

Supporting Information

Disiloxanes with cyclic or non-cyclic carbamate moieties as electrolytes for lithium-ion batteries

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General Remarks

Materials

All reactions were carried out under nitrogen atmosphere using standard Schlenck techniques and with dried solvents. Reagents were purchased from Sigma Aldrich, ABCR and ACROS and used as received.

Sigma Aldrich	allyl bromide, iodomethane, lithium hexamethyldisilazide
ABCR	pentamethyldisiloxane, Platinum-divinyltetramethyldisiloxane complex in xylene (2.1-2.4%Pt),
ACROS	oxazolidin-2-one, allyl amine, methyl chloroformate, ethyl chloroformate, potassium carbonate

Measurements

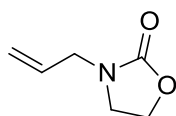
- ¹H and ¹³C NMR measurements were performed on a Bruker AVANCE(III) 400 UltraShield® spectrometer with 400.03 MHz. Chemical shifts are reported in delta (δ) units, in parts per million (ppm) relative to non-deuterated solvent residual signal. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublet. Spectra were analyzed using Mestrelab Research S.L. MestReNova v8.0.0-10524.
- Mass spectrometric measurements were performed on Thermo Quest FinniganGCQ with gas chromatograph Thermo FOCUS®, CTC A200S autosampler using MeOH and SGE HT5 carborane modified siloxane column.
- Ionic conductivity was determined by Agilent Technologies Precision LCR-Meter E4980A combined with multiplexer Agilent Technologies E5250A with two E5252A 10 × 12 matrix switches. The conductivity measurement cells were tempered using JULABO Labortechnik GmbH FP45 thermostat. Spectra were analyzed using Scribner Associates, Inc. ZView v3.1c.
- Relative permittivity measurements were performed using Novocontrol GmbH Novotherm Alpha-A High Performance Frequency Analyzer. Spectra were analyzed using Scribner Associates, Inc. ZView v3.1c.
- Linear sweep and cyclic voltammetry were performed using Deutsche Metrohm Autolab PGSTAT302N® potentiostat.
- Viscosity of disiloxanes model compounds was measured on Anton Paar MCR301 rheometer.
- HOMO/LUMO energies were calculated with the semiempirical PM3¹ method using Mopac2009².

¹ J. J. P. Stewart. Optimization of Parameters for Semi-Empirical Methods I-Method. *J. Comp. Chem.*, 1989, **10**, 209.

² MOPAC2009, J. J. P. Stewart, Stewart Computational Chemistry, Version 11.366L web: [HTTP://OpenMOPAC.net](http://OpenMOPAC.net)

Experimental

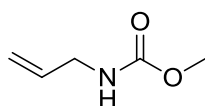
N-allyl oxazolidin-2-one (1)



Oxazolidin-2-one (9.0 g, 102.3 mmol), allyl bromide (25.0 g, 204.7 mmol), 220 ml acetonitrile and 50 g potassium carbonate are placed in a 500-ml round-flask and equipped with reflux condenser. The mixture is refluxed for three days. After cooling to room temperature the solid is filtered and the resulting filtrate concentrated in vacuum using rotary evaporator. The residue is distilled under reduced pressure and the major fraction is collected to afford the title compound (65 °C at 4×10^{-4} mbar). Yield: 12.1 g (95.3 mmol, 93%).

^1H NMR (400 MHz, CDCl_3): δ = 5.67 (ddt, 1H, CH), 5.15 (dd, 1H of $\text{H}_2\text{C}=\text{CH}$), 5.12 (d, 1H of $\text{H}_2\text{C}=\text{CH}$), 4.22 (dd, 2H, OCH_2), 3.74 (dd, 2H, NCH_2CH), 3.43 (dd, 2H, NCH_2CH_2); ^{13}C NMR (101 MHz, CDCl_3): δ = 157.97, 131.69, 118.18, 61.53, 46.55, 43.84.

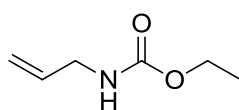
Methyl N-allylcarbamate (2)³



Allyl amine (14.6 g, 253.0 mmol) and 200 ml methylene chloride are placed in a 500-ml round-flask and stirred at temperature of 0 °C with reflux condenser. To the mixture methyl chloroformate (11.5 g, 120.5 mmol) is added dropwise via syringe with care holding temperature for one hour. The mixture is allowed to warm to room temperature over one hour and then extracted with 50 ml of aqueous 1M HCl solution, 50 ml of saturated aqueous NaHCO_3 solution, and 50 ml of saturated aqueous NaCl solution. The organic phase is dried over MgSO_4 , filtered, and concentrated by rotary evaporation. Yield: 13.3 g (115.5 mmol, 96%).

^1H NMR (400 MHz, CDCl_3): δ = 5.71 (ddd, 1H, CH), 5.31 (s, 1H, NH), 5.05 (dd, 1H of $\text{H}_2\text{C}=\text{CH}$), 4.97 (dd, 1H of $\text{H}_2\text{C}=\text{CH}$), 3.65 (s, 2H, CH_2), 3.53 (s, 3H, OCH_3); ^{13}C NMR (101 MHz, CDCl_3): δ = 156.84, 134.44, 115.30, 51.65, 43.08; GC-MS: R_t = 4.21 min., m/z (%) = 115(20) [M], 100(100) [M - CH_3], 83(30), 82(24), 56(78) [$\text{C}_3\text{H}_6\text{N}^+$].

Ethyl N-allylcarbamate (3)³

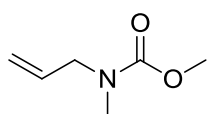


Allyl amine (12.7 g, 220.3 mmol) and 200 ml methylene chloride are placed in a 500-ml round-flask and stirred at temperature of 0 °C with reflux condenser. To the mixture ethyl chloroformate (11.5 g, 104.9 mmol) is added dropwise via syringe with care holding temperature for one hour. The mixture is allowed to warm to room temperature over one hour and then extracted with 50 ml of aqueous 1M HCl solution, 50 ml of saturated aqueous NaHCO_3 solution, and 50 ml of saturated aqueous NaCl solution. The organic phase is dried over MgSO_4 , filtered, and concentrated by rotary evaporation. Yield: 12.9 g (99.9 mmol, 95%).

^1H NMR (400 MHz, CDCl_3): δ = 5.80 – 5.63 (m, 1H, CH), 5.23 (s, 1H, NH), 5.06 (d, 1H of $\text{H}_2\text{C}=\text{CH}$), 4.97 (d, 1H of $\text{H}_2\text{C}=\text{CH}$), 4.01 (t, 2H, CH_2), 3.65 (s, 2H, CH_2CH_3), 1.14 (dt, 3H, CH_3); ^{13}C NMR (101 MHz, CDCl_3): δ = 156.45, 134.53, 115.31, 60.40, 43.03, 14.28; GC-MS: R_t = 4.78 min., m/z (%) = 129(10) [M], 100(100) [M - C_2H_5], 82(16), 70(20), 56(96) [$\text{C}_3\text{H}_6\text{N}^+$].

