Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information

Copper-Catalyzed Aerobic Oxyamination of Alkenes of Unsaturated Keto Oximes in EtOH Toward Cyclic Nitrones

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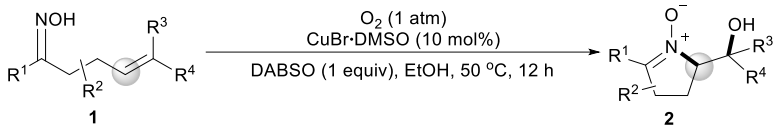
Contents

(A) General Information

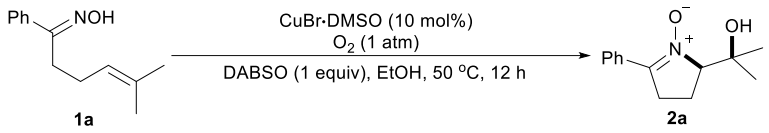
^{1}H-NMR and ^{13}C-NMR spectra were recorded at room temperature using a Bruker Avance-500 instruments or Avance-400 instruments (^{1}H NMR at 500 MHz and ^{13}C NMR at 125 MHz), NMR spectra of all products were reported in ppm with reference to solvent signals [^{1}H NMR: $CD(H)Cl_3$ (7.26 ppm), ^{13}C NMR: $CD(H)Cl_3$ (77.00 ppm)]. Highresolution mass spectra (HRMS) was recorded on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. Melting Points were recorded on Hanon MP100 Apparatus and were uncorrected. All the unsaturated oximes **1** were prepared according to the known procedures.[1] Unless otherwise noted, all reactions were carried out using standard Schlenk techniques, and the starting materials and solvents were commercially available and were used without further purification. Column chromatography was performed on silica gel (200-300 mesh) using petroleum ether (PE)/ethyl acetate (EA).

(a) General procedure for the synthesis of compounds 2



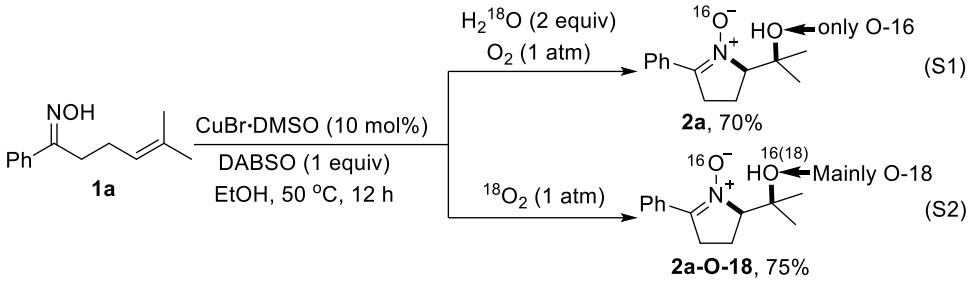
To a Schlenk tube were added 4-en-1-one oxime **1** (40.6 mg, 0.2 mmol), CuBr·DMSO (0.02 mmol; 10 mol%), DABSO (1 equiv) and EtOH (2 mL). Then the tube was charged with O_2 three times, and the mixture was stirred at 50 °C for 12 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was washed by saturated NaCl solution (5 mL × 3), and diluted in diethyl ether. The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate = 2:1) to afford **2**.

(b) General Procedure for 1 mmol Scale of 1a.

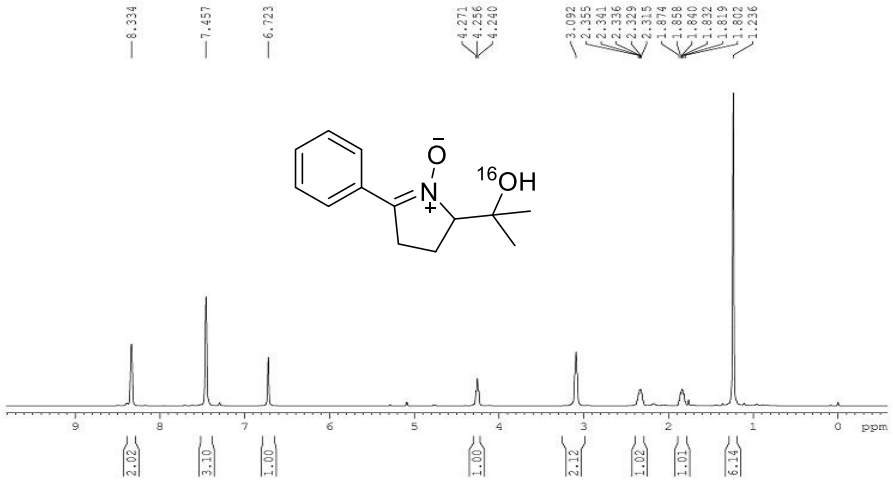


To a Schlenk tube were added 5-methyl-1-phenylhex-4-en-1-one oxime **1a** (1 mmol), CuBr·DMSO (10 mol%), DABSO (1 equiv) and EtOH (4 mL). Then the tube was charged with O_2 three times, and was stirred at 50 °C for 12 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was washed by saturated NaCl solution (5 mL × 3), and diluted in diethyl ether. The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate = 2:1) to afford **2** (64% yield; 140.2 mg).

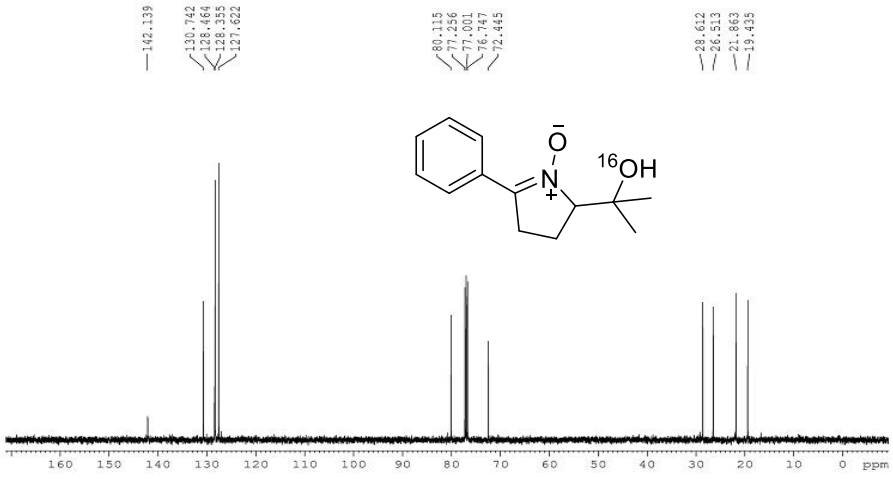
(c) The ^{18}O isotope Labelling Experiments.



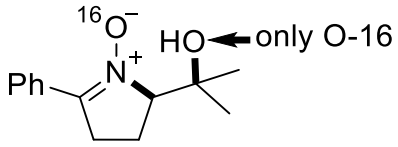
The product **2a** was purified by flash chromatography to give 30.7 mg (70%) as yellow solid. mp 126−128 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 8.33 (s, 2H), 7.46 (s, 3H), 6.72 (s, 1H), 4.26 (t, *J* = 7.5 Hz, 1H), 3.09 (s, 1H), 2.31-2.35 (m, 1H), 1.80-1.87 (m, 1H), 1.24 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 142.1, 130.7, 128.5, 128.4, 127.6, 80.1, 72.4, 28.6, 26.5, 21.9, 19.4. HRMS (ESI) m/z calcd for $C_{13}H_{18}NO_2^+$ $(M+H)^+$ 220.1332, found 220.1335.



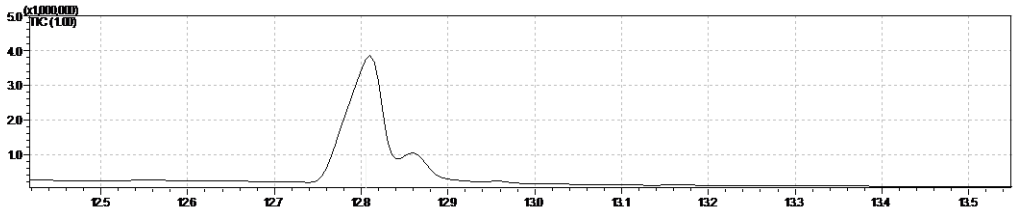
^{1}H NMR (500 MHz, $CDCl_3$)

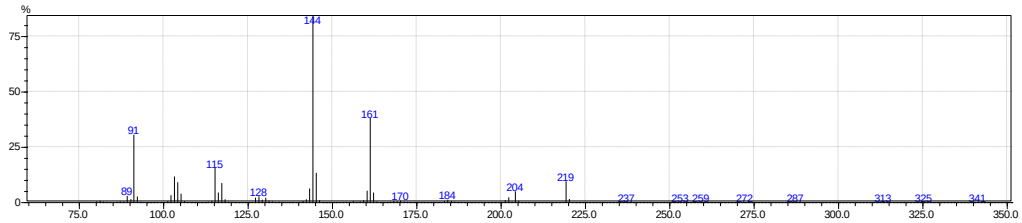


^{13}C NMR (125 MHz, $CDCl_3$)



(MW=219)





[MS Spectrum]

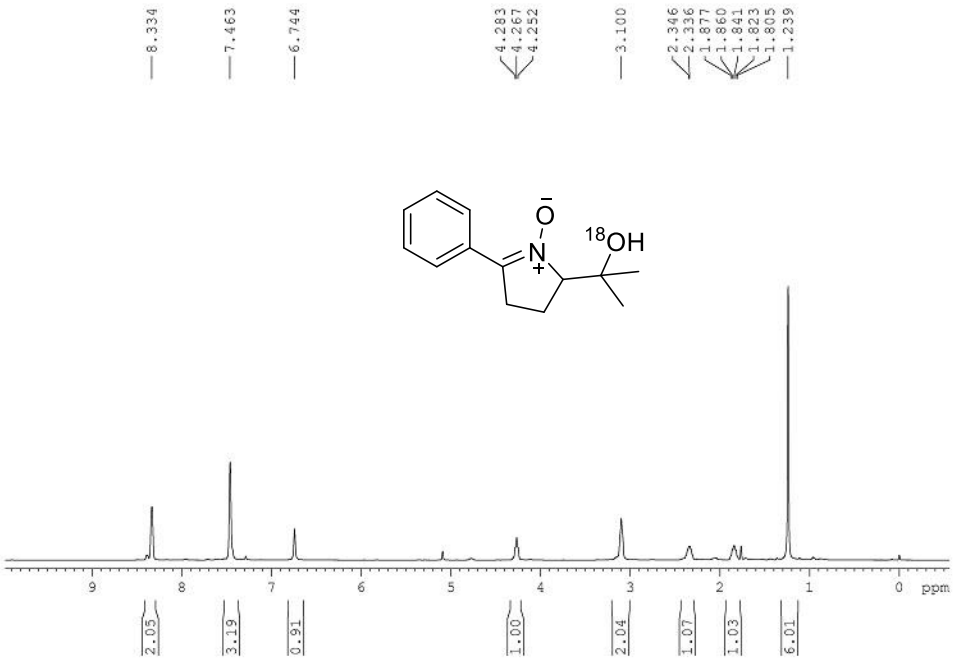
# of Peaks 516

Raw Spectrum 12.805 (scan: 1762) Base Peak m/z 144.20 (Inten : 1,180,594)

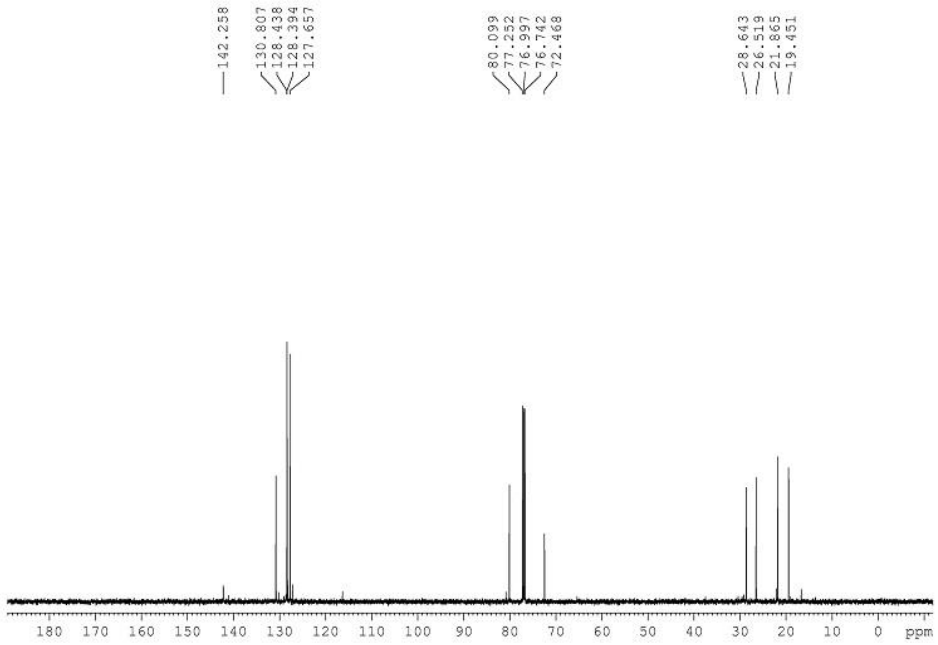
Background No Background Spectrum

m/z	Absolute Intensity	Relative Intensity	m/z	Absolute Intensity	Relative Intensity	m/z	Absolute Intensity	Relative Intensity
89.15	34681	2.94	118.20	15558	1.32	161.20	449729	38.09
90.25	16749	1.42	127.20	24751	2.10	162.20	52257	4.43
91.15	360127	30.50	128.20	31860	2.70	201.25	11797	1.00
92.15	31160	2.64	129.20	14356	1.22	202.25	26447	2.24
102.15	38335	3.25	130.20	23620	2.00	204.20	58708	4.97
103.15	137639	11.66	142.25	16233	1.37	**219.25**	**112557**	**9.53**
104.15	106717	9.04	143.25	73315	6.21	**220.25**	**17441**	**1.48**
105.15	46081	3.90	144.20	1180594	100.00	**221.20**	**1999**	**0.17**
114.25	8085	0.68	145.20	157036	13.30	222.20	292	0.02
115.20	182546	15.46	158.20	5444	0.46	223.20	209	0.02
116.20	52273	4.43	159.25	10839	0.92			
117.20	102249	8.66	160.25	61843	5.24			

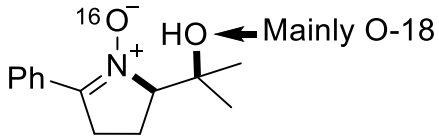
The product **2a-O-18** was purified by flash chromatography to give 32.8 mg (75%) as yellow solid. mp 126−128 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 8.33 (s, 2H), 7.46 (s, 3H), 6.74 (s, 1H), 4.27 (t, *J* = 8.0 Hz, 1H), 3.10 (s, 2H), 2.34-2.35 (m, 1H), 1.81-1.88 (m, 1H), 1.24 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 142.3, 130.8, 128.4, 128.4, 127.7, 80.1, 72.6, 72.5, 28.6, 26.5, 21.9, 19.5.



