

Supplementary Material

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1. General Information

All reactions involving air or moisture sensitive reagents, or intermediates were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Solvent purification was conducted according to Purification of Laboratory Chemicals (Peerrin, D. D. Armarego, W. L. and Perrins, D. R., Pergamon Press: Oxford, 1980). Yields refer to isolated compounds, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Tsingdao silica gel plates (60F-254).

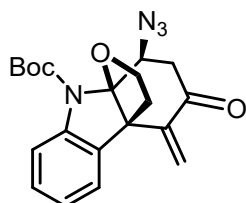
Visualization on TLC was achieved by use of UV light at 254 nm, exposure to iodine vapor. Staining was performed with an ethanolic solution of phosphomolybdic acid (PMA) and cerium sulfate, or by oxidative staining with an aqueous basic potassium permanganate (KMnO₄) solution and subsequent heating. Tsingdao silica gel (60, particle size 0.040 – 0.063 mm) was used for flash column chromatography. NMR spectra were recorded on a Brüker AVANCE 400 (¹H: 400 MHz, ¹³C: 100 MHz) or a Brüker AVANCE 500 (¹H: 500 MHz, ¹³C: 125 MHz) instrument. Chemical shifts were reported in parts per million (ppm) with respect to the residual solvent signal CDCl₃ (¹H NMR: δ = 7.26; ¹³C NMR: δ = 77.16). Peak multiplicities were reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, m = multiplet, br = broad signal. High resolution mass spectra (HRMS) were recorded on an Agilent Mass spectrometer using ESI-TOF (electrospray ionization-time of flight). Optical rotation values were recorded on a Rudolph Research Analytical Autopol I polarimeter (Rudolph Research Co.) The substrates were prepared according to literature methods.^{1,2}

Note: There exist rotational isomers for few compounds containing the acetal group, which are difficult to separate using column chromatography.

2. Analytical data of desired products

Compound 9

tert-butyl(4bS,8S,8aR)-8-azido-5-methylene-6-oxo-5,6,7,8-tetrahydro-9H-8a,4b-(epoxyethano) carbazole-9-carboxylate



A white solid, 91 mg, 85% yield.

TLC: R_f = 0.45 (Petroleum ether/EtOAc = 4:1) [UV].

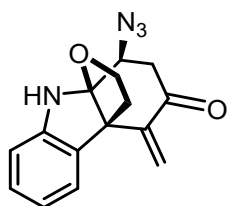
^1H NMR (400 MHz, CDCl_3) δ 7.72 – 7.65 (m, 1H), 7.20 (ddd, J = 8.5, 6.2, 2.6 Hz, 1H), 7.05 – 6.95 (m, 2H), 6.21 (s, 1H), 5.64 (s, 1H), 5.34 – 5.29 (m, 1H), 4.32 (ddd, J = 8.6, 7.4, 1.1 Hz, 1H), 3.76 (ddd, J = 11.9, 9.1, 4.9 Hz, 1H), 2.66 – 2.51 (m, 2H), 2.48 (d, J = 4.7 Hz, 1H), 2.35 (dd, J = 17.4, 2.4 Hz, 1H), 1.62 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 195.5, 151.8, 147.0, 142.4, 130.5, 129.2, 124.2, 123.9, 120.5, 115.0, 105.3, 83.0, 67.9, 60.0, 58.0, 42.3, 39.2, 28.3.

HRMS (ESI): $\text{C}_{20}\text{H}_{22}\text{N}_4\text{NaO}_4^+$ [(M+Na) $^+$]: calcd: 405.1533; found: 405.1531.

Compound 10

(4bS,8S,8aR)-8-azido-5-methylene-7,8-dihydro-9H-8a,4b-(epoxyethano) carbazol-6(5H)-one



A white solid, 26.8 mg, 40% yield.

TLC: R_f = 0.38 (Petroleum ether/EtOAc = 2:1) [UV].

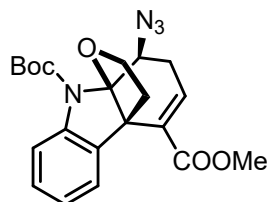
^1H NMR (400 MHz, CDCl_3) δ 7.09 (td, J = 7.6, 1.3 Hz, 1H), 7.01 (dd, J = 7.6, 1.3 Hz, 1H), 6.80 (td, J = 7.5, 1.0 Hz, 1H), 6.61 (d, J = 7.8 Hz, 1H), 6.23 (d, J = 0.8 Hz, 1H), 5.68 (s, 1H), 4.42 (s, 1H), 4.29 (ddd, J = 8.8, 4.9, 3.0 Hz, 1H), 4.17 (dd, J = 4.9, 2.8 Hz, 1H), 3.82 – 3.68 (m, 1H), 2.77 (dd, J = 17.3, 2.9 Hz, 1H), 2.62 (dd, J = 17.3, 4.9 Hz, 1H), 2.55 – 2.48 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 196.4, 148.0, 147.0, 129.8, 129.1, 124.2, 121.6, 120.3, 108.8, 103.1, 68.0, 60.5, 60.1, 43.0, 40.1.

HRMS (ESI): $C_{15}H_{15}N_4O_2^+$ $[(M+H)^+]$: calcd: 283.1190; found: 283.1189.

Compound 13

9-(tert-butyl) 5-methyl (4bS,8S,8aR)-8-azido-7,8-dihydro-9H-8a,4b-(epoxyethano) carbazole-5,9-dicarboxylate



A white solid, 55 mg, 78% yield.

TLC: R_f = 0.62 (Petroleum ether/EtOAc = 5:1) [UV].

1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.3 Hz, 1H), 7.61 (ddd, J = 7.7, 1.5, 0.6 Hz, 1H), 7.20 (ddd, J = 8.2, 7.4, 1.5 Hz, 1H), 6.98 (td, J = 7.5, 1.1 Hz, 1H), 6.87 (td, J = 4.7, 0.8 Hz, 1H), 5.46 (s, 1H), 3.69 (ddd, J = 12.3, 8.6, 4.9 Hz, 1H), 3.07 (dd, J = 12.6, 4.9 Hz, 1H), 2.56 (td, J = 12.5, 7.9 Hz, 1H), 2.43 (dd, J = 4.6, 3.1 Hz, 2H), 1.63 (s, 9H).

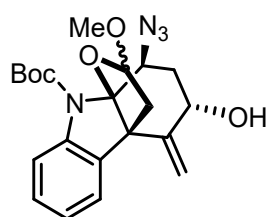
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 152.3, 142.2, 135.4, 134.5, 132.0, 128.7, 124.9, 123.4, 115.4, 105.3, 82.9, 68.8, 57.8, 57.6, 51.2, 39.3, 28.6, 28.4.

HRMS (ESI): $C_{21}H_{24}N_4NaO_5^+$ $[(M+Na)^+]$: calcd: 435.1639; found: 435.1642.

Compound 5

tert-butyl

(4bS,6S,8S,8aR)-8-azido-6-hydroxy-11-methoxy-5-methylene-5,6,7,8-tetrahydro-9H-8a,4b-(epoxyethano) carbazole-9-carboxylate



dr = 2:1

A white solid, 68 mg, 88% yield.

TLC: R_f = 0.63 (Petroleum ether/EtOAc = 2:1) [UV].

1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.2 Hz, 1H), 7.68 (s, 1H), 7.24 – 7.15 (m, 2H), 7.14 – 7.06 (m, 2H), 7.00 (tdd, J = 7.5, 4.3, 1.0 Hz, 2H), 5.44 – 5.32 (m, 4H), 5.30 (d, J = 5.1 Hz, 1H), 5.13 (s, 1H), 5.06 (dd, J = 6.7, 5.0 Hz, 1H), 4.99 (t, J = 3.7 Hz, 1H), 4.43 (t, J = 7.5 Hz, 1H), 4.37 (t, J = 7.7 Hz, 1H), 3.50 (s, 3H), 3.19 (s, 2H), 2.65 (dd, J = 12.7, 5.2 Hz, 1H), 2.60 – 2.46 (m, 3H), 2.46 – 2.30 (m, 2H), 1.63 (s, 3H), 1.61 (s, 6H), 0.97 (s, 1H), 0.82 (s, 1H).

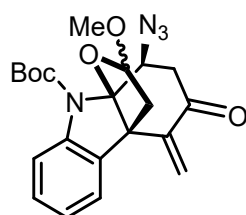
^{13}C NMR (101 MHz, CDCl_3) δ 152.2, 152.0, 151.8, 150.3, 141.6, 134.1, 133.4, 128.9, 128.6, 123.4, 123.2, 122.9, 115.7, 115.6, 115.4, 114.9, 106.1, 105.7, 105.6, 104.6, 82.4, 82.3, 68.5, 68.1, 58.9, 57.9, 57.4, 54.9, 46.9, 45.4, 33.1, 32.5, 28.4.

HRMS (ESI): $\text{C}_{21}\text{H}_{26}\text{N}_4\text{NaO}_5^+$ $[(\text{M}+\text{Na})^+]$: calcd: 437.1795; found: 437.1782.

Compound 6

tert-butyl

(4bS,8S,8aR)-8-azido-11-methoxy-5-methylene-6-oxo-5,6,7,8-tetrahydro-9H-8a,4b-(epoxyethano) carbazole-9-carboxylate



dr = 2:1

A white solid, 43 mg, 86% yield.

TLC: R_f = 0.49 (Petroleum ether/EtOAc = 4:1) [UV].

^1H NMR (400 MHz, CDCl_3) δ 7.66 (s, 1H), 7.18 (ddd, J = 8.5, 4.9, 3.8 Hz, 1H), 6.99 (dd, J = 4.0, 0.9 Hz, 2H), 6.18 (s, 1H), 5.58 (s, 1H), 5.42 (dd, J = 3.3, 2.2 Hz, 1H), 5.37 (s, 1H), 3.23 (s, 3H), 2.72 – 2.66 (m, 2H), 2.58 (dd, J = 17.6, 4.3 Hz, 1H), 2.40 (dd, J = 17.6, 2.4 Hz, 1H), 1.65 (s, 9H).

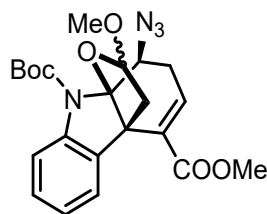
^{13}C NMR (101 MHz, CDCl_3) δ 195.2, 151.7, 147.3, 132.0, 128.9, 123.9, 123.8, 120.3, 115.4, 106.8, 105.4, 82.8, 55.1, 48.1, 39.0, 28.4.

HRMS (ESI): $\text{C}_{21}\text{H}_{24}\text{N}_4\text{NaO}_5^+$ $[(\text{M}+\text{Na})^+]$: calcd: 435.1639; found: 435.1640.

Compound 8(up)

9-(tert-butyl) 5-methyl

(4bS,8S,8aR)-8-azido-11-methoxy-7,8-dihydro-9H-8a,4b-(epoxyethano) carbazole-5,9-dicarboxylate



dr = 2:1

A white solid, 67 mg, 59% yield.

TLC: R_f = 0.58 (Petroleum ether/EtOAc = 7:1) [UV].

^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, J = 8.2 Hz, 1H), 7.61 (dd, J = 7.7, 1.4 Hz, 1H), 7.21 (ddd, J = 8.3, 7.4, 1.4 Hz, 1H), 6.99 (td, J = 7.5, 1.1 Hz, 1H), 6.86 – 6.79 (m, 1H), 5.42 (s, 1H), 5.06 (dd, J = 7.8, 4.9 Hz, 1H), 3.74 (s, 3H), 3.49 (s, 3H), 3.34 (dd, J = 13.4, 4.9 Hz, 1H), 2.54 – 2.44 (m, 3H), 1.62 (s, 9H).

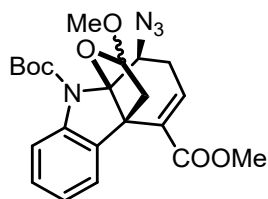
¹³C NMR (101 MHz, CDCl₃) δ 165.5, 152.3, 141.3, 134.9, 133.9, 132.3, 128.9, 125.1, 123.5, 116.0, 107.2, 104.0, 82.9, 58.6, 57.4, 55.9, 51.8, 44.1, 29.2, 28.4.

HRMS (ESI): C₂₂H₂₆N₄NaO₆⁺ [(M+Na)⁺]: calcd: 465.1745; found: 465.1743.

Compound 8(down)

9-(*tert*-butyl) 5-methyl

(4bS,8S,8aR)-8-azido-11-methoxy-7,8-dihydro-9H-8a,4b-(epoxyethano) carbazole-5,9-dicarboxylate



dr = 2:1

A white solid, 67 mg, 59% yield.

TLC: *R_f* = 0.56 (Petroleum ether/EtOAc = 7:1) [UV].

¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.64 – 7.51 (m, 1H), 7.25 – 7.12 (m, 1H), 6.97 (td, *J* = 7.5, 1.1 Hz, 1H), 6.84 (dt, *J* = 9.8, 4.6 Hz, 1H), 5.43 (t, *J* = 3.1 Hz, 1H), 5.30 (d, *J* = 5.1 Hz, 1H), 3.76 (d, *J* = 13.9 Hz, 3H), 3.59 – 3.46 (m, 1H), 3.17 (d, *J* = 13.6 Hz, 1H), 3.10 (s, 2H), 2.58 (dd, *J* = 13.6, 5.2 Hz, 1H), 2.53 – 2.38 (m, 2H), 1.63 (d, *J* = 6.2 Hz, 9H).

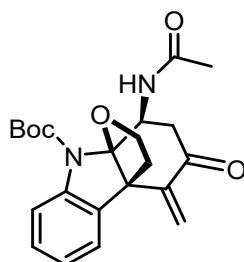
¹³C NMR (101 MHz, CDCl₃) δ 165.6, 152.2, 140.6, 135.2, 134.9, 134.3, 128.1, 124.1, 123.5, 115.6, 106.1, 105.8, 82.6, 58.2, 55.9, 54.6, 51.8, 45.8, 28.4, 28.0.

HRMS (ESI): C₂₂H₂₆N₄NaO₆⁺ [(M+Na)⁺]: calcd: 465.1745; found: 465.1739.

Compound 17a

tert-butyl

(4bS,8S,8aR)-8-acetamido-5-methylene-6-oxo-5,6,7,8-tetrahydro-9H-8a,4b-(epoxyethano) carbazole-9-carboxylate



A white solid, 38 mg, 72% yield.

TLC: *R_f* = 0.42 (Petroleum ether/EtOAc = 4:1) [UV].

¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 8.3 Hz, 1H), 7.20 (ddd, *J* = 8.4, 6.5, 2.3 Hz, 1H), 7.02 – 6.92 (m, 2H), 6.29 (s, 1H), 5.67 (d, *J* = 5.8 Hz, 2H), 5.39 (q, *J* = 2.0 Hz, 1H), 4.30 – 4.21 (m, 1H), 3.75 (ddd, *J* = 11.8, 9.4, 5.2 Hz, 1H), 3.07 (dd, *J* = 17.6, 4.4 Hz, 1H), 2.53 – 2.35 (m, 2H), 2.32 (dd, *J* = 17.6, 2.6 Hz, 1H), 1.93 (s, 3H), 1.59

(s, 9H).

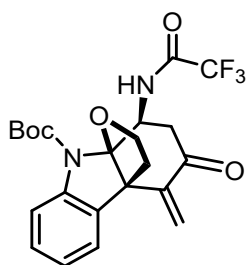
^{13}C NMR (101 MHz, CDCl_3) δ 196.5, 170.2, 151.4, 146.6, 142.8, 130.1, 129.3, 124.1, 123.7, 121.3, 115.0, 104.1, 82.9, 67.2, 60.2, 48.6, 42.4, 38.9, 28.3, 23.5.

HRMS (ESI): $\text{C}_{22}\text{H}_{26}\text{N}_2\text{NaO}_5^+$ [(M+Na) $^+$]: calcd: 421.1734; found: 421.1737.