³ A. Kohnen, J. Dunetz and R. Danheiser, *Org. Synth.*, 2007, **84**, 88.

Methyl *N*-allylmethylcarbamate (**4**)⁴



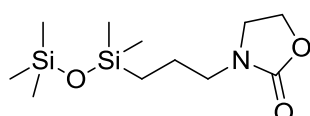
Lithium hexamethyldisilazide (14.0 g, 83.0 mmol) and 130 ml THF are placed in a 250-mL round-flask and stirred at a temperature of -78 °C. To the mixture methyl allylcarbamate **3** (7.2 g, 55.3 mmol) is added dropwise via syringe. The ensuing mixture was stirred for 30 minutes holding temperature and then, dropwise, treated with methyl iodide (15.9 g, 110.7 mmol) before being allowed to warm to ambient temperature overnight. The mixture is treated with 50 ml saturated aqueous solution of ammonium chloride and extracted with ethyl acetate (3 × 50 ml). The combined organic layers are washed with brine (3 × 50 ml) then dried over MgSO₄, filtered, and concentrated by rotary evaporation to give colorless oil. Yield: 7.5 g (58.2 mmol, 98%).

¹H NMR (400 MHz, CDCl₃): δ = 5.65 (dq, 1H), 5.12 – 4.91 (m, 2H, H₂C=CH), 3.77 (s, 2H, CH₂), 3.59 (s, 3H, OCH₃), 2.75 (s, 3H, NCH₃); ¹³C NMR (101 MHz, CDCl₃): δ = 156.62, 133.08, 116.67 – 116.21, 52.29, 51.23 – 50.92, 33.85 – 33.12; GC-MS: R_t = 4.45 min., m/z(%) = 129(48) [M], 114(100) [M - CH₃], 70 (52) [C₄H₈N⁺].

Disiloxanes - General Procedure -

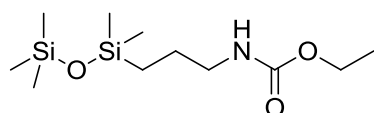
To a mixture of pentamethyldisiloxane (7.7 g, 50 mmol) and *N*-allyl sidechain **1 - 4** (5.7 g, 44 mmol) in 100-mL flask toluene (40 mL) and 50 μL of platinum divinyltetramethyldisiloxane (2.1-2.4% solution in xylene) are added and the temperature is raised to 70 °C. The reaction mixture is stirred until no allyl signal (≈ 5.6 ppm) was detected in ¹H NMR spectrum. The mixture is stirred with active charcoal to remove residual catalyst and filtered through Celite. The raw product is concentrated by rotary evaporation and purified by silica gel column chromatography.

3-(3-(1,1,3,3,3-pentamethyldisiloxanyl)propyl)oxazolidin-2-one (**5**)



¹H NMR (200 MHz, CDCl₃): δ = 4.22 (dd, 2H, OCH₂), 3.56 – 3.39 (m, 2H, NCH₂CH₂O), 3.14 (dd, NCH₂), 1.46 (dddd, 2H, CH₂), 0.50 – 0.31 (m, 2H, SiCH₂), -0.03 (s, 15H, SiCH₃); ¹³C NMR (101 MHz, CDCl₃): δ = 158.35, 61.47, 46.92, 44.31, 21.13, 14.93, 1.76, 0.07; ²⁹Si NMR (79 MHz, CDCl₃): δ = 7.64, 7.10; GC-MS: R_t = 9.45 min., m/z(%) = 260(40) [M - CH₃], 174(78), 149(100), 147(80) [C₅H₁₅OSi₂⁺], 133(22).

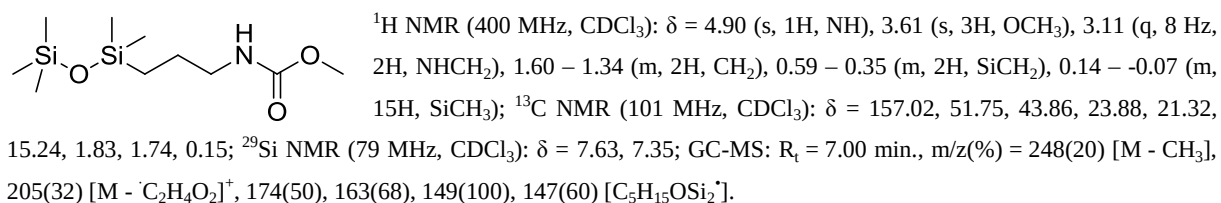
Ethyl (3-(1,1,3,3,3-pentamethyldisiloxanyl)propyl)carbamate (**6**)



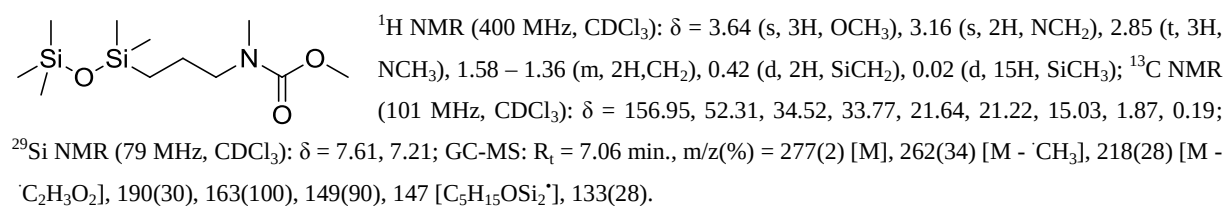
¹H NMR (400 MHz, CDCl₃): δ = 4.93 (s, 1H, NH), 4.03 (q, 2H, OCH₂), 3.07 (q, 2H, NHCH₂), 1.53 – 1.34 (m, 2H, CH₂), 1.15 (t, 3H, CH₂CH₃), 0.57 – 0.33 (m, 2H, SiCH₂), -0.02 (d, 15H, SiCH₃); ¹³C NMR (101 MHz, CDCl₃): δ = 156.58, 60.31, 43.70, 23.83, 15.21, 14.51, 1.76, 0.08; ²⁹Si NMR (79 MHz, CDCl₃): δ = 7.54, 7.33; GC-MS: R_t = 7.37 min., m/z(%) = 262(10) [M - CH₃], 204(60) [M - C₃H₆O₂], 149(100), 147(70) [C₅H₁₅OSi₂⁺].

⁴ L. V. White, B. D. Schwartz, M. G. Banwell and A. C. Willis, *J. Org. Chem.*, 2011, **76**, 6250.

Methyl (3-(1,1,3,3,3-pentamethyldisiloxanyl)propyl)carbamate (7)



N-methyl methyl(3-(1,1,3,3,3-pentamethyldisiloxanyl)propyl)carbamate (8)



Relative permittivity measurements

About 100 µL of disiloxane were filled in a coin cell (area A 1.0×10^{-4} m², thickness d 1.1×10^{-3} m) and an impedance measurement was carried out in frequency range of 0.01 Hz to 1.0×10^7 Hz. In Nyquist plot the resulting semi cycle was fitted with an equivalent circuit to obtain the capacitance C (Fig. S1).

