

Supporting Information

Hydrophilic Reduction-Resistant Spin Labels of Pyrrolidine and Pyrroline Series from 3,4-Bis-hydroxymethyl-2,2,5,5-tetraethylpyrrolidine-1-oxyl

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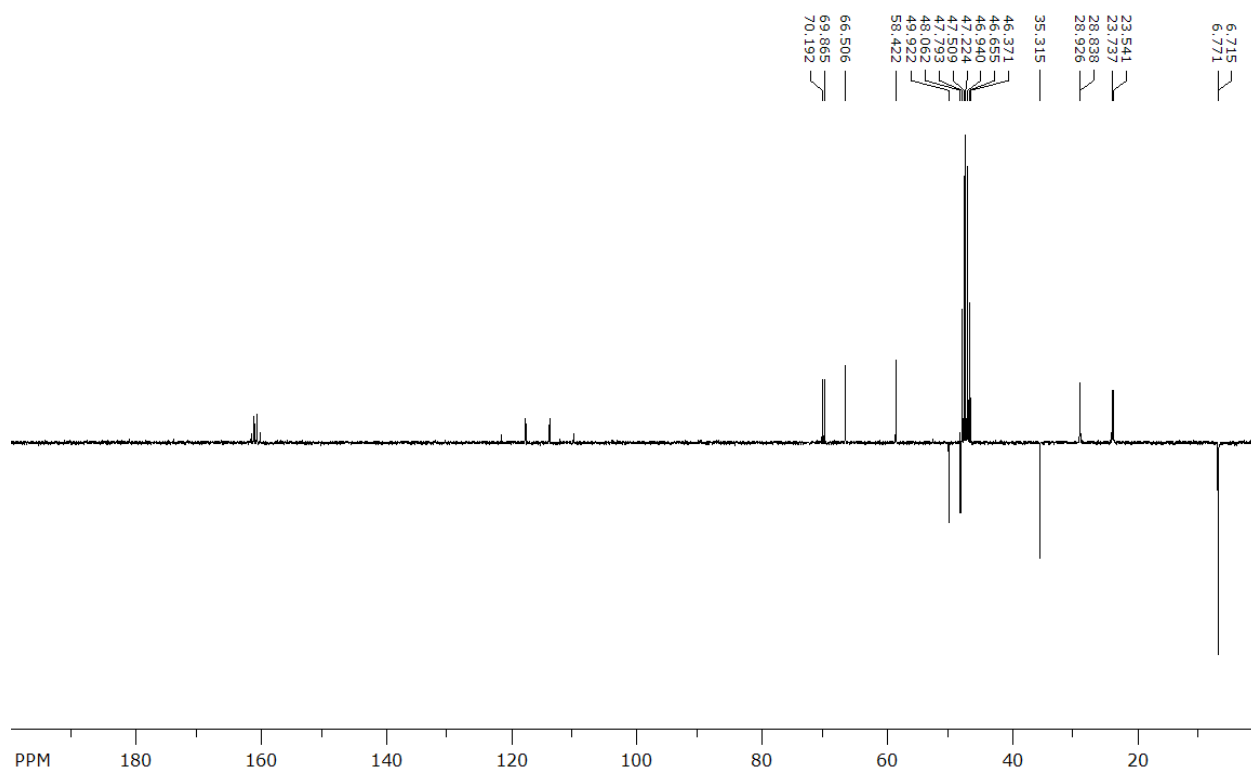
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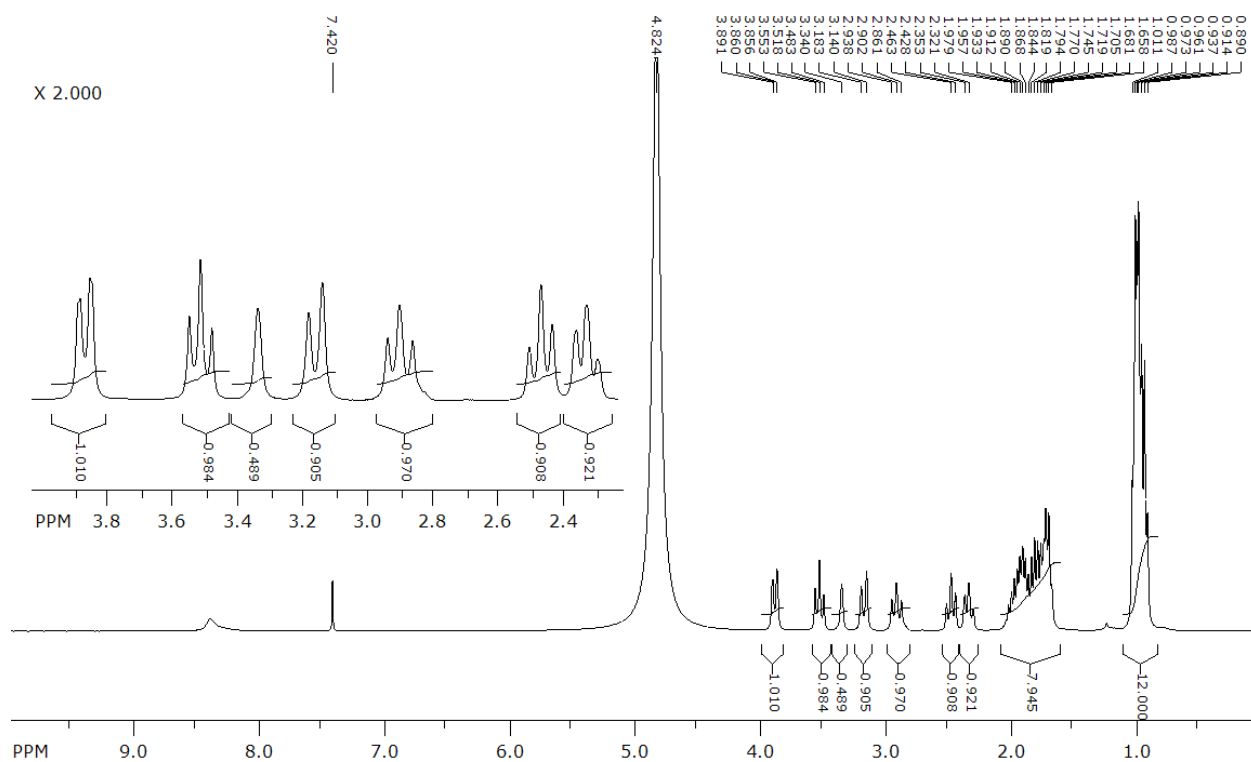
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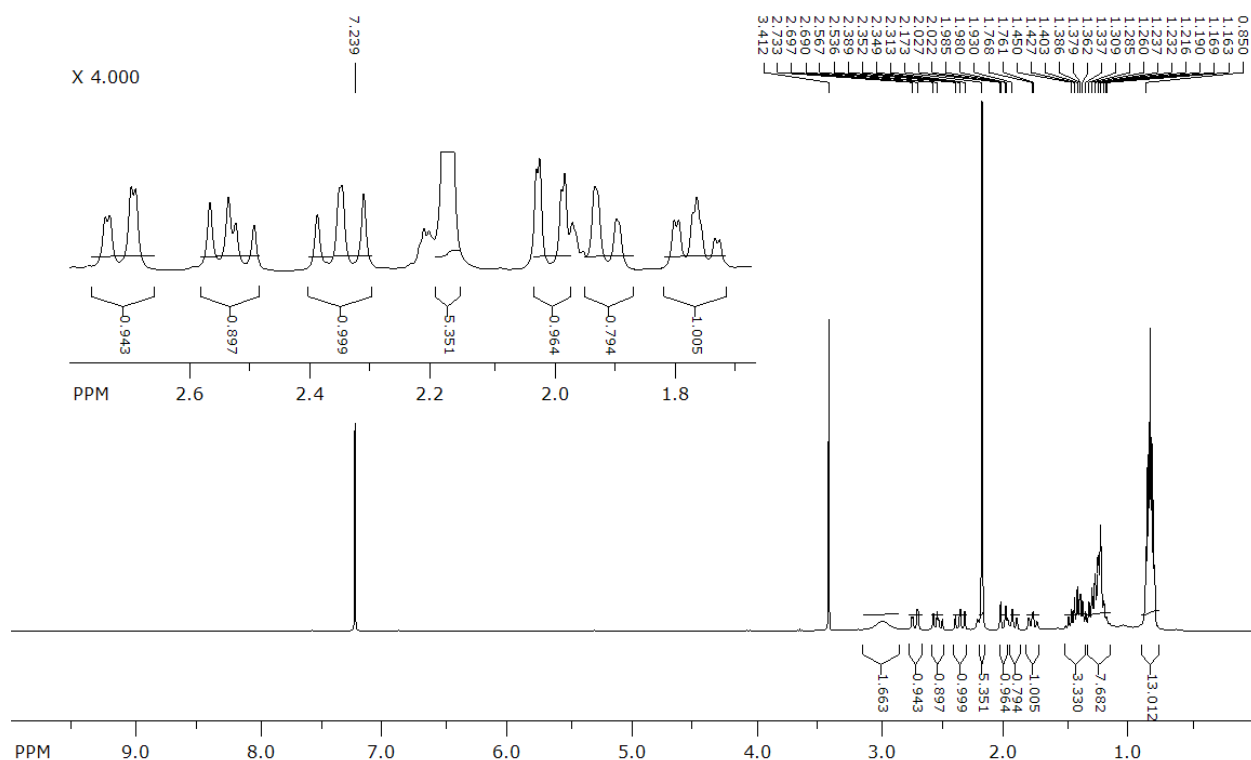
$^{13}\text{C}\{^1\text{H}\}$ (75 MHz; CD_3OD ; $\text{Zn}/\text{CF}_3\text{COOH}$) of 2,2,5,5-tetraethyl-3-(hydroxymethyl)-4-((methylsulfonyloxy)methyl)pyrrolidin-1-oxyl (4)



