Supporting Information

Modifications of Terpenoids via Inert Aliphatic C−H Bonds Heteroarylation with Heteroarenes

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Table of Contents

1) General Experimental Procedures

All solvents and reagents used in the experiments were purchased from commercial sources and some reagents were dried or protected by inert gas protection according to standard methods before use. TBADT was synthesized according to the protocol previously described.[1] The reactions were monitored by thin layer chromatography (TLC) using silica gel HSGF254 with ultraviolet fluorescence at 254 nm. All compounds were purified using silica gel column chromatography (200–300 mesh). The ^{1}H (400 Hz) and ^{13}C (100 Hz) NMR spectra of compounds were determined by Bruker av400 (Bruker, GER), and the internal standard was tetramethylsilane (TMS). High-resolution mass spectra (HR-MS) were recorded by using Agilent QTOF6520 (Agilent Technologies Co. Ltd., USA), or Q ExactiveTM Orbitrap MS system (Thermo Scientific, USA).

Unless otherwise noted, all reactions were performed using standard Schlenk techniques. The other starting materials and solvents were commercially available and were used without further purification. Column chromatography was performed on silica gel (200-300 mesh) using petroleum ether/ethyl acetate.

2) Photochemical Reaction Setup

A 10 mL oven dried Schlenk tube equipped with a stirring bar, reaction solution and filled with argon, the stirred reaction mixture is irradiated with 390 nm LEDs (30 W LED barrel and 20 W LED lamp). Fans are employed to maintain the reaction temperature at 25 °C.

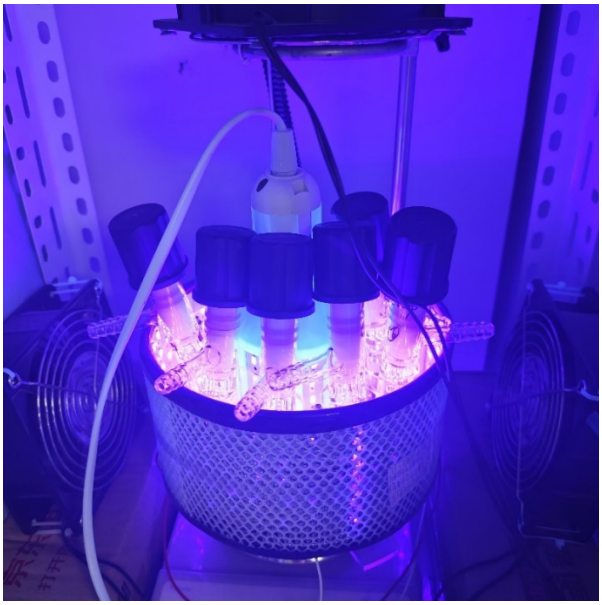
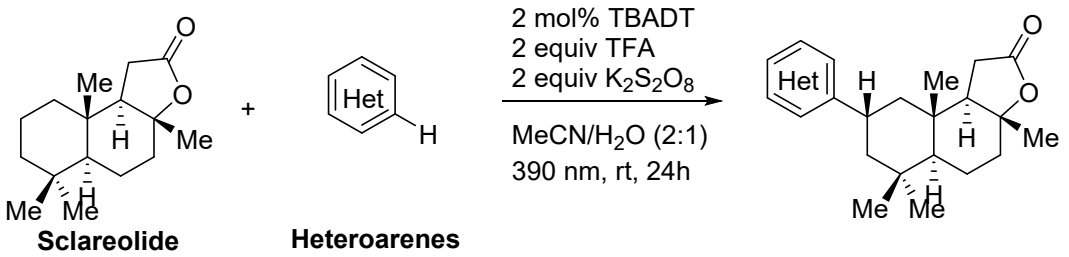


Figure S1. Details for the photochemical reaction setup.

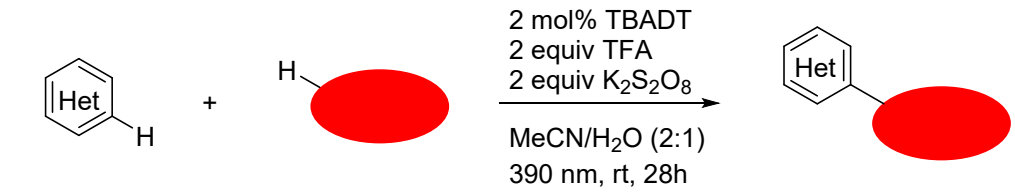
3) Procedure A: Reaction of Sclareolide with Respect to N-Heteroarenes



To an oven dried 10 mL Schlenk tube with a magnetic stirring bar under an inert atmosphere was added TBADT (13.2 mg, 0.002 mmol), $K_2S_2O_8$ (108.2 mg, 0.4 mmol), heteroarenes (0.2 mmol), sclareolide (0.6 mmol), TFA (30 μL, 0.4 mmol) followed by

MeCN (1.0 mL) and H_2O (0.5 mL), reaction for 24 hours. The organic phase was separated and the aqueous layer was extracted with EtOAc. The combined organic phase was washed with saturated brine and dried over Na_2SO_4. The solvent was removed by rotary evaporation and the residue was transferred to a column on silica gel using petroleum ether/ethyl acetate as the eluents.

4) Procedure B: Heteroarylation of Terpenoids with Heteroarenes

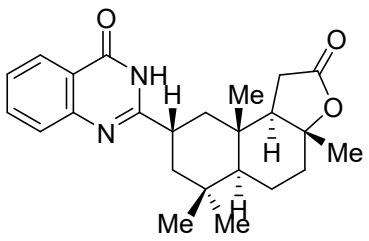


Heteroarenes **Terpenoids**

To an oven dried 10 mL Schlenk tube with a magnetic stirring bar under an inert atmosphere was added TBADT (13.2 mg, 0.002 mmol), $K_2S_2O_8$ (108.2 mg, 0.4 mmol), heteroarens (0.2 mmol), terpenoids (0.6 mmol), TFA (30 μL, 0.4 mmol) followed by MeCN (1.0 mL) and H_2O (0.5 mL), reaction for 24 hours. The organic phase was separated and the aqueous layer was extracted with EtOAc. The combined organic phase was washed with saturated brine and dried over Na_2SO_4. The solvent was removed by rotary evaporation and the residue was transferred to a column on silica gel using petroleum ether/ethyl acetate as the eluents.

5) Characterization Data of Products

2-((3aR,5aS,9aS,9bR)-3a,6,6,9a-tetramethyl-2-oxododecahydronaphtho[2,1-b]furan-8-yl)quinazolin-4(3H)-one (8)



Following general procedure of Sclareolide with Respect to N-Heteroarenes, purified by silica gel columchromatography (PE/EtOAc=3/1) and recrystallisation to obtain **8** as white powder (38% yield, 65% brsm).

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.25 (s, 1H), 8.20 (d, *J* = 6.3 Hz, 1H), 7.79 (t, *J* = 6.8 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 3.21 (t, *J* = 12.5 Hz, 1H), 2.49 – 2.40 (m, 1H), 2.29 (dd, *J* = 16.1, 6.4 Hz, 1H), 2.19 – 2.11 (m, 2H), 2.05 – 1.99 (m, 1H), 1.86 – 1.76 (m, 4H), 1.70 – 1.63 (m, 3H), 1.40 (s, 3H), 1.15 (s, 3H), 1.07 (s, 3H), 1.03 (s, 3H).

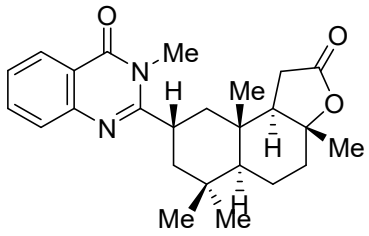
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.48, 164.67, 159.45, 149.64, 134.99, 127.62, 126.70, 125.95, 120.77, 86.18, 58.99, 56.11, 45.68, 42.88, 38.82, 36.65, 36.60, 33.97, 33.09, 28.77, 21.78, 21.44, 20.54, 15.80.

m.p. 312.5-313.8 ℃

R_f = 0.52 (PE/EtOAc = 3:1)

HRMS-ESI (m/z) calc. for $C_{24}H_{31}N_2O_3$ $[M + H]^+$: 395.2329; Found 395.2328.

3-methyl-2-((3aR,5aS,8S,9aS,9bR)-3a,6,6,9a-tetramethyl-2-oxododecahydronaphtho[2,1-b]furan-8-yl)quinazolin-4(3H)-one (9)



Purified by silica gel column chromatography (PE/EtOAc=4/1) to obtain **9** as white powder (40% yield, 64% brsm).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.71 (ddd, *J* = 8.5, 7.0, 1.6 Hz, 1H), 7.63 (d, *J* = 8.3 Hz, 1H), 7.43 (ddd, *J* = 8.1, 7.0, 1.3 Hz, 1H), 3.68 (s, 3H), 3.36 – 3.26 (m, 1H), 2.45 (dd, *J* = 16.1, 14.6 Hz, 1H), 2.33 (dd, *J* = 16.2, 6.5 Hz, 1H), 2.18 – 2.15 (m, 1H), 2.14 – 2.11 (m, 1H), 2.01 – 1.94 (m, 1H), 1.76 (d, *J* = 4.5 Hz, 1H), 1.74 (s, 1H), 1.71 (s, 2H), 1.69 – 1.66 (m, 1H), 1.66 – 1.62 (m, 1H), 1.38 (s, 3H), 1.32 (dd, *J* = 12.6, 2.5 Hz, 1H), 1.08 (s, 3H), 1.02 (s, 6H).

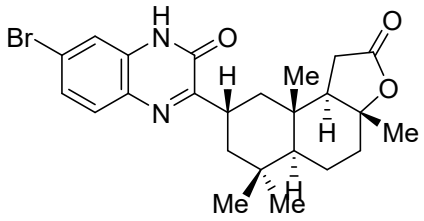
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.26, 162.66, 159.18, 147.13, 134.10, 127.00, 126.72, 126.44, 120.20, 86.00, 58.71, 56.07, 46.36, 43.26, 38.59, 36.64, 34.03, 33.86, 32.79, 29.80, 28.63, 21.71, 21.35, 20.39, 16.02.

m.p. 311.6-312.7 ℃

R_f = 0.28 (PE/EtOAc = 4:1)

HRMS-ESI (m/z) calc. for $C_{25}H_{33}N_2O_3$ $[M + H]^+$: 409.2486; Found 409.2484.

7-bromo-3-((3aR,5aS,8S,9aS,9bR)-3a,6,6,9a-tetramethyl-2-oxododecahydronaphtho[2,1-b]furan-8-yl)quinoxalin-2(1H)-one (10)



Purified by silica gel column chromatography (PE/EtOAc=8/1) to obtain **10** as white powder (22% yield, 34% brsm).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.64 (s, 1H), 7.67 (d, *J* = 9.1 Hz, 1H), 7.45 – 7.42 (m, 2H), 3.81 (ddd, *J* = 12.4, 9.0, 3.3 Hz, 1H), 2.51 – 2.42 (m, 1H), 2.26 (dd, *J* = 16.3, 6.4 Hz, 1H), 2.15 – 2.06 (m, 2H), 1.96 (dd, *J* = 13.8, 3.7 Hz, 1H), 1.77 – 1.68 (m, 4H), 1.57 (d, *J* = 12.9 Hz, 1H), 1.46 (dd, *J* = 13.7, 3.3 Hz, 1H), 1.38 (s, 3H), 1.26 – 1.21 (m, 1H), 1.14 (s, 3H), 1.04 (s, 3H), 1.00 (s, 3H).

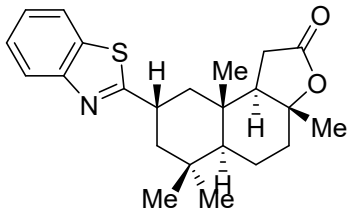
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.83, 164.22, 155.64, 131.87, 131.67, 130.41, 127.64, 123.58, 118.14, 86.45, 59.06, 56.50, 45.51, 43.08, 38.78, 36.86, 34.05, 33.14, 32.13, 28.87, 21.78, 21.45, 20.60, 15.84.

m.p. 312.5-313.5 ℃

R_f = 0.58 (PE/EtOAc = 2:1)

HRMS-ESI (m/z) calc. for $C_{24}H_{30}BrN_2O_3$ $[M+H]^+$: 473.1434; Found 473.1434.

(3aR,5aS,8S,9aS,9bR)-8-(benzo[d]thiazol-2-yl)-3a,6,6,9a-tetramethyldecahydronaphtho[2,1-b]furan-2(1H)-one (11)



Purified by silica gel column chromatography (PE/EtOAc = 12/1) to obtain **11** as white powder (36% yield, 37% brsm).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.9 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.37 – 7.32 (m, 1H), 3.56 (ddd, *J* = 12.6, 8.9, 3.5 Hz, 1H), 2.44 (dd, *J* = 16.3, 14.7 Hz, 1H), 2.28 (dd, *J* = 16.2, 6.5 Hz, 1H), 2.15 – 2.03 (m, 2H), 2.00 – 1.92 (m, 3H), 1.78 – 1.70 (m, 1H), 1.62 (t, *J* = 13.0 Hz, 1H), 1.50 – 1.41 (m, 2H), 1.36 (s, 3H), 1.24 (dd, *J* = 12.6, 2.7 Hz, 1H), 1.07 (s, 3H), 1.00 (s, 3H), 0.99 (s, 3H).

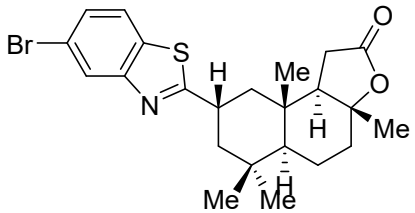
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.45, 176.28, 152.90, 134.30, 126.06, 124.81, 122.56, 121.61, 86.01, 58.77, 56.20, 48.59, 45.99, 38.56, 36.82, 35.69, 34.12, 32.93, 28.64, 21.65, 21.33, 20.40, 15.76.

m.p. 209.5-211.3 ℃

R_f = 0.25 (PE/EtOAc = 3:1)

HRMS-ESI (m/z) calc. for $C_{23}H_{30}NO_2S$ $[M + H]^+$: 384.1992; Found 384.1990.

(3aR,5aS,8S,9aS,9bR)-8-(5-bromobenzo[d]thiazol-2-yl)-3a,6,6,9a-tetramethyldecahydronaphtho[2,1-b]furan-2(1H)-one (12)



Purified by silica gel column chromatography (PE/EtOAc = 10/1) to obtain **12** as white powder (34% yield, 43% brsm).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 2.0 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.47 (dd, *J* = 8.5, 1.9 Hz, 1H), 3.61 – 3.51 (m, 1H), 2.50 – 2.41 (m, 1H), 2.29 (dd, *J* = 16.2, 6.5 Hz, 1H), 2.14 (dt, *J* = 12.0, 3.2 Hz, 1H), 2.07 (dd, *J* = 15.1, 6.5 Hz, 1H), 1.99 (s, 1H), 1.94 (dd, *J* = 11.3, 3.7 Hz, 2H), 1.77 (dd, *J* = 12.6, 4.0 Hz, 1H), 1.59 (d, *J* = 13.0

Hz, 1H), 1.46 (dtd, *J* = 12.8, 8.8, 3.9 Hz, 2H), 1.38 (s, 3H), 1.26 (d, *J* = 2.1 Hz, 1H), 1.08 (s, 3H), 1.02 (s, 3H), 1.00 (s, 3H).

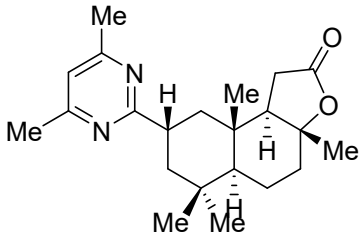
^{13}C NMR (100 MHz, $CDCl_3$) δ 178.27, 176.24, 154.19, 133.17, 127.93, 125.56, 122.65, 119.63, 85.99, 58.75, 56.19, 48.53, 45.90, 38.55, 36.82, 35.79, 34.12, 32.91, 28.64, 21.65, 21.32, 20.39, 15.76.

m.p. 160.1-161.2 ℃

R_f = 0.3 (PE/EtOAc = 4:1)

HRMS-ESI (m/z) calc. for $C_{23}H_{29}BrNO_2S$ $[M + H]^+$: 462.1097; Found 462.1097.

(3aR,5aS,8S,9aS,9bR)-8-(4,6-dimethylpyrimidin-2-yl)-3a,6,6,9a-tetramethyldeca hydronaphtho[2,1-b]furan-2(1H)-one (13)



Purified by silica gel column chromatography (PE/EtOAc=15/1) to obtain **13** as white powder (28% yield, 46% brsm).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 1H), 3.25 – 3.17 (m, 1H), 2.42 (s, 6H), 2.24 (dd, *J* = 16.2, 6.5 Hz, 1H), 2.08 (dd, *J* = 9.1, 5.7 Hz, 2H), 1.92 (d, *J* = 14.0 Hz, 1H), 1.75 – 1.59 (m, 5H), 1.53 (d, *J* = 12.4 Hz, 1H), 1.41 (dd, *J* = 13.6, 3.4 Hz, 1H), 1.34 (s, 3H), 1.25 (d, *J* = 2.6 Hz, 1H), 1.04 (s, 3H), 0.95 (s, 6H).

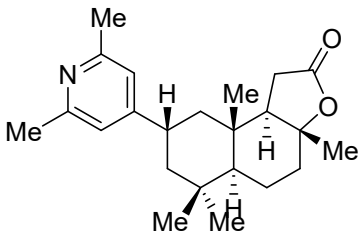
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.87, 173.12, 166.63, 117.80, 86.44, 59.00, 56.06, 47.34, 44.50, 39.58, 38.79, 36.62, 33.85, 33.16, 28.81, 24.11, 21.71, 21.64, 20.55, 15.92.

m.p. 237.2-238.3 ℃

R_f = 0.31 (PE/EtOAc = 2:1)

HRMS-ESI (m/z) calc. for $C_{22}H_{33}N_2O_2$ $[M + H]^+$: 357.2537; Found 357.2534.

(3aR,9aS)-8-(2,6-dimethylpyridin-4-yl)-3a,6,6,9a-tetramethyldecahydronaphtho[2,1-b]furan-2(1H)-one (14)



Purified by silica gel column chromatography (PE/EtOAc=2/1) to obtain **14** as white powder (13% yield, 33% brsm).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (s, 2H), 2.89 (tt, *J* = 12.4, 3.5 Hz, 1H), 2.51 (s, 6H), 2.42 (dd, *J* = 16.2, 14.8 Hz, 1H), 2.27 – 2.22 (m, 1H), 2.16 – 2.11 (m, 1H), 2.05 – 1.92 (m, 2H), 1.79 – 1.70 (m, 1H), 1.59 (ddt, *J* = 14.1, 12.4, 1.6 Hz, 2H), 1.46 – 1.41 (m, 2H), 1.37 (s, 3H), 1.28 – 1.25 (m, 2H), 1.04 (s, 3H), 0.97 (s, 3H), 0.96 (s, 3H).

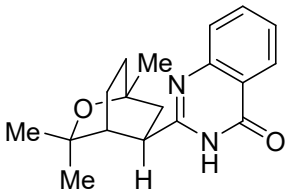
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.37, 157.71, 155.69, 119.15, 86.10, 59.02, 56.39, 48.99, 46.22, 38.64, 36.79, 35.08, 34.01, 33.09, 28.63, 24.31, 21.67, 21.29, 20.45, 15.75.

m.p. 236.5-237.8 ℃

R_f = 0.32 (PE/EtOAc = 2:1)

HRMS-ESI (m/z) calc. for $C_{23}H_{34}NO_2$ $[M + H]^+$: 356.2584; Found 356.2584.

((1R,4S)-1,3,3-trimethyl-2-oxabicyclo[2.2.2]octan-5-yl)quinazolin-4(3H)-one (15)



Following General procedure of Late-Stage Heteroarylation of Terpenoids, Purified by silica gel column chromatography (PE/EtOAc = 12/1) to obtain **15** as white powder (45% yield, 68% brsm).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.24 (s, 1H), 8.24 (dd, *J* = 8.0, 2.3 Hz, 1H), 7.72 – 7.62 (m, 2H), 7.40 (ddd, *J* = 8.0, 6.8, 1.5 Hz, 1H), 4.31 (d, *J* = 7.7 Hz, 1H), 2.29 (dtd, *J* = 12.6, 4.6, 2.1 Hz, 1H), 2.16 – 2.04 (m, 2H), 1.99 (q, *J* = 3.7 Hz, 1H), 1.83 – 1.78 (m, *J* = 5.7 Hz, 1H), 1.65 – 1.58 (m, 2H), 1.53 (s, 3H), 1.48 (d, *J* = 0.9 Hz, 3H), 1.29 – 1.28 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.49, 162.06, 148.88, 134.18, 127.63, 126.34,

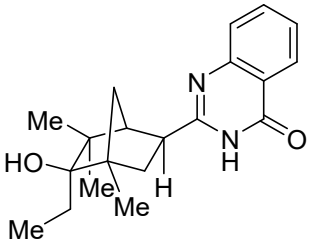
121.44, 119.78, 83.91, 81.51, 44.34, 41.80, 32.69, 31.73, 30.18, 24.29, 22.87, 20.19.

m.p. 181.5-182.3 ℃

R_f = 0.34 (PE/EtOAc = 2:1)

HRMS-ESI (m/z) calc. for $C_{18}H_{23}N_2O_2$ $[M + H]^+$:299.1754; Found 299.1750

2-((1S,4S,5R)-5-ethyl-5-hydroxy-4,6,6-trimethylbicyclo[2.2.1]heptan-2-yl)quinazolin-4(3H)-one (16)



Purified by silica gel column chromatography (PE/EtOAc = 15/1) to obtain **16** as white powder (38% yield, 55% brsm).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.35 (s, 1H), 8.23 (d, *J* = 7.7 Hz, 1H), 7.75 – 7.71 (m, 2H), 7.43 (td, *J* = 5.7, 2.7 Hz, 1H), 3.29 (dd, *J* = 9.3, 4.6 Hz, 1H), 2.42 (ddd, *J* = 11.6, 9.0, 2.6 Hz, 1H), 2.07 (s, 1H), 1.97 (dd, *J* = 12.6, 5.2 Hz, 1H), 1.62 (ddd, *J* = 28.9, 14.5, 7.1 Hz, 4H), 1.51 (d, J = 10.7 Hz, 1H), 1.29 (s, 3H), 1.18 (s, 3H), 1.11 (s, 3H), 1.03 (t, J = 7.3 Hz, 3H).

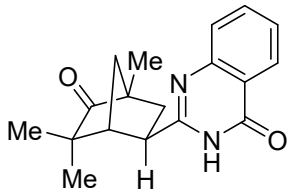
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.24, 159.37, 149.37, 134.58, 127.73, 126.33, 126.22, 120.66, 80.60, 55.45, 52.80, 45.33, 41.91, 38.16, 34.38, 27.92, 27.42, 22.57, 17.72, 9.47.

m.p. 230.5-231.5℃

R_f = 0.32 (PE/EtOAc = 3:1)

HRMS-ESI (m/z) calc. for $C_{21}H_{27}N_2O_2$ $[M+H]^+$: 327.2067; Found 327.2065.

((1R,2R,4S)-4,6,6-trimethyl-5-oxobicyclo[2.2.1]heptan-2-yl)quinazolin-4(3H)-one (17)



Purified by silica gel column chromatography (PE/EtOAc = 12/1) to obtain **17** as white

powder (47% yield, 56% brsm).

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.65 (s, 1H), 8.23 (d, *J* = 7.6 Hz, 1H), 7.83 – 7.76 (m, 2H), 7.51 (ddd, *J* = 8.2, 6.3, 2.0 Hz, 1H), 3.47 (dd, *J* = 9.6, 3.8 Hz, 1H), 2.75 (dd, *J* = 13.0, 4.0 Hz, 1H), 2.64 (s, 1H), 2.02 (d, *J* = 12.8 Hz, 1H), 1.82 – 1.71 (m, 2H), 1.44 (s, 3H), 1.28 (s, 3H), 1.17 (s, 3H).

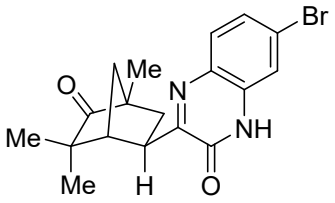
^{13}C NMR (100 MHz, $CDCl_3$) δ 222.48, 164.90, 157.78, 149.05, 134.79, 127.80, 126.72, 125.96, 120.42, 54.03, 51.14, 47.75, 41.83, 37.91, 34.02, 23.57, 21.60, 14.23.

m.p. 256.5-257.8 ℃

R_f = 0.6 (PE/EtOAc = 1:1)

HRMS-ESI (m/z) calc. for $C_{18}H_{21}N_2O_2$ $[M + H]^+$:297.1598; Found 297.1597

7-bromo-3-((1R,2R,4S)-4,6,6-trimethyl-5-oxobicyclo[2.2.1]heptan-2-yl)quinoxali-2(1H)-one (18)



Purified by silica gel column chromatography (PE/EtOAc = 15/1) to obtain **18** as white powder (40% yield, 72% brsm).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.79 (s, 1H), 7.75 – 7.71 (m, 1H), 7.47 – 7.44 (m, 2H), 3.92 (dd, *J* = 9.5, 4.6 Hz, 1H), 2.47 (q, *J* = 5.5 Hz, 2H), 1.84 (dd, *J* = 10.8, 1.9 Hz, 1H), 1.77 – 1.72 (m, 1H), 1.69 (d, *J* = 11.8 Hz, 1H), 1.35 (s, 3H), 1.25 (s, 3H), 1.14 (s, 3H).

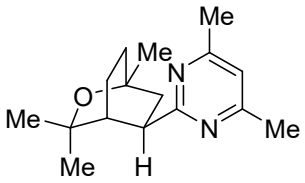
^{13}C NMR (100 MHz, $CDCl_3$) δ 223.11, 162.51, 156.05, 131.81, 131.38, 130.57, 127.68, 123.74, 118.19, 54.40, 50.03, 48.06, 39.48, 37.91, 34.52, 23.67, 21.55, 14.54.

m.p. 257.6-258.9 ℃

R_f = 0.45 (PE/EtOAc = 2:1)

HRMS-ESI (m/z) calc. for $C_{18}H_{20}BrN_2O_2$ $[M + H]^+$ 375.0703; Found 375.0703.

4,6-dimethyl-2-((1R,4S)-1,3,3-trimethyl-2-oxabicyclo[2.2.2]octan-5-yl)pyrimidine (19)



Purified by silica gel column chromatography (PE/EtOAc = 15/1) to obtain **19** as white powder (43% yield, 59% brsm).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 1H), 3.70 (d, *J* = 9.3 Hz, 1H), 2.56 (dd, *J* = 13.7, 4.8 Hz, 1H), 2.46 (s, 6H), 2.02 – 1.98 (m, 1H), 1.95 – 1.87 (m, 1H), 1.62 – 1.54 (m, 4H), 1.44 (s, 3H), 1.32 (s, 3H), 1.17 (s, 3H).

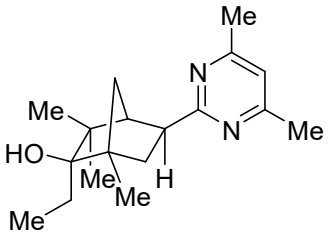
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.26, 166.10, 116.99, 74.04, 70.74, 40.54, 38.59, 34.28, 31.30, 29.06, 28.85, 27.50, 24.09, 16.93.

m.p. 174.6-175.9℃

R_f = 0.2 (PE/EtOAc = 2:1)

HRMS-ESI (m/z) calc. for $C_{16}H_{25}N_2O$ $[M + H]^+$: 261.1961; Found 261.1960.

(1S,2S,4R,6R)-6-(4,6-dimethylpyrimidin-2-yl)-2-ethyl-1,3,3-trimethylbicyclo[2.2.1]heptan-2-ol (20)



Purified by silica gel column chromatography (PE/EtOAc = 18/1) to obtain **20** as colorless oil (43% yield, 62% brsm).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (s, 1H), 3.44 (dd, *J* = 9.5, 5.3 Hz, 1H), 2.43 (s, 6H), 2.06 (s, 1H), 1.68 – 1.65 (m, 2H), 1.60 – 1.55 (m, 2H), 1.27 (d, *J* = 12.1 Hz, 2H), 1.16 (d, *J* = 3.5 Hz, 6H), 1.12 (d, *J* = 6.9 Hz, 1H), 1.06 (s, 3H), 1.01 (t, *J* = 7.3 Hz, 3H).

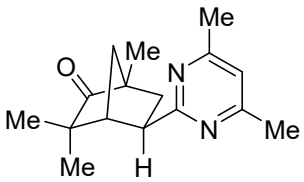
^{13}C NMR (100 MHz, $CDCl_3$) δ 174.14, 166.16, 116.91, 80.87, 55.46, 52.90, 45.20, 44.89, 38.58, 37.65, 27.92, 27.48, 24.18, 22.72, 17.93, 9.56.

R_f = 0.45 (PE/EtOAc = 3:1)

HRMS-ESI (m/z) calc. for $C_{18}H_{29}N_2O$ $[M + H]^+$: 289.2274; Found 289.2273.

(1S,4R,5R)-5-(4,6-dimethylpyrimidin-2-yl)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-

one (21)



Purified by silica gel column chromatography (PE/EtOAc = 16/1) to obtain **21** as white powder (38% yield, 54% brsm).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 1H), 3.52 (dd, *J* = 8.8, 4.6 Hz, 1H), 2.64 (s, 1H), 2.46 (s, 6H), 2.39 (dd, *J* = 13.4, 5.5 Hz, 1H), 1.98 (dd, *J* = 10.7, 1.8 Hz, 1H), 1.85 (ddd, *J* = 13.3, 9.0, 2.3 Hz, 1H), 1.68 (dq, *J* = 10.9, 1.8 Hz, 1H), 1.22 (s, 3H), 1.20 (s, 3H), 1.11 (s, 3H).

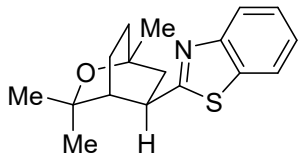
^{13}C NMR (100 MHz, $CDCl_3$) δ 223.68, 172.32, 166.30, 117.20, 54.43, 50.81, 47.66, 45.08, 38.46, 37.09, 24.07, 23.49, 21.73, 14.46.

m.p. 175.5-176.8 ℃

R_f = 0.25 (PE/EtOAc = 2:1)

HRMS-ESI (m/z) calc. for $C_{16}H_{23}N_2O$ $[M + H]^+$: 259.1805; Found 259.1804.

2-((1R,4S)-1,3,3-trimethyl-2-oxabicyclo[2.2.2]octan-5-yl)benzo[d]thiazole (22)



Purified by silica gel column chromatography (PE/EtOAc = 10/1) to obtain **22** as white powder (34% yield, 45% brsm).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.45 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.37 – 7.32 (m, 1H), 3.96 (ddd, *J* = 11.3, 5.3, 2.7 Hz, 1H), 2.37 – 2.31 (m, 1H), 2.19 (ddd, *J* = 14.0, 11.1, 3.3 Hz, 1H), 1.99 – 1.96 (m, 1H), 1.88 – 1.80 (m, 1H), 1.73 – 1.66 (m, 1H), 1.57 – 1.54 (m, 1H), 1.42 (s, 3H), 1.35 (s, 3H), 1.28 – 1.24 (m, 1H), 1.18 (s, 3H).

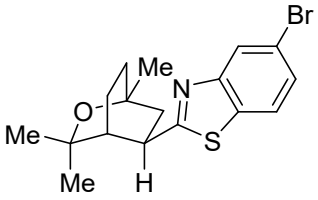
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.95, 153.25, 135.02, 126.02, 124.81, 122.74, 121.60, 74.01, 70.56, 40.46, 37.99, 36.87, 31.28, 28.95, 28.85, 27.31, 17.17.

m.p. 158.5-159.7℃

R_f = 0.22 (PE/EtOAc = 3:1)

HRMS-ESI (m/z) calc. for $C_{17}H_{22}NOS$ $[M+H]^+$: 288.1417; Found 288.1417.

5-bromo-2-((1R,4S)-1,3,3-trimethyl-2-oxabicyclo[2.2.2]octan-5-yl)benzo[d]thiazol e (23)



Purified by silica gel column chromatography (PE/EtOAc = 15/1) to obtain **23** as white powder (41% yield, 50% brsm).

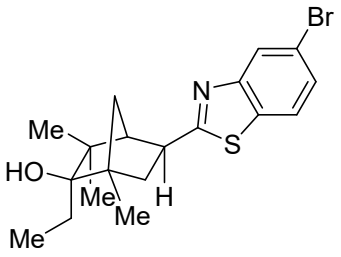
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 2.0 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.41 (dd, *J* = 8.5, 2.0 Hz, 1H), 4.43 (d, *J* = 6.2 Hz, 1H), 2.55 – 2.44 (m, 1H), 2.34 – 2.25 (m, 1H), 2.01 (d, *J* = 12.0 Hz, 1H), 1.96 (d, *J* = 3.7 Hz, 1H), 1.92 – 1.78 (m, 3H), 1.45 (s, 3H), 1.43 (s, 3H), 1.22 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 183.09, 154.00, 134.27, 127.58, 125.78, 122.49, 119.11, 83.12, 82.61, 46.62, 41.88, 32.71, 31.94, 30.34, 24.71, 24.66, 22.85.

