

4-Dialkylamino-2,5-dihydroimidazol-1-oxyls with Functional Groups at the Position 2 and at the Exocyclic Nitrogen: The pH-Sensitive Spin Labels

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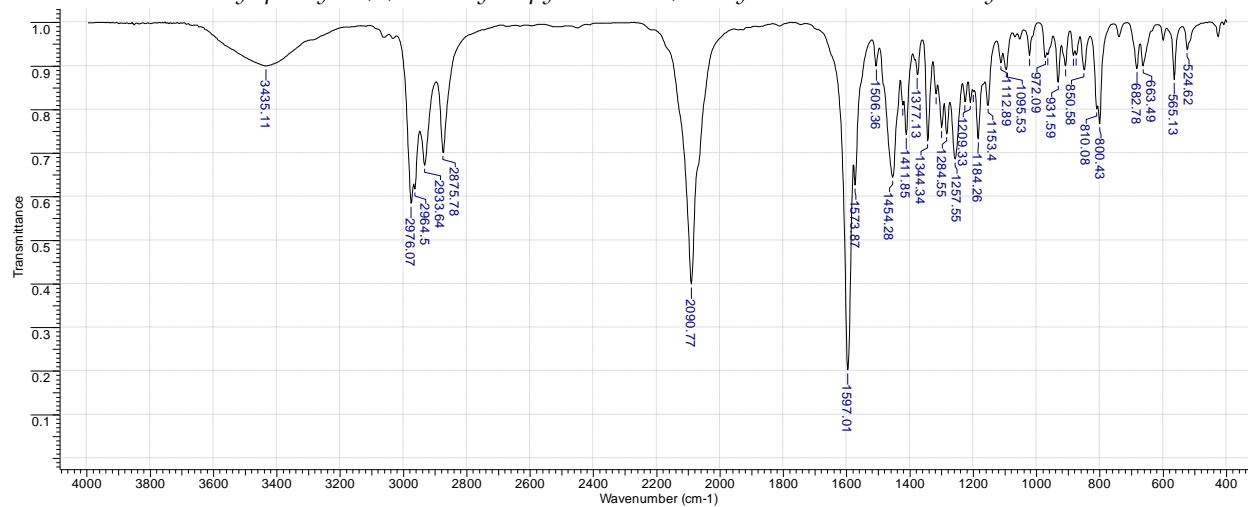
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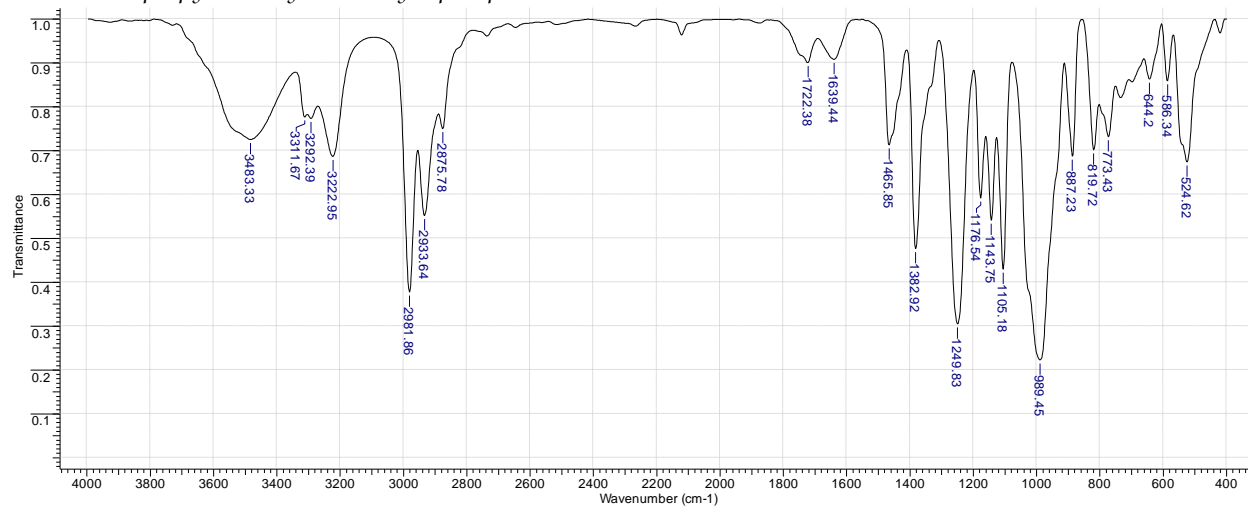
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1. IR Spectra

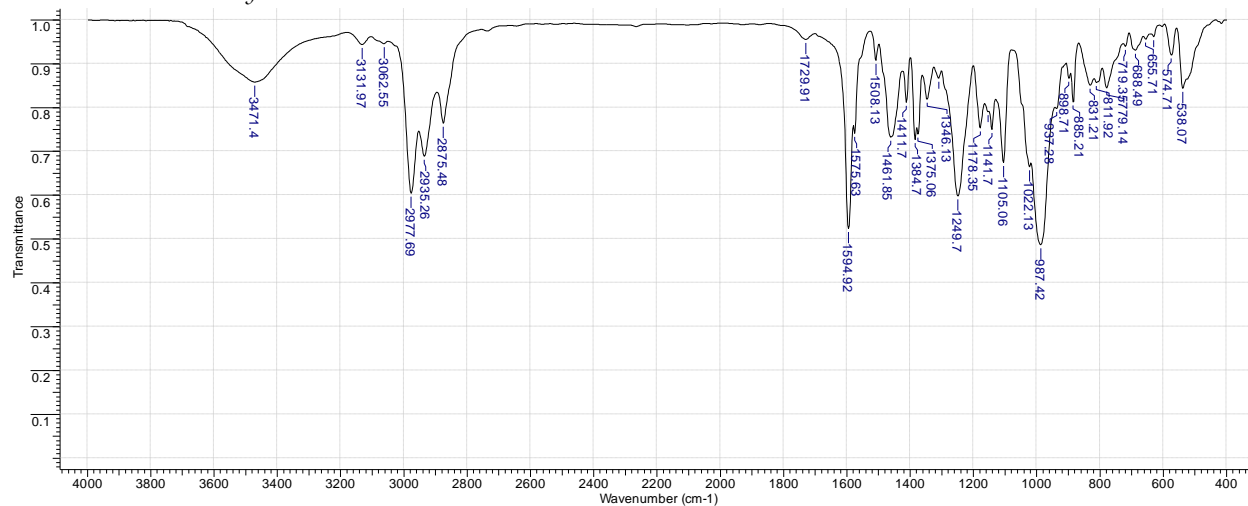
1.1. 2-(4-(Azidomethyl)phenyl)-2,5,5-triethyl-4-pyrrolidino-2,5-dihydro-1H-imidazol-1-oxyl (5) (KBr)



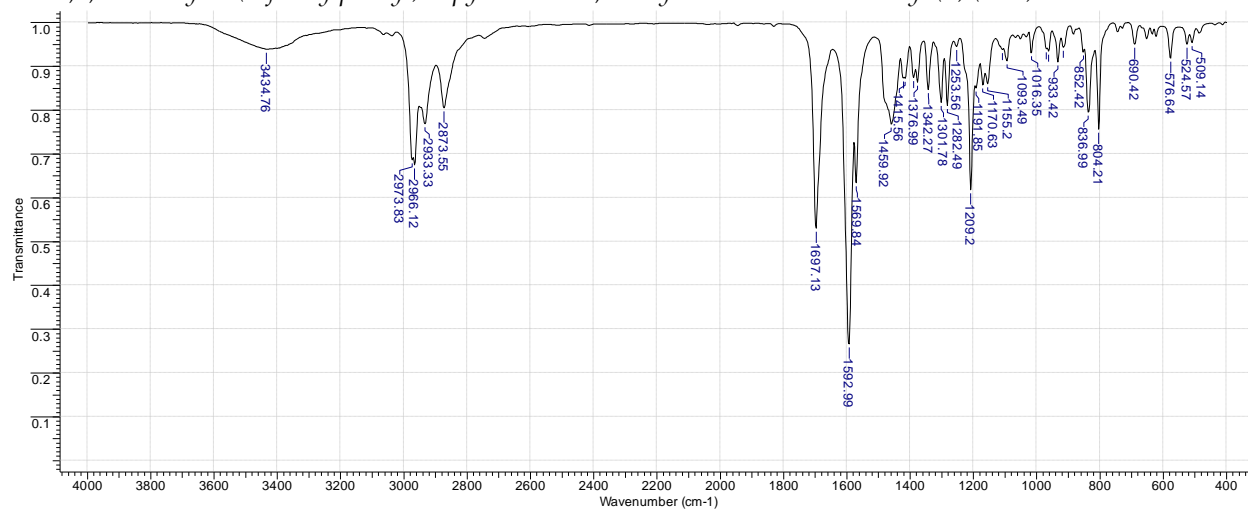
1.2. Tetraisopropyl but-3-yne-1,1-diylidphosphonate (6) (neat)



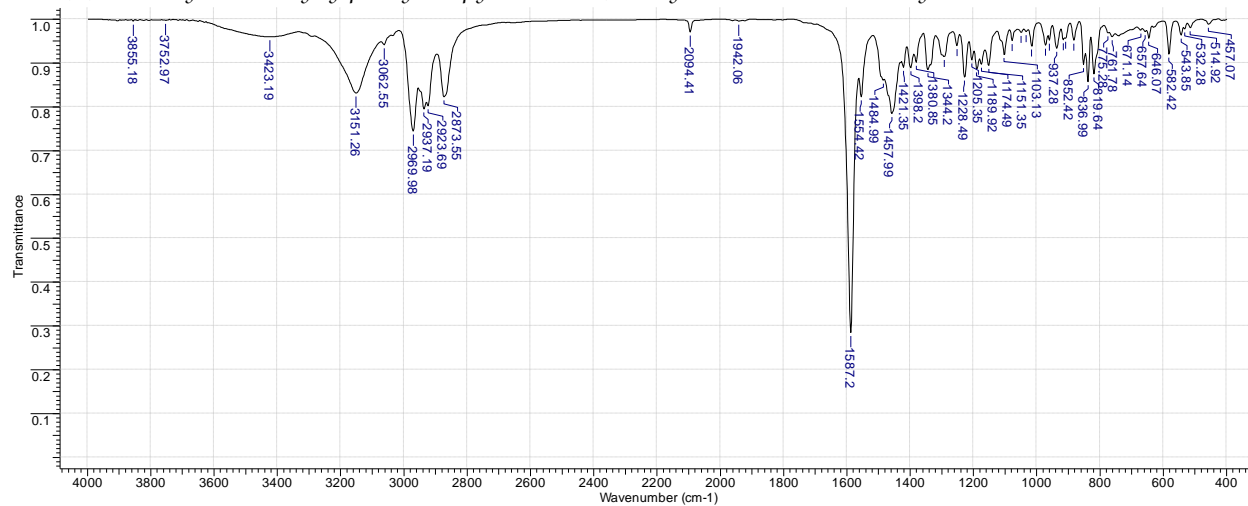
1.3. 2-(4-((4-(2,2-Bis(diisopropoxyphosphoryl)ethyl)-1H-1,2,3-triazol-1-yl)methyl)phenyl)-2,5,5-triethyl-4-pyrrolidino-2,5-dihydro-1H-imidazol-1-oxyl(7) (neat)



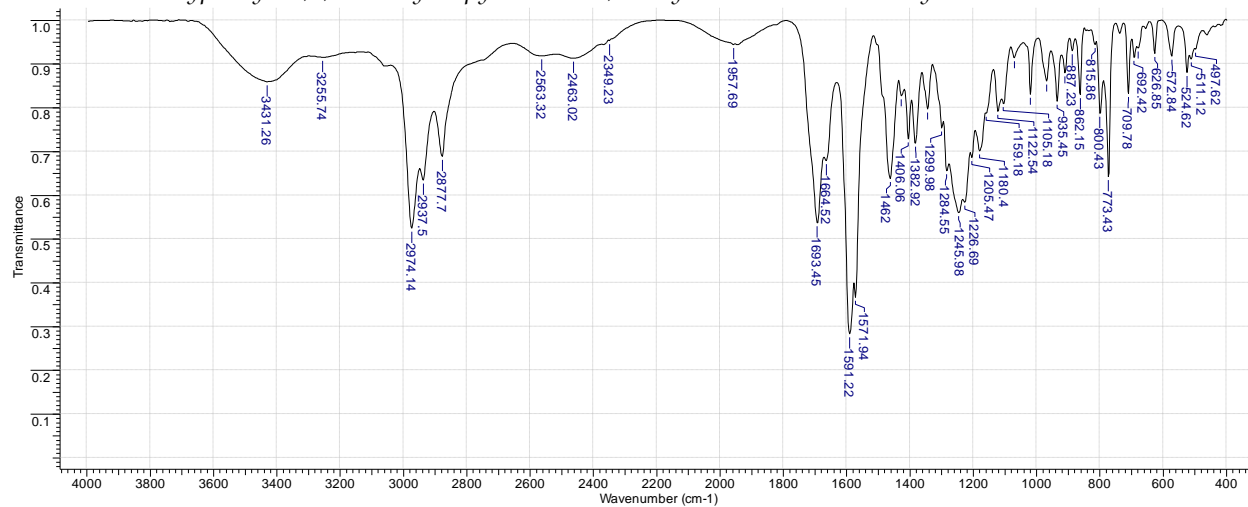
1.4. 2,5,5-Triethyl-2-(4-formylphenyl)-4-pyrrolidino-2,5-dihydro-1H-imidazol-1-oxyl (9) (KBr)



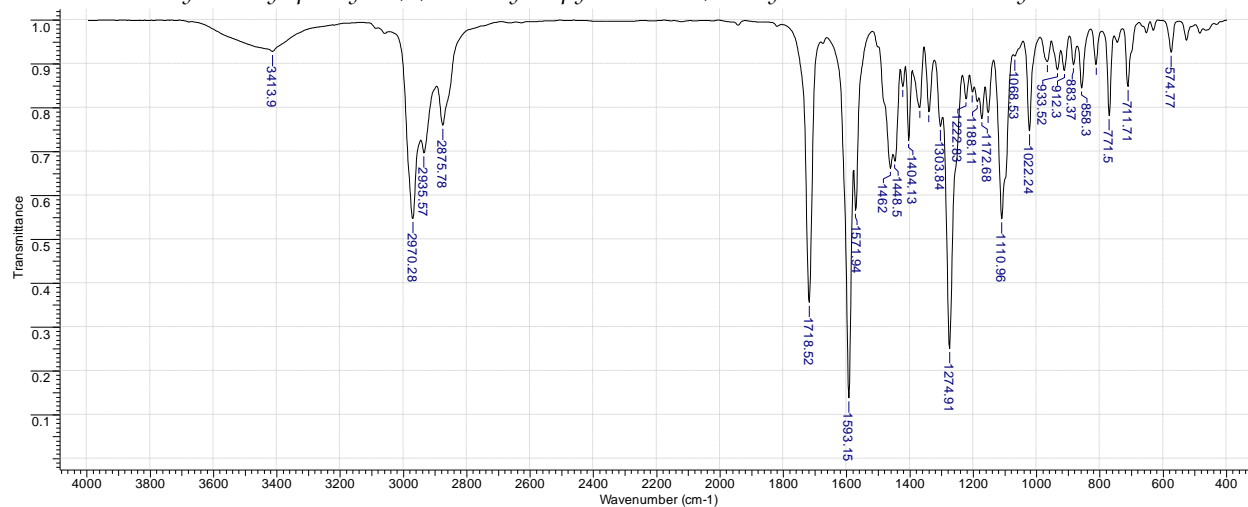
1.5. 2,5,5-Triethyl-2-(4-ethynylphenyl)-4-pyrrolidino-2,5-dihydro-1H-imidazol-1-oxyl (11) (KBr)



