Electronic Supplementary Information

Design, synthesis and anticancer activities of novel otobain derivatives

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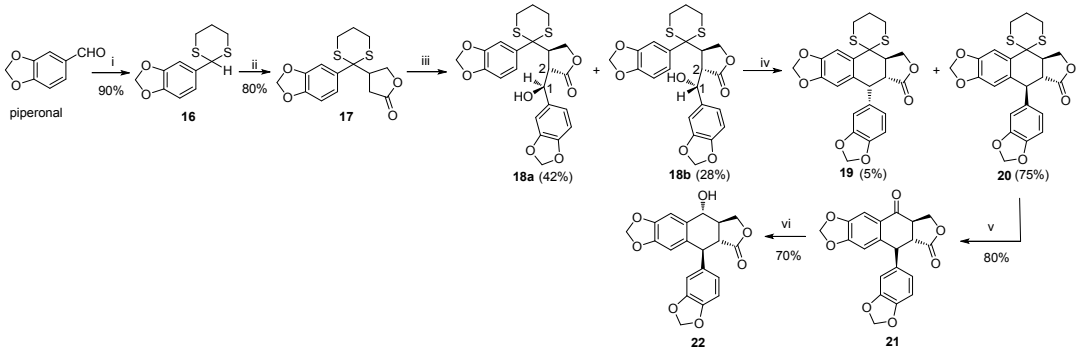
1. General information.

All reagents and chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. ^{1}H (500 Mz) and ^{13}C (125 Mz) NMR spectra were recorded on a Varian INOVA spectrometer with $CDCl_3$ or DMSO-d_6 and tetramethylsilane (TMS) as the internal standard. All chemical shift values were reported in units of δ (ppm). The following abbreviations were used to indicate the peak multiplicity: s = singlet; d = doublet; t = triplet; m = multiplet; br = broad. Analytical thin-layer chromatography (TLC) was carried out on precoated plates (silica gel 60 F254), and spots were visualized with ultraviolet (UV) light. Flash column chromatography was carried out with silica gel (300-350 mesh). Melting points were determined on Yanano MP 500. High-resolution mass data were obtained on a Bruker microOTOFQ II spectrometer.

2. General procedures and characterizations of intermediate compounds 16-22,24 and 25.



Scheme 1 Synthesis of **22**. Reagents and conditions: (i) SH $(CH_2)_3SH$, *p*-TsOH, DCM, rt; (ii) n-BuLi, furan-2(5H)-one, THF, -78°C; (iii) LDA, piperonal, THF, -78°C; (iv) TFA, DCM, rt; (v) HgO, $BF_3{\cdot}Et_2O$, THF/H_2O (85/15), 0°C-rt; (vi) $NaBH_4$, THF, 0°C.

Synthesis of 5-(1,3-dithian-2-yl)benzo[d][1,3]dioxole (16)

To a solution of piperonal (15.00 g, 100 mmol) in dichloromethane (150 mL), propanedithiol (11.02 mL, 110 mmol) and monohydrated p-toluensulfonic acid (1.90 g, 10 mmol) were added. The mixture was stirred for 24 h at room temperature. Upon completion, saturated sodium carbonate (100 mL) was added and stirred for 2 h. The organic layer was washed with saturated brine (3×50 mL), dried over anhydrous Na_2SO_4, filtered, concentrated in vacuo, and recrystallized from ethanol to give white solid of 5-(1,3-dithian-2-yl)benzo[d][1,3]dioxole (**16**) (21.50 g, 90%): m.p. 97 °C (lit.[1] 93-94 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.87-1.94(m, 1H), 2.12-2.17(m, 1H), 2.89(d, *J* = 14.2 Hz, 2H), 3.01-3.07(m, 2H), 5.09(s, 1H), 5.95(s, 2H), 6.75(d, *J* = 8.0 Hz, 1H), 6.93(d, *J* = 8.0 Hz, 1H), 6.98(s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.05, 32.19, 51.19, 101.23, 108.39, 121.31, 132.95, 147.64, 147.76.

Synthesis of 4-(2-(benzo[d][1,3]dioxol-5-yl)-1,3-dithian-2-yl)dihydrofuran-2(3H)-one (17)

To a solution of **16** (4.00 g, 16.64 mmol) in dry THF (60 mL) at -78°C was added n-BuLi (6.96 mL, 2.4 M, in hexane, 16.64 mmol) dropwise within a period of 30 min. Stirring was continued for 30 min, and then a solution of furan-2(5H)-one (1.44 g, 16.64 mmol) in dry THF (10 mL) was added dropwise over a period of 20 min at -78°C. The reaction was kept in the same conditions for two more hours. After the addition of concentrated acetic acid (3 mL), the mixture was allowed to reach the room temperature. The crude of the reaction was extracted with ethyl acetate and the organic phase was dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure yielded yellowish colored oil, which was recrystallized from ethyl acetate to provide white solid of 4-(2-(benzo[d][1,3]dioxol-5-yl)-1,3-dithian-2-yl)dihydrofuran-2(3H)-one (**17**) (4.36 g, 80%): m.p. 162-163 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.85-1.99(m, 2H), 2.40-2.46(m, 1H), 2.66-2.76(m, 4H), 2.82-2.87(m, 1H), 2.98-3.04(m, 1H), 4.18-4.22(m, 1H), 4.39-4.43(m, 1H), 6.01(s, 2H), 6.84(d, *J* = 8.5 Hz, 1H), 7.46(d, *J* = 5.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.75, 27.20, 30.19, 48.20, 60.67, 68.54, 101.57, 108.33, 109.37, 123.16, 132.95, 147.22, 148.67, 175.76; HRMS (ESI): calc.for $C_{15}H_{16}O_4S_2Na$ $(M+Na)^+$ 347.0382, found: 347.0379.

Synthesis of 3-(benzo[d][1,3]dioxol-5-yl(hydroxy)methyl)-4-(2-(benzo[d][1,3]dioxol-5-yl)-1,3-dithian-2-yl)dihydrofuran-2(3H)-one (18)

To a solution of diisopropylamine (1.2 mL, 7.40 mmol) in dry THF (5 mL) at at -78°C was added n-BuLi (3.20 mL, 2.4 M, in hexane, 7.40 mmol) dropwise within a period of 30 min. Stirring was continued for 30 min, and then a solution of (**17**) (2.00 g, 6.17 mmol) in dry THF (15 mL) was added dropwise over a period of 30 min at -78°C. The reaction was stirred at -78°C for one more hour. At this point, a solution of piperonal (1.11 g, 7.40 mmol) in dry THF (5 mL) was added. After 1 h, acetic acid (1.60 mL) was added and allowed the mixture to rise to the room

temperature. The mixture of the reaction was extracted with ethyl acetate and the product was purified by silica column chromatography (ethyl acetate/petroleum ether, 3:7) to give **18a (**1.23 g, 42%**)** and 1**8b** (0.82 g, 28%).

3-(benzo[d][1,3]dioxol-5-yl(hydroxy)methyl)-4-(2-(benzo[d][1,3] dioxol-5-yl)-1,3-dithian-2-yl)dihydrofuran-2(3H)-one (**18a**): white solid, m.p. 181-184 °C; ^{1}H NMR (500 MHz, $CDCl_3$)：δ 1.76-1.90(m, 2H), 2.50-2.54(m, 3H), 2.56-2.67(m, 2H), 2.76 (dt, J_1 = 7.9, J_2 = 2.3 Hz, 1H), 2.90(s, 1H), 4.33(dd, J_1 = 9.2, J_2 = 8.2 Hz, 1H), 4.88(dd, J_1 = 9.3, J_2 = 1.9 Hz, 1H), 5.08(t, J = 3.6 Hz, 1H), 5.94(t, J = 1.8 Hz, 2H), 5.99(d, J = 1.6 Hz, 1H), 6.02(d, J = 1.6 Hz, 1H), 6.52(d, J = 8.0 Hz, 2H), 6.60(d, J = 8.2 Hz, 1H), 6.63(d, J = 8.2 Hz, 1H), 7.08(s, 1H), 7.19(dd, J_1 = 8.2, J_2 = 1.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.45, 26.70, 27.21, 47.83, 49.49, 62.96, 70.31, 73.62, 101.19, 101.55, 105.89, 107.54, 107.94, 109.27, 118.60, 123.31, 132.55, 134.28, 146.78, 146.97, 147.63, 148.10, 178.31; HRMS (ESI): calc.for $C_{23}H_{22}O_7S_2Na$ $(M+Na)^+$ 497.0699, found: 497.0702.

3-(-benzo[d][1,3]dioxol-5-yl(hydroxy)methyl)-4-(2-(benzo[d][1,3] dioxol-5-yl)-1,3-dithian-2-yl)dihydrofuran-2(3H)-one (**18b**): white solid, m.p. 169-170 °C; ^{1}H NMR (500 MHz, $CDCl_3$)：δ 1.81-1.95(m, 2H), 2.59-2.75(m, 6H), 3.15(d, J = 5.9 Hz, 1H), 3.92(t, J = 9.0 Hz, 1H), 4.67(d, J = 9.9 Hz, 1H), 4.72(d, J = 5.9 Hz, 1H), 5.94(s, 1H), 5.97(s, 1H), 5.99(s, 1H), 6.03(s, 1H), 6.65(d, J = 7.9 Hz, 1H), 6.70(d, J = 9.5 Hz, 2H), 6.75(d, J = 8.1 Hz, 1H), 7.32(s, 1H), 7.35(d, J = 8.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.43, 26.86, 27.12, 49.48, 50.34, 62.35, 68.35, 73.56, 101.17, 101.60, 106.62, 107.95, 108.05, 109.49, 119.85, 123.40, 132.60, 133.46, 147.15, 147.48, 147.78, 148.50, 176.58; HRMS (ESI): calc.for $C_{23}H_{22}O_7S_2Na$ $(M+Na)^+$ 497.0708, found: 497.0699.

Synthesis of lactones (19) and (20)

TFA (4.27 mL) was added dropwise to a solution of **18** (1.78 g, 3.59 mmol) in CH_2Cl_2 (25 mL). The reaction mixture was stirred for 24 h at room temperature, and then the reaction was quenched with $NaHCO_3$ (concentrated solution). The organic layer was washed with saturated brine (3×20 mL), dried over anhydrous Na_2SO_4, filtered, concentrated in vacuo to give the crude product, which was purified by silica column chromatography (ethyl acetate/petroleum ether, 3:7) to give **19** (86 mg, 5%)and **20** (1.29 g, 75%).

9'-(benzo[d][1,3]dioxol-5-yl)-8a',9'-dihydro-5a'H-spiro[[1,3] dithiane-2,5'-furo[3',4':6,7]naphtho[2,3-d][1,3]dioxol]-8'(6'H)-one (**19**): white solid, m.p. 234-236 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.05-2.13(m, 1H), 2.20-2.28(m, 1H), 2.80-2.96(m, 4H), 3.29(dd, J_1 = 13.8 Hz, J_2 = 5.1 Hz, 1H), 3.53-3.59(m, 1H), 4.49 (d, J = 5.1 Hz, 1H), 4.55(dd, J_1 = 10.8 Hz, J_2 = 7.7 Hz, 1H), 4.65-4.68(m, 1H), 5.89-5.95(m, 4H), 6.36(s, 1H), 6.58(dd, J_1 = 8.1 Hz, J_2 = 1.6 Hz, 1H), 6.65(d, J = 1.6 Hz, 1H), 6.69(d, J = 8.1 Hz, 1H), 7.70(s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.68, 29.46, 31.21, 43.52, 43.74, 50.84, 53.49, 70.11, 101.01, 101.63, 107.78, 109.08, 110.79, 111.20, 124.27, 132.25, 133.15, 133.26, 146.71, 147.18, 147.36, 148.46, 173.80; HRMS (ESI): calc.for $C_{23}H_{20}O_6S_2Na$ $(M+Na)^+$ 479.0594, found: 479.0595.

9'-(benzo[d][1,3]dioxol-5-yl)-8a',9'-dihydro-5a'H-spiro[[1,3] dithiane-2,5'-furo[3',4':6,7]naphtho[2,3-d][1,3]dioxol]-8'(6'H)-one (**20**)：white solid, m.p. 281-284 °C, ^{1}H NMR (500 MHz, $CDCl_3$)：δ 2.05-2.14(m, 1H), 2.23-2.27(m, 1H), 2.82-2.92(m, 2H), 2.96-3.04(m, 2H), 3.21-3.27(m, 1H), 3.33(dd, J_1 = 13.7 Hz, J_2 = 11.1 Hz, 1H), 3.99(d, J = 11.0 Hz, 1H), 4.53(dd, J_1 = 10.6 Hz, J_2 = 8.0 Hz, 1H), 4.71(t, J = 7.2 Hz, 1H), 5.90(d, J = 3.6 Hz, 2H), 5.93(s, 2H), 6.23(s, 1H), 6.60(s, 1H), 6.77(s, 2H), 7.64(s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.61, 29.31, 30.54, 44.27, 46.39, 52.62, 56.53, 68.80, 101.03, 101.52, 108.20, 108.95, 109.14, 109.27, 123.09, 132.81, 134.08, 136.86, 146.60, 146.64, 147.91, 148.01, 174.95; HRMS (ESI): calc.for $C_{23}H_{20}O_6S_2Na$ $(M+Na)^+$ 479.0595, found: 479.0594.

Synthesis of 9'-(benzo[d][1,3]dioxol-5-yl)-8a',9'-dihydro-5a'H-spiro[[1,3]dithiane-2,5'-furo[3',4':6,7]naphtho[2,3-d][1,3]dioxol]-8'(6'H)-one (21)

A solution of **20** (1.50 g, 3.29 mmol) in 60 mL of 85:15 THF/H_2O was added to a suspension of HgO (1.55 g, 7.51 mmol) in 85:15 THF/H_2O at 0 °C under argon followed by $BF_3.Et_2O$ (0.52 mL, 7.51 mmol). The reaction mixture was stirred for 1 h at room temperature, and then CH_2Cl_2 (30 mL) was added and the precipitate filtered. concentrated in vacuo to give the crude product, which was isolated by silica column chromatography (ethyl acetate/petroleum ether, 3:7) to give **21** (0.96 g, 80%): white solid, m.p. 216-218 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.01(dd, J_1 = 15.5 Hz, J_2 = 11.4 Hz, 1H), 3.39(ddd, J_1 = 15.5 Hz, J_2 = 10.6 Hz, J_3 = 7.0 Hz, 1H), 4.23(d, J = 11.4 Hz, 1H), 4.42(dd, J_1 = 10.5 Hz, J_2 = 9.5 Hz, 1H), 4.63(dd, J_1 = 9.3 Hz, J_2 = 7.0 Hz, 1H), 5.96-6.01(m, 4H), 6.39(s, 1H), 6.57(s, 1H), 6.75(d, J = 7.2 Hz, 1H), 6.82(d, J = 7.9 Hz, 1H), 7.44(s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 47.43, 47.52, 49.67, 66.22, 101.26, 102.25, 105.52, 108.49, 109.63, 127.95, 134.00, 143.72, 147.20, 147.61, 148.18, 152.99, 172.79, 192.15; HRMS (ESI): calc.for $C_{20}H_{14}O_7Na$ $(M+Na)^+$ 389.0632, found: 389.0632.

Synthesis of 5-(benzo[d][1,3]dioxol-5-yl)-9-hydroxy-5,5a,8a,9-tetrahydrofuro[3',4':6,7]naphtho[2,3-d][1,3]dioxol-6(8H)-one (22)

To a mixture of **21** (500 mg, 1.37 mmol) in THF (20 mL) $NaBH_4$ (150 mg, 4.01 mmol) was added and allowed to react at room temperature, for 1h. The reaction was quenched with a saturated NH_4Cl solution. The aqueous phase was extracted with Et_2O (3×20 mL). The collected organic phases were dried, concentrated in vacuum, and purified by flash chromatography (dichloromethane/acetone, 20:1) to give **22** (353 mg, 70%): white solid, m.p.

261-263°C ; ^{1}H NMR (500 MHz, *d*-DMSO): δ 2.53-2.56(m, 1H), 3.07(dd, J_1 = 13.8 Hz, J_2 = 11.5 Hz, 1H), 4.06(d, J = 11.4 Hz, 1H), 4.13(dd, J_1= 10.6 Hz, J_2= 8.6 Hz, 1H), 4.51(dd, J_1= 8.2 Hz, J_2= 7.1 Hz, 1H), 4.82(d, J = 10.0 Hz, 1H), 5.91(s, 1H), 5.94(s, 1H), 5.99(d, J = 3.6 Hz, 1H), 6.09(s, 1H), 6.70-6.72(m, 2H), 6.86(d, J = 7.8 Hz, 1H). 7.05(s, 1H); ^{13}C NMR (125 MHz, CDCl3): δ 45.18, 45.81, 46.78, 70.22, 70.67, 101.29. 101.41, 106.23, 108.32, 108.70, 109.57, 123.22, 133.45, 135.37, 137.94, 146.25, 146.39, 146.65, 147.65,175.85; HRMS (ESI): calc.for $C_{20}H_{16}O_7S_2Na$ $(M+Na)^+$ 391.0788, found: 391.0783.

Synthesis of 9-azido-5-(benzo[d][1,3]dioxol-5-yl)-5,5a,8a,9-tetrahydrofuro[3',4':6,7]naphtho[2,3-d][1,3]dioxol-6(8H)-one (24)

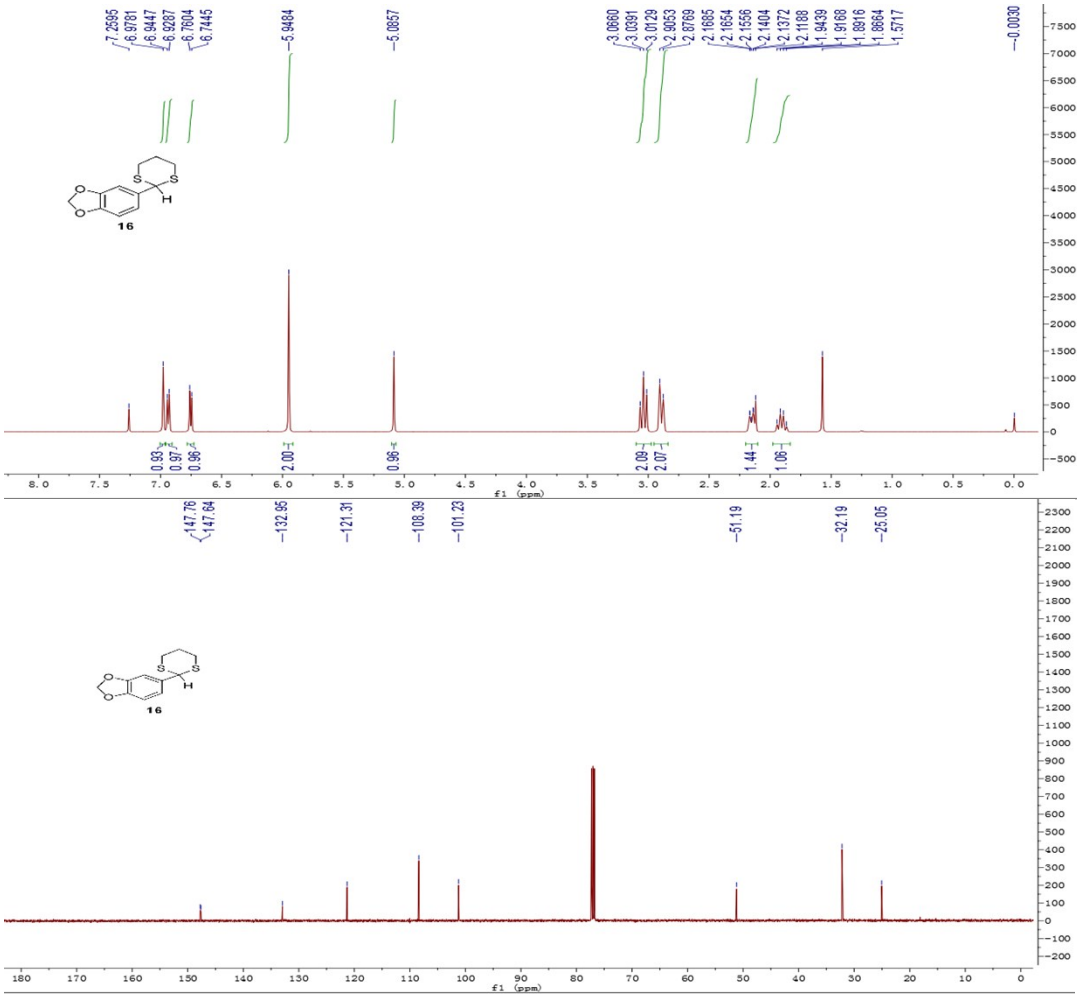
To a solution of **22** (294.4 mg, 0.80 mmol) and sodium azide (264.0 mg, 4.00 mmol) in $CHCl_3$ (20 mL), was added trifluoroacetic acid (1.6 mL, 2.07 mmol) dropwise in an ice bath. The reaction mixture was brought up to room temperature stirred for 5 h. Saturated aqueous sodium bicarbonate solution was added (2×20 mL). The organic layer was washed with water (1×20 mL), brine (1×20 mL) and dried over Na_2SO_4. After the solvent was removed, the crude product was purified by column chromatography (ethyl acetate/petroleum ether, 1:3) to afford compound **24** (267 mg, 85%): white solid, m.p. 174-176 °C ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.71-2.78(m, 1H), 2.99(dd, J_1 = 13.9, J_2 = 11.4 Hz, 1H), 3.99(d, J = 11.4 Hz, 1H), 4.25(dd, J_1 = 10.6 Hz, J_2 = 8.7 Hz, 1H), 4.36-4.40(m, 1H), 4.71 (d, J = 3.1 Hz, 1H), 5.95(d, J = 6.3 Hz, 4H), 6.42(s, 1H), 6.61(s, 1H), 6.71(s, 1H), 6.76(d, J = 8.2 Hz, 1H), 6.79(d, J = 8.2 Hz, 1H); ^{13}C NMR(125 MHz, $CDCl_3$): 42.20, 43.35, 45.84, 59.37, 67.09, 101.10, 101.70, 108.31, 108.83, 109.08, 110.62, 123.01, 126.00, 134.07, 136.11, 146.76, 147.77, 147.95, 148.96, 174.83; HRMS (ESI): calc.for $C_{20}H_{15}N_3O_6Na$ $(M+Na)^+$ 416.0853, found: 416.0863.

