Electronic Supplementary Information

Facile synthesis of spiroisoquinolines based on photocycloaddition of isoquinoline-1,3,4-trione with oxazoles

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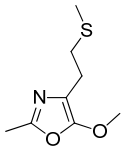
Experimental description

General

All non-aqueous reactions were run under an inert atmosphere (nitrogen or argon) with rigid exclusion of moisture from reagents and glassware using standard techniques for manipulating air-sensitive compounds. All glassware was stored in the oven and/or was flame-dried prior to use under an inert atmosphere of gas. Flash column chromatography was performed using 300-400 mesh silica of the indicated solvent system according to standard technique. Nuclear magnetic resonance spectra were recorded on 300 MHz spectrometers. Chemical shifts for ^{1}HNMR spectra are recorded in parts per million from tetramethylsilane with the solvent resonance as the internal standard (chloroform, 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q=quartet, m = multiplet and br = broad), coupling constant in Hz, integration, and assignment. Mass spectra were recorded on a LCQ FLEET mass spectrometer (ESI). Elemental analyses were performed on a Elementar Vario MICRO analyzer. Reagents: Commercial reagents were used as supplied or purified by standard techniques where necessary. Dichloromethane (DCM) and Chloroform were freshly distillated over calcium hydride prior use. CH_3CN was distillated from P_2O_5 firstly, then distillated from K_2CO_3.

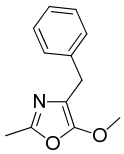
Synthesis of substituted oxazoles.

1a-1d were prepared according to reported method reference 4c. **1e** and **1f** were prepared from L-Methionine methyl ester hydrochloride and L-Phenylalanine methyl ester hydrochloride respectively using similar method.



1e

1e: yellow oil separated by petroleum ether/ ethyl acetate; yield 16%; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 3.71 (s, 3H), 2.42 (m, 4H), 2.13 (s, 3H), 1.92 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 154.8, 151.9, 113.6, 61.0, 32.7, 24.5, 15.1, 14.0; **MS** (ESI) *m/z* 188 $[M+H]^+$; **EA** Calcd for $C_8H_{13}NO_2S$ C, 51.31; H, 7.00; N, 7.48; found: C, 51.30; H, 7.11; N, 7.47.

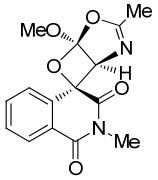


1f

1f: colorless oil separated by petroleum ether/ ethyl acetate; yield 53%; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.33–7.23 (m, 4H), 7.22–7.14 (m, 1H), 3.82 (s, 3H), 3.71 (s, 2H), 2.29 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 154.9, 152.2, 139.5, 128.5 (2C), 128.4(2C), 126.2, 114.7, 61.1, 30.9, 14.24; **MS** (ESI) *m/z* 204 $[M+H]^+$; **EA** Calcd for $C_{12}H_{13}NO_2$ C,70.92; H, 6.45; N, 6.89; found: C, 70.96; H, 6.30; N, 6.87.

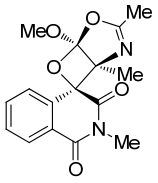
General procedures for preparative photolysis of IQT with 1a-1f.

The light source was a medium-pressure mercury lamp (500 W) in a cooling water jacket which was further surrounded by a layer of filter solution (1 cm thick, saturated aqueous $NaNO_2$) to cut off light of wavelength shorter than 400 nm. The solution of **IQT** (0.02M) and corresponding oxazoles **1a-1f** (0.08M) in anhydrous acetonitrile was purged with dry argon for 10 min and then irradiated under continuous argon purging. The reaction course was monitored by TLC. At the end of the reaction, the solvent was removed under reduced pressure and petroleum ether was added to the residue to precipitate the products. The crude products were further purified by recrystalization with acetone and petroleum ether to give pure spiroisoquinolineoxetane products **2a-2f**.



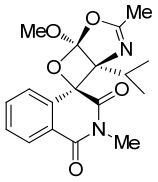
2a

2a, white solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.20(d, *J* = 7.8 Hz, 1H), 7.62(t, *J* = 7.8 Hz, 1H), 7.53(t, *J* = 7.5 Hz, 1H), 7.30(d, *J* = 7.5 Hz, 1H), 5.06(s, 1H), 3.42(s, 3H), 3.11(s, 3H), 2.32(s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.1, 167.7, 167.4, 163.2, 134.0, 133.7, 129.8, 128.5, 125.4, 125.2, 83.9, 80.9, 52.0, 27.8, 14.0; **MS** (ESI) *m/z* 303 $[M+H]^+$; **EA** Calcd for $C_{15}H_{14}N_2O_5$ C, 59.60; H, 4.67; N, 9.27; Found: C, 59.66; H, 4.601; N, 9.19.



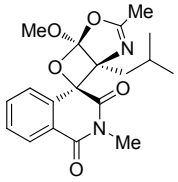
2b

2b, colourless crystal from acetone/petroleum ether; m.p. 164–166˚C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.20–8.17 (m, 1H), 7.82–7.79 (m, 1H), 7.74(dt, *J* = 7.8, 1.5 Hz, 1H), 7.58(dt, *J* = 7.2, 1.2 Hz, 1H), 3.76(s, 3H), 3.31(s, 3H), 2.16(s, 3H), 0.88(s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 169.6, 168.4, 163.6, 135.2, 133.6, 129.6, 128.9, 125.9, 125.2, 124.0, 88.6, 82.2, 52.3, 27.6, 14.8, 14.0; **MS** (ESI) *m/z* 317 $[M+H]^+$; **EA** Calcd for $C_{16}H_{16}N_2O_5$ C, 60.75; H, 5.10; N, 8.86; Found: C, 60.80; H, 5.20; N, 8.78.



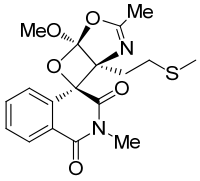
2c

2c, colourless crystal from acetone/petroleum ether; m.p. 178–180˚C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.16(dd, *J* = 7.8, 0.9 Hz, 1H), 7.84(dd, *J*=7.5, 0.9 Hz, 1H), 7.74(dt, *J* = 7.8, 1.5 Hz, 1H), 7.58(dt, *J* = 7.8, 1.5 Hz, 1H), 3.79(s, 3H), 3.33(s, 3H), 2.20(s, 3H), 1.88–1.79(m, 1H), 0.73(d, *J* = 6.6 Hz, 3H), 0.40(d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 170.0, 168.6, 163.8, 136.0, 134.9, 134.4, 133.4, 129.7, 128.4, 127.0, 126.2, 88.5, 52.0, 27.7, 25.9, 17.3, 15.2, 14.8; **MS** (ESI) *m/z* 345 $[M+H]^+$; **EA** Calcd for $C_{18}H_{20}N_2O_5$ C, 62.78; H, 5.85; N, 8.13; Found: C, 62.80; H, 5.81; N, 8.08.



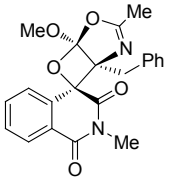
2d

2d, colourless crystal from acetone/petroleum ether; m.p. 148–150˚C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.17–8.14(m, 1H), 7.78–7.75(m, 1H), 7.71(dt, *J* = 7.2, 1.2 Hz, 1H), 7.55(dt, *J* = 7.8, 1.5 Hz, 1H), 3.77(s, 3H), 3.30(s, 3H), 2.16(s, 3H), 1.49–1.39(m, 1H), 1.11–0.95(m, 2H), 0.63(d, *J* = 6.6 Hz, 3H), 0.55(d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 169.7, 167.7, 163.7, 135.1, 133.4, 129.5, 128.6, 126.2, 125.5, 88.9, 84.8, 76.6, 52.1, 35.8, 27.6, 23.7, 23.6, 22.5, 14.8; **MS** (ESI) *m/z* 359 $[M+H]^+$; **EA** Calcd for $C_{19}H_{22}N_2O_5$ C, 63.67; H, 6.19; N, 7.82; Found: C, 63.68; H, 6.20; N, 7.85; **IR** (KBr pallet) 2872.1, 1736.6, 1690.5, 1678.1, 1664.3, 1658.8, 1600.6, 1423.2, 1225.2, 765.9 cm^{-1}.



2e

2e, colourless crystal from acetone/ petroleum ether; m.p. 132–134˚C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.18(dd, *J* = 7.8, 0.6 Hz, 1H), 7.80(dd, *J* = 7.8, 1.2 Hz, 1H), 7.75(dt, *J* = 7.2, 1.2 Hz, 1H), 7.59(dt, *J* = 7.5, 1.5 Hz, 1H), 3.78(s, 3H), 3.31(s, 3H), 2.33–2.23(m, 1H), 2.17(s, 3H), 2.09–1.99(m, 1H), 1.78(s, 3H), 1.6–1.4(m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 169.5, 169.1, 163.5, 134.7, 133.7, 129.9, 129.0, 126.2, 125.4, 123.7, 88.5, 84.0, 52.3, 27.8, 27.7, 15.2, 14.9; **MS** (ESI) *m/z* 377 $[M+H]^+$; **EA** Calcd for $C_{18}H_{20}N_2O_5S$ C, 57.43; H, 5.36; N, 7.44; Found: C, 57.48; H, 5.31; N, 7.48.

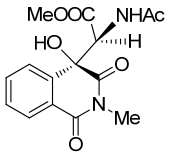


2f

2f, colourless crystal from acetone/ petroleum ether; m.p. 190–192˚C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.91(dd, *J* = 7.2, 5.1 Hz, 2H), 7.74(dt, *J* = 7.5, 1.2 Hz, 1H), 7.51(dt, *J* = 7.5, 1.2 Hz, 1H), 7.11–7.00(m, 3H), 6.87(d, *J* = 7.2 Hz, 2H), 3.82(s, 3H), 3.25(s, 3H), 2.76(d, *J* = 14.7 Hz, 1H), 2.54(d, *J* = 15 Hz, 1H), 2.12(s, 3H); **^{13}C NMR** (75 MHz, CDCl3) δ 169.7, 168.1, 163.1, 134.8, 133.3, 129.5, 129.2, 128.5, 128.0, 126.6, 126.0, 125.8, 124.0, 87.8, 84.4, 52.4, 33.9, 27.6, 14.8; **MS** (ESI) *m/z* 393 $[M+H]^+$; **EA** Calcd for $C_{22}H_{20}N_2O_5$ C, 67.34; H, 5.14; N, 7.14; Found: C, 67.41; H, 5.17; N, 7.18.

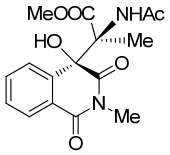
Hydrolysis of 2a-2f using concentrated HCl

To a solution of the spirooxetane (**2a-2f**) in DCM (0.1M) was added corresponding amount of concentrated HCl. The mixture was stirred at room temperature and monitored by TLC. Upon complete conversion, the reaction mixture was poured into water and neutralized to pH=8 with $NaHCO_3$. The mixture was extracted with DCM. The organic layer was dried over $MgSO_4$. The solvent was removed under vacum, and the crude product were separated by flash column chromatography on 300-400 mesh silica gel (petroleum ether/ethyl acetate) to give the final products.



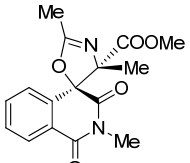
3a

3a, white powder; m.p. 180–182˚C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.17(d, *J* = 8.1 Hz, 1H), 7.66(dd, *J* = 5.1, 1.2 Hz, 2H), 7.57–7.51(m, 1H), 6.27(d, *J* = 9.0 Hz, 1H), 5.04(d, *J* = 8.1 Hz, 1H), 4.57(s, 1H), 3.51(s, 3H), 3.36(s, 3H), 2.00(s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 173.9, 170.0, 168.0, 163.7, 136.0, 133.5, 129.4, 128.6, 125.5, 125.0, 76.1, 61.3, 52.7, 27.8, 22.8; **MS** (ESI) *m/z* 321 $[M+H]^+$; **EA** Calcd for $C_{15}H_{16}N_2O_6$ C, 56.25; H, 5.04; N, 8.75; Found: C, 56.18; H, 5.11; N, 8.78.



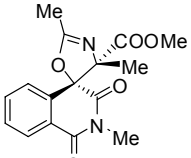
3b

3b, colourless crystal from acetone/ petroleum ether; m.p. 164–166˚C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.13(d, *J* = 7.8 Hz, 1H), 7.68–7.59(m, 2H), 7.54(dt, *J* = 6.9, 1.5 Hz, 1H), 6.54(s, 1H), 5.30(s, 1H), 3.65(s, 3H), 3.34(s, 3H), 1.94(s, 3H), 1.51(s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 173.0, 171.1, 170.0, 164.2, 135.7, 133.0, 129.4, 128.1, 126.7, 126.2, 77.9, 66.8, 53.1, 27.9, 23.6, 18.2; **MS** (ESI) *m/z* 335 $[M+H]^+$; **EA** Calcd for $C_{16}H_{18}N_2O_6$ C, 57.48; H, 5.43; N, 8.38; Found: C, 57.51; H, 5.34; N, 8.38.



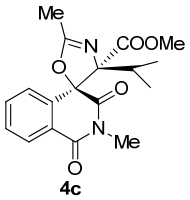
4b

4b, colourless crystal from acetone/ petroleum ether; m.p. 142–144˚C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.16(dd, *J* = 7.2, 1.5 Hz, 1H), 7.57(dt, *J*=7.2, 1.5 Hz, 1H), 7.51(dt, *J* = 7.5, 1.5 Hz, 1H), 7.30(dd, *J* = 7.5, 1.2 Hz, 1H), 3.39(s, 3H), 3.07(s, 3H), 2.33(s, 3H), 1.49(s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 169.9, 169.3, 165.8, 163.6, 134.7, 133.3, 129.6, 128.5, 125.8, 124.8, 88.2, 85.3, 52.2, 27.3, 22.3, 14.1; **MS** (ESI) *m/z* 317 $[M+H]^+$; **EA** Calcd for $C_{16}H_{16}N_2O_5$ C, 60.75; H, 5.10; N, 8.86; Found: C, 60.69; H, 5.14; N, 8.78.



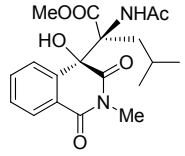
4bi

4bi, colourless crystal from acetone/ petroleum ether; m.p. 135–137˚C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.24(dd, *J* = 7.8, 1.2 Hz, 1H), 7.68(dt, *J* = 7.5, 1.2 Hz, 1H), 7.58(dt, *J* = 7.5, 1.2 Hz, 1H), 7.43(dd, *J* = 7.5, 1.5 Hz, 1H), 3.70(s, 3H), 3.30(s, 3H), 2.31(s, 3H), 1.02(s,3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.1, 170.4, 165.5, 163.5, 133.9, 133.0, 129.7, 129.2, 126.1, 125.7, 87.8, 84.4, 53.2, 27.6, 24.5, 14.1; **MS** (ESI) *m/z* 317 $[M+H]^+$; **EA** Calcd for $C_{16}H_{16}N_2O_5$ C, 60.75; H, 5.10; N, 8.86; Found: C, 60.71; H, 5.08; N, 8.84.



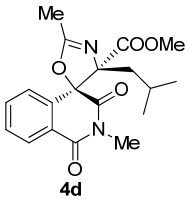
4c

4c, colourless crystal from acetone/petroleum ether; m.p. 139–142˚C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.13(dd, *J* = 7.8, 1.2 Hz, 1H), 7.61–7.48(m, 2H), 7.15(dd, *J* = 7.8, 0.9 Hz, 1H), 3.42(s, 3H), 3.14(s, 3H), 2.44(s, 3H), 2.16–2.07(m, 1H), 1.04(d, *J* = 6.6 Hz, 3H), 0.91(d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 169.3, 164.9, 164.0, 135.0, 133.2, 129.5, 127.9, 126.4, 124.4, 93.1, 89.0, 51.6, 35.1, 27.9, 20.3, 17.5, 13.8; **MS** (ESI) *m/z* 345 $[M+H]^+$; **EA** Calcd for $C_{18}H_{20}N_2O_5$ C, 62.78; H, 5.85; N, 8.13; Found: C, 62.72; H, 5.79; N, 8.18.



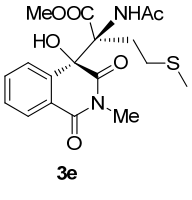
3d

3d, colourless crystal from acetone/petroleum ether; m.p. 128–130˚C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.08(d, *J* = 7.5 Hz, 1H), 7.70–7.61(m, 2H), 7.50(dt, *J* = 7.8, 1.8 Hz, 1H), 6.49(s, 1H), 5.47(s, 1H), 3.72(s, 3H), 3.33(s, 3H), 2.87(dd, *J* = 14.4, 4.2 Hz, 1H), 1.92(s, 3H), 1.90–1.82(m, 1H), 1.39–1.31(m, 1H), 0.84(d, *J* = 6.6 Hz, 3H), 0.65(d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 173.4, 171.6, 170.2, 164.6, 136.0, 132.7, 129.2, 127.9, 127.2, 126.1, 80.2, 72.7, 53.4, 35.7, 27.8, 25.1, 24.2, 23.8, 21.7; **MS** (ESI) *m/z* 377 $[M+H]^+$; **EA** Calcd for $C_{19}H_{24}N_2O_6$ C, 60.63; H, 6.43; N, 7.44; Found: C, 60.69; H, 6.50; N, 7.48; **IR** (KBr pallet) 3326.6, 2871.4, 1743.3, 1724.0, 1674.6, 1639.2, 1605.9, 1523.2, 1420.8, 1236.1, 1208.3, 1163.4, 761.8 cm^{-1}.



4d

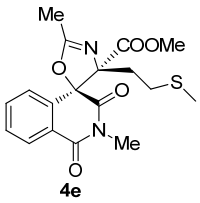
4d, colourless crystal from acetone/petroleum ether; m.p. 148–150˚C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.14(dd, *J* = 7.5, 1.2 Hz, 1H), 7.58(dt, *J* = 7.5, 1.2 Hz, 1H), 7.50(dt, *J* = 7.5, 0.9 Hz, 1H), 7.23(d, *J* = 8.1 Hz, 1H), 3.39(s, 3H), 3.04(s, 3H), 2.34(s, 3H), 1.79–1.58(m, 3H), 0.95(d, *J* = 6.3 Hz, 3H), 0.76(d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 169.8, 167.8, 163.8, 135.2, 133.5, 129.6, 128.7, 126.3, 125.6, 124.1, 88.9, 84.8, 52.2, 35.8, 27.7, 23.8, 23.7, 22.5, 14.9; **MS** (ESI) *m/z* 359 $[M+H]^+$; **EA** Calcd for $C_{19}H_{22}N_2O_5$ C, 63.67; H, 6.19; N, 7.82; Found: C, 63.69; H, 6.14; N, 7.78; **IR** (KBr pallet) 2871.1, 1754.1, 1726.6; 1678.1, 1600.8, 1428.7, 1238.7, 1147.5, 765.3 cm^{-1}.



3e

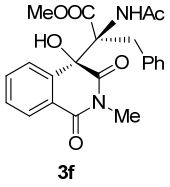
3e, colourless crystal from acetone/petroleum ether; m.p. 124–126˚C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.08(dd, *J* = 7.8, 0.9 Hz, 1H), 7.72(dd, *J* = 8.1, 1.2 Hz, 1H), 7.64(dt, *J* = 7.2, 1.2 Hz, 1H), 7.52(dt, *J* = 7.8, 1.2 Hz, 1H), 6.40(s, 1H), 4.95(s, 1H), 3.77(s, 3H), 3.32(s, 3H), 3.19–3.10(m, 1H), 2.39–2.19(m, 2H), 2.06–1.99(m, 1H), 1.97(s, 3H), 1.86(s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 173.6, 170.7, 169.4, 164.5, 135.3, 132.9, 129.4, 127.9, 127.1, 126.2, 79.7, 72.7, 53.8, 29.3, 27.8, 27.6, 24.2, 15.4; **MS** (ESI)

m/z 395 $[M+H]^+$; **EA** Calcd for $C_{18}H_{22}N_2O_6S$ C, 54.81; H, 5.62; N, 7.10; Found: C, 54.71; H, 5.64; N, 7.18.