Compound 17b

tert-butyl

(4bS,8S,8aR)-5-methylene-6-oxo-8-(2,2,2-trifluoroacetamido)-5,6,7,8-tetrahydro-9H-8a,4b-(epoxyethano) carbazole-9-carboxylate



A white solid, 44 mg, 69% yield.

TLC: R_f = 0.39 (Petroleum ether/EtOAc = 4:1) [UV].

^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, J = 8.2 Hz, 1H), 7.22 (ddd, J = 8.5, 6.5, 2.3 Hz, 1H), 7.05 – 6.94 (m, 2H), 6.70 (s, 1H), 6.29 (s, 1H), 5.71 (s, 1H), 5.40 (td, J = 4.9, 2.9 Hz, 1H), 4.35 – 4.24 (m, 1H), 3.84 – 3.72 (m, 1H), 3.08 (dd, J = 17.9, 4.7 Hz, 1H), 2.51 – 2.39 (m, 3H), 1.59 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 195.3, 157.5, 157.1, 156.8, 156.4, 151.4, 146.1, 142.4, 129.6, 129.4, 124.1, 124.0, 122.3, 119.7, 116.8, 115.1, 113.9, 111.1, 103.4, 83.4, 67.5, 60.3, 49.2, 42.3, 37.9, 28.2.

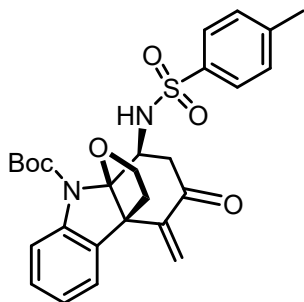
^{19}F NMR (376 MHz, CDCl_3) δ -76.0.

HRMS (ESI): $\text{C}_{22}\text{H}_{23}\text{F}_3\text{N}_2\text{NaO}_5^+$ [(M+Na) $^+$]: calcd: 475.1451; found: 475.1452.

Compound 17c

tert-butyl (4bS,8S,8aR)-5-methylene-8-((4-methylphenyl)

sulfonamido)-6-oxo-5,6,7,8-tetrahydro-9H-8a,4b-(epoxyethano) carbazole-9-carboxylate



A white solid, 84 mg, 78% yield.

TLC: R_f = 0.48 (Petroleum ether/EtOAc = 4:1) [UV].

^1H NMR (400 MHz, CDCl_3) δ 7.74 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 8.2 Hz, 1H), 7.31

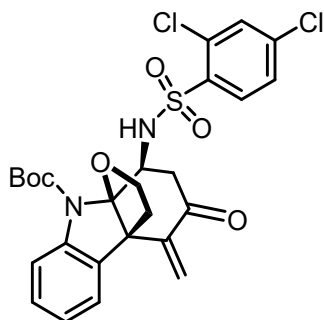
(d, $J = 8.0$ Hz, 2H), 7.16 (ddd, $J = 8.5, 6.5, 2.3$ Hz, 1H), 7.00 – 6.90 (m, 2H), 6.15 (s, 1H), 5.56 (s, 1H), 5.24 (s, 1H), 4.74 (dt, $J = 3.9, 1.8$ Hz, 1H), 4.16 (dd, $J = 9.2, 7.3$ Hz, 1H), 3.65 (ddd, $J = 12.1, 9.2, 4.8$ Hz, 1H), 2.95 (dd, $J = 17.9, 4.3$ Hz, 1H), 2.49 (dt, $J = 12.1, 6.0$ Hz, 1H), 2.43 (s, 3H), 2.33 (dd, $J = 11.9, 4.7$ Hz, 1H), 2.25 (dt, $J = 17.9, 1.7$ Hz, 1H), 1.41 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 195.5, 151.4, 146.6, 143.8, 142.6, 136.2, 130.2, 129.7, 129.1, 127.3, 124.2, 123.9, 120.2, 114.9, 103.5, 82.7, 67.6, 60.2, 51.1, 42.0, 38.2, 28.0, 21.5.

HRMS (ESI): $\text{C}_{27}\text{H}_{30}\text{N}_2\text{NaO}_6\text{S}^+$ [(M+H) $^+$]: calcd: 533.1717; found: 533.1720.

Compound 17d

tert-butyl (4bS,8S,8aR)-8-((2,4-dichlorophenyl)sulfonamido)-5-methylene-6-oxo-5,6,7,8-tetrahydro-9H-8a,4b-(epoxyethano)carbazole-9-carboxylate



A white solid, 63 mg, 74% yield.

TLC: $R_f = 0.45$ (Petroleum ether/EtOAc = 4:1) [UV].

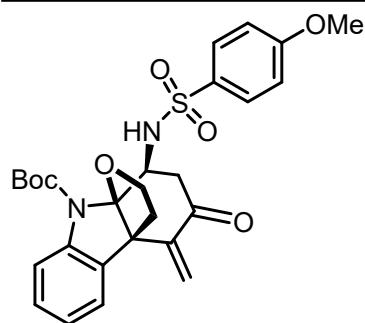
^1H NMR (400 MHz, CDCl_3) δ 8.01 (d, $J = 8.5$ Hz, 1H), 7.65 (d, $J = 8.3$ Hz, 1H), 7.53 (d, $J = 2.0$ Hz, 1H), 7.42 (dd, $J = 8.5, 2.0$ Hz, 1H), 7.17 (ddd, $J = 8.5, 6.9, 1.9$ Hz, 1H), 7.02 – 6.90 (m, 2H), 6.17 – 6.12 (m, 1H), 5.63 (s, 1H), 5.50 (d, $J = 2.7$ Hz, 1H), 4.97 – 4.90 (m, 1H), 4.10 (dd, $J = 9.3, 7.3$ Hz, 1H), 3.67 (ddd, $J = 12.2, 9.3, 4.8$ Hz, 1H), 2.85 (dd, $J = 18.0, 4.1$ Hz, 1H), 2.50 (td, $J = 12.0, 7.4$ Hz, 1H), 2.38 (dd, $J = 11.9, 4.7$ Hz, 1H), 2.34 – 2.24 (m, 1H), 1.49 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 195.4, 151.3, 146.4, 142.6, 139.7, 135.9, 132.8, 132.0, 131.3, 129.9, 129.3, 127.5, 124.2, 124.0, 120.9, 115.1, 103.4, 83.0, 67.7, 60.2, 51.5, 42.1, 38.7, 28.2.

HRMS (ESI): $\text{C}_{26}\text{H}_{26}\text{Cl}_2\text{N}_2\text{NaO}_6\text{S}^+$ [(M+Na) $^+$]: calcd: 587.0781; found: 587.0781.

Compound 17e

tert-butyl (4bS,8S,8aR)-8-((4-methoxyphenyl)sulfonamido)-5-methylene-6-oxo-5,6,7,8-tetrahydro-9H-8a,4b-(epoxyethano)carbazole-9-carboxylate



A white solid, 54 mg, 70% yield.

TLC: R_f = 0.47 (Petroleum ether/EtOAc = 4:1) [UV].

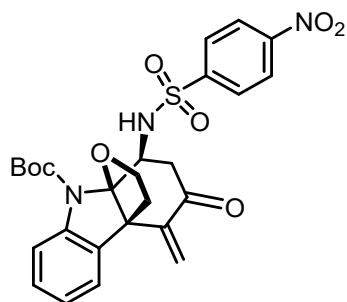
^1H NMR (400 MHz, CDCl_3) δ 7.83 – 7.74 (m, 2H), 7.66 (d, J = 8.2 Hz, 1H), 7.17 (ddd, J = 8.5, 6.6, 2.2 Hz, 1H), 7.02 – 6.91 (m, 4H), 6.16 (s, 0H), 5.57 (s, 1H), 5.11 (s, 1H), 4.77 (dt, J = 3.8, 1.7 Hz, 1H), 4.19 (dd, J = 9.3, 7.3 Hz, 1H), 3.88 (s, 3H), 3.68 (ddd, J = 12.2, 9.3, 4.8 Hz, 1H), 2.94 (dd, J = 17.9, 4.2 Hz, 1H), 2.49 (td, J = 12.1, 7.4 Hz, 1H), 2.36 (dd, J = 11.9, 4.7 Hz, 1H), 2.25 (ddd, J = 17.8, 2.1, 1.2 Hz, 1H), 1.45 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 195.4, 163.2, 151.4, 146.7, 142.6, 130.8, 130.2, 129.5, 129.2, 124.2, 124.0, 120.2, 115.0, 114.4, 103.5, 82.8, 67.6, 60.2, 55.6, 51.2, 42.2, 38.1, 28.1.

HRMS (ESI): $\text{C}_{27}\text{H}_{30}\text{N}_2\text{NaO}_7\text{S}^+$ $[(\text{M}+\text{Na})^+]$: calcd: 549.1666; found: 549.1669.

Compound 17f

tert-butyl (4bS,8S,8aR)-5-methylene-8-((4-nitrophenyl)sulfonamido)-6-oxo-5,6,7,8-tetrahydro-9H-8a,4b-(epoxyethano)carbazole-9-carboxylate



A brown solid, 58 mg, 73% yield.

TLC: R_f = 0.36 (Petroleum ether/EtOAc = 4:1) [UV].

^1H NMR (400 MHz, CDCl_3) δ 8.38 (d, J = 8.9 Hz, 2H), 8.06 (d, J = 8.9 Hz, 2H), 7.60 (d, J = 8.3 Hz, 1H), 7.19 (ddd, J = 8.5, 7.1, 1.7 Hz, 1H), 7.03 – 6.91 (m, 2H), 6.18 (s, 1H), 5.63 (s, 1H), 5.38 – 5.33 (m, 1H), 5.00 (dt, J = 4.4, 2.2 Hz, 1H), 4.20 – 4.11 (m, 1H), 3.69 (ddd, J = 12.0, 9.3, 5.0 Hz, 1H), 2.90 (dd, J = 17.8, 4.2 Hz, 1H), 2.47 (td, J = 12.0, 7.4 Hz, 1H), 2.40 – 2.35 (m, 1H), 2.32 (ddd, J = 17.8, 2.3, 1.0 Hz, 1H), 1.52 (s, 9H).

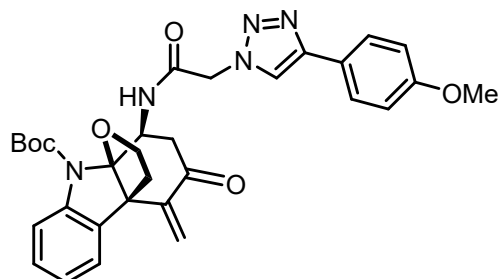
^{13}C NMR (101 MHz, CDCl_3) δ 195.0, 151.2, 150.2, 146.2, 145.2, 142.3, 129.9, 129.4, 128.7, 124.3, 124.2, 124.1, 121.3, 115.0, 103.3, 83.3, 67.6, 60.1, 51.3, 42.3,

38.8, 28.2.

HRMS (ESI): $C_{26}H_{27}N_3NaO_8S^+$ $[(M+Na)^+]$: calcd: 567.1411; found: 567.1412.

Compound 20a

tert-butyl (4bS,8S,8aR)-8-(2-(4-(4-methoxyphenyl)-1H-1,2,3-triazol-1-yl)acetamido)-5-methylene-6-oxo-5,6,7,8-tetrahydro-9H-8a,4b-(epoxyethano)carbazole-9-carboxylate



A white solid, 39 mg, 65% yield.

TLC: R_f = 0.55 (Petroleum ether/EtOAc = 3:1) [UV].

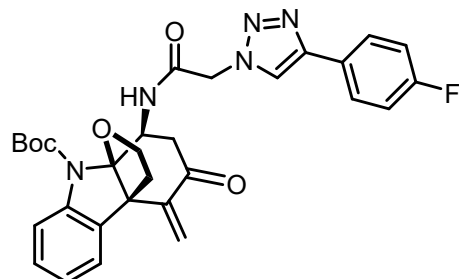
1H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.72 (m, 3H), 7.66 (d, J = 8.3 Hz, 1H), 7.17 (ddd, J = 8.4, 7.3, 1.4 Hz, 1H), 7.04 – 6.98 (m, 2H), 6.94 (td, J = 7.5, 1.0 Hz, 1H), 6.86 (dd, J = 7.7, 1.5 Hz, 1H), 6.23 (d, J = 5.4 Hz, 1H), 5.97 (s, 1H), 5.53 – 5.45 (m, 1H), 5.40 (s, 1H), 5.12 (d, J = 16.5 Hz, 1H), 4.98 (d, J = 16.5 Hz, 1H), 4.14 (dd, J = 9.0, 7.3 Hz, 1H), 3.87 (s, 3H), 3.63 (ddd, J = 11.8, 9.2, 5.0 Hz, 1H), 3.01 (dd, J = 17.8, 4.1 Hz, 1H), 2.34 (dd, J = 17.8, 2.5 Hz, 1H), 2.28 – 2.13 (m, 2H), 1.60 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2, 165.2, 160.0, 151.4, 148.6, 146.3, 142.7, 129.9, 129.3, 127.0, 124.1, 123.9, 122.4, 121.7, 120.3, 115.0, 114.5, 103.6, 83.1, 67.4, 60.1, 55.3, 53.4, 48.3, 41.9, 38.4, 29.7, 28.3.

HRMS (ESI): $C_{31}H_{34}N_5O_6^+$ $[(M+H)^+]$: calcd: 572.2504; found: 572.2505.

Compound 20b

tert-butyl (4bS,8S,8aR)-8-(2-(4-(4-fluorophenyl)-1H-1,2,3-triazol-1-yl)acetamido)-5-methylene-6-oxo-5,6,7,8-tetrahydro-9H-8a,4b-(epoxyethano)carbazole-9-carboxylate



A white solid, 46 mg, 71% yield.

TLC: R_f = 0.51 (Petroleum ether/EtOAc = 3:1) [UV].

1H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.76 (m, 3H), 7.64 (d, J = 8.3 Hz, 1H), 7.16 (dtd, J = 8.8, 7.2, 1.8 Hz, 3H), 6.94 (td, J = 7.5, 1.0 Hz, 1H), 6.86 (dd, J = 7.7, 1.4 Hz, 1H), 6.30 (d, J = 5.3 Hz, 1H), 5.97 (s, 1H), 5.48 (td, J = 4.5, 2.4 Hz, 1H), 5.41 (s, 1H),

5.11 (d, $J = 16.4$ Hz, 1H), 4.99 (d, $J = 16.4$ Hz, 1H), 4.17 – 4.06 (m, 1H), 3.63 (ddd, $J = 11.7, 9.2, 5.1$ Hz, 1H), 3.01 (dd, $J = 17.7, 4.2$ Hz, 1H), 2.33 (dd, $J = 17.8, 2.5$ Hz, 2H), 2.29 – 2.15 (m, 1H), 1.58 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 196.1, 165.0, 164.1, 161.6, 151.4, 147.7, 146.3, 142.6, 129.8, 129.3, 127.5, 127.4, 126.1, 126.0, 124.1, 123.9, 121.6, 121.0, 116.2, 116.0, 115.0, 103.6, 83.1, 67.4, 60.0, 53.4, 48.4, 42.0, 38.4, 28.3.

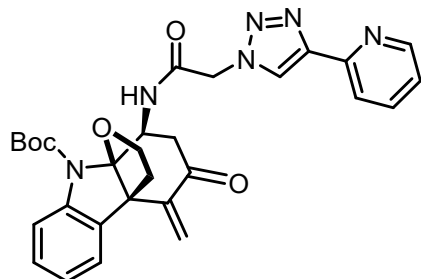
^{19}F NMR (376 MHz, CDCl_3) δ -112.5.

HRMS (ESI): $\text{C}_{30}\text{H}_{31}\text{FN}_5\text{O}_5^+$ [(M+H) $^+$]: calcd: 560.2304; found: 560.2308.

Compound 20c

tert-butyl

(4bS,8S,8aR)-5-methylene-6-oxo-8-(2-(4-(pyridin-2-yl)-1H-1,2,3-triazol-1-yl)acetamido)-5,6,7,8-tetrahydro-9H-8a,4b-(epoxyethano) carbazole-9-carboxylate



A white solid, 32 mg, 60% yield.