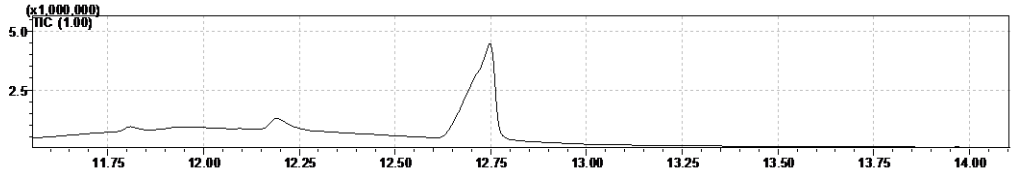
^{1}H NMR (500 MHz, $CDCl_3$)

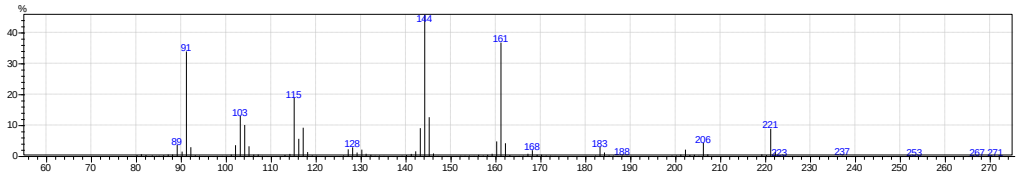


^{13}C NMR (125 MHz, $CDCl_3$)



(MW=221)





[MS Spectrum]

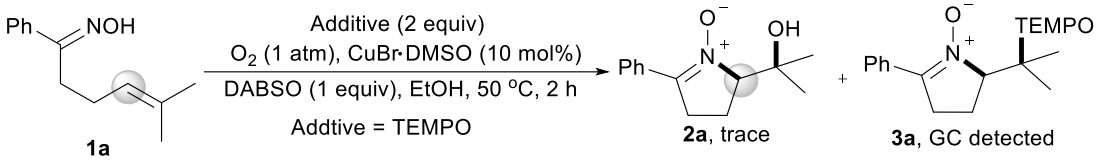
# of Peaks 483

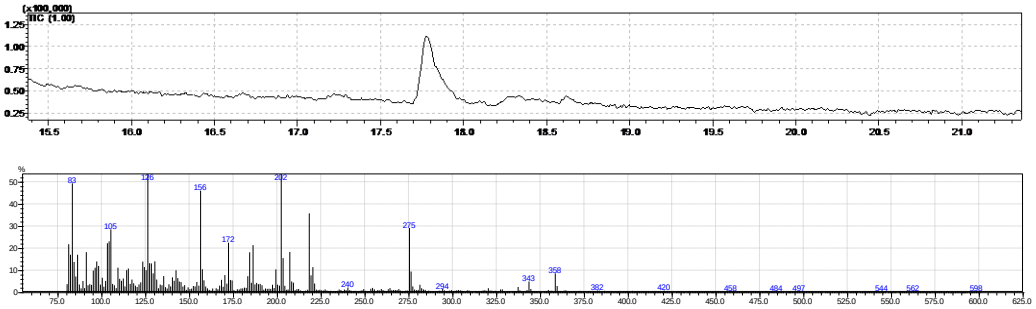
Raw Spectrum 12.745 (scan : 1750) Base Peak m/z 144.15 (Inten : 1,339,450)

Background No Background Spectrum

m/z	Absolute Intensity	Relative Intensity	m/z	Absolute Intensity	Relative Intensity	m/z	Absolute Intensity	Relative Intensity
89.05	49073	3.66	128.10	38140	2.85	184.15	15715	1.17
90.15	20024	1.49	129.10	15967	1.19	202.15	28148	2.10
91.10	45432	33.92	130.15	28547	2.13	206.15	57425	4.29
92.10	39252	2.93	142.15	20801	1.55	219.15	8052	0.60
102.05	47524	3.55	143.15	12162	9.08	220.20	4713	0.35
103.10	17444	13.02	144.15	13394	100.00	**221.15**	**1189**	**8.88**
104.10	13502	10.08	145.15	16883	12.60	222.15	1872	1.40
105.05	42823	3.20	159.15	10575	0.79	223.15	1639	0.12
115.10	25295	18.88	160.15	63993	4.78	224.10	268	0.02
116.10	75062	5.60	161.1049236		36.76	225.10	95	0.01
117.10	12347	9.22	162.10	56369	4.21			
118.10	18038	1.35	168.10	25980	1.94			
127.10	29986	2.24	183.15	40380	3.01			

(d) The TEMPO-trapped Experiments.





[MS Spectrum]

# of Peaks 509

Raw Spectrum 17.790 (scan : 2759) Base Peak m/z 126.20 (Inten : 7,908)

Background No Background Spectrum

m/z	Absolute Intensity	Relative Intensity	m/z	Absolute Intensity	Relative Intensity	m/z	Absolute Intensity	Relative Intensity
80.15	292	3.69	105.10	2249	28.44	130.15	1109	14.02
81.10	1721	21.76	106.10	302	3.82	131.20	458	5.79
82.10	1346	17.02	107.10	254	3.21	132.20	148	1.87
83.10	3903	49.36	108.10	151	1.91	133.20	279	3.53
84.15	1086	13.73	109.15	884	11.18	134.20	255	3.22
85.15	570	7.21	110.15	483	6.11	135.20	582	7.36
86.10	1346	17.02	111.15	415	5.25	136.20	188	2.38
87.10	278	3.52	112.15	499	6.31	137.20	138	1.75
88.10	142	1.80	113.10	215	2.72	138.20	287	3.63
89.15	406	5.13	114.10	796	10.07	139.20	212	2.68
90.10	151	1.91	115.05	854	10.80	140.20	537	6.79
91.10	1439	18.20	116.10	302	3.82	141.15	414	5.24
92.10	254	3.21	117.10	457	5.78	142.20	791	10.00
93.10	292	3.69	118.10	326	4.12	143.20	510	6.45
94.10	265	3.35	119.10	239	3.02	144.10	385	4.87
95.10	782	9.89	120.10	193	2.44	145.10	369	4.67
96.10	882	11.15	121.10	282	3.57	146.10	207	2.62
97.05	1104	13.96	122.15	360	4.55	147.10	258	3.26
98.15	944	11.94	123.25	1100	13.91	148.10	90	1.14
99.10	274	3.46	124.20	906	11.46	149.10	178	2.25
100.15	526	6.65	125.20	794	10.04	150.10	114	1.44
101.10	202	2.55	**126.20**	**7908**	**100.00**	151.10	135	1.71
102.10	407	5.15	127.20	1044	13.20	152.10	225	2.85
103.10	1758	22.23	128.15	1034	13.08	153.10	215	2.72
104.10	1823	23.05	129.15	680	8.60	154.10	375	4.74

155.20	239	3.02	190.20	302	3.82	235.20	102	1.29
156.20	3642	46.05	191.20	255	3.22	236.20	82	1.04
157.20	828	10.47	192.20	94	1.19	240.20	172	2.18
158.15	430	5.44	193.20	138	1.75	241.20	81	1.02
159.10	207	2.62	194.20	124	1.57	249.20	116	1.47
160.10	140	1.77	195.20	129	1.63	253.20	129	1.63
161.10	90	1.14	196.20	124	1.57	254.20	162	2.05
165.10	148	1.87	197.20	273	3.45	269.20	116	1.47
166.10	113	1.43	198.10	156	1.97	275.25	2305	29.15
167.10	239	3.02	199.10	822	10.39	276.20	745	9.42
168.15	448	5.67	200.10	274	3.46	277.20	212	2.68
169.10	202	2.55	201.20	239	3.02	281.20	271	3.43
170.05	618	7.81	202.20	7294	92.24	282.20	148	1.87
171.20	311	3.93	203.20	1225	15.49	283.20	102	1.29
172.15	1780	22.51	204.20	234	2.96	284.20	90	1.14
173.20	442	5.59	205.20	87	1.10	294.20	121	1.53
174.20	428	5.41	206.10	103	1.30	320.20	146	1.85
177.20	111	1.40	207.10	1446	18.29	327.20	102	1.29
178.20	100	1.26	208.10	386	4.88	328.20	108	1.37
179.20	137	1.73	209.10	345	4.36	342.20	81	1.02
180.20	140	1.77	210.10	74	0.94	343.35	387	4.89
181.20	169	2.14	211.10	113	1.43	344.40	118	1.49
182.20	158	2.00	212.10	122	1.54	354.40	86	1.09
183.15	579	7.32	217.20	94	1.19	355.40	54	0.68
184.20	1434	18.13	218.15	2826	35.74	356.40	58	0.73
185.15	343	4.34	219.15	608	7.69	357.40	41	0.52
186.15	1692	21.40	220.20	903	11.42	**358.35**	**680**	**8.60**
187.20	286	3.62	221.20	314	3.97	359.40	228	2.88
188.20	338	4.27	222.20	97	1.23	360.40	44	0.56
189.20	294	3.72	227.20	102	1.29			

(e) EPR spectra Experiments

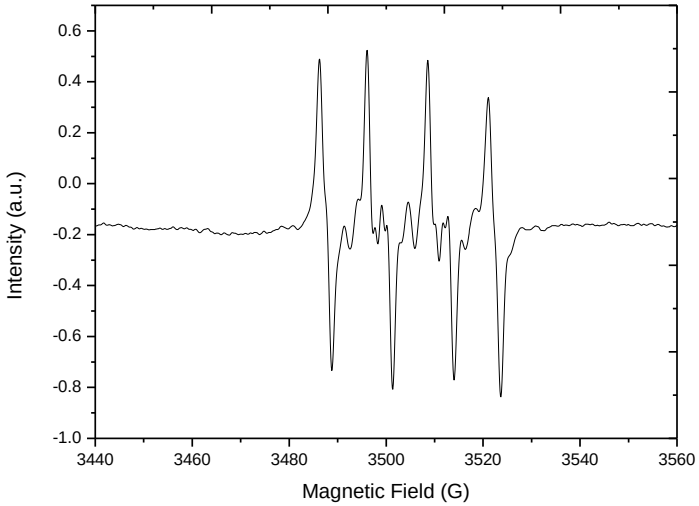


Figure S1. EPR spectra of reaction system: 1a (0.20 mmol), CuBr·DMSO (0.020 mmol), DABSO(0.2 mmol), EtOH (2 mL), stirred at 50 °C under O_2 (1 atm), 0.5 h. 0.01 mL of this reaction solution was taken out into a small tube, followed by the addition of 0.01 mL DMPO (5*10-2 M). Then, this mixture was analyzed by EPR. There are classical 4 peaks the signals corresponding to (DMPO–O(H)).

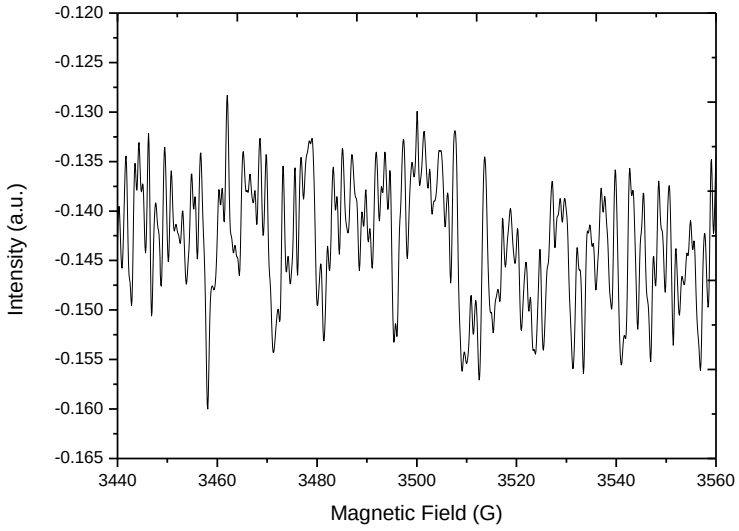


Figure S2. EPR spectra of reaction system: 1a (0.20 mmol), CuBr·DMSO (0.020 mmol), DABSO(0.2 mmol), EtOH (2 mL), stirred at 50 °C under O_2 (1 atm), 0.5 h. 0.01 mL of this reaction solution was taken out into a small tube, mixed well with 0.01 mL SOD solvent (1*10-2 M), followed by the addition of 0.01 mL DMPO (5*10-2 M). Then, this mixture was analyzed by EPR analysis.

In the EPR spectra monitored with the addition of the radical trap 5-,5-dimethyl-1-pyrroline N-oxide (DMPO), the signal corresponding to DMPO−O(H) has been identified which are classical four peaks. Furthermore, the EPR analysis results demonstrate that the hydroxyl radical may be derived from a superoxide compound.

(f) The UV-Visible Spectroscopic Analyses DABSO and 1a effect of catalyst.

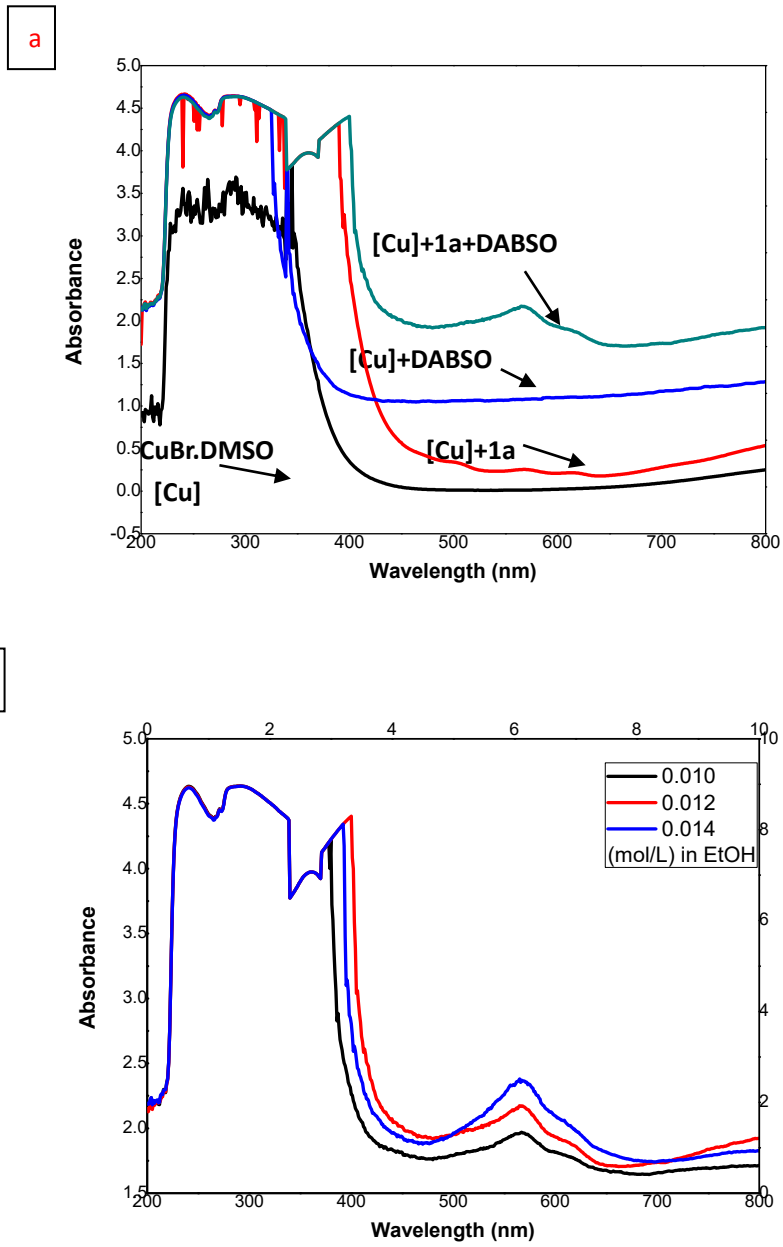
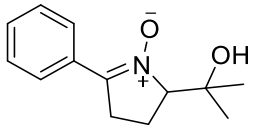


Figure S3: The UV-Visible spectroscopic experiment. (a) CuBr·DMSO (0.01mmol/mL) in EtOH (dark line); both CuBr·DMSO (0.01 mmol/mL) and 1a (0.01 mmol/mL) in EtOH (red line); both CuBr·DMSO (0.01 mmol/mL) and DABSO (0.01 mmol/mL) in EtOH (blue line); CuBr·DMSO (0.01 mmol/mL), 1a (0.01 mmol/mL) and DABSO (0.01 mmol/mL) in EtOH (green line). (b) CuBr·DMSO (0.01 mmol/mL),DABSO (0.01 mmol/mL) and various concentrations of 1a in EtOH.

Figure S3 (a) shows that coordination of the **1a** with the **Cu**^{I} forms the new complex **Cu-DABSO-1a** as the maximum absorption (Figure 1). But in the absence of **DABSO**, CuBr·DMSO or CuBr·DMSO /**1a** has no absorption peaks in the visible light region. Meanwhile, a variation of the absorbance was also along with the solution concentration of **1a** changing, suggesting that the DABSO is indispensable and a coordination the Cu^{I} species with **DABSO** and **1a** occurs.

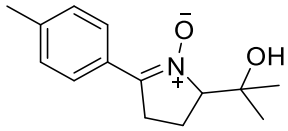
(B) Analytical Data

2-(2-hydroxypropan-2-yl)-5-phenyl-3,4-dihydro-2H-pyrrole 1-oxide (2a)



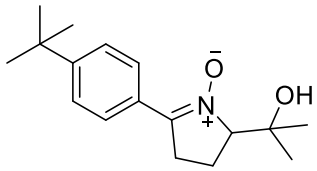
The product was purified by flash chromatography to give 32.9 mg (75%) as a yellow solid. mp 126−128 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 8.33 (s, 2H), 7.46 (s, 3H), 6.72 (s, 1H), 4.26 (t, *J* = 7.5 Hz, 1H), 3.09 (s, 1H), 2.31-2.35 (m, 1H), 1.80-1.87 (m, 1H), 1.24 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 142.1, 130.7, 128.5, 128.4, 127.6, 80.1, 72.4, 28.6, 26.5, 21.9, 19.4. HRMS (ESI) m/z calcd for $C_{13}H_{18}NO_2^+$ $(M+H)^+$ 220.1332, found 220.1335.

