Supplementary Information

Catalytic Regio- and Stereoselective Intermolecular [5+2] Cycloaddition via Conjugative Activation of Oxidopyrylium

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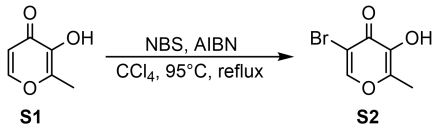
1. Experimental procedures and spectroscopic data

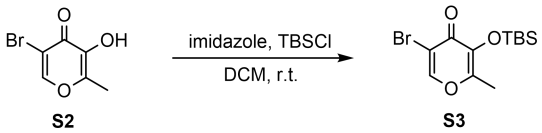
1.1 General information

All reactions were carried out under an inert atmosphere of dry N_2 in Schlenk tube. ^1H, ^{13}C, ^{19}F NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz for ^1H; 100 MHz for ^{13}C; 376 MHz for ^{19}F), ^1H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as external standard. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Mass spectra (MS) were obtained using ESI, DART mass spectrometer. Melting points were determined using a hot stage apparatus. All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature.

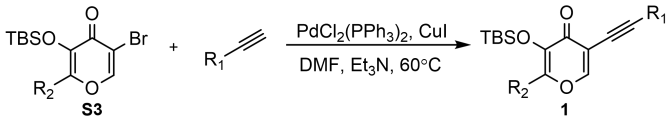
1.2 Preparation of Maltol derived alkynes[1-2]



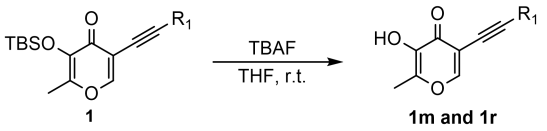
S1 (3.78 g, 30 mmol, 1.0 equiv), *N*-bromosuccinimide (5.87 g, 31 mmol, 1.1 equiv), and azobisisobutyronitrile (147 mg, 9 mmol, 0.3 equiv) were added to an oven dried 500mL round bottom flask containing anhydrous carbon tetrachloride (100 mL) under an atmosphere of argon. The mixture was then heated to reflux at 95°C for 18 h, After the reaction was finished, the mixture was filtered through a short silica gel and then concentrated. The crude product was purified by flash chromatography using a gradient (PE/EA: from 5:1 to 3:1) to give pure product **S2** 5.3g (52% yield) as a yellow solid.



To a magnetically stirred solution of **S2** (20 mmol, 1.0 equiv) in dry DCM (40 mL) was added imidazole (40 mmol, 2.0 equiv) at room temperature under air atmosphere, and then followed by TBSCl (30 mmol, 1.5 equiv)**.** The mixture was allowed to stir at room temperatureuntil the starting materials were completely consumed (monitored by TLC). After the reaction was finished, the mixture was filtered through a short silica gel, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (PE/EA = 20/1) as elute to afford the pure product **S3**.

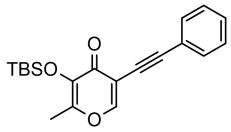


To a magnetically stirred solution of **S3** (1.0 mmol, 1.0 equiv) in DMF (8 mL) was added $Pd(PPh_3)_2Cl_2$ (3.0 mmol%) and CuI (5.0 mmol%) under nitrogen atmosphere, and then followed by the alkynes (1.2 equiv) and Et_3N (5 mmol, 5.0 equiv). The mixture was allowed to stir at 60℃ until the starting materials was completely consumed (monitored by TLC). After the reaction was finished, then the aqueous phase was extracted with EtOAc. The combined organic phases were dried over Na_2SO_4, filtered and evaporated under reduced pressure. the residue was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent to afford **1**.



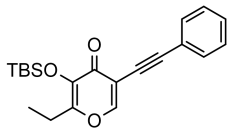
To a magnetically stirred solution of **1** (1.0 mmol, 1.0 equiv) in THF (8 mL) was added TBAF (3.0 mmol, 3 equiv) under atmosphere. The mixture was allowed to stir at room temperature until the starting materials was completely consumed (monitored by TLC). After the reaction was finished, then the aqueous phase was extracted with EtOAc. The combined organic phases were dried over Na_2SO_4, filtered and evaporated under reduced pressure. the residue was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent to afford **1m** and **1r**

***3-((tert-butyldimethylsilyl)oxy)-2-methyl-5-(phenylethynyl)-4H-pyran-4-one*(1a)**



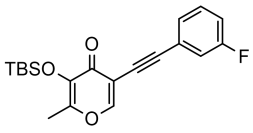
Yellow solid, m.p.= 138 °C, purified by chromatography (petroleum/ethyl acetate = 20:1), R_f = 0.3 (PE/EA = 20/1), 170 mg, yield =50%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.56 – 7.49 (m, 2H), 7.33 – 7.27 (m, 3H), 2.31 (s, 3H), 0.96 (s, 9H), 0.29 (s, 6H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 172.3, 155.7, 154.5, 142.2, 132.0, 128.7, 128.3, 122.7, 114.1, 95.4, 79.2, 26.0, 18.8, 15.1, -3.6; **IR** (KBr, cm^{-1}) 3678, 3568, 2931, 2362, 1917, 1740, 1645, 1533, 1453, 1398, 1253, 1166, 1073, 924, 899, 761; **HRMS** (ESI) Calcd for $C_{20}H_{24}O_3SiNa$ $(M+Na)^+$ 363.1387, found: 363.1392.

***3-((tert-butyldimethylsilyl)oxy)-2-ethyl-5-(phenylethynyl)-4H-pyran-4-one* (1b)**



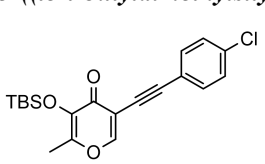
Yellow solid, m.p. = 120-121 °C, purified by chromatography (petroleum/ethyl acetate = 20:1), R_f = 0.3 (PE/EA = 20/1), 127 mg, yield = 36%; **^{1}HNMR** (500 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.44 (d, *J* = 1.9 Hz, 2H), 7.21 (d, *J* = 2.7 Hz, 3H), 2.63-2.60 (m, 2H), 1.12 – 1.09 (m, 3H), 0.88 (s, 9H), 0.22 (s, 6H); **^{13}CNMR** (125 MHz, $CDCl_3$) δ 172.5, 158.7, 155.8, 151.8, 141.3, 131.9, 128.6, 128.2, 122.7, 95.2, 79.2, 26.0, 21.9, 18.8, 11.0, -3.7; **IR** (KBr, cm^{-1}) 3286, 2975, 2358, 1602, 1530, 1450, 1352, 1294, 1186, 1156, 994, 929, 888, 761, 732, 687; **HRMS** (ESI) Calcd for $C_{21}H_{26}O_3SiNa(M+Na)^+$ 377.1543, found: 377.1544.

***3-((tert-butyldimethylsilyl)oxy)-5-((3-fluorophenyl)ethynyl)-2-methyl-4H-pyran-4-one(*1c)**



Yellow solid, m.p.=152-153 °C, purified by chromatography (petroleum/ethyl acetate = 20:1), R_f = 0.25 (PE/EA = 20/1), 143 mg, yield = 40%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.32 (t, *J* = 5.7 Hz, 1H), 7.30 – 7.21 (m, 2H), 7.03 (t, *J* = 8.8 Hz, 1H), 2.34 (s, 3H), 0.98 (s, 9H), 0.30 (s, 6H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 172.3, 162.4 (d, *J* = 246.7 Hz), 156.0, 142.3, 130.0 (d, *J* = 8.5 Hz), 127.9 (d, *J* = 3.0 Hz), 124.6 (d, *J* = 9.5 Hz), 118.8 (d, *J* = 23.1 Hz), 116.1 (d, *J* = 21.2 Hz), 113.8, 94.1, 80.3, 26.1, 18.9, 15.2, -3.6; **^{19}FNMR** (376 MHz, $CDCl_3$) δ -113.0; **IR** (KBr, cm^{-1}) 3743, 3649,1835, 1740, 1645, 1515, 1465, 1337, 1252, 1009, 876, 704; **HRMS** (ESI) Calcd for $C_{20}H_{23}FO_3SiNa$ $(M+Na)^+$ 381.1293, found: 381.1292.

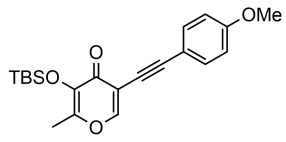
***3-((tert-butyldimethylsilyl)oxy)-5-((4-chlorophenyl)ethynyl)-2-methyl-4H-pyran-4-one* (1d)**



Yellow solid, m.p. = 149 °C, purified by chromatography (petroleum/ethyl acetate = 20:1), R_f = 0.2 (PE/EA = 20/1), 179 mg, yield = 48%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 2.34 (s, 3H), 0.97 (s, 9H), 0.29 (s, 6H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 172.4, 155.9, 154.7, 142.3, 134.9, 133.3, 128.7, 121.3, 114.0, 94.3, 80.3, 26.1, 18.88, 15.2, -3.6; **IR** (KBr, cm^{-1}) 3743, 3566, 2857, 1835, 1793,

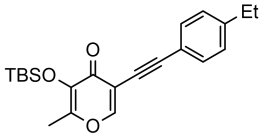
1644, 1515, 1428, 1366, 1244, 1079, 837, 782, 679; **HRMS** (ESI) Calcd for $C_{20}H_{23}ClO_3SiH$ $(M+H)^+$ 375.1178, found: 375.1176.

3-((tert-butyldimethylsilyl)oxy)-5-((4-methoxyphenyl)ethynyl)-2-methyl-4H-pyran-4-one **(1e)**



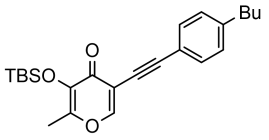
Yellow solid, m.p.= 106-107 °C, purified by chromatography (petroleum/ethyl acetate = 20 :1), R_f = 0.25 (PE/EA = 20/1), 159 mg, yield = 43 %; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.47 (d, *J* = 8.9 Hz, 2H), 6.83 (d, *J* = 8.9 Hz, 2H), 3.80 (s, 3H), 2.33 (s, 3H), 0.97 (s, 9H), 0.29 (s, 6H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 172.4, 159.9, 155.4, 154.4, 142.1, 133.4, 114.8, 114.3, 113.8, 95.4, 77.8, 55.3, 26.0, 18.8, 15.1, -3.7; **IR** (KBr, cm^{-1}) 3429, 2954, 2855, 1668, 1508, 1440, 1168, 1029, 834, 786; **HRMS** (ESI) Calcd for $C_{21}H_{26}O_4SiH$ $(M+H)^+$ 371.1673, found: 371.1675.

3-((tert-butyldimethylsilyl)oxy)-5-((4-ethylphenyl)ethynyl)-2-methyl-4H-pyran-4-one**(1f)**



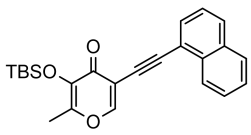
Yellow solid, m.p. = 146 °C, purified by chromatography (petroleum/ethyl acetate = 20:1), R_f = 0.2 (PE/EA = 20/1), 118 mg, yield = 32%; **^{1}HNMR** (500 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 2.64 (q, *J* = 7.6 Hz, 2H), 2.33 (s, 3H), 1.23 (d, *J* = 7.7 Hz, 3H), 0.97 (s, 9H), 0.30 (s, 6H); **^{13}CNMR** (125 MHz, $CDCl_3$) δ 172.5, 155.7, 154.5, 145.2, 142.2, 132.0, 127.9, 119.9, 114.3, 95.7, 78.5, 29.0, 26.1, 18.9, 15.4, 15.2, -3.6; **IR** (KBr, cm^{-1}) 3742, 3677, 3589, 2361, 1916, 1835, 1740, 1646, 1583, 1428, 1396, 902, 857, 674; **HRMS** (ESI) Calcd for $C_{22}H_{28}O_3SiH$ $(M+H)^+$ 369.1880, found: 369.1883.

3-((tert-butyldimethylsilyl)oxy)-5-((4-butylphenyl)ethynyl)-2-methyl-4H-pyran-4-one **(1g)**



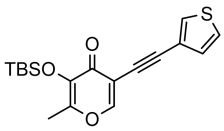
Yellow solid, m.p.= 98-99 °C, purified by chromatography (petroleum/ethyl acetate = 20:1), R_f = 0.3 (PE/EA = 20/1), 158 mg, yield = 40%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 2.61 – 2.56 (m, 2H), 2.31 (s, 3H), 160-1.54 (m, 2H), 1.35 – 1.30 (m, 2H), 0.97 (s, 9H), 0.91 (t, *J* = 7.4 Hz, 3H), 0.30 (s, 6H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 172.4, 155.6, 154.4, 143.8, 142.1, 131.9, 128.4, 119.9, 114.3, 95.6, 78.5, 35.7, 33.4, 26.0, 22.4, 18.8, 15.1, 14.0, -3.7; **IR** (KBr, cm^{-1}) 3028, 2839, 1677, 1607, 1587, 1441, 1329, 1293, 1177, 1026, 923, 833, 756; **HRMS** (ESI) Calcd for $C_{24}H_{32}O_3SiH$ $(M+H)^+$ 397.2193, found: 397.2197.

3-((tert-butyldimethylsilyl)oxy)-2-methyl-5-(naphthalen-1-ylethynyl)-4H-pyran-4-one **(1h)**



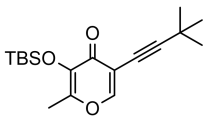
White solid, m.p.= 142 °C, purified by chromatography (petroleum/ethyl acetate = 20:1), R_f = 0.3 (PE/EA = 20/1), 195 mg, yield = 50%; **^{1}HNMR** (500 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.3 Hz, 1H), 8.05 (s, 1H), 7.84 (dd, *J* = 8.1, 3.6 Hz, 2H), 7.79 (d, *J* = 7.0 Hz, 1H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.46 – 7.40 (m, 1H), 2.35 (s, 3H), 1.00 (s, 9H), 0.34 (s, 6H); **^{13}CNMR** (125 MHz, $CDCl_3$) δ 172.4, 155.6, 154.6, 142.3, 133.3, 133.2, 130.9, 129.3, 128.3, 127.0, 126.6, 126.5, 125.2, 120.4, 114.3, 93.8, 84.1, 26.1, 18.9, 15.2, -3.6; **IR** (KBr, cm^{-1}) 3456, 2968, 2934, 1678, 1605, 1496, 1365, 1297, 1026, 976, 740; **HRMS** (ESI) Calcd for $C_{24}H_{26}O_3SiH$ $(M+H)^+$ 391.1724, found: 391.1725.

***3-((tert-butyldimethylsilyl)oxy)-2-methyl-5-(thiophen-3-ylethynyl)-4H-pyran-4-one* (1i)**



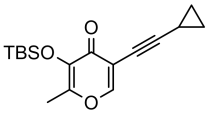
Brown solid, m.p. = 150 °C, purified by chromatography (petroleum/ethyl acetate = 20:1), R_f = 0.3 (PE/EA = 20/1), 138 mg, yield = 40%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.55 (dd, *J* = 2.9, 1.0 Hz, 1H), 7.26 – 7.24 (m, 1H), 7.19 (dd, *J* = 5.0, 1.0 Hz, 1H), 2.33 (s, 3H), 0.96 (s, 9H), 0.29 (s, 6H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 172.4, 155.7, 154.6, 142.3, 130.1, 129.8, 125.3, 121.8, 114.2, 90.6, 78.8, 26.1, 18.9, 15.2, -3.6; **IR** (KBr, cm^{-1}) 3743, 3649, 3620, 2353, 1917, 1793, 1694, 1621, 1515, 1465, 1426, 1396, 1252, 1076, 675; **HRMS** (ESI) Calcd for $C_{18}H_{22}O_3SSiH$ $(M+H)^+$ 347.1132, found: 347.1122.

***3-((tert-butyldimethylsilyl)oxy)-5-(3,3-dimethylbut-1-yn-1-yl)-2-methyl-4H-pyran-4-one* (1j)**



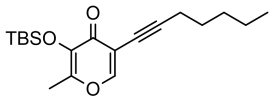
White solid, m.p. = 96-97 °C, purified by chromatography (petroleum/ethyl acetate = 20:1), R_f = 0.4 (PE/EA = 20/1), 163mg, yield = 51%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 2.30 (s, 3H), 1.31 (s, 9H), 0.97 (s, 9H), 0.28 (s, 6H); **^{13}CNMR** (100MHz, $CDCl_3$) δ 172.6, 155.5, 154.2, 142.1, 114.5, 104.5, 68.9, 31.0, 28.3, 26.1,18.8, 15.1, -3.7; **IR** (KBr, cm^{-1}) 3273, 296, 2870, 1693, 1613, 1519, 1454, 1312, 1216, 1185, 1029, 945, 874; **HRMS** (ESI) Calcd for $C_{18}H_{28}O_3SiNa$ $(M+Na)^+$ 343.1700, found: 343.1700.

***3-((tert-butyldimethylsilyl)oxy)-5-(cyclopropylethynyl)-2-methyl-4H-pyran-4-one* (1k)**



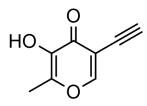
White solid, m.p.= 142 °C, purified by chromatography (petroleum/ethyl acetate = 20:1), R_f = 0.4 (PE/EA = 20/1), 158 mg, yield =54%; **^{1}HNMR** (500 MHz,$CDCl_3$) δ 7.78 (s, 1H), 2.29 (s, 3H), 1.47 (tt, *J* = 8.1, 5.3 Hz, 1H), 0.95 (s, 9H), 0.82 (tq, *J* = 7.6, 2.8 Hz, 4H), 0.27 (s, 6H); **^{13}CNMR** (125 MHz, $CDCl_3$) 173.0, 155.5, 154.3, 142.1, 114.5, 100.0, 65.4, 26.1, 18.9, 15.2, 8.9, 0.6, -3.6; **IR** (KBr, cm^{-1}) 3743, 3678, 3620, 2362, 1917, 1793, 1694, 1538, 1464, 1386, 754, 679; **HRMS** (ESI) Calcd for $C_{17}H_{24}O_3SiNa$ $(M+Na)^+$ 327.1387, found: 327.1290.

***3-((tert-butyldimethylsilyl)oxy)-5-(hept-1-yn-1-yl)-2-methyl-4H-pyran-4-one* (1l)**



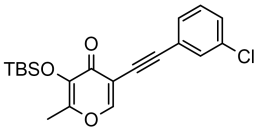
Yellow oil, purified by chromatography (petroleum/ethyl acetate = 20:1), R_f = 0.3 (PE/EA = 20/1), 107 mg, yield = 32%; **^{1}HNMR** (500 MHz, $CDCl_3$) 7.81 (s, 1H), 2.41 (t, *J* = 7.3 Hz, 2H), 2.30 (s, 3H), 1.61 – 1.55 (m, 2H), 1.38 – 1.31 (m, 4H), 0.95 (s, 9H), 0.89 (t, *J* = 7.1 Hz, 3H), 0.27 (s, 6H); **^{13}CNMR** (100MHz, $CDCl_3$) δ 173.0, 155.4, 154.4, 142.2, 114.5, 97.3, 70.1, 31.3, 28.4, 26.1, 22.3, 19.9, 18.9, 15.1, 14.1, -3.6; **IR** (KBr, cm^{-1}) 2956, 2930, 2361, 1686, 1528, 1437, 1370, 1292, 1183, 1073, 968, 817, 727; **HRMS** (ESI) Calcd for $C_{19}H_{30}O_3SiH$ $(M+H)^+$ 335.2037, found : 335.2036.

***5-ethynyl-3-hydroxy-2-methyl-4H-pyran-4-one* (1m)**



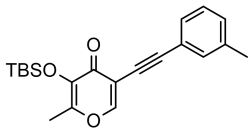
White solid, m.p. = 146-147 °C, purified by chromatography (petroleum/ethyl acetate = 2:1), R_f = 0.2 (PE/EA = 2/1), 45 mg, yield = 30%; **^{1}HNMR** (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 3.29 (s, 1H), 2.37 (s, 3H); **^{13}CNMR** (125 MHz, $CDCl_3$) δ 171.7, 157.8, 149.1,142.4,110.6, 84.3, 73.0, 14.5; **IR** (KBr, cm^{-1}) 3568, 3058, 1717, 1679, 1526, 1481, 1294, 1019, 926, 807; **HRMS** (ESI) Calcd for $C_8H_6O_3Na$ $(M+Na)^+$ 173.0209, found: 173.0206.

3-((tert-butyldimethylsilyl)oxy)-5-((3-chlorophenyl)ethynyl)-2-methyl-4H-pyran-4-one **(1n)**



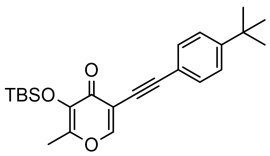
Yellow solid, m.p.= 156-157 ºC, purified by chromatography (petroleum/ethyl acetate = 20 :1), R_f = 0.25 (PE/EA = 20/1), 161 mg, yield = 43%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 1.0 Hz, 1H), 7.53 (t, *J* = 1.6 Hz, 1H), 7.41 (s, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 2.34 (s, 3H), 0.97 (s, 9H), 0.29 (s, 6H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 172.2, 155.9, 154.6, 142.2, 134.1, 131.7, 130.0, 129.5, 128.9, 124.4, 113.7, 93.8, 80.4, 26.0, 18.8, 15.1, -3.7; **IR** (KBr, cm^{-1}) 2958, 2930, 1675, 1515, 1428, 1112, 1009, 975, 902, 867, 702; **HRMS** (ESI) Calcd for $C_{20}H_{23}ClO_3SiNa$ $(M+Na)^+$ 397.0997, found: 397.0990.

3-((tert-butyldimethylsilyl)oxy)-2-methyl-5-(m-tolylethynyl)-4H-pyran-4-one**(1o)**



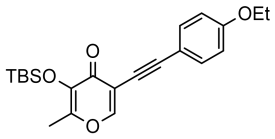
Yellow solid, m.p. = 150 ºC, purified by chromatography (petroleum/ethyl acetate = 20:1), R_f = 0.3 (PE/EA = 20/1), 141 mg, yield = 40%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.37 (s, 1H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 2.32 (s, 3H), 2.31 (s, 3H), 0.97 (s, 9H), 0.30 (s, 6H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 172.4, 155.7, 154.5, 142.2, 137.9, 132.6, 129.6, 129.0, 128.2, 122.5, 114.2, 95.6, 78.9, 26.1, 21.2, 18.8, 15.1, -3.6; **IR** (KBr, cm^{-1}) 3743, 3568, 2857, 2334, 1916, 1740, 1678, 1516, 1396, 1256, 1063, 942, 838, 782, 698; **HRMS** (ESI) Calcd for $C_{21}H_{26}O_3SiNa$ $(M+Na)^+$ 377.1543, found: 377.1544.

5-((4-(tert-butyl)phenyl)ethynyl)-3-((tert-butyldimethylsilyl)oxy)-2-methyl-4H-pyran-4-one(**1p)**



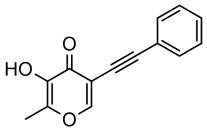
Yellow solid, m.p. = 154 ºC, purified by chromatography (petroleum/ethyl acetate = 20:1), R_f = 0.3 (PE/EA = 20/1), 178 mg, yield = 45%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 2.33 (s, 3H), 1.31 (s, 9H), 0.98 (s, 9H), 0.30 (s, 6H); **^{13}CNMR** (100MHz, $CDCl_3$) δ 172.5, 155.7, 154.5, 152.0, 142.3, 131.8, 125.3, 119.7, 114.4, 95.6, 78.6, 34.9, 31.3, 26.1, 18.9, 15.2, -3.6; **IR** (KBr, cm^{-1}) 3743, 3678, 3620, 2958, 2335, 1918, 1793, 1693, 1539, 1428, 1387, 1203, 1001, 836, 785, 674; **HRMS** (ESI) Calcd for $C_{24}H_{32}O_3SiNa$ $(M+Na)^+$ 419.2013, found: 419.2016.

3-((tert-butyldimethylsilyl)oxy)-5-((4-ethoxyphenyl)ethynyl)-2-methyl-4H-pyran-4-one **(1q)**



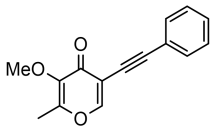
Yellow solid, m.p. = 186 ºC, purified by chromatography (petroleum/ethyl acetate = 20:1), R_f = 0.2 (PE/EA = 20/1), 161 mg, yield = 42%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.46 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 4.03 (q, *J* = 6.9 Hz, 2H), 2.33 (s, 3H), 1.41 (t, *J* = 6.9 Hz, 3H), 0.97 (s, 9H), 0.29 (s, 6H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 172.5, 159.4, 155.5, 154.5, 152.8, 142.2, 133.5, 114.7, 114.5, 95.6, 77.8, 63.6, 26.1, 18.9, 15.2, 14.9, -3.6; **IR** (KBr, cm^{-1}) 3743, 3678, 3620, 2362, 1967, 1835, 1770, 1694, 1538, 1465, 1391, 1250, 753, 673; **HRMS** (ESI) Calcd for $C_{22}H_{28}O_4SiNa$ $(M+Na)^+$ 407.1649, found: 407.1653.

3-hydroxy-2-methyl-5-(phenylethynyl)-4H-pyran-4-one**(1r)**



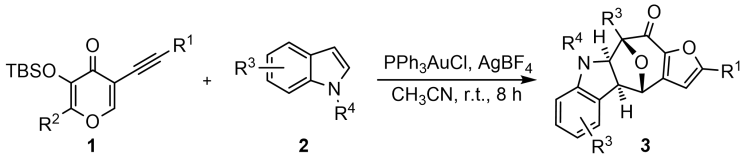
Yellow solid, m.p.= 138 ºC, purified by chromatography (petroleum/ethyl acetate = 4:1), R_f = 0.2 (PE/EA = 4/1), 172 mg, yield =76%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.54 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.33 (dd, *J* = 5.1, 1.9 Hz, 3H), 6.45 (s, 1H), 2.38 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 171.6, 156.8, 148.7, 142.4, 132.0, 129.0, 128.4, 122.5, 111.8, 95.9, 78.4, 14.5; **IR** (KBr, cm^{-1}) 3528, 2968, 2870, 1693, 1613, 1567, 1454, 1313, 1253, 1185, 1029, 945, 874; **HRMS** (ESI) Calcd for $C_{14}H_{10}O_3Na$ $(M+Na)^+$ 249.0522, found: 249.0526.

3-methoxy-2-methyl-5-(phenylethynyl)-4H-pyran-4-one **(1s)**



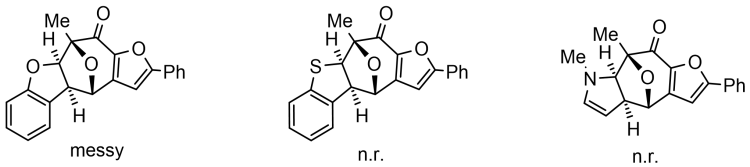
Brown solid, m.p. = 120-122 ºC, R_f = 0.3 (PE/EA = 5/1), 108 mg, yield =45%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.54 (s, 2H), 7.34 (s, 3H), 3.90 (s, 3H), 2.34 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 172.8, 158.9, 156.2, 144.8, 131.8, 128.8, 128.3, 122.5, 115.5, 96.1, 78.8, 60.0, 14.6; **IR** (KBr, cm^{-1}) 3059, 2362, 1917, 1835, 1770, 1678, 1515, 1455, 1340, 1087, 932, 700; **HRMS** (ESI) Calcd for $C_{15}H_{12}O_3Na$ $(M+Na)^+$ 263.0679, found: 263.0680.

1.3 General procedure for the synthesis of 3



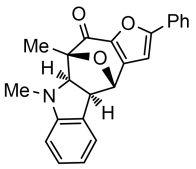
To a 25 mL Schlenk tube with a magnetic bar under nitrogen atmosphere was PPh_3AuCl (5 mmol%) and $AgBF_4$ (5 mmol%) in acetonitrile (CH_3CN, 2 mL) , then the substrates 1(0.1mmol) and Indole derivatives (1.5 eq) were added. The resulting mixture was stirred at room temperature for 8 h. After the reaction was finished, the mixture was filtered by short silica, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as elute to afford the product **3** .

Unsatisfactory results from other heterocycles



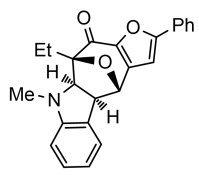
Note: When other heteroarenes were used, the catalytic system was out of function.

9,10-dimethyl-2-phenyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one **(3aa)**



Yellow solid, m.p. = 185-186 ºC, purified by chromatography (petroleum/ethyl acetate = 15:1), R_f = 0.2 (PE/EA = 15/1), 29 mg, yield = 81%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.3 Hz, 2H), 7.50 – 7.38 (m, 3H), 7.17 (dd, *J* = 12.1, 7.3 Hz, 2H), 6.84 (s, 1H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.49 (s, 1H), 5.34 (s, 1H), 4.23 (d, *J* = 8.5 Hz, 1H), 3.96 (d, *J* = 8.5 Hz, 1H), 2.98 (s, 3H), 1.66 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 185.6, 160.2, 153.9, 147.1, 144.3, 130.2, 129.2, 129.1, 128.9, 127.5, 125.7, 124.0, 117.9, 107.2, 102.9, 93.6, 78.9, 74.6, 56.1, 37.1, 15.1; **IR** (KBr, cm^{-1}) 3743, 3678, 3649, 3620, 2933, 1835, 1740, 1676, 1497, 1455, 1367, 1296, 1263, 1119, 1026, 972, 829, 743; **HRMS** (ESI) Calcd for $C_{23}H_{19}NO_3$ $(M+Na)^+$ 380.1257, found: 380.1252.

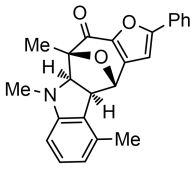
10-ethyl-9-methyl-2-phenyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-on e **(3ba)**



Yellow solid, m.p. = 131-132 ºC, purified by chromatography (petroleum/ethyl acetate = 15:1), R_f = 0.2 (PE/EA = 15/1), 27 mg, yield = 72%; **^{1}HNMR** (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.1 Hz, 2H), 7.44 (dt, *J* = 12.8, 6.9 Hz, 3H), 7.19 – 7.13 (m, 2H), 6.84 (s, 1H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.46 (d, *J* = 7.8 Hz, 1H), 5.36 (s, 1H), 4.21 (d, *J* = 8.5 Hz, 1H), 3.96 (d, *J* = 8.5 Hz, 1H), 2.96 (s, 3H), 2.49 (dq, *J* = 14.6, 7.3 Hz, 1H), 1.89 (dq, *J* = 14.5, 7.3 Hz, 1H), 1.04 (t, *J* = 7.3 Hz, 3H); **^{13}CNMR** (125 MHz, $CDCl_3$) δ 185.4, 160.2 153.9, 147.1, 145.2, 130.2, 129.2, 129.15,

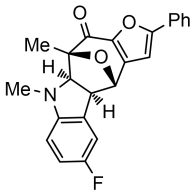
129.0, 127.6, 125.7, 124.0, 117.8, 107.1, 102.9, 97.3, 78.6, 75.1, 56.2, 37.2, 22.6, 8.9; **IR** (KBr, cm^{-1}) 3740, 3061, 2974, 1679, 1527, 1474, 1427, 1356, 1258, 1030, 973, 921, 880, 765, 738, 693; **HRMS** (ESI) Calcd for $C_{24}H_{21}NO_3H$ $(M+H)^+$372.1594, found: 372.1593.

***5,9,10-trimethyl-2-phenyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one* (3ab)**



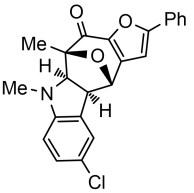
Yellow solid, m.p. = 119-120 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), R_f = 0.2 (PE/EA = 15/1), 33 mg, yield = 88%; **^{1}HNMR** (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.1 Hz, 2H), 7.45 (dt, *J* = 12.1, 6.9 Hz, 3H), 7.09 (t, *J* = 7.7 Hz, 1H), 6.82 (s, 1H), 6.55 (d, *J* = 7.5 Hz, 1H), 6.35 (d, *J* = 7.9 Hz, 1H), 5.35 (s, 1H), 4.17 (d, *J* = 8.5 Hz, 1H), 3.96 (d, *J* = 8.5 Hz, 1H), 2.96 (s, 3H), 2.36 (s, 3H), 1.68 (s, 3H); **^{13}CNMR** (125 MHz, $CDCl_3$) δ 185.6, 160.4, 154.2, 147.4, 144.3, 133.5, 130.2, 129.4, 129.1, 128.9, 125.9, 125.7, 119.4, 105.1, 102.5, 93.5, 77.3, 74.8, 55.9, 37.7, 18.6, 15.3; **IR** (KBr, cm^{-1}) 3742, 3442, 2933, 2362, 1676, 1453, 1364, 1268, 1128, 1009, 973, 803, 765, 733; **HRMS** (ESI) Calcd for $C_{24}H_{21}NO_3H$ $(M+H)^+$ 372.1594, found: 372.1590.

***6-fluoro-9,10-dimethyl-2-phenyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one* (3ac)**



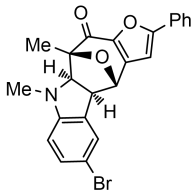
Green solid, m.p. = 189-190 °C, purified by chromatography (petroleum/ethyl acetate = 12:1), R_f = 0.25 (PE/EA = 10/1), 32 mg, yield = 84%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.83 7.44 (q, *J* = 8.2, 7.3 Hz, 3H), 6.91 (d, *J* = 7.9 Hz, 1H), 6.87 (d, *J* = 8.9 Hz, 1H), 6.83 (s, 1H), 6.37 (dd, *J* = 8.5, 3.9 Hz, 1H), 5.31 (s, 1H), 4.19 (d, *J* = 8.5 Hz, 1H), 3.95 (d, *J* = 8.5 Hz, 1H), 2.94 (s, 3H), 1.65 (s, 3H).**^{13}CNMR** (100 MHz, $CDCl_3$) δ 185.4, 160.3, 156.6 (d, *J* = 234.4 Hz), 150.3,146.8, 144.3, 130.2, 129.2, 128.9, 128.7 (d, *J* = 8.1 Hz), 125.7, 115.1 (d, *J* = 23.2 Hz), 111.5 (d, *J* = 24.5 Hz), 107.5 (d, *J* = 8.2 Hz), 102.8, 93.6, 78.7, 75.2, 56.0, 37.9, 15.0; **^{19}FNMR** (376 MHz,$CDCl_3$) δ -127.5; **IR** (KBr, cm^{-1}) 3743, 3638, 3566, 2935, 2361, 1835, 1741, 1483, 1396, 1222, 1128, 1028, 975, 874, 763; **HRMS** (ESI) Calcd for $C_{23}H_{18}FNO_3Na$ $(M+Na)^+$ 398.1163, found: 398.1165.

***6-chloro-9,10-dimethyl-2-phenyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one* (3ad)**



Green solid, m.p. = 191-192 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), R_f = 0.2 (PE/EA = 15/1), 29 mg, yield = 74%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.0 Hz, 2H), 7.45 (q, *J* = 8.3, 7.3 Hz, 3H), 7.14 (s, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 6.82 (s, 1H), 6.36 (d, *J* = 8.4 Hz, 1H), 5.31 (s, 1H), 4.18 (d, *J* = 8.4 Hz, 1H), 3.98 (d, *J* = 8.5 Hz, 1H), 2.96 (s, 3H), 1.63 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 185.3, 160.4, 152.4, 146.7, 144.3, 130.3, 129.2, 129.17, 128.9, 128.8, 125.8, 124.3, 122.3, 107.8, 102.8, 93.5, 78.7, 74.9, 55.8, 37.1, 15.1; **IR** (KBr, cm^{-1}) 3743, 3678, 3565, 2985, 1835, 1740, 1677, 1497, 1305, 1100, 973, 875, 802, 740; **HRMS**(ESI) Calcd for $C_{23}H_{18}ClNO_3H$ $(M+H)^+$ 392.1048, found: 392.1052.

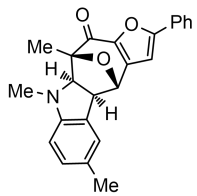
***6-bromo-9,10-dimethyl-2-phenyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one* (3ae)**



Yellow solid, m.p. = 195-196 °C, purified by chromatography (petroleum/ethyl acetate = 12:1), R_f = 0.2 (PE/EA = 12/1), 33 mg, yield = 76%; **^{1}HNMR** (500 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 2H), 7.40 – 7.33 (m, 3H), 7.23 – 7.19 (m, 1H), 7.15 (dt, *J* = 8.4, 2.5 Hz, 1H), 6.74 (s, 1H), 6.25 (dd, *J* = 8.3, 3.0 Hz, 1H), 5.24 (s, 1H), 4.11 (d, *J* = 8.5 Hz, 1H), 3.91 (d, *J* = 8.5 Hz, 1H), 2.88 (s, 3H), 1.56 (s, 3H); **^{13}CNMR** (125 MHz, $CDCl_3$) δ 185.2, 160.4, 152.8,

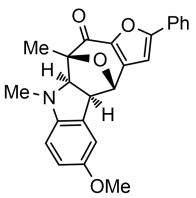
146.7, 144.3, 131.8, 130.3, 129.7, 129.2, 128.8, 127.0, 125.7, 109.1, 108.4, 102.8, 93.5, 78.7, 74.8, 55.7, 37.0, 15.1; **IR** (KBr, cm^{-1}) 3059, 2935, 2364, 1675, 1525, 1453, 1367, 1271, 1099, 973, 803, 755, 692; **HRMS** (ESI) Calcd for $C_{23}H_{18}BrNO_3H$ $(M+H)^+$436.0543, found: 436.0542.

6,9,10-trimethyl-2-phenyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one **(3af)**



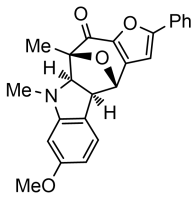
Yellow solid, m.p. = 188-189 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), R_f = 0.2 (PE/EA = 15/1), 29 mg, yield = 77%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 6.7 Hz, 2H), 7.45 (q, *J* = 9.5, 8.0 Hz, 3H), 7.02 (s, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.82 (s, 1H), 6.41 (d, *J* = 7.9 Hz, 1H), 5.32 (s, 1H), 4.19 (d, *J* = 8.4 Hz, 1H), 3.92 (d, *J* = 8.5 Hz, 1H), 2.95 (s, 3H), 2.29 (s, 3H), 1.65 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 185.8, 160.2, 151.9, 147.10, 144.4, 130.2, 129.5, 129.1, 129.0, 127.7, 127.3, 125.7, 124.8, 107.3, 102.8, 93.6, 78.9, 74.9, 56.2, 37.7, 20.8, 15.0; **IR** (KBr, cm^{-1}) 3733, 3620, 2932, 2362, 1868, 1740, 1616, 1502, 1454, 1396, 1285, 1026, 922, 878, 763; **HRMS** (ESI) Calcd for $C_{24}H_{21}NO_3Na$ $(M+Na)^+$ 394.1414, found: 394.1416.

6-methoxy-9,10-dimethyl-2-phenyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one **(3ag)**



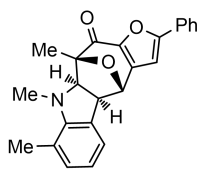
Green solid, m.p. = 113-115 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.2 (PE/EA = 10/1), 29 mg, yield = 76%; **^{1}HNMR** (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.2 Hz, 2H), 7.44 (dt, *J* = 12.8, 6.9 Hz, 3H), 6.84 (s, 1H), 6.82 (s, 1H), 6.74 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.43 (d, *J* = 8.5 Hz, 1H), 5.32 (s, 1H), 4.20 (d, *J* = 8.4 Hz, 1H), 3.90 (d, *J* = 8.5 Hz, 1H), 3.77 (s, 3H), 2.92 (s, 3H), 1.65 (s, 3H); **^{13}CNMR** (125MHz, $CDCl_3$) δ 185.8, 160.2, 153.2, 148.5, 147.0, 144.4, 134.3, 130.2, 129.2, 128.8, 125.7, 114.1, 111.3, 108.2, 102.9, 93.6, 78.8, 75.3, 56.4, 56.3, 38.5, 15.0; **IR** (KBr, cm^{-1}) 3058, 2935, 2362, 1674, 1525, 1496, 1365, 1227, 1145, 1097, 1028, 924, 875, 733; **HRMS** (ESI) Calcd for $C_{24}H_{21}NO_4Na$ $(M+Na)^+$410.1363, found: 410.1362.

7-methoxy-9,10-dimethyl-2-phenyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one **(3ah)**



Yellow solid, m.p.= 195-196 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.2 (PE/EA = 10/1), 27 mg, yield = 70%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.48 – 7.38 (m, 3H), 7.05 (d, *J* = 8.1 Hz, 1H), 6.82 (s, 1H), 6.25 (dd, *J* = 8.1, 2.2 Hz, 1H), 6.05 (d, *J* = 2.2 Hz, 1H), 5.28 (s, 1H), 4.15 (d, *J* = 8.4 Hz, 1H), 3.99 (d, *J* = 8.4 Hz, 1H), 3.79 (s, 3H), 2.97 (s, 3H), 1.64 (s, 3H); **^{13}CNMR** (100MHz, $CDCl_3$) δ 185.6, 161.6, 160.3, 155.2, 147.1, 144.3, 130.2, 129.2, 129.0, 125.7, 124.3, 120.1, 102.9, 102.5, 94.2, 93.5, 78.9, 75.3, 55.6, 55.5, 36.9, 15.2; **IR** (KBr, cm^{-1}) 3743, 3678, 3655, 2934, 2363, 1835, 1771, 1541, 1427, 1368, 1200, 1028, 972, 817, 783; **HRMS** (ESI) Calcd for $C_{24}H_{21}NO_4Na$ $(M+Na)^+$ 410.1363, found: 410.1360.

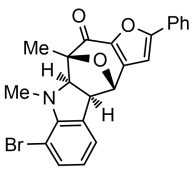
8,9,10-trimethyl-2-phenyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one **(3ai)**



Yellow solid, m.p. = 165-166 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), R_f = 0.2 (PE/EA = 15/1), 28 mg, yield = 76%; **^{1}HNMR** (500 MHz, $CDCl_3$) δ 7.87 – 7.82 (m, 2H), 7.48 – 7.40 (m, 3H), 7.09 (d, *J* = 7.3 Hz, 1H), 6.97 (d, *J* = 7.4 Hz, 1H), 6.83 (s, 1H), 6.79 (t, *J* = 7.4 Hz, 1H), 5.26 (s, 1H), 4.27 (d, *J* = 8.2 Hz, 1H), 3.77 (d, *J* = 8.2 Hz, 1H), 3.02 (s, 3H), 2.36 (s, 3H), 1.70 (s, 3H); **^{13}CNMR** (125 MHz, $CDCl_3$) δ 186.1, 160.1,

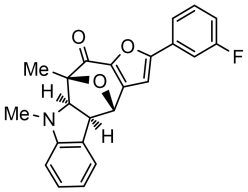
152.7, 146.9, 144.5, 131.8, 130.1, 129.6, 129.1, 129.0, 125.7, 121.7, 121.6, 120.5, 102.9, 93.2, 79.2, 76.2, 55.5, 42.0 19.2, 14.9; **IR** (KBr, cm^{-1}) 3049, 2934, 1675, 1597, 1476, 1366, 1266, 1134, 1026, 925, 822, 766, 734; **HRMS** (ESI) Calcd for $C_{24}H_{21}NO_3H$ $(M+H)^+$ 372.1594, found: 372.1589.

8-bromo-9,10-dimethyl-2-phenyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one **(3aj)**



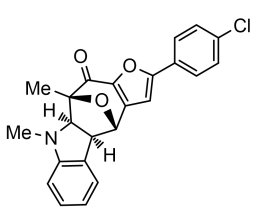
Yellow solid, m.p. = 185-186 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), R_f = 0.2 (PE/EA = 15/1), 24 mg, yield = 56%; **^{1}HNMR** (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.3 Hz, 2H), 7.45 (dt, *J* = 11.8, 6.8 Hz, 3H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.14 (d, *J* = 7.3 Hz, 1H), 6.82 (s, 1H), 6.68 (t, *J* = 7.6 Hz, 1H), 5.26 (s, 1H), 4.28 (d, *J* = 8.3 Hz, 1H), 3.85 (d, *J* = 8.2 Hz, 1H), 3.21 (s, 3H), 1.69 (s, 3H); **^{13}CNMR** (125 MHz, $CDCl_3$) δ 185.5, 160.4, 151.0, 146.4, 134.1, 132.0, 130.3, 129.2, 128.9, 125.7, 123.0, 121.1, 104.4, 102.9, 93.3, 79.1, 76.3, 55.4, 41.3, 29.8, 14.9; **IR** (KBr, cm^{-1}) 3059, 2935, 2364, 1675, 1525, 1453, 1367, 1271, 1099, 973, 803, 755, 692; **HRMS** (ESI) Calcd for $C_{23}H_{18}BrNO_3H$ $(M+H)^+$436.0543, found: 436.0541.

2-(3-fluorophenyl)-9,10-dimethyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one **(3ca)**



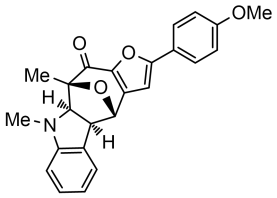
Yellow solid, m.p. = 148-149 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), R_f = 0.2 (PE/EA = 15/1), 26 mg, yield = 70%; **^{1}HNMR** (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 9.4 Hz, 1H), 7.42 (q, *J* = 8.0 Hz, 1H), 7.17 (dd, *J* = 11.7, 7.5 Hz, 2H), 7.11 (t, *J* = 8.3 Hz, 1H), 6.86 (s, 1H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.49 (d, *J* = 7.8 Hz, 1H), 5.34 (s, 1H), 4.23 (d, *J* = 8.5 Hz, 1H), 3.96 (d, *J* = 8.5 Hz, 1H), 2.98 (s, 3H), 1.65 (s, 3H); **^{13}CNMR** (125 MHz, $CDCl_3$) δ 184.5, 163.2 (d, *J* = 247.0 Hz), 158.2, 146.5, 146.4, 137.3, 131.2 (d, *J* = 8.3 Hz), 130.8 (d, *J* = 8.4 Hz), 128.8, 127.8, 127.5, 121.3, 121.3, 116.8 (d, *J* = 21.3 Hz), 112.5 (d, *J* = 23.8 Hz), 103.5, 91.5, 73.2, 52.9, 38.8, 19.6; **^{19}FNMR** (471 MHz, $CDCl_3$) δ -111.7; **IR** (KBr, cm^{-1}) 3654, 2928, 2362, 1678, 1525, 1464, 1298, 1204, 1157, 1025, 977, 862, 789, 731; **HRMS** (ESI) Calcd for $C_{23}H_{18}FO_3H$ $(M+H)^+$ 376.1343, found: 376.1344.

2-(4-chlorophenyl)-9,10-dimethyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one **(3da)**



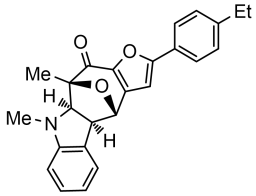
Yellow solid, m.p. = 145-146 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), R_f = 0.2 (PE/EA = 15/1), 28 mg, yield = 72%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.16 (t, *J* = 8.1 Hz, 2H), 6.82 (d, *J* = 3.1 Hz, 1H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.48 (d, *J* = 7.7 Hz, 1H), 5.33 (s, 1H), 4.22 (d, *J* = 8.4 Hz, 1H), 3.95 (d, *J* = 8.5 Hz, 1H), 2.98 (s, 3H), 1.65 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 185.7, 159.0, 153.9, 147.0, 144.5, 136.2, 129.5, 129.2, 127.4, 126.9, 124.0, 117.9, 107.3, 103.3, 93.6, 78.8, 74.5, 56.1, 37.1, 29.8, 15.1; **IR** (KBr, cm^{-1}) 3056, 2933, 2342, 1677, 1602, 1470, 1353, 1236, 1090, 1021, 937, 827, 738, 704; **HRMS** (ESI) Calcd for $C_{23}H_{18}NO_3ClH$ $(M+H)^+$ 392.1048, found: 392.1044.

2-(4-methoxyphenyl)-9,10-dimethyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one **(3ea)**



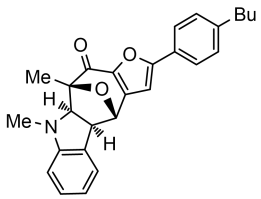
Yellow solid, m.p. = 189-190 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.2 (PE/EA = 10:1), 26 mg, yield = 68%; **^{1}HNMR** (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.19 – 7.13 (m, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.71 (d, *J* = 6.3 Hz, 2H), 6.48 (d, *J* = 7.8 Hz, 1H), 5.32 (s, 1H), 4.21 (d, *J* = 8.4 Hz, 1H), 3.96 (d, *J* = 8.4 Hz, 1H), 3.86 (s, 3H), 2.98 (s, 3H), 1.65 (s, 3H); **^{13}CNMR** (125 MHz, $CDCl_3$) δ 185.2, 161.3, 160.6, 153.9, 147.5, 143.8, 129.1, 127.5, 127.4, 124.0, 121.7, 117.8, 114.6, 107.2, 93.5, 78.9, 74.6, 56.2, 55.6, 37.1, 15.1; **IR** (KBr, cm^{-1}) 3029, 2964, 2360, 1676, 1603, 1515, 1481, 1367, 1298, 1112, 1024, 973, 807; **HRMS** (ESI) Calcd for $C_{24}H_{21}NO_4Na$ $(M+Na)^+$ 410.1363, found: 410.1356.

2-(4-ethylphenyl)-9,10-dimethyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one **(3fa)**



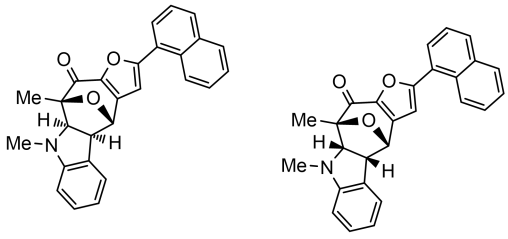
White solid, m.p. =150-152 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.3 (PE/EA = 10/1), 27 mg, yield = 70%; **^{1}HNMR** (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.16 (dd, *J* = 12.1, 7.4 Hz, 2H), 6.78 (s, 1H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.48 (d, *J* = 7.8 Hz, 1H), 5.32 (s, 1H), 4.22 (d, *J* = 8.5 Hz, 1H), 3.96 (d, *J* = 8.5 Hz, 1H), 2.98 (s, 3H), 2.70 (q, *J* = 7.6 Hz, 2H), 1.65 (s, 3H), 1.27 (t, *J* = 7.6 Hz, 3H); **^{13}CNMR** (125 MHz, $CDCl_3$) δ 185.6, 160.8, 154.0, 147.4, 147.0, 144.2, 129.3, 128.8, 127.7, 126.6, 125.0, 124.1, 118.0, 107.3, 102.4, 93.7, 79.0, 74.7, 56.3, 37.3, 29.1, 15.5, 15.2; **IR** (KBr, cm^{-1}) 3054, 2929, 2362, 1675, 1605, 1481, 1441, 1368, 1297, 1265, 1123, 973, 927, 890, 728; **HRMS** (ESI) Calcd for $C_{25}H_{23}NO_3H$ $(M+H)^+$ 386.1751, found: 386.1751.

2-(4-butylphenyl)-9,10-dimethyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one **(3ga)**



Yellow solid, m.p. = 122-124 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), R_f = 0.25 (PE/EA = 15/1), 31 mg, yield = 75%; **^{1}HNMR** (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 7.7 Hz, 2H), 7.11 – 7.05 (m, 2H), 6.70 (s, 1H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.39 (d, *J* = 7.8 Hz, 1H), 5.24 (s, 1H), 4.13 (d, *J* = 8.5 Hz, 1H), 3.87 (d, *J* = 8.5 Hz, 1H), 2.89 (s, 3H), 2.60 – 2.54 (m, 2H), 1.57 (s, 3H), 1.55 – 1.50 (m, 2H), 1.32 – 1.26 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H); **^{13}CNMR** (125 MHz, $CDCl_3$) δ 185.4, 160.7, 153.9, 147.2, 145.6, 144.1, 129.2, 129.1, 127.5, 126.4, 125.7, 124.0, 117.9, 107.2, 102.3, 93.5, 78.9, 74.6, 56.2, 37.1, 35.7, 33.5, 29.8, 22.5, 15.1, 14.0; **IR** (KBr, cm^{-1}) 3054, 2929, 2362, 1675, 1605, 1481, 1441, 1368,1297, 1265, 1123, 973, 927, 890, 834; **HRMS** (ESI) Calcd for $C_{27}H_{27}NO_3H$ $(M+H)^+$414.2064, found: 414.2061.

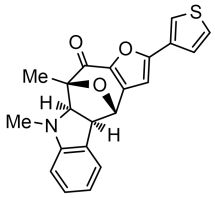
9,10-dimethyl-2-(naphthalen-1-yl)-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one **(3ha)**



White solid, m.p. = 166-168 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.2 (PE/EA = 10/1) (exo:endo=1:1) 40 mg, yield = 98%; **^{1}HNMR** (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.4 Hz, 1H), 7.82 (dd, *J* = 11.0, 8.1 Hz, 2H), 7.77 (d, *J* = 7.2 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.44 (dd, *J* = 8.7, 4.3 Hz, 3H), 7.39 –

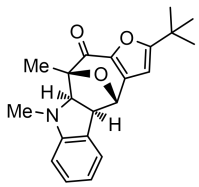
7.29 (m, 3H), 7.12 (d, *J* = 7.3 Hz, 1H), 7.07 (t, *J* = 7.7 Hz, 1H), 7.02 (d, *J* = 7.3 Hz, 1H), 6.86 (t, *J* = 7.7 Hz, 1H), 6.81 (s, 1H), 6.65 (d, *J* = 7.4 Hz, 1H), 6.55 (t, *J* = 7.4 Hz, 1H), 6.39 (d, *J* = 7.9 Hz, 1H), 6.19 (s, 1H), 6.07 (d, *J* = 8.0 Hz, 1H), 5.48 (d, *J* = 7.0 Hz, 1H), 5.31 (s, 1H), 4.45 (dd, *J* = 10.4, 7.0 Hz, 1H), 4.20 (d, *J* = 8.5 Hz, 1H), 4.10 (d, *J* = 10.4 Hz, 1H), 3.91 (d, *J* = 8.5 Hz, 1H), 2.89 (s, 3H), 2.62 (s, 3H), 1.71 (s, 3H), 1.59 (s, 3H); **^{13}CNMR** (125 MHz, $CDCl_3$) δ 185.7, 184.5, 160.0, 157.3, 153.8, 153.2, 146.6, 146.3, 144.6, 141.6, 134.0, 133.7, 130.9, 130.5, 130.3, 130.1, 129.2, 128.9, 128.5, 128.0, 127.6, 127.5, 127.4, 127.0, 127.0, 126.5, 126.48, 126.2, 125.3, 125.2, 125.1, 125.0, 124.3, 124.0, 117.9, 117.2, 109.0, 107.6, 107.2, 93.6, 91.0, 79.6, 78.9, 77.9, 74.5, 56.1, 53.6, 37.1, 35.6, 19.5, 15.1; **IR**(KBr, cm^{-1}) 3428, 2980, 2364, 1683, 1521, 1494, 1285, 1163, 1065, 982, 896, 736; **HRMS** (ESI) Calcd for $C_{27}H_{21}O_3NNa$ $(M+Na)^+$ 430.1414, found: 430.1411.

9,10-dimethyl-2-(thiophen-3-yl)-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one **(3ia)**



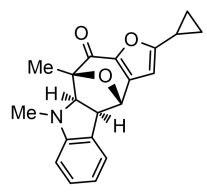
Green solid, m.p. = 138-139 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), R_f = 0.2 (PE/EA = 15/1), 26 mg, yield = 72%; **^{1}HNMR** (500 MHz, $CDCl_3$) δ 7.85 – 7.80 (m, 1H), 7.44 (d, *J* = 4.5 Hz, 1H), 7.40 (dd, *J* = 5.1, 3.0 Hz, 1H), 7.16 (t, *J* = 8.1 Hz, 2H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.67 (s, 1H), 6.48 (d, *J* = 7.8 Hz, 1H), 5.32 (s, 1H), 4.21 (d, *J* = 8.4 Hz, 1H), 3.95 (d, *J* = 8.5 Hz, 1H), 2.98 (s, 3H), 1.65 (s, 3H); **^{13}CNMR** (125MHz, $CDCl_3$) δ 185.5, 156.7, 153.8, 147.1, 143.7, 130.7, 129.2, 127.44, 127.3, 125.2, 124.2, 124.0, 117.9, 107.2, 102.7, 93.5, 78.8, 74.5, 56.1, 37.1, 15.1; **IR** (KBr, cm^{-1}) 3108, 2935, 1673, 1603, 1552, 1495, 1364, 1297, 1020, 975, 858, 789, 739, 702; **HRMS** (ESI) Calcd for $C_{21}H_{17}NO_3SH$ $(M+H)^+$ 364.1002, found: 364.1001.

2-(tert-butyl)-9,10-dimethyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one **(3ja)**



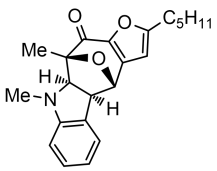
White solid, m.p. = 156-157 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), R_f = 0.2 (PE/EA = 15/1), 24 mg, yield = 72%; **^{1}HNMR** (500 MHz, $CDCl_3$) δ 7.14 (dt, *J* = 7.4, 4.0 Hz, 2H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.47 (d, *J* = 8.2 Hz, 1H), 6.24 (s, 1H), 5.24 (s, 1H), 4.17 (d, *J* = 8.5 Hz, 1H), 3.93 (d, *J* = 8.5 Hz, 1H), 2.97 (s, 3H), 1.62 (s, 3H), 1.35 (s, 9H); **^{13}CNMR** (125 MHz, $CDCl_3$) δ 185.4, 172.4, 153.9, 146.6, 143.8, 129.1, 127.6, 124.0, 117.8, 107.2, 101.6, 93.4, 78.9, 74.5, 56.0, 37.1, 33.7, 28.9, 15.1; **IR** (KBr, cm^{-1}) 3054, 2930, 2364, 1677, 1570, 1461, 1382, 1264, 1160, 975, 882, 782, 704; **HRMS** (ESI) Calcd for $C_{21}H_{23}NO_3H$ $(M+H)^+$ 338.1751, found: 338.1748.

2-cyclopropyl-9,10-dimethyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one **(3ka)**



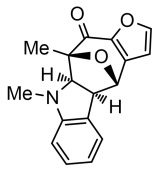
White solid, m.p.= 153-155 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), R_f = 0.2 (PE/EA = 15/1), 20 mg, yield = 61%; **^{1}HNMR** (500 MHz, $CDCl_3$) δ 7.18 – 7.10 (m, 2H), 6.69 (t, *J* = 7.4 Hz, 1H), 6.46 (d, *J* = 8.1 Hz, 1H), 6.20 (s, 1H), 5.21 (s, 1H), 4.14 (d, *J* = 8.5 Hz, 1H), 3.89 (d, *J* = 8.5 Hz, 1H), 2.95 (s, 3H), 2.06 – 1.97 (m, 1H), 1.60 (s, 3H), 1.13 – 1.00 (m, 4H); **^{13}CNMR** (125 MHz, $CDCl_3$) δ 184.7, 166.3, 153.9, 147.2, 143.1, 129.1, 127.6, 124.0, 117.8, 107.1, 102.5, 93.3, 78.8, 74.6, 56.1, 37.1, 15.0, 10.0, 9.0; **IR** (KBr, cm^{-1}) 2983, 2935, 1674, 1529, 1495, 1368, 1298, 1158, 978, 958, 832, 742; **HRMS** (ESI) Calcd for $C_{20}H_{19}NO_3H$ $(M+H)^+$ 322.1438, found: 322.1425.

9,10-dimethyl-2-pentyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one **(3la)**



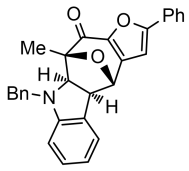
White solid, m.p. = 100-101 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), R_f = 0.2 (PE/EA = 15/1), 27 mg, yield = 78%; **^{1}HNMR** (500 MHz, $CDCl_3$) δ 7.14 (dt, *J* = 7.3, 3.7 Hz, 2H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.46 (d, *J* = 8.1 Hz, 1H), 6.23 (s, 1H), 5.24 (s, 1H), 4.15 (d, *J* = 8.5 Hz, 1H), 3.91 (d, *J* = 8.5 Hz, 1H), 2.96 (s, 3H), 2.72 (t, *J* = 7.7 Hz, 2H), 1.76 – 1.68 (m, 2H), 1.62 (s, 3H), 1.35 (dt, *J* = 7.0, 3.6 Hz, 4H), 0.93 – 0.88 (m, 3H); **^{13}CNMR** (125 MHz, $CDCl_3$) δ 185.2, 165.1, 153.8, 146.6, 143.8, 129.0, 127.4, 123.9, 117.7, 107.0, 104.0, 93.2, 78.7, 74.4, 56.0, 37.0, 31.3, 28.5, 27.3, 22.3, 14.9, 13.9; **IR** (KBr, cm^{-1}) 3054, 2931, 2866, 1677, 1606, 1520, 1495, 1336,1265, 1120, 1026, 981, 739, 704; **HRMS** (ESI) Calcd for $C_{22}H_{25}NO_3H$ $(M+H)^+$ 352.1907, found: 352.1902.

9,10-dimethyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one **(3ma)**



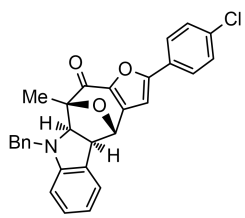
White solid, m.p. = 174-175 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), R_f = 0.2 (PE/EA = 15/1), 19 mg, yield = 67%; **^{1}HNMR** (500 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.16 (t, *J* = 8.2 Hz, 2H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.61 (s, 1H), 6.48 (d, *J* = 7.8 Hz, 1H), 5.32 (s, 1H), 4.18 (d, *J* = 8.5 Hz, 1H), 3.92 (d, *J* = 8.5 Hz, 1H), 2.97 (s, 3H), 1.63 (s, 3H); **^{13}CNMR** (125 MHz, $CDCl_3$) δ 186.3, 153.8, 148.8, 145.3, 145.0, 129.2, 127.4, 124.0, 117.9, 108.2, 107.2, 93.5, 78.9, 74.3, 56.1, 37.1, 15.0; **IR** (KBr, cm^{-1}) 3056, 2993, 2890, 2362, 1717, 1625, 1525, 1442, 1335, 1220, 1119, 1050, 970, 792; **HRMS** (ESI) Calcd for $C_{17}H_{15}NO_3Na(M+Na)^+$ 304.0944, found: 304.0950.

9-benzyl-10-methyl-2-phenyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one **(3ak)**



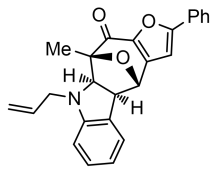
Yellow solid, m.p. = 190-191 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), R_f = 0.2 (PE/EA = 15/1), 39 mg, yield = 91%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.4 Hz, 1H), 7.92 (dd, *J* = 11.3, 8.1 Hz, 2H), 7.84 (d, *J* = 7.2 Hz, 1H), 7.61 – 7.51 (m, 3H), 7.25 – 7.19 (m, 5H), 7.14 (dd, *J* = 23.3, 7.3 Hz, 3H), 6.90 (s, 1H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.58 (d, *J* = 7.9 Hz, 1H), 5.43 (s, 1H), 4.80 (d, *J* = 16.4 Hz, 1H), 4.38 – 4.29 (m, 2H), 4.19 (d, *J* = 8.5 Hz, 1H), 1.70 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 185.7, 160.0, 153.1, 146.2, 144.7, 137.5, 134.0, 130.9, 130.3, 129.2, 129.0, 128.8, 128.0, 127.7, 127.6, 127.4, 126.6, 126.55, 125.3, 125.1, 124.2, 118.3, 108.3, 107.2, 93.6, 78.7, 71.2, 56.0, 52.6, 15.3; **IR** (KBr, cm^{-1}) 3649, 3054, 2829, 1677, 1515, 1454, 1365, 1228, 1110, 1034, 970, 825, 704; **HRMS**(ESI)Calcd for $C_{29}H_{23}NO_3Na(M+Na)^+$ 456.1570,found: 456.1573.

9-benzyl-2-(4-chlorophenyl)-10-methyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one **(3dk)**



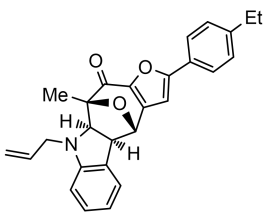
Yellow solid, m.p. = 117-118 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), R_f = 0.2 (PE/EA = 15/1), 34 mg, yield = 72%; **^{1}HNMR** (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.19 – 7.11 (m, 4H), 7.07 (d, *J* = 7.6 Hz, 2H), 7.03 (d, *J* = 7.7 Hz, 1H), 6.72 (s, 1H), 6.66 (t, *J* = 7.4 Hz, 1H), 6.49 (d, *J* = 7.9 Hz, 1H), 5.27 (s, 1H), 4.70 (d, *J* = 16.3 Hz, 1H), 4.24 (d, *J* = 16.4 Hz, 1H), 4.13 (d, *J* = 8.5 Hz, 1H), 4.03 (d, *J* = 8.5 Hz, 1H), 1.58 (s, 3H); **^{13}CNMR** (125 MHz, $CDCl_3$) δ 185.7, 158.9, 153.1, 146.6, 144.5, 137.4, 136.2, 129.5, 129.2, 128.8, 127.7, 127.6, 127.4, 127.4, 126.8, 124.2, 118.3, 108.3, 103.3, 93.5, 78.6, 71.2, 55.9, 52.7, 15.2; **IR** (KBr, cm^{-1}) 3656, 2980, 2362, 1675,1515, 1442, 1368, 1217, 1112, 1098, 927, 856, 742, 702; **HRMS** (ESI) Calcd for $C_{29}H_{22}NO_3ClH$ $(M+H)^+$ 468.1361, found: 468.1363.

***9-allyl-10-methyl-2-phenyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one* (3al)**



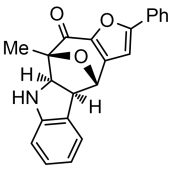
White solid, m.p. = 148-150 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), R_f = 0.2 (PE/EA = 15/1), 23 mg, yield = 60%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 1.7 Hz, 1H), 7.82 (d, *J* = 1.3 Hz, 1H), 7.49 – 7.40 (m, 3H), 7.19 (d, *J* = 7.3 Hz, 1H), 7.14 (t, *J* = 7.7 Hz, 1H), 6.84 (s, 1H), 6.79 – 6.72 (m, 1H), 6.57 (d, *J* = 7.9 Hz, 1H), 5.83-5.7` (m, 1H), 5.35 (s, 1H), 5.18 (dd, J = 7.9, 1.4 Hz, 1H), 5.15 (t, *J* = 1.4 Hz, 1H), 4.23 (d, *J* = 8.5 Hz, 1H), 4.16 – 4.05 (m, 2H), 3.74 (dd, *J* = 16.4, 6.6 Hz, 1H), 1.65 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 185.8, 160.2, 152.9, 146.9, 144.4, 132.9, 130.2, 129.2, 129.0, 128.96, 128.1, 125.7, 124.1, 118.5, 118.2, 108.7, 102.9, 93.4, 78.8, 71.6, 56.1, 52.3, 15.3; **IR** (KBr, cm^{-1}) 3768, 3649, 1886, 1770, 1676, 1516, 1425, 1396, 1236, 1115, 1025, 971, 827; **HRMS** (ESI) Calcd for $C_{25}H_{21}NO_3Na$ $(M+Na)^+$ 406.1414, found: 406.1409.

***9-allyl-2-(4-ethylphenyl)-10-methyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one* (3fl)**



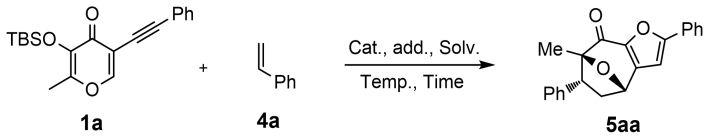
Yellow solid, m.p. = 151-152 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), R_f = 0.2 (PE/EA = 15/1), 28 mg, yield = 68%; **^{1}HNMR** (400 MHz, $CDCl_3$) 7.67 (d, *J* = 7.9 Hz, 2H), 7.26 – 7.16 (m, 2H), 7.10 (d, *J* = 7.3 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.70 (s, 1H), 6.67 (d, *J* = 7.4 Hz, 1H), 6.49 (d, *J* = 7.9 Hz, 1H), 5.69 (td, *J* = 10.7, 5.3 Hz, 1H), 5.25 (s, 1H), 5.15 – 5.02 (m, 2H), 4.14 (d, *J* = 8.5 Hz, 1H), 4.02 (dd, *J* = 19.2, 6.7 Hz, 2H), 3.66 (dd, *J* = 16.4, 6.6 Hz, 1H), 2.61 (q, *J* = 7.7 Hz, 2H), 1.57 (s, 3H), 1.19 (t, *J* = 7.6 Hz, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 185.6, 160.6, 152.9, 147.1, 146.8, 144.1, 132.9, 129.0, 128.7, 128.2, 126.4, 125.8, 124.1, 118.4, 118.2, 108.6, 102.3, 93.3, 78.8, 71.6, 56.1, 52.3, 28.9, 15.4, 15.3; **IR** (KBr, cm^{-1}) 3542, 2980, 2832, 1617, 1549, 1444, 1328, 1259, 1198, 1009, 928, 843, 765; **HRMS** (ESI) Calcd for $C_{24}H_{21}NO_3H$ $(M+H)^+$412.1907, found: 412.1901.

***10-methyl-2-phenyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one* (3am)**



Green solid, m.p. = 178-179 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.2 (PE/EA = 10/1), 24 mg, yield =70%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.1 Hz, 2H), 7.51 – 7.42 (m, 3H), 7.25 (d, *J* = 7.3 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.87 (s, 1H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 1H), 5.36 (s, 1H), 4.31 (d, *J* = 8.2 Hz, 1H), 4.24 (d, *J* = 8.2 Hz, 1H), 1.64 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 185.8, 160.3, 151.5, 146.7, 144.5, 130.2, 129.1, 129.0, 128.9, 127.2, 125.7, 124.2, 119.0, 109.0, 103.0, 92.6, 79.1, 66.2, 56.6, 15.1; **IR** (KBr, cm^{-1}) 3687, 3421, 2927, 1670, 1528, 1466, 1368, 1257, 1106, 1022, 973, 828, 754; **HRMS** (ESI) Calcd for $C_{22}H_{17}NO_3Na$ $(M+Na)^+$366.1101, found: 366.1103.

1.4 Optimization of reaction conditions[a]



1a 4a 5aa

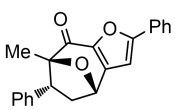
Entry	Cat. (mol %)	Solv. (mL)	Temp. (°C)	Time (h)	Conv. (%)	Yield (%) (endo:exo)[b]
1	$PPh_3AuCl/AgBF_4$ (5)	DCE	rt	12	85	65 (10:1)
2	$IPrAuCl/AgBF_4$ (5)	DCE	rt	12	80	61 (10:1)
3	$PdCl_2(CN)_2$ (5)	DCE	80	12	78	65
4	$C_2H_3AgO_2$ (5)	DCE	80	12	100	Messy
5	$In(OTf)_3$ (20)	DCE	rt	12	100	40
6	$Bi(OTf)_3$ (20)	DCE	rt	12	100	20
7	$Sn(OTf)_2$ (20)	DCE	rt	12	100	28
8	$Cu(OTf)_2$ (20)	DCE	rt	12	100	36
9	**ZnI_2 (20)**	**DCE**	**rt**	**12**	**100**	**99 (>15:1)**
10	$ZnBr_2$ (20)	DCE	rt	12	100	Trace
11	CuCl (20)	DCE	rt	12	100	Trace

[a]Reaction conditions: **1a** (0.1 mmol), **4a** (0.15 mmol) and catalyst in 2 mL DCE were stirred for 12 h. [b]isolated yield.

1.5 General procedure for the synthesis of 5

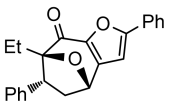
To a 25 mL Schlenk tube with a magnetic bar under nitrogen atmosphere were added substrates **1** (0.1 mmol) and olefin (1.5eq) in 1,2-dichloroethane (DCE, 2 mL), then ZnI_2 (20 mmol%) was added. The resulting mixture was stirred at room temperature for 12 h. After the reaction was finished, the mixture was filtered by short silica. the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as elute to afford the product **5** .

7-methyl-2,6-diphenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one **(5aa)**



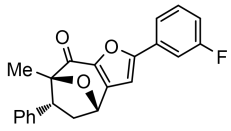
Yellow solid, m.p. = 179-181 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.3 (PE/EA = 1/1), 32 mg, yield = 99%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.5 Hz, 2H), 7.50 – 7.37 (m, 3H), 7.19 (d, *J* = 5.2 Hz, 3H), 6.82 (d, *J* = 5.3 Hz, 3H), 5.44 (d, *J* = 7.1 Hz, 1H), 3.57 (dd, *J* = 11.0, 4.5 Hz, 1H), 3.04 (td, *J* = 11.9, 7.4 Hz, 1H), 2.22 (dd, *J* = 12.7, 4.6 Hz, 1H), 1.68 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 184.3, 159.7, 146.6, 146.2, 137.4, 129.9, 129.1 129.08, 128.7, 127.9, 127.4, 125.6, 102.6, 91.4, 73.2, 55.0, 38.9, 19.6; **IR** (KBr, cm^{-1}) 3743, 3678, 2981, 1832, 1741, 1690, 1530, 1453, 1389, 1258, 1112, 979, 766, 695; **HRMS** (ESI) Calcd for $C_{22}H_{18}O_3Na$ $(M+Na)^+$ 353.1148, found: 353.1147.

7-ethyl-2,6-diphenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one **(5ba)**



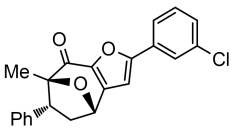
Yellow solid, m.p. = 155-156 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.25 (PE/EA = 10/1), 30 mg, yield = 86%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.17 (dd, *J* = 5.0, 2.1 Hz, 3H), 6.74 (dd, *J* = 6.4, 2.5 Hz, 2H), 6.20 (s, 1H), 5.34 (d, *J* = 7.0 Hz, 1H), 3.52 (dd, *J* = 11.0, 4.6 Hz, 1H), 2.98 (td, *J* = 11.9, 11.3, 7.1 Hz, 1H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.14 (dd, *J* = 12.7, 4.6 Hz, 1H), 1.73 (d, *J* = 7.0 Hz, 2H), 1.63 (s, 3H), 1.35 (dt, *J* = 7.2, 3.9 Hz, 4H), 0.92 (t, *J* = 6.8 Hz, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 183.8, 159.5, 146.8, 146.4, 137.5, 129.9, 129.1, 129.1, 128.6, 128.0, 127.3, 125.6, 102.6, 94.4, 73.0, 51.0, 38.7, 26.3, 8.5; **IR** (KBr, cm^{-1}) 3657, 2972, 1672, 1605, 1525, 1494, 1297, 1032, 886, 738, 690; **HRMS** (ESI) Calcd for $C_{23}H_{20}O_3Na$ $(M+Na)^+$ 367.1305, found: 367.1299.

2-(3-fluorophenyl)-7-methyl-6-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one **(5ca)**



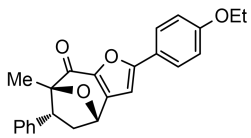
Yellow solid, m.p. = 188 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.2 (PE/EA = 10/1), 27 mg, yield = 78%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 9.5 Hz, 1H), 7.42 (q, *J* = 7.9 Hz, 1H), 7.18 (s, 3H), 7.11 (t, *J* = 8.2 Hz, 1H), 6.81 (d, *J* = 9.0 Hz, 3H), 5.44 (d, *J* = 7.0 Hz, 1H), 3.57 (dd, *J* = 11.0, 4.6 Hz, 1H), 3.05 (td, *J* = 12.0, 7.3 Hz, 1H), 2.22 (dd, *J* = 12.7, 4.5 Hz, 1H), 1.67 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 184.5, 163.2 (d, *J* = 247.0 Hz), 158.2, 146.5, 146.4, 137.3, 131.2 (d, *J* = 8.3 Hz), 130.8 (d, *J* = 8.4 Hz), 128.8, 127.8, 127.5, 121.3 (d, *J* = 3.0 Hz), 116.8 (d, *J* = 21.3 Hz), 112.5(d, *J* = 23.8 Hz), 103.5, 91.5, 73.2, 52.9, 38.8, 19.6; **^{19}FNMR** (376 MHz, CDCl3) δ -111.8; **IR** (KBr, cm^{-1}) 3743, 3649, 3620, 2981, 2362, 1917, 1679, 1516, 1397, 1202, 1113, 980, 821, 787; **HRMS** (ESI) Calcd for $C_{22}H_{17}FO_3Na$ $(M+Na)^+$ 371.1054, found: 371.1056.

2-(3-chlorophenyl)-7-methyl-6-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one **(5na)**



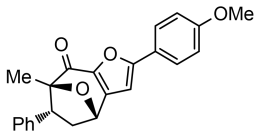
Yellow solid, m.p. = 154-155 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.3 (PE/EA = 10/1), 26 mg, yield = 72%; **^{1}HNMR** (500 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.71 (d, *J* = 6.3 Hz, 1H), 7.38 (d, *J* = 5.7 Hz, 2H), 7.18 (d, *J* = 6.1 Hz, 3H), 6.83 (s, 1H), 6.80 (d, *J* = 5.6 Hz, 2H), 5.44 (d, *J* = 7.0 Hz, 1H), 3.57 (dd, *J* = 11.0, 4.6 Hz, 1H), 3.05 (td, *J* = 12.0, 7.2 Hz, 1H), 2.22 (dd, *J* = 12.8, 4.7 Hz, 1H), 1.67 (s, 3H); **^{13}CNMR** (125 MHz, $CDCl_3$) δ 184.5, 158.0, 146.6, 146.3, 137.2, 135.3, 130.8, 130.4, 129.8, 128.8, 127.8, 127.5, 126.0, 123.6, 103.5, 91.4, 73.2, 52.9, 38.8, 19.6; **IR** (KBr, cm^{-1}) 3768, 3649, 1886, 1770, 1676, 1516, 1425, 1396, 1236, 1115, 1025, 971, 827; **HRMS** (ESI) Calcd for $C_{22}H_{17}ClO_3Na$ $(M+Na)^+$ 387.0758, found: 387.0750.

2-(4-ethoxyphenyl)-7-methyl-6-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one **(5qa)**



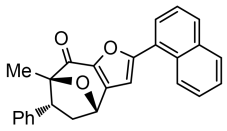
White solid, m.p.=185-186 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.15 (PE/EA = 10/1) , 33 mg, yield = 87%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.8 Hz, 2H), 7.21 – 7.15 (m, 3H), 6.96 (d, *J* = 8.9 Hz, 2H), 6.82 (dd, *J* = 7.3, 2.0 Hz, 2H), 6.66 (s, 1H), 5.41 (d, *J* = 7.0 Hz, 1H), 4.09 (q, *J* = 7.0 Hz, 2H), 3.55 (dd, *J* = 11.1, 4.8 Hz, 1H), 3.03 (ddd, *J* = 12.6, 11.2, 7.2 Hz, 1H), 2.20 (dd, *J* = 12.7, 4.8 Hz, 1H), 1.66 (s, 3H), 1.45 (t, *J* = 7.0 Hz, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 183.9, 160.6, 160.2, 147.0, 145.7, 137.5, 128.7, 127.9, 127.4, 127.3, 121.8, 115.1, 101.0, 91.3, 73.3, 63.8, 53.1, 39.0, 19.7, 14.9; **IR** (KBr, cm^{-1}) 3649, 3566, 2980, 1868, 1793, 1618, 1539, 1478, 1368, 1253, 1112, 1036, 978, 830, 746; **HRMS** (ESI) Calcd for $C_{24}H_{22}O_4Na$ $(M+Na)^+$ 397.1410, found: 397.1414.

2-(4-methoxyphenyl)-7-methyl-6-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one **(5ea)**



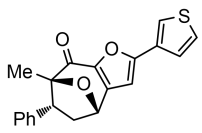
Yellow solid, m.p. = 110-112°C, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.2 (PE/EA = 10/1), 31 mg, yield = 86%; **^{1}HNMR** (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 6.6 Hz, 3H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 7.6 Hz, 2H), 6.68 (s, 1H), 5.42 (d, *J* = 7.1 Hz, 1H), 3.86 (s, 3H), 3.55 (dd, *J* = 11.1, 4.8 Hz, 1H), 3.03 (td, *J* = 11.9, 7.1 Hz, 1H), 2.20 (dd, *J* = 12.7, 4.7 Hz, 1H), 1.67 (s, 3H); **^{13}CNMR** (125 MHz, $CDCl_3$) δ 183.9, 161.1, 160.0, 147.0, 145.6, 137.4, 128.7, 127.9, 127.4, 127.3, 121.9, 114.5, 101.1, 91.3, 73.2, 55.5, 53.0, 38.9, 19.6; **IR** (KBr, cm^{-1}) 3028, 2980, 1683, 1521, 1474, 1352, 1245, 1163, 1024, 982, 859, 736; **HRMS** (ESI) Calcd for $C_{23}H_{20}O_4Na$ $(M+Na)^+$ 383.1254, found: 383.1247.

7-methyl-2-(naphthalen-1-yl)-6-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one **(5ha)**



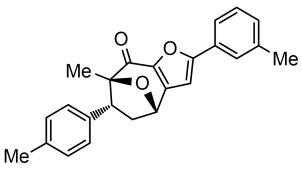
Yellow solid, m.p. = 150-152 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.2 (PE/EA = 10/1), 33 mg, yield = 86%; **^{1}HNMR** (500 MHz, $CDCl_3$) δ 8.43 (d, *J* = 8.4 Hz, 1H), 7.94 (t, *J* = 9.0 Hz, 2H), 7.89 (d, *J* = 6.9 Hz, 1H), 7.63 – 7.52 (m, 3H), 7.22 (q, *J* = 6.2 Hz, 3H), 6.89 (s, 1H), 6.87 (d, *J* = 6.7 Hz, 2H), 5.52 (d, *J* = 7.0 Hz, 1H), 3.62 (dd, *J* = 11.0, 4.5 Hz, 1H), 3.12 – 3.05 (m, 1H), 2.31 (dd, *J* = 12.8, 4.5 Hz, 1H), 1.73 (s, 3H); **^{13}CNMR** (125 MHz, $CDCl_3$) δ 184.4, 159.7, 146.6, 146.0, 137.5, 134.0, 130.7, 130.3, 128.9, 128.7, 127.9, 127.8, 127.6, 127.5, 126.8, 126.5, 125.3, 125.1, 106.8, 91.4, 73.4, 52.9, 38.9, 19.6; **IR** (KBr, cm^{-1}) 2963, 2930, 2361, 1686, 1528, 1437, 1370, 1292, 1183, 1073, 968, 817, 727; **HRMS** (ESI) Calcd for $C_{26}H_{20}O_3Na$ $(M+Na)^+$ 403.1305, found: 403.1303.

7-methyl-6-phenyl-2-(thiophen-3-yl)-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one **(5ia)**



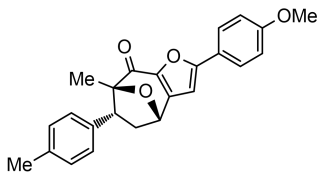
Yellow solid, m.p. = 195 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.3 (PE/EA = 10/1), 26 mg, yield = 78%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 2.9, 1.2 Hz, 1H), 7.46 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.41 (dd, *J* = 5.1, 2.9 Hz, 1H), 7.22 – 7.15 (m, 3H), 6.82 (d, *J* = 2.4 Hz, 1H), 6.81 (d, *J* = 1.6 Hz, 1H), 6.63 (s, 1H), 5.42 (d, *J* = 7.0 Hz, 1H), 3.56 (dd, *J* = 11.0, 4.8 Hz, 1H), 3.03 (m, 1H), 2.21 (dd, *J* = 12.7, 4.8 Hz, 1H), 1.66 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 184.2, 156.3, 146.7, 145.6, 137.4, 131.0, 128.7, 127.9, 127.5, 127.2, 125.3, 124.0, 102.4, 91.4, 73.2, 53.0, 38.9, 19.6; **IR** (KBr, cm^{-1}) 3768, 3620, 2979, 1740, 1679, 1531, 1429, 1369, 1264, 1110, 955, 887, 746, 699; **HRMS** (ESI) Calcd for $C_{20}H_{16}O_3SNa$ $(M+Na)^+$ 359.0712, found: 359.0713.

7-methyl-2-(m-tolyl)-6-(p-tolyl)-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one **(5ob)**



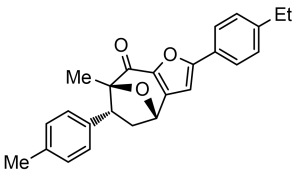
Yellow solid, m.p. = 152-154 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.2 (PE/EA = 10/1), 31 mg, yield = 87%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.9 Hz, 2H), 6.68 (s, 1H), 6.60 (d, *J* = 7.9 Hz, 2H), 5.31 (d, *J* = 7.1 Hz, 1H), 3.43 (dd, *J* = 11.1, 4.6 Hz, 1H), 2.91 (td, *J* = 11.9, 7.3 Hz, 1H), 2.31 (s, 3H), 2.14 (s, 3H), 2.08 (dd, *J* = 12.7, 4.6 Hz, 1H), 1.57 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 184.4, 159.8, 146.6, 146.1, 138.9, 137.0, 134.3, 130.7, 129.4, 129.0, 128.9, 127.6, 126.2, 122.8, 102.5, 91.3, 73.2, 52.6, 38.8, 21.4, 21.0, 19.6; **IR** (KBr, cm^{-1}) 3756, 2983, 1681, 1566, 1482, 1387, 1253, 1162, 925, 892,784; **HRMS** (ESI) Calcd for $C_{24}H_{22}O_3Na$ $(M+Na)^+$ 381.1461, found: 381.1463.

7-methyl-2,6-di-p-tolyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one **(5eb)**



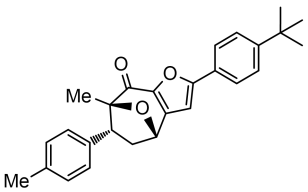
White solid, m.p. = 146-148 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.3 (PE/EA = 10/1), 33 mg, yield = 88%; **^{1}HNMR** (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 5.6 Hz, 2H), 6.74 (s, 1H), 6.71 (d, *J* = 2.5 Hz, 4H), 5.39 (d, *J* = 7.0 Hz, 1H), 3.70 (s, 3H), 3.50 (dd, *J* = 11.1, 4.7 Hz, 1H), 3.06 – 2.96 (m, 1H), 2.39 (s, 3H), 2.14 (dd, *J* = 12.7, 4.7 Hz, 1H), 1.64 (s, 3H); **^{13}CNMR** (125 MHz, $CDCl_3$) δ 184.4, 160.0, 158.8, 146.8, 145.9, 140.3, 129.8, 129.3, 128.8, 126.4, 125.6, 114.1, 101.9, 91.1, 73.1, 55.2, 52.2, 39.0, 21.6, 19.6; **IR** (KBr, cm^{-1}) 3078, 2394, 1625, 1559, 1452, 1375, 1254, 1182, 1059, 970,835; **HRMS** (ESI) Calcd for $C_{24}H_{22}O_4H$ $(M+H)^+$ 397.1610, found: 397.1613.