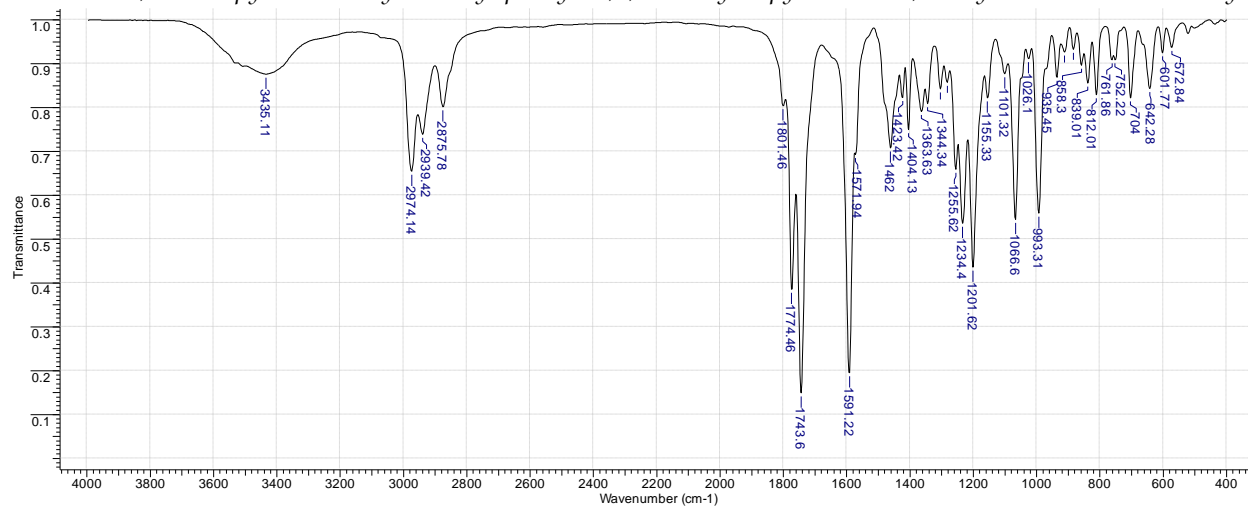
1.6. 2-(4-Carboxyphenyl)-2,5,5-triethyl-4-pyrrolidino-2,5-dihydro-1H-imidazol-1-oxyl (12)(KBr)



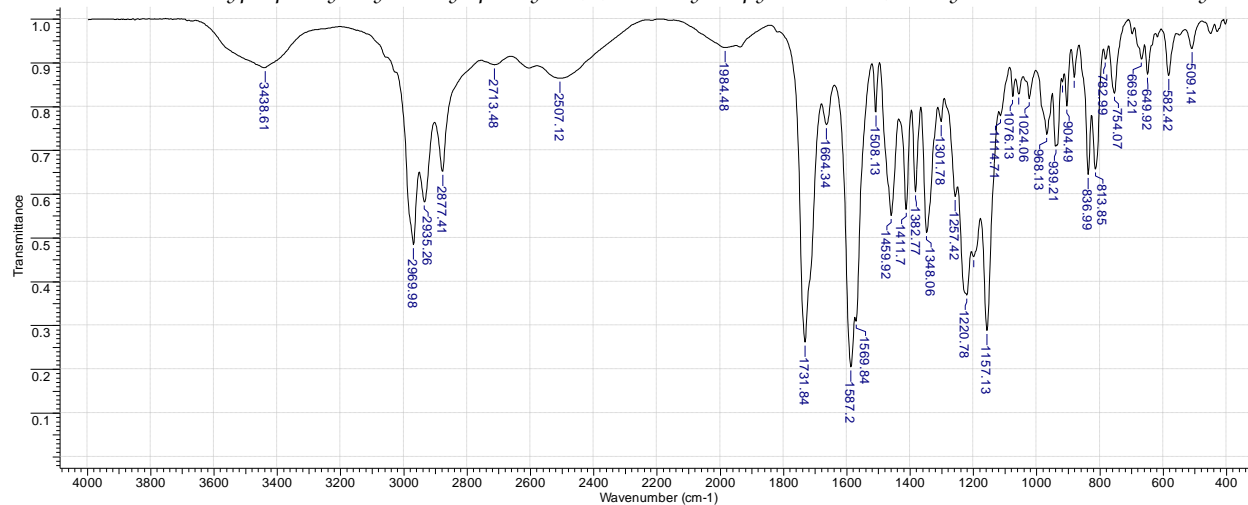
1.7. 2-(4-(Ethoxycarbonyl)phenyl)-2,5,5-triethyl-4-pyrrolidino-2,5-dihydro-1H-imidazol-1-oxyl (**14**) (KBr)



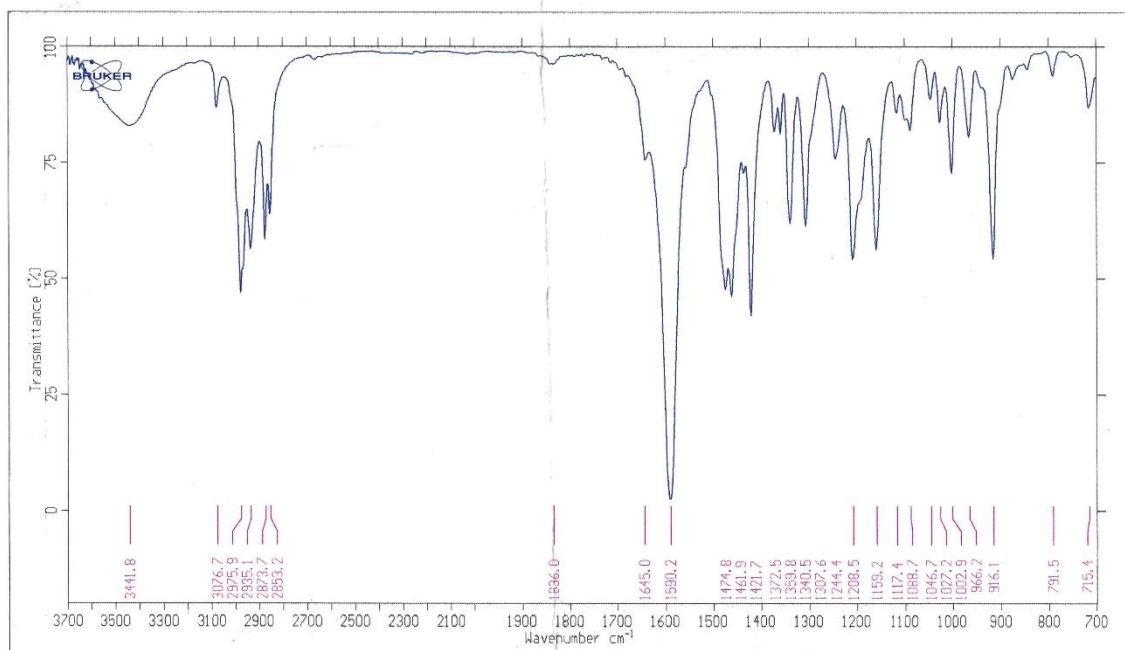
1.8. 2-(4-((2,5-Dioxypyrrolidinooxy)carbonyl)phenyl)-2,5,5-triethyl-4-pyrrolidino-2,5-dihydro-1H-imidazol-1-oxyl (**15**) (KBr)



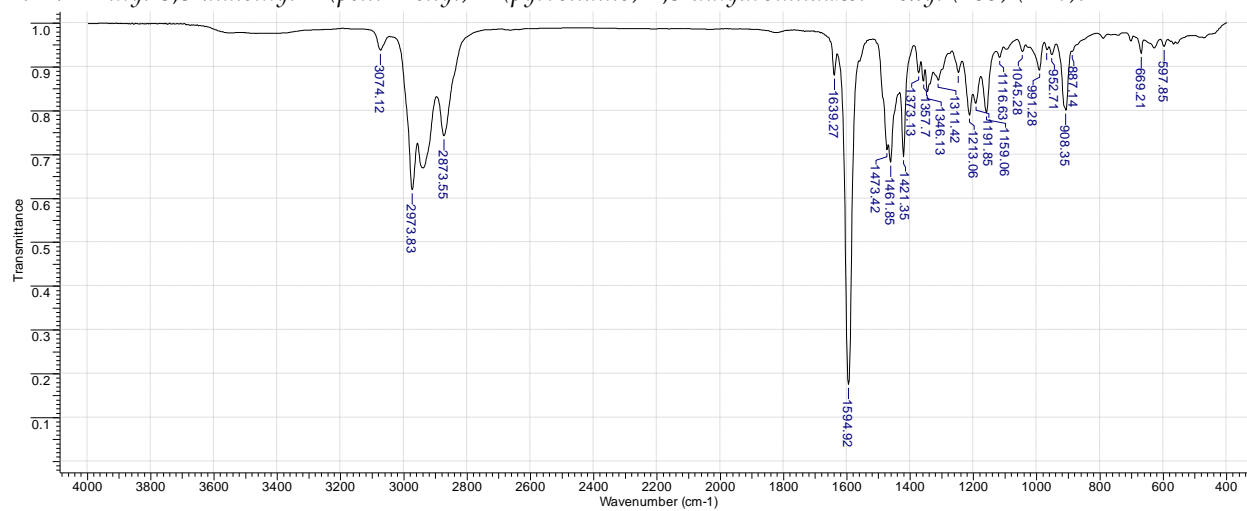
1.9. 2-(4-((3-Carboxypropanoyloxy)methyl)phenyl)-2,5,5-triethyl-4-pyrrolidino-2,5-dihydro-1H-imidazol-1-oxyl (**16**) (KBr)



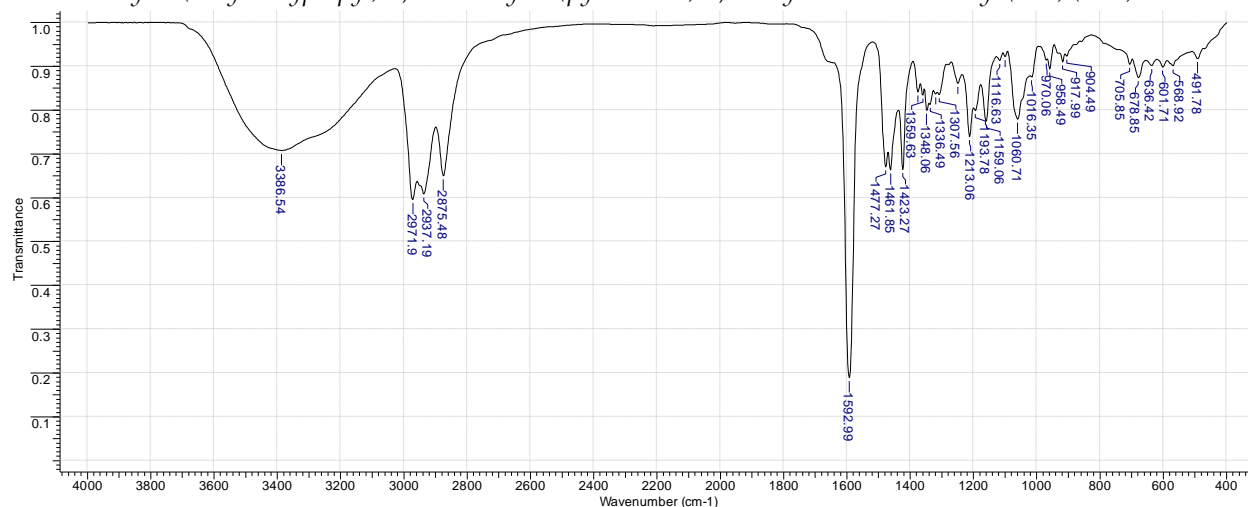
1.10. 2-Allyl-2-ethyl-5,5-dimethyl-4-(pyrrolidino)-2,5-dihydroimidazol-1-oxyl (**18a**) (KBr)



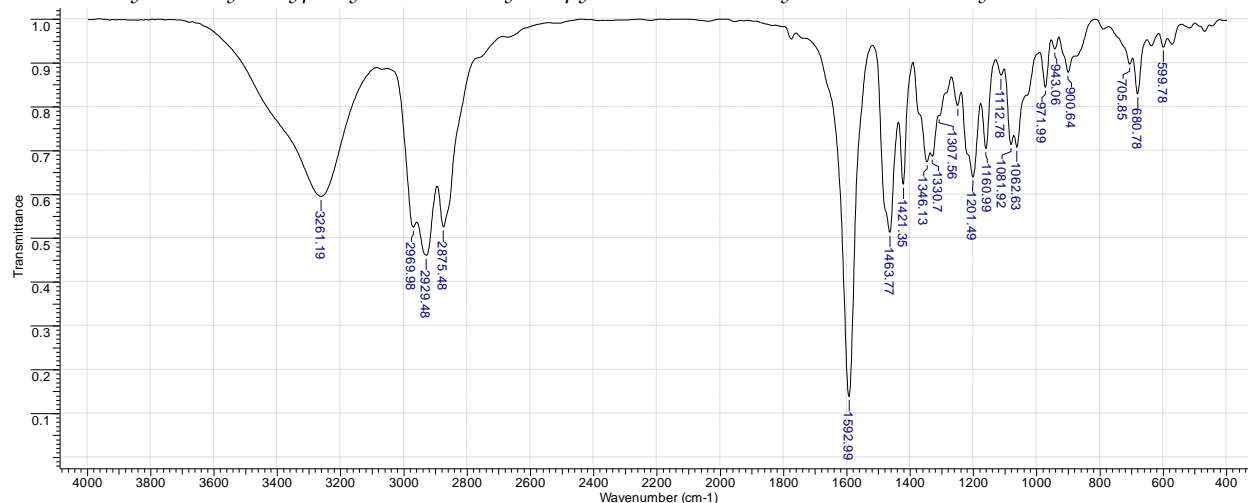
1.11. 2-Ethyl-5,5-dimethyl-2-(pent-4-enyl)-4-(pyrrolidino)-2,5-dihydroimidazol-1-oxyl (**18b**) (KBr).



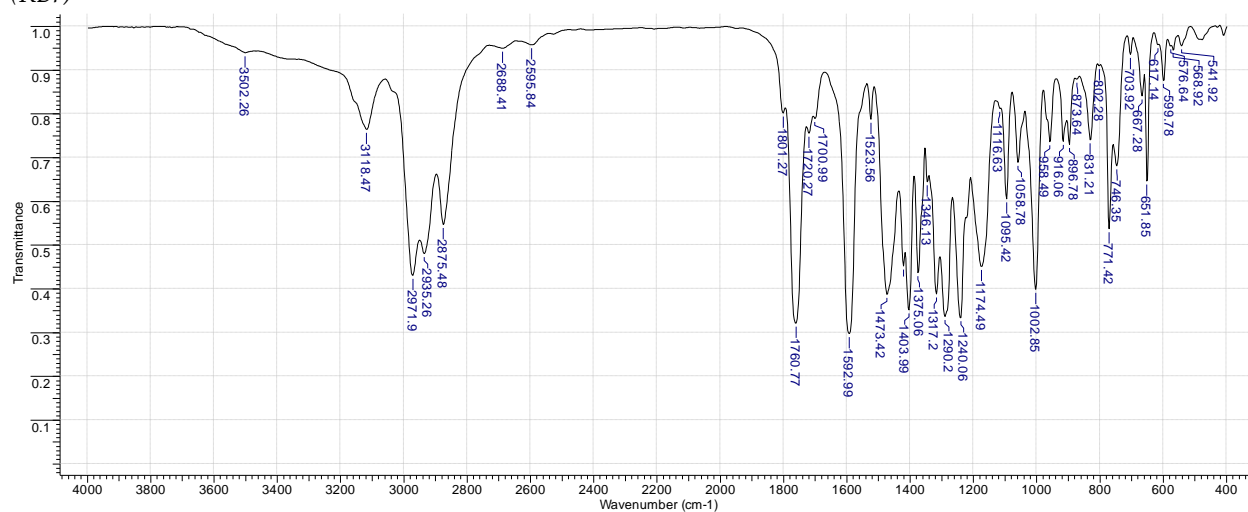
1.12. 2-Ethyl-2-(3-hydroxypropyl)-5,5-dimethyl-4-(pyrrolidino)-2,5-dihydroimidazol-1-oxyl (19a) (KBr)



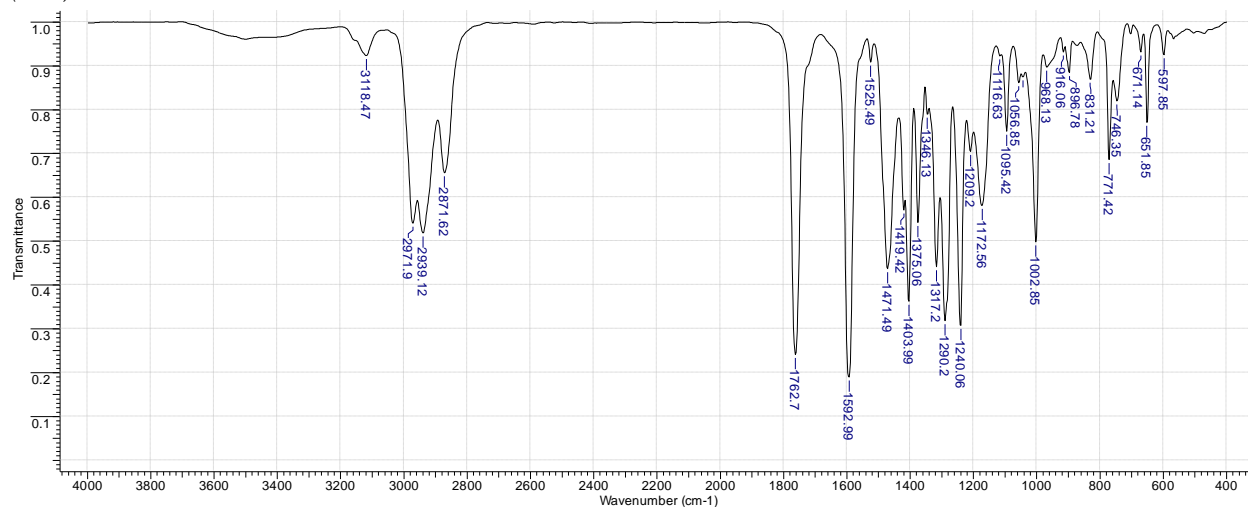
1.13. 2-Ethyl-2-(5-hydroxypentyl)-5,5-dimethyl-4-(pyrrolidino)-2,5-dihydroimidazol-1-oxyl (19b) (KBr)