R_f = 0.43 (PE/EtOAc = 3:1)

HRMS-ESI (m/z) calc. for $C_{17}H_{21}BrNOS$ $[M + H]^+$: 366.0522; Found 366.0521.

(1S,2R,4S)-5-(5-bromobenzo[d]thiazol-2-yl)-2-ethyl-1,3,3-trimethylbicyclo[2.2.1] heptan-2-ol (24)



Purified by silica gel column chromatography (PE/EtOAc = 16/1) to obtain **24** as Colorless oil (48% yield, 62% brsm).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 2.0 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.43 (dd, *J* = 8.5, 1.9 Hz, 1H), 3.69 (dd, *J* = 7.3, 5.2 Hz, 1H), 2.72 (ddd, *J* = 12.0, 9.1, 2.8 Hz, 1H), 2.07 (s, 1H), 1.70 (d, *J* = 7.2 Hz, 2H), 1.62 (s, 1H), 1.61 – 1.56 (m, 2H), 1.50

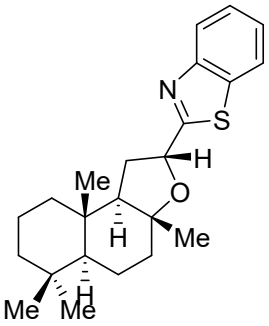
(dd, *J* = 10.9, 1.8 Hz, 1H), 1.17 (d, *J* = 5.2 Hz, 6H), 1.10 (s, 3H), 1.01 (d, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.54, 154.54, 133.86, 127.64, 125.59, 122.53, 119.44, 80.44, 57.34, 53.09, 45.39, 42.14, 39.37, 38.94, 27.93, 27.33, 22.58, 17.74, 9.40.

R_f = 0.4 (PE/EtOAc = 2:1)

HRMS-ESI (m/z) calc. for $C_{19}H_{25}BrNOS$ $[M + H]^+$:394.0835; Found 394.0833.

2-((2R,3aR,5aS,9aS,9bR)-3a,6,6,9a-tetramethyldodecahydronaphtho[2,1-b]furan-2-yl)benzo[d]thiazole (25)



Purified by silica gel column chromatography (PE/EtOAc = 15/1) to obtain **25** as yellow oil (25% yield, 41% brsm).

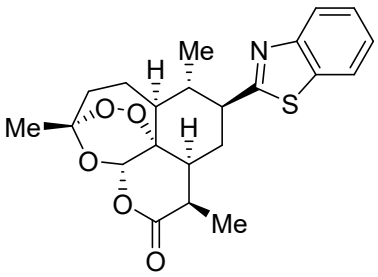
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.88 (ddd, *J* = 7.9, 1.3, 0.7 Hz, 1H), 7.46 (ddd, *J* = 8.3, 7.3, 1. Hz, 1H), 7.36 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 5.47 (dd, *J* = 9.5, 2.2 Hz, 1H), 2.43 (ddd, *J* = 13.9, 12.0, 9.5 Hz, 1H), 2.12 (dt, *J* = 11.7, 3.2 Hz, 1H), 2.08 – 2.03 (m, 1H), 1.87 – 1.81 (m, 1H), 1.69 – 1.60 (m, 3H), 1.42 – 1.33 (m, 5H), 1.28 (d, *J* = 1.0 Hz, 3H), 1.17 – 1.10 (m, 1H), 0.99 (dd, *J* = 12.6, 2.7 Hz, 1H), 0.88 (s, 6H), 0.84 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 178.36, 153.67, 134.70, 125.91, 124.61, 122.67, 121.68, 83.29, 76.03, 58.20, 57.17, 42.31, 39.93, 39.79, 36.26, 33.50, 33.08, 31.58, 21.94, 21.09, 20.70, 18.27, 15.24.

R_f = 0.32 (PE/EtOAc = 2:1)

HRMS-ESI (m/z) calc. for $C_{23}H_{32}NOS$ $[M + H]^+$: 370.2199; Found 370.2195.

(3R,5aS,6S,7R,8aS,9R,12S,12aR)-7-(benzo[d]thiazol-2-yl)-3,6,9-trimethyloctahydro-12H-3,12-epoxy[1,2]dioxepino[4,3-i]isochromen-10(3H)-one (26)



Purified by silica gel column chromatography (PE/EtOAc = 13/1) to obtain **26** as white powder (16% yield, 32% brsm).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 6.12 (s, 1H), 3.50 – 3.42 (m, 1H), 2.97 – 2.89 (m, 1H), 2.55 – 2.44 (m, 1H), 2.23 (dd, *J* = 14.0, 3.9 Hz, 1H), 2.15 – 1.97 (m, 5H), 1.67 – 1.60 (m, 2H), 1.49 (s, 3H), 1.20 (d, *J* = 7.3 Hz, 3H), 0.98 (d, *J* = 6.3 Hz, 3H).

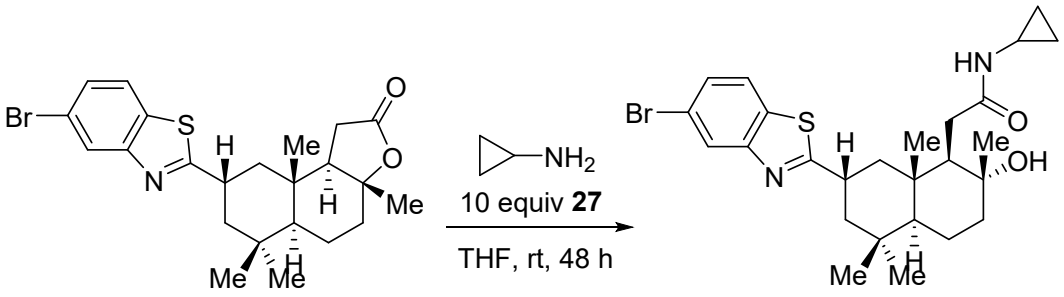
^{13}C NMR (100 MHz, $CDCl_3$) δ 173.15, 171.40, 152.95, 134.31, 126.28, 125.20, 122.82, 121.71, 105.52, 93.43, 78.84, 49.60, 48.92, 44.19, 42.31, 35.80, 32.72, 31.39, 25.15, 24.87, 17.67, 12.53.

m.p. 211.5-213.6 ℃

R_f = 0.3 (PE/EtOAc = 2:1)

HRMS-ESI (m/z) calc. for $C_{22}H_{26}NO_5S$ $[M + H]^+$: 416.1526; Found 416.1524.

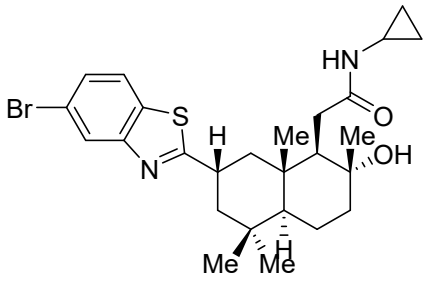
6) Synthetic Applications



12, 1 equiv

28, 51%

2-((1R,2R,4aS,7S,8aS)-7-(6-bromobenzo[d]thiazol-2-yl)-2-hydroxy-2,5,5,8a-tetramethyldecahydronaphthalen-1-yl)-N-cyclopropylacetamide (28)



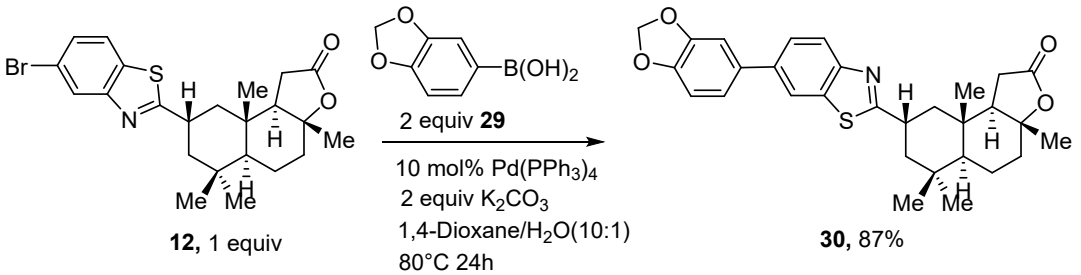
12 (25 mg, 0.05 mmol) was dissolved in THF (1.5 mL), **27** (17 μL, 10 mmol) were added and the reaction was allowed to continue at room temperature for 48h. The reaction was diluted with dichloromethane and the organic layer was washed with deionised water and saturated sodium chloride solution, dried with anhydrous Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography (DCM/MeOH = 40/1) to obtain colorless oil (13 mg, 51% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 1.8 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.47 (dd, *J* = 8.5, 1.9 Hz, 1H), 5.89 (s, 1H), 3.47 (t, *J* = 12.7 Hz, 1H), 2.63 (s, 1H), 2.38 (dd, *J* = 15.4, 5.7 Hz, 1H), 2.15 – 2.07 (m, 2H), 2.03 – 1.97 (m, 1H), 1.96 – 1.88 (m, 2H), 1.76 (d, *J* = 14.0 Hz, 1H), 1.53 (t, *J* = 13.0 Hz, 2H), 1.32 (t, *J* = 12.6 Hz, 2H), 1.25 (s, 1H), 1.16 (s, 3H), 1.01 (s, 3H), 0.94 (s, 6H), 0.84 (d, 1H), 0.69 (d, *J* = 7.6 Hz, 2H), 0.42 (t, *J* = 4.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.64, 176.12, 127.96, 125.43, 122.80, 119.70, 117.95, 108.19, 72.84, 57.34, 55.54, 48.07, 46.06, 44.26, 39.61, 36.16, 34.34, 33.21, 32.23, 23.76, 22.87, 21.90, 20.45, 16.32, 6.71, 6.53.

R_f = 0.26 (DCM/MeOH = 40:1)

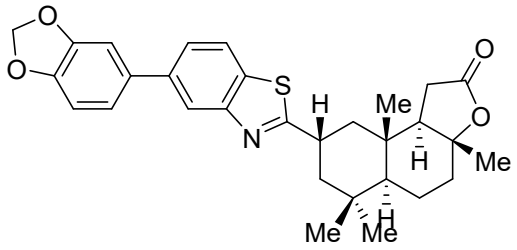
HRMS-ESI (m/z) calc. for $C_{26}H_{36}BrN_2O_2S$ $[M + H]^+$:519.1675; Found 519.1673.



The reaction of Sclareolide with heterocycles is described in the previous section.**12** (25 mg, 0.05 mmol), **29** (18 mg, 0.1 mmol), $Pd(PPh_3)_4$ (6.5 mg, 0.005 mmol), K_2CO_3 (15 mg, 0.01 mmol)as dissolved in 1,4-dioxane/H_2O (10:1) with 10 mL Schlenk

tube and the reaction was stirred for 24 h at 80°C temperature. The reaction system was diluted with dichloromethane, washed with deionised water and saturated NaCl solution. The organic layer was dried with anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by silica gel column chromatography obtain pure product (23 mg, 87% yield).

(3aR,5aS,8S,9aS,9bR)-8-(6-(benzo[d][1,3]dioxol-5-yl)benzo[d]thiazol-2-yl)-3a,6,6,9a-tetramethyldecahydronaphtho[2,1-b]furan-2(1H)-one (30)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.08 (m, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.52 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.13 – 7.08 (m, 2H), 6.91 – 6.87 (m, 1H), 6.00 (s, 2H), 3.62 – 3.51 (m, 1H), 2.45 (dd, *J* = 16.2, 14.6 Hz, 1H), 2.28 (dd, *J* = 16.2, 6.5 Hz, 1H), 2.16 – 2.03 (m, 2H), 2.02 – 1.93 (m, 3H), 1.74 (td, *J* = 12.2, 3.8 Hz, 1H), 1.63 (t, *J* = 13.1 Hz, 1H), 1.46 (d, *J* = 6.1 Hz, 1H), 1.37 (s, 3H), 1.27 – 1.22 (m, 2H), 1.08 (s, 3H), 1.00 (d, *J* = 6.3 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.22, 176.26, 153.61, 148.24, 147.25, 139.44, 135.07, 132.87, 124.13, 121.70, 120.84, 120.52, 108.71, 107.80, 101.21, 86.00, 58.76, 56.20, 48.54, 45.94, 38.56, 36.83, 35.75, 34.12, 32.92, 28.64, 21.65, 21.33, 20.40, 15.76.

m.p. 251.6-253.4℃

R_f = 0.37 (PE/EtOAc = 3:1)

HRMS-ESI (m/z) calc. for $C_{30}H_{34}NO_4S$ $[M + H]^+$: 504.2203; Found 504.2200.

7) Cell viability analyses

RAW264.7 cells were seeded in 96-well plates at a density of 5 × 10^4 cells/well

and incubated for 24 h. Subsequently, the cells were treated with various compounds at a concentration of 40 μM for another 24 h. MTT assay was performed by adding 20.0 μL of 0.5 mg/mL MTT reagent to each well and incubating for 4 h. Media was then removed and replaced with 150 μL of DMSO, and plates were incubated for 10 min in the dark. A microplate reader (Spectra Max iD3) was then used to measure absorbance in each well at 570 nm.

8) Assay for NO production

The Griess reaction was used to analyze nitrite concentrations in supernatants to assess NO production. Briefly, RAW264.7 cells were plated in 96-well plates (5×10^4) for 24 h, followed by pretreatment for 2 h with a range of compound concentrations. Cells were then stimulated using 20 μL LPS (1 μg/mL) and cultured for 24 h, after which supernatants were combined with an equivalent volume of Griess reagent and incubated for 10 min while shielded from light. Absorbance at 540 nm was then assessed with a microplate reader.

Table S1 Compounds inhibitory activity against LPS-induced NO release in RAW264.7 cells.

Cpd.	Cell viability (%)	Inhibition rate (%)			
	40 μM	2.5 μM	5 μM	10 μM	20 μM
8	109.05	1.09	7.2	13.53	20.08
9	98.35	18.34	21.17	24.45	26.85
10	100.73	18.34	21.02	30.87	33.77
11	99.45	-1.07	17.09	21.15	31.19
12	97.23	20.08	26.92	31.4	34.61
13	73	—	—	—	—
14	85.37	8.28	10.29	19.46	31.31
15	104.98	13.41	15	23.18	25.9
16	77.25	—	—	—	—
17	92.24	3.86	6.59	17.5	35.45
18	71.95	—	—	—	—
19	82.26	—	—	—	—
20	96.25	9.87	15.45	26.17	29.39
21	104.96	-0.68	4.5	9.91	17.11
22	67.13	—	—	—	—
23	83.84	—	—	—	—
24	72.52	—	—	—	—
25	79.46	—	—	—	—
26	88.46	67.63	70.57	74.42	76
28	92.13	13.49	14.52	19.83	37.82
30	90.59	17.58	22.9	29.44	31.9
sclareolide	99.18	7.39	13.69	19.78	30.21
fenchone	97.7	12.39	14.13	20.43	27.6
ethyl fenchol	94.81	2.6	12.05	15.13	24.58
eucalyptol	94.84	8.04	13.24	26.23	30.49
(−)-ambroxane	99.44	6.37	12.74	15.92	30.78
artemisinin	97.91	69.41	72.38	74.72	77.69

9) Assay for antitumour production

HCC1806 (American Type Culture Collection) and HUVEC cells were planted into the 96-well plate overnight, then treated with compounds at the concentration of 25 μM for 48 h. At the endpoint of this experiment, cells were incubated with 2.5 mg/mL MTT (MCE, HY-15924) at 37℃ for 4 h. After centrifugation, the formazan was dissolved in DMSO and the absorbance was measured at 570 nm by a microplate reader (BioTek, USA)

Table S2 Compounds inhibitory activity antitumour in HCC1806 and HUVEC cells.

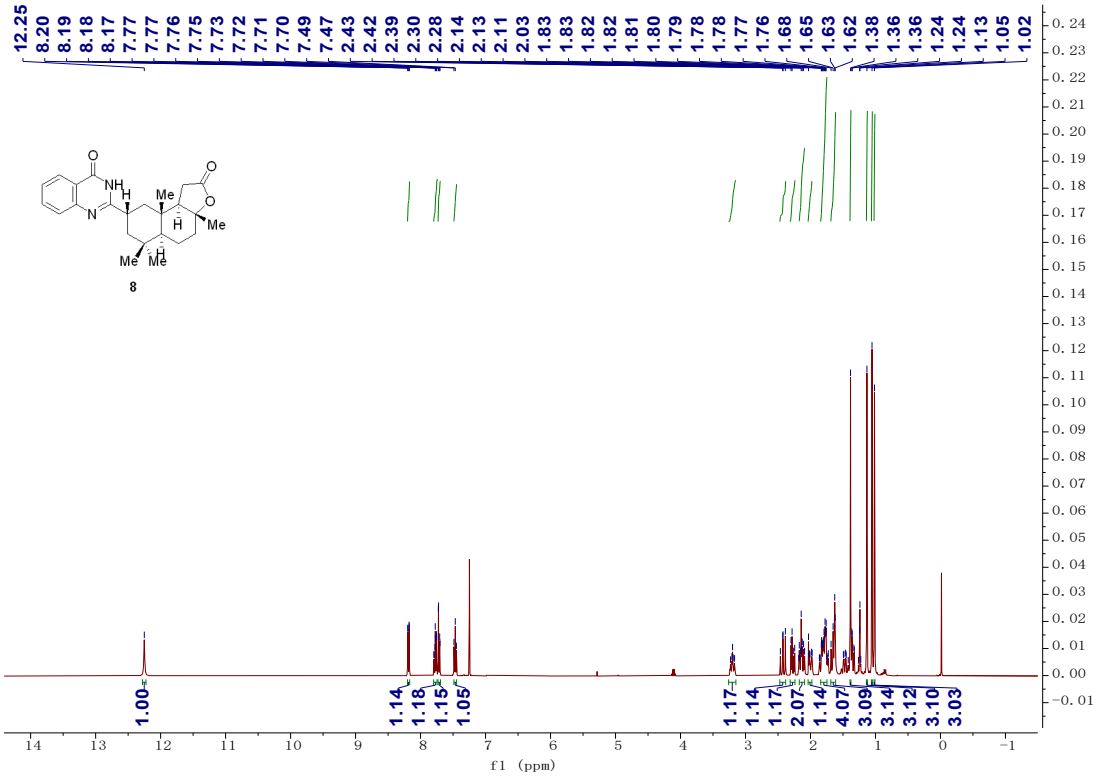
Cpd.(25μM)	Inhibition rate (%)		Cpd.(25μM)	Inhibition rate (%)	
	HUVEC	HCC1806		HUVEC	HCC1806
8	7.01	7.02	**22**	4.03	25.24
9	9.58	7.16	**23**	9.57	2.31
10	-0.9	25.1	**24**	11.12	13.66
11	8.4	9.47	**25**	-1.36	17.42
12	12.07	15.93	**26**	14.54	21
13	3.53	11.4	**28**	5.36	6.7
14	11.95	6.84	**30**	5.17	12.95
15	4.29	12.63	**sclareolide**	12.43	4.8
16	-2.33	24.45	**fenchone**	12.65	-0.76
17	5.87	10.4	**ethyl fenchol**	11.16	0.72
18	3.96	14.35	**eucalyptol**	10.25	-3.28
19	1.68	-1.4	**(−)-ambroxane**	16.73	-0.14
20	3.89	2.51	**artemisinin**	42.73	21.58
21	4.33	-6.68			

10) Reference

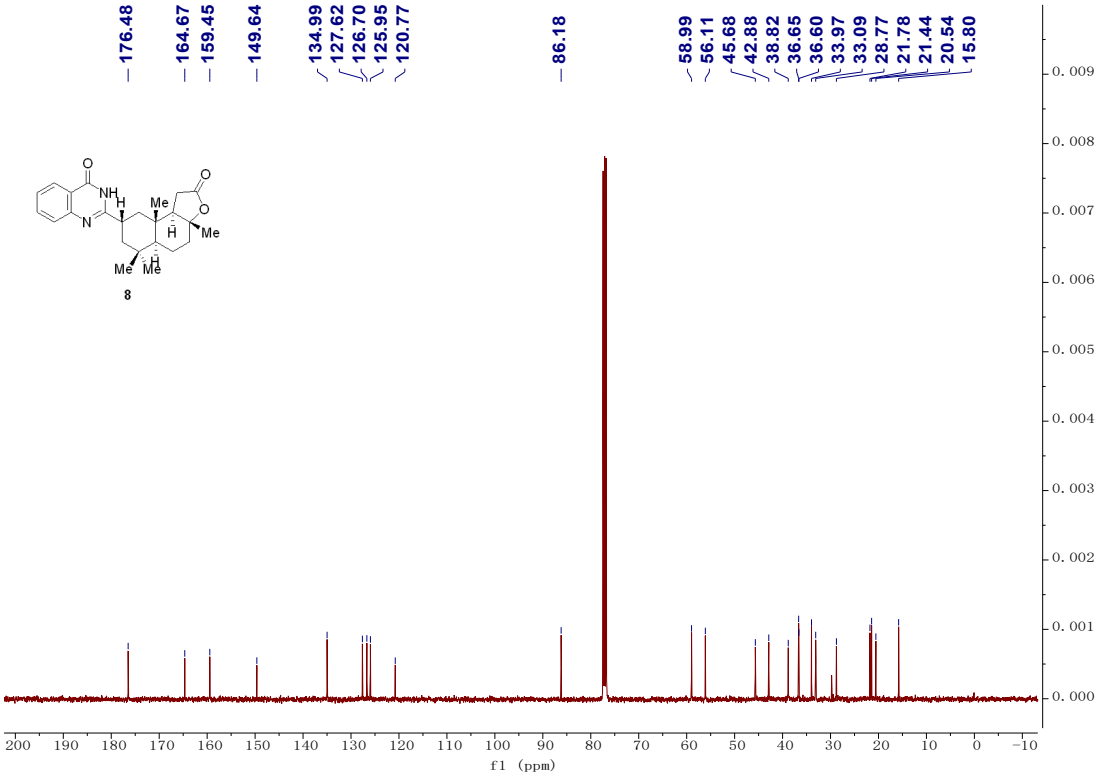
[1] Protti, S.; Ravelli, D.; Fagnoni, M.; Albini, A. *Chem. Commun.* **2009**, 7351–7353.

11) NMR Spectral Data

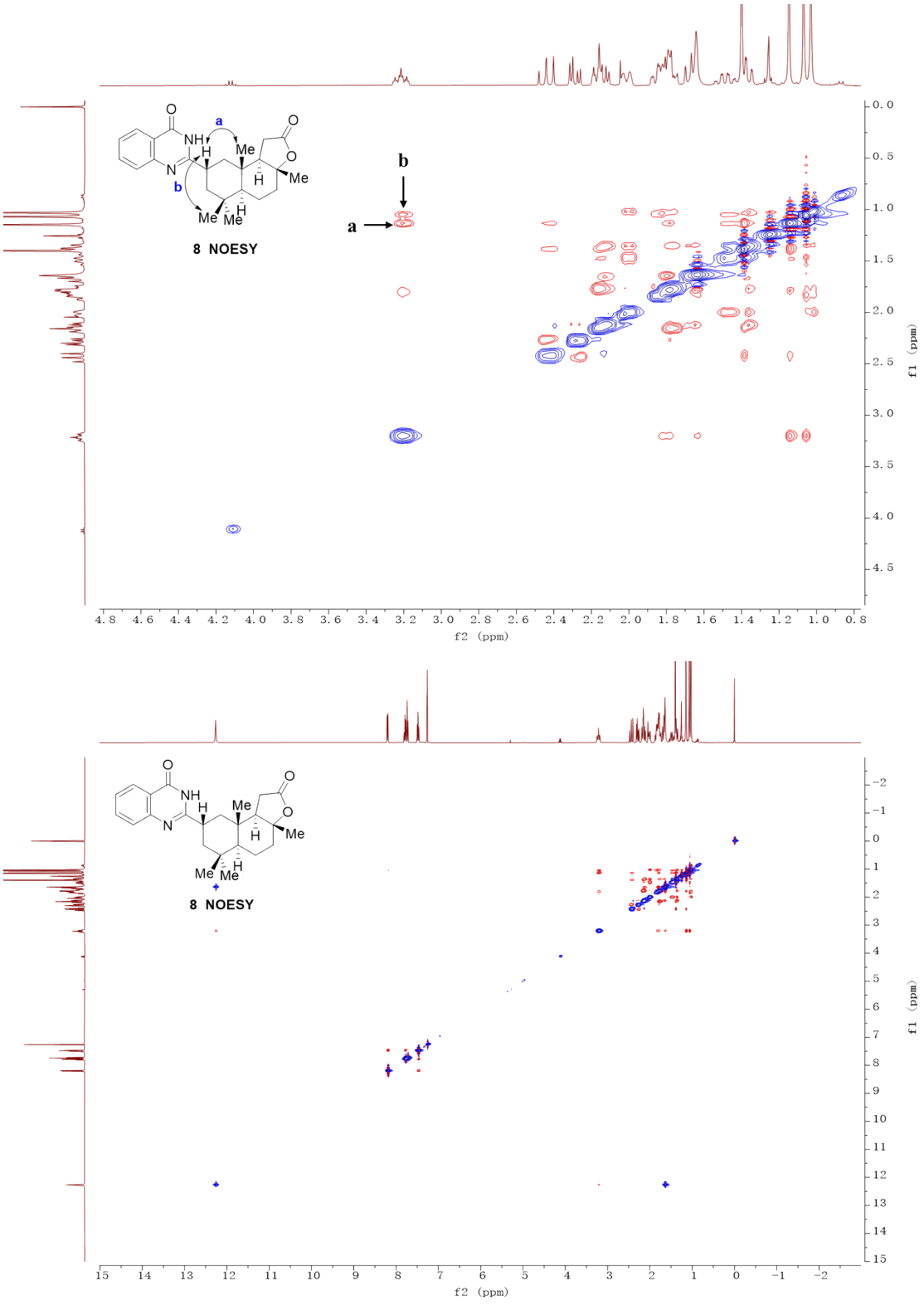
^{1}H NMR of compound 8 in $CDCl_3$ at 400 MHz



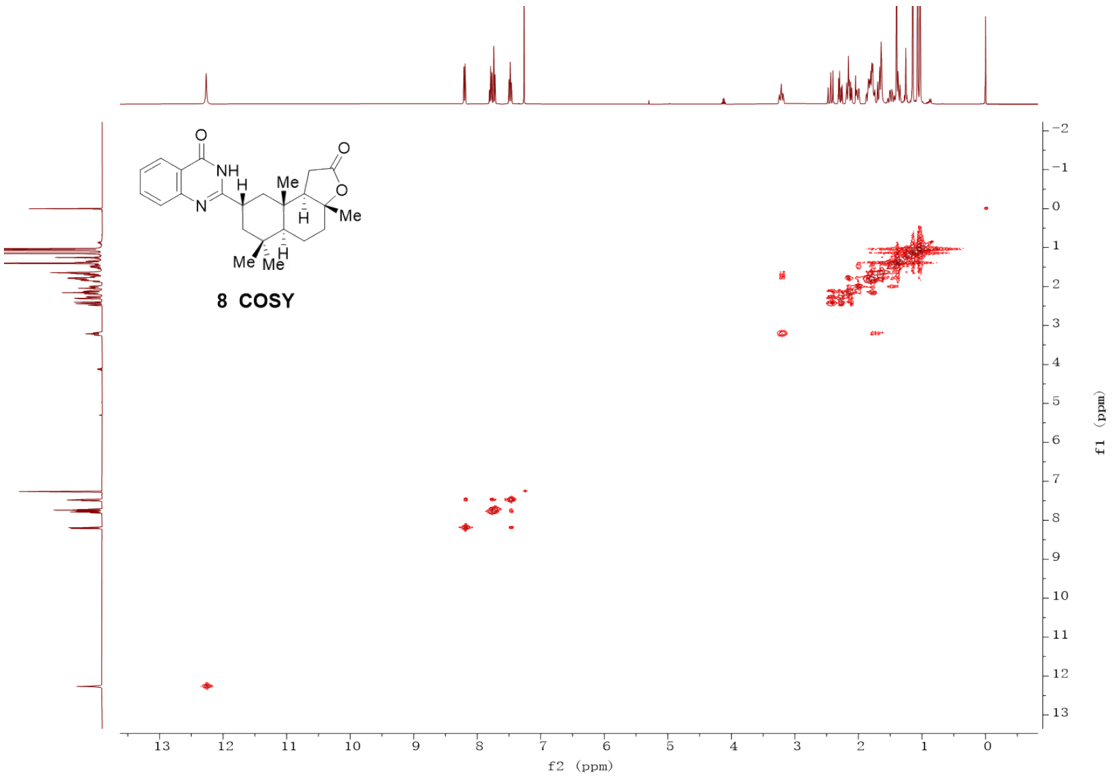
^{13}C NMR of compound 8 in $CDCl_3$ at 100 MHz



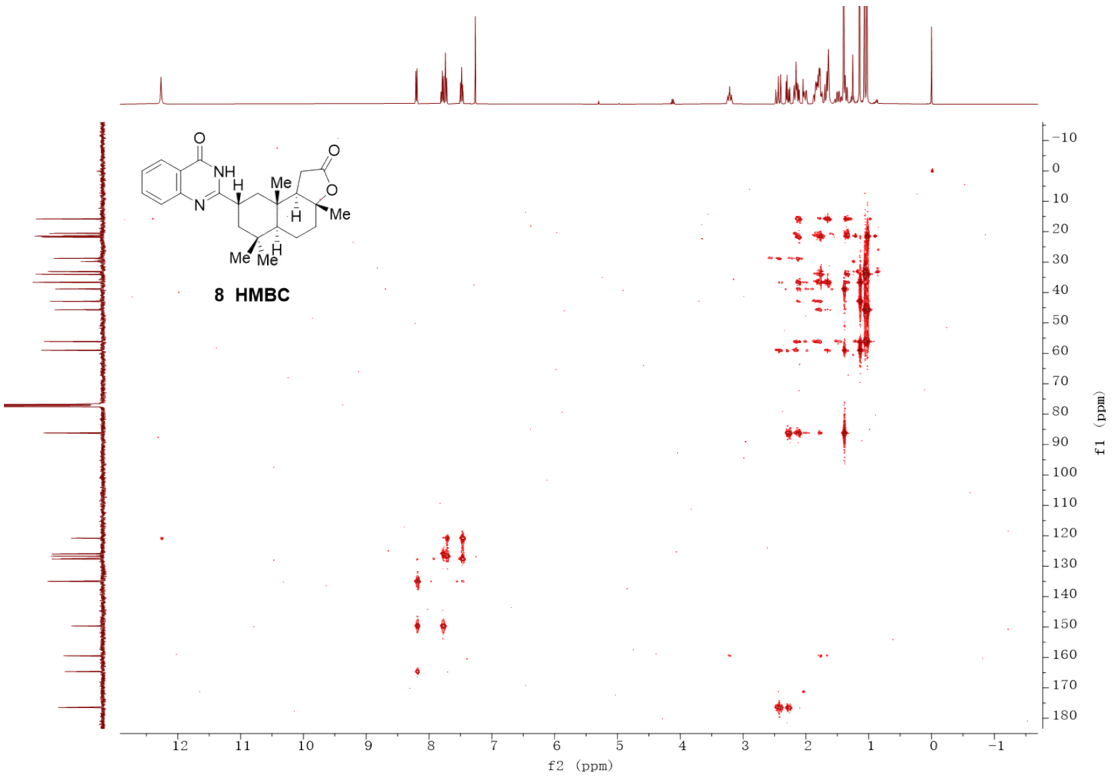
^{1}H-^{1}H –NOESY spectrum of compound 8 in $CDCl_3$ at 400 MHz



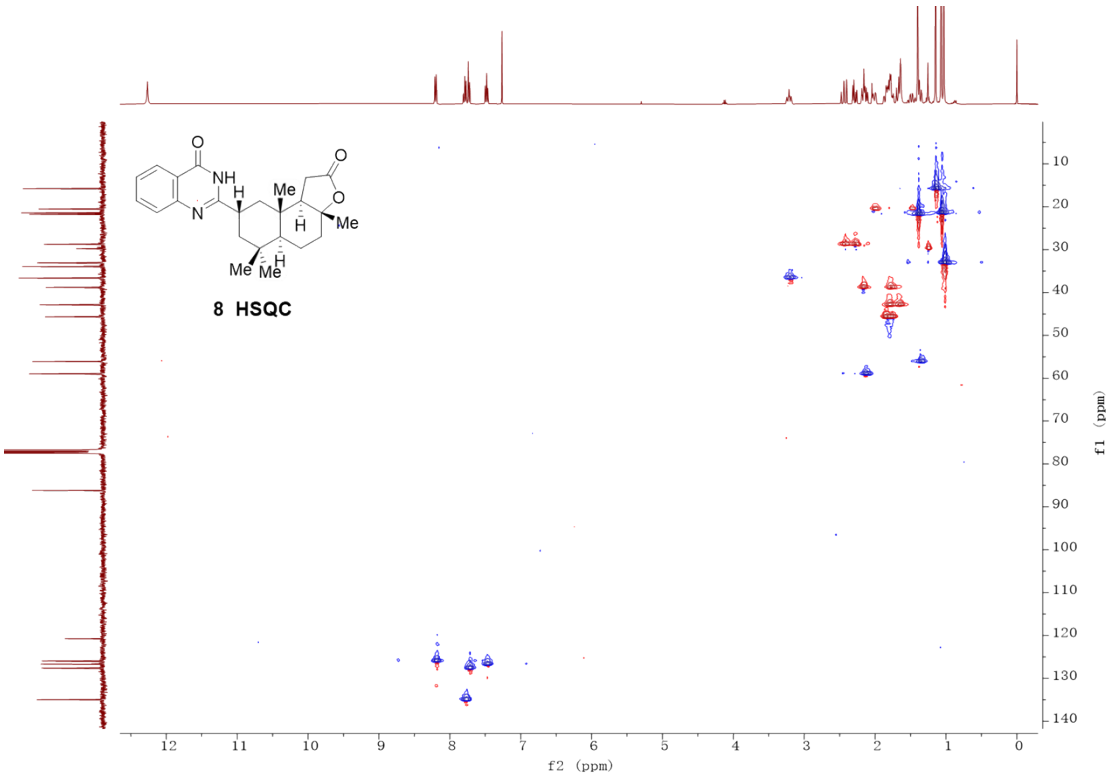
^{1}H-^{1}H –COSY spectrum of compound 8 in $CDCl_3$ at 400 MHz