2-(4-ethylphenyl)-7-methyl-6-(p-tolyl)-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one **(5fb)**



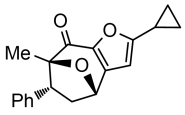
White solid, m.p. = 167 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.3 (PE/EA = 10/1), 33 mg, yield = 89%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 7.8 Hz, 2H), 6.76 (s, 1H), 6.71 (d, *J* = 7.9 Hz, 2H), 5.42 (d, *J* = 7.0 Hz, 1H), 3.53 (dd, *J* = 11.0, 4.6 Hz, 1H), 3.02 (td, *J* = 11.9, 7.3 Hz, 1H), 2.71 (q, *J* = 7.6 Hz, 2H), 2.25 (s, 3H), 2.19 (dd, *J* = 12.7, 4.7 Hz, 1H), 1.67 (s, 3H), 1.29 (d, *J* = 7.6 Hz, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 184.3, 160.0, 146.7, 146.6, 145.9, 137.0, 134.3, 129.4, 128.6, 127.7, 126.6, 125.7, 102.0, 91.3, 73.2, 52.6, 38.9, 28.9, 21.1, 19.6, 15.5; **IR** (KBr, cm^{-1}) 3743, 3620, 2930, 2362, 1741, 1680, 1515, 1480, 1368, 1290, 1186, 1114, 1024, 979, 871, 675; **HRMS** (ESI) Calcd for $C_{25}H_{24}O_3Na$ $(M+Na)^+$ 395.1618, found: 395.1620.

2-(4-(tert-butyl)phenyl)-7-methyl-6-(p-tolyl)-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one **(5pb)**



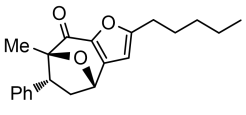
White solid, m.p. = 150 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.2 (PE/EA = 10/1), 32 mg, yield = 80%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 6.99 (d, *J* = 7.6 Hz, 2H), 6.78 (s, 1H), 6.70 (d, *J* = 7.7 Hz, 2H), 5.42 (d, *J* = 7.0 Hz, 1H), 3.53 (dd, *J* = 11.0, 4.4 Hz, 1H), 3.02 (td, *J* = 11.8, 7.3 Hz, 1H), 2.25 (s, 3H), 2.19 (dd, *J* = 12.7, 4.5 Hz, 1H), 1.67 (s, 3H), 1.37 (s, 9H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 184.3, 159.9, 153.4, 146.7, 146.0, 137.0, 134.3, 129.4, 127.7, 126.4, 126.0, 125.4, 102.1, 91.3, 73.2, 52.6, 38.9, 35.0, 31.3, 21.1, 19.6; **IR** (KBr, cm^{-1}) 3754, 2938, 1606, 1496, 1368, 1296, 1119, 922, 836, 701; **HRMS** (ESI) Calcd for $C_{27}H_{28}O_3Na$ $(M+Na)^+$ 423.1931, found: 423.1935.

2-cyclopropyl-7-methyl-6-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one **(5ka)**



Yellow oil, purified by chromatography (petroleum/ethyl acetate = 15:1), R_f = 0.3 (PE/EA = 15/1), 22 mg, yield =75%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.24 – 7.09 (m, 3H), 6.82 – 6.71 (m, 2H), 6.15 (s, 1H), 5.31 (d, *J* = 7.0 Hz, 1H), 3.50 (dd, *J* = 11.0, 4.8 Hz, 1H), 2.97 (td, *J* = 11.9, 11.2, 7.1 Hz, 1H), 2.12 (dd, *J* = 12.6, 4.8 Hz, 1H), 2.08 – 1.98 (m, 1H), 1.62 (s, 3H), 1.10 – 0.99 (m, 4H); **^{13}CNMR** (100MHz, $CDCl_3$) δ 183.5, 165.7, 146.6, 145.1, 137.6, 128.6, 127.9, 127.4, 102.0, 91.1, 73.2, 53.0, 38.9, 19.6, 10.0, 9.0, 8.8; **IR** (KBr, cm^{-1}) 3678, 3620, 1835, 1770, 1740, 1646, 1515, 1465, 1396, 1284, 1019, 787; **HRMS** (ESI) Calcd for $C_{19}H_{18}O_3H$ $(M+H)^+$ 295.1329, found: 295.13232.

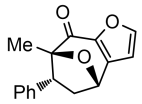
7-methyl-2-pentyl-6-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one**(5la)**



Yellow oil, purified by chromatography (petroleum/ethyl acetate = 15:1), R_f = 0.3 (PE/EA = 15/1), 26 mg, yield = 85%; **^{1}HNMR** (500 MHz, $CDCl_3$) δ 7.17 (dd, *J* = 5.0, 2.1 Hz, 3H), 6.74 (dd, *J* = 6.4, 2.5 Hz, 2H), 6.20 (s, 1H), 5.34 (d, *J* = 7.0 Hz, 1H), 3.52

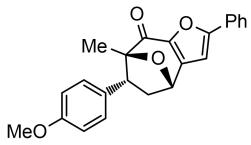
(dd, *J* = 11.0, 4.6 Hz, 1H), 2.98 (td, *J* = 11.9, 11.3, 7.1 Hz, 1H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.14 (dd, *J* = 12.7, 4.6 Hz, 1H), 1.73 (d, *J* = 7.0 Hz, 2H), 1.63 (s, 3H), 1.35 (dt, *J* = 7.2, 3.9 Hz, 4H), 0.92 (t, *J* = 6.8 Hz, 3H); **^{13}CNMR** (125 MHz, $CDCl_3$) δ 184.0, 164.6, 146.1, 145.8, 137.6, 128.6, 127.8, 127.4, 103.8, 91.1, 73.3, 52.9, 38.9, 31.3, 28.6, 27.5, 22.4, 19.6, 14.1; **IR** (KBr, cm^{-1}) 3054, 3029, 2956, 2364, 1675, 1445, 1372, 1286, 1165, 1024, 977, 870, 792, 739; **HRMS** (ESI) Calcd for $C_{21}H_{24}O_3H$ $(M+H)^+$ 325.1798, found: 325.1797.

7-methyl-6-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one **(5ma)**



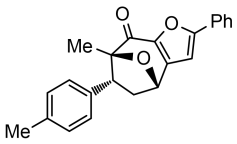
White solid, m.p. = 190-191°C, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.25 (PE/EA = 10/1), 19 mg, yield = 75%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 1.8 Hz, 1H), 7.18 (dd, *J* = 5.1, 1.9 Hz, 3H), 6.72 (dd, *J* = 6.7, 2.9 Hz, 2H), 6.58 (d, *J* = 1.8 Hz, 1H), 5.42 (d, *J* = 7.0 Hz, 1H), 3.55 (dd, *J* = 11.1, 4.7 Hz, 1H), 3.01 (td, *J* = 11.9, 11.3, 7.1 Hz, 1H), 2.17 (dd, *J* = 12.7, 4.6 Hz, 1H), 1.65 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 184.8, 148.3, 147.2, 144.4, 137.3, 128.7, 127.8, 127.5, 107.9, 91.3, 73.3, 52.8, 38.8, 19.5; **IR** (KBr, cm^{-1}) 3725, 3286, 2986, 1606, 1445, 1386, 1297, 1132, 1025, 973, 824; **HRMS** (ESI) Calcd for$C_{16}H_{14}O_3Na$ $(M+Na)^+$ 277.0835, found: 277.0837.

6-(4-methoxyphenyl)-7-methyl-2-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one **(5ac)**



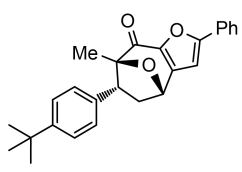
Brown solid, m.p. = 156-157 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.3 (PE/EA = 1/1), 35 mg, yield = 98%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.6 Hz, 2H), 7.51 – 7.37 (m, 3H), 6.81 (s, 1H), 6.72 (s, 4H), 5.41 (d, *J* = 7.4 Hz, 1H), 3.71 (s, 3H), 3.52 (dd, *J* = 11.1, 4.5 Hz, 1H), 3.02 (td, *J* = 11.9, 7.3 Hz, 1H), 2.16 (dd, *J* = 12.7, 4.6 Hz, 1H), 1.66 (s, 3H); **^{13}CNMR** (100MHz, $CDCl_3$) δ 184.6, 159.6, 158.8, 146.6, 146.2, 129.9, 129.3, 129.1, 129.06, 128.8, 125.6, 114.1, 102.6, 91.2, 73.1, 55.2, 52.1, 39.0, 19.6; **IR** (KBr, cm^{-1}) 3743, 3678, 3620, 2990, 2883, 1740, 1691, 1515, 1454, 1369, 1266, 1114, 929, 825, 766. 690; **HRMS** (ESI) Calcd for $C_{23}H_{20}O_4Na$ $(M+Na)^+$ 383.1254, found: 383.1254.

7-methyl-2-phenyl-6-(p-tolyl)-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one **(5ad)**



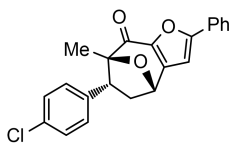
Yellow solid, m.p. = 150-151 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.2 (PE/EA = 10/1), 32 mg, yield = 92%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.5 Hz, 2H), 7.44 (dt, *J* = 11.6, 7.0 Hz, 3H), 6.99 (d, *J* = 7.6 Hz, 2H), 6.81 (s, 1H), 6.70 (d, *J* = 7.7 Hz, 2H), 5.43 (d, *J* = 7.1 Hz, 1H), 3.53 (dd, *J* = 11.0, 4.5 Hz, 1H), 3.02 (td, *J* = 11.9, 7.4 Hz, 1H), 2.24 (s, 3H), 2.19 (dd, *J* = 12.7, 4.5 Hz, 1H), 1.66 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 184.5, 159.6, 146.6, 146.2, 137.0, 134.3, 129.9, 129.5, 129.2, 129.1, 127.7, 125.6, 102.6, 91.3, 73.2, 52.6, 38.9, 21.1, 19.6; **IR** (KBr, cm^{-1}) 3743, 3620, 3565, 2979, 1835, 1740, 1690, 1517, 1426, 1388, 1259, 1112, 923, 870, 811, 765, 699,540; **HRMS** (ESI) Calcd for $C_{23}H_{20}O_3Na$ $(M+Na)^+$ 367.1305, found: 367.1303.

6-(4-(tert-butyl)phenyl)-7-methyl-2-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one **(5ae)**



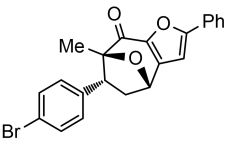
Yellow solid, m.p. = 158 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.2 (PE/EA = 10/1), 34 mg, yield =89%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.3 Hz, 2H), 7.45 (dt, *J* = 12.2, 6.9 Hz, 3H), 7.20 (d, *J* = 7.9 Hz, 2H), 6.81 (s, 1H), 6.75 (d, *J* = 8.0 Hz, 2H), 5.42 (d, *J* = 7.0 Hz, 1H), 3.53 (dd, *J* = 11.0, 4.6 Hz, 1H), 3.04 (td, *J* = 11.9, 7.2 Hz, 1H), 2.18 (dd, *J* = 12.6, 4.7 Hz, 1H), 1.66 (s, 3H), 1.24 (s, 9H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 184.5, 159.7, 150.1, 146.8, 146.2, 134.3, 129.9, 129.2, 129.1, 127.7, 125.7, 102.6, 91.3, 73.2, 52.6, 39.4, 34.5, 31.4, 19.7; **IR**(KBr, cm^{-1}) 3743, 3649, 3566, 3961, 2365, 1867, 1679, 1515, 1456, 1397, 1261, 1024, 979, 823, 763; **HRMS** (ESI) Calcd for $C_{26}H_{26}O_3Na$ $(M+Na)^+$ 409.1774, found: 409.1775.

6-(4-chlorophenyl)-7-methyl-2-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one **(5af)**



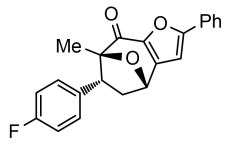
Yellow solid, m.p.= 210-211 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.2 (PE/EA = 10/1), 35 mg, yield = 96 %; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.5 Hz, 2H), 7.50 – 7.39 (m, 3H), 7.14 (d, *J* = 8.2 Hz, 2H), 6.81 (s, 1H), 6.74 (d, *J* = 8.2 Hz, 2H), 5.43 (d, *J* = 7.1 Hz, 1H), 3.53 (dd, *J* = 11.0, 4.6 Hz, 1H), 3.04 (td, *J* = 11.9, 7.2 Hz, 1H), 2.15 (dd, *J* = 12.8, 4.7 Hz, 1H), 1.66 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 184.0, 159.9, 146.7, 146.0, 136.0, 133.3, 130.1, 129.1, 129.12, 129.0, 128.9, 125.6, 102.6, 91.3, 73.1, 52.4, 38.9, 19.6; **IR** (KBr, cm^{-1}) 3743, 3678, 3620, 3566, 2982, 2854, 1835, 1741, 1679, 1530, 1497, 1426, 1369, 1288, 1257, 1094, 1027, 980, 924, 818, 764, 687; **HRMS** (ESI) Calcd for $C_{22}H_{17}ClO_3Na$ $(M+Na)^+$ 387.0758, found: 387.0757.

6-(4-bromophenyl)-7-methyl-2-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one **(5ag)**



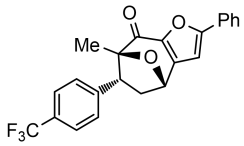
Brown solid, m.p.= 195 °C, purified by chromatography (petroleum/ethyl acetate = 8:1), R_f = 0.2 (PE/EA = 1/1), 35 mg, yield = 85%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.44 (p, *J* = 6.4 Hz, 3H), 7.30 (d, *J* = 8.1 Hz, 2H), 6.81 (s, 1H), 6.68 (d, *J* = 8.1 Hz, 2H), 5.43 (d, *J* = 7.1 Hz, 1H), 3.51 (dd, *J* = 11.1, 4.7 Hz, 1H), 3.04 (td, *J* = 11.9, 7.1 Hz, 1H), 2.15 (dd, *J* = 12.8, 4.7 Hz, 1H), 1.65 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 184.0, 160.0, 146.7, 146.0, 136.5, 131.9, 130.1, 129.5, 129.1, 129.0, 125.7, 121.5, 102.6, 91.3, 73.2, 52.5, 38.9, 19.6; **IR** (KBr, cm^{-1}) 3743, 3678, 3649, 3521, 2980, 2352, 1680, 1529, 1454, 1368, 1258, 1111, 1009, 1027, 980, 924, 818, 764, 687; **HRMS** (ESI) Calcd for $C_{22}H_{17}BrO_3Na$ (M+Na)+ 431.0253, found: 431.0255.

6-(4-fluorophenyl)-7-methyl-2-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one **(5ah)**



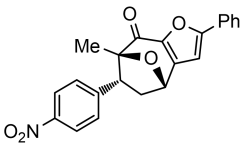
Brown solid, m.p. = 198 °C, purified by chromatography (petroleum/ethyl acetate = 9:1), R_f = 0.2 (PE/EA = 9/1), 30 mg, yield =87%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.1 Hz, 2H), 7.44 (q, *J* = 9.9, 8.2 Hz, 3H), 6.87 (t, *J* = 8.5 Hz, 2H), 6.81 (s, 1H), 6.80 – 6.74 (m, 2H), 5.43 (d, *J* = 7.0 Hz, 1H), 3.54 (dd, *J* = 11.1, 4.6 Hz, 1H), 3.04 (td, *J* = 12.0, 7.2 Hz, 1H), 2.15 (dd, *J* = 12.8, 4.6 Hz, 1H), 1.66 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 184.2, 162.1 (d, *J* = 245.9 Hz), 159.9, 146.7, 146.1, 133.2 (d, *J* = 3.3 Hz), 130.0, 129.3(d, *J* = 8.1 Hz), 129.1, 129.0, 125.6, 115.6 (d, *J* = 21.4 Hz), 102.6, 91.2, 73.1, 52.2, 39.1, 19.5; **^{19}FNMR** (376 MHz, $CDCl_3$) δ -115.3; **IR** (KBr, cm^{-1}) 3743, 3650, 2980, 2362, 1741, 1680, 1515, 1426, 1287, 1162, 980, 821, 765; **HRMS** (ESI) Calcd for $C_{22}H_{17}FONa$ $(M+Na)^+$ 371.1054, found: 371.1055.

7-methyl-2-phenyl-6-(4-(trifluoromethyl)phenyl)-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one **(5ai)**



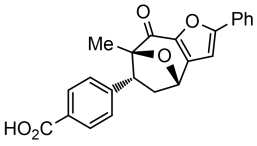
Yellow solid, m.p.= 184-185 °C, purified by chromatography (petroleum/ethyl acetate = 8:1), R_f = 0.2 (PE/EA = 8/1), 26 mg, yield = 66%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.3 Hz, 2H), 7.48 – 7.41 (m, 5H), 6.93 (d, *J* = 7.9 Hz, 2H), 6.83 (s, 1H), 5.46 (d, *J* = 7.0 Hz, 1H), 3.61 (dd, *J* = 10.9, 4.4 Hz, 1H), 3.07 (td, *J* = 11.9, 7.5 Hz, 1H), 2.20 (dd, *J* = 12.8, 4.4 Hz, 1H), 1.68 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 183.7, 160.1, 146.8, 146.0, 141.7, 130.1, 129.6 (q, *J* = 32.5 Hz), 129.1, 128.9, 128.3, 125.7 (q, *J* = 3.4 Hz),124.1(q, *J* = 272.0 Hz) 102.6, 102.6, 91.4, 73.2, 52.8, 39.0, 19.6; **^{19}FNMR** (376 MHz, $CDCl_3$) δ -62.6; **IR** (KBr, cm^{-1}) 3743, 3620, 2993, 1741, 1624, 1529, 1424, 1369, 1325, 1257, 1164, 1068, 929, 765, 625; **HRMS**(ESI) Calcd for $C_{23}H_{17}F_3O_3Na$ $(M+Na)^+$ 421.1022, found: 421.1019.

7-methyl-6-(4-nitrophenyl)-2-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one **(5aj)**



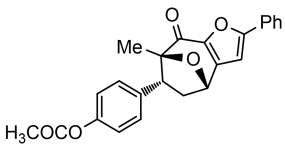
Brown solid, m.p. = 160-161 °C, purified by chromatography (petroleum/ethyl acetate = 8:1), R_f = 0.2 (PE/EA = 1/1), 29 mg, yield = 76%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.6 Hz, 2H), 7.84 (d, *J* = 6.6 Hz, 2H), 7.45 (q, *J* = 7.5, 6.8 Hz, 3H), 6.96 (d, *J* = 8.6 Hz, 2H), 6.84 (s, 1H), 5.48 (d, *J* = 7.0 Hz, 1H), 3.66 (dd, *J* = 10.9, 4.5 Hz, 1H), 3.09 (td, *J* = 12.0, 11.2, 7.2 Hz, 1H), 2.23 (dd, *J* = 12.9, 4.5 Hz, 1H), 1.69 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 183.4, 160.4, 147.3, 146.8, 145.9, 145.2, 130.3, 129.2, 128.8, 128.7, 125.7, 123.9, 102.6, 91.6, 73.3, 52.8, 38.8, 19.6; **IR** (KBr, cm^{-1}) 3742, 3678, 3566, 2983, 2335, 1917, 1740, 1618, 1517, 1426, 1345, 1275, 1111, 1025, 980, 882, 765; **HRMS** (ESI) Calcd for $C_{22}H_{17}NO_5H$ $(M+H)^+$ 376.1179, found: 376.1178.

7-methyl-8-oxo-2-phenyl-5,6,7,8-tetrahydro-4H-4,7-epoxycyclohepta[b]furan-6-yl)benzoic acid **(5ak)**



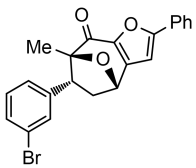
Brown solid, m.p. = 196 °C, purified by chromatography (petroleum/ethyl acetate =7:1), R_f = 0.2 (PE/EA =7/1), 28 mg, yield = 75%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.49 – 7.41 (m, 3H), 6.90 (d, *J* = 8.2 Hz, 2H), 6.82 (s, 1H), 5.47 (d, *J* = 7.0 Hz, 1H), 3.62 (dd, *J* = 11.0, 4.6 Hz, 1H), 3.06 (td, *J* = 12.0, 11.4, 7.2 Hz, 1H), 2.24 (dd, *J* = 12.8, 4.6 Hz, 1H), 1.68 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 183.7, 172.2, 160.1, 146.7, 146.0, 143.7, 130.7, 130.6, 130.1, 129.2, 129.0, 128.0, 125.7, 102.6, 91.6, 70.2, 53.1, 38.8, 19.7; **IR** (KBr, cm^{-1}) 3743, 3678, 3590, 2362, 1868, 1740, 1675, 1517, 1454, 1387, 1262, 1101, 1071, 971, 829, 760, 689; **HRMS** (ESI) Calcd for $C_{23}H_{18}O_5Na$ $(M+Na)^+$ 397.1046, found: 397.1044.

4-(7-methyl-8-oxo-2-phenyl-5,6,7,8-tetrahydro-4H-4,7-epoxycyclohepta[b]furan-6-yl)phenyl acetate(5al)



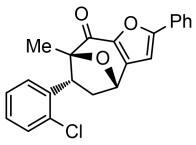
Yellow solid, m.p.= 185 °C, purified by chromatography (petroleum/ethyl acetate = 8:1), R_f = 0.1 (PE/EA = 8/1), 35 mg, yield = 86%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.0 Hz, 2H), 7.50 – 7.38 (m, 3H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 6.7 Hz, 3H), 5.42 (d, *J* = 7.0 Hz, 1H), 3.55 (dd, *J* = 11.1, 4.7 Hz, 1H), 3.03 (td, *J* = 12.0, 11.4, 7.2 Hz, 1H), 2.23 (s, 3H), 2.16 (dd, *J* = 12.8, 4.7 Hz, 1H), 1.66 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 184.1, 169.4, 159.8, 149.9, 146.7, 146.1, 135.0, 130.0, 129.1, 129.0, 128.9, 125.6, 121.8, 102.6, 91.3, 73.1, 52.4, 39.2, 21.2, 19.6; **IR** (KBr, cm^{-1}) 3743, 3620, 2981, 2362, 1835, 1680, 1514, 1454, 1368, 1257, 1114, 979, 873, 690; **HRMS** (ESI) Calcd for $C_{24}H_{20}O_5Na$ $(M+Na)^+$ 411.1203, found: 411.1205.

6-(3-bromophenyl)-7-methyl-2-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one **(5am)**



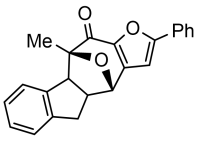
Yellow solid, m.p. = 207-211°C, purified by chromatography (petroleum/ethyl acetate = 9:1), R_f = 0.25 (PE/EA = 9/1), 38 mg, yield = 93%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.6 Hz, 2H), 7.31 (q, *J* = 9.9, 8.5 Hz, 3H), 7.17 – 7.11 (m, 1H), 6.90 (t, *J* = 7.9 Hz, 1H), 6.84 (s, 1H), 6.67 (s, 1H), 6.54 (d, *J* = 7.7 Hz, 1H), 5.30 (d, *J* = 7.0 Hz, 1H), 3.37 (dd, *J* = 11.0, 4.4 Hz, 1H), 2.89 (td, *J* = 11.9, 7.1 Hz, 1H), 2.03 (dd, *J* = 12.8, 4.5 Hz, 1H), 1.54 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 183.9, 160.1, 146.5, 146.2, 140.0, 131.5, 130.6, 130.3, 130.1, 129.2, 129.1, 126.3, 125.8, 122.8, 102.7, 91.4, 73.4, 52.7, 39.0, 19.7; **IR**(KBr, cm^{-1}) 3743, 3678, 3620, 3566, 2982, 2854, 1835, 1741, 1679, 1530, 1497, 1426,1369, 1288, 1257, 1094, 1027, 980, 924, 818, 764, 687; **HRMS** (ESI) Calcd for $C_{22}H_{17}BrO_3Na(M+Na)^+$ 431.0253, found: 431.0252.

6-(2-chlorophenyl)-7-methyl-2-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one **(5an)**



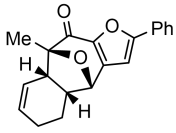
Yellow solid, m.p.=158-159 °C, purified by chromatography (petroleum/ethyl acetate = 9:1), R_f = 0.2 (PE/EA = 9/1), 33 mg, yield = 92%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 6.8 Hz, 2H), 7.45 (q, *J* = 9.9, 8.3 Hz, 3H), 7.34 (d, *J* = 8.8 Hz, 1H), 7.07 (t, *J* = 6.9 Hz, 1H), 6.99 (t, *J* = 7.1 Hz, 1H), 6.83 (s, 1H), 6.37 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.45 (d, *J* = 7.1 Hz, 1H), 4.36 (dd, *J* = 11.2, 4.9 Hz, 1H), 3.19 – 3.05 (m, 1H), 2.07 (dd, *J* = 12.8, 5.0 Hz, 1H), 1.74 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 184.1, 159.9, 146.8, 146.3, 135.3, 135.1, 130.0, 129.96, 129.1, 129.0, 128.4, 128.4, 127.2, 125.6, 102.7, 92.1, 73.0, 47.3, 40.4, 20.1; **IR** (KBr, cm^{-1}) 3742, 3649, 3064, 2982, 2361, 1681, 1527, 1473, 1370, 1260, 1110, 1049, 980, 825; **HRMS** (ESI) Calcd for $C_{22}H_{17}ClO_3Na$ $(M+Na)^+$ 387.0758, found: 387.0759.

10-methyl-2-phenyl-4a,5,9b,10-tetrahydro-4,10-epoxybenzo[1,2]azuleno[6,5-b]furan-11(4H)-one**(5ao)**



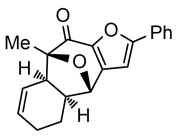
White solid, m.p. = 165-167 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.2 (PE/EA = 10/1), 16 mg, yield = 46%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.1 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 3H), 7.08 (d, *J* = 5.4 Hz, 2H), 6.97 (t, *J* = 7.1 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.69 (s, 1H), 5.40 (d, *J* = 7.2 Hz, 1H), 4.07 (d, *J* = 9.7 Hz, 1H), 3.72 (q, *J* = 9.1 Hz, 1H), 3.02 (dd, *J* = 17.4, 9.9 Hz, 1H), 2.58 (d, *J* = 17.2 Hz, 1H), 1.85 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 185.2, 158.5, 146.2, 143.2, 141.7, 139.4, 129.7, 129.0, 128.9, 127.7, 126.7, 125.5, 125.0, 124.5, 104.4, 90.2, 60.0, 46.0, 32.4, 29.8, 21.0; **IR** (KBr, cm^{-1}) 3704, 3066, 2655, 1681, 1574, 1464, 1256, 1106, 1016, 920, 869, 814, 754, 683; **HRMS** (ESI) Calcd for $C_{23}H_{18}O_3Na$ $(M+Na)^+$ 365.1148, found: 365.1150.

9-methyl-2-phenyl-4,4a,5,6,8a,9-hexahydro-10H-4,9-epoxybenzo[4,5]cyclohepta[1,2-b]furan-10-one**(5ap)**



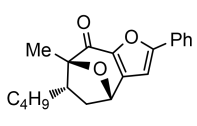
Yellow oil, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.4 (PE/EA = 10/1), 13 mg, yield = 43%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.2 Hz, 2H), 7.42 (q, *J* = 5.9, 5.0 Hz, 3H), 6.72 (s, 1H), 5.73 (d, *J* = 12.0 Hz, 1H), 5.60 (d, *J* = 10.3 Hz, 1H), 5.23 (d, *J* = 6.8 Hz, 1H), 3.08 (dt, *J* = 12.5, 6.3 Hz, 1H), 2.76 (d, *J* = 10.3 Hz, 1H), 1.82 – 1.74 (m, 1H), 1.67 (s, 3H), 1.39 – 1.18 (m, 3H); **^{13}CNMR** (100 MHz,$CDCl_3$) δ 186.1, 159.1, 145.6, 144.5, 130.0, 129.8, 129.1, 129.05, 125.6, 124.3, 104.1, 90.5, 66.4, 44.2, 39.9, 21.7, 21.4, 20.0; **IR** (KBr, cm^{-1}) 3743, 2935, 2362, 1917, 1793, 1741, 1493, 1367, 1222, 1023, 975, 874, 802; **HRMS** (ESI) Calcd for $C_{20}H_{18}O_3Na$ $(M+Na)^+$ 329.1148, found: 329.1152.

9-methyl-2-phenyl-4,4a,5,6,8a,9-hexahydro-10H-4,9-epoxybenzo[4,5]cyclohepta[1,2-b]furan-10-one**(5ap')**



Yellow oil, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.4 (PE/EA = 10/1), 13 mg, yield = 43%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.3 Hz, 2H), 7.41 (dt, *J* = 12.5, 6.9 Hz, 3H), 6.71 (s, 1H), 6.03 (d, *J* = 8.5 Hz, 1H), 5.66 (d, *J* = 10.0 Hz, 1H), 4.92 (s, 1H), 2.67 – 2.57 (m, 1H), 2.37 (ddd, *J* = 12.8, 7.7, 4.8 Hz, 1H), 2.20 – 2.08 (m, 1H), 2.04 – 1.99 (m, 1H), 1.94 (d, *J* = 15.5 Hz, 1H), 1.56 (dd, *J* = 12.2, 4.6 Hz, 1H), 1.48 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 187.6, 159.4, 144.5, 143.9, 130.3, 129.8, 129.2, 129.1, 125.5, 124.1, 103.0, 88.8, 78.2, 42.2, 40.7, 27.0, 23.7, 16.2; **IR** (KBr, cm^{-1}) 3607, 3568, 2936, 1792, 1745, 1525, 1427, 1319, 1219, 1109, 1011, 970, 875, 842; **HRMS** (ESI) Calcd for $C_{20}H_{18}O_3Na$ $(M+Na)^+$ 329.1148, found: 329.1155.

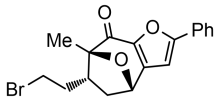
6-butyl-7-methyl-2-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one**(5aq)**



Brown oil, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.3 (PE/EA = 10/1), 17 mg, yield = 56%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.1 Hz, 2H), 7.45-7.35 (m, 3H), 6.68 (s, 1H), 5.24 (d, *J* = 7.1 Hz, 1H), 2.73 – 2.62 (m, 1H), 2.17 (dt, *J* = 10.5, 6.1 Hz, 1H), 1.60 (s, 3H), 1.53 (dd, *J* = 12.3, 4.3 Hz, 1H), 1.30 – 1.21 (m, 4H), 0.91 (s,

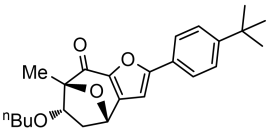
2H), 0.84 (d, *J* = 6.8 Hz, 3H).; **^{13}CNMR** (100 MHz,$CDCl_3$) δ 185.8, 159.5, 147.8, 145.2, 129.8, 129.2, 129.0, 125.5, 102.6, 89.9, 72.7, 46.4, 37.2, 31.8, 31.7, 22.7, 19.7, 14.1; **IR** (KBr, cm^{-1})2678, 3649, 2928, 2859, 1835, 1741, 1679, 1529, 1454, 1370, 1258, 1122, 1021, 981, 838,765; **HRMS** (ESI) Calcd for $C_{20}H_{22}O_3Na$ $(M+Na)^+$ 333.1461, found: 333.1367.

6-(2-bromoethyl)-7-methyl-2-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one **(5ar)**



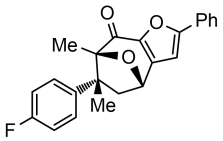
Yellow oil, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.3 (PE/EA = 10/1), 32 mg, yield = 88%; **^{1}HNMR** (400 MHz,$CDCl_3$) δ 7.80 (d, *J* = 6.8 Hz, 2H), 7.47 – 7.39 (m, 3H), 6.69 (s, 1H), 5.28 (d, *J* = 7.2 Hz, 1H), 3.43 (dt, *J* = 12.3, 6.4 Hz, 1H), 3.38 – 3.27 (m, 1H), 2.87 – 2.68 (m, 1H), 2.51 (dt, *J* = 9.8, 5.2 Hz, 1H), 1.94 (dq, *J* = 13.4, 6.5 Hz, 1H), 1.63 (s, 3H), 1.55 (dd, *J* = 12.3, 4.1 Hz, 2H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 185.2, 160.0, 147.9, 145.0, 130.1, 129.1, 129.0, 125.6, 102.6, 89.6, 72.7, 44.2, 37.0, 34.9, 32.2, 19.7; **IR** (KBr, cm^{-1}) 3742, 3620, 2974, 2361, 1867, 1740, 1518, 1454, 1258, 1023, 923, 819, 702; **HRMS** (ESI) Calcd for $C_{18}H_{17}BrO_3Na$ $(M+Na)^+$ 383.0253, found: 383.0250.

6-butoxy-2-(4-(tert-butyl)phenyl)-7-methyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one**(5ps)**



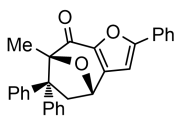
Yellow oil, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.3 (PE/EA = 10/1), 33 mg, yield = 87%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 6.64 (s, 1H), 5.20 (d, *J* = 6.9 Hz, 1H), 4.03 (d, *J* = 7.9 Hz, 1H), 3.50 (q, *J* = 6.6 Hz, 1H), 3.31 (q, *J* = 6.6 Hz, 1H), 2.73 (dt, *J* = 12.8, 8.3 Hz, 1H), 1.89 (d, *J* = 12.7 Hz, 1H), 1.67 (s, 3H), 1.40 (d, *J* = 6.9 Hz, 1H), 1.33 (s, 9H), 1.21 (dt, *J* = 13.9, 7.2 Hz, 3H), 0.81 (t, *J* = 7.3 Hz, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 184.1, 159.3, 153.1, 145.9, 145.7, 126.6, 126.0, 125.3, 102.2, 88.8, 85.4, 72.9, 71.5, 39.3, 35.0, 31.8, 31.3, 19.4, 19.3, 13.9; **IR** (KBr, cm^{-1}) 3743, 3678, 2959, 2362, 1917, 1687, 1538, 1480, 1437, 1095, 981, 928, 833, 669; **HRMS** (ESI) Calcd for $C_{24}H_{30}O_4Na$ $(M+Na)^+$ 405.2036, found: 405.2041.

6-(4-fluorophenyl)-6,7-dimethyl-2-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one**(5at)**



Brown solid, m.p. = 165-166 °C, purified by chromatography (petroleum/ethyl acetate = 8:1), R_f = 0.25 (PE/EA = 8/1),30 mg, yield =82%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 6.9 Hz, 2H), 7.41 (q, *J* = 8.3, 7.3 Hz, 3H), 6.98 (dd, *J* = 8.7, 5.2 Hz, 2H), 6.84 (t, *J* = 8.6 Hz, 2H), 6.74 (s, 1H), 5.37 (d, *J* = 7.2 Hz, 1H), 2.82 (d, *J* = 13.1 Hz, 1H), 2.52 (dd, *J* = 13.1, 7.3 Hz, 1H), 1.63 (s, 3H), 1.60 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 185.4, 161.5 (d, *J* = 246.5 Hz), 159.6, 145.8, 145.5, 138.1 (d, *J* = 3.3 Hz), 129.9, 129.1, 129.0, 128.2 (d, *J* = 8.0 Hz), 125.6, 115.1 (d, *J* = 21.2 Hz), 102.4, 92.5, 71.9, 49.6, 46.0, 28.7, 16.3; **^{19}FNMR** (376 MHz, CDCl3) δ -116.2; **IR** (KBr, cm^{-1}) 3742, 3568, 2931, 2362, 1917, 1740, 1645, 1533, 1454, 1398, 1253, 1166, 1073, 924, 839, 761; **HRMS** (ESI) Calcd for $C_{23}H_{19}FO_3Na$ $(M+Na)^+$ 385.1210, found: 385.1211.

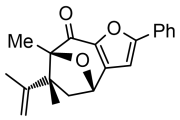
7-methyl-2,6,6-triphenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one**(5au)**



Yellow solid, m.p. =154-155 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.2 (PE/EA = 10/1), 33 mg, yield = 82%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.1 Hz, 2H), 7.29 (d, *J* = 7.4 Hz, 3H), 7.21 (d, *J* = 8.2 Hz, 3H), 7.15 (dd, *J* = 15.7, 8.9 Hz, 5H), 6.99 (d, *J* = 7.5 Hz, 2H), 6.63 (s, 1H), 5.46 (d, *J* = 7.5 Hz, 1H), 3.36 (dd, *J* = 12.9, 7.8 Hz, 1H), 3.12 (d, *J* = 13.1 Hz, 1H), 1.35 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 185.5, 159.4, 148.2, 147.7, 144.7, 141.3, 129.8, 129.0, 128.99, 128.9, 128.1, 127.9, 127.0, 126.5, 125.6, 102.3, 94.1, 71.7, 59.9, 50.3, 19.6; **IR** (KBr, cm^{-1}) 3743, 3678, 3565, 2986, 2336, 1835, 1770, 1676, 1516, 1454, 1368, 1023, 935, 815, 758; **HRMS**

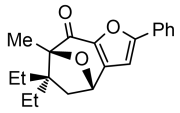
(ESI) Calcd for $C_{28}H_{22}O_3Na$ $(M+Na)^+$ 429.1461, found: 429.1462.

***6,7-dimethyl-2-phenyl-6-(prop-1-en-2-yl)-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one*(5av)**



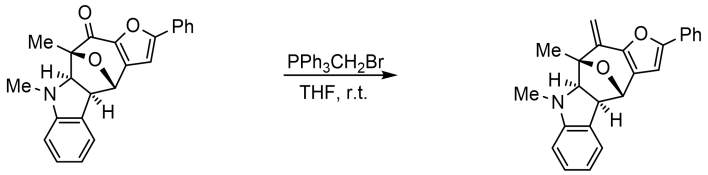
White solid, m.p. = 156 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.4 (PE/EA = 10/1), 17 mg, yield = 56%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 6.9 Hz, 2H), 7.39 (dd, *J* = 12.8, 7.3 Hz, 3H), 6.68 (s, 1H), 5.24 (d, *J* = 7.2 Hz, 1H), 4.69 (s, 1H), 4.39 (s, 1H), 2.55 (d, *J* = 12.9 Hz, 1H), 2.22 (dd, *J* = 12.9, 7.3 Hz, 1H), 1.72 (s, 3H), 1.59 (s, 3H), 1.36 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 185.8, 159.3, 146.9, 145.8, 145.4, 129.8, 129.2, 129.0, 125.5, 113.0, 102.4, 91.6, 71.8, 51.1, 44.5, 25.8, 21.6, 17.1; **IR** (KBr, cm^{-1}) 3768, 3649, 2987, 1741, 1646, 1531, 1455, 1365, 1263, 1098, 974, 898, 812, 764, 690; **HRMS** (ESI) Calcd for $C_{20}H_{20}O_3Na$ $(M+Na)^+$ 331.1305, found: 331.1310.

***6,6-diethyl-7-methyl-2-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one*(5aw)**



White solid, m.p. = 140 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.3 (PE/EA = 10/1), 27 mg, yield = 86%; **^{1}HNMR** (400 MHz, $CDCl_3$）δ 7.81 (d, *J* = 7.5 Hz, 2H), 7.41 (dt, *J* = 12.1, 6.8 Hz, 3H), 6.67 (s, 1H), 5.14 (d, *J* = 7.6 Hz, 1H), 2.42 (dd, *J* = 12.4, 7.7 Hz, 1H), 1.82 (dd, *J* = 13.8, 7.2 Hz, 1H), 1.62 – 1.56 (m, 2H), 1.52 (s, 3H), 1.41 (dt, *J* = 13.8, 7.3 Hz, 1H), 1.26 – 1.16 (m, 1H), 0.95 – 0.90 (m, 3H), 0.82 (t, *J* = 7.4 Hz, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 187.0, 159.4, 147.9, 144.8, 129.8, 129.2, 129.1, 125.5, 102.5, 92.4, 71.5, 48.0, 44.7, 29.0, 26.4, 17.4, 9.3, 9.1; **IR** (KBr, cm^{-1}) 3768, 3619, 3591, 2867, 2362, 1917, 1792, 1619, 1516, 1428, 1395, 1264, 1109, 1021, 976, 822, 762; **HRMS** (ESI) Calcd for $C_{20}H_{22}O_3Na$ $(M+Na)^+$ 333.1461, found: 333.1464.

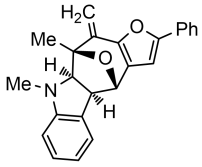
1.6 Product further transformation



3aa **6**

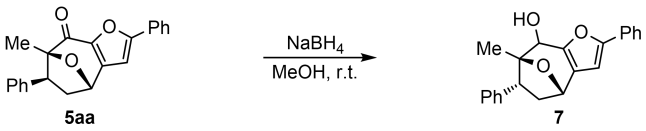
To a solution of CH_2PPh_3Br (71mg, 0.2 mmol) in THF (2 mL), was added *t*-BuOK (22 mg, 0.2 mmol). The resulting solution was stirred at rt for 30 min, and then compound **3a** (36 mg, 0.1 mmol) in THF (2 mL) was added. The mixture was stirred at room temperature. After the reaction was finished, the reaction mixture was quenched by NH_4Cl The solution was extracted with Ethyl Acetate. the combined organic layers were washed with brine, dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE:EA=15:1) afforded the compound **6**.

***9,10-dimethyl-11-methylene-2-phenyl-4,4a,9,9a,10,11-hexahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indole* (6)**



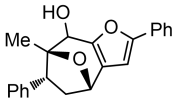
Yellow solid, m.p. = 120-121 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), R_f = 0.3 (PE/EA = 15/1), 27 mg, yield = 75%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.7 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.13 (dd, *J* = 12.9, 7.1 Hz, 2H), 6.71 – 6.65 (m, 2H), 6.42 (d, *J* = 7.8 Hz, 1H), 5.45 (s, 1H), 5.14 (s, 1H), 5.04 (s, 1H), 4.23 (d, *J* = 8.5 Hz, 1H), 3.88 (d, *J* = 8.5 Hz, 1H), 2.98 (s, 3H), 1.67 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 154.1, 153.4, 147.4, 140.6, 130.6, 129.4, 129.1, 128.9, 128.8, 128.8, 127.9, 124.1, 124.0, 117.4, 106.6, 102.9, 101.5, 88.0, 78.8, 78.7, 59.1, 37.3, 18.2; **IR** (KBr, cm^{-1}) 3052, 2963, 2837, 2364, 1672, 1581,

1367,1256, 1177, 1026, 973, 834, 738; **HRMS** (ESI) Calcd for$C_{24}H_{21}NO_2Na$ $(M+Na)^+$ 378.1465, found: 378.1472.



Cycloadduct **3a** (33.0 mg, 0.1 mmol) was dissolved in MeOH (2 ml) in a round-bottom flask. To the resultant solution was added $NaBH_4$ (7.6 mg, 0.2 mmol, 2.0 equiv), The reaction was stirred at room temperature for 30 min. The reaction was the quenched with NH_4Cl (5 mL). The aqueous phase was separated and extracted with EtOAc (5 x 5 mL). The combined organic fractions were washed with brine (5 mL), All combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by column chromatography (silica gel, PE:EA=10:1) to afford diastereomerically pure **7**.

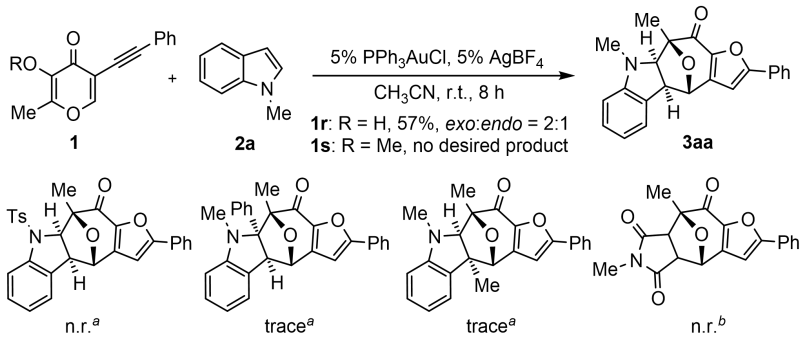
7-methyl-2,6-diphenyl-5,6,7,8-tetrahydro-4H-4,7-epoxycyclohepta[b]furan-8-ol **(7)**



White solid, m.p. = 173-174 ºC, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.25 (PE/EA = 10/1), 33 mg, yield = 99%; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.7 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 7.4 Hz, 1H), 7.27 (d, *J* = 7.3 Hz, 3H), 6.96 (d, *J* = 6.9 Hz, 2H), 6.64 (s, 1H), 5.18 (d, *J* = 6.2 Hz, 1H), 4.92 (d, *J* = 12.3 Hz, 1H), 3.59 (dd, *J* = 11.9, 3.4 Hz, 1H), 2.93 (td, *J* = 12.1, 6.3 Hz, 1H), 2.40 (dd, *J* = 12.5, 3.4 Hz, 1H), 1.78 (s, 3H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 154.3, 149.3, 139.8, 130.8, 129.2, 128.8, 128.5, 127.6, 127.5, 126.9, 123.8, 101.8, 86.4, 74.7, 73.9, 53.6, 42.8, 24.8; **IR** (KBr, cm^{-1}) 3563, 2935, 2862, 1677, 1580, 1481, 1369, 1255, 1117, 1026, 980, 833, 736; **HRMS** (ESI) Calcd for $C_{22}H_{20}O_3Na$ $(M+Na)^+$ 355.1305, found: 355.1303.

1.7 Control experiments

From following experiments, it's easy to find that the TBS group should preserve during the cycloaddition course to ensure the stereoselectivity and the leaving of protecting group might be synchronous with the cycloaddition, or at least not later than the latter, because once a post-cycloaddition oxonium species was formed, it would convert into **3a** inevitably. The inefficient results of other dipolarphiles indicated that reaction was influence by the electronic nature and steric property of these heterocycles.



Reaction conditions: [a]**1a** (0.1 mmol), **2** (0.15 mmol), 5 mmol% PPh_3AuCl and 5 mmol% $AgBF_4$ in 2 mL acetonitrile were stirred at 25 ºC for 8 h. [b]**1a** (0.1 mmol), **4** (0.15 mmol) and 5 mmol% ZnI_2 in 2 mL DCE was stirred at 25 ºC for 12 h.

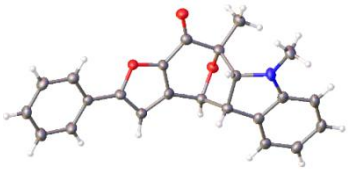
2 References

[1] Groß, T .; Metzeter, P. *Chem. Eur. J.* **2013**, *19*, 14787.

[2] Zhang, L., Cao, T., Jiang, H., Zhu, S. *Angew. Chem., Int. Ed.* **2020**, *59*, 4670.

3 Crystal data

3.1 X-ray diffraction analysis data of 3aa



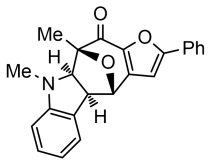
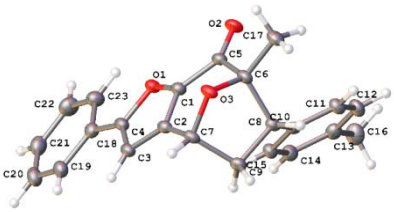


Table 1 Crystal data and structure refinement for 3aa.

CCDC	1984647
Empirical formula	$C_{23}H_{19}NO_3$
Formula weight	357.39
Temperature/K	99.99(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	4.9097(6)
b/Å	20.9012(19)
c/Å	16.8201(14)
α/°	90
β/°	96.123(9)
γ/°	90
Volume/Å^3	1716.2(3)
Z	4
ρ_{calc}g/cm^3	1.383
μ/mm^{-1}	0.738
F(000)	752.0
Crystal size/mm^3	0.12 × 0.11 × 0.09
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.284 to 147.482
Index ranges	-5 ≤ h ≤ 3, -25 ≤ k ≤ 25, -19 ≤ l ≤ 20
Reflections collected	6214
Independent reflections	4638 [R_{int} = 0.0440, R_{sigma} = 0.0590]
Data/restraints/parameters	4638/1/491
Goodness-of-fit on F^2	1.076
Final R indexes [I>=2σ (I)]	R_1 = 0.0576, wR_2 = 0.1515
Final R indexes [all data]	R_1 = 0.0641, wR_2 = 0.1584
Largest diff. peak/hole / e Å^{-3}	0.28/-0.31
Flack parameter	-0.2(3)

3.2 X-ray diffraction analysis data of 5ad



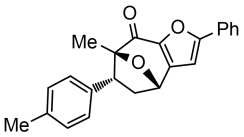
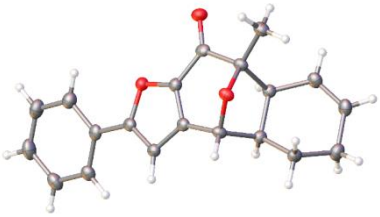


Table 1 Crystal data and structure refinement for 5ad

CCDC	1984385
Empirical formula	$C_{23}H_{20}O_3$
Formula weight	344.39
Temperature/K	100.01(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	6.8575(3)
b/Å	17.6675(7)
c/Å	29.0079(11)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3514.4(2)
Z	8
ρ_{calc}g/cm^3	1.302
μ/mm^{-1}	0.681
F(000)	1456.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.094 to 147.312
Index ranges	-5 ≤ h ≤ 8, -21 ≤ k ≤ 18, -27 ≤ l ≤ 36
Reflections collected	8491
Independent reflections	3431 [R_{int} = 0.0297, R_{sigma} = 0.0308]
Data/restraints/parameters	3431/0/237
Goodness-of-fit on F^2	1.084
Final R indexes [I>=2σ (I)]	R_1 = 0.0456, wR_2 = 0.1110
Final R indexes [all data]	R_1 = 0.0540, wR_2 = 0.1178
Largest diff. peak/hole / e Å^{-3}	0.23/-0.28

3.3 X-ray diffraction analysis data of 5ap'



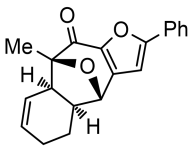
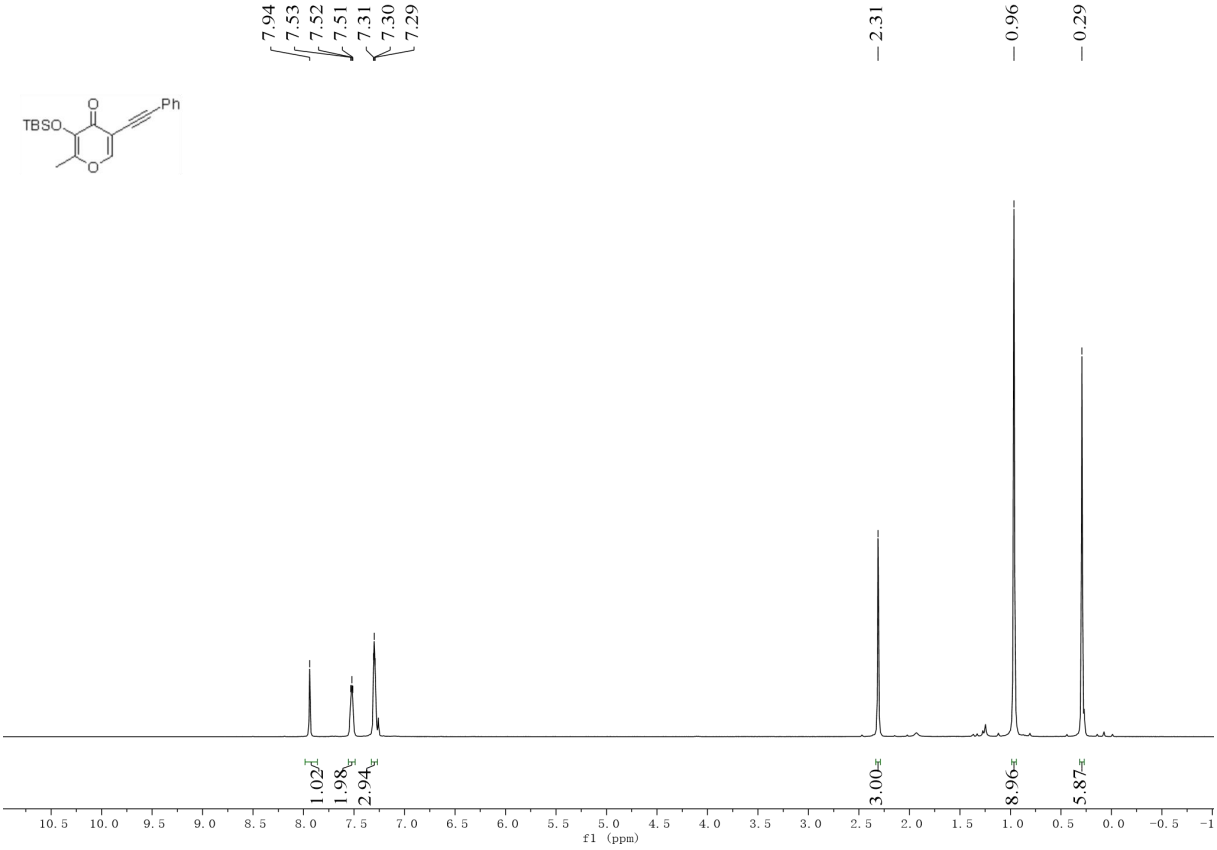


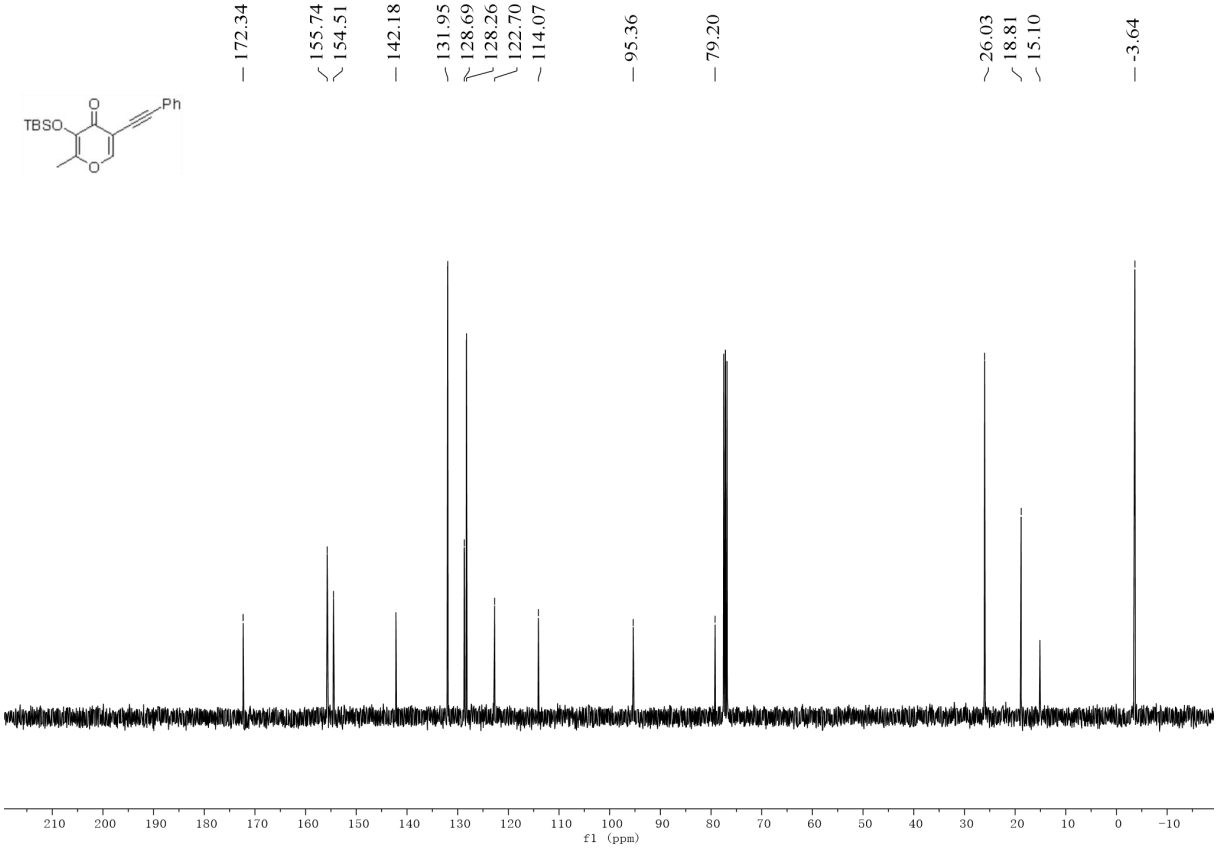
Table 1 Crystal data and structure refinement for 5ap'

CCDC	1997501
Empirical formula	$C_{20}H_{18}O_3$
Formula weight	306.34
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.3935(6)
b/Å	25.0493(16)
c/Å	8.8978(6)
α/°	90
β/°	111.188(8)
γ/°	90
Volume/Å^3	1536.5(2)
Z	4
ρ_{calc}g/cm^3	1.324
μ/mm^{-1}	0.709
F(000)	648.0
Crystal size/mm^3	0.12 × 0.11 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.058 to 146.716
Index ranges	$-7 \le h \le 9$, $-30 \le k \le 30$, $-10 \le l \le 6$
Reflections collected	5741
Independent reflections	2996 [R_{int} = 0.0361, R_{sigma} = 0.0458]
Data/restraints/parameters	2996/0/209
Goodness-of-fit on F^2	1.090
Final R indexes [I>=2σ (I)]	R_1 = 0.0492, wR_2 = 0.1220
Final R indexes [all data]	R_1 = 0.0617, wR_2 = 0.1307
Largest diff. peak/hole / e Å^{-3}	0.27/-0.29

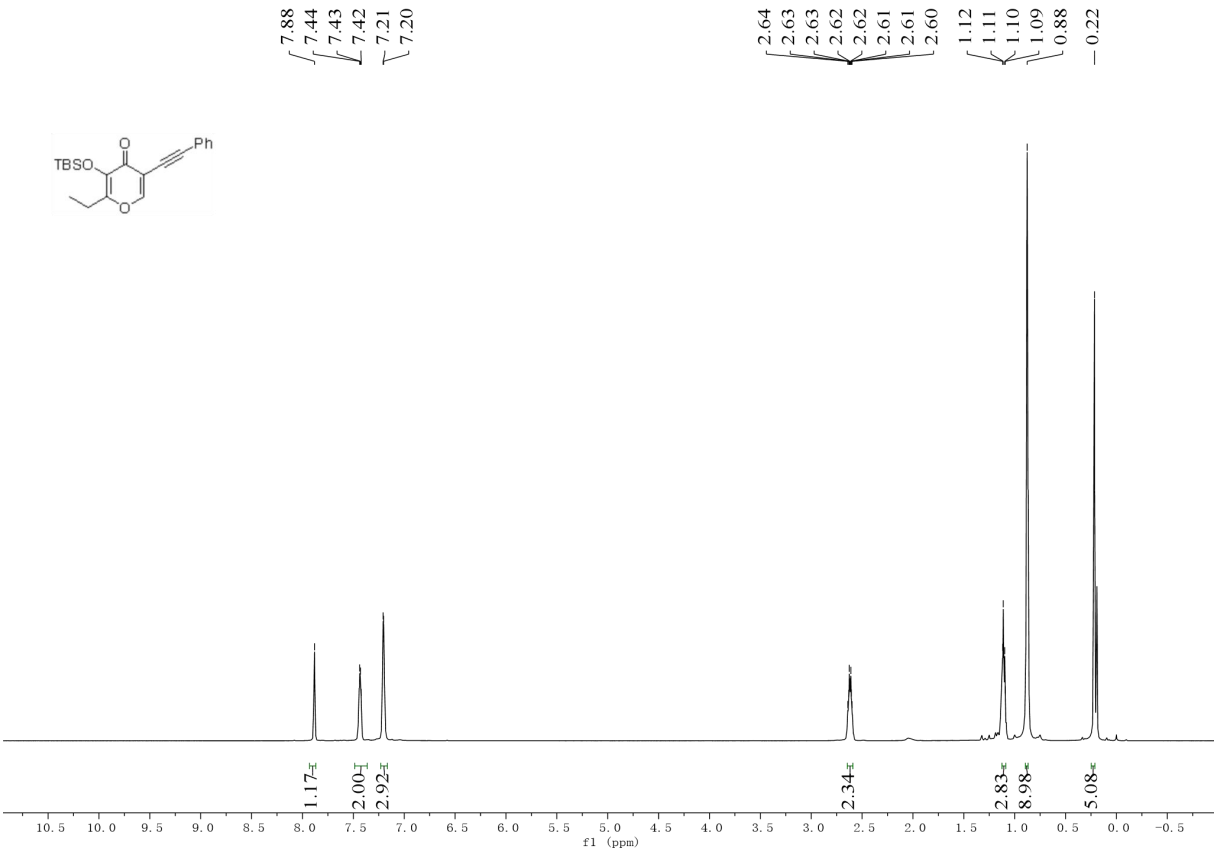
4. Copies of NMR spectrum

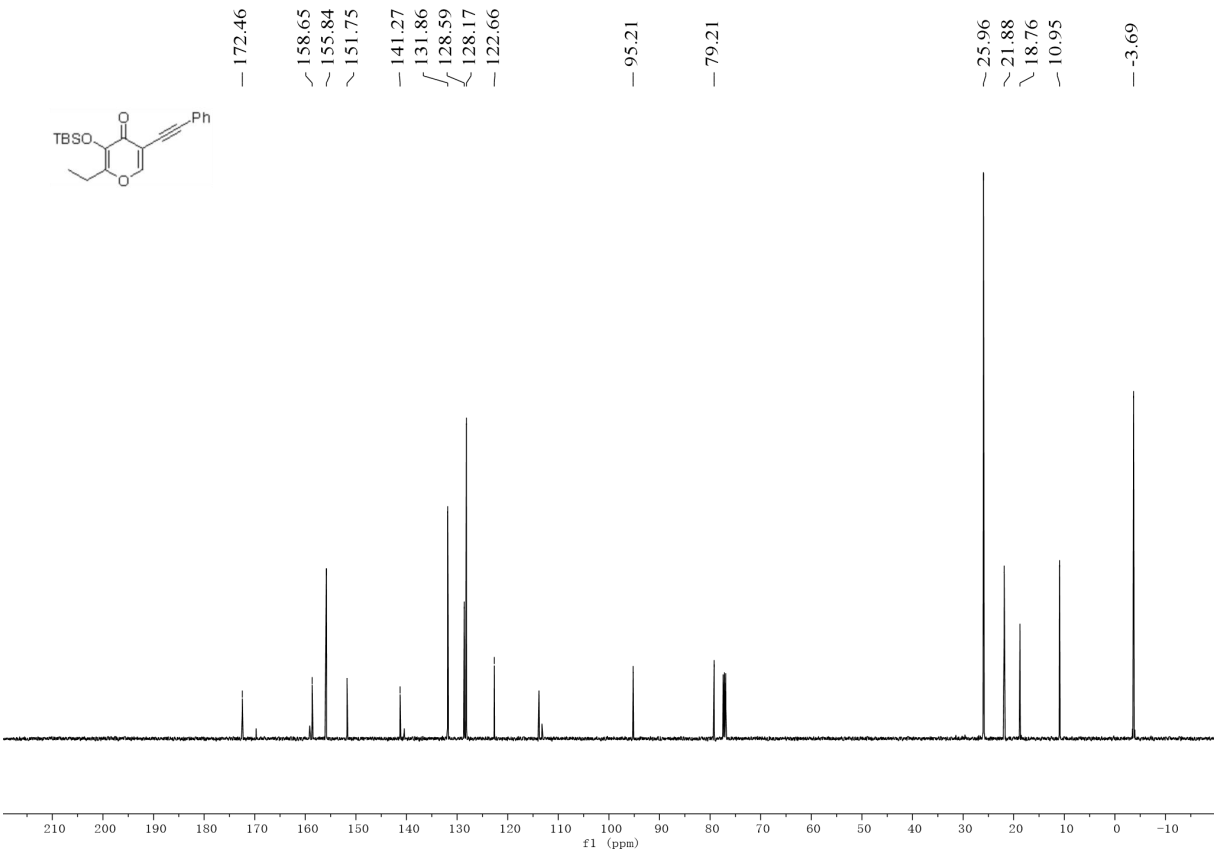
^{1}H and ^{13}C NMR spectra of 1a



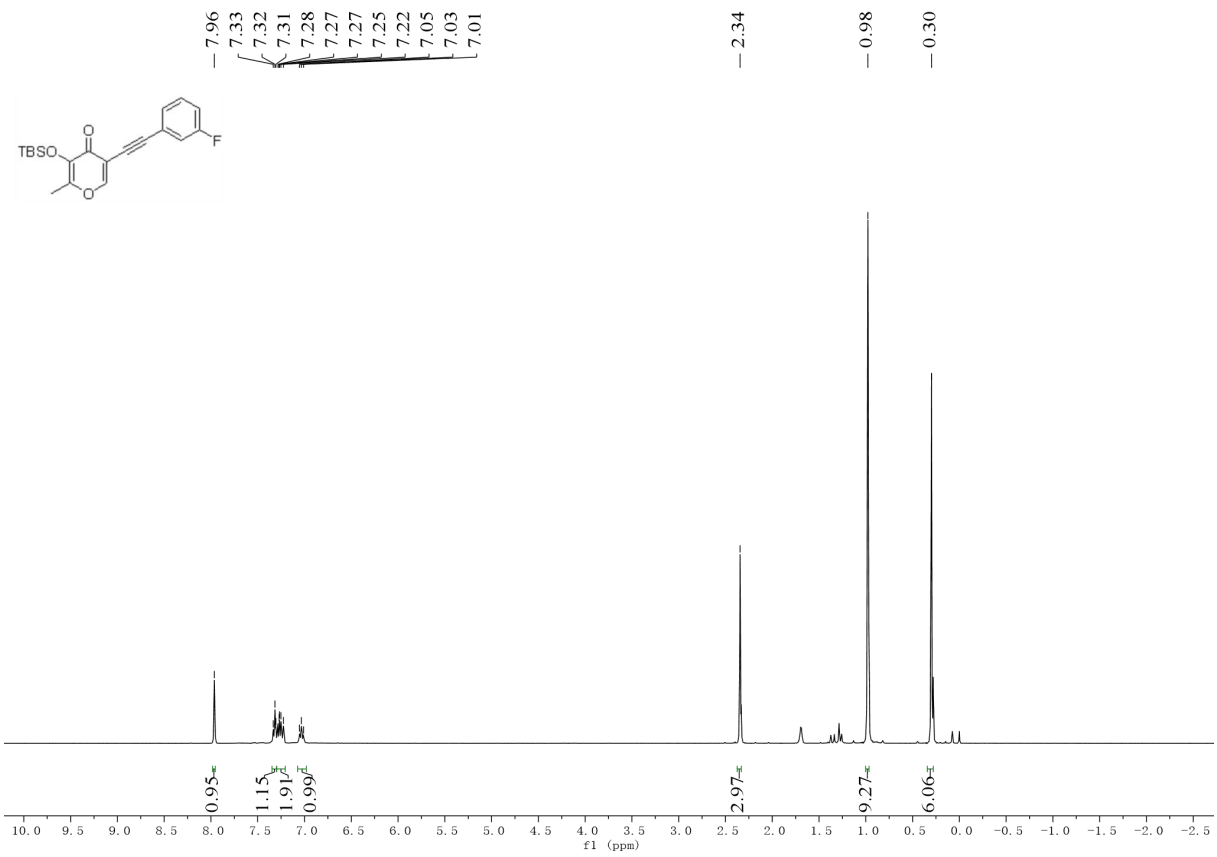


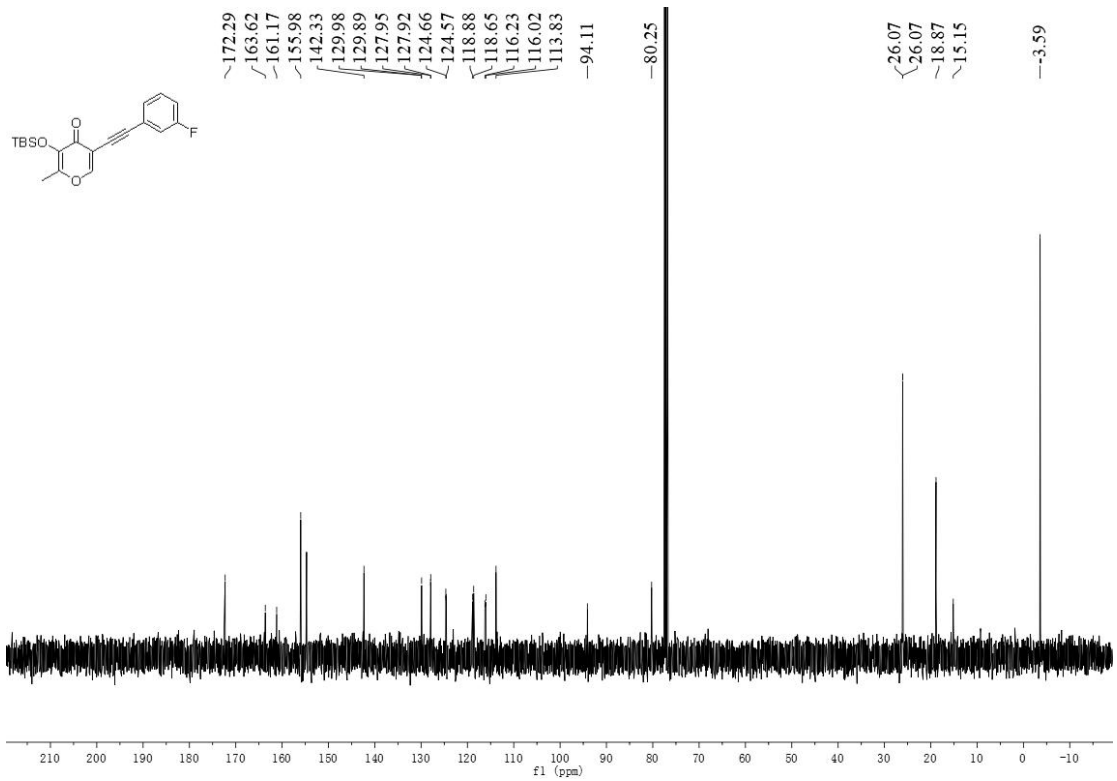
^{1}H and ^{13}C NMR spectra of 1b





^{1}H and ^{13}C NMR and $^{19}FNMR$ spectra of 1c





TBSO
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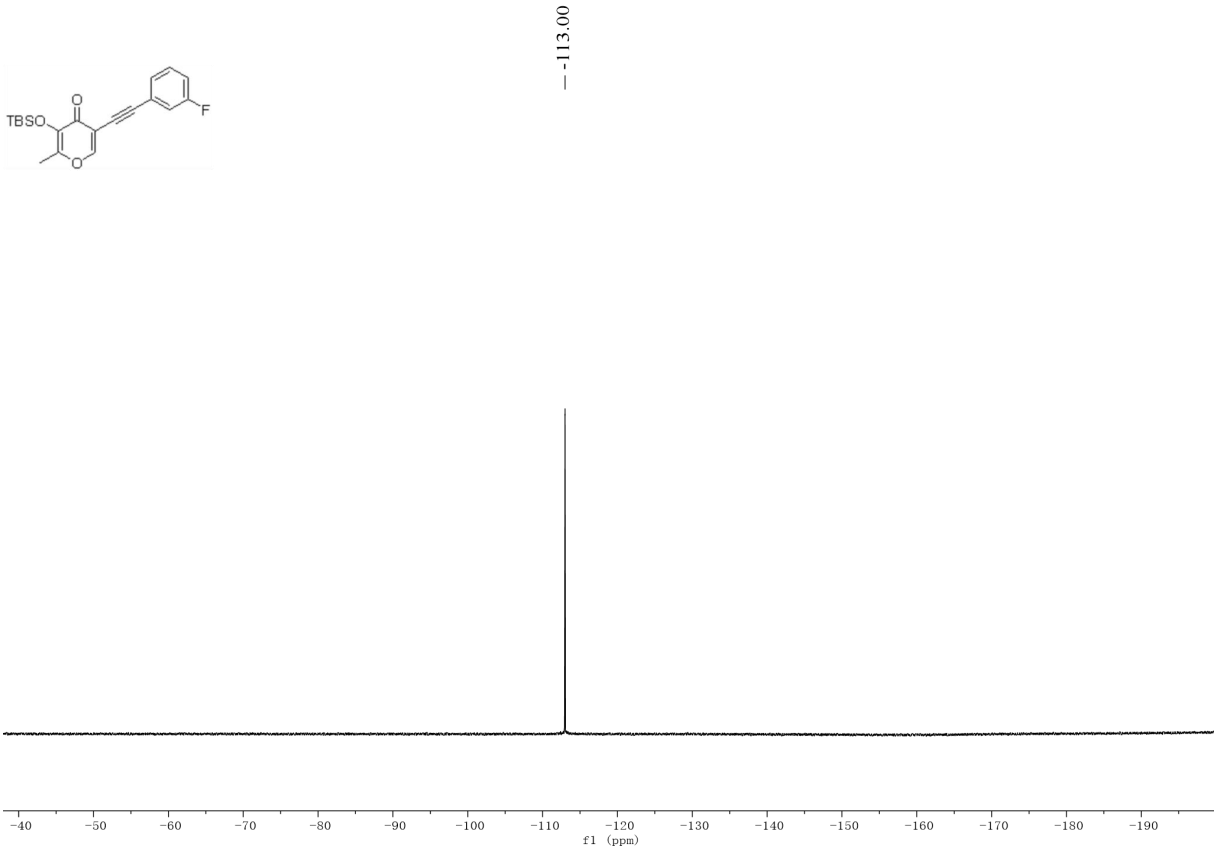
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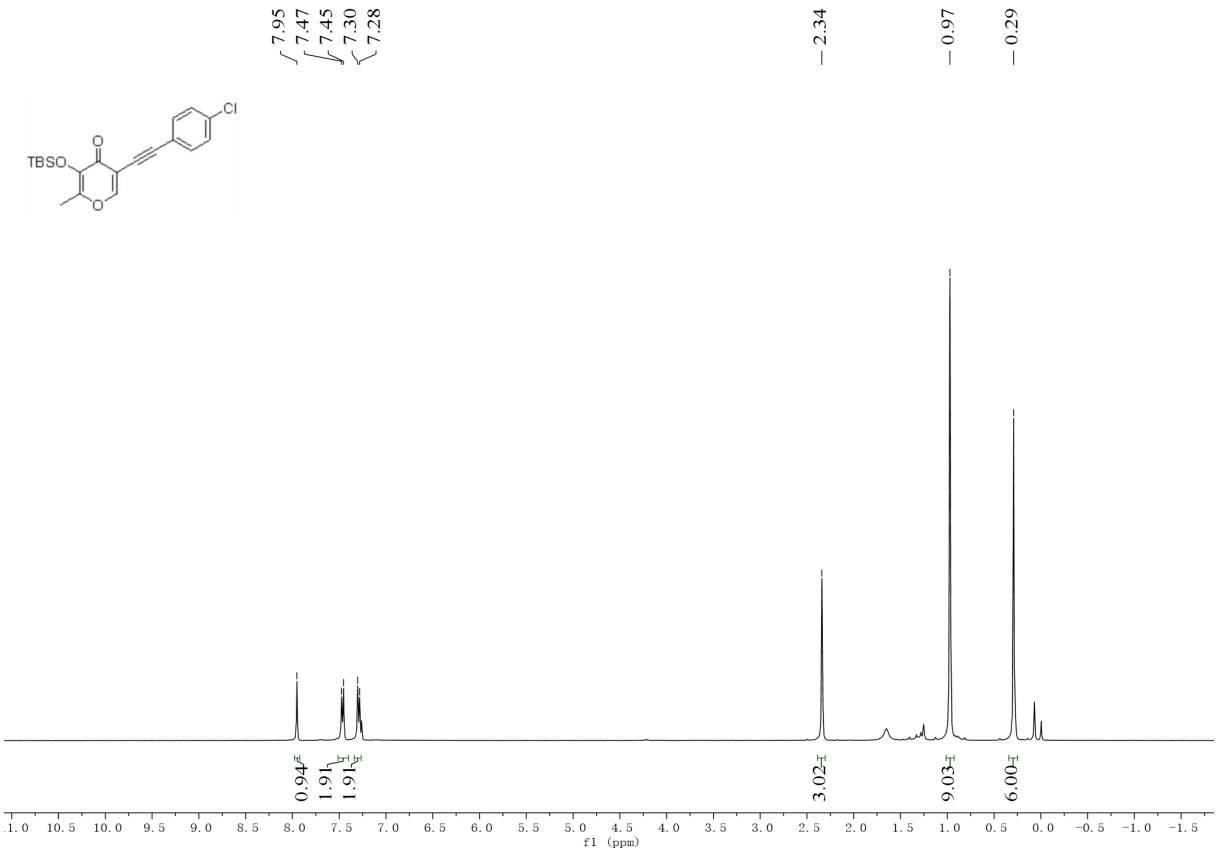
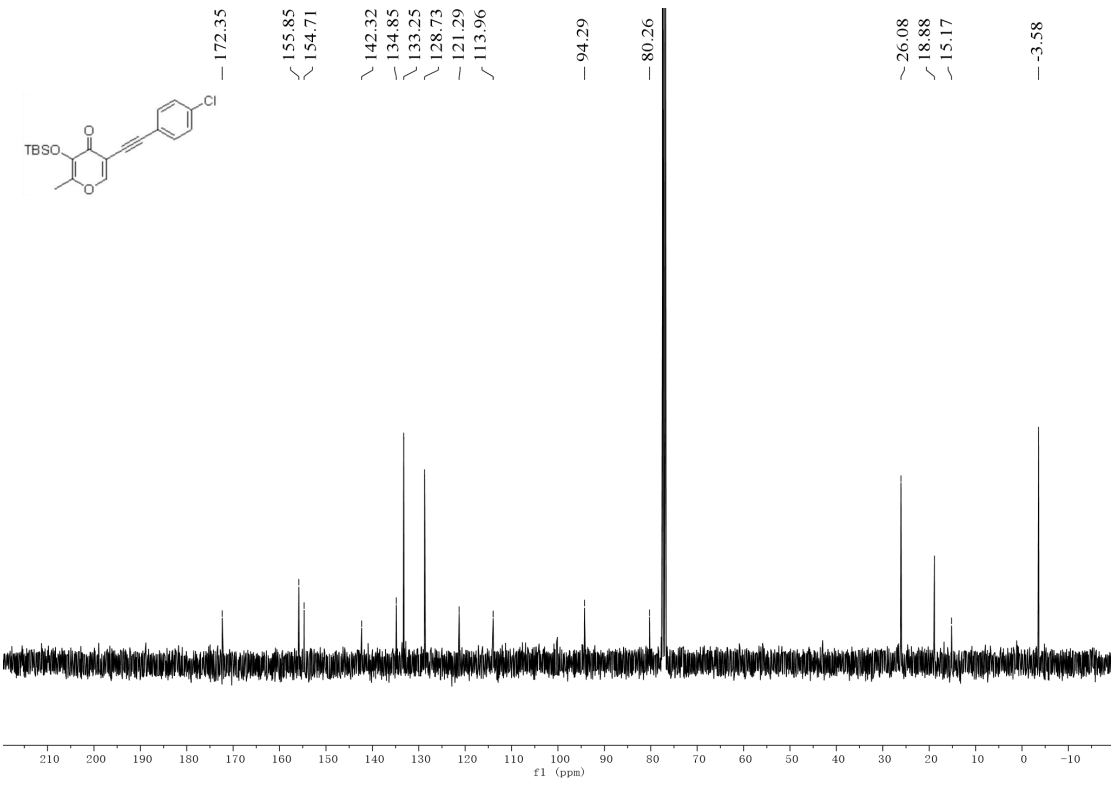
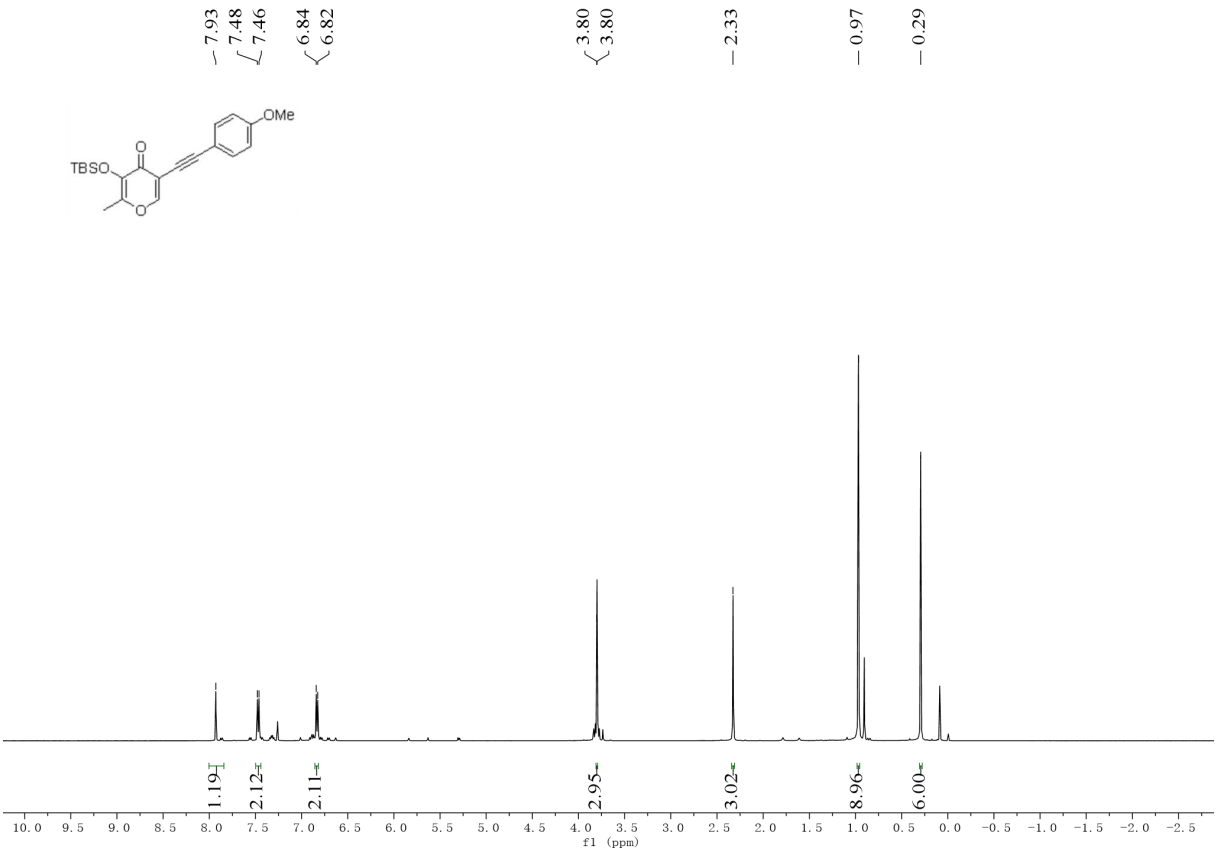
f1 (ppm)