2-(2-hydroxypropan-2-yl)-5-(p-tolyl)-3,4-dihydro-2H-pyrrole 1-oxide (2b)



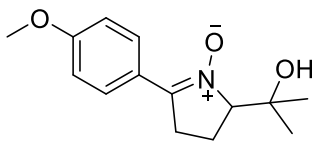
The product was purified by flash chromatography to give 35.0 mg (75%) as a yellow solid. mp 132−134 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 8.24 (d, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 7.0 Hz, 2H), 6.78 (s, 1H), 4.26 (t, *J* = 7.5 Hz, 1H), 3.08 (d, *J* = 6.5 Hz, 2H), 2.40 (s, 3H), 2.31-2.37 (m, 1H), 1.79-1.87 (m, 1H), 1.23 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 142.3, 141.4, 129.2, 127.7, 125.8, 80.0, 72.6, 28.7, 26.6, 21.9, 21.6, 19.5. HRMS (ESI) m/z calcd for $C_{14}H_{20}NO_2^+$ $(M+H)^+$ 234.1489, found 234.1478.

5-(4-(tert-butyl)phenyl)-2-(2-hydroxypropan-2-yl)-3,4-dihydro-2H-pyrrole 1-oxide (2c)



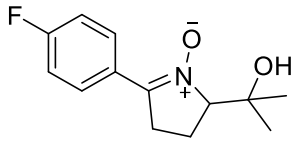
The product was purified by flash chromatography to give 41.8 mg (76%) as a yellow solid. mp 105−107 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 8.26 (d, *J* = 10.5 Hz, 2H), 7.48 (d, *J* = 10.5 Hz, 2H), 6.79 (s, 1H), 4.25 (t, *J* = 9.5 Hz, 1H), 3.06-3.10 (m, 2H), 2.28-2.37 (m, 1H), 1.77-1.87 (m, 1H), 1.32 (s, 9H), 1.22 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 154.4, 142.1, 127.6, 125.9, 125.4, 80.0, 72.6, 35.0, 31.0, 28.7, 26.6, 21.9, 19.6. HRMS (ESI) m/z calcd for $C_{17}H_{26}NO_2^+$ $(M+H)^+$ 276.1958, found 276.1934.

2-(2-hydroxypropan-2-yl)-5-(4-methoxyphenyl)-3,4-dihydro-2H-pyrrole 1-oxide (2d)



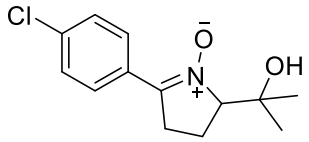
The product was purified by flash chromatography to give 38.8 mg (78%) as a yellow solid. mp 127−129 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 8.34 (d, *J* = 7.5 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.85 (s, 1H), 4.24 (s, 1H), 3.86 (s, 3H), 3.07 (s, 2H), 2.30-2.36 (m, 1H), 1.80-1.84 (m, 1H), 1.23 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 161.3, 142.0, 129.7, 121.4, 113.8, 79.7, 72.6, 55.3, 28.7, 26.6, 22.0, 19.5. HRMS (ESI) m/z calcd for $C_{14}H_{20}NO_3^+$ $(M+H)^+$ 250.1438, found 250.1445.

5-(4-fluorophenyl)-2-(2-hydroxypropan-2-yl)-3,4-dihydro-2H-pyrrole 1-oxide (2e)



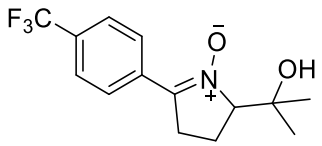
The product was purified by flash chromatography to give 33.7 mg (71%) as a yellow solid. mp 105−107 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 8.40 (s, 2H), 7.15 (t, *J* = 7.5 Hz, 2H), 6.68 (s, 1H), 4.28 (t, *J* = 8.0 Hz, 1H), 3.09 (s, 2H), 2.36 (t, *J* = 6.0 Hz, 1H), 1.82-1.89 (m, 1H), 1.24 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 163.5 (d, *J* = 252.0 Hz), 141.3, 130.1 (d, *J* = 8.4 Hz), 124.9, 115.6 (d, *J* = 21.5 Hz), 80.0, 72.5, 28.7, 26.5, 21.9, 19.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ (ppm) -107.0. HRMS (ESI) m/z calcd for $C_{13}H_{17}FNO_2^+$ $(M+H)^+$ 238.1238, found 238.1246.

5-(4-chlorophenyl)-2-(2-hydroxypropan-2-yl)-3,4-dihydro-2H-pyrrole 1-oxide (2f)



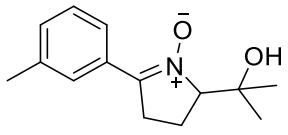
The product was purified by flash chromatography to give 36.9 mg (73%) as a yellow solid. mp 120−122 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 8.31 (d, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 7.5 Hz, 2H), 6.58 (s, 1H), 4.27 (t, *J* = 8.5 Hz, 1H), 3.08 (s, 2H), 2.36 (t, *J* = 5.5 Hz, 1H), 1.84-1.88 (m, 1H), 1.24 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 141.2, 136.5, 129.0, 128.7, 127.0, 80.2, 72.5, 28.6, 26.6, 21.9, 19.5. HRMS (ESI) m/z calcd for $C_{13}H_{17}{}^{35}ClNO_2^+$ $(M+H)^+$ 254.0942, found 254.0943.

2-(2-hydroxypropan-2-yl)-5-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2H-pyrrole 1-oxide (2g)



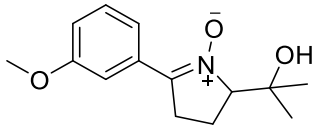
The product was purified by flash chromatography to give 39.6 mg (69%) as a yellow solid. mp 142−144 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 8.46 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 7.0 Hz, 2H), 6.43 ((s, 1H), 4.32 (t, *J* = 8.0 Hz, 1H), 3.14 (s, 2H), 2.37-2.41 (m, 1H), 1.86-1.94 (m, 1H), 1.26 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 141.0, 132.0 (d, *J* = 32.4 Hz), 131.7, 127.9, 125.5(q, *J* = 3.8 Hz), 123.7 (d, *J* = 269.4 Hz), 80.8, 72.7, 28.7, 26.7, 22.0, 19.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ (ppm) -73.6. HRMS (ESI) m/z calcd for $C_{14}H_{17}F_3NO_2^+$ $(M+H)^+$ 288.1206, found 288.1218.

2-(2-hydroxypropan-2-yl)-5-(m-tolyl)-3,4-dihydro-2H-pyrrole 1-oxide (2h)



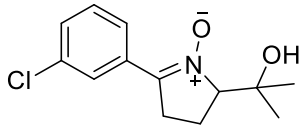
The product was purified by flash chromatography to give 34.5 mg (74%) as a yellow solid. mp 113−115 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 8.27 (s, 1H), 8.05 (d, *J* = 9.5 Hz, 1H), 7.37 (t, *J* = 9.5 Hz, 1H), 7.29 (d, *J* = 10.0 Hz, 1H), 6.76 (s, 1H), 4.28 (t, *J* = 10.5 Hz, 1H), 3.11 (s, 1H), 2.42 (s, 3H), 2.31-2.38 (m, 1H), 1.80-1.90 (m, 1H), 1.25 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 142.5, 138.2, 131.8, 128.4, 128.3, 128.2, 125.0, 80.2, 72.6, 28.8, 26.6, 21.9, 21.5, 19.6. HRMS (ESI) m/z calcd for $C_{14}H_{20}NO_2^+$ $(M+H)^+$ 234.1489, found 234.1494.

2-(2-hydroxypropan-2-yl)-5-(3-methoxyphenyl)-3,4-dihydro-2H-pyrrole 1-oxide (2i)



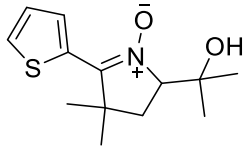
The product was purified by flash chromatography to give 39.8 mg (80%) as a yellow solid. mp 125−127 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 8.23 (s, 1H), 7.66 (d, *J* = 10.0 Hz, 1H), 7.36 (t, *J* = 10.5 Hz, 1H), 7.02 (dd, *J* = 10.5 Hz, 1H), 6.66 (s, 1H), 4.27 (t, *J* = 10.5 Hz, 1H), 3.86 (s, 3H), 3.06-3.11 (m, 2H), 2.29-2.38 (m, 1H), 1.82-1.88 (m, 1H), 1.23 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 159.5, 142.1, 129.8, 129.4, 120.3, 117.3, 112.5, 80.5, 72.6, 55.4, 28.9, 26.7, 22.0, 19.6. HRMS (ESI) m/z calcd for $C_{14}H_{20}NO_3^+$ $(M+H)^+$ 250.1438, found 250.1449.

5-(3-chlorophenyl)-2-(2-hydroxypropan-2-yl)-3,4-dihydro-2H-pyrrole 1-oxide (2j)



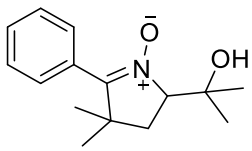
The product was purified by flash chromatography to give 34.4 mg (68%) as a yellow solid. mp 105−107 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 8.44 (s, 1H), 8.12 (d, *J* = 9.5 Hz, 1H), 7.36-7.43 (m, 2H), 6.49 (s, 1H), 4.27 (t, *J* = 10.5 Hz, 1H), 3.05-3.09 (m, 2H), 2.31-2.40 (m, 1H), 1.82-1.90 (m, 1H), 1.23 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 140.9, 134.6, 130.8, 130.2, 129.7, 127.5, 125.7, 80.6, 72.6, 28.6, 26.6, 22.0, 19.6. HRMS (ESI) m/z calcd for $C_{13}H_{17}{}^{35}ClNO_2^+$ $(M+H)^+$ 254.0942, found 254.0943.

2-(2-hydroxypropan-2-yl)-4,4-dimethyl-5-(thiophen-2-yl)-3,4-dihydro-2H-pyrrole 1-oxide (2k)



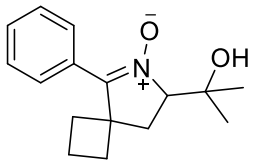
The product was purified by flash chromatography to give 35.4 mg (70%) as a yellow solid. mp 95−97 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.70 (d, *J* = 3.5 Hz, 1H), 7.55 (d, *J* = 5.0 Hz, 1H), 7.17 (t, *J* = 4.0 Hz, 1H), 6.33 (s, 1H), 4.20 (t, *J* = 9.5 Hz, 1H), 2.15-2.19 (m, 1H), 1.68-1.72 (m, 1H), 1.59 (s, 3H), 1.47 (s, 3H), 1.20 (s, 3H), 1.17 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 146.5, 129.5, 128.7, 127.7, 126.3, 75.2, 72.0, 42.4, 38.9, 28.7, 27.0, 26.3, 21.8. HRMS (ESI) m/z calcd for $C_{13}H_{20}NO_2S^+$ $(M+H)^+$ 254.1209, found 254.1213.

2-(2-hydroxypropan-2-yl)-4,4-dimethyl-5-phenyl-3,4-dihydro-2H-pyrrole 1-oxide (2l)



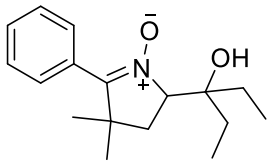
The product was purified by flash chromatography to give 33.6 mg (68%) as a yellow solid. mp 96−98 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.79 (d, *J* = 9.0 Hz, 2H), 7.41-7.47 (m, 3H), 6.74 (s, 1H), 4.23 (t, *J* = 11.5 Hz, 1H), 2.11-2.16 (m, 1H), 1.69 (t, *J* = 14.5 Hz, 1H), 1.43 (s, 3H), 1.31 (s, 6H), 1.19 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 150.9, 129.9, 128.4, 128.3, 128.2, 76.1, 71.9, 42.8, 38.6, 27.8, 27.0, 26.5, 21.8. HRMS (ESI) m/z calcd for $C_{15}H_{22}NO_2^+$ $(M+H)^+$ 248.1645, found 248.1662.

7-(2-hydroxypropan-2-yl)-5-phenyl-6-azaspiro[3.4]oct-5-ene 6-oxide (2m)



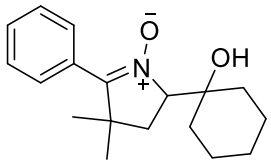
The product was purified by flash chromatography to give 39.4 mg (76%) as a yellow solid. mp 101−103 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.84 (d, *J* = 9.0 Hz, 2H), 7.43-7.52 (m, 3H), 6.65 (s, 1H), 4.16 (t, *J* = 10.5 Hz, 1H), 2.53-2.70 (m, 3H), 2.14-2.22 (m, 1H), 1.92-2.12 (m, 3H), 1.83-1.91 (m, 1H), 1.27 (s, 3H), 1.22 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 149.1, 130.0, 128.6, 128.3, 76.5, 71.9, 48.2, 38.2, 33.5, 32.5, 26.6, 21.9, 15.7. HRMS (ESI) m/z calcd for $C_{16}H_{22}NO_2^+$ $(M+H)^+$ 260.1645, found 260.1649.

2-(3-hydroxypentan-3-yl)-4,4-dimethyl-5-phenyl-3,4-dihydro-2H-pyrrole 1-oxide (2n)



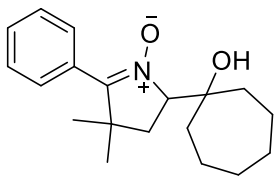
The product was purified by flash chromatography to give 40.7 mg (74%) as a yellow solid. mp 98−100 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.76 (d, *J* = 9.0 Hz, 2H), 7.42-7.51 (m, 3H), 6.40 (s, 1H), 4.40 (t, *J* = 11.5 Hz, 1H), 2.07-2.12 (m, 1H), 2.04(s, 1H), 1.66-1.81 (m, 3H), 1.47-1.54 (m, 1H), 1.42 (s, 3H), 1.32 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 131.5, 130.0, 129.9, 128.5, 128.4, 74.9, 74.0, 43.0, 37.7, 28.6, 27.8, 27.3, 26.1, 7.5, 7.1. HRMS (ESI) m/z calcd for $C_{17}H_{26}NO_2^+$ $(M+H)^+$ 276.1958, found 276.1967.

2-(1-hydroxycyclohexyl)-4,4-dimethyl-5-phenyl-3,4-dihydro-2H-pyrrole 1-oxide (2o)



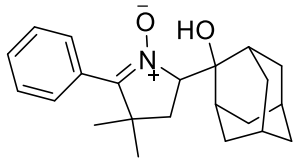
The product was purified by flash chromatography to give 40.8 mg (71%) as a yellow solid. mp 115−117 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.75 (d, *J* = 7.5 Hz, 2H), 7.39-7.46 (m, 3H), 6.46 (s, 1H), 4.21 (t, *J* = 9.5 Hz, 1H), 2.07-2.11 (m, 1H), 1.71-1.86 (m, 6H), 1.51-1.61 (m, 3H), 1.42 (s, 3H), 1.31 (s, 3H), 1.11-1.20 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 151.0, 129.9, 128.5, 128.4, 128.2, 76.4, 72.7, 42.9, 38.0, 34.3, 28.6, 27.8, 27.1, 26.0, 20.8, 20.4. HRMS (ESI) m/z calcd for $C_{18}H_{26}NO_2^+$ $(M+H)^+$ 288.1958, found 288.1964.

2-(1-hydroxycycloheptyl)-4,4-dimethyl-5-phenyl-3,4-dihydro-2H-pyrrole 1-oxide (2p)



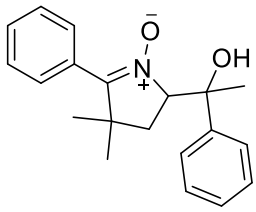
The product was purified by flash chromatography to give 39.7 mg (66%) as a yellow solid. mp 124−126 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.75 (s, 2H), 7.45 (d, *J* = 8.5 Hz, 3H), 6.68 (s, 1H), 4.22 (t, *J* = 10.0 Hz, 1H), 2.09-2.13 (m, 1H), 1.80-1.88 (m, 4H), 1.48-1.72 (m, 9H), 1.41 (s, 3H), 1.32 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 151.2, 129.9, 128.5, 128.4, 128.2, 77.4, 75.4, 42.8, 38.9, 38.0, 32.8, 28.8, 28.8, 27.8, 26.9, 22.1, 21.5. HRMS (ESI) m/z calcd for $C_{19}H_{28}NO_2^+$ $(M+H)^+$ 302.2115, found 302.2115.