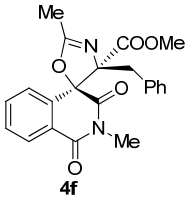
4e

4e, colourless crystal from acetone/ petroleum ether; m.p. 143–145˚C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.14(dd, *J* = 7.5, 1.5 Hz, 1H), 7.58(dt, *J* = 7.5, 1.5 Hz, 1H), 7.50(dd, *J* = 7.5, 1.2 Hz, 1H), 7.24(dd, *J* = 7.5, 0.9 Hz, 1H), 3.39(s, 3H), 3.05(s, 3H), 2.70(dt, *J* = 10.8, 4.5 Hz, 1H), 2.32(s, 3H), 2.25(dt, *J* = 11.4, 5.4 Hz, 1H), 2.06(dt, *J* = 12.3, 5.1 Hz, 1H), 2.01(s, 3H), 1.92(dt, *J* = 12.6, 4.5 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 169.0, 166.0, 163.5, 134.5, 133.3, 129.6, 128.5, 125.8, 124.7, 88.7, 52.1, 36.1, 29.8, 27.4, 15.5, 14.1; **MS** (ESI) *m/z* 377 $[M+H]^+$; **EA** Calcd for $C_{18}H_{20}N_2O_5S$ C, 57.43; H, 5.36; N, 7.44; Found: C, 57.42; H, 5.34; N, 7.40.



3f

3f, colourless crystal from acetone/petroleum ether; m.p. 133–135˚C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.12(dd, *J* = 7.8, 0.9 Hz, 1H), 7.74(dd, *J* = 7.8, 0.9 Hz, 1H), 7.67(dt, *J* = 7.5, 1.5 Hz, 1H), 7.54(dt, *J* = 7.5, 1.5 Hz, 1H), 7.18–7.16(m, 3H), 6.99–6.96(m, 2H), 6.33(s, 1H), 6.15(s, 1H), 4.24(d, *J* = 13.8 Hz, 1H), 3.72(s, 3H), 3.43(d, *J* = 14.1 Hz, 1H), 3.37(s, 3H), 1.86(s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 173.1, 171.4, 170.0, 164.4, 136.5, 135.1, 132.9, 129.7, 129.4, 128.3, 128.1, 128.0, 127.3, 127.1, 126.0, 79.8, 74.5, 53.6, 33.1, 27.8, 24.3; **MS** (ESI) *m/z* 411 $[M+H]^+$; **EA** Calcd for $C_{22}H_{22}N_2O_6$ C, 64.38; H, 5.40; N, 6.83; Found: C, 64.31; H, 5.39; N, 6.88.



4f

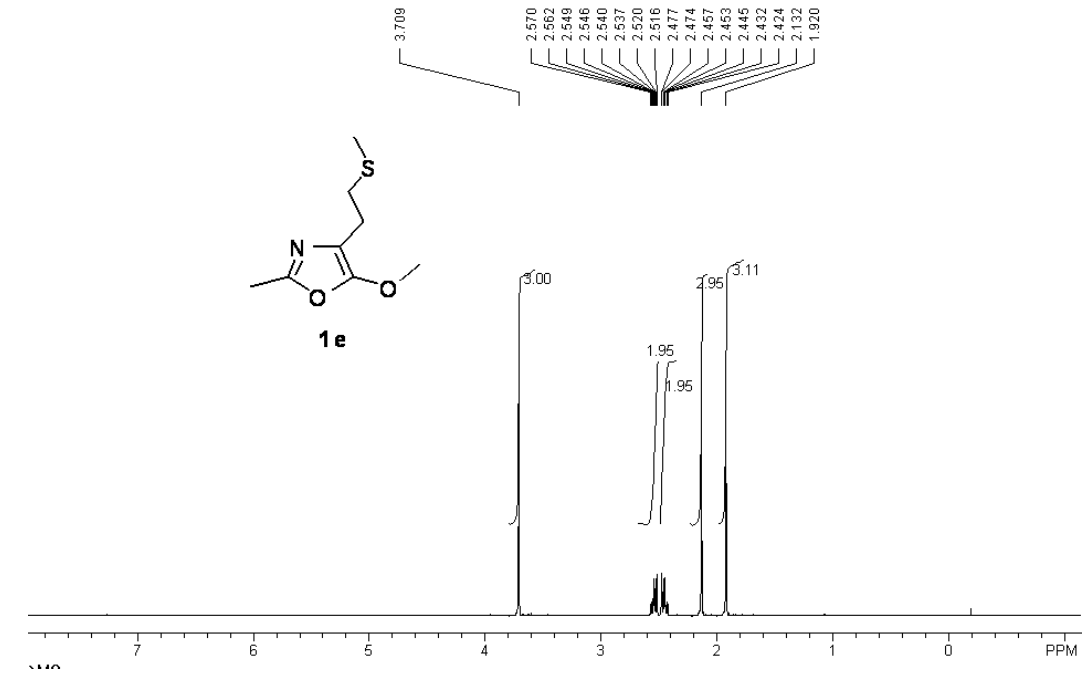
4f, colourless crystal from acetone/petroleum ether; m.p. 179–181˚C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.19(d, *J* = 7.5 Hz, 1H), 7.60–7.48(m, 2H), 7.26–7.17(m, 6H), 3.45(s, 3H), 3.01(s, 2H), 2.94(s, 3H), 2.38(s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 169.3, 168.6, 165.4, 163.7, 135.1, 134.9, 133.5, 130.5, 129.6, 128.5, 128.1, 127.1, 125.9, 124.6, 90.2, 88.3, 51.7, 42.2, 27.5, 14.2; **MS** (ESI) *m/z* 393 $[M+H]^+$; **EA** Calcd for $C_{22}H_{20}N_2O_5$ C, 67.34; H, 5.14; N, 7.14; Found: C, 67.31; H, 5.09; N, 7.08.

Transformation of 2b to 4b and 4bi catalyzed by different acids:

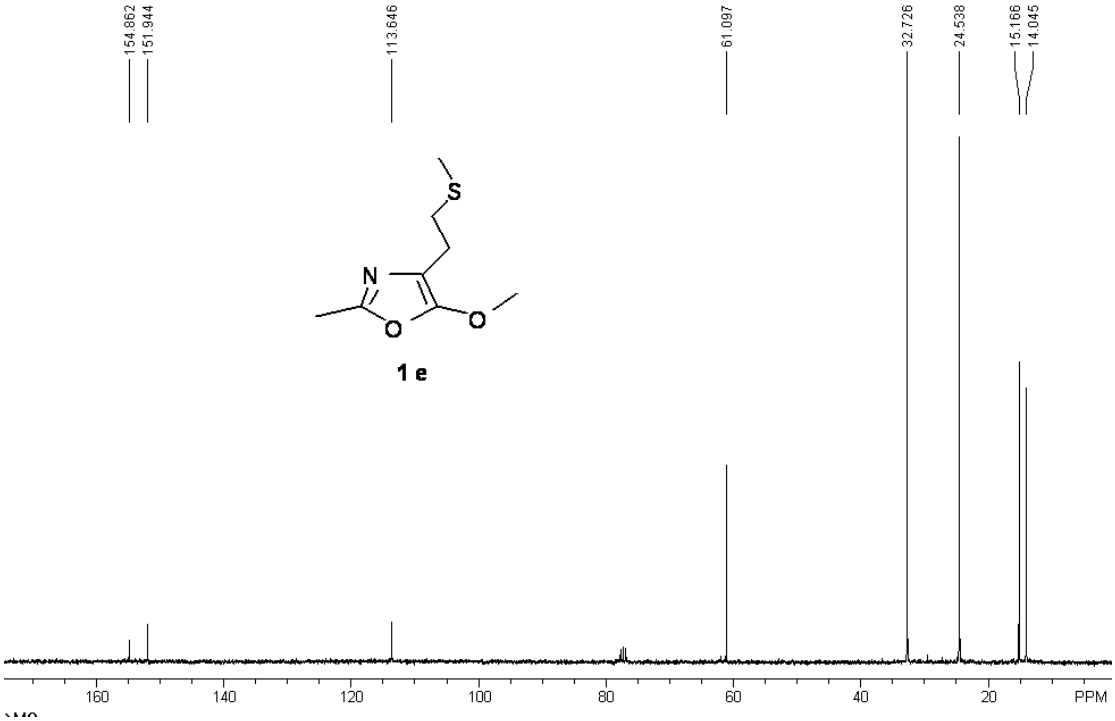
To a solution of the spirooxetane **2b** in anhydrous acetonitrile (0.02M) was added corresponding amount of organic acid or Lewis acid. The mixture was stirred at room temperature and monitored by TLC. Upon complete conversion, the reaction mixture was poured into water (When 10eq. amount of Lewis acid was used, the mixture should be poured into saturated aqueous $NaHCO_3$ instead of water) and extracted with ethyl acetate. The combined organic layer was washed by brine and dried over $MgSO_4$. The solvent was removed under vacum, and the crude products were separated by flash column chromatography on 300-400 mesh silica gel (petroleum ether/ethyl acetate) to give the final products.

Copies of ^{1}HNMR and ^{13}CNMR spectra of all the new compounds and IR spectra of 2d 3d and 4d

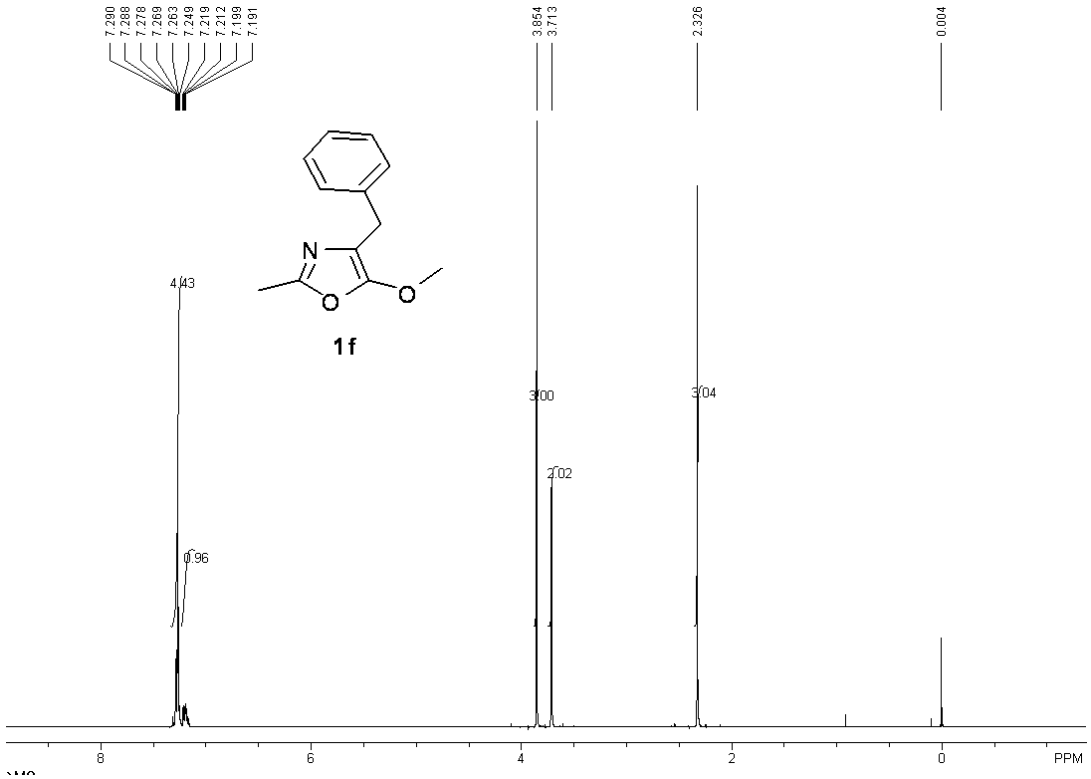
1e-^{1}H NMR($CDCl_3$):



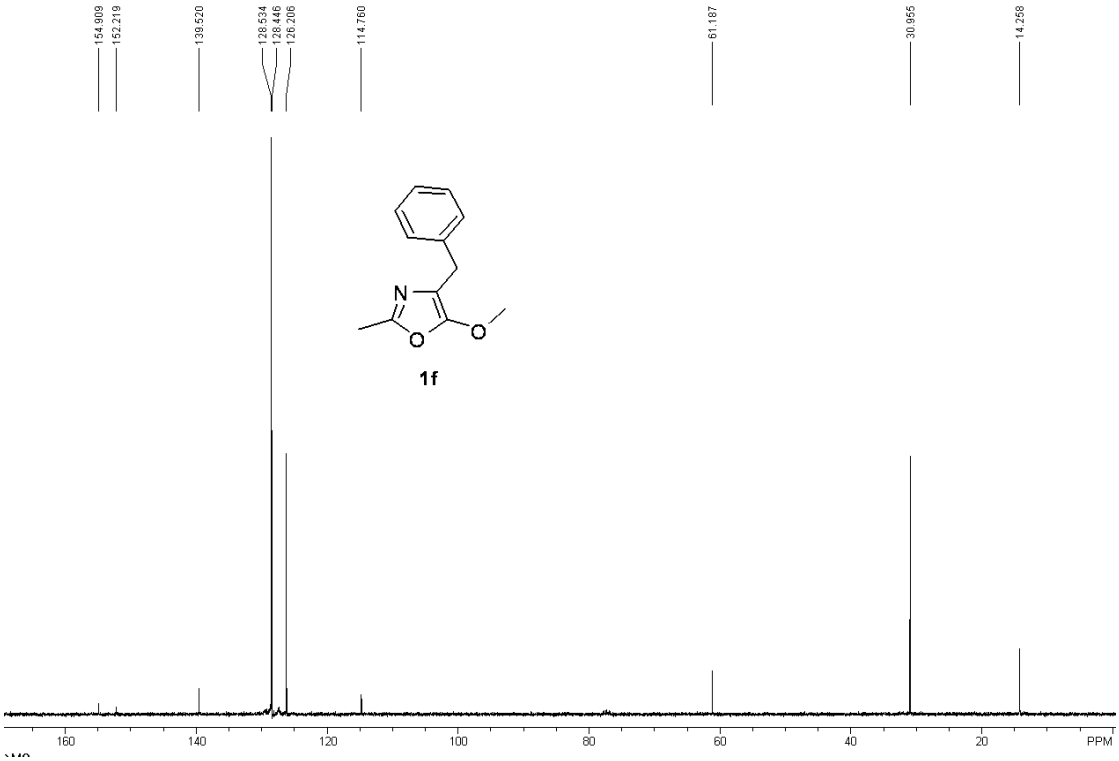
1e-^{13}C NMR($CDCl_3$):



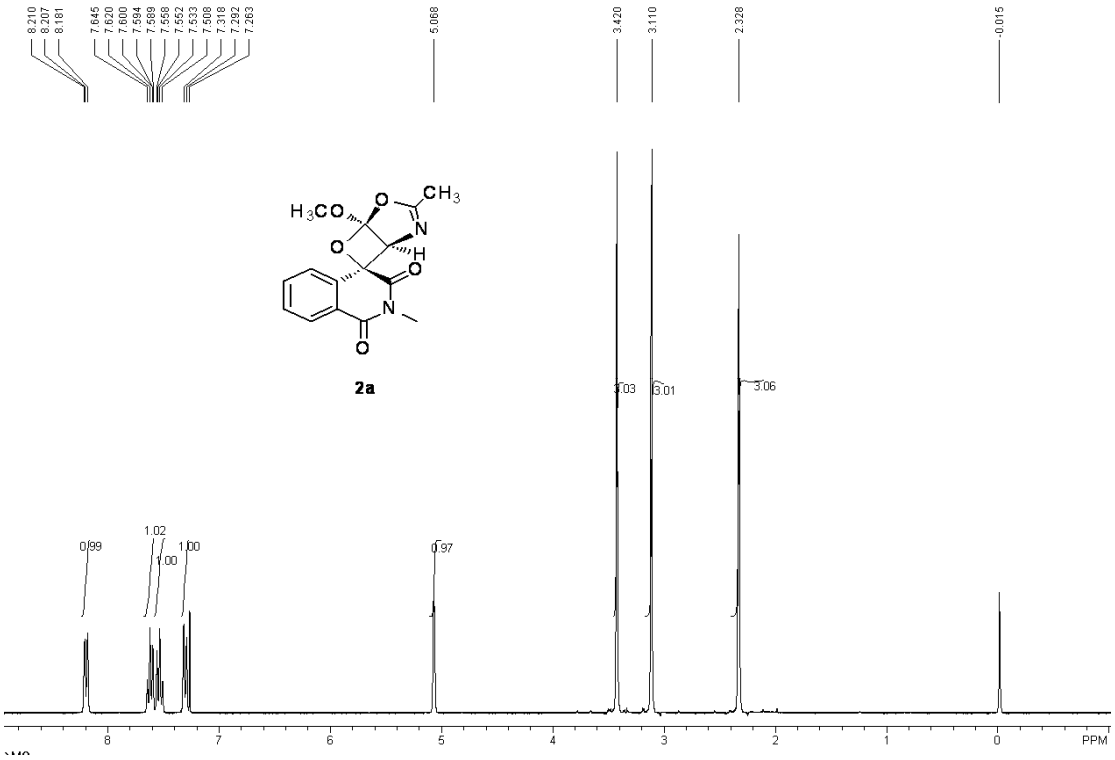
1f-^{1}H NMR($CDCl_3$):



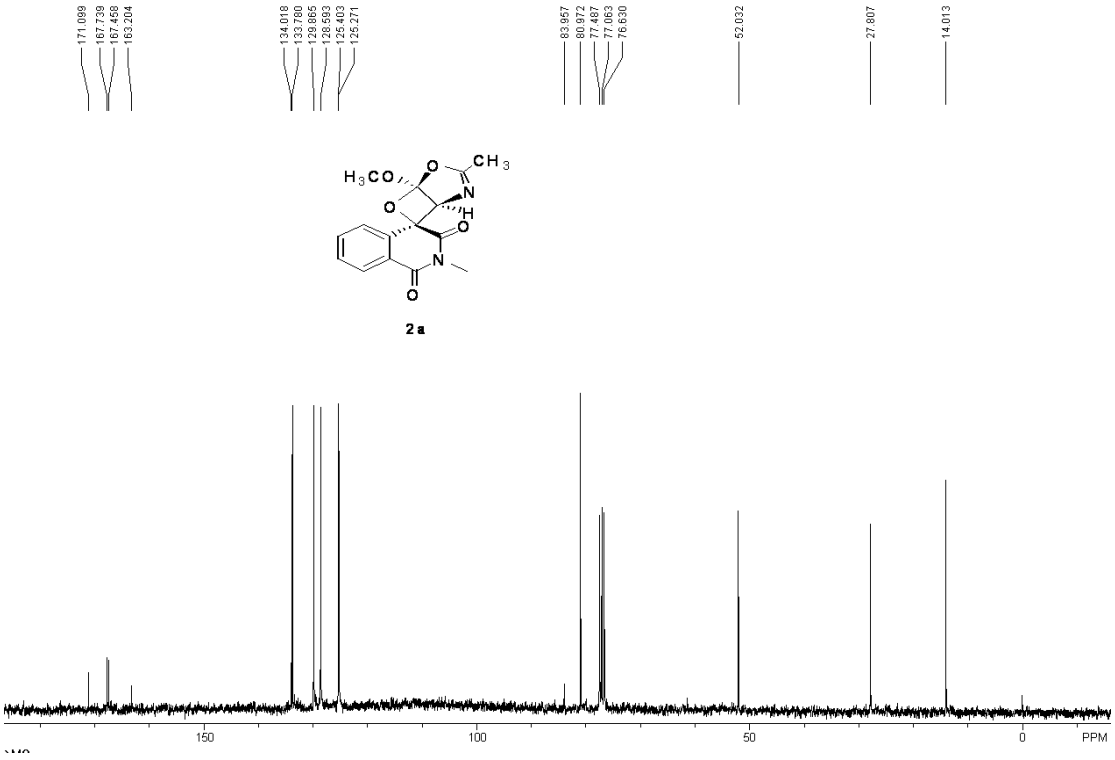
1f-^{13}C NMR($CDCl_3$):