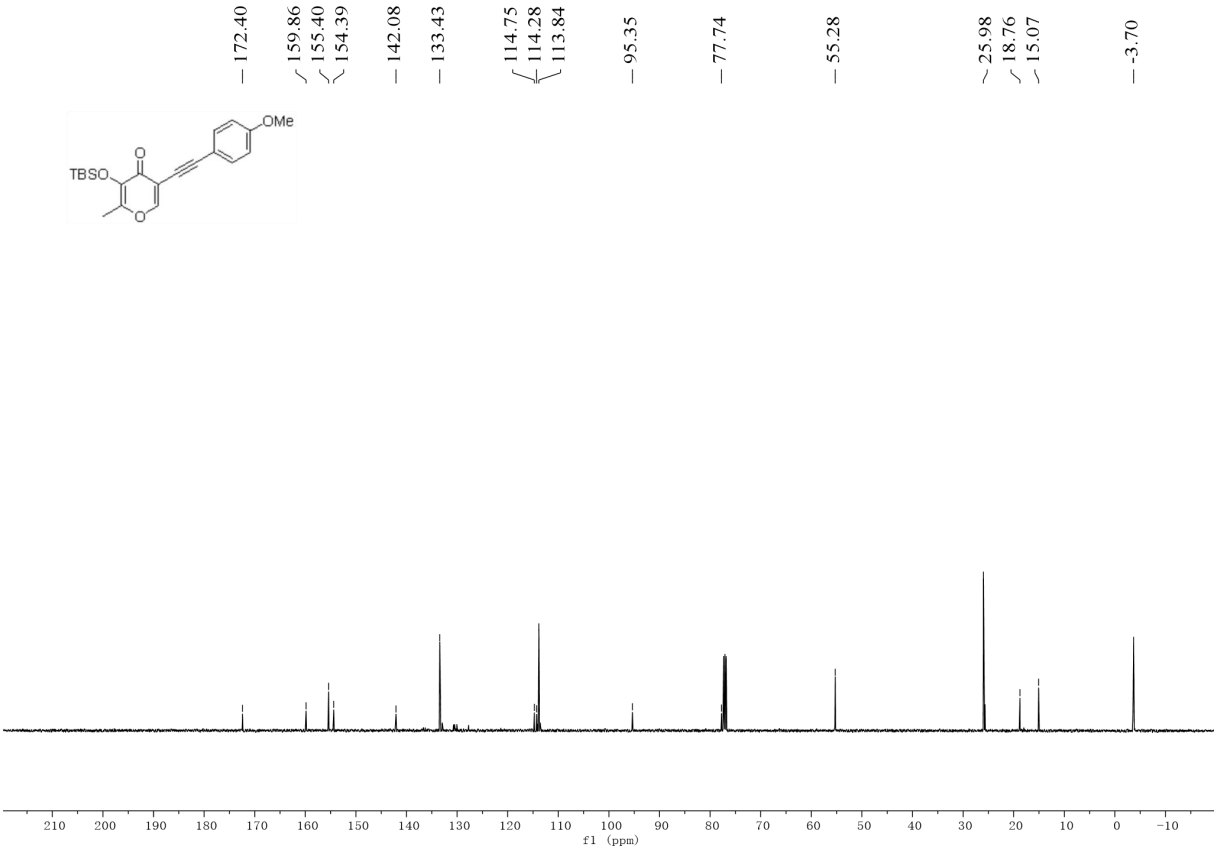
^{1}H and ^{13}C NMR spectra of 1d



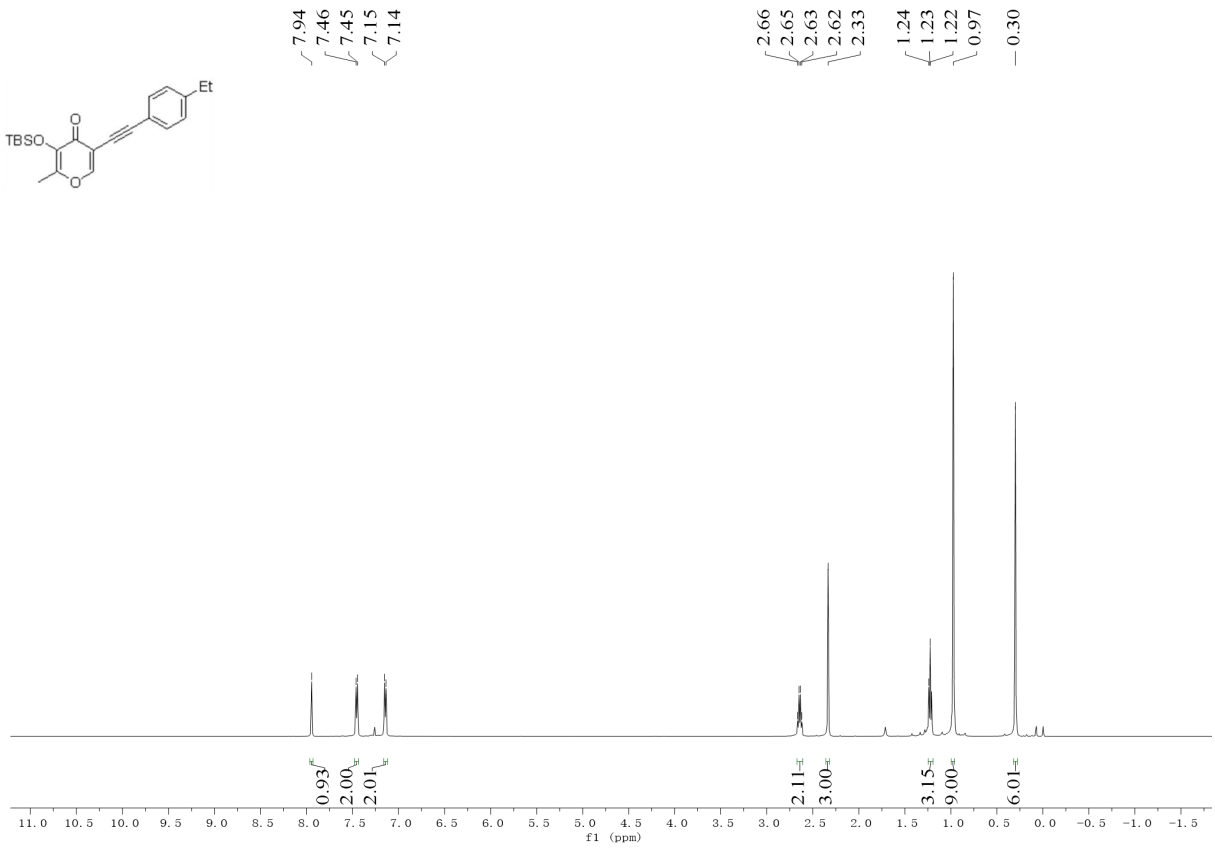


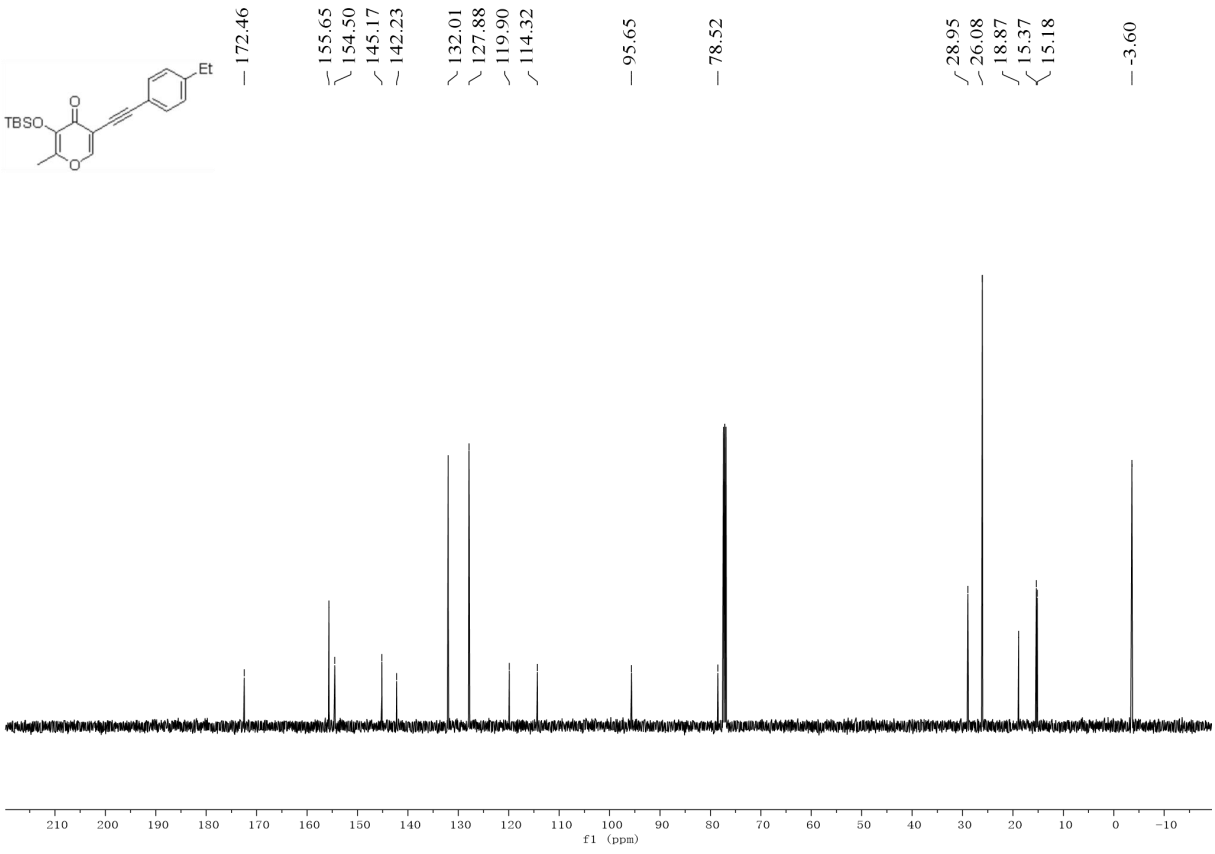
^{1}H and ^{13}C NMR spectra of 1e



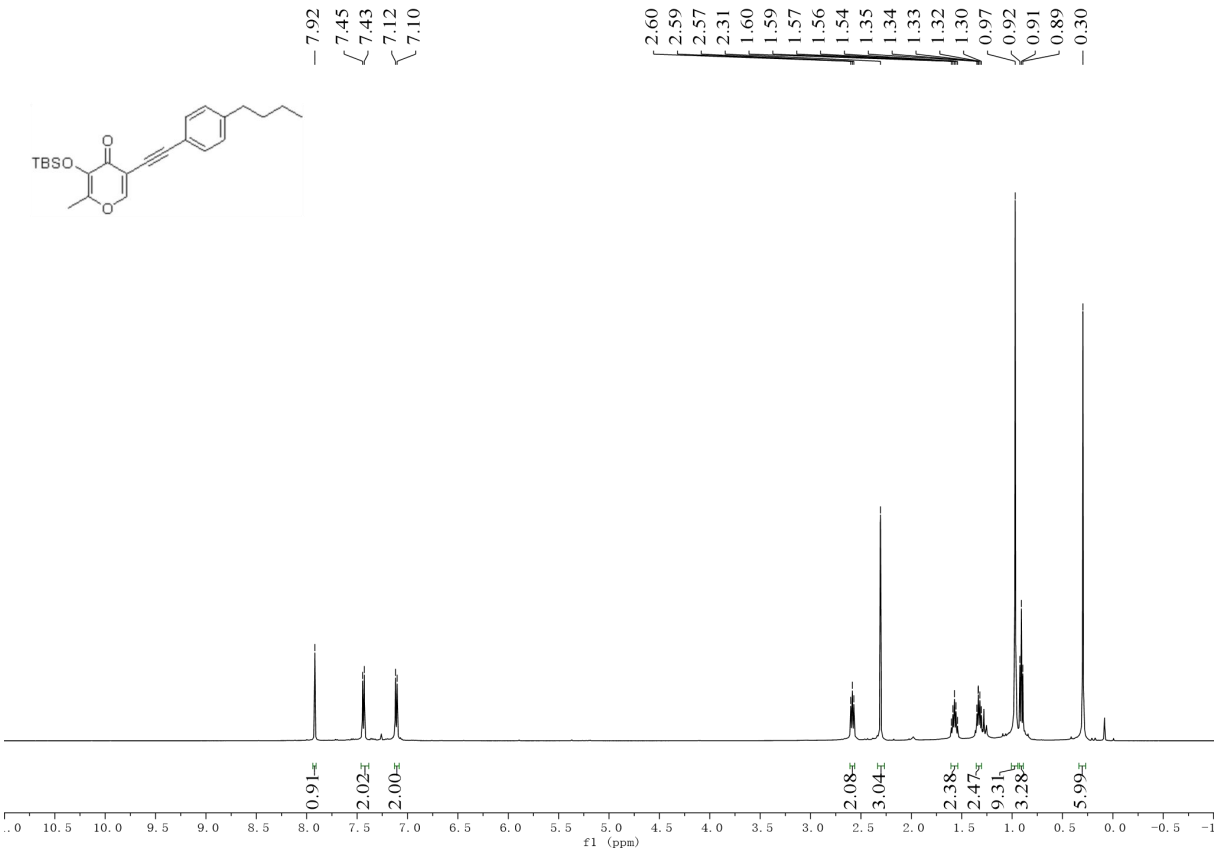


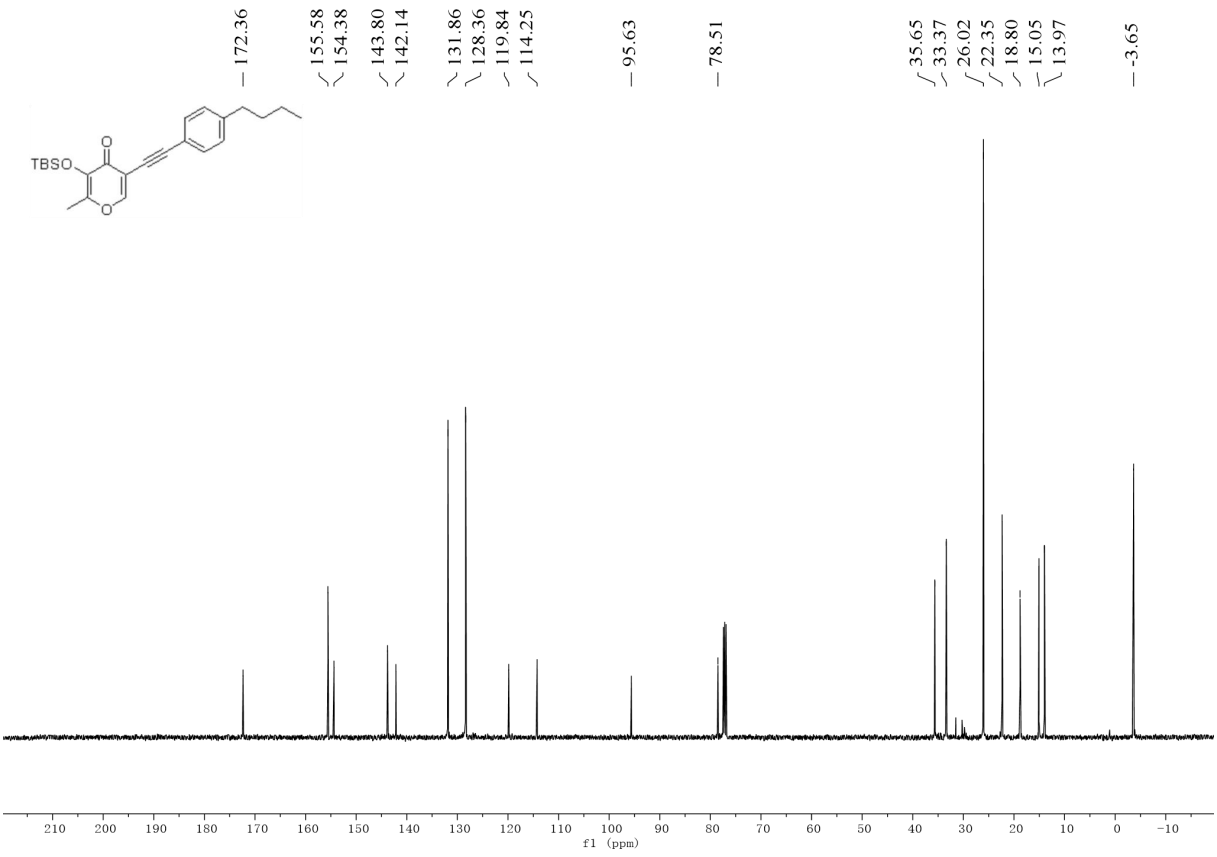
^{1}H and ^{13}C NMR and $^{19}FNMR$ spectra of 1f



