Electronic Supplementary Material (ESI) for Chemical Communications.

Discovery of a ^{19}F MRI sensitive salinomycin derivative with high cytotoxicity towards cancer cells

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Note added after first publication: This Supplementary Information file replaces that originally published on 21st March 2016, and contains additional information on the MTT assay of library compounds.

Table of contents

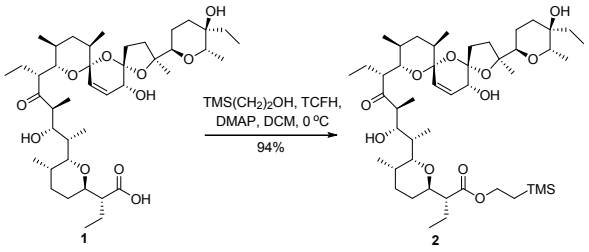
1. General information

^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on a 400 MHz. Chemical shifts are in ppm and coupling constants (*J*) are in Hertz (Hz). ^{1}H NMR spectra were referenced to tetramethylsilane (d, 0.00 ppm) using $CDCl_3$ as solvent. ^{13}C NMR spectra were referenced to solvent carbons (77.16 ppm for $CDCl_3$). ^{19}F NMR spectra were referenced to 2% perfluorobenzene (s, -164.90 ppm) in $CDCl_3$. The splitting patterns for ^{1}H NMR spectra are denoted as follows: s (singlet), d (doublet), q (quartet), m (multiplet).

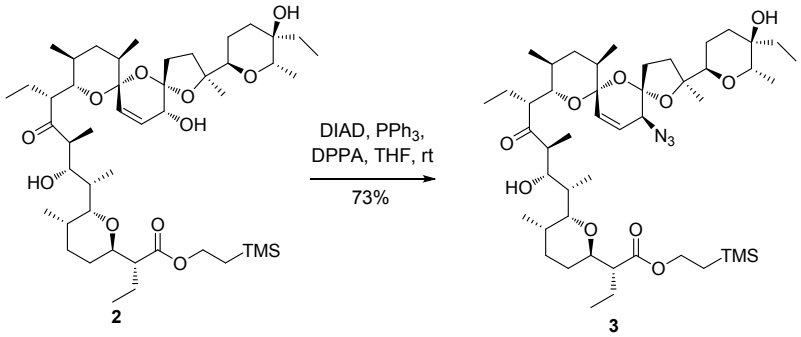
^{19}F MRI experiments were performed on a 9.4 T microimaging system with a 10 mm inner diameter ^{19}F coil (376.4 MHz) for both radiofrequency transmission and reception. The MSME (Multi Slice Multi Echo) pulse sequence was employed for all MRI acquisitions with single average. FOV = 8 x 8 mm^2, SI = 40.0 mm TR = 2500 ms and TE = 7.6 ms were used. The data collection time was 128 s. ^{19}F NMR relaxation experiments were carried out on a 376.4 MHz spectrometer at a ^{19}F concentration of 0.1 M.

Unless otherwise indicated, all reagents were obtained from commercial supplier and used without prior purification. DMF, Et_3N, MeOH and THF were dried and freshly distilled prior to use. Flash chromatography was performed on silica gel (200-300 mesh) with petroleum ether/ethyl acetate as eluents.

2. Synthesis of library compounds

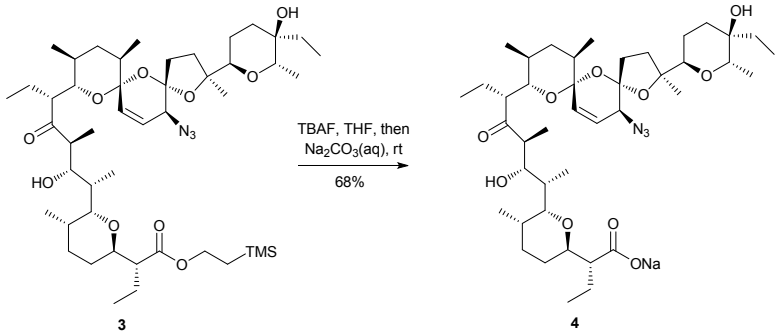


Preparation of compound 2. To a stirring solution of compound **1** (7.51 g, 10.00 mmol) in DCM (150 mL) was added DMAP (5.61 g, 50.00 mmol), TMSEtOH (7.10 g, 60.00 mmol) and *N*'-tetramethyl chloroformamidinium hexafluorophosphate (TCFH) (3.37 g, 12.00 mmol) at 0 °C. The resulting mixture was stirred at rt overnight. Then, it was diluted with EtOAc (150 mL) and washed with brine (3 × 150 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under vacuum to give a residue which was purified by flash chromatography on silica gel (5-33% petroleum ether/ethyl acetate) to give compound **2** as white amorphous solid (8.02 g, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (dd, *J* = 10.8 , 2.4 Hz, 1H), 5.98 (dd, *J* = 10.8, 0.8 Hz, 1H), 4.52-4.33 (m, 2H), 4.10-3.97 (m, 3H), 3.88-3.80 (m, 1H), 3.74-3.64 (m, 2H), 3.61-3.54 (m, 1H), 3.61-3.54 (m, 1H), 3.04-2.94 (m, 1H), 2.77-2.67 (m, 1H), 2.45-2.32 (m, 1H), 2.28-2.16 (m, 1H), 2.08-0.64 (m, 57H), 0.08 (s, 9H).



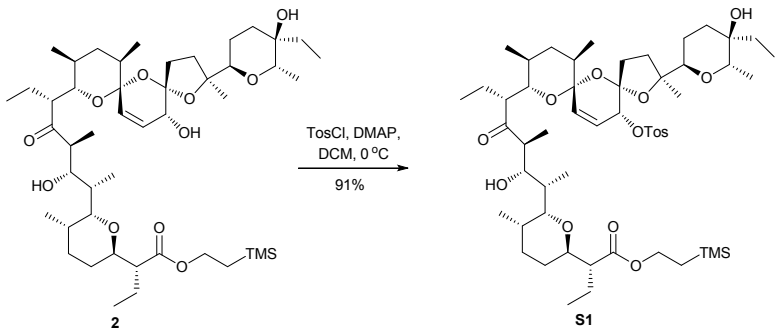
Preparation of compound 3. Under an atmosphere of argon, to a stirring solution of triphenylphosphine (9.35 g, 35.66 mmol) in anhydrous THF (200 mL) was added diisopropyl azodicarboxylate (7.21 g, 35.66 mmol, in 20 mL THF) at 0 °C. After the resulting solution was stirred for 10 min at this temperature, compound **2** (15.18 g, 17.83 mmol, in 30 mL THF) was added. The mixture was allowed to warm to rt and stirred for another 10 min. Then diphenylphosphoryl azide (9.81 g, 35.66 mmol, in 40 mL THF) was added and the resulting mixture was stirred at rt overnight. The solution was concentrated under vacuum to give a residue which was purified by flash chromatography on silica gel (0-33% petroleum ether/ethyl acetate) to give compound **3** as white amorphous solid (11.47 g, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.52-6.41 (m, 1H), 6.14 (dd, *J* = 10.4, 5.2 Hz, 1H), 4.55-

4.31 (m, 2H), 4.09-3.99 (m, 2H), 3.93-3.86 (m, 1H), 3.83-3.74 (m, 1H), 3.73-3.64 (m, 1H), 3.62-3.50 (m, 1H),3.47-3.40 (m, 1H), 3.17-3.06 (m, 2H), 3.04-2.94 (m, 1H), 2.72-2.67 (m, 1H), 2.23-0.62 (m, 57H), 0.08 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.9, 175.8, 128.0, 124.2, 107.0, 98.7, 88.5, 80.6, 75.1, 73.6, 71.8, 71.0, 69.1, 63.6, 57.9, 56.8, 48.8, 47.8, 39.5, 39.2, 36.9, 36.5, 33.1, 32.0, 30.6, 29.4, 28.2, 26.4, 24.9, 22.7, 21.8, 20.6, 19.8, 17.6, 17.5, 16.3, 14.5, 13.9, 13.1, 11.9, 11.1, 7.4, 6.6, -1.4. IR (KBr): 3414, 2960, 2930, 2875, 2099, 1715, 1248, 1089 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{81}N_3NaO_{10}Si^+$ ([M+Na]$^+$), 898.5583; found, 898.5589.

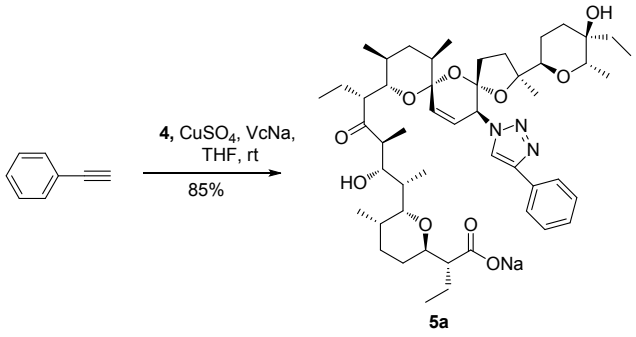


3 4

Preparation of compound 4. To a stirring solution of compound **3** (3.00 g, 3.42 mmol) in THF (30 mL) at rt was added TBAF (3.24 g, 10.26 mmol, in 5 mL THF). The resulting mixture was stirred at rt and monitored by TLC. The solution was concentrated under vacuum to give a residue which was diluted with EtOAc (40 mL) and washed with Na_2CO_3 (3 × 50 mL, 0.10 M aqueous solution). The organic layer was collected, dried over anhydrous Na_2SO_4 and concentrated under vacuum to give a residue which was purified by flash chromatography on silica gel (10-100% petroleum ether/ethyl acetate) to give compound **4** as white amorphous solid (1.86 g, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.53-6.35 (m, 1H), 6.35-6.15 (m, 1H), 5.23-4.83 (m, 1H), 4.45-4.27 (m, 1H), 4.26-4.11 (m, 1H), 4.03-3.83 (m, 3H), 3.76-3.50 (m, 3H), 3.43-3.32 (m, 1H), 2.92-2.79 (m, 1H), 2.76-2.54 (m, 3H), 2.16-0.60 (m, 52H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 217.0, 184.4, 127.9, 122.6, 106.6, 98.9, 89.6, 75.8, 75.6, 75.2, 74.2, 71.4, 70.0, 67.3, 56.2, 55.3, 51.1, 50.1, 39.9, 38.8, 37.1, 35.9, 32.8, 32.3, 28.7, 27.9, 27.7, 26.8, 23.9, 21.0, 19.9, 17.4, 16.3, 15.9, 14.6, 13.1, 12.5, 11.8, 10.6, 6.6, 6.4. IR (KBr): 3491, 2963, 2876, 2101, 1712, 1565, 1386, 1247, 1111 cm^{-1}. HRMS (ESI) calcd for $C_{42}H_{69}N_3NaO_{10}^+$ ([M+H]$^+$), 798.4875; found, 798.4860.

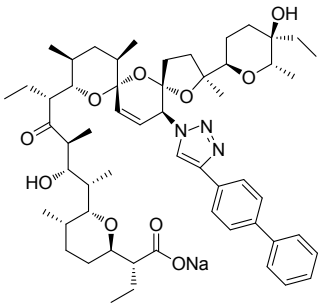


Preparation of compound S1. At 0 °C, to a stirring solution of compound **2** (1.70 g, 2.00 mmoL) and DMAP (1.95 g, 16.00 mmol) in DCM (15 mL) was added 4-toluene-sulfonyl chloride (2.29 g, 12.00 mmoL, in 10 mL DCM) over 1 hour. The resulting mixture was stirred at rt overnight. The solution was concentrated under vacuum to give a residue which was purified by flash chromatography on silica gel (5-60% petroleum ether/ethyl acetate) to give compound **S1** as white amorphous solid (1.80 g, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 6.17 (dd, *J* = 10.9, 2.3 Hz, 1H), 5.72 (m, 1H), 4.95 (s, 1H), 4.54-4.28 (m, 2H), 4.12-3.96 (m, 2H), 3.74-3.62 (m, 2H), 3.50-3.43 (m, 1H), 3.38-3.30 (m, 1H), 3.23-3.12 (m, 1H), 3.05-2.94 (m, 1H), 2.84-2.70 (m, 3H), 2.46 (s, 3H), 2.35-0.63 (m, 56 H), 0.07 (s, 9H). ^{13}C NMR (100 MHz, $CO(CD_3)_2$) δ 214.6, 177.2, 147.2, 136.0, 132.0, 129.6, 128.2, 126.7, 105.8, 100.8, 89.1, 82.0, 80.3, 78.8, 76.5, 75.7, 73.2, 72.9, 72.0, 70.7, 64.9, 59.0, 50.6, 49.2, 42.1, 40.7, 38.3, 36.1, 35.0, 34.6, 32.8, 29.9, 28.0, 24.4, 23.8, 22.9, 22.4, 22.3, 21.4, 19.1, 19.0, 17.1, 16.1, 15.5, 14.5, 13.4, 12.6, 8.8, 8.1, 0.0. HRMS (ESI) calcd for $C_{54}H_{92}NO_{13}SSi^+$ ($[M+NH_4]^+$), 1022.6053; found, 1022.6053.



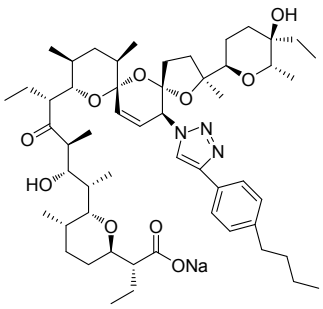
General procedure for the CuAAC reaction (Using the synthesis of **5a** as an example). Under an atmosphere of argon, to a stirring solution of compound **4** (0.12 g, 0.15 mmol) in THF (2 mL) was added phenylacetylene (0.031 g, 0.30 mmol, in 1mL THF) at rt, flowed by $CuSO_4$ (0.12 g, 0.75 mmol, 1.00 M aqueous solution) and sodium ascorbate (0.30 g, 1.50 mmol, 1.00 M aqueous solution). The resulting mixture was stirred at rt overnight. The resulting mixture was filtered, diluted with EtOAc (15 mL) and washed with brine (3 × 10 mL). The organic

layer was collected, dried over anhydrous Na_2SO_4 and concentrated under vacuum to give a residue which was purified by flash chromatography on silica gel (10-100% petroleum ether/ethyl acetate) to give compound **5a** as white amorphous solid (0.12 g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.81 (d, *J* = 7.6 Hz, 2H), 7.45-7.35 (m, 2H), 7.34-7.28 (m, 1H), 6.66-6.44 (m, 1H), 6.39-6.15 (m, 1H), 5.54-5.41 (m, 1H), 4.39-4.08 (m, 2H), 4.05-3.74 (m, 3H), 3.62-3.42 (m, 2H), 2.87-2.56 (m, 3H), 2.11-0.60 (m, 55H).7.96 (s, 1H), 7.81 (d, *J* = 7.6 Hz ,2H), 7.45-7.35 (m, 2H), 7.34-7.28 (m, 1H), 6.66-6.44 (m, 1H), 6.39-6.15 (m, 1H), 5.54-5.41 (m, 1H), 4.39-4.08 (m, 2H), 4.05-3.74 (m, 3H), 3.62-3.42 (m, 2H), 2.87-2.56 (m, 3H), 2.11-0.60 (m, 55H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.6, 178.2, 147.0, 130.8, 128.8, 128.0, 127.6, 125.8, 125.6, 120.7, 108.6, 98.7, 89.0, 76.5, 76.2, 74.9, 73.6, 71.6, 71.4, 67.9, 58.8, 55.2, 49.4, 48.8, 39.7, 38.4, 36.5, 35.7, 32.6, 32.0, 29.7, 27.9, 26.2, 25.4, 22.7, 21.8, 19.8, 17.8, 16.7, 16.1, 14.3, 13.2, 12.0, 10.9, 6.9, 6.5. IR (KBr): 3427, 2964, 2933, 2876, 1713, 1566, 1231, 1112, 768, 697 cm^{-1}. HRMS (ESI) calcd for $C_{50}H_{76}N_3O_{10}^+$ ([M+H]$^+$), 878.5525; found, 878.5502.



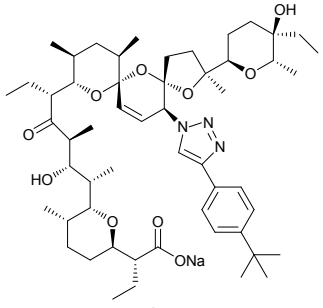
5b

Compound 5b was prepared from compound **4** and (1,1'-biphenyl-4-yl)acetylene by following the general procedure for the CuAAC reaction with a 90% yield as white amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.94-7.84 (m, 2H), 7.68-7.59 (m, 4H), 7.49-7.41 (m. 2H), 7.39-7.32 (m, 1H), 6.76-6.50 (m, 1H), 6.47-6.18 (m. 1H), 5.60-5.44 (m, 1H), 4.38-4.11 (m, 2H), 4.01-3.77 (m, 3H), 3.63-3.44 (m, 2H), 2.89-2.54 (m, 3H), 2.12-0.57 (m, 55H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.6, 178.3, 146.8, 140.7, 129.8, 128.9, 127.8, 127.5, 127.0, 126.0, 125.9, 120.9, 110.1, 108.7, 98.8, 89.1, 76.6, 76.2, 75.0, 73.8, 71.7, 71.6, 67.9, 59.0, 55.2, 49.5, 48.8, 39.7, 38.4, 36.6, 35.8, 32.7, 32.2, 29.9, 28.0, 26.2, 25.6, 22.8, 21.9, 19.8, 17.8, 16.8, 16.1, 14.3, 13.4, 13.3, 12.1, 11.0, 7.0, 6.6. IR (KBr): 3403, 2963, 2934, 2876, 1714, 1564, 1405, 1115, 800, 766, 699 cm^{-1}. HRMS (ESI) calcd for $C_{56}H_{80}N_3O_{10}^+$ ([M+H]$^+$), 954.5838; found, 954.5834.



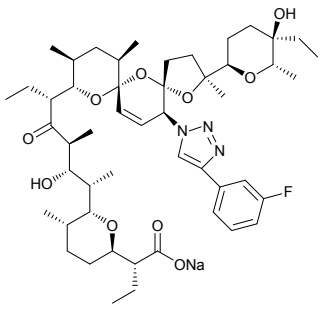
5c

Compound 5c was prepared from compound **4** and (*p*-butylphenyl)acetylene by following the general procedure for the CuAAC reaction with a 71% yield as white amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.54 (dd, *J* = 10.4, 1.6 Hz, 1H), 6.30 (dd, *J* = 10.4, 3.6 Hz, 1H), 5.53-5.44 (m, 1H), 4.22-4.13 (m, 1H), 4.03-3.87 (m, 2H), 3.86-3.78 (m, 1H), 3.61-3.51 (m, 2H), 2.87-2.56 (m, 5H), 2.09-0.64 (m, 63H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.3, 147.3, 142.9, 128.9, 128.2, 127.8, 125.7, 125.6, 120.2, 108.6, 98.7, 89.4, 76.5, 75.0, 74.0, 71.71, 71.66, 68.0, 58.9, 55.2, 49.6, 48.9, 39.8, 38.5, 36.6, 35.5, 33.7, 32.7, 30.0, 28.0, 26.3, 25.6, 22.8, 22.4, 22.0, 17.9, 16.9, 16.1, 14.3, 14.1, 13.3, 12.1, 11.0, 7.0, 6.6. IR (KBr): 3502, 2962, 2934, 2875, 1712, 1116, 1087 cm^{-1}. HRMS (ESI) calcd for $C_{54}H_{84}N_3O_{10}^+$ ([M+H]$^+$), 934.6151; found 934.6164.



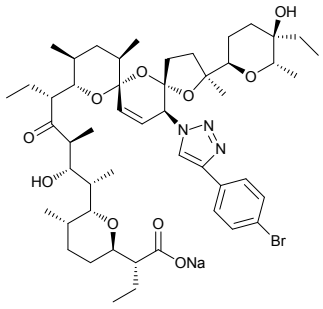
5d

Compound 5d was prepared from compound **4** and (4-*tert*-butylphenyl)enthyne by following the general procedure for the CuAAC reaction with an 80% yield as white amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 6.66-6.51 (m, 1H), 6.28 (dd, *J* = 10.4, 3.6 Hz, 1H), 4.22-4.11 (m, 1H), 4.07-3.90 (m, 2H), 3.87-3.74 (m, 1H), 3.62-3.49 (m, 2H), 2.89-2.56 (m, 3H), 2.10-0.58 (m, 65H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.4, 178.0, 151.0, 146.9, 127.9, 127.6, 125.6, 125.3, 120.5, 108.7, 98.7, 91.6, 89.0, 76.0, 74.9, 73.6, 71.6, 67.9, 59.0, 55.1, 49.3, 48.5, 41.1, 39.6, 38.4, 36.7, 36.4, 35.4, 34.6, 33.9, 32.6, 32.3, 31.9, 31.3, 29.9, 29.7, 29.3, 29.0, 28.5, 27.9, 26.2, 25.1, 24.8, 24.0, 23.7, 22.7, 21.8, 21.0, 20.7, 19.8, 17.6, 17.3, 16.6, 16.2, 14.7, 14.2, 14.1, 13.2, 12.0, 10.9, 8.0, 6.9, 6.5. IR (KBr): 3421, 2963, 2935, 2875, 1713, 1564, 1405, 1116, 799 cm^{-1}. HRMS (ESI) calcd for $C_{54}H_{84}N_3O_{10}^+$ ([M+H]$^+$), 934.6151 ; found, 934.6173.



5e

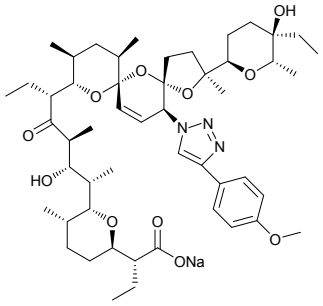
Compound 5e was prepared from compound **4** and (3-fluorophenyl)ethyne by following the general procedure for the CuAAC reaction with an 81% yield as white amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.61-7.47 (m, 2H), 7.41-7.30 (m, 1H), 7.06-6.91 (m, 1H), 6.68-6.50 (m, 1H), 6.40-6.14 (m, 1H), 5.59-5.45 (m, 1H), 4.44-4.11 (m, 2H), 4.00-3.89 (m, 1H), 3.74-3.55 (m, 2H), 3.51-3.36 (m, 1H), 2.86-2.62(m, 3H), 2.11-0.62 (m, 56H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 161.9, 145.8, 132.8, 130.4, 130.3, 127.6, 121.2, 114.9, 114.7, 112.6, 112.3, 98.6, 76.3, 75.9, 75.4, 74.2, 71.5, 70.3, 67.5, 57.7, 55.3, 51.0, 49.7, 40.2, 38.4, 36.4, 36.0, 32.4, 29.7, 29.1, 27.9, 26.7, 23.6, 21.2, 19.9, 17.6, 17.0, 15.7, 14.5, 13.1, 12.3, 10.7, 6.8, 6.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.97. IR (KBr): 3430, 2964, 2935, 2876, 1713, 1563, 1404, 1115, 885, 787, 682 cm^{-1}. HRMS (ESI) calcd for $C_{50}H_{74}FN_3NaO_{10}^+$ ([M+H]$^+$), 918.5250; found, 918.5253.



5f

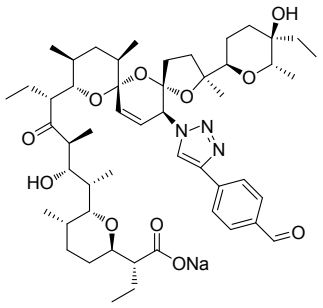
Compound 5f was prepared from compound **4** and (4-bromomphenyl)ethyne by following the general procedure for the CuAAC reaction with a 92% yield as white amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.71 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 6.60-6.46 (m, 1H), 6.42-6.23 (m, 1H), 5.57-5.50 (m, 1H), 4.27-4.12 (m, 1H), 4.00-3.89 (m, 1H), 3.78-3.66 (m, 1H), 3.66-3.53 (m, 1H), 3.47-3.38 (m, 1H), 2.86-2.60 (m, 3H), 2.05-0.63 (m, 57H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 131.6, 129.5, 127.3, 126.9, 121.5, 121.0, 108.0, 98.6, 88.6, 76.2, 76.0, 74.9, 73.5, 71.3, 70.6, 67.5, 58.1, 55.0, 49.8, 49.0, 39.6, 38.1, 35.8, 32.3, 32.0, 30.1, 29.5, 28.9, 27.8, 26.2, 23.5, 22.8, 22.5, 21.0, 19.8, 17.4, 16.5, 15.6, 14.2, 14.0, 13.9, 13.0, 12.5, 11.9, 10.7, 6.7, 6.2. IR (KBr):

3498, 2964, 2934, 2876, 1713, 1563, 1404, 1116 cm^{-1}. HRMS (ESI) calcd for $C_{50}H_{74}BrN_3NaO_{10}^+$ ([M+H]$^+$), 978.4450; found, 978.4451.



5g

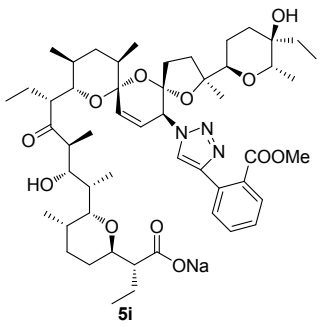
Compound 5g was prepared from compound **4** and (4-methoxyphenyl)acetylene by following the general procedure for the CuAAC reaction with a 77% yield as white amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.72 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.64-6.53 (m, 1H), 6.28-6.14 (m, 1H), 5.44 (s, 1H), 4.39-4.19 (m, 2H), 3.99-3.88 (m, 1H), 3.83 (s, 3H), 3.73-3.60 (m, 2H), 3.49-3.37 (m, 1H), 2.91-2.63 (m, 3H), 2.09-0.65 (m, 56H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 146.7, 127.3, 126.8, 123.3, 119.1, 114.1, 107.5, 98.5, 89.7, 76.3, 75.8, 75.4, 74.4, 71.5, 70.2, 67.5, 57.5, 55.3, 55.2, 51.1, 49.8, 40.3, 38.5, 36.4, 32.4, 29.7, 29.0, 28.0, 27.6, 26.8, 23.6, 21.0, 17.6, 17.0, 15.7, 14.6, 14.1, 13.1, 12.4, 6.8, 6.4. IR (KBr): 3421, 2963, 2934, 2876, 1714, 1563, 1404, 1250, 1177, 1114, 797 cm^{-1}. HRMS (ESI) calcd for $C_{51}H_{78}N_3O_{11}^+$ ([M+H]$^+$), 908.5631; found, 908.5648.



5h

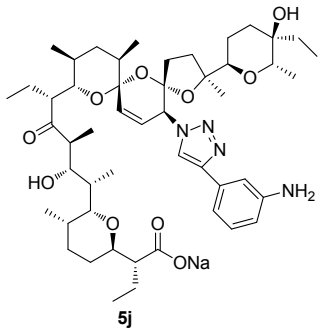
Compound 5h was prepared from compound **4** and 4-ethynylbenzaldehyde by following the general procedure for the CuAAC reaction with an 80% yield as white amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 8.09 (s, 1H), 8.01-7.96 (m, 2H), 7.95-7.90 (m, 2H), 6.68-6.55 (m, 1H), 6.28-6.18 (m, 1H), 5.56-5.45 (m, 1H), 4.38-4.19 (m, 2H), 4.01-3.88 (m, 1H), 3.74-3.60 (m, 2H), 3.52-3.35 (m, 1H), 2.91-2.60 (m, 3H), 2.12-0.62 (m, 56H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 217.0, 191.4, 184.4, 145.3, 136.2, 135.4, 130.1, 127.5, 125.7, 122.9, 121.3, 107.1, 98.4, 89.5, 75.7, 75.3, 74.1, 71.2, 70.0, 67.2, 57.5, 55.0, 50.8, 49.4, 40.0, 38.2, 36.4, 35.6, 32.2, 29.4, 28.7, 27.7, 27.3, 26.6, 23.4, 20.8, 19.8, 17.3, 16.8, 15.5, 14.3, 12.8, 12.2, 12.0, 10.5, 6.6, 6.2. IR (KBr): 3411, 2964, 2934,

2876, 1702, 1563, 1404, 1115, 800 cm^{-1}. HRMS (ESI) calcd for $C_{51}H_{75}N_3NaO_{11}^+$ ([M+H]$^+$), 928.5294; found, 928.5301.



5i

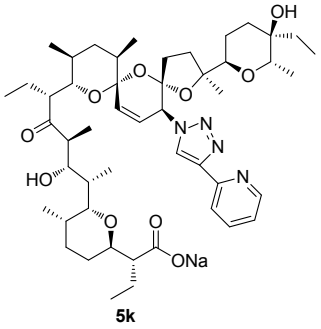
Compound 5i was prepared from compound **4** and methyl 2-ethynylbenzoic acid methyl ester by following the general procedure for the CuAAC reaction with a 51% yield as white amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.81-7.71 (m, 2H), 7.57-7.48 (m, 1H), 7.42-7.35 (m, 1H), 6.66-6.57 (m, 1H), 6.24 (dd, *J* = 10.4, 4.8 Hz, 1H), 5.46 (d, *J* = 4.4 Hz, 1H), 4.39-4.19 (m, 2H), 4.02-3.87 (m, 1H), 3.77 (s, 3H), 3.73-3.60 (m, 2H), 3.48-3.36 (m, 1H), 2.88-2.63 (m, 3H), 2.14-0.63 (m, 56H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 217.4, 184.6, 168.6, 144.9, 131.3, 130.3, 130.2, 129.9, 129.6, 127.9, 127.5, 123.2, 122.5, 107.5, 98.5, 89.9, 76.4, 75.7, 74.4, 71.4, 70.1, 67.5, 57.5, 55.4, 52.2, 51.1, 49.9, 40.3, 38.5, 36.4, 35.8, 32.4, 32.2, 31.9, 29.7, 29.3, 29.0, 28.0, 27.6, 26.9, 23.7, 22.7, 21.0, 20.0, 17.6, 17.2, 15.7, 14.6, 14.1, 13.1, 12.4, 12.1, 10.7, 6.8, 6.4. IR (KBr): 3428, 2962, 2932, 2875, 1727, 1563, 1404, 1292, 1119, 1089, 762 cm^{-1}. HRMS (ESI) calcd for $C_{52}H_{77}N_3NaO_{12}^+$ ([M+H]$^+$), 958.5399; found, 958.5404.



5j

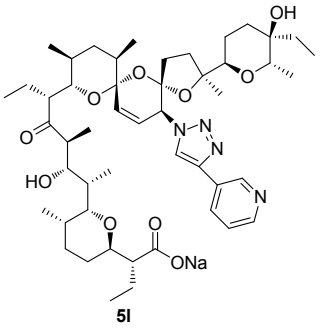
Compound 5j was prepared from compound **4** and (3-aminophenyl)acetylene by following the general procedure for the CuAAC reaction with a 53% yield as yellow amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.25-7.03 (m, 3H), 6.69-6.51 (m, 2H), 6.21 (dd, *J* = 10.4, 4.8 Hz, 1H), 5.44 (d, *J* = 4.4 Hz, 1H), 4.40-4.19 (m, 2H), 3.97-3.90 (m, 1H), 3.72-3.60 (m, 2H), 3.46-3.35 (m, 1H), 2.88-2.56 (m, 4H), 2.14-0.58 (m, 55H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 217.4, 184.7, 147.3, 147.0, 131.2, 129.6, 127.3, 123.1, 119.8, 115.3, 114.7, 111.9, 107.3, 98.5, 89.7, 76.2, 75.7, 74.3, 71.4, 70.1, 67.3, 57.4, 55.3, 51.0, 49.8, 40.3, 38.4, 36.4, 35.8, 32.4, 28.8, 27.9, 27.6, 26.7,

23.7, 20.9, 19.9, 17.5, 17.0, 15.6, 14.5, 13.0, 12.4, 12.0, 10.6, 6.7, 6.4. IR (KBr): 3371, 2963, 2934, 2876, 1714, 1563, 1404, 1115, 882, 774 cm^{-1}. HRMS (ESI) calcd for $C_{50}H_{76}N_4NaO_{10}^+$ ([M+H]$^+$), 915.5454; found, 915.5454.



5k

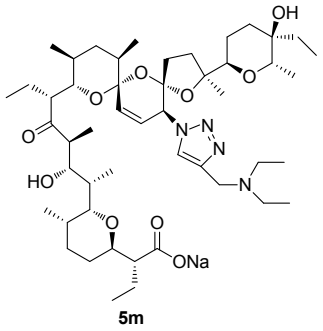
Compound 5k was prepared from compound **4** and 2-ethynylpyridine by following the general procedure for the CuAAC reaction with a 96% yield as white amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65-8.44 (m, 2H), 8.25-8.08 (m, 1H), 7.82-7.68(m. 1H), 7.24-7.14 (m, 1H), 6.65-6.37 (m, 2H), 5.65-5.50 (m, 1H), 4.28-4.14 (m, 1H), 4.00-3.88 (m, 2H), 3.74-3.65 (m, 1H), 3.59-3.37 (m, 2H), 2.77-2.54 (m, 3H), 2.10-0.49 (m, 56H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.1, 177.9, 150.4, 149.2, 147.1, 137.0, 127.8, 125.8, 124.2, 122.7, 120.4, 108.6, 98.8, 88.0, 76.4, 75.9, 75.0, 73.6, 71.6, 71.3, 67.9, 59.1, 55.2, 49.3, 49.0, 41.1, 39.5, 38.4, 36.8, 36.4, 35.6, 32.6, 32.2, 30.7, 29.7, 28.6, 28.0, 26.3, 25.7, 24.8, 24.0, 23.6, 22.5, 21.5, 20.8, 19.8, 17.7, 17.3, 16.5, 16.1, 14.7, 14.3, 13.2, 11.7, 10.9, 8.0, 7.0, 6.6. IR (KBr): 3489, 2965, 2936, 2876, 1712, 1604, 1115, 1087, 786 cm^{-1}. HRMS (ESI) calcd for $C_{49}H_{75}N_4O_{10}^+$ ([M+H]$^+$), 879.5478; found 879.5488.



5l

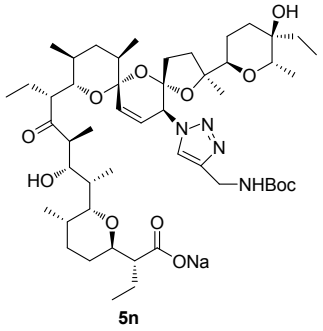
Compound 5l was prepared from compound **4** and 3-ethynylpyridine by following the general procedure for the CuAAC reaction with a 42% yield as white amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 8.59-8.50 (m, 1H), 8.24-8.15 (m, 1H), 8.07 (s, 1H), 7.41-7.31 (m, 1H), 6.68-6.51 (m, 1H), 6.29-6.16 (m, 1H), 5.54 (d, *J* = 4.0 Hz, 1H), 4.36-4.14 (m, 2H), 4.02-3.87 (m, 2H), 3.77-3.59 (m, 3H), 3.50-3.35 (m, 1H), 2.88-2.65 (m, 3H), 2.12-0.65 (m, 54H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 217.5, 184.6, 149.1, 146.8, 143.9, 132.9, 127.8, 123.8, 123.1, 120.0, 107.2, 98.6, 89.9, 76.3, 75.8, 75.7, 74.5, 71.5, 69.9, 67.4, 57.7, 55.4, 51.1, 50.0, 40.4, 38.5, 36.6, 32.5, 32.4, 32.3, 31.9, 29.7, 29.4, 29.1, 28.0, 27.7, 26.9, 23.7, 22.7, 21.1, 17.6, 17.2, 15.7, 14.6, 14.1, 13.1, 12.5, 12.1, 10.7,

6.8, 6.5. IR (KBr): 3410, 2963, 2933, 2875, 1714, 1563,1406, 1116, 878, 796, 705 cm^{-1}. HRMS (ESI) calcd for $C_{49}H_{74}N_4NaO_{10}^+$ ($[M+H]^+$), 901.5297; found 901.5304.



5m

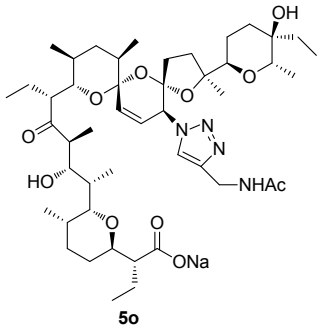
Compound 5m was prepared from compound **4** and 1-(diethylamino)-2-propyne by following the general procedure for the CuAAC reaction with a 71% yield as white amorphous solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 6.66-6.51 (m, 1H), 6.20 (dd, *J* = 10.0, 3.6 Hz, 1H), 5.44-5.30 (m, 1H), 4.19-4.04 (m, 3H), 4.02-3.86 (m, 2H), 3.76-3.61 (m, 2H), 3.56-3.38 (m, 1H), 3.00-2.53 (m, 7H), 2.10-0.65 (m, 62H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 217.5, 184.7, 142.0, 127.5, 123.3, 123.1, 107.4, 98.6, 89.9, 76.4, 75.7, 74.5, 71.4, 70.1, 67.4, 57.4, 55.4, 51.1, 50.0, 46.5, 40.4, 38.5, 36.4, 35.9, 32.6, 32.4, 32.2, 31.9, 29.7, 29.6, 29.4, 28.9, 28.0, 27.7, 26.9, 23.8, 22.7, 21.0, 20.0, 17.6, 17.1, 15.7, 14.6, 14.1, 13.1, 12.4, 12.1, 11.3, 10.7, 6.8, 6.4. IR (KBr): 3408, 2964, 2932, 2875, 1717, 1564, 1405, 1116 cm^{-1}. HRMS (ESI) calcd for $C_{49}H_{83}N_4O_{10}^+$ ($[M+H]^+$), 887.6104; found,887.6170.



5n

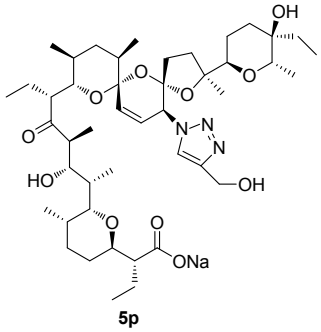
Compound 5n was prepared from compound **4** and 2-propynylcarbamic acid *tert*-butyl ester by following the general procedure for the CuAAC reaction with an 85% yield as white amorphous solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 6.62-6.51 (m, 1H), 6.16 (dd, *J* =10.4, 4.8 Hz, 1H), 5.40 (d, *J* = 4.4 Hz, 1H), 5.12 (s, 1H), 4.38-4.18 (m, 4H), 3.98-3.88 (m, 1H), 3.72-3.61 (m, 2H), 3.45-3.36 (m, 1H), 2.88-2.57 (m, 3H), 2.10-0.64 (m, 65H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 217.2, 184.2, 155.6, 144.7, 127.2, 122.9, 121.3, 107.0, 98.2, 89.6, 79.0, 76.0, 75.4, 74.2, 71.1, 69.6, 67.1, 57.2, 55.1, 50.8, 49.7, 40.1, 38.2, 36.1, 35.9, 35.6, 32.1, 32.0, 29.4, 28.8, 28.0, 27.7, 27.4, 26.6, 23.4, 20.7, 19.7, 17.3, 17.0, 15.4, 14.3, 12.8, 12.2, 11.8, 10.4, 6.5, 6.2. IR (KBr): 3370, 2964,

2935, 2876, 1714, 1564, 1405, 1250, 1174, 1118 cm^{-1}. HRMS (ESI) calcd for $C_{50}H_{82}N_4NaO_{12}^+$ ([M+H]$^+$), 953.5821; found, 953.5831.



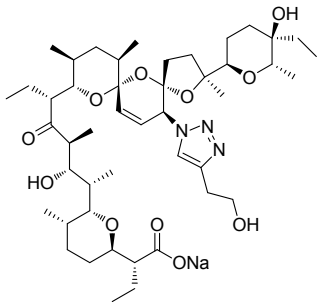
5o

Compound 5o was prepared from compound **4** and 3-acetamidopropyne by following the general procedure for the CuAAC reaction with an 87% yield as white amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 6.62-6.46 (m, 1H), 6.27-6.12 (m, 1H), 5.54-5.39 (m, 1H), 4.52-4.36 (m, 2H), 4.30-4.11 (m, 2H), 3.98-3.87 (m, 1H), 3.73-3.56 (m, 2H), 3.50-3.38 (m, 1H), 2.88-2.62 (m, 3H), 2.04-0.63 (m, 59H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 217.2, 184.1, 170.2, 144.3, 127.2, 122.8, 121.7, 107.0, 98.2, 89.5, 76.0, 75.4, 75.2, 74.1, 71.2, 69.7, 67.2, 57.2, 55.1, 50.8, 49.6, 40.0, 38.1, 36.0, 35.5, 34.5, 32.1, 29.3, 28.8, 27.7, 27.3, 26.5, 23.3, 22.5, 20.7, 19.8, 17.2, 16.8, 15.4, 14.3, 13.7, 12.8, 12.1, 11.7, 10.5, 6.5, 6.1. IR (KBr): 3405, 2963, 2935, 2876, 1714, 1660, 1563, 1405, 1254, 1116 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{76}N_4NaO_{11}^+$ ([M+H]$^+$), 895.5403; found, 895.5411.



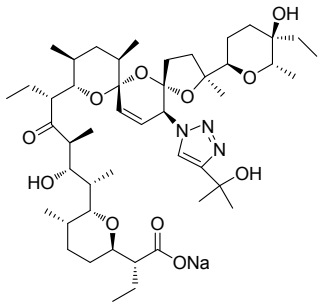
5p

Compound 5p was prepared from compound **4** and 1-hydroxy-2-propyne by following the general procedure for the CuAAC reaction with a 95% yield as white solid powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 6.618-6.445 (m, 1H), 6.30-6.07 (m, 1H), 5.46 (d, J = 3.6 Hz, 1H), 4.73 (s, 2H), 4.26-4.16 (m, 1H), 3.99-3.88 (m, 1H), 3.71-3.59 (m, 2H), 3.45-3.36 (m, 1H), 2.89-2.76 (m, 2H), 2.75-2.62 (m, 3H), 2.07-0.64 (m, 56H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 216.9, 147.2, 127.2, 122.4, 107.5, 98.5, 89.4, 76.2, 75.7, 75.4, 74.2, 71.4, 70.4, 67.5, 57.5, 55.9, 55.2, 50.8, 49.6, 40.2, 38.4, 36.1, 35.7, 32.3, 31.8, 29.6, 28.7, 28.0, 27.3, 26.6, 23.5, 20.8, 20.1, 17.5, 16.9, 15.7, 14.5, 13.0, 12.23, 12.17, 10.8, 6.8, 6.3. IR (KBr): 3403, 2965, 2931, 2875, 1712, 1567, 1403, 1114 cm^{-1}. HRMS (ESI) calcd for $C_{45}H_{74}N_3O_{11}^+$ ([M+H]$^+$), 832.5318; found, 832.5245.



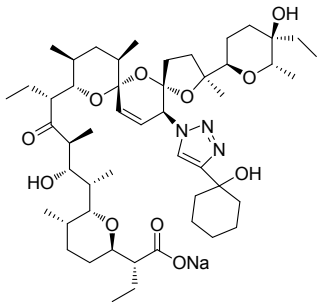
5q

Compound 5q was prepared from compound **4** and (2-hydroxyethyl)acetylene by following the general procedure for the CuAAC reaction with a 76% yield as white amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 6.64-6.41 (m, 1H), 6.17 (dd, *J* = 10.0, 2.8 Hz, 1H), 5.42 (d, *J* = 3.6 Hz, 1H), 4.29-4.17 (m, 2H), 3.98-3.85 (m, 4H), 3.70-3.61 (m, 2H), 3.49-3.36 (m, 1H), 2.89 (t, *J* = 6.0 Hz, 2H), 2.86-2.76 (m, 1H), 2.76-2.62 (m, 2H), 2.10-0.65 (m, 56H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 127.2, 121.9, 107.5, 98.5, 89.4, 76.2, 75.8, 75.4, 74.2, 71.5, 70.4, 67.5, 61.2, 57.4, 55.3, 49.6, 40.1, 38.4, 36.2, 35.8, 32.4, 29.6, 28.9, 28.7, 28.0, 26.7, 23.4, 21.0, 20.0, 17.5, 16.9, 15.7, 14.5, 13.0, 12.3, 10.8, 6.8, 6.4. IR (KBr): 3415, 2964, 2935, 2876, 1713, 1564, 1404, 1116 cm^{-1}. HRMS (ESI) calcd for $C_{46}H_{76}N_3O_{11}^+$ ([M+H]$^+$), 846.5474; found, 846.5472.



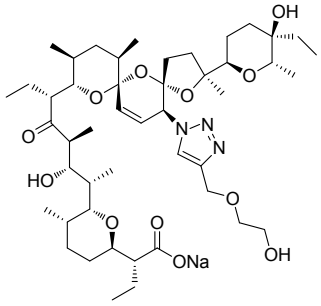
5r

Compound 5r was prepared from compound **4** and (1-hydroxy-1-methylethyl)acetylene by following the general procedure for the CuAAC reaction with a 99% yield as white amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 6.65-6.44 (m, 1H), 6.18 (dd, *J* = 10.2, 4.1 Hz, 1H), 5.36 (d, *J* = 4.1 Hz, 1H), 4.40-4.17 (m, 3H), 3.98-3.85 (m, 1H), 3.69-3.62 (m, 2H), 3.45-3.35 (m, 1H), 2.90-2.60 (m, 4H), 2.10-0.55 (m, 61H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 217.1, 184.2, 154.9, 127.0, 123.1, 119.3, 107.2, 98.3, 89.4, 76.0, 75.5, 75.3, 74.2, 71.1, 69.8, 67.9, 67.1, 57.2, 55.0, 50.7, 49.6, 40.1, 38.3, 36.1, 35.6, 32.2, 30.3, 30.0, 29.4, 28.8, 27.7, 27.4, 26.6, 23.4, 20.7, 19.8, 17.3, 16.8, 15.5, 14.4, 13.9, 12.8, 12.2, 11.8, 10.4, 6.5, 6.2. IR (KBr): 3408, 2965, 2934, 2876, 1714, 1563, 1404, 1116 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{77}N_3NaO_{11}^+$ ([M+H]$^+$), 882.5450; found, 882.5415.



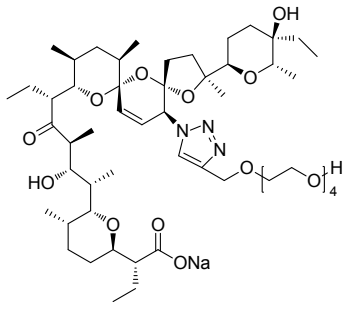
5s

Compound 5s was prepared from compound **4** and (1-hydroxycyclohexyl)acetylene by following the general procedure for the CuAAC reaction with a 94% yield as white amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 6.66-6.46 (m, 1H), 6.29-6.09 (m, 1H), 5.43 (d, J = 2.4 Hz, 1H), 4.34-4.15 (m, 2H), 3.98-3.88 (m, 1H), 3.72-3.58 (m, 2H), 3.51-3.35 (m,1H), 2.88-2.77 (m, 1H), 2.76-2.60 (m, 2H), 2.10-0.63 (m, 57H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 127.2, 120.0, 107.4, 98.4, 89.4, 76.2, 75.7, 75.4, 74.2, 71.3, 70.1, 69.2, 67.4, 57.4, 55.2, 50.6, 49.4, 40.1, 38.4, 38.0, 37.8, 36.1, 35.8, 32.3, 29.6, 29.0, 27.8, 26.6, 25.3, 23.5, 22.6, 21.9, 20.9, 19.8, 17.4, 16.9, 15.7, 14.4, 13.0, 12.3, 10.6, 6.7, 6.3. IR (KBr): 3420, 2933, 2869, 1712, 1564, 1114 cm^{-1}. HRMS (ESI) calcd for $C_{50}H_{81}N_3NaO_{11}^+$ ([M+H]$^+$), 922.5763; found, 922.5771.



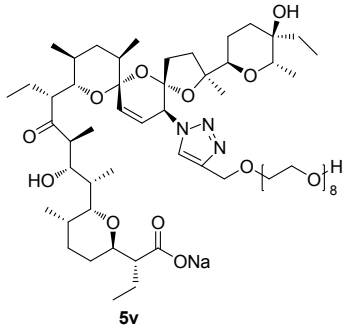
5t

Compound 5t was prepared from compound **4** and 2-(2-propynyloxy)ethanol by following the general procedure for the CuAAC reaction with a 91% yield as white amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 6.64-6.48 (m, 1H), 6.30-6.11 (m, 1H), 5.46-5.31 (m, 1H), 4.64 (s, 2H), 4.42-4.12 (m, 2H), 4.05-3.85 (m, 1H), 3.83-3.54 (m, 7H), 3.51-3.34 (m, 1H), 2.88-2.55 (m, 3H), 2.127-0.565 (m, 57H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 216.8, 143.9, 127.1, 122.7, 107.2, 98.2, 89.2, 76.0, 75.5, 75.2, 73.9, 71.6, 71.1, 70.1, 67.2, 64.0, 60.9, 57.3, 55.0, 50.5, 49.3, 39.9, 38.1, 36.0, 35.6, 32.1, 31.6, 29.3, 28.6, 27.6, 27.0, 26.4, 23.2, 20.68, 19.7, 17.2, 16.6, 15.4, 14.2, 12.8, 12.0, 10.5, 6.5, 6.1. IR (KBr): 3413, 2963, 2935, 2876, 1714, 1563, 1405, 1116 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{77}N_3NaO_{12}^+$ ([M+H]$^+$), 898.5399; found, 898.5407.



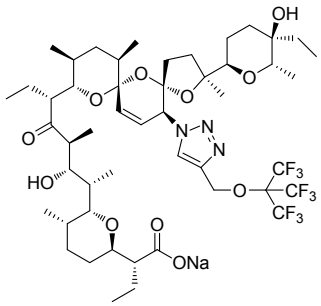
5u

Compound 5u was prepared from compound **4** and 3,6,9,12-tetraoxapentadec-14-yn-1-ol by following the general procedure for the CuAAC reaction with a 74% yield as white amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 6.61-6.46 (m, 1H), 6.29-6.18 (m, 1H), 5.42-5.38 (m, 1H), 4.64 (s, 2H), 4.24-4.10 (m, 2H), 3.99-3.91 (m, 1H), 3.79-3.71 (m, 3H), 3.70-3.57 (m, 16H), 3.54-3.42 (m, 1H), 2.88-2.53 (m, 3H), 2.09-0.59 (m, 56H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 127.2, 122.9, 107.6, 98.2, 88.8, 76.0, 74.7, 72.2, 71.2, 70.2, 70.12, 70.10, 70.06, 69.9, 69.2, 67.5, 64.2, 61.0, 58.0, 55.2, 51.1, 48.9, 39.5, 38.1, 35.6, 33.7, 32.2, 31.5, 30.0, 29.3, 29.0, 28.5, 27.7, 26.1, 22.6, 22.3, 21.0, 19.6, 17.3, 16.5, 15.8, 14.1, 13.8, 12.8, 11.8, 10.6, 6.5, 6.1. IR (KBr): 3447, 2933, 2875, 1714, 1565, 1114 cm^{-1}. HRMS (ESI) calcd for $C_{53}H_{89}N_3NaO_{15}^{+}$ ([M+H]$^{+}$), 1030.6186; found, 1030.6167.



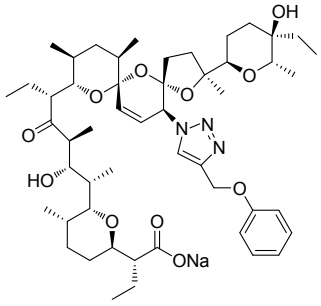
5v

Compound 5v was prepared from compound **4** and 3,6,9,12,15,18,21,24-octaoxaheptacos-26-yn-1-ol by following the general procedure for the CuAAC reaction with an 88% yield as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 6.64-6.49 (m, 1H), 6.17 (dd, J = 10.4, 4.8 Hz, 1H), 5.42 (d, J = 5.2 Hz, 1H), 4.63 (s, 2H), 4.40-4.18 (m, 2H), 3.98-3.87 (m, 1H), 3.78-3.55 (m, 40H), 3.49-3.37 (m, 2H), 2.88-2.62 (m, 3H), 2.08-0.66 (m, 50H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 217.3, 184.5, 144.2, 127.3, 123.0, 122.4, 107.2, 98.4, 89.7, 76.2, 75.6, 74.3, 72.5, 71.2, 70.4, 70.0, 69.9, 69.4, 67.2, 64.3, 61.3, 57.3, 55.2, 50.9, 49.8, 40.2, 38.4, 36.3, 35.7, 32.4, 32.3, 32.0, 31.7, 29.5, 29.2, 28.8, 27.8, 27.5, 26.7, 23.6, 22.5, 20.8, 19.8, 17.4, 17.0, 15.6, 14.5, 14.0, 13.0, 12.3, 11.9, 10.6, 6.6, 6.3. IR (KBr): 3412, 2925, 2874, 1714, 1564, 1405, 1113 cm^{-1}. HRMS (ESI) calcd for $C_{61}H_{105}N_3NaO_{19}^{+}$ ([M+H]$^{+}$), 1206.7234; found, 1206.7229.



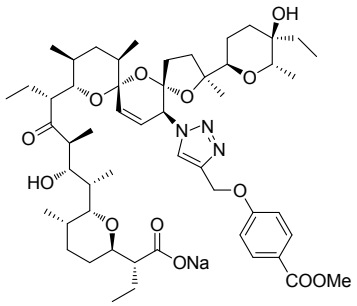
5w

Compound 5w was repared from compound **4** and 3-((1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl) propan-2-yl)oxy) prop-1-yne by following the general procedure for the CuAAC reaction with a 68% yield as white amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 6.58 (dd, *J* =10.6, 1.7 Hz, 1H), 6.20 (dd, *J* =10.5, 4.4 Hz, 1H), 5.47-5.35 (m, 1H), 5.17 (s, 2H), 4.19-4.10 (m, 1H), 4.03-3.91 (m, 2H), 3.88-3.82 (m, 1H), 3.72-3.53 (m, 2H), 2.88-2.54 (m ,3H), 2.08-0.64 (m, 56H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.9, 178.5, 142.1, 128.4, 124.3, 123.0, 107.7, 98.5, 90.1, 76.3, 76.1, 75.0, 74.0, 71.7, 71.5, 68.1, 63.8, 58.8, 55.6, 49.7, 49.2, 40.0, 38.6, 36.6, 36.5, 32.8, 32.0, 31.7, 29.9, 29.8, 29.5, 28.0, 26.3, 25.9, 22.8, 22.1, 19.9, 18.0, 16.9, 16.0, 14.3, 14.2, 13.3, 13.2, 12.1, 11.0, 6.8, 6.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.50. IR (KBr): 3492, 2966, 2877, 17127, 15647, 1154, 1152, 1123 cm^{-1}. HRMS (ESI) calcd for $C_{49}H_{72}F_9N_3NaO_{11}^+$ ([M+H]), 1072.4915; found, 1072.4924.



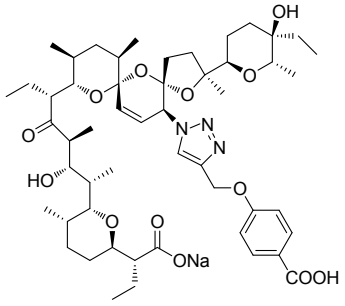
5x

Compound 5x was prepared from compound **4** and (2-propynyloxy)benzene by following the general procedure for the CuAAC reaction with a 77% yield as white solid powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.30-7.24 (m, 2H), 6.99-6.88 (m, 3H), 6.61-6.44 (m, 1H), 6.17 (dd, *J* = 10.4, 4.8 Hz, 1H), 5.44 (d, *J* = 4.0 Hz, 1H), 5.17 (s, 2H), 4.40-4.10 (m, 2H), 4.00-3.86 (m,1H), 3.77-3.54 (m, 2H), 3.46-3.36 (m, 1H), 2.88-2.76 (m,1H), 2.74-2.63 (m, 2H), 2.11-0.63 (m, 56H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 217.3, 184.3, 157.8, 143.3, 129.2, 127.4, 123.0, 122.4, 120.9, 114.6, 107.1, 98.3, 89.6, 76.1, 75.5, 74.2, 71.2, 69.7, 67.2, 61.7, 57.3, 55.2, 50.8, 49.8, 40.1, 38.2, 36.1, 35.7, 32.2, 29.4, 28.8, 27.8, 27.4, 26.6, 23.5, 20.8, 19.7, 17.4, 16.8, 15.5, 14.3, 14.0, 12.9, 12.2, 10.5, 6.6, 6.2. IR (KBr): 3492, 2964, 2932, 2876, 1712, 1564, 1243, 1119, 754, 688 cm^{-1}. HRMS (ESI) calcd for $C_{51}H_{77}N_3NaO_{11}^+$ ([M+H]$^+$), 930.5450; found, 930.5457.



5y

Compound 5y was prepared from compound **4** and methyl 4-(2-propynyloxy)benzoate by following the general procedure for the CuAAC reaction with a 95% yield as white amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.8, 2.8 Hz, 2H), 7.68 (s, 1H), 6.96 (dd, *J* =8.8, 2.0 Hz, 2H), 6.64-6.49 (m, 1H), 6.24-6.11 (m, 1H), 5.42 (d, *J* = 4.0 Hz, 1H), 5.22 (s, 2H), 4.37-4.18 (m, 2H), 3.98-3.90 (m, 1H), 3.89-3.86 (m, 3H), 3.71-3.59 (m, 2H), 3.44-3.34 (m, 1H), 2.89-2.59 (m, 3H), 2.10-0.63 (m, 56H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 217.3, 184.2, 166.3, 161.6, 142.5, 131.3, 127.4, 122.8, 122.7, 122.5, 114.2, 107.0, 98.2, 89.6, 76.1, 75.5, 74.2, 71.1, 69.6, 67.2, 61.7, 57.3, 55.2, 51.6, 50.8, 49.7, 40.0, 38.2, 36.2, 35.6, 32.2, 29.4, 28.8, 27.7, 27.4, 26.6, 23.5, 22.4, 20.7, 19.7, 17.3, 16.8, 15.4, 14.3, 13.9, 12.8, 12.2, 11.8, 10.4, 6.5, 6.2. IR (KBr): 3389, 2957, 2934, 2876, 1717, 1564, 1394, 1251, 1173, 1111 cm^{-1}. HRMS (ESI) calcd for $C_{53}H_{79}N_3NaO_{13}^+$ ([M+H]$^+$), 988.5505; found, 988.5510.



5z

Compound 5z was prepared from compound **4** and 4-(2-propynyloxy)benzoic acid by following the general procedure for the CuAAC reaction with an 87% yield as white amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.86 (s, 1H), 6.95 (d, *J* = 9.2 Hz, 2H), 6.56-6.46 (m, 1H), 6.36-6.18 (m, 1H), 5.48 (d, *J* = 2.0 Hz, 1H), 5.18 (s, 2H), 4.25-4.12 (m, 1H), 4.03-3.95 (m, 1H), 3.81-3.69 (m, 1H), 3.67-3.55 (m, 1H), 3.49-3.41 (m, 1H), 2.91-2.58 (m, 3H), 2.05-0.59 (m, 57H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 161.8, 142.5, 131.8, 128.6, 127.5, 123.8, 123.4, 114.1, 107.9, 98.5, 89.0, 76.2, 74.8, 71.5, 71.1, 68.0, 61.8, 58.4, 55.2, 49.0, 39.6, 38.2, 36.0, 32.4, 31.8, 30.2, 29.6, 29.2, 28.8, 27.9, 26.3, 25.3, 23.6, 22.8, 22.6, 21.2, 19.6, 17.5, 16.6, 15.8, 14.2, 14.0, 13.0, 11.9, 10.8, 6.8, 6.3. IR (KBr): 3450, 2964, 2934, 2876, 1712, 1606, 1384, 1247, 1169, 1116 cm^{-1}. HRMS (ESI) calcd for $C_{52}H_{77}N_3NaO_{13}^+$ ([M+H]$^+$), 974.5349; found, 974.5361.

General procedure for chelation of salinomycin derivatives 5f with metal ions. To a stirring solution of **5f**-Na^+ (97.8 mg, 0.1 mmol) in ethyl ether (2 mL) was added of hydrochloric acid (2 N, 2 mL) and the mixture was stirred for 5 min at rt. After removal of the aqueous layer, the organic lay was washed with another portion of hydrochloric acid (2N, 2 mL). Note: **5f**-H^+ was obtained through concentrating the organic layer and purifying the residue with a short pad of silica gel. Then the organic lay was collected and washed twice with KOH (2 N aqueous solution, 2 mL) by stirring the mixture for 5 min at rt. The organic lay was collected, concentrated under vacuum and purified by a short pad of silica gel to give the **5f**-K^+ (99.2 mg, 97%).

5f-Li^+, **5f**-Cs^+, **5f**-Mg^{2+}, **5f**-Zn^{2+} were prepared by using the above procedure.