TLC: $R_f = 0.68$ (Petroleum ether/EtOAc = 2:1) [UV].

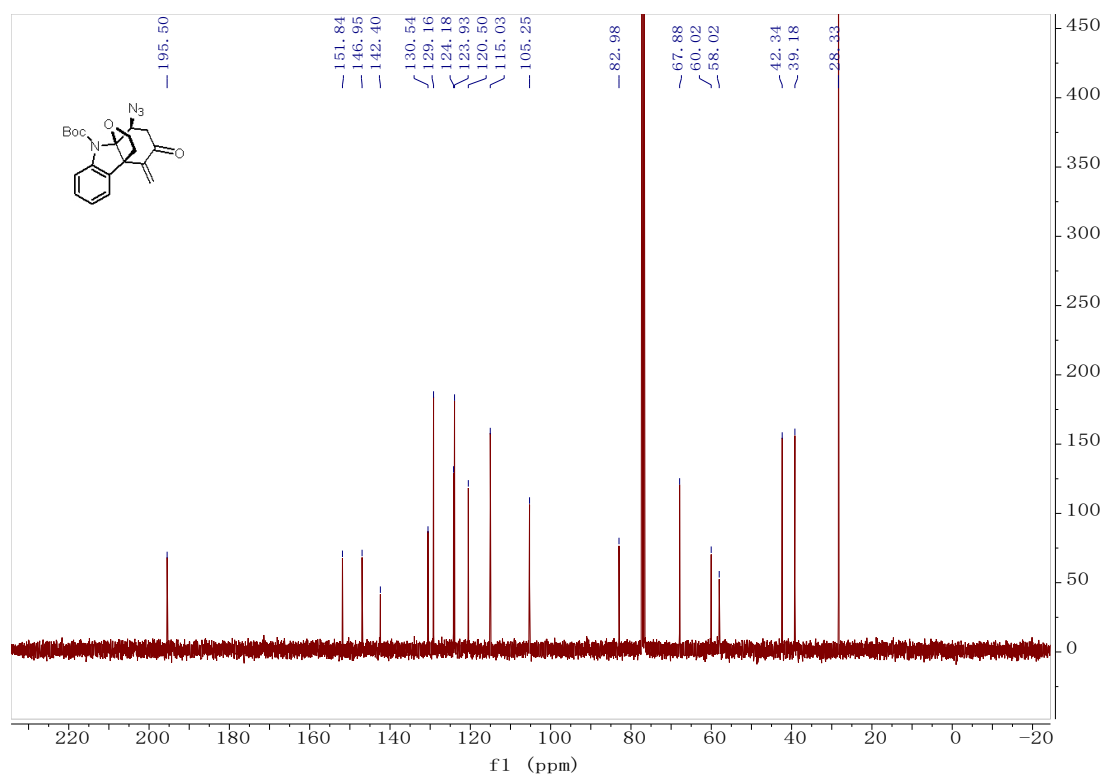
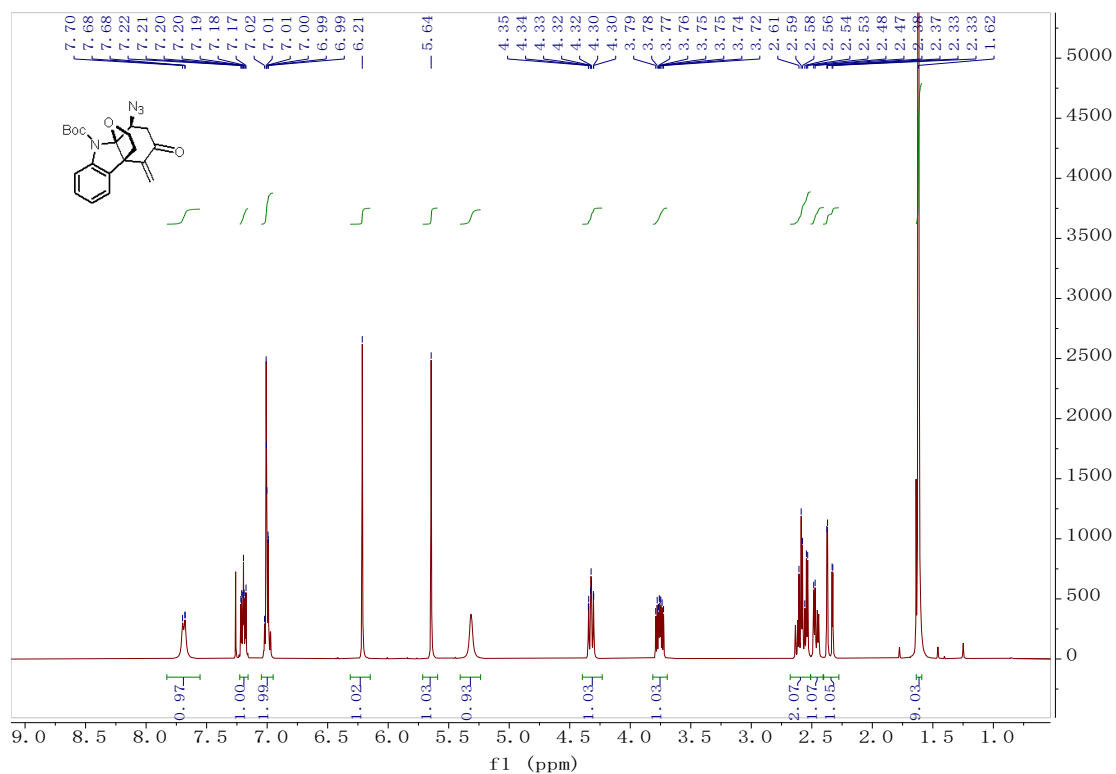
^1H NMR (400 MHz, CDCl_3) δ 8.62 (ddd, $J = 4.9, 1.8, 1.0$ Hz, 1H), 8.19 (s, 1H), 8.17 – 8.13 (m, 1H), 7.82 (td, $J = 7.8, 1.8$ Hz, 1H), 7.67 (d, $J = 8.3$ Hz, 1H), 7.28 (ddd, $J = 7.7, 4.9, 1.2$ Hz, 1H), 7.17 (ddd, $J = 8.4, 7.3, 1.5$ Hz, 1H), 6.94 (td, $J = 7.4, 1.0$ Hz, 1H), 6.86 (dd, $J = 7.7, 1.4$ Hz, 1H), 6.26 (d, $J = 5.6$ Hz, 1H), 6.01 (s, 1H), 5.51 (ddd, $J = 6.2, 4.1, 2.5$ Hz, 1H), 5.42 (s, 1H), 5.13 (d, $J = 16.6$ Hz, 1H), 5.04 (d, $J = 16.6$ Hz, 1H), 4.18 – 4.10 (m, 1H), 3.63 (ddd, $J = 10.9, 9.2, 5.6$ Hz, 1H), 2.99 (dd, $J = 18.0, 4.1$ Hz, 1H), 2.35 (dd, $J = 17.9, 2.6$ Hz, 1H), 2.29 – 2.15 (m, 2H), 2.10 (d, $J = 9.9$ Hz, 1H), 1.59 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 196.2, 164.8, 151.4, 149.7, 149.4, 149.2, 146.4, 142.7, 137.0, 129.8, 129.3, 124.1, 123.8, 123.7, 123.3, 121.6, 120.1, 115.0, 103.7, 83.1, 67.4, 60.1, 53.4, 48.3, 41.8, 38.4, 28.3.

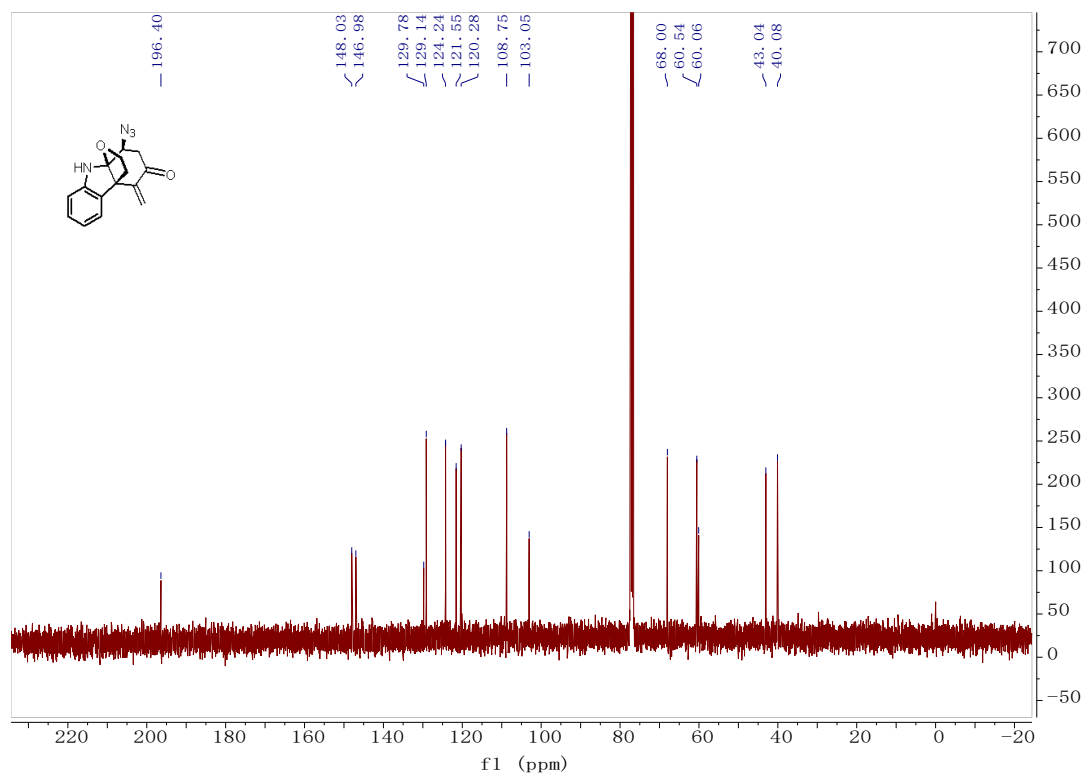
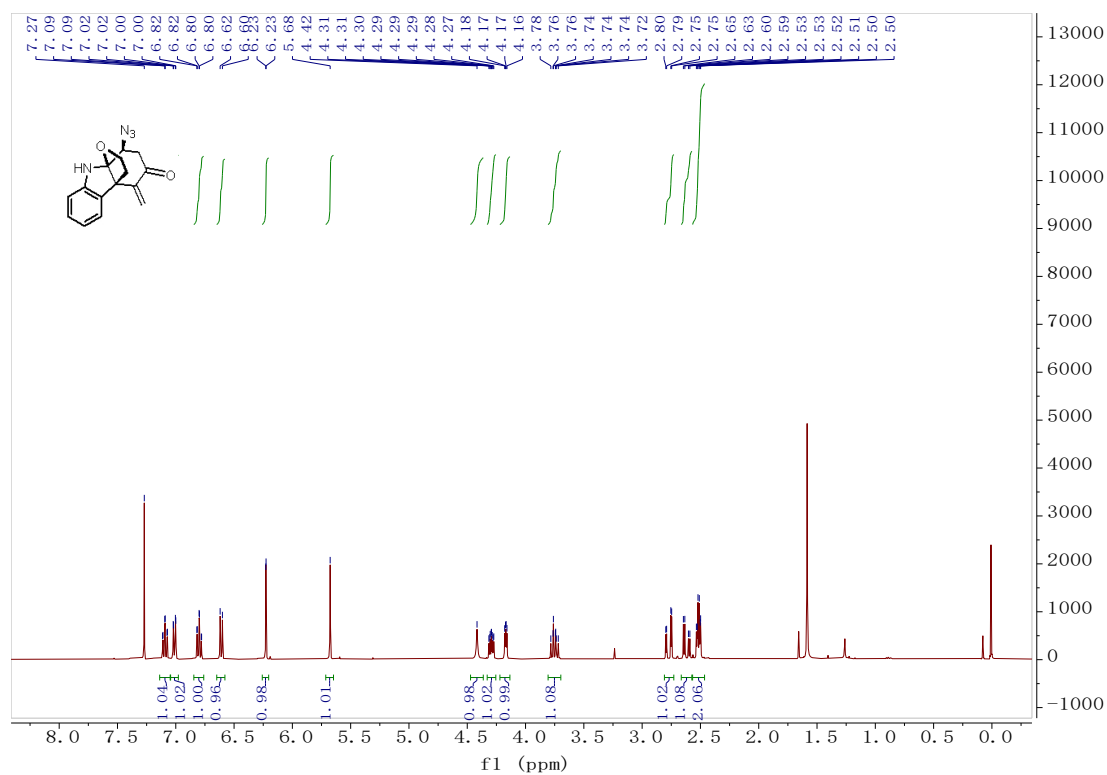
HRMS (ESI): $\text{C}_{29}\text{H}_{31}\text{N}_6\text{O}_5^+$ [(M+H) $^+$]: calcd: 543.2350; found: 543.2352.

3. Copies of ^1H and ^{13}C NMR spectra of products

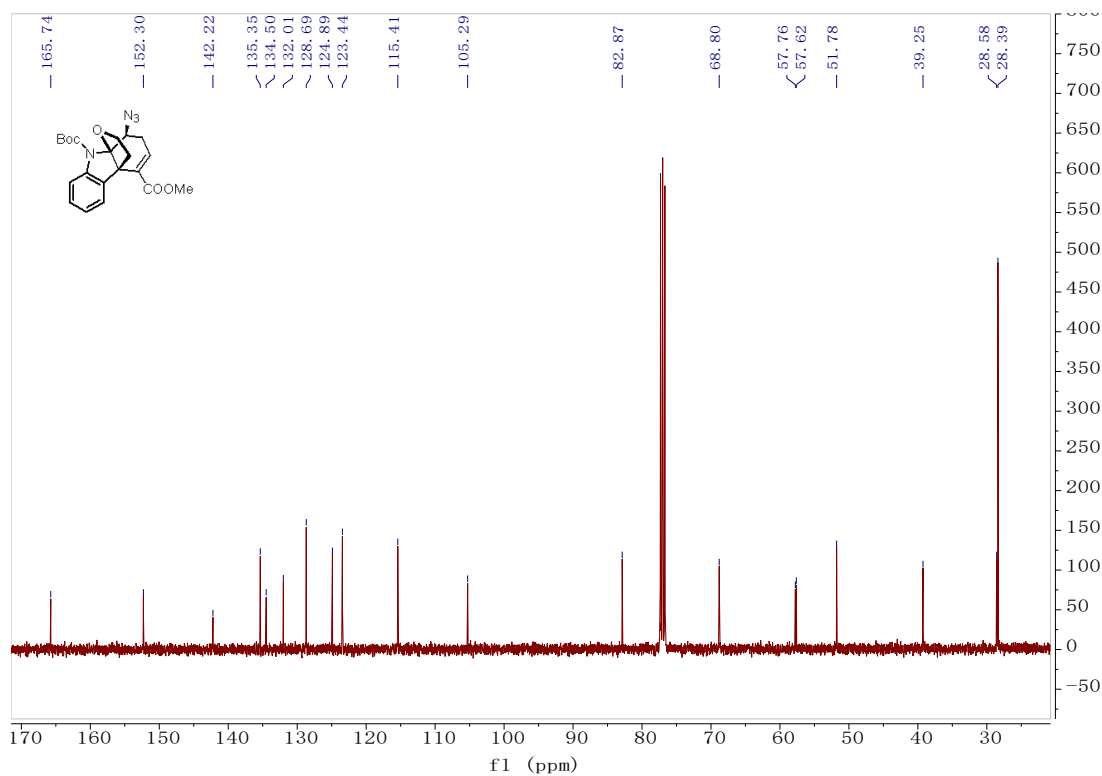
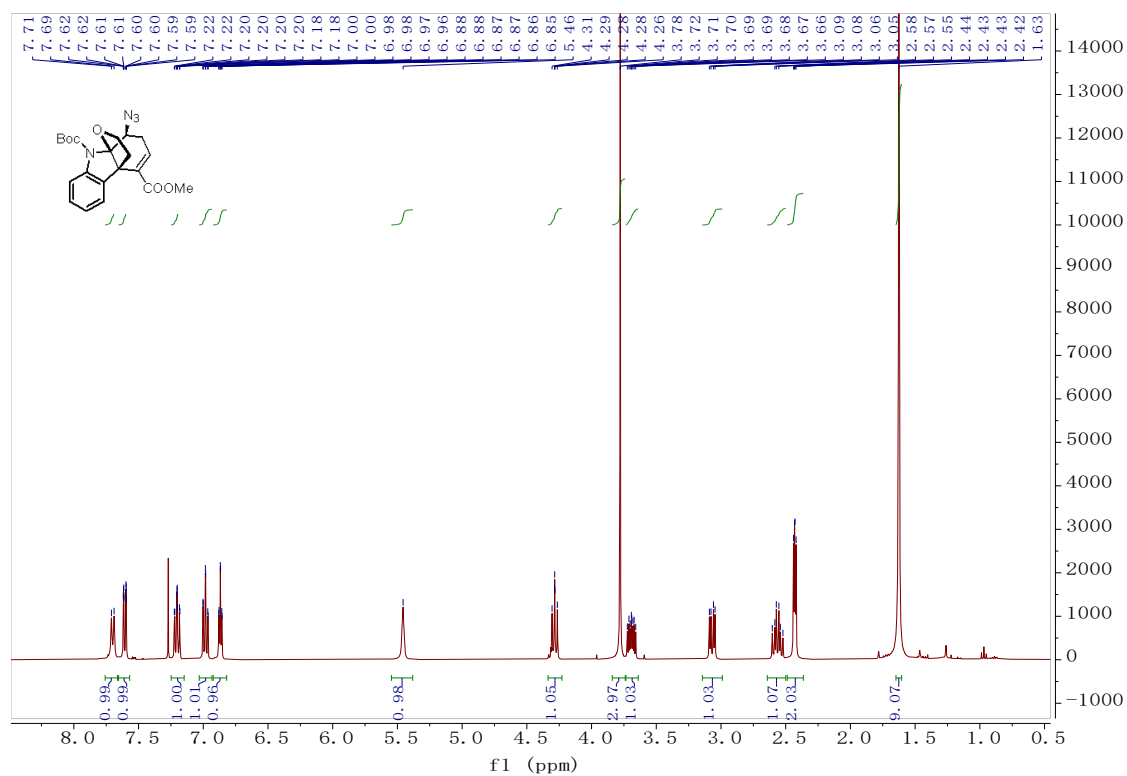
Compound 9