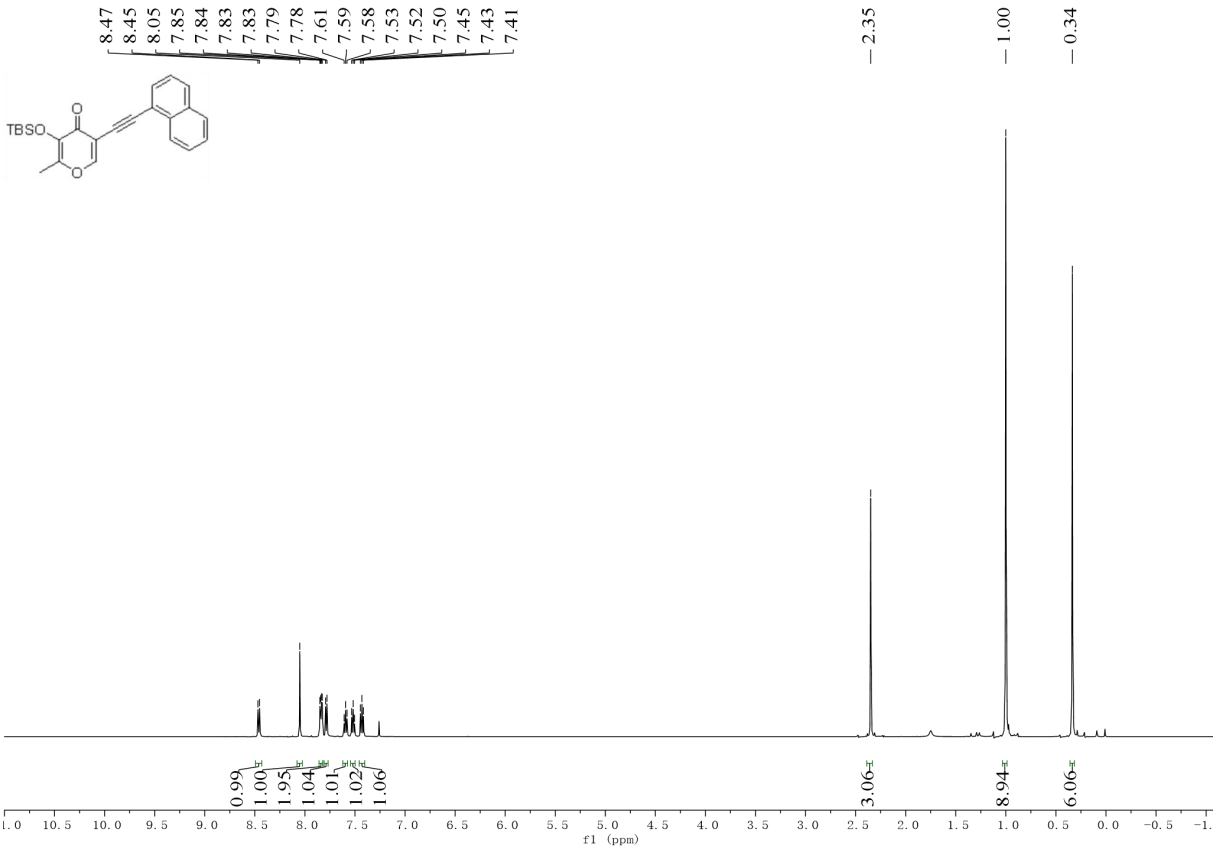


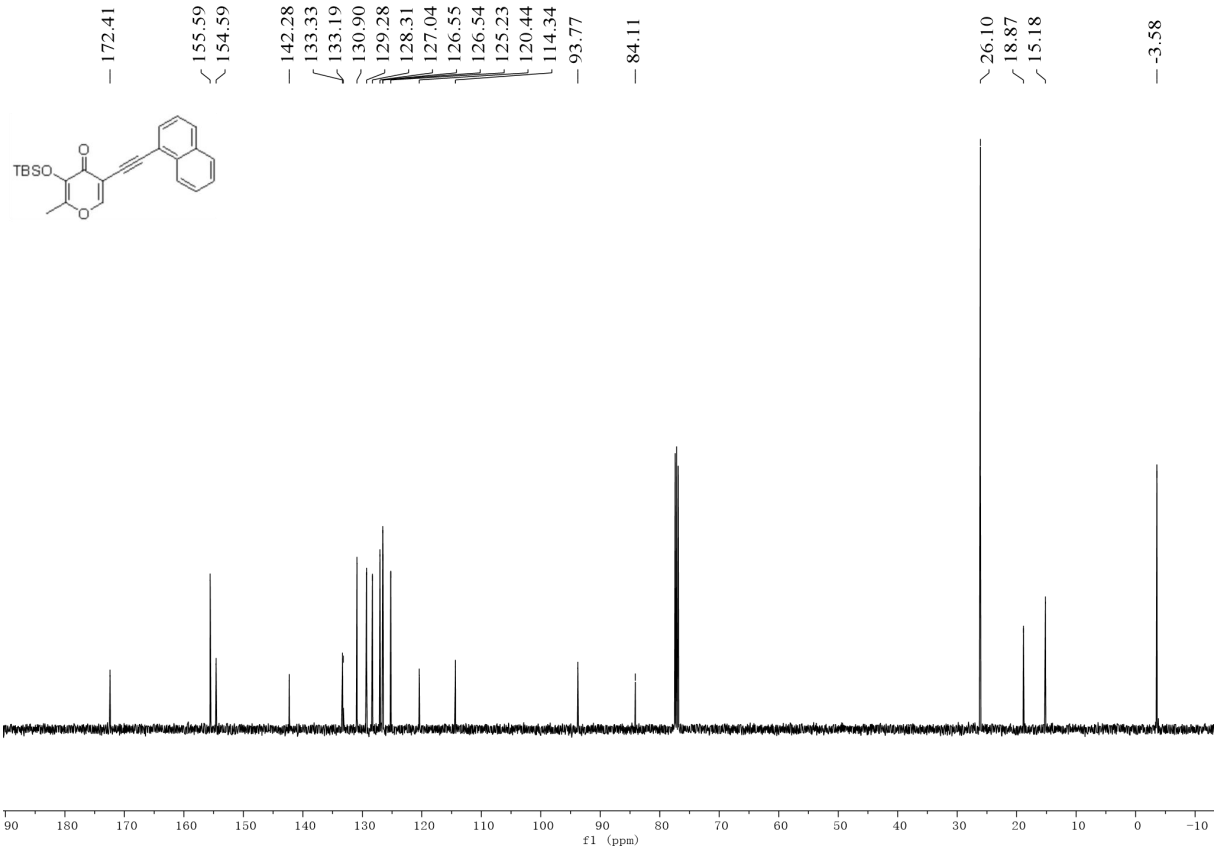
^{1}H and ^{13}C NMR spectra of 1g



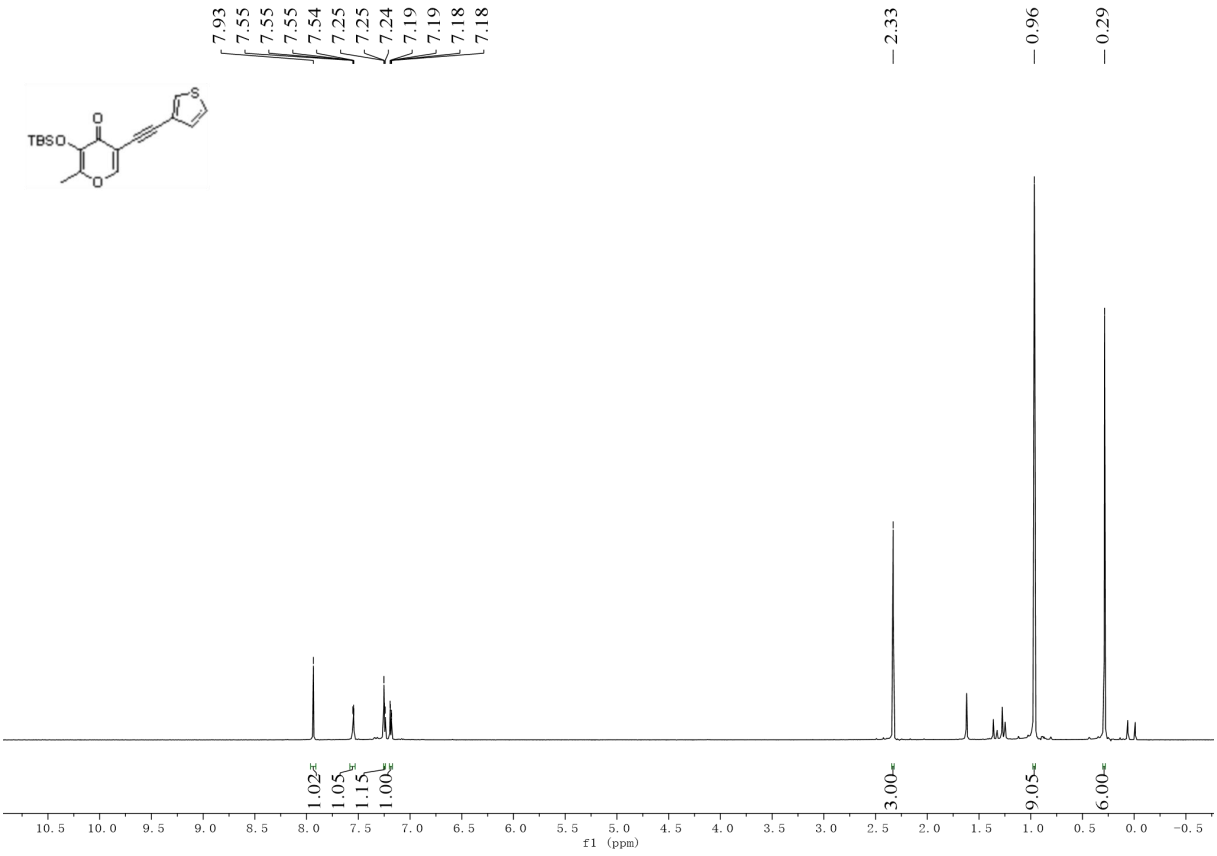


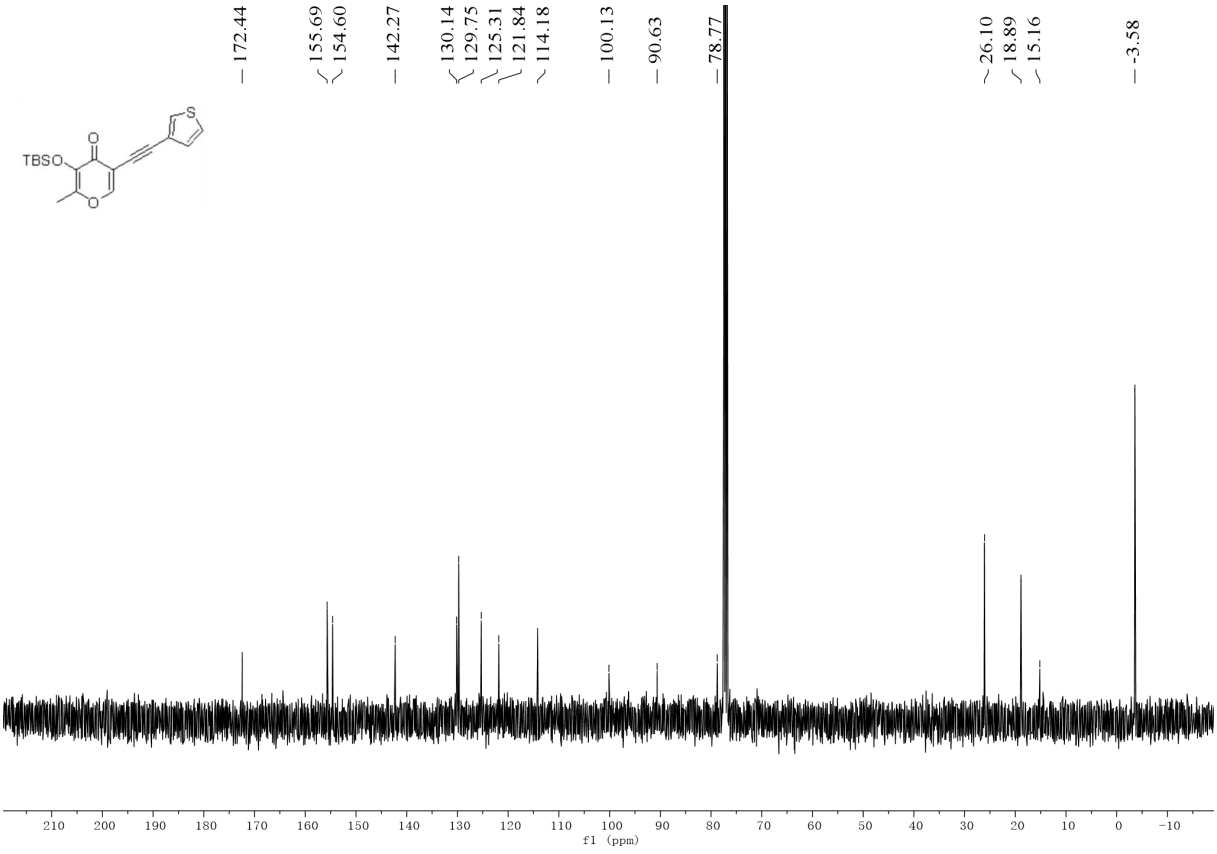
^{1}H and ^{13}C NMR spectra of 1h



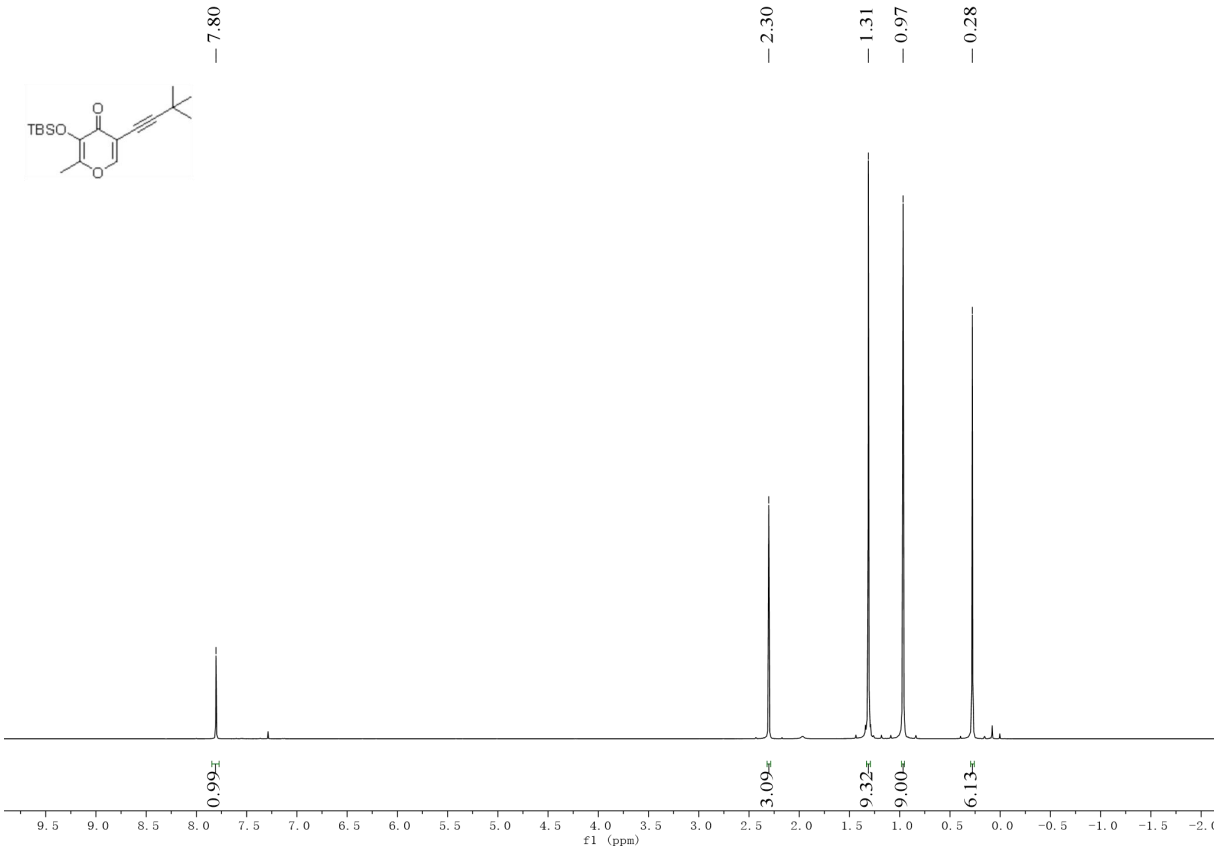


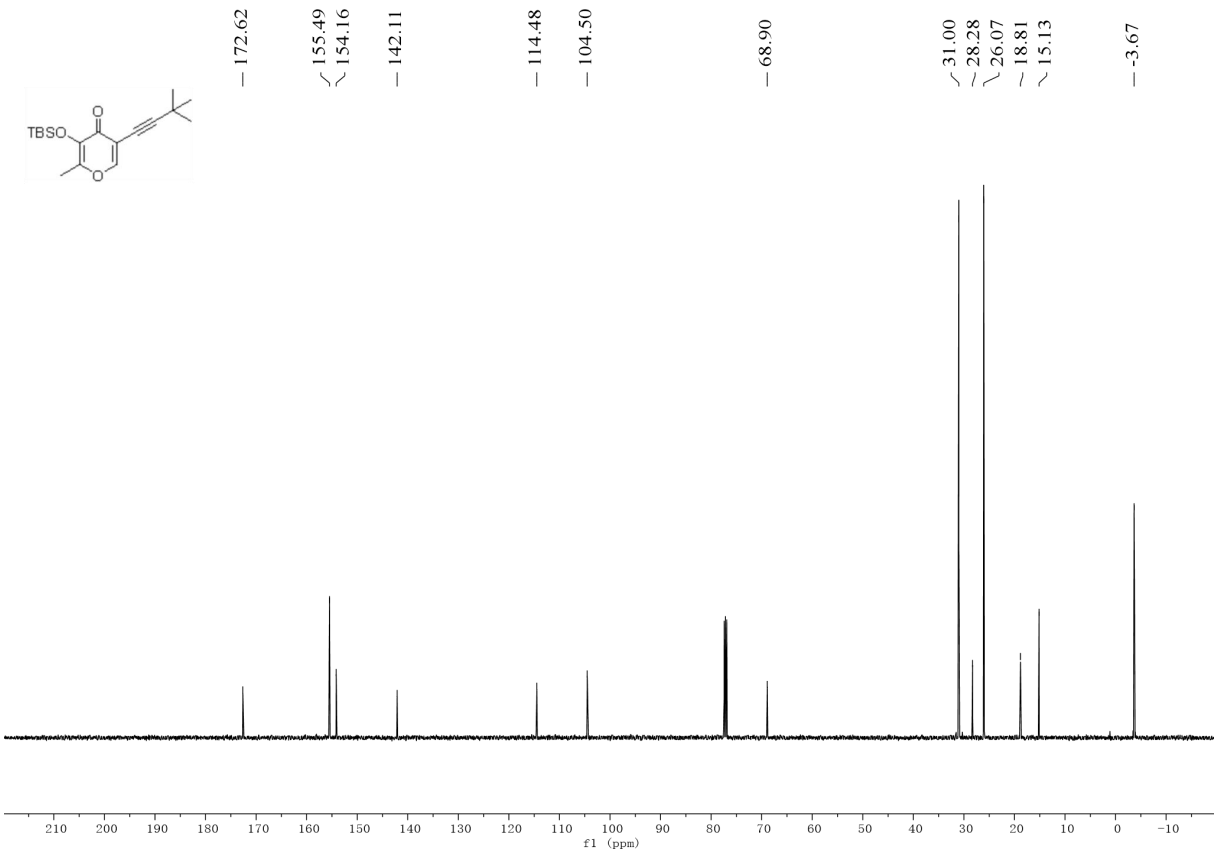
^{1}H and ^{13}C NMR spectra of 1i



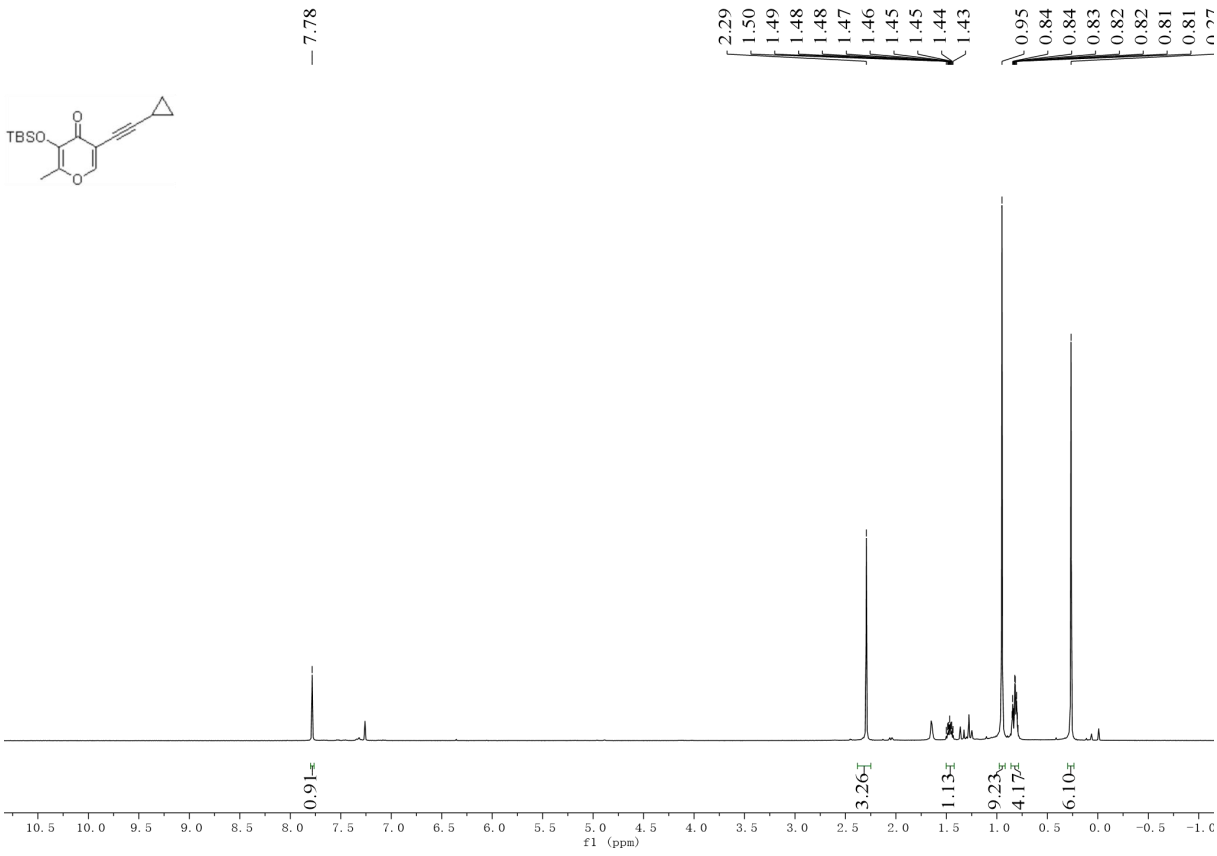


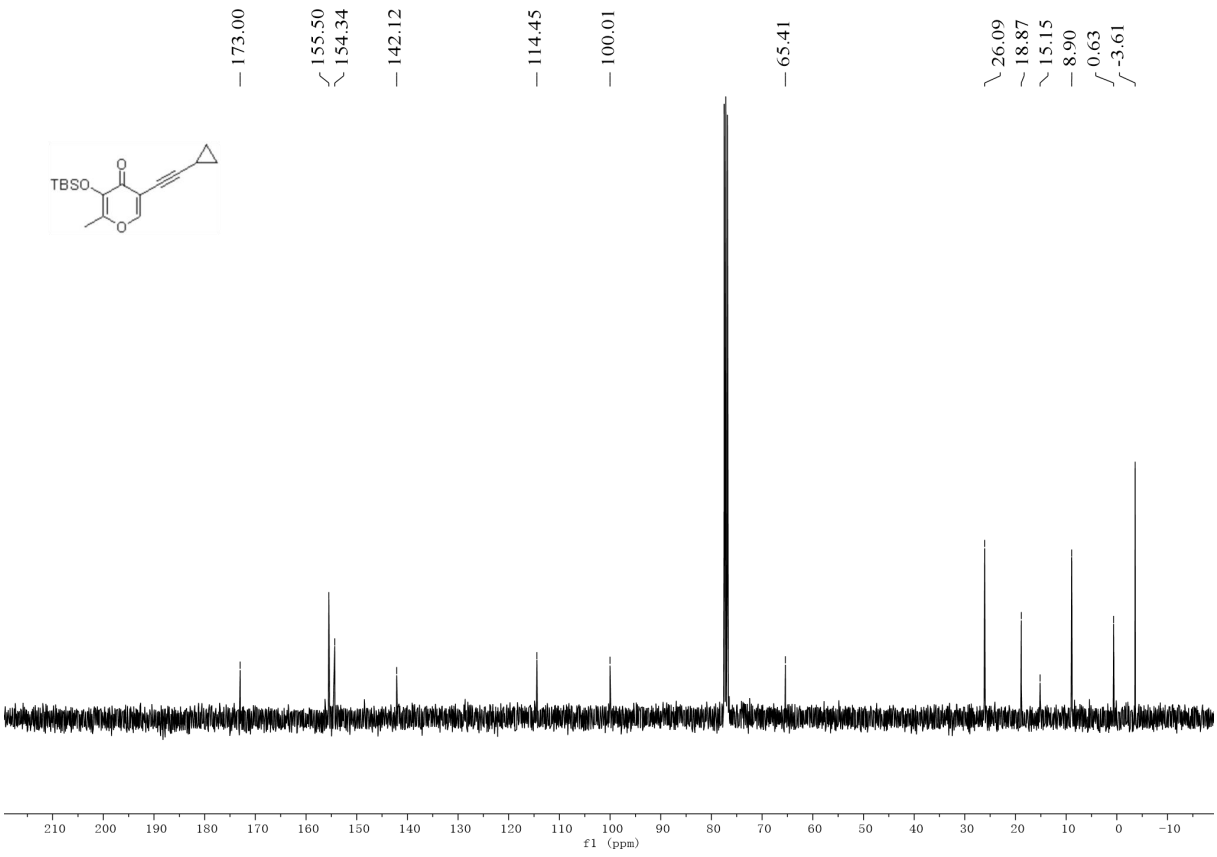
^{1}H and ^{13}C NMR spectra of 1j



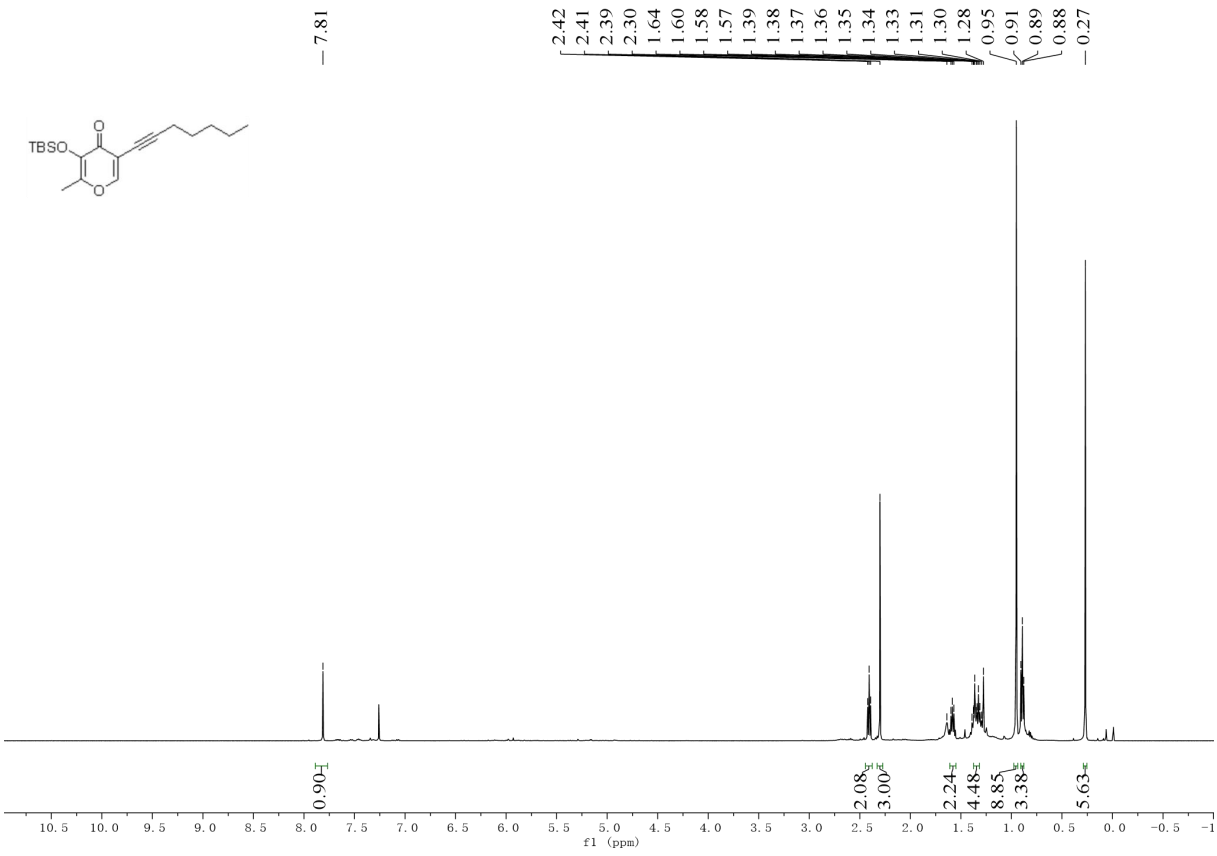


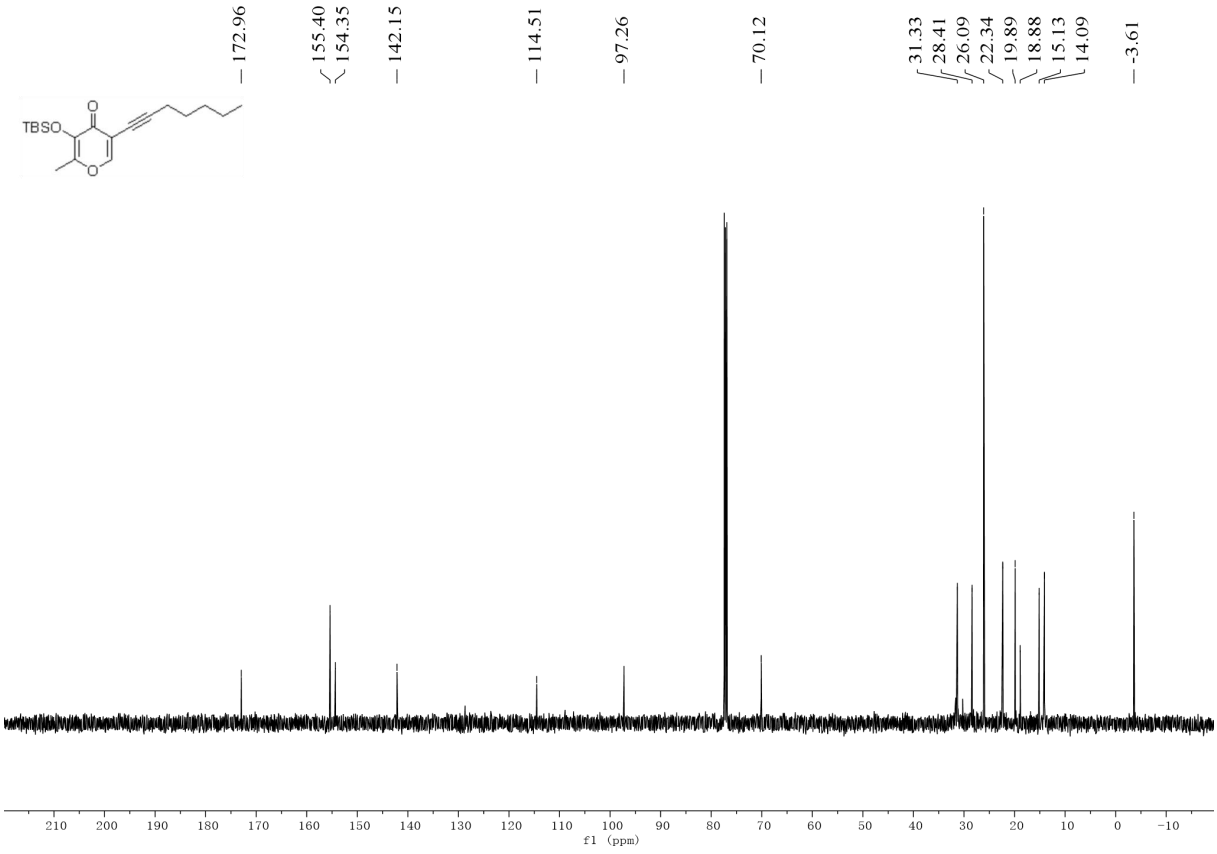
^{1}H and ^{13}C NMR spectra of 1k



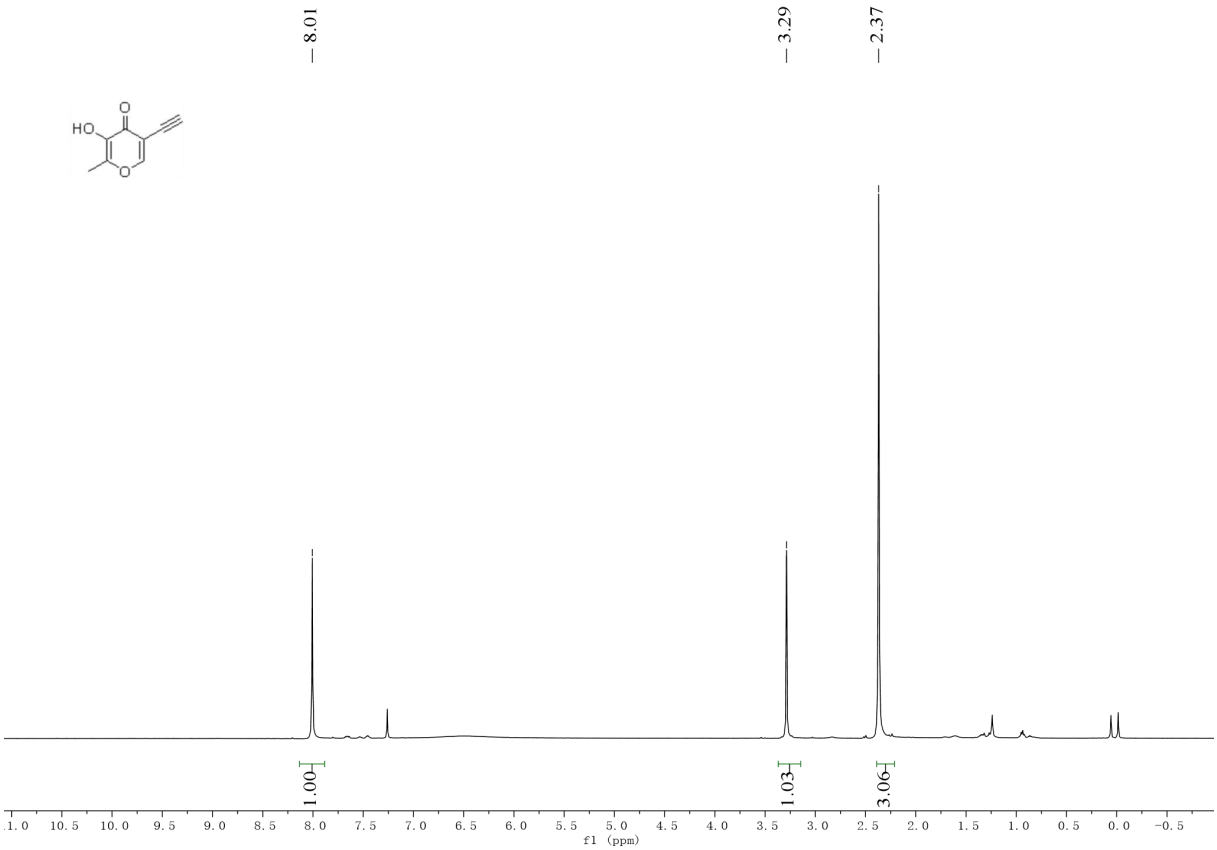


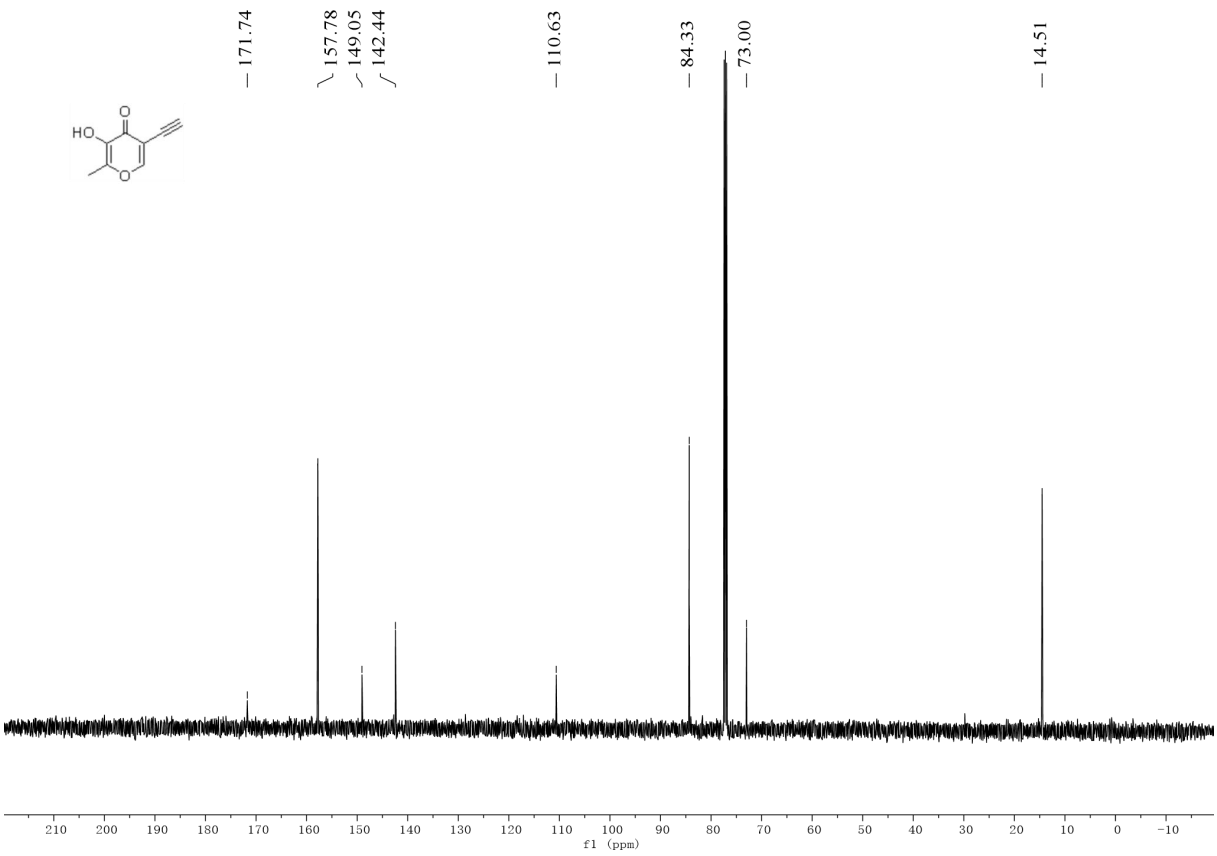
^{1}H and ^{13}C NMR spectra of 1l



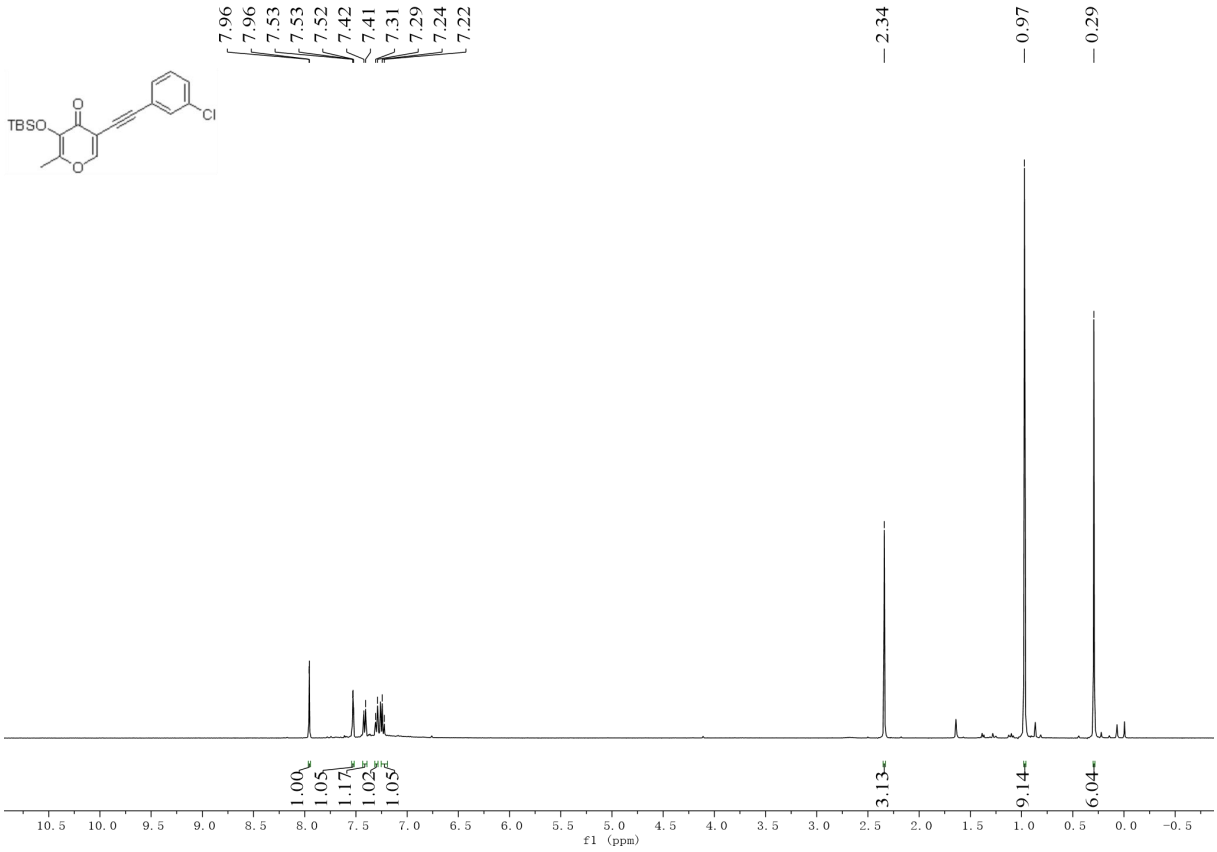


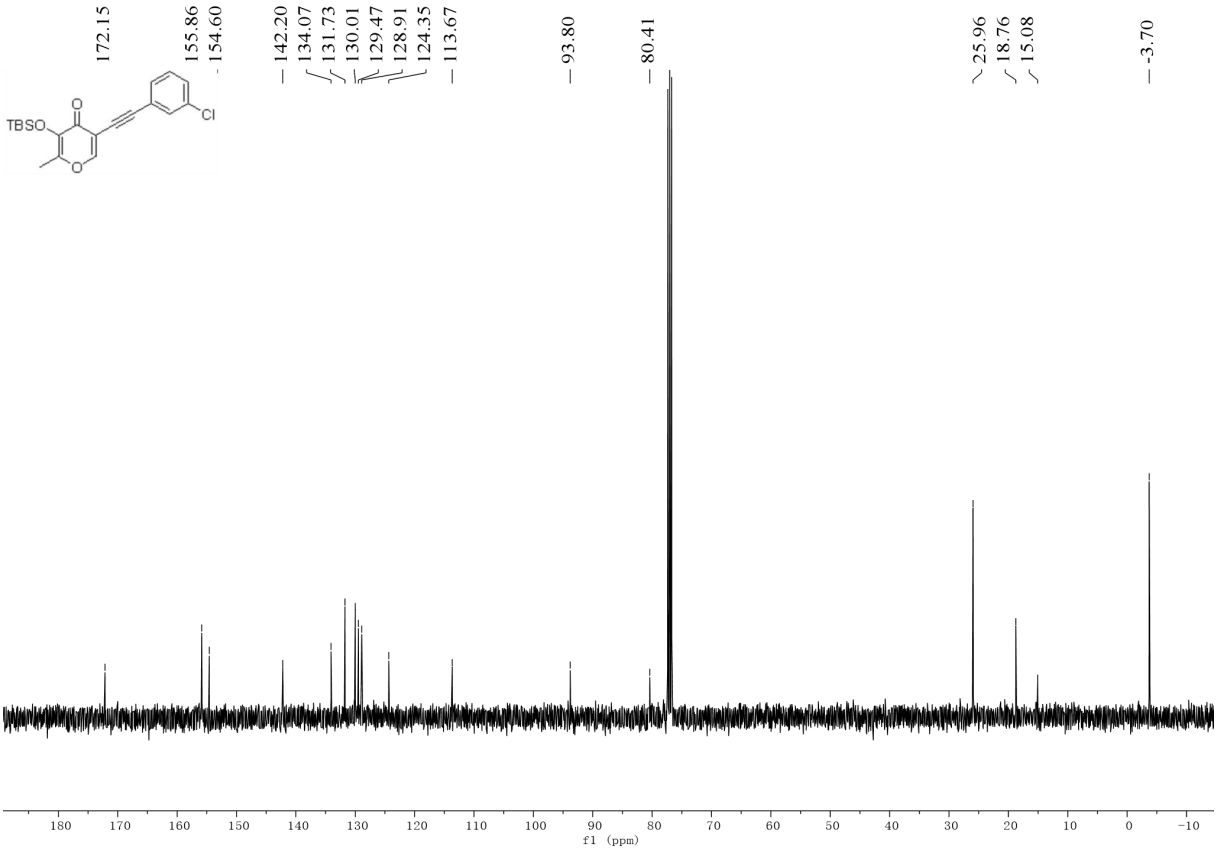
^{1}H and ^{13}C NMR spectra of 1m



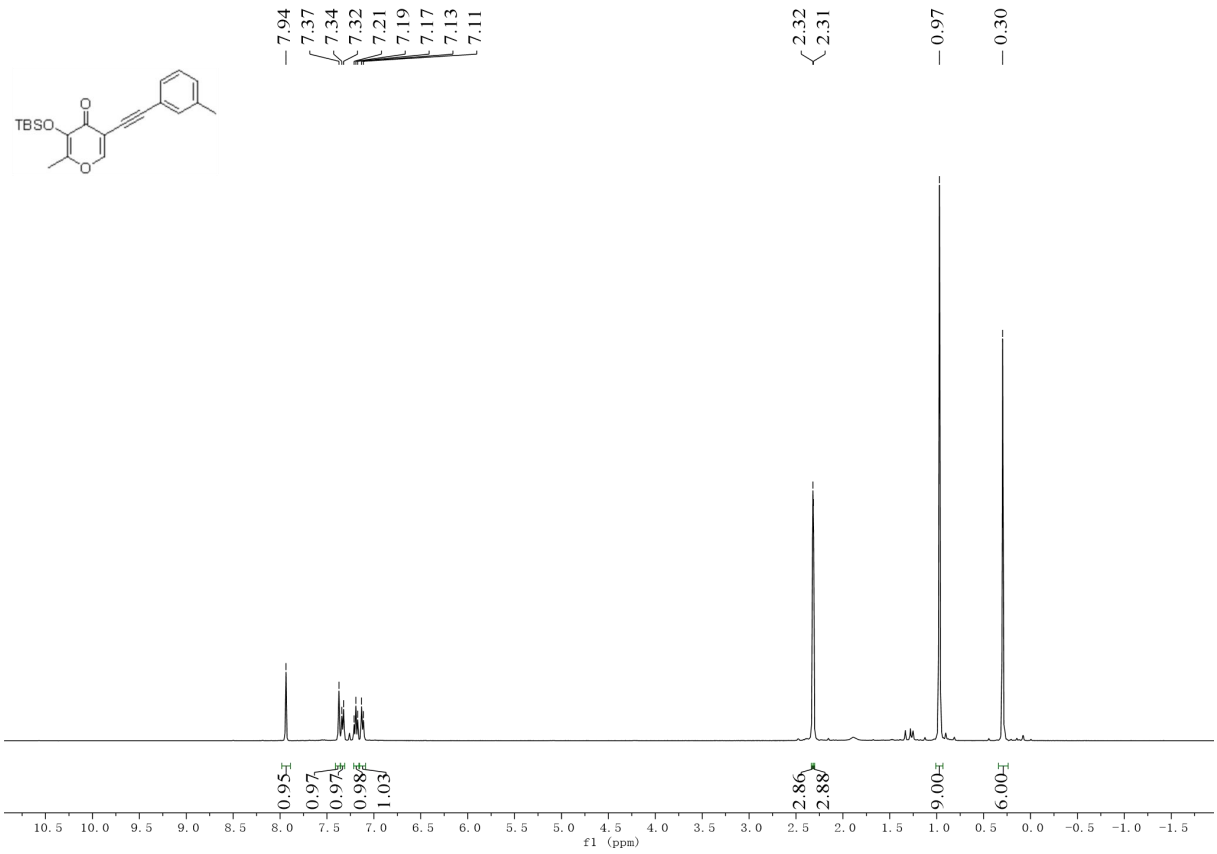


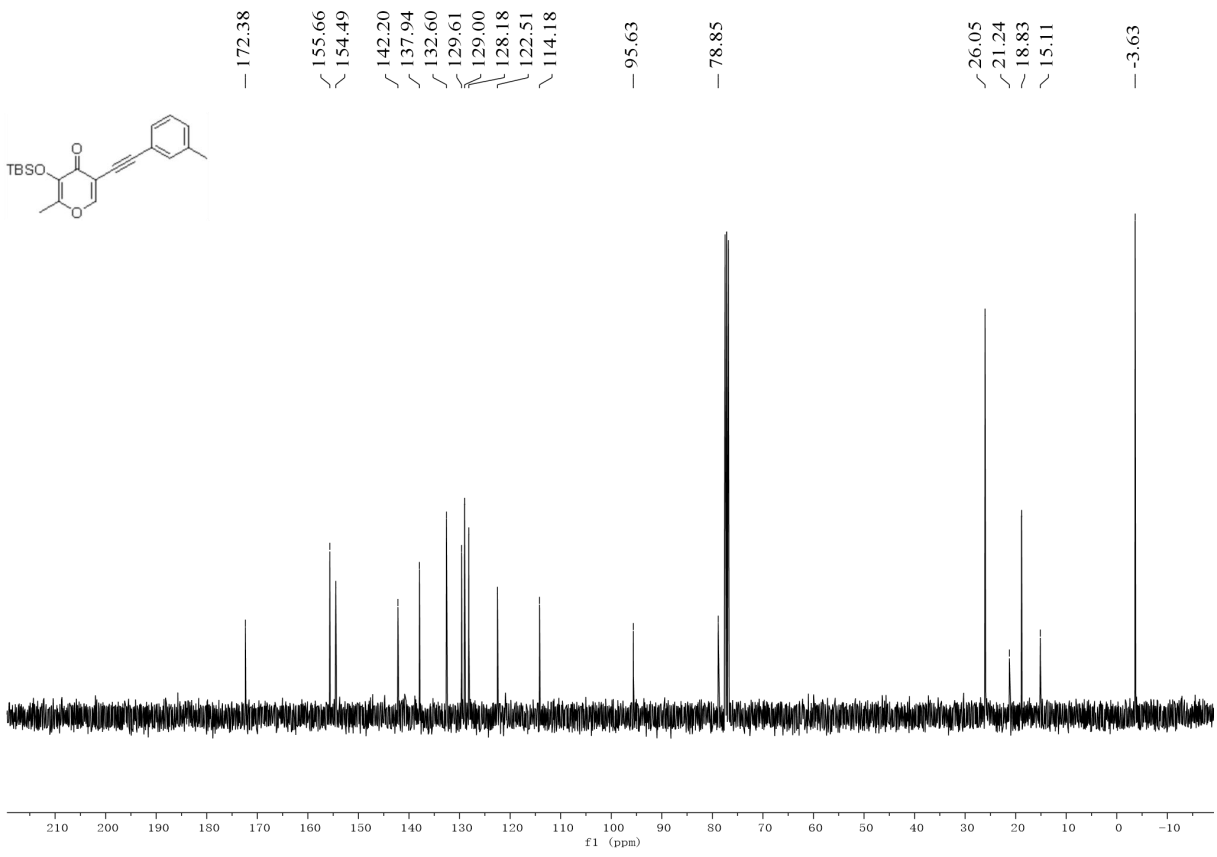
^{1}H and ^{13}C NMR spectra of 1n



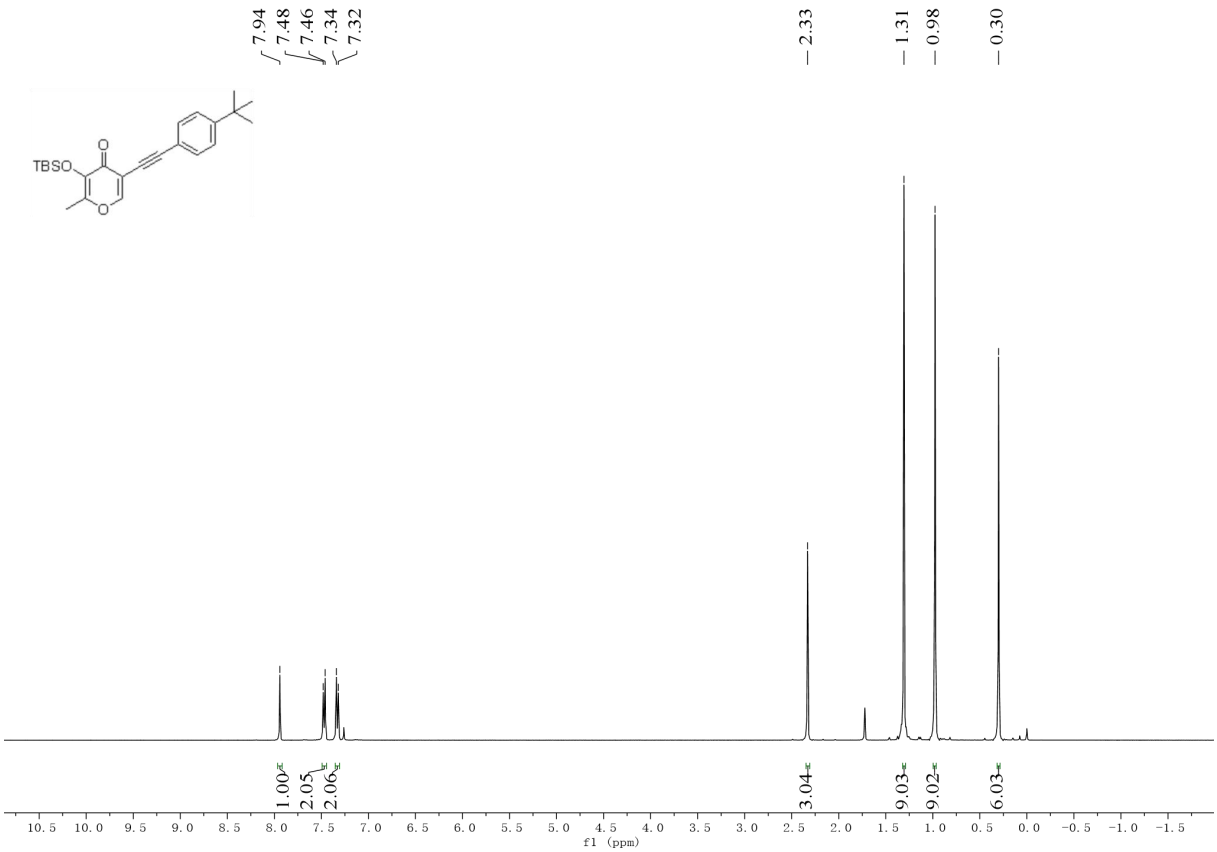


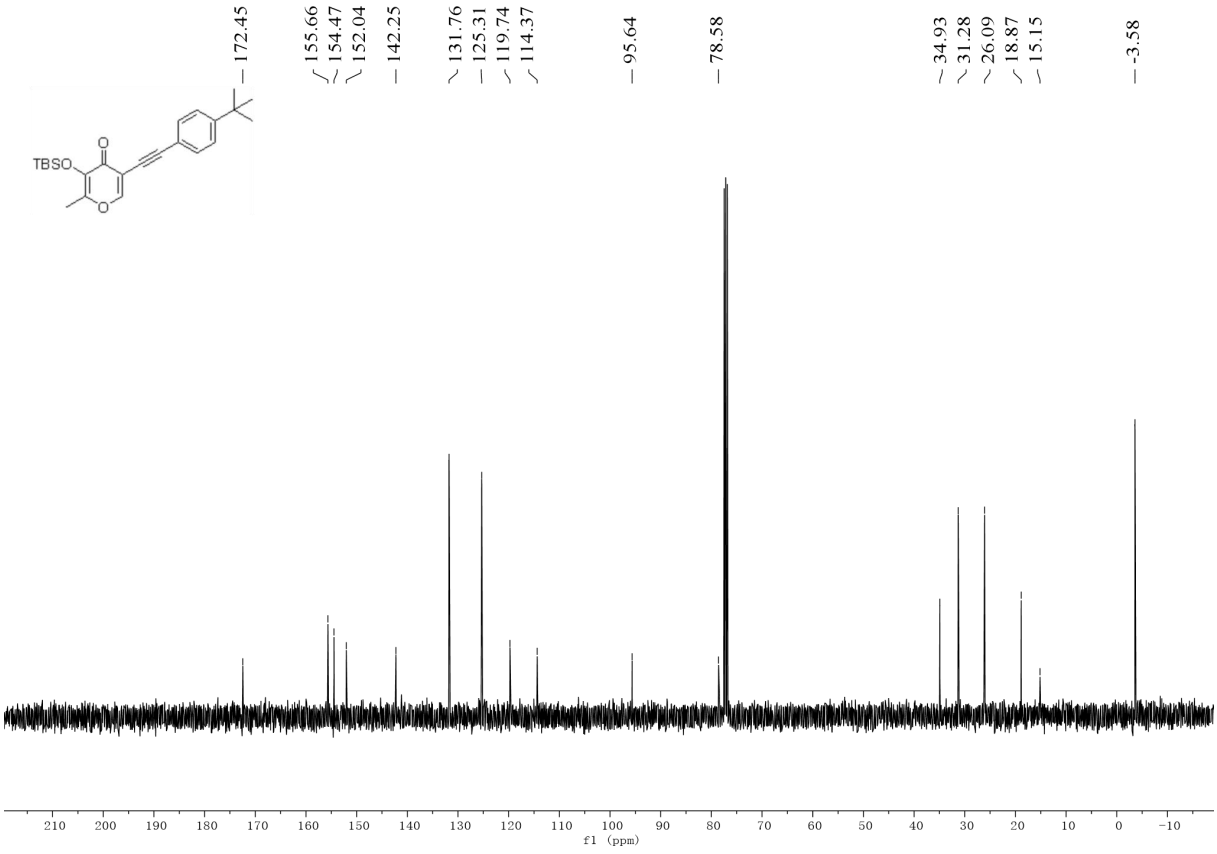
^{1}H and ^{13}C NMR spectra of 1o



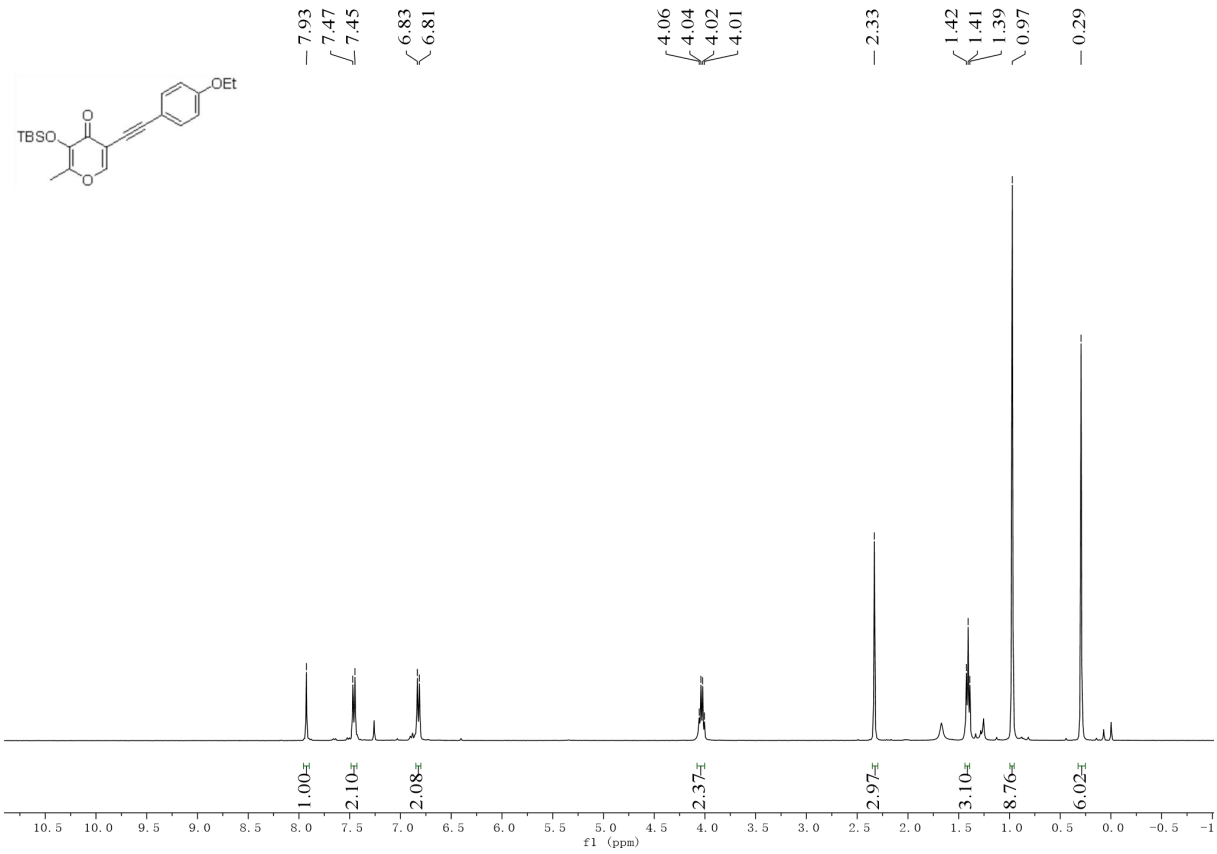


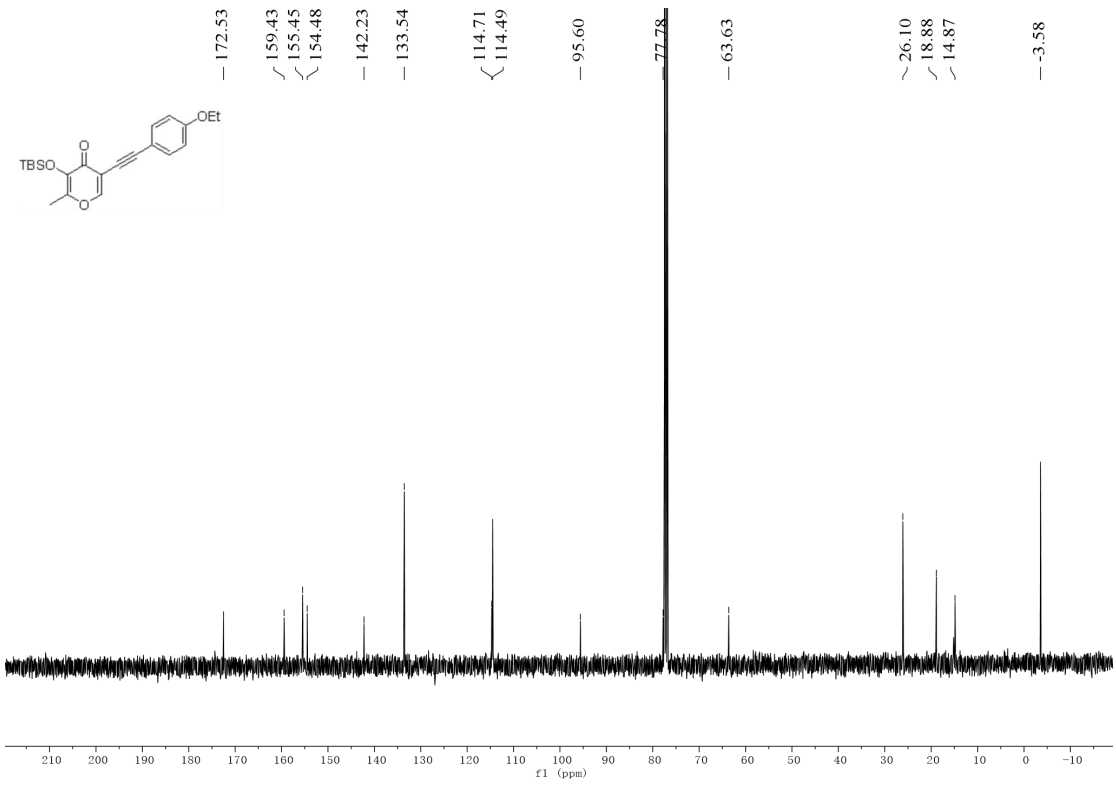
^{1}H and ^{13}C NMR spectra of 1p



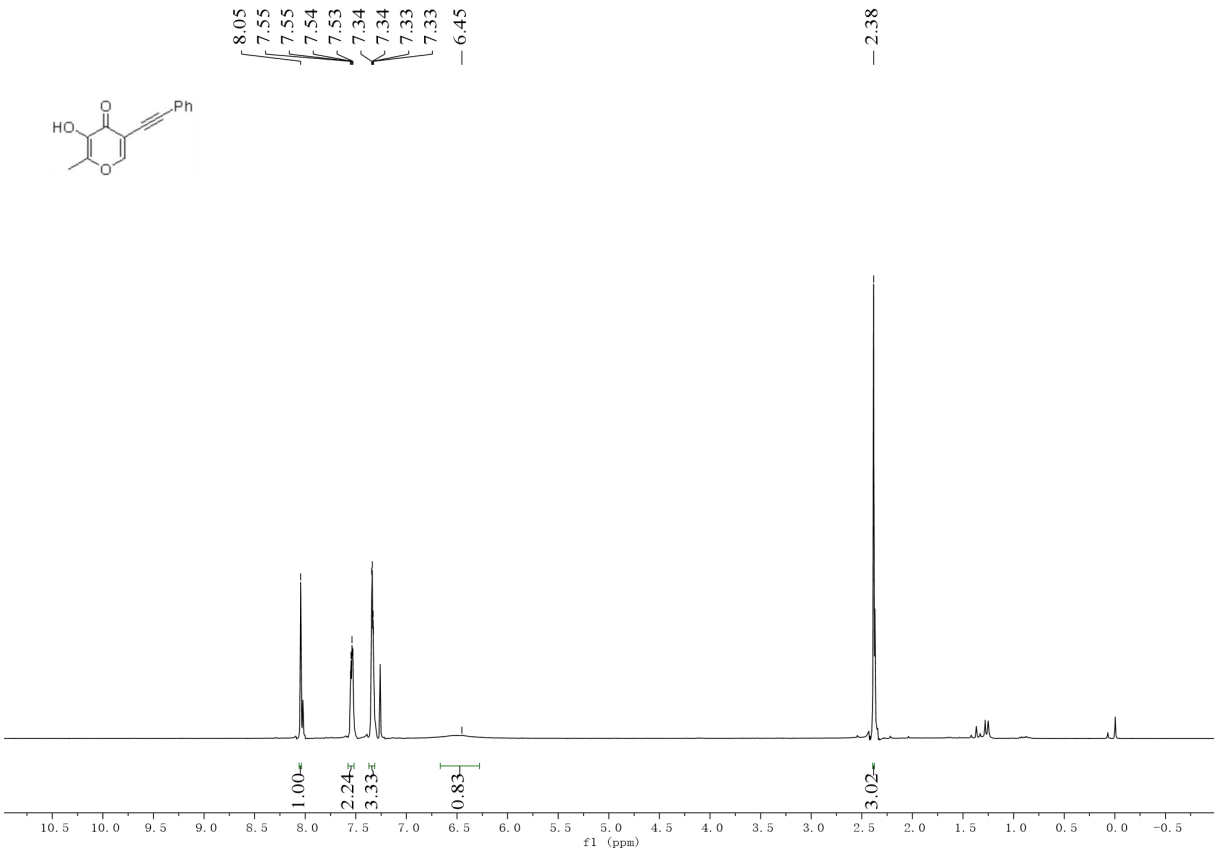


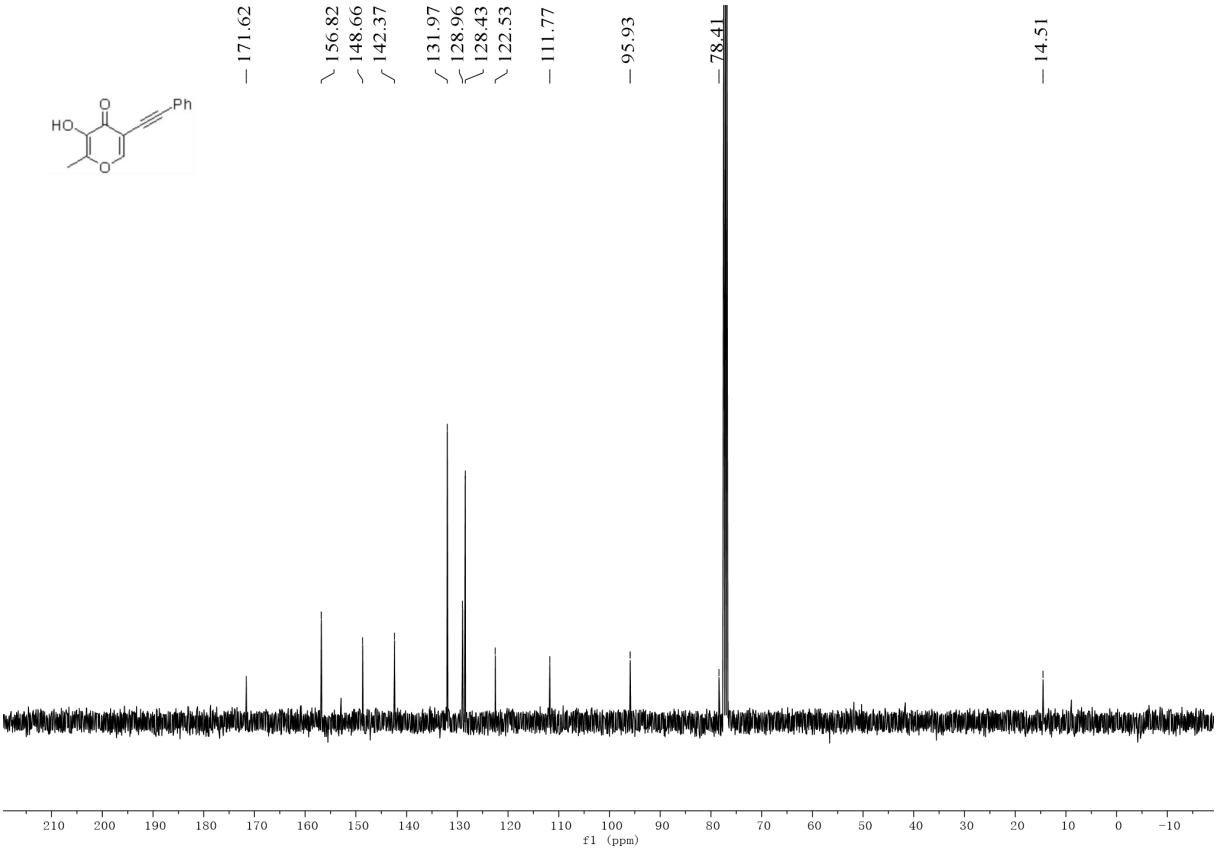
^{1}H and ^{13}C NMR spectra of 1q



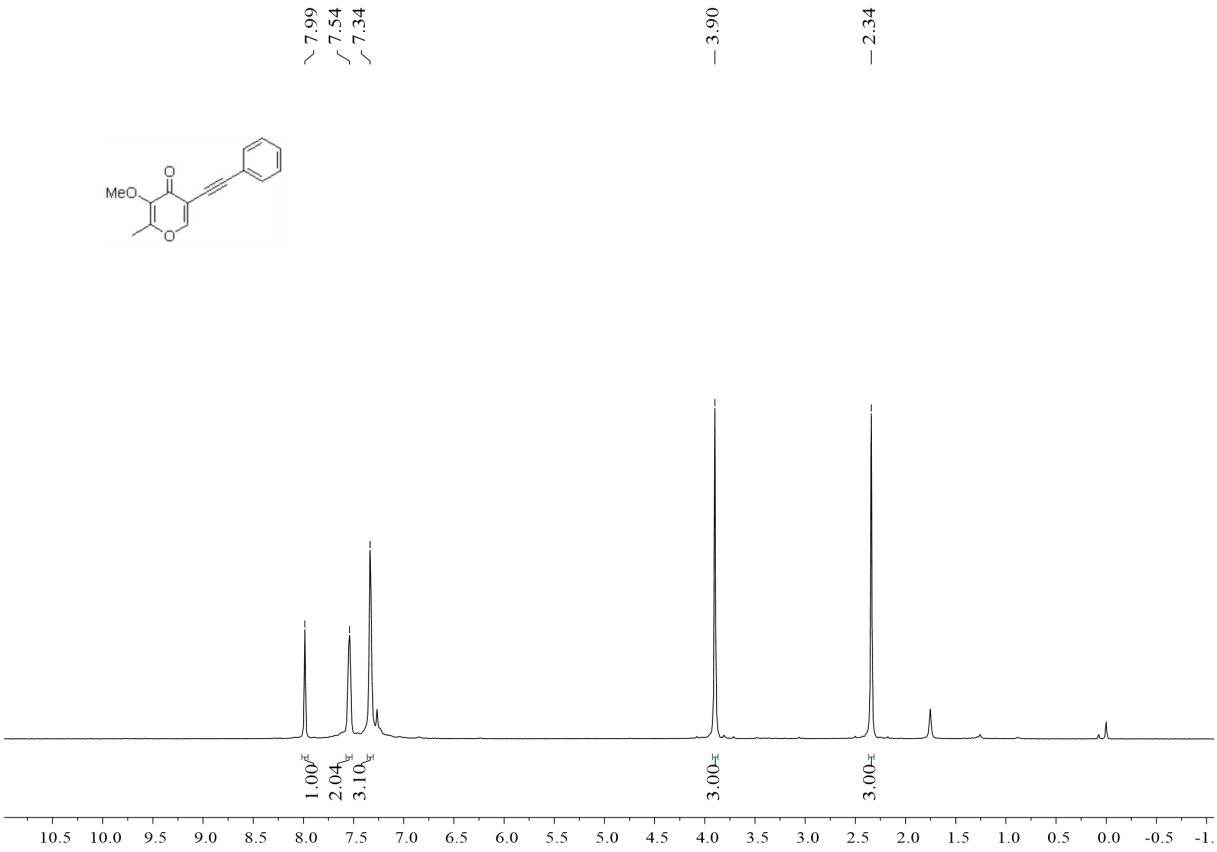


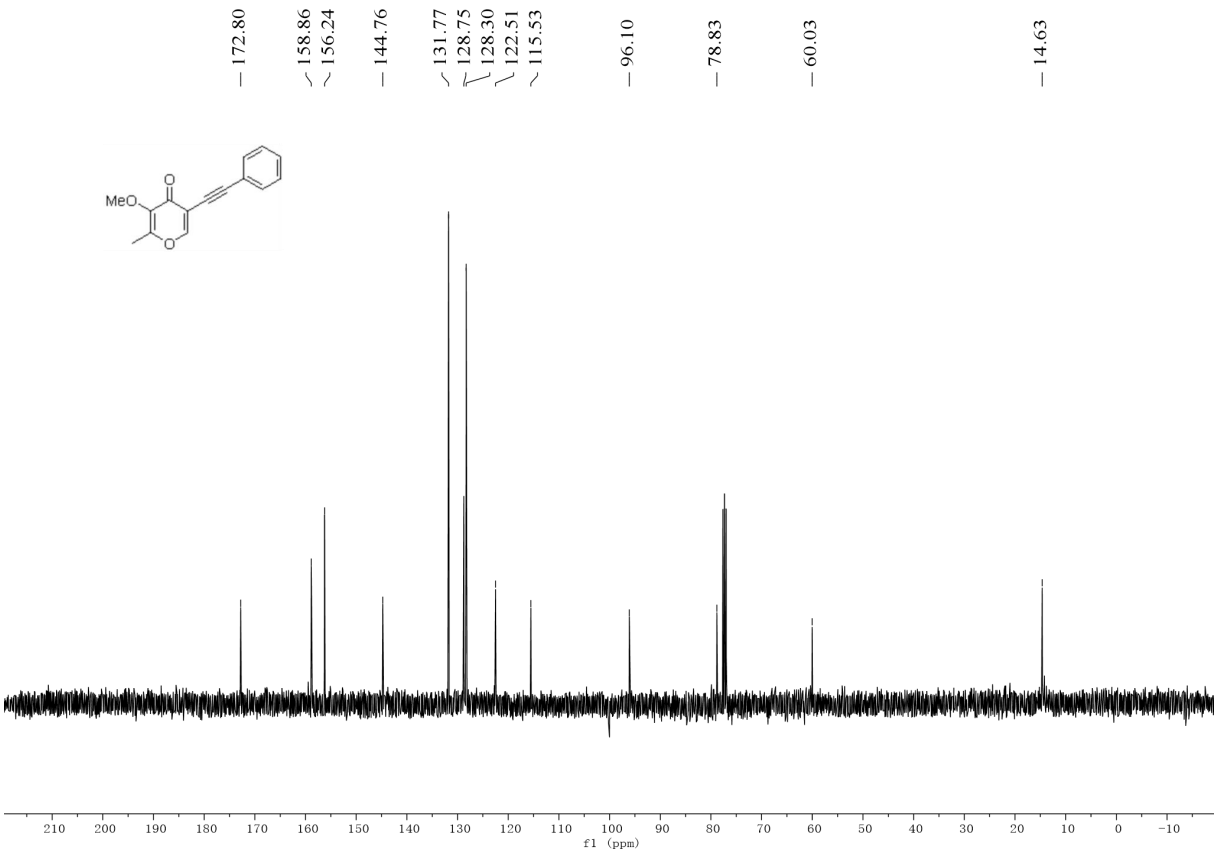
^{1}H and ^{13}C NMR spectra of 1r



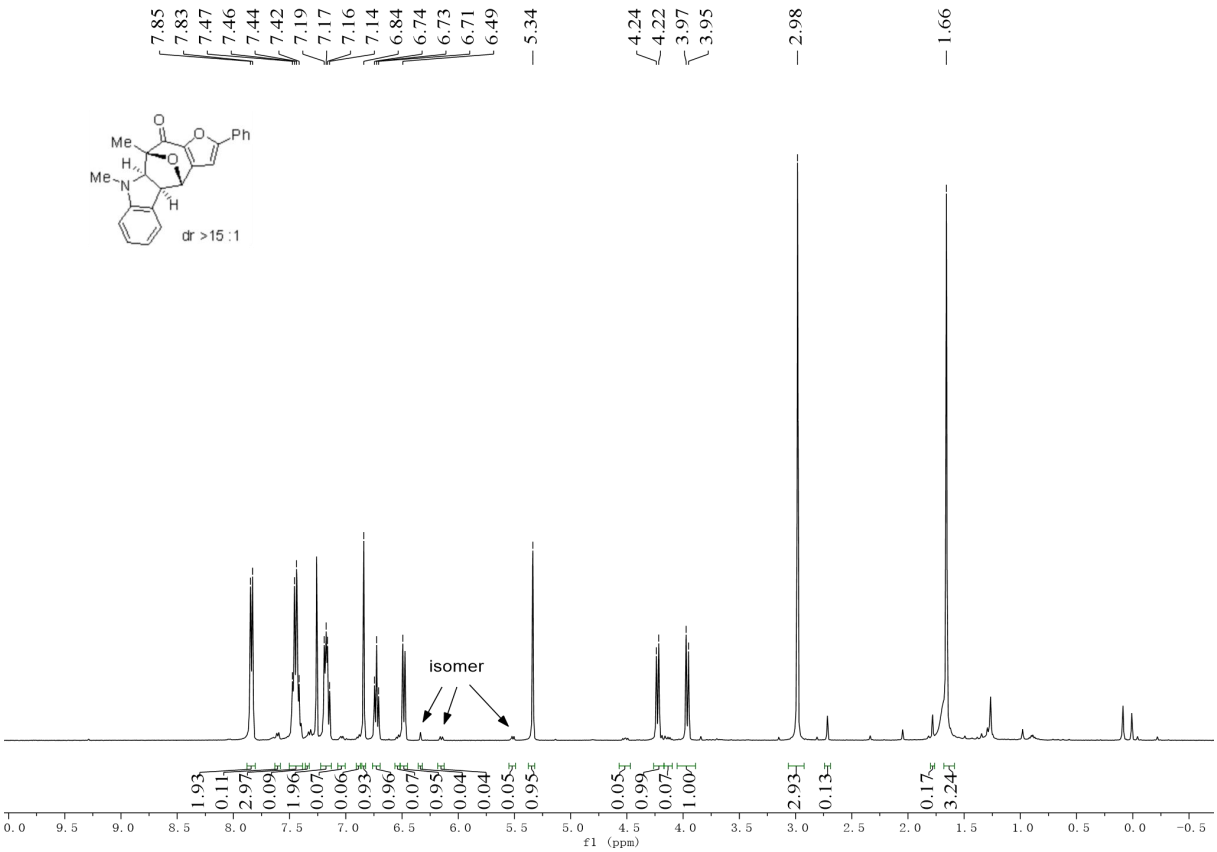


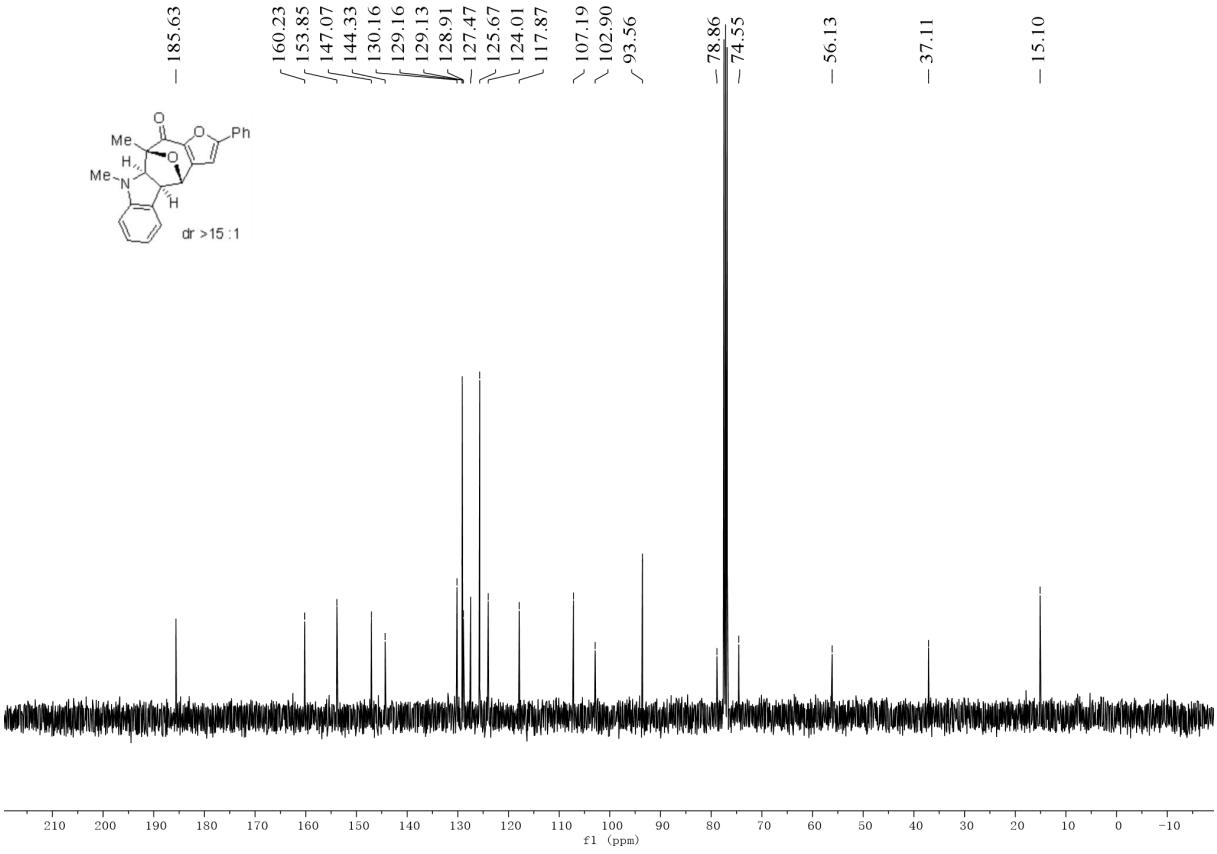
^{1}H and ^{13}C NMR spectra of 1s



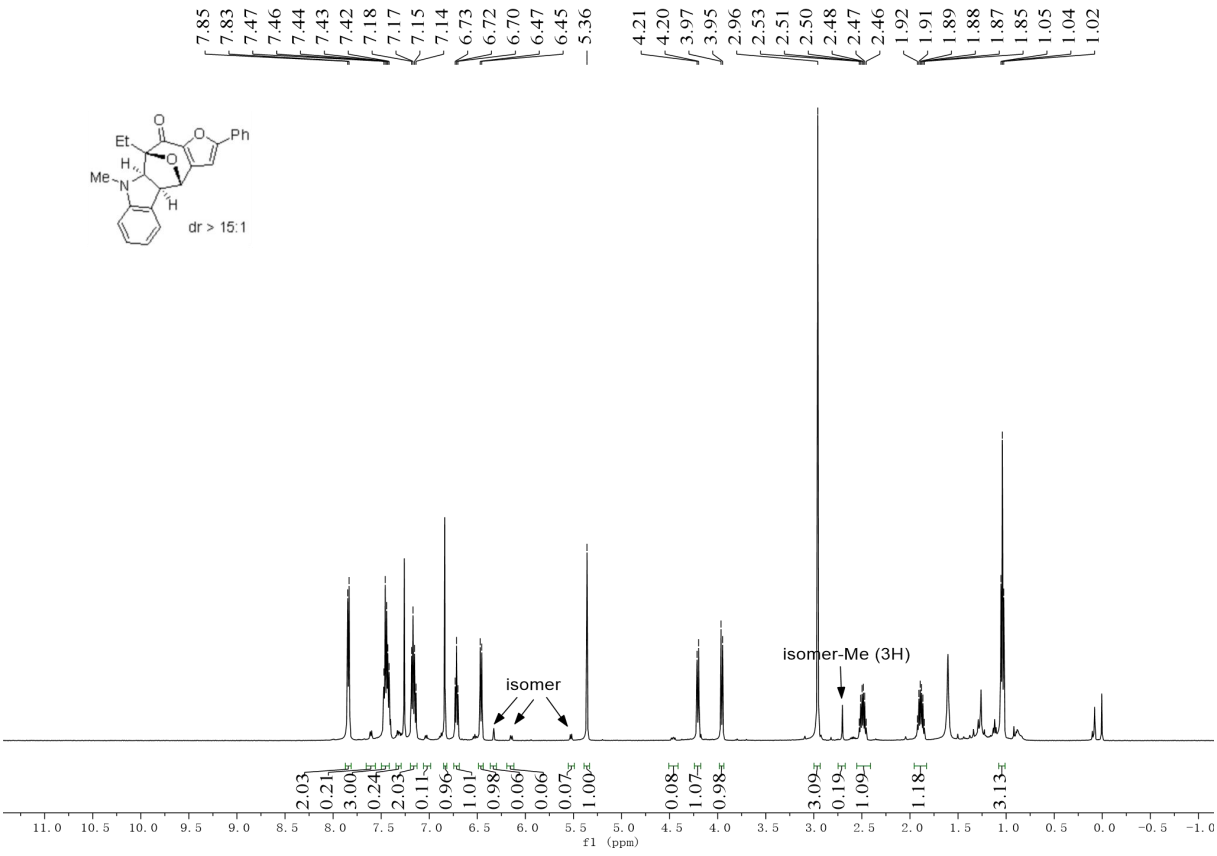


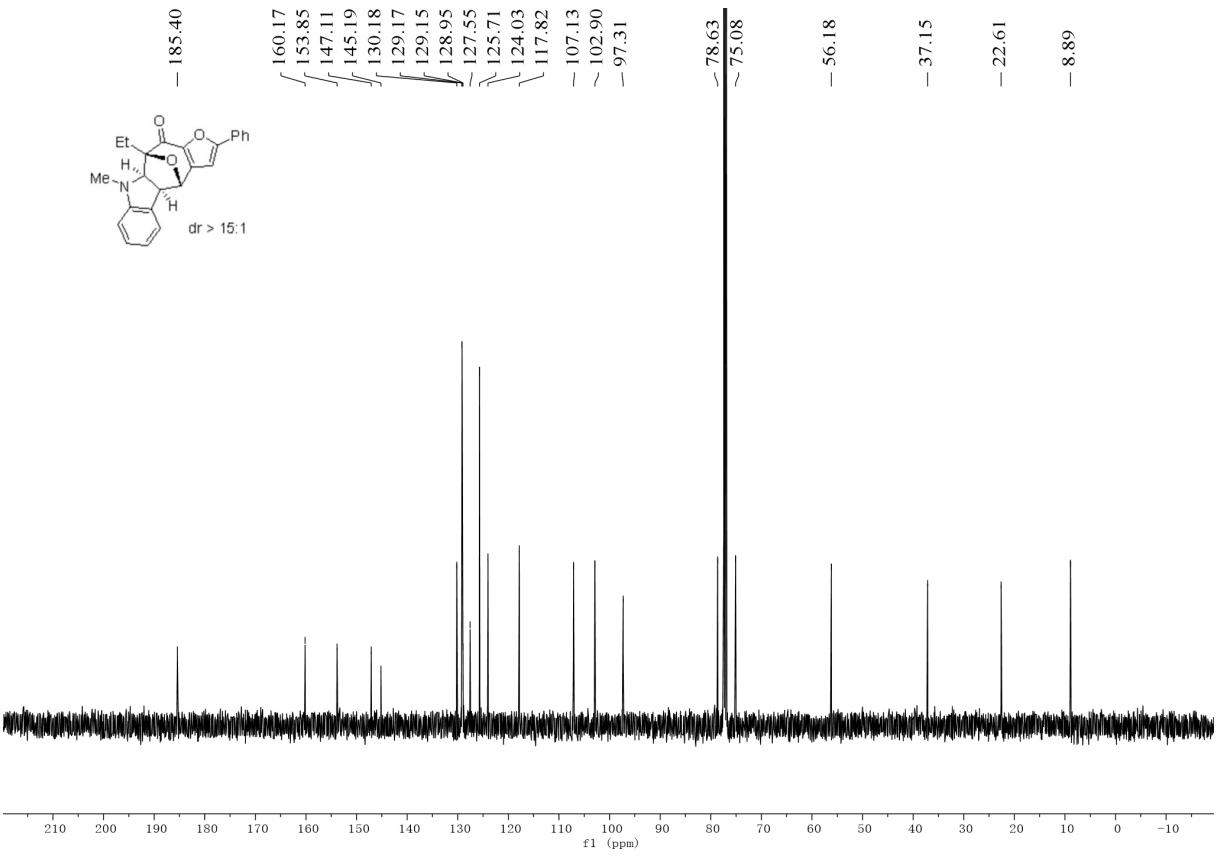
^{1}H and ^{13}C NMR spectra of 3aa



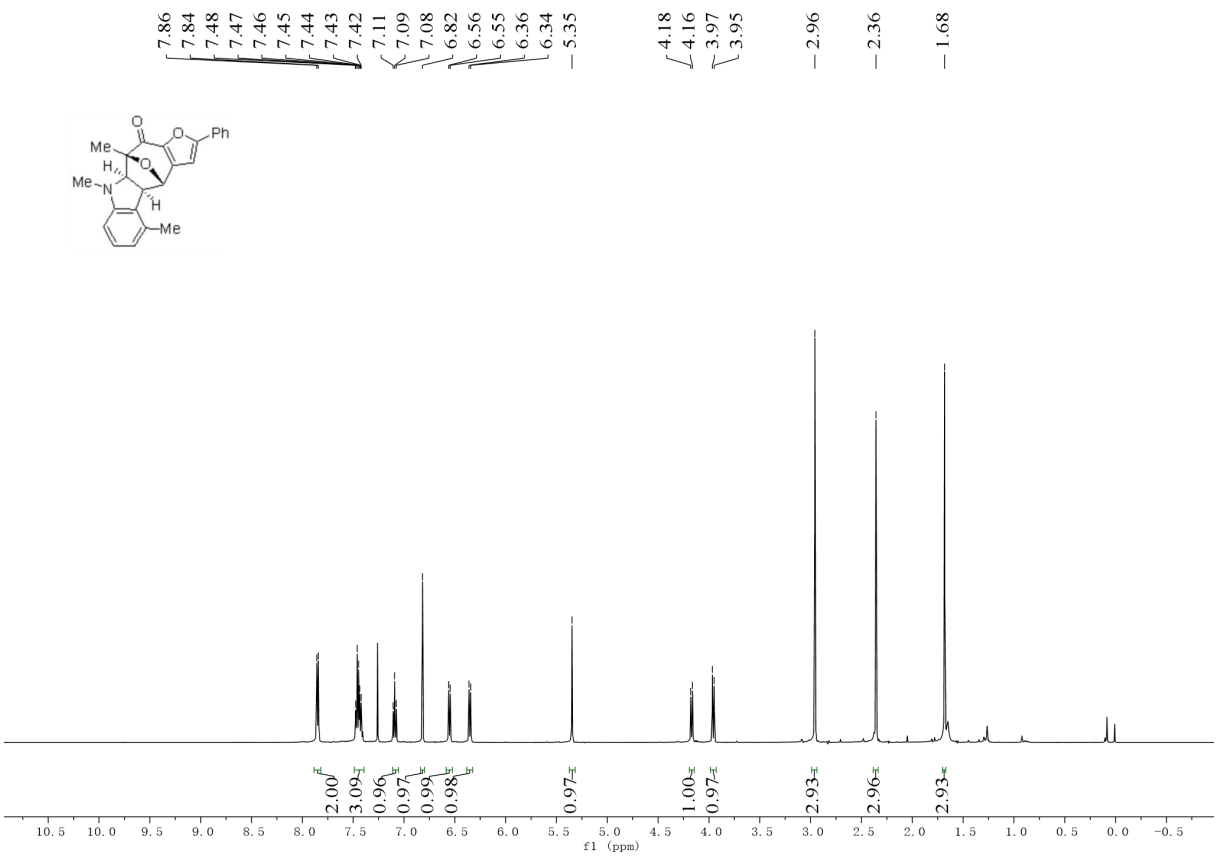