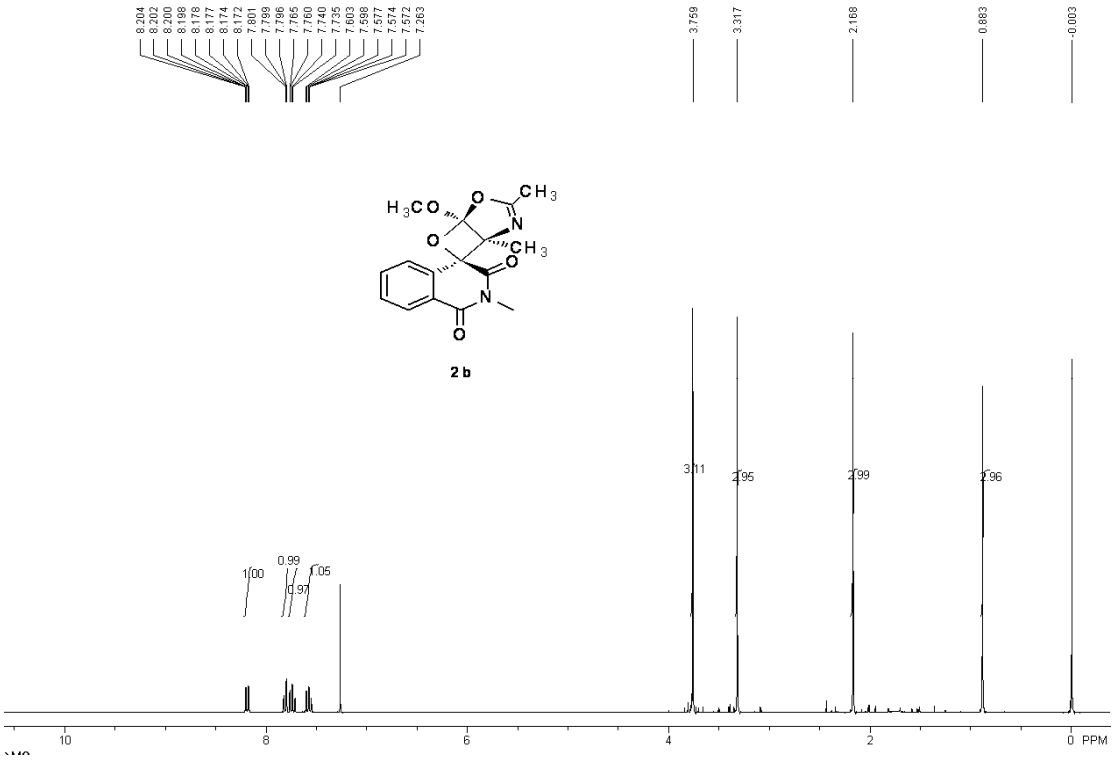
2a-^{1}H NMR($CDCl_3$):



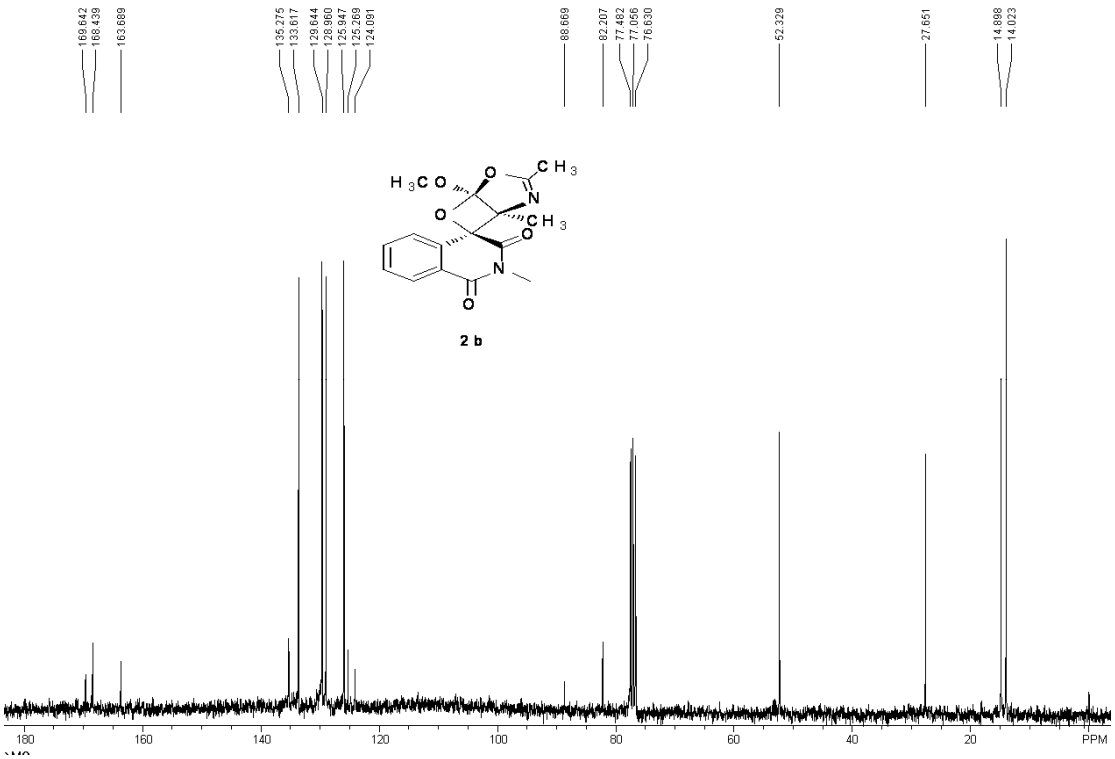
2a-^{13}C NMR($CDCl_3$):



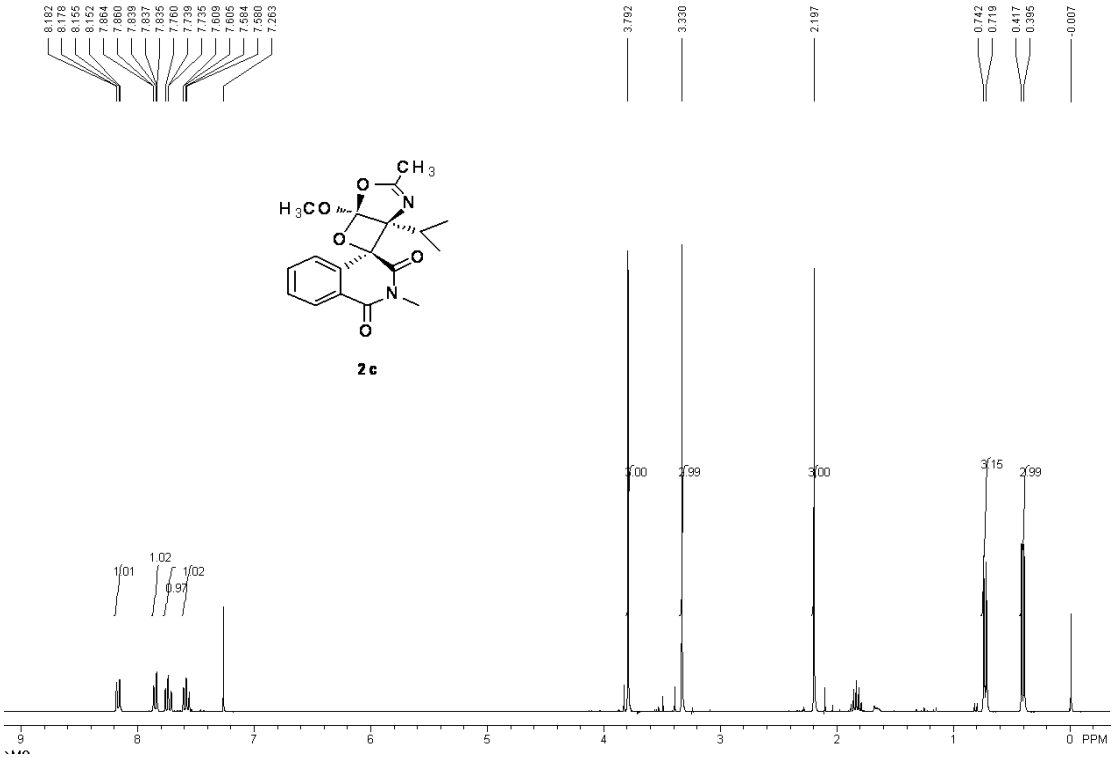
2b-^{1}H NMR($CDCl_3$):



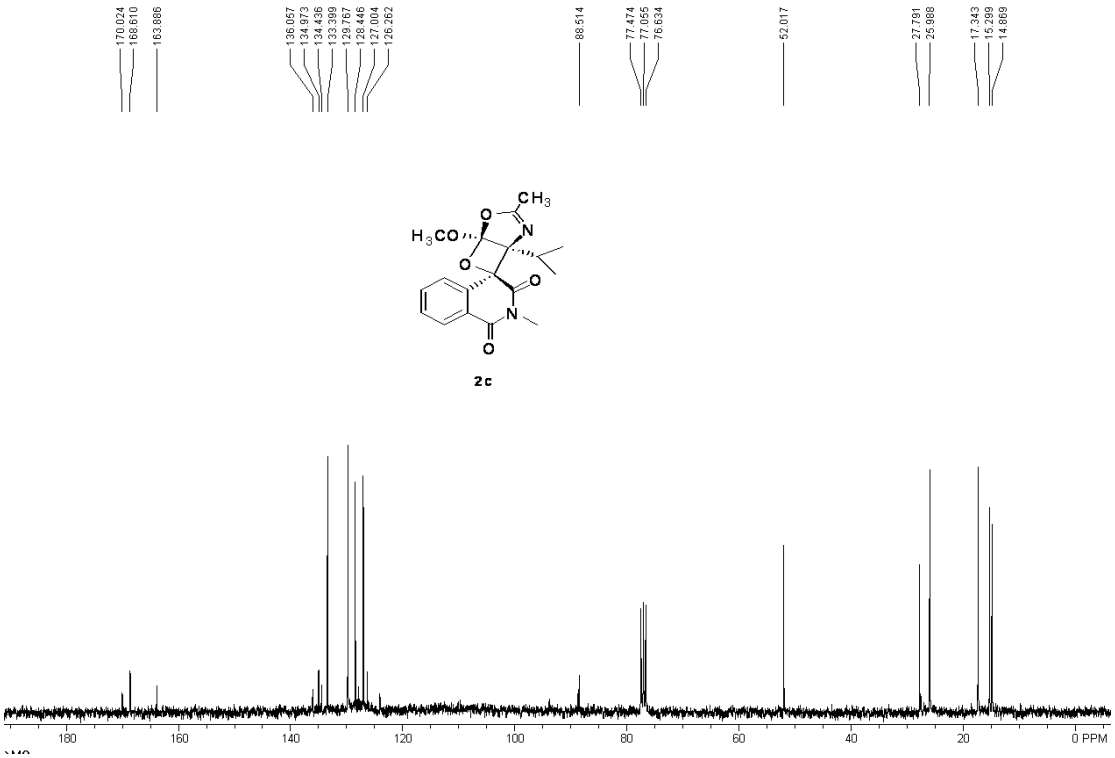
2b-^{13}C NMR($CDCl_3$):



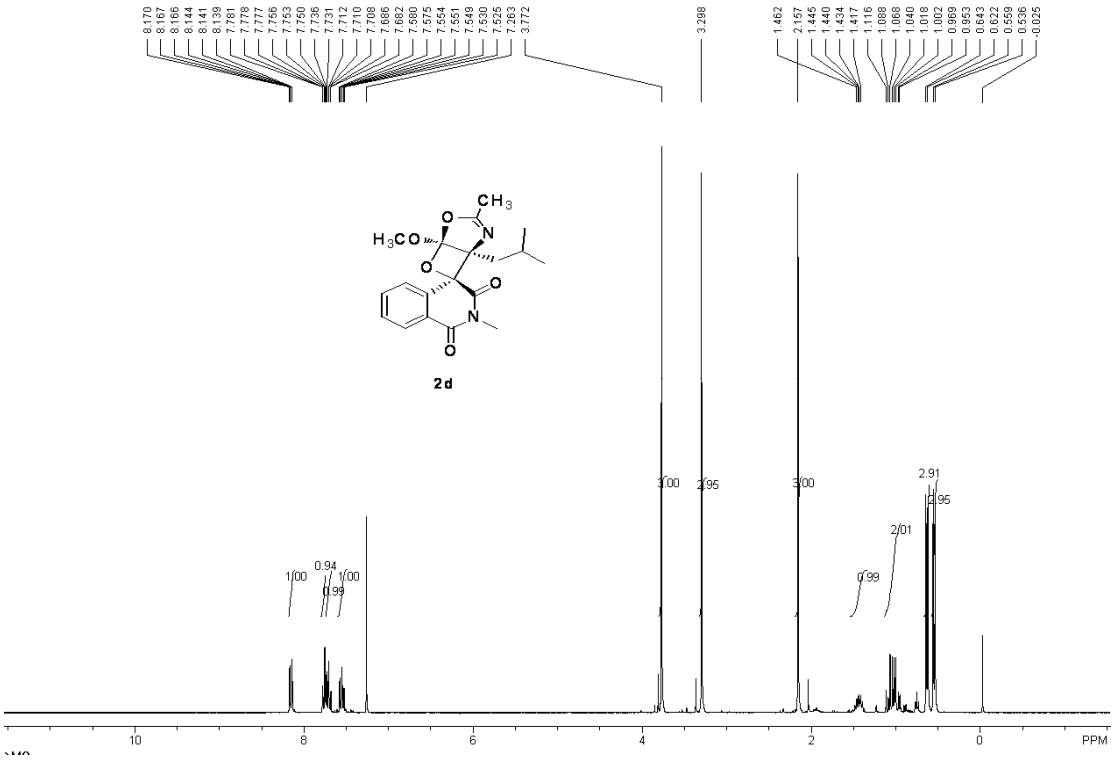
2c-^{1}H NMR($CDCl_3$):



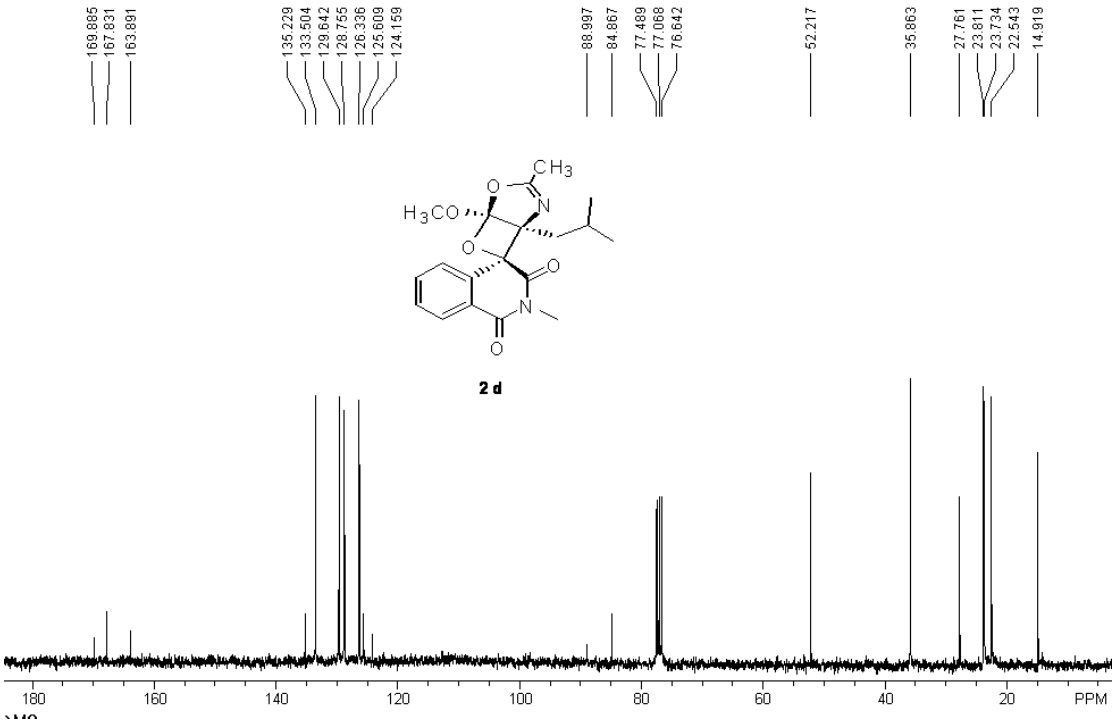
2c-^{13}C NMR($CDCl_3$):



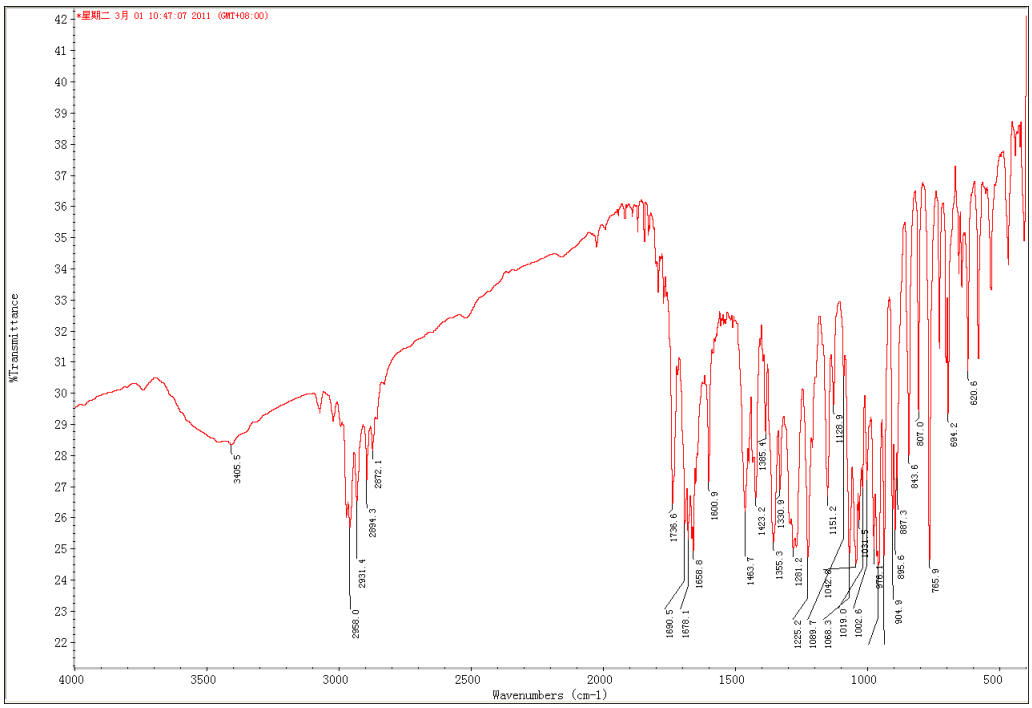
2d-^{1}H NMR($CDCl_3$):



