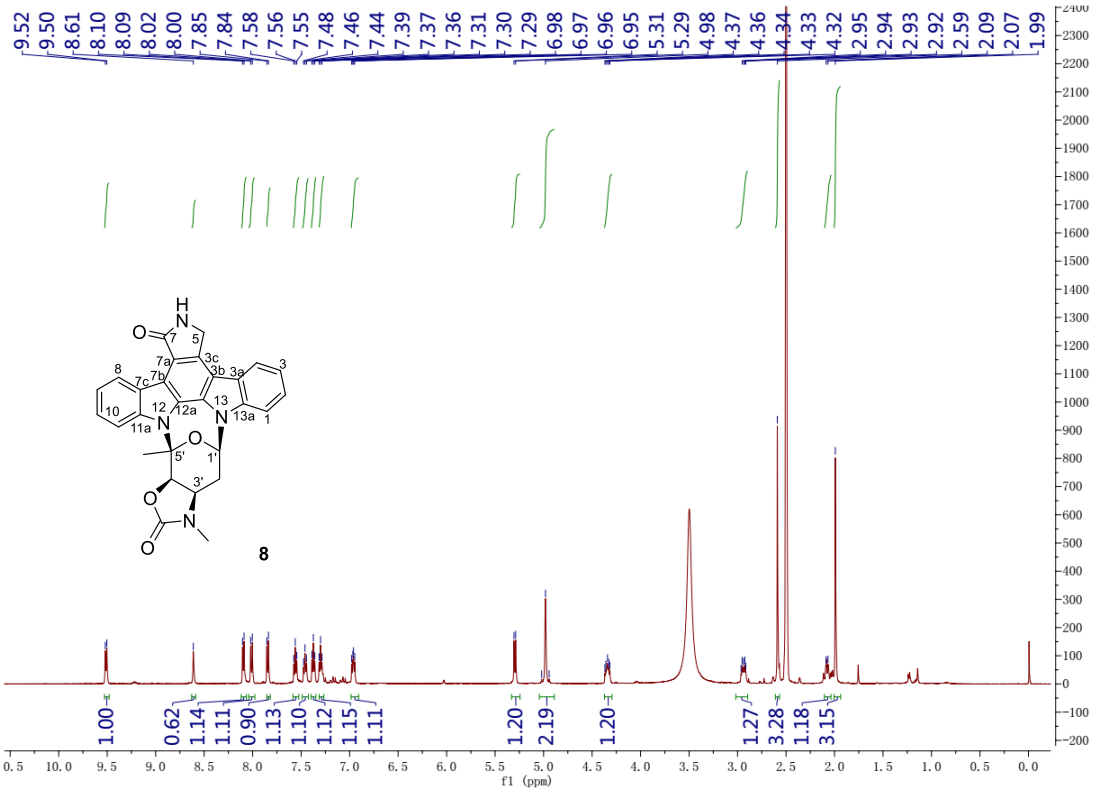
7


7
f2 (ppm)
f1 (ppm)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2.92
2.59
2.09
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1.99
1.00
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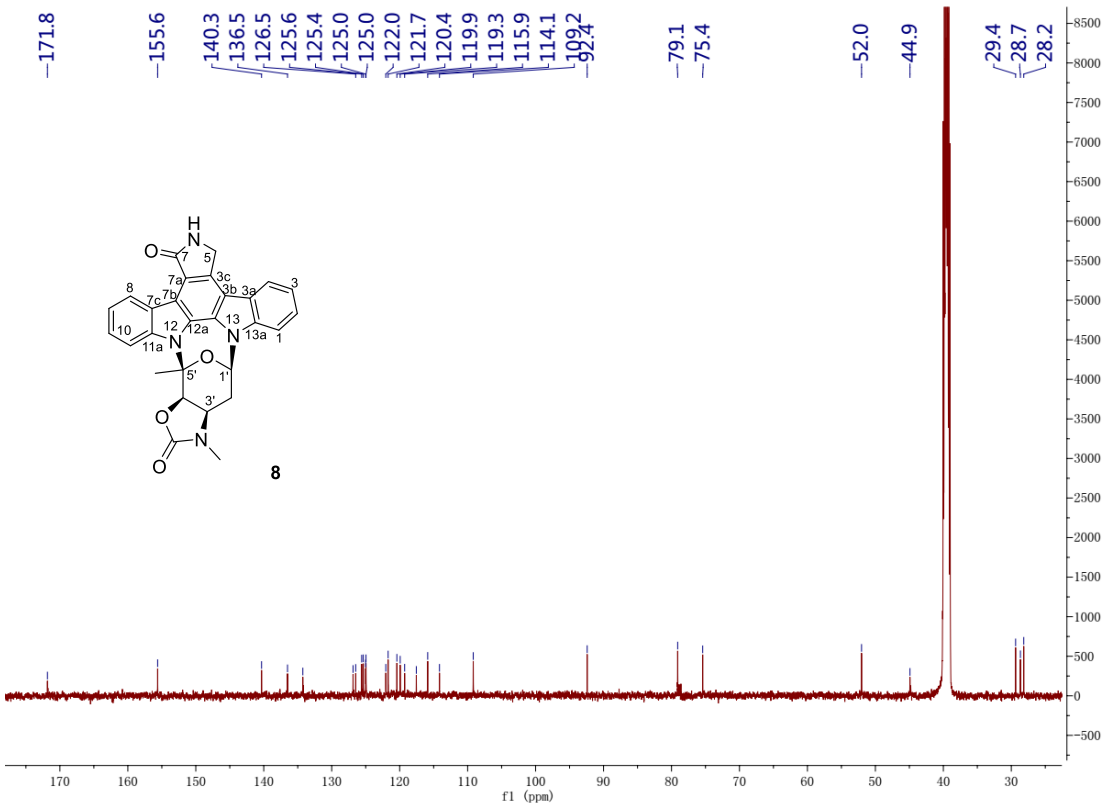
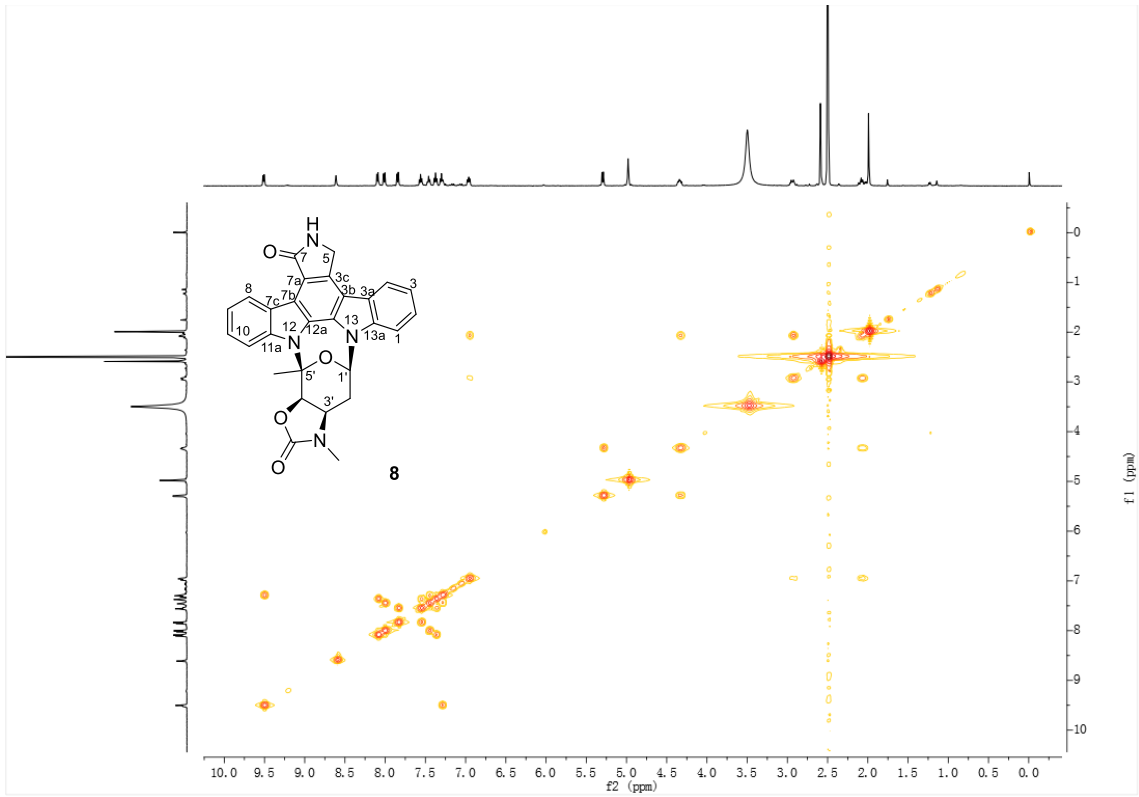
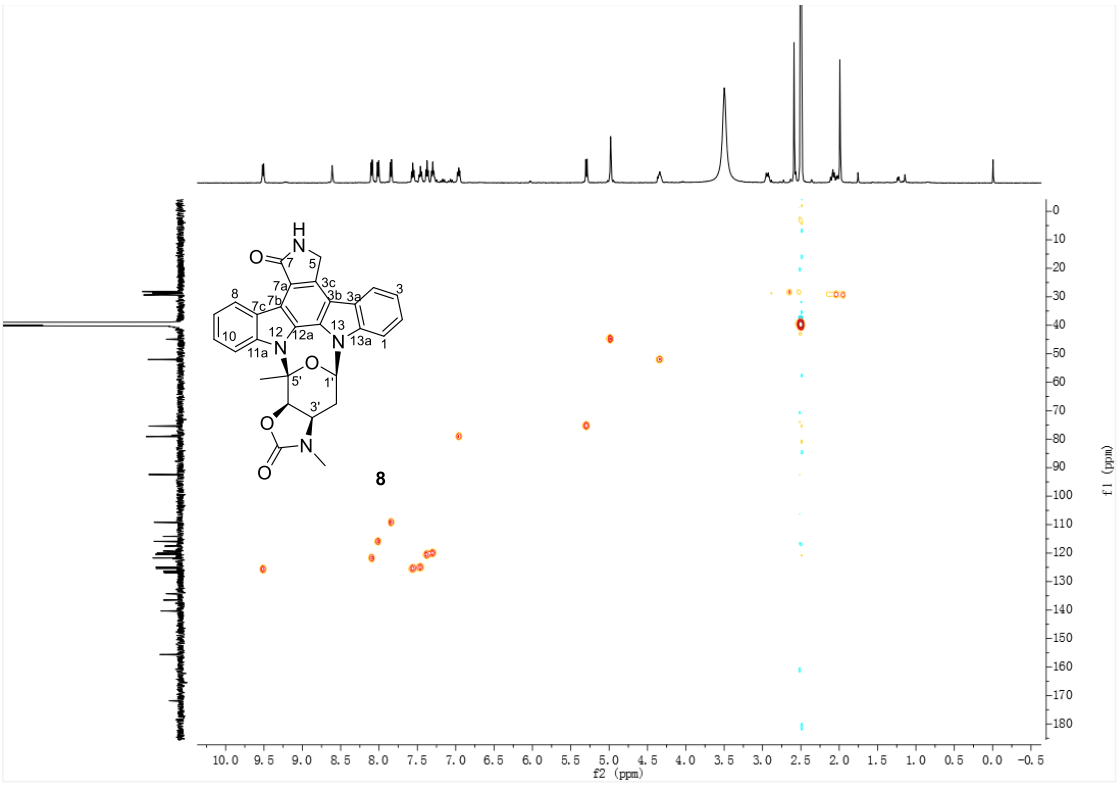
1.11
0.90
1.13
1.10
1.12
1.15
1.11
1.20
2.19
1.20
1.27
3.28
1.18
3.15
8
f1 (ppm)

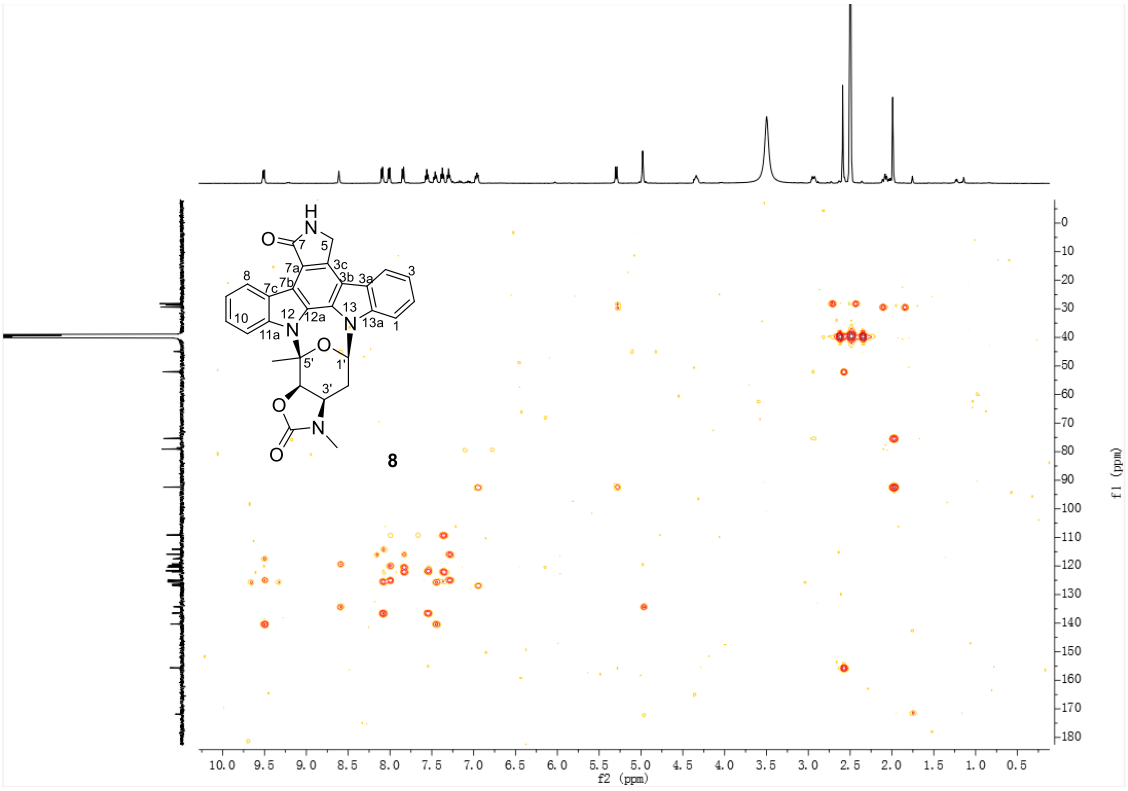

171.8
155.6
140.3
136.5
126.5
125.6
125.4
125.0
125.0
122.0
121.7
120.4
119.9
119.3
115.9
114.1
109.2
92.4
79.1
75.4
52.0
44.9
29.4
28.7
28.2
f1 (ppm)

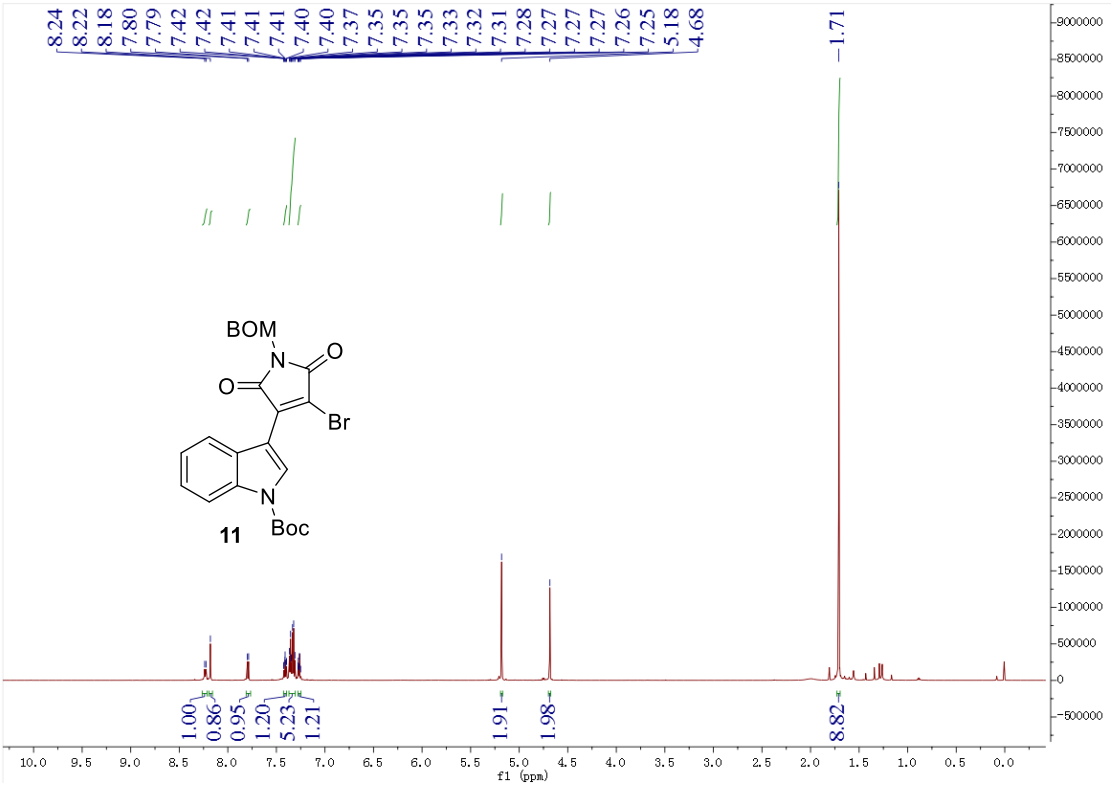
8

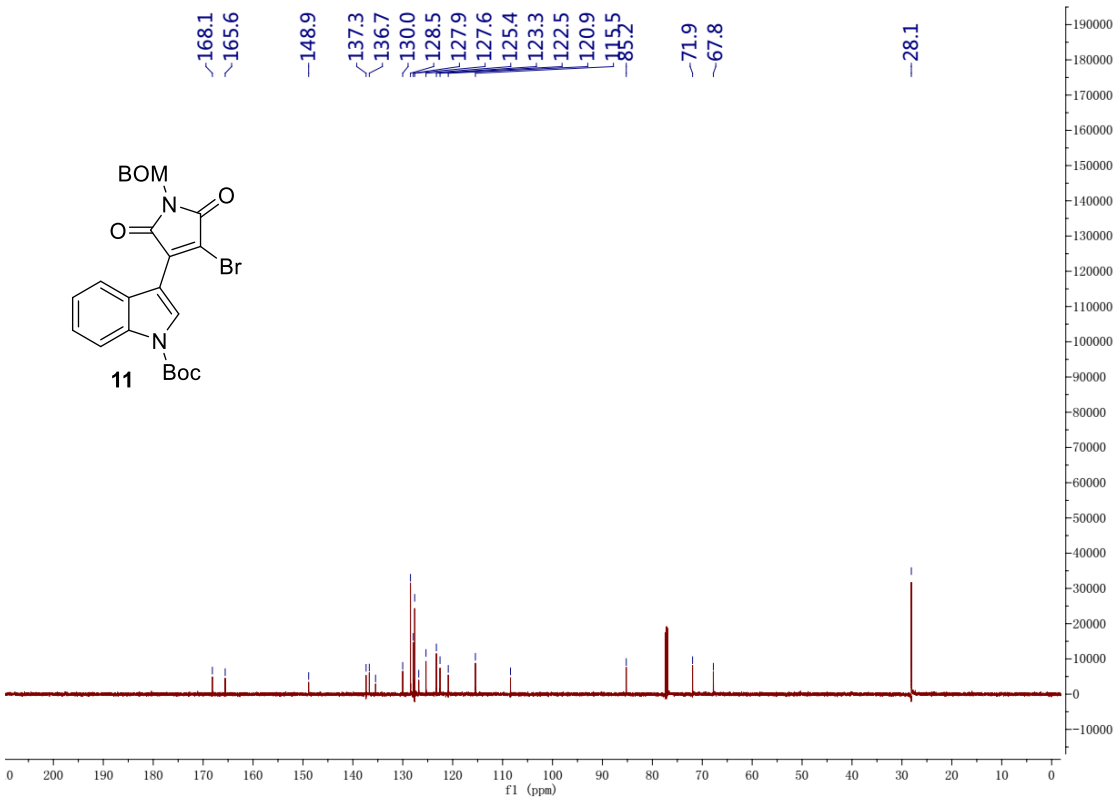

f2 (ppm)
f1 (ppm)

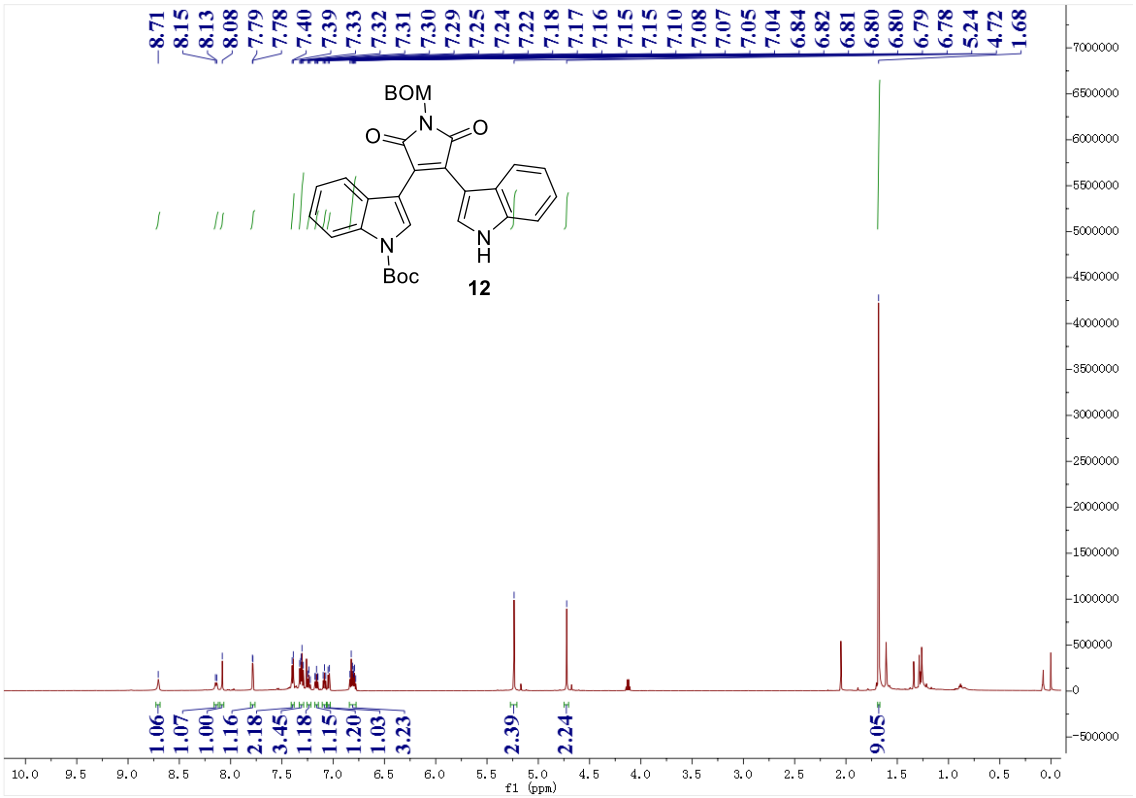
8

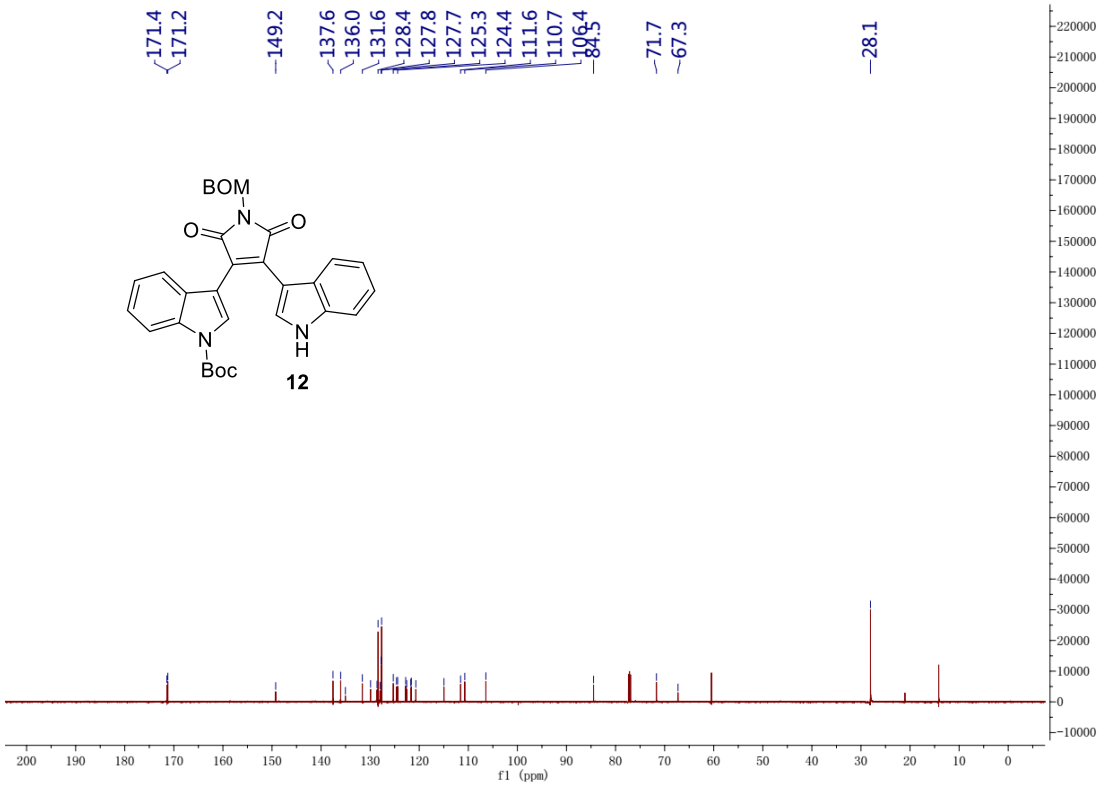

8
f2 (ppm)
f1 (ppm)

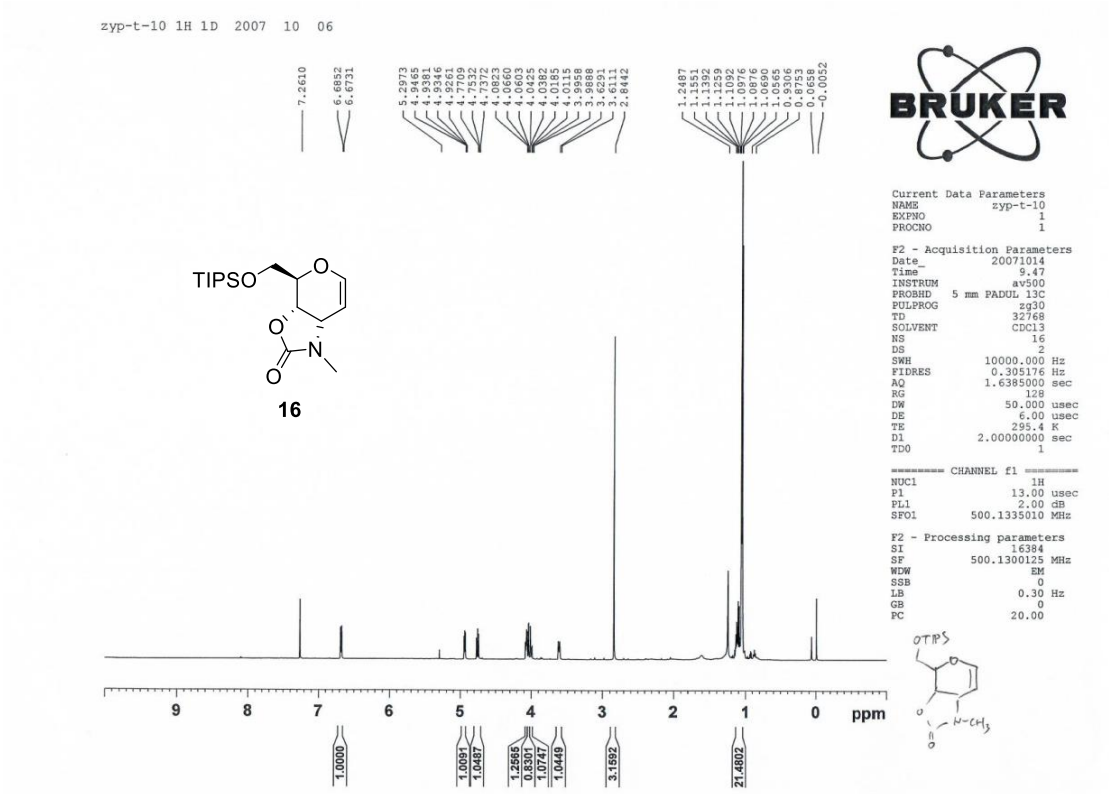

8
f2 (ppm)
f1 (ppm)

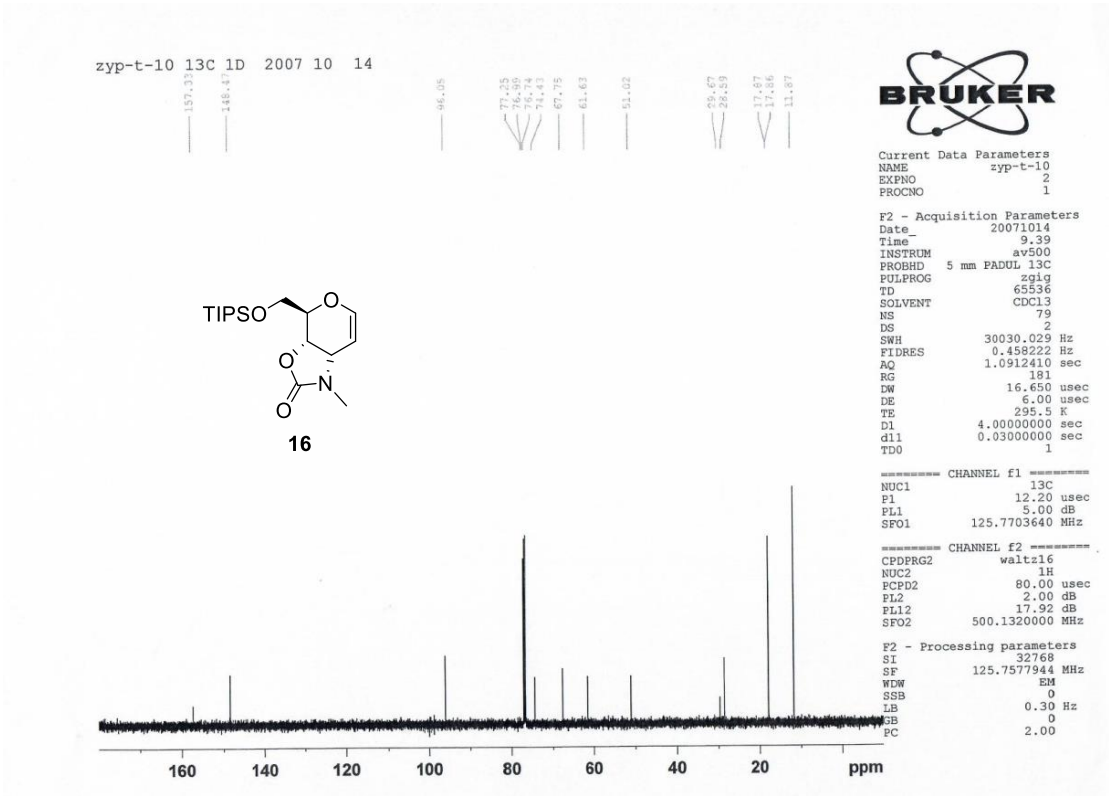

8.24
8.22
8.18
7.80
7.79
7.42
7.42
7.41
7.41
7.41
7.40
7.40
7.37
7.35
7.35
7.35
7.33
7.32
7.31
7.28
7.27
7.27
7.27
7.26
7.25
5.18
4.68
1.71
BOM
N
O
O
Br
N
Boc
11
1.00
0.86
0.95
1.20
5.23
1.21
1.91
1.98
8.82
f1 (ppm)