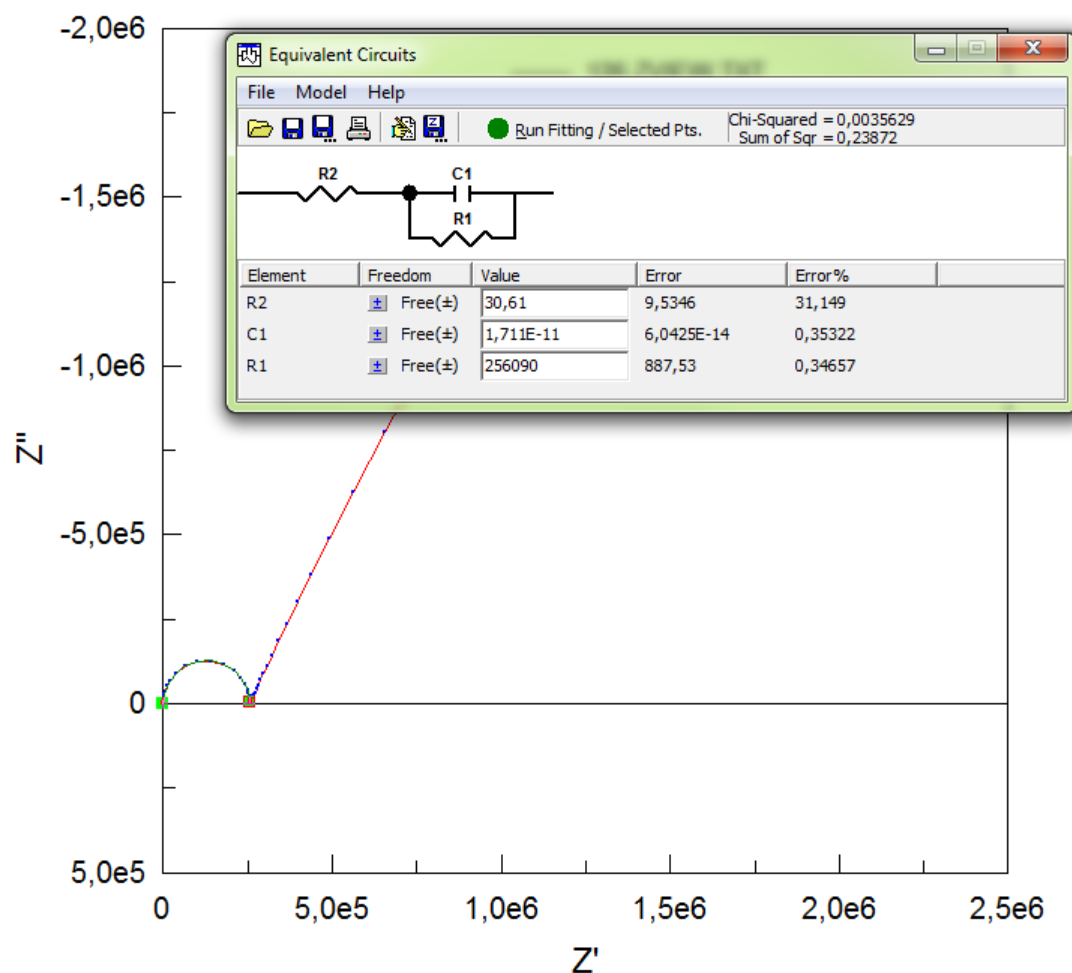


Fig. S1 Nyquist plot of compound **5** with equivalent circuit und calculated capacitance C , here $C1 = 1.711 \times 10^{-11}$.

The relative permittivity was calculated using the following equation, with vacuum permittivity ϵ_0 and correction factor f .

$$\epsilon_r = f \cdot \frac{C}{\epsilon_0} \cdot \frac{d}{A}$$

The correction factor was determined by performing relative permittivity measurements of H₂O ($\epsilon_r = 80.1$)⁵ and THF ($\epsilon_r = 7.2$)⁵ as described.

⁵ Wohlfarth, C.(2001) *Permittivity (Dielectric Constant) of Liquids*, In: *CRC Handbook of Chemistry and Physics 82nd Edition* (eds. David R. Lide), 2001, CRC Press LLC, Boca Raton, Florida.

Molecular Orbital Calculations

It was found that molecular orbital calculations of HOMO and LUMO values are roughly proportional to oxidation and reduction potentials measured by linear sweep or cyclic voltammetry.⁶

Table S1 Calculated HOMO/LUMO energies of disiloxanes **5** - **8**.

	5	6	7	8
HOMO/eV	-9.504	-9.329	-9.323	-9.296
LUMO/eV	0.900	0.983	0.996	1.037

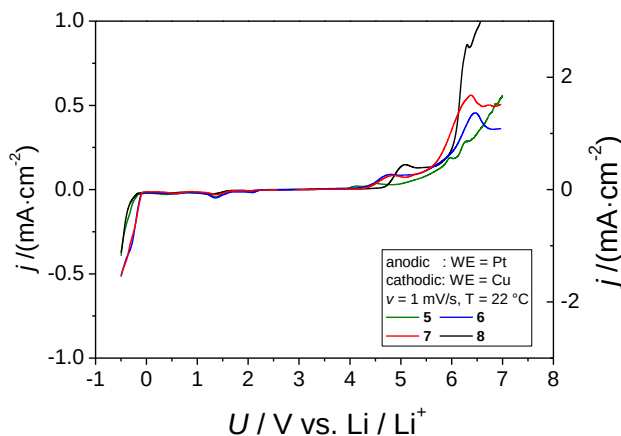


Fig. S2 Linear sweep voltammogram of disiloxanes **5** - **8**.

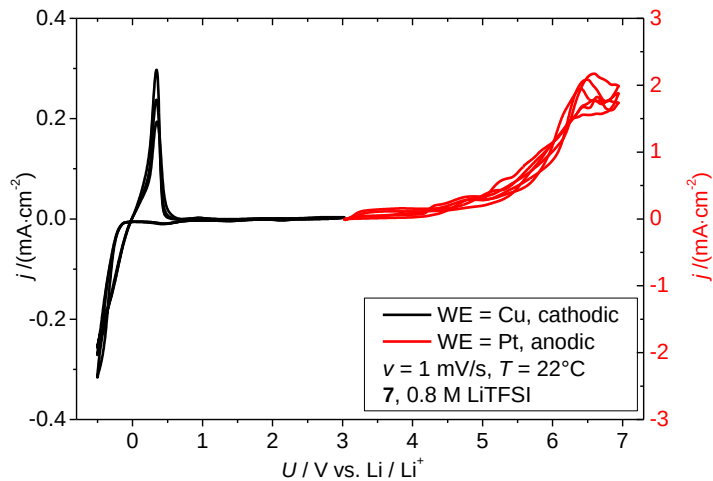


Fig. S3 Cyclic voltammogram of disiloxane **7**.

⁶ H. Yoshitake (2009) *Functional Electrolytes #specially Designated for Lithium-Ion Batteries*, In: *Lithium-Ion Batteries* (eds. M. Yoshio, R. J. Brodd, A. Kozawa), 2009, New York, Springer Science + Business Media.