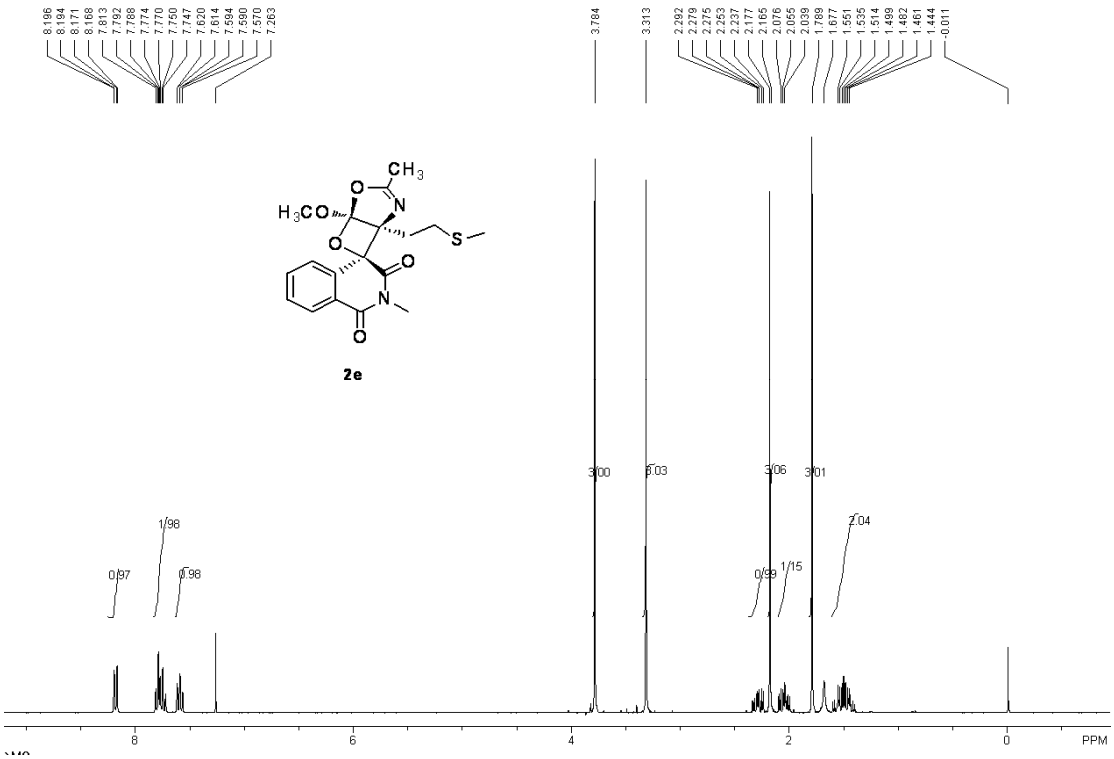
2d-^{13}C NMR($CDCl_3$):



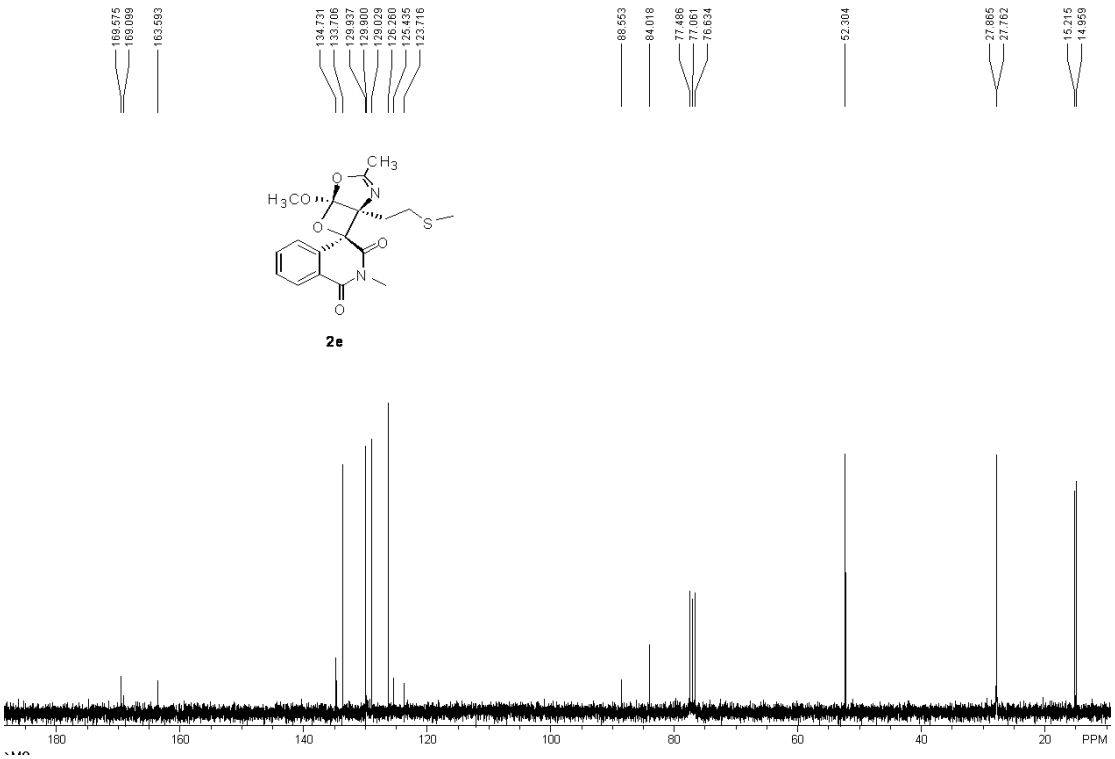
2d-IR (KBr pallet):



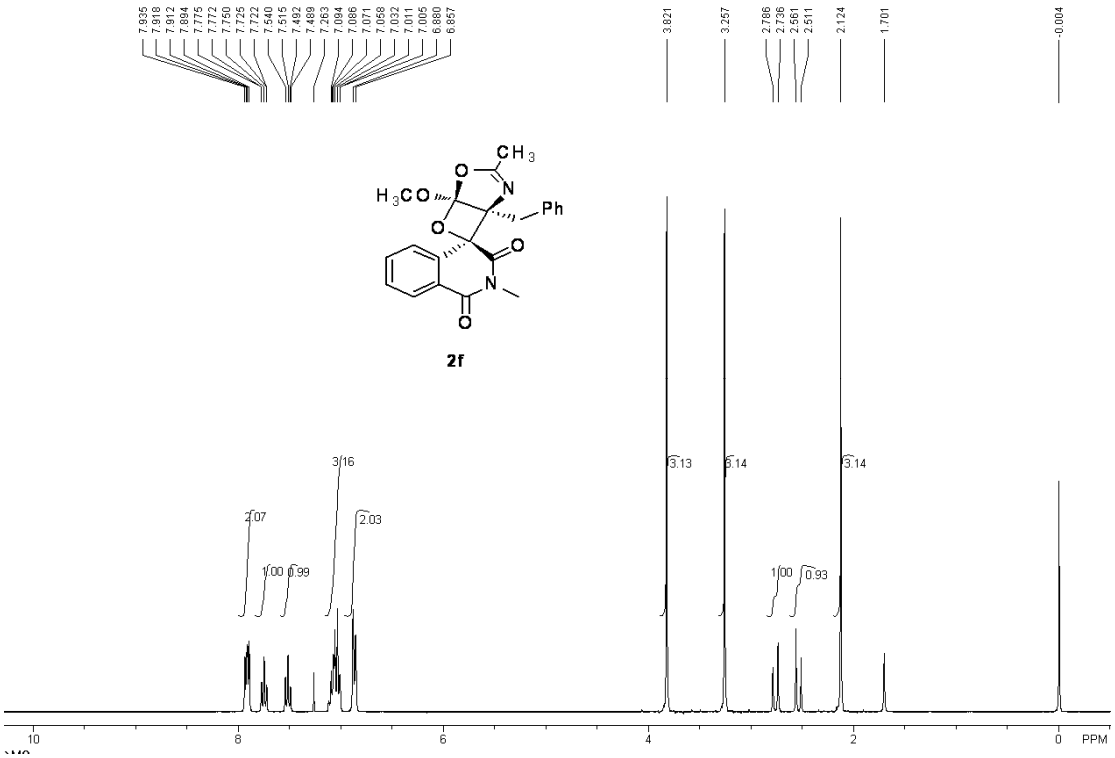
2e-^{1}H NMR($CDCl_3$):



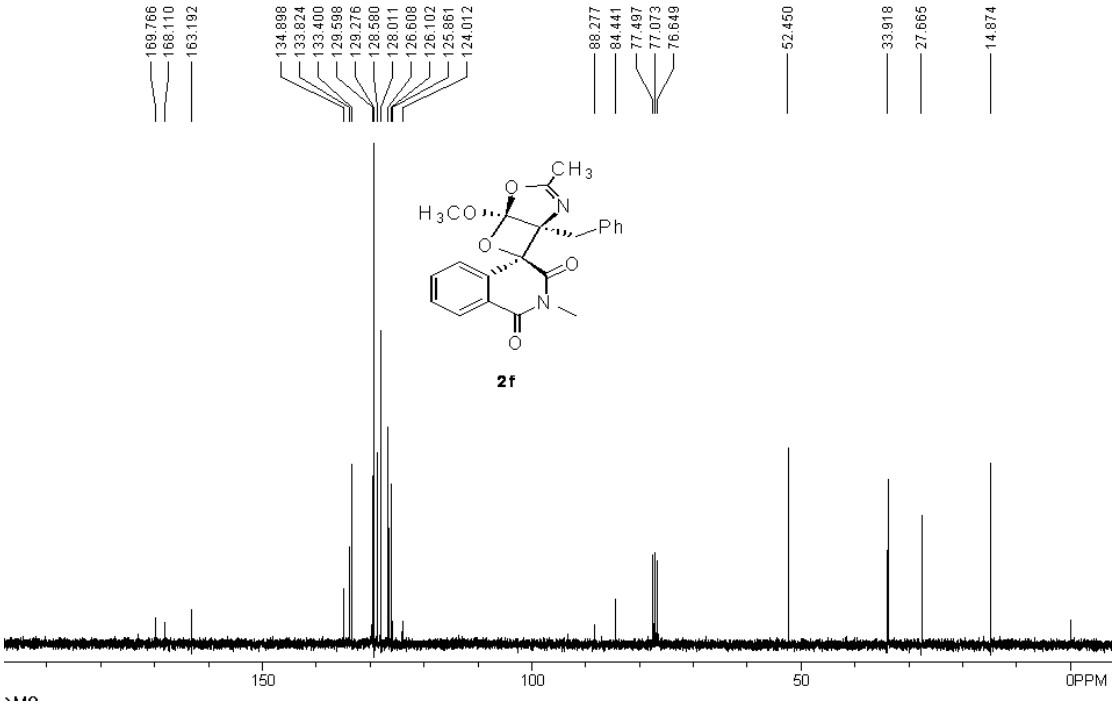
2e-^{13}C NMR($CDCl_3$):



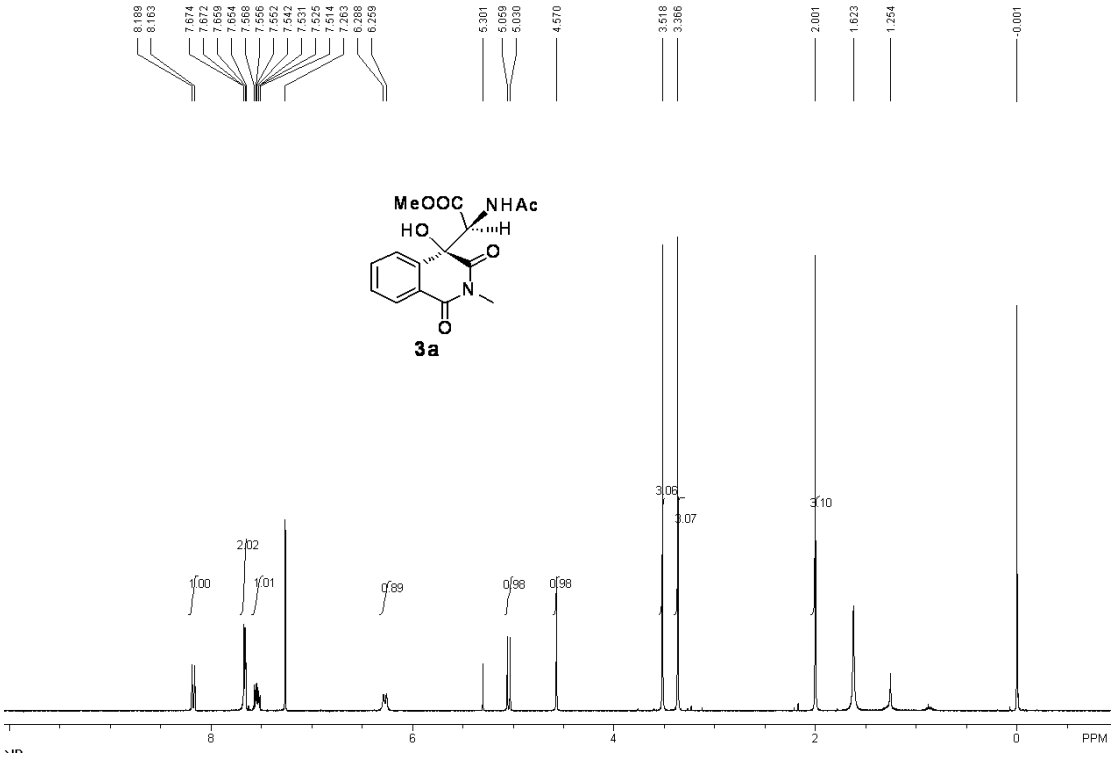
2f-^{1}H NMR($CDCl_3$):



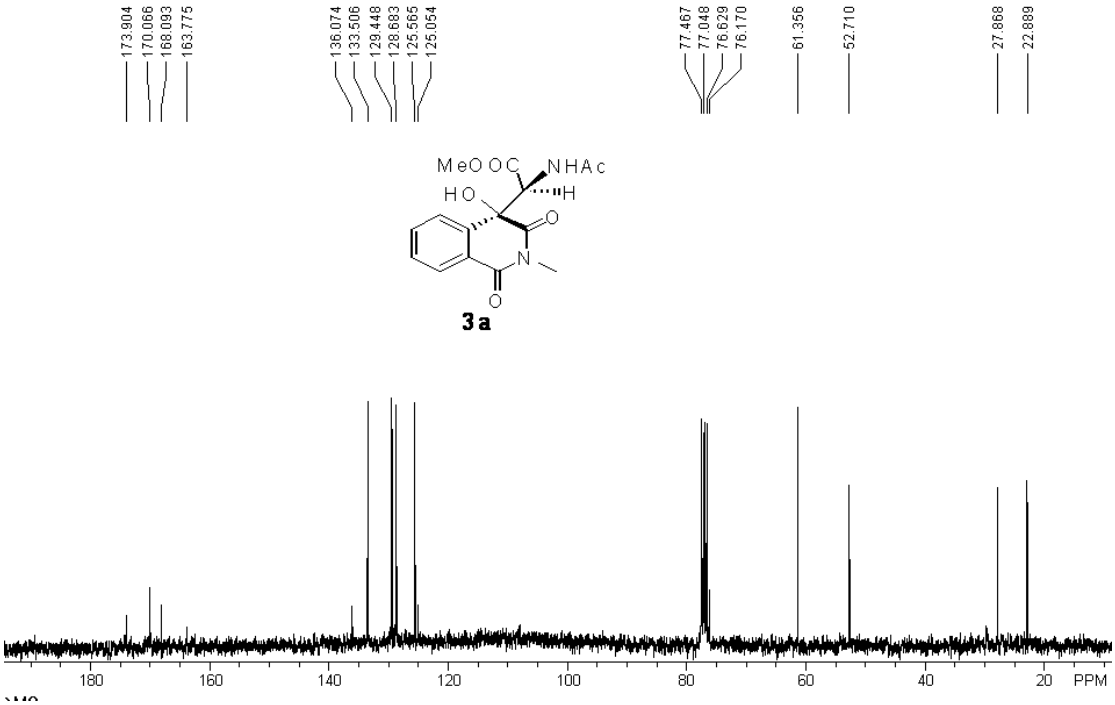
2f-^{13}C NMR($CDCl_3$):



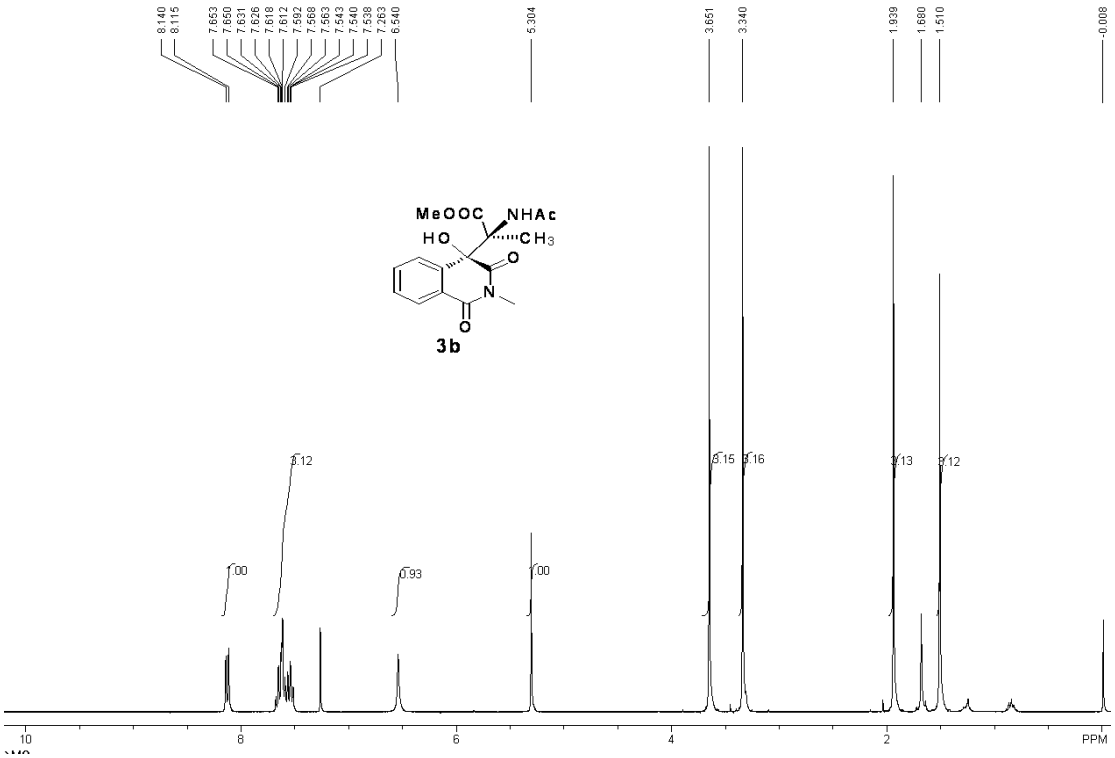
3a-^{1}H NMR($CDCl_3$):



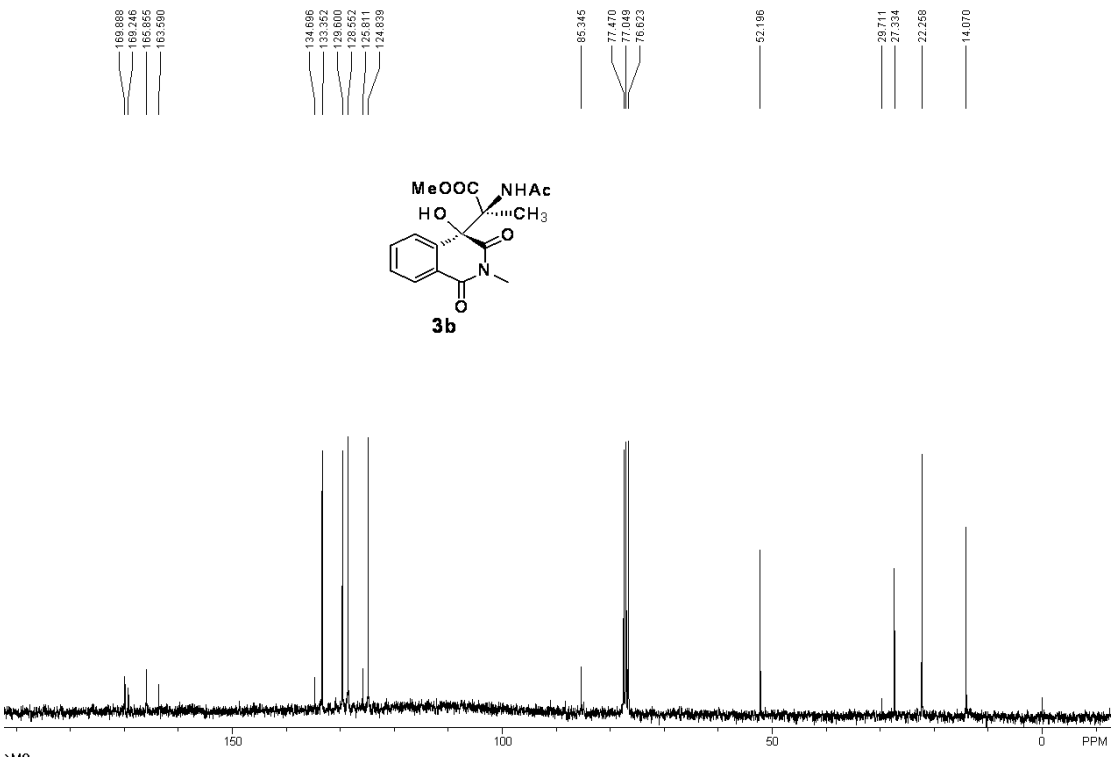
3a-^{13}C NMR($CDCl_3$):



