# Supporting Information

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## NMR Spectra

**Figure S1**. $^1$H NMR (400 MHz; $CDCl_3$) of 2,2-dimethylpentan-3-ol

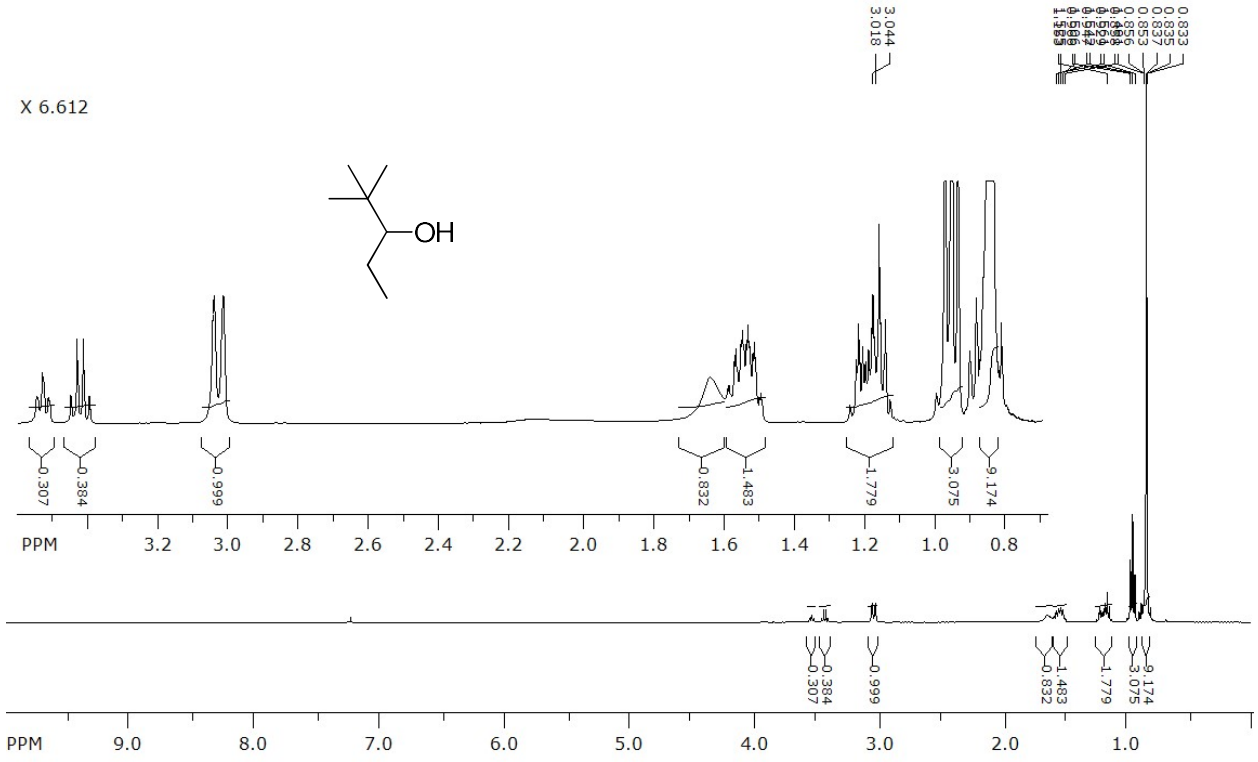



**Figure S2.** $^1$H NMR (400 MHz; $CDCl_3$) of 2,2-dimethylpentan-3-one

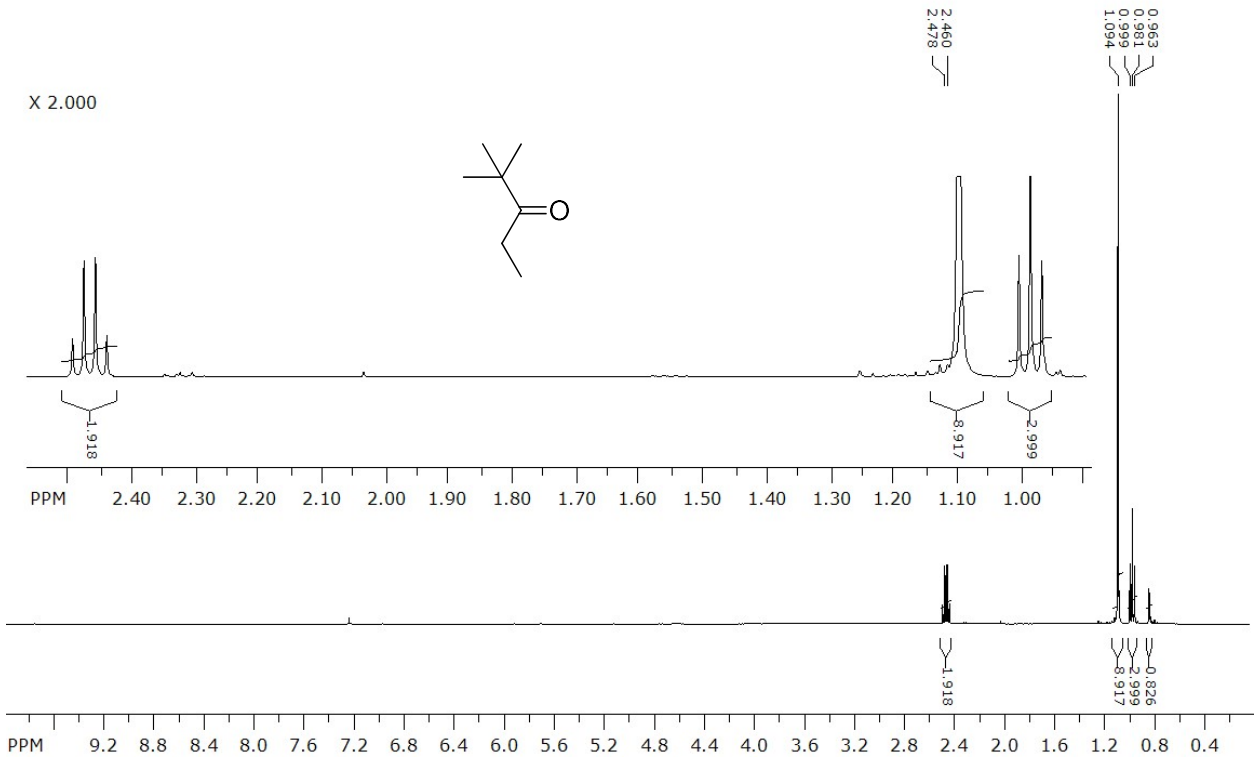


**Figure S3.** $^{1}H$ NMR (500 MHz; $CDCl_3$) of (2R(S),3R(S),4R(S),5S(R))-2,5-di-*tert*-butyl-3,4-bis(methoxycarbonyl)-2-ethylpyrrolidine (**8**)

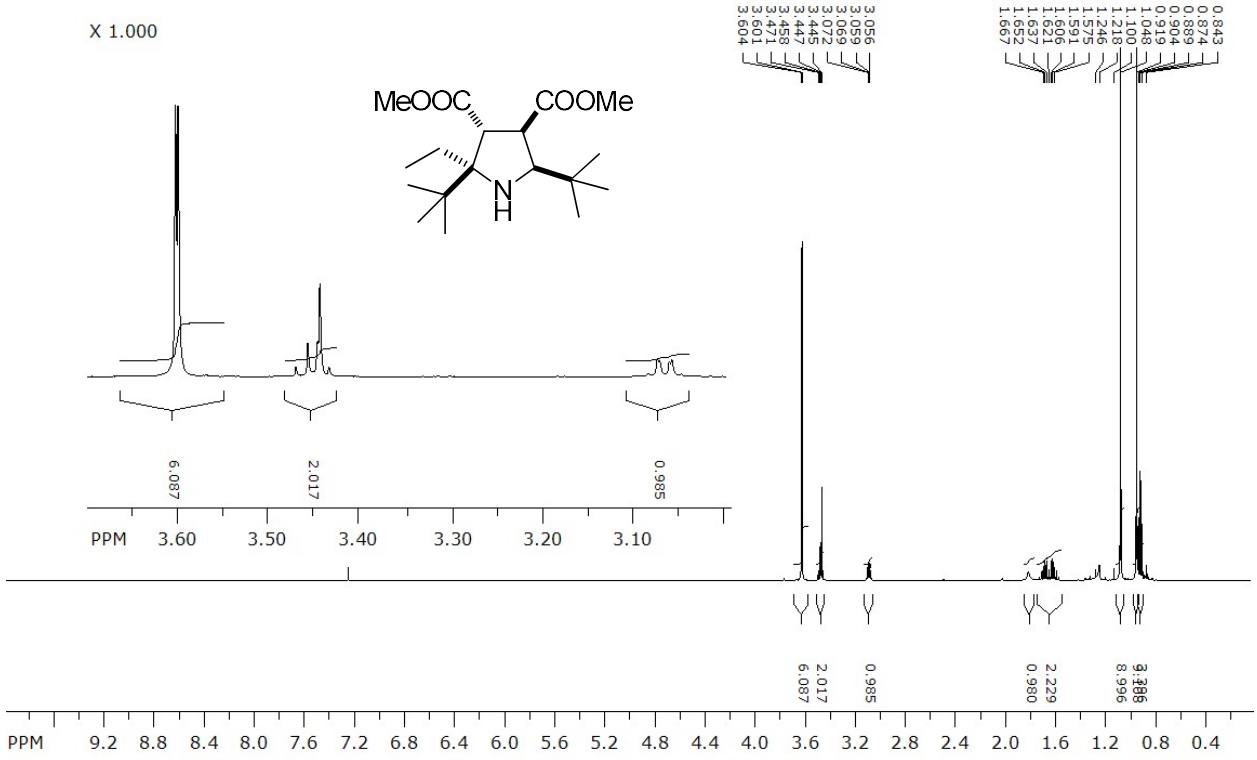



**Figure S4**. $^{13}C$ NMR (125 MHz; $CDCl_3$) of (2R(S),3R(S),4R(S),5S(R))-2,5-di-*tert*-butyl-3,4-bis(methoxycarbonyl)-2-ethylpyrrolidine (**8**)

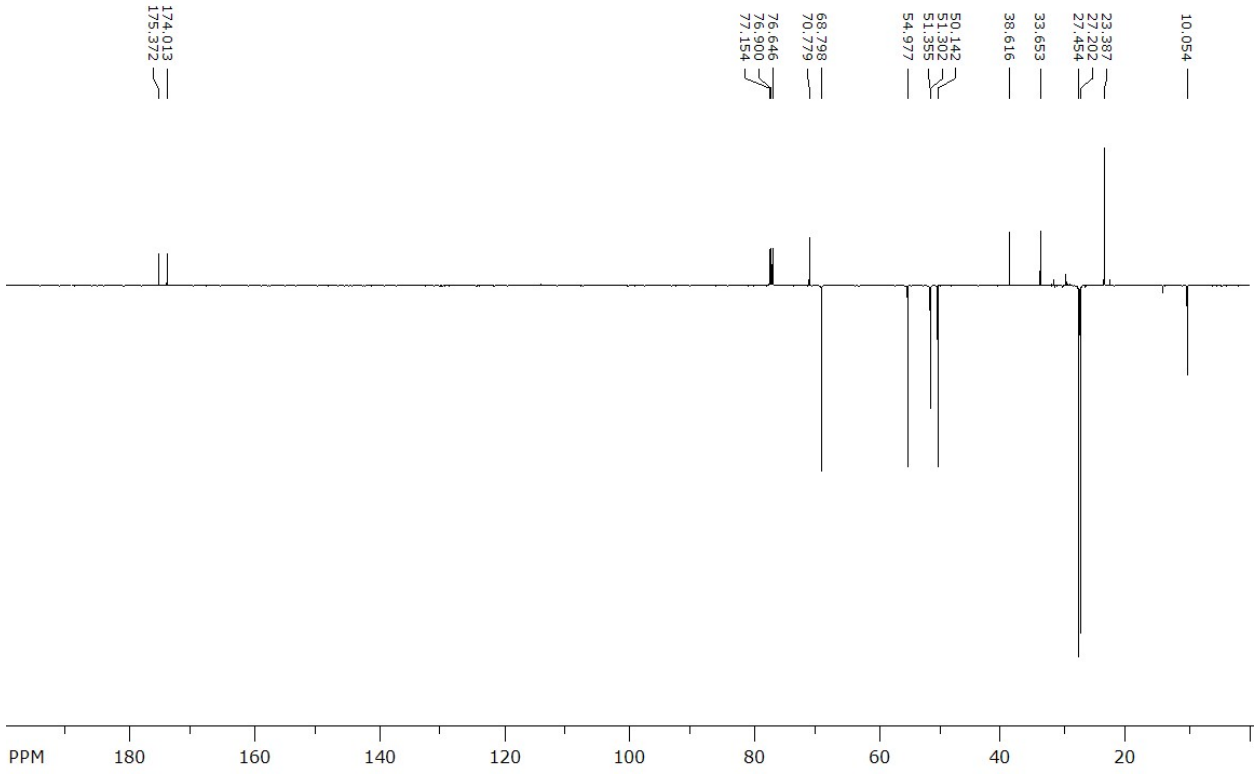


**Figure S5**. $^{1}H$ NMR (400 MHz; $(CD_3)_2CO$; $CF_3COOH$) of (2R(S),3R(S),4R(S),5S(R))-2,5-di-*tert*-butyl-3,4-bis(methoxycarbonyl)-2-ethylpyrrolidine (**8**)

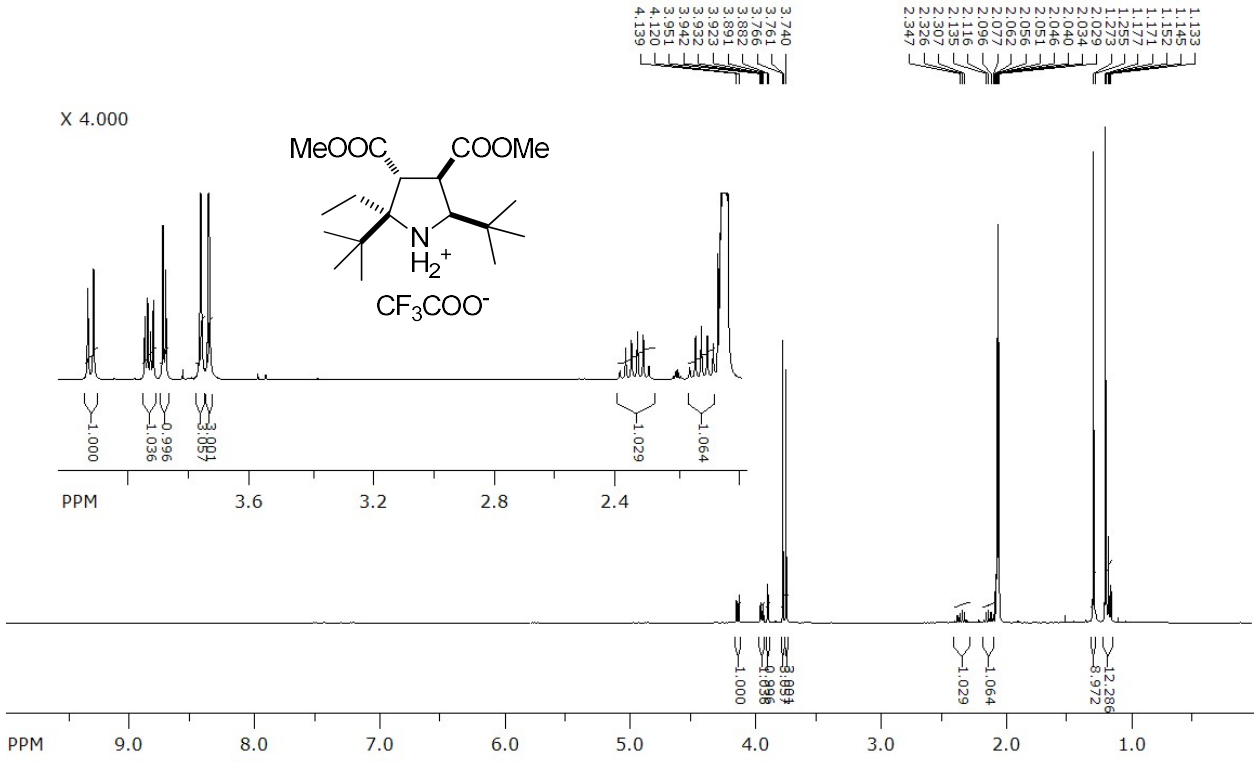



**Figure S6**. $^{13}C$ NMR (100 MHz; $(CD_3)_2CO$; $CF_3COOH$) of (2R(S),3R(S),4R(S),5S(R))-2,5-di-tert-butyl-3,4-bis(methoxycarbonyl)-2-ethylpyrrolidine (**8**)

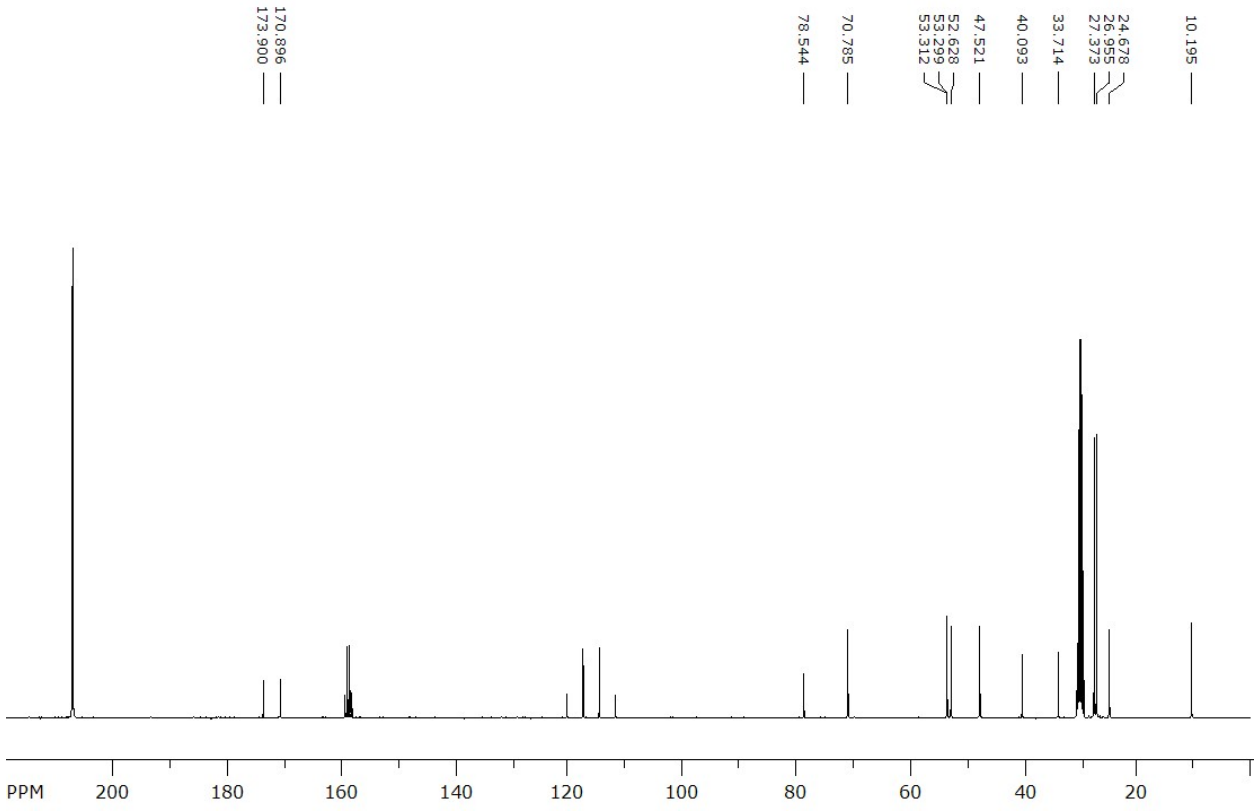


**Figure S7**. $^{1}H$ NMR (500 MHz; $CDCl_3$) of (2S(R),3R(S),4R(S),5R(S))-2,5-di-*tert*-butyl-3,4-bis(methoxycarbonyl)-2-ethylpyrrolidine (**9**)

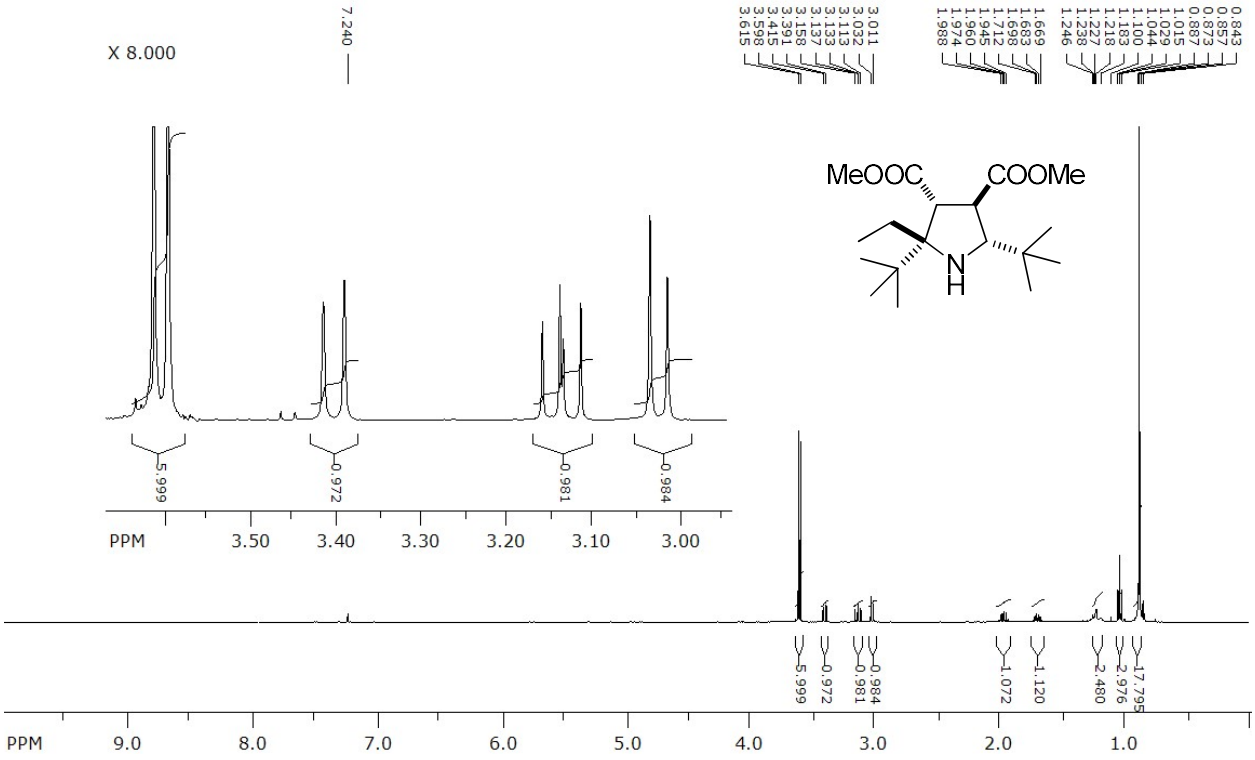



**Figure S8**. $^{13}C$ NMR (125 MHz; $CDCl_3$) of (2S(R),3R(S),4R(S),5R(S))-2,5-di-*tert*-butyl-3,4-bis(methoxycarbonyl)-2-ethylpyrrolidine (**9**)

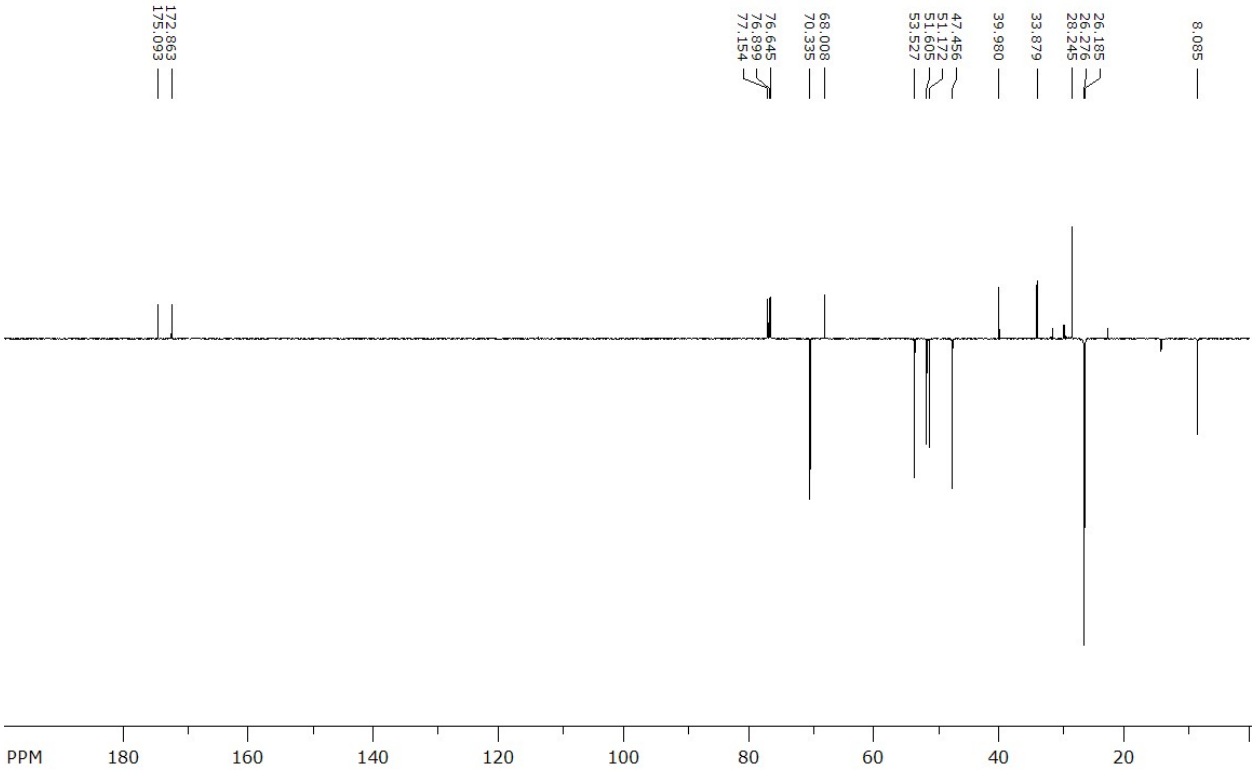


**Figure S9**. $^{1}H$ NMR (500 MHz; $CDCl_3$) of dimethyl 2-(1-((2,2-dimethylpentan-3-ylidene)amino)-2,2-dimethylpropyl)succinate (**10**)