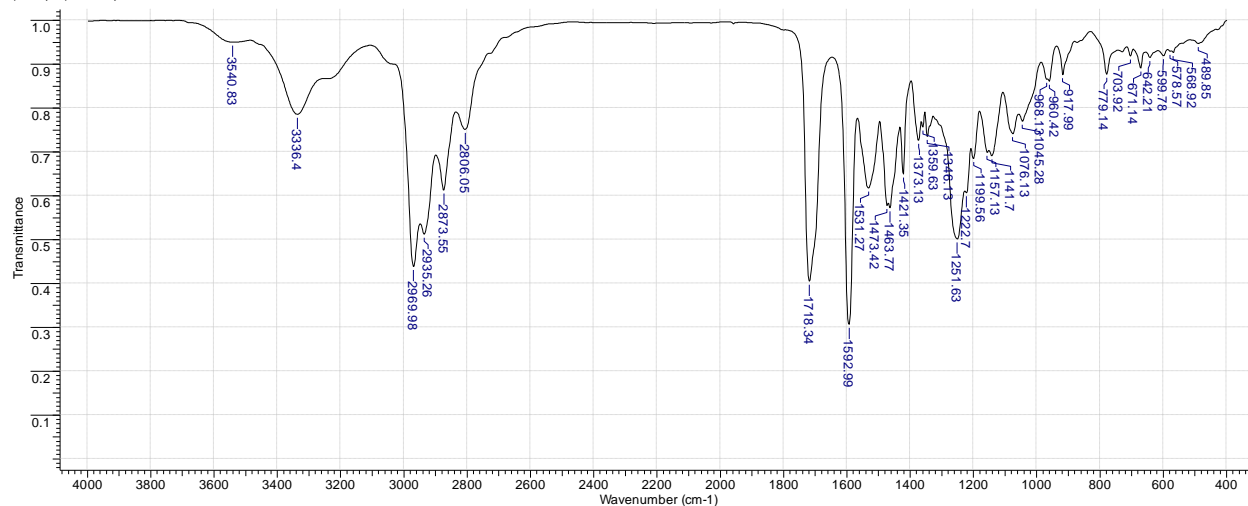
1.14. 2-(3-(1H-Imidazole-1-carboxyloxy)propyl)-2-ethyl-5,5-dimethyl-4-(pyrrolidino)-2,5-dihydro-1H-imidazol-1-oxyl (20a) (KBr)



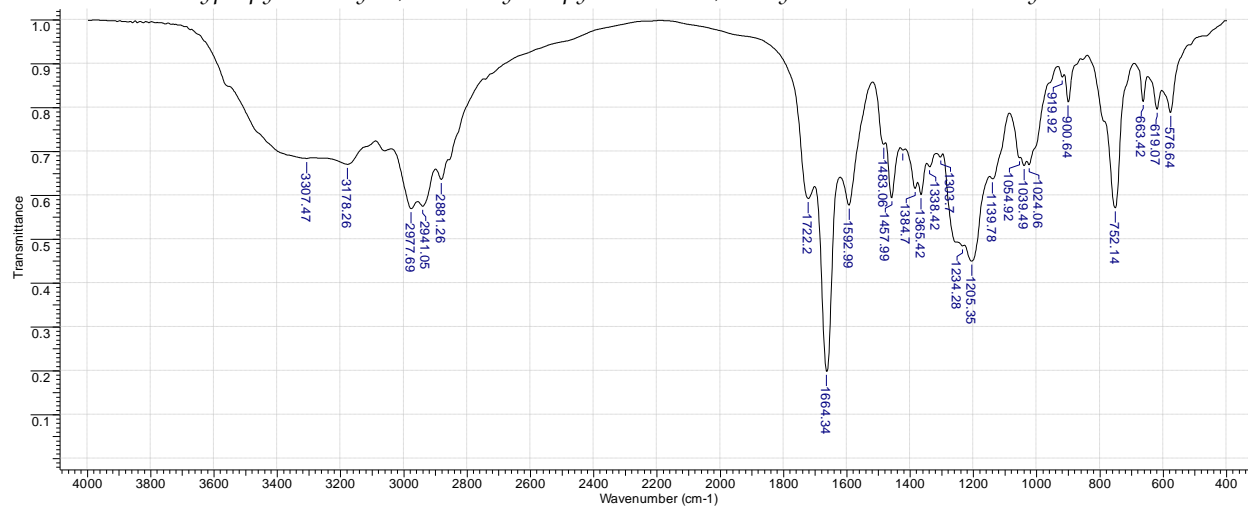
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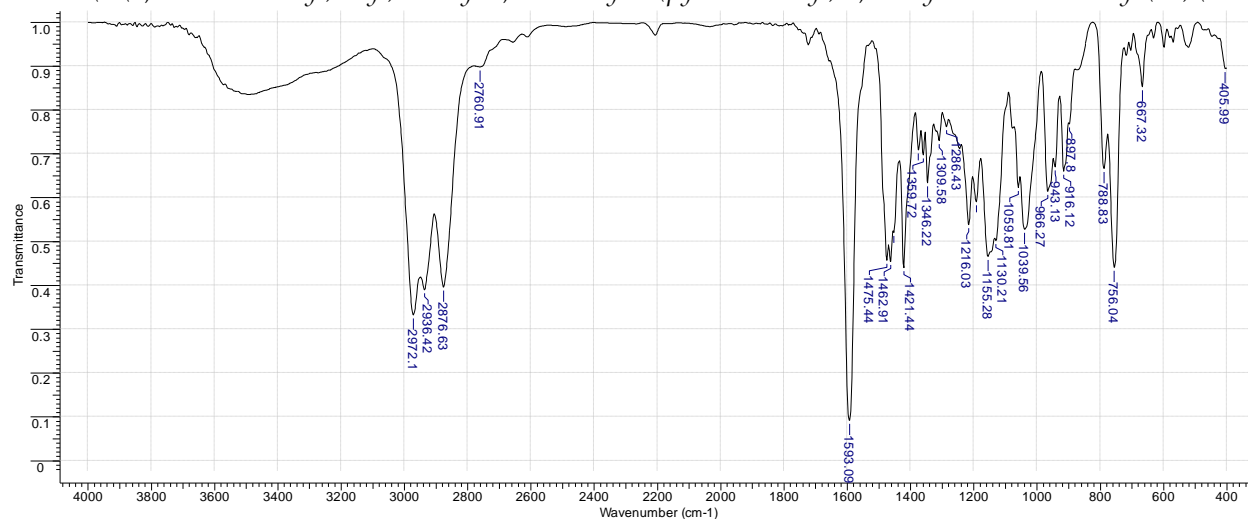
1.16. 2-(3-(3-(Diethylamino)propylcarbamoyloxy)propyl)-2-ethyl-5,5-dimethyl-4-(pyrrolidino)-2,5-dihydro-1H-imidazol-1-oxyl (21) (KBr)



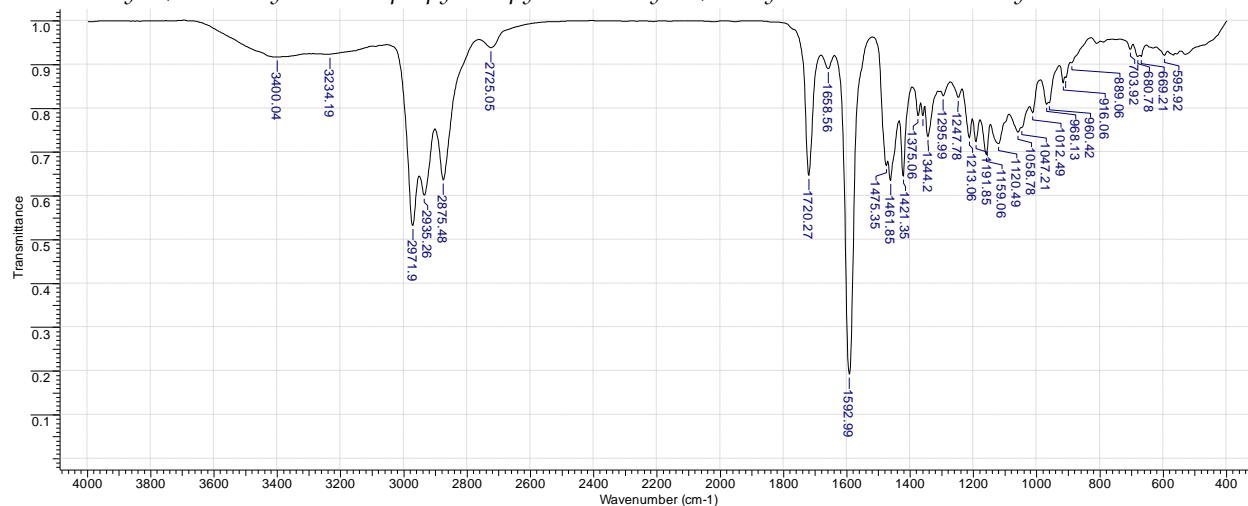
1.17. 2-(3-Carboxypropyl)-2-ethyl-5,5-dimethyl-4-(pyrrolidino)-2,5-dihydro-1H-imidazol-1-oxyl (22) (neat)



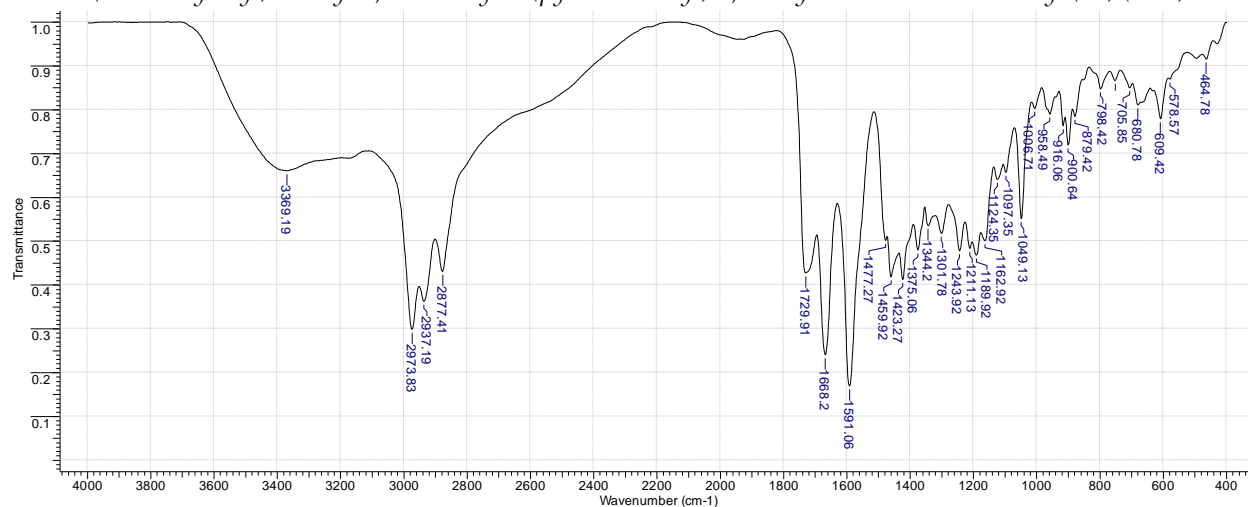
1.18. 2-(2-(1,3-Dioxolan-2-yl)ethyl)-2-ethyl-5,5-dimethyl-4-(pyrrolidin-1-yl)-2,5-dihydroimidazol-1-oxyl (23) (neat)



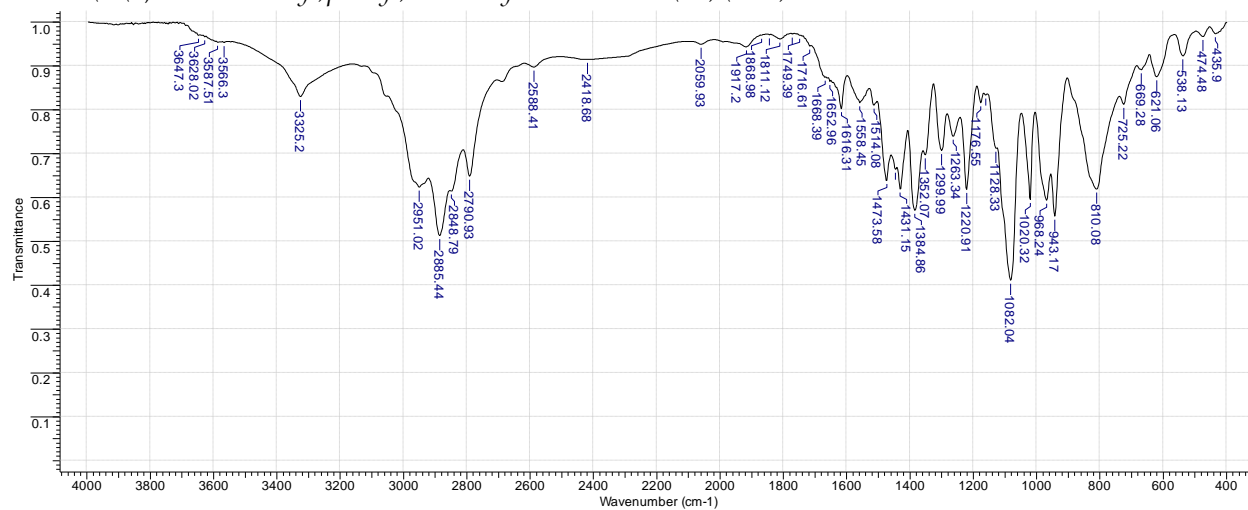
1.19. 2-ethyl-5,5-dimethyl-2-(3-oxopropyl)-4-(pyrrolidin-1-yl)-2,5-dihydro-1H-imidazol-1-oxyl (24) (neat)



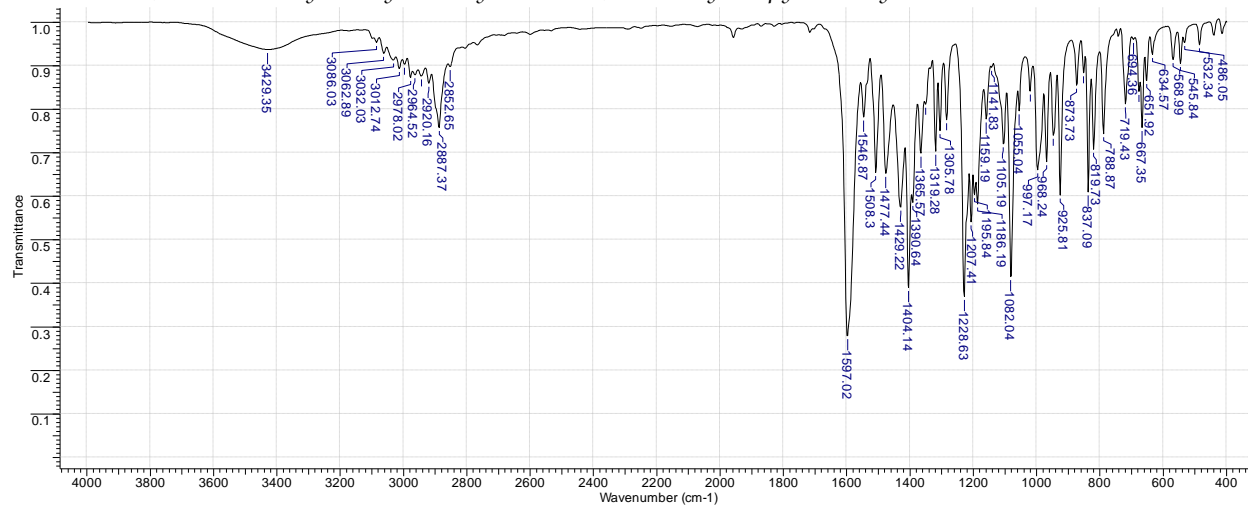
1.20. 2-(2-carboxyethyl)-2-ethyl-5,5-dimethyl-4-(pyrrolidin-1-yl)-2,5-dihydro-1H-imidazol-1-oxyl (25) (neat)