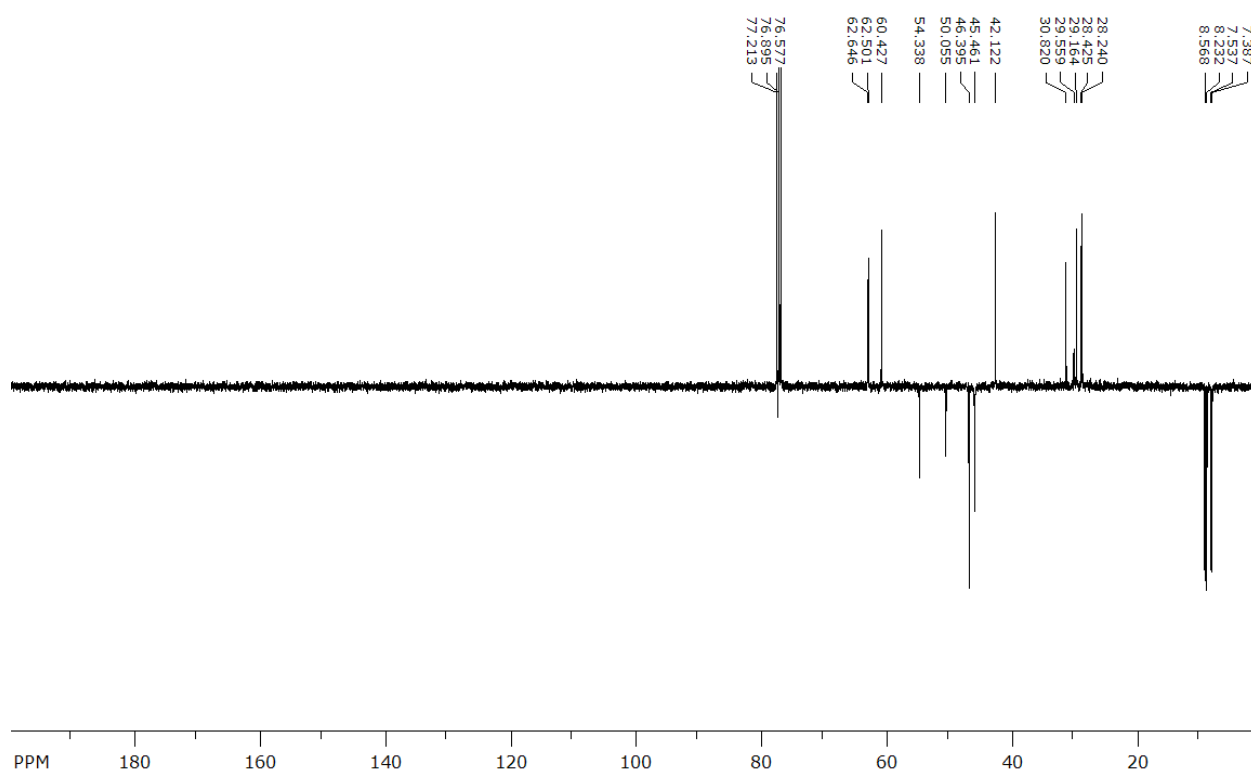
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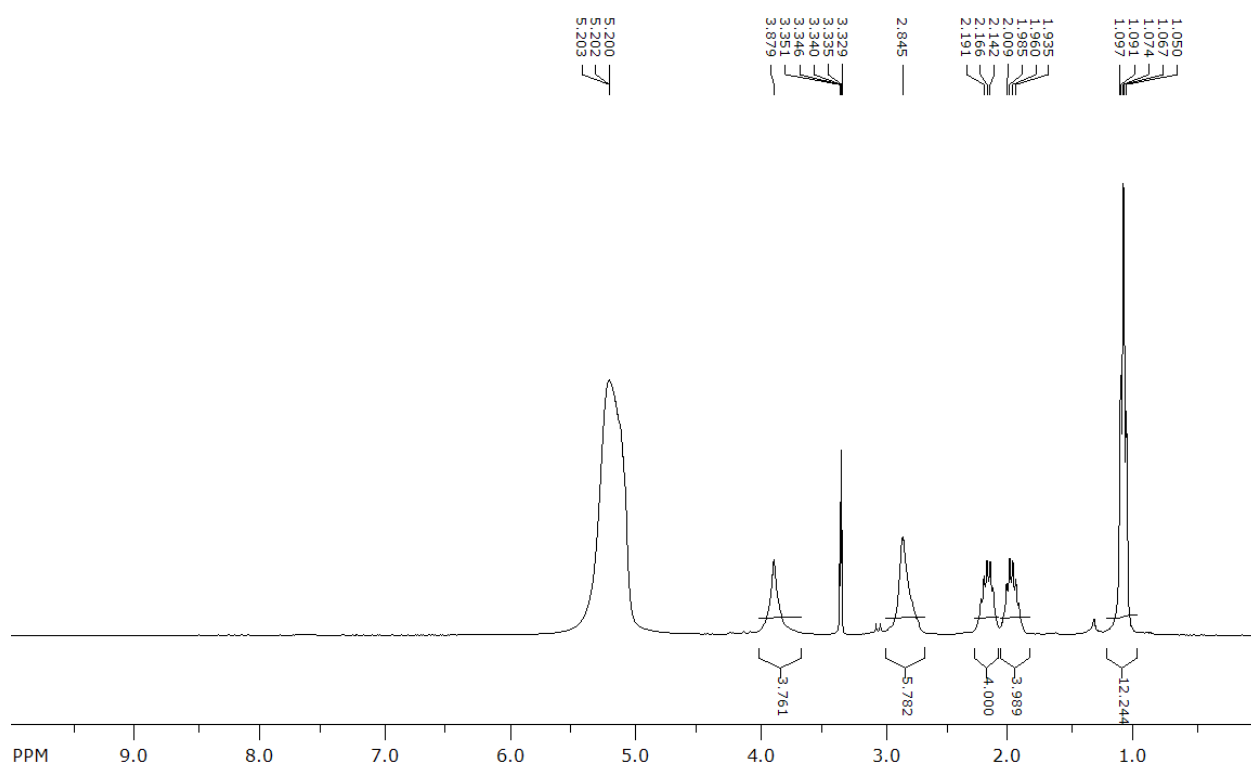
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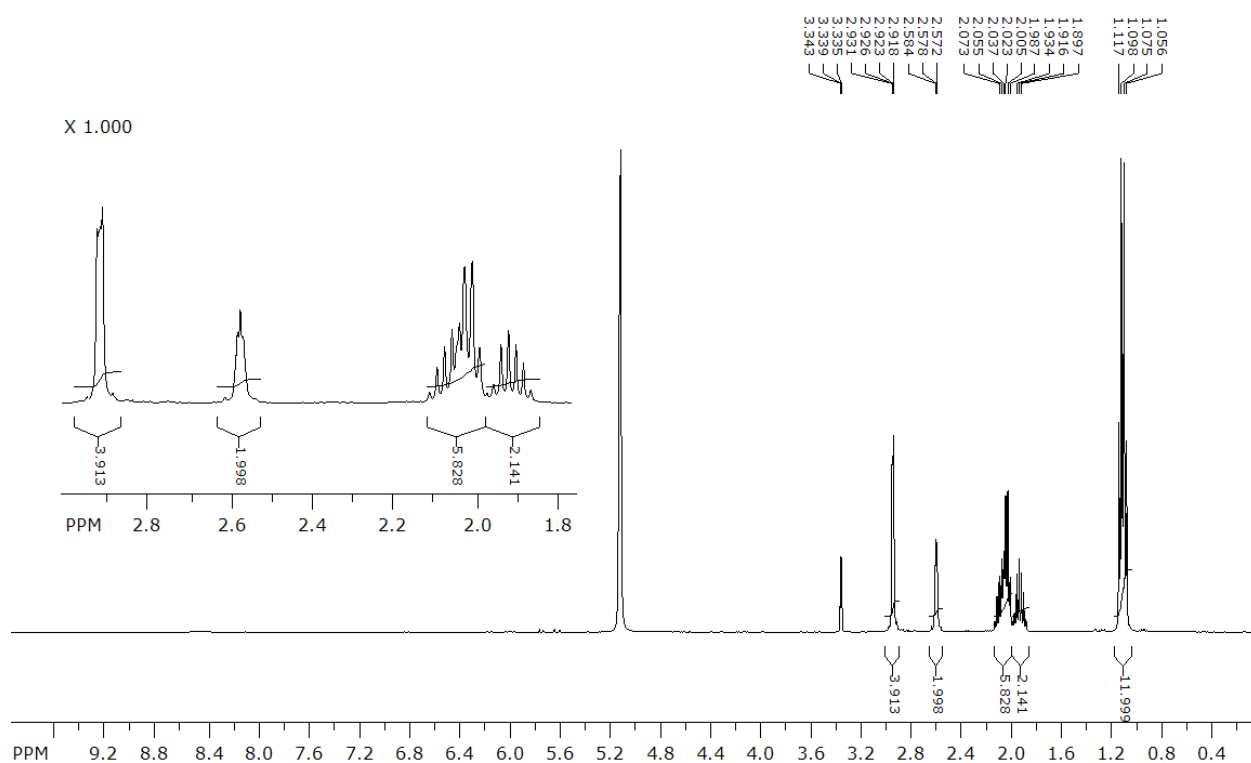
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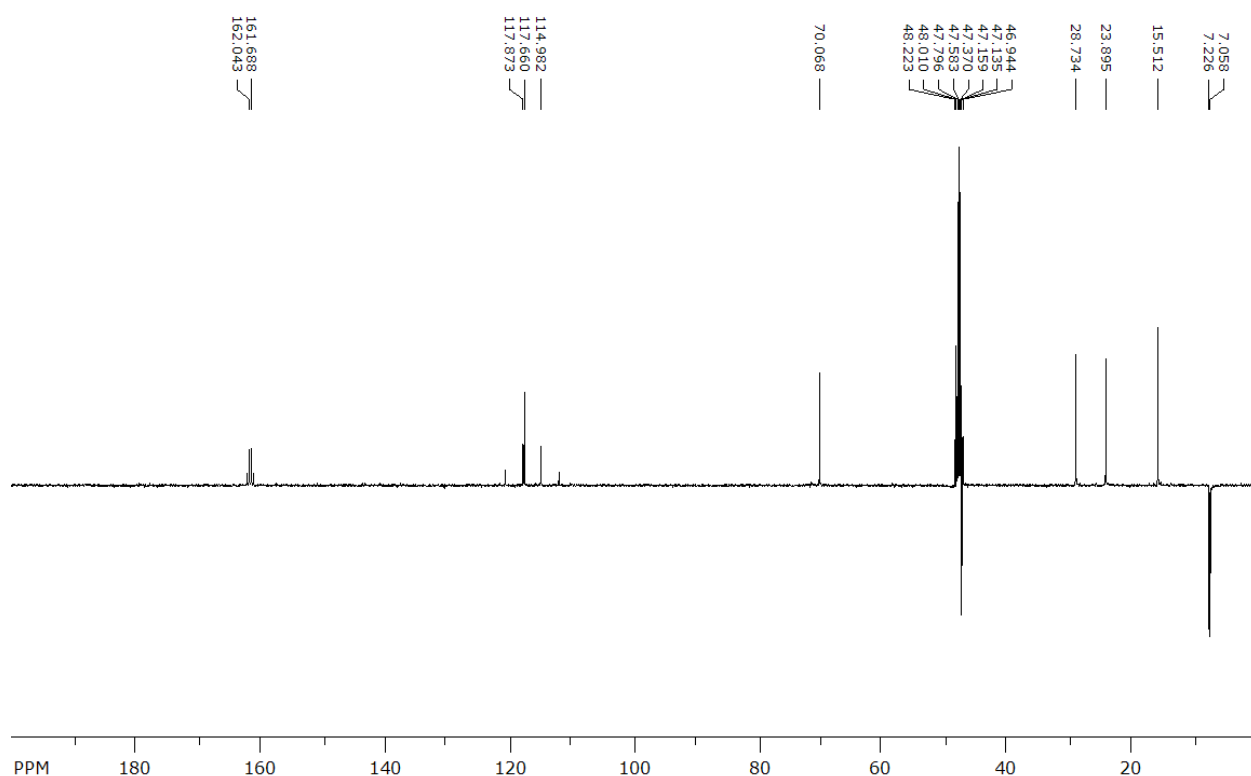
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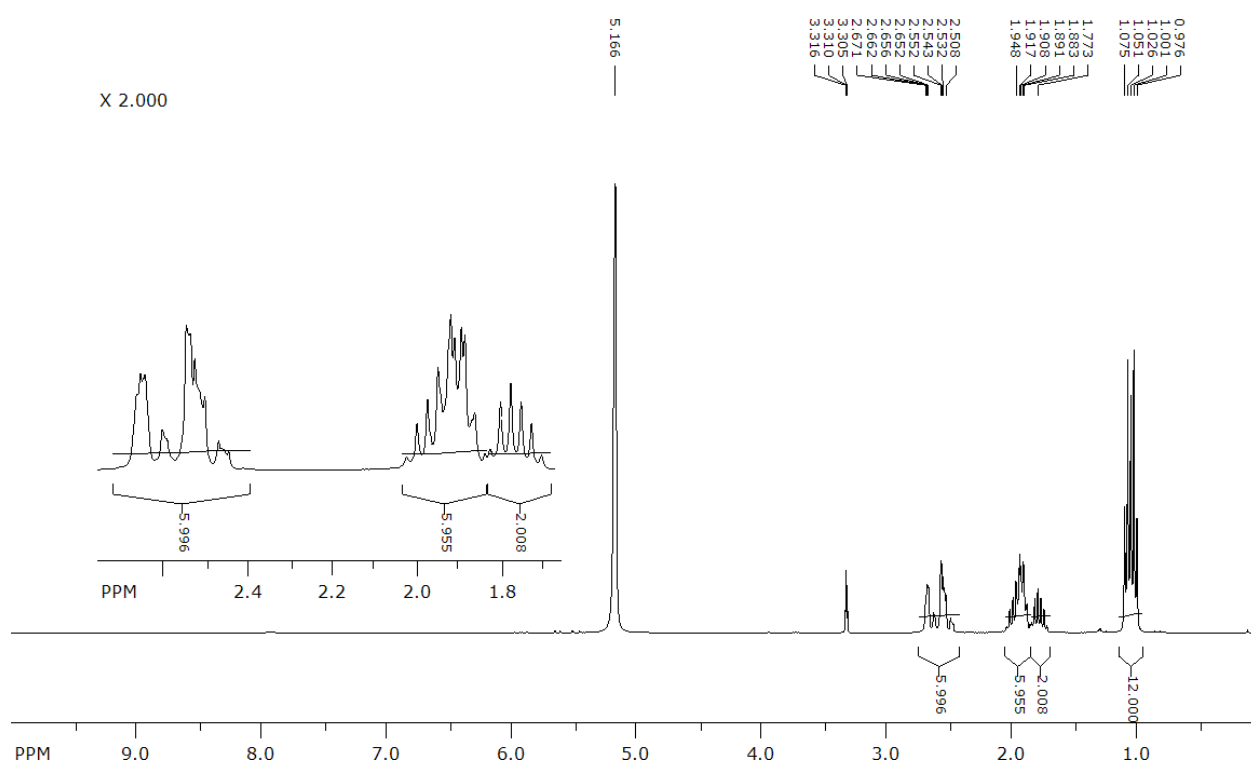
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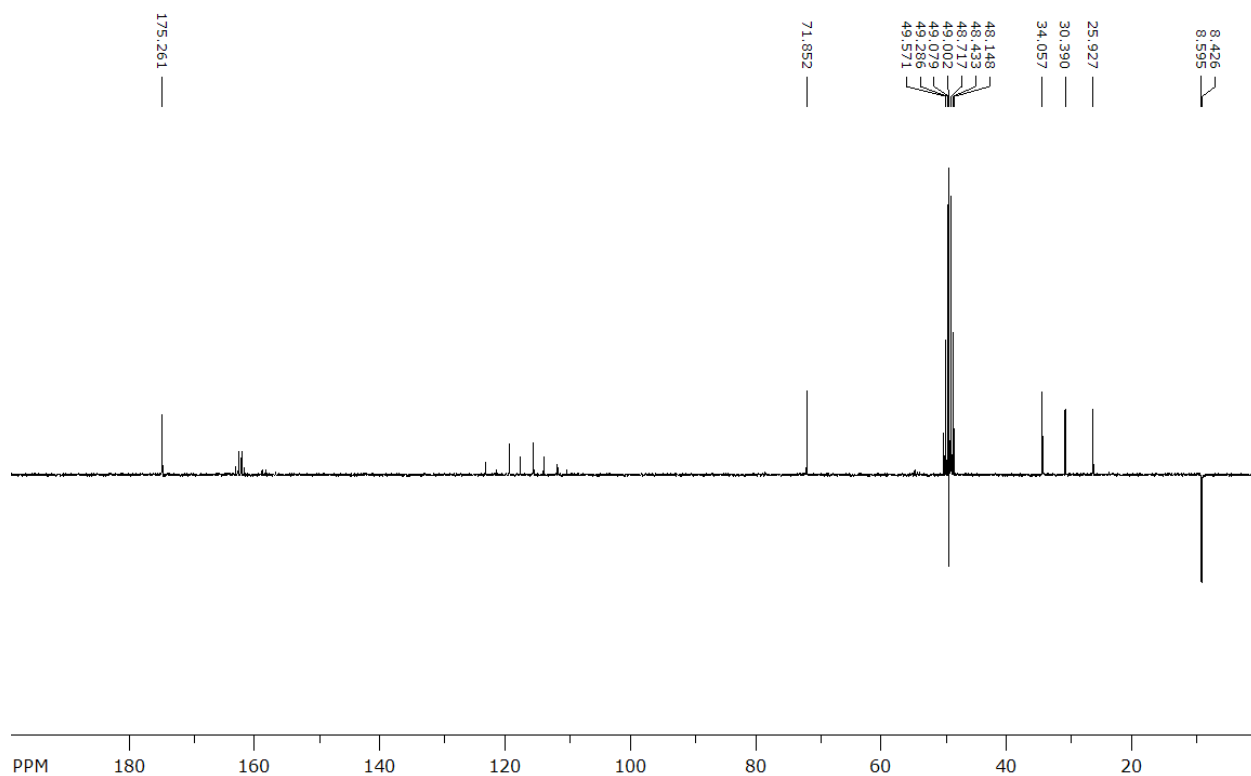
$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz; CD_3OD , $\text{Zn}/\text{CF}_3\text{COOH}$) of 3,4-bis(carboxymethyl)-2,2,5,5-tetraethylpyrrolidin-1-oxyl (23)



