SUPPORTING INFORMATION

Synthesis and reactivity of furoquinolines bearing an external methylene-bond: access to reduced and spirocyclic structures

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1. General considerations

Dichloromethane was distilled on CaH_2. THF and toluene were distilled on sodium/benzophenone. All other reagents and solvents were used without further purification. ^1H NMR (300 MHz) and ^{13}C-{^1H} NMR (75 MHz) were recorded on a Bruker ACP-300 spectrometer using the residual peak of chloroform-d as internal standard (7.26 ppm for ^1H NMR and 77.16 ppm for ^{13}C NMR). Chemical shifts are reported in ppm and coupling constants J in Hertz. Flash chromatography was performed using 40-63 µm silica. Analytical TLC's were performed on Merck pre-coated silica 60-F254 plates. IR spectra were recorded on a FTIR spectrometer. Compounds **6**, **7**, **8**, **9**, **11**, **13**, **15** and **17** were already described.[1]

2. Procedures description

a. General procedure for silver catalyzed cyclization

To the appropriate quinoline (1 equiv), $[Ag(Im)]_n$ (5 mol%) and PPh_3 (5 mol%) was added the appropriate alcohol (0.5 M). The solution was stirred at rt for 2h (TLC monitoring) and evaporated under vacuum. The crude mixture was purified by flash chromatography on silica gel using mixtures of pentane and diethyl ether to afford the pure product.

b. Procedure for silver catalyzed cyclization using p-methoxybenzylalcohol and p-nitrobenzylalcohol

To the appropriate quinoline (1 equiv), $[Ag(Im)]_n$ (5 mol%) and PPh_3 (5 mol%) were added dichloroethane (0.5 M) and the appropriate benzylalcohol (1.0 equiv). The solution was stirred at rt for 8h (TLC monitoring) and evaporated under vacuum. The crude mixture was purified by flash chromatography on silica gel using mixtures of pentane/diethyl ether (gradient 9:1 to 7:3) to afford the pure product in 79% yield (for p-methoxybenzylalcohol, respectively 73% for *p*-nitrobenzylalcohol).

c. Procedure for reduction by palladium-catalyzed hydrogenation

To a solution of the appropriate furoquinoline (1 equiv.) in degassed (argon bubbling for 5 min) methanol (0.06 M) was added Pd/C (20% in mass). The mixture was stirred under argon bubbling for 5 min and hydrogen was then bubbled for 5 min. The reaction media was then stirred at room temperature for 4h under 1atm of hydrogen. The mixture was flushed with argon and dissolved in ethyl acetate. After filtration through a pad of celite, the filtrate was

[1] T. Godet, C. Vaxelaire, C. Michel, A. Milet and P. Belmont, *Chem. Eur. J.*, 2007, **13**, 5632-5641.

washed with water (x3) and brine. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by preparative TLC or flash chromatography on silica gel using mixtures of cyclohexane and ethyl acetate to afford the pure product.

d. Procedure for Hetero-Diels-Alder reaction with acrolein

In a sealed tube, to a solution of the appropriate furoquinoline (0.2 mmol) in toluene/THF (0.8/0.2 mL) were successively added acrolein (40 µL, 0.6 mmol) and $ZnCl_2$ (1M in Et_2O, 200 µL, 0.2 mmol). The mixture was then stirred at 50°C for 8h, allowed to cool to room temperature and evaporated. The crude product was purified by flash chromatography on silica gel using mixtures of pentane and diethyl ether to afford the pure product.

e. Procedure for [3+2] cycloaddition

In a sealed tube, to a solution of the appropriate furoquinoline (0.2 mmol) in toluene (0.07M, 2.9 mL) were successively added sodium carbonate (106.0 mg, 1.0 mmol) and dibromoformaldoxime (121.7 mg, 0.6 mmol). The mixture was then stirred at room temperature for 16h and water was added. The mixture was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were washed with brine (5 mL) and dried over $MgSO_4$. The crude product was purified by flash chromatography on silica gel using mixtures of pentane and diethyl ether to afford the pure product.

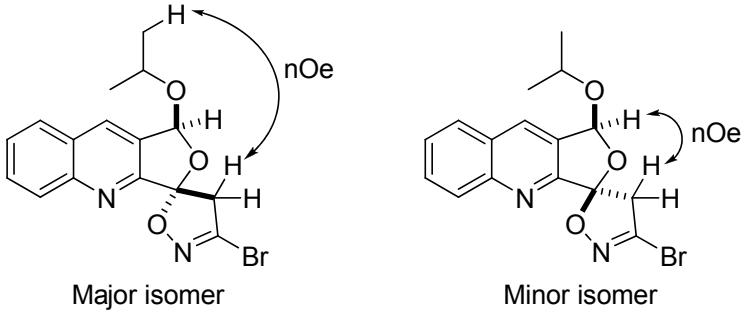
f. Procedure for [4+2] cycloaddition

To a solution of the appropriate furoquinoline (0.2 mmol) in dichloroethane (0.1 M, 2.0 mL) was added sodium carbonate (106.0 mg, 1.0 mmol). The mixture was heated at 50°C and a solution of ethyl 3-bromo-2-(hydroxyimino)propanoate (126.2 mg, 0.6 mmol) in dichloroethane (0.75 mL) was then added via syringe pump over 24 h. $HCl_{aq.}$ 1M (2.5 mL) was added and the mixture was extracted with dichloromethane (3 x 5 mL). The combined organic layers were washed with brine (5 mL) and dried over $MgSO_4$. The crude product was purified by flash chromatography on silica gel using mixtures of pentane and diethyl ether to afford the pure product.

g. Assignment of the diastereoisomers by NOESY experiments

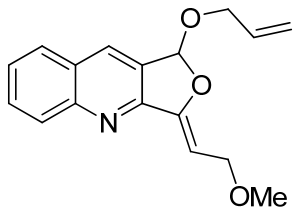
NOESY experiments were run on a single product for each family of compound and assignment was assumed to be correct for the other products. In the [3+2] family, a nOe was

observed in the major isomer between the methyl groups of the *iso*-propyl moiety and the CH_2 of the newly formed cycle, proving the spatial arrangement of this isomer (Scheme 1). In addition, a nOe was found in the minor isomer between the proton in α of the *iso*-propyloxy group and the CH_2 of the newly formed cycle.

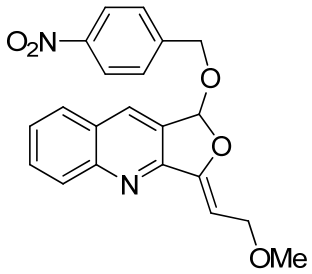


Scheme 1 NOESY experiments proving the spatial arrangement of the isomers.

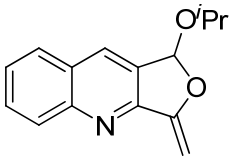
3. Description of products



According to the procedure described above, **10** was isolated in 95% yield (yellow solid).
^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 8.20 (s, 1H), 8.13 (d, 1H, *J* = 8.5 Hz), 7.84 (d, 1H, *J* = 8.1 Hz), 7.75 (t, 1H, *J* = 7.1 Hz), 7.54 (t, 1H, *J* = 7.2 Hz), 6.59 (s, 1H), 6.06-5.95 (m, 1H), 5.95 (t, 1H, *J* = 7.2 Hz), 5.36 (dd, 1H, *J* = 1.4, 17.2 Hz), 5.25 (dd, 1H, *J* = 1.0, 10.4 Hz), 4.42-4.25 (m, 4H), 3.42 (s, 3H).
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): δ (ppm) = 153.5, 153.0, 150.0, 133.7, 131.6, 130.7, 129.7, 129.4, 128.6, 127.9, 127.0, 118.2, 103.2, 97.6, 69.2, 66.3, 57.9.
HRMS(ESI$^+$) m/z calculated for (MH^+): 284.1281. Found: 284.1281.
SM (ESI$^+$): 284 (MH^+).
IR (CH_2Cl_2): ν 2928, 1726, 1627, 1505, 1264 cm^{-1}.

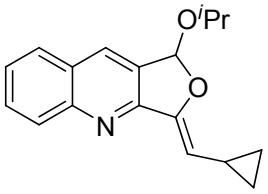


According to the procedure described above, **12** was isolated in 73% yield (yellow solid).
^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 8.24 (s, 1H), 8.22 (d, 2H, *J* = 8.8 Hz), 8.17 (d, 1H, *J* = 8.7 Hz), 7.88 (d, 1H, *J* = 8.1 Hz), 7.80 (dt, 1H, *J* = 1.4, 7.1, 8.5 Hz), 7.59 (dt, 1H, *J* = 1.4, 7.0, 8.0 Hz), 7.55 (d, 2H, *J* = 8.7 Hz), 6.72 (s, 1H), 6.00 (t, 1H, *J* = 7.3 Hz), 4.91 (AB system, 2H), 4.37-4.23 (m, 2H), 3.41 (s, 3H).
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): δ (ppm) = 153.1, 152.6, 150.0, 147.5, 144.8, 131.7, 130.9, 129.6, 128.7, 128.6, 128.0, 127.7, 127.2, 123.6, 103.4, 98.0, 68.4, 66.2, 58.0.
HRMS(ESI$^+$) m/z calculated for (MH^+): 379.1288. Found: 379.1302.
SM (ESI$^+$): 379 (MH^+).
IR (CH_2Cl_2): ν 2928, 2824, 1690, 1626, 1608, 1524, 1348 cm^{-1}.

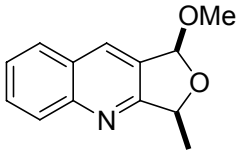


According to the procedure described above, **14** was isolated in >99% yield (yellow solid).
^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 8.06 (d, 1H, *J* = 8.5 Hz), 8.00 (s, 1H), 7.69 (d, 1H, *J* = 8.2 Hz), 7.63 (t, 1H, *J* = 8.4 Hz), 7.41 (t, 1H, *J* = 7.5 Hz), 6.45 (s, 1H), 5.30 (d, 1H, *J* = 1.9

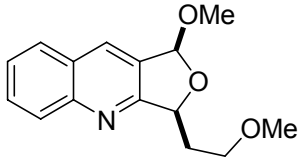
Hz), 4.74 (d, 1H, *J* = 1.9 Hz), 4.13 (sept, 1H, *J* = 6.2 Hz), 1.28 (d, 3H, *J* = 6.2 Hz), 1.25 (d, 3H, *J* = 6.2 Hz).
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): δ (ppm) = 157.0, 153.4, 149.7, 131.2, 130.3, 129.9, 129.4, 128.3, 127.7, 126.7, 102.4, 83.6, 71.9, 23.5, 22.3.
HRMS(ESI$^+$) m/z calculated for (MH^+): 242.1176. Found: 242.1175.
SM (ESI$^+$): 242 (MH^+).
IR (CH_2Cl_2): ν 2975, 1784, 1631, 1605, 1506 cm^{-1}.



According to the procedure described above, **16** was isolated in 96% yield (yellow solid).
^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 8.10 (s, 1H), 8.04 (d, 1H, *J* = 8.5 Hz), 7.79 (d, 1H, *J* = 8.1 Hz), 7.68 (t, 1H, *J* = 8.3 Hz), 7.47 (t, 1H, *J* = 7.2 Hz), 6.62 (s, 1H), 5.33 (d, 1H, *J* = 10.1 Hz), 4.23 (sept, 1H, *J* = 6.2 Hz), 2.00-1.88 (m, 1H), 1.36 (d, 3H, *J* = 3.0 Hz), 1.34 (d, 3H, *J* = 3.0 Hz), 0.91 (dd, 2H, *J* = 2.2, 8.1 Hz), 0.67-0.57 (m, 2H).
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): δ (ppm) = 153.9, 150.4, 149.8, 131.3, 130.3, 129.8, 129.2, 128.5, 127.6, 126.3, 107.0, 102.6, 71.9, 23.8, 22.6, 8.7, 7.9, 7.7.
HRMS(ESI$^+$) m/z calculated for (MH^+): 282.1489. Found: 282.1491.
SM (ESI$^+$): 282 (MH^+).
IR (CH_2Cl_2): ν 2977, 2930, 1683, 1627, 1506, 1416, 1373 cm^{-1}.



According to the procedure described above, **18** was obtained as a mixture of diastereoisomers 88:12 in 73% yield. The major isomer was isolated pure in 46% yield (yellow oil).
^{1}H NMR ($CDCl_3$, 300 MHz): Major isomer δ (ppm) = 8.13 (s, 1H), 8.11 (d, *J* = 8.6 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.73 (ddd, *J* = 1.3, 6.9, 8.6 Hz, 1H), 7.53 (ddd, *J* = 0.9, 6.9, 8.1 Hz, 1H), 6.21 (s, 1H), 5.31 (q, *J* = 6.7 Hz, 1H), 3.54 (s, 3H), 1.70 (d, *J* = 6.7 Hz, 3H).
Minor isomer δ (ppm) (selected peak) = 6.22 (s, 1H).
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): Major isomer δ (ppm) = 164.5, 149.3, 131.4, 130.2, 129.3 (2C), 128.6, 127.5, 126.5, 104.8, 78.9, 54.8, 22.1.
HRMS(ESI$^+$) m/z calculated for (MH^+): 216.1015. Found: 216.1019.
GC/MS: m/z $C_{13}H_{13}NO_2$ ($MH^{+\bullet}$) 215.
IR (neat): ν 2976, 2927, 2826, 1632, 1504, 1306 cm^{-1}.



According to the procedure described above, **19** was obtained as a mixture of diastereoisomers 89:11 in 71% yield. The major isomer was isolated pure in 45% yield (yellow solid).

^{1}H NMR ($CDCl_3$, 500 MHz): Major isomer δ (ppm) = 8.15 (s, 1H), 8.11 (d, *J* = 8.7 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.74 (ddd, *J* = 1.6, 7.0, 8.7 Hz, 1H), 7.54 (ddd, *J* = 1.1, 7.0, 7.6 Hz, 1H), 6.22 (s, 1H), 5.33 (dd, *J* = 3.7, 9.0 Hz, 1H), 3.77-3.70 (part of AB system, 1H), 3.69-3.67 (part of AB system, 1H), 3.58 (s, 3H), 3.39 (s, 3H), 2.48-2.42 (part of AB system, 1H), 2.12-2.04 (part of AB system, 1H)

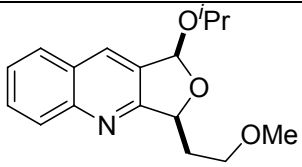
Minor isomer δ (ppm) (selected peak) = 6.26 (s, 1H).

^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz): Major isomer δ (ppm) = 164.4, 149.4, 131.4, 130.2, 129.4, 129.3, 128.6, 127.5, 126.6, 105.0, 79.8, 69.4, 58.8, 55.3, 36.6.

HRMS(EI) m/z calculated for ($M^{+\bullet}$): 259.1208. Found: 259.1209.

GC/MS: m/z $C_{15}H_{17}NO_3$ ($MH^{+\bullet}$) 259.

IR (neat): *ν* 2956, 2921, 2883, 2829, 1631, 1580, 1504, 1420 cm^{-1}.



According to the procedure described above, **20** was obtained as a mixture of diastereoisomers 94:6 in 75% yield. The major isomer was isolated pure in 49% yield (yellow solid).

^{1}H NMR ($CDCl_3$, 300 MHz): Major isomer δ (ppm) = 8.11 (s, 1H), 8.09 (d, *J* = 8.7 Hz, 1H), 7.85 (dd, *J* = 1.0, 8.1 Hz, 1H), 7.72 (ddd, *J* = 1.4, 7.0, 8.7 Hz, 1H), 7.52 (ddd, *J* = 1.0, 7.0, 8.1 Hz, 1H), 6.37 (s, 1H), 5.29 (dd, *J* = 3.9, 8.9 Hz, 1H), 4.23 (sept, *J* = 6.2 Hz, 1H), 3.80-3.68 (part of AB system, 1H), 3.67-3.62 (part of AB system, 1H), 3.38 (s, 3H), 2.49-2.38 (part of AB system, 1H), 2.18-2.06 (part of AB system, 1H) .

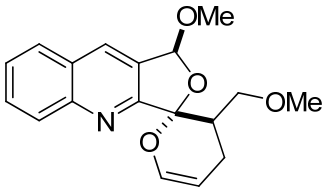
Minor isomer δ (ppm) (selected peak) = 6.40 (s, 1H).

^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz): Major isomer δ (ppm) = 164.7, 149.3, 131.2, 130.2, 130.1, 129.3, 128.6, 127.7, 126.5, 102.7, 79.6, 71.0, 69.4, 58.8, 36.7, 23.9, 22.4.

HRMS(ESI$^+$) m/z calculated for (MH^+): 288.1591. Found: 288.1594.

GC/MS: m/z $C_{17}H_{21}NO_3$ ($M^{+\bullet}$) 287.

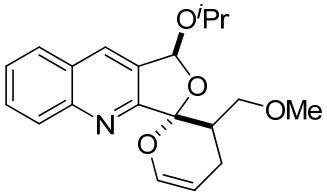
IR (neat): *ν* 2963, 2918, 2868, 2823, 1630, 1504, 1332 cm^{-1}.



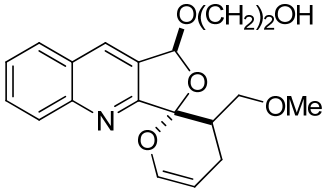
According to the procedure described above, **21** was isolated in 80% yield as a single isomer (white solid).

^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 8.24 (d, 1H, *J* = 8.5 Hz), 8.20 (s, 1H), 7.88 (d, 1H, *J* = 8.1 Hz), 7.76 (t, 1H, *J* = 7.6 Hz), 7.58 (t, 1H, *J* = 7.4 Hz), 6.43 (d, 1H, *J* = 7.9 Hz), 6.39 (s, 1H), 5.05 (t, 1H, *J* = 5.1 Hz), 3.66 (s, 3H), 3.24-3.00 (m, 3H), 3.00 (s, 3H), 2.43-2.34 (m, 1H), 2.22-2.12 (m, 1H).

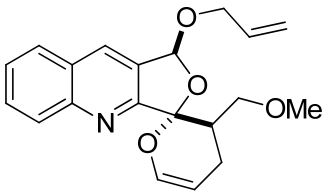
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): δ (ppm) = 159.7, 149.9, 141.4, 131.9, 130.4, 130.1, 129.5, 128.5, 128.3, 127.3, 105.9, 104.5, 101.4, 73.2, 58.4, 56.3, 37.8, 20.9.
HRMS(ESI$^+$) m/z calculated for (MH^+): 314.1387. Found: 314.1383.
SM (ESI$^+$): 314 (MH^+).
IR (CH_2Cl_2): ν 2929, 1658, 1630, 1505, 1447, 1397 cm^{-1}.



According to the procedure described above, **22** was isolated in 89% yield as a single isomer (white solid).
^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 8.23 (d, 1H, *J* = 8.4 Hz), 8.17 (s, 1H), 7.88 (d, 1H, *J* = 8.1 Hz), 7.75 (ddd, 1H, *J* = 1.3, 6.9, 8.4 Hz), 7.57 (ddd, 1H, *J* = 1.0, 6.9, 8.0 Hz), 6.58 (s, 1H), 6.43 (dd, 1H, *J* = 1.4, 6.2 Hz), 5.04 (dt, 1H, *J* = 1.9, 5.9 Hz), 4.26 (sept, 1H, *J* = 6.2 Hz), 3.28-3.22 (m, 1H), 3.17-3.12 (m, 1H), 3.04-2.96 (m, 1H), 3.03 (s, 3H), 2.43-2.34 (m, 1H), 2.21-2.10 (m, 1H), 1.35 (d, 6H, *J* = 6.2 Hz).
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): δ (ppm) = 159.7, 149.9, 141.5, 131.7, 130.2, 130.1, 128.5, 128.3, 127.1, 105.8, 102.5, 101.3, 73.3, 72.2, 58.5, 38.0, 24.0, 22.5, 21.0.
HRMS(ESI$^+$) m/z calculated for (MH^+): 342.1700. Found: 342.1697.
SM (ESI$^+$): 342 (MH^+).
IR (CH_2Cl_2): ν 2977, 2927, 1658, 1631, 1506, 1401, 1383 cm^{-1}.



According to the procedure described above, **23** was isolated in 68% yield as a single isomer (white solid).
^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 8.24 (s, 1H), 8.23 (d, 1H, *J* = 8.8 Hz), 7.89 (d, 1H, *J* = 8.3 Hz), 7.77 (ddd, 1H, *J* = 1.3, 6.9, 8.4 Hz), 7.59 (ddd, 1H, *J* = 1.1, 7.0, 8.0 Hz), 6.52 (s, 1H), 6.43-6.39 (m, 1H), 5.04 (dt, 1H, *J* = 2.1, 5.9 Hz), 4.10-3.94 (m, 2H), 3.85 (t, 2H, *J* = 4.3 Hz), 3.21-3.19 (m, 2H), 3.09-2.98 (m, 1H), 3.02 (s, 3H), 2.40-2.30 (m, 1H), 2.26-2.15 (m, 1H).
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): δ (ppm) = 159.5, 149.9, 141.3, 132.1, 130.5, 130.1, 129.3, 128.6, 128.3, 127.4, 106.0, 104.3, 101.5, 73.0, 72.0, 62.3, 58.6, 37.8, 20.8.
HRMS(ESI$^+$) m/z calculated for (MH^+): 344.1492. Found: 344.1500.
SM (ESI$^+$): 344 (MH^+).
IR (CH_2Cl_2): ν 2928, 2882, 1658, 1631, 1506, 1397 cm^{-1}.



According to the procedure described above, **24** was isolated in 73% yield as a single isomer (white solid).

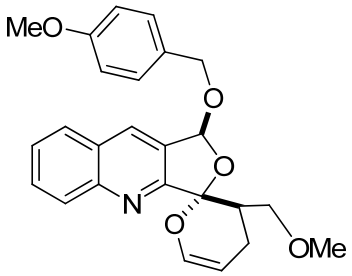
^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 8.25 (d, 1H, *J* = 8.8 Hz), 8.22 (s, 1H), 7.89 (d, 1H, *J* = 8.3 Hz), 7.76 (ddd, 1H, *J* = 1.5, 6.9, 8.4 Hz), 7.59 (ddd, 1H, *J* = 1.1, 7.0, 8.1 Hz), 6.53 (s, 1H), 6.43 (ddd, 1H, *J* = 1.2, 1.3, 6.2 Hz), 6.10-5.97 (m, 1H), 5.39 (dq, 1H, *J* = 1.6, 17.2 Hz), 5.26 (dq, 1H, *J* = 1.2, 10.4 Hz), 5.05 (dt, 1H, *J* = 1.9, 5.9 Hz), 4.53-4.29 (AB system, 2H), 3.26-3.20 (m, 1H), 3.16-3.11 (m, 1H), 3.07-2.97 (m, 1H), 3.01 (s, 3H), 2.44-2.34 (m, 1H), 2.23-2.11 (m, 1H).

^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): δ (ppm) = 159.8, 150.0, 141.4, 134.1, 131.9, 130.4, 130.1, 129.6, 128.5, 128.3, 127.2, 117.8, 106.0, 103.0, 101.4, 73.3, 69.8, 58.5, 38.0, 20.9.

HRMS(ESI$^+$) m/z calculated for (MH^+): 340.1543. Found: 340.1551.

SM (ESI$^+$): 340 (MH^+).

IR (CH_2Cl_2): ν 2926, 2893, 1658, 1631, 1506, 1399 cm^{-1}.



According to the procedure described above, **25** was isolated in 65% yield as a single isomer (colorless oil that crystallized on standing).

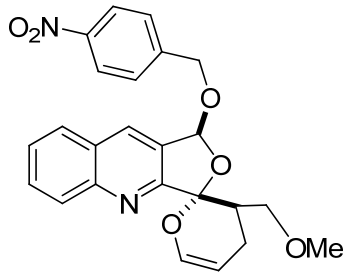
^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 8.24 (d, 1H, *J* = 8.5 Hz), 8.18 (s, 1H), 7.87 (d, 1H, *J* = 8.0 Hz), 7.76 (t, 1H, *J* = 8.1 Hz), 7.58 (t, 1H, *J* = 7.5 Hz), 7.38 (d, 2H, *J* = 8.5 Hz), 6.92 (d, 2H, *J* = 8.5 Hz), 6.59 (s, 1H), 6.46 (dd, 1H, *J* = 1.2, 6.0 Hz), 5.05 (dt, 1H, *J* = 1.6, 5.8 Hz), 4.88 (AB system, 2H), 3.81 (s, 3H), 3.26-3.00 (m, 3H), 3.00 (s, 3H), 2.47-2.37 (m, 1H), 2.25-2.15 (m, 1H).

^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): δ (ppm) = 159.6, 149.9, 141.4, 132.0, 131.9, 130.4, 130.0, 129.9, 129.6, 129.5, 128.5, 128.2, 127.2, 114.0, 106.0, 102.7, 101.4, 73.2, 70.7, 58.5, 55.4, 37.9, 20.9.

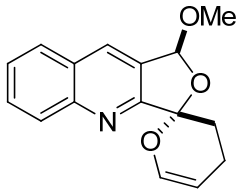
HRMS(ESI$^+$) m/z calculated for (MH^+): 420.1805. Found: 420.1817.

SM (ESI$^+$): 420 (MH^+).

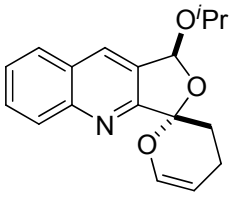
IR (CH_2Cl_2): ν 2926, 1658, 1631, 1607, 1505, 1392 cm^{-1}.



According to the procedure described above, **26** was isolated in 74% yield as a single isomer (colorless oil that crystallized on standing).
^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 8.27-8.22 (m, 4Hz), 7.92 (dd, 1H, *J* = 0.7, 7.4 Hz), 7.80 (ddd, 1H, *J* = 1.5, 7.0, 8.4 Hz), 7.65-7.58 (m, 3H), 6.63 (s, 1H), 6.44 (dd, 1H, *J* = 1.4, 6.2 Hz), 5.07 (dt, 1H, *J* = 2.0, 6.0 Hz), 5.04 (AB system, 2H), 3.21-3.02 (m, 3H), 2.98 (s, 3H), 2.43-2.33 (part of AB system, 1H), 2.19-2.08 (part of AB system, 1H).
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): δ (ppm) = 159.5, 150.0, 147.6, 145.0, 141.4, 132.0, 130.7, 130.1, 129.0, 128.6, 128.4, 128.1, 127.5, 123.9, 106.3, 103.3, 101.4, 73.2, 69.4, 58.5, 37.7, 20.9.
HRMS(ESI$^+$) m/z calculated for (MH^+): 435.1551. Found: 435.1543.
SM (ESI$^+$): 435 (MH^+).
IR (CH_2Cl_2): ν 3057, 2926, 1658, 1631, 1607, 1524, 1348 cm^{-1}.

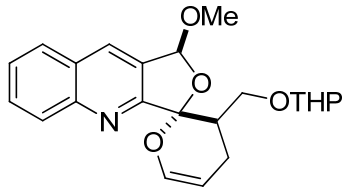


According to the procedure described above, **27** was isolated in 76% yield (white solid).
^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 8.24 (d, 1H, *J* = 9.6 Hz), 8.23 (s, 1H), 7.92 (d, 1H, *J* = 8.2 Hz), 7.78 (ddd, 1H, *J* = 1.2, 7.0, 9.6 Hz), 7.63 (dd, 1H, *J* = 1.2, 7.0, 8.2 Hz), 6.49 (d, 1H, *J* = 8.5 Hz), 6.47 (s, 1H), 5.05 (dd, 1H, *J* = 4.7, 6.2 Hz), 3.59 (s, 3H), 2.60-2.54 (m, 2H), 2.10 (m, 1H), 2.05 (m, 1H).
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): δ (ppm) = 160.9, 150.5, 142.2, 132.9, 132.4, 130.8, 130.2, 129.1, 127.7, 105.0, 104.3, 102.2, 55.7, 30.5, 17.0.
HRMS(ESI$^+$) m/z calculated for (MH^+): 270.1125. Found: 270.1128.
SM (ESI$^+$): 270 (MH^+).
IR (CH_2Cl_2): ν 2933, 2852, 1654, 1631, 1506, 1399, 1297 cm^{-1}.

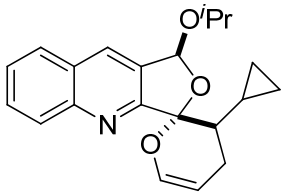


According to the procedure described above, **28** was isolated in 81% yield (white solid).
^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 8.21 (d, 1H, *J* = 9.0 Hz), 8.19 (s, 1H), 7.88 (d, 1H, *J* = 8.1 Hz), 7.77 (t, 1H, *J* = 7.5 Hz), 7.57 (t, 1H, *J* = 7.5 Hz), 6.58 (s, 1H), 6.47 (d, 1H, *J* = 5.9

Hz), 5.02 (t, 1H, *J* = 5.6 Hz), 4.23 (sept, 1H, *J* = 6.1 Hz), 2.63-2.46 (m, 2H), 2.32-2.06 (m, 2H).
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): δ (ppm) = 160.8, 149.7, 142.0, 131.8, 130.3, 130.2, 130.0, 128.5, 128.4, 127.2, 104.7, 102.1, 101.8, 71.7, 30.5, 23.9, 22.6, 16.8.
HRMS(ESI$^+$) m/z calculated for (MNa^+): 320.1257. Found: 320.1261.
SM (ESI$^+$): 320 (MNa^+).
IR (CH_2Cl_2): ν 2975, 2931, 2851, 1654, 1632, 1506, 1400, 1384, 1332, 1294 cm^{-1}.

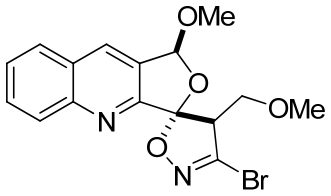


According to the procedure described above, **29** was isolated in 86% yield (white solid).
Presence of 2 diastereoisomers (50:50) due to the presence of a THP group.
^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 8.24-8.17 (m, 2H), 7.86 (d, 1H, *J* = 8.1 Hz), 7.74 (ddd, 1H, *J* = 1.3, 7.1, 8.2 Hz), 7.56 (ddd, 1H, *J* = 1.1, 7.0, 8.0 Hz), 6.45-6.38 (m, 2H), 5.04 (dt, 1H, *J* = 1.9, 5.9 Hz), 4.41 (t, 1H, *J* = 3.2 Hz, 50%), 4.13 (t, 1H, *J* = 3.2 Hz, 50%), 3.64 (s, 3H), 3.61-3.15 (m, 4H), 3.03 (sept, 1H, *J* = 6.1 Hz), 2.42-2.10 (m, 2H), 1.38-0.55 (m, 6H).
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): δ (ppm) = 160.1, 159.8, 149.9, 141.4, 131.7, 131.6, 130.2, 130.0, 129.6, 129.5, 128.4, 128.4, 128.3, 128.2, 127.2, 127.1, 106.3, 106.1, 104.6, 104.5, 101.4, 101.2, 98.5, 98.1, 67.8, 67.7, 61.6, 61.5, 56.3, 56.2, 38.4, 38.3, 30.4, 30.2, 30.0, 29.8, 25.4, 25.3, 21.0, 20.8, 18.6.
HRMS(ESI$^+$) m/z calculated for (MH^+): 384.1805. Found: 384.1798.
SM (ESI$^+$): 384 (MH^+).
IR (CH_2Cl_2): ν 2941, 2878, 2852, 1658, 1631, 1506, 1398, 1355, 1299 cm^{-1}.

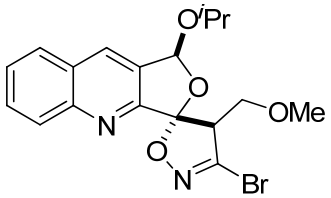


According to the procedure described above, **30** was isolated in 75% yield as a single isomer (white solid).
^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 8.21 (d, 1H, *J* = 8.8 Hz), 8.20 (s, 1H), 7.90 (d, 1H, *J* = 8.1 Hz), 7.75 (ddd, 1H, *J* = 1.1, 6.9, 8.1 Hz), 7.59 (ddd, 1H, *J* = 1.0, 7.0, 8.0 Hz), 6.63 (s, 1H), 6.43-6.40 (m, 1H), 5.00 (dt, 1H, *J* = 2.0, 5.9 Hz), 4.29 (sept, 1H, *J* = 6.1 Hz), 2.42-2.20 (m, 2H), 1.89-1.79 (m, 1H), 1.84 (ddd, 1H, *J* = 6.0, 6.0, 9.8 Hz), 1.35 (d, 3H, *J* = 5.2 Hz), 1.34 (d, 3H, *J* = 5.2 Hz), 0.79-0.67 (m, 1H), 0.35-0.26 (m, 1H), 0.10-0.02 (m, 1H), (-)0.24- (-)0.35 (m, 2H).
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): δ (ppm) = 160.2, 149.6, 141.4, 131.6, 130.6, 130.2, 129.9, 128.5, 128.3, 127.1, 108.1, 102.6, 101.9, 72.1, 43.5, 24.0, 23.6, 22.5, 11.7, 5.2, 2.5.
HRMS(ESI$^+$) m/z calculated for (MH^+): 338.1751. Found: 338.1754.
SM (ESI$^+$): 338 (MH^+).

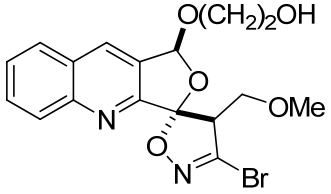
IR (CH_2Cl_2): ν 2976, 2928, 1656, 1632, 1506, 1384, 1294 cm^{-1}.



According to the procedure described above, **31** was isolated in 79% yield (white solid).
Mixture of diastereoisomers 77:23
^{1}H NMR ($CDCl_3$, 300 MHz): Major isomer δ (ppm) = 8.23 (s, 1H), 8.18 (d, 1H, *J* = 8.5 Hz), 7.90 (d, 1H, *J* = 8.1 Hz), 7.78 (t, 1H, *J* = 8.4 Hz), 7.61 (t, 1H, *J* = 8.0 Hz), 6.50 (s, 1H), 4.38 (t, 1H, *J* = 6.2 Hz), 3.83-3.71 (m, 2H), 3.64 (s, 3H), 3.22 (s, 3H). Minor isomer (selected signals) δ (ppm) = 6.28 (s, 1H), 3.50 (s, 3H), 3.14 (s, 3H).
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): Major isomer δ (ppm) = 156.5, 150.0, 140.8, 132.1, 130.9, 130.0, 129.3, 128.6, 128.5, 127.8, 114.4, 105.3, 66.9, 59.0, 56.6, 56.4. Minor isomer (selected signals) δ (ppm) = 157.0, 150.0, 139.7, 113.1, 104.0, 67.3, 59.0, 56.0, 54.3.
HRMS(ESI$^+$) m/z calculated for (MH^+): 379.0288. Found: 379.0286.
SM (ESI$^+$): 379 (MH^+).
IR (CH_2Cl_2): ν 2932, 2838, 1723, 1628, 1584, 1506, 1448, 1397, 1299 cm^{-1}.

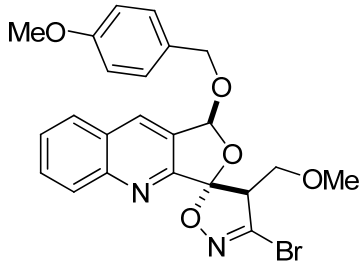


According to the procedure described above, **32** was isolated in 96% yield (white solid).
Mixture of diastereoisomers 84:16
^{1}H NMR ($CDCl_3$, 300 MHz): Major isomer δ (ppm) = 8.21-8.17 (m, 2H), 7.90 (d, 1H, *J* = 8.1 Hz), 7.77 (t, 1H, *J* = 7.5 Hz), 7.60 (t, 1H, *J* = 7.4 Hz), 6.65 (s, 1H), 4.37 (t, 1H, *J* = 6.0 Hz), 4.24 (sept, 1H, *J* = 6.1 Hz), 3.77 (d, 2H, *J* = 6.1 Hz), 3.24 (s, 3H), 1.36 (t, 6H, *J* = 5.7 Hz). Minor isomer (selected signals) δ (ppm) = 6.34 (s, 1H), 3.14 (s, 3H).
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): Major isomer δ (ppm) = 156.5, 150.0, 141.0, 132.0, 130.7, 130.1, 129.9, 128.6, 128.5, 127.7, 114.4, 103.4, 72.9, 67.1, 59.0, 56.6, 23.8, 22.5.
HRMS(ESI$^+$) m/z calculated for (MH^+): 407.0601. Found: 407.0599.
SM (ESI$^+$): 407 (MH^+).
IR (CH_2Cl_2): ν 2977, 2929, 1724, 1628, 1583, 1506, 1467, 1385, 1337, 1295 cm^{-1}.

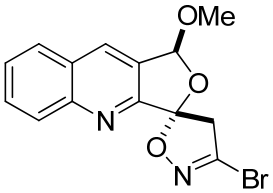


According to the procedure described above, **33** was isolated in 85% yield (white solid).
Mixture of diastereoisomers 58:42

^{1}H NMR ($CDCl_3$, 300 MHz): mixture of isomers δ (ppm) = 8.27-8.26 (m, 2H), 8.18 (d, 1H, *J* = 8.4 Hz), 7.80-7.75 (m, 1H), 7.60 (t, 1H, *J* = 7.6 Hz), 6.62 (s, 1H, major isomer), 6.34 (s, 1H, minor isomer), 4.47-4.41 (m, 1H), 4.00-3.69 (m, 6H), 3.20 (s, 3H, major isomer), 3.14 (s, 3H, minor isomer), 2.72 (br s, 1H).
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): Major isomer δ (ppm) = 156.3, 149.9, 140.5, 132.4, 131.0, 129.8, 129.2, 128.7, 128.5, 127.9, 114.3, 104.8, 71.6, 66.8, 61.9, 58.9, 56.1. Minor isomer δ (ppm) = 156.7, 149.8, 140.0, 132.3, 130.9, 129.8, 128.8, 128.7, 128.4, 127.9, 113.2, 103.7, 70.0, 67.1, 62.0, 58.9, 56.0.
HRMS(ESI$^+$) m/z calculated for (MH^+): 409.0394. Found: 409.0388.
SM (ESI$^+$): 409 (MH^+).
IR (CH_2Cl_2): ν 2930, 1725, 1628, 1584, 1507, 1459, 1396, 1298 cm^{-1}.

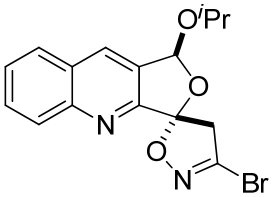


According to the procedure described above, **34** was isolated in 79% yield (white solid).
Mixture of diastereoisomers 77:23
^{1}H NMR ($CDCl_3$, 300 MHz): Major isomer δ (ppm) = 8.20-8.17 (m, 2H), 7.89 (d, 1H, *J* = 8.1 Hz), 7.78 (dt, 1H, *J* = 1.0, 7.2, 8.2 Hz), 7.60 (t, 1H, *J* = 7.1 Hz), 7.36 (d, 2H, *J* = 8.7 Hz), 6.92 (d, 2H, *J* = 8.6 Hz), 6.66 (s, 1H, major isomer), 6.38 (s, 1H, minor isomer), 4.84 (AB system, 2H), 4.40 (dd, 1H, *J* = 5.5, 6.6 Hz), 3.81 (s, 3H), 3.80-3.77 (m, 2H), 3.19 (s, 3H).
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): Major isomer δ (ppm) = 159.6, 156.4, 149.9, 141.0, 132.2, 130.8, 129.9, 129.5, 129.1, 129.0, 128.6, 128.4, 127.8, 114.5, 114.1, 103.3, 70.6, 66.9, 59.1, 56.7, 55.4.
HRMS(ESI$^+$) m/z calculated for (MH^+): 485.0707. Found: 485.0694.
SM (ESI$^+$): 485 (MH^+).
IR (CH_2Cl_2): ν 2930, 1613, 1585, 1514, 1464, 1392, 1342, 1300 cm^{-1}.

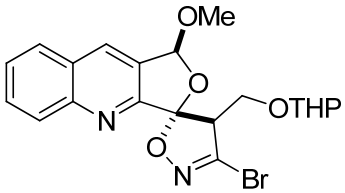


According to the procedure described above, **35** was isolated in 74% yield (white solid).
Mixture of diastereoisomers 77:23
^{1}H NMR ($CDCl_3$, 300 MHz): Major isomer δ (ppm) = 8.25 (s, 1H), 8.20 (d, 1H, *J* = 8.5 Hz), 7.93 (d, 1H, *J* = 8.1 Hz), 7.81 (ddd, 1H, *J* = 1.4, 6.9, 8.4 Hz), 7.64 (ddd, 1H, *J* = 1.1, 6.9, 8.1 Hz), 6.48 (s, 1H), 4.16 (part of AB system, 1H, *J* = 18.2 Hz), 3.59 (s, 3H), 3.51 (part of AB system, 1H, *J* = 18.2 Hz). Minor isomer (selected signals) δ (ppm) = 6.25 (s, 1H), 4.17 (part of AB system, 1H, *J* = 18.2 Hz), 3.57 (s, 3H), 3.42 (part of AB system, 1H, *J* = 18.2 Hz).

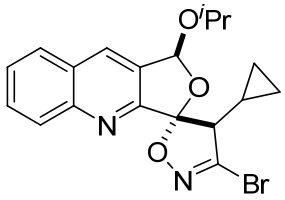
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): Major isomer δ (ppm) = 156.2, 150.1, 137.7, 132.1, 131.0, 129.9, 129.4, 128.7, 128.4, 128.0, 114.3, 104.9, 56.2, 50.2.
HRMS(ESI$^+$) m/z calculated for (MH^+): 335.0026. Found: 335.0028.
SM (ESI$^+$): 335 (MH^+).
IR (CH_2Cl_2): ν 2931, 2854, 1724, 1628, 1582, 1507, 1399, 1336, 1313 cm^{-1}.



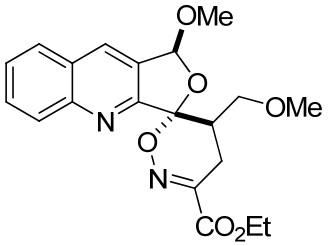
According to the procedure described above, **36** was isolated in 74% yield (white solid).
Mixture of diastereoisomers 85:15
^{1}H NMR ($CDCl_3$, 300 MHz): Major isomer δ (ppm) = 8.20 (s, 1H), 8.18 (d, 1H, *J* = 8.5 Hz), 7.91 (d, 1H, *J* = 8.1 Hz), 7.79 (t, 1H, *J* = 7.1 Hz), 7.62 (t, 1H, *J* = 7.5 Hz), 6.61 (s, 1H), 4.24 (sept, 1H, *J* = 6.2 Hz), 4.16 (part of AB system, 1H, *J* = 18.2 Hz), 3.48 (part of AB system, 1H, *J* = 18.2 Hz), 1.36 (d, 3H, *J* = 6.1 Hz), 1.33 (d, 3H, *J* = 6.1 Hz). Minor isomer (selected signals) δ (ppm) = 6.33 (s, 1H), 3.37 (part of AB system, 1H, *J* = 18.2 Hz).
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): Major isomer δ (ppm) = 156.3, 150.0, 137.6, 132.0, 131.8, 130.8, 130.3, 129.8, 128.6, 128.5, 127.8, 114.2, 102.9, 72.9, 50.1, 23.7, 22.4.
HRMS(ESI$^+$) m/z calculated for (MNa^+): 385.0158. Found: 385.0148.
SM (ESI$^+$): 385 (MNa^+).
IR (CH_2Cl_2): ν 2977, 2929, 1725, 1630, 1582, 1507, 1405, 1385 cm^{-1}.



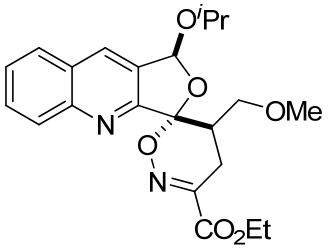
According to the procedure described above, **37** was isolated in 78% yield (white solid).
Mixture of diastereoisomers 40:40:10:10
^{1}H NMR ($CDCl_3$, 300 MHz): Major isomers δ (ppm) = 8.25-8.17 (m, 2H), 7.91 (d, 1H, *J* = 8.1 Hz), 7.81-7.76 (m, 1H), 7.64-7.59 (m, 1H), 6.48 & 6.46 (s, 1H), 4.63 (br s, 1H, 50%), 4.49 (br s, 1H, 50%), 4.48-4.41 (m, 1H), 4.18-4.07 (m, 1H), 3.81-3.71 (m, 2H), 3.65 & 3.63 (s, 3H), 3.53-3.39 (m, 1H), 1.50-1.06 (m, 6H). Minor isomers (selected signals) δ (ppm) = 6.32 & 6.23 (s, 1H), 3.50 & 3.49 (s, 3H).
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): Major isomers δ (ppm) = 156.5, 156.4, 149.9, 141.3, 140.8, 132.0, 131.9, 130.9, 129.9, 129.5, 128.6, 128.4, 127.8, 127.7, 114.6, 114.4, 105.5, 105.3, 99.3, 98.8, 62.5, 61.9, 61.6, 56.9, 56.8, 56.7, 56.3, 30.1, 29.8, 25.3, 18.7, 18.6.
HRMS(ESI$^+$) m/z calculated for (MH^+): 449.0707. Found: 449.0699.
SM (ESI$^+$): 449 (MH^+).
IR (CH_2Cl_2): ν 2944, 2854, 1724, 1628, 1584, 1507, 1446, 1398, 1356, 1298 cm^{-1}.



According to the procedure described above, **38** was isolated in 65% yield (white solid).
Mixture of diastereoisomers 86:14
^{1}H NMR ($CDCl_3$, 300 MHz): Major isomer δ (ppm) = 8.25-8.22 (m, 1H), 8.15 (d, 1H, *J* = 8.5 Hz), 7.92 (d, 1H, *J* = 8.2 Hz), 7.78 (t, 1H, *J* = 8.3 Hz), 7.64-7.59 (m, 1H), 6.69 (s, 1H, major isomer), 6.40 (s, 1H, minor isomer), 4.24 (sept, 1H, *J* = 6.2 Hz), 3.35 (d, 1H, *J* = 10.8 Hz), 1.35 (d, 3H, *J* = 6.1 Hz), 1.29 (d, 3H, *J* = 6.2 Hz), 1.18-1.06 (m, 1H), 0.87-0.70 (m, 1H), 0.51-0.23 (m, 2H).
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): Major isomer δ (ppm) = 156.8, 149.9, 144.8, 132.1, 130.8, 130.7, 129.8, 128.7, 128.6, 127.8, 114.6, 103.2, 72.5, 62.4, 23.7, 22.4, 7.0, 4.7, 2.4.
HRMS(ESI$^+$) m/z calculated for (MH^+): 403.0652. Found: 403.0647.
SM (ESI$^+$): 403 (MH^+).
IR (CH_2Cl_2): ν 2977, 2928, 1724, 1628, 1582, 1506, 1403, 1384 cm^{-1}.

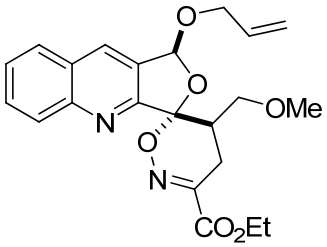


According to the procedure described above, **39** was isolated in 83% yield.
Mixture of diastereoisomers 88:12
^{1}H NMR ($CDCl_3$, 300 MHz): Major isomer δ (ppm) = 8.23-8.18 (m, 2H), 7.89 (d, 1H, *J* = 7.8 Hz), 7.77 (t, 1H, *J* = 7.3 Hz), 7.59 (t, 1H, *J* = 7.6 Hz), 6.39 (s, 1H), 4.36 (q, 2H, *J* = 7.1 Hz), 3.60 (s, 3H), 3.23-3.04 (m, 4H), 3.07 (s, 3H), 2.51-2.39 (m, 1H), 1.37 (t, 3H, *J* = 7.1 Hz).
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): Major isomer δ (ppm) = 163.1, 157.3, 150.7, 149.8, 132.0, 130.6, 130.0, 129.8, 128.6, 128.3, 127.6, 105.1, 104.9, 72.4, 62.2, 58.7, 56.4, 33.5, 21.9, 14.3.
HRMS(ESI$^+$) m/z calculated for (MNa^+): 409.1370. Found: 409.1370.
SM (ESI$^+$): 409 (MNa^+).
IR (CH_2Cl_2): ν 2985, 2932, 1721, 1628, 1506, 1447, 1398 cm^{-1}.

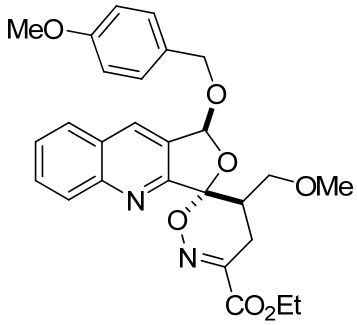


According to the procedure described above, **40** was isolated in 51% yield (white solid).
Mixture of diastereoisomers 88:12

^{1}H NMR ($CDCl_3$, 300 MHz): Major isomer δ (ppm) = 8.23-8.19 (m, 2H), 7.91 (dd, 1H, *J* = 1.0, 8.2 Hz), 7.78 (ddd, 1H, *J* = 1.4, 7.0, 8.4 Hz), 7.61 (ddd, 1H, *J* = 1.0, 7.0, 8.0 Hz), 6.58 (s, 1H), 4.38 (q, 2H, *J* = 7.1 Hz), 4.19 (sept, 1H, *J* = 6.2 Hz), 3.26-3.05 (m, 4H), 3.11 (s, 3H), 2.43 (AB system, 1H), 1.39 (t, 3H, *J* = 7.1 Hz), 1.35 (d, 3H, *J* = 6.1 Hz), 1.33 (d, 3H, *J* = 6.1 Hz).
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): Major isomer δ (ppm) = 163.3, 157.3, 150.7, 149.9, 131.9, 130.7, 130.6, 130.1, 128.6, 128.5, 127.6, 105.1, 103.1, 72.8, 72.6, 62.3, 58.8, 33.6, 23.9, 22.5, 22.0, 14.3.
HRMS(ESI$^+$) m/z calculated for (MH^+): 415.1864. Found: 415.1865.
SM (ESI$^+$): 415 (MH^+).
IR (CH_2Cl_2): ν 2979, 2929, 1721, 1629, 1506, 1378 cm^{-1}.



According to the procedure described above, **41** was isolated in 20% yield (white solid).
Mixture of diastereoisomers 86:14
^{1}H NMR ($CDCl_3$, 300 MHz): Major isomer δ (ppm) = 8.24-8.21 (m, 2H), 7.92 (dd, 1H, *J* = 1.0, 8.3 Hz), 7.79 (ddd, 1H, *J* = 1.4, 6.9, 8.3 Hz), 7.62 (ddd, 1H, *J* = 1.0, 7.0, 8.0 Hz), 6.54 (s, 1H), 6.01 (ddt, 1H, *J* = 6.0, 10.5, 16.5 Hz), 5.38 (dd, 1H, *J* = 1.5, 17.2 Hz), 5.27 (dd, 1H, *J* = 1.3, 10.4 Hz), 4.45-4.26 (m, 4H), 3.26-3.04 (m, 4H), 3.09 (s, 3H), 2.51-2.39 (m, 1H), 1.39 (t, 3H, *J* = 7.1 Hz).
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): Major isomer δ (ppm) = 163.2, 157.4, 150.7, 149.9, 133.7, 132.1, 130.7, 130.1, 128.6, 128.4, 127.7, 118.3, 105.2, 103.5, 72.5, 70.1, 62.3, 58.8, 33.6, 21.9, 14.3.
HRMS(ESI$^+$) m/z calculated for (MH^+): 413.1707. Found: 413.1704.
SM (ESI$^+$): 413 (MH^+).
IR (CH_2Cl_2): ν 2985, 2929, 1721, 1628, 1582, 1506, 1399, 1377 cm^{-1}.



According to the procedure described above, **42** was isolated in 51% yield (white solid).
Mixture of diastereoisomers 90:10
^{1}H NMR ($CDCl_3$, 300 MHz): Major isomer δ (ppm) = 8.23-8.19 (m, 2H), 7.89 (dd, 1H, *J* = 1.0, 8.2 Hz), 7.78 (ddd, 1H, *J* = 1.4, 7.3, 8.4 Hz), 7.60 (ddd, 1H, *J* = 1.0, 7.0, 8.0 Hz), 7.35 (d,

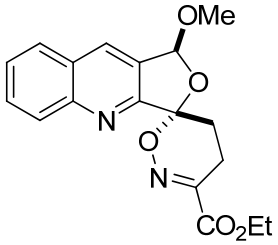
2H, *J* = 8.6 Hz), 6.9 (d, 2H, *J* = 8.6 Hz), 6.58 (s, 1H), 4.81 (AB system, 2H), 4.39 (q, 2H, *J* = 7.1 Hz), 3.81 (s, 3H), 3.23-3.04 (m, 4H), 3.07 (s, 3H), 2.50-2.38 (m, 1H), 1.40 (t, 3H, *J* = 7.1 Hz).

^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): Major isomer δ (ppm) = 163.2, 159.7, 157.3, 150.7, 149.8, 132.1, 130.6, 130.1, 129.2, 128.6, 128.4, 127.6, 114.1, 105.2, 103.2, 72.5, 71.0, 62.3, 58.8, 55.4, 33.7, 22.0, 14.3.

HRMS(ESI$^+$) m/z calculated for (MH^+): 493.1969. Found: 493.1970.

SM (ESI$^+$): 493 (MH^+).

IR (CH_2Cl_2): ν 2983, 2931, 2840, 1721, 1613, 1514, 1299 cm^{-1}.



According to the procedure described above, **43** was isolated in 59% yield (white solid).
Mixture of diastereoisomers 88:12

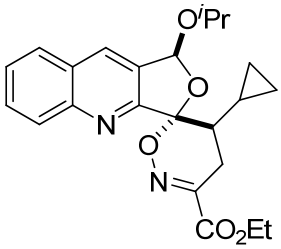
^{1}H NMR ($CDCl_3$, 300 MHz): Major isomer δ (ppm) = 8.25 (s, 1H), 8.19 (d, 1H, *J* = 8.5 Hz), 7.92 (d, 1H, *J* = 8.2 Hz), 7.79 (ddd, 1H, *J* = 1.4, 7.1, 8.4 Hz), 7.63 (ddd, 1H, *J* = 1.0, 7.1, 8.1 Hz), 6.48 (s, 1H), 4.38 (q, 2H, *J* = 7.1 Hz), 3.56 (s, 3H), 3.04-2.96 (part of AB system, 1H), 2.87-2.64 (part of AB system, 2H), 2.32-2.26 (part of AB system, 1H), 1.39 (t, 3H, *J* = 7.1 Hz).

^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): Major isomer δ (ppm) = 163.4, 158.5, 150.6, 149.8, 132.2, 130.7, 130.0, 129.8, 128.7, 128.5, 127.7, 104.7, 103.9, 62.3, 55.8, 24.9, 17.9, 14.3.

HRMS(ESI$^+$) m/z calculated for (MH^+): 343.1288. Found: 343.1288.

SM (ESI$^+$): 343 (MH^+).

IR (CH_2Cl_2): ν 2983, 2938, 1720, 1628, 1506, 1398, 1378, 1296 cm^{-1}.



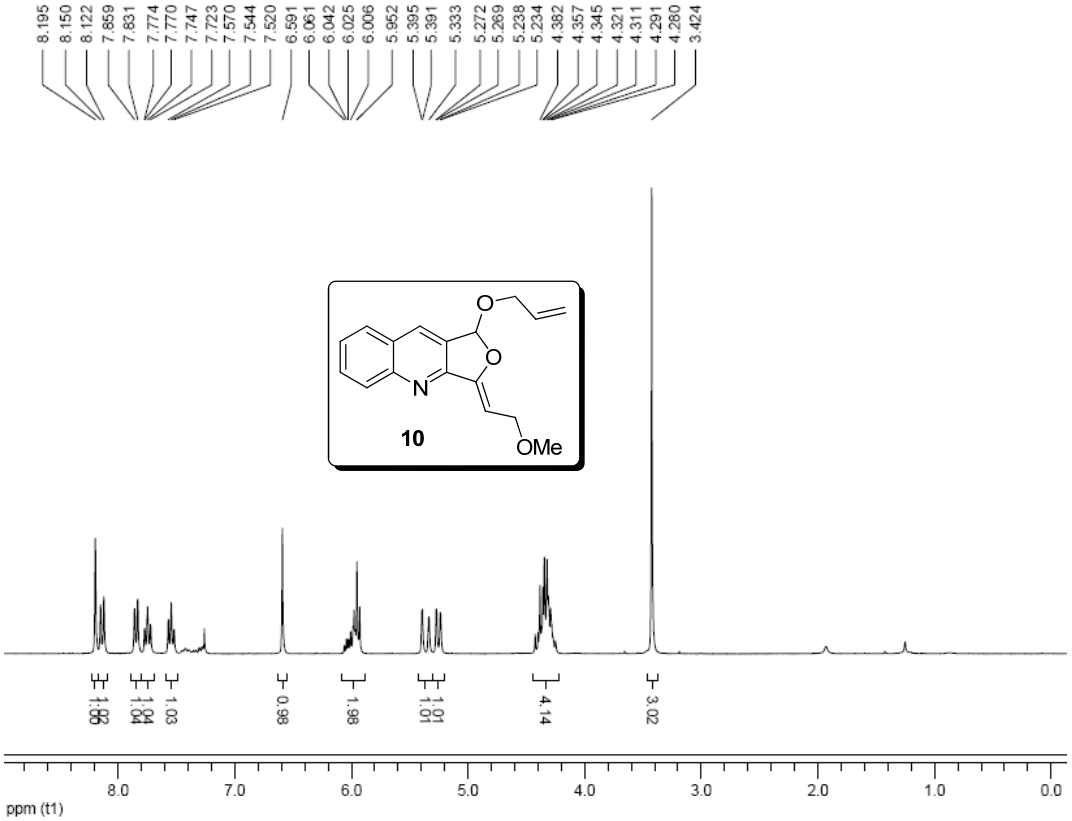
According to the procedure described above, **44** was isolated in 63% yield (white solid).
Mixture of diastereoisomers 86:14

^{1}H NMR ($CDCl_3$, 300 MHz): Major isomer δ (ppm) = 8.25-8.17 (m, 2H), 7.93 (d, 1H, *J* = 8.2 Hz), 7.79 (t, 1H, *J* = 7.1 Hz), 7.62 (t, 1H, *J* = 7.1 Hz), 6.63 (s, 1H), 4.37 (q, 2H, *J* = 7.1 Hz), 4.21 (sept, 1H, *J* = 6.2 Hz), 3.00-2.89 (part of AB system, 1H), 2.63-2.52 (part of AB system, 1H), 2.01-1.92 (m, 1H), 1.39 (t, 3H, *J* = 7.1 Hz), 1.35 (d, 3H, *J* = 6.2 Hz), 1.31 (d, 3H, *J* = 6.2 Hz), 0.77-0.65 (m, 1H), 0.43-0.34 (m, 1H), 0.18-0.07 (m, 1H), -0.04-(-)0.18 (m, 2H). Minor isomer δ (ppm) (selected peak) = 6.45 (s, 1H).

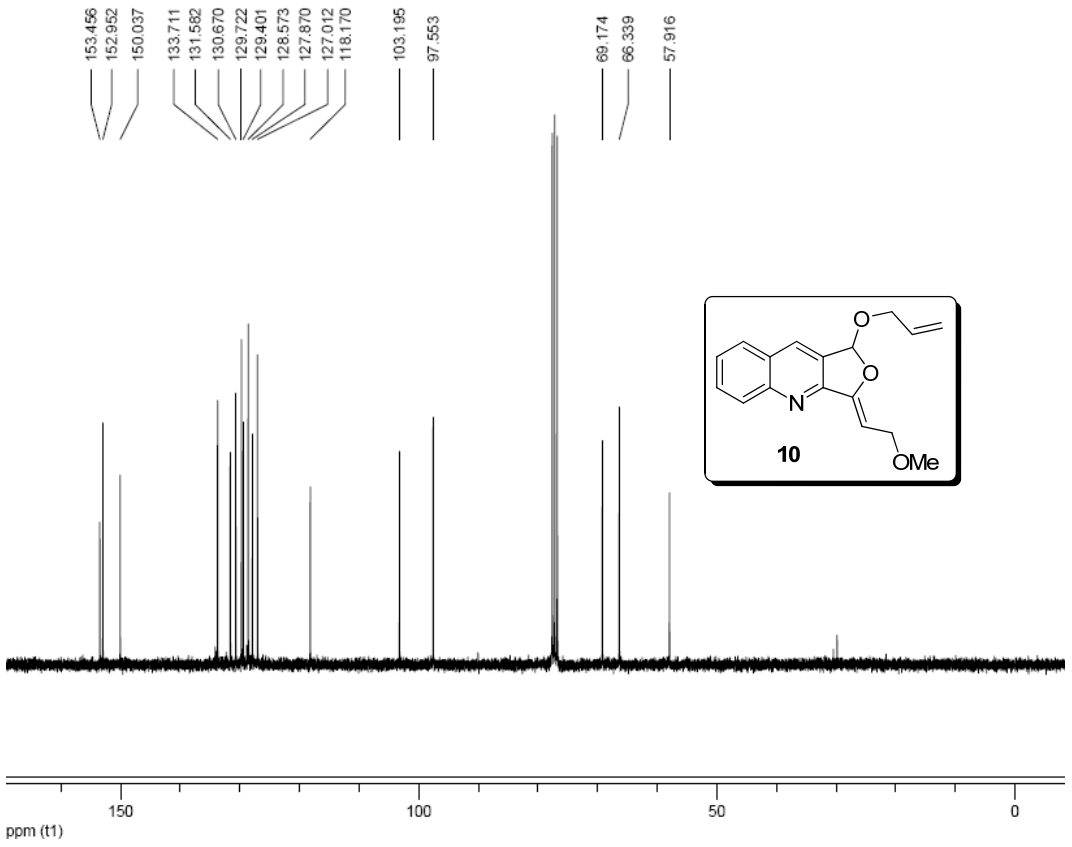
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): Major isomer δ (ppm) = 163.5, 157.9, 150.8, 149.6, 131.8, 131.1, 130.5, 129.9, 128.6, 128.5, 127.5, 107.4, 103.3, 72.7, 62.2, 38.6, 24.2, 23.9, 22.6, 14.3, 11.4, 5.0, 2.3.
HRMS(ESI$^+$) m/z calculated for (MH^+): 411.1914. Found: 411.1914.
SM (ESI$^+$): 411 (MH^+).
IR (CH_2Cl_2): ν 2979, 2928, 1720, 1629, 1608, 1506, 1376, 1299 cm^{-1}.

4. NMR spectra of new compounds

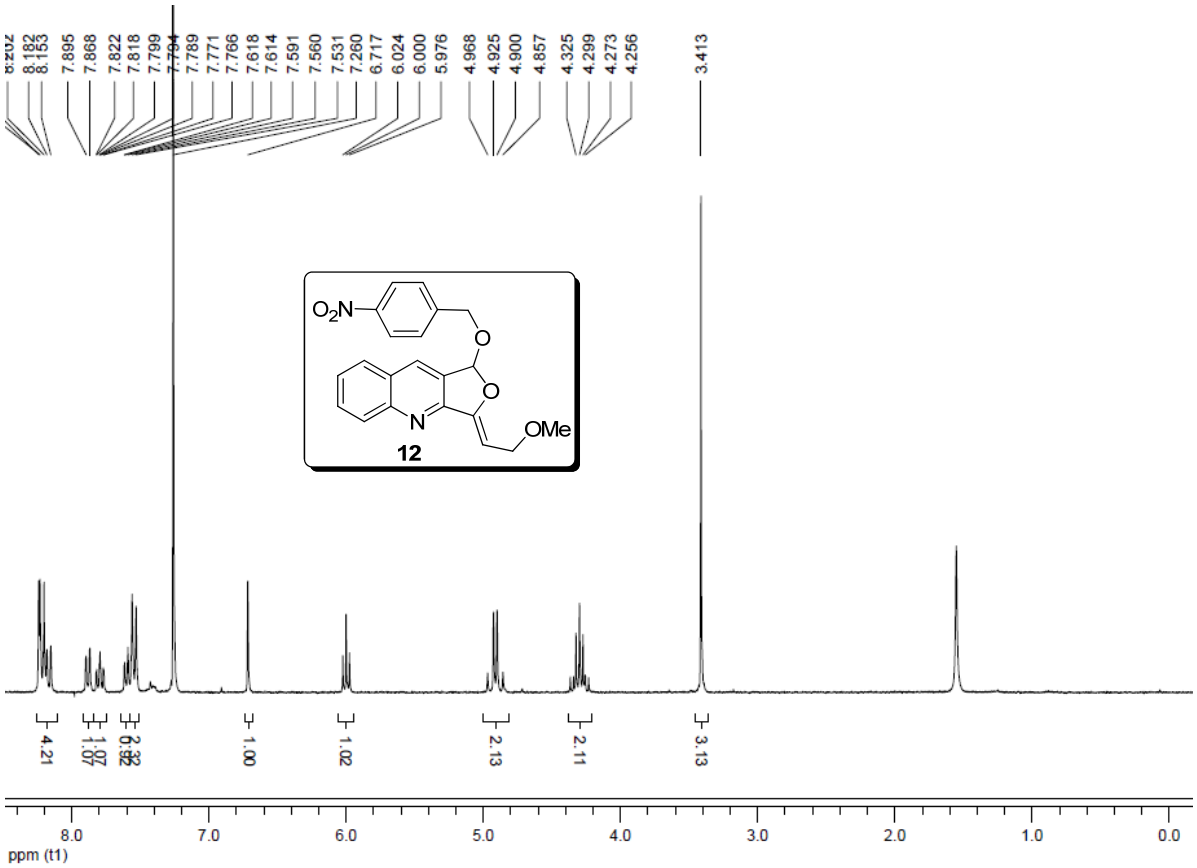
^{1}H NMR ($CDCl_3$, 300 MHz) of **10**



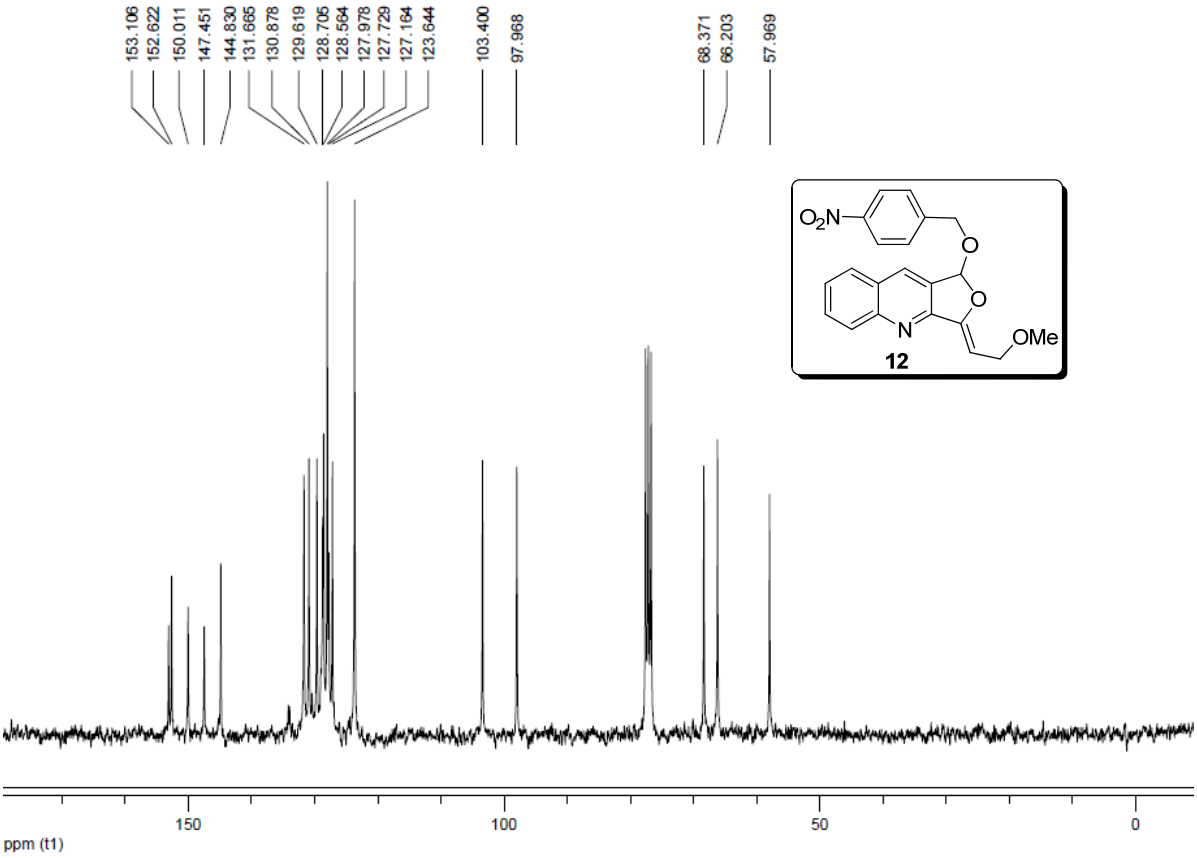
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz) of **10**



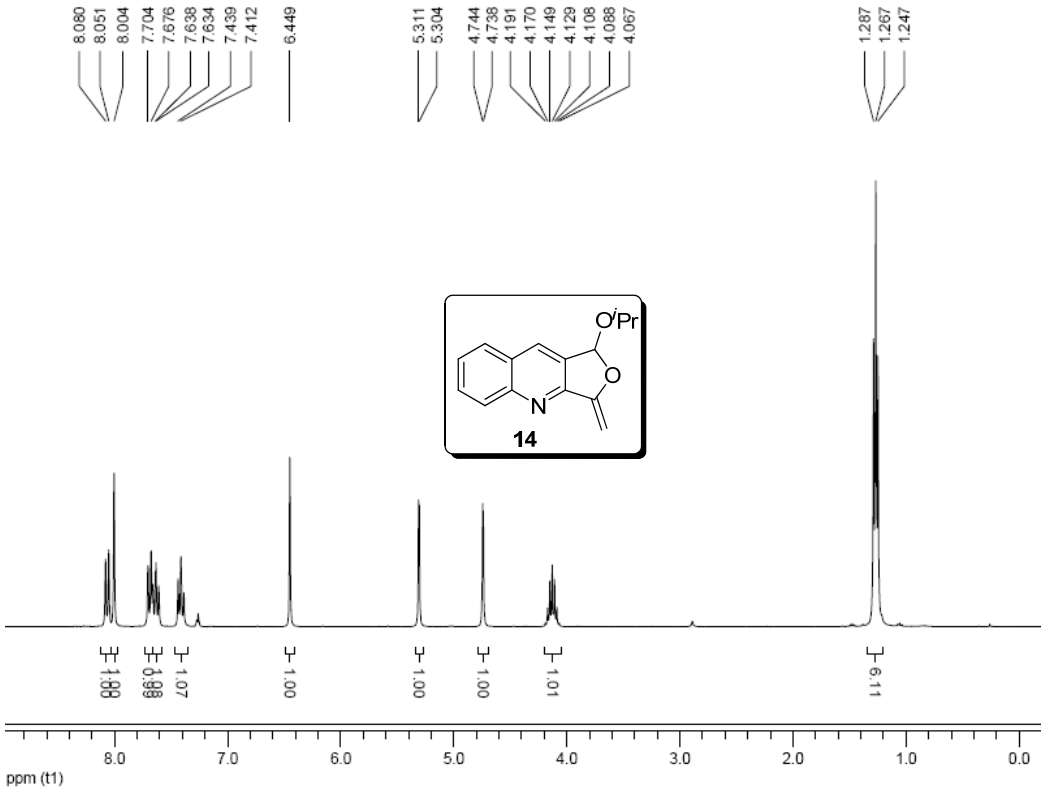
^{1}H NMR ($CDCl_3$, 300 MHz) of **12**



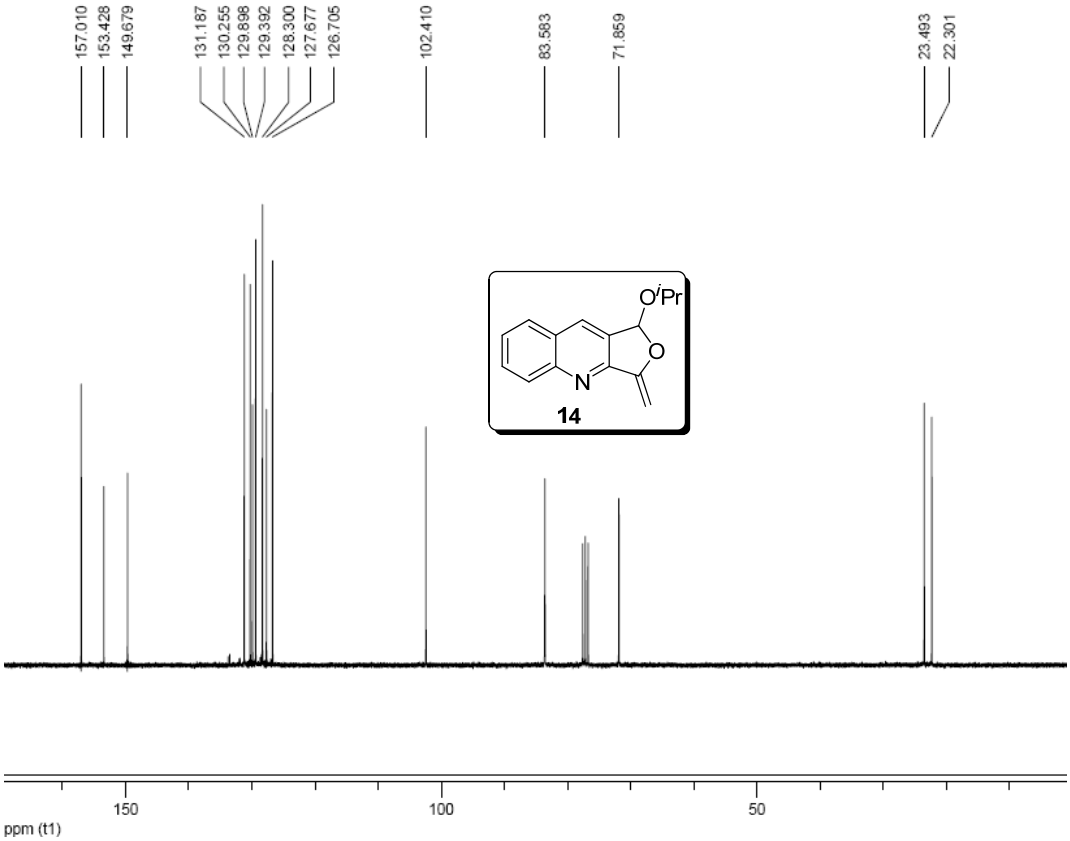
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz) of **12**



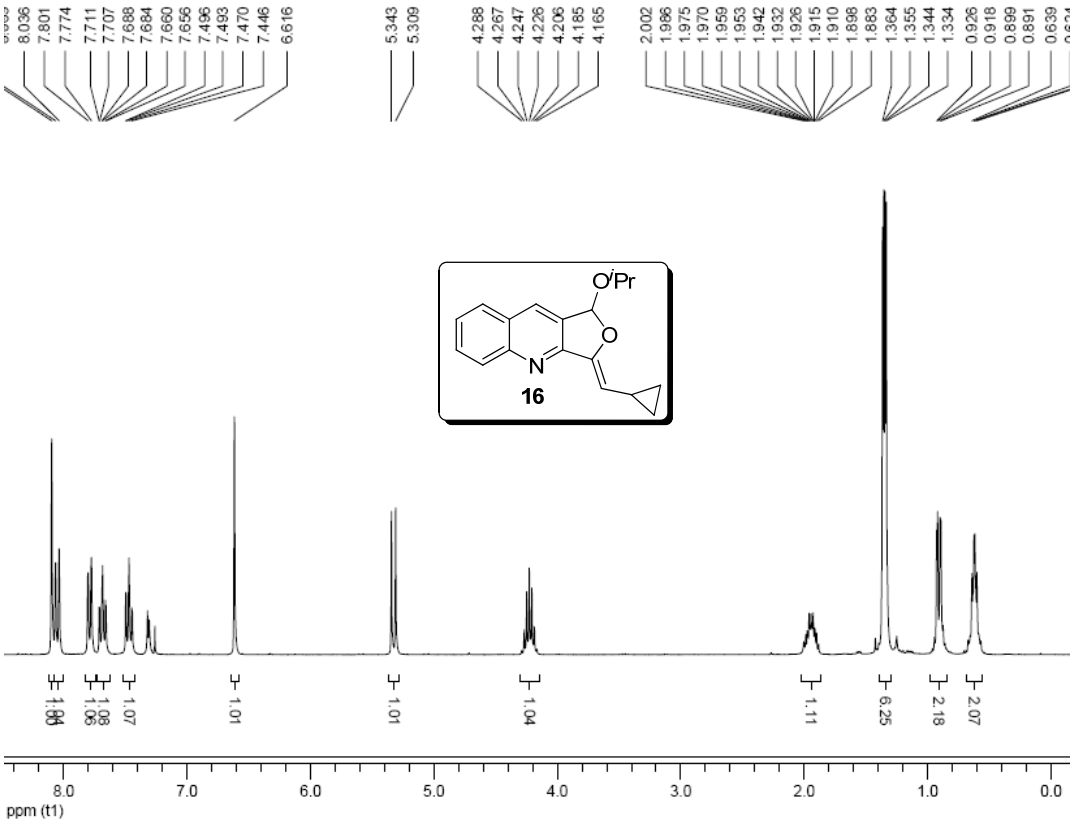
^{1}H NMR ($CDCl_3$, 300 MHz) of **14**



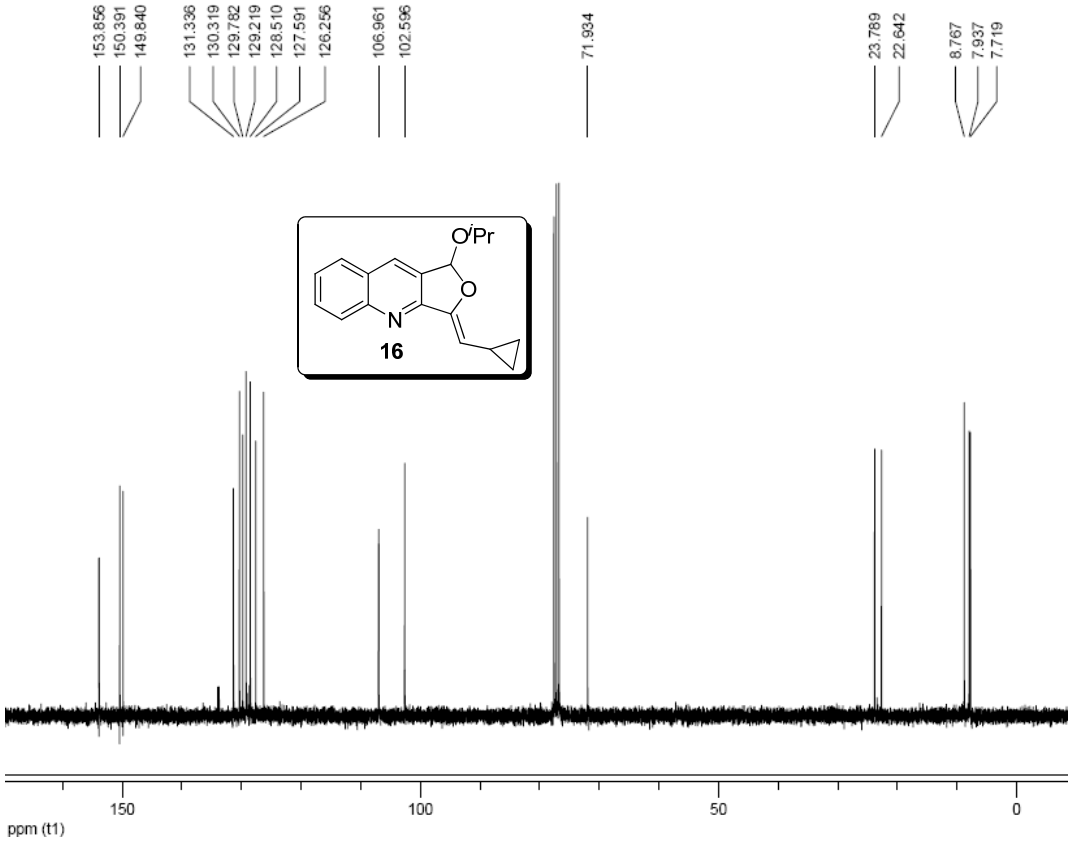
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz) of **14**



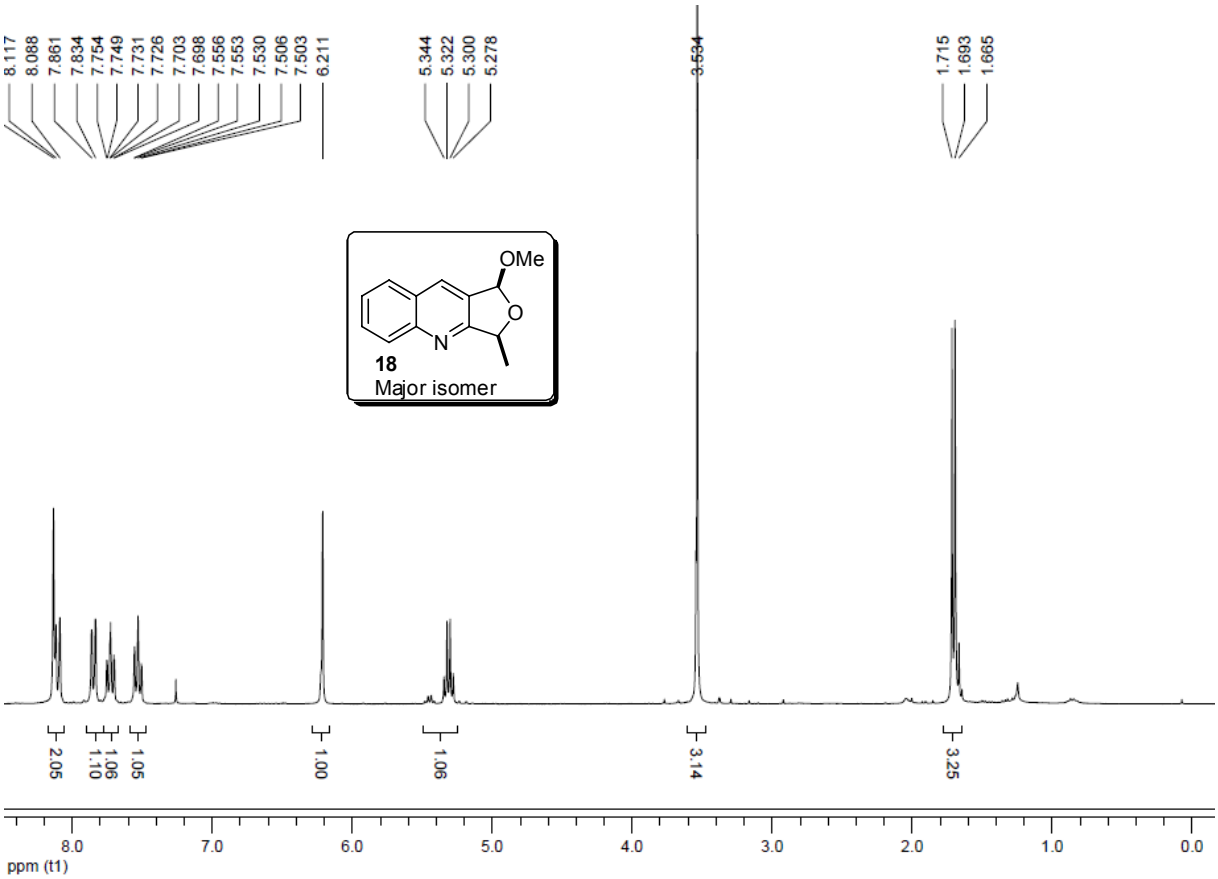
^{1}H NMR ($CDCl_3$, 300 MHz) of **16**



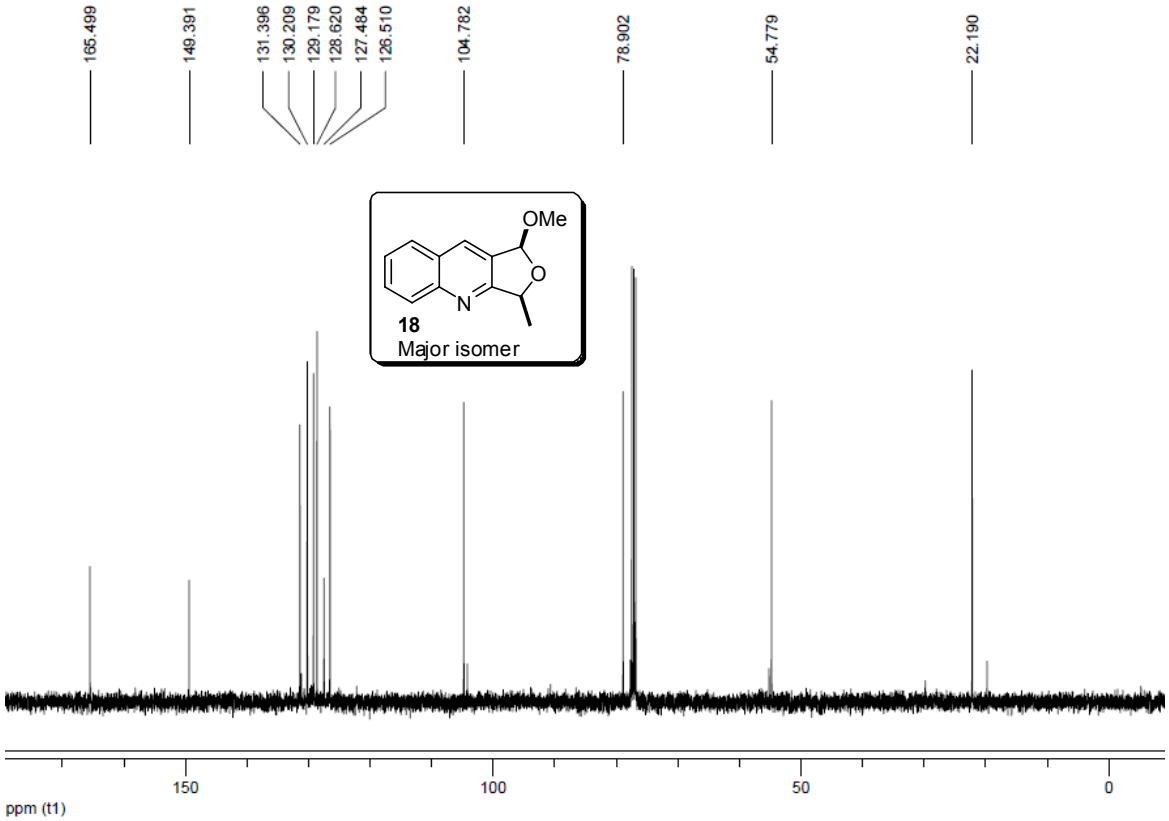
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz) of **16**



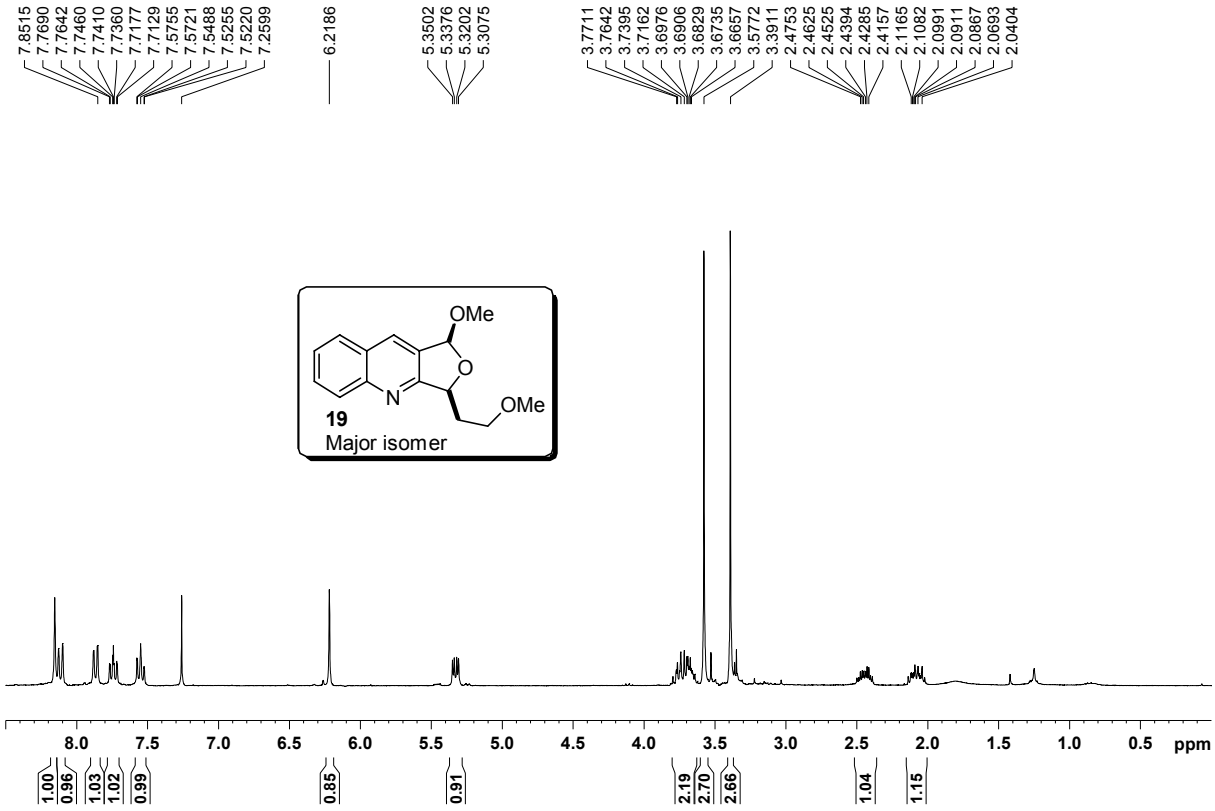
^{1}H NMR ($CDCl_3$, 300 MHz) of **18**



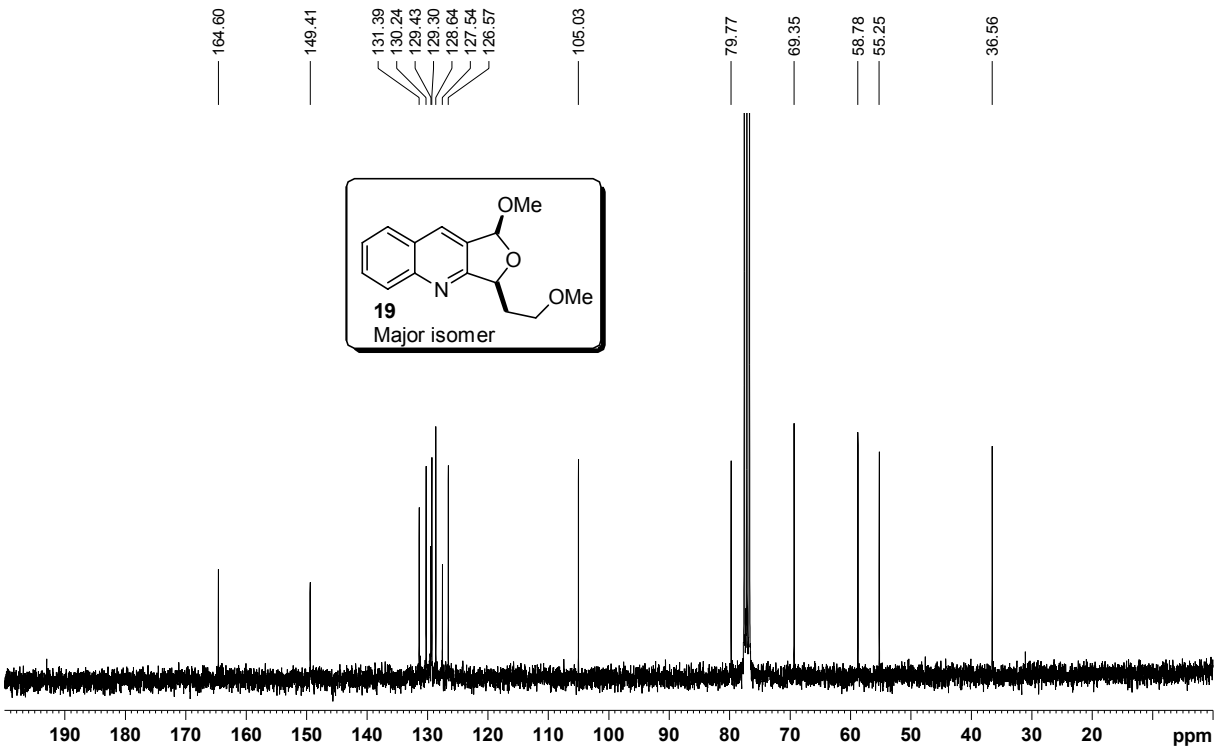
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz) of **18**



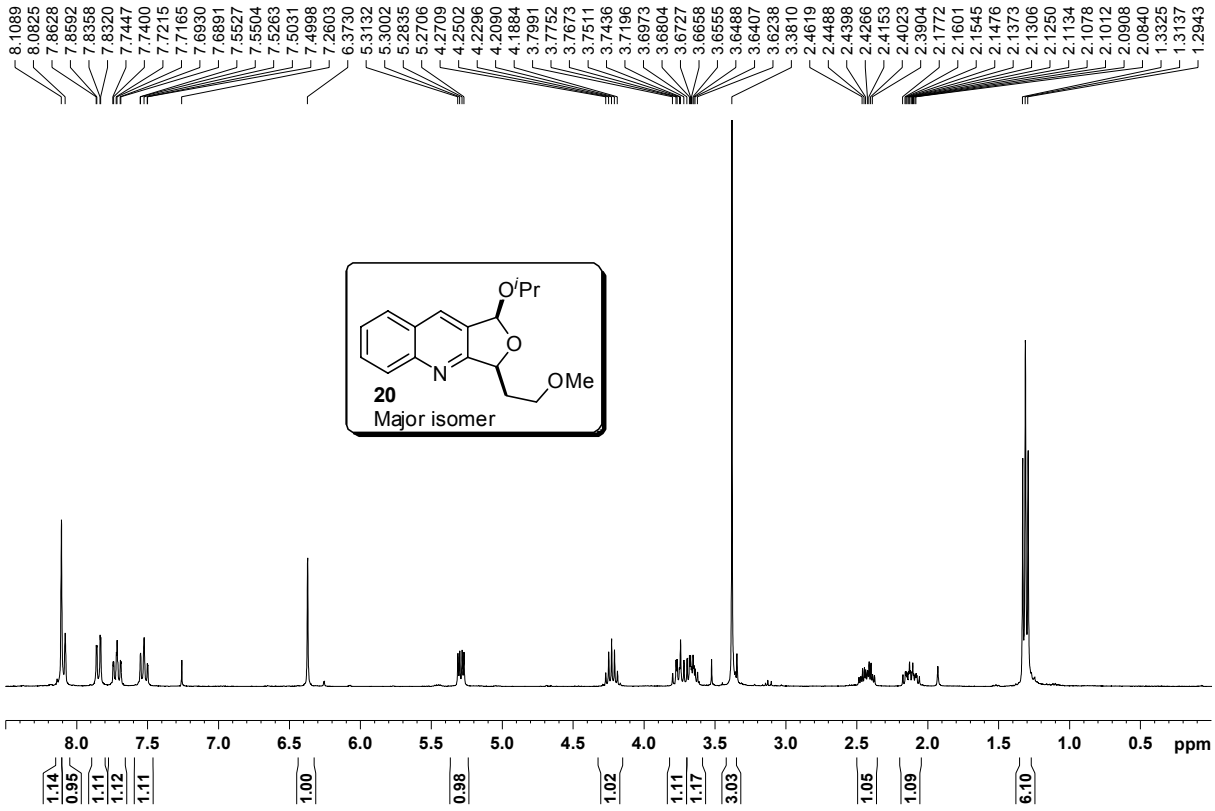
^{1}H NMR ($CDCl_3$, 500 MHz) of **19**



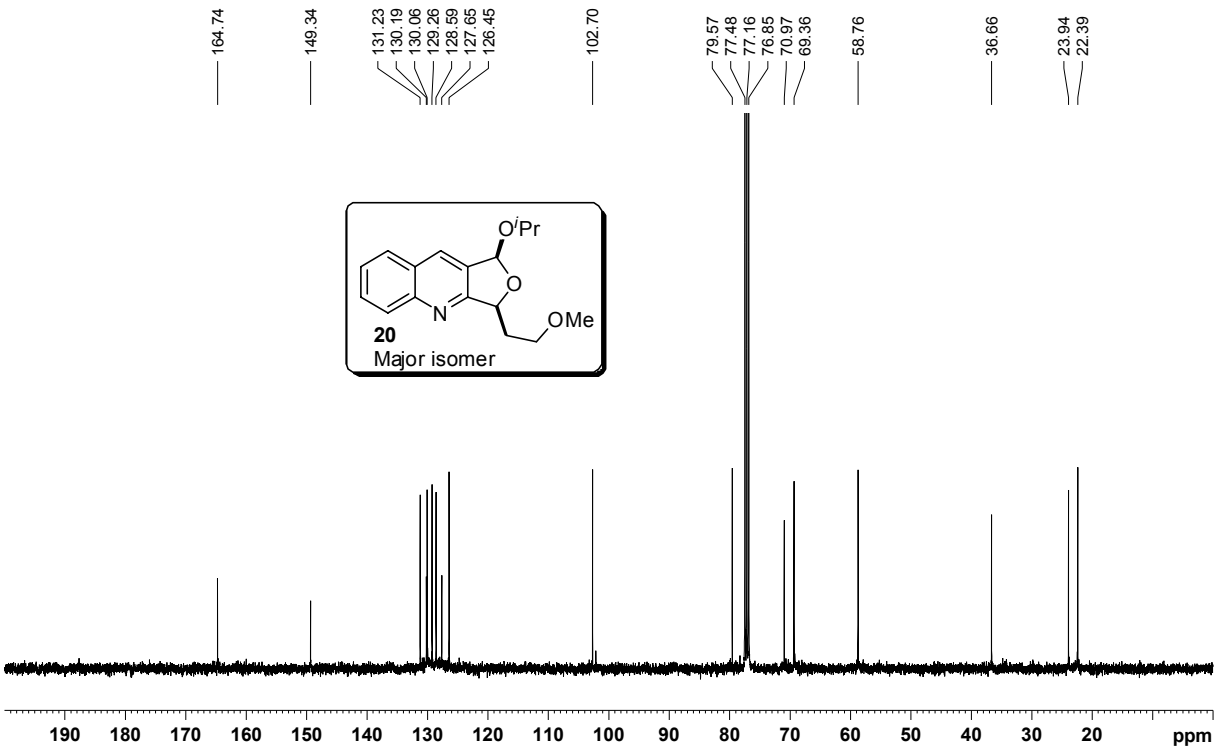
^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz) of **19**



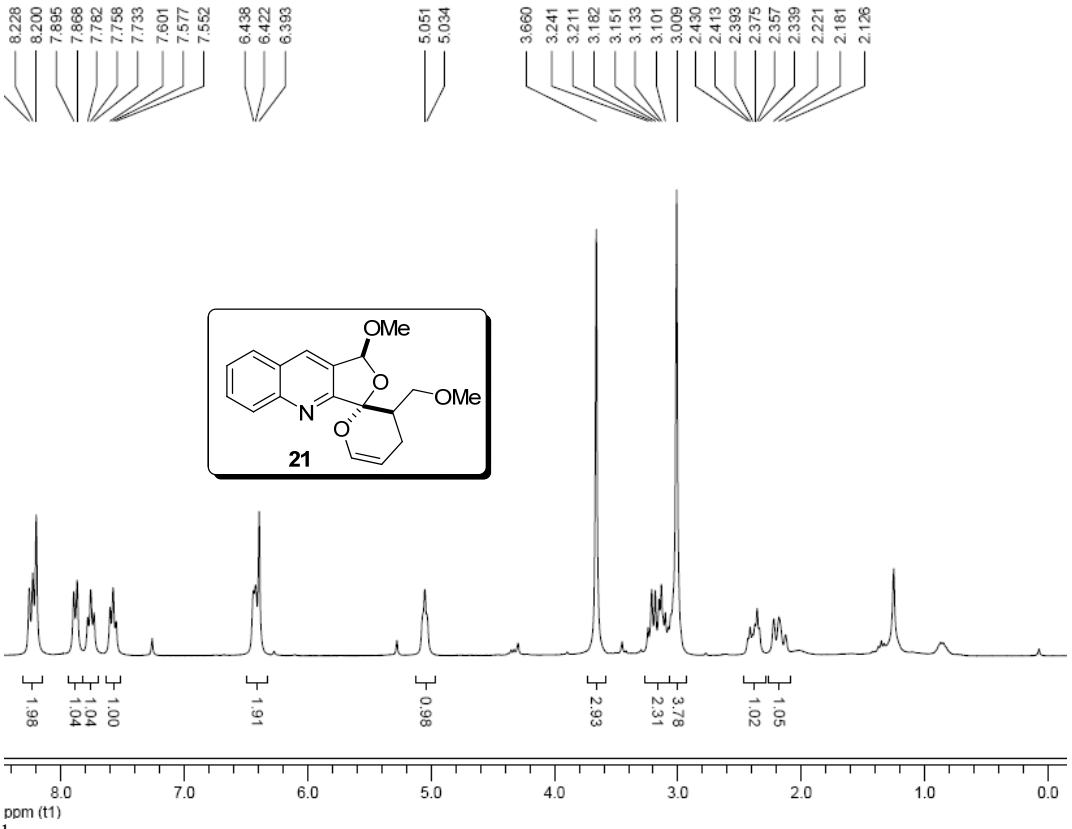
^{1}H NMR ($CDCl_3$, 300 MHz) of **20**



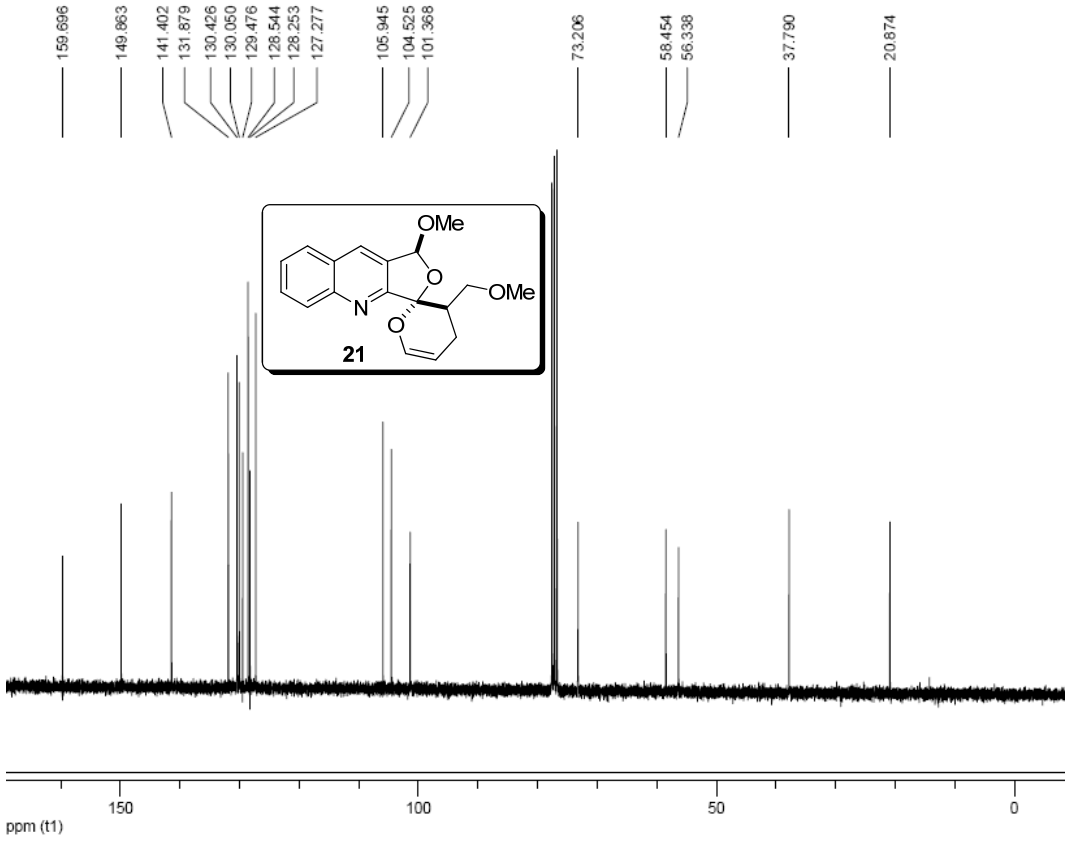
^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz) of **20**



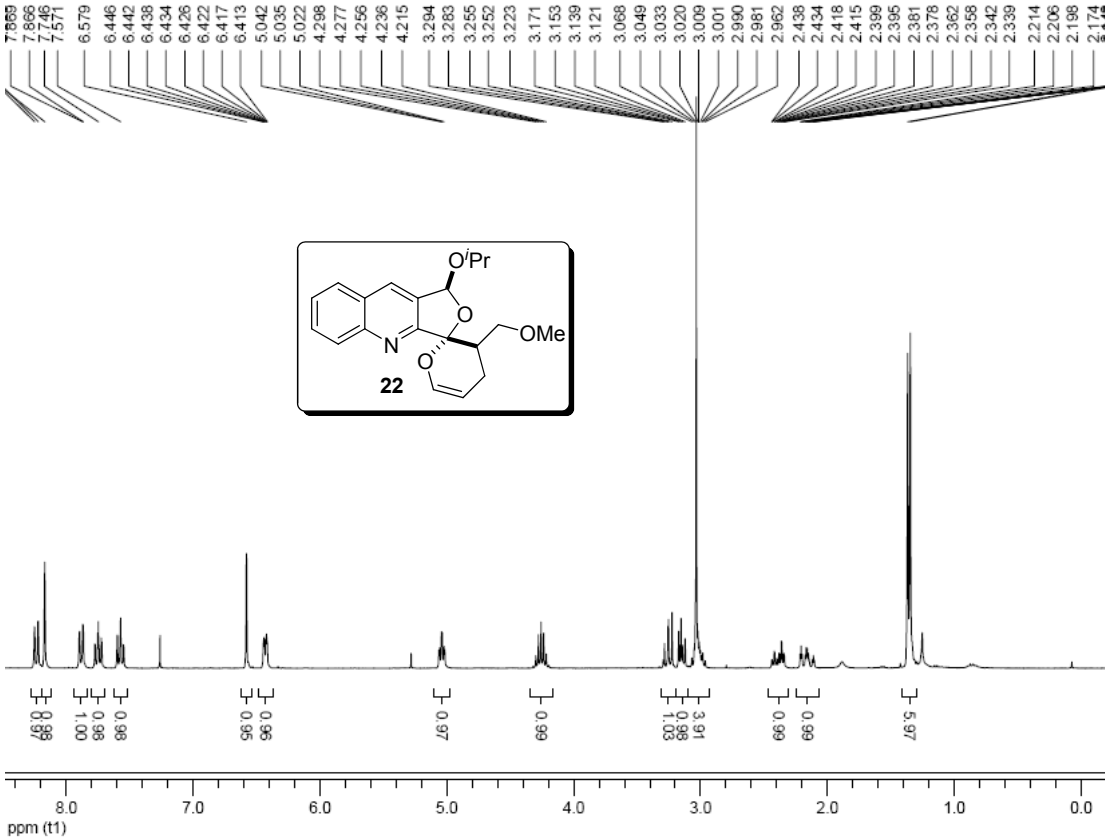
^{1}H NMR ($CDCl_3$, 300 MHz) of **21**



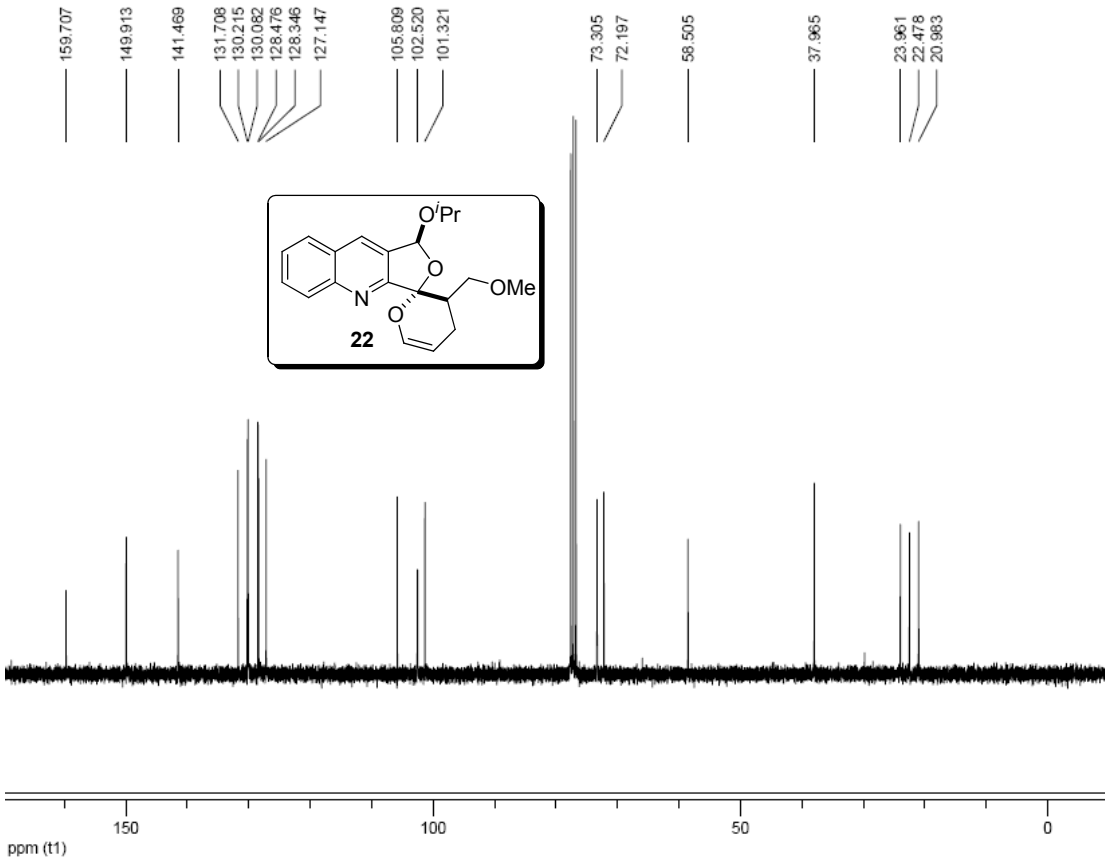
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz) of **21**



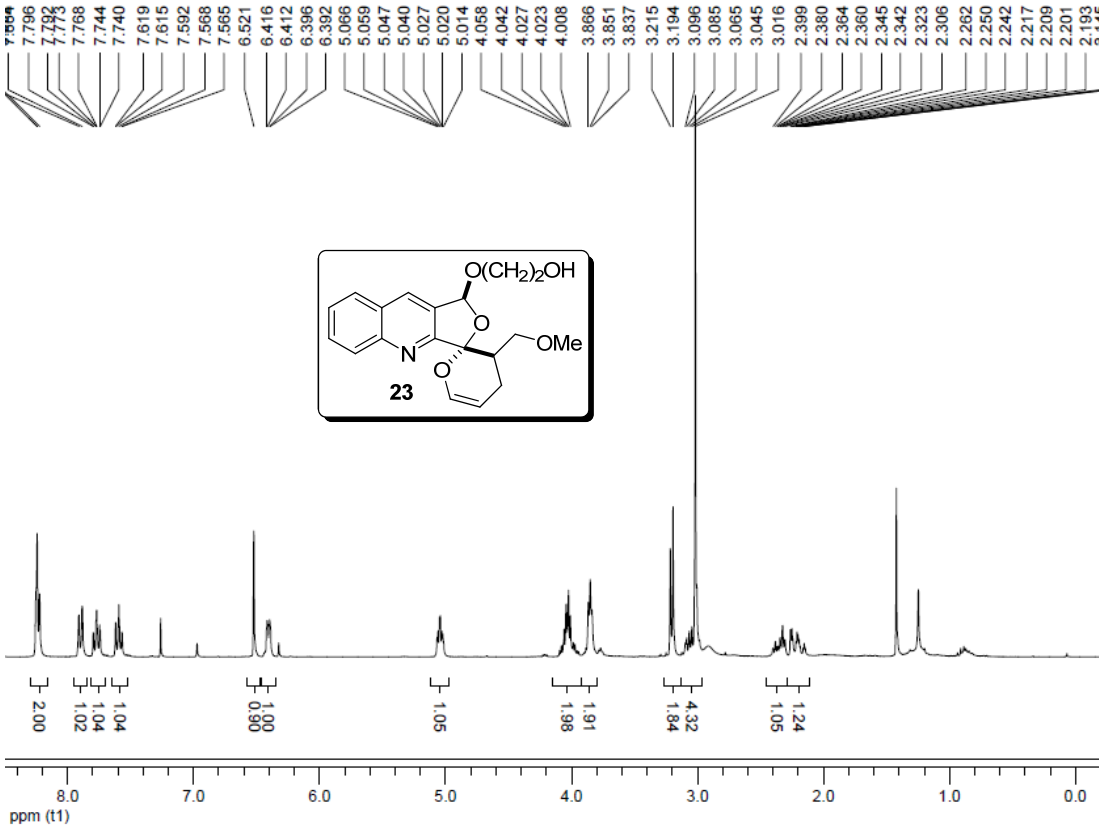
^{1}H NMR ($CDCl_3$, 300 MHz) of **22**



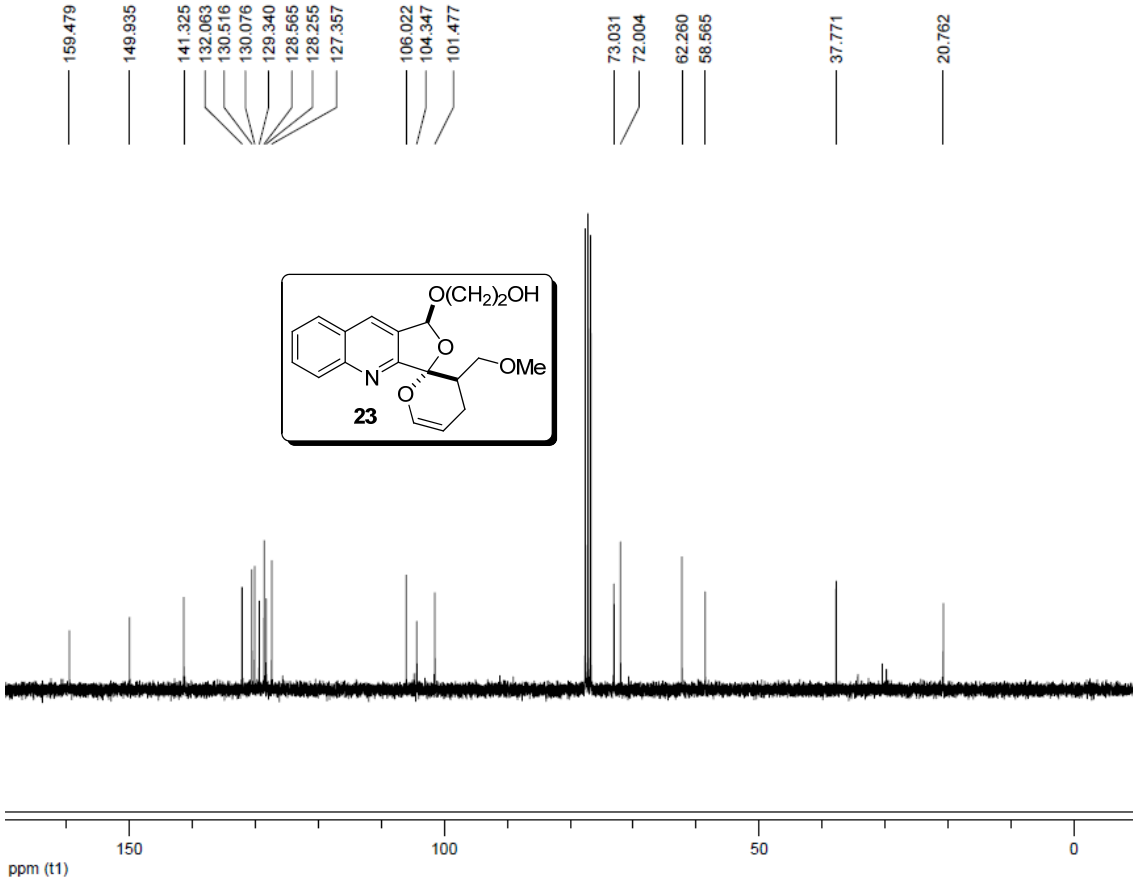
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz) of **22**



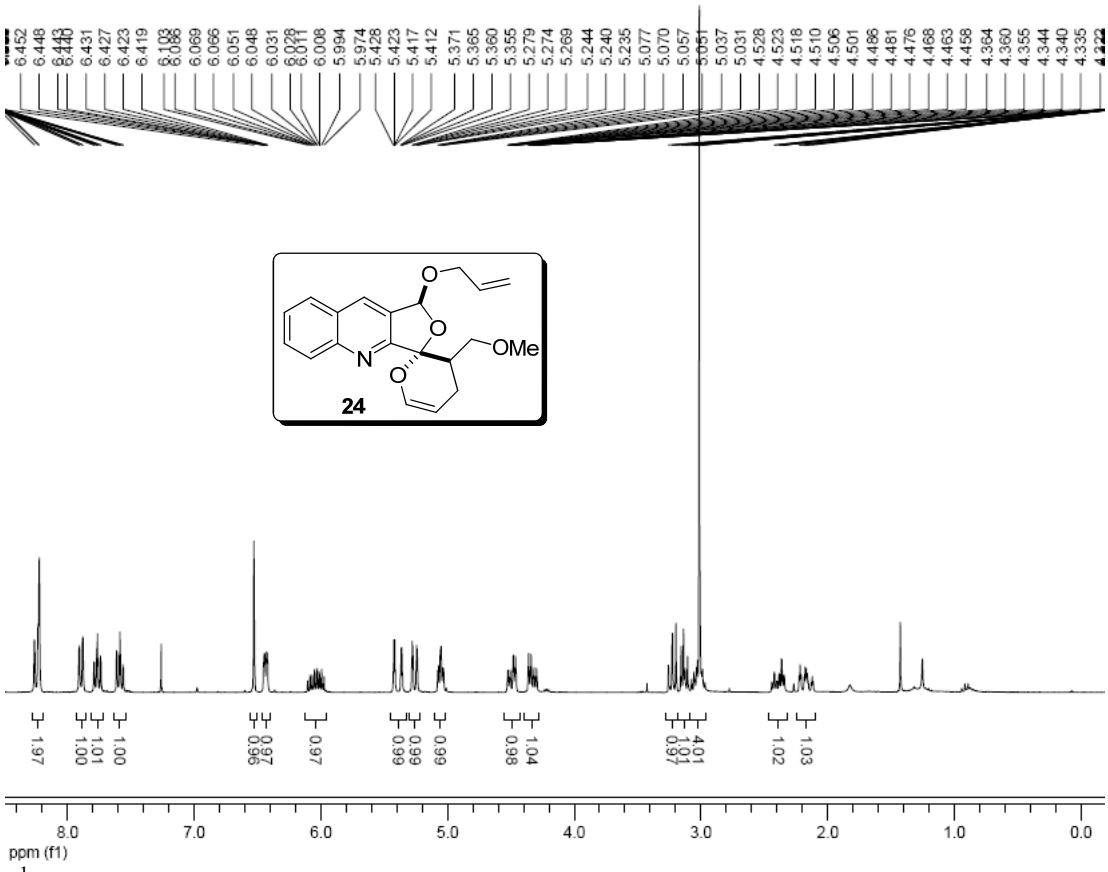
^{1}H NMR ($CDCl_3$, 300 MHz) of **23**



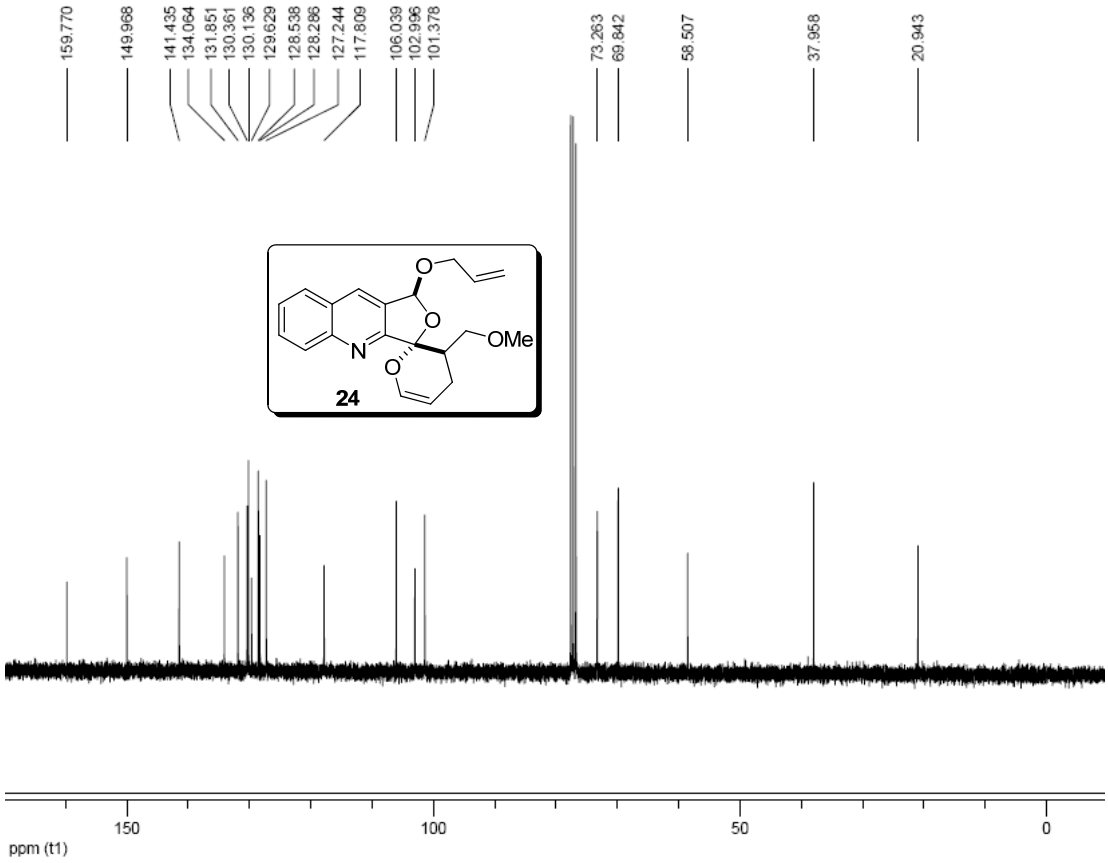
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz) of **23**



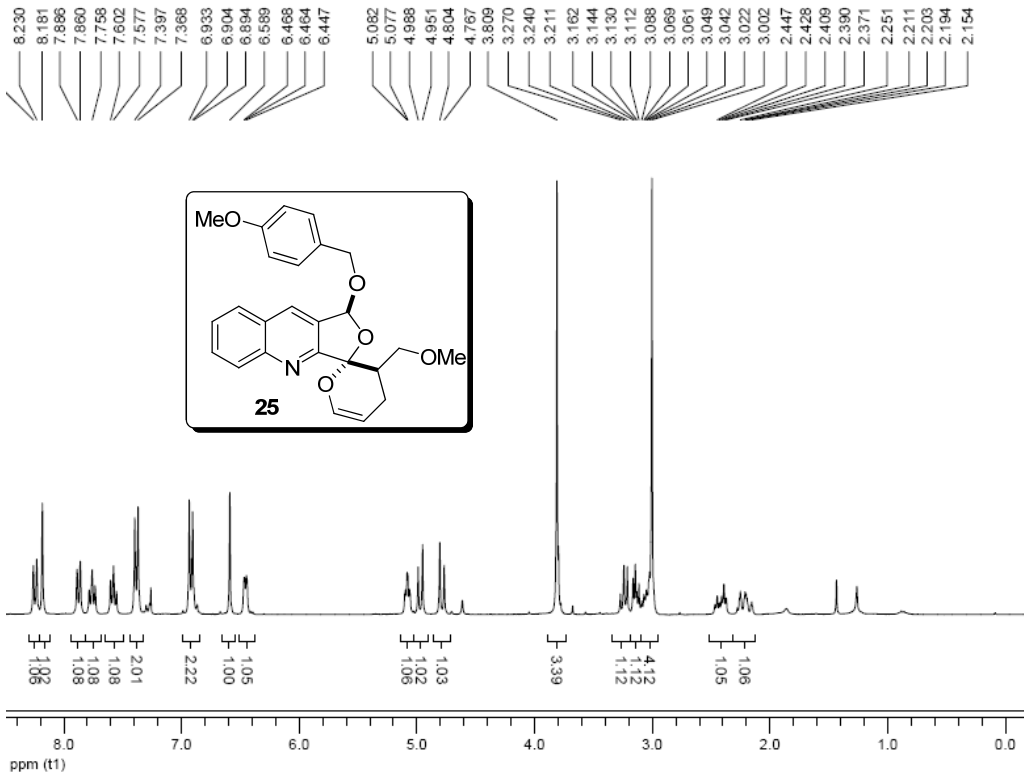
^{1}H NMR ($CDCl_3$, 300 MHz) of **24**



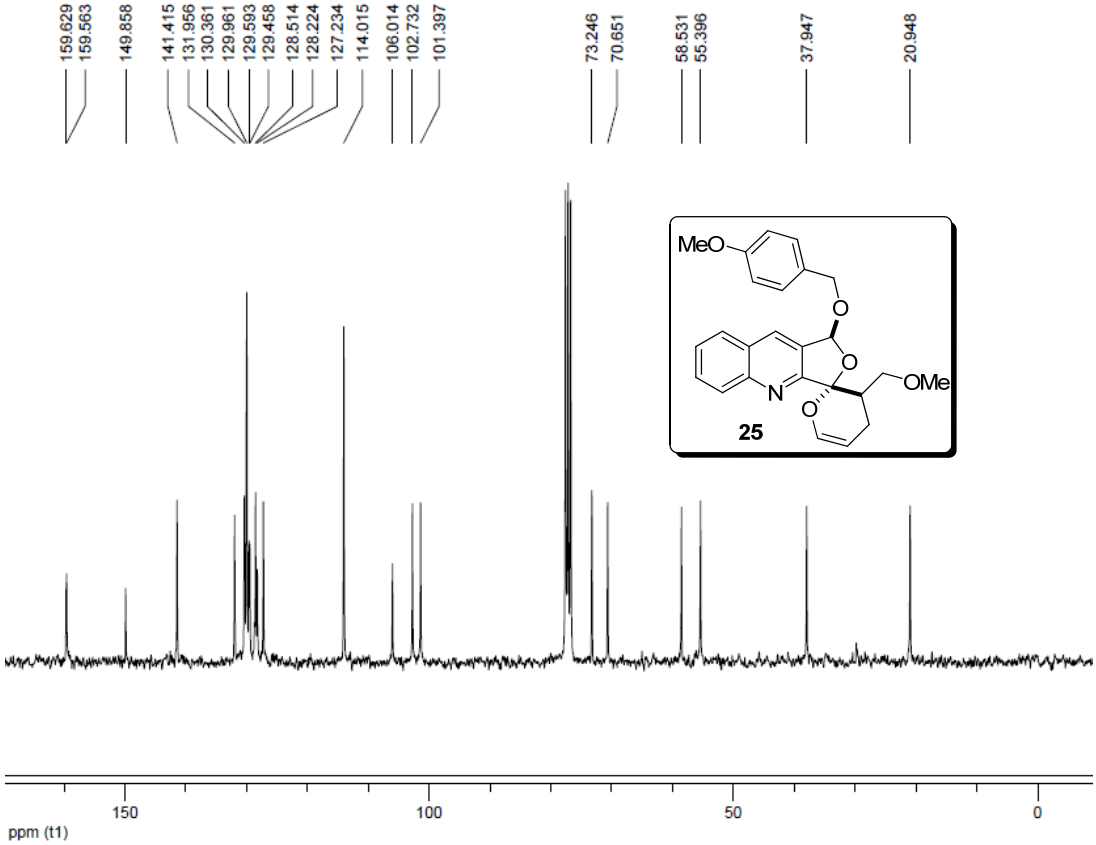
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz) of **24**



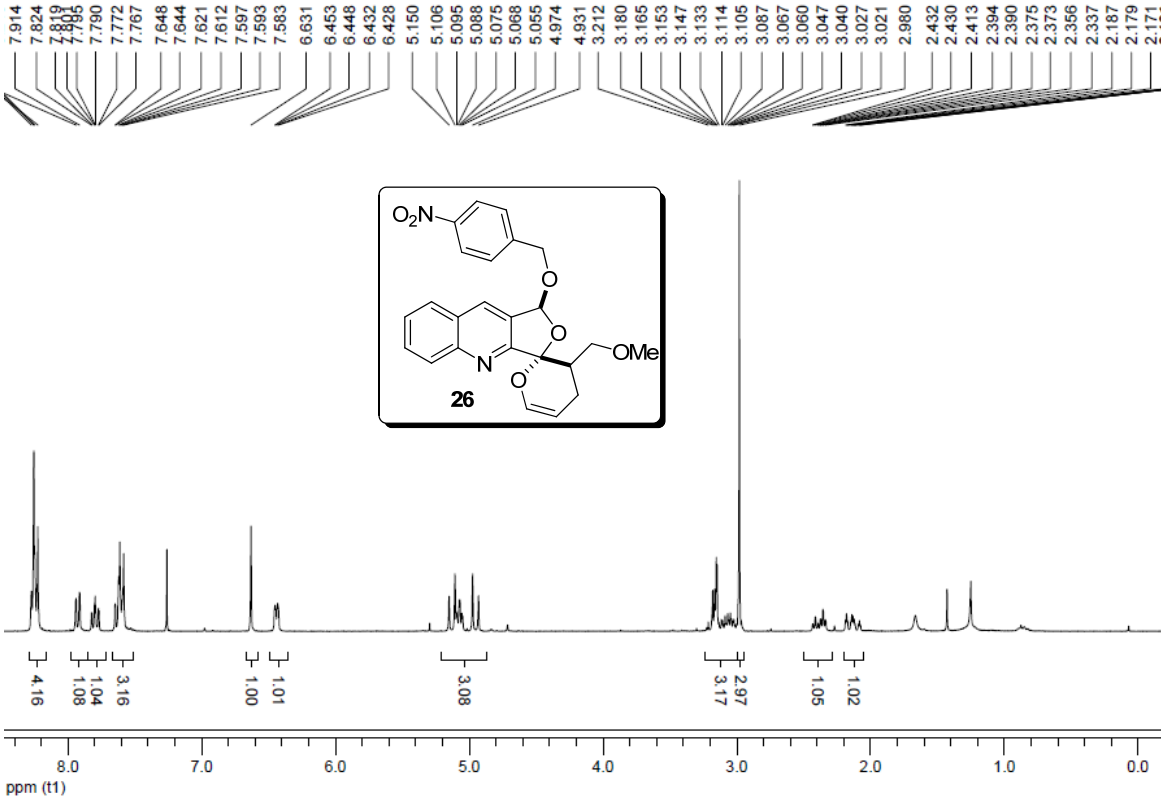
^{1}H NMR ($CDCl_3$, 300 MHz) of **25**



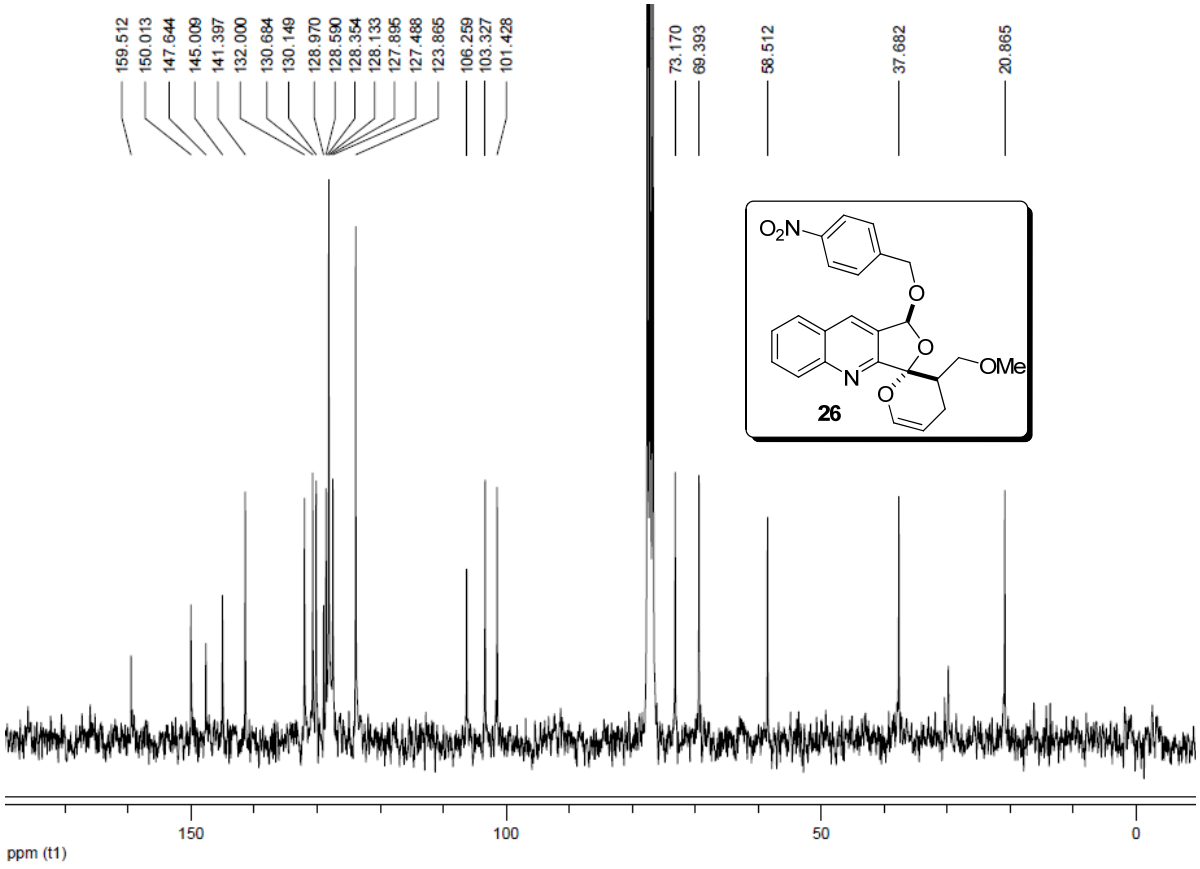
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz) of **25**



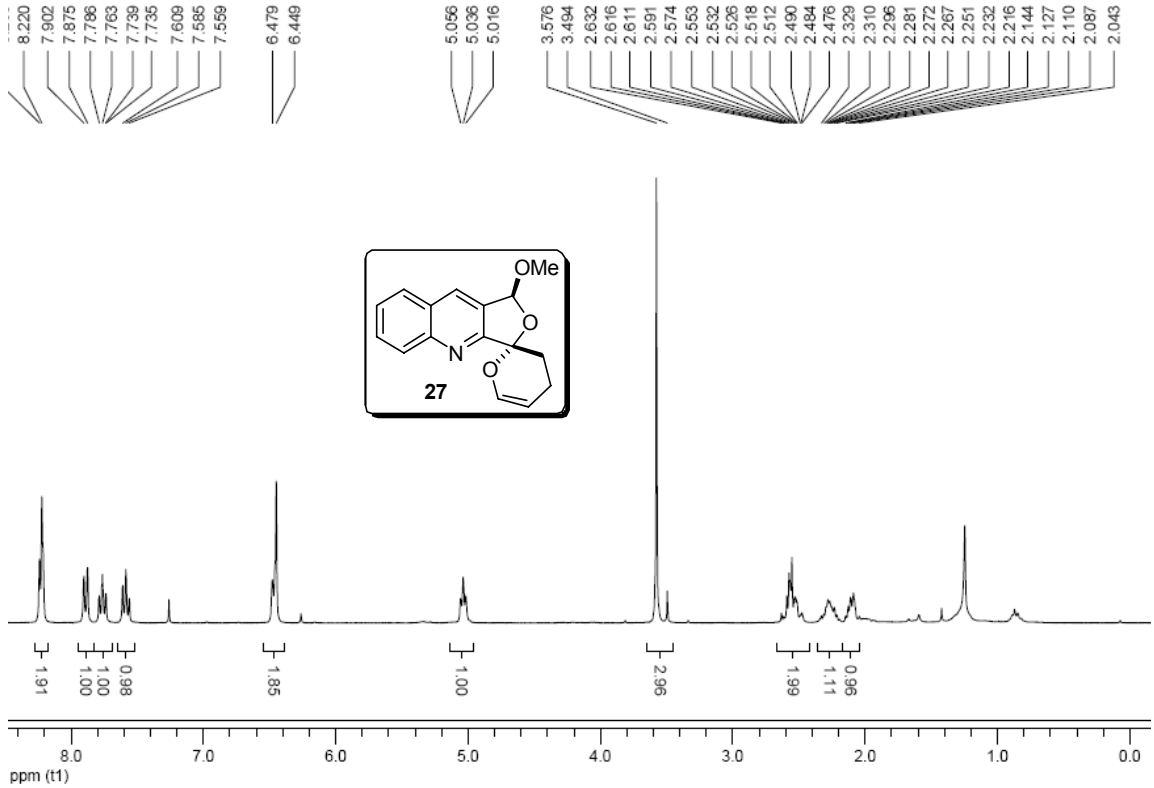
^{1}H NMR ($CDCl_3$, 300 MHz) of **26**



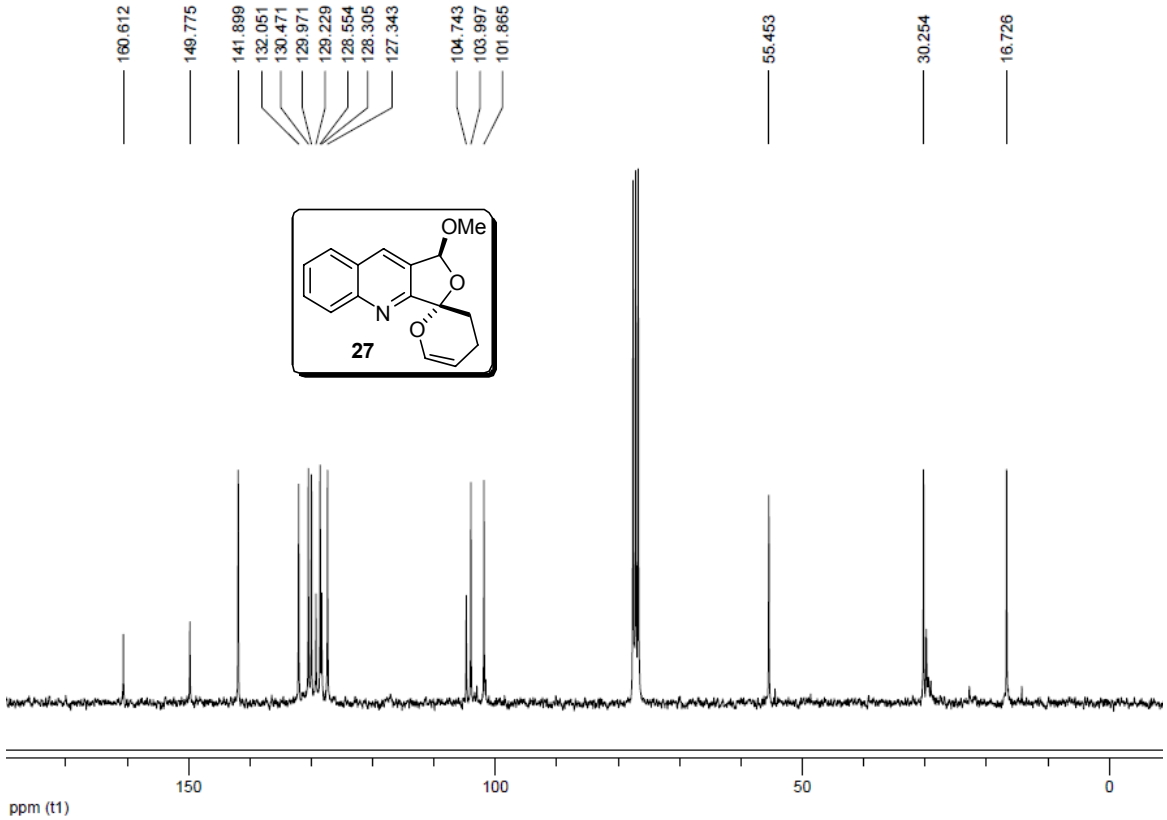
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz) of **26**



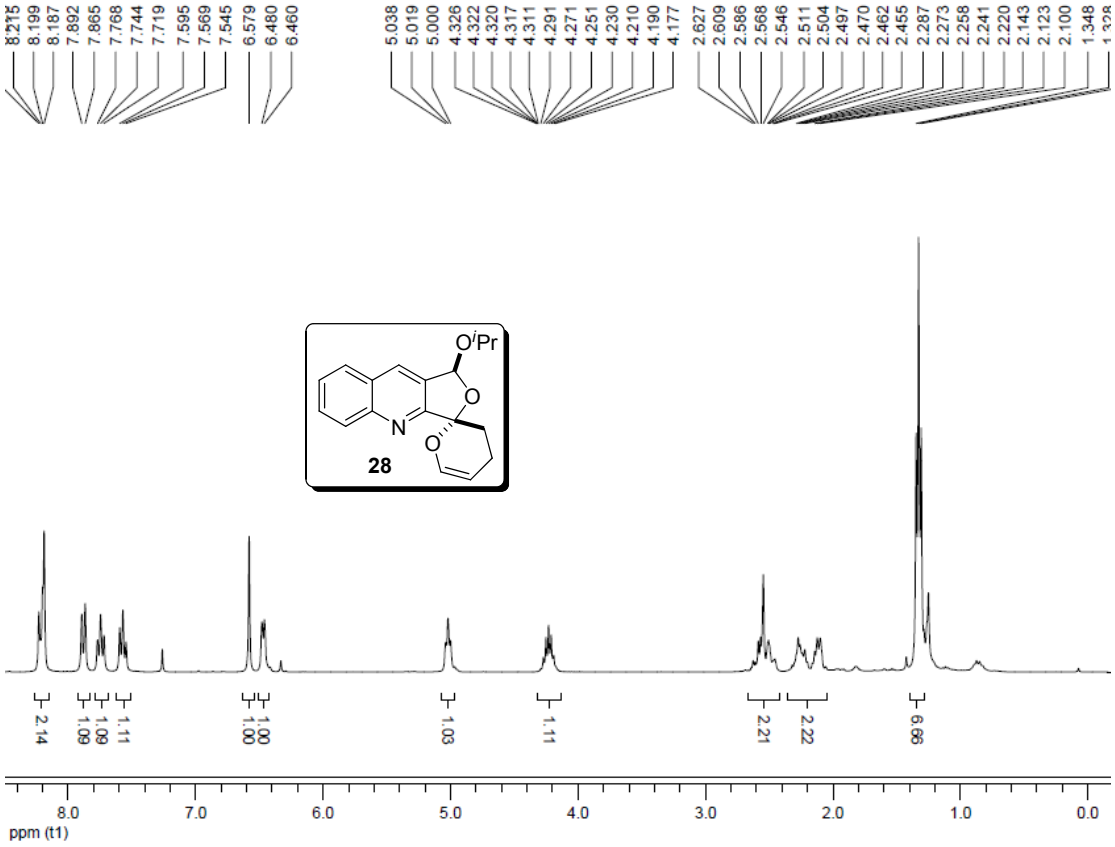
^{1}H NMR ($CDCl_3$, 300 MHz) of **27**



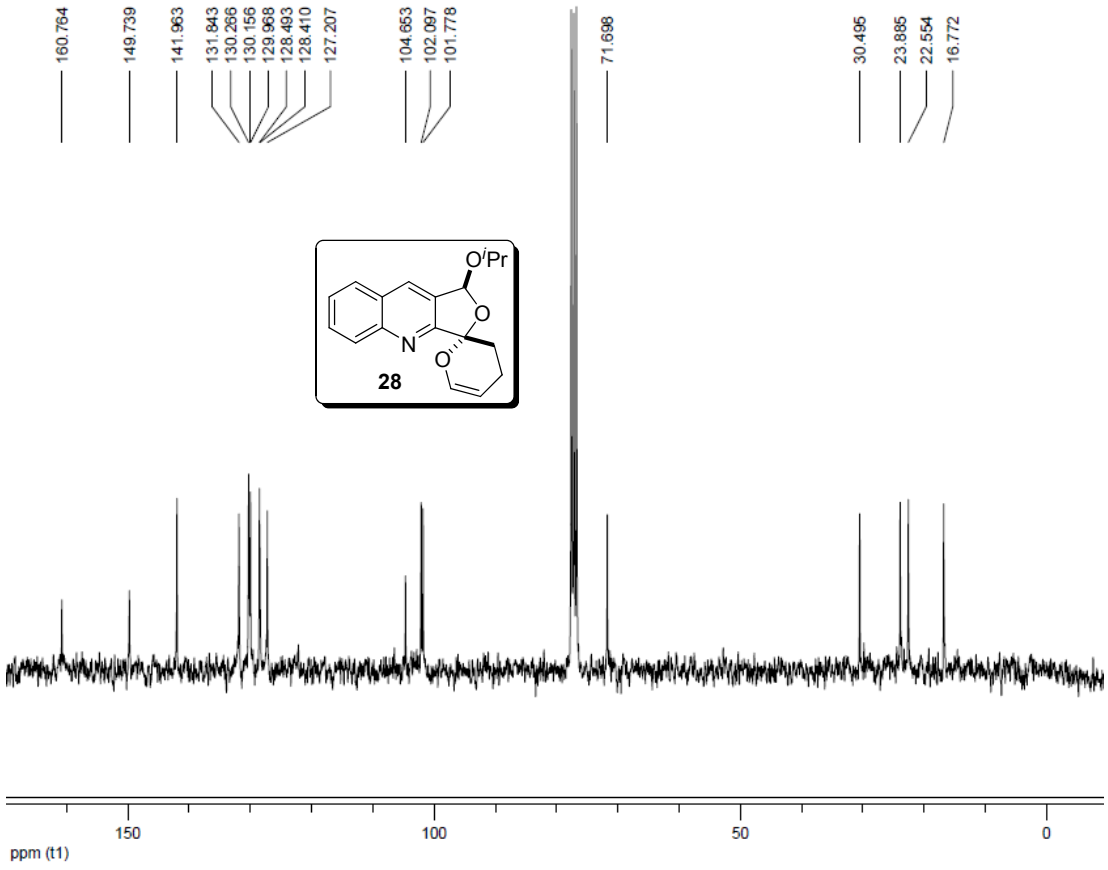
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz) of **27**



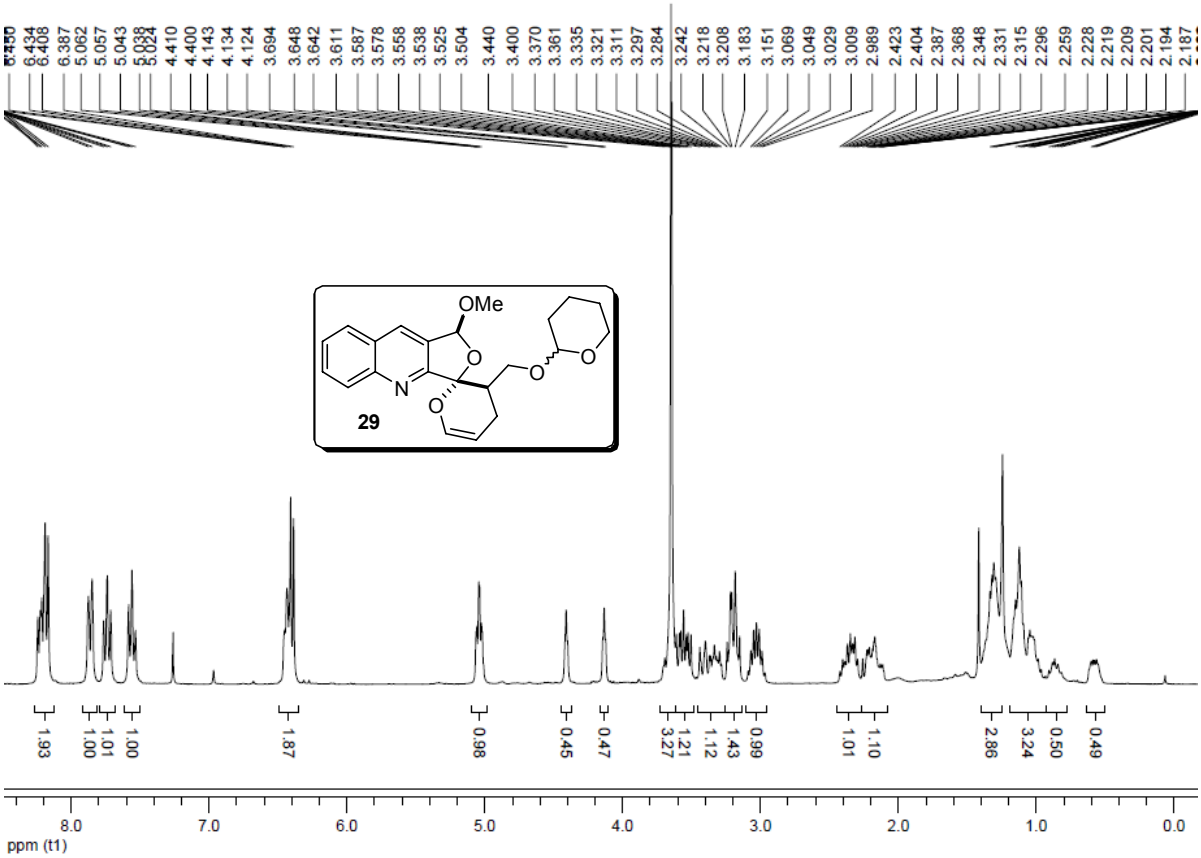
^{1}H NMR ($CDCl_3$, 300 MHz) of **28**



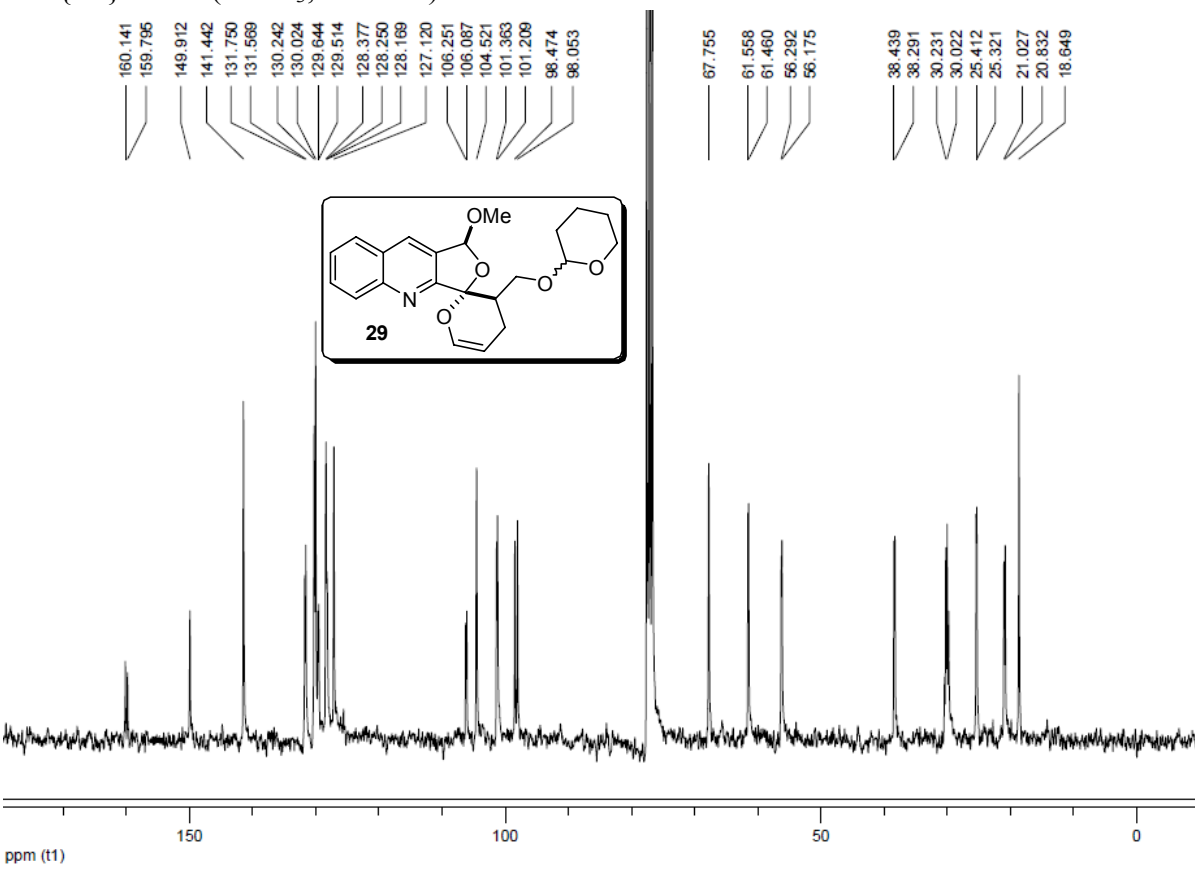
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz) of **28**



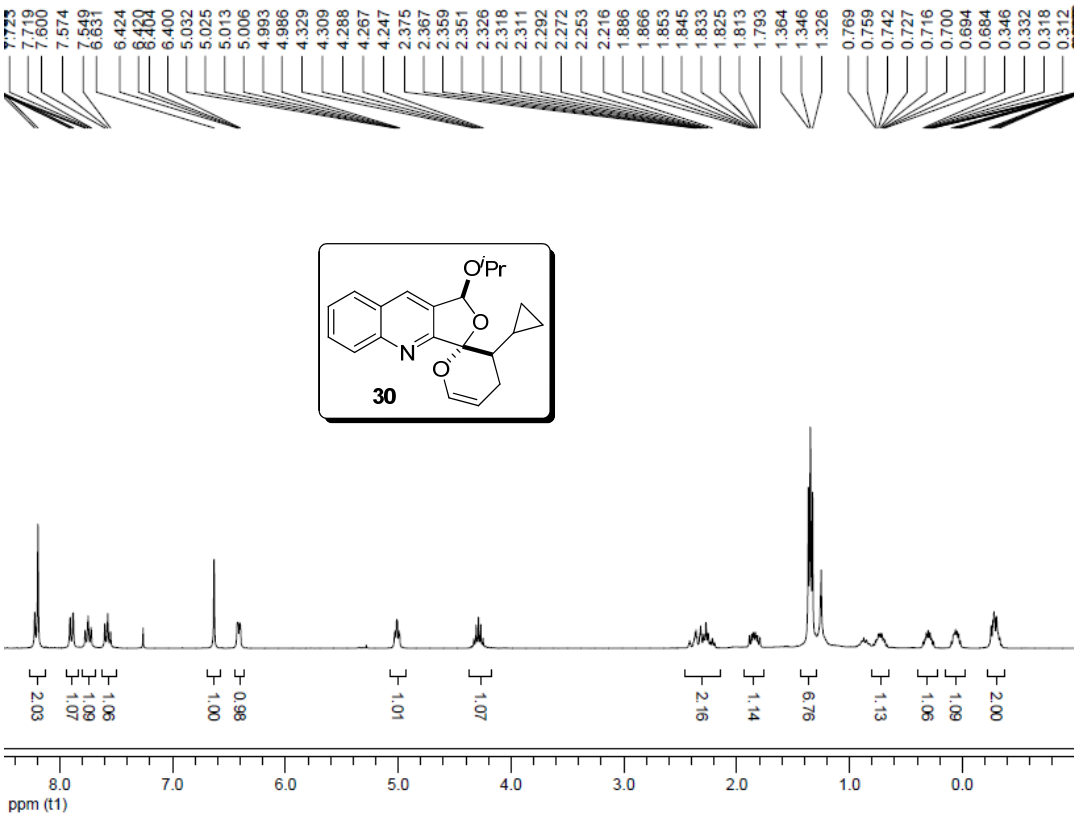
^{1}H NMR ($CDCl_3$, 300 MHz) of **29**



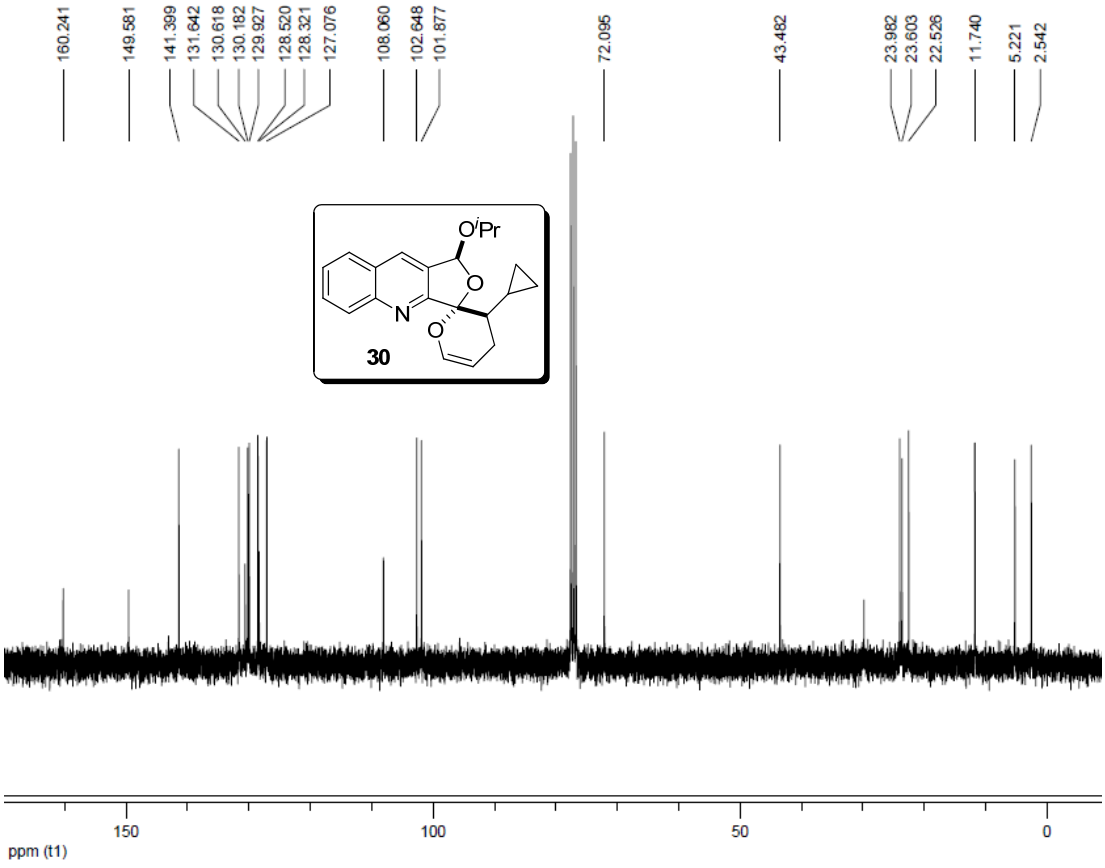
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz) of **29**



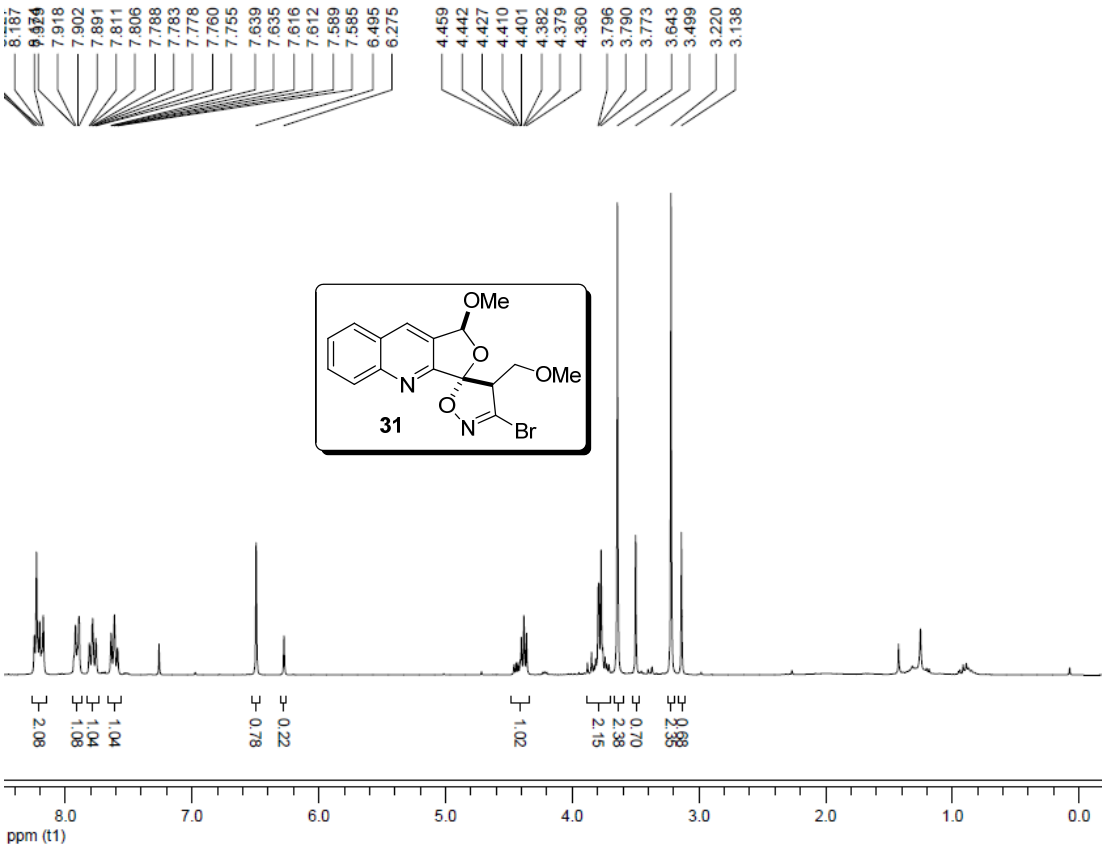
^{1}H NMR ($CDCl_3$, 300 MHz) of **30**



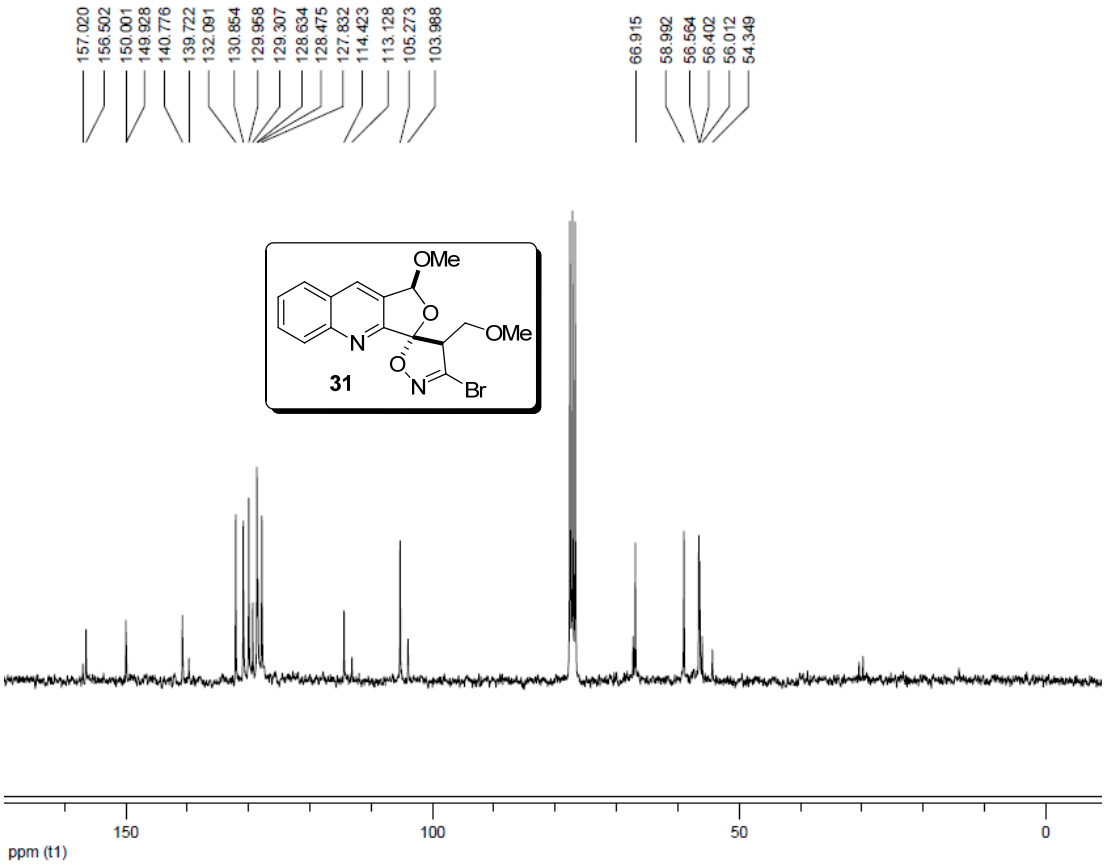
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz) of **30**



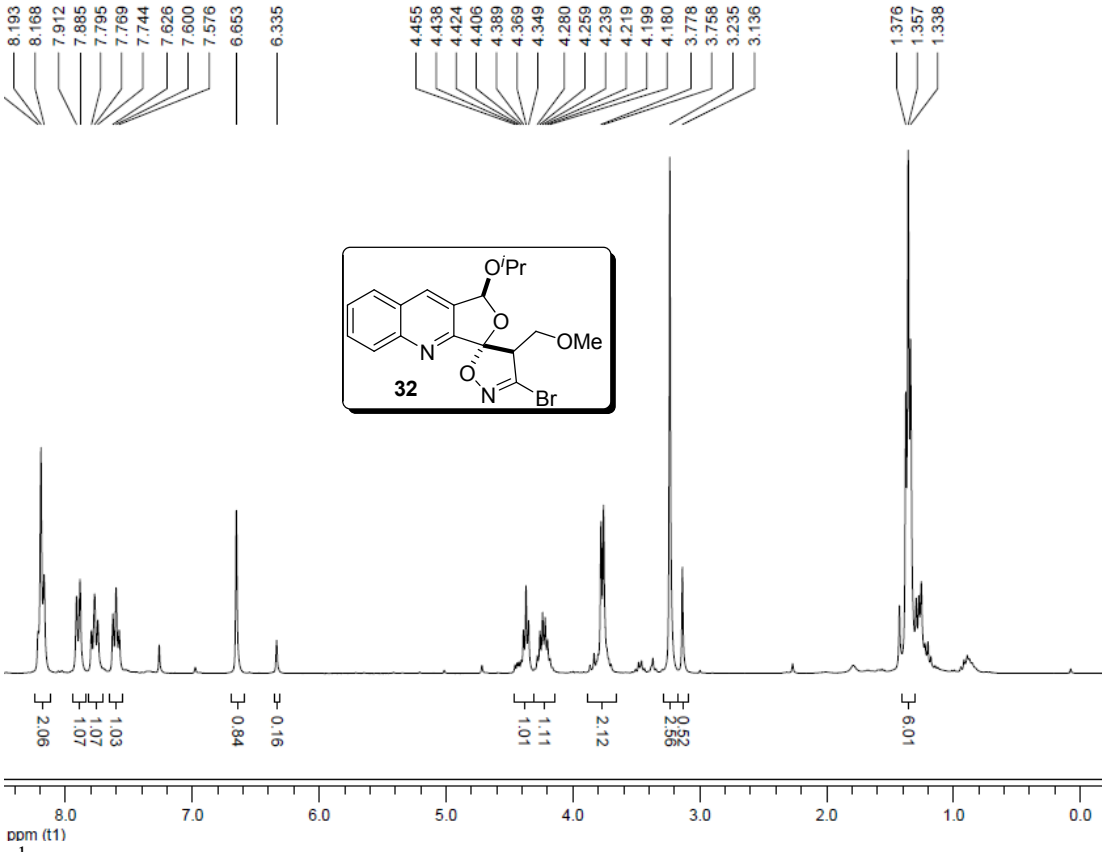
^{1}H NMR ($CDCl_3$, 300 MHz) of **31**



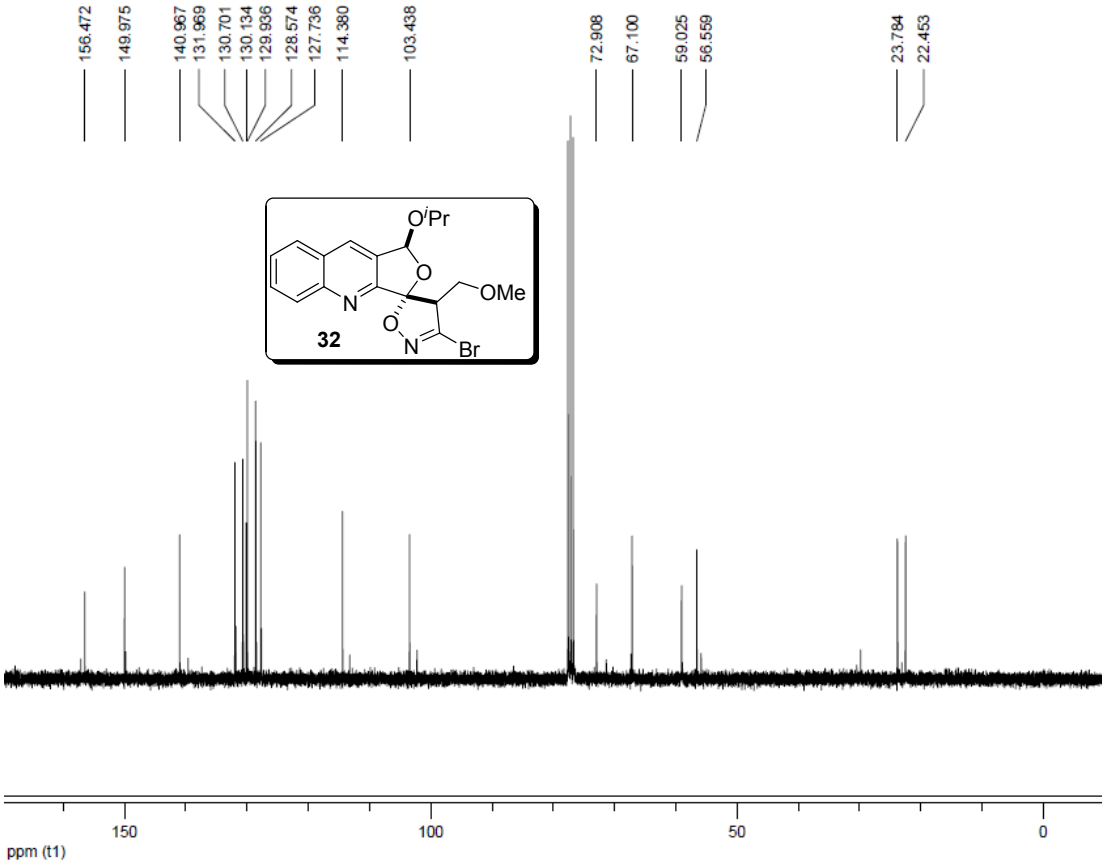
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz) of **31**



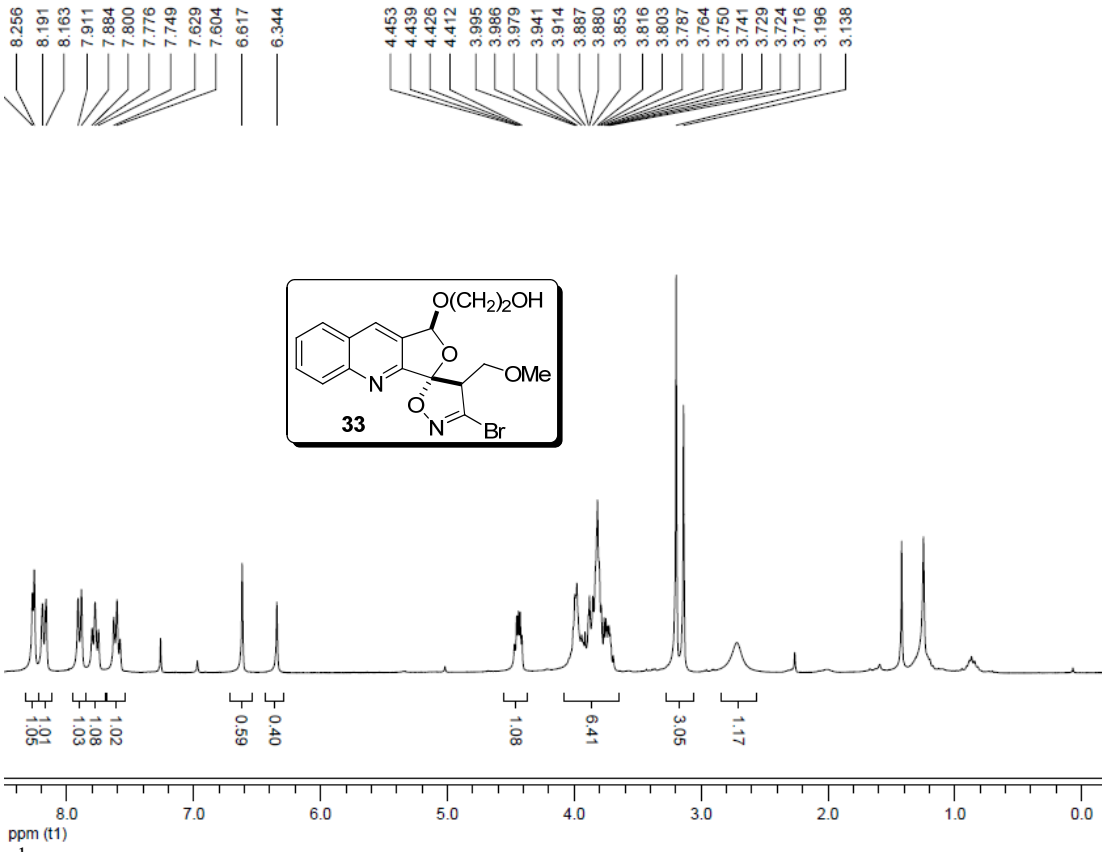
^{1}H NMR ($CDCl_3$, 300 MHz) of **32**



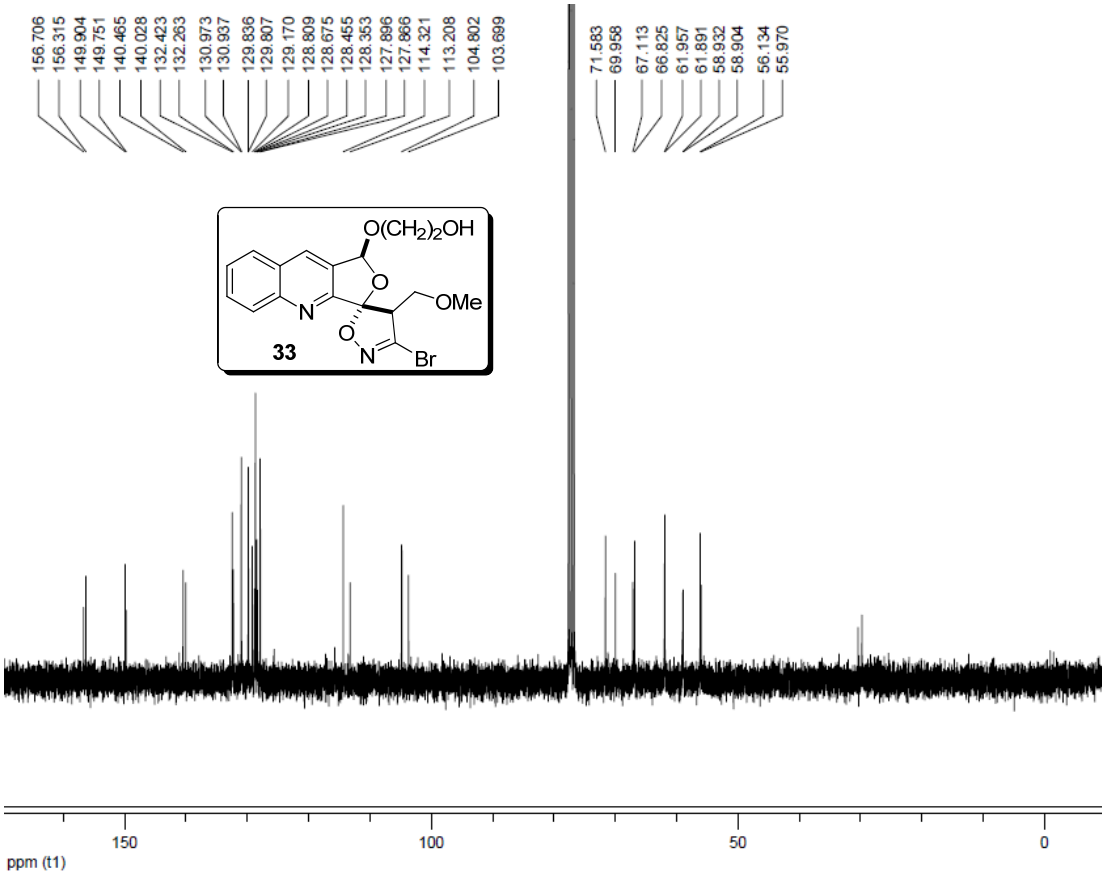
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz) of **32**



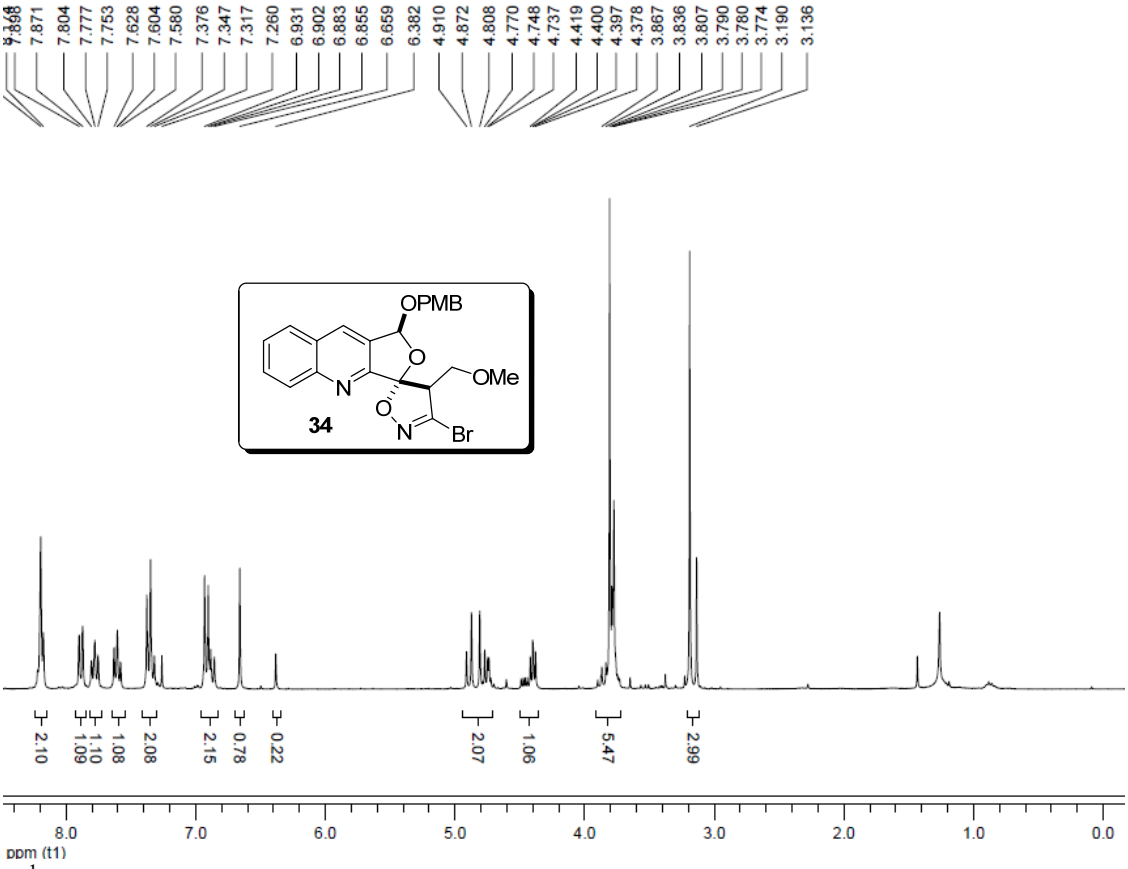
^{1}H NMR ($CDCl_3$, 300 MHz) of **33**



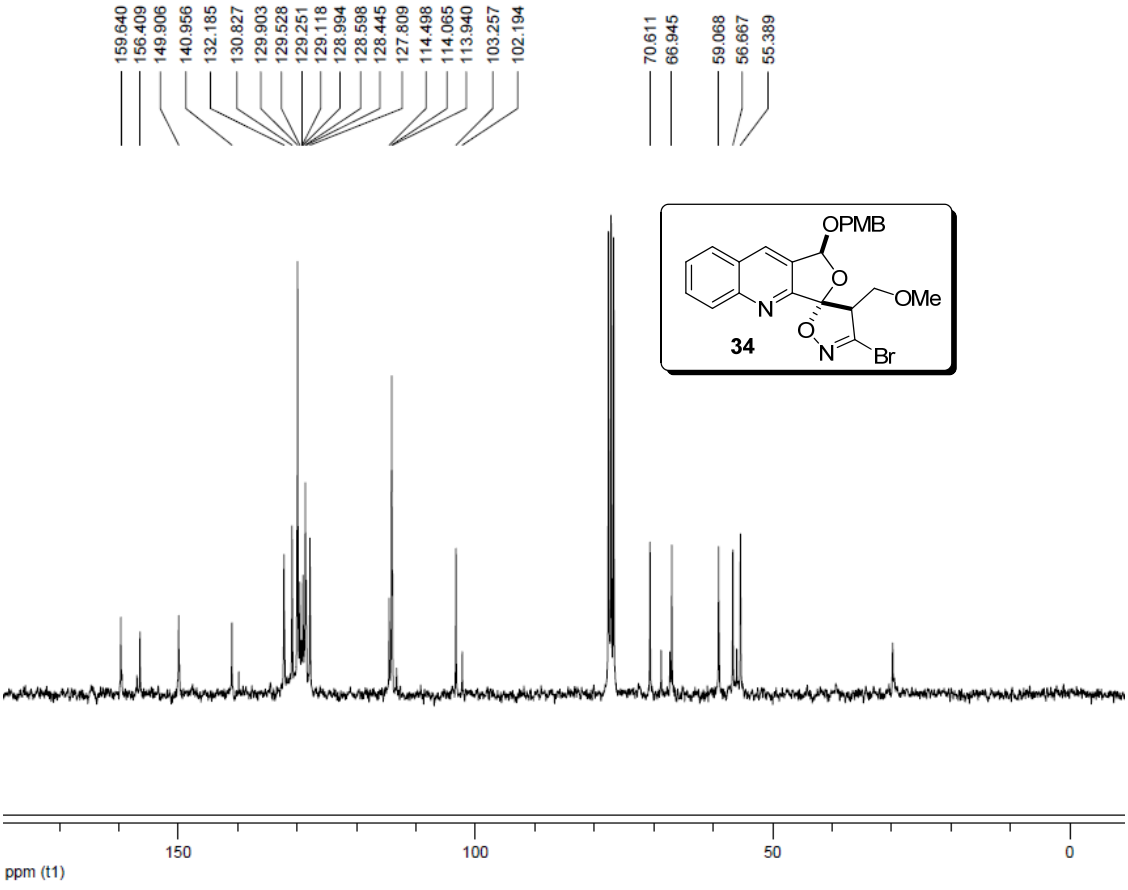
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz) of **33**



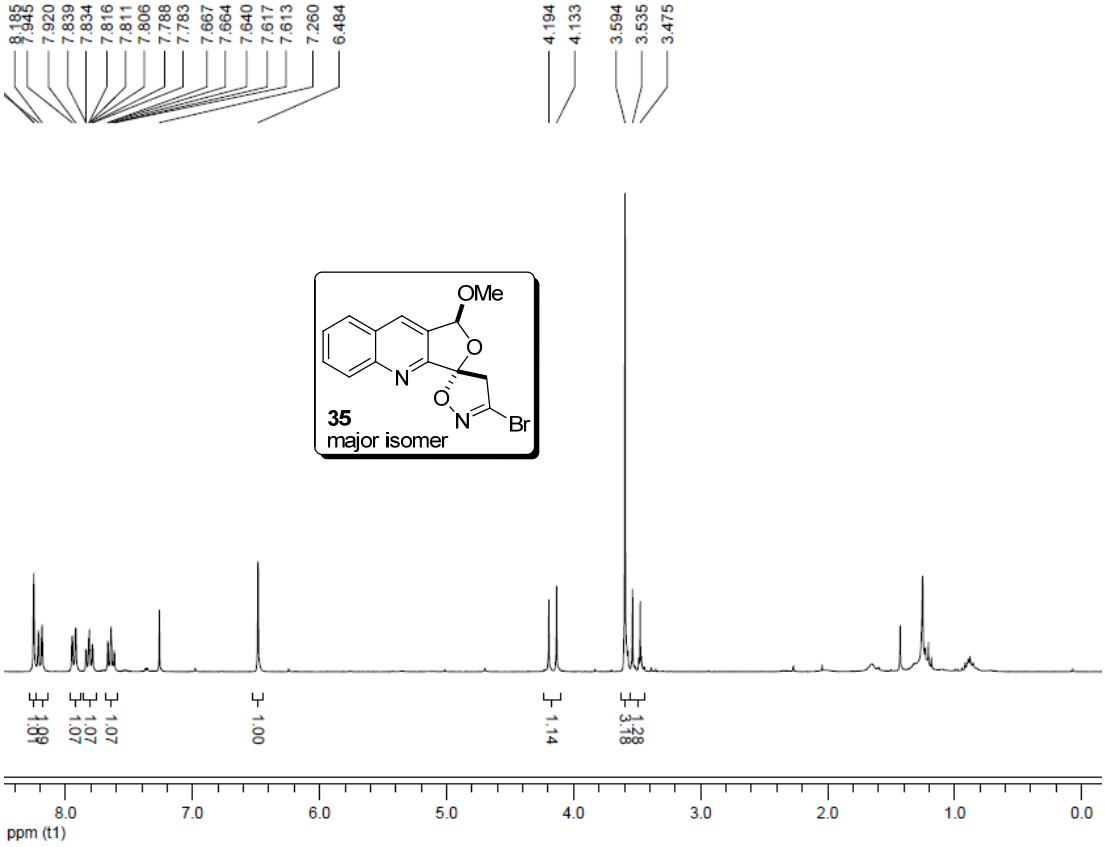
^{1}H NMR ($CDCl_3$, 300 MHz) of **34**



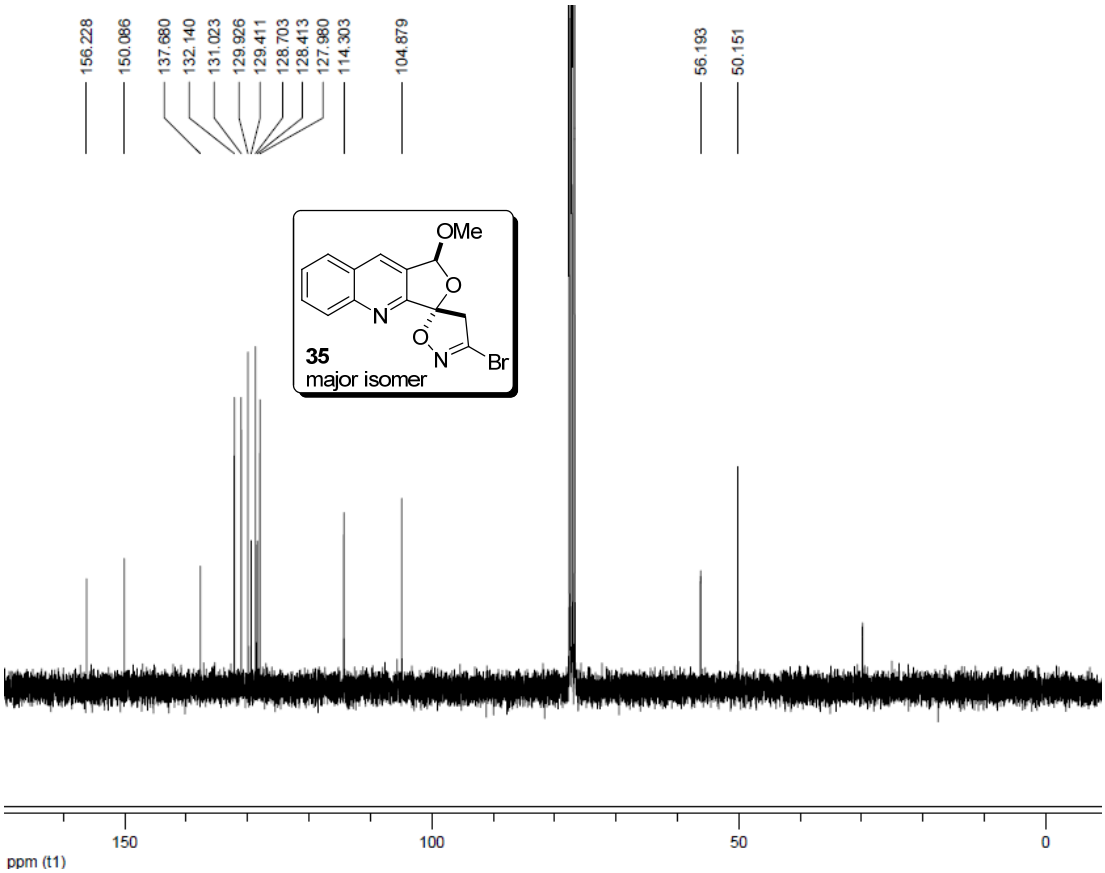
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz) of **34**



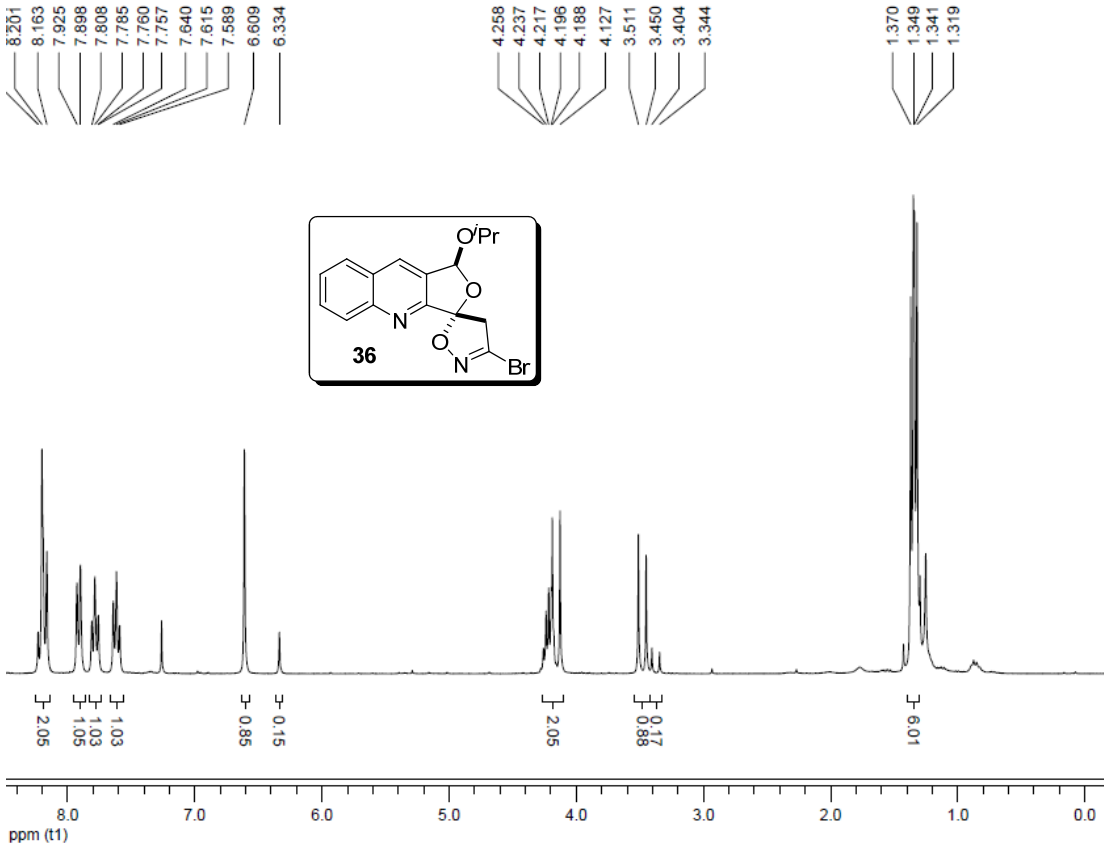
^{1}H NMR ($CDCl_3$, 300 MHz) of **35**



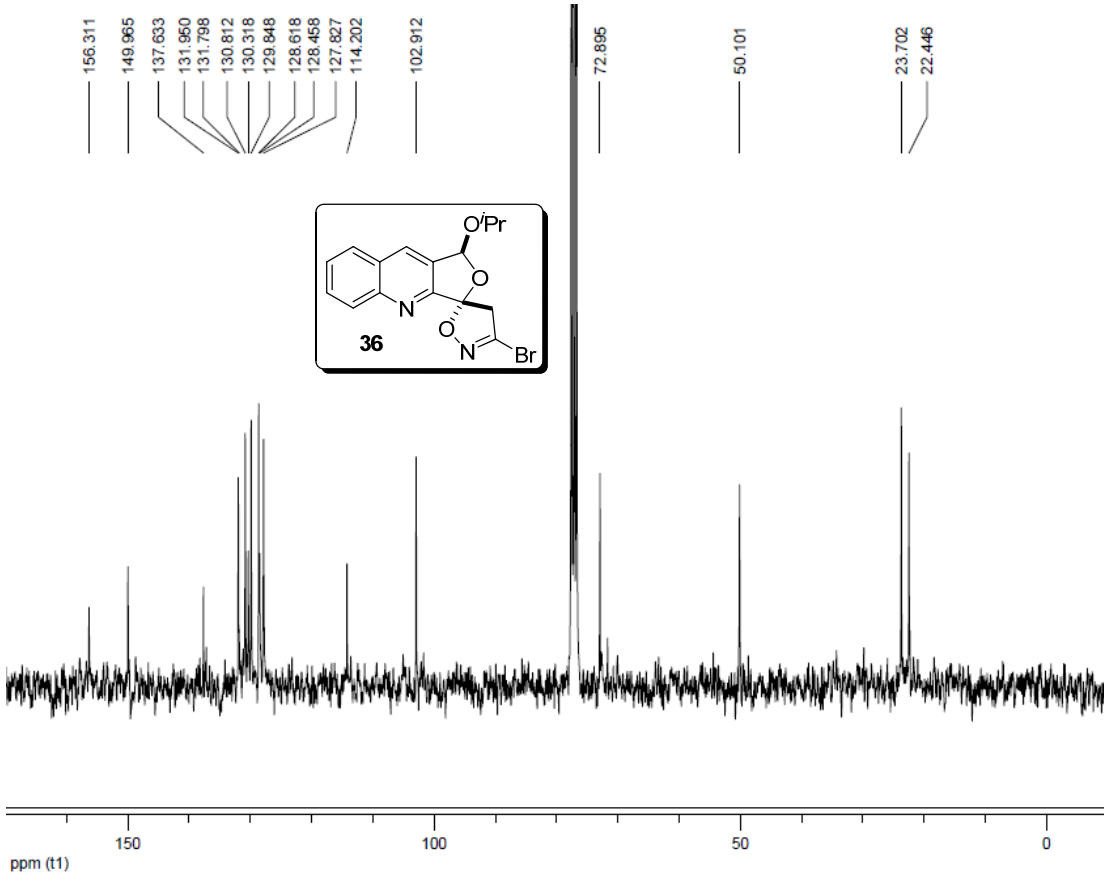
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz) of **35**



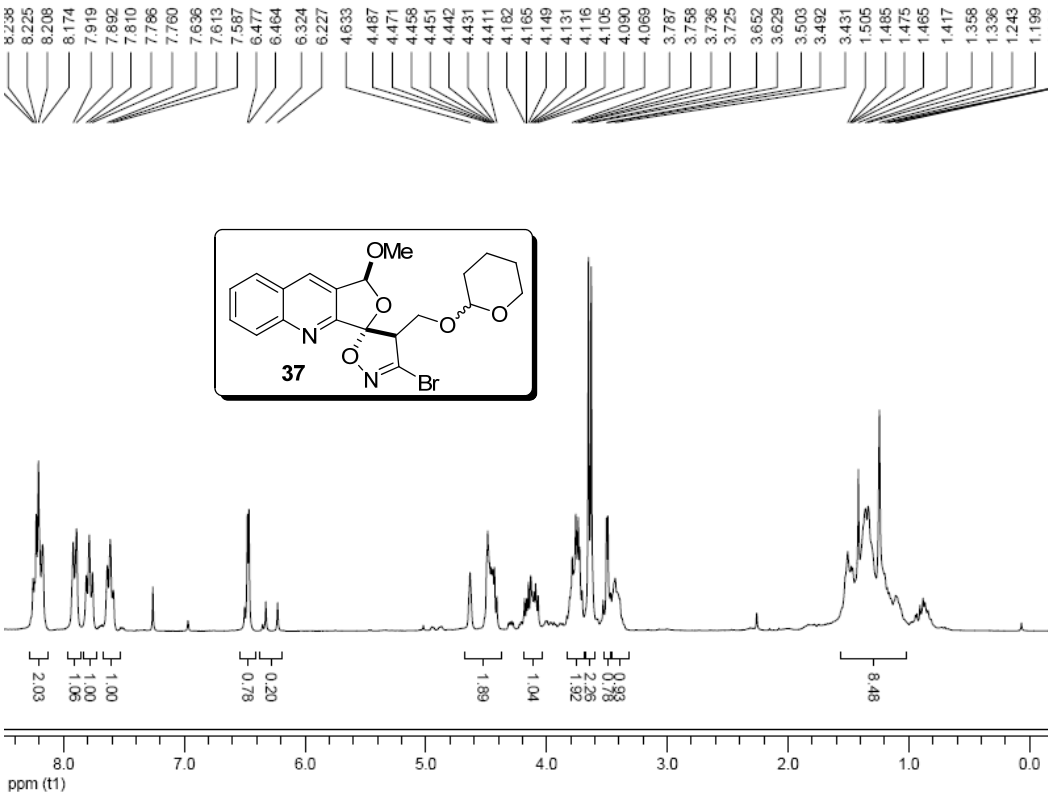
^{1}H NMR ($CDCl_3$, 300 MHz) of **36**



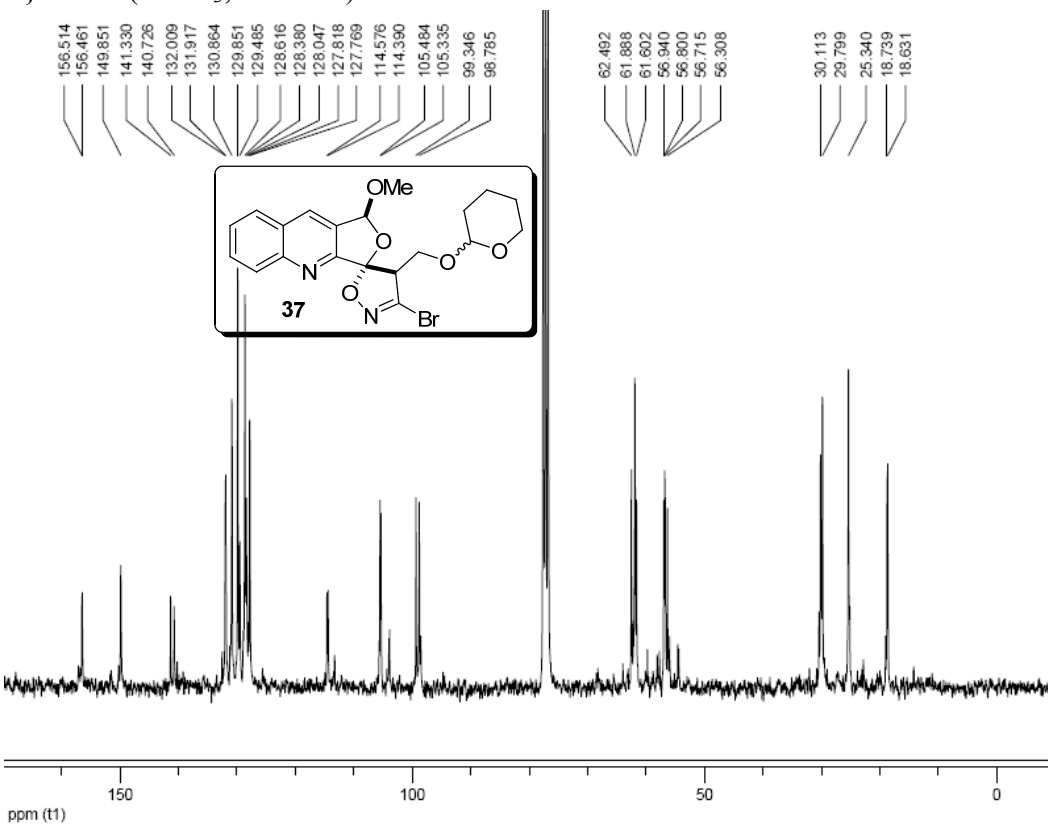
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz) of **36**



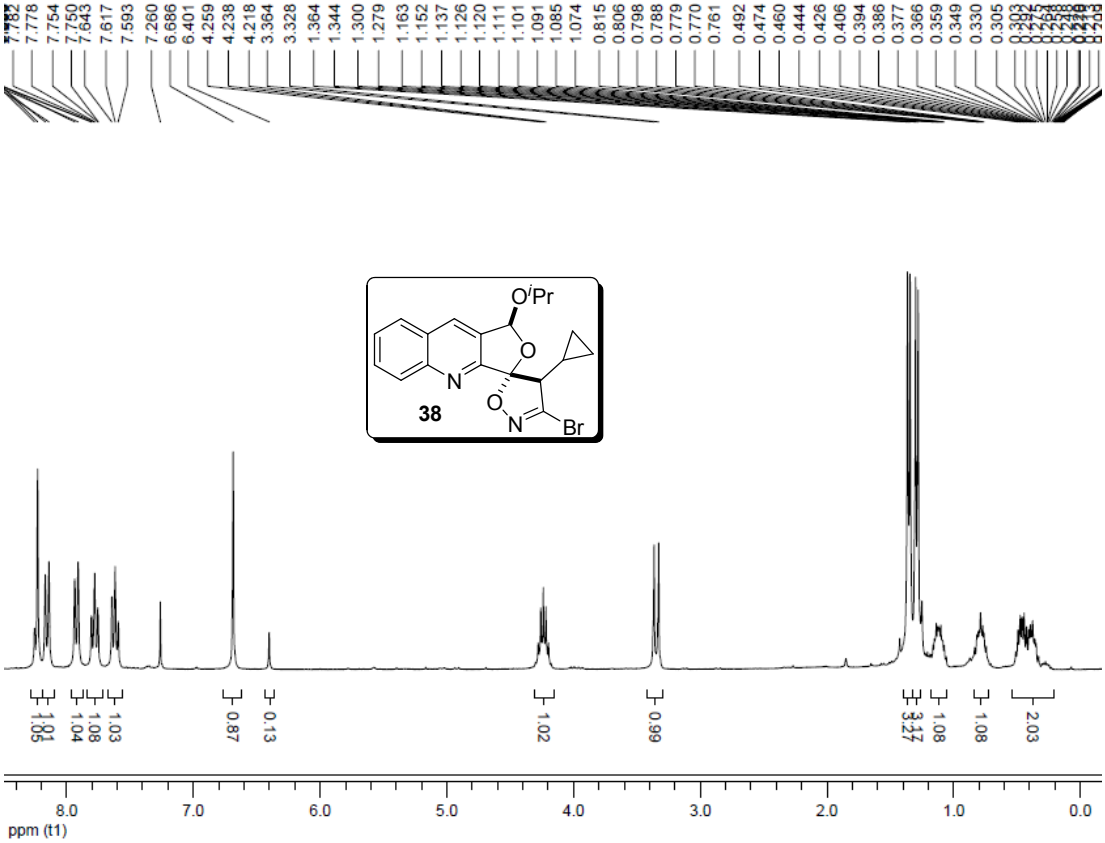
^{1}H NMR ($CDCl_3$, 300 MHz) of **37**



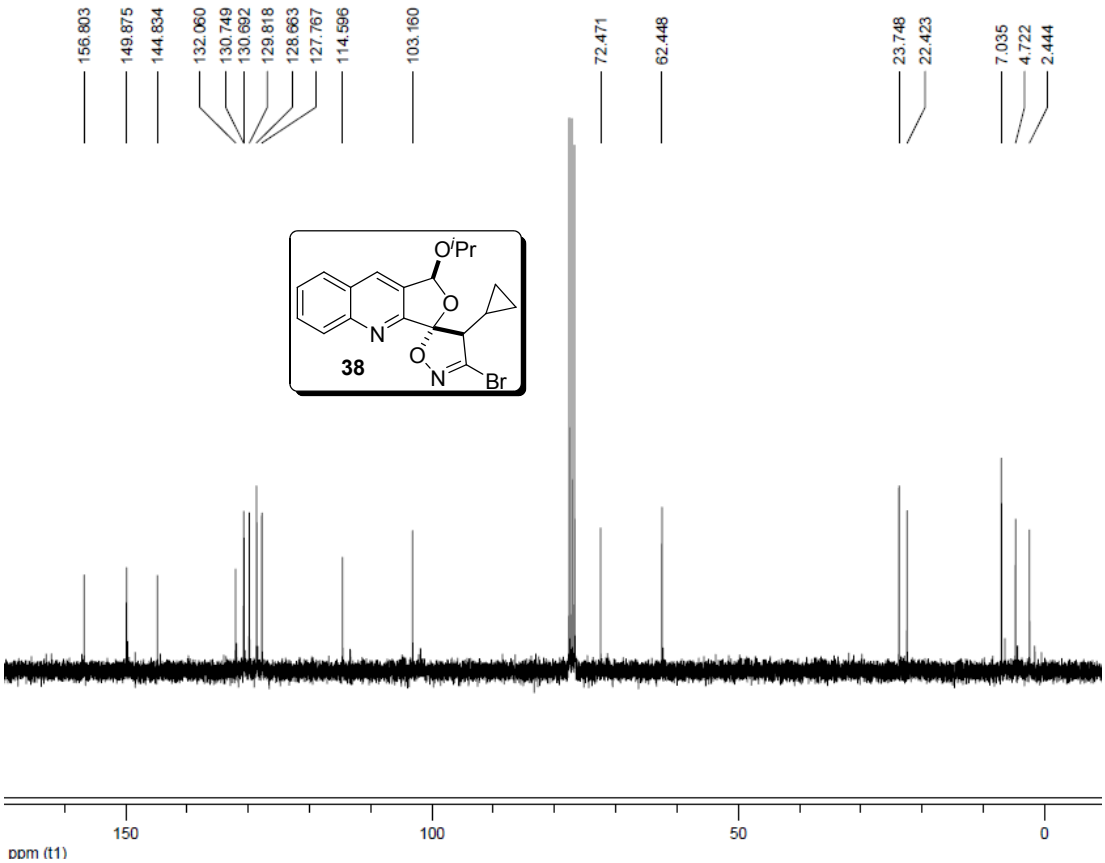
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz) of **37**



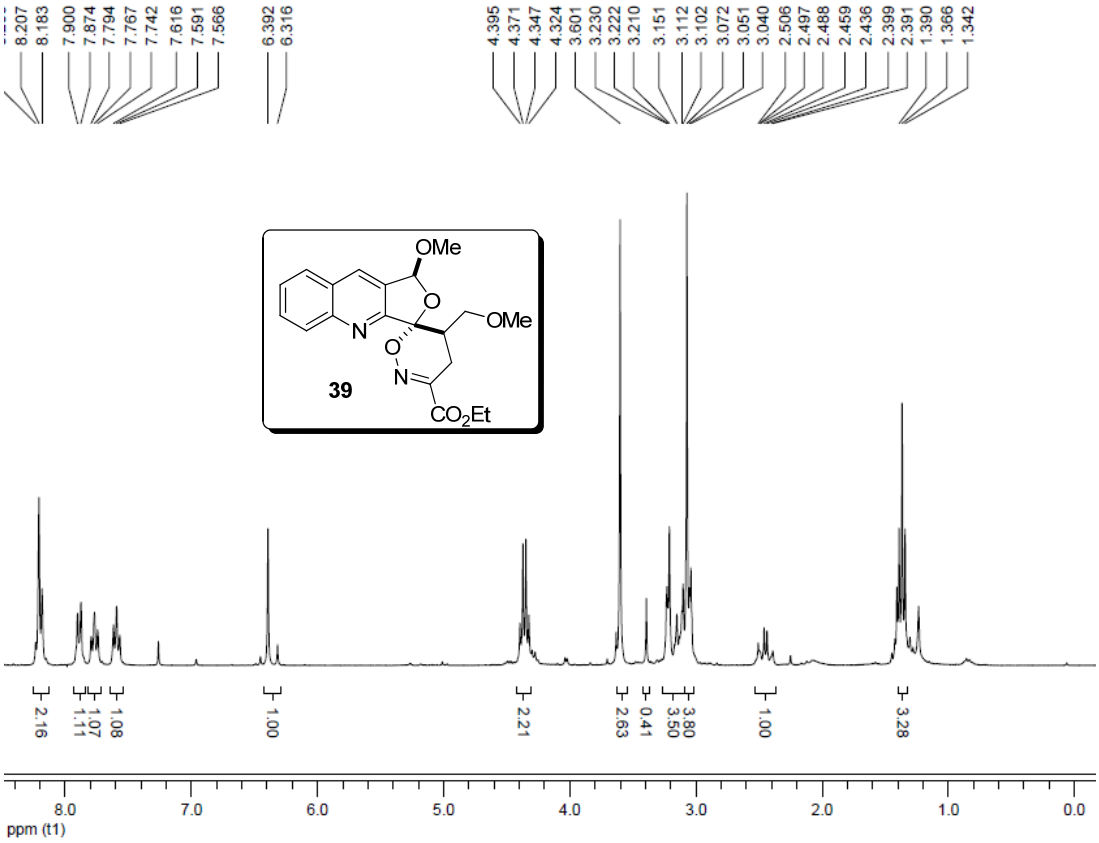
^{1}H NMR ($CDCl_3$, 300 MHz) of **38**



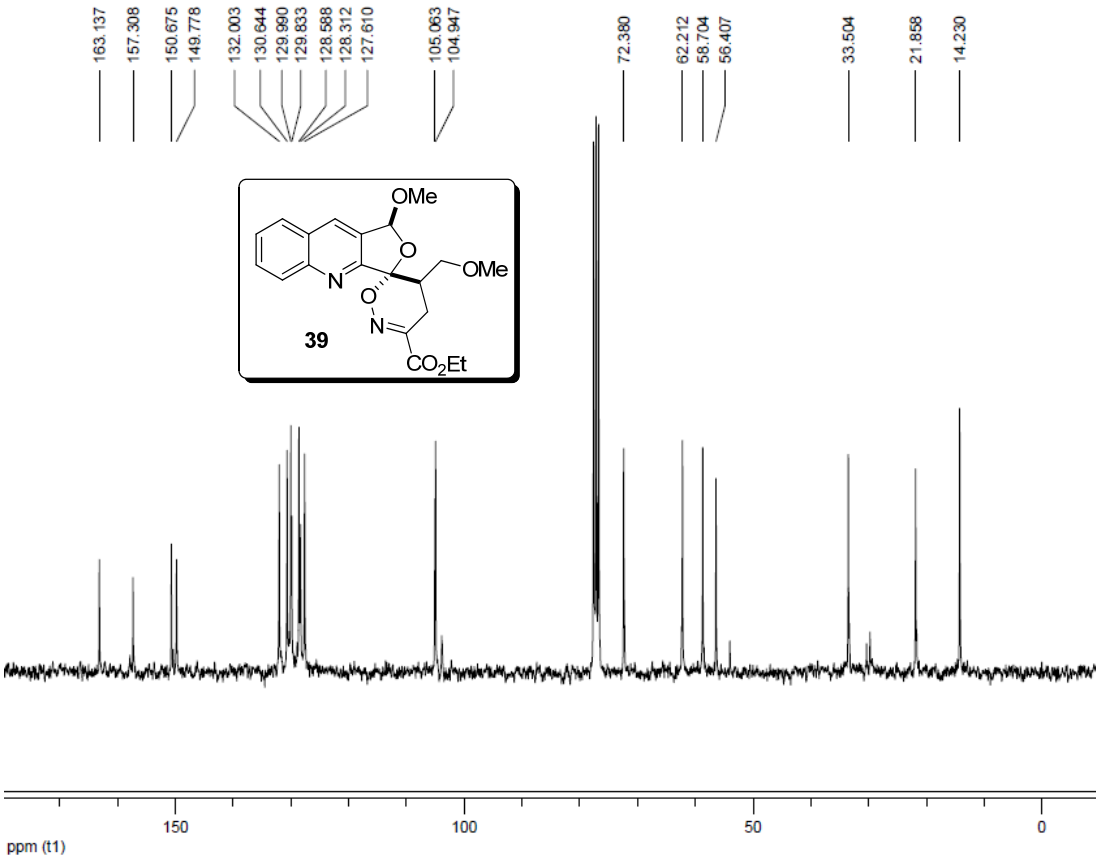
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz) of **38**