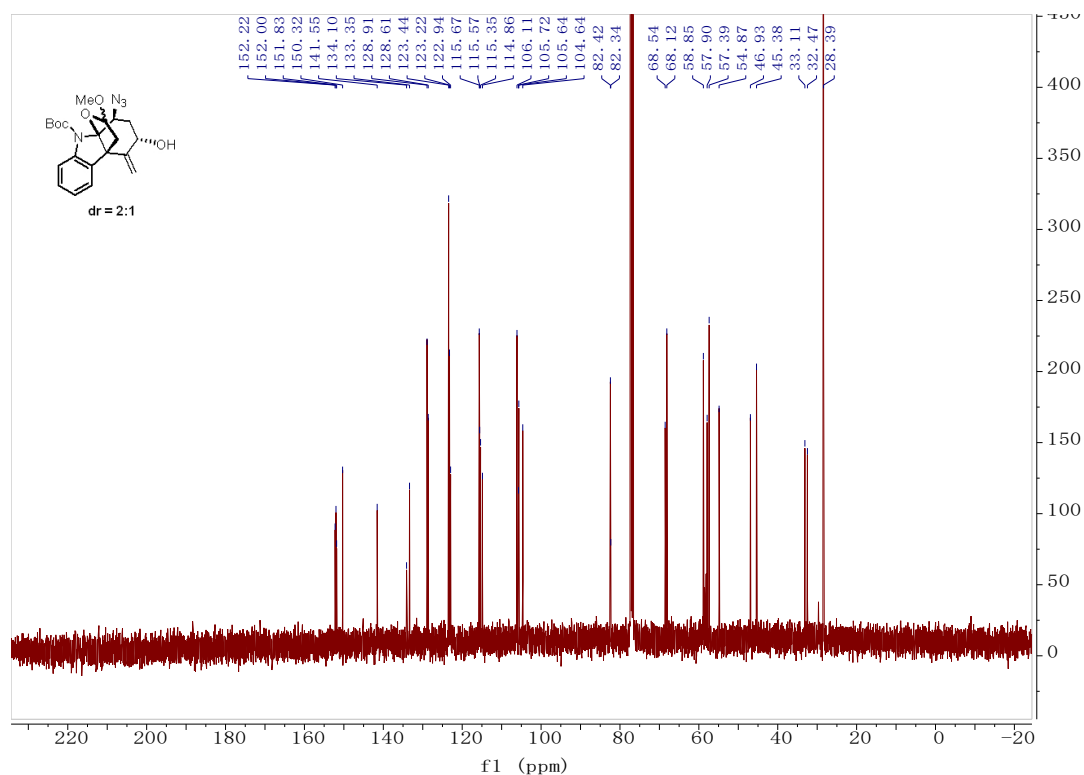
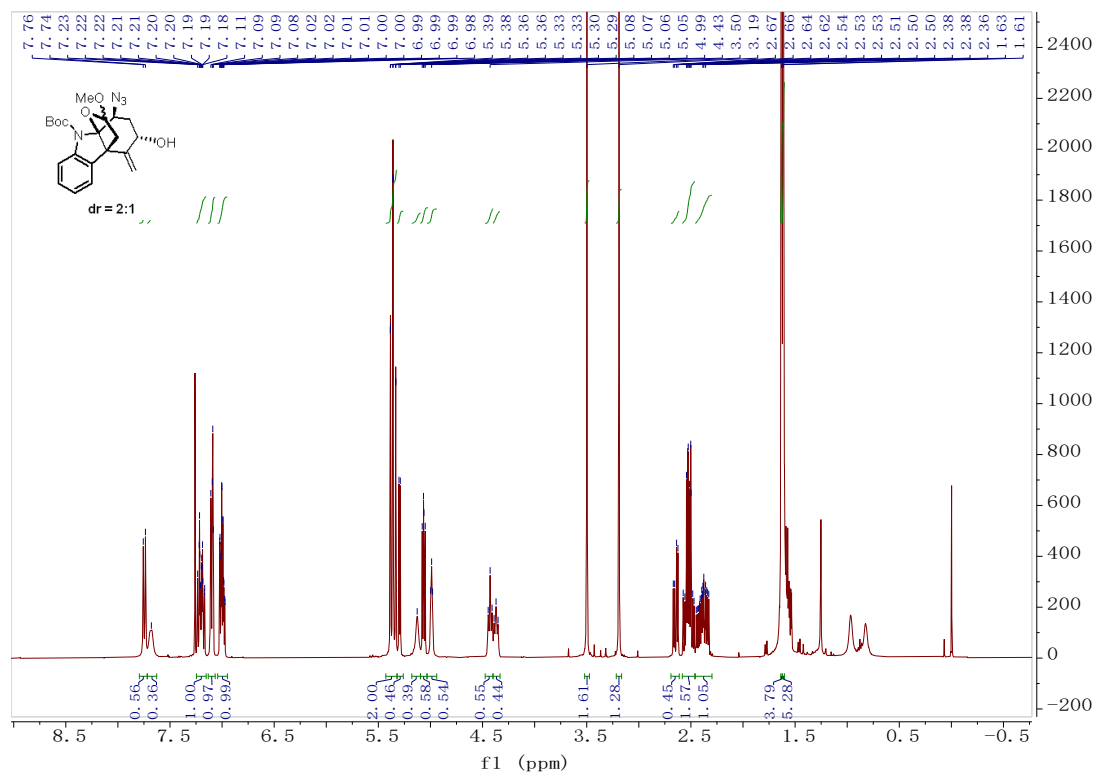
Compound 10



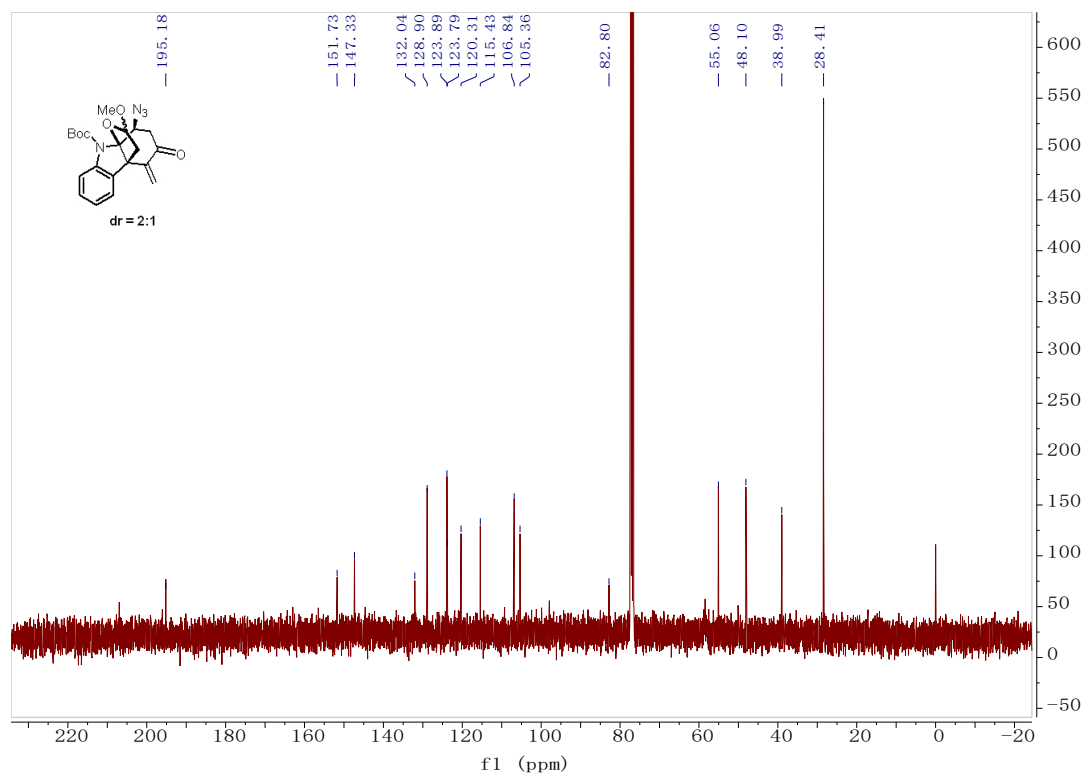
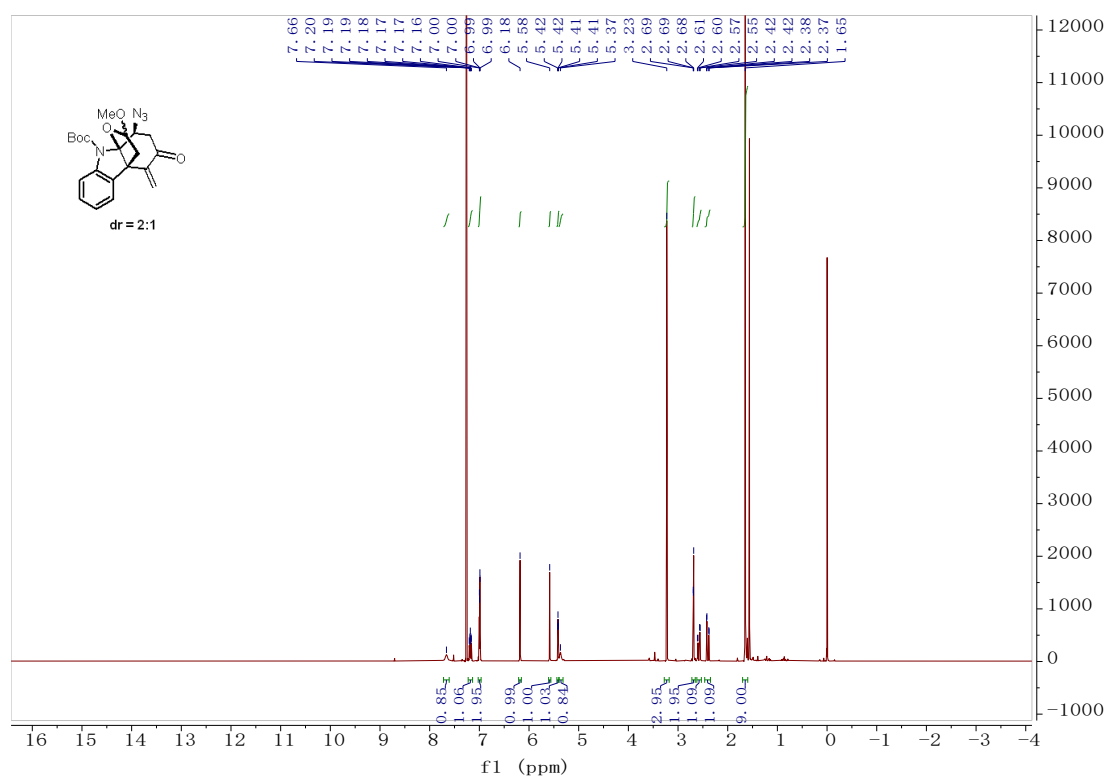
Compound 13