Synthesis of 9-amino-5-(benzo[d][1,3]dioxol-5-yl)-5,5a,8a,9-tetrahydrofuro[3',4':6,7]naphtho[2,3-d][1,3]dioxol-6(8H)-one (25)

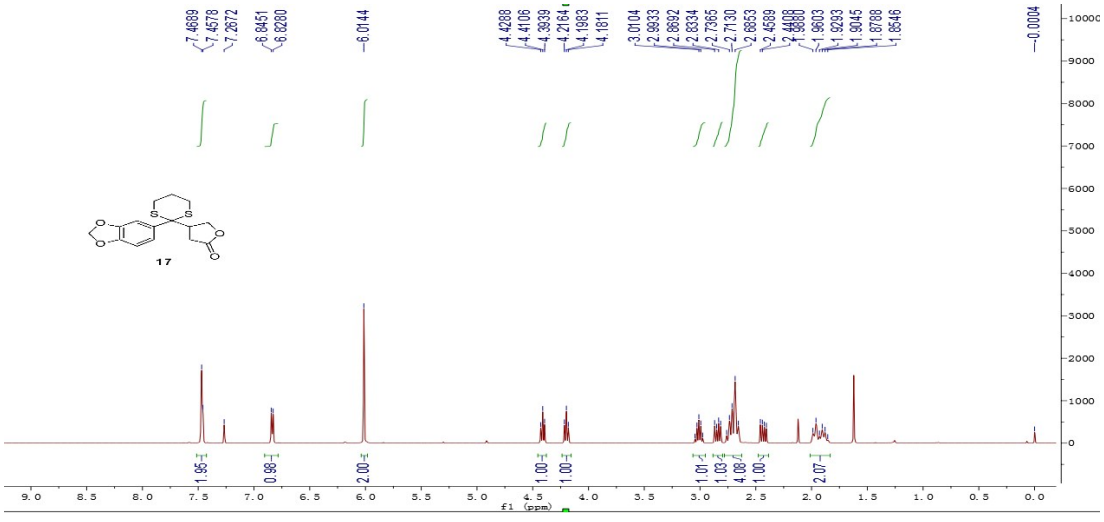
To a solution of **24** (100 mg, 0.25 mmol) in ethyl acetate (10 mL) was added 5% palladium on activated carbon (45 mg). The mixture was stirred overnight under hydrogen. The reaction mixture was filtered, and the filtrate was evaporated. The crude product was purified by column chromatography (dichloromethane/methanol, 120:1) to afford compound **25** (74 mg, 80%): white solid, m.p. 246-248 °C; ^{1}H NMR (500 MHz, *d*-DMSO) δ 2.07(s, 2H), 2.51-2.68(m, 1H), 3.19(dd, J_1 = 13.8 Hz, J_2 = 11.6 Hz, 1H), 3.91(d, J = 11.4 Hz, 1H), 3.99(d, J = 3.8 Hz, 1H), 4.25(dd, J_1 = 10.8 Hz, J_2 = 8.5 Hz, 1H), 4.34(t, J = 7.8 Hz, 1H), 5.90(s, 1H), 5.92(s, 1H), 5.99(d, J = 2.6 Hz, 2H), 6.08(s, 1H), 6.76-6.78(m, 2H), 6.86(d, J = 7.8 Hz, 1H), 6.88(s, 1H); ^{13}C NMR(125 MHz, *d*-DMSO): 40.39, 44.36, 45.97, 49.20, 68.39, 101.26, 101.38, 108.24, 108.81, 109.66, 109.78, 123.40, 133.09, 135.48, 137.93, 146.15, 146.21, 146.81, 147.67, 176.57; HRMS (ESI): calc.for $C_{20}H_{17}NO_6Na$ $(M+Na)^+$ 390.0948, found: 390.0963.

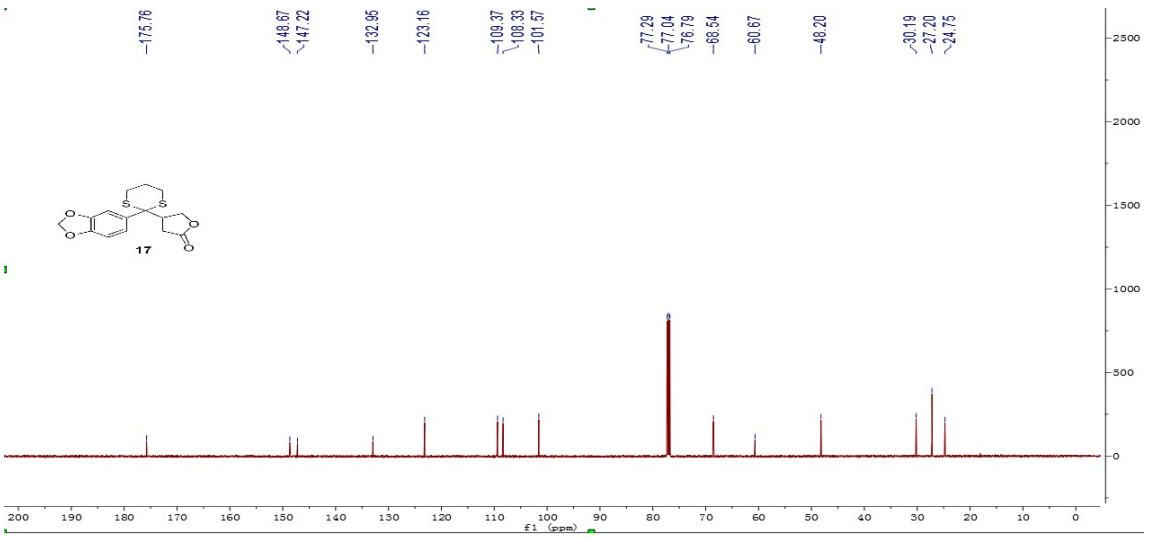
3. Copies of NMR Data for All Compounds.

^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of compound **16**.

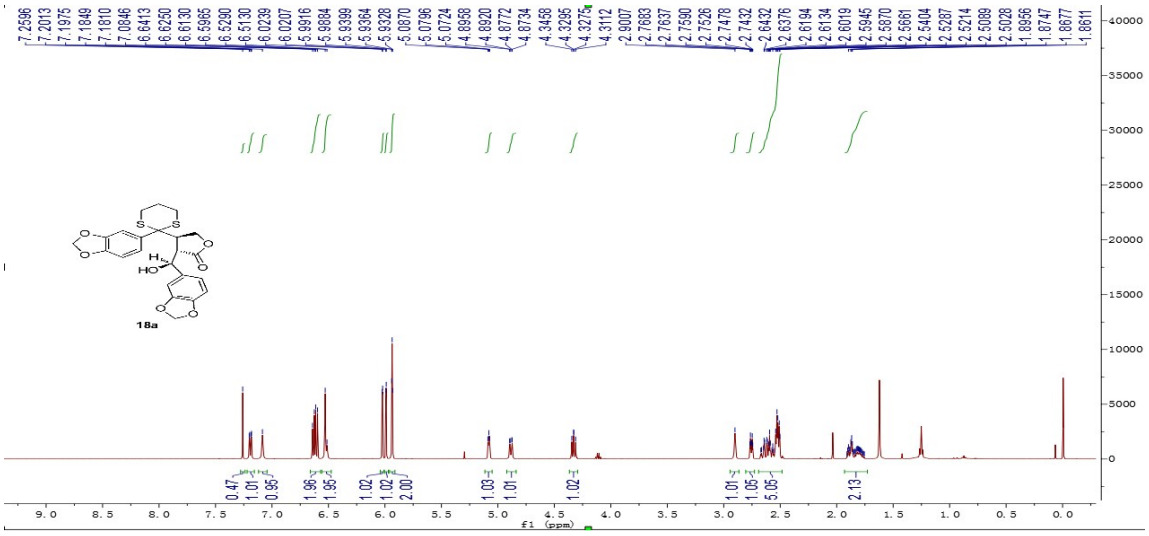


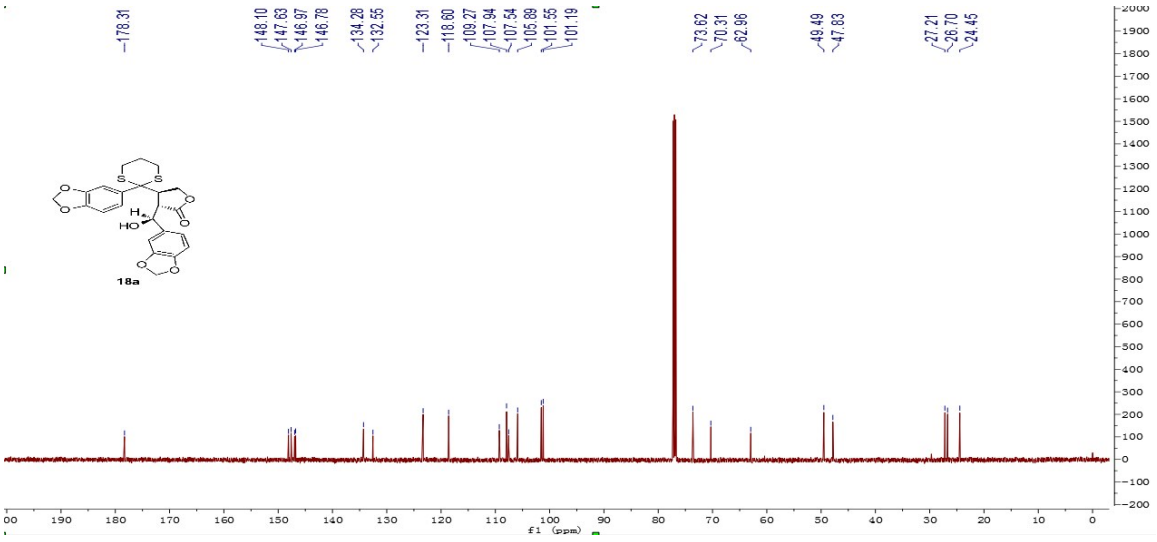
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of compound **17**.

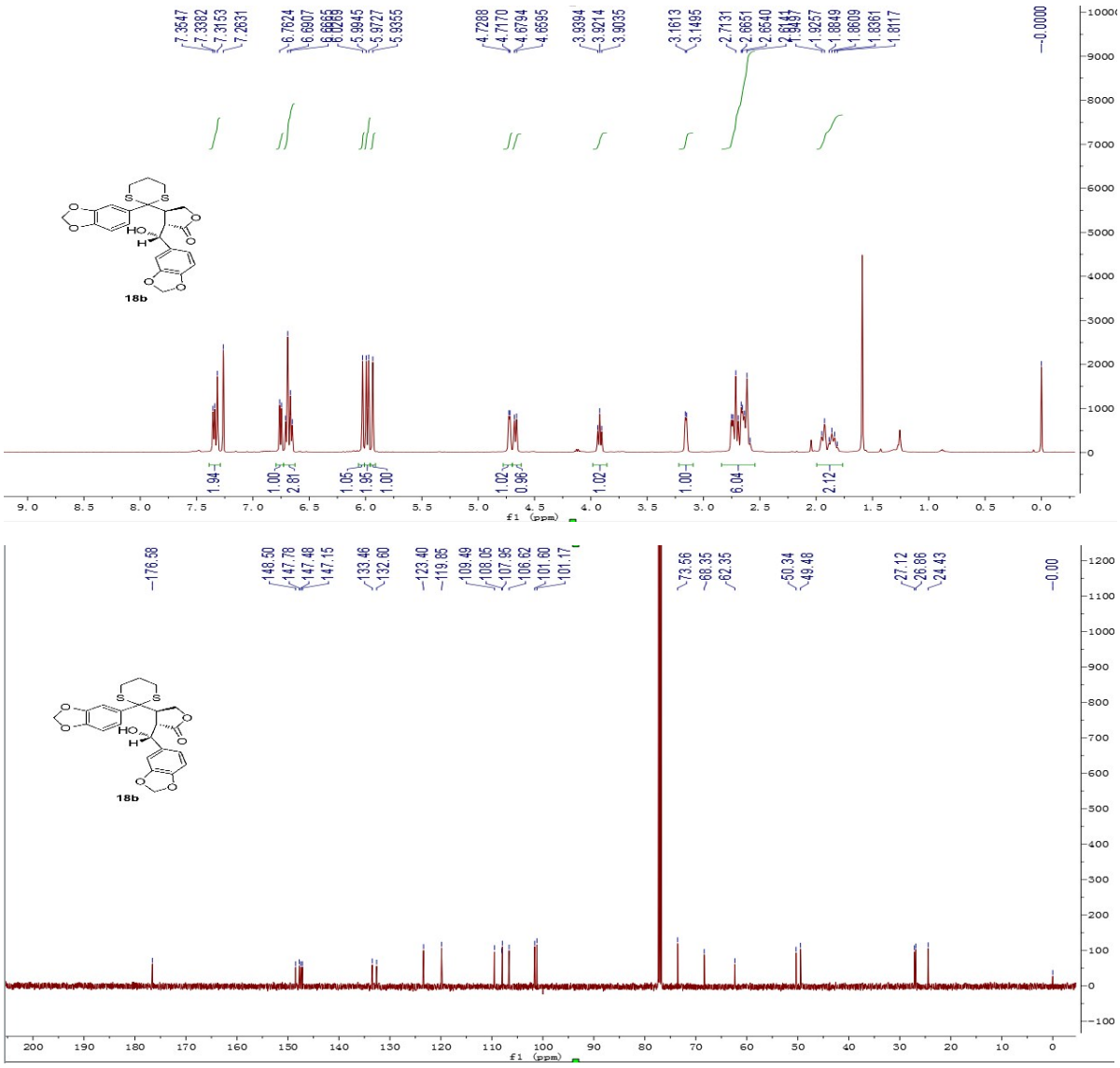




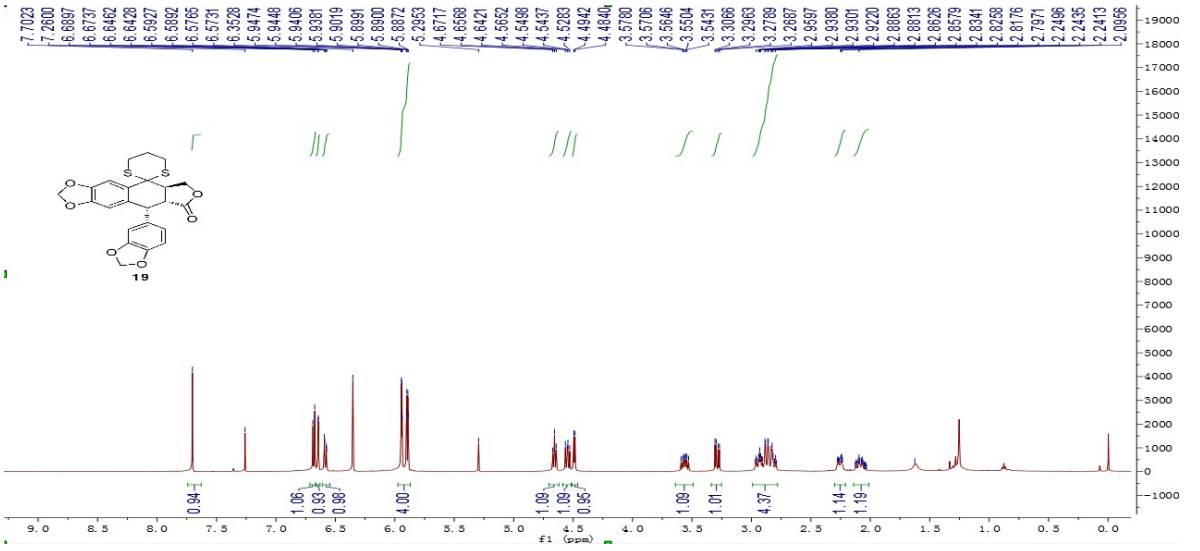
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of compound **18a** and **18b**.

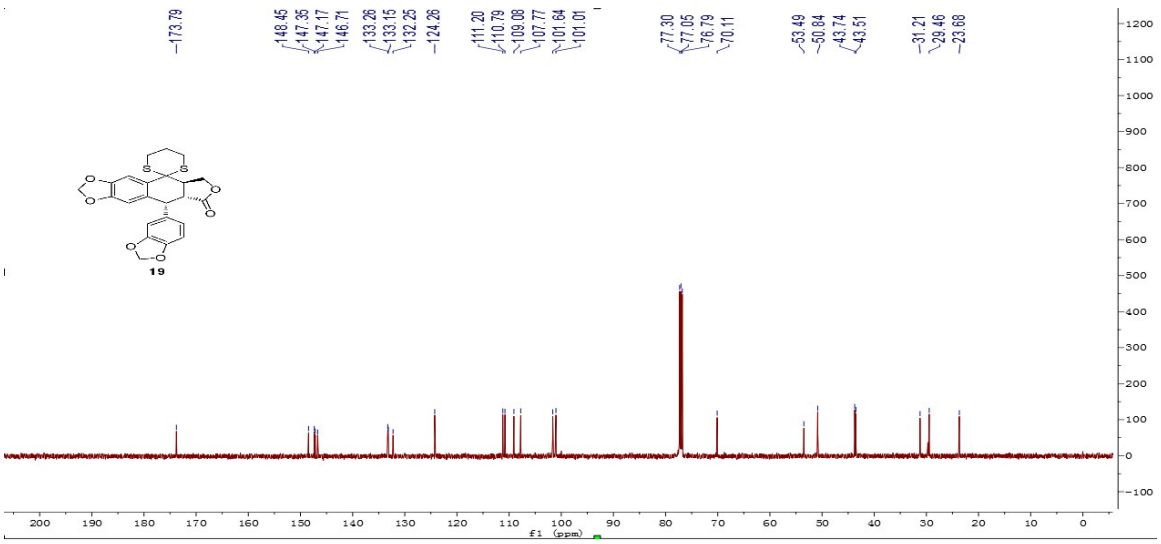




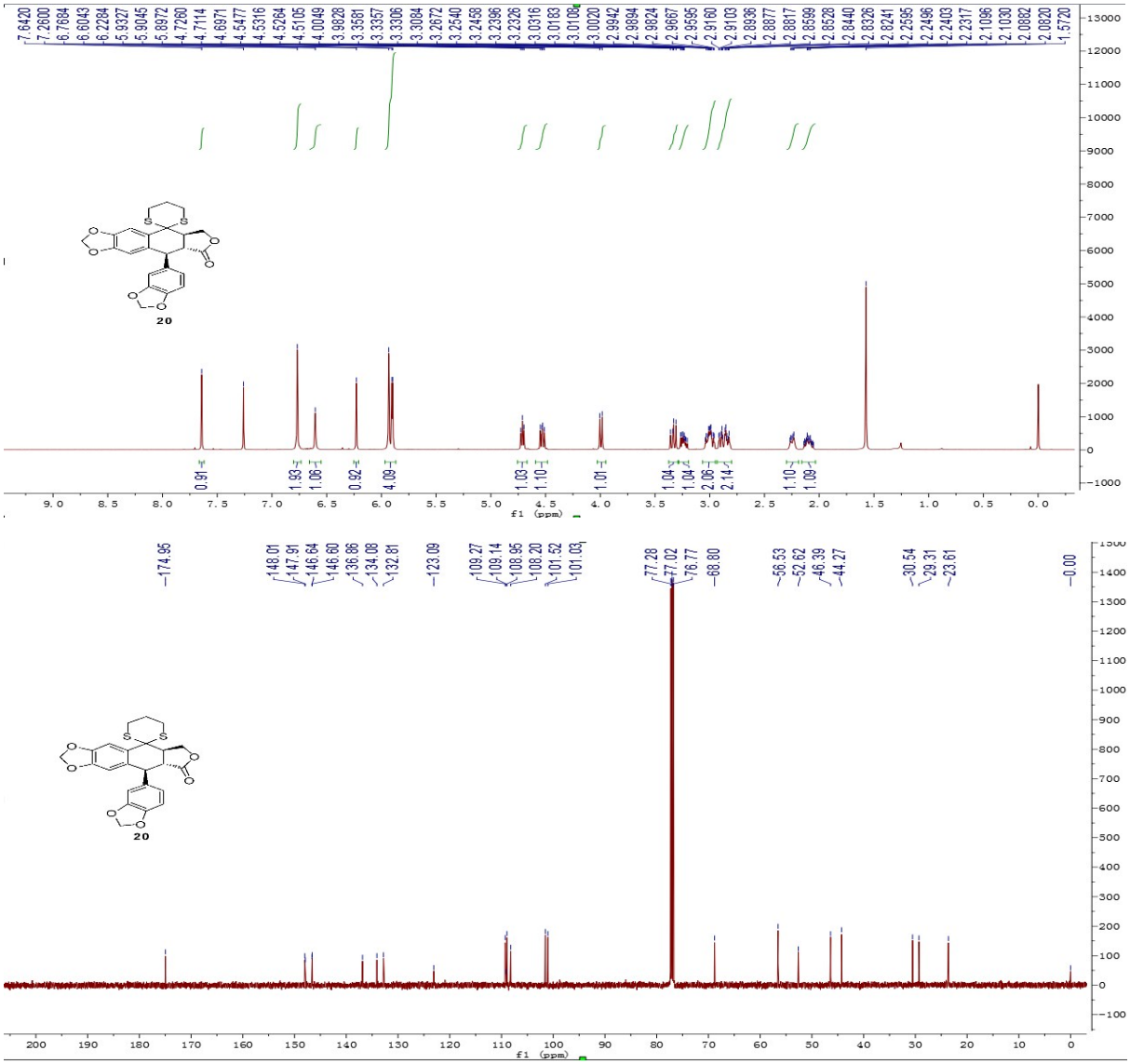


^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of compound **19**.