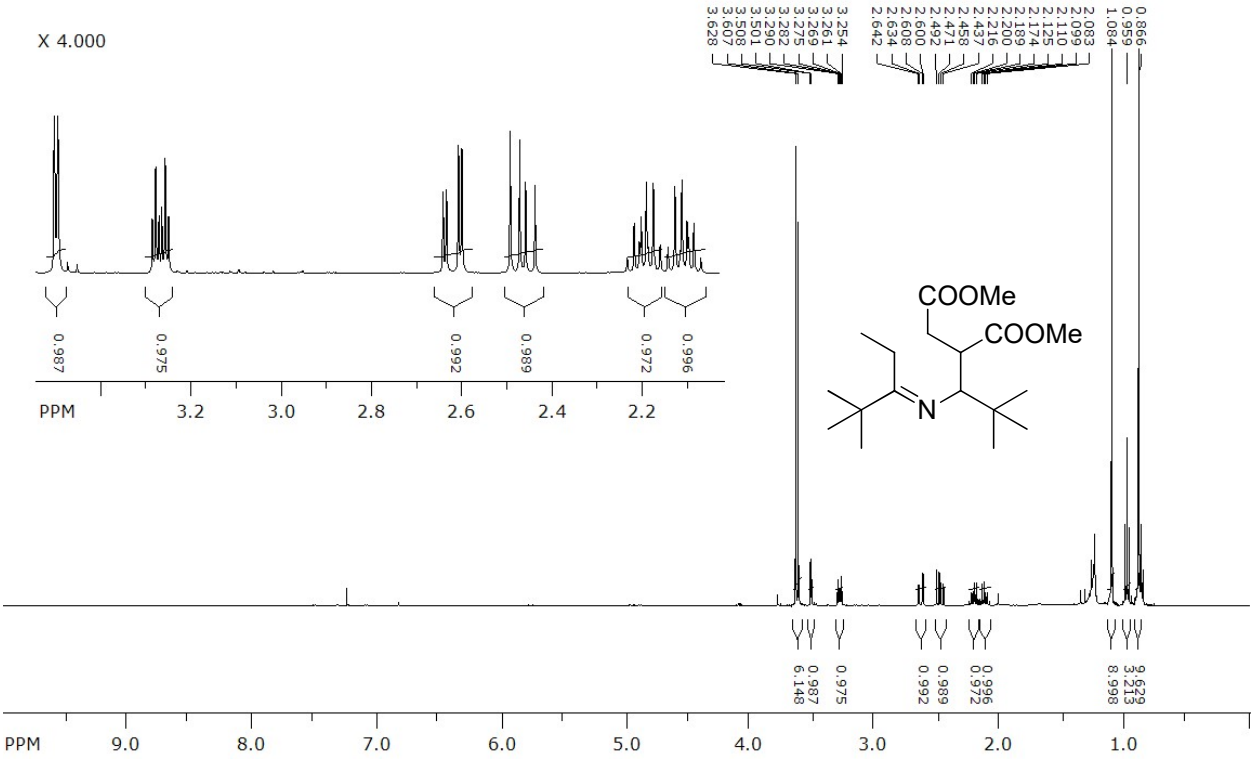



**Figure S10**. $^{13}C$ NMR (125 MHz; $CDCl_3$) of dimethyl 2-(1-((2,2-dimethylpentan-3-ylidene)amino)-2,2-dimethylpropyl)succinate (**10**)

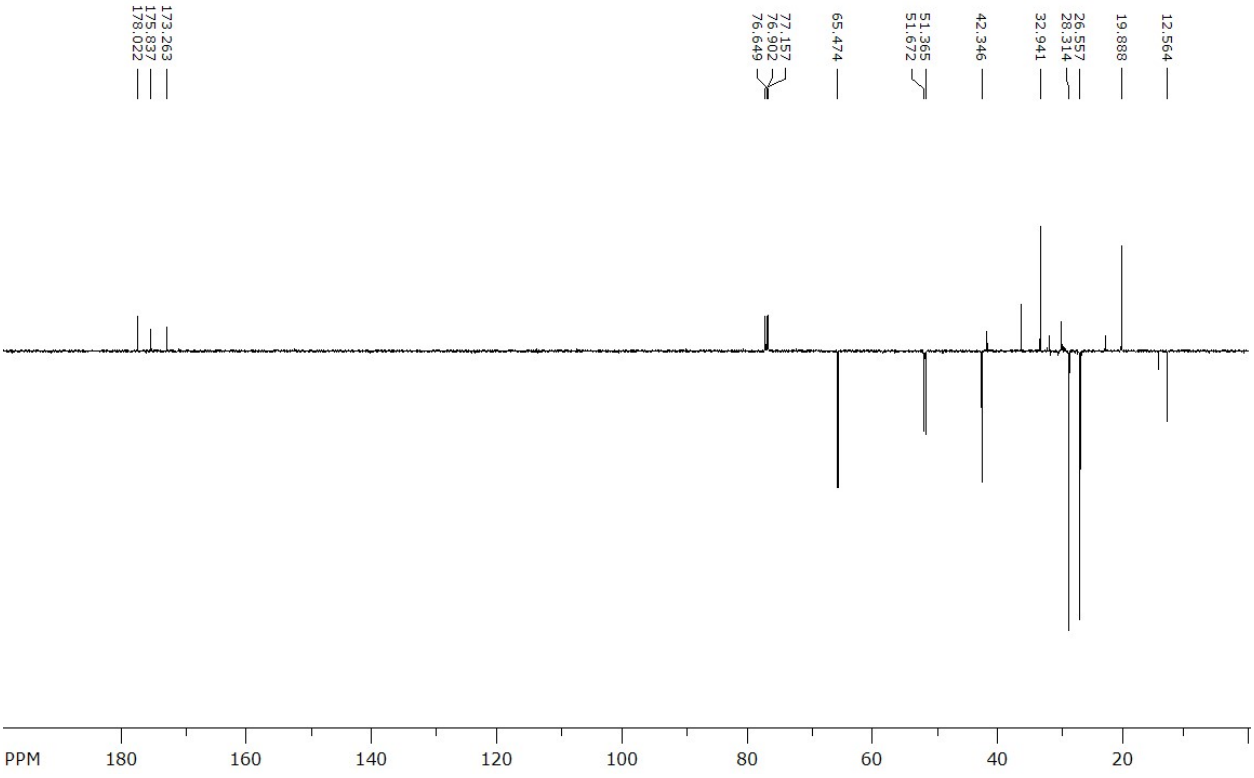


**Figure S11**. $^{1}H$ NMR (500 MHz; $CDCl_3$) of (2R(S),3R(S),4R(S),5S(R))-2,5-di-*tert*-butyl-3,4-bis(hydroxymethyl)-2-ethylpyrrolidine (**11**)

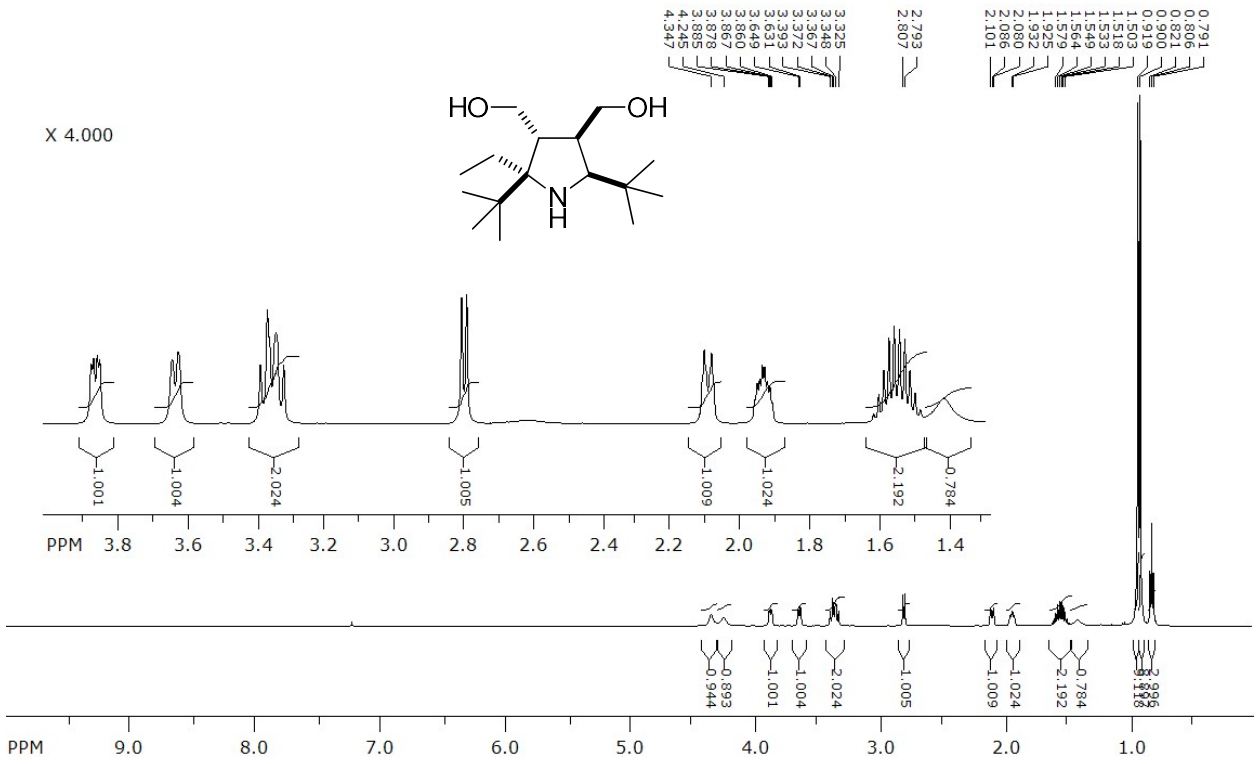



**Figure S12**. $^{13}C$ NMR (125 MHz; $CDCl_3$) of (2R(S),3R(S),4R(S),5S(R))-2,5-di-tert-butyl-3,4-bis(hydroxymethyl)-2-ethylpyrrolidine (**11**)

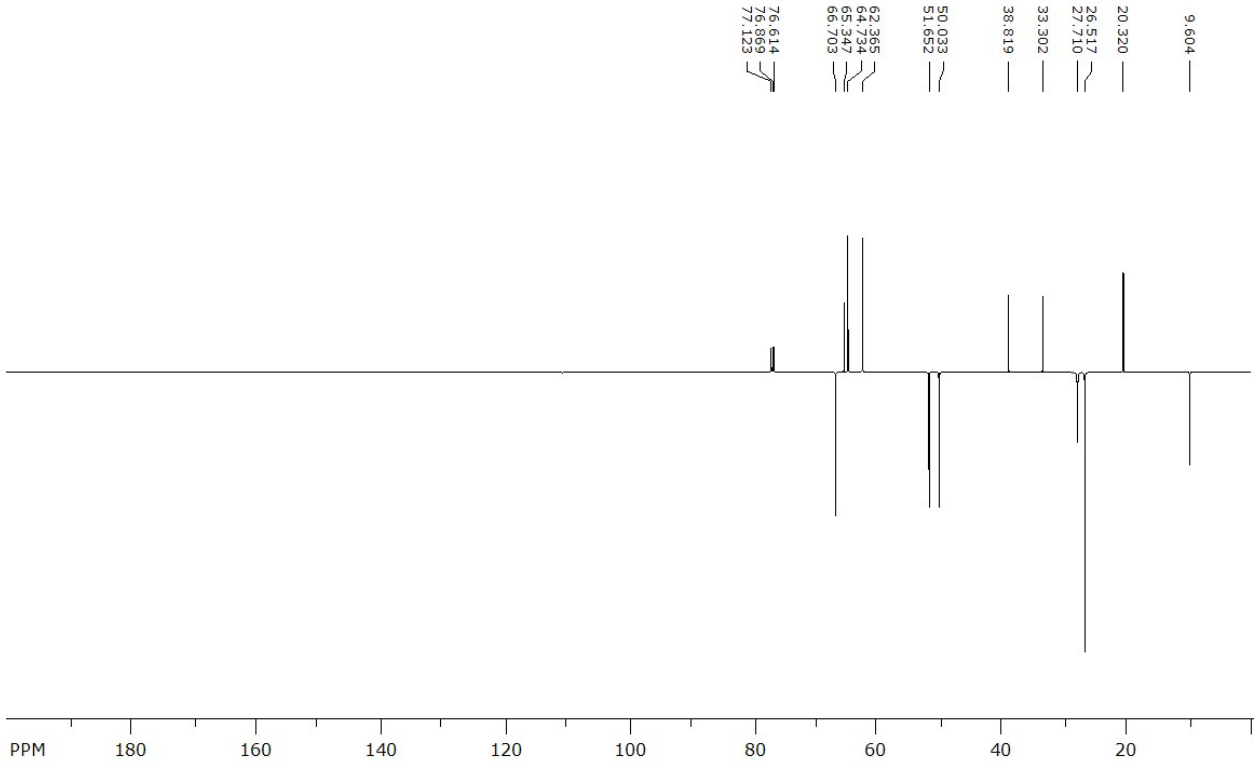


**Figure S13**. $^{1}H$ NMR (400 MHz, $CDCl_3$) of (2R(S),3R(S),4R(S))-2,5-di-*tert*-butyl-2-ethyl-3,4-bis(hydroxymethyl)-3,4-dihydro-2*H*-pyrrole 1-oxide (**12**)

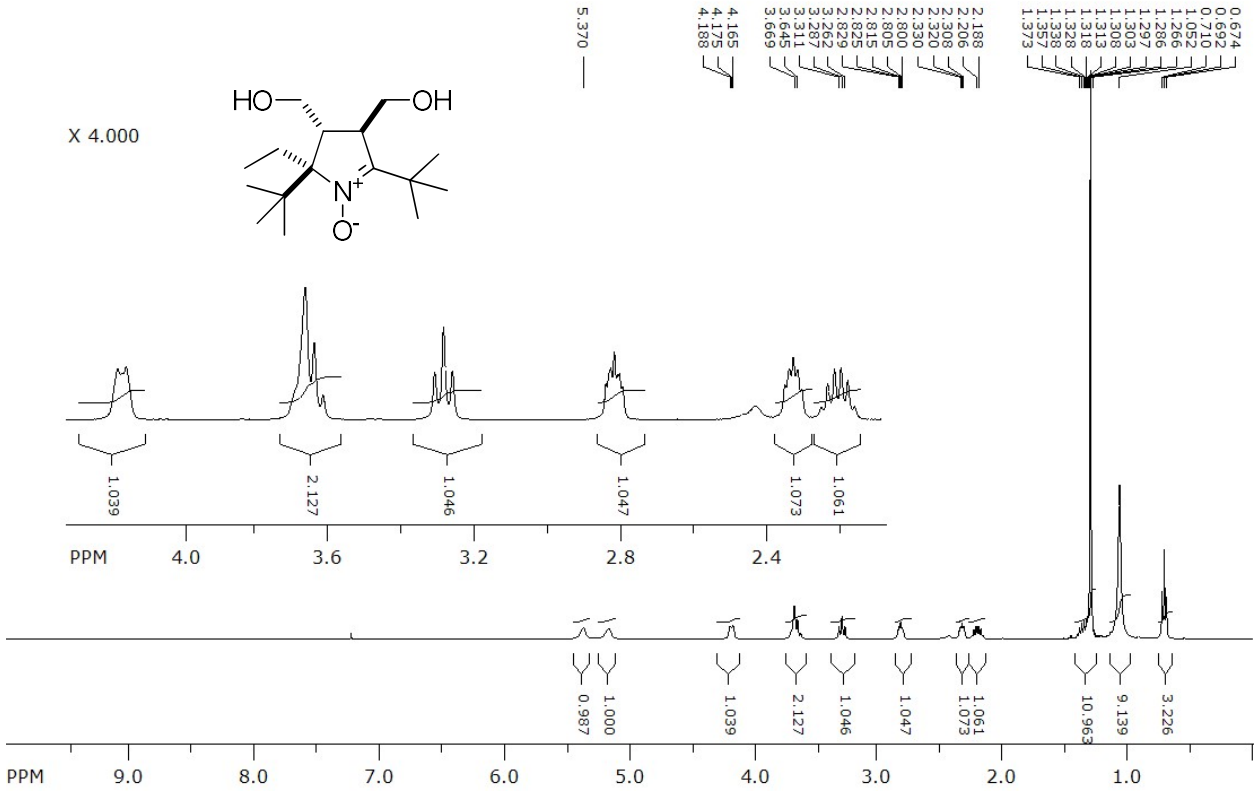



**Figure S14**. $^{13}C$ NMR (100 MHz, $CDCl_3$) of (2R(S),3R(S),4R(S))-2,5-di-*tert*-butyl-2-ethyl-3,4-bis(hydroxymethyl)-3,4-dihydro-2*H*-pyrrole 1-oxide (**12**)

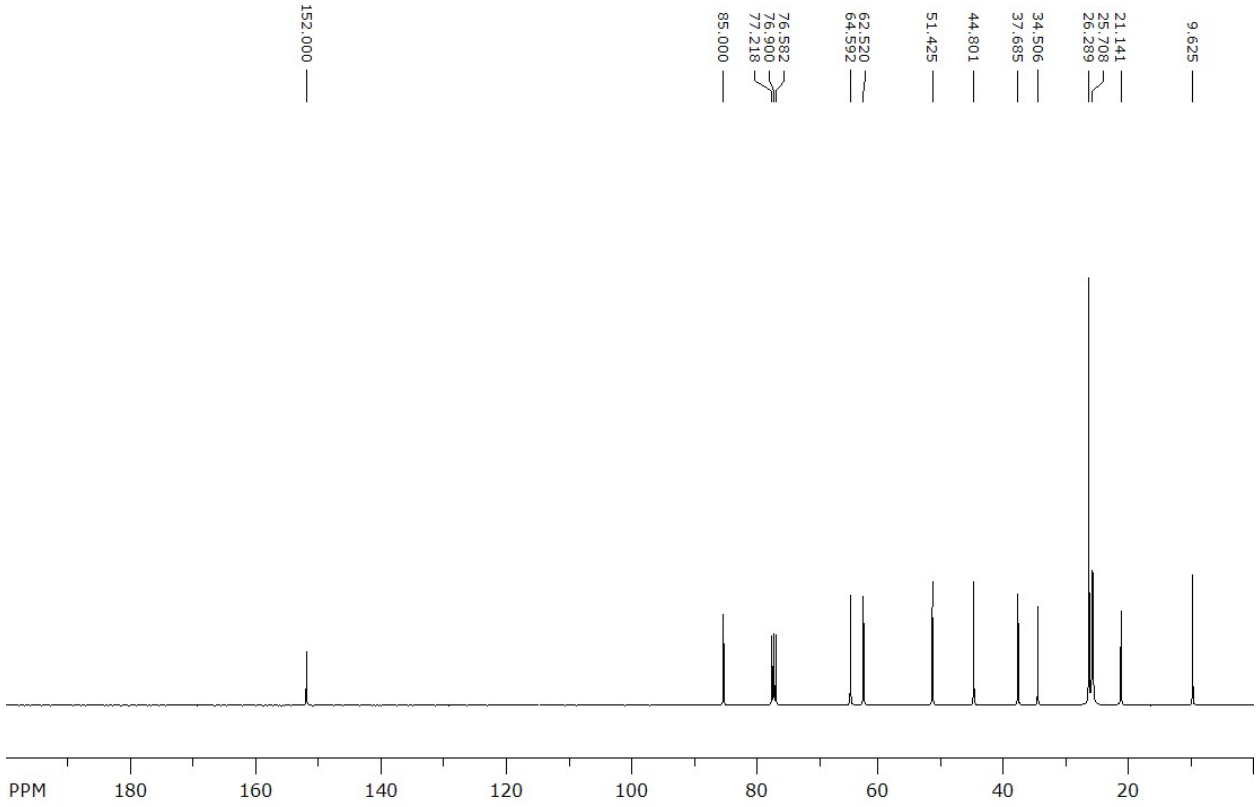


**Figure S15**. $^{1}H$ NMR (500 MHz, $CDCl_3$) of (2R(S),3R(S),4R(S))-2,5-di-*tert*-butyl-2-ethyl-3,4-bis(((2-methoxypropan-2-yl)oxy)methyl)-3,4-dihydro-2*H*-pyrrole 1-oxide (**14**)

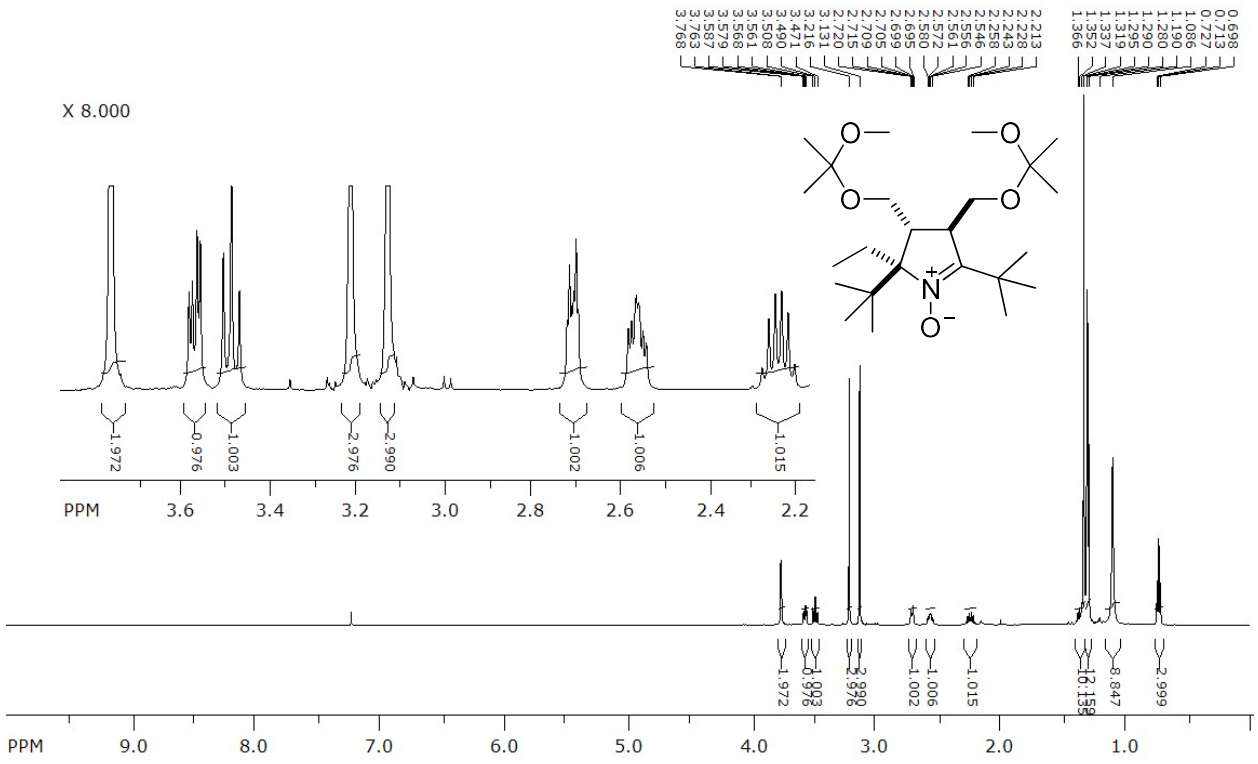



**Figure S16**. $^{13}C$ NMR (125 MHz, $CDCl_3$) of (2R(S),3R(S),4R(S))-2,5-di-tert-butyl-2-ethyl-3,4-bis(((2-methoxypropan-2-yl)oxy)methyl)-3,4-dihydro-2*H*-pyrrole 1-oxide (**14**)

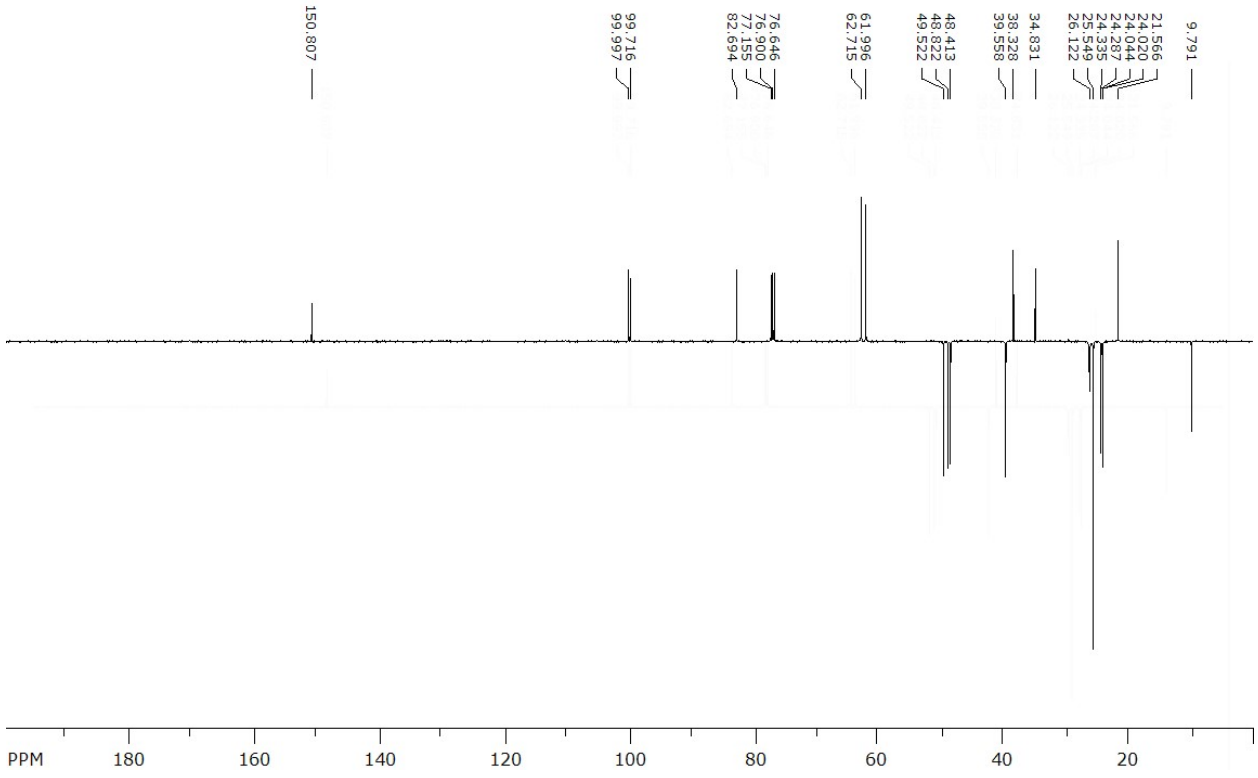


**Figure S17**. $^{1}H$ NMR (400 MHz; $CD_3OD$, Zn/$CF_3COOH$ system) of (2R(S),3R(S),4R(S),5S(R))-2,2,5-triethyl-5-*tert*-butyl-3,4-bis(hydroxymethyl)-pyrrolidine-1-oxyl

