Practical Access to Spiroacetal Enol Ethers via Nucleophilic Dearomatization of 2-Furylmethylenepalladium Halides Generated by Pd-Catalyzed Coupling of Furfural Tosylhydrazones with Aryl Halides

Biaolin Yin*, Xiaoyu Zhang, Jianchao Liu, Xuehui Li and Huanfeng Jiang

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, Guangdong, 510640, China.

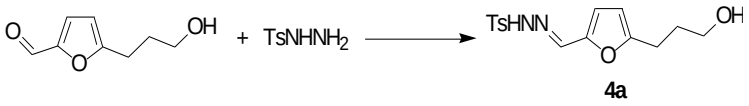
blyin@scut.edu.cn

Content **Page**

General Experimental details

IR spectra were recorded with FT-IR as a thin film or using KBr pellets and are expressed in cm^{-1}. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded using $CDCl_3$ as a solvent. Chemical shifts are reported in ppm downfield to tetramethylsilane. Coupling constants are reported and expressed in Hz; splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (double doublet), dt (double triplet), dq (double quartet). Infrared (IR) spectra were obtained on a Bruker Vector 22 spectrometer. Mass spectra were obtained from high resolution ESI mass spectrometer. All reactions were carried out using freshly distilled and dry solvents. Column chromatography was performed over silica gel (100-200 Mesh) using petroleum ether and ethyl acetate as the eluent.

Preparation of tosylhydrazone (4a)

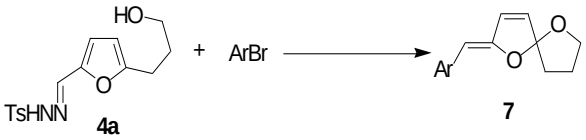


4a

To a stirred suspension of *p*-tosylhydrazide (1.86 g, 10 mmol) in methanol (20 mL) was added 5-(3-hydroxypropyl)furan-2-carbaldehyde (1.54 g, 10 mmol). The mixture was stirred for 2 h at room temperature, and then the solvent was removed under reduced pressure. The crude products could be obtained as precipitates. The precipitates were washed by petroleum ether then removed in vacuo to afford the pure product **4a**.

Yellow solid (3.09 g, 96%), m.p. 129–130 ℃; IR (KBr) ν: 3438, 3047, 2386, 1438, 1162, 1105, 619, 550 cm^{-1}; ^{1}H NMR (400 MHz, DMSO) δ 11.30 (s, 1H), 7.78-7.67 (m, 3H), 7.40 (d, J = 8.1 Hz, 2H), 6.70 (d, J = 3.3 Hz, 1H), 6.21 (d, J = 3.2 Hz, 1H), 3.42 (t, J = 6.3 Hz, 2H), 2.65 (t, J = 7.6 Hz, 2H), 2.37 (s, 3H), 1.76-1.62 (m, 2H); ^{13}C NMR (101 MHz, DMSO) δ 158.53, 147.02, 143.38, 137.11, 136.21, 129.65, 127.09, 115.22, 107.60, 59.76, 30.64, 24.07, 20.96; HRMS (ESI) m/z calcd for $C_{15}H_{18}N_2NaO_4S$: $[M + Na]^+$ 345.0885, Found: 345.0882;

General procedure for the preparation of 7

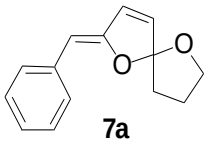


4a **7**

Bromobenzene (0.36 mmol, 56 mg) was added to a mixture of $Pd_2(dba)_3$ (5.0 mol%, 14 mg), tricyclohexylphosphine (10 mol%, 9 mg), Li*O*t*Bu (1.05 mmol, 84 mg), **4a** (0.3 mmol, 97 mg), and toluene (3 mL) in a Schlenk tube under nitrogen. The mixture was stirred at 90 ℃ for 2 h, cooled to room temperature, and filtered through a short column of silica gel (ethyl acetate). The solvent was removed in vacuo, and the residue was purified by flash column chromatography on silica gel (ethyl acetate/petroleum ether= 1:15) to give **7**.

Characterization of 7

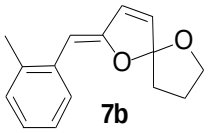
(Z)-2-benzylidene-1,6-dioxaspiro[4.4]non-3-ene (7a)



7a

Yellow oil (79 mg, 74%), IR (film) 2950, 1693, 1449, 1359, 1091, 944, 816, 754, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.3 Hz, 2H), 7.21 (t, J = 7.7 Hz, 2H), 7.09-7.02 (m, 1H), 6.26 (d, J = 5.6 Hz, 1H), 5.96 (d, J = 5.6 Hz, 1H), 5.32 (s, 1H), 4.21-3.91 (m, 2H), 2.30-2.14 (m, 2H), 2.04-1.97 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 136.2, 131.0, 129.9, 128.3, 128.2, 125.7, 121.1, 101.3, 69.1, 36.0, 24.6; HRMS (ESI) m/z calcd for $C_{14}H_{14}NaO_2$: $[M + Na]^+$ 237.0891, Found: 237.0886.

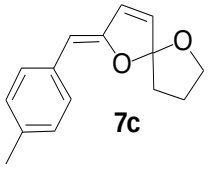
(Z)-2-(2-methylbenzylidene)-1,6-dioxaspiro[4.4]non-3-ene (7b)



7b

Yellow oil (83 mg, 73%), IR (KBr) 2952, 2359, 1644, 1456, 1129, 944, 818, 750, 619 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.02 (m, 4H), 6.37 (d, J = 5.5 Hz, 1H), 6.02 (d, J = 5.6 Hz, 1H), 5.50 (s, 1H), 4.32-3.90 (m, 3H), 2.31 (s, 3H), 2.27-2.19 (m, 2H), 2.10-2.01 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 135.0, 134.5, 134.1, 130.9, 130.1, 129.9, 128.5, 125.9, 125.8, 121.0, 98.0, 69.1, 49.4, 36.0, 24.7, 20.3; HRMS (ESI) m/z calcd for $C_{15}H_{16}NaO_2$: $[M + Na]^+$ 251.1048, Found: 251.1043.

(Z)-2-(4-methylbenzylidene)-1,6-dioxaspiro[4.4]non-3-ene (7c)

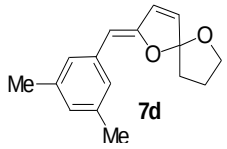


7c

Yellow oil (86 mg, 76 %), IR (film) 2925, 1640, 1446, 1106, 816 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.5 Hz, 2H), 7.14 (d, J = 7.1 Hz, 2H), 6.37 (d, J = 6.4 Hz, 1H), 6.05 (d, J = 6.0 Hz, 1H), 5.40 (s, 1H), 4.31-4.00 (m, 2H), 2.35 (s, 1H), 2.30-2.20 (m, 2H), 2.14-2.06(m,

2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 135.4, 133.3, 130.4, 129.9, 129.0, 128.1, 120.9, 101.3, 69.0, 36.0, 24.6, 21.2; HRMS (ESI) m/z calcd for $C_{15}H_{16}NaO_2$: $[M + Na]^+$ 251.1048, Found: 251.1043.

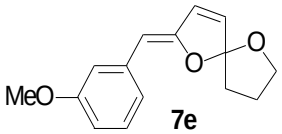
(Z)-2-(3,5-dimethylbenzylidene)-1,6-dioxaspiro[4.4]non-3-ene (7d)



7d

Yellow oil (91 mg, 75 %), IR (film) 2978, 2874, 1518, 1488, 1372, 1280, 1158, 1116, 1063, 978, 876 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.0 Hz, 1H), 6.96 (d, J = 13.6 Hz, 2H), 6.37 (d, J = 5.5 Hz, 1H), 6.01 (d, J = 5.6 Hz, 1H), 5.48 (s, 1H), 4.23-3.99 (m, 2H), 2.30-2.22 (m, 12H), 2.12-2.04 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.46, 130.72, 130.30, 130.14, 128.45, 120.85, 100.68, 98.05, 69.04, 35.94, 24.63, 20.19; HRMS (ESI) m/z calcd for $C_{16}H_{18}O_2$: $[M + H]^+$ 243.1385, Found: 243.1390.

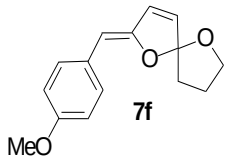
(Z)-2-(3-methoxybenzylidene)-1,6-dioxaspiro[4.4]non-3-ene (7e)



7e

Yellow oil (85 mg, 70%), IR (film) 2942, 1648, 1487, 1266, 1093, 974, 874, 775, 688 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.18 (m, 3H), 6.75-6.69 (m, 1H), 6.38 (d, J = 5.6 Hz, 1H), 6.08 (d, J = 5.6 Hz, 1H), 5.42 (s, 1H), 4.31-4.01 (m, 2H), 3.85 (s, 3H), 2.44-0.59 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 156.3, 137.5, 131.1, 129.9, 129.1, 121.0, 113.3, 111.8, 101.2, 69.1, 55.0, 36.0, 24.6; HRMS (ESI) m/z calcd for $C_{15}H_{16}NaO_3$: $[M + Na]^+$ 267.0997, Found: 267.0991.

(Z)-2-(4-methoxybenzylidene)-1,6-dioxaspiro[4.4]non-3-ene (7f)

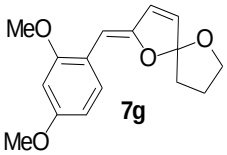


7f

Yellow oil (94 mg, 77 %), IR (film) 2950, 1510, 1451, 1358, 1249, 1176, 1029, 840 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 6.36 (d, J =

5.6 Hz, 1H), 6.01 (d, *J* = 5.5 Hz, 1H), 5.39 (s, 1H), 4.34-4.01 (m, 2H), 3.83 (s, 3H), 2.42-2.23 (m, 2H), 2.16-2.03 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 154.6, 133.8, 129.9, 129.8, 129.4, 129.1, 120.9, 114.0, 113.8, 100.9, 69.0, 55.2, 36.0, 24.7; HRMS (ESI) m/z calcd for $C_{15}H_{16}NaO_3$: $[M + Na]^+$ 267.0997, Found: 267.0992.

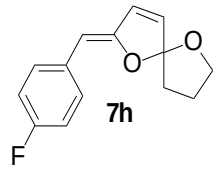
(Z)-2-(2,4-dimethoxybenzylidene)-1,6-dioxaspiro[4.4]non-3-ene (7g)



7g

Yellow oil (113 mg, 83 %), IR (film) 2941, 1608, 1504, 1460, 1291, 1158, 1035, 832 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.6 Hz, 1H), 6.51 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.42 (d, *J* = 2.4 Hz, 1H), 6.36 (d, *J* = 5.6 Hz, 1H), 5.95 (d, *J* = 5.5 Hz, 1H), 5.75 (s, 1H), 4.26-3.97 (m, 2H), 3.81 (s, 6H), 2.35-2.17 (m, 2H), 2.12-2.02 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 157.1, 154.7, 130.2, 129.8, 129.3, 120.8, 118.1, 104.6, 98.1, 94.2, 69.0, 55.6, 55.3, 36.0, 24.7; HRMS (ESI) m/z calcd for $C_{16}H_{18}NaO_4$: $[M + Na]^+$ 297.1103, Found: 297.1097.

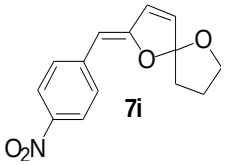
(Z)-2-(4-fluorobenzylidene)-1,6-dioxaspiro[4.4]non-3-ene (7h)



7h

Yellow oil (74 mg, 64 %), IR (film) 2983, 1693, 1507, 1359, 1315, 1090, 944, 771, cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.52 (m, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.33 (d, *J* = 5.6 Hz, 1H), 6.03 (d, *J* = 5.6 Hz, 1H), 5.36 (s, 1H), 4.27-3.99 (m, 2H), 2.36-2.20 (m, 2H), 2.13-2.06 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.7, 132.4, 132.3, 130.9, 129.7, 129.7, 129.6, 129.5, 129.4, 125.3, 121.1, 115.2, 115.0, 100.2, 69.2, 36.0, 24.6; HRMS (ESI) m/z calcd for $C_{14}H_{13}FNaO_2$: $[M + Na]^+$ 255.0797, Found: 255.0792.

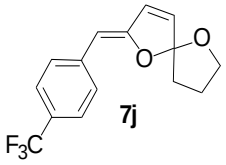
(Z)-2-(4-nitrobenzylidene)-1,6-dioxaspiro[4.4]non-3-ene (7i)



7i

Yellow oil (63 mg, 49 %); IR (film), 2983, 1642, 1388, 1111, 993, 619 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.8 Hz, 2H), 7.71 (d, J = 8.9 Hz, 2H), 6.38 (d, J = 5.6 Hz, 1H), 6.22 (d, J = 5.6 Hz, 1H), 5.48 (s, 1H), 4.34-3.99 (m, 3H), 2.33-2.22 (m, 2H), 2.20-2.11 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.1, 159.3, 134.0, 129.4, 128.1, 127.9, 123.7, 121.9, 99.5, 69.6, 49.4, 30.6; HRMS (ESI) m/z calcd for $C_{14}H_{13}NNaO_4$: $[M + Na]^+$ 282.0742, Found: 282.0737.

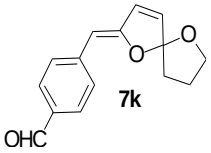
(Z)-2-(4-(trifluoromethyl)benzylidene)-1,6-dioxaspiro[4.4]non-3-ene (7j)



7j

Yellow oil (78 mg, 56 %), IR (film) 2895, 1653, 1419, 1363, 1243, 1068, 945, 849, 759 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.2 Hz, 2H), 7.52 (d, J = 8.3 Hz, 2H), 6.35 (d, J = 5.6 Hz, 1H), 6.12 (d, J = 5.5 Hz, 1H), 5.42 (s, 1H), 4.32-3.97 (m, 2H), 2.40-2.20 (m, 2H), 2.16-2.01 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 139.8, 132.6, 129.6, 128.0, 127.2 (q, $J_{C\text{-}F}$ = 32 Hz), 125.8, 125.1 (q, $J_{C\text{-}F}$ = 23 Hz), 123.1, 121.5, 99.9, 77.4, 77.1, 76.7, 69.4, 35.9, 24.6; HRMS (ESI) m/z calcd for $C_{15}H_{13}F_3NaO_2$: $[M + Na]^+$ 305.0765, Found: 305.0760.