2-((1r,3r,5r,7r)-2-hydroxyadamantan-2-yl)-4,4-dimethyl-5-phenyl-3,4-dihydro-2H-pyrrole 1-oxide (2q)



The product was purified by flash chromatography to give 32.5 mg (48%) as a yellow solid. mp 157−159 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.77 (d, *J* = 9.0 Hz, 2H), 7.42 (d, *J* = 9.5 Hz, 3H), 4.80-4.84 (m, 1H), 3.30 (s, 1H), 3.10 (s, 1H), 2.33 (d, *J* = 12.5 Hz, 2H), 2.16 (t, *J* = 14.5 Hz, 1H), 2.06 (d, *J* = 17.0 Hz, 1H), 1.87-1.96 (m, 3H), 1.74-1.81 (m, 4H), 1.53-1.62 (m, 4H), 1.42 (s, 3H), 1.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 151.3, 129.6, 128.3, 127.7, 127.4, 74.4, 71.2, 42.0, 38.0, 37.4, 35.6, 34.9, 34.1, 34.1, 33.0, 32.5, 27.4, 26.9, 26.7, 25.3. HRMS (ESI) m/z calcd for $C_{22}H_{30}NO_2^+$ $(M+H)^+$ 340.2271, found 340.2294.

2-(1-hydroxy-1-phenylethyl)-4,4-dimethyl-5-phenyl-3,4-dihydro-2H-pyrrole 1-oxide (2r)

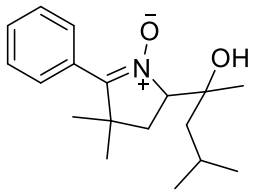


1:1.2 dr.

The product was purified by flash chromatography to give 19.2 mg (31%) as a yellow solid. mp 122−124 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.82 (d, *J* = 7.5 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.37-7.50 (m, 6H), 7.32 (t, *J* = 7.0 Hz, 1H), 4.40 (t, *J* = 8.5 Hz, 1H), 1.76 (s, 3H), 1.62-1.68 (m, 2H), 1.32 (s, 3H), 1.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 151.7, 143.4, 130.1, 128.5, 128.4, 128.3, 128.1, 127.7, 126.1, 76.5, 75.3, 42.6, 38.8, 27.8, 27.0, 19.7. HRMS (ESI) m/z calcd for $C_{20}H_{24}NO_2^+$ $(M+H)^+$ 310.1802, found 310.1814.

The product was purified by flash chromatography to give 23.5mg (38%) as a yellow solid. mp 120−122 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 8.32 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.36-7.42 (m, 6H), 7.30 (t, *J* = 7.0 Hz, 1H), 4.47 (t, *J* = 9.0 Hz, 1H), 2.11-2.16 (m, 1H), 1.72-1.76 (m, 1H), 1.68 (s, 3H), 1.25 (s, 3H), 0.49 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 152.7, 141.9, 129.9, 128.5, 128.1, 128.1, 128.0, 127.7, 127.2, 76.5, 76.2, 43.1, 36.3, 28.5, 26.8, 25.8.

2-(2-hydroxy-4-methylpentan-2-yl)-4,4-dimethyl-5-phenyl-3,4-dihydro-2H-pyrrole 1-oxide (2s)

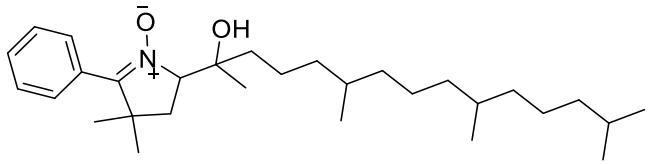


1:1.2 dr.

The product was purified by flash chromatography to give 19.1 mg (33%) as a yellow solid. mp 128−130 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.78 (d, *J* = 7.5 Hz, 2H), 7.41-7.48 (m, 3H), 6.40 (s, 1H), 4.22 (t, *J* = 10.0 Hz, 1H), 2.09-2.13 (m, 1H), 1.97-2.02 (m, 1H), 1.74 (t, *J* = 12.5 Hz, 1H), 1.53-1.57 (m, 1H), 1.41 (s, 3H), 1.35-1.38 (m, 1H), 1.33 (s, 3H), 1.17 (s, 3H), 1.07 (d, *J* = 6.5 Hz, 3H), 0.98 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 151.1, 129.9, 128.5, 128.4, 128.2, 77.3, 73.9, 42.8, 41.2, 38.1, 27.8, 27.0, 25.3, 24.6, 24.0, 23.6. HRMS (ESI) m/z calcd for $C_{18}H_{28}NO_2^+$ $(M+H)^+$ 290.2115, found 290.2120.

The product was purified by flash chromatography to give 23.1 mg (40%) as a yellow solid. mp 126−128 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.76 (d, *J* = 7.5 Hz, 2H), 7.42-7.47 (m, 3H), 6.75 (s, 1H), 4.31 (t, *J* = 9.0 Hz, 1H), 2.10-2.14 (m, 1H), 1.94-1.99 (m, 1H), 1.69 (t, *J* = 11.0 Hz, 2H), 1.42 (s, 3H), 1.31 (s, 3H), 1.29 (s, 3H), 1.25 (s, 1H), 1.05 (d, *J* = 6.5 Hz, 3H), 1.00 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 151.2, 129.9, 128.5, 128.3, 128.2, 75.2, 74.4, 47.7, 42.8, 38.7, 27.8, 27.2, 25.0, 24.7, 23.5, 21.1.

2-(2-hydroxy-6,10,14-trimethylpentadecan-2-yl)-4,4-dimethyl-5-phenyl-3,4-dihydro-2H-pyrrole 1-oxide (2t)

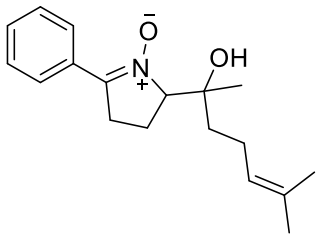


1:1.1 dr.

The product was purified by flash chromatography to give 28.3 mg (31%) as a yellow solid. mp 143−145 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.80 (d, *J* = 8.5 Hz, 2H), 7.46 (t, *J* = 10.0 Hz, 3H), 6.79 (s, 1H), 4.29 (t, *J* = 11.0 Hz, 1H), 2.11-2.16 (m, 1H), 1.71 (t, *J* = 15.0 Hz, 1H), 1.56-1.63 (m, 1H), 1.53 (t, *J* = 8.0 Hz, 1H), 1.40-1.45 (m, 8H), 1.28-1.33 (m, 15H), 1.10-1.16 (m, 6H), 0.86-0.89 (m, 12H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 151.1, 129.9, 128.4, 128.3, 128.1, 76.6, 73.4, 42.8, 39.3, 38.0, 37.7, 37.7, 37.4, 37.4, 37.3, 37.2, 33.7, 33.0, 32.9, 32.7, 27.9, 27.7, 27.0, 24.7, 24.4, 23.6, 22.7, 22.6, 20.3, 20.3, 19.8, 19.7. HRMS (ESI) m/z calcd for $C_{30}H_{52}NO_2^+$ $(M+H)^+$ 458.3993, found 458.3997.

The product was purified by flash chromatography to give 31.1 mg (34%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.77 (d, *J* = 7.5 Hz, 2H), 7.41-7.47 (m, 3H), 6.77 (s, 1H), 4.27 (t, *J* = 9.0 Hz, 1H), 2.09-2.13 (m, 1H), 1.69 (t, *J* = 11.0 Hz, 1H), 1.52 (d, *J* = 6.5 Hz, 1H), 1.36-1.42 (m, 8H), 1.25-1.31 (m, 15H), 1.11-1.15 (m, 3H), 1.05-1.09 (m, 3H), 0.83-0.88 (m, 12H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 151.0, 129.9, 128.4, 128.3, 128.1, 75.0, 75.0, 73.7, 42.9, 39.8, 39.3, 38.4, 37.5, 37.4, 37.3, 37.3, 37.2, 32.8, 32.7, 27.9, 27.7, 27.1, 24.7, 24.4, 22.7, 22.6, 20.4, 20.3, 19.9, 19.9, 19.7, 19.7, 19.6.

2-(2-hydroxy-6-methylhept-5-en-2-yl)-5-phenyl-3,4-dihydro-2H-pyrrole 1-oxide (2u)



1:1.2 dr.

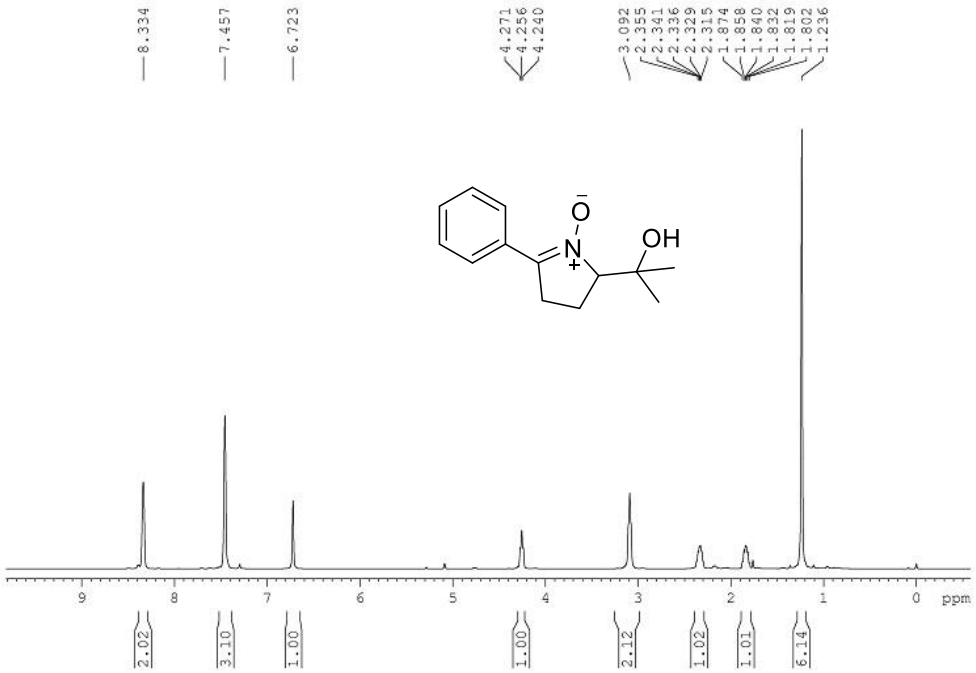
The product was purified by flash chromatography to give 18.9 mg (33%) as a yellow solid. mp 133−135 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 8.32-8.34 (m, 2H), 7.45-7.47 (m, 3H), 6.69 (s, 1H), 5.10-5.14 (m, 1H), 4.33 (t, *J* = 9.5 Hz, 1H), 2.08-2.12 (m, 2H), 2.29-2.36 (m, 1H), 2.20-2.27 (m, 1H), 2.11-2.19 (m, 1H), 1.80-1.89 (m, 1H), 1.69 (s, 3H), 1.64 (s, 3H), 1.46-1.52 (m, 2H), 1.20 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 142.2, 131.9, 130.9, 128.6, 128.5, 127.7, 124.2, 79.0, 74.1, 39.5, 28.9, 25.7, 21.3, 20.7, 19.3, 17.7. HRMS (ESI) m/z calcd for $C_{18}H_{26}NO_2^+$ $(M+H)^+$ 288.1958, found 288.1972.

The product was purified by flash chromatography to give 23.0 mg (40%) as a yellow solid. mp 131−133 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 8.32 (s, 2H), 7.46 (s, 3H), 6.41 (s, 1H), 5.07 (t, *J* =

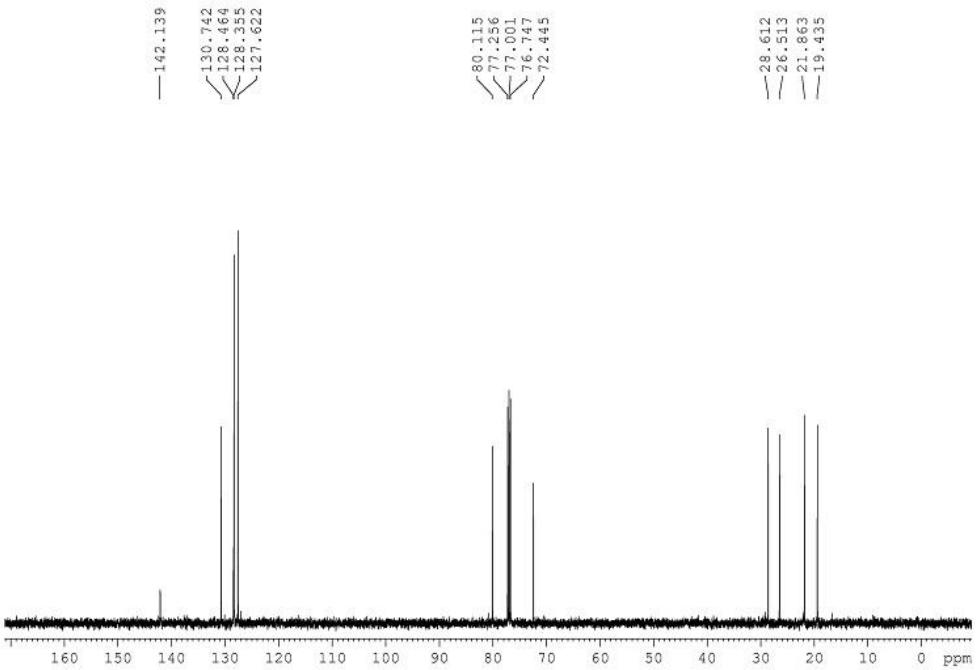
6.5 Hz, 1H), 4.31 (t, *J* = 8.5 Hz, 1H), 3.10 (t, *J* = 7.0 Hz, 1H), 2.28-2.37 (m, 2H), 2.06-2.11 (m, 1H), 1.87-1.94 (m, 1H), 1.63 (s, 3H), 1.58 (s, 3H), 1.50-1.55 (m, 1H), 1.35-1.41 (m, 1H), 1.19 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 142.4, 131.6, 130.9, 128.6, 128.5, 127.8, 124.5, 80.9, 74.1, 33.7, 28.8, 25.6, 23.6, 21.5, 19.0, 17.6.