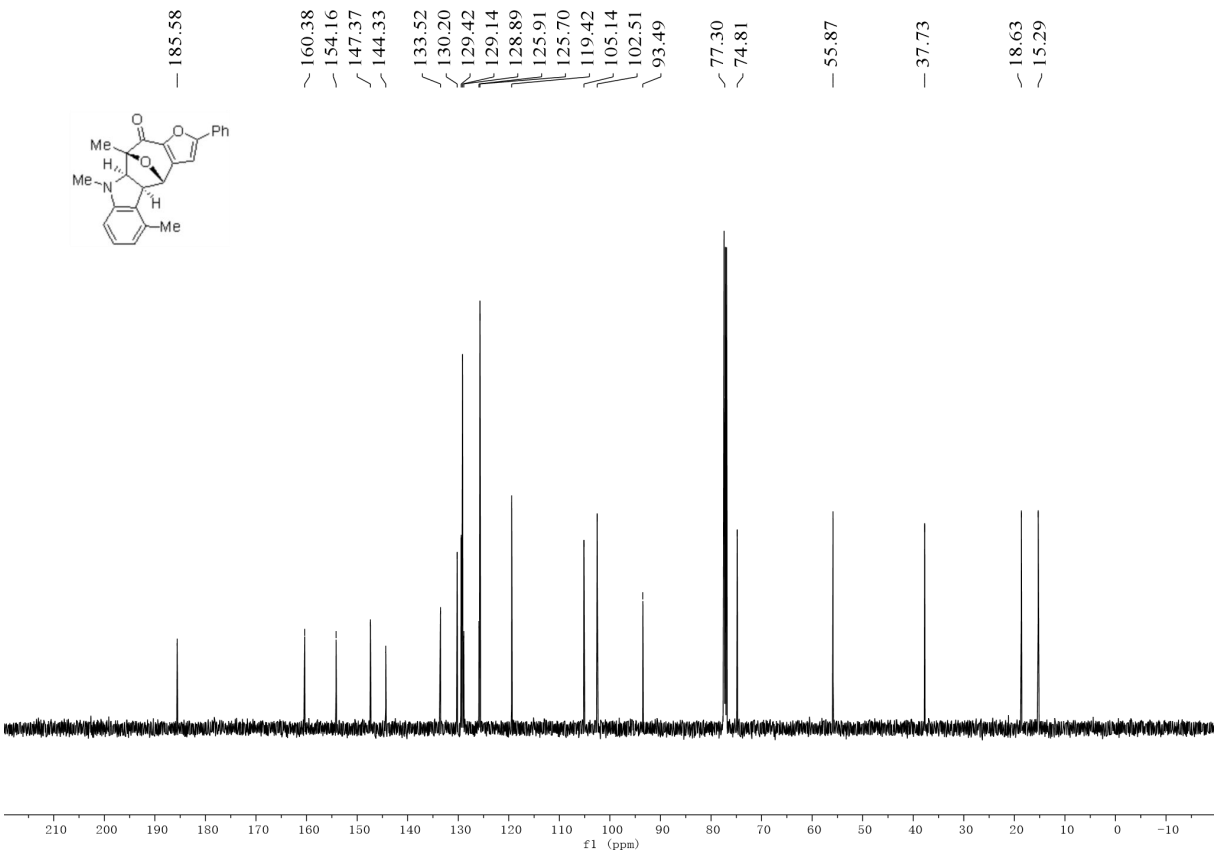
^{1}H and ^{13}C NMR spectra of 3ba



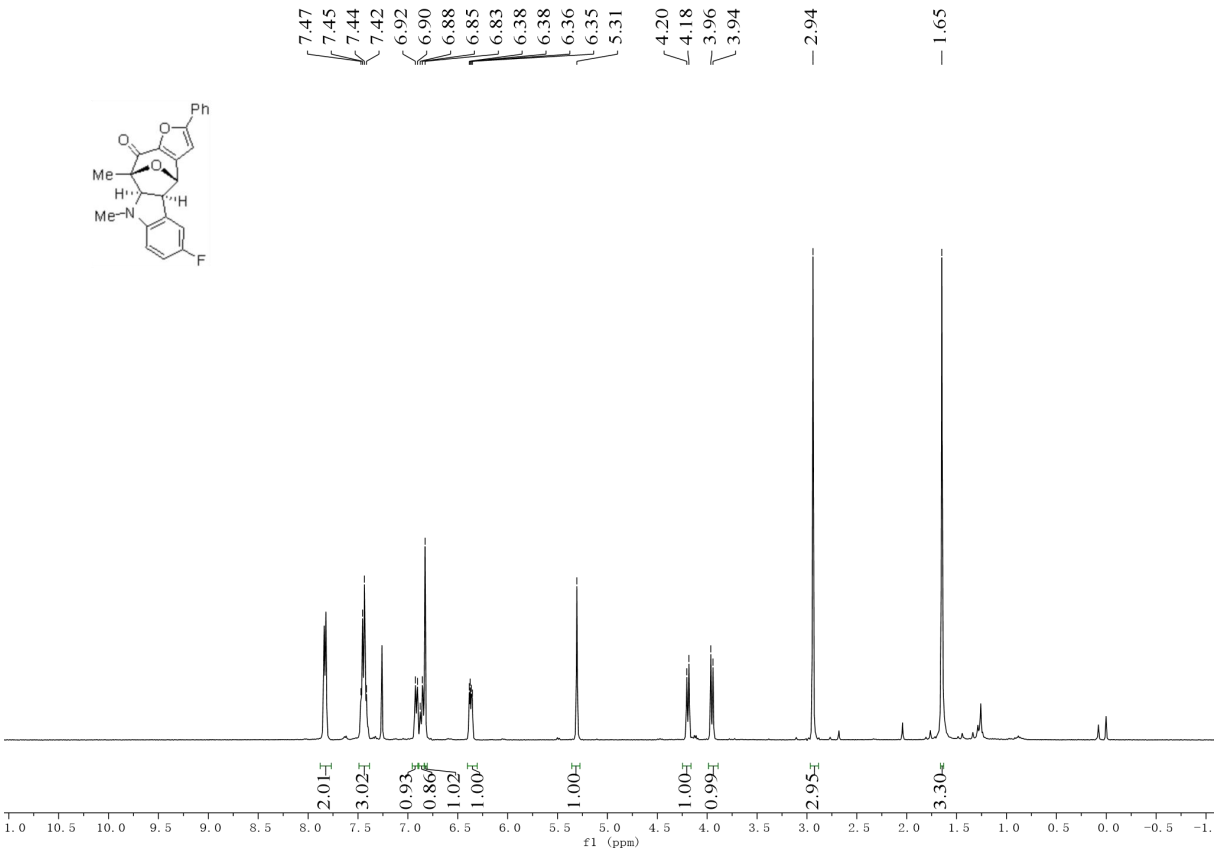


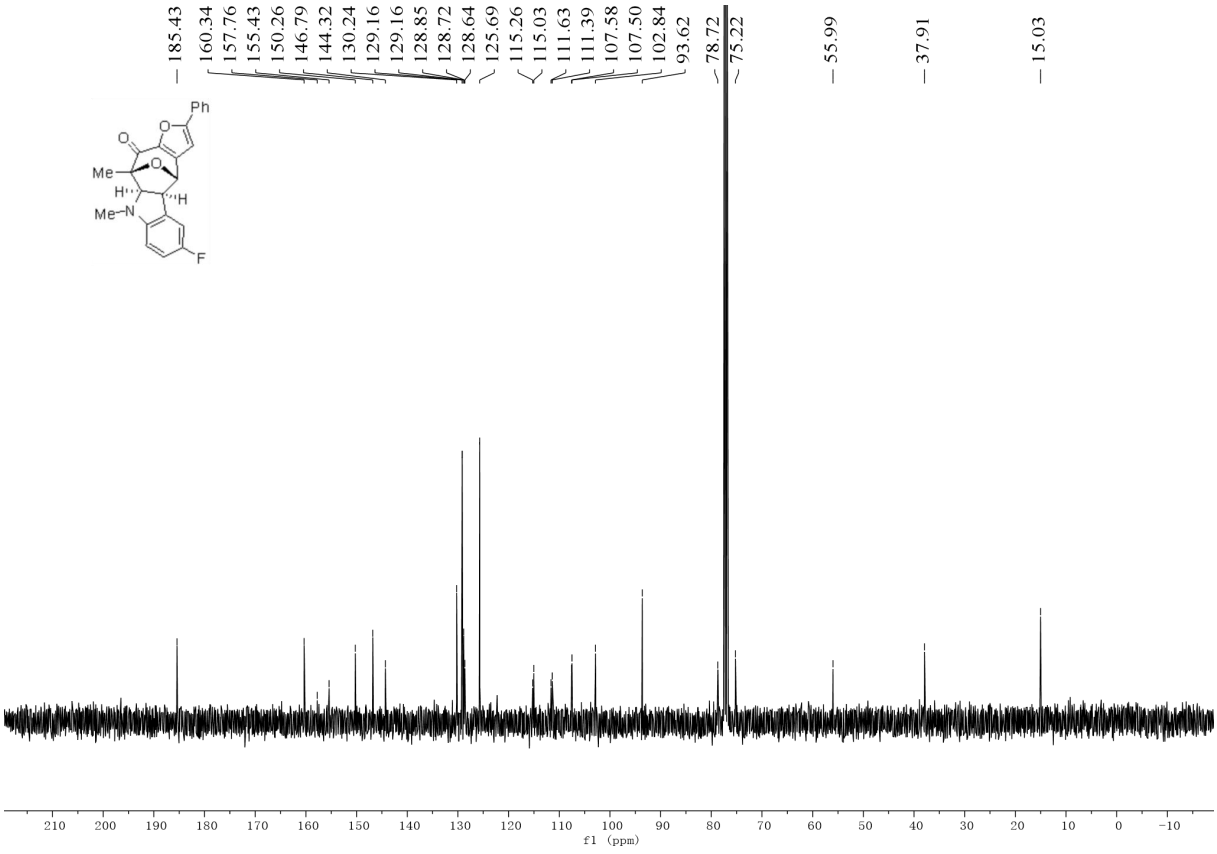
^{1}H and ^{13}C NMR spectra of 3ab



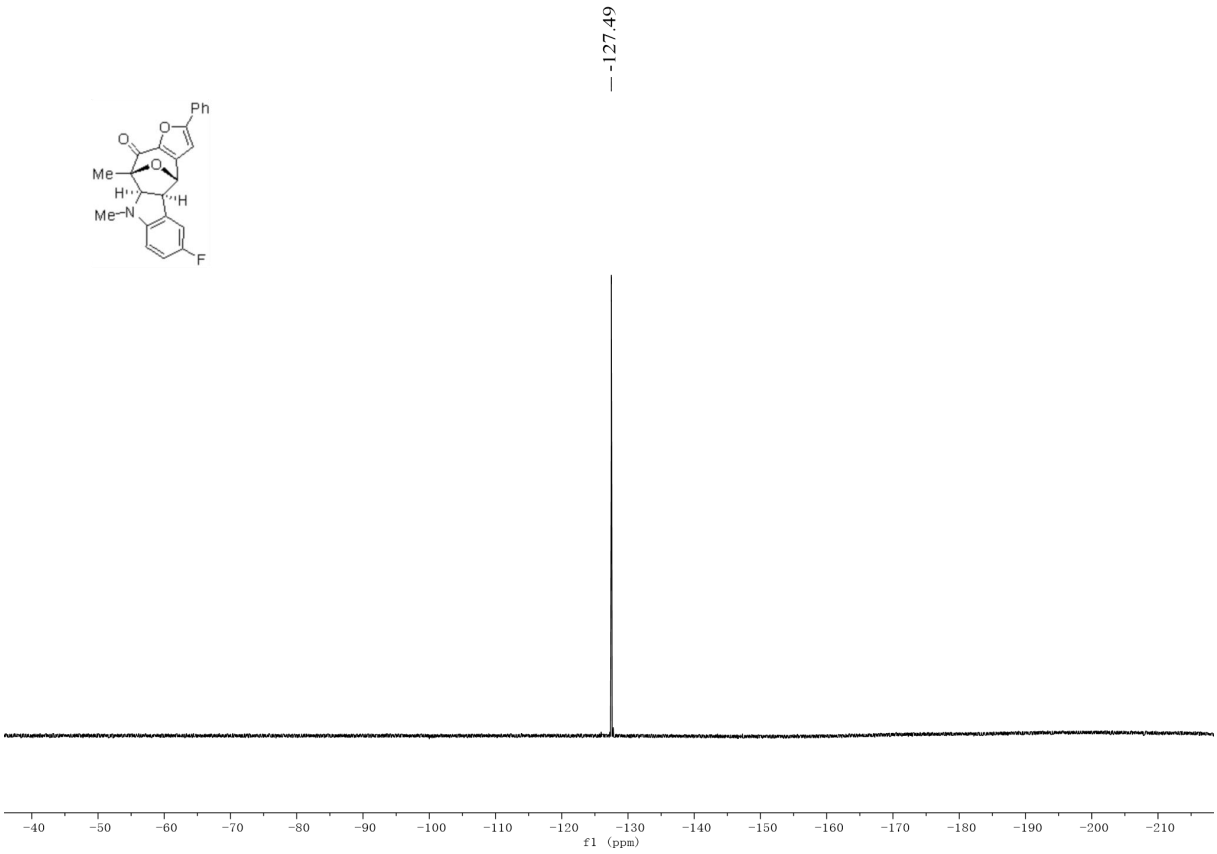


^{1}H and ^{13}C NMR and $^{19}FNMR$ spectra of 3ac

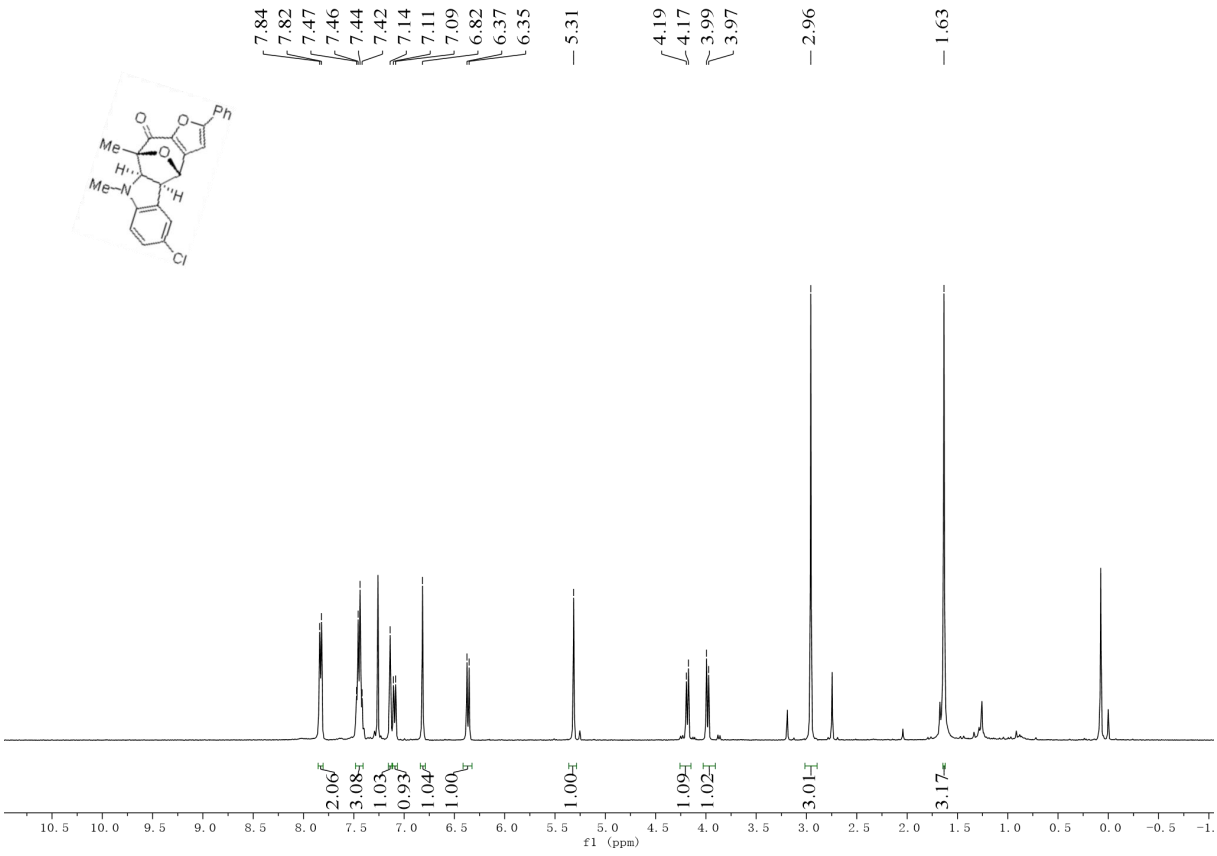


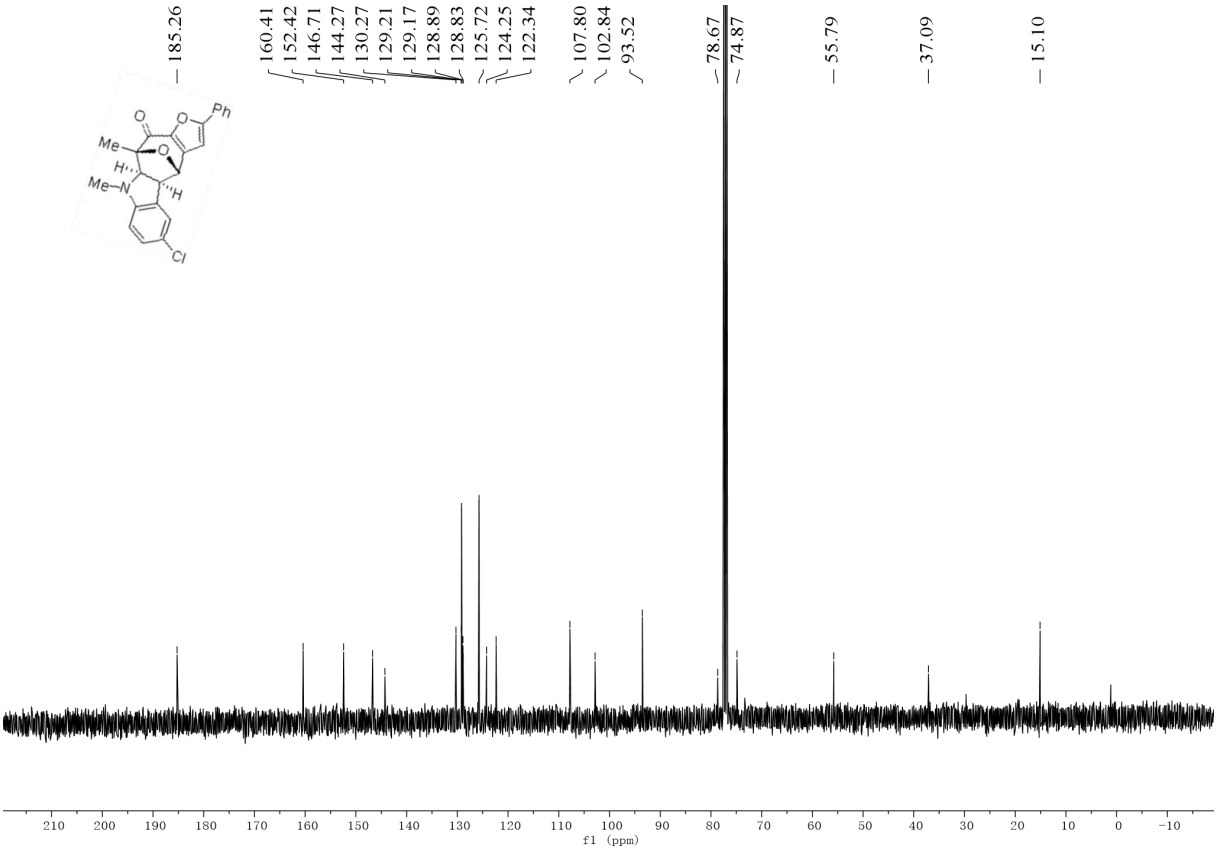


Ph
O
O
Me
H
Me
N
H
F

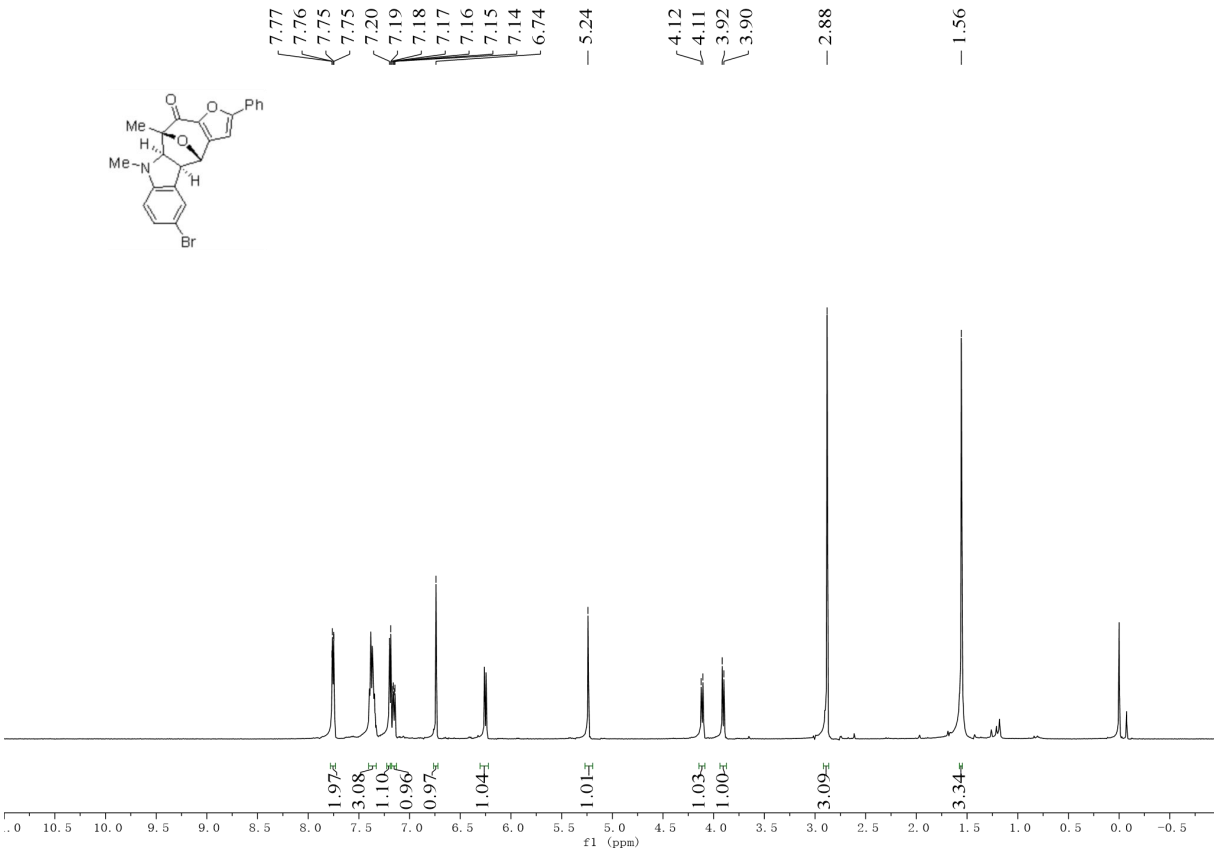

-127.49
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

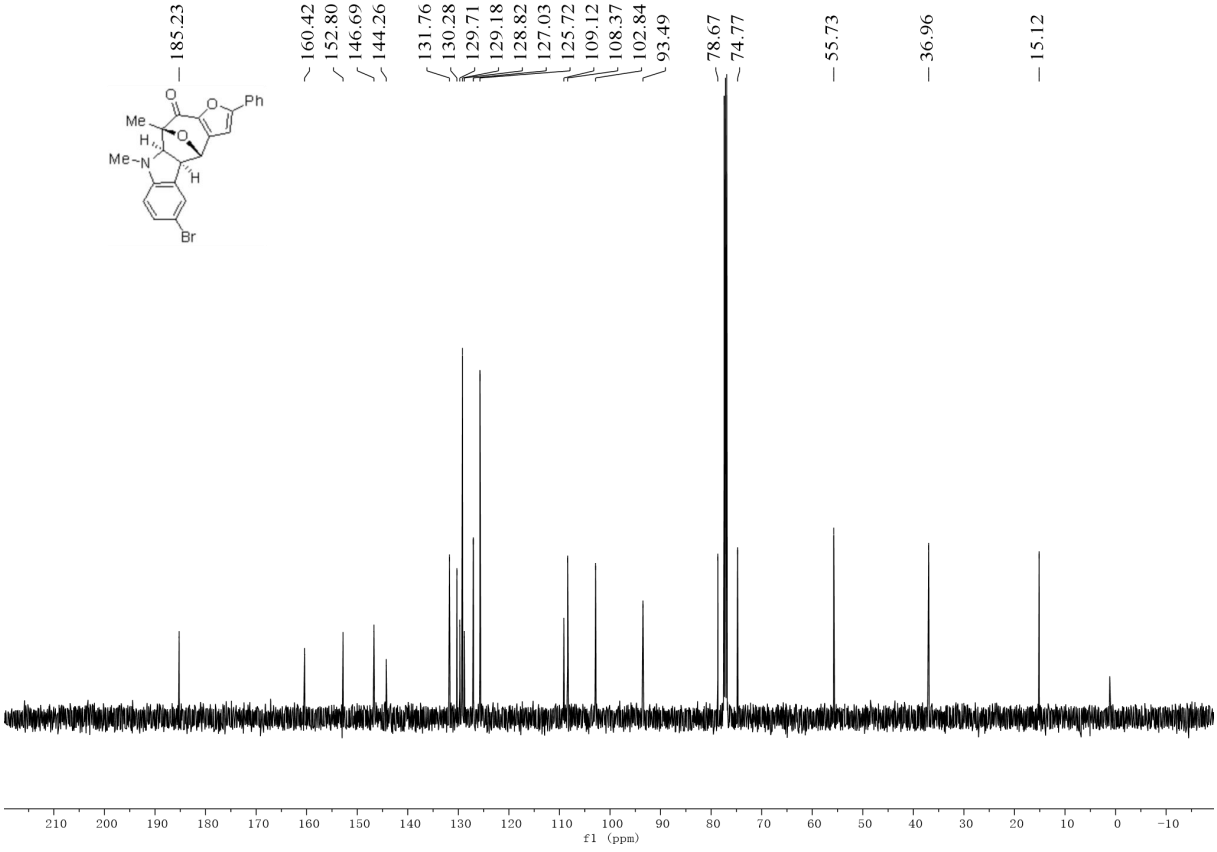
^{1}H and ^{13}C NMR spectra of 3ad



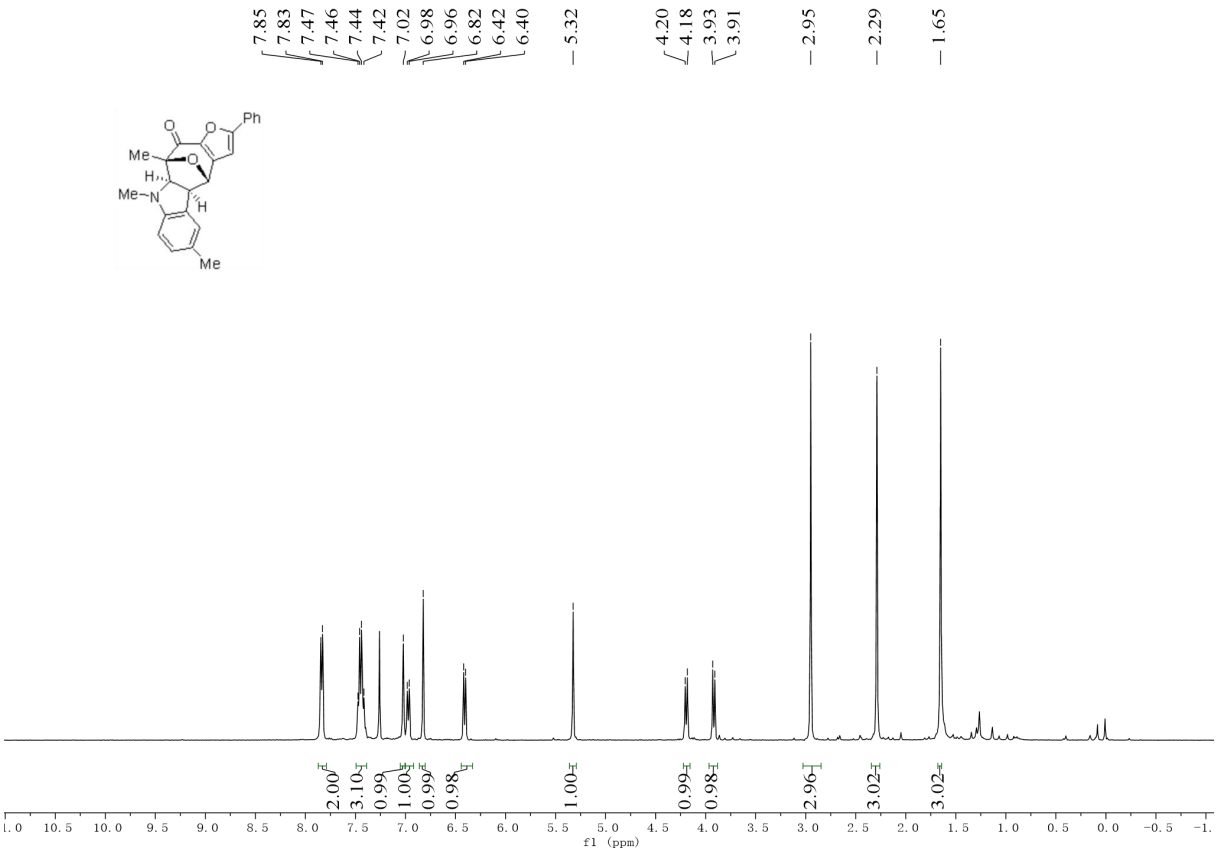


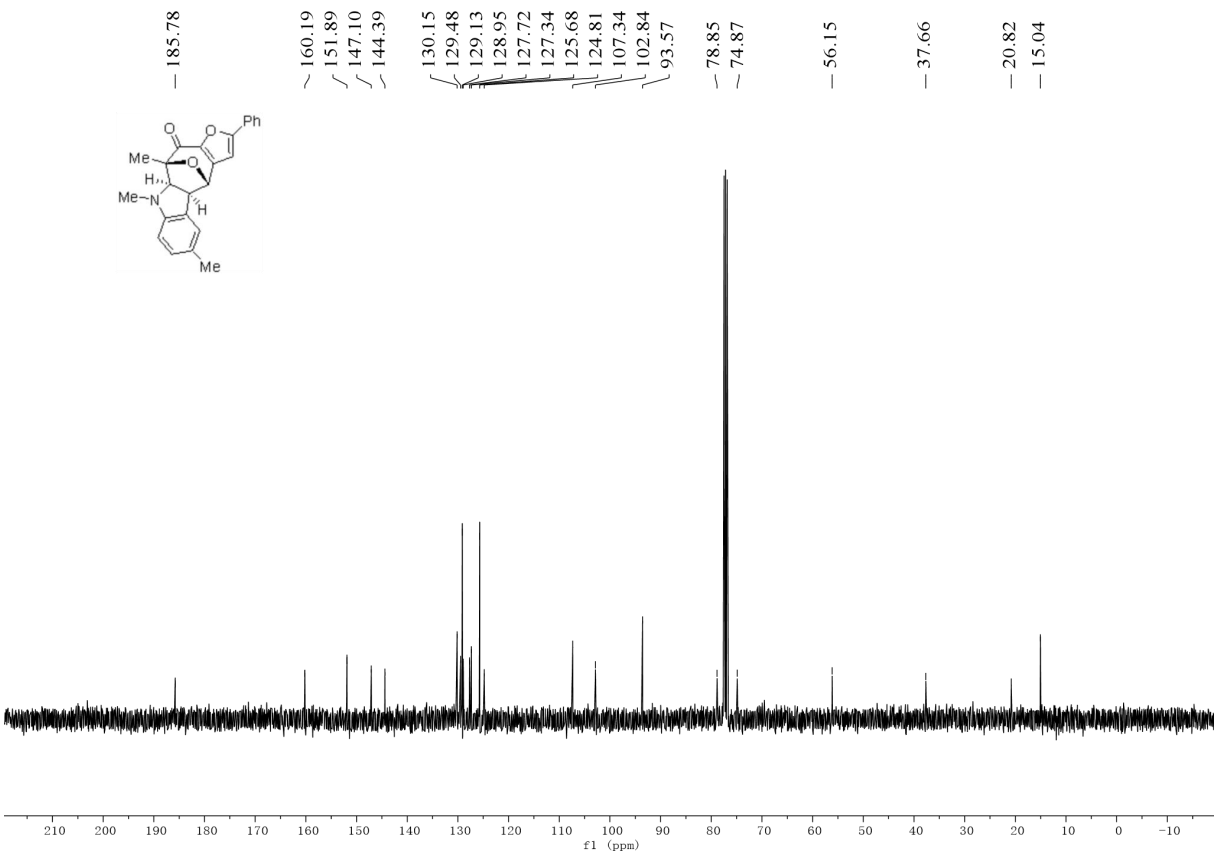
^{1}H and ^{13}C NMR spectra of 3ae



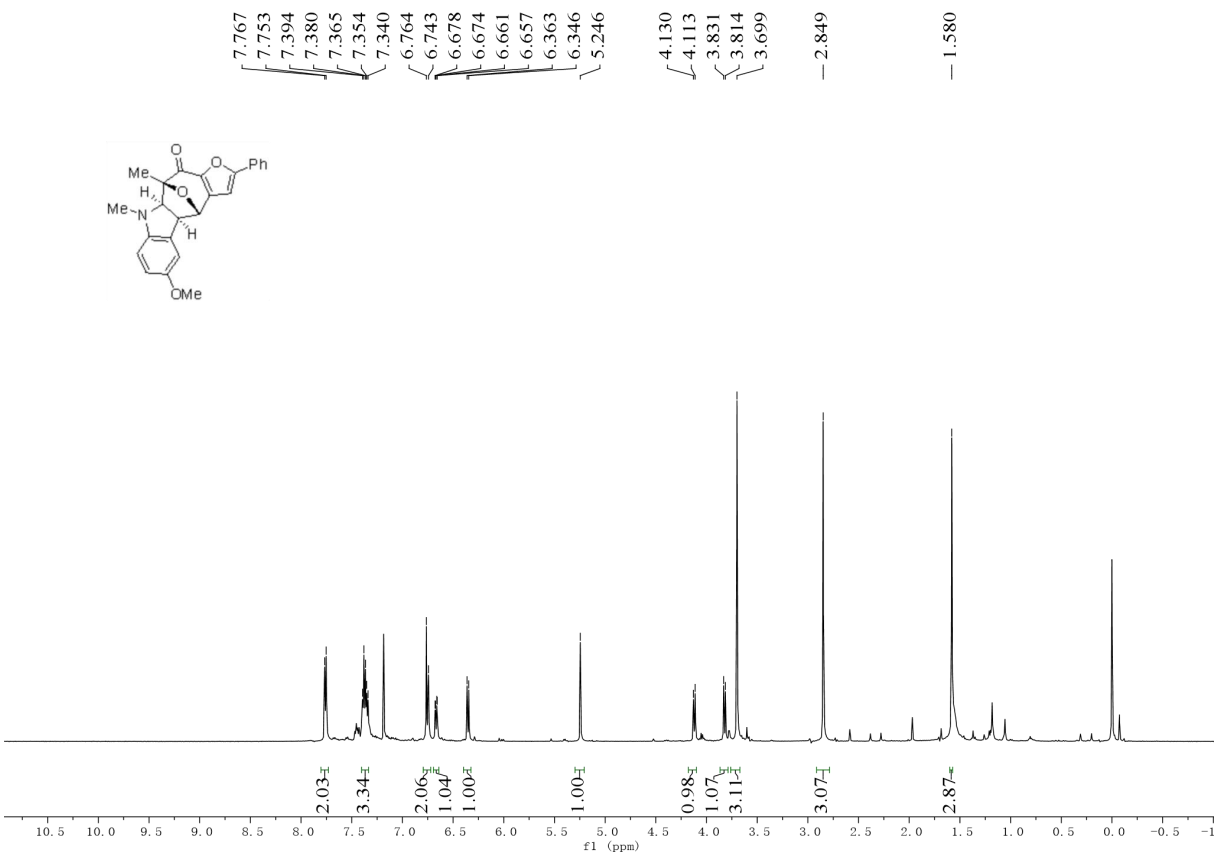


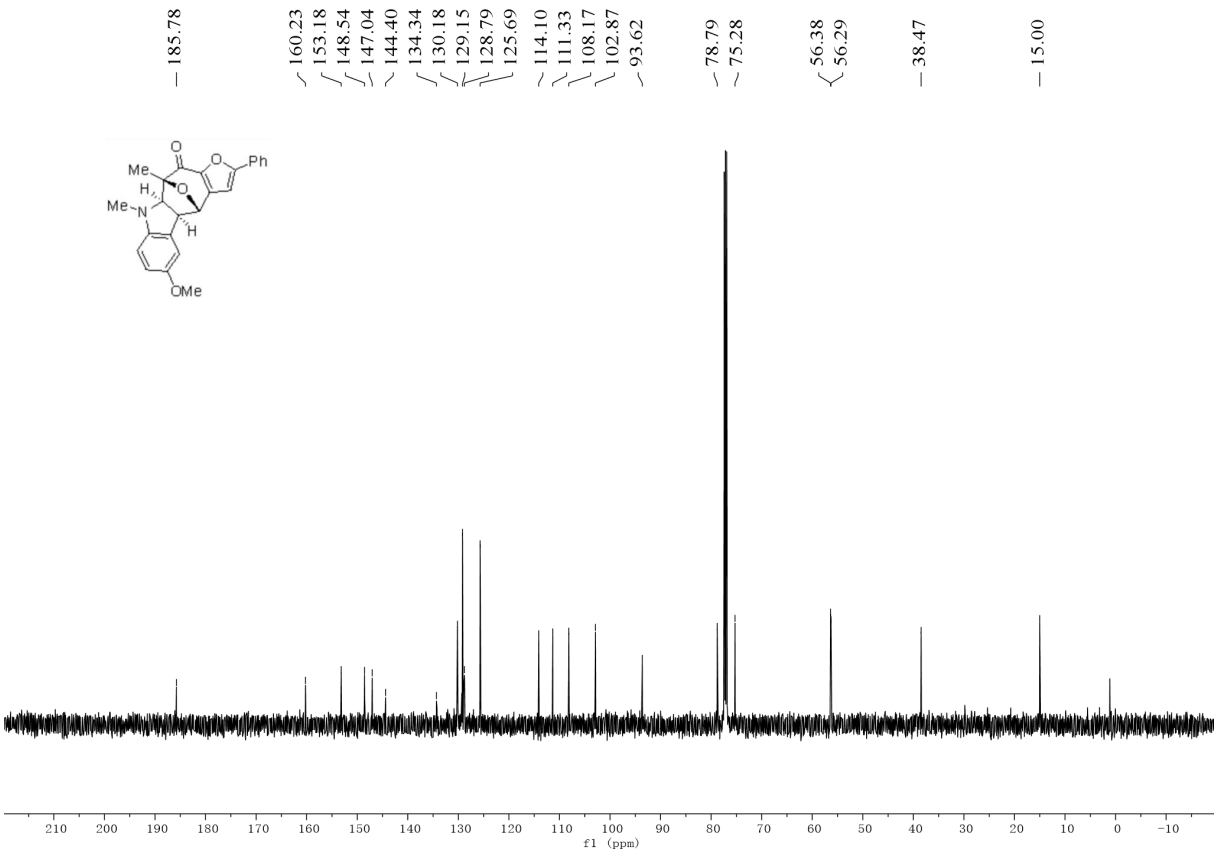
^{1}H and ^{13}C NMR spectra of 3af



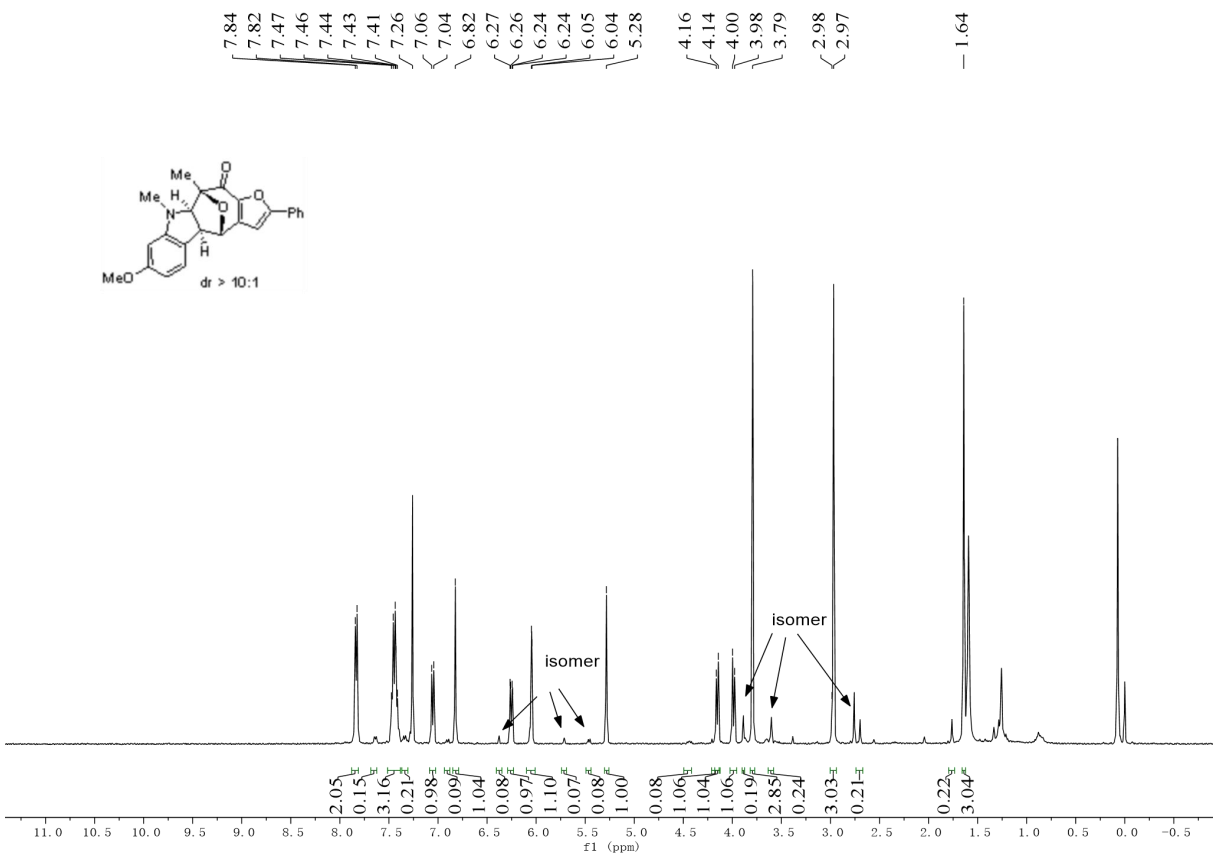


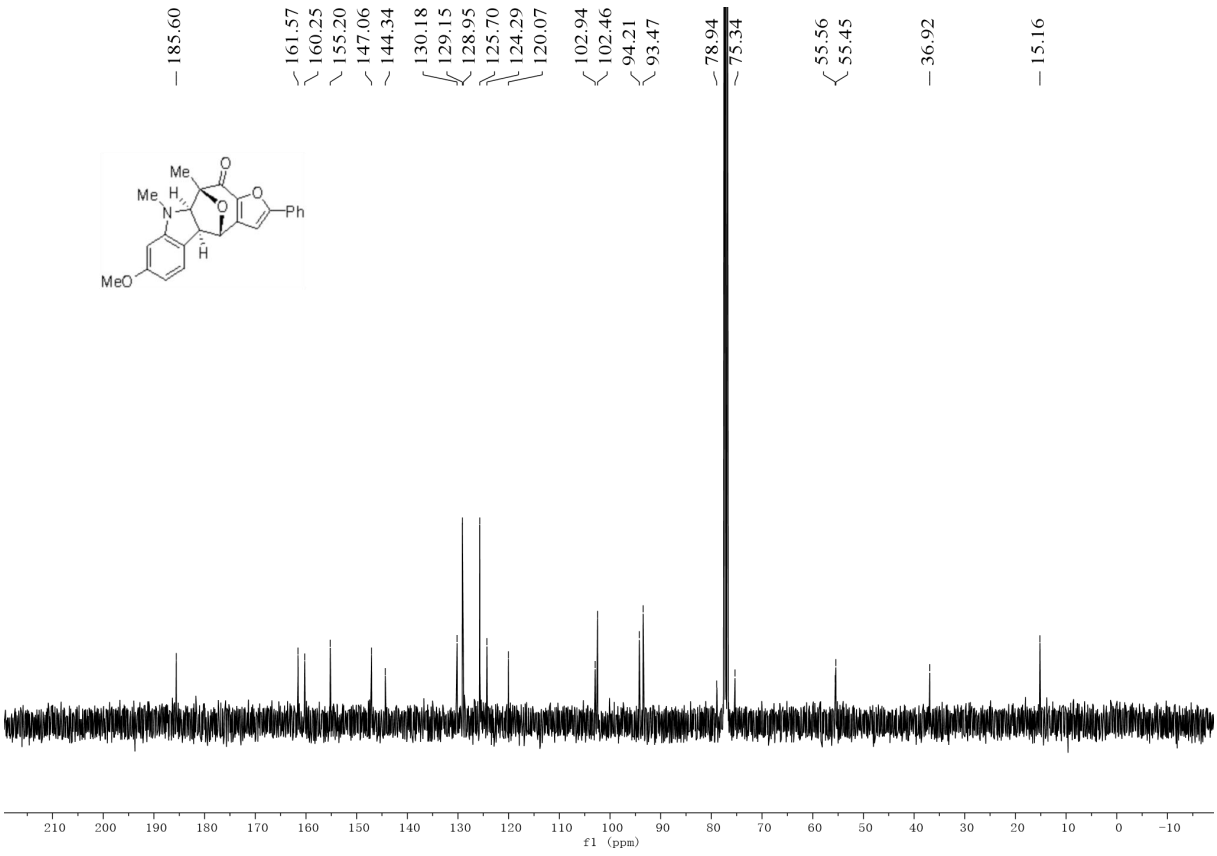
^{1}H and ^{13}C NMR spectra of 3ag



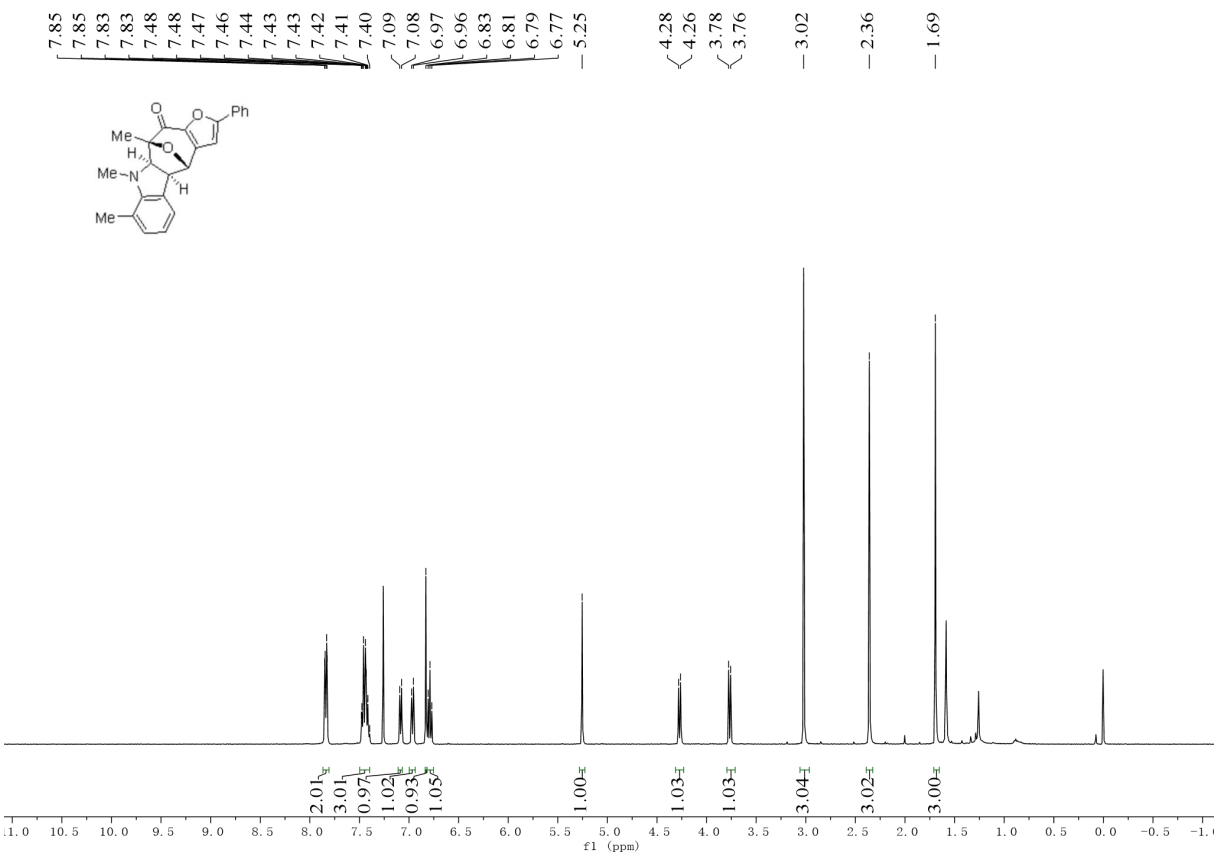


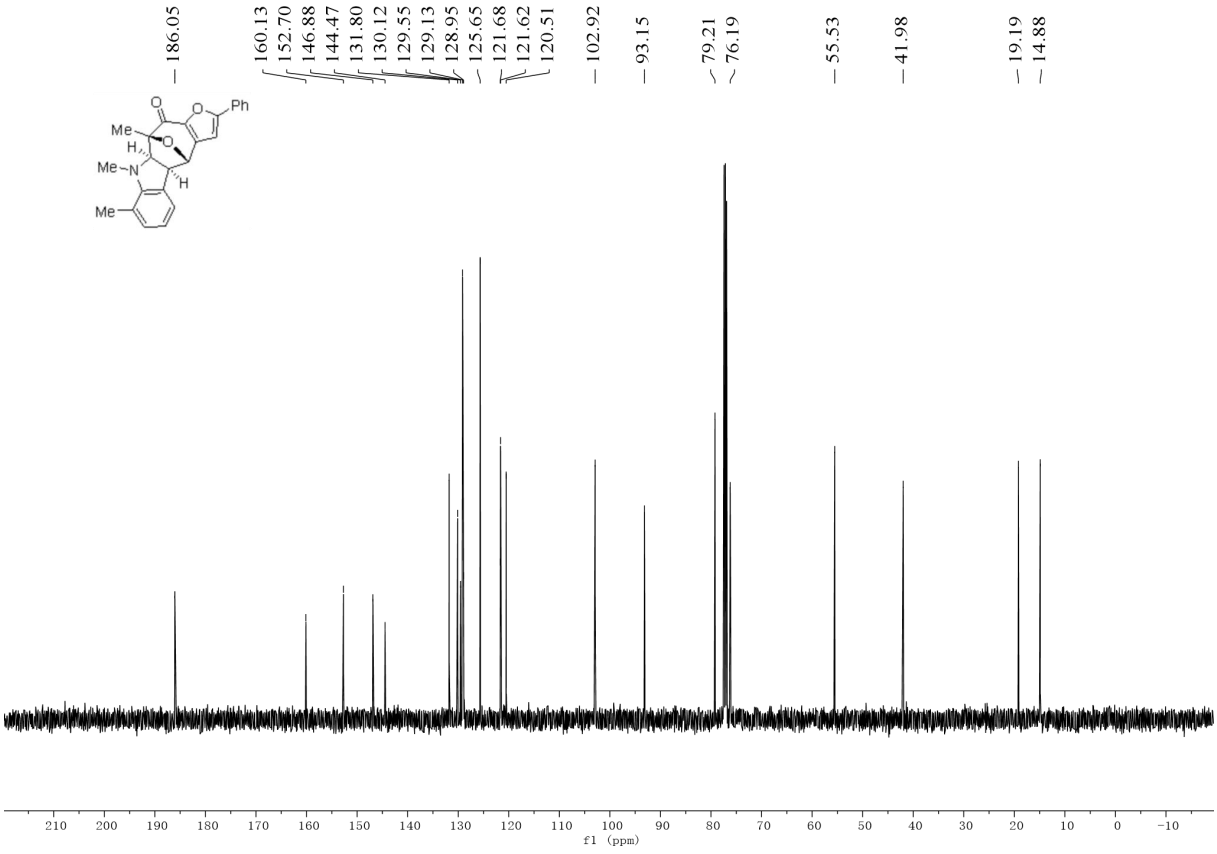
^{1}H and ^{13}C NMR spectra of 3ah



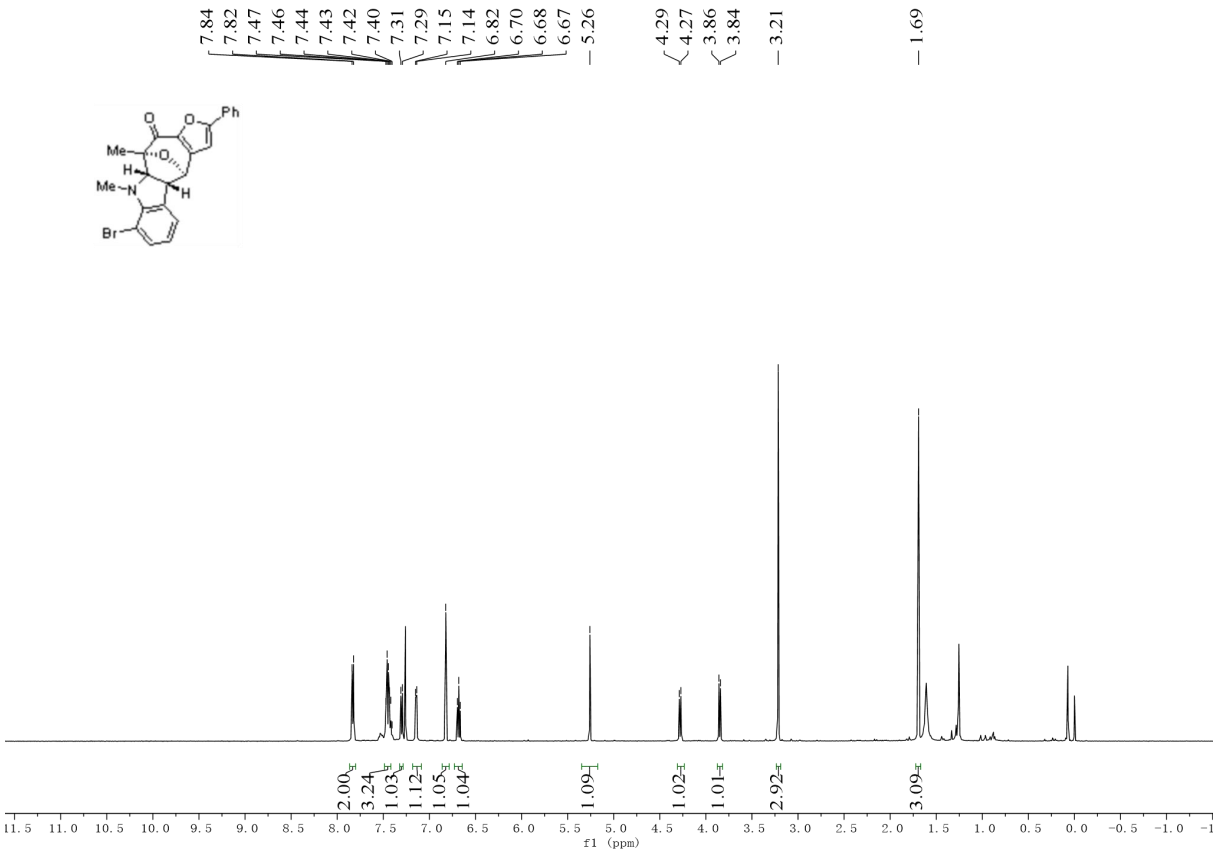


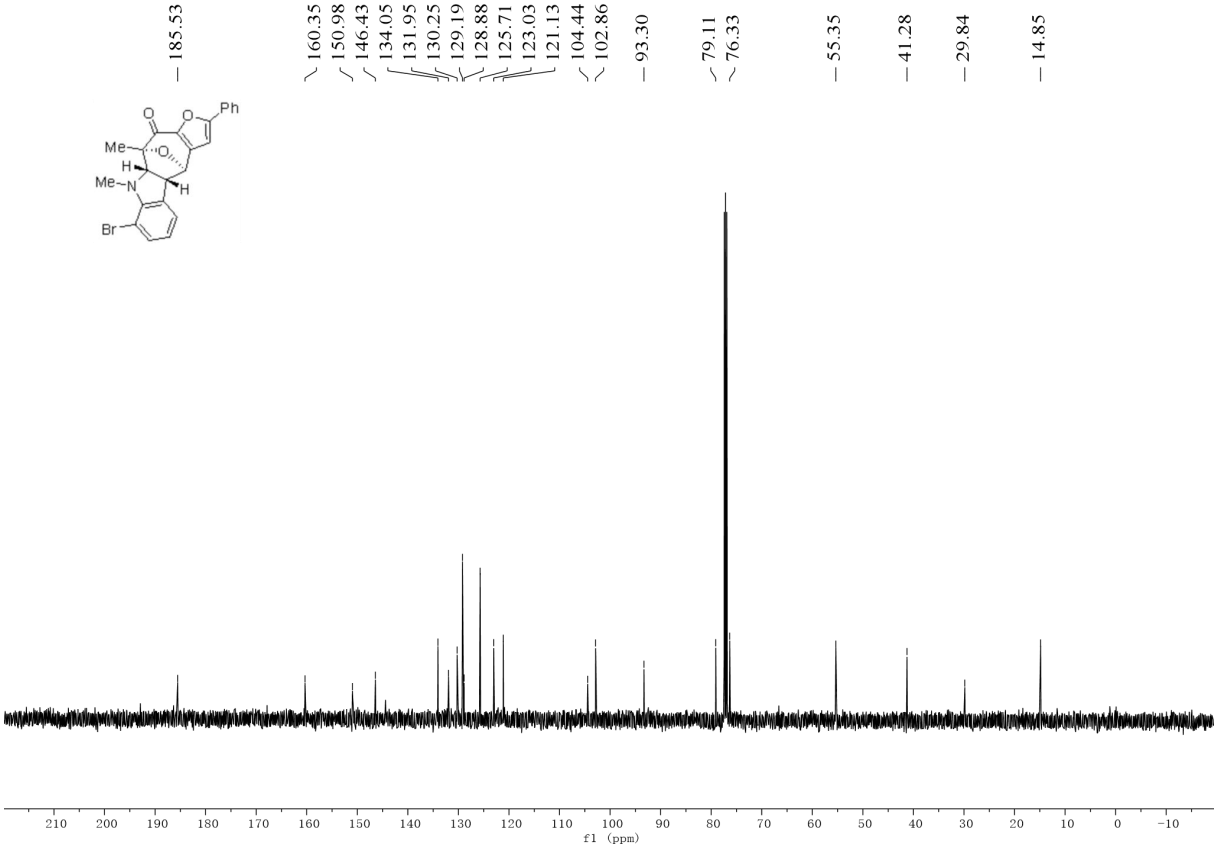
^{1}H and ^{13}C NMR spectra of 3ai



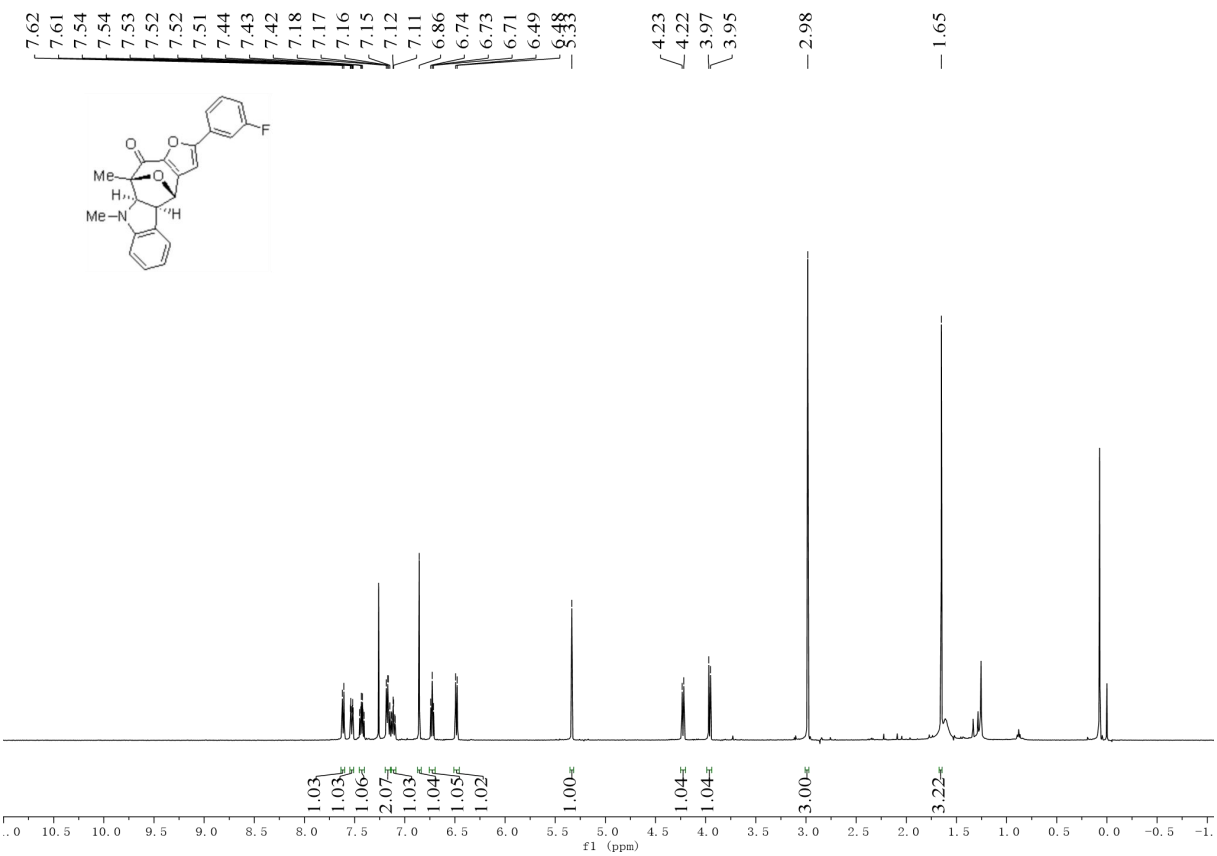


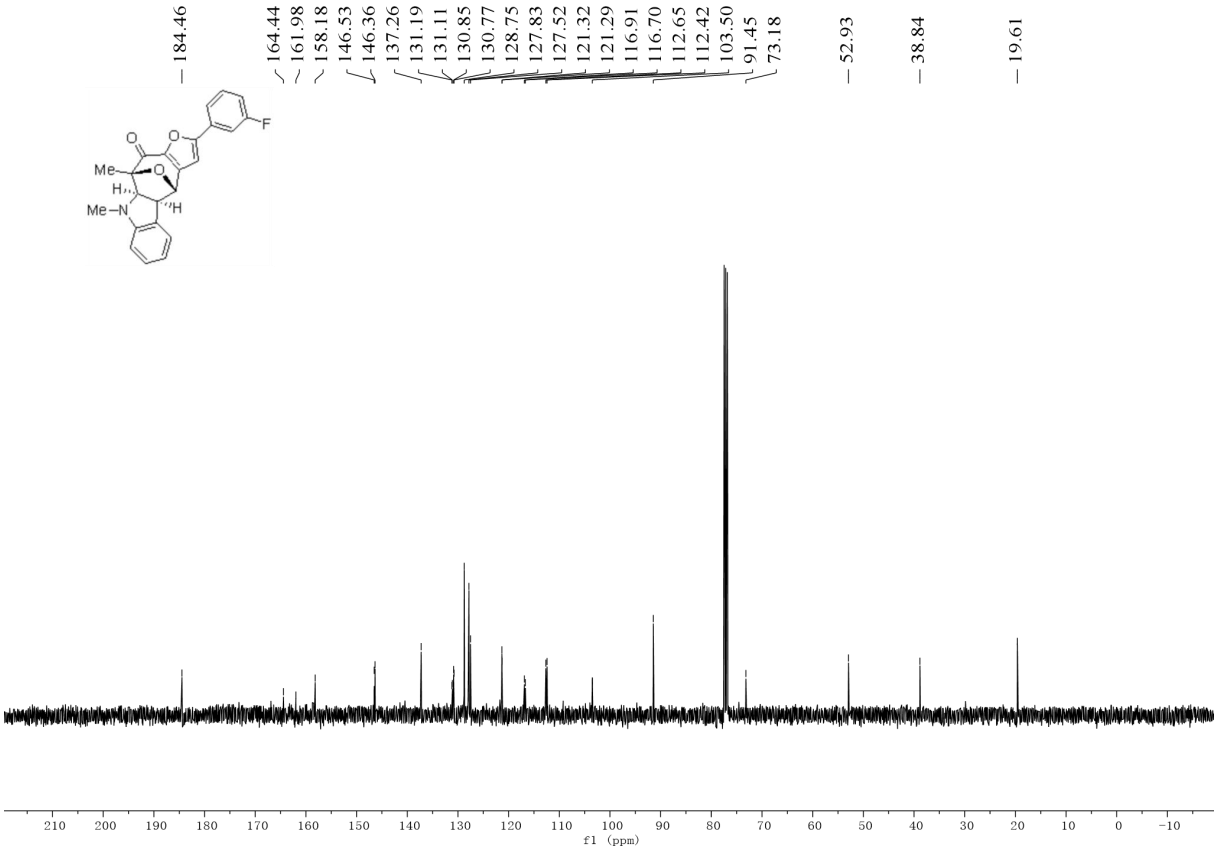
^{1}H and ^{13}C NMR spectra of 3aj



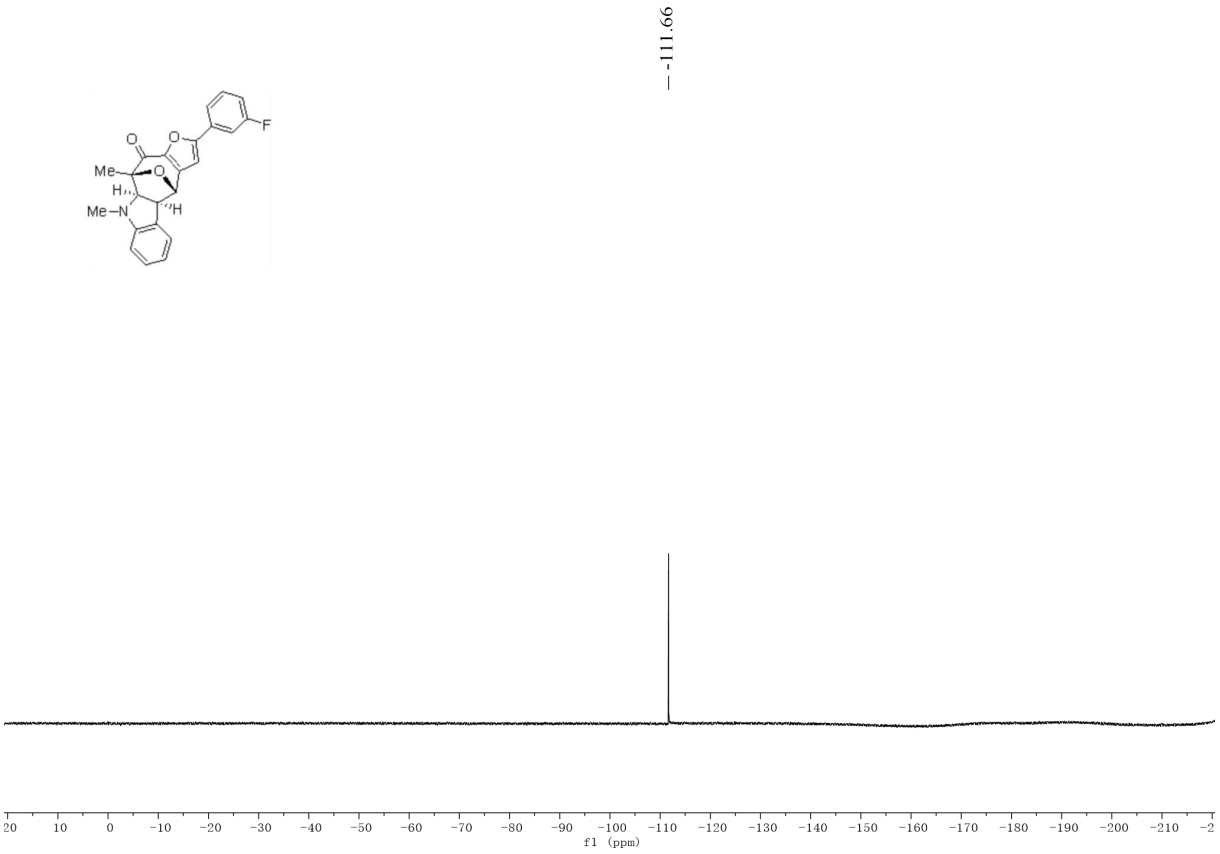


^{1}H and ^{13}C NMR and $^{19}FNMR$ spectra of 3ca





O
O
F
Me
H
O
Me–N
H


-111.66
20
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-130
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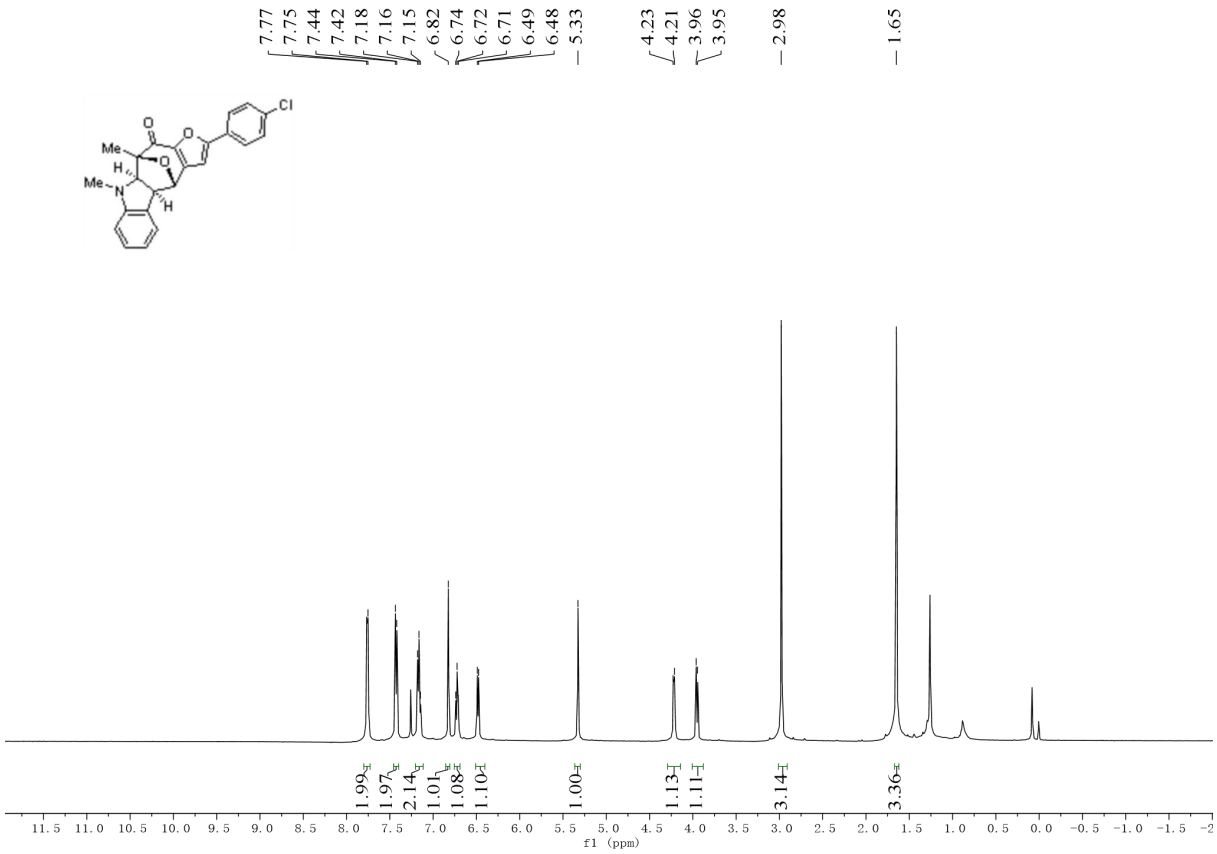
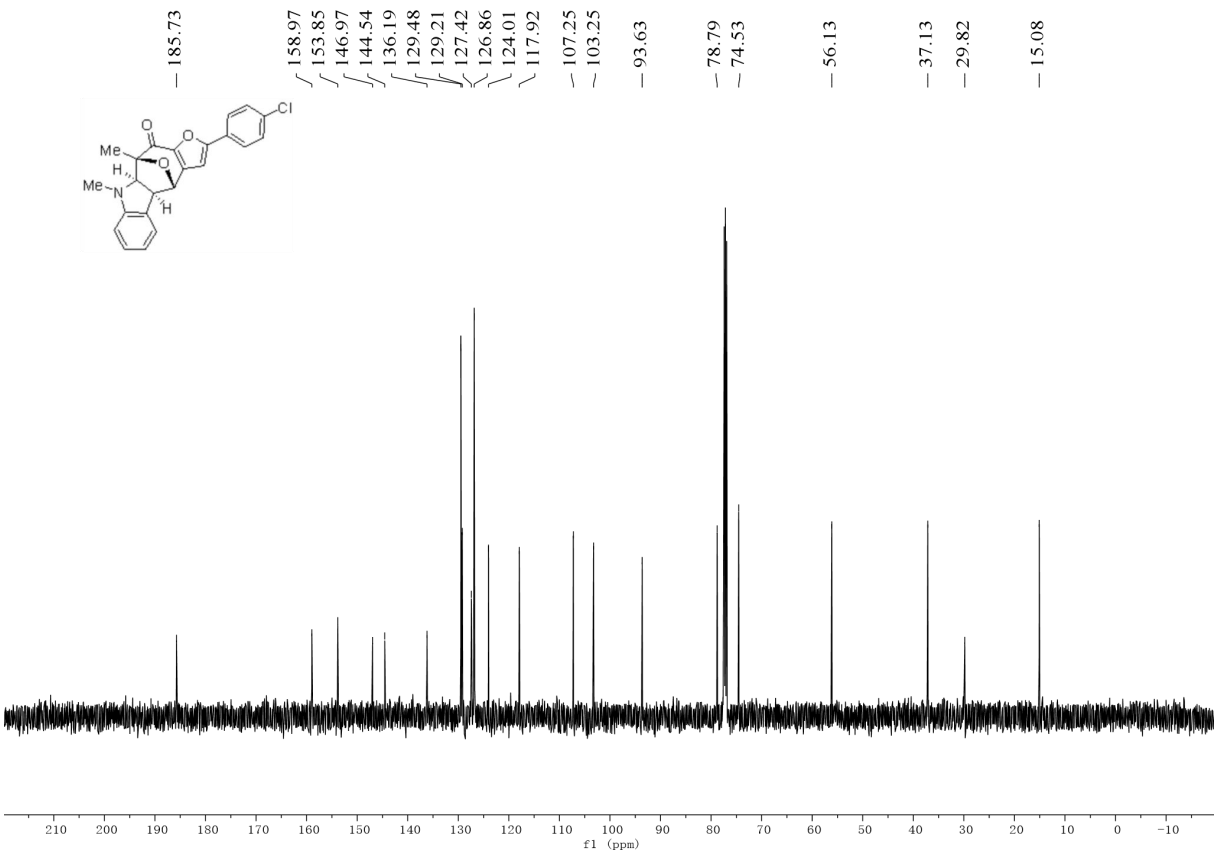
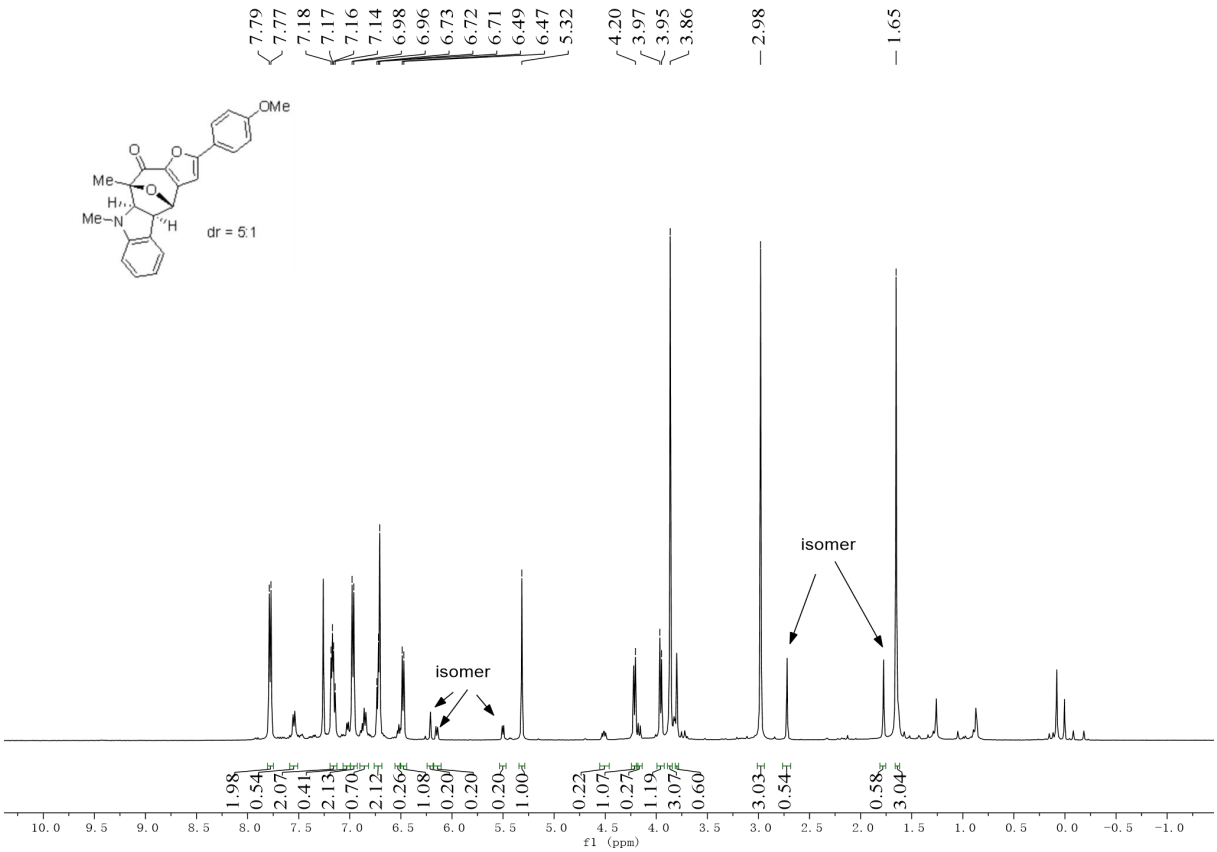
-160
-170
-180
-190
-200
-210
f1 (ppm)