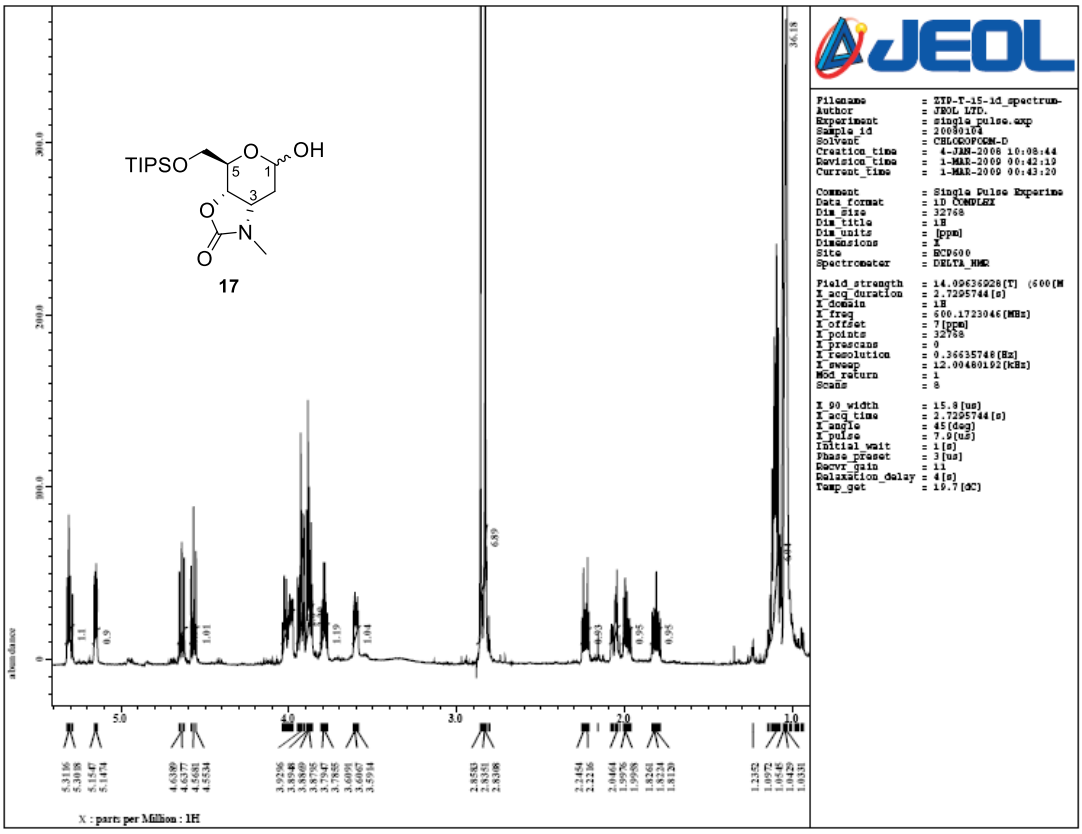

168.1
165.6
148.9
137.3
136.7
130.0
128.5
127.9
127.6
125.4
123.3
122.5
120.9
115.5
85.2
71.9
67.8
28.1
BOM
N
O
O
Br
N
Boc
11
f1 (ppm)

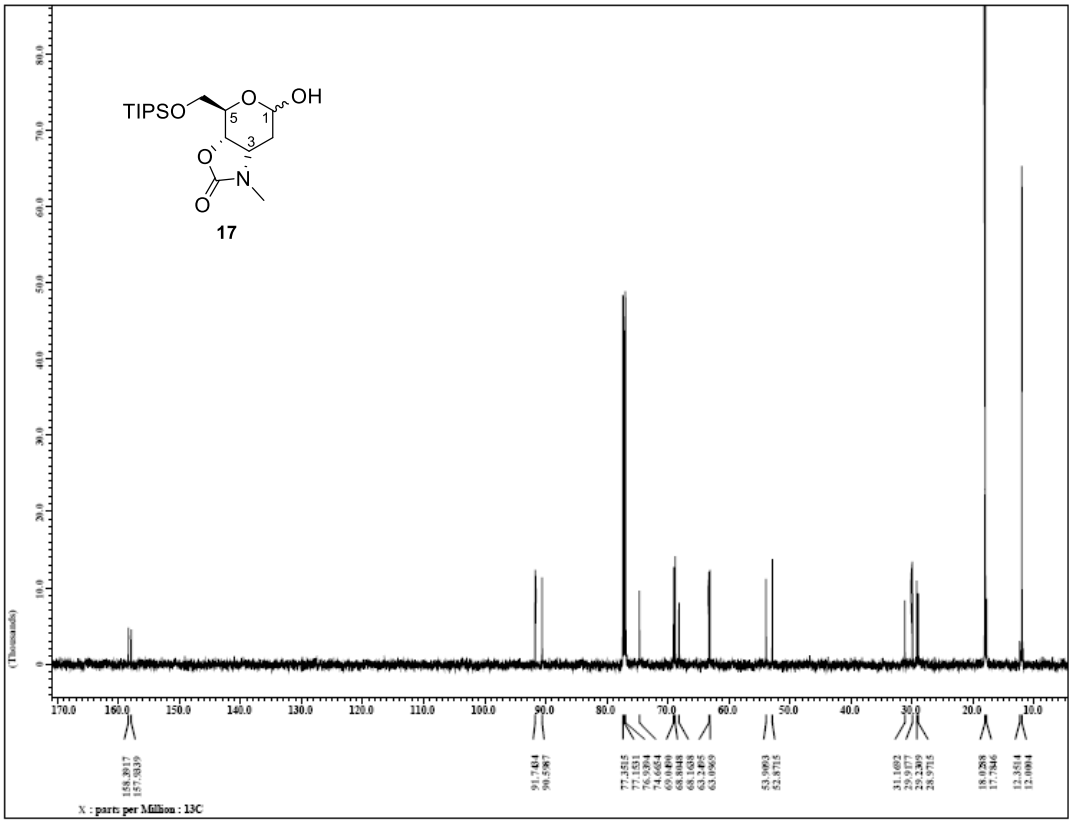

8.71
8.15
8.13
8.08
7.79
7.78
7.40
7.39
7.33
7.32
7.31
7.30
7.29
7.25
7.24
7.22
7.18
7.17
7.16
7.15
7.15
7.10
7.08
7.07
7.05
7.04
6.84
6.82
6.81
6.80
6.80
6.79
6.78
5.24
4.72
1.68
BOM
N
O
O
N
Boc
N
H
12
1.06
1.07
1.00
1.16
2.18
3.45
1.18
1.15
1.20
1.03
3.23
2.39
2.24
9.05
f1 (ppm)

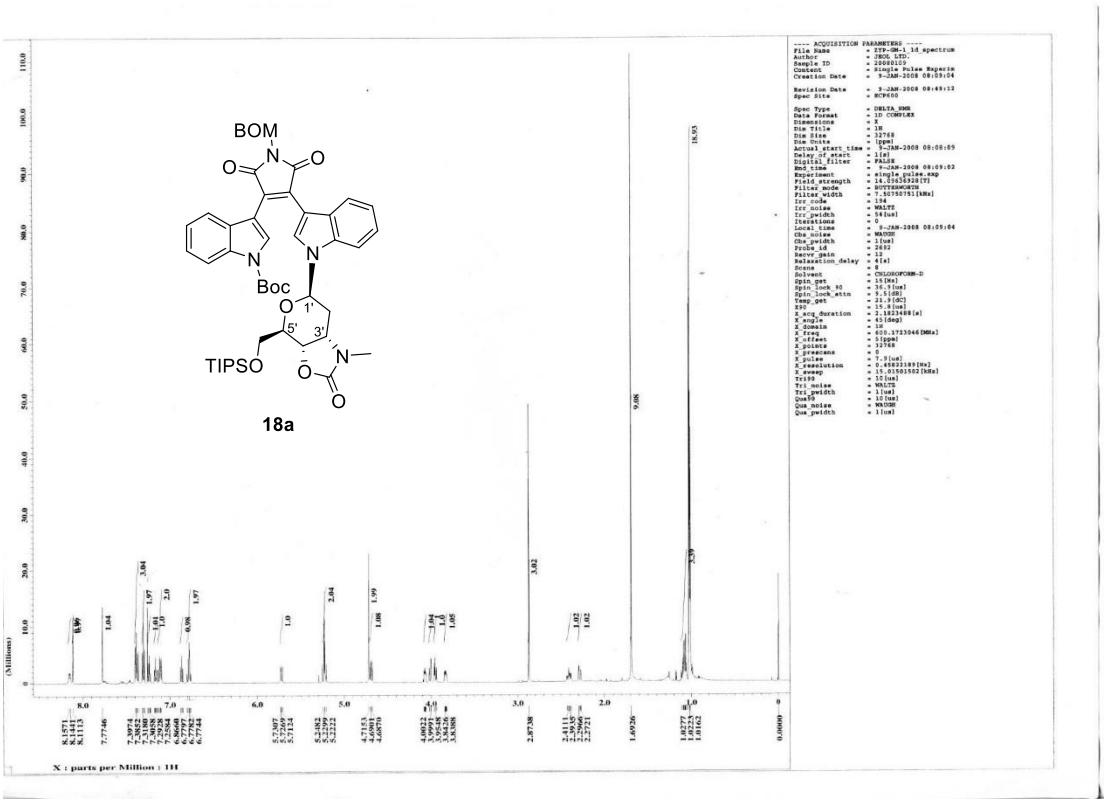

171.4
171.2
149.2
137.6
136.0
131.6
128.4
127.8
127.7
125.3
124.4
111.6
110.7
106.4
84.5
71.7
67.3
28.1
BOM
N
O
O
N
Boc
N
H
12
f1 (ppm)

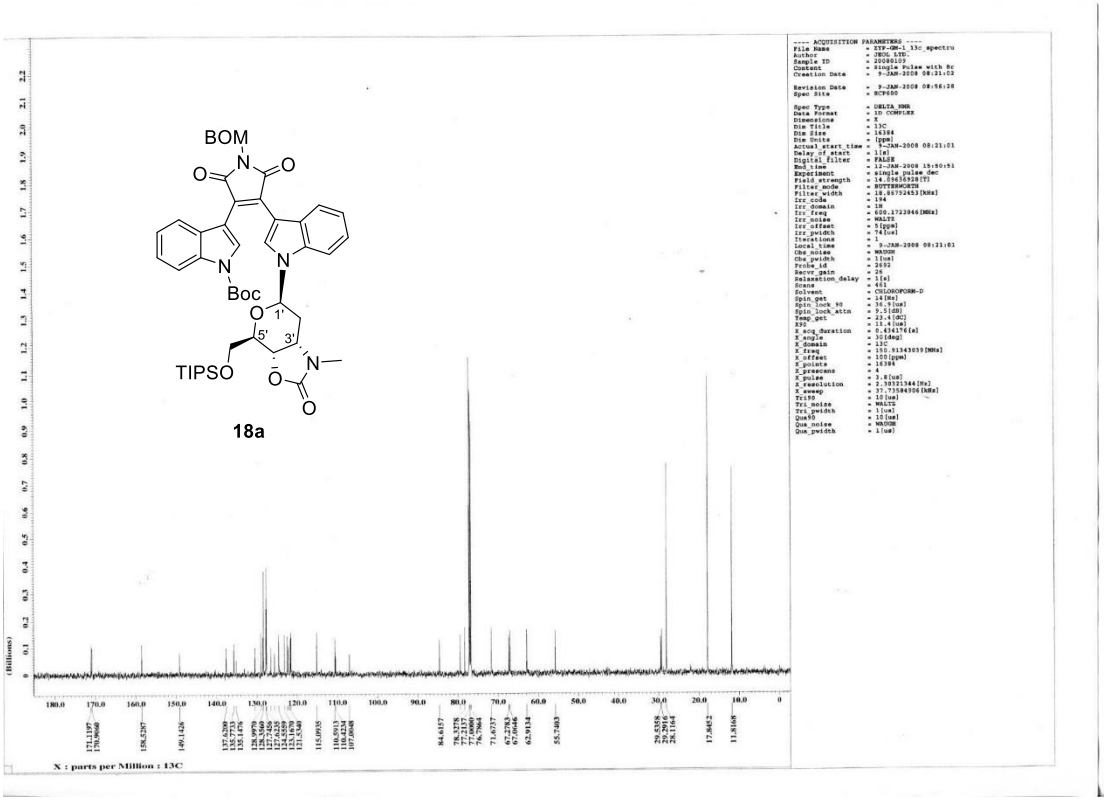

zyp-t-10 1H 1D 2007 10 06
TIPSO
16
Current Data Parameters
NAME zyp-t-10
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071014
Time 9.47
INSTRUM av500
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 1.6385000 sec
RG 128
DW 50.000 usec
DE 6.00 usec
TE 295.4 K
D1 2.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 13.00 usec
PL1 2.00 dB
SFO1 500.1335010 MHz
F2 - Processing parameters
SI 16384
SF 500.1300125 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 20.00
ppm

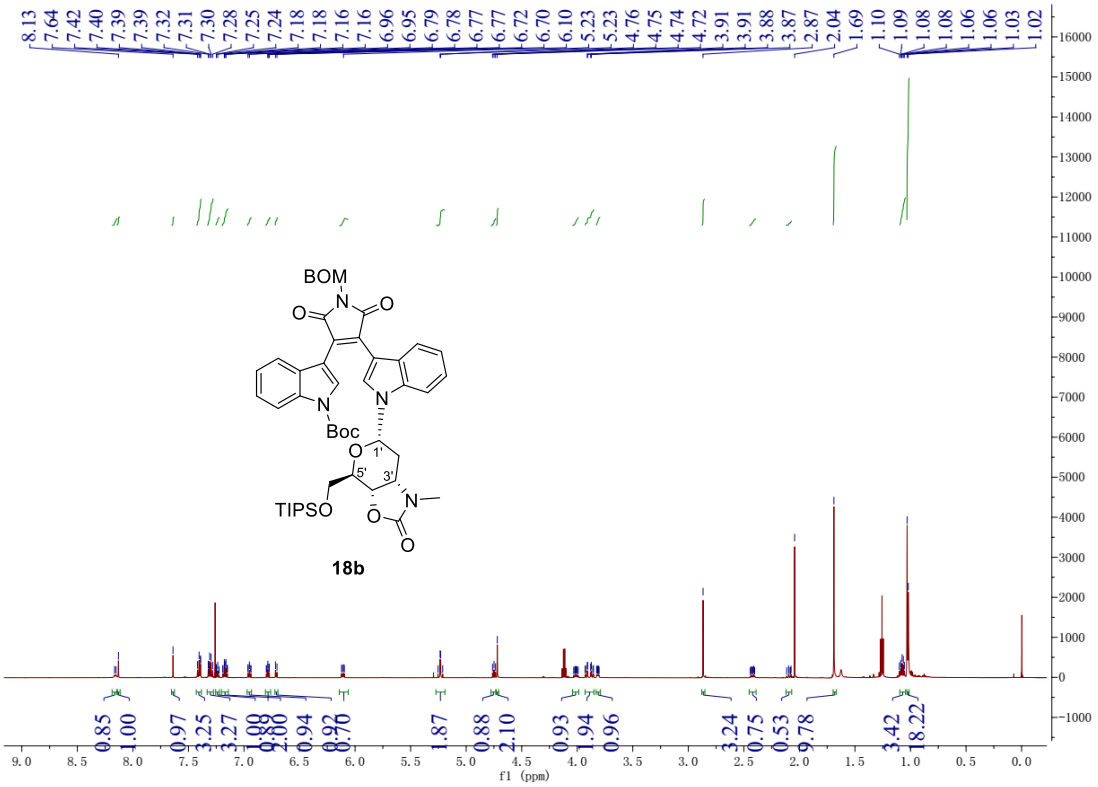

zyp-t-10 13C 1D 2007 10 14
TIPSO
16
Current Data Parameters
NAME zyp-t-10
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071014
Time 9.39
INSTRUM av500
PROBHD 5 mm PADUL 13C
PULPROG zgig
TD 65536
SOLVENT CDCl3
NS 79
DS 2
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912410 sec
RG 181
DW 16.650 usec
DE 6.00 usec
TE 295.5 K
D1 4.00000000 sec
d11 0.03000000 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 12.20 usec
PL1 5.00 dB
SFO1 125.7703640 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 2.00 dB
PL12 17.92 dB
SFO2 500.1320000 MHz
F2 - Processing parameters
SI 32768
SF 125.7577944 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 2.00
ppm

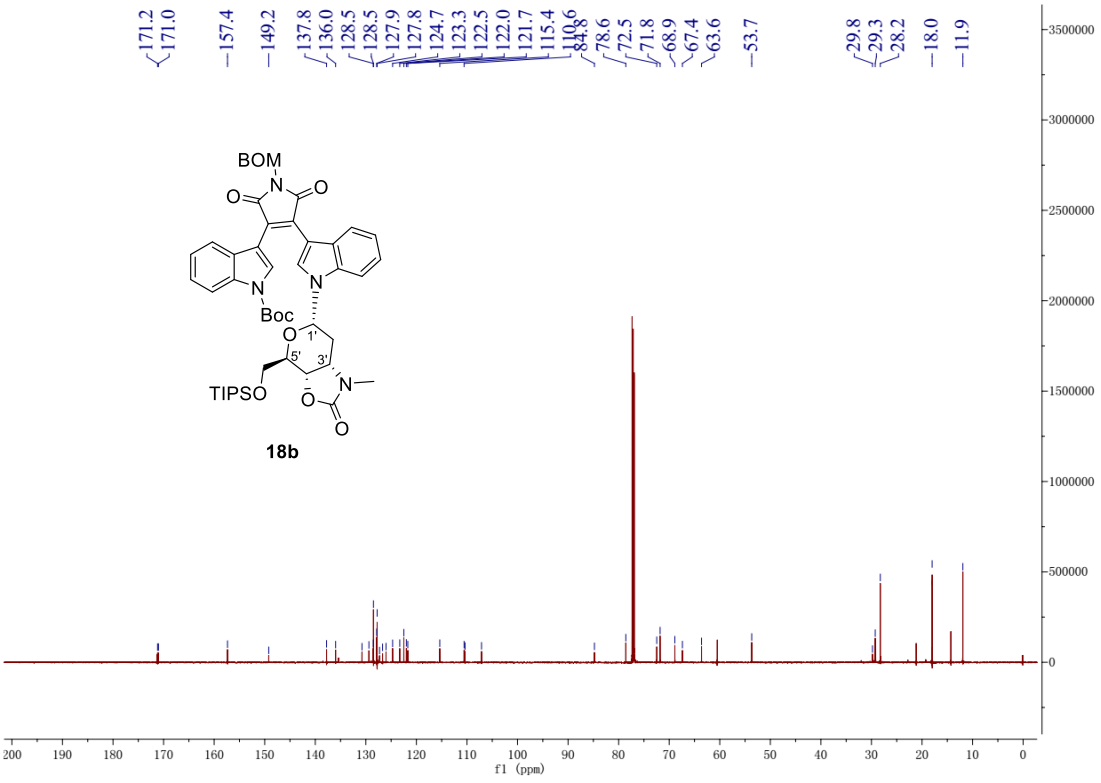

TIPSO
OH
O
5
1
3
O
N
O
17
JEOL
Filename : ETP-T-15-1d_spectrum-
Author : JEOL LTD.
Experiment : single_pulse.exp
Sample_id : 20080108
Solvent : CHLOROFORM-D
Creation_time : 4-JAN-2008 10:08:44
Revision_time : 1-MAR-2009 00:42:19
Current_time : 1-MAR-2009 00:43:20
Comment : Single Pulse Experime
Data_format : 1D COMPLEX
Dim_size : 32768
Dim_title : 1H
Dim_units : [ppm]
Dimensions : 1
Site : NCP600
Spectrometer : DELTA_NMR
Field_strength : 14.09636928[T] (600[M
X_acq_duration : 2.7295744[s]
X_domain : 1H
X_freq : 600.1723046[MHz]
X_offset : 7[ppm]
X_points : 32768
X_prescans : 0
X_resolution : 0.36635746[Hz]
X_sweep : 12.00480192[kHz]
Mod_return : 1
Scans : 8
X_90_width : 15.8[us]
X_acq_time : 2.7295744[s]
X_angle : 45[deg]
X_pulse : 7.9[us]
Initial_wait : 1[s]
Phase_preset : 3[us]
Recvr_gain : 11
Relaxation_delay : 4[s]
Temp_get : 19.7[dC]
X : parts per Million : 1H

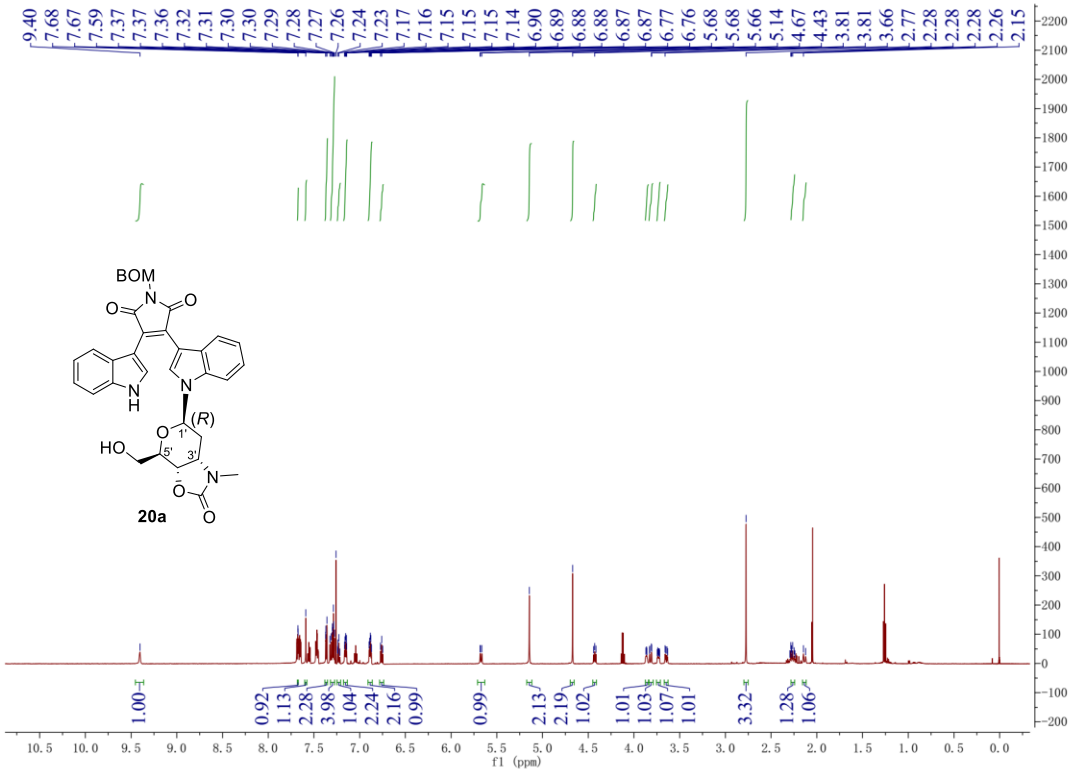

TIPSO
OH
O
5
1
3
O
N
O
17
X : parts per Million : 13C

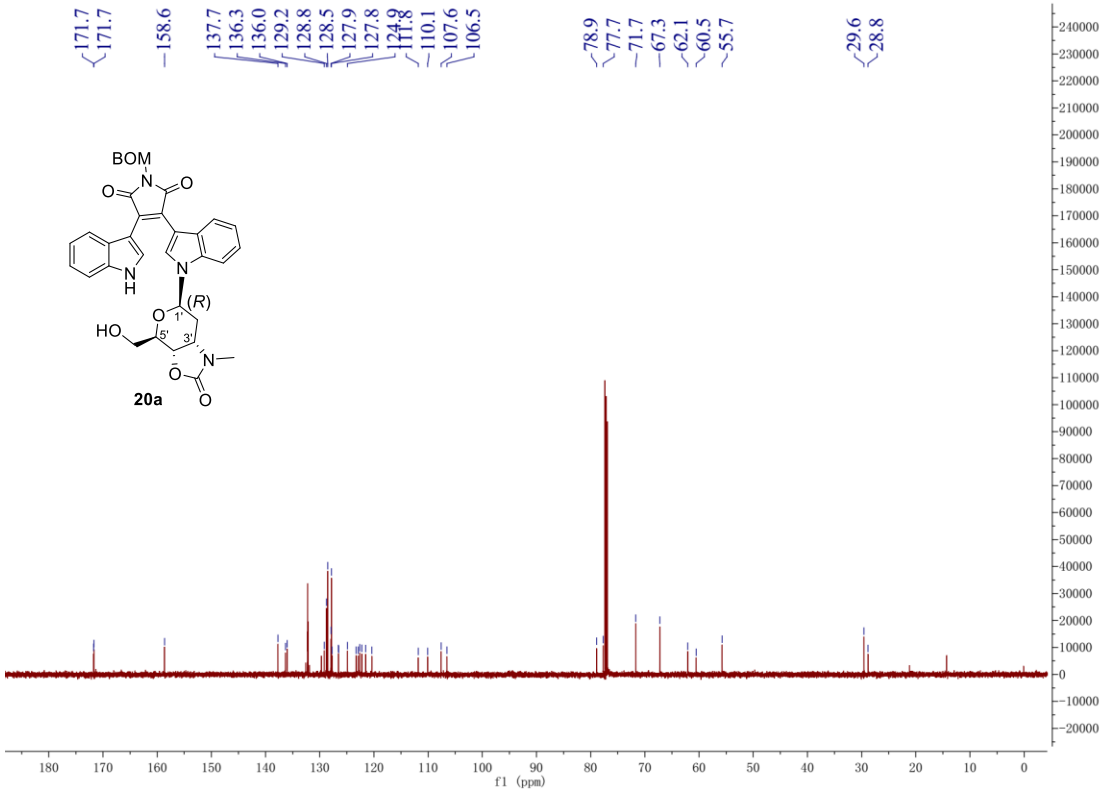

BOM
Boc
TIPSO
18a
X : parts per Million : 1H

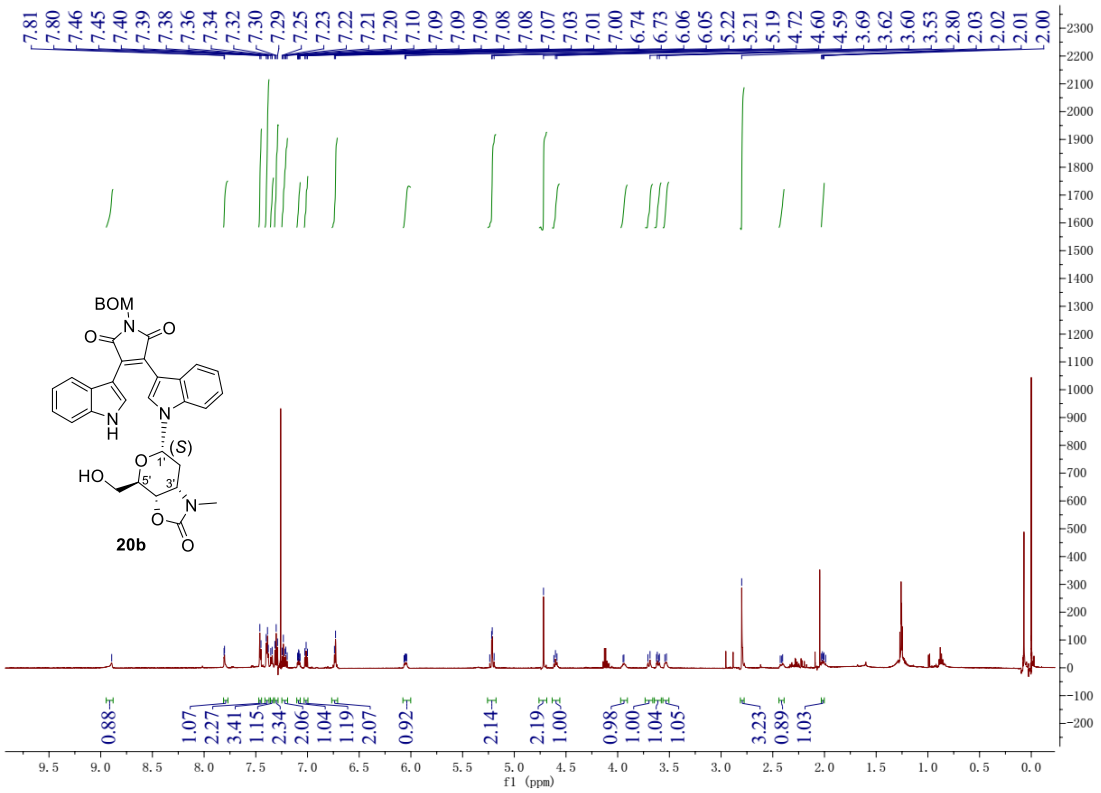

BOM
Boc
TIPSO
18a
X : parts per Million : 13C

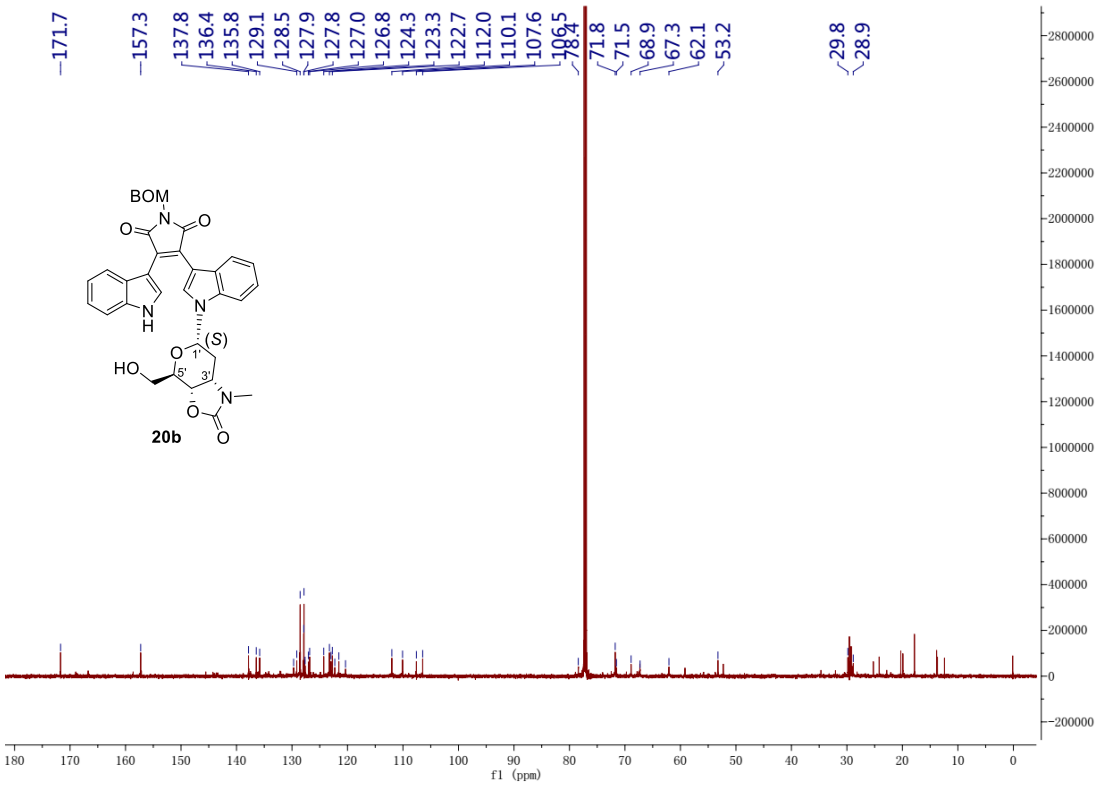

8.13 7.64 7.42 7.40 7.39 7.39 7.32 7.31 7.30 7.28 7.25 7.24 7.18 7.18 7.16 7.16 6.96 6.95 6.79 6.78 6.77 6.77 6.72 6.70 6.10 5.23 5.23 4.76 4.75 4.74 4.72 3.91 3.91 3.88 3.87 2.87 2.04 1.69 1.10 1.09 1.08 1.08 1.06 1.06 1.03 1.02
BOM
Boc
TIPSO
18b
0.85 1.00 0.97 3.25 3.27 1.00 2.00 0.94 0.92 8.70 1.87 0.88 2.10 0.93 1.94 0.96 3.24 0.75 0.53 9.78 3.42 18.22
f1 (ppm)