(C) NMR Spectra of 2

2-(2-hydroxypropan-2-yl)-5-phenyl-3,4-dihydro-2H-pyrrole 1-oxide (2a)

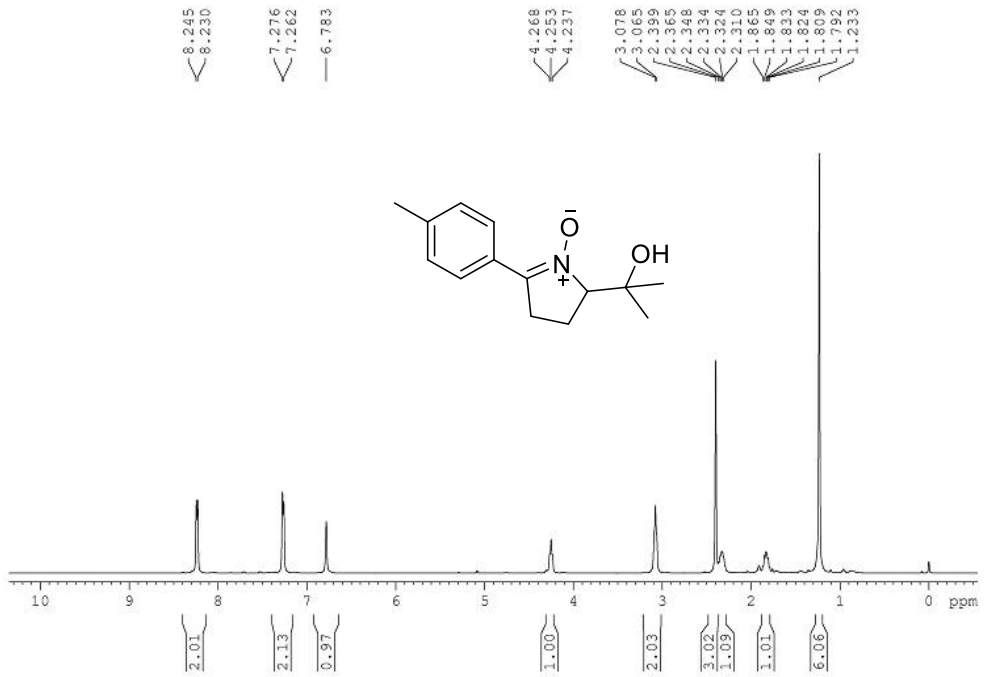


^{1}H NMR (500 MHz, $CDCl_3$)

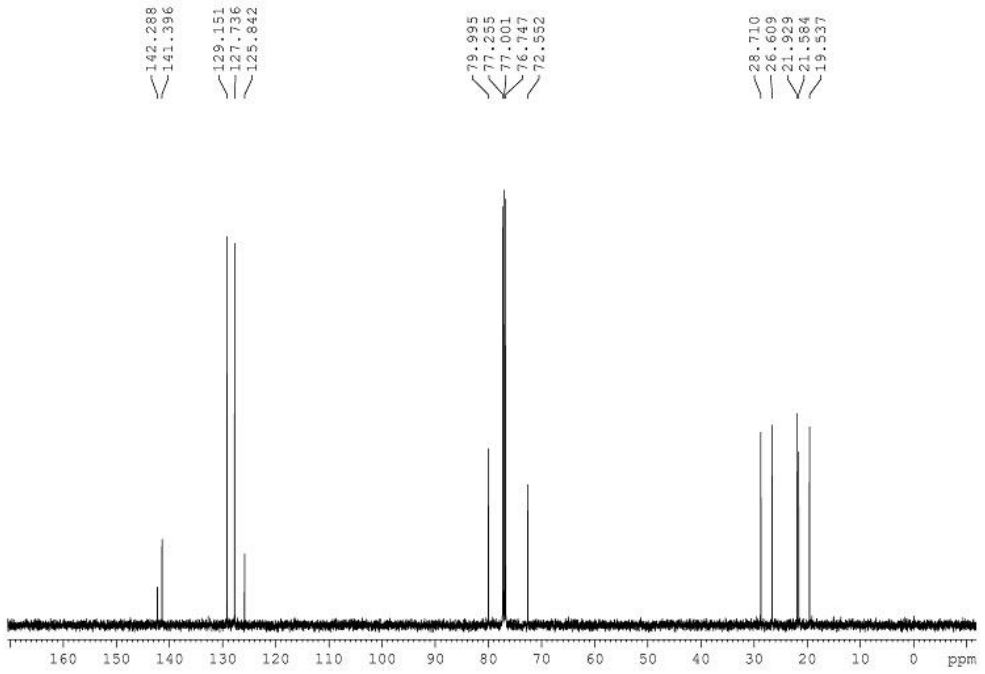


^{13}C NMR (125 MHz, $CDCl_3$)

2-(2-hydroxypropan-2-yl)-5-(p-tolyl)-3,4-dihydro-2H-pyrrole 1-oxide (2b)

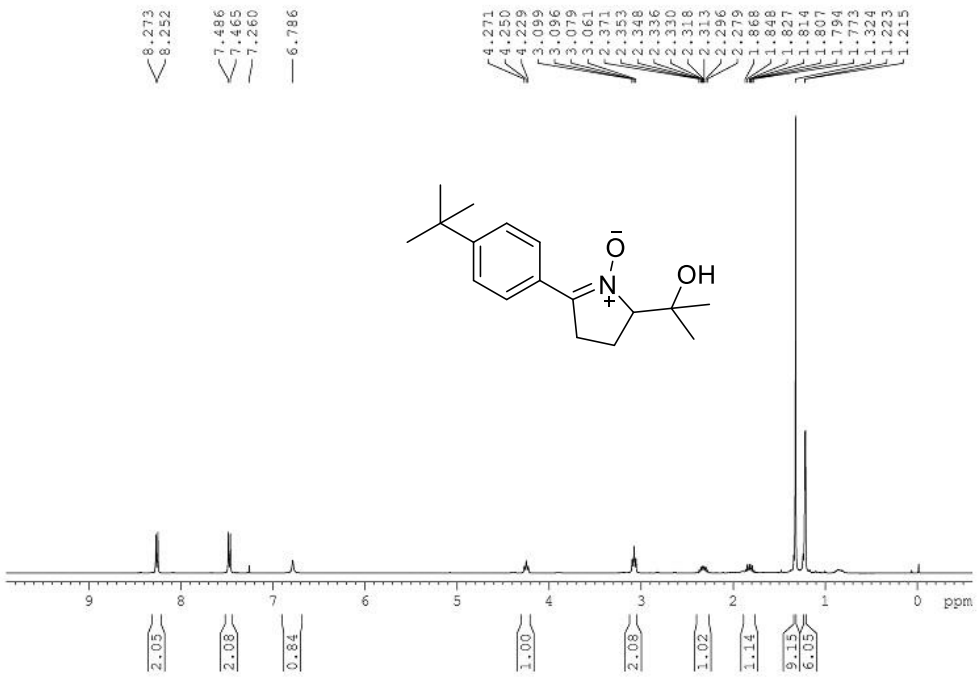


^{1}H NMR (500 MHz, $CDCl_3$)

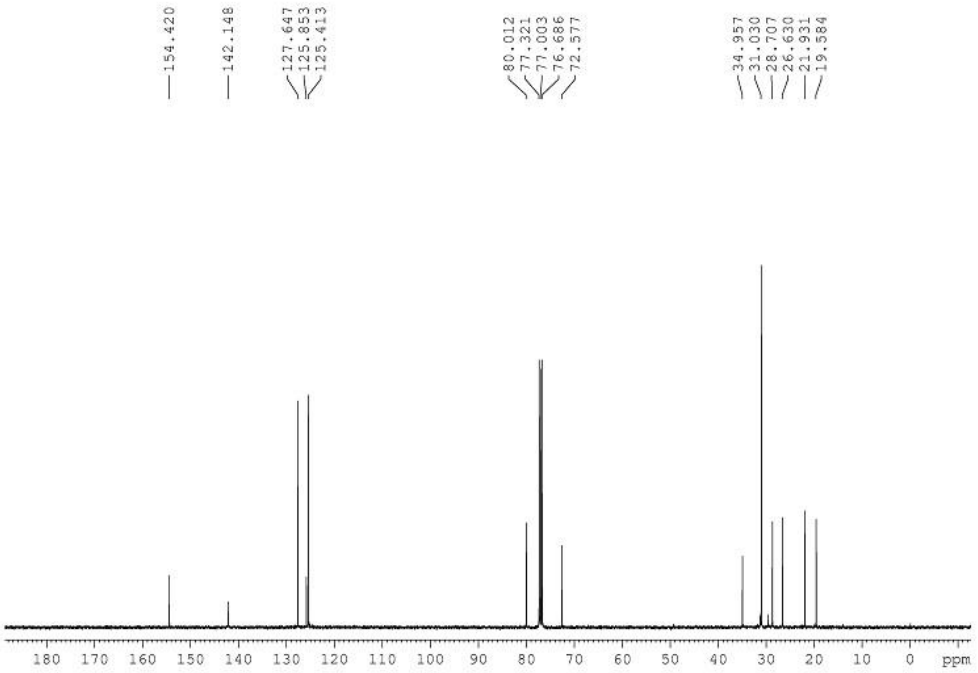


^{13}C NMR (125 MHz, $CDCl_3$)

5-(4-(tert-butyl)phenyl)-2-(2-hydroxypropan-2-yl)-3,4-dihydro-2H-pyrrole 1-oxide (2c)

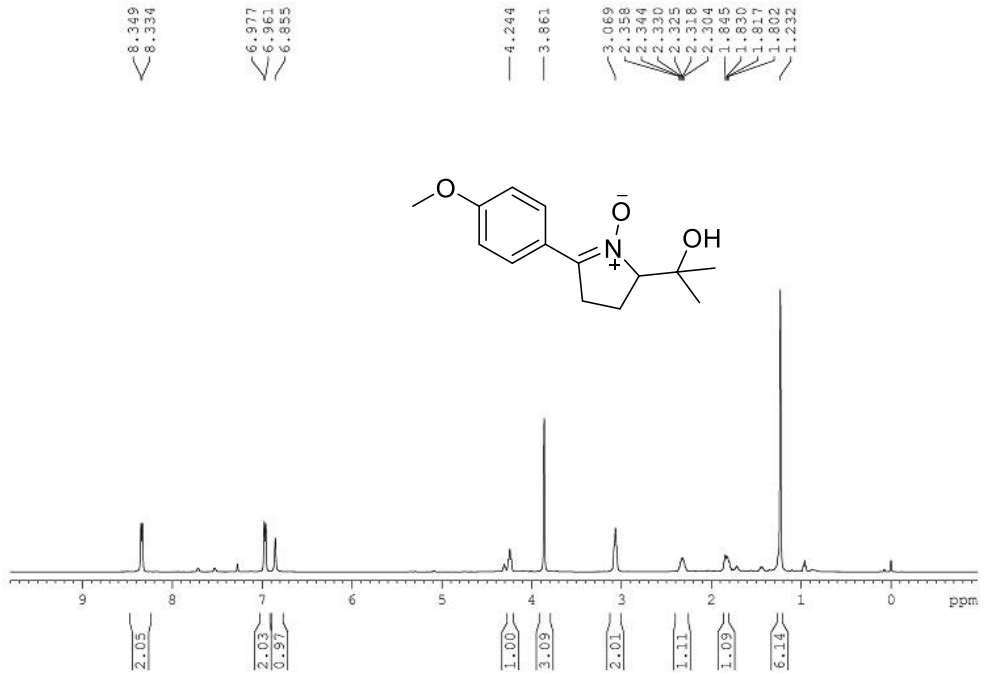


^{1}H NMR (500 MHz, $CDCl_3$)

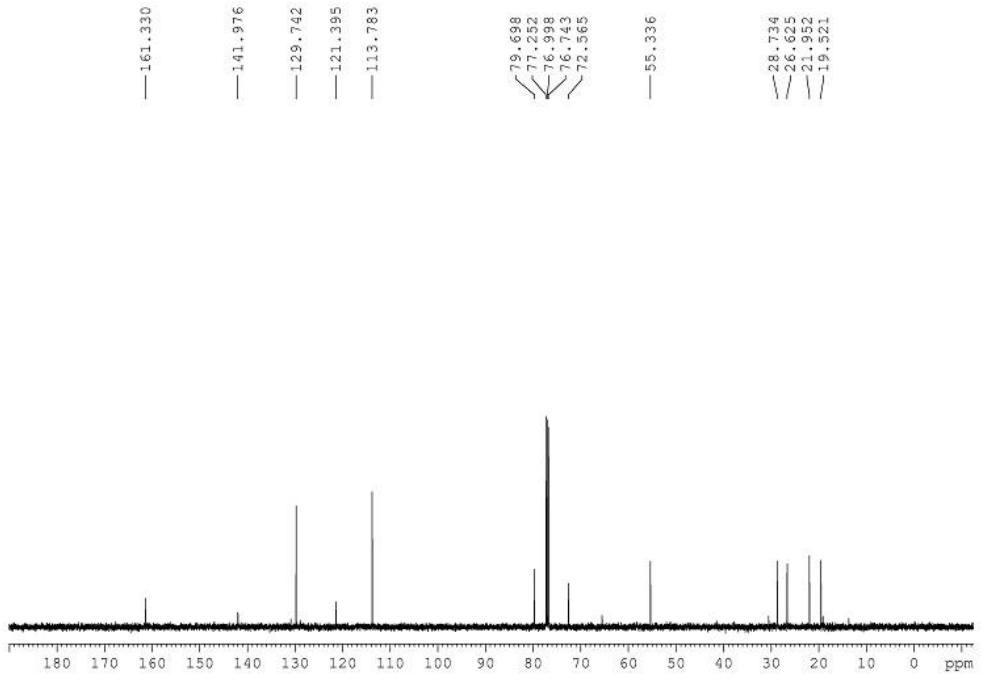


^{13}C NMR (125 MHz, $CDCl_3$)

2-(2-hydroxypropan-2-yl)-5-(4-methoxyphenyl)-3,4-dihydro-2H-pyrrole 1-oxide (2d)

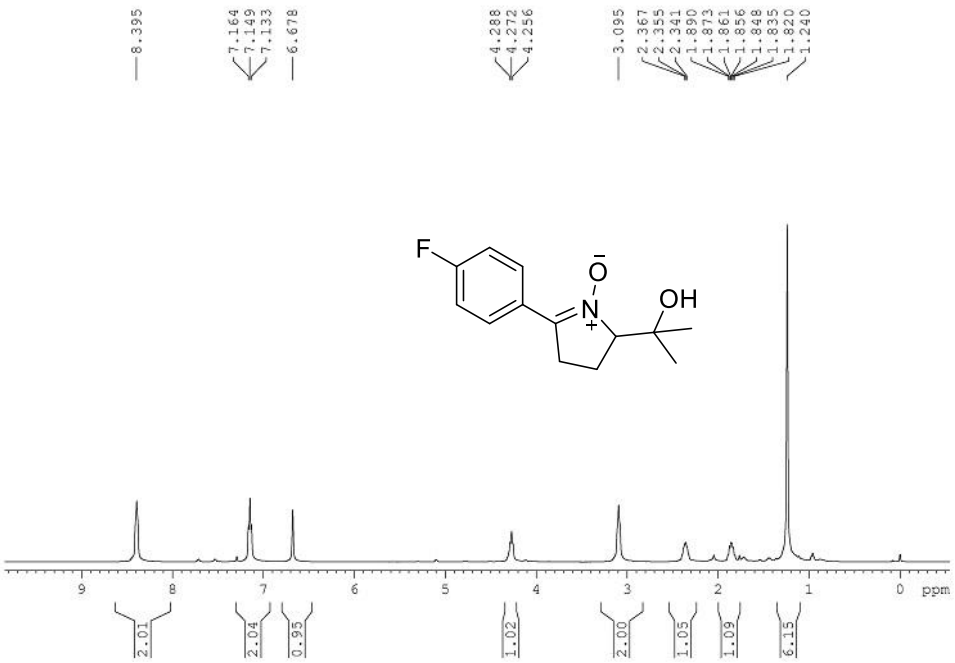


^{1}H NMR (500 MHz, $CDCl_3$)

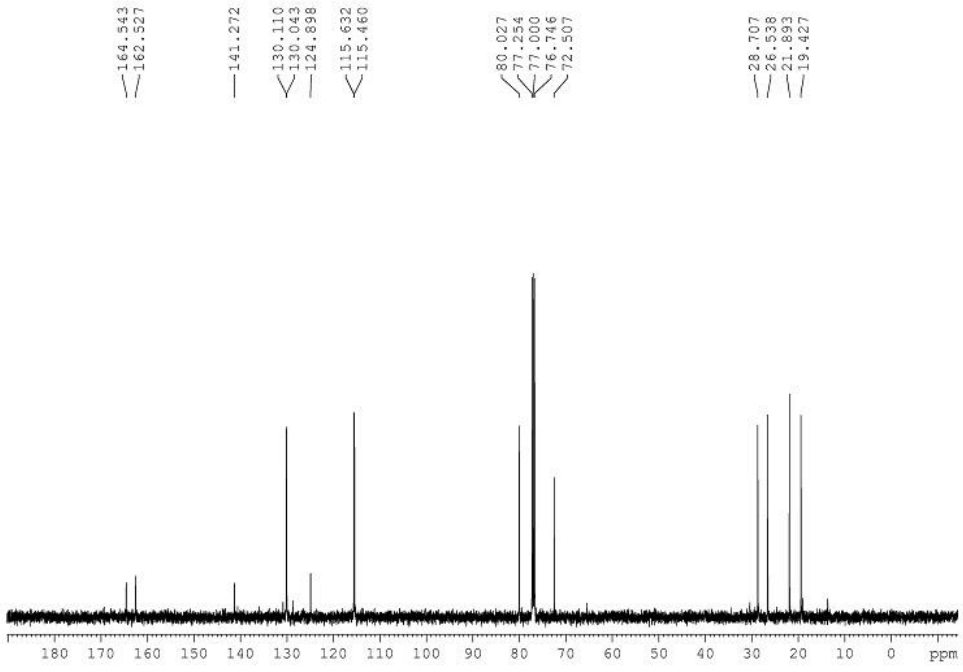


^{13}C NMR (125 MHz, $CDCl_3$)