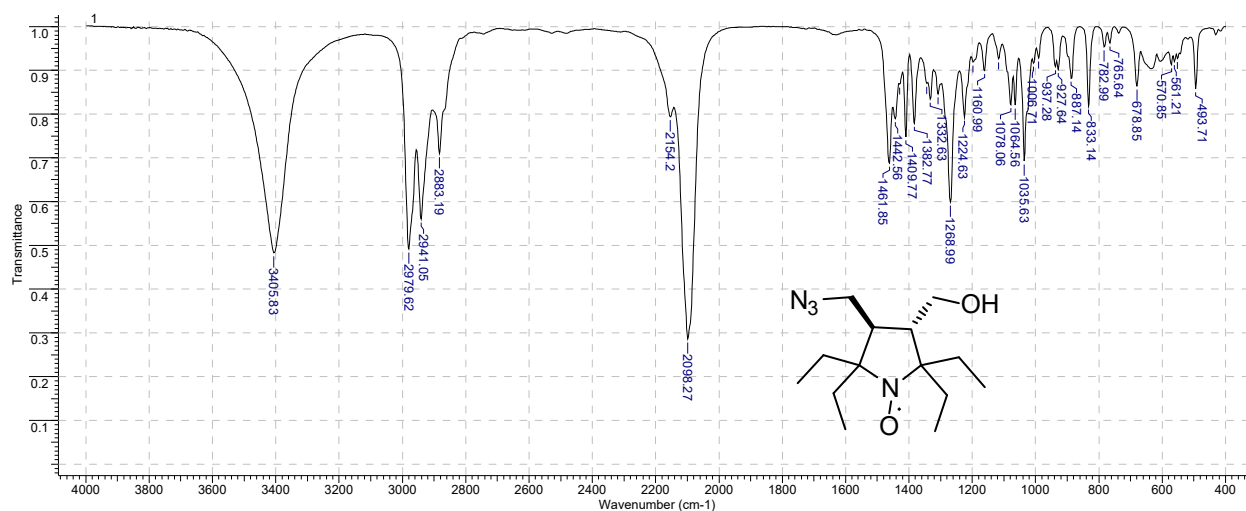
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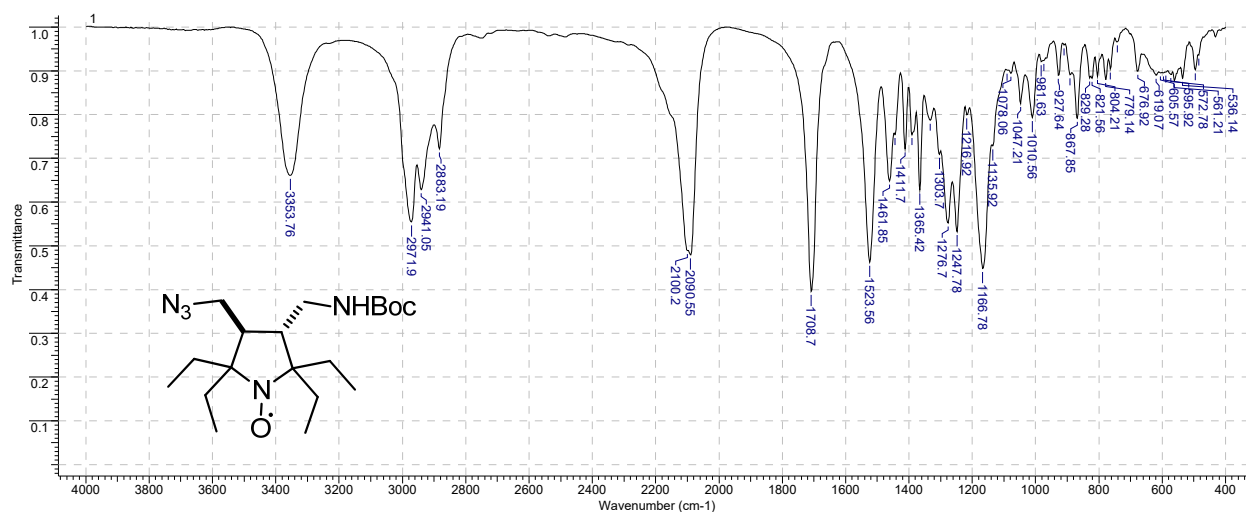
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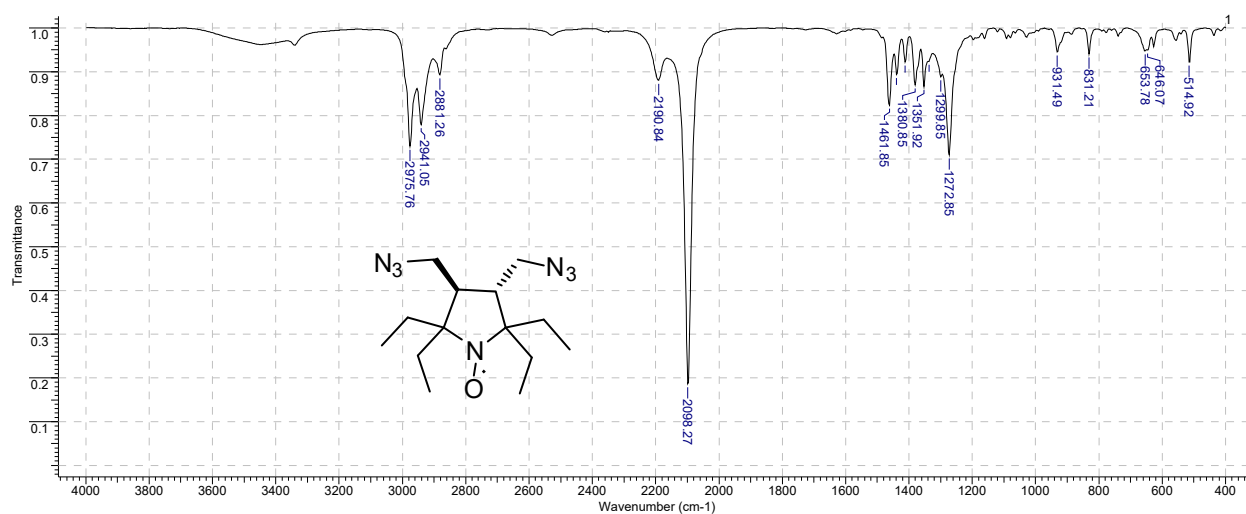
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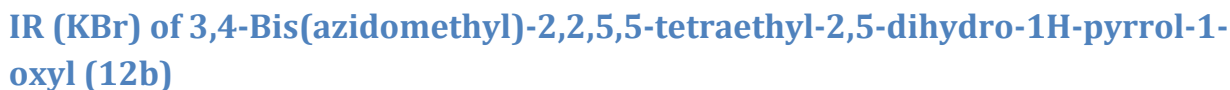


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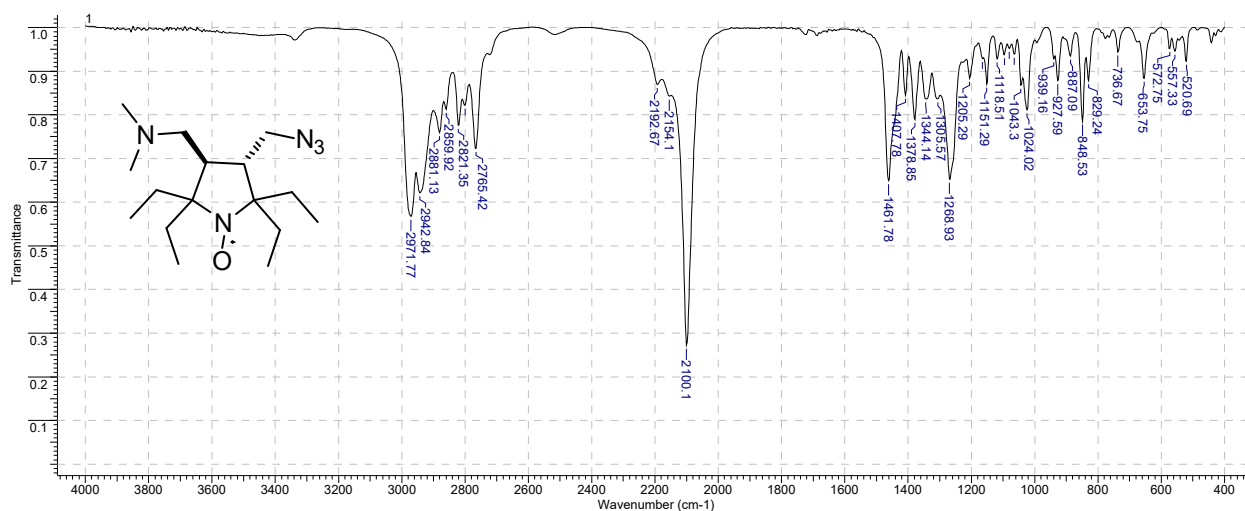