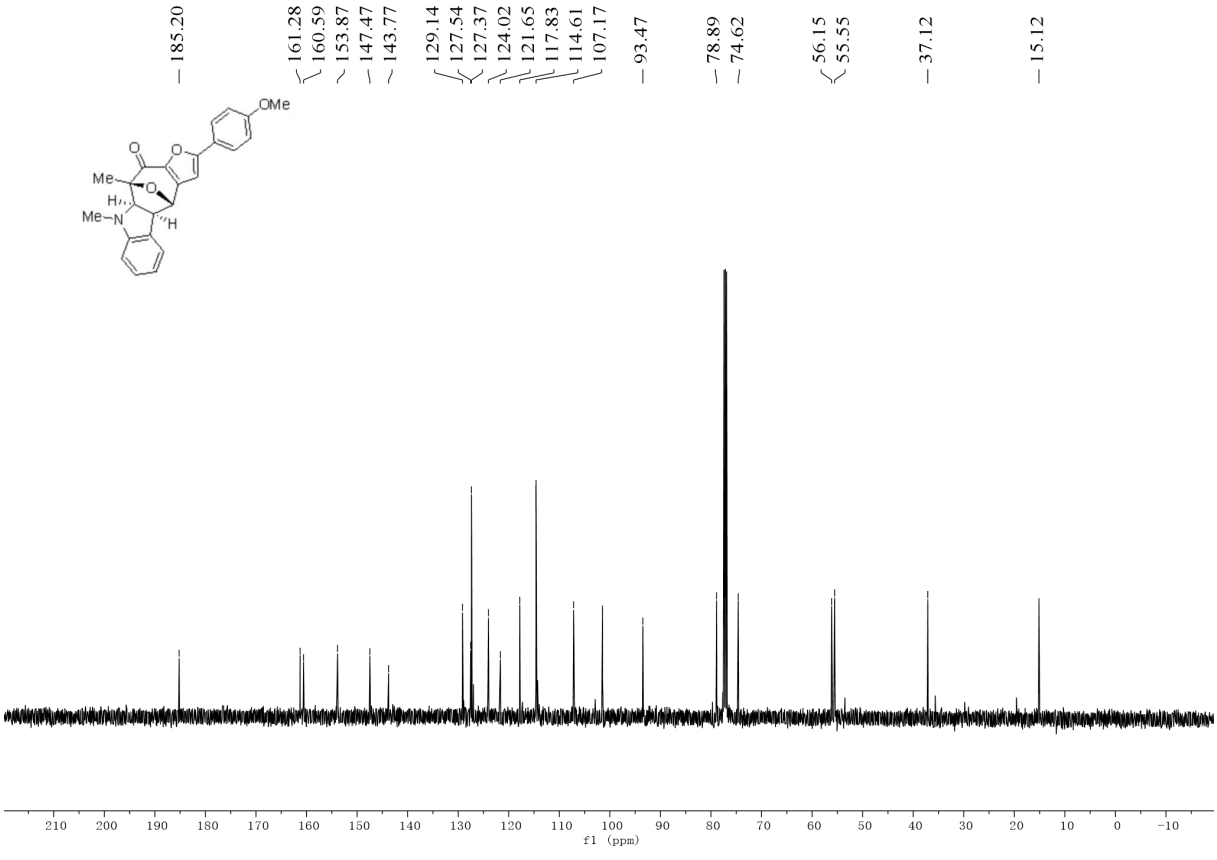
^{1}H and ^{13}C NMR spectra of 3da



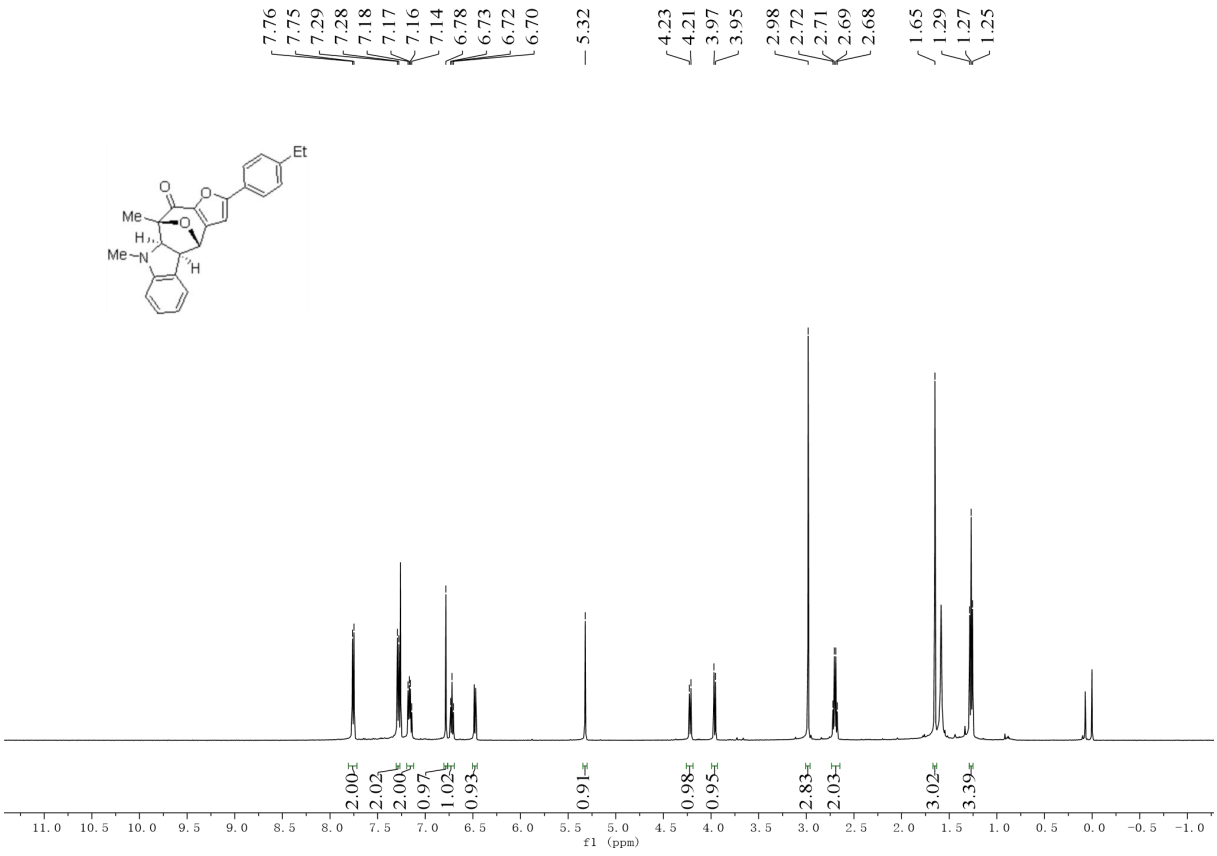


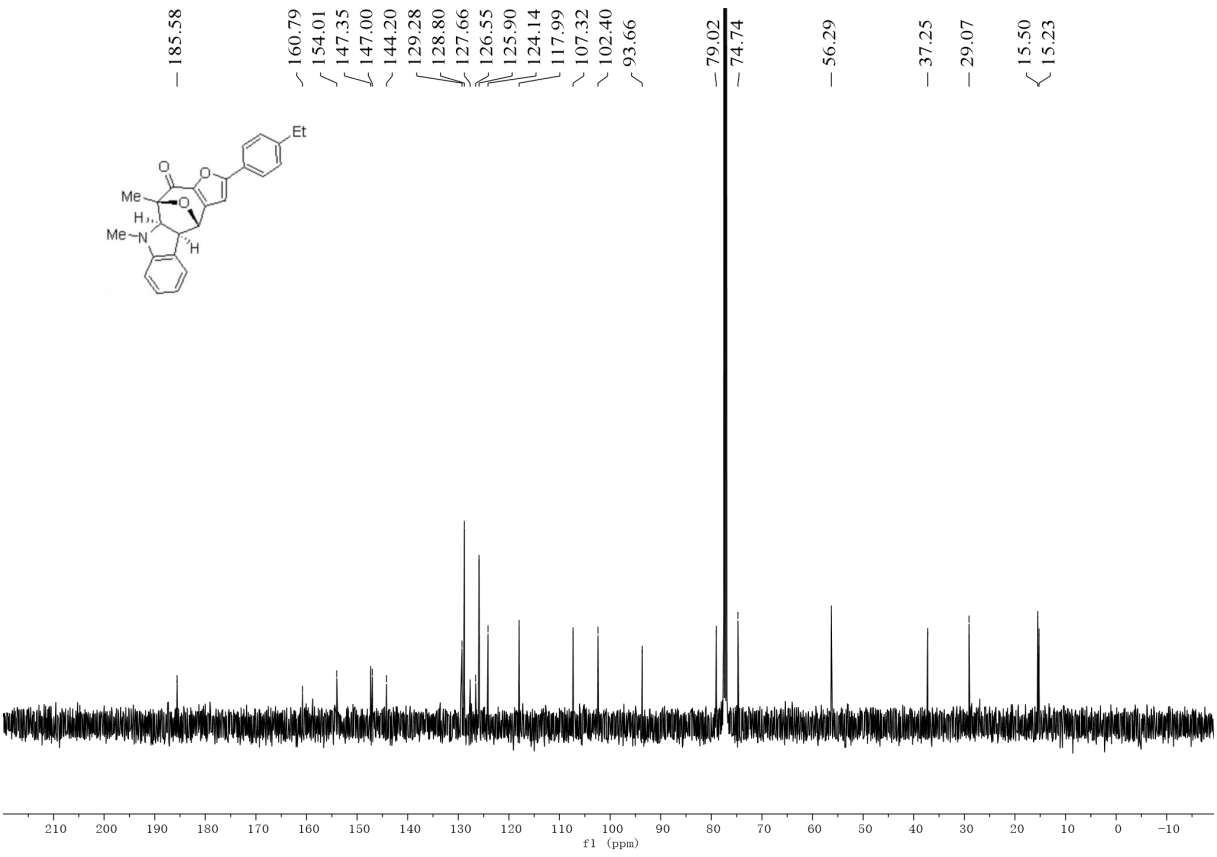
^{1}H and ^{13}C NMR spectra of 3ea



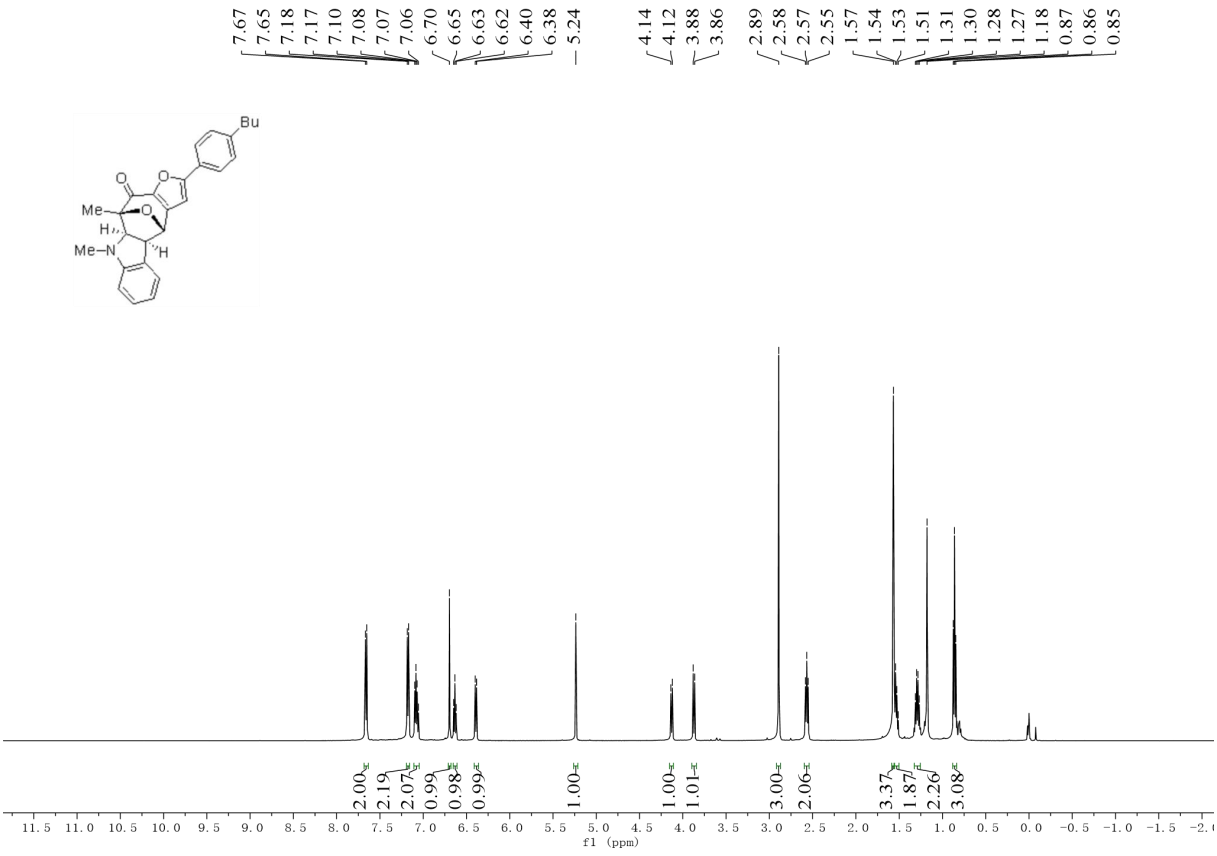


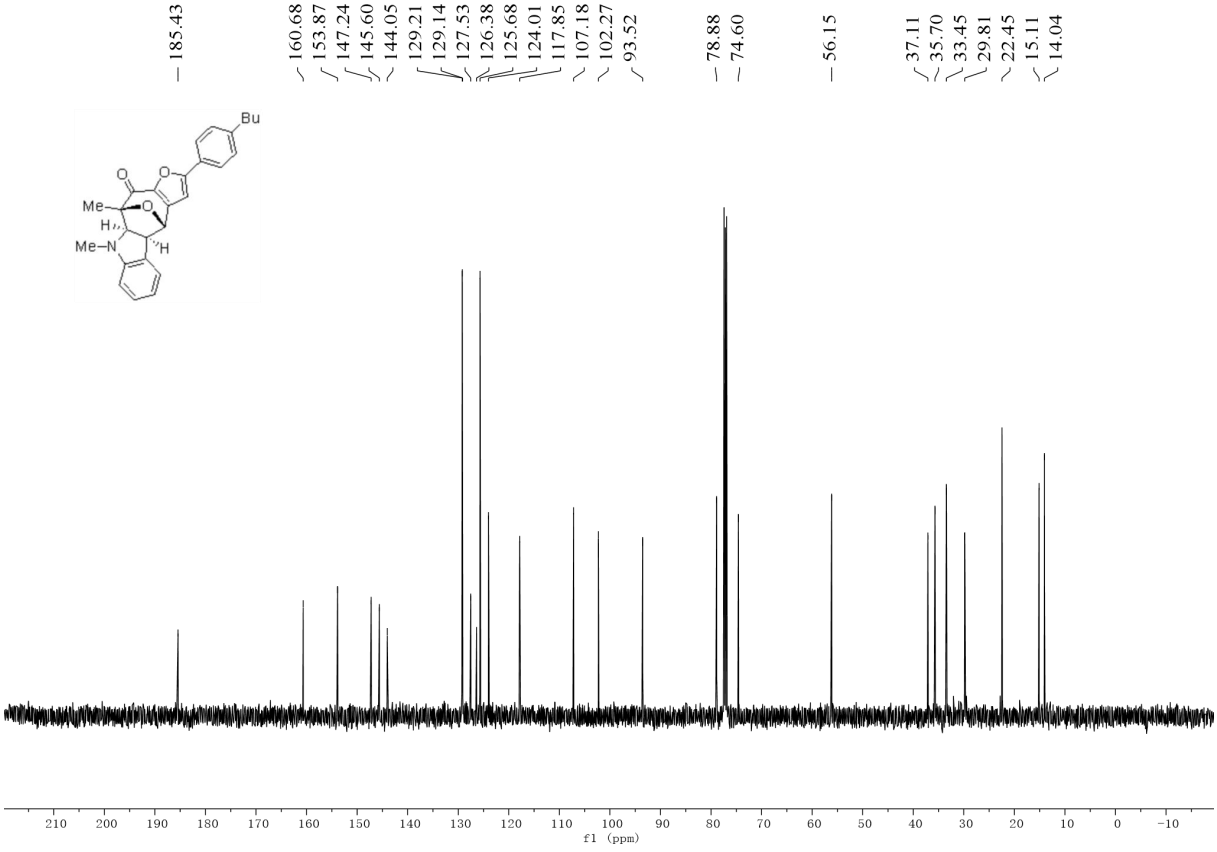
^{1}H and ^{13}C NMR spectra of 3fa



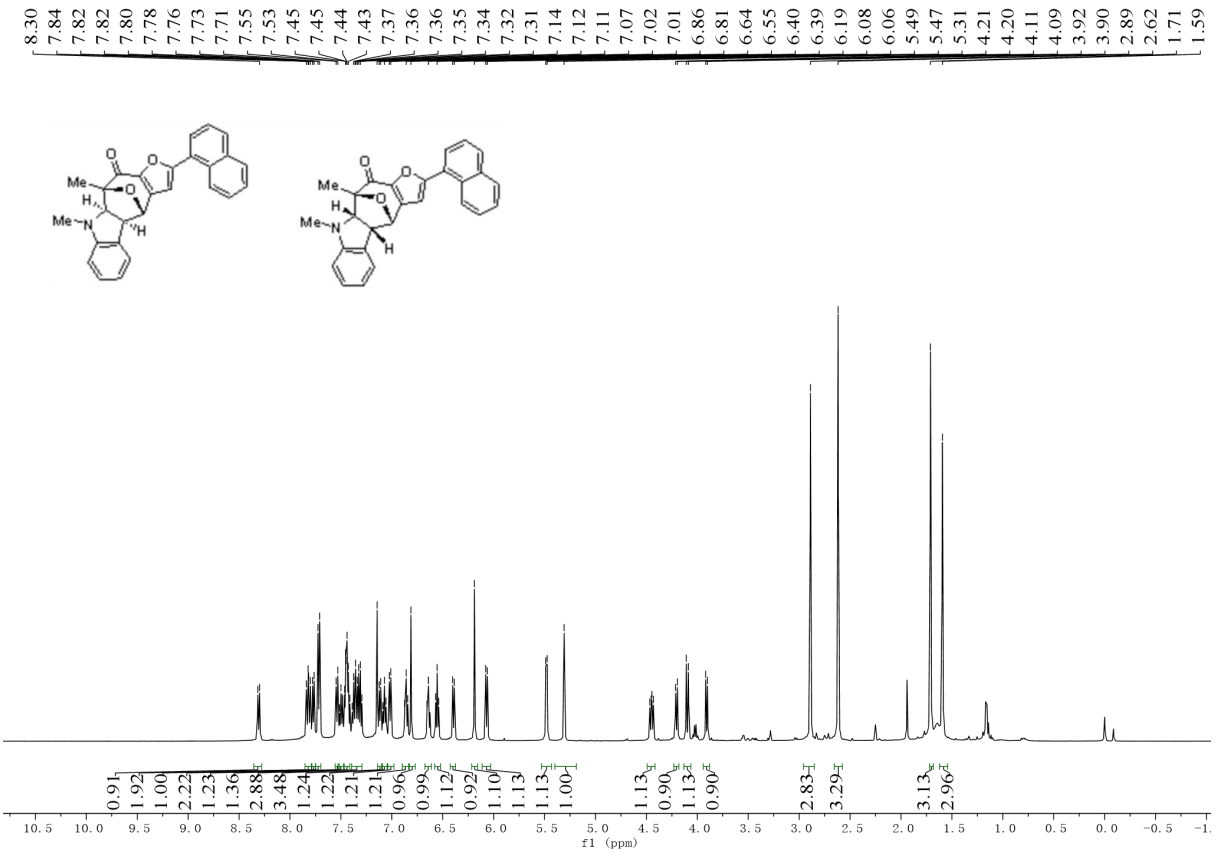


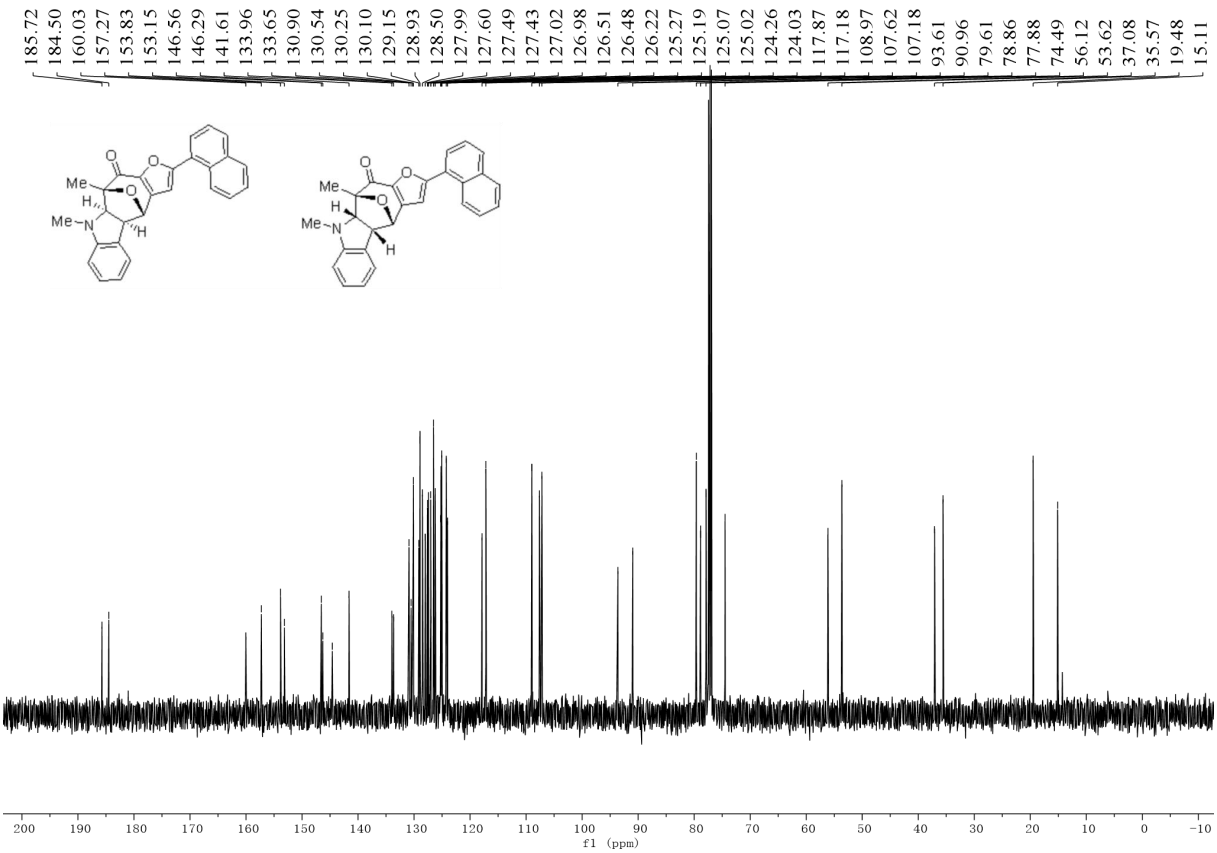
^{1}H and ^{13}C NMR spectra of 3ga



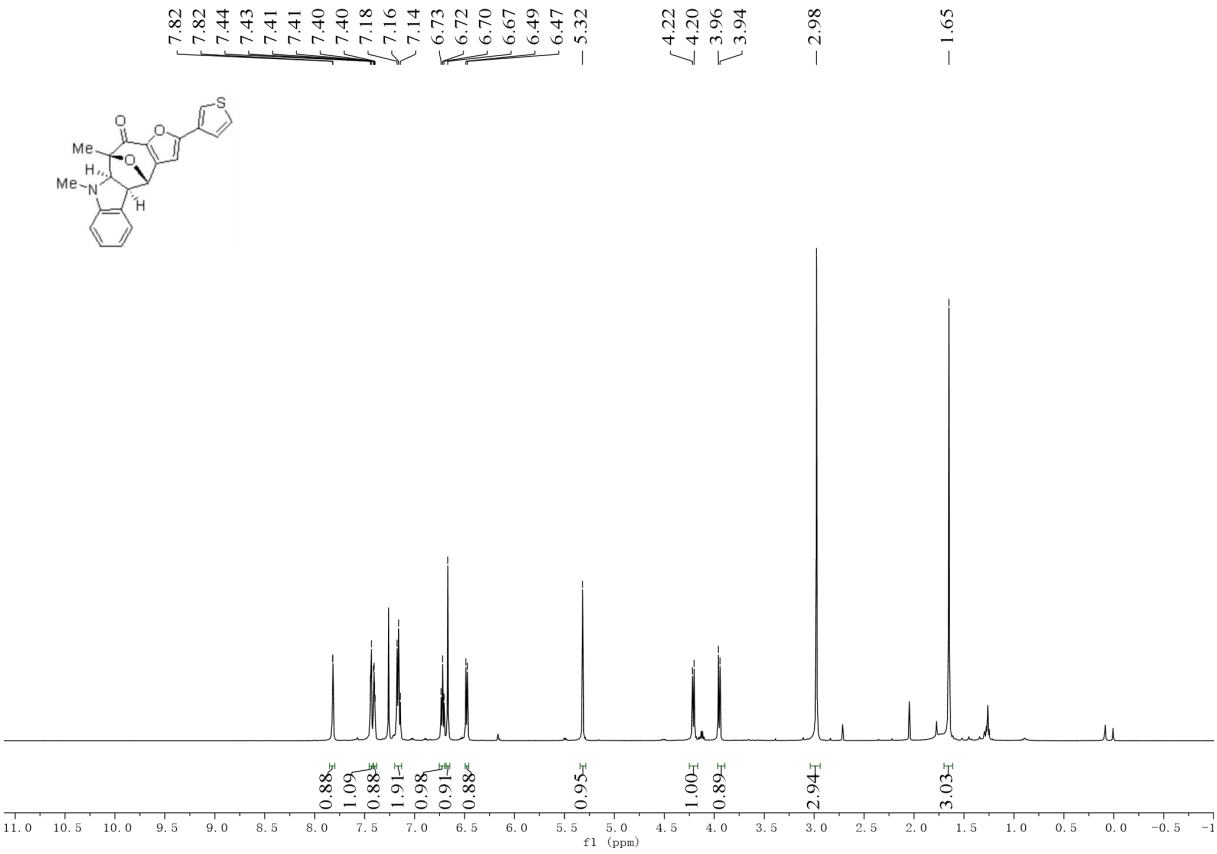


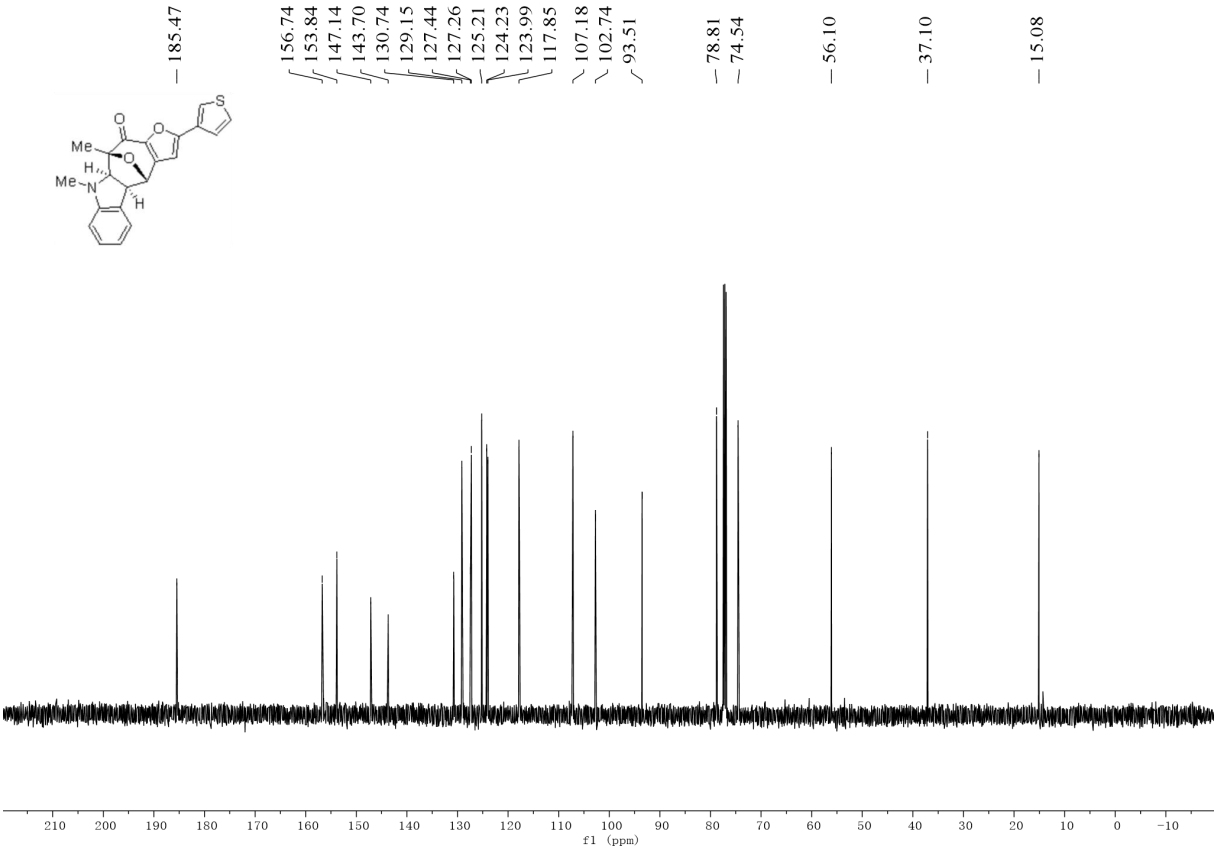
^{1}H and ^{13}C NMR spectra of 3ha



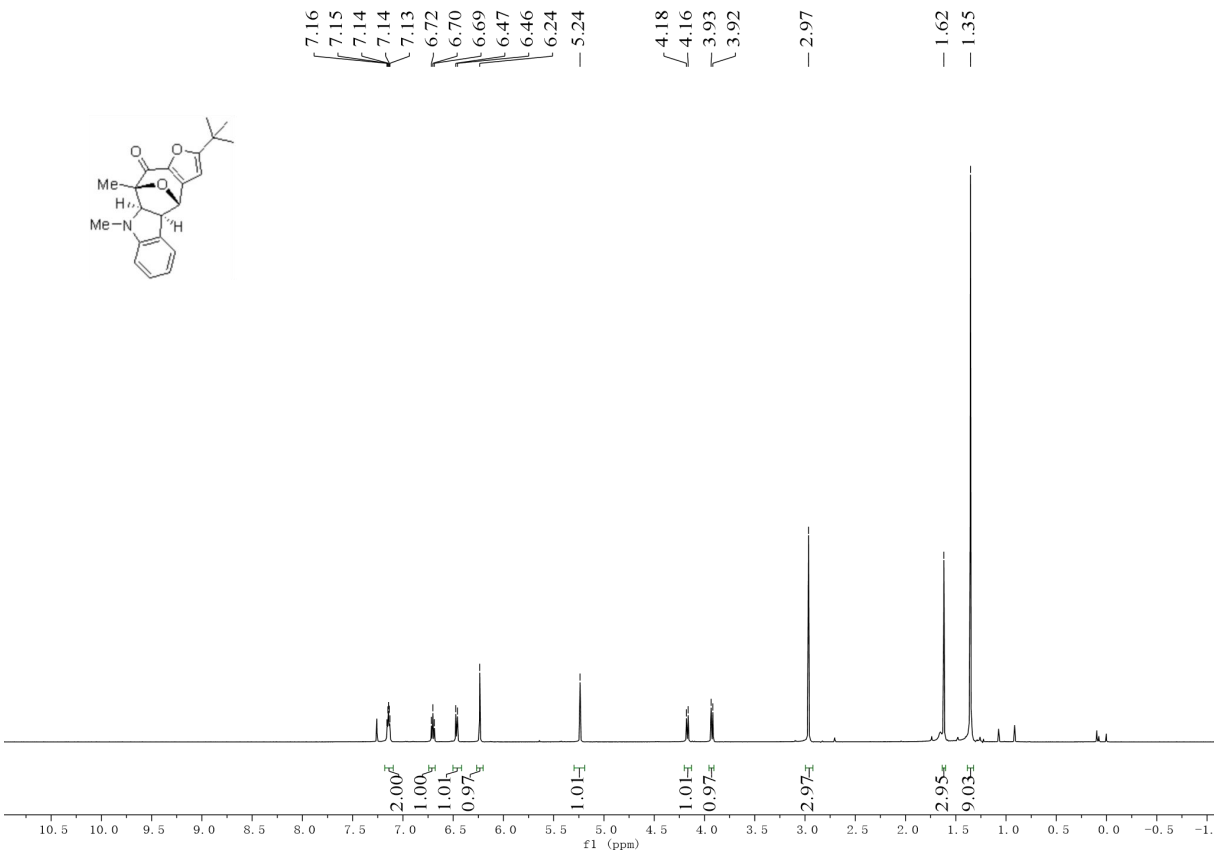


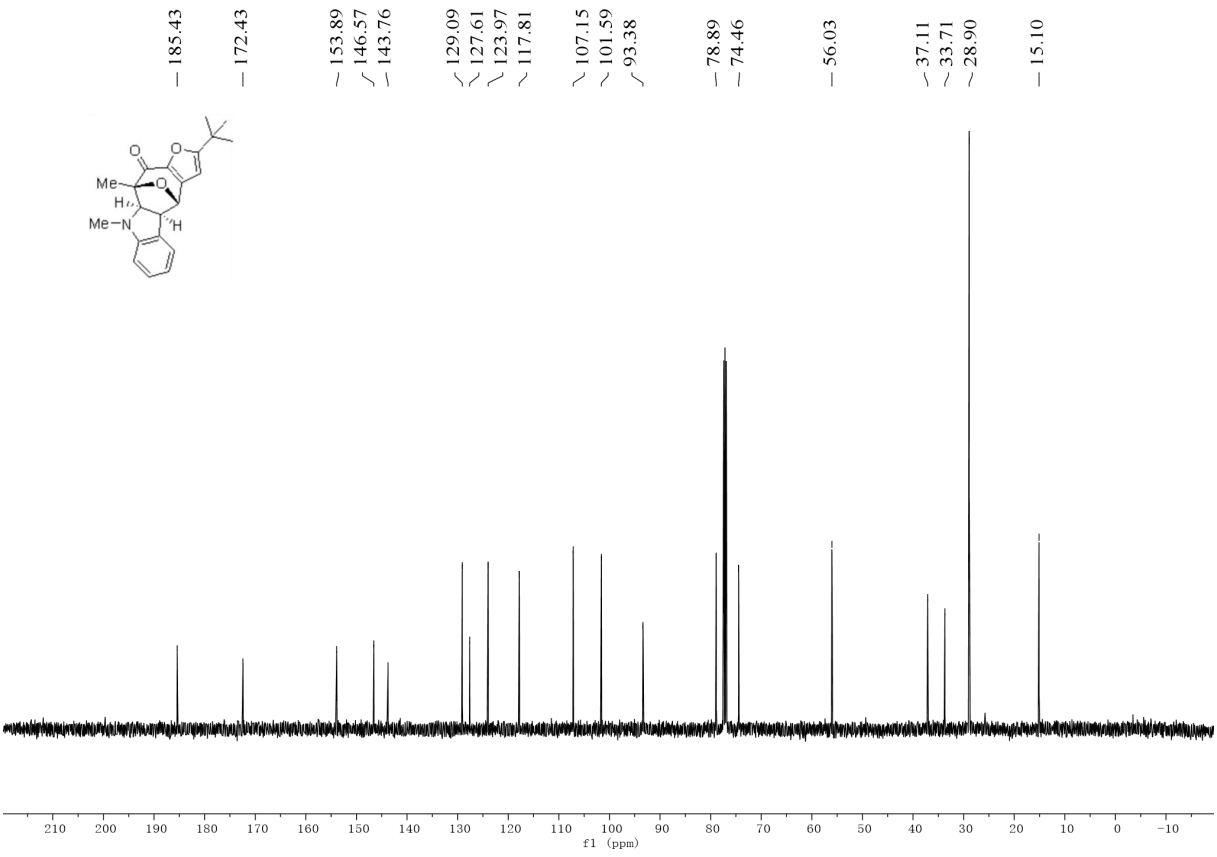
^{1}H and ^{13}C NMR spectra of 3ia



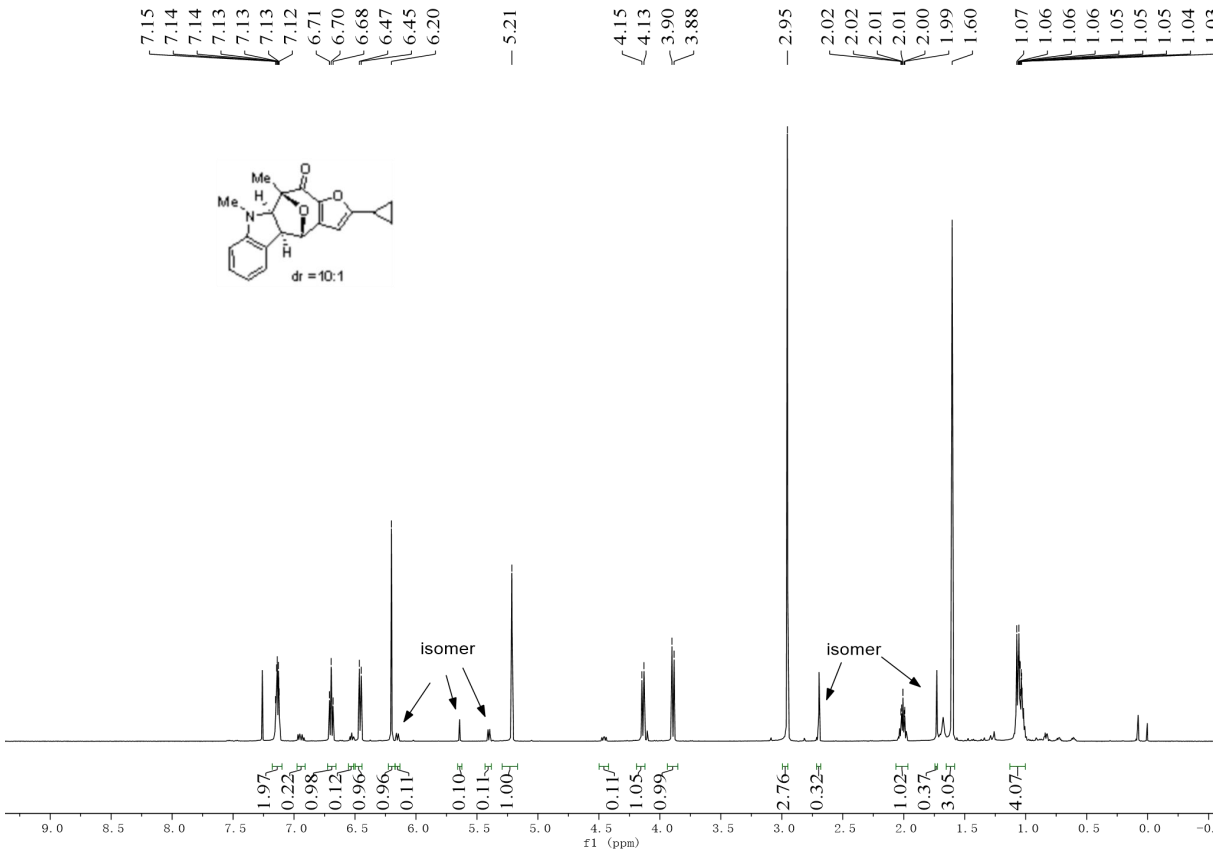


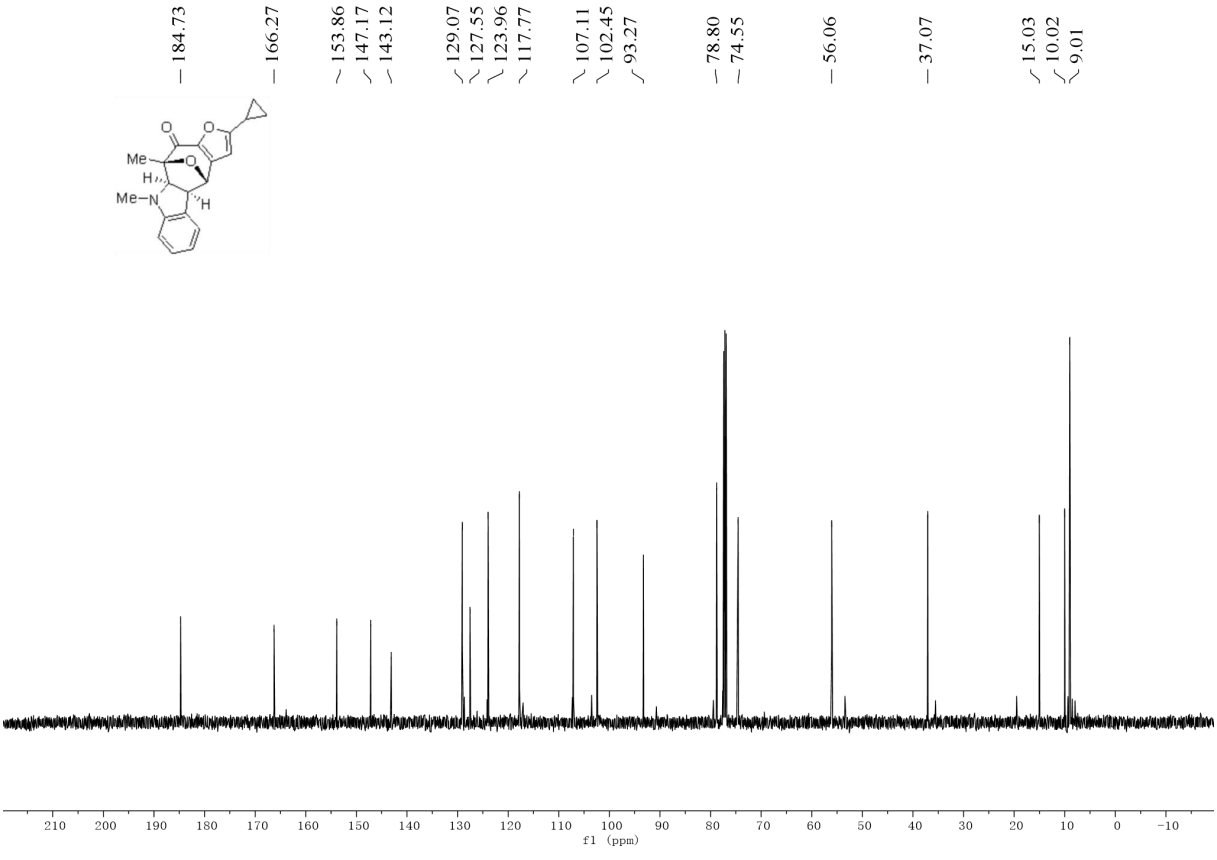
^{1}H and ^{13}C NMR spectra of 3ja



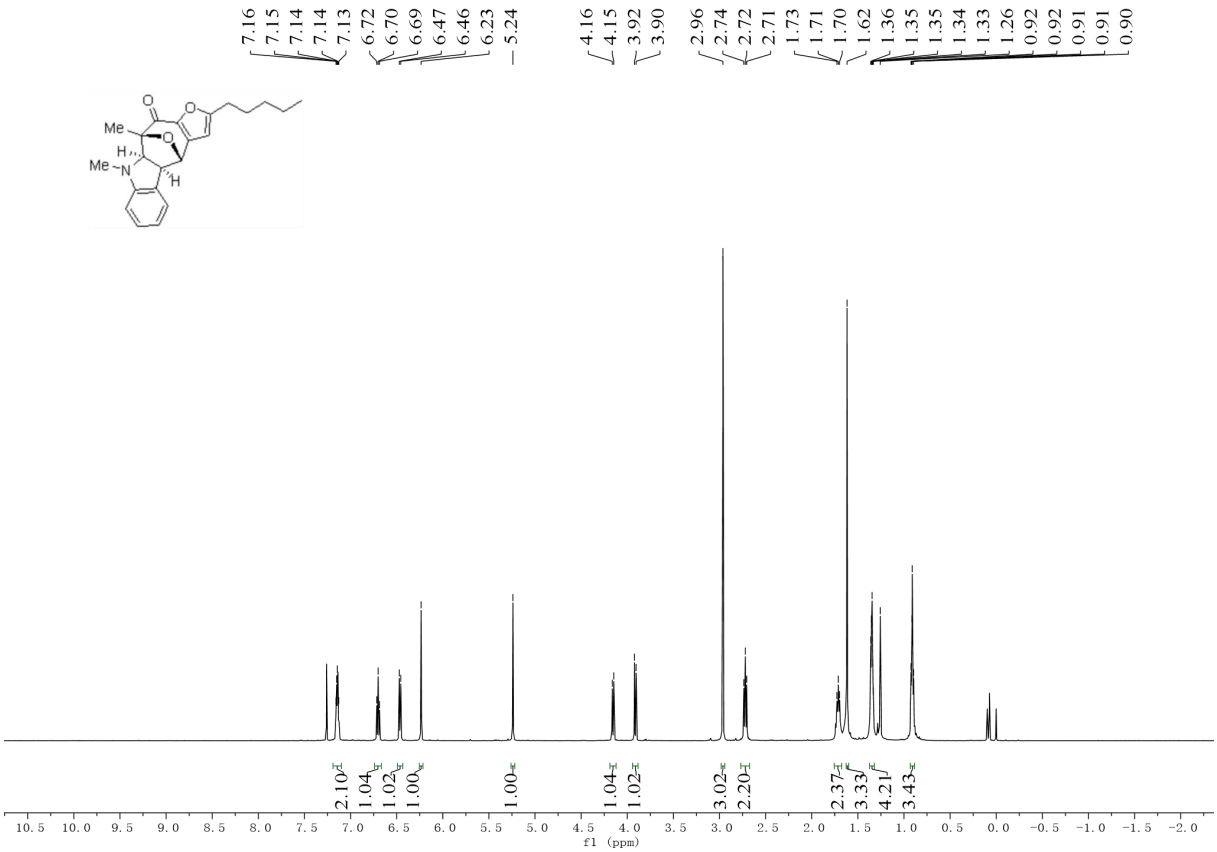


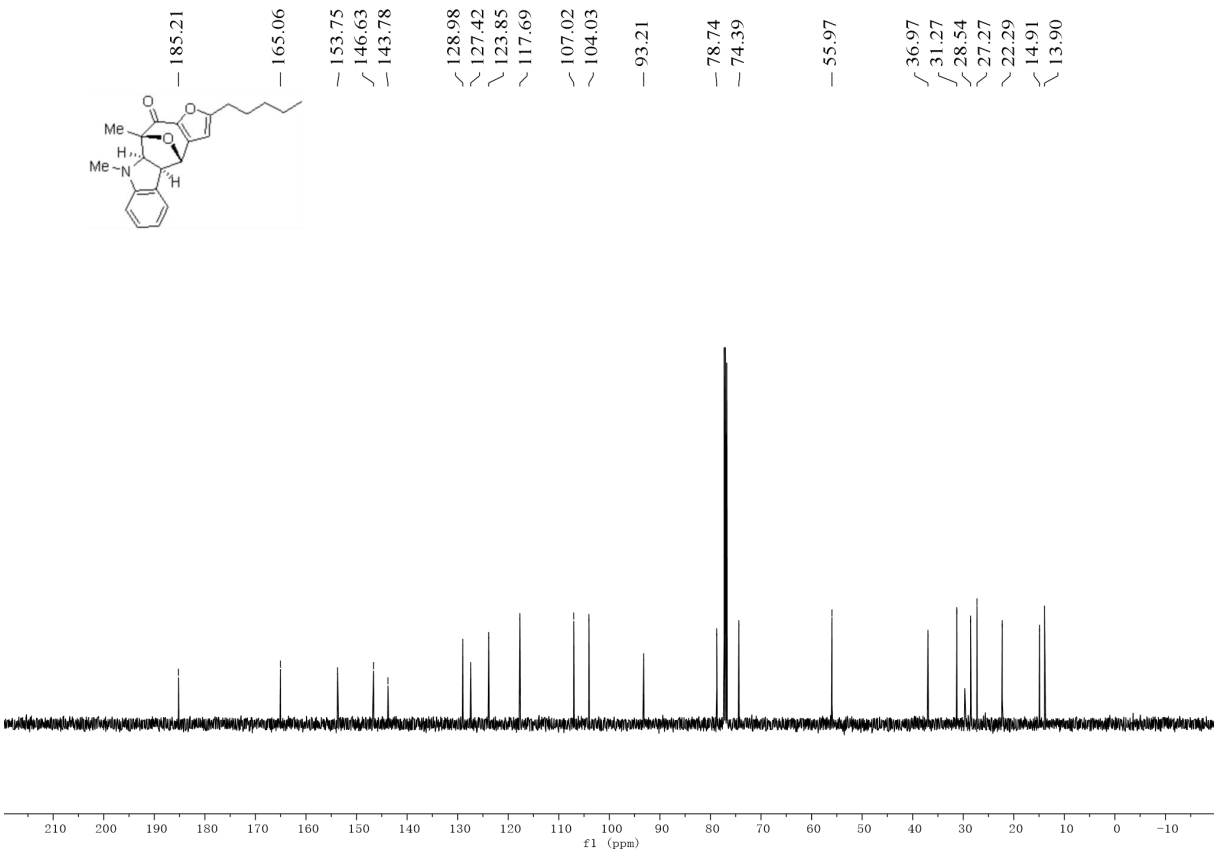
^{1}H and ^{13}C NMR spectra of 3ka



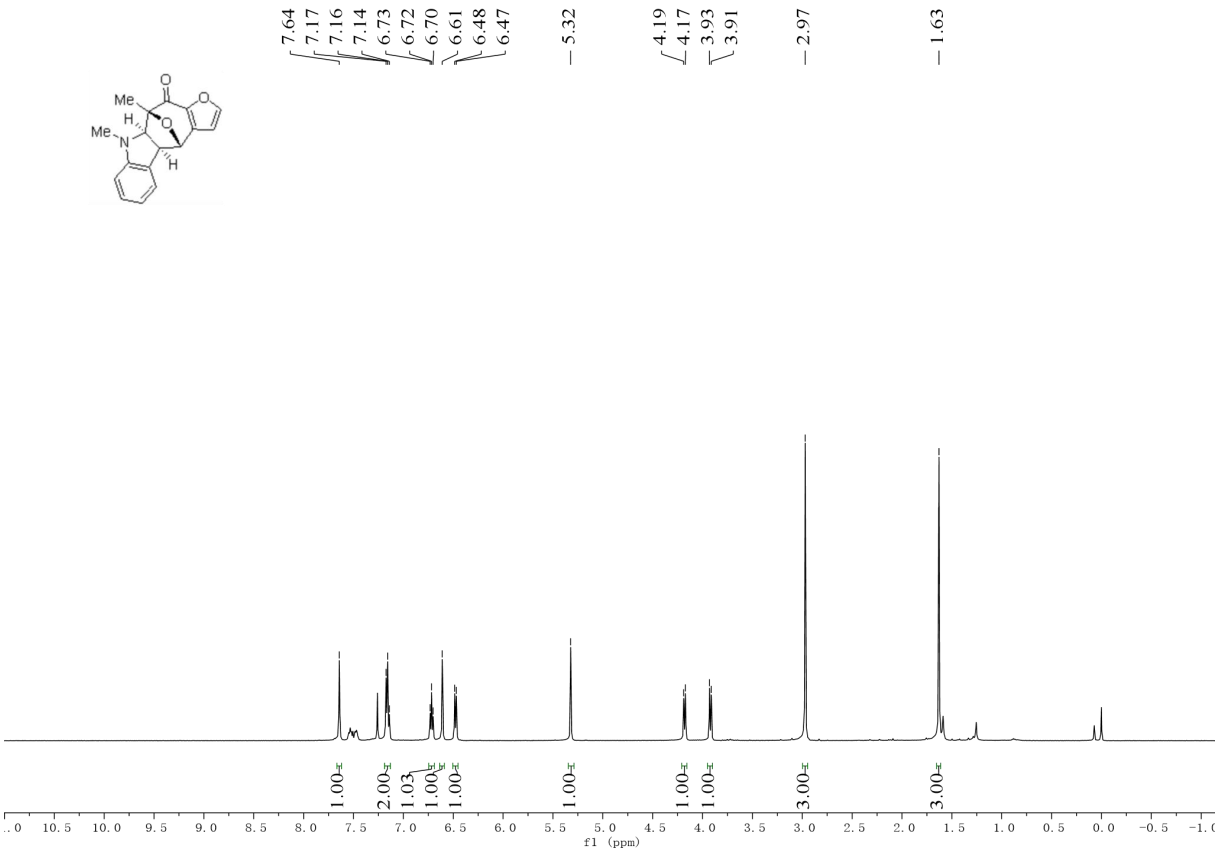


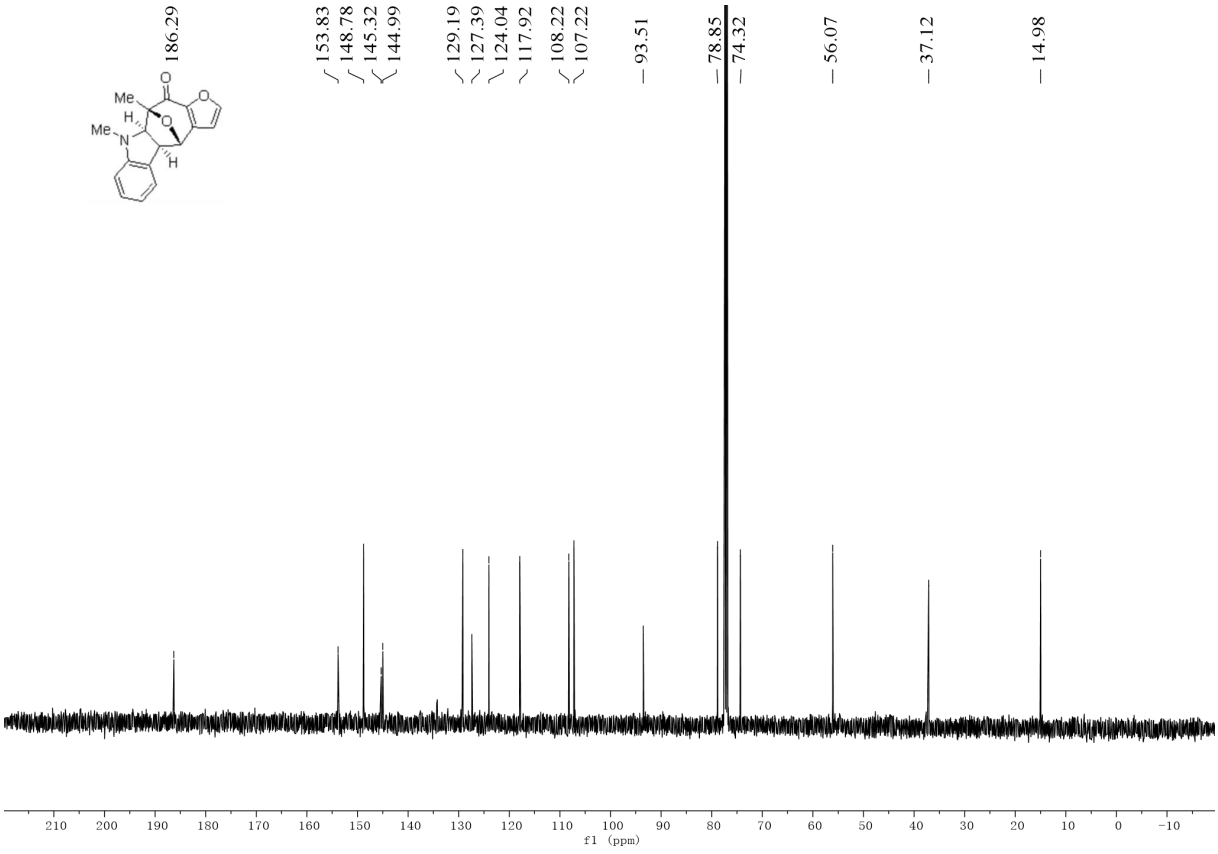
^{1}H and ^{13}C NMR spectra of 3la



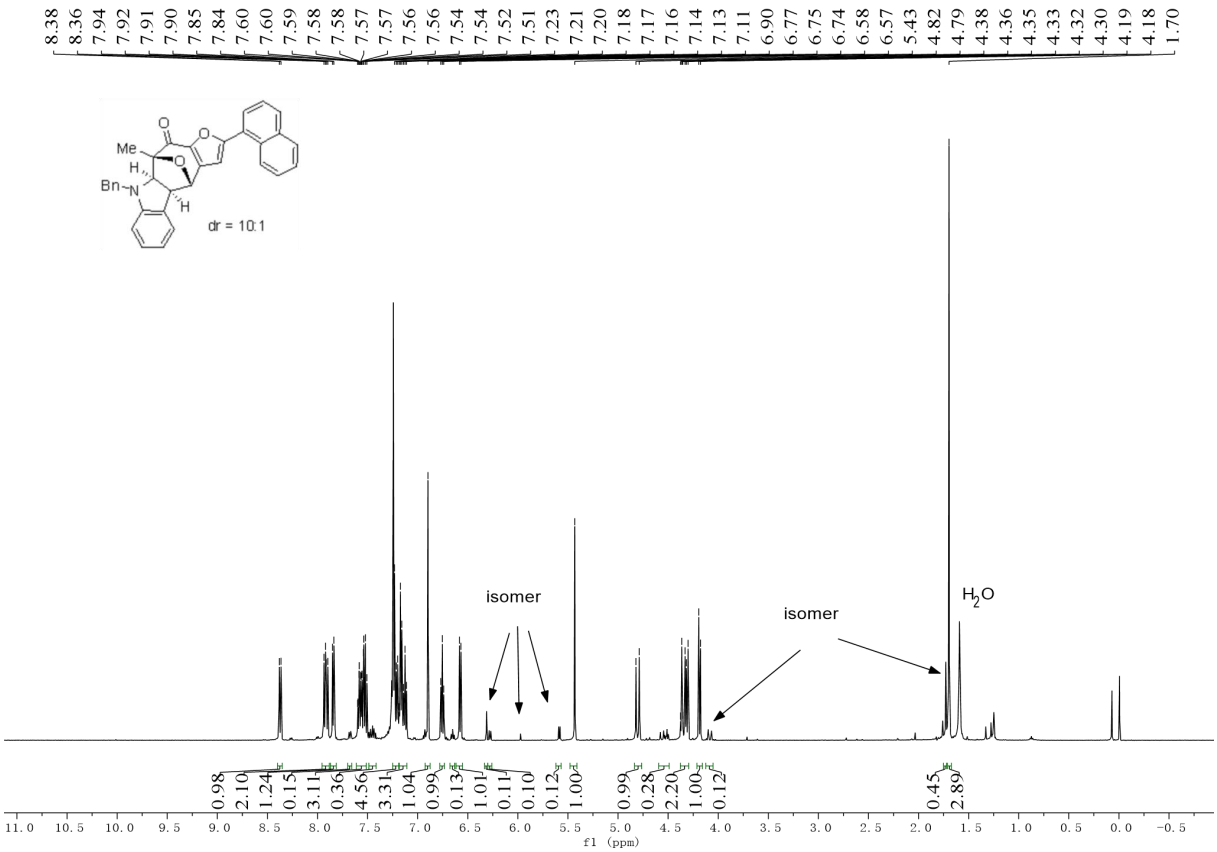


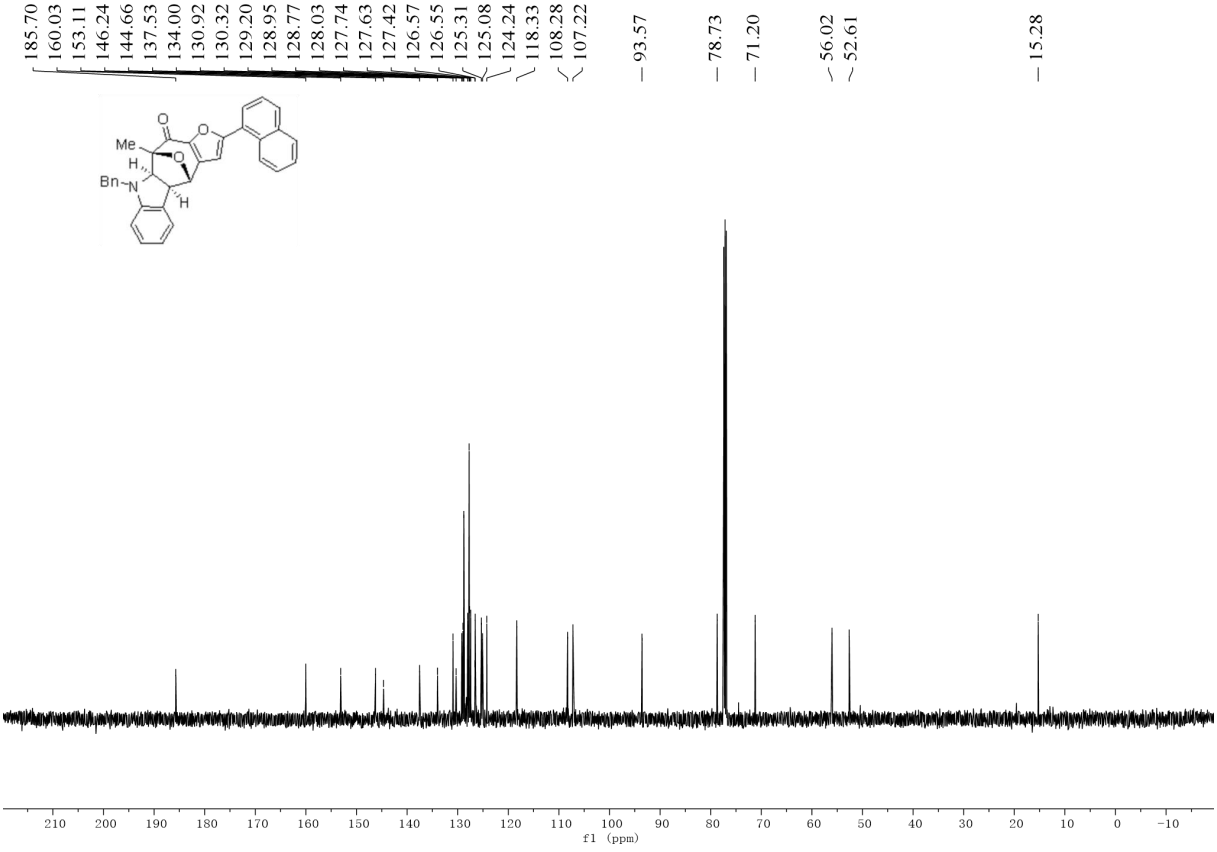
^{1}H and ^{13}C NMR spectra of 3ma



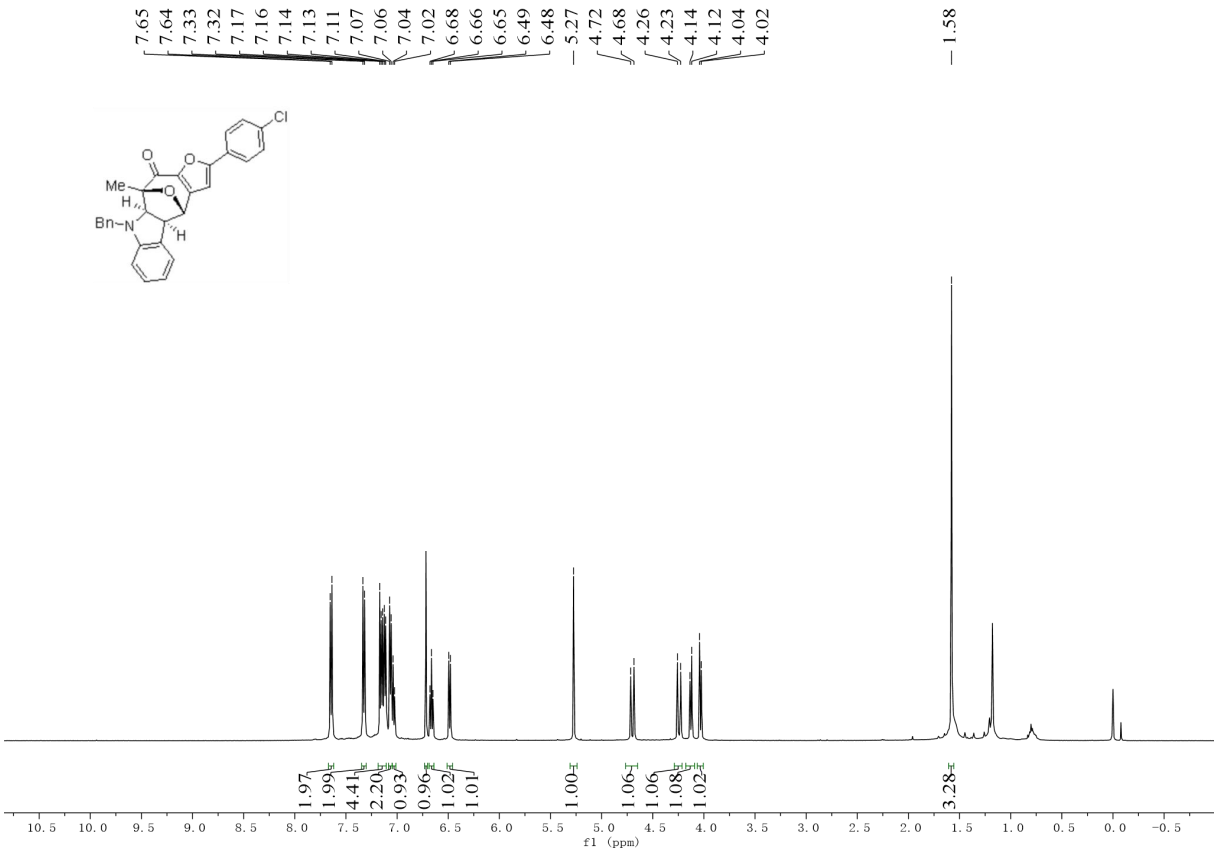


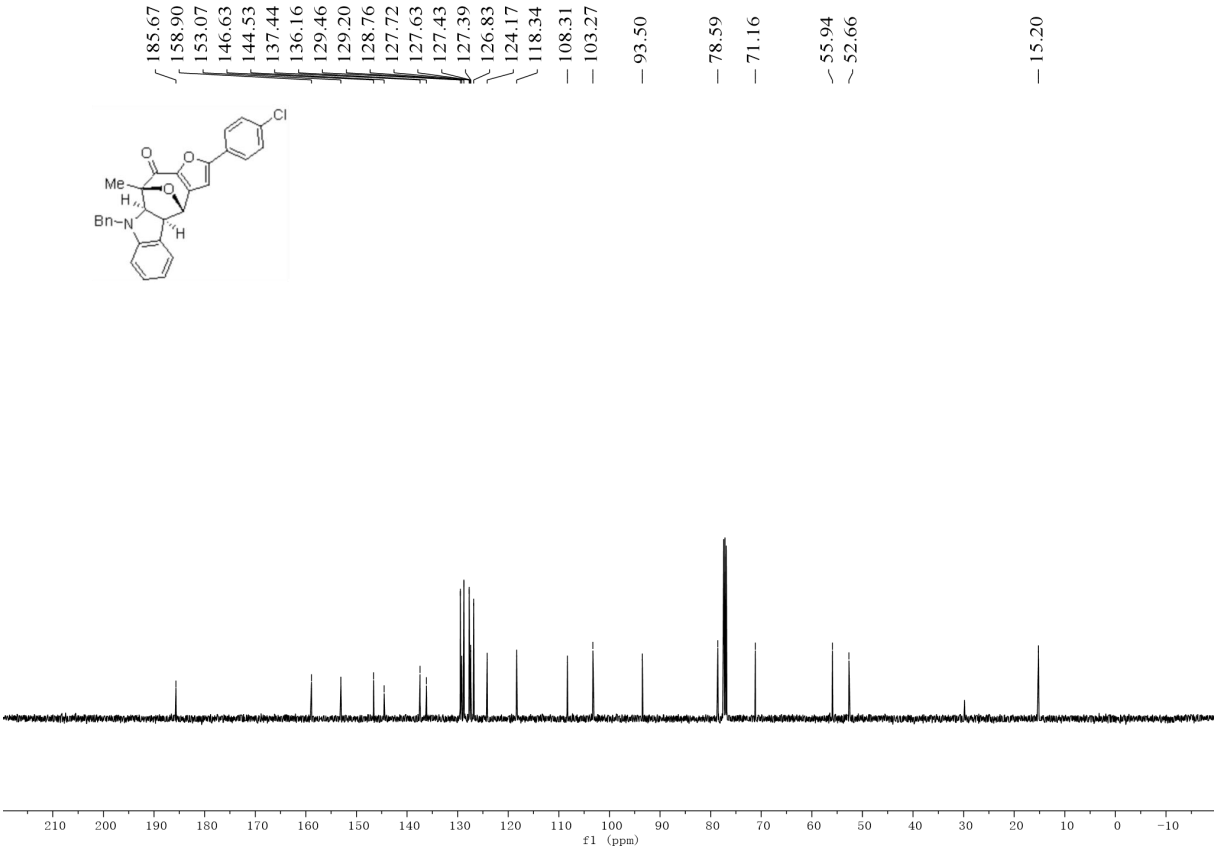
^{1}H and ^{13}C NMR spectra of 3ak



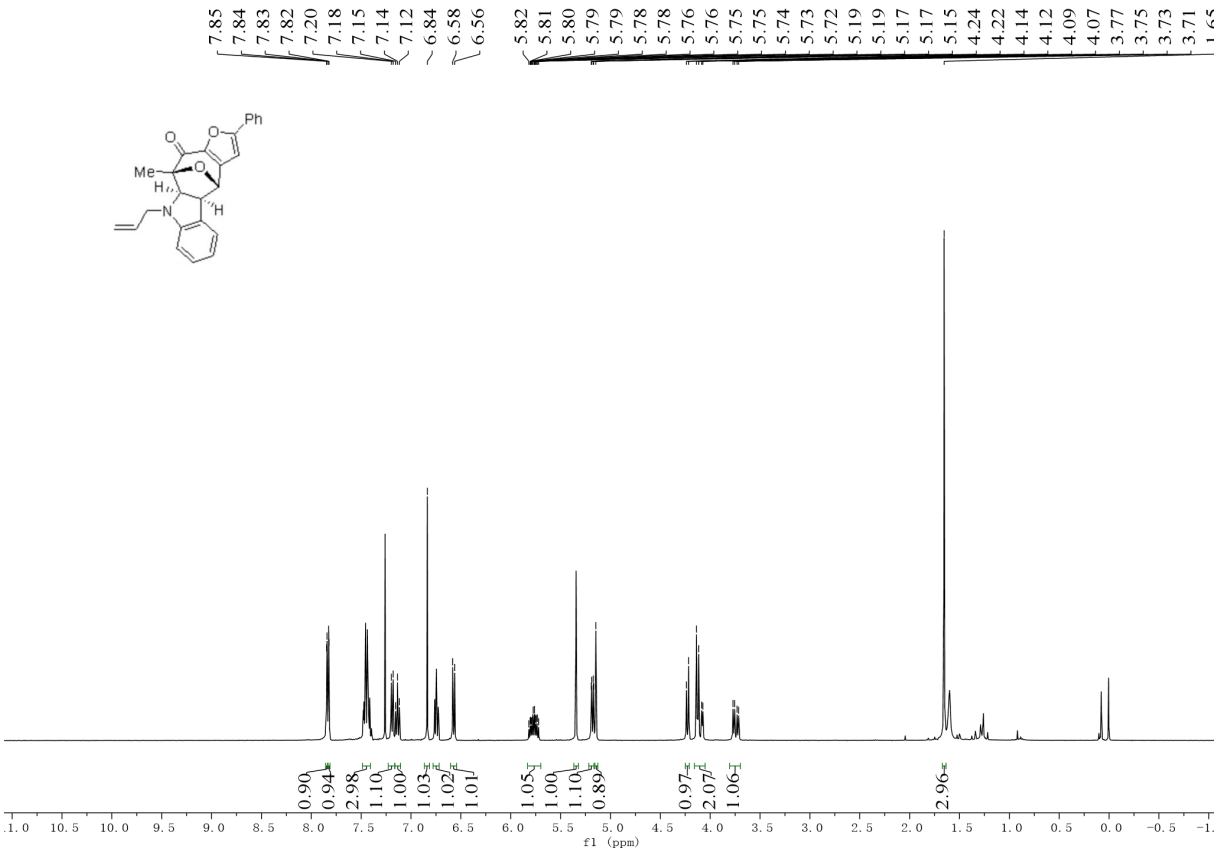


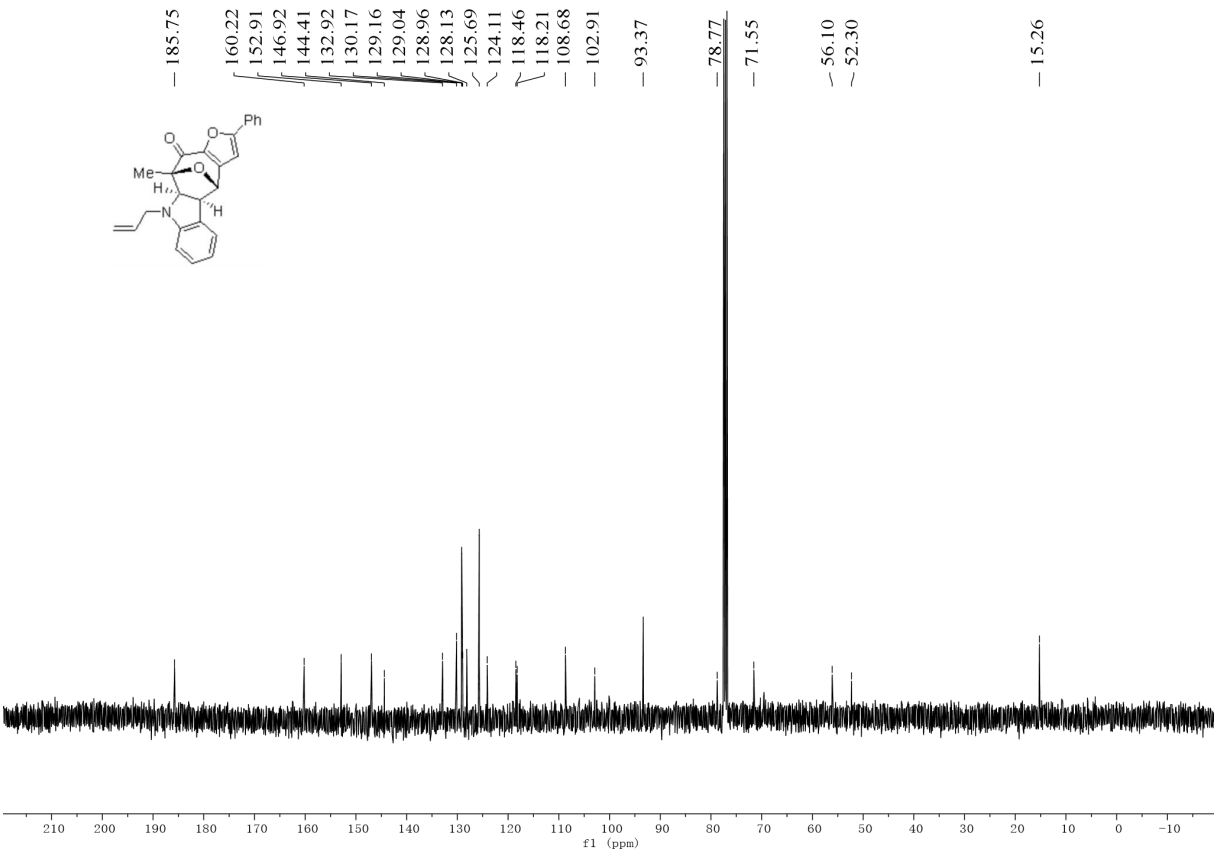
^{1}H and ^{13}C NMR spectra of 3dk



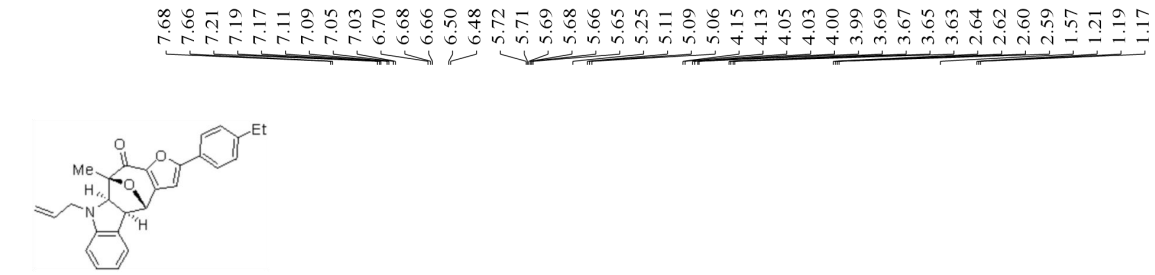


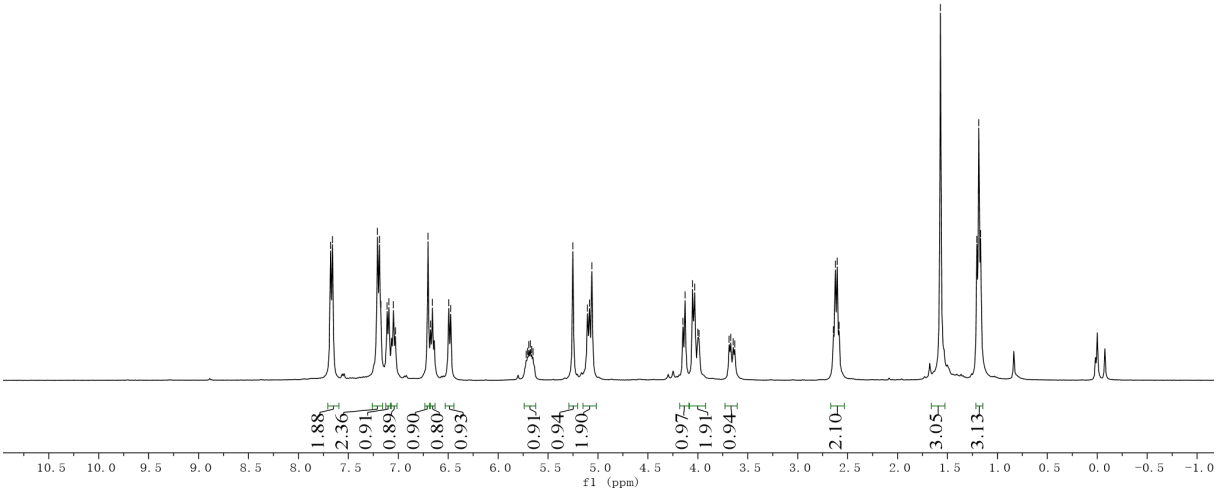
^{1}H and ^{13}C NMR spectra of 3al

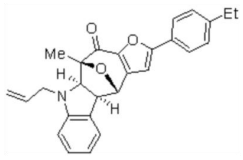


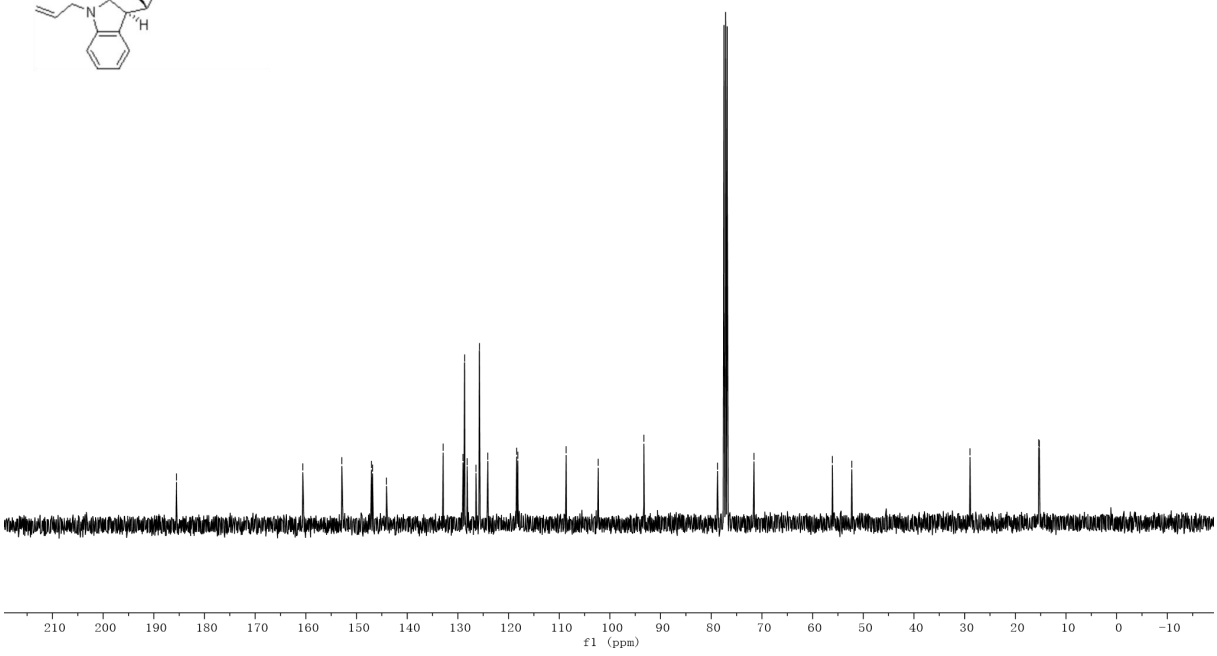


^{1}H and ^{13}C NMR spectra of 3fl

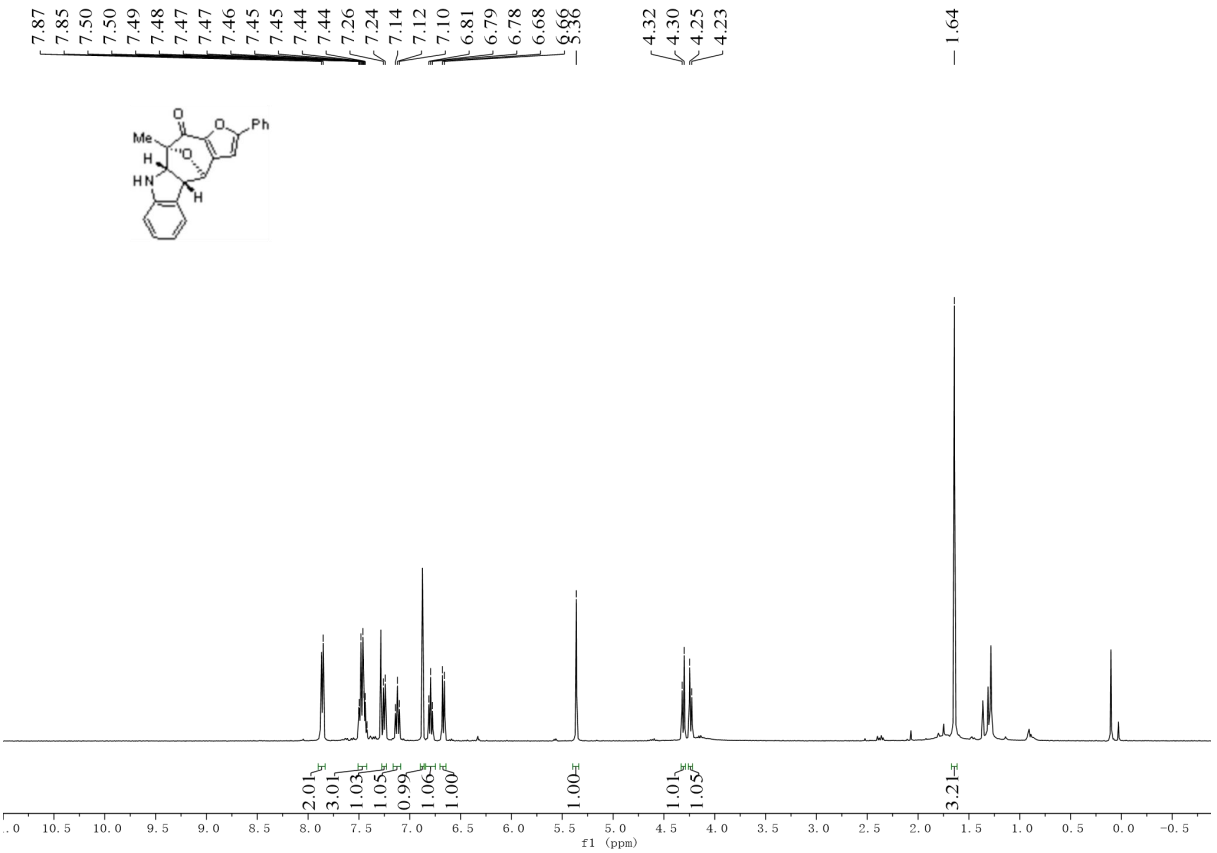


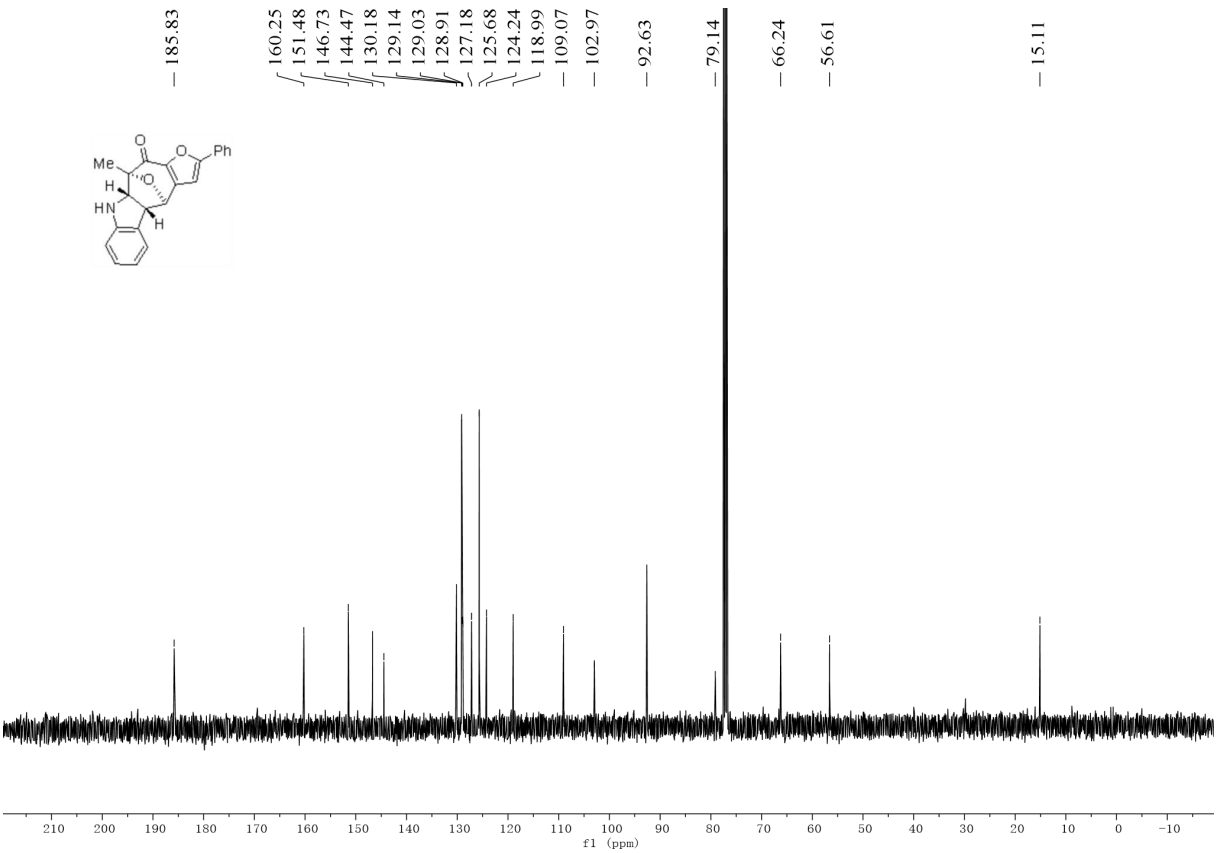




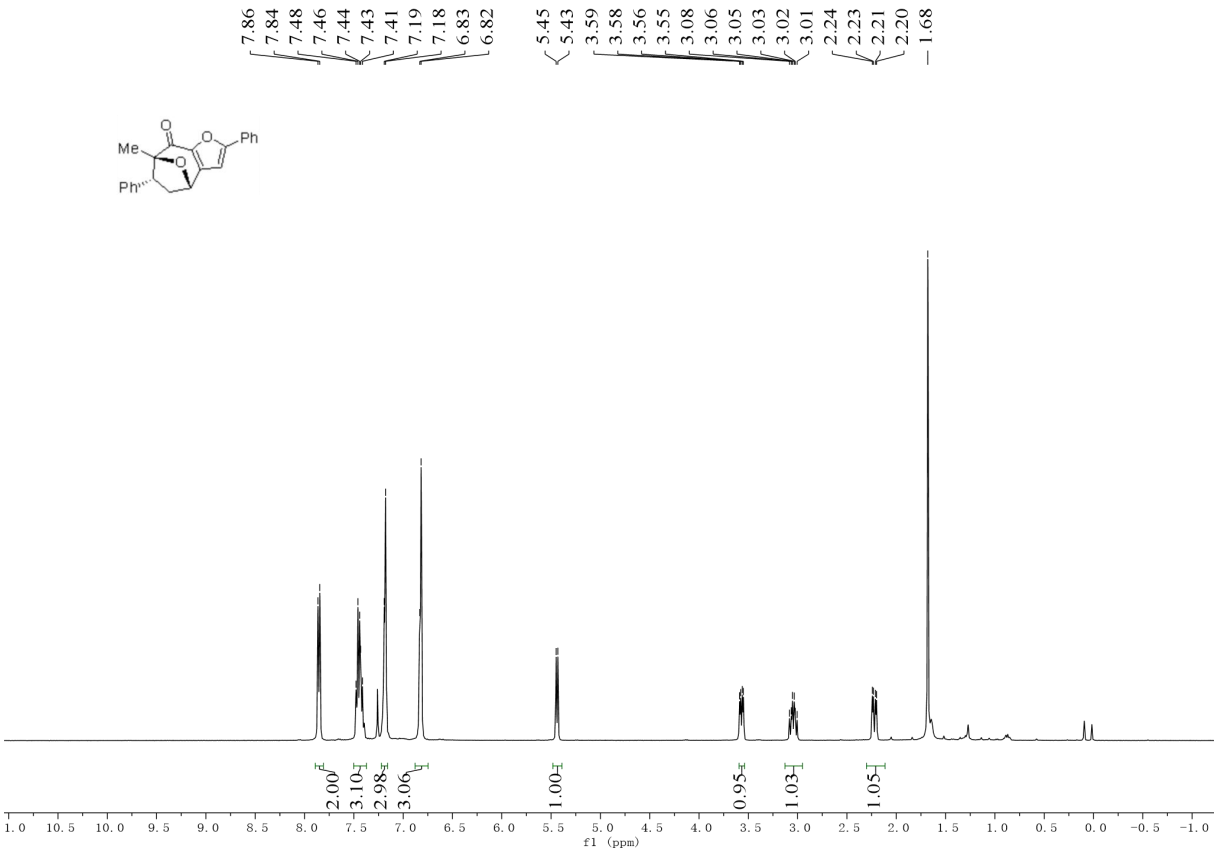


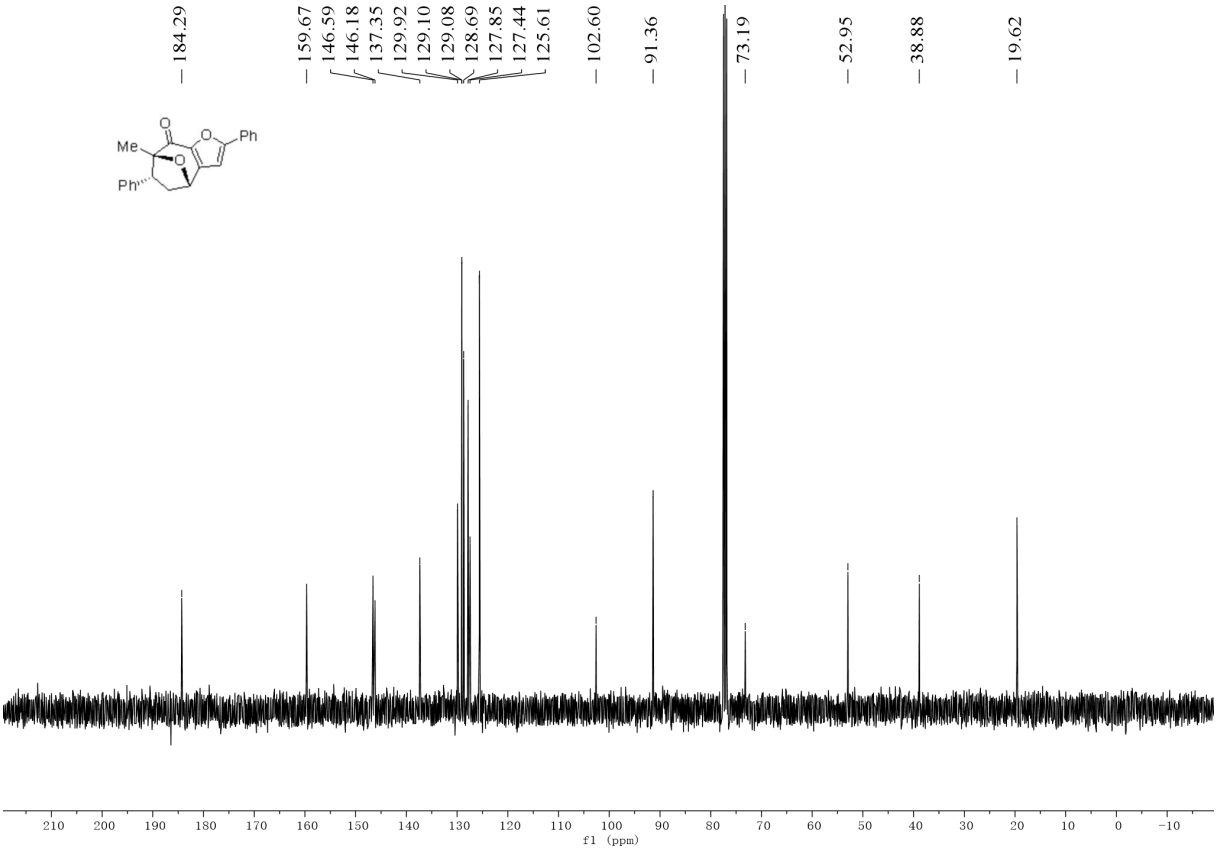
^{1}H and ^{13}C NMR spectra of 3am



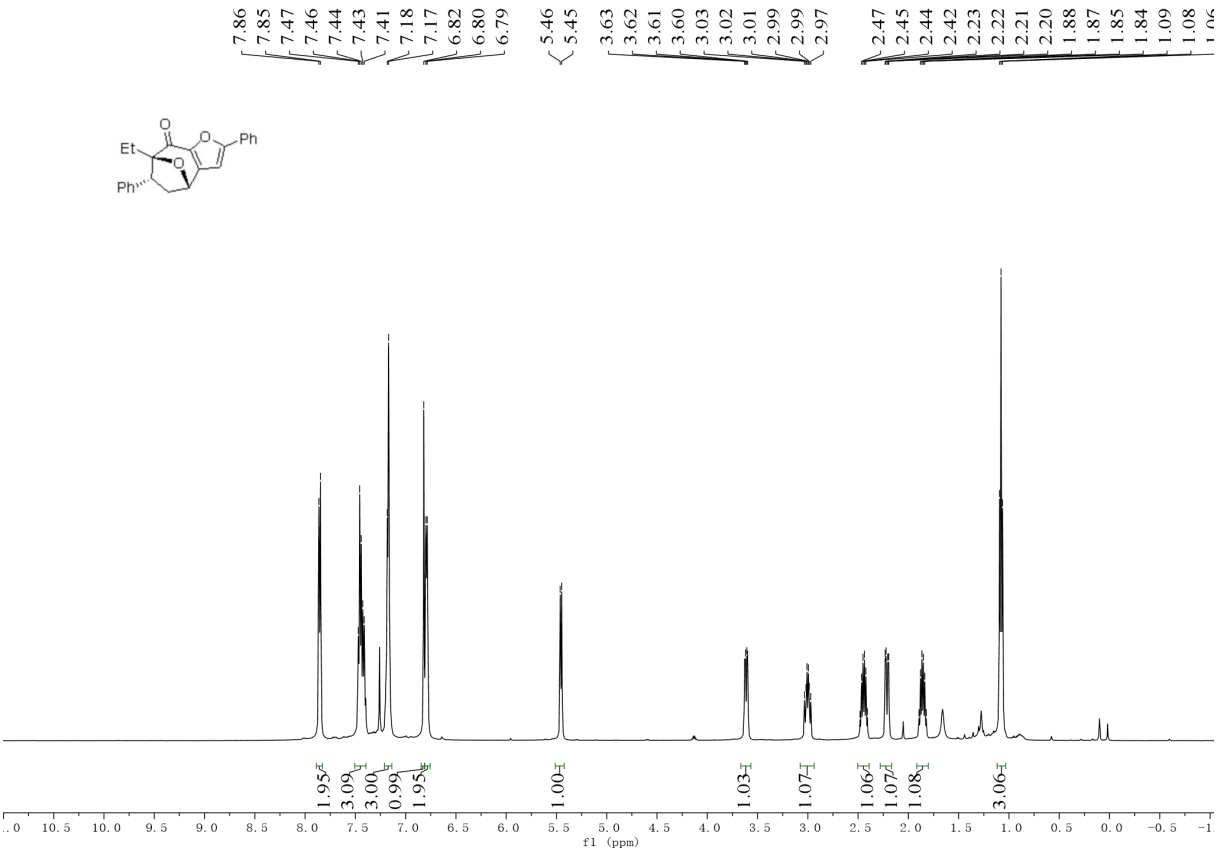


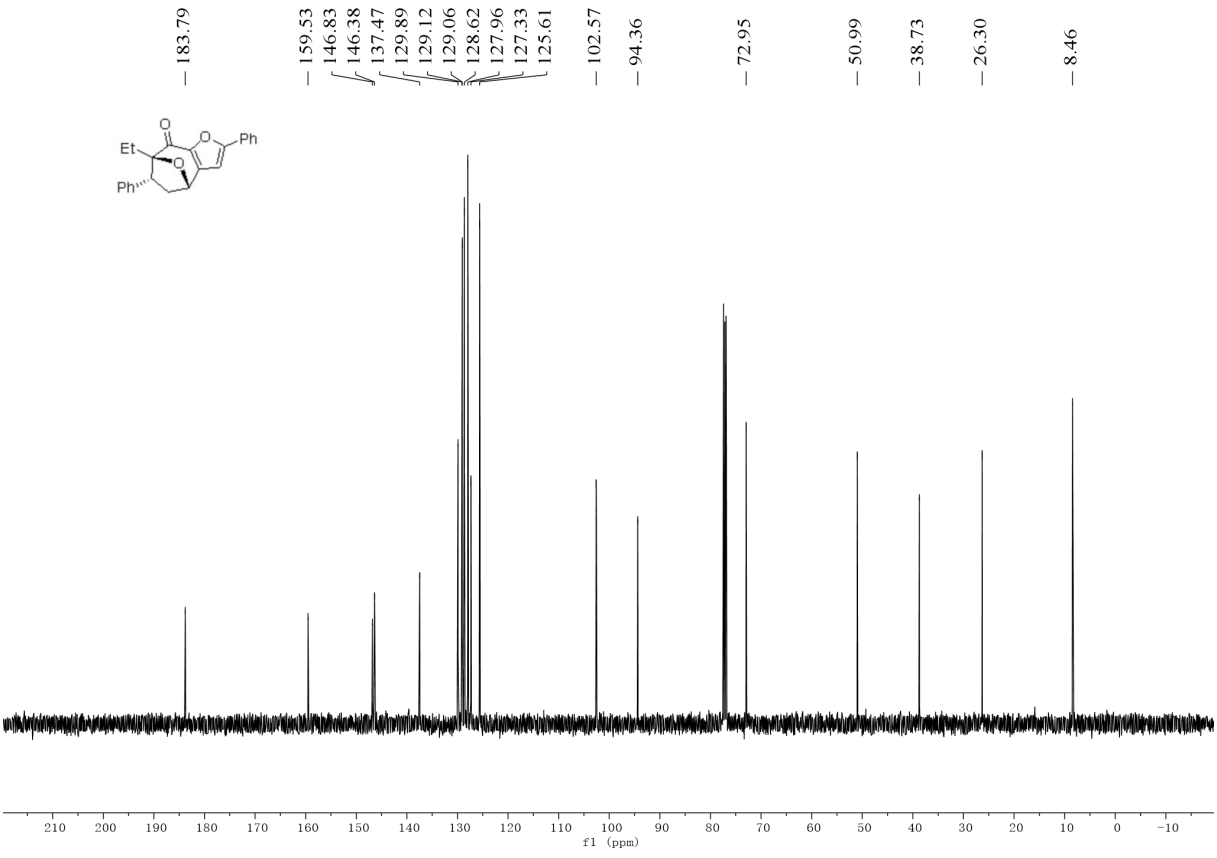
^{1}H and ^{13}C NMR spectra of 5aa



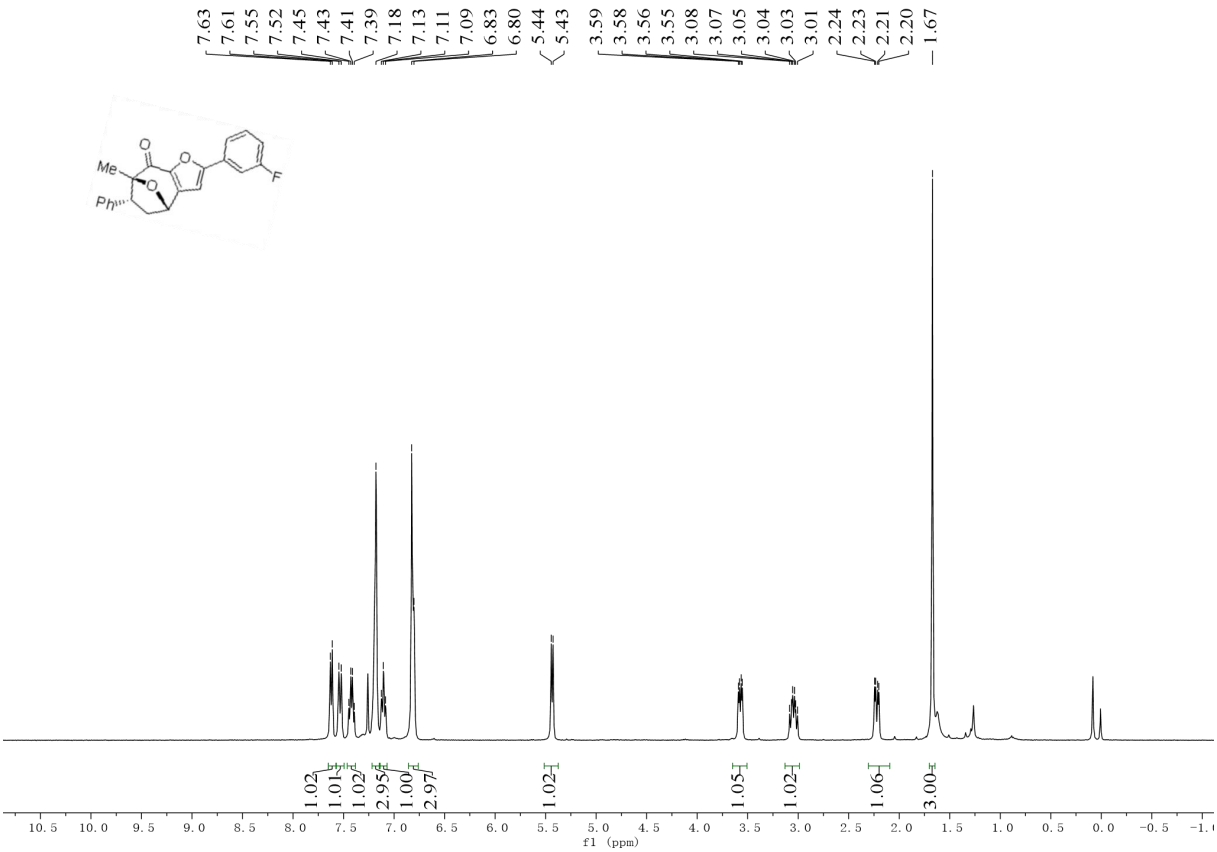


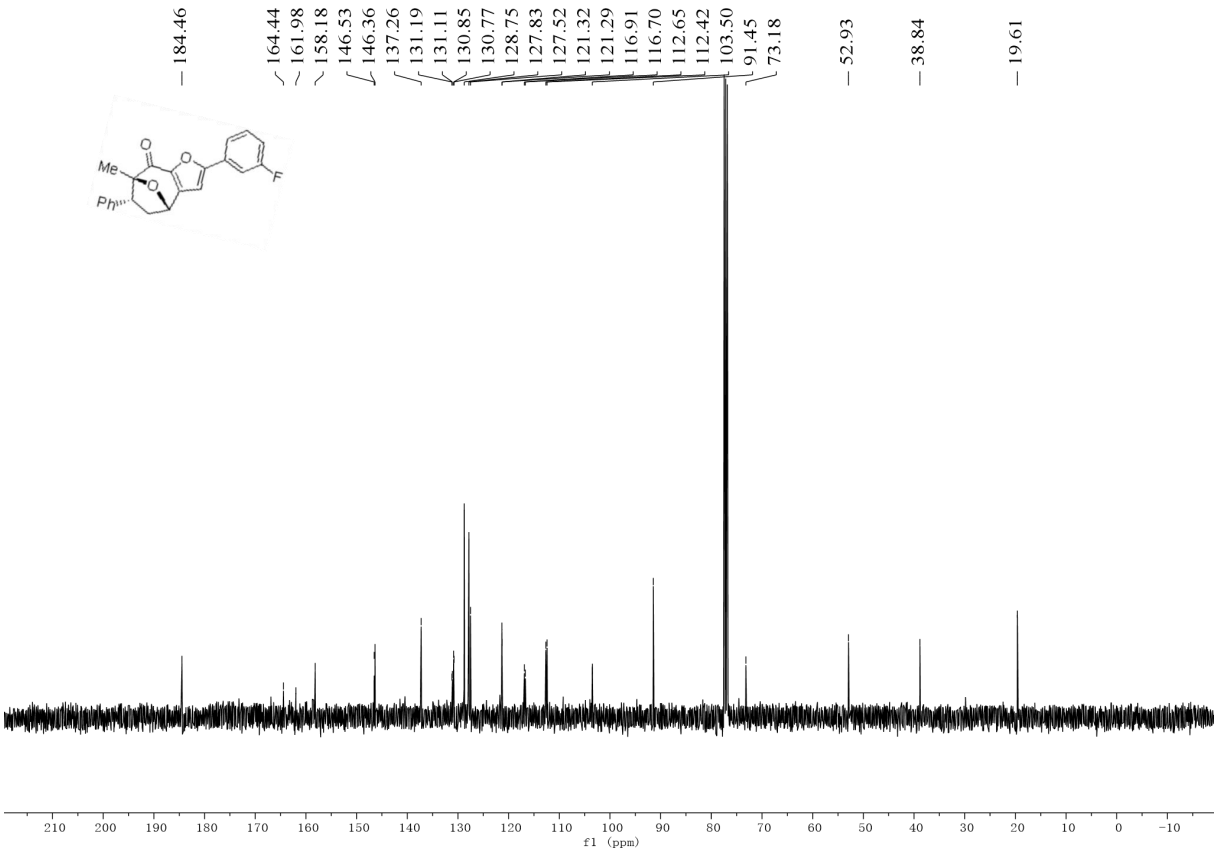
^{1}H and ^{13}C NMR spectra of 5ba



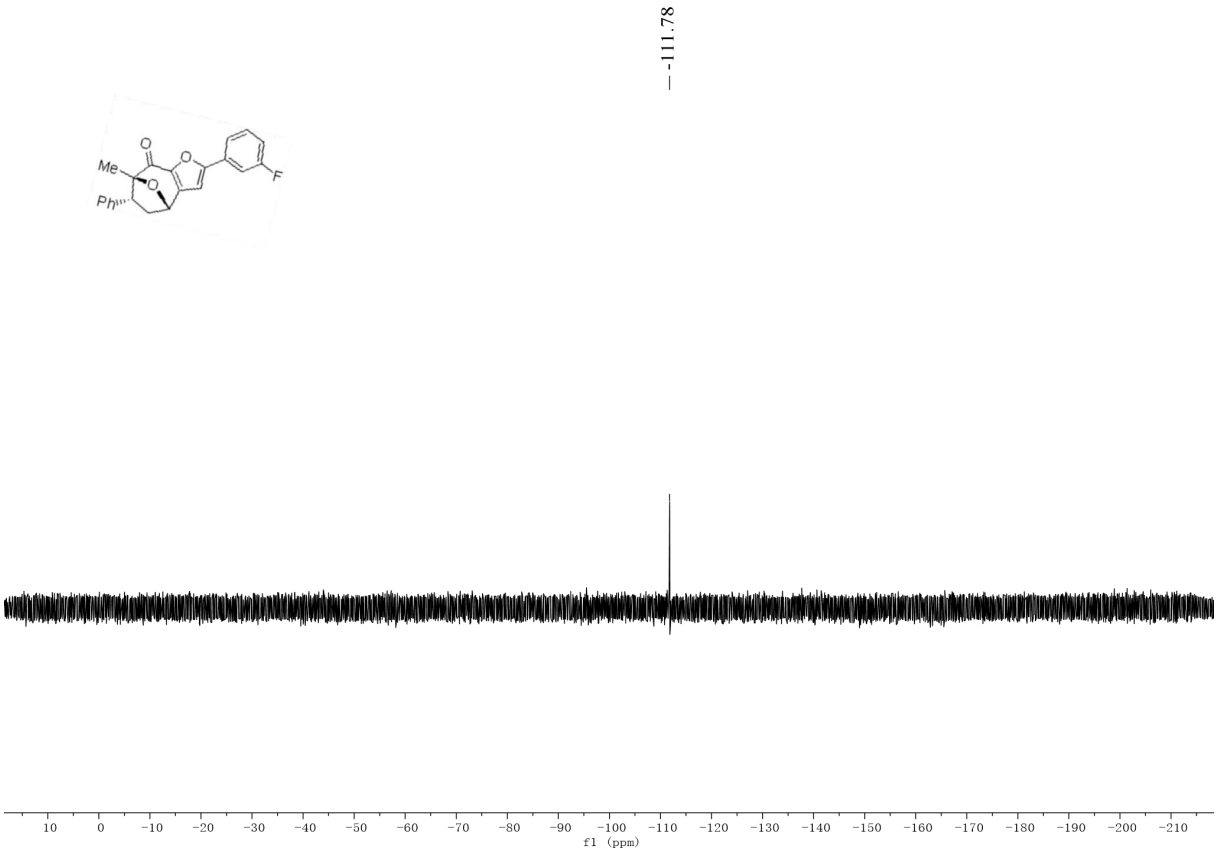


^{1}H and ^{13}C NMR and $^{19}FNMR$ spectra of 5ca

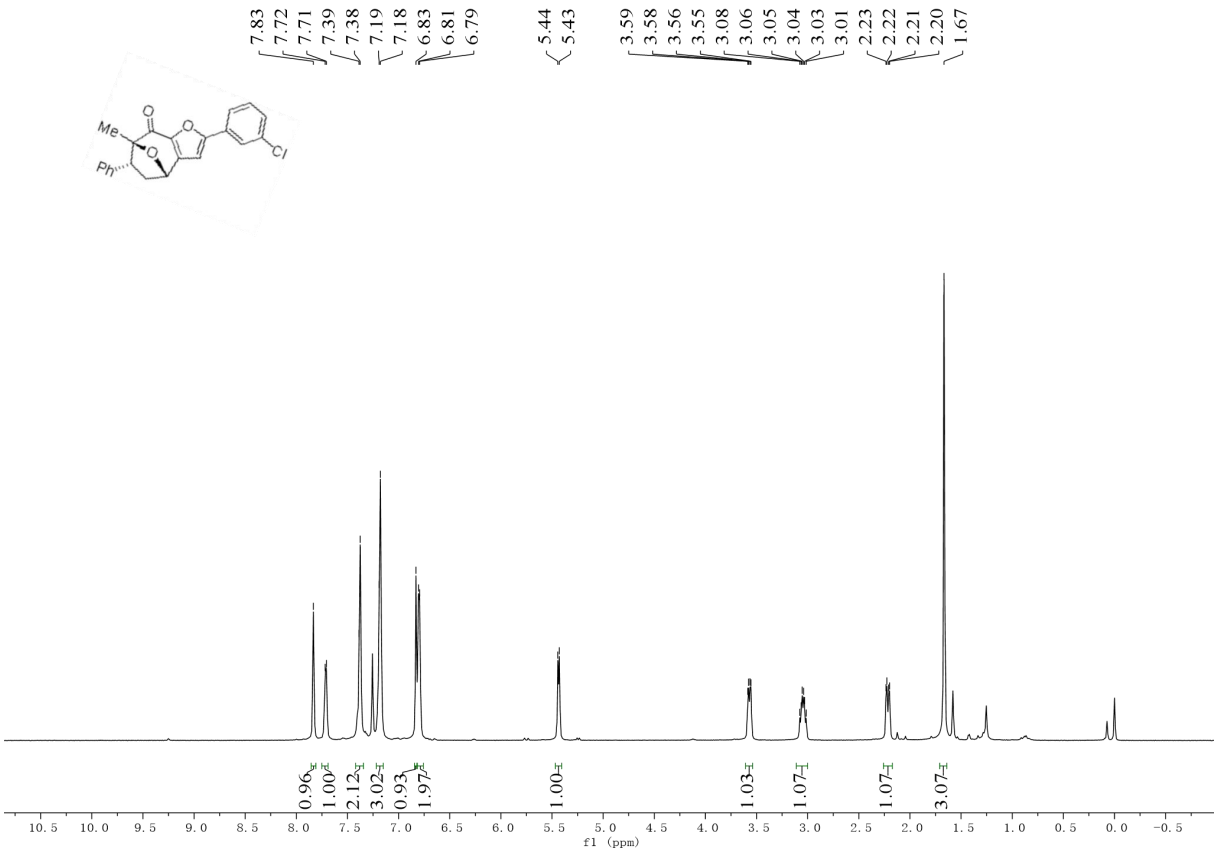


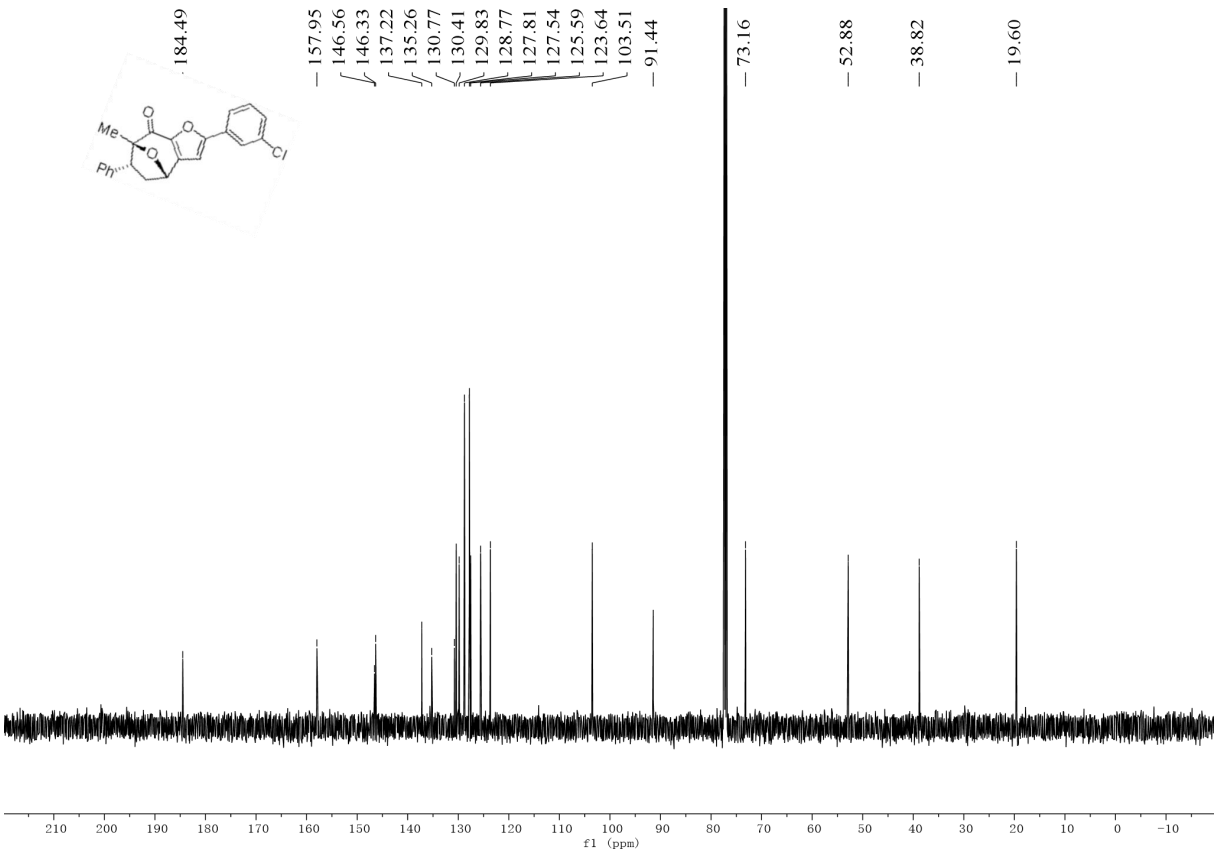


O
Me
O
Ph
O
F

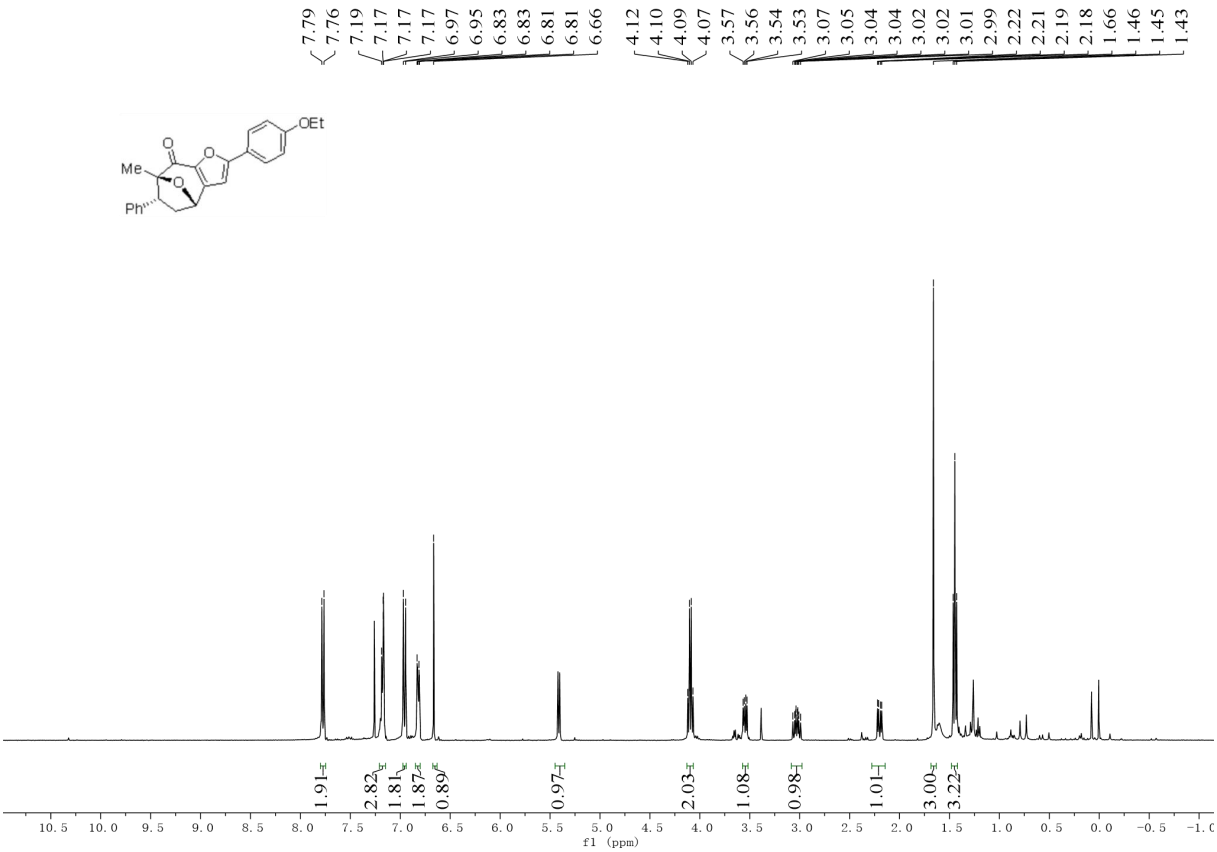

-111.78
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

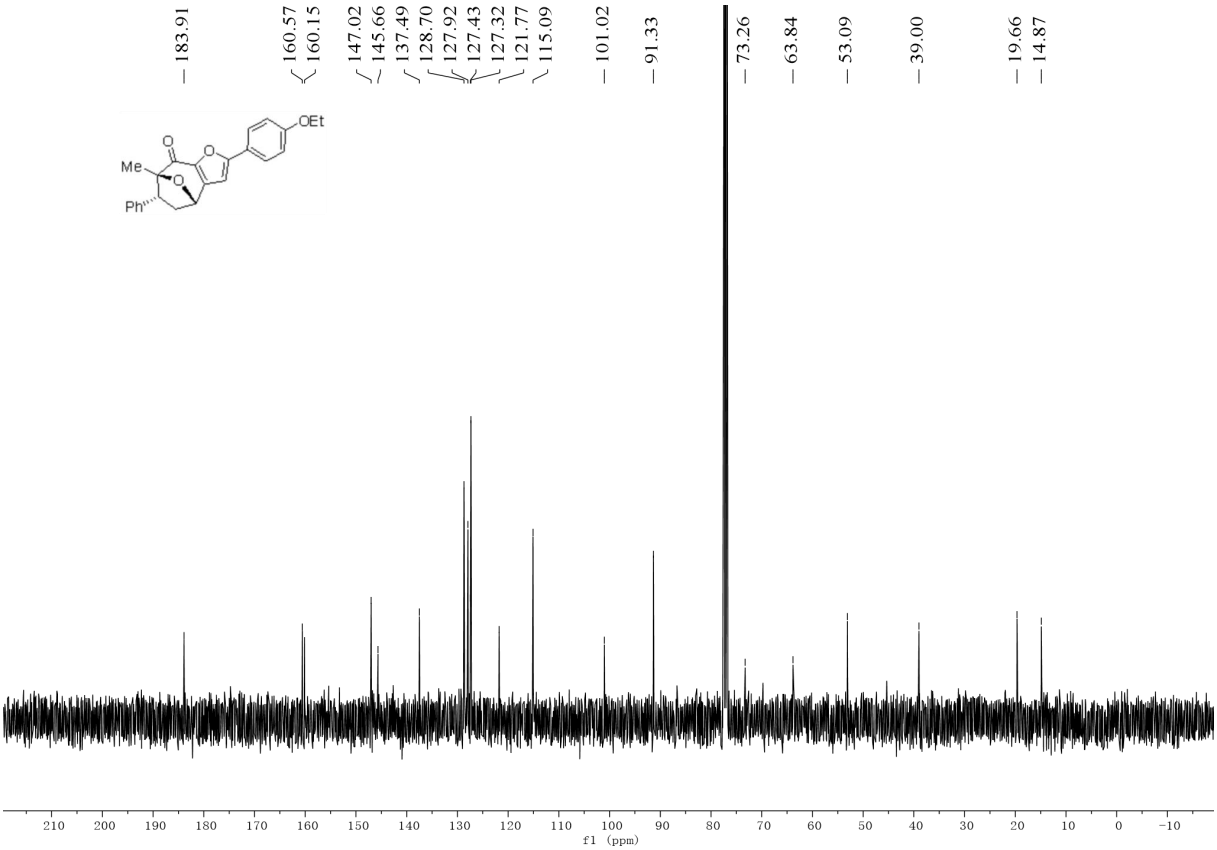
^{1}H and ^{13}C NMR spectra of 5na