3. MTT assay of library compounds

4T1 was purchased from American Type Culture Collection (Rockville, MD, USA).[1] L02, U87, Hela, Caco2, MCF-7 were purchased from Wuhan University Culture Collection (Wuhan, Hubei, China). 4T1 cells were maintained in monolayer cultures within an RPMI 1640 medium supplemented with 10% FBS. Cells were maintained at 37 °C humidified atmosphere with 5% CO_2. 1640 medium was used to culture MCF-7 cell lines whereas L02, HeLa, U87 and Caco2 cell lines were grown in DMEM high glucose medium. Both media were supplemented with 10% (v/v) fetal bovine serum (FBS), 1% penicillin-streptomycin solution (v/v). All cell lines were maintained at 37 ^{o}C in a humidified atmosphere containing 5% CO_2 in an incubator.[2-7]

3,000 4T1 cells were seeded in wells of 96-well plates in 100 μL RPMI-1640 media. The media contained serially diluted derivatives of Sali. After 48 hours of incubation, live cells were quantified using the CellTiter 96® AQueous One Solution Cell Proliferation Assay (Promega, WI, USA). The plates were read with a SpectraMax M2 plate reader (Molecular Devices, Inc. CA, USA). Quantities of live cells in each well were represented by the absorbance values at 490 nm of that well. Consequently, cell viabilities in each treated well were expressed as the absorbance values in percentage after the values were normalized with the mean absorbance value of the wells containing untreated cells. The viability data was fitted into a sigmoidal dose-response curve using the GraphPad Prism 5.0 (GraphPad Software, Inc., CA, USA). The EC_{50} and 95% confidence index (CI) were obtained from the fitting. The assay was carried out side-by-side 3 times and the average cell viability was used for plotting of the dose-response curve.

L02, U87, MCF7, Hela and Caco2 cells were plated at a density of 8×10^3 cells per well into a 96-well plate. One day (24 h) after seeding, serial concentrations of the compounds (100 μL) were added and further incubated for 72 h (final concentrations of each compound: 100 μM, 33 μM, 10 μM, 3.3 μM and 1 μM). The culture plates

were incubated for 4 h after adding 100 μL MTT.[4-6] The supernatant was then removed and 150 μL DMSO was added into each well with samples being shaken for further 10 min. Three independent samples were used at each concentration. The optical density (OD) was measured at 490 nm. Cell viability data was fitted into a sigmoidal dose-response curve using the Origin 8.0 and the IC_{50} were obtained from the SPSS 19.0. The IC_{50} concentration represents the concentration resulting in a 50% decrease in cell growth after 3 days incubation. The assay was carried out side-by-side 3 times and the average cell viability was used for plotting of the dose-response curve.

References：

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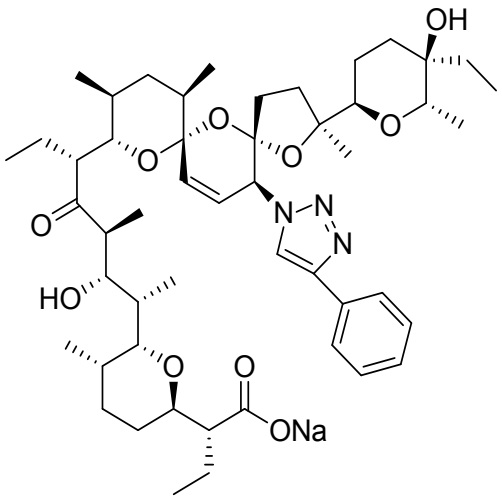
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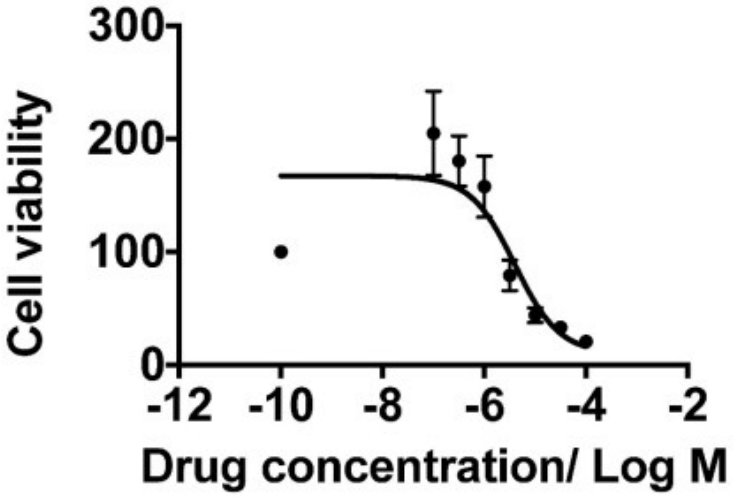
N
N
N
HO
O
O
ONa

5a


Cell viability
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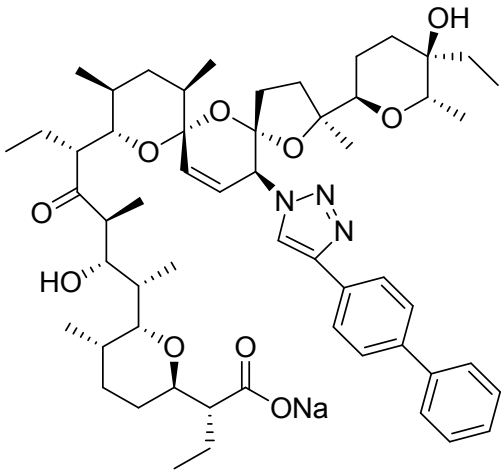
200
100
0
-12
-10
-8
-6
-4
-2
Drug concentration/ Log M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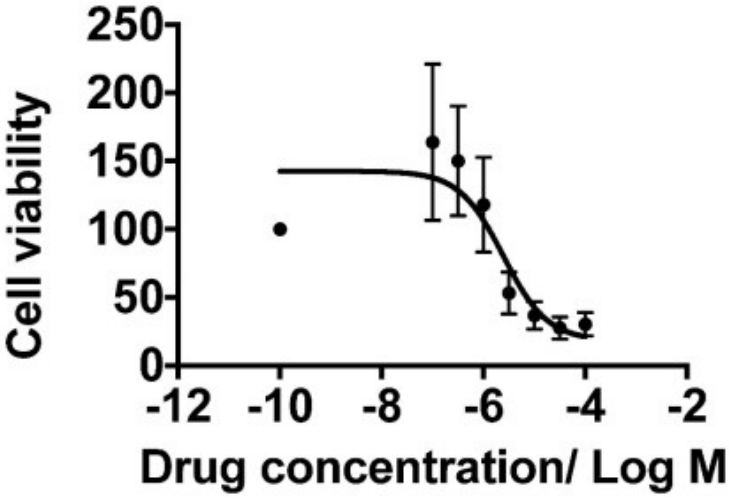
N
N
HO
O
O
ONa

5b


Cell viability
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200
150
100
50
0
-12
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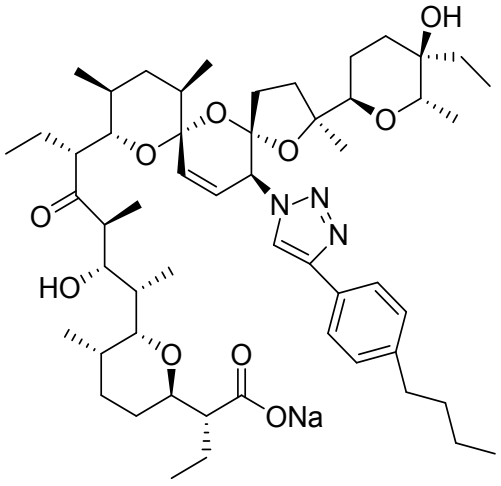
-8
-6
-4
-2
Drug concentration/ Log M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N
HO
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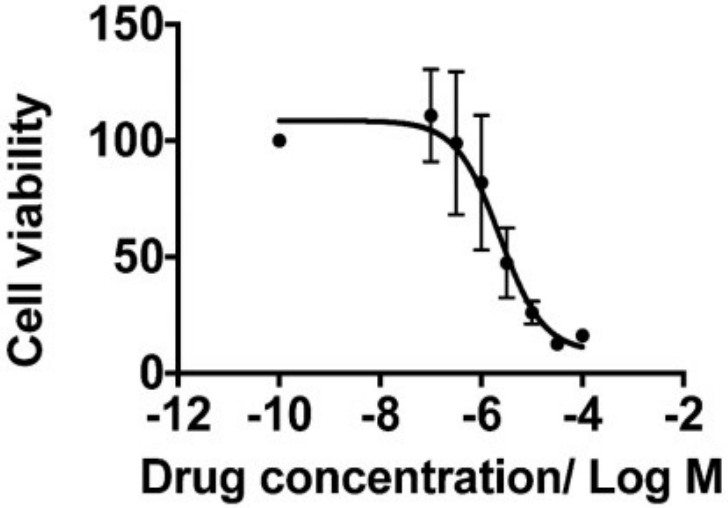
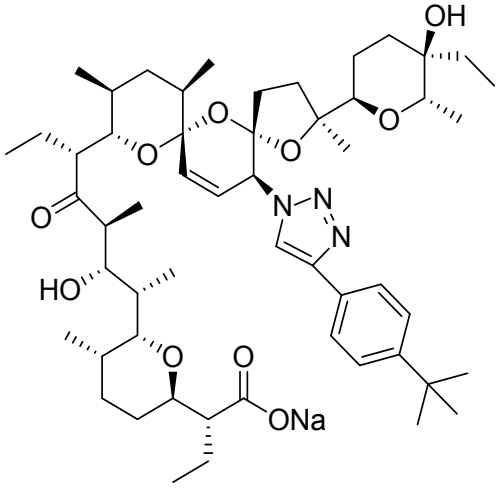
ONa

5c


Cell viability
150
100
50
0
-12
-10
-8
-6
-4
-2
Drug concentration/ Log M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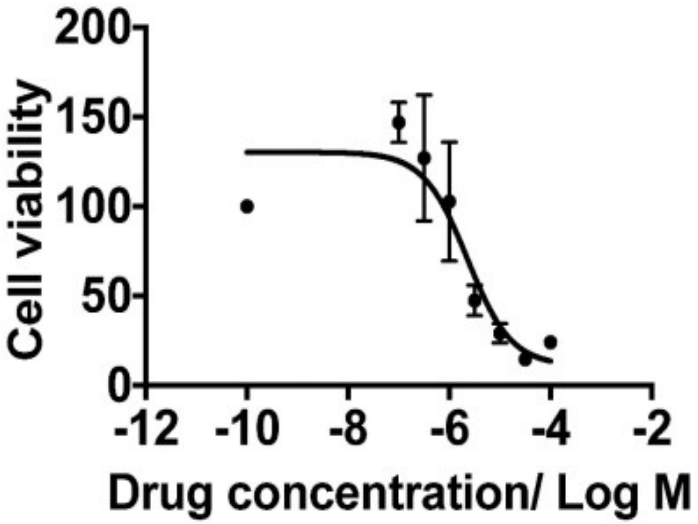
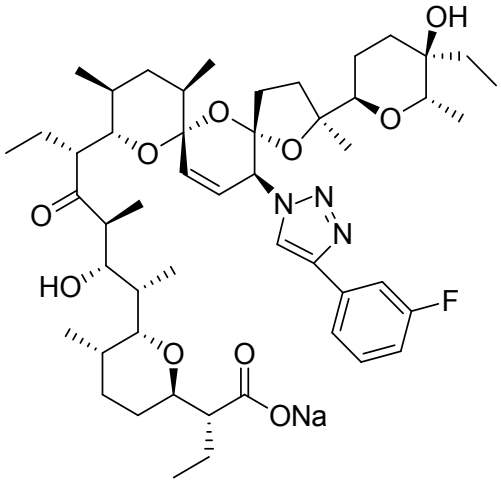
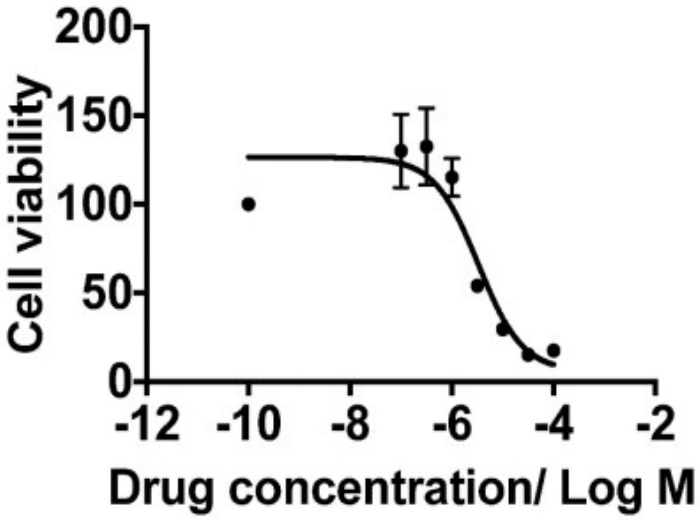
O
O
N
N
N
HO
O
O
ONa

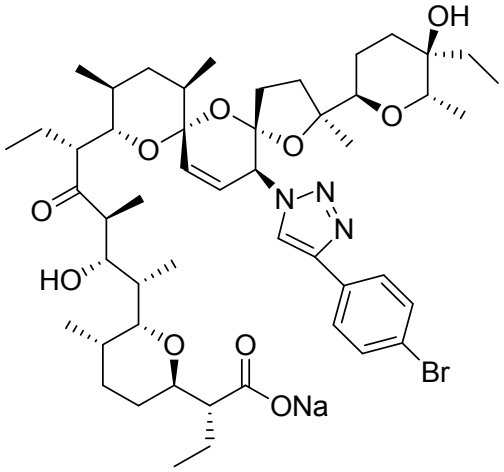
5d


Cell viability
200
150
100
50
0
-12
-10
-8
-6
-4
-2
Drug concentration/ Log M

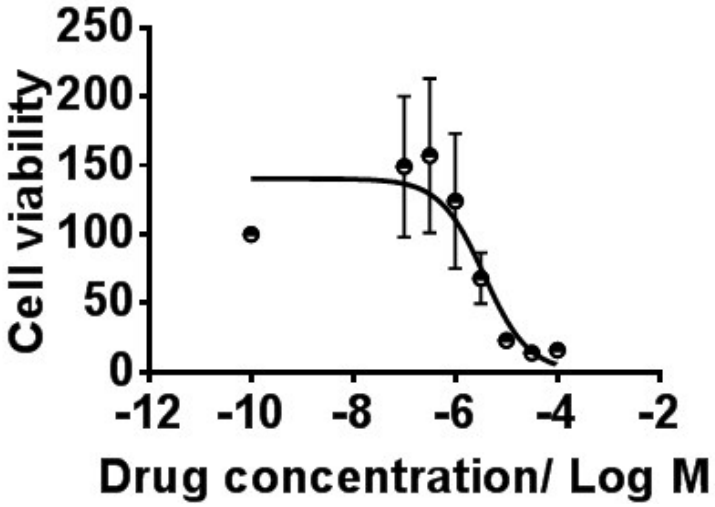

OH
O
O
O
O
N
N
N
HO
F
O
O
ONa

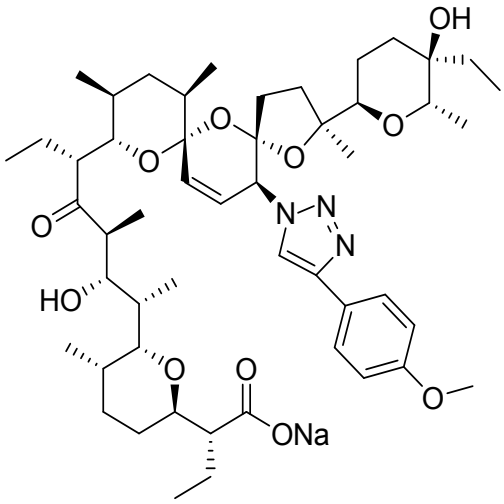
5e


Cell viability
200
150
100
50
0
-12
-10
-8
-6
-4
-2
Drug concentration/ Log M

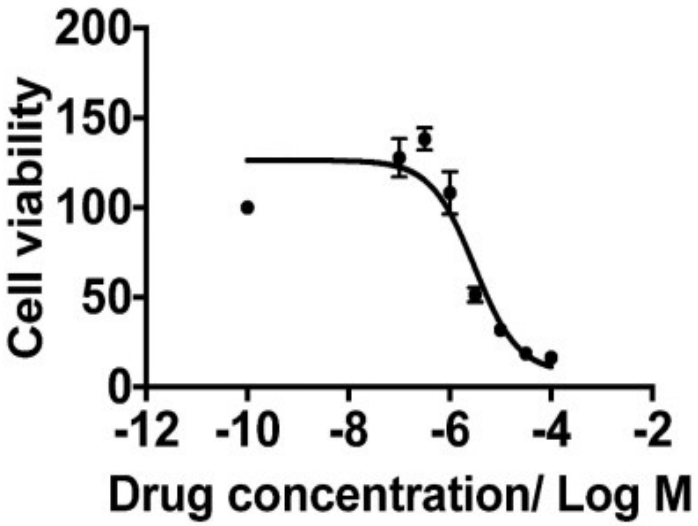

OH
O
O
O
O
N
N
N
HO
O
O
ONa
Br

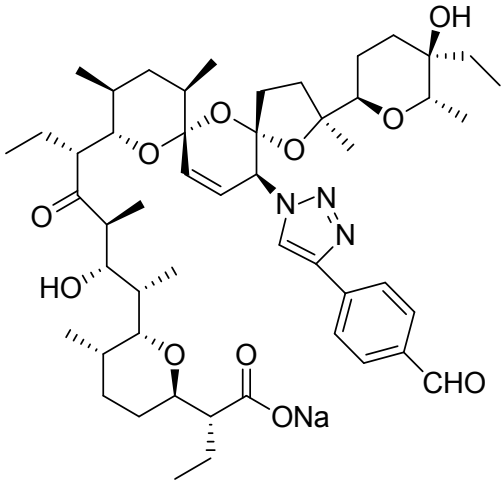
5f


Cell viability
250
200
150
100
50
0
-12
-10
-8
-6
-4
-2
Drug concentration/ Log M

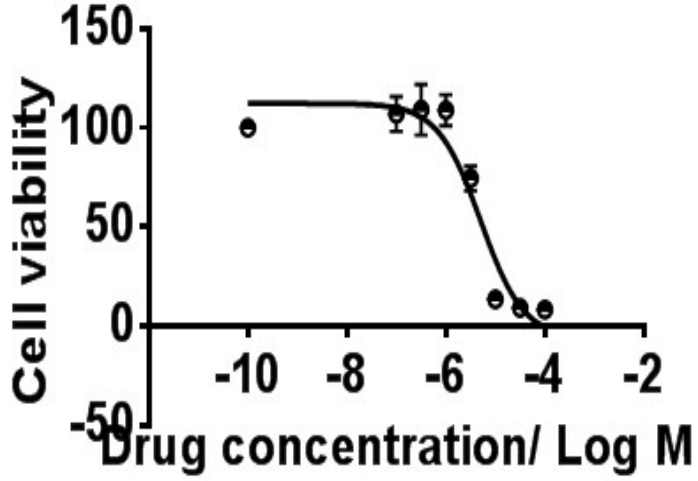

OH
O
O
O
O
N
N
N
HO
O
O
ONa
O

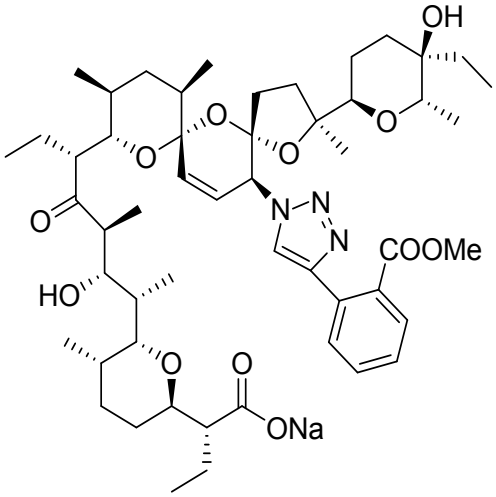
5g


Cell viability
200
150
100
50
0
-12
-10
-8
-6
-4
-2
Drug concentration/ Log M

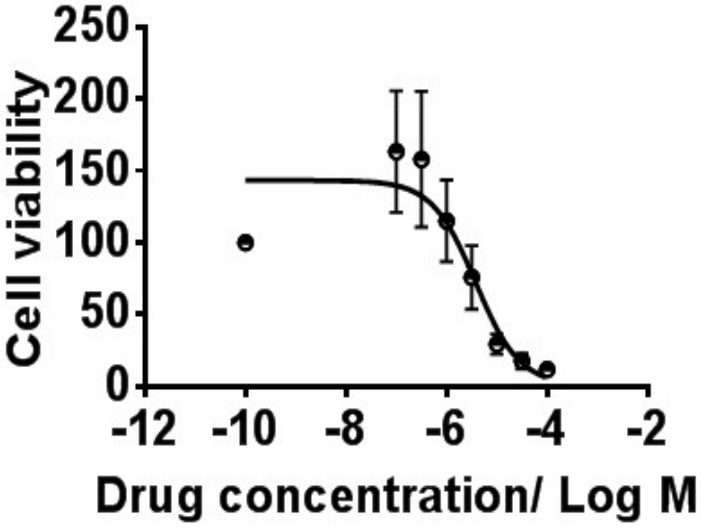

OH
O
O
O
O
N
N
N
HO
O
O
ONa
CHO

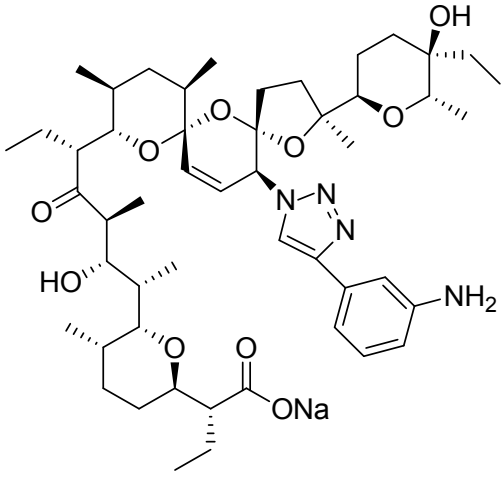
5h


Cell viability
150
100
50
0
-50
-10
-8
-6
-4
-2
Drug concentration/ Log M

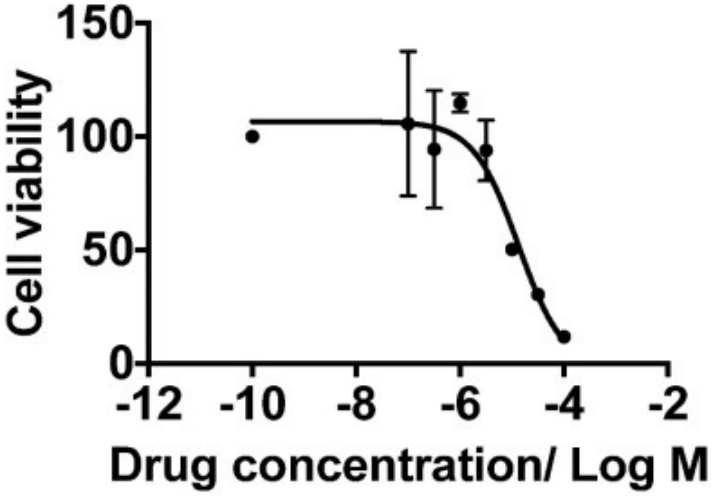

OH
O
O
O
O
N
N
N
COOMe
HO
O
O
ONa

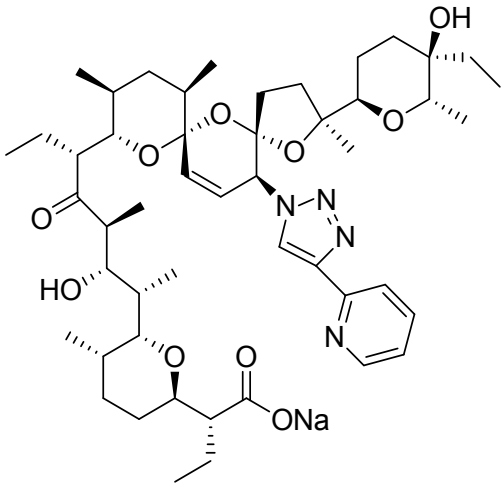
5i


Cell viability
250
200
150
100
50
0
-12
-10
-8
-6
-4
-2
Drug concentration/ Log M

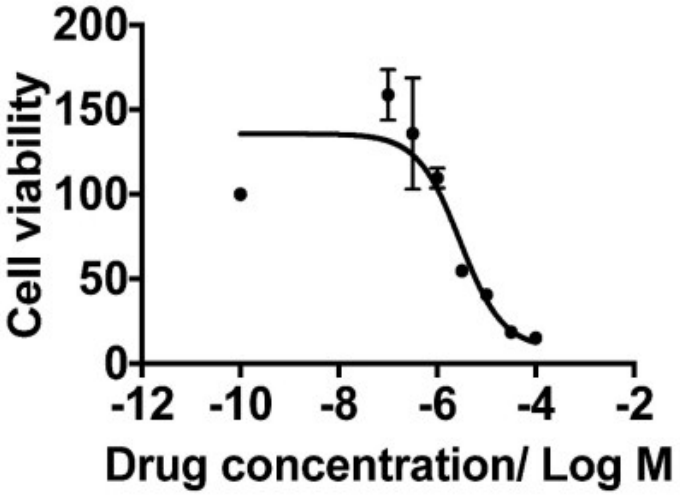

OH
O
O
O
O
N
N
N
HO
NH2
O
O
ONa

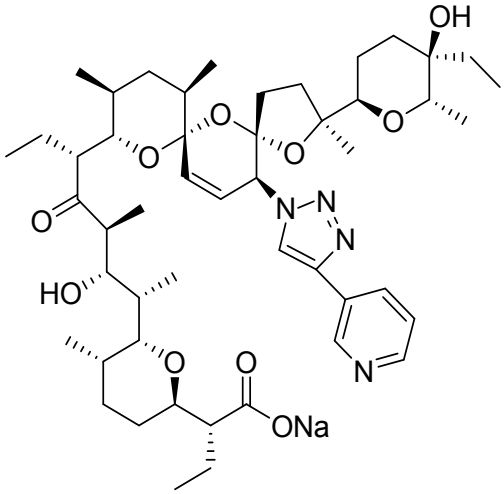
5j


Cell viability
150
100
50
0
-12
-10
-8
-6
-4
-2
Drug concentration/ Log M

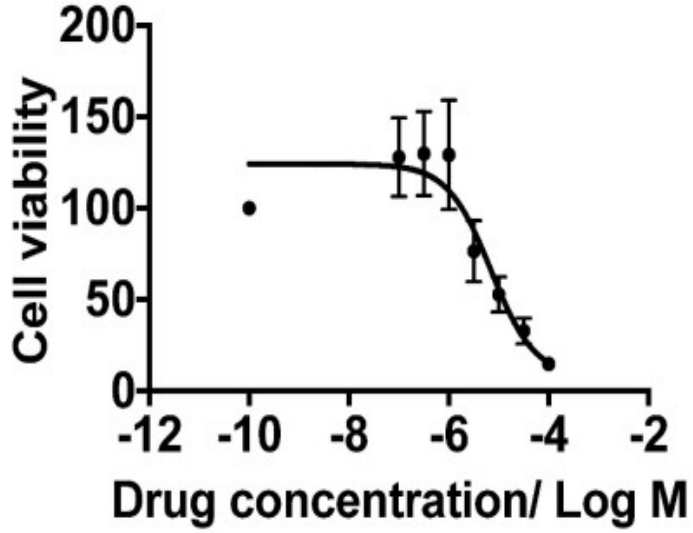

OH
O
O
O
O
N
N
N
HO
O
O
ONa

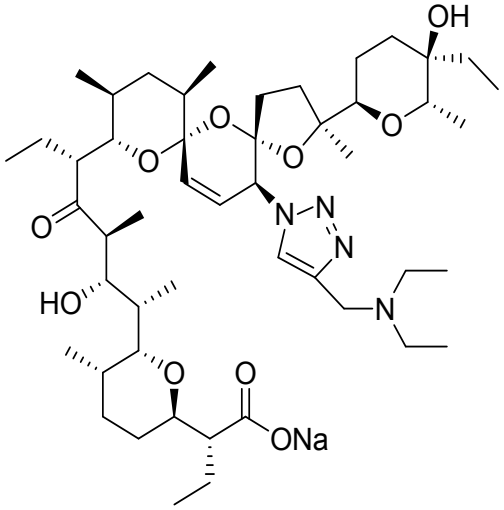
5k


Cell viability
200
150
100
50
0
-12
-10
-8
-6
-4
-2
Drug concentration/ Log M

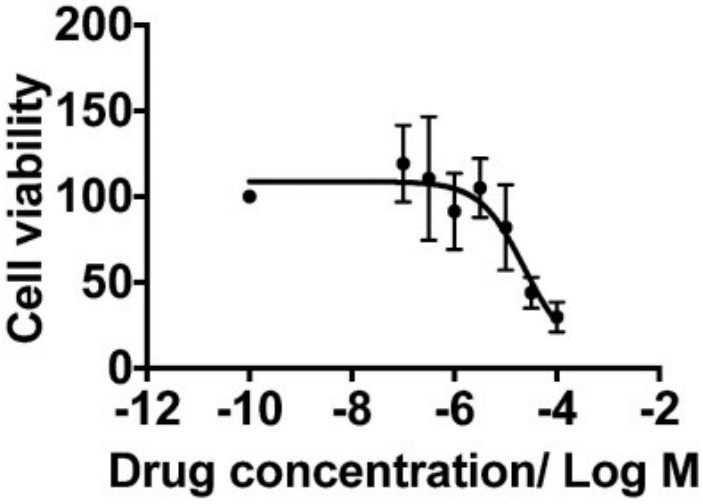

OH
O
O
O
O
N
N
N
HO
O
O
ONa

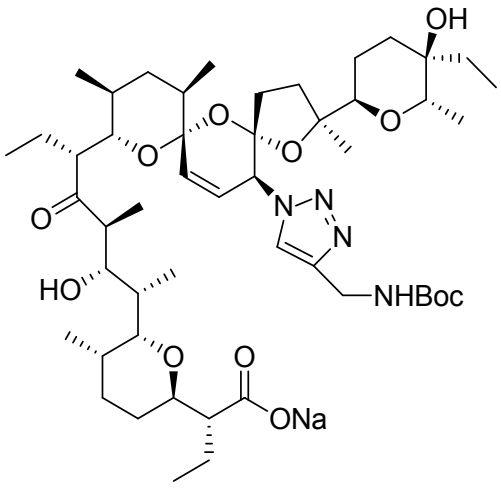
5l


Cell viability
200
150
100
50
0
-12
-10
-8
-6
-4
-2
Drug concentration/ Log M

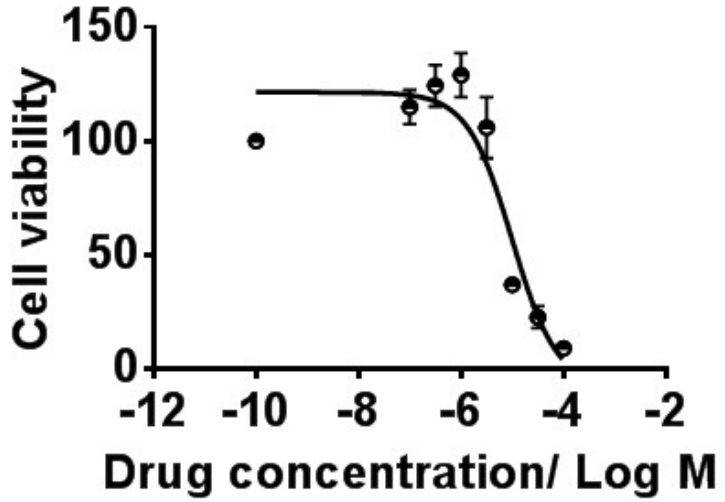

OH
O
O
O
O
N
N
N
HO
O
O
ONa

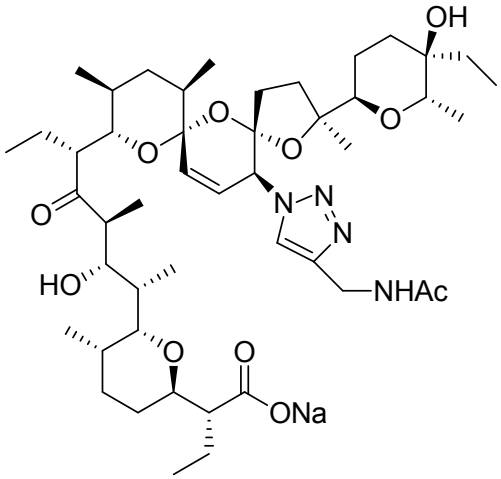
5m


Cell viability
200
150
100
50
0
-12
-10
-8
-6
-4
-2
Drug concentration/ Log M

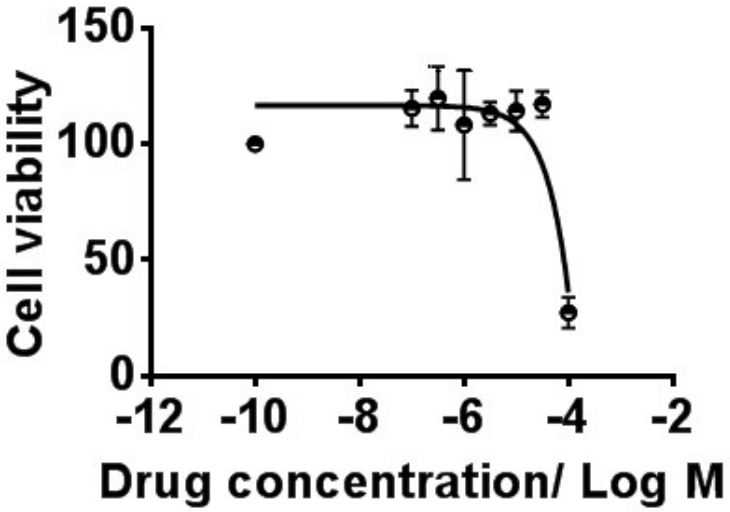

OH
O
O
O
O
N
N
N
HO
NHBoc
O
O
ONa

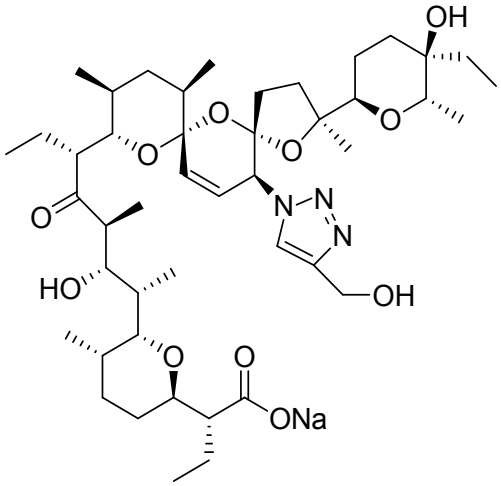
5n


Cell viability
150
100
50
0
-12
-10
-8
-6
-4
-2
Drug concentration/ Log M

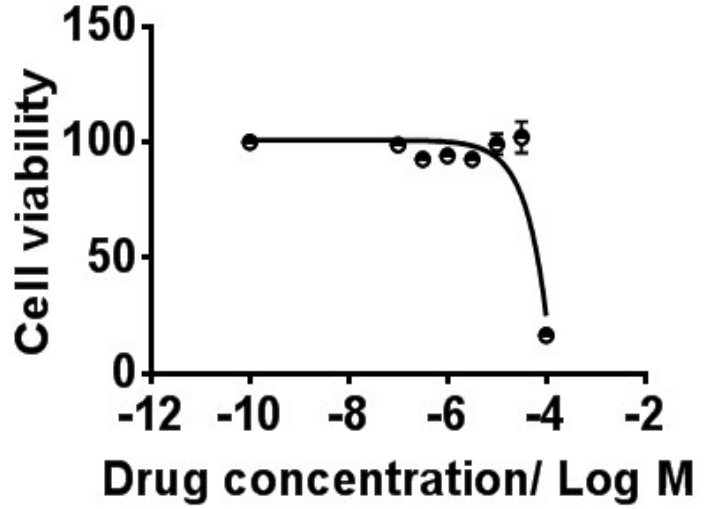

OH
O
O
O
O
N
N
N
HO
NHAc
O
O
ONa

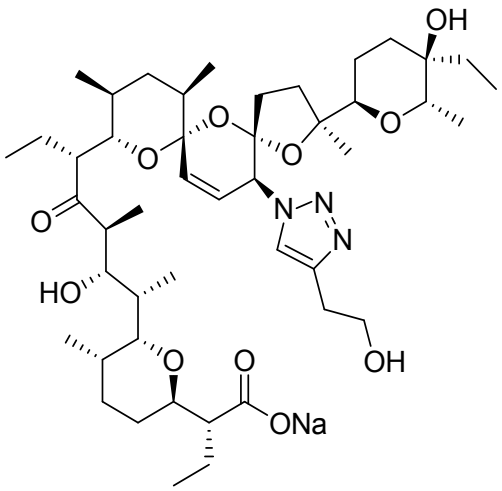
5o


Cell viability
150
100
50
0
-12
-10
-8
-6
-4
-2
Drug concentration/ Log M

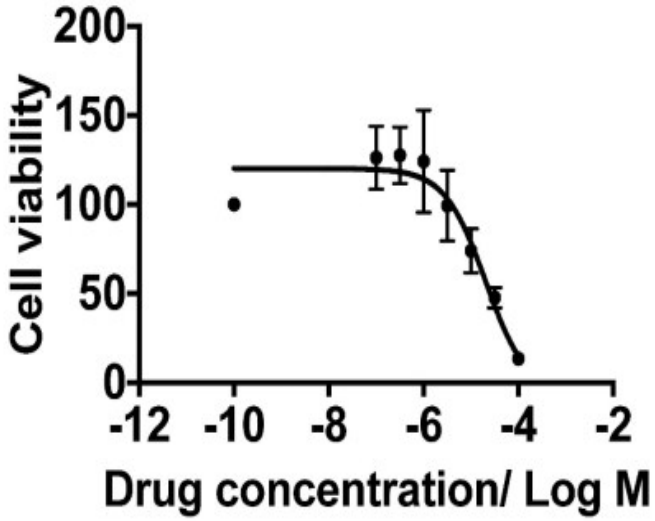

OH
O
O
O
O
N
N
N
HO
OH
O
O
ONa

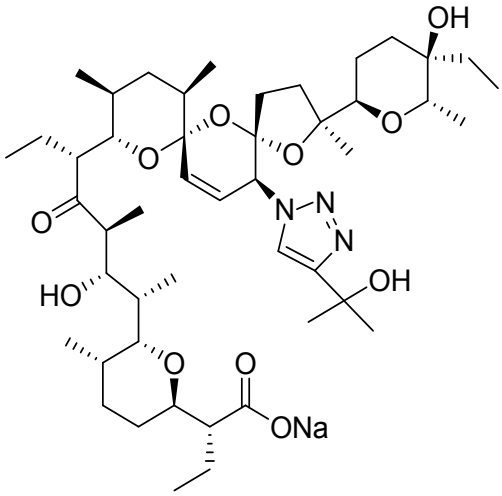
5p


Cell viability
150
100
50
0
-12
-10
-8
-6
-4
-2
Drug concentration/ Log M

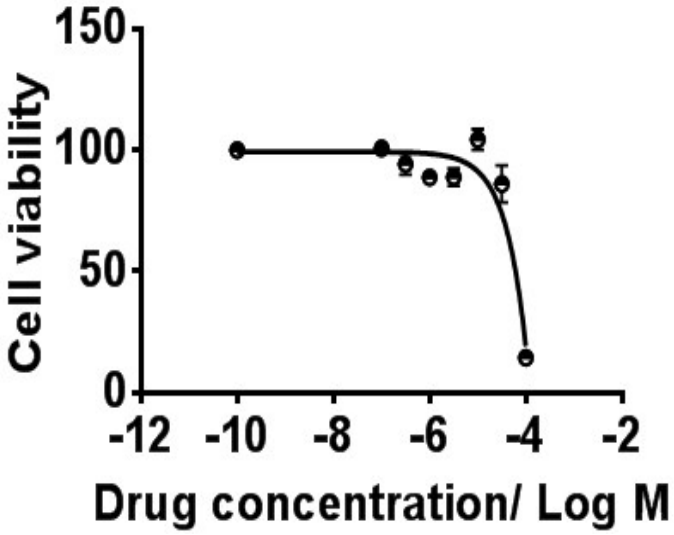

OH
O
O
O
O
N
N
N
HO
O
O
OH
ONa

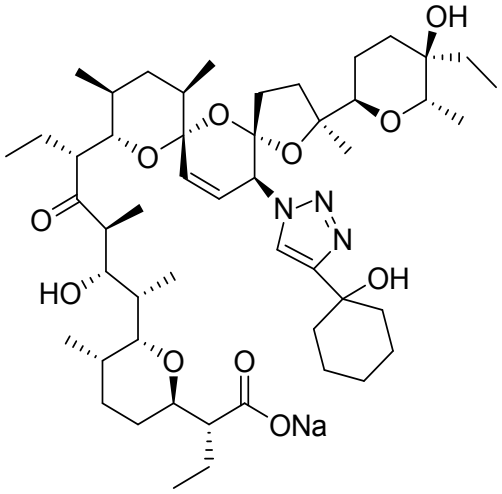
5q


200
150
100
50
0
Cell viability
-12
-10
-8
-6
-4
-2
Drug concentration/ Log M

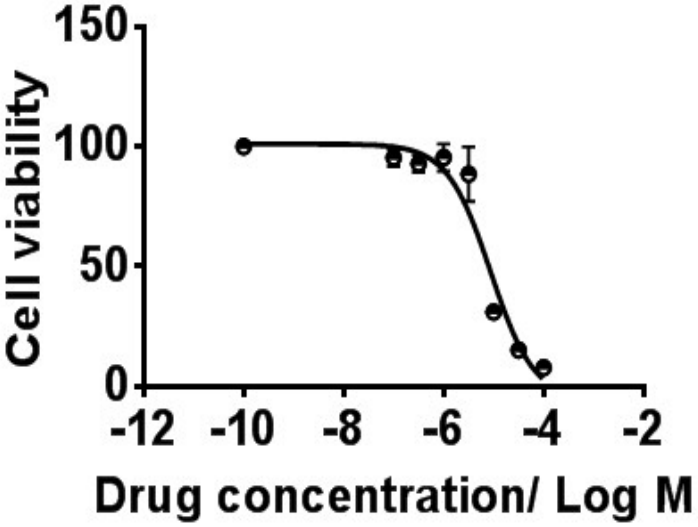

OH
O
O
O
O
N
N
N
HO
OH
O
O
ONa

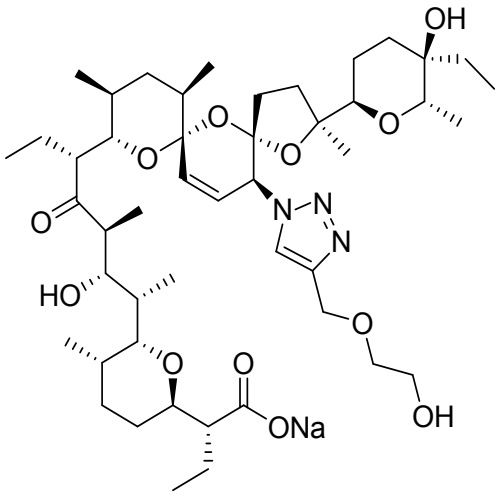
5r


150
100
50
0
Cell viability
-12
-10
-8
-6
-4
-2
Drug concentration/ Log M

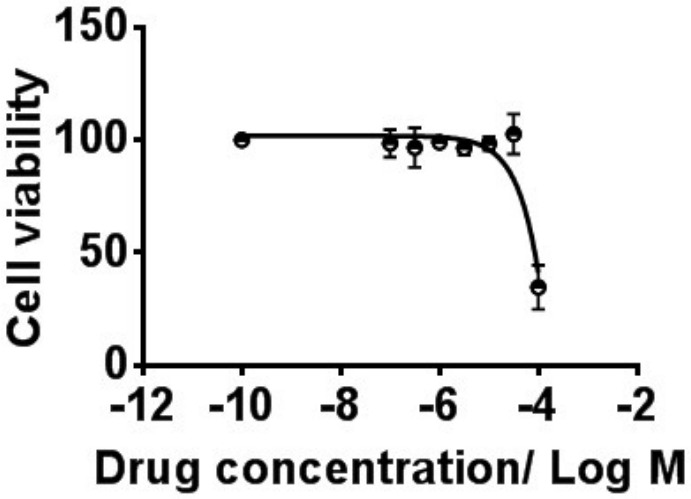

OH
O
O
O
O
N
N
N
HO
OH
O
O
ONa

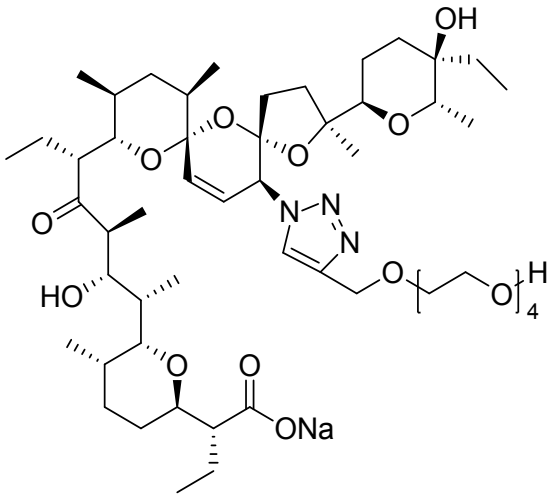
5s


150
100
50
0
Cell viability
-12
-10
-8
-6
-4
-2
Drug concentration/ Log M

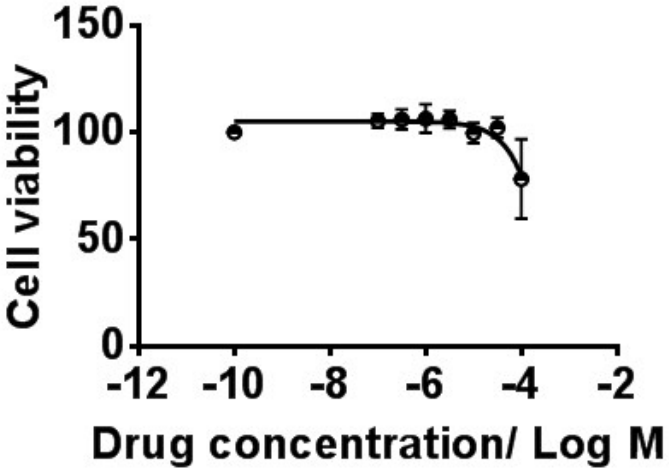

OH
O
O
O
O
N
N
N
HO
O
O
O
ONa
O
OH

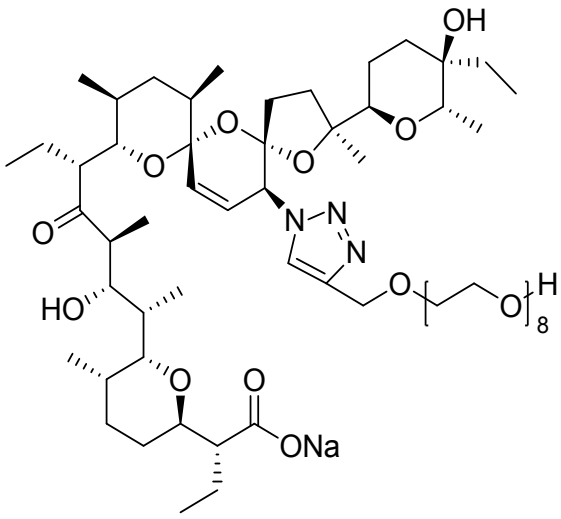
5t


Cell viability
150
100
50
0
-12
-10
-8
-6
-4
-2
Drug concentration/ Log M

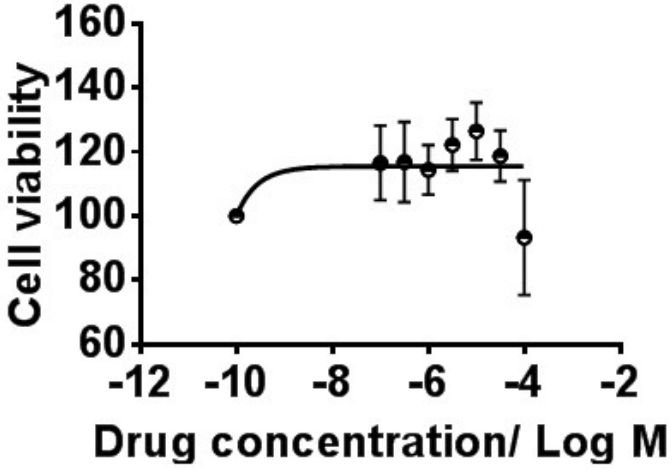

OH
O
O
O
O
N
N
N
HO
O
O
O
ONa
O
H
4

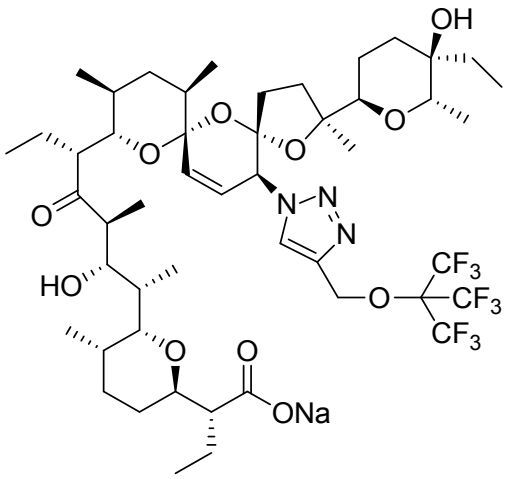
5u


Cell viability
150
100
50
0
-12
-10
-8
-6
-4
-2
Drug concentration/ Log M

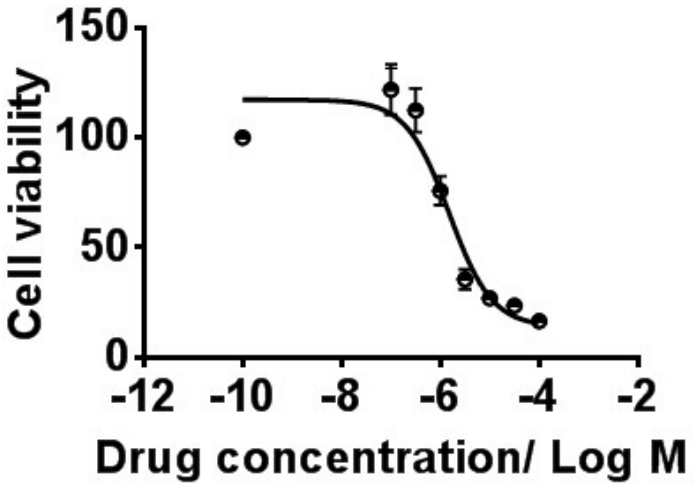

OH
O
O
O
O
N
N
N
HO
O
O
O
ONa
O
H
8

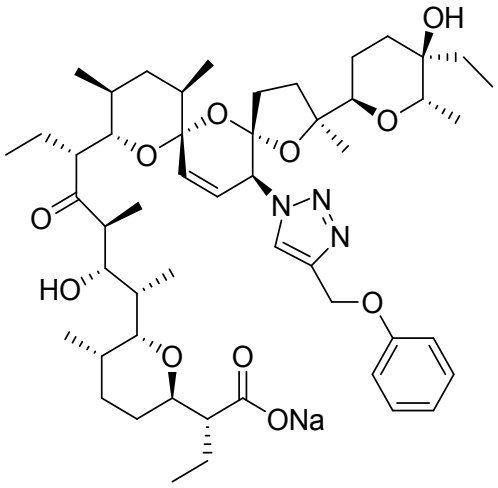
5v


Cell viability
160
140
120
100
80
60
-12
-10
-8
-6
-4
-2
Drug concentration/ Log M