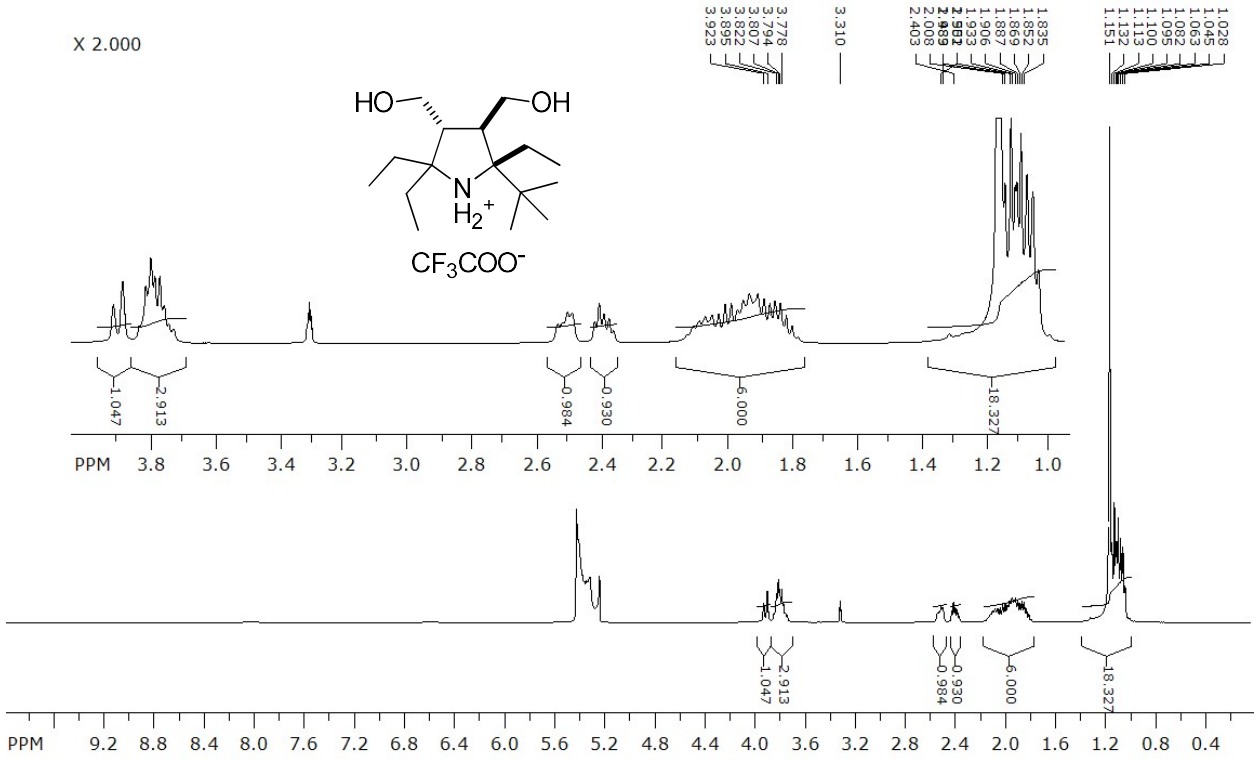



**Figure S18**. $^{13}C$ NMR (100 MHz; $CD_3OD$, Zn/$CF_3COOH$ system) of (2R(S),3R(S),4R(S),5S(R))-2,2,5-triethyl-5-*tert*-butyl-3,4-bis(hydroxymethyl)-pyrrolidine-1-oxyl

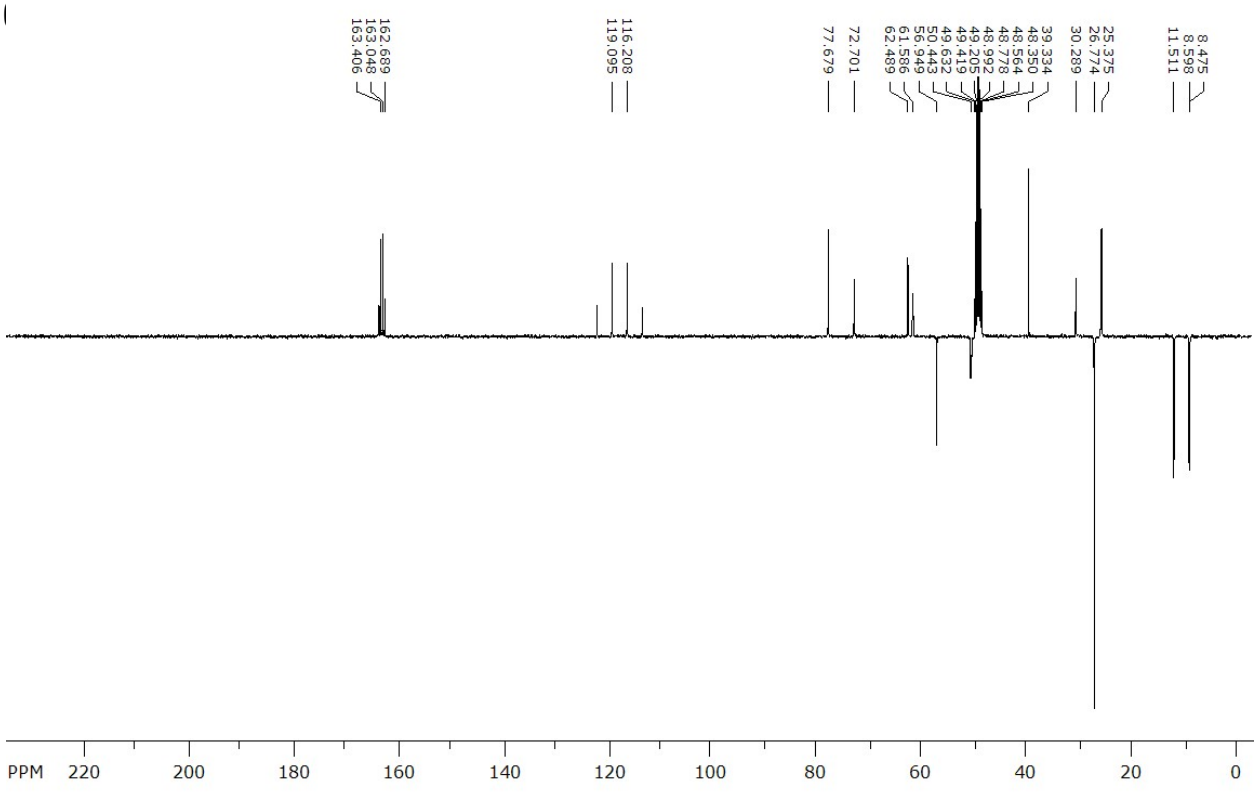


**Figure S19**. $^{1}H$ NMR (400 MHz; $CDCl_3$) of (1S(R),4R(S),5R(S))-2,4-di-*tert*-butyl-4-ethyl-1-propyl-3-azabicyclo[3.1.0]hex-2-ene (**15**)

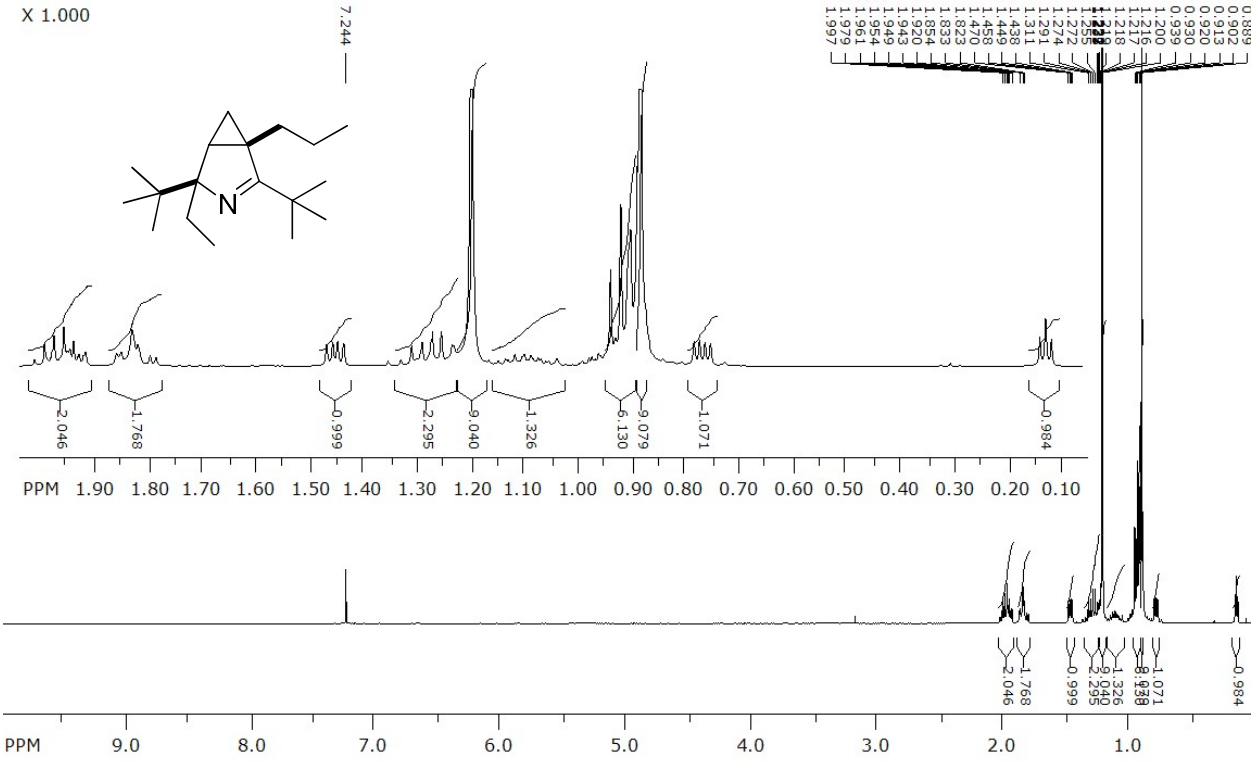



**Figure S20**. $^{13}C$ NMR (100 MHz; $CDCl_3$) of (1S(R),4R(S),5R(S))-2,4-di-*tert*-butyl-4-ethyl-1-propyl-3-azabicyclo[3.1.0]hex-2-ene (**15**)

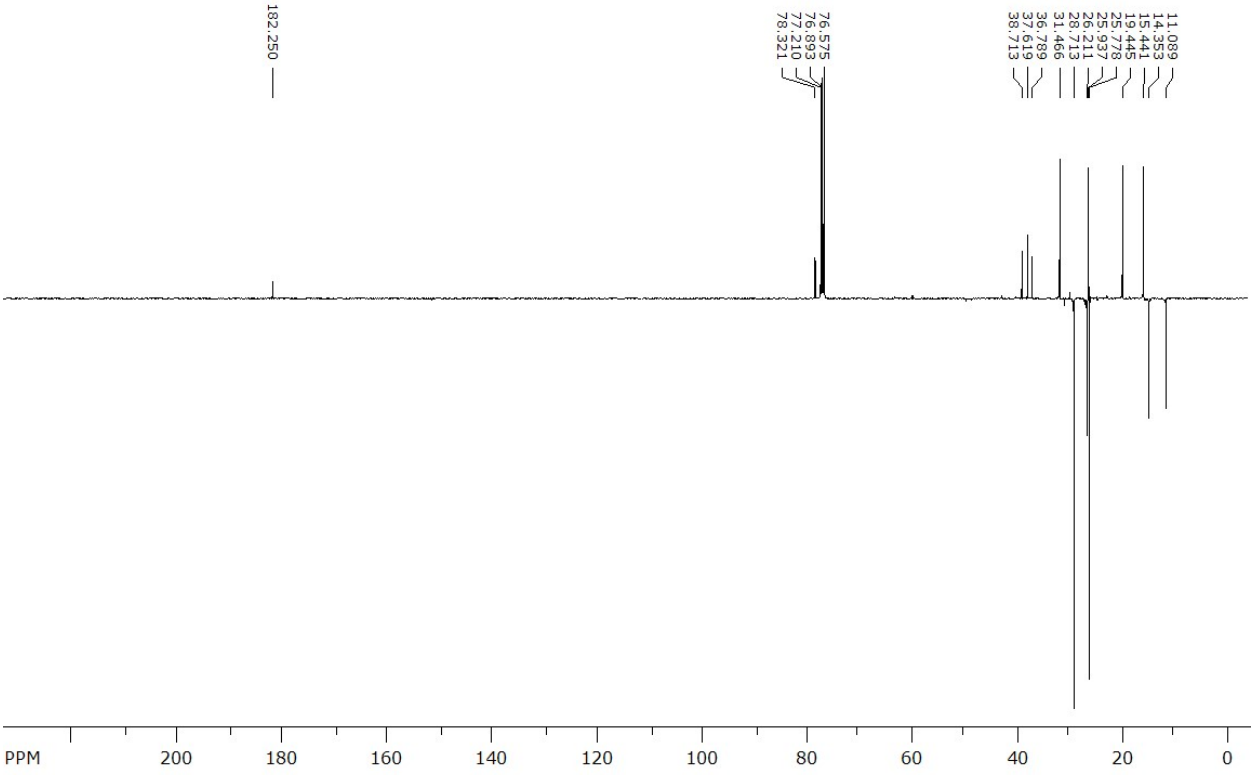


**Figure S21**. $^{1}H$ NMR (500 MHz; $CDCl_3$) of (2S(R),3R(S),4R(S))-2,5-di-*tert*-butyl-2-ethyl-3,4-bis(methoxycarbonyl)-3,4-dihydro-2H-pyrrole 1-oxide (**16**)

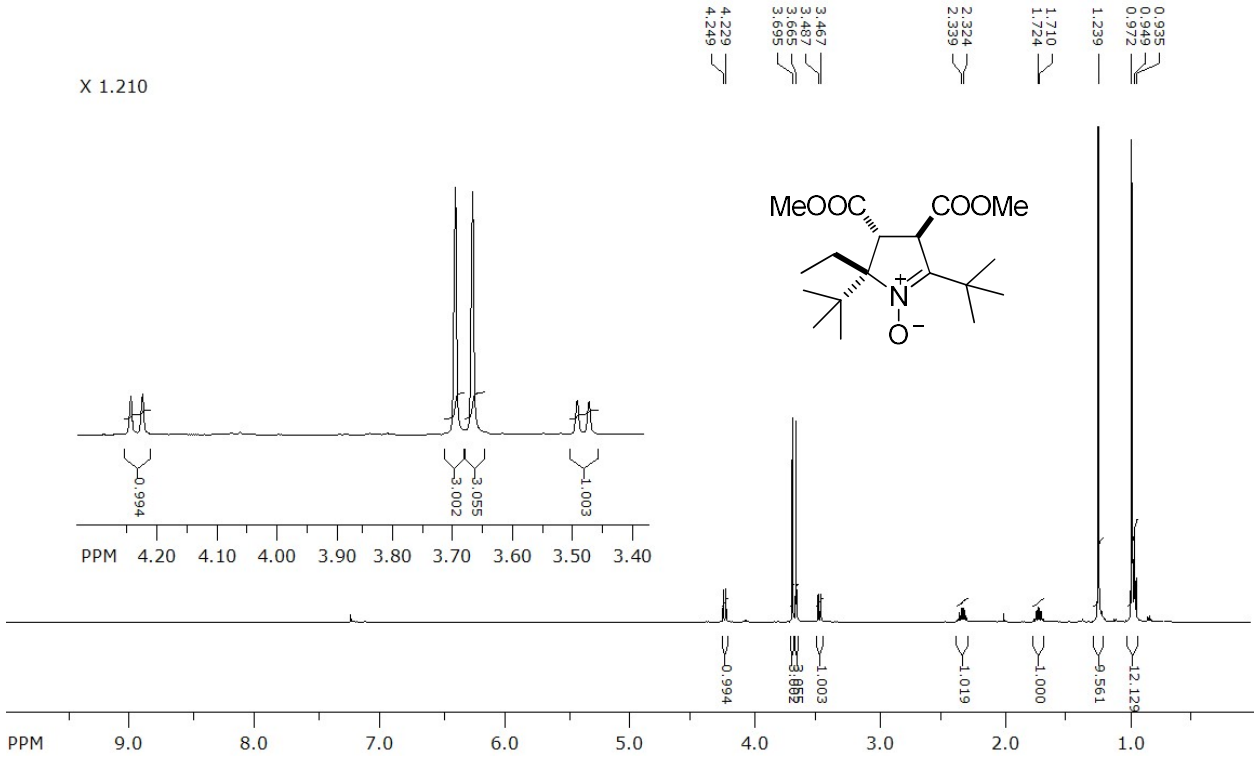



**Figure S22**. $^{13}C$ NMR (125 MHz; $CDCl_3$) of (2S(R),3R(S),4R(S))-2,5-di-*tert*-butyl-2-ethyl-3,4-bis(methoxycarbonyl)-3,4-dihydro-2H-pyrrole 1-oxide (**16**)

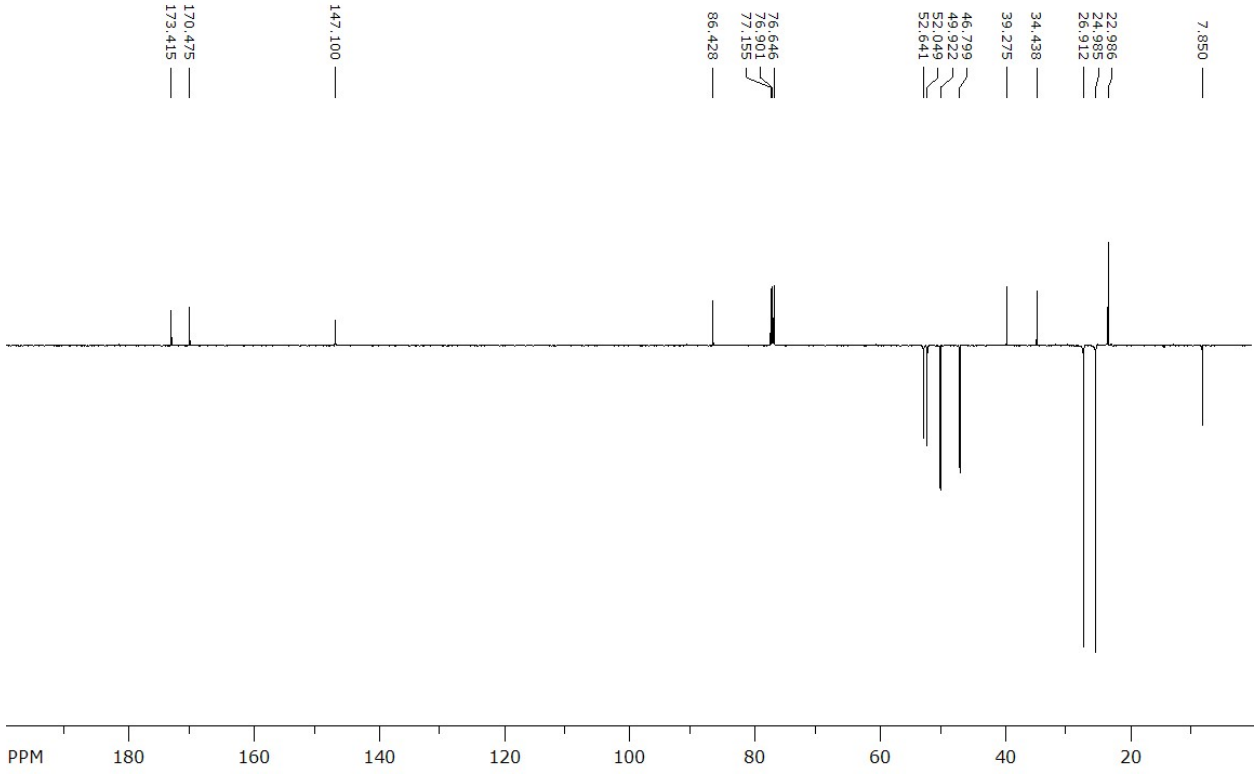


**Figure S23**. $^{1}H$ NMR (400 MHz; $CDCl_3$) of (2S(R),3R(S))-2,5-di-*tert*-butyl-2-ethyl-3-(methoxycarbonyl)-3,4-dihydro-2H-pyrrole 1-oxide (**17**)

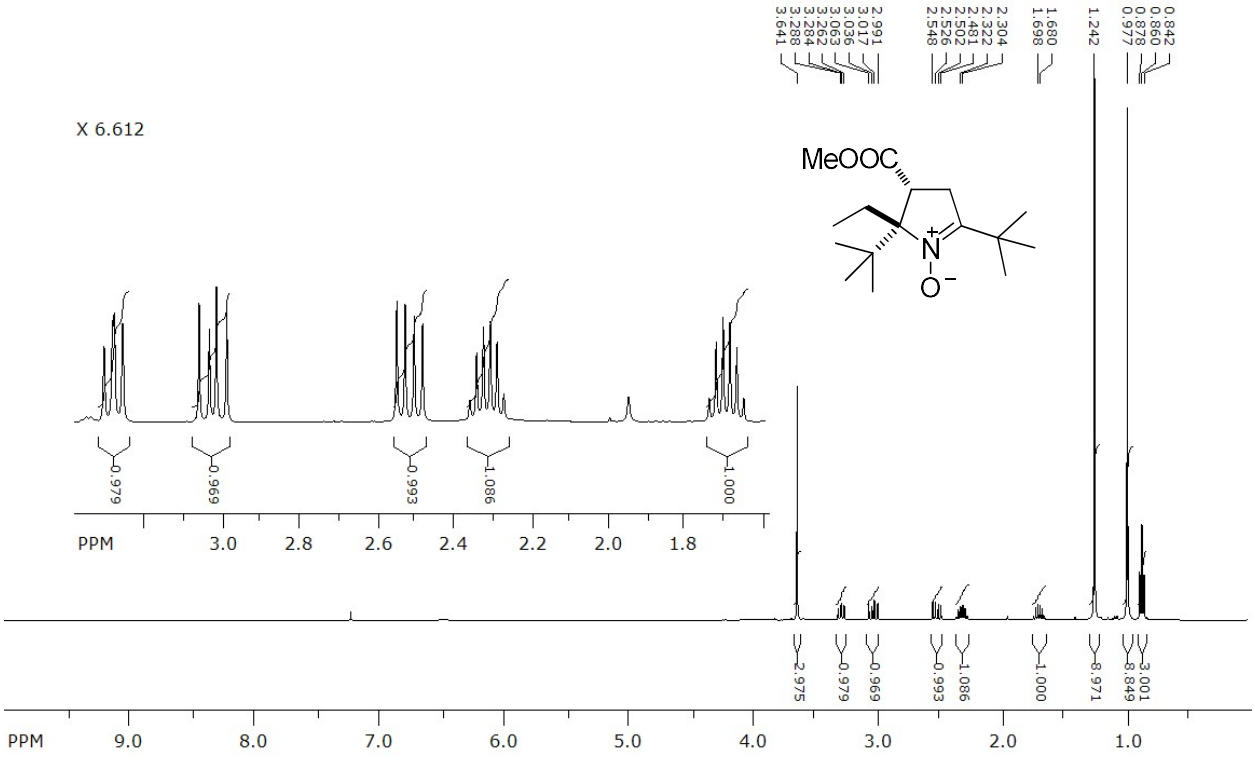



**Figure S24**. $^{13}C$ NMR (100 MHz; $CDCl_3$) of (2S(R),3R(S))-2,5-di-*tert*-butyl-2-ethyl-3-(methoxycarbonyl)-3,4-dihydro-2H-pyrrole 1-oxide (**17**)

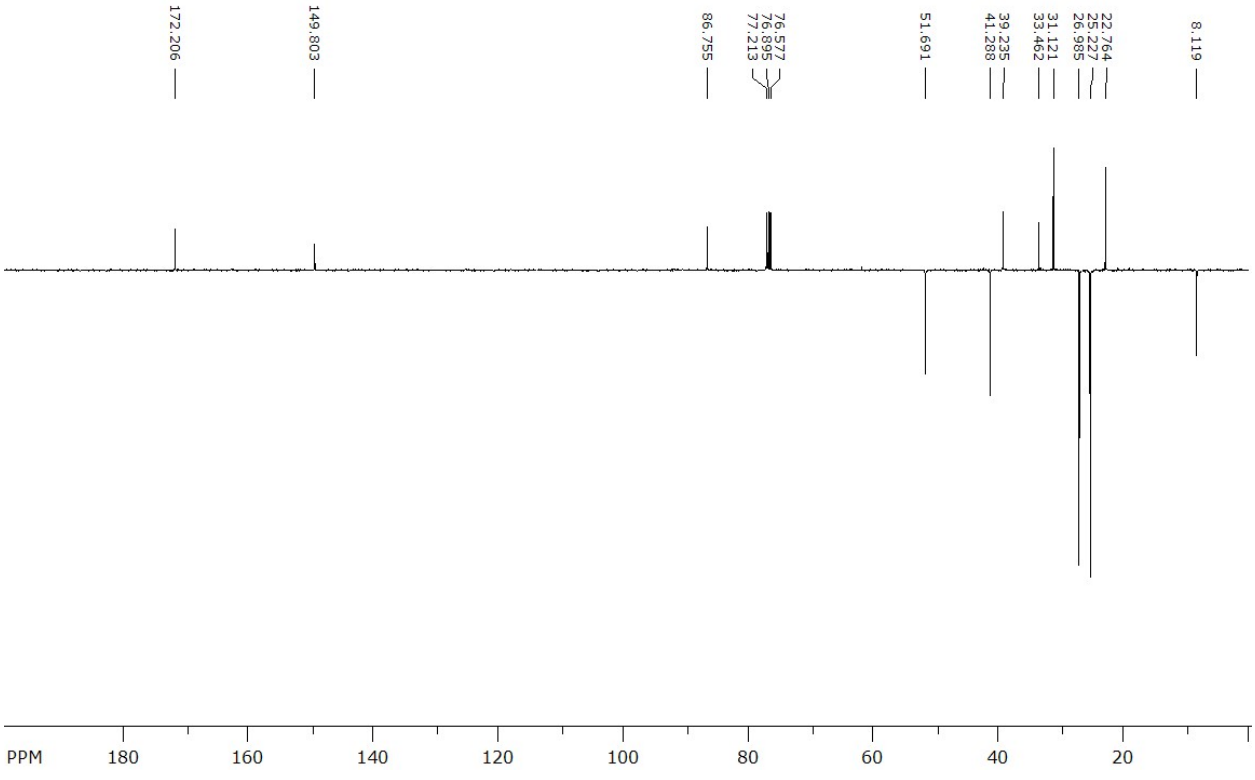


**Figure S25**. $^{1}H$ NMR (500 MHz; $CDCl_3$) of (2S(R),3S(R))-2,5-di-*tert*-butyl-2-ethyl-3-(methoxycarbonyl)-3,4-dihydro-2H-pyrrole 1-oxide (**18**)