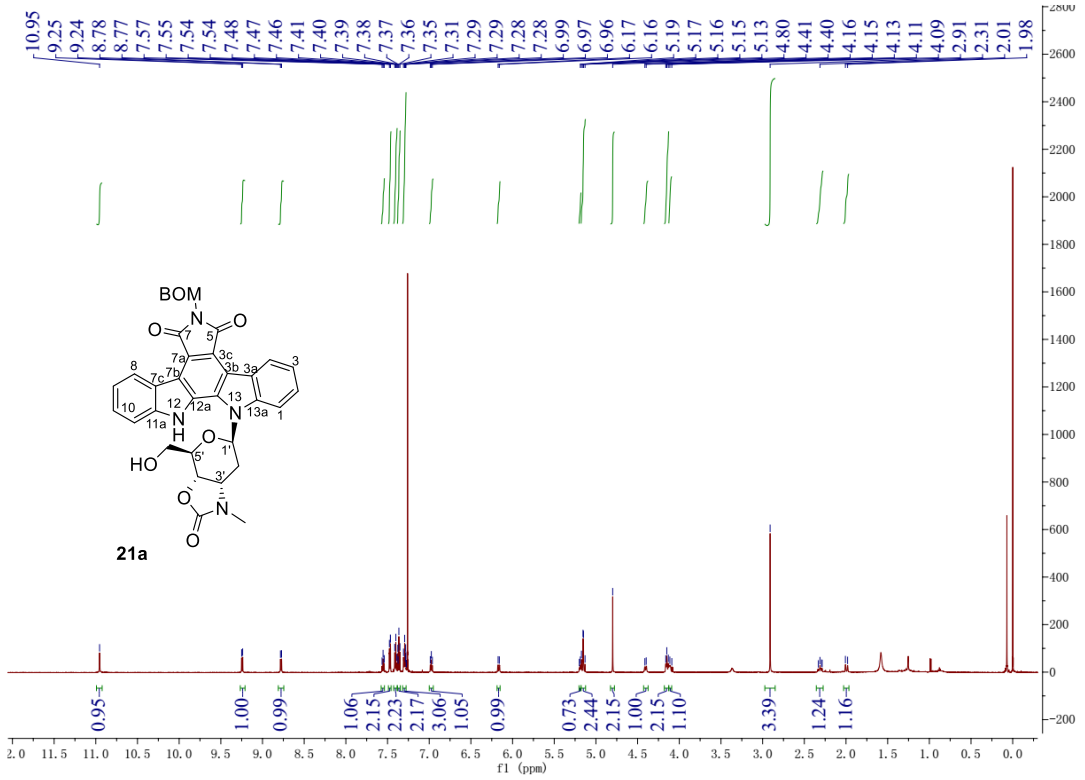

171.2 171.0 157.4 149.2 137.8 136.0 128.5 128.5 127.9 127.8 124.7 123.3 122.5 122.0 121.7 115.4 110.6 84.8 78.6 72.5 71.8 68.9 67.4 63.6 53.7 29.8 29.3 28.2 18.0 11.9
BOM
Boc
TIPSO
18b
f1 (ppm)

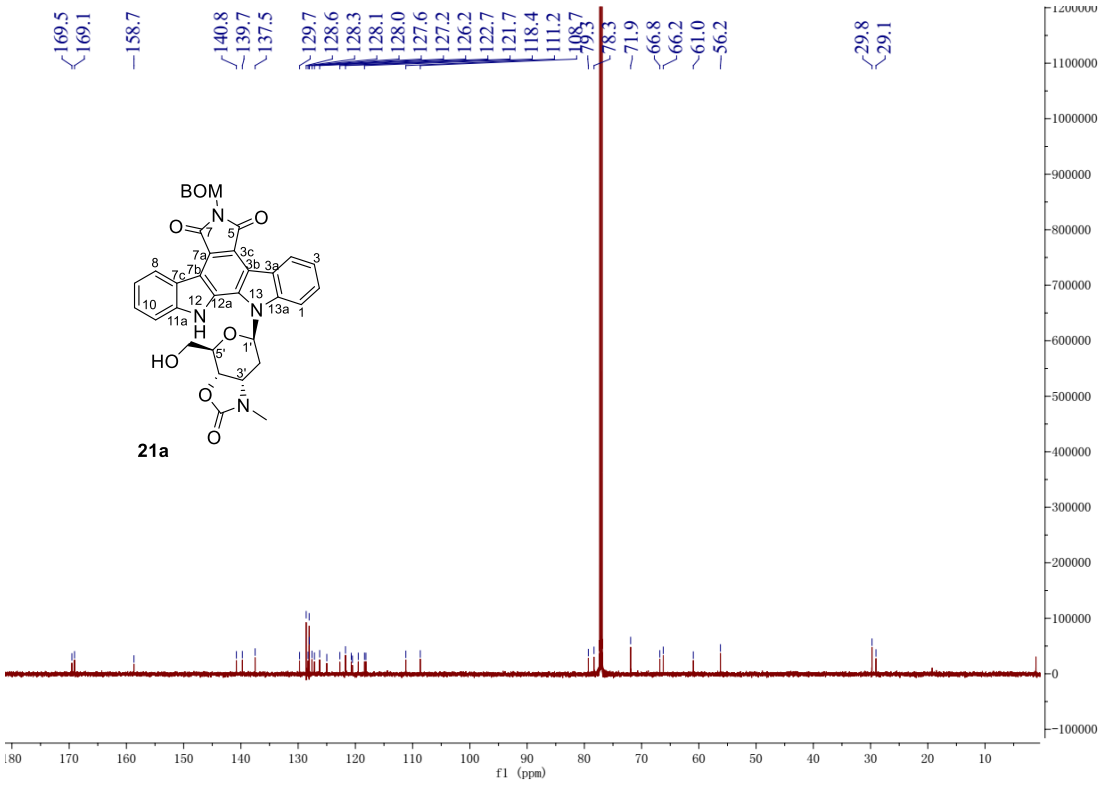

9.40
7.68
7.67
7.59
7.37
7.37
7.36
7.32
7.31
7.30
7.30
7.29
7.28
7.27
7.26
7.24
7.23
7.17
7.16
7.15
7.15
7.15
7.14
6.90
6.89
6.88
6.88
6.87
6.87
6.77
6.76
5.68
5.66
5.14
4.67
4.43
3.81
3.81
3.66
2.77
2.28
2.28
2.28
2.26
2.15
BOM
HO
(R)
20a
1.00
0.92
1.13
2.28
3.98
1.04
2.24
2.16
0.99
0.99
2.13
2.19
1.02
1.01
1.03
1.07
1.01
3.32
1.28
1.06
f1 (ppm)

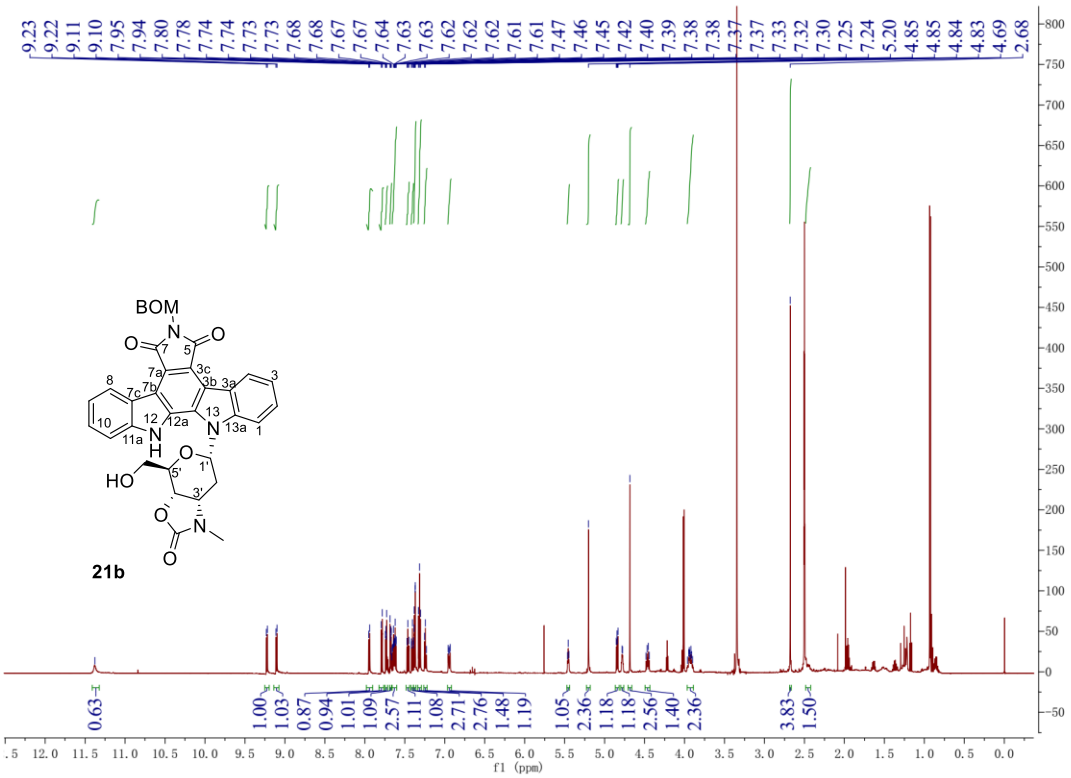

171.7
171.7
158.6
137.7
136.3
136.0
129.2
128.8
128.5
127.9
127.8
124.9
111.8
110.1
107.6
106.5
78.9
77.7
71.7
67.3
62.1
60.5
55.7
29.6
28.8
BOM
HO
(R)
20a
f1 (ppm)

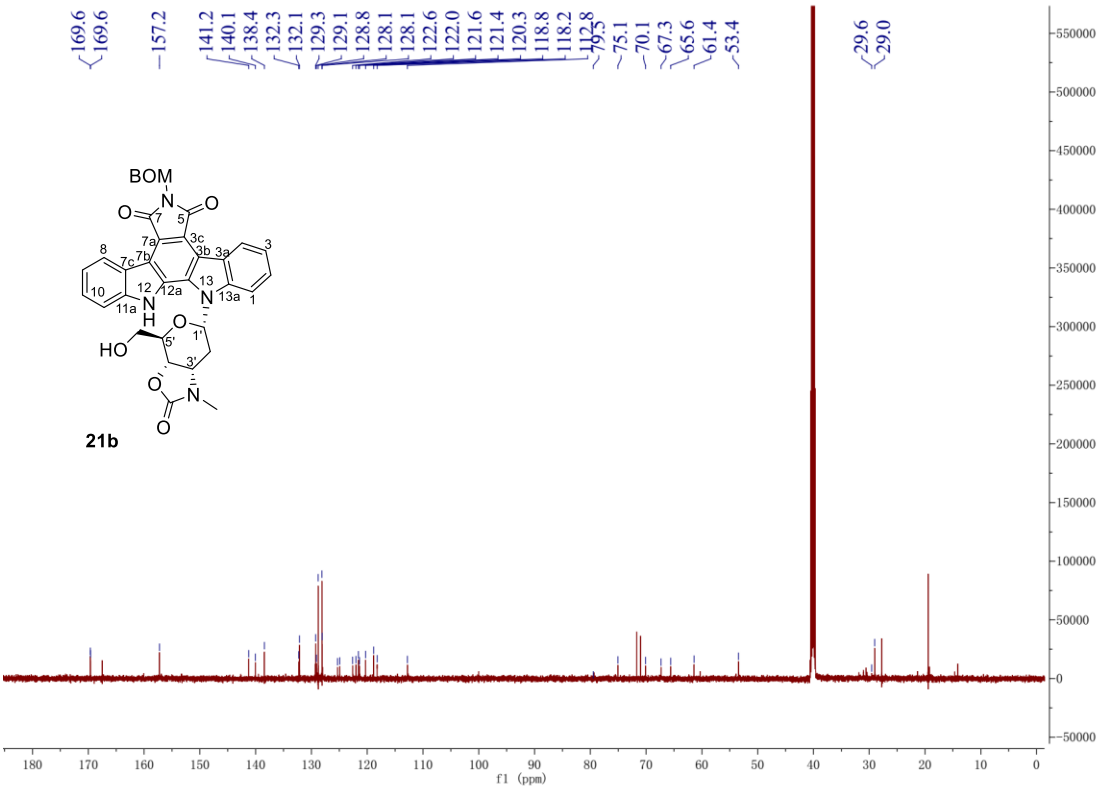

7.81 7.80 7.46 7.45 7.40 7.39 7.38 7.36 7.34 7.32 7.30 7.29 7.25 7.23 7.22 7.21 7.20 7.10 7.09 7.09 7.09 7.08 7.08 7.07 7.03 7.01 7.00 6.74 6.73 6.06 6.05 5.22 5.21 5.19 4.72 4.60 4.59 3.69 3.62 3.60 3.53 2.80 2.03 2.02 2.01 2.00
BOM
HO
(S)
20b
0.88 1.07 2.27 3.41 1.15 2.34 2.06 1.04 1.19 2.07 0.92 2.14 2.19 1.00 0.98 1.00 1.04 1.05 3.23 0.89 1.03
f1 (ppm)

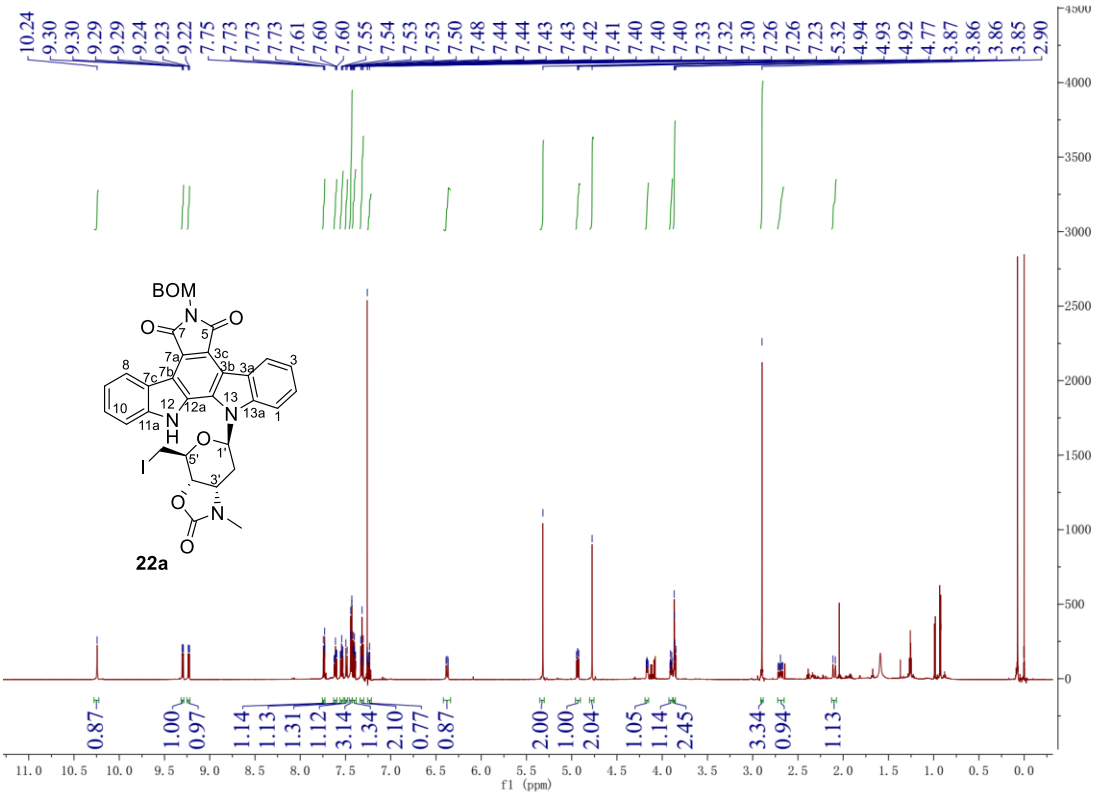

171.7 157.3 137.8 136.4 135.8 129.1 128.5 127.9 127.8 127.0 126.8 124.3 123.3 122.7 112.0 110.1 107.6 106.5 78.4 71.8 71.5 68.9 67.3 62.1 53.2 29.8 28.9
BOM
HO
(S)
20b
f1 (ppm)

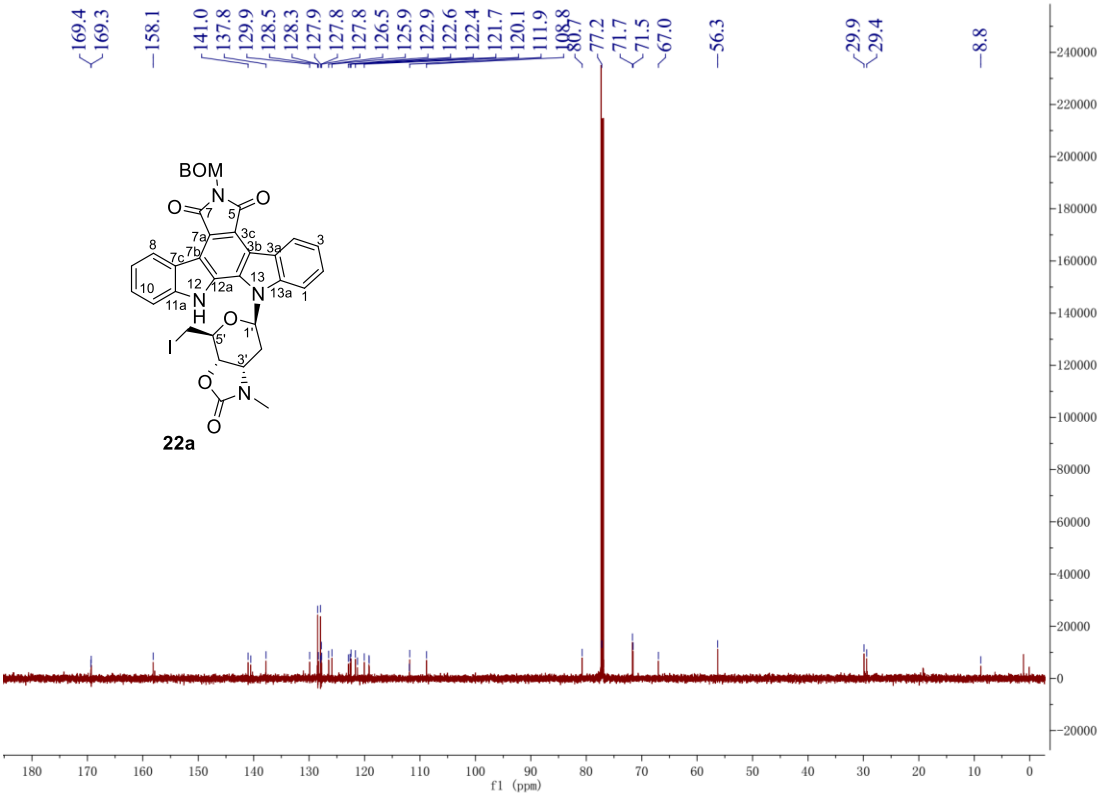

BOM
HO
21a
f1 (ppm)

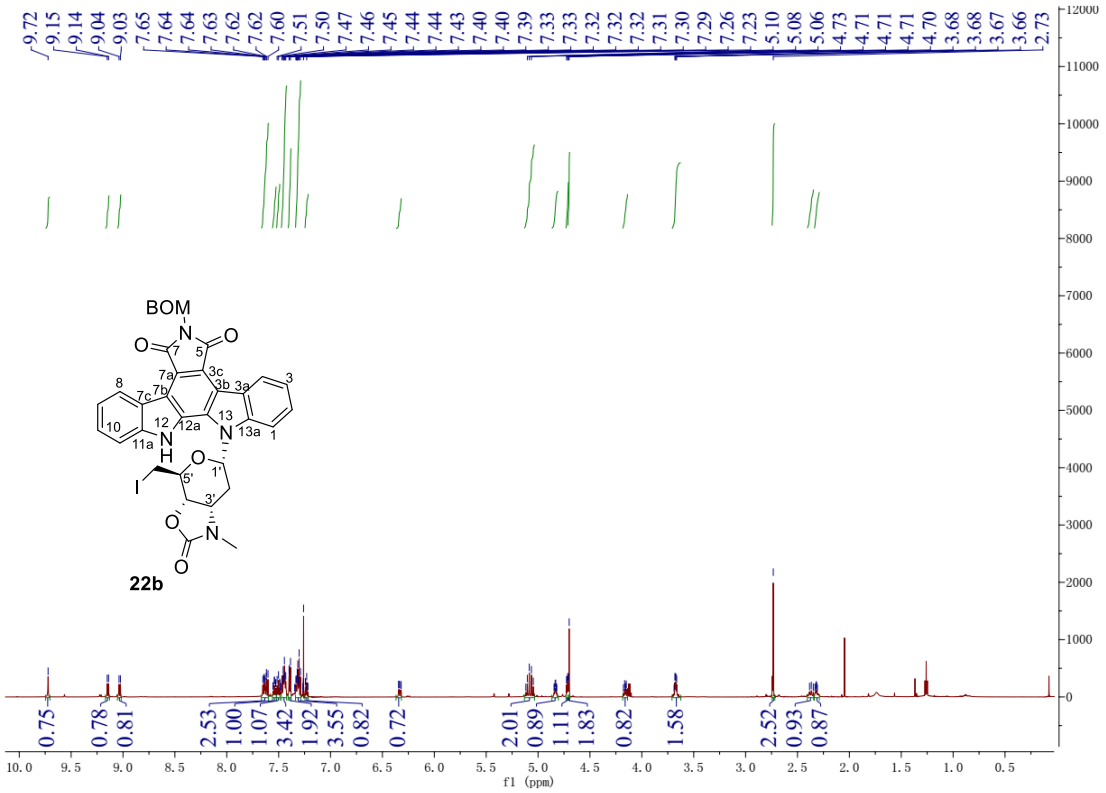

BOM
HO
21a
f1 (ppm)

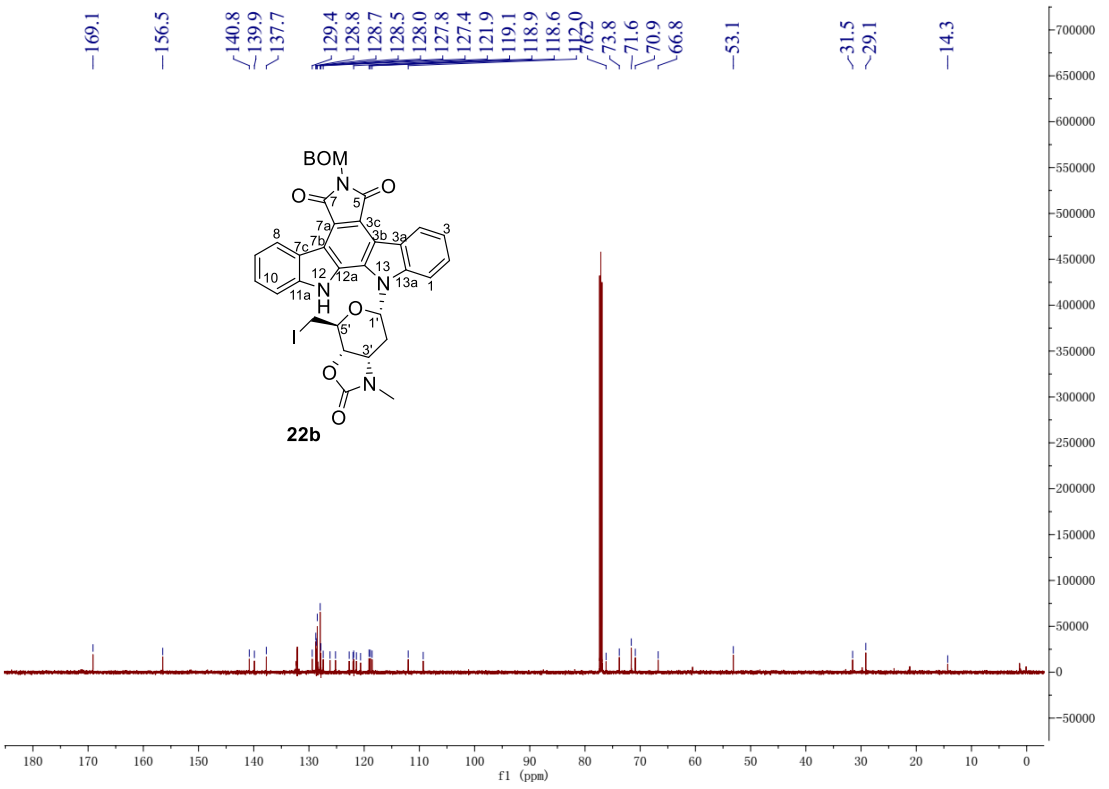

BOM
HO
21b
f1 (ppm)

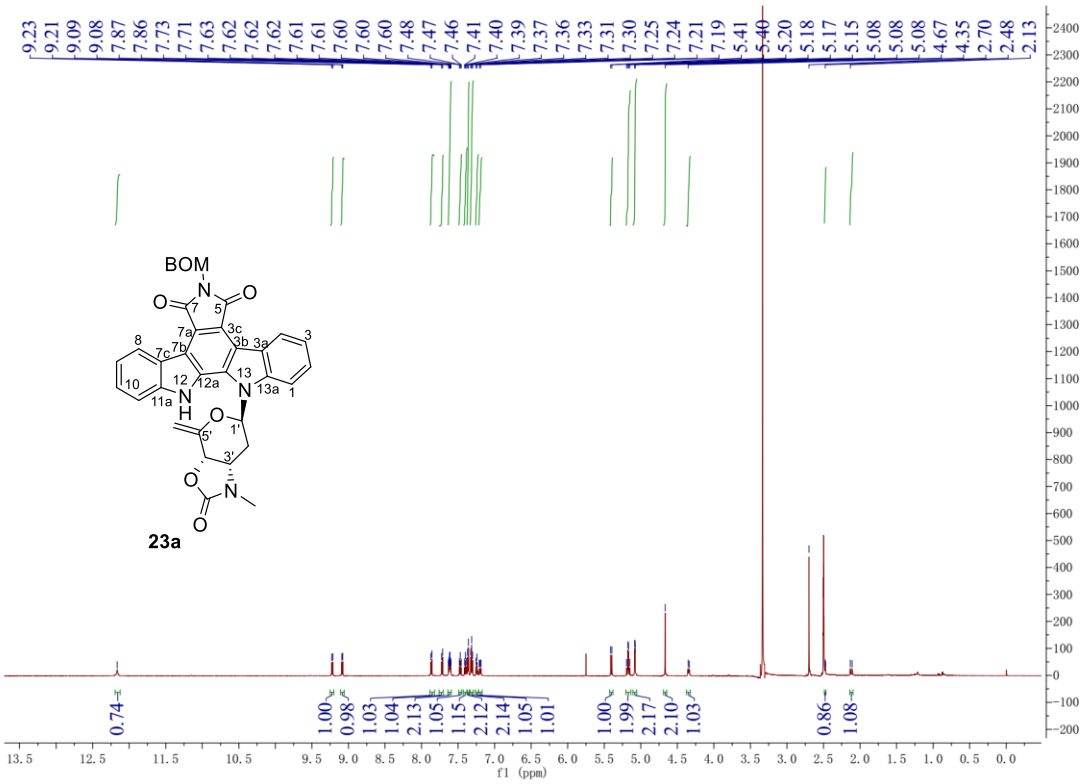

BOM
HO
21b
f1 (ppm)

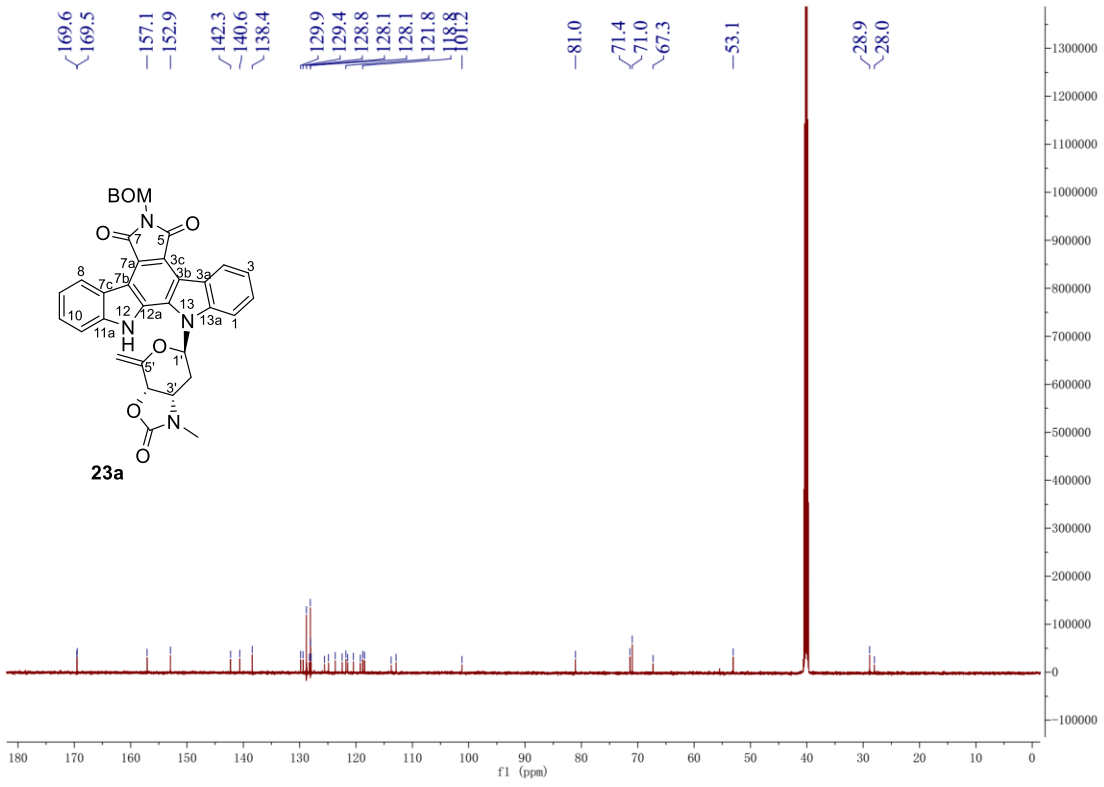

10.24
9.30
9.30
9.29
9.29
9.24
9.23
9.22
7.75
7.73
7.73
7.73
7.61
7.60
7.60
7.55
7.54
7.53
7.53
7.50
7.48
7.44
7.44
7.43
7.43
7.42
7.41
7.40
7.40
7.40
7.33
7.32
7.30
7.26
7.26
7.23
5.32
4.94
4.93
4.92
4.77
3.87
3.86
3.86
3.85
2.90
BOM
22a
0.87
1.00
0.97
1.14
1.13
1.31
1.12
3.14
1.34
2.10
0.77
0.87
2.00
1.00
2.04
1.05
1.14
2.45
3.34
0.94
1.13
f1 (ppm)

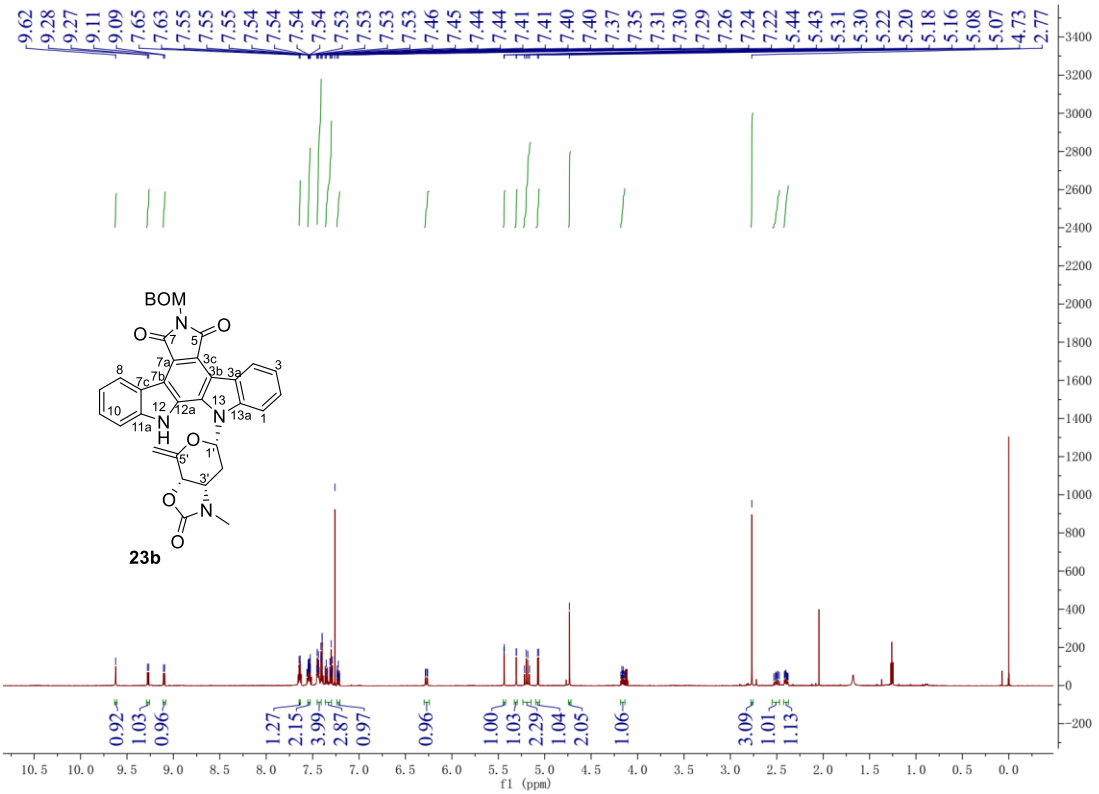

169.4
169.3
158.1
141.0
137.8
129.9
128.5
128.3
127.9
127.8
127.8
126.5
125.9
122.9
122.6
122.4
121.7
120.1
111.9
108.8
80.7
77.2
71.7
71.5
67.0
56.3
29.9
29.4
8.8
BOM
22a
f1 (ppm)