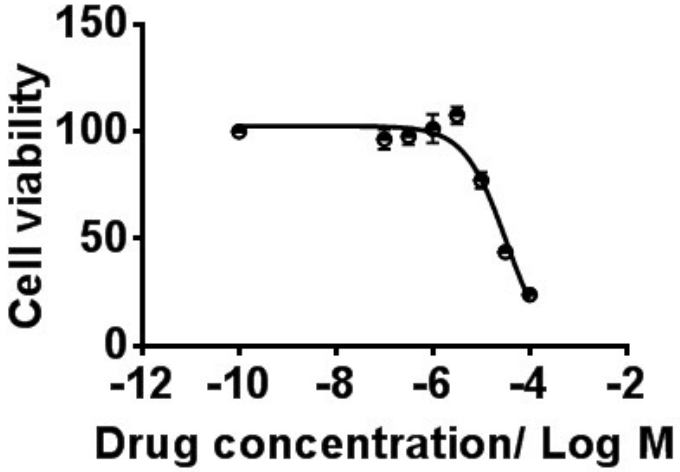

OH
O
O
O
O
N
N
N
HO
CF3
CF3
CF3
O
O
O
ONa

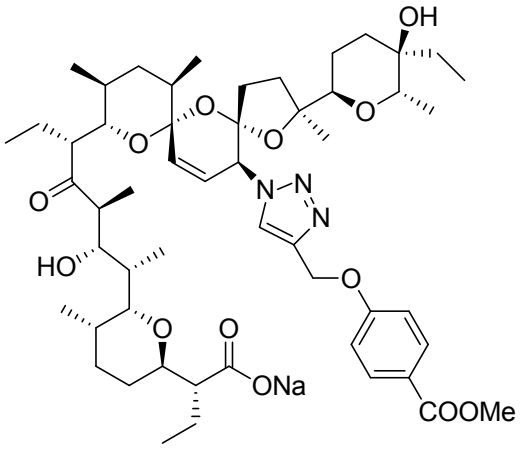
5w


Cell viability
150
100
50
0
-12
-10
-8
-6
-4
-2
Drug concentration/ Log M

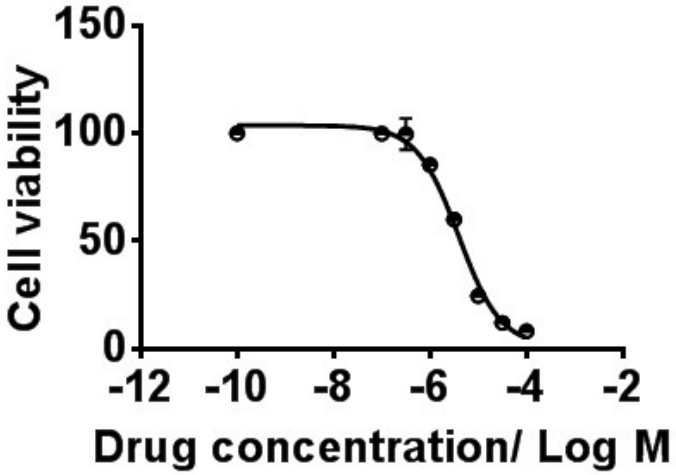

OH
O
O
O
O
N
N
N
HO
O
O
O
ONa

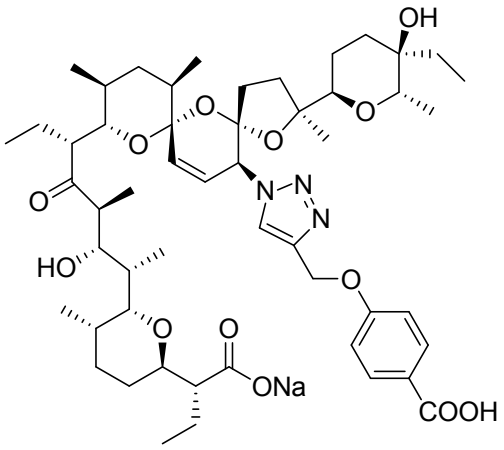
5x


Cell viability
150
100
50
0
-12
-10
-8
-6
-4
-2
Drug concentration/ Log M

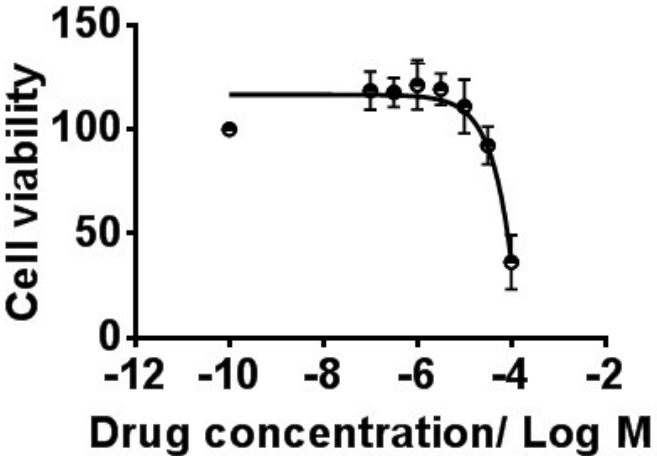

OH
O
O
O
O
N
N
N
HO
O
O
O
ONa
COOMe

5y


Cell viability
150
100
50
0
-12
-10
-8
-6
-4
-2
Drug concentration/ Log M

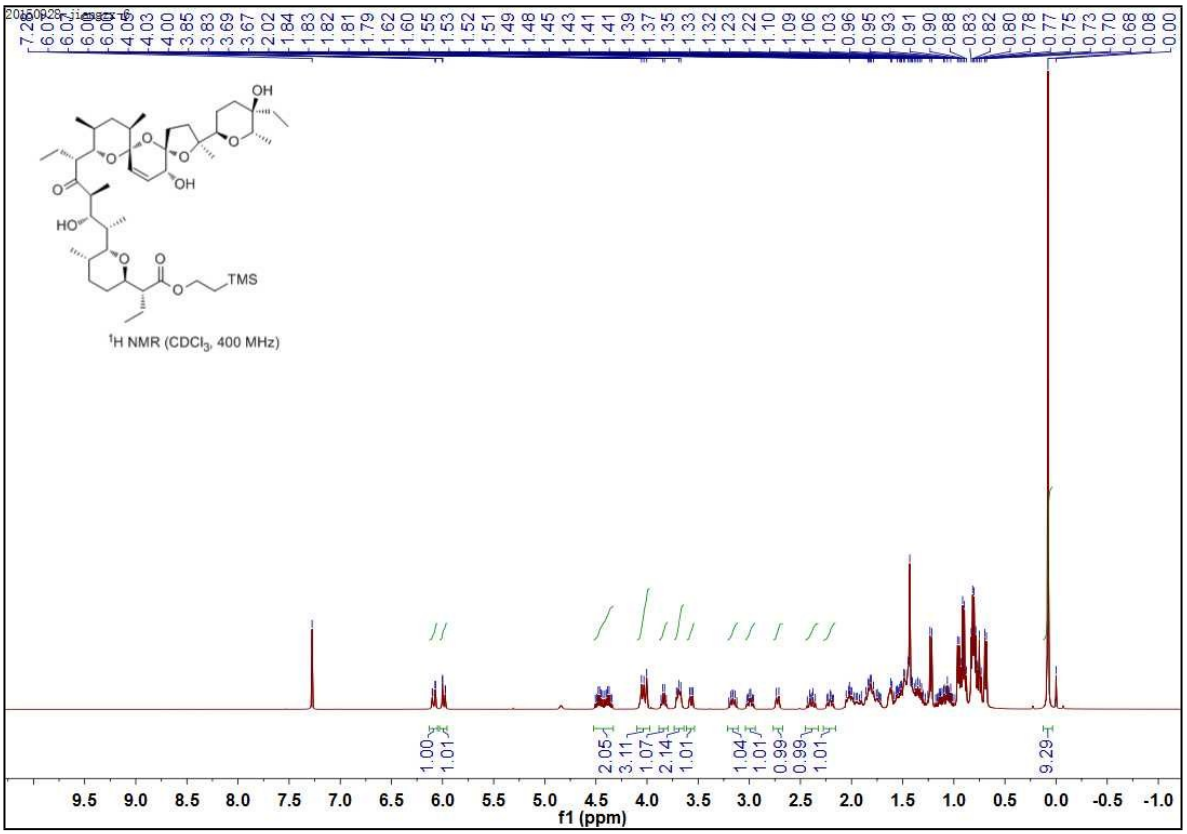

OH
O
O
O
O
N
N
N
O
HO
O
O
ONa
COOH

5z

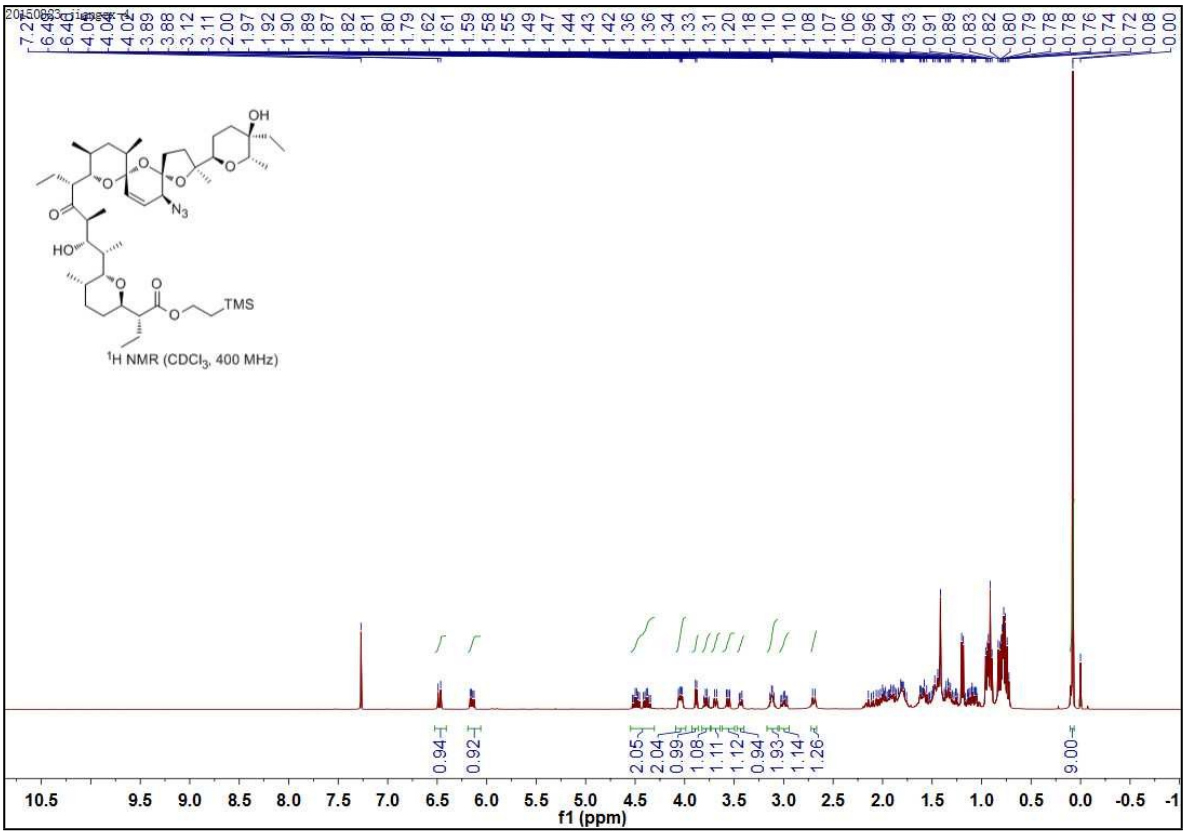

Cell viability
150
100
50
0
-12
-10
-8
-6
-4
-2
Drug concentration/ Log M

4. Copies of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, IR, and HRMS spectra of compounds

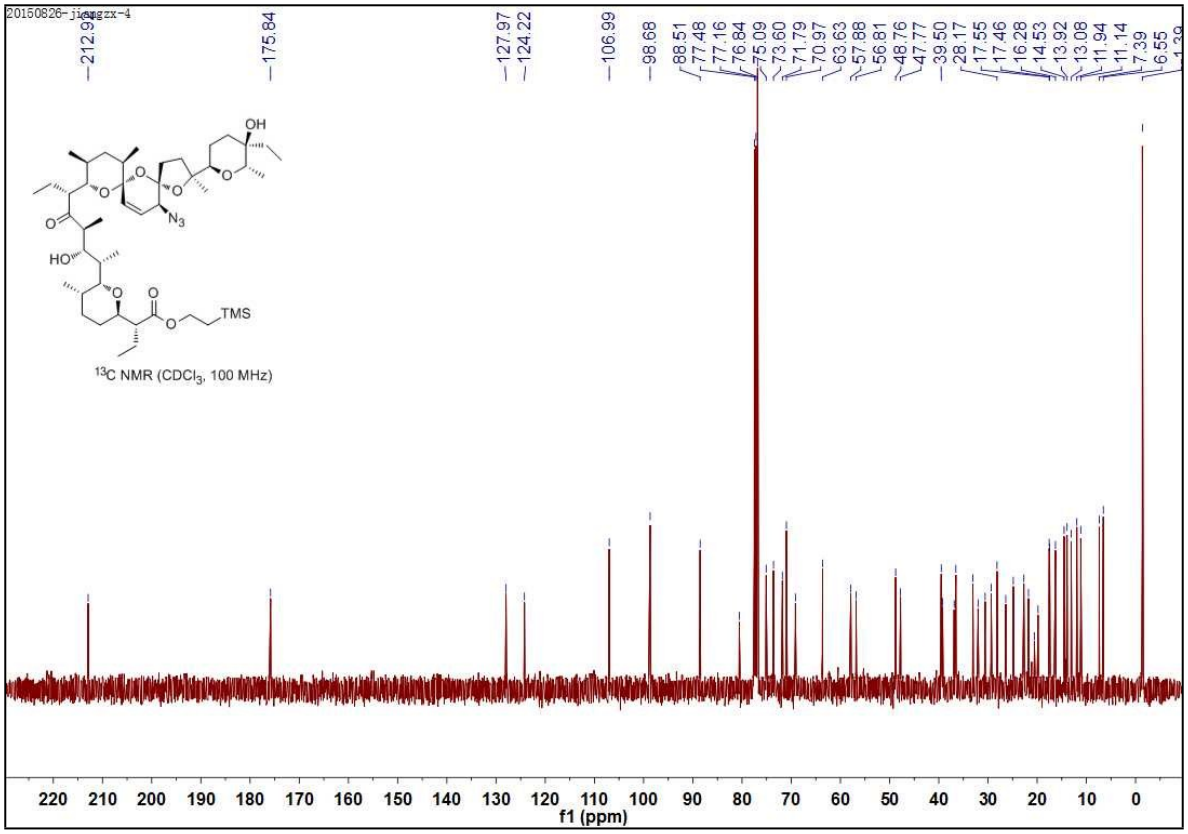
^{1}H NMR of compound **2**



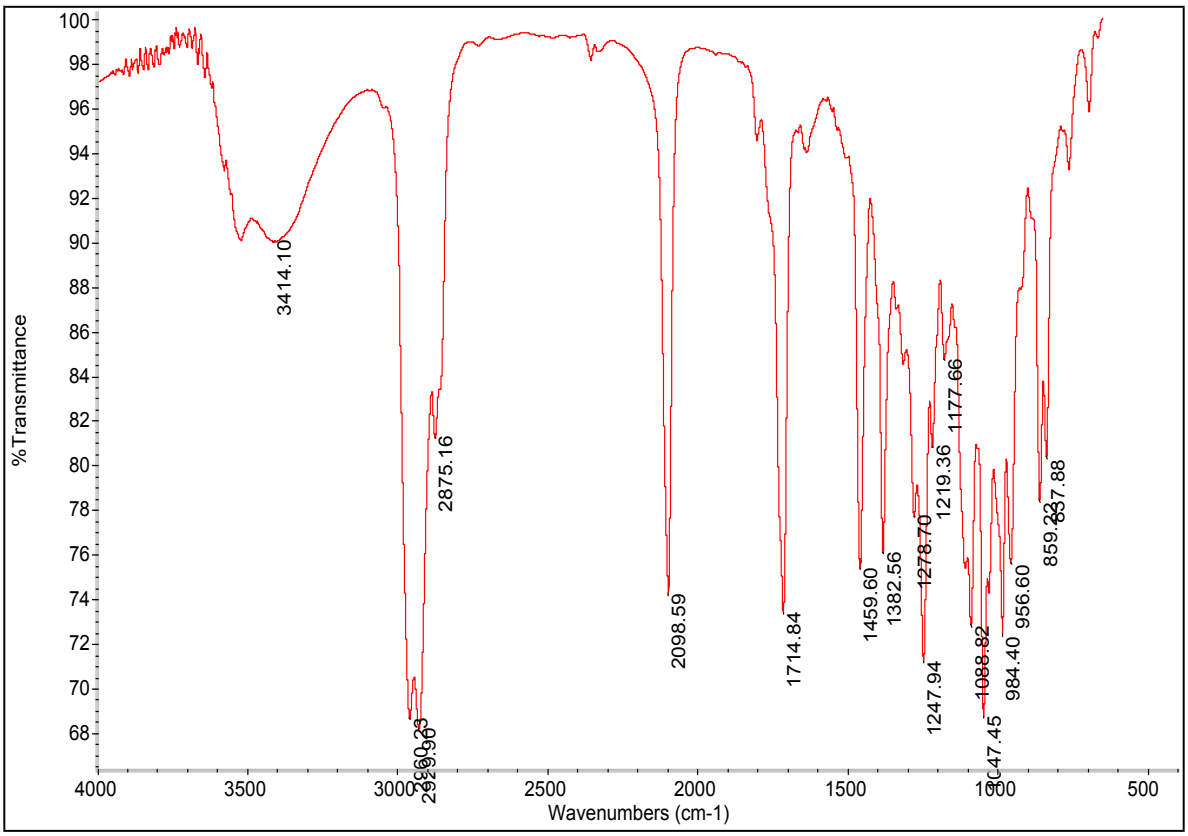
^{1}H NMR of compound **3**



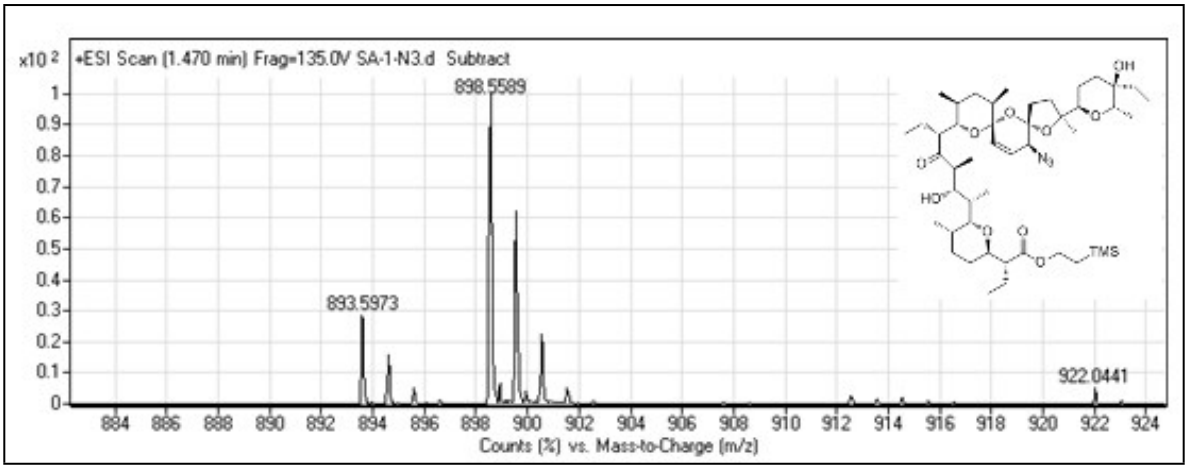
^{13}C NMR of compound **3**



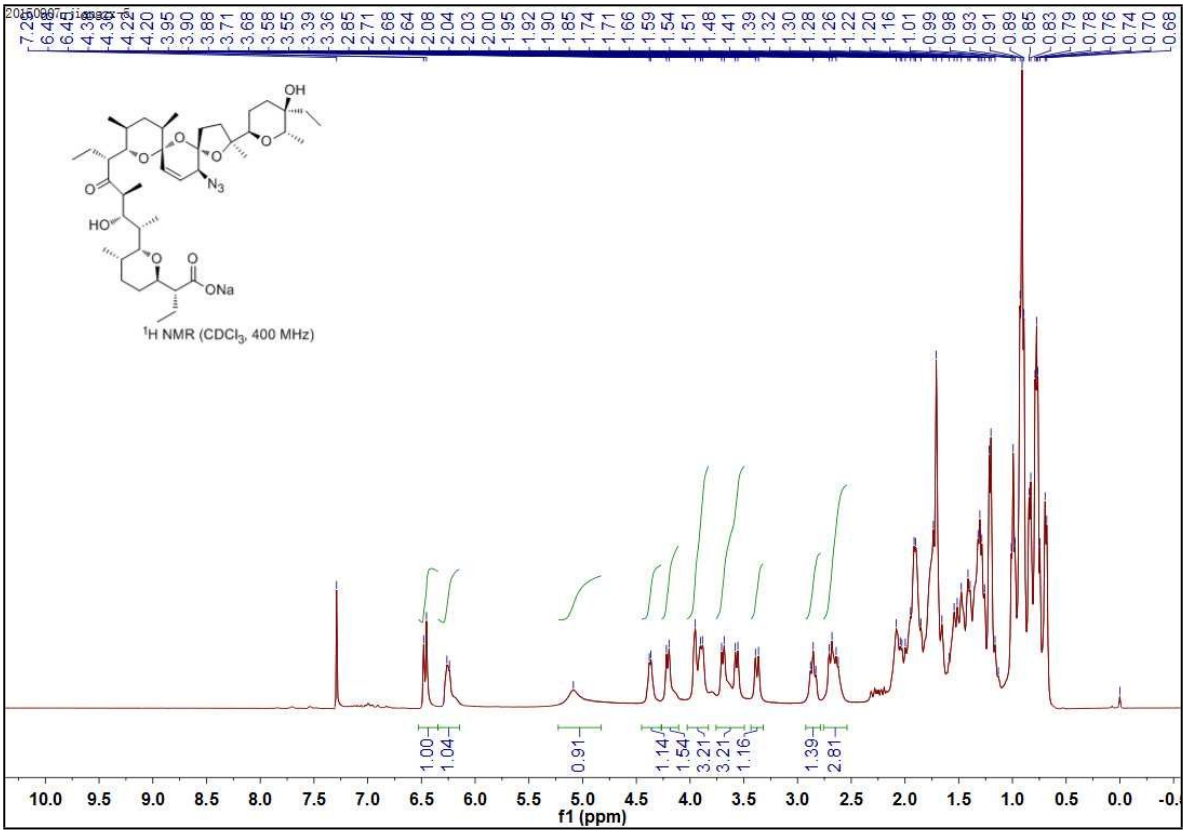
IR (KBr) of compound **3**



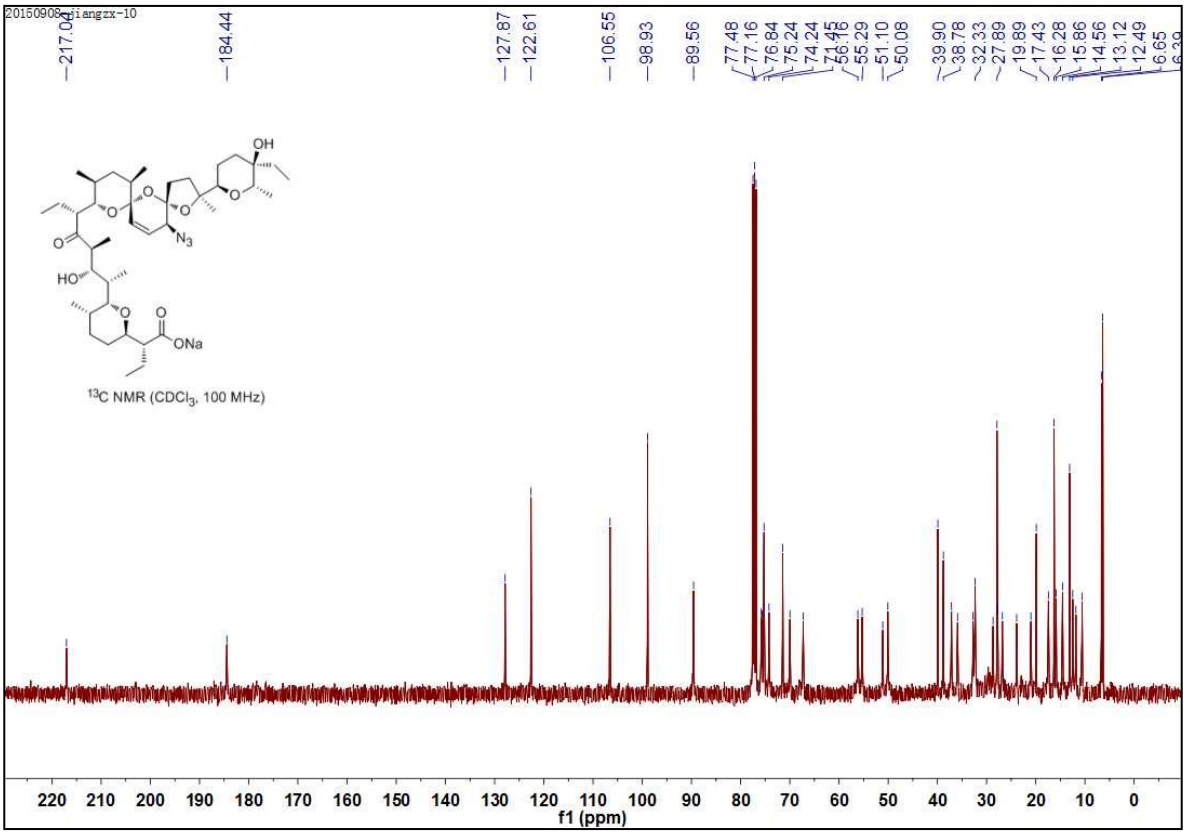
HRMS of compound **3**



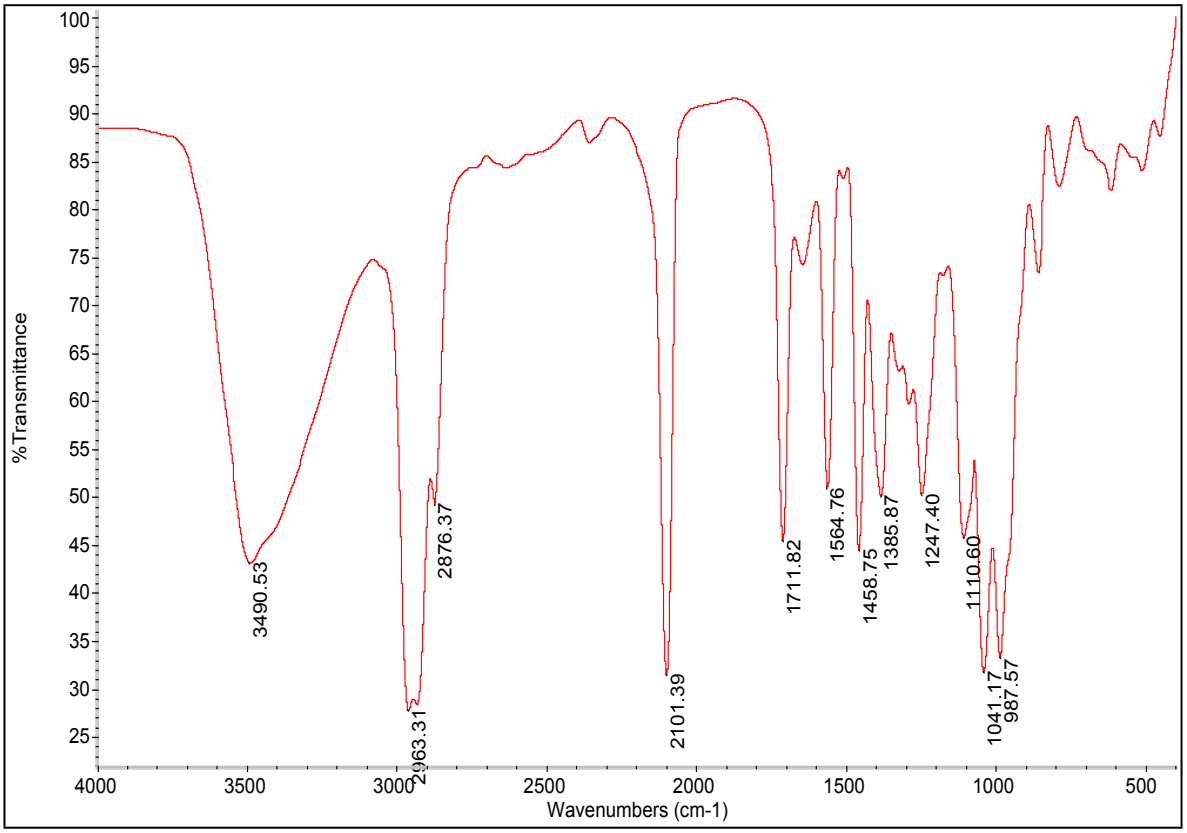
^{1}H NMR of compound **4**



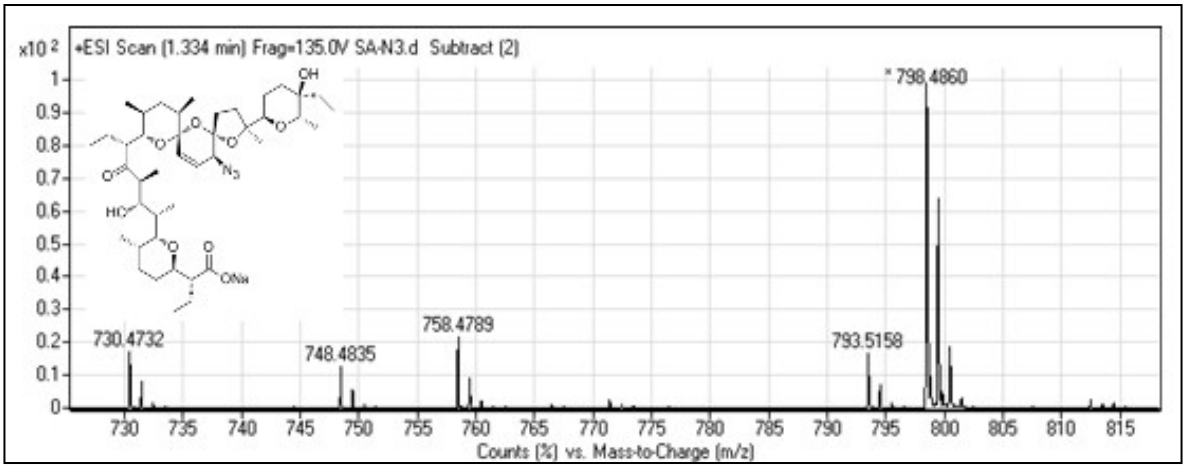
^{13}C NMR of compound **4**



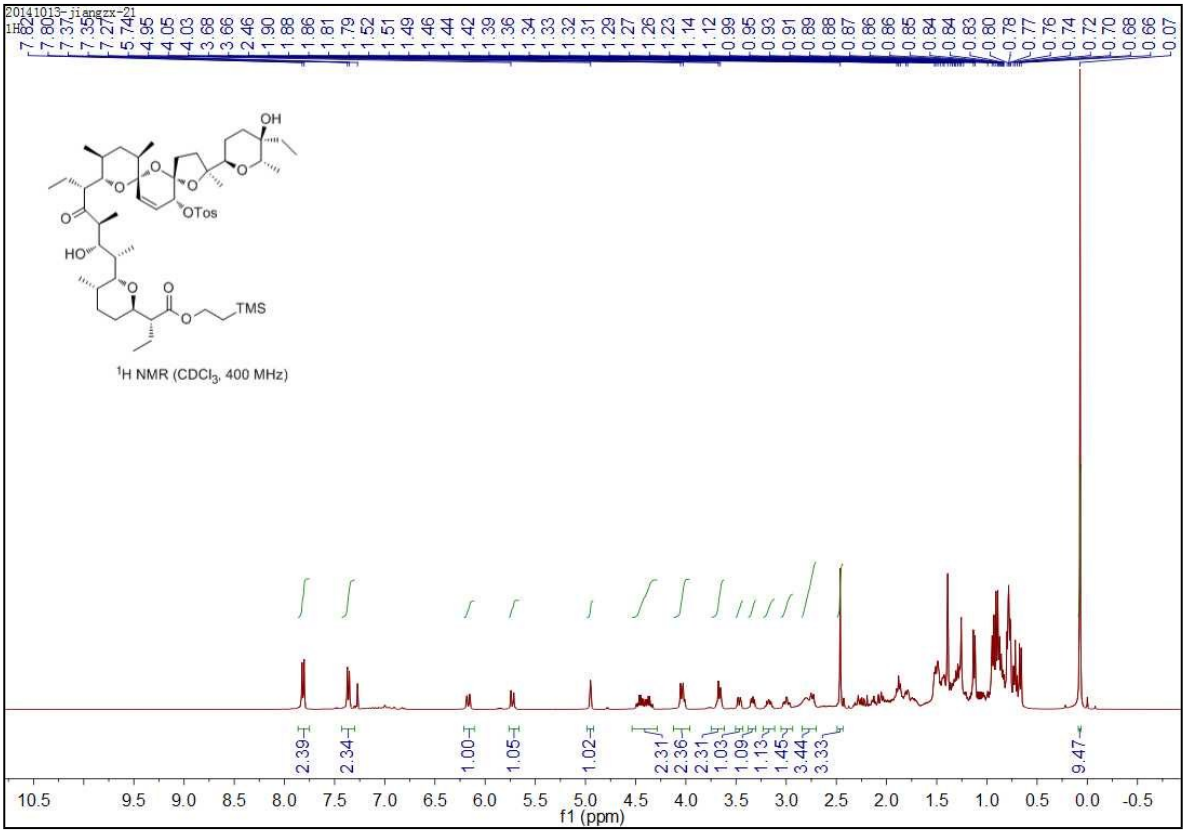
IR (KBr) of compound **4**



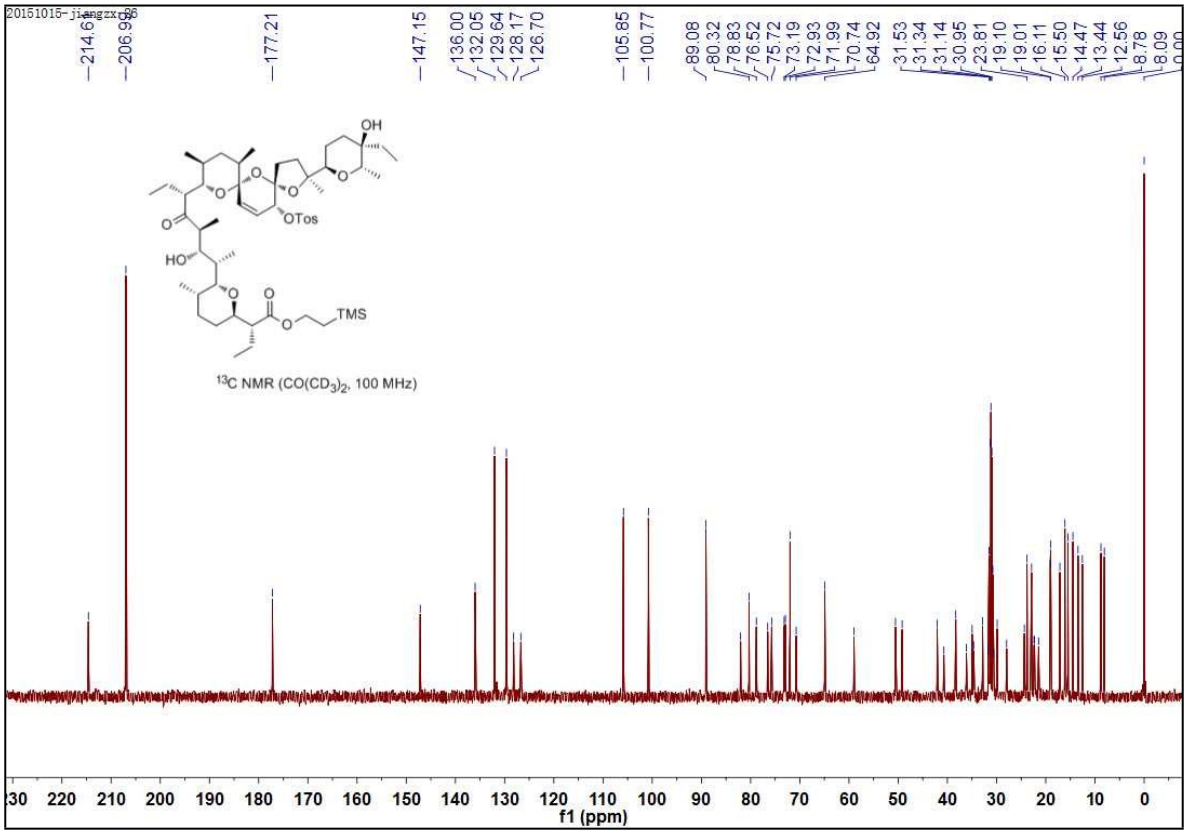
HRMS of compound **4**



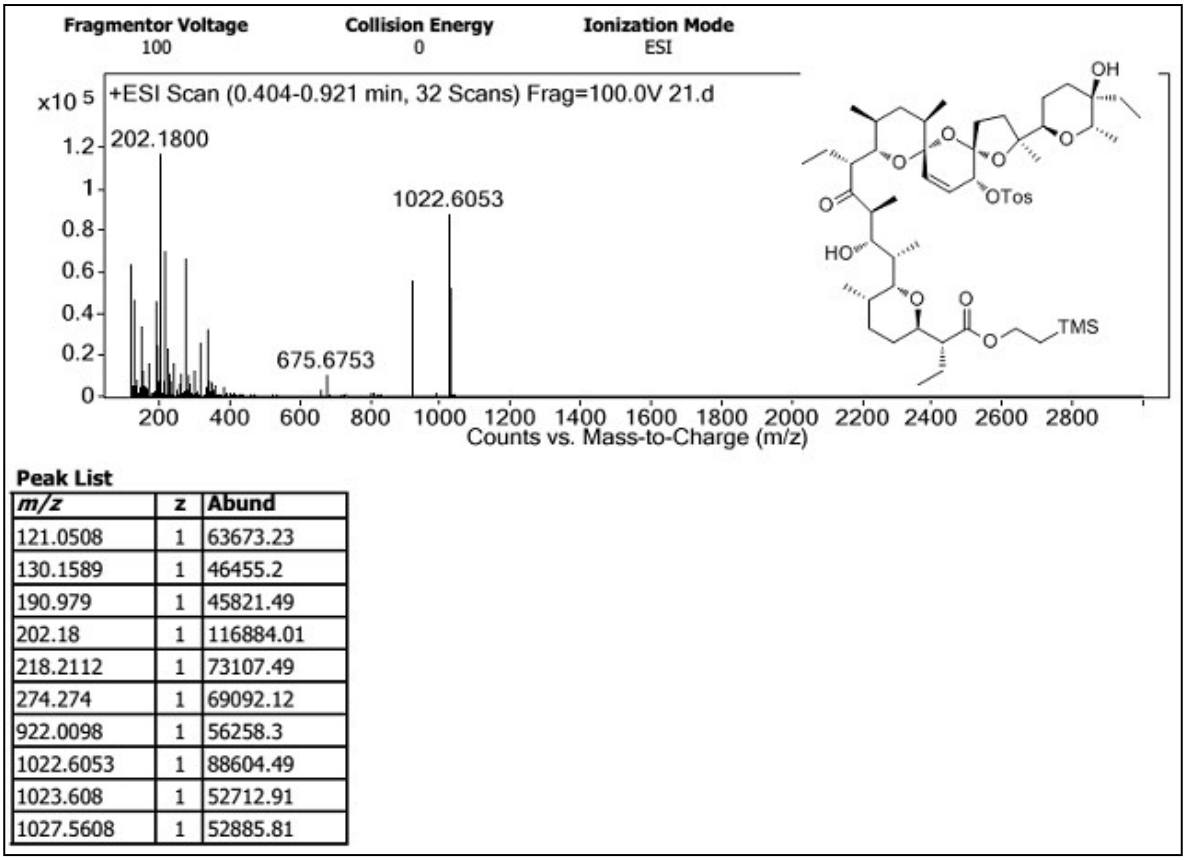
^{1}H NMR of compound **S1**



^{13}C NMR of compound **S1**



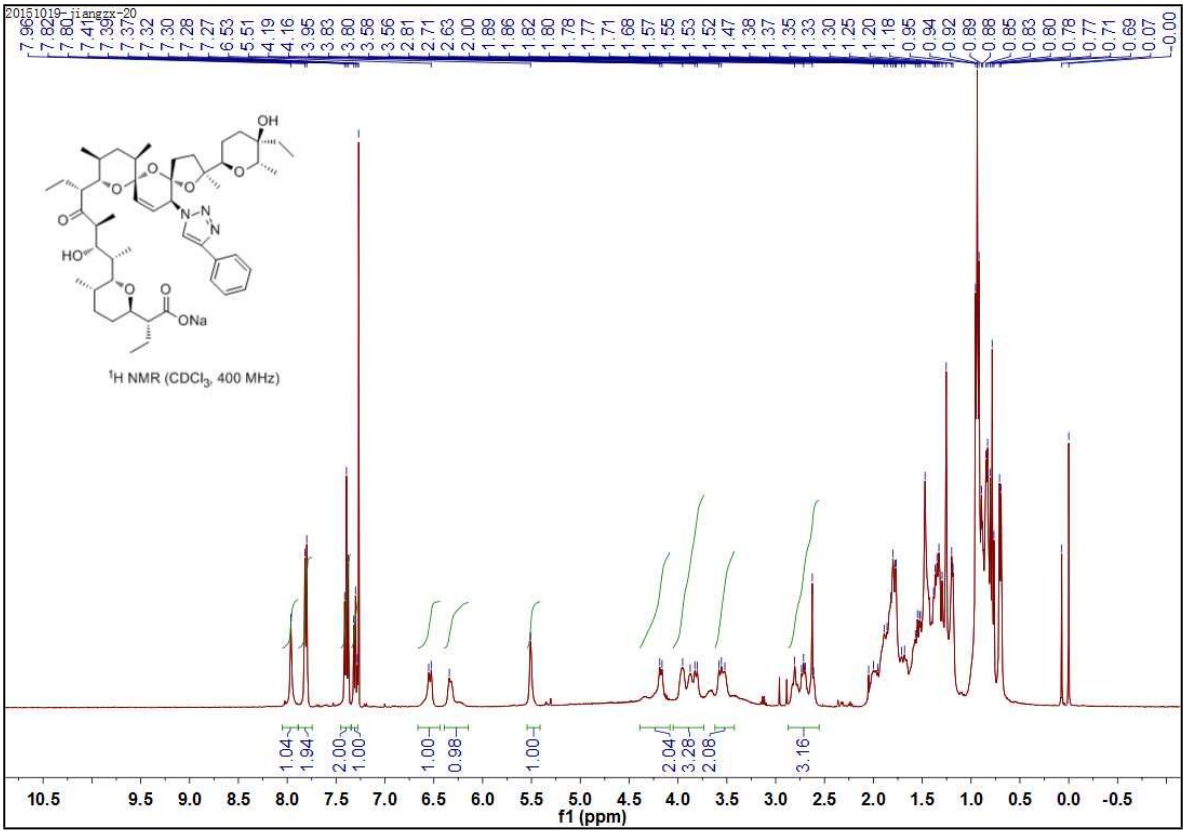
HRMS of compound **S1**



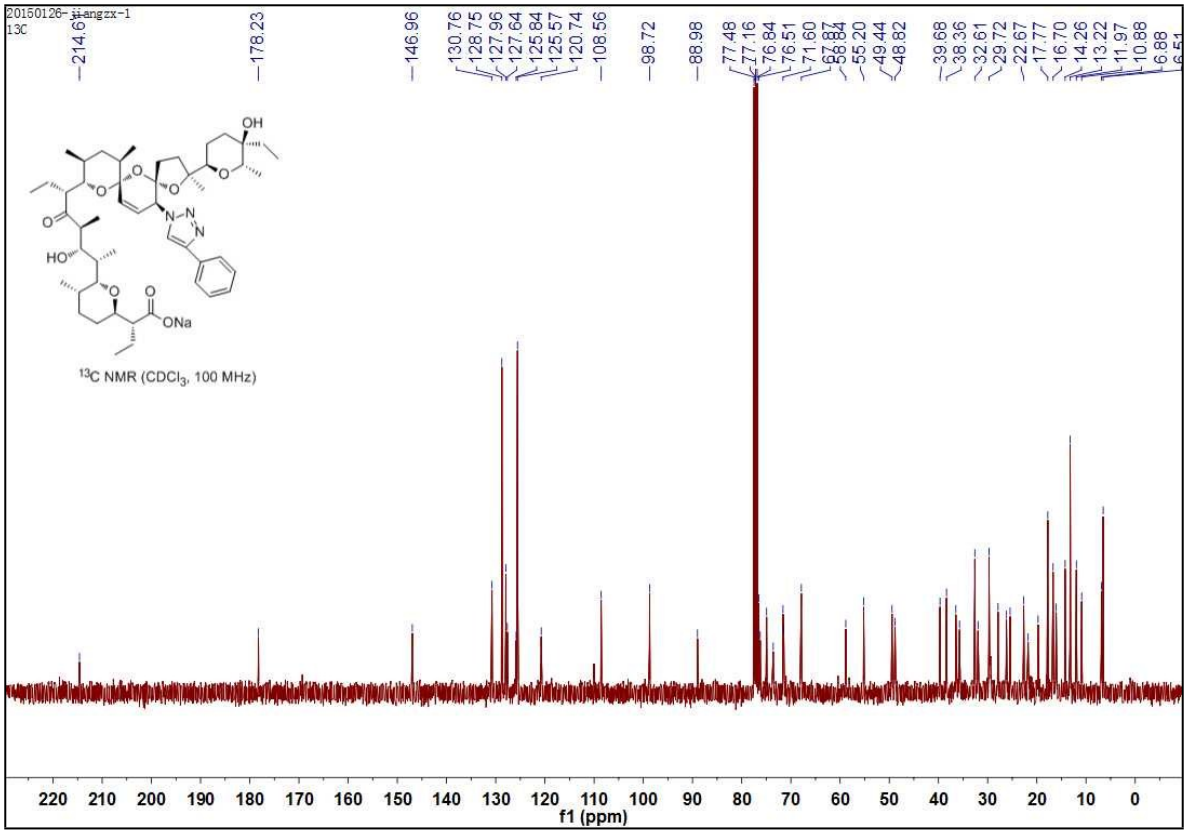
Peak List

m/z	z	Abund
121.0508	1	63673.23
130.1589	1	46455.2
190.979	1	45821.49
202.18	1	116884.01
218.2112	1	73107.49
274.274	1	69092.12
922.0098	1	56258.3
1022.6053	1	88604.49
1023.608	1	52712.91
1027.5608	1	52885.81