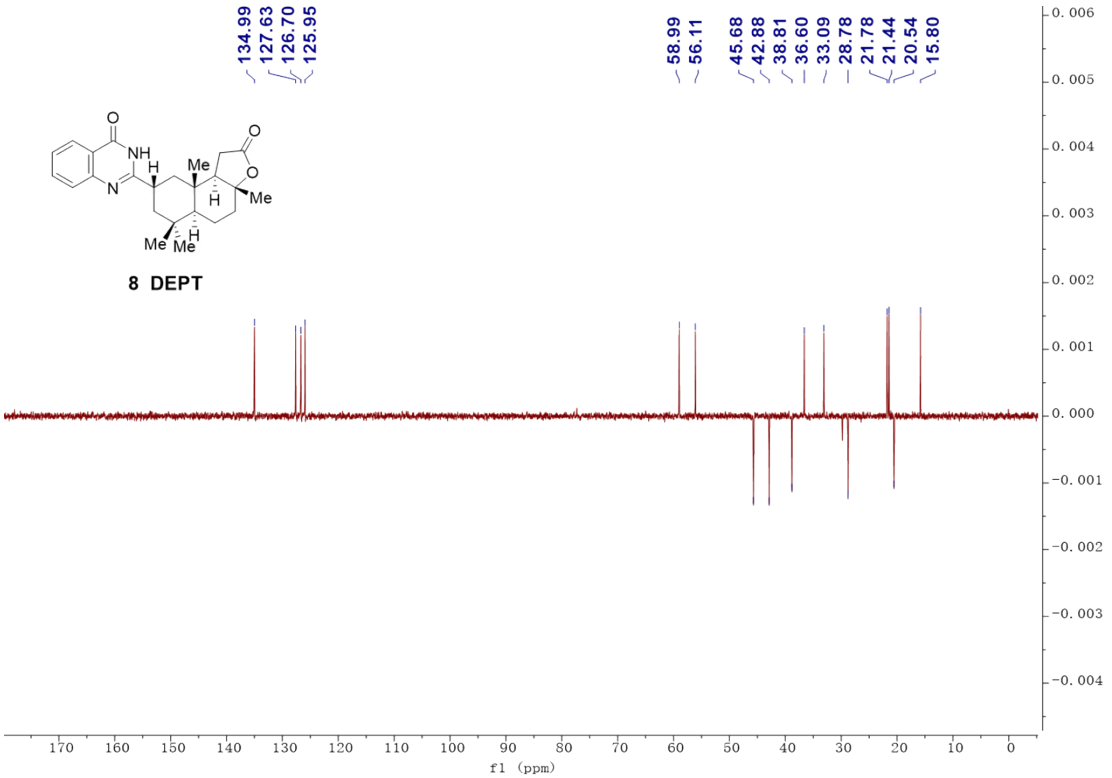
^{1}H-^{13}C –HMBC spectrum of compound 8 in $CDCl_3$ at 400 MHz



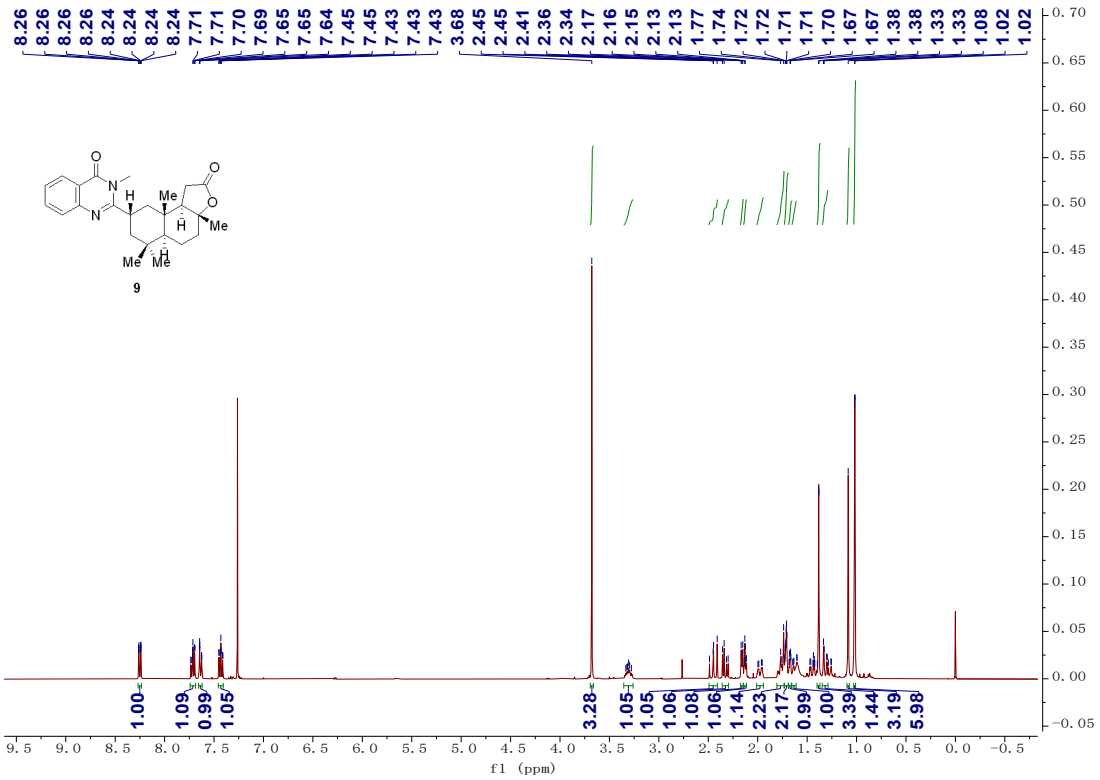
^{1}H-^{13}C –HSQC spectrum of compound 8 in $CDCl_3$ at 400 MHz



DEPT spectrum of compound 8 in $CDCl_3$ at 400 MHz



^{1}H NMR of compound 9 in $CDCl_3$ at 400 MHz



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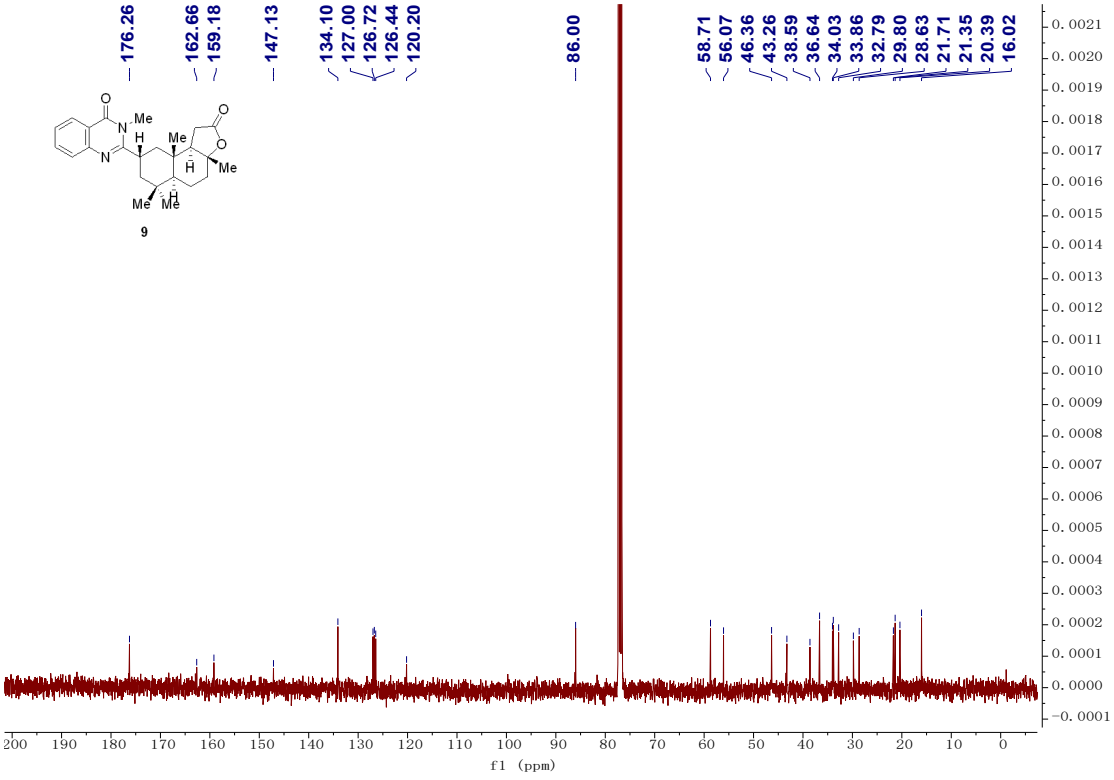
^{13}C NMR of compound 9 in $CDCl_3$ at 100 MHz



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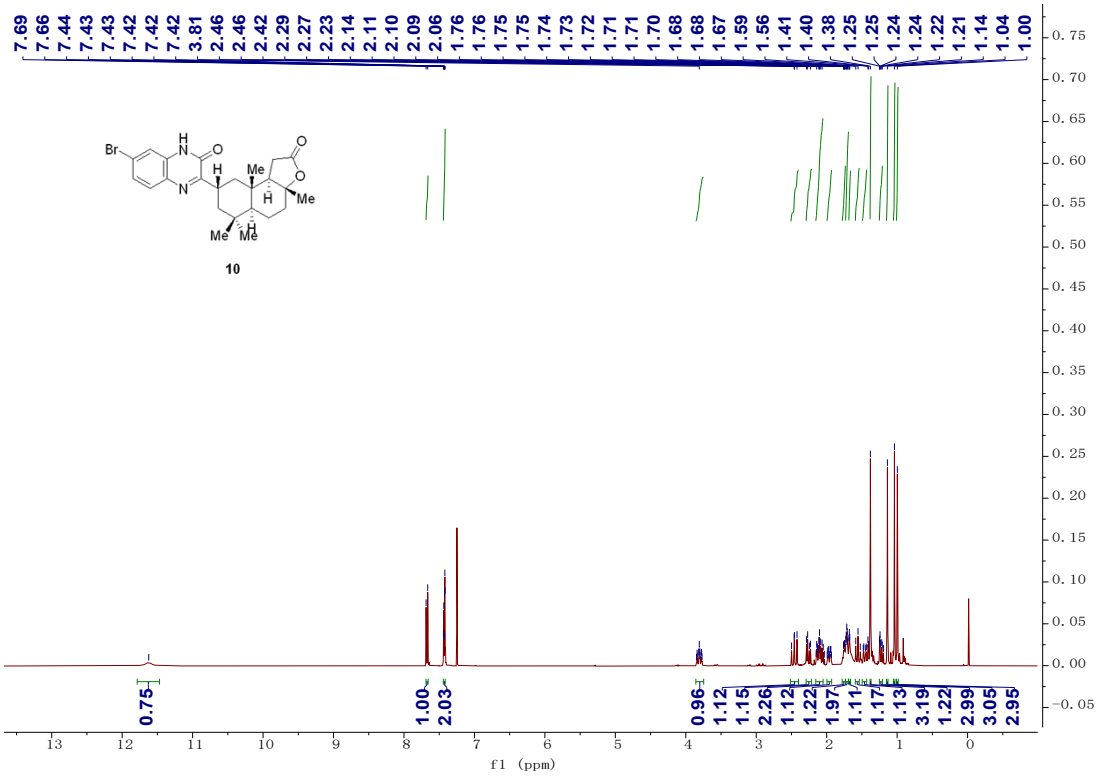
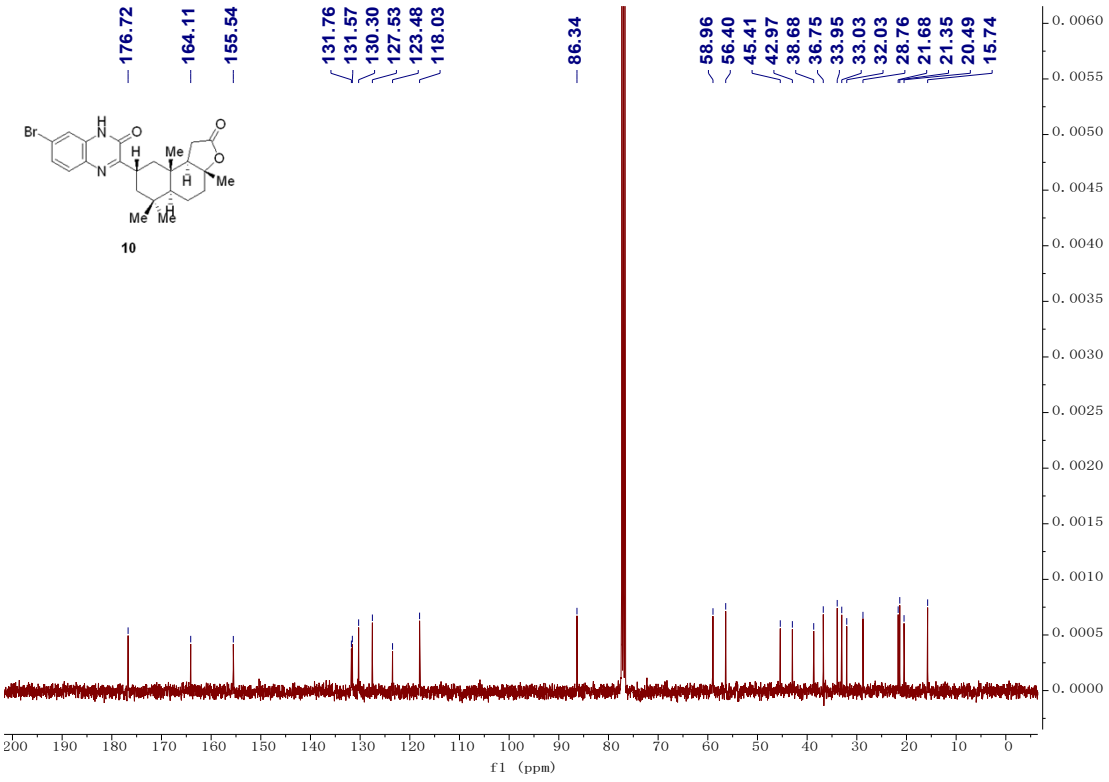
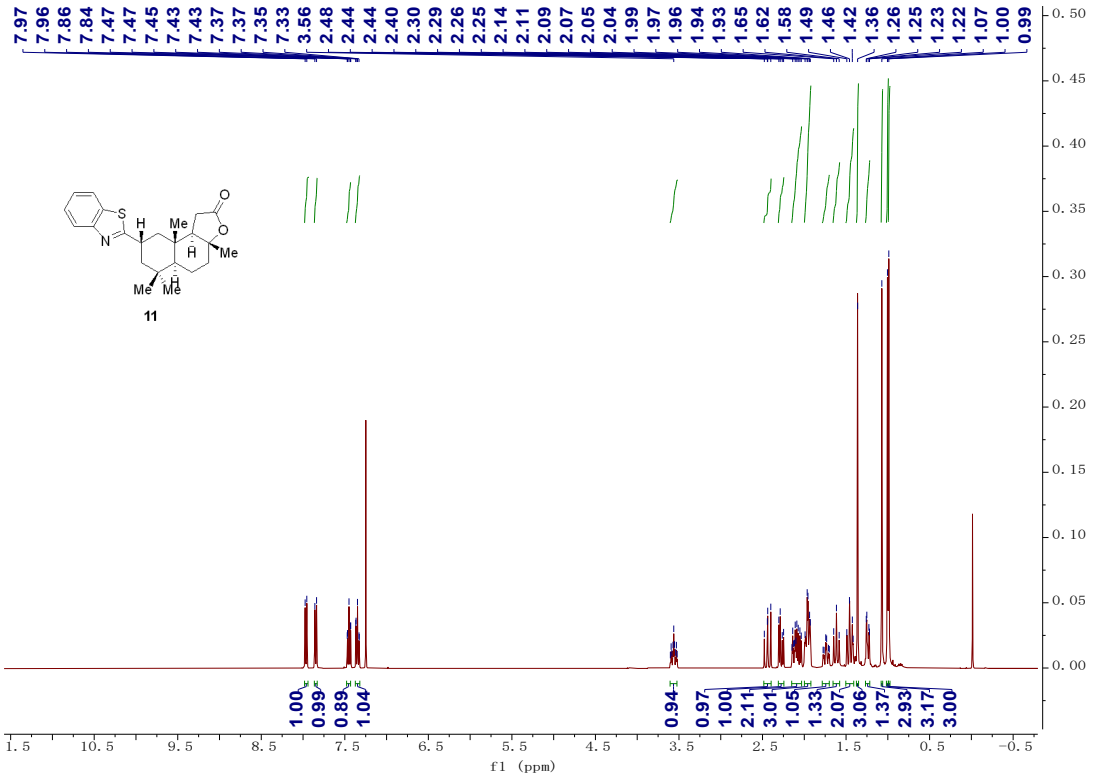
^{1}H NMR of compound 10 in $CDCl_3$ at 400 MHz



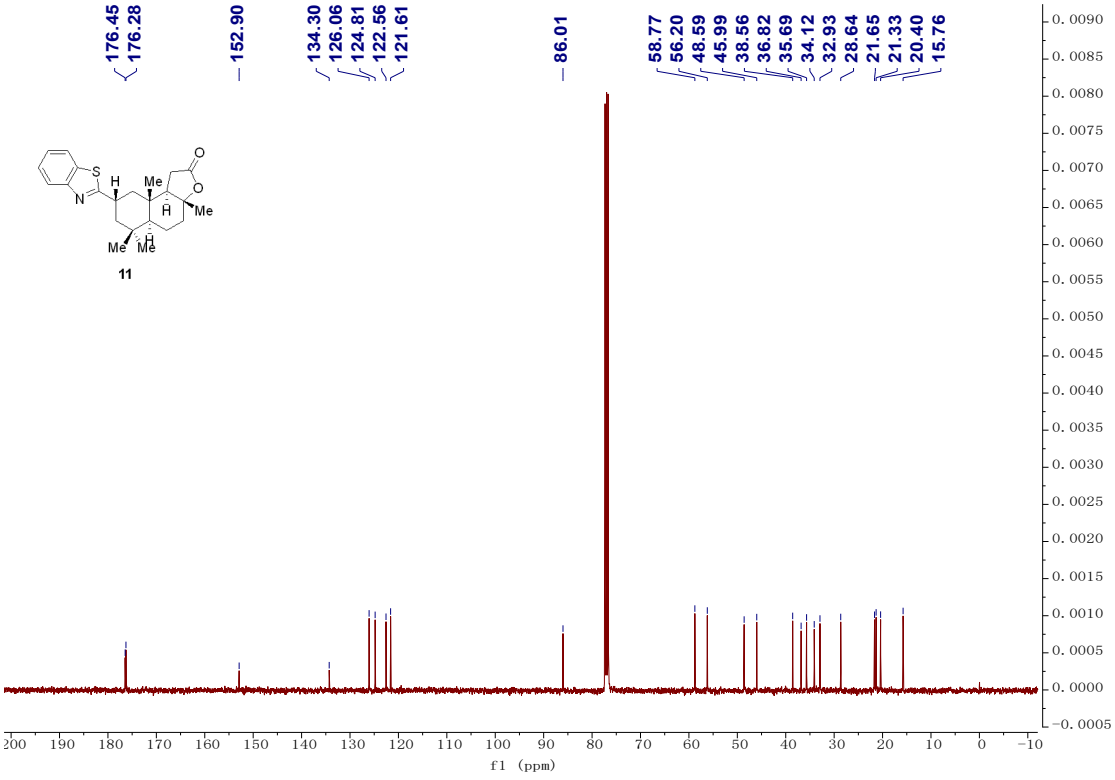
^{13}C NMR of compound 10 in $CDCl_3$ at 100 MHz



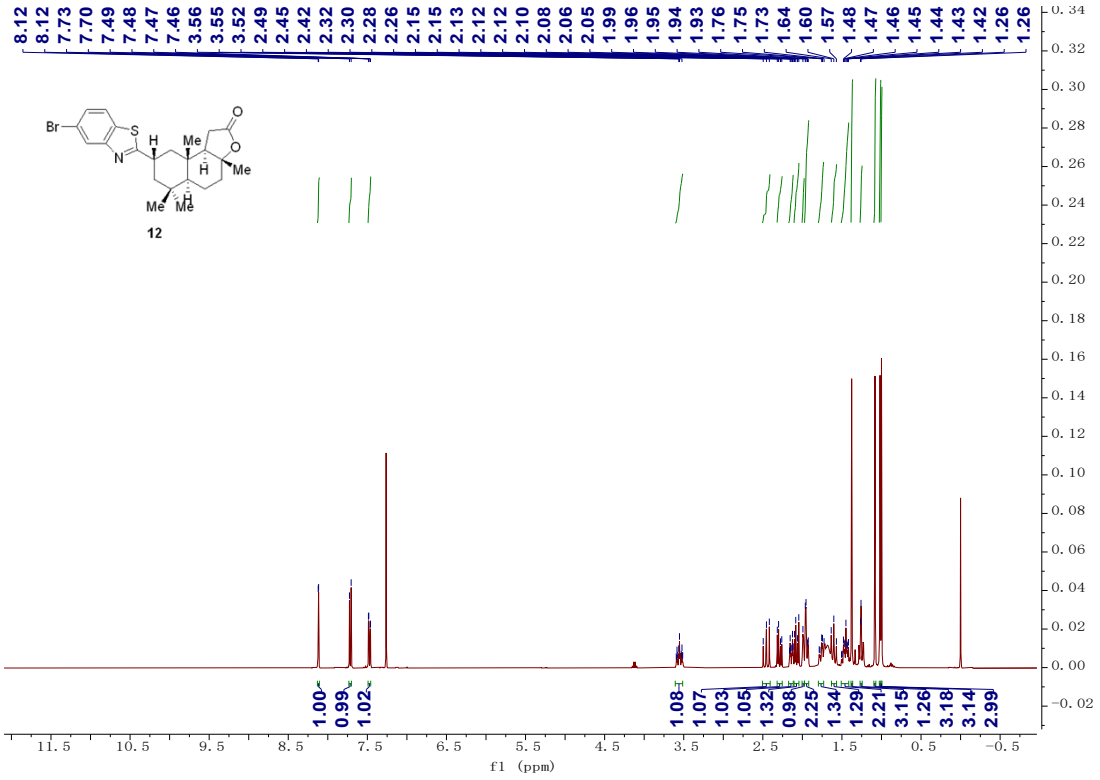
^{1}H NMR of compound 11 in $CDCl_3$ at 400 MHz



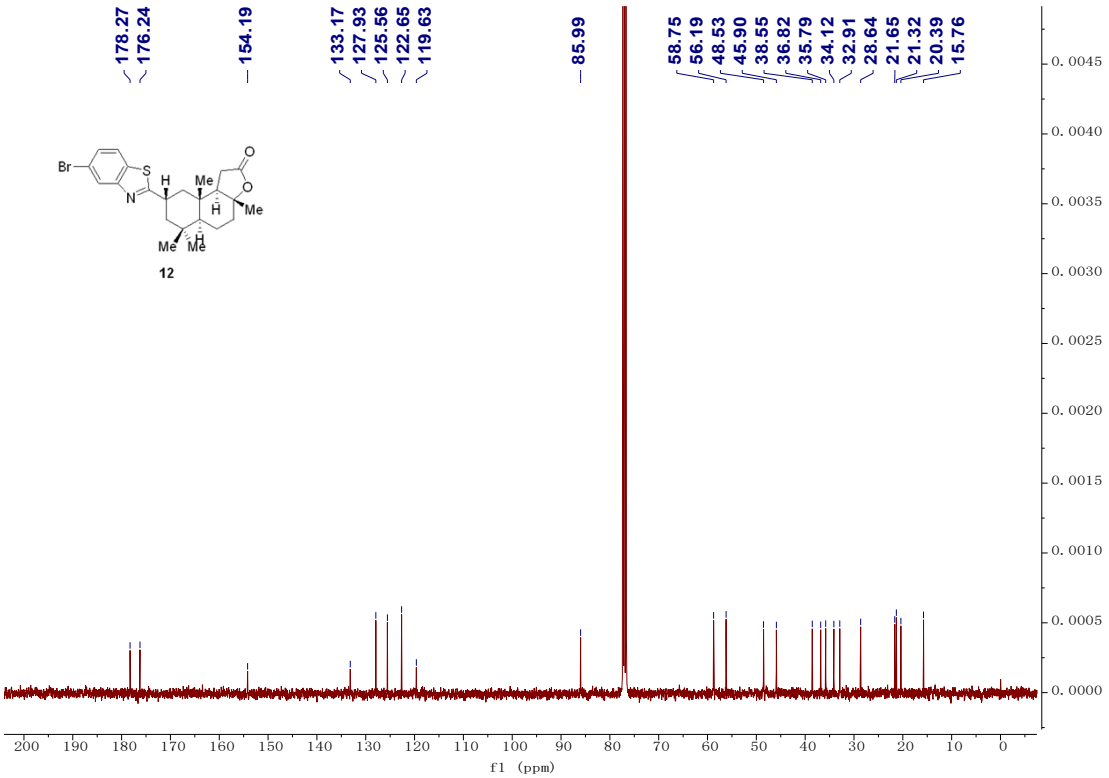
^{13}C NMR of compound 11 in $CDCl_3$ at 100 MHz



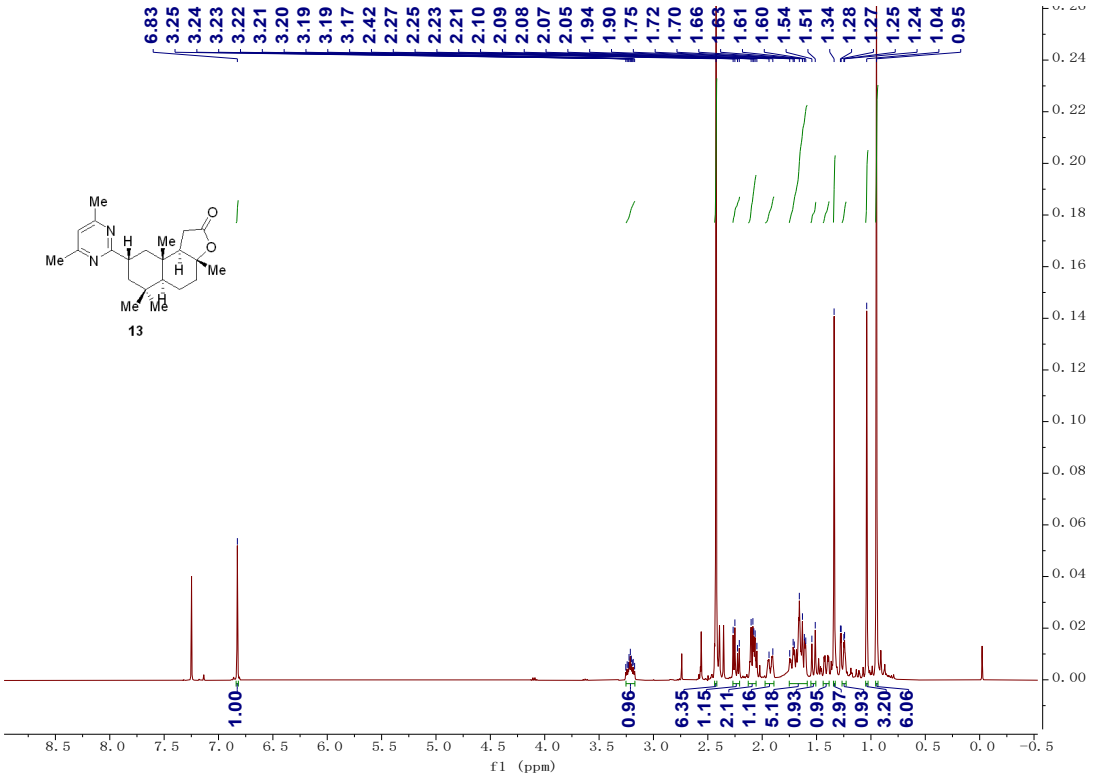
^{1}H NMR of compound 12 in $CDCl_3$ at 400 MHz



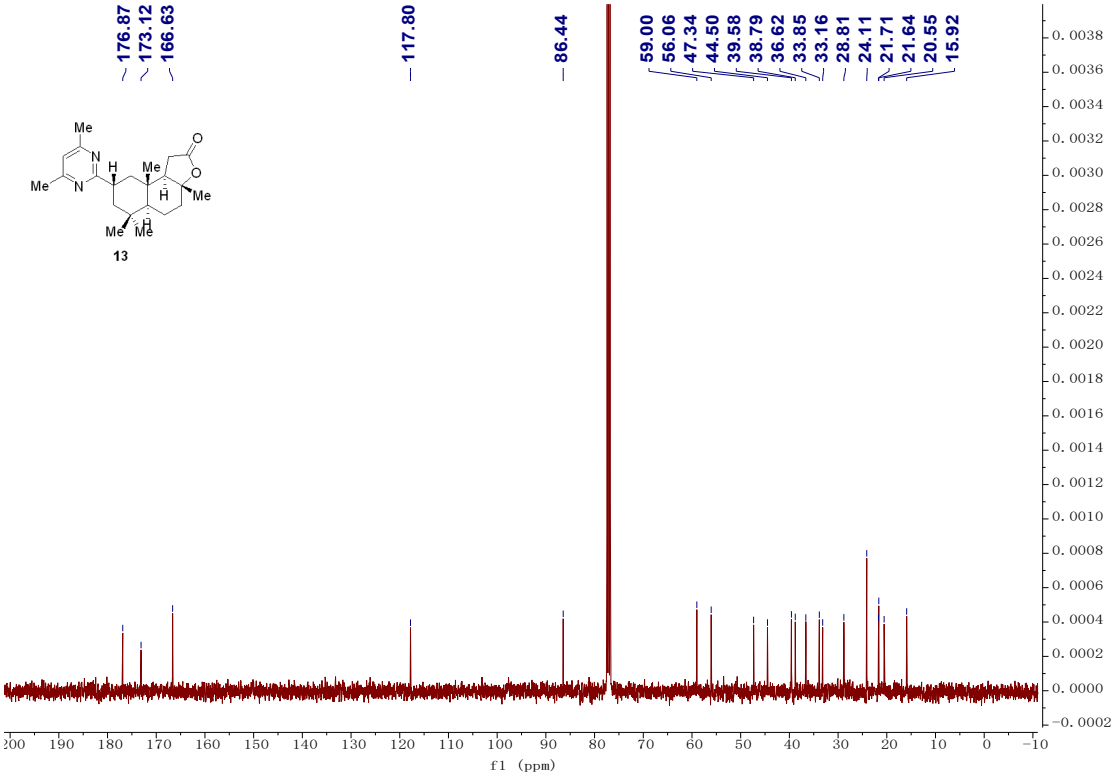
^{13}C NMR of compound 12 in $CDCl_3$ at 100 MHz