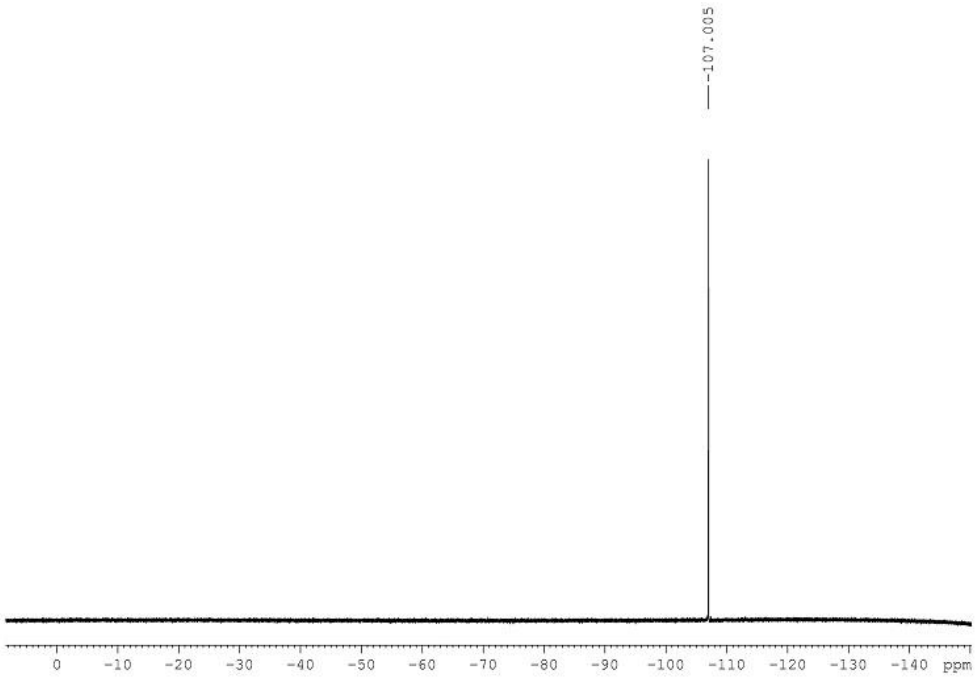
5-(4-fluorophenyl)-2-(2-hydroxypropan-2-yl)-3,4-dihydro-2H-pyrrole 1-oxide (2e)



^{1}H NMR (500 MHz, $CDCl_3$)

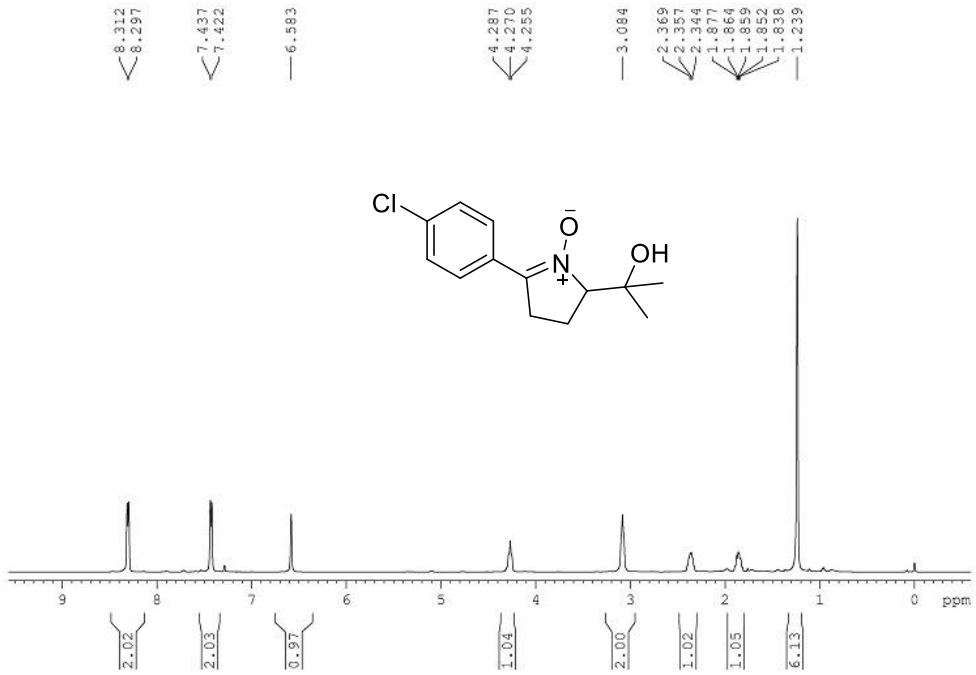


^{13}C NMR (125 MHz, $CDCl_3$)

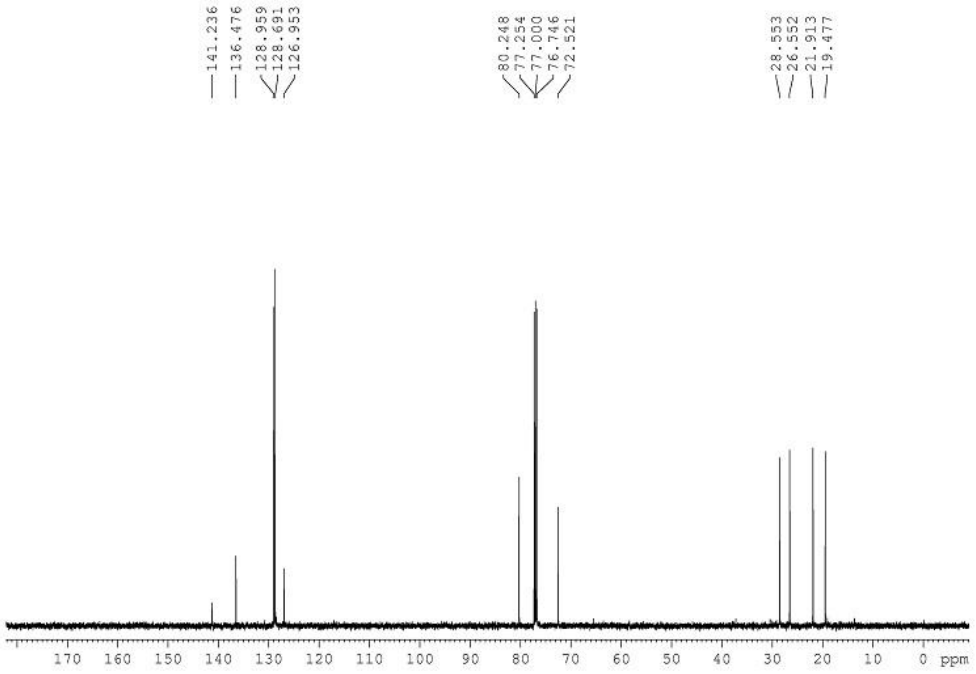


^{19}F NMR (471 MHz, $CDCl_3$)

5-(4-chlorophenyl)-2-(2-hydroxypropan-2-yl)-3,4-dihydro-2H-pyrrole 1-oxide (2f)

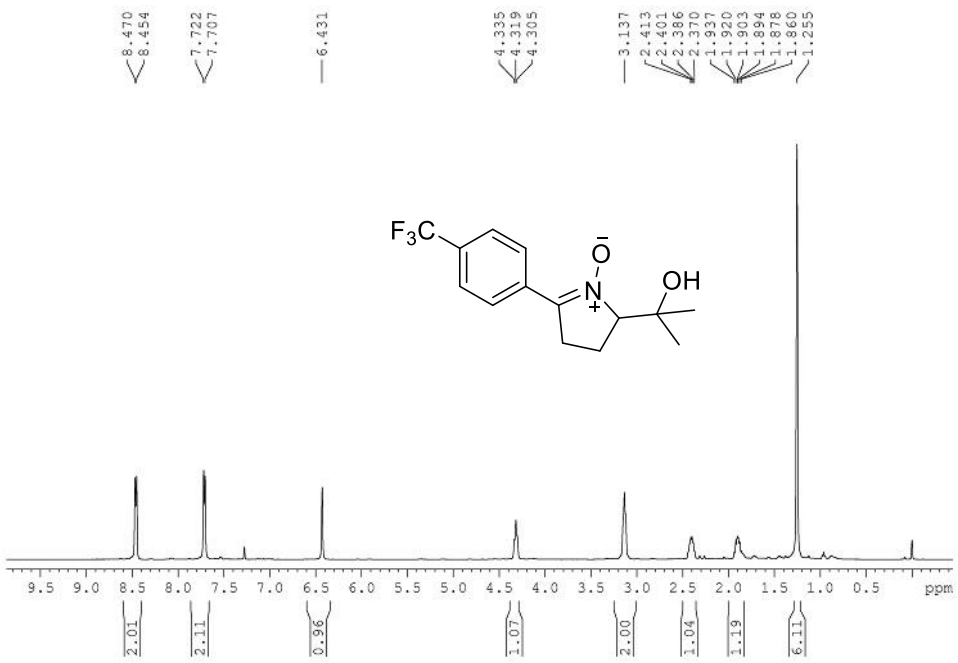


^{1}H NMR (500 MHz, $CDCl_3$)

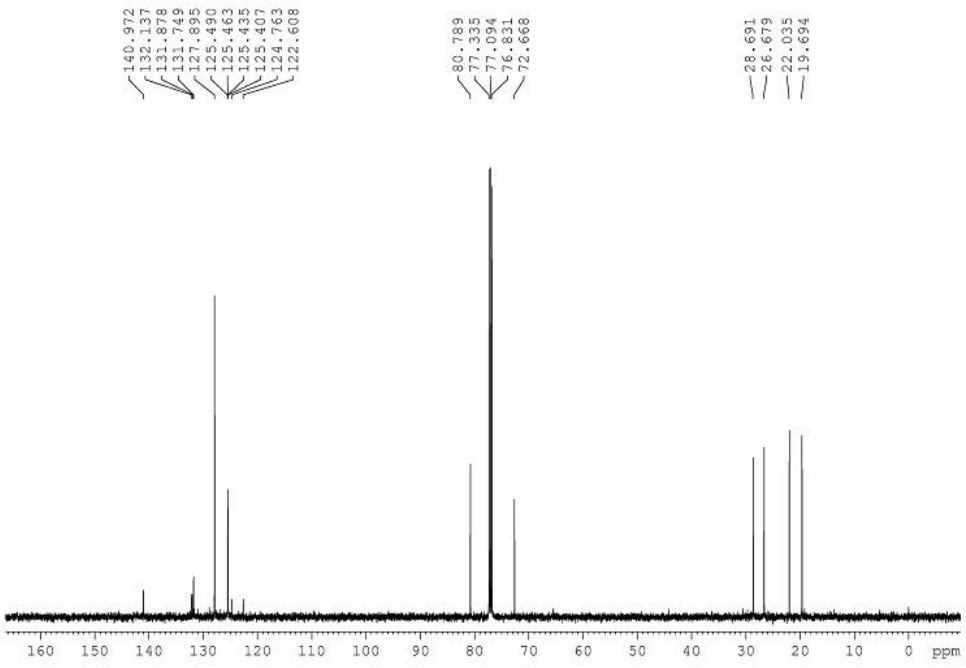


^{13}C NMR (125 MHz, $CDCl_3$)

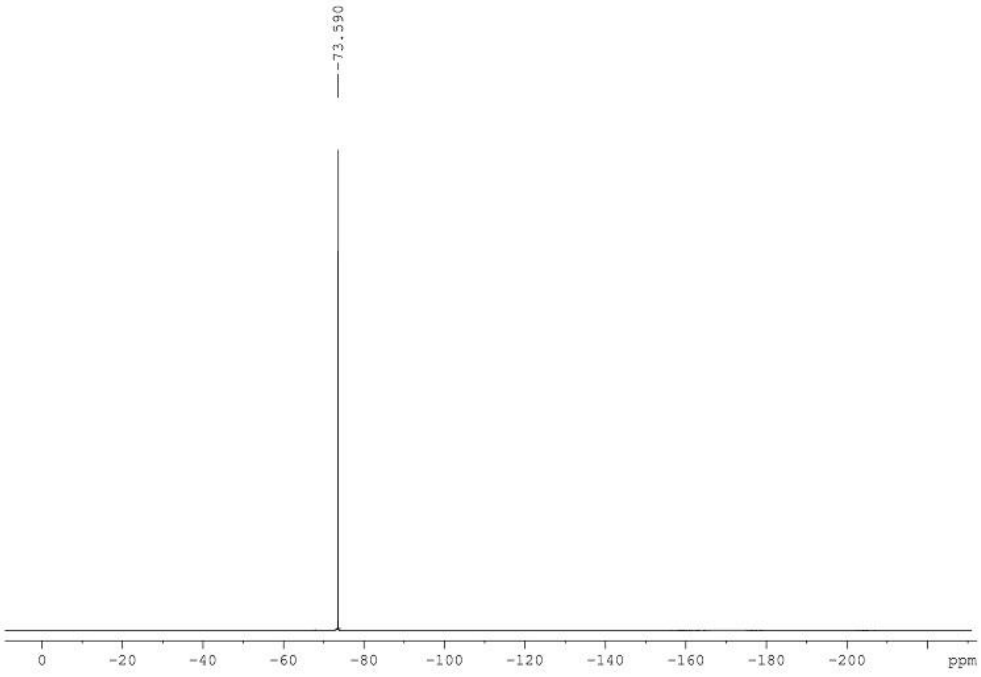
2-(2-hydroxypropan-2-yl)-5-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2H-pyrrole 1-oxide (2g)



^{1}H NMR (500 MHz, $CDCl_3$)

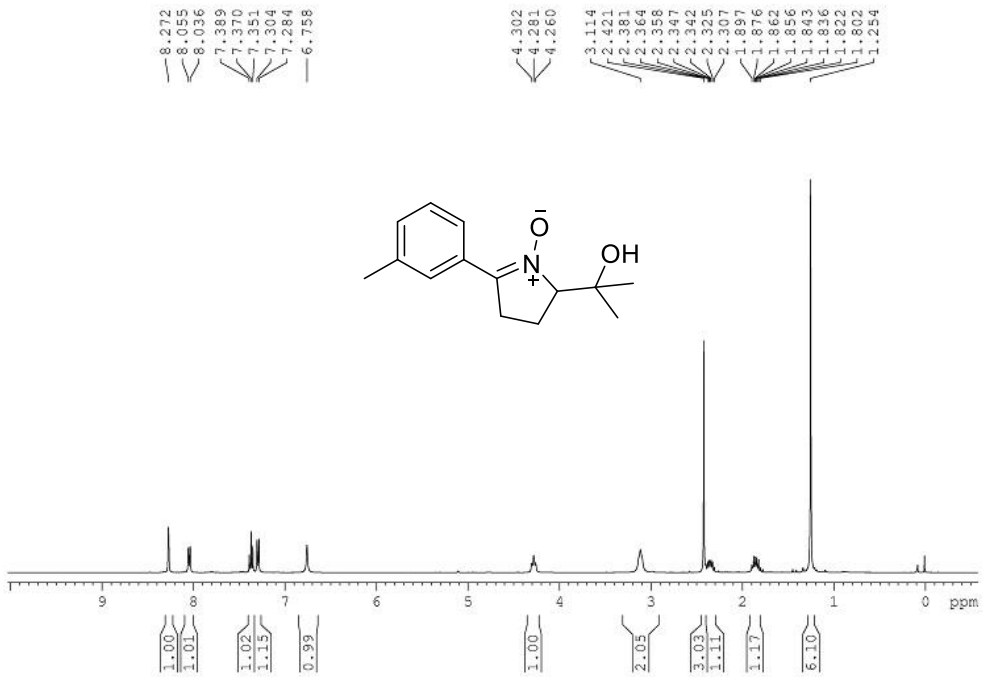


^{13}C NMR (125 MHz, $CDCl_3$)

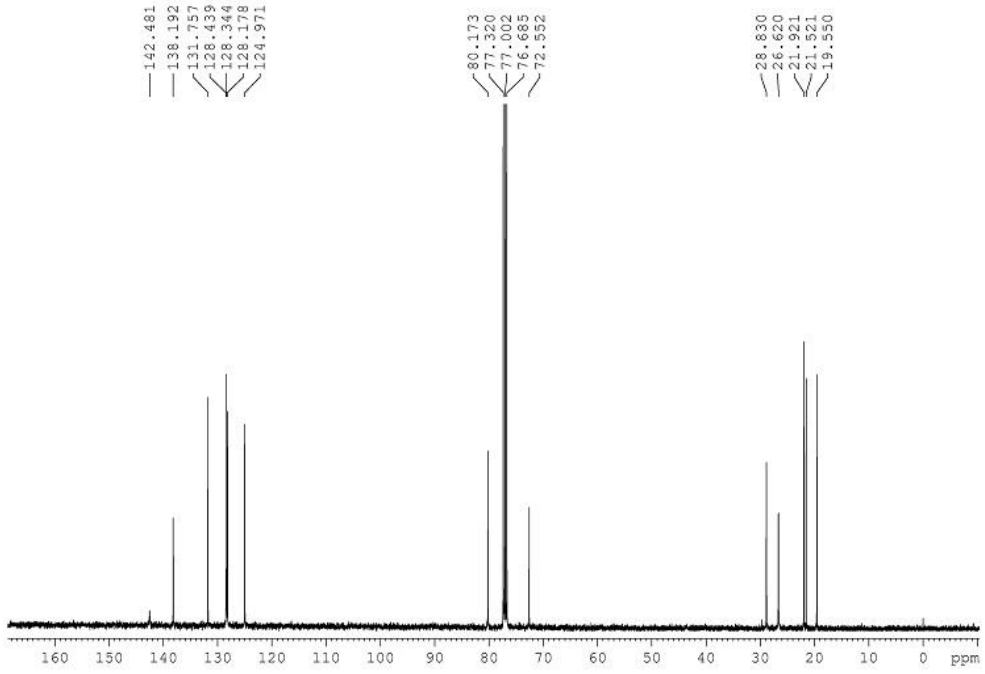


^{19}F NMR (471 MHz, $CDCl_3$)