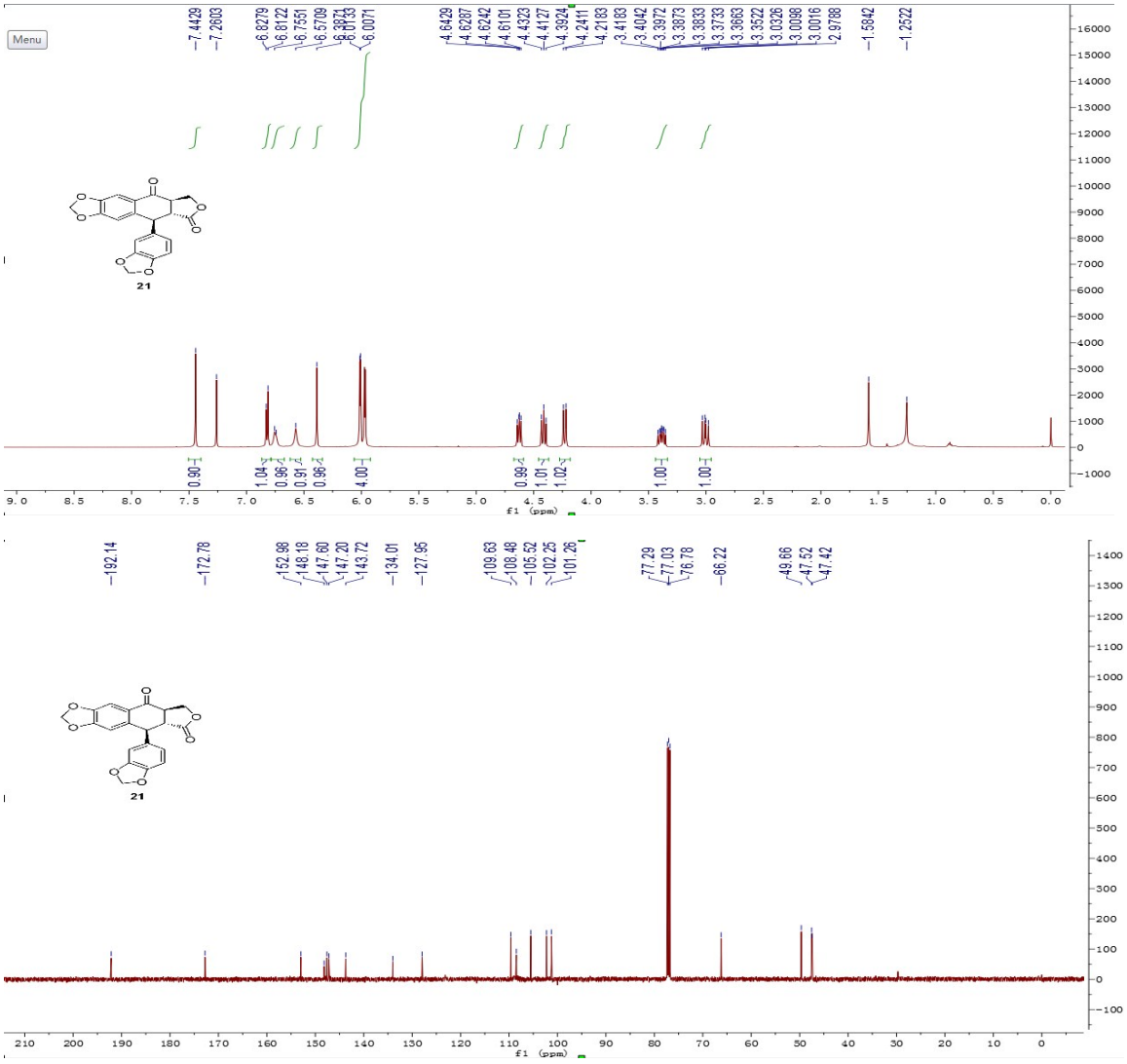




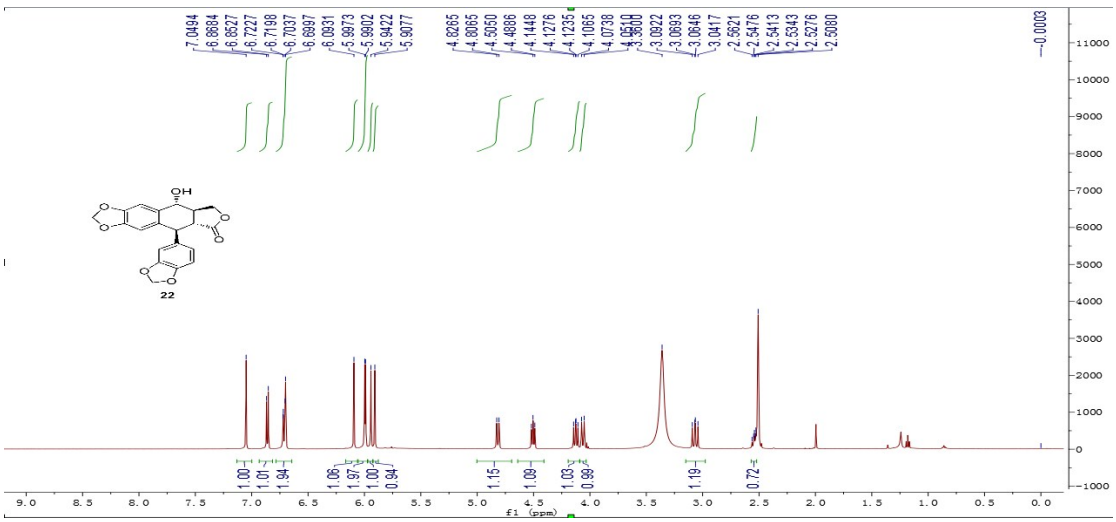
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of compound **20**.

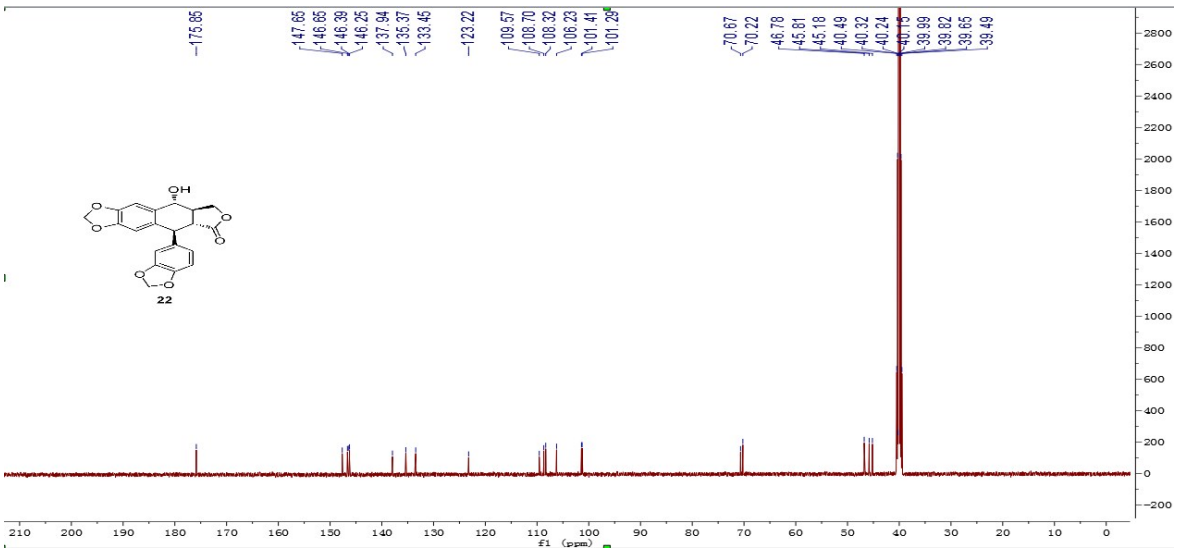


^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of compound **21**.

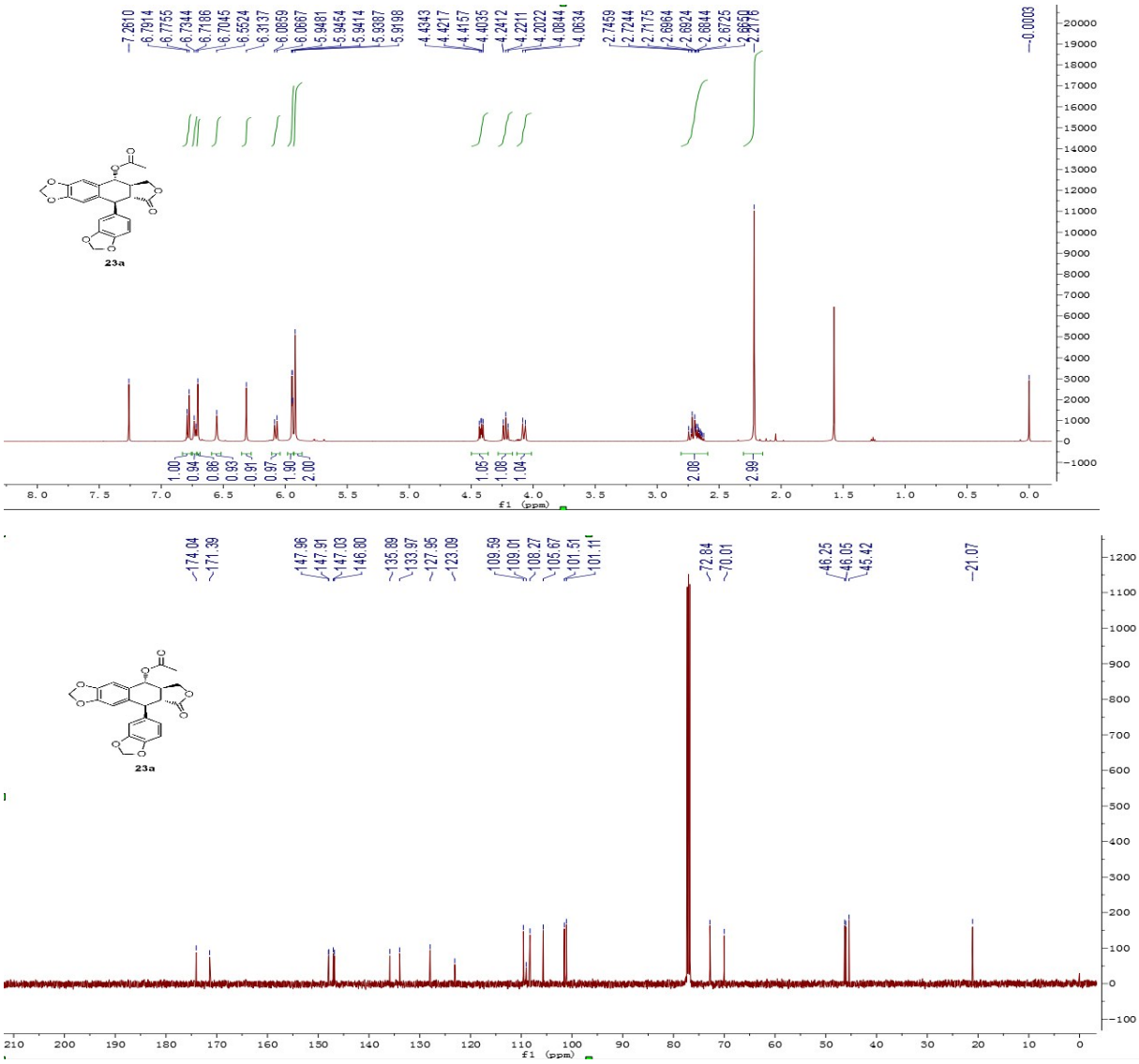


^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of compound **22**.

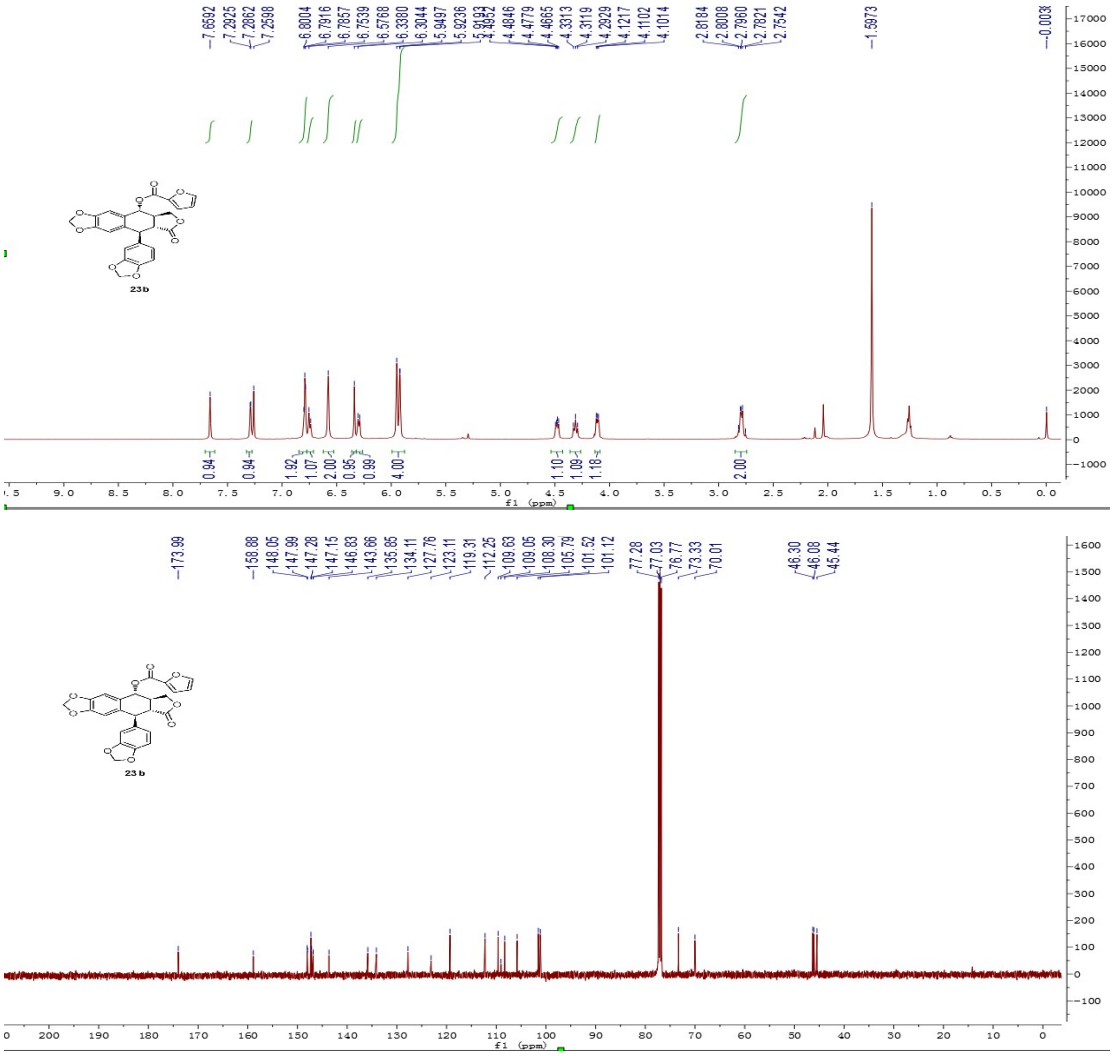




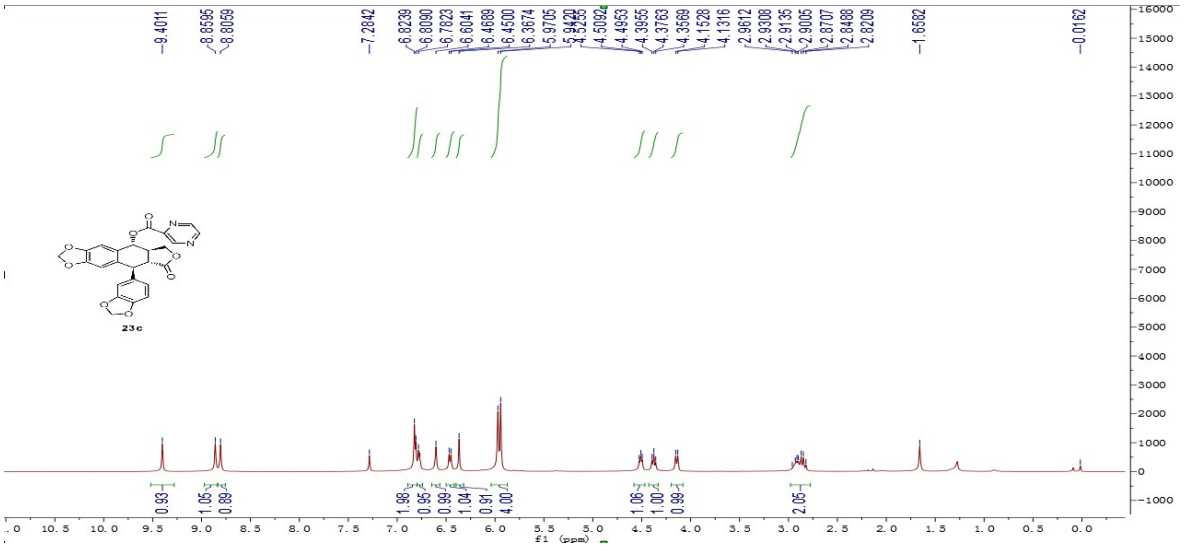
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of compound **23a**.

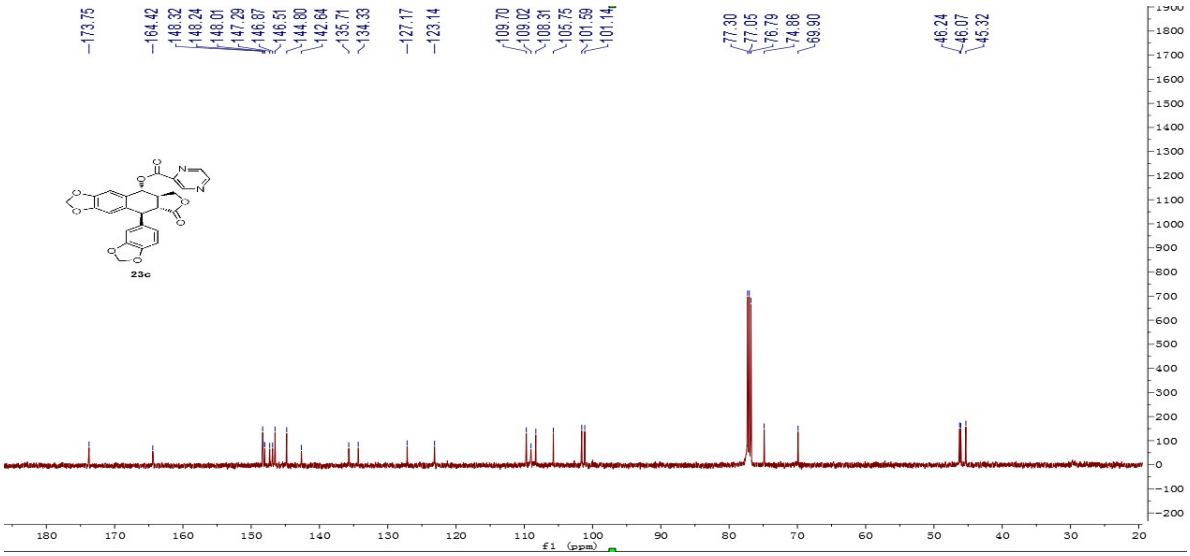


^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of compound **23b**.