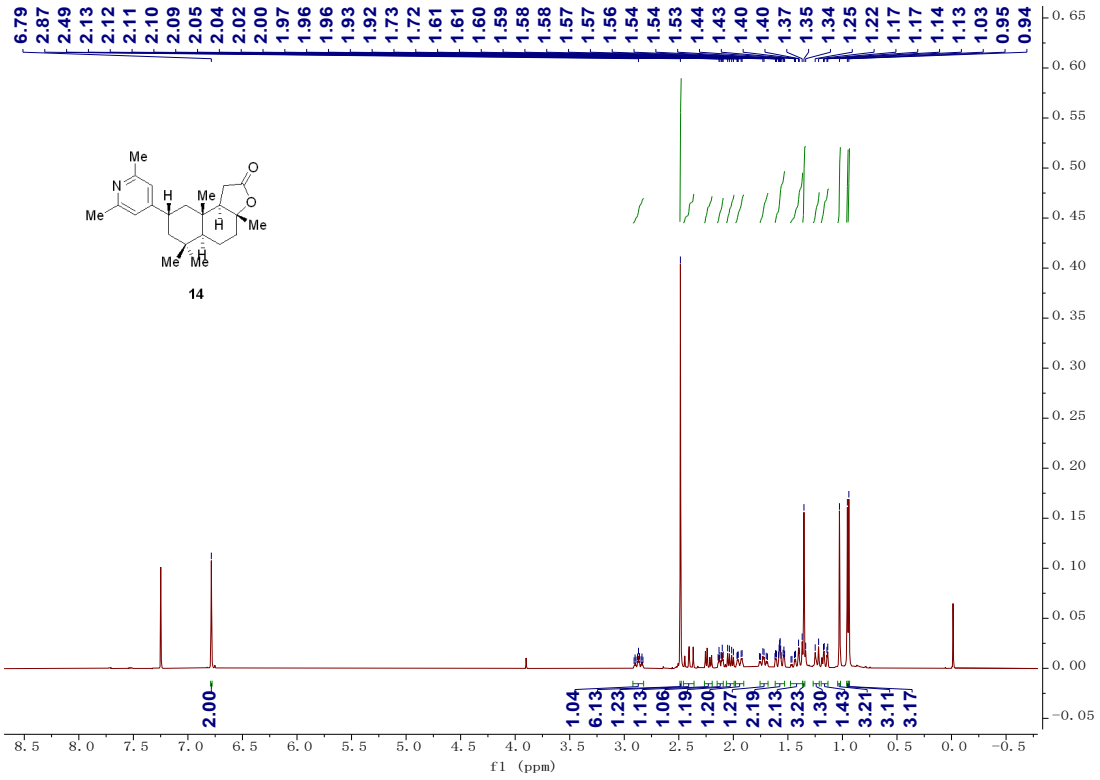
^{1}H NMR of compound 13 in $CDCl_3$ at 400 MHz



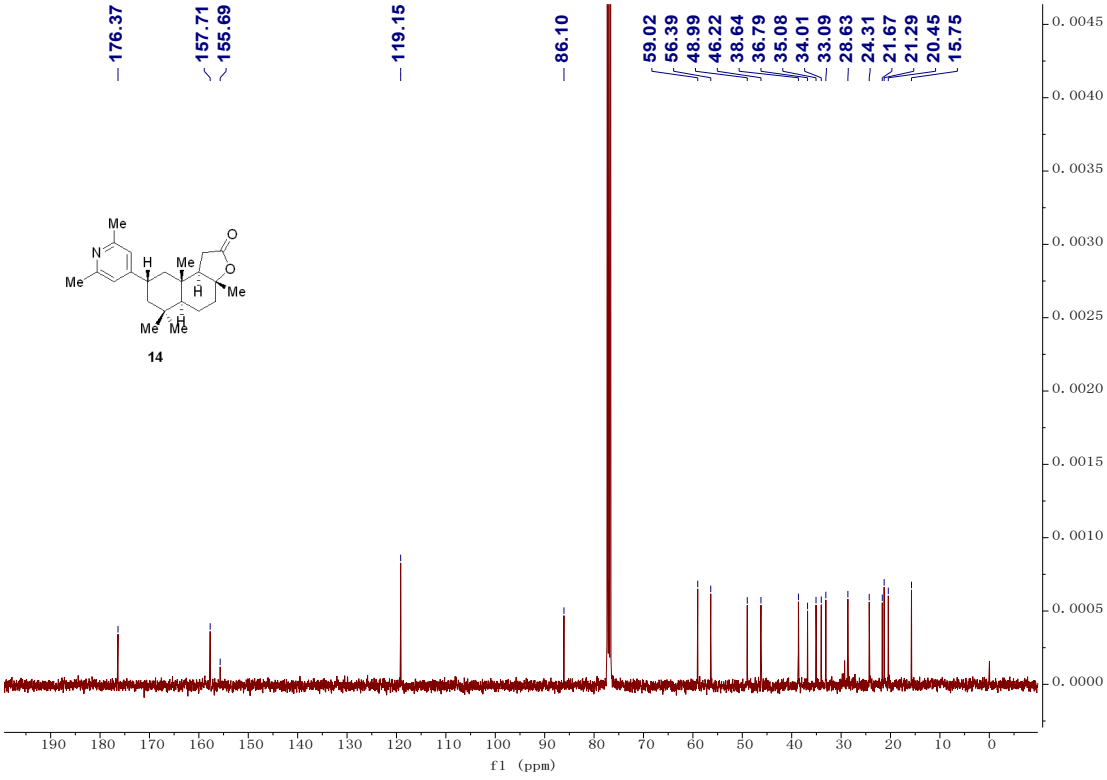
^{13}C NMR of compound 13 in $CDCl_3$ at 100 MHz



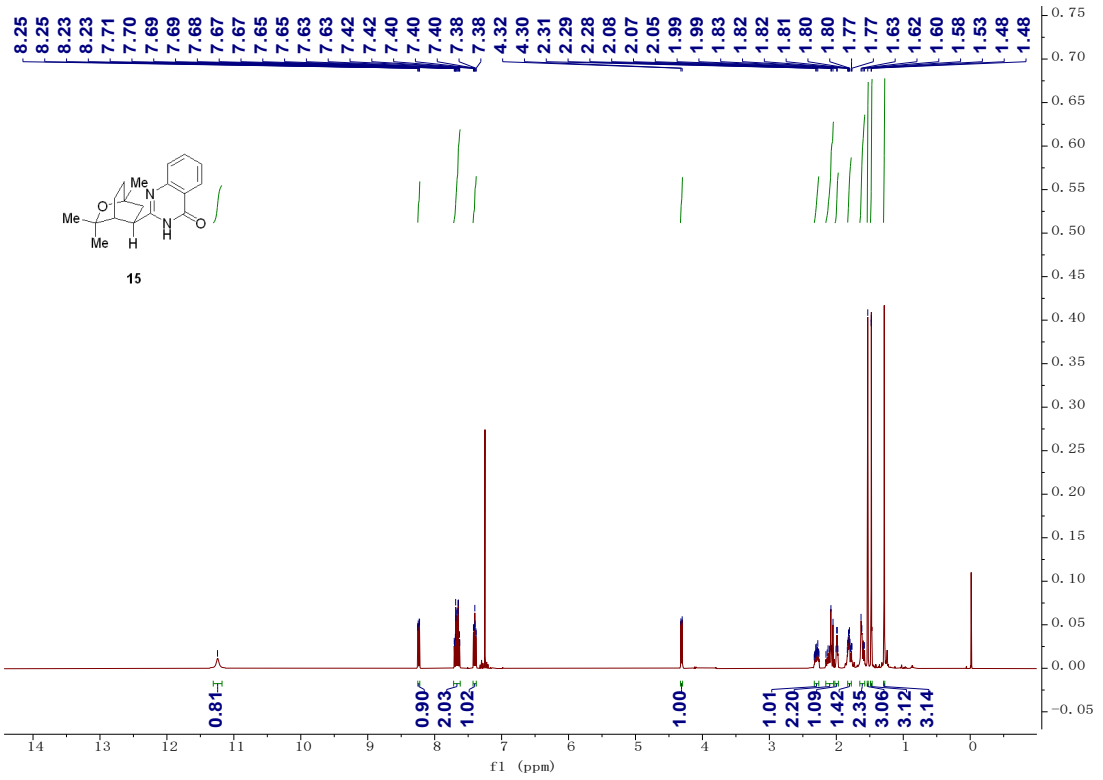
^{1}H NMR of compound 14 in $CDCl_3$ at 400 MHz



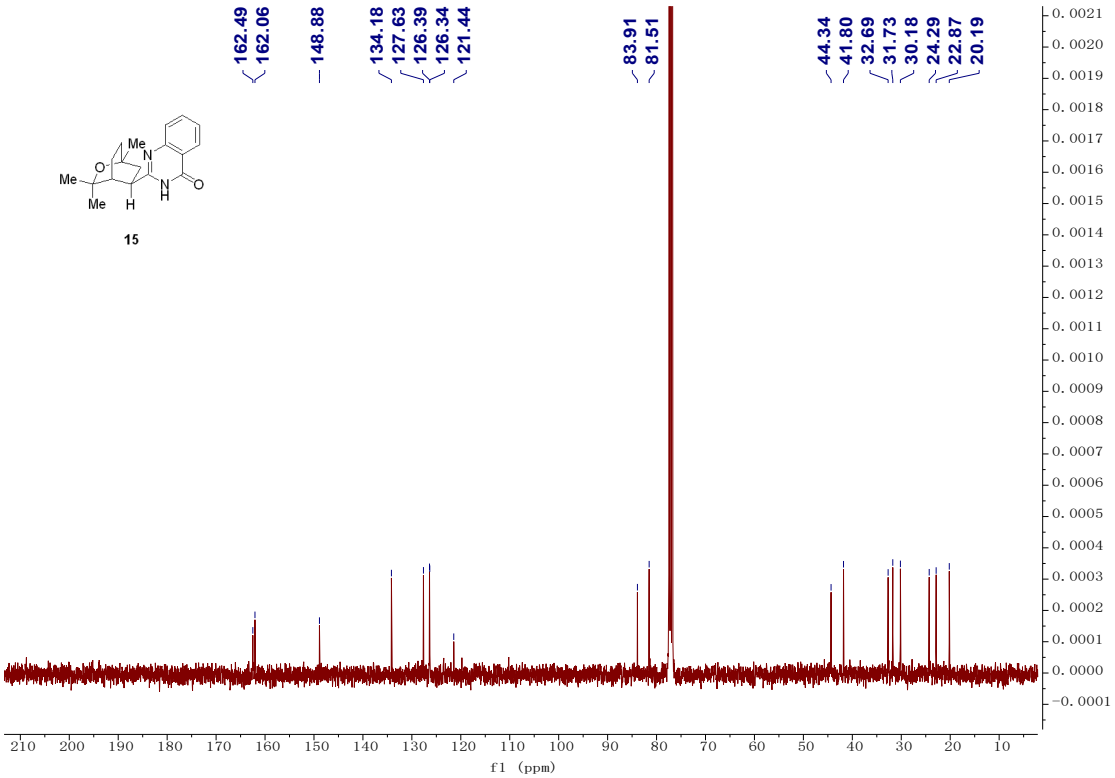
^{13}C NMR of compound 14 in $CDCl_3$ at 100 MHz



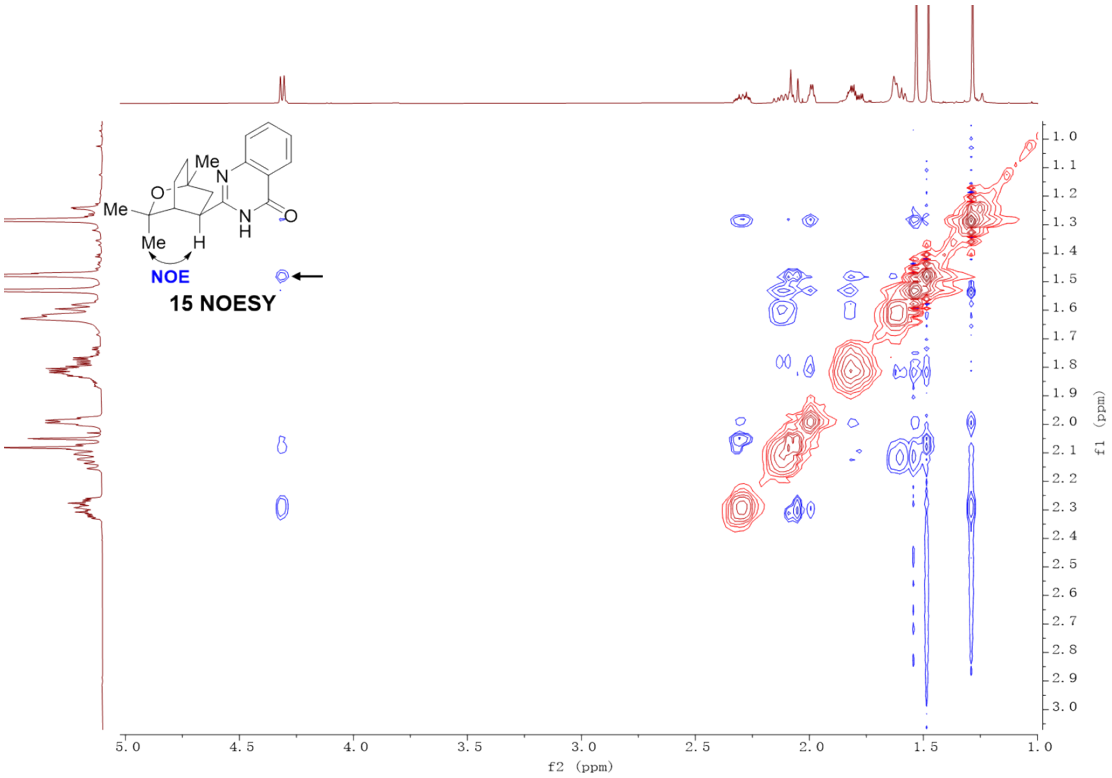
^{1}H NMR of compound 15 in $CDCl_3$ at 400 MHz

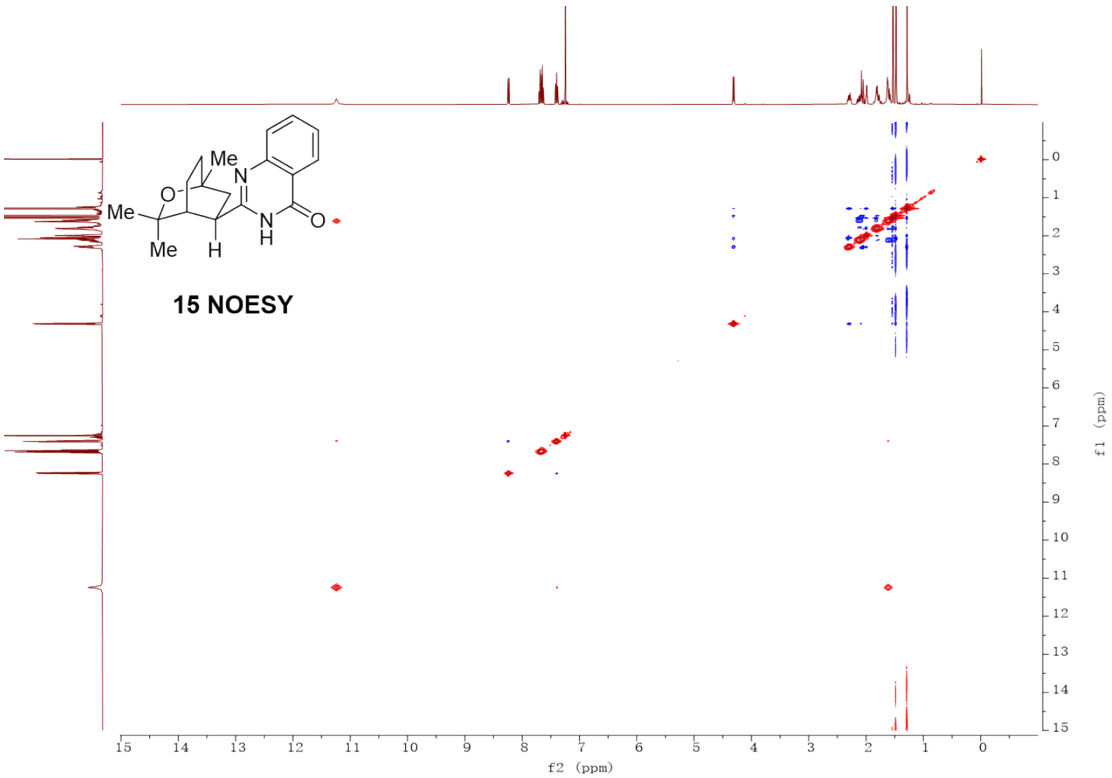


^{13}C NMR of compound 15 in $CDCl_3$ at 100 MHz

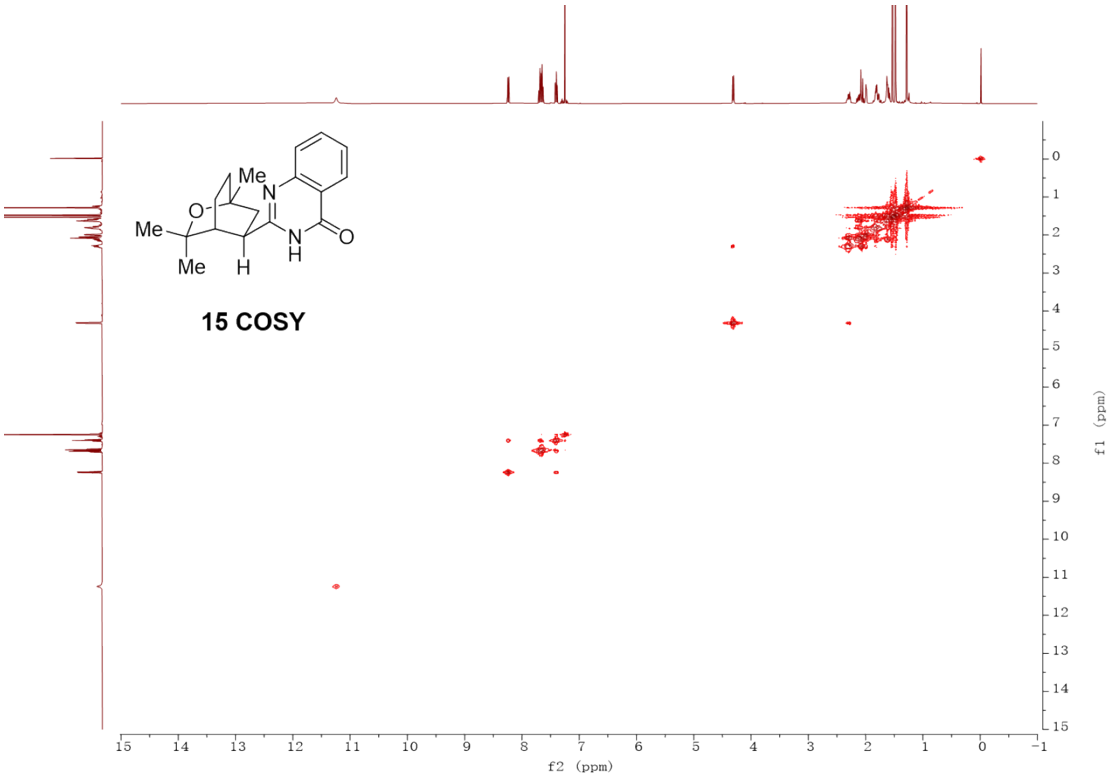


^{1}H-^{1}H –NOESY spectrum of compound 15 in $CDCl_3$ at 400 MHz

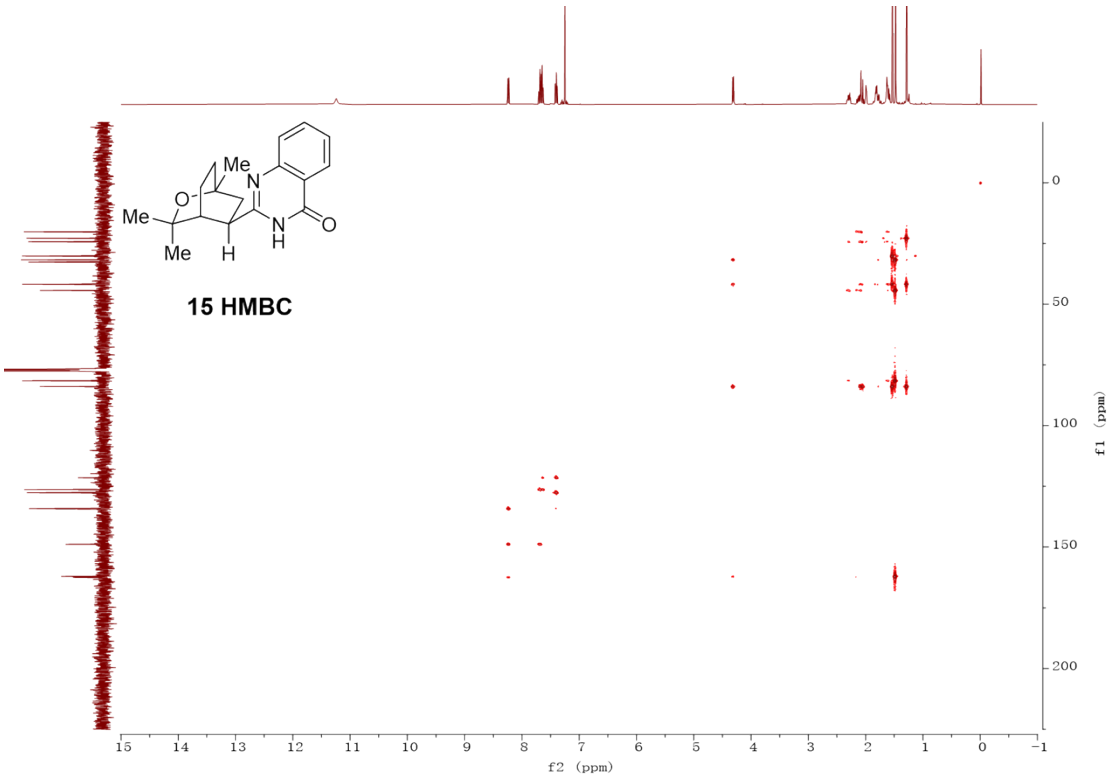




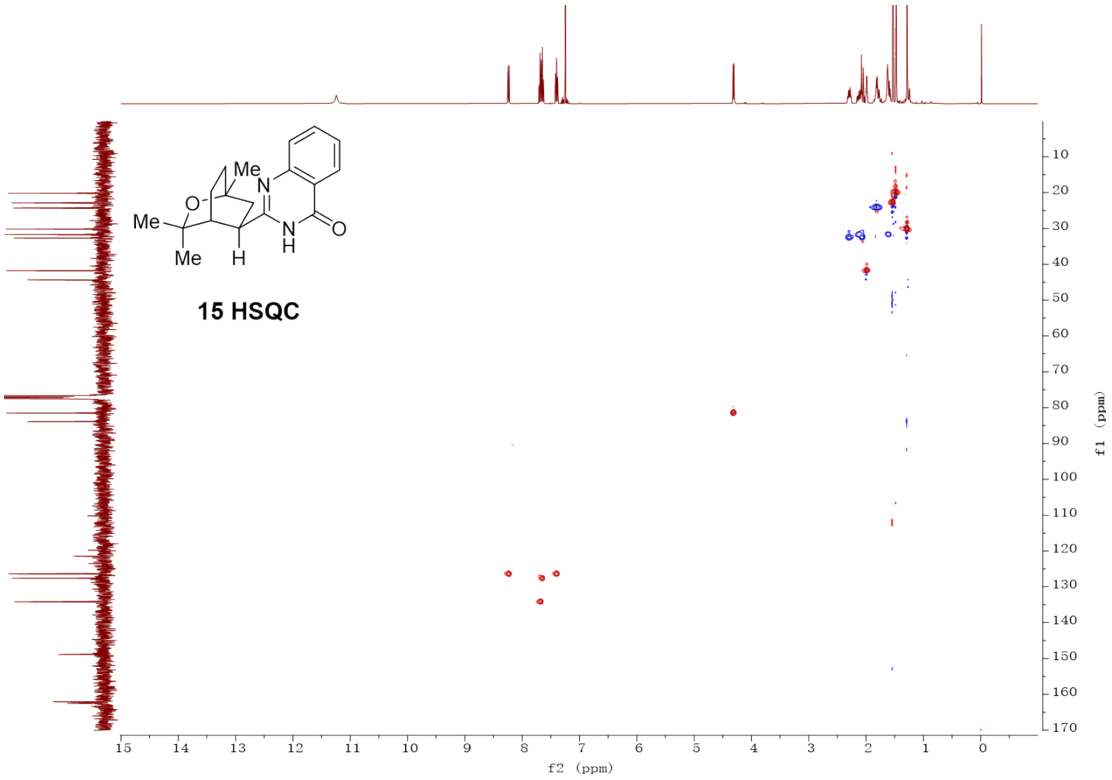
^{1}H-^{1}H –COSY spectrum of compound 15 in $CDCl_3$ at 400 MHz



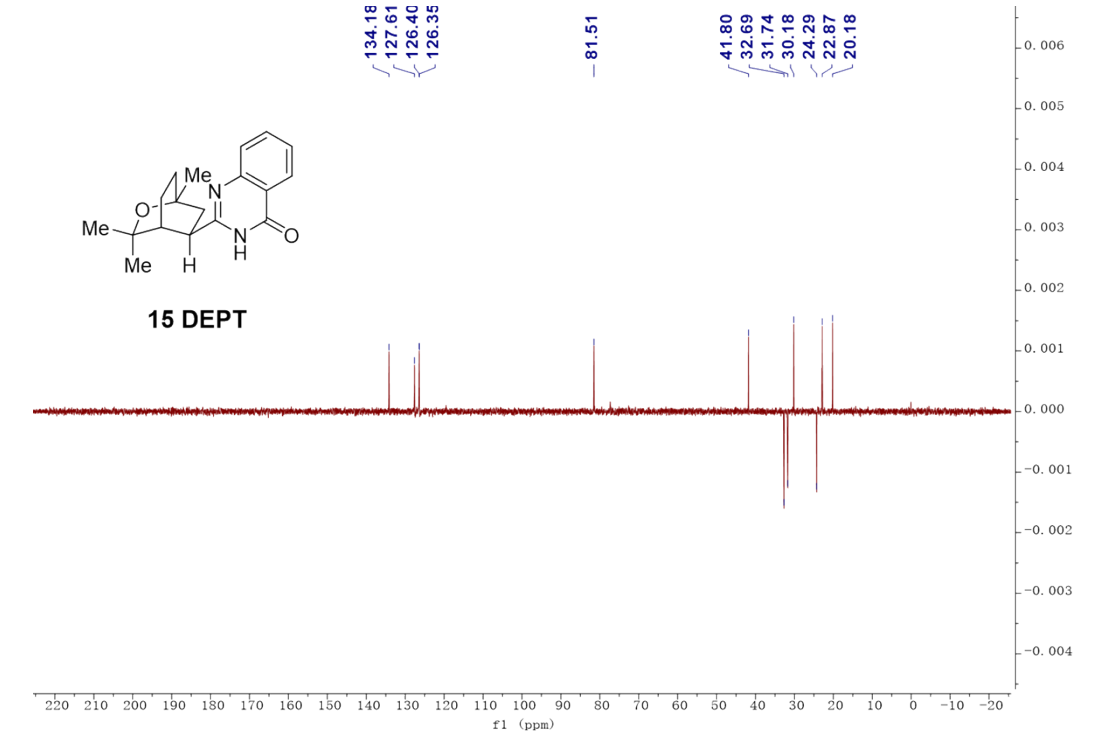
^{1}H-^{13}C –HMBC spectrum of compound 15 in $CDCl_3$ at 400 MHz



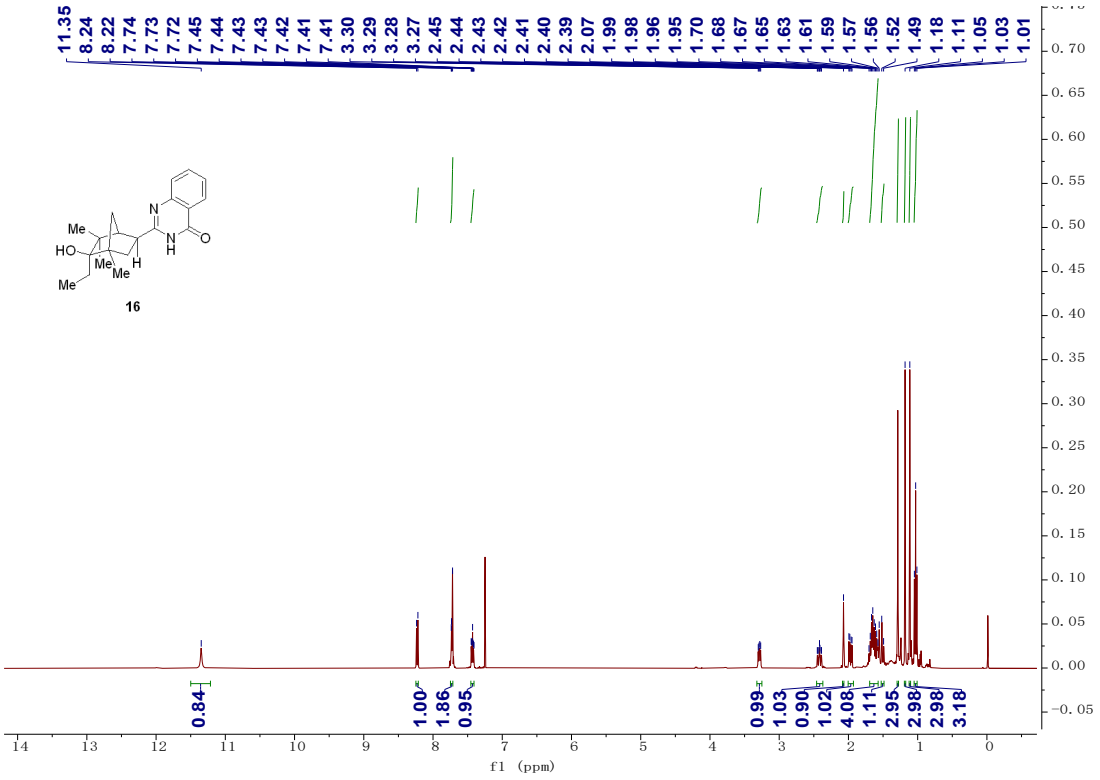
^{1}H-^{13}C –HSQC spectrum of compound 15 in $CDCl_3$ at 400 MHz



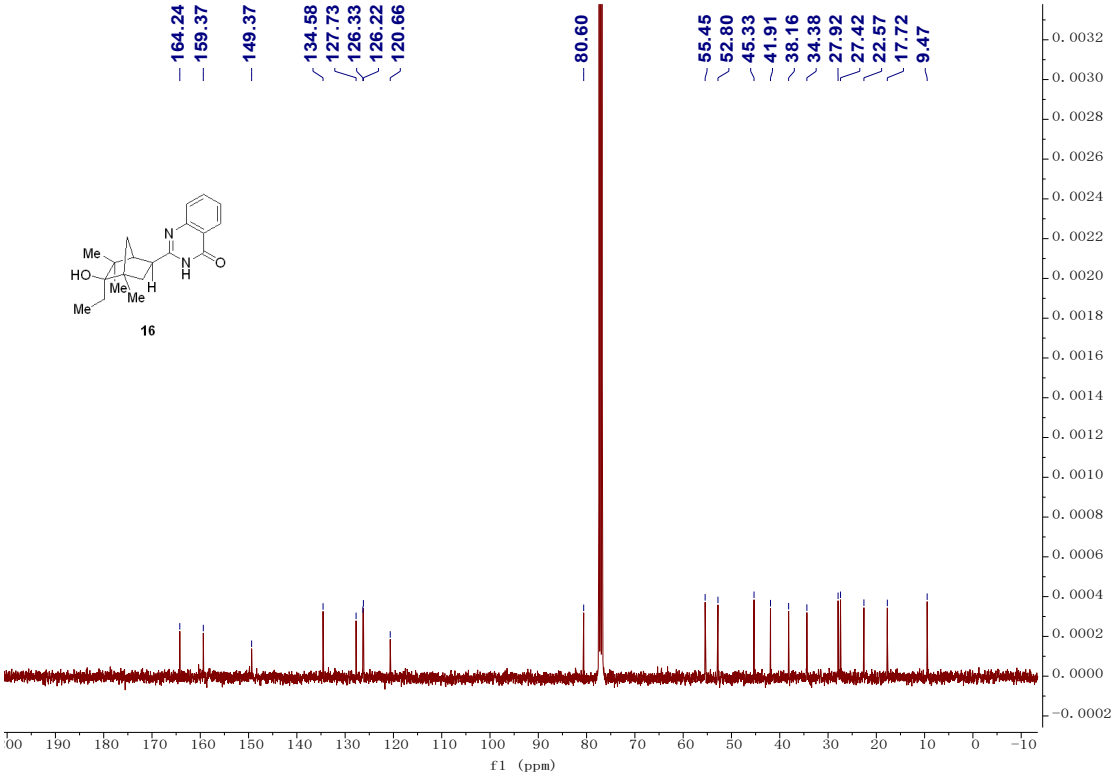
DEPT spectrum of compound 15 in $CDCl_3$ at 400 MHz