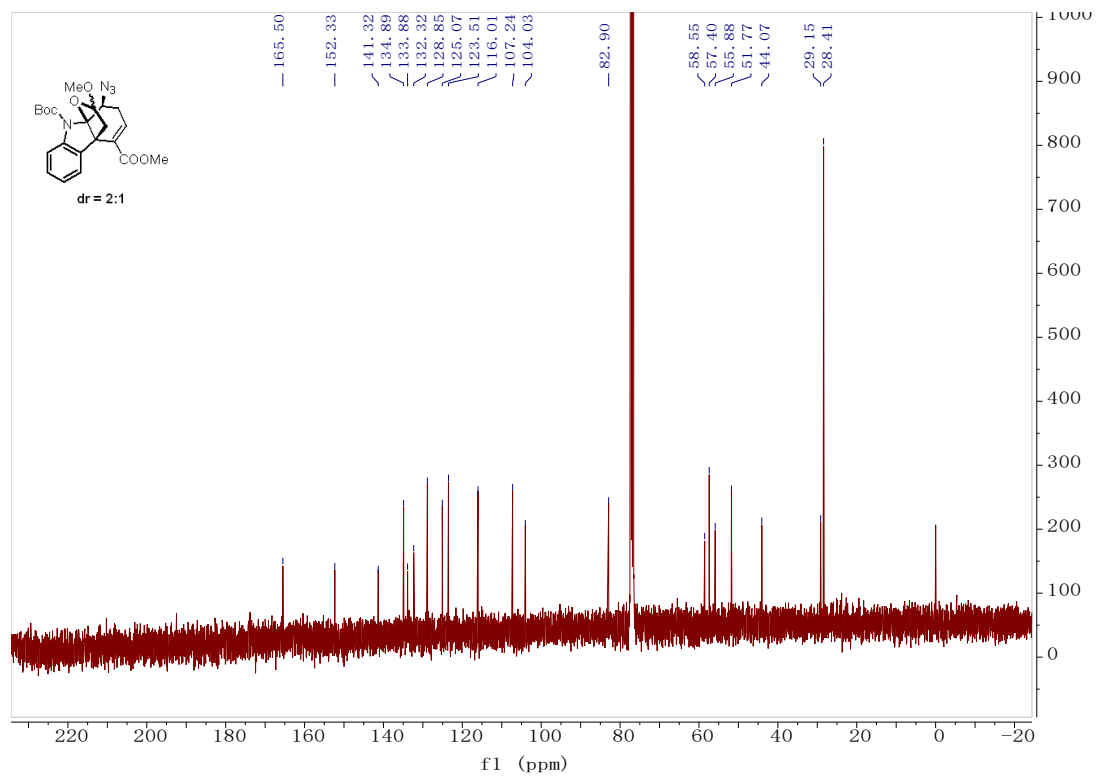
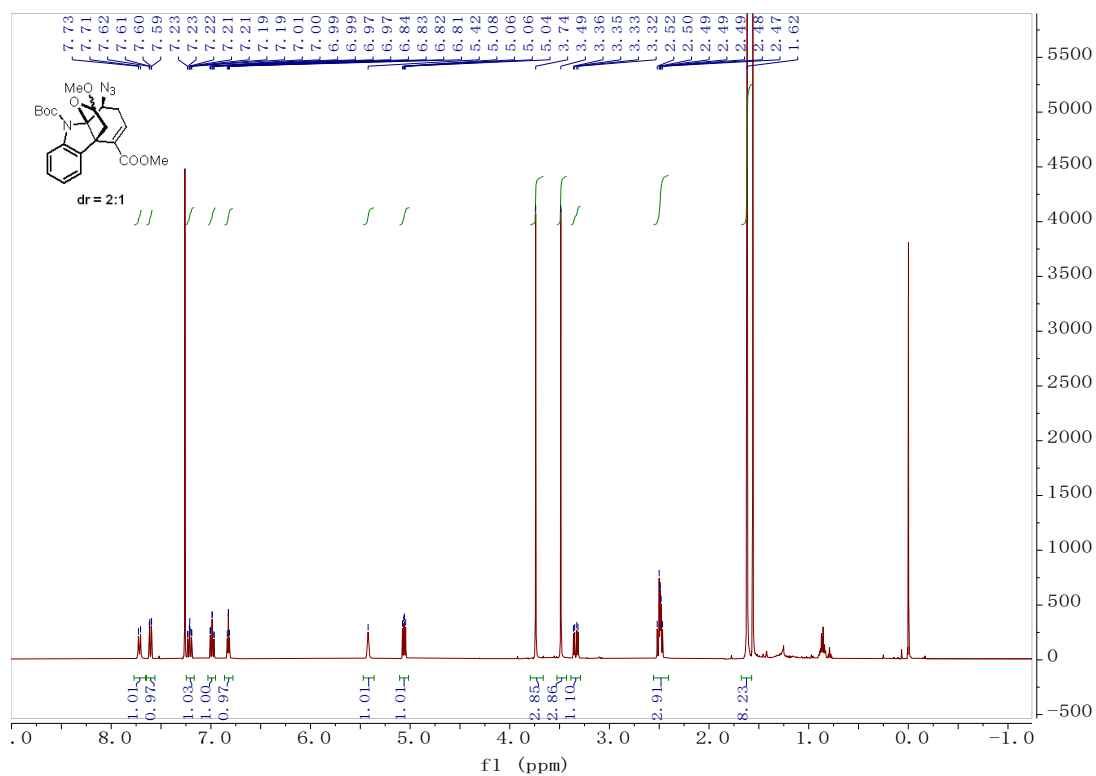


Compound 5

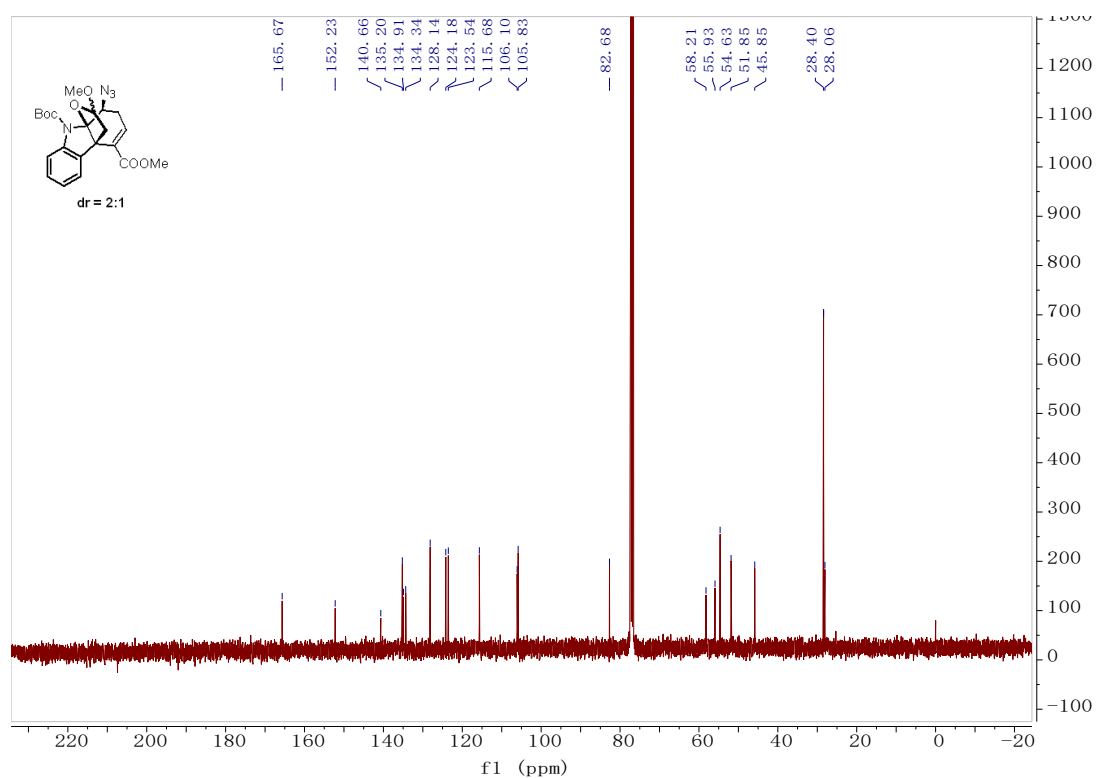
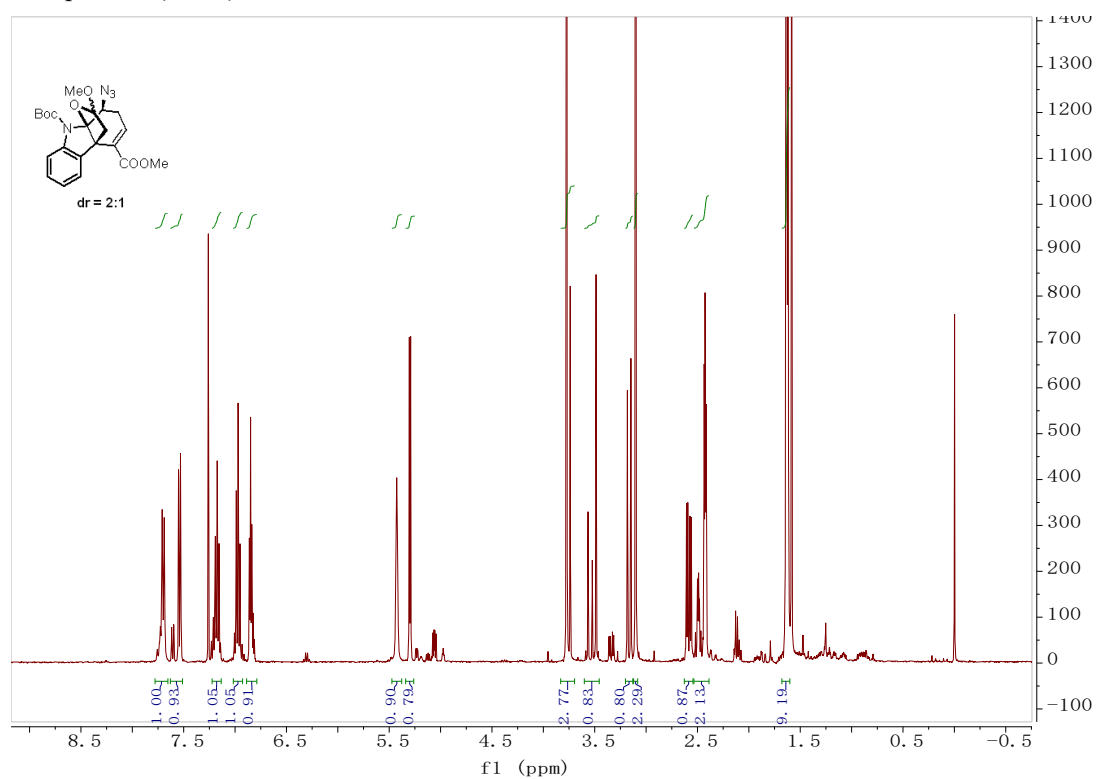


Compound 6

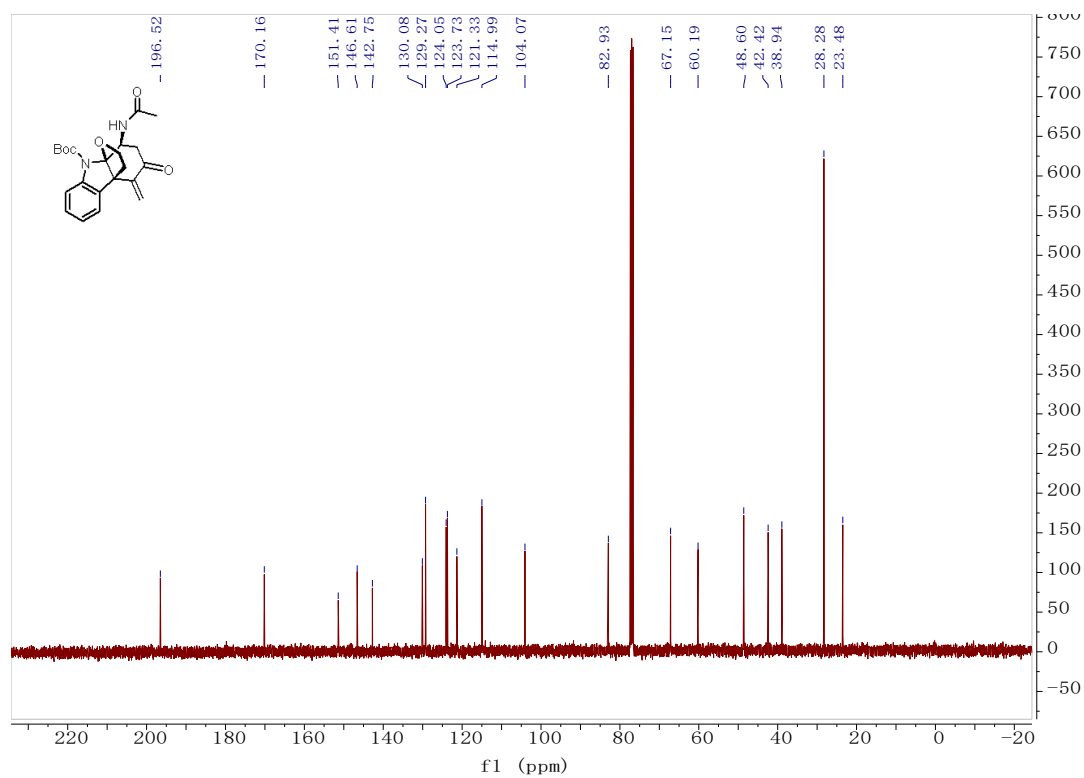
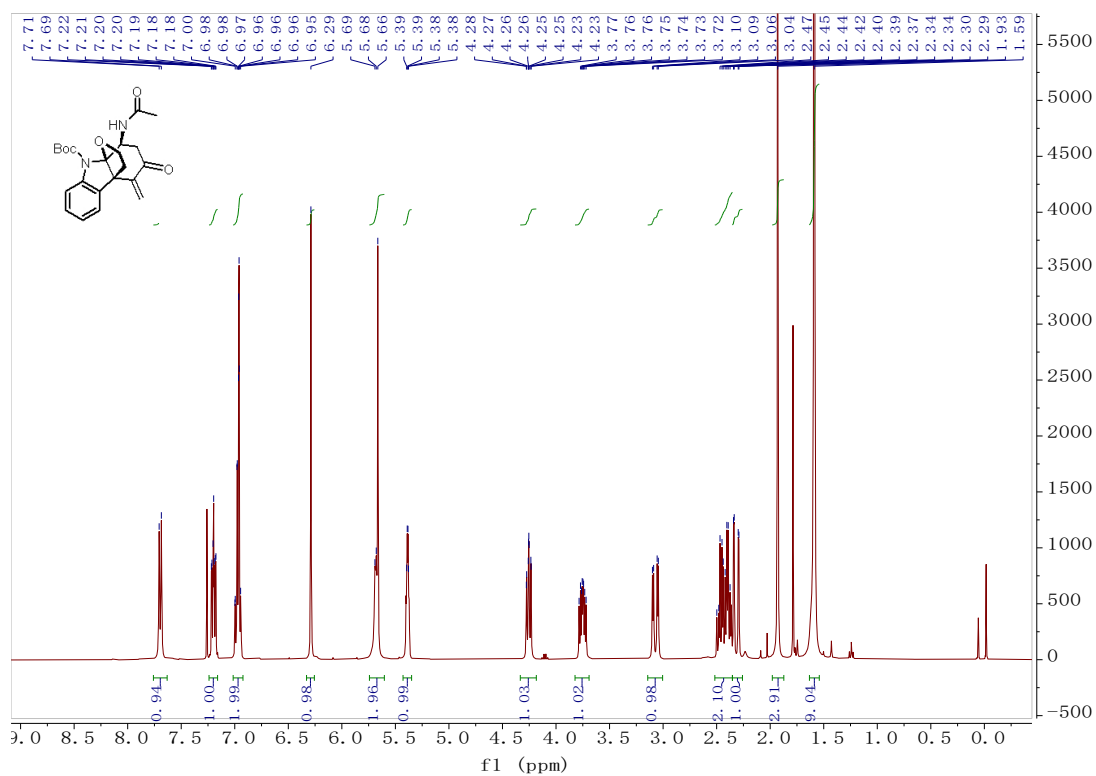


Compound **8** (up)