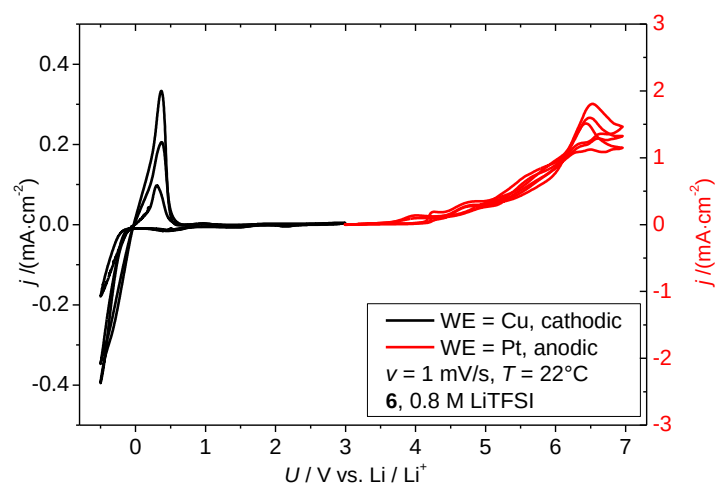


Fig. S4 Cyclic voltammogram of disiloxane **6**.

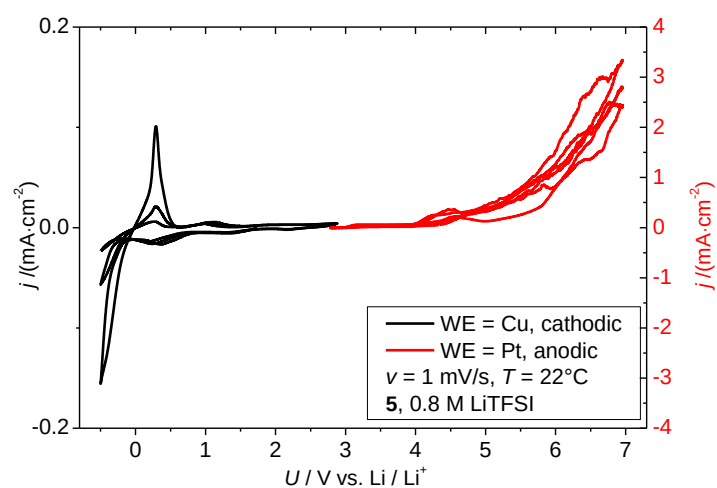
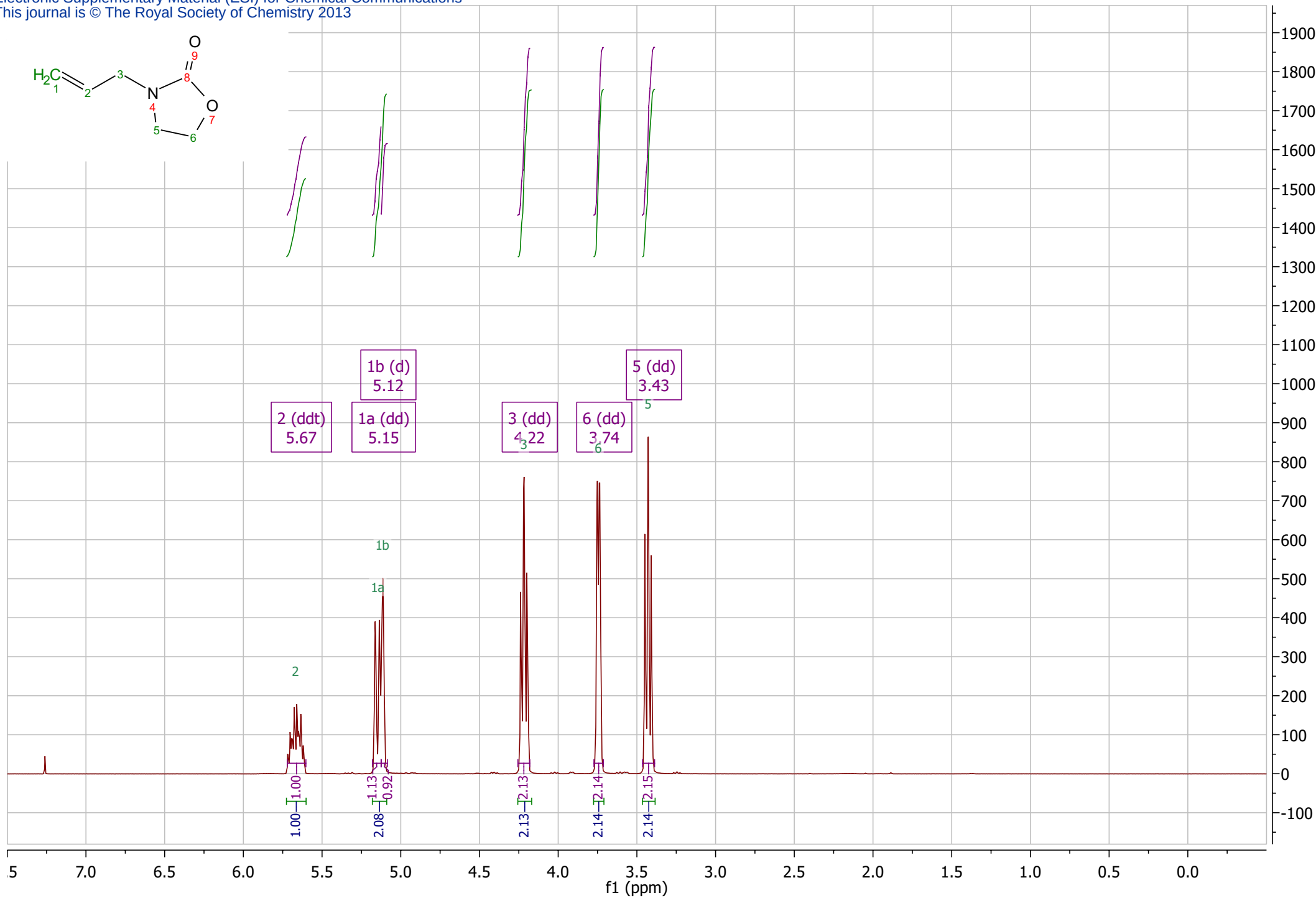
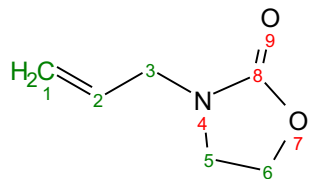
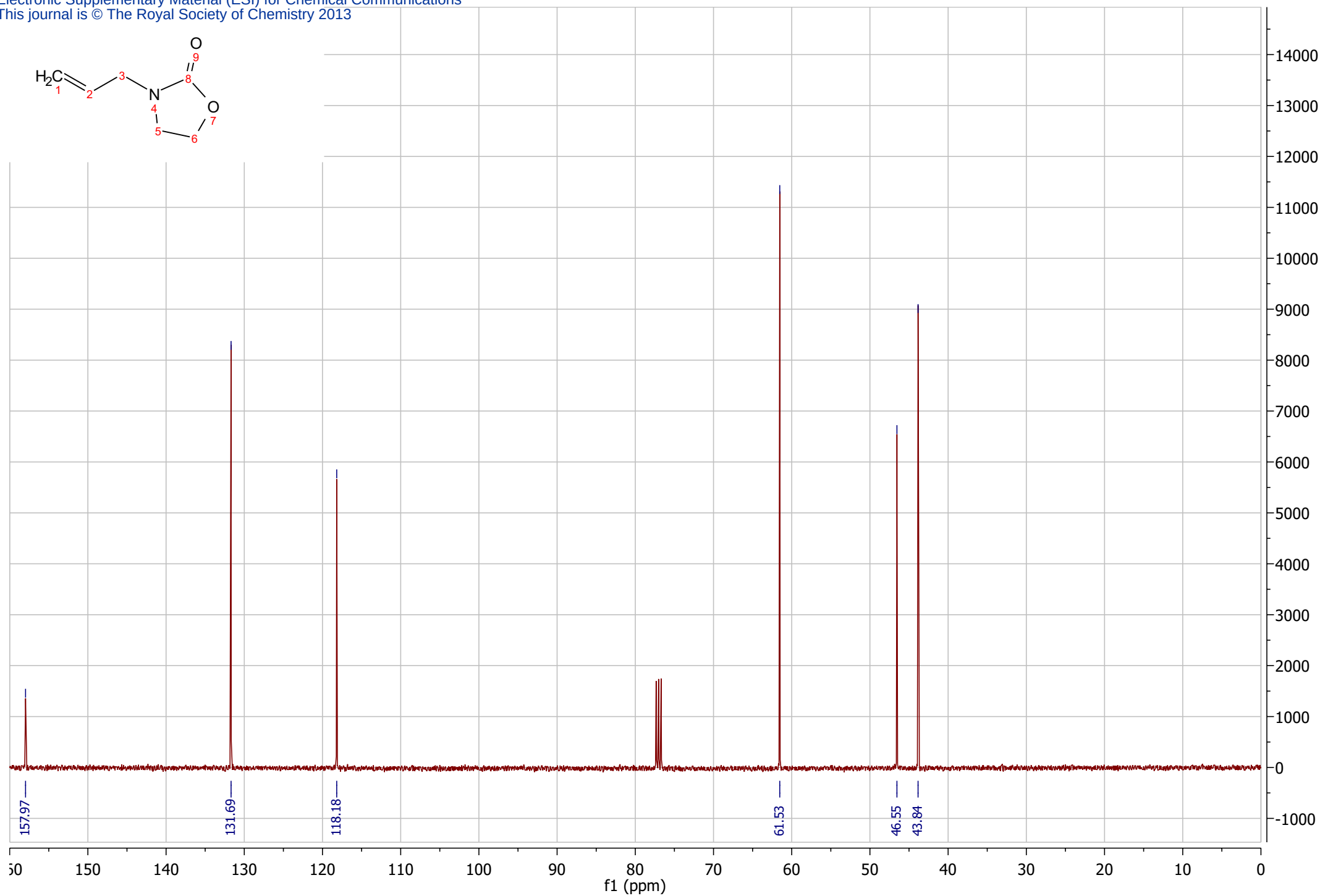
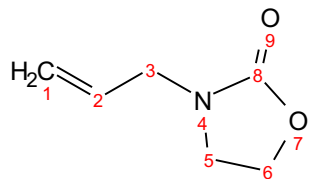