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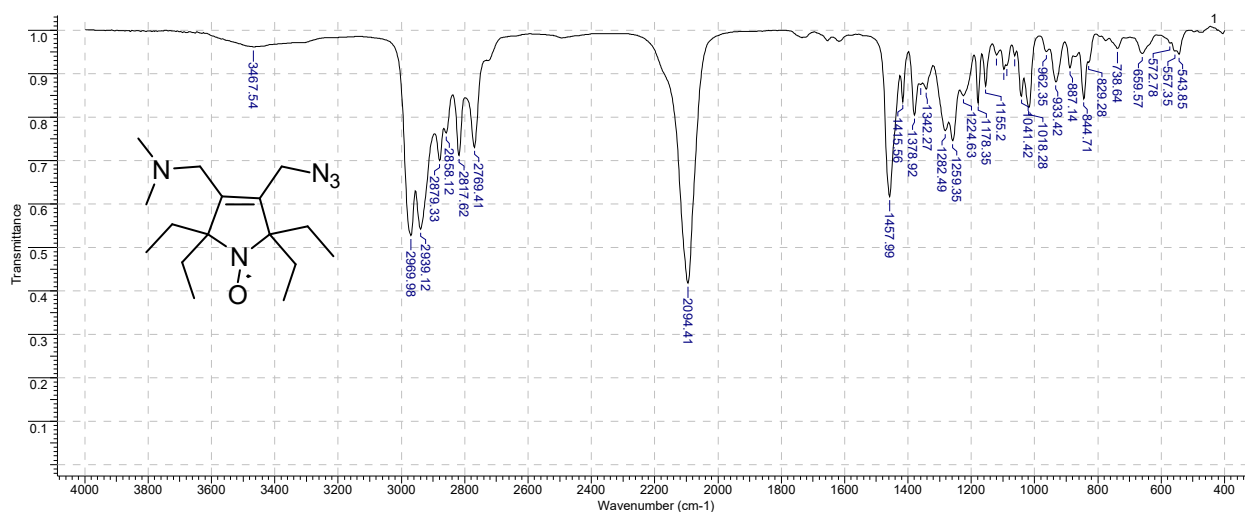