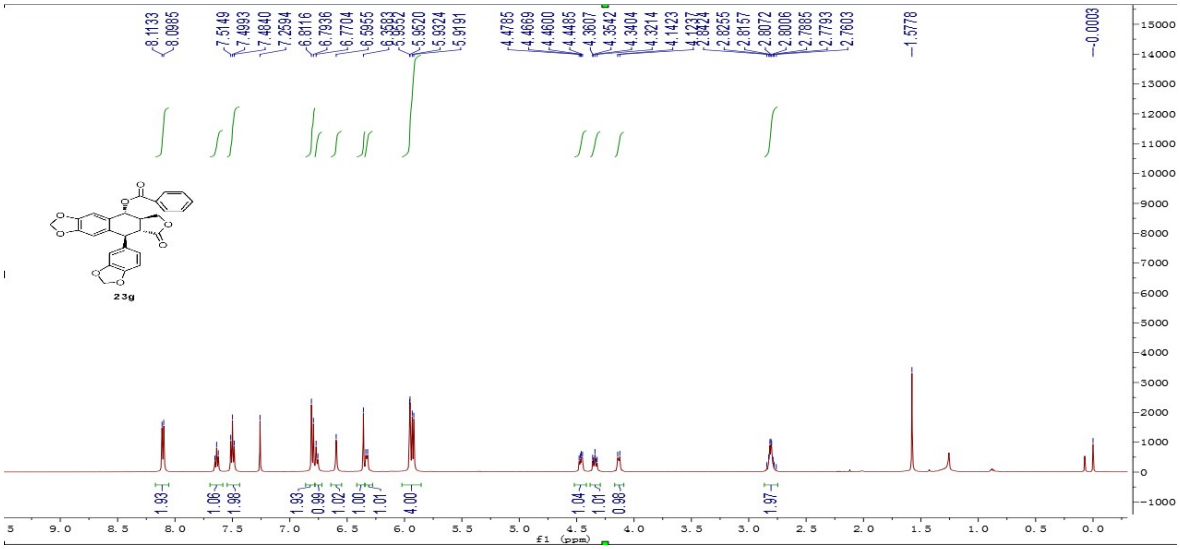


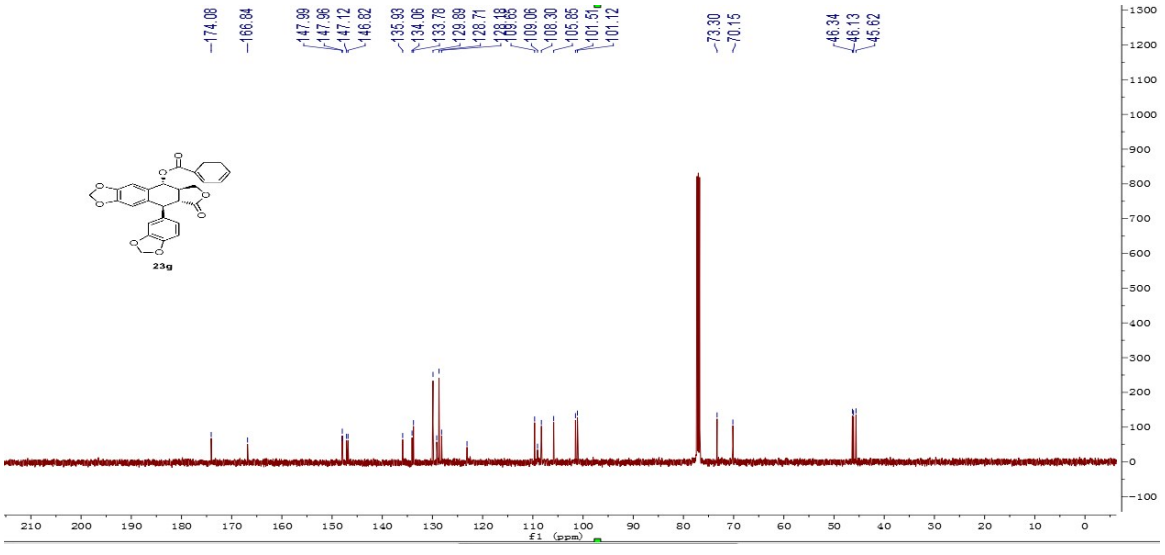
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of compound **23c**.



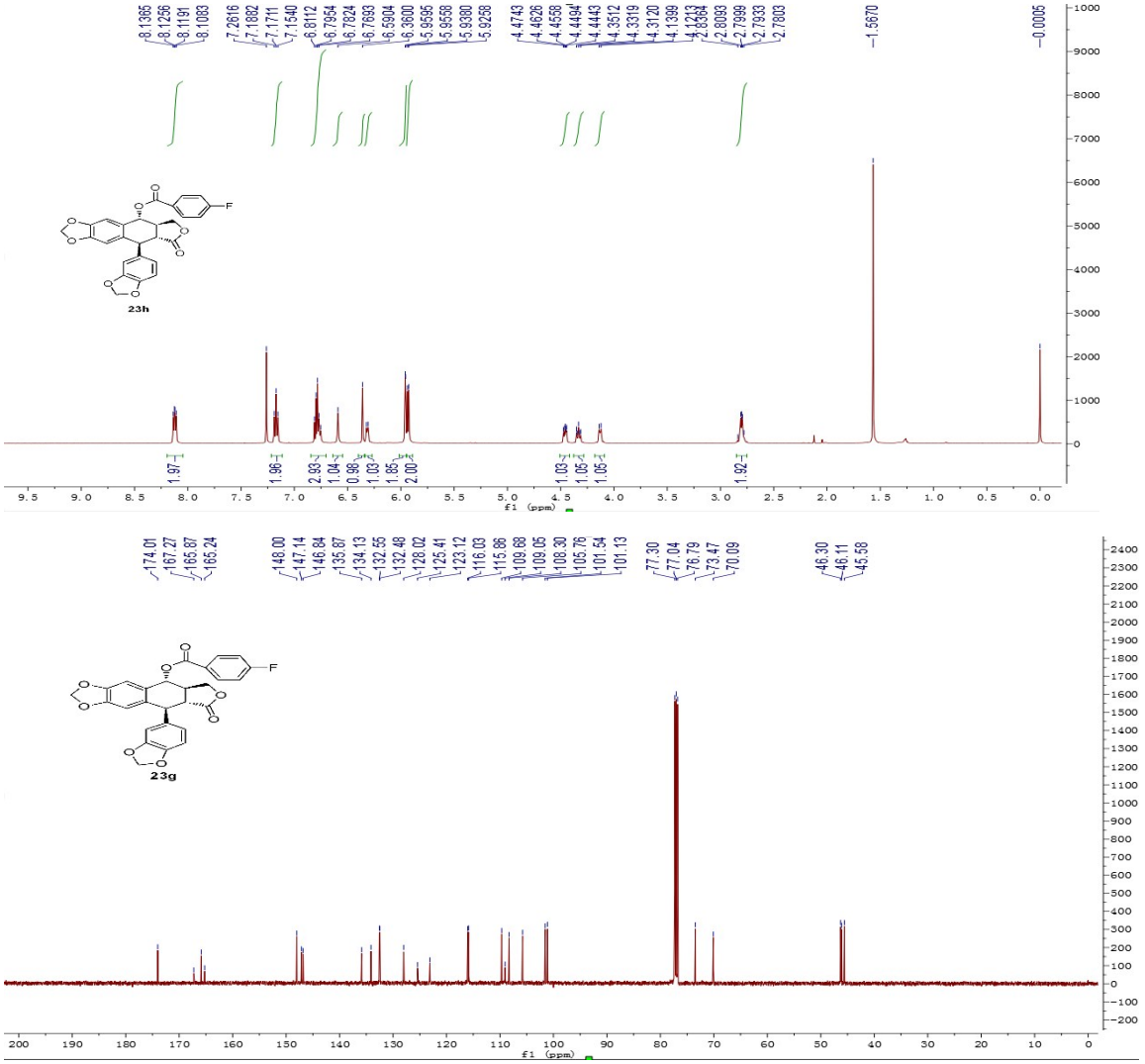


^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of compound **23g**.

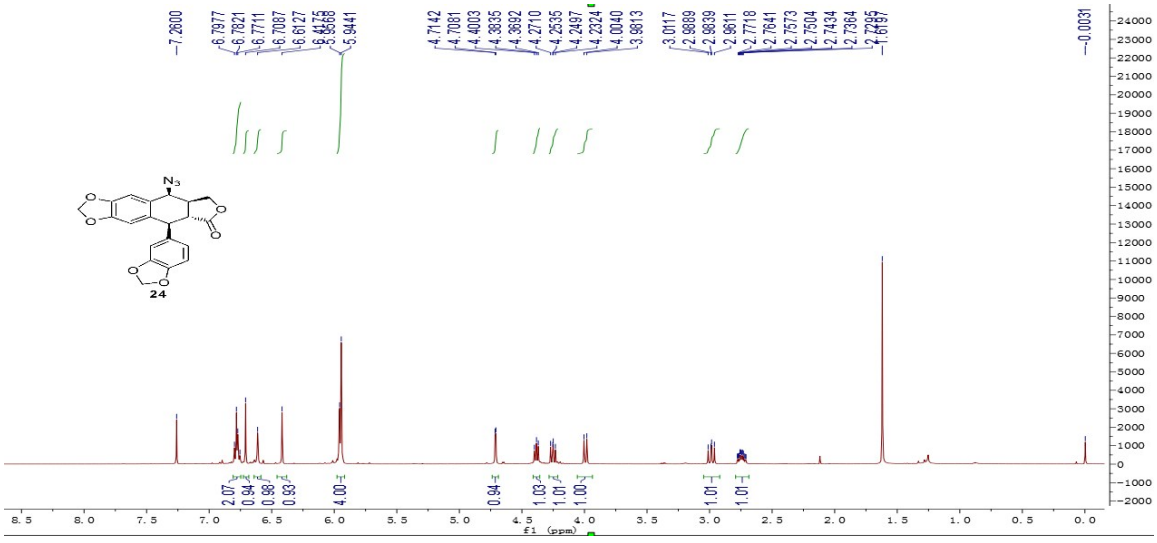


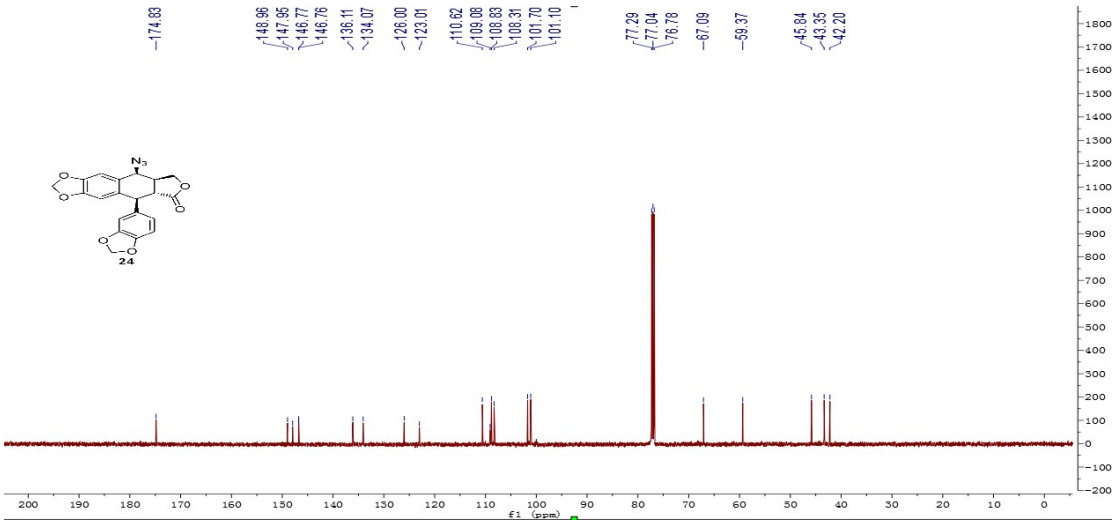


^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of compound **23h**.

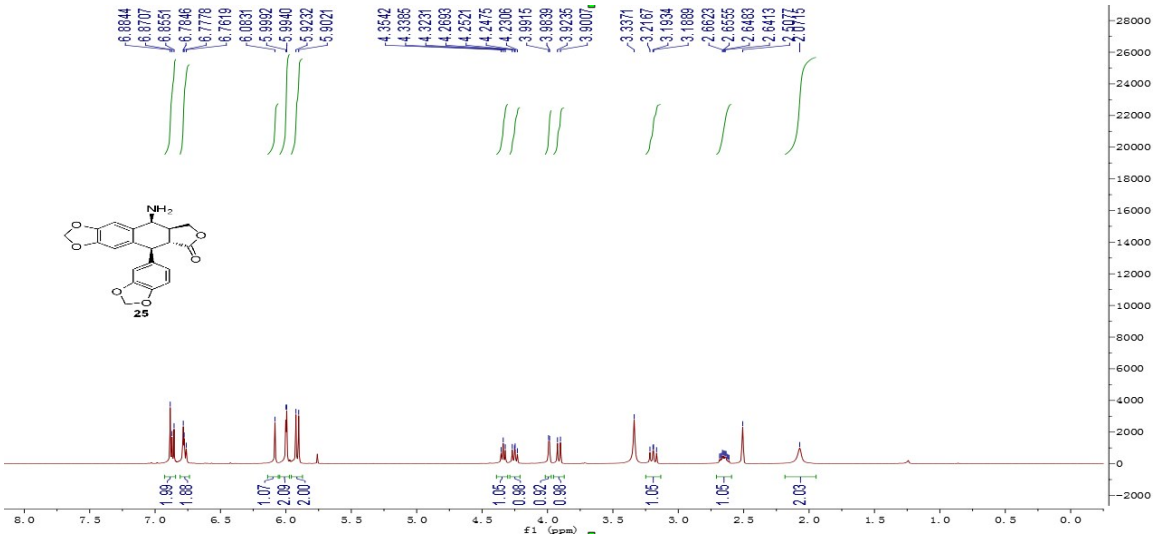


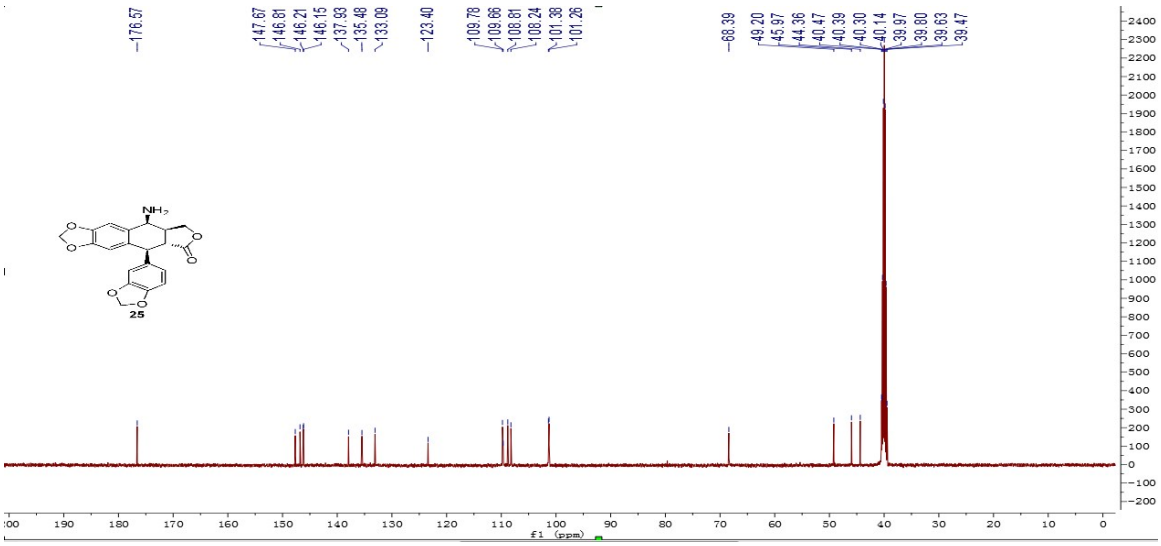
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of compound **24**.



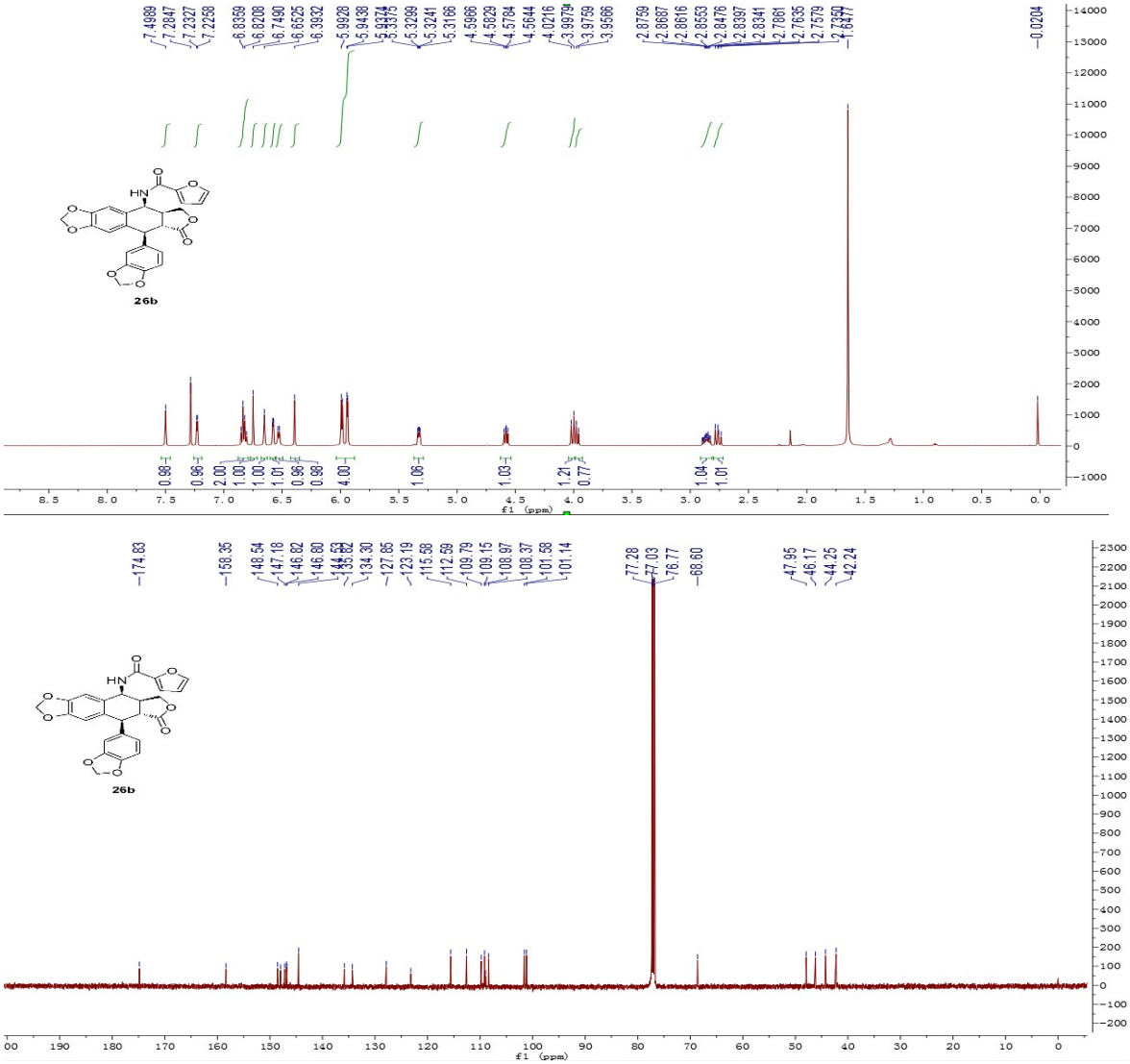


^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of compound **25**.

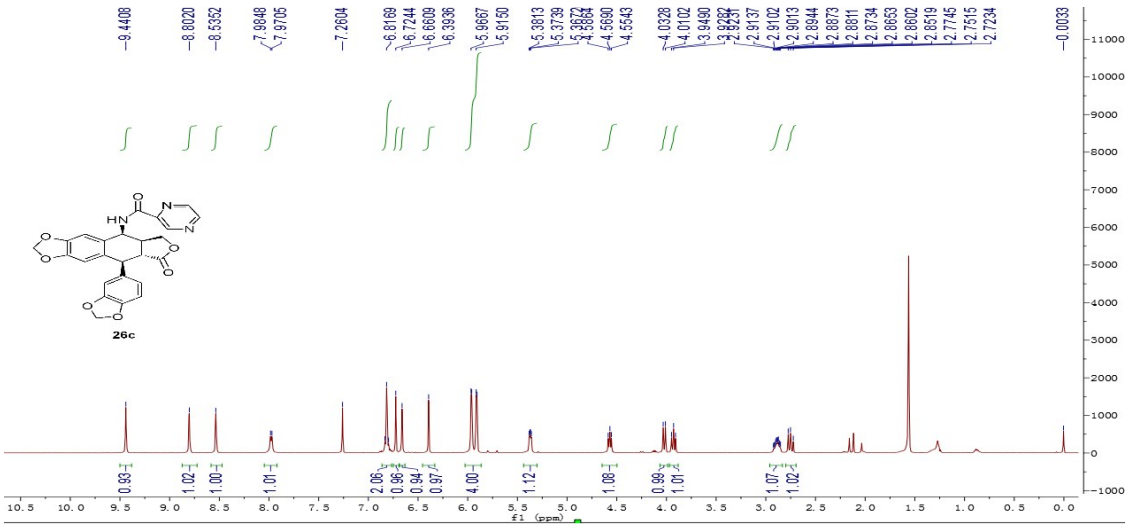


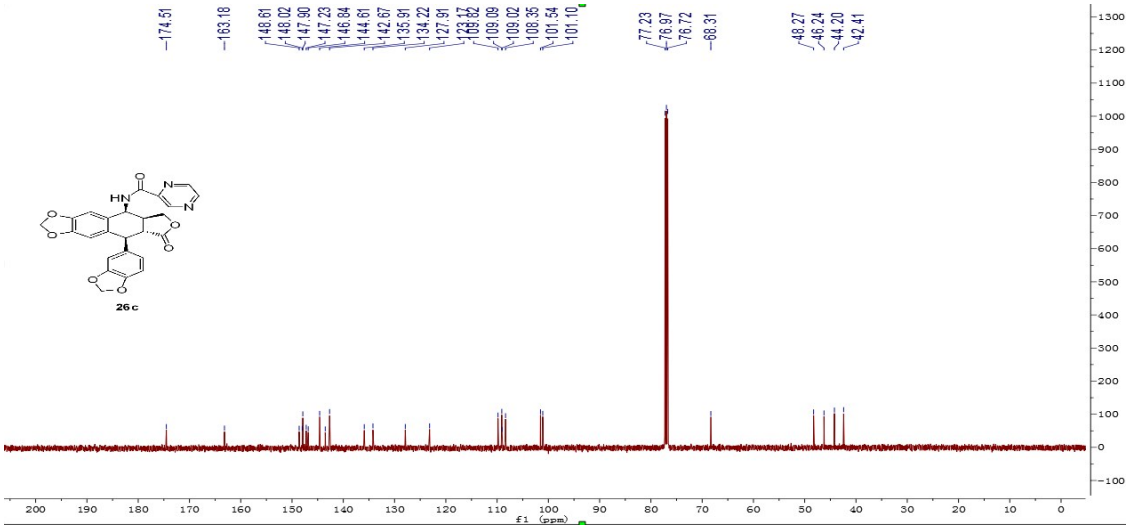


^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of compound **26b**.