2-(2-hydroxypropan-2-yl)-5-(m-tolyl)-3,4-dihydro-2H-pyrrole 1-oxide (2h)

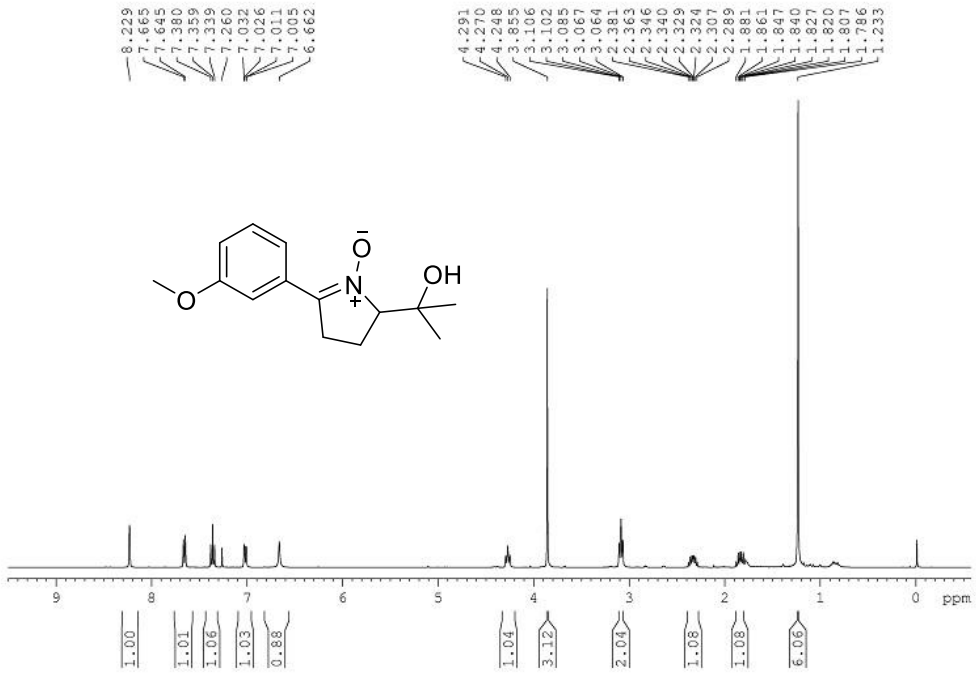


^{1}H NMR (500 MHz, $CDCl_3$)

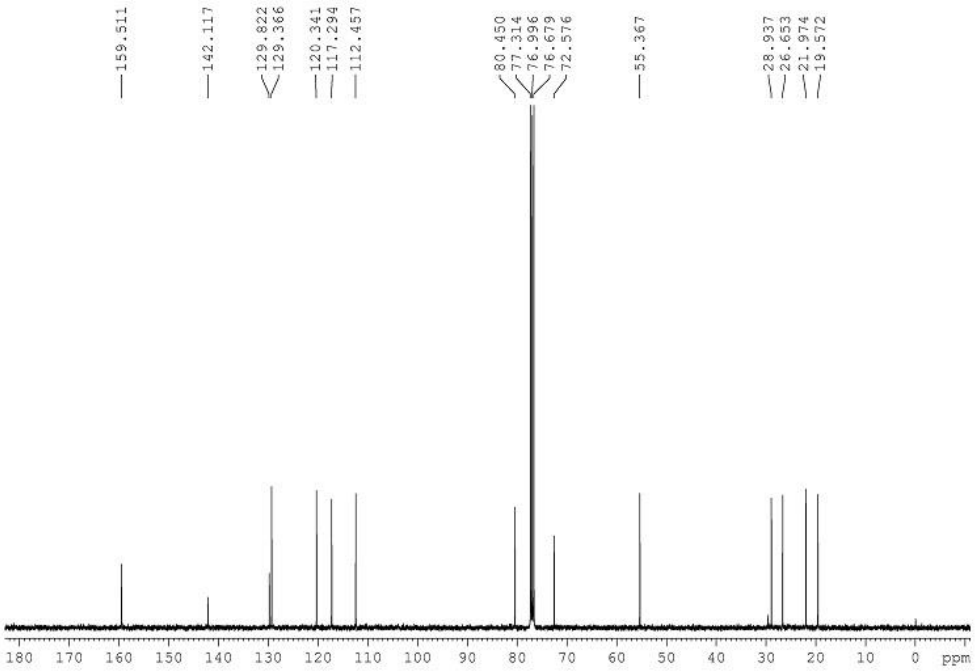


^{13}C NMR (125 MHz, $CDCl_3$)

2-(2-hydroxypropan-2-yl)-5-(3-methoxyphenyl)-3,4-dihydro-2H-pyrrole 1-oxide (2i)

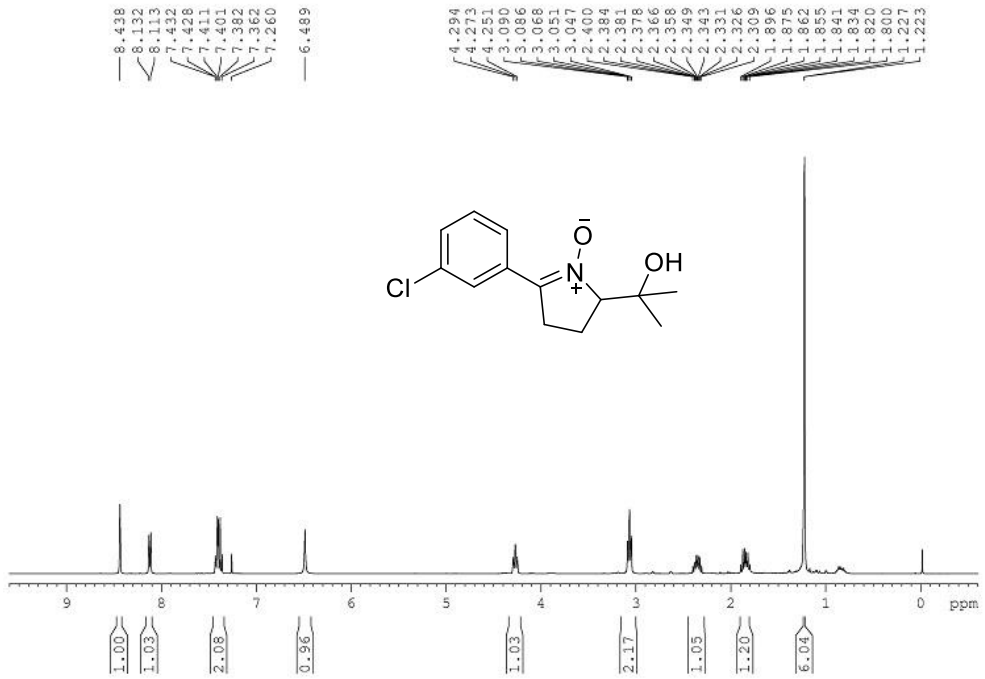


^{1}H NMR (500 MHz, $CDCl_3$)

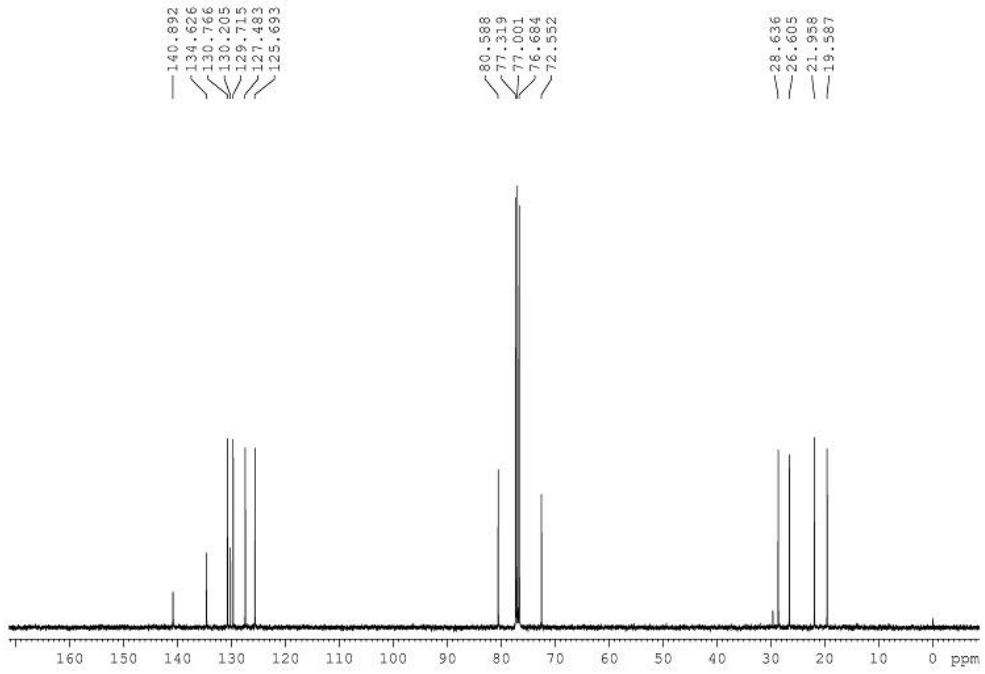


^{13}C NMR (125 MHz, $CDCl_3$)

5-(3-chlorophenyl)-2-(2-hydroxypropan-2-yl)-3,4-dihydro-2H-pyrrole 1-oxide (2j)

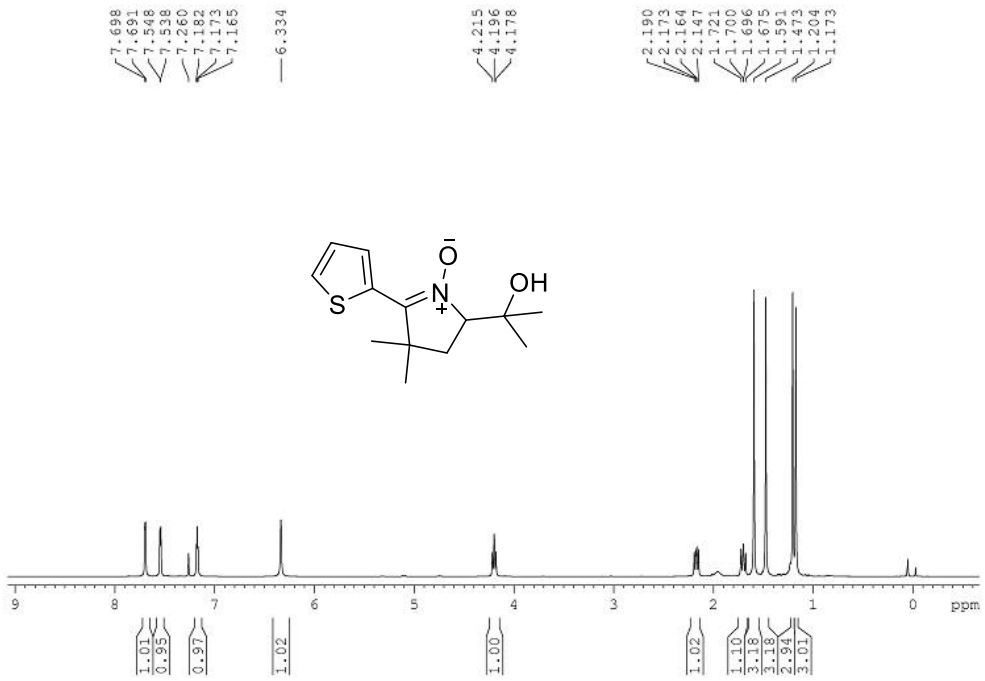


^{1}H NMR (500 MHz, $CDCl_3$)

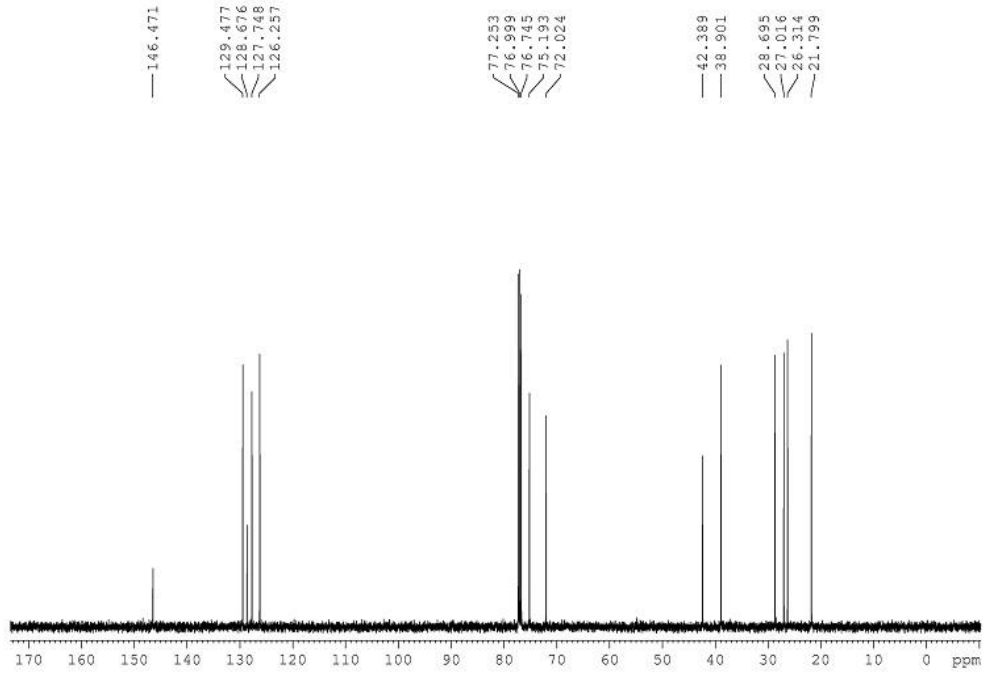


^{13}C NMR (125 MHz, $CDCl_3$)

2-(2-hydroxypropan-2-yl)-4,4-dimethyl-5-(thiophen-2-yl)-3,4-dihydro-2H-pyrrole 1-oxide (2k)

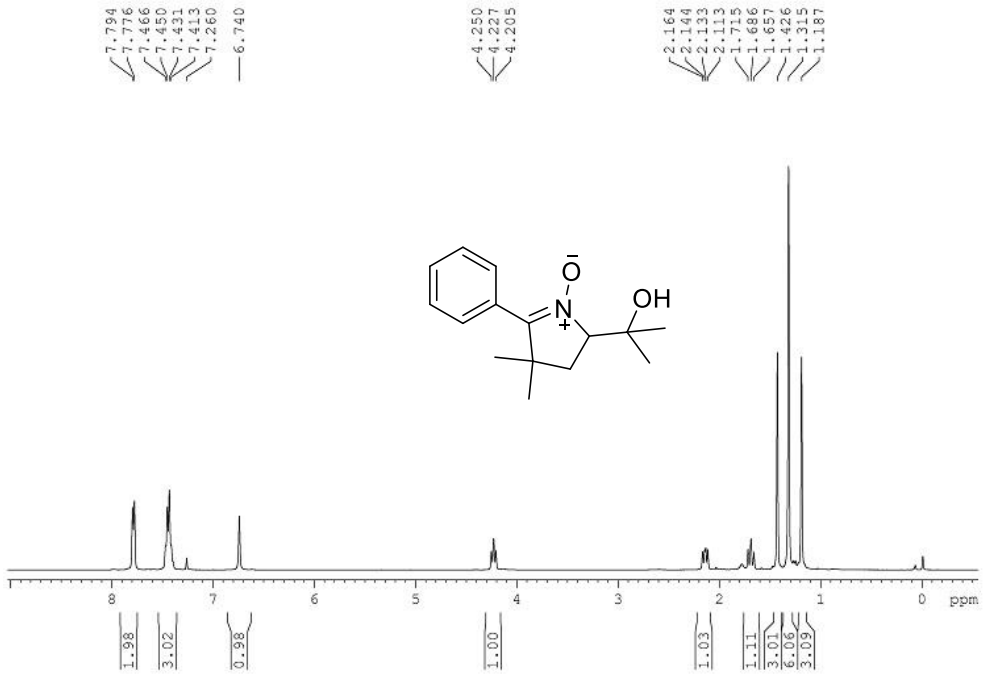


^{1}H NMR (500 MHz, $CDCl_3$)