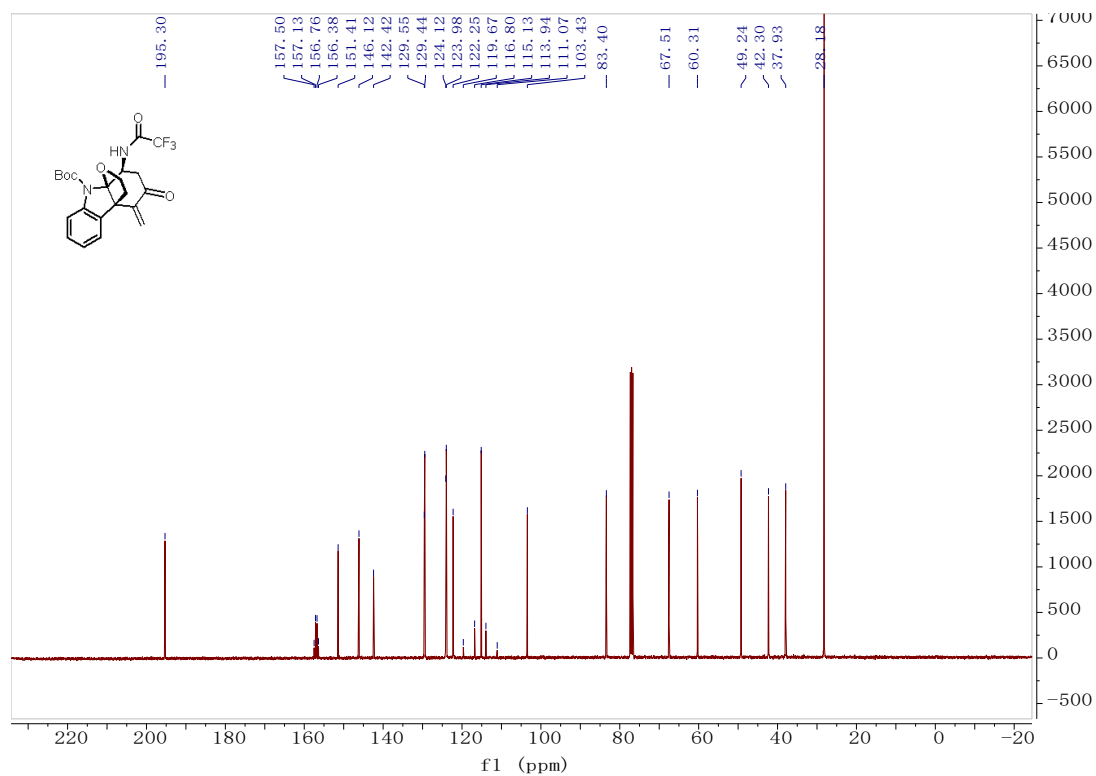
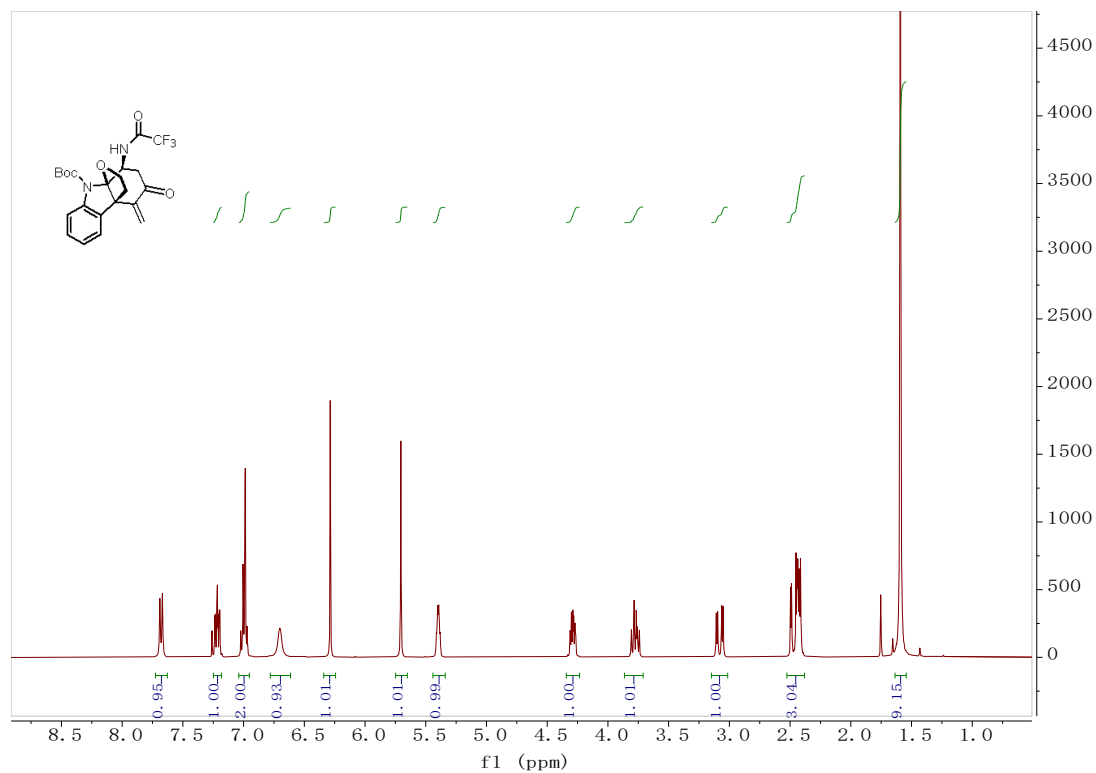
Compound 8(down)

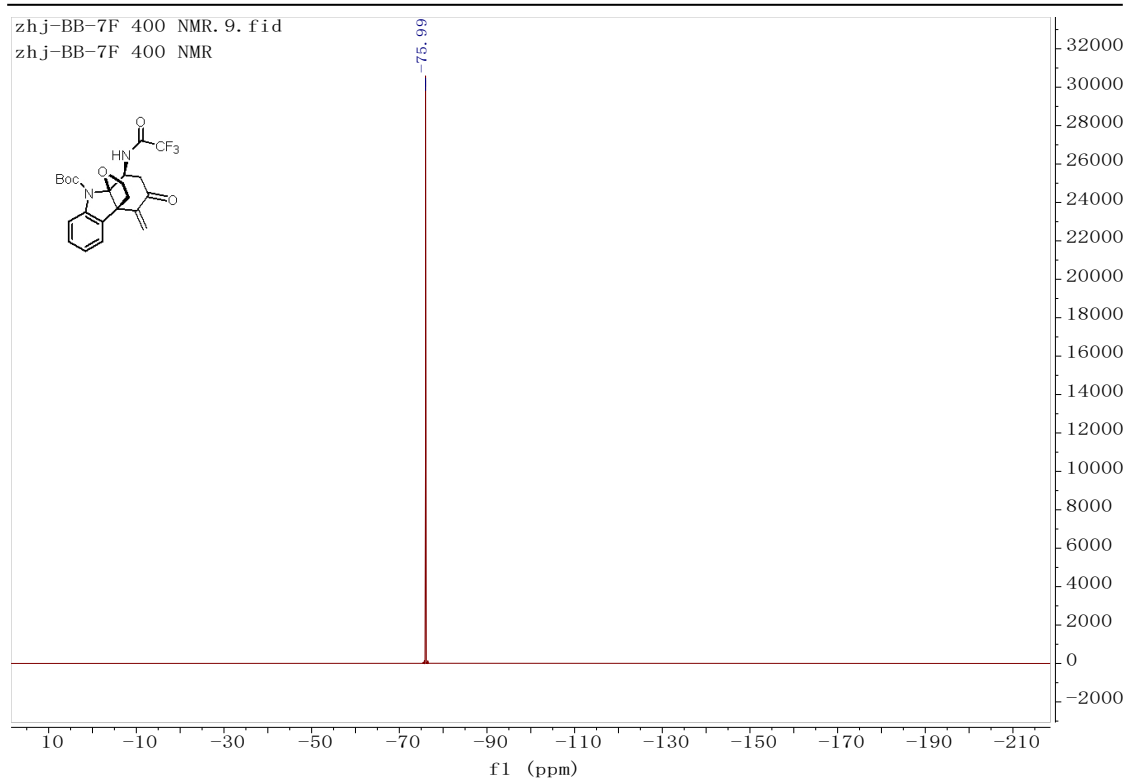


Compound 17a

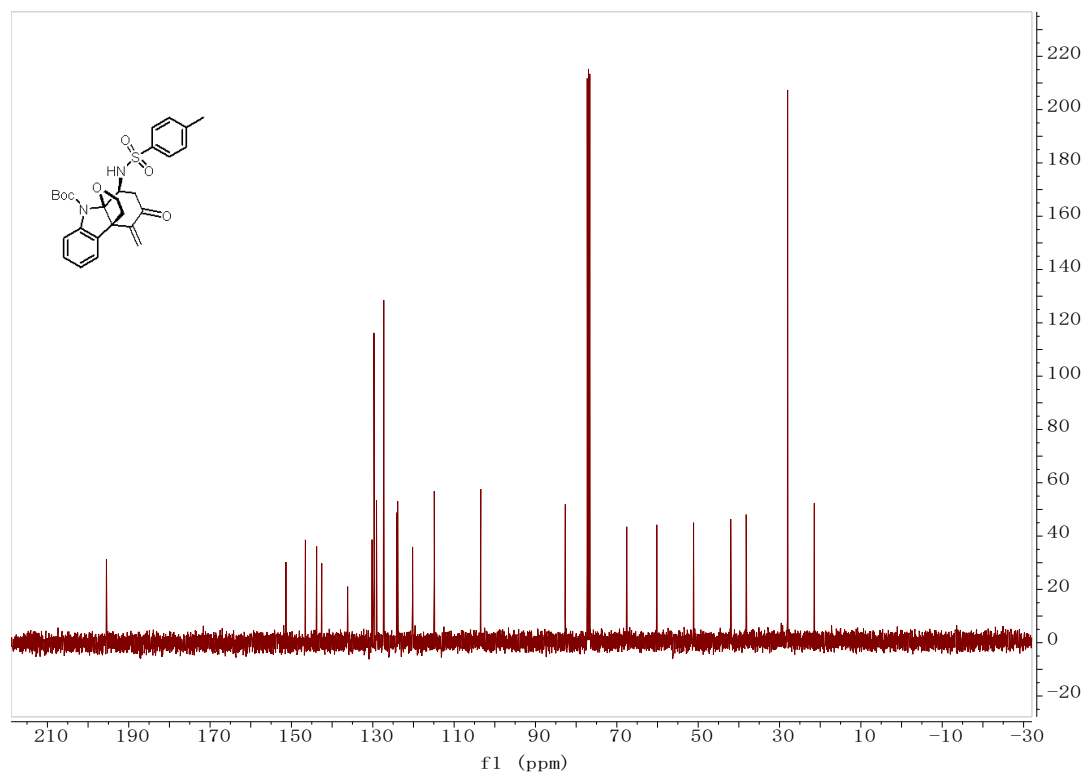
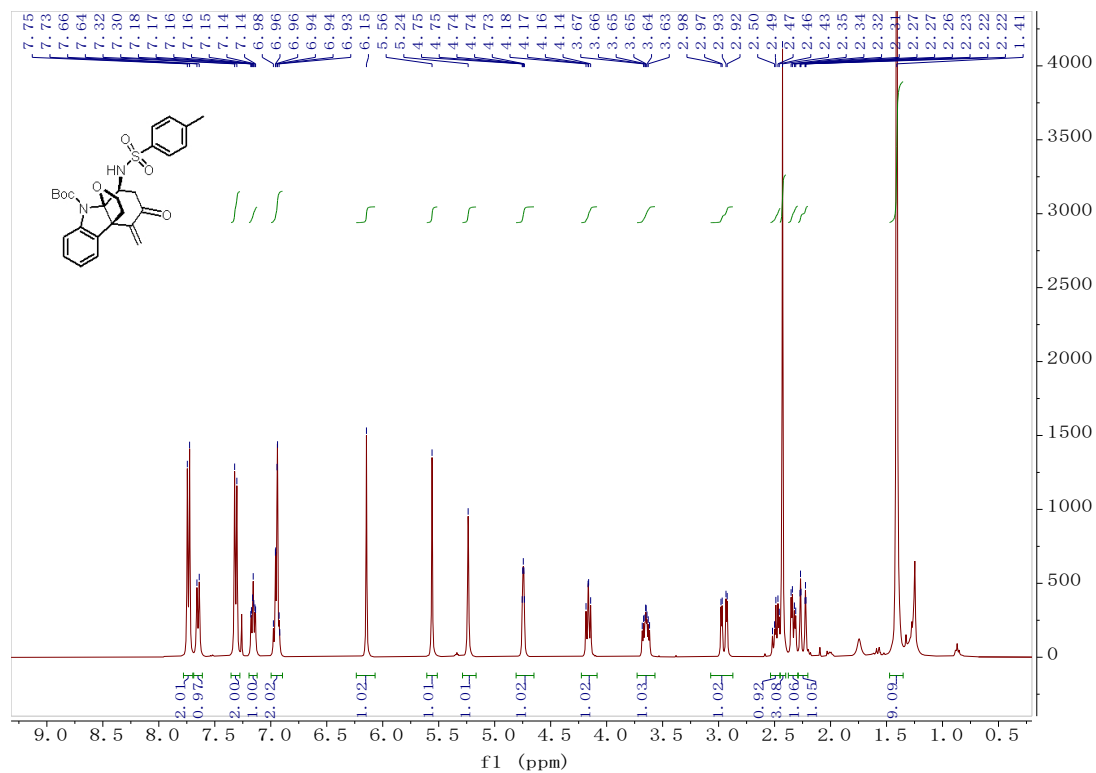


Compound 17b

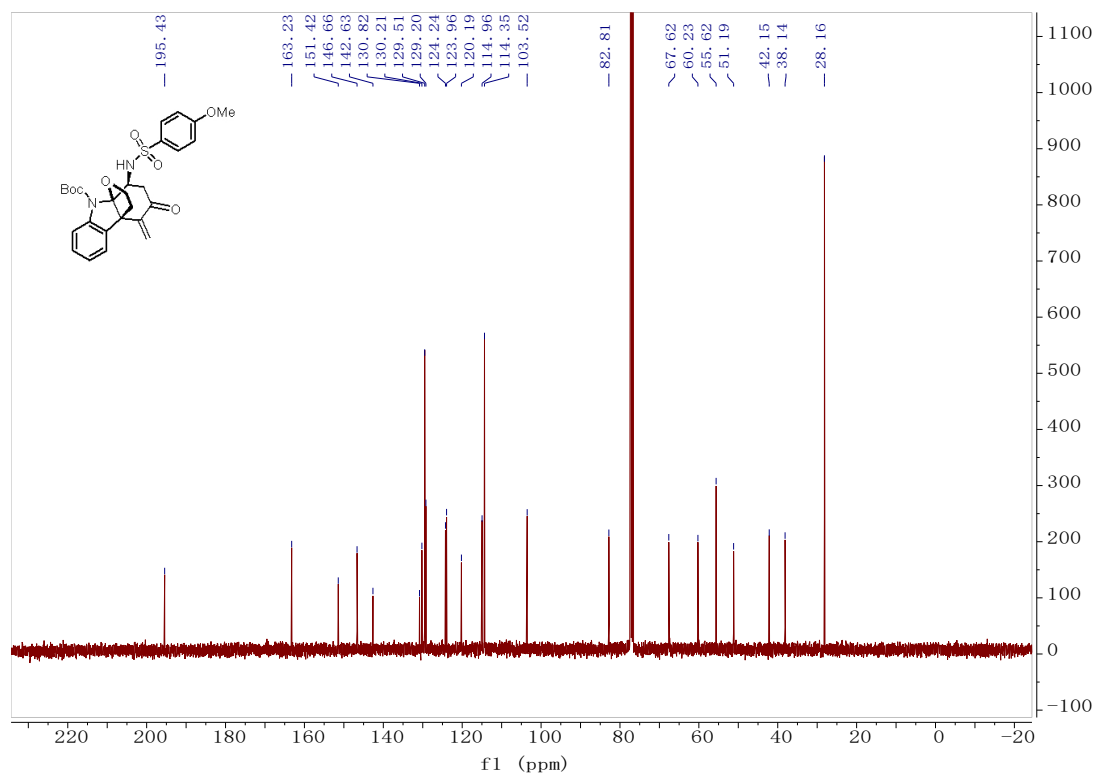
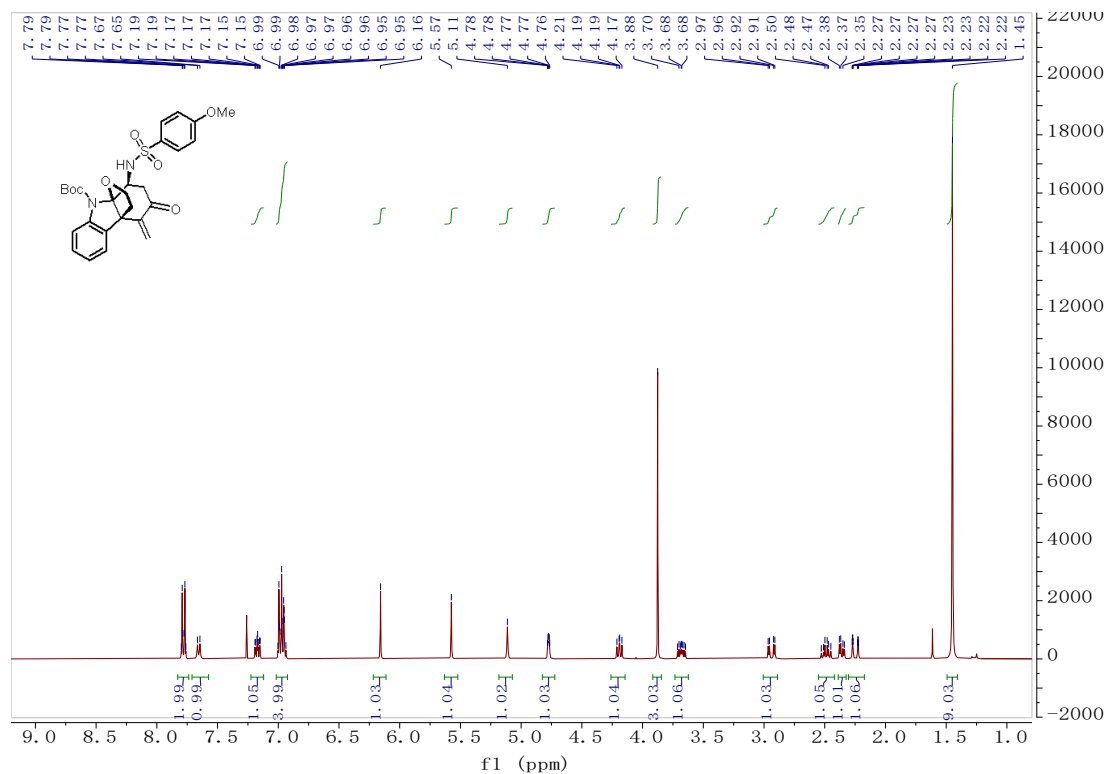