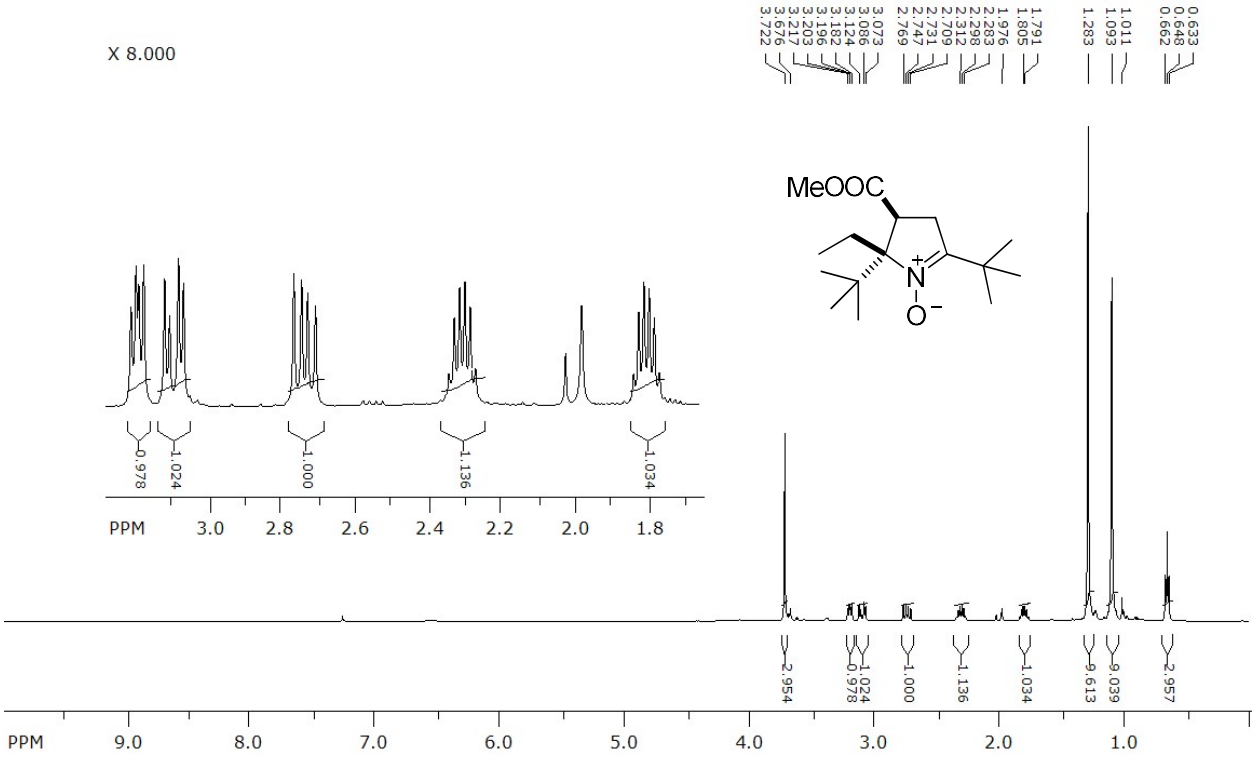



**Figure S26**. $^{13}C$ NMR (125 MHz; $CDCl_3$) of (2S(R),3S(R))-2,5-di-*tert*-butyl-2-ethyl-3-(methoxycarbonyl)-3,4-dihydro-2H-pyrrole 1-oxide (**18**)

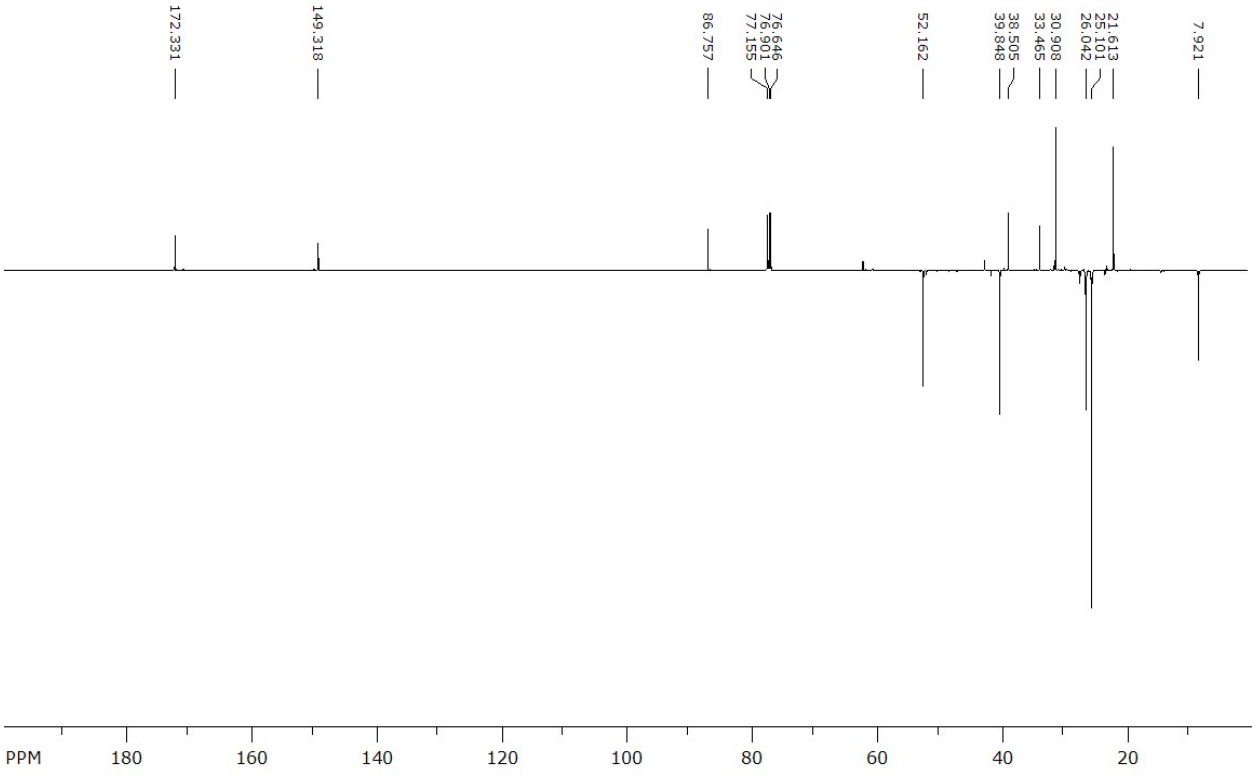


**Figure S27**. $^{1}H$ NMR (600 MHz; $CDCl_3$) of (2S(R),3R(S))-2,5-di-*tert*-butyl-2-ethyl-3-(hydroxymethyl)-3,4-dihydro-2H-pyrrole 1-oxide (**20**)

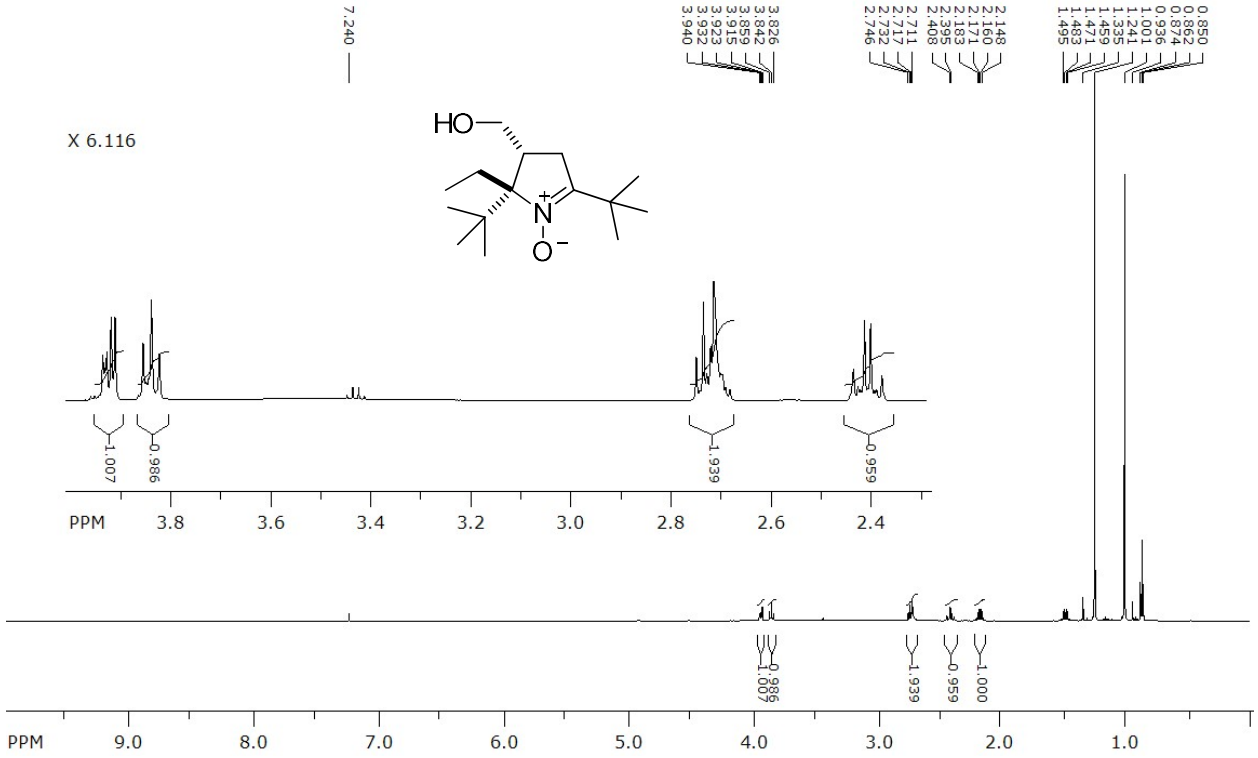



**Figure S28**. $^{13}C$ NMR (150 MHz; $CDCl_3$) of (2S(R),3R(S))-2,5-di-*tert*-butyl-2-ethyl-3-(hydroxymethyl)-3,4-dihydro-2H-pyrrole 1-oxide (**20**)

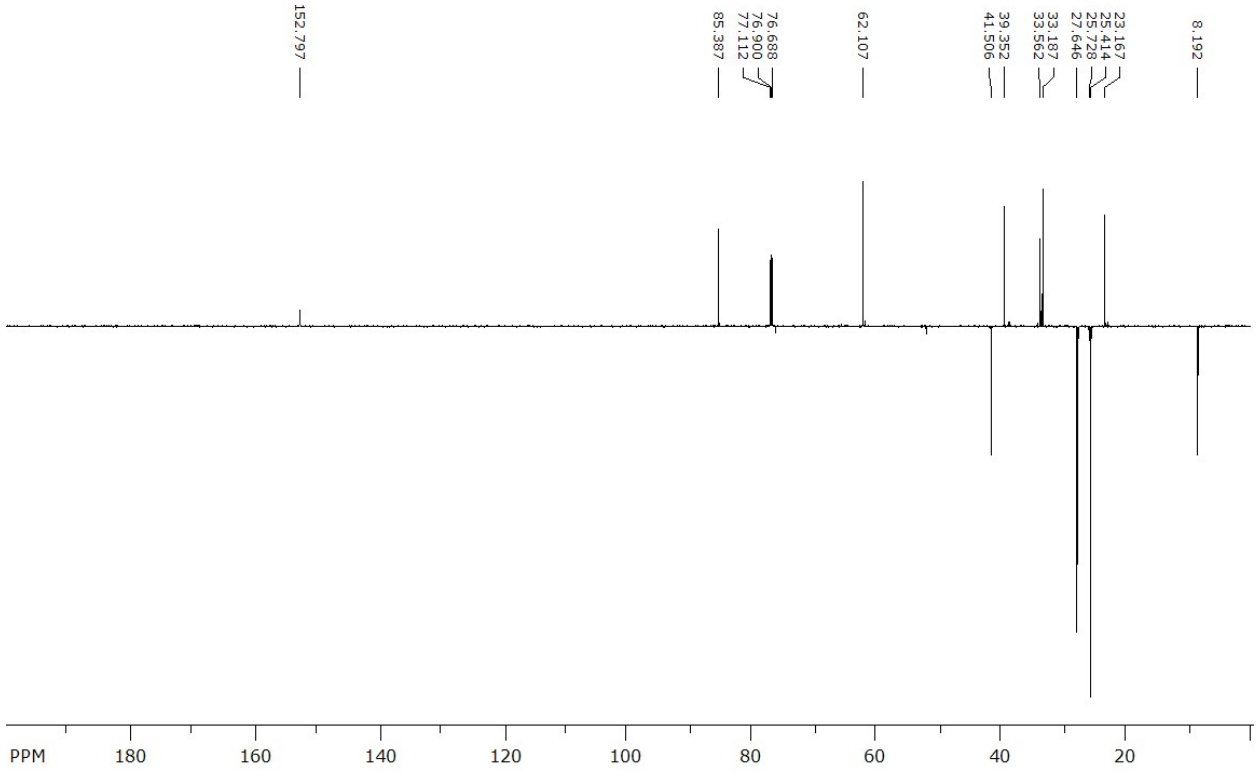


**Figure S29**. $^{1}H$ NMR (400 MHz; $CDCl_3$) of (2S(R),3S(R))-2,5-di-*tert*-butyl-2-ethyl-3-(hydroxymethyl)-3,4-dihydro-2H-pyrrole 1-oxide (**21**)

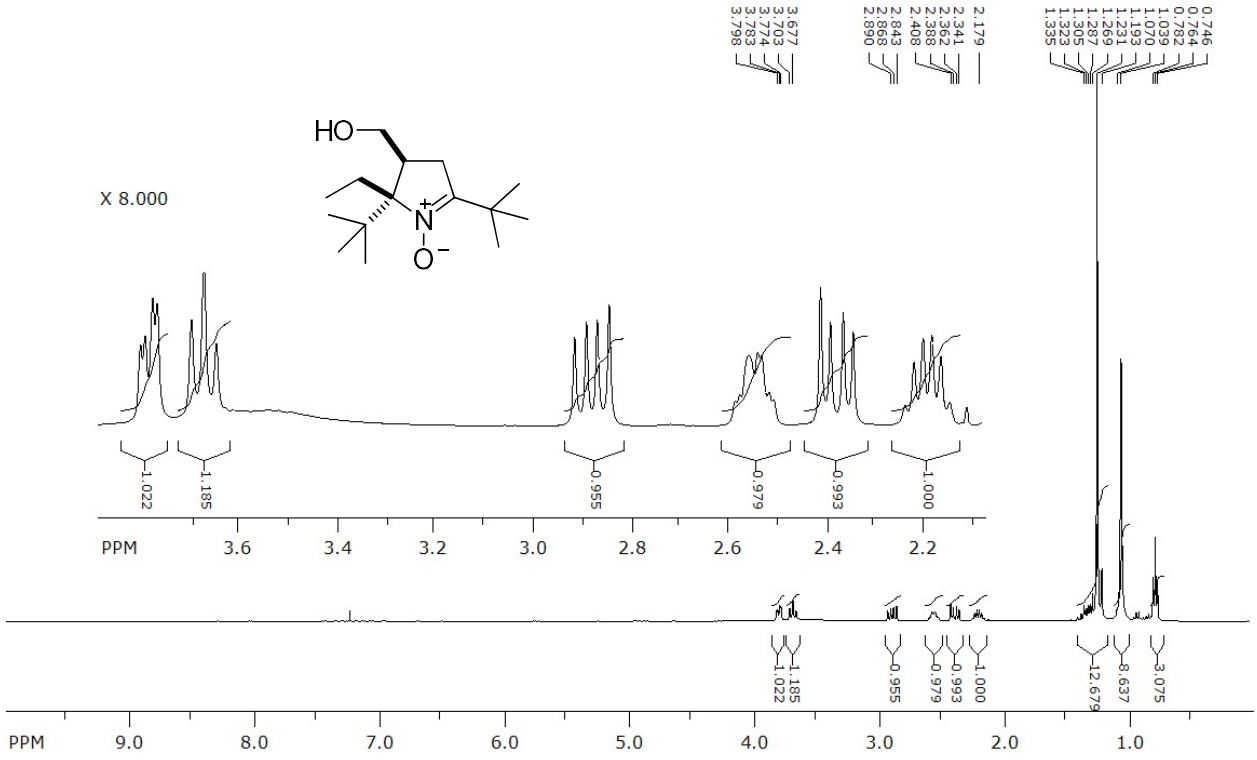



**Figure S30**. $^{13}C$ NMR (125 MHz; $CDCl_3$) of (2S(R),3S(R))-2,5-di-*tert*-butyl-2-ethyl-3-(hydroxymethyl)-3,4-dihydro-2H-pyrrole 1-oxide (**21**)

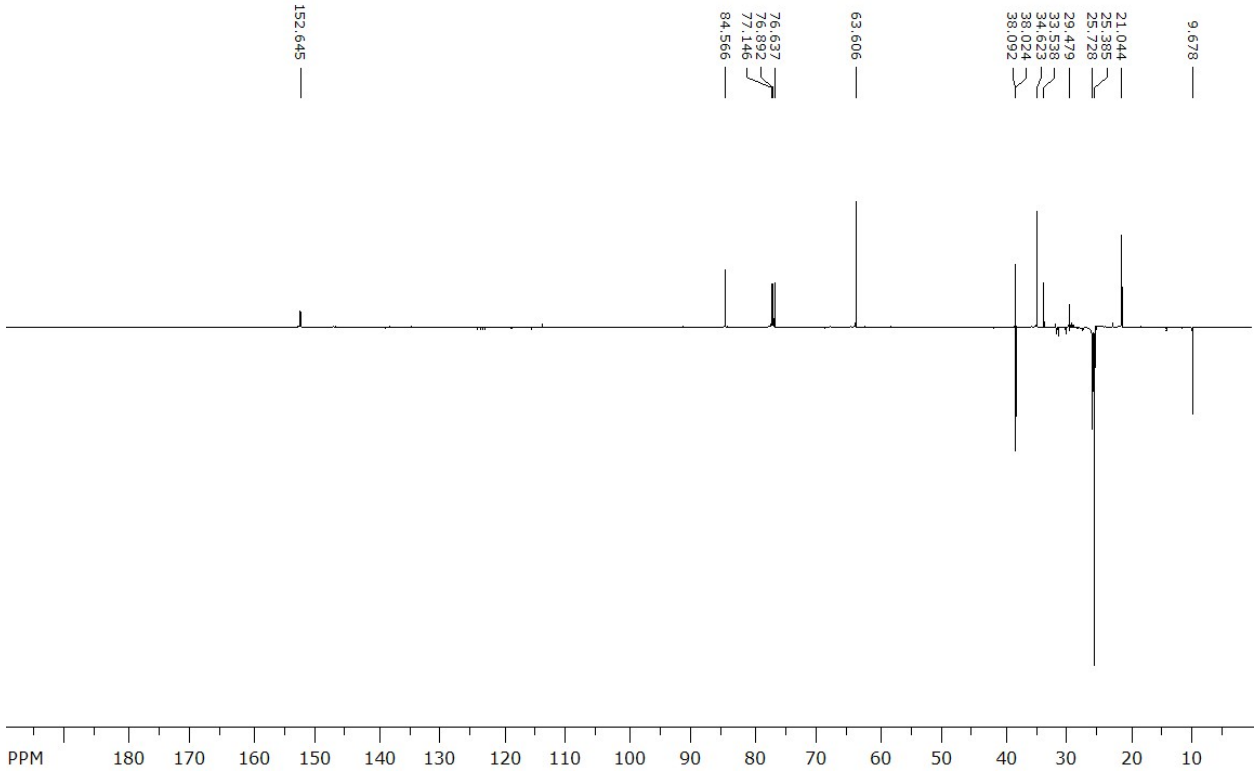


**Figure S31**. $^{1}H$ NMR (400 MHz; $CD_3OD$, Zn/$CF_3COOH$ system) of (2S(R),3R(S))-2,5-di-tert-butyl-2,5-diethyl-3-(hydroxymethyl)pyrrolidin-1-oxyl (**23**)

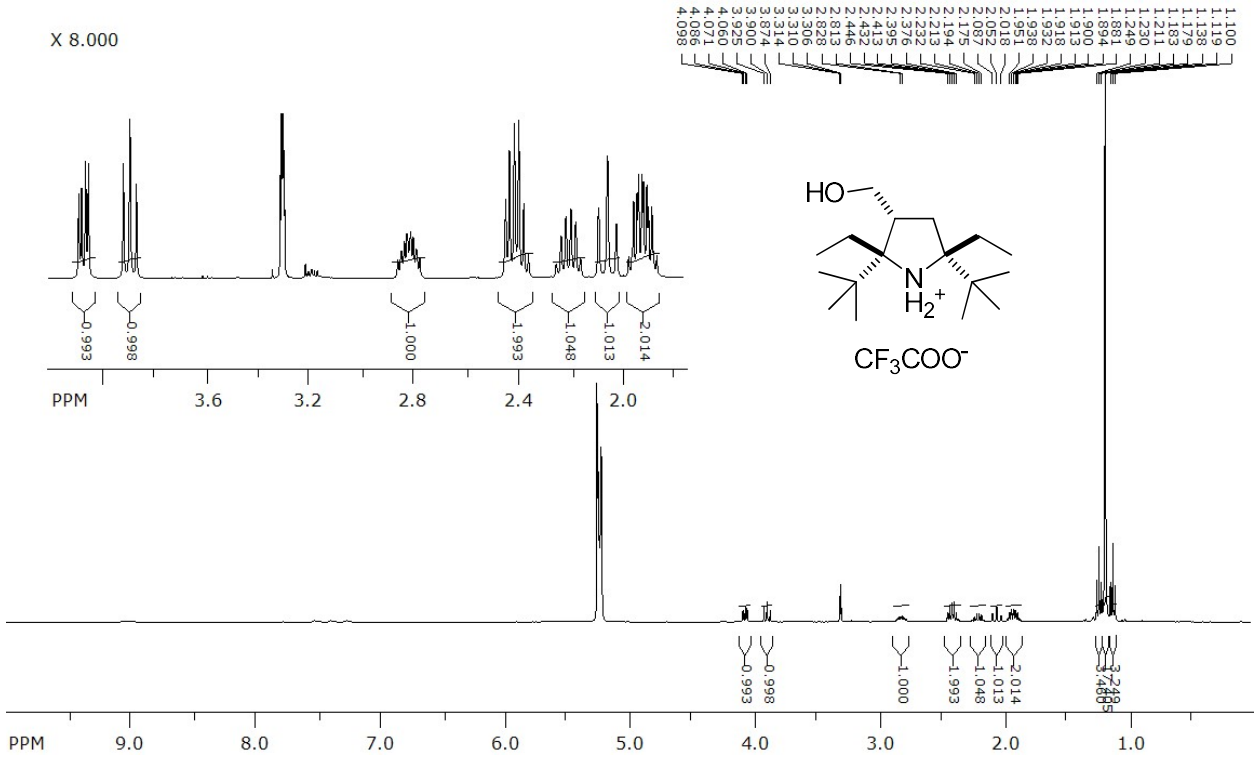



**Figure S32**. $^{13}C$ NMR (75 MHz; $CD_3OD$, Zn/$CF_3COOH$ system) of (2S(R),3R(S))-2,5-di-tert-butyl-2,5-diethyl-3-(hydroxymethyl)pyrrolidin-1-oxyl (**23**)