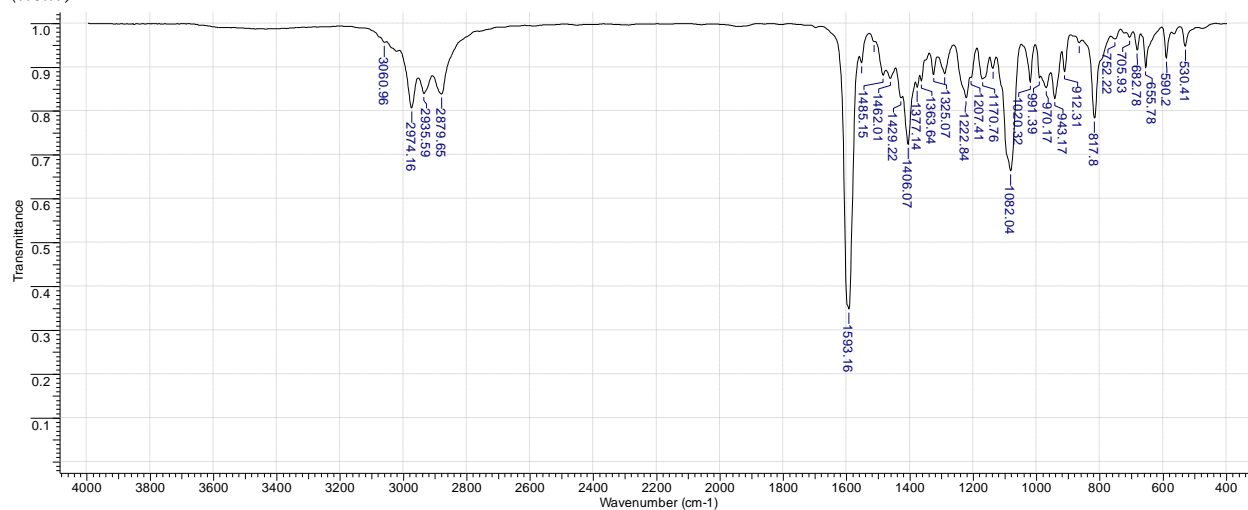
1.21. 1-(4-(1,3-dioxolan-2-yl)phenyl)-N-methylmethanamine (26) (neat)



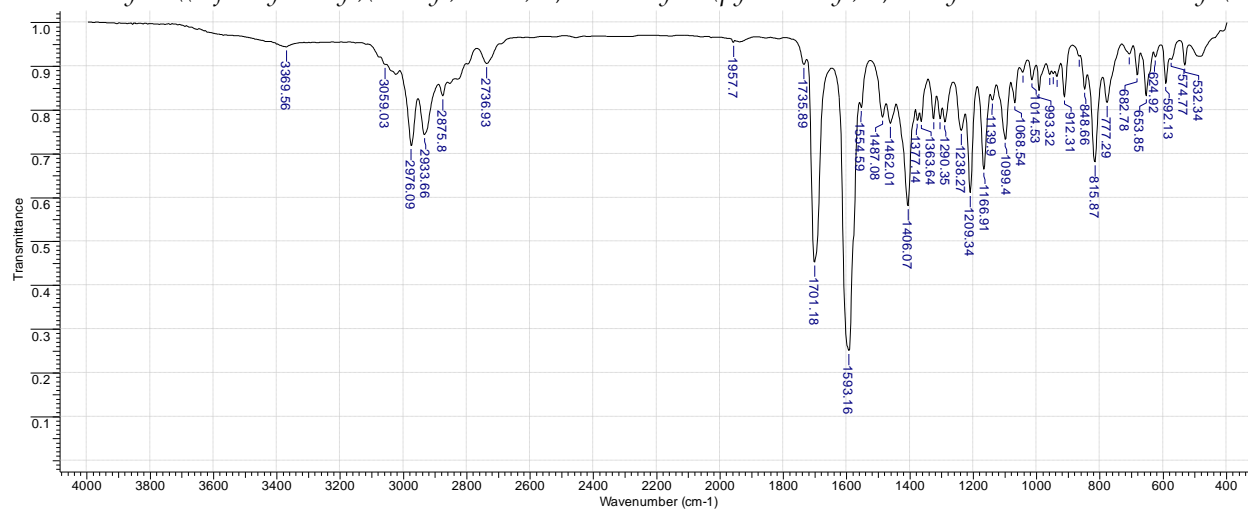
1.22. 5-((4-(1,3-dioxolan-2-yl)benzyl)(methyl)amino)-4,4-dimethyl-2-(pyridin-4-yl)-4H-imidazole 3-oxide (30) (KBr)



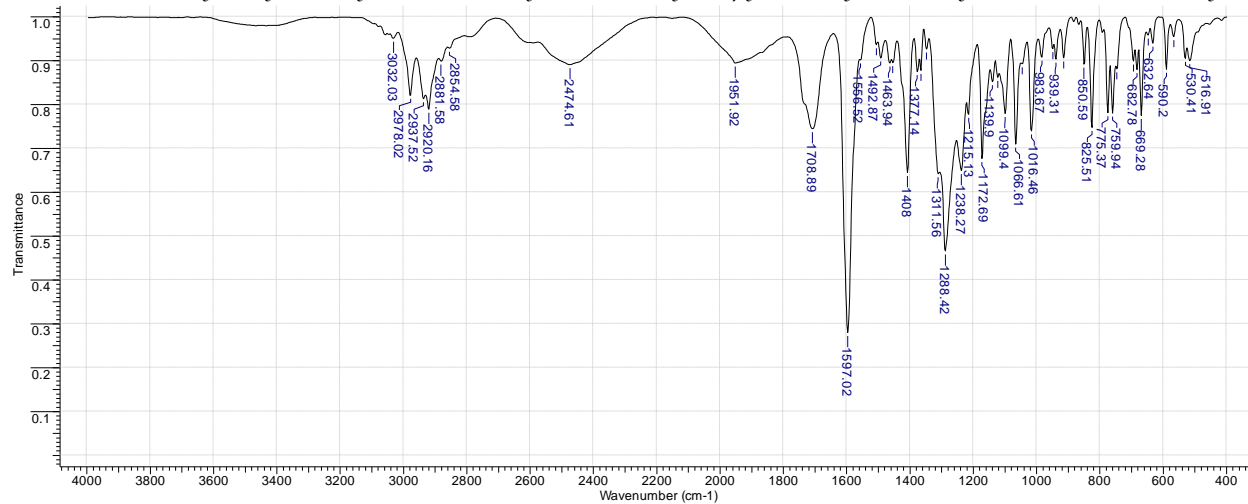
1.23. 4-((4-(1,3-dioxolan-2-yl)benzyl)(methyl)amino)-2-ethyl-5,5-dimethyl-2-(pyridin-4-yl)-2,5-dihydro-1H-imidazol-1-oxyl (31) (neat)



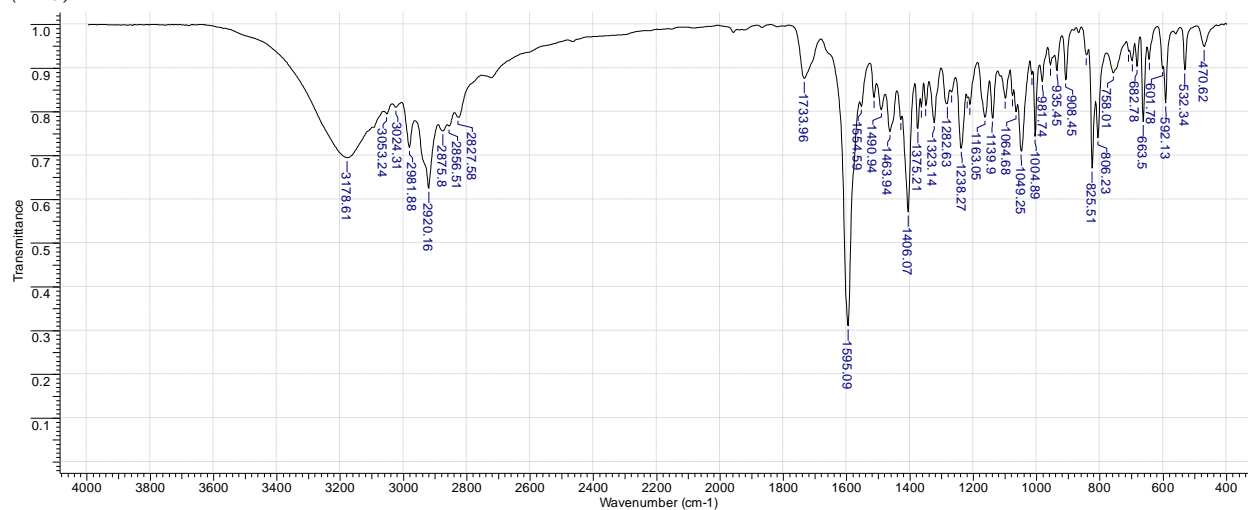
1.24. 2-ethyl-4-((4-formylbenzyl)(methyl)amino)-5,5-dimethyl-2-(pyridin-4-yl)-2,5-dihydro-1H-imidazol-1-oxyl (32) (KBr)



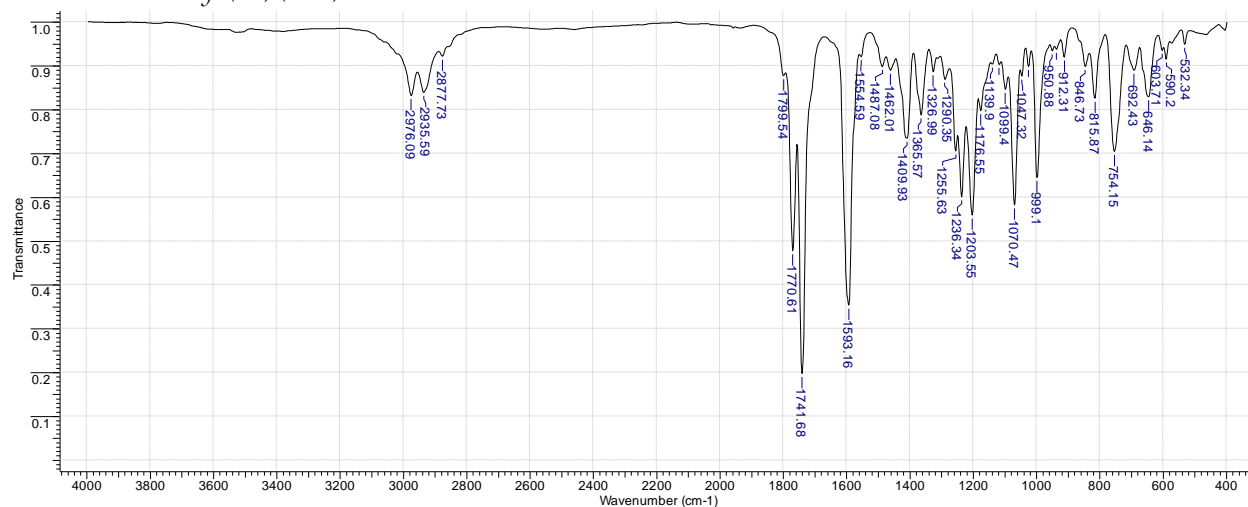
1.25. 4-((4-carboxybenzyl)(methyl)amino)-2-ethyl-5,5-dimethyl-2-(pyridin-4-yl)-2,5-dihydro-1H-imidazol-1-oxyl (33) (KBr)



1.26. 2-ethyl-4-((4-(hydroxymethyl)benzyl)(methyl)amino)-5,5-dimethyl-2-(pyridin-4-yl)-2,5-dihydro-1H-imidazol-1-oxyl (34) (KBr)

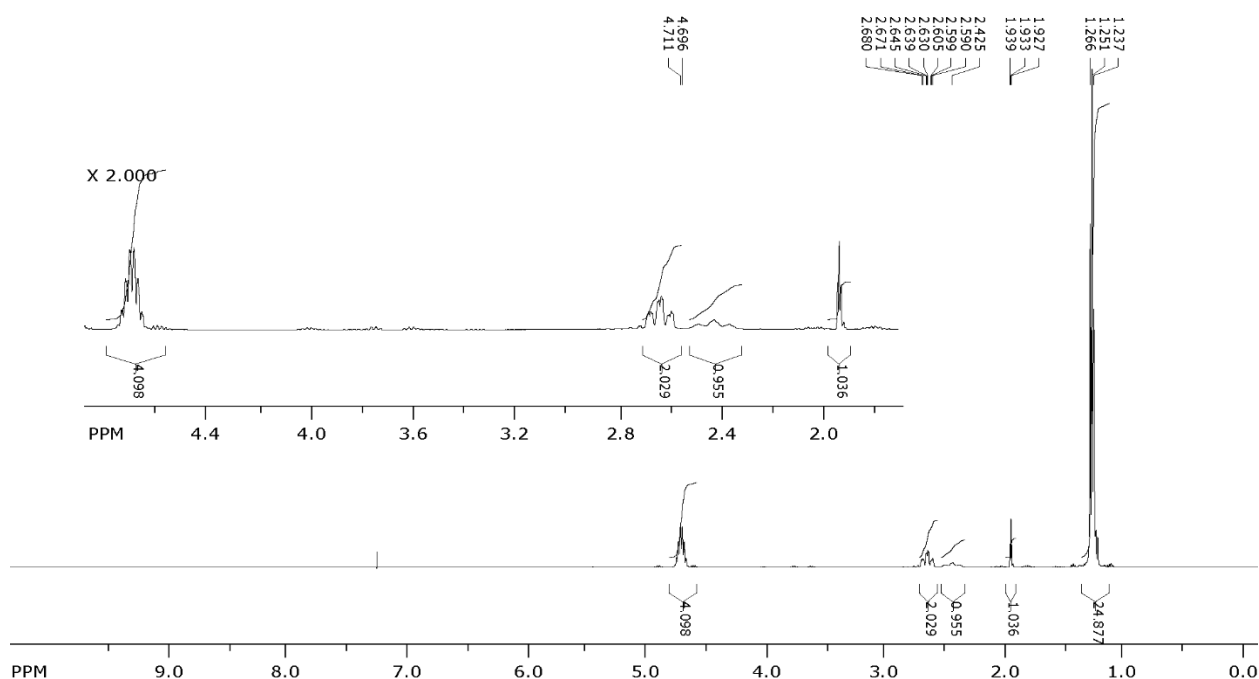


1.27. 4-((4-(((2,5-dioxopyrrolidin-1-yl)oxy)carbonyl)benzyl)(methyl)amino)-2-ethyl-5,5-dimethyl-2-(pyridin-4-yl)-2,5-dihydro-1H-imidazol-1-oxyl (35) (KBr)



2. ¹H NMR Spectra.

2.1. Tetraisopropyl but-3-yne-1,1-diylidphosphonate(6)(400 MHz, CDCl₃)

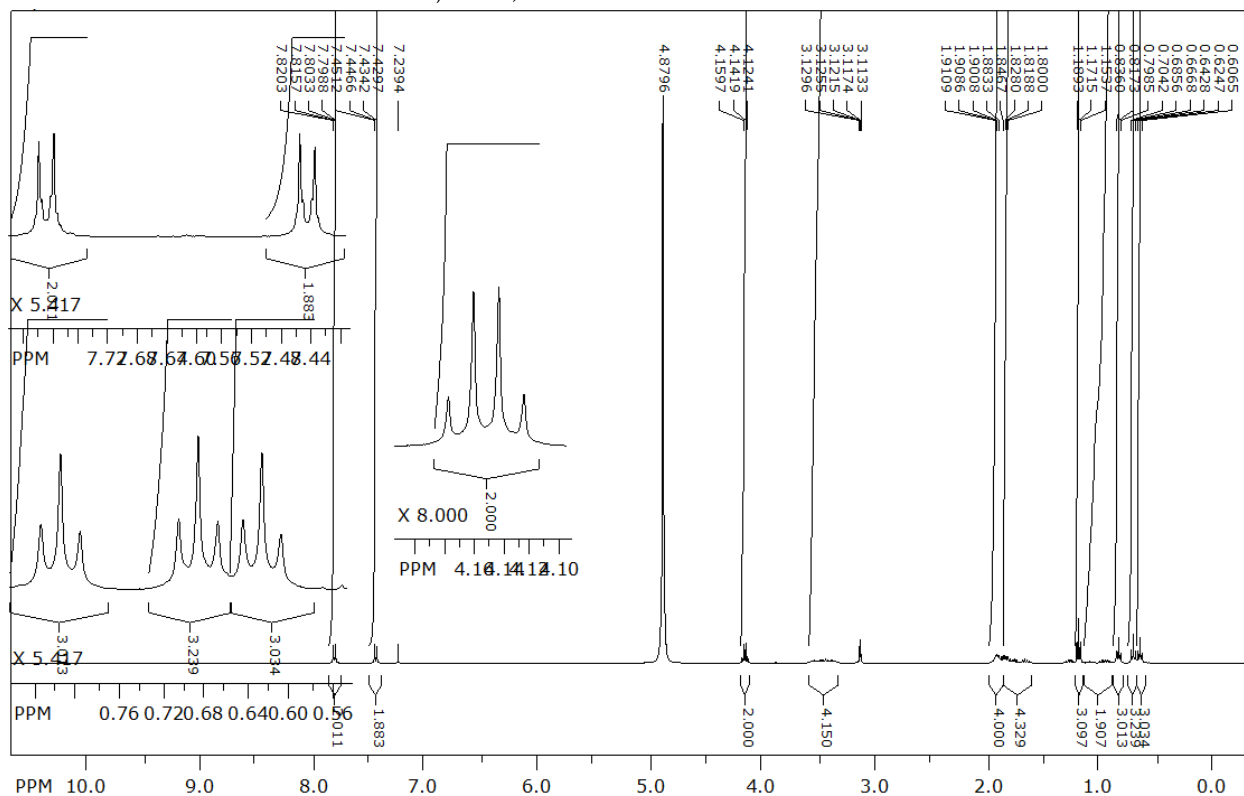


¹H NMR spectrum (400 MHz, CDCl₃) of 1,3-bis(4-methylphenyl)propan-2-one. The spectrum shows peaks from 0 to 10 ppm. Key features include a singlet at ~7.6 ppm (aromatic), a singlet at ~4.6 ppm (CH), a singlet at ~3.9 ppm (CH₃), a multiplet at ~3.3 ppm (CH₂), a multiplet at ~2.1 ppm (CH₂), a multiplet at ~1.4 ppm (CH₃), and a multiplet at ~0.7 ppm (CH₃). Integration values are shown below the peaks.