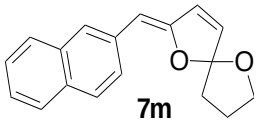
(Z)-4-(1,6-dioxaspiro[4.4]non-3-en-2-ylidenemethyl)benzaldehyde (7k)



7k

Yellow syrup (60 mg, 50 %), IR (film) 2936, 1644, 1598, 1387, 1110, 848, 619 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.72 (d, J = 8.2 Hz, 2H), 7.66 (d, J = 8.3 Hz, 2H), 6.30 (d, J = 5.6 Hz, 1H), 6.10 (d, J = 5.6 Hz, 1H), 5.39 (s, 1H), 4.24-3.95 (m, 2H), 2.34-2.26 (m, 2H), 2.11-2.03 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 158.6, 142.8, 133.3, 129.9, 129.6, 128.3, 128.1, 121.7, 100.4, 69.5, 35.9, 24.6; HRMS (ESI) m/z calcd for $C_{15}H_{14}NaO_3$: $[M + Na]^+$ 265.0841, Found: 265.0835.

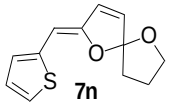
(Z)-2-(naphthalen-2-ylmethylene)-1,6-dioxaspiro[4.4]non-3-ene (7m)



7m

Yellow oil (89 mg, 68 %), IR (film) 2952, 2892, 1650, 1591, 1440, 1346, 1089, 943, 705 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.82 (dd, J = 8.6, 1.6 Hz, 1H), 7.78-7.71 (m, 3H), 7.43-7.34 (m, 2H), 6.36 (d, J = 5.6 Hz, 1H), 6.05 (d, J = 5.6 Hz, 1H), 5.54 (s, 1H), 4.34-3.97 (m, 2H), 2.42-2.21 (m, 2H), 2.16-2.02 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 133.9, 133.8, 132.0, 131.2, 129.9, 127.9, 127.7, 127.6, 127.0, 126.6, 125.9, 125.2, 121.3, 101.5, 69.3, 36.0, 24.7; HRMS (ESI) m/z calcd for $C_{18}H_{16}NaO_2$: $[M + Na]^+$ 287.1048, Found: 287.1043.

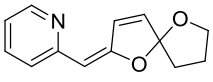
(Z)-2-(thiophen-2-ylmethylene)-1,6-dioxaspiro[4.4]non-3-ene (7n)



7n

Yellow oil (72 mg, 66 %), IR (film) 2945, 1642, 1440, 1356, 1056, 912, 669 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, J = 5.1 Hz, 1H), 7.05 (d, J = 3.4 Hz, 1H), 6.96 (dd, J = 5.1, 3.6 Hz, 1H), 6.35 (d, J = 5.6 Hz, 1H), 6.06 (d, J = 5.6 Hz, 1H), 5.75 (s, 1H), 4.37-3.94 (m, 2H), 2.47-2.18 (m, 2H), 2.16-1.98 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 139.3, 131.4, 128.5, 126.7, 125.0, 124.2, 120.8, 95.3, 69.0, 36.0, 24.4; HRMS (ESI) m/z calcd for $C_{12}H_{12}NaO_2S$: $[M + Na]^+$ 243.0456, Found: 243.0450.

(Z)-2-(1,6-dioxaspiro[4.4]non-3-en-2-ylidenemethyl)pyridine (7o)

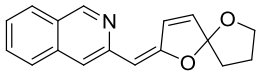


7o

Yellow syrup (47 mg, 44 %), IR (film) 2955, 1648, 1587, 1345, 1257, 1085, 936, 741 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52-8.44 (m, 1H), 7.69 (d, J = 5.7 Hz, 1H), 7.51 (td, J = 7.7, 1.9 Hz, 1H), 7.07-6.92 (m, 2H), 6.26 (dd, J = 5.8, 1.7 Hz, 1H), 5.93 (d, J = 1.2 Hz, 1H), 4.42-3.83 (m, 2H), 2.32-2.17 (m, 2H), 2.12-2.03 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 156.0, 149.2, 136.0, 135.7, 127.6, 122.8, 119.8, 118.1, 101.1, 69.3, 35.5, 24.7 cm^{-1}; HRMS (ESI) m/z

calcd for $C_{13}H_{14}NO_2$: $[M + H]^+$ 216.1025, Found: 216.1019

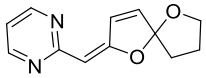
(Z)-2-(1,6-dioxaspiro[4.4]non-3-en-2-ylidenemethyl)quinolone (7p)



7p

Yellow oil (77 mg, 58 %), IR (film) 3048, 2924, 1648, 1593, 1498, 1429, 1345, 1170, 977, 754 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, J = 6.8, 4.8 Hz, 3H), 7.69 (d, J = 8.2 Hz, 1H), 7.63 (t, J = 7.6 Hz, 1H), 7.40 (t, J = 7.4 Hz, 1H), 7.17 (d, J = 8.5 Hz, 1H), 6.36 (d, J = 5.8 Hz, 1H), 6.08 (s, 1H), 4.23-3.97 (m, 2H), 2.36-2.19 (m, 2H), 2.22-2.03 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0, 156.1, 148.3, 136.7, 135.7, 129.3, 128.8, 128.0, 127.4, 126.2, 125.2, 122.3, 118.4, 101.2, 69.5, 35.5, 24.7; HRMS (ESI) m/z calcd for $C_{17}H_{16}NO_2$: $[M + H]^+$ 266.1181, Found: 266.1176.

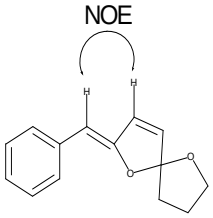
(Z)-2-(1,6-dioxaspiro[4.4]non-3-en-2-ylidenemethyl)pyrimidine (7q)

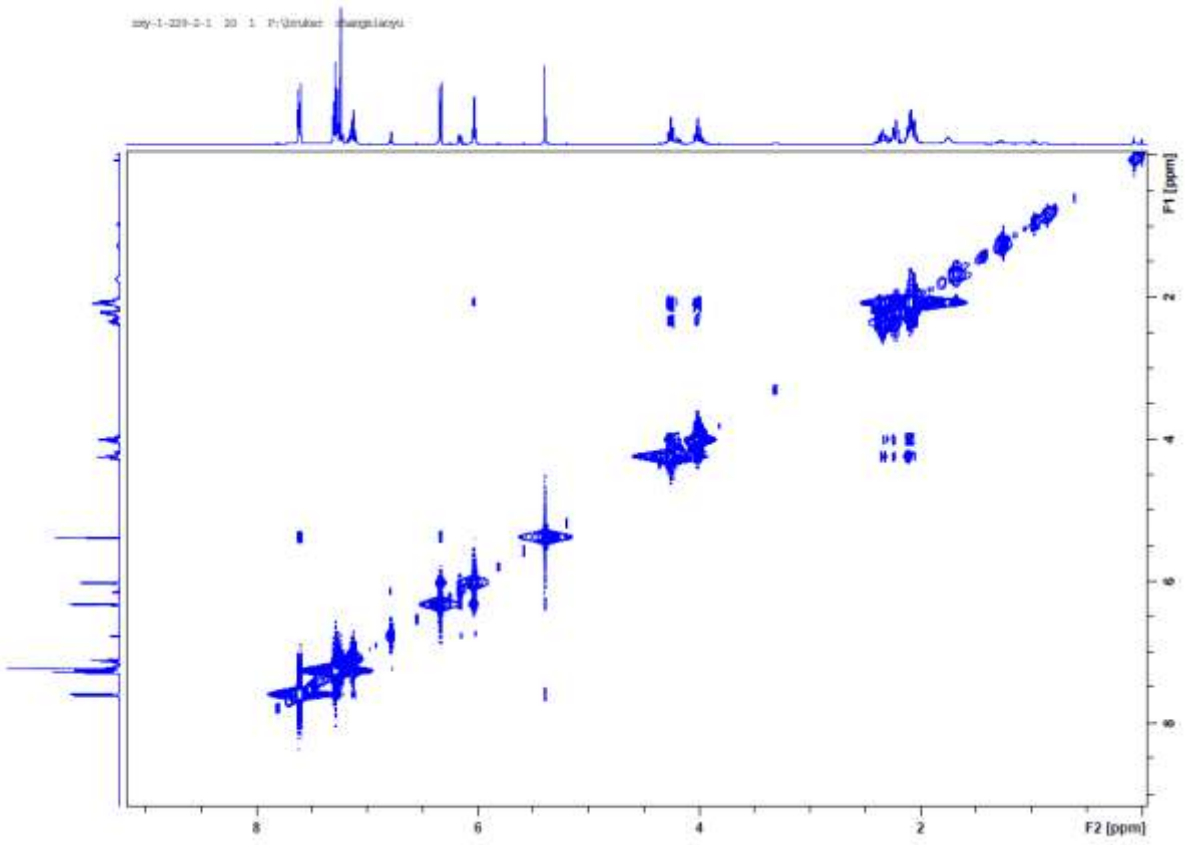


7q

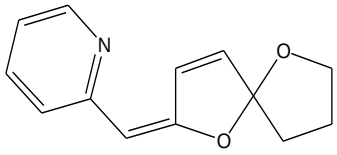
Yellow syrup (64 mg, 58 %), IR (KBr) 3043, 2916, 1648, 1568, 1425, 1124, 985, 767 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J = 4.8 Hz, 2H), 7.81 (d, J = 5.8 Hz, 1H), 6.91 (t, J = 4.9 Hz, 1H), 6.36 (dd, J = 5.8, 1.6 Hz, 1H), 6.07 (s, 1H), 4.28-3.96 (m, 2H), 2.36-2.19 (m, 2H), 2.15-2.07 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 164.7, 156.6, 137.4, 127.6, 118.6, 116.4, 101.5, 69.7, 35.4, 24.7; HRMS (ESI) m/z calcd for $C_{12}H_{13}N_2O_2$: $[M + H]^+$ 217.0977, Found: 217.0972.