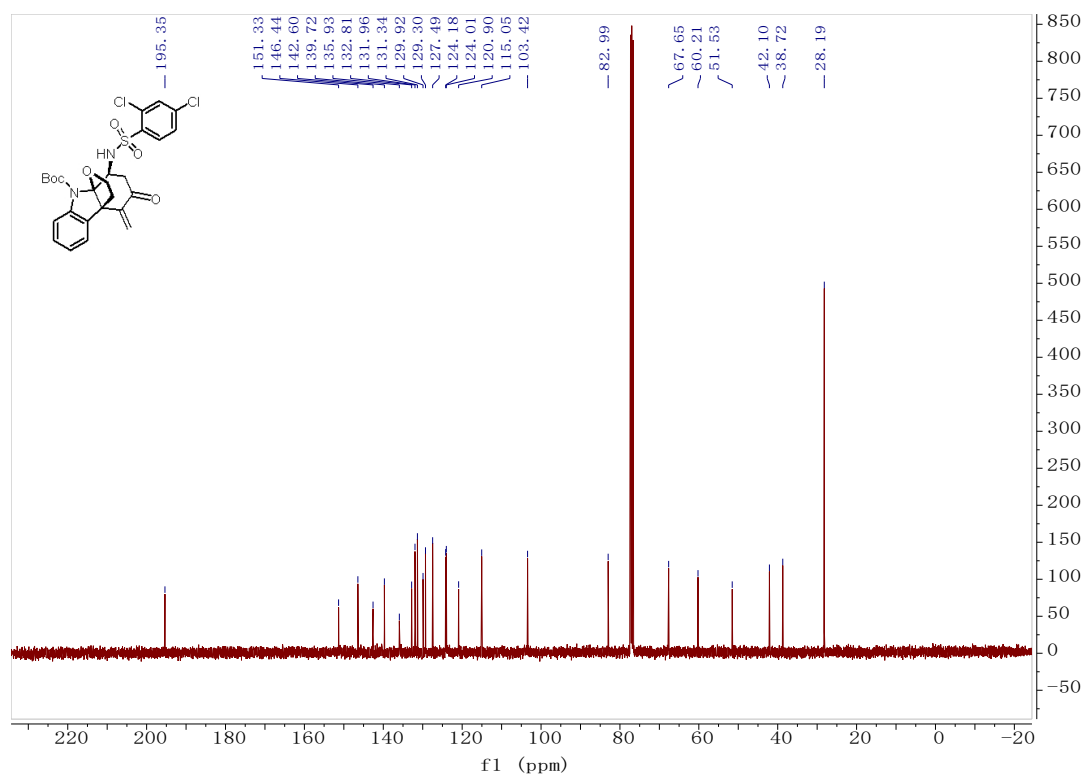
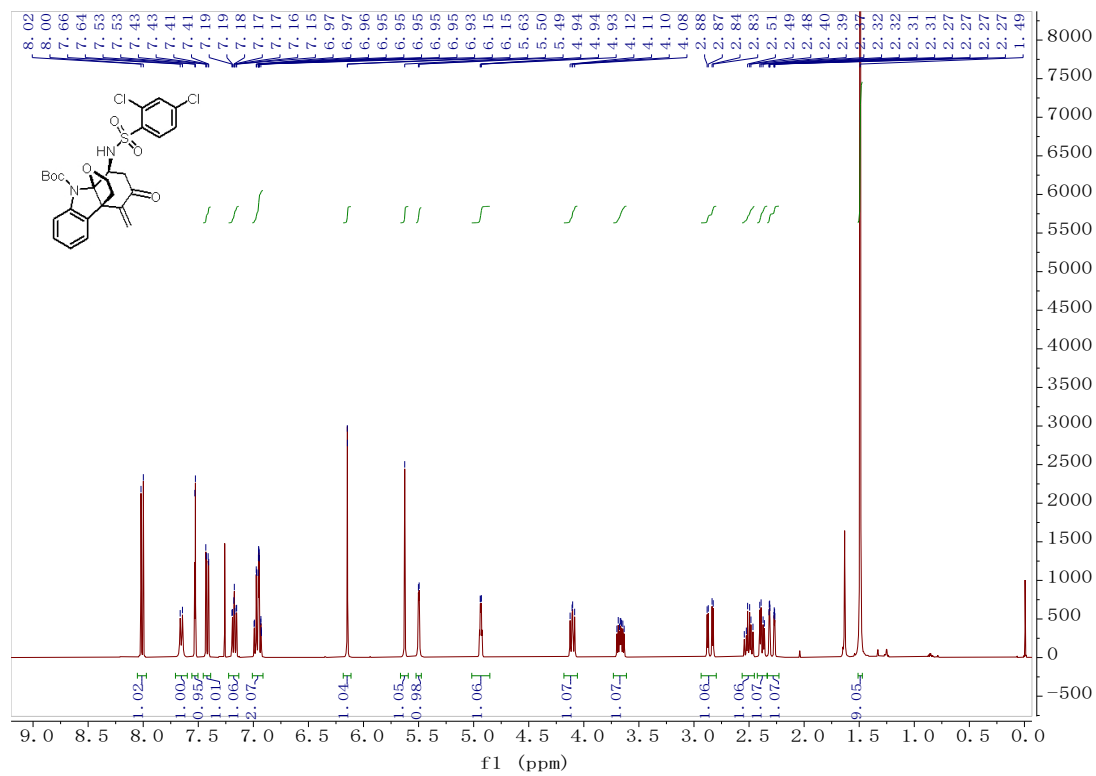
Compound 17c



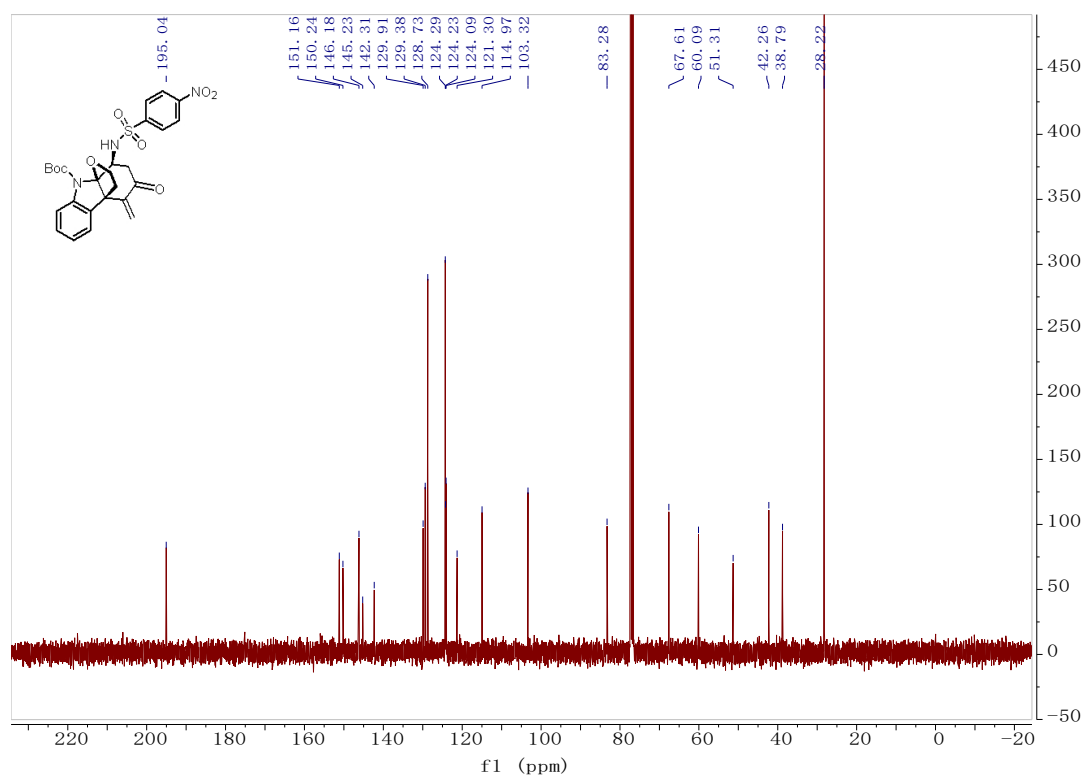
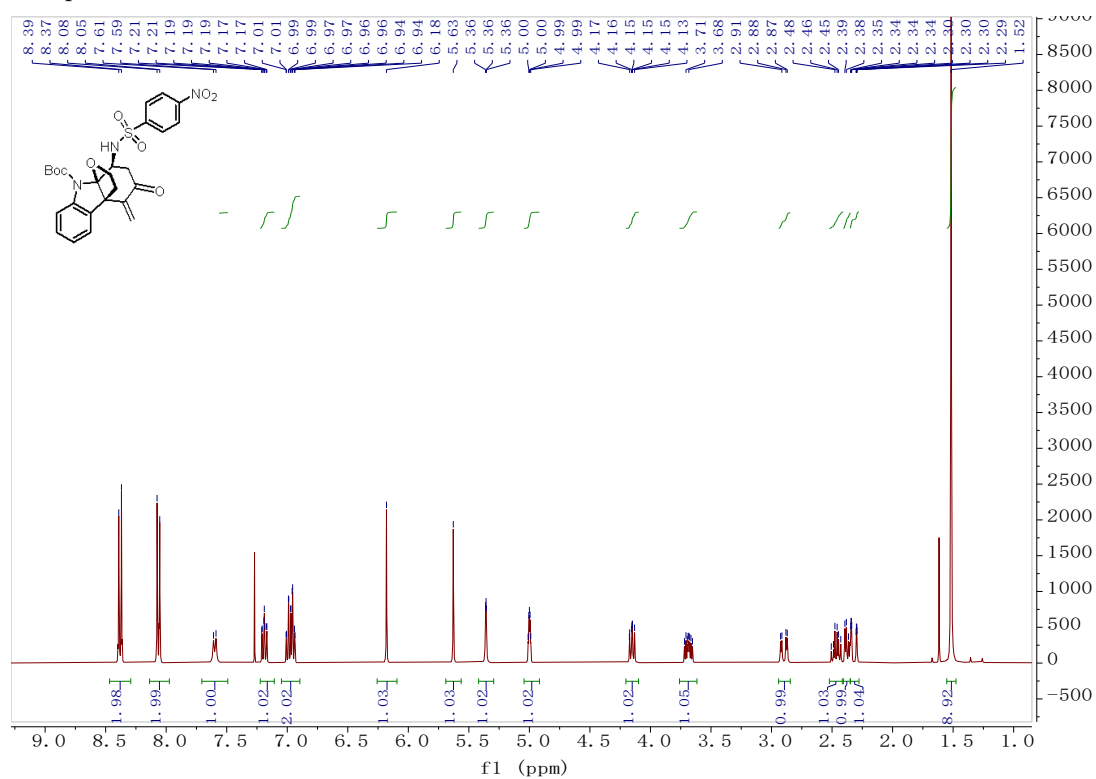
Compound 17d



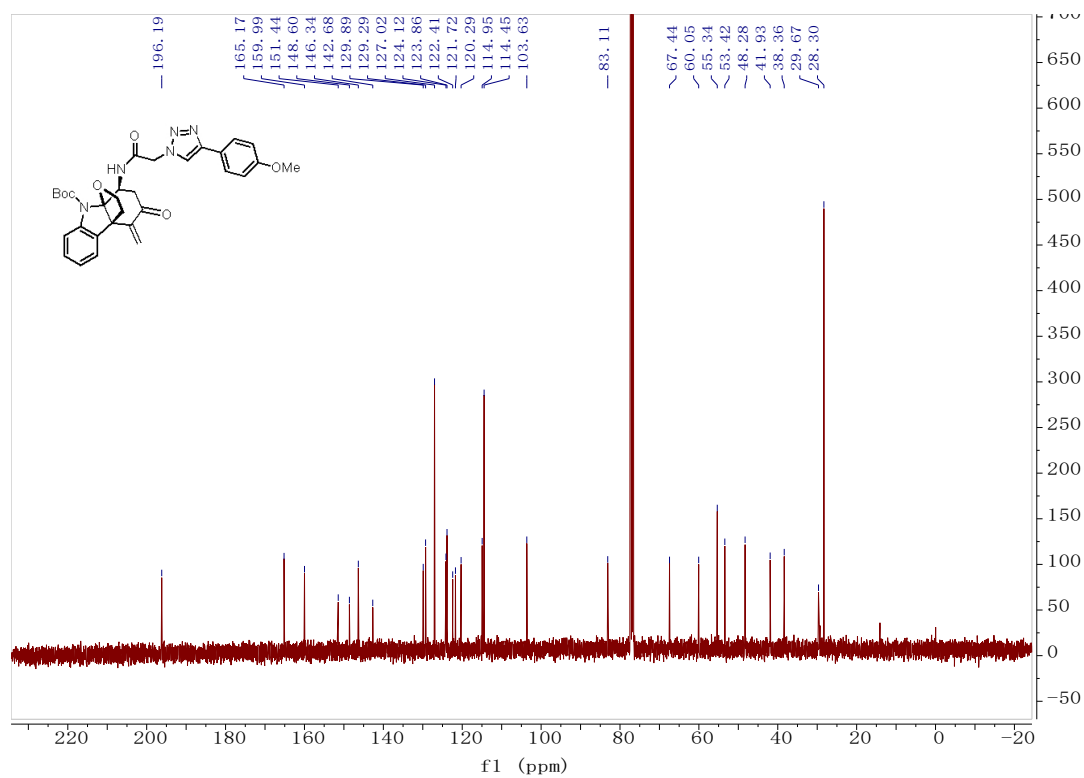
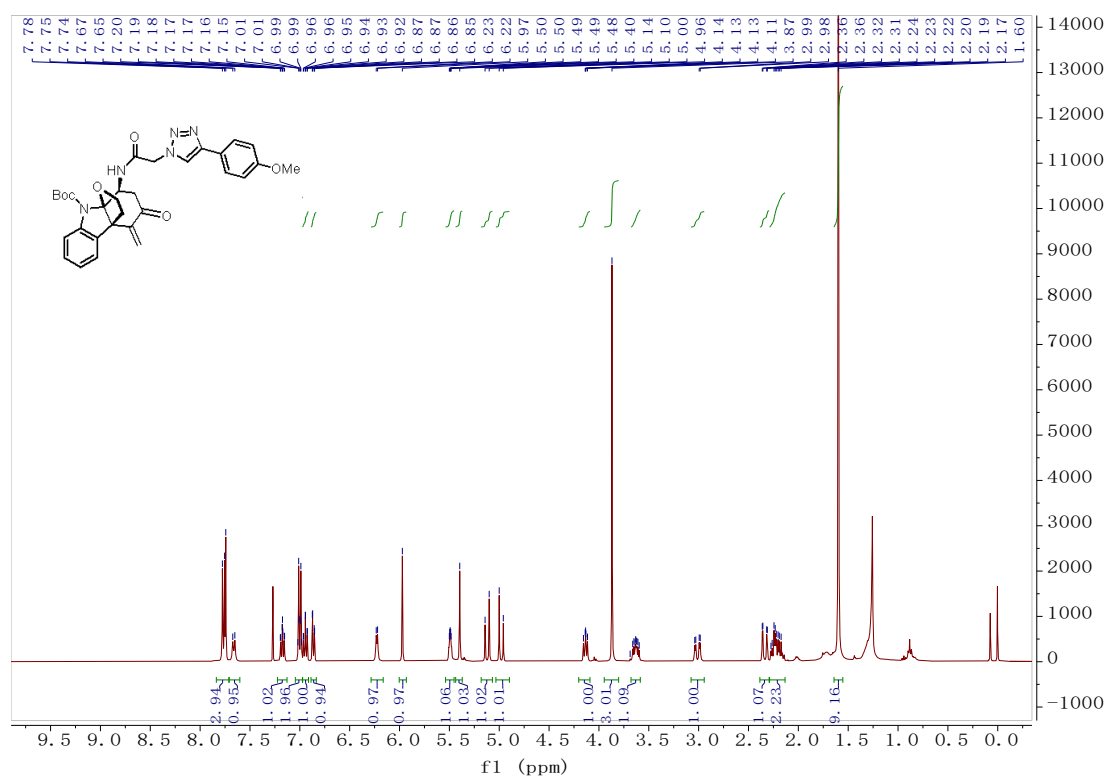
Compound 17e