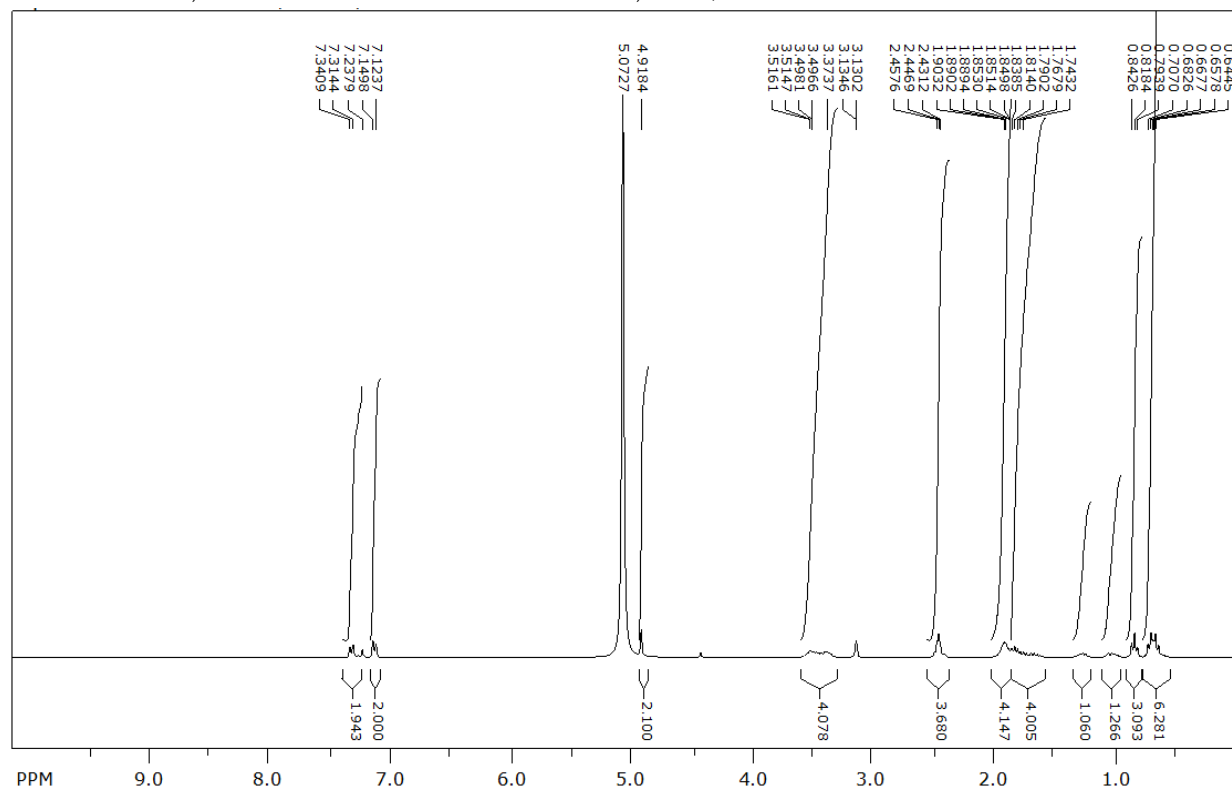
Chemical Shift (ppm)	Integration
~7.607	~0.925
~4.691	~5.081
~3.922	~4.652
~3.259	~2.413
~2.858	~0.452
~2.123	~2.737
~1.847	~1.270
~1.468	~2.433
~1.382	~2.736
~1.239	~3.728
~1.039	~3.526
~0.904	~3.225

[illegible]

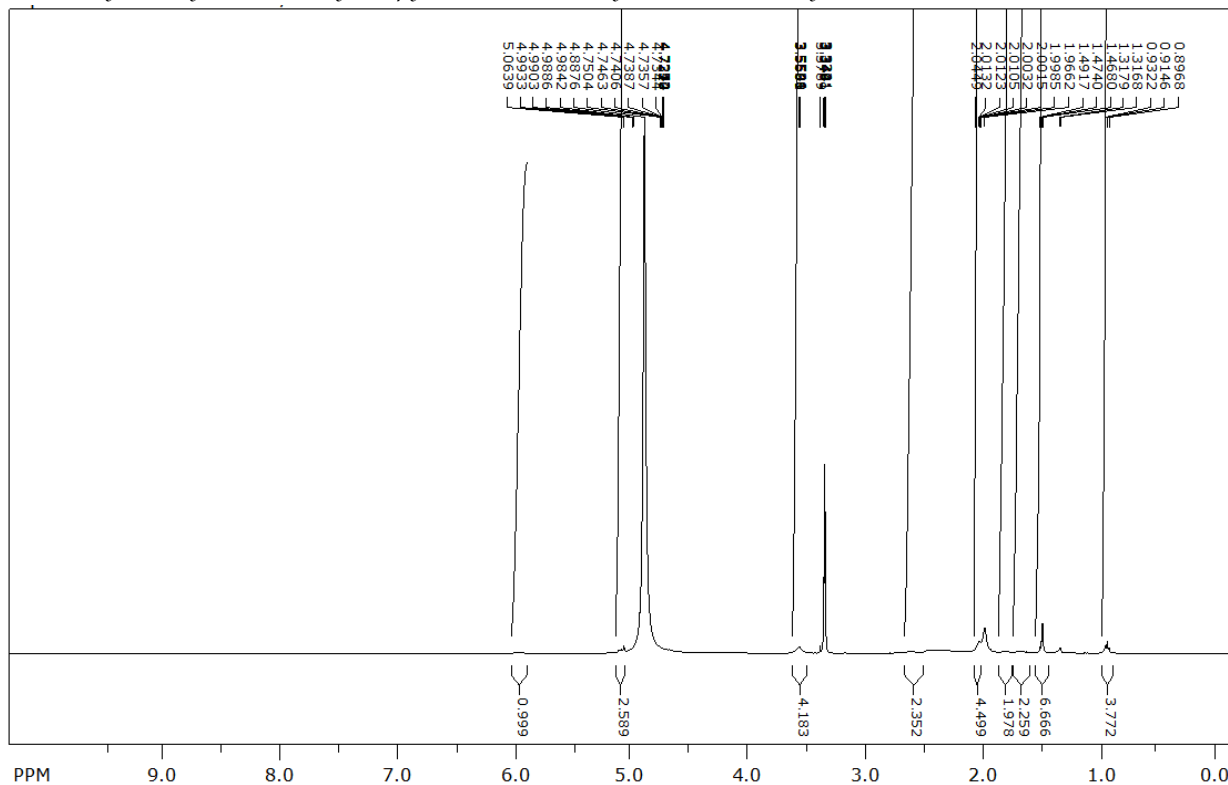
2.4. 2-(4-(Ethoxycarbonyl)phenyl)-2,5,5-triethyl-4-pyrrolidino-2,5-dihydro-1H-imidazol-1-oxyl (**14**) (300 MHz; CDCl₃-CD₃OD, reduced with Zn/CF₃COOH in CD₃OD, 65 °C)



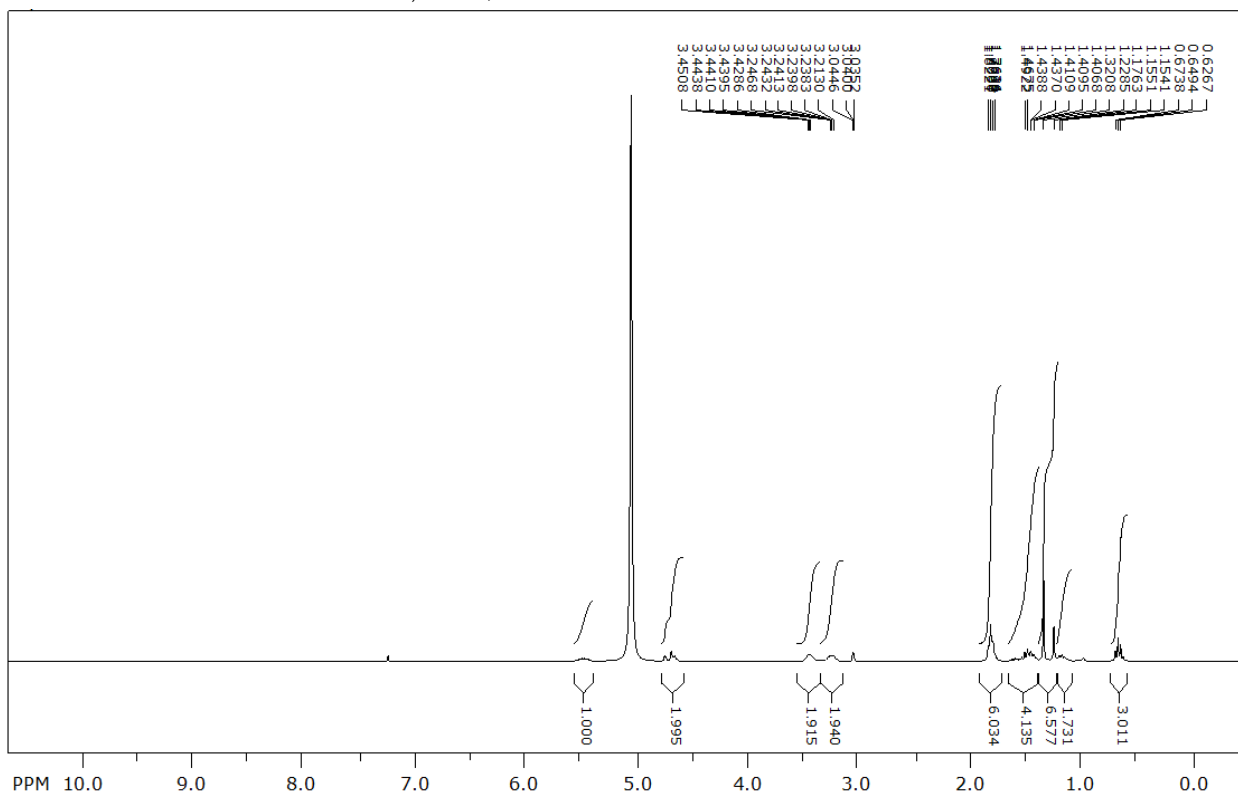
2.5. 2-(4-((3-Carboxypropanoyloxy)methyl)phenyl)-2,5,5-triethyl-4-pyrrolidino-2,5-dihydro-1H-imidazol-1-oxyl (**16**) (300 MHz; CDCl₃ - CD₃OD, reduced with Zn/CF₃COOH in CD₃OD, 65 °C)



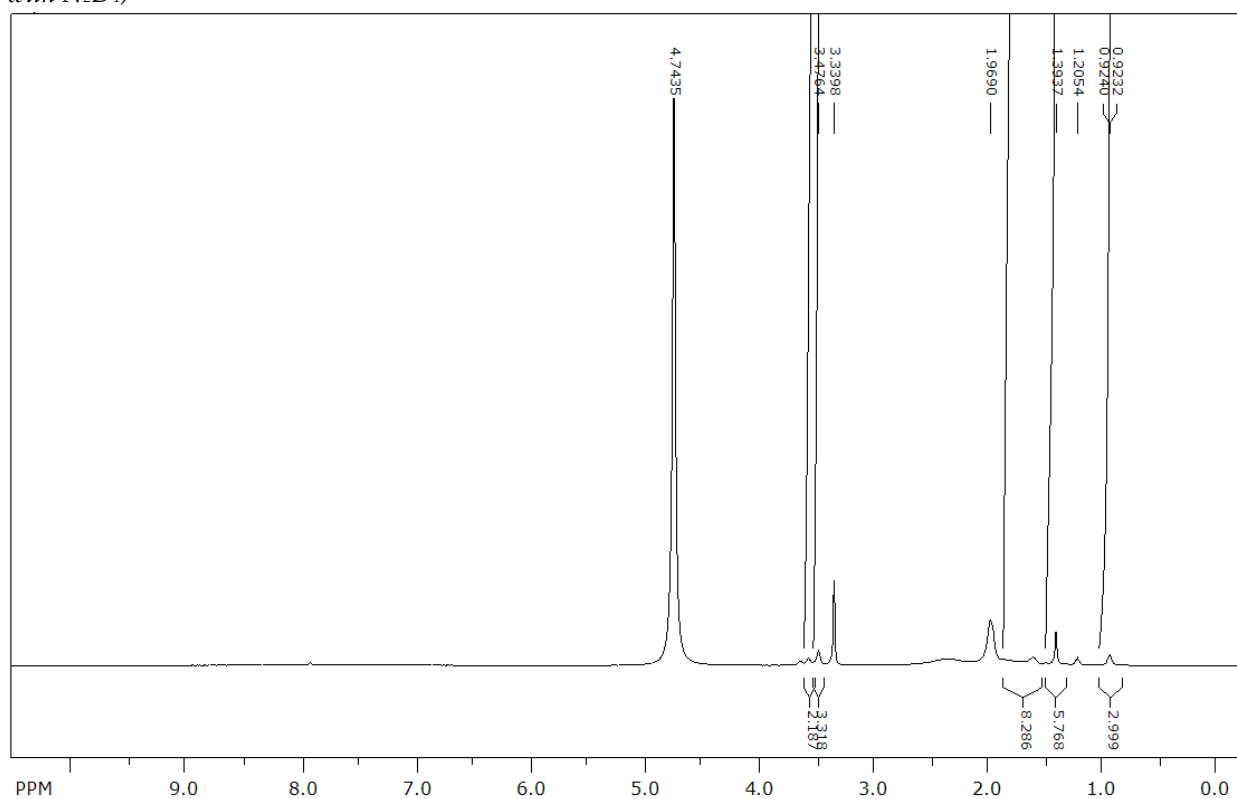
2.6. 2-Allyl-2-ethyl-5,5-dimethyl-4-(pyrrolidino)-2,5-dihydroimidazol-1-oxyl (**18a**) (400 MHz; CD₃OD, reduced with N₂D₄)