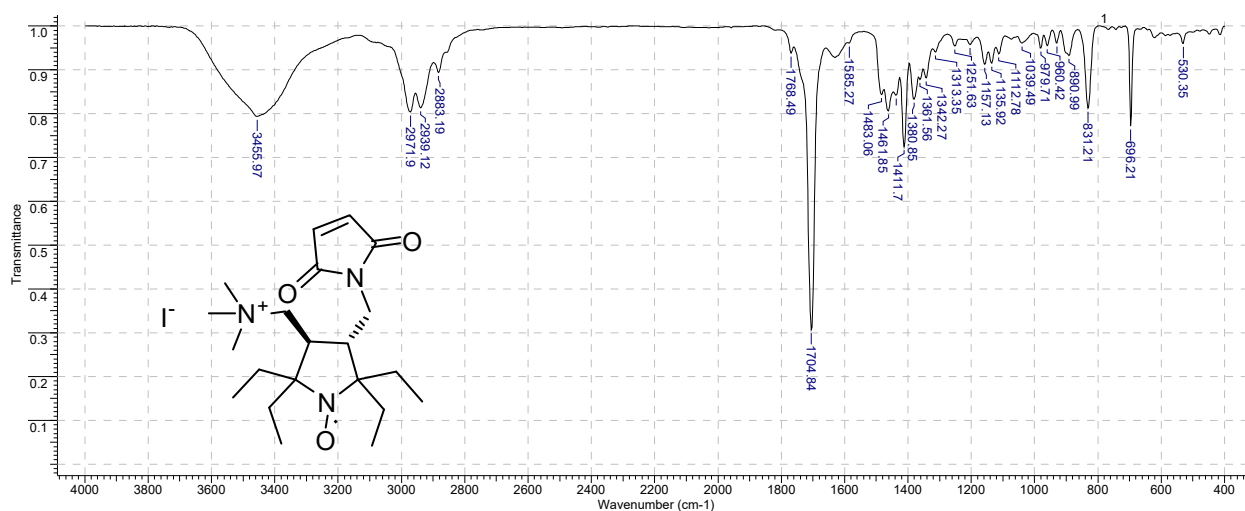
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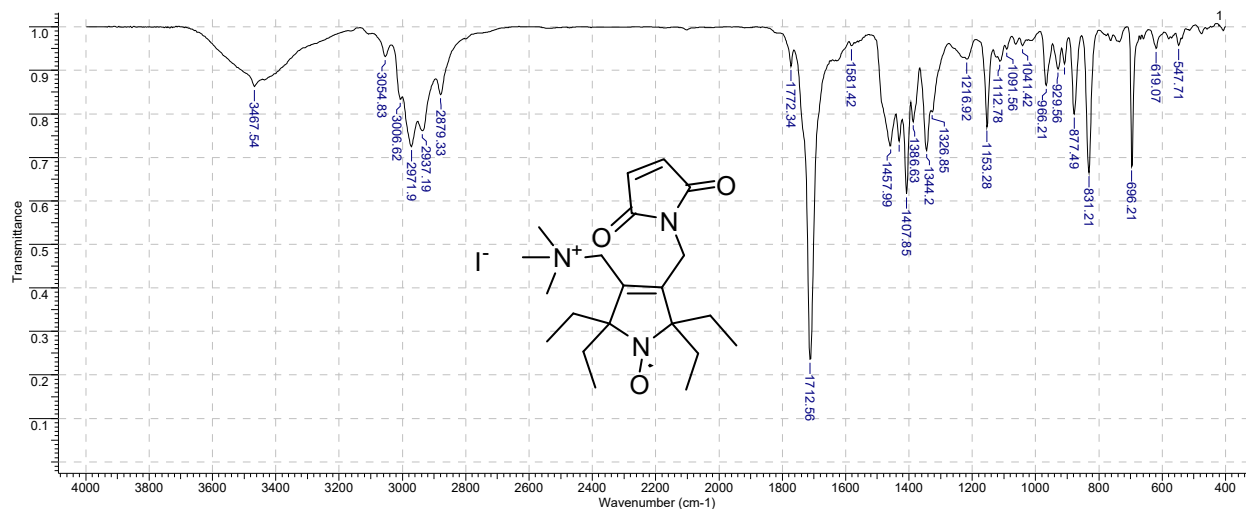
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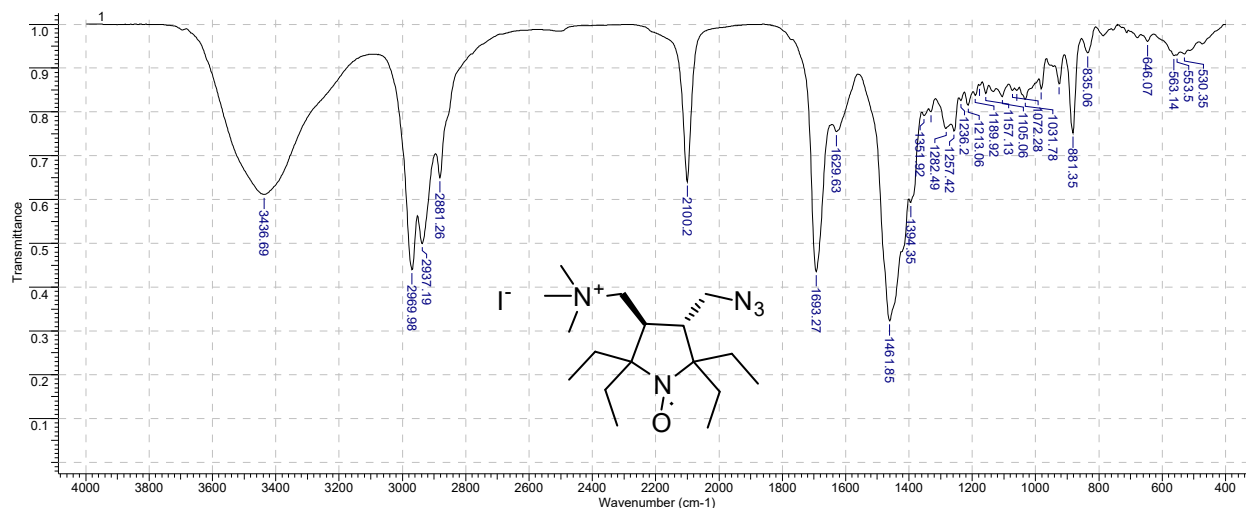
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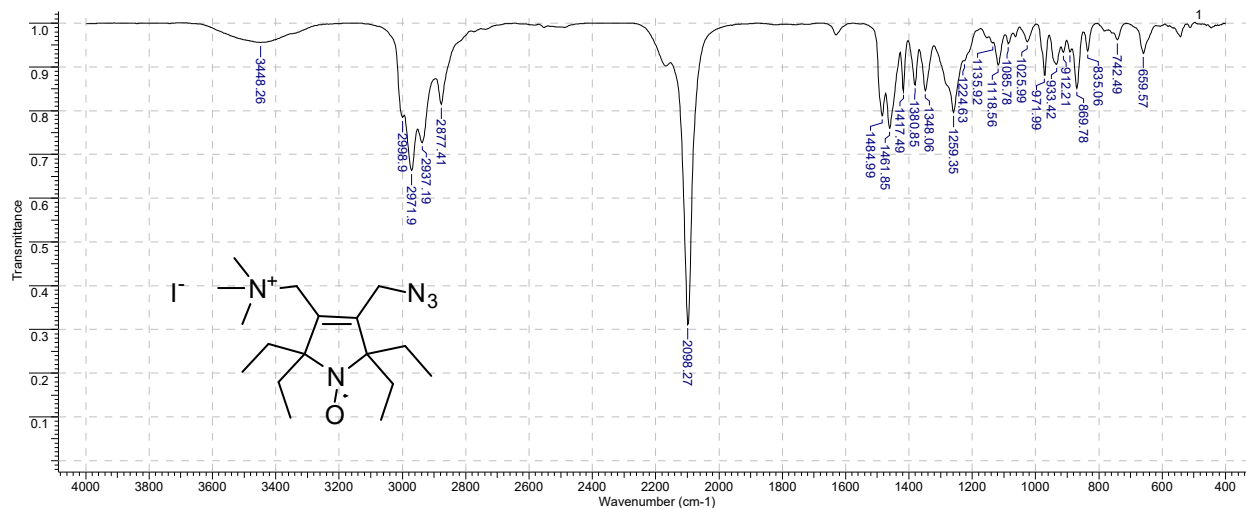
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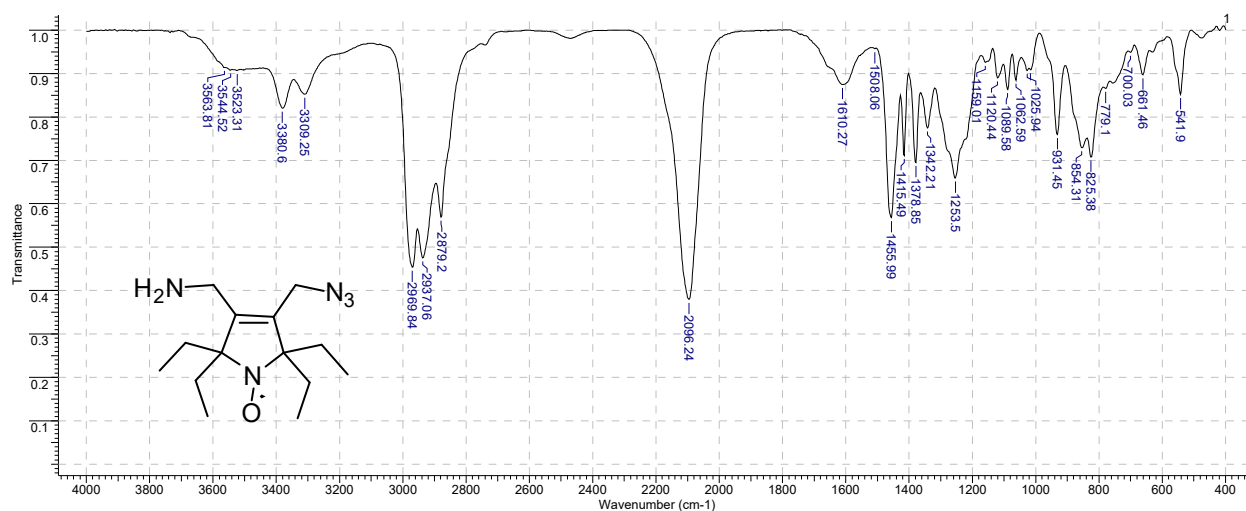
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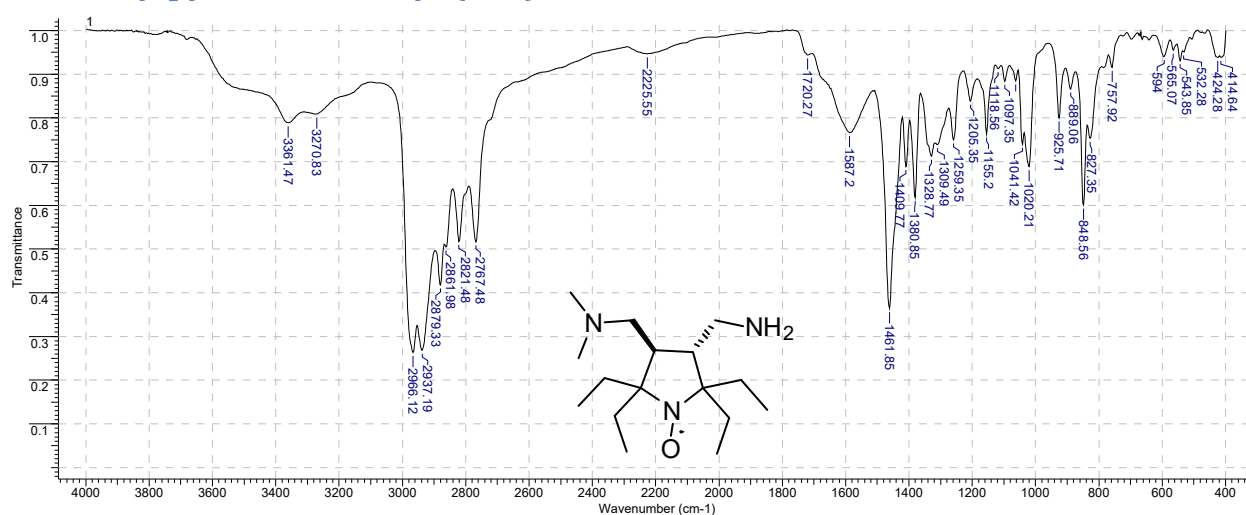
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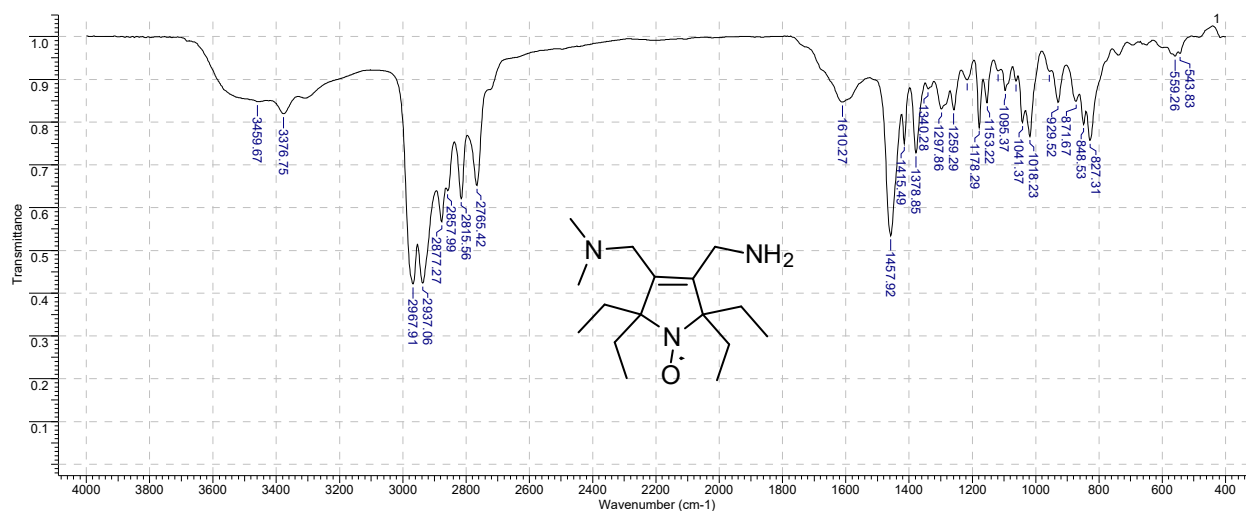
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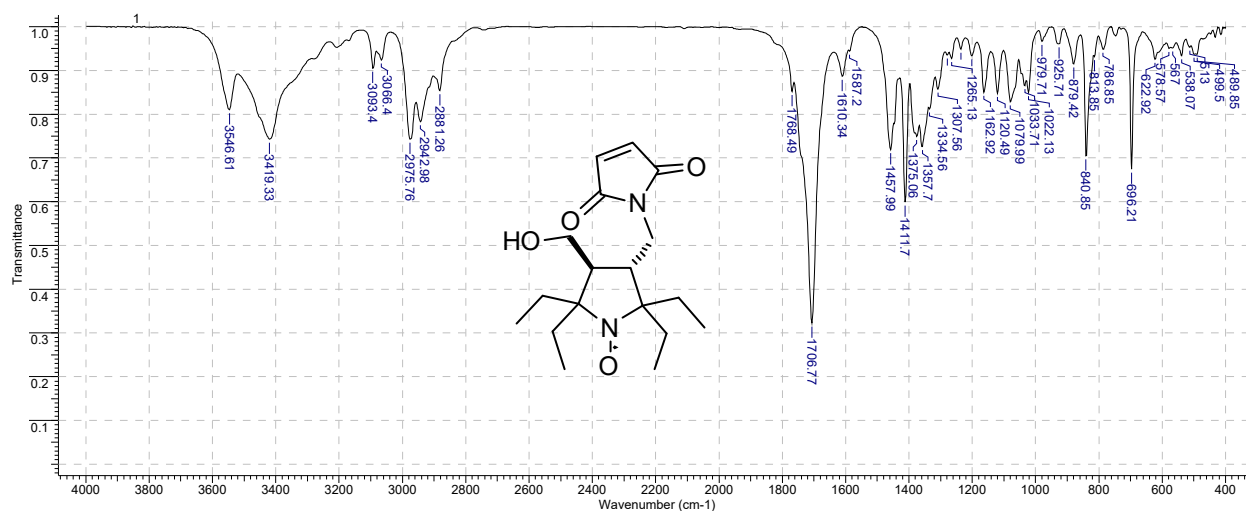
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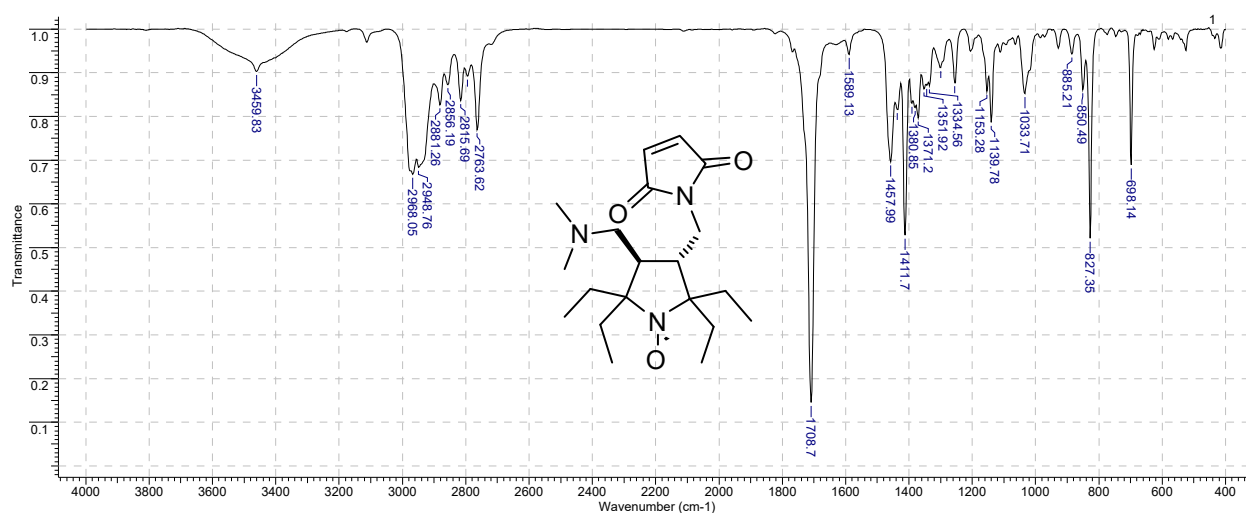
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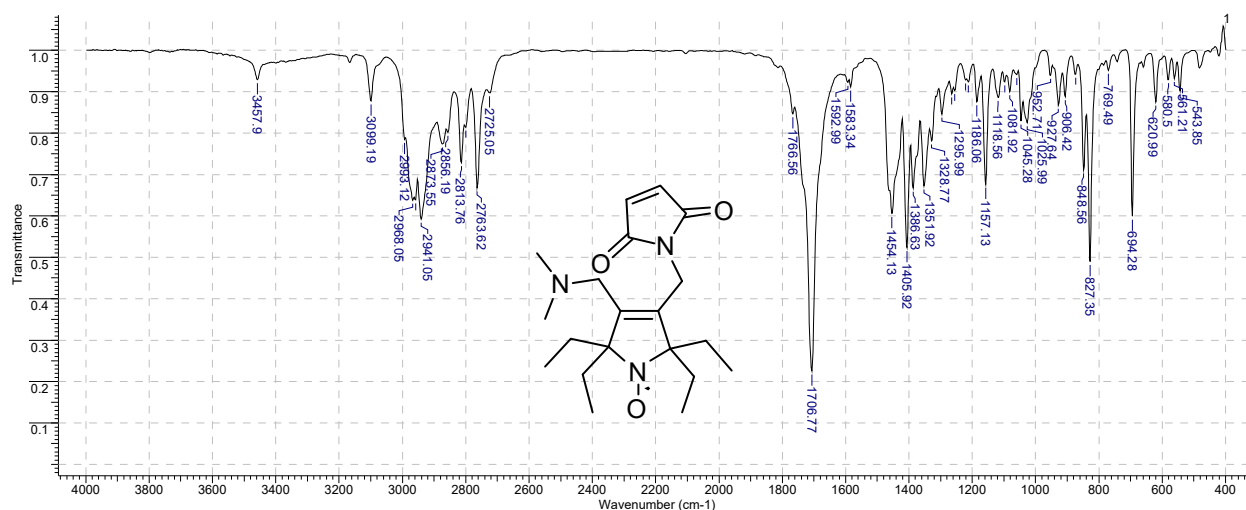
IR (KBr) of 3-((2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)methyl)-2,2,5,5-tetraethyl-4-(hydroxymethyl)pyrrolidin-1-oxyl (7)