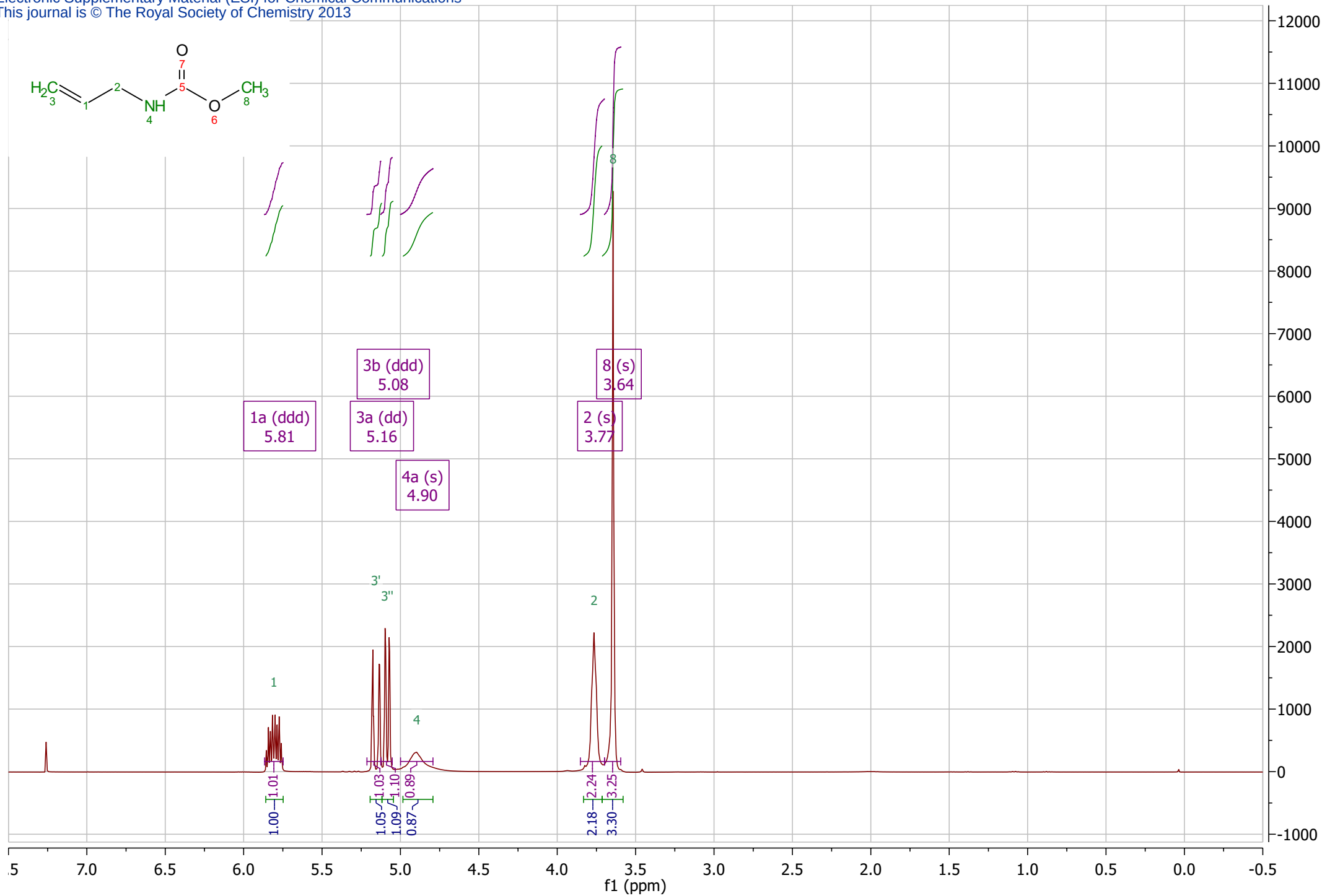
Fig. S5 Cyclic voltammogram of disiloxane **5**.