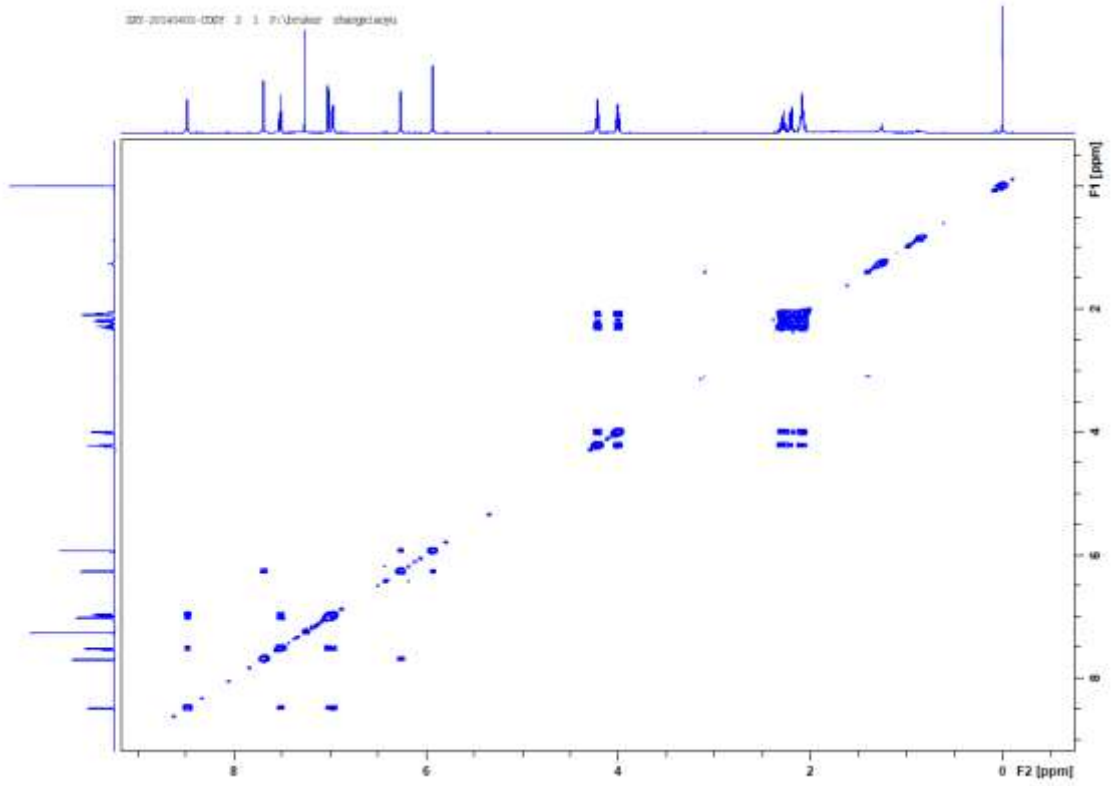
NOESY Of 7a



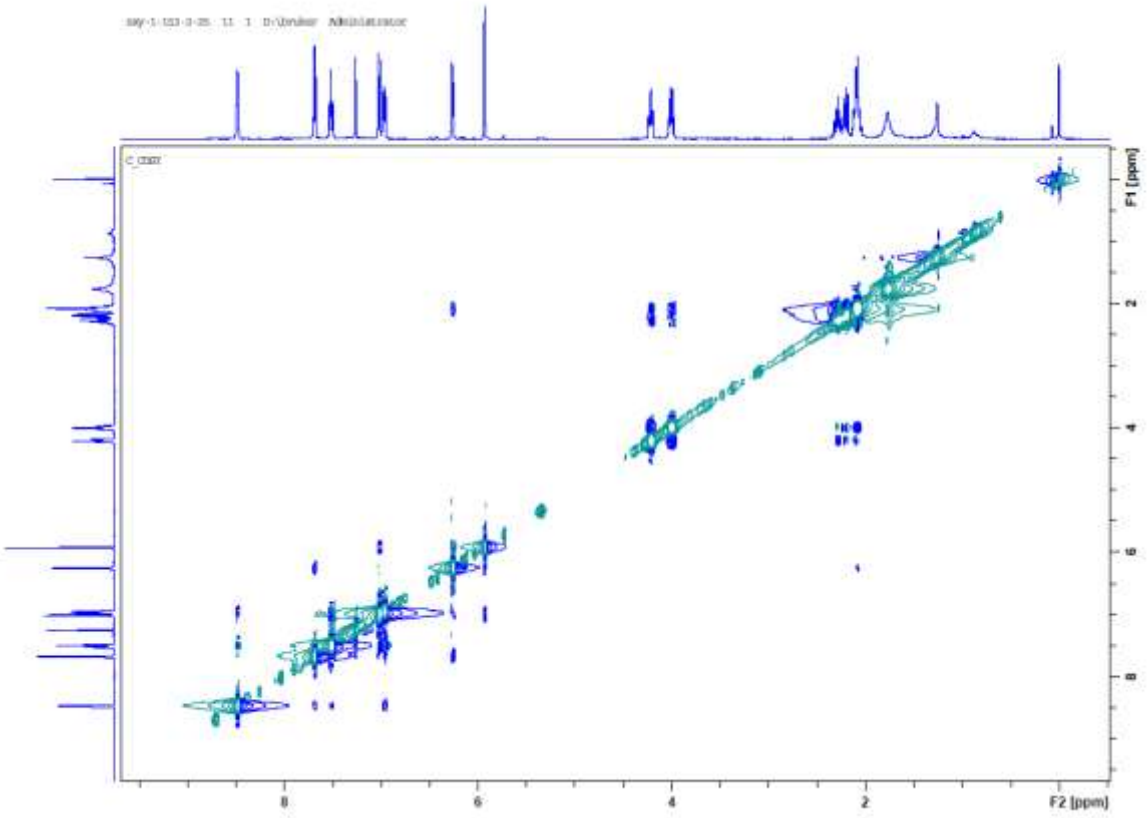


COSY of **7o**

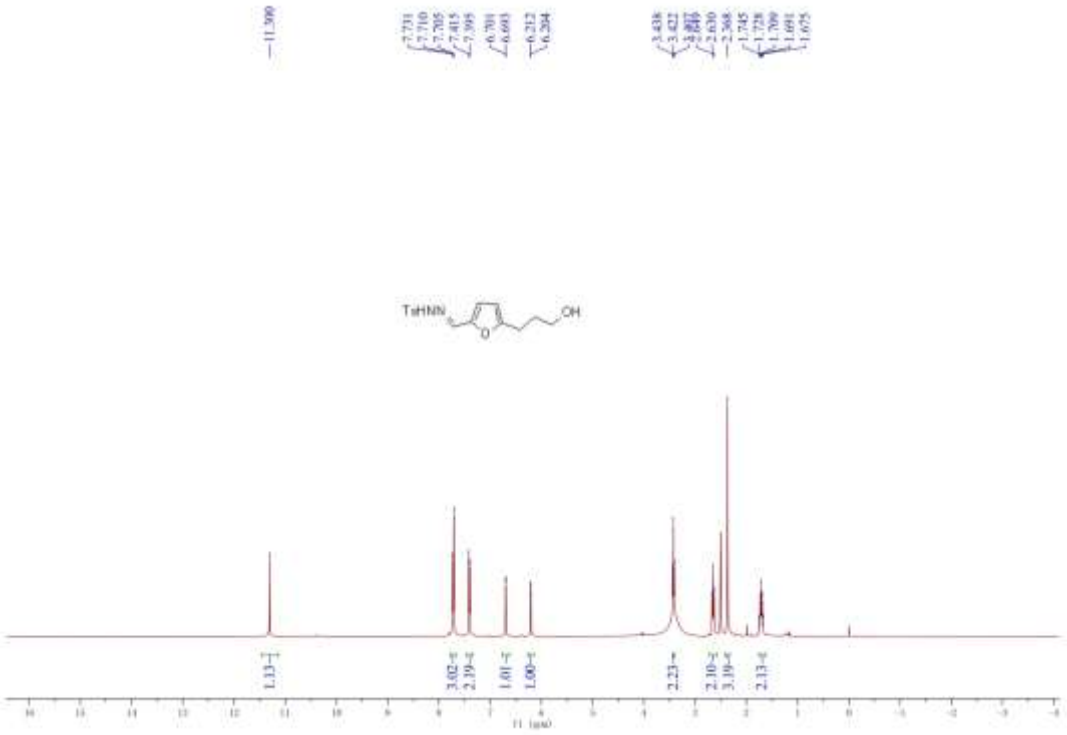




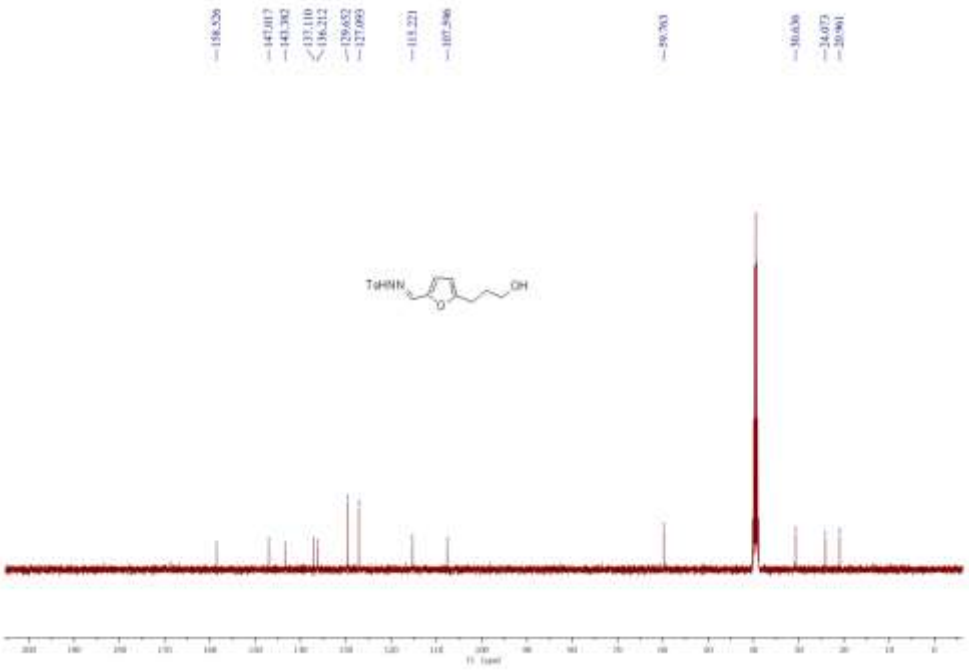
NOESY Of 7o



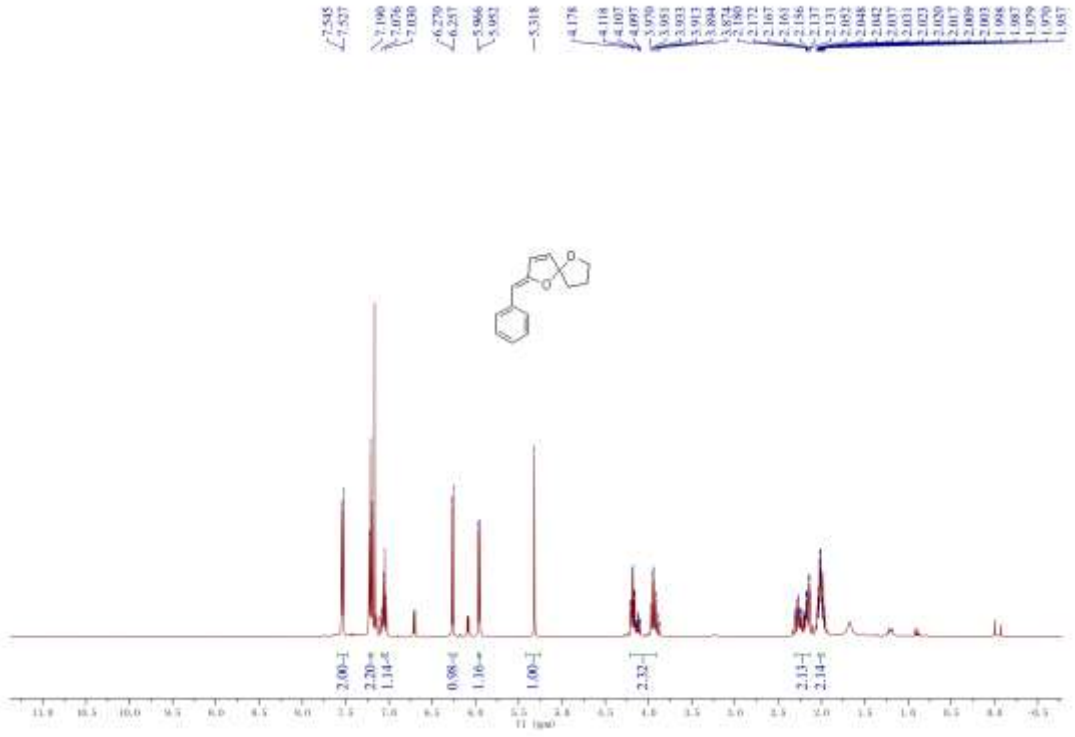
^{1}H NMR of **4a**



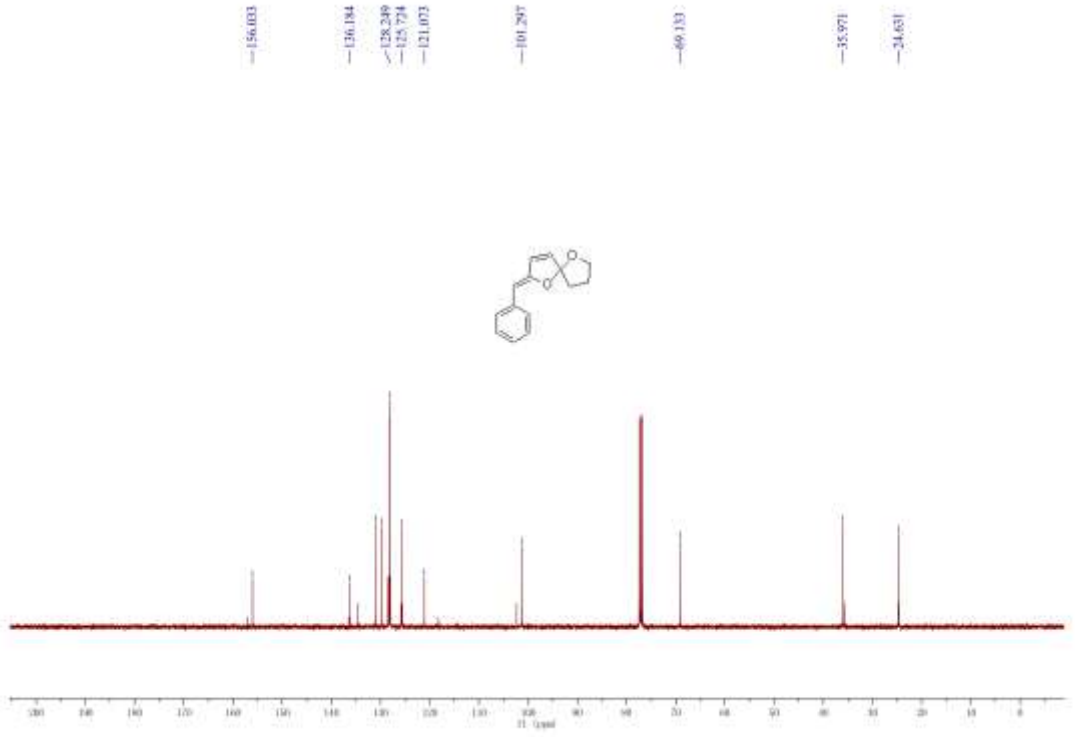
^{13}C NMR of **4a**



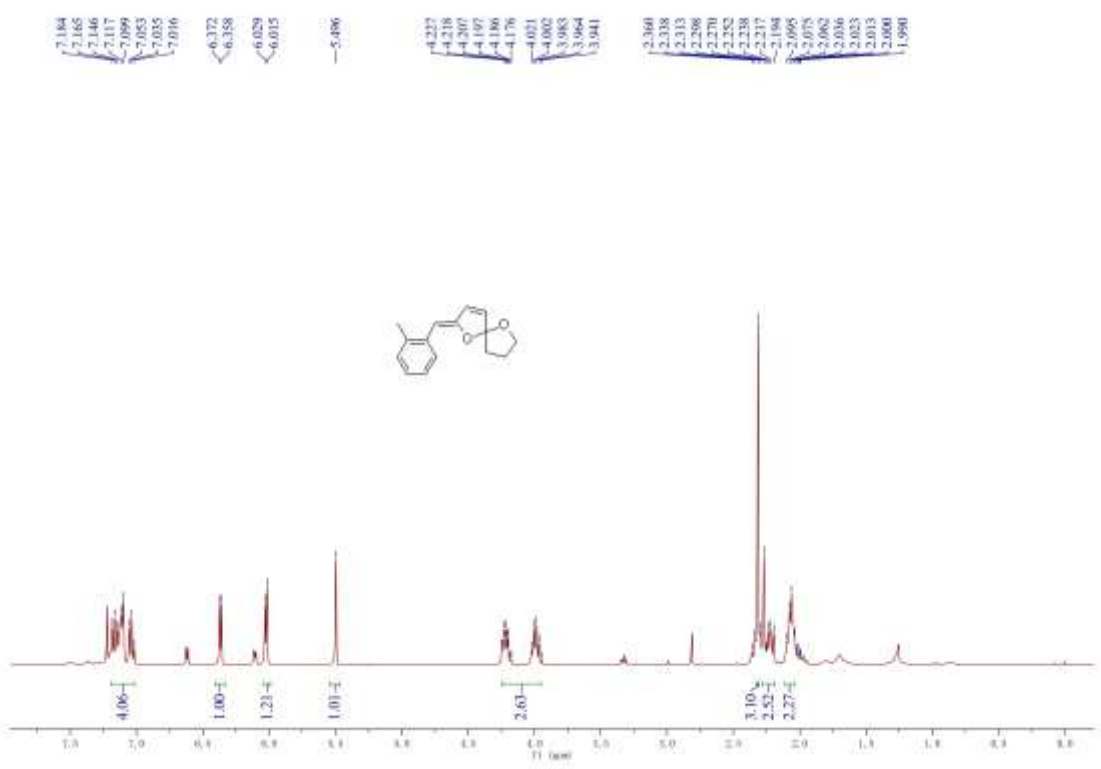
^{1}H NMR of **7a** (Z/E=4:1)



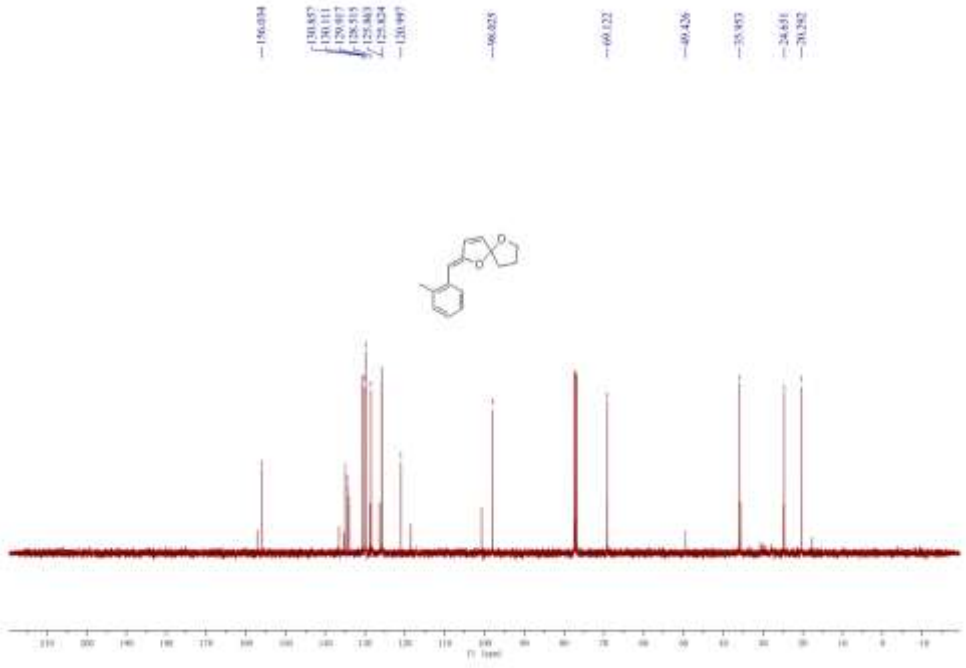
^{13}C NMR of **7a** (Z/E=4:1)