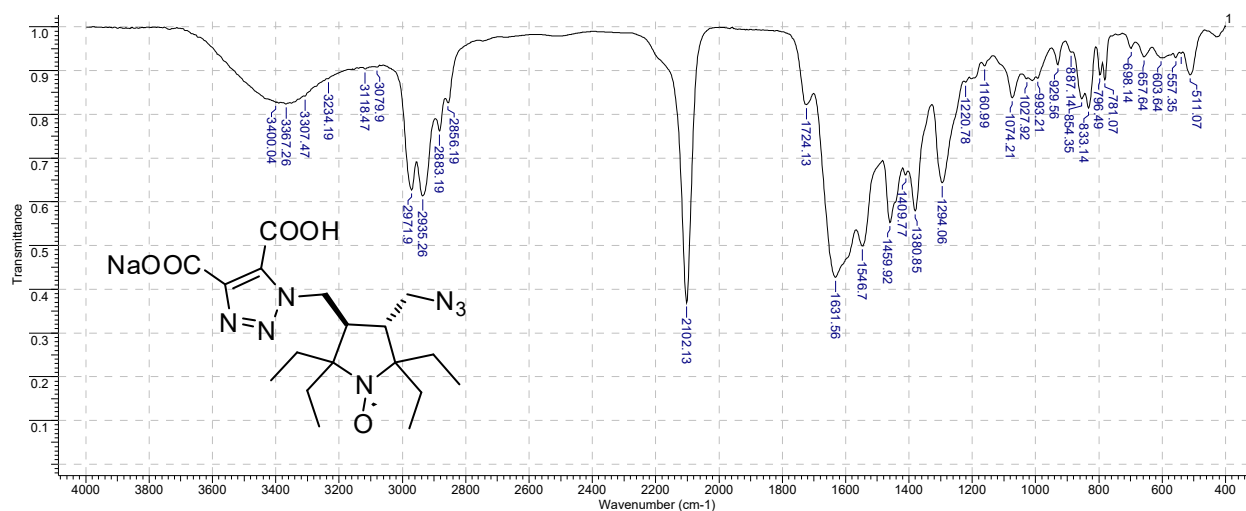
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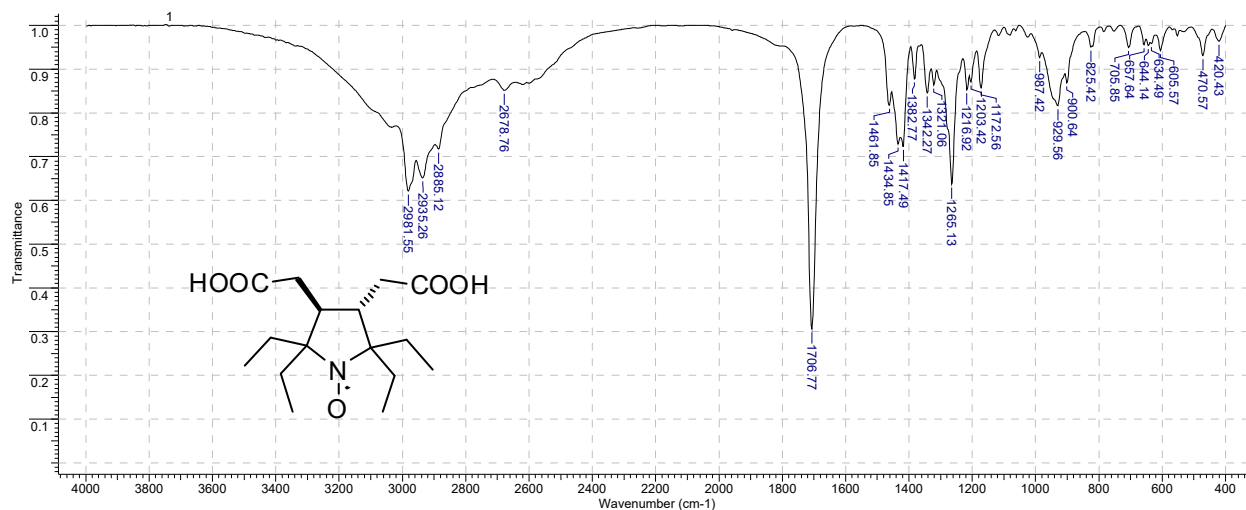
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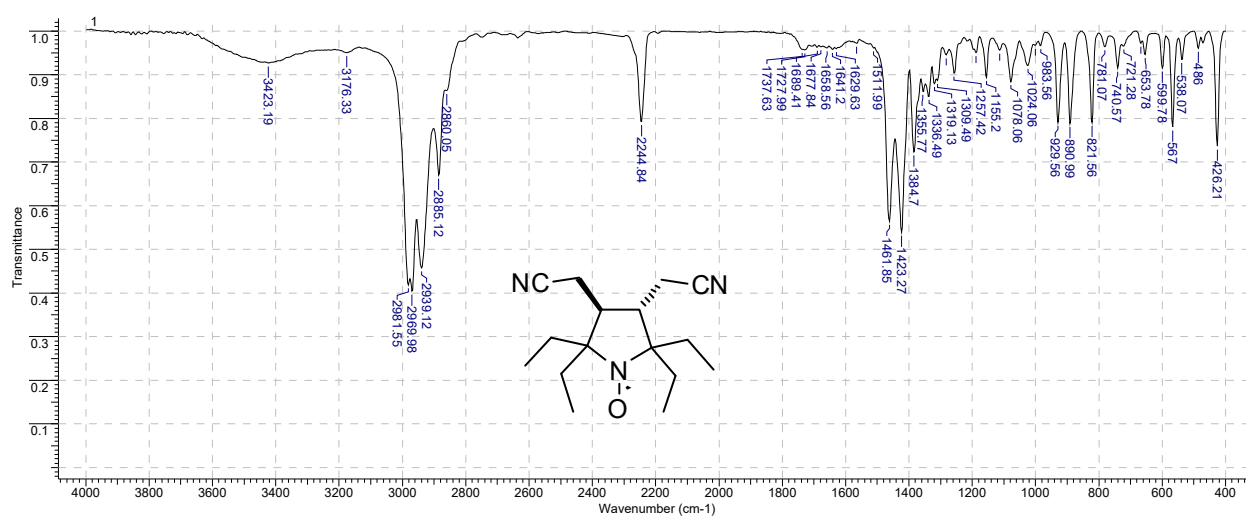
IR (KBr) of 3-(azidomethyl)-4-((4,5-dicarboxy-1H-1,2,3-triazol-1-yl)methyl)-2,2,5,5-tetraethylpyrrolidin-1-oxyl monosodium salt (20)



IR (KBr) of 3,4-bis(carboxymethyl)-2,2,5,5-tetraethylpyrrolidin-1-oxyl (23)



IR (KBr) of 3,4-bis(cyanomethyl)-2,2,5,5-tetraethylpyrrolidin-1-oxyl (24)



XRD Data

Table 1

XRD data for compounds **3**, **4**, **6**, **8**, **10**, **12a**, **15a**, **15b**, **20**.

Compound	3	4
Empirical formula	C ₁₆ H ₃₂ NO ₇ S ₂	C ₁₅ H ₃₀ NO ₅ S
Formula weight	414.54	336.46
Temperature K	296(2)	296(2)
Wavelength Å	0.71073	0.71073
Crystal system	Tetragonal	Triclinic
Space group	I4 ₁ /a	P-1
Unit cell dimensions <i>a</i> Å	11.2559(3)	9.1916(5)
<i>b</i> Å	11.2559(3)	13.3515(9)
<i>c</i> Å	34.1134(15)	14.9892(10)
α °	90	97.112(2)
β °	90	92.783(2)
γ °	90	93.154(2)
Volume Å ³	4322.0(3)	1819.7(2)
<i>Z</i>	8	4
Density (calcd.) Mg.m ⁻³	1.274	1.228
Abs. coefficient mm ⁻¹	0.280	0.199
F(000)	1784	732
Crystal size mm ³	0.35 x 0.6 x 0.6	0.05 x 0.30 x 0.80
Θ range for data collection °	1.9 – 27.6	1.9 – 25.1
Index ranges	-14 ≤ <i>h</i> ≤ 14, -14 ≤ <i>k</i> ≤ 14, -44 ≤ <i>l</i> ≤ 42	-10 ≤ <i>h</i> ≤ 10, -15 ≤ <i>k</i> ≤ 15, -17 ≤ <i>l</i> ≤ 17
Reflections collected	27582	20336
Independent reflections	2506 R(int) = 0.042	6443 R(int) = 0.039
Completeness to θ %	99.8	99.6
Data / restraints / parameters	2606 / 0 / 122	6443 / 12 / 409
Goodness-of-fit on F^2	1.01	1.00
Final R indices $I > 2\sigma(I)$	R ₁ = 0.0464, wR ₂ = 0.1222	R ₁ = 0.0698, wR ₂ = 0.1848
Final R indices (all data)	R ₁ = 0.0552, wR ₂ = 0.1318	R ₁ = 0.1227, wR ₂ = 0.1978
Largest diff. peak / hole e.Å ⁻³	0.56/ -0.27	0.86/ -0.26
CCDC	2308349	2308350

Table 1 (*continued*)

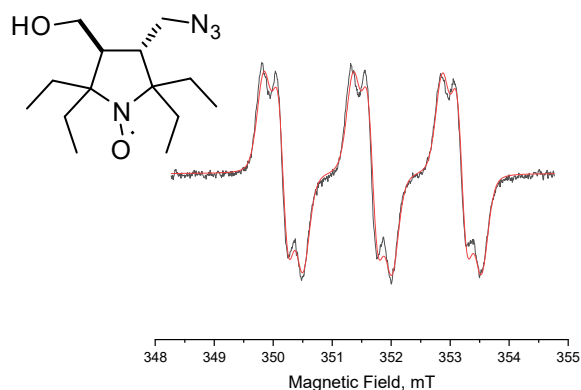
Compound	6	8	10
Empirical formula	C ₁₄ H ₂₉ N ₂ O ₂	C ₁₉ H ₃₇ N ₂ O ₄	C ₁₉ H ₃₆ N ₅ O ₃
Formula weight	257.39	357.50	382.53
Temperature K	296(2)	296(2)	200(2)
Wavelength Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	Cc	P2 ₁ /n	Cc
Unit cell dimensions <i>a</i> Å	8.1003(10)	8.1312(3)	16.0849(11)
<i>b</i> Å	30.326(4)	24.0467(8)	12.2256(11)
<i>c</i> Å	13.2222(16)	12.0626(4)	12.2167(9)
α °	90	90	90
β °	106.333(4)	108.7839(17)	113.772(4)
γ °	90	90	90
Volume Å ³	3116.9(7)	2232.96(14)	2198.6(3)
<i>Z</i>	8	4	4
Density (calcd.) Mg.m ⁻³	1.097	1.063	1.156
Abs. coefficient mm ⁻¹	0.073	0.074	0.079
<i>F</i> (000)	1144	788	836
Crystal size mm ³	0.20 x 0.40 x 0.80	0.07 x 0.12 x 0.68	0.10 x 0.30 x 0.35
Θ range for data collection °	1.3 – 26.1	2.7 – 25.1	2.2 – 25.0
Index ranges	-10 ≤ <i>h</i> ≤ 9, -37 ≤ <i>k</i> ≤ 37, -16 ≤ <i>l</i> ≤ 16	-9 ≤ <i>h</i> ≤ 6, -28 ≤ <i>k</i> ≤ 28, -13 ≤ <i>l</i> ≤ 14	-18 ≤ <i>h</i> ≤ 19, -14 ≤ <i>k</i> ≤ 14, -14 ≤ <i>l</i> ≤ 13
Reflections collected	22931	21652	10723
Independent reflections	6163 <i>R</i> (int) = 0.058	3970 <i>R</i> (int) = 0.059	3780 <i>R</i> (int) = 0.050
Completeness to θ %	99.6	99.5	97.2
Data / restraints / parameters	6163 / 2 / 336	3970 / 0 / 241	3780 / 39 / 250
Goodness-of-fit on <i>F</i> ²	1.10	0.99	1.04
Final <i>R</i> indices <i>I</i> > 2 σ (<i>I</i>)	<i>R</i> ₁ = 0.0713, <i>wR</i> ₂ = 0.1709	<i>R</i> ₁ = 0.0475, <i>wR</i> ₂ = 0.1208	<i>R</i> ₁ = 0.0793, <i>wR</i> ₂ = 0.2009
Final <i>R</i> indices (all data)	<i>R</i> ₁ = 0.0978, <i>wR</i> ₂ = 0.1852	<i>R</i> ₁ = 0.0634, <i>wR</i> ₂ = 0.1320	<i>R</i> ₁ = 0.1098, <i>wR</i> ₂ = 0.2153
Largest diff. peak / hole e.Å ⁻³	0.26 / -0.35	0.20 / -0.15	0.77 / -0.29
CCDC	2309021	2308351	23082352

Table 1 (*continued*)