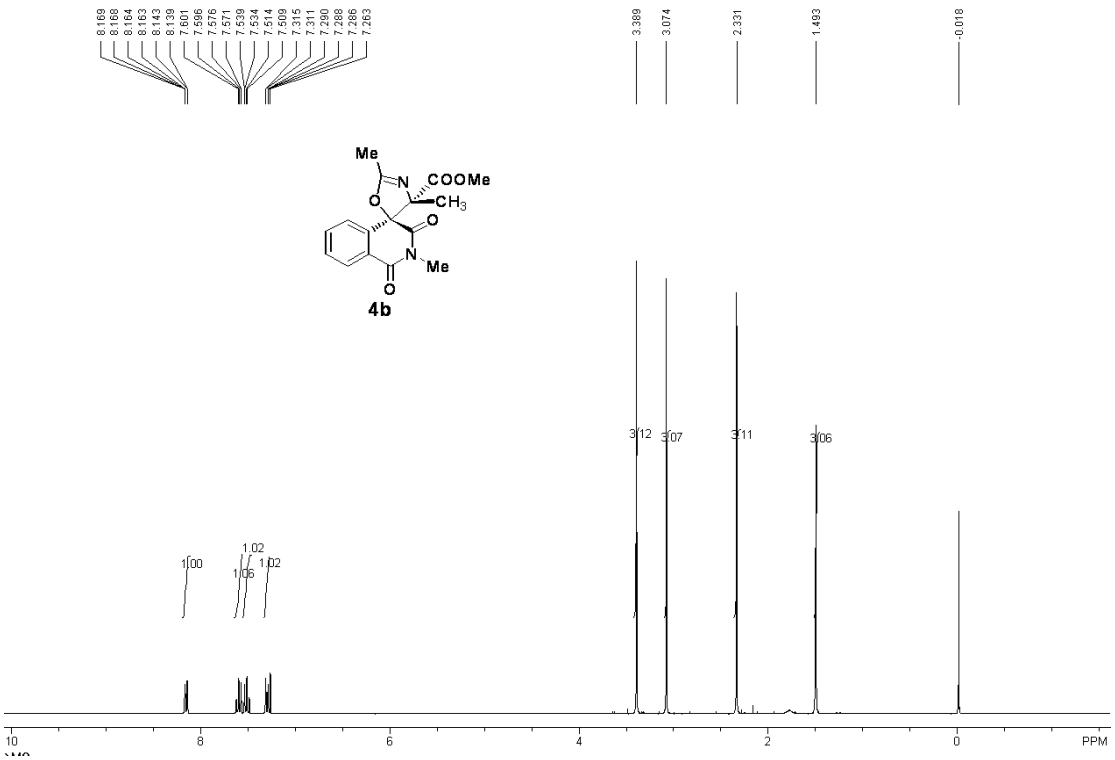
3b-^{1}H NMR($CDCl_3$):



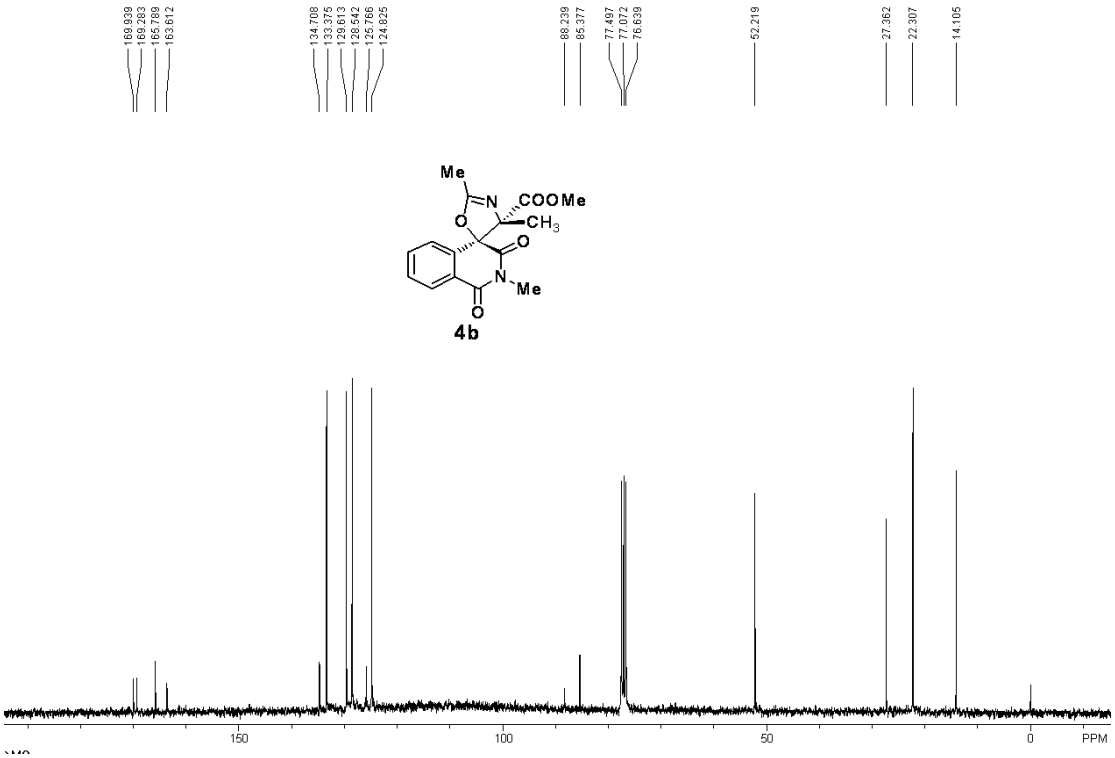
3b-^{13}C NMR($CDCl_3$):



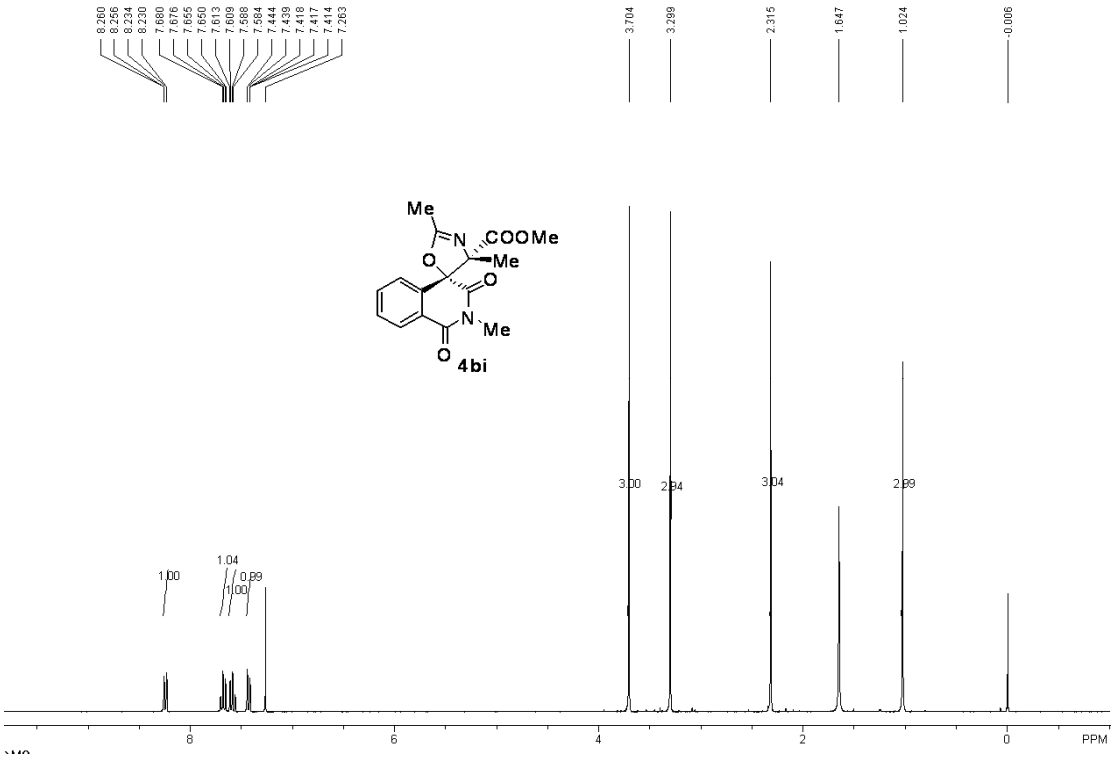
4b-^{1}H NMR($CDCl_3$):



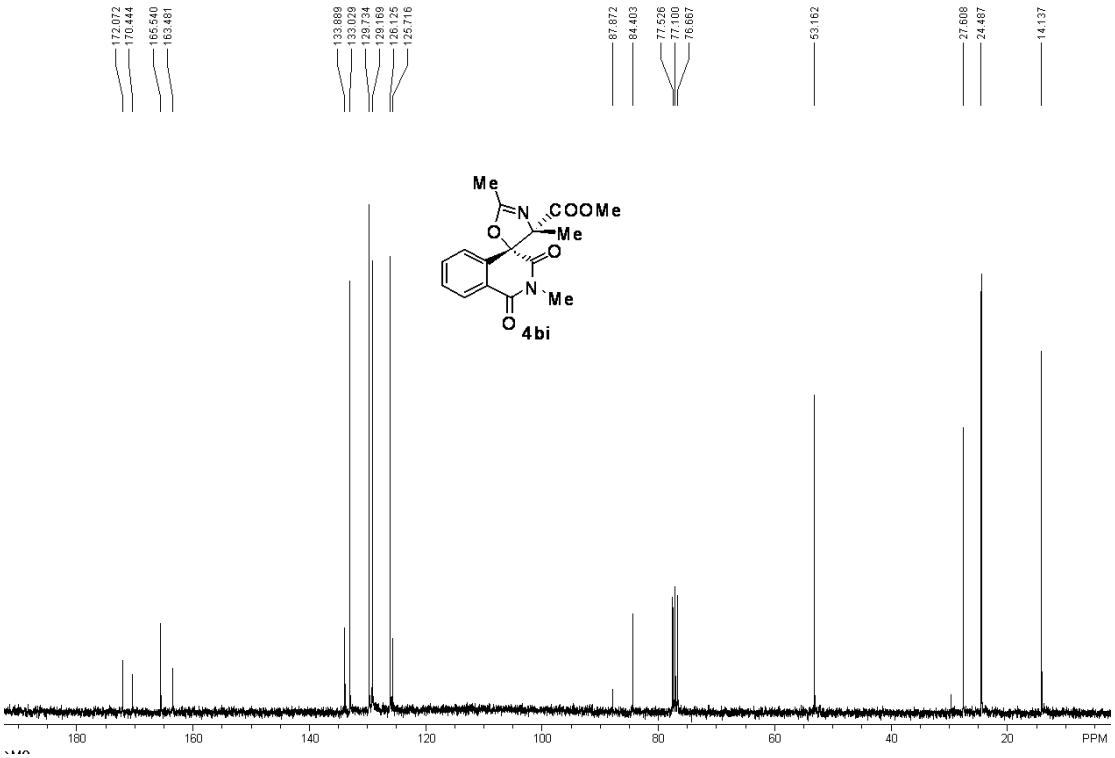
4b-^{13}C NMR($CDCl_3$):



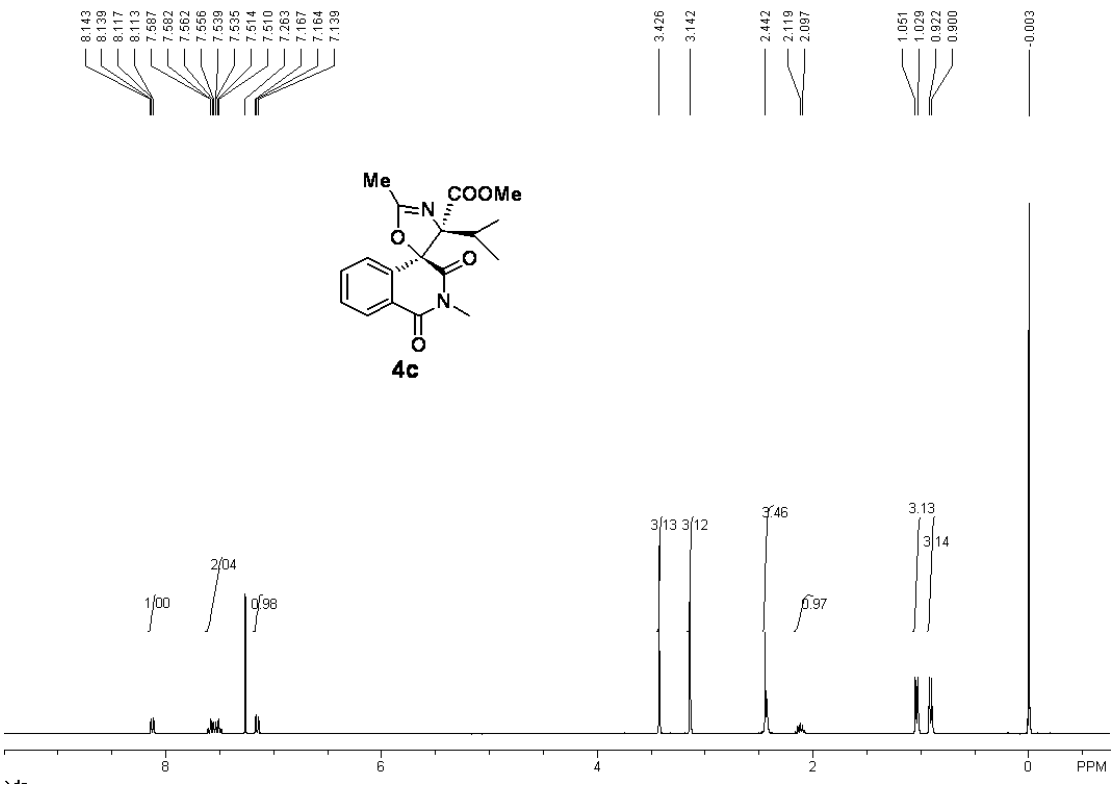
4bi-^{1}H NMR($CDCl_3$):



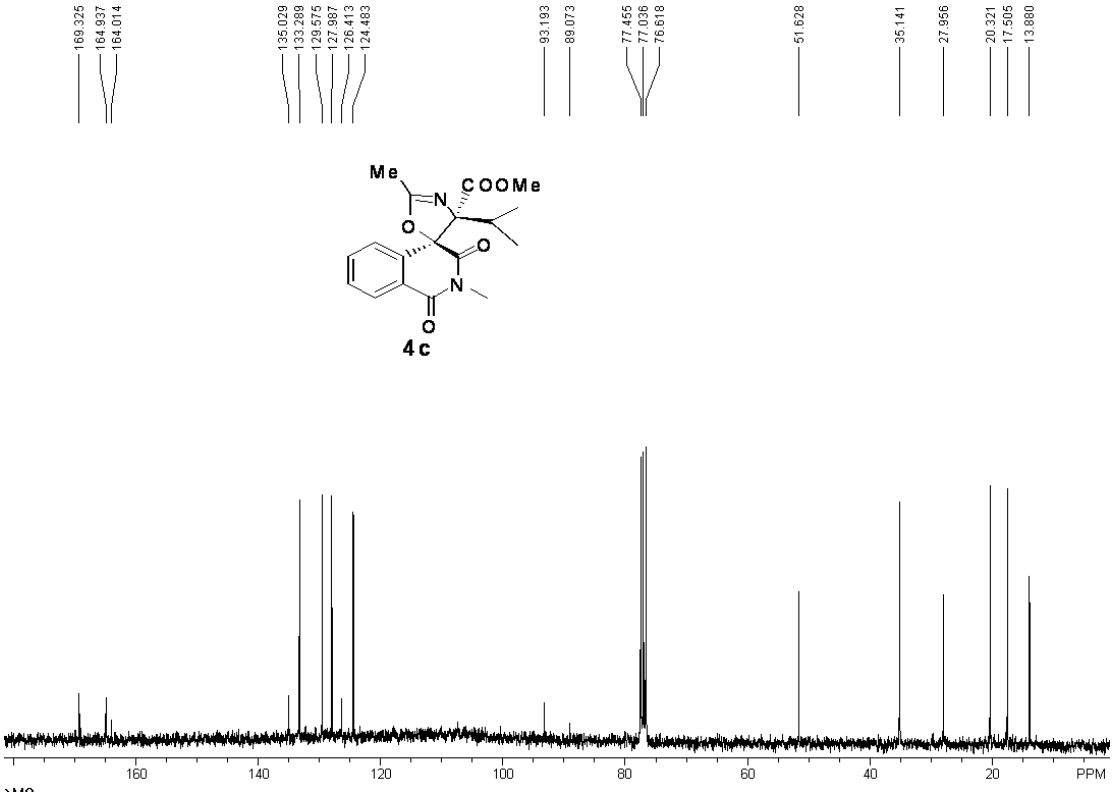
4bi-^{13}C NMR($CDCl_3$):



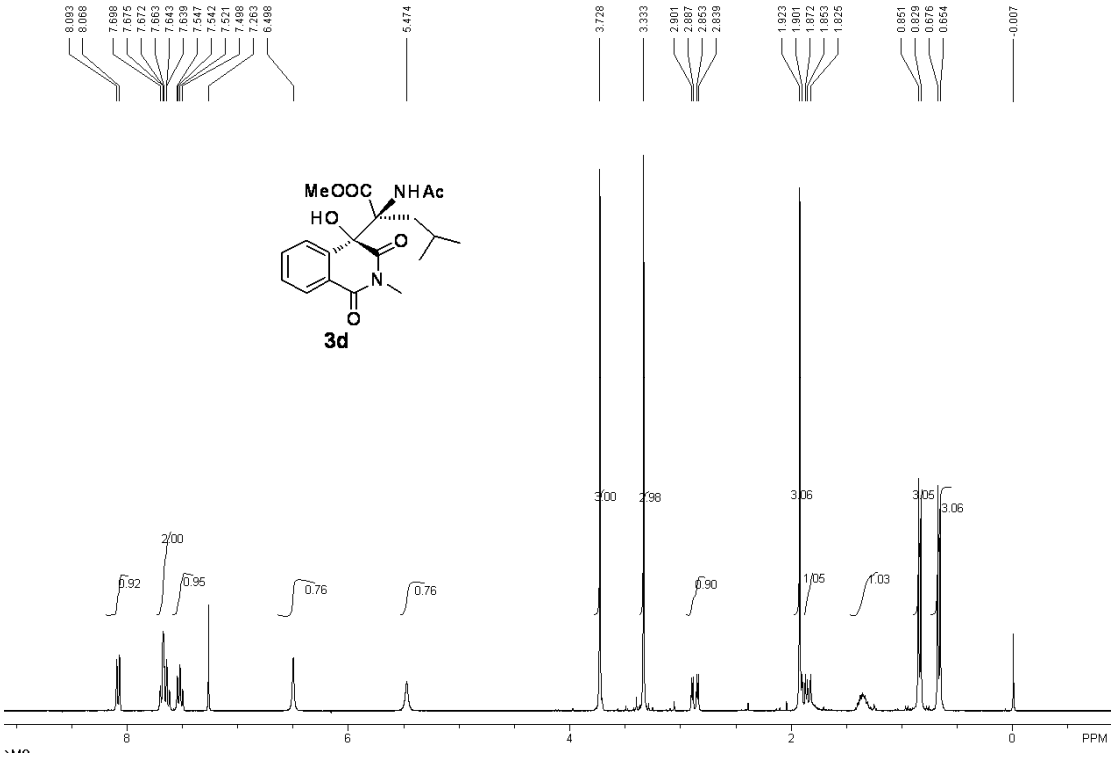
4c-^{1}H NMR($CDCl_3$):