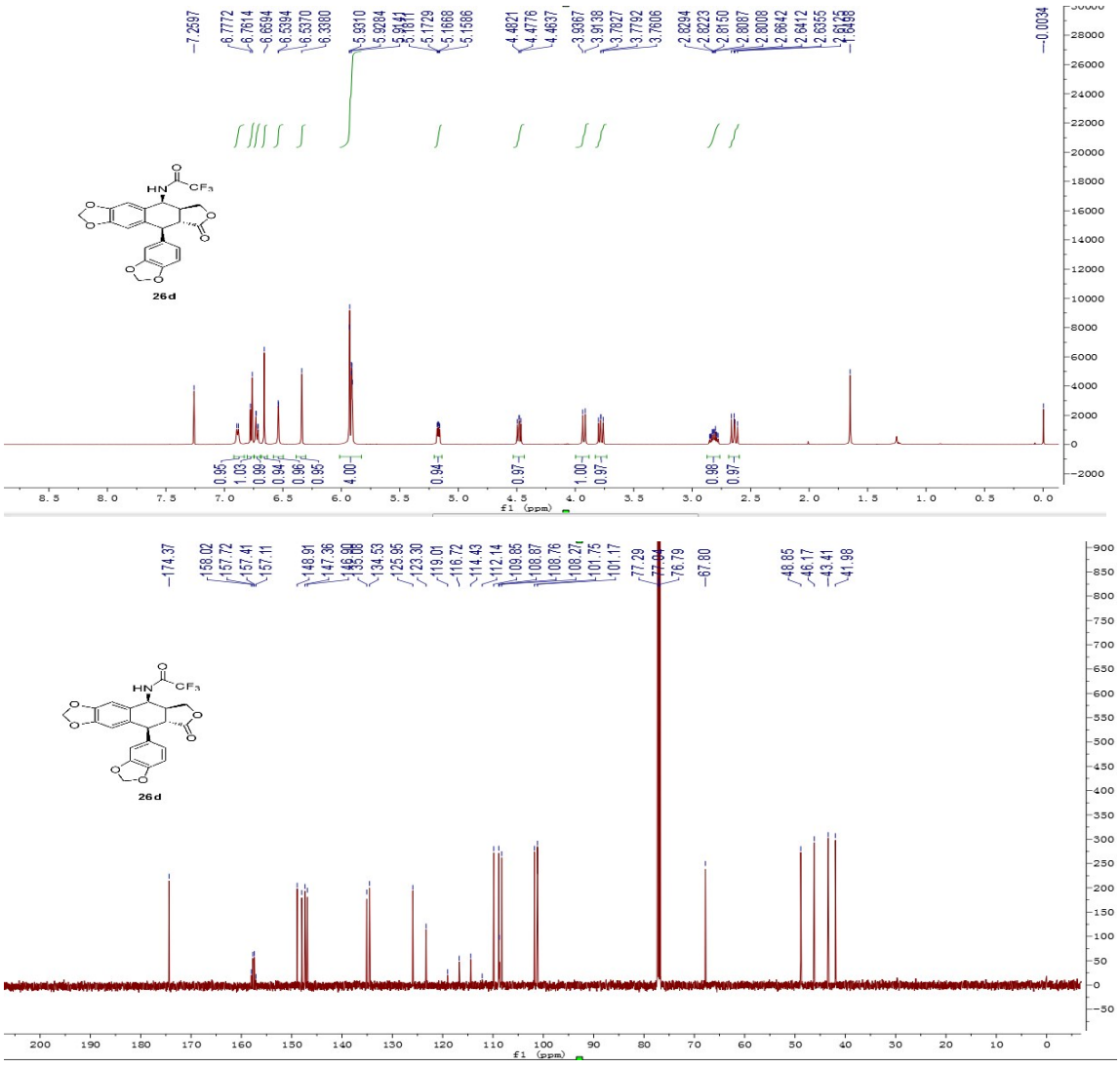


^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of compound **26c**.

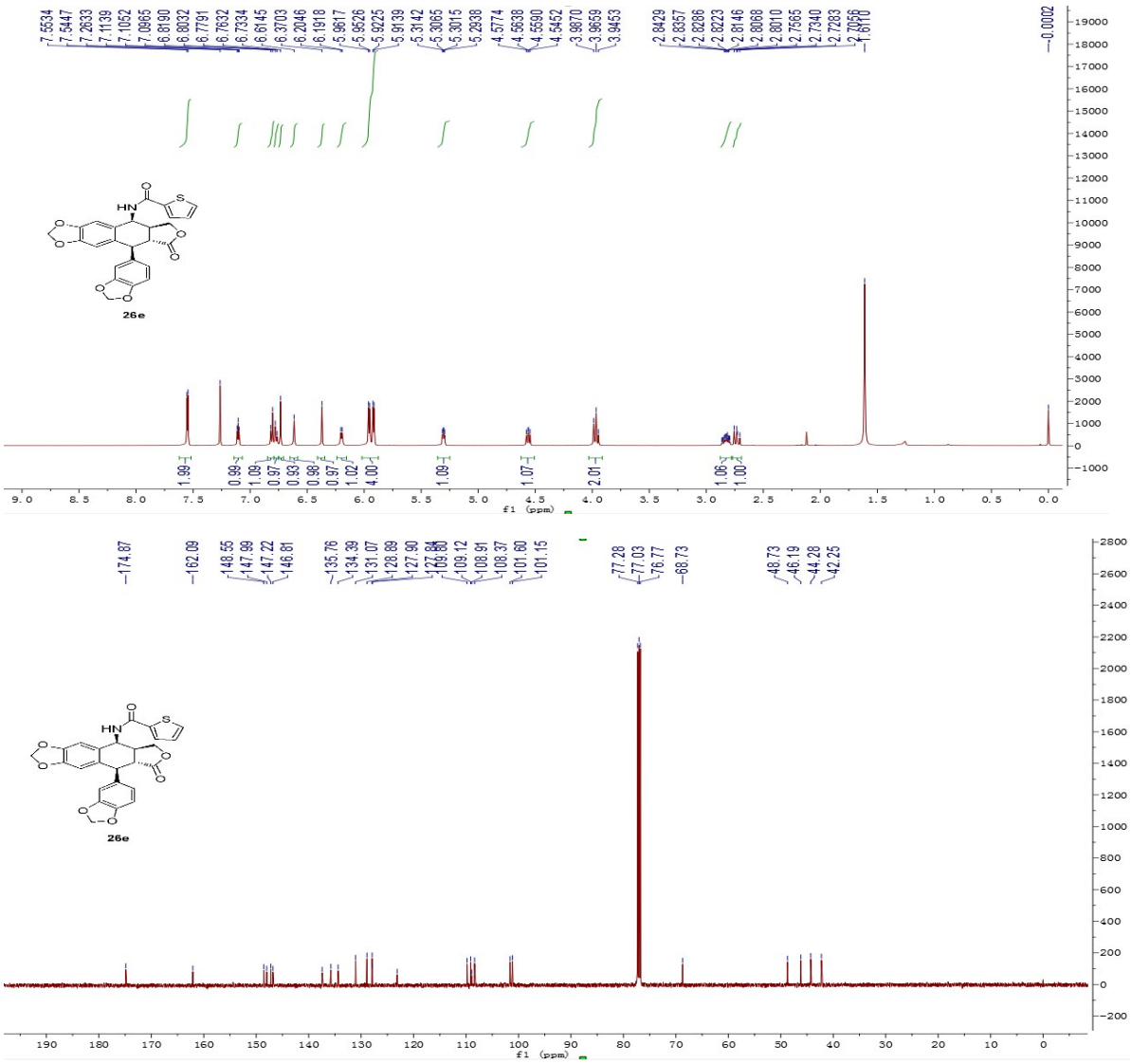




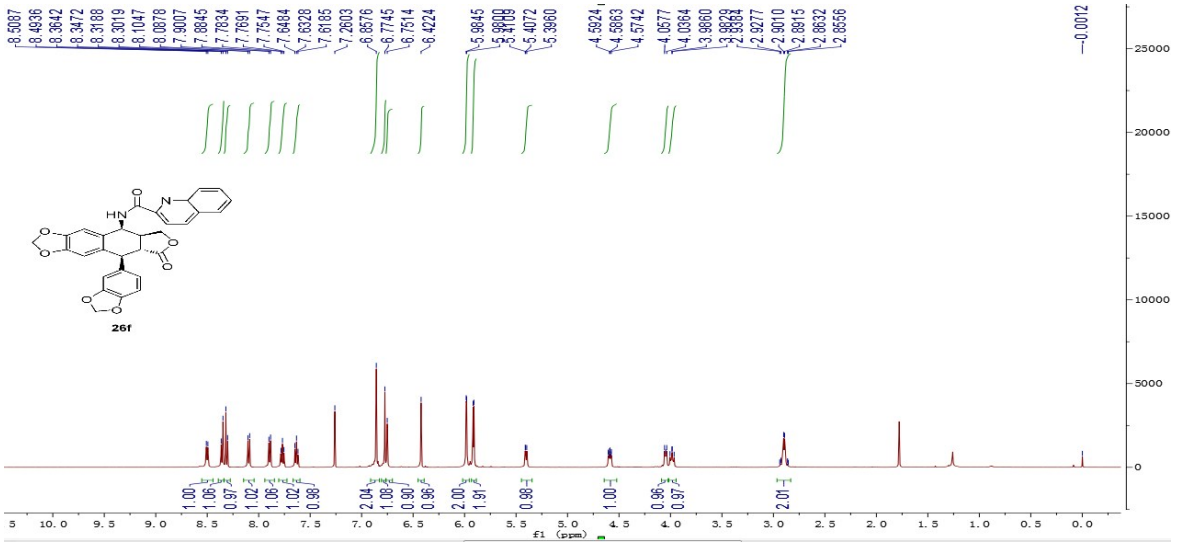
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of compound **26d**.

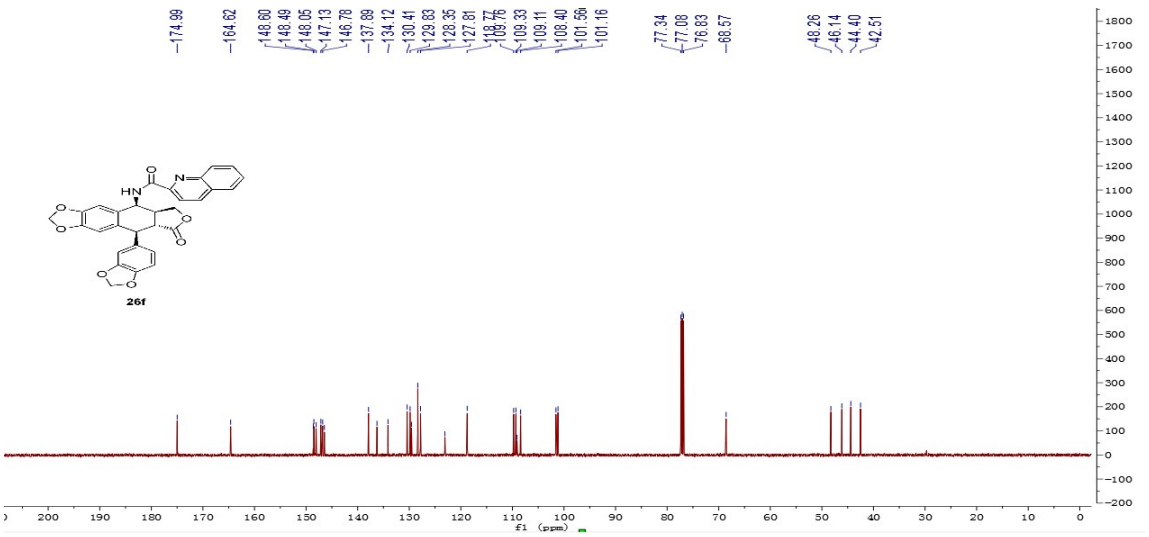


^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of compound **26e**.

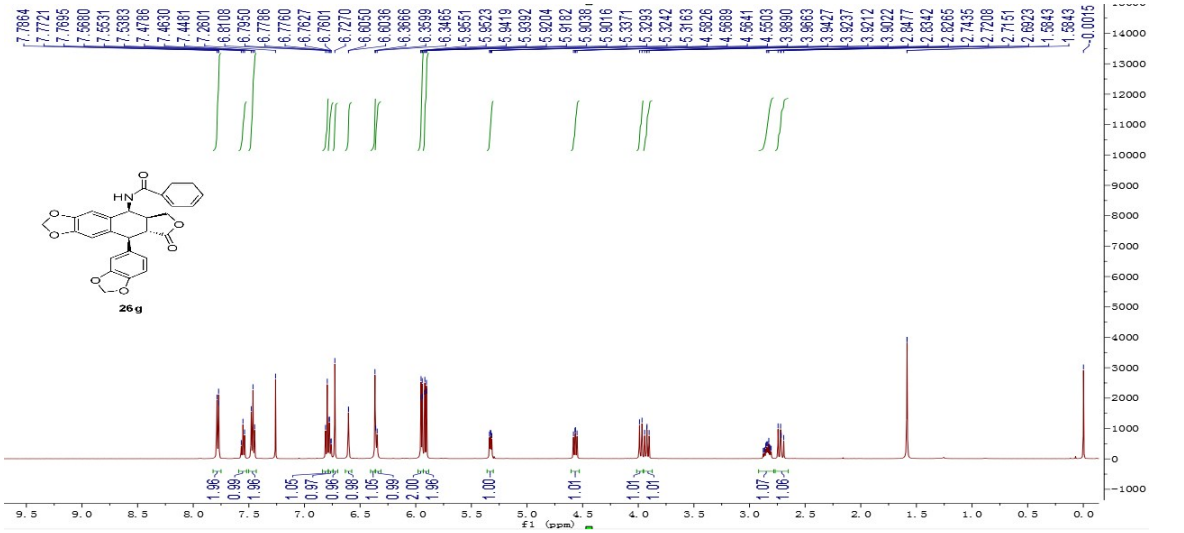


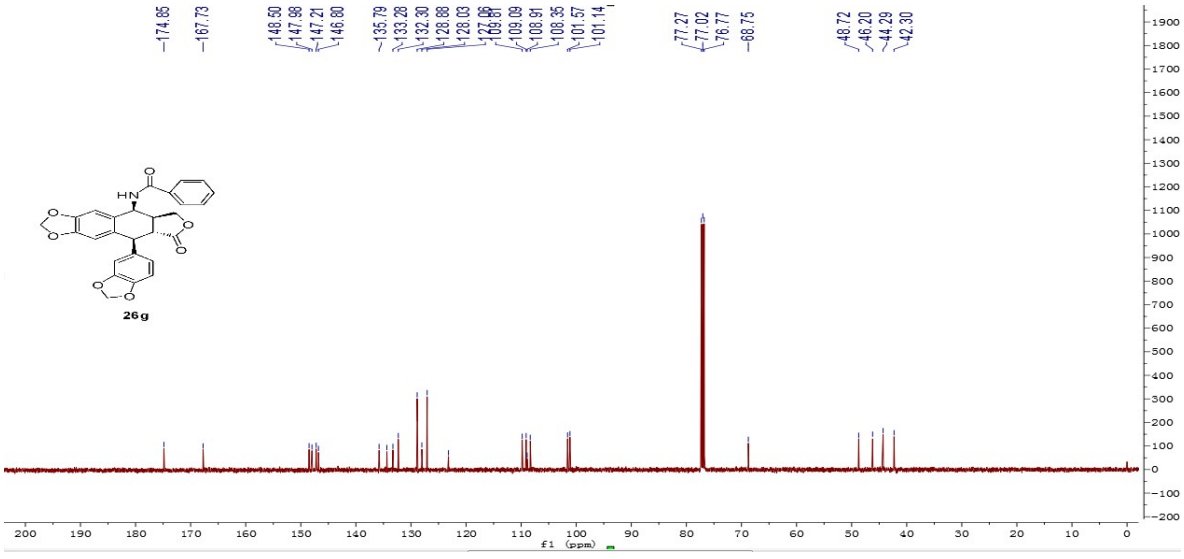
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of compound **26f**.



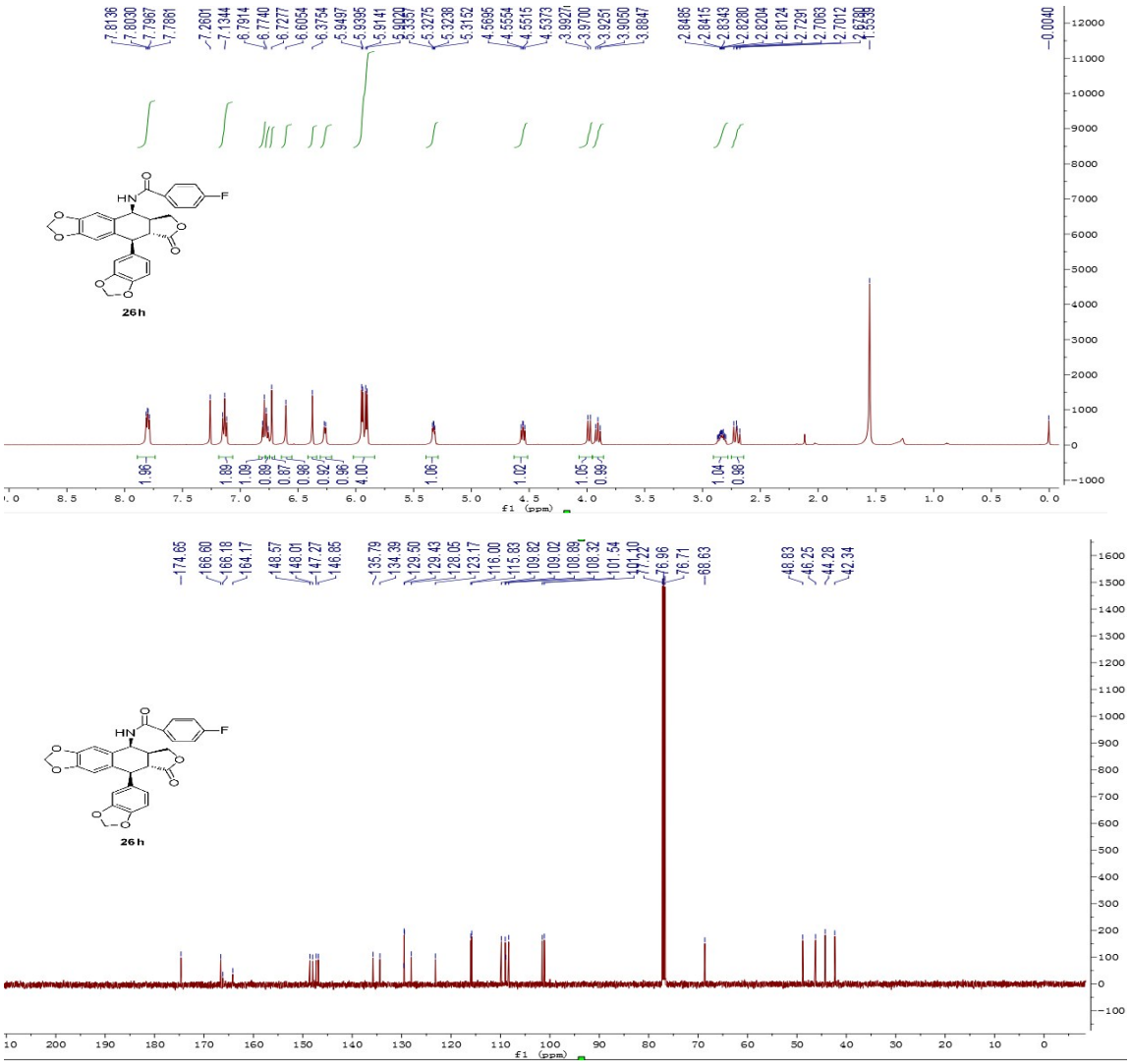


^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of compound **26g**.

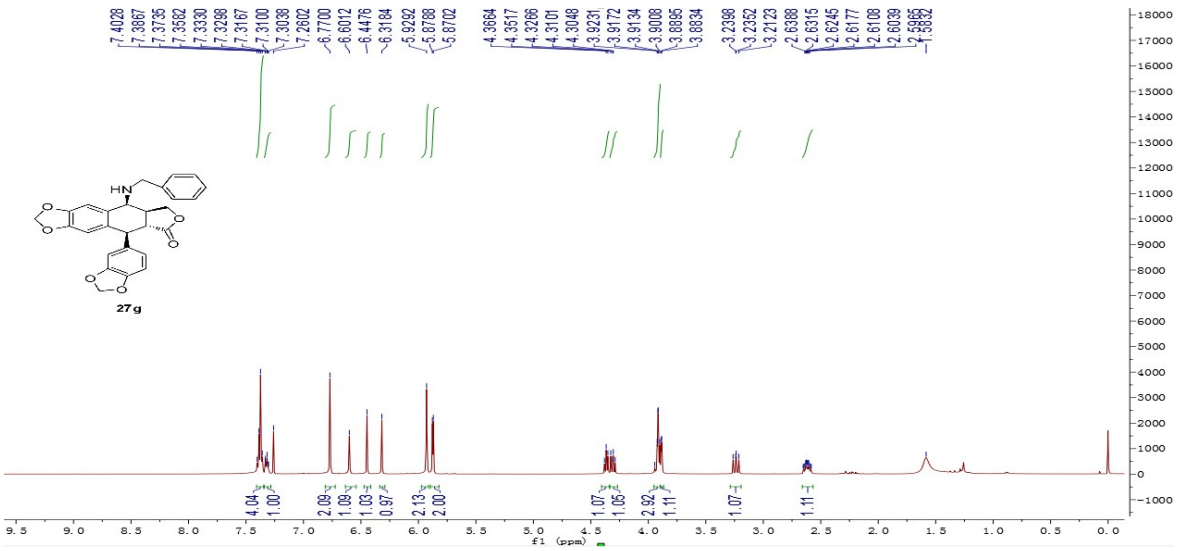


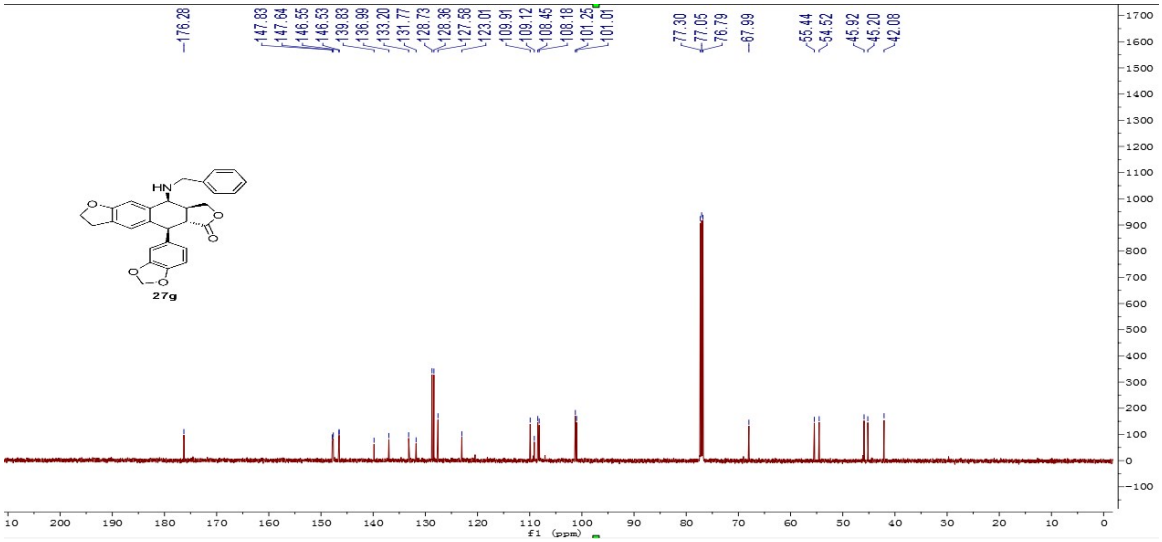


^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of compound **26h**.