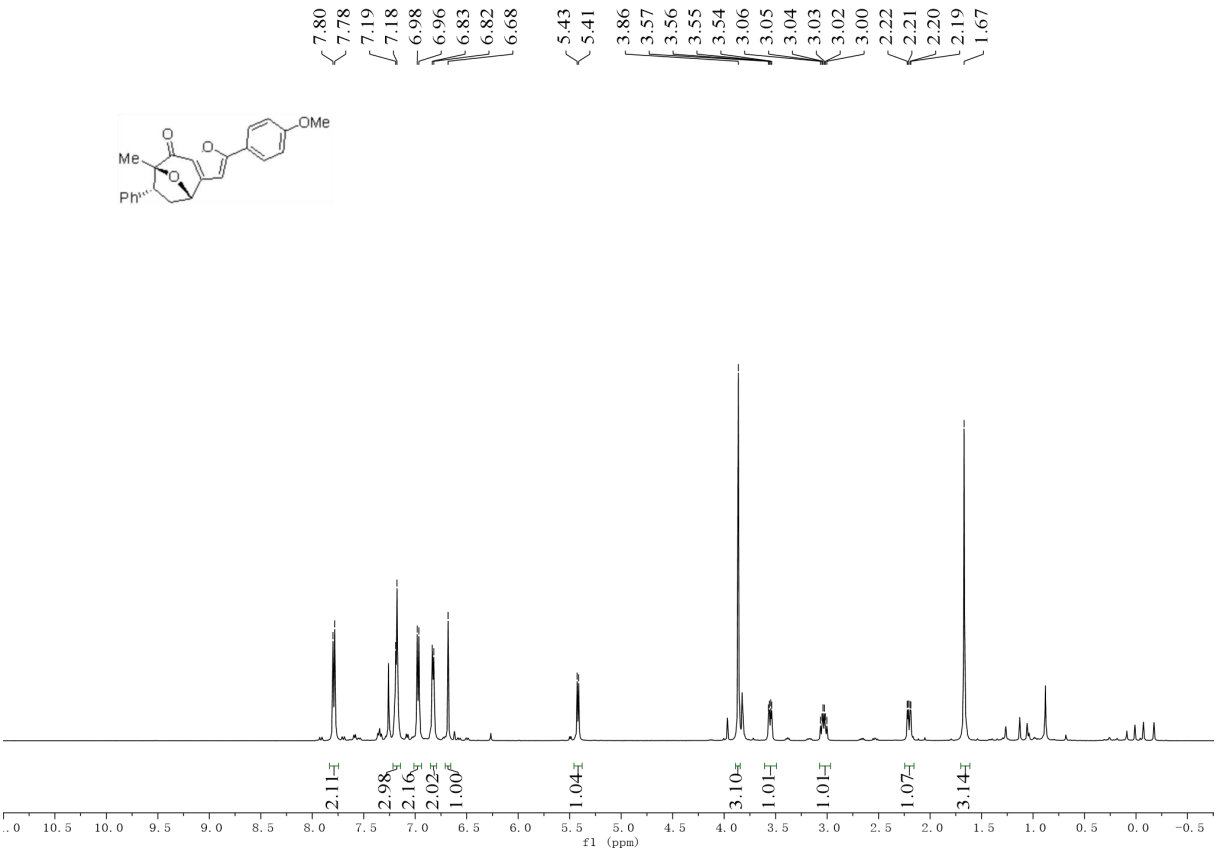


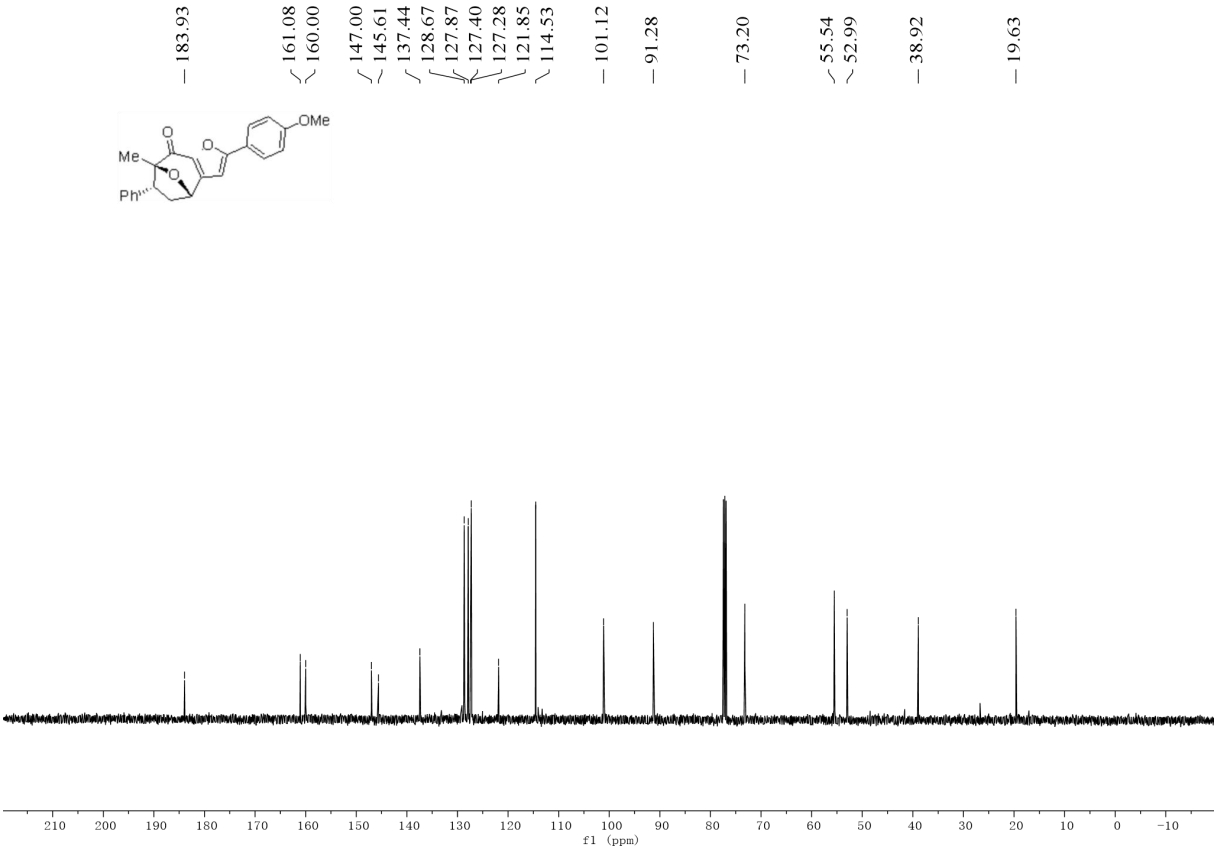
^{1}H and ^{13}C NMR spectra of 5qa



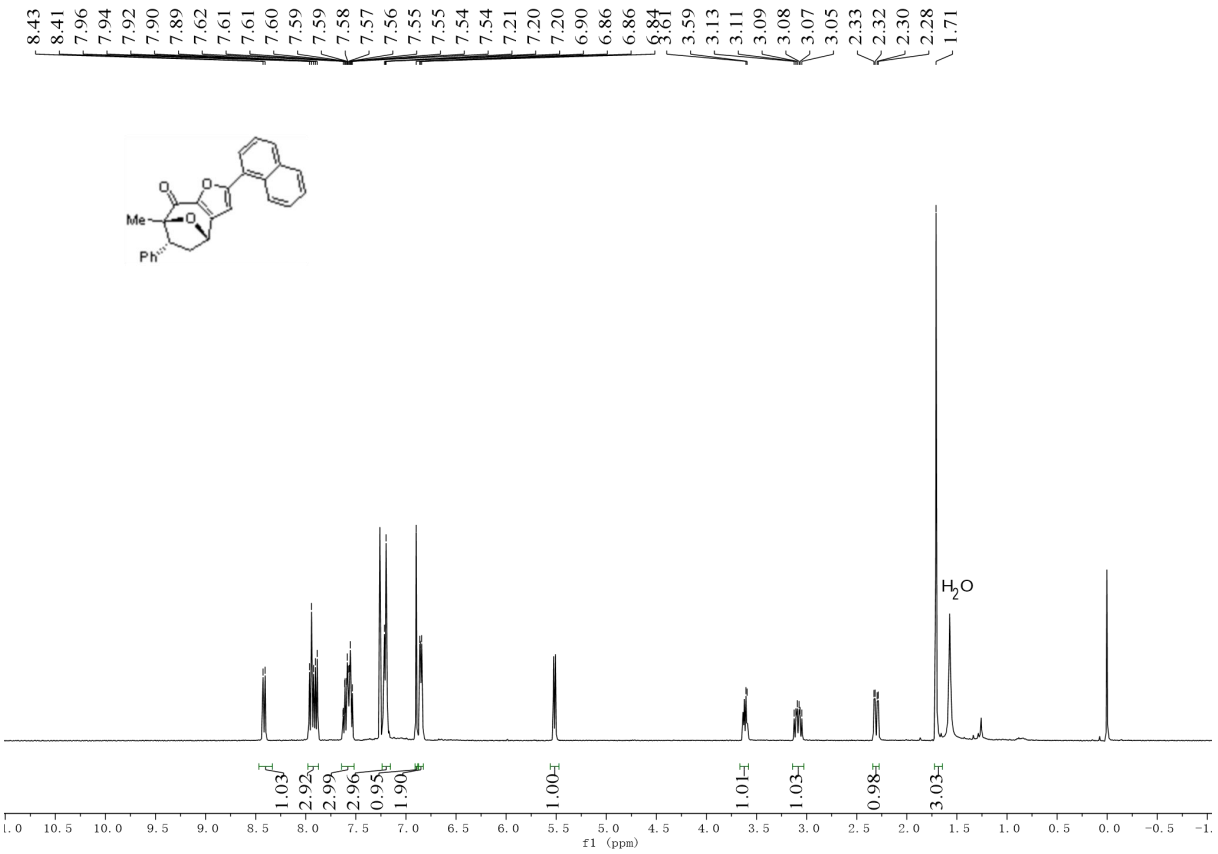


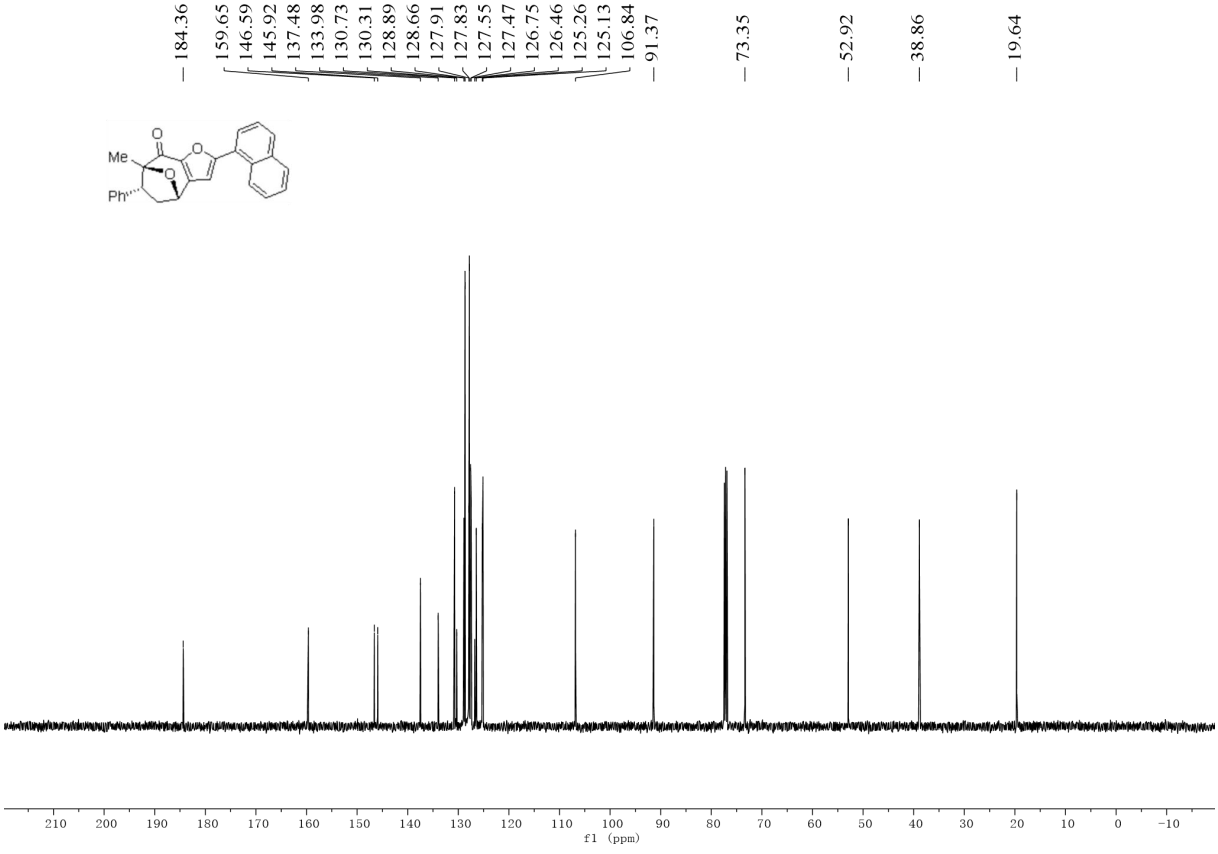
^{1}H and ^{13}C NMR spectra of 5ea



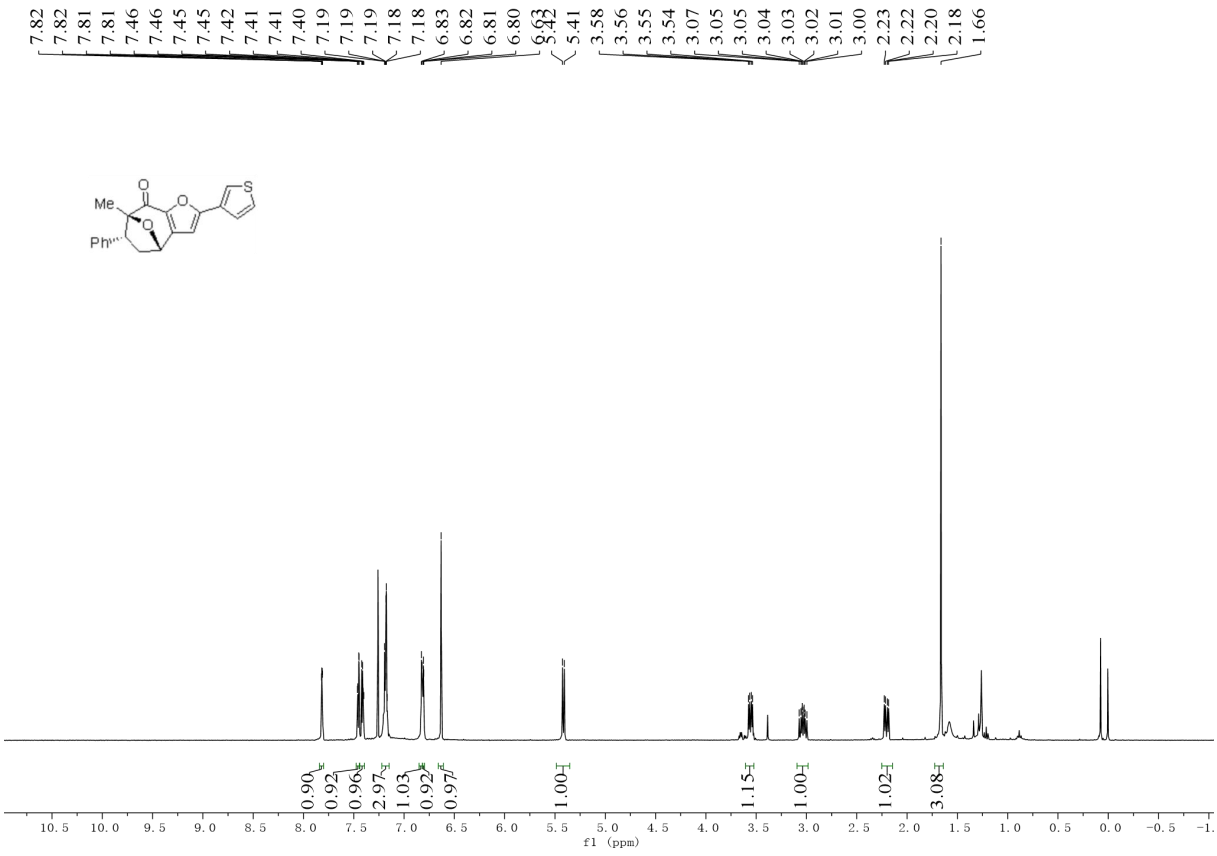


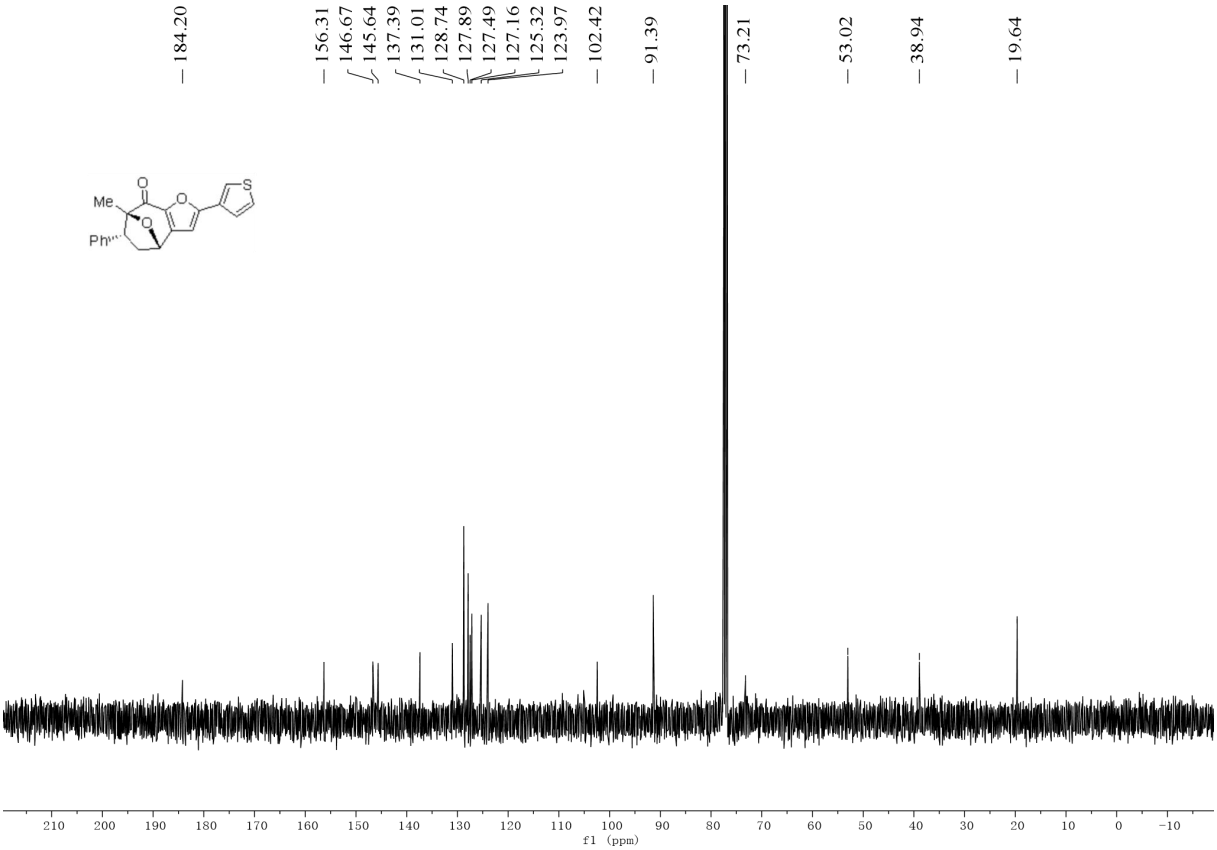
^{1}H and ^{13}C NMR spectra of 5ha



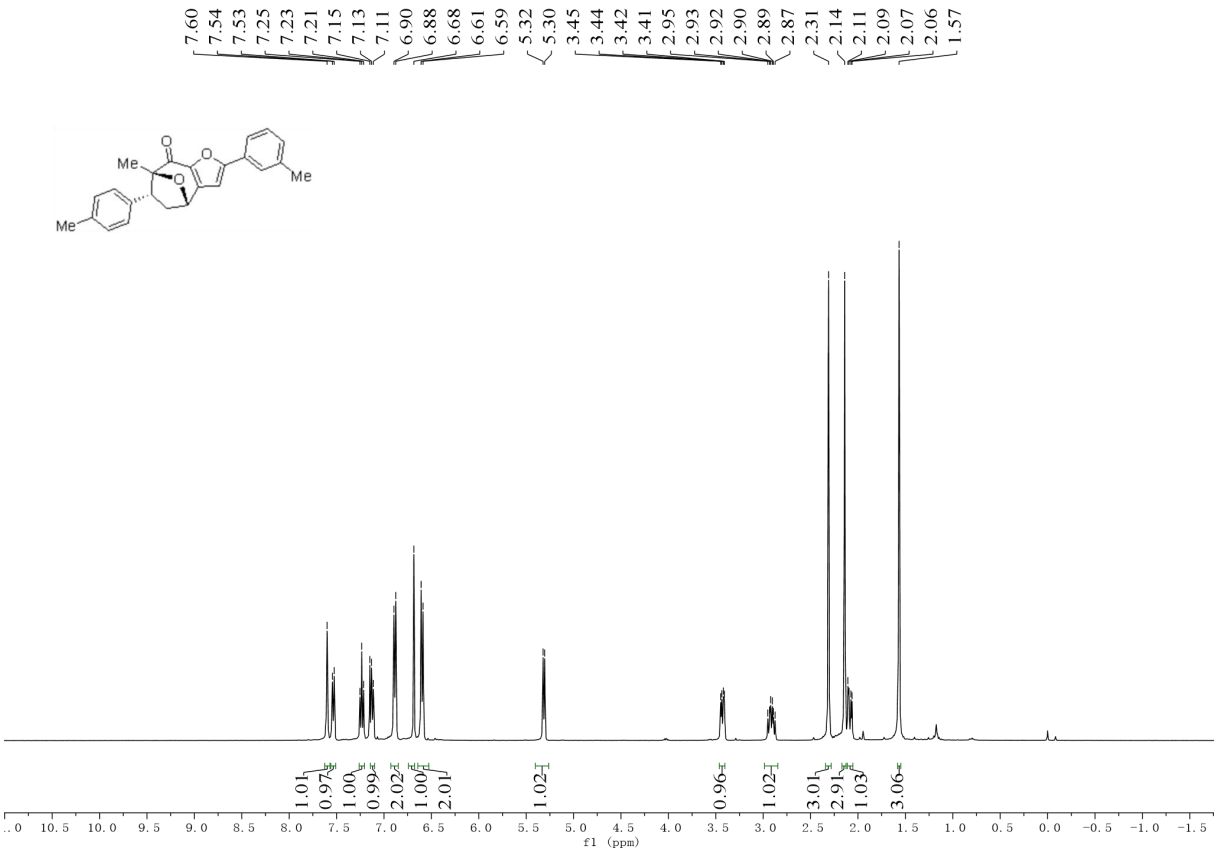


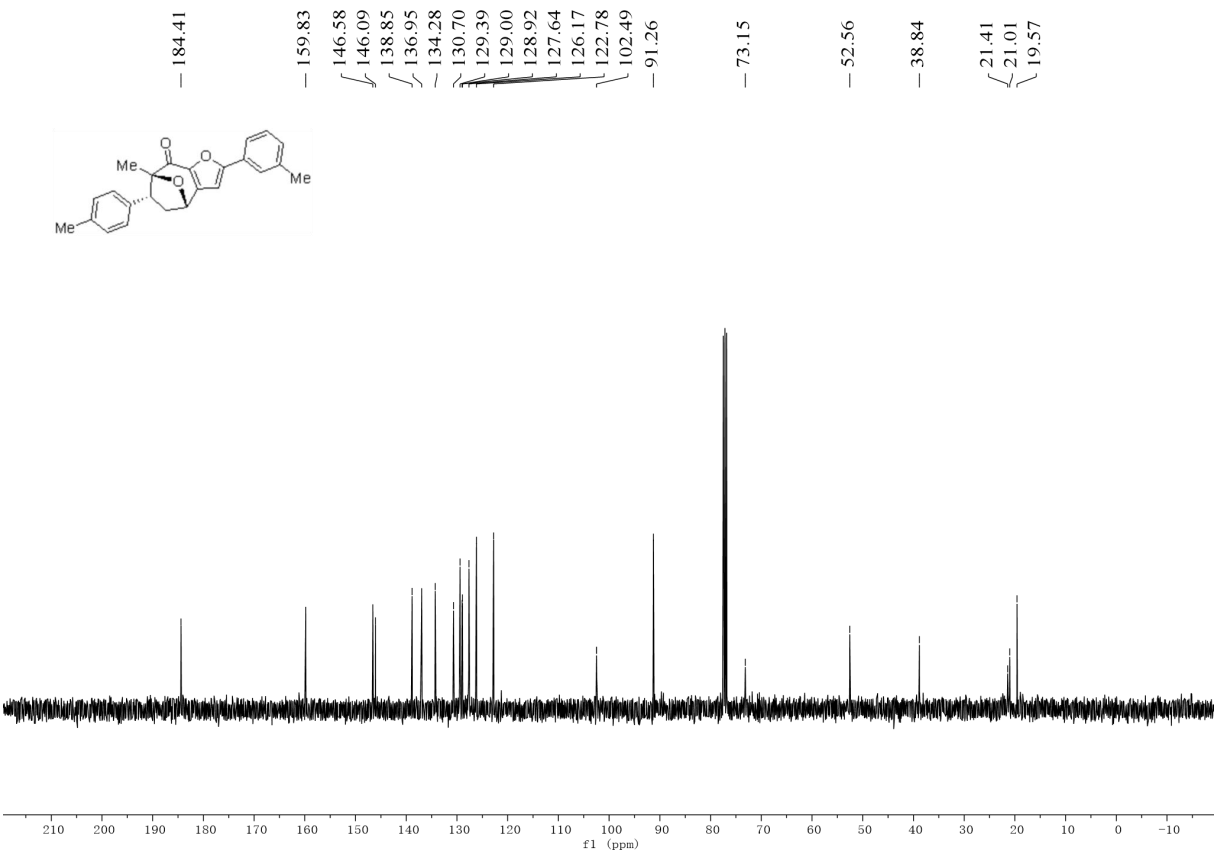
^{1}H and ^{13}C NMR spectra of 5ia



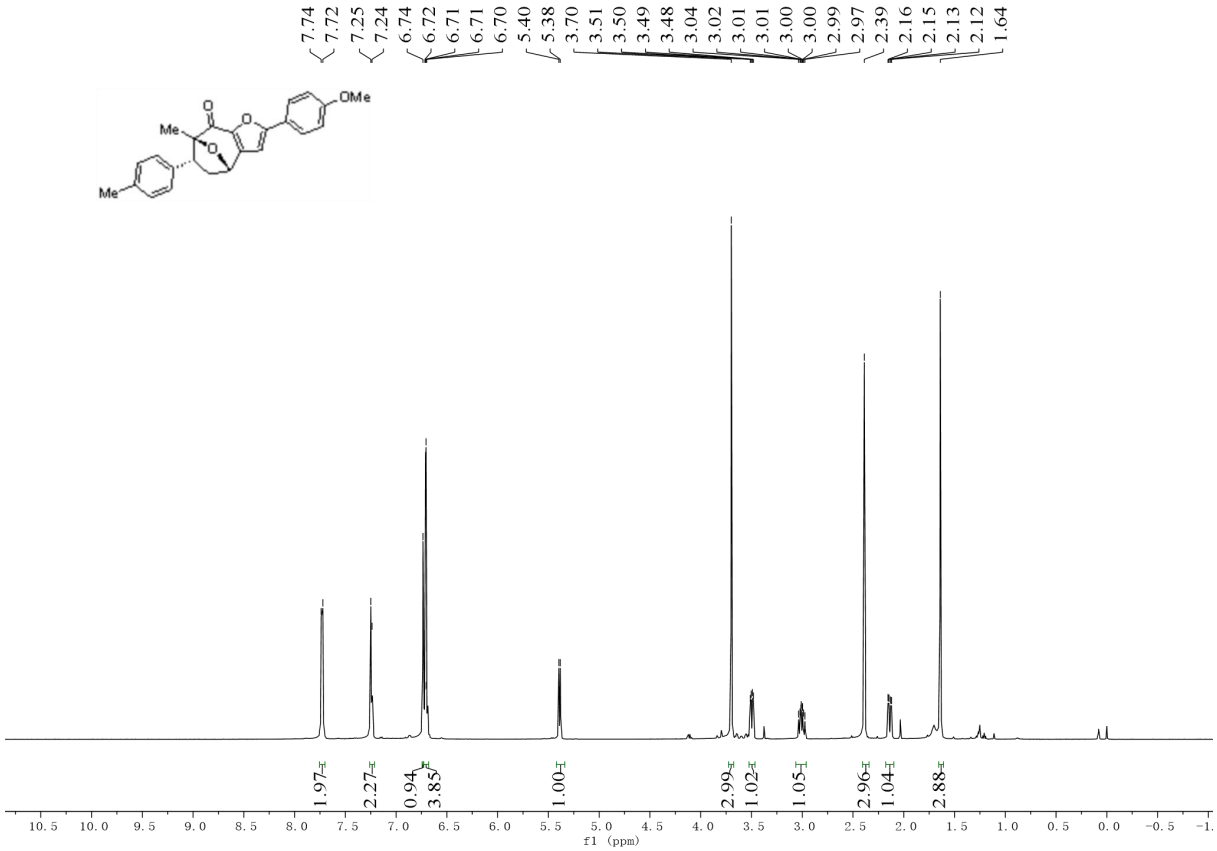


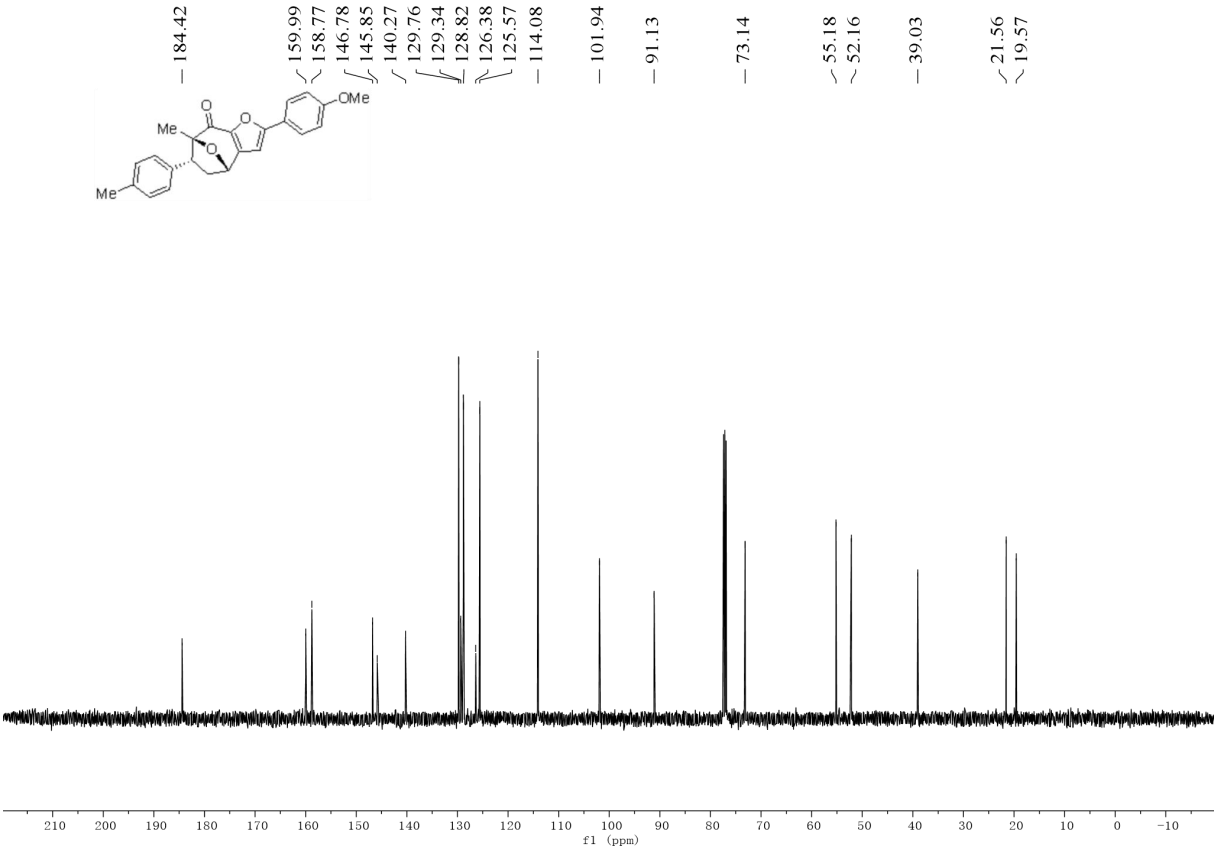
^{1}H and ^{13}C NMR spectra of 5ob



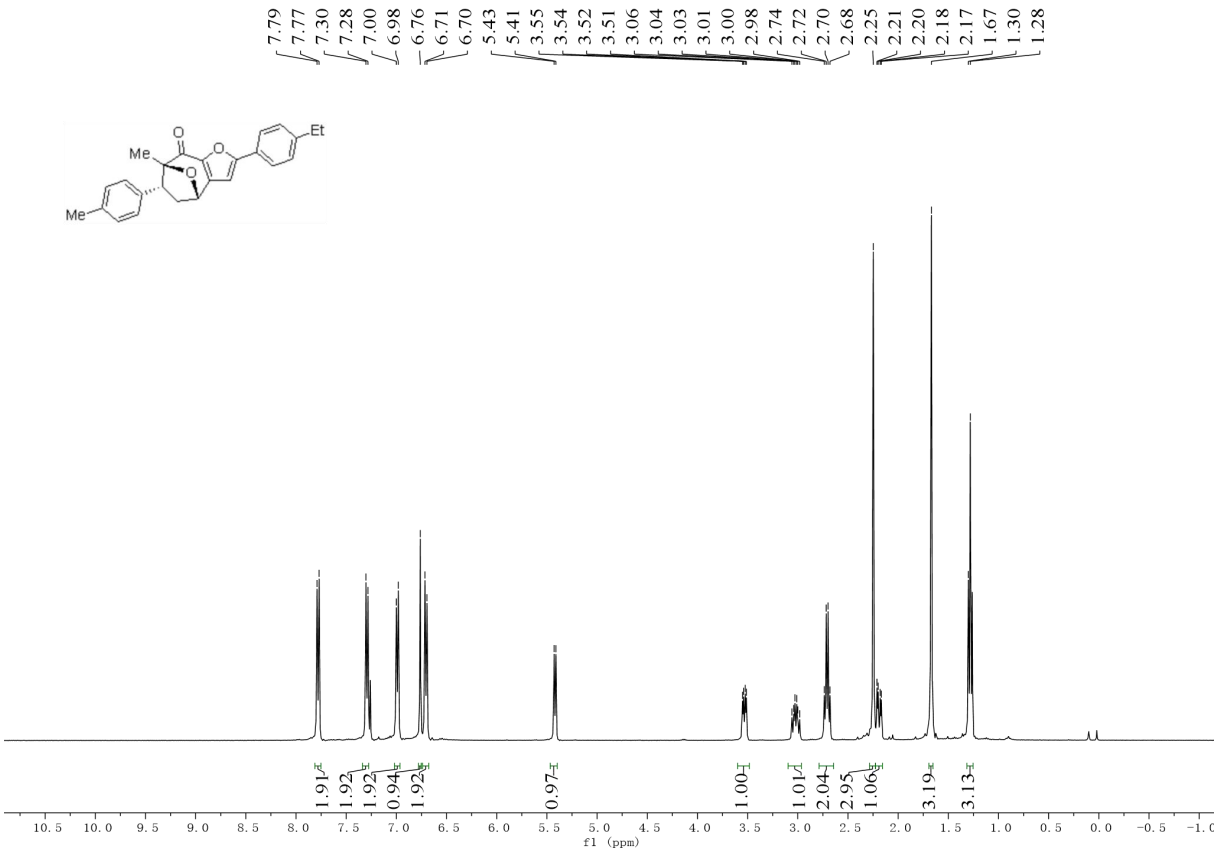


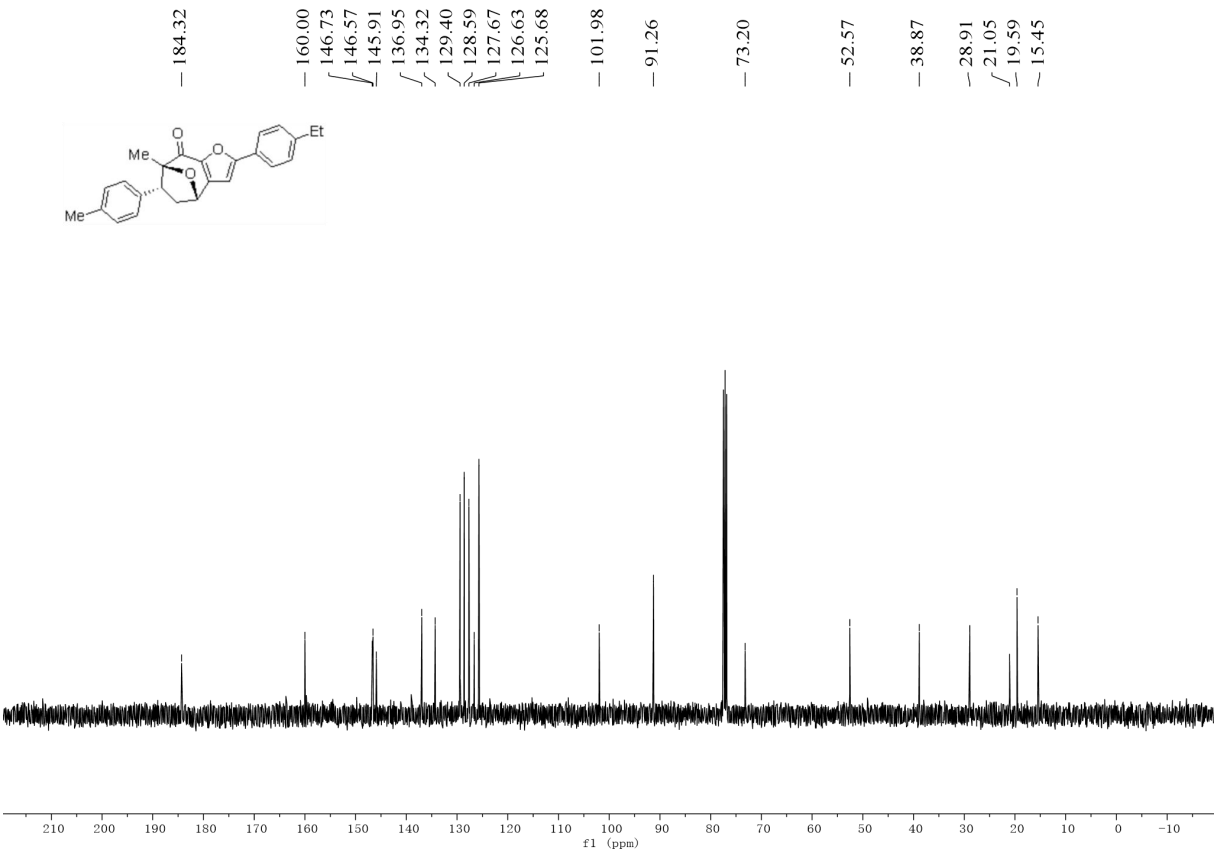
^{1}H and ^{13}C NMR spectra of 5eb



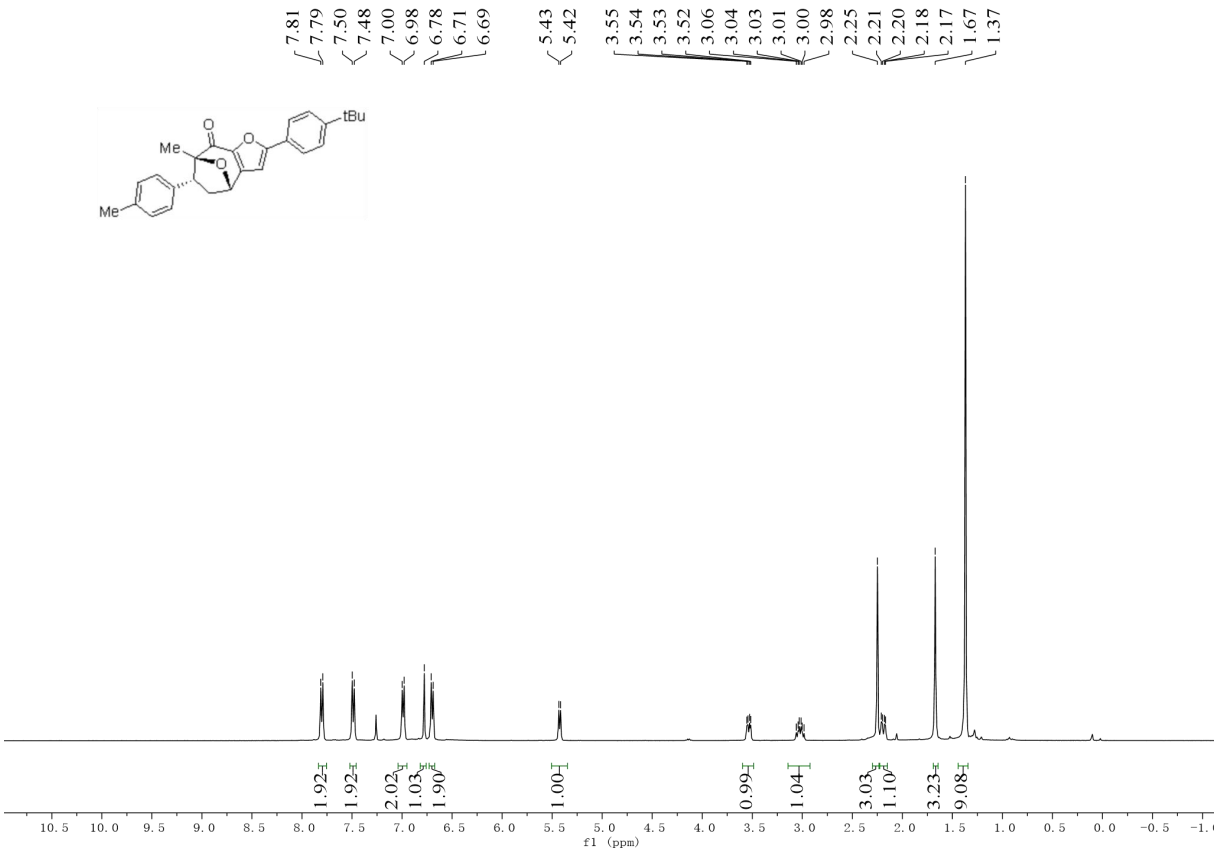


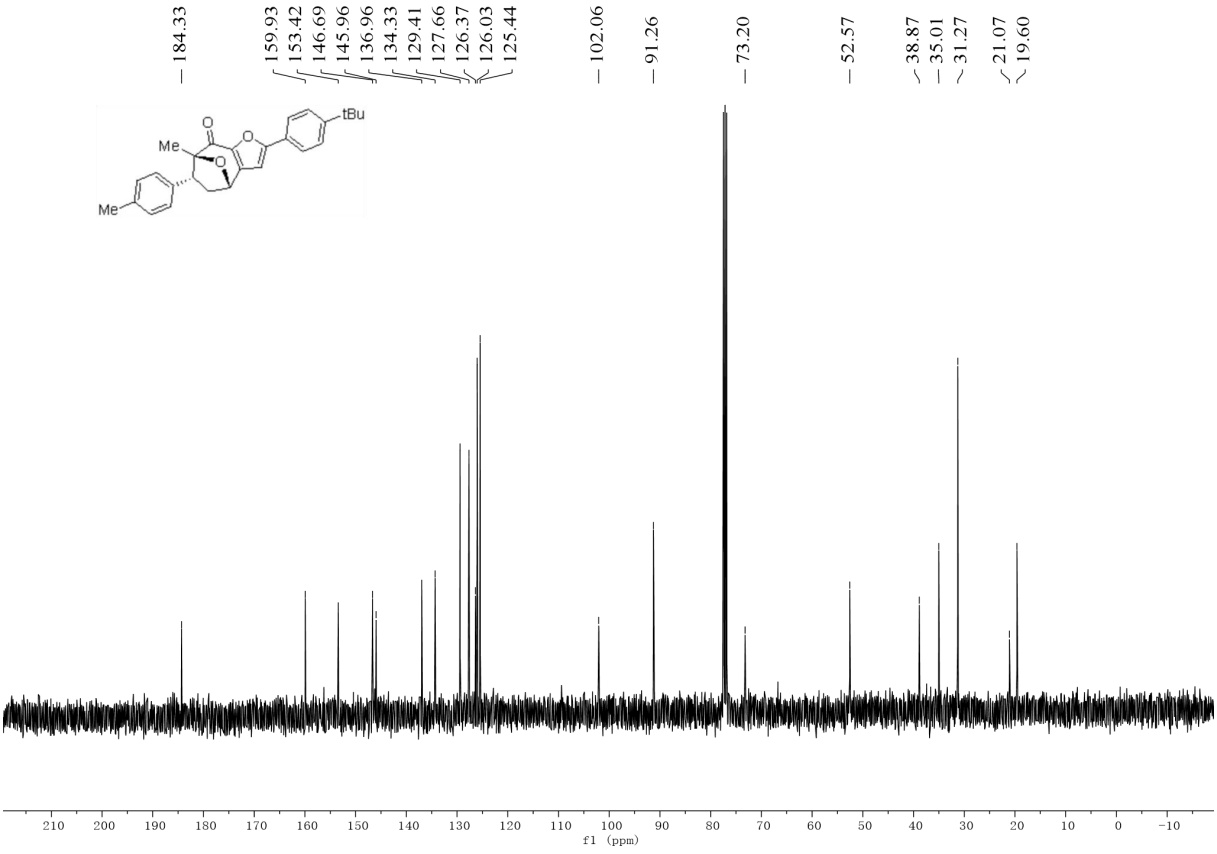
^{1}H and ^{13}C NMR spectra of 5fb



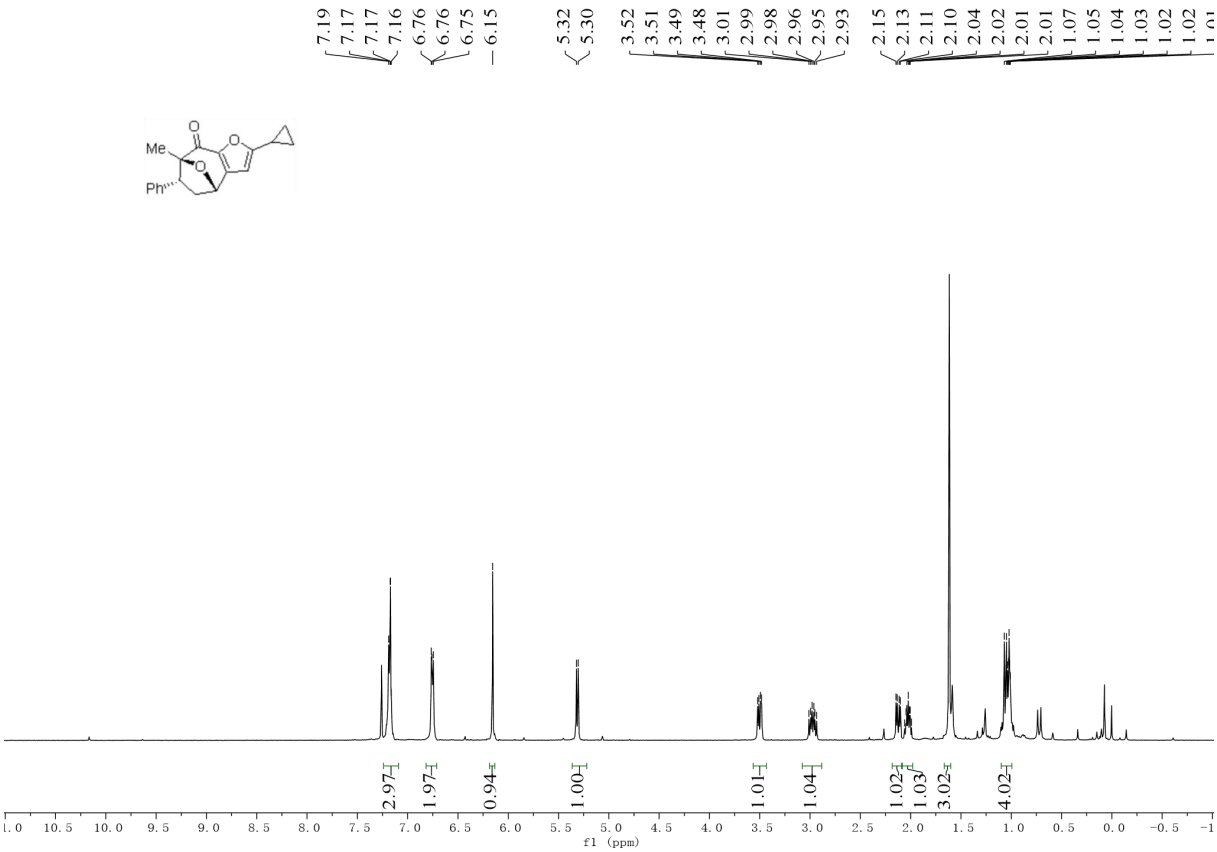


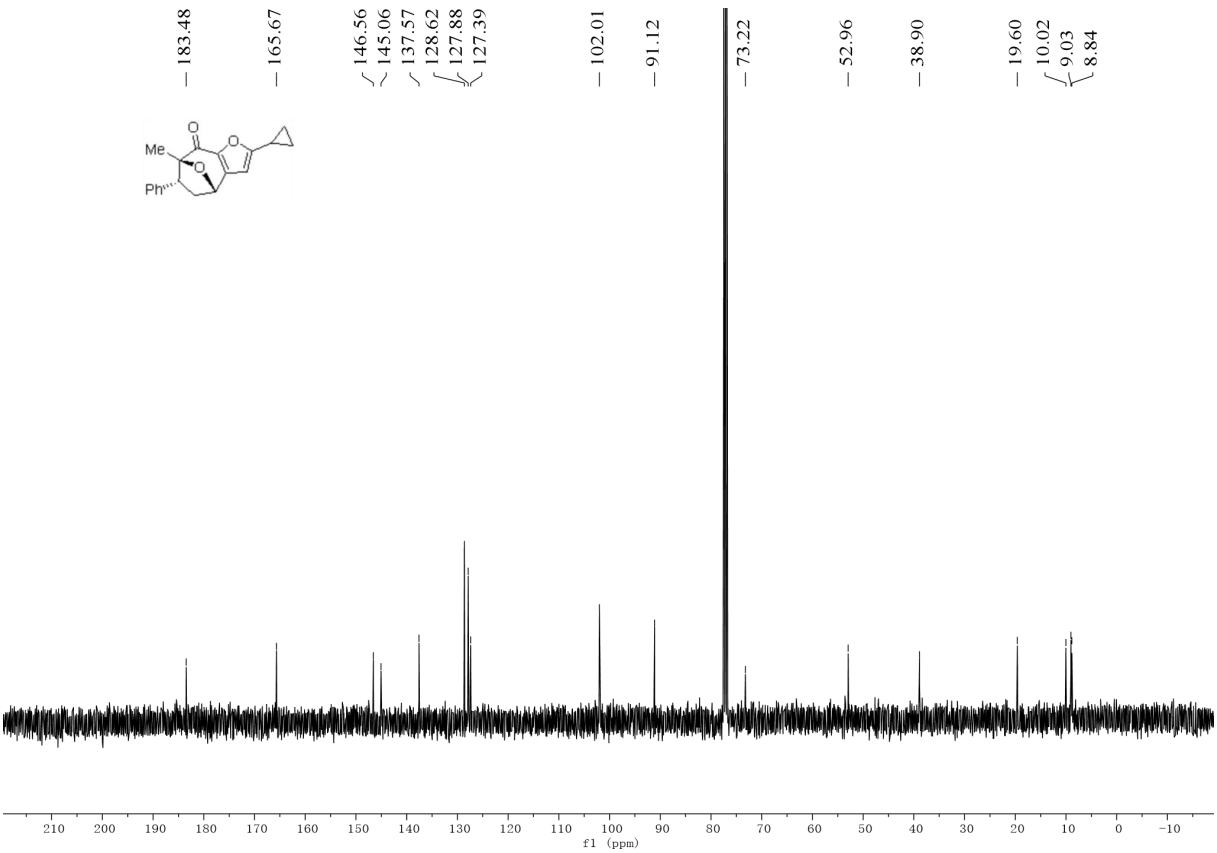
^{1}H and ^{13}C NMR spectra of 5pb



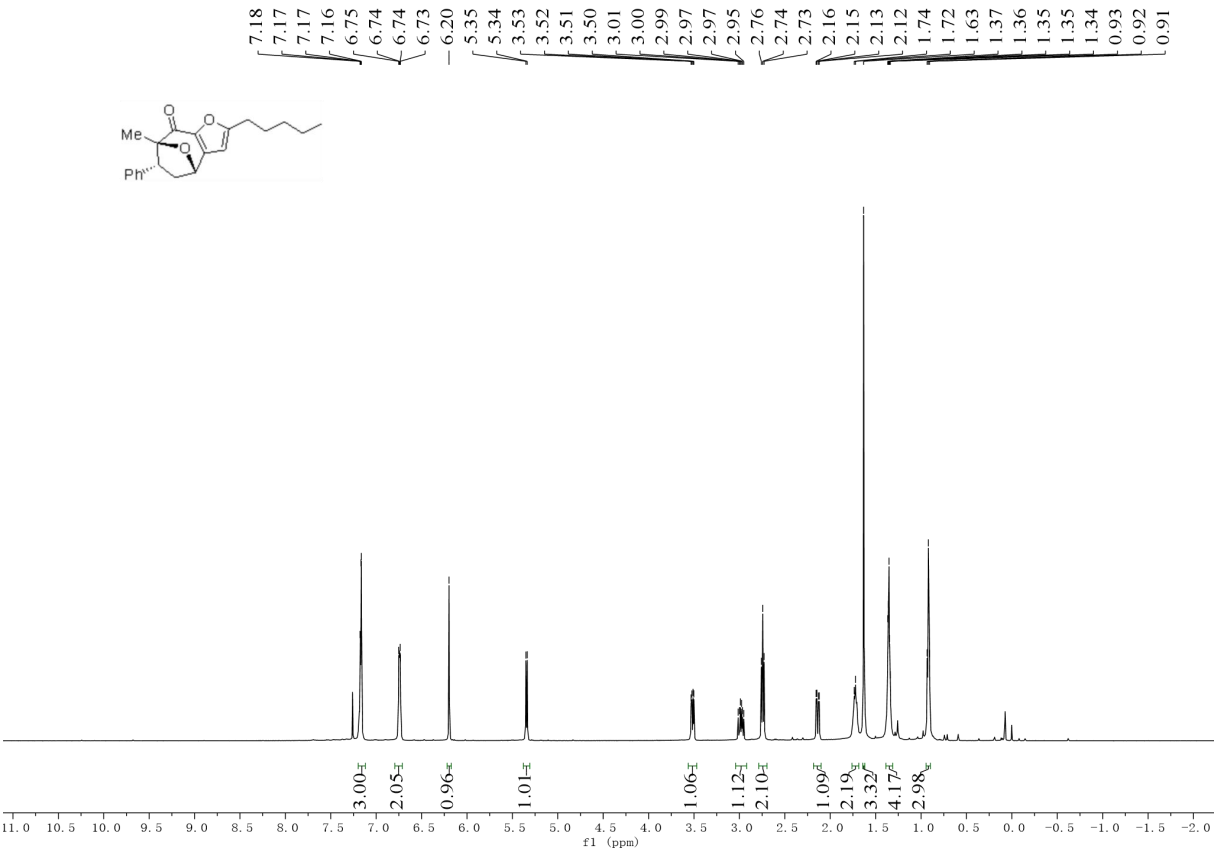


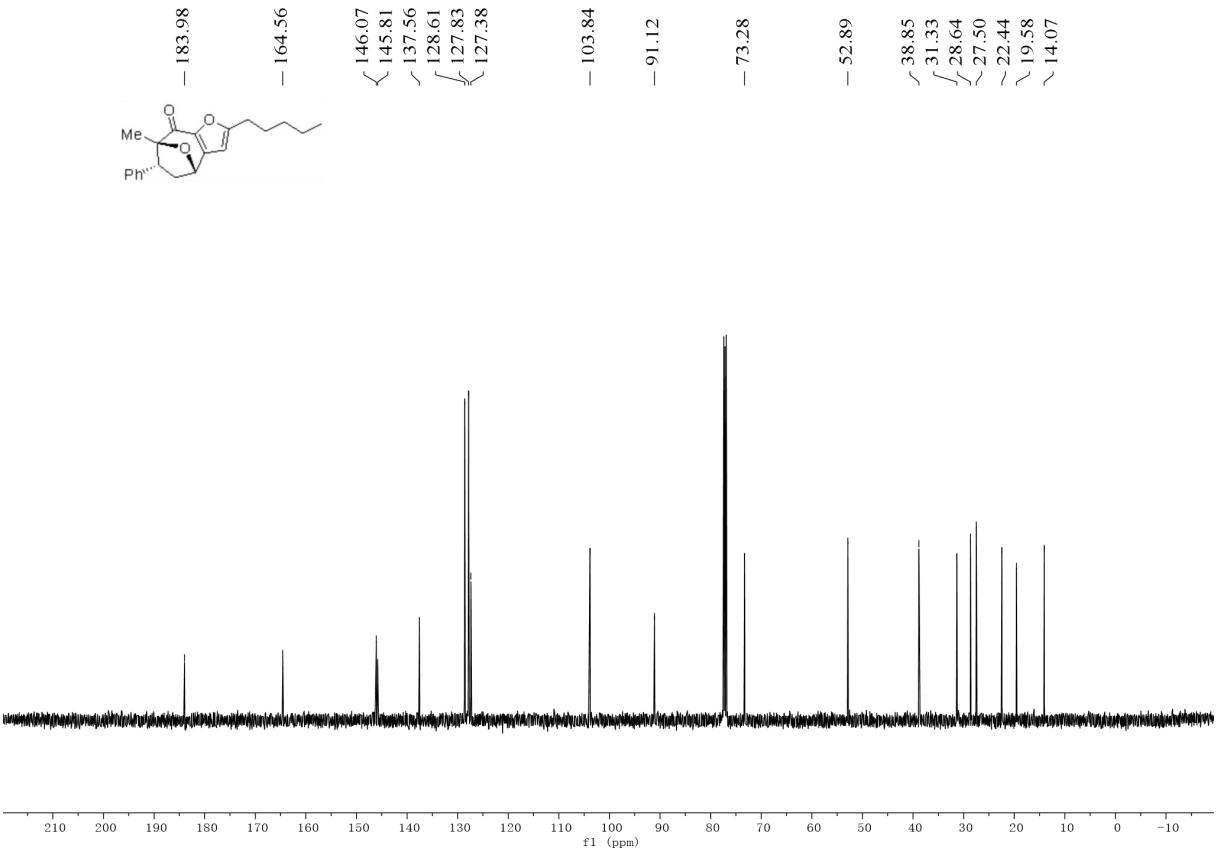
^{1}H and ^{13}C NMR spectra of 5ka



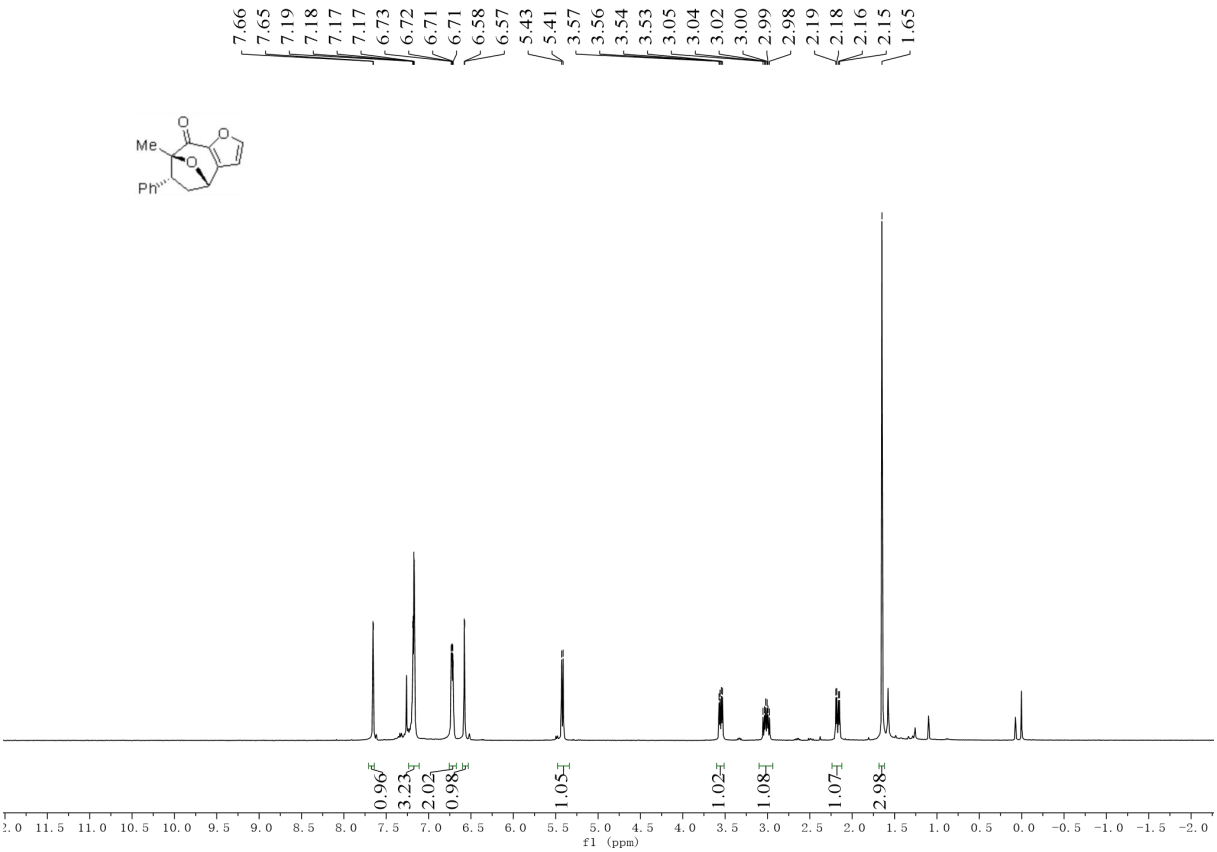


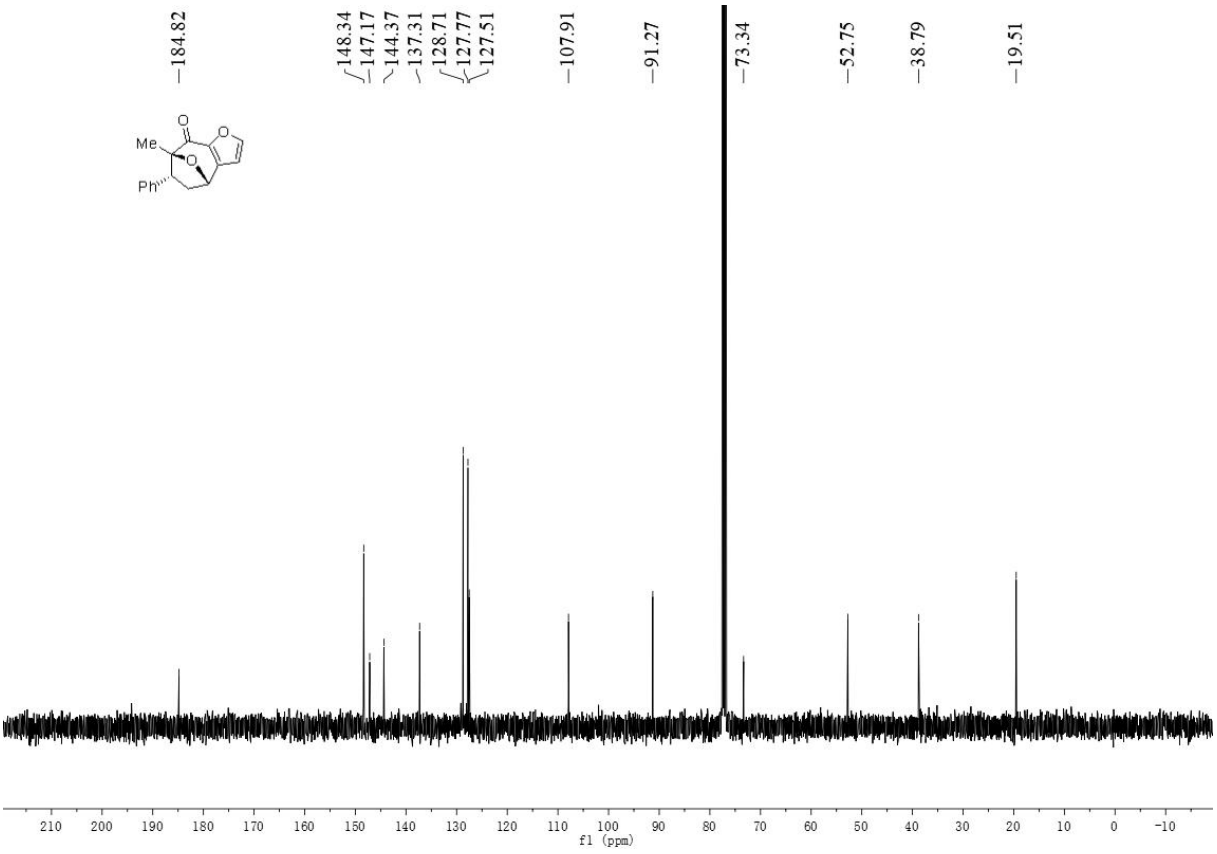
^{1}H and ^{13}C NMR spectra of 5la



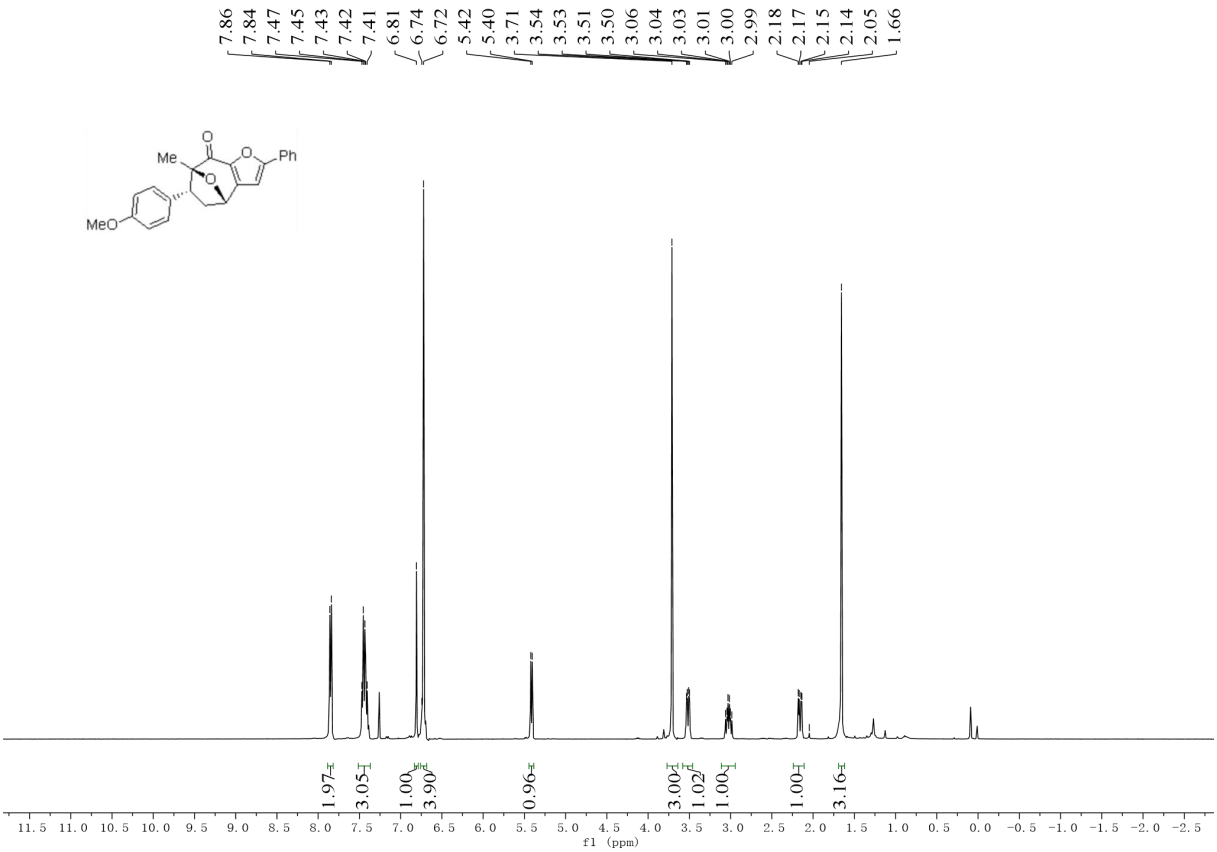


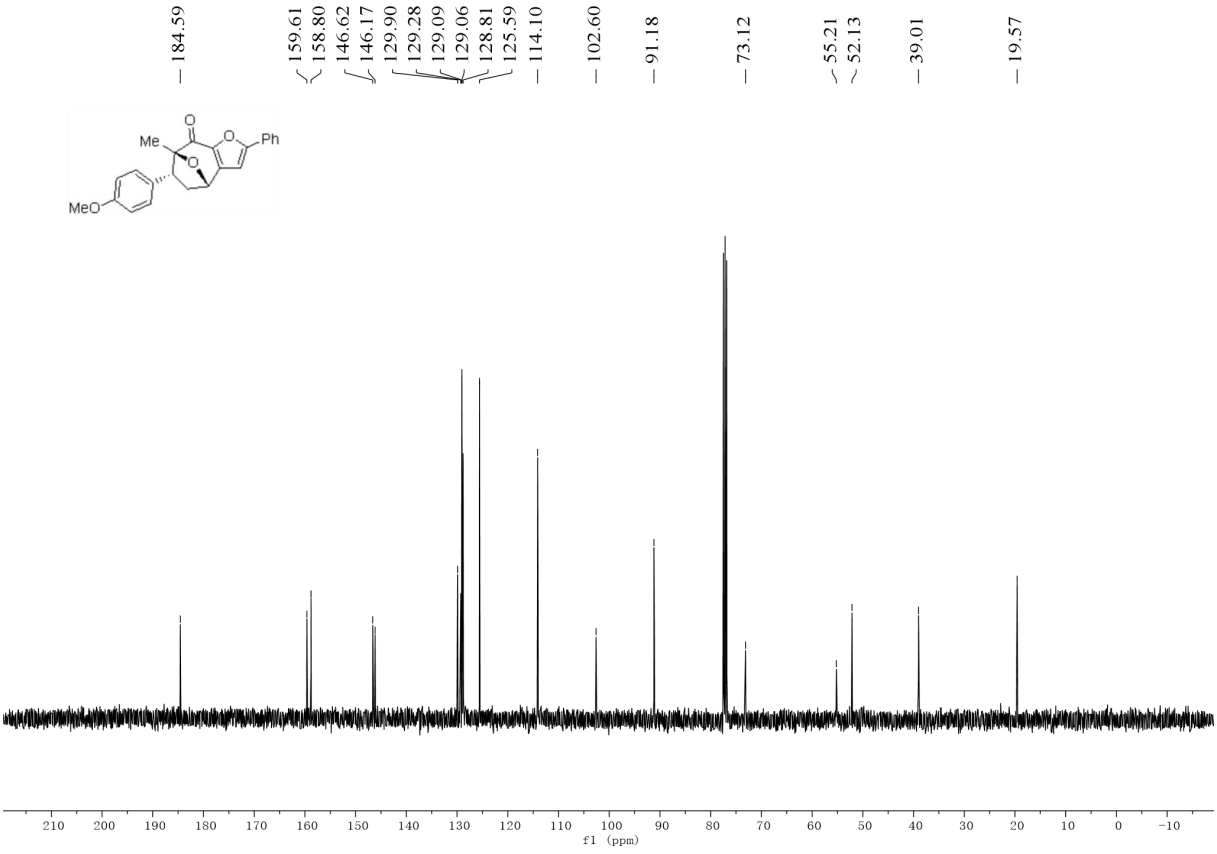
H and ^{13}C NMR spectra of 5ma



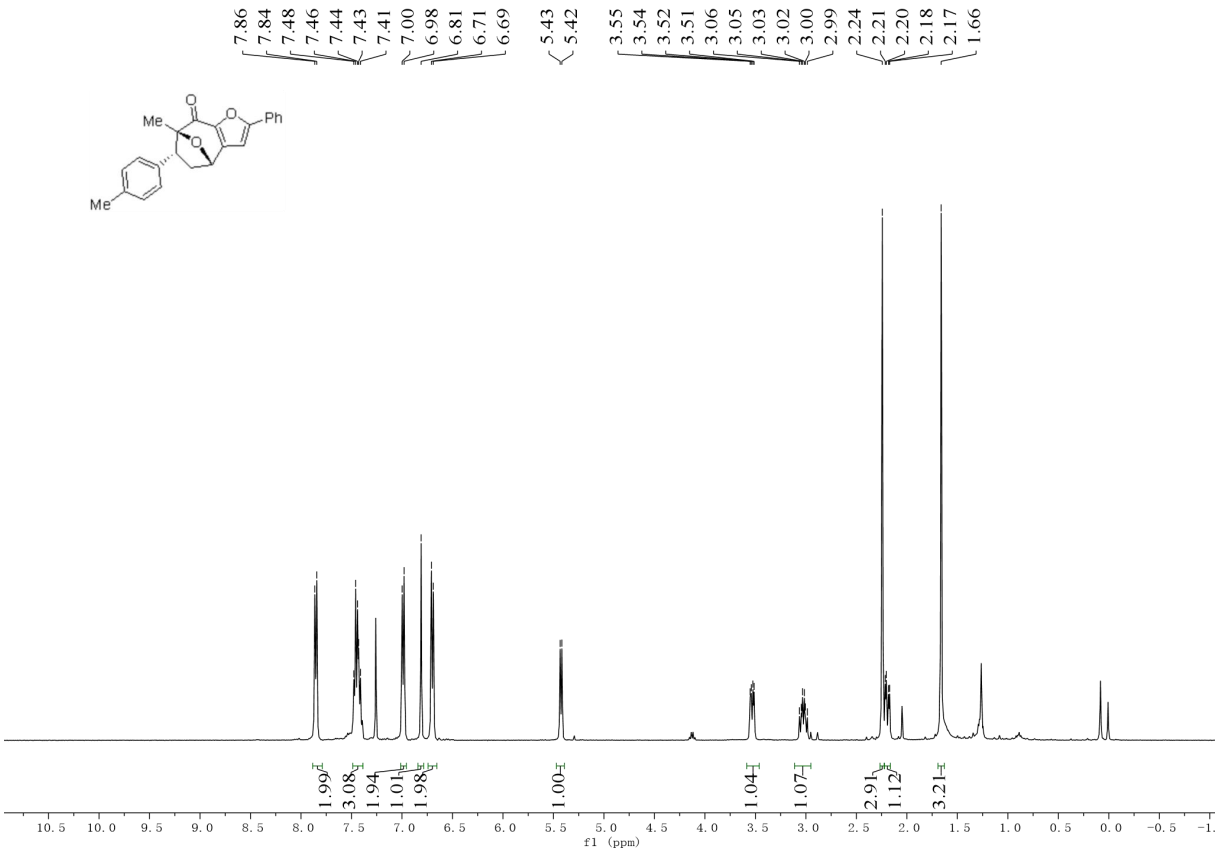


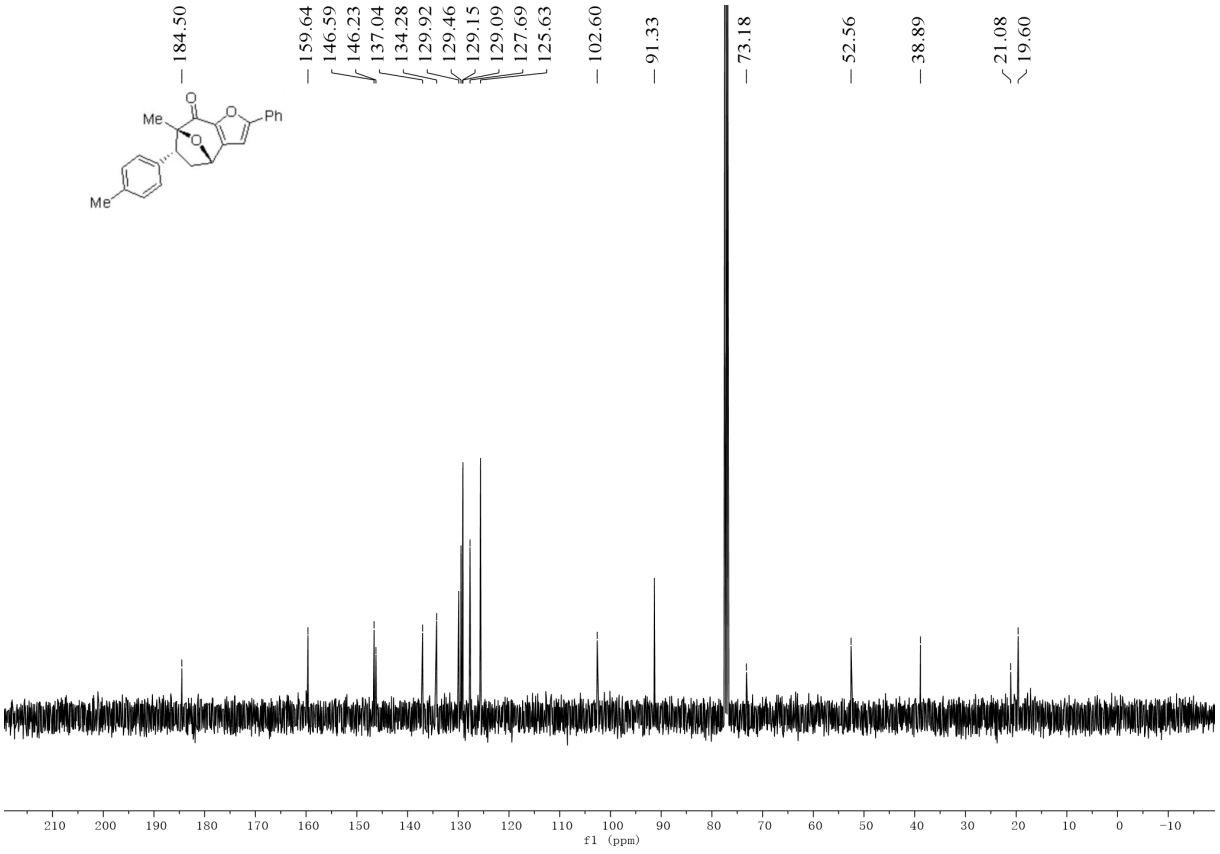
^{1}H and ^{13}C NMR spectra of 5ac



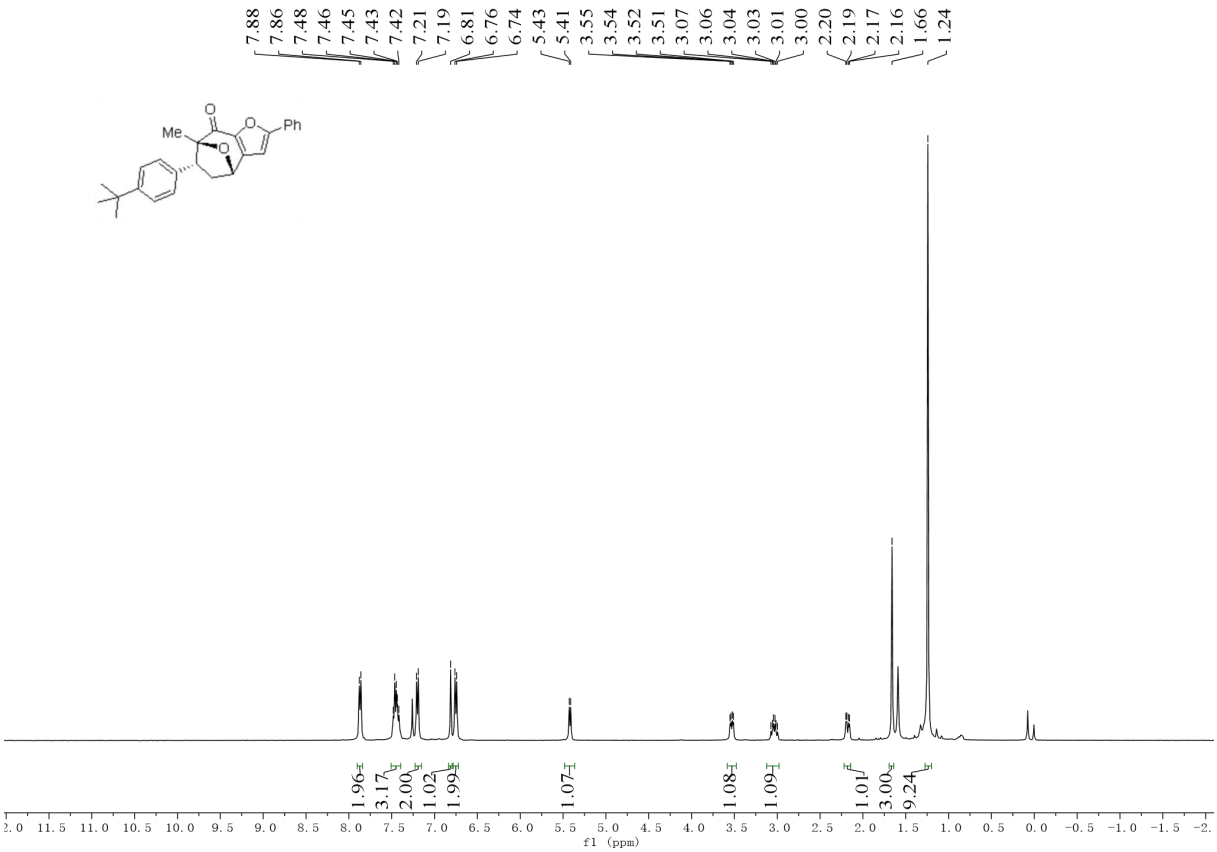


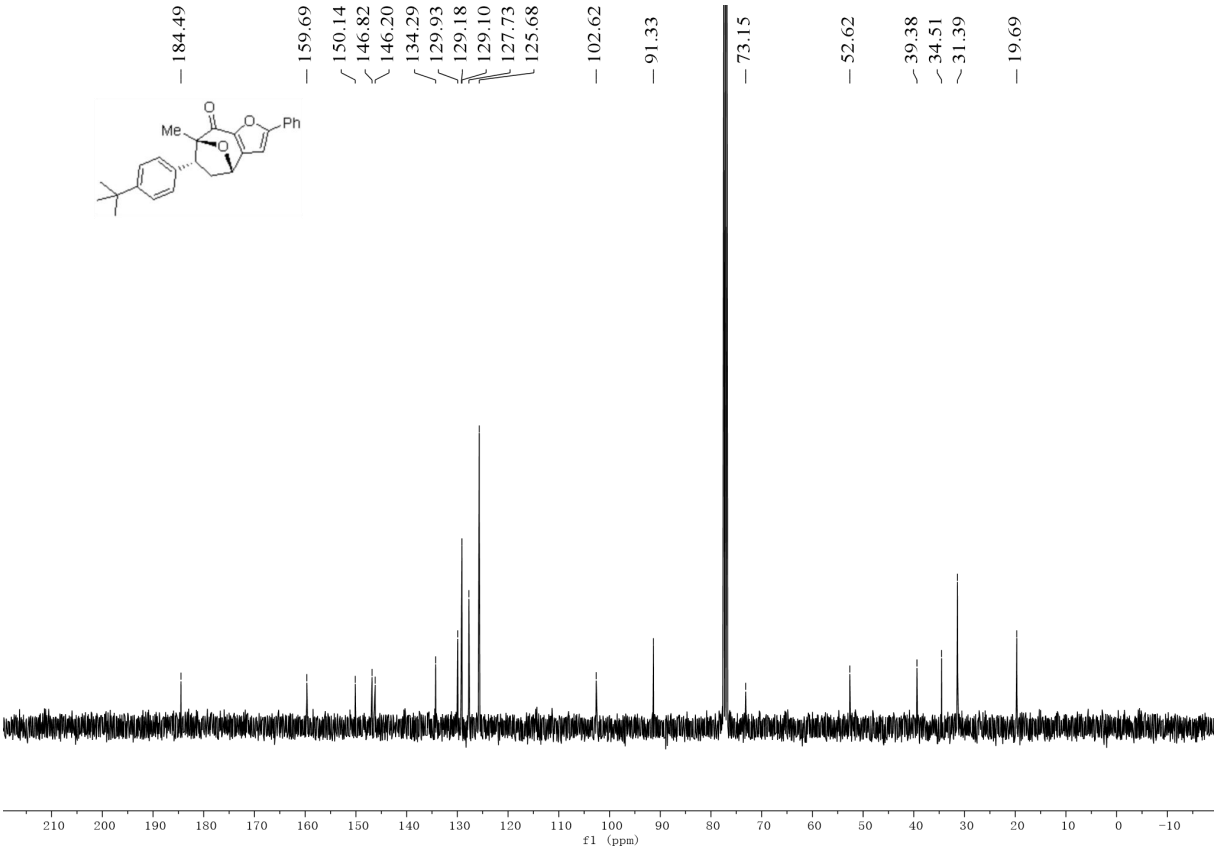
^{1}H and ^{13}C NMR spectra of 5ad



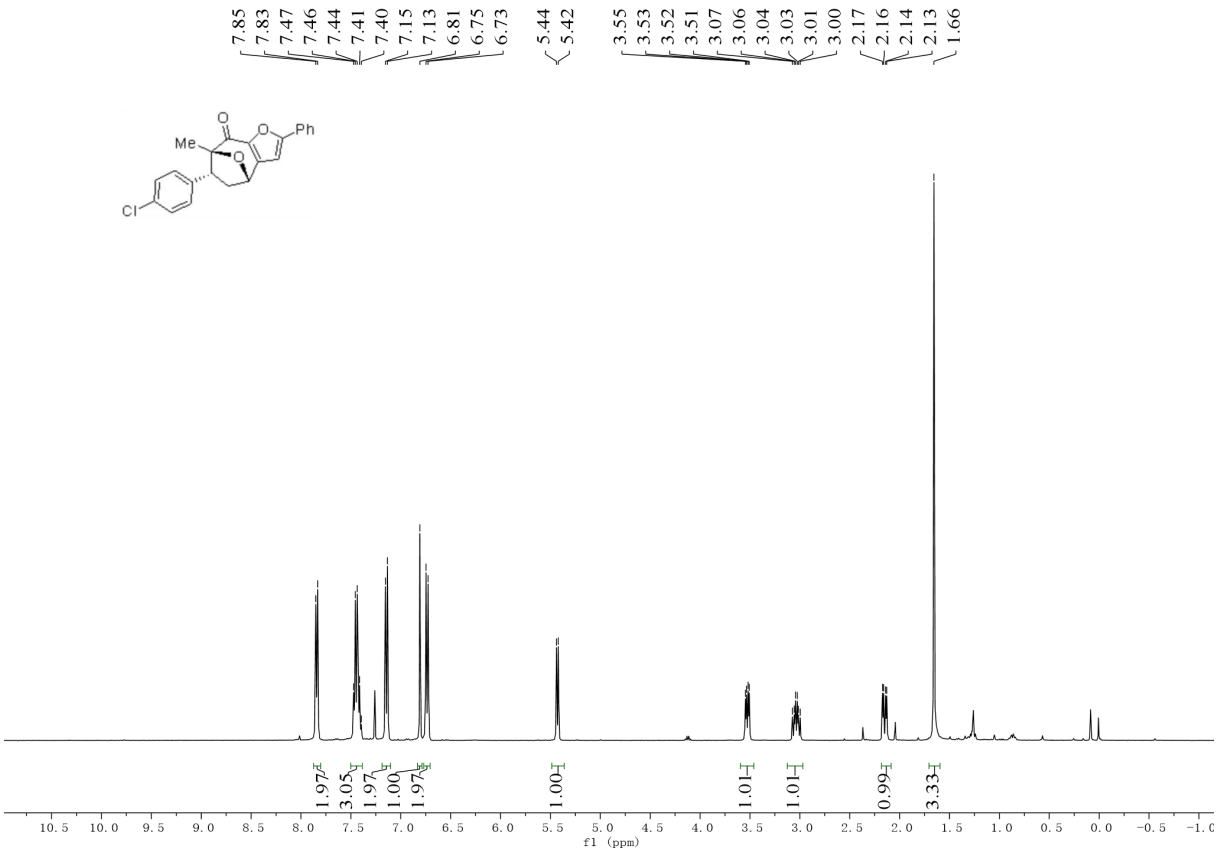


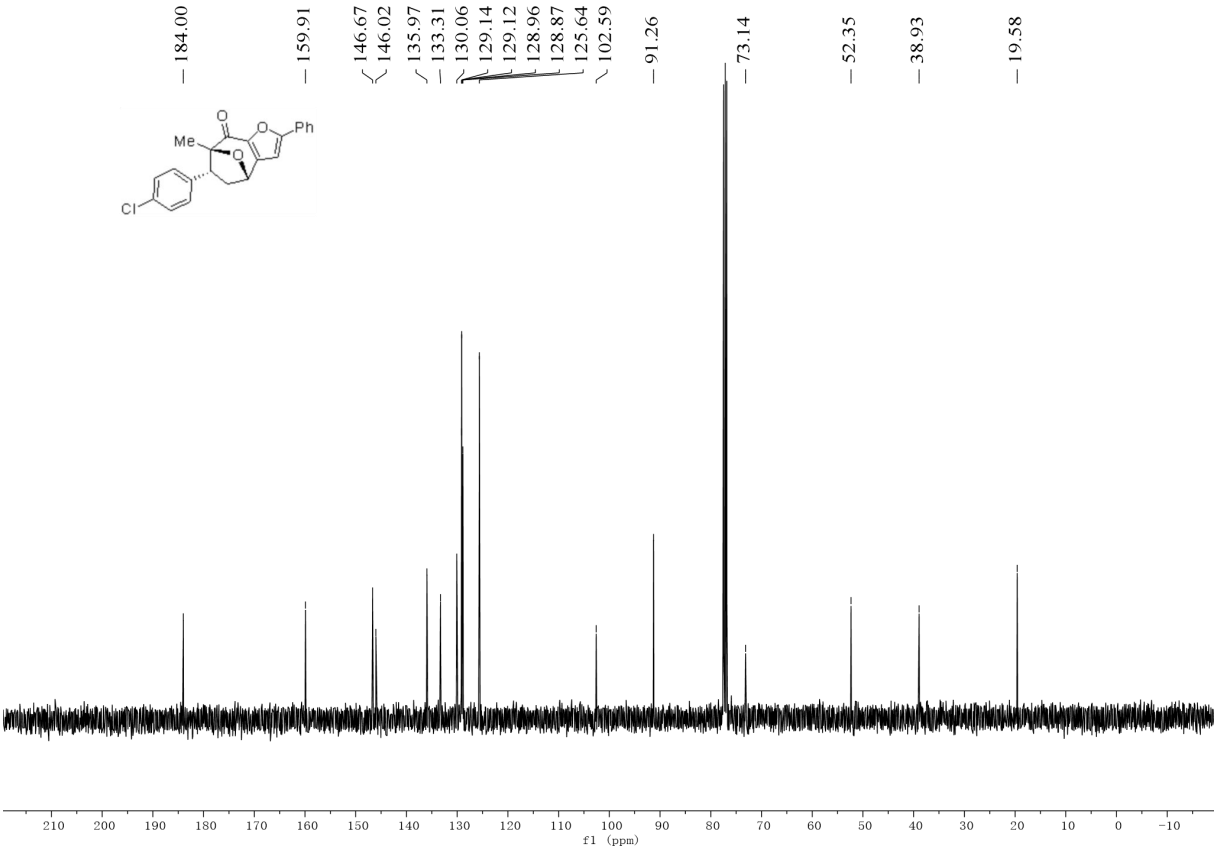
^{1}H and ^{13}C NMR spectra of 5ae



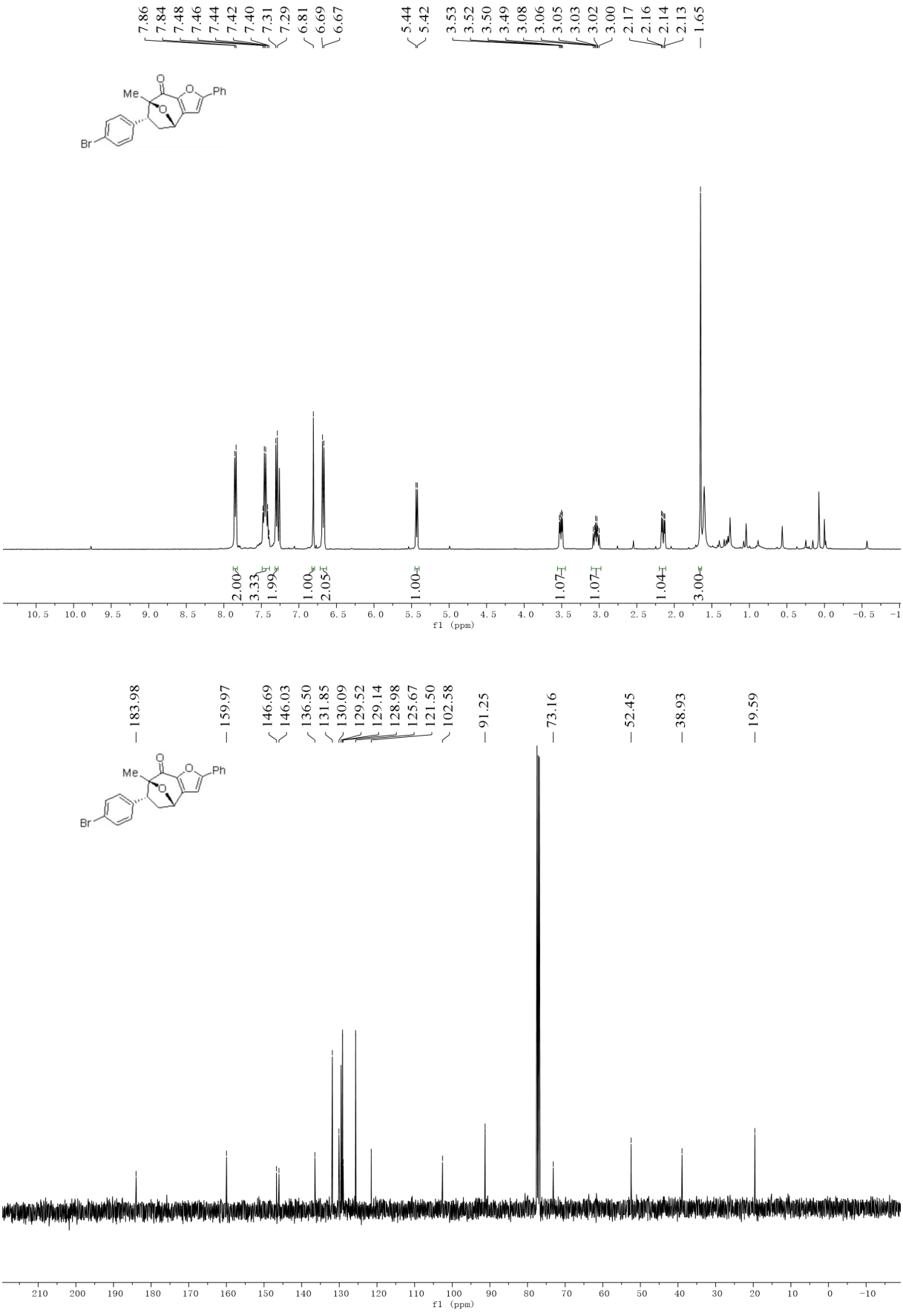


^{1}H and ^{13}C NMR spectra of 5af

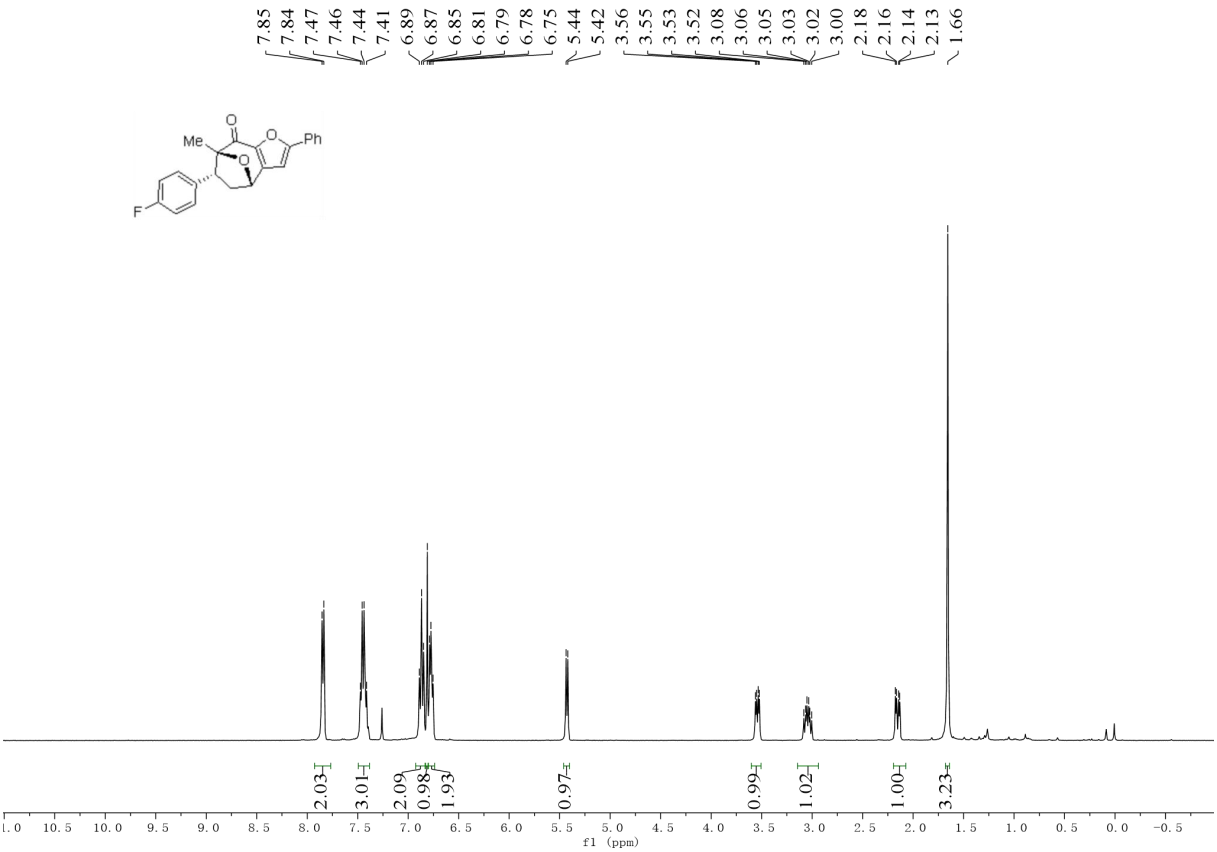


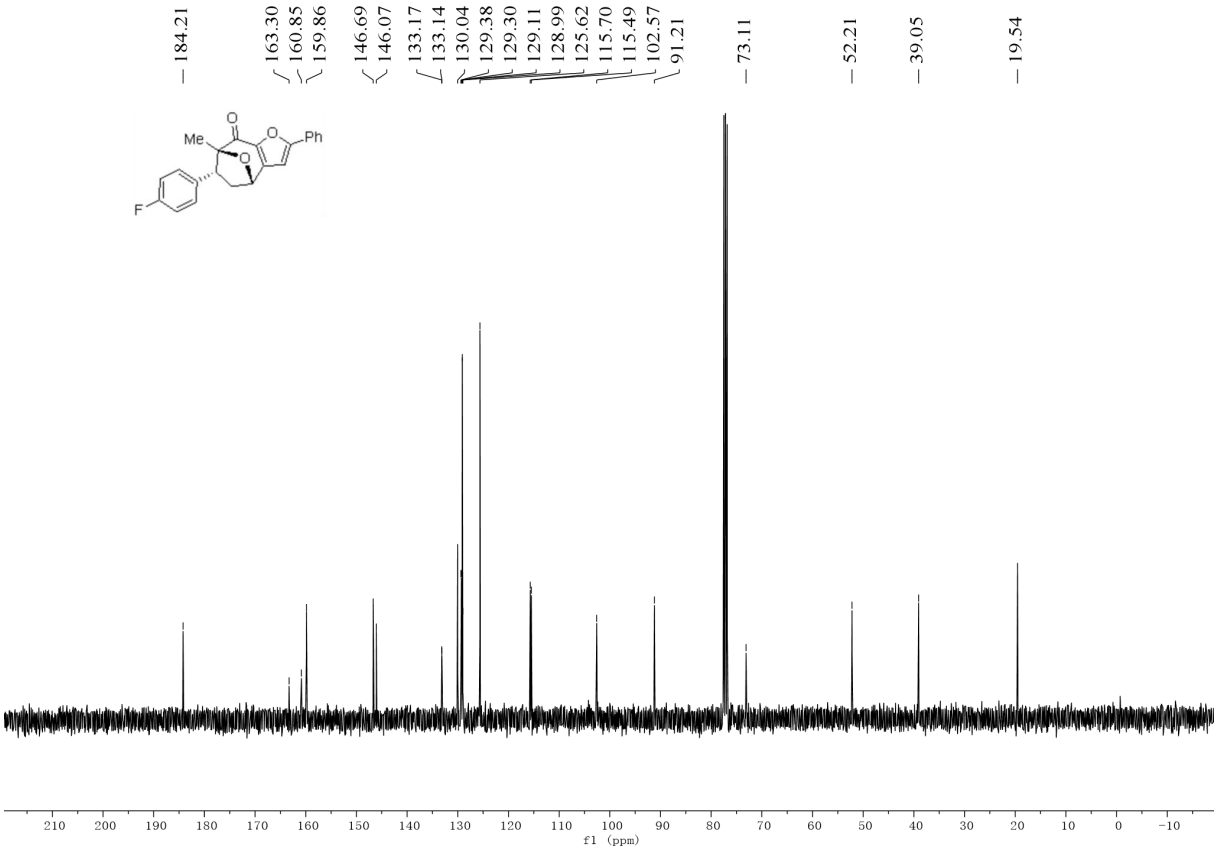


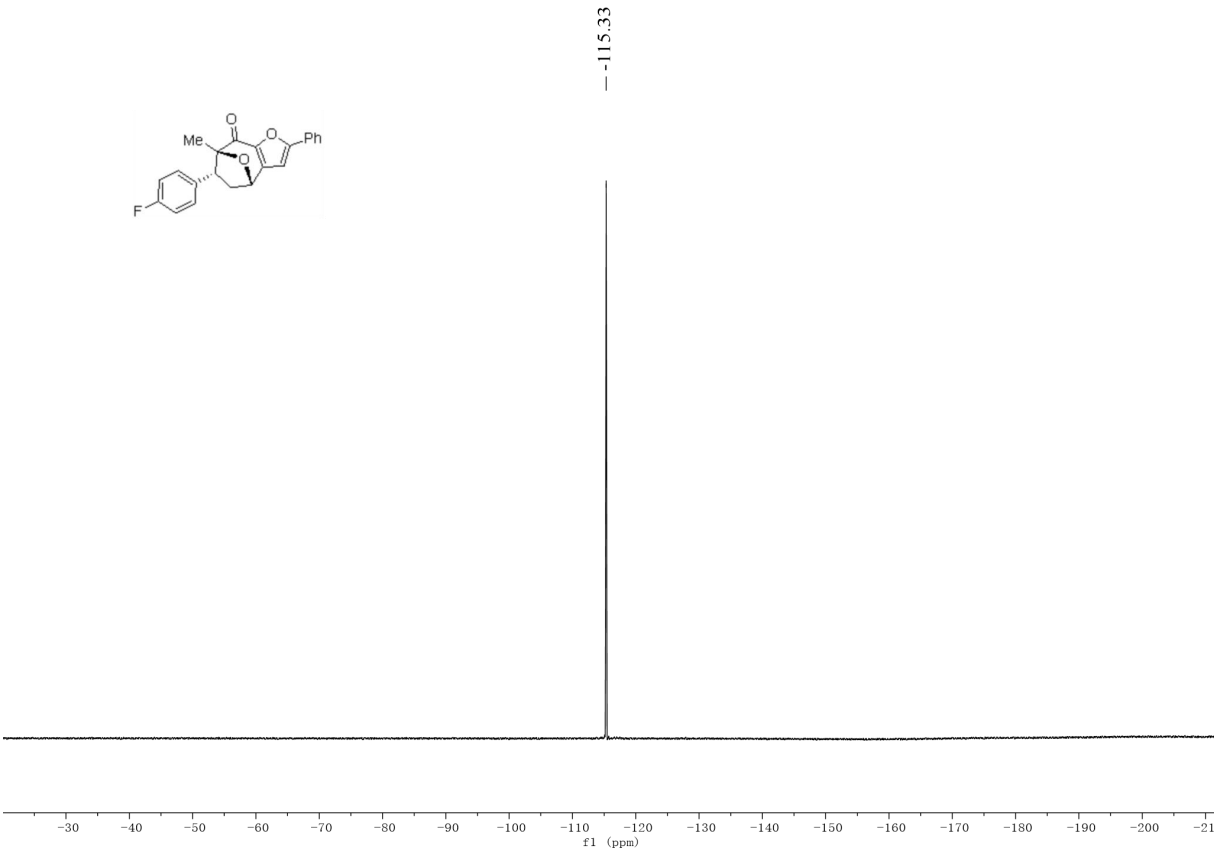
^{1}H and ^{13}C NMR spectra of 5ag



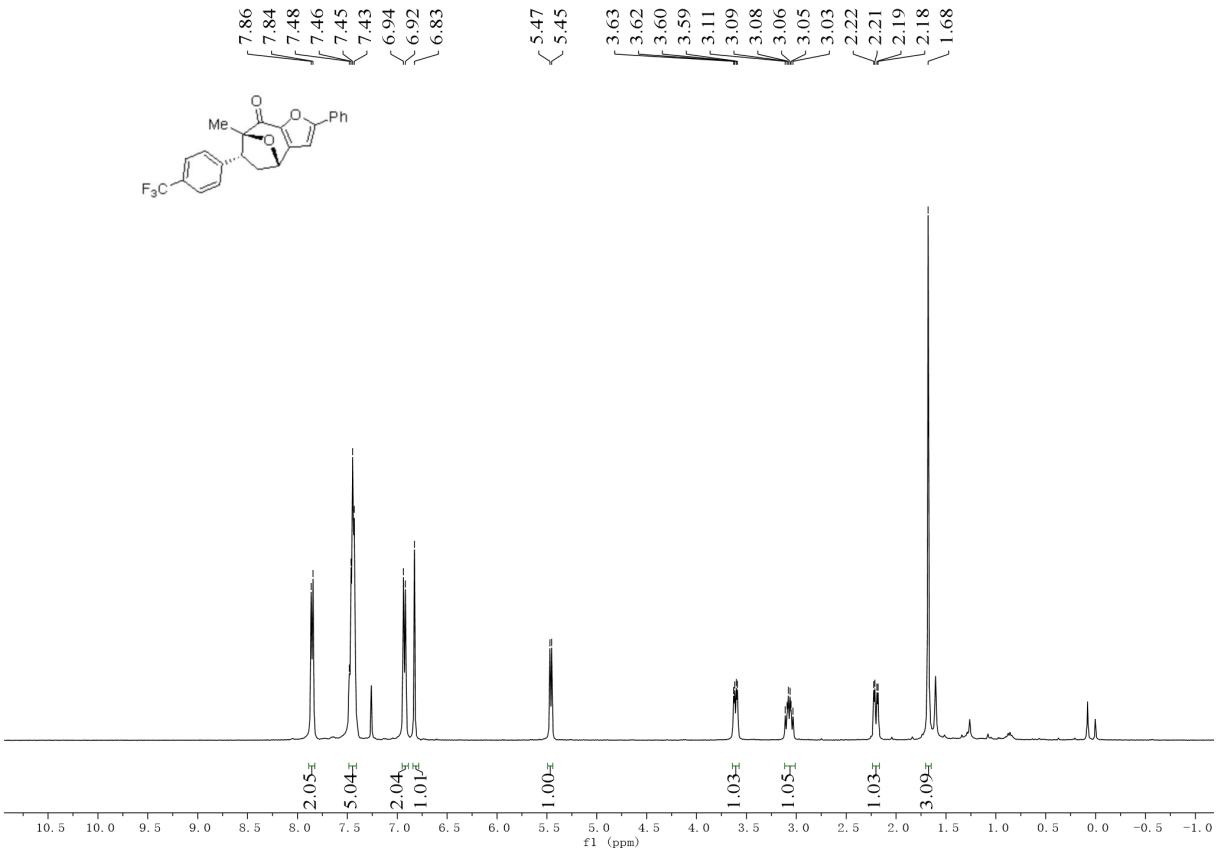
^{1}H and ^{13}C NMR and $^{19}FNMR$ spectra of 5ah

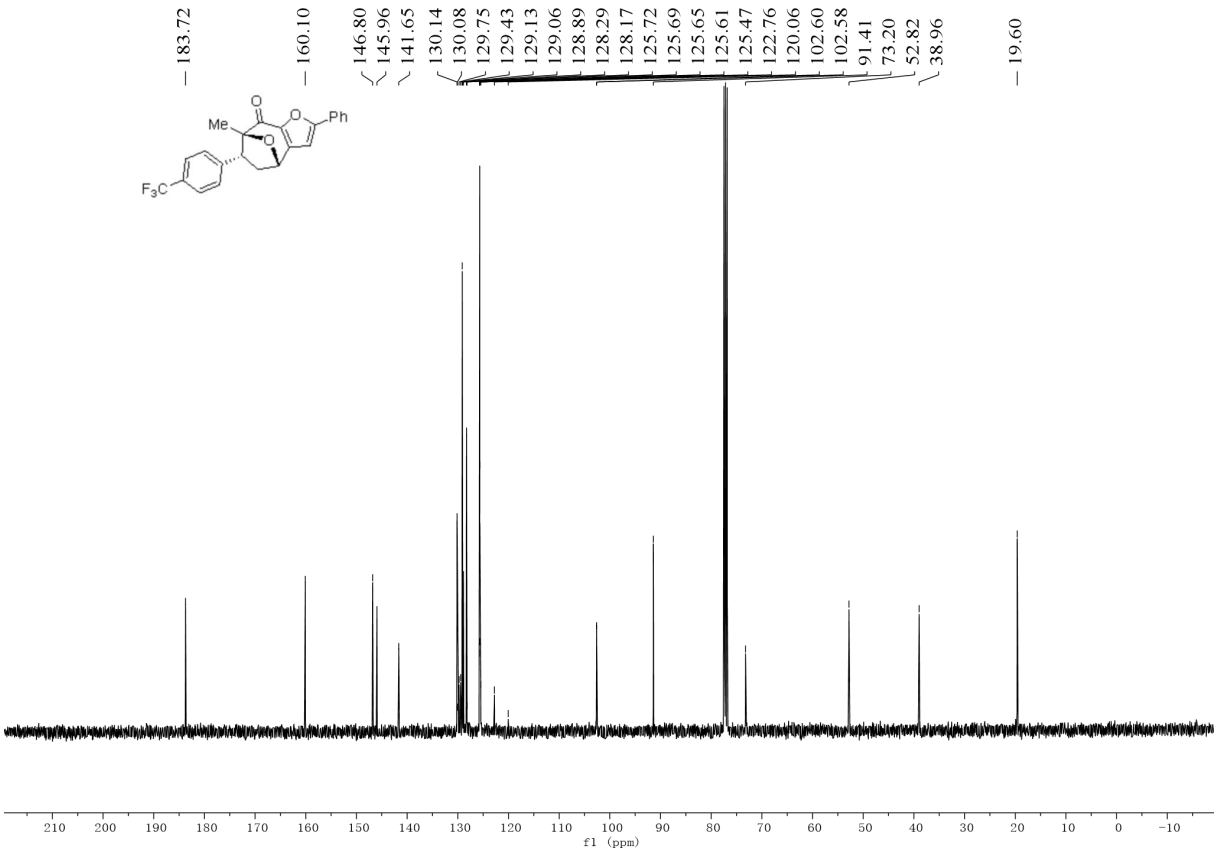


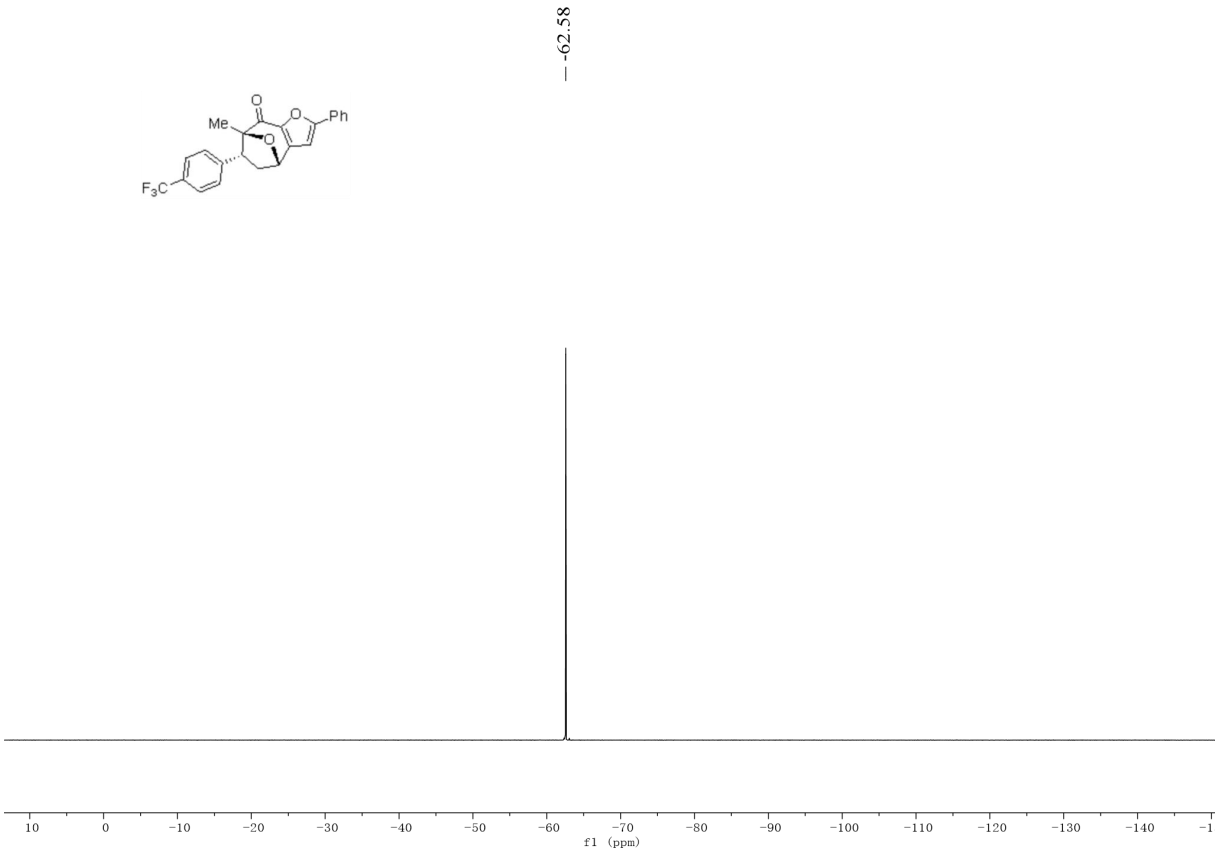



-115.33
Me
O
O
O
Ph
F
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-21
f1 (ppm)

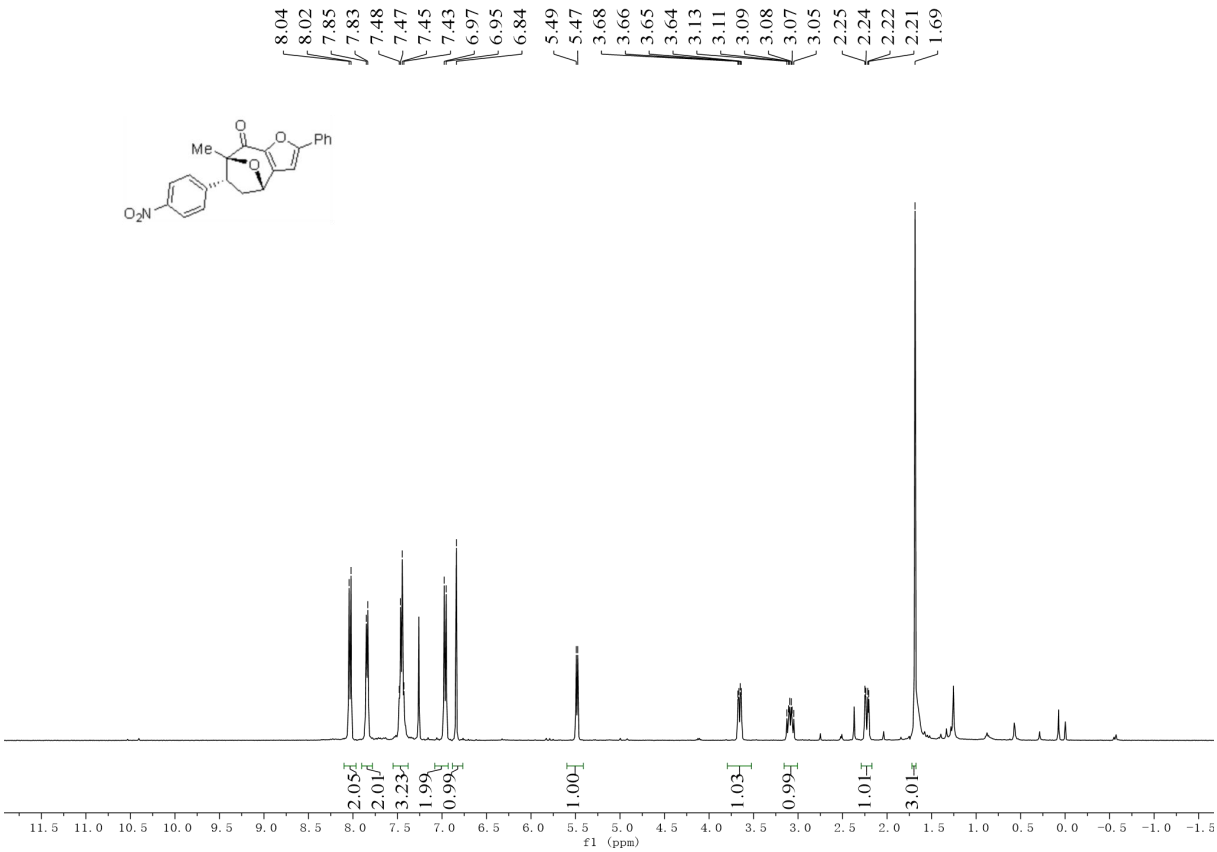
^{1}H and ^{13}C NMR and $^{19}FNMR$ spectra of 5ai

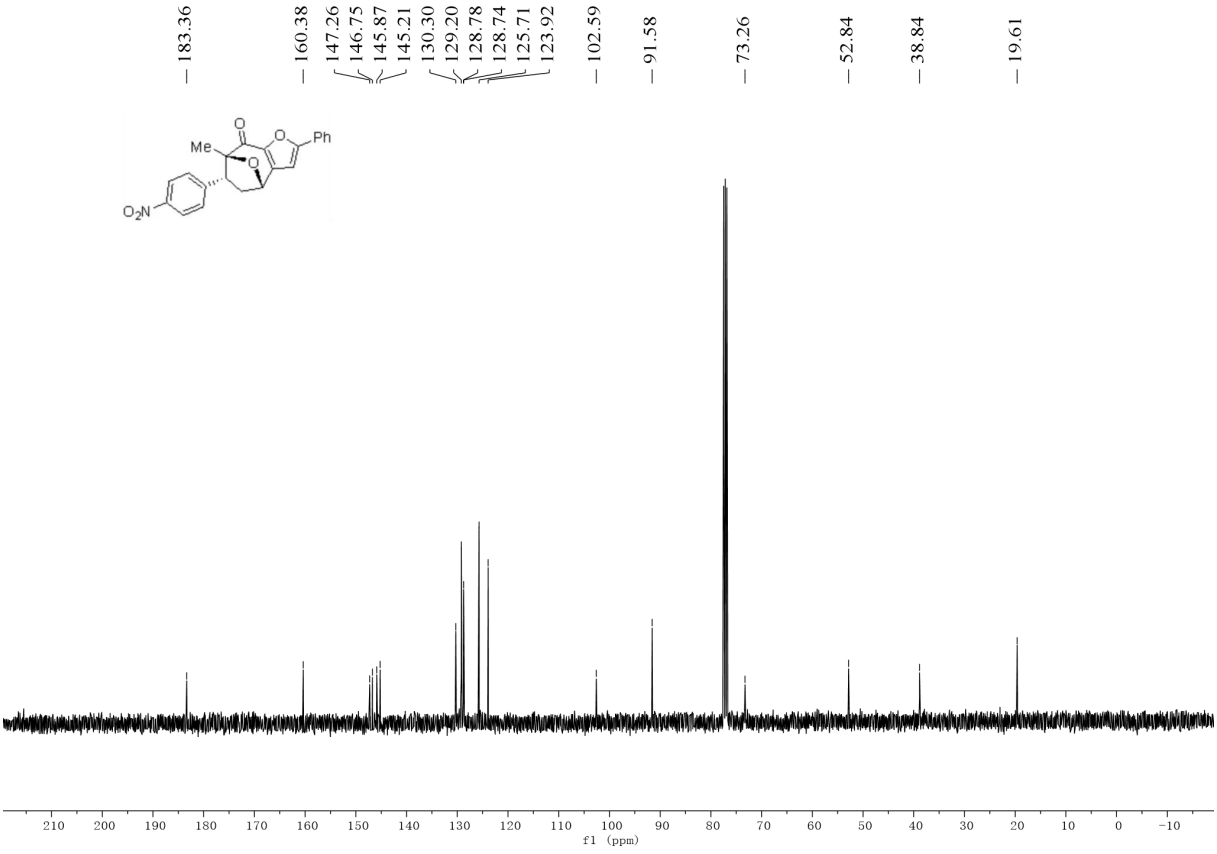




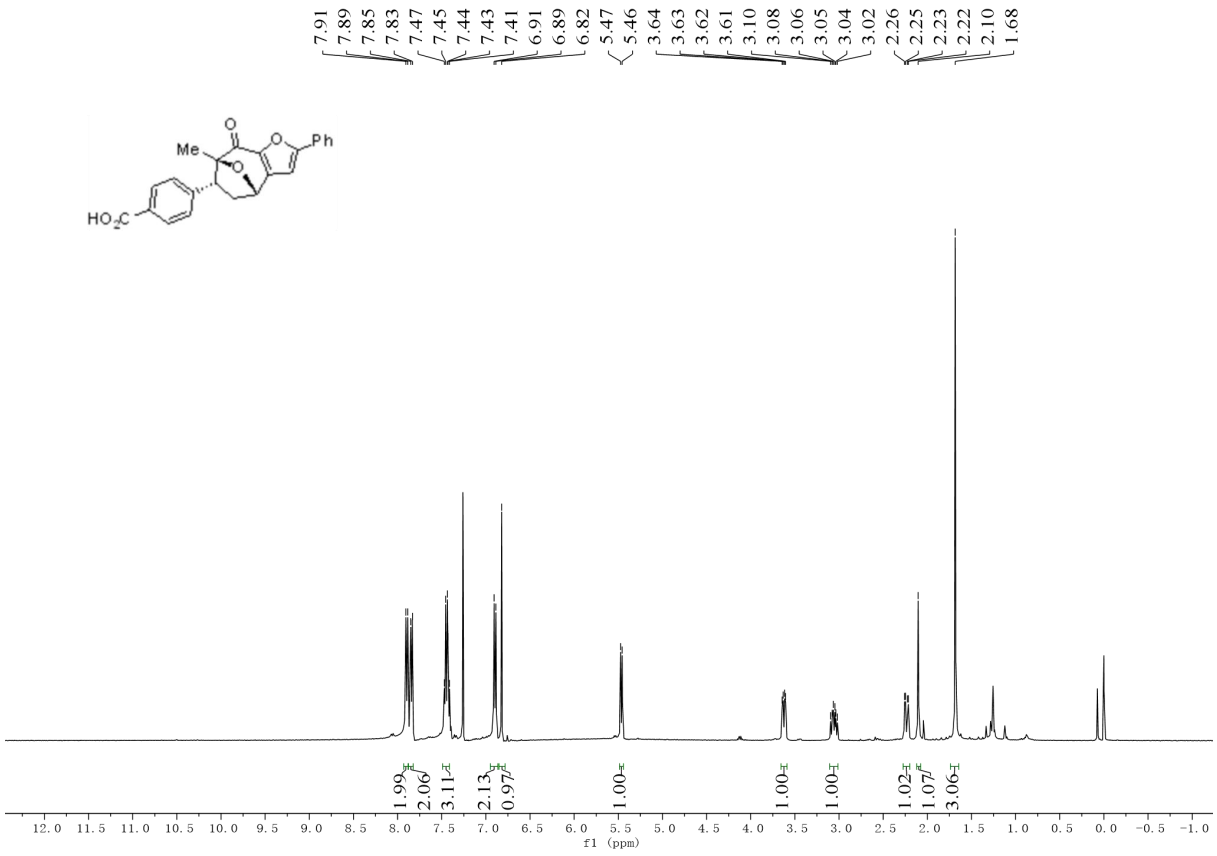

-62.58
O
Me
O
O
Ph
F3C
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
f1 (ppm)