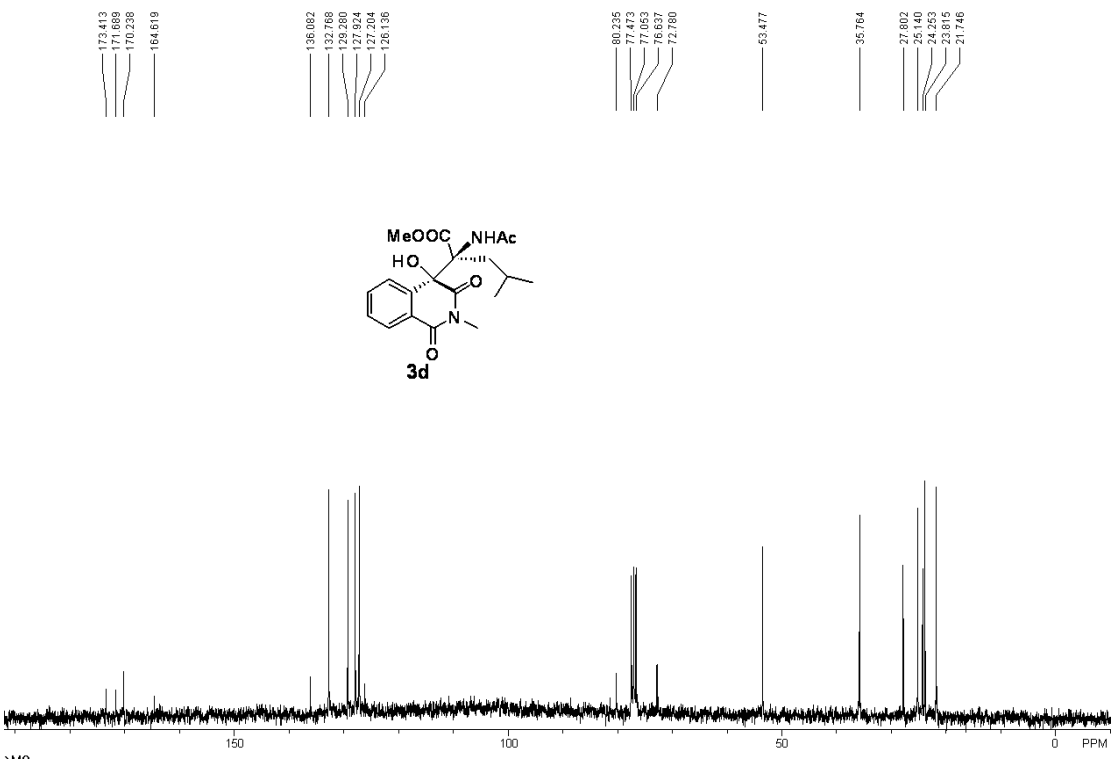
4c-^{13}C NMR($CDCl_3$):



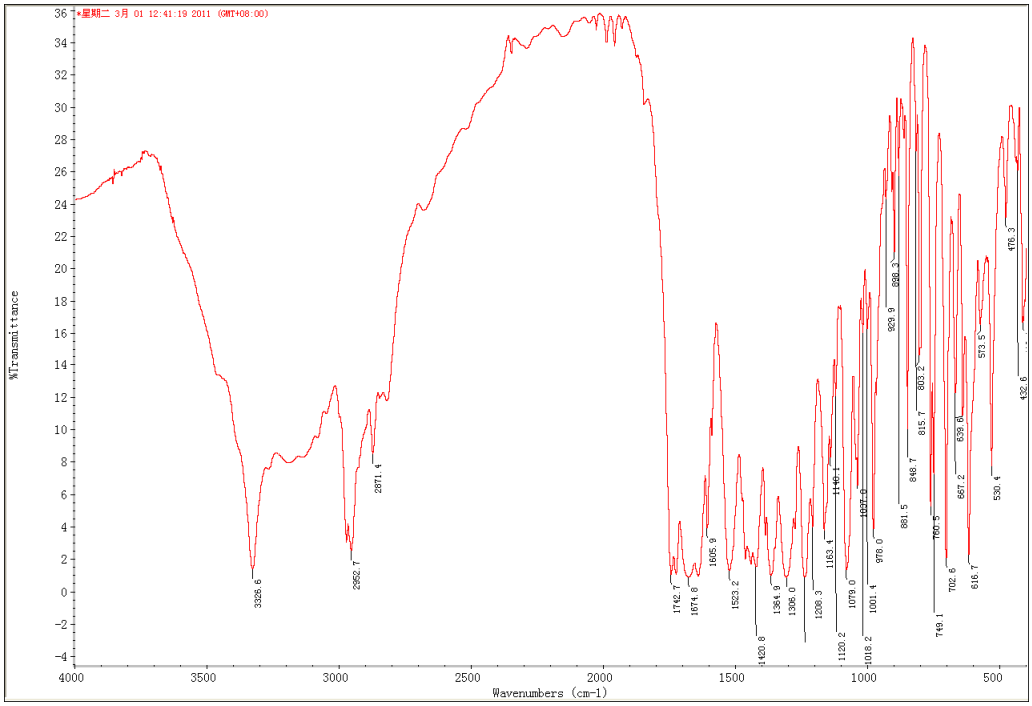
3d-^{1}H NMR($CDCl_3$):



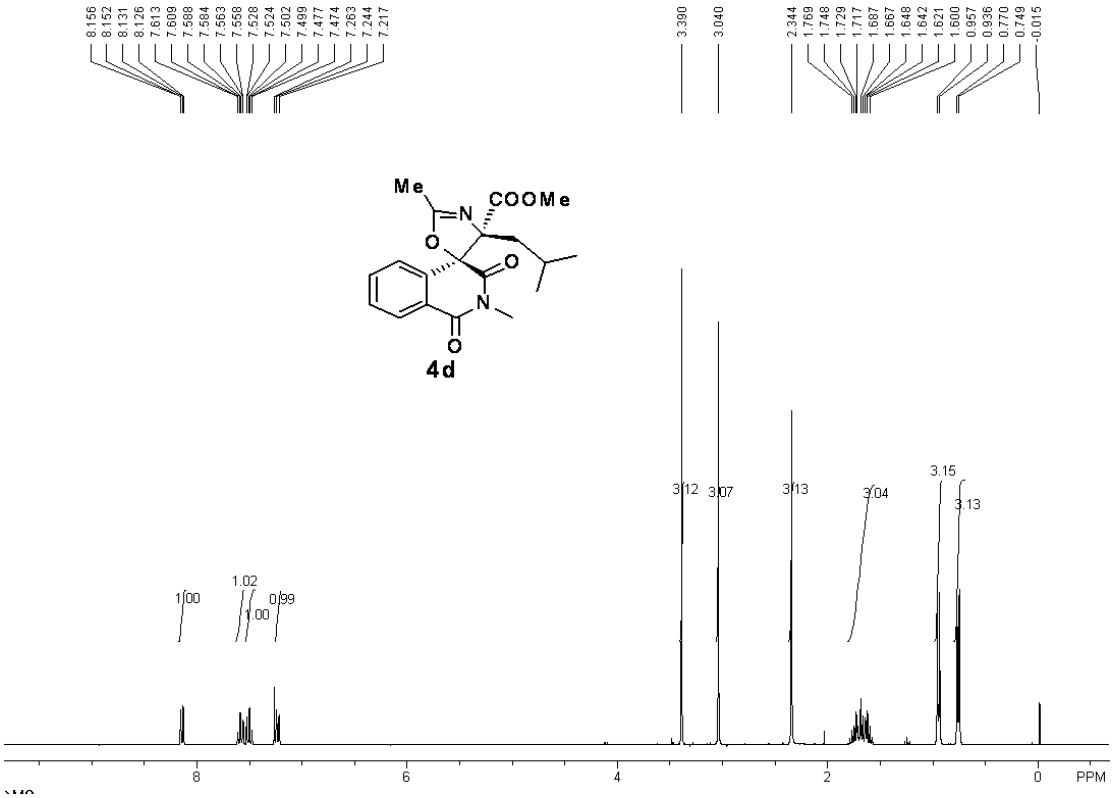
3d-^{13}C NMR($CDCl_3$):



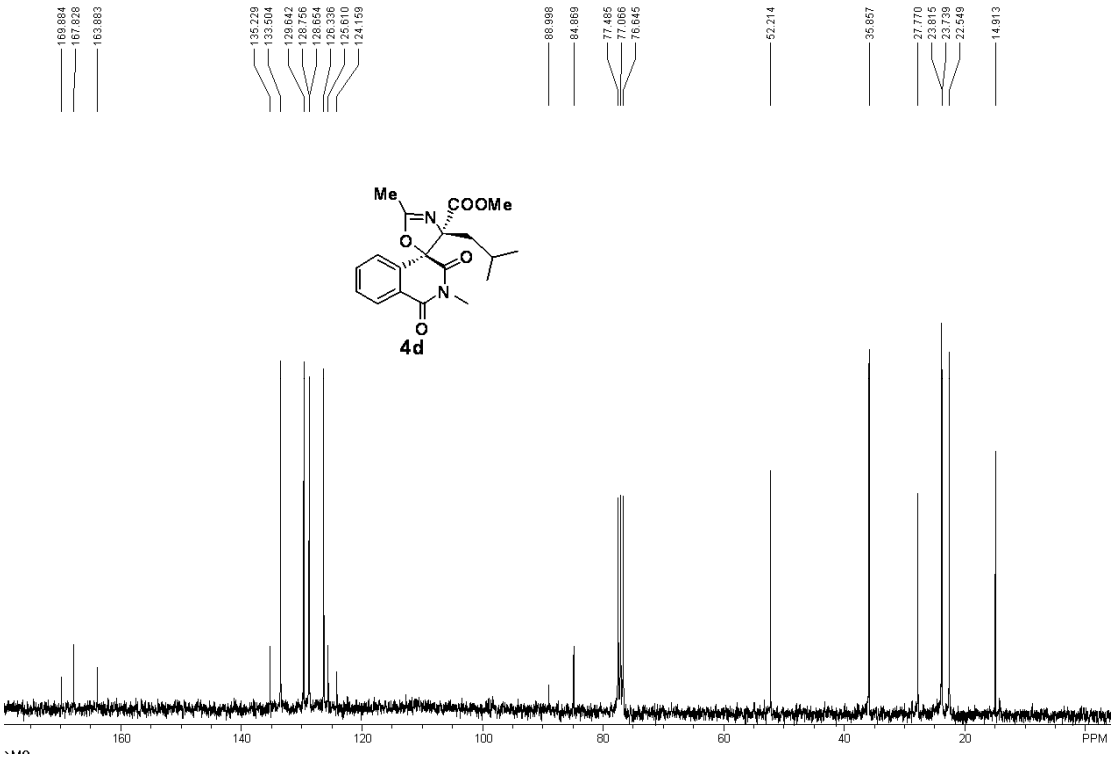
3d-IR (KBr, pallet):



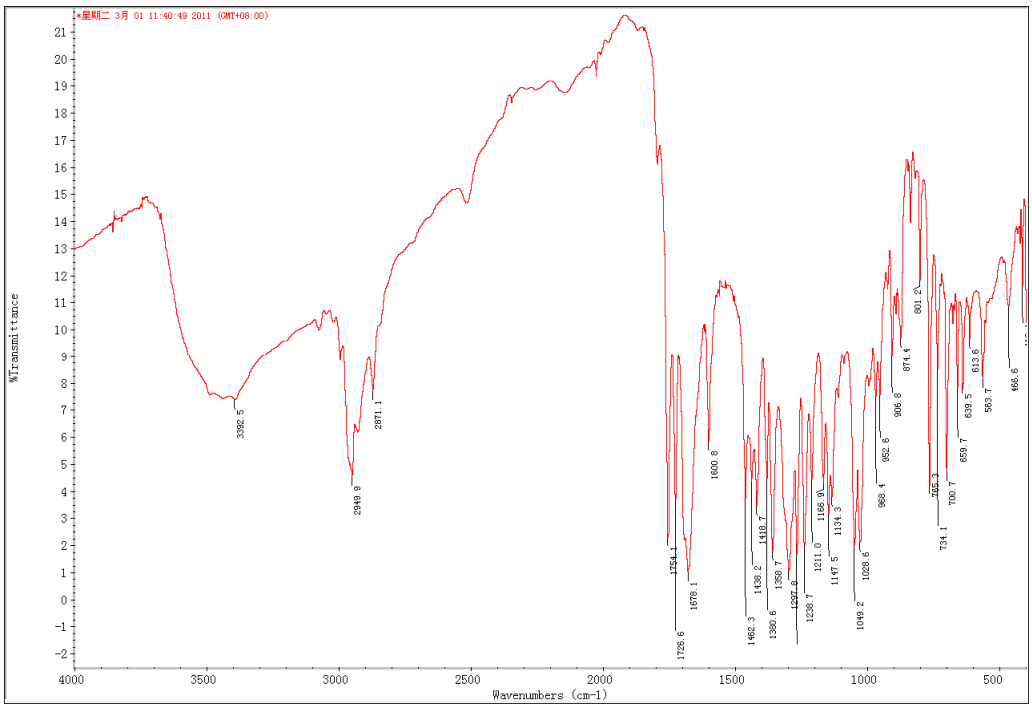
4d-^{1}H NMR($CDCl_3$):



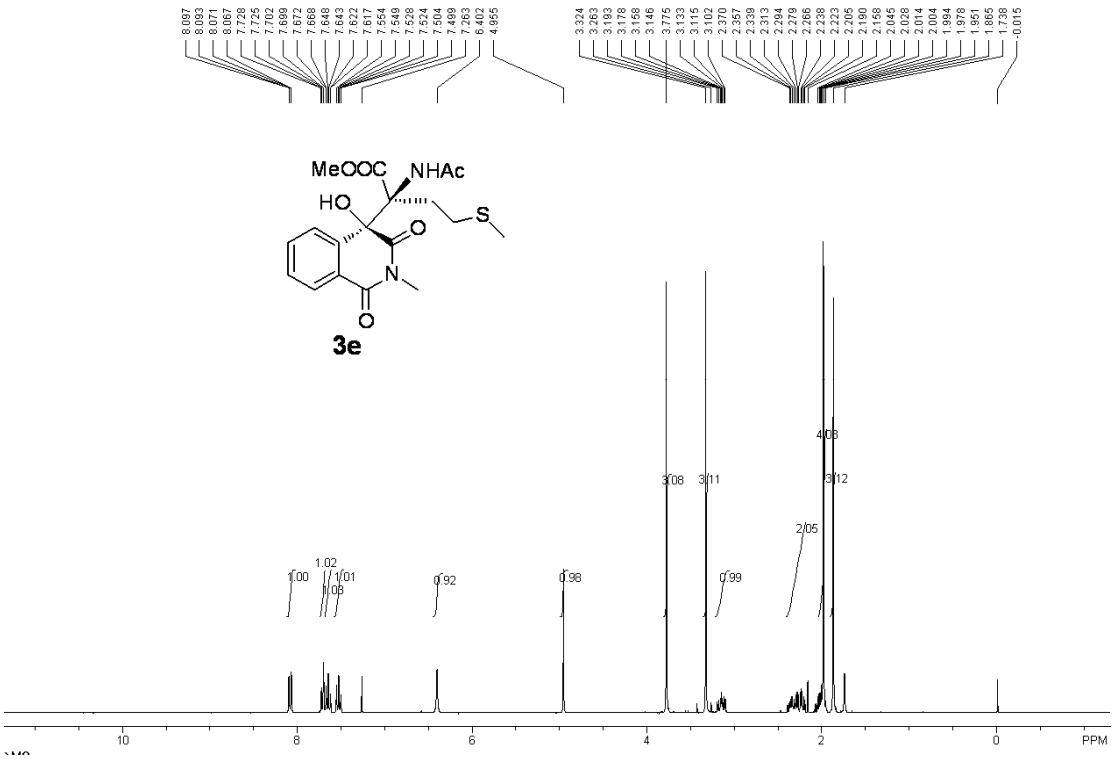
4d-^{13}C NMR($CDCl_3$):



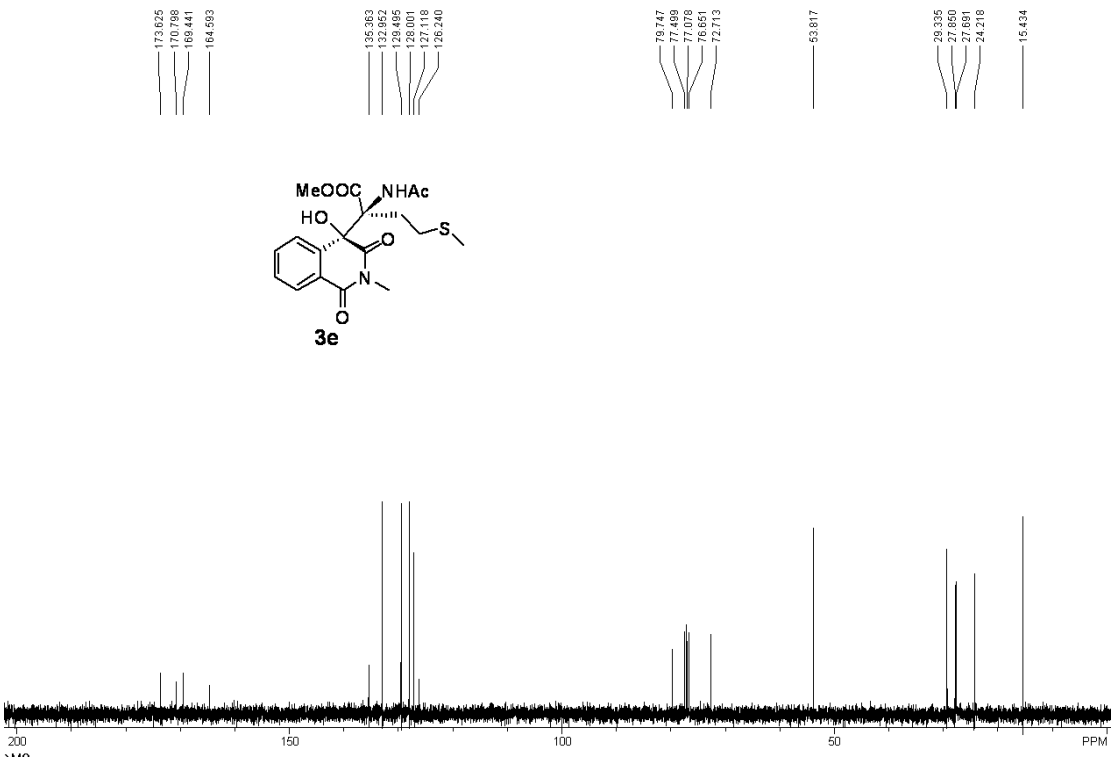
4d-IR (KBr, pallet):