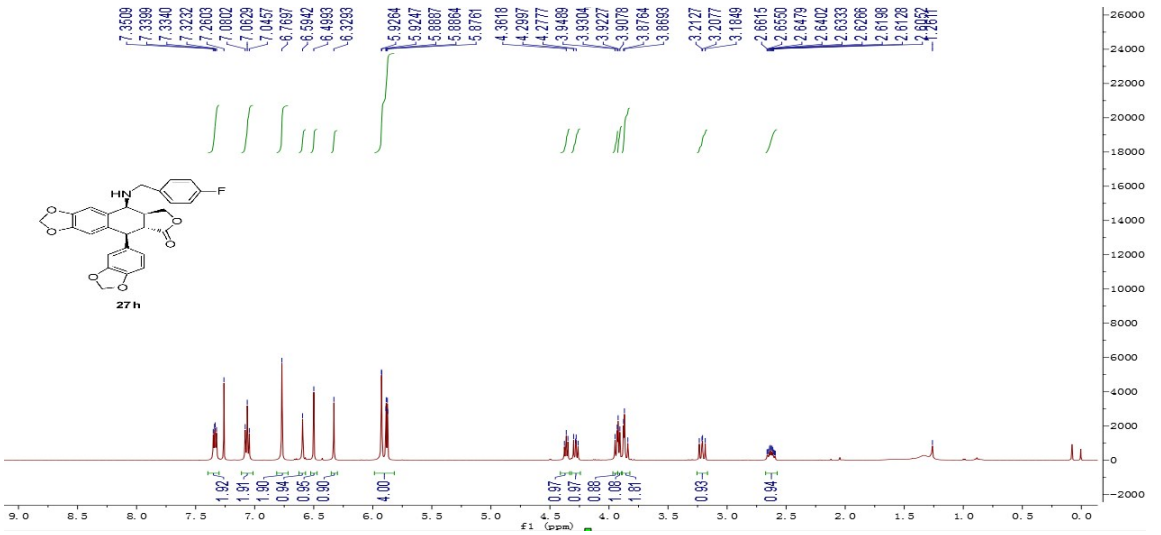


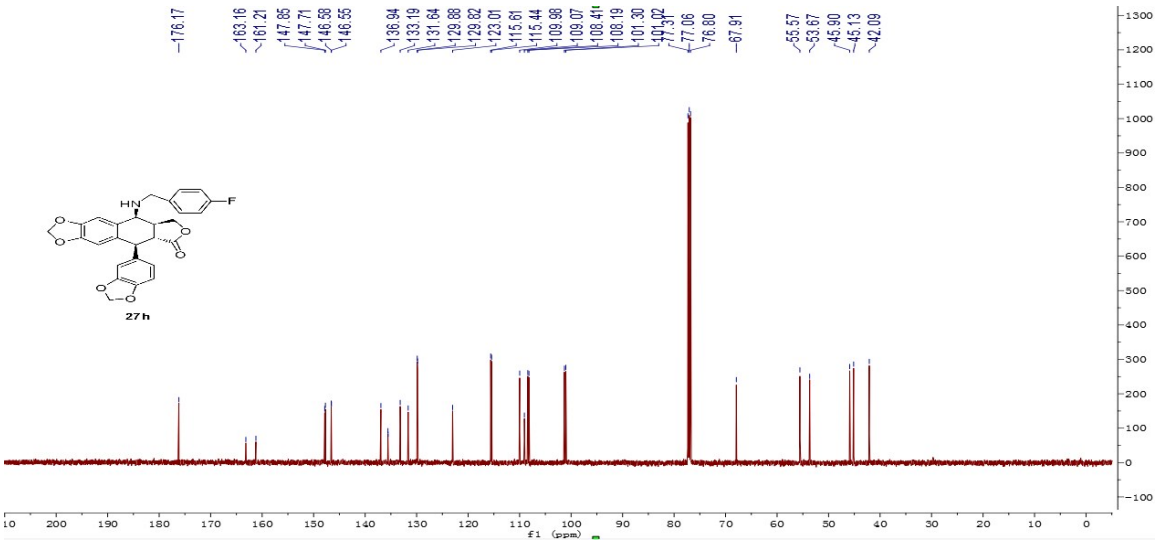
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of compound **27g**.



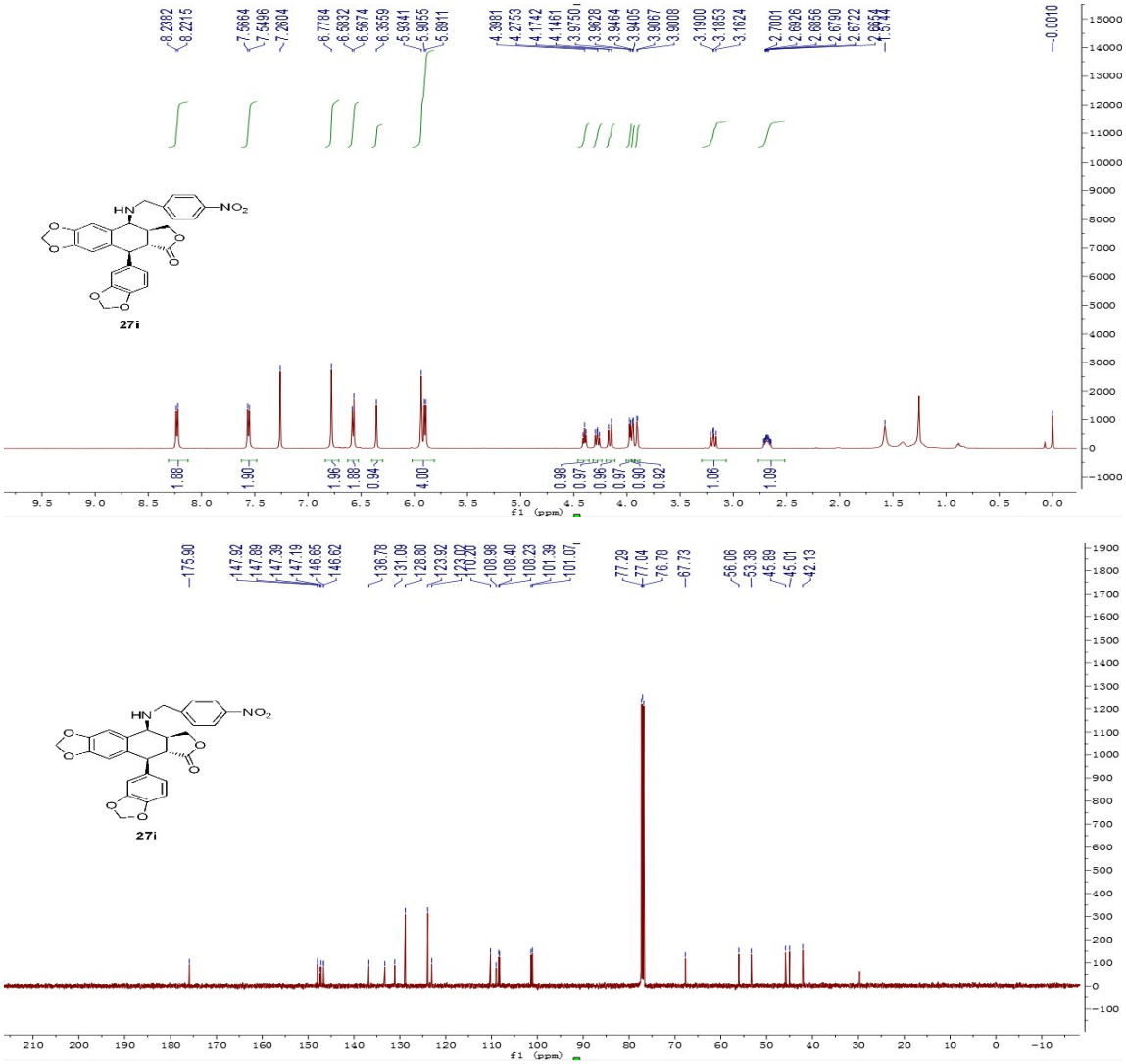


^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of compound **27h**.

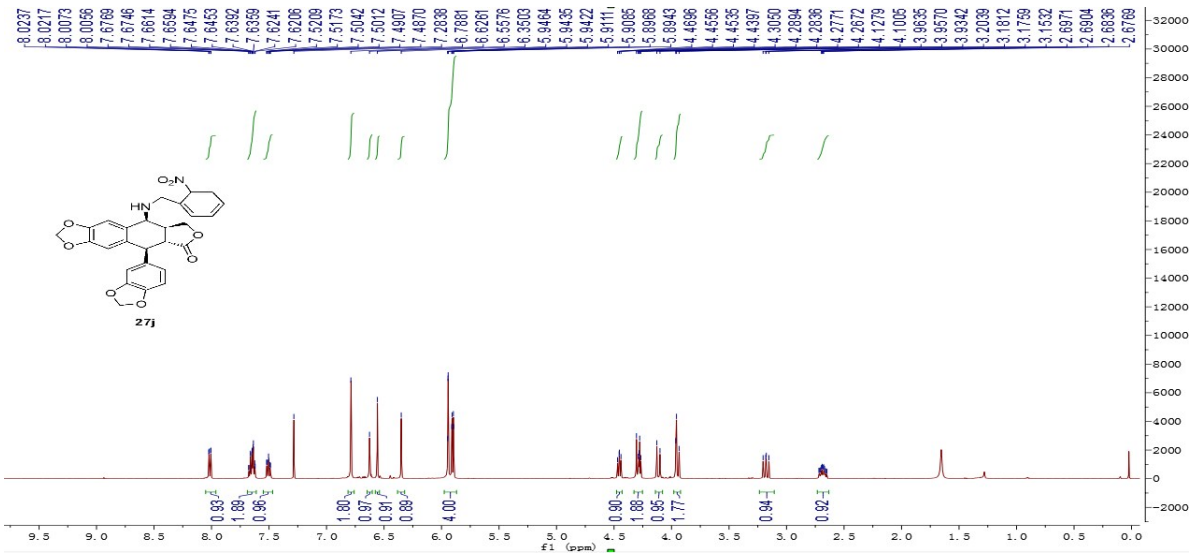


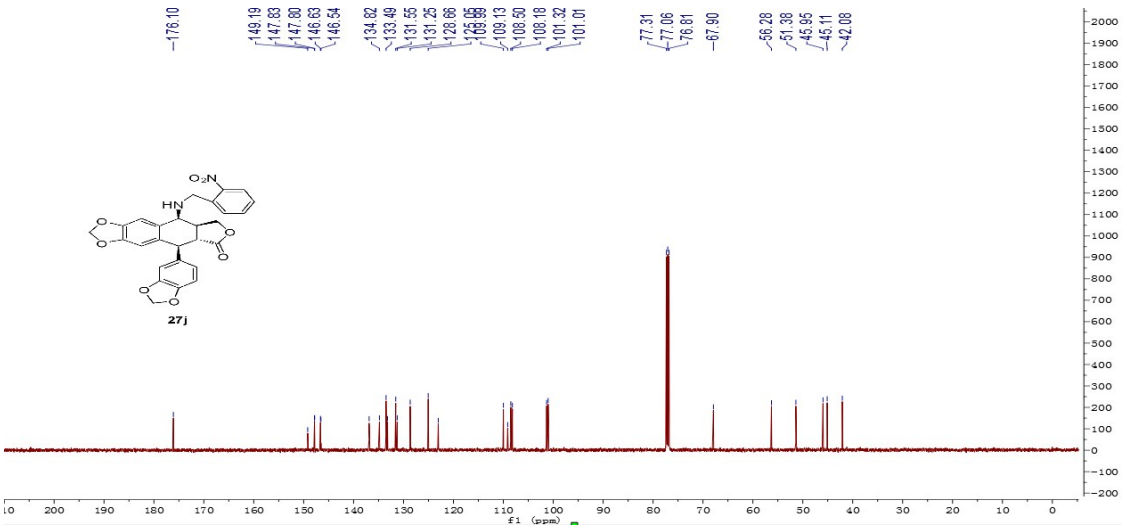


^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of compound **27i**.

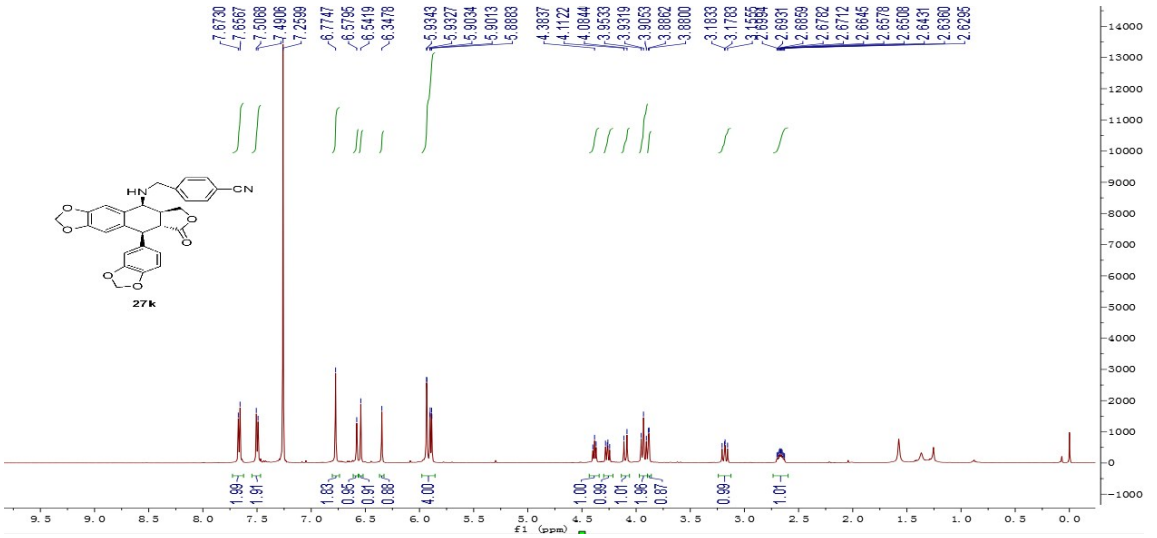


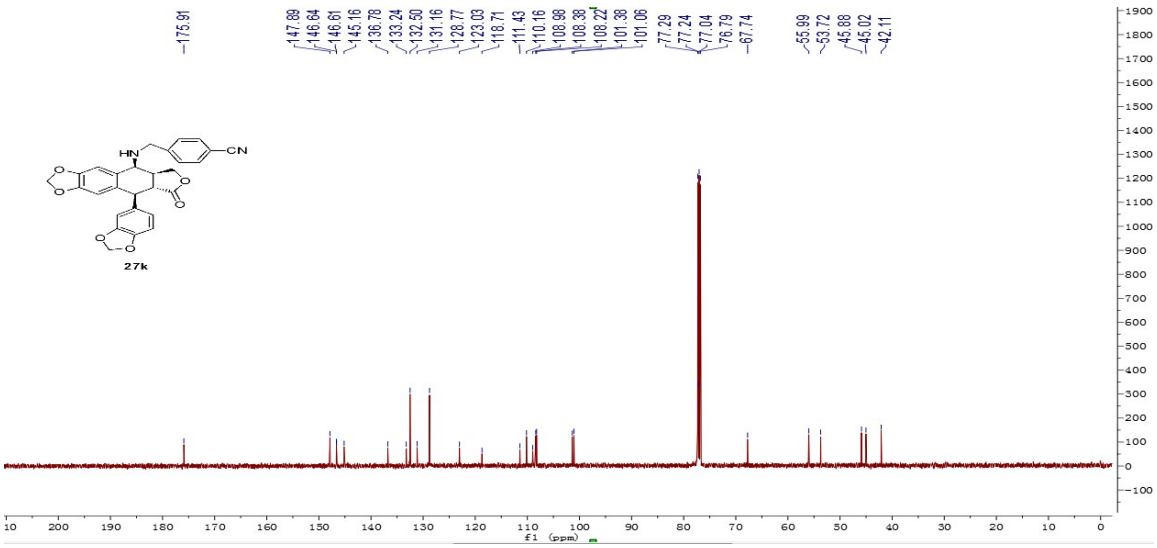
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of compound **27j**.



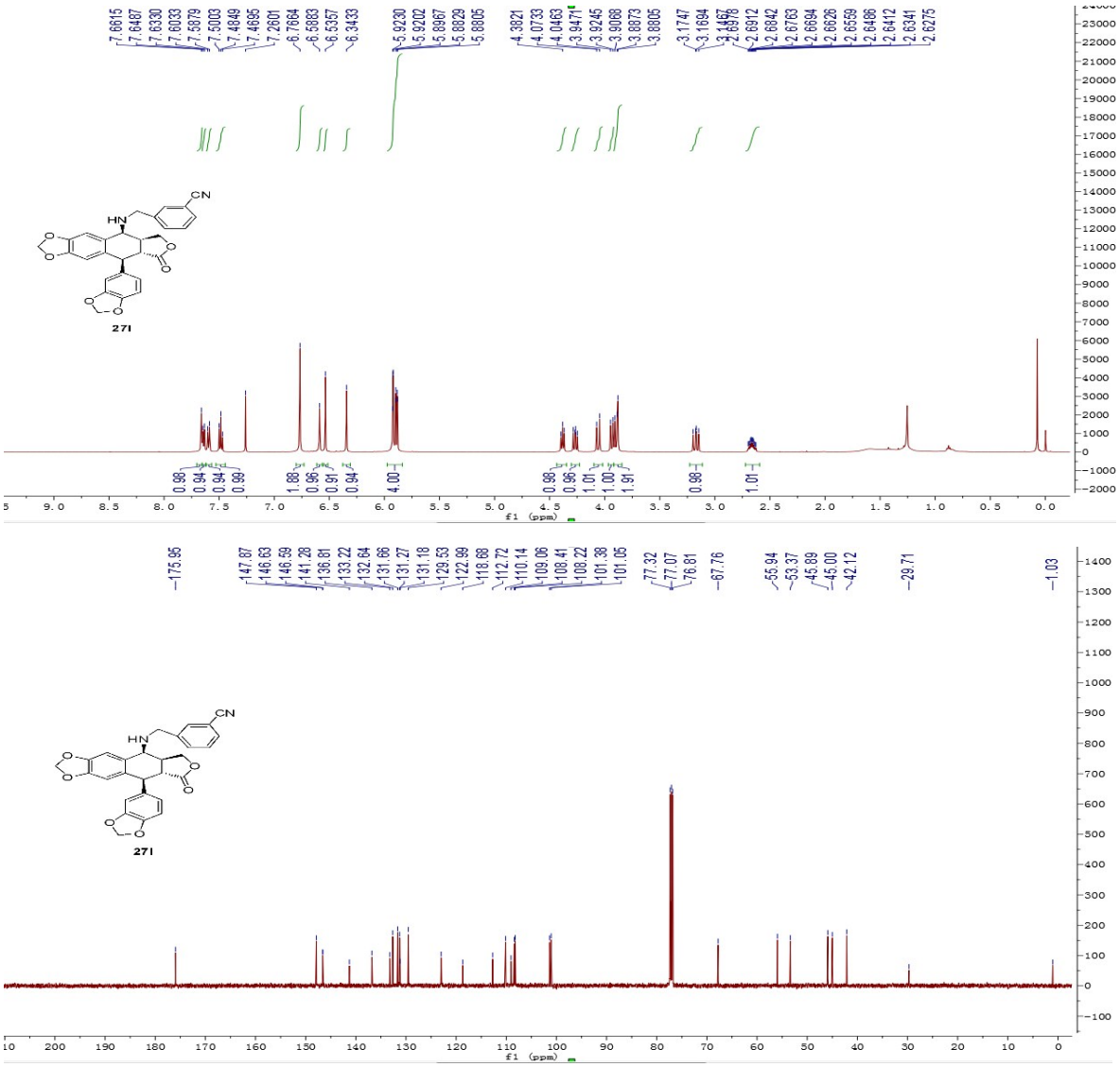


^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of compound **27k**.