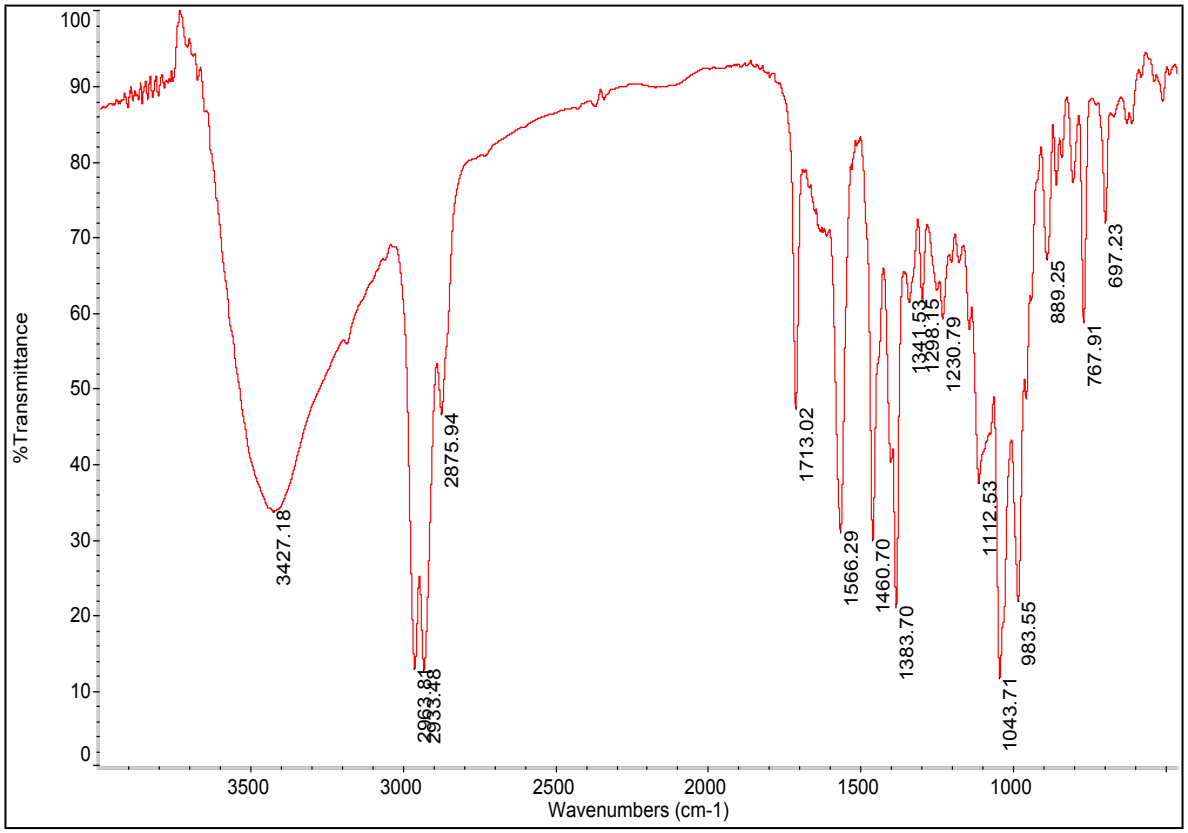
^{1}H NMR of compound **5a**



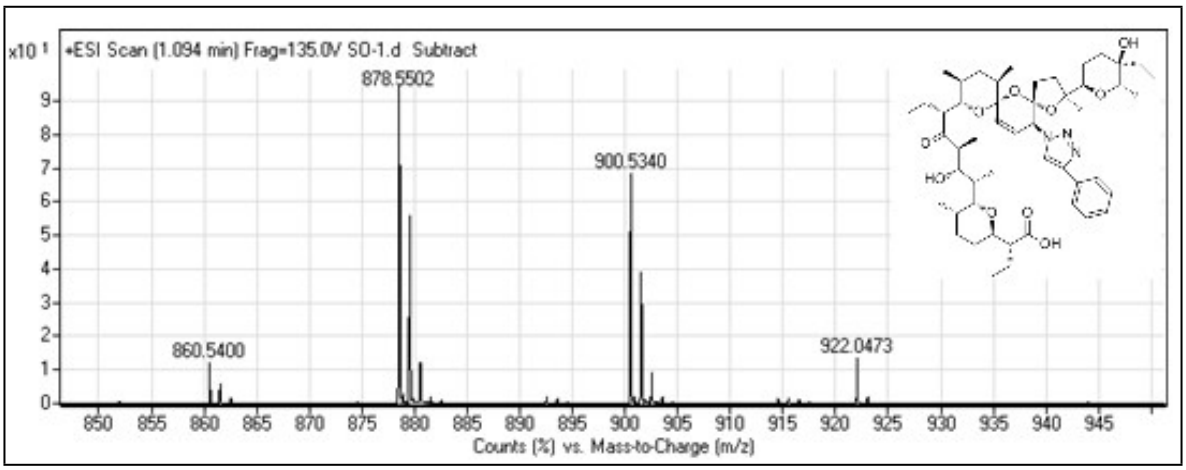
^{13}C NMR of compound **5a**



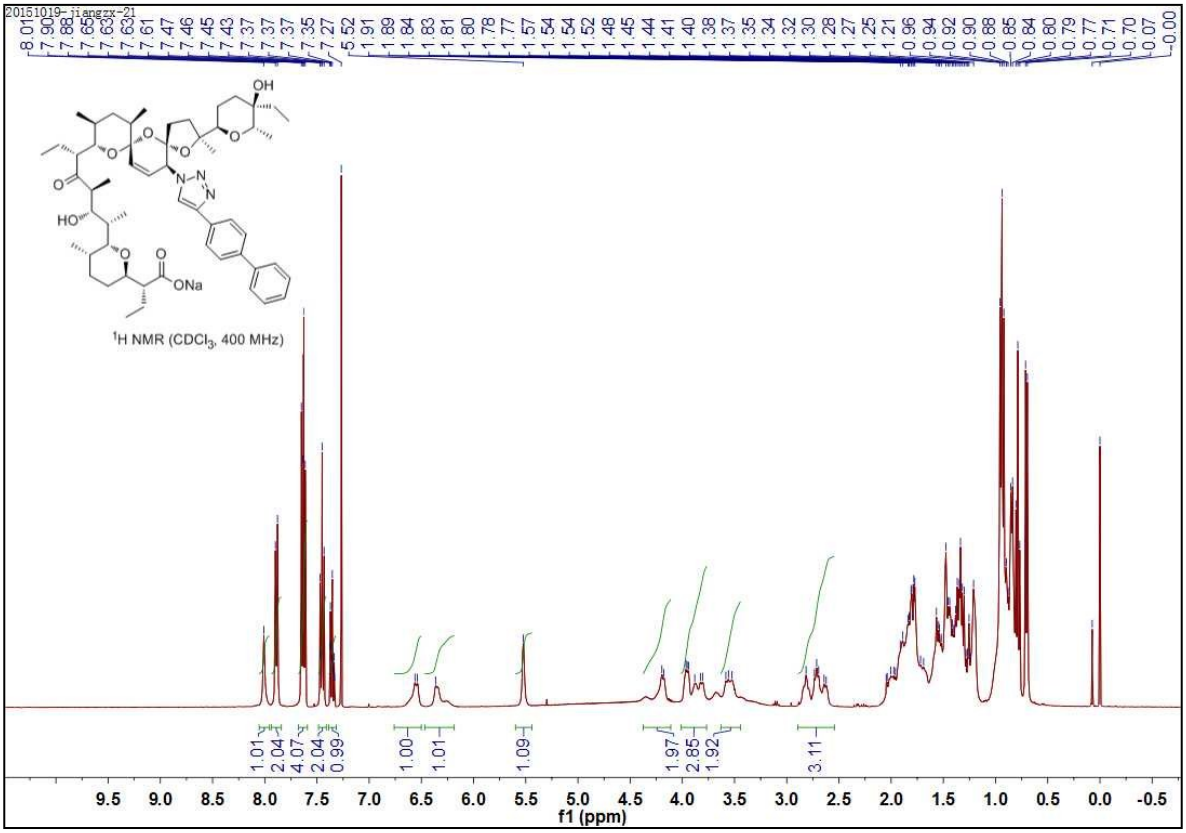
IR (KBr) of compound **5a**



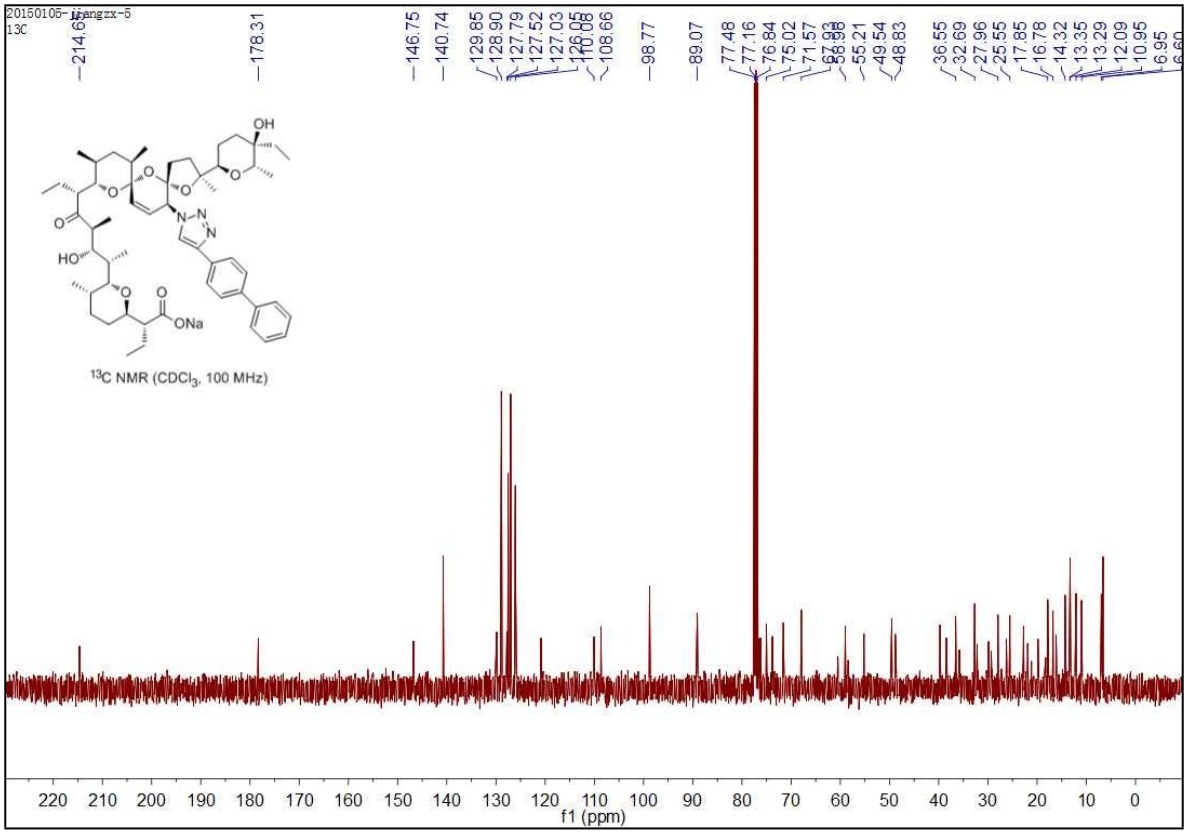
HRMS of compound **5a**



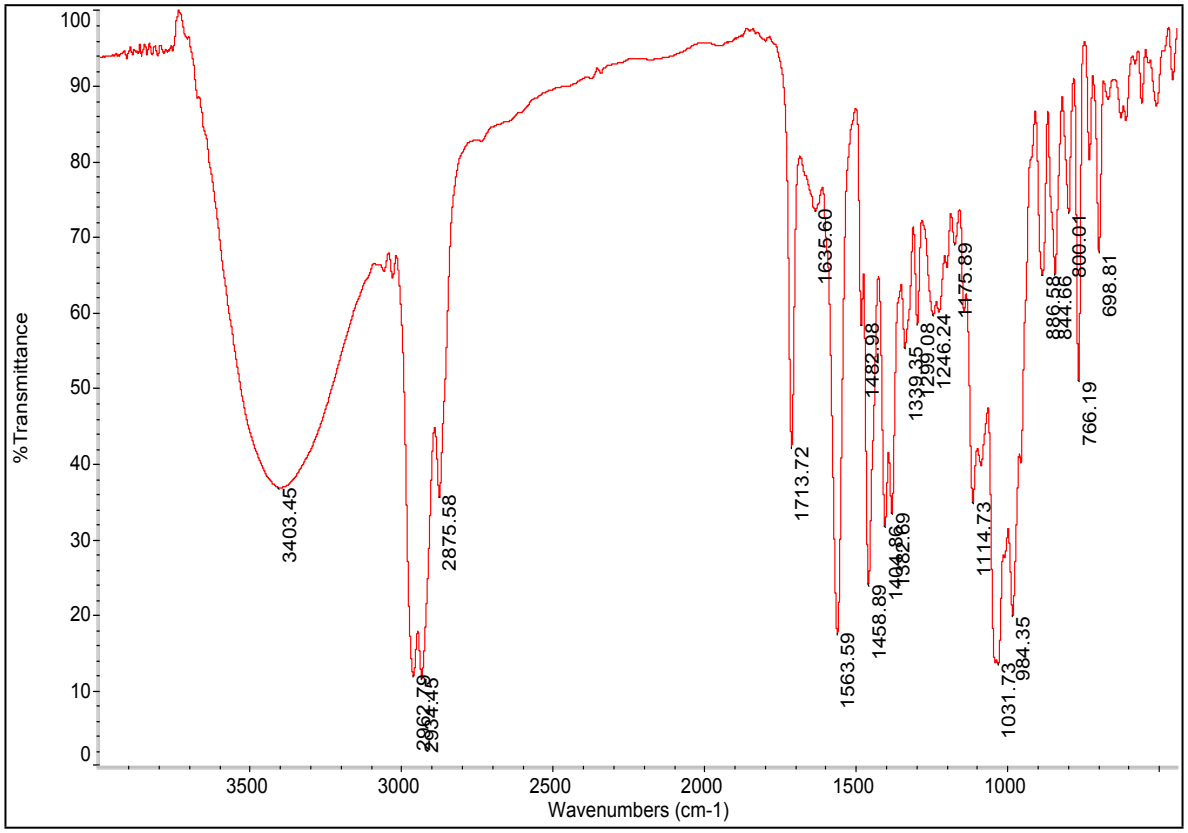
^{1}H NMR of compound **5b**



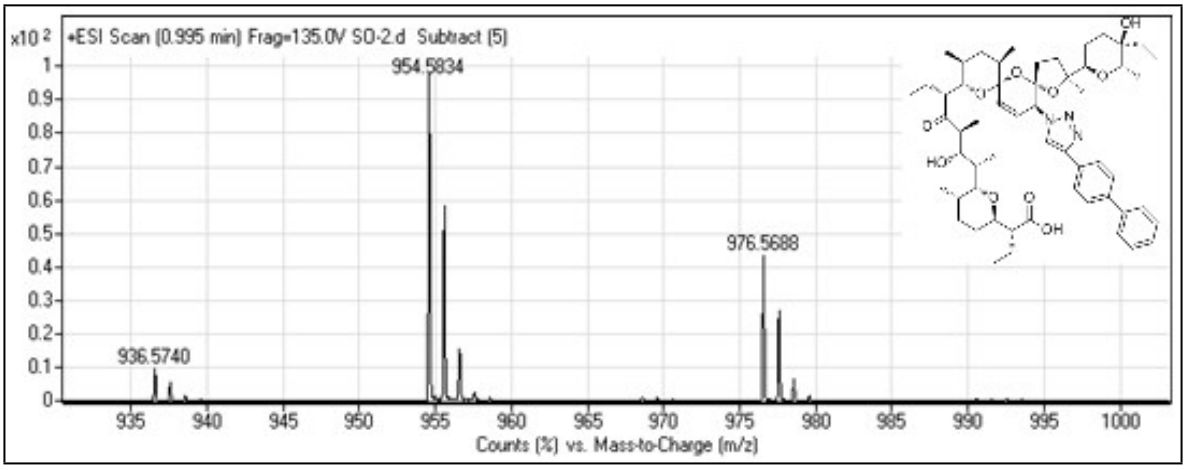
^{13}C NMR of compound **5b**



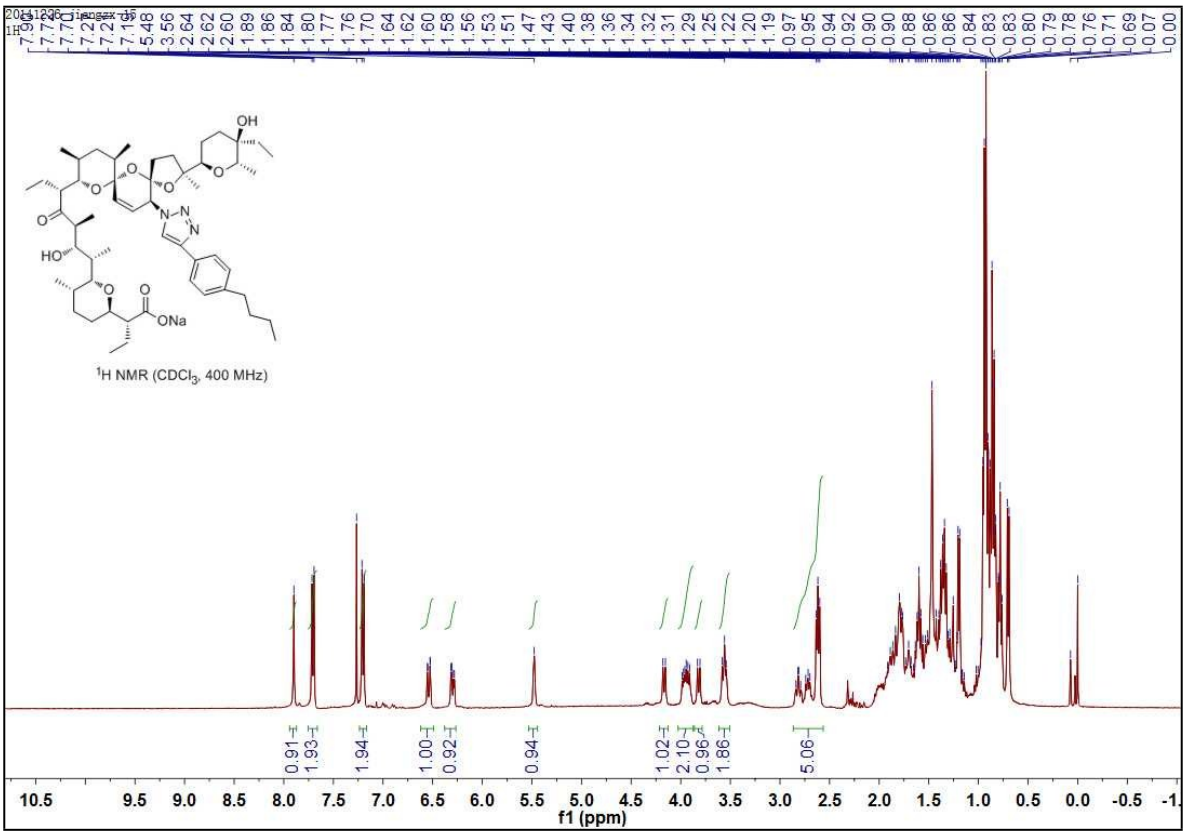
IR (KBr) of compound **5b**



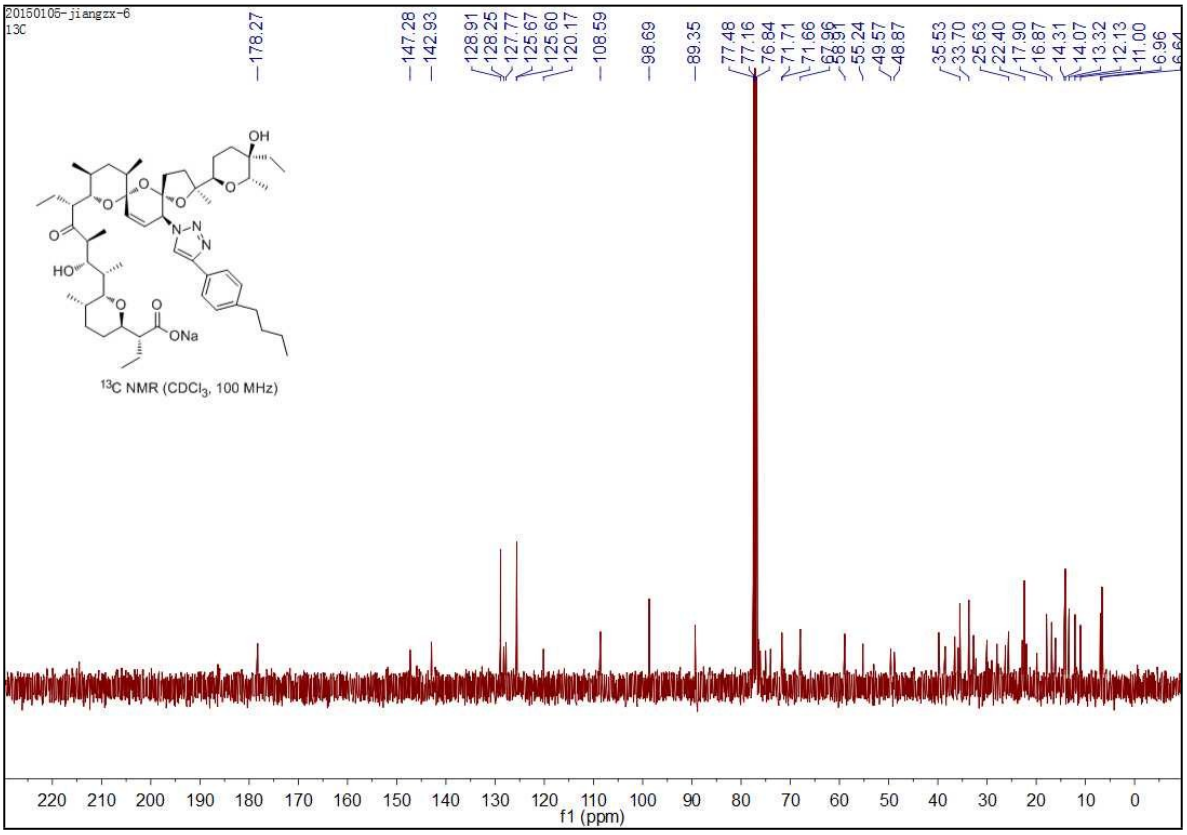
HRMS of compound **5b**



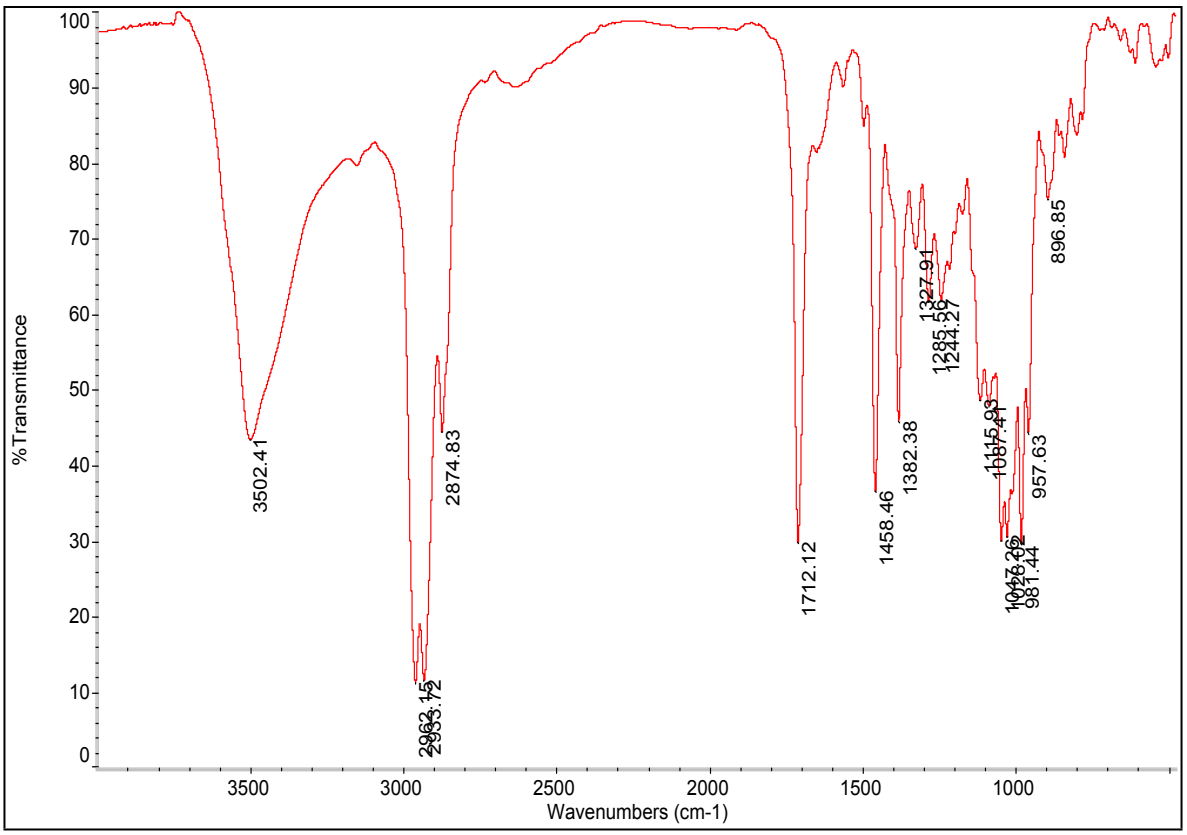
^{1}H NMR of compound **5c**



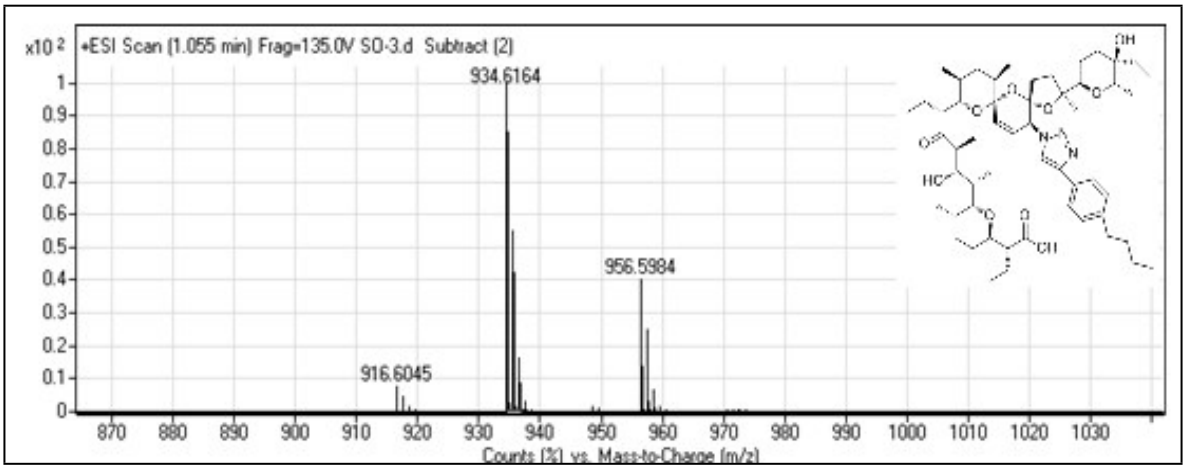
^{13}C NMR of compound **5c**



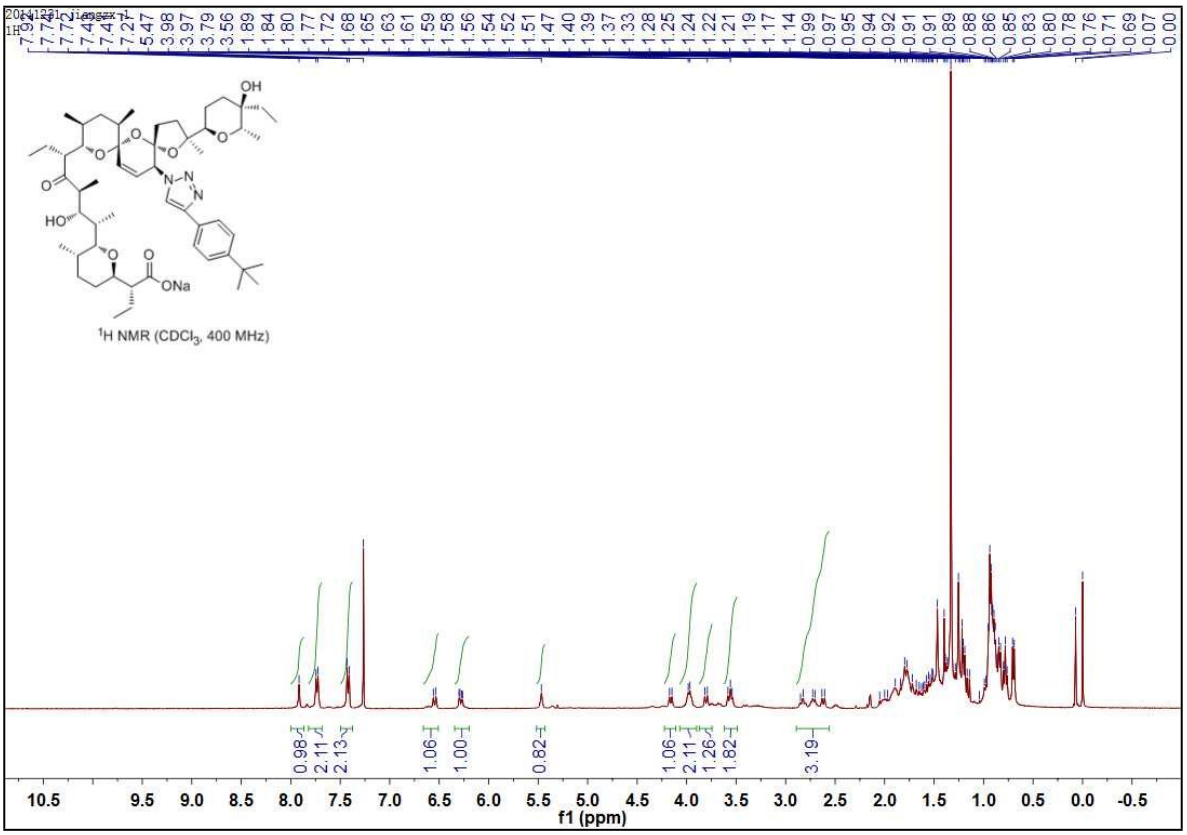
IR (KBr) of compound **5c**



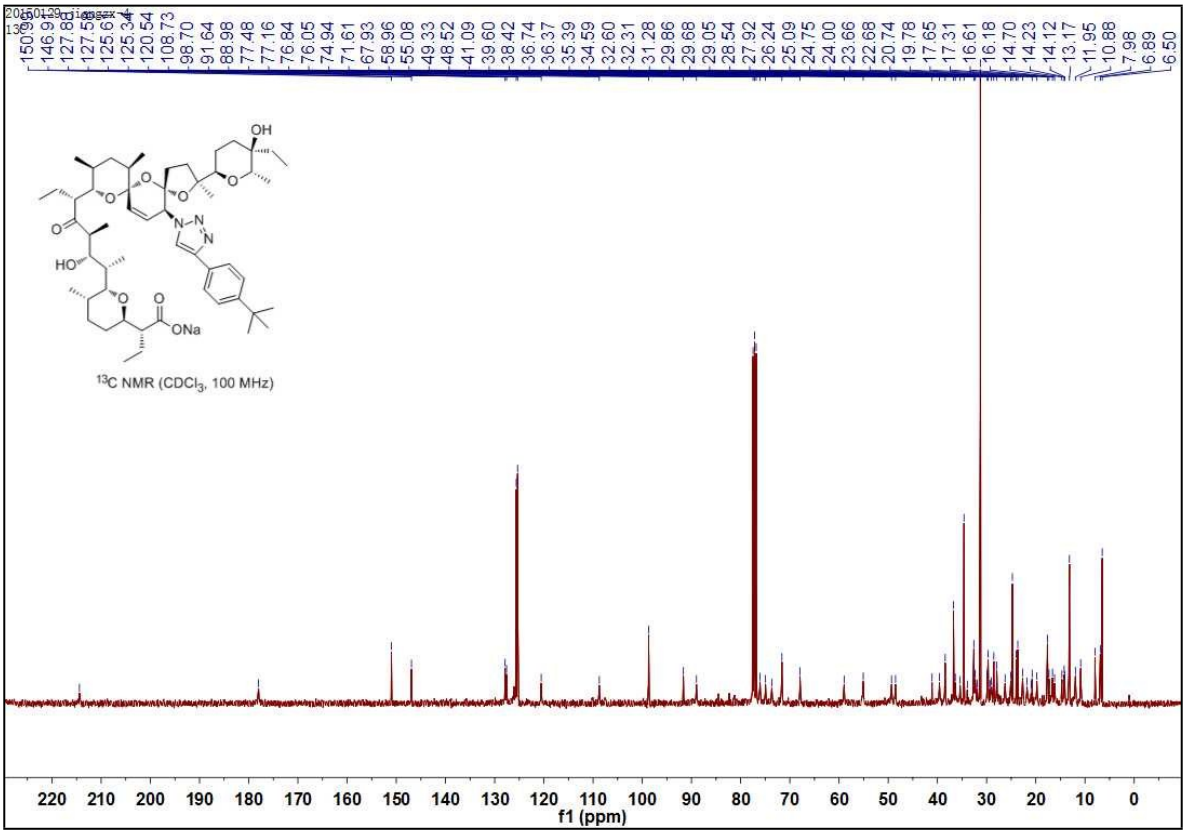
HRMS of compound **5c**



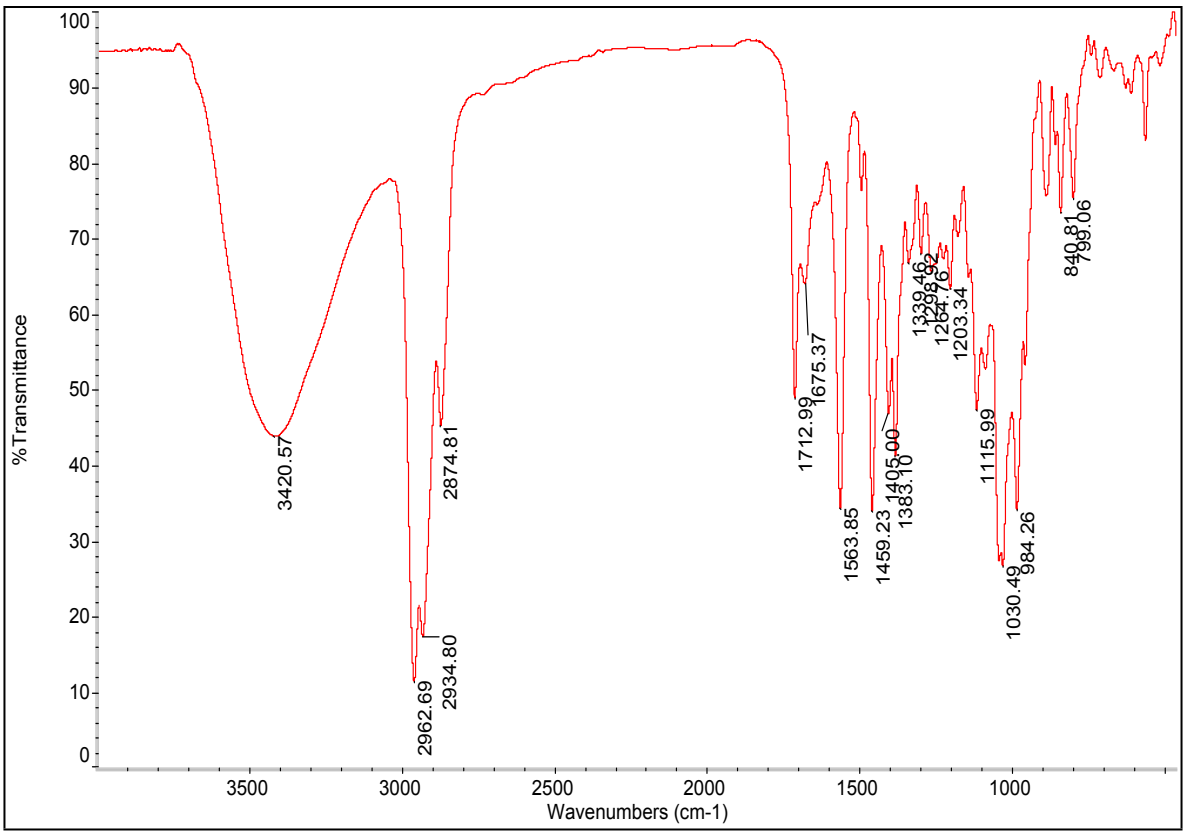
^{1}H NMR of compound **5d**



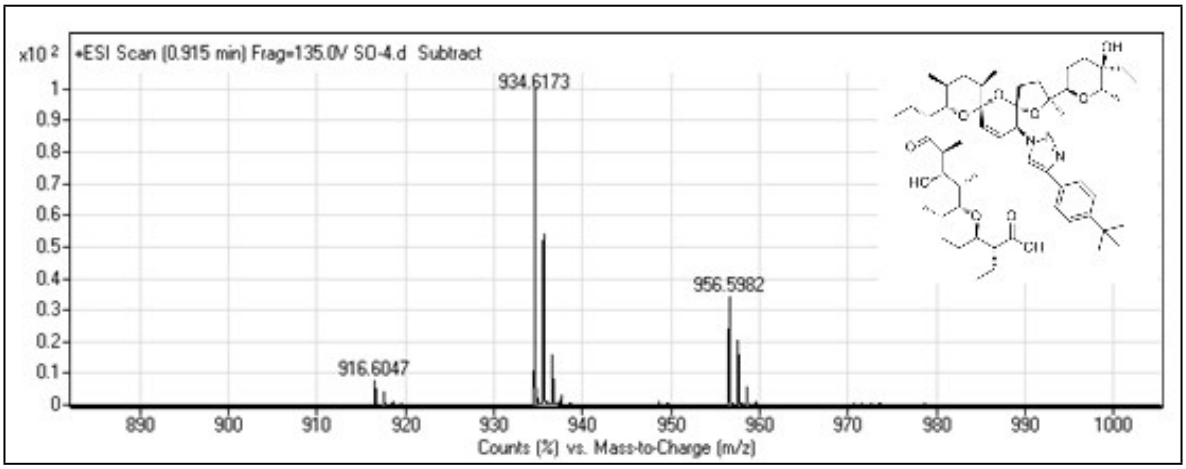
^{13}C NMR of compound **5d**



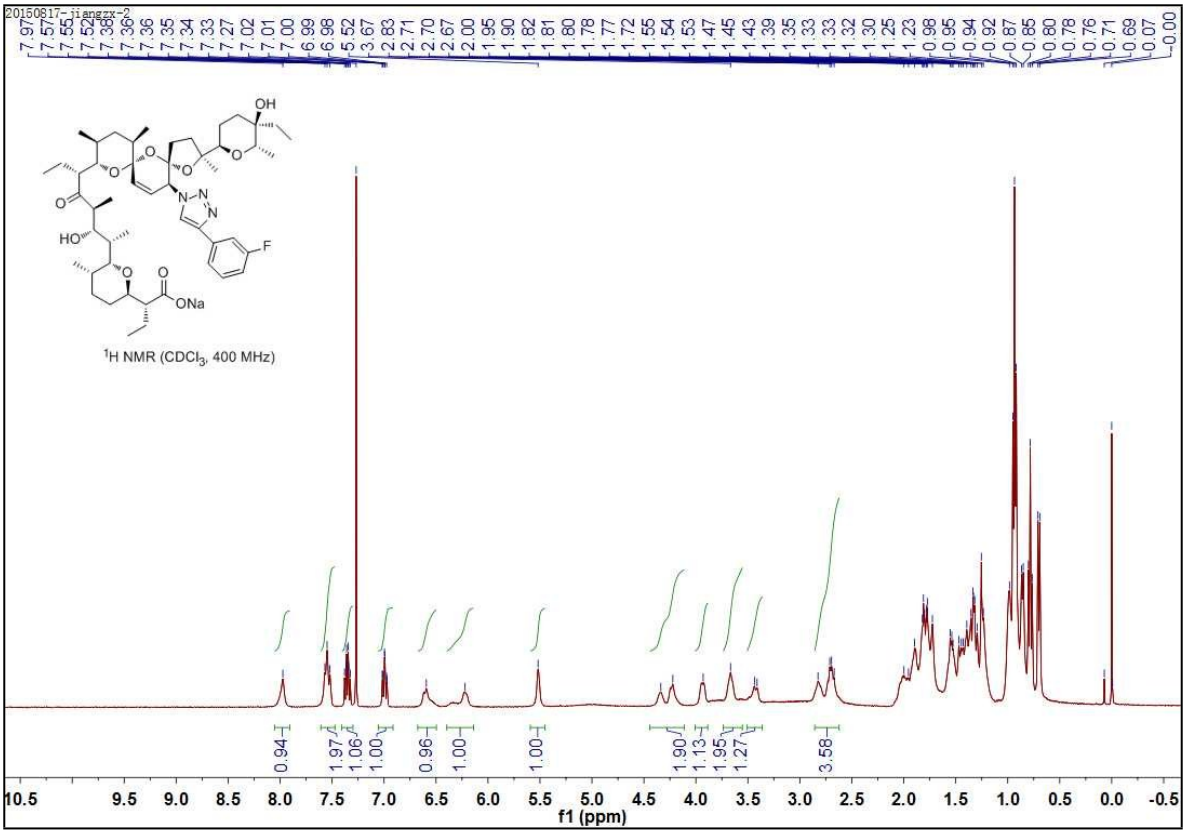
IR (KBr) of compound **5d**



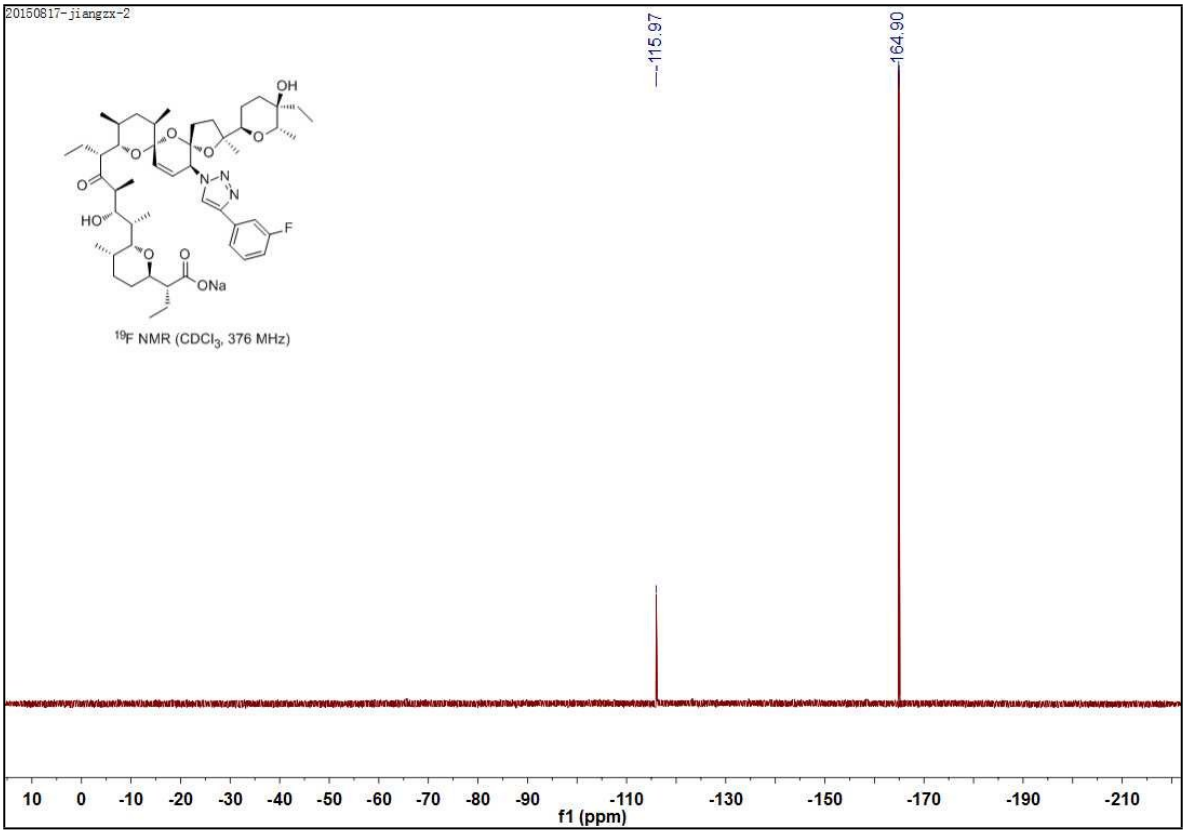
HRMS of compound **5d**



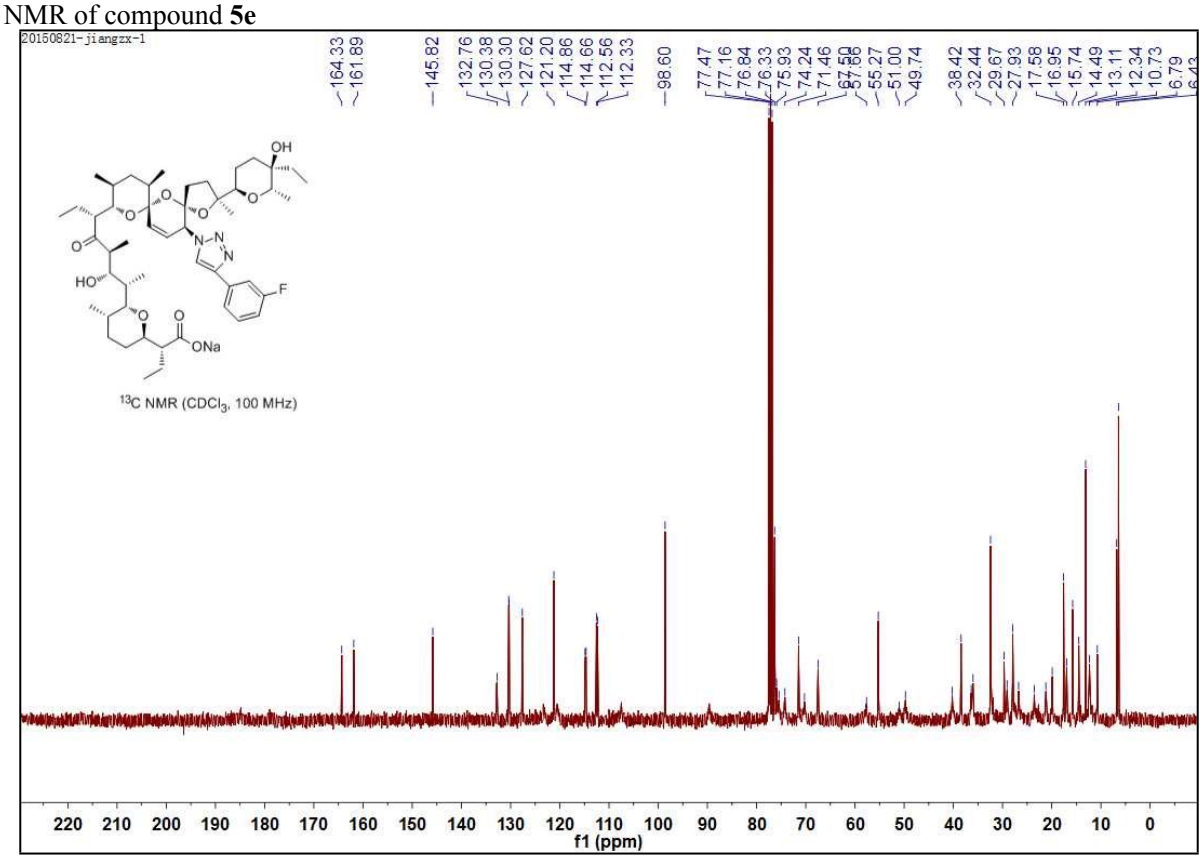
^{1}H NMR of compound **5e**



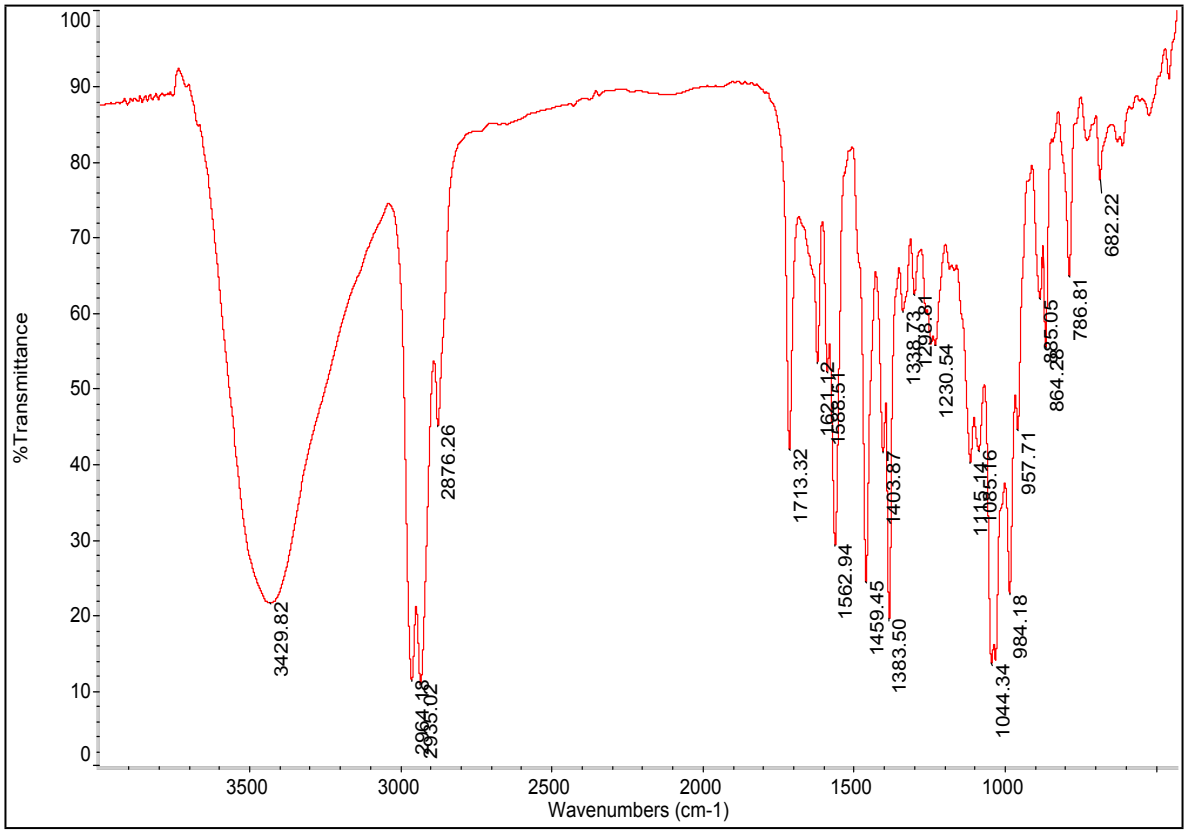
^{19}F NMR of compound **5e**



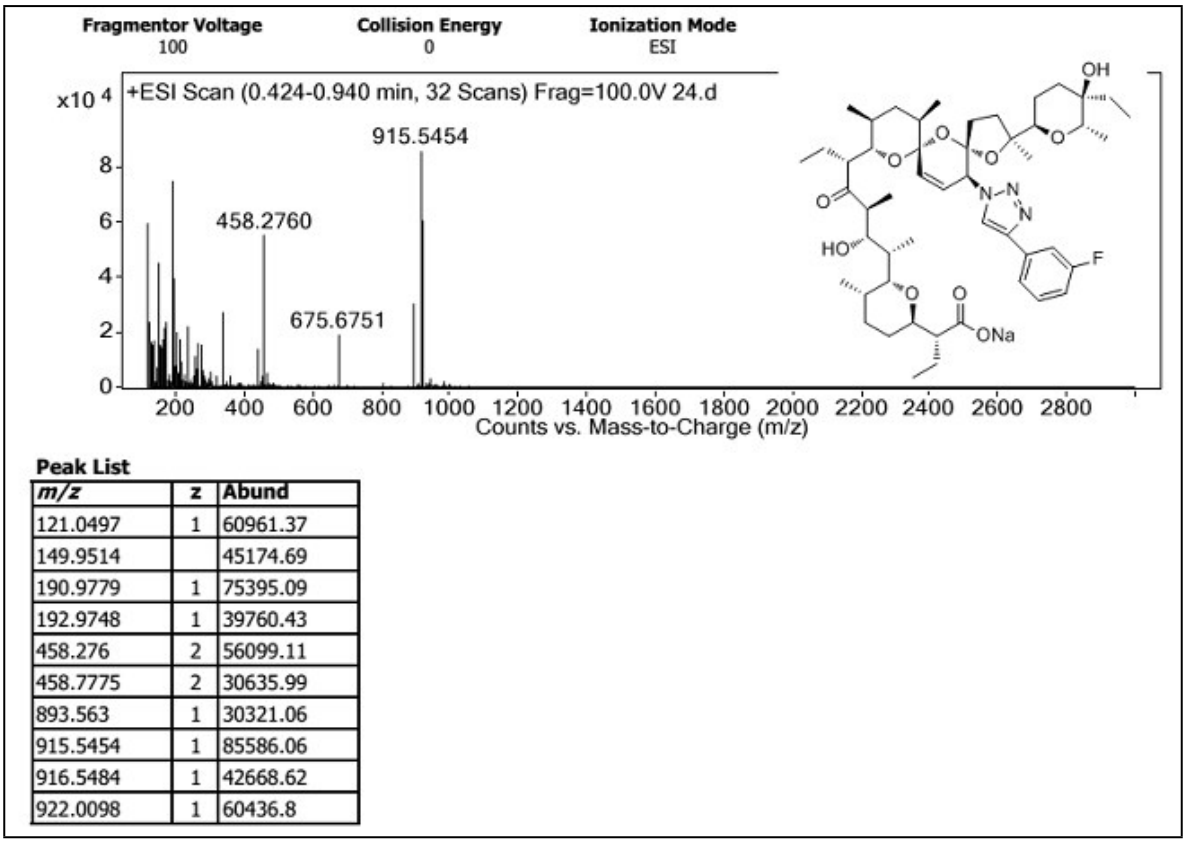
^{13}C NMR of compound **5e**



IR (KBr) of compound **5e**



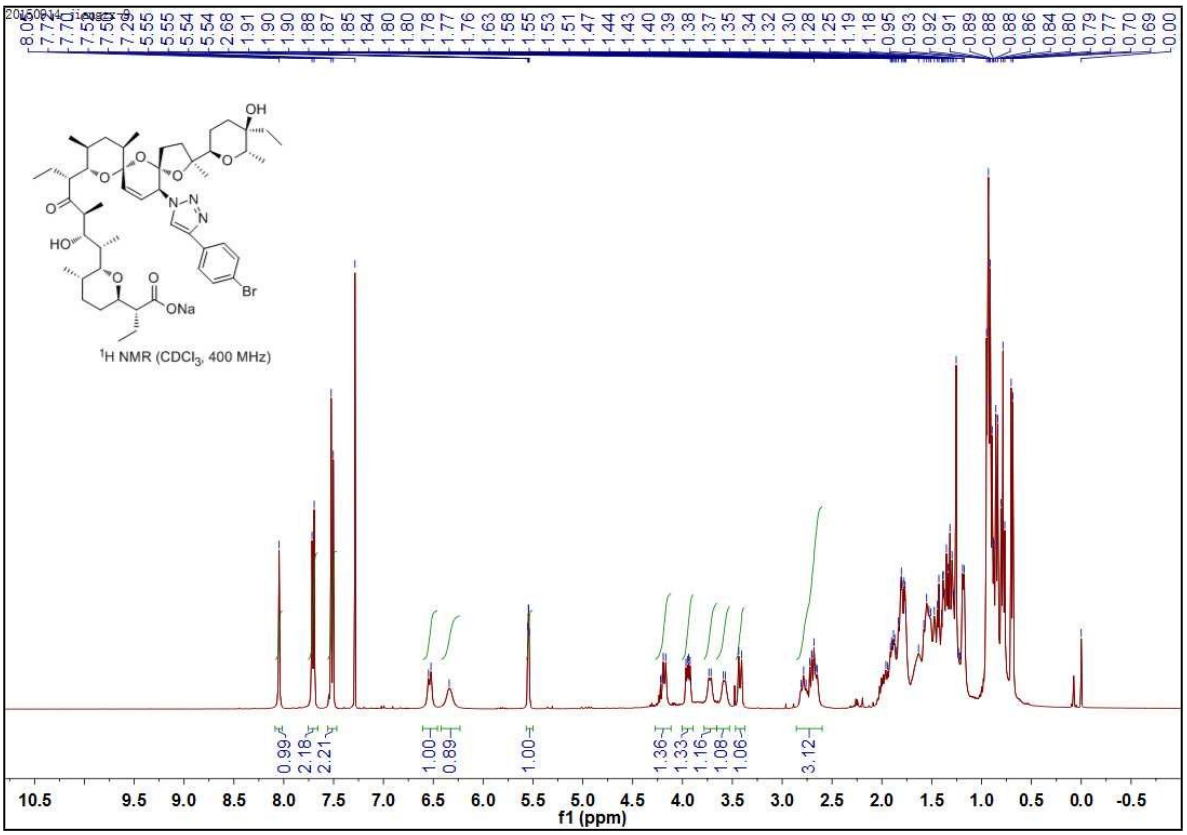
HRMS of compound **5e**



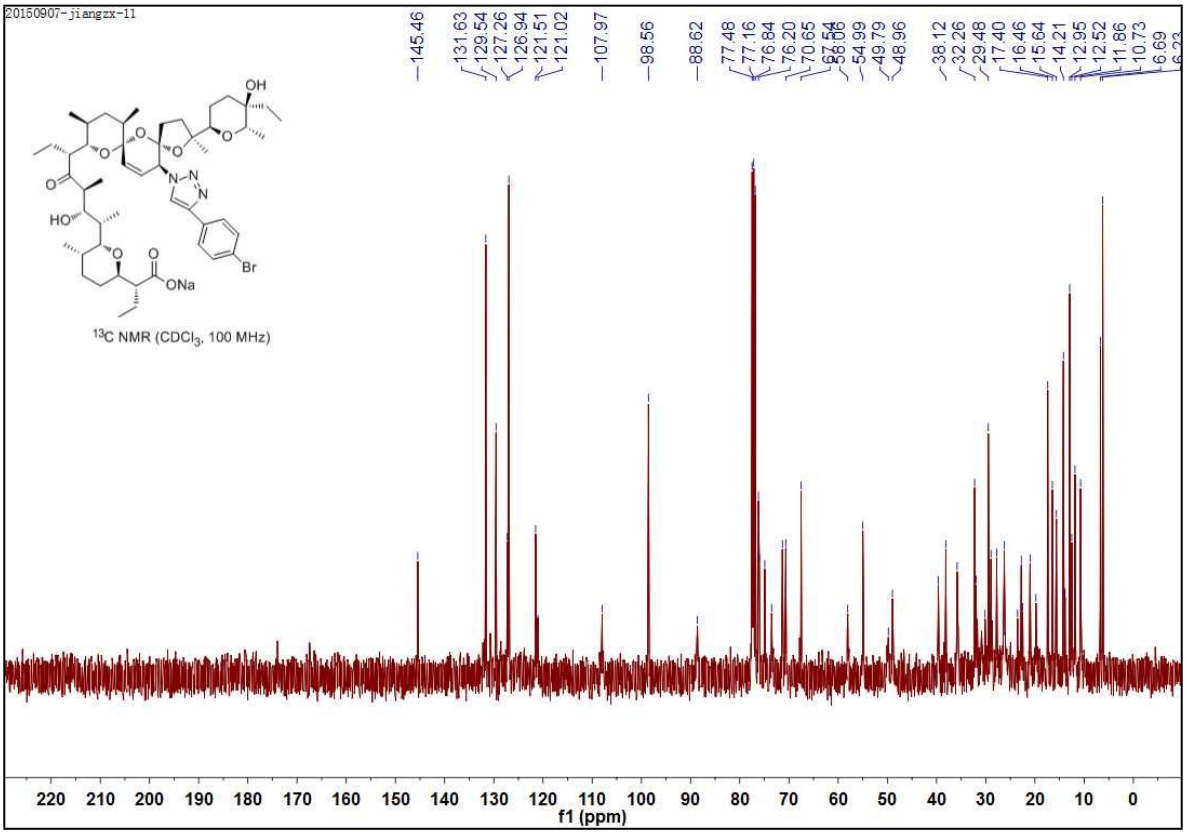
Peak List

m/z	z	Abund
121.0497	1	60961.37
149.9514		45174.69
190.9779	1	75395.09
192.9748	1	39760.43
458.276	2	56099.11
458.7775	2	30635.99
893.563	1	30321.06
915.5454	1	85586.06
916.5484	1	42668.62
922.0098	1	60436.8