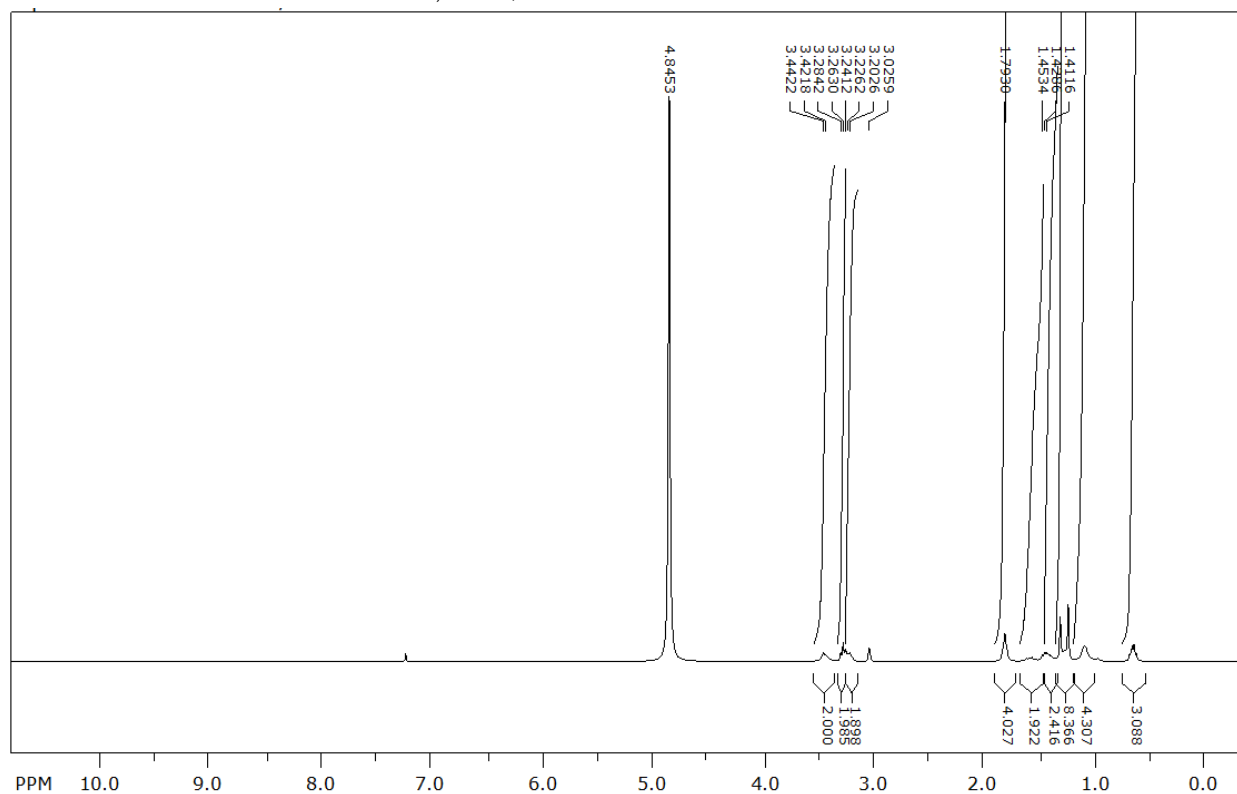
2.7. 2-Ethyl-5,5-dimethyl-2-(pent-4-enyl)-4-(pyrrolidino)-2,5-dihydroimidazol-1-oxyl (**18b**) (300 MHz; CDCl₃ – CD₃OD, reduced with Zn/CF₃COOH in CD₃OD, 65 °C)



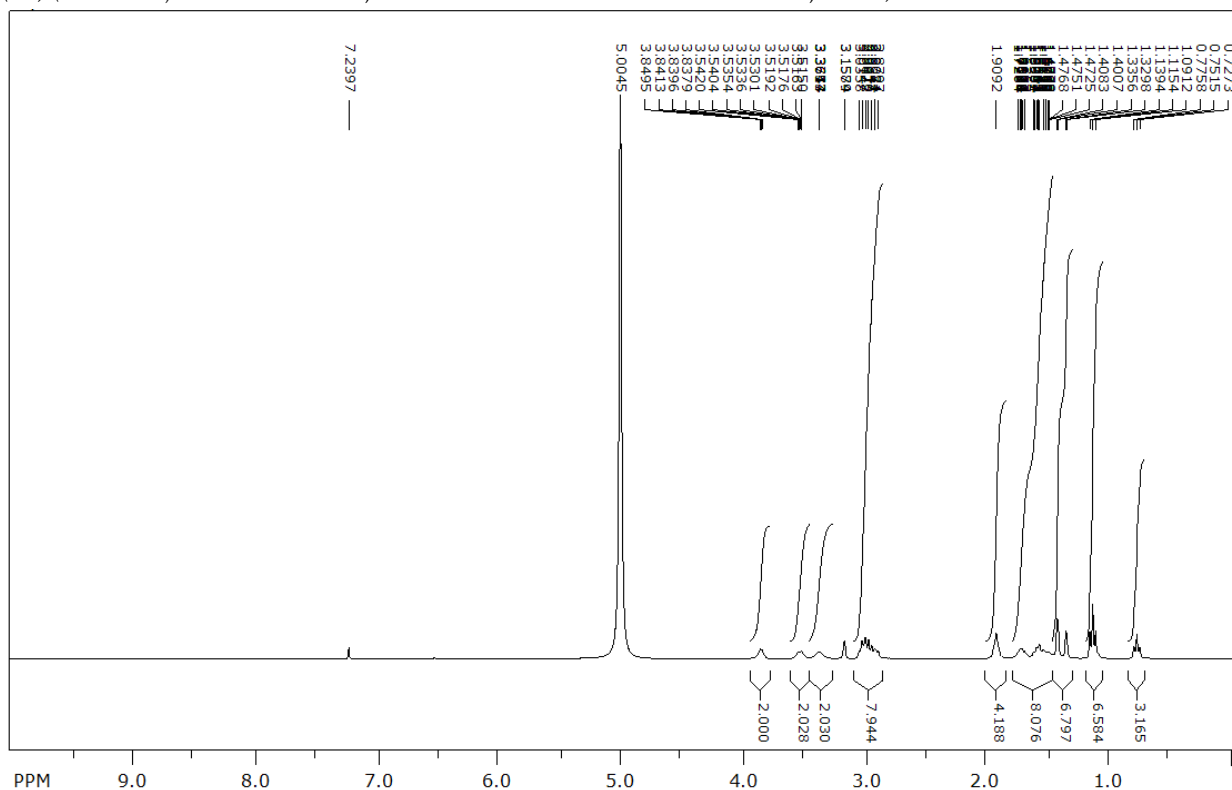
2.8. 2-Ethyl-2-(3-hydroxypropyl)-5,5-dimethyl-4-(pyrrolidino)-2,5-dihydroimidazol-1-oxyl (**19a**) (400 MHz; CD₃OD, reduced with N₂D₄)



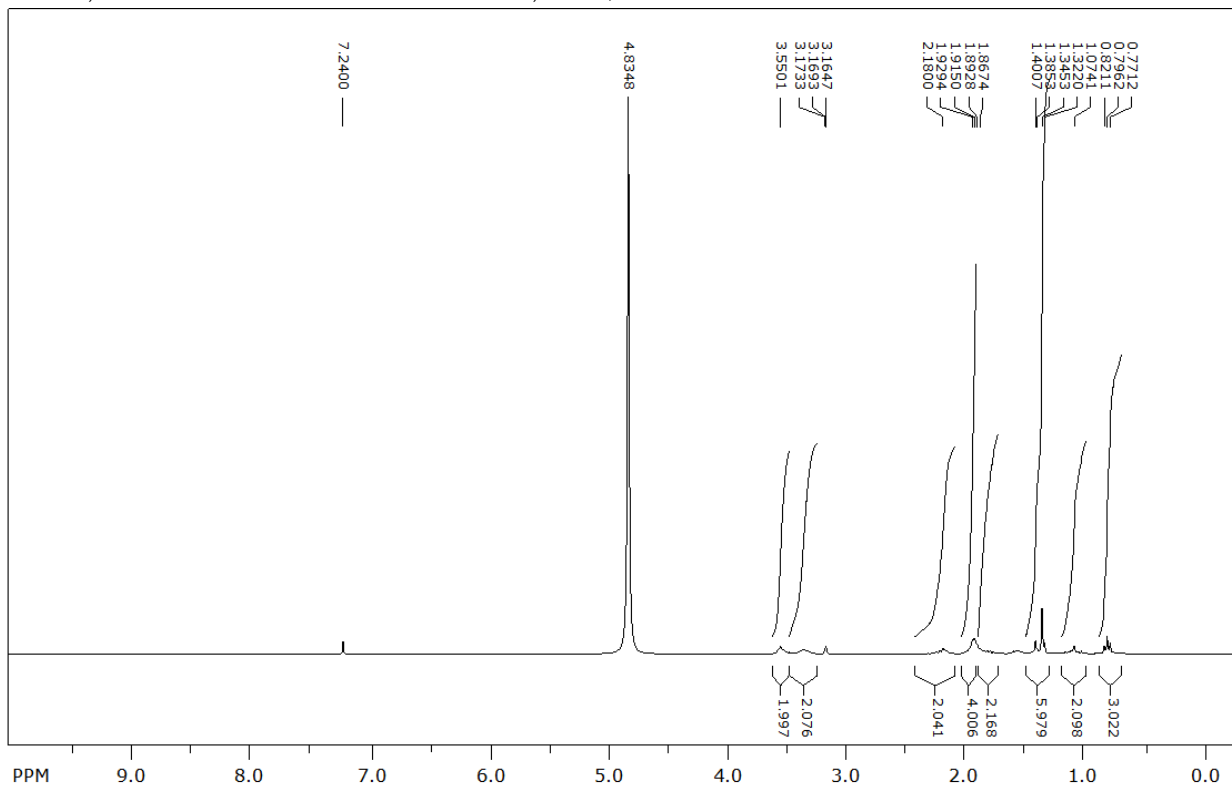
2.9. 2-Ethyl-2-(5-hydroxypentyl)-5,5-dimethyl-4-(pyrrolidino)-2,5-dihydroimidazol-1-oxyl (**19b**) (300 MHz; CDCl₃-CD₃OD, reduced with Zn/CF₃COOH in CD₃OD, 65 °C)



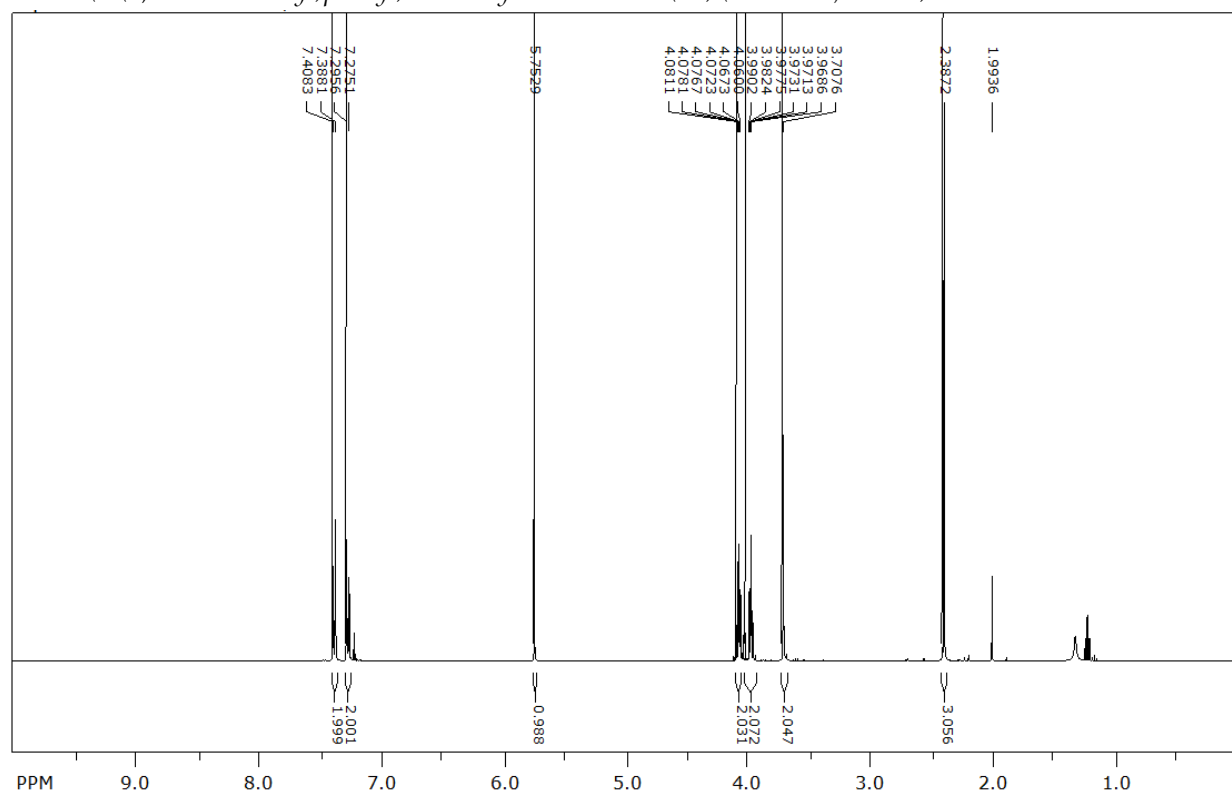
2.10. 2-(3-(3-(Diethylamino)propylcarbamoyloxy)propyl)-2-ethyl-5,5-dimethyl-4-(pyrrolidino)-2,5-dihydro-1H-imidazol-1-oxyl (**21**) (300 MHz; CDCl₃ – CD₃OD, reduced with Zn/CF₃COOH in CD₃OD, 65 °C)



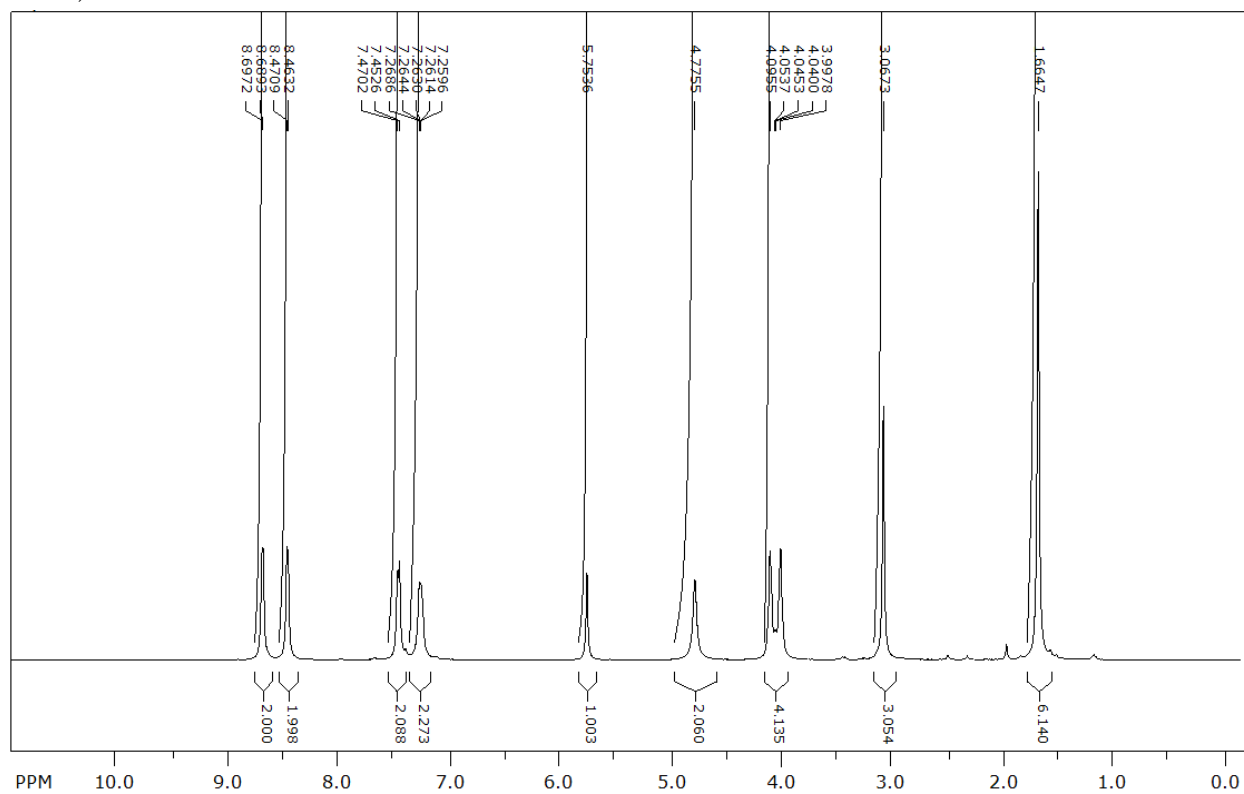
2.11. 2-(2-(2-carboxyethyl)-2-ethyl-5,5-dimethyl-4-(pyrrolidin-1-yl)-2,5-dihydro-1H-imidazol-1-oxyl (**25**) (300 MHz; CDCl₃ – CD₃OD, reduced with Zn/CF₃COOH in CD₃OD, 65 °C)