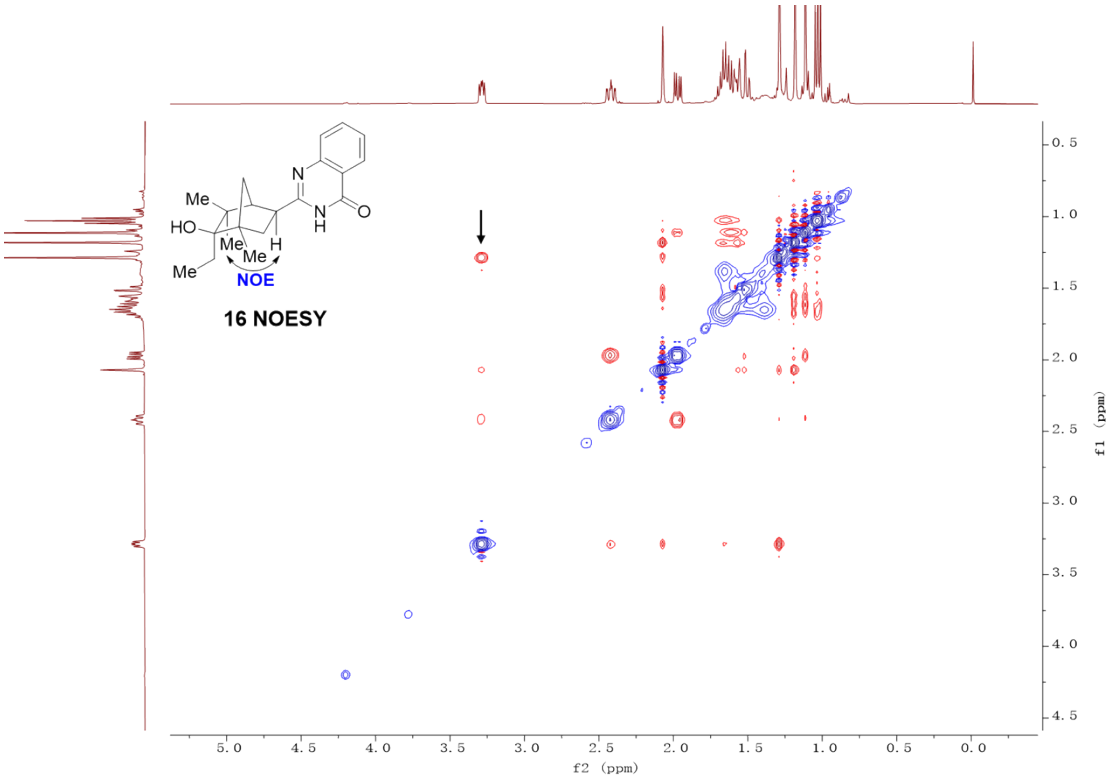
^{1}H NMR of compound 16 in $CDCl_3$ at 400 MHz

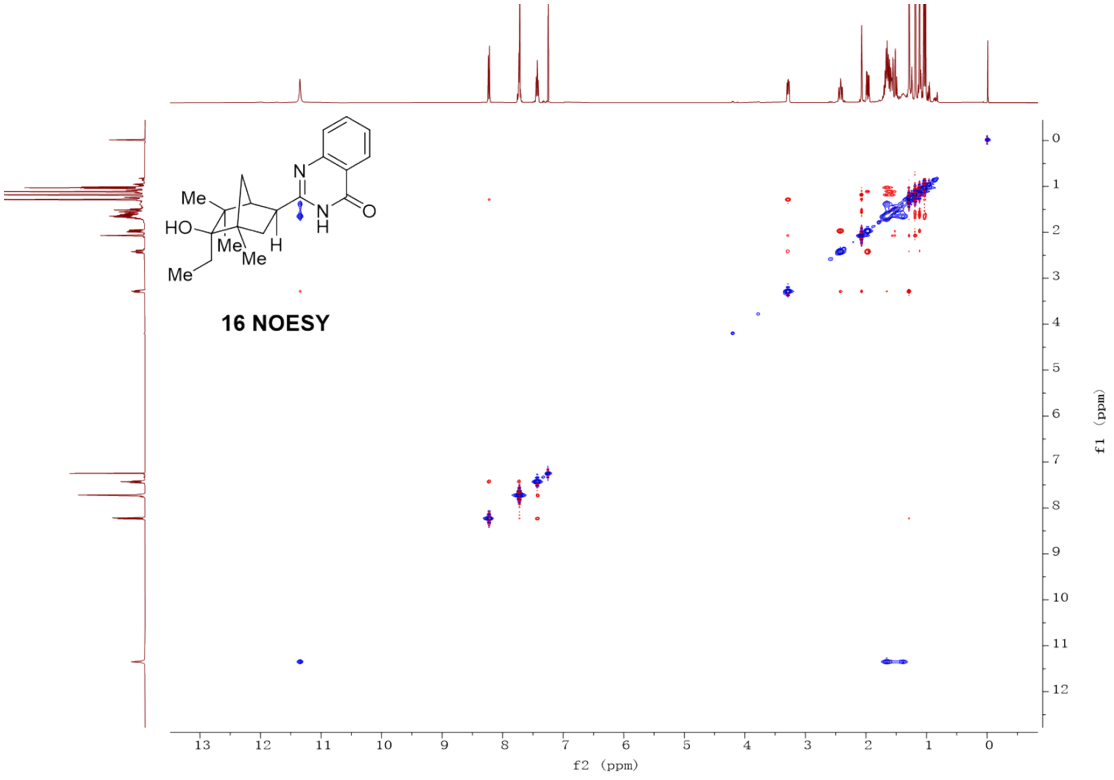


^{13}C NMR of compound 16 in $CDCl_3$ at 100 MHz

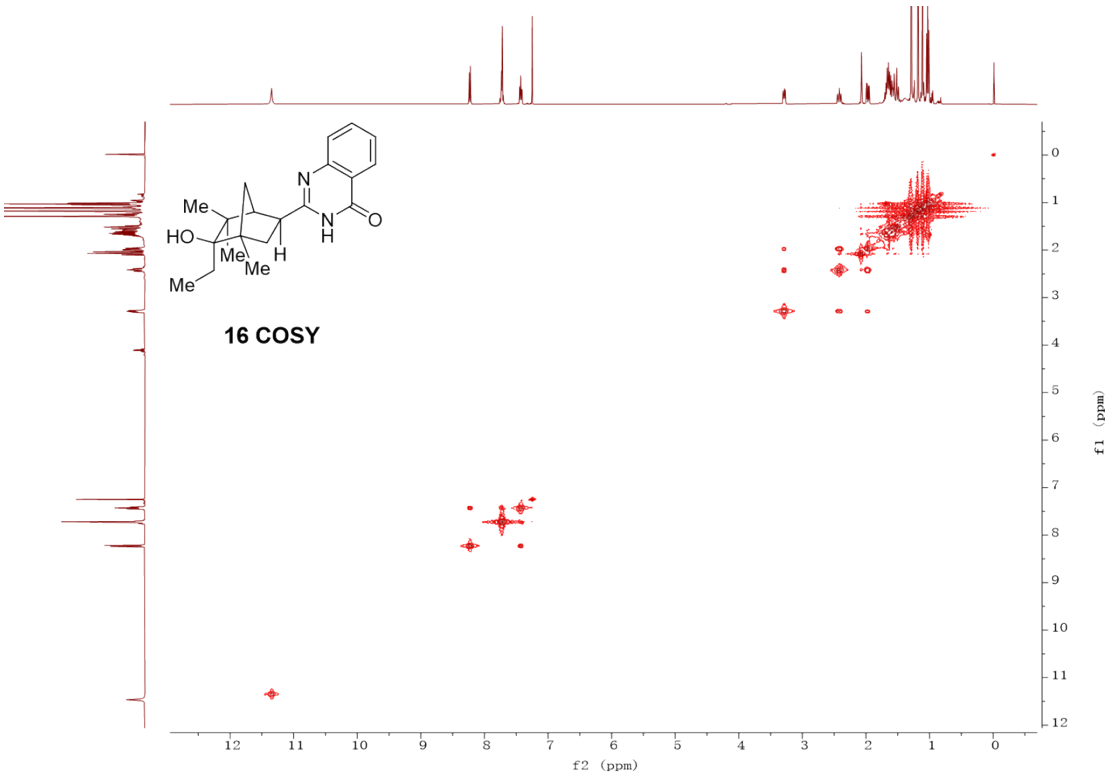


^{1}H-^{1}H –NOESY spectrum of compound 16 in $CDCl_3$ at 400 MHz

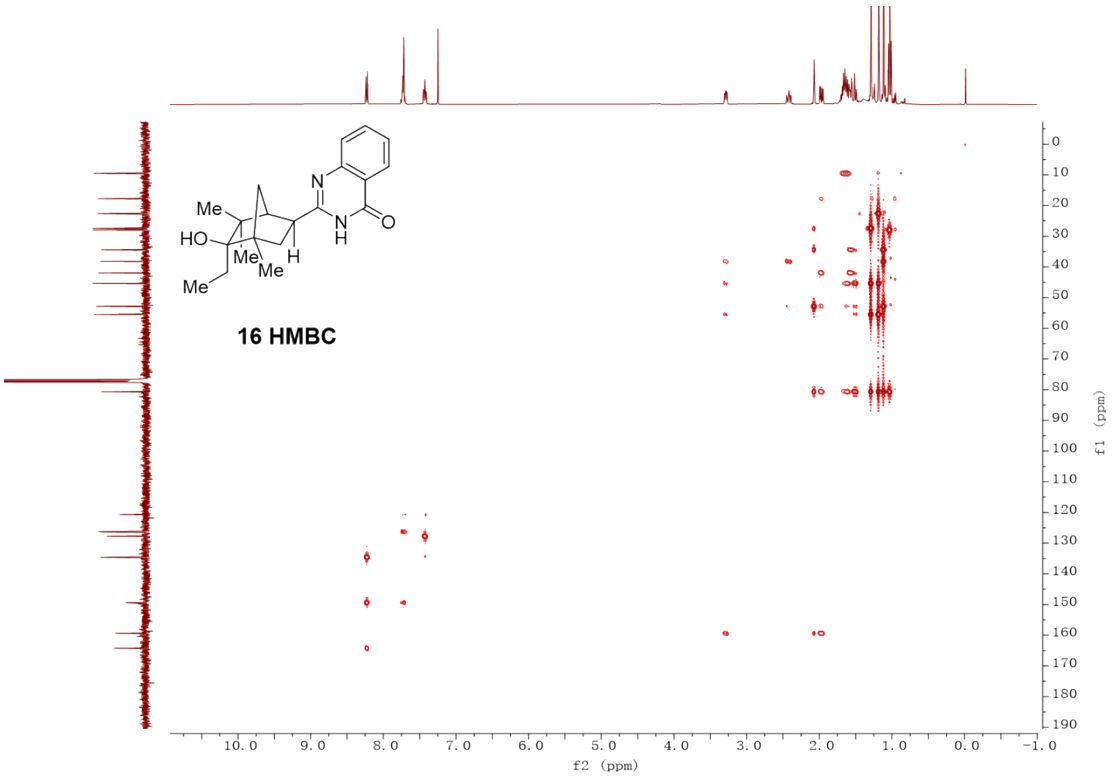




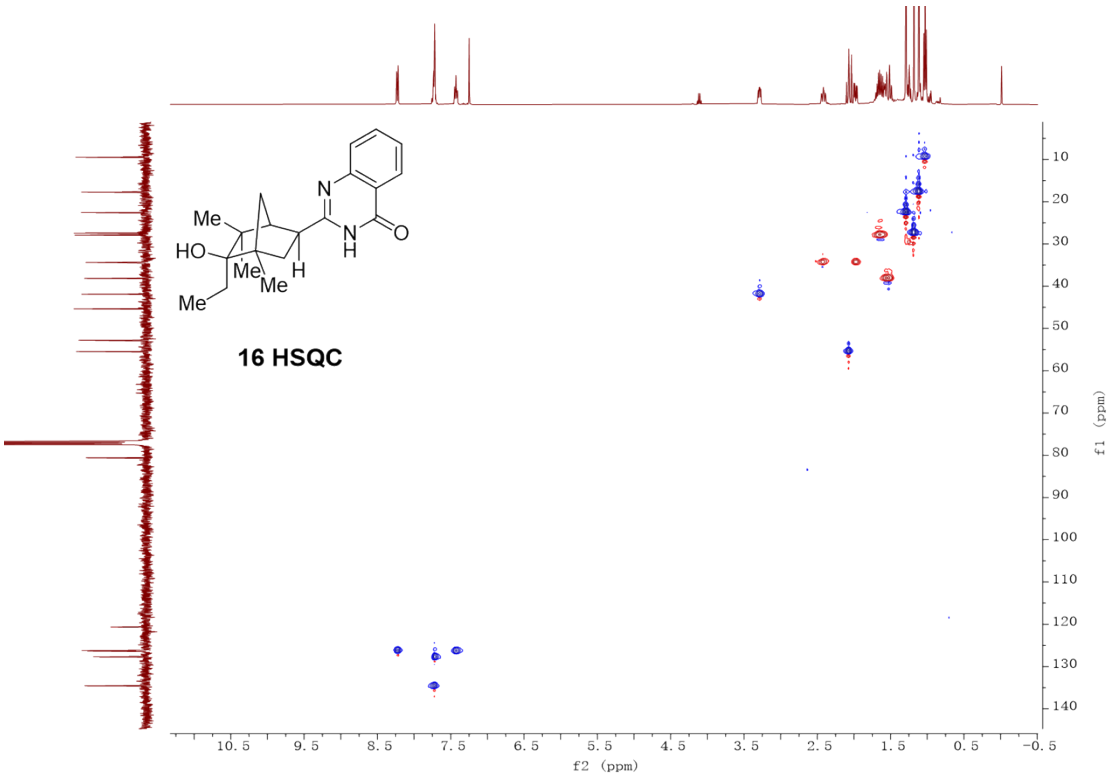
^{1}H-^{1}H –COSY spectrum of compound 16 in $CDCl_3$ at 400 MHz



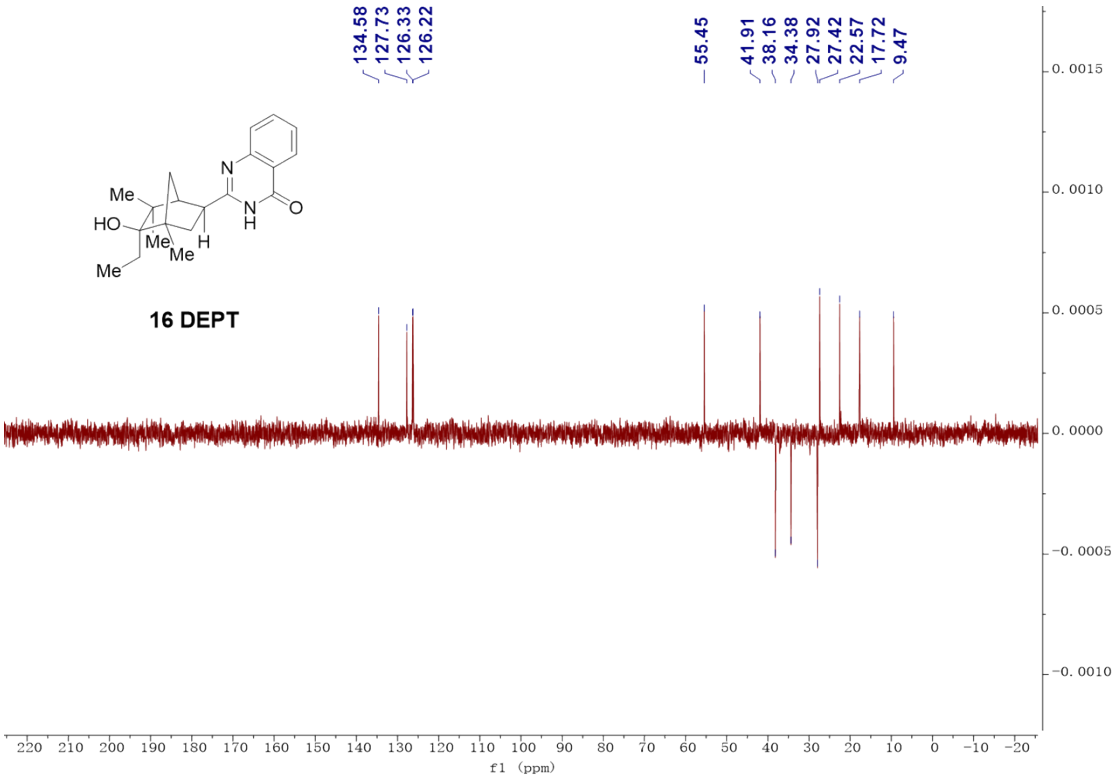
^{1}H-^{13}C –HMBC spectrum of compound 16 in $CDCl_3$ at 400 MHz



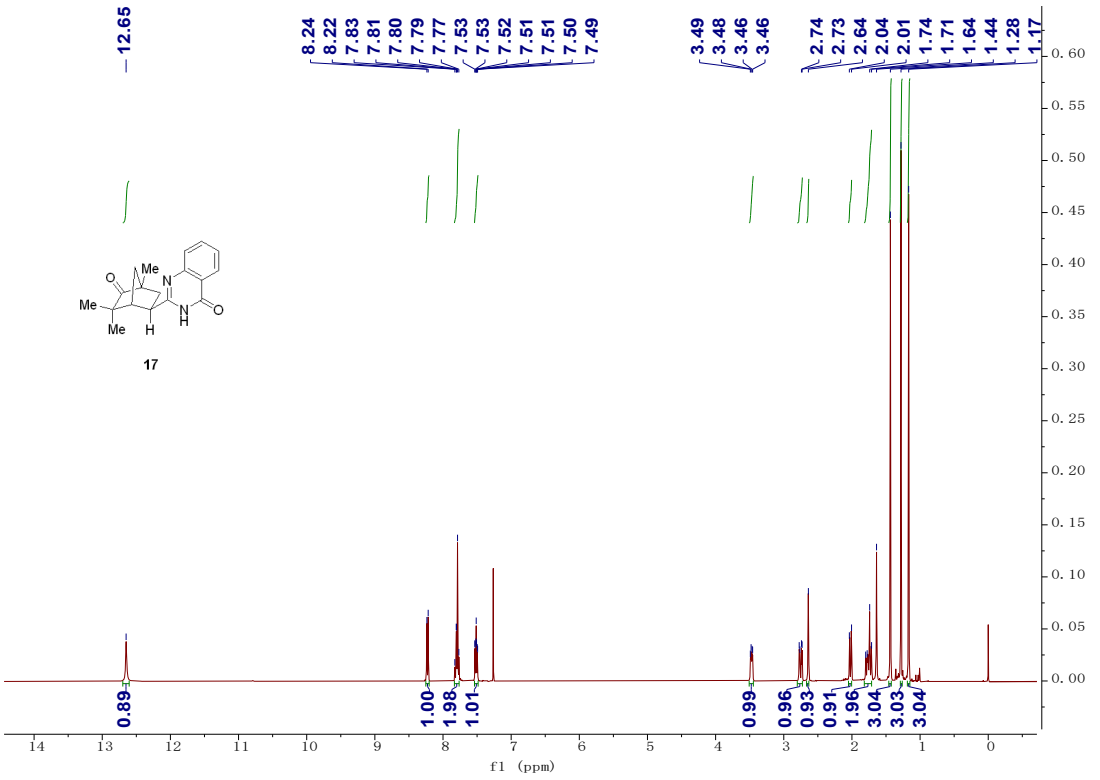
^{1}H-^{13}C –HSQC spectrum of compound 16 in $CDCl_3$ at 400 MHz



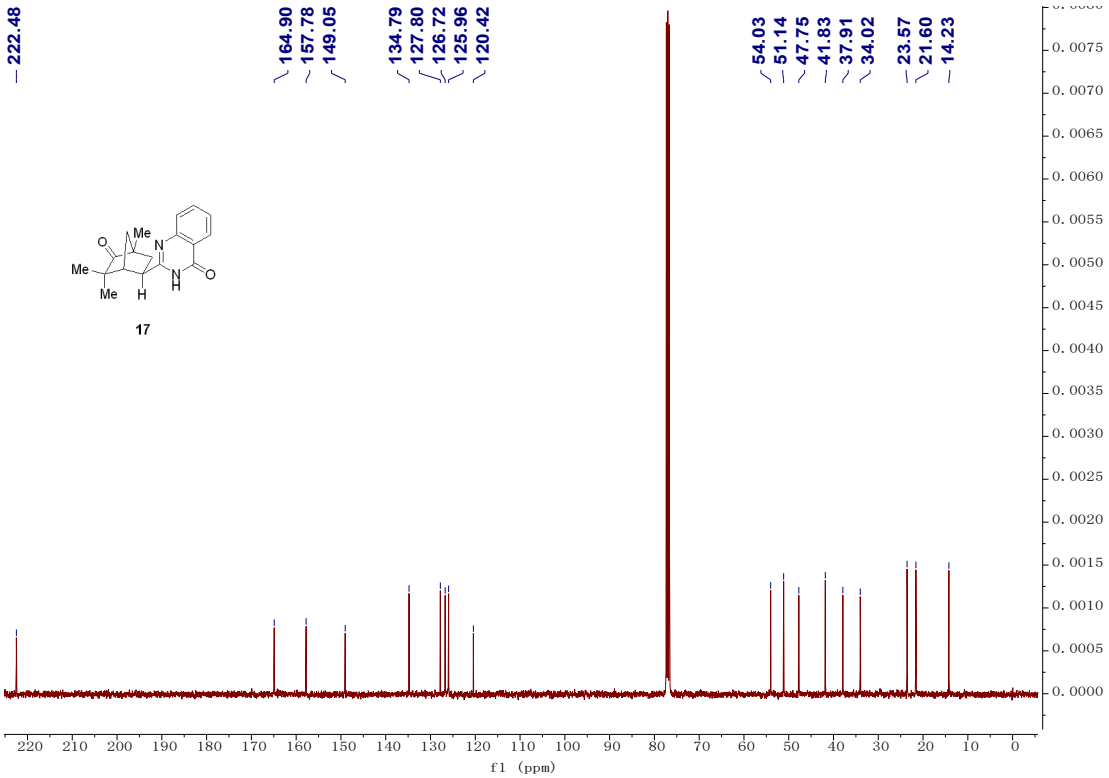
DEPT spectrum of compound 16 in $CDCl_3$ at 400 MHz



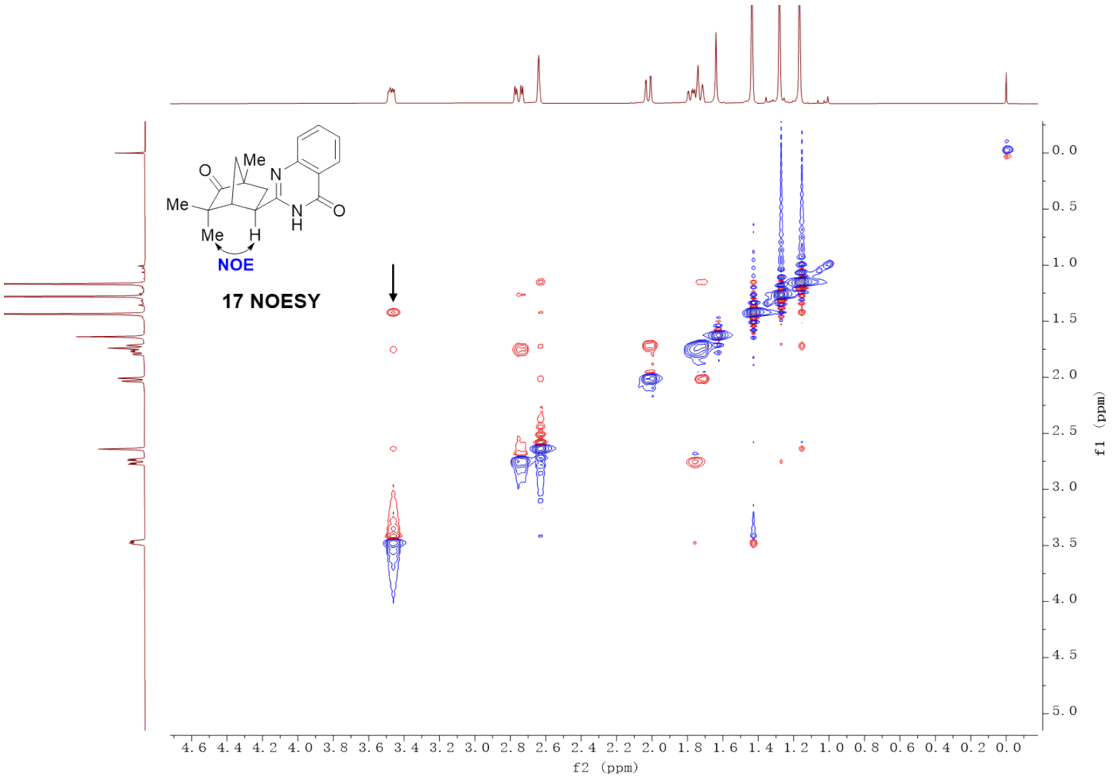
^{1}H NMR of compound 17 in $CDCl_3$ at 400 MHz

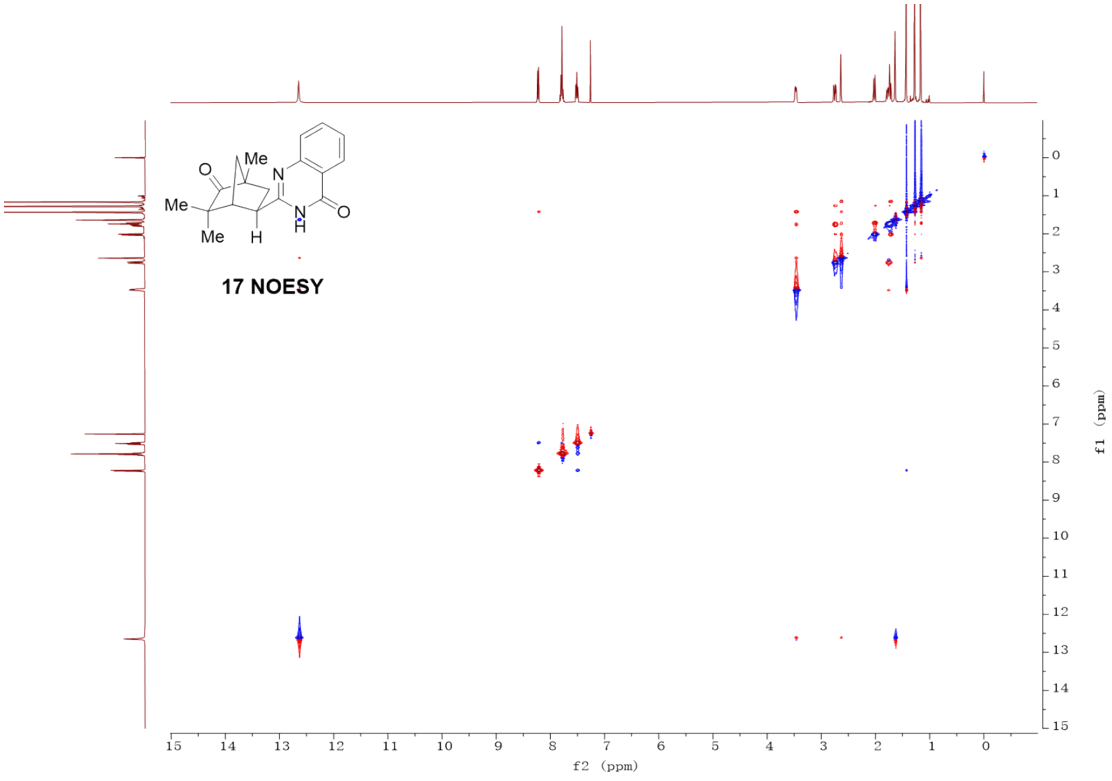


^{13}C NMR of compound 17 in $CDCl_3$ at 100 MHz

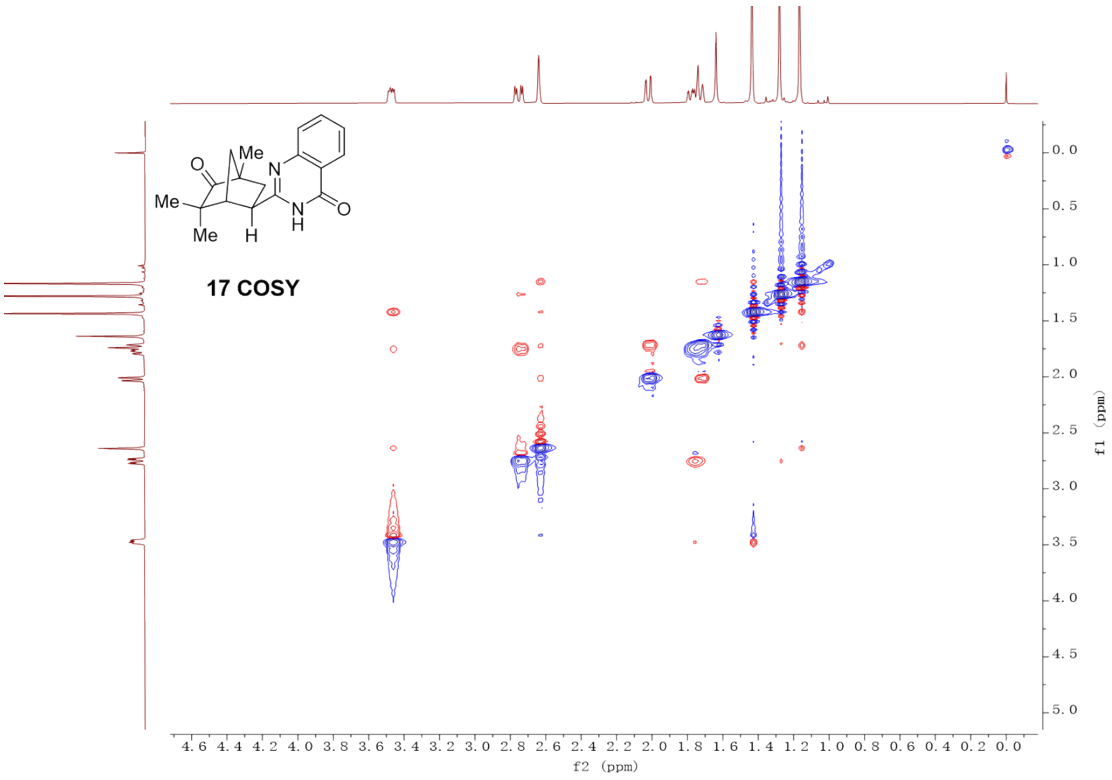


^{1}H-^{1}H –NOESY spectrum of compound 17 in $CDCl_3$ at 400 MHz

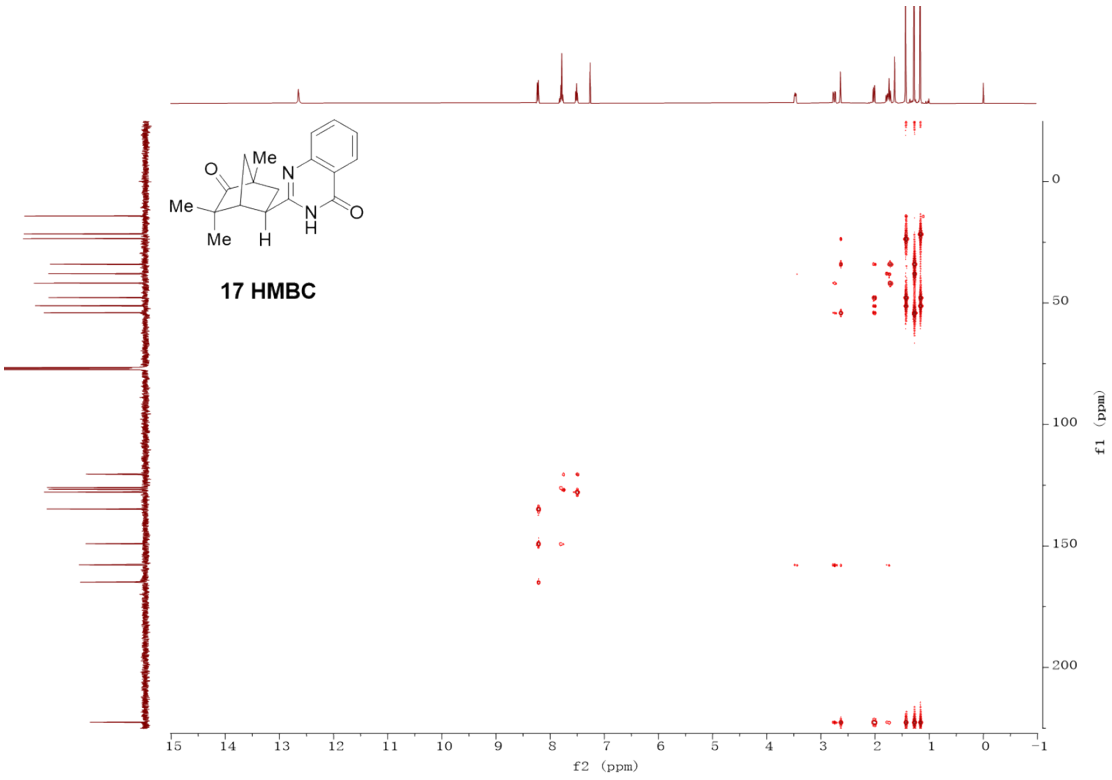




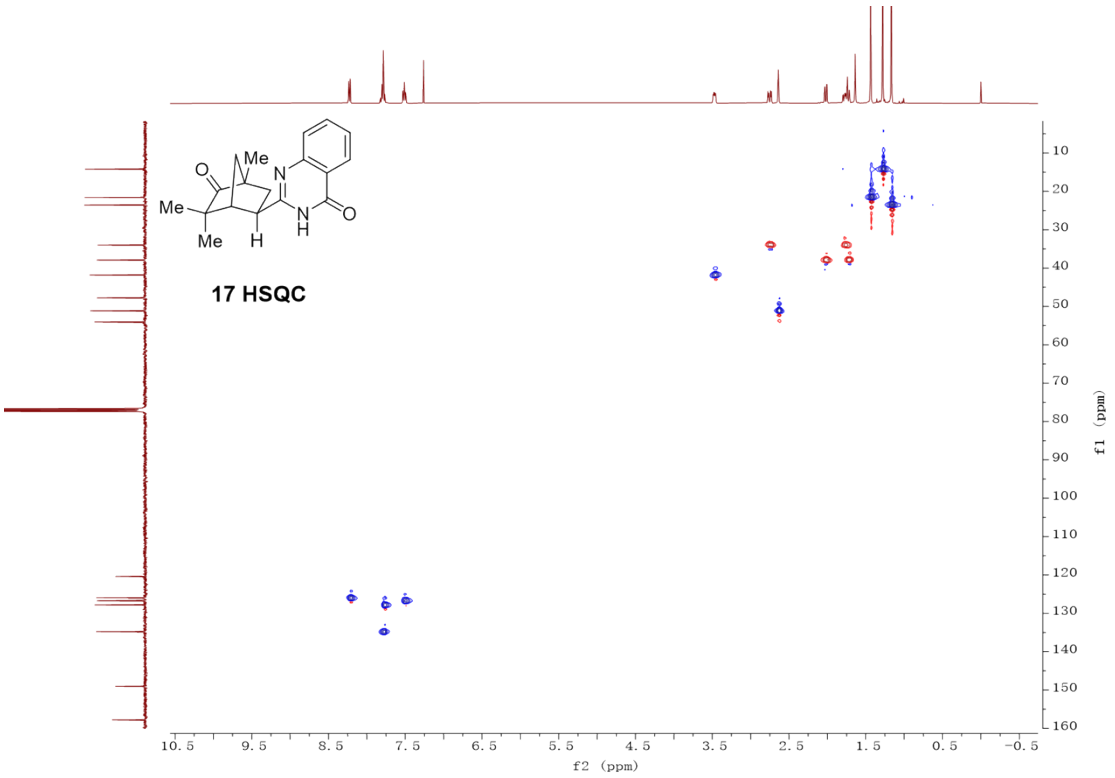
^{1}H-^{1}H –COSY spectrum of compound 17 in $CDCl_3$ at 400 MHz