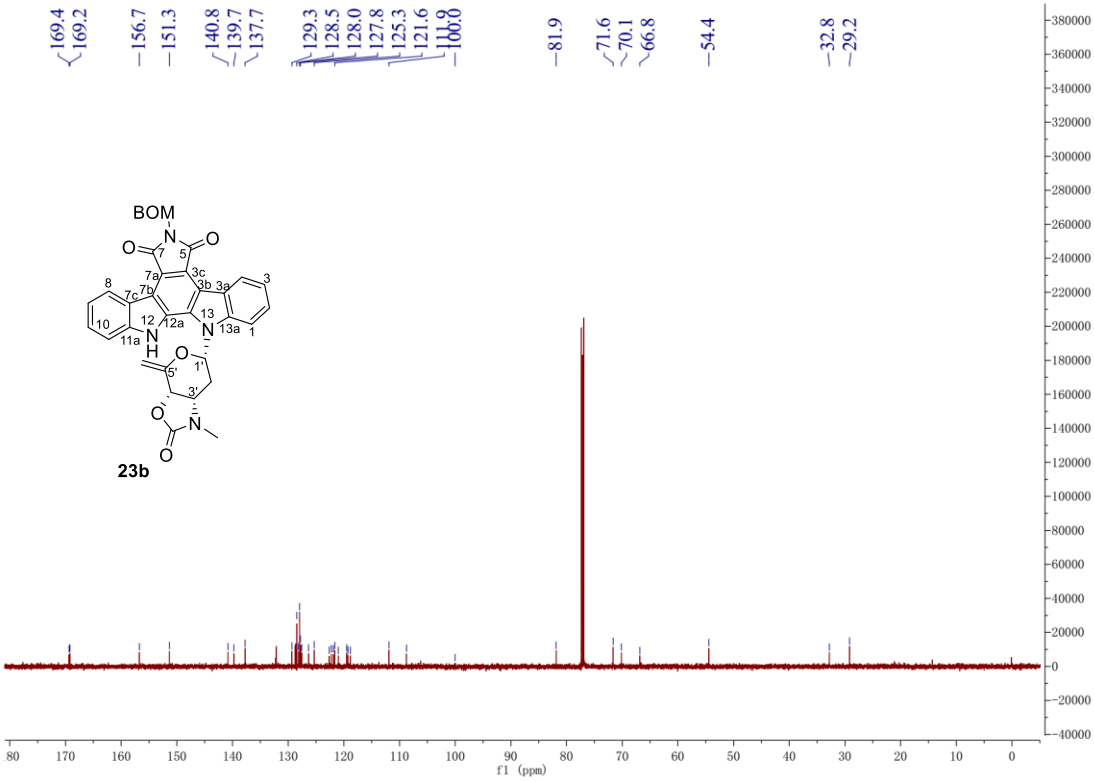

9.72
9.15
9.14
9.04
9.03
7.65
7.64
7.64
7.63
7.62
7.62
7.60
7.51
7.50
7.47
7.46
7.45
7.44
7.44
7.43
7.40
7.40
7.39
7.33
7.33
7.32
7.32
7.32
7.31
7.30
7.29
7.26
7.23
5.10
5.08
5.06
4.73
4.71
4.71
4.71
4.70
3.68
3.68
3.67
3.66
2.73
BOM
22b
0.75
0.78
0.81
2.53
1.00
1.07
3.42
1.92
3.55
0.82
0.72
2.01
0.89
1.11
1.83
0.82
1.58
2.52
0.93
0.87
f1 (ppm)

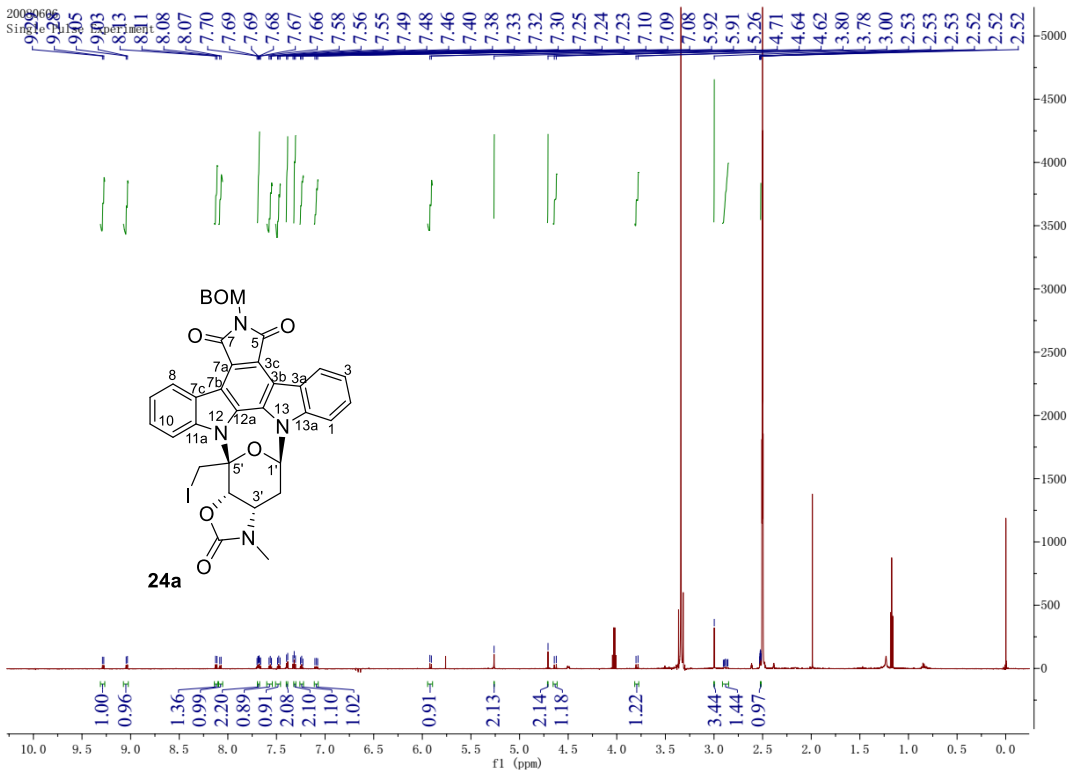

169.1
156.5
140.8
139.9
137.7
129.4
128.8
128.7
128.5
128.0
127.8
127.4
121.9
119.1
118.9
118.6
112.0
76.2
73.8
71.6
70.9
66.8
53.1
31.5
29.1
14.3
BOM
22b
f1 (ppm)

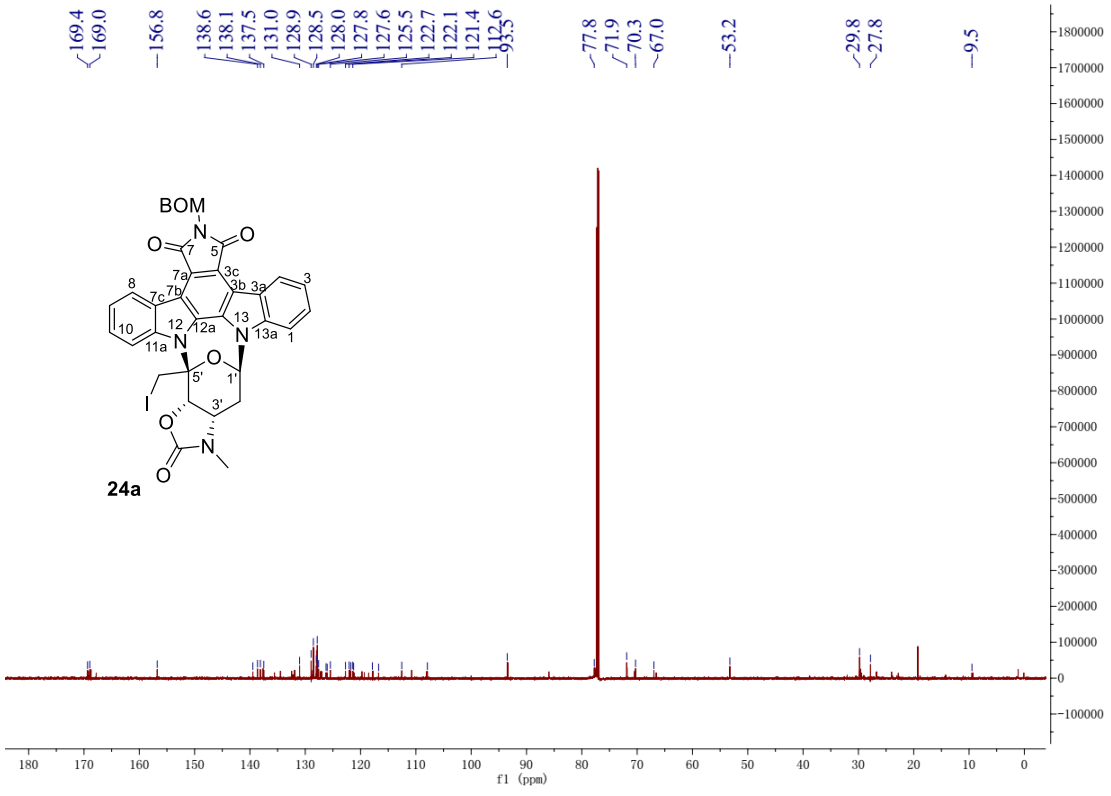

BOM
23a
f1 (ppm)

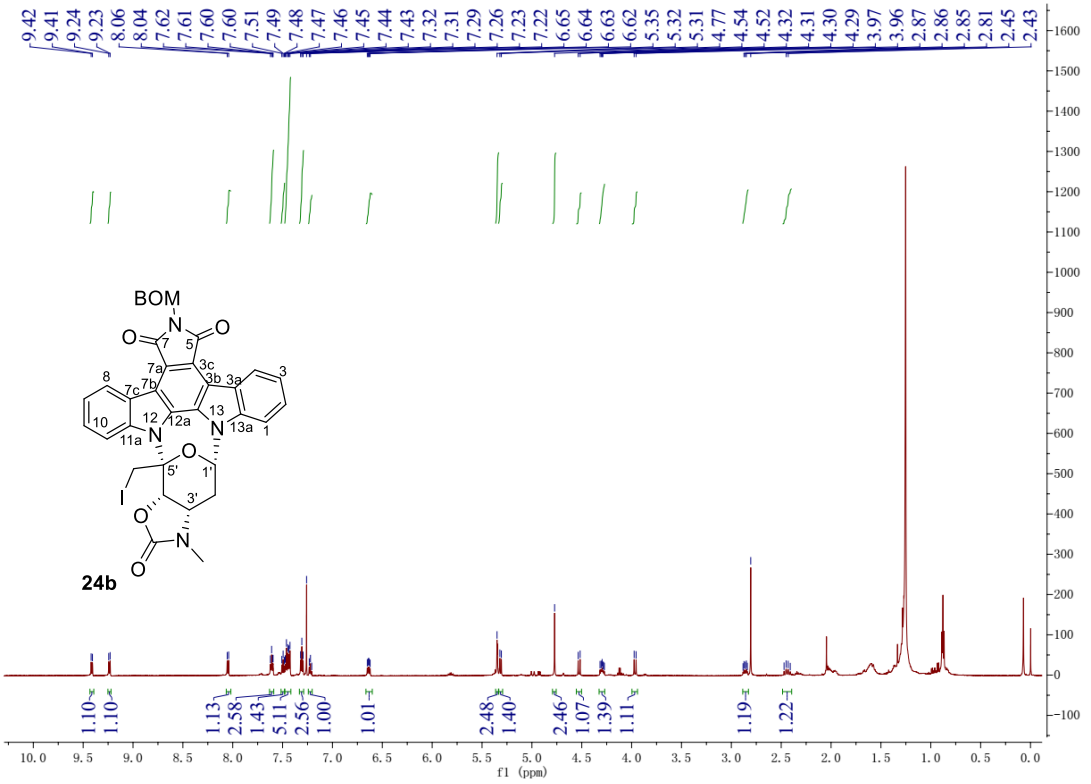

BOM
23a
f1 (ppm)

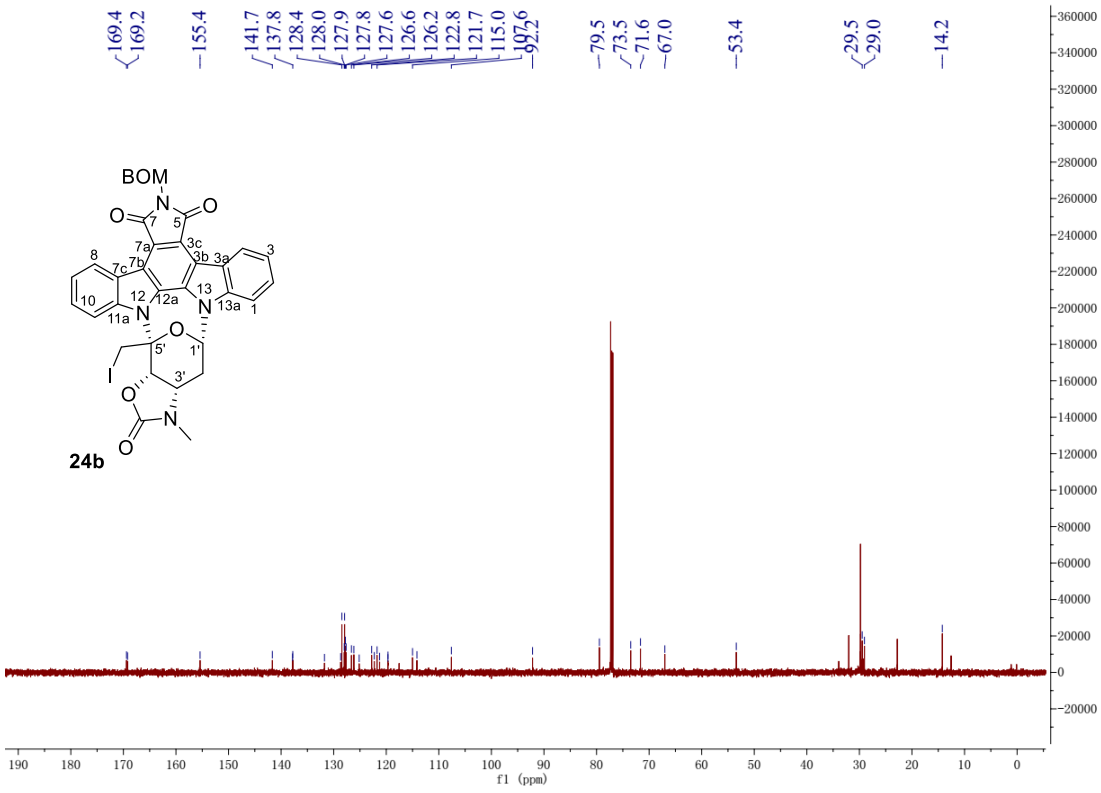

9.62 9.28 9.27 9.11 9.09 7.65 7.63 7.55 7.55 7.55 7.54 7.54 7.54 7.54 7.53 7.53 7.53 7.53 7.46 7.45 7.44 7.44 7.41 7.41 7.40 7.40 7.37 7.35 7.31 7.30 7.29 7.26 7.24 7.22 5.44 5.43 5.31 5.30 5.22 5.20 5.18 5.16 5.08 5.07 4.73 2.77
BOM
23b
0.92 1.03 0.96 1.27 2.15 3.99 2.87 0.97 0.96 1.00 1.03 2.29 1.04 2.05 1.06 3.09 1.01 1.13
f1 (ppm)

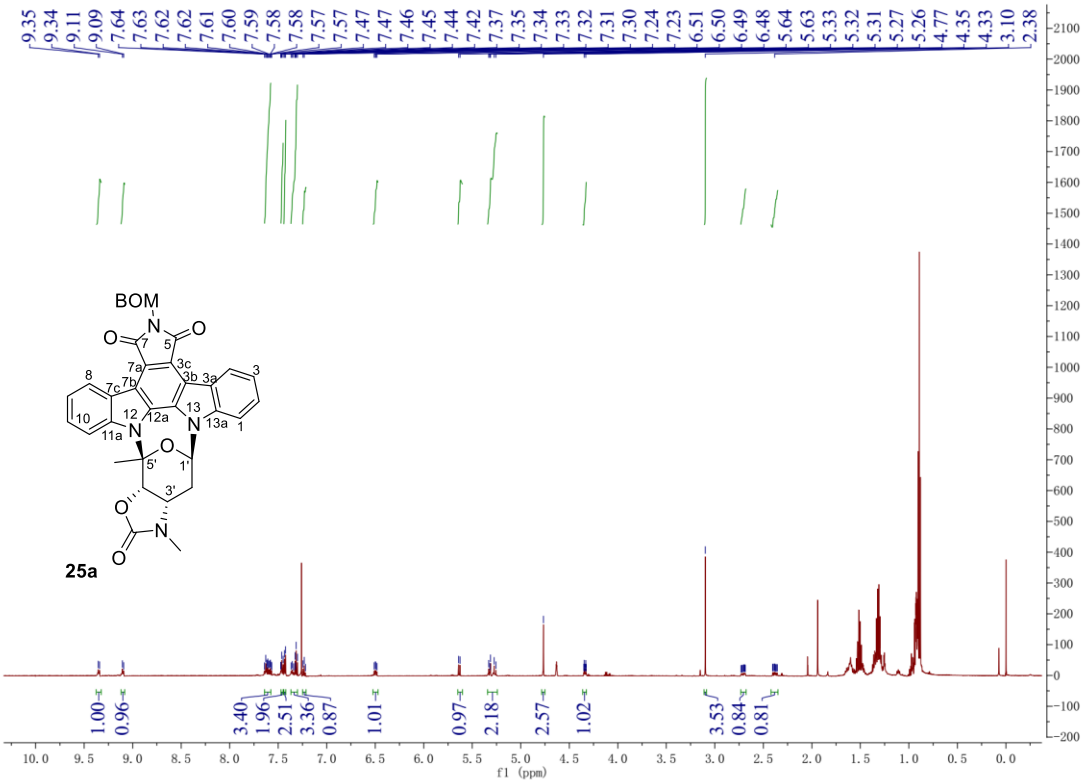

169.4 169.2 156.7 151.3 140.8 139.7 137.7 129.3 128.5 128.0 127.8 125.3 121.6 111.9 100.0 81.9 71.6 70.1 66.8 54.4 32.8 29.2
BOM
23b
f1 (ppm)

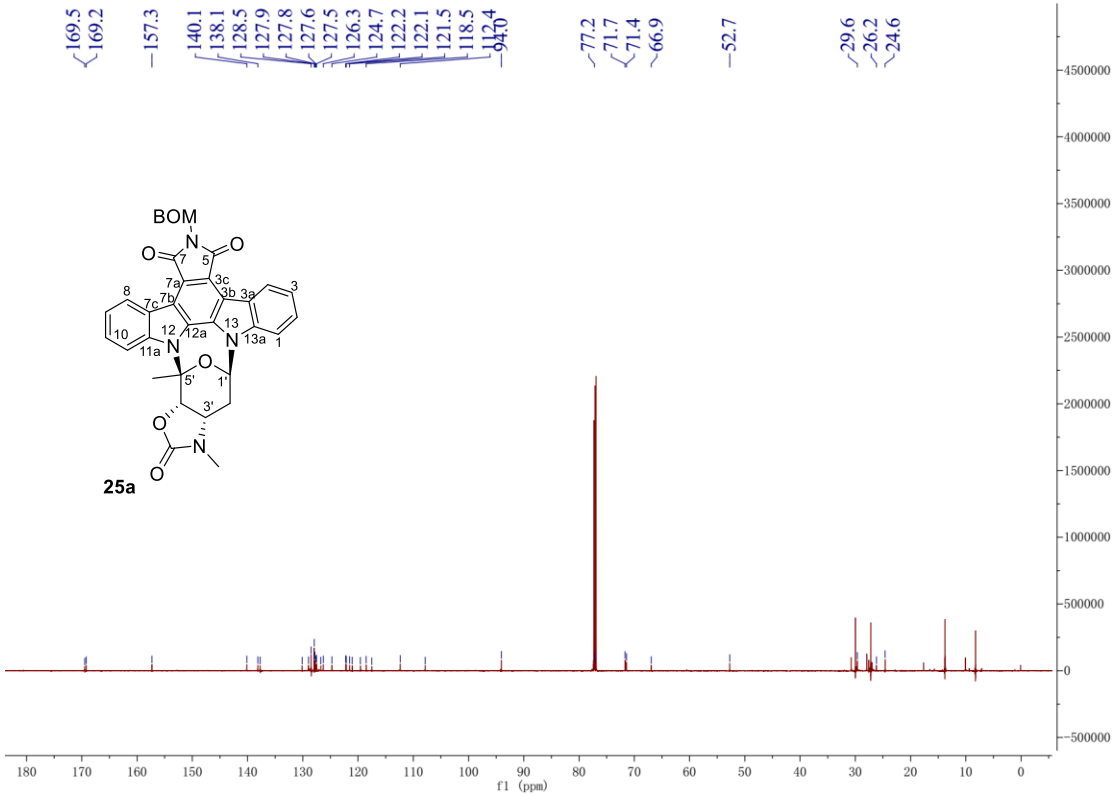

20080606
Single Pulse Experiment
9.26
9.05
9.03
8.13
8.11
8.08
8.07
7.70
7.69
7.69
7.68
7.67
7.66
7.58
7.56
7.55
7.49
7.48
7.46
7.40
7.38
7.33
7.32
7.30
7.25
7.24
7.23
7.10
7.09
7.08
5.92
5.91
5.26
4.71
4.64
4.62
3.80
3.78
3.00
2.53
2.53
2.53
2.52
2.52
2.52
BOM
24a
1.00
0.96
1.36
0.99
2.20
0.89
0.91
2.08
2.10
1.10
1.02
0.91
2.13
2.14
1.18
1.22
3.44
1.44
0.97
f1 (ppm)

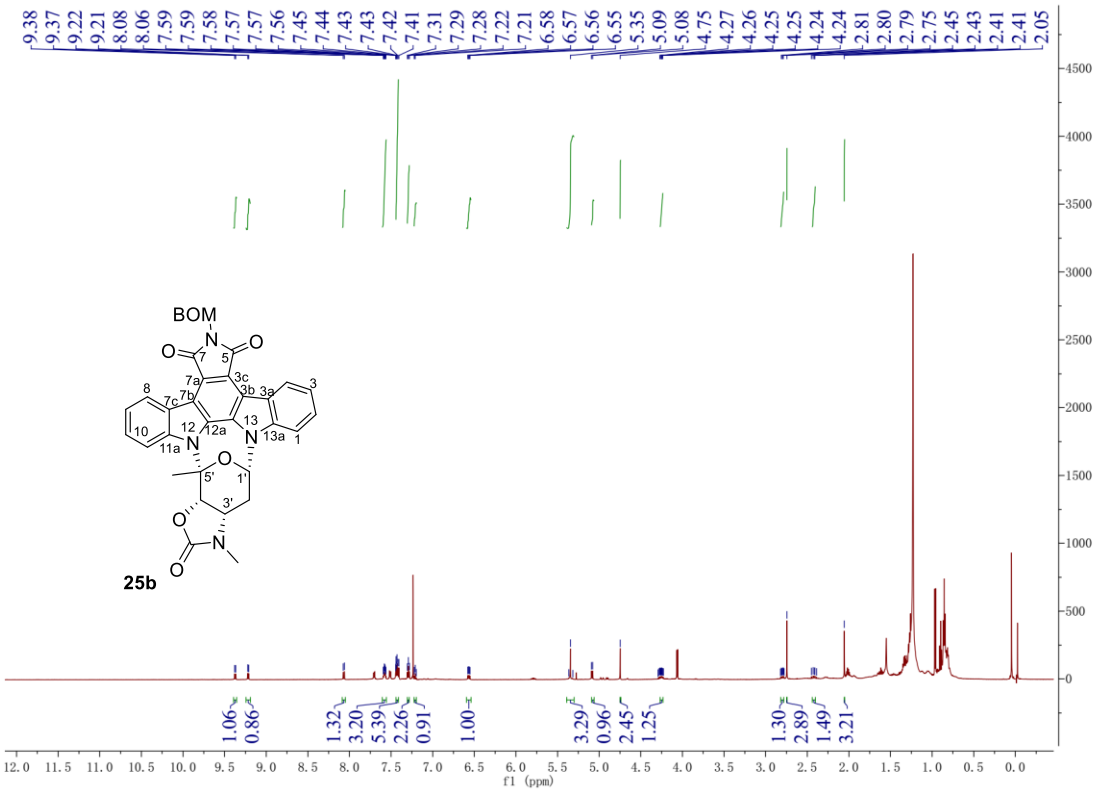

169.4
169.0
156.8
138.6
138.1
137.5
131.0
128.9
128.5
128.0
127.8
127.6
125.5
122.7
122.1
121.4
112.6
93.5
77.8
71.9
70.3
67.0
53.2
29.8
27.8
9.5
BOM
24a
f1 (ppm)

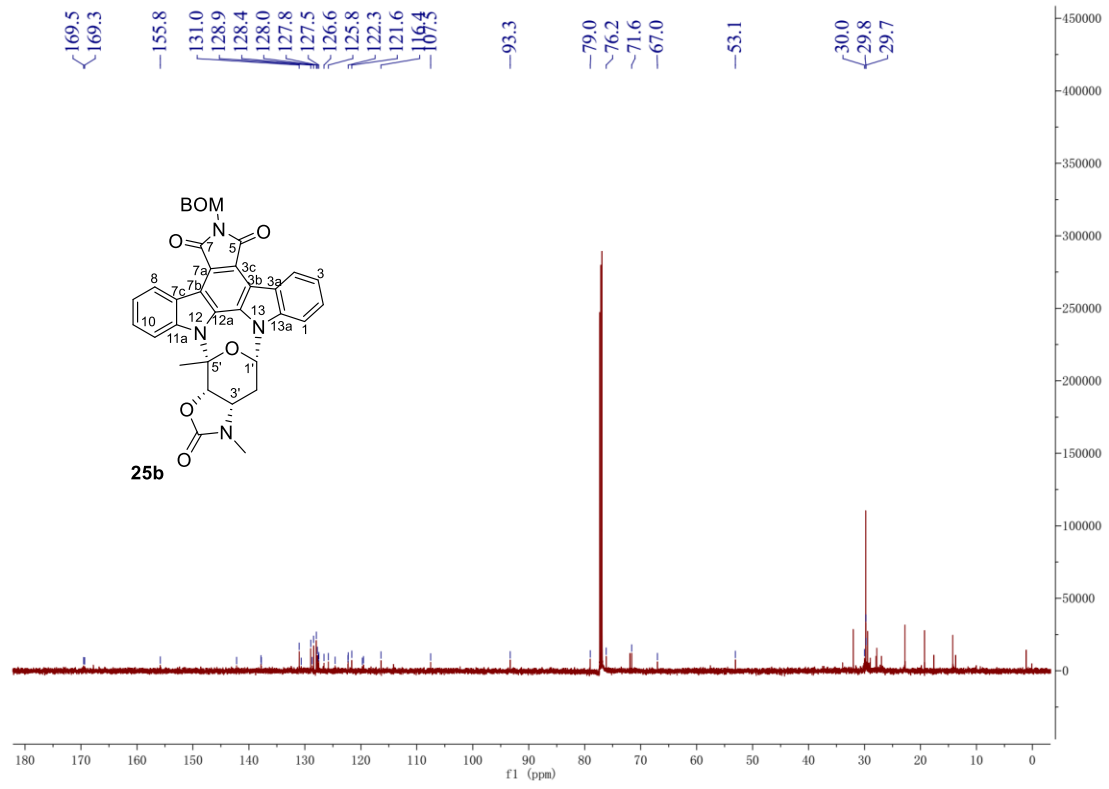

9.42 9.41 9.24 9.23 8.06 8.04 7.62 7.61 7.60 7.60 7.51 7.49 7.48 7.47 7.46 7.45 7.44 7.43 7.32 7.31 7.29 7.26 7.23 7.22 6.65 6.64 6.63 6.62 5.35 5.32 5.31 4.77 4.54 4.52 4.32 4.31 4.30 4.29 3.97 3.96 2.87 2.86 2.85 2.81 2.45 2.43
BOM
24b
1.10 1.10 1.13 2.58 1.43 5.11 2.56 1.00 1.01 2.48 1.40 2.46 1.07 1.39 1.11 1.19 1.22
f1 (ppm)

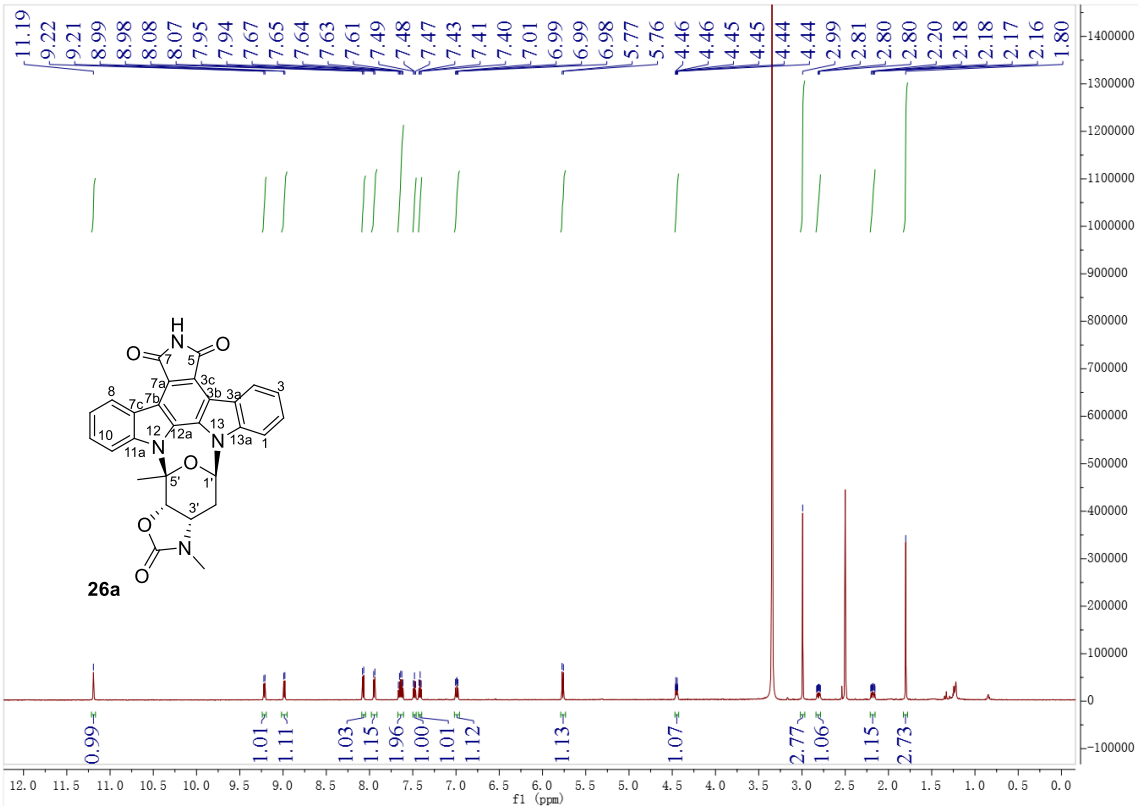

169.4 169.2 155.4 141.7 137.8 128.4 128.0 127.9 127.8 127.6 126.6 126.2 122.8 121.7 115.0 107.6 92.2 79.5 73.5 71.6 67.0 53.4 29.5 29.0 14.2
BOM
24b
f1 (ppm)


9.35
9.34
9.11
9.09
7.64
7.63
7.62
7.62
7.61
7.60
7.59
7.58
7.58
7.57
7.57
7.47
7.47
7.46
7.45
7.44
7.42
7.37
7.35
7.34
7.33
7.32
7.31
7.30
7.24
7.23
6.51
6.50
6.49
6.48
5.64
5.63
5.33
5.32
5.31
5.27
5.26
4.77
4.35
4.33
3.10
2.38
BOM
25a
1.00
0.96
3.40
1.96
2.51
3.36
0.87
1.01
0.97
2.18
2.57
1.02
3.53
0.84
0.81
f1 (ppm)