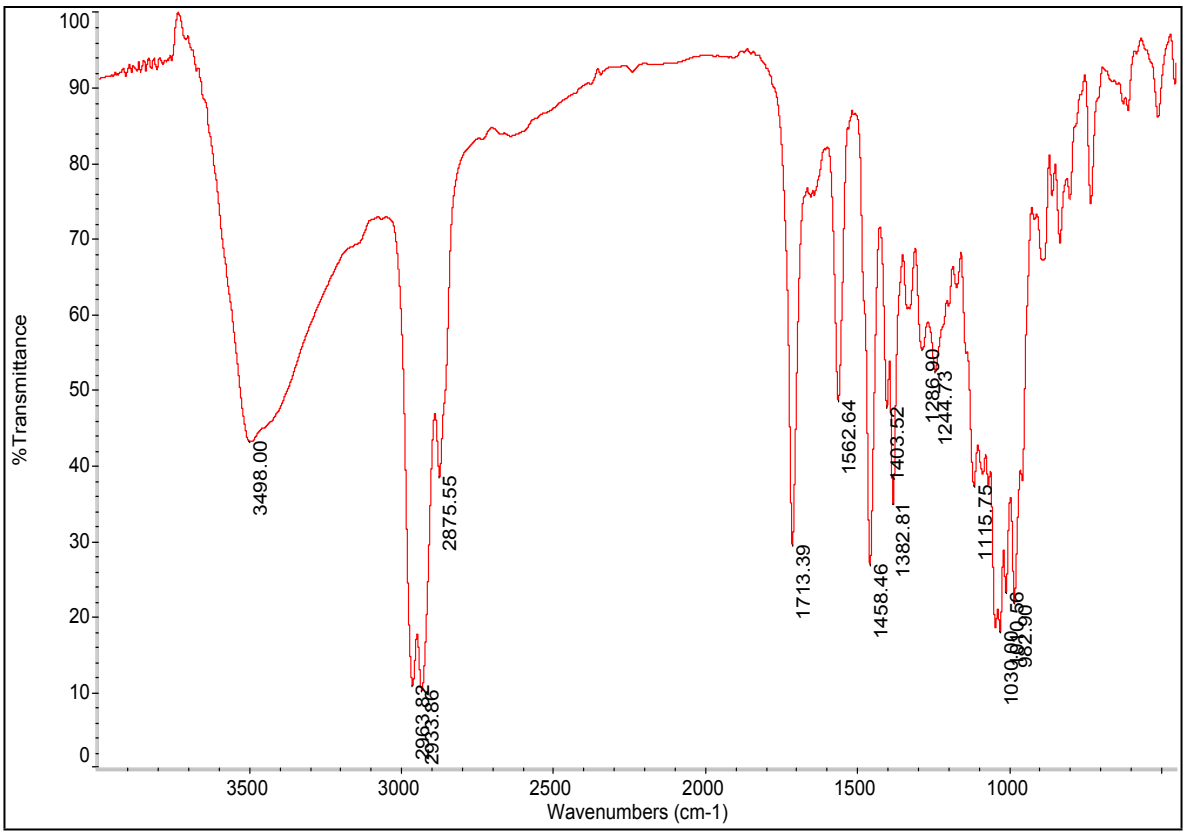
^{1}H NMR of compound **5f**



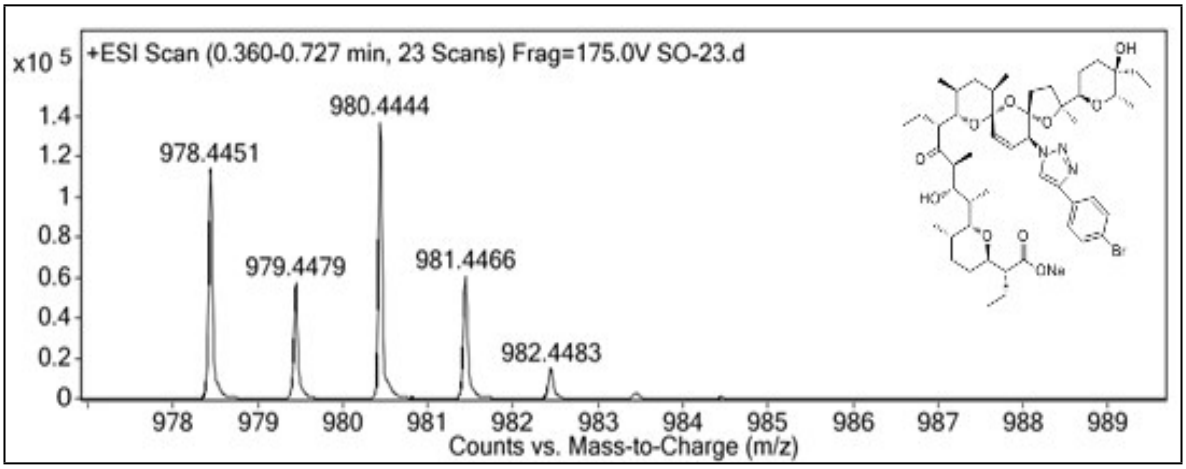
^{13}C NMR of compound **5f**



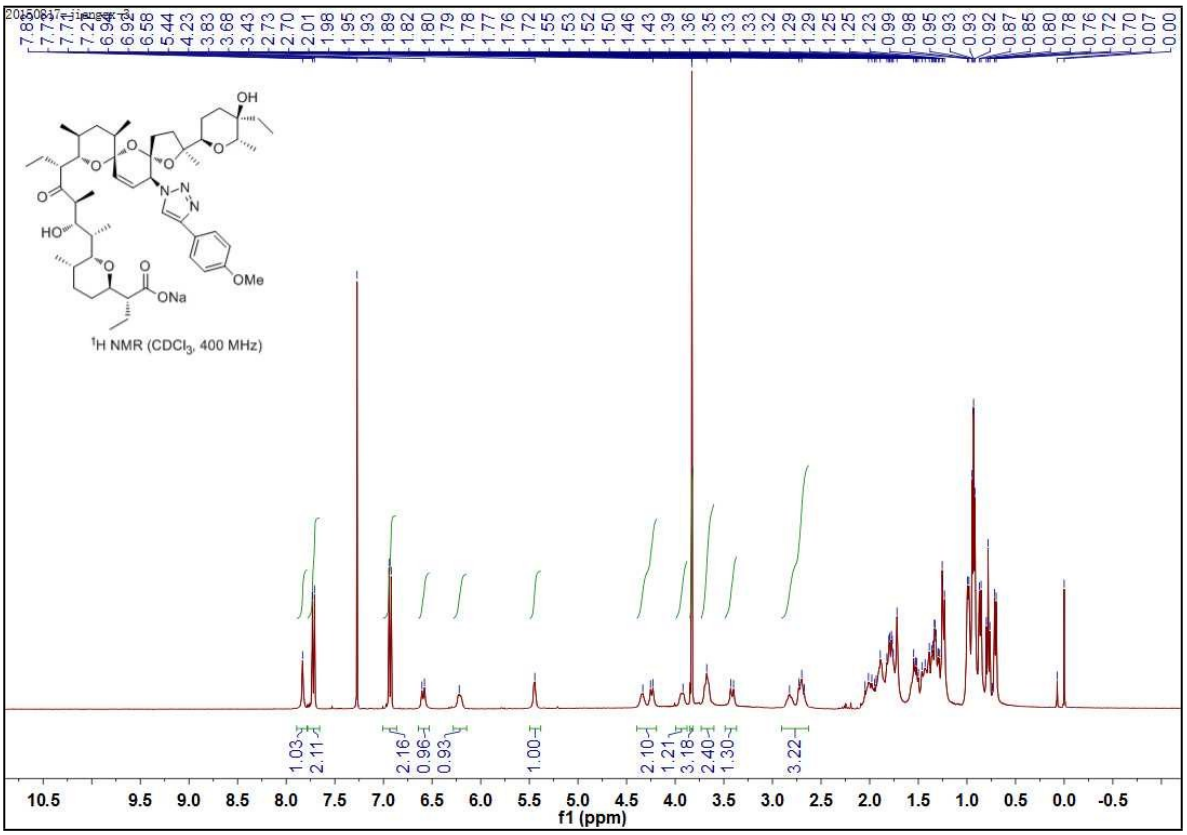
IR (KBr) of compound **5f**



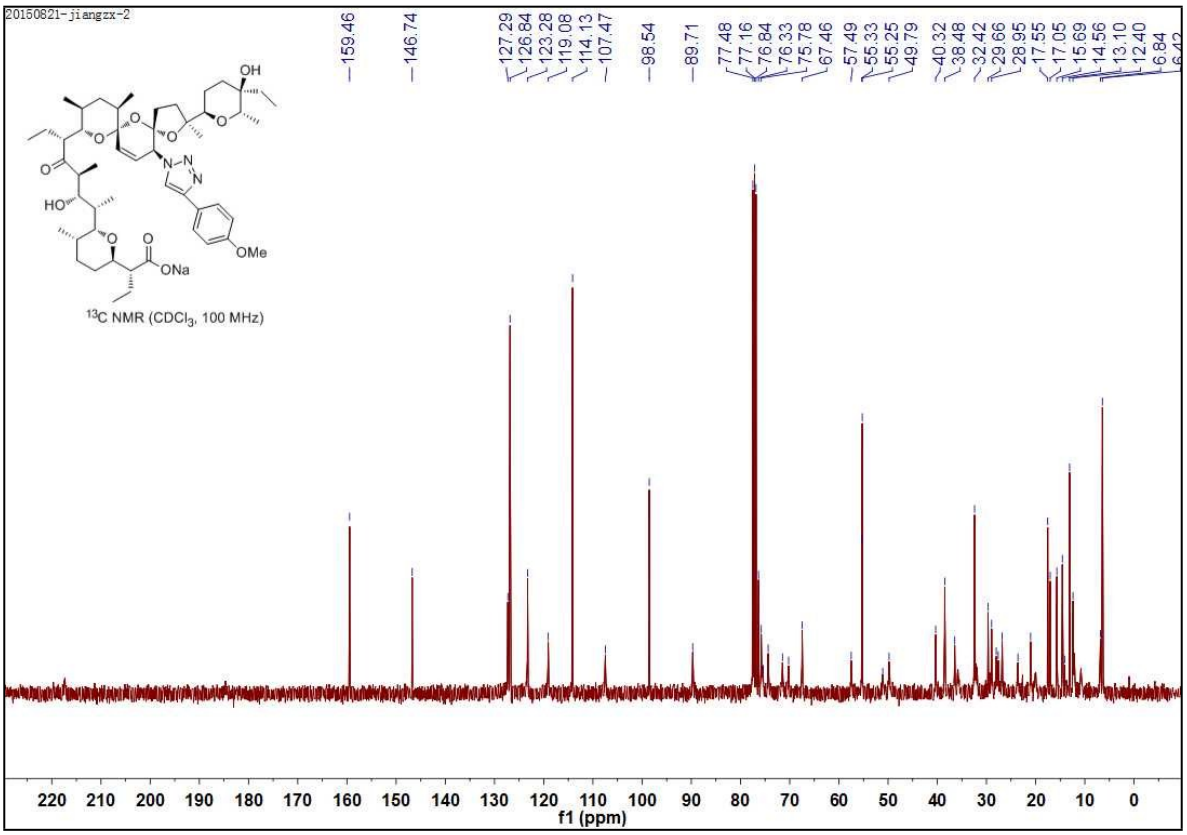
HRMS of compound **5f**



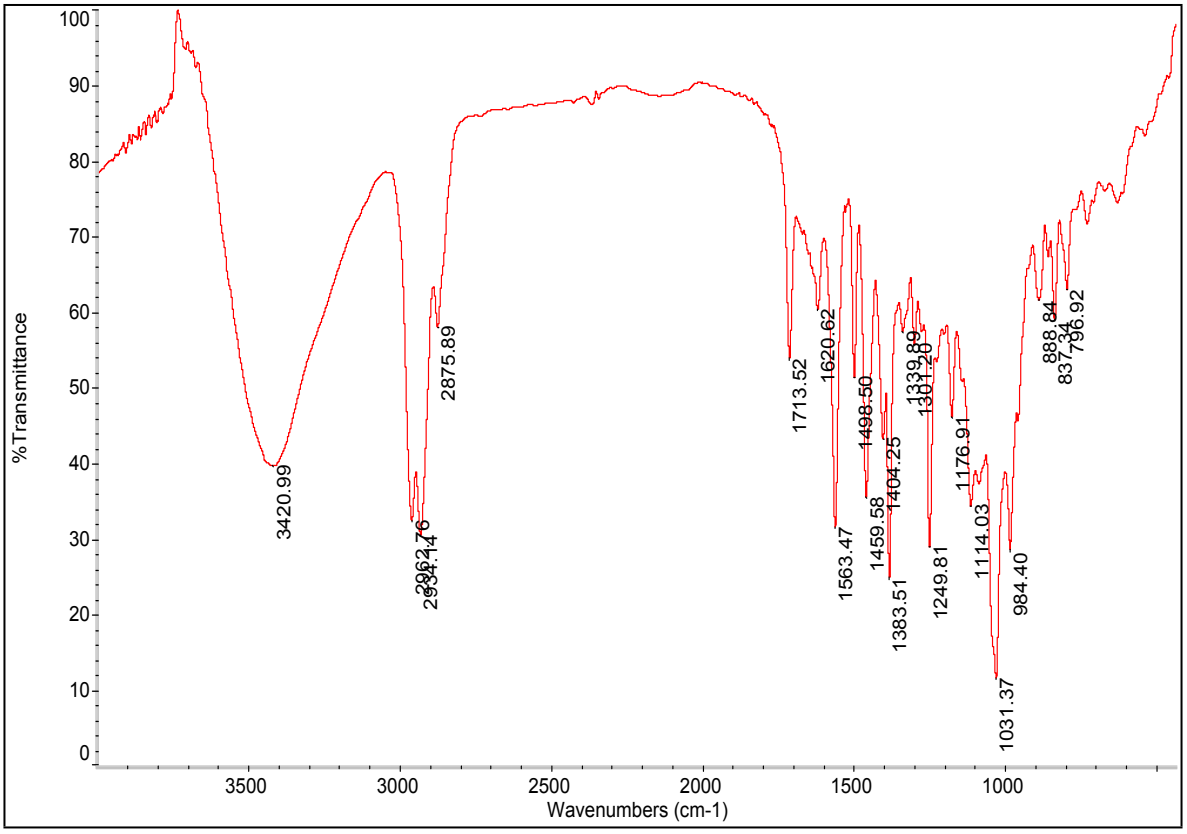
^{1}H NMR of compound **5g**



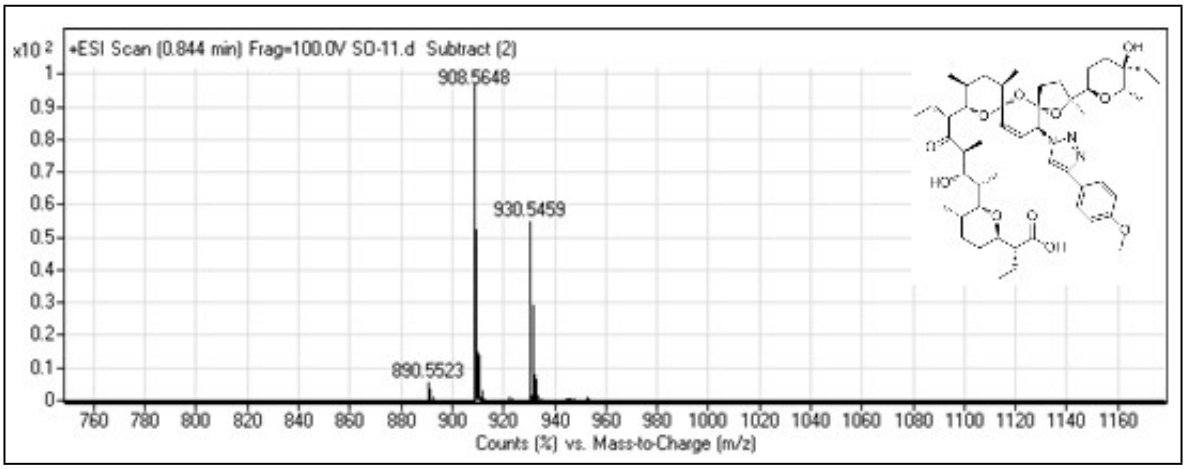
^{13}C NMR of compound **5g**



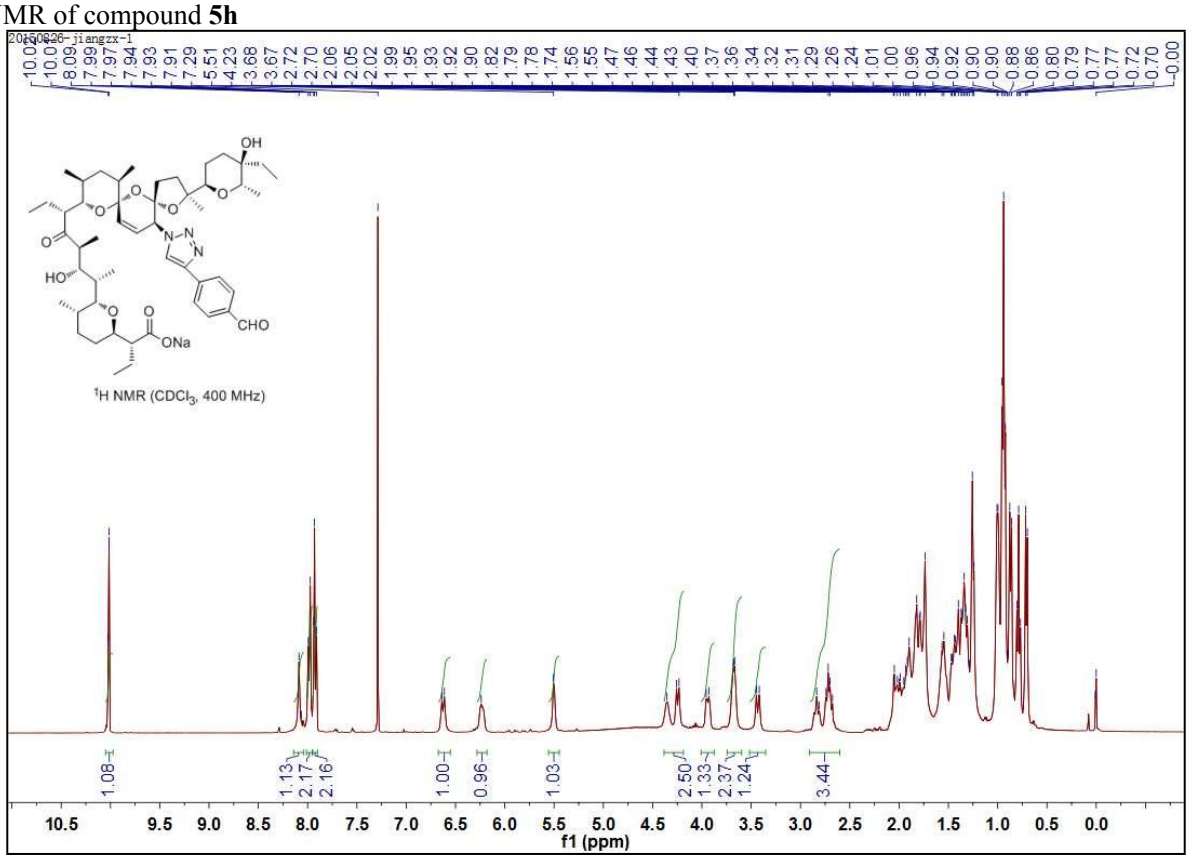
IR (KBr) of compound **5g**



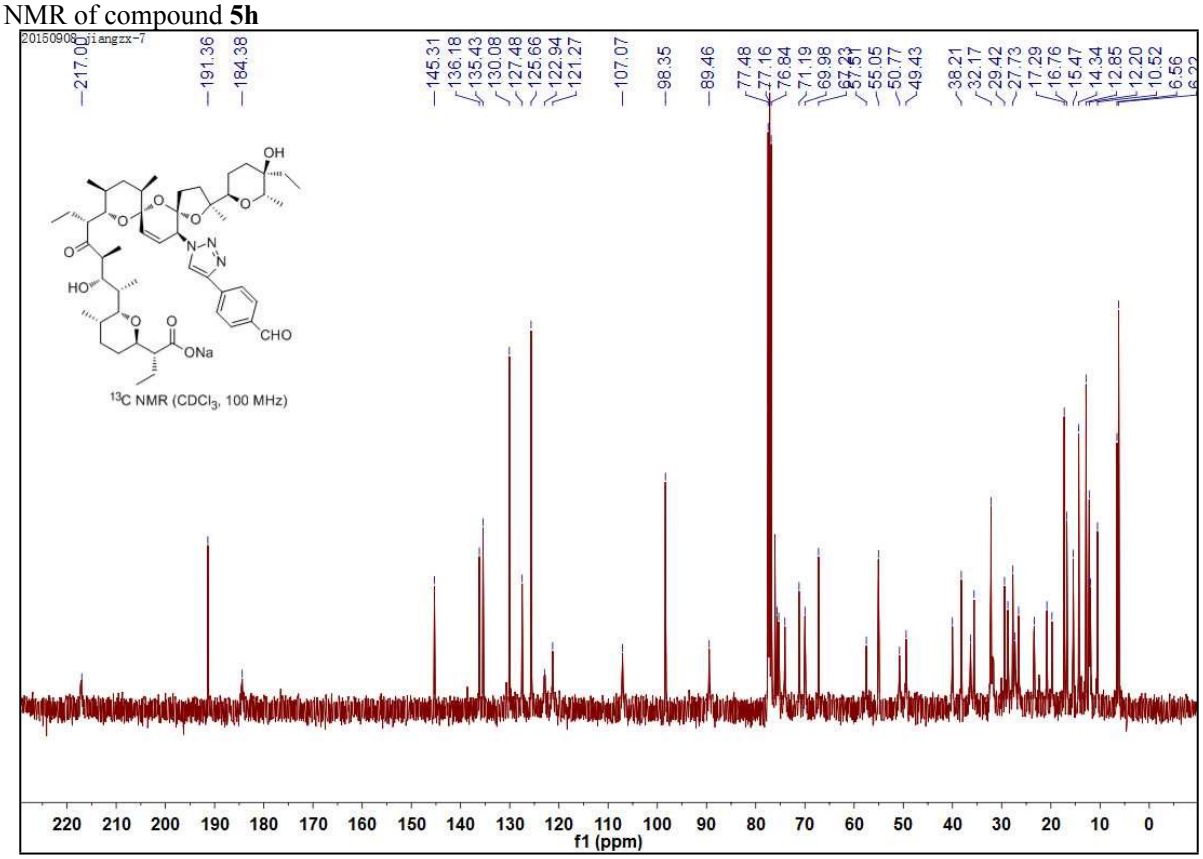
HRMS of compound **5g**



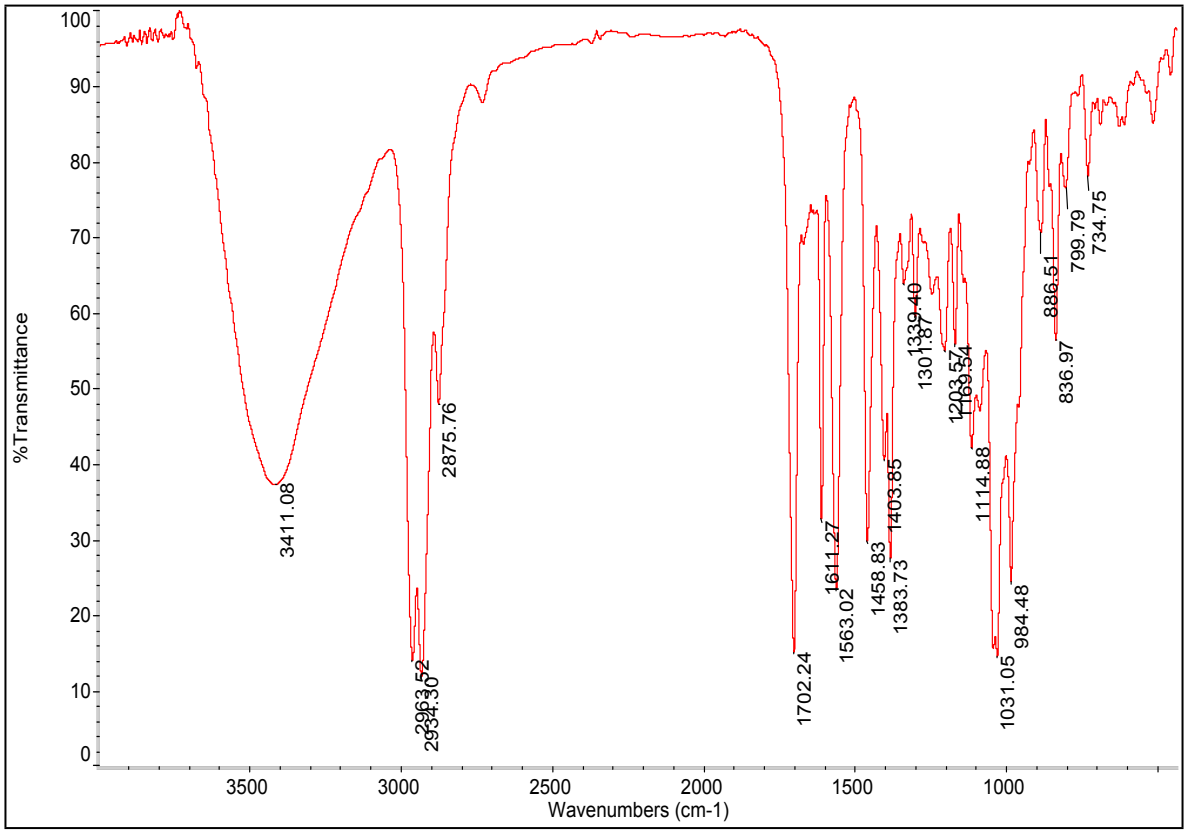
^{1}H NMR of compound **5h**



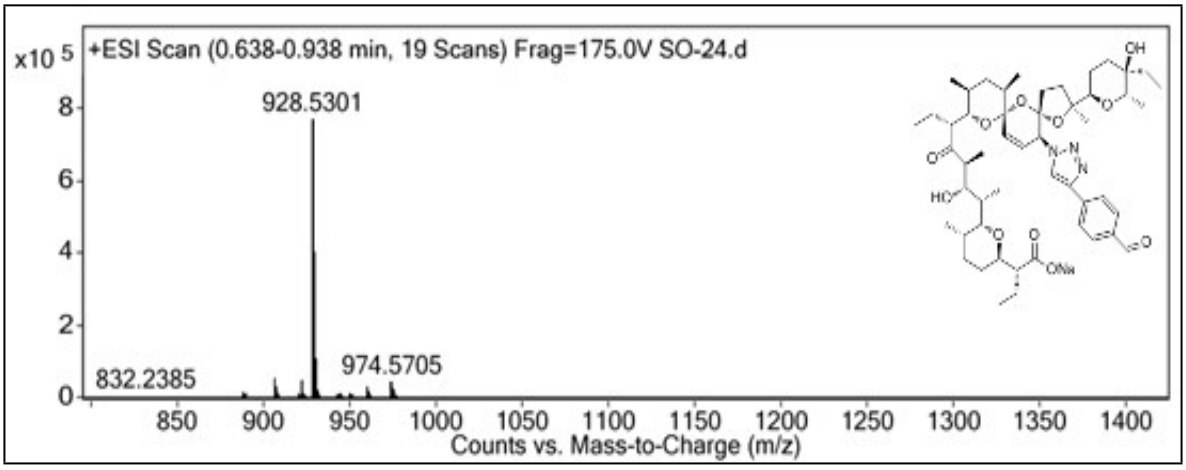
^{13}C NMR of compound **5h**



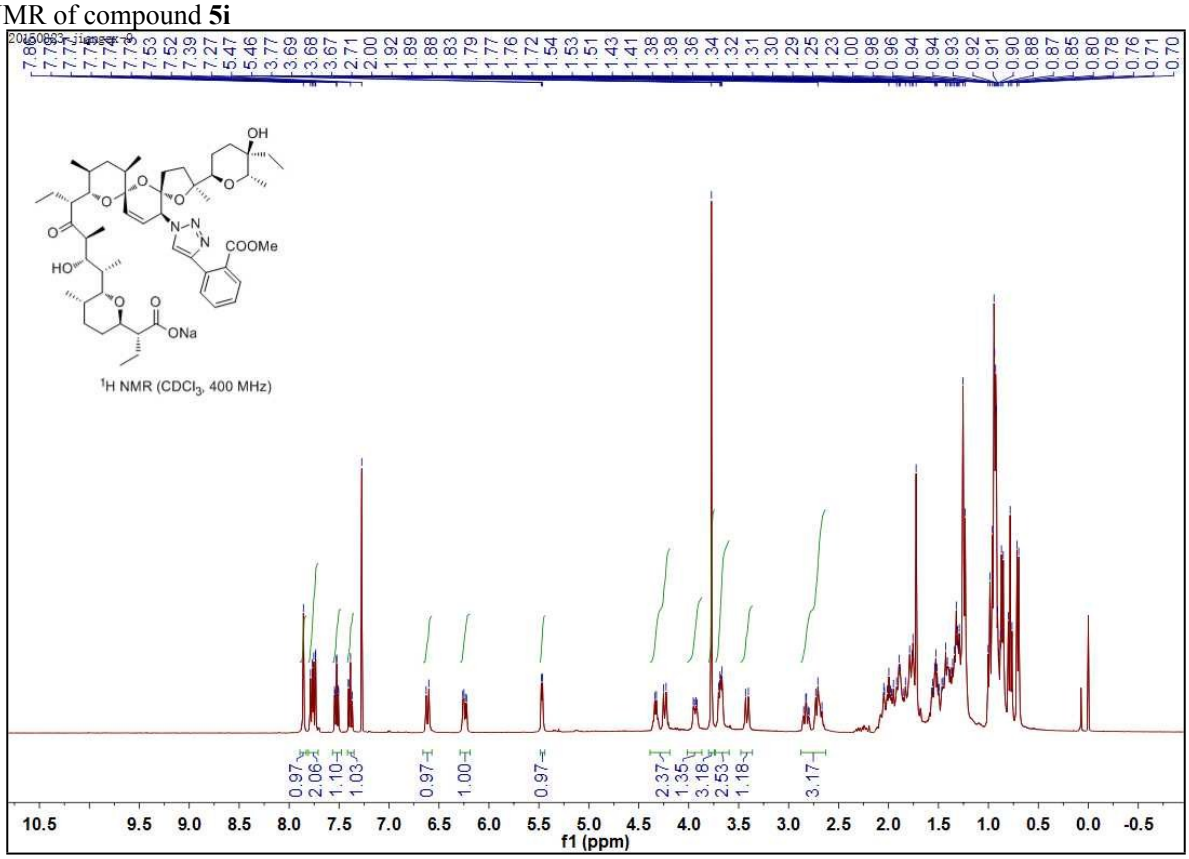
IR (KBr) of compound **5h**



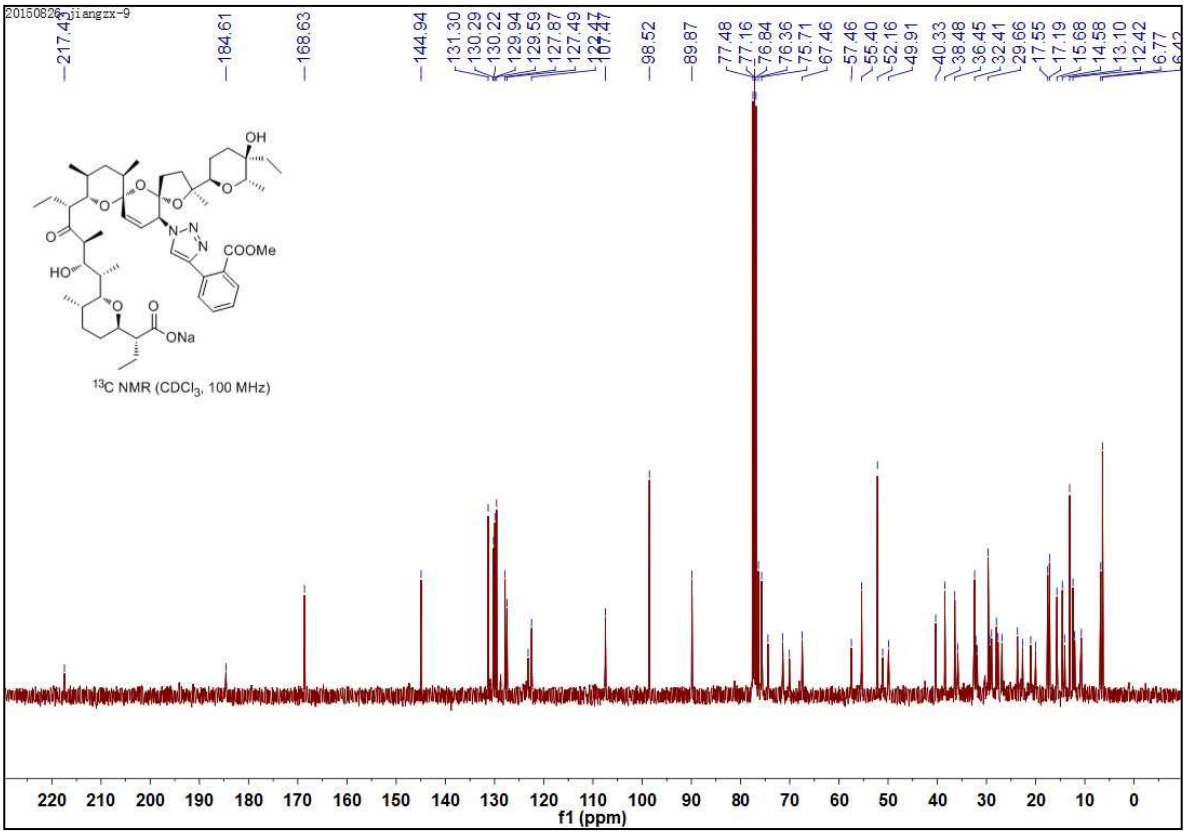
HRMS of compound **5h**



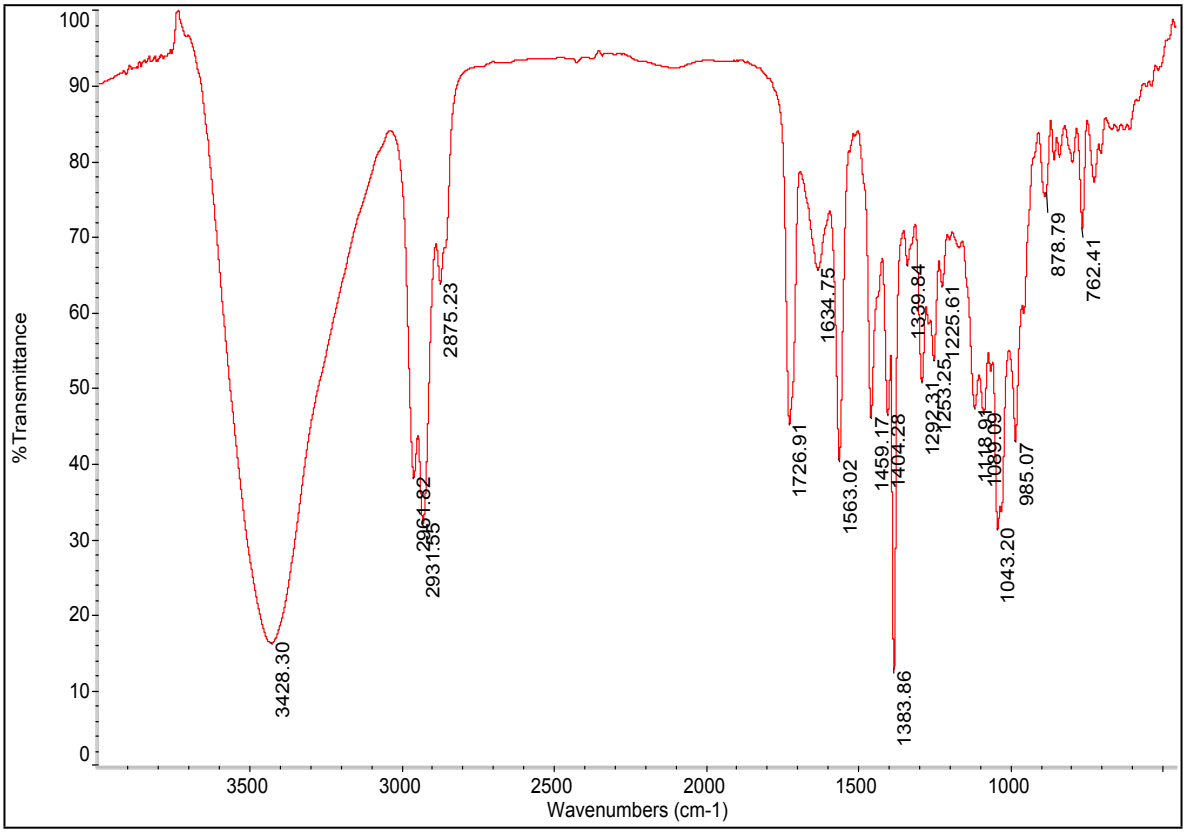
^{1}H NMR of compound **5i**



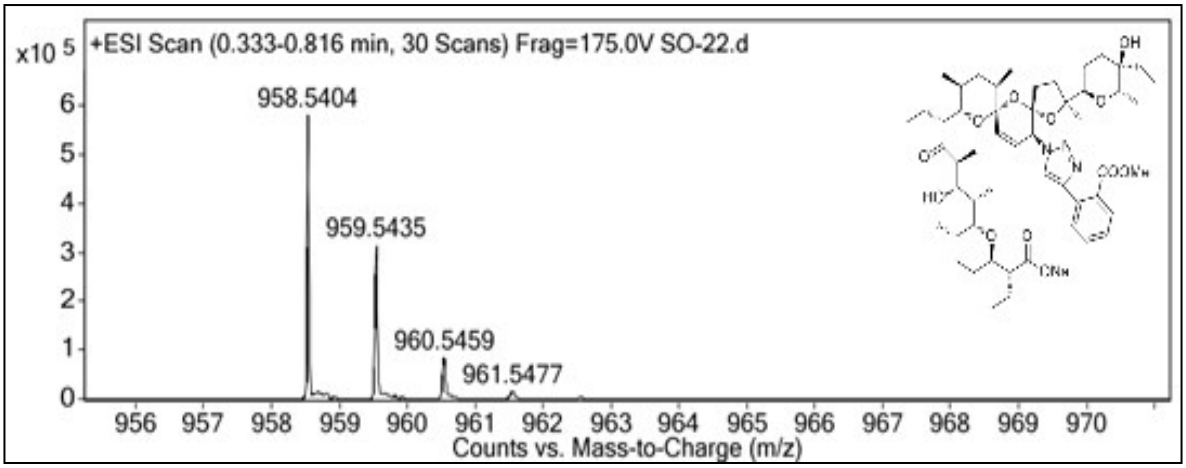
^{13}C NMR of compound **5i**



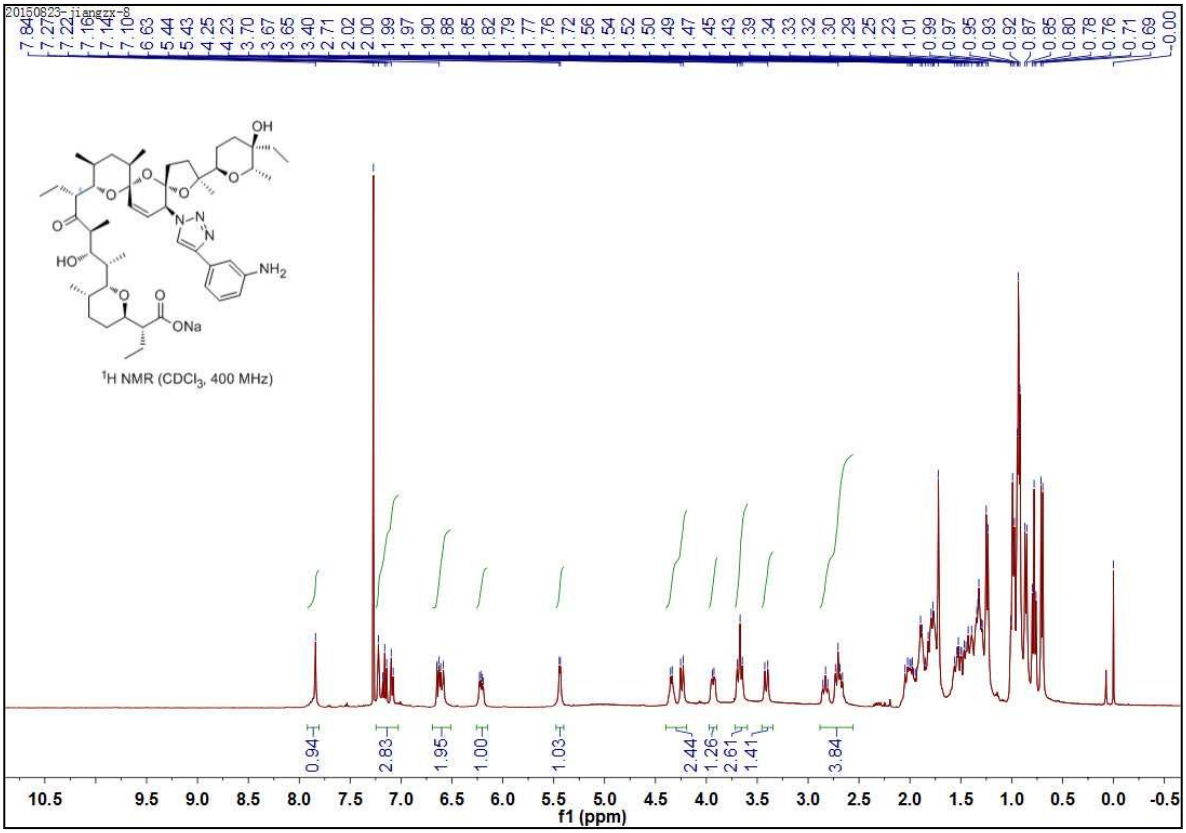
IR (KBr) of compound **5i**



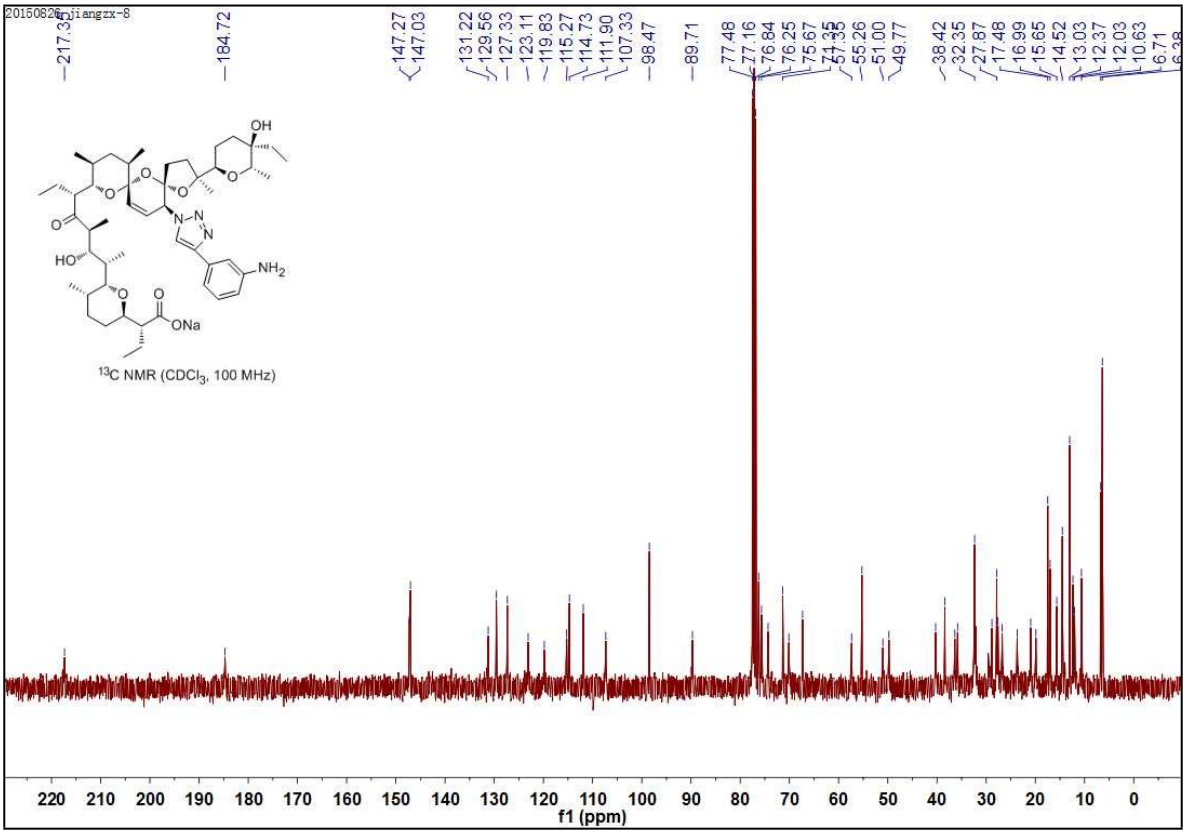
HRMS of compound **5i**



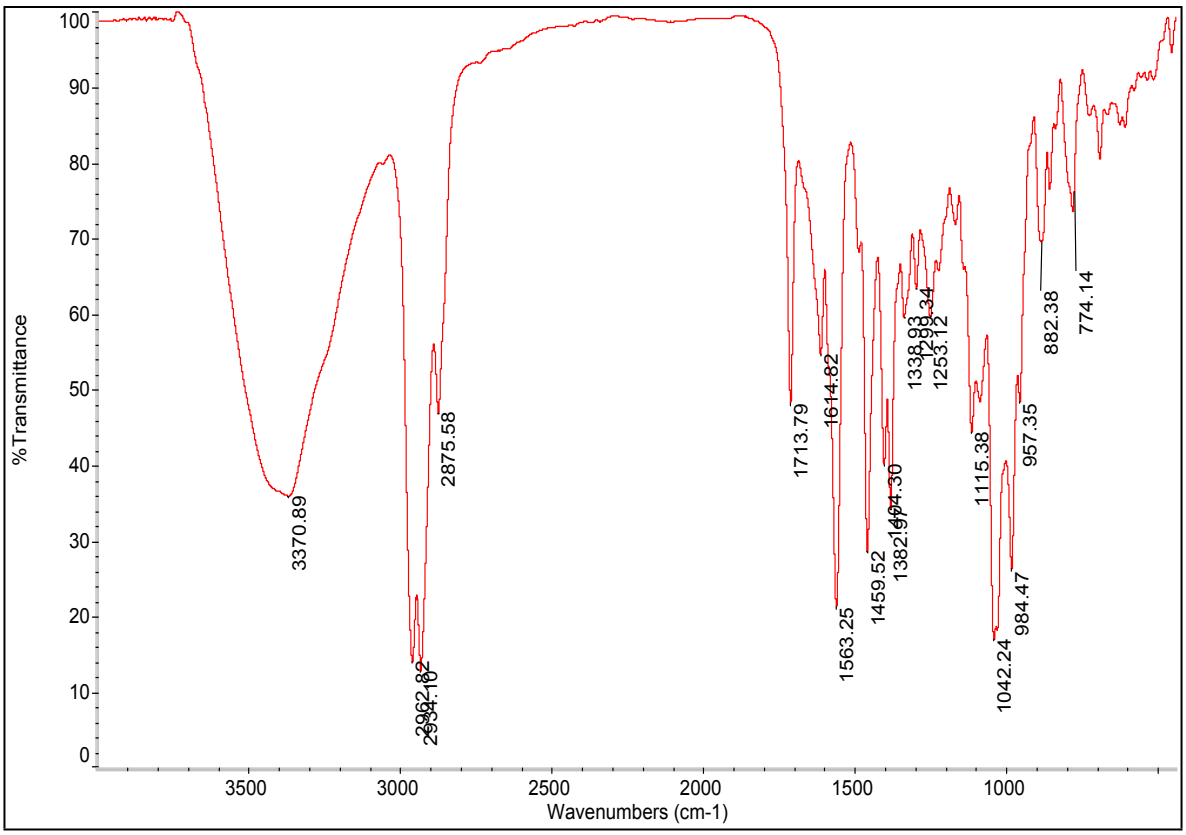
^{1}H NMR of compound **5j**



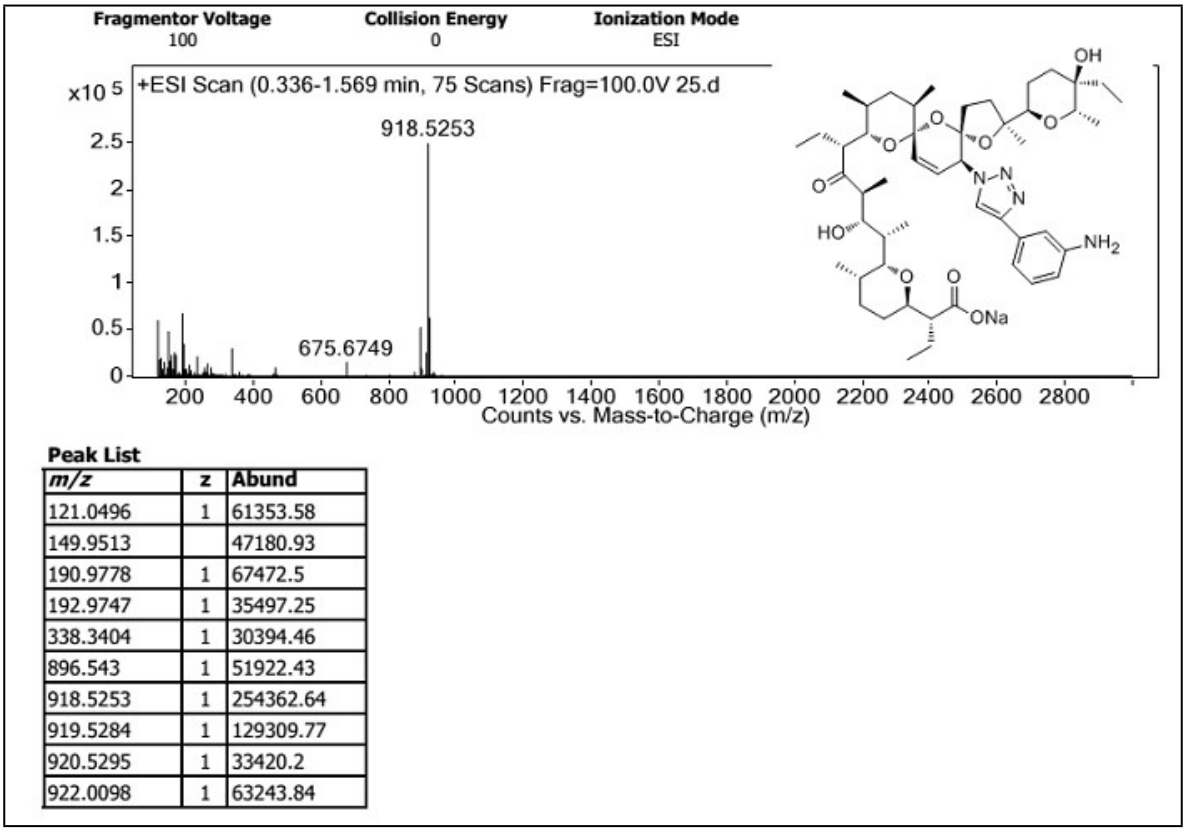
^{13}C NMR of compound **5j**



IR (KBr) of compound **5j**



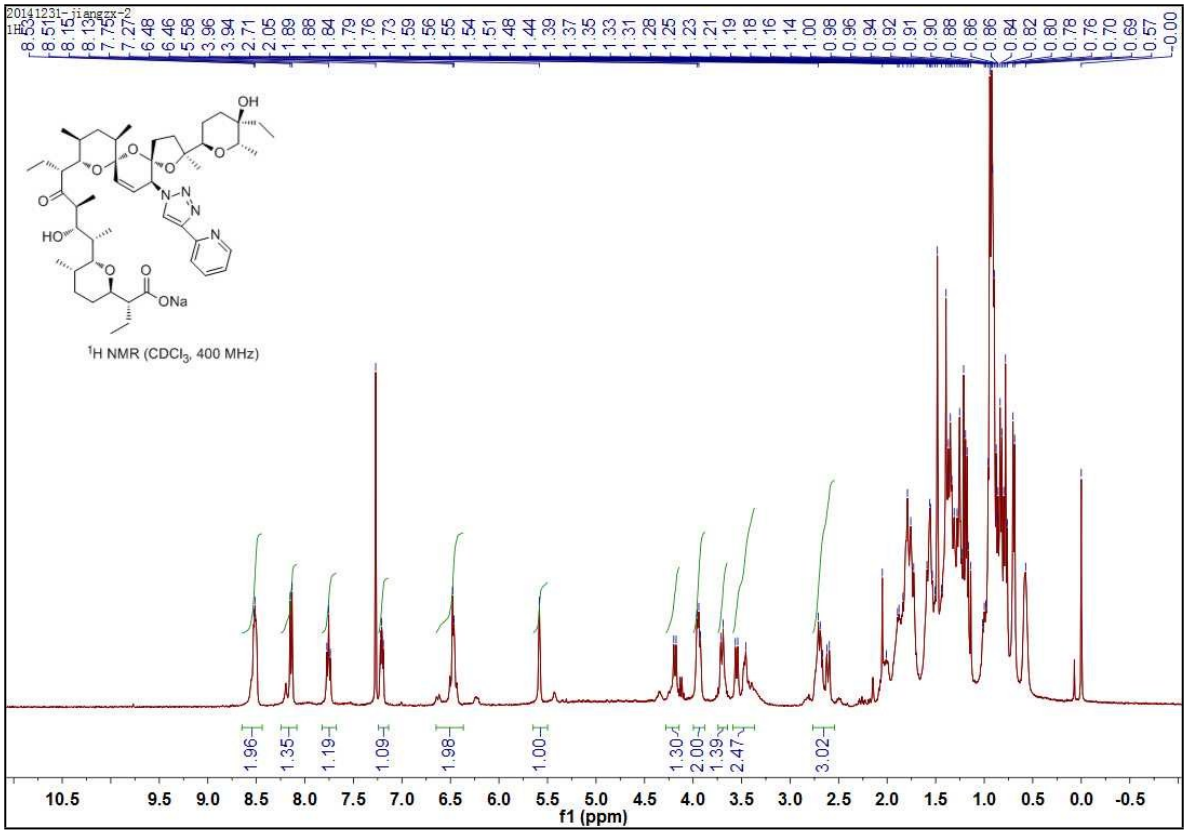
HRMS of compound **5j**



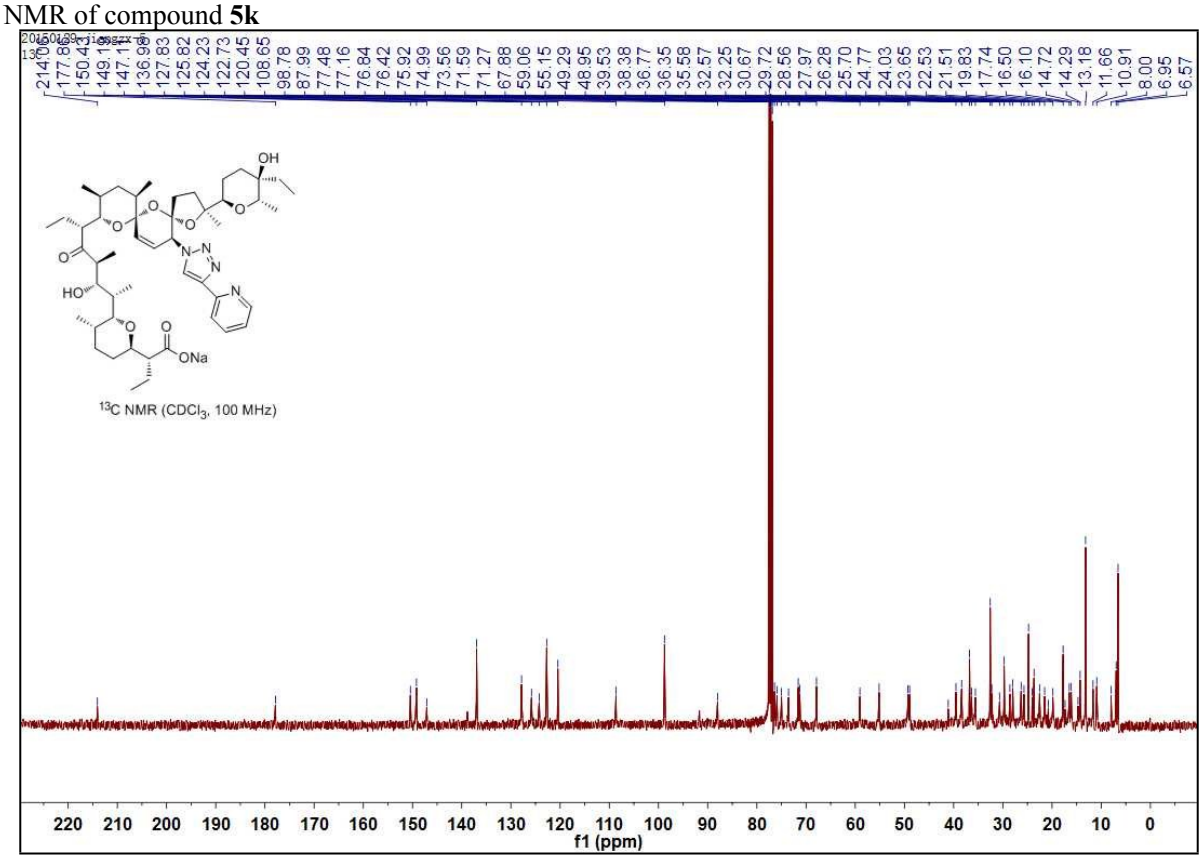
Peak List

m/z	z	Abund
121.0496	1	61353.58
149.9513		47180.93
190.9778	1	67472.5
192.9747	1	35497.25
338.3404	1	30394.46
896.543	1	51922.43
918.5253	1	254362.64
919.5284	1	129309.77
920.5295	1	33420.2
922.0098	1	63243.84

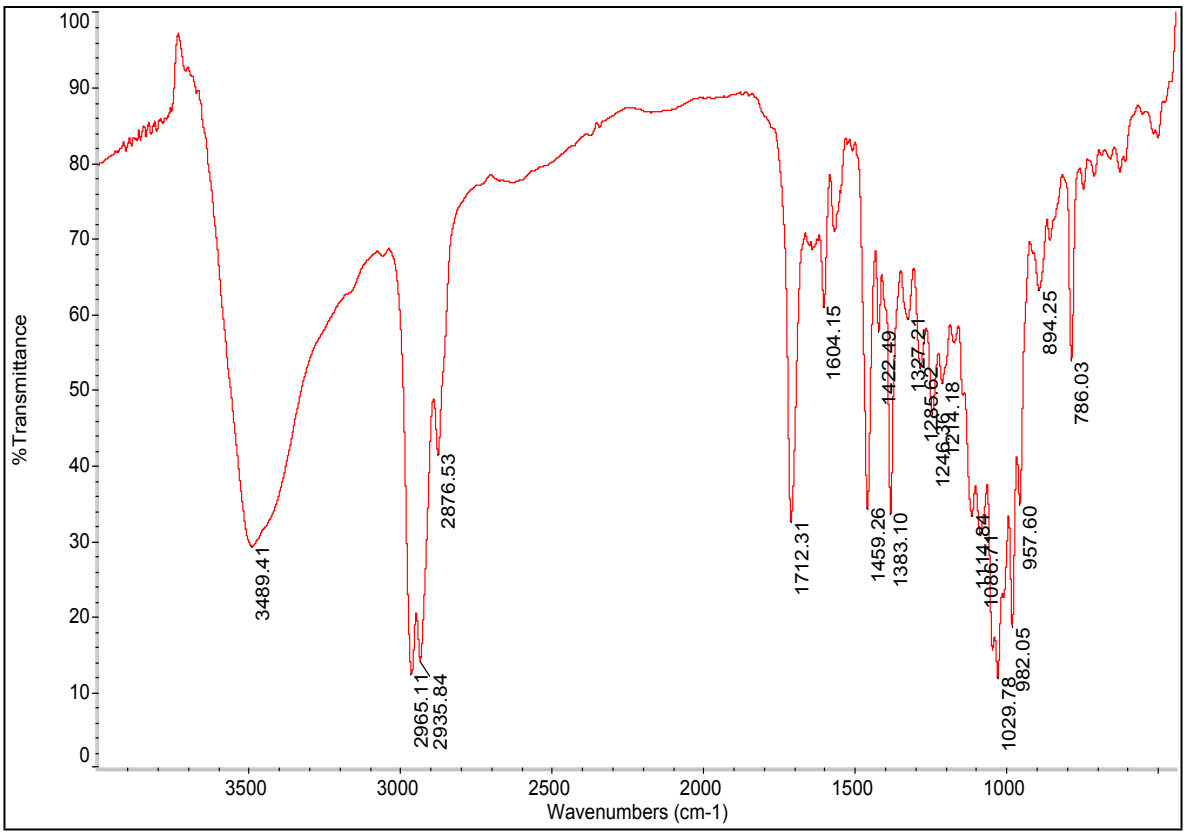
^{1}H NMR of compound **5k**



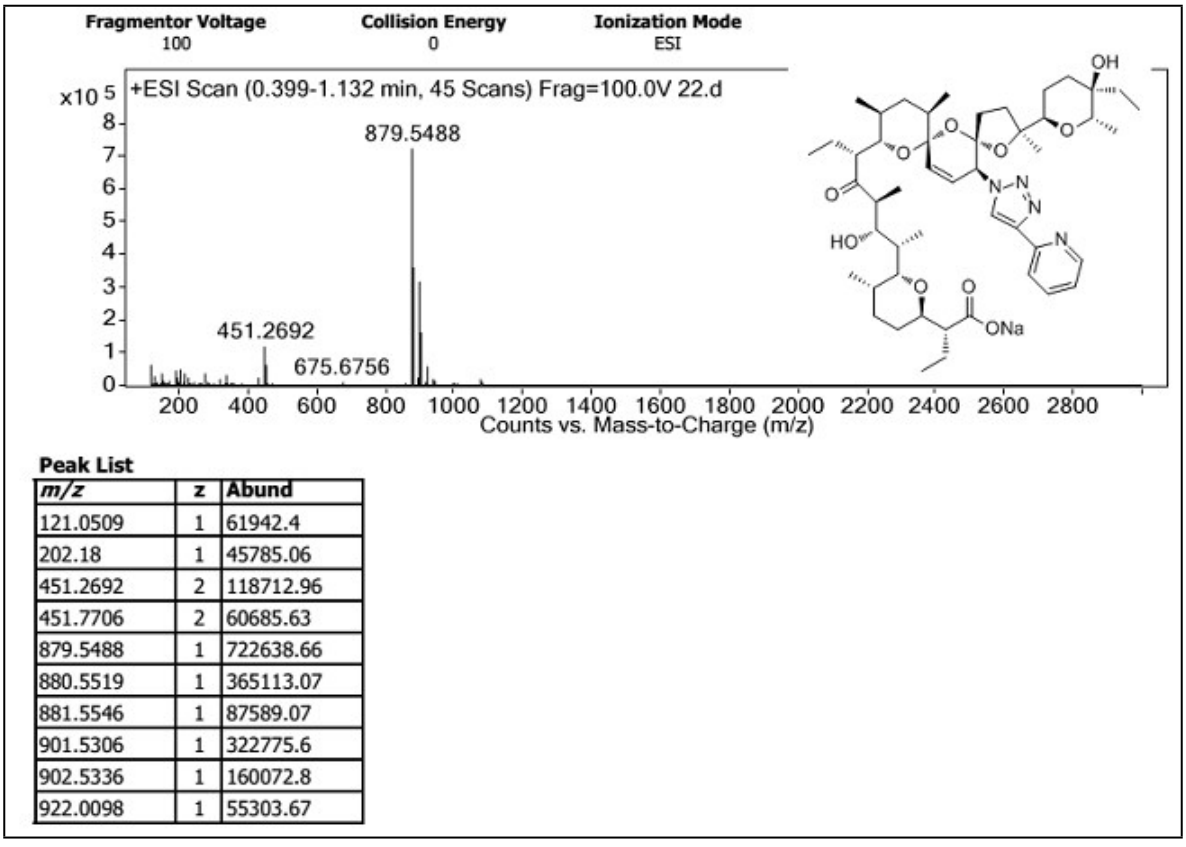
^{13}C NMR of compound **5k**



IR (KBr) of compound **5k**



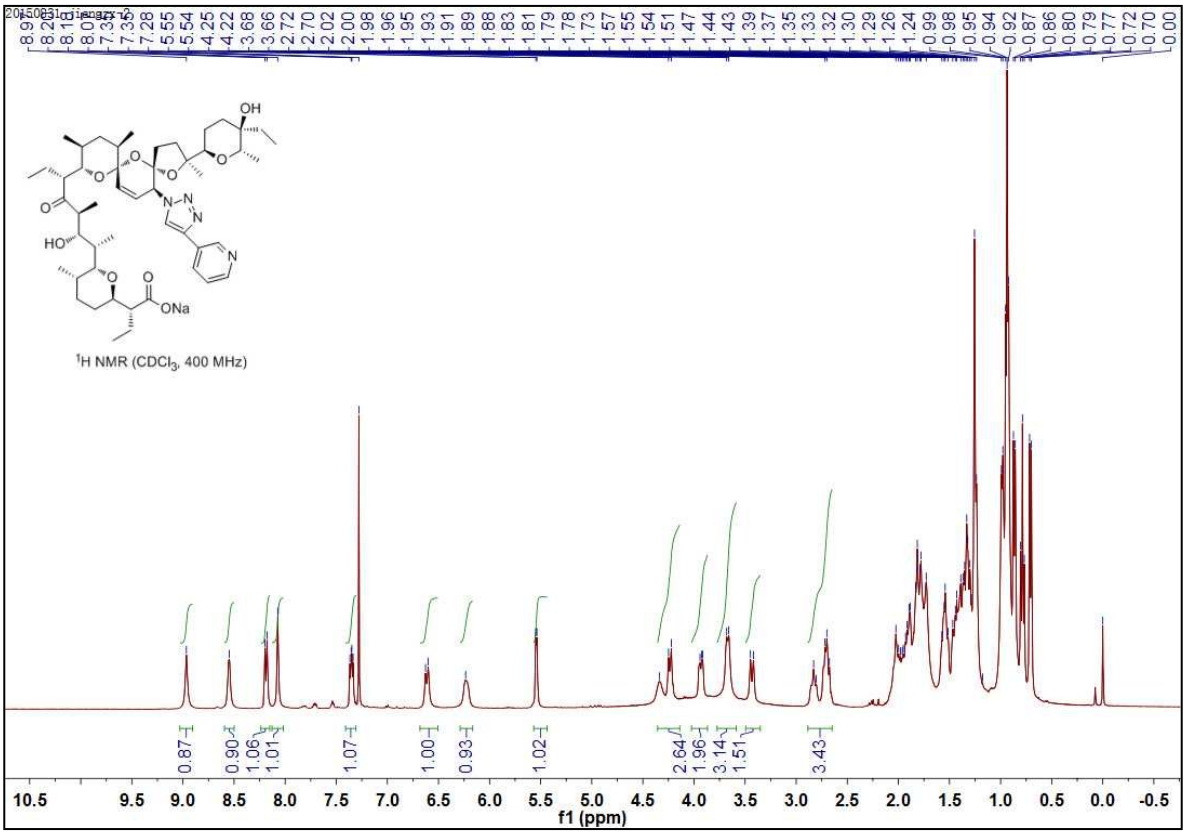
HRMS of compound **5k**



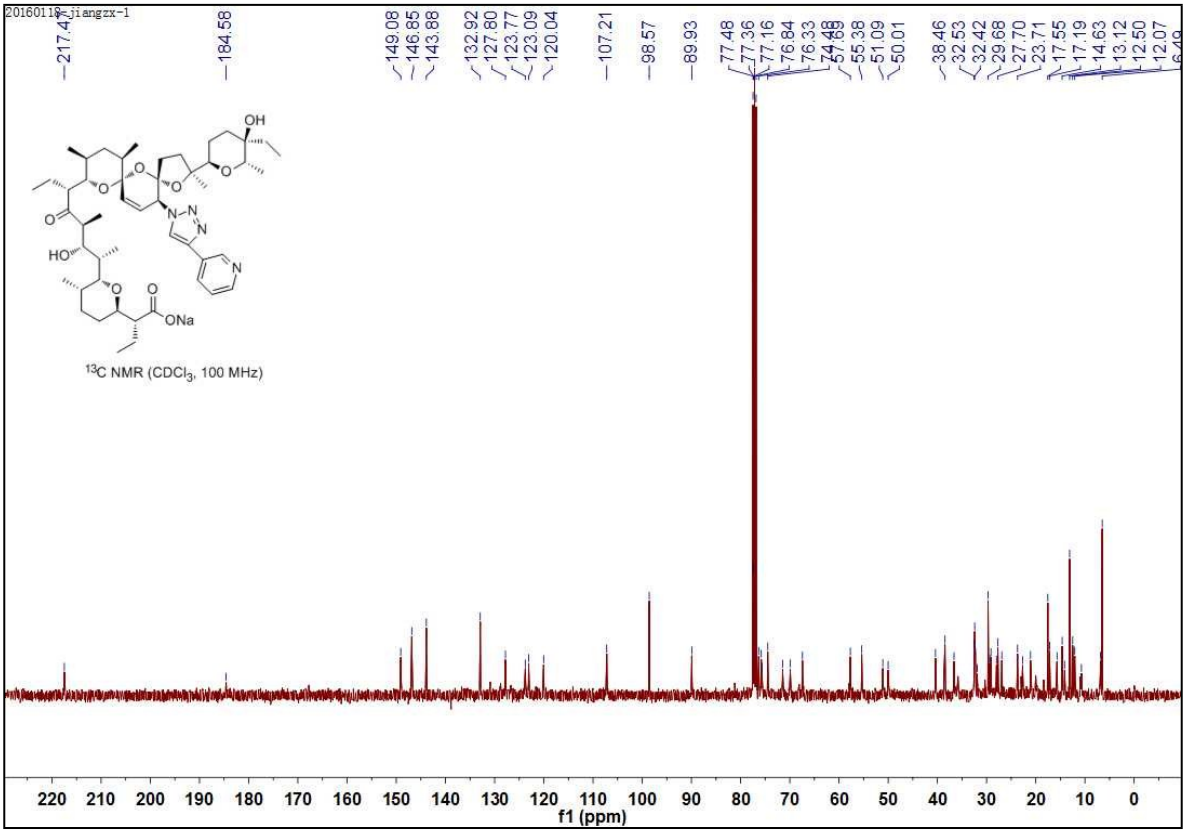
Peak List

m/z	z	Abund
121.0509	1	61942.4
202.18	1	45785.06
451.2692	2	118712.96
451.7706	2	60685.63
879.5488	1	722638.66
880.5519	1	365113.07
881.5546	1	87589.07
901.5306	1	322775.6
902.5336	1	160072.8
922.0098	1	55303.67

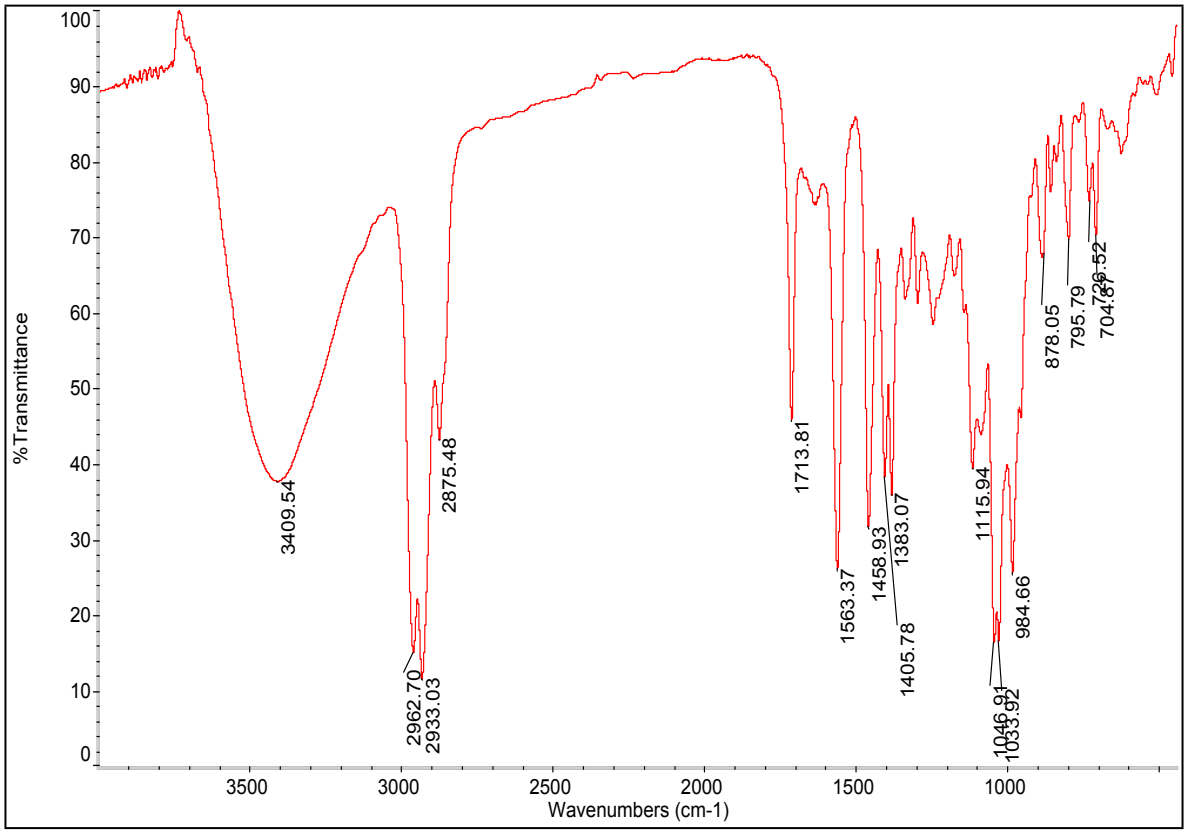
^{1}H NMR of compound **5l**



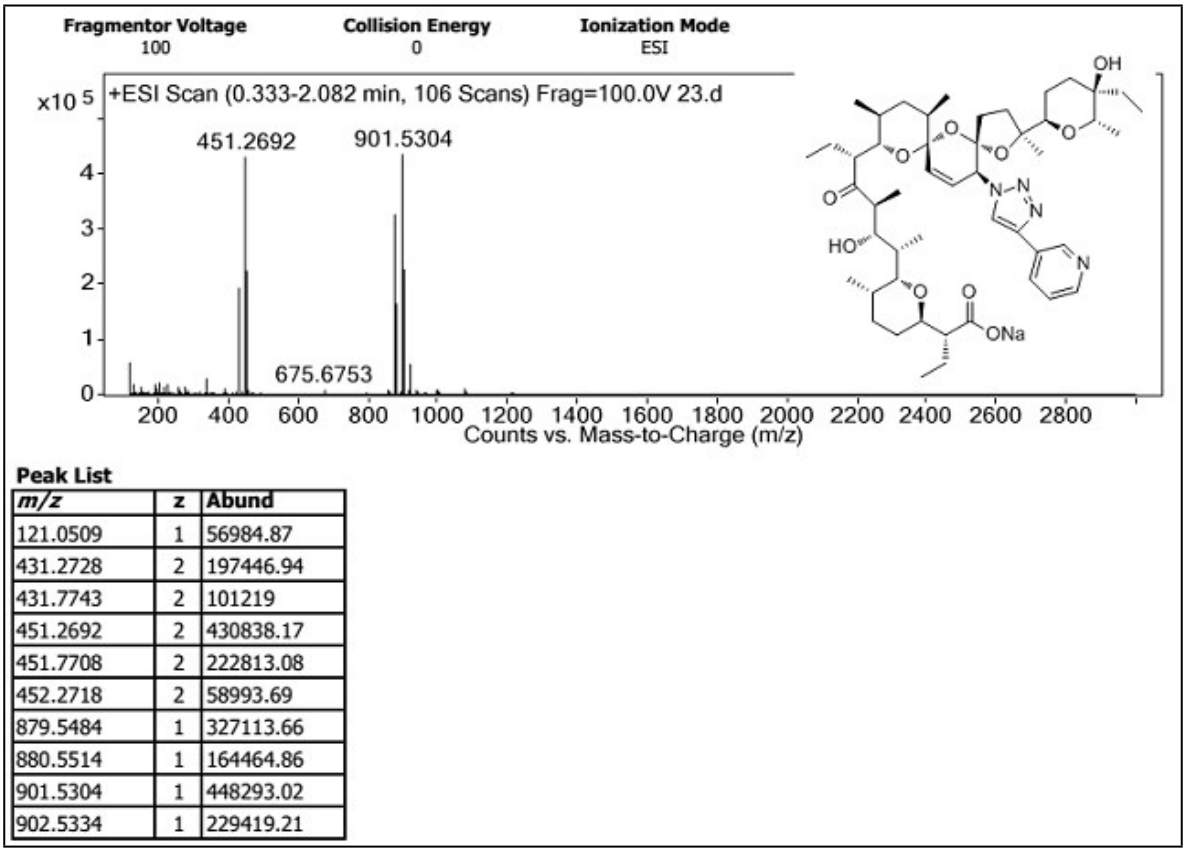
^{13}C NMR of compound **5l**



IR (KBr) of compound **5l**



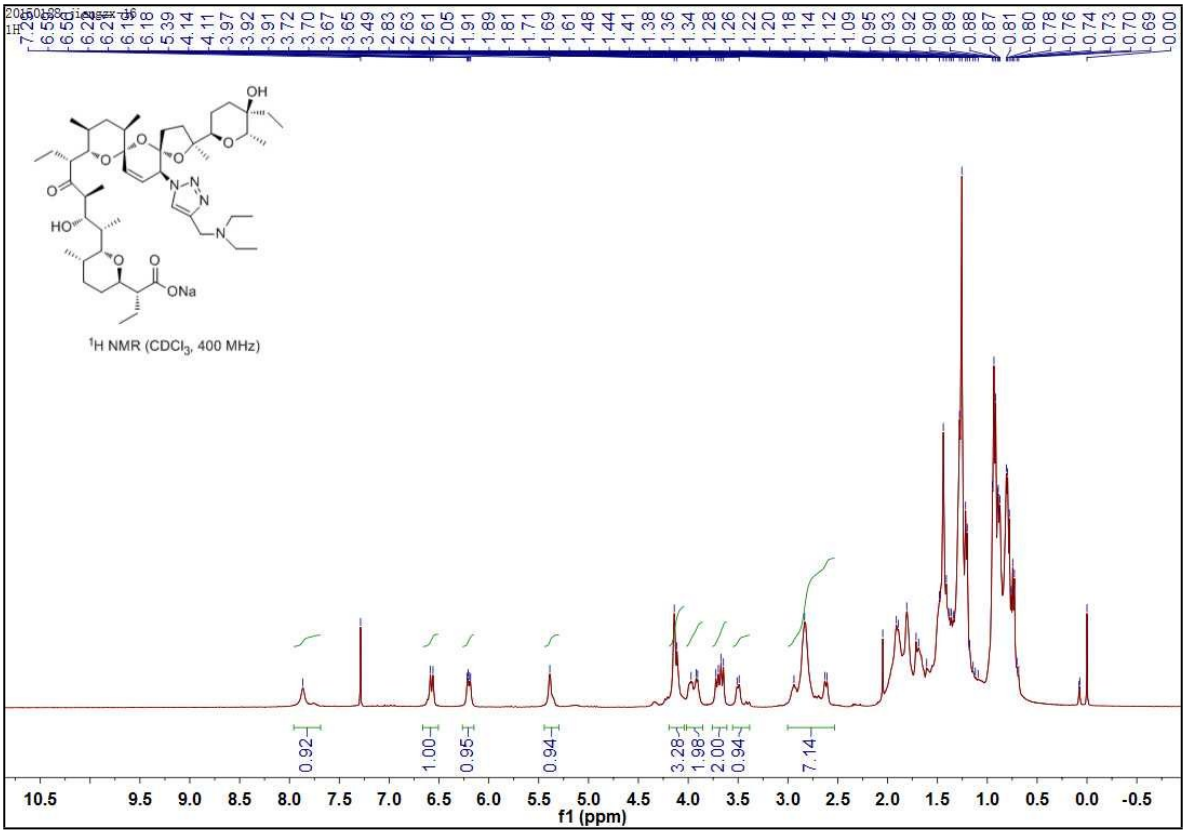
HRMS of compound **5l**



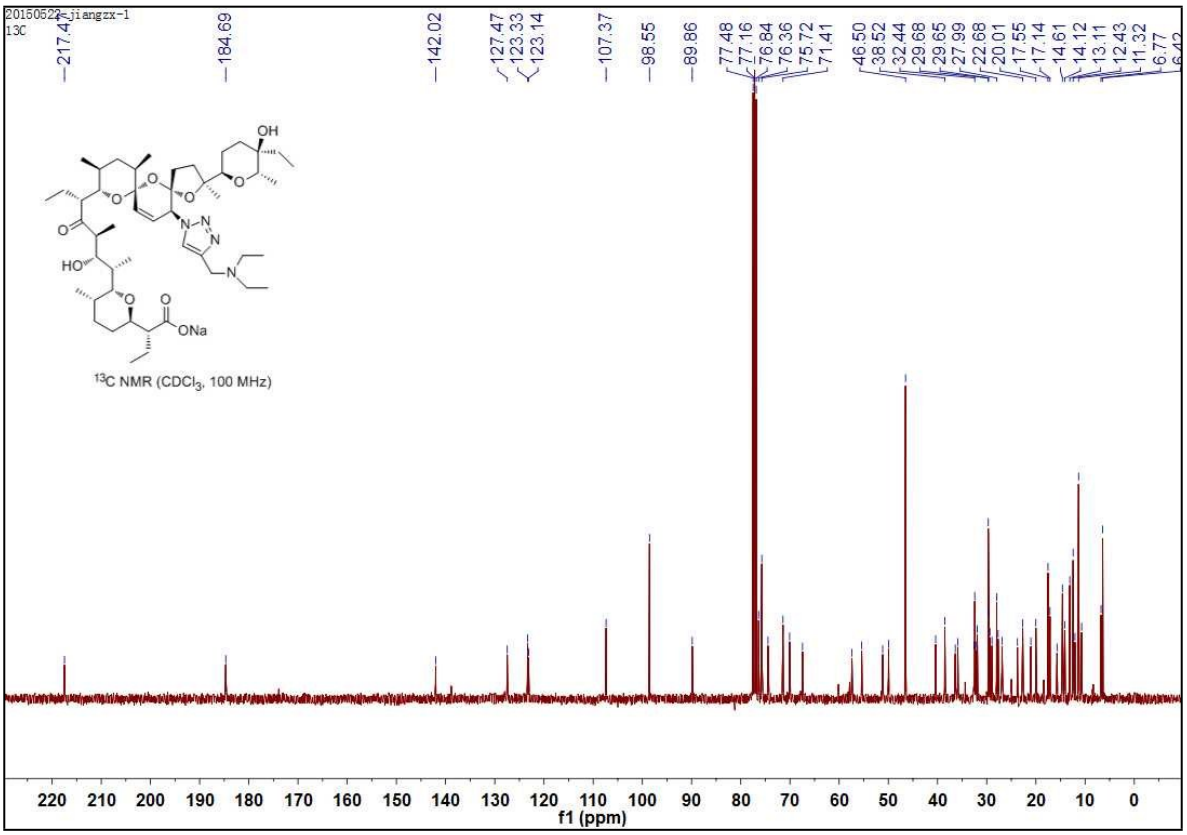
Peak List

m/z	z	Abund
121.0509	1	56984.87
431.2728	2	197446.94
431.7743	2	101219
451.2692	2	430838.17
451.7708	2	222813.08
452.2718	2	58993.69
879.5484	1	327113.66
880.5514	1	164464.86
901.5304	1	448293.02
902.5334	1	229419.21