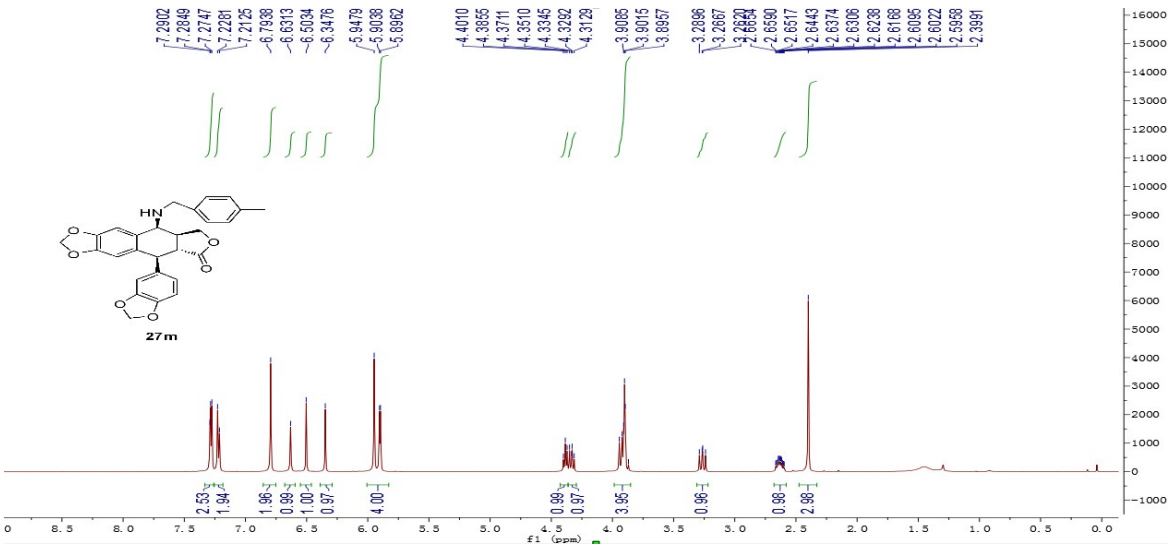


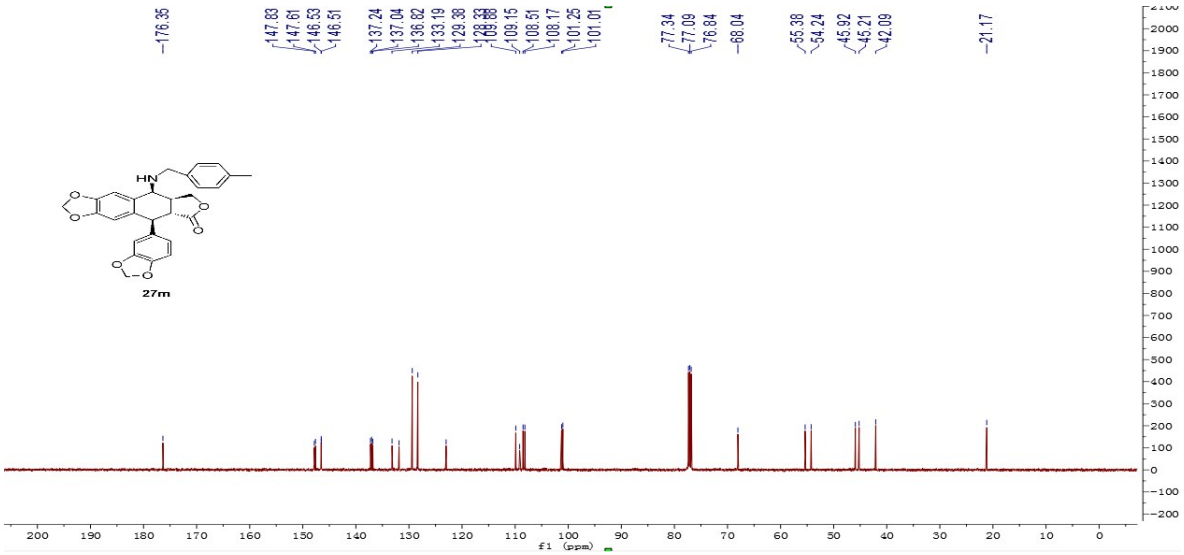


^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of compound **27l**.



^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of compound **27m**.

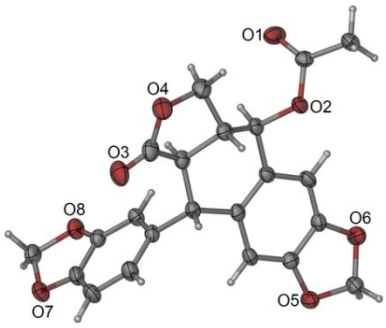


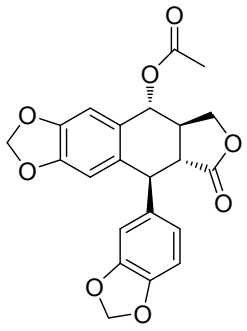


4. X-ray Data of Compound 23a and 24

4.1. Single Crystal X-ray Crystallography of compound **23a** (CCDC 1430247)

Data intensity of **23a** was collected using a Bruker SMART APEX II (Mo radiation). The X-ray condition of was 50 kV × 30 mA. Data collection and reduction were done by using the Bruker ApexII software package. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. Crystal data for **23a**: $C_{22}H_{18}O_8$, M = 410.36, T = 173(2) K, λ = 0.71073 Å, triclinic, space group P-1, a = 9.4301(6) Å, b = 9.8683(6) Å, c = 11.5227(8) Å, V = 923.30(10) Å^3, z = 2, d_{calc} = 1.476 mg/m^3, 10831 reflections measured, 3228 unique [R_{int} = 0.0296]. R_1 = 0.0403, wR_2 = 0.1065 ($I > 2\sigma(I)$, final). R_1 = 0.0527, wR_2 = 0.1185 (all data). GOF = 1.080, and 271 parameters.





23a

Table 1. Crystal data and structure refinement for z.

Identification code	z
Empirical formula	C22 H18 O8
Formula weight	410.36
Temperature	173(2) K
Wavelength	0.71073 A

Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.4301(6) A alpha = 81.308(2) deg.
	b = 9.8683(6) A beta = 68.130(2) deg.
	c = 11.5227(8) A gamma = 68.113(2) deg.
Volume	923.30(10) A^3
Z, Calculated density	2, 1.476 Mg/m^3
Absorption coefficient	0.114 mm^-1
F(000)	428
Crystal size	0.48 x 0.29 x 0.13 mm
Theta range for data collection	1.90 to 25.01 deg.
Limiting indices	-11<=h<=11, -11<=k<=11, -13<=l<=13
Reflections collected / unique	10831 / 3228 [R(int) = 0.0296]
Completeness to theta = 25.01	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9854 and 0.9475
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3228 / 0 / 271
Goodness-of-fit on F^2	1.080
Final R indices [I>2sigma(I)]	R1 = 0.0403, wR2 = 0.1065
R indices (all data)	R1 = 0.0527, wR2 = 0.1185
Largest diff. peak and hole	0.226 and -0.223 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for z.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	8533(2)	5524(2)	1594(2)	42(1)

O(2)	8438(2)	7821(2)	1005(1)	31(1)
O(3)	15354(2)	6848(2)	35(2)	45(1)
O(4)	13304(2)	6285(2)	1501(1)	42(1)
O(5)	9704(2)	11104(2)	-4049(1)	34(1)
O(6)	7476(2)	10409(2)	-2907(2)	38(1)
O(7)	18654(2)	5857(2)	-5663(1)	39(1)
O(8)	16764(2)	4701(2)	-5012(1)	34(1)
C(1)	8005(3)	11425(2)	-3828(2)	34(1)
C(2)	10028(2)	10142(2)	-3100(2)	27(1)
C(3)	11431(2)	9605(2)	-2828(2)	26(1)
C(4)	11469(2)	8650(2)	-1782(2)	25(1)
C(5)	13038(2)	8123(2)	-1471(2)	26(1)
C(6)	12951(2)	6989(2)	-428(2)	28(1)
C(7)	14045(3)	6727(2)	331(2)	36(1)
C(8)	11719(3)	6260(3)	1607(2)	38(1)
C(9)	11294(2)	7346(2)	596(2)	29(1)
C(10)	10071(2)	7287(2)	79(2)	28(1)
C(11)	10100(2)	8274(2)	-1074(2)	26(1)
C(12)	8694(2)	8808(2)	-1412(2)	29(1)
C(13)	8696(2)	9735(2)	-2414(2)	28(1)
C(14)	7817(3)	6818(2)	1703(2)	29(1)
C(15)	6158(3)	7514(3)	2597(2)	39(1)
C(16)	14558(2)	7564(2)	-2611(2)	26(1)
C(17)	15724(3)	8235(2)	-3003(2)	33(1)
C(18)	17157(3)	7745(2)	-4028(2)	37(1)
C(19)	17375(2)	6545(2)	-4618(2)	32(1)
C(20)	16234(2)	5862(2)	-4232(2)	27(1)
C(21)	14800(2)	6356(2)	-3255(2)	27(1)
C(22)	18460(3)	4491(2)	-5662(2)	36(1)

Table 3. Bond lengths [A] and angles [deg] for z.

O(1)-C(14)	1.203(2)
O(2)-C(14)	1.346(2)
O(2)-C(10)	1.459(2)
O(3)-C(7)	1.200(3)
O(4)-C(7)	1.358(3)
O(4)-C(8)	1.463(3)
O(5)-C(2)	1.381(2)
O(5)-C(1)	1.440(2)
O(6)-C(13)	1.374(2)
O(6)-C(1)	1.427(3)
O(7)-C(19)	1.386(3)
O(7)-C(22)	1.425(3)
O(8)-C(20)	1.385(2)
O(8)-C(22)	1.439(2)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-C(3)	1.367(3)
C(2)-C(13)	1.380(3)
C(3)-C(4)	1.416(3)
C(3)-H(3A)	0.9500
C(4)-C(11)	1.397(3)
C(4)-C(5)	1.534(3)
C(5)-C(6)	1.514(3)
C(5)-C(16)	1.520(3)
C(5)-H(5A)	1.0000
C(6)-C(9)	1.516(3)
C(6)-C(7)	1.517(3)
C(6)-H(6A)	1.0000
C(8)-C(9)	1.523(3)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.503(3)

C(9)-H(9A)	1.0000
C(10)-C(11)	1.522(3)
C(10)-H(10A)	1.0000
C(11)-C(12)	1.410(3)
C(12)-C(13)	1.360(3)
C(12)-H(12A)	0.9500
C(14)-C(15)	1.480(3)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-C(17)	1.390(3)
C(16)-C(21)	1.401(3)
C(17)-C(18)	1.397(3)
C(17)-H(17A)	0.9500
C(18)-C(19)	1.366(3)
C(18)-H(18A)	0.9500
C(19)-C(20)	1.380(3)
C(20)-C(21)	1.369(3)
C(21)-H(21A)	0.9500
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900

C(14)-O(2)-C(10)	117.34(15)
C(7)-O(4)-C(8)	109.86(16)
C(2)-O(5)-C(1)	105.06(15)
C(13)-O(6)-C(1)	106.22(15)
C(19)-O(7)-C(22)	103.50(16)
C(20)-O(8)-C(22)	103.65(15)
O(6)-C(1)-O(5)	107.63(16)
O(6)-C(1)-H(1A)	110.2
O(5)-C(1)-H(1A)	110.2
O(6)-C(1)-H(1B)	110.2

O(5)-C(1)-H(1B)	110.2
H(1A)-C(1)-H(1B)	108.5
C(3)-C(2)-C(13)	121.67(19)
C(3)-C(2)-O(5)	128.11(19)
C(13)-C(2)-O(5)	110.22(17)
C(2)-C(3)-C(4)	118.08(19)
C(2)-C(3)-H(3A)	121.0
C(4)-C(3)-H(3A)	121.0
C(11)-C(4)-C(3)	119.77(18)
C(11)-C(4)-C(5)	123.63(18)
C(3)-C(4)-C(5)	116.57(17)
C(6)-C(5)-C(16)	111.84(16)
C(6)-C(5)-C(4)	109.81(16)
C(16)-C(5)-C(4)	112.60(16)
C(6)-C(5)-H(5A)	107.4
C(16)-C(5)-H(5A)	107.4
C(4)-C(5)-H(5A)	107.4
C(5)-C(6)-C(9)	113.65(16)
C(5)-C(6)-C(7)	117.85(18)
C(9)-C(6)-C(7)	101.09(16)
C(5)-C(6)-H(6A)	107.9
C(9)-C(6)-H(6A)	107.9
C(7)-C(6)-H(6A)	107.9
O(3)-C(7)-O(4)	121.5(2)
O(3)-C(7)-C(6)	130.1(2)
O(4)-C(7)-C(6)	108.39(18)
O(4)-C(8)-C(9)	102.77(17)
O(4)-C(8)-H(8A)	111.2
C(9)-C(8)-H(8A)	111.2
O(4)-C(8)-H(8B)	111.2
C(9)-C(8)-H(8B)	111.2
H(8A)-C(8)-H(8B)	109.1

C(10)-C(9)-C(6)	109.46(16)
C(10)-C(9)-C(8)	120.08(18)
C(6)-C(9)-C(8)	100.37(16)
C(10)-C(9)-H(9A)	108.8
C(6)-C(9)-H(9A)	108.8
C(8)-C(9)-H(9A)	108.8
O(2)-C(10)-C(9)	109.76(16)
O(2)-C(10)-C(11)	107.72(15)
C(9)-C(10)-C(11)	109.76(17)
O(2)-C(10)-H(10A)	109.9
C(9)-C(10)-H(10A)	109.9
C(11)-C(10)-H(10A)	109.9
C(4)-C(11)-C(12)	120.53(18)
C(4)-C(11)-C(10)	121.48(17)
C(12)-C(11)-C(10)	117.99(17)
C(13)-C(12)-C(11)	118.00(18)
C(13)-C(12)-H(12A)	121.0
C(11)-C(12)-H(12A)	121.0
C(12)-C(13)-O(6)	128.74(19)
C(12)-C(13)-C(2)	121.88(18)
O(6)-C(13)-C(2)	109.38(17)
O(1)-C(14)-O(2)	123.40(19)
O(1)-C(14)-C(15)	125.1(2)
O(2)-C(14)-C(15)	111.45(18)
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(17)-C(16)-C(21)	119.87(19)
C(17)-C(16)-C(5)	120.10(18)

C(21)-C(16)-C(5)	120.03(18)
C(16)-C(17)-C(18)	122.3(2)
C(16)-C(17)-H(17A)	118.8
C(18)-C(17)-H(17A)	118.8
C(19)-C(18)-C(17)	116.4(2)
C(19)-C(18)-H(18A)	121.8
C(17)-C(18)-H(18A)	121.8
C(18)-C(19)-C(20)	121.9(2)
C(18)-C(19)-O(7)	128.3(2)
C(20)-C(19)-O(7)	109.74(19)
C(21)-C(20)-C(19)	122.43(19)
C(21)-C(20)-O(8)	128.36(19)
C(19)-C(20)-O(8)	109.16(18)
C(20)-C(21)-C(16)	117.05(19)
C(20)-C(21)-H(21A)	121.5
C(16)-C(21)-H(21A)	121.5
O(7)-C(22)-O(8)	107.02(16)
O(7)-C(22)-H(22A)	110.3
O(8)-C(22)-H(22A)	110.3
O(7)-C(22)-H(22B)	110.3
O(8)-C(22)-H(22B)	110.3
H(22A)-C(22)-H(22B)	108.6

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for z.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

U11	U22	U33	U23	U13	U12

O(1)	50(1)	28(1)	35(1)	-2(1)	-3(1)	-12(1)
O(2)	26(1)	27(1)	32(1)	-2(1)	0(1)	-8(1)
O(3)	30(1)	63(1)	42(1)	-3(1)	-16(1)	-11(1)
O(4)	37(1)	54(1)	30(1)	2(1)	-13(1)	-10(1)
O(5)	30(1)	39(1)	32(1)	7(1)	-12(1)	-13(1)
O(6)	31(1)	40(1)	51(1)	10(1)	-21(1)	-17(1)
O(7)	28(1)	40(1)	34(1)	-5(1)	2(1)	-8(1)
O(8)	29(1)	35(1)	30(1)	-9(1)	-4(1)	-6(1)
C(1)	29(1)	38(1)	32(1)	4(1)	-10(1)	-12(1)
C(2)	28(1)	26(1)	24(1)	-4(1)	-7(1)	-7(1)
C(3)	21(1)	27(1)	29(1)	-6(1)	-4(1)	-8(1)
C(4)	22(1)	24(1)	25(1)	-6(1)	-5(1)	-5(1)
C(5)	22(1)	28(1)	26(1)	-5(1)	-5(1)	-7(1)
C(6)	25(1)	28(1)	25(1)	-6(1)	-6(1)	-5(1)
C(7)	31(1)	38(1)	31(1)	-7(1)	-9(1)	-2(1)
C(8)	34(1)	43(1)	30(1)	1(1)	-9(1)	-9(1)
C(9)	28(1)	28(1)	25(1)	-5(1)	-4(1)	-6(1)
C(10)	23(1)	26(1)	26(1)	-4(1)	-2(1)	-5(1)
C(11)	24(1)	23(1)	25(1)	-4(1)	-3(1)	-7(1)
C(12)	24(1)	29(1)	33(1)	-2(1)	-4(1)	-13(1)
C(13)	23(1)	28(1)	32(1)	-3(1)	-10(1)	-8(1)
C(14)	32(1)	30(1)	24(1)	2(1)	-9(1)	-12(1)
C(15)	30(1)	41(1)	38(1)	5(1)	-3(1)	-13(1)
C(16)	21(1)	28(1)	27(1)	-1(1)	-8(1)	-6(1)
C(17)	27(1)	32(1)	38(1)	-5(1)	-8(1)	-10(1)
C(18)	26(1)	38(1)	43(1)	-1(1)	-4(1)	-14(1)
C(19)	22(1)	36(1)	31(1)	-2(1)	-4(1)	-6(1)
C(20)	26(1)	28(1)	25(1)	-3(1)	-8(1)	-5(1)
C(21)	23(1)	32(1)	28(1)	-2(1)	-8(1)	-11(1)
C(22)	28(1)	35(1)	34(1)	-3(1)	-4(1)	-5(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for z.

	x	y	z	U(eq)
H(1A)	7366	12436	-3527	40
H(1B)	7850	11329	-4611	40
H(3A)	12355	9865	-3325	32
H(5A)	13099	8980	-1152	32
H(6A)	13203	6038	-800	33
H(8A)	10903	6577	2445	45
H(8B)	11796	5273	1448	45
H(9A)	10954	8358	892	35
H(10A)	10331	6260	-145	34
H(12A)	7773	8528	-954	35
H(15A)	5741	6757	3090	59
H(15B)	5439	8100	2135	59
H(15C)	6196	8146	3156	59
H(17A)	15539	9056	-2558	40
H(18A)	17937	8222	-4300	44
H(21A)	14005	5900	-3024	33
H(22A)	19136	3732	-5232	43
H(22B)	18797	4178	-6530	43

Table 6. Torsion angles [deg] for z.