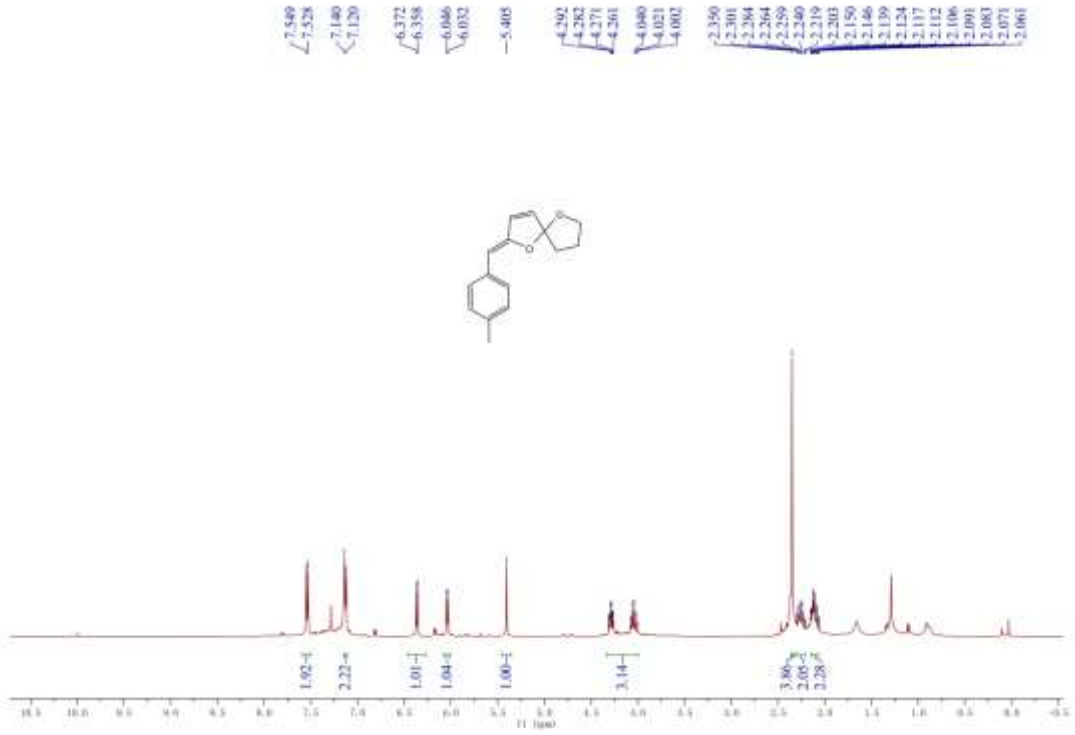
^{1}H NMR of **7b** (Z/E =4.5:1)



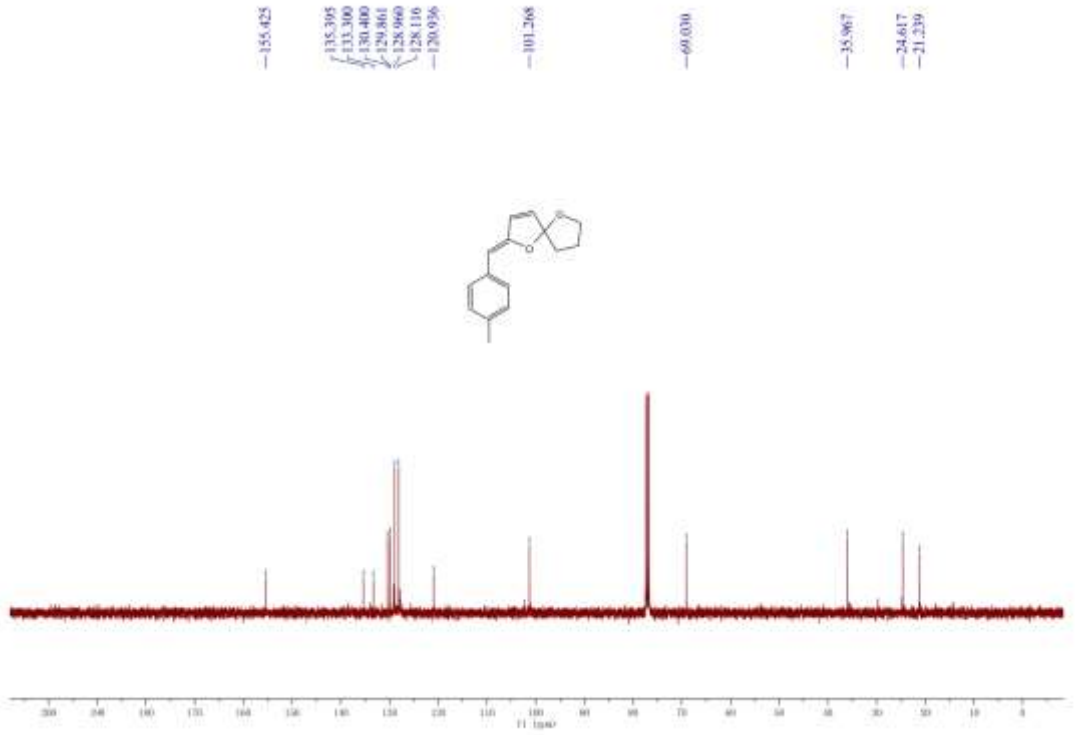
^{13}C NMR of **7b** (Z/E =4.5:1)



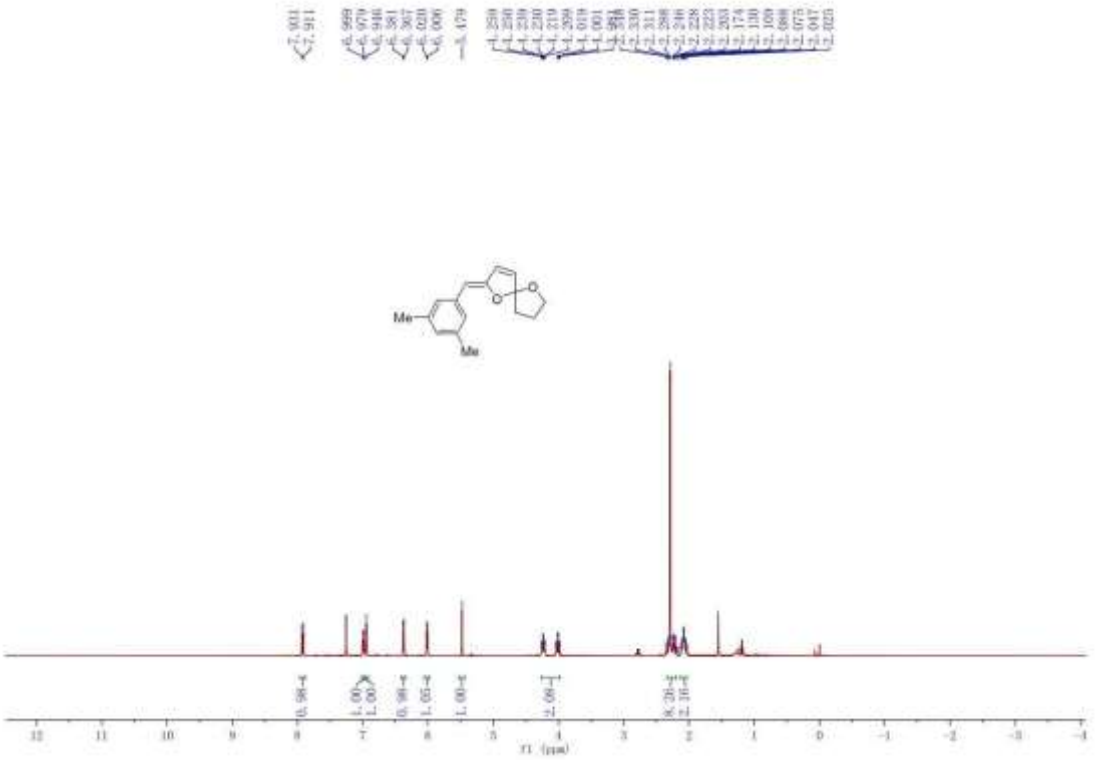
^{1}H NMR of **7c** (Z/E =5:1)



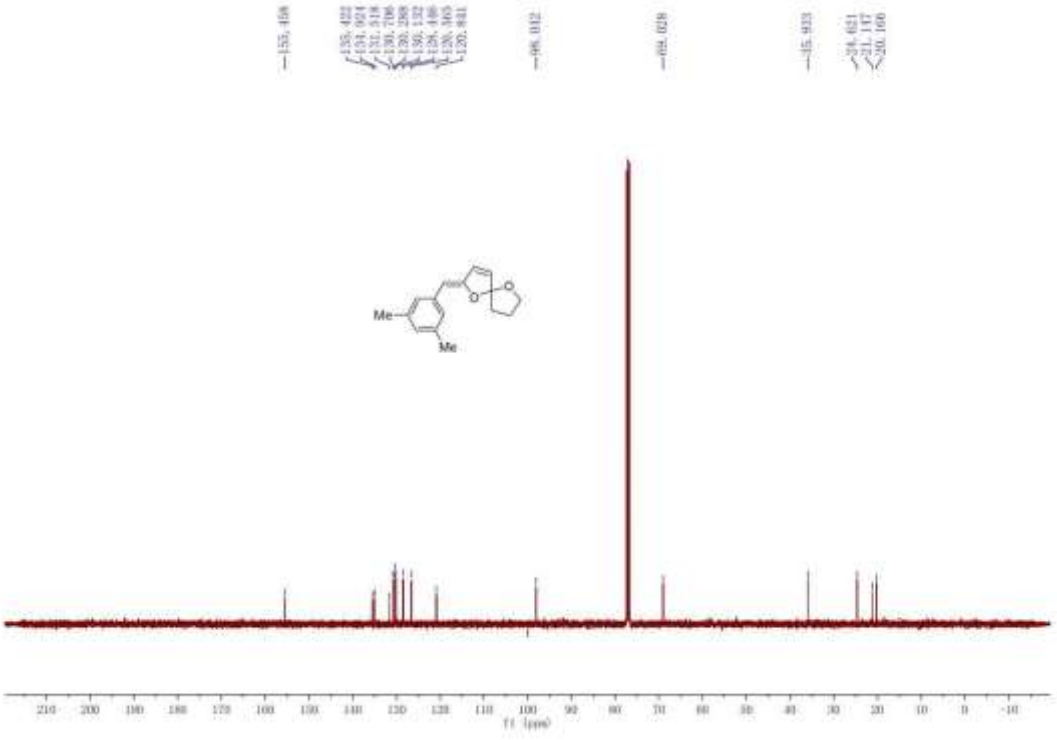
^{13}C NMR of **7c** (Z/E =5:1)