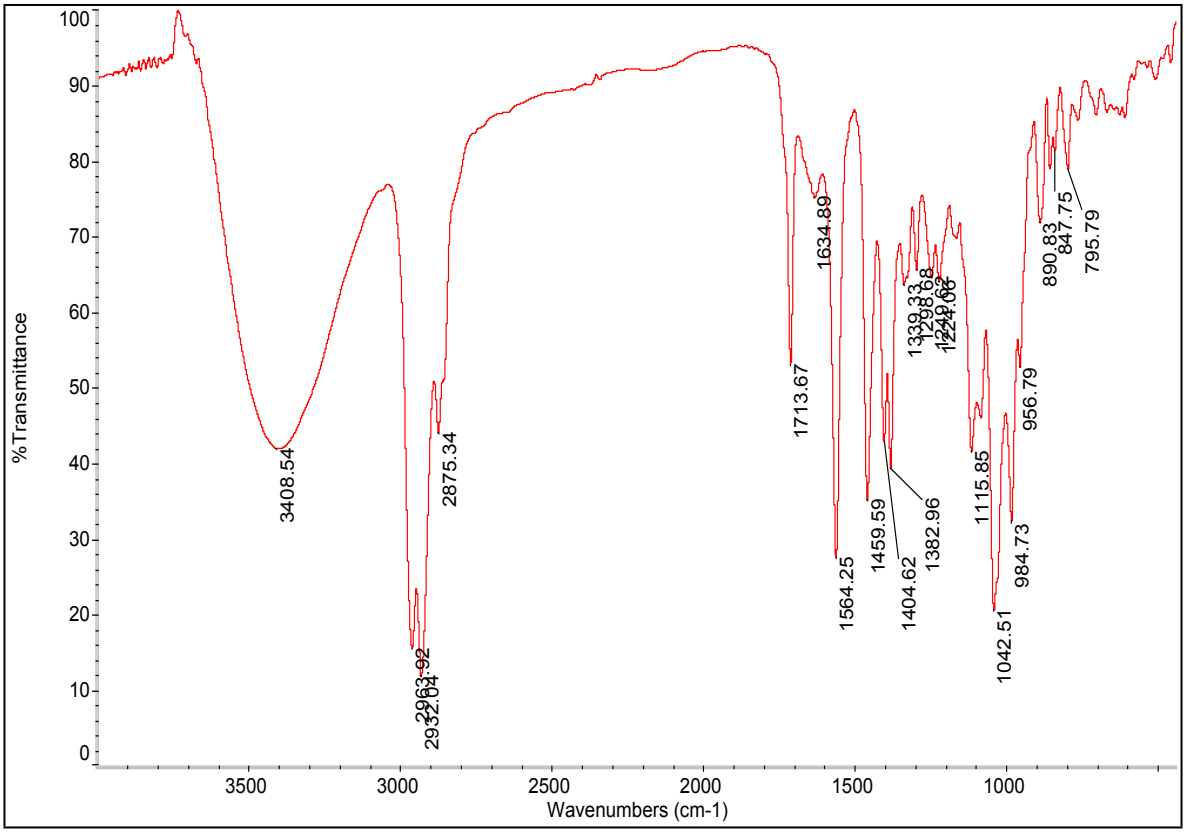
^{1}H NMR of compound **5m**



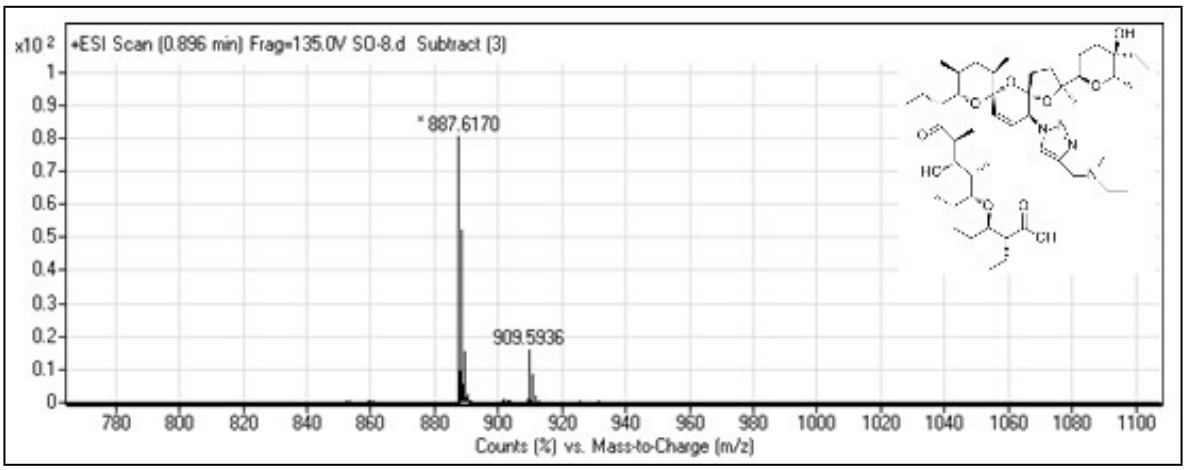
^{13}C NMR of compound **5m**



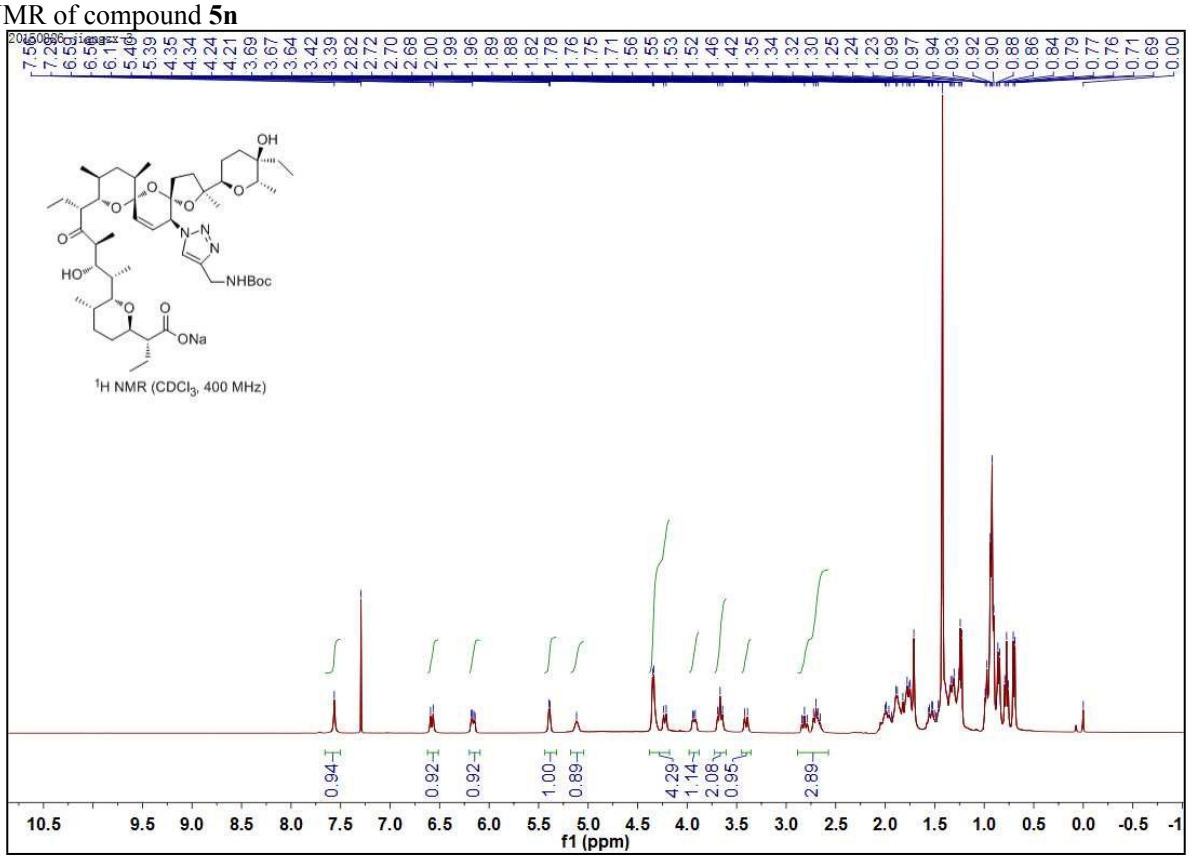
IR (KBr) of compound **5m**



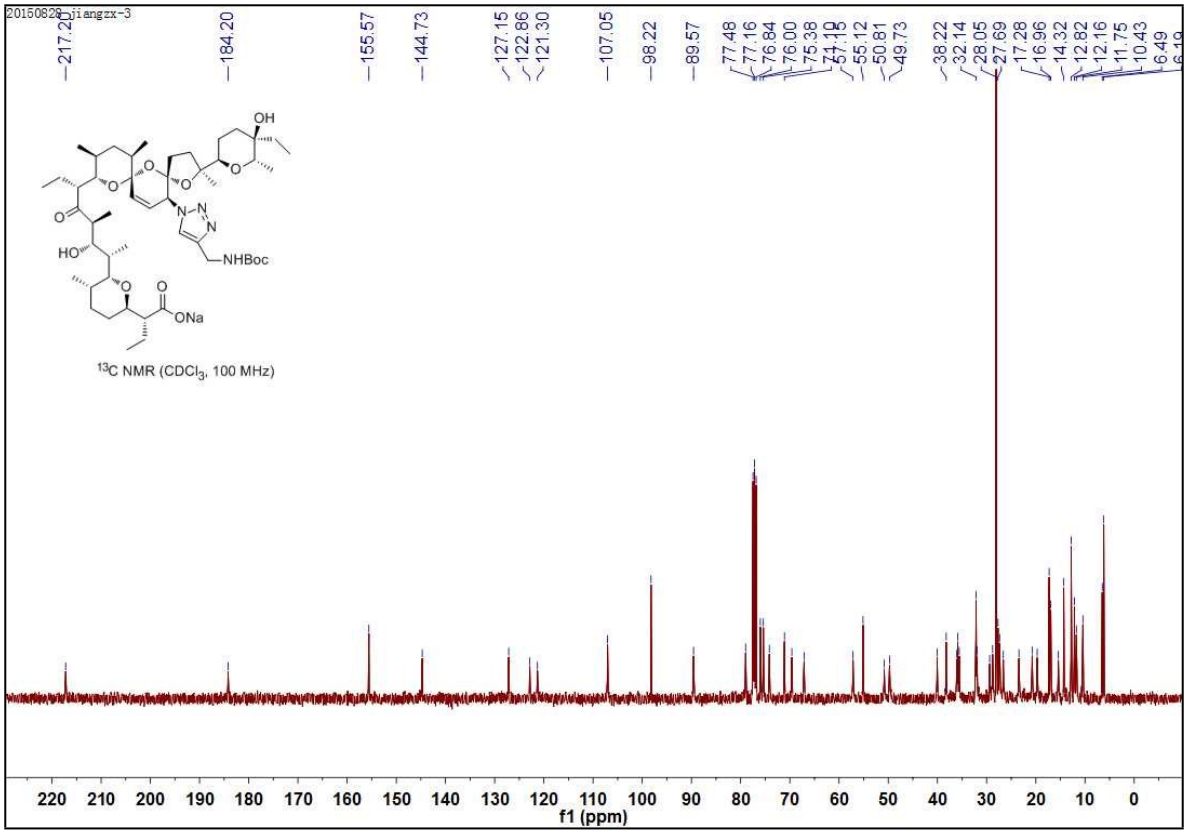
HRMS of compound **5m**



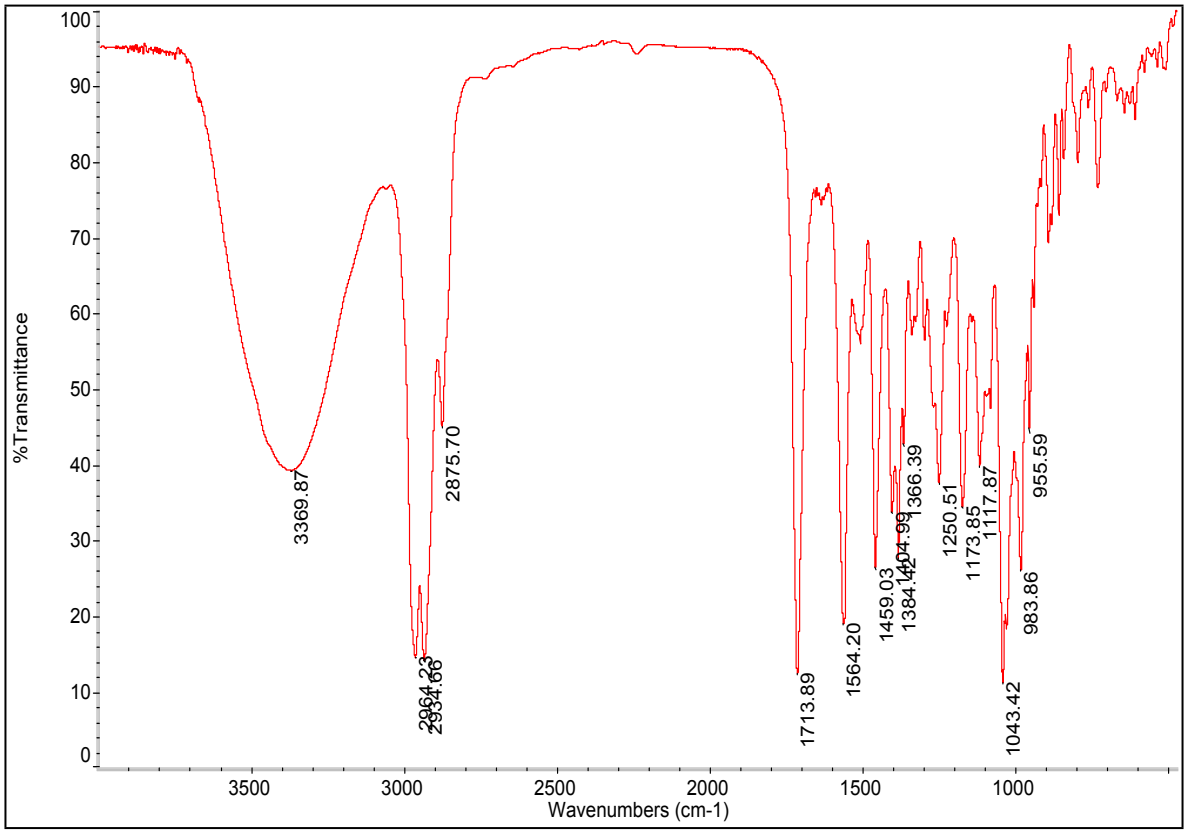
^{1}H NMR of compound **5n**



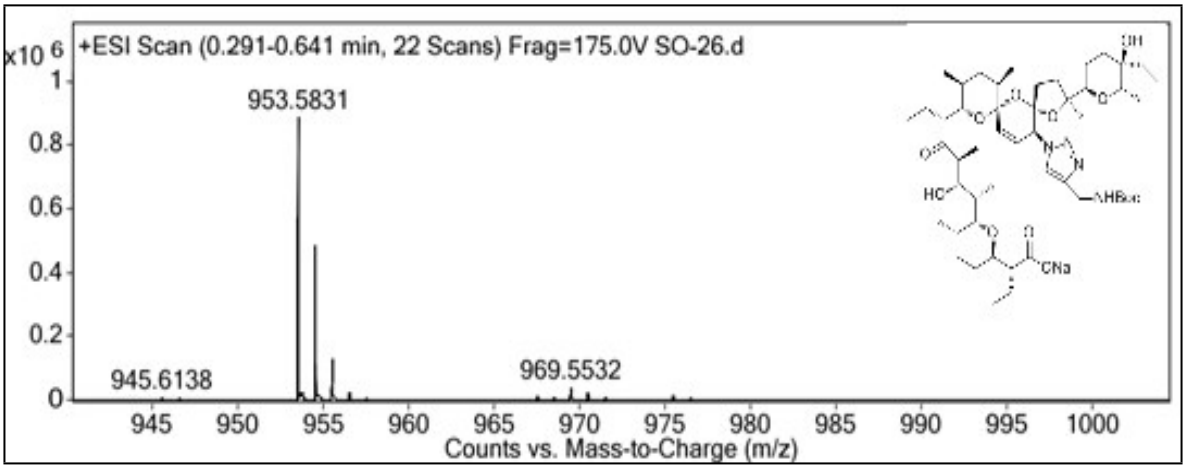
^{13}C NMR of compound **5n**



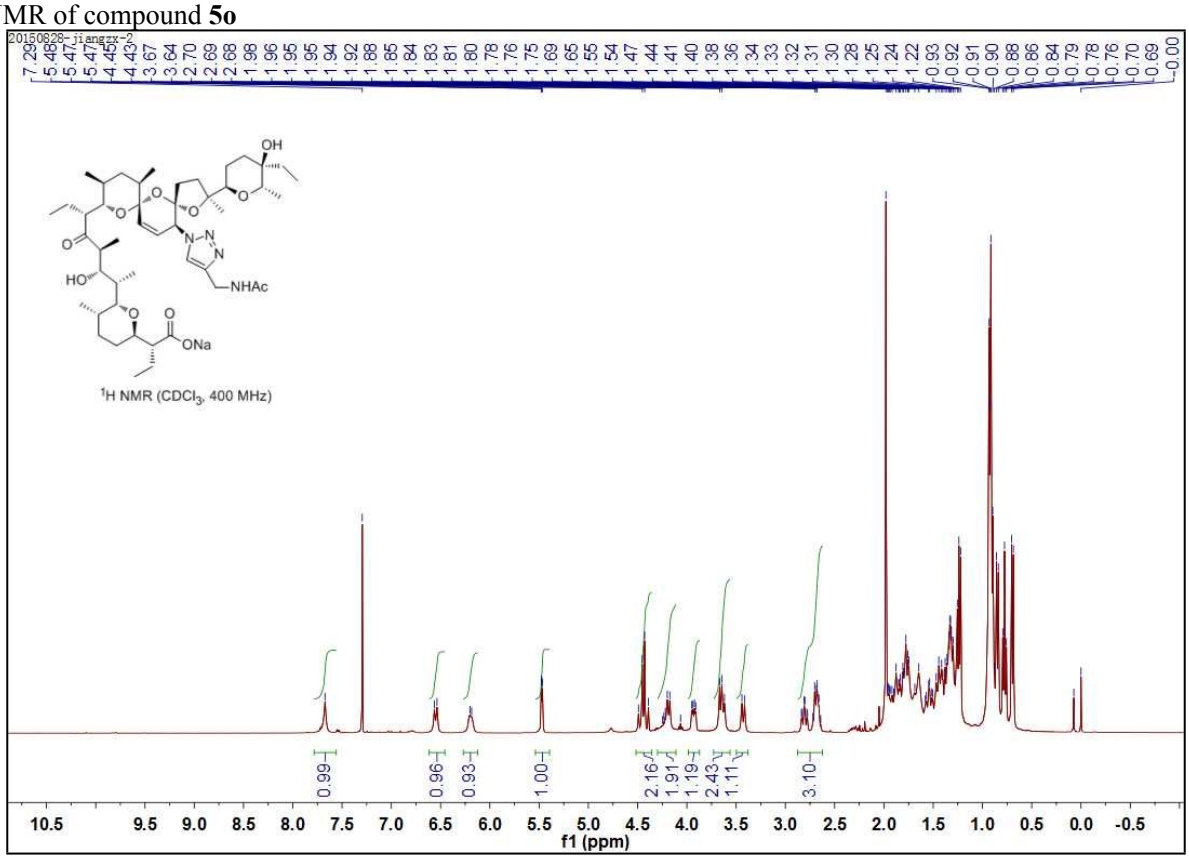
IR (KBr) of compound **5n**



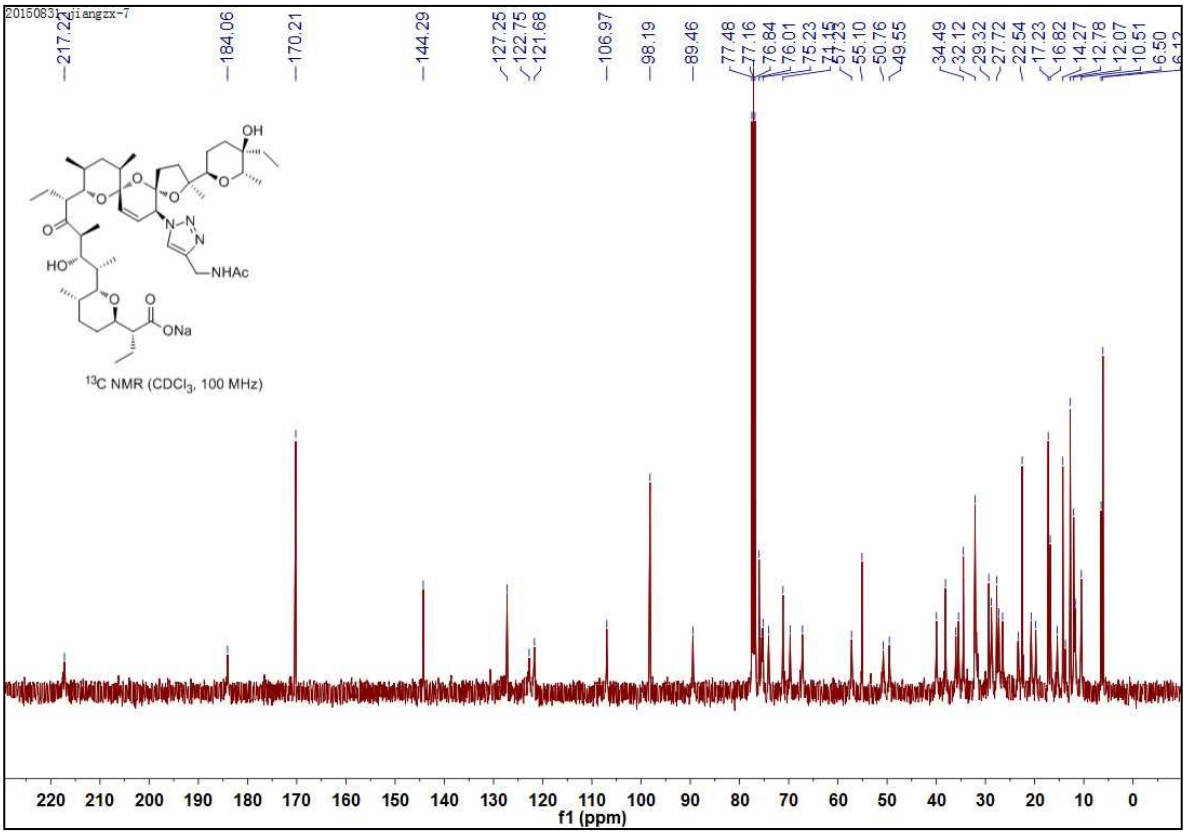
HRMS of compound **5n**



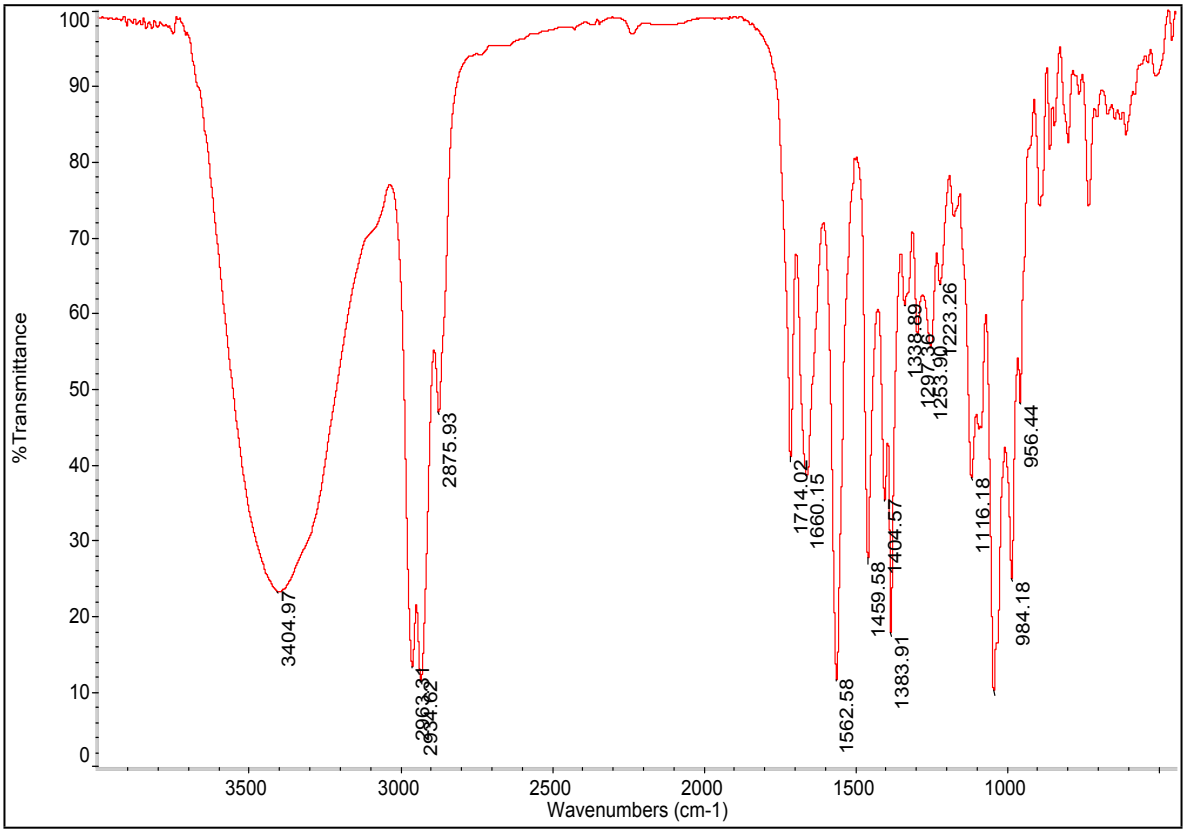
^{1}H NMR of compound **5o**



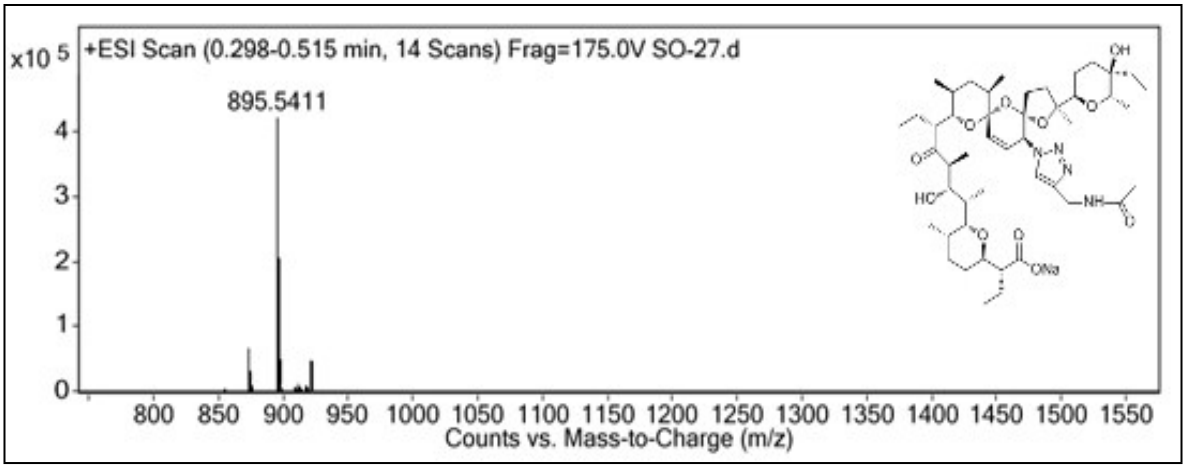
^{13}C NMR of compound **5o**



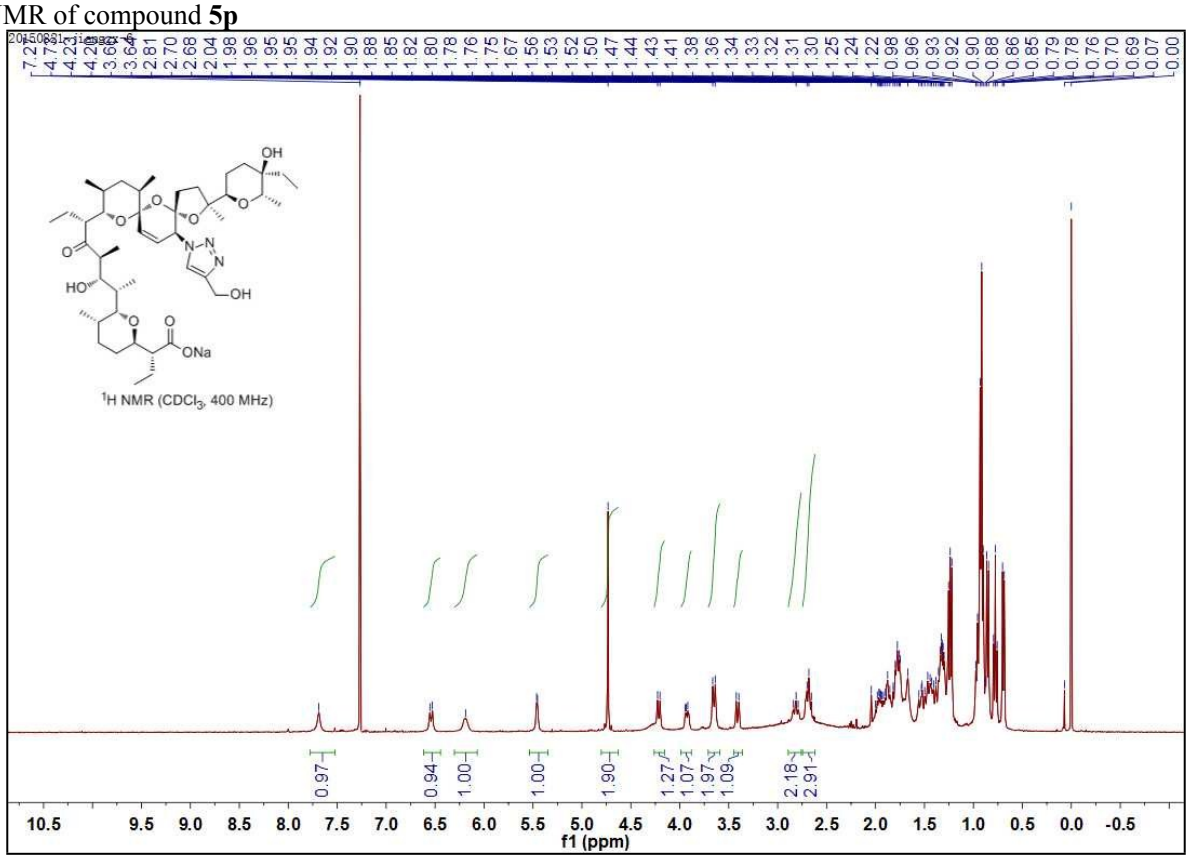
IR (KBr) of compound **5o**



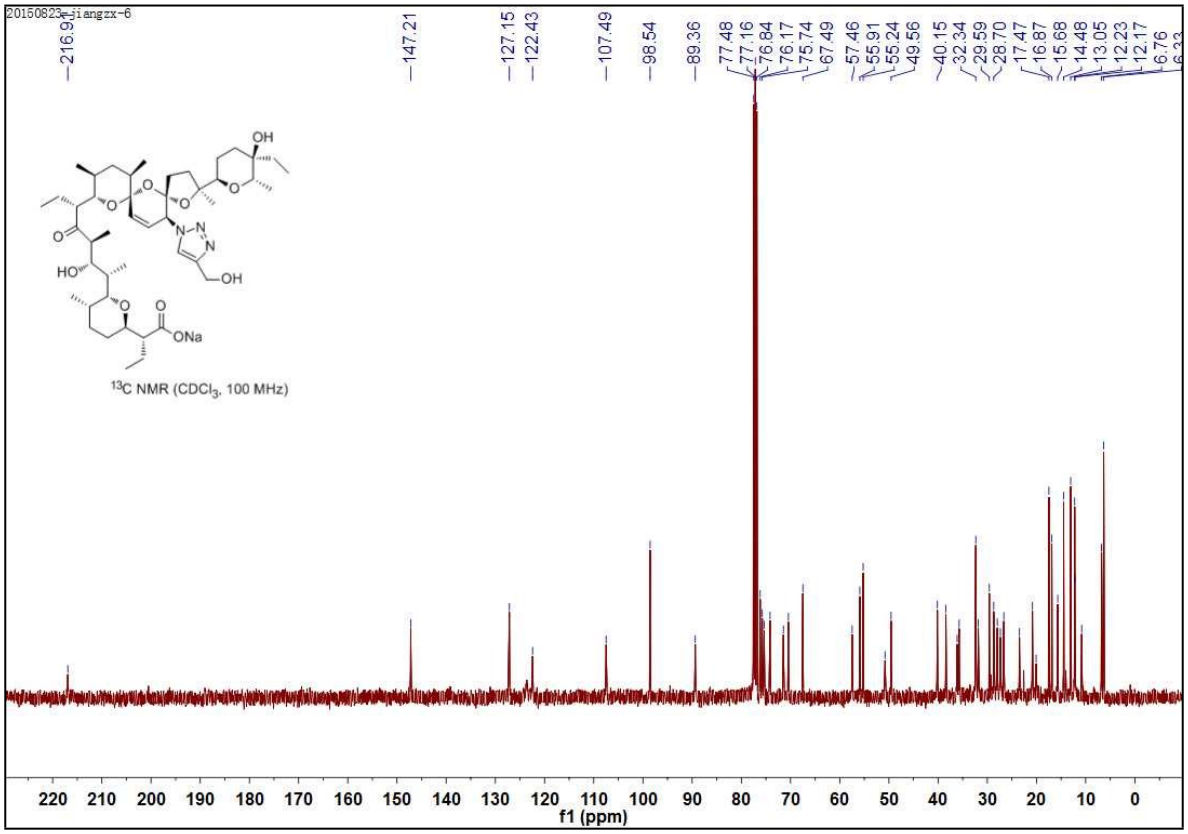
HRMS of compound **5o**



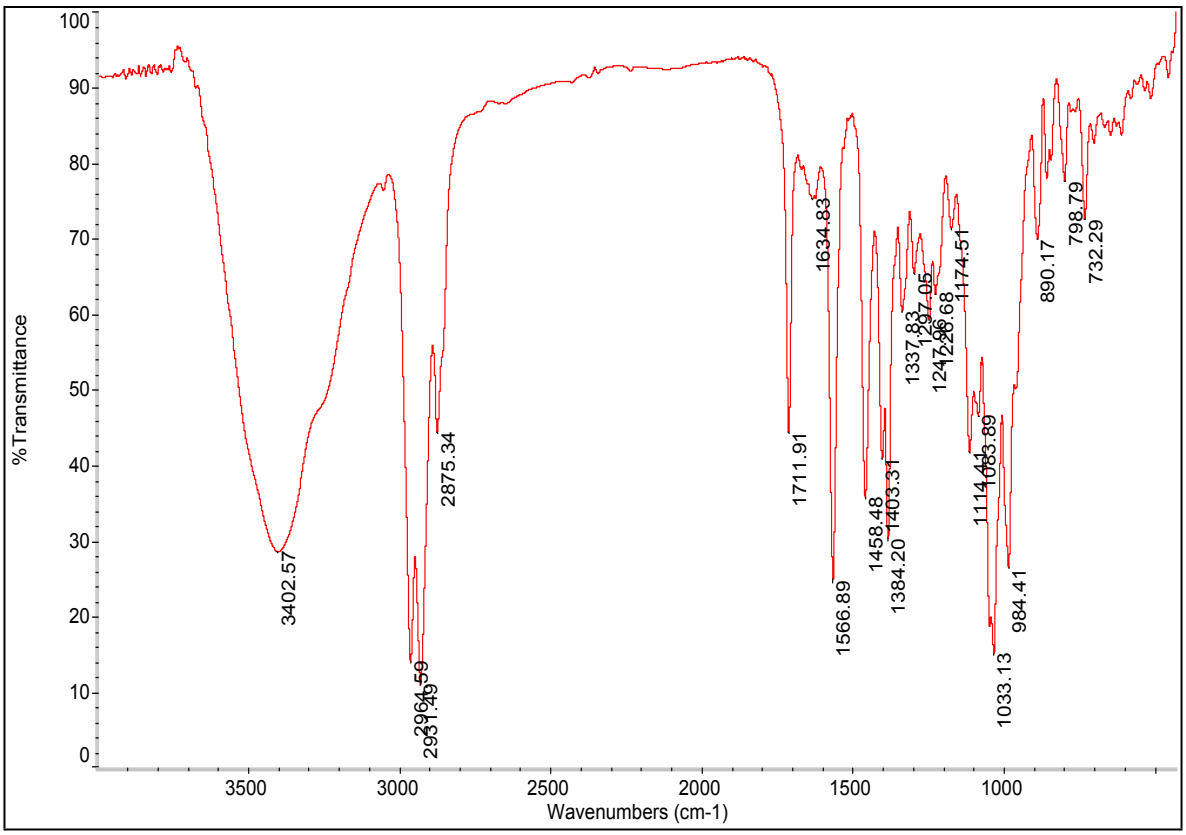
^{1}H NMR of compound **5p**



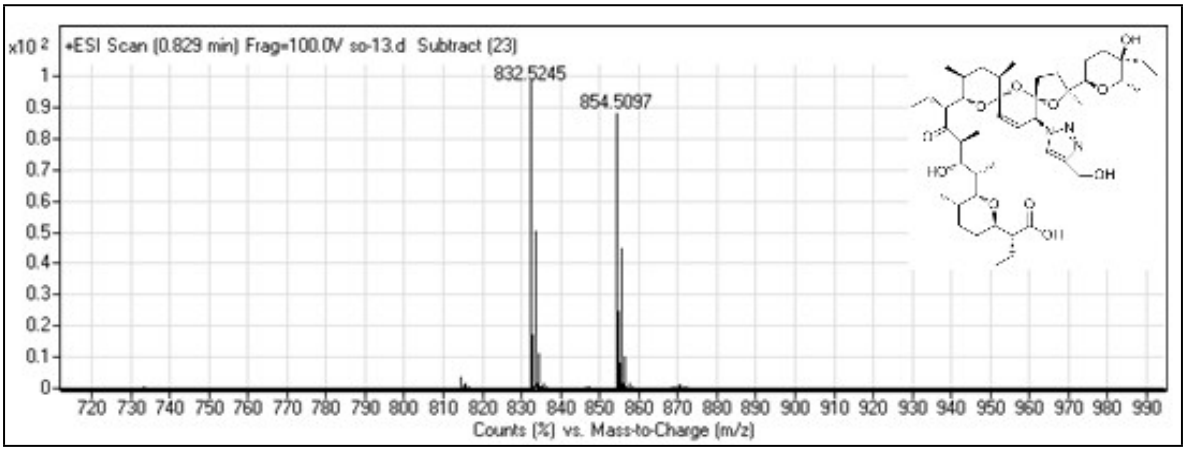
^{13}C NMR of compound **5p**



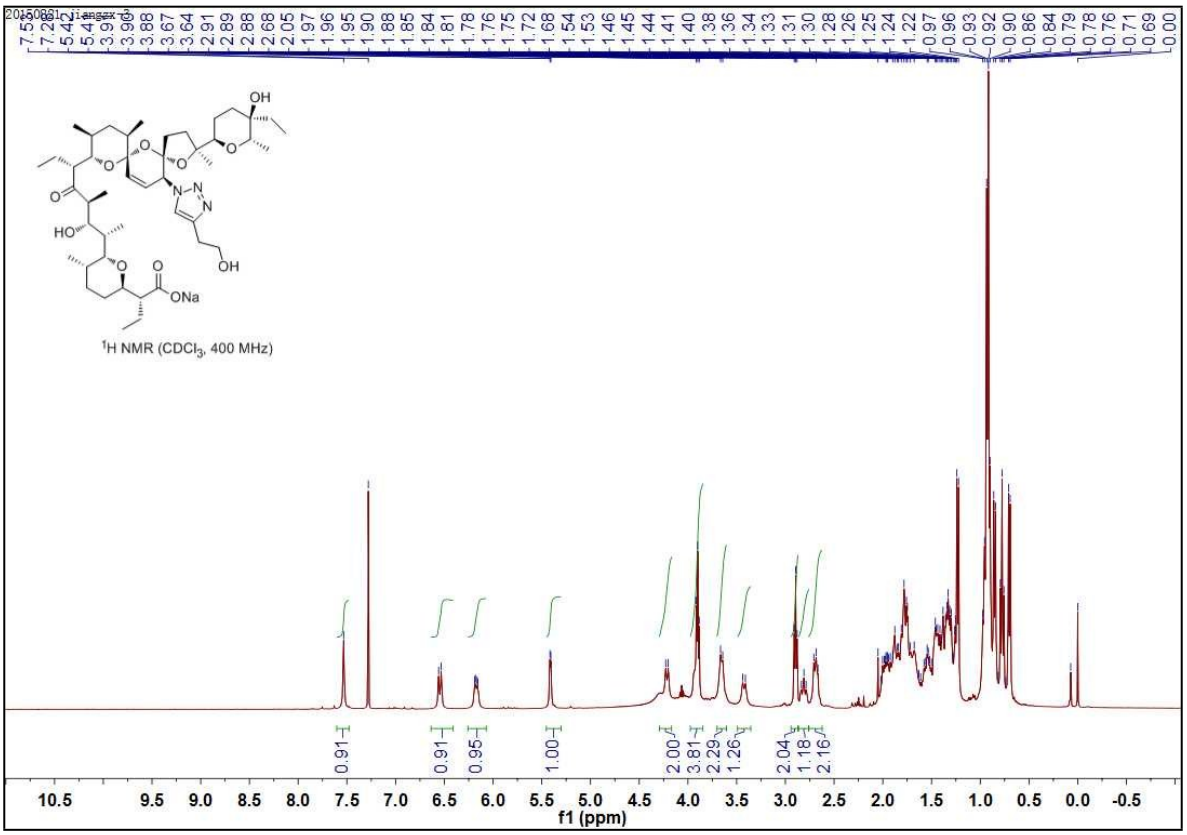
IR (KBr) of compound **5p**



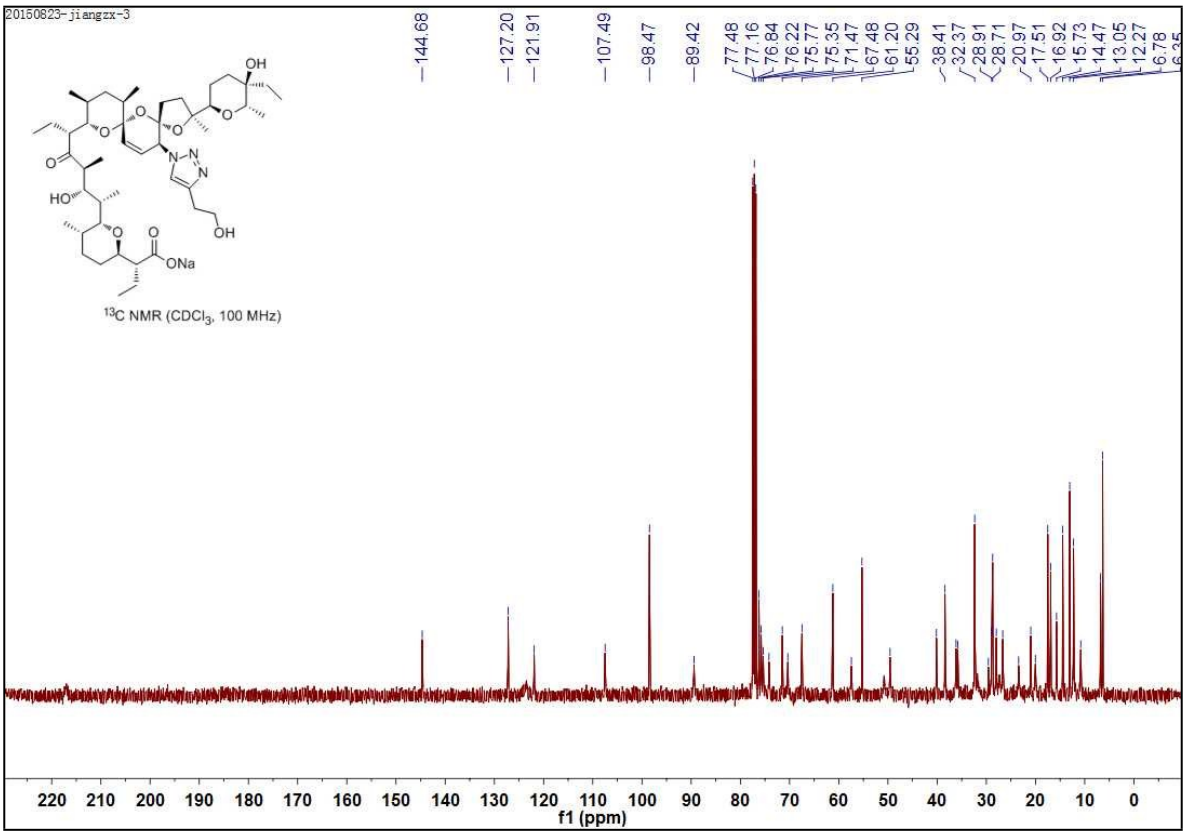
HRMS of compound **5p**



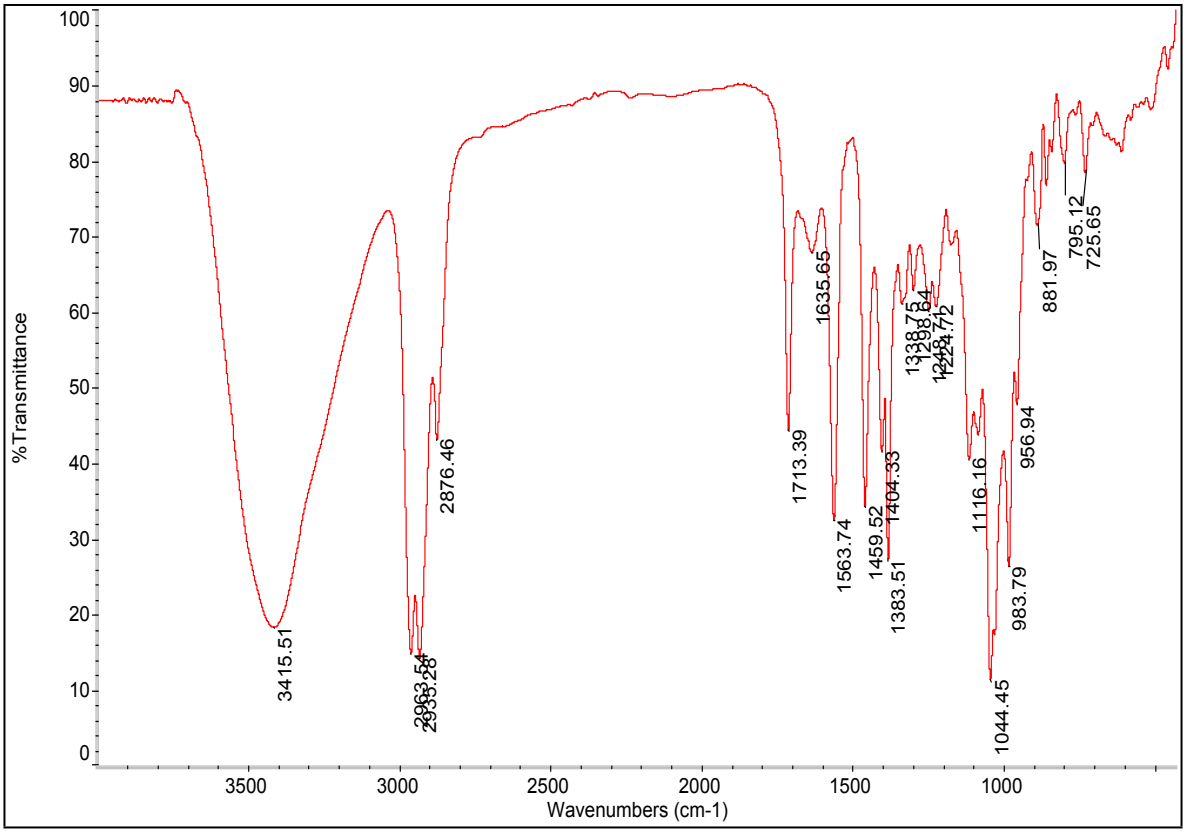
^{1}H NMR of compound **5q**



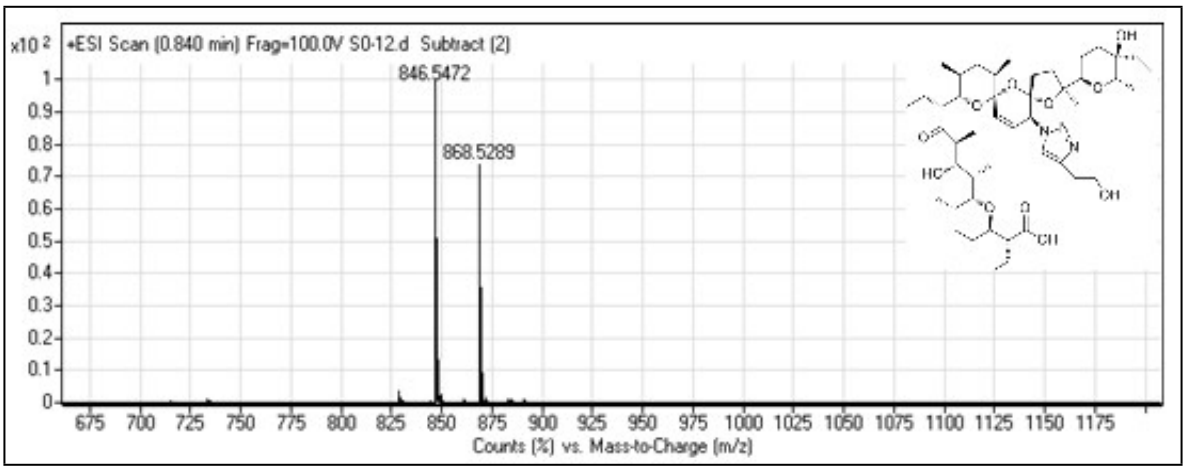
^{13}C NMR of compound **5q**



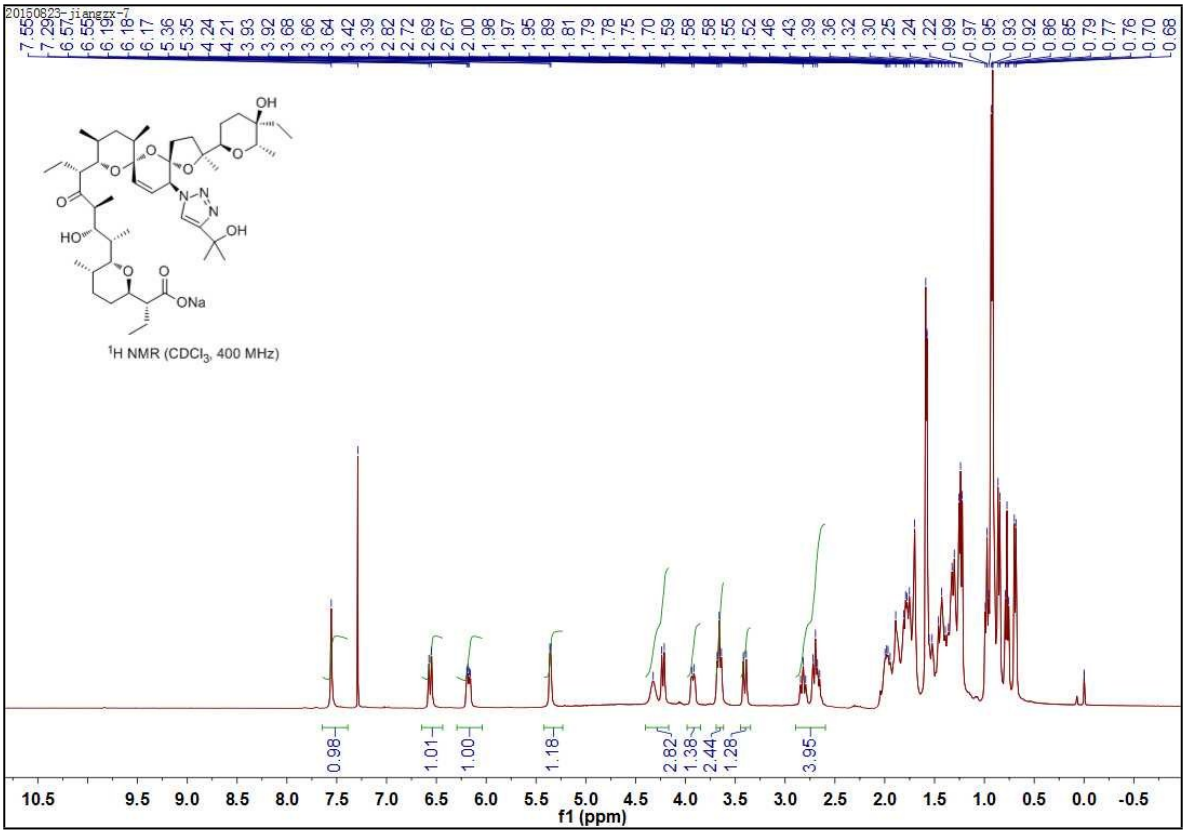
IR (KBr) of compound **5q**



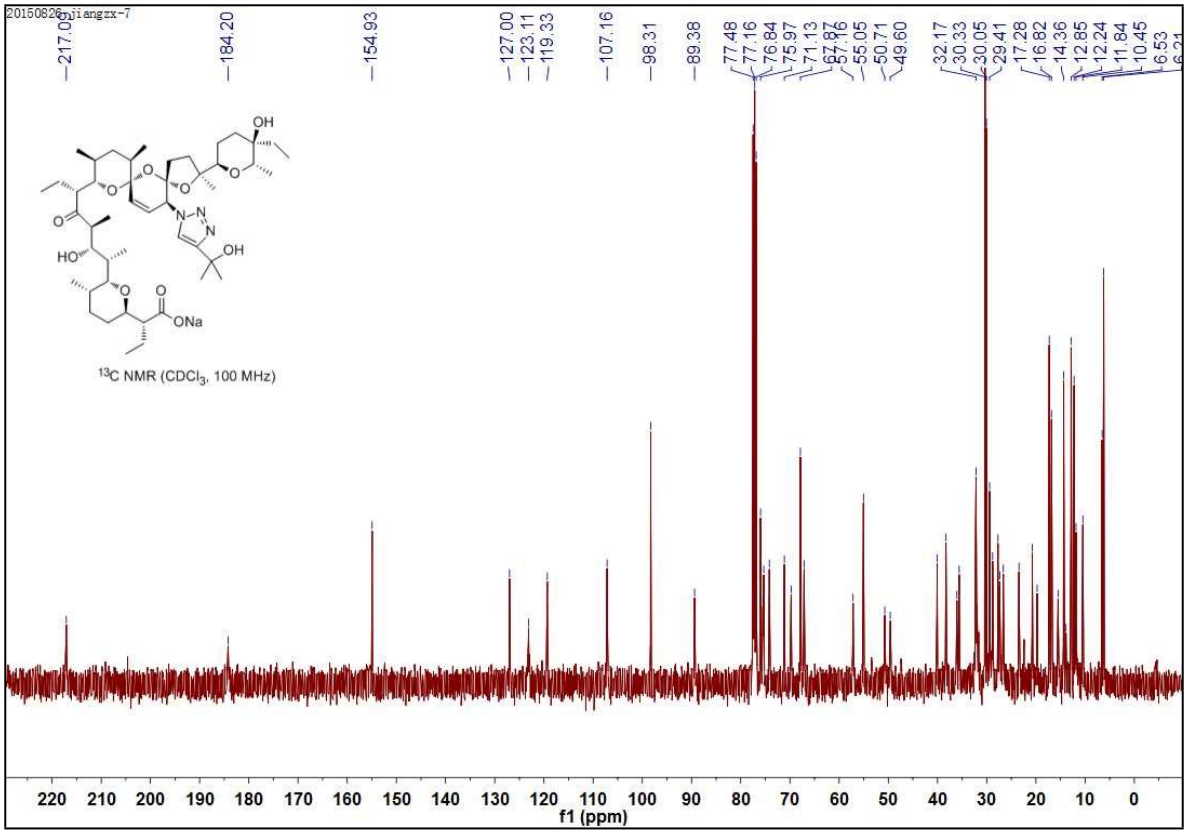
HRMS of compound **5q**



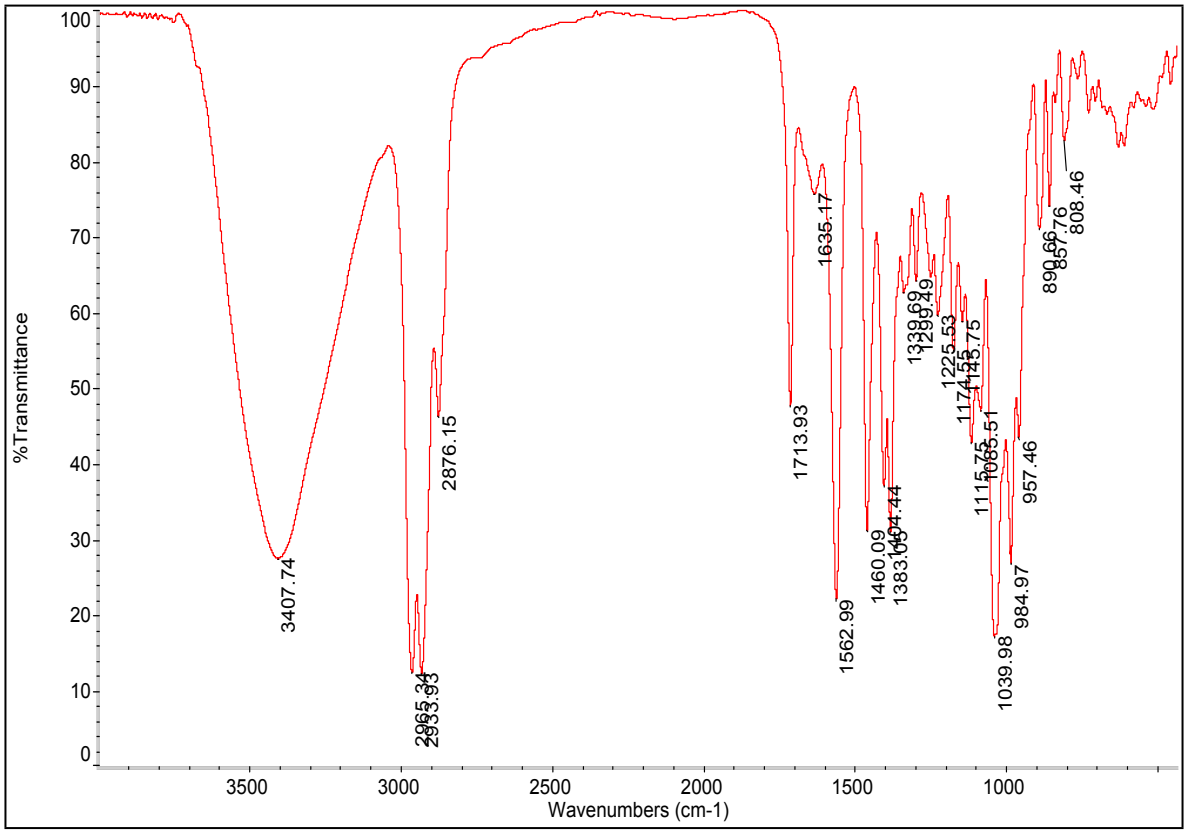
^{1}H NMR of compound **5r**



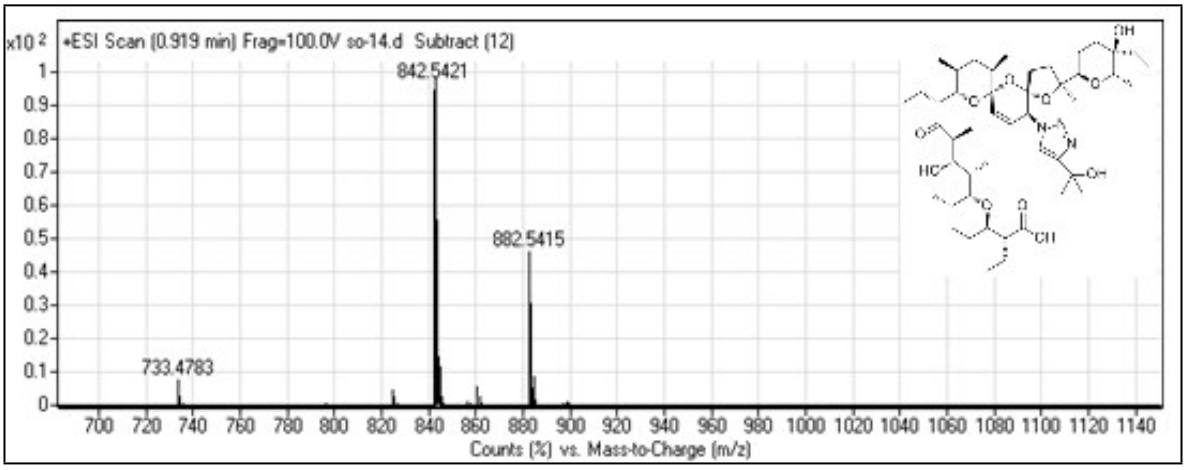
^{13}C NMR of compound **5r**



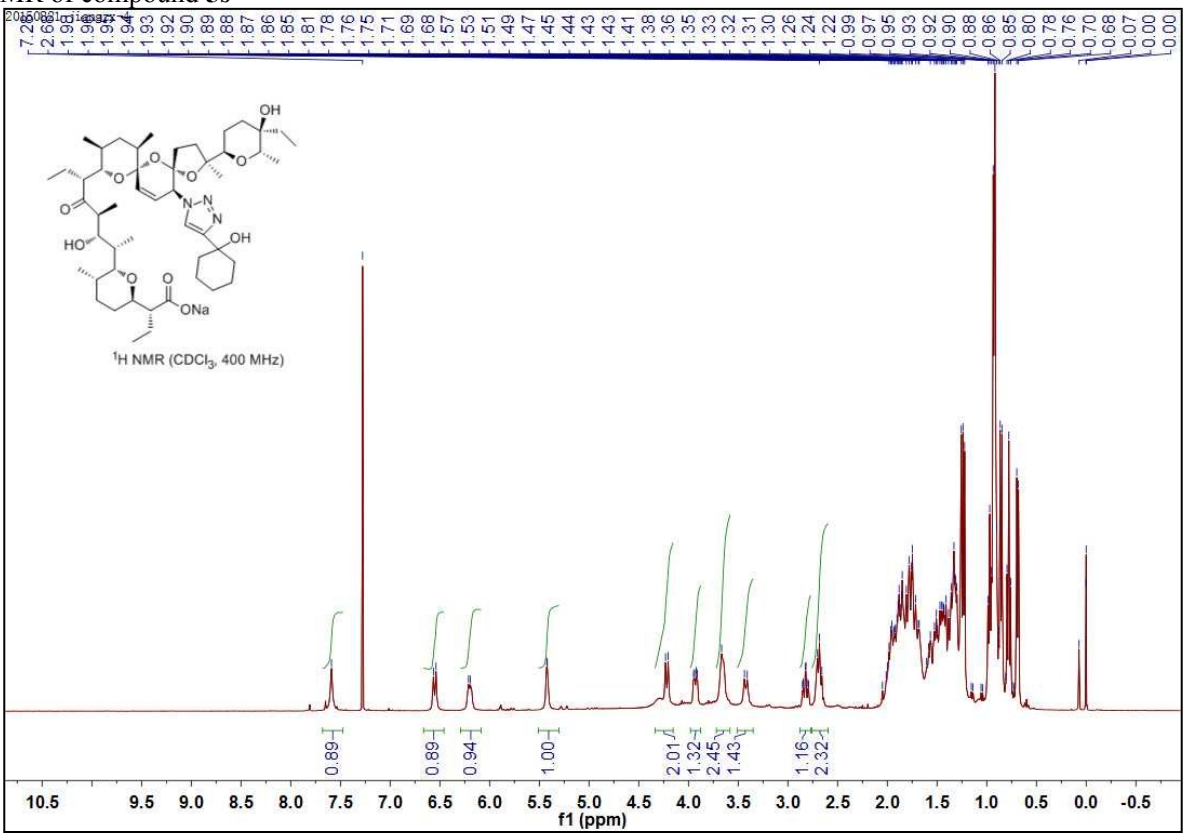
IR (KBr) of compound **5r**



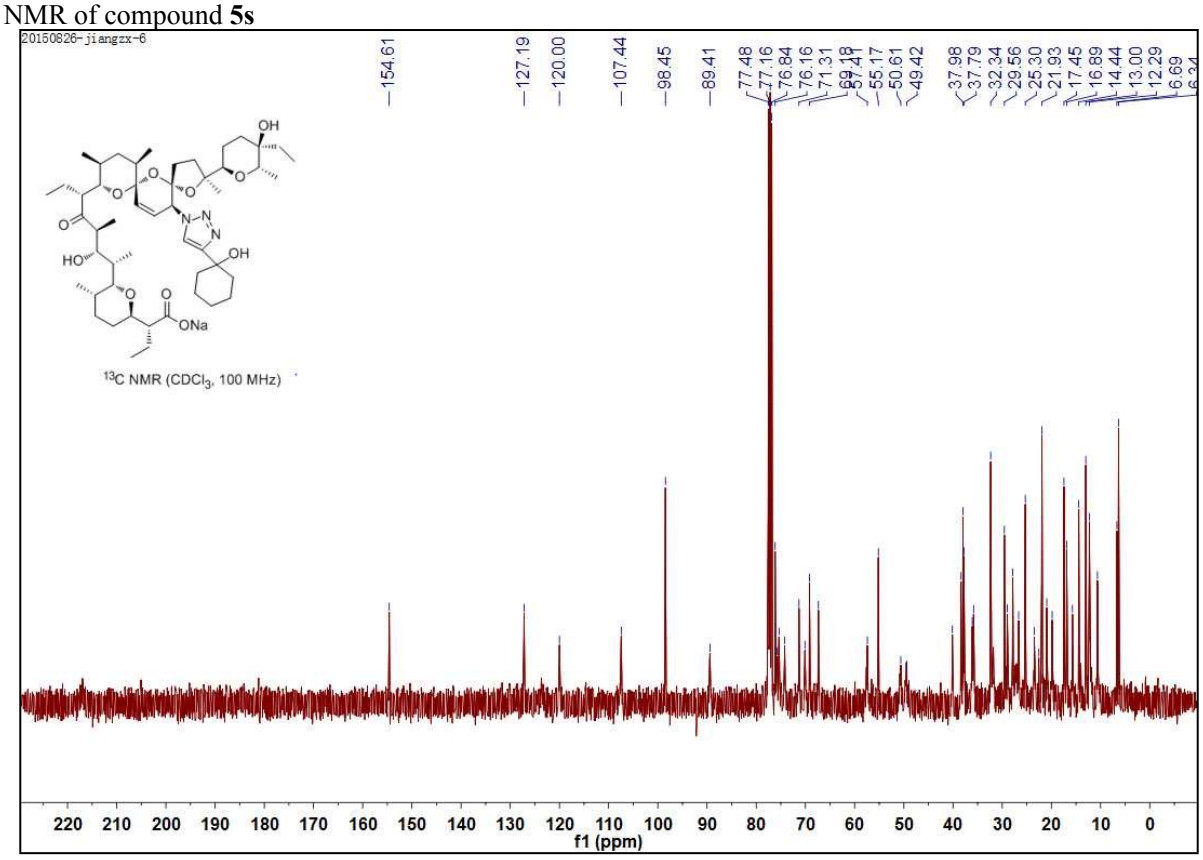
HRMS of compound **5r**



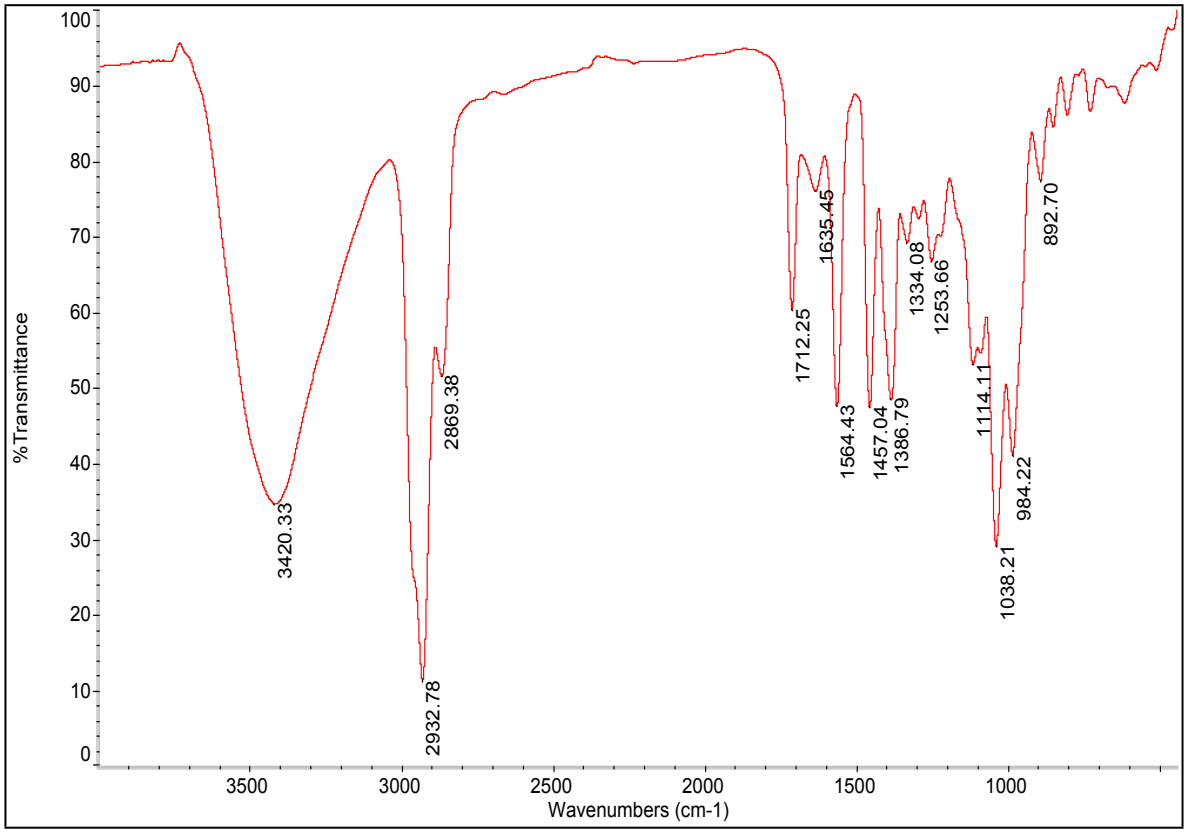
^{1}H NMR of compound **5s**



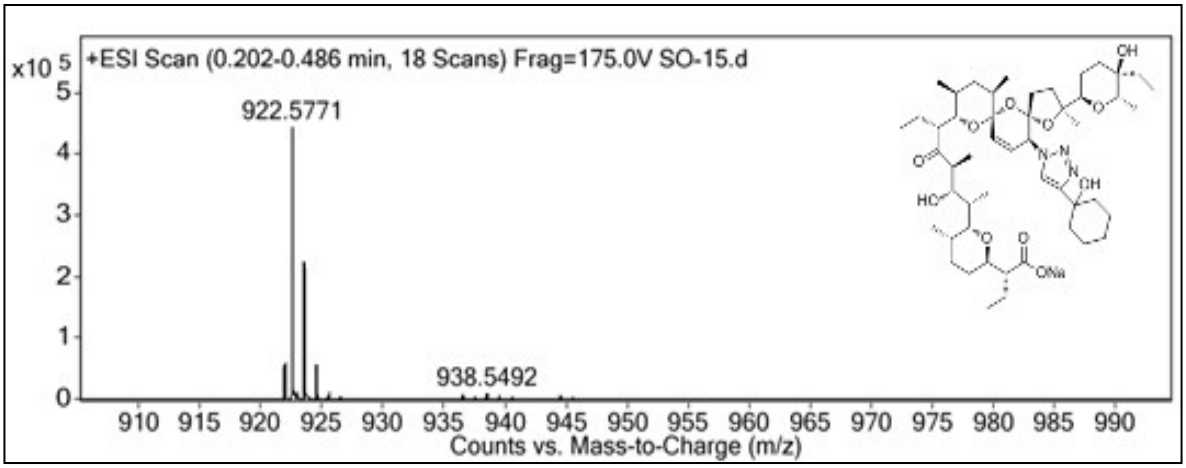
^{13}C NMR of compound **5s**



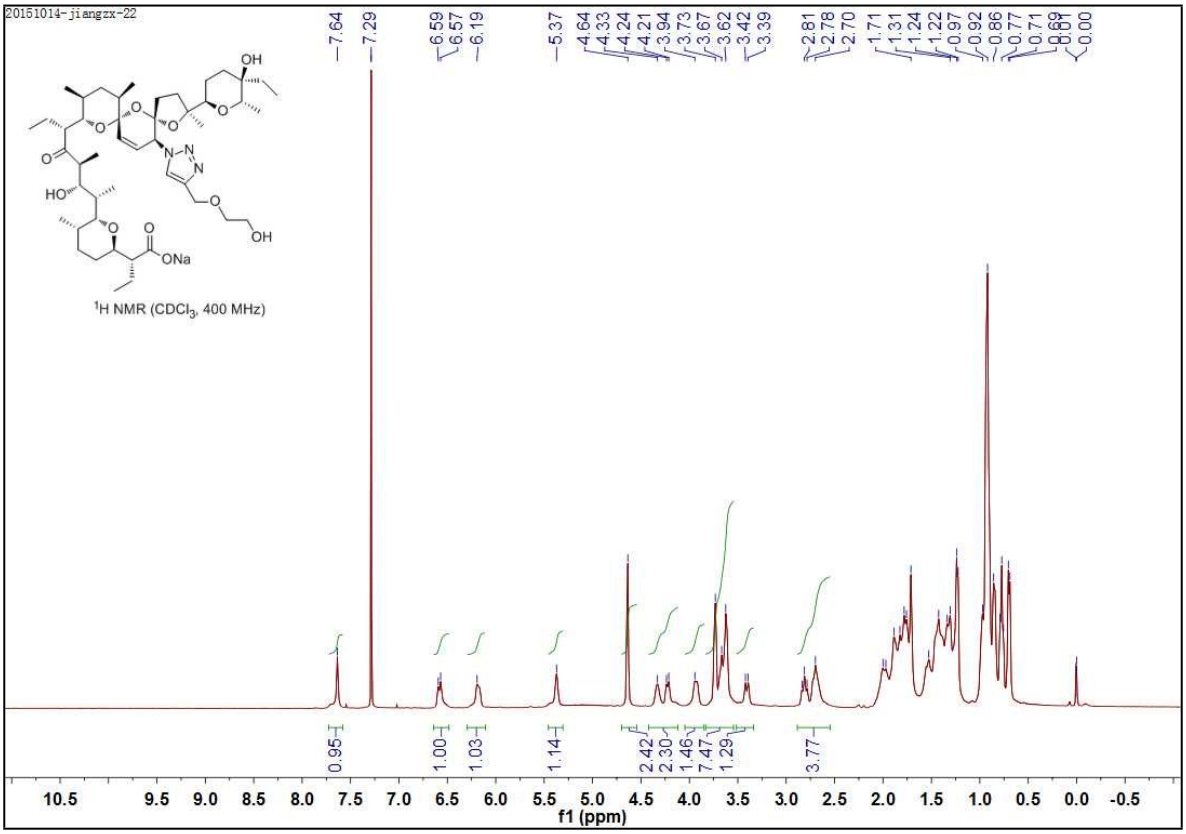
IR (KBr) of compound **5s**



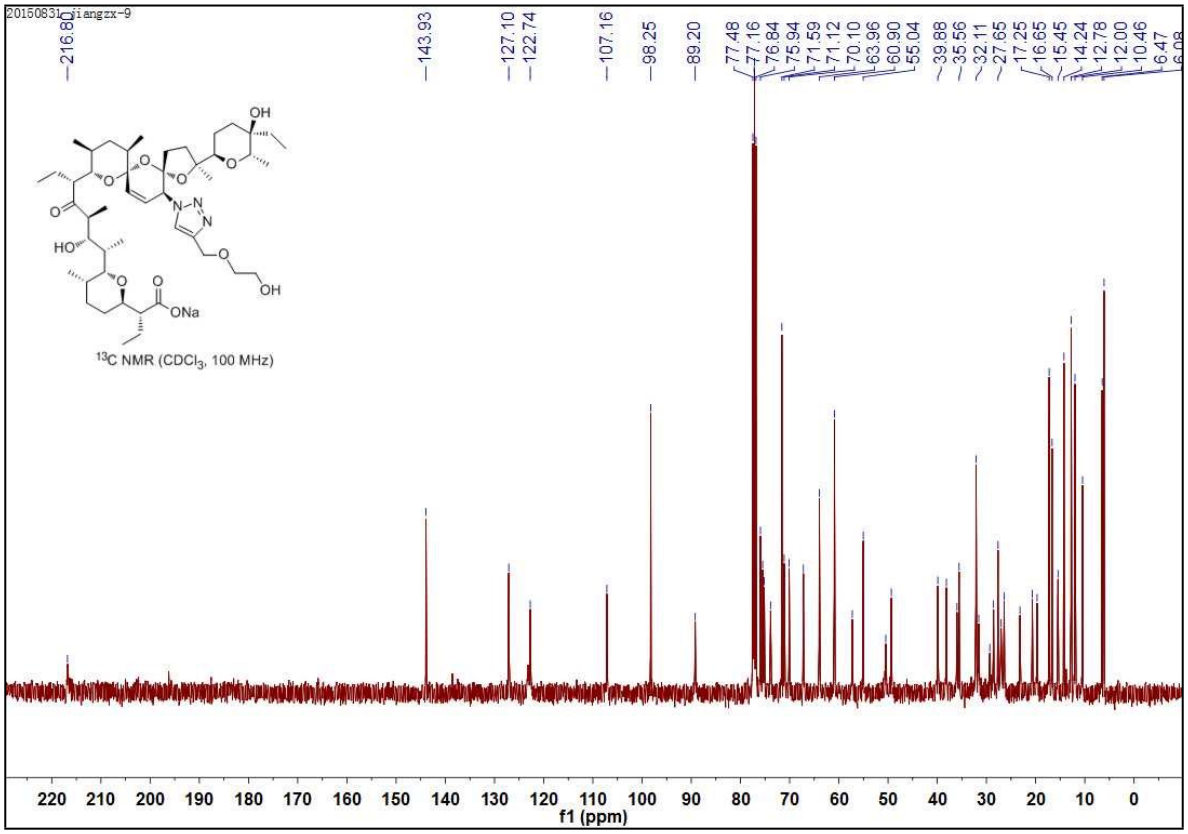
HRMS of compound **5s**



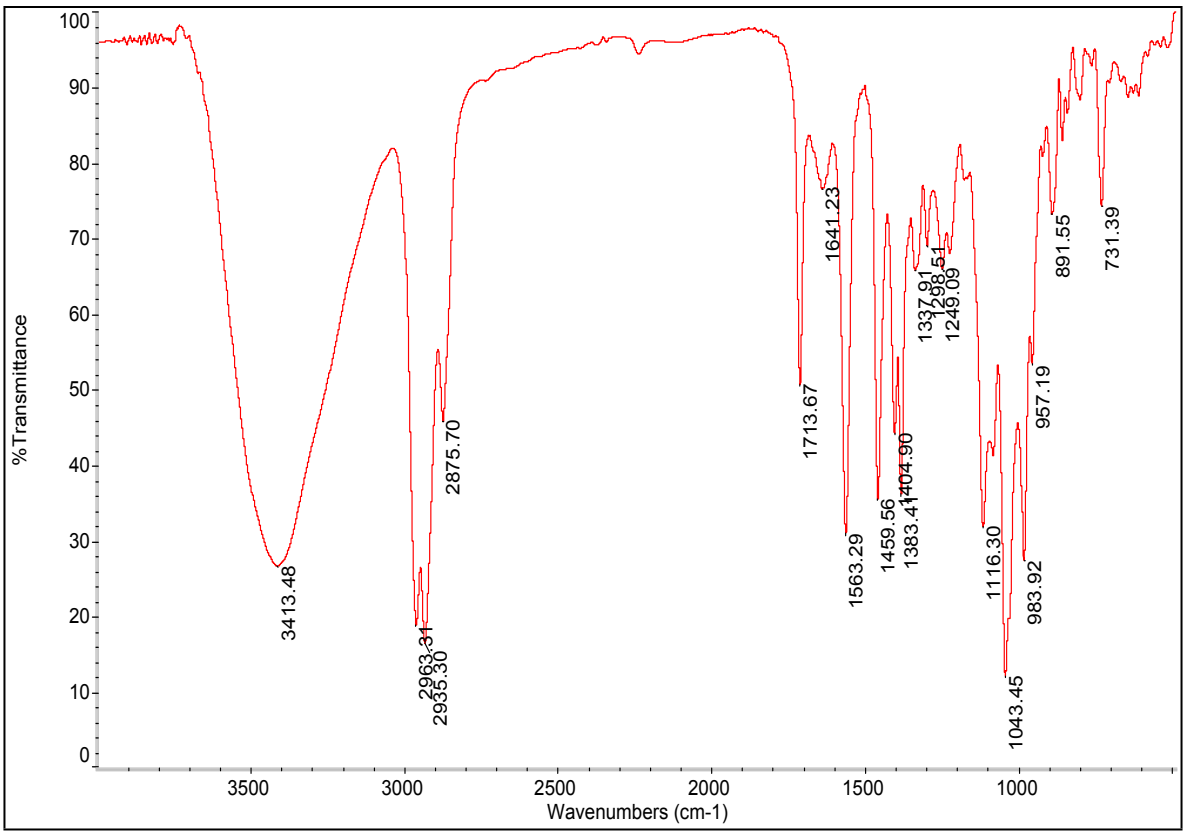
^{1}H NMR of compound **5t**



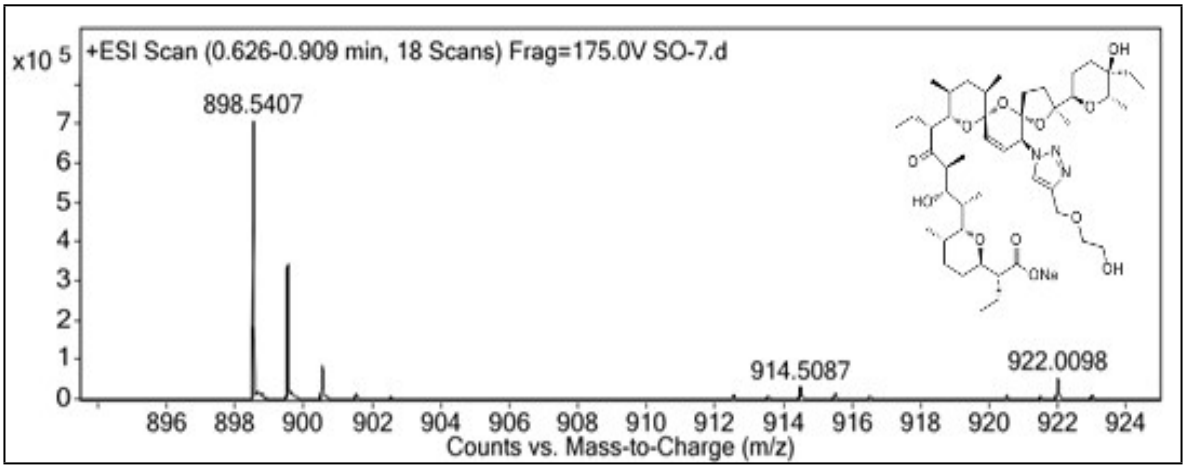
^{13}C NMR of compound **5t**



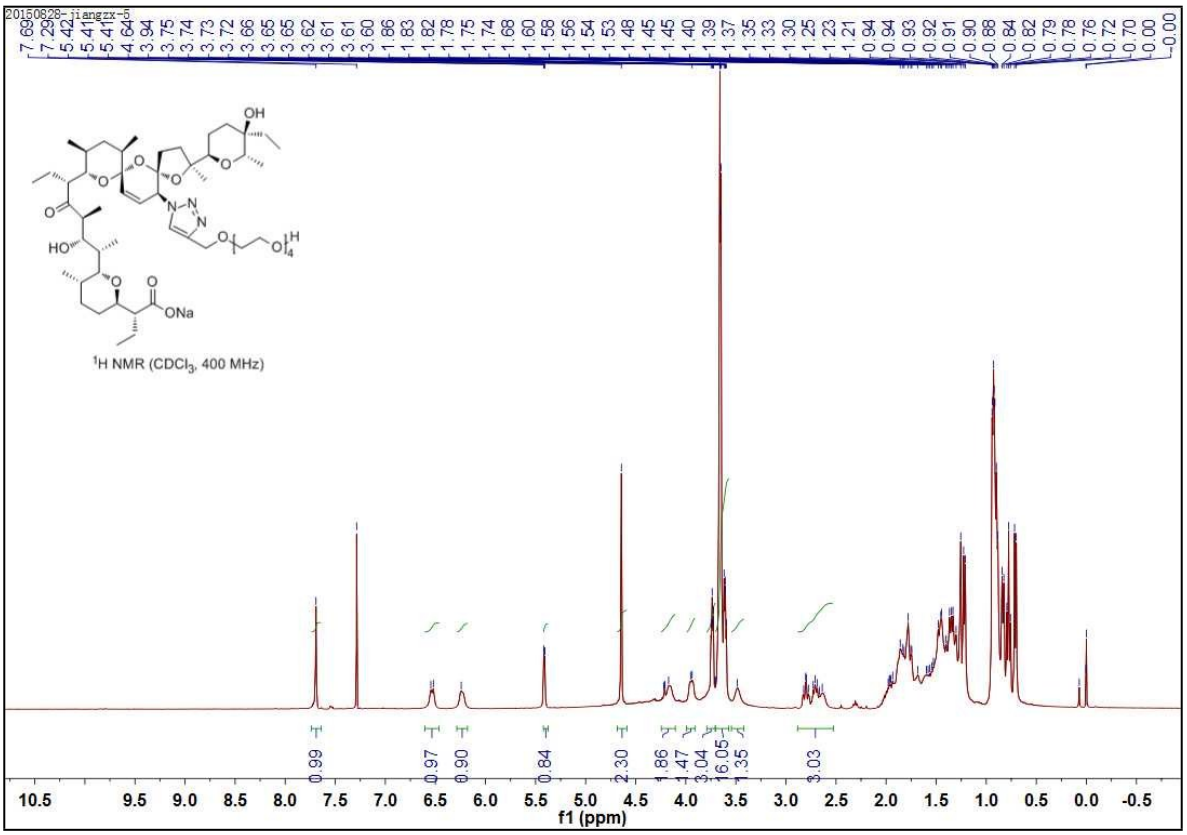
IR (KBr) of compound **5t**



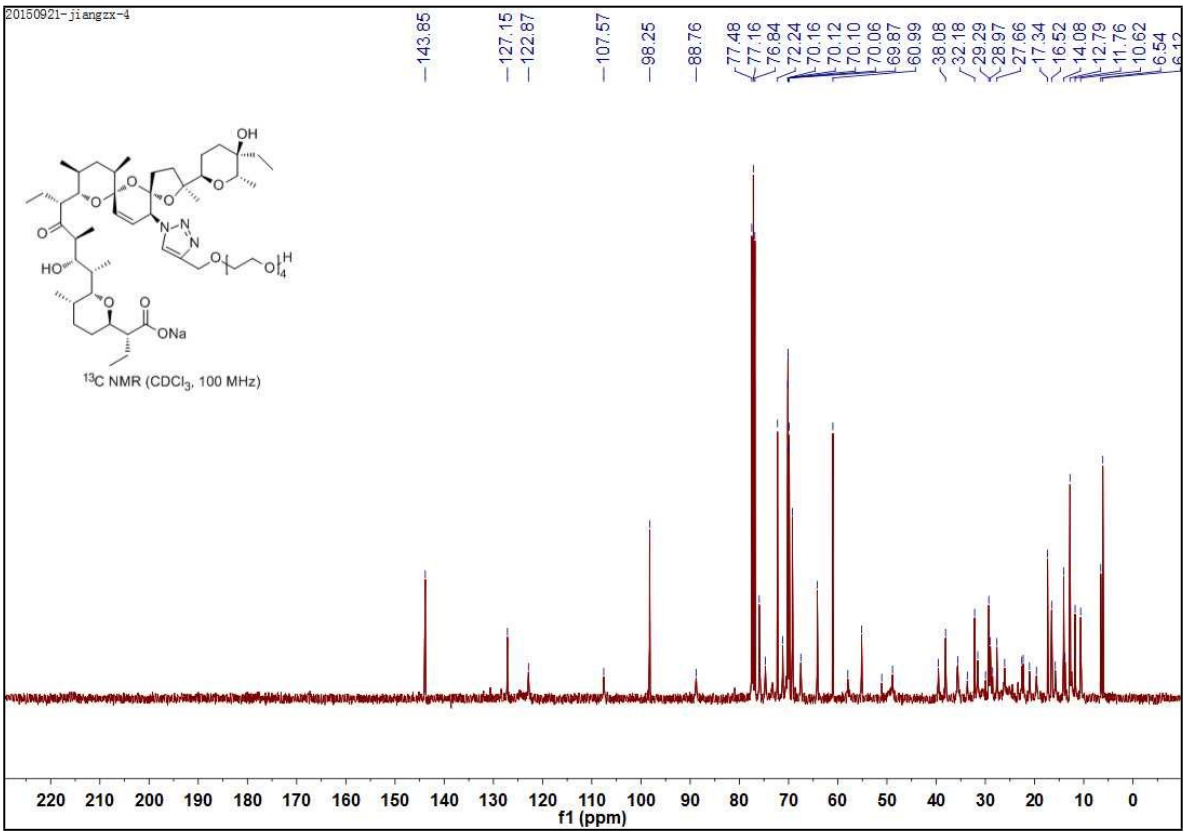
HRMS of compound **5t**



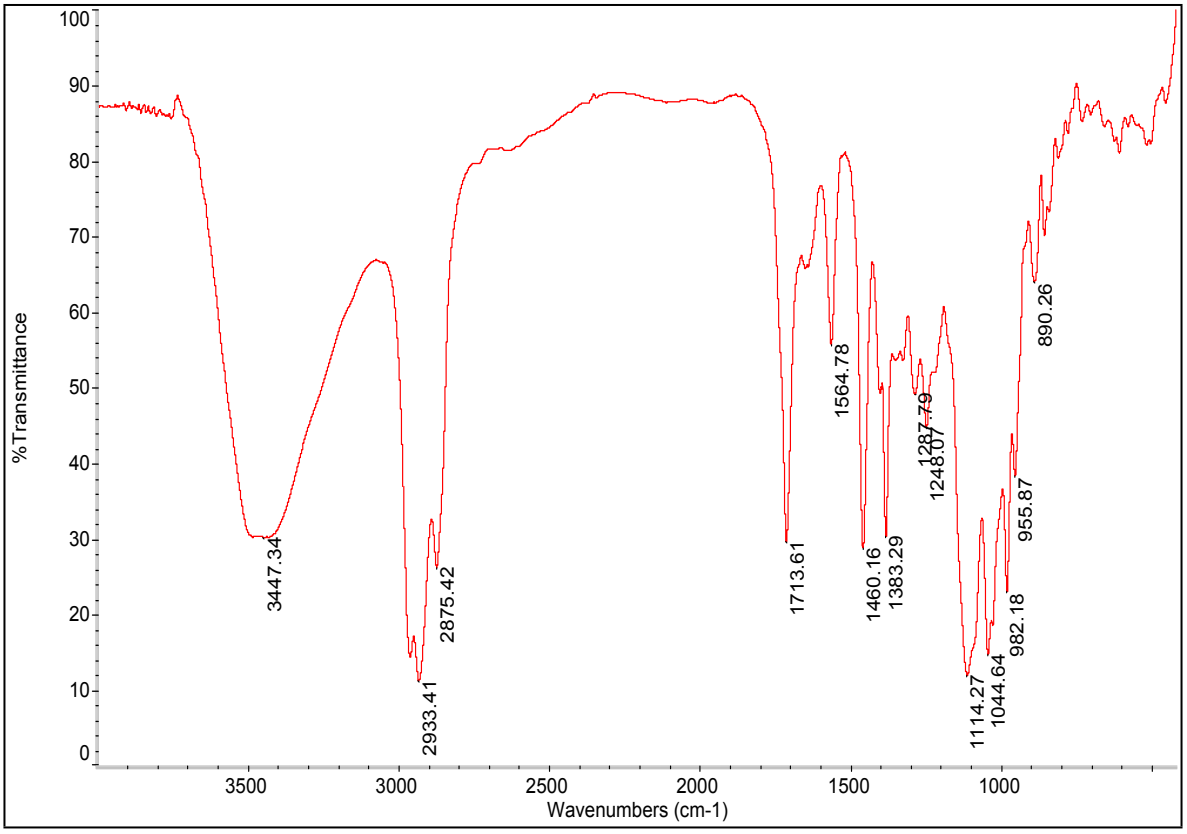
^{1}H NMR of compound **5u**



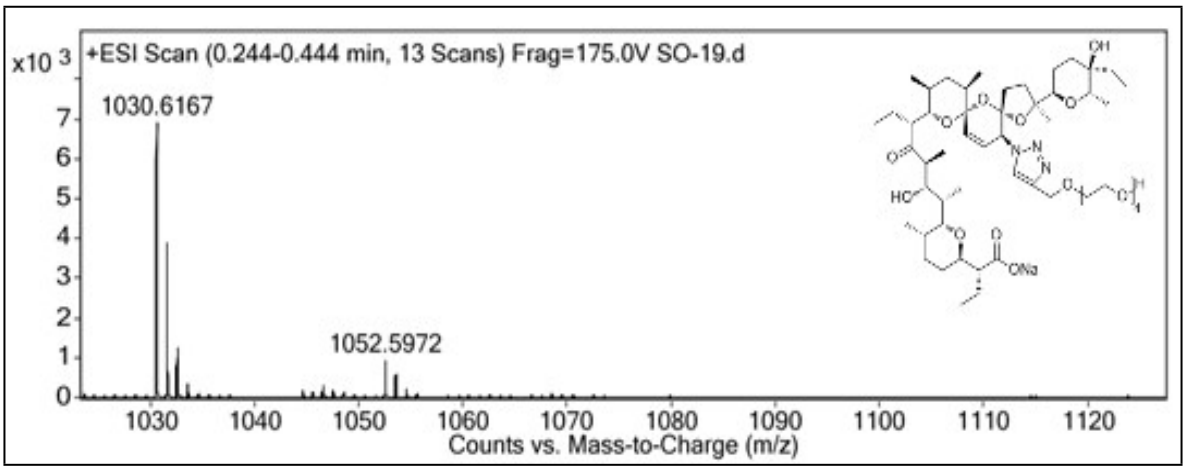
^{13}C NMR of compound **5u**



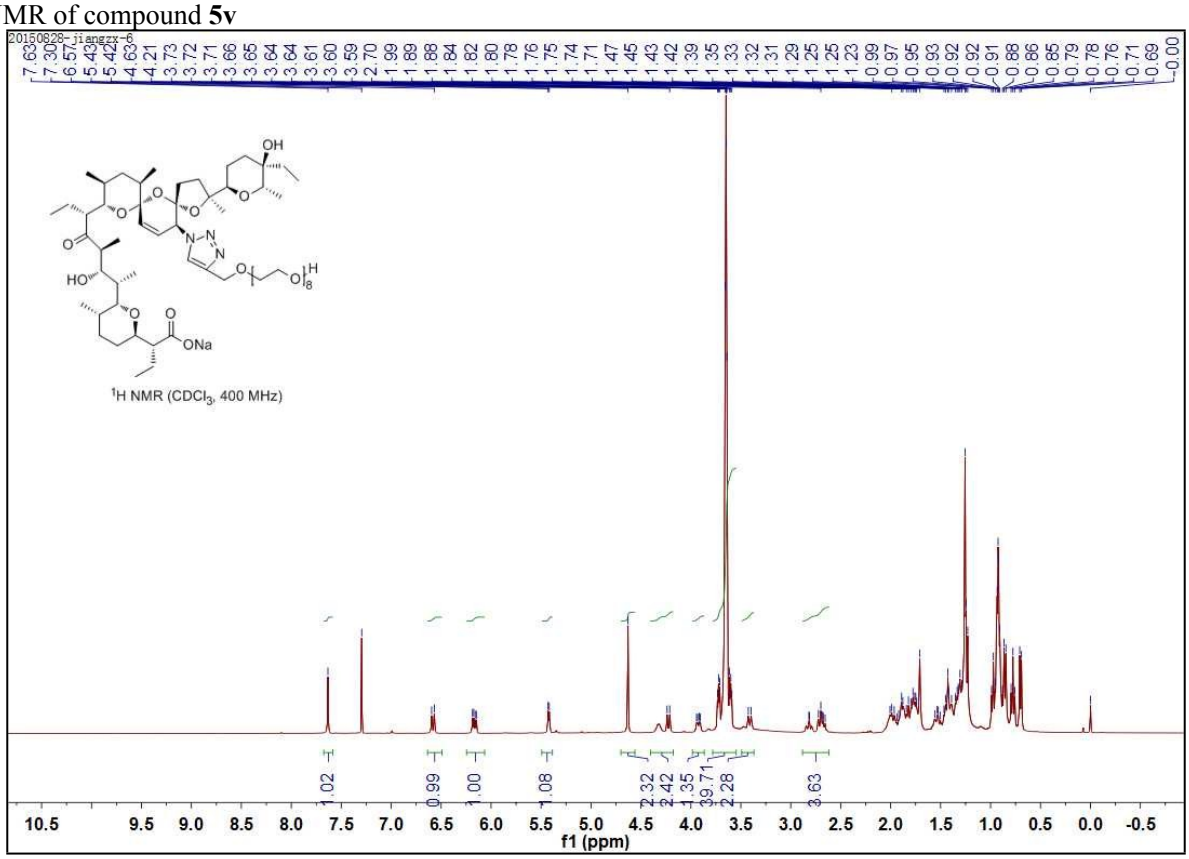
IR (KBr) of compound **5u**



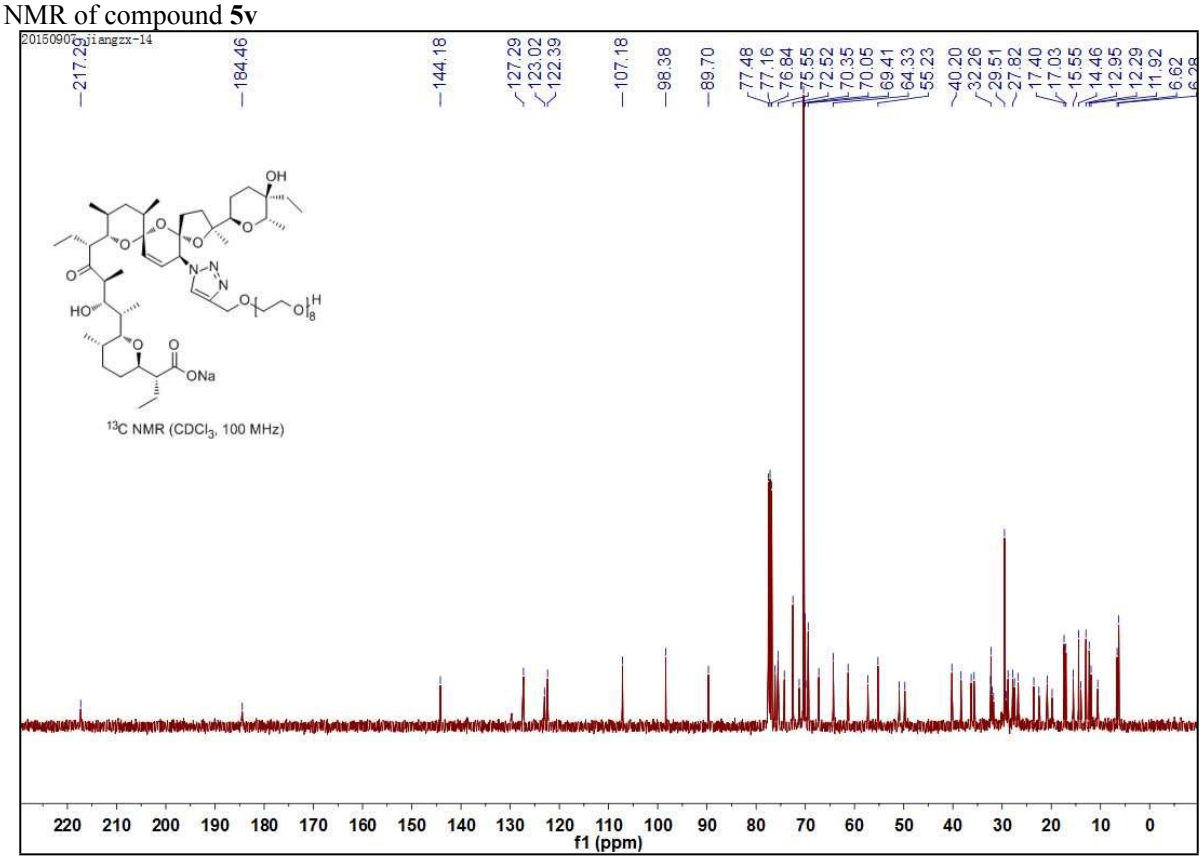
HRMS of compound **5u**



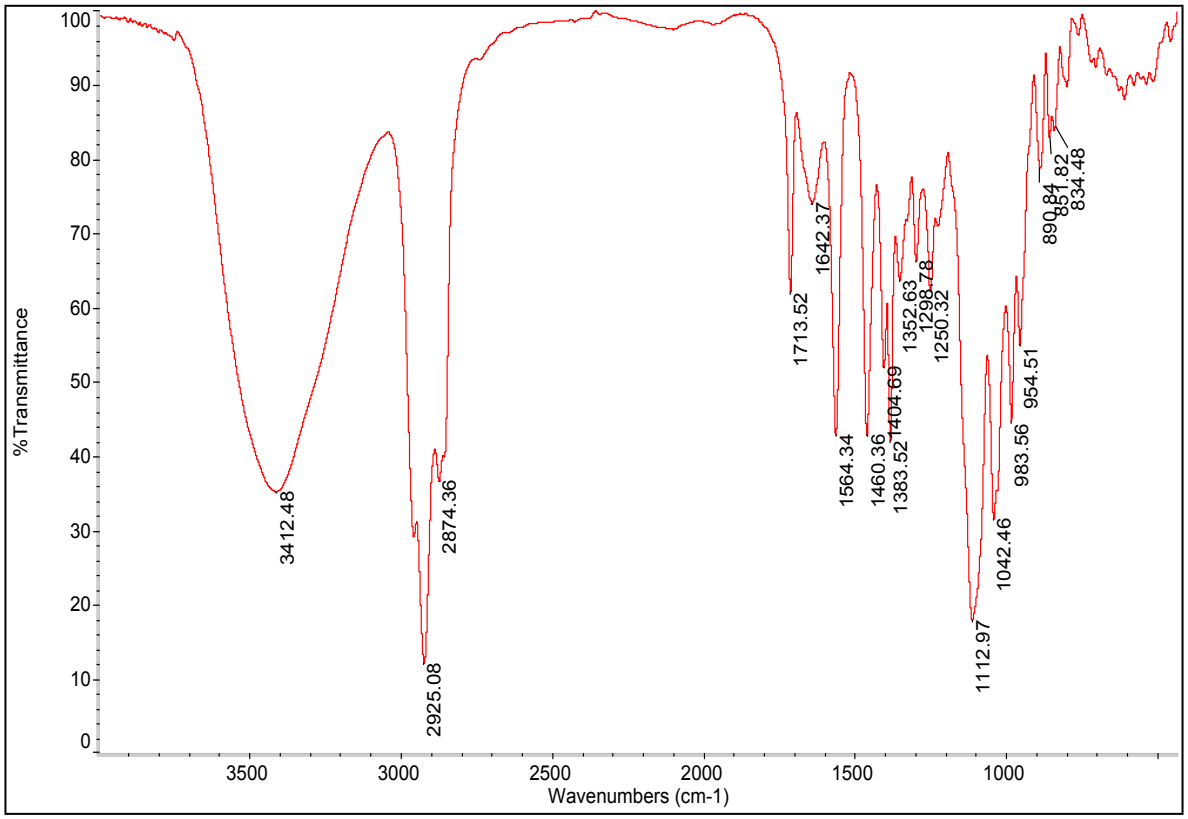
^{1}H NMR of compound **5v**



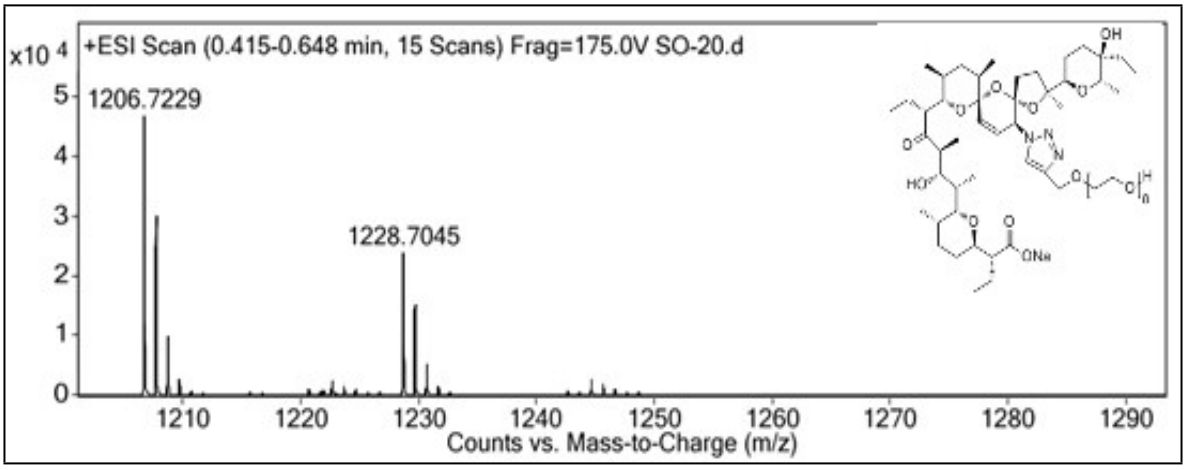
^{13}C NMR of compound **5v**



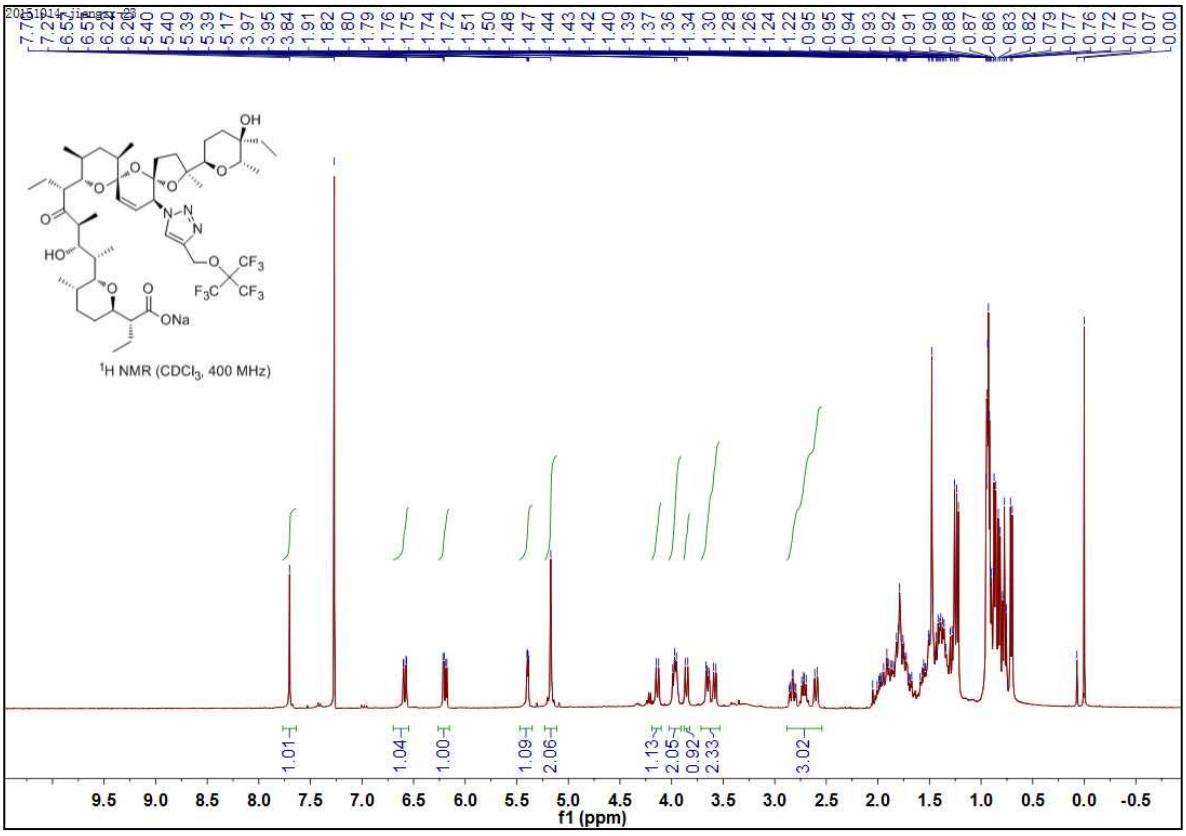
IR (KBr) of compound **5v**



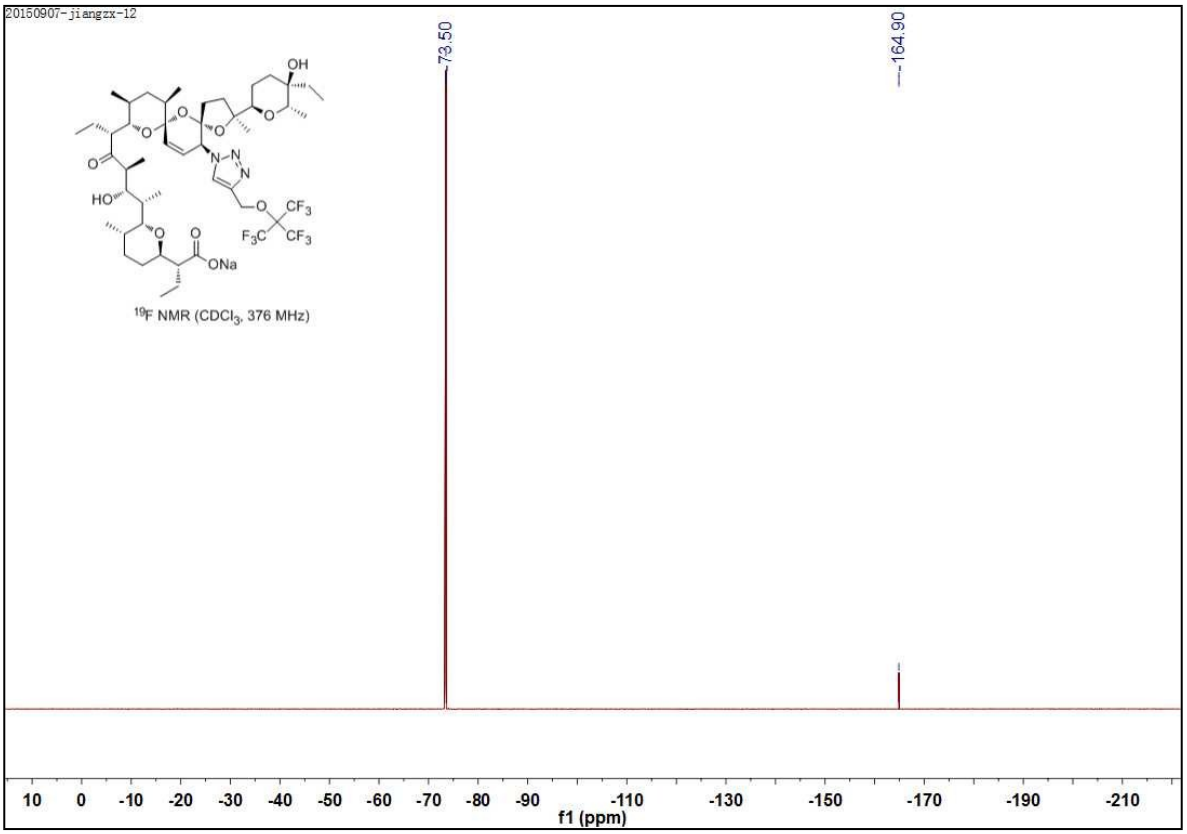
HRMS of compound **5v**



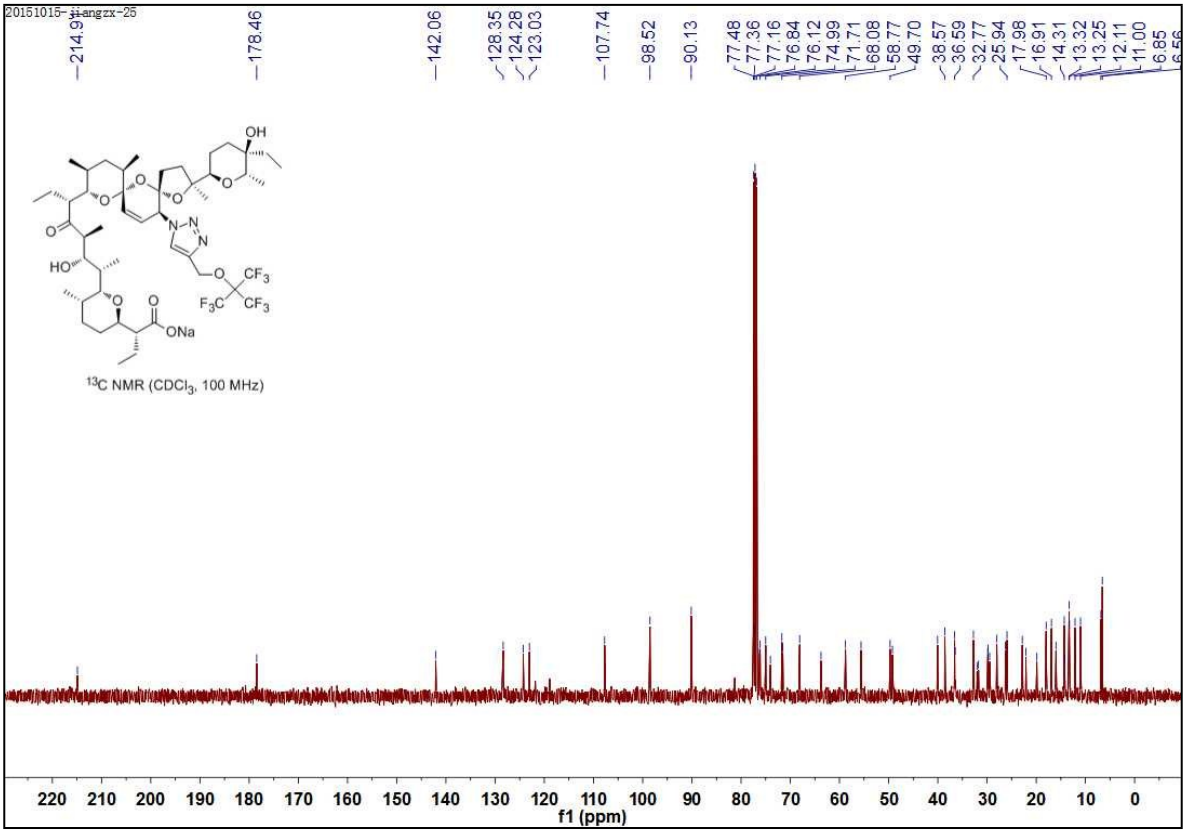
^{1}H NMR of compound **5w**



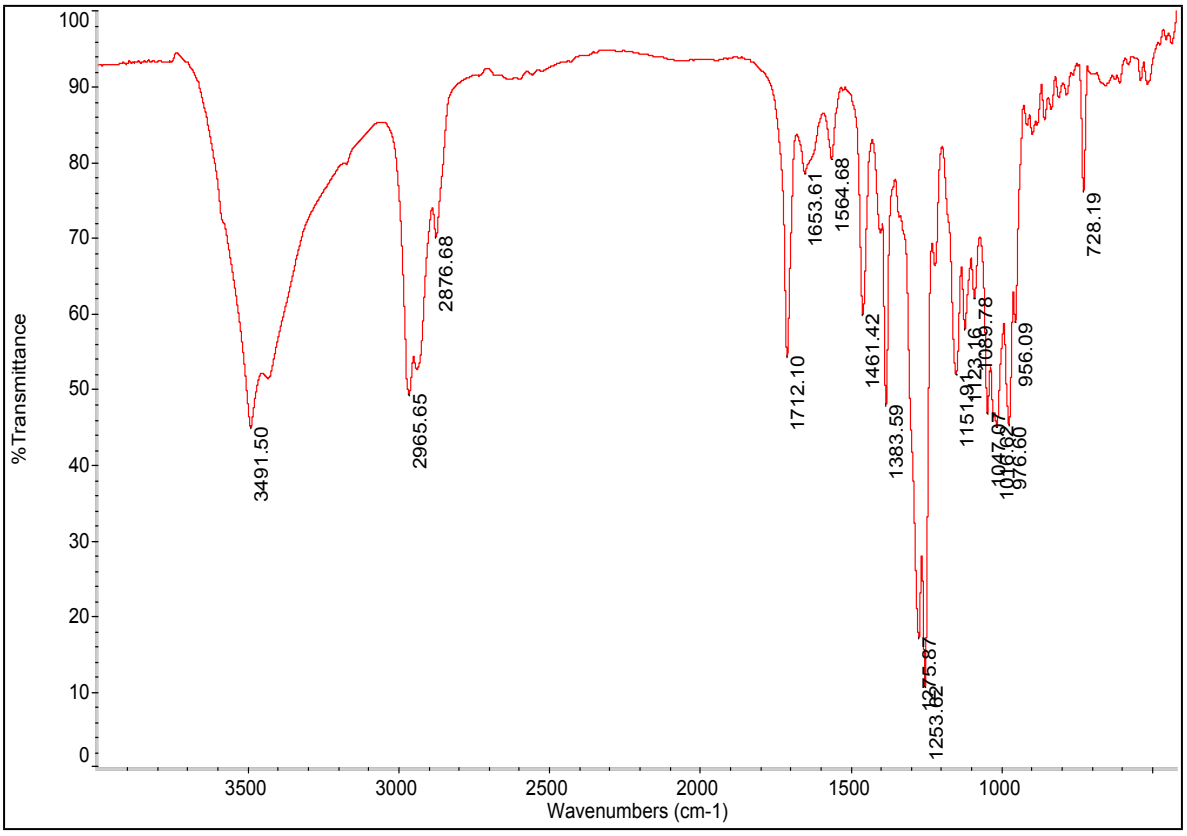
^{19}F NMR of compound **5w**



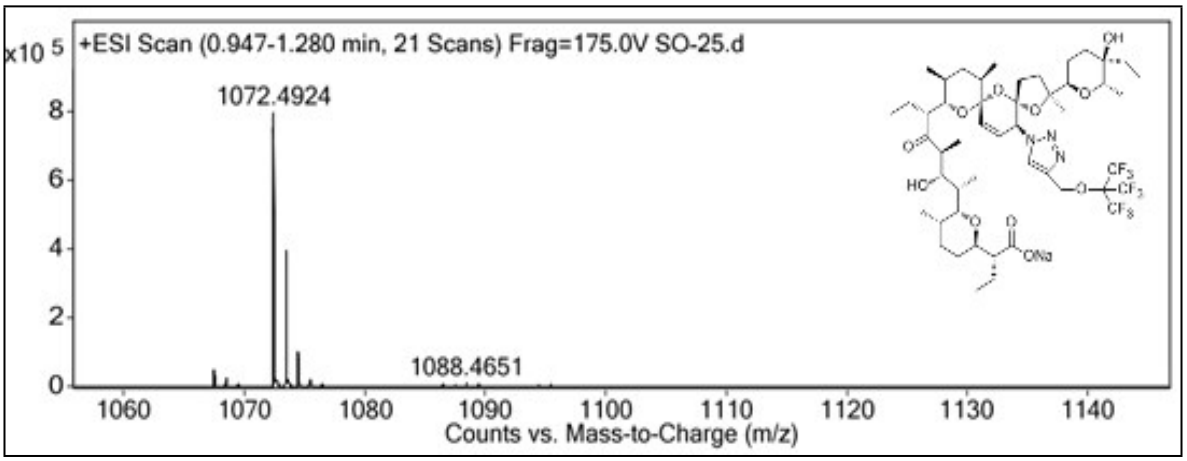
^{13}C NMR of compound **5w**



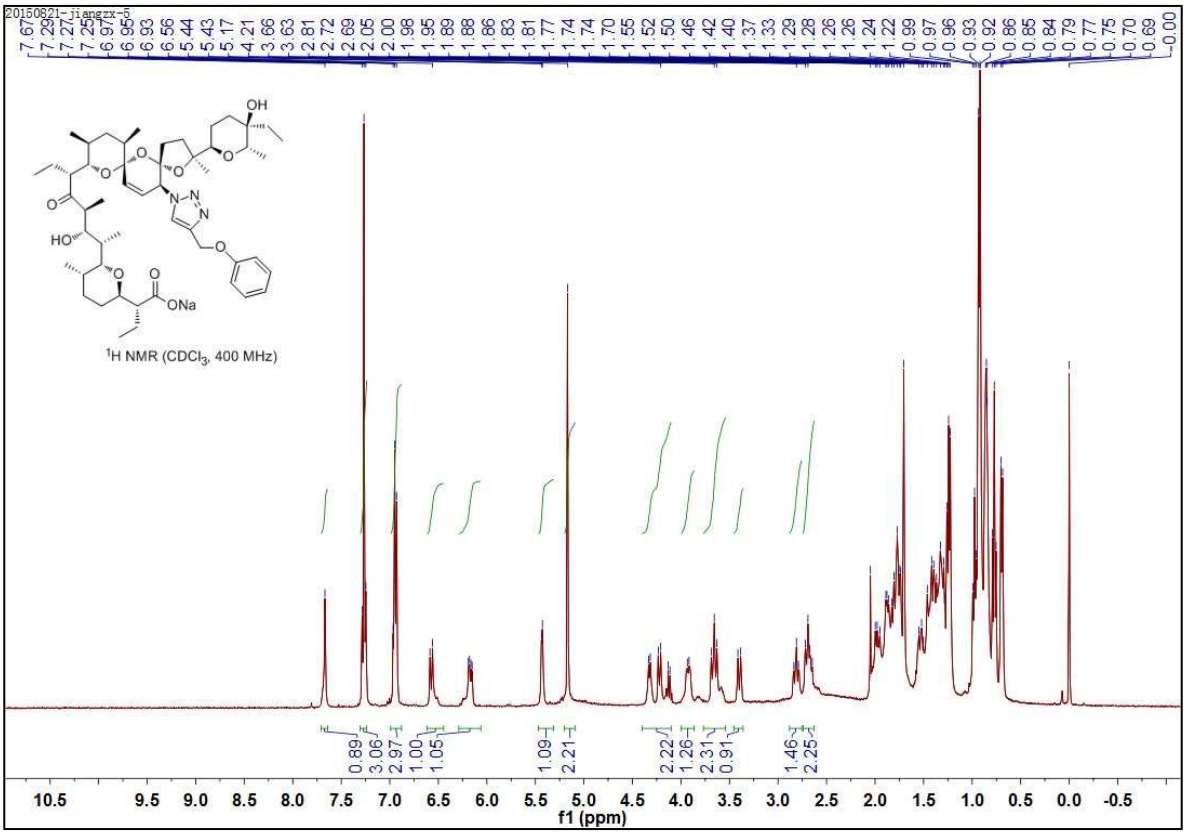
IR (KBr) of compound **5w**



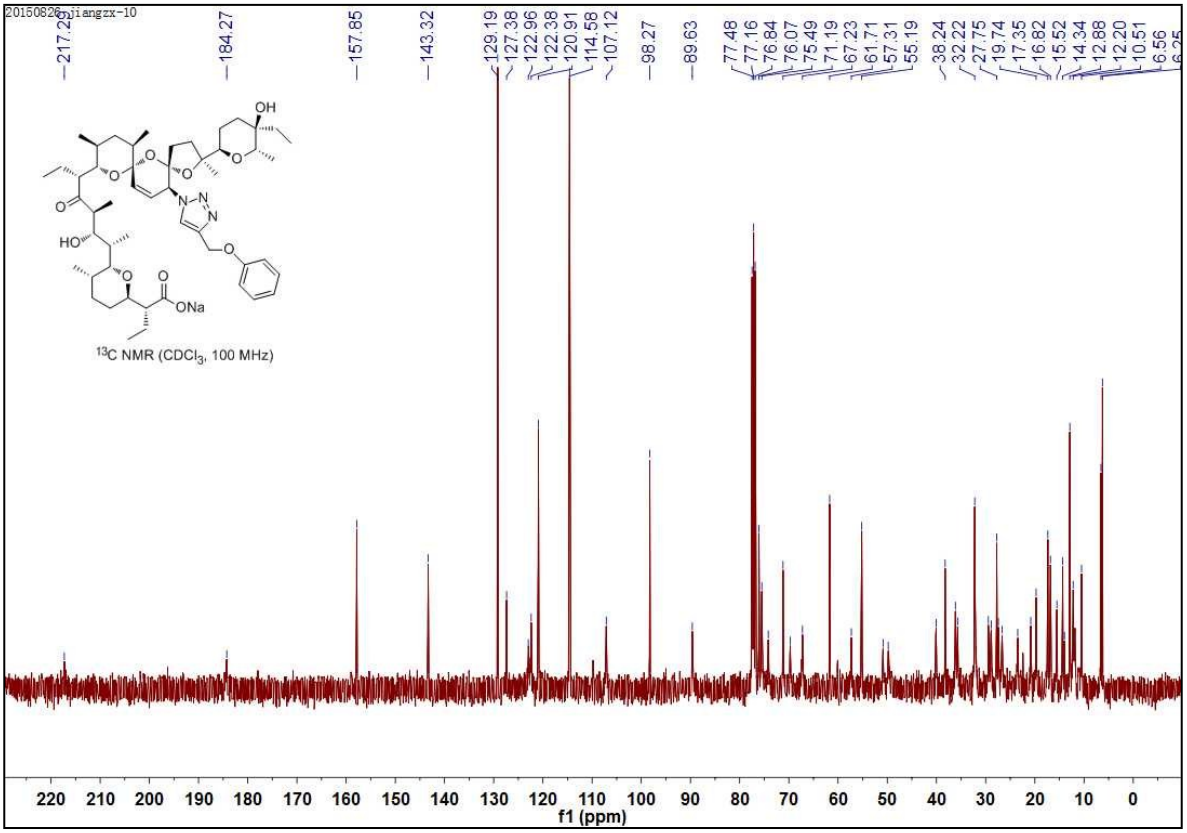
HRMS of compound **5w**



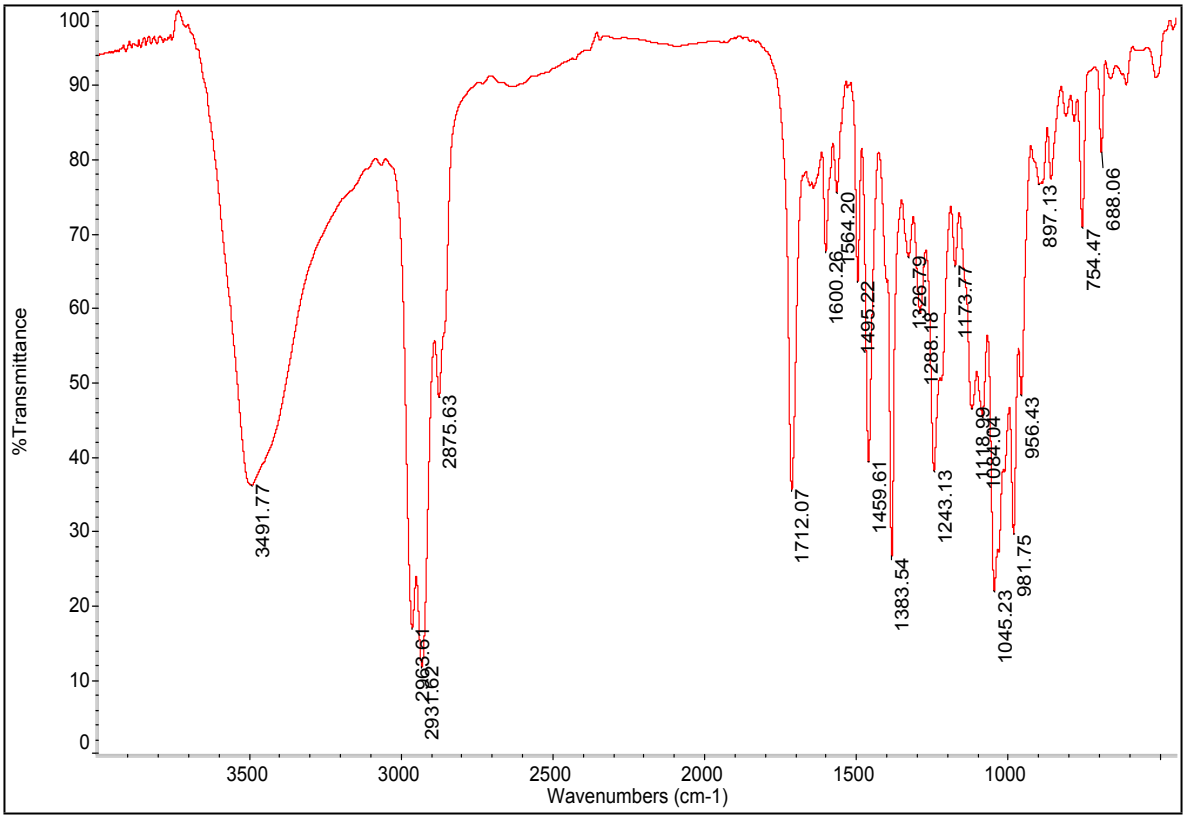
^{1}H NMR of compound **5x**



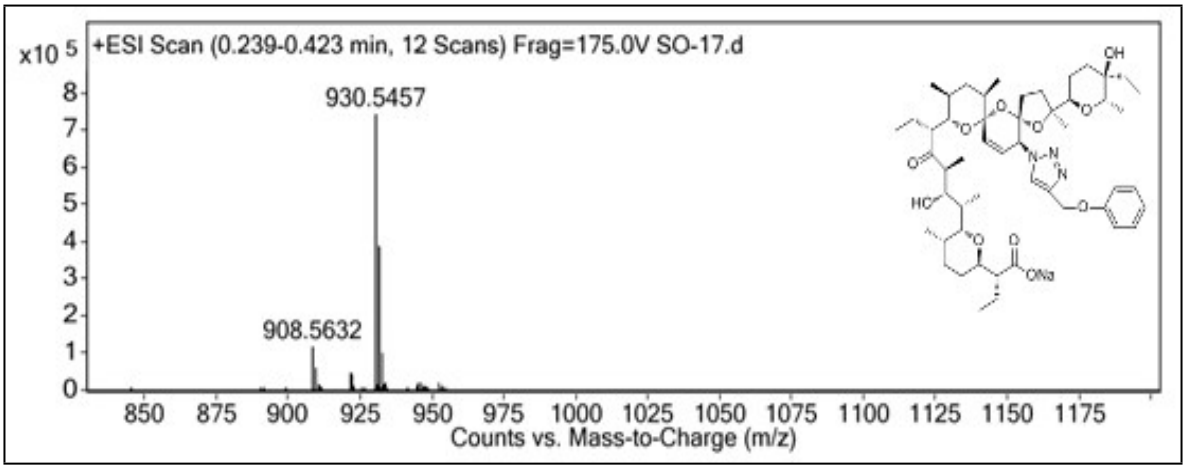
^{13}C NMR of compound 5x



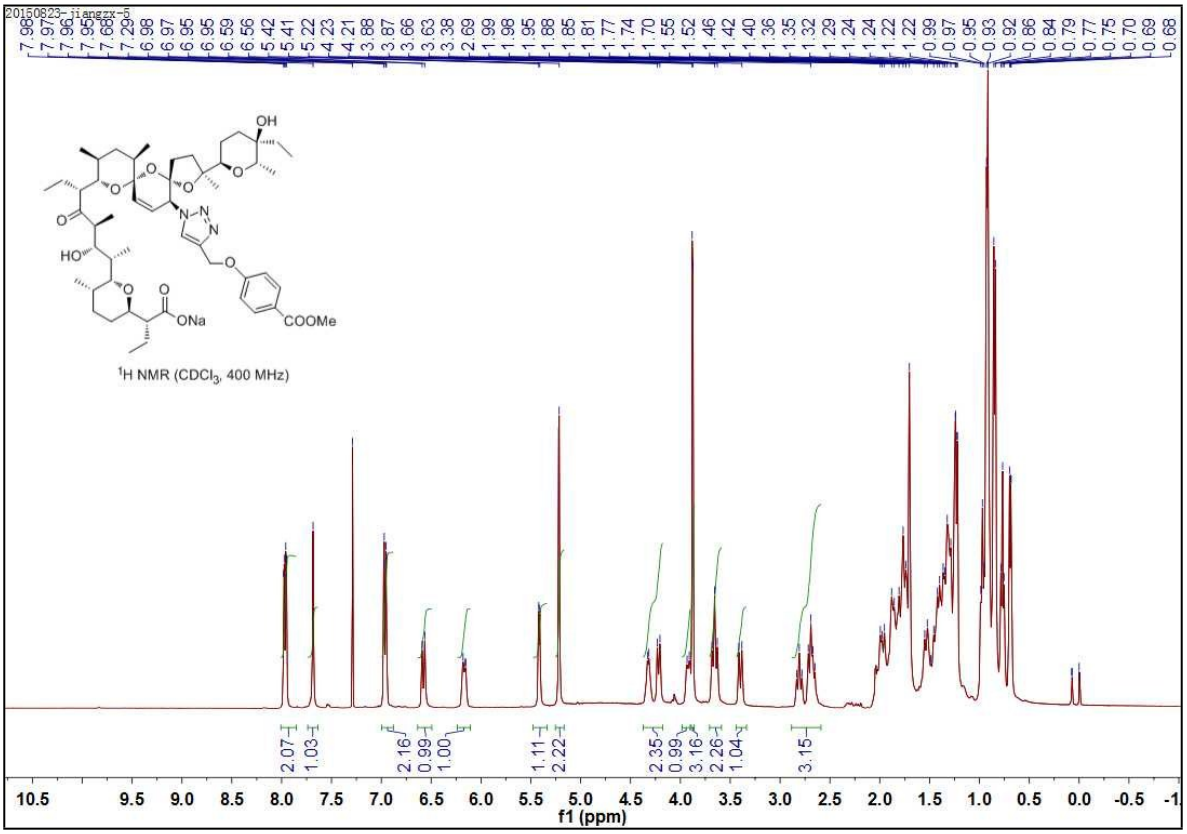
IR (KBr) of compound **5x**



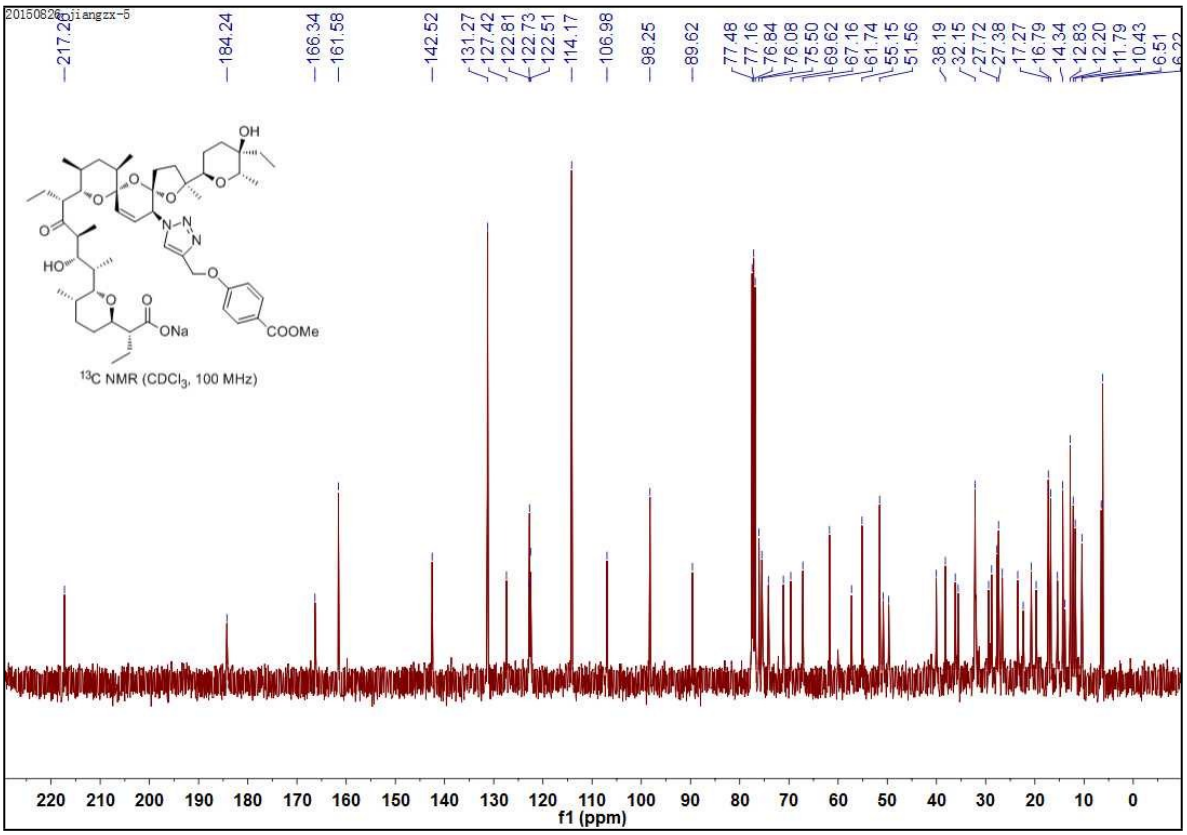
HRMS of compound **5x**



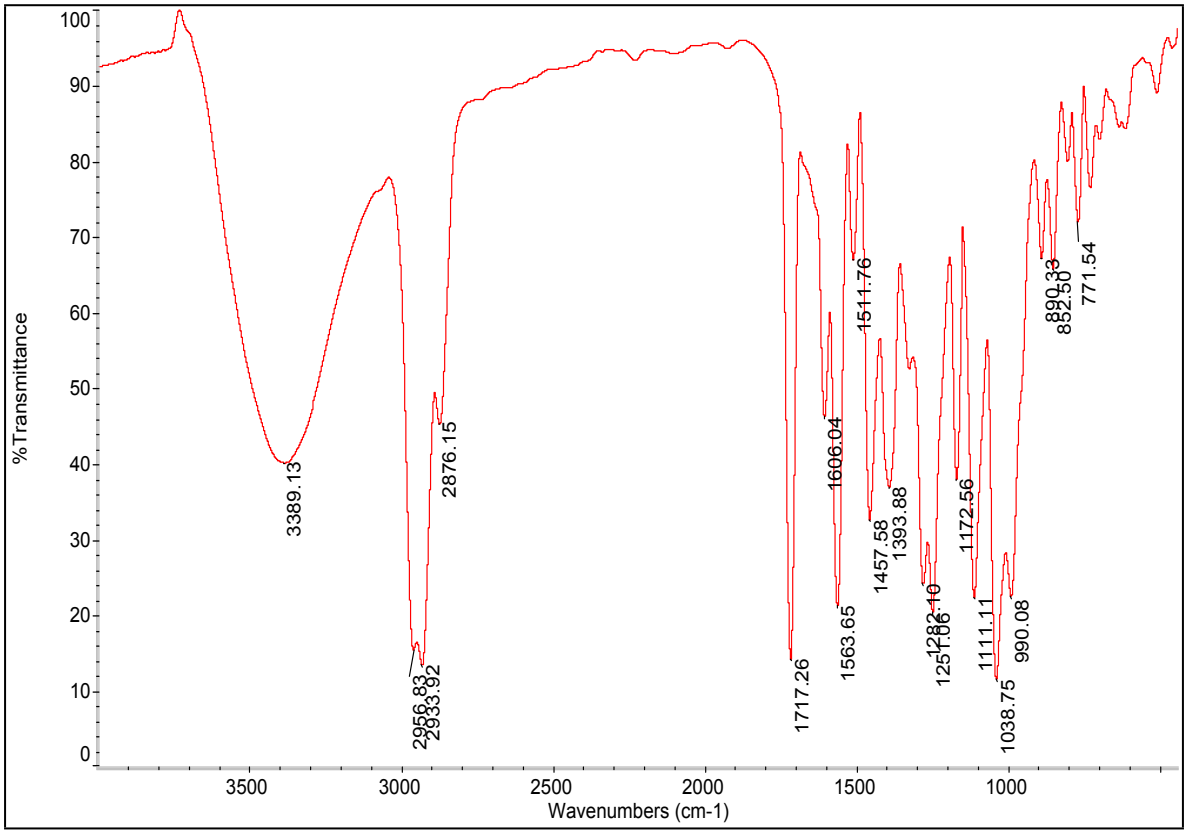
^{1}H NMR of compound **5y**



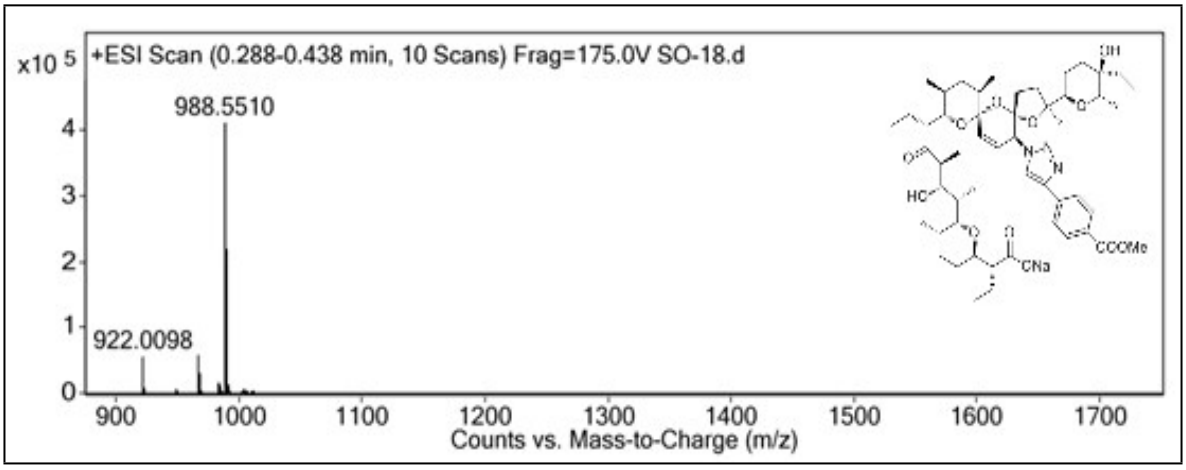
^{13}C NMR of compound **5y**



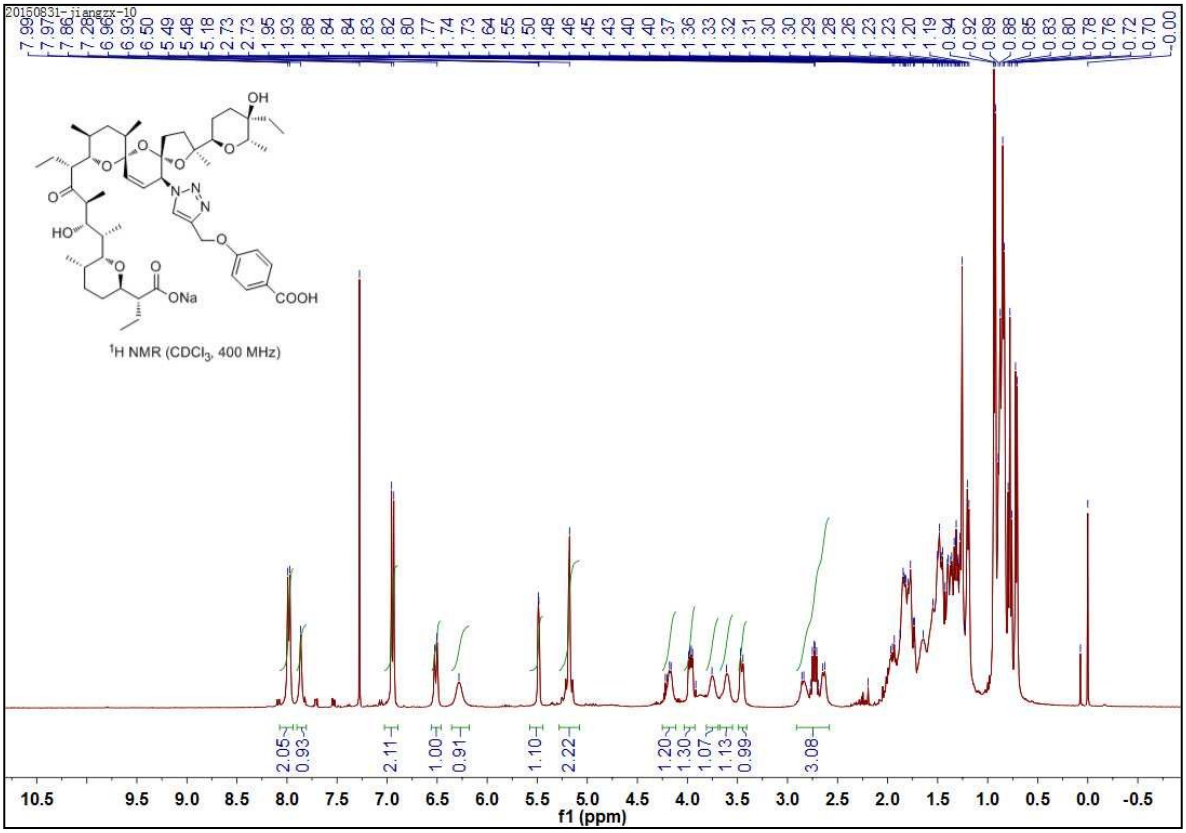
IR (KBr) of compound **5y**



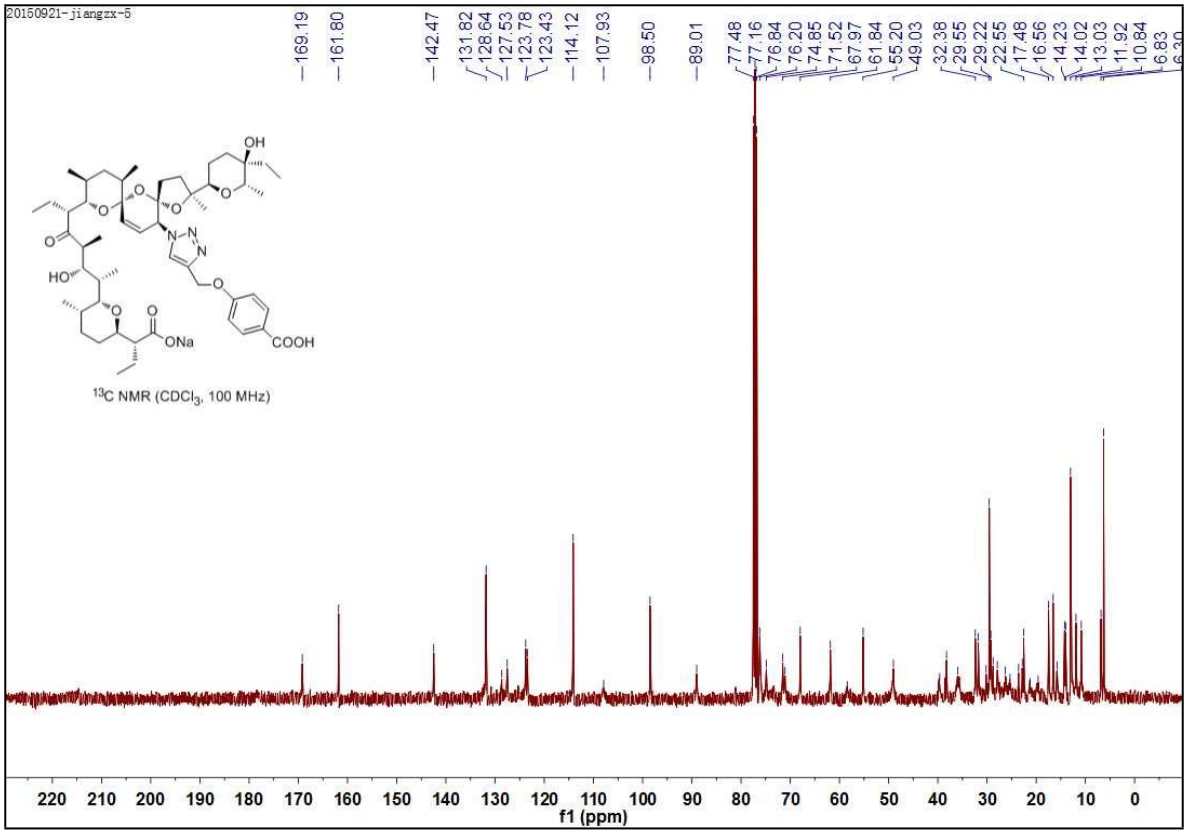
HRMS of compound **5y**



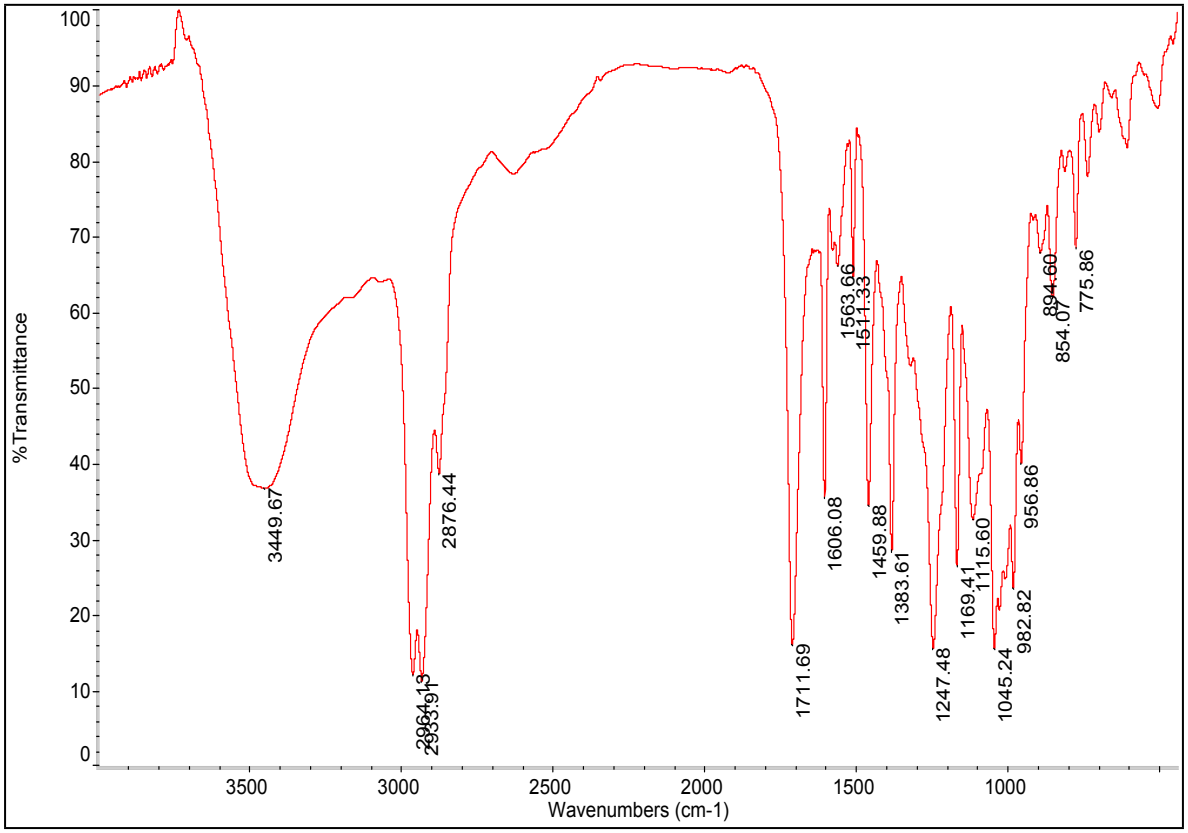
^{1}H NMR of compound **5z**



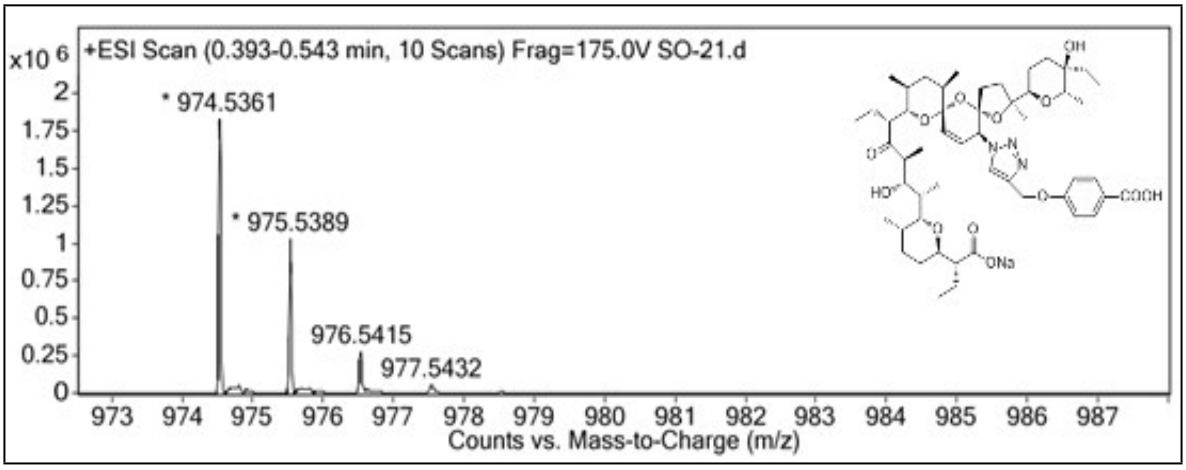
^{13}C NMR of compound **5z**



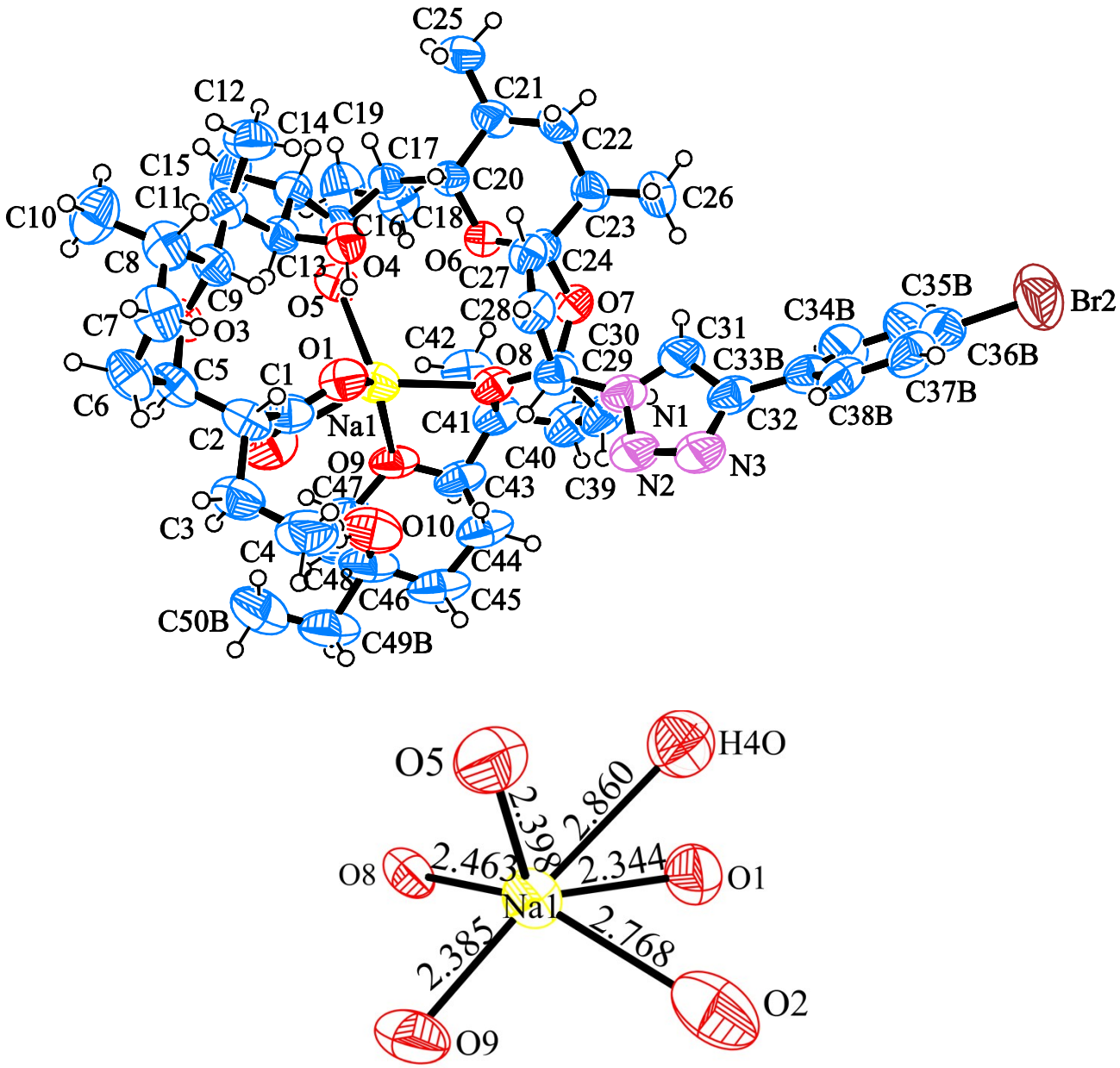
IR (KBr) of compound **5z**



HRMS of compound **5z**



5. Single-crystal X-ray structural data of compound **5f**



Single-crystal X-ray structural of compound **5f** complexed with Na^+ and detailed coordination of Na^+ (H_4O is a coordinated water)

Important geometric parameters (Å, °)

Na1—O1	2.344 (2)	C17—C20	1.537 (3)
Na1—O9	2.385 (2)	C18—C19	1.498 (4)
Na1—O5	2.398 (2)	C20—C21	1.538 (3)
Na1—O8	2.463 (2)	C21—C25	1.493 (5)

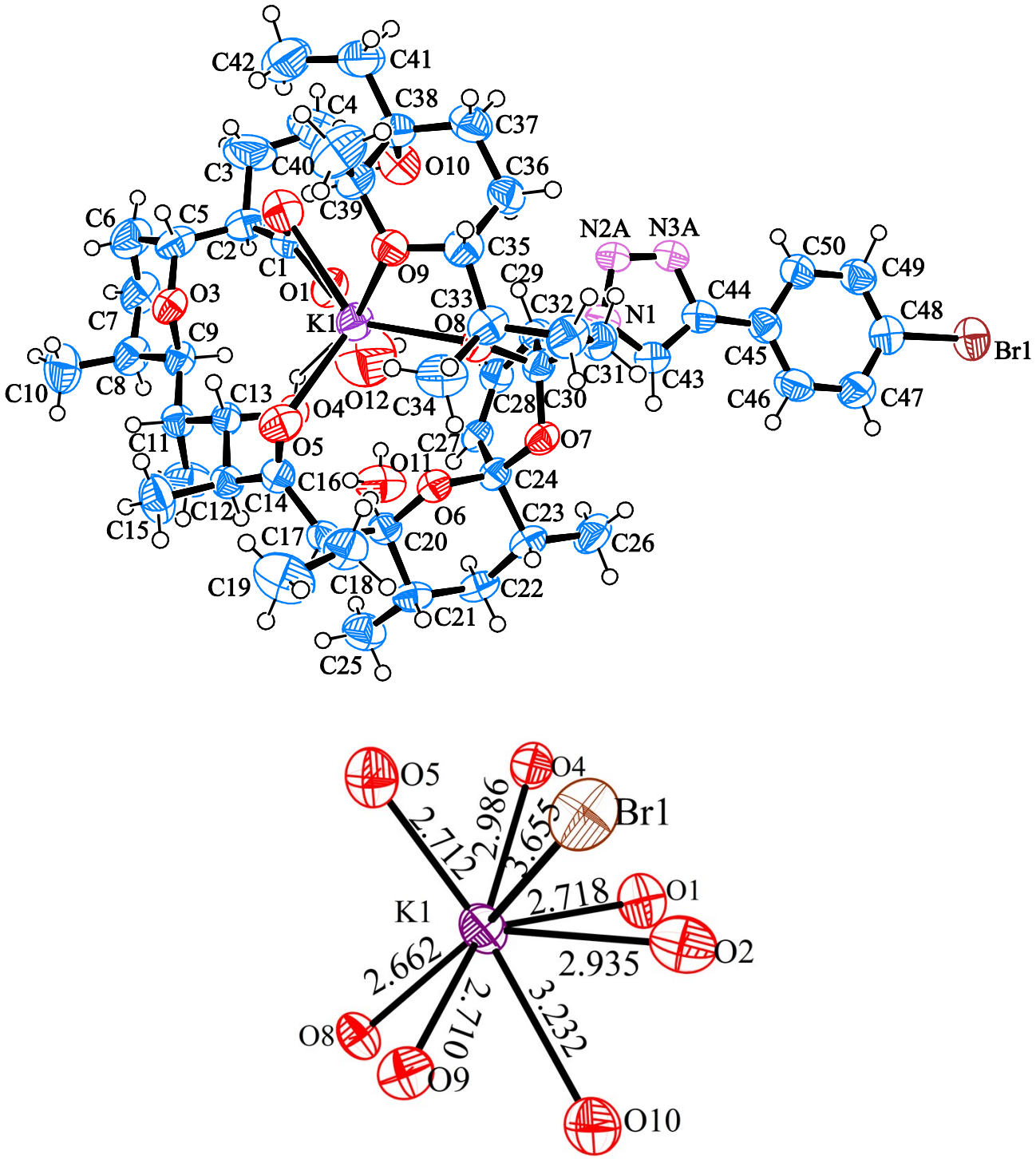
Na1—O2	2.768 (4)	C21—C22	1.493 (4)
Na1—C1	2.913 (3)	C22—C23	1.520 (4)
N1—N2	1.327 (3)	C23—C26	1.501 (5)
N1—C31	1.337 (4)	C23—C24	1.537 (3)
N1—C29	1.478 (4)	C24—C27	1.504 (3)
C1—O2	1.241 (4)	C27—C28	1.305 (4)
C1—O1	1.259 (4)	C28—C29	1.487 (4)
C1—C2	1.529 (4)	C29—C30	1.546 (3)
C2—C5	1.524 (4)	C30—C39	1.526 (4)
C2—C3	1.546 (4)	C31—C32	1.368 (4)
N2—N3	1.306 (4)	C32—C33A	1.376 (14)
C3—C4	1.473 (6)	C32—C33B	1.522 (11)
O3—C5	1.432 (3)	C33A—C38A	1.362 (11)
O3—C9	1.433 (3)	C33A—C34A	1.371 (11)