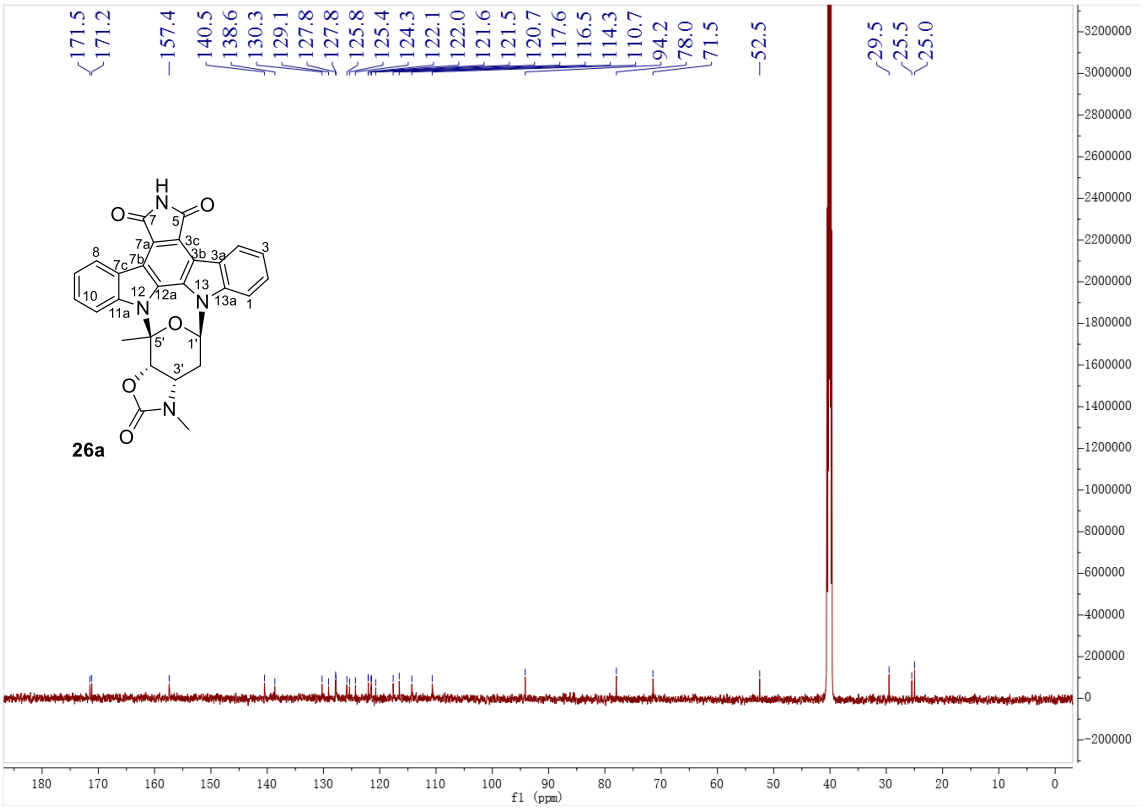

169.5
169.2
157.3
140.1
138.1
128.5
127.9
127.8
127.6
127.5
126.3
124.7
122.2
122.1
121.5
118.5
112.4
94.0
77.2
71.7
71.4
66.9
52.7
29.6
26.2
24.6
BOM
25a
f1 (ppm)


9.38
9.37
9.22
9.21
8.08
8.06
7.59
7.59
7.58
7.57
7.57
7.56
7.45
7.44
7.43
7.43
7.42
7.41
7.31
7.29
7.28
7.22
7.21
6.58
6.57
6.56
6.55
5.35
5.09
5.08
4.75
4.27
4.26
4.25
4.25
4.24
4.24
2.81
2.80
2.79
2.75
2.45
2.43
2.41
2.41
2.05
BOM
25b
1.06
0.86
1.32
3.20
5.39
2.26
0.91
1.00
3.29
0.96
2.45
1.25
1.30
2.89
1.49
3.21
f1 (ppm)

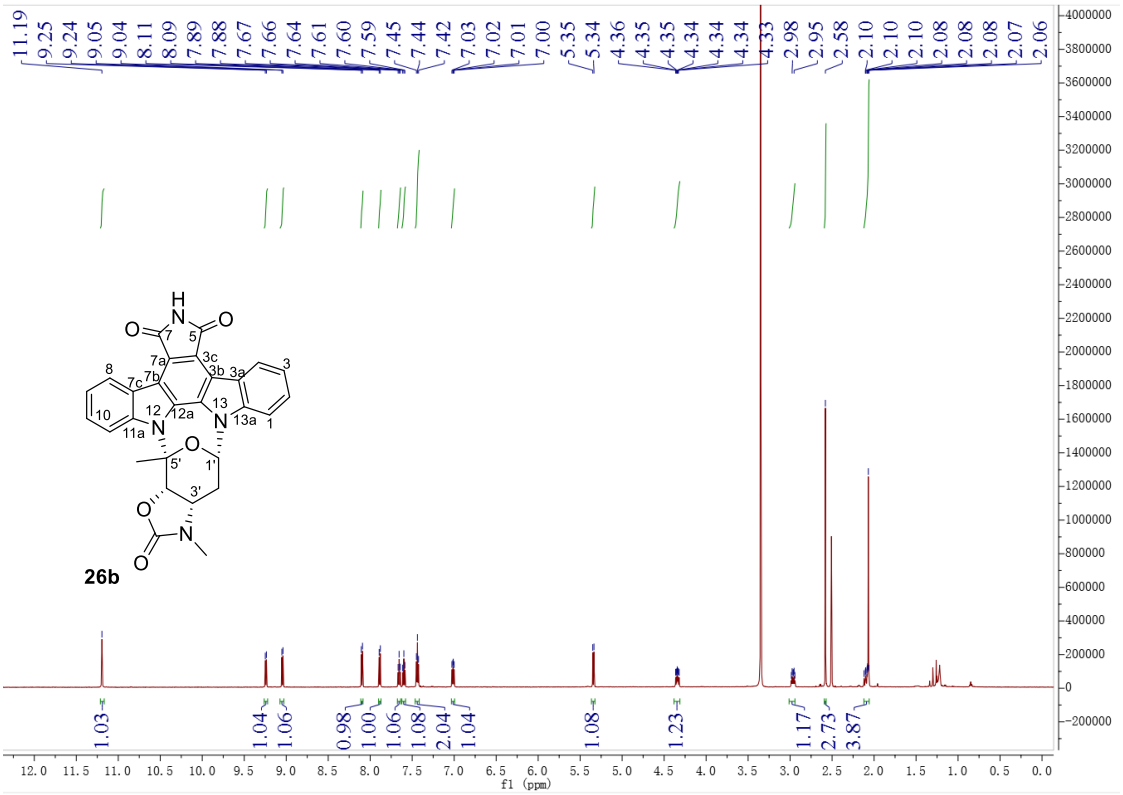

169.5
169.3
155.8
131.0
128.9
128.4
128.0
127.8
127.5
126.6
125.8
122.3
121.6
93.3
79.0
76.2
71.6
67.0
53.1
30.0
29.8
29.7
BOM
25b
f1 (ppm)

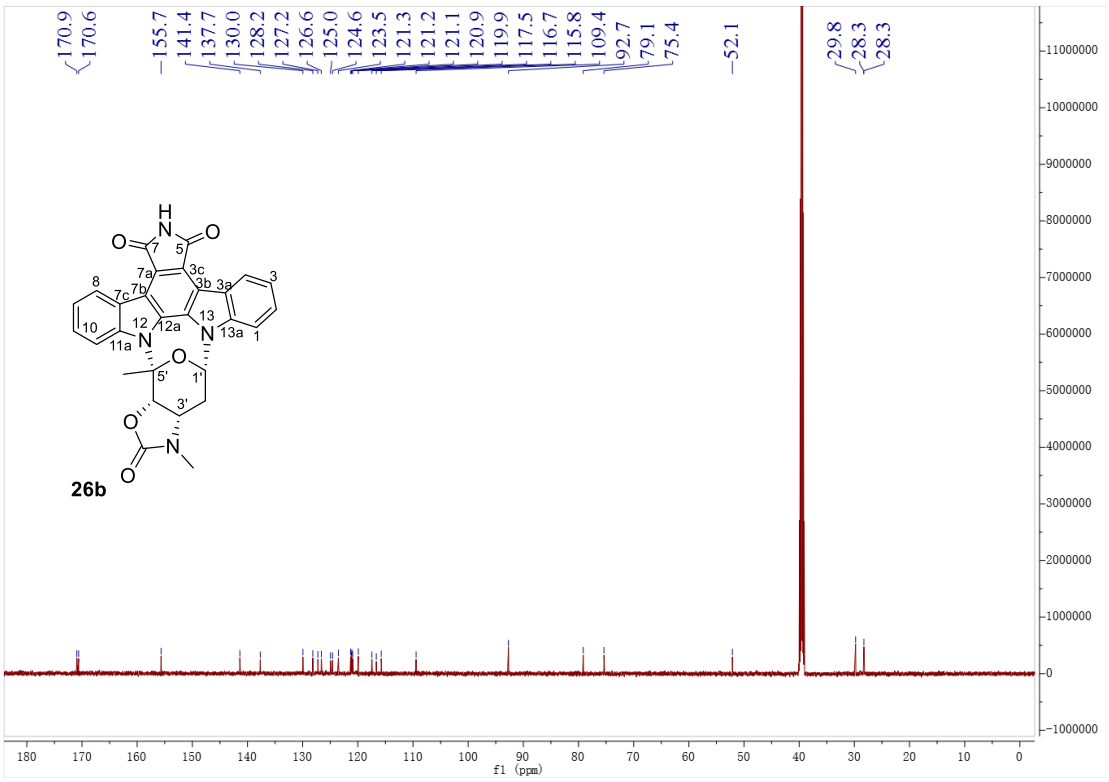

11.19
9.22
9.21
8.99
8.98
8.08
8.07
7.95
7.94
7.67
7.65
7.64
7.63
7.61
7.49
7.48
7.47
7.43
7.41
7.40
7.01
6.99
6.99
6.98
5.77
5.76
4.46
4.46
4.45
4.45
4.44
4.44
2.99
2.81
2.80
2.80
2.20
2.18
2.18
2.17
2.16
1.80
0.99
1.01
1.11
1.03
1.15
1.96
1.00
1.01
1.12
1.13
1.07
2.77
1.06
1.15
2.73
f1 (ppm)

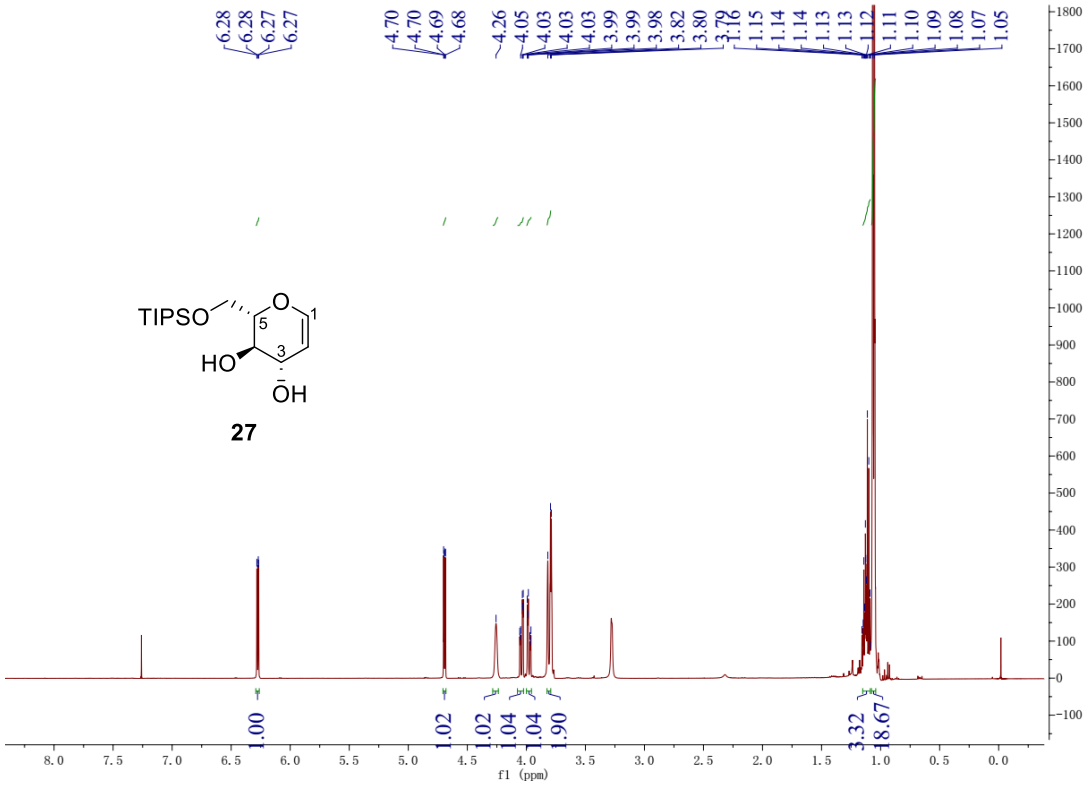
26a

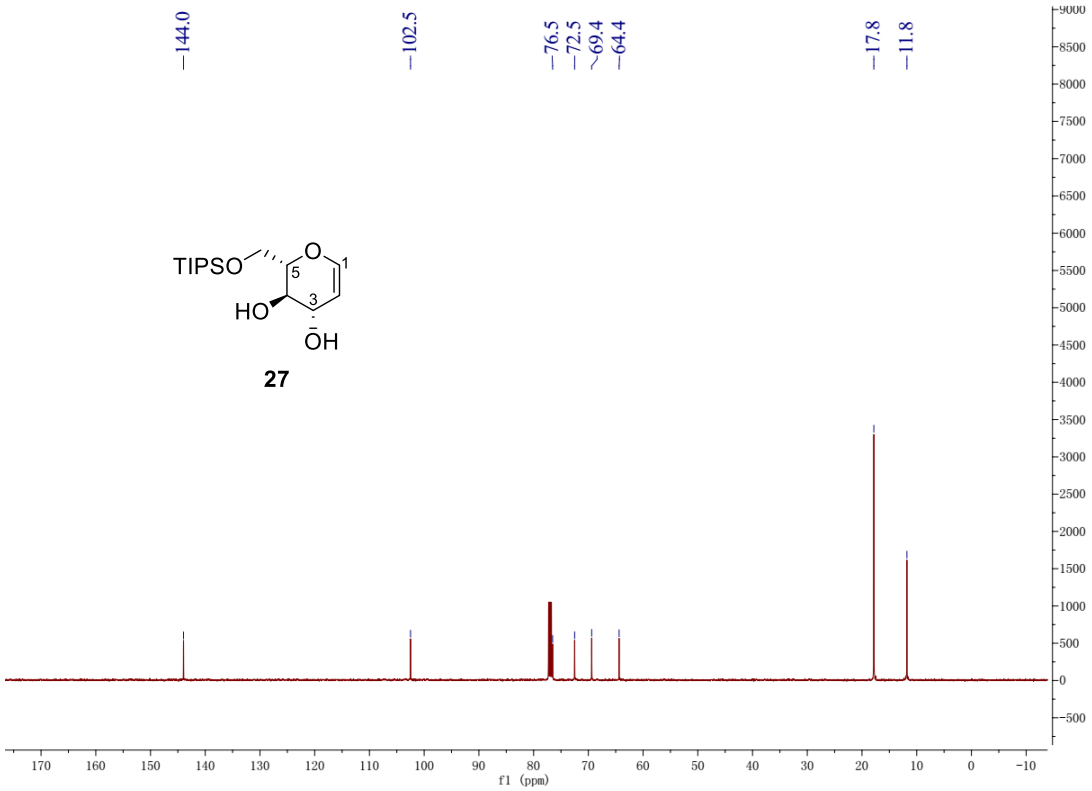

171.5
171.2
157.4
140.5
138.6
130.3
129.1
127.8
127.8
125.8
125.4
124.3
122.1
122.0
121.6
121.5
120.7
117.6
116.5
114.3
110.7
94.2
78.0
71.5
52.5
29.5
25.5
25.0
f1 (ppm)

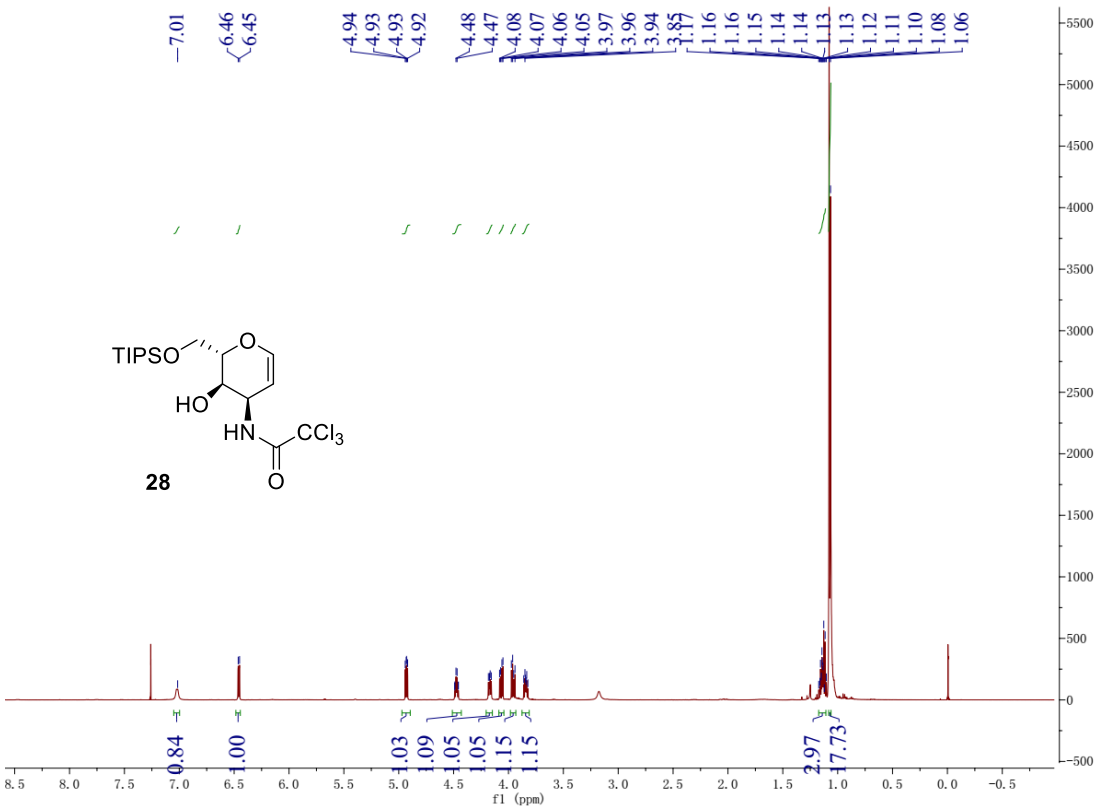
26a

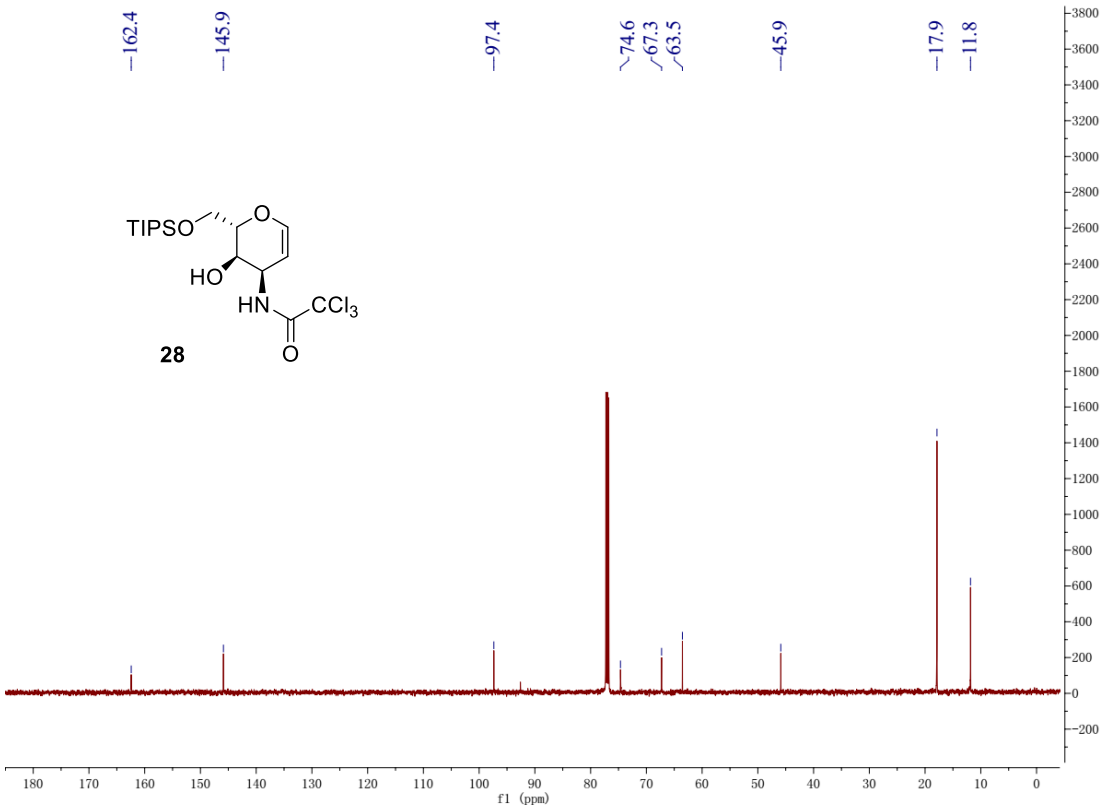

11.19
9.25
9.24
9.05
9.04
8.11
8.09
7.89
7.88
7.67
7.66
7.64
7.61
7.60
7.59
7.45
7.44
7.42
7.03
7.02
7.01
7.00
5.35
5.34
4.36
4.35
4.35
4.34
4.34
4.34
4.33
2.98
2.95
2.58
2.10
2.10
2.10
2.08
2.08
2.08
2.07
2.06
26b
1.03
1.04
1.06
0.98
1.00
1.06
1.08
2.04
1.04
1.08
1.23
1.17
2.73
3.87
f1 (ppm)

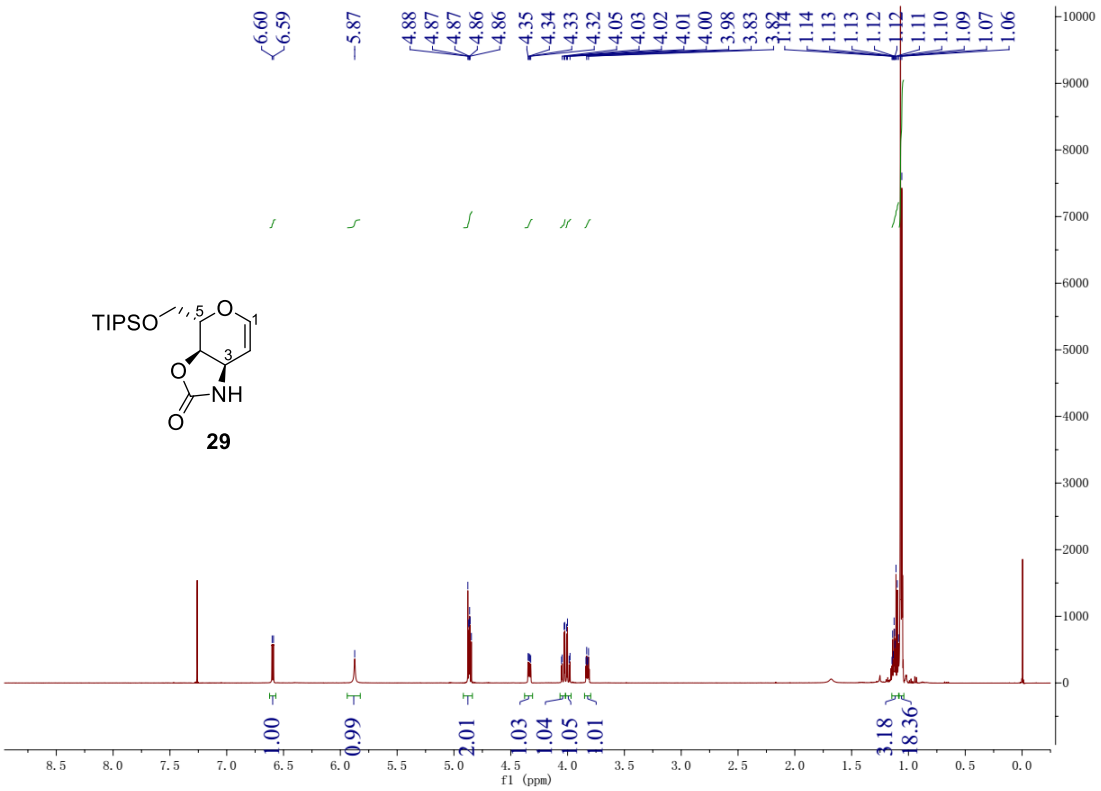

170.9
170.6
155.7
141.4
137.7
130.0
128.2
127.2
126.6
125.0
124.6
123.5
121.3
121.2
121.1
120.9
119.9
117.5
116.7
115.8
109.4
92.7
79.1
75.4
52.1
29.8
28.3
28.3
26b
f1 (ppm)

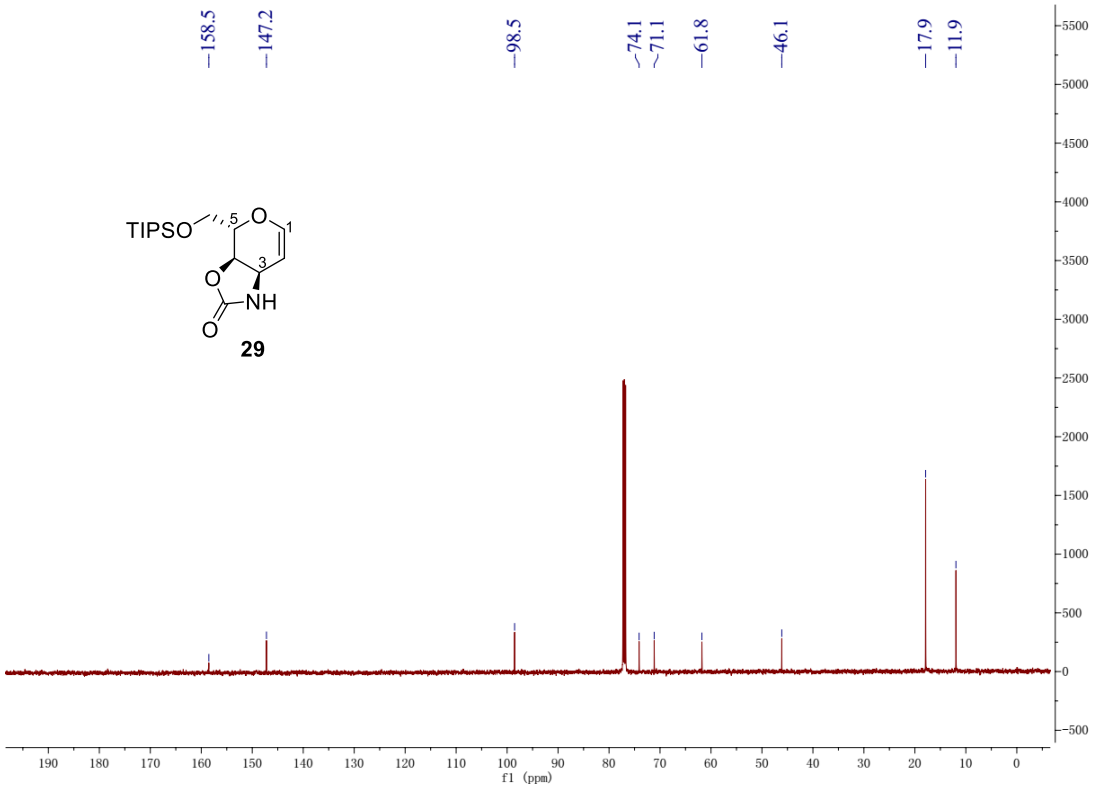

6.28
6.28
6.27
6.27
4.70
4.70
4.69
4.68
4.26
4.05
4.03
4.03
4.03
3.99
3.99
3.98
3.82
3.80
3.79
1.16
1.15
1.14
1.14
1.13
1.13
1.12
1.11
1.10
1.09
1.08
1.07
1.05
TIPSO
HO
OH
27
1.00
1.02
1.02
1.04
1.04
1.90
3.32
18.67
f1 (ppm)

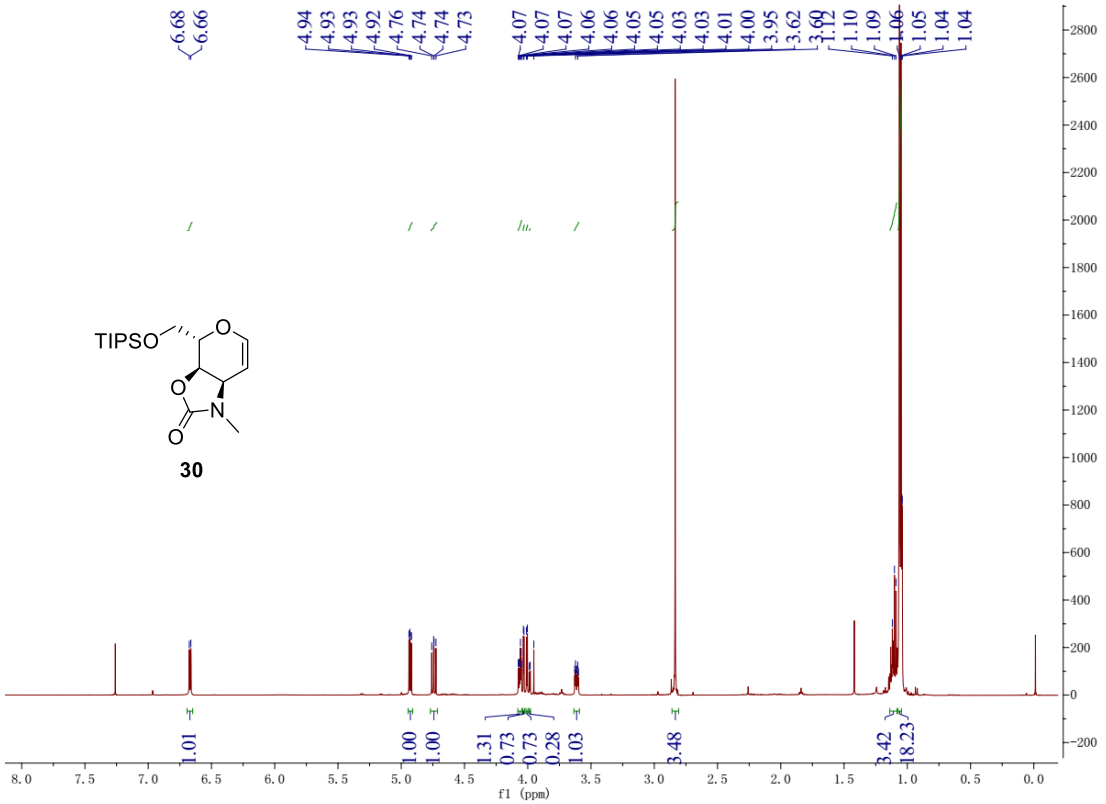

144.0
102.5
76.5
72.5
69.4
64.4
17.8
11.8
TIPSO
HO
OH
27
f1 (ppm)