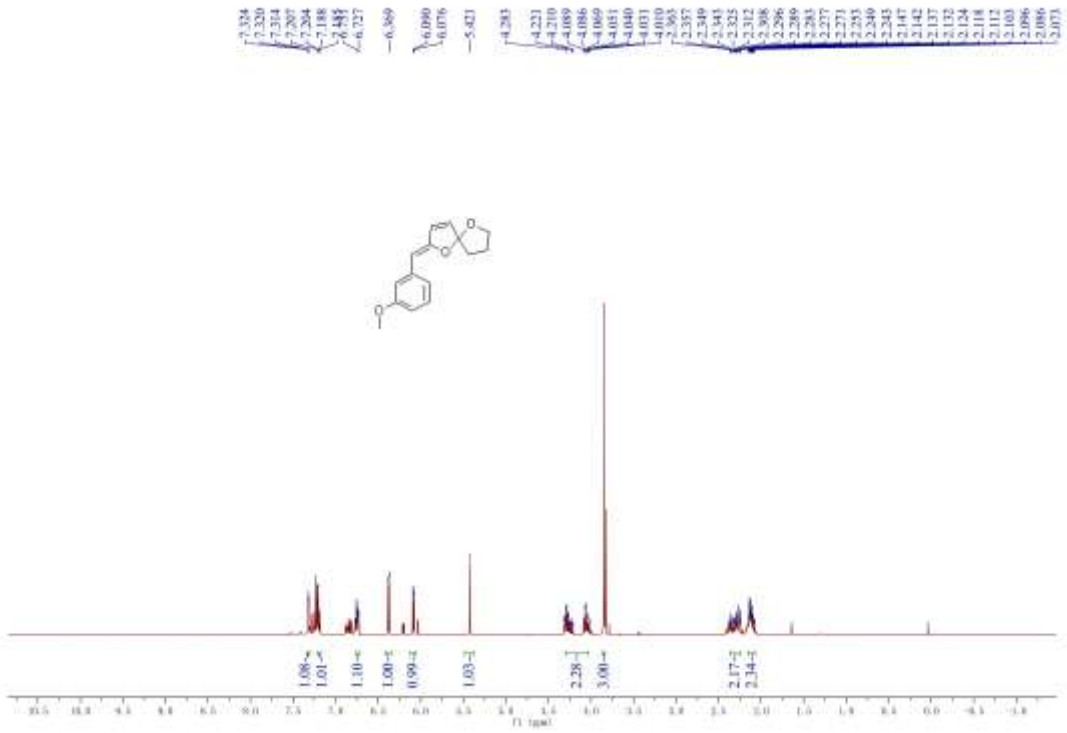
^{1}H NMR of **7d**



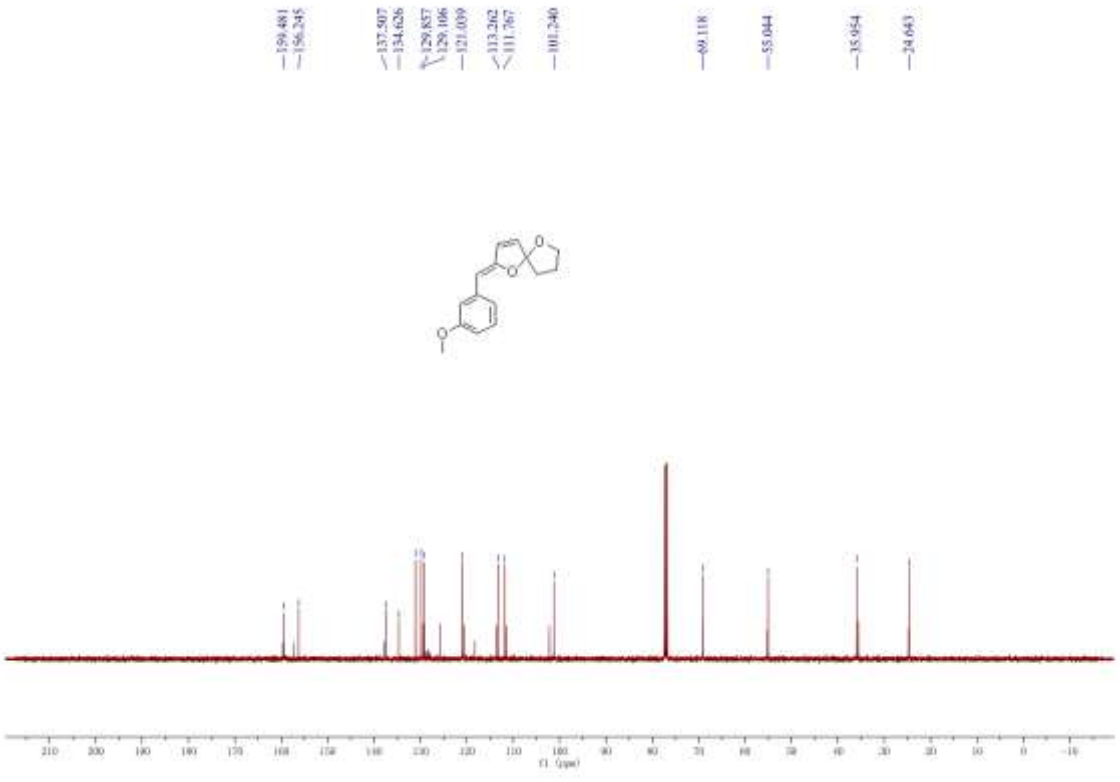
^{13}C NMR of **7d**



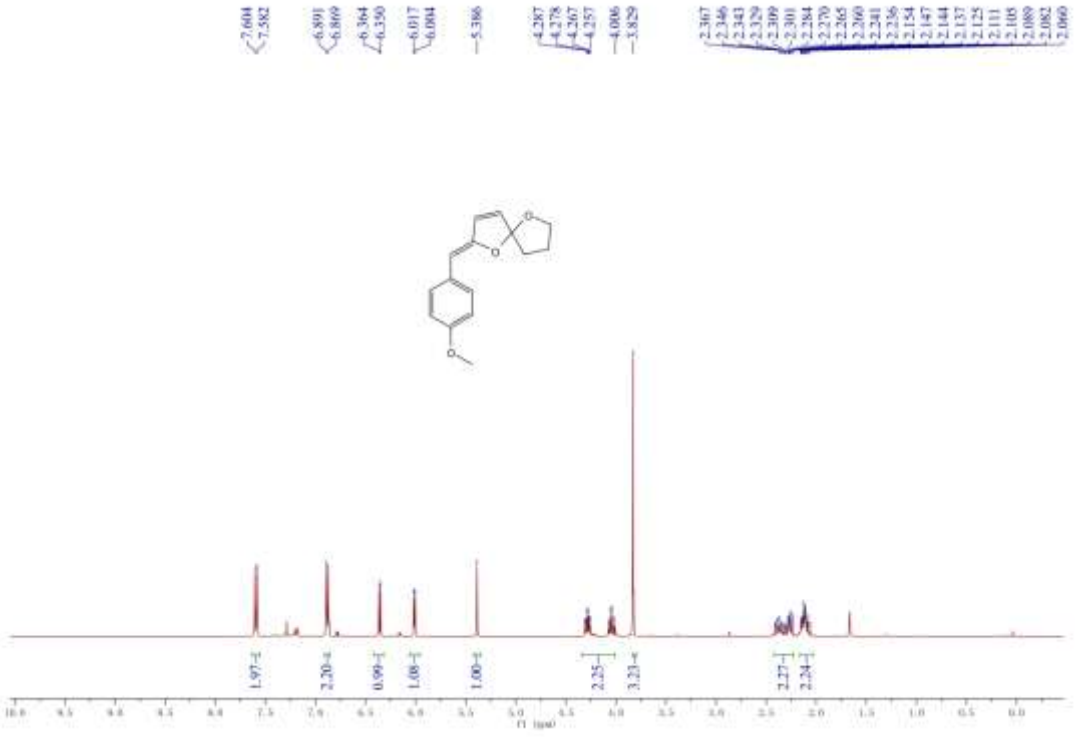
^{1}H NMR of **7e** (Z/E =3.3:1)



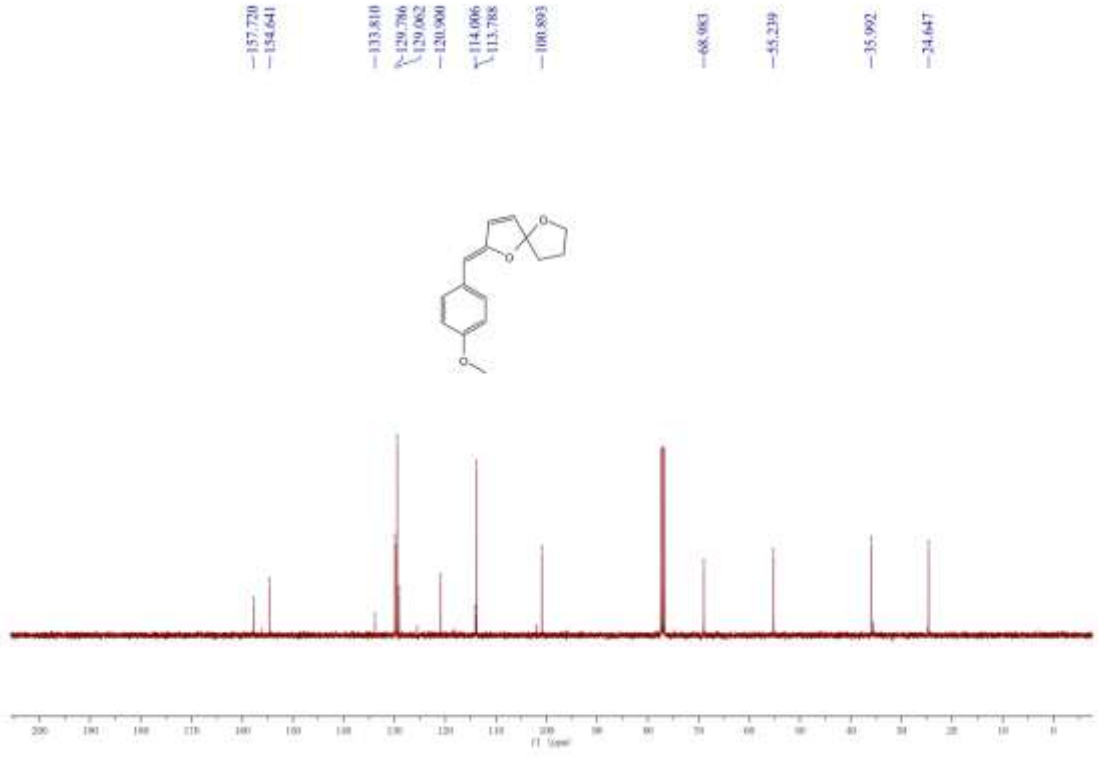
^{13}C NMR of **7e** (Z/E =3.3:1)



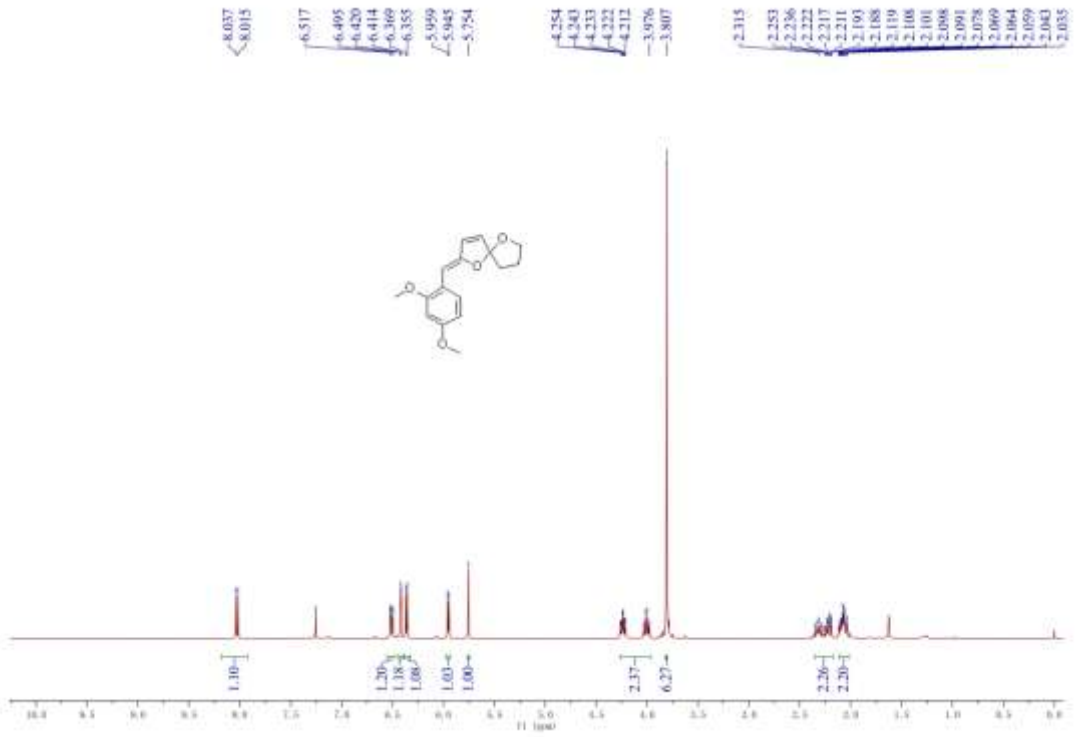
^{1}H NMR of **7f** (Z/E =10:1)



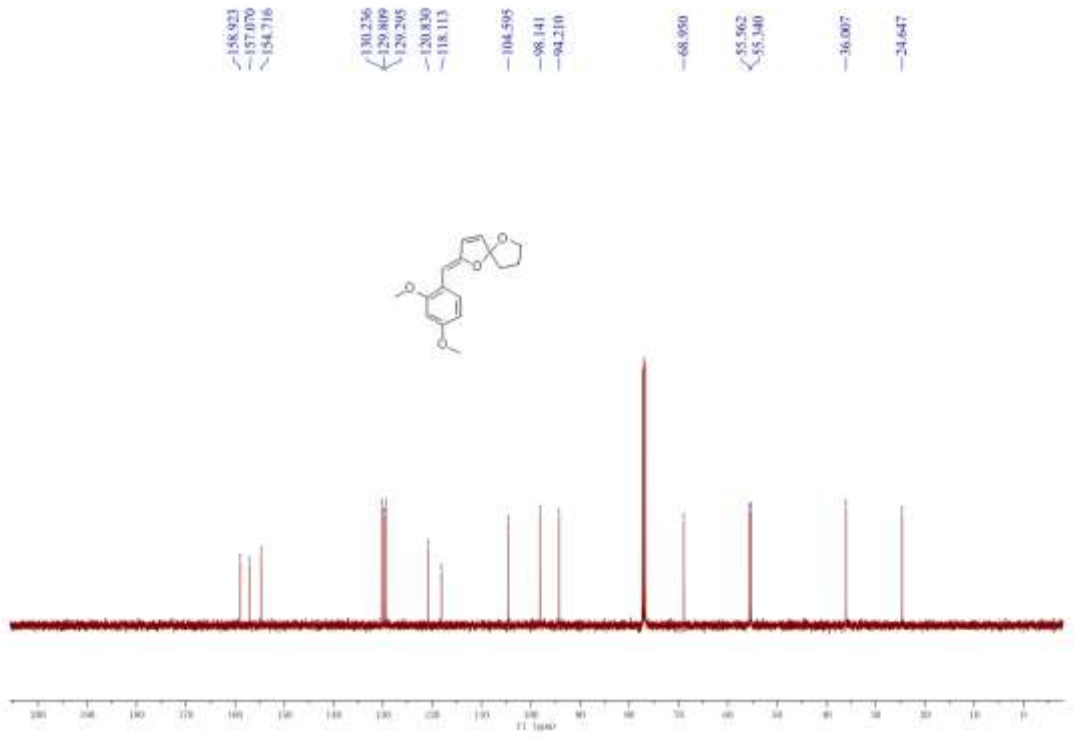
^{13}C NMR of **7f** (Z/E =10:1)