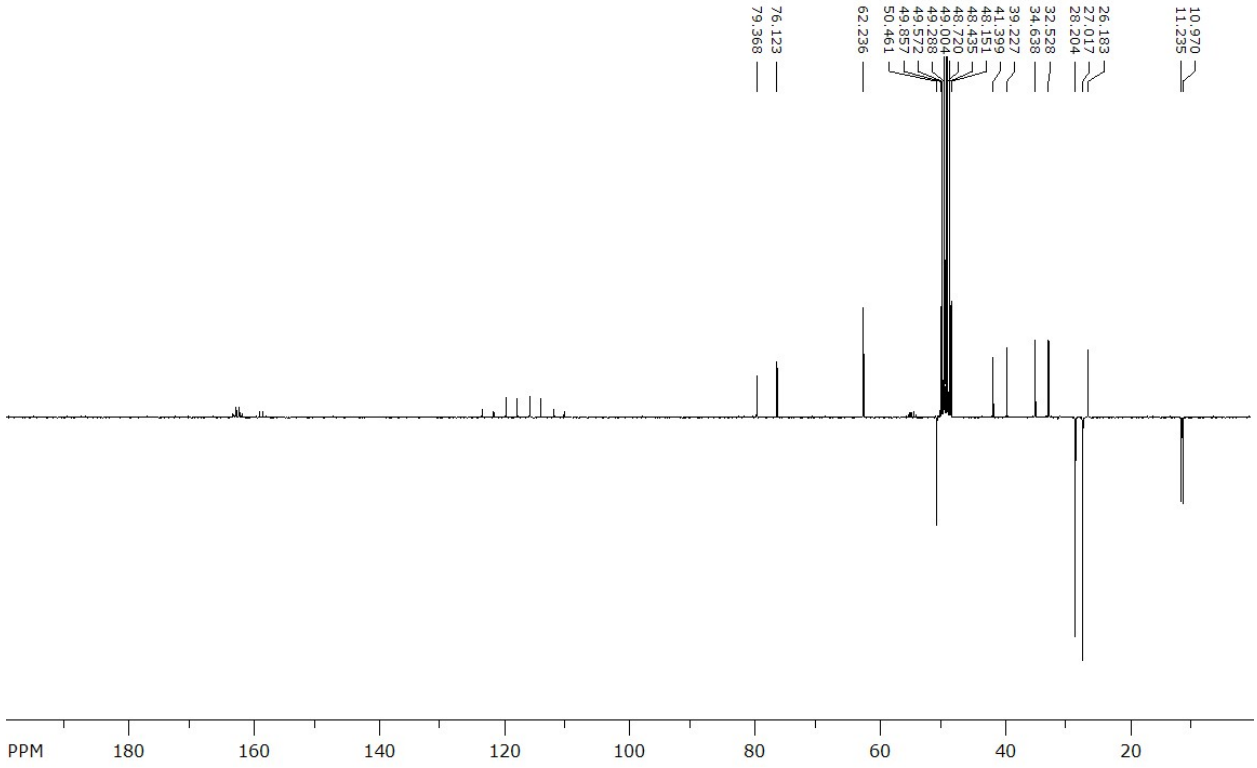


**Figure S33**. $^{1}H$ NMR (400 MHz; $CD_3OD$, Zn/$CF_3COOH$ system) of ((2S(R),3R(S),5S(R))-2,5-di-*tert*-butyl-2,5-diethyl-3-((((3-(trimethylammonio)propyl)carbamoyl)oxy)methyl)pyrrolidin-1-oxyl) monoiodide (**26**)

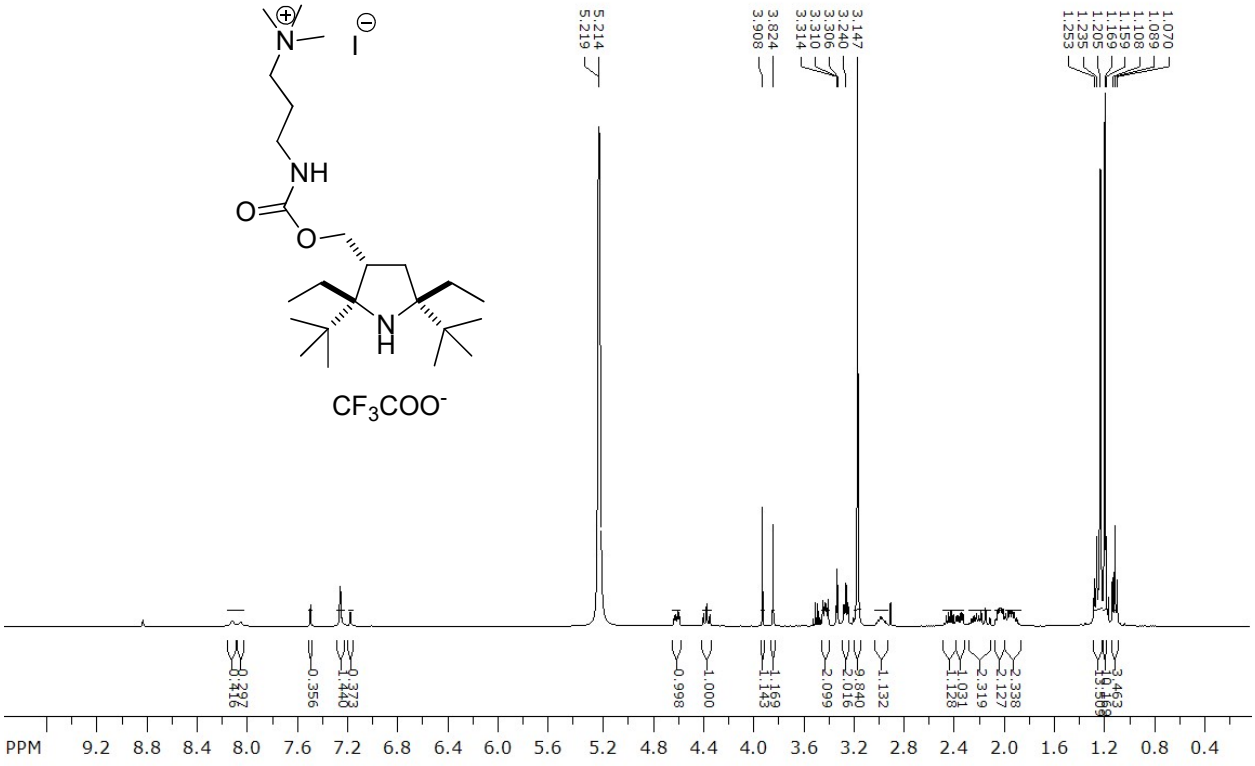
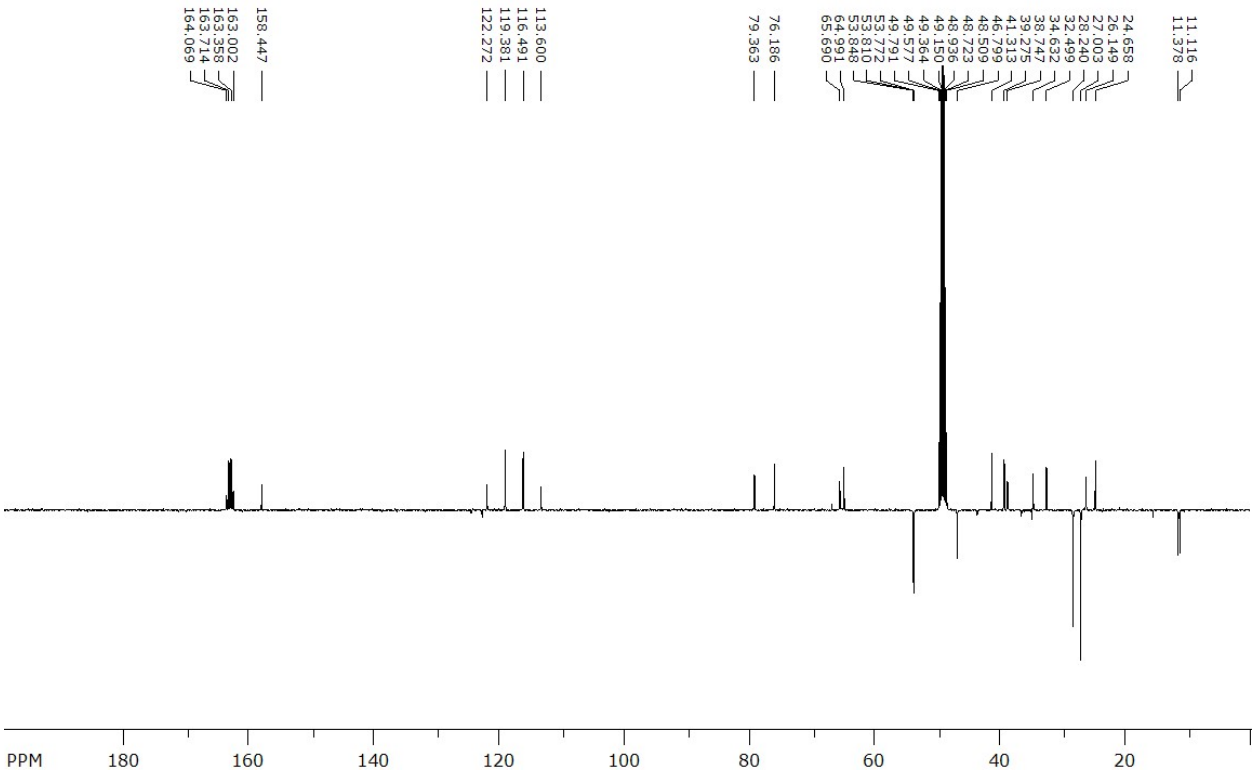



**Figure S34**. $^{13}C$ NMR (100 MHz; $CD_3OD$, Zn/$CF_3COOH$ system) of ((2S(R),3R(S),5S(R))-2,5-di-*tert*-butyl-2,5-diethyl-3-((((3-(trimethylammonio)propyl)carbamoyl)oxy)methyl)pyrrolidin-1-oxyl) monoiodide (**26**)



## 2D NMR Spectra

**Figure S35**. HMBC (400 MHz; $(CD_3)_2CO$; $CF_3COOH$) of (2R(S),3R(S),4R(S),5S(R))-2,5-di-*tert*-butyl-3,4-bis(methoxycarbonyl)-2-ethylpyrrolidine (**8**)

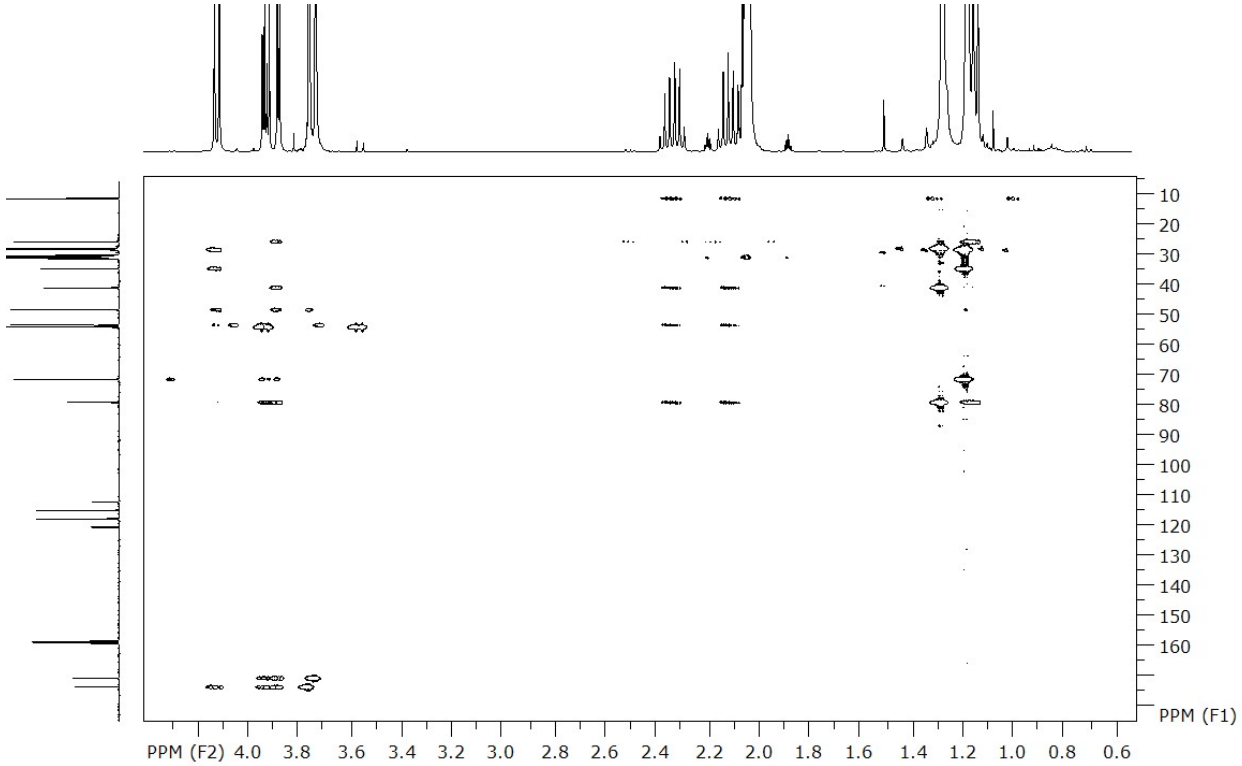



**Figure S36**. NOESY (400 MHz; $(CD_3)_2CO$; $CF_3COOH$) of (2R(S),3R(S),4R(S),5S(R))-2,5-di-*tert*-butyl-3,4-bis(methoxycarbonyl)-2-ethylpyrrolidine (**8**)

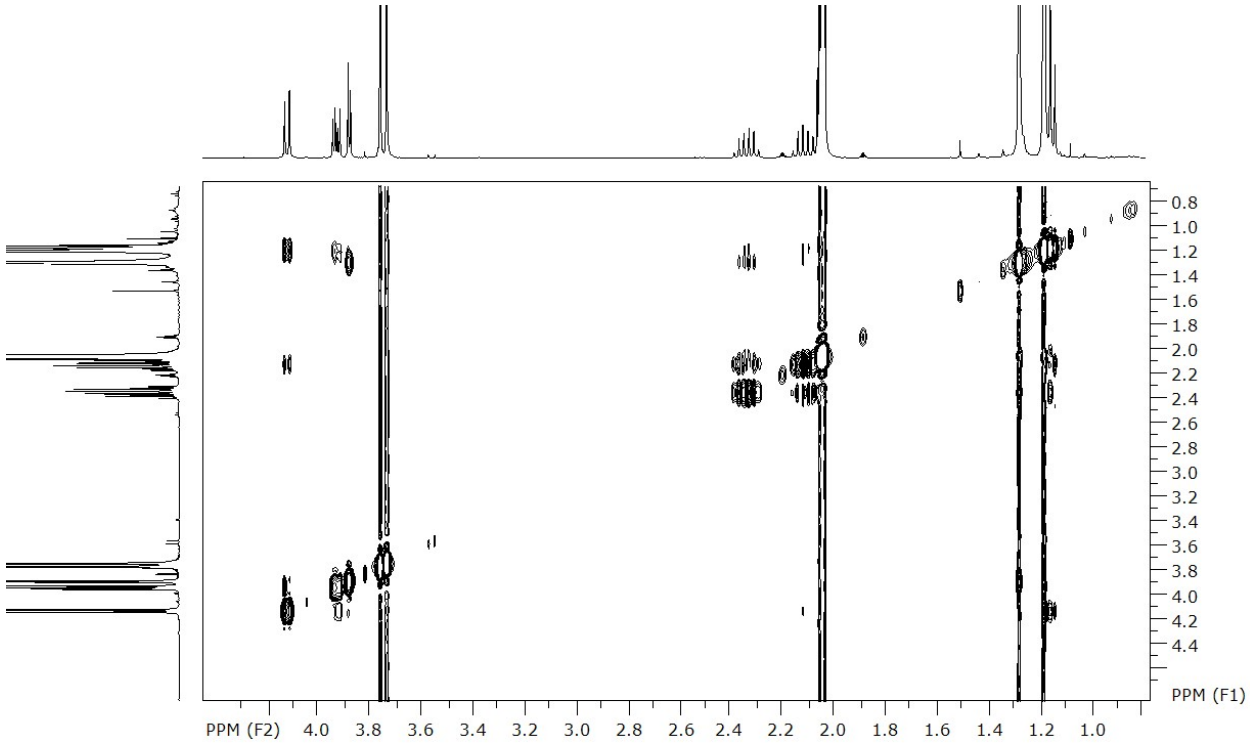


**Figure S37**. NOESY (600 MHz; $CDCl_3$) of (2S(R),3R(S),4R(S),5R(S))-2,5-di-*tert*-butyl-3,4-bis(methoxycarbonyl)-2-ethylpyrrolidine (**9**)

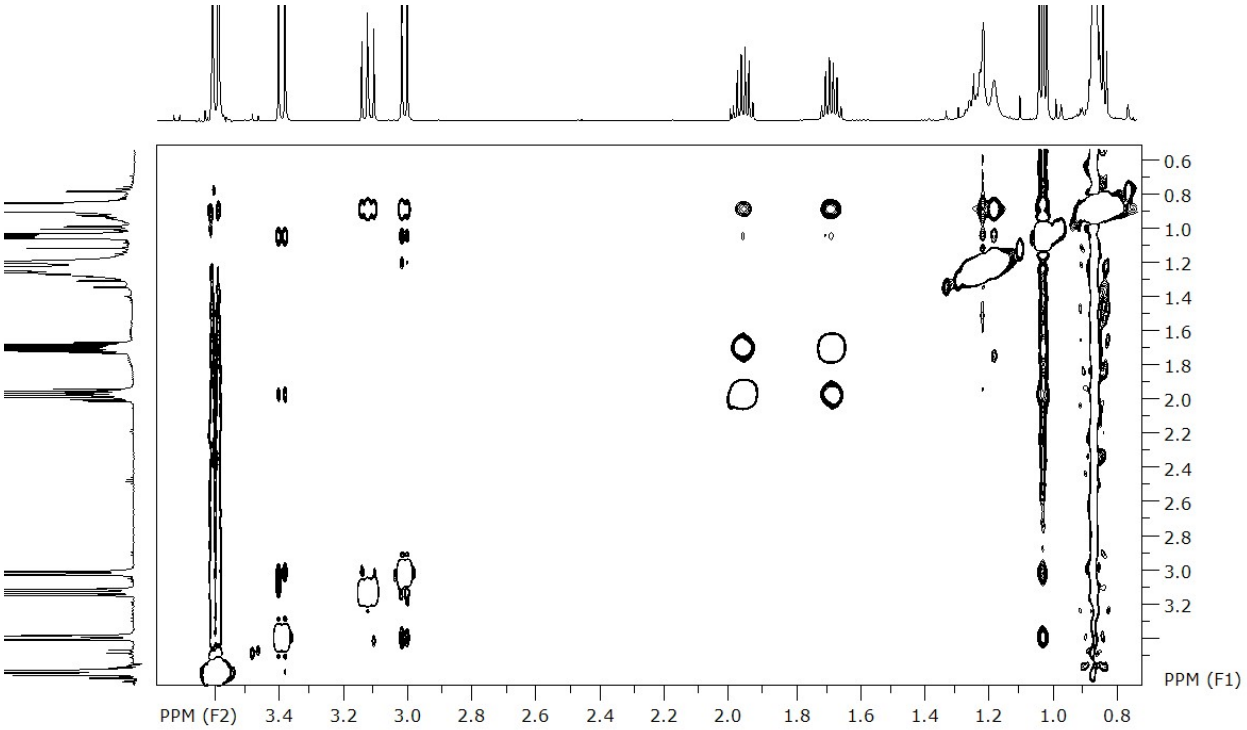



**Figure S38.** HMBC (400 MHz; $CDCl_3$) of (2R(S),3R(S),4R(S))-2,5-di-*tert*-butyl-2-ethyl-3,4-bis(hydroxymethyl)-3,4-dihydro-2*H*-pyrrole 1-oxide (**12**)

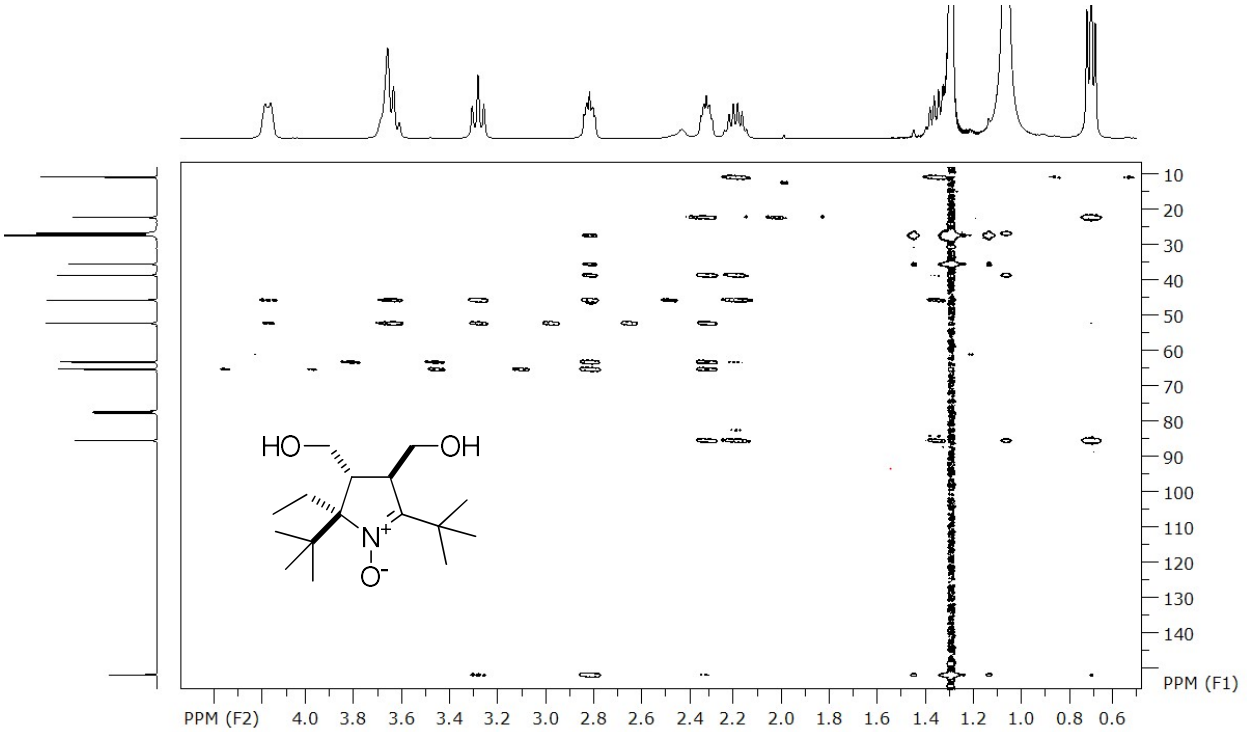


**Figure S39**. NOESY (400 MHz; $CDCl_3$) of (2R(S),3R(S),4R(S))-2,5-di-*tert*-butyl-2-ethyl-3,4-bis(hydroxymethyl)-3,4-dihydro-2*H*-pyrrole 1-oxide (**12**)

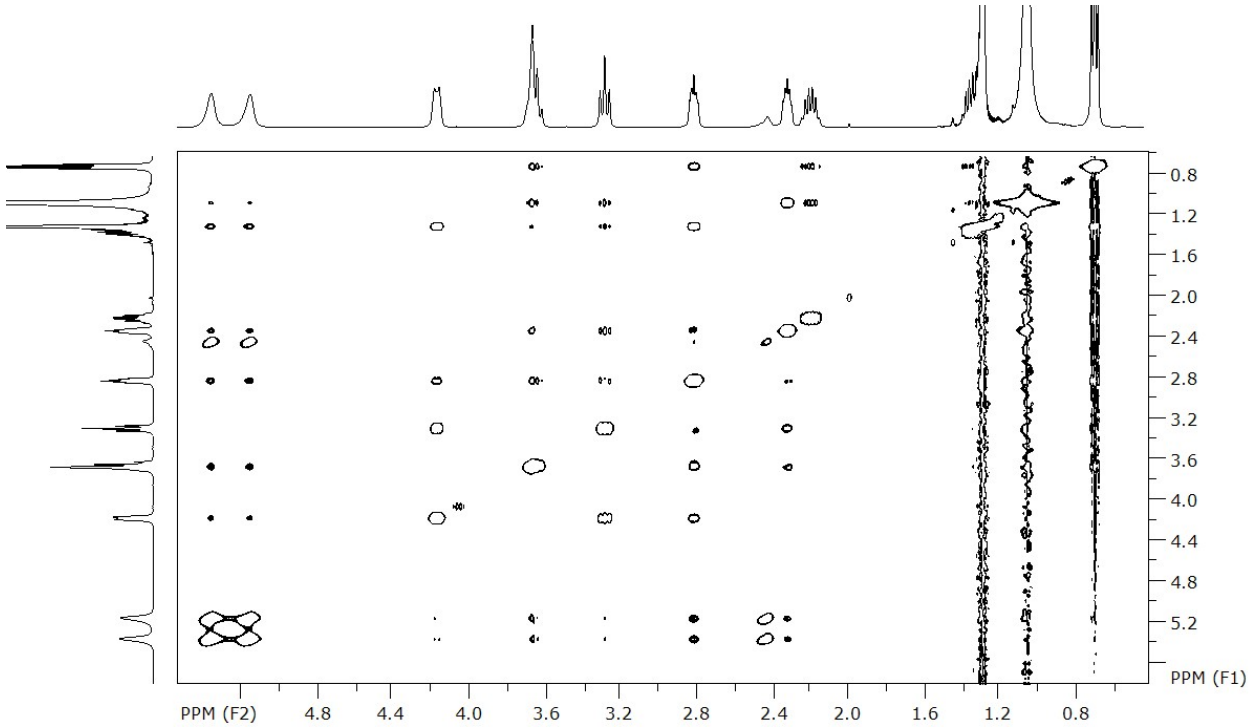



**Figure S40**. COSY (400 MHz, $CDCl_3$) of (1S(R),4R(S),5R(S))-2,4-di-*tert*-butyl-4-ethyl-1-propyl-3-azabicyclo[3.1.0]hex-2-ene (**15**)