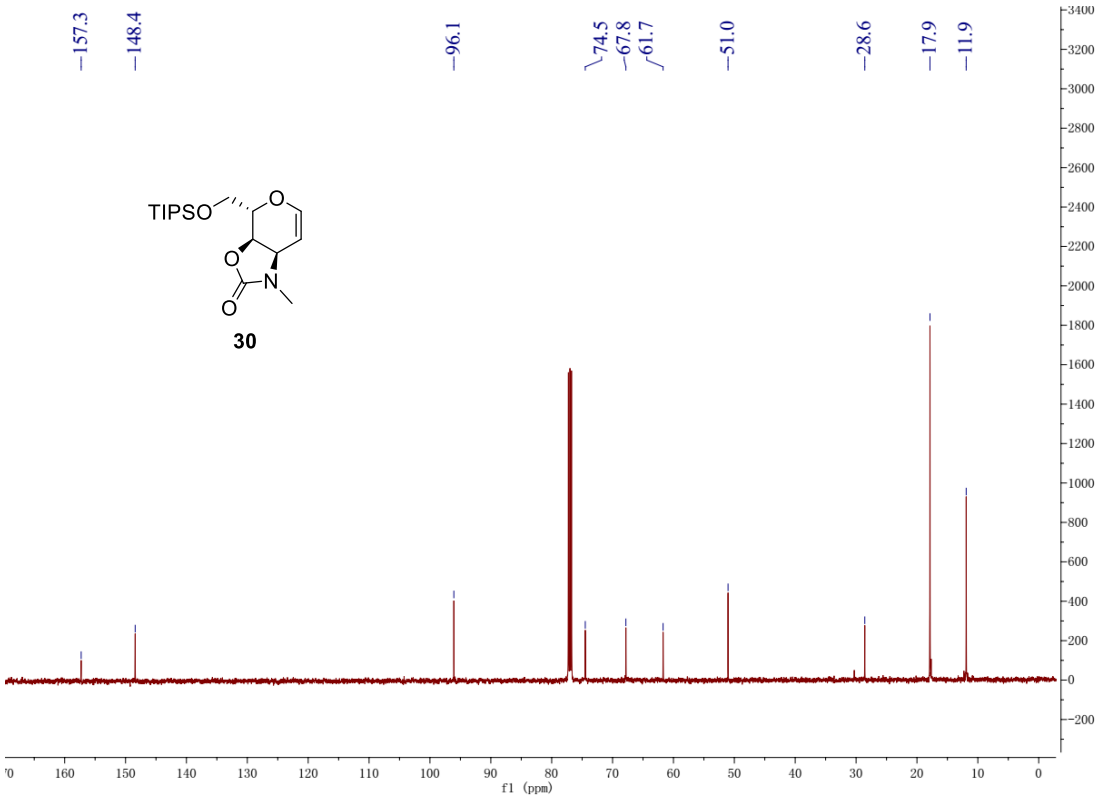

7.01
6.46
6.45
4.94
4.93
4.93
4.92
4.48
4.47
4.08
4.07
4.06
4.05
3.97
3.96
3.94
3.85
1.17
1.16
1.16
1.15
1.14
1.14
1.13
1.13
1.12
1.11
1.10
1.08
1.06
TIPSO
O
HO
HN
CCl3
O
28
0.84
1.00
1.03
1.09
1.05
1.05
1.15
1.15
2.97
17.73
f1 (ppm)

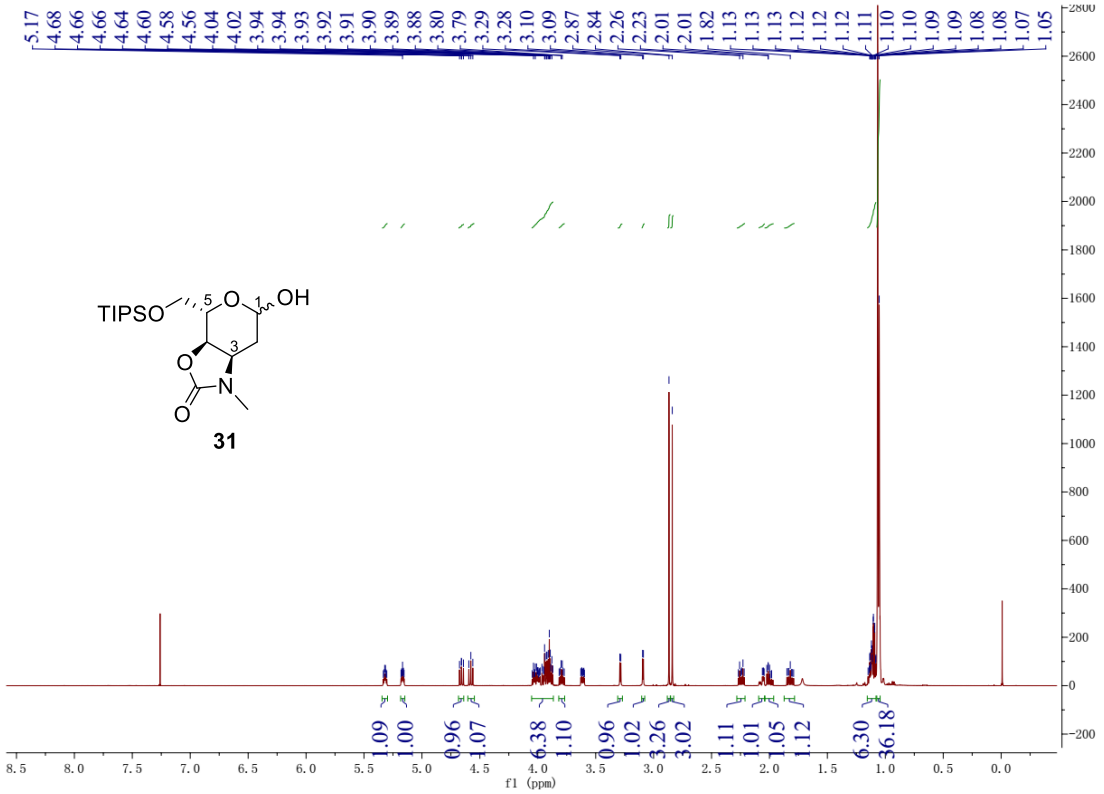

162.4
145.9
97.4
74.6
67.3
63.5
45.9
17.9
11.8
TIPSO
O
HO
HN
CCl3
O
28
f1 (ppm)

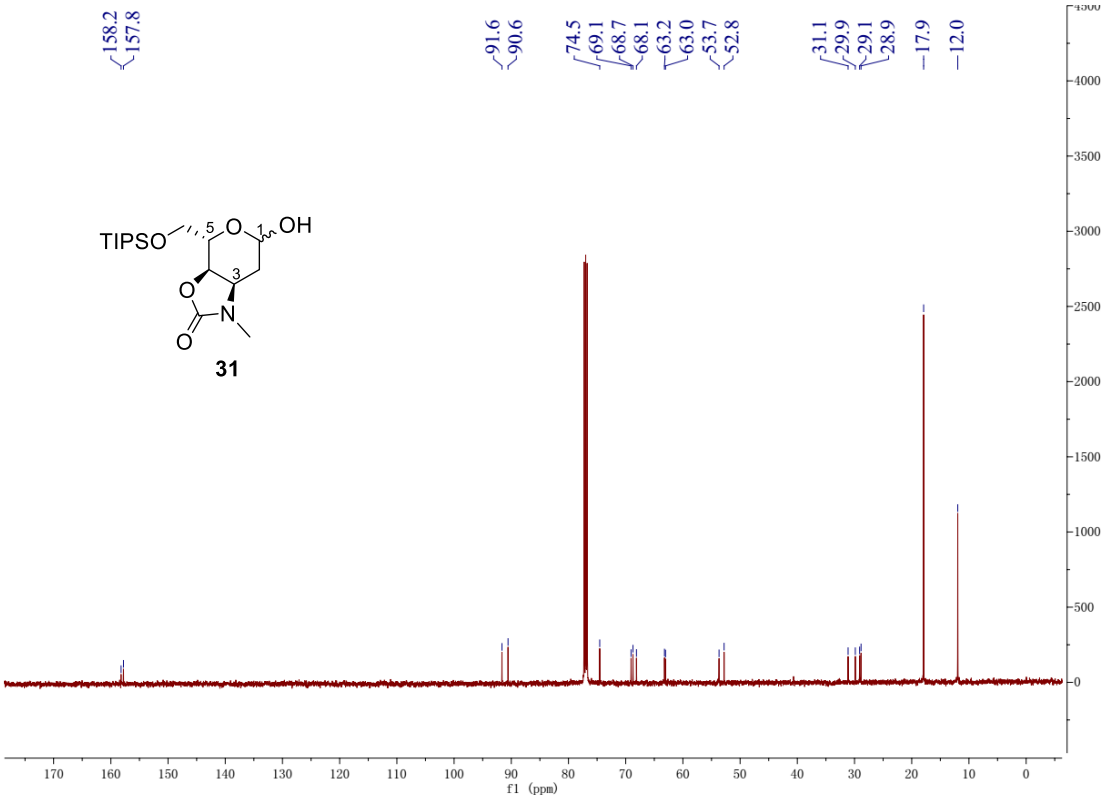

6.60
6.59
5.87
4.88
4.87
4.87
4.86
4.86
4.35
4.34
4.33
4.32
4.05
4.03
4.02
4.01
4.00
3.98
3.83
3.82
1.14
1.14
1.13
1.13
1.12
1.12
1.11
1.10
1.09
1.07
1.06
TIPSO
O
1
5
3
O
NH
O
29
1.00
0.99
2.01
1.03
1.04
1.05
1.01
3.18
18.36
f1 (ppm)

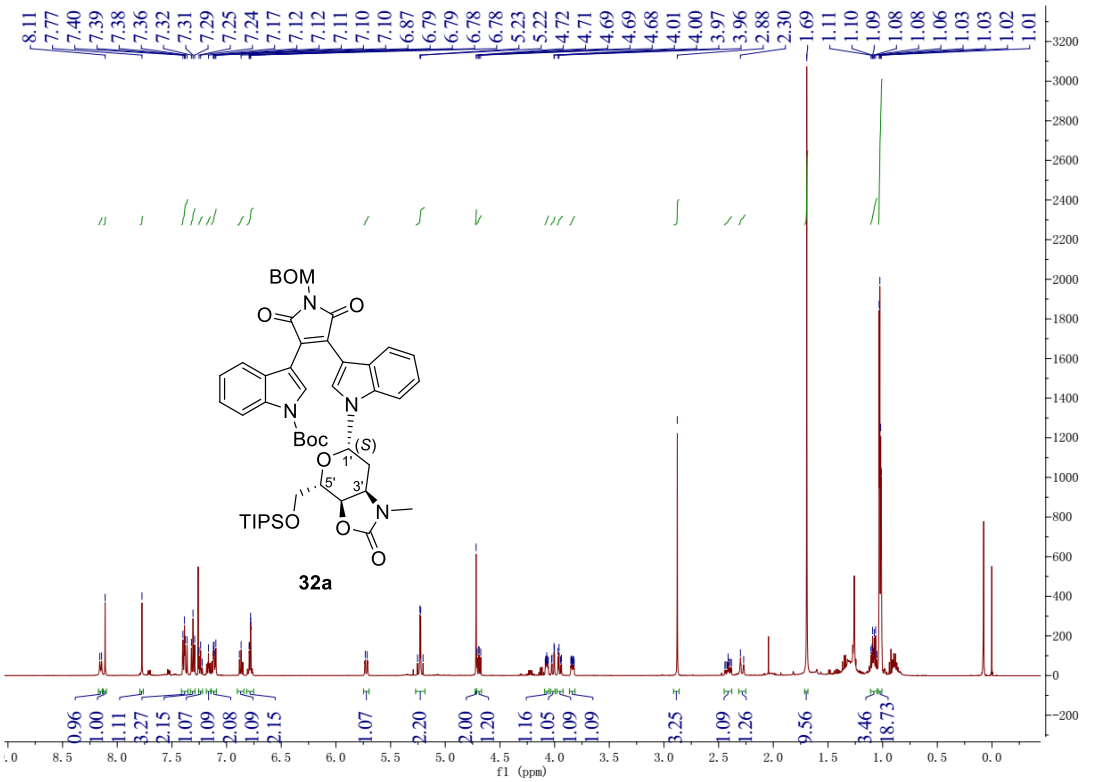

158.5
147.2
98.5
74.1
71.1
61.8
46.1
17.9
11.9
TIPSO
O
1
5
3
O
NH
O
29
f1 (ppm)

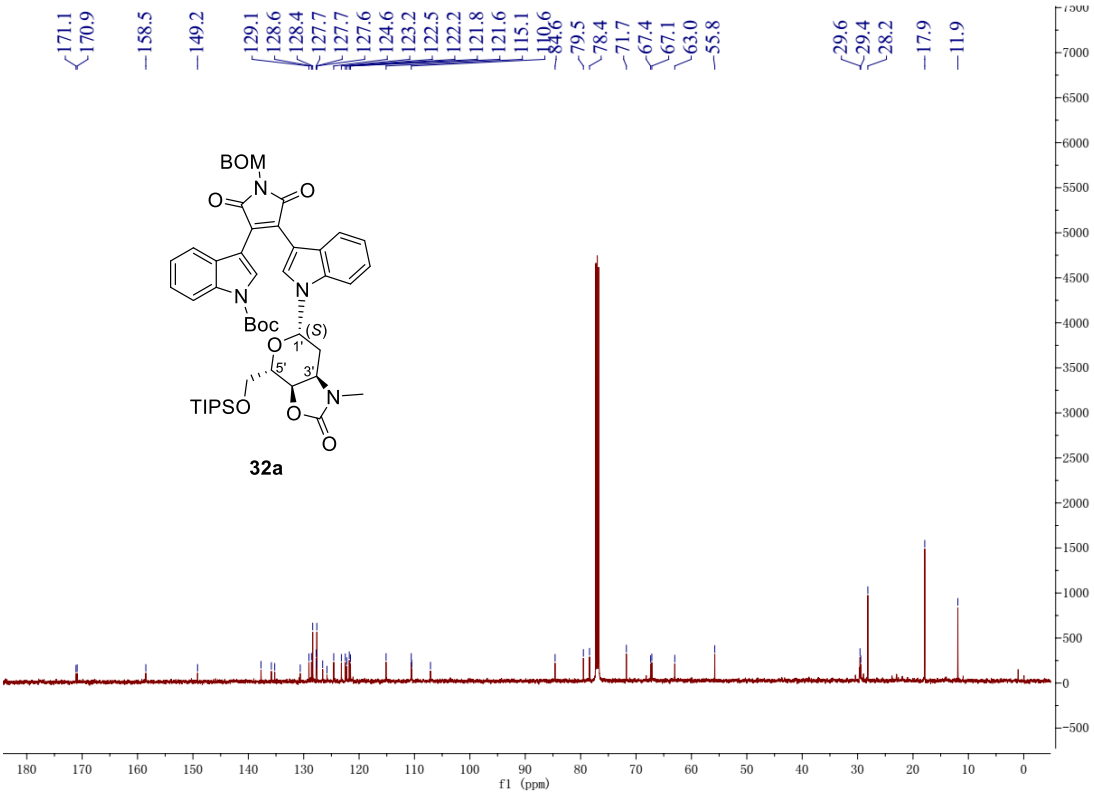

6.68
6.66
4.94
4.93
4.93
4.92
4.76
4.74
4.74
4.73
4.07
4.07
4.07
4.06
4.06
4.05
4.05
4.03
4.03
4.01
4.00
3.95
3.62
3.60
1.12
1.10
1.09
1.06
1.05
1.04
1.04
TIPSO
O
O
N
O
30
1.01
1.00
1.00
1.31
0.73
0.73
0.28
1.03
3.48
3.42
18.23
f1 (ppm)

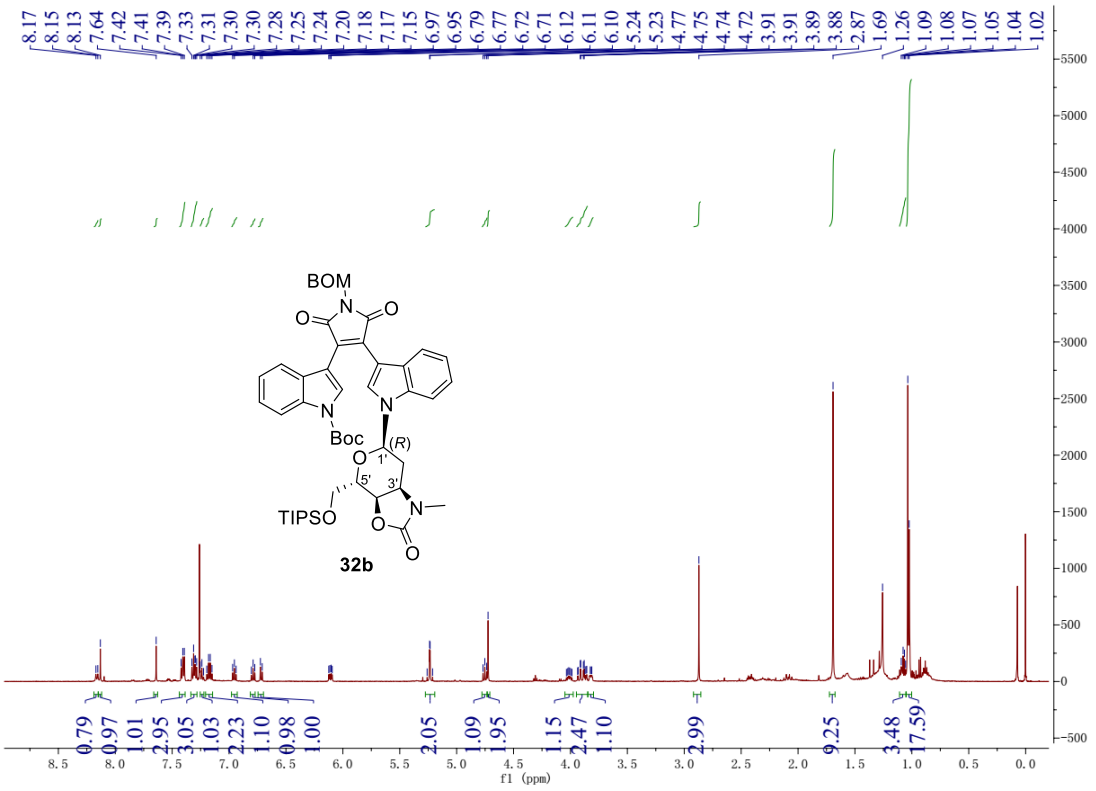

157.3
148.4
96.1
74.5
67.8
61.7
51.0
28.6
17.9
11.9
TIPSO
O
O
N
O
30
f1 (ppm)

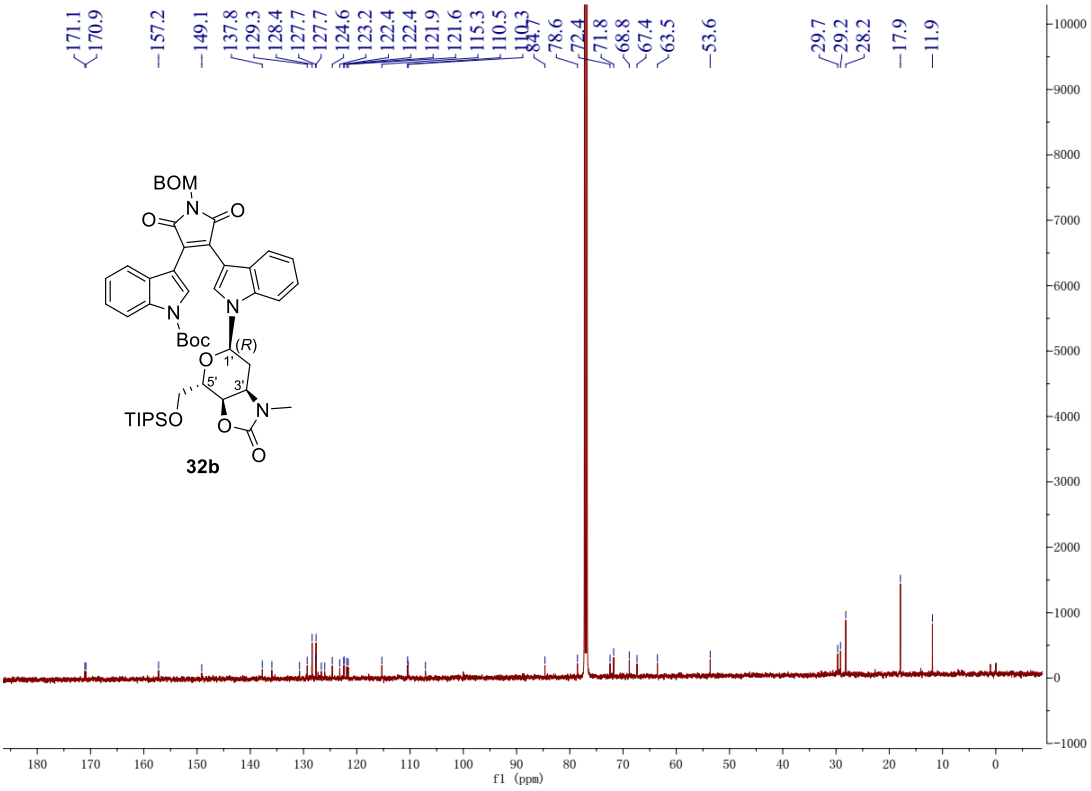

TIPSO
OH
O
N
O
5
1
3
31
f1 (ppm)

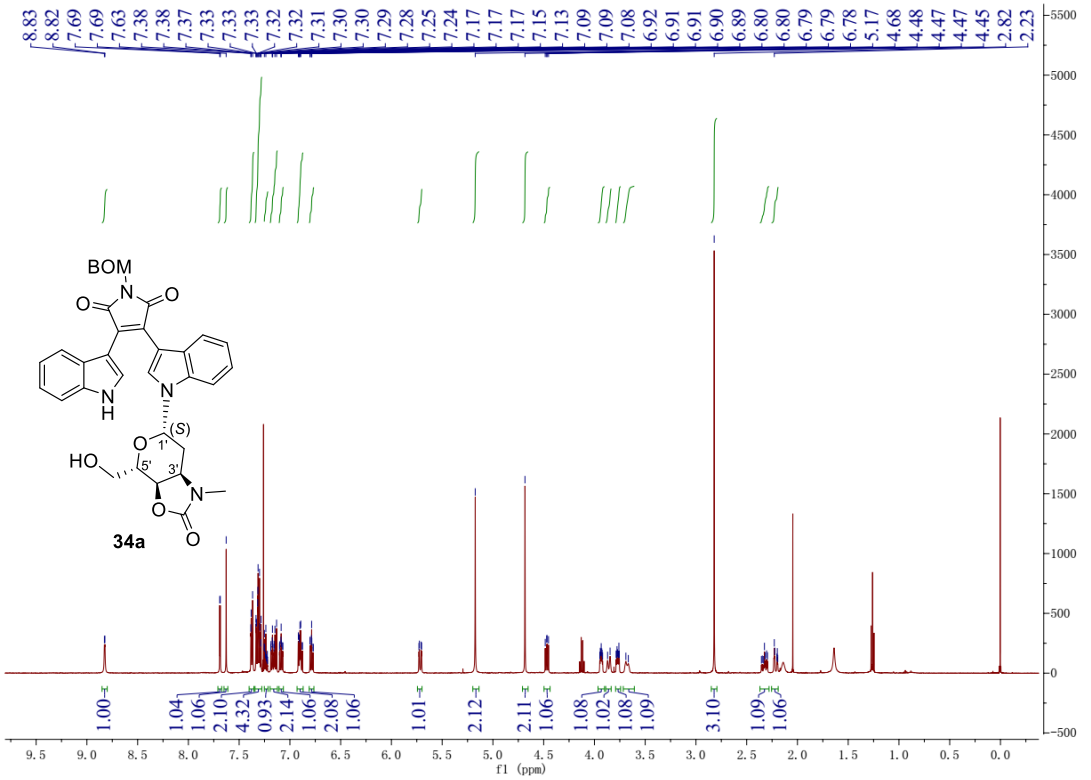

TIPSO
OH
O
N
O
5
1
3
31
f1 (ppm)

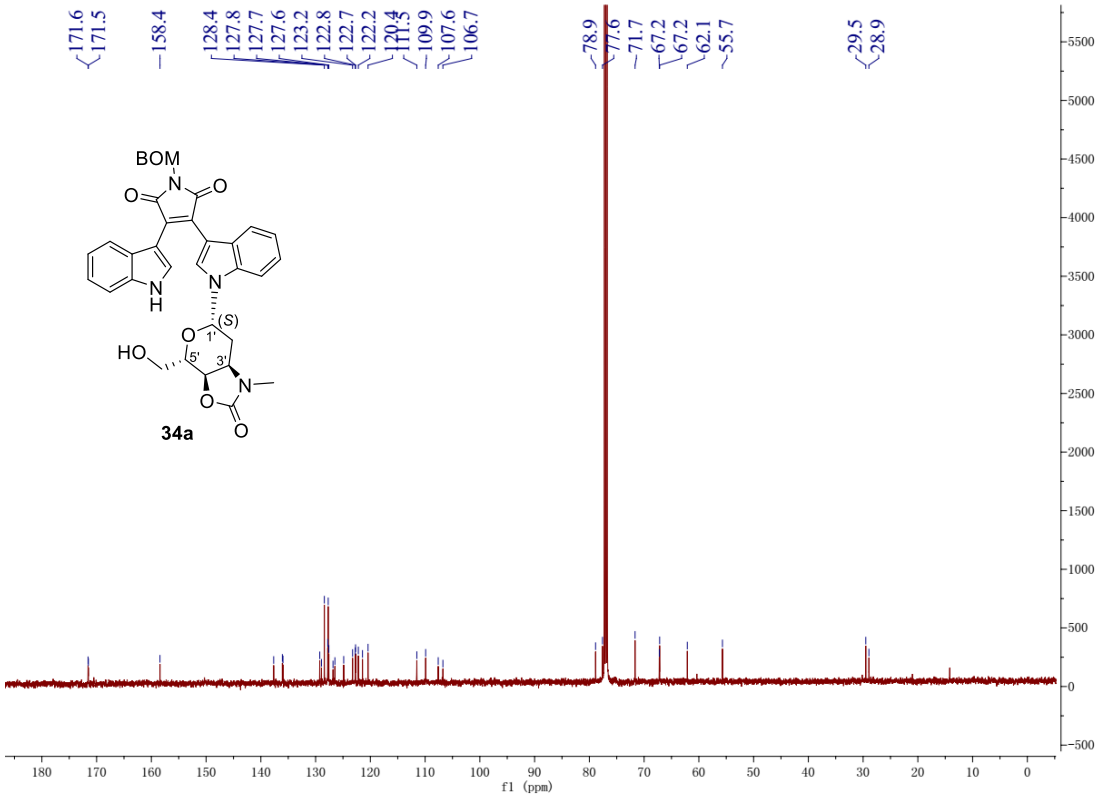

BOM
Boc
TIPSO
(S)
32a
f1 (ppm)

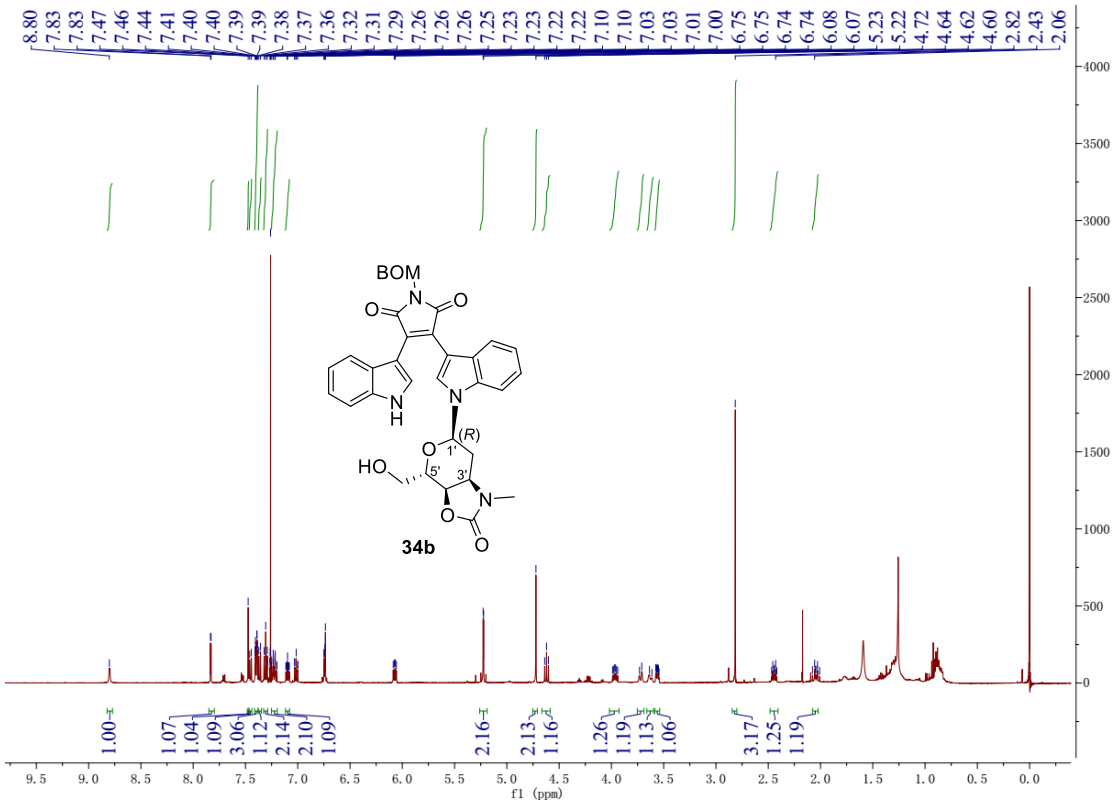

BOM
Boc
TIPSO
(S)
32a
f1 (ppm)

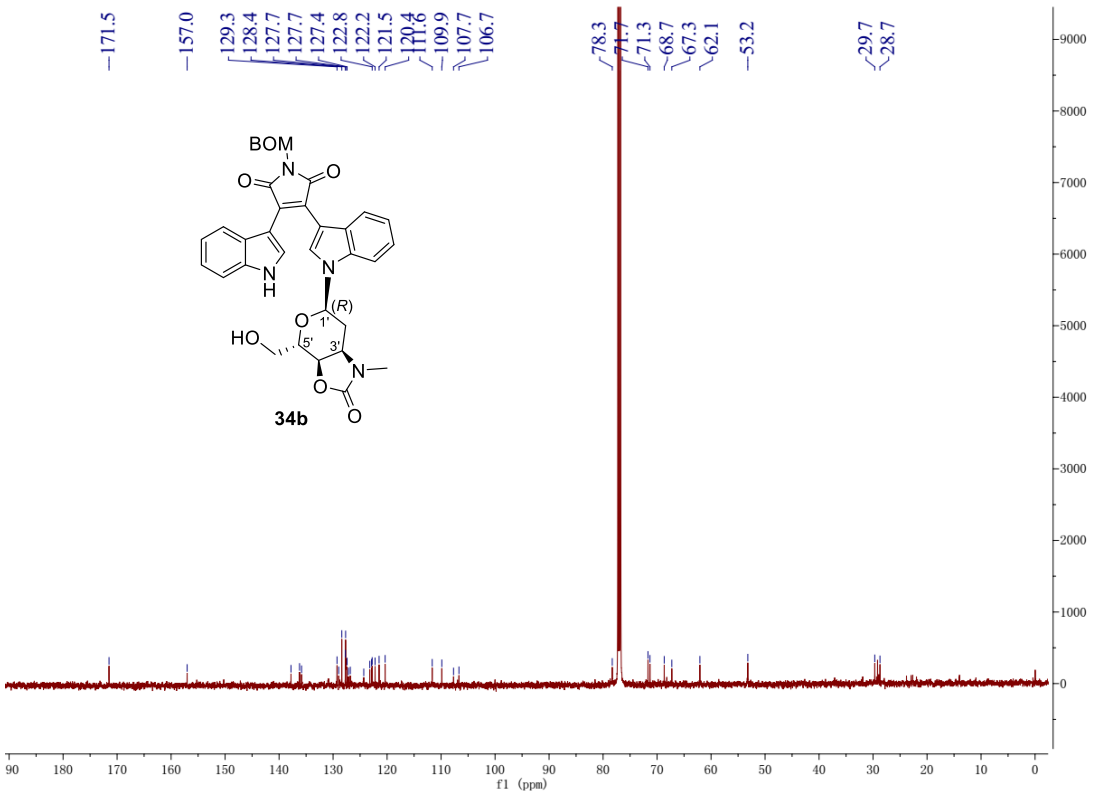

BOM
Boc
(R)
TIPSO
32b
f1 (ppm)