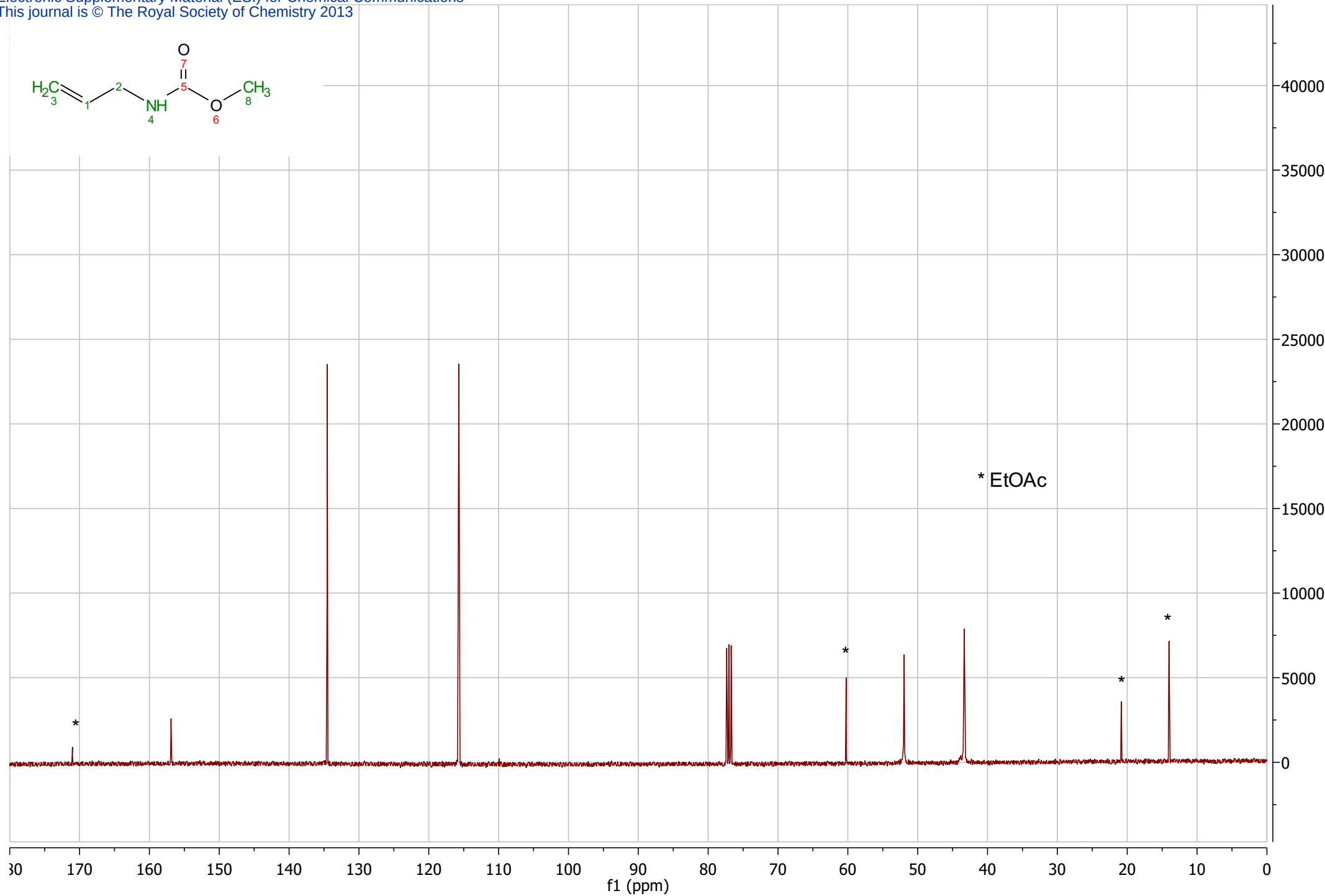
^1H NMR (400 MHz, CDCl_3) δ = 5.67 (ddt, J =12.3, 10.2, 6.1, 1H), 5.15 (dd, J =12.0, 2.8, 1H), 5.12 (d, J =2.6, 1H), 4.22 (dd, J =8.5, 7.5, 2H), 3.74 (dd, J =6.0, 1.1, 2H), 3.43 (dd, J =8.3, 7.7, 2H).