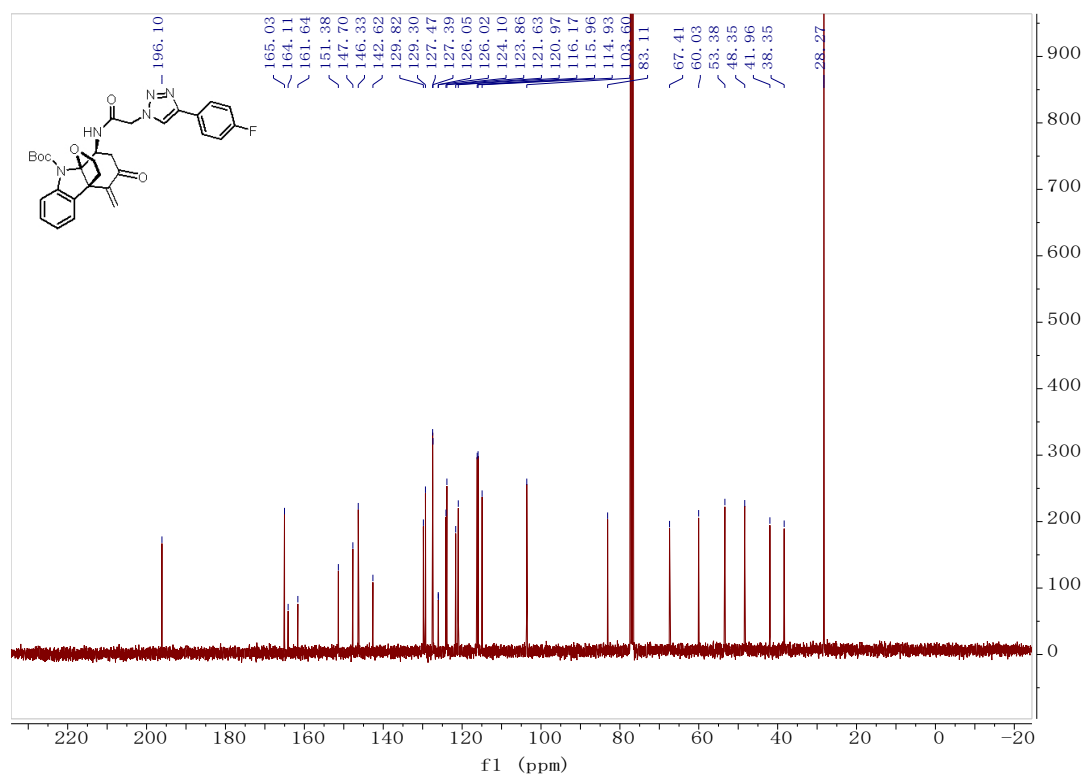
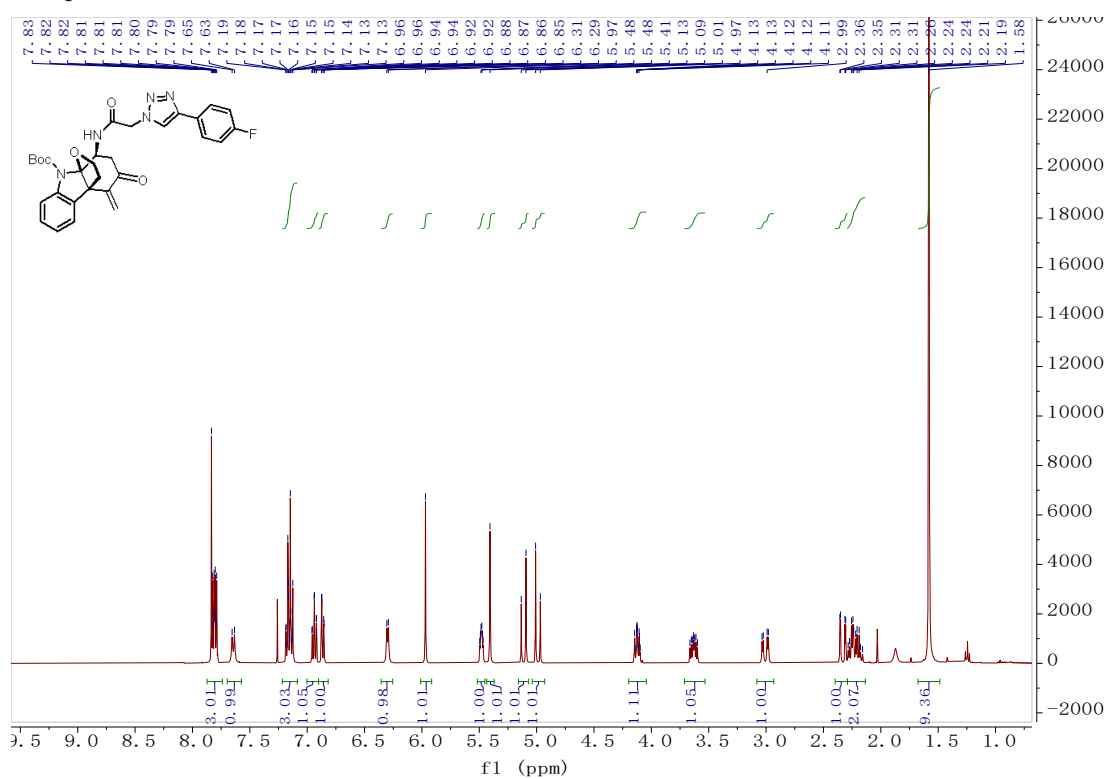
Compound 17f

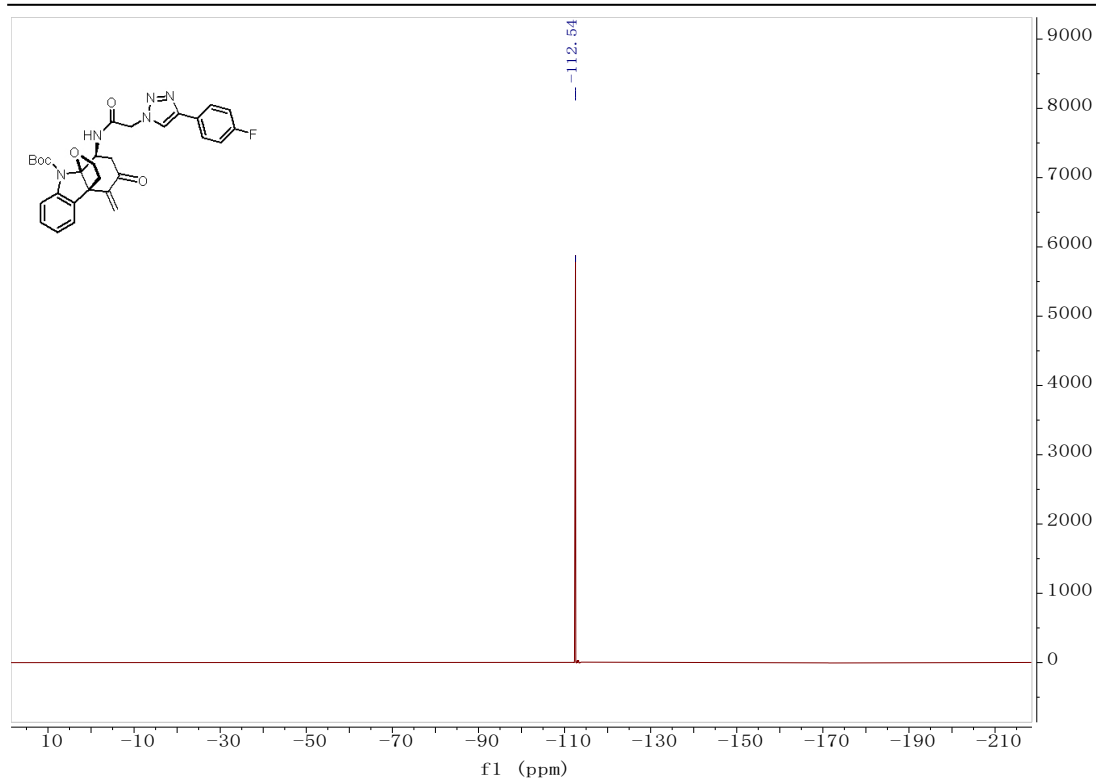


Compound 20a

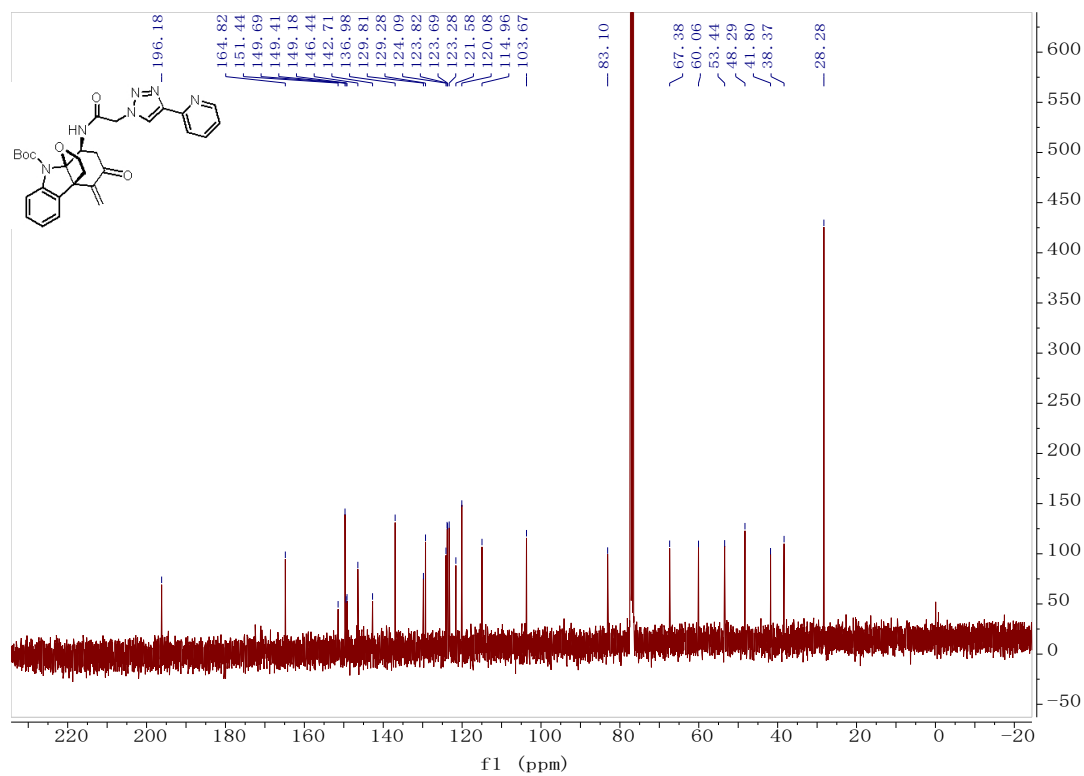
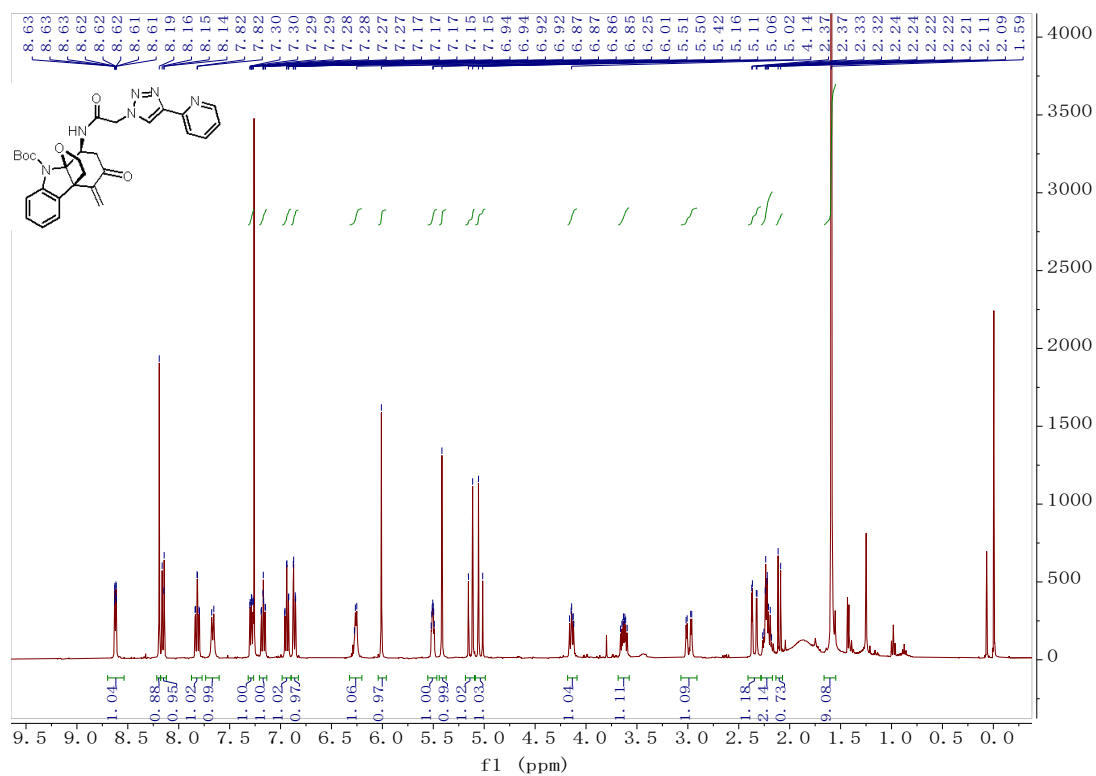


Compound 20b





Compound 20c



4. Details of Biological evaluation

MH7A cells were cultured in 10 cm² cell culture dishes with DMEM medium (Gibco, USA) containing 10% fetal bovine serum (Gibco, USA) at 37 °C in an incubator with CO₂ (5%). For cell viability detection, MH7A cells were collected and seeded in 96-well plates (5,000 cells per well) overnight. Then the adherent cells were stimulated with or without different dosages (2.5, 5, 10, and 20 μM) of compounds for 24 h. After treatment, cells were incubated with CCK-8 solution (10 μL/well) for 1 h. Finally, the absorbance of each well was tested through a microplate reader (450 nm; BioTek, USA). The viability rate of the control group was taken as 100%, and the 24 h-IC₅₀ of each compound in MH7A was calculated according to the viability rate.

5. Reference

1. T. Wang, X. Duan, H. Zhao, S. Zhai, C. Tao, H. Wang, Y. Li, B. Cheng and H. Zhai, *Org Lett*, 2017, **19**, 1650-1653.
2. P. Zou, H. Yang, J. Wei, T. Wang and H. Zhai, *Org Lett*, 2021, **23**, 6836-6840.