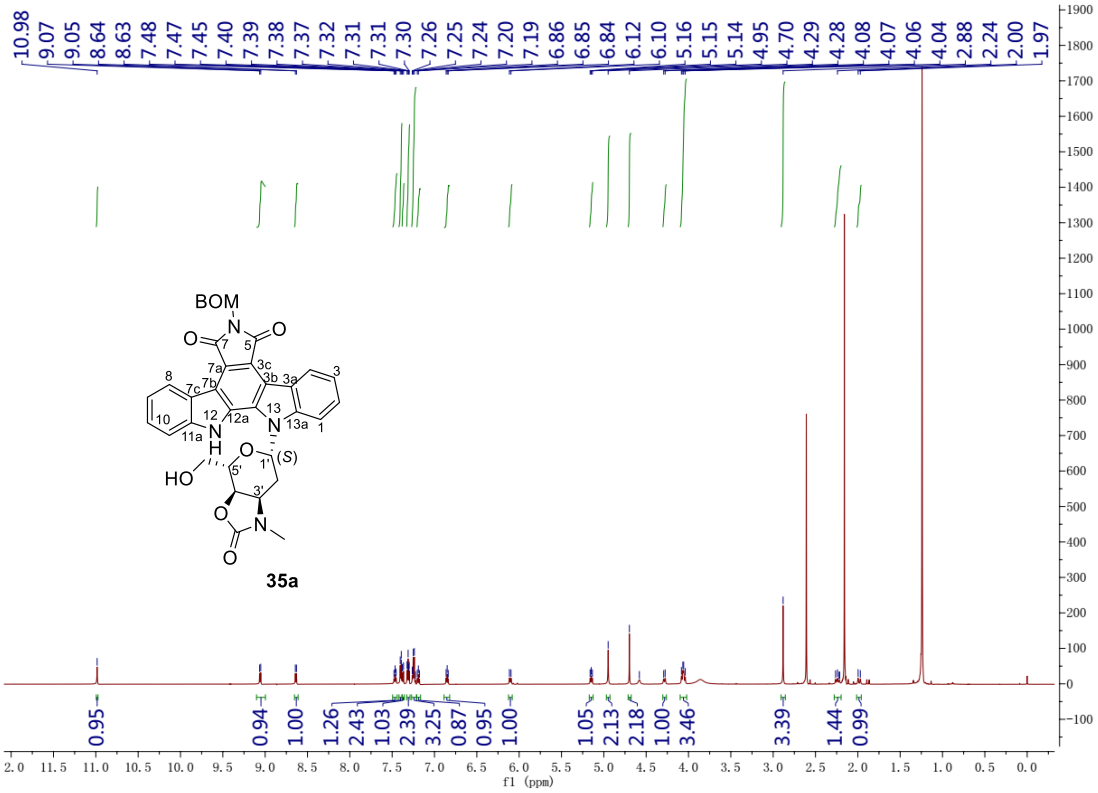

BOM
Boc
(R)
TIPSO
32b
f1 (ppm)

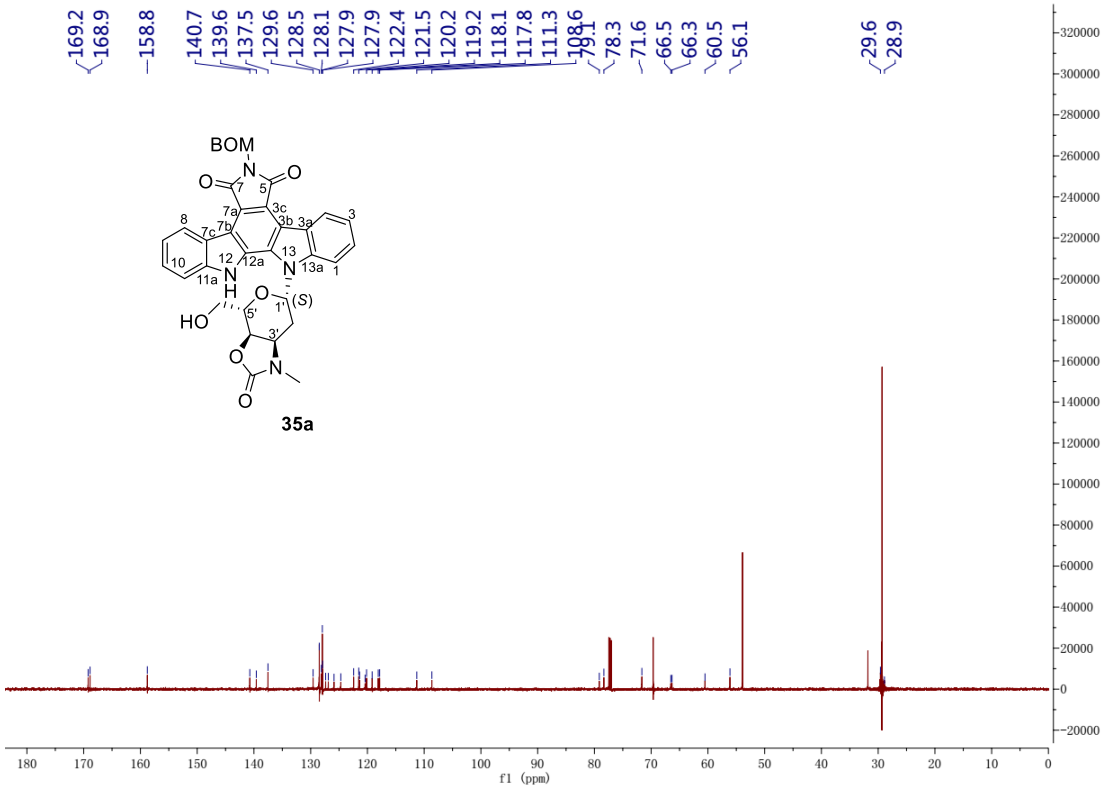

8.83 8.82 7.69 7.69 7.63 7.38 7.38 7.37 7.33 7.33 7.33 7.32 7.32 7.31 7.30 7.30 7.29 7.28 7.25 7.24 7.17 7.17 7.17 7.15 7.13 7.09 7.09 7.08 6.92 6.91 6.91 6.90 6.89 6.80 6.80 6.79 6.79 6.78 5.17 4.68 4.48 4.47 4.47 4.45 2.82 2.23
BOM
HO
34a
1.00 1.04 1.06 2.10 4.32 0.93 2.14 1.06 2.08 1.06 1.01 2.12 2.11 1.06 1.08 1.02 1.08 1.09 3.10 1.09 1.06
f1 (ppm)

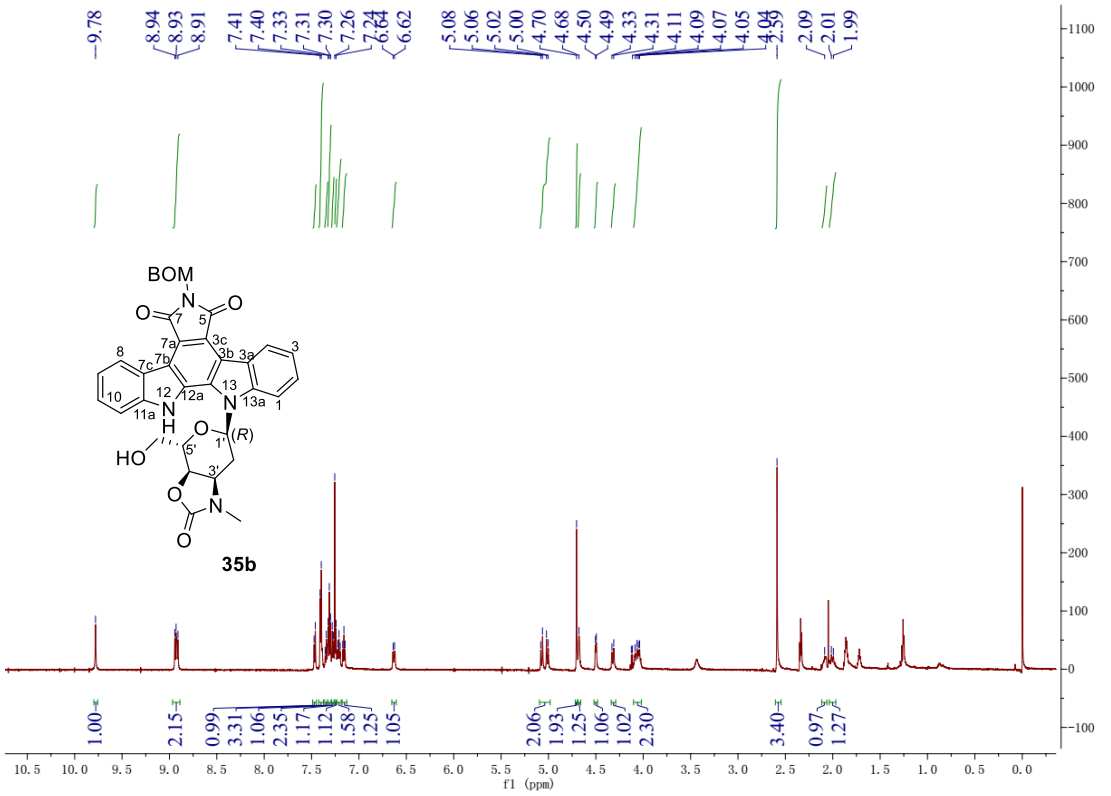

171.6 171.5 158.4 128.4 127.8 127.7 127.6 123.2 122.8 122.7 122.2 120.4 111.5 109.9 107.6 106.7 78.9 77.6 71.7 67.2 67.2 62.1 55.7 29.5 28.9
BOM
HO
34a
f1 (ppm)

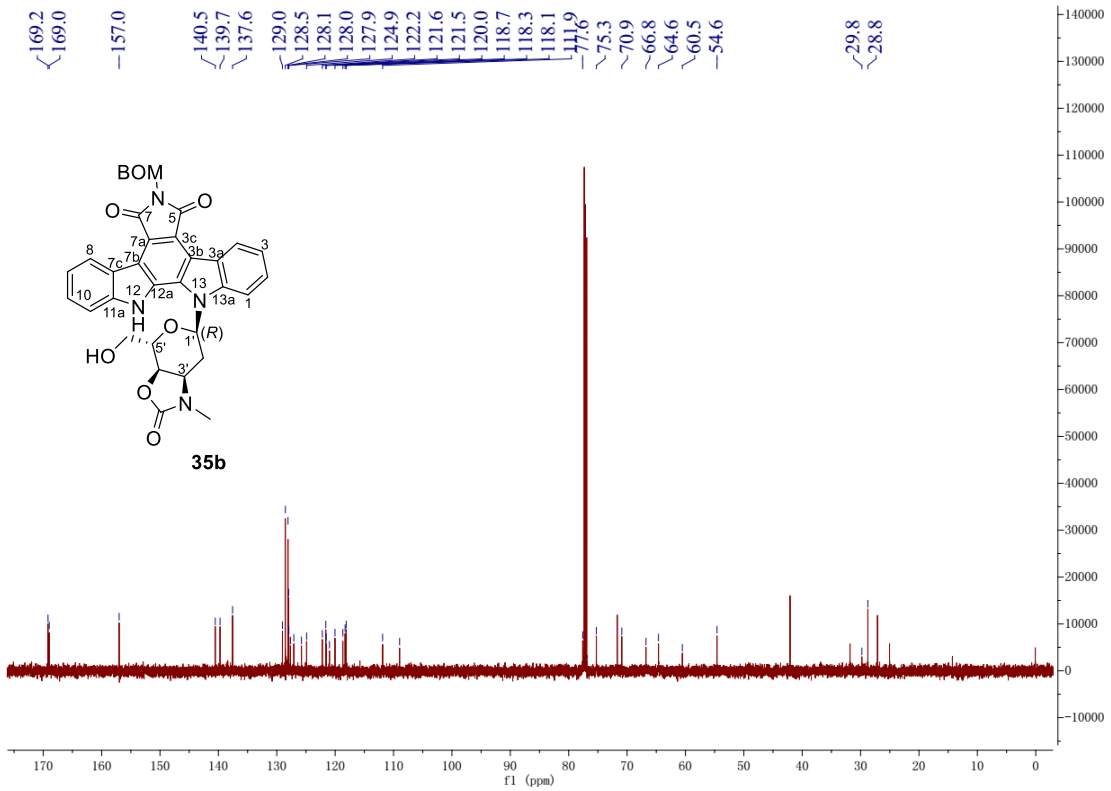

8.80 7.83 7.83 7.47 7.46 7.44 7.41 7.40 7.40 7.39 7.39 7.38 7.37 7.36 7.32 7.31 7.29 7.26 7.26 7.26 7.25 7.23 7.23 7.22 7.22 7.10 7.10 7.03 7.03 7.01 7.00 6.75 6.75 6.74 6.74 6.08 6.07 5.23 5.22 4.72 4.64 4.62 4.60 2.82 2.43 2.06
BOM
34b
1.00 1.07 1.04 1.09 3.06 1.12 2.14 2.10 1.09 2.16 2.13 1.16 1.26 1.19 1.13 1.06 3.17 1.25 1.19
f1 (ppm)

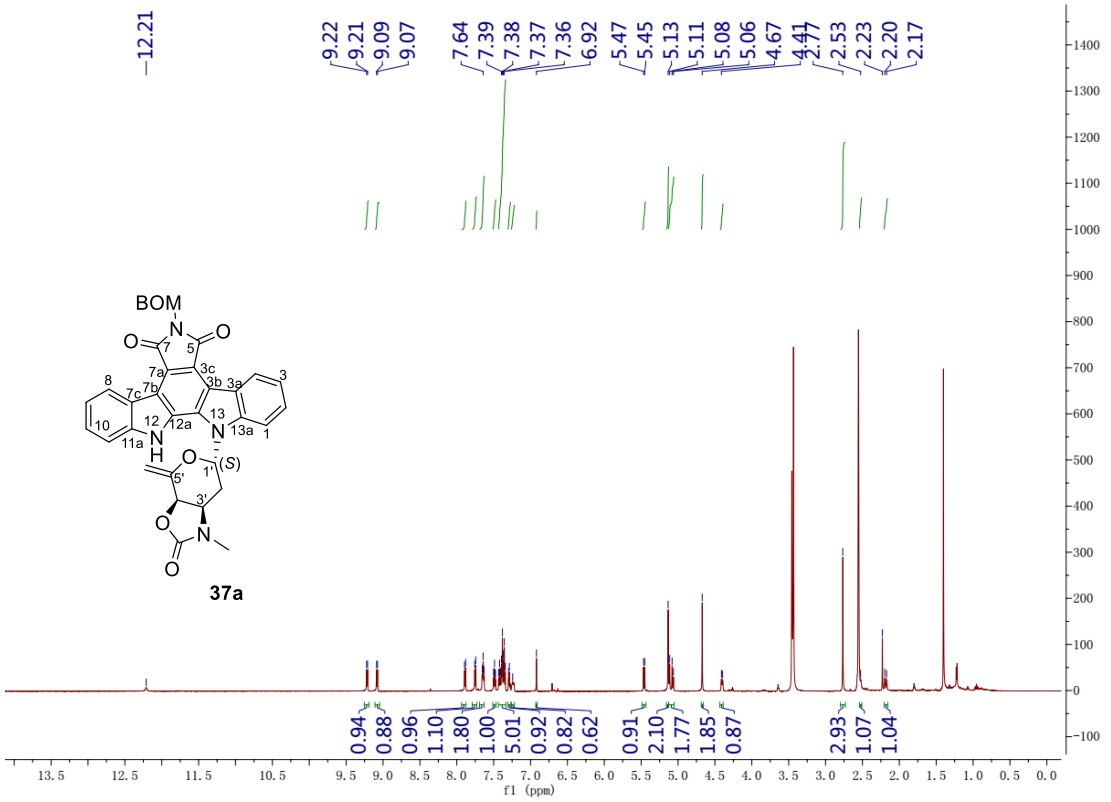

171.5 157.0 129.3 128.4 127.7 127.7 127.4 122.8 122.2 121.5 120.4 111.6 109.9 107.7 106.7 78.3 71.7 71.3 68.7 67.3 62.1 53.2 29.7 28.7
BOM
34b
f1 (ppm)

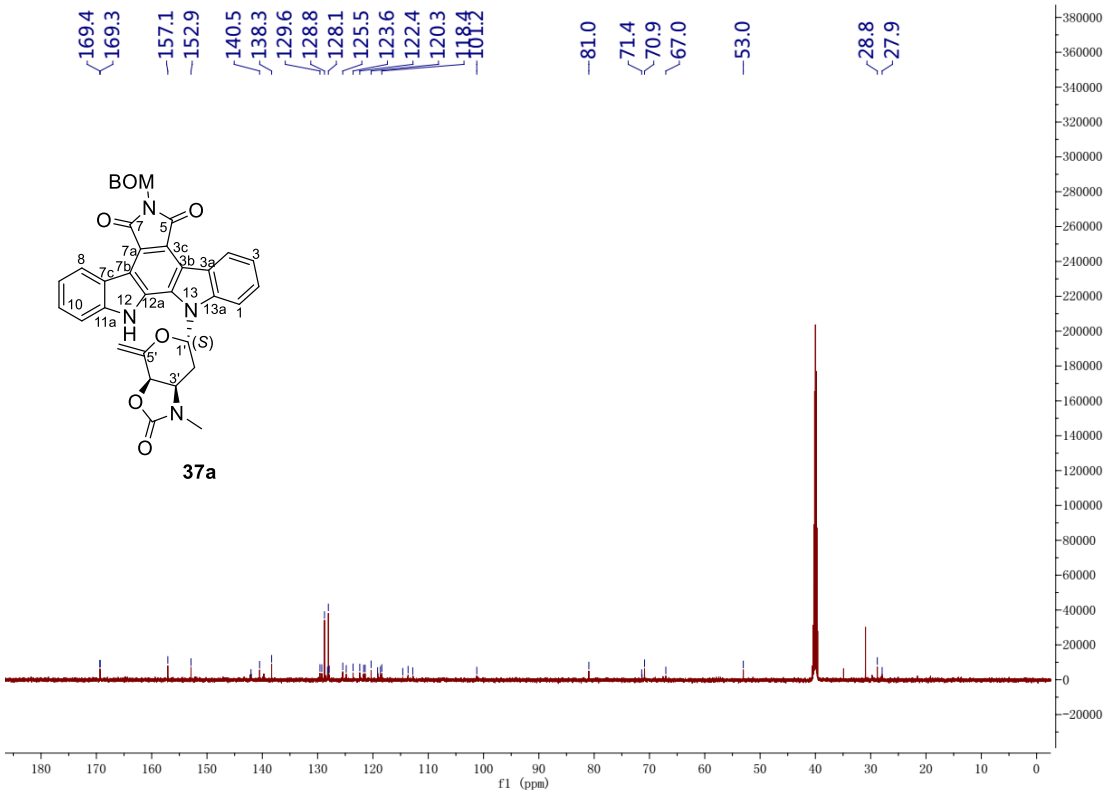

10.98
9.07
9.05
8.64
8.63
7.48
7.47
7.45
7.40
7.39
7.38
7.37
7.32
7.31
7.31
7.30
7.26
7.25
7.24
7.20
7.19
6.86
6.85
6.84
6.12
6.10
5.16
5.15
5.14
4.95
4.70
4.29
4.28
4.08
4.07
4.06
4.04
2.88
2.24
2.00
1.97
BOM
HO
(S)
35a
0.95
0.94
1.00
1.26
2.43
1.03
2.39
3.25
0.87
0.95
1.00
1.05
2.13
2.18
1.00
3.46
3.39
1.44
0.99
f1 (ppm)

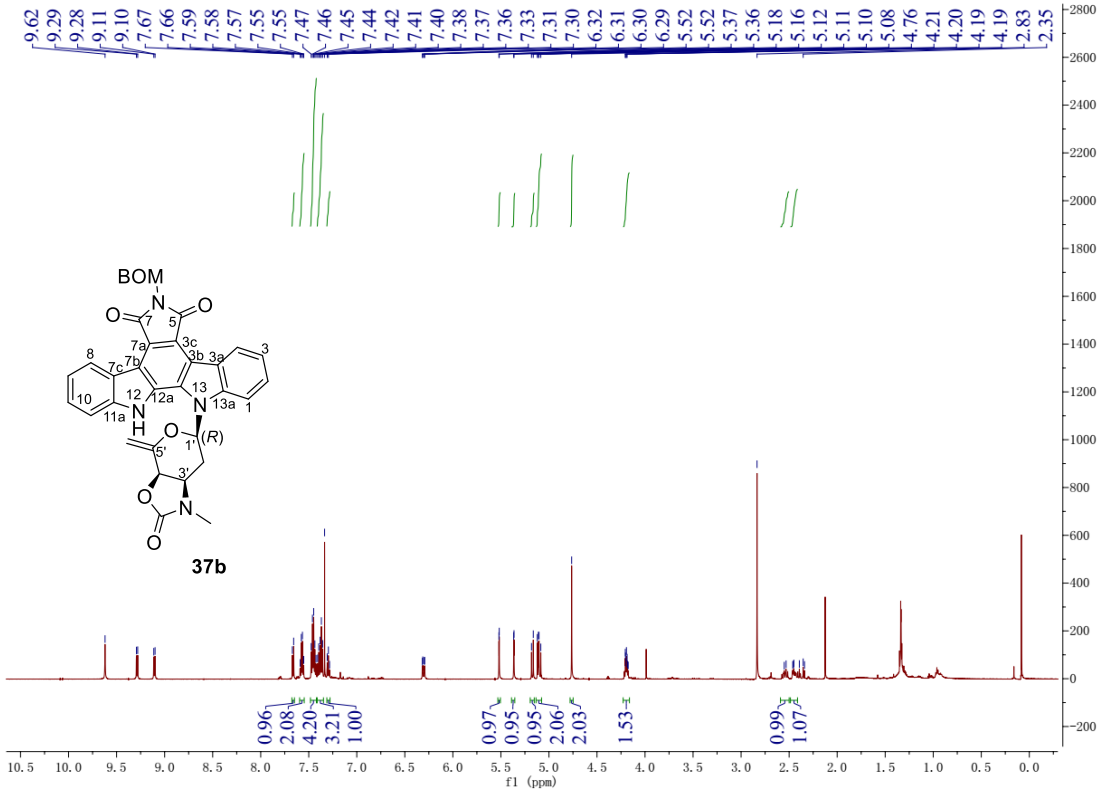

169.2
168.9
158.8
140.7
139.6
137.5
129.6
128.5
128.1
127.9
127.9
122.4
121.5
120.2
119.2
118.1
117.8
111.3
108.6
79.1
78.3
71.6
66.5
66.3
60.5
56.1
29.6
28.9
BOM
HO
(S)
35a
f1 (ppm)

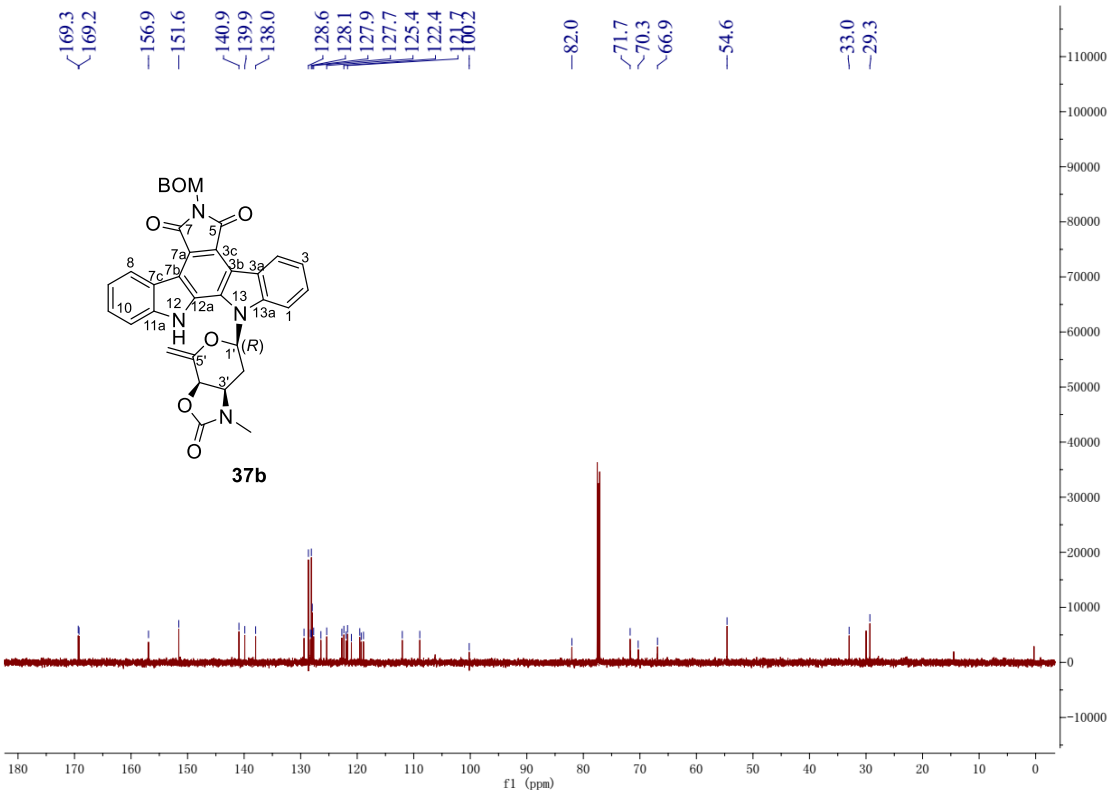

9.78
8.94
8.93
8.91
7.41
7.40
7.33
7.31
7.30
7.26
7.24
6.64
6.62
5.08
5.06
5.02
5.00
4.70
4.68
4.50
4.49
4.33
4.31
4.11
4.09
4.07
4.05
4.04
2.59
2.09
2.01
1.99
BOM
HO
(R)
35b
1.00
2.15
0.99
3.31
1.06
2.35
1.17
1.12
1.58
1.25
1.05
2.06
1.93
1.25
1.06
1.02
2.30
3.40
0.97
1.27
f1 (ppm)

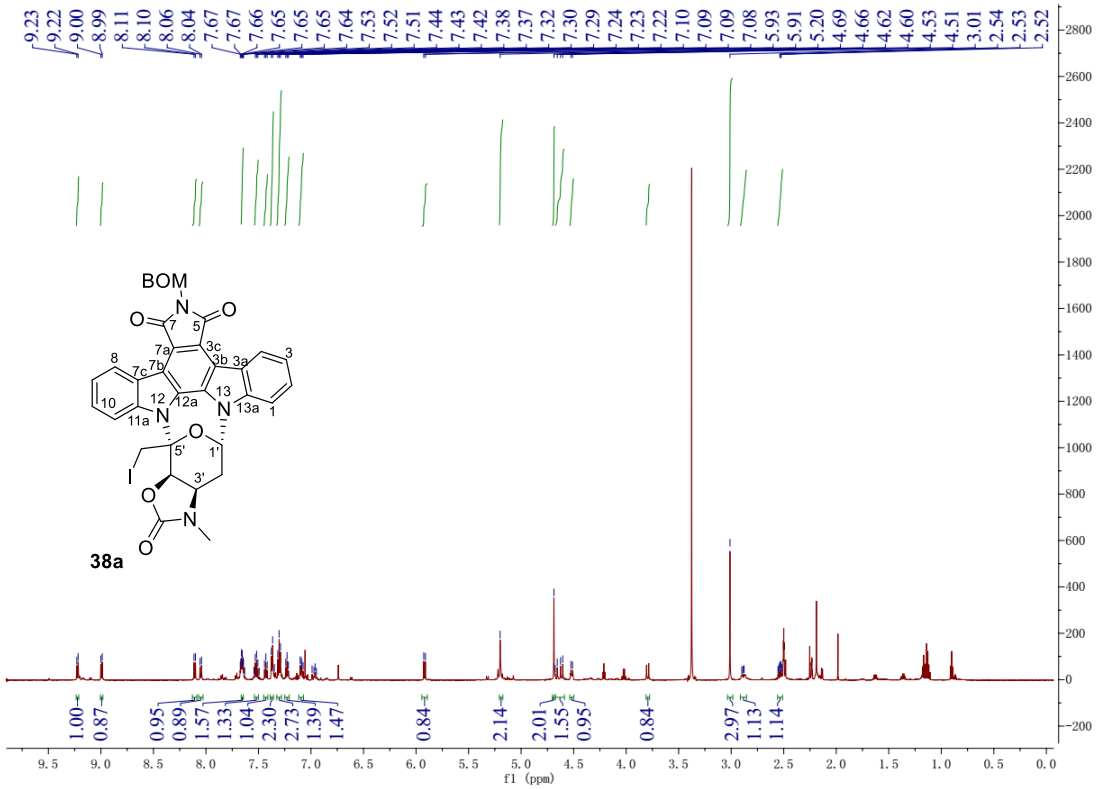

169.2
169.0
157.0
140.5
139.7
137.6
129.0
128.5
128.1
128.0
127.9
124.9
122.2
121.6
121.5
120.0
118.7
118.3
118.1
111.9
77.6
75.3
70.9
66.8
64.6
60.5
54.6
29.8
28.8
BOM
HO
(R)
35b
f1 (ppm)


12.21
9.22
9.21
9.09
9.07
7.64
7.39
7.38
7.37
7.36
6.92
5.47
5.45
5.13
5.11
5.08
5.06
4.67
4.41
2.77
2.53
2.23
2.20
2.17
BOM
37a
0.94
0.88
0.96
1.10
1.80
1.00
5.01
0.92
0.82
0.62
0.91
2.10
1.77
1.85
0.87
2.93
1.07
1.04
f1 (ppm)


169.4
169.3
157.1
152.9
140.5
138.3
129.6
128.8
128.1
125.5
123.6
122.4
120.3
118.4
101.2
81.0
71.4
70.9
67.0
53.0
28.8
27.9
BOM
37a
f1 (ppm)


9.62 9.29 9.28 9.11 9.10 7.67 7.66 7.59 7.58 7.57 7.55 7.55 7.47 7.46 7.45 7.44 7.42 7.41 7.40 7.38 7.37 7.36 7.33 7.31 7.30 6.32 6.31 6.30 6.29 5.52 5.52 5.37 5.36 5.18 5.16 5.12 5.11 5.10 5.08 4.76 4.21 4.20 4.19 4.19 2.83 2.35
BOM
37b
0.96 2.08 4.20 3.21 1.00 0.97 0.95 0.95 2.06 2.03 1.53 0.99 1.07
f1 (ppm)


169.3 169.2 156.9 151.6 140.9 139.9 138.0 128.6 128.1 127.9 127.7 125.4 122.4 121.7 100.2 82.0 71.7 70.3 66.9 54.6 33.0 29.3
BOM
37b
f1 (ppm)