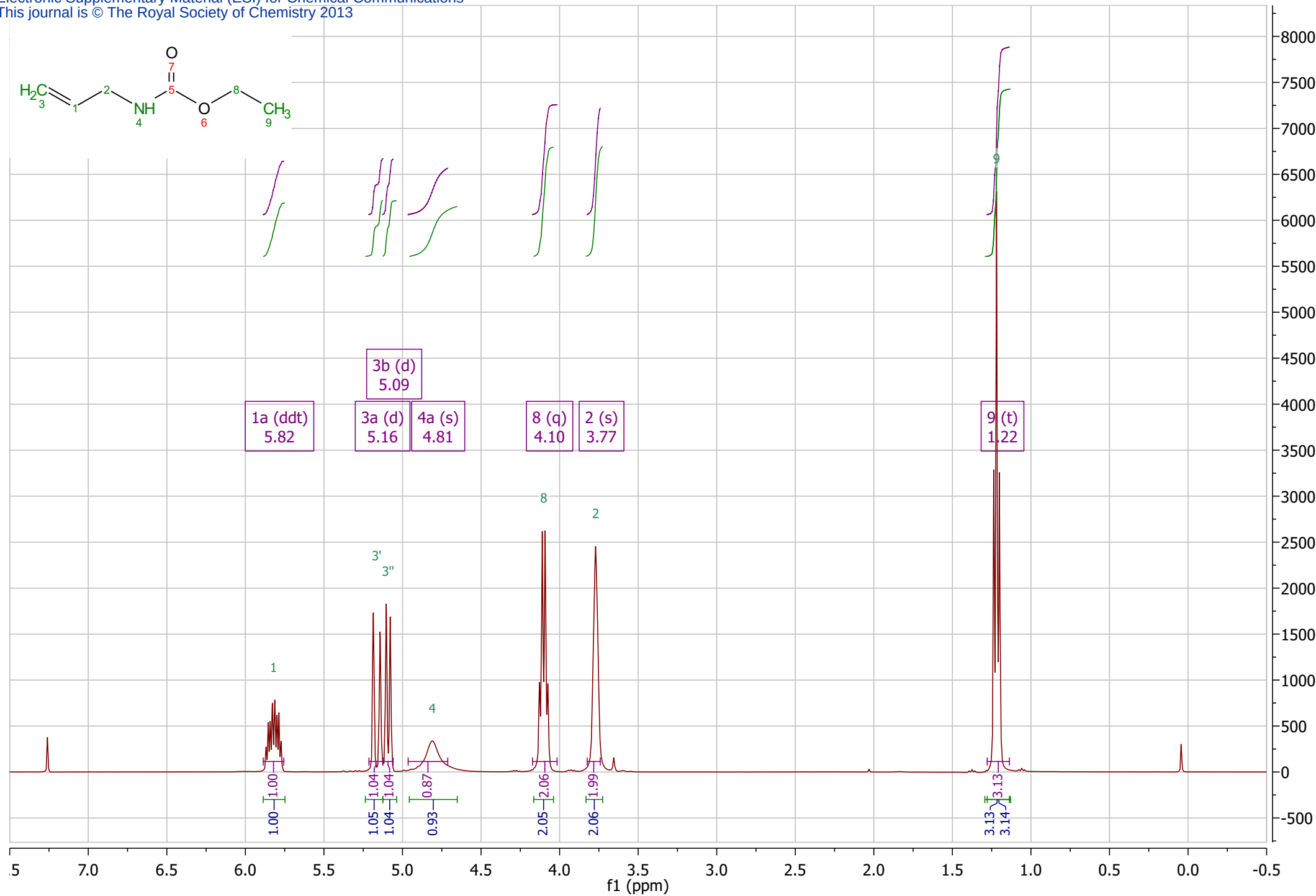


^{13}C NMR (101 MHz, CDCl_3) δ 157.97, 131.69, 118.18, 61.53, 46.55, 43.84.

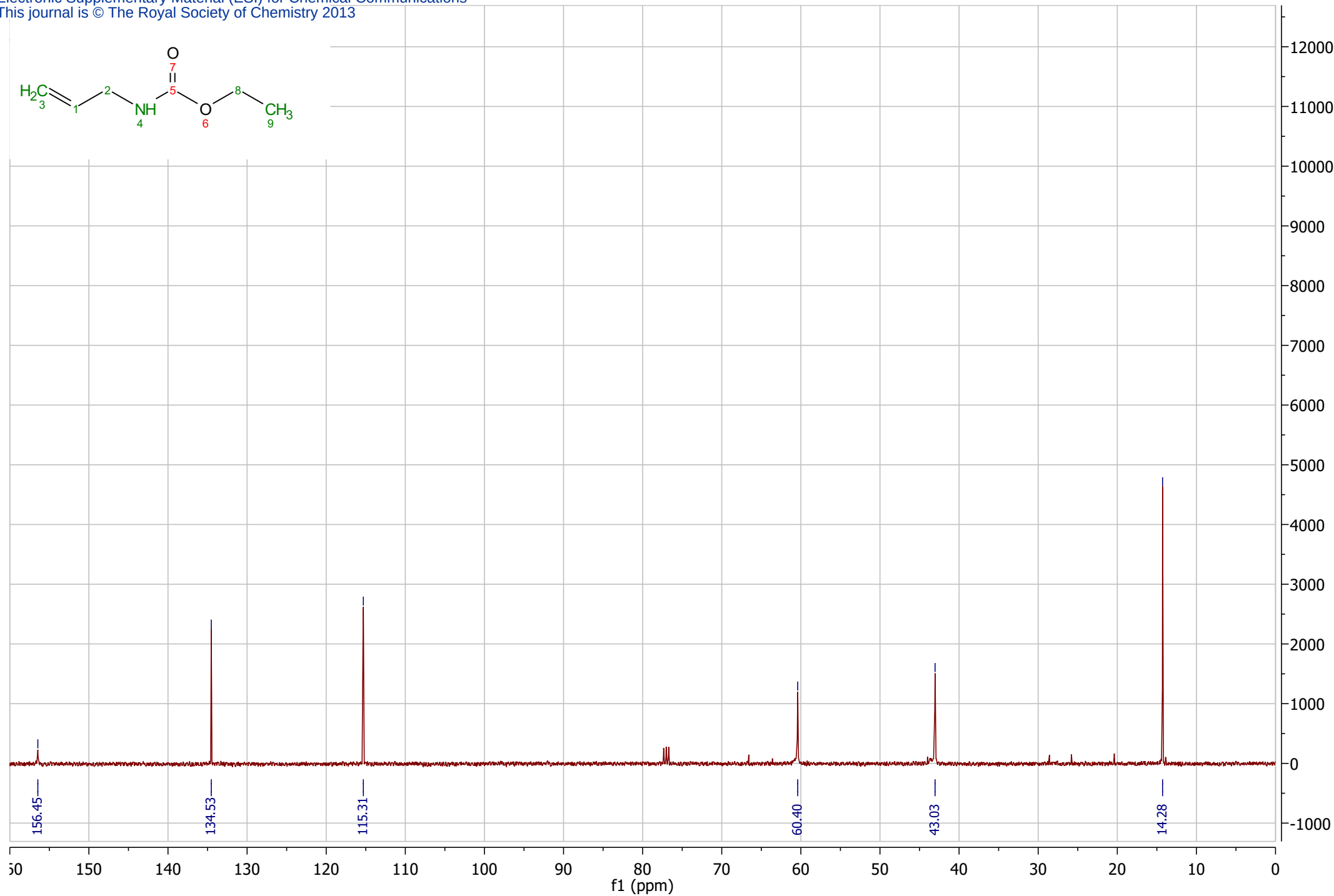


¹H NMR (400 MHz, CDCl₃) δ = 5.81 (ddd, *J*=22.6, 10.6, 5.5, 1H), 5.16 (dd, *J*=17.2, 1.4, 1H), 5.08 (ddd, *J*=10.3, 2.7, 1.4, 1H), 4.90 (s, 1H), 3.77 (s, 2H), 3.64 (s, 3H).