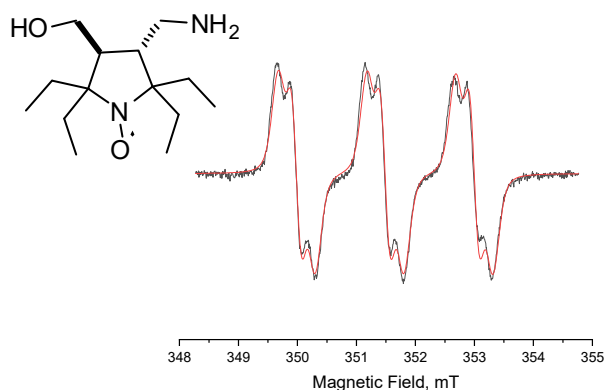
Compound	12a	15a	15b
Empirical formula	C ₁₄ H ₂₆ N ₇ O	C ₂₀ H ₃₄ N ₃ O ₃	C ₂₀ H ₃₂ N ₃ O ₃
Formula weight	308.42	364.50	357.50
Temperature K	296(2)	296(2)	296(2)
Wavelength Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	P2 ₁ /n	P2 ₁ 2 ₁ 2 ₁	P2 ₁
Unit cell dimensions <i>a</i> Å	15.2867(11)	8.0517(11)	9.063(2)
<i>b</i> Å	7.7128(5)	9.9408(12)	10.668(2)
<i>c</i> Å	15.5815(12)	26.754(3)	11.401(3)
α °	90	90	90
β °	112.088(3)	90	110.718(8)
γ °	90	90	90
Volume Å ³	1702.3(2)	2141.4(5)	1031.1(4)
<i>Z</i>	4	4	2
Density (calcd.) Mg.m ⁻³	1.203	1.131	1.168
Abs. coefficient mm ⁻¹	0.082	0.076	0.079
F(000)	668	796	788
Crystal size mm ³	0.08 x 0.15 x 0.55	0.22 x 0.40 x 0.64	0.20 x 0.40 x 0.80
Θ range for data collection °	2.4 - 26.1	2.6 – 25.6	2.75 – 26.1
Index ranges	-18 ≤ <i>h</i> ≤ 18, -9 ≤ <i>k</i> ≤ 9, -19 ≤ <i>l</i> ≤ 19	-7 ≤ <i>h</i> ≤ 9, -10 ≤ <i>k</i> ≤ 12, -32 ≤ <i>l</i> ≤ 29	-11 ≤ <i>h</i> ≤ 11, -13 ≤ <i>k</i> ≤ 13, -13 ≤ <i>l</i> ≤ 14
Reflections collected	21917	12566	8396
Independent reflections	3367 R(int) = 0.040	3993 R(int) = 0.051	3973 R(int) = 0.064
Completeness to θ %	99.7	99.7	99.8
Data / restraints / parameters	3367 / 0 / 203	3993 / 0 / 235	3973 / 1 / 241
Goodness-of-fit on F^2	1.04	1.09	1.01
Final R indices $I > 2\sigma(I)$	R ₁ = 0.0541, wR ₂ = 0.1327	R ₁ = 0.0673, wR ₂ = 0.1779	R ₁ = 0.0588, wR ₂ = 0.1538
Final R indices (all data)	R ₁ = 0.0895, wR ₂ = 0.1530	R ₁ = 0.0916, wR ₂ = 0.1917	R ₁ = 0.0779, wR ₂ = 0.1724
Largest diff. peak / hole e.Å ⁻³	0.25 / -0.17	0.22 / -0.23	0.36 / -0.23
CCDC	2308353	2308354	2308355

Compound	20
Empirical formula	C ₁₈ H ₂₈ N ₇ O ₇ Na
Formula weight	477.46
Temperature K	200(2)
Wavelength Å	0.71073
Crystal system	Monoclinic
Space group	P2 ₁ /n
Unit cell dimensions <i>a</i> Å	12.0326(6)
<i>b</i> Å	10.6711(4)
<i>c</i> Å	18.4973(8)
α °	90
β °	92.254(2)
γ °	90
Volume Å ³	2373.24(18)
<i>Z</i>	4
Density (calcd.) Mg.m ⁻³	1.336
Abs. coefficient mm ⁻¹	0.119
F(000)	1008
Crystal size mm ³	0.10 x 0.40 x 0.50
Θ range for data collection °	2.1 – 27.6
Index ranges	-15 ≤ <i>h</i> ≤ 15, -13 ≤ <i>k</i> ≤ 13, -19 ≤ <i>l</i> ≤ 24
Reflections collected	37337
Independent reflections	5462 R(int) = 0.053
Completeness to θ %	99.9
Data / restraints / parameters	5462 / 18 / 342
Goodness-of-fit on F^2	1.05
Final R indices $I > 2\sigma(I)$	R ₁ = 0.069, wR ₂ = 0.1726
Final R indices (all data)	R ₁ = 0.1018, wR ₂ = 0.1936
Largest diff. peak / hole e.Å ⁻³	1.68 / -0.43
CCDC	2308356

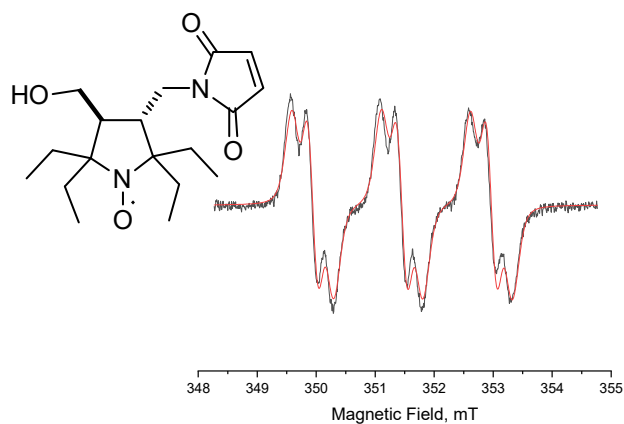
EPR Spectra



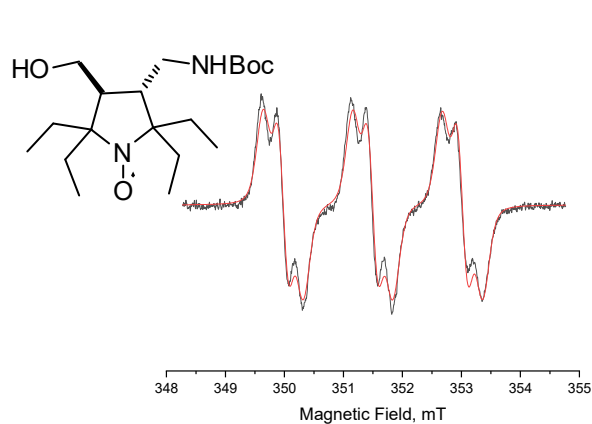
EPR of 3-(Azidomethyl)-2,2,5,5-tetraethyl-4-(hydroxymethyl)pyrrolidin-1-oxyl (5)



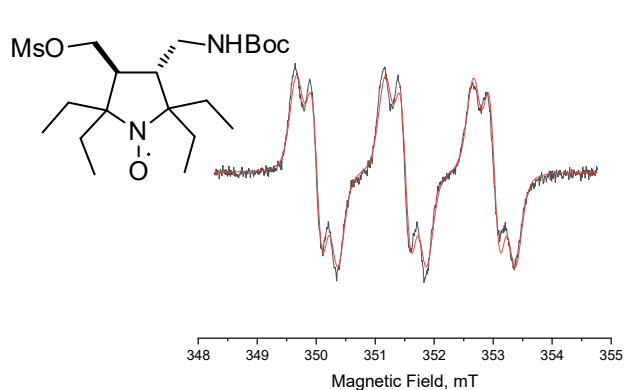
EPR of 3-(Aminomethyl)-2,2,5,5-tetraethyl-4-(hydroxymethyl)pyrrolidin-1-oxyl (6)



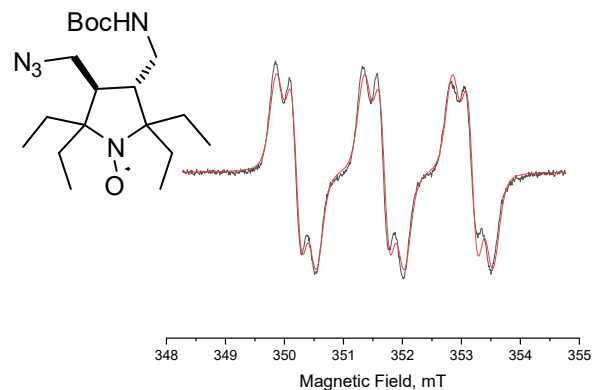
EPR of 3-((2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)methyl)-2,2,5,5-tetraethyl-4-(hydroxymethyl)pyrrolidin-1-oxyl (7)



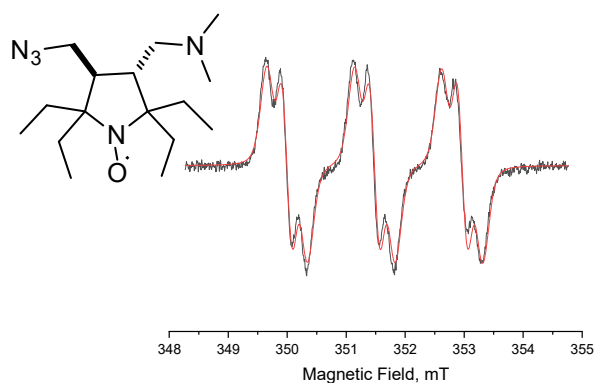
EPR of 3-(((tert-Butoxycarbonyl)amino)methyl)-2,2,5,5-tetraethyl-4-(hydroxymethyl)pyrrolidin-1-oxyl (8)



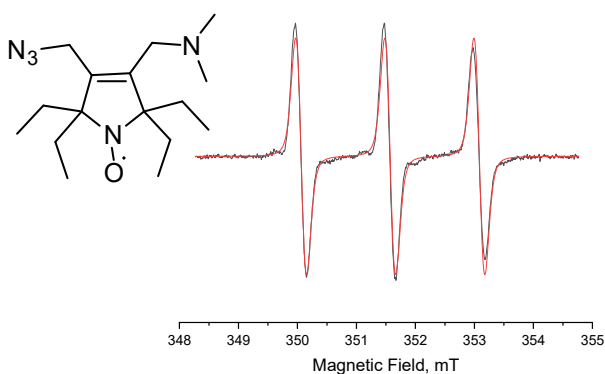
EPR of 3-(((tert-Butoxycarbonyl)amino)methyl)-2,2,5,5-tetraethyl-4-(((methylsulfonyl)oxy)methyl)pyrrolidin-1-oxyl (9)



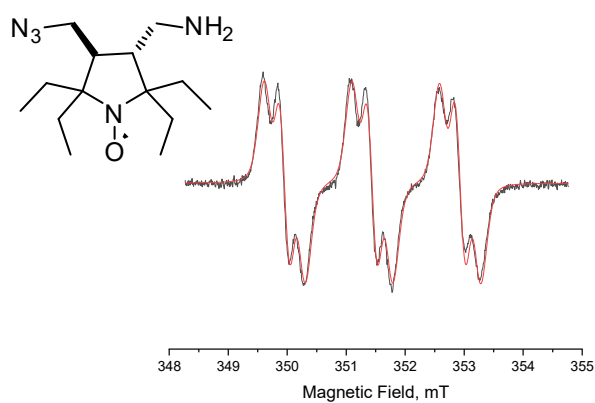
EPR of 3-(Azidomethyl)-4-(((tert-butoxycarbonyl)amino)methyl)-2,2,5,5-tetraethylpyrrolidin-1-oxyl (10)



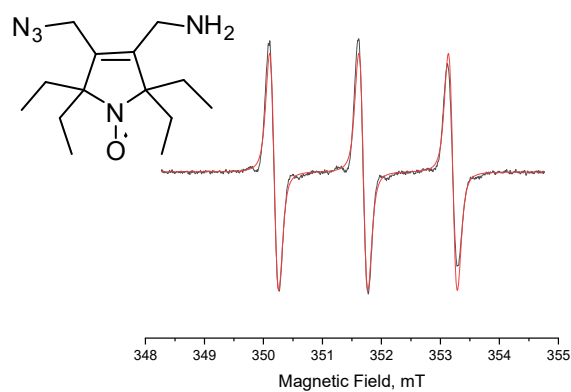
EPR of 3-(azidomethyl)-4-((dimethylamino)methyl)-2,2,5,5-tetraethylpyrrolidin-1-oxyl (11a)