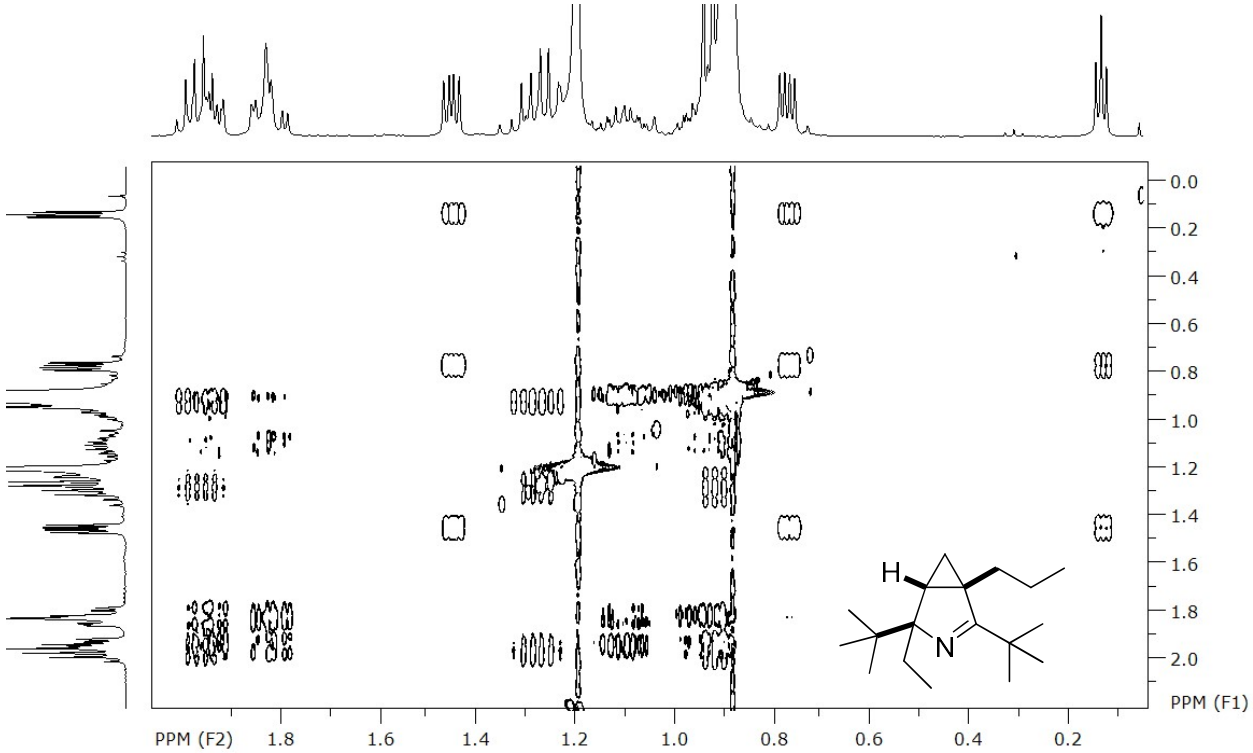


**Figure S41**. HSQC (400 MHz, $CDCl_3$) of (1S(R),4R(S),5R(S))-2,4-di-*tert*-butyl-4-ethyl-1-propyl-3-azabicyclo[3.1.0]hex-2-ene (**15**)

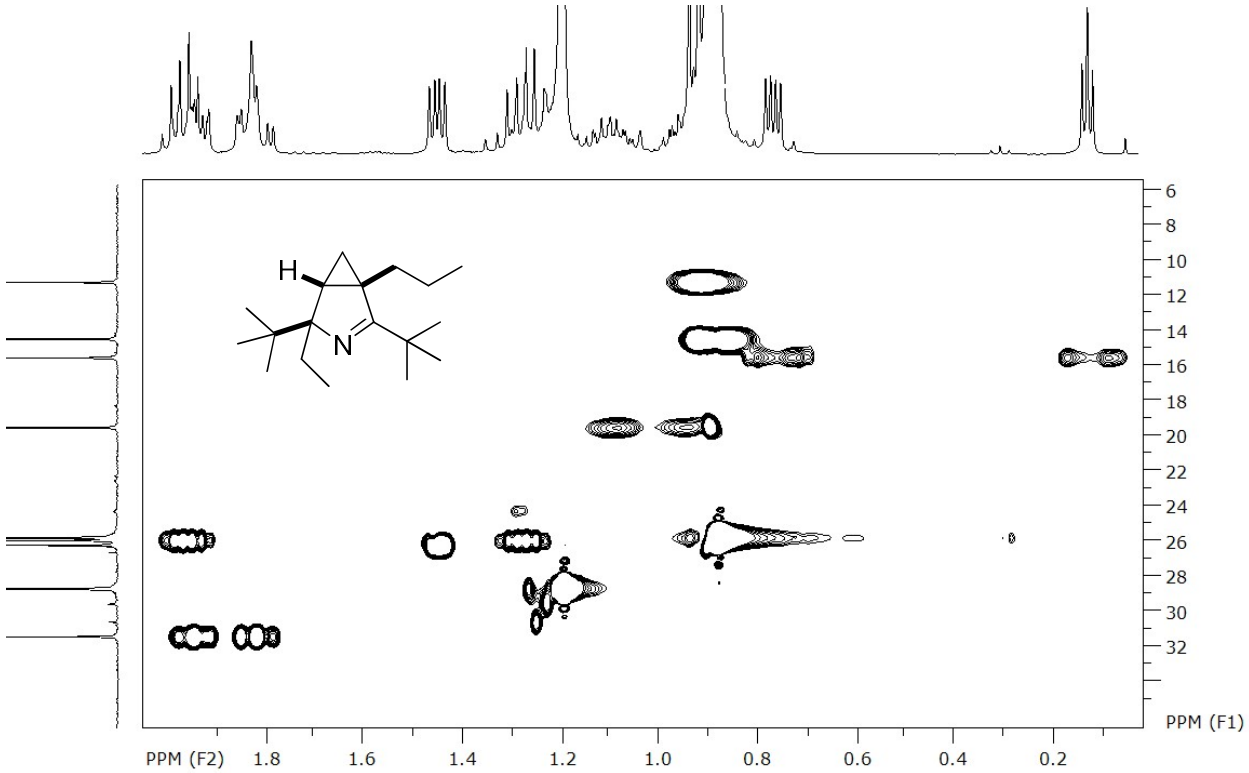



**Figure S42**. HMBC (400 MHz, $CDCl_3$) of (1S(R),4R(S),5R(S))-2,4-di-*tert*-butyl-4-ethyl-1-propyl-3-azabicyclo[3.1.0]hex-2-ene (**15**)

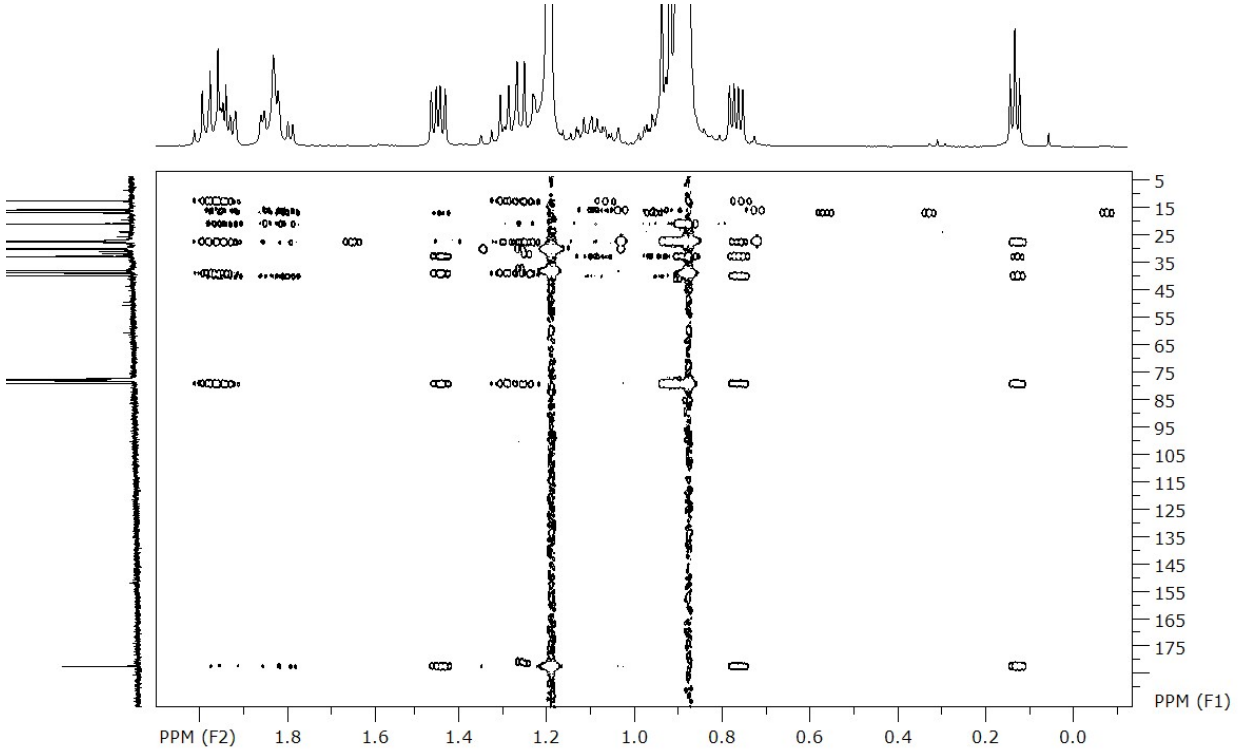


**Figure S43**. NOESY (400 MHz, $CDCl_3$) of (1S(R),4R(S),5R(S))-2,4-di-*tert*-butyl-4-ethyl-1-propyl-3-azabicyclo[3.1.0]hex-2-ene (**15**)

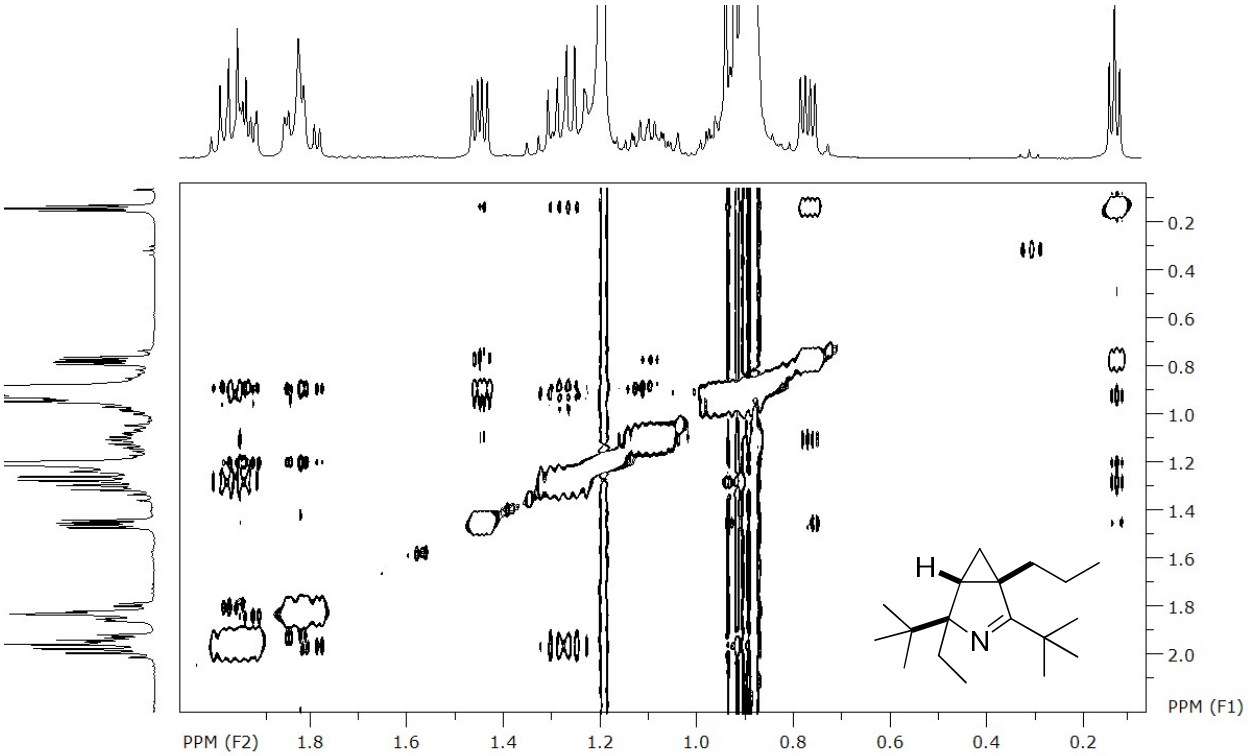



**Figure S44**. COSY (400 MHz; $CD_3OD$, Zn/$CF_3COOH$ system) of ((2S(R),3R(S),5S(R))-2,5-di-*tert*-butyl-2,5-diethyl-3-((((3-(trimethylammonio)propyl)carbamoyl)oxy)methyl)pyrrolidin-1-oxyl) monoiodide (**26**)

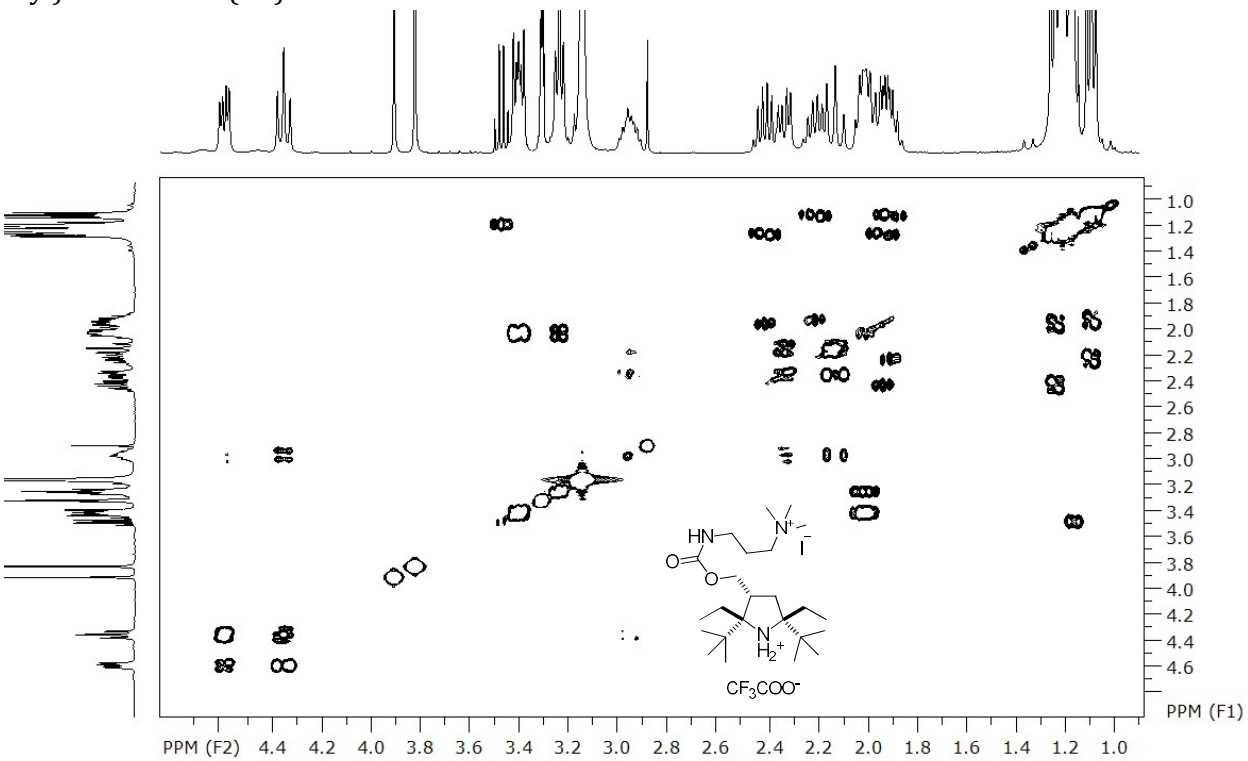


**Figure S45**. HSQC (400 MHz; $CD_3OD$, Zn/$CF_3COOH$ system) of ((2S(R),3R(S),5S(R))-2,5-di-*tert*-butyl-2,5-diethyl-3-((((3-(trimethylammonio)propyl)carbamoyl)oxy)methyl)pyrrolidin-1-oxyl) monoiodide (**26**)

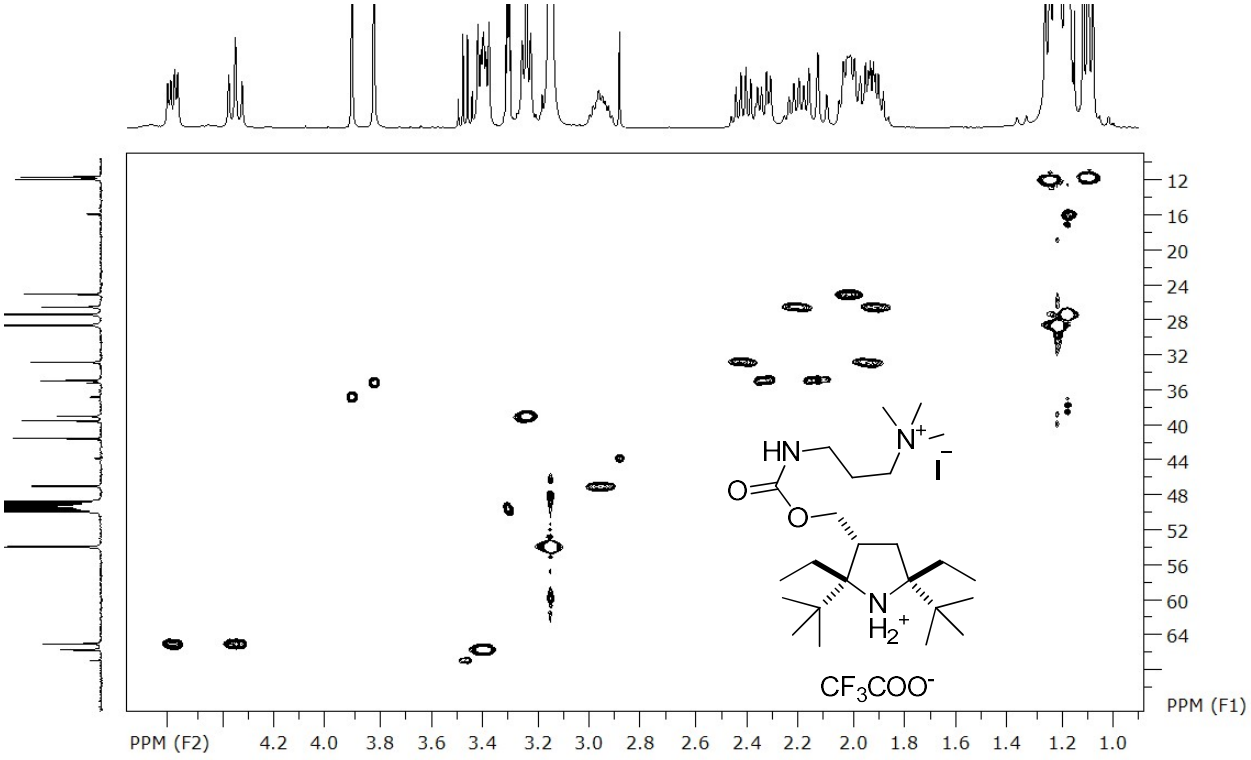



**Figure S46**. HMBC (400 MHz; $CD_3OD$, Zn/$CF_3COOH$ system) of ((2S(R),3R(S),5S(R))-2,5-di-*tert*-butyl-2,5-diethyl-3-((((3-(trimethylammonio)propyl)carbamoyl)oxy)methyl)pyrrolidin-1-oxyl) monoiodide (**26**)

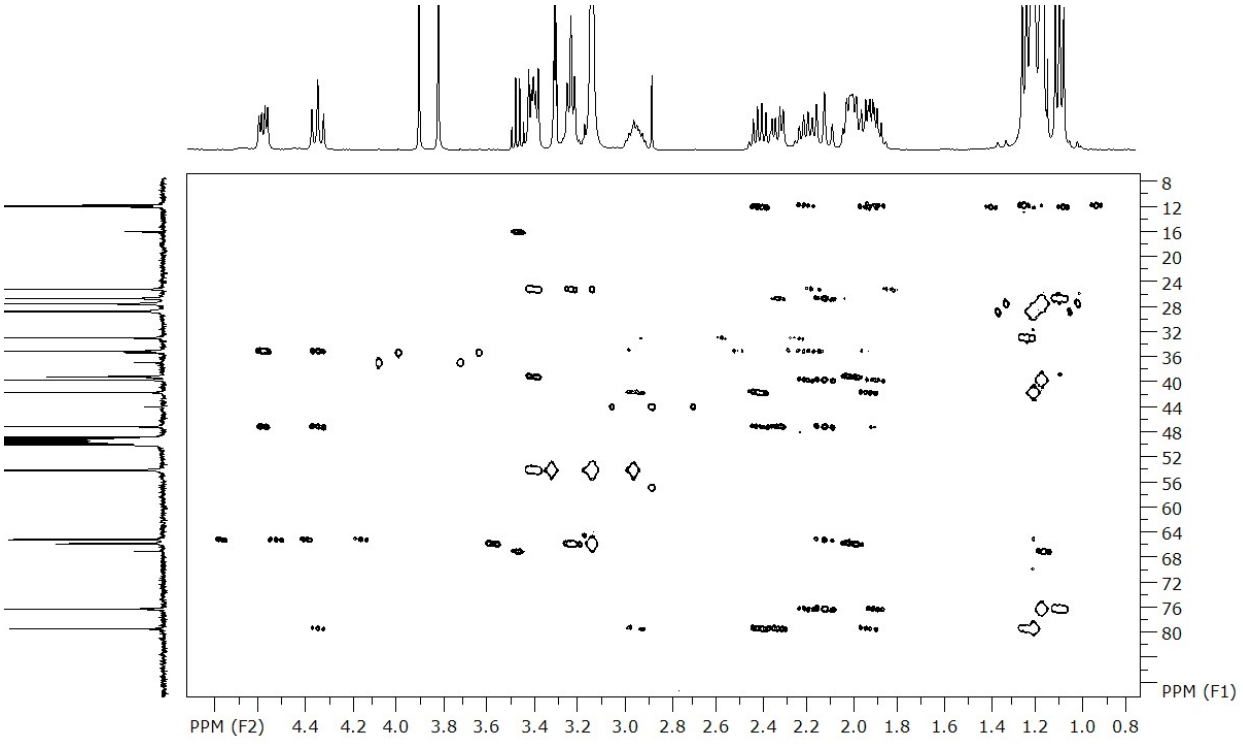
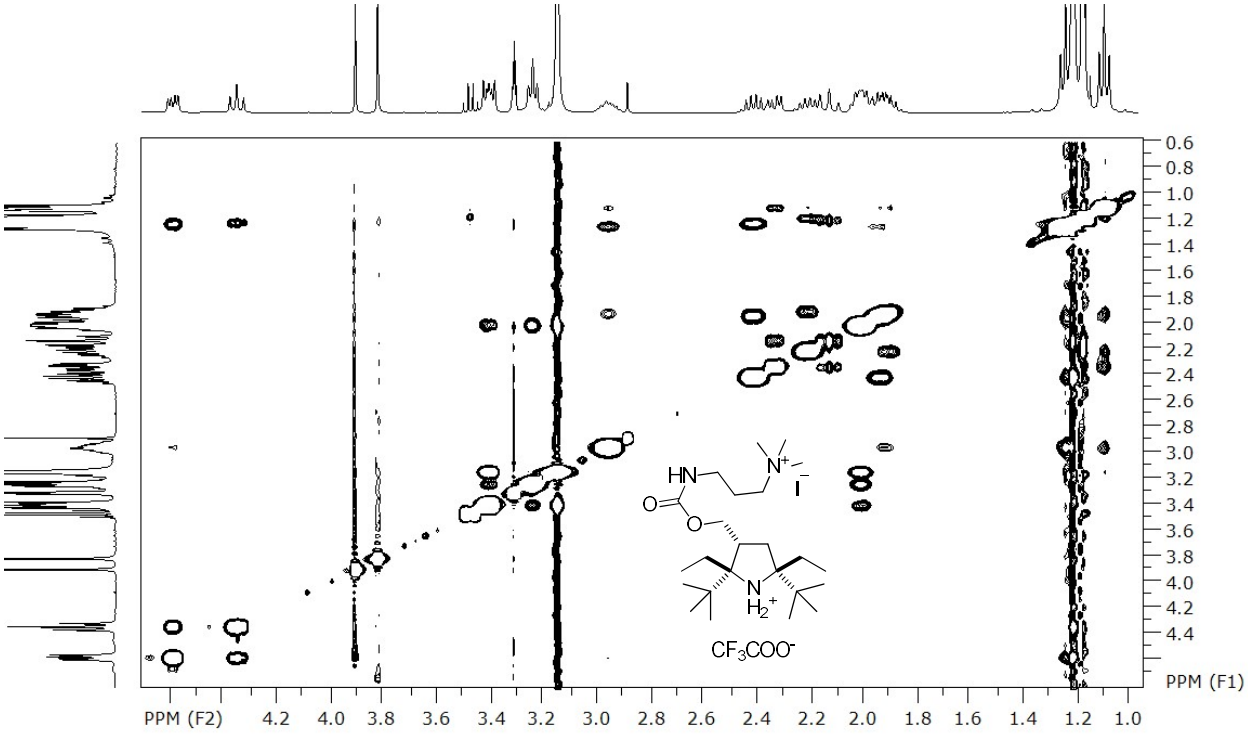


**Figure S47**. NOESY (400 MHz; $CD_3OD$, Zn/$CF_3COOH$ system) of ((2S(R),3R(S),5S(R))-2,5-di-*tert*-butyl-2,5-diethyl-3-((((3-(trimethylammonio)propyl)carbamoyl)oxy)methyl)pyrrolidin-1-oxyl) monoiodide (**26**)



## Line shape analysis

The analysis was performed using the gNMR 5.0 software [Budzelaar, P. H. M. "gNMR, version 5.0. 6.0." *Ivorysoft, Nijmegen, Netherlands* (2006).].