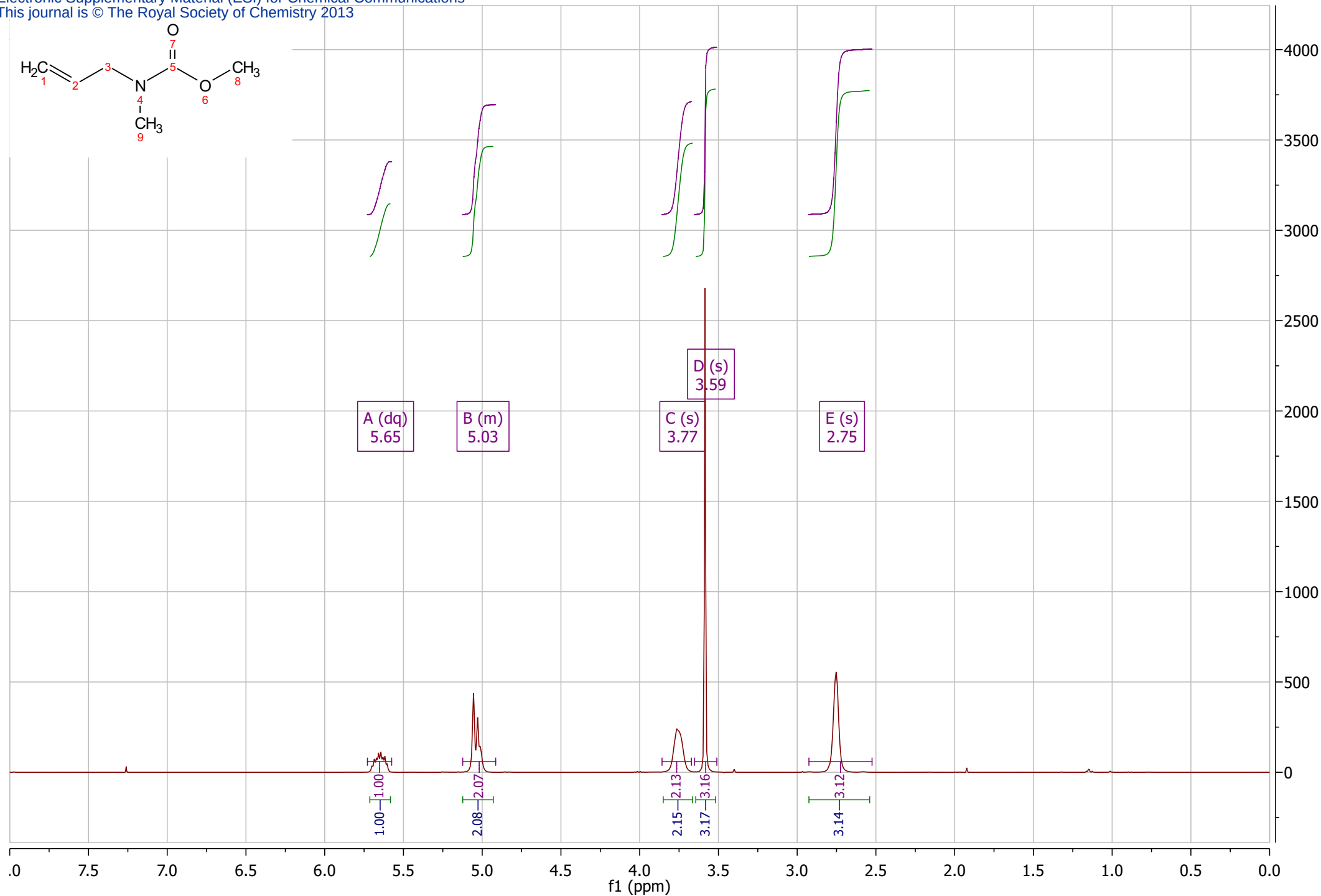




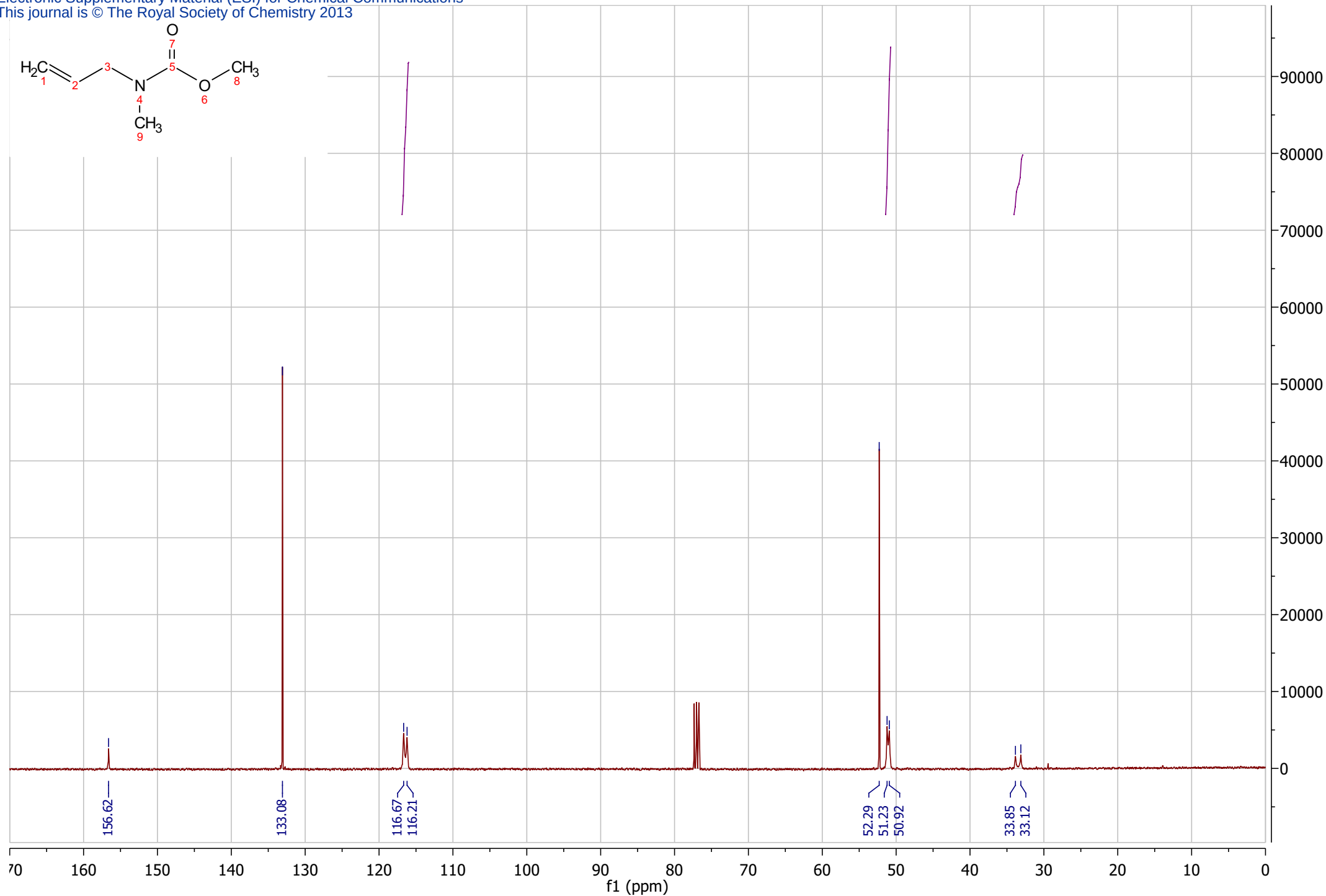
¹H NMR (400 MHz, CDCl₃) δ = 5.82 (ddt, *J*=16.0, 10.5, 5.4, 1H), 5.16 (d, *J*=17.2, 1H), 5.09 (d, *J*=10.3, 1H), 4.81 (s, 1H), 4.10 (q, *J*=7.0, 2H), 3.77 (s, 2H), 1.22 (t, *J*=7.1, 3H).



¹³C NMR (101 MHz, CDCl₃) δ 156.45, 134.53, 115.31, 60.40, 43.03, 14.28.



^1H NMR (400 MHz, CDCl_3) δ 5.65 (dq, J = 10.7, 5.6 Hz, 1H), 5.12 – 4.91 (m, 2H), 3.77 (s, 2H), 3.59 (s, 3H), 2.75 (s, 3H).



^{13}C NMR (101 MHz, CDCl_3) δ 156.62, 133.08, 116.67, 116.21, 52.29, 51.23, 50.92, 33.85, 33.12.