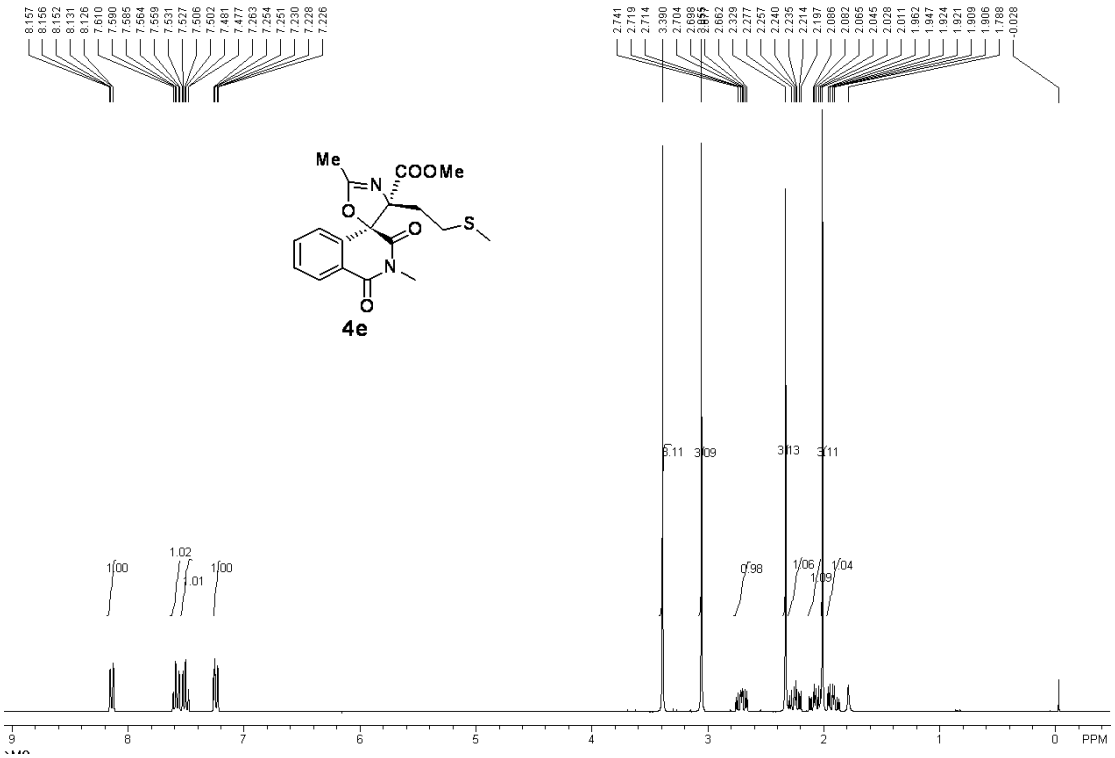
3e-^{1}H NMR($CDCl_3$):



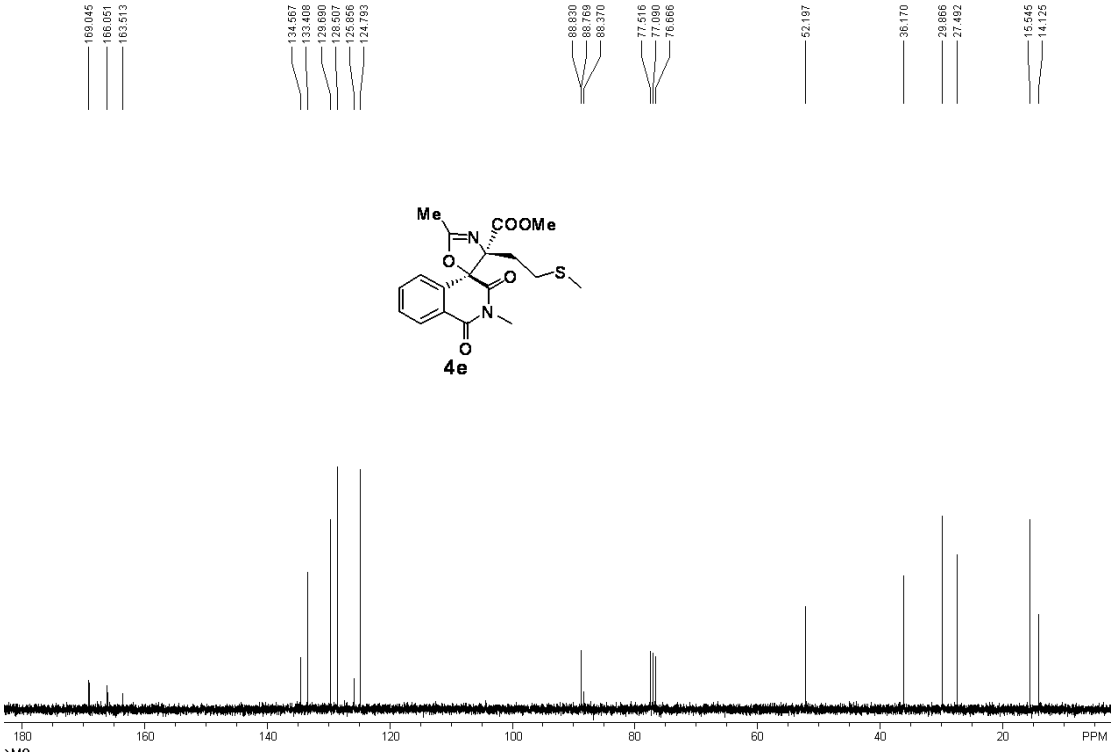
3e-^{13}C NMR($CDCl_3$):



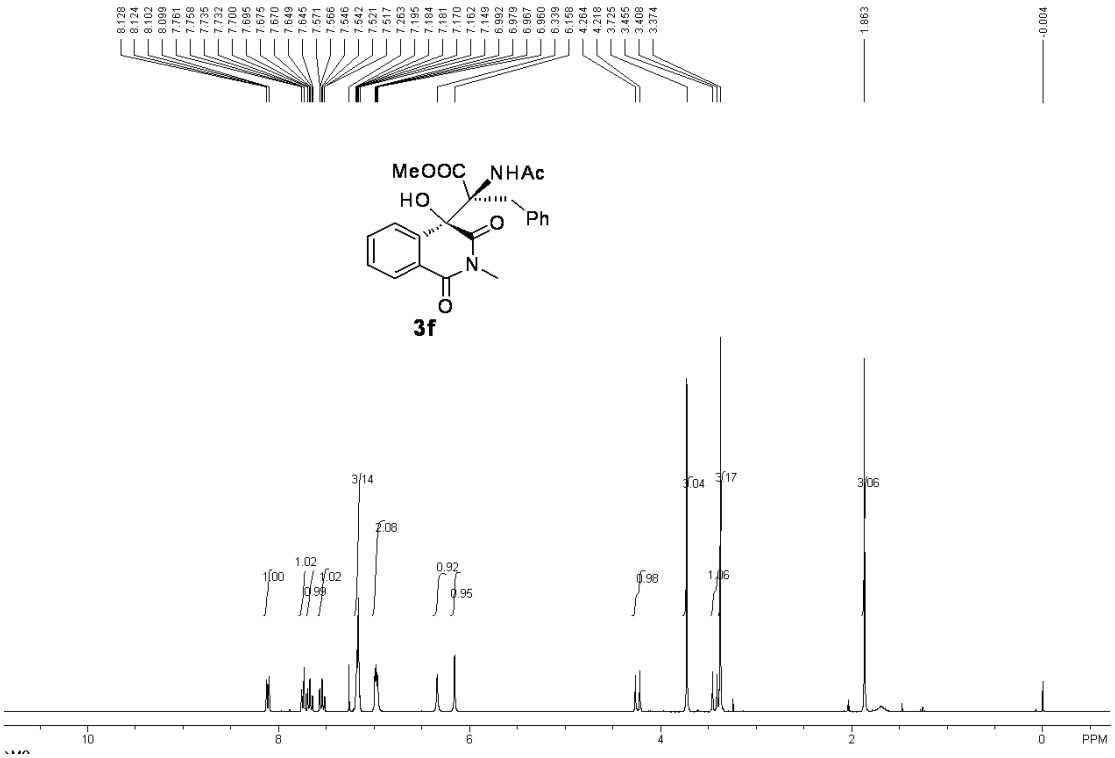
4e-^{1}H NMR($CDCl_3$):



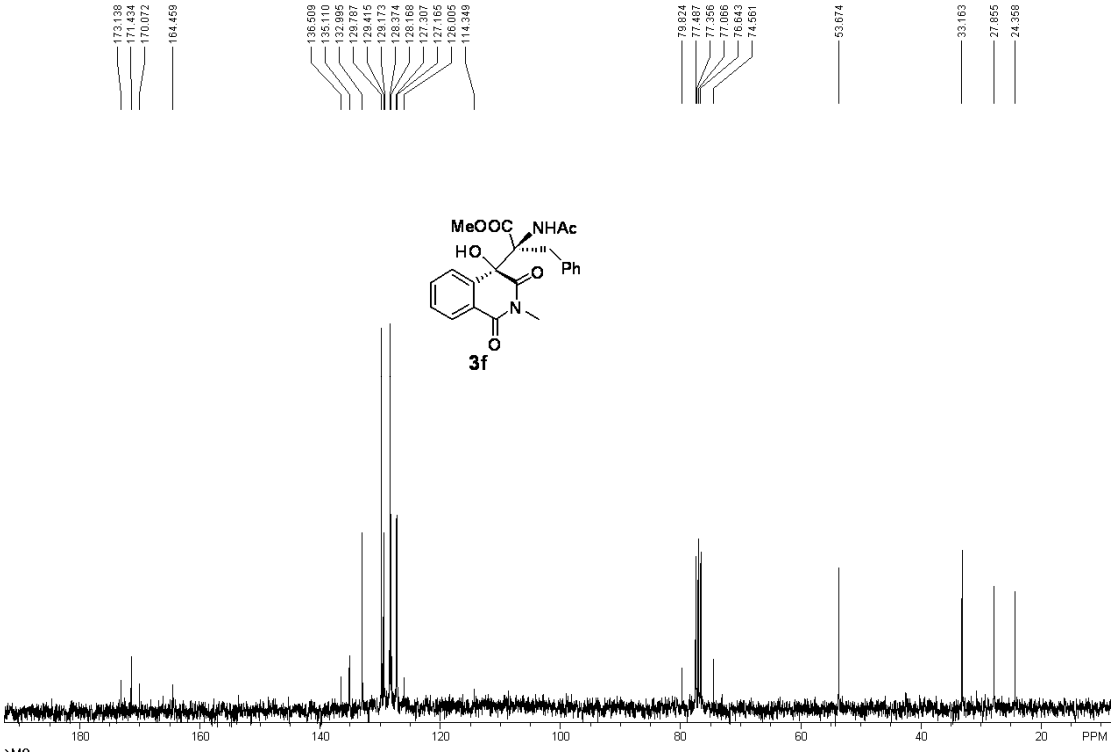
4e-^{13}C NMR($CDCl_3$):



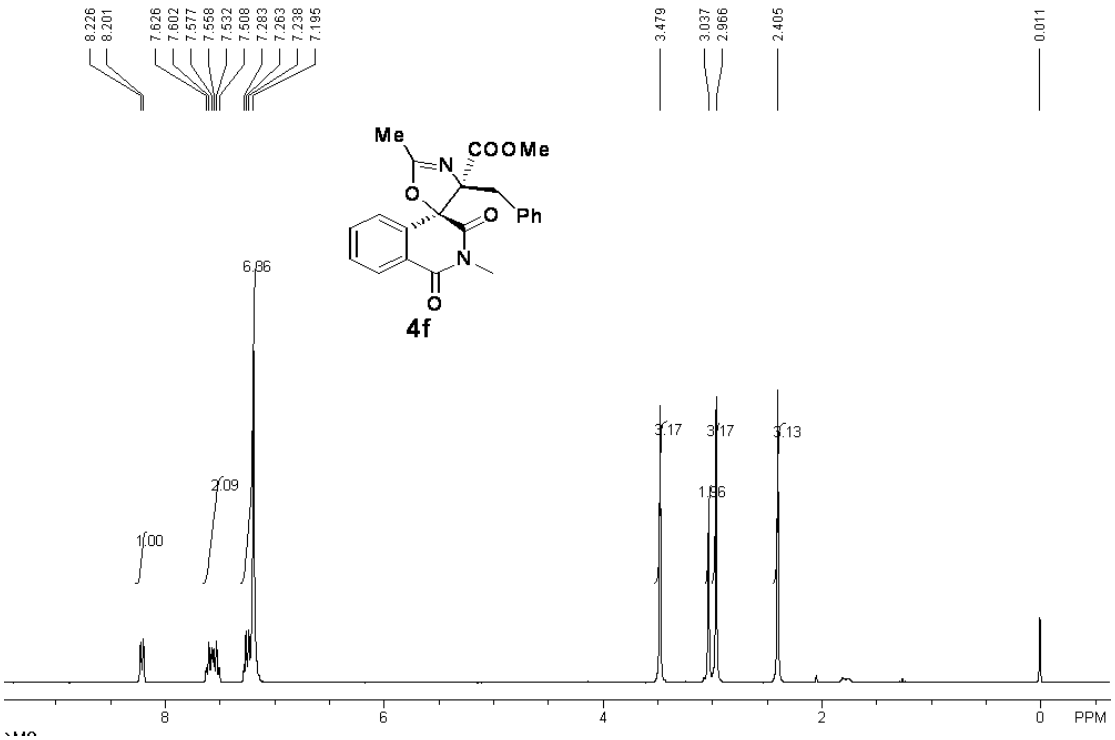
3f-^{1}H NMR($CDCl_3$):



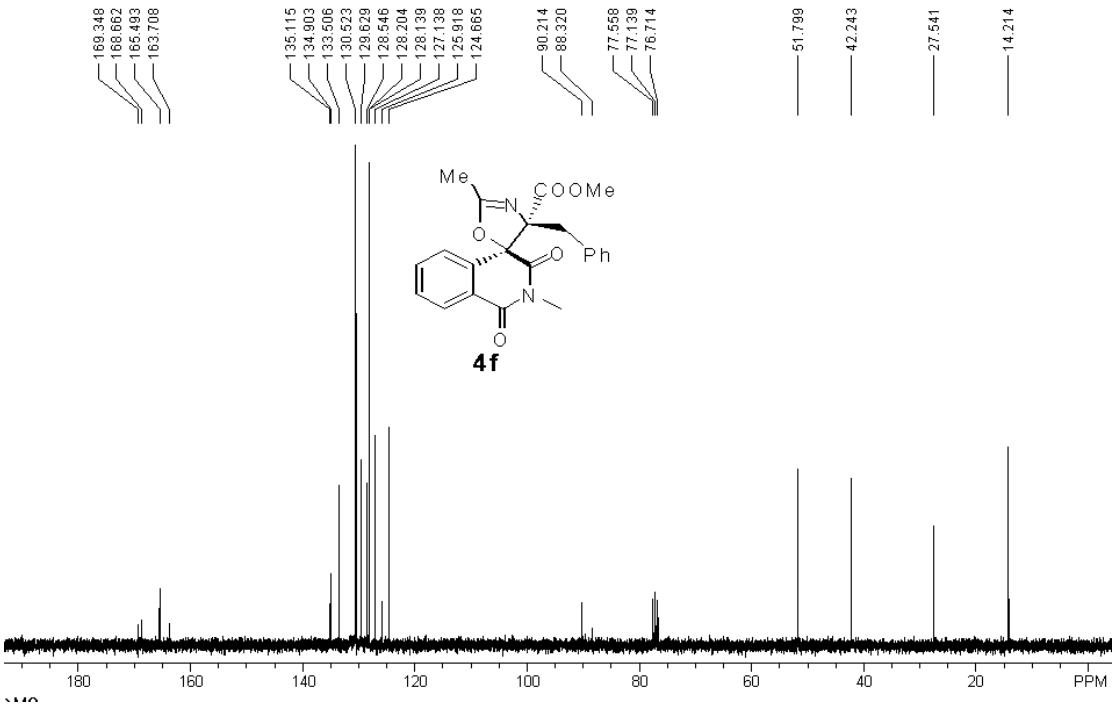
3f-^{13}C NMR($CDCl_3$):



4f-^{1}H NMR($CDCl_3$):

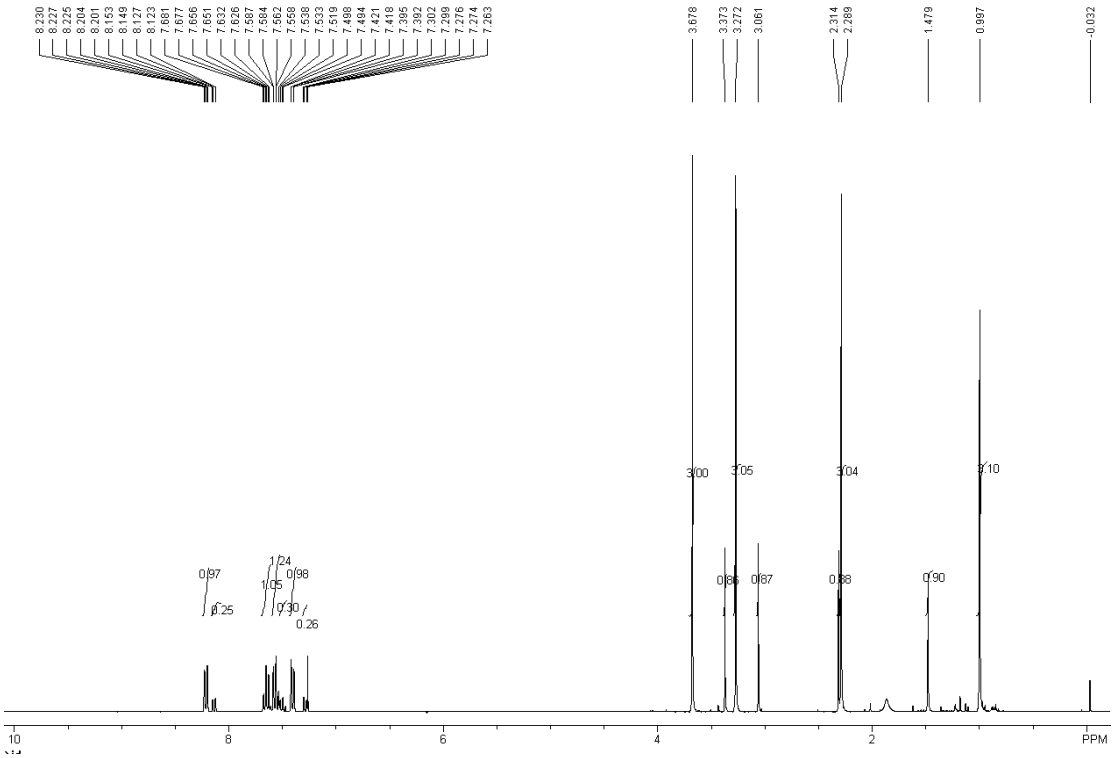


4f-^{13}C NMR($CDCl_3$):