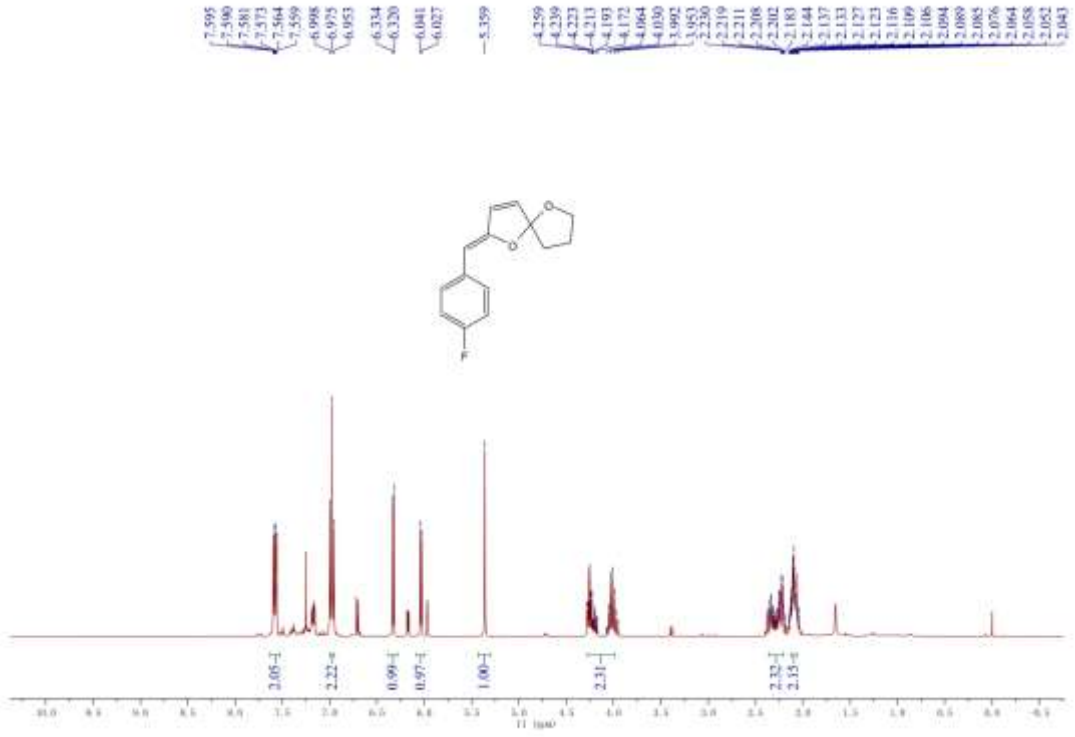
^{1}H NMR of **7g**



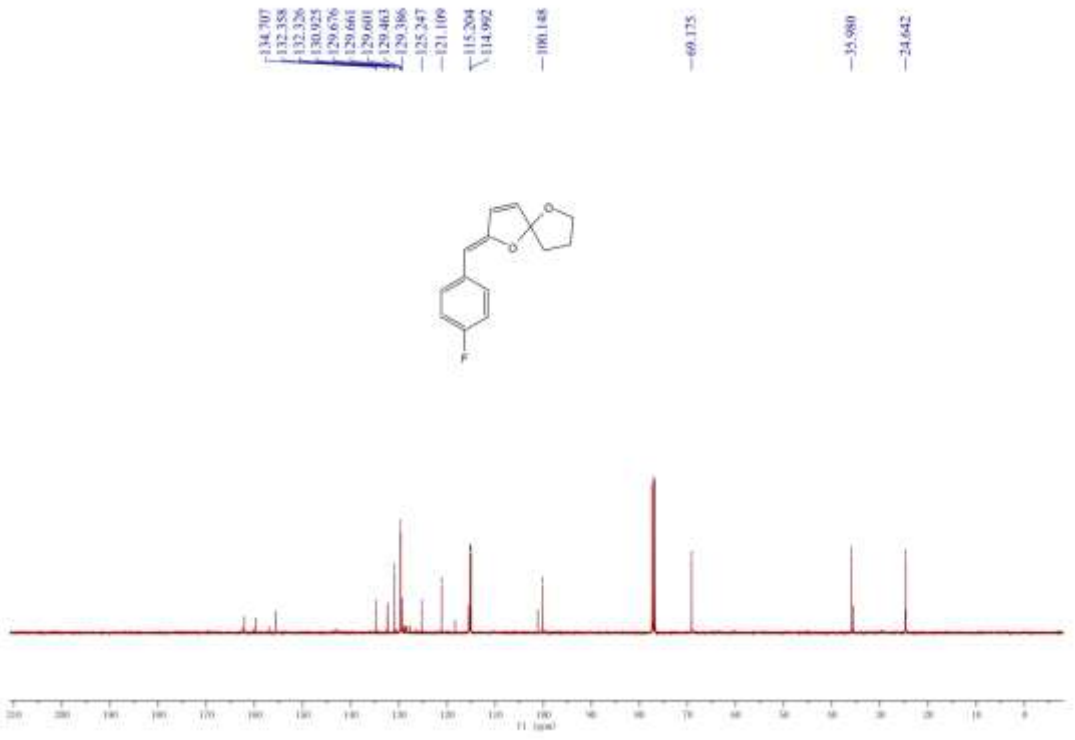
^{13}C NMR of **7g**



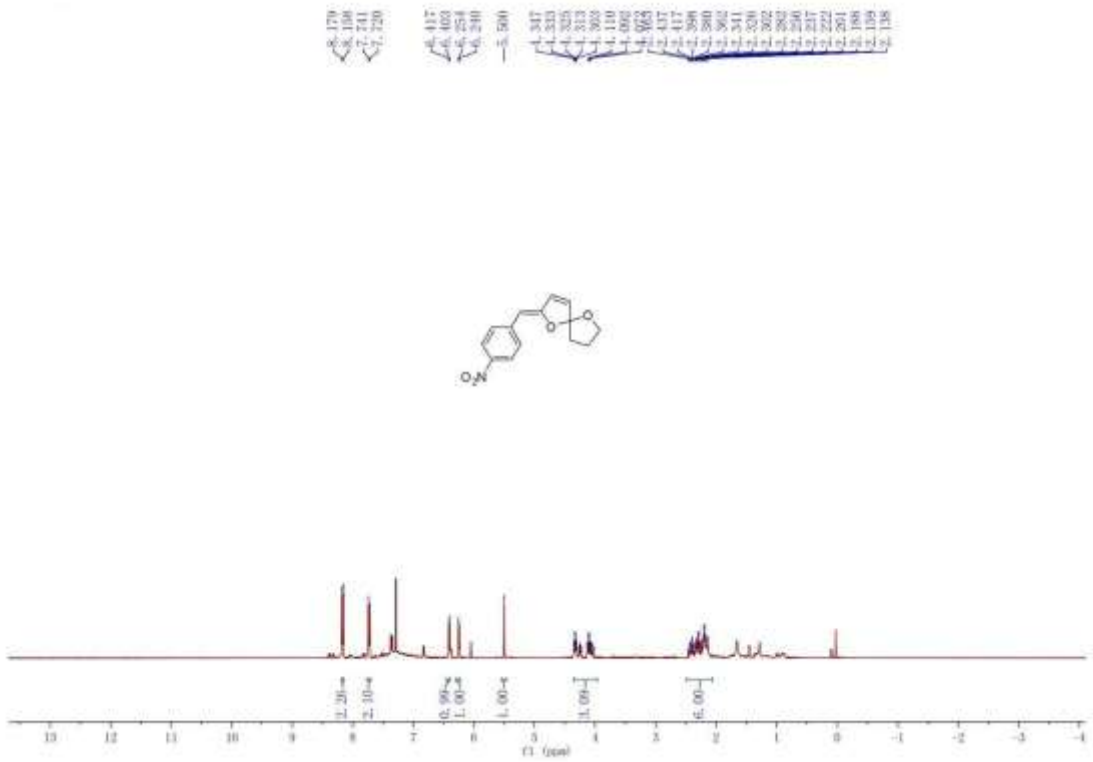
^{1}H NMR of **7h** (Z/E =3:1)



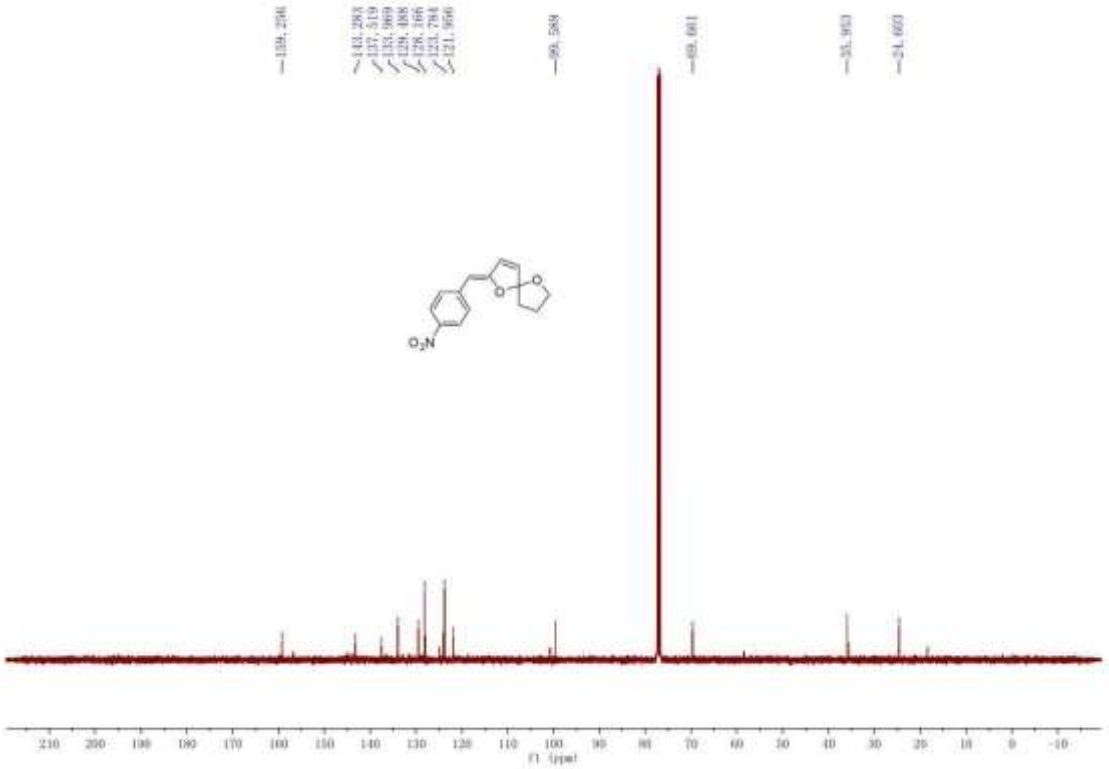
^{13}C NMR of **7h** (Z/E =3:1)



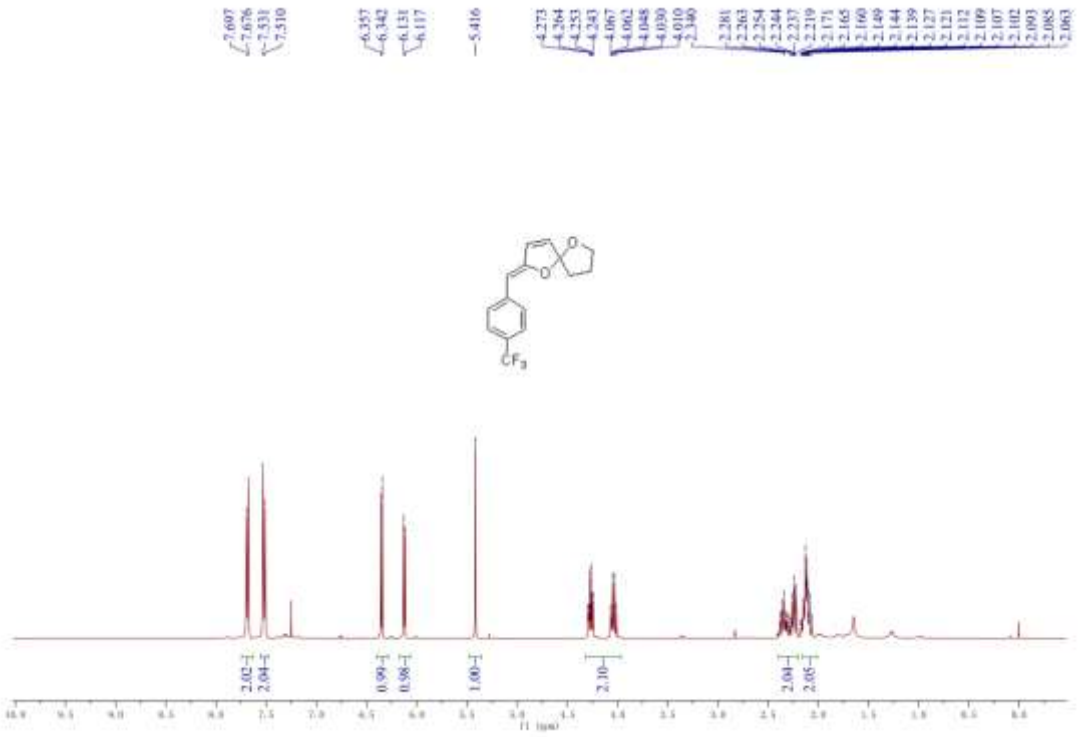
^{1}H NMR of **7i** (Z/E =4/1)



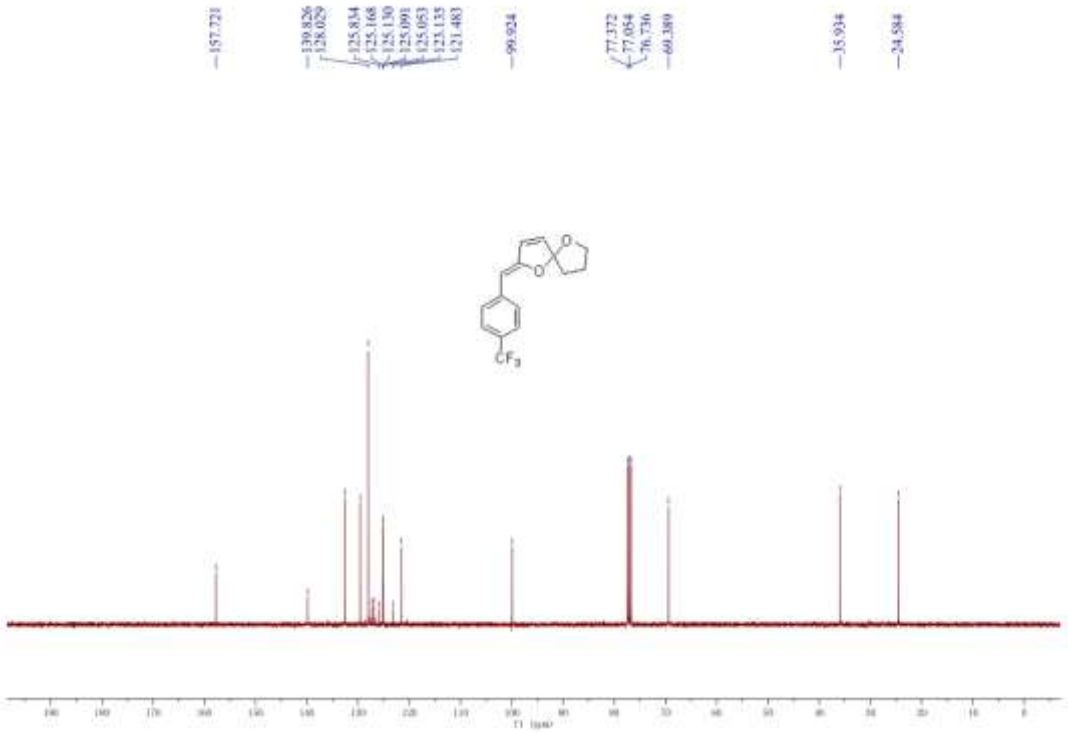
^{13}C NMR of **7i** (Z/E =4/1)