N3—C32	1.337 (4)	C34A—C35A	1.388 (11)
O4—C13	1.425 (3)	C35A—C36A	1.361 (11)
C5—C6	1.523 (4)	C36A—C37A	1.356 (10)
O5—C16	1.216 (3)	C36A—Br1	1.898 (9)
C6—C7	1.524 (5)	C37A—C38A	1.336 (10)
O6—C20	1.428 (3)	C33B—C34B	1.386 (9)
O6—C24	1.432 (3)	C33B—C38B	1.400 (9)
C7—C8	1.518 (5)	C34B—C35B	1.353 (9)
O7—C24	1.409 (3)	C35B—C36B	1.366 (9)
O7—C30	1.421 (3)	C36B—C37B	1.368 (10)
C8—C10	1.514 (5)	C36B—Br2	1.921 (7)
C8—C9	1.542 (4)	C37B—C38B	1.393 (10)
O8—C30	1.410 (3)	C39—C40	1.514 (5)
O8—C41	1.478 (3)	C40—C41	1.544 (5)
C9—C11	1.525 (4)	C41—C42	1.515 (4)
O9—C43	1.432 (4)	C41—C43	1.520 (5)
O9—C47	1.449 (4)	C43—C44	1.526 (4)
O10—C46	1.423 (4)	C48—C47	1.527 (5)

C11—C12	1.535 (4)	C47—C46	1.534 (5)
C11—C13	1.542 (4)	C46—C45	1.519 (6)
C13—C14	1.519 (3)	C46—C49B	1.529 (9)
C14—C16	1.515 (4)	C46—C49A	1.606 (14)
C14—C15	1.529 (4)	C45—C44	1.505 (6)
C16—C17	1.523 (3)	C49A—C50A	1.486 (18)
C17—C18	1.536 (4)	C49B—C50B	1.475 (14)

O1—Na1—O9	137.59 (8)	C26—C23—C22	111.8 (3)
O1—Na1—O5	106.42 (8)	C26—C23—C24	114.2 (2)
O9—Na1—O5	110.50 (8)	C22—C23—C24	111.0 (2)
O1—Na1—O8	121.24 (8)	O7—C24—O6	107.56 (17)
O9—Na1—O8	69.03 (7)	O7—C24—C27	111.32 (18)
O5—Na1—O8	103.59 (7)	O6—C24—C27	109.65 (17)
O1—Na1—O2	49.85 (8)	O7—C24—C23	104.70 (17)
O9—Na1—O2	98.68 (8)	O6—C24—C23	109.22 (18)
O5—Na1—O2	107.19 (9)	C27—C24—C23	114.1 (2)
O8—Na1—O2	149.21 (9)	C28—C27—C24	123.6 (2)
O1—Na1—C1	24.82 (8)	C27—C28—C29	123.1 (2)
O9—Na1—C1	120.09 (9)	N1—C29—C28	108.5 (2)
O5—Na1—C1	107.55 (8)	N1—C29—C30	111.3 (2)
O8—Na1—C1	140.16 (9)	C28—C29—C30	112.42 (19)
O2—Na1—C1	25.07 (8)	O8—C30—O7	111.96 (18)
N2—N1—C31	110.0 (2)	O8—C30—C39	106.0 (2)
N2—N1—C29	120.9 (2)	O7—C30—C39	106.0 (2)
C31—N1—C29	128.9 (2)	O8—C30—C29	106.5 (2)
O2—C1—O1	122.2 (3)	O7—C30—C29	111.66 (19)
O2—C1—C2	119.3 (3)	C39—C30—C29	114.6 (2)
O1—C1—C2	118.5 (2)	N1—C31—C32	106.2 (2)
O2—C1—Na1	70.9 (2)	N3—C32—C31	106.1 (3)
O1—C1—Na1	51.42 (14)	N3—C32—C33A	120.3 (5)

C2—C1—Na1	169.4 (2)	C31—C32—C33A	132.4 (5)
C1—O2—Na1	84.0 (2)	N3—C32—C33B	128.6 (3)
C5—C2—C1	110.3 (2)	C31—C32—C33B	125.2 (3)
C5—C2—C3	111.0 (2)	C38A—C33A—C34A	116.5 (10)
C1—C2—C3	109.4 (3)	C38A—C33A—C32	125.0 (10)
N3—N2—N1	106.8 (3)	C34A—C33A—C32	118.5 (9)
C4—C3—C2	112.5 (3)	C33A—C34A—C35A	122.7 (9)
C5—O3—C9	113.94 (19)	C36A—C35A—C34A	117.5 (8)
N2—N3—C32	110.8 (2)	C37A—C36A—C35A	120.2 (8)
O3—C5—C6	109.6 (3)	C37A—C36A—Br1	120.7 (6)
O3—C5—C2	111.78 (19)	C35A—C36A—Br1	119.1 (8)
C6—C5—C2	115.4 (2)	C38A—C37A—C36A	120.9 (7)
C16—O5—Na1	136.89 (18)	C37A—C38A—C33A	122.1 (9)
C5—C6—C7	111.6 (2)	C34B—C33B—C38B	118.0 (8)
C20—O6—C24	115.21 (16)	C34B—C33B—C32	122.5 (7)
C8—C7—C6	111.8 (3)	C38B—C33B—C32	119.4 (7)
C24—O7—C30	121.23 (17)	C35B—C34B—C33B	122.0 (7)
C10—C8—C7	111.7 (3)	C34B—C35B—C36B	118.6 (7)
C10—C8—C9	114.2 (3)	C35B—C36B—C37B	122.9 (7)
C7—C8—C9	107.1 (3)	C35B—C36B—Br2	118.9 (6)
C30—O8—C41	110.16 (19)	C37B—C36B—Br2	118.2 (6)
C30—O8—Na1	140.04 (13)	C36B—C37B—C38B	117.9 (7)
C41—O8—Na1	109.79 (15)	C37B—C38B—C33B	120.5 (7)
O3—C9—C11	105.2 (2)	C40—C39—C30	102.8 (2)
O3—C9—C8	110.0 (2)	C39—C40—C41	105.1 (2)
C11—C9—C8	117.1 (2)	O8—C41—C42	108.3 (2)
C43—O9—C47	116.4 (2)	O8—C41—C43	106.6 (2)
C43—O9—Na1	116.40 (15)	C42—C41—C43	111.6 (3)
C47—O9—Na1	113.0 (2)	O8—C41—C40	104.9 (2)
C9—C11—C12	111.9 (2)	C42—C41—C40	111.6 (3)
C9—C11—C13	108.5 (2)	C43—C41—C40	113.4 (2)
C12—C11—C13	111.5 (2)	O9—C43—C41	106.0 (2)

O4—C13—C14	105.58 (18)	O9—C43—C44	110.1 (3)
O4—C13—C11	110.0 (2)	C41—C43—C44	115.7 (3)
C14—C13—C11	115.8 (2)	O9—C47—C48	111.1 (4)
C16—C14—C13	110.0 (2)	O9—C47—C46	108.8 (3)
C16—C14—C15	107.0 (3)	C48—C47—C46	114.2 (3)
C13—C14—C15	114.4 (2)	O10—C46—C45	105.3 (3)
O5—C16—C14	122.6 (2)	O10—C46—C49B	113.4 (6)
O5—C16—C17	121.2 (2)	C45—C46—C49B	104.5 (5)
C14—C16—C17	116.2 (2)	O10—C46—C47	108.0 (3)
C16—C17—C18	113.9 (2)	C45—C46—C47	109.1 (4)
C16—C17—C20	106.71 (17)	C49B—C46—C47	115.8 (6)
C18—C17—C20	114.2 (2)	O10—C46—C49A	103.5 (8)
C19—C18—C17	112.7 (3)	C45—C46—C49A	123.8 (7)
O6—C20—C17	107.04 (18)	C47—C46—C49A	106.2 (7)
O6—C20—C21	112.29 (19)	C44—C45—C46	111.7 (3)
C17—C20—C21	113.20 (18)	C45—C44—C43	112.1 (3)
C25—C21—C22	110.6 (3)	C1—O1—Na1	103.75 (18)
C25—C21—C20	112.9 (3)	C50A—C49A—C46	118.6 (13)
C22—C21—C20	109.27 (19)	C50B—C49B—C46	107.4 (7)
C21—C22—C23	114.0 (2)		



Single-crystal X-ray structural of compound **5f** complexed with K^+ and detailed coordination of K^+

Important geometric parameters (Å, °)

Br1—C48	1.900 (4)	C11—C12	1.531 (7)
Br1—K1^{i}	3.6546 (11)	C13—C14	1.524 (6)

K1—O8	2.662 (3)	C14—C16	1.526 (6)
K1—O9	2.707 (3)	C14—C15	1.532 (6)
K1—O5	2.711 (4)	C16—C17	1.513 (6)
K1—O1	2.719 (3)	C17—C18	1.520 (7)
K1—O2	2.934 (4)	C17—C20	1.552 (6)
K1—O4	2.987 (3)	C18—C19	1.515 (8)
K1—C1	3.170 (5)	C20—C21	1.529 (6)
K1—O10	3.231 (4)	C21—C22	1.519 (7)
K1—C16	3.402 (4)	C21—C25	1.519 (7)
K1—C39	3.476 (5)	C22—C23	1.521 (7)
K1—Br1^{ii}	3.6546 (11)	C23—C26	1.519 (7)
O1—C1	1.268 (6)	C23—C24	1.535 (6)
N1—C43	1.332 (6)	C24—C27	1.509 (5)
N1—N2A	1.346 (12)	C27—C28	1.308 (6)
N1—N2B	1.39 (2)	C28—C29	1.495 (6)
N1—C29	1.479 (6)	C29—C30	1.527 (6)
C1—O2	1.246 (5)	C30—C31	1.521 (6)