C(13)-O(6)-C(1)-O(5)	12.1(2)
C(2)-O(5)-C(1)-O(6)	-11.6(2)
C(1)-O(5)-C(2)-C(3)	-173.9(2)
C(1)-O(5)-C(2)-C(13)	6.9(2)

C(13)-C(2)-C(3)-C(4)	-2.4(3)
O(5)-C(2)-C(3)-C(4)	178.49(18)
C(2)-C(3)-C(4)-C(11)	0.7(3)
C(2)-C(3)-C(4)-C(5)	-177.41(17)
C(11)-C(4)-C(5)-C(6)	8.3(3)
C(3)-C(4)-C(5)-C(6)	-173.73(16)
C(11)-C(4)-C(5)-C(16)	133.60(19)
C(3)-C(4)-C(5)-C(16)	-48.4(2)
C(16)-C(5)-C(6)-C(9)	-166.27(16)
C(4)-C(5)-C(6)-C(9)	-40.5(2)
C(16)-C(5)-C(6)-C(7)	75.8(2)
C(4)-C(5)-C(6)-C(7)	-158.47(17)
C(8)-O(4)-C(7)-O(3)	179.0(2)
C(8)-O(4)-C(7)-C(6)	-1.4(2)
C(5)-C(6)-C(7)-O(3)	-29.6(3)
C(9)-C(6)-C(7)-O(3)	-154.0(2)
C(5)-C(6)-C(7)-O(4)	150.85(18)
C(9)-C(6)-C(7)-O(4)	26.4(2)
C(7)-O(4)-C(8)-C(9)	-24.1(2)
C(5)-C(6)-C(9)-C(10)	66.4(2)
C(7)-C(6)-C(9)-C(10)	-166.30(17)
C(5)-C(6)-C(9)-C(8)	-166.34(17)
C(7)-C(6)-C(9)-C(8)	-39.1(2)
O(4)-C(8)-C(9)-C(10)	158.86(17)
O(4)-C(8)-C(9)-C(6)	39.0(2)
C(14)-O(2)-C(10)-C(9)	-98.3(2)
C(14)-O(2)-C(10)-C(11)	142.21(17)
C(6)-C(9)-C(10)-O(2)	-172.29(15)
C(8)-C(9)-C(10)-O(2)	72.5(2)
C(6)-C(9)-C(10)-C(11)	-54.1(2)
C(8)-C(9)-C(10)-C(11)	-169.26(17)
C(3)-C(4)-C(11)-C(12)	1.7(3)

C(5)-C(4)-C(11)-C(12)	179.61(18)
C(3)-C(4)-C(11)-C(10)	-178.19(17)
C(5)-C(4)-C(11)-C(10)	-0.2(3)
O(2)-C(10)-C(11)-C(4)	142.99(18)
C(9)-C(10)-C(11)-C(4)	23.5(2)
O(2)-C(10)-C(11)-C(12)	-36.9(2)
C(9)-C(10)-C(11)-C(12)	-156.33(17)
C(4)-C(11)-C(12)-C(13)	-2.3(3)
C(10)-C(11)-C(12)-C(13)	177.53(18)
C(11)-C(12)-C(13)-O(6)	-178.86(19)
C(11)-C(12)-C(13)-C(2)	0.7(3)
C(1)-O(6)-C(13)-C(12)	171.6(2)
C(1)-O(6)-C(13)-C(2)	-8.0(2)
C(3)-C(2)-C(13)-C(12)	1.7(3)
O(5)-C(2)-C(13)-C(12)	-179.00(18)
C(3)-C(2)-C(13)-O(6)	-178.67(18)
O(5)-C(2)-C(13)-O(6)	0.6(2)
C(10)-O(2)-C(14)-O(1)	-0.4(3)
C(10)-O(2)-C(14)-C(15)	-179.82(17)
C(6)-C(5)-C(16)-C(17)	-116.6(2)
C(4)-C(5)-C(16)-C(17)	119.1(2)
C(6)-C(5)-C(16)-C(21)	62.3(2)
C(4)-C(5)-C(16)-C(21)	-61.9(2)
C(21)-C(16)-C(17)-C(18)	-0.3(3)
C(5)-C(16)-C(17)-C(18)	178.65(19)
C(16)-C(17)-C(18)-C(19)	-1.3(3)
C(17)-C(18)-C(19)-C(20)	0.8(3)
C(17)-C(18)-C(19)-O(7)	178.4(2)
C(22)-O(7)-C(19)-C(18)	165.6(2)
C(22)-O(7)-C(19)-C(20)	-16.5(2)
C(18)-C(19)-C(20)-C(21)	1.4(3)
O(7)-C(19)-C(20)-C(21)	-176.71(18)

C(18)-C(19)-C(20)-O(8)	178.94(19)
O(7)-C(19)-C(20)-O(8)	0.9(2)
C(22)-O(8)-C(20)-C(21)	-167.6(2)
C(22)-O(8)-C(20)-C(19)	15.0(2)
C(19)-C(20)-C(21)-C(16)	-2.9(3)
O(8)-C(20)-C(21)-C(16)	-179.95(18)
C(17)-C(16)-C(21)-C(20)	2.3(3)
C(5)-C(16)-C(21)-C(20)	-176.63(17)
C(19)-O(7)-C(22)-O(8)	25.7(2)
C(20)-O(8)-C(22)-O(7)	-25.3(2)

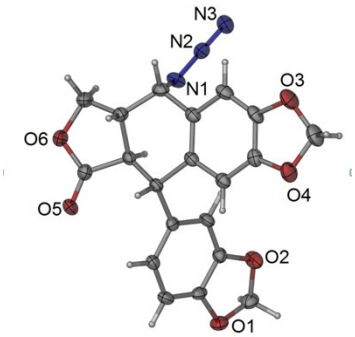
Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for z [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

4.2. Single Crystal X-ray Crystallography of compound **24** (CCDC 1430248)

Data intensity of **24** was collected using a Bruker SMART APEX II (Mo radiation). The X-ray condition of was 50 kV × 30 mA. Data collection and reduction were done by using the Bruker ApexII software package. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. Crystal data for compound **24**: $C_{20}H_{15}N_3O_6$, M = 393.35, T = 173(2) K, λ = 0.71073 Å, monoclinic, space group P2(1)/c, a = 8.8536(5) Å, b = 11.6840(7) Å, c = 16.8730(10) Å, V = 1724.97(17) Å^3, z = 4, d_{calc} = 1.515 mg/m^3, 19705 reflections measured, 3046 unique [R_{int} = 0.0523]. R_1 = 0.0354, wR_2 = 0.0758 ($I > 2\sigma(I)$, final). R_1 = 0.0528, wR_2 = 0.0854 (all data). GOF = 1.037, and 262 parameters.



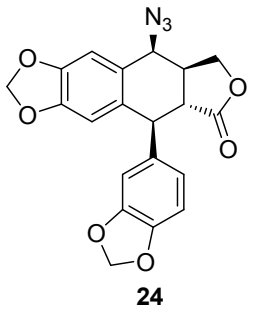


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Table 1. Crystal data and structure refinement for z.

Identification code	z
Empirical formula	C20 H15 N3 O6

Formula weight	393.35
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 8.8536(5) A alpha = 90 deg.
	b = 11.6840(7) A beta = 98.782(2) deg.
	c = 16.8730(10) A gamma = 90 deg.
Volume	1724.97(17) A^3
Z, Calculated density	4, 1.515 Mg/m^3
Absorption coefficient	0.114 mm^-1
F(000)	816
Crystal size	0.27 x 0.26 x 0.15 mm
Theta range for data collection	2.13 to 25.00 deg.
Limiting indices	-10<=h<=10, -13<=k<=13, -20<=l<=20
Reflections collected / unique	19705 / 3046 [R(int) = 0.0523]
Completeness to theta = 25.00	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9831 and 0.9698
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3046 / 1 / 262
Goodness-of-fit on F^2	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0354, wR2 = 0.0758
R indices (all data)	R1 = 0.0528, wR2 = 0.0854
Largest diff. peak and hole	0.190 and -0.177 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for z.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	9825(1)	4690(1)	1354(1)	34(1)

O(2)	11114(1)	6285(1)	1007(1)	40(1)
O(3)	7886(2)	12444(1)	689(1)	43(1)
O(4)	7531(2)	10987(1)	1573(1)	38(1)
O(5)	5302(2)	6030(1)	-1696(1)	37(1)
O(6)	5479(2)	7236(1)	-2695(1)	41(1)
N(1)	8682(2)	9696(1)	-1893(1)	35(1)
N(2)	9460(2)	10572(1)	-1914(1)	31(1)
N(3)	10268(2)	11316(1)	-1950(1)	41(1)
C(1)	6054(2)	8397(2)	-2790(1)	40(1)
C(2)	6121(2)	8903(2)	-1957(1)	30(1)
C(3)	7106(2)	9930(2)	-1702(1)	30(1)
C(4)	7148(2)	10126(1)	-810(1)	26(1)
C(5)	7478(2)	11244(1)	-529(1)	32(1)
C(6)	7604(2)	11426(1)	276(1)	30(1)
C(7)	8165(2)	12119(2)	1513(1)	43(1)
C(8)	7371(2)	10563(2)	799(1)	29(1)
C(9)	6979(2)	9477(1)	539(1)	27(1)
C(10)	6881(2)	9244(1)	-284(1)	24(1)
C(11)	6435(2)	8024(1)	-562(1)	24(1)
C(12)	6637(2)	7870(1)	-1437(1)	25(1)
C(13)	5757(2)	6925(2)	-1913(1)	30(1)
C(14)	7288(2)	7110(1)	-30(1)	22(1)
C(15)	8873(2)	7210(1)	206(1)	27(1)
C(16)	9598(2)	6347(1)	664(1)	26(1)
C(17)	8827(2)	5400(1)	878(1)	25(1)
C(18)	7291(2)	5281(2)	662(1)	30(1)
C(19)	6527(2)	6165(1)	205(1)	26(1)
C(20)	11307(2)	5166(2)	1338(1)	33(1)

Table 3. Bond lengths [A] and angles [deg] for z.

O(1)-C(17)	1.377(2)

O(1)-C(20)	1.429(2)
O(2)-C(16)	1.379(2)
O(2)-C(20)	1.423(2)
O(3)-C(6)	1.381(2)
O(3)-C(7)	1.426(2)
O(4)-C(8)	1.384(2)
O(4)-C(7)	1.446(2)
O(5)-C(13)	1.198(2)
O(6)-C(13)	1.355(2)
O(6)-C(1)	1.466(2)
N(1)-N(2)	1.237(2)
N(1)-C(3)	1.504(2)
N(2)-N(3)	1.134(2)
C(1)-C(2)	1.516(3)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-C(3)	1.507(2)
C(2)-C(12)	1.521(2)
C(2)-H(2A)	1.0000
C(3)-C(4)	1.516(2)
C(3)-H(3A)	1.0000
C(4)-C(10)	1.404(2)
C(4)-C(5)	1.405(2)
C(5)-C(6)	1.364(3)
C(5)-H(5A)	0.9500
C(6)-C(8)	1.376(2)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(9)	1.369(2)
C(9)-C(10)	1.405(2)
C(9)-H(9A)	0.9500
C(10)-C(11)	1.533(2)

C(11)-C(14)	1.520(2)
C(11)-C(12)	1.525(2)
C(11)-H(11A)	1.0000
C(12)-C(13)	1.509(2)
C(12)-H(12A)	1.0000
C(14)-C(19)	1.383(2)
C(14)-C(15)	1.404(2)
C(15)-C(16)	1.369(2)
C(15)-H(15A)	0.9500
C(16)-C(17)	1.377(2)
C(17)-C(18)	1.360(2)
C(18)-C(19)	1.400(2)
C(18)-H(18A)	0.9500
C(19)-H(19A)	0.9500
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(17)-O(1)-C(20)	105.29(13)
C(16)-O(2)-C(20)	105.32(13)
C(6)-O(3)-C(7)	104.70(14)
C(8)-O(4)-C(7)	104.32(14)
C(13)-O(6)-C(1)	109.85(13)
N(2)-N(1)-C(3)	113.22(14)
N(3)-N(2)-N(1)	174.14(19)
O(6)-C(1)-C(2)	103.00(14)
O(6)-C(1)-H(1A)	111.2
C(2)-C(1)-H(1A)	111.2
O(6)-C(1)-H(1B)	111.2
C(2)-C(1)-H(1B)	111.2
H(1A)-C(1)-H(1B)	109.1
C(3)-C(2)-C(1)	120.99(15)
C(3)-C(2)-C(12)	110.90(14)
C(1)-C(2)-C(12)	100.99(14)

C(3)-C(2)-H(2A)	107.7
C(1)-C(2)-H(2A)	107.7
C(12)-C(2)-H(2A)	107.7
N(1)-C(3)-C(2)	108.00(14)
N(1)-C(3)-C(4)	110.92(14)
C(2)-C(3)-C(4)	109.28(14)
N(1)-C(3)-H(3A)	109.5
C(2)-C(3)-H(3A)	109.5
C(4)-C(3)-H(3A)	109.5
C(10)-C(4)-C(5)	121.07(16)
C(10)-C(4)-C(3)	122.32(15)
C(5)-C(4)-C(3)	116.61(15)
C(6)-C(5)-C(4)	117.55(16)
C(6)-C(5)-H(5A)	121.2
C(4)-C(5)-H(5A)	121.2
C(5)-C(6)-C(8)	121.78(16)
C(5)-C(6)-O(3)	128.18(16)
C(8)-C(6)-O(3)	109.96(16)
O(3)-C(7)-O(4)	107.44(15)
O(3)-C(7)-H(7A)	110.2
O(4)-C(7)-H(7A)	110.2
O(3)-C(7)-H(7B)	110.2
O(4)-C(7)-H(7B)	110.2
H(7A)-C(7)-H(7B)	108.5
C(9)-C(8)-C(6)	122.00(17)
C(9)-C(8)-O(4)	128.20(16)
C(6)-C(8)-O(4)	109.74(15)
C(8)-C(9)-C(10)	118.07(16)
C(8)-C(9)-H(9A)	121.0
C(10)-C(9)-H(9A)	121.0
C(4)-C(10)-C(9)	119.43(15)
C(4)-C(10)-C(11)	123.39(15)

C(9)-C(10)-C(11)	117.16(14)
C(14)-C(11)-C(12)	111.59(13)
C(14)-C(11)-C(10)	113.04(13)
C(12)-C(11)-C(10)	110.04(13)
C(14)-C(11)-H(11A)	107.3
C(12)-C(11)-H(11A)	107.3
C(10)-C(11)-H(11A)	107.3
C(13)-C(12)-C(2)	100.88(13)
C(13)-C(12)-C(11)	118.28(14)
C(2)-C(12)-C(11)	113.32(14)
C(13)-C(12)-H(12A)	107.9
C(2)-C(12)-H(12A)	107.9
C(11)-C(12)-H(12A)	107.9
O(5)-C(13)-O(6)	120.76(16)
O(5)-C(13)-C(12)	130.32(16)
O(6)-C(13)-C(12)	108.91(14)
C(19)-C(14)-C(15)	119.68(15)
C(19)-C(14)-C(11)	120.71(15)
C(15)-C(14)-C(11)	119.59(14)
C(16)-C(15)-C(14)	117.47(15)
C(16)-C(15)-H(15A)	121.3
C(14)-C(15)-H(15A)	121.3
C(15)-C(16)-C(17)	122.09(16)
C(15)-C(16)-O(2)	128.16(15)
C(17)-C(16)-O(2)	109.69(14)
C(18)-C(17)-O(1)	128.37(15)
C(18)-C(17)-C(16)	121.80(16)
O(1)-C(17)-C(16)	109.74(15)
C(17)-C(18)-C(19)	116.86(16)
C(17)-C(18)-H(18A)	121.6
C(19)-C(18)-H(18A)	121.6
C(14)-C(19)-C(18)	122.08(16)

C(14)-C(19)-H(19A)	119.0
C(18)-C(19)-H(19A)	119.0
O(2)-C(20)-O(1)	107.99(14)
O(2)-C(20)-H(20A)	110.1
O(1)-C(20)-H(20A)	110.1
O(2)-C(20)-H(20B)	110.1
O(1)-C(20)-H(20B)	110.1
H(20A)-C(20)-H(20B)	108.4

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for z.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	39(1)	27(1)	35(1)	10(1)	0(1)	3(1)
O(2)	27(1)	30(1)	58(1)	10(1)	-6(1)	1(1)
O(3)	50(1)	26(1)	54(1)	-11(1)	10(1)	-6(1)
O(4)	41(1)	35(1)	39(1)	-12(1)	8(1)	-4(1)
O(5)	44(1)	29(1)	35(1)	0(1)	0(1)	-13(1)
O(6)	56(1)	37(1)	27(1)	1(1)	-5(1)	-14(1)
N(1)	38(1)	29(1)	40(1)	3(1)	10(1)	-4(1)
N(2)	36(1)	32(1)	26(1)	0(1)	3(1)	-4(1)
N(3)	44(1)	39(1)	39(1)	-1(1)	3(1)	-11(1)
C(1)	50(1)	34(1)	33(1)	6(1)	-2(1)	-10(1)
C(2)	30(1)	29(1)	29(1)	7(1)	-1(1)	-1(1)
C(3)	30(1)	24(1)	35(1)	8(1)	2(1)	2(1)
C(4)	21(1)	21(1)	36(1)	2(1)	3(1)	2(1)
C(5)	28(1)	21(1)	46(1)	4(1)	6(1)	0(1)
C(6)	26(1)	19(1)	47(1)	-6(1)	7(1)	0(1)

C(7)	41(1)	31(1)	56(1)	-14(1)	6(1)	-3(1)
C(8)	22(1)	29(1)	35(1)	-6(1)	3(1)	3(1)
C(9)	22(1)	24(1)	34(1)	1(1)	3(1)	0(1)
C(10)	19(1)	20(1)	33(1)	1(1)	2(1)	1(1)
C(11)	21(1)	22(1)	28(1)	2(1)	1(1)	-2(1)
C(12)	22(1)	23(1)	29(1)	2(1)	-1(1)	-3(1)
C(13)	29(1)	32(1)	28(1)	1(1)	-1(1)	-2(1)
C(14)	26(1)	19(1)	21(1)	-3(1)	2(1)	0(1)
C(15)	26(1)	20(1)	34(1)	3(1)	3(1)	-4(1)
C(16)	24(1)	24(1)	28(1)	-1(1)	1(1)	1(1)
C(17)	36(1)	19(1)	20(1)	2(1)	4(1)	3(1)
C(18)	36(1)	22(1)	31(1)	3(1)	6(1)	-6(1)
C(19)	26(1)	25(1)	26(1)	-1(1)	3(1)	-4(1)
C(20)	38(1)	28(1)	33(1)	5(1)	0(1)	7(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for z.

	x	y	z	U(eq)
H(1A)	5350	8837	-3190	48
H(1B)	7080	8380	-2955	48
H(2A)	5053	9092	-1879	36
H(3A)	6671	10620	-2005	36
H(5A)	7609	11851	-887	38
H(7A)	7672	12668	1840	51
H(7B)	9277	12112	1711	51
H(9A)	6779	8899	905	32
H(11A)	5323	7930	-532	29
H(12A)	7749	7746	-1455	30
H(15A)	9421	7852	53	32
H(18A)	6762	4629	814	35

H(19A)	5451	6113	51	31
H(20A)	11886	5201	1888	40
H(20B)	11884	4682	1007	40

Table 6. Torsion angles [deg] for z.

C(3)-N(1)-N(2)-N(3)	-179(100)
C(13)-O(6)-C(1)-C(2)	-22.0(2)
O(6)-C(1)-C(2)-C(3)	159.99(15)
O(6)-C(1)-C(2)-C(12)	37.27(18)
N(2)-N(1)-C(3)-C(2)	161.48(15)
N(2)-N(1)-C(3)-C(4)	-78.79(18)
C(1)-C(2)-C(3)-N(1)	-50.2(2)
C(12)-C(2)-C(3)-N(1)	67.67(18)
C(1)-C(2)-C(3)-C(4)	-170.96(16)
C(12)-C(2)-C(3)-C(4)	-53.09(19)
N(1)-C(3)-C(4)-C(10)	-94.51(18)
C(2)-C(3)-C(4)-C(10)	24.5(2)
N(1)-C(3)-C(4)-C(5)	85.16(18)
C(2)-C(3)-C(4)-C(5)	-155.88(15)
C(10)-C(4)-C(5)-C(6)	3.2(3)
C(3)-C(4)-C(5)-C(6)	-176.49(15)
C(4)-C(5)-C(6)-C(8)	-2.1(3)
C(4)-C(5)-C(6)-O(3)	-178.45(16)
C(7)-O(3)-C(6)-C(5)	-170.22(18)
C(7)-O(3)-C(6)-C(8)	13.04(19)
C(6)-O(3)-C(7)-O(4)	-19.42(18)
C(8)-O(4)-C(7)-O(3)	18.54(18)
C(5)-C(6)-C(8)-C(9)	-0.9(3)
O(3)-C(6)-C(8)-C(9)	176.07(16)
C(5)-C(6)-C(8)-O(4)	-178.46(16)
O(3)-C(6)-C(8)-O(4)	-1.5(2)

C(7)-O(4)-C(8)-C(9)	172.07(18)
C(7)-O(4)-C(8)-C(6)	-10.58(19)
C(6)-C(8)-C(9)-C(10)	2.7(3)
O(4)-C(8)-C(9)-C(10)	179.78(16)
C(5)-C(4)-C(10)-C(9)	-1.4(2)
C(3)-C(4)-C(10)-C(9)	178.24(15)
C(5)-C(4)-C(10)-C(11)	176.73(15)
C(3)-C(4)-C(10)-C(11)	-3.6(3)
C(8)-C(9)-C(10)-C(4)	-1.5(2)
C(8)-C(9)-C(10)-C(11)	-179.78(15)
C(4)-C(10)-C(11)-C(14)	136.57(16)
C(9)-C(10)-C(11)-C(14)	-45.3(2)
C(4)-C(10)-C(11)-C(12)	11.1(2)
C(9)-C(10)-C(11)-C(12)	-170.77(14)
C(3)-C(2)-C(12)-C(13)	-167.67(14)
C(1)-C(2)-C(12)-C(13)	-38.21(17)
C(3)-C(2)-C(12)-C(11)	64.87(19)
C(1)-C(2)-C(12)-C(11)	-165.67(14)
C(14)-C(11)-C(12)-C(13)	75.50(19)
C(10)-C(11)-C(12)-C(13)	-158.17(14)
C(14)-C(11)-C(12)-C(2)	-166.77(14)
C(10)-C(11)-C(12)-C(2)	-40.44(19)
C(1)-O(6)-C(13)-O(5)	175.80(17)
C(1)-O(6)-C(13)-C(12)	-3.1(2)
C(2)-C(12)-C(13)-O(5)	-152.1(2)
C(11)-C(12)-C(13)-O(5)	-27.9(3)
C(2)-C(12)-C(13)-O(6)	26.68(18)
C(11)-C(12)-C(13)-O(6)	150.81(15)
C(12)-C(11)-C(14)-C(19)	-99.29(17)
C(10)-C(11)-C(14)-C(19)	136.04(15)
C(12)-C(11)-C(14)-C(15)	78.76(18)
C(10)-C(11)-C(14)-C(15)	-45.9(2)

C(19)-C(14)-C(15)-C(16)	0.1(2)
C(11)-C(14)-C(15)-C(16)	-177.96(15)
C(14)-C(15)-C(16)-C(17)	1.3(3)
C(14)-C(15)-C(16)-O(2)	-175.57(16)
C(20)-O(2)-C(16)-C(15)	-173.59(18)
C(20)-O(2)-C(16)-C(17)	9.26(18)
C(20)-O(1)-C(17)-C(18)	175.84(17)
C(20)-O(1)-C(17)-C(16)	-7.72(18)
C(15)-C(16)-C(17)-C(18)	-1.6(3)
O(2)-C(16)-C(17)-C(18)	175.75(15)
C(15)-C(16)-C(17)-O(1)	-178.32(15)
O(2)-C(16)-C(17)-O(1)	-0.96(19)
O(1)-C(17)-C(18)-C(19)	176.53(16)
C(16)-C(17)-C(18)-C(19)	0.5(2)
C(15)-C(14)-C(19)-C(18)	-1.2(2)
C(11)-C(14)-C(19)-C(18)	176.83(15)
C(17)-C(18)-C(19)-C(14)	0.9(2)
C(16)-O(2)-C(20)-O(1)	-13.95(18)
C(17)-O(1)-C(20)-O(2)	13.39(18)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for z [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

5. **References**.

1、R. B. Kothapalli, R. Niddana, R. Balamurugan, *Org. Lett.*, 2014, **16**, 1278-1281.