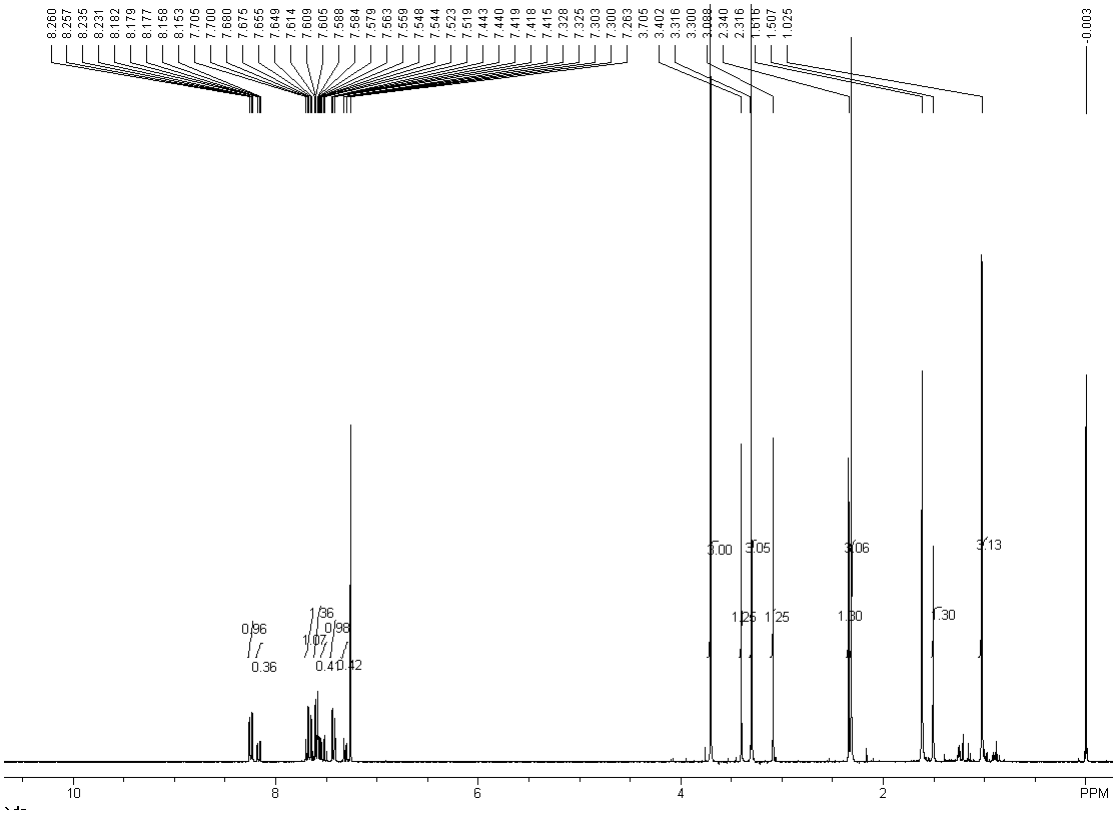


^{1}HNMR of crude products from different acids catalyzed transformation of 2b to 4b:

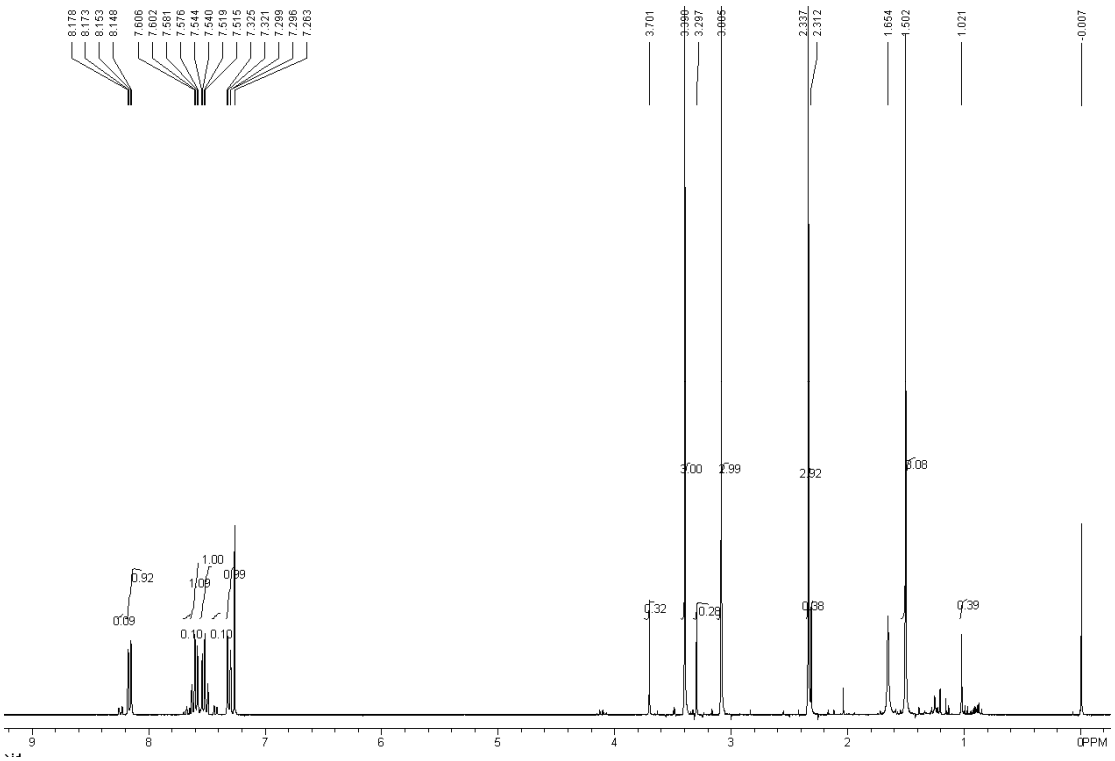
2b treated with 0.15eq. $BF_3{\cdot}OEt_2$



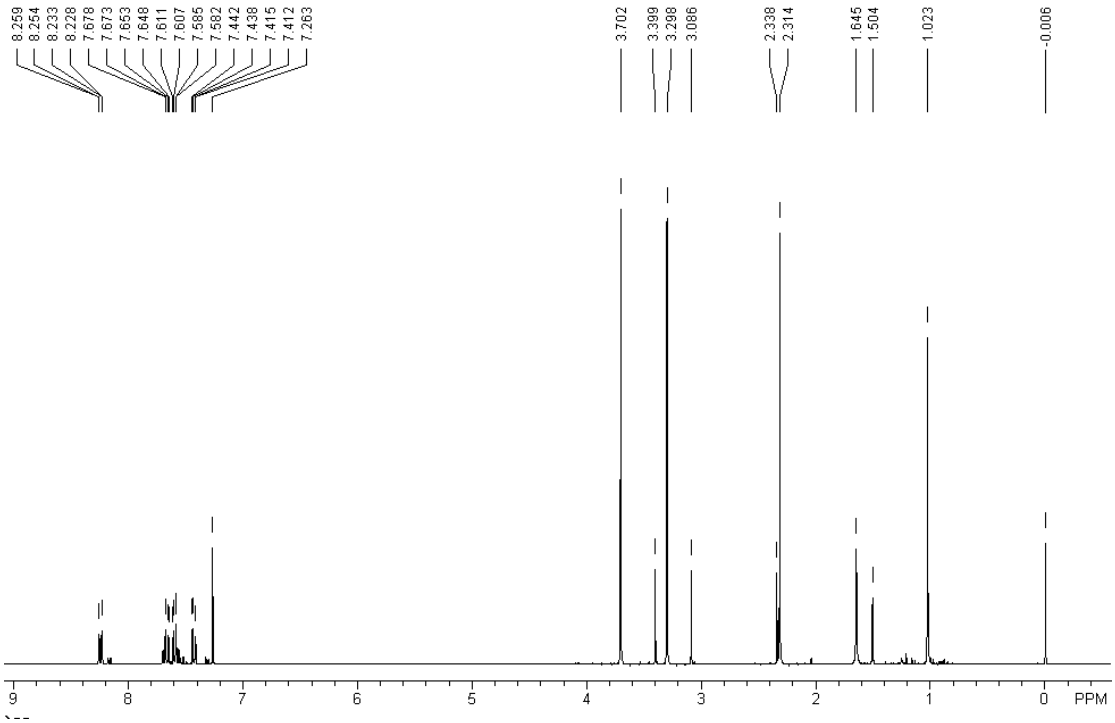
2b treated with 10eq. $BF_3{\cdot}OEt_2$



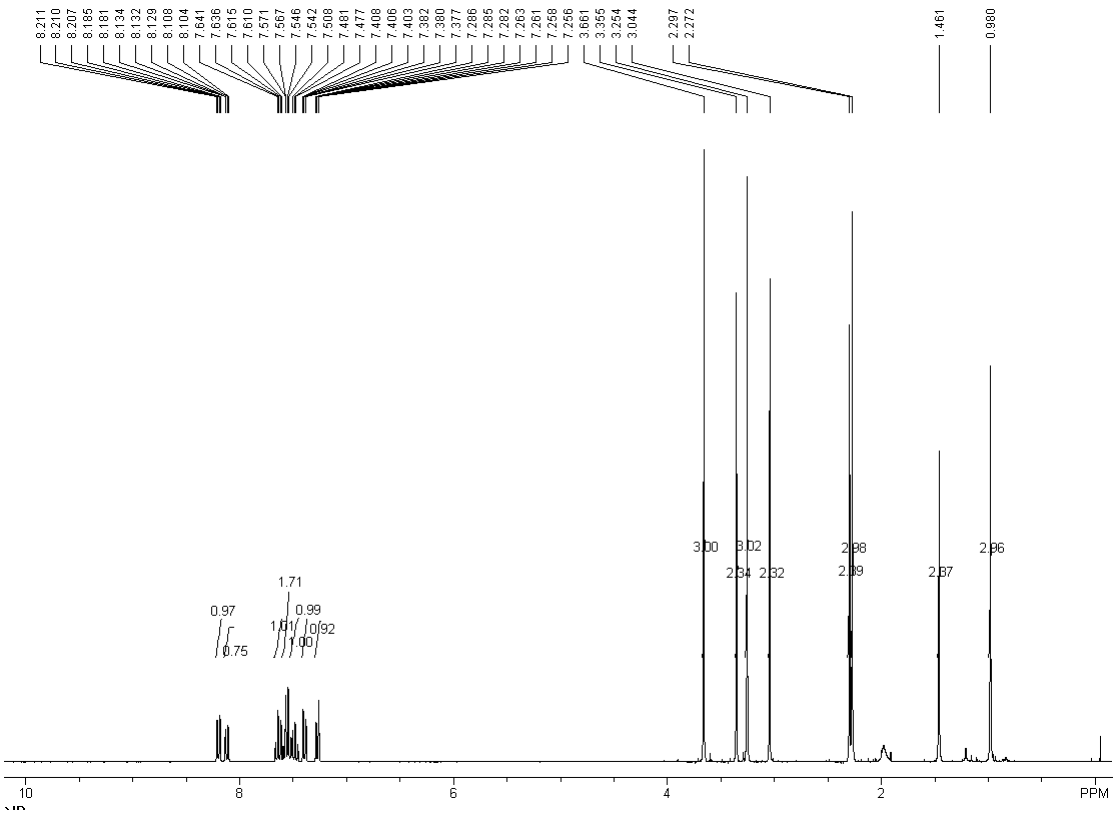
2b treated with 0.15eq. $TiCl_4$



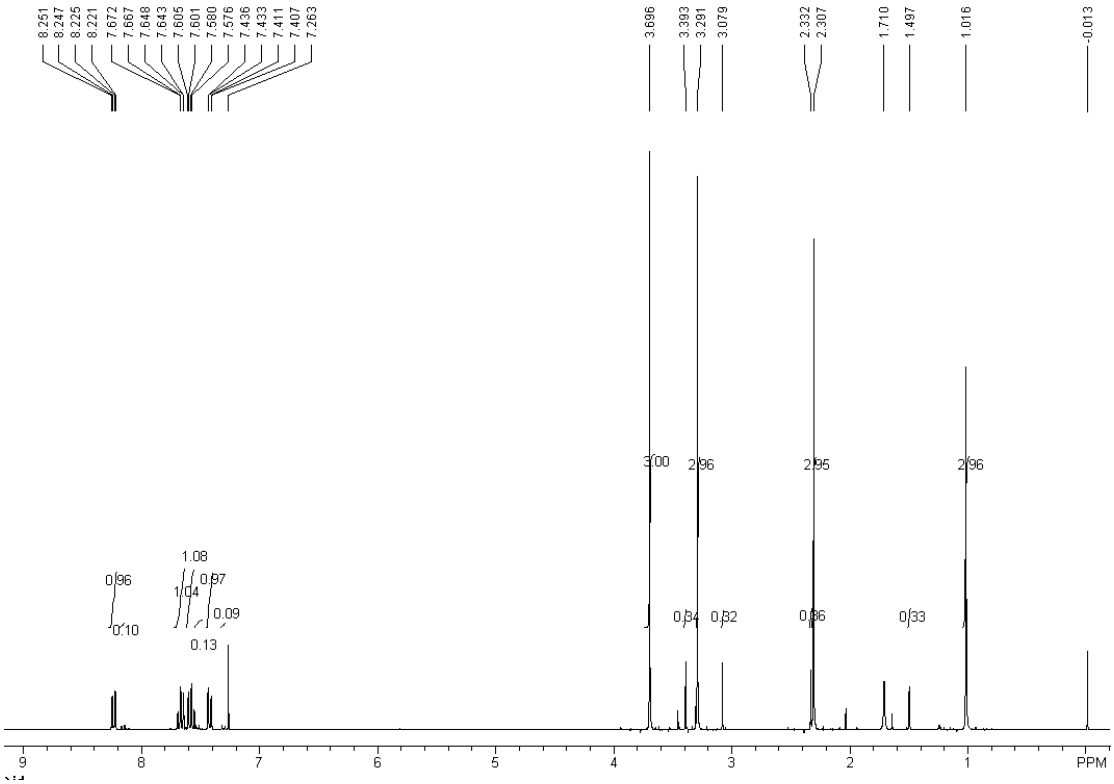
2b treated with 10eq. $TiCl_4$



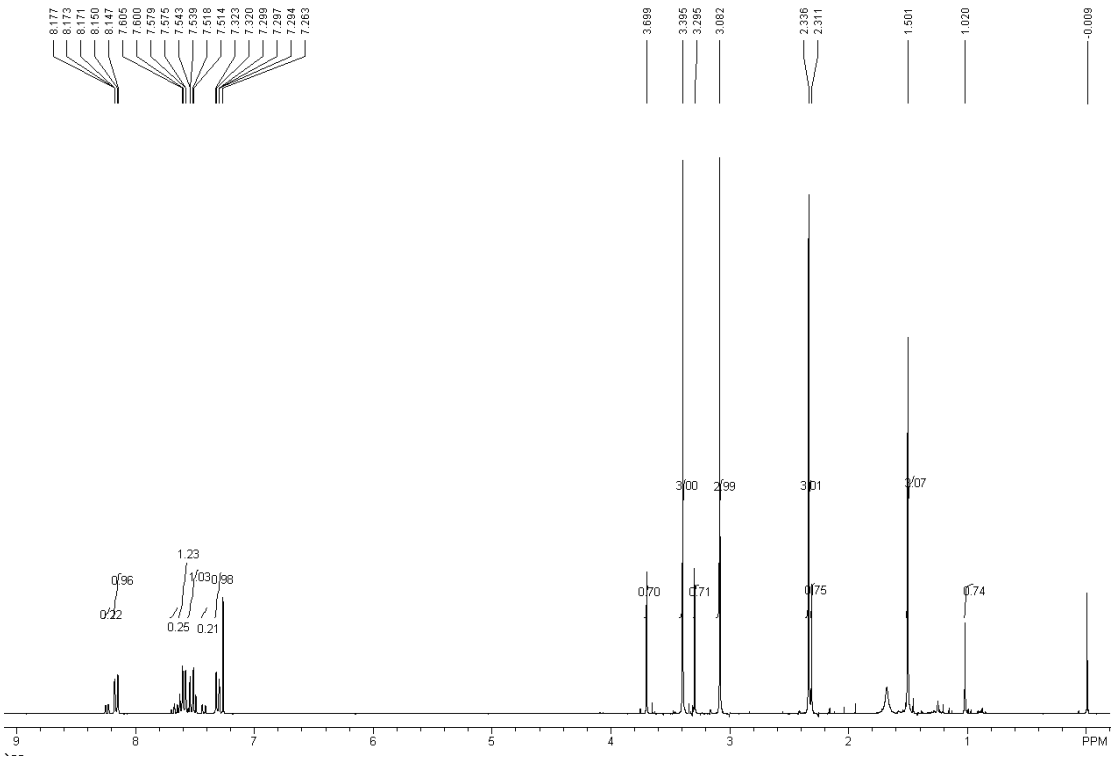
2b treated with 0.15eq. CH_3SO_3H



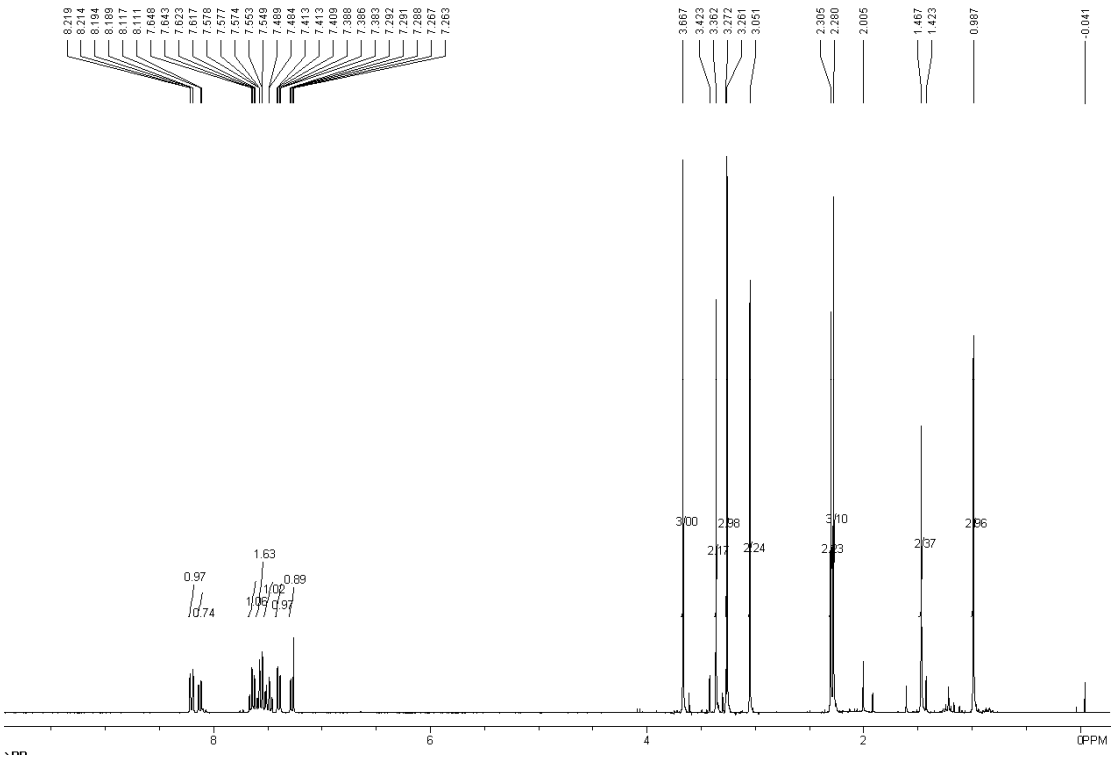
2b treated with 10eq. CH_3SO_3H



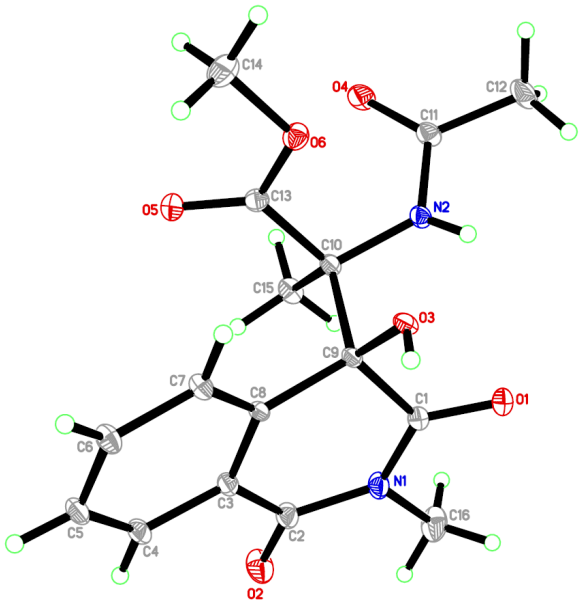
2b treated with 0.5eq. TFA



2b treated with 10eq.TFA



Crystal structure of 3b:



Crystal structure of 4bi: