# Photosensitized Oxidations of Substituted Pyrroles: Unanticipated Radical-Derived Oxygenated Products

*Mariza N. Alberti, Georgios C. Vougioukalakis[†] and Michael Orfanopoulos[*]*

Department of Chemistry, University of Crete, 71003 Voutes, Heraklion, Crete, Greece

[†] Present address: Institute of Physical Chemistry, NCSR Demokritos, 15310 Agia Paraskevi, Attiki, Greece

## Supporting Information

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[*] To whom correspondence should be addressed. Email: orfanop@chemistry.uoc.gr

## (A) General Experimental Considerations

$^{1}H$ NMR and $^{13}C$ NMR spectra were recorded on 500 MHz and 300 MHz spectrometers, in $CDCl_3$ solutions. All spectra are reported in $\delta$ (ppm) relative to the solvent residual peak (7.26 and 77.16 ppm in $CDCl_3$). GC-MS analysis was performed on an apparatus equipped with a capillary column (MDN-5, 30m × 0.25mm, 0.25μm film thickness) and a 5971A MS detector. Electrospray ionization mass spectra (ESI-MS) were acquired using positive ions detection. All of the samples were sodiated and NaAc was added in order to improve the intensities. Photooxidations were achieved with a Xenon 300W lamp. TLC was carried out on $SiO_2$ (silica gel $F_{254}$) and flash chromatography was carried out on $SiO_2$ (silica gel 60, particle size 0.040–0.063 mm). Diethylether was distilled from Na under $N_2$ just prior to use.

## (B) Experimental Procedures for the Synthesis of Pyrroles 7–10

**1-(2-Hydroxyethyl)-pyrrole (7).** Pyrrole **7** was prepared according to a literature procedure:[i] 2-hydroxyethanolamine (1.52 mL, 25.2 mmol) was added to ice-cooled glacial acetic acid (28 mL) at such a rate that the temperature of the solution was kept below 15 °C. Then, 2,5-dimethoxytetrahydrofuran (0.75 mL, 5.8 mmol) was added in one portion and the solution was heated at 80–90 °C for 3h. Acetic acid was then completely removed from the reaction mixture under vacuum with careful heating. The residue was cooled to room temperature, diluted with $H_2O$, and extracted three times with $CH_2Cl_2$. The organic extract was washed two times with saturated aqueous solutions of $Na_2CO_3$, dried over $MgSO_4$, and then evaporated. The residue was chromatographed on silica gel (hexanes/EtOAc = 3:2 v/v) to give pyrrole 7 (0.386 mg, 3.48 mmol). Overall yield 60%. $^{1}H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 6.71 (br s, 2H), 6.18 (br s, 2H), 4.03 (t, 2H, $J$ = 5.5 Hz), 3.86 (t, 2H, $J$ = 5.5 Hz), 1.69 (br s, 1H, OH) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 120.5, 107.7, 62.0, 51.3 ppm; MS $m/z$ = 111 (100, $m/z$ = 80).

**5-Chloro-3-pentene-2-one.** This chloro enone was prepared according to a literature procedure:[ii] Acetyl chloride (3 mL, 42 mmol) was added dropwise to an ice-cooled slurry of aluminium chloride (7.2 g, 54 mmol) in $CH_2Cl_2$ (80 mL). The solution was then filtered. The filtrate was cooled to 0 $^{o}$C and

allyl bromide (2.6 mL, 30 mmol), dissolved in $CH_2Cl_2$ (30 mL), was added dropwise. This mixture was stirred at 0 $^oC$ for 1h and then poured into a mixture of ice (40 g), water (40 mL) and HCl 3N (100 mL). The aqueous layer was separated and extracted two times with $CH_2Cl_2$. The combined organic layers were washed two times with a 10 w/w % aqueous $NaHCO_3$ solution, dried over $Na_2SO_4$, filtered and then evaporated. The residue was used in the next steps without further purification. Yield 80% (2.84 g, 24 mmol).

**1-(2-Hydroxyethyl)-2-methylpyrrole (8) and 1-(3-Hydroxypropyl)-2-methylpyrrole (9).** Pyrroles **8** and **9** were prepared according to a published procedure:[iii] A solution of 5-chloro-3-pentene-2-one (1.42 g, 12 mmol) and the appropriate amino alcohol (12 mmol) was refluxed for 5-6 h in dry $Et_2O$ (100 mL) containing $Et_3N$ (1.66 mL, 12 mmol). The mixture was then cooled to rt and 12 mL of water was added. The aqueous layer was separated and extracted two times with $Et_2O$. The combined organic layers were washed two times with brine and dried over $MgSO_4$. After the evaporation of the solvent the crude product was purified by flash column chromatography over silica gel (hexanes/EtOAc = 4:1 → 1:1 v/v). Overall yield 40–50%. The spectroscopic data of pyrroles **8** and **9** are the following:

**1-(2-Hydroxyethyl)-2-methylpyrrole (8).** $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 6.63 (br s, 1H), 6.07 (br s, 1H), 5.89 (br s, 1H), 3.96 (t, 2H, $J$ = 5.5 Hz), 3.81 (t, 2H, $J$ = 5.5 Hz), 2.24 (s, 3H), 1.78 (br s, 1H, OH) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 128.8, 120.4, 107.4, 107.2, 62.8, 48.9, 12.1 ppm; ESI-MS m/z = 148.5 $[M + Na]^+$.

**1-(3-Hydroxypropyl)-2-methylpyrrole (9).** $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 6.60 (br s, 1H), 6.05 (t, 1H, $J$ = 3.0 Hz), 5.87 (br s, 1H), 3.95 (t, 2H, $J$ = 7.0 Hz), 3.66 (t, 2H, $J$ = 6.0 Hz), 2.24 (s, 3H), 1.94 (m, 2H), 1.35 (br s, 1H, OH) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 127.9, 119.5, 106.3, 106.2, 58.8, 42.6, 33.3, 11.4 ppm; ESI-MS $m/z$ = 162.4 $[M + Na]^+$.

**1-(2-Hydroxyethyl)-2,5-dimethylpyrrole (10).** Pyrrole **10** was prepared according to a published procedure:[iv] A mixture of ethanolamine (1 mL, 16.6 mmol) and 2,5-hexanedione (1 mL, 8.5 mmol) was heated under an argon atmosphere for 1h. The mixture was then cooled to rt and then 50 mL of $Et_2O$ was added. This mixture was washed three times with brine and dried over $MgSO_4$. After evaporation of

the solvent the crude product was purified by flash column chromatography over silica gel (hexanes/EtOAc = 3:1 → 1:1 v/v). Overall yield 80% (0.94 g, 6.8 mmol). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 5.78 (s, 2H), 3.92 (t, 2H, $J$ = 6.0 Hz), 3.77 (t, 2H, $J$ = 6.0 Hz), 2.24 (s, 6H), 1.85 (br s, 1H, OH) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 127.7, 105.1, 61.6, 45.2, 12.3 ppm; MS $m/z$ = 139 (100, $m/z$ = 108).

## (C) Analytical and Spectroscopic Data for Compounds 15–27

**7a-Methyl-2,3-dihydropyrrolo[2,1-*b*]oxazol-5(7a*H*)-one (15).** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.09 (d, 1H, $J$ = 5.5 Hz), 6.02 (d, 1H, $J$ = 5.5 Hz), 4.17 (m, 1H), 3.94 (m, 2H), 3.26 (m, 1H), 1.53 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 177.8, 151.5, 127.9, 100.1, 69.7, 42.8, 22.4 ppm; ESI-MS $m/z$ = 162.3 $[M + Na]^+$.

**1-(2-Hydroxyethyl)-5-methylene-1*H*-pyrrol-2(5*H*)-one (16).** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.98 (d, 1H, $J$ = 5.0 Hz), 6.19 (d, 1H, $J$ = 5.0 Hz), 5.02 (s, 1H), 4.88 (s, 1H), 3.77 (br s, 4H), 2.95 (br s, 1H, OH) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 171.6, 145.9, 137.7, 125.0, 97.4, 61.4, 42.3 ppm; MS $m/z$ = 139 (100, $m/z$ = 108).

**5-Hydroxy-1-(2-hydroxyethyl)-5-methyl-1*H*-pyrrol-2(5*H*)-one (17).** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.96 (d, 1H, $J$ = 6.0 Hz), 6.04 (d, 1H, $J$ = 6.0 Hz), 4.75 (br s, 1H, OH), 3.80 (m, 4H), 3.27 (m, 1H), 1.90 (br s, 1H, OH), 1.51 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 170.4, 151.1, 125.6, 89.8, 61.9, 41.31, 22.8 ppm; ESI-MS $m/z$ = 180.3 $[M + Na]^+$.

**1-(2-Hydroxyethyl)-5-methoxy-5-methyl-1*H*-pyrrol-2(5*H*)-one (18).** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.82 (d, 1H, $J$ = 6.0 Hz), 6.22 (d, 1H, $J$ = 6.0 Hz), 3.89 (br s, 1H, OH), 3.79 (m, 2H), 3.52 (m, 1H), 3.36 (m, 1H), 3.04 (s, 3H), 1.51 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 171.0, 148.8, 128.5, 94.2, 62.5, 51.1, 42.4, 22.7 ppm; ESI-MS $m/z$ = 194.3 $[M + Na]^+$.

**a-Methyl-3,4-dihydro-2*H*-pyrrolo[2,1-*b*][1,3]oxazin-6(8a*H*)-one (19).** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.96 (d, 1H, $J$ = 5.5 Hz), 6.17 (d, 1H, $J$ = 5.5 Hz), 4.24 (dd, 1H, $J_1$ = 5.5 Hz, $J_2$ = 13.5 Hz), 4.00 (dt,

1H, $J_1$ = 2.5 Hz, $J_2$ = 12.0 Hz), 3.86 (m, 1H), 3.11 (dt, 1H, $J_1$ = 3.5 Hz, $J_2$ = 13.5 Hz), 1.70 (m, 2H), 1.59 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 168.9, 149.4, 127.6, 89.3, 61.2, 35.0, 25.1, 17.8 ppm; ESI-MS *m/z* = 176.3 $[M + Na]^+$.

**1-(3-Hydroxypropyl)-5-methylene-1*H*-pyrrol-2(5*H*)-one (20).** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.00 (d, 1H, *J* = 5.5 Hz), 6.23 (d, 1H, *J* = 5.5 Hz), 5.00 (s, 1H), 4.91 (s, 1H), 3.78 (t, 2H, *J* = 6.0 Hz), 3.52 (t, 2H, *J* = 5.5 Hz), 3.10 (br s, 1H, OH), 1.76 (m, 2H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 170.0, 149.5, 137.5, 124.9, 97.5, 58.5, 35.2, 31.1 ppm; MS *m*/*z* = 153 (100, *m*/*z* = 138).

**5-Hydroxy-1-(3-hydroxypropyl)-5-methyl-1*H*-pyrrol-2(5*H*)-one (21).** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.94 (d, 1H, *J* = 6.0 Hz), 6.07 (d, 1H, *J* = 6.0 Hz), 3.65 (br s, 4H), 3.43 (br s, 2H), 1.84 (m, 2H, OH), 1.54 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 170.3, 150.9, 126.1, 90.5, 59.8, 34.9, 31.6, 22.8 ppm; MS *m*/*z* = 153 (100, *m*/*z* = 138).

**1-(3-Hydroxypropyl)-5-methoxy-5-methyl-1*H*-pyrrol-2(5*H*)-one (22).** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.79 (d, 1H, *J* = 6.0 Hz), 6.22 (d, 1H, *J* = 6.0 Hz), 3.84 (br s, 1H), 3.65 (br s, 1H), 3.54 (m, 2H), 3.34 (dt, 1H, $J_1$ = 5.5 Hz, $J_2$ = 14.5 Hz), 2.98 (s, 3H), 1.74 (m, 2H), 1.51 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 171.0, 148.8, 128.4, 94.3, 58.9, 50.9, 34.1, 32.0, 23.2 ppm; ESI-MS *m/z* = 208.2 $[M + Na]^+$.

**1-(2-Hydroxyethyl)-2-formyl-5-methylpyrrole (23).** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 9.36 (s, 1H), 6.90 (d, 1H, *J* = 4.0 Hz), 6.06 (d, 1H, *J* = 4.0 Hz), 4.43 (t, 2H, *J* = 5.5 Hz), 3.92 (br s, 2H), 2.39 (br s, 1H, OH), 2.32 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 179.0, 141.6, 132.0, 126.1, 110.6, 63.0, 47.4, 12.6 ppm; ESI-MS *m/z* = 176.4 $[M + Na]^+$.

**1-(2-Hydroxyethyl)-2-methoxymethyl-5-methylpyrrole (24).** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.09 (d, 1H, *J* = 3.5 Hz), 5.86 (d, 1H, *J* = 3.5 Hz), 4.39 (s, 2H), 4.04 (t, 2H, *J* = 5.5 Hz), 3.82 (q, 2H, *J* = 5.5 Hz), 3.34 (s, 3H), 3.29 (br s, 1H, OH), 2.24 (s, 3H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 130.7, 127.9, 110.0, 106.3, 66.2, 62.5, 57.0, 46.5, 12.7 ppm; MS *m*/*z* = 137 (100, *m*/*z* = 137).

**1-(2-Hydroxyethyl)-2,5-dimethoxymethylpyrrole (25).** $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.13 (s, 2H), 4.39 (s, 4H), 4.16 (t, 2H, $J$ = 5.0 Hz), 3.85 (br s, 2H), 3.69 (br s, 1H, OH), 3.32 (s, 6H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 130.4, 110.2, 66.1, 63.2, 57.2, 47.1 ppm; MS $m/z$ = 199 (100, $m/z$ = 136).

**1-(2-Hydroxyethyl)-2-ethoxymethyl-5-methylpyrrole (26).** $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.08 (br s, 1H), 5.86 (br s, 1H), 4.42 (s, 2H), 4.04 (t, 2H, $J$ = 5.0 Hz), 3.83 (t, 2H, $J$ = 5.0 Hz), 3.54 (q, 3H, $J$ = 7.0 Hz), 2.24 (s, 3H), 1.21 (t, 3H, $J$ = 7.0 Hz) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 130.6, 128.3, 109.7, 106.4, 65.1, 64.3, 62.6, 46.6, 15.0, 12.8 ppm; MS $m/z$ = 137 (100, $m/z$ = 137).

**1-(2-Hydroxyethyl)-2,5-diethoxymethylpyrrole (27).** $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.11 (s, 2H), 4.43 (s, 4H), 4.18 (t, 2H, $J$ = 4.5 Hz), 3.93 (t, 1H, OH, $J$ = 5.5 Hz), 3.88 (t, 2H, $J$ = 4.5 Hz), 3.52 (q, 4H, $J$ = 7.0 Hz), 1.20 (t, 6H, $J$ = 7.0 Hz) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 130.5, 109.8, 65.1, 64.2, 63.1, 47.1, 15.0 ppm; ESI-MS $m/z$ = 250.5 $[M + Na]^+$.

## References


(i) Reference 16.

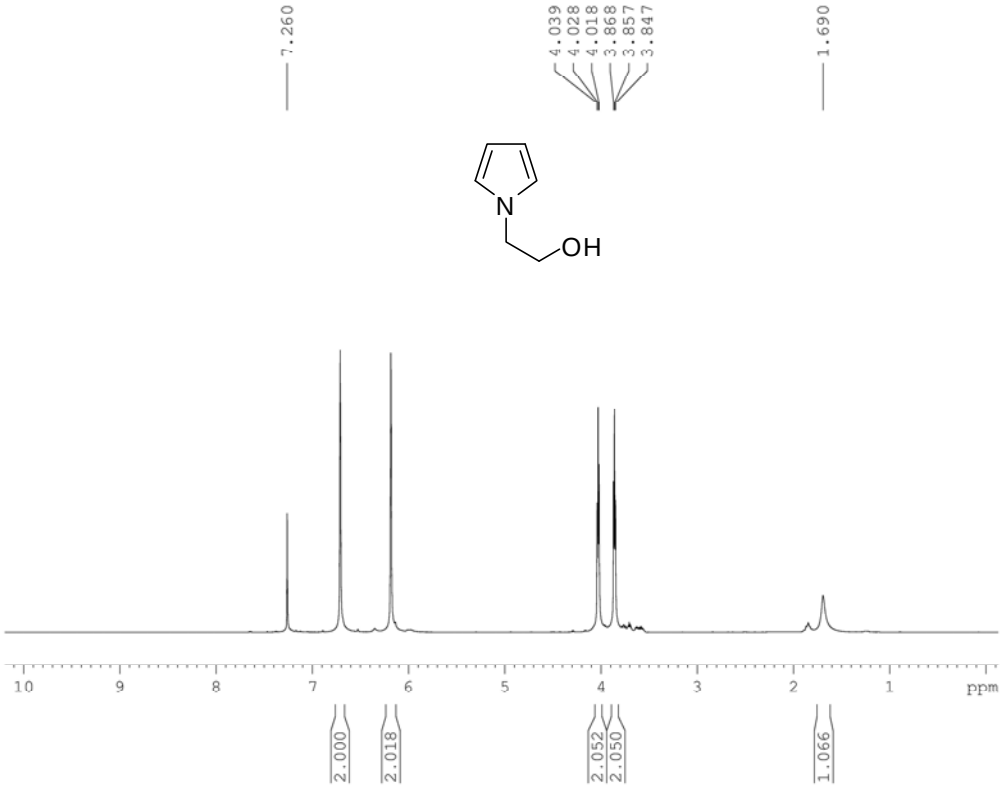
(ii) Reference 28a.

(iii) References 28b and 28c.

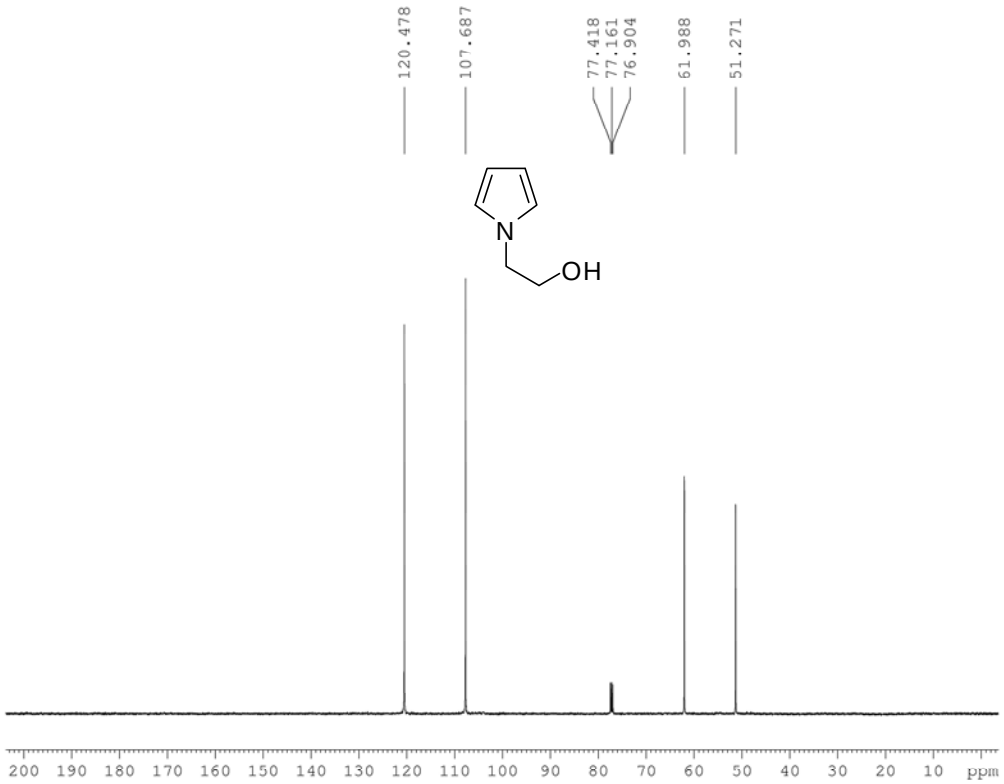
(iv) Reference 31.

## (D) NMR Spectra Section

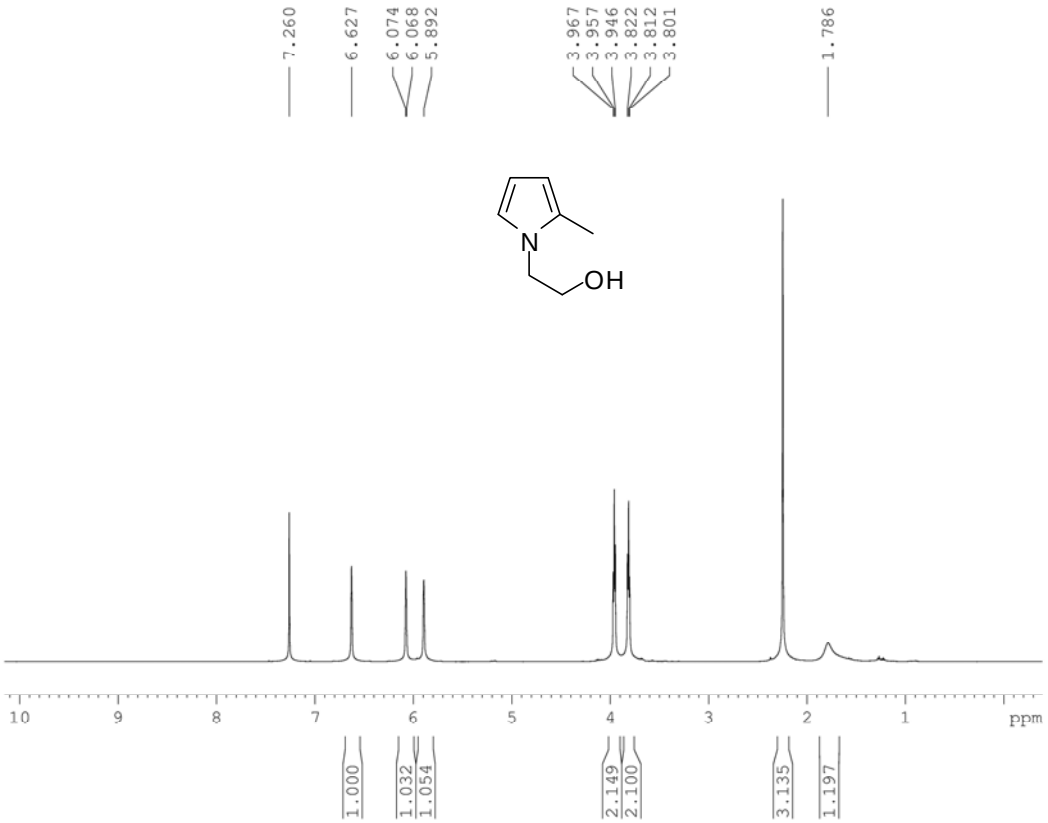
$^{1}$H NMR (500 MHz, $CDCl_3$) of compound **7**



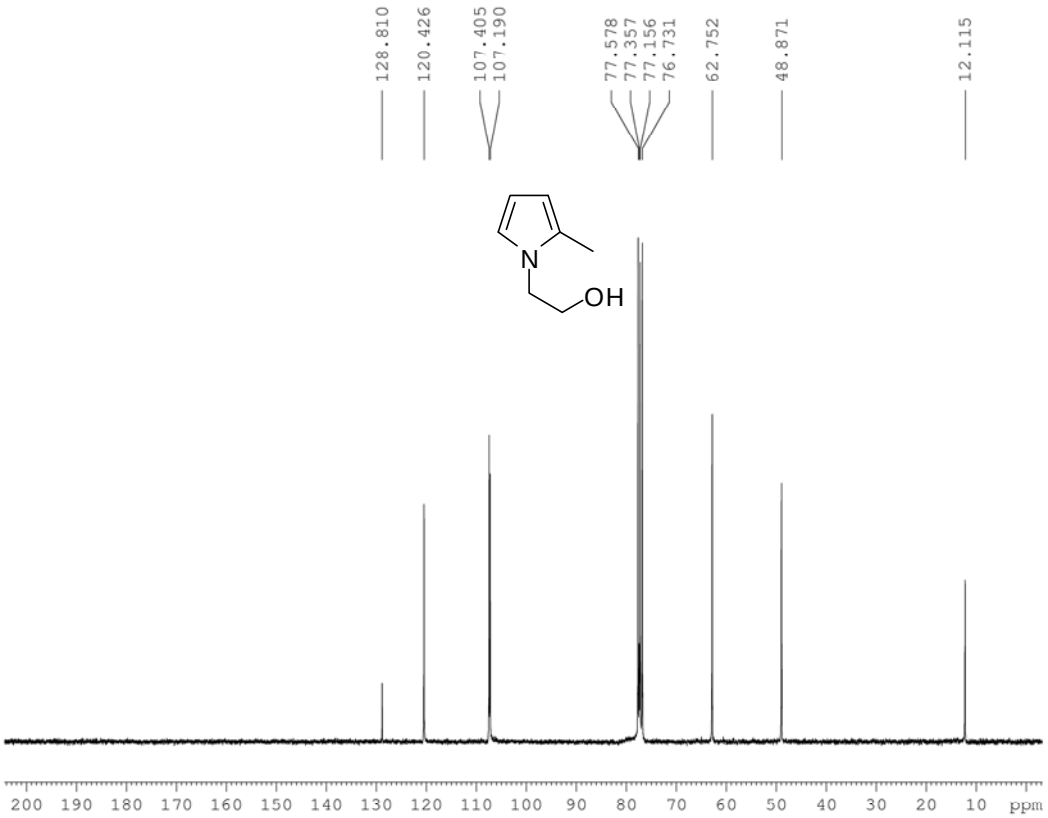

$^{13}$C NMR (125 MHz, $CDCl_3$) of compound **7**



$^{1}$H NMR (500 MHz, $CDCl_3$) of compound **8**

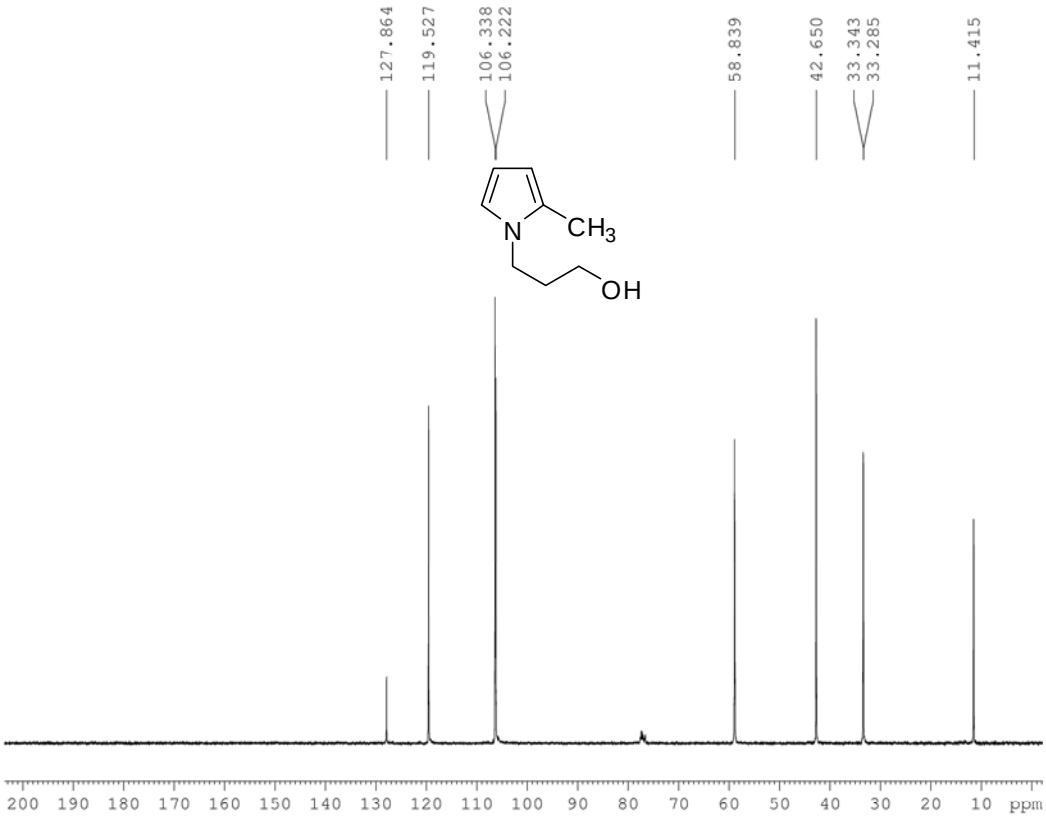



$^{13}$C NMR (75 MHz, $CDCl_3$) of compound **8**

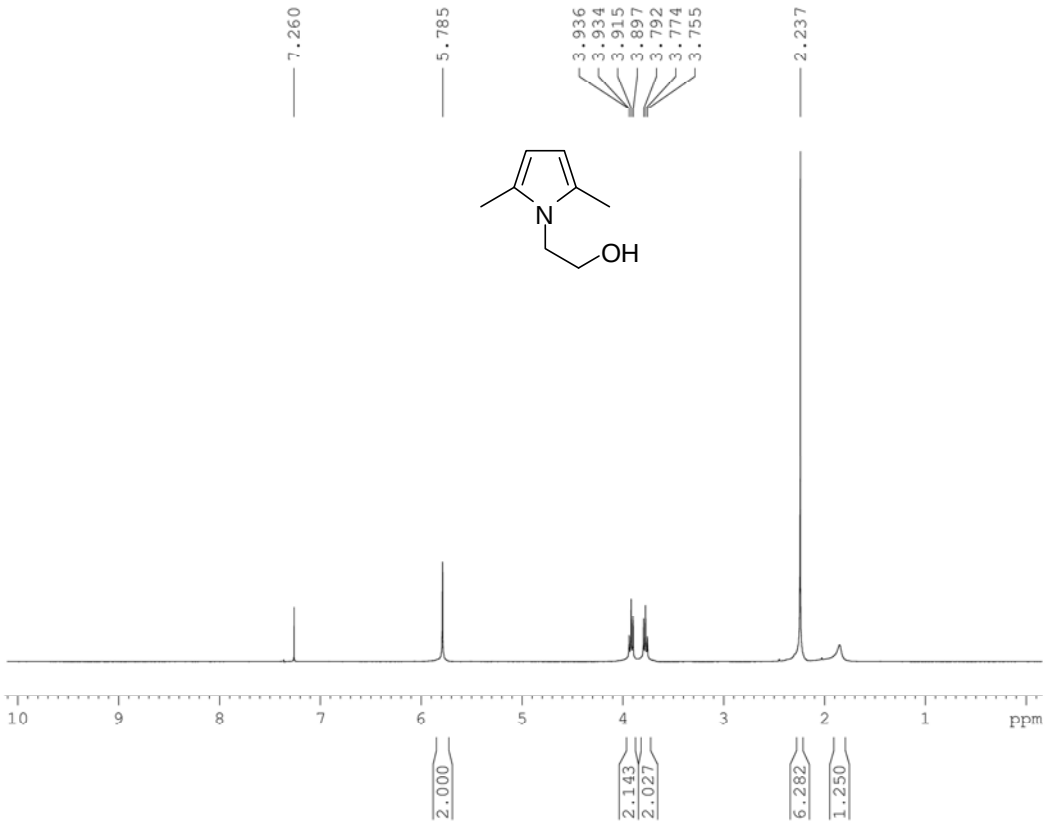


$^{1}$H NMR (500 MHz, $CDCl_3$) of compound **9**

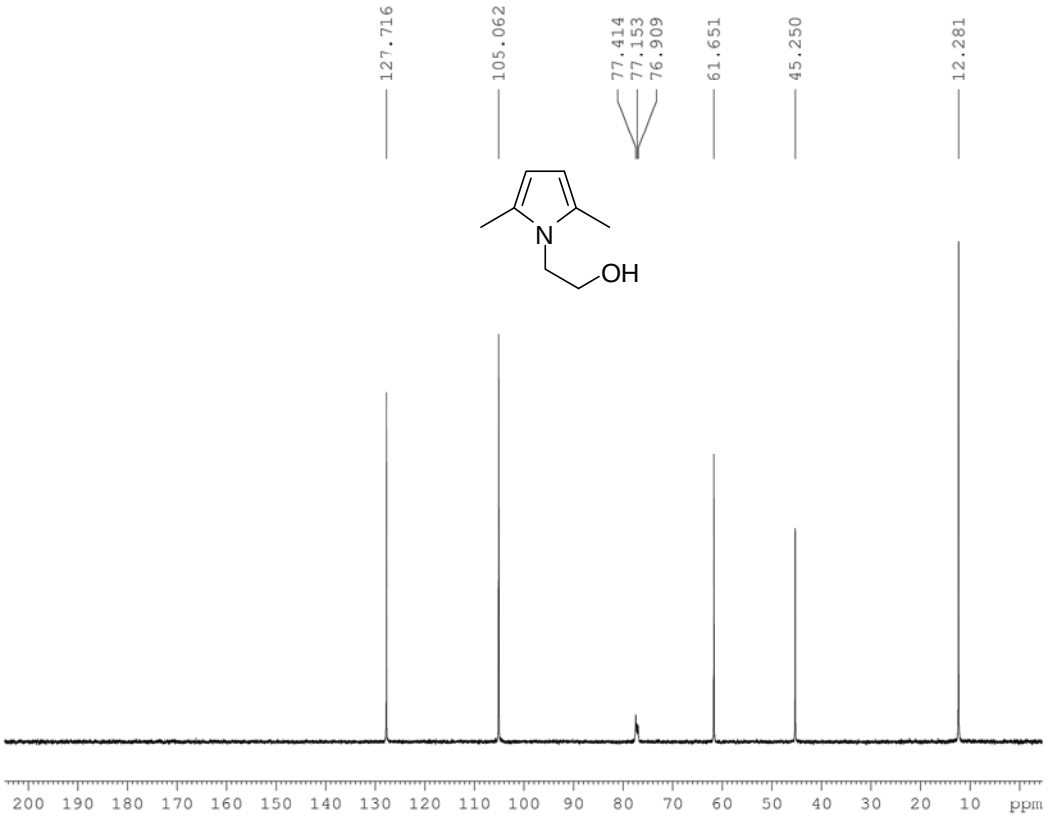

$^{13}$C NMR (75 MHz, $CDCl_3$) of compound **9**



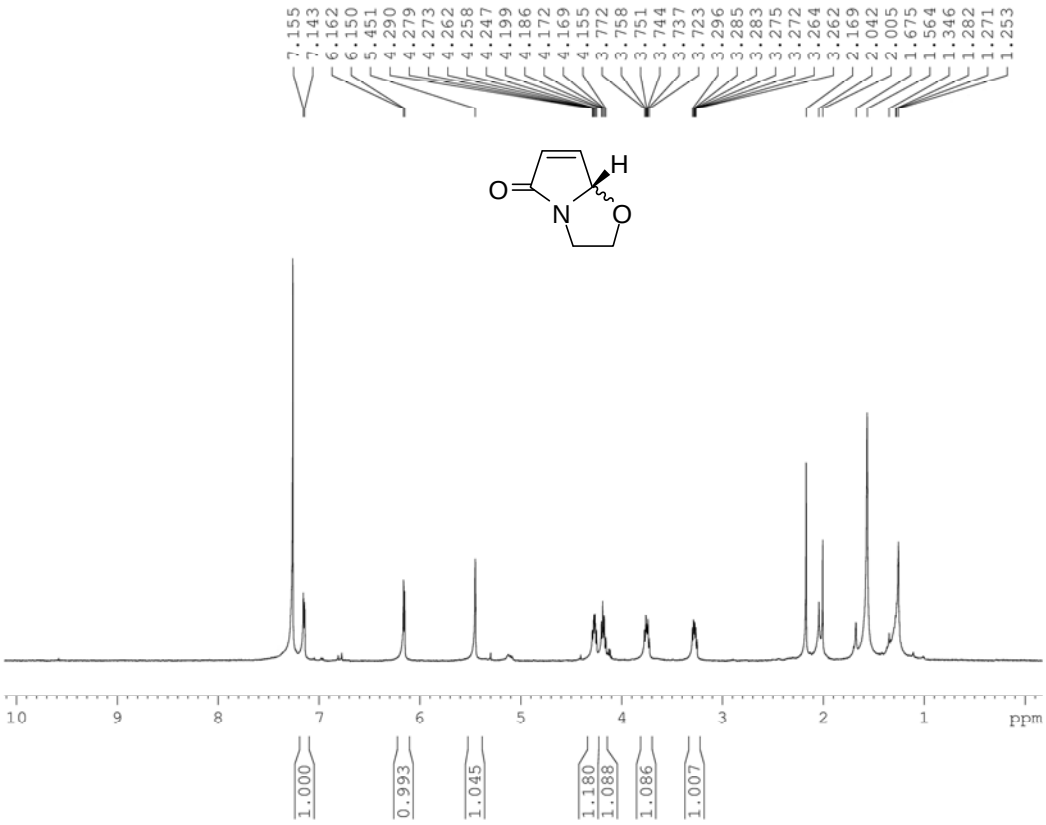
$^{1}$H NMR (300 MHz, $CDCl_3$) of compound **10**



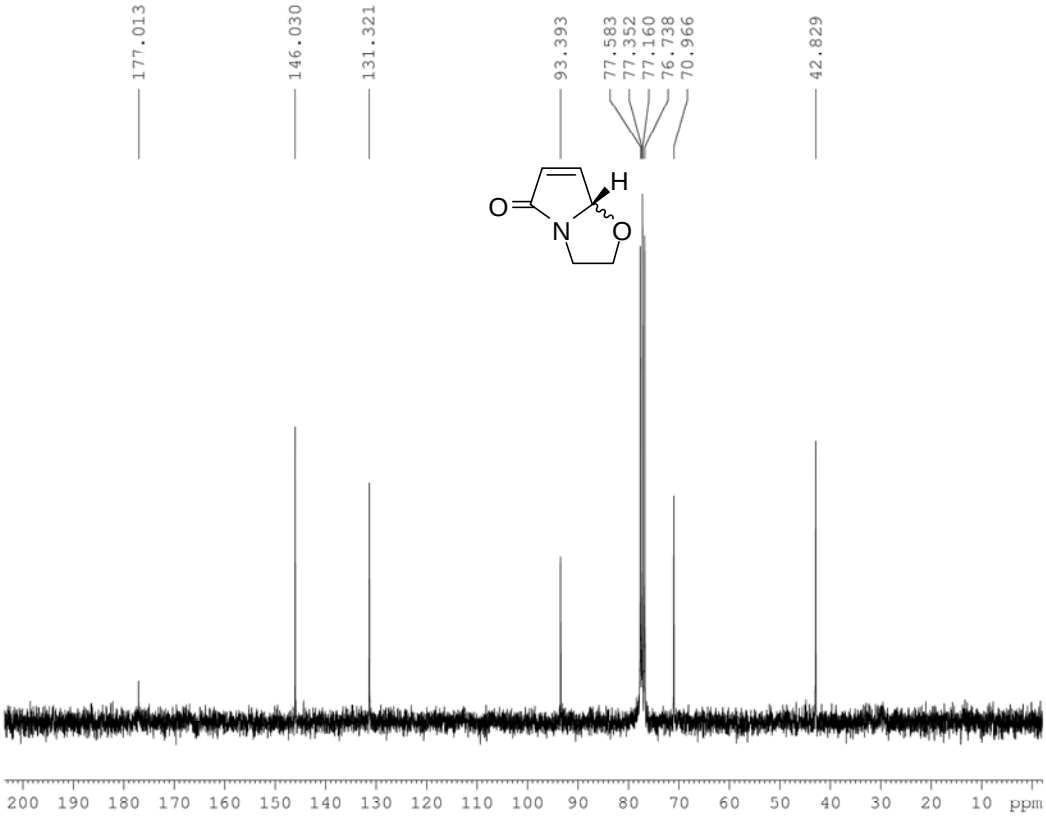

$^{13}$C NMR (125 MHz, $CDCl_3$) of compound **10**



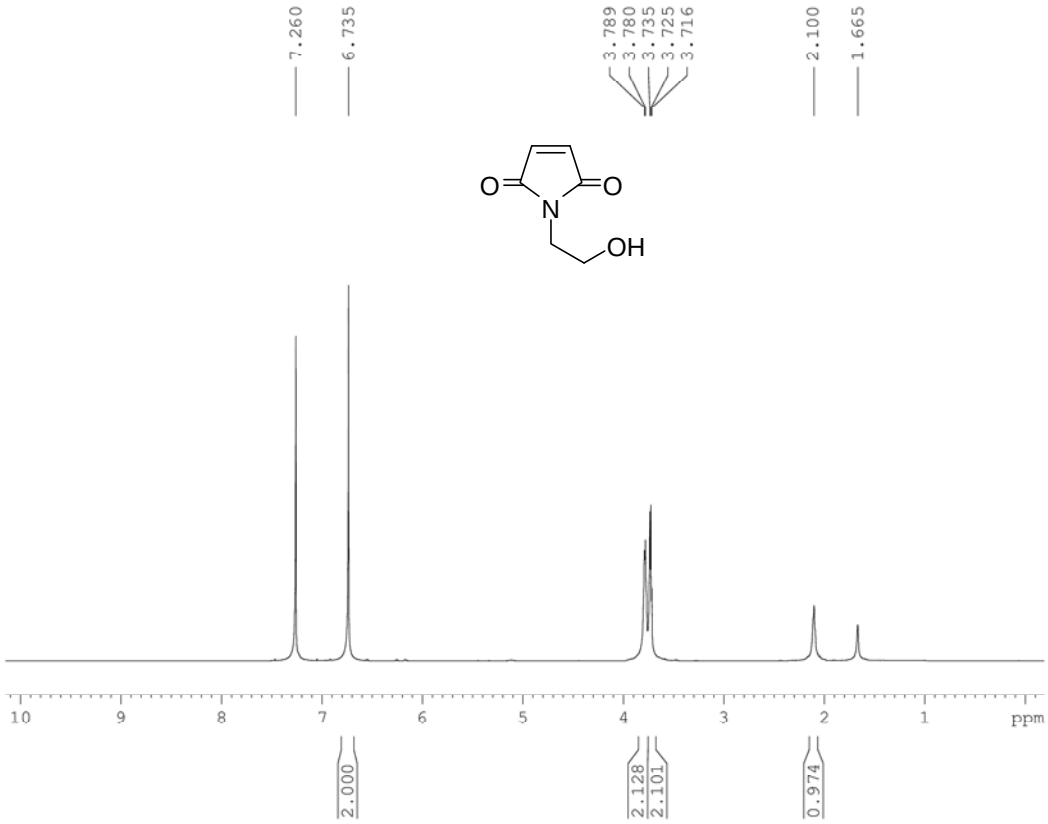
$^{1}$H NMR (500 MHz, $CDCl_3$) of compound **11**



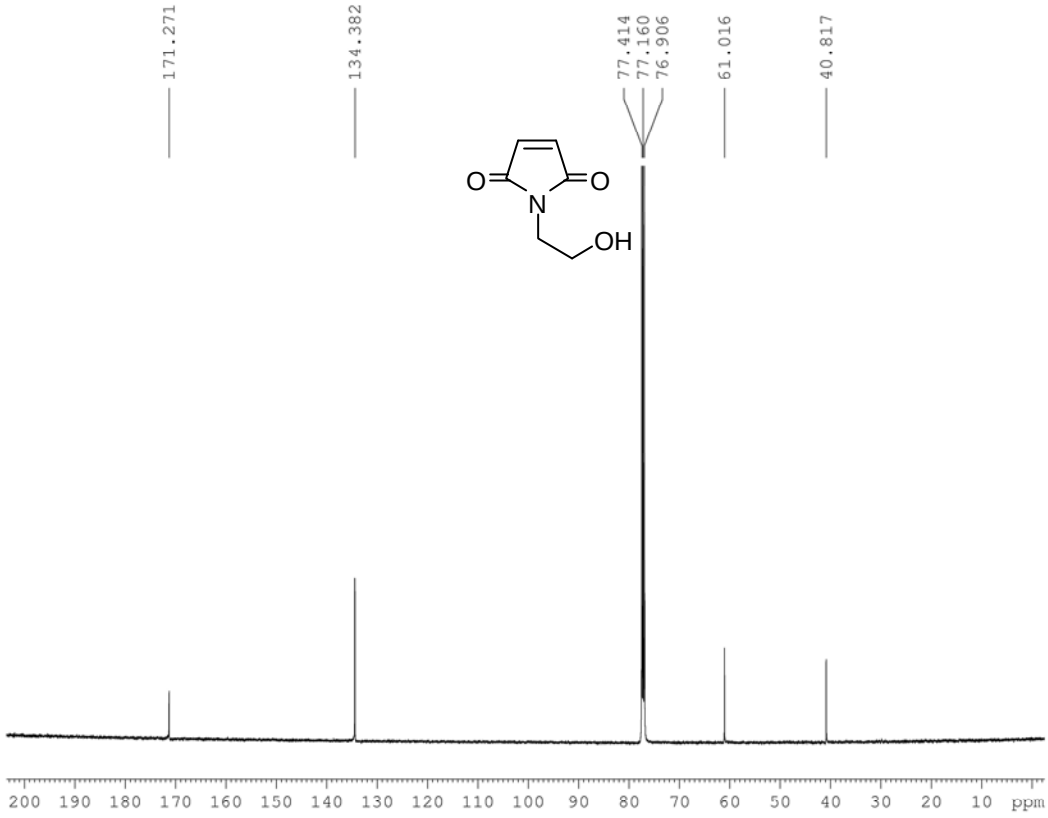

$^{13}$C NMR (75 MHz, $CDCl_3$) of compound **11**



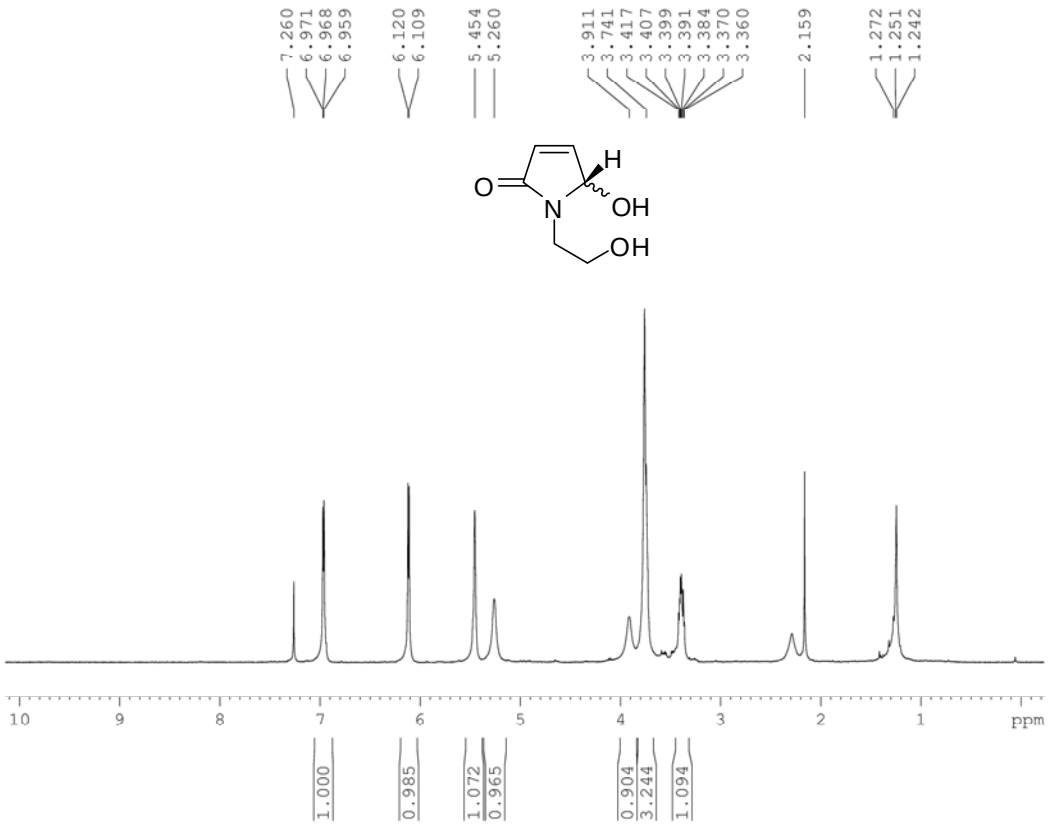
$^{1}$H NMR (500 MHz, $CDCl_3$) of compound **12**



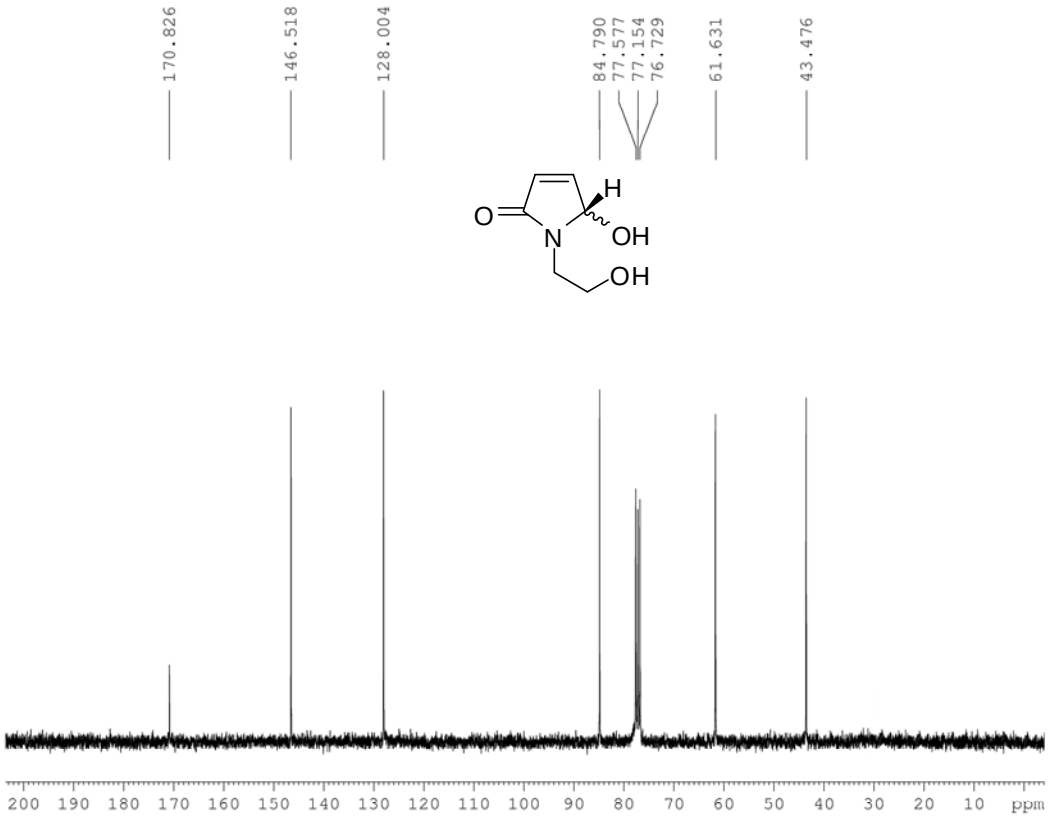

$^{13}$C NMR (125 MHz, $CDCl_3$) of compound **12**



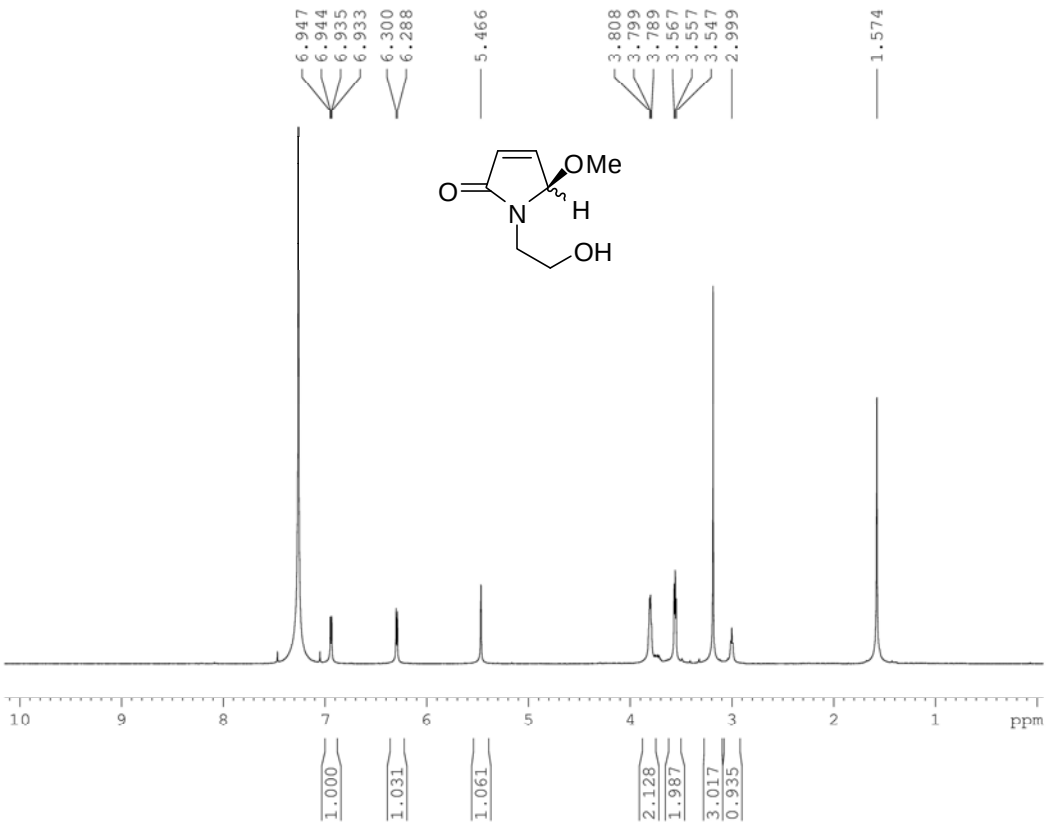
$^{1}$H NMR (500 MHz, $CDCl_3$) of compound **13**



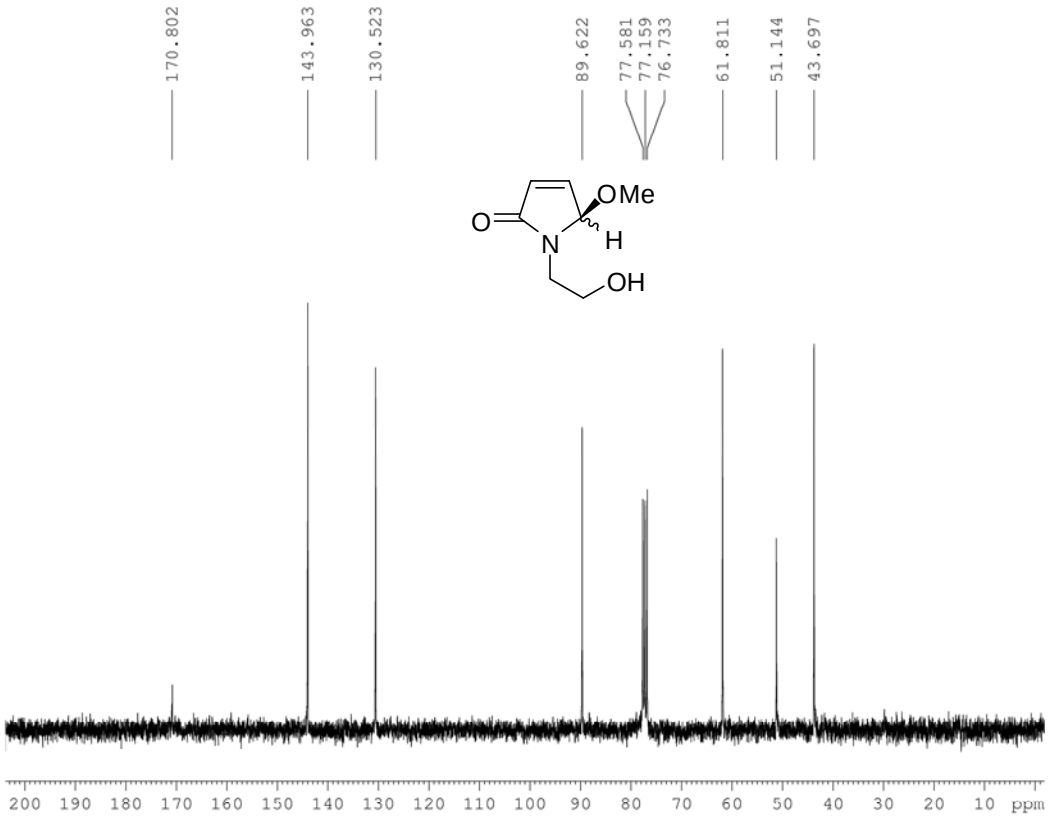

$^{13}$C NMR (75 MHz, $CDCl_3$) of compound **13**



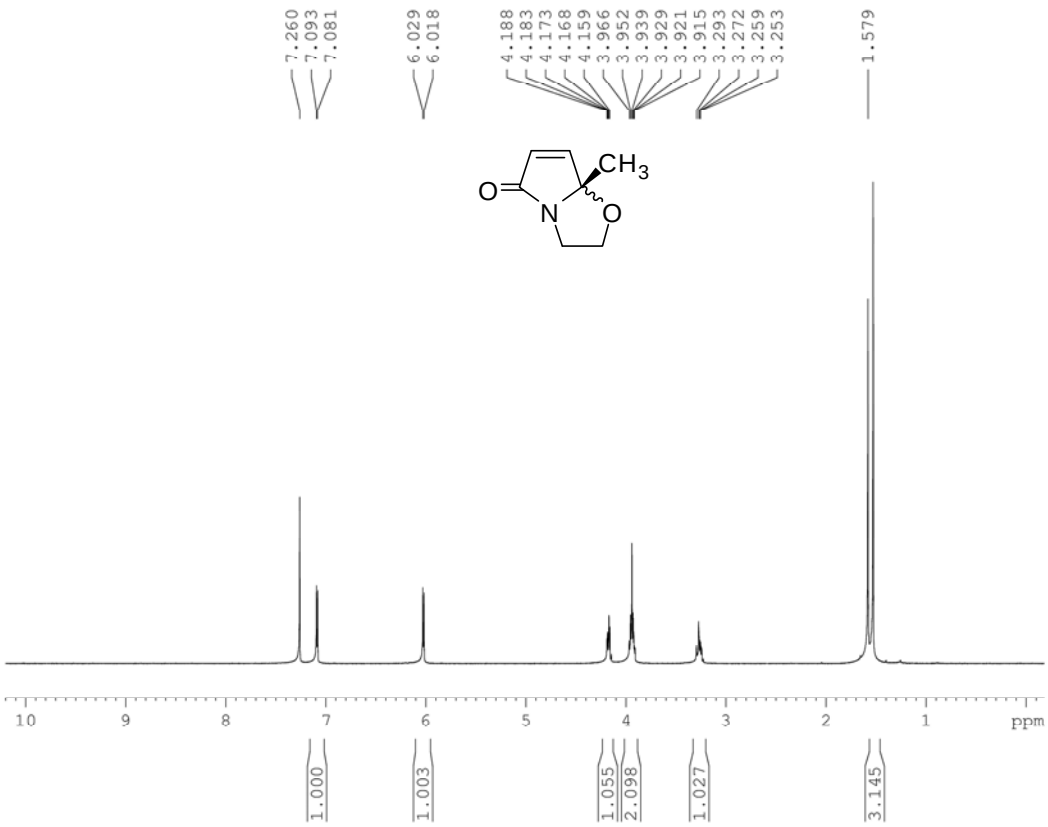
$^{1}$H NMR (500 MHz, $CDCl_3$) of compound **14**



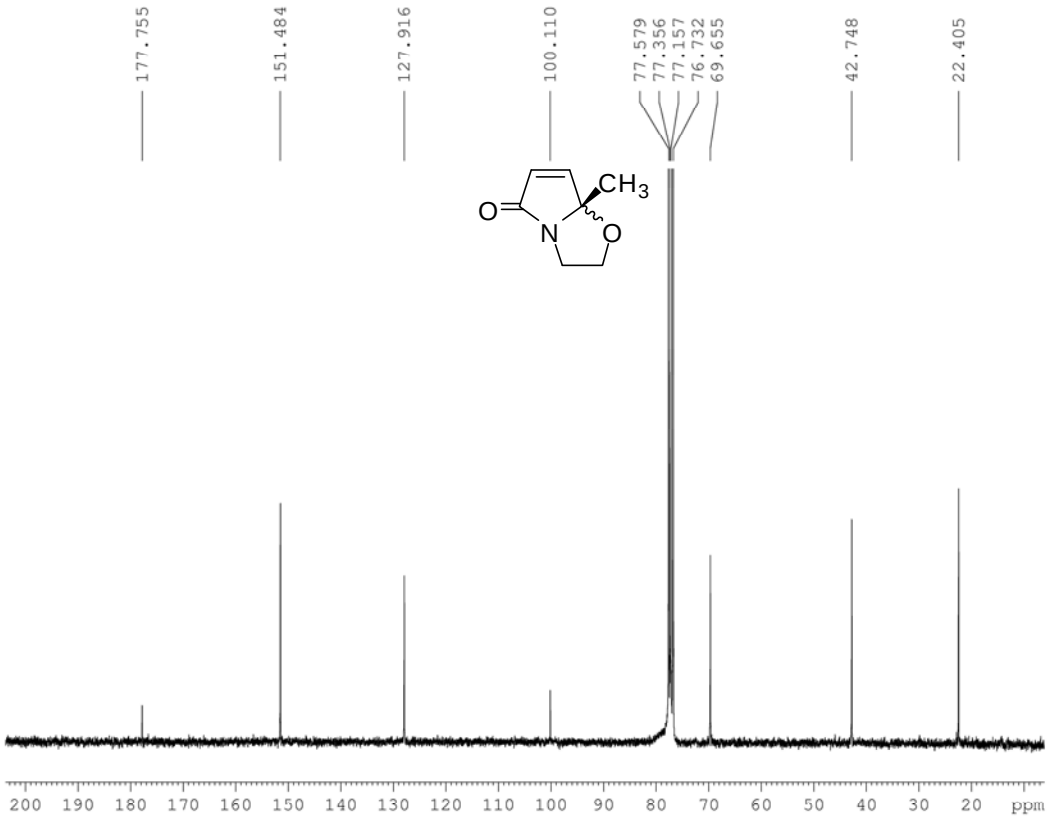

$^{13}$C NMR (75 MHz, $CDCl_3$) of compound **14**



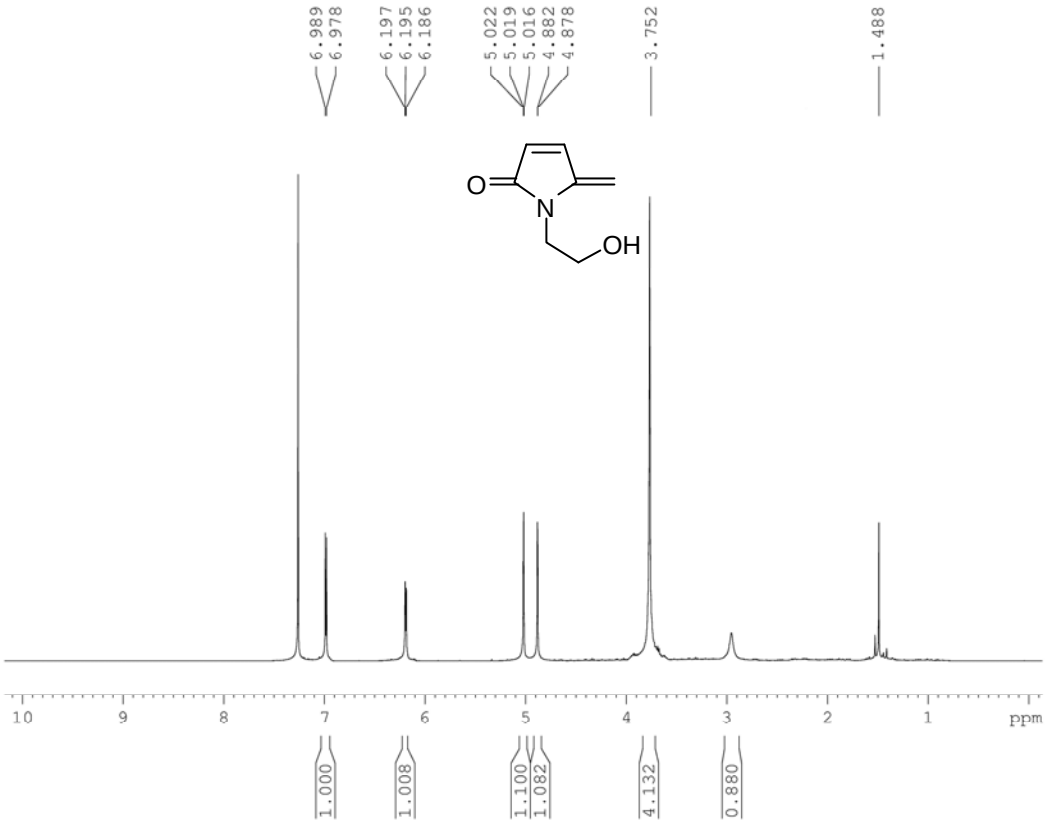
$^{1}$H NMR (500 MHz, $CDCl_3$) of compound **15**



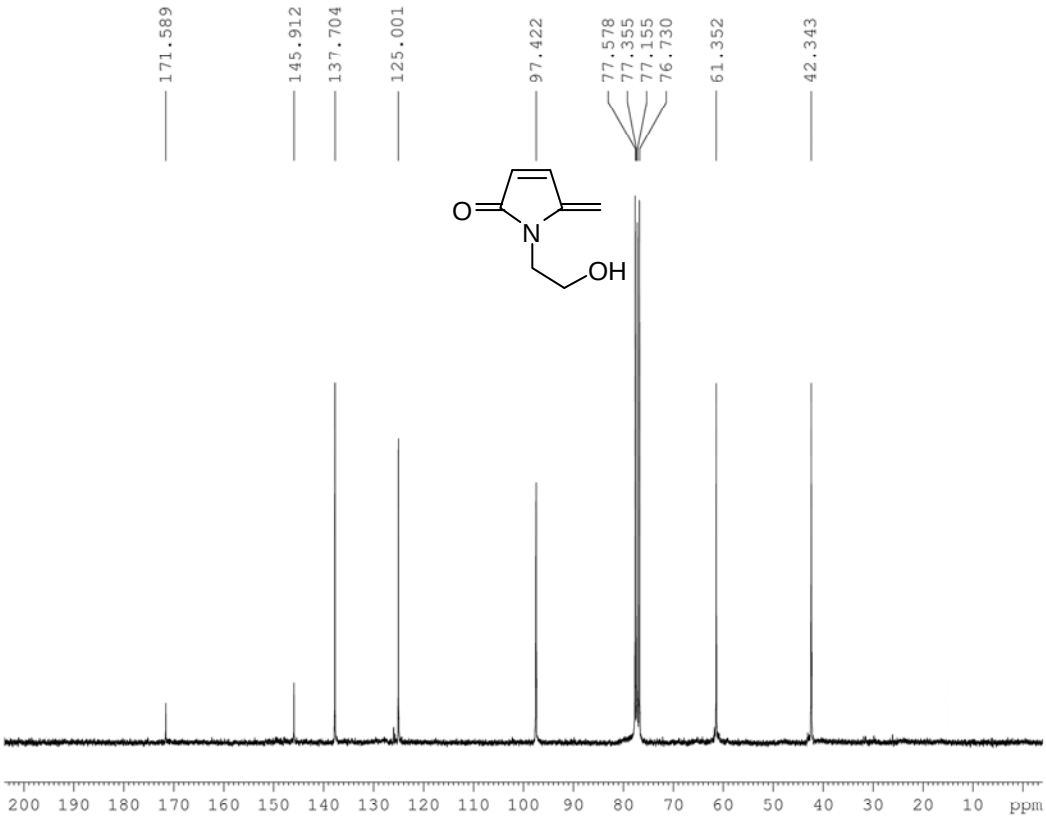

$^{13}$C NMR (75 MHz, $CDCl_3$) of compound **15**



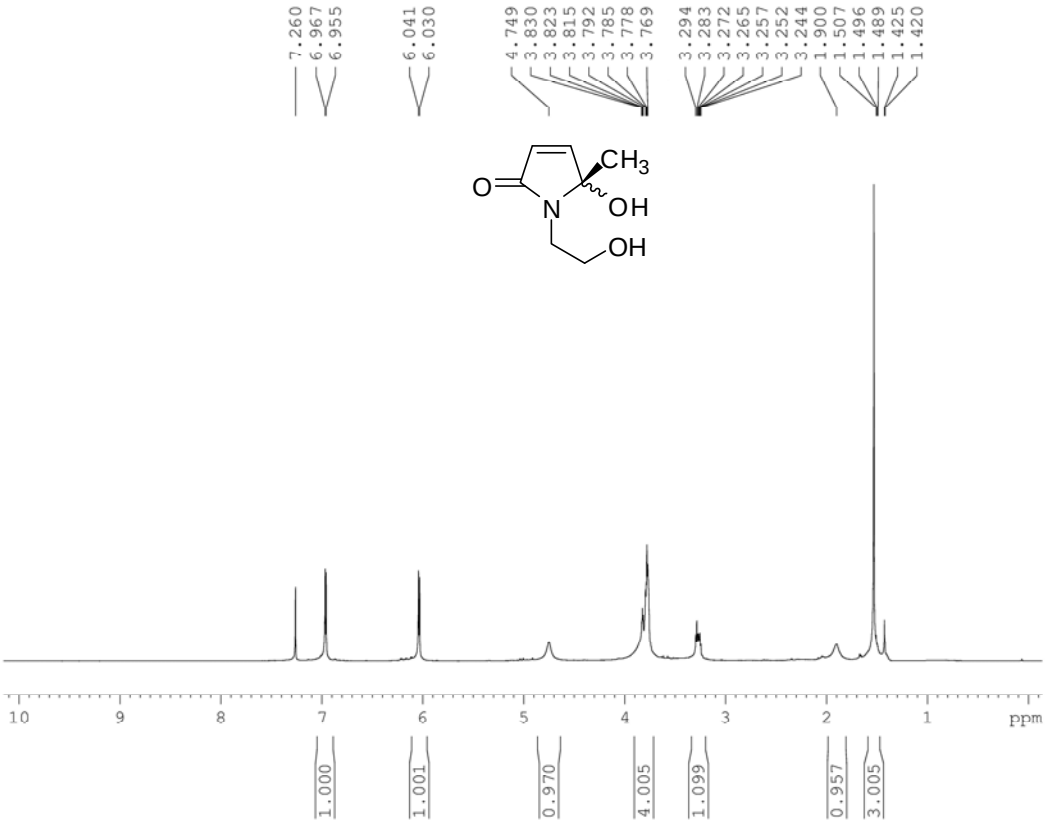
$^{1}$H NMR (500 MHz, $CDCl_3$) of compound **16**




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

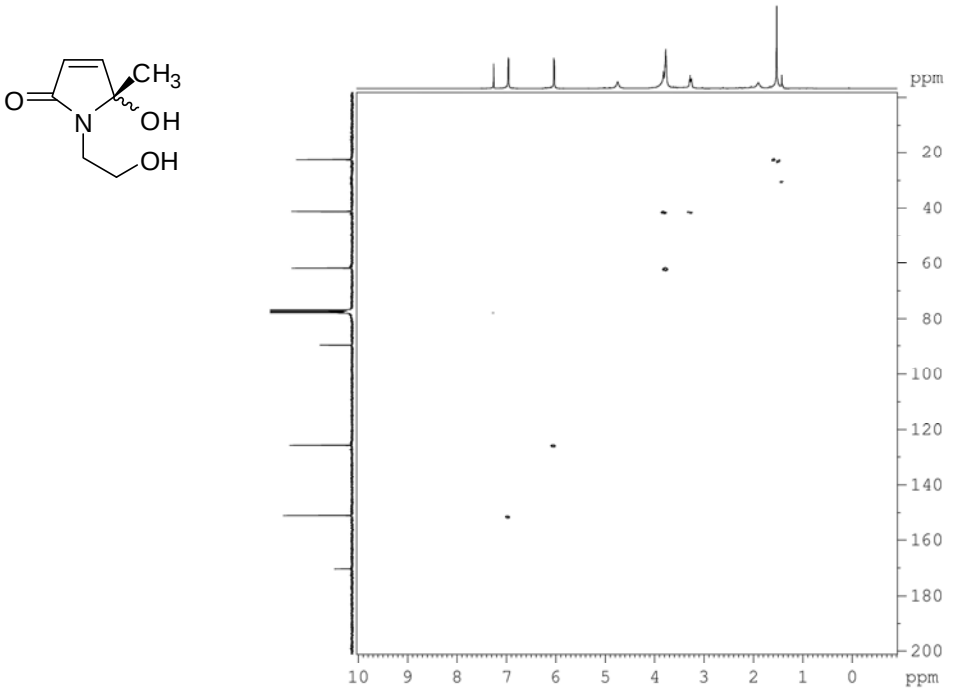


$^{1}$H NMR (500 MHz, $CDCl_3$) of compound **17**

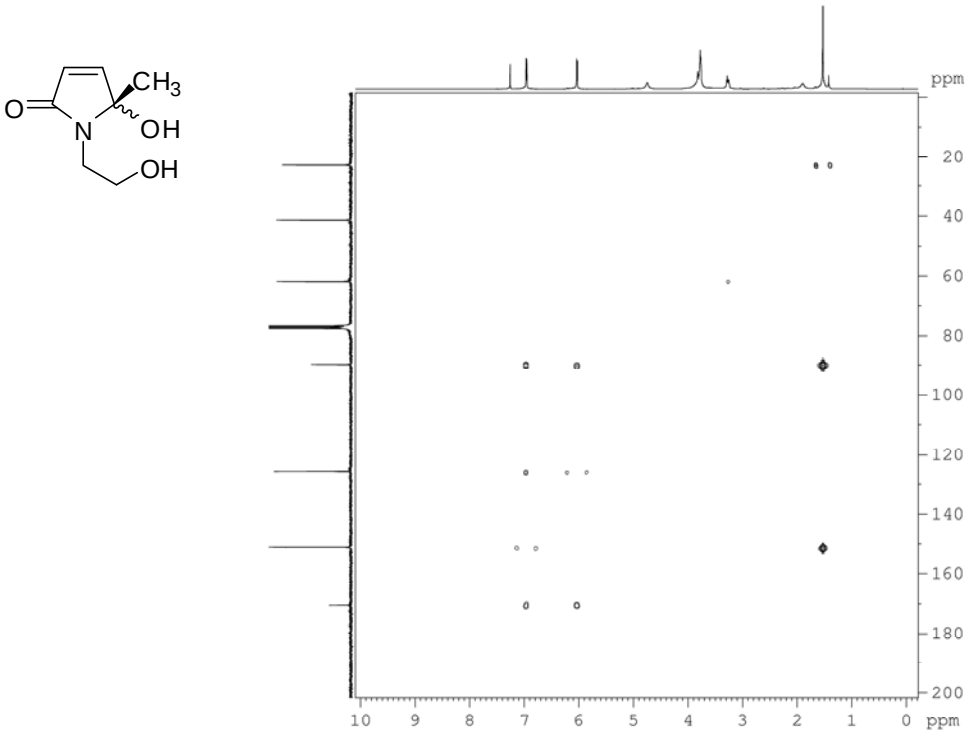



$^{13}$C NMR (75 MHz, $CDCl_3$) of compound **17**

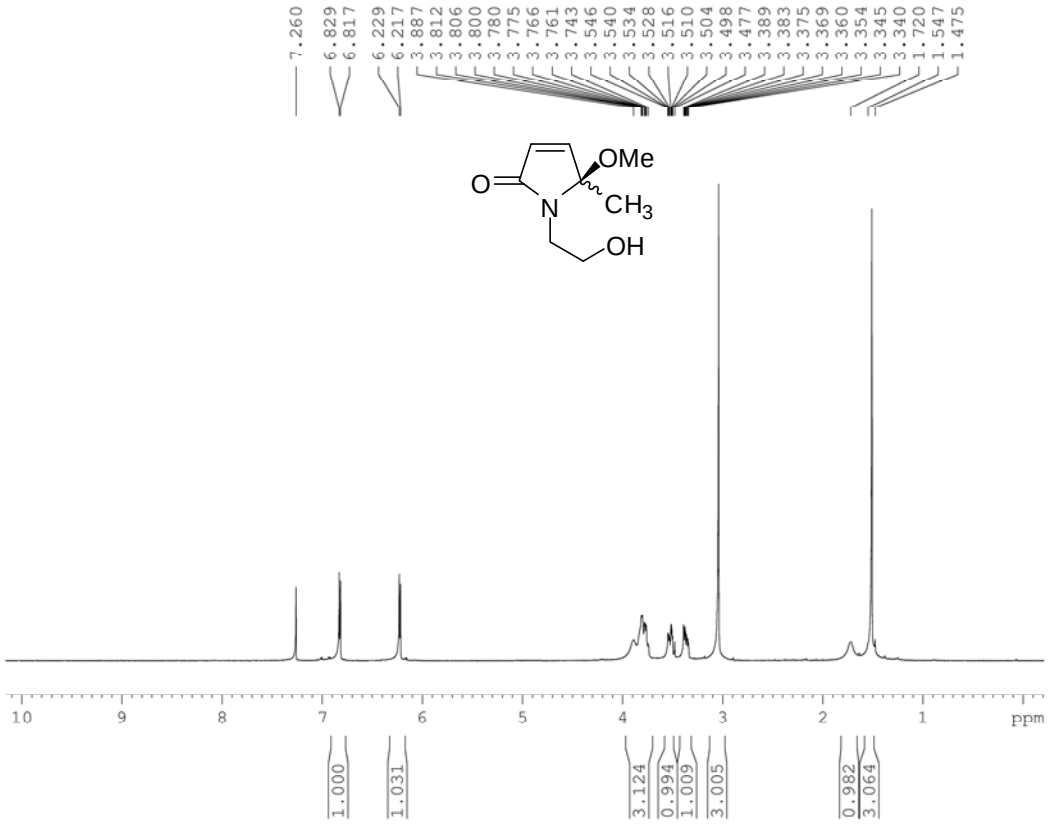
HMQC (500 MHz, $CDCl_3$) of compound **17**



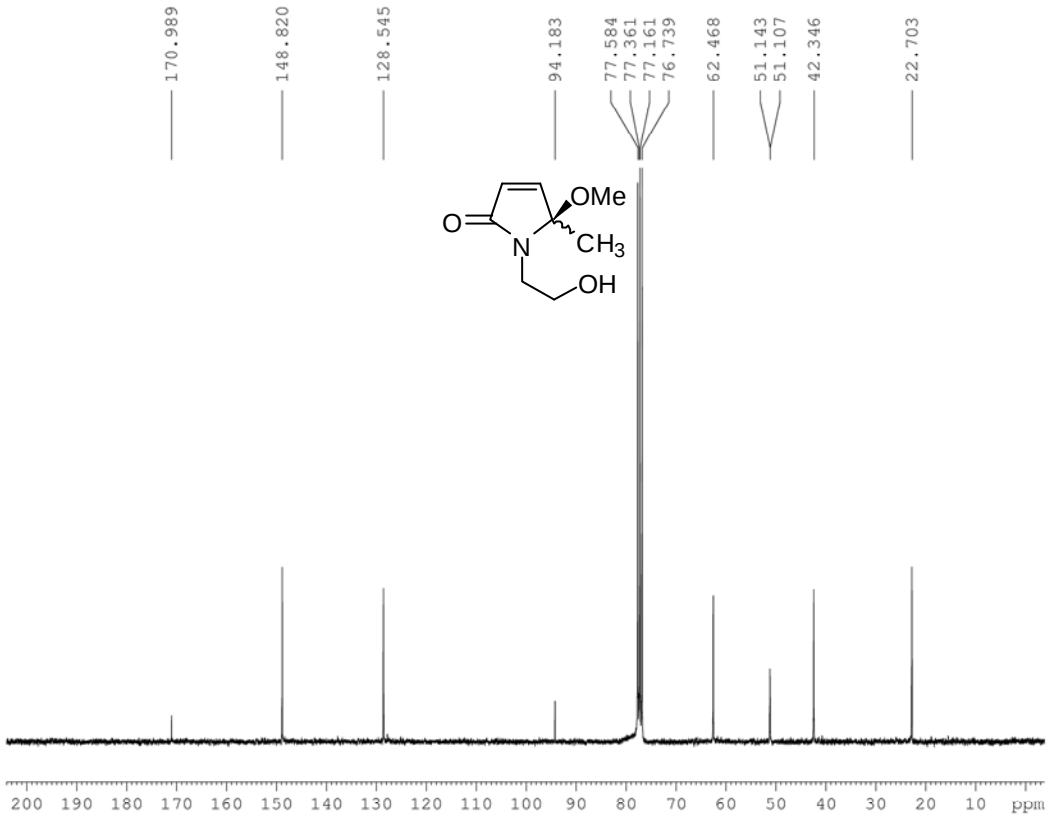

HMBC (500 MHz, $CDCl_3$) of compound **17**



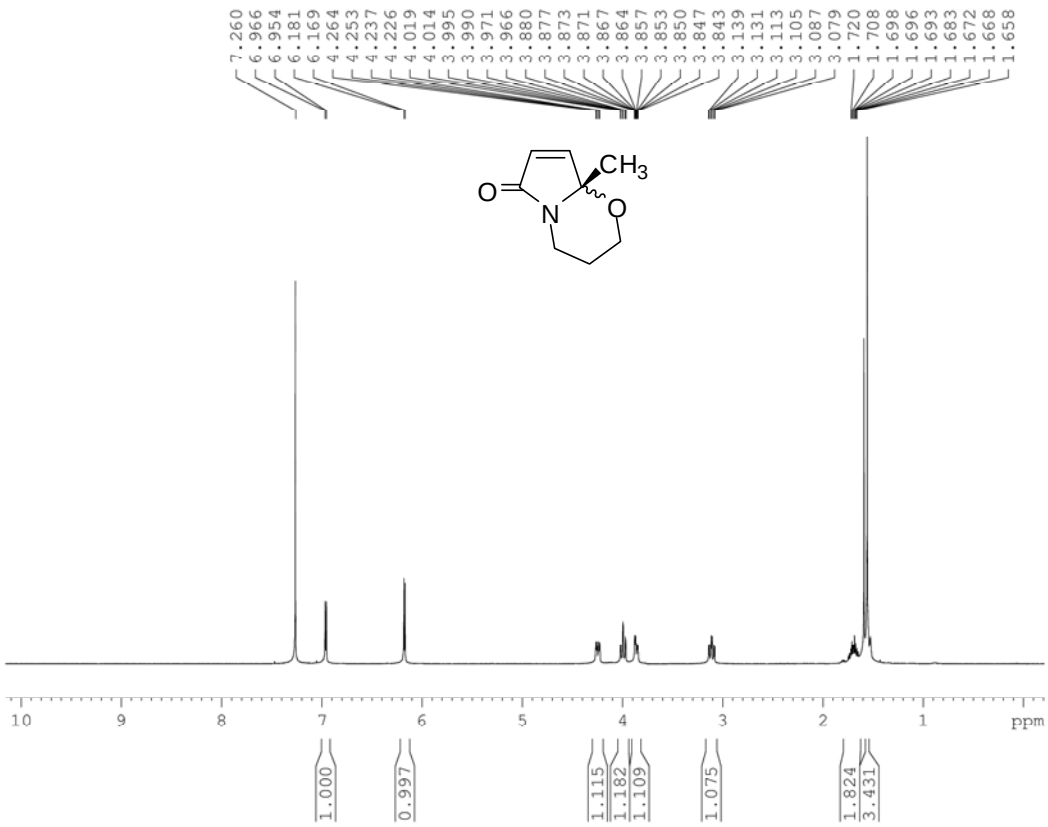
$^{1}$H NMR (500 MHz, $CDCl_3$) of compound **18**



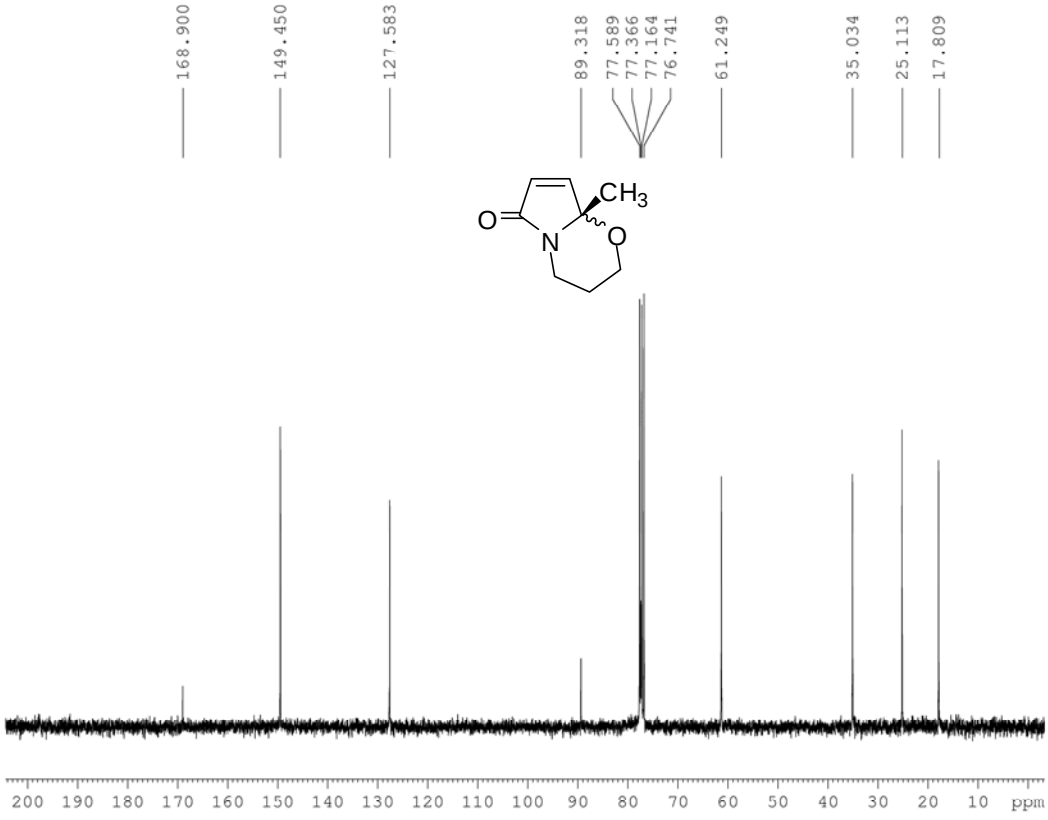

$^{13}$C NMR (75 MHz, $CDCl_3$) of compound **18**



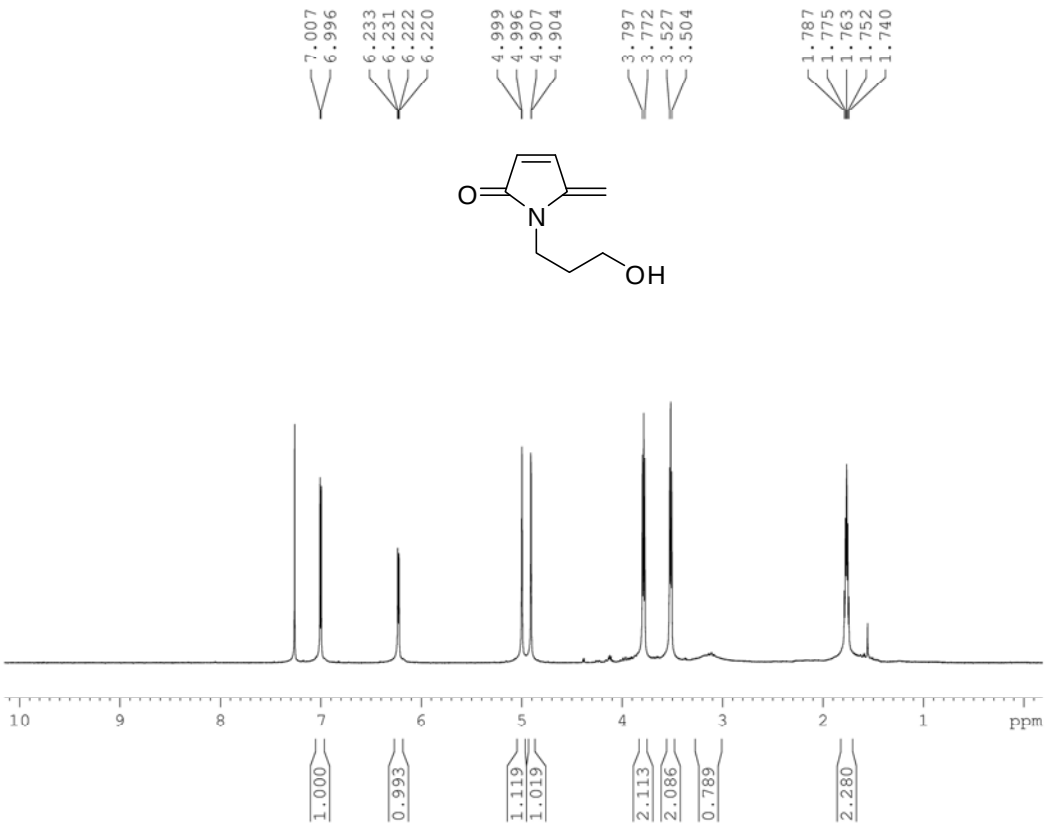
$^{1}$H NMR (500 MHz, $CDCl_3$) of compound **19**



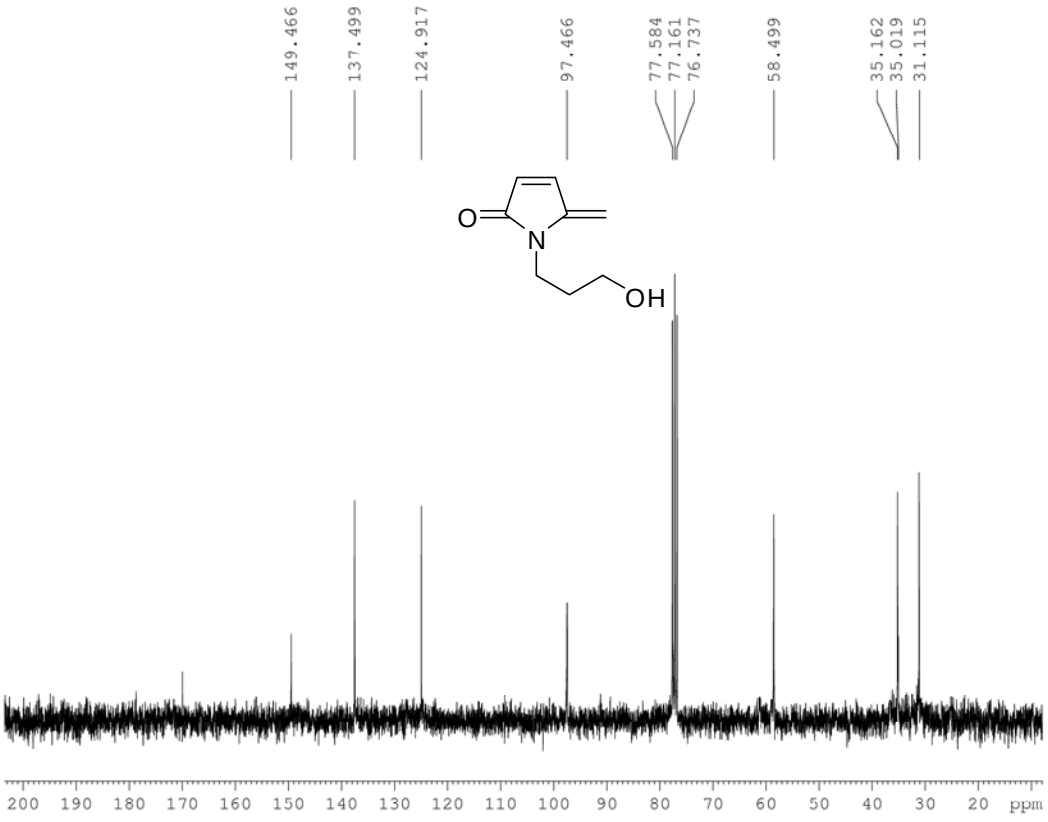

$^{13}$C NMR (75 MHz, $CDCl_3$) of compound **19**



$^{1}$H NMR (500 MHz, $CDCl_3$) of compound **20**

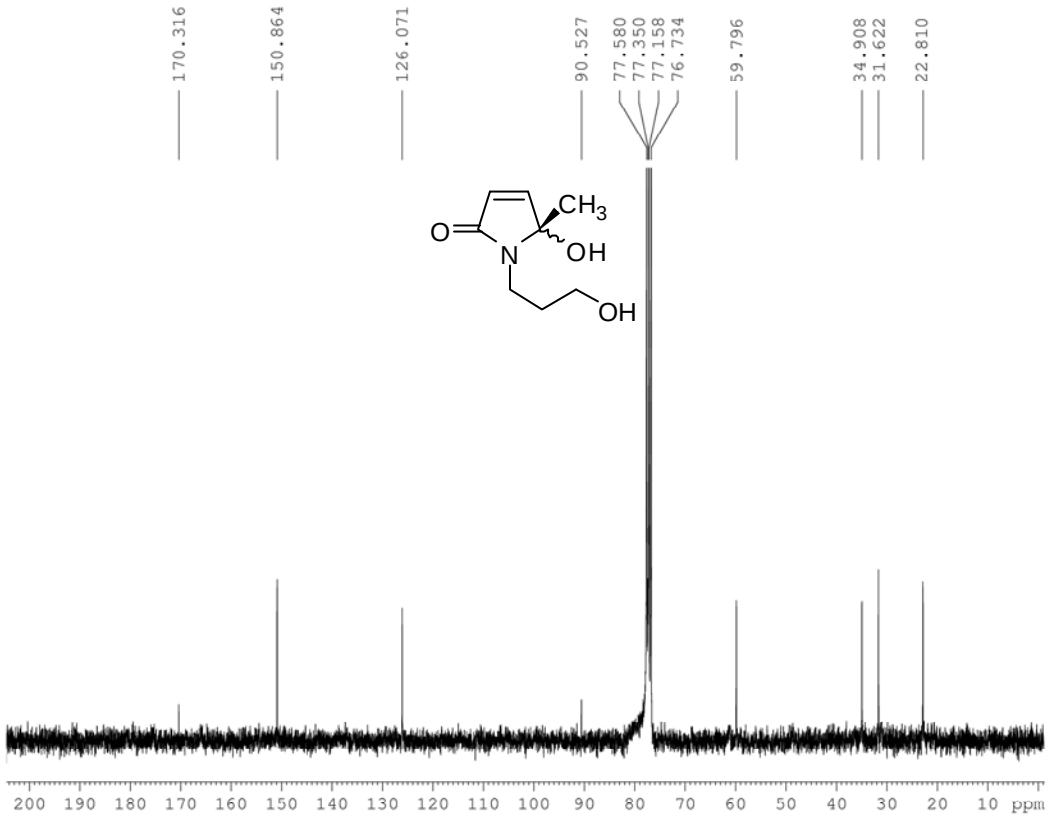



$^{13}$C NMR (75 MHz, $CDCl_3$) of compound **20**

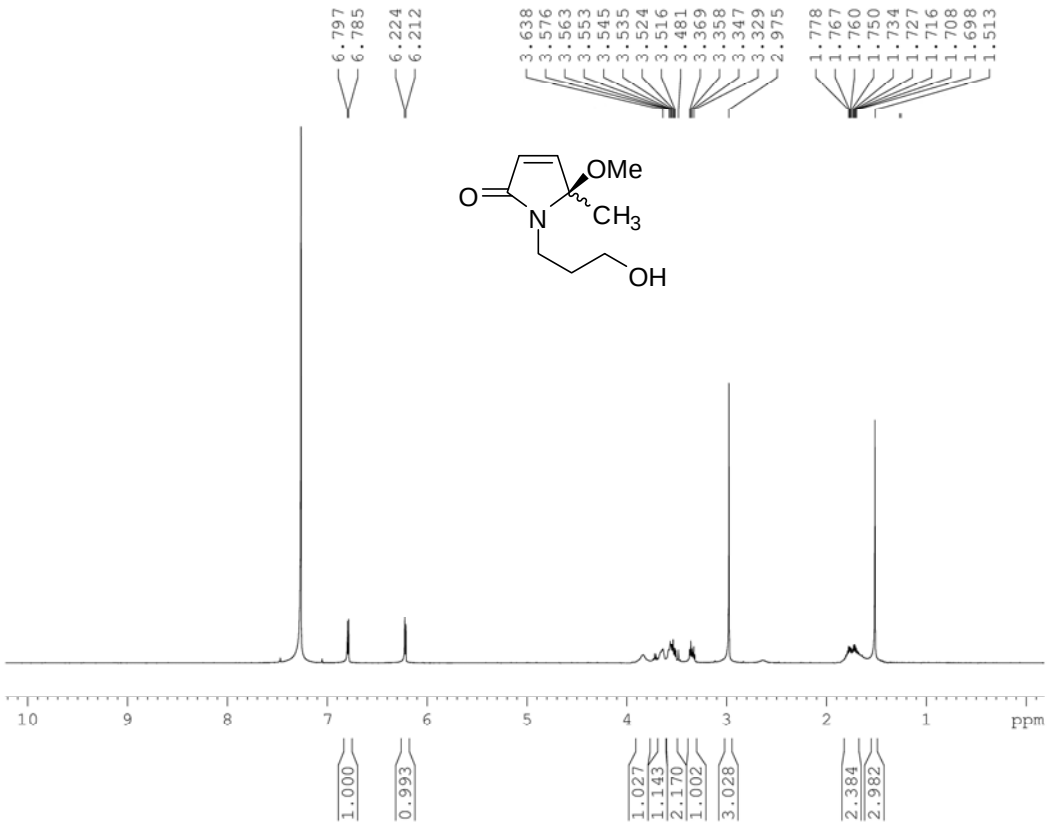


$^{1}$H NMR (500 MHz, $CDCl_3$) of compound **21**

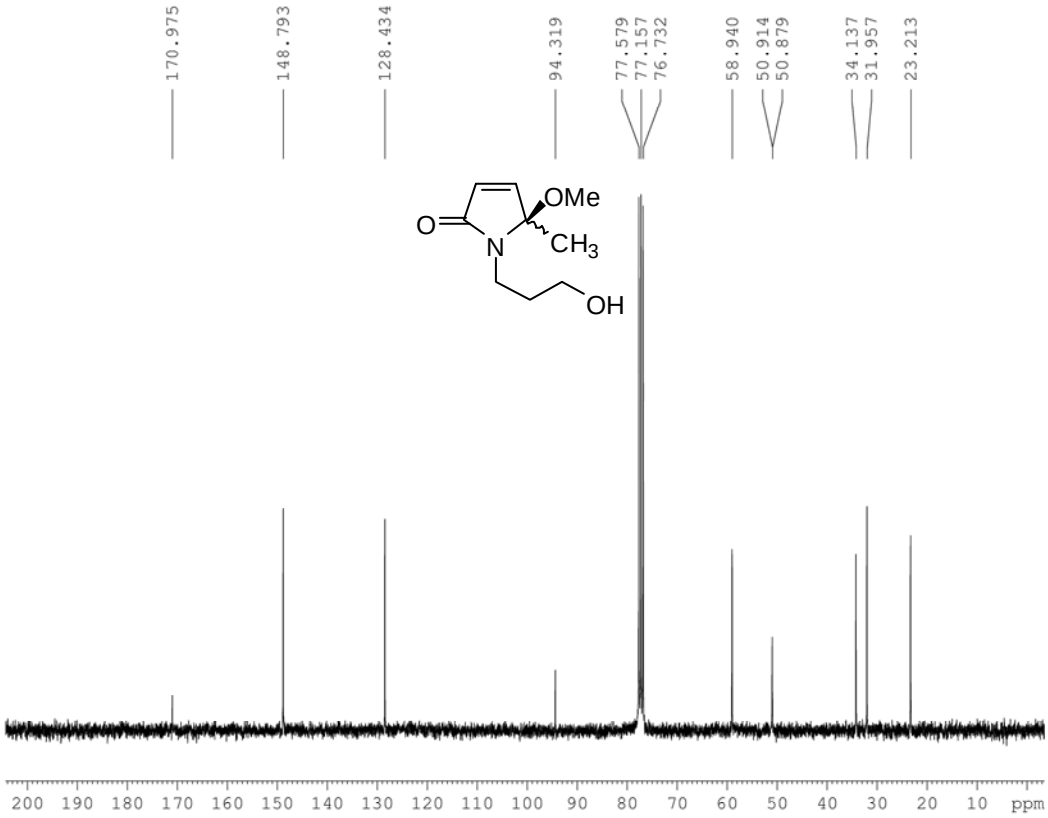

$^{13}$C NMR (75 MHz, $CDCl_3$) of compound **21**



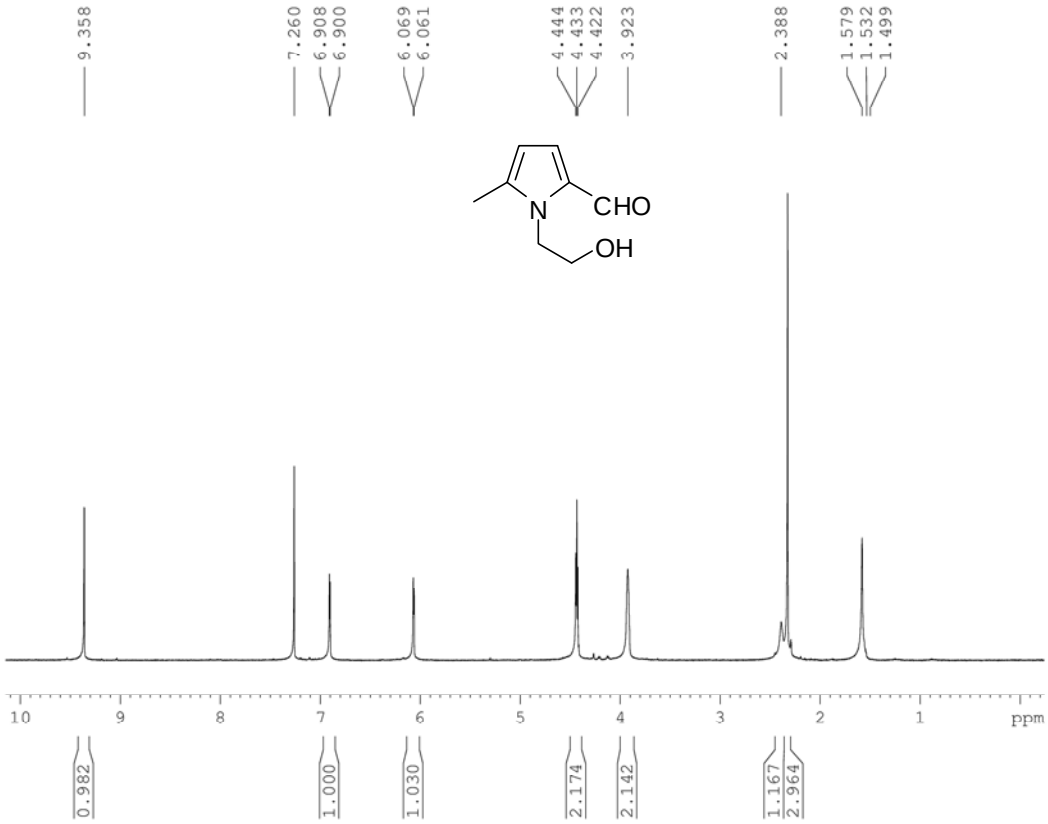
$^{1}$H NMR (500 MHz, $CDCl_3$) of compound **22**



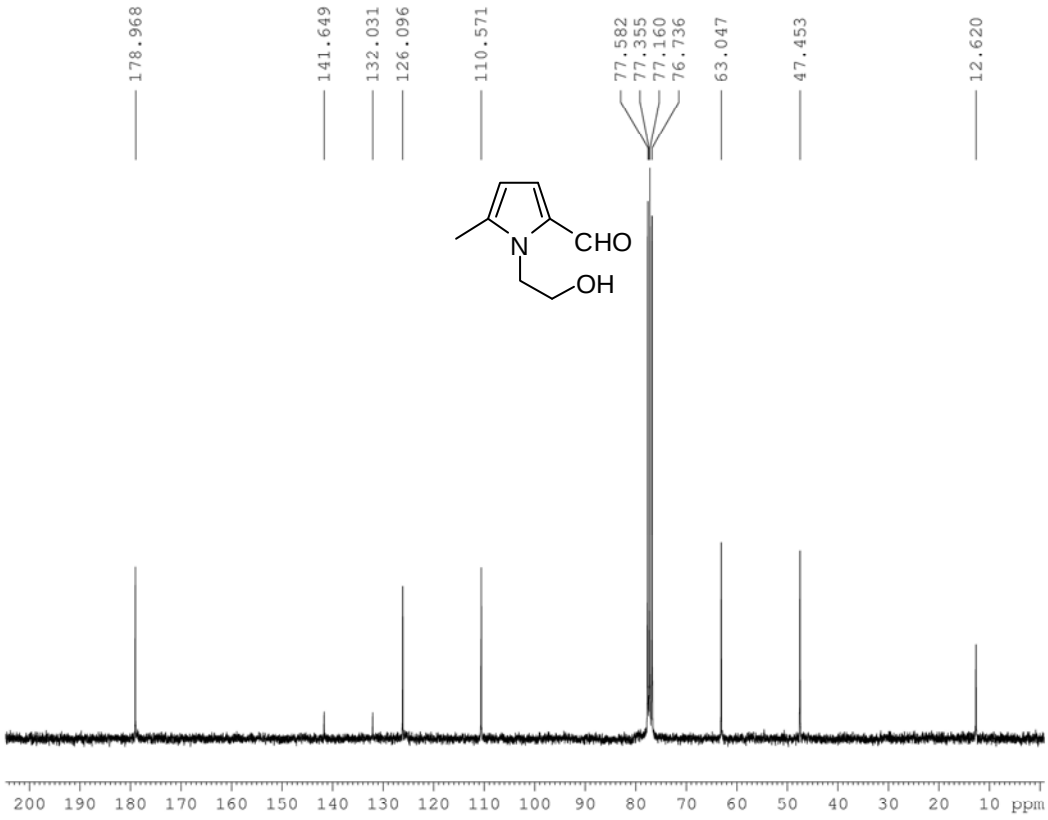

$^{13}$C NMR (75 MHz, $CDCl_3$) of compound **22**



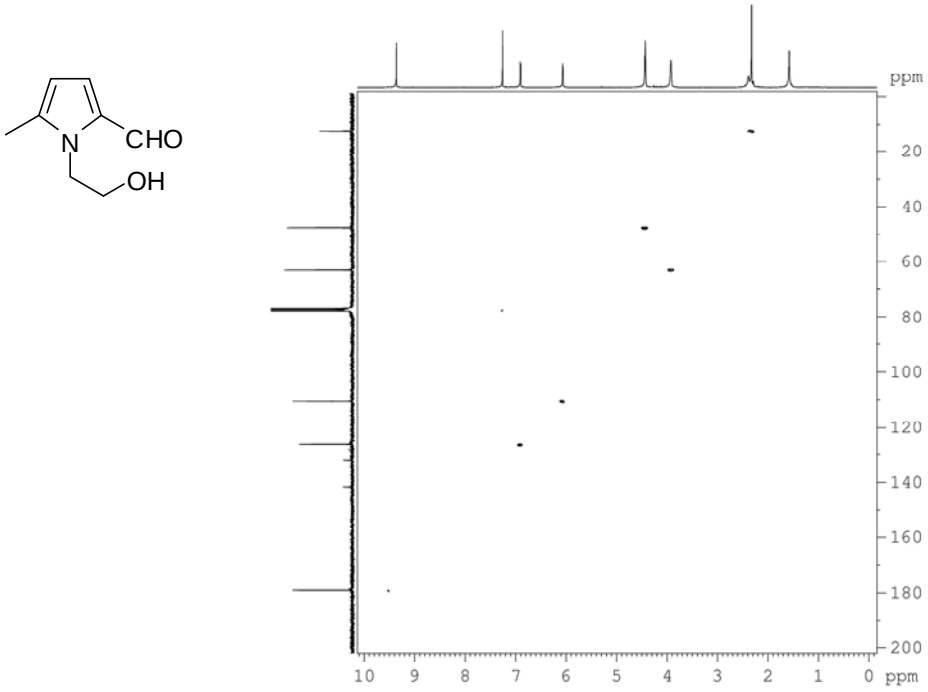
$^{1}$H NMR (500 MHz, $CDCl_3$) of compound **23**



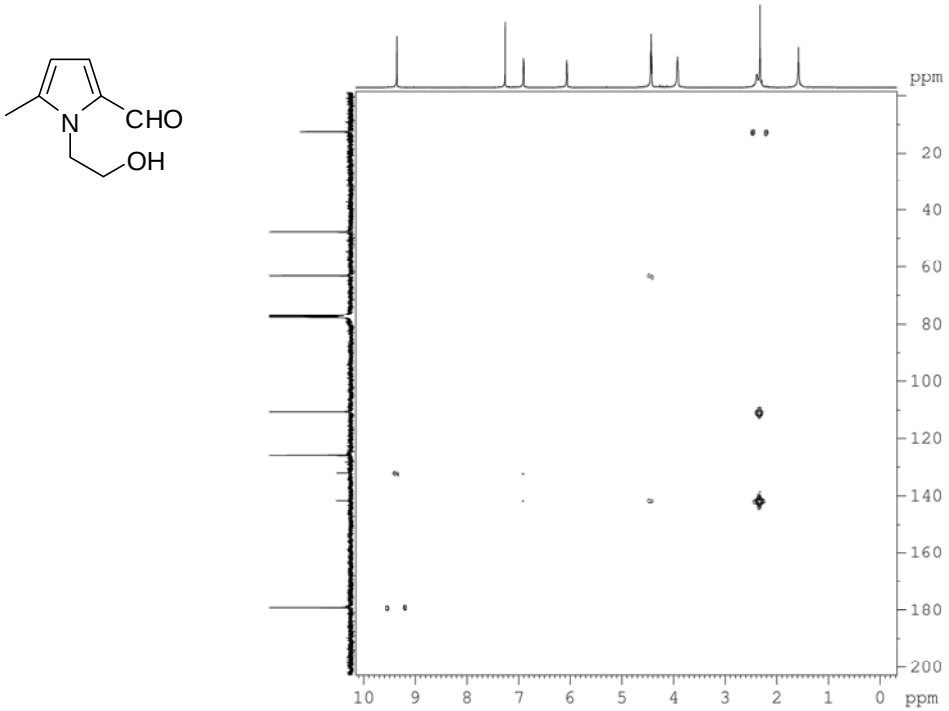

$^{13}$C NMR (75 MHz, $CDCl_3$) of compound **23**



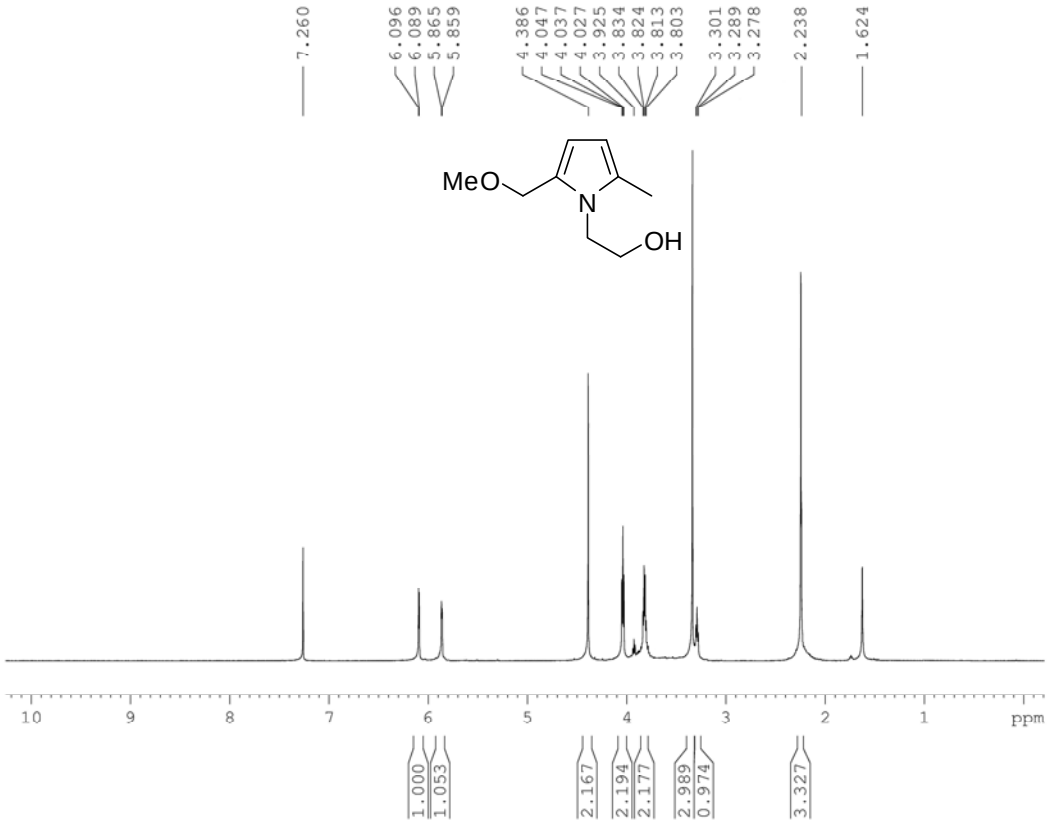
HMQC (500 MHz, $CDCl_3$) of compound **23**



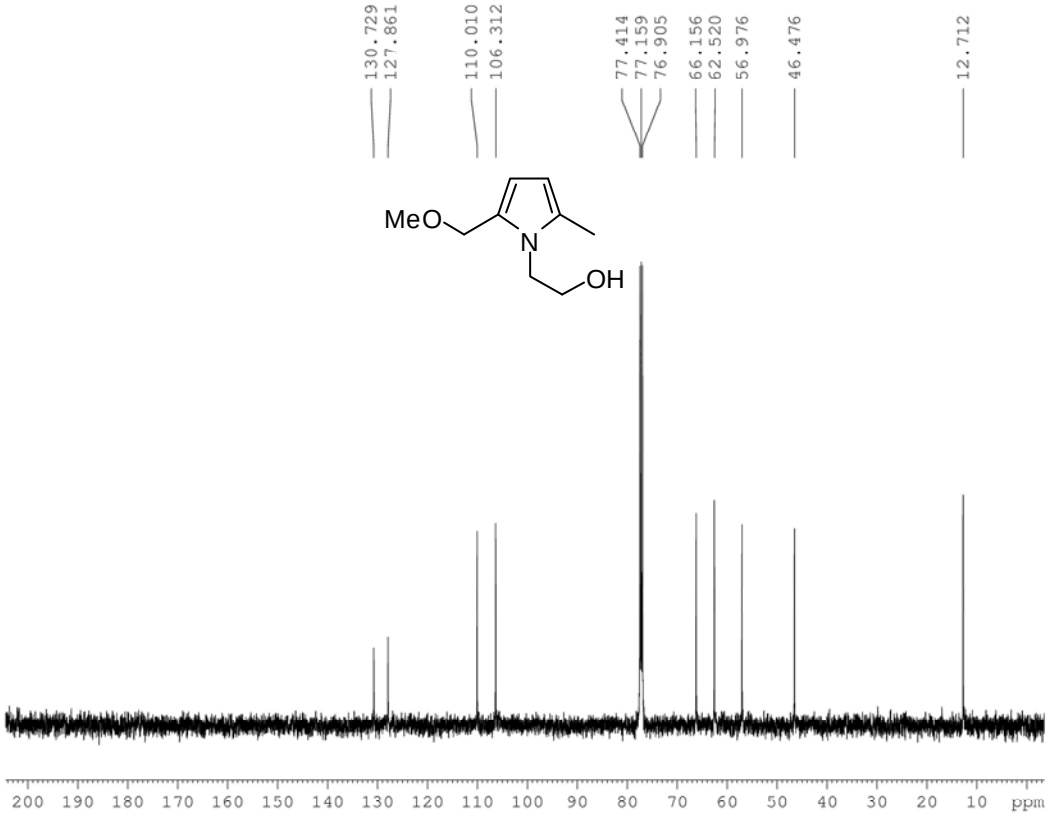

HMBC (500 MHz, $CDCl_3$) of compound **23**



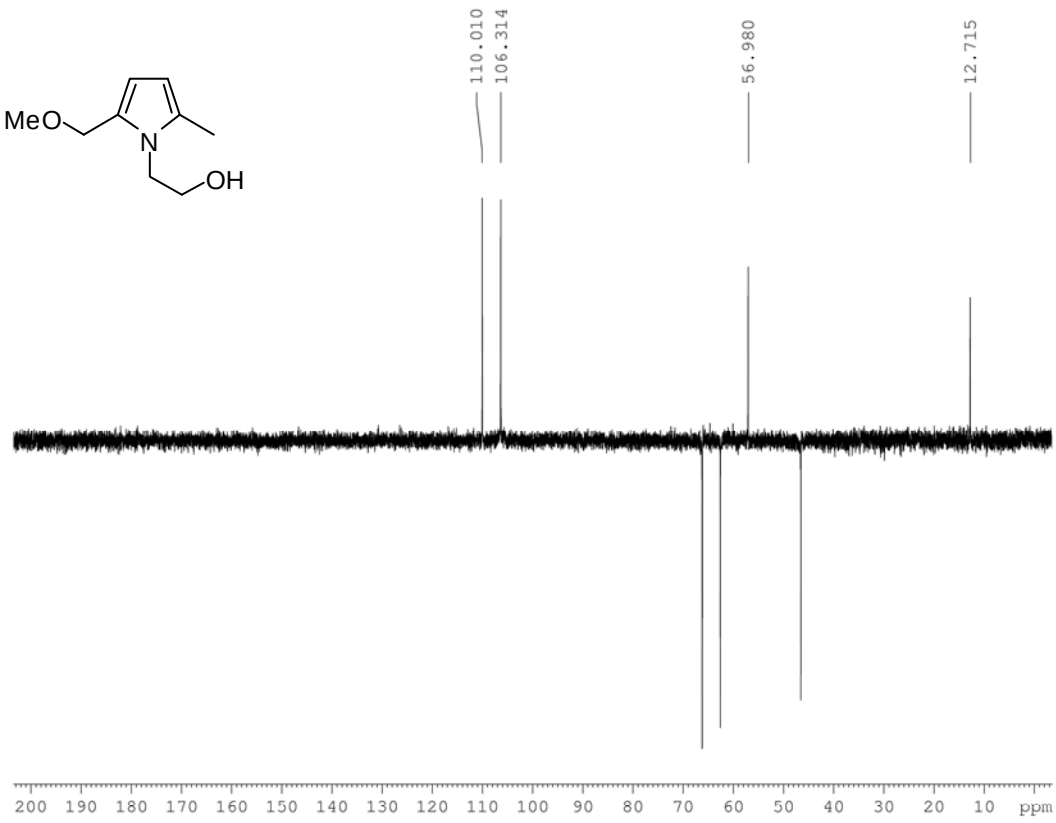
$^{1}$H NMR (500 MHz, $CDCl_3$) of compound **24**



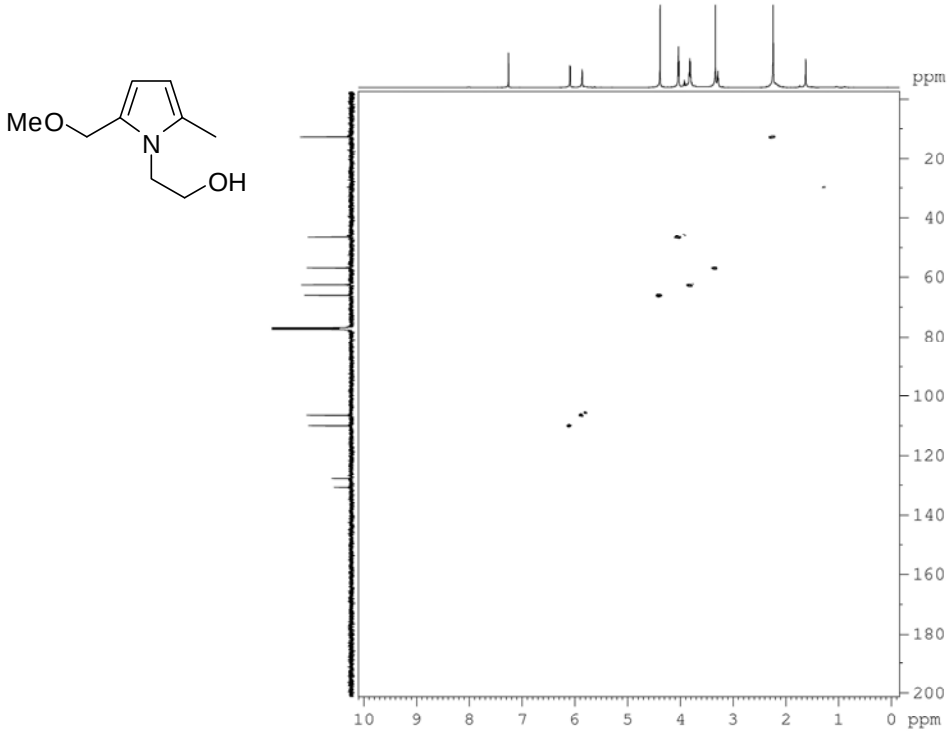

$^{13}$C NMR (125 MHz, $CDCl_3$) of compound **24**



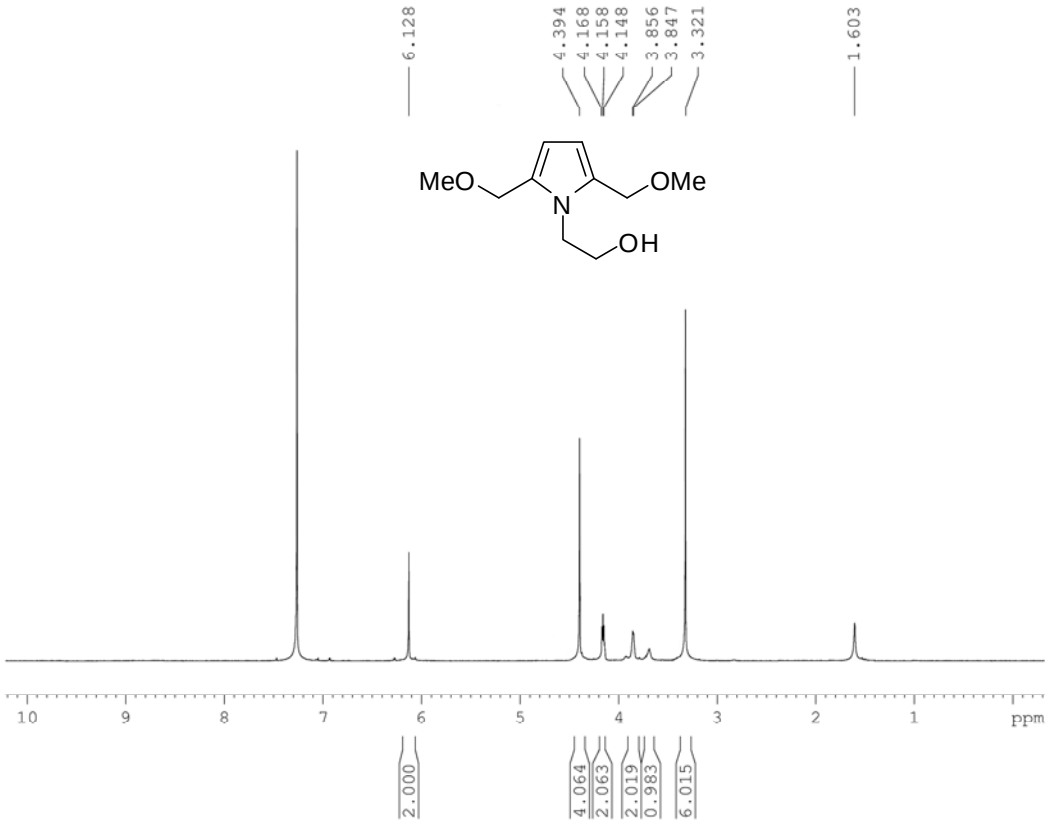
DEPT 135 (125 MHz, $CDCl_3$) of compound **24**