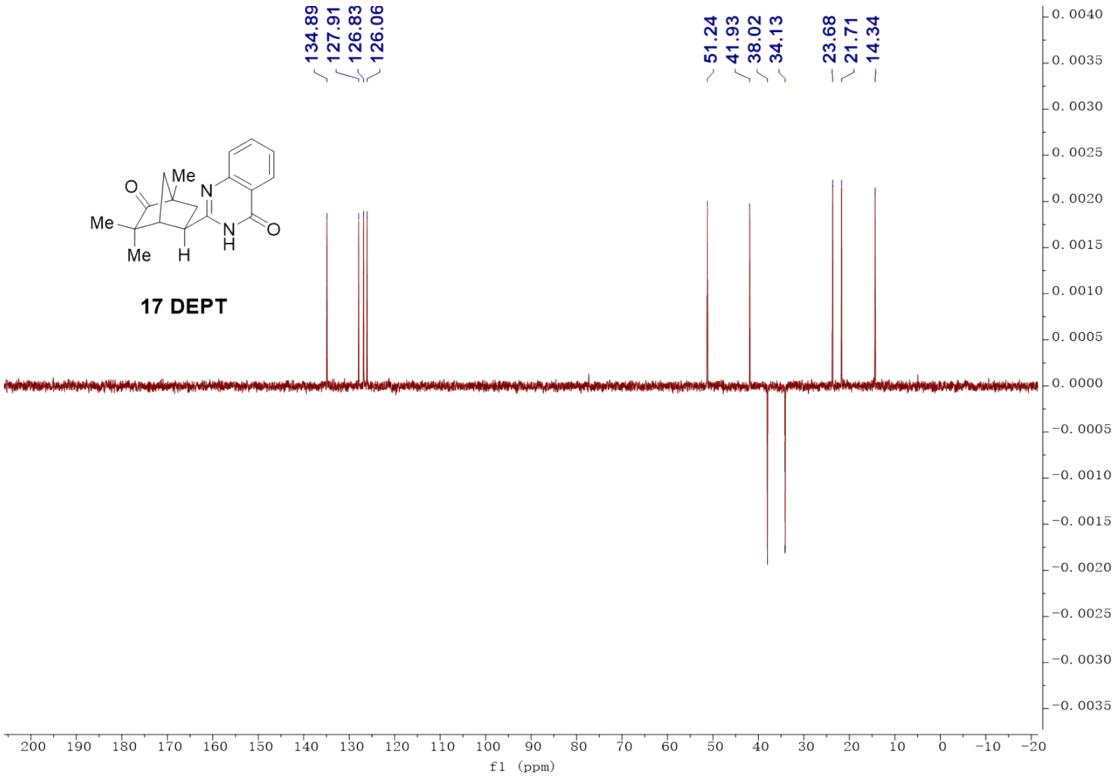
^{1}H-^{13}C –HMBC spectrum of compound 17 in $CDCl_3$ at 400 MHz



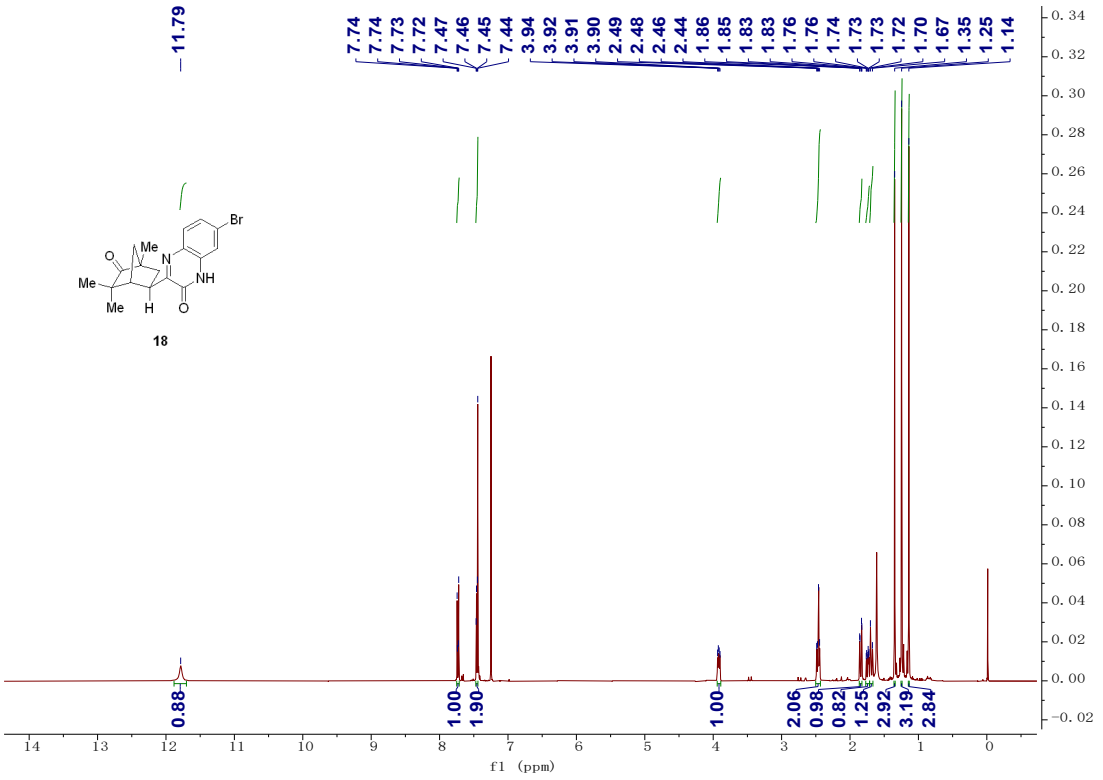
^{1}H-^{13}C –HSQC spectrum of compound 17 in $CDCl_3$ at 400 MHz



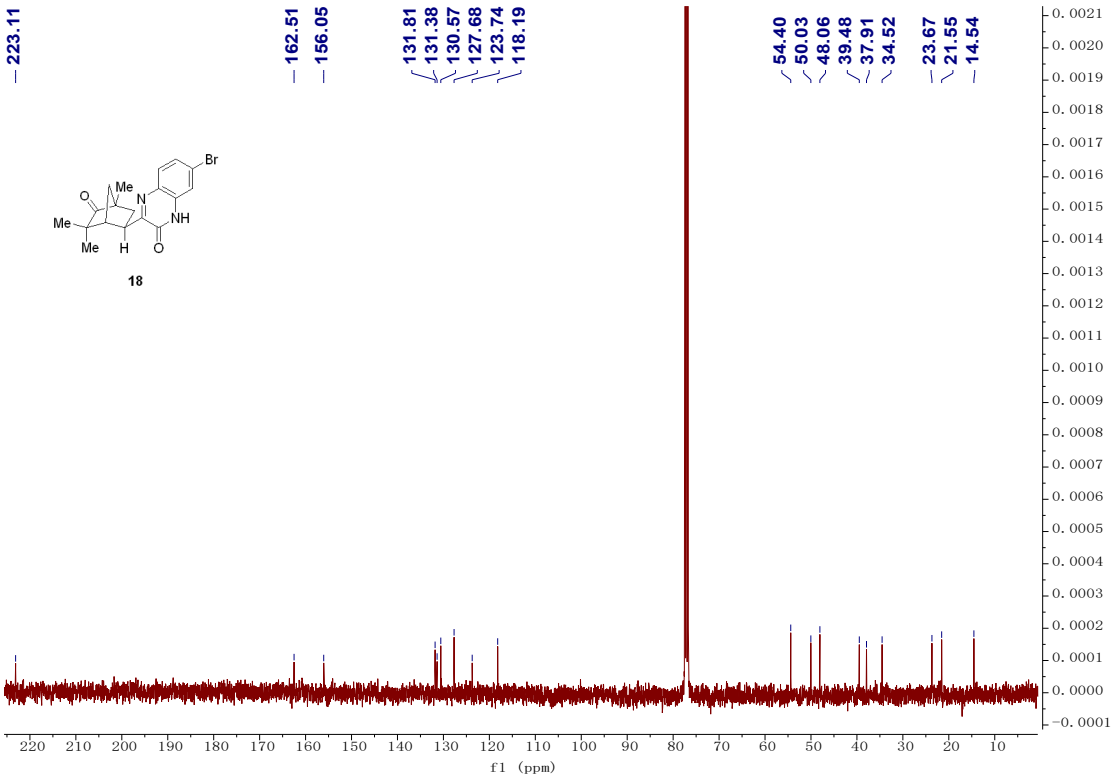
DEPT spectrum of compound 17 in $CDCl_3$ at 400 MHz



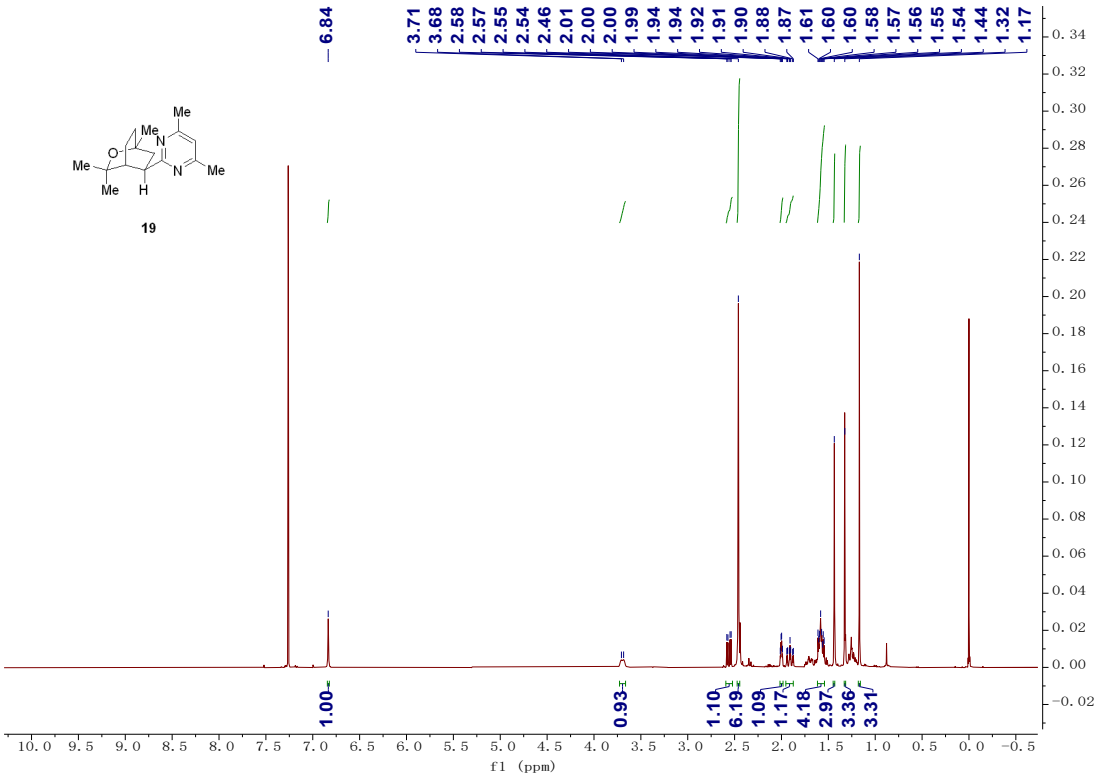
^{1}H NMR of compound 18 in $CDCl_3$ at 400 MHz



^{13}C NMR of compound 18 in $CDCl_3$ at 100 MHz

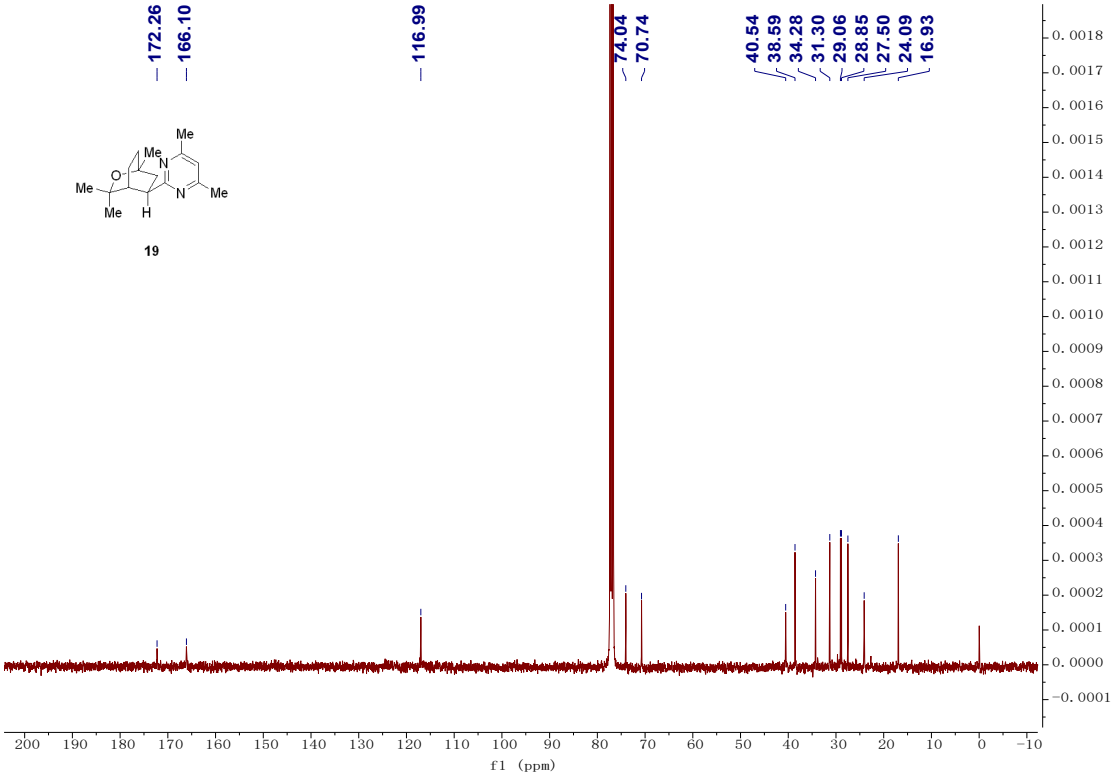


^{1}H NMR of compound 19 in $CDCl_3$ at 400 MHz



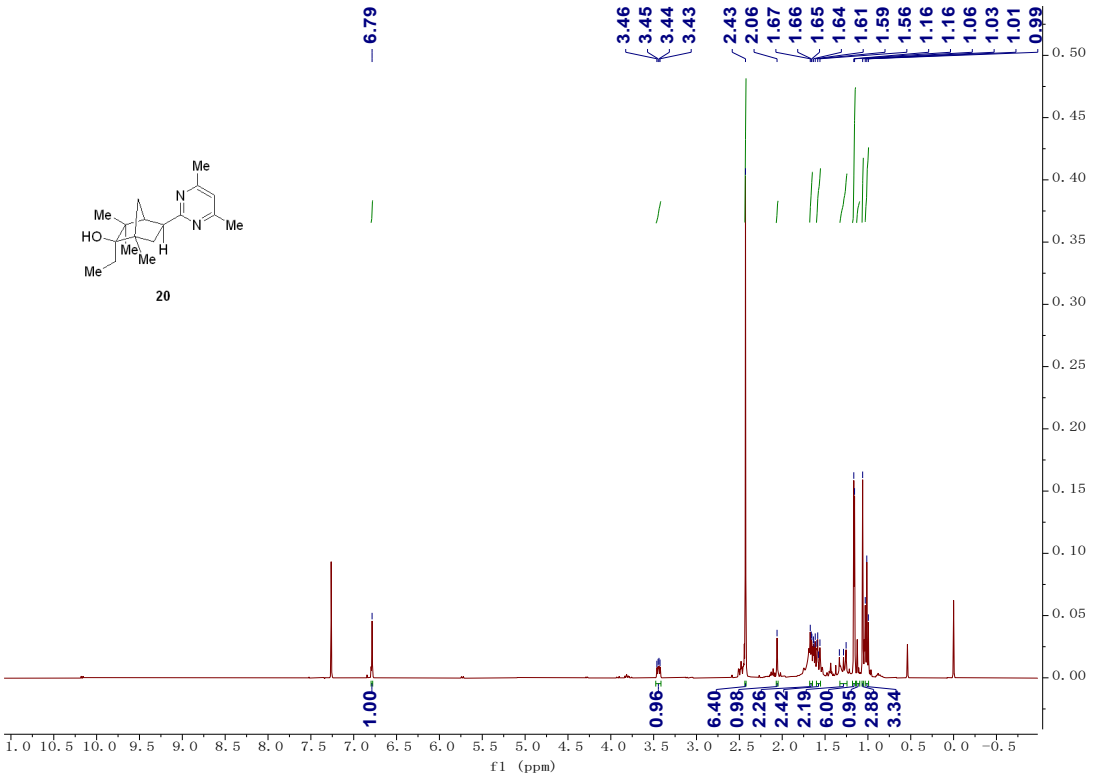
19

^{13}C NMR of compound 19 in $CDCl_3$ at 100 MHz

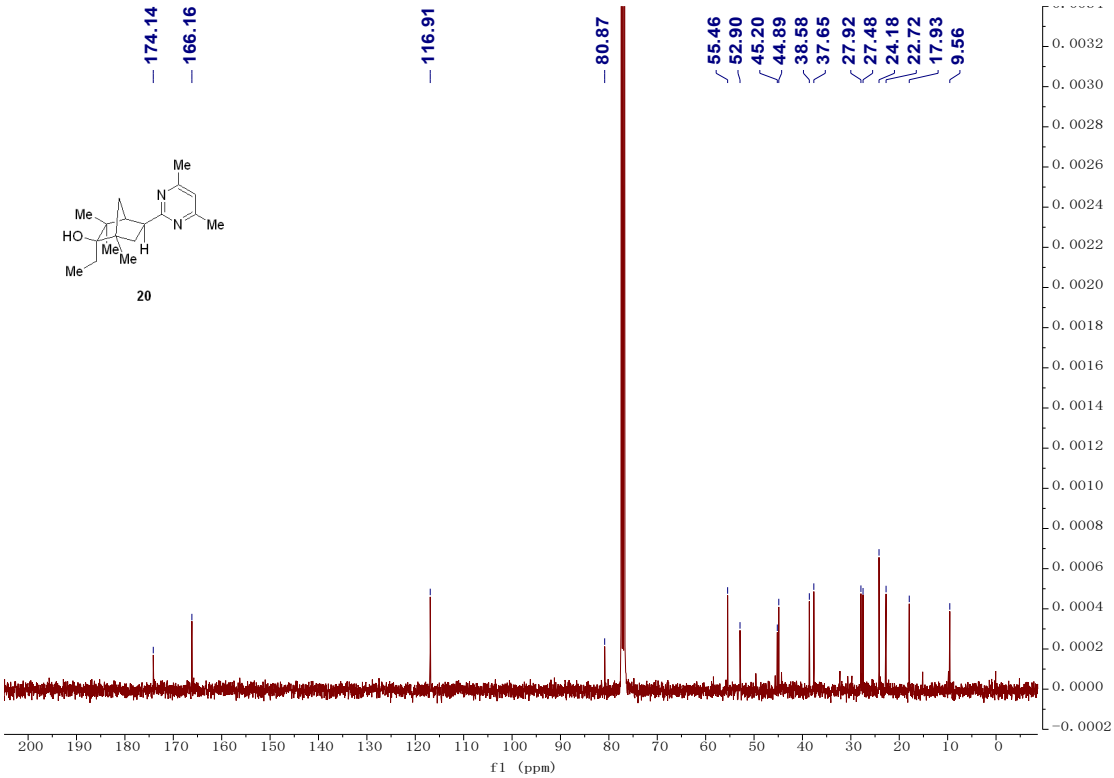


19

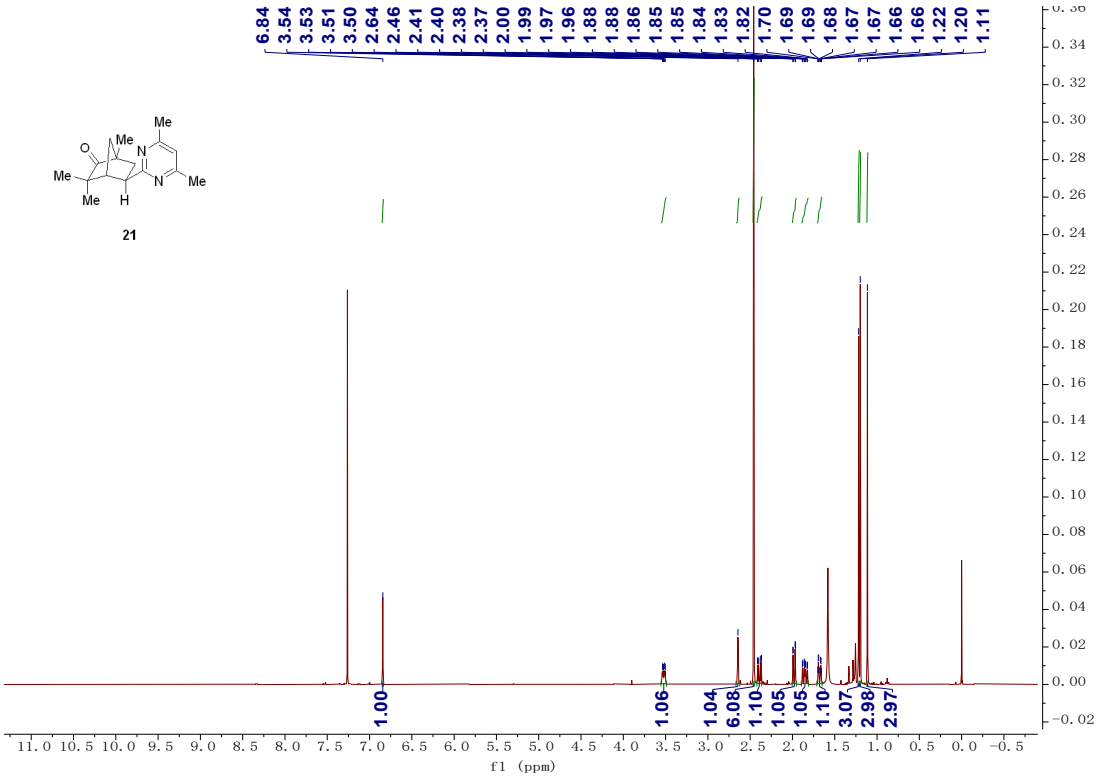
^{1}H NMR of compound 20 in $CDCl_3$ at 400 MHz



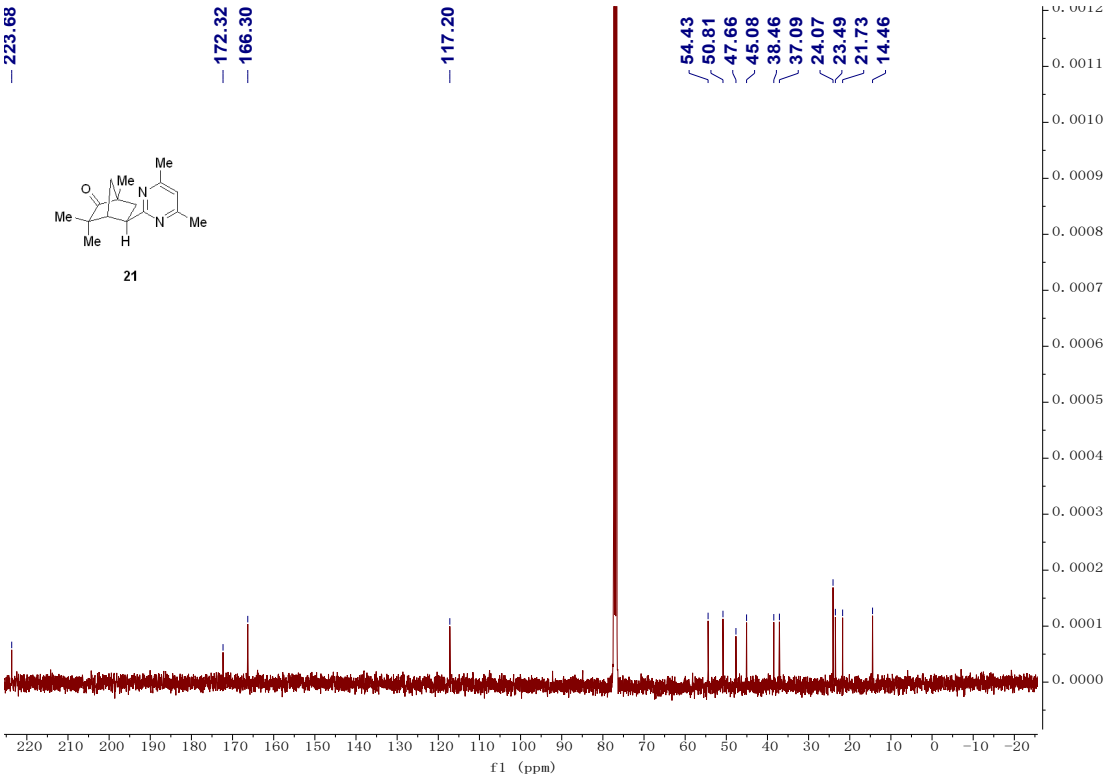
^{13}C NMR of compound 20 in $CDCl_3$ at 100 MHz



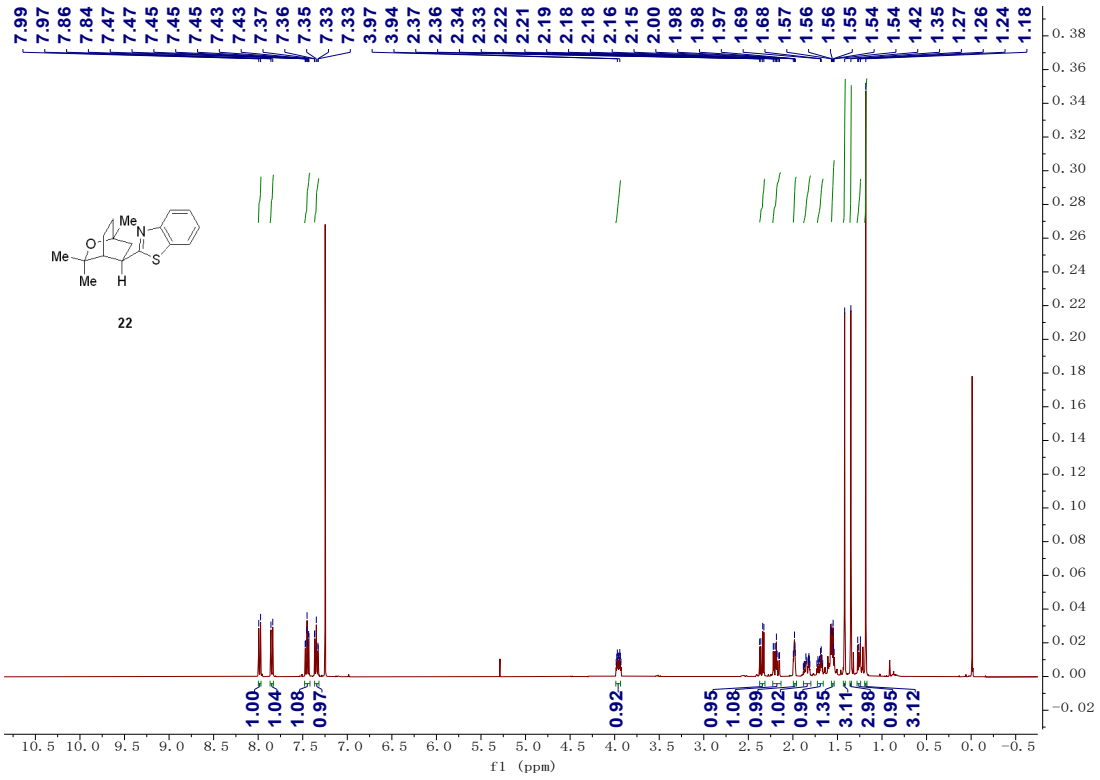
^{1}H NMR of compound 21 in $CDCl_3$ at 400 MHz



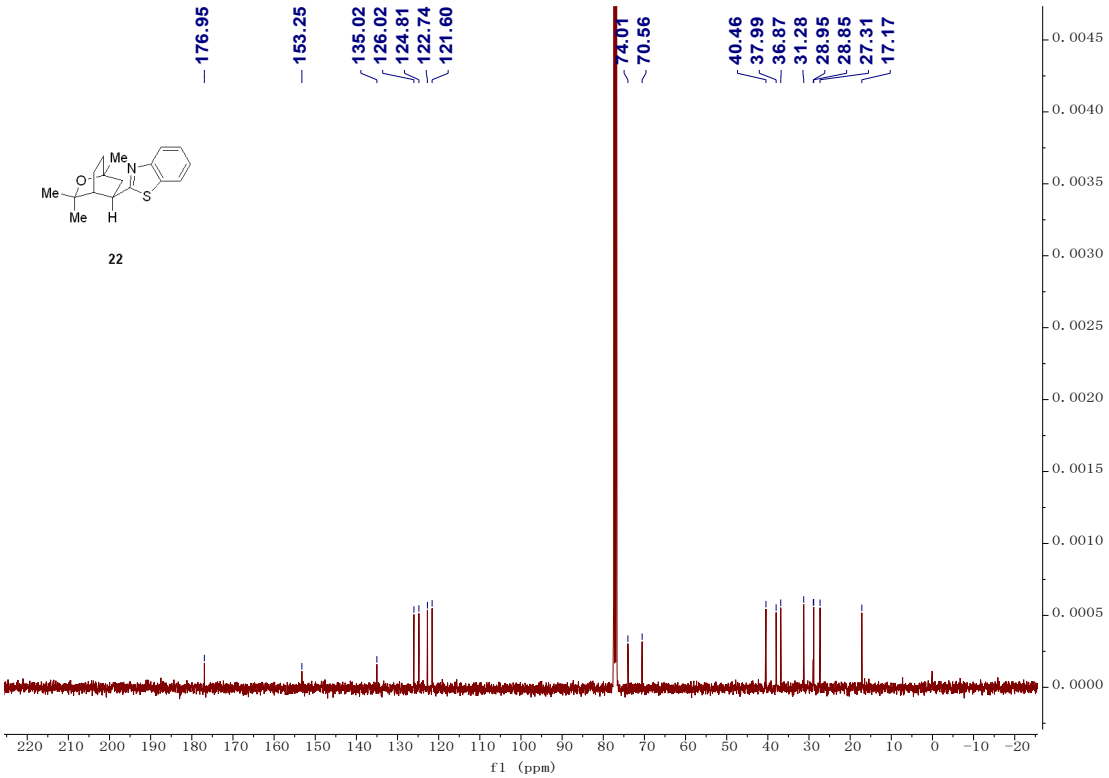
^{13}C NMR of compound 21 in $CDCl_3$ at 100 MHz