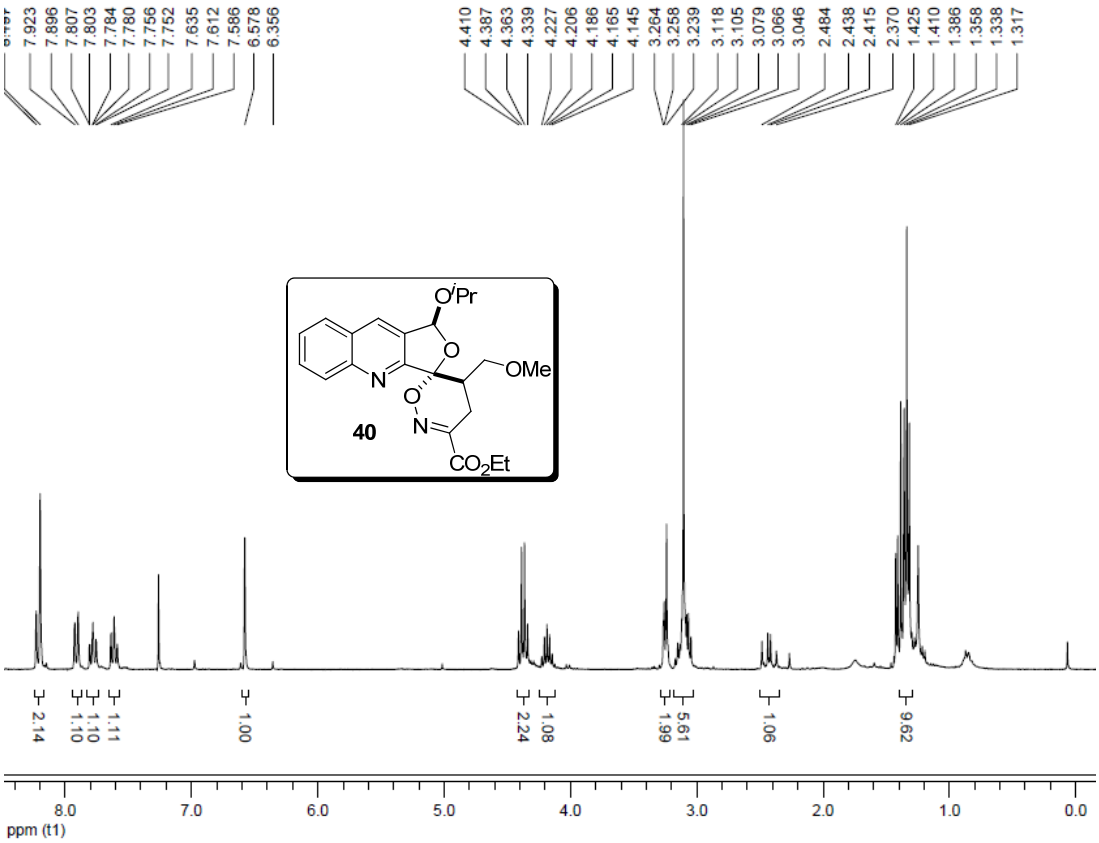
^{1}H NMR ($CDCl_3$, 300 MHz) of **39**



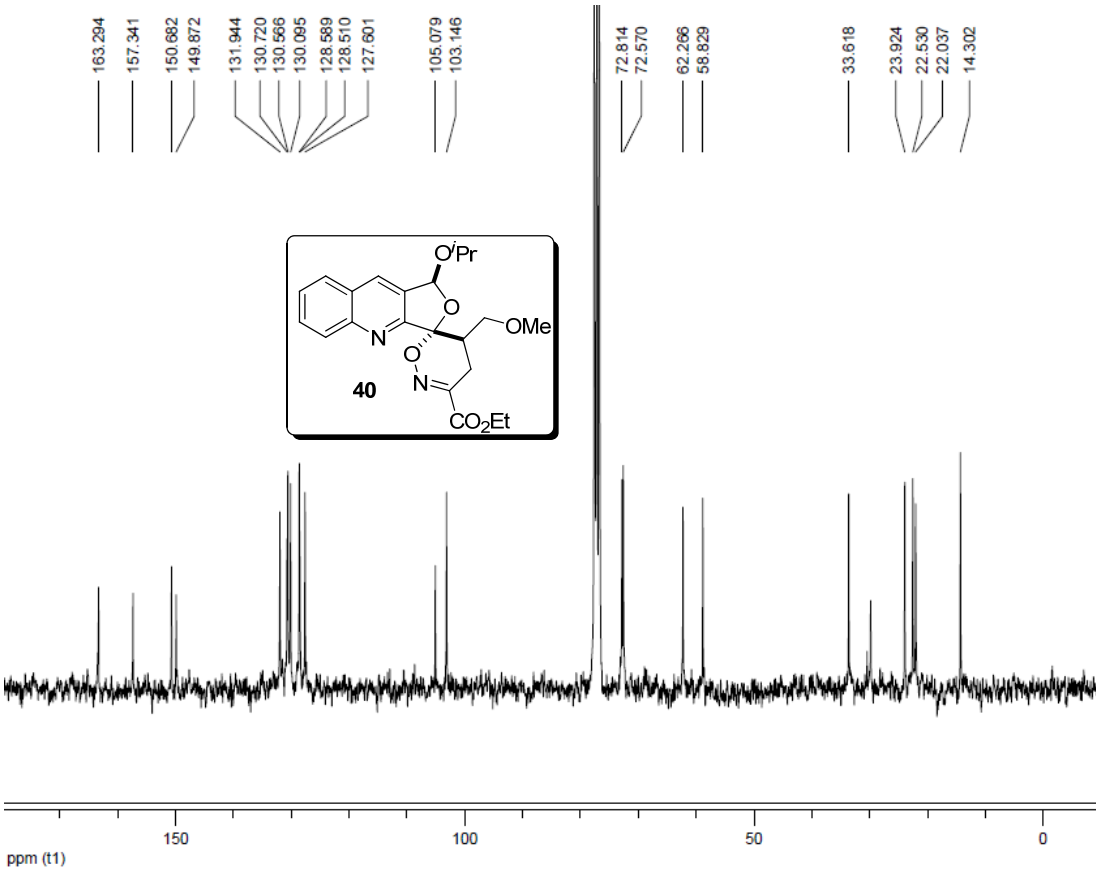
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz) of **39**



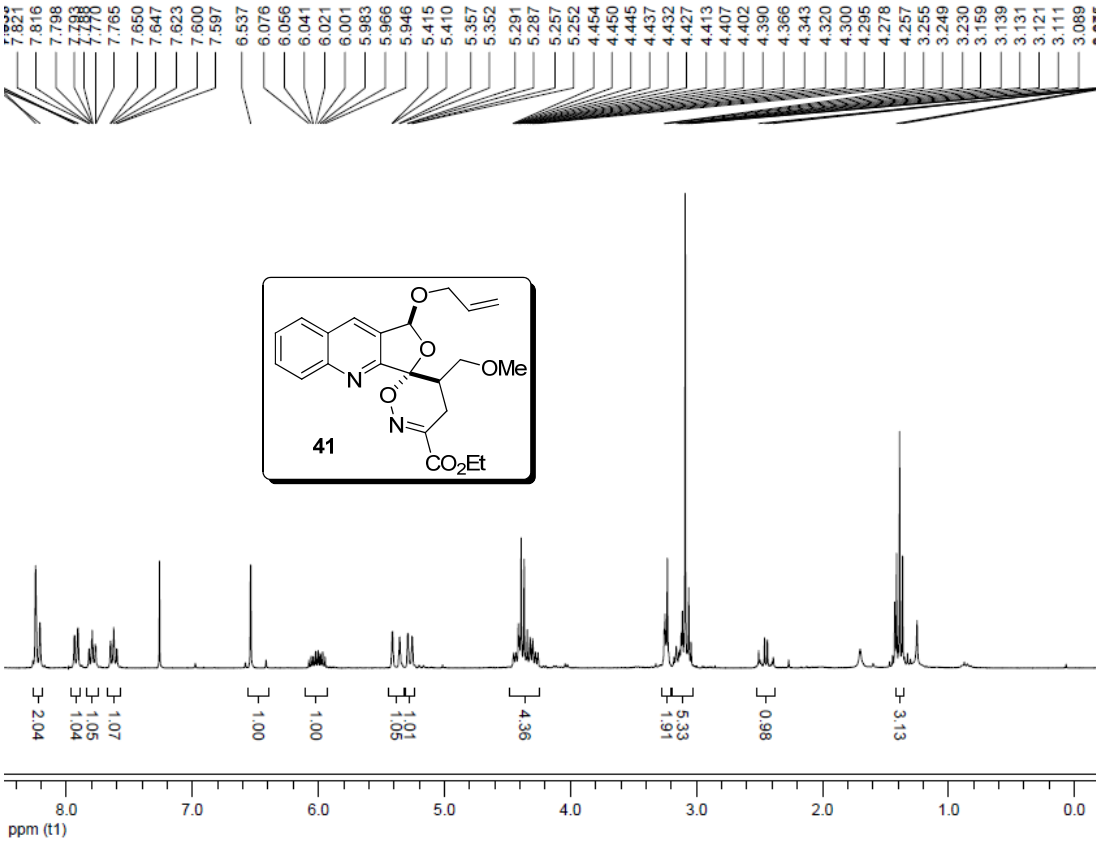
^{1}H NMR ($CDCl_3$, 300 MHz) of **40**



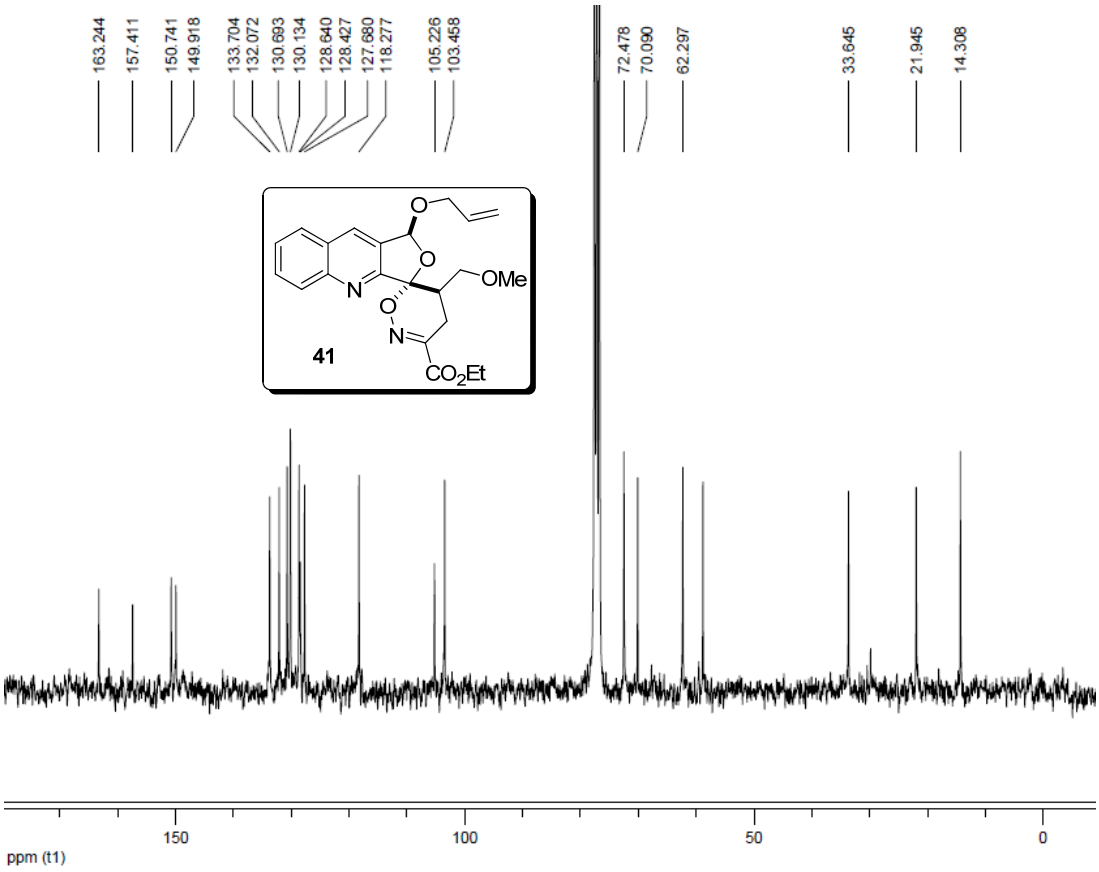
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz) of **40**



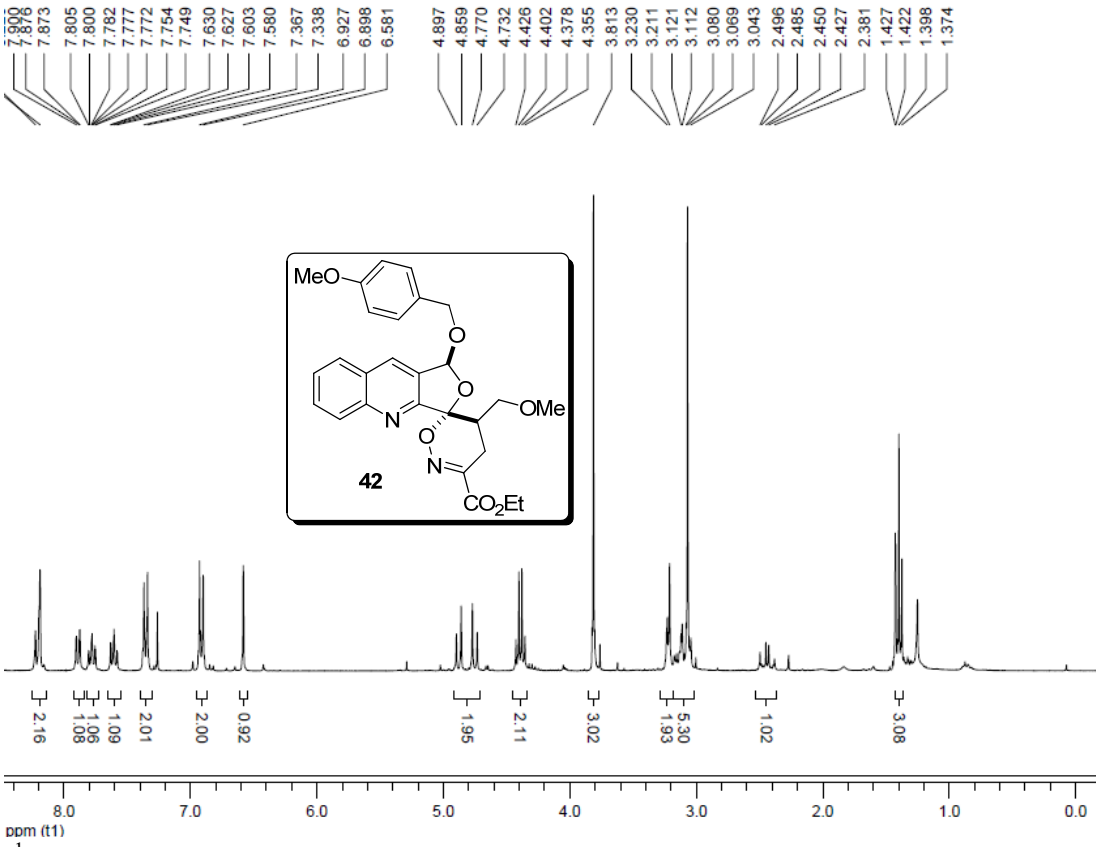
^{1}H NMR ($CDCl_3$, 300 MHz) of **41**



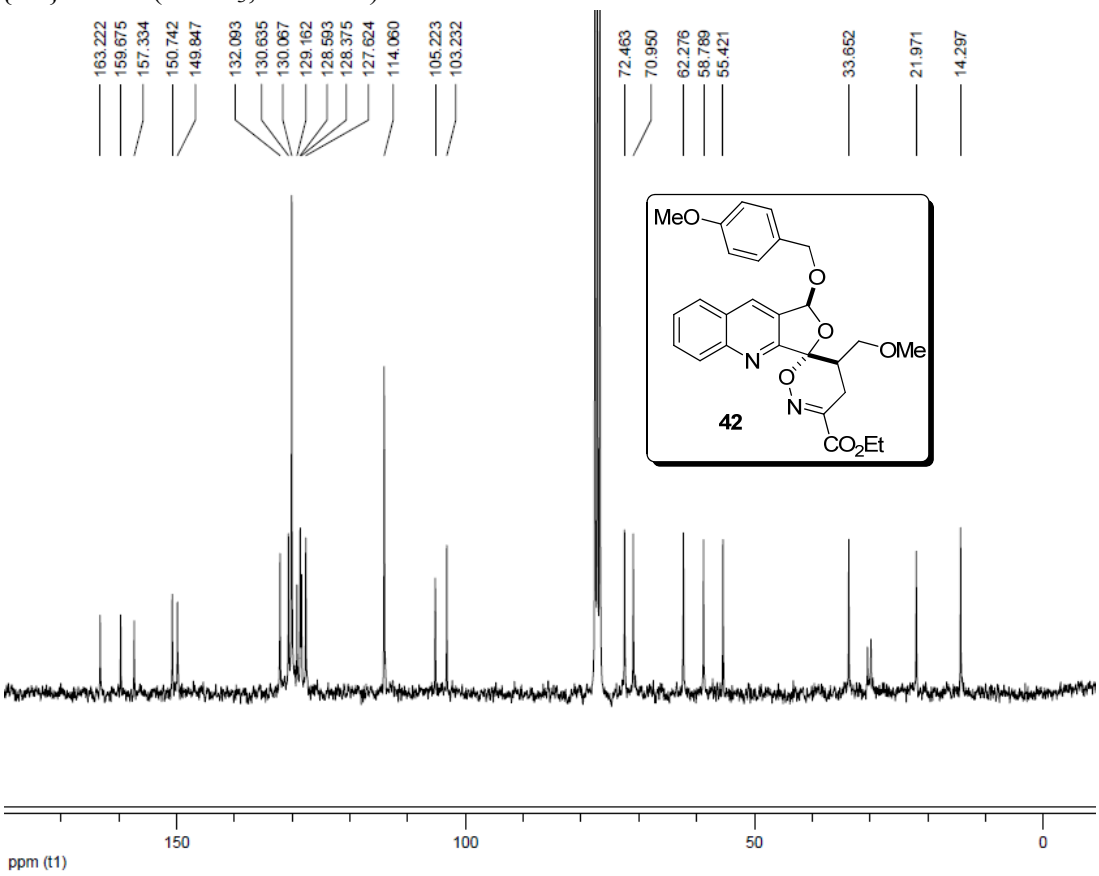
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz) of **41**



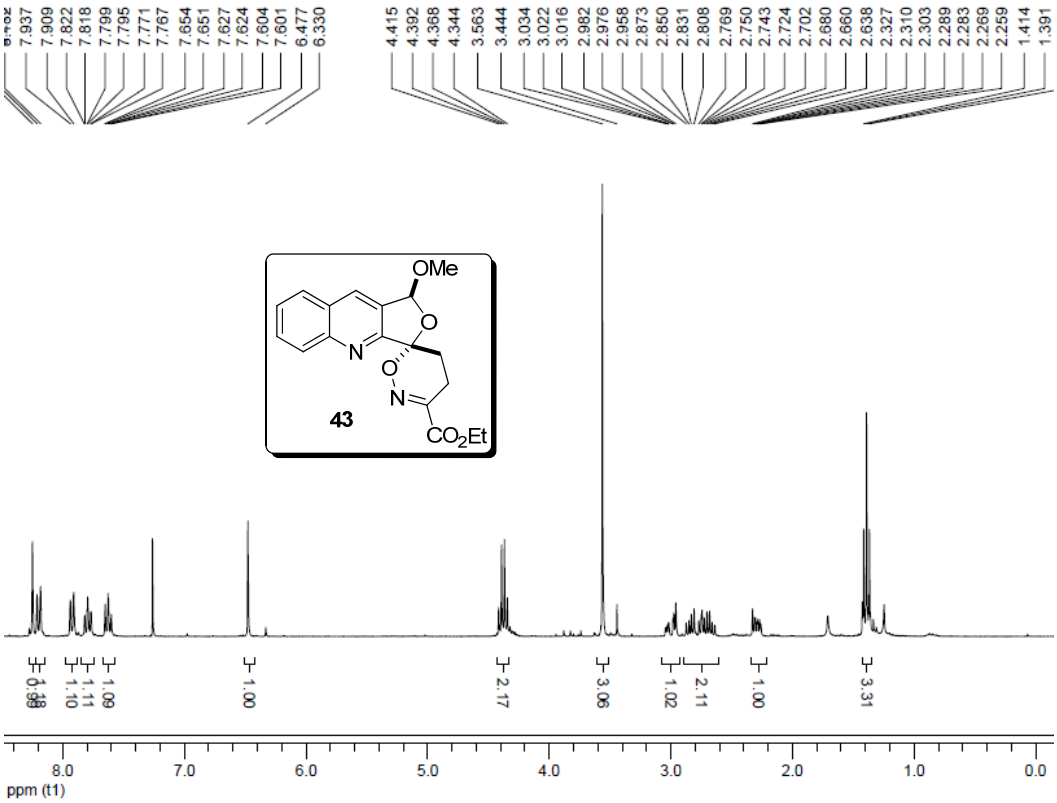
^{1}H NMR ($CDCl_3$, 300 MHz) of **42**



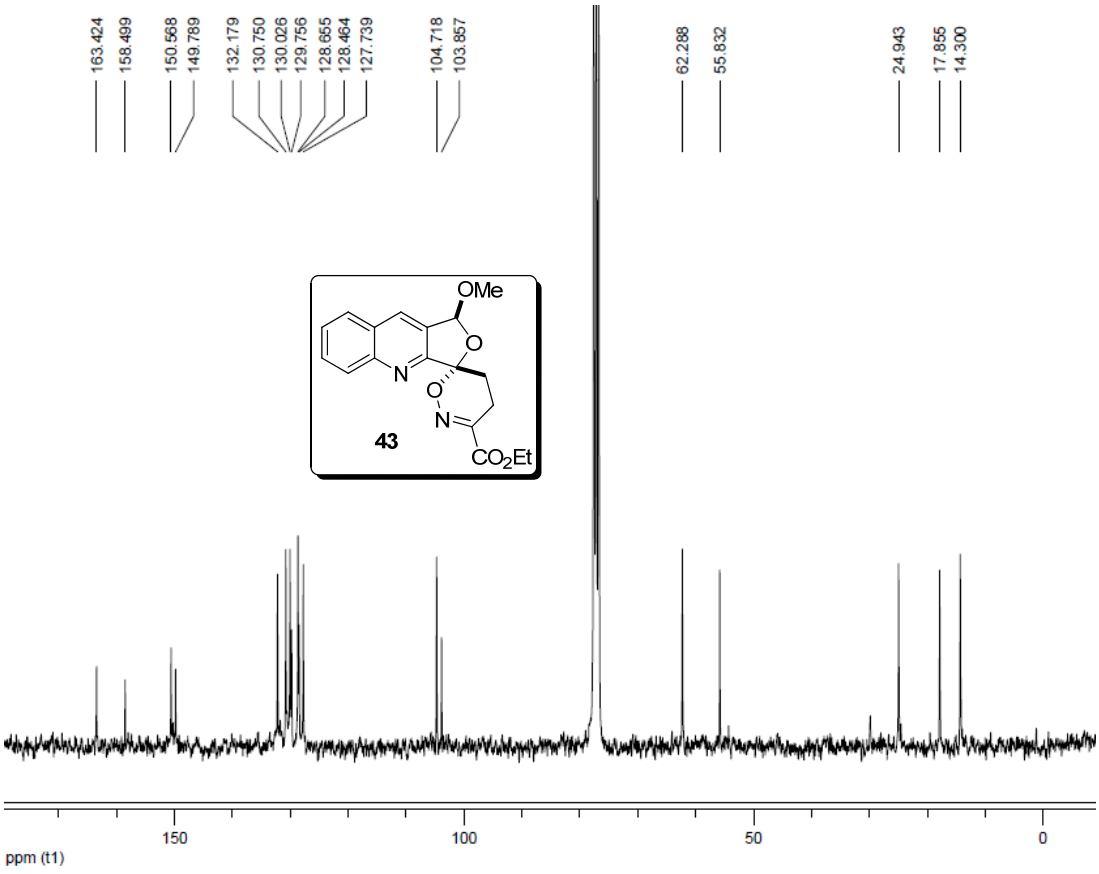
^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz) of **42**



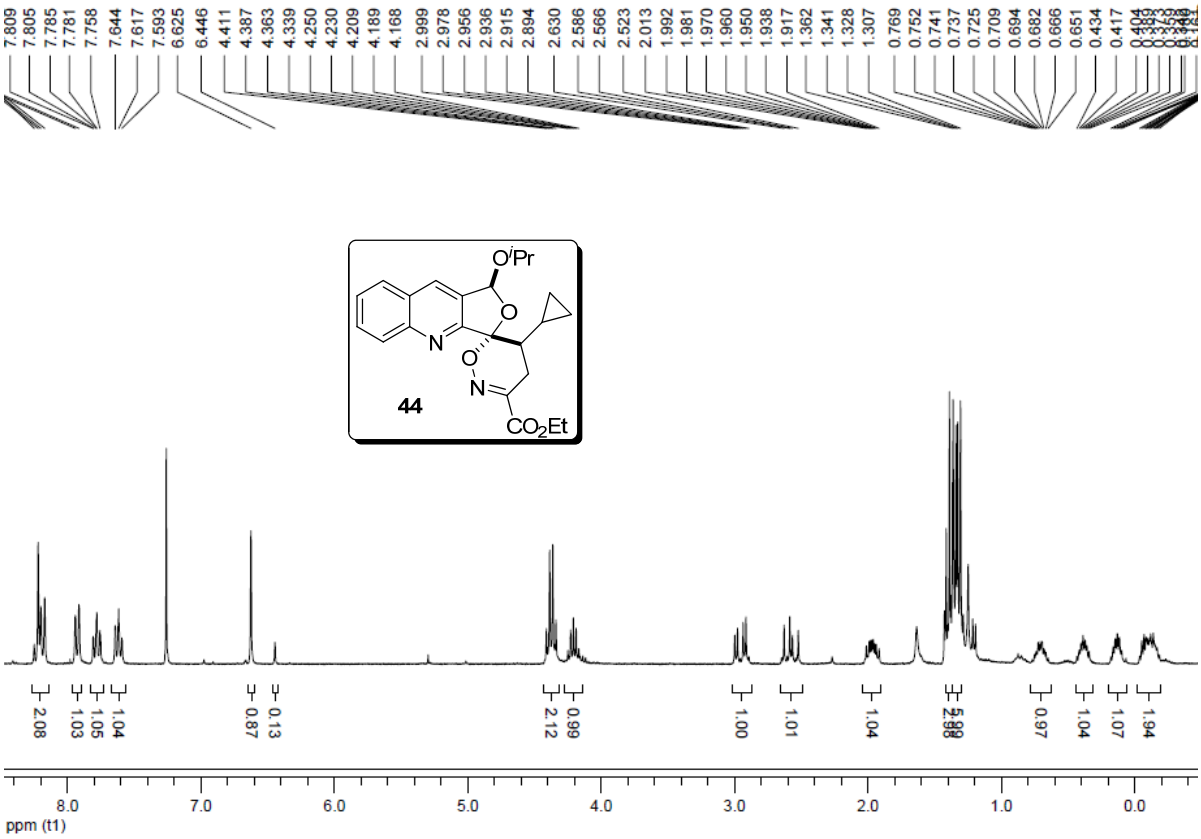
^{1}H NMR ($CDCl_3$, 300 MHz) of **43**



^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz) of **43**



^{1}H NMR ($CDCl_3$, 300 MHz) of **44**



^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz) of **44**