**Figure S48.**Simulated spectrum for (1S(R),4R(S),5R(S))-2,4-di-tert-butyl-4-ethyl-1-propyl-3-azabicyclo[3.1.0]hex-2-ene (**15**)

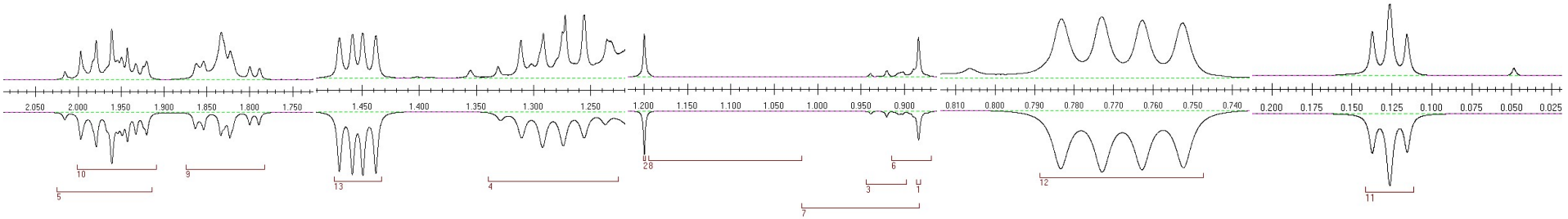



**Table S1.** Parameters of spins system (1S(R),4R(S),5R(S))-2,4-di-tert-butyl-4-ethyl-1-propyl-3-azabicyclo[3.1.0]hex-2-ene (**15**)

| # | n | Shift | Width | J[1] | J[2] | J[3] | J[4] | J[5] | J[6] | J[7] | J[8] | J[9] | J[10] | J[11] | J[12] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 9 | 0.884 | 1.53 | | | | | | | | | | | | |
| 2 | 9 | 1.200 | 1.41 | - | | | | | | | | | | | |
| 3 | 3 | 0.921 | 1.24 | - | - | | | | | | | | | | |
| 4 | 1 | 1.283 | 2.94 | - | - | 7.85 | | | | | | | | | |
| 5 | 1 | 1.969 | 1.72 | - | - | 7.21 | -14.54 | | | | | | | | |
| 6 | 3 | 0.892 | 1.25 | - | - | - | - | - | 7.4* | | | | | | |
| 7 | 1 | 0.951* | - | - | - | - | - | - | 7.4* | -14.4* | | | | | |
| 8 | 1 | 1.106* | - | - | - | - | - | - | - | 4.31 | 12.31 | | | | |
| 9 | 1 | 1.829 | 1.77 | - | - | - | - | - | - | 5.18 | 11.42 | -13.57 | | | |
| 10 | 1 | 1.955 | 1.82 | - | - | - | - | - | - | - | - | - | - | | |
| 11 | 1 | 0.126 | 1.78 | - | - | - | - | - | - | - | - | - | - | | |
| 12 | 1 | 0.768 | 1.97 | - | - | - | - | - | - | - | - | - | - | -4.20 | |
| 13 | 1 | 1.454 | 1.70 | - | - | - | - | - | - | - | - | - | - | 4.56 | 8.24 |

*the data is not reliably determined

**Figure S49.** Simulated spectrum for mono((2S(R),3R(S),5S(R))-2,5-di-*tert*-butyl-2,5-diethyl-3-((((3-(trimethylammonio)propyl)carbamoyl)oxy)methyl)pyrrolidin-1-oxyl) monoiodide (**26**)

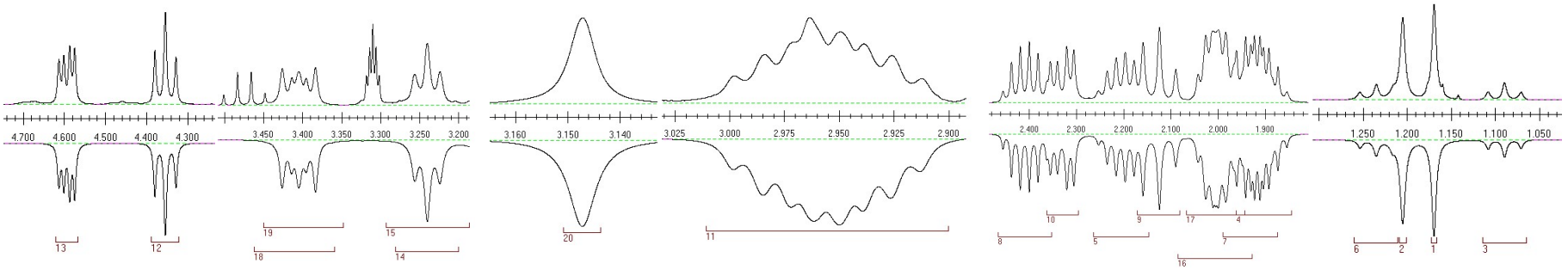



**Table S2.** Parameters of spins system for mono((2S(R),3R(S),5S(R))-2,5-di-*tert*-butyl-2,5-diethyl-3-((((3-(trimethylammonio)propyl)carbamoyl)oxy)methyl)pyrrolidin-1-oxyl) monoiodide (**26**)

| # | n | Shift | Width | J[1] | J[2] | J[3] | J[4] | J[5] | J[6] | J[7] | J[8] | J[9] | J[10] | J[11] | J[12] | J[13] | J[14] | J[15] | J[16] | J[17] | J[18] | J[19] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 9 | 1.169 | 2.45 | | | | | | | | | | | | | | | | | | | |
| 2 | 9 | 1.205 | 2.84 | - | | | | | | | | | | | | | | | | | | |
| 3 | 3 | 1.090 | 2.25 | - | - | | | | | | | | | | | | | | | | | |
| 4 | 1 | 1.903 | 2.89 | - | - | 7.59 | | | | | | | | | | | | | | | | |
| 5 | 1 | 2.205 | 3.33 | - | - | 7.37 | -15.41 | | | | | | | | | | | | | | | |
| 6 | 3 | 1.235 | 2.59 | - | - | - | - | - | | | | | | | | | | | | | | |
| 7 | 1 | 1.933 | 2.75 | - | - | - | - | - | 7.43 | | | | | | | | | | | | | |
| 8 | 1 | 2.409 | 2.44 | - | - | - | - | - | 7.25 | -15.23 | | | | | | | | | | | | |
| 9 | 1 | 2.126 | 3.73 | - | - | - | - | - | - | - | - | | | | | | | | | | | |
| 10 | 1 | 2.329 | 3.35 | - | - | - | - | - | - | - | - | -13.94 | | | | | | | | | | |
| 11 | 1 | 2.955 | 3.92 | - | - | - | - | - | - | - | - | 13.72 | 5.99 | | | | | | | | | |
| 12 | 1 | 4.355 | 3.10 | - | - | - | - | - | - | - | - | - | - | 9.98 | | | | | | | | |
| 13 | 1 | 4.594 | 3.19 | - | - | - | - | - | - | - | - | - | - | 4.85 | -10.59 | | | | | | | |
| 14 | 1 | 3.241 | 4.20 | - | - | - | - | - | - | - | - | - | - | - | - | - | | | | | | |
| 15 | 1 | 3.240 | 2.88 | - | - | - | - | - | - | - | - | - | - | - | - | - | -16.26* | | | | | |
| 16 | 1 | 2.006 | 2.63 | - | - | - | - | - | - | - | - | - | - | - | - | - | 4.75 | 9.92 | | | | |
| 17 | 1 | 2.005 | 3.40 | - | - | - | - | - | - | - | - | - | - | - | - | - | 2.98 | 8.09 | -16.53* | | | |
| 18 | 1 | 3.410 | 2.85 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 6.83 | 10.43 | | |
| 19 | 1 | 3.399 | 2.62 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 14.69 | 2.46 | -15.78* | |
| 20 | 9 | 3.147 | 2.47 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |

***the data is not reliably determined**

## IR Spectra

**Figure S50.** IR (neat) of (2R(S),3R(S),4R(S),5S(R))-2,5-di-*tert*-butyl-3,4-bis(methoxycarbonyl)-2-ethylpyrrolidine (**8**)

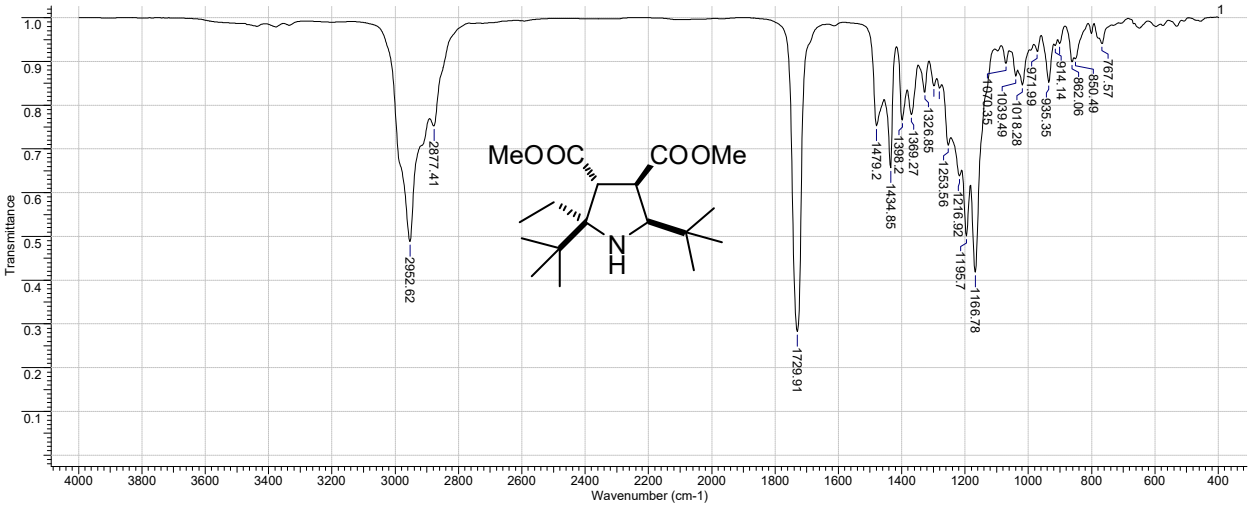



**Figure S51.** IR (neat) of (2S(R),3R(S),4R(S),5R(S))-2,5-di-*tert*-butyl-3,4-bis(methoxycarbonyl)-2-ethylpyrrolidine (**9**)

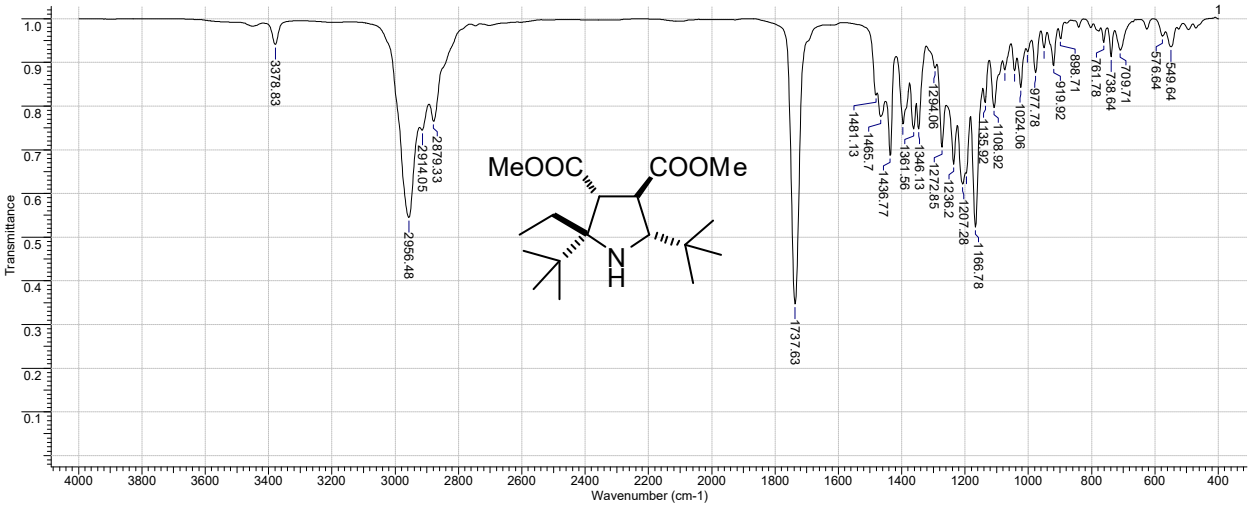



**Figure S52.** IR (neat) of dimethyl 2-(1-((2,2-dimethylpentan-3-ylidene)amino)-2,2-dimethylpropyl)succinate (**10**)

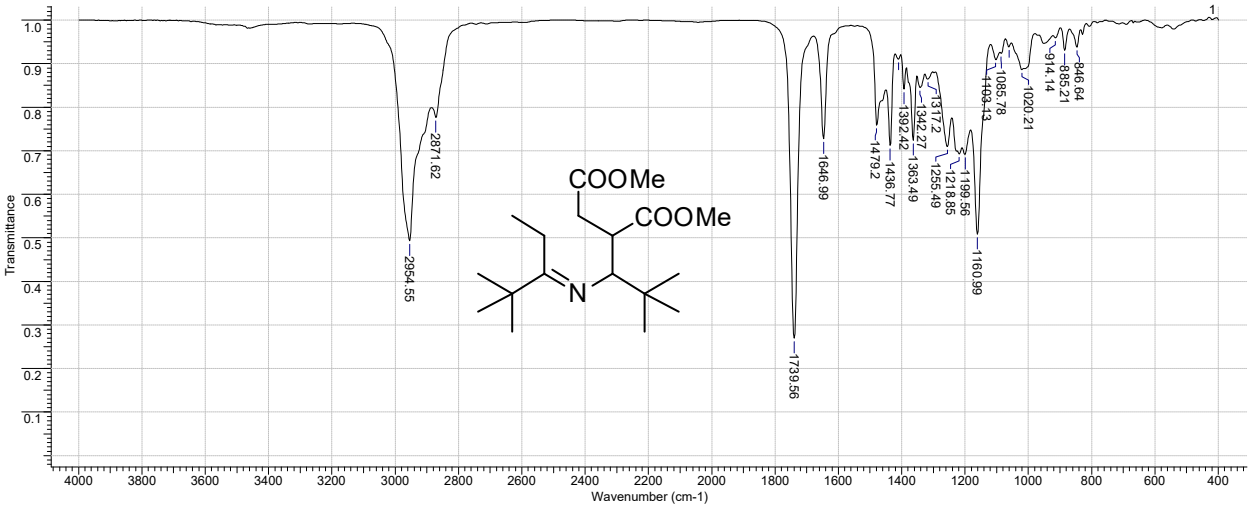


**Figure S53.** IR (KBr) of (2R(S),3R(S),4R(S),5S(R))-2,5-di-tert-butyl-3,4-bis(hydroxymethyl)-2-ethylpyrrolidine (**11**)

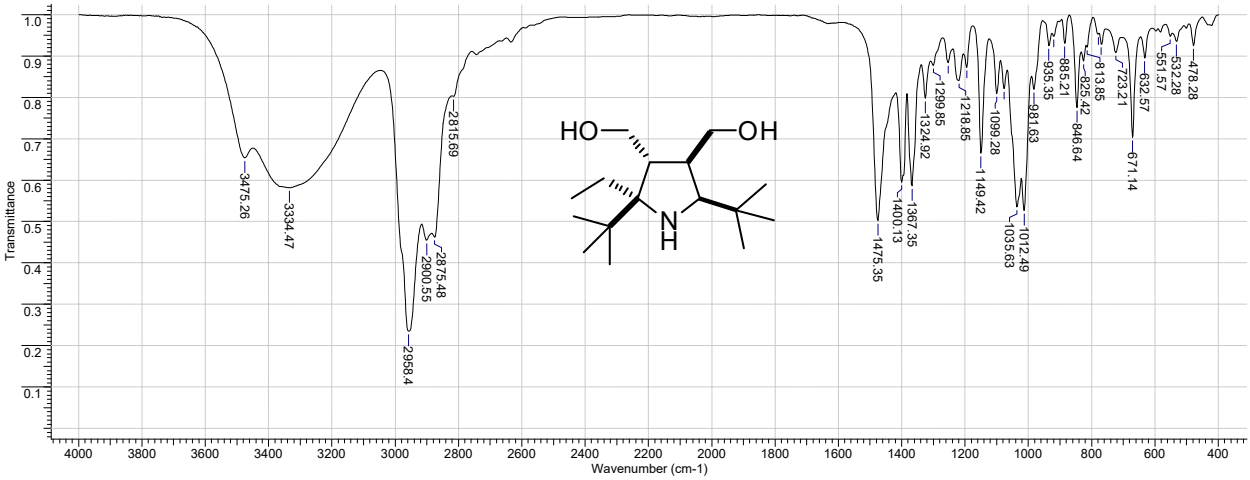



**Figure S54.** IR (KBr) of (2R(S),3R(S),4R(S))-2,5-di-tert-butyl-2-ethyl-3,4-bis(hydroxymethyl)-3,4-dihydro-2H-pyrrole 1-oxide (**12**)

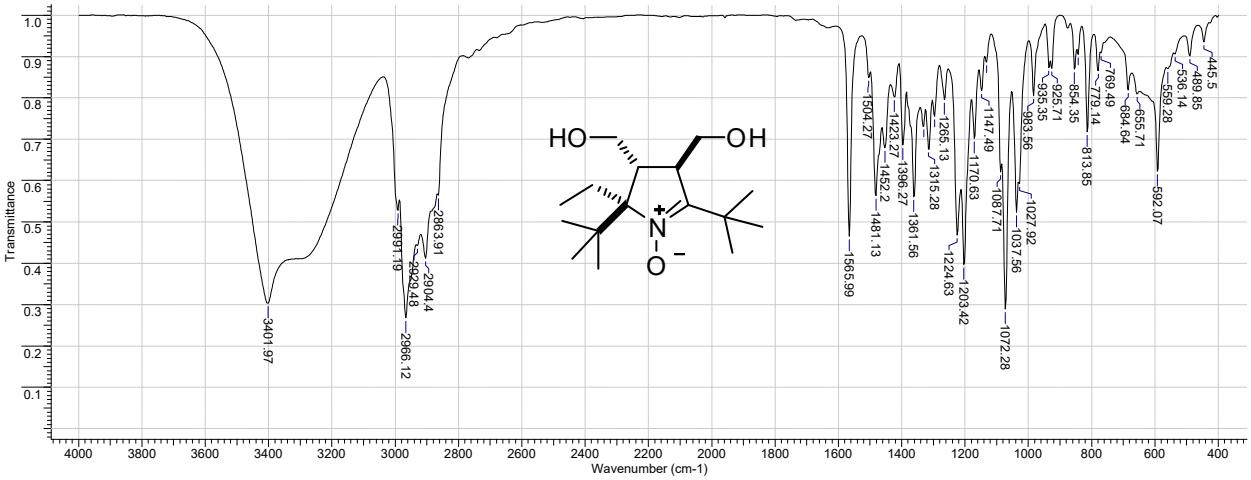



**Figure S55.** IR (KBr) of 2,2,5-Triethyl-5-tert-butyl-3,4-bis(hydroxymethyl)-pyrrolidine-1-oxyl (**1a**)

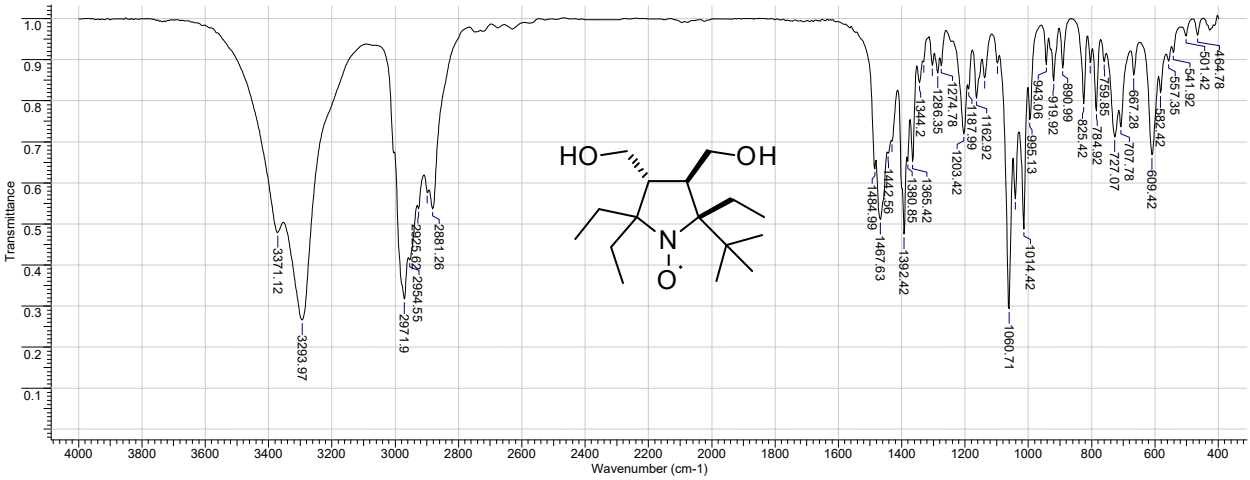


**Figure S56.** IR(KBr) of (2R(S),3R(S),4R(S))-2,5-di-tert-butyl-2-ethyl-3,4-bis(((2-methoxypropan-2-yl)oxy)methyl)-3,4-dihydro-2H-pyrrole 1-oxide (**14**)

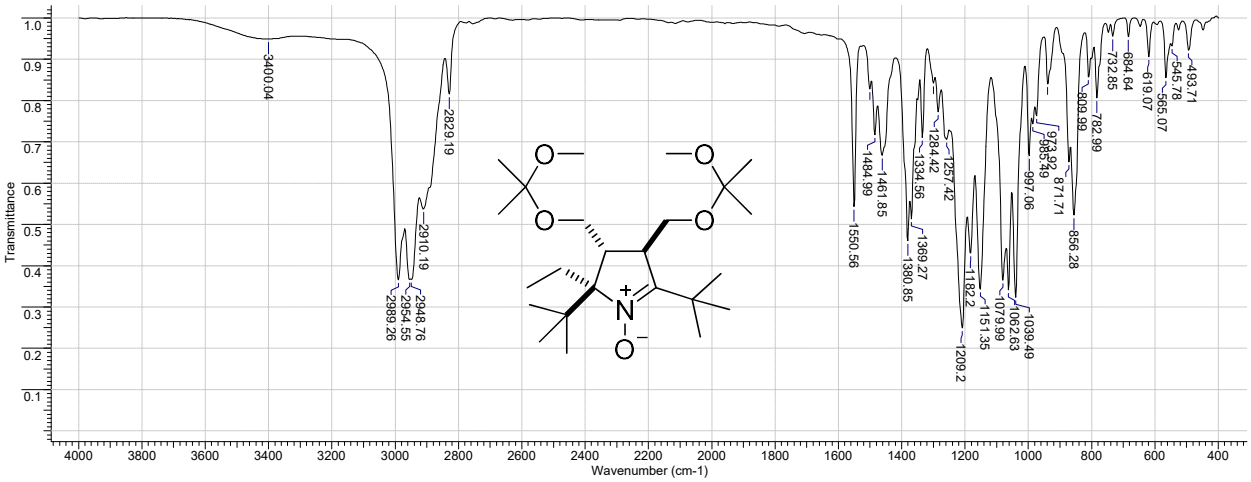



**Figure S57.** IR (neat) of (1S(R),4R(S),5R(S))-2,4-di-*tert*-butyl-4-ethyl-1-propyl-3-azabicyclo[3.1.0]hex-2-ene (**15**)

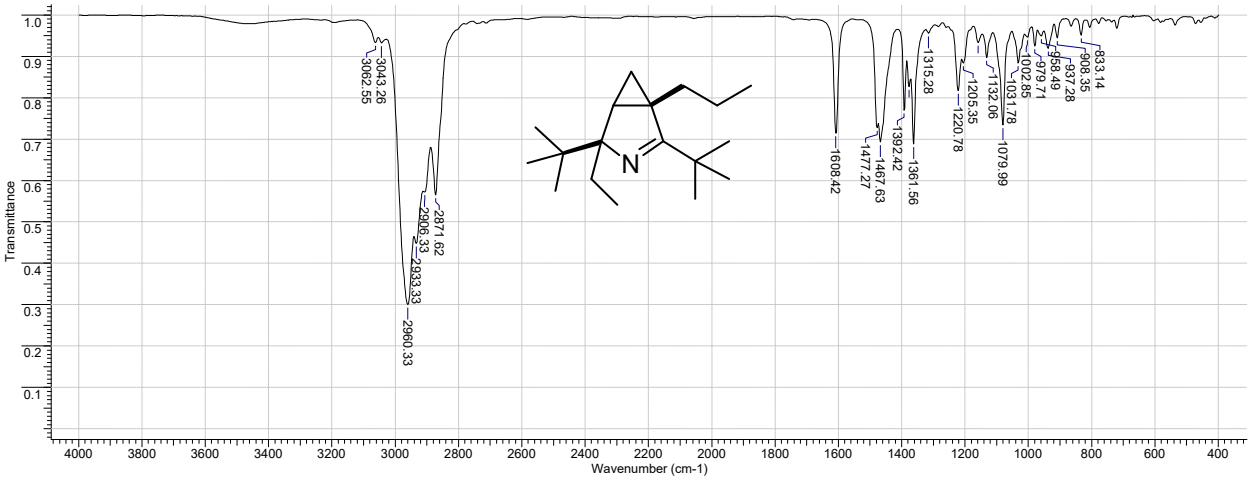



**Figure S58.** IR (neat) of (2S(R),3R(S),4R(S))-2,5-di-*tert*-butyl-2-ethyl-3,4-bis(methoxycarbonyl)-3,4-dihydro-2*H*-pyrrole 1-oxide (**16**)

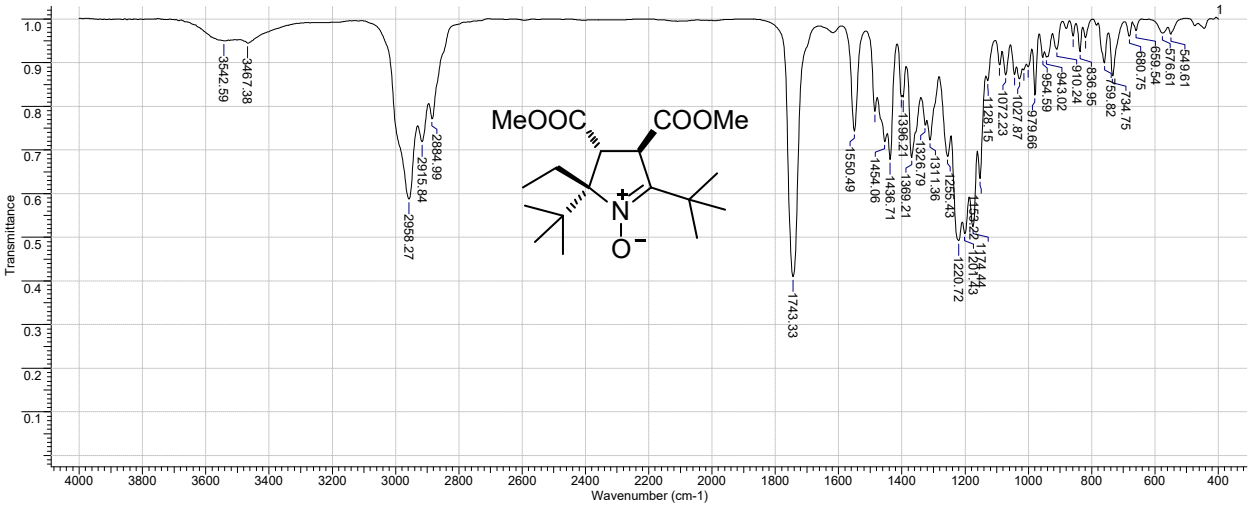


**Figure S59.** IR (KBr) of (2S(R),3R(S))-2,5-di-tert-butyl-2-ethyl-3-(methoxycarbonyl)-3,4-dihydro-2H-pyrrole 1-oxide (**17**)