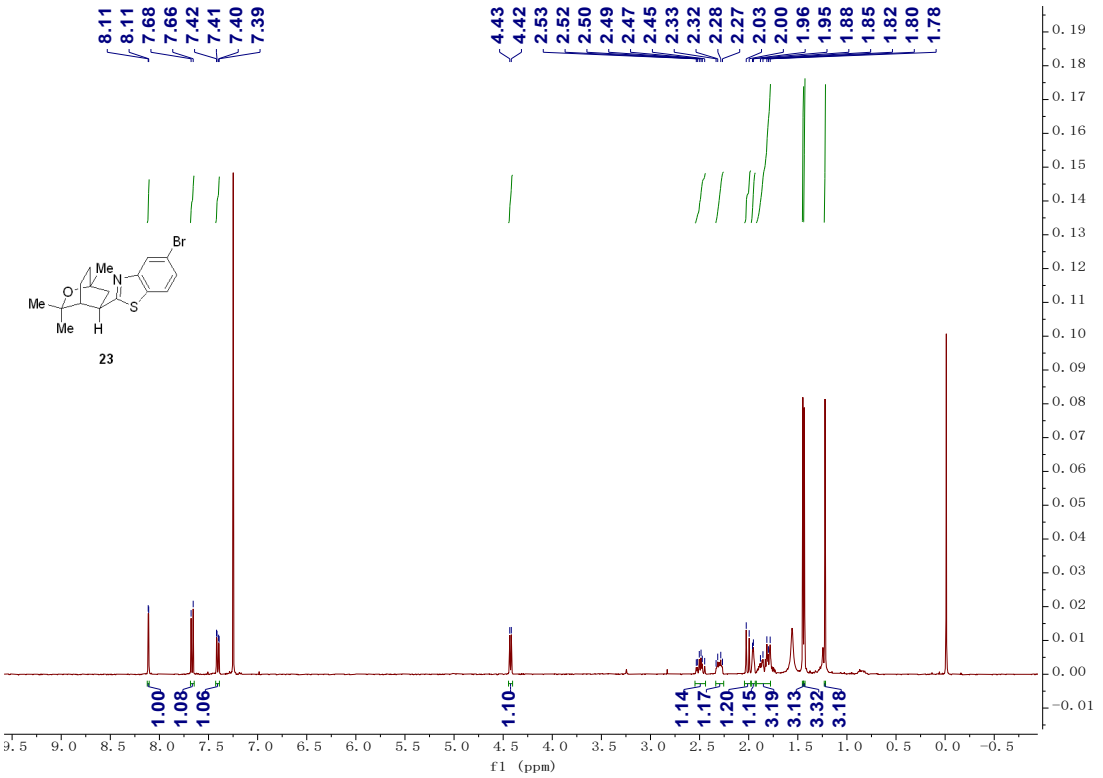
^{1}H NMR of compound 22 in $CDCl_3$ at 400 MHz



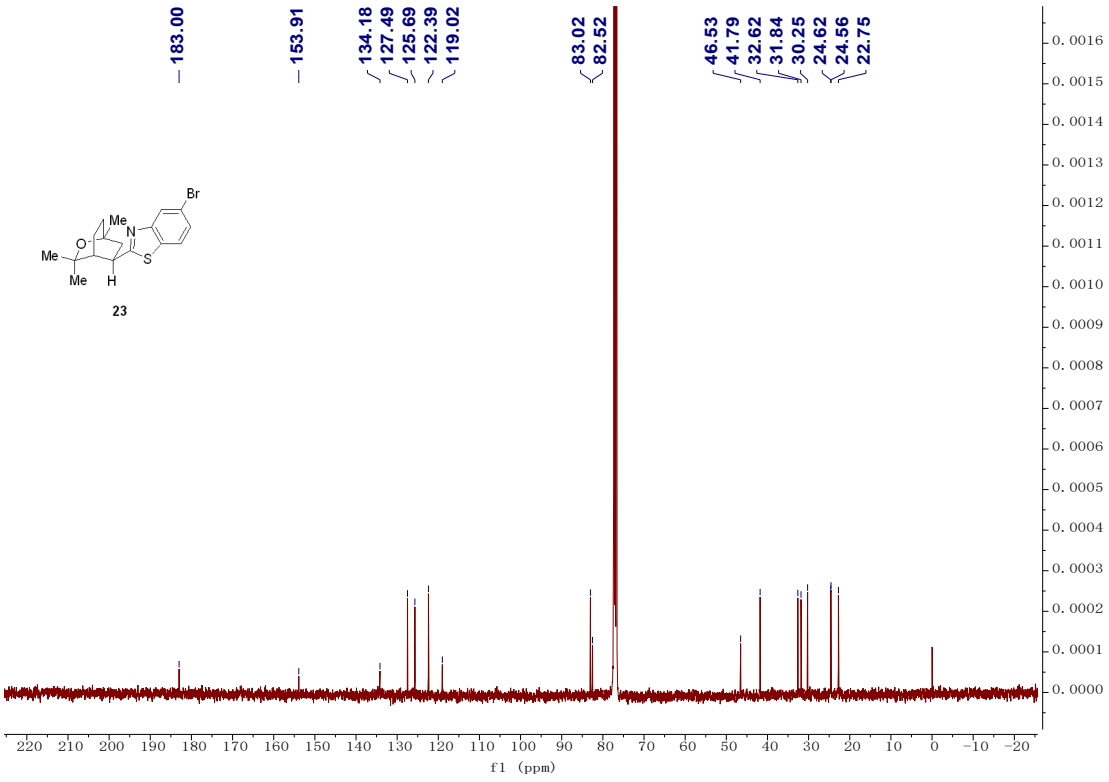
^{13}C NMR of compound 22 in $CDCl_3$ at 100 MHz



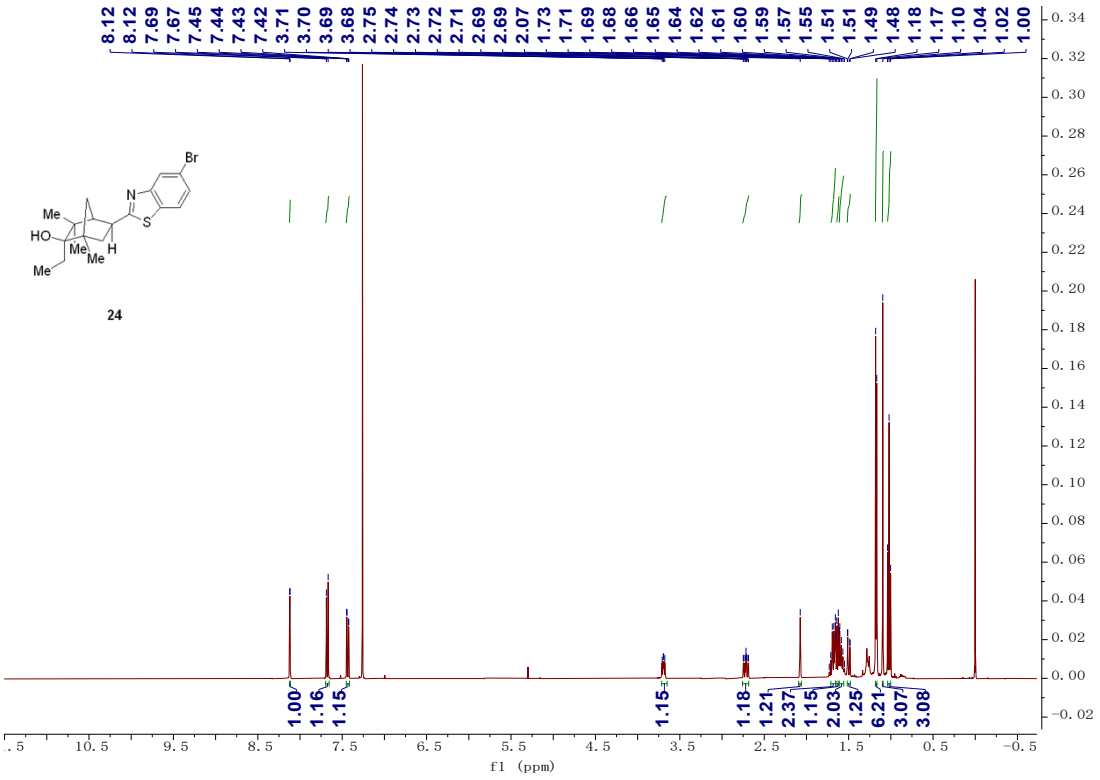
^{1}H NMR of compound 23 in $CDCl_3$ at 400 MHz



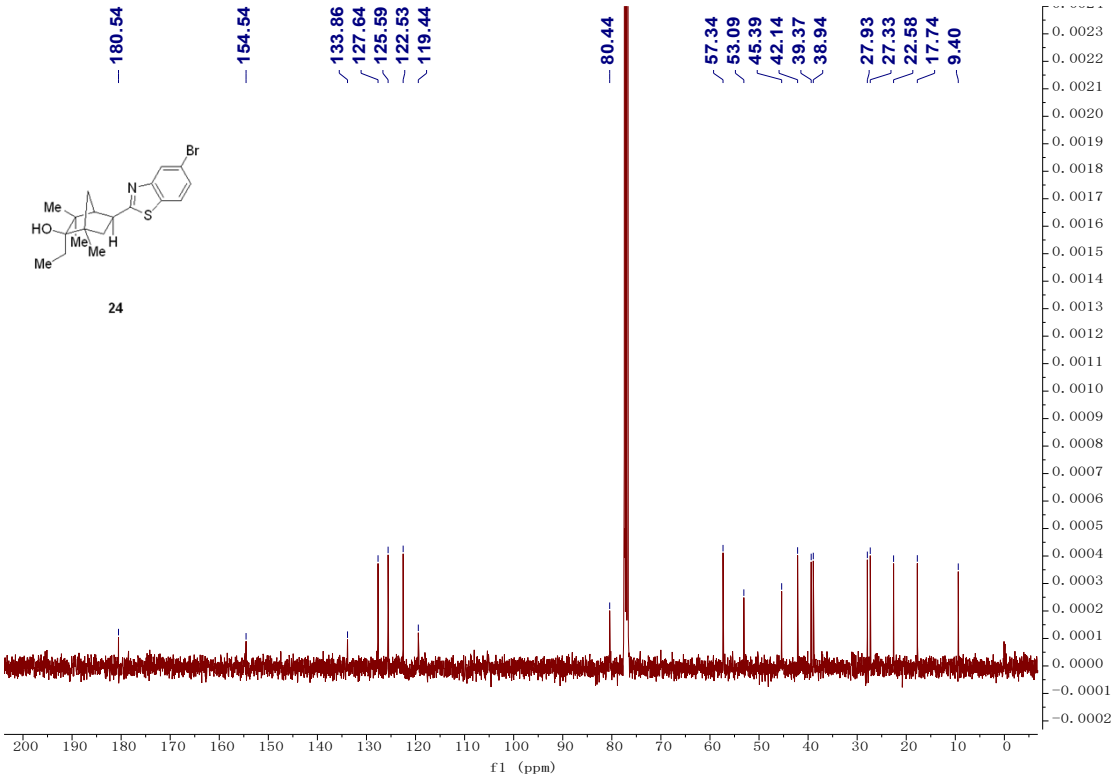
^{13}C NMR of compound 23 in $CDCl_3$ at 100 MHz



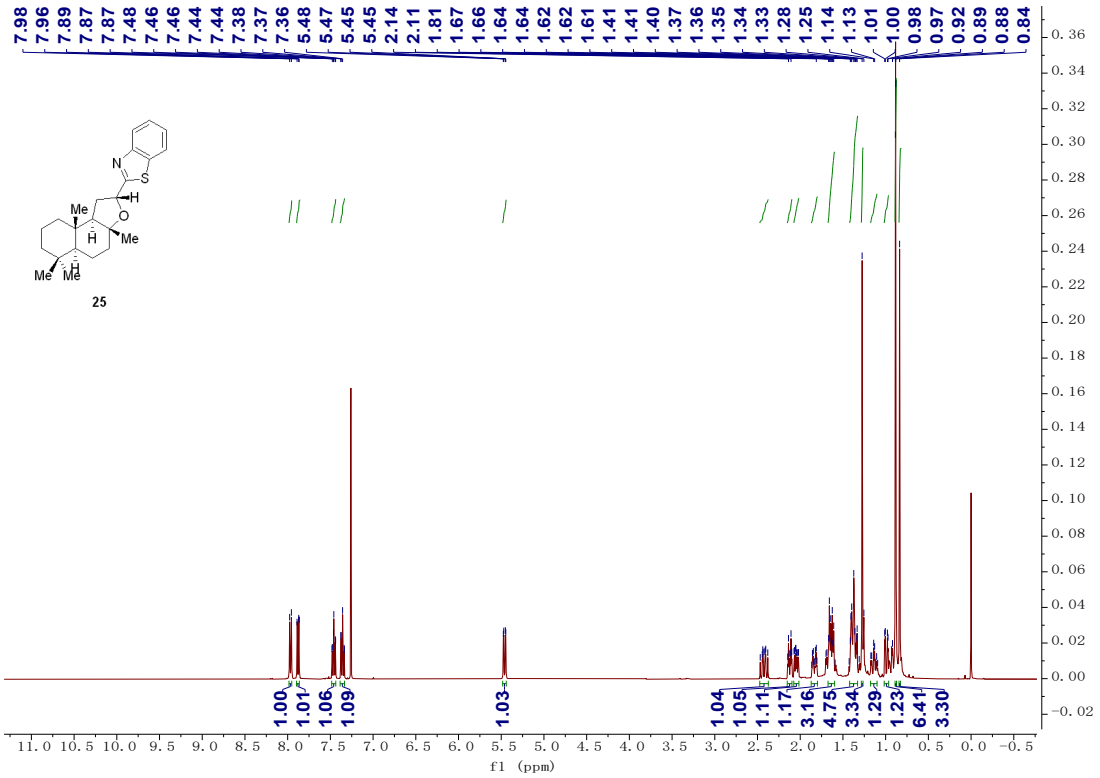
^{1}H NMR of compound 24 in $CDCl_3$ at 400 MHz



^{13}C NMR of compound 24 in $CDCl_3$ at 100 MHz

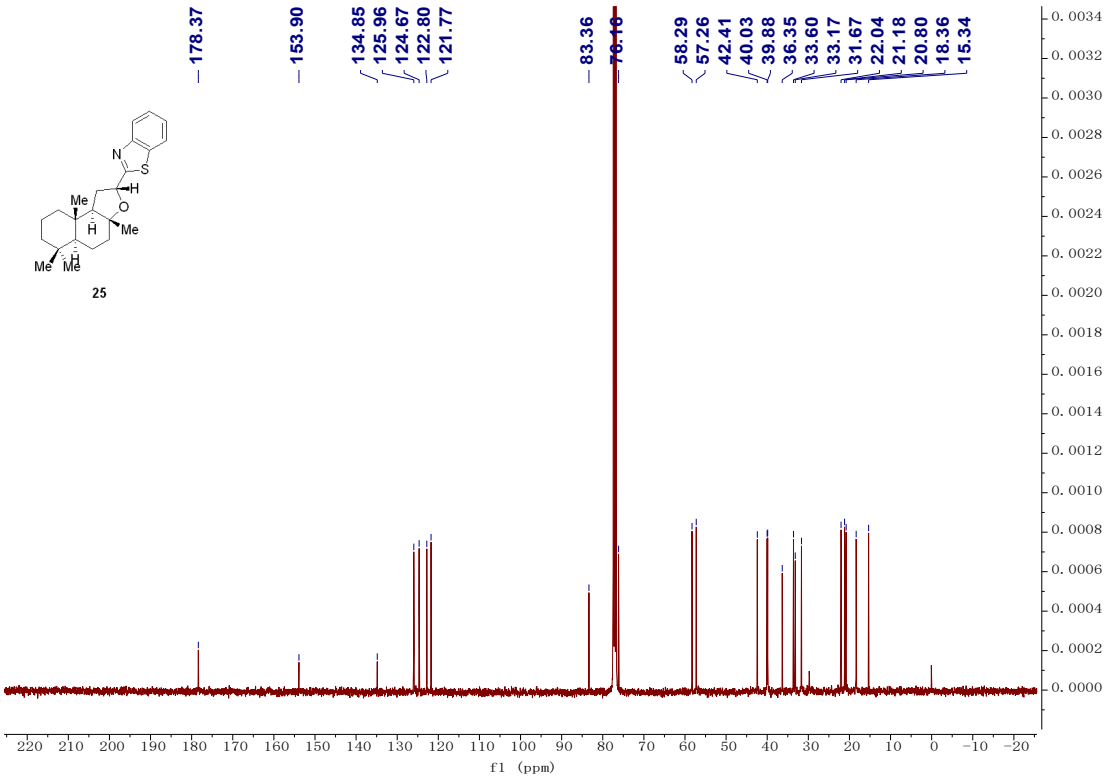


^{1}H NMR of compound 25 in $CDCl_3$ at 400 MHz



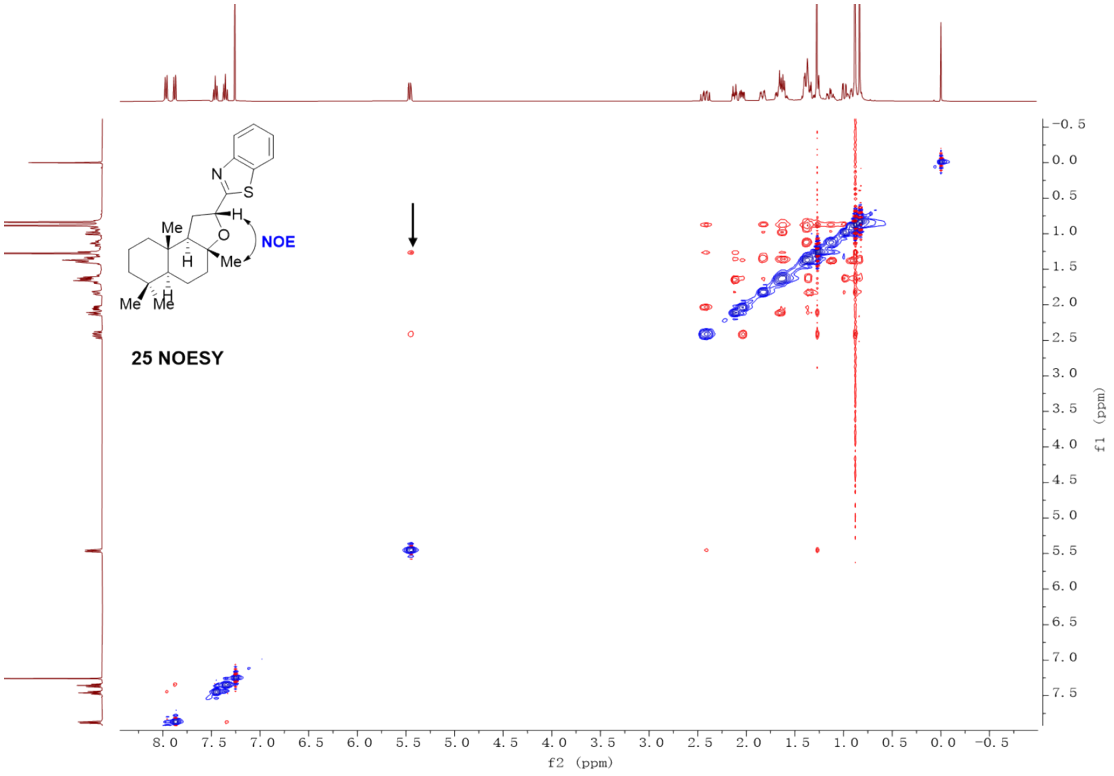
25

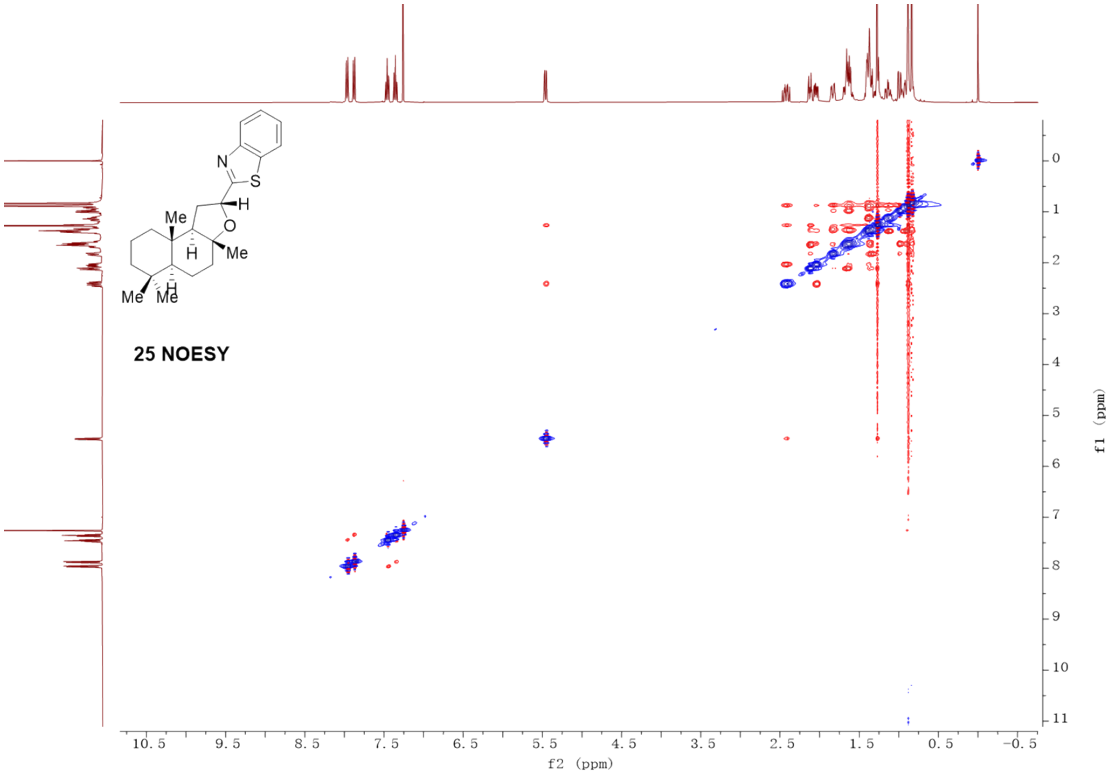
^{13}C NMR of compound 25 in $CDCl_3$ at 100 MHz



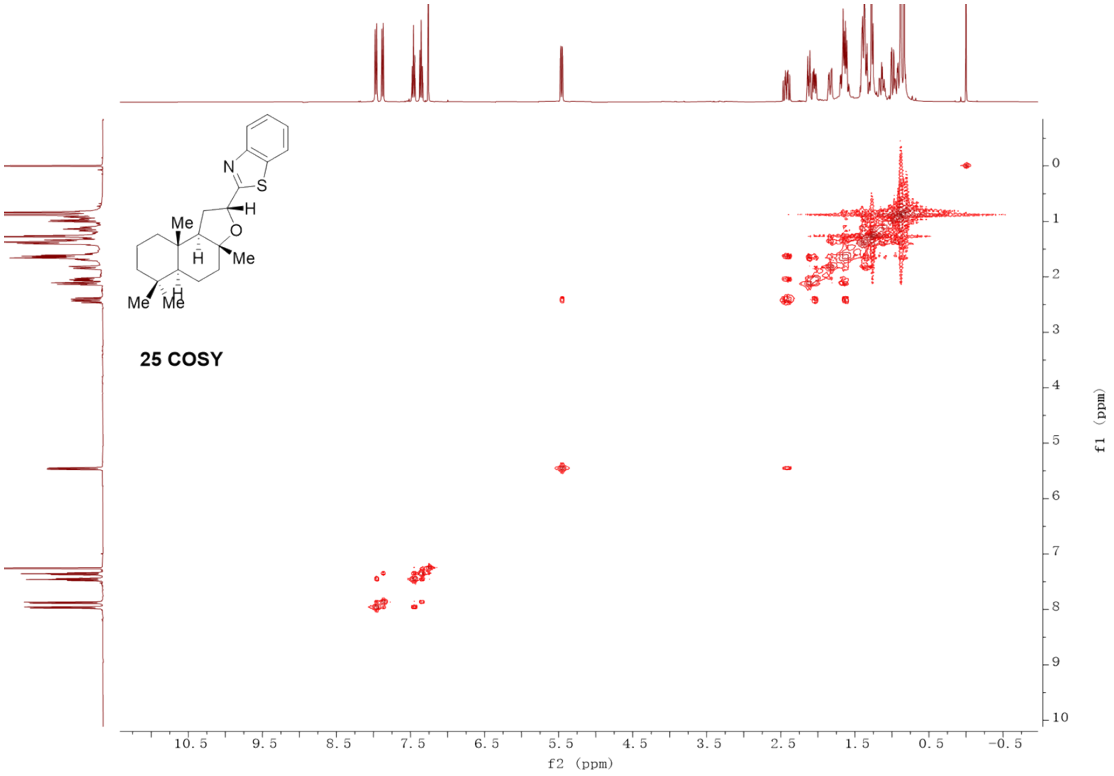
25

^{1}H-^{1}H –NOESY spectrum of compound 25 in $CDCl_3$ at 400 MHz

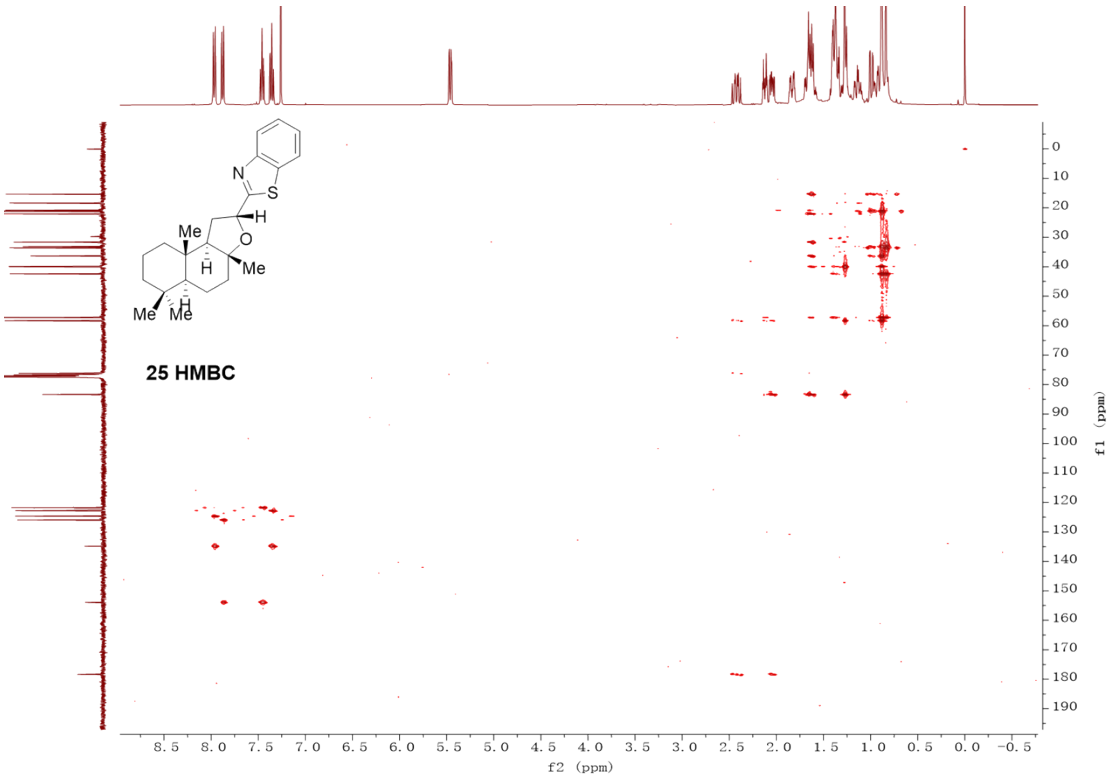




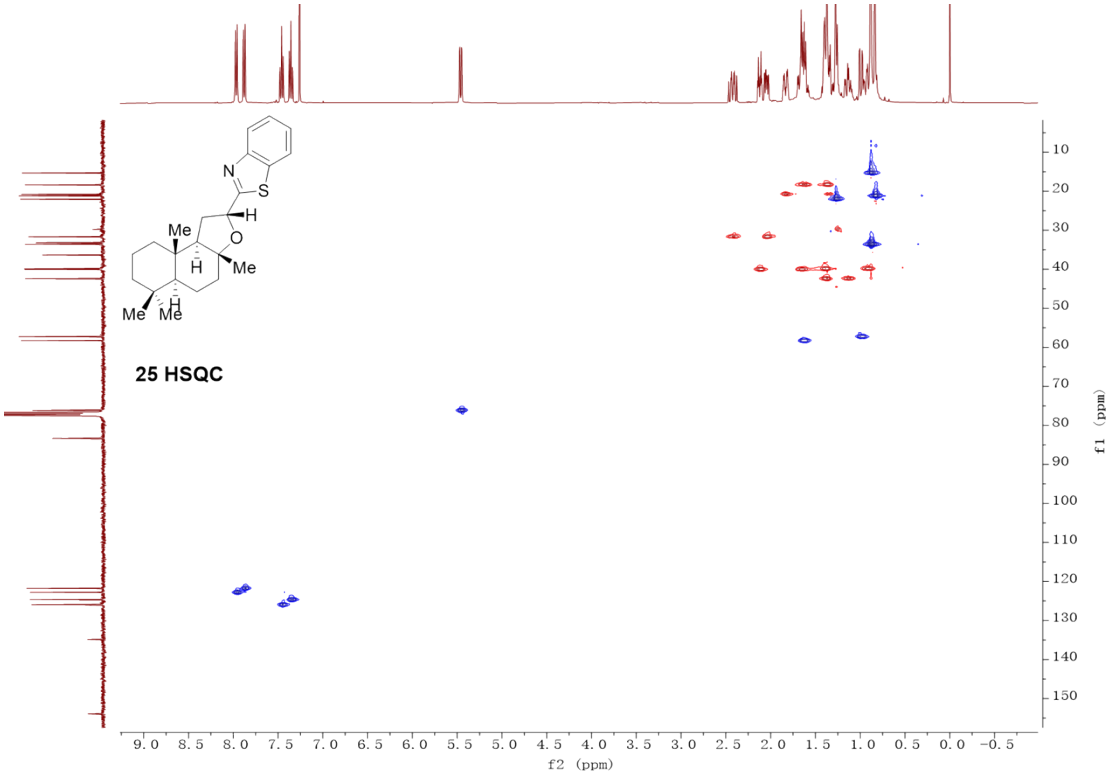
^{1}H-^{1}H –COSY spectrum of compound 25 in $CDCl_3$ at 400 MHz



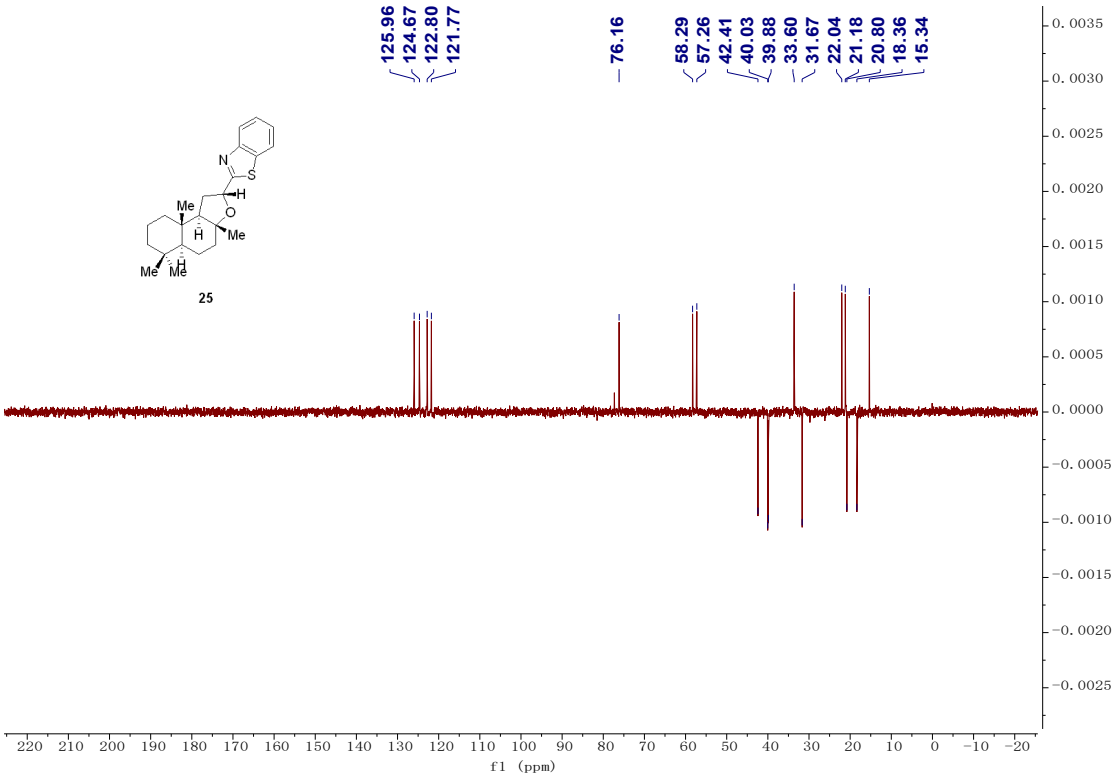
^{1}H-^{13}C –HMBC spectrum of compound 25 in $CDCl_3$ at 400 MHz