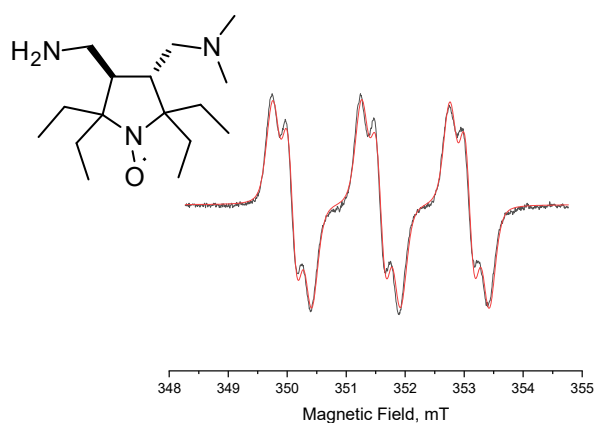
EPR of 3-(azidomethyl)-4-((dimethylamino)methyl)-2,2,5,5-tetraethyl-2,5-dihydro-1H-pyrrol-1-oxyl (11b)



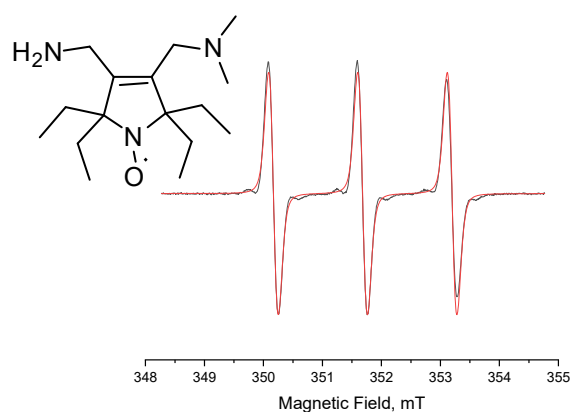
EPR of 3-(aminomethyl)-4-(azidomethyl)-2,2,5,5-tetraethylpyrrolidin-1-oxyl (13a)



EPR of 3-(aminomethyl)-4-(azidomethyl)-2,2,5,5-tetraethyl-2,5-dihydro-1H-pyrrol-1-oxyl (13b)

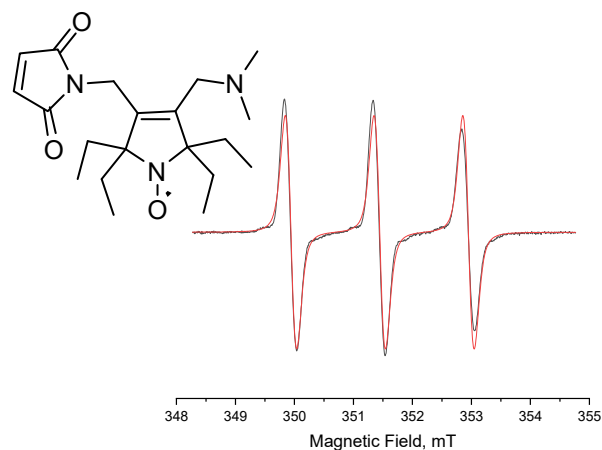
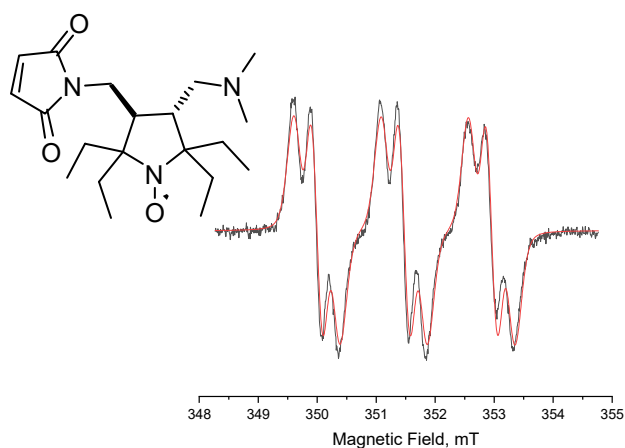


EPR of 3-(aminomethyl)-4-((dimethylamino)methyl)-2,2,5,5-tetraethylpyrrolidin-1-oxyl (14a)



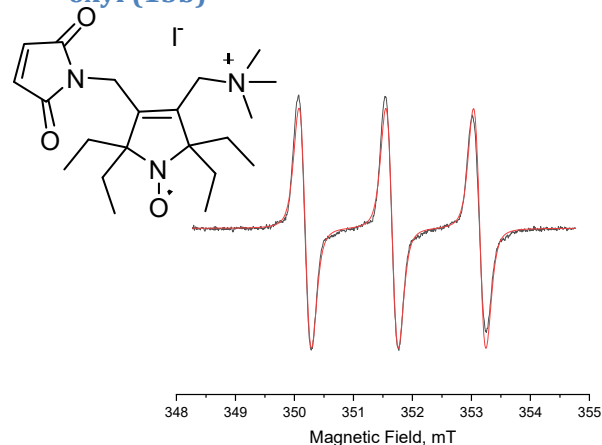
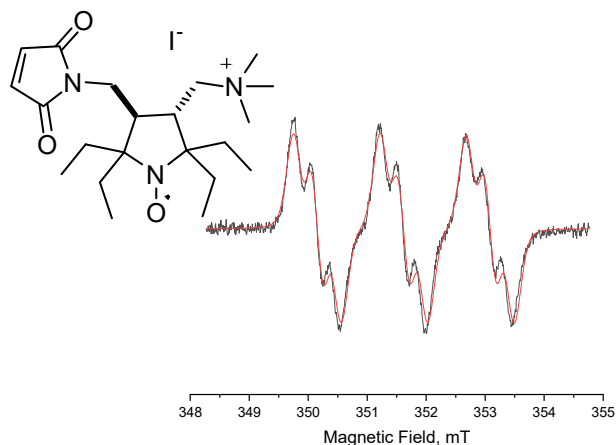
EPR of 3-(aminomethyl)-4-((dimethylamino)methyl)-2,2,5,5-tetraethyl-2,5-dihydro-1H-pyrrol-1-oxyl (14b)

S25



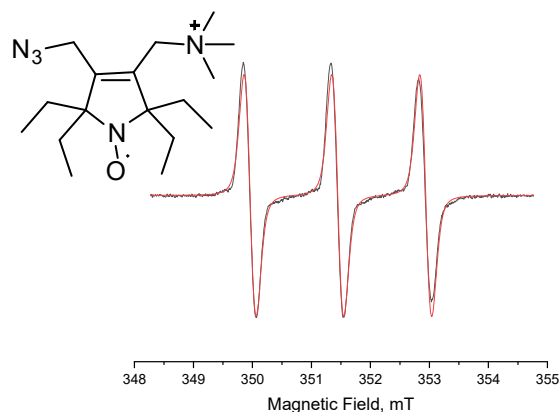
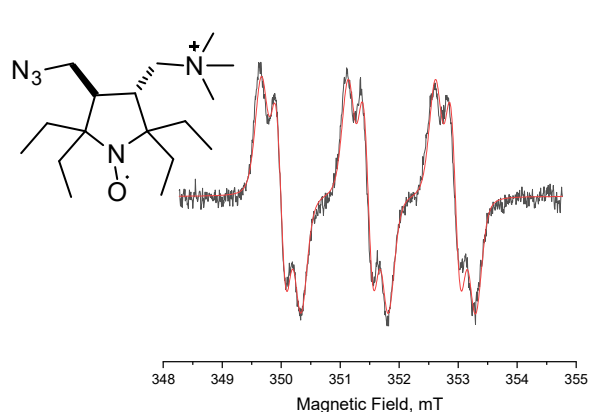
EPR of 3-((dimethylamino)methyl)-4-((2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)methyl)-2,2,5,5-tetraethylpyrrolidin-1-oxyl (15a)

EPR of 3-((dimethylamino)methyl)-4-((2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)methyl)-2,2,5,5-tetraethyl-2,5-dihydro-1H-pyrrol-1-oxyl (15b)



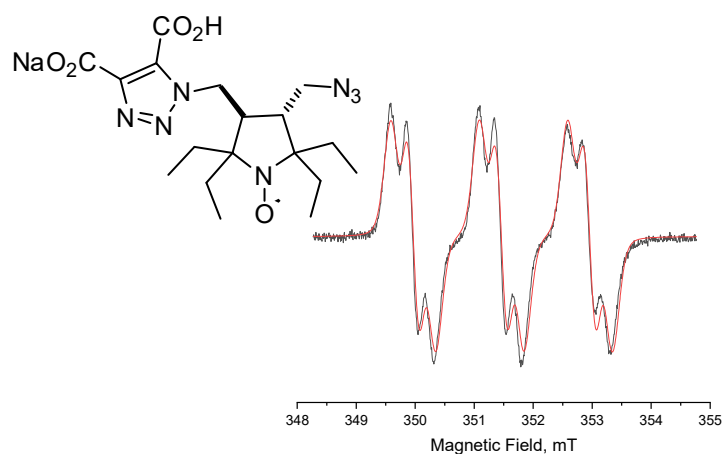
EPR of 3-((2,5-Dioxo-2,5-dihydro-1H-pyrrol-1-yl)methyl)-2,2,5,5-tetraethyl-4-((trimethylammonio)methyl)pyrrolidin-1-oxyl monoiodide (16a)

EPR of 3-((2,5-Dioxo-2,5-dihydro-1H-pyrrol-1-yl)methyl)-2,2,5,5-tetraethyl-4-((trimethylammonio)methyl)-2,5-dihydro-1H-pyrrol-1-oxyl monoiodide (16b)

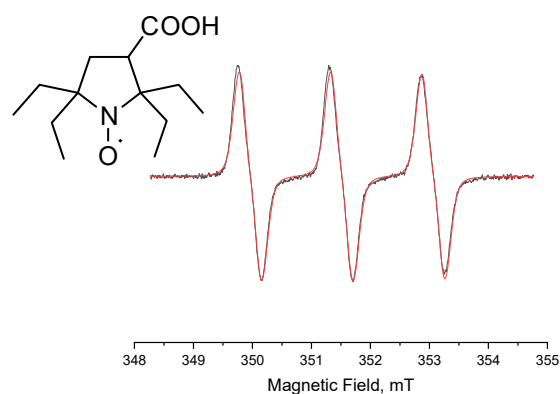


EPR of 3-(azidomethyl)-2,2,5,5-tetraethyl-4-((trimethylammonio)methyl)pyrrolidin-1-oxyl monoiodide (17a)

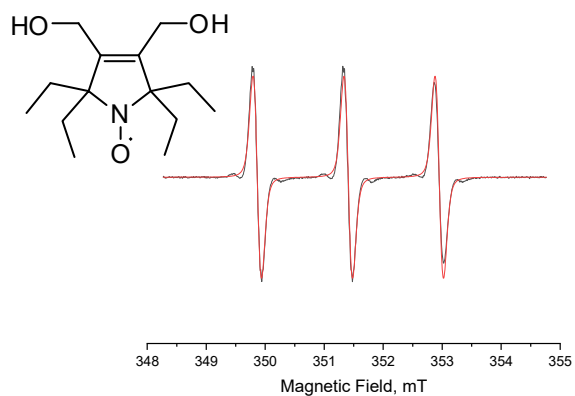
EPR of 3-(azidomethyl)-2,2,5,5-tetraethyl-4-((trimethylammonio)methyl)-2,5-dihydro-1H-pyrrol-1-oxyl monoiodide (17b)



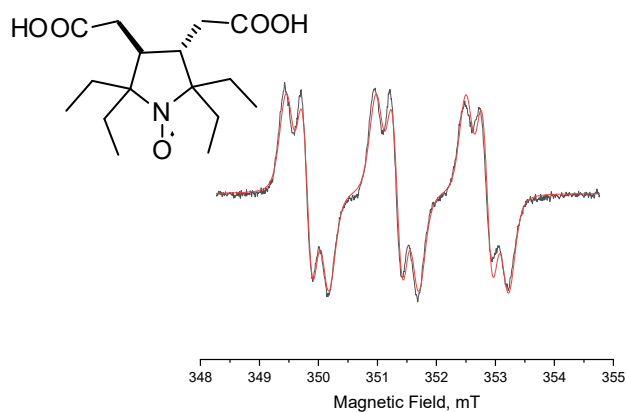
EPR of 3-(azidomethyl)-4-((4,5-dicarboxy-1H-1,2,3-triazol-1-yl)methyl)-2,2,5,5-tetraethylpyrrolidin-1-oxyl monosodium salt (20)



EPR of 3-carboxy-2,2,5,5-tetraethylpyrrolidin-1-oxyl (21)



EPR of 3,4-bis(hydroxymethyl)-2,2,5,5-tetraethyl-2,5-dihydro-1H-pyrrol-1-oxyl (22)



EPR of 3,4-bis(carboxymethyl)-2,2,5,5-tetraethylpyrrolidin-1-oxyl (23)