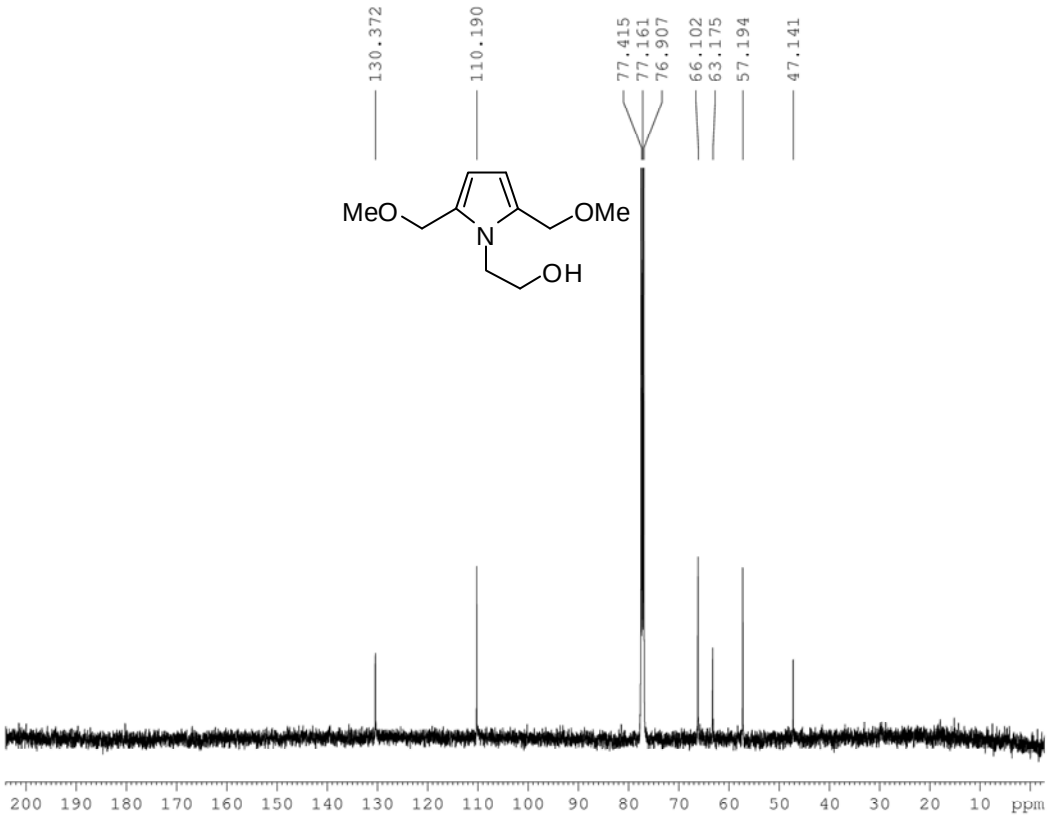

HMQC (500 MHz, $CDCl_3$) of compound **24**



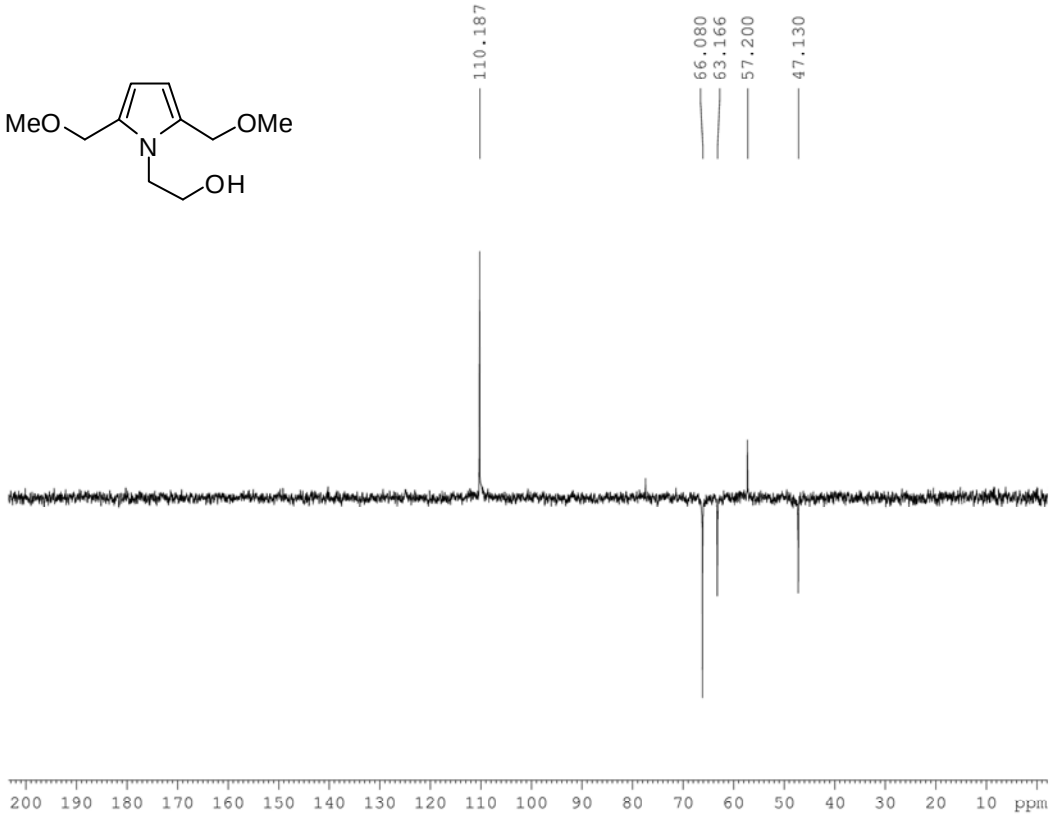
$^{1}$H NMR (500 MHz, $CDCl_3$) of compound **25**



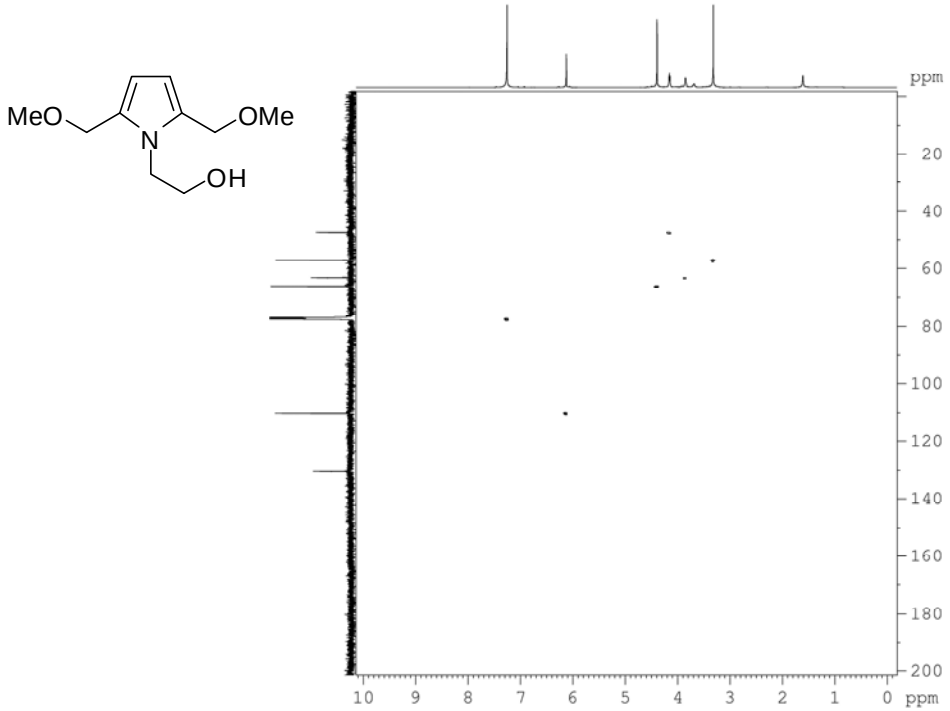

$^{13}$C NMR (125 MHz, $CDCl_3$) of compound **25**



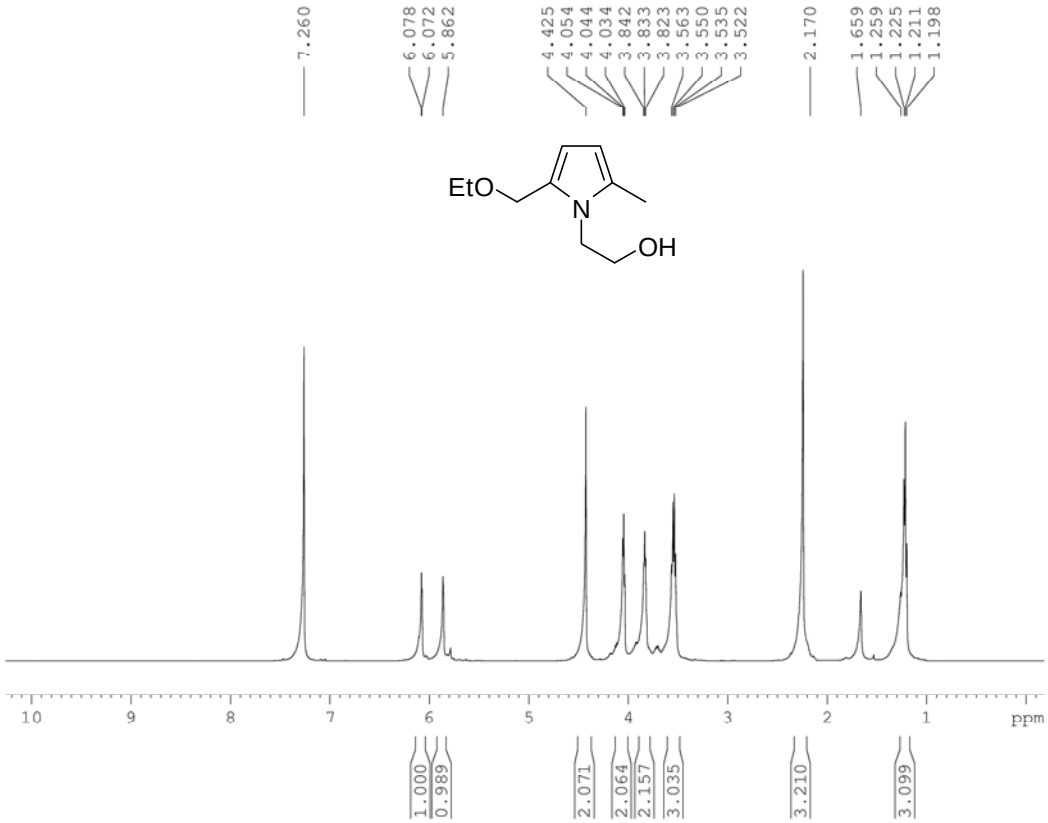
DEPT 135 (75 MHz, $CDCl_3$) of compound **25**



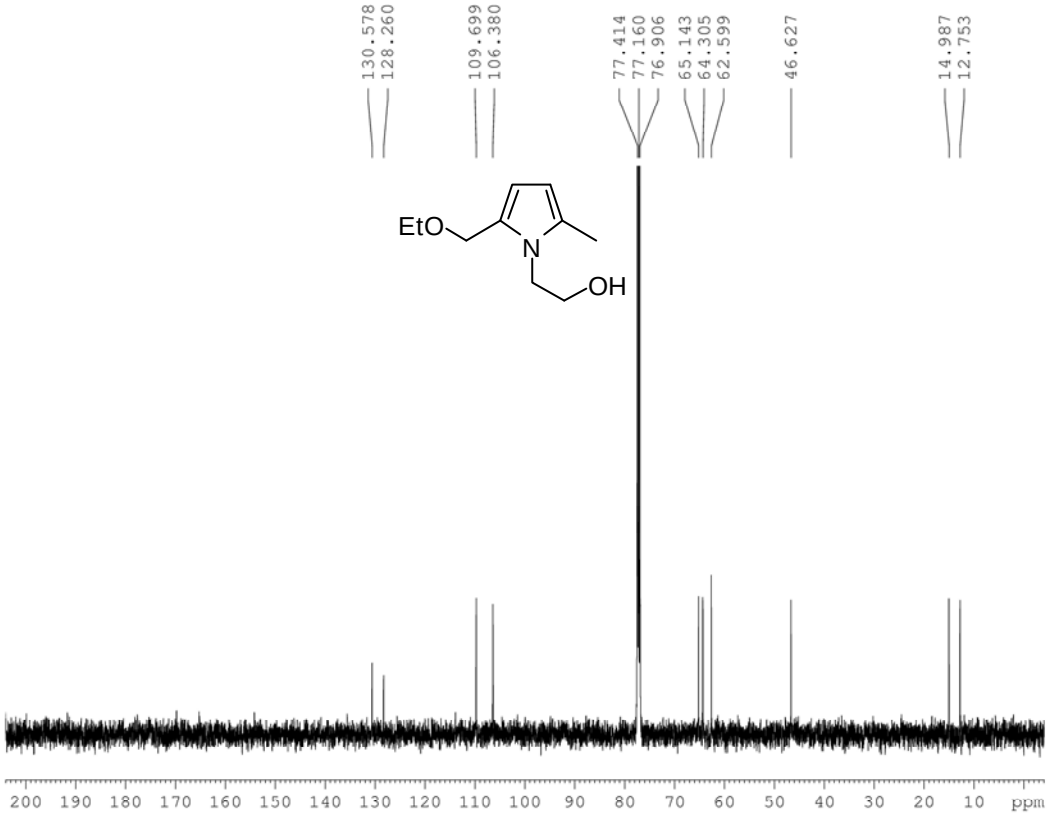

HMQC (500 MHz, $CDCl_3$) of compound **25**



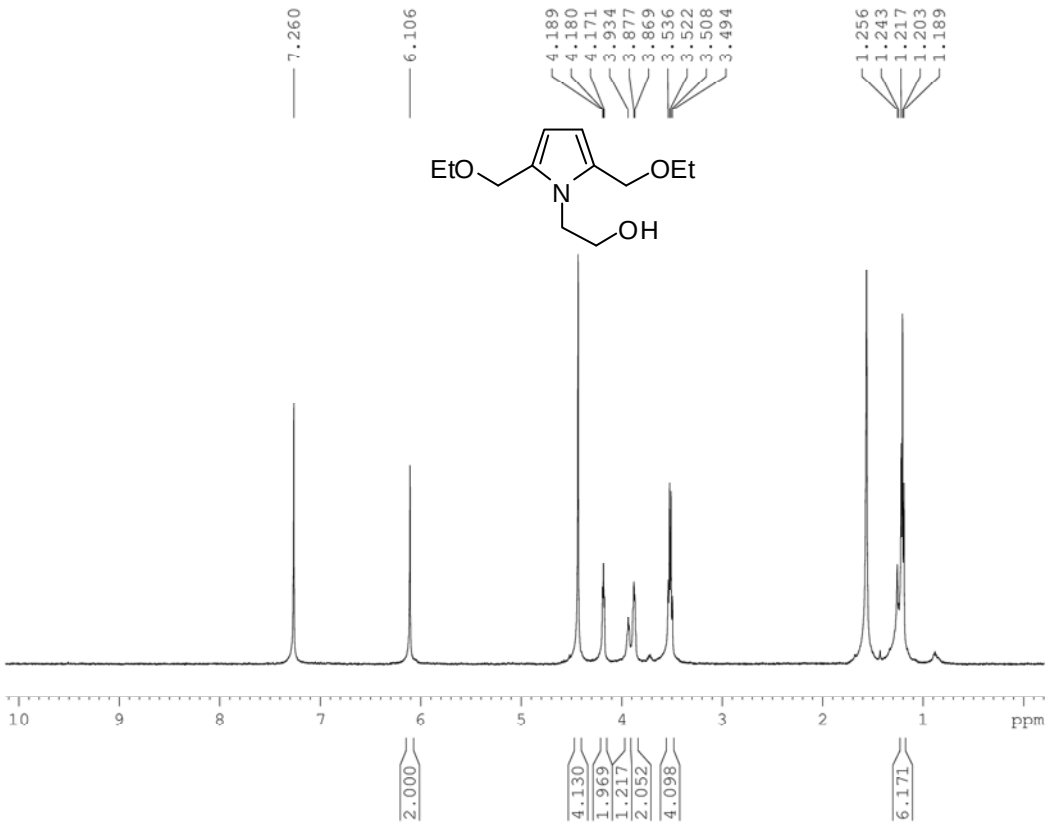
$^{1}$H NMR (500 MHz, $CDCl_3$) of compound **26**




$^{13}$C NMR (125 MHz, $CDCl_3$) of compound **26**



$^{1}$H NMR (500 MHz, $CDCl_3$) of compound **27**




$^{13}$C NMR (125 MHz, $CDCl_3$) of compound **27**