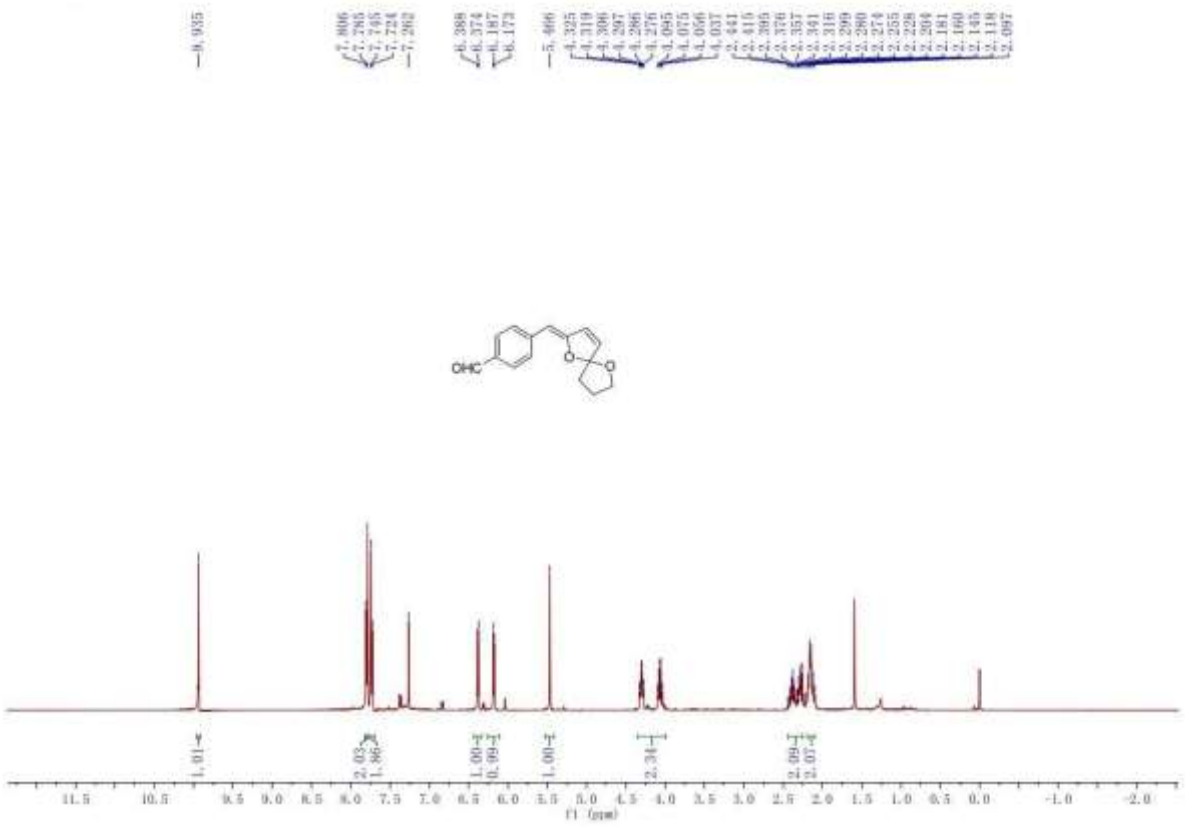
^{1}H NMR of **7j**



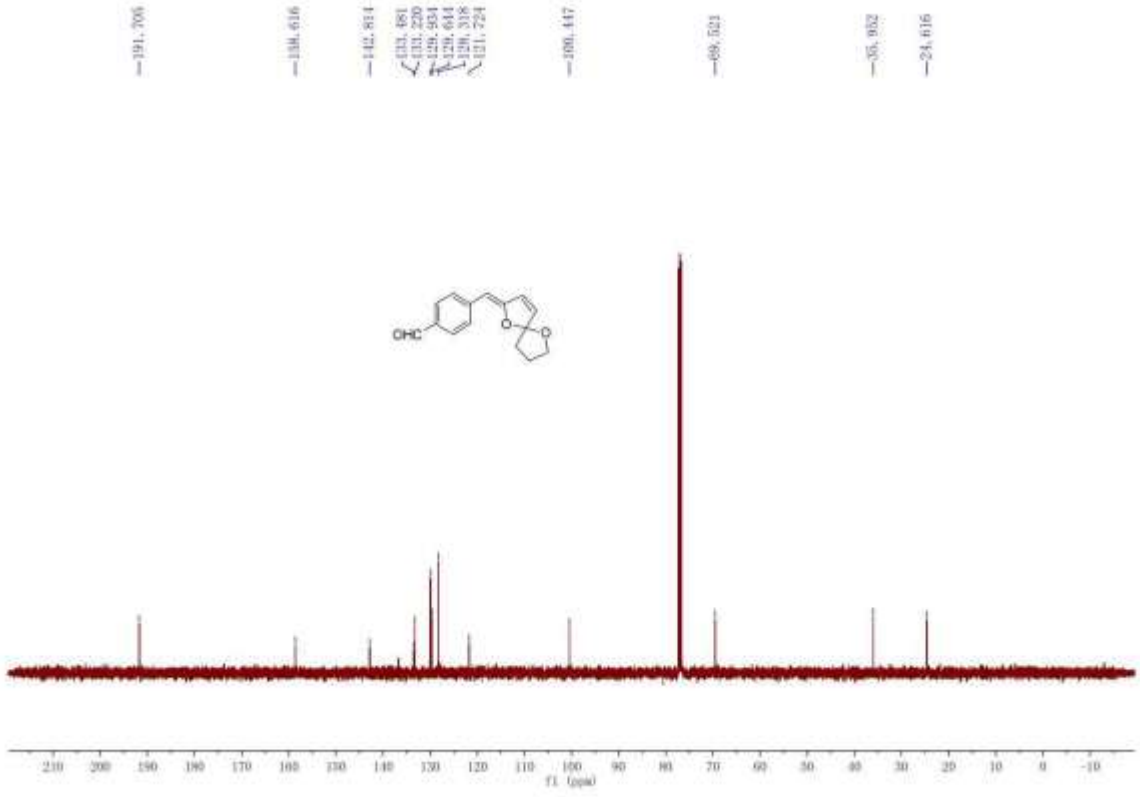
^{13}C NMR of **7j**



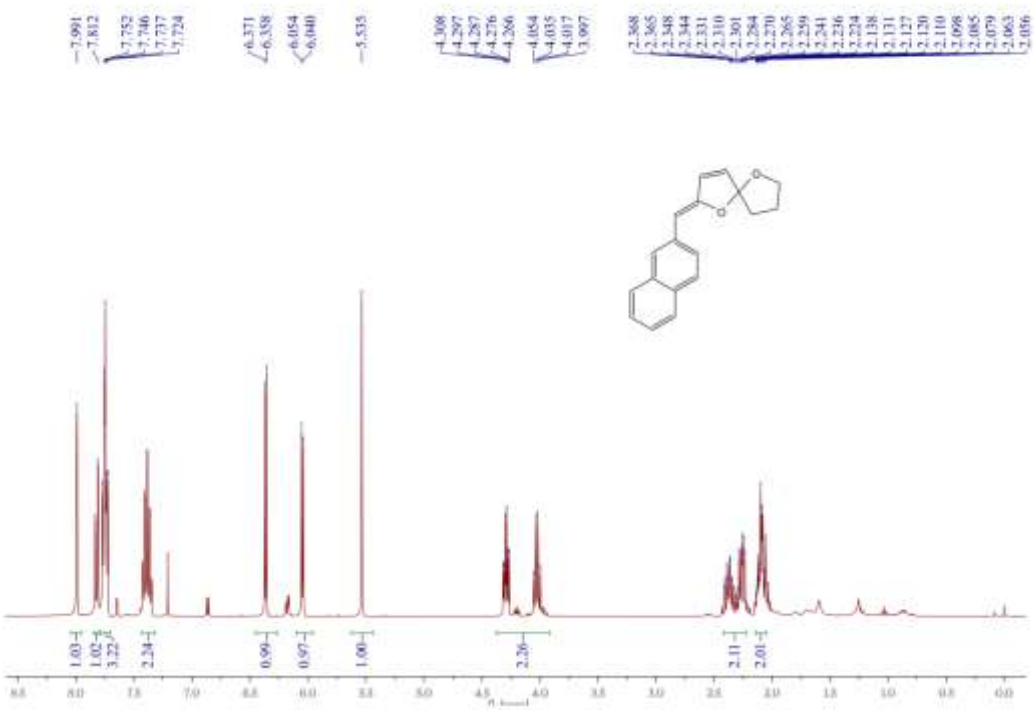
^{1}H NMR of **7k** (Z/E =5:1)



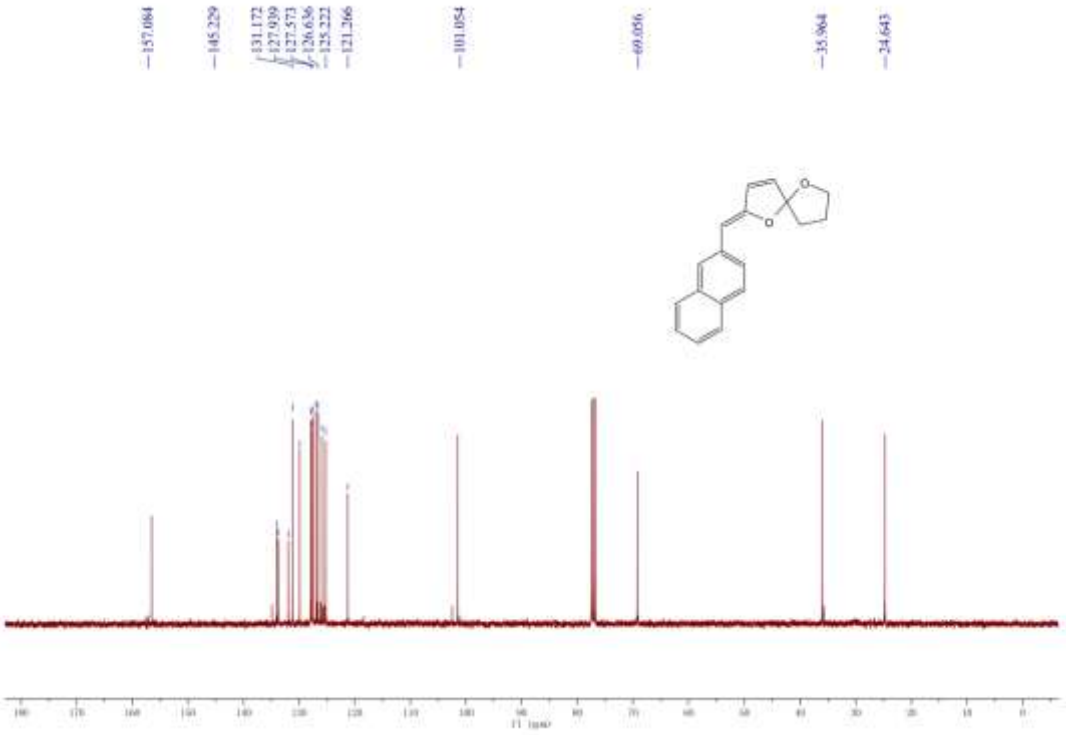
^{13}C NMR of **7k** (Z/E =5:1)



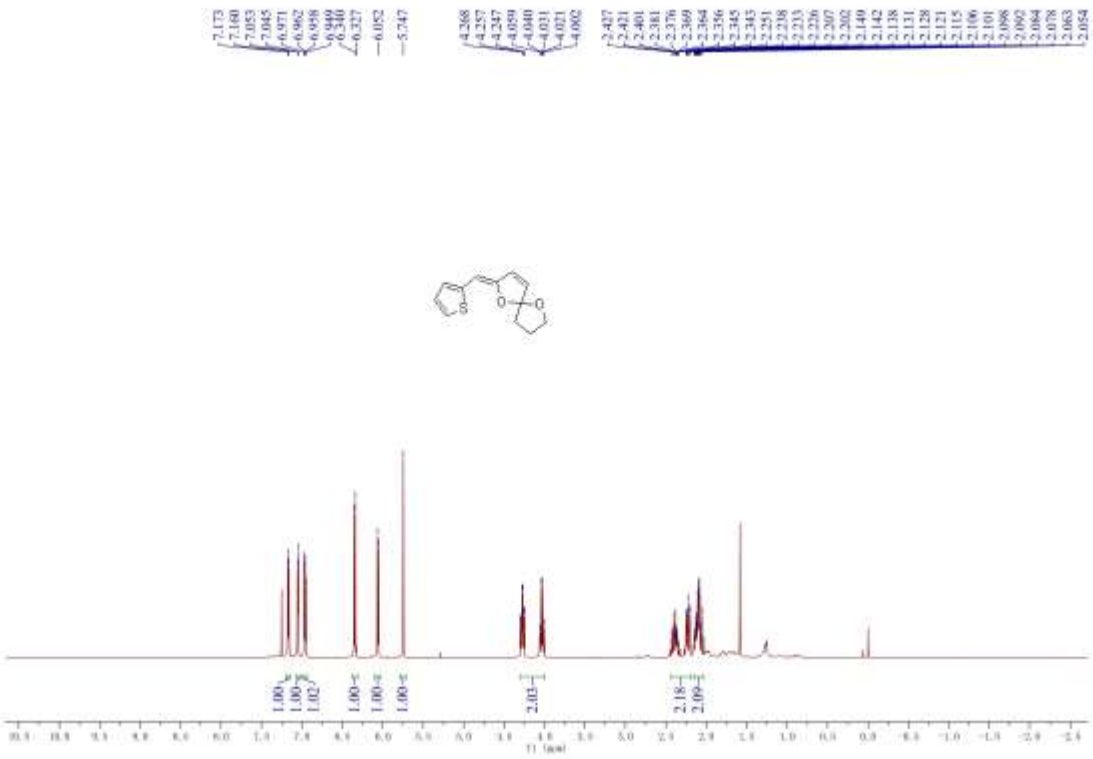
^{1}H NMR of **7m** (Z/E =10:1)



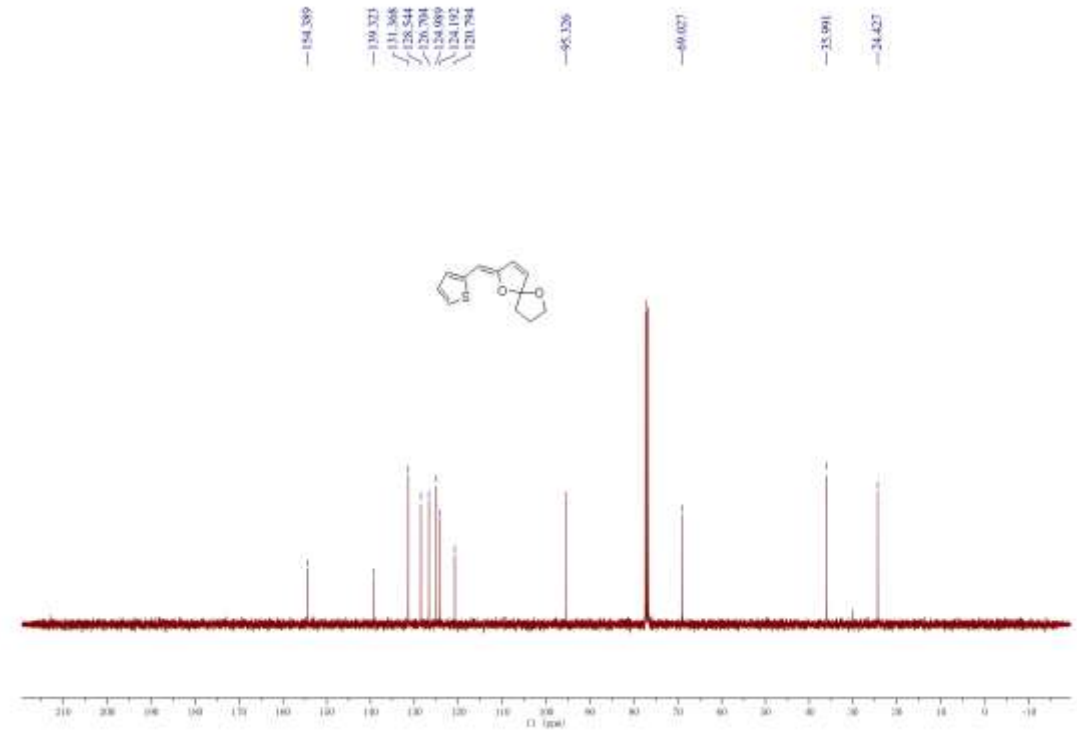
^{13}C NMR of **7m** (Z/E =10:1)