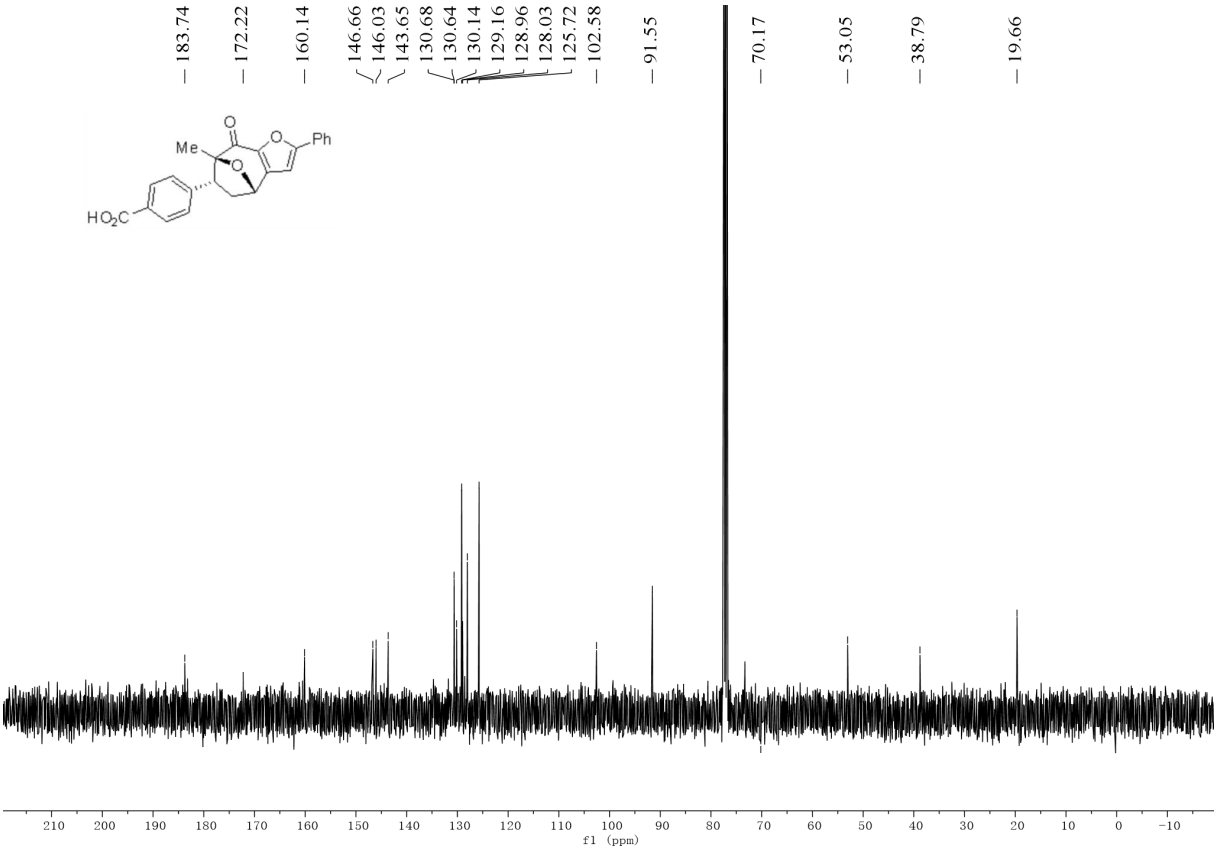
^{1}H and ^{13}C NMR spectra of 5aj



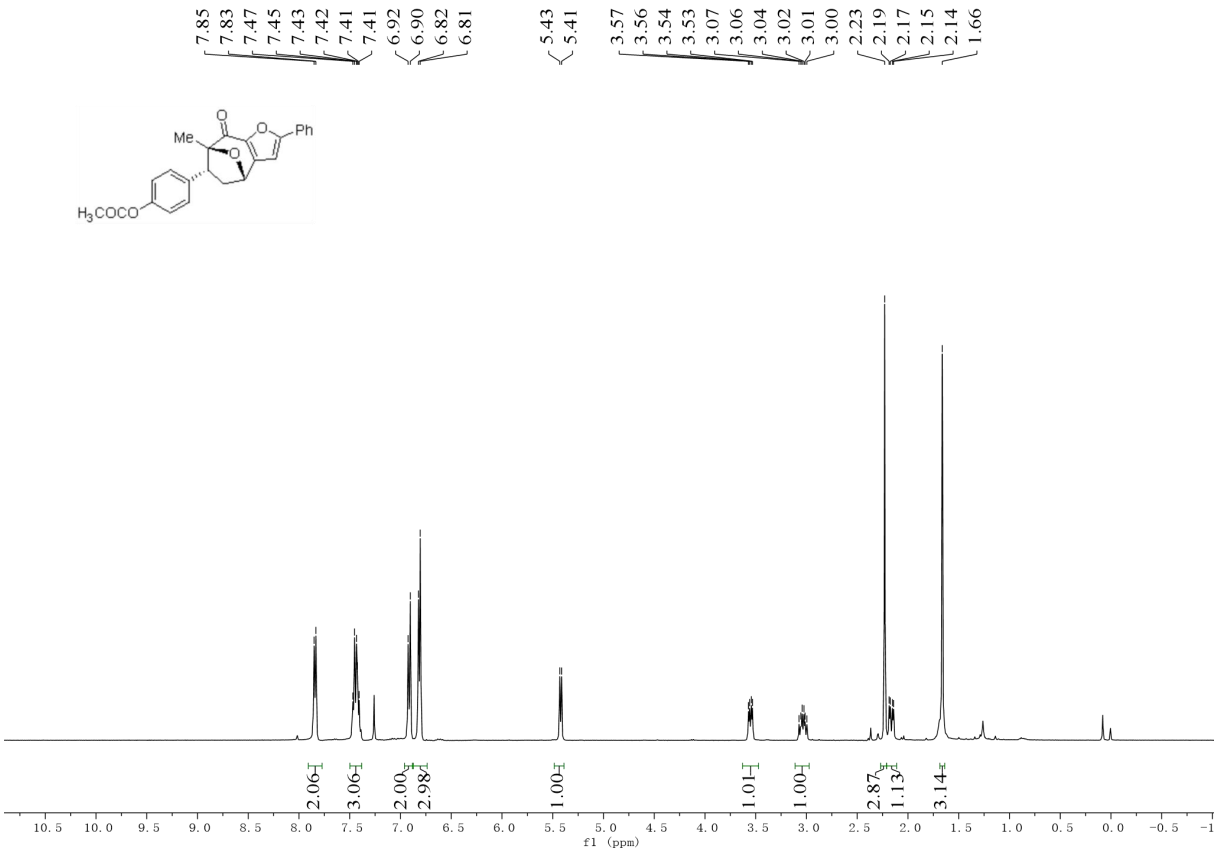


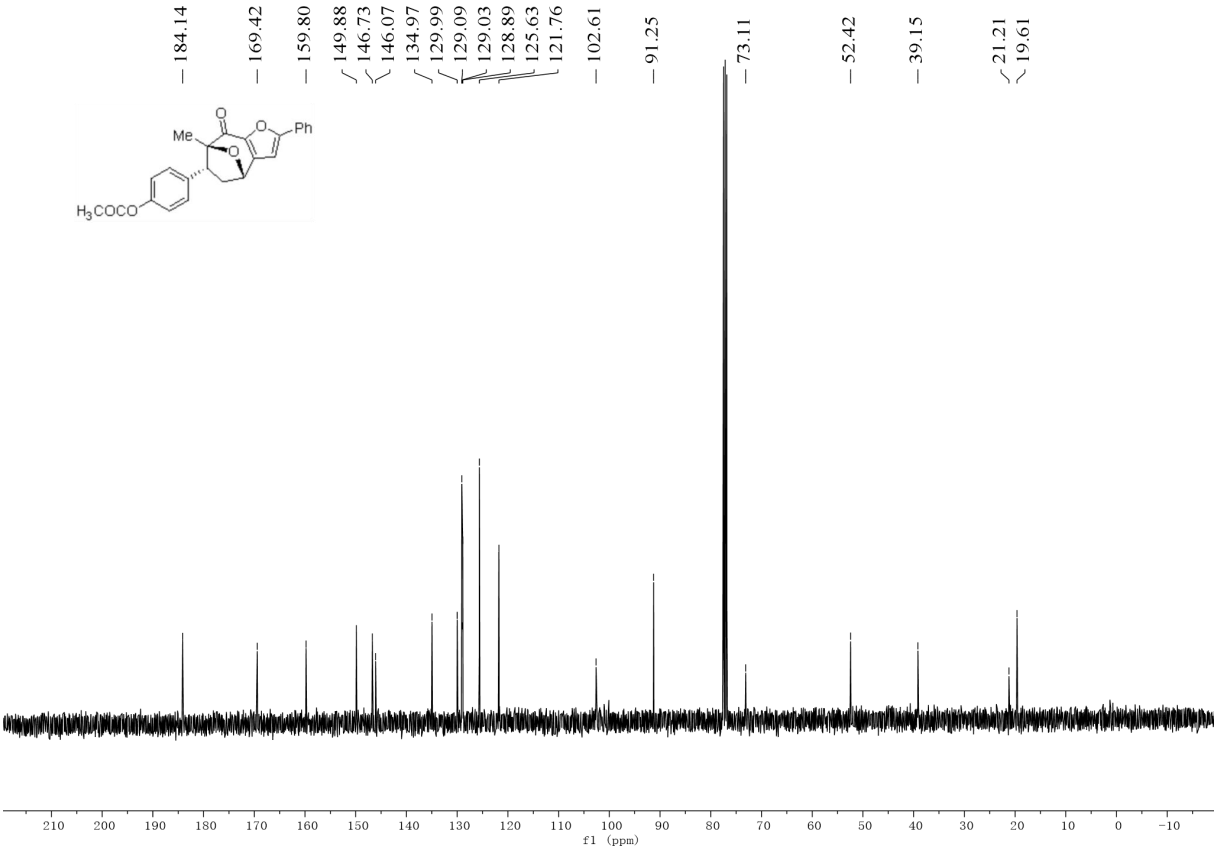
^{1}H and ^{13}C NMR spectra of 5ak



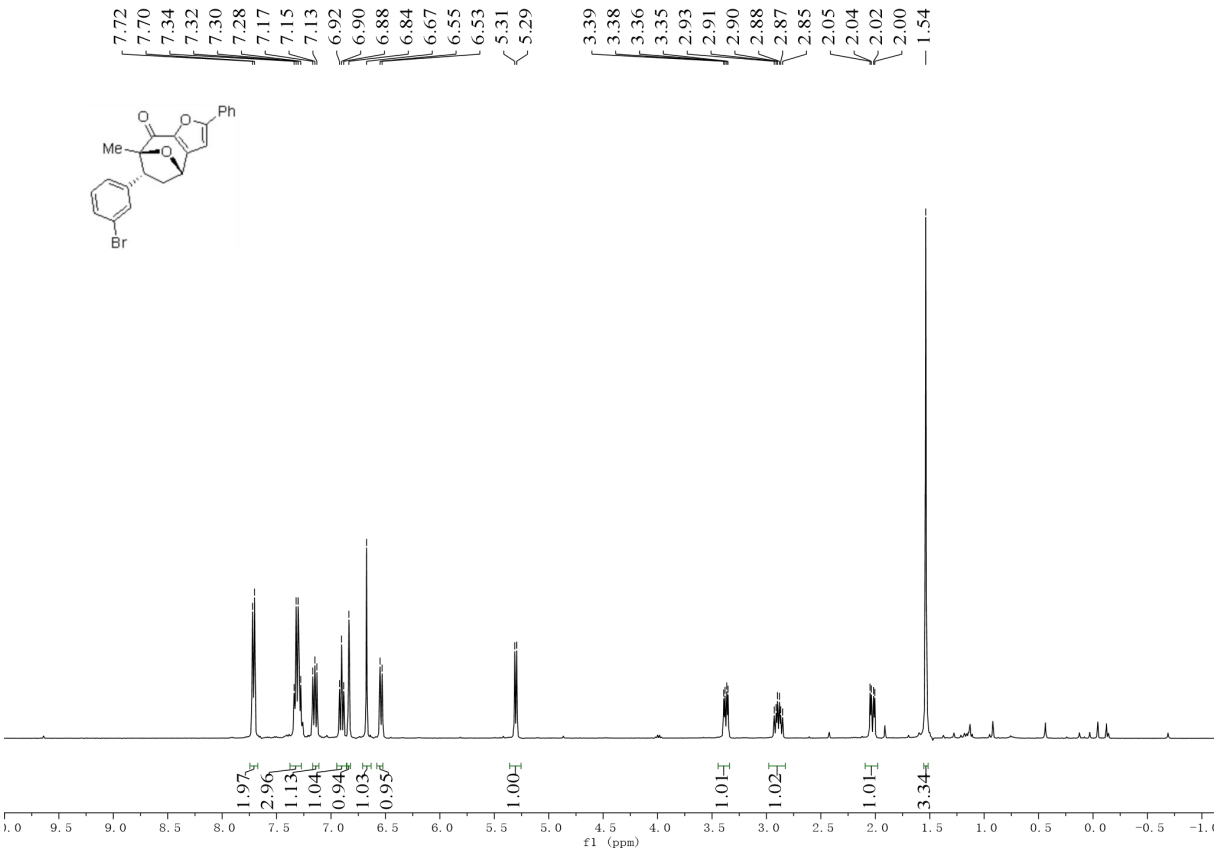


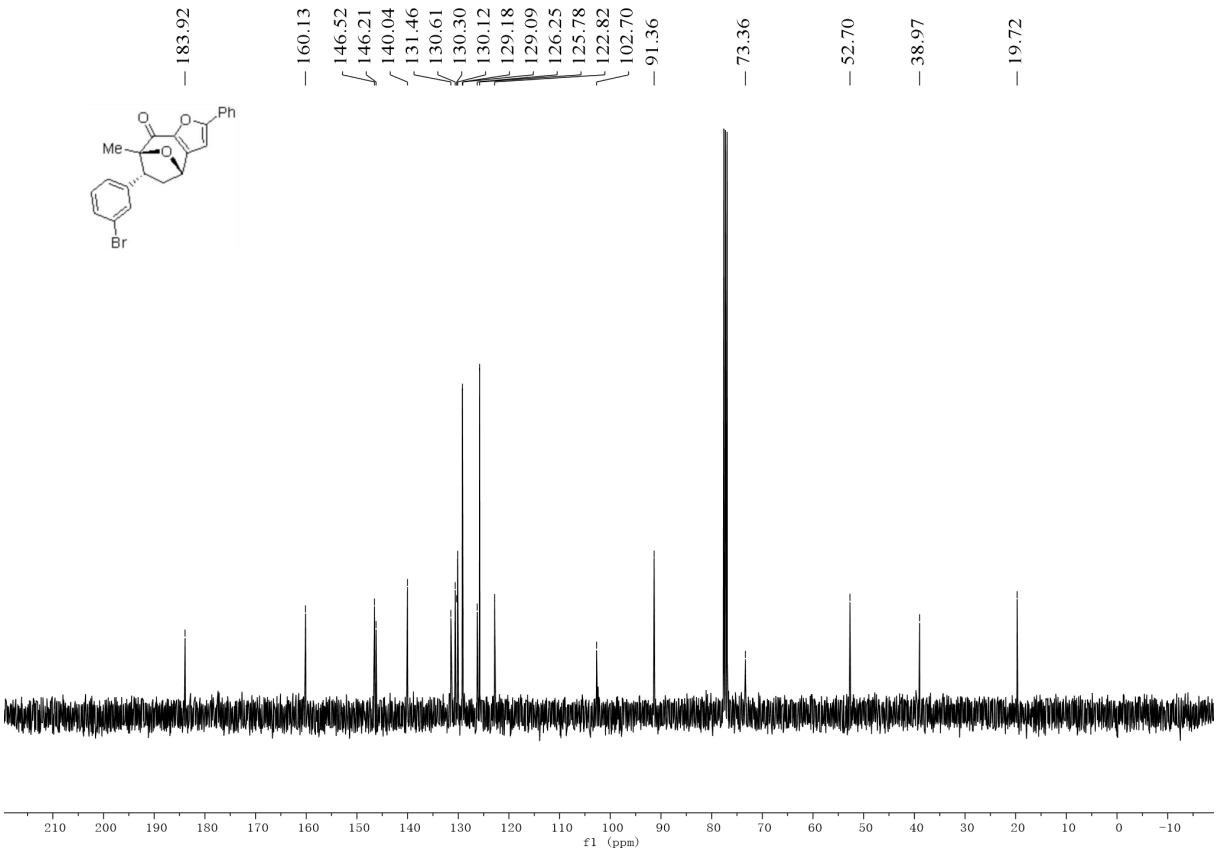
^{1}H and ^{13}C NMR spectra of 5al



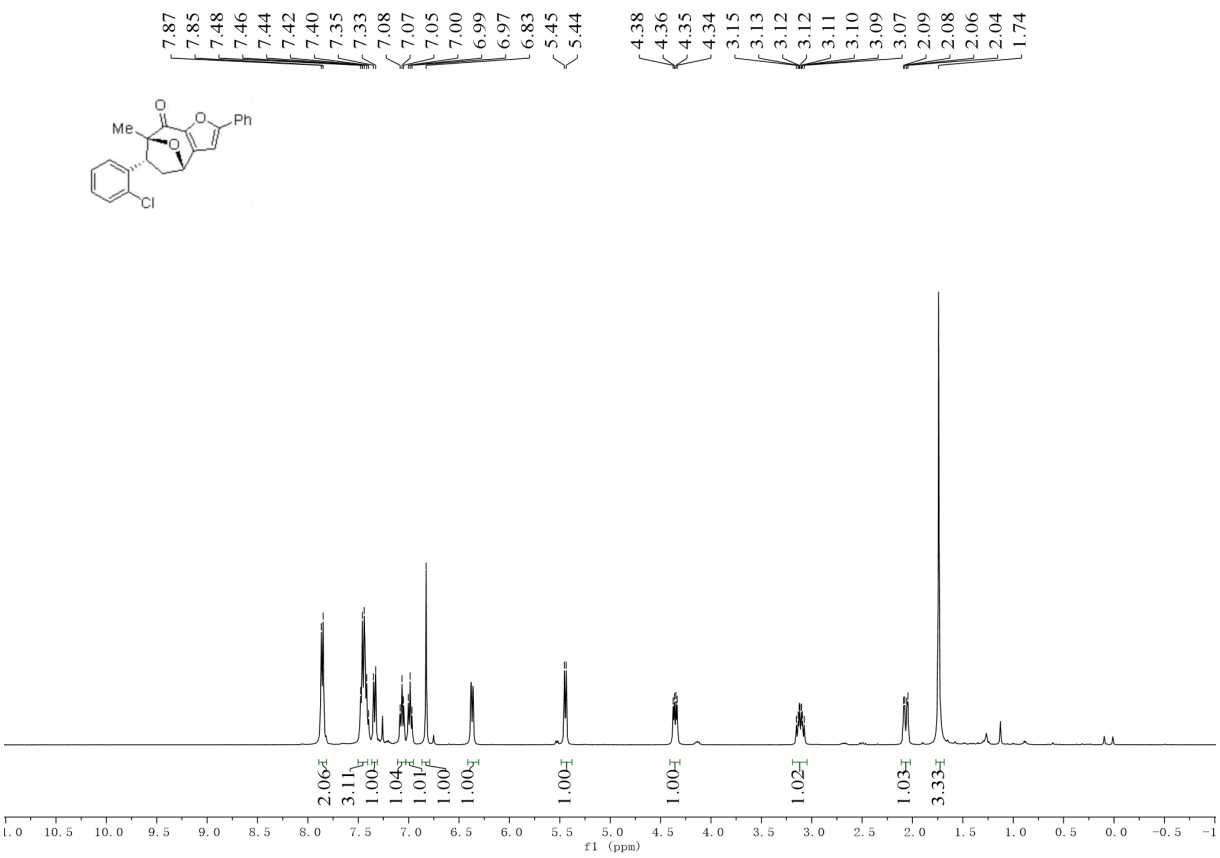


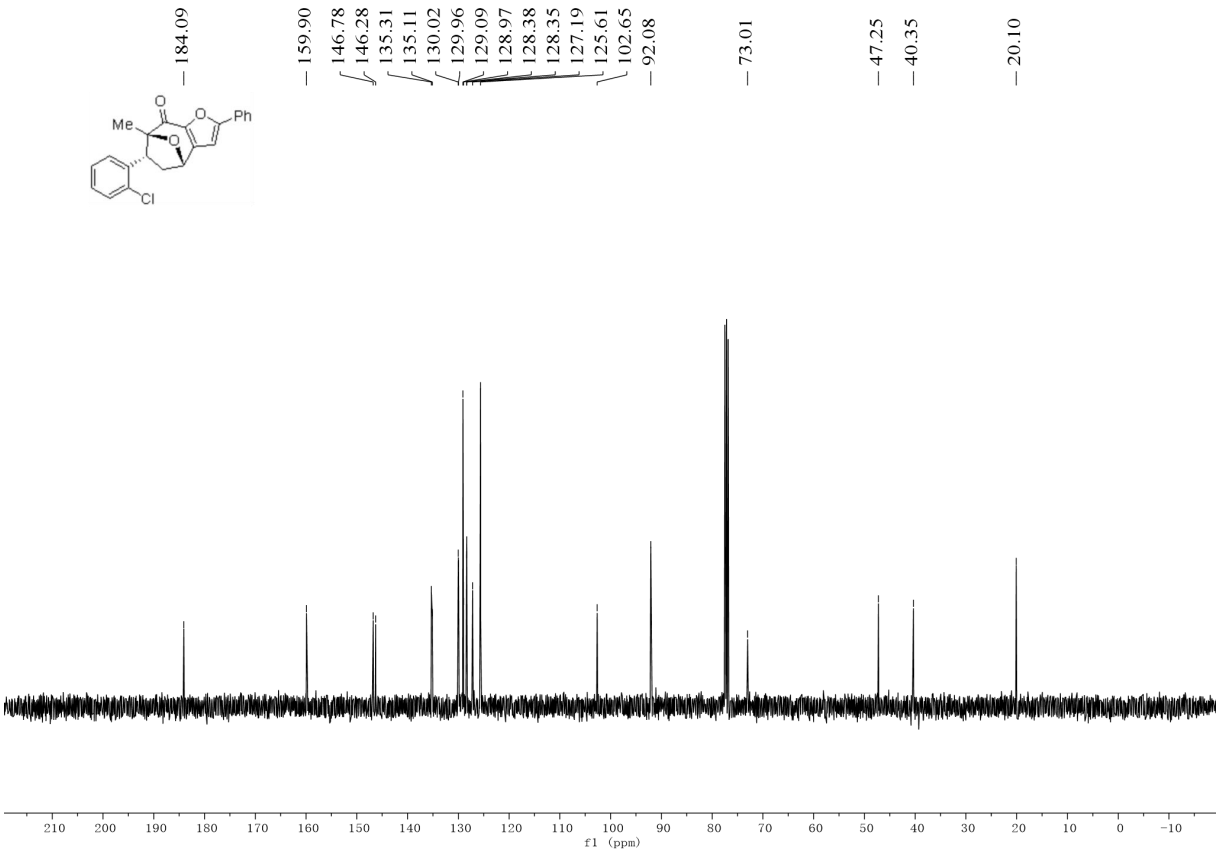
^{1}H and ^{13}C NMR spectra of 5am



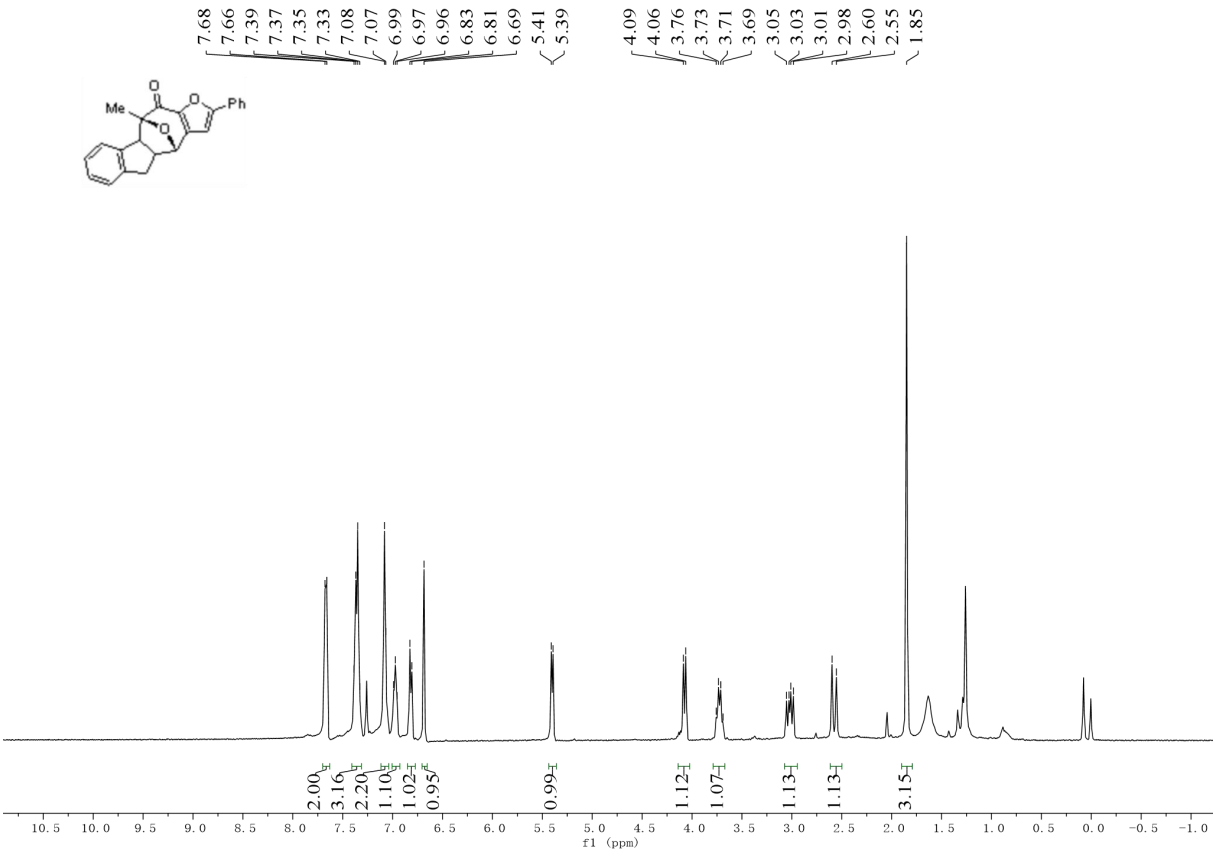


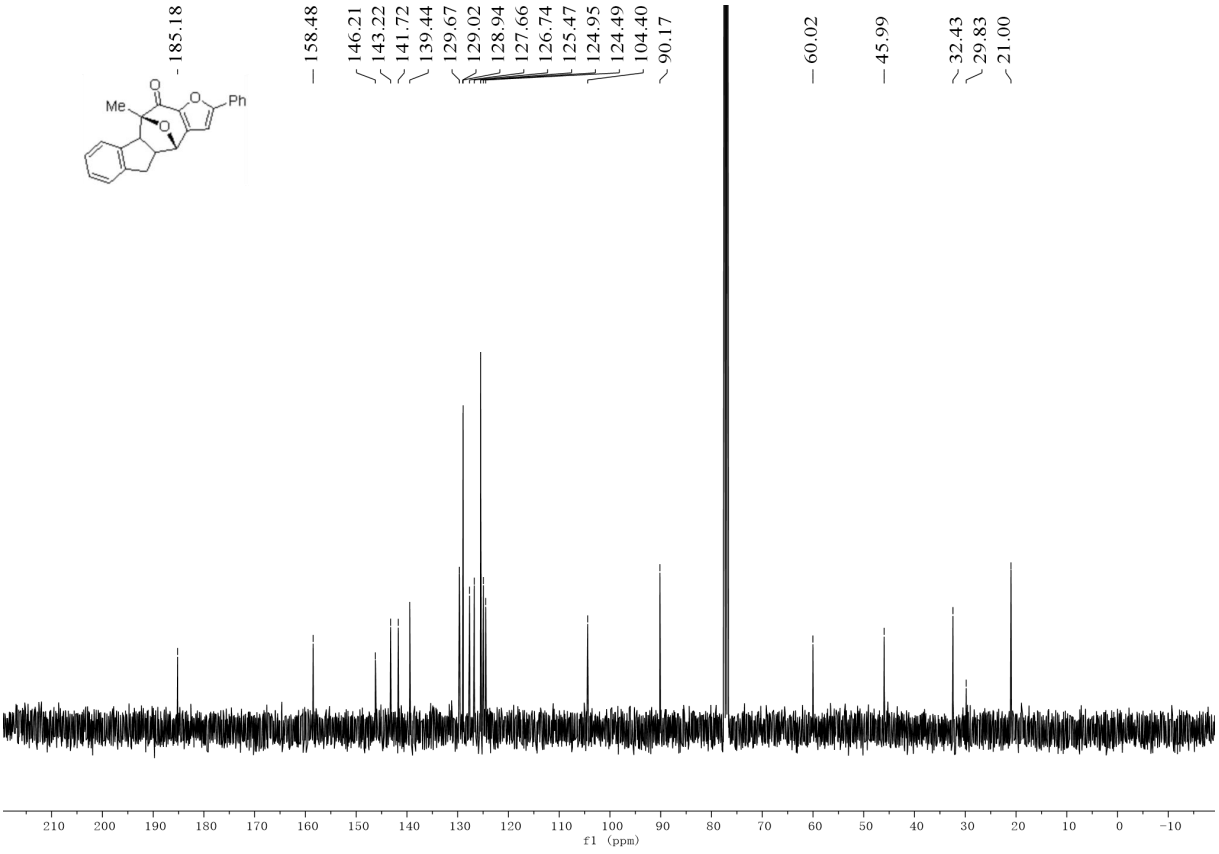
^{1}H and ^{13}C NMR spectra of 5an



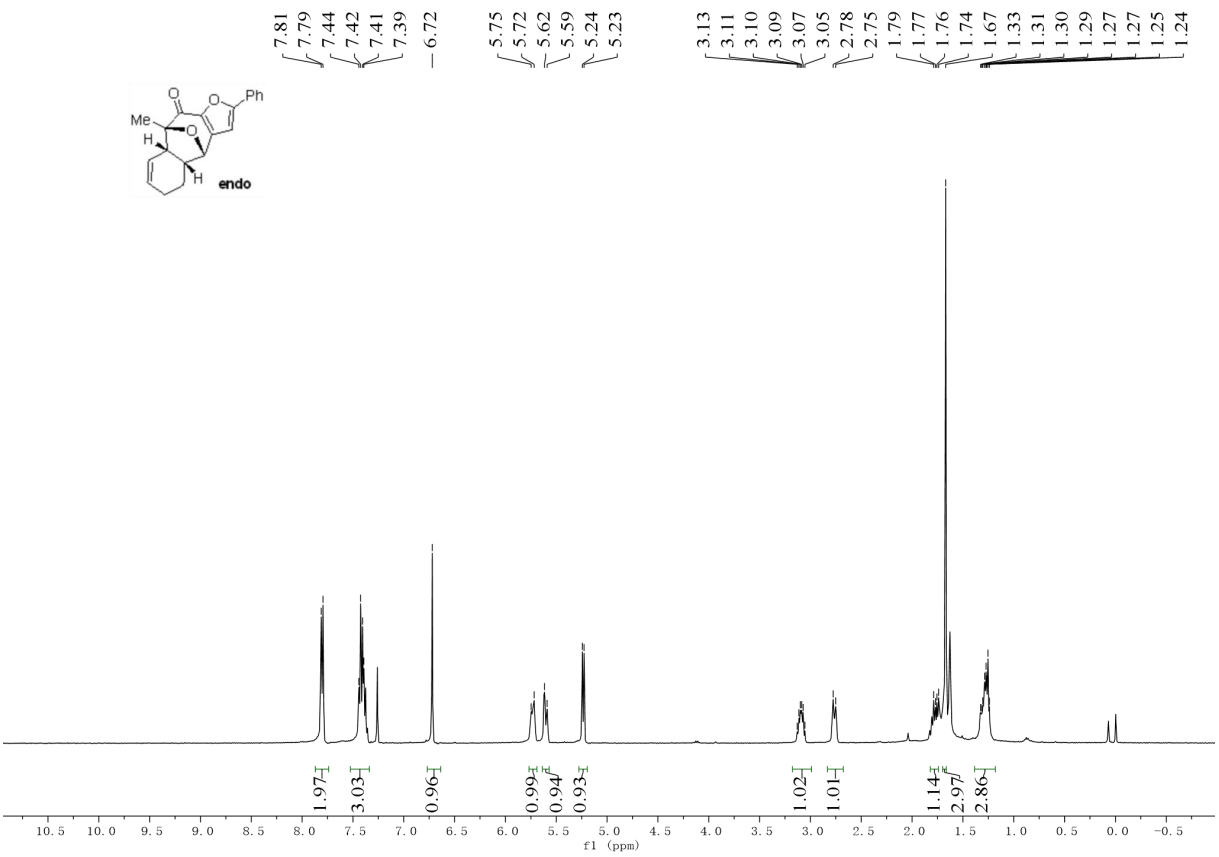


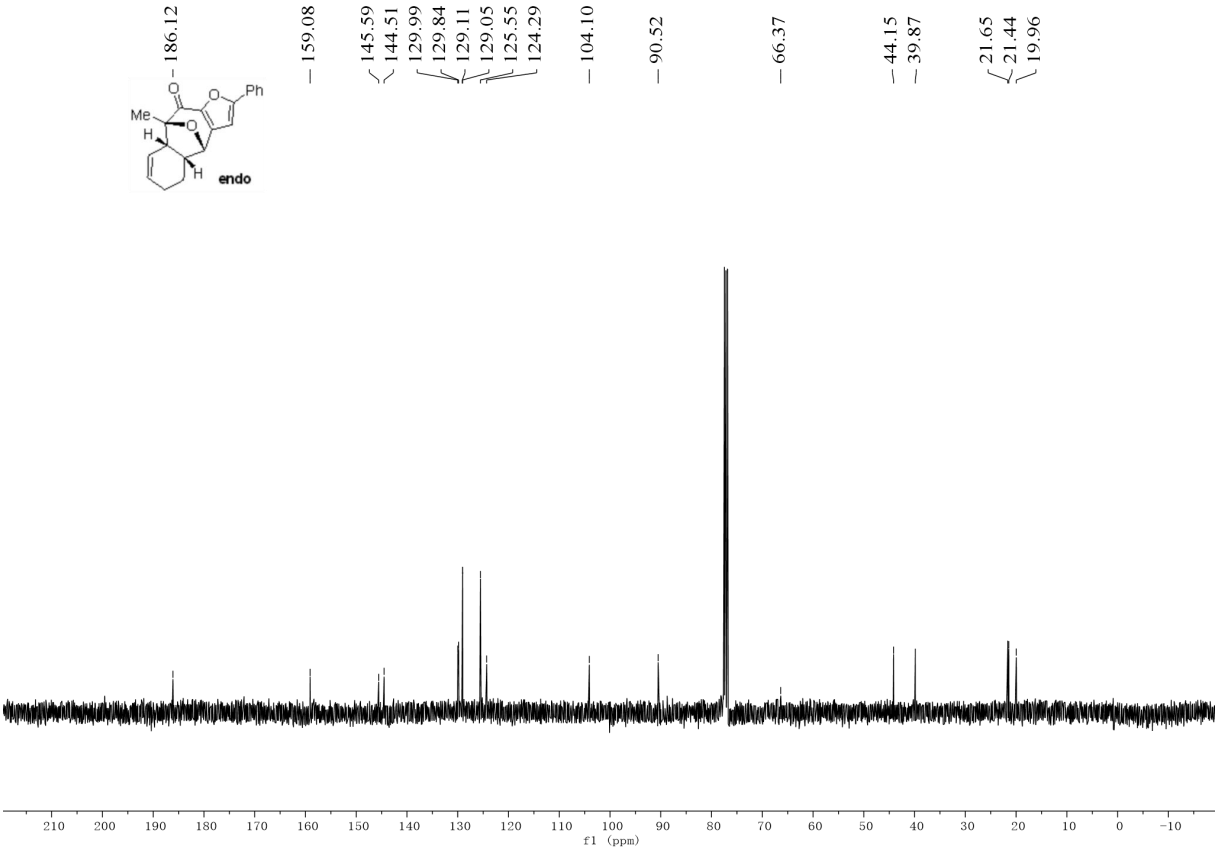
^{1}H and ^{13}C NMR spectra of 5ao



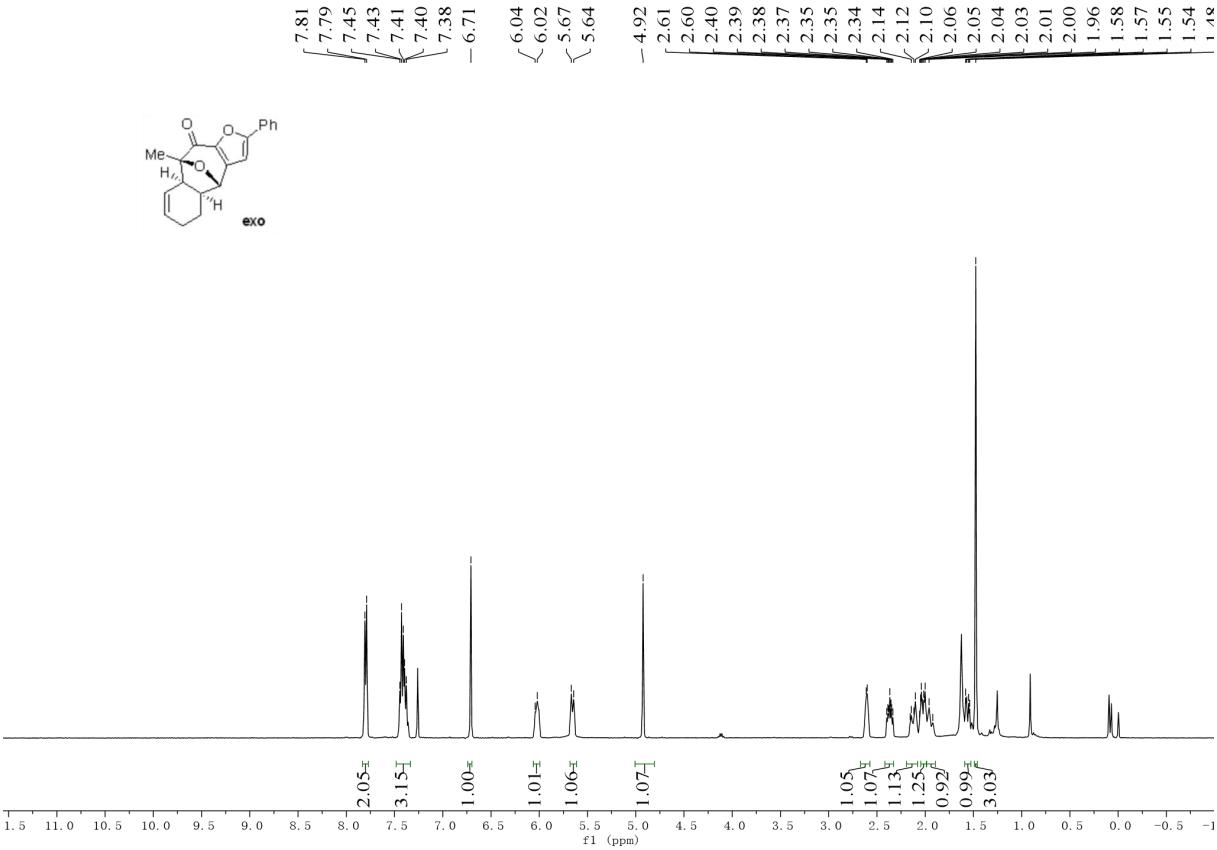


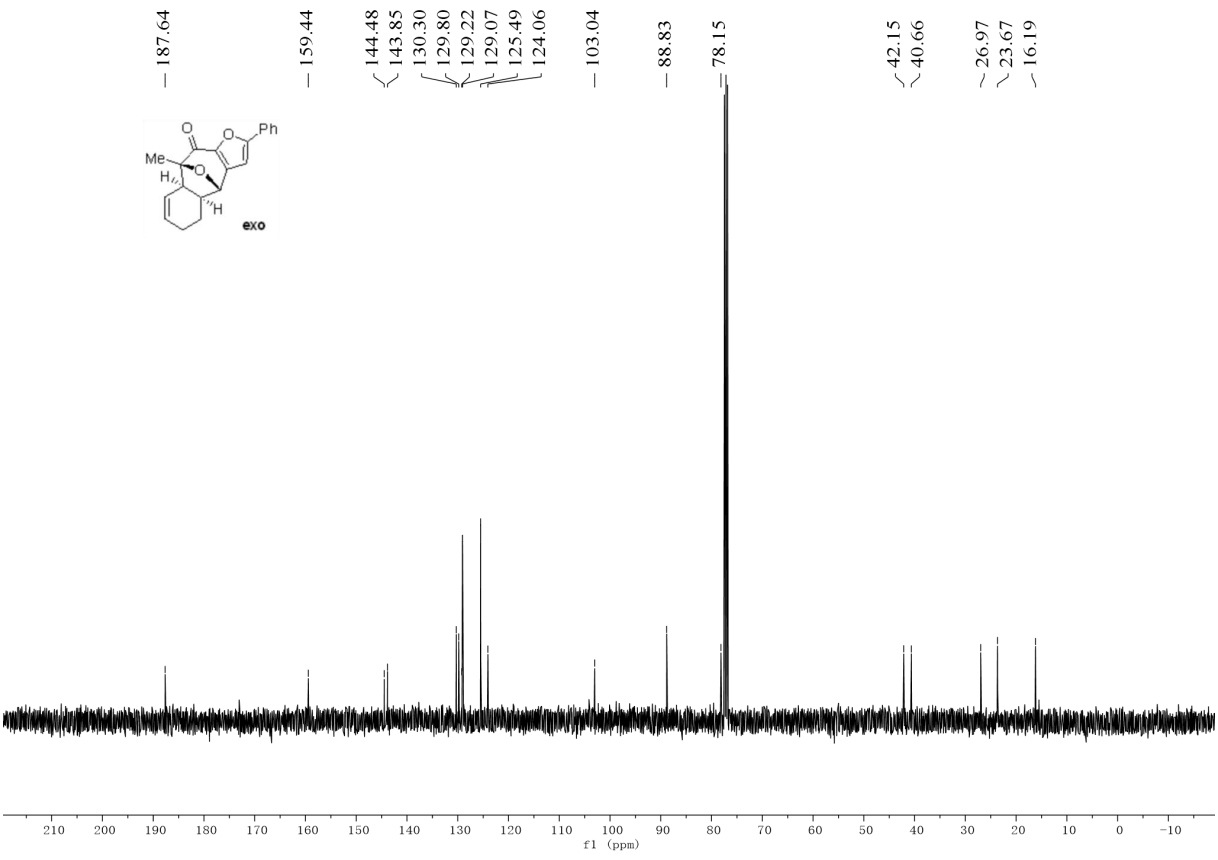
^{1}H and ^{13}C NMR spectra of 5ap



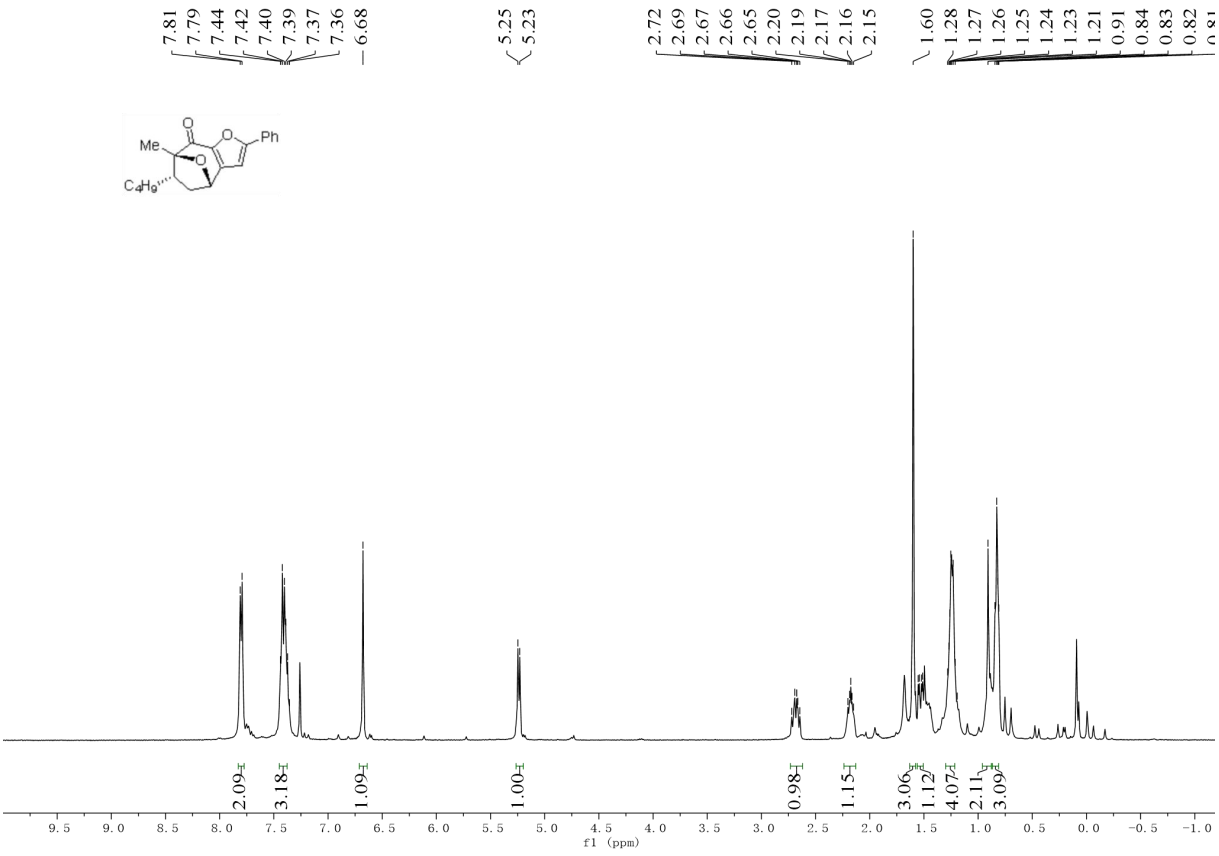


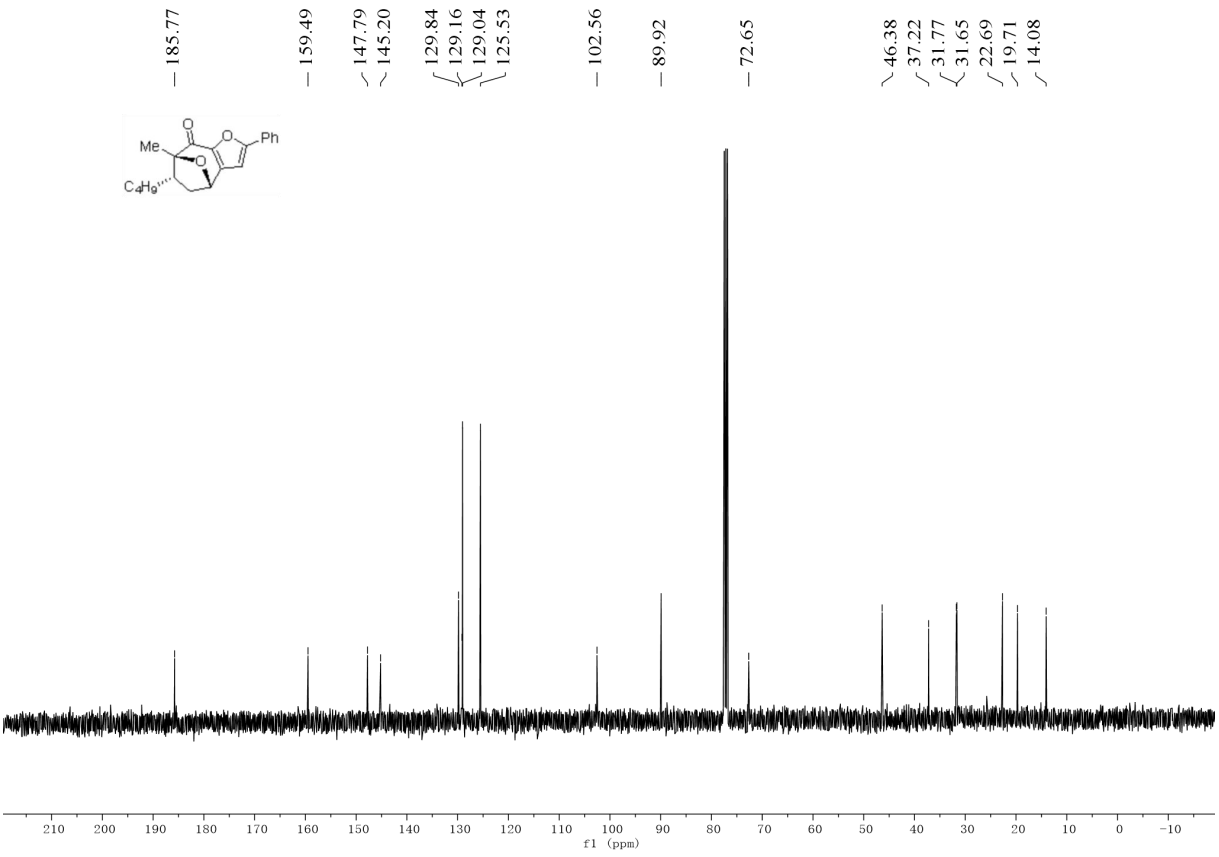
^{1}H and ^{13}C NMR spectra of 5ap´



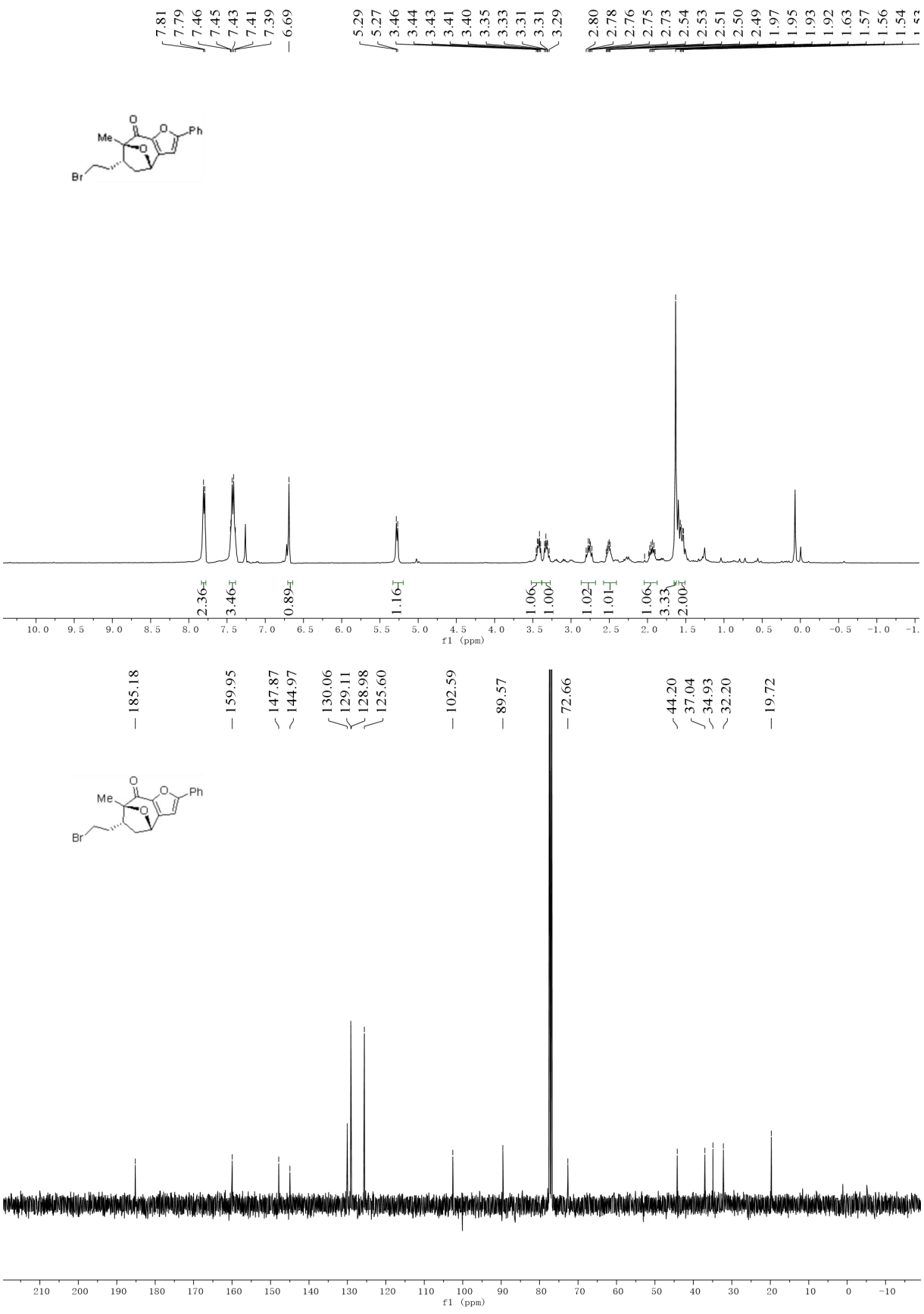


^{1}H and ^{13}C NMR spectra of 5aq

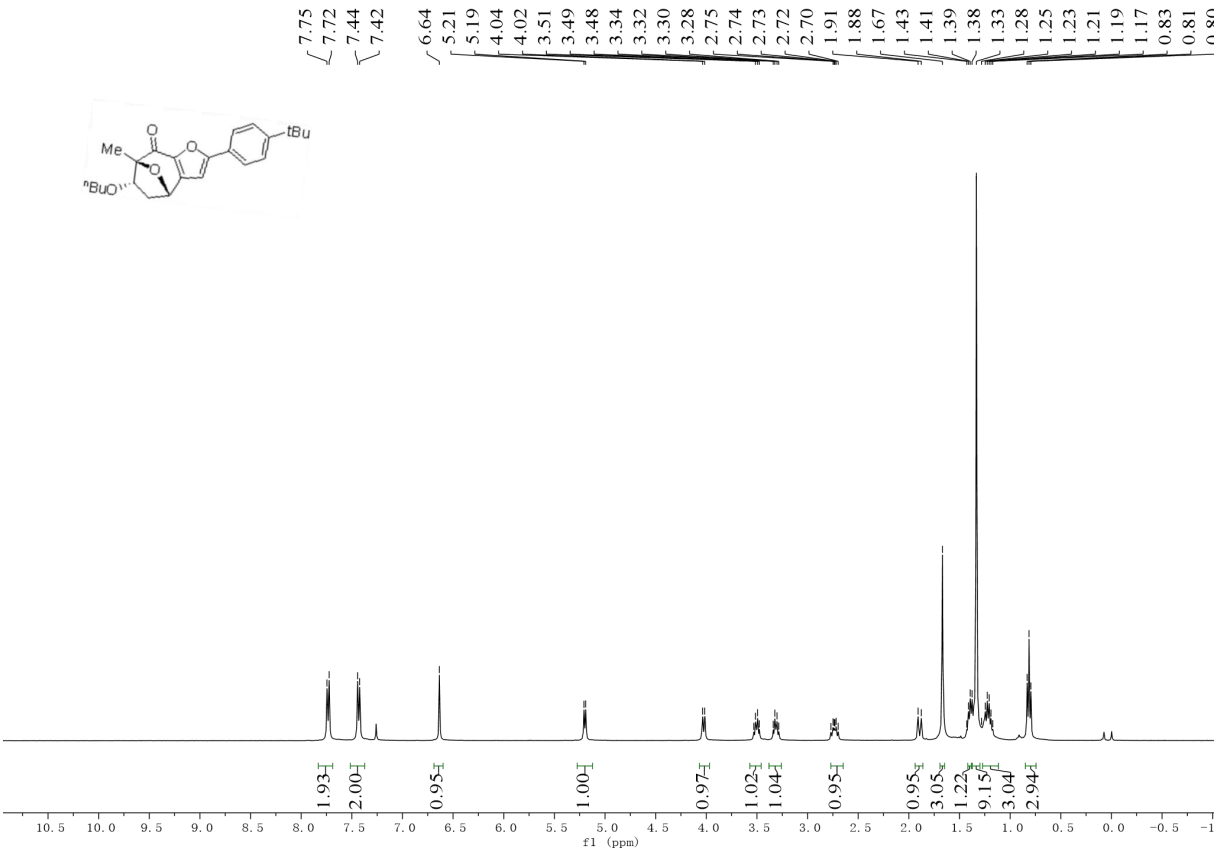


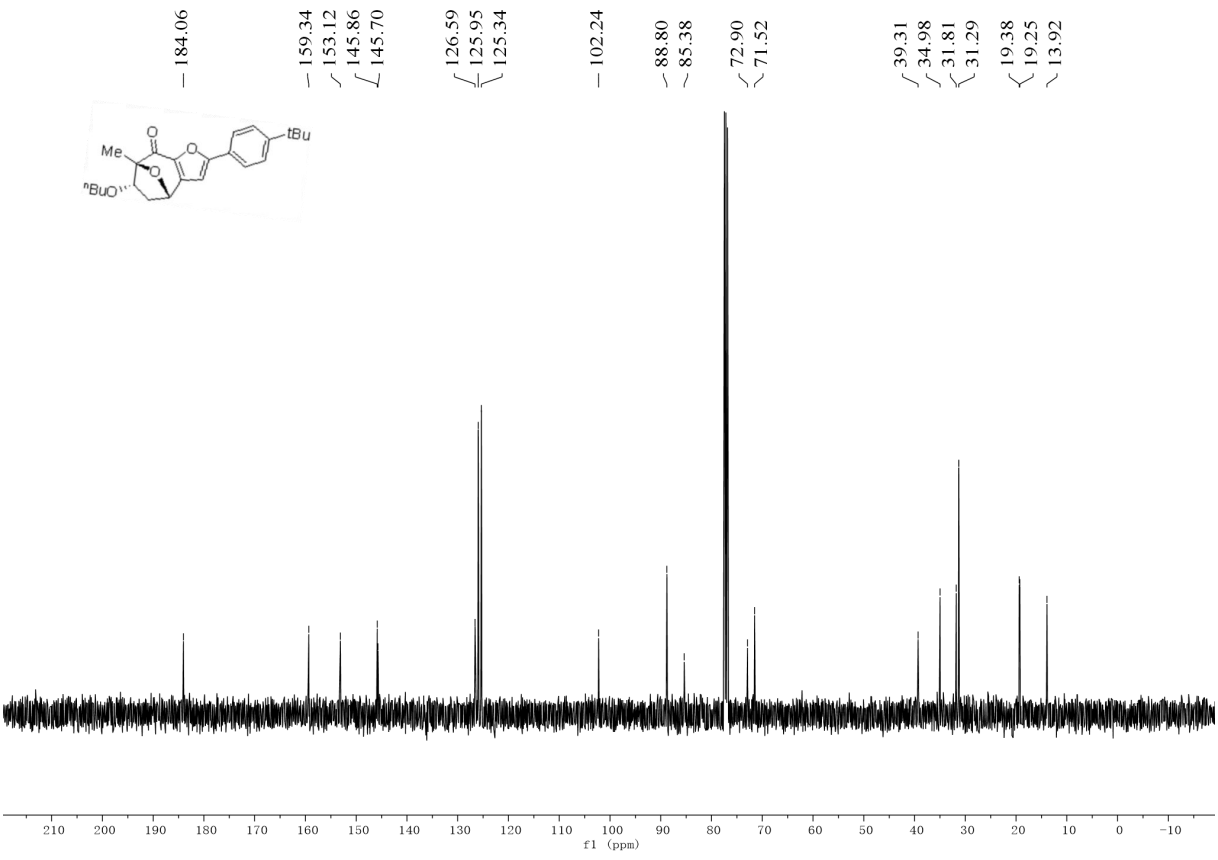


^{1}H and ^{13}C NMR spectra of 5ar

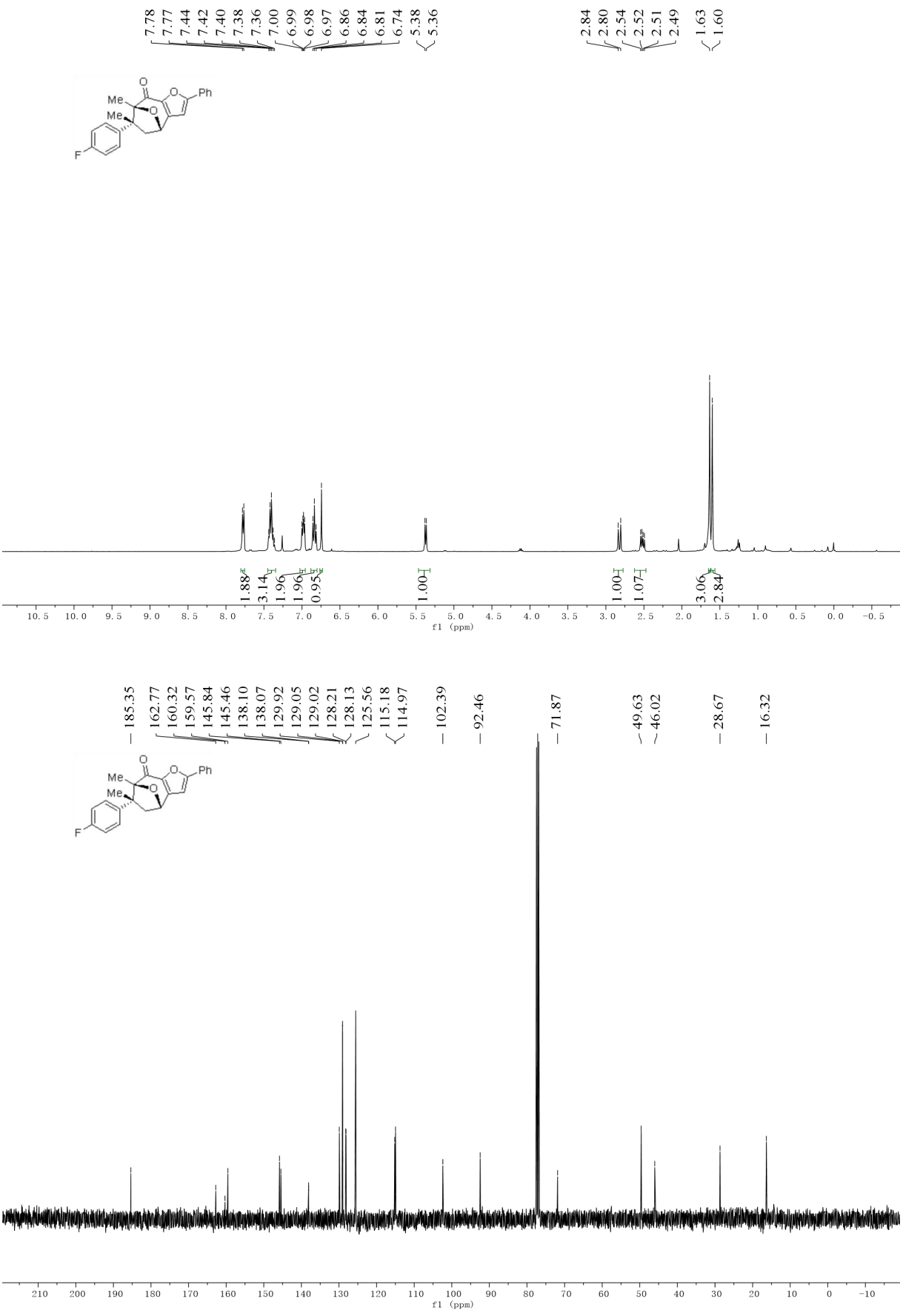


^{1}H and ^{13}C NMR spectra of 5ps

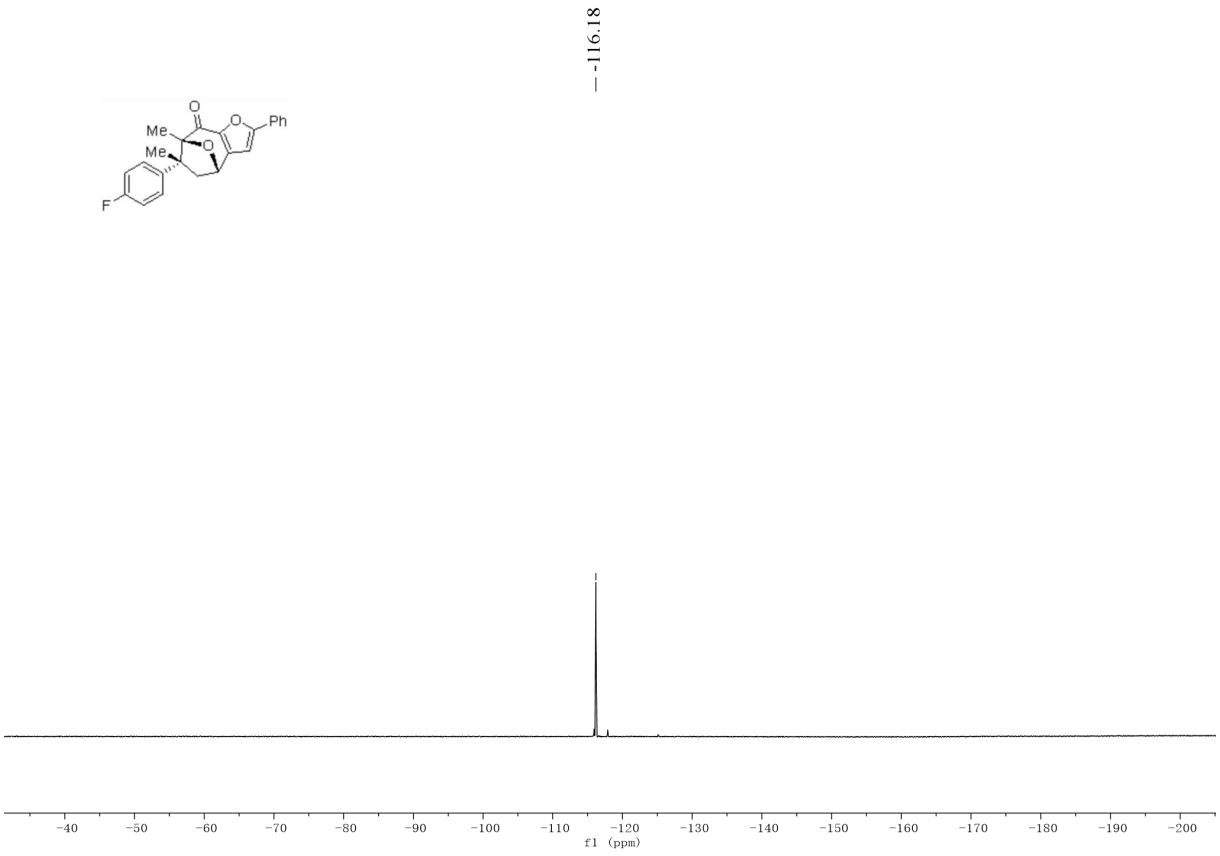




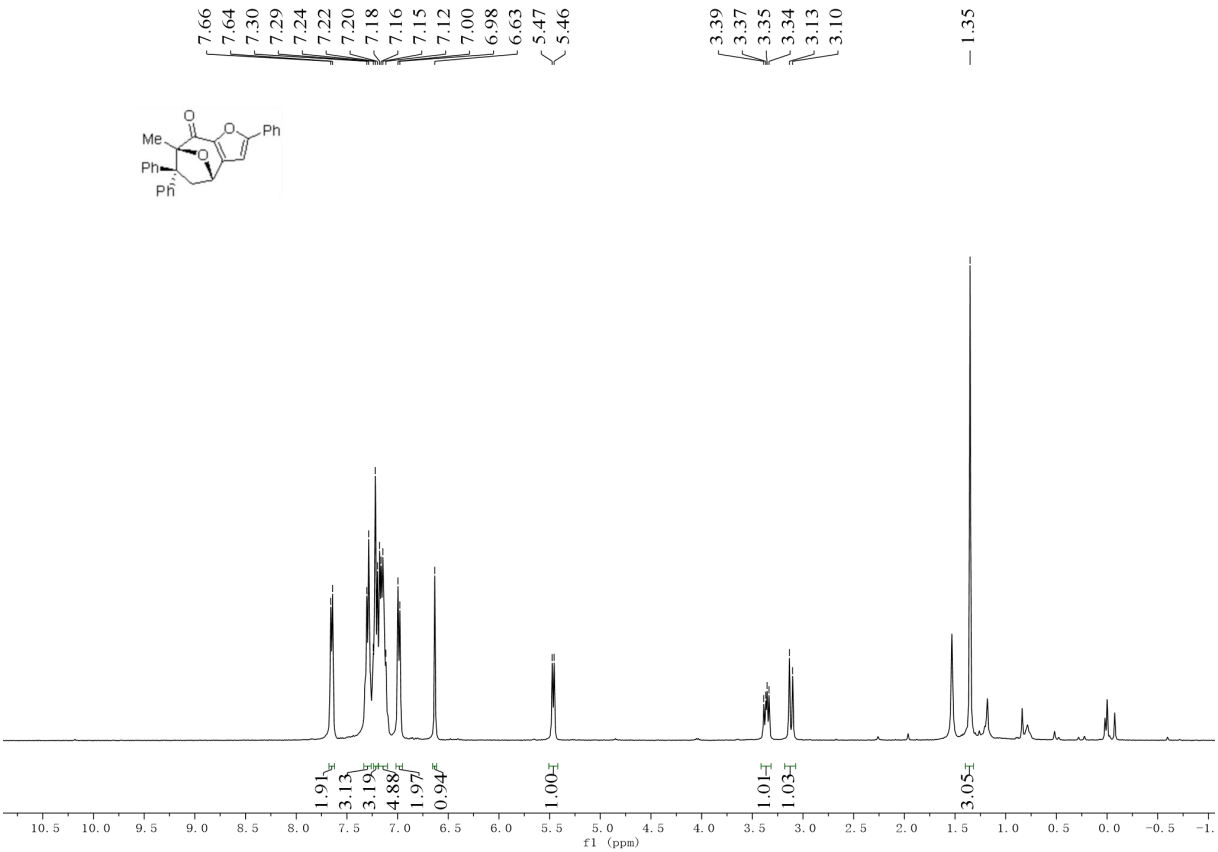
^{1}H and ^{13}C NMR and $^{19}FNMR$ spectra of 5at

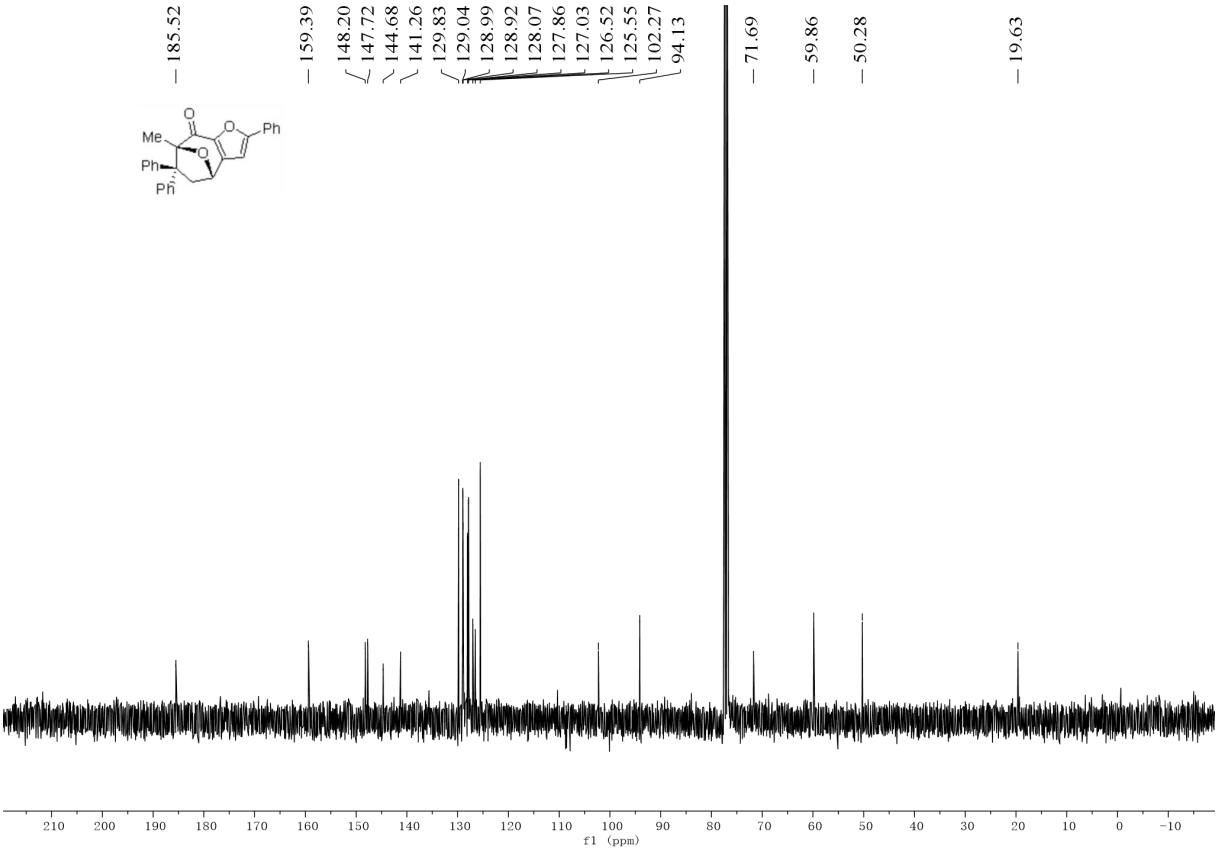


O
Me
Me
O
O
Ph
F

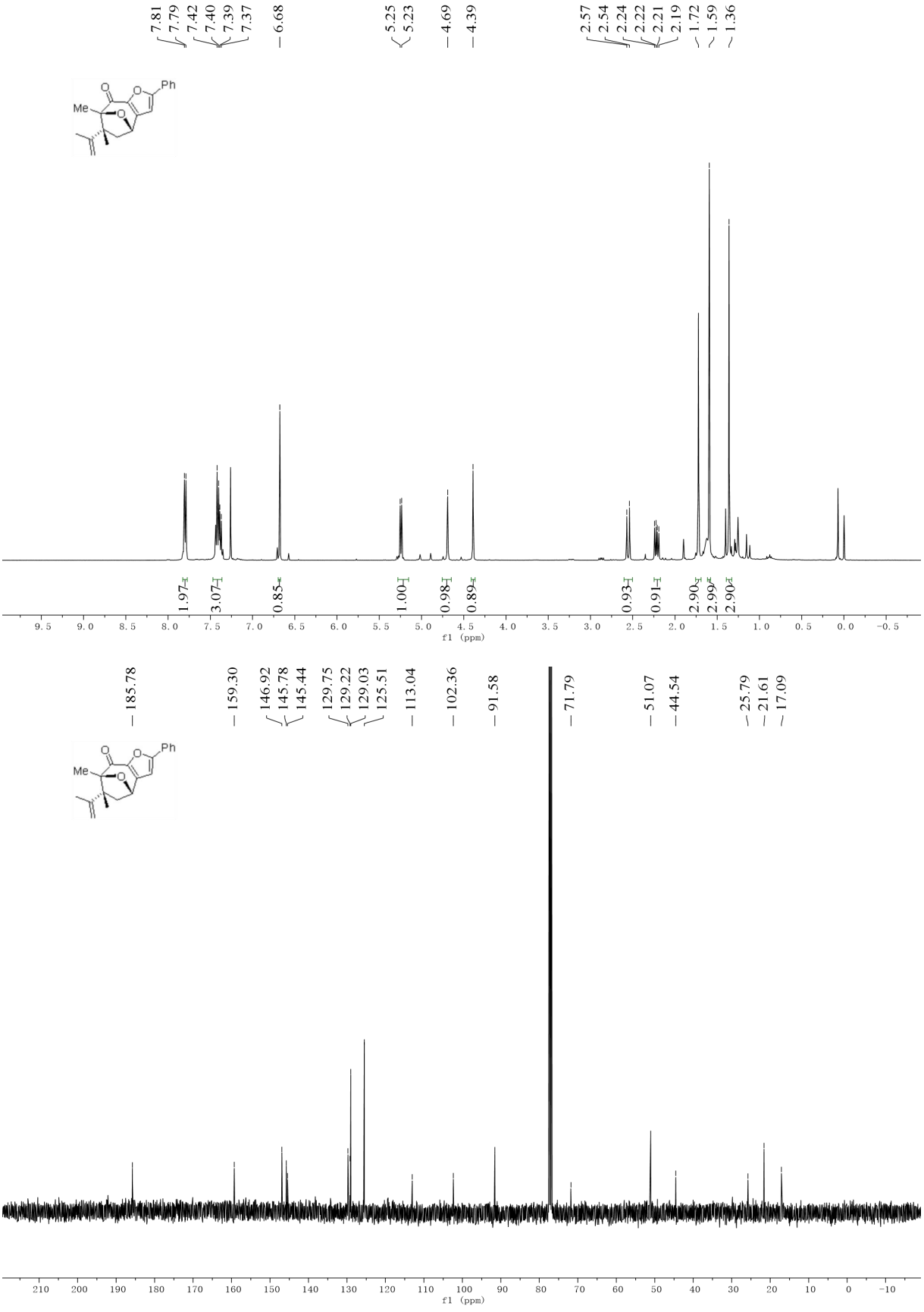

-116.18
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

^{1}H and ^{13}C NMR spectra of 5au

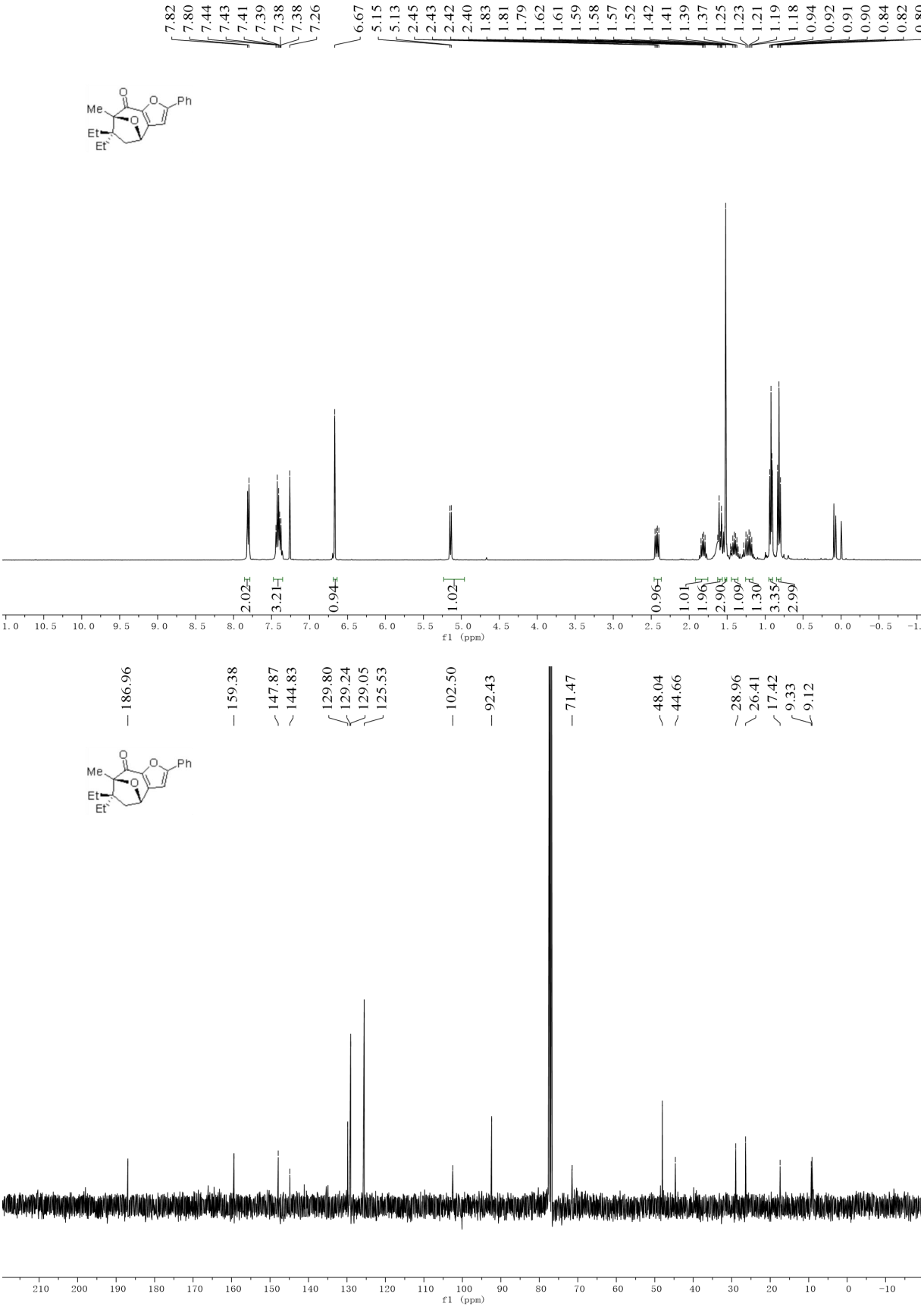




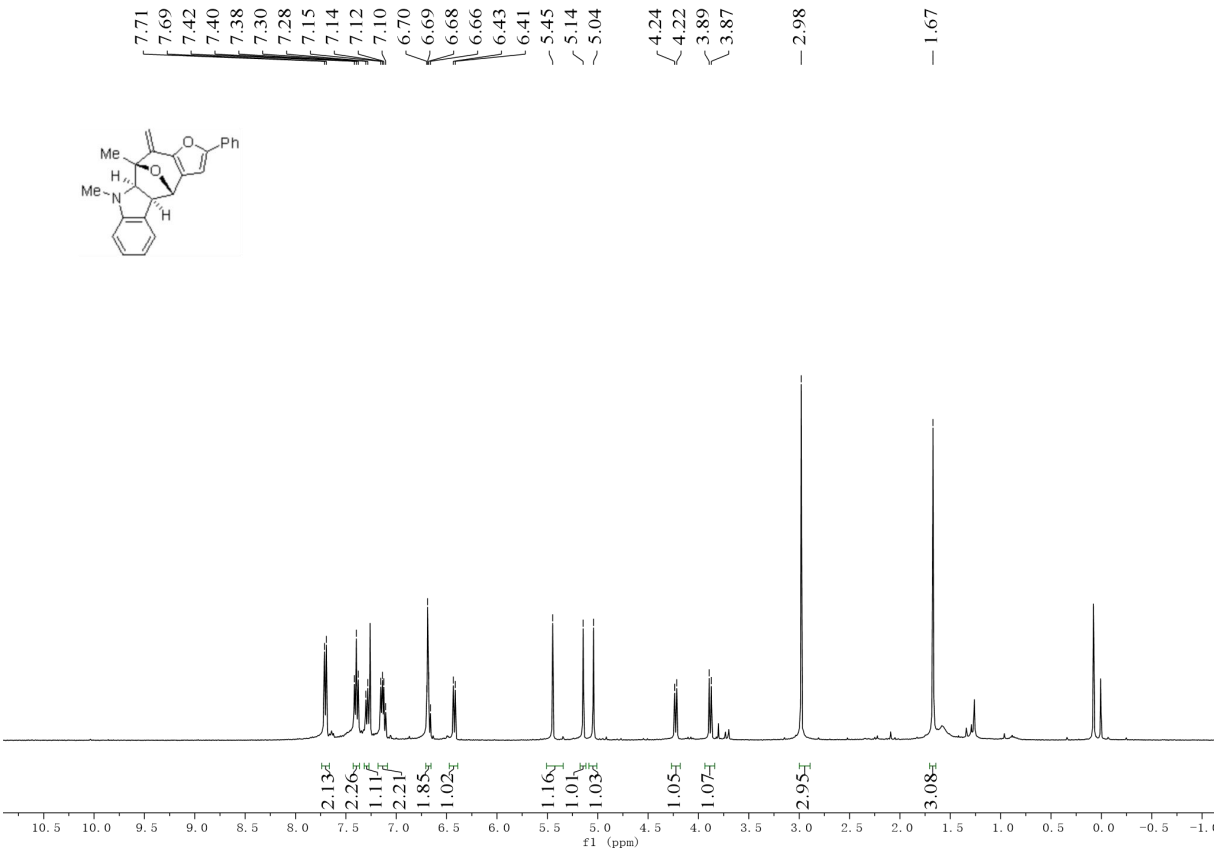
^{1}H and ^{13}C NMR spectra of 5av

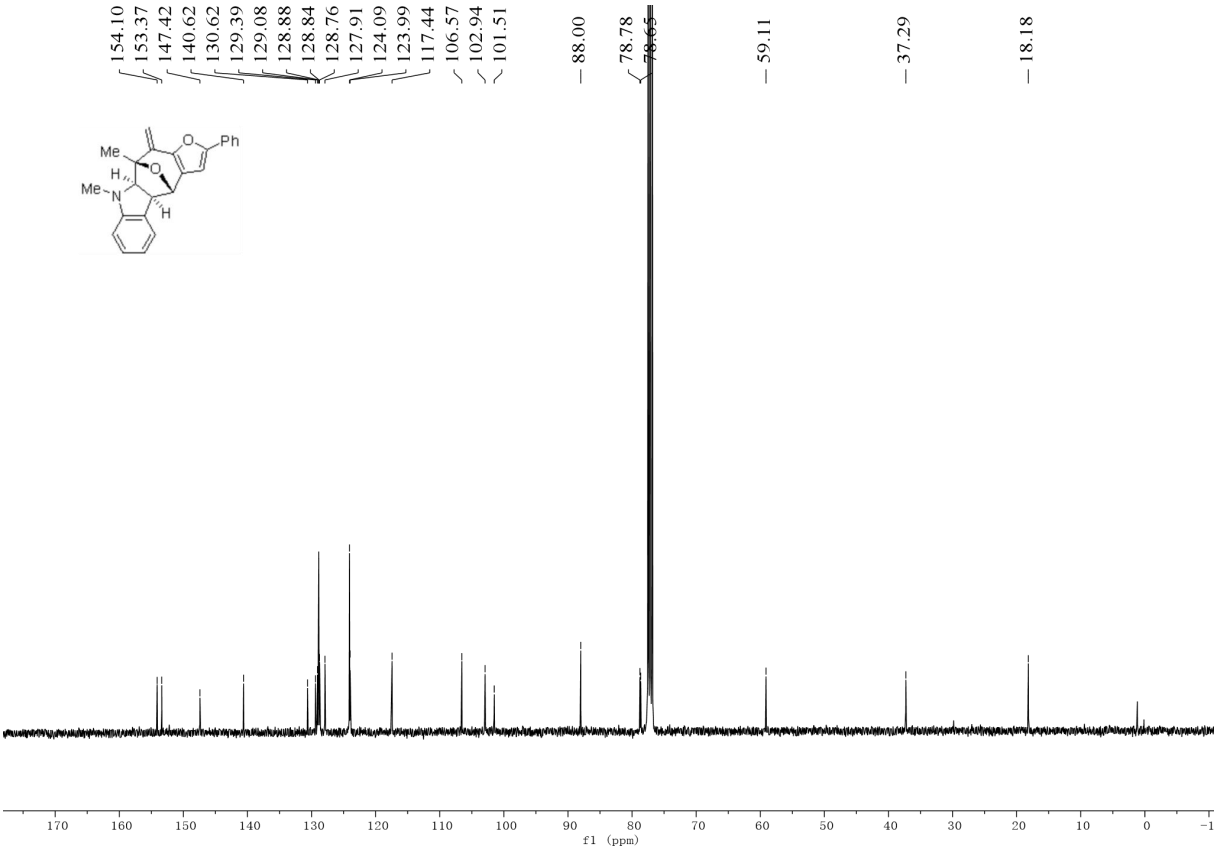


^{1}H and ^{13}C NMR spectra of 5aw



^{1}H and ^{13}C NMR spectra of 6





^{1}H and ^{13}C NMR spectra of 7