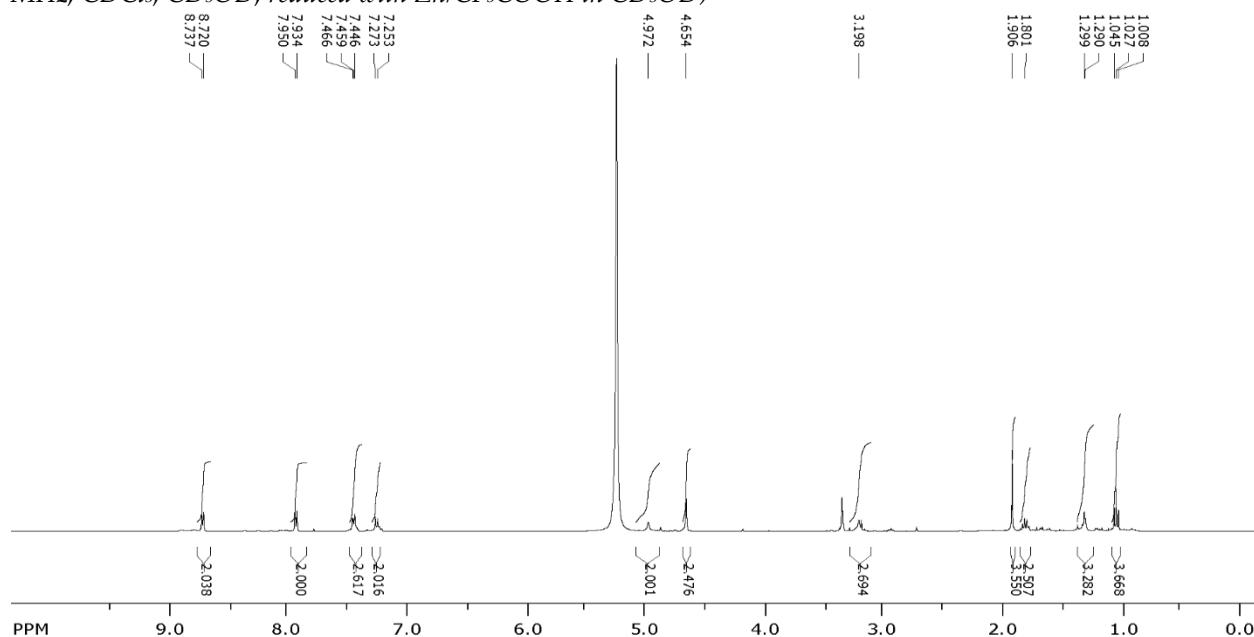
2.12. 1-(4-(1,3-dioxolan-2-yl)phenyl)-N-methylmethanamine (**26**) (300 MHz; CDCl₃)



2.13. 5-((4-(1,3-dioxolan-2-yl)benzyl)(methyl)amino)-4,4-dimethyl-2-(pyridin-4-yl)-4H-imidazole 3-oxide (**30**) (400 MHz; CDCl₃)

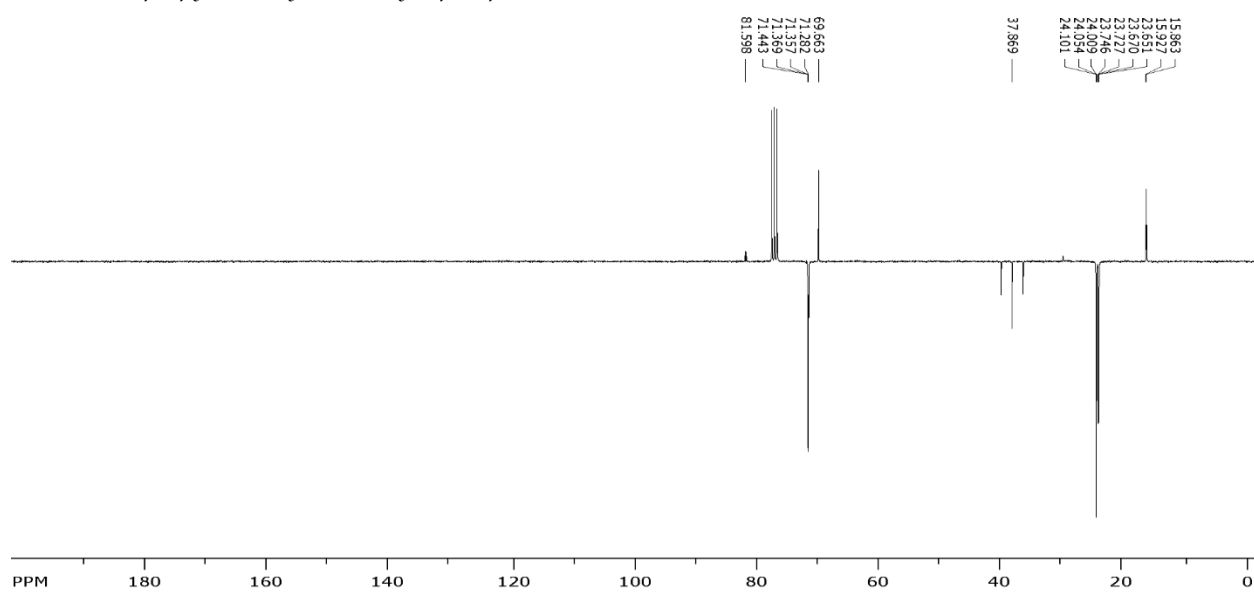


2.14. 2-Ethyl-4-((4-(hydroxymethyl)benzyl)(methyl)amino)-5,5-dimethyl-2-(pyridin-4-yl)-2,5-dihydroimidazol-1-oxyl (**34**) (400 MHz; CDCl₃, CD₃OD, reduced with Zn/CF₃COOH in CD₃OD)



3. ¹³C NMR Spectra

3.1. Tetraisopropyl but-3-yne-1,1-diylldiphosphonate(**6**)(75 MHz, CDCl₃)



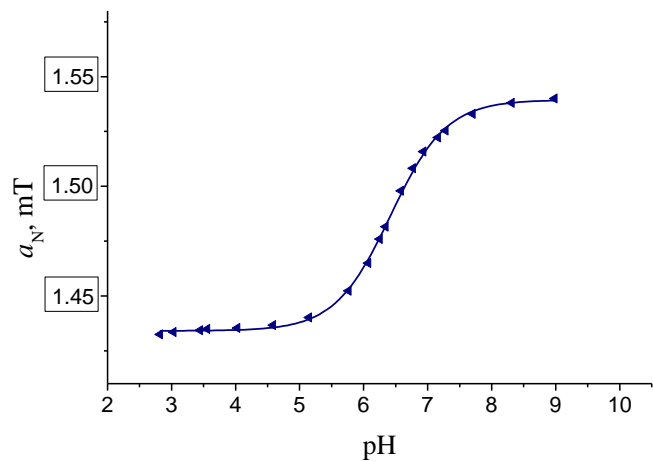
¹³C NMR spectrum of compound 10. The x-axis represents the chemical shift in PPM, ranging from 0 to 180. The spectrum shows several peaks, with the following chemical shifts labeled above the baseline:

- 35.7588
- 55.5462
- 65.0449
- 76.5793
- 76.8974
- 77.2159
- 103.4212
- 126.2842
- 127.8916
- 136.3100
- 141.1237

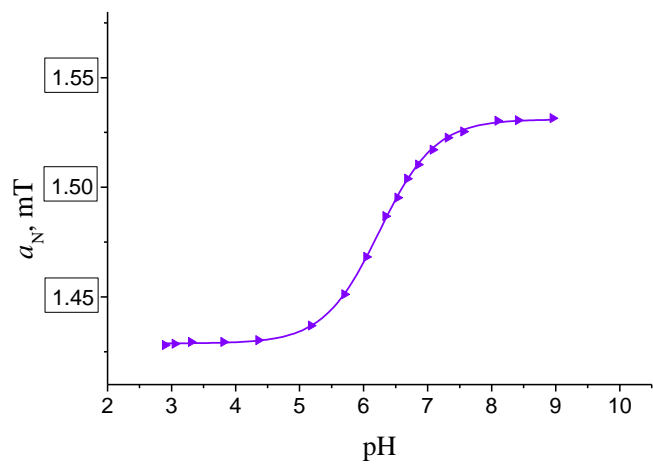
¹³C NMR spectrum (CDCl₃) of compound 10. The x-axis represents the chemical shift in PPM, ranging from 0 to 180. The spectrum shows several sharp peaks, with the most intense at 76.7267 ppm (CDCl₃ solvent). Other labeled peaks include 21.4496, 21.4738, 21.4932, 21.5104, 21.5484, 21.5967, 35.1938, 35.2142, 53.0537, 64.9527, 75.7267, 76.2072, 76.6327, 77.0533, 102.8513, 120.8831, 120.9665, 126.6629, 126.7684, 133.8546, 136.3742, 136.3921, 137.4360, 149.7963, and 172.2938 ppm.

4. Titration Data.

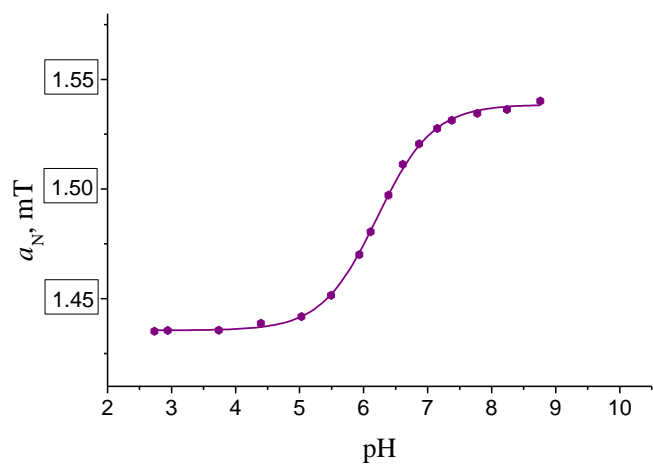
4.1. 2-(4-(Azidomethyl)phenyl)-2,5,5-triethyl-4-pyrrolidino-2,5-dihydro-1H-imidazol-1-oxyl (5)



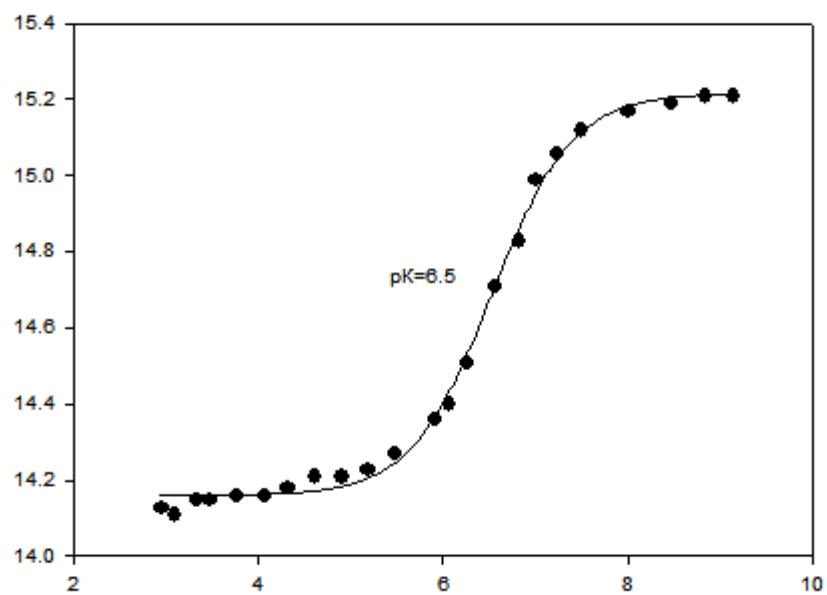
4.2. 2-(4-((4-(2,2-Bis(diisopropoxyphosphoryl)ethyl)-1H-1,2,3-triazol-1-yl)methyl)phenyl)-2,5,5-triethyl-4-pyrrolidino-2,5-dihydro-1H-imidazol-1-oxyl (7)



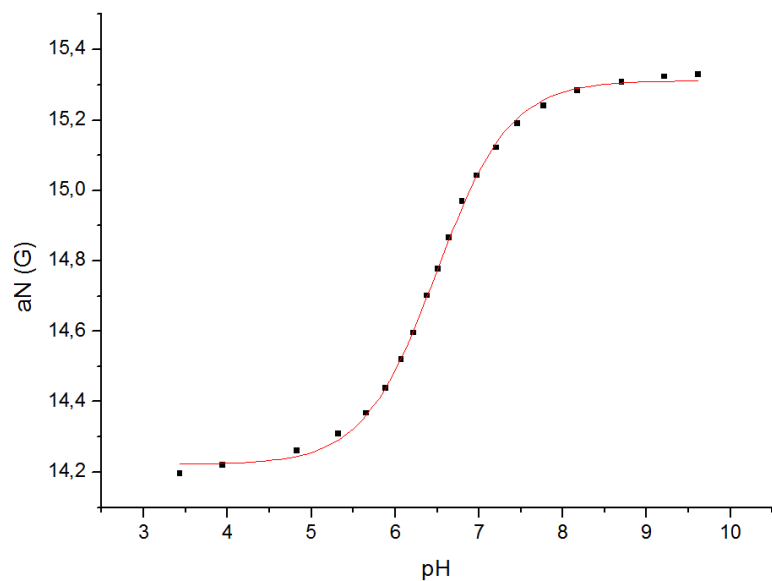
4.3. 2,5,5-Triethyl-2-(4-ethynylphenyl)-4-pyrrolidino-2,5-dihydro-1H-imidazol-1-oxyl (**11**)



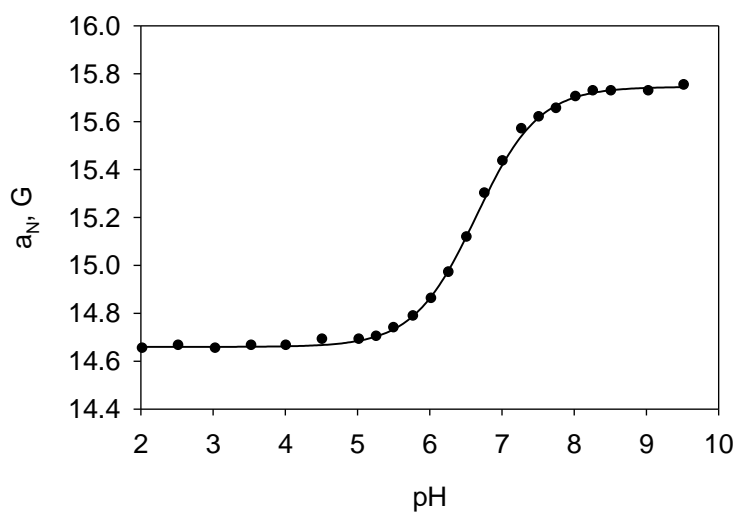
4.4 2-(4-Carboxyphenyl)-2,5,5-triethyl-4-pyrrolidino-2,5-dihydro-1H-imidazol-1-oxyl (**12**)



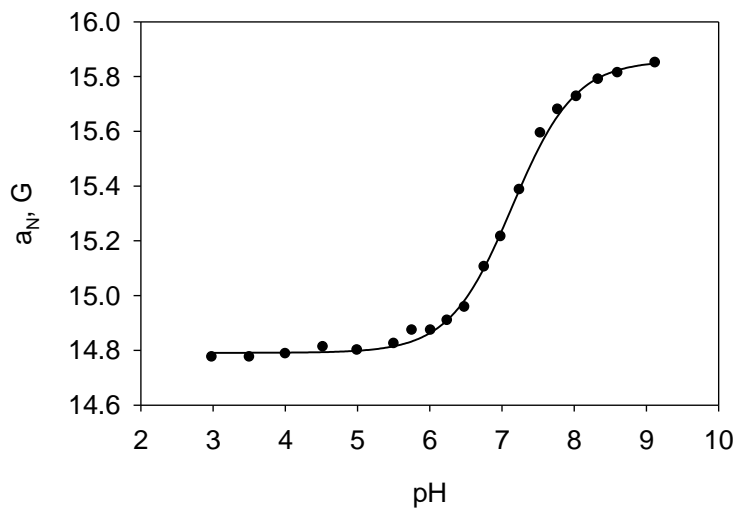
4.5. 2-(4-((2,5-Dioxopyrrolidinoxy)carbonyl)phenyl)-2,5,5-triethyl-4-pyrrolidino-2,5-dihydro-1H-imidazol-1-oxyl (**15**)



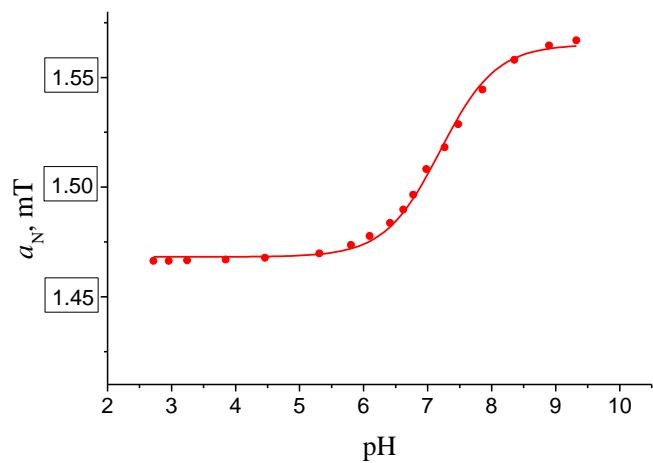
4.6. 2-(4-((3-Carboxypropanoyloxy)methyl)phenyl)-2,5,5-triethyl-4-pyrrolidino-2,5-dihydro-1H-imidazol-1-oxyl (**16**)