9.23
9.22
9.00
8.99
8.11
8.10
8.06
8.04
7.67
7.67
7.66
7.65
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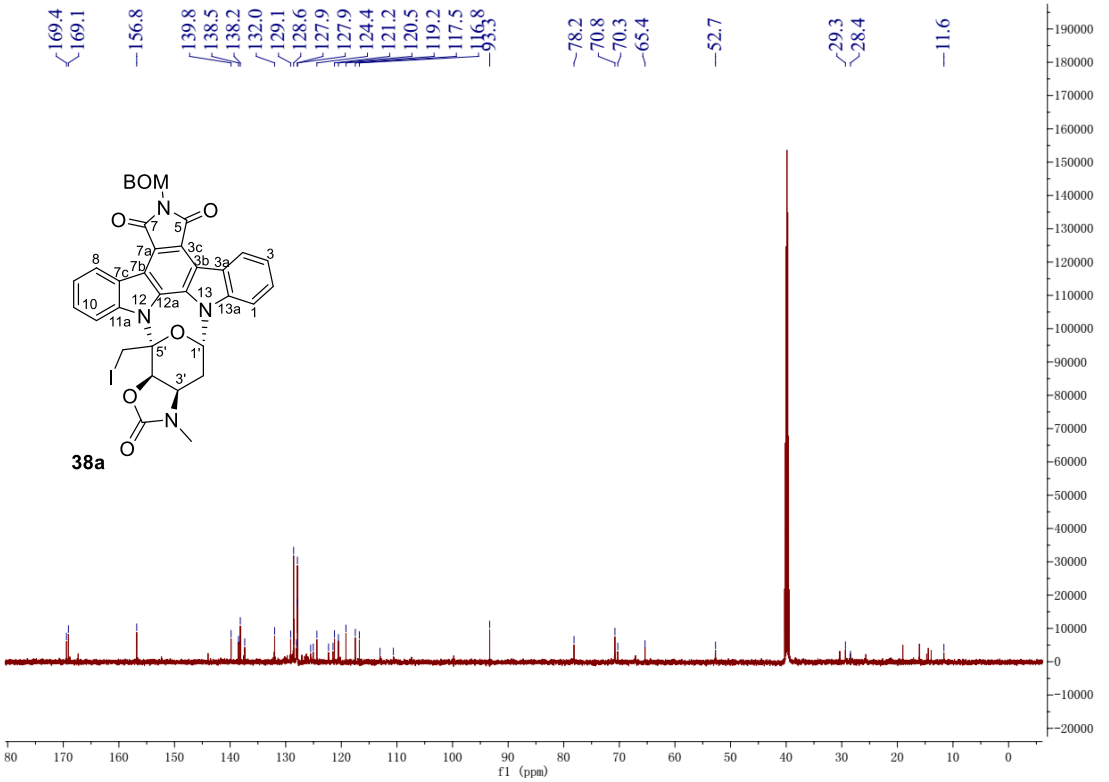
7.65
7.64
7.53
7.52
7.51
7.44
7.43
7.42
7.38
7.37
7.32
7.30
7.29
7.24
7.23
7.22
7.10
7.09
7.09
7.08
5.93
5.91
5.20
4.69
4.66
4.62
4.60
4.53
4.51
3.01
2.54
2.53
2.52
BOM
38a
1.00
0.87
0.95
0.89
1.57
1.33
1.04
2.30
2.73
1.39
1.47
0.84
2.14
2.01
1.55
0.95
0.84
2.97
1.13
1.14
f1 (ppm)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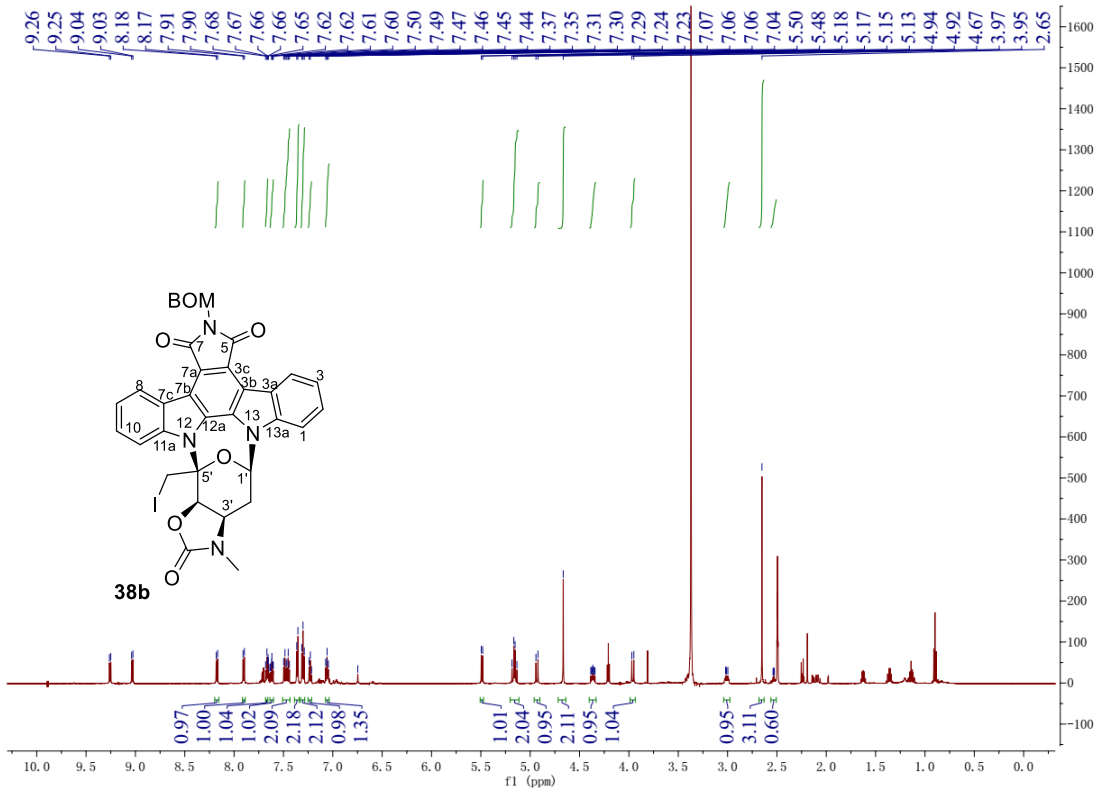
169.1
156.8
139.8
138.5
138.2
132.0
129.1
128.6
127.9
127.9
124.4
121.2
120.5
119.2
117.5
116.8
93.3
78.2
70.8
70.3
65.4
52.7
29.3
28.4
11.6
BOM
38a
f1 (ppm)


9.26
9.25
9.04
9.03
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8.17
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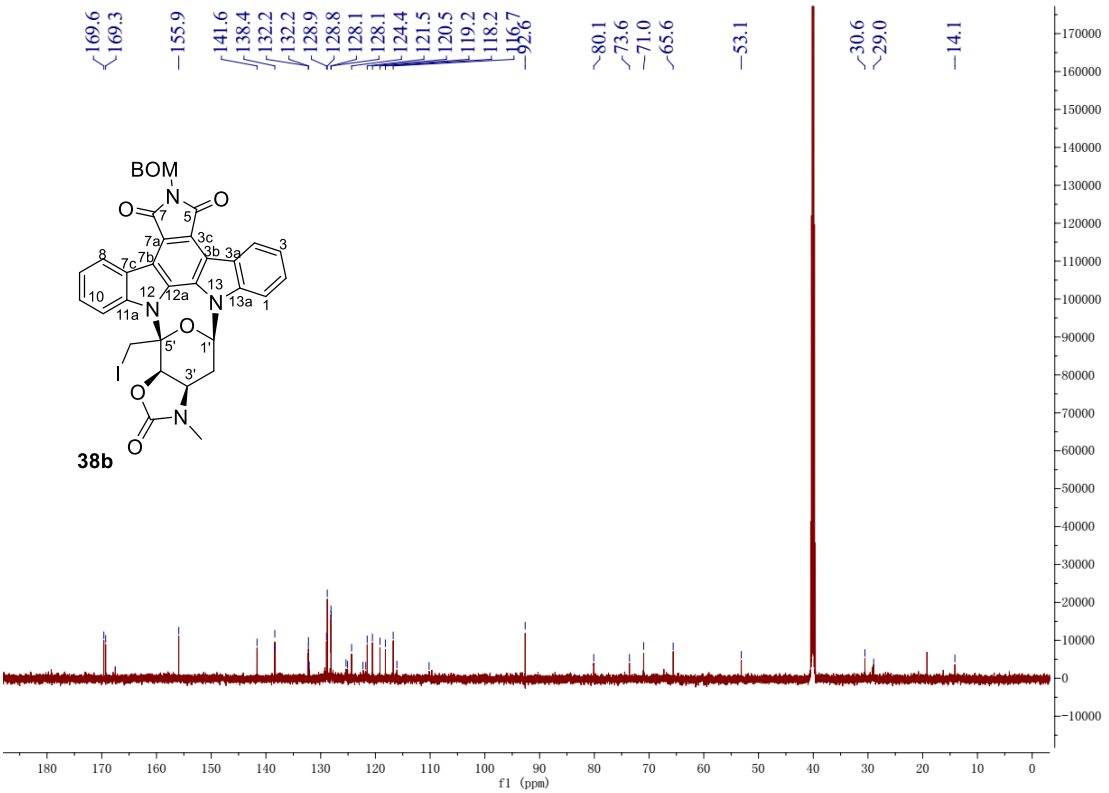
7.90
7.68
7.67
7.66
7.66
7.65
7.62
7.62
7.61
7.60
7.50
7.49
7.47
7.46
7.45
7.44
7.37
7.35
7.31
7.30
7.29
7.24
7.23
7.07
7.06
7.06
7.04
5.50
5.48
5.18
5.17
5.15
5.13
4.94
4.92
4.67
3.97
3.95
2.65
BOM
38b
0.97
1.00
1.04
1.02
2.09
2.18
2.12
0.98
1.35
1.01
2.04
0.95
2.11
0.95
1.04
0.95
3.11
0.60
f1 (ppm)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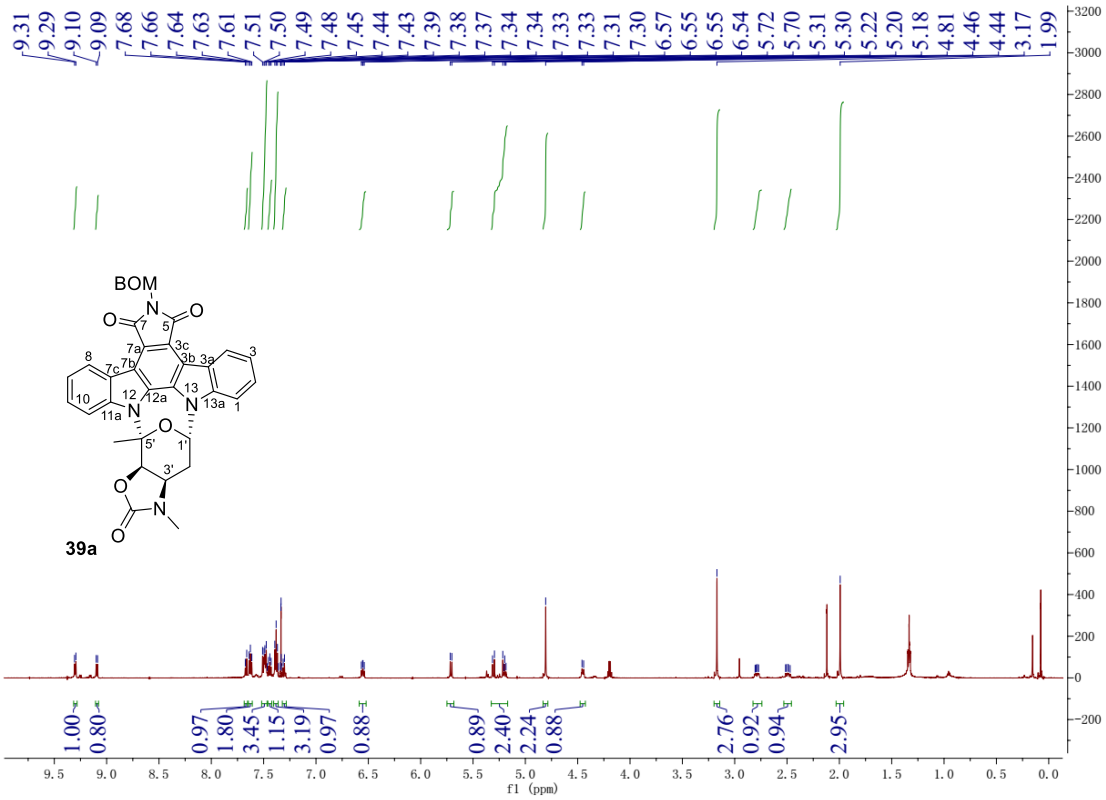
169.3
155.9
141.6
138.4
132.2
132.2
128.9
128.8
128.1
128.1
124.4
121.5
120.5
119.2
118.2
116.7
92.6
80.1
73.6
71.0
65.6
53.1
30.6
29.0
14.1
BOM
38b
f1 (ppm)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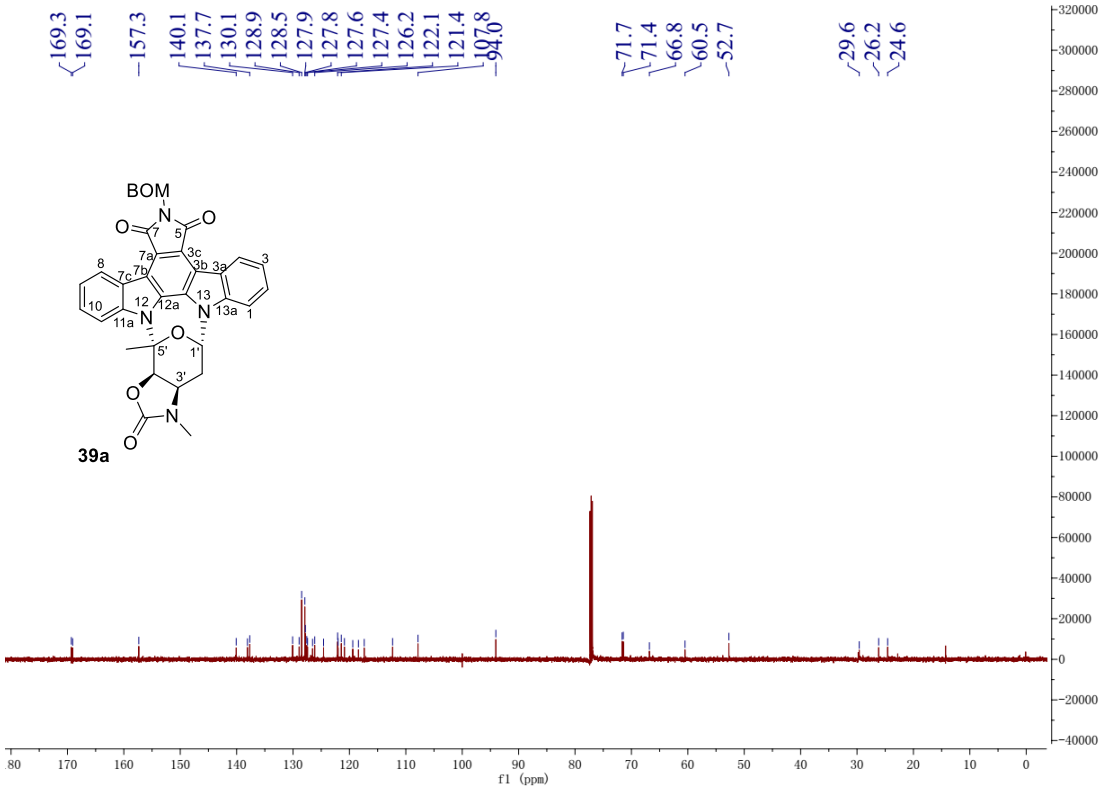
9.29
9.10
9.09
7.68
7.66
7.64
7.63
7.61
7.51
7.50
7.49
7.48
7.45
7.44
7.43
7.39
7.38
7.37
7.34
7.34
7.33
7.33
7.31
7.30
6.57
6.55
6.55
6.54
5.72
5.70
5.31
5.30
5.22
5.20
5.18
4.81
4.46
4.44
3.17
1.99
BOM
39a
1.00
0.80
0.97
1.80
3.45
1.15
3.19
0.97
0.88
0.89
2.40
2.24
0.88
2.76
0.92
0.94
2.95
f1 (ppm)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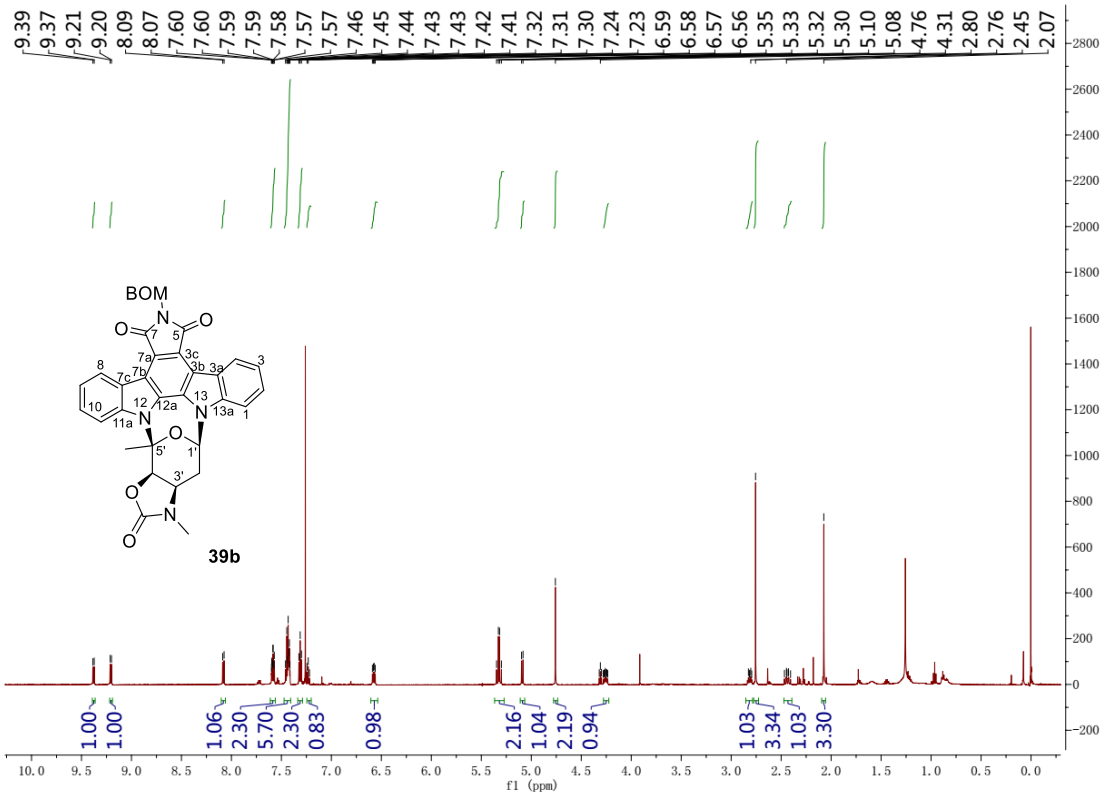
169.1
157.3
140.1
137.7
130.1
128.9
128.5
127.9
127.8
127.6
127.4
126.2
122.1
121.4
107.8
94.0
71.7
71.4
66.8
60.5
52.7
29.6
26.2
24.6
BOM
39a
f1 (ppm)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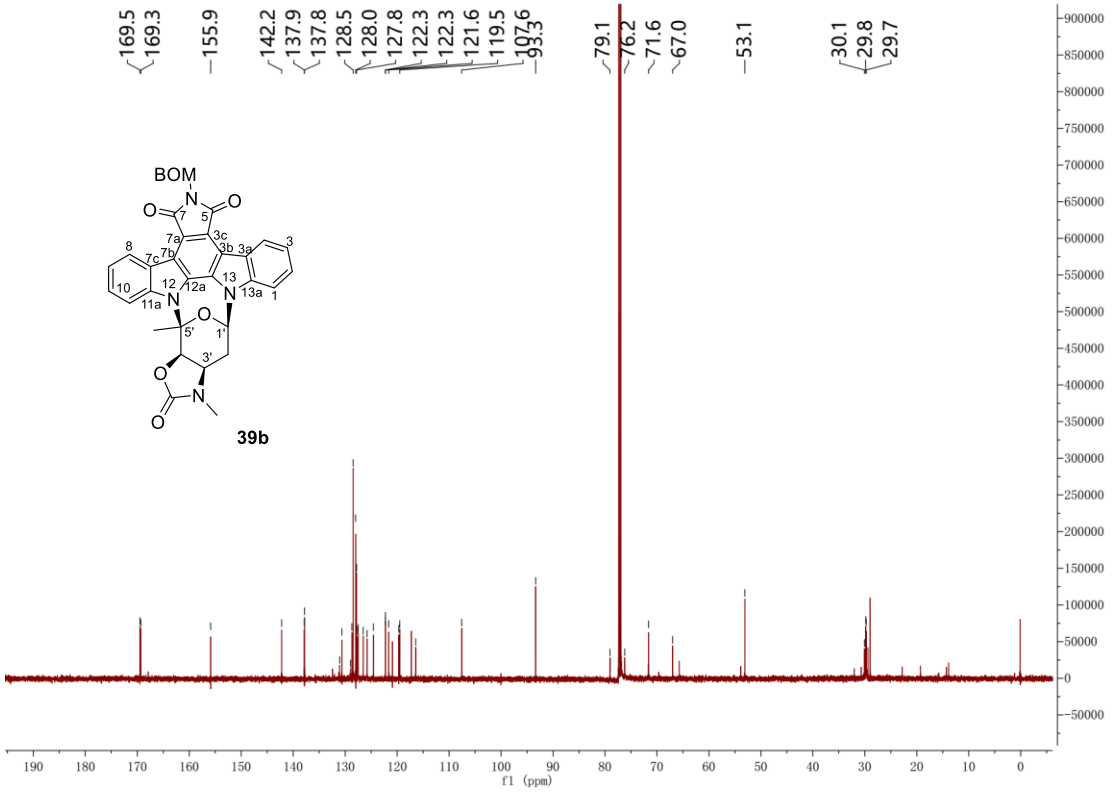
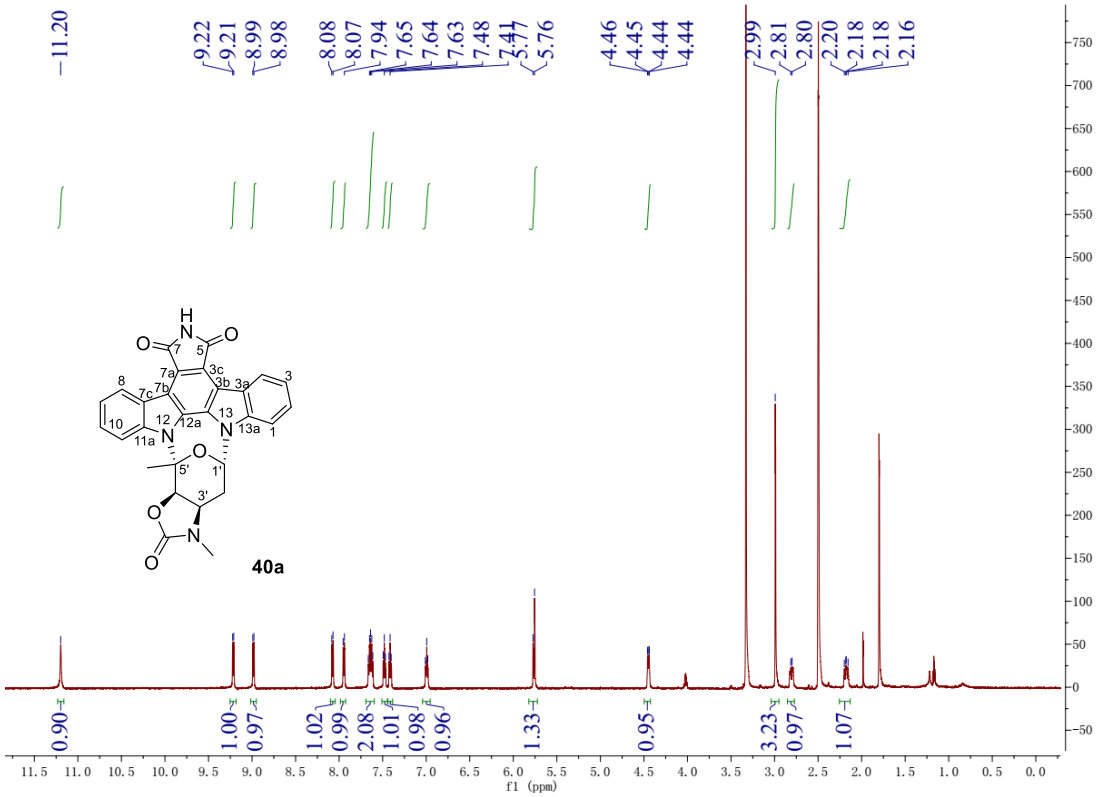
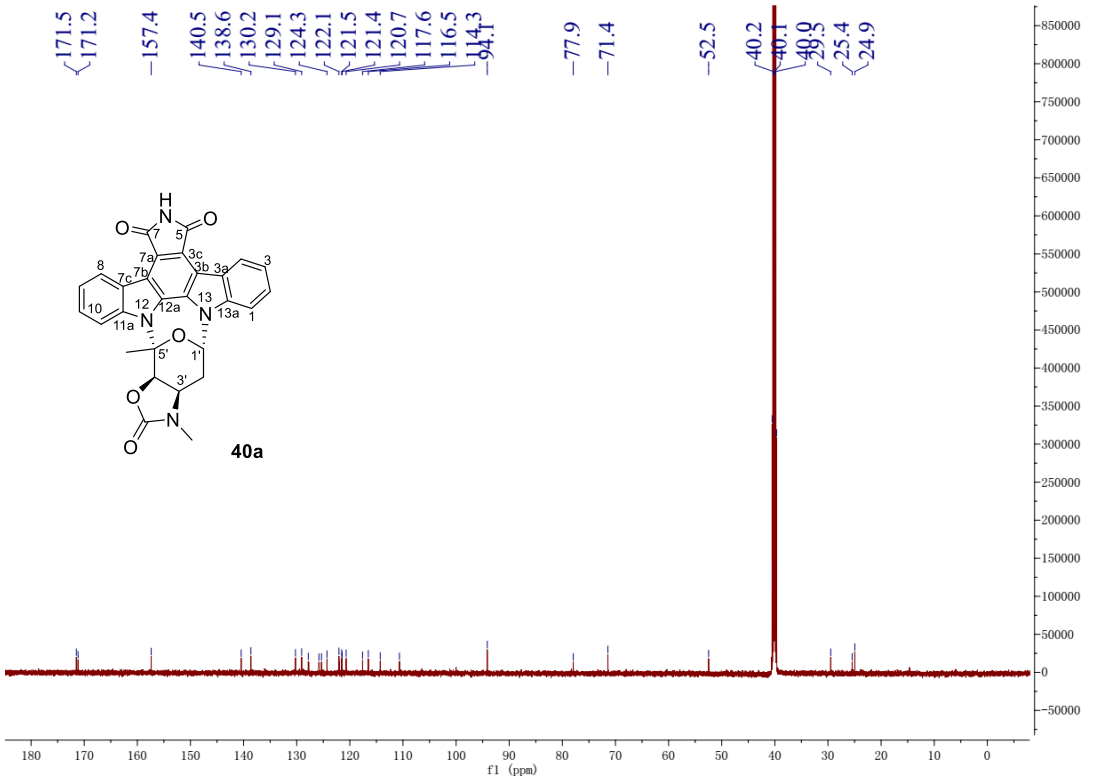
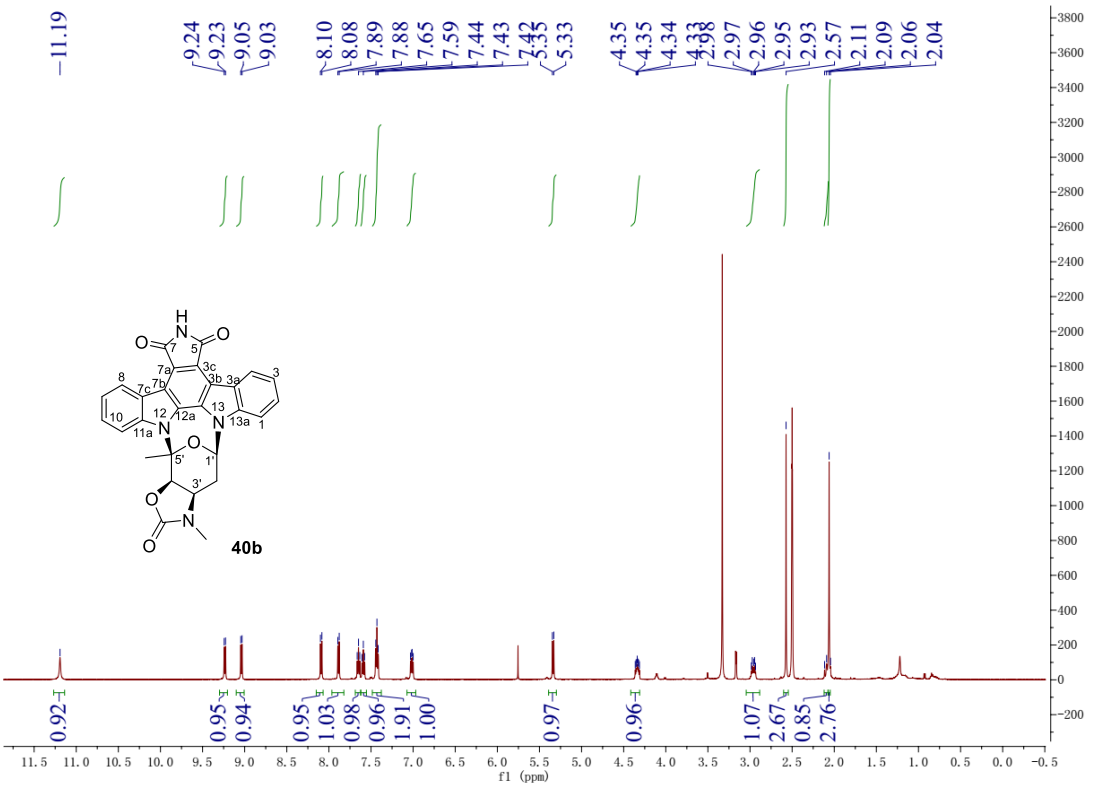
9.37
9.21
9.20
8.09
8.07
7.60
7.60
7.59
7.59
7.58
7.57
7.57
7.46
7.45
7.44
7.43
7.43
7.42
7.41
7.32
7.31
7.30
7.24
7.23
6.59
6.58
6.57
6.56
5.35
5.33
5.32
5.30
5.10
5.08
4.76
4.31
2.80
2.76
2.45
2.07
BOM
39b
1.00
1.00
1.06
2.30
5.70
2.30
0.83
0.98
2.16
1.04
2.19
0.94
1.03
3.34
1.03
3.30
f1 (ppm)

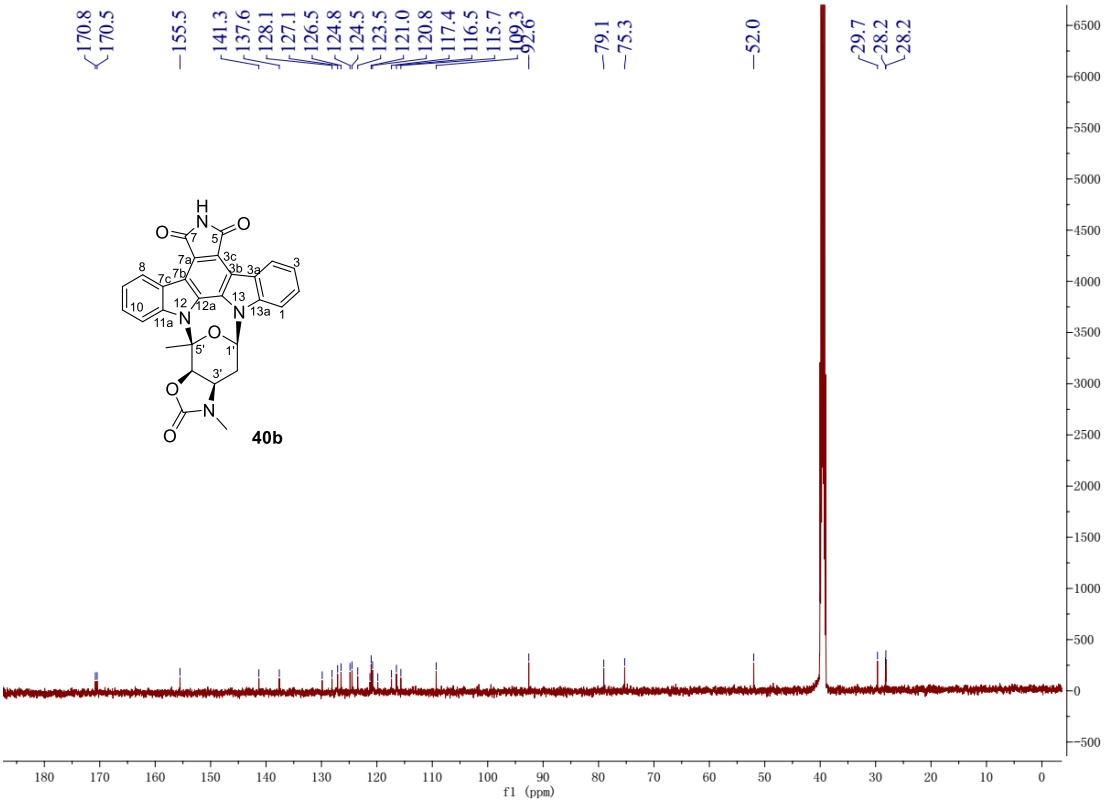

169.5
169.3
155.9
142.2
137.9
137.8
128.5
128.0
127.8
122.3
122.3
121.6
119.5
107.6
93.3
79.1
76.2
71.6
67.0
53.1
30.1
29.8
29.7
BOM
39b
f1 (ppm)


11.20
9.22
9.21
8.99
8.98
8.08
8.07
7.94
7.65
7.64
7.63
7.48
7.41
7.41
5.77
5.76
4.46
4.45
4.44
4.44
2.99
2.81
2.80
2.20
2.18
2.18
2.16
0.90
1.00
0.97
1.02
0.99
2.08
1.01
0.98
0.96
1.33
0.95
3.23
0.97
1.07
f1 (ppm)
40a


171.5
171.2
157.4
140.5
138.6
130.2
129.1
124.3
122.1
121.5
121.4
120.7
117.6
116.5
114.3
94.1
77.9
71.4
52.5
40.2
40.1
40.0
29.5
25.4
24.9
f1 (ppm)
40a


11.19
9.24
9.23
9.05
9.03
8.10
8.08
7.89
7.88
7.65
7.59
7.44
7.43
7.42
5.35
5.33
4.35
4.35
4.34
4.33
2.97
2.96
2.95
2.93
2.57
2.11
2.09
2.06
2.04
0.92
0.95
0.94
0.95
1.03
0.98
0.96
1.91
1.00
0.97
0.96
1.07
2.67
0.85
2.76
f1 (ppm)

40b


170.8
170.5
155.5
141.3
137.6
128.1
127.1
126.5
124.8
124.5
123.5
121.0
120.8
117.4
116.5
115.7
109.3
92.6
79.1
75.3
52.0
29.7
28.2
28.2
f1 (ppm)

40b