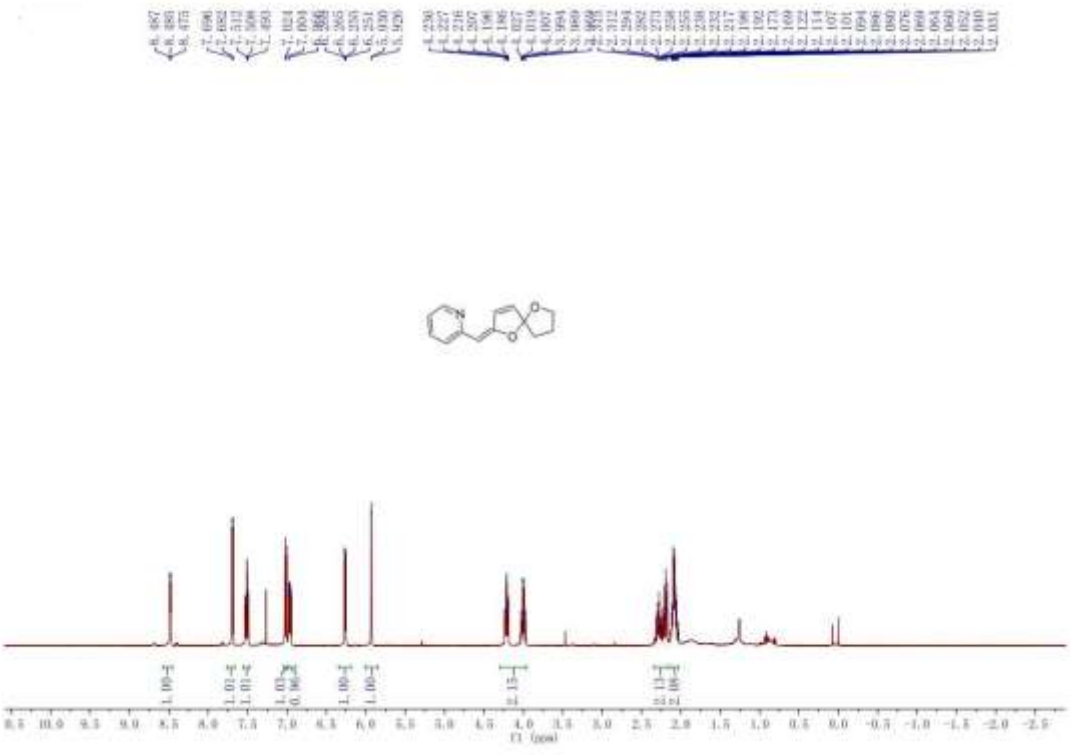
^{1}H NMR of **7n**



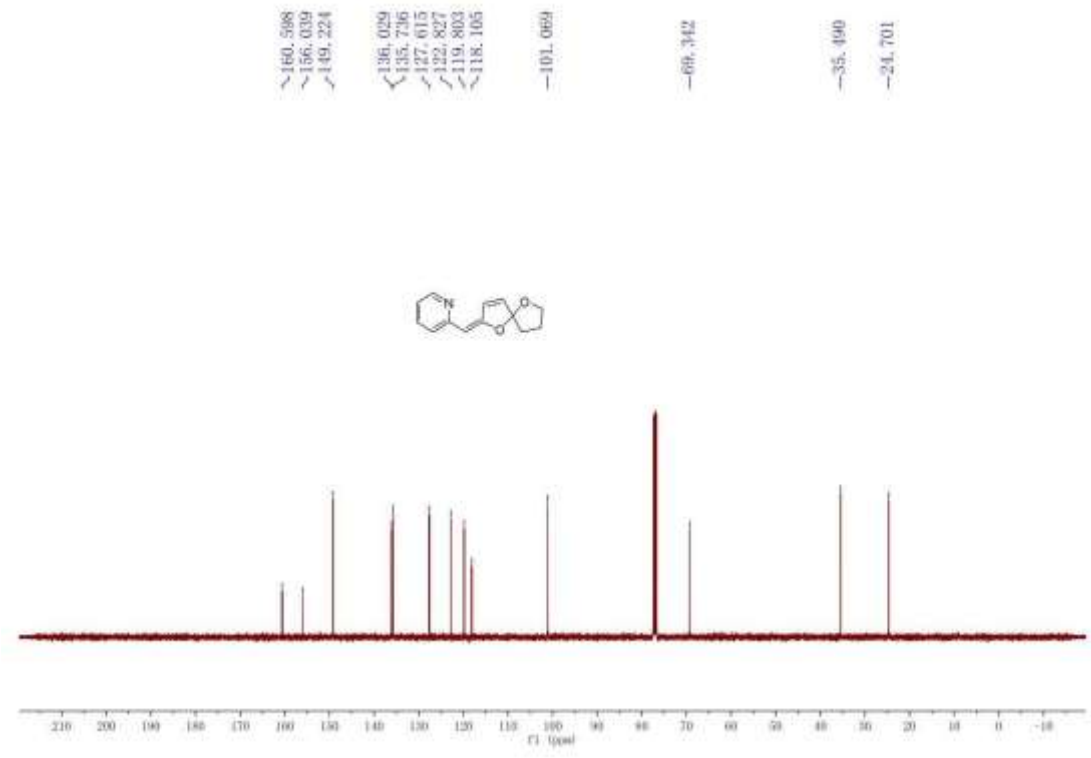
^{13}C NMR of **7n**



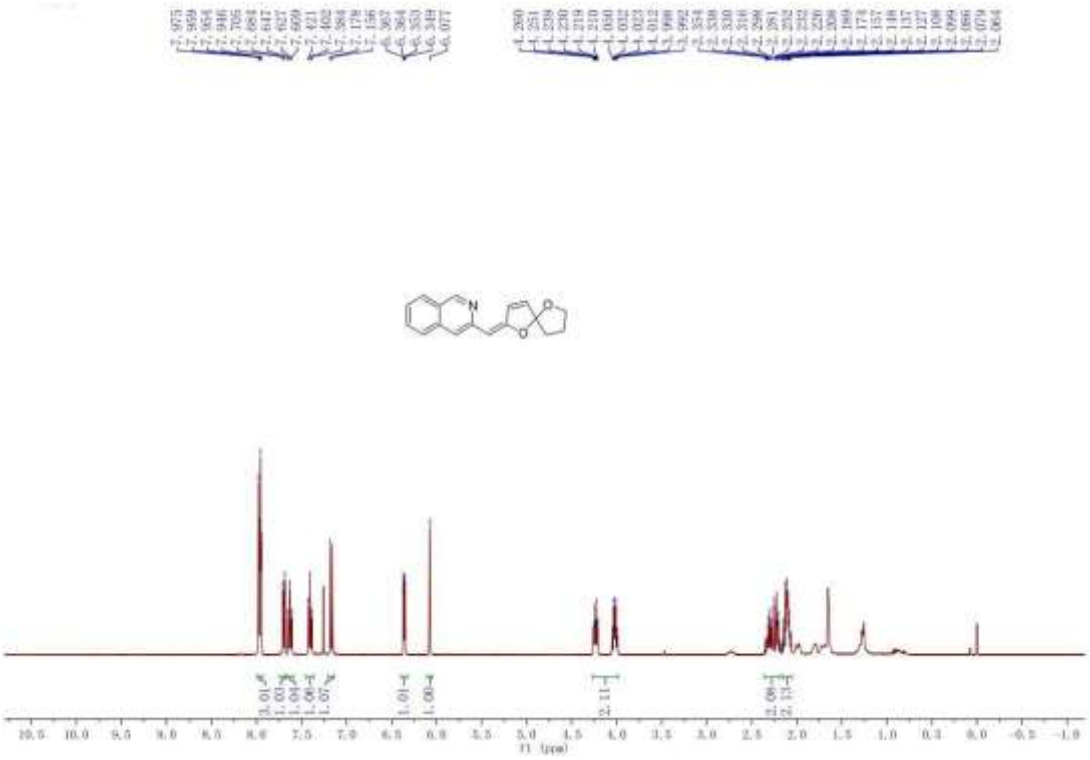
^{1}H NMR of **7o**



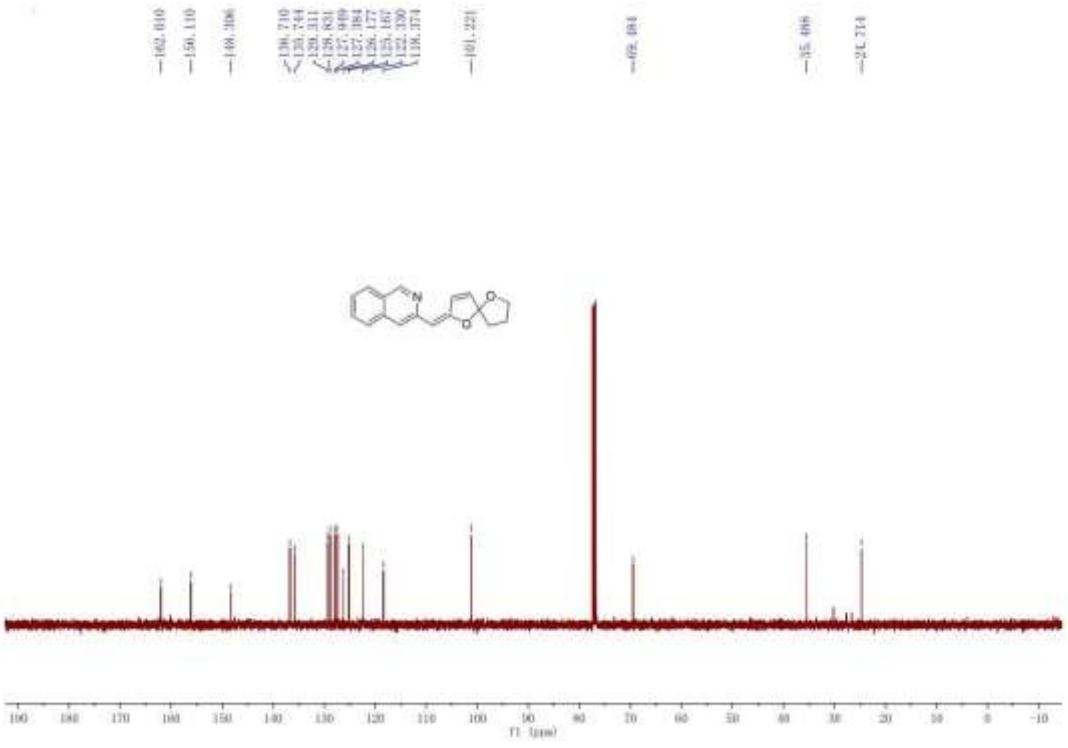
^{13}C NMR of **7o**



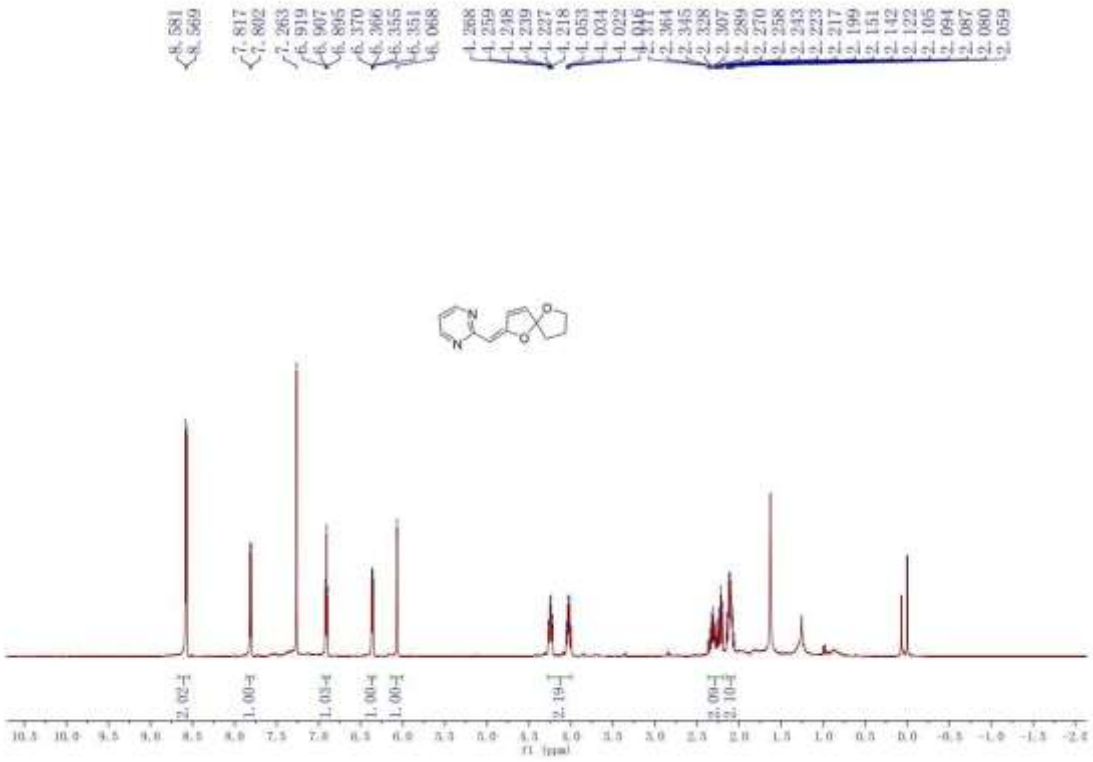
^{1}H NMR of **7p**



^{13}C NMR of **7p**



^{1}H NMR of **7q**



^{13}C NMR of **7q**