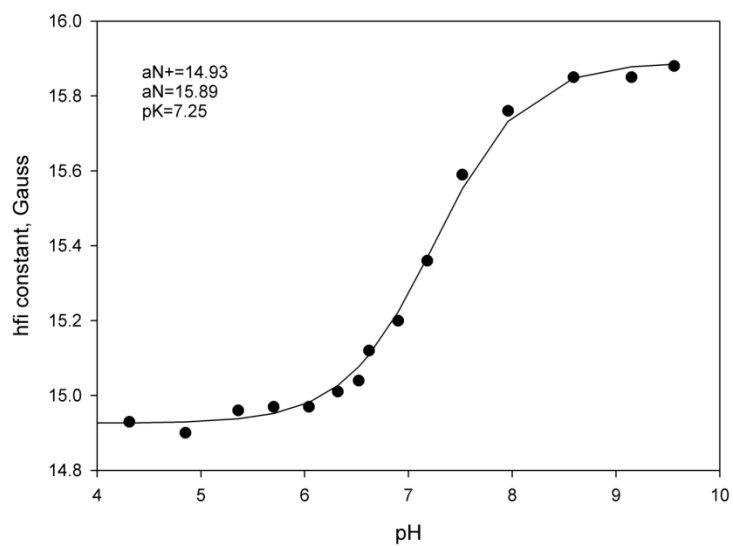
4.7. 2-Allyl-2-ethyl-5,5-dimethyl-4-(pyrrolidino)-2,5-dihydroimidazol-1-oxyl (**18a**)



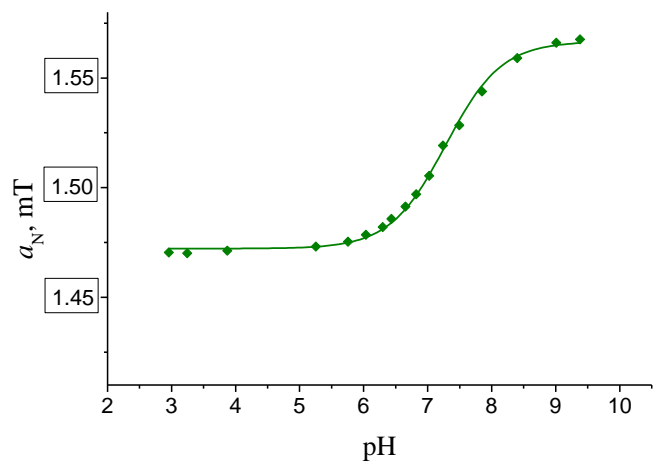
4.8. 2-Ethyl-5,5-dimethyl-2-(pent-4-enyl)-4-(pyrrolidino)-2,5-dihydroimidazol-1-oxyl (**18b**)



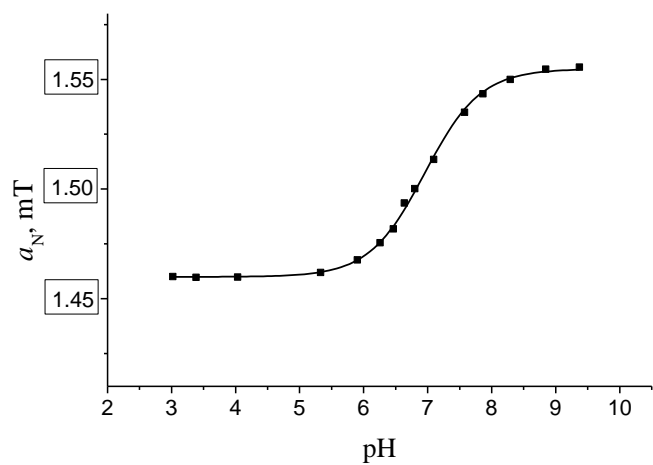
4.9. 2-Ethyl-2-(3-hydroxypropyl)-5,5-dimethyl-4-(pyrrolidino)-2,5-dihydroimidazol-1-oxyl (**19a**)



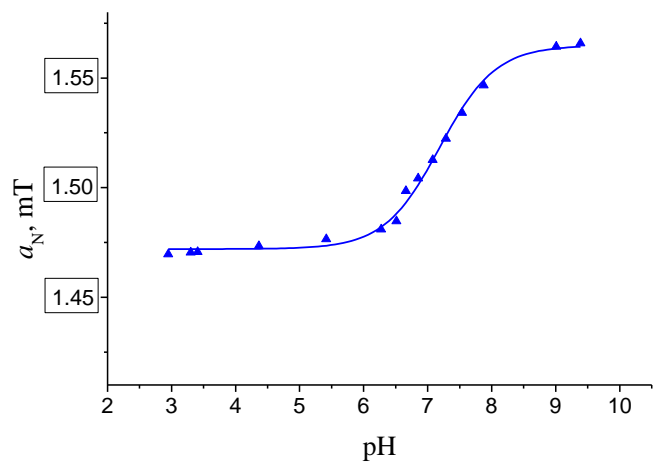
4.10. 2-Ethyl-2-(5-hydroxypentyl)-5,5-dimethyl-4-(pyrrolidino)-2,5-dihydroimidazol-1-oxyl (**19b**)



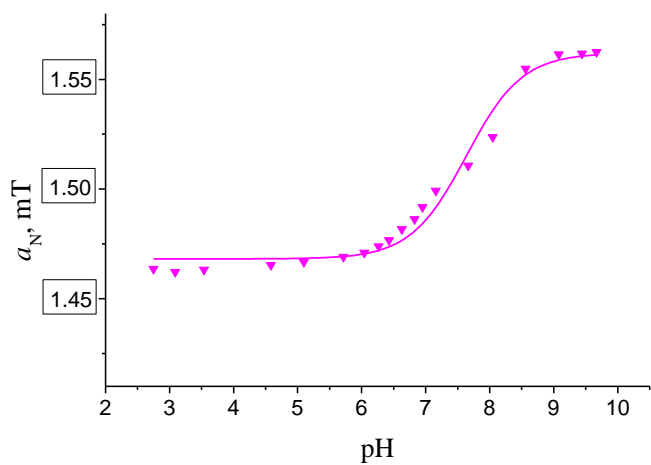
4.11. 2-(3-(1H-Imidazole-1-carboxyloxy)propyl)-2-ethyl-5,5-dimethyl-4-(pyrrolidino)-2,5-dihydro-1H-imidazol-1-oxyl (**20a**)



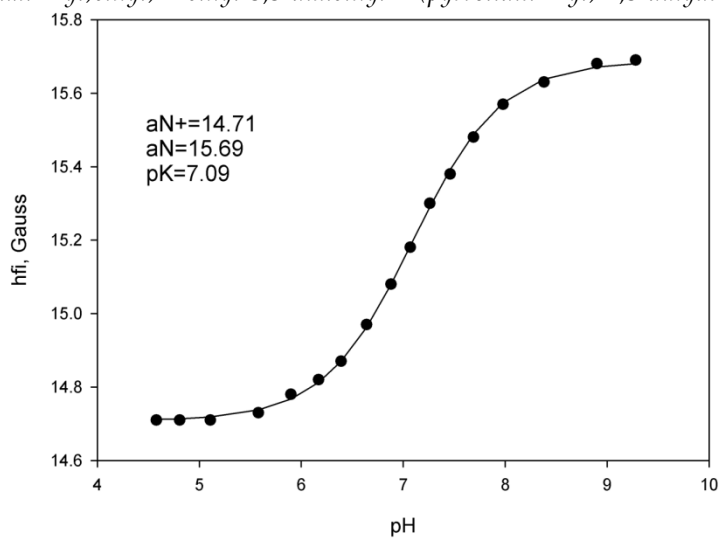
4.12. 2-(3-(3-(Diethylamino)propylcarbamoyloxy)propyl)-2-ethyl-5,5-dimethyl-4-(pyrrolidino)-2,5-dihydro-1H-imidazol-1-oxyl (**21**)



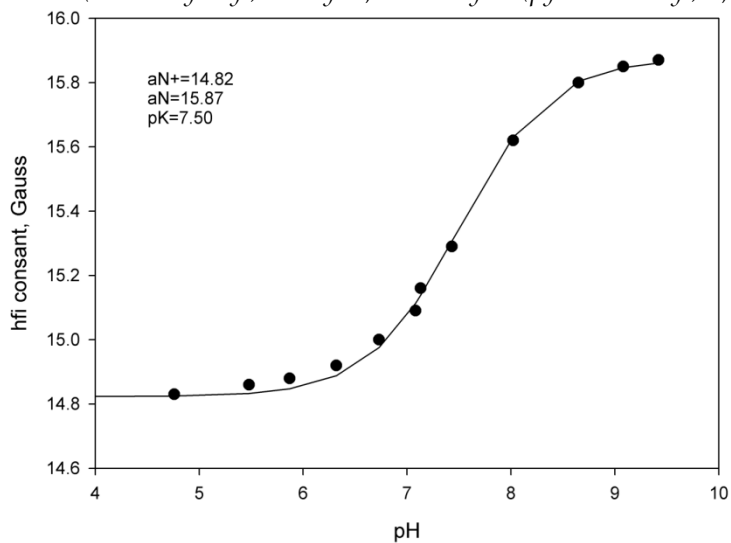
4.13. 2-(3-Carboxypropyl)-2-ethyl-5,5-dimethyl-4-(pyrrolidino)-2,5-dihydro-1H-imidazol-1-oxyl (22)



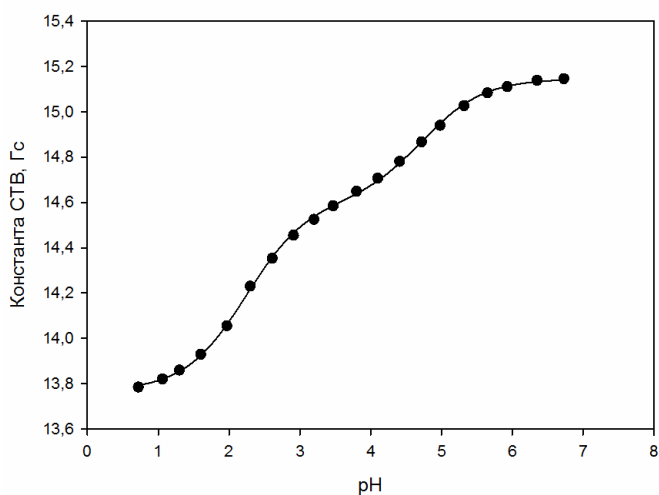
4.14. 2-(2-(1,3-dioxo-lan-2-yl)ethyl)-2-ethyl-5,5-dimethyl-4-(pyrrolidin-1-yl)-2,5-dihydro-1H-imidazol-1-oxyl (23)



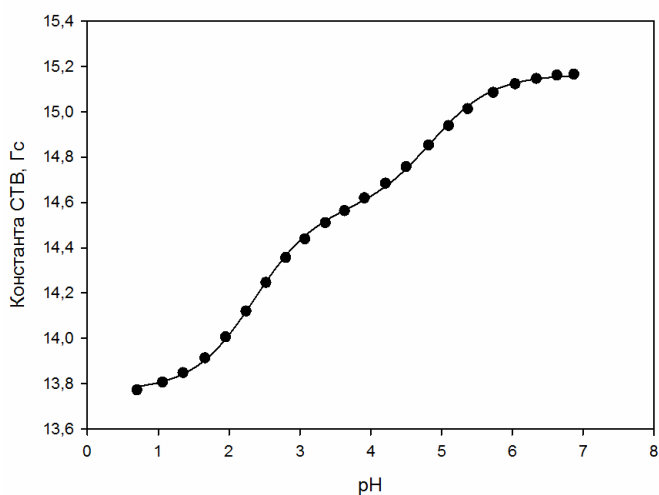
4.15. 2-(2-carboxyethyl)-2-ethyl-5,5-dimethyl-4-(pyrrolidin-1-yl)-2,5-dihydro-1H-imidazol-1-oxyl (25)



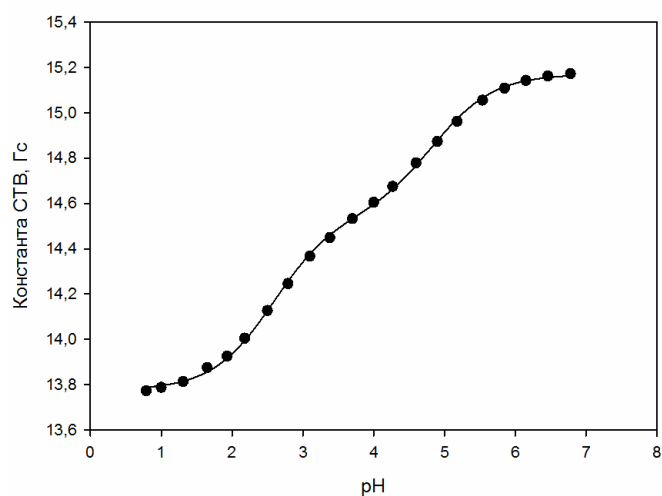
4.16. 2-ethyl-4-((4-formylbenzyl)(methyl)amino)-5,5-dimethyl-2-(pyridin-4-yl)-2,5-dihydro-1H-imidazol-1-oxyl (32)



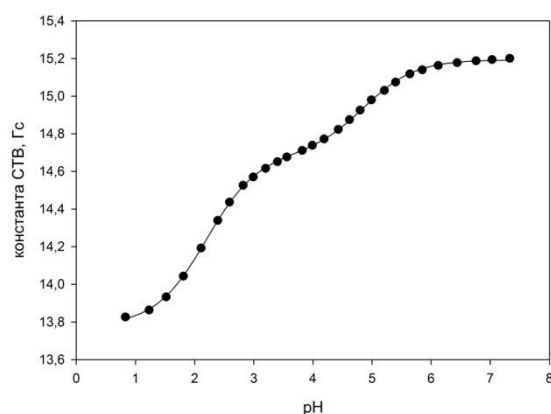
4.17. 4-((4-carboxybenzyl)(methyl)amino)-2-ethyl-5,5-dimethyl-2-(pyridin-4-yl)-2,5-dihydro-1H-imidazol-1-oxyl (33)



4.18. 2-ethyl-4-((4-(hydroxymethyl)benzyl)(methyl)amino)-5,5-dimethyl-2-(pyridin-4-yl)-2,5-dihydro-1H-imidazol-1-oxyl (34)



4.19. 4-((4-(((2,5-dioxopyrrolidin-1-yl)oxy)carbonyl)benzyl)(methyl)amino)-2-ethyl-5,5-dimethyl-2-(pyridin-4-yl)-2,5-dihydro-1H-imidazol-1-oxyl (35)



5. X-Ray Data for Nitroxide 11.

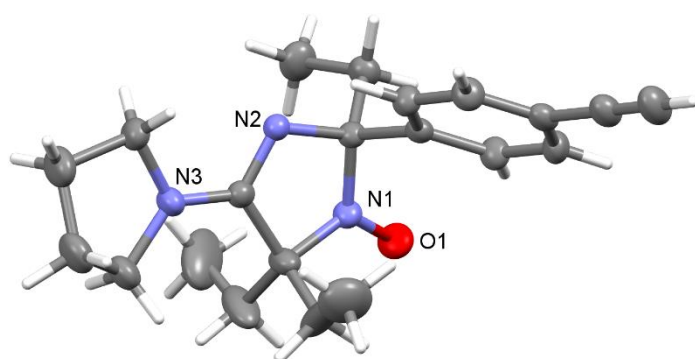


Figure S1. The molecular structure of 2,5,5-triethyl-2-(4-ethynylphenyl)-4-pyrrolidino-2,5-dihydro-1H-imidazol-1-oxyl (11) (minor position of disordered geminal ethyl group is omitted).

Crystallographic data for **11**: $C_{21}H_{28}N_3O$, M 338.46, monoclinic, $P2_1/c$, a 8.7388(3), b 15.2737(6), c 14.5589(6) Å, β 100.656(2)° V 1909.7(1) Å³, Z 4, D_{calcd} 1.177 g·cm⁻³, $\mu(\text{Mo-K}\alpha)$ 0.073 mm⁻¹, $F(000)$ 732, (θ 2.67 – 25.36°, completeness 99.9%), T 200(2) K, orange needle, (1.00 × 0.32 × 0.14) mm³, transmission 0.782 – 0.862, 18099 measured reflections in index range $-10 \leq h \leq 10$, $-18 \leq k \leq 18$, $-17 \leq l \leq 17$, 3513 independent (R_{int} 0.0351), 243 parameters, R_1 0.0434 (for 2820 observed $I > 2\sigma(I)$), wR_2 0.1154 (all data), GOOF 1.025, largest diff. peak and hole 0.27 and -0.28 e.Å⁻³.