C1—C2	1.520 (7)	C31—C32	1.538 (7)
C2—C5	1.525 (8)	C32—C33	1.528 (7)
C2—C3	1.548 (8)	C33—C34	1.524 (7)
O3—C9	1.435 (5)	C33—C35	1.536 (7)
O3—C5	1.441 (6)	C35—C36	1.525 (7)
C3—C4	1.511 (12)	C36—C37	1.521 (8)
O4—C13	1.441 (5)	C37—C38	1.509 (7)
O5—C16	1.207 (5)	C38—C41	1.540 (7)
C5—C6	1.541 (7)	C38—C39	1.542 (7)
O6—C20	1.438 (5)	C39—C40	1.522 (7)
O6—C24	1.442 (5)	C41—C42	1.505 (10)
C6—C7	1.505 (9)	C43—C44	1.347 (6)
O7—C24	1.416 (5)	C44—N3A	1.371 (14)
O7—C30	1.428 (5)	C44—N3B	1.42 (2)
C7—C8	1.517 (9)	C44—C45	1.478 (7)

O8—C30	1.405 (5)	C45—C46	1.378 (7)
O8—C33	1.466 (5)	C45—C50	1.386 (7)
C8—C10	1.528 (8)	C46—C47	1.390 (8)
C8—C9	1.537 (6)	C47—C48	1.384 (8)
O9—C35	1.435 (6)	C48—C49	1.360 (7)
O9—C39	1.440 (6)	C49—C50	1.366 (7)
C9—C11	1.537 (6)	N2A—N3A	1.290 (14)
O10—C38	1.420 (6)	N2B—N3B	1.31 (2)
C11—C13	1.529 (6)		

C48—Br1—K1^{i}	122.27 (14)	C13—C11—C12	112.2 (4)
O8—K1—O9	60.64 (9)	C13—C11—C9	111.7 (3)
O8—K1—O5	99.68 (10)	C12—C11—C9	110.8 (4)
O9—K1—O5	98.05 (10)	O4—C13—C14	104.5 (3)
O8—K1—O1	127.75 (10)	O4—C13—C11	111.6 (3)
O9—K1—O1	133.64 (11)	C14—C13—C11	114.7 (3)
O5—K1—O1	120.58 (11)	C13—C14—C16	111.2 (3)
O8—K1—O2	137.64 (10)	C13—C14—C15	113.3 (4)
O9—K1—O2	94.78 (9)	C16—C14—C15	106.8 (4)
O5—K1—O2	118.69 (10)	O5—C16—C17	122.4 (4)
O1—K1—O2	45.92 (9)	O5—C16—C14	121.2 (4)
O8—K1—O4	124.04 (9)	C17—C16—C14	116.4 (4)
O9—K1—O4	165.18 (9)	O5—C16—K1	46.2 (2)
O5—K1—O4	67.74 (9)	C17—C16—K1	116.8 (3)
O1—K1—O4	57.03 (9)	C14—C16—K1	106.4 (2)
O2—K1—O4	88.88 (9)	C16—C17—C18	113.5 (4)
O8—K1—C1	140.66 (11)	C16—C17—C20	107.6 (3)
O9—K1—C1	116.56 (11)	C18—C17—C20	114.3 (4)
O5—K1—C1	118.92 (11)	C19—C18—C17	112.2 (5)
O1—K1—C1	23.29 (10)	O6—C20—C21	113.7 (3)
O2—K1—C1	23.15 (10)	O6—C20—C17	105.6 (3)

O4—K1—C1	69.73 (10)	C21—C20—C17	112.1 (3)
O8—K1—O10	84.46 (10)	O6—C20—H20	103 (3)
O9—K1—O10	54.96 (9)	C21—C20—H20	112 (2)
O5—K1—O10	146.51 (9)	C17—C20—H20	110 (2)
O1—K1—O10	79.28 (10)	C22—C21—C25	110.3 (4)
O2—K1—O10	53.77 (9)	C22—C21—C20	110.2 (4)
O4—K1—O10	136.12 (9)	C25—C21—C20	111.0 (4)
C1—K1—O10	67.93 (10)	C21—C22—C23	113.3 (4)
O8—K1—C16	100.61 (10)	C26—C23—C22	112.3 (4)
O9—K1—C16	115.04 (10)	C26—C23—C24	112.8 (4)
O5—K1—C16	18.75 (9)	C22—C23—C24	110.1 (4)
O1—K1—C16	107.87 (11)	O7—C24—O6	107.1 (3)
O2—K1—C16	121.55 (10)	O7—C24—C27	112.5 (3)
O4—K1—C16	51.67 (9)	O6—C24—C27	109.6 (3)
C1—K1—C16	113.43 (11)	O7—C24—C23	105.9 (3)
O10—K1—C16	164.76 (9)	O6—C24—C23	109.0 (3)
O8—K1—C39	81.17 (11)	C27—C24—C23	112.5 (3)
O9—K1—C39	22.89 (11)	C28—C27—C24	123.2 (4)
O5—K1—C39	105.77 (11)	C27—C28—C29	122.4 (4)
O1—K1—C39	114.06 (12)	N1—C29—C28	111.3 (3)
O2—K1—C39	72.12 (11)	N1—C29—C30	113.2 (4)
O4—K1—C39	154.23 (10)	C28—C29—C30	112.8 (4)
C1—K1—C39	94.48 (12)	O8—C30—O7	110.9 (3)
O10—K1—C39	41.60 (10)	O8—C30—C31	106.2 (3)
C16—K1—C39	124.51 (11)	O7—C30—C31	106.6 (3)
O8—K1—Br1^{ii}	138.71 (6)	O8—C30—C29	105.6 (3)
O9—K1—Br1^{ii}	81.18 (7)	O7—C30—C29	112.1 (3)
O5—K1—Br1^{ii}	68.90 (7)	C31—C30—C29	115.4 (4)
O1—K1—Br1^{ii}	89.37 (7)	C30—C31—C32	103.7 (4)
O2—K1—Br1^{ii}	54.40 (7)	C33—C32—C31	105.1 (4)
O4—K1—Br1^{ii}	89.39 (6)	O8—C33—C34	108.1 (4)
C1—K1—Br1^{ii}	68.93 (8)	O8—C33—C32	105.0 (3)

O10—K1—Br1^{ii}	86.01 (7)	C34—C33—C32	111.6 (4)
C16—K1—Br1^{ii}	80.72 (7)	O8—C33—C35	105.9 (3)
C39—K1—Br1^{ii}	65.52 (9)	C34—C33—C35	111.3 (4)
C1—O1—K1	98.7 (3)	C32—C33—C35	114.3 (4)
C43—N1—N2A	109.5 (6)	O9—C35—C36	111.4 (4)
C43—N1—N2B	108.1 (10)	O9—C35—C33	105.5 (4)
C43—N1—C29	133.5 (4)	C36—C35—C33	115.2 (4)
N2A—N1—C29	116.3 (6)	C37—C36—C35	112.0 (4)
N2B—N1—C29	116.2 (10)	C38—C37—C36	111.9 (4)
O2—C1—O1	123.4 (4)	O10—C38—C37	105.7 (4)
O2—C1—C2	118.8 (4)	O10—C38—C41	110.0 (4)
O1—C1—C2	117.7 (4)	C37—C38—C41	111.0 (4)
O2—C1—K1	67.8 (3)	O10—C38—C39	107.7 (4)
O1—C1—K1	58.0 (2)	C37—C38—C39	109.3 (4)
C2—C1—K1	161.0 (3)	C41—C38—C39	112.8 (4)
C1—O2—K1	89.1 (3)	O9—C39—C40	111.2 (4)
C1—C2—C5	109.1 (4)	O9—C39—C38	109.5 (3)
C1—C2—C3	110.1 (5)	C40—C39—C38	116.3 (5)
C5—C2—C3	110.8 (5)	O9—C39—K1	46.97 (19)
C9—O3—C5	115.8 (3)	C40—C39—K1	145.7 (4)
C4—C3—C2	113.0 (7)	C38—C39—K1	97.5 (3)
C13—O4—K1	100.9 (2)	C42—C41—C38	115.6 (5)
C16—O5—K1	115.0 (3)	N1—C43—C44	106.8 (4)
O3—C5—C2	113.0 (4)	C43—C44—N3A	105.5 (7)
O3—C5—C6	109.9 (5)	C43—C44—N3B	107.4 (10)
C2—C5—C6	113.7 (5)	C43—C44—C45	134.6 (4)
C20—O6—C24	115.4 (3)	N3A—C44—C45	119.2 (7)
C7—C6—C5	111.5 (5)	N3B—C44—C45	116.4 (10)
C24—O7—C30	119.8 (3)	C46—C45—C50	118.0 (4)
C6—C7—C8	111.4 (5)	C46—C45—C44	123.0 (4)
C30—O8—C33	112.4 (3)	C50—C45—C44	119.0 (4)
C30—O8—K1	130.5 (2)	C45—C46—C47	121.3 (5)

C33—O8—K1	116.9 (2)	C48—C47—C46	118.5 (5)
C7—C8—C10	113.4 (5)	C49—C48—C47	121.0 (5)
C7—C8—C9	107.6 (4)	C49—C48—Br1	118.5 (4)
C10—C8—C9	113.0 (4)	C47—C48—Br1	120.4 (4)
C35—O9—C39	116.3 (3)	C48—C49—C50	119.7 (5)
C35—O9—K1	119.6 (2)	C49—C50—C45	121.6 (5)
C39—O9—K1	110.1 (3)	N3A—N2A—N1	106.6 (9)
O3—C9—C8	110.3 (3)	N2A—N3A—C44	110.3 (9)
O3—C9—C11	105.9 (3)	N3B—N2B—N1	108.3 (15)
C8—C9—C11	115.5 (4)	N2B—N3B—C44	106.6 (15)
C38—O10—K1	111.8 (2)		

Symmetry codes: (i) *y*−1/2, −*x*+3/2, *z*−1/4; (ii) −*y*+3/2, *x*+1/2, *z*+1/4.