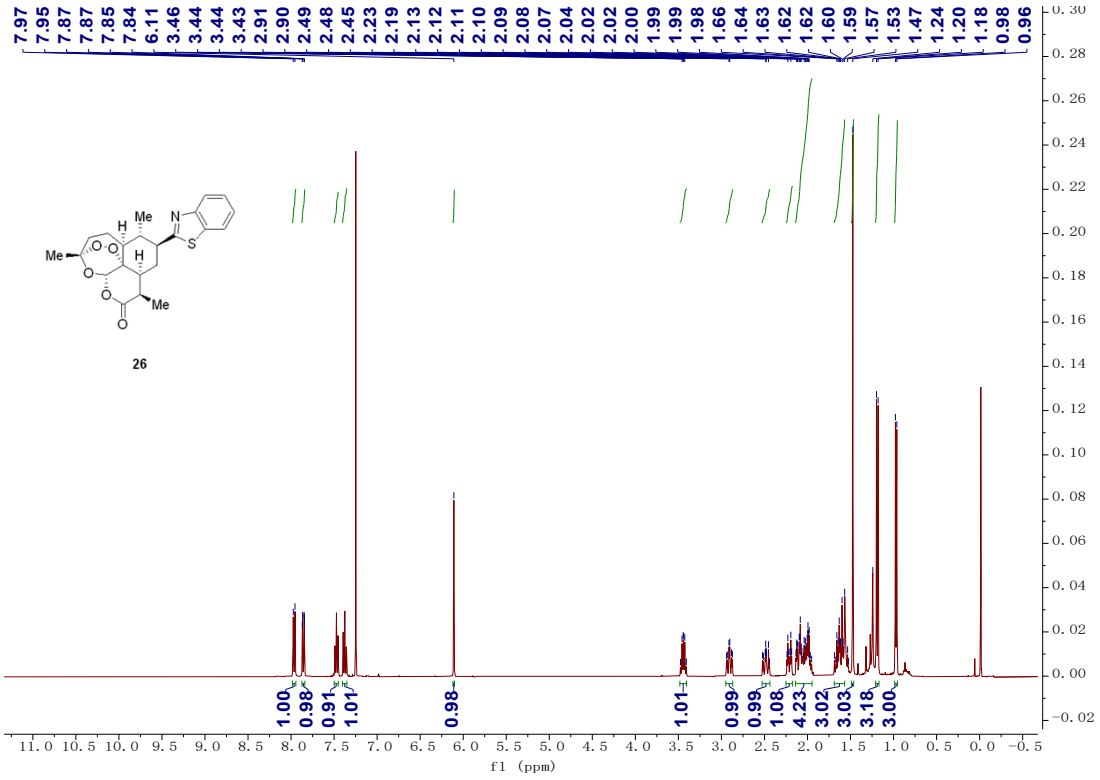
^{1}H-^{13}C –HSQC spectrum of compound 25 in $CDCl_3$ at 400 MHz



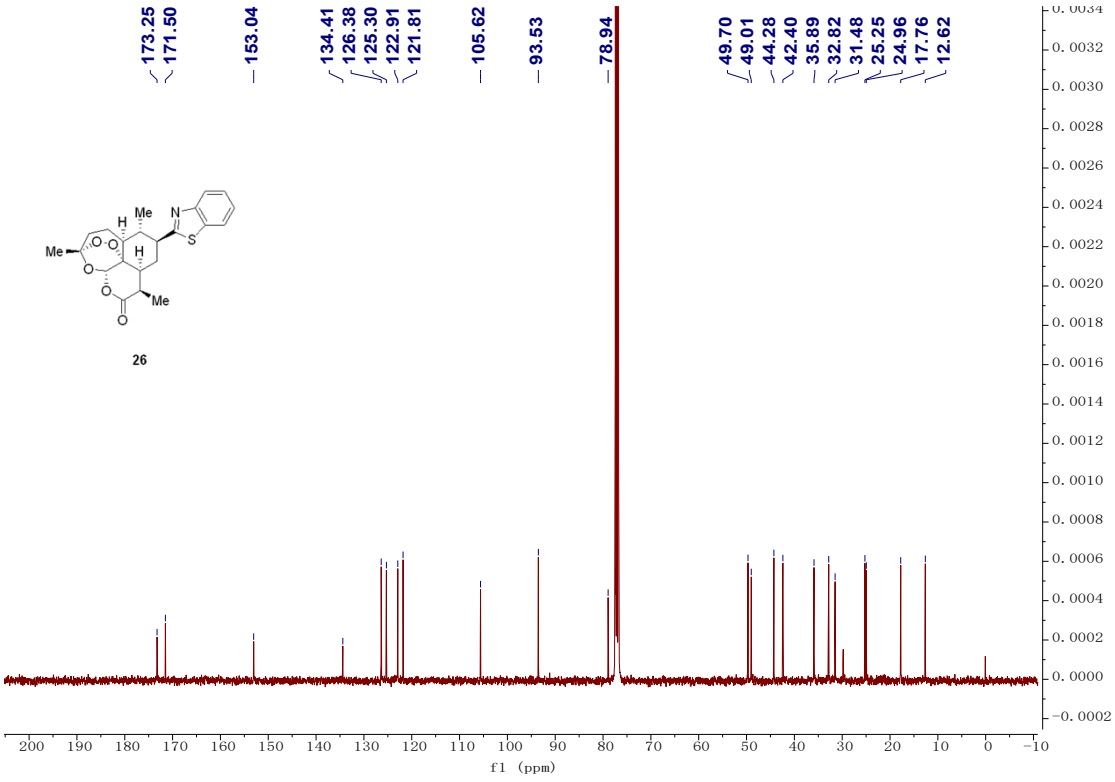
DEPT spectrum of compound 25 in $CDCl_3$ at 400 MHz



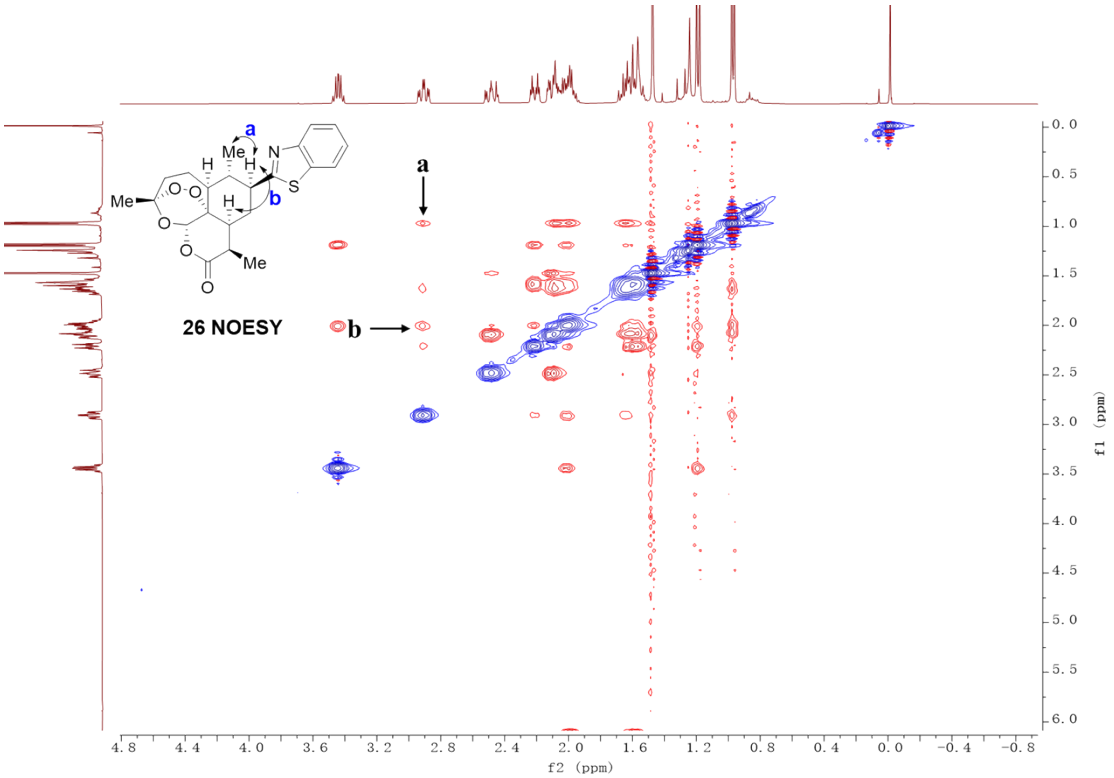
^{1}H NMR of compound 26 in $CDCl_3$ at 400 MHz

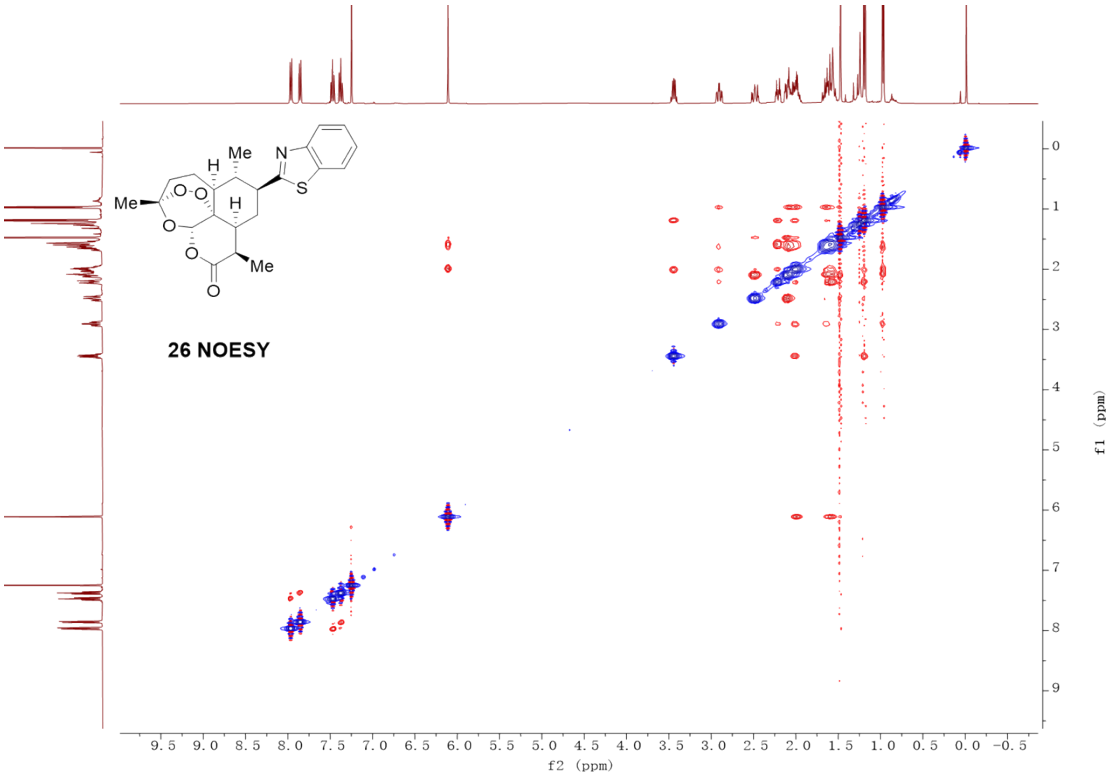


^{13}C NMR of compound 26 in $CDCl_3$ at 100 MHz

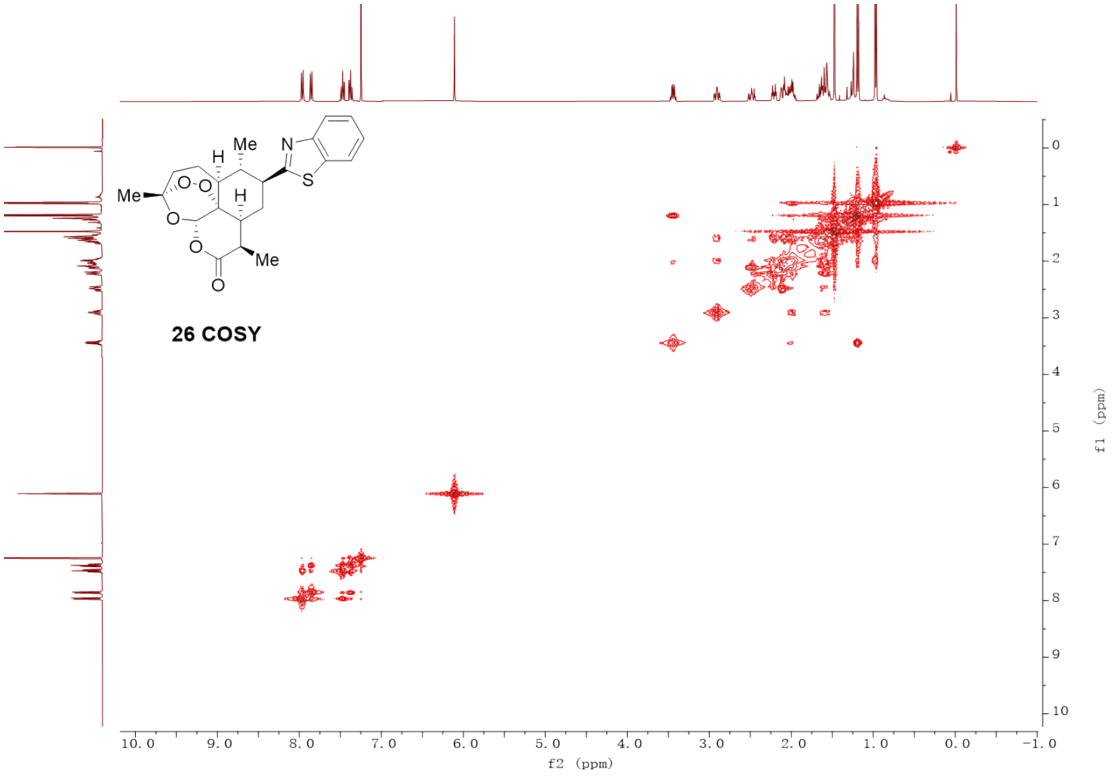


^{1}H-^{1}H –NOESY spectrum of compound 26 in $CDCl_3$ at 400 MHz

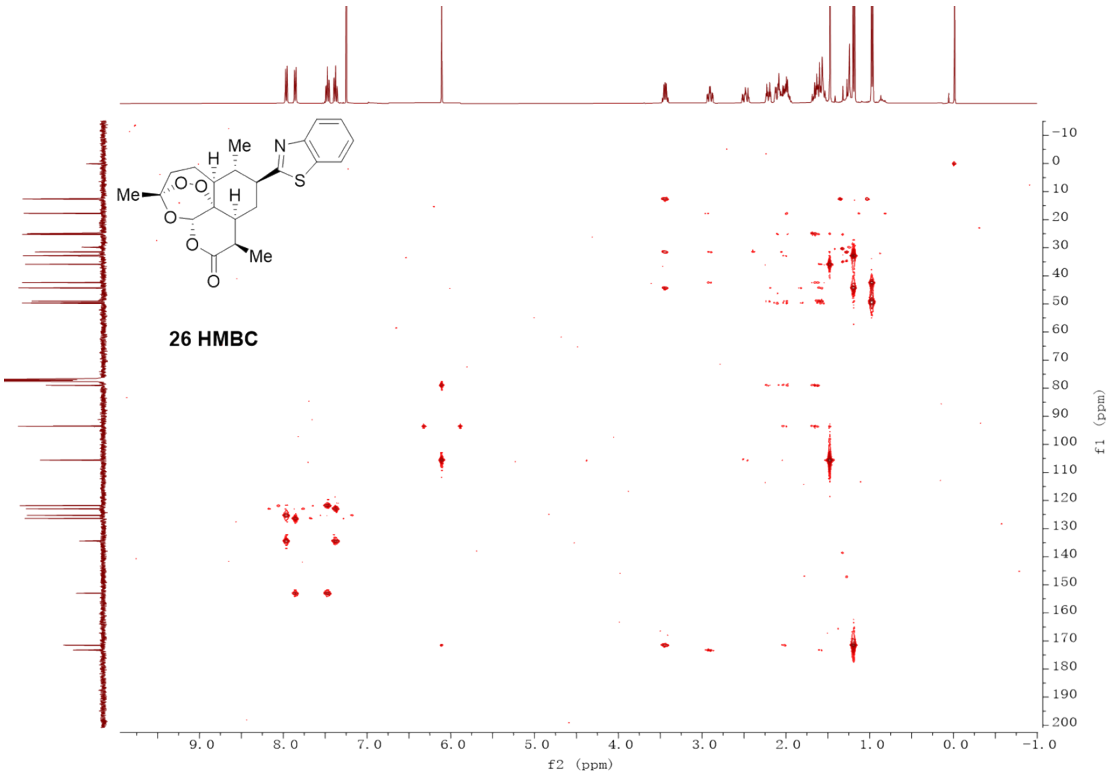




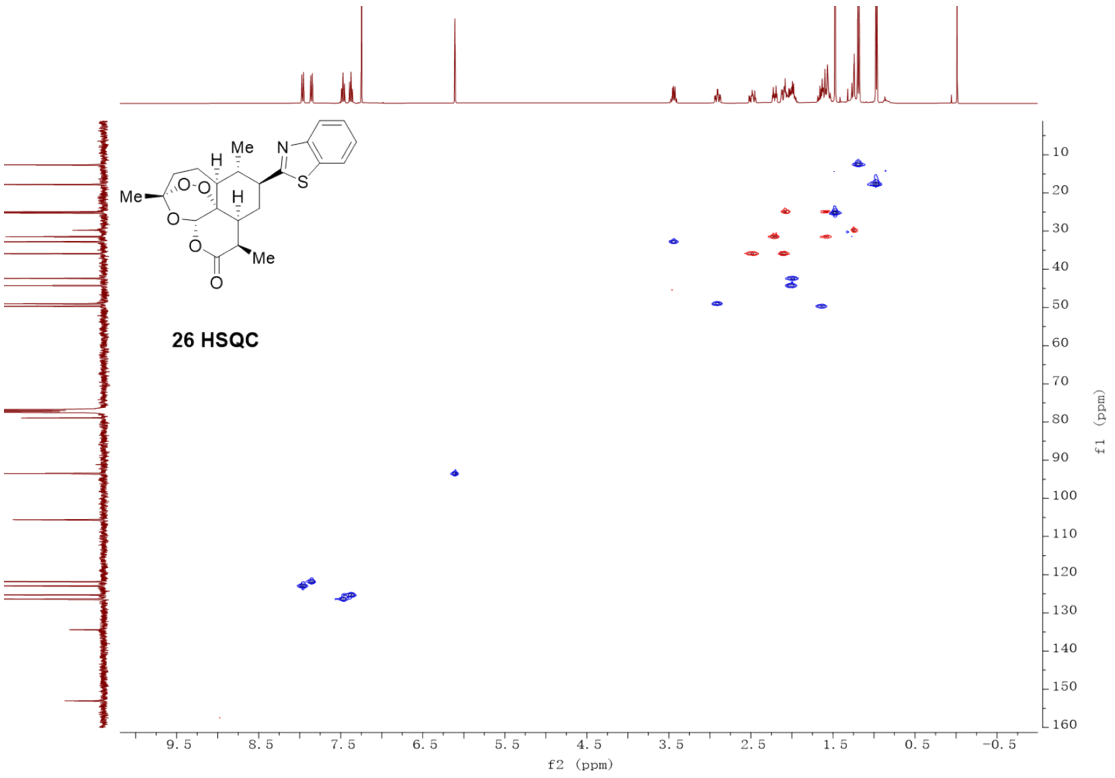
^{1}H-^{1}H –COSY spectrum of compound 26 in $CDCl_3$ at 400 MHz



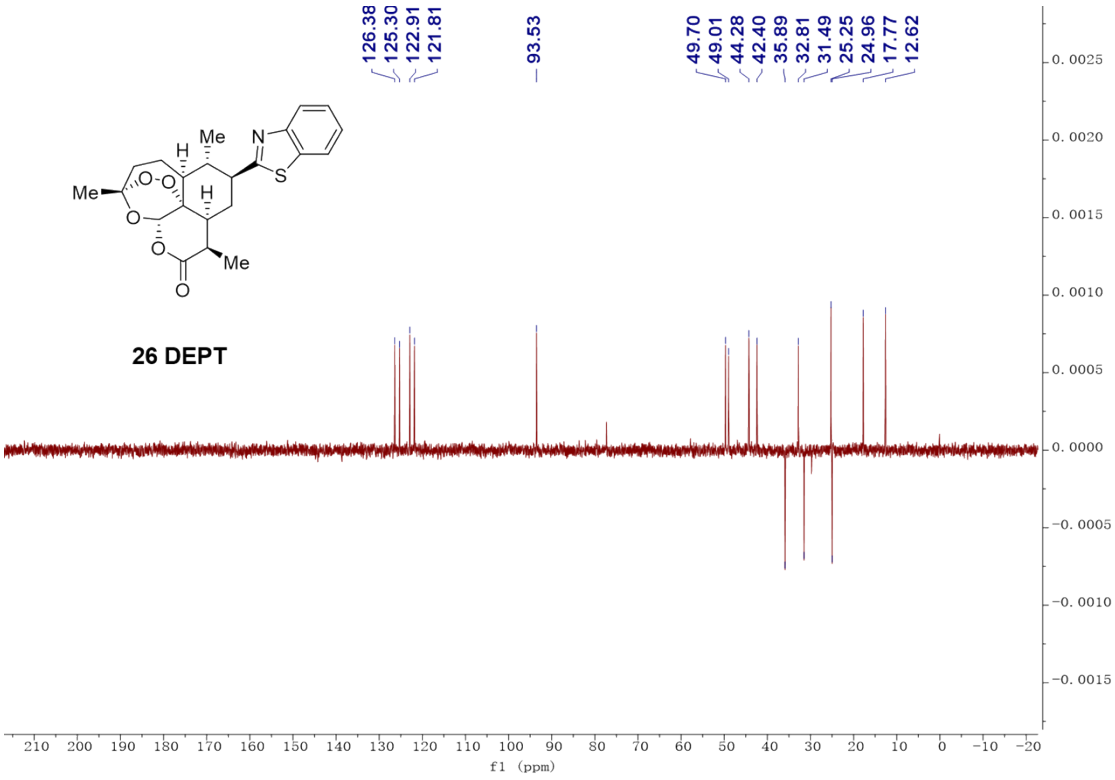
^{1}H-^{13}C –HMBC spectrum of compound 26 in $CDCl_3$ at 400 MHz



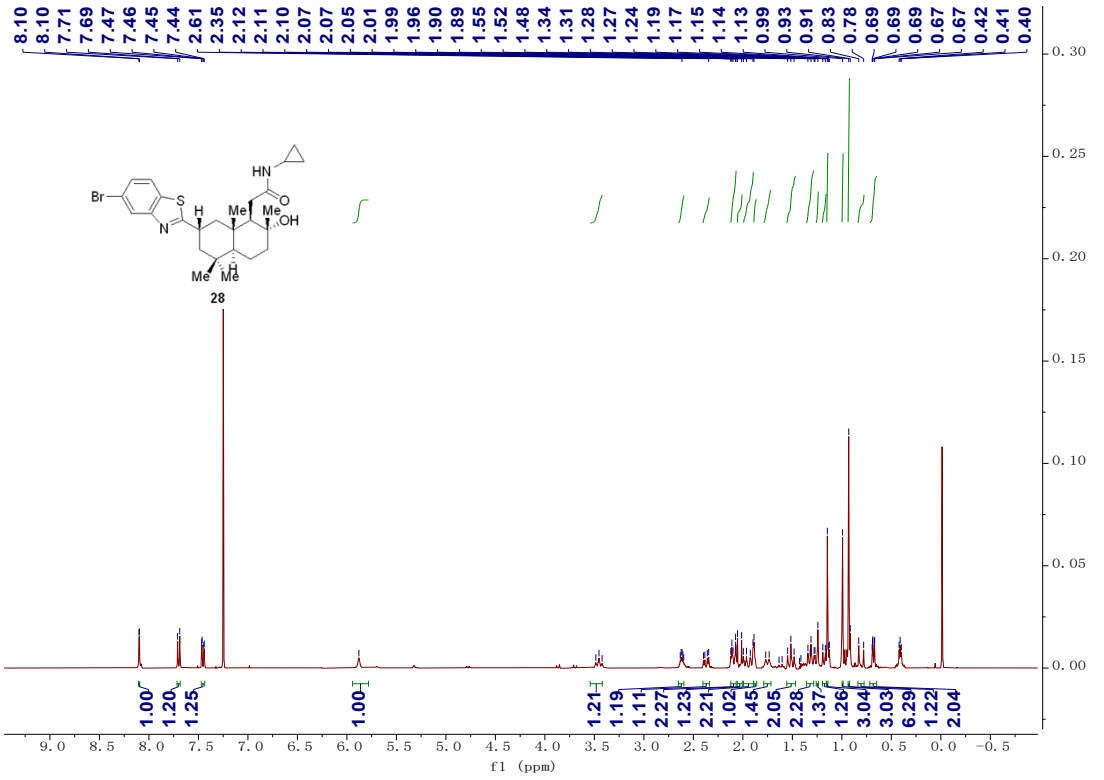
^{1}H-^{13}C –HSQC spectrum of compound 26 in $CDCl_3$ at 400 MHz



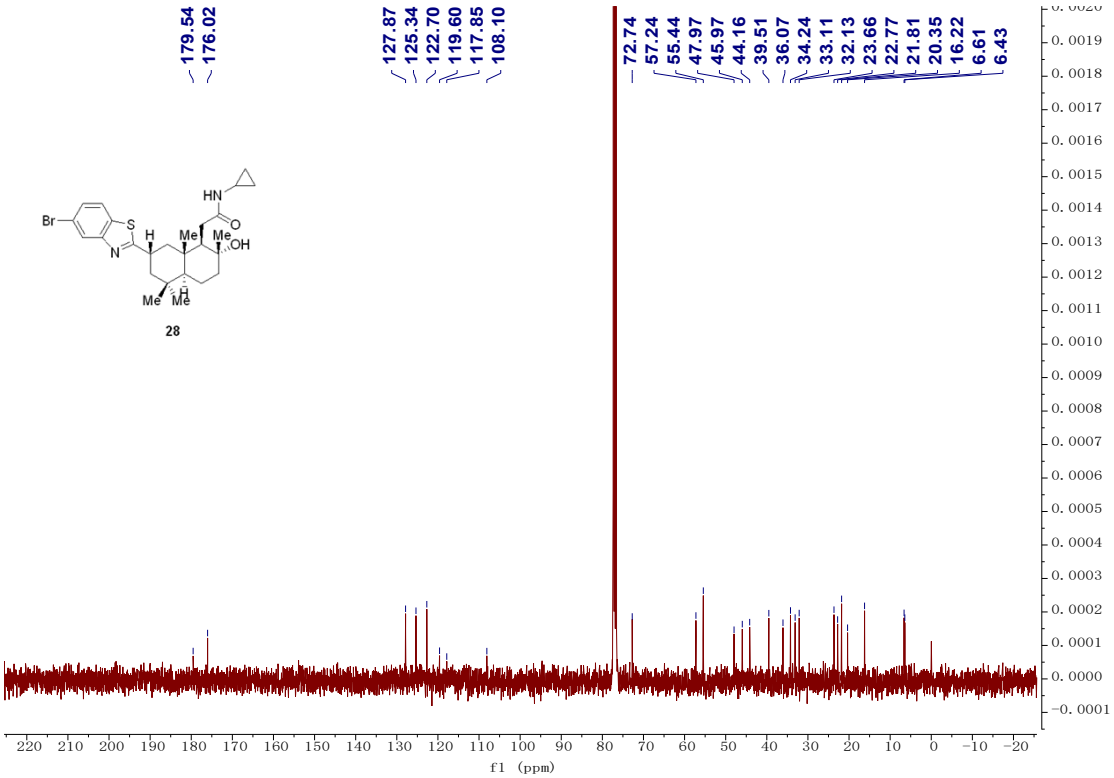
DEPT spectrum of compound 26 in $CDCl_3$ at 400 MHz



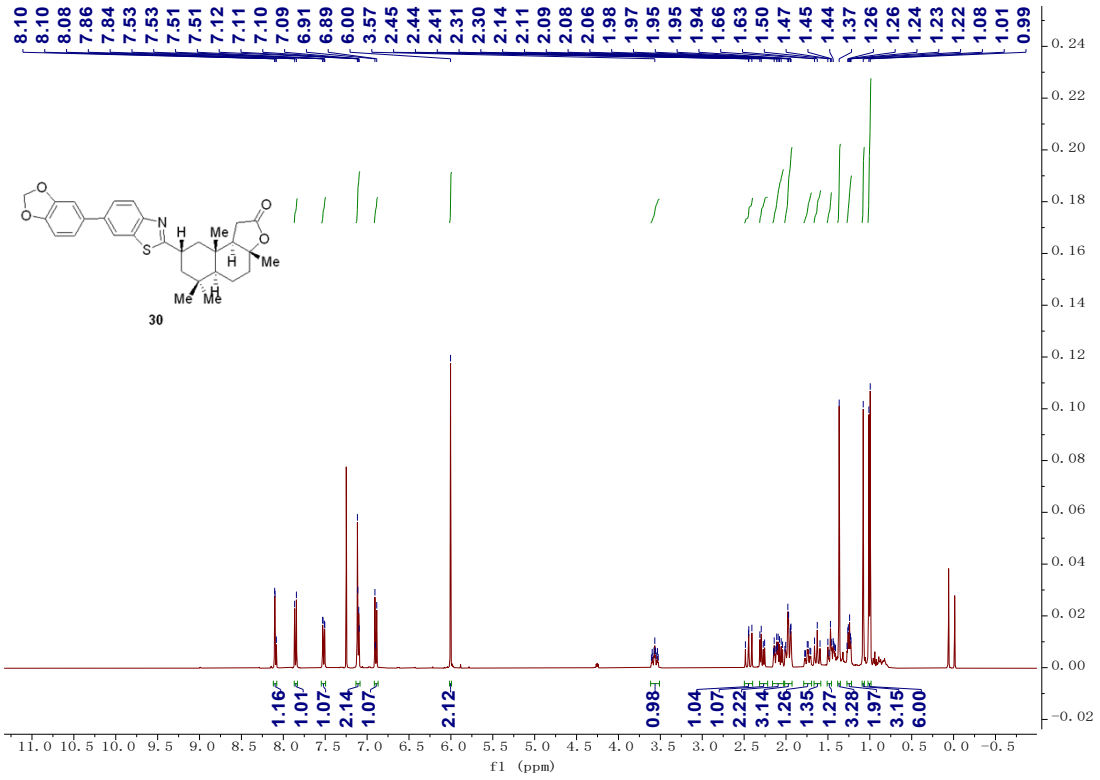
^{1}H NMR of compound 28 in $CDCl_3$ at 400 MHz



^{13}C NMR of compound 28 in $CDCl_3$ at 100 MHz

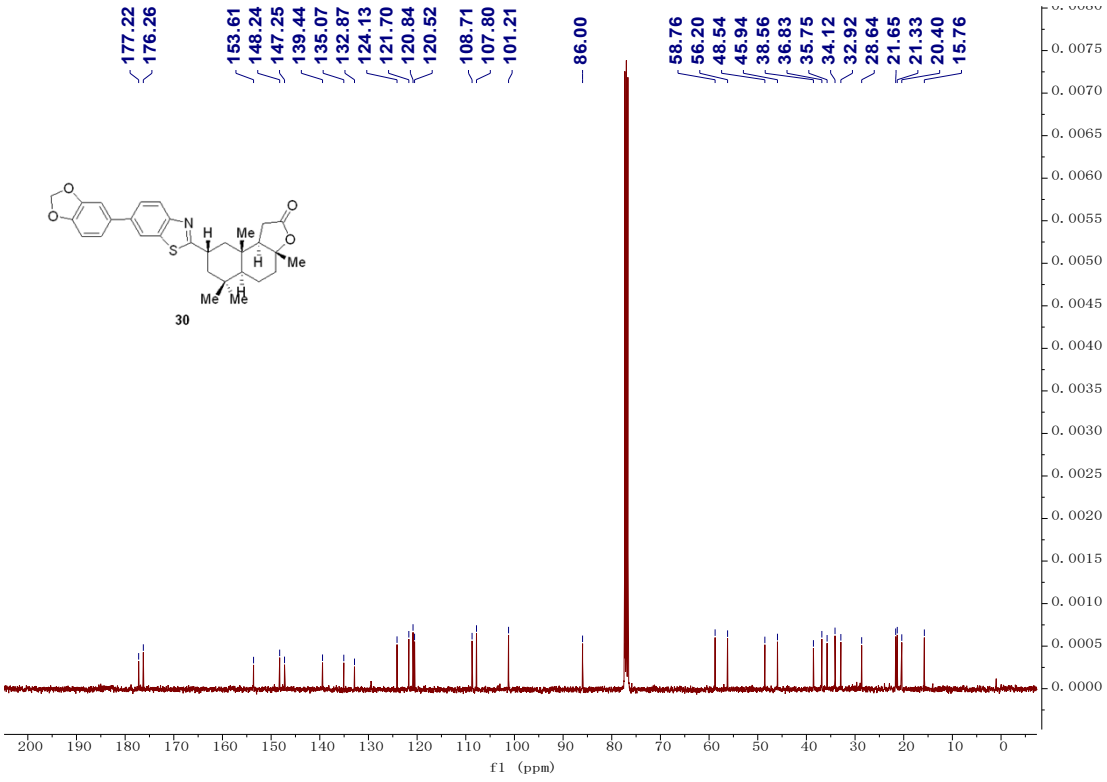


^{1}H NMR of compound 30 in $CDCl_3$ at 400 MHz



30

^{13}C NMR of compound 30 in $CDCl_3$ at 100 MHz



30