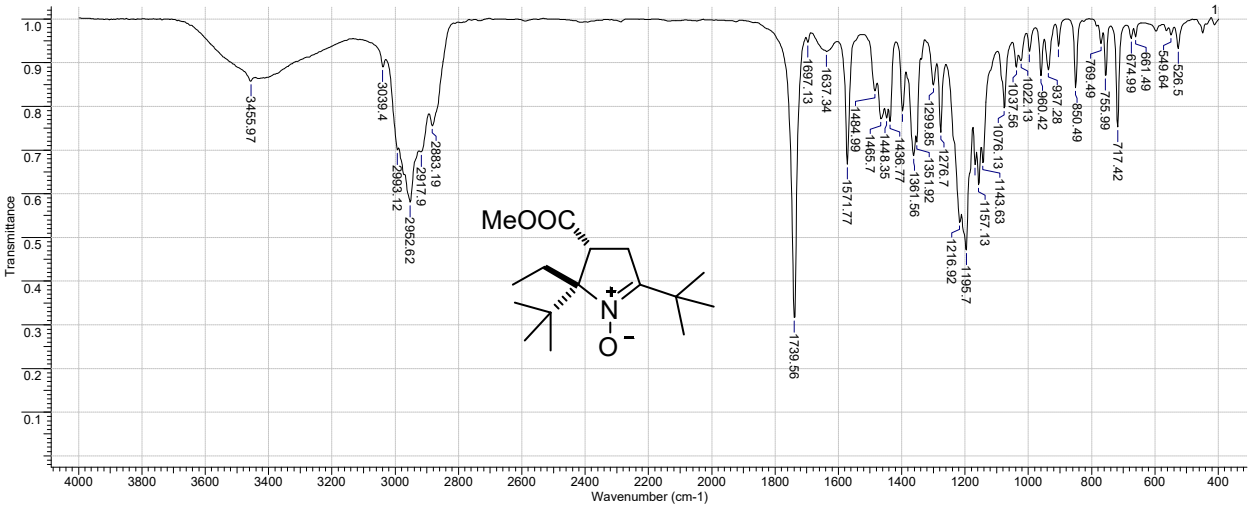



**Figure S60.** IR (KBr) of (2S(R),3S(R))-2,5-di-tert-butyl-2-ethyl-3-(methoxycarbonyl)-3,4-dihydro-2H-pyrrole 1-oxide (**18**)

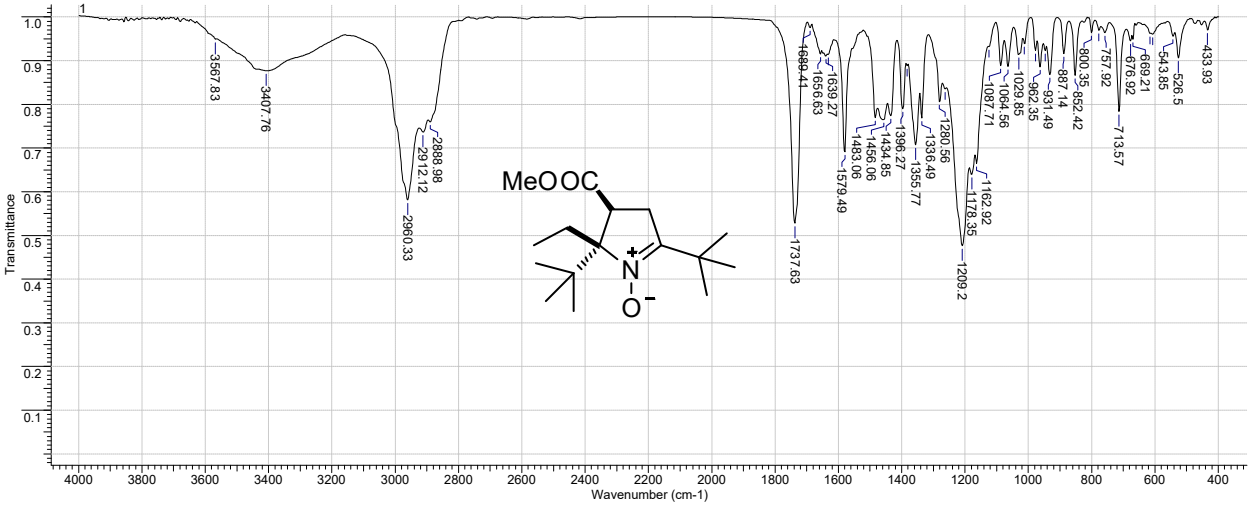



**Figure S61.** IR (KBr) of (2S(R),3R(S))-2,5-di-tert-butyl-2-ethyl-3-(hydroxymethyl)-3,4-dihydro-2H-pyrrole 1-oxide (**20**)

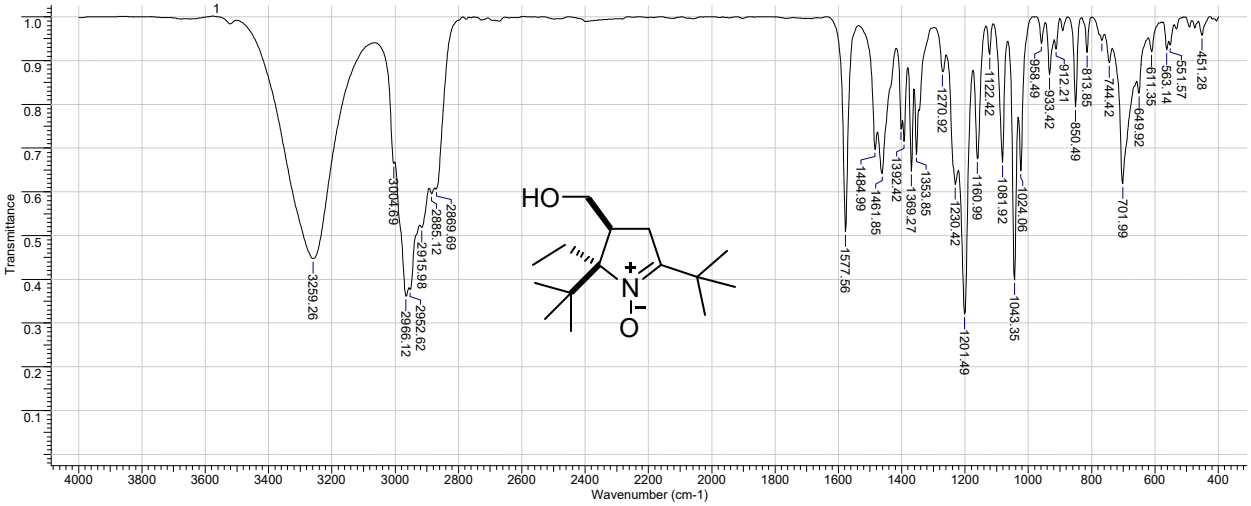


**Figure S62.** IR (KBr) of (2S(R),3S(R))-2,5-di-tert-butyl-2-ethyl-3-(hydroxymethyl)-3,4-dihydro-2H-pyrrole 1-oxide (**21**)

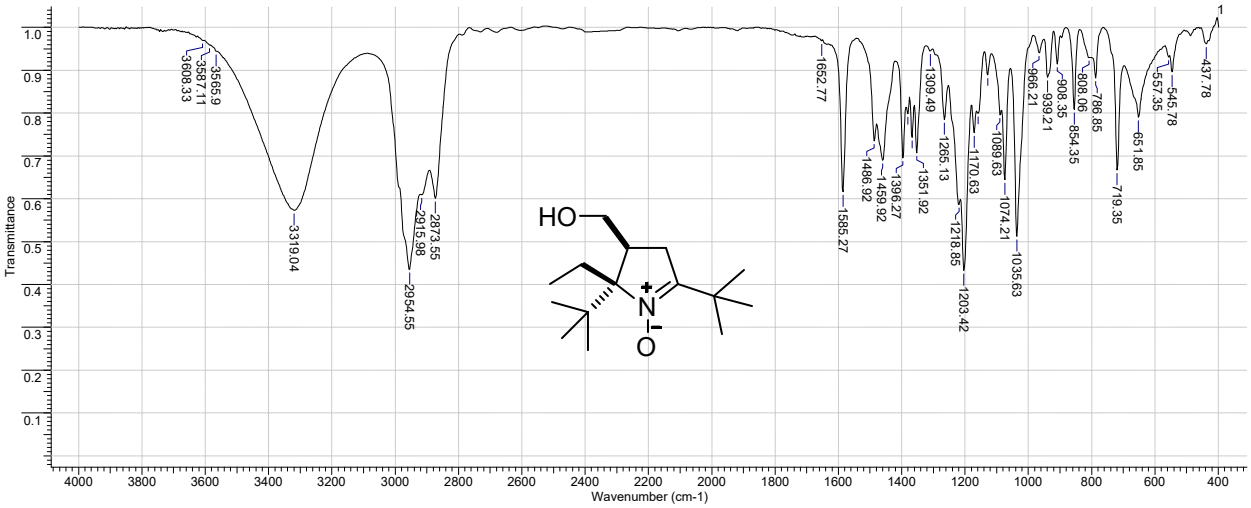



**Figure S63.** IR (neat) of (2S(R),3R(S))-2,5-di-tert-butyl-2,5-diethyl-3-(hydroxymethyl)pyrrolidin-1-oxyl (**23**)

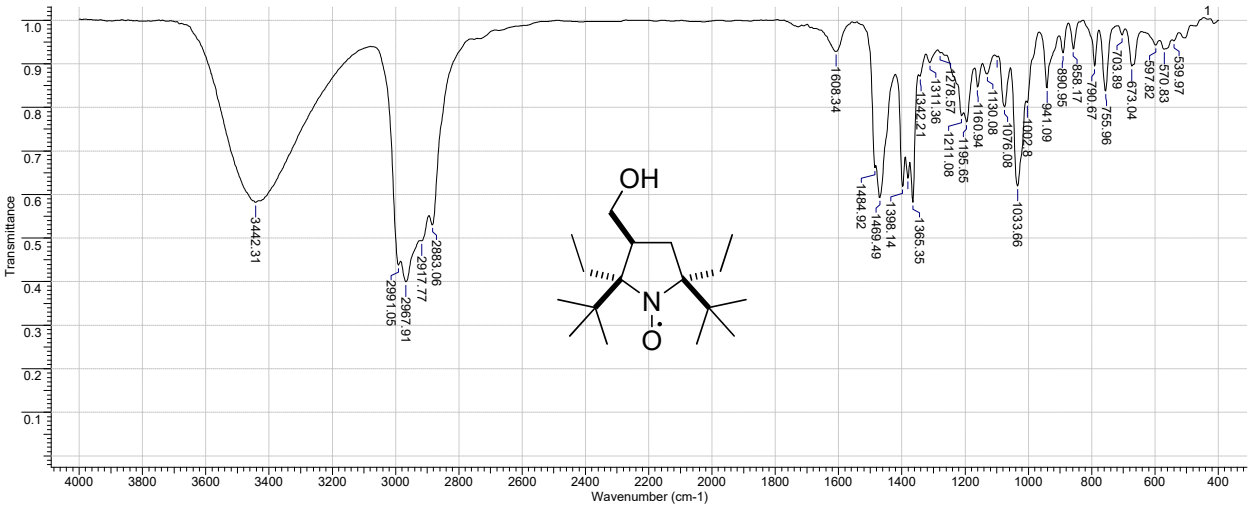



**Figure S64.** IR (neat) of (2S(R),3R(S),5S(R))-2,5-di-*tert*-butyl-3-((((3-(dimethylamino)propyl)carbamoyl)oxy)methyl)-2,5-diethylpyrrolidin-1-oxyl (**25**)

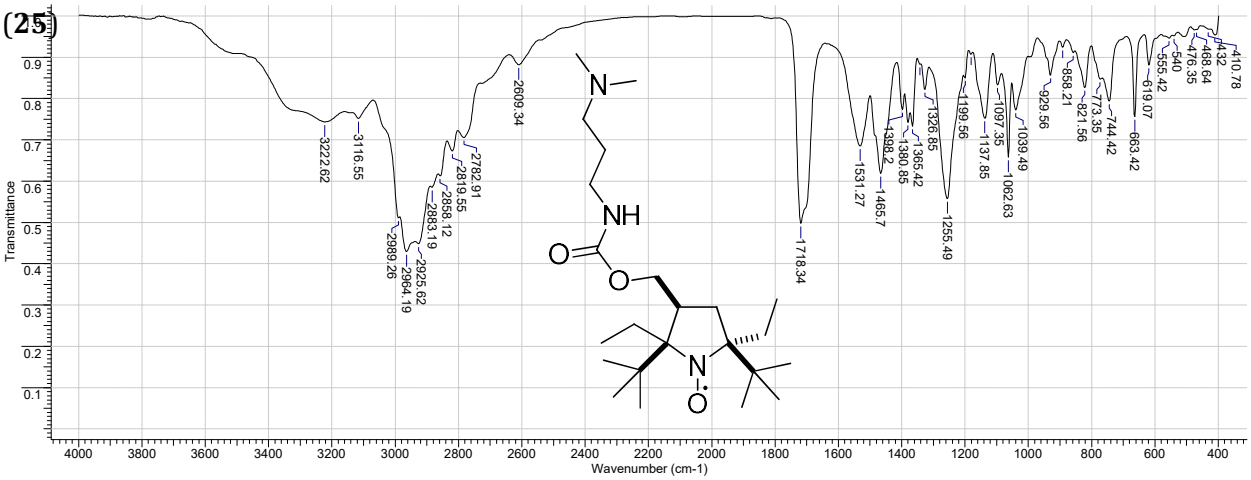
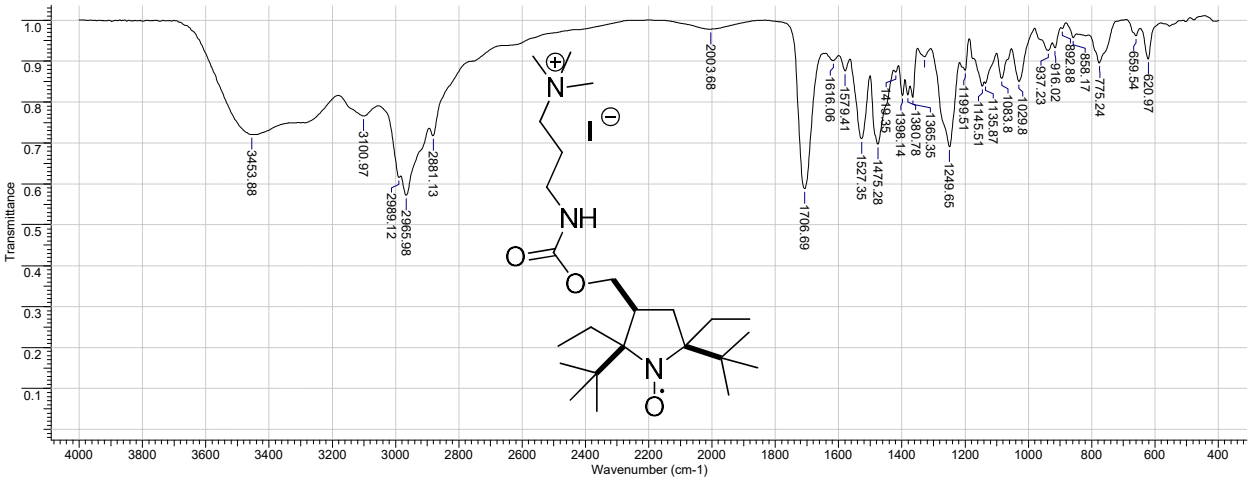


**Figure S65.** IR (neat) of mono((2S(R),3R(S),5S(R))-2,5-di-*tert*-butyl-2,5-diethyl-3-((((3-(trimethylammonio)propyl)carbamoyl)oxy)methyl)pyrrolidin-1-oxyl) monoiodide (**26**)



## XRD Data

Chemical structures of the molecules **20** and **21** obtained by X-ray single crystal diffractometry:

**Figure S66.** Crystal structure for (2S(R),3R(S))-2,5-di-tert-butyl-2-ethyl-3-(hydroxymethyl)-3,4-dihydro-2H-pyrrole 1-oxide (**20**)

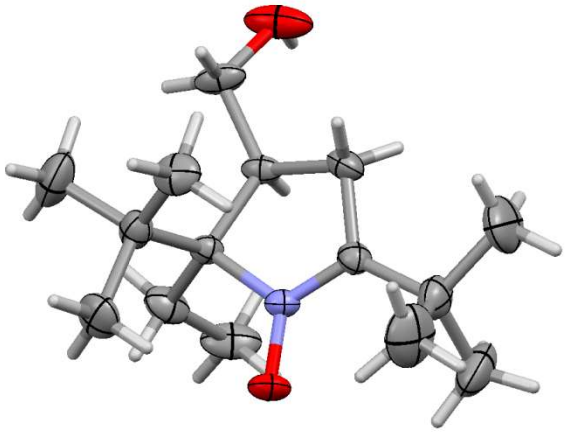
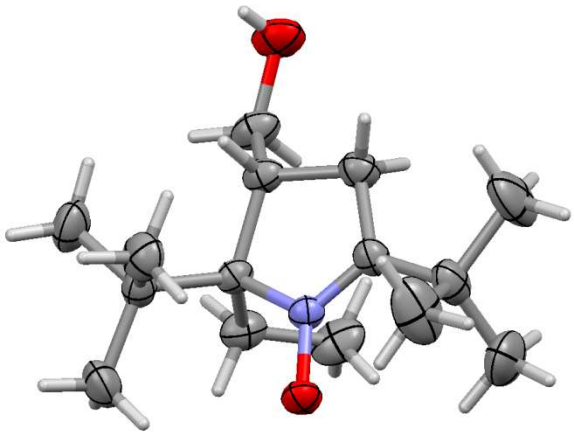


**Figure S67.** Crystal structure for (2S(R),3S(R))-2,5-di-tert-butyl-2-ethyl-3-(hydroxymethyl)-3,4-dihydro-2H-pyrrole 1-oxide (**21**)



Crystal data **20**: $C_{15}H_{29}NO_2$, M = 255.39, monoclinic, space group C2/c, at 296 K: a = 20.1597(14), b = 15.1070(10), c = 12.4016(7) Å , β = 119.835(2)°, V = 3276.3(4) $Å^3$, Z = 8, $d_{calc}$ = 1.036 $g·cm^{-3}$, μ = 0.067 $mm^{-1}$, a total of 26540 ($\theta_{max}$ = 28.02°), 3964 I unique ($R_{int}$ = 0.0623), 2877 [I > 2σ(I)], 170 parameters. GooF = 1.001, $R_1$ = 0.0887, $wR_2$ = 0.2676 [I > 2σ(I)], $R_1$ = 0.1107, $wR_2$ = 0.3048 (all data), max/min diff. peak 1.39/-0.32 $e·Å^{-3}$. CCDC 2312570.

Crystal data **21**: $C_{15}H_{29}NO_2$, M = 255.39, triclinic, space group P-1, at 296 K: a = 9.5627(8), b = 12.9565(13), c = 13.4896(14) Å , α = 85.641(4), β = 88.100(4), γ = 79.040(3)°, V = 1635.8(3) $Å^3$ , Z = 4, $d_{calc}$ = 1.037 $g·cm^{-3}$, μ = 0.067 $mm^{-1}$, a total of 16573I ($\theta_{max}$ = 25.21°), 5832 unique ($R_{int}$ = 0.0642), 3298 [I > 2σ(I)], 339 parameters. GooF = 1.015, $R_1$ = 0.0616, $wR_2$ = 0.1775 [I > 2σ(I)], $R_1$ = 0.1144, $wR_2$ = 0.2142 (all data), max/min diff. peak 0.34/-0.18 $e·Å^{-3}$. CCDC 2312569.

## EPR Data

**Figure S68.** Reduction profiles of **1a** (0.2 mM) in anaerobic conditions in phosphate-citrate-borate buffer (5 mM, pH 7.4) in presence of GSH (5 mM) and ascorbate (200 ( ,)■300●( )mM). The amplitude of the low-field component of the EPR spectrum was followed, spectrometer settings: frequency, 9.87 GHz; centerfield, 350.6 mT; sweep range, 10 mT; microwave power, 2.0 mW; modulation amplitude, 0.1 mT; time constant, 10.24 ms; and conversion time, 20.48 ms.

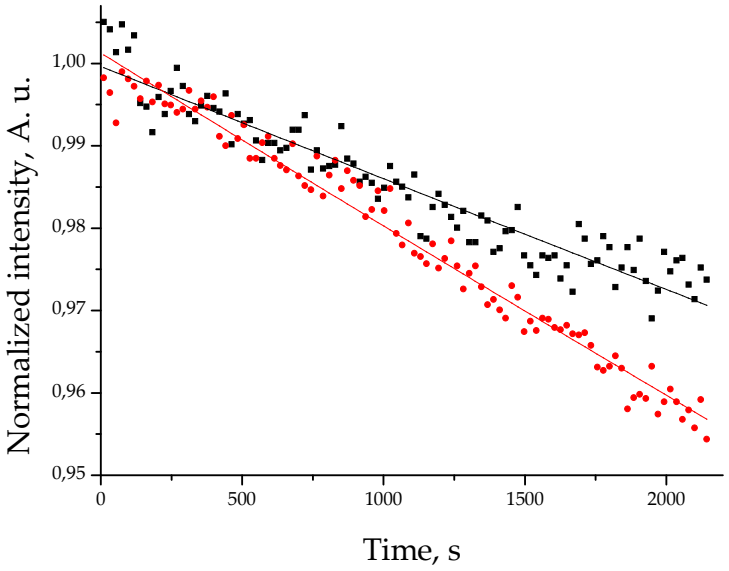



**Figure S69.** The plot of the nitroxide **1a** first order decay constant $k_1$ versus ascorbate concentration and the linear fitcorresponding to $k_2$ = (7.0 ±2× ) $10^{-5}$ $M^{-1}s^{-1}$.

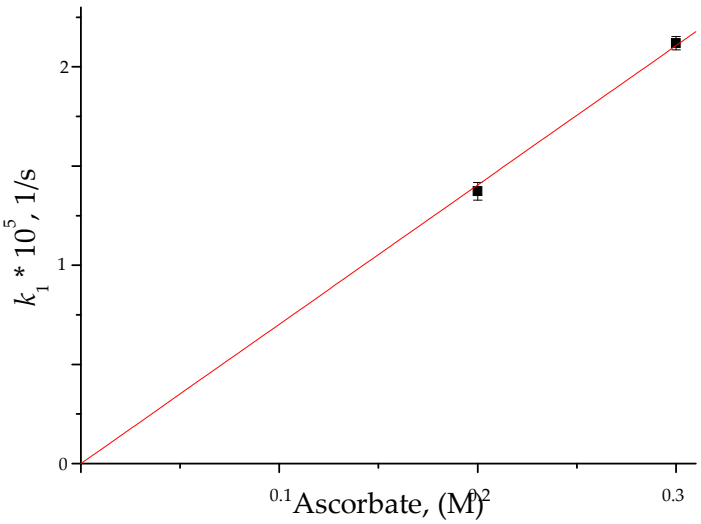


**Figure S70.** EPR spectrum of **26** (0.2 mM) in distilled water. Spectrometer settings: frequency, 9.87 GHz; microwave power, 5.0 mW; modulation amplitude, 0.05 mT; time constant, 50–100 ms; and conversion time, 5.12 ms.

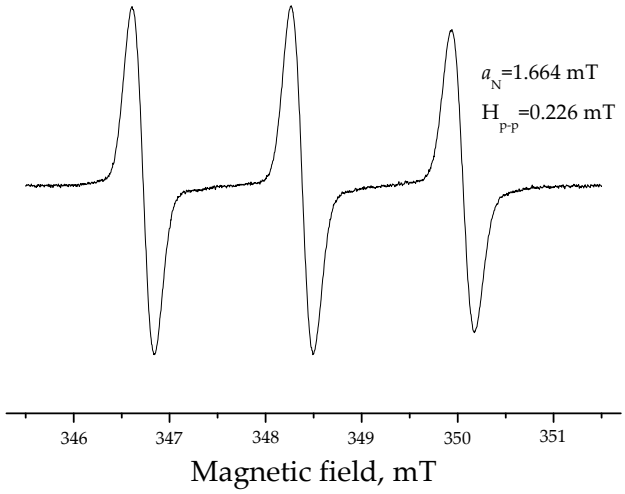



**Figure S71.** Reduction profiles of **26** (0.2 mM) in anaerobic conditions in phosphate-citrate-borate buffer (5 mM, pH 7.4) in presence of GSH (5 mM) and ascorbate (100 ( ,)■200●( ) and 300 (◆) mM). The amplitude of the low-field component of the EPR spectrum was followed, spectrometer settings: frequency, 9.87 GHz; centerfield, 350.6 mT; sweep range, 10 mT; microwave power, 2.0 mW; modulation amplitude, 0.1 mT; time constant, 10.24 ms; and conversion time, 20.48 ms.

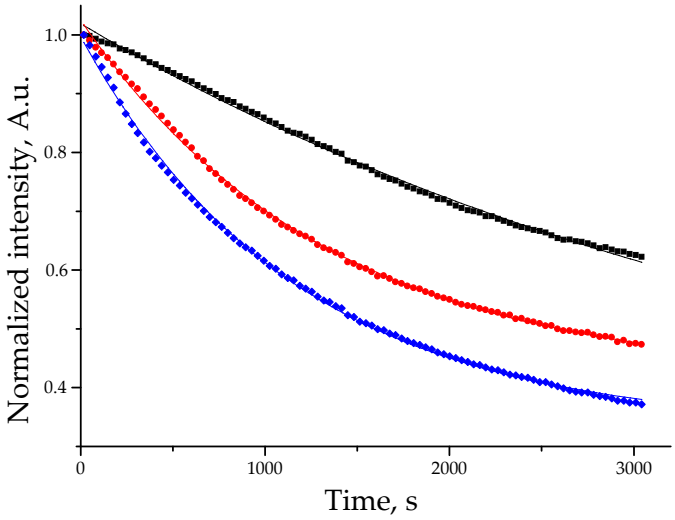


**Figure S72.** The plot of the nitroxide **26** first order decay constant $k_1$ versus ascorbate concentration and the linear fit corresponding to $k_2$ = (2.0 ±0.1× ) $10^{-3}$ $M^{-1}s^{-1}$.