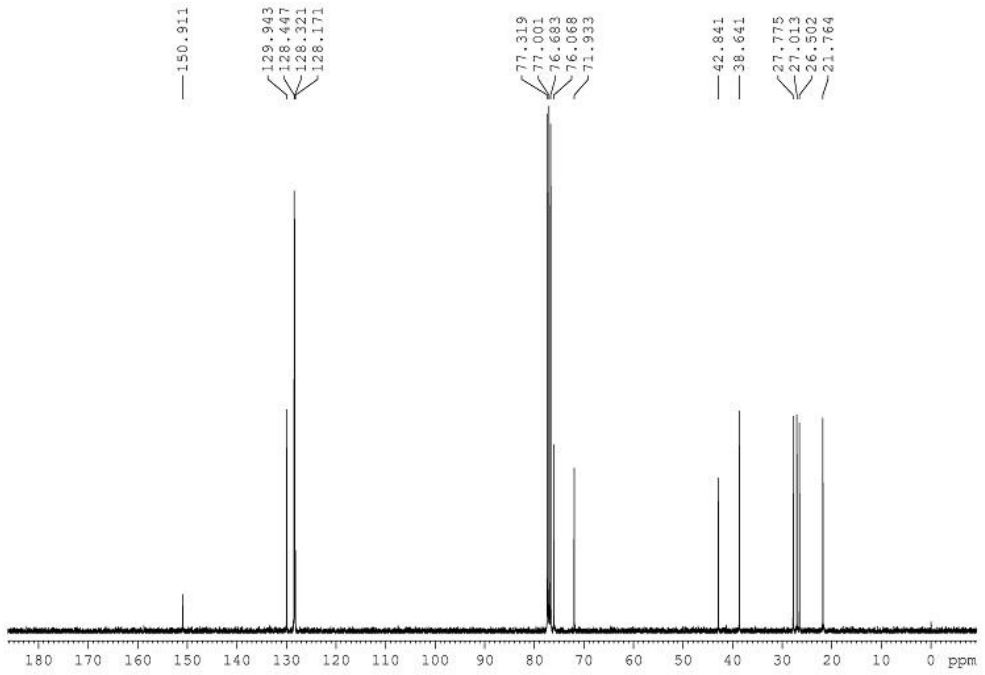


^{13}C NMR (125 MHz, $CDCl_3$)

2-(2-hydroxypropan-2-yl)-4,4-dimethyl-5-phenyl-3,4-dihydro-2H-pyrrole 1-oxide (2l)

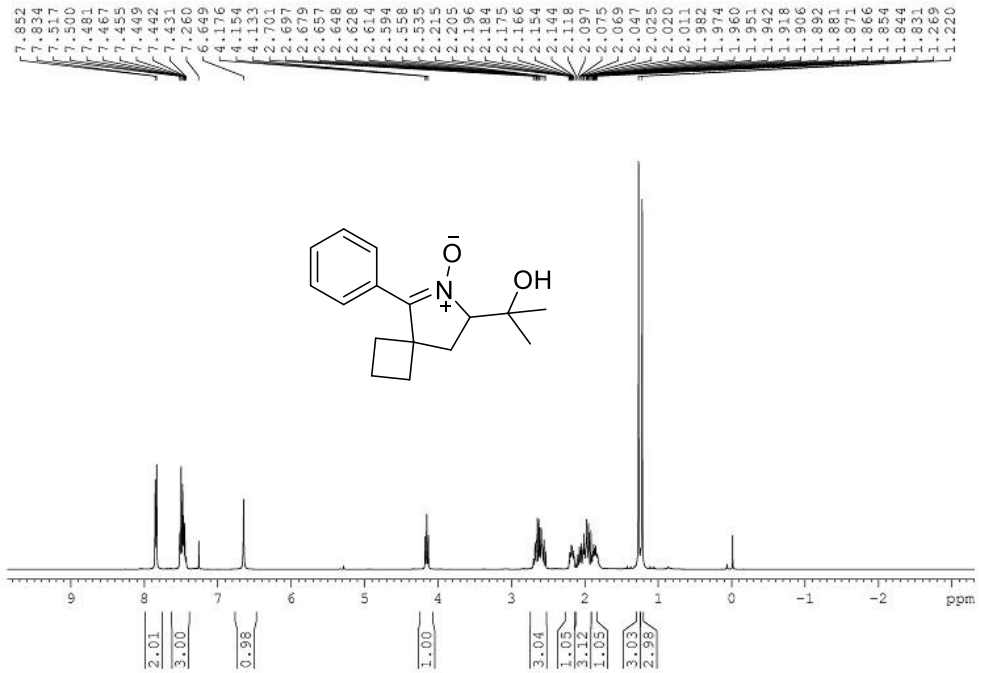


^{1}H NMR (500 MHz, $CDCl_3$)

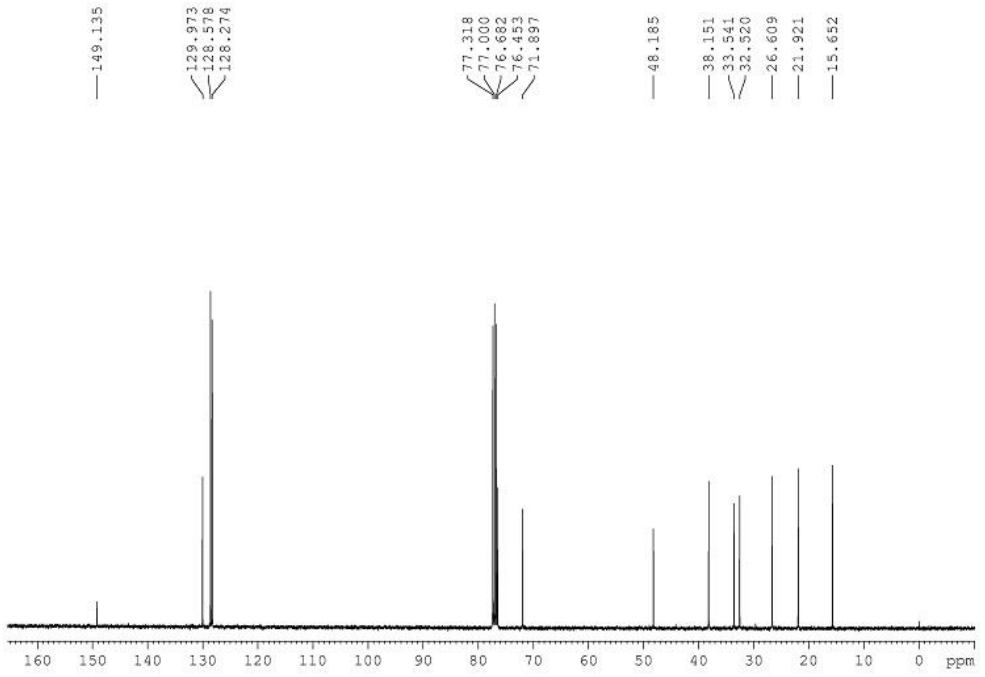


^{13}C NMR (125 MHz, $CDCl_3$)

7-(2-hydroxypropan-2-yl)-5-phenyl-6-azaspiro[3.4]oct-5-ene 6-oxide (2m)

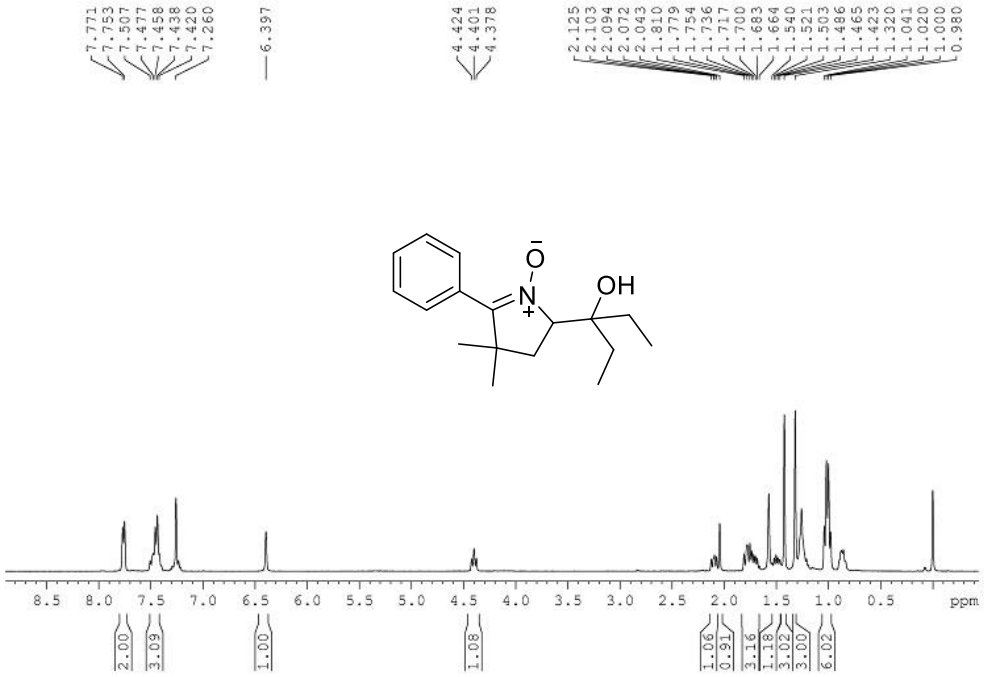


^{1}H NMR (500 MHz, $CDCl_3$)

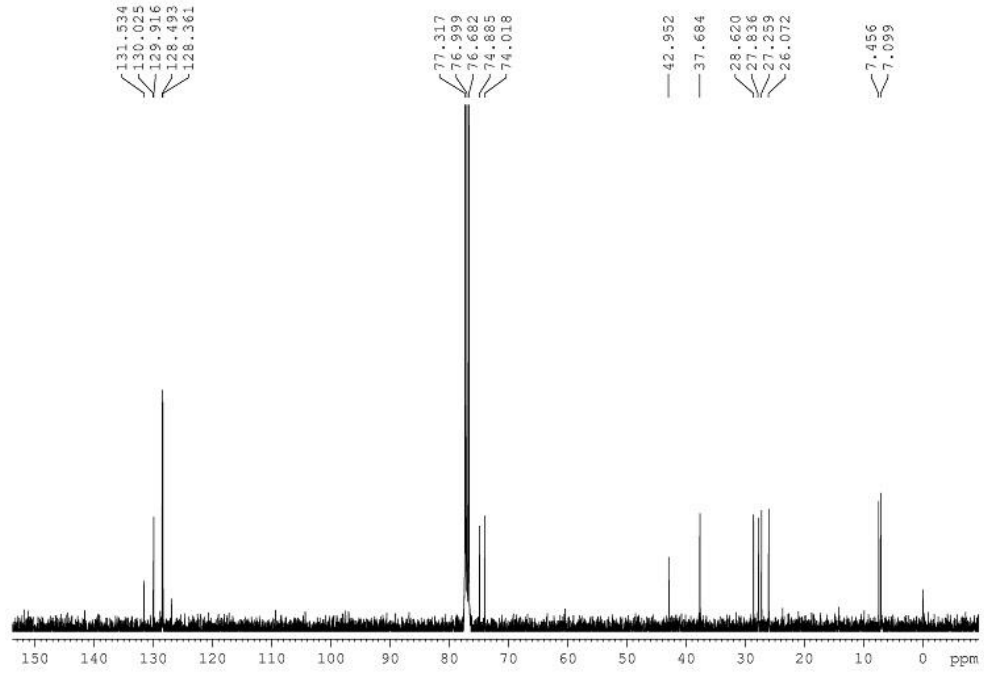


^{13}C NMR (125 MHz, $CDCl_3$)

2-(3-hydroxypentan-3-yl)-4,4-dimethyl-5-phenyl-3,4-dihydro-2H-pyrrole 1-oxide (2n)

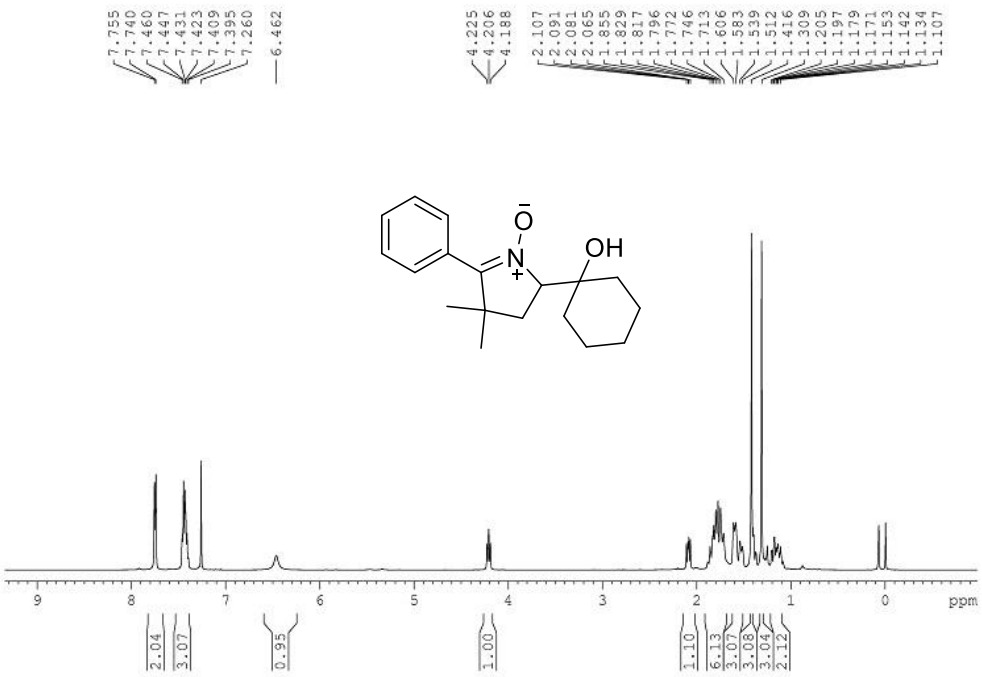


^{1}H NMR (500 MHz, $CDCl_3$)

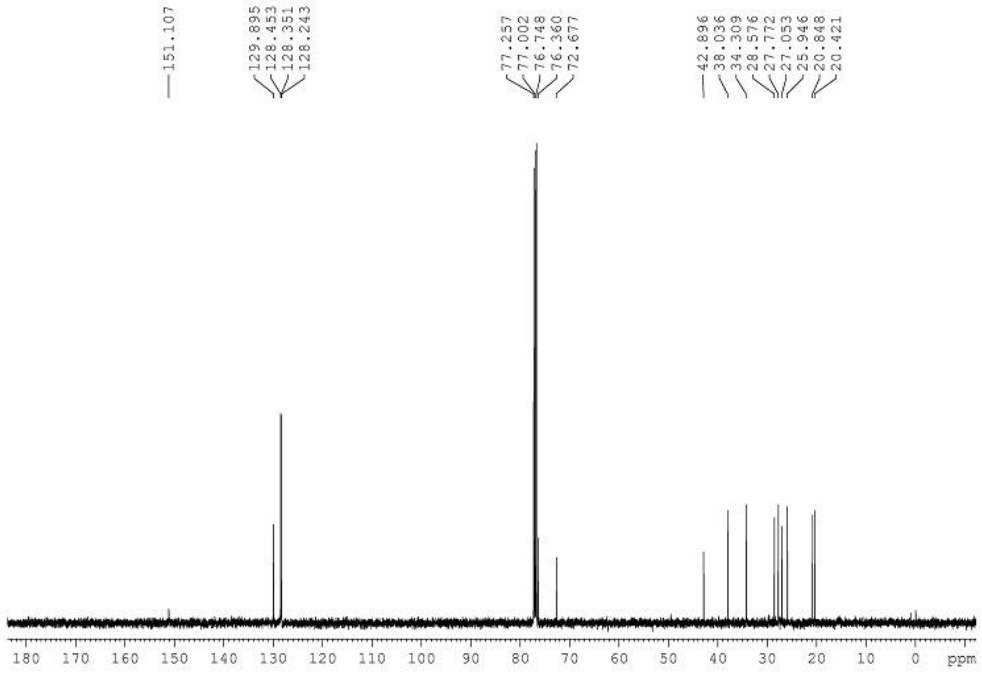


^{13}C NMR (125 MHz, $CDCl_3$)

2-(1-hydroxycyclohexyl)-4,4-dimethyl-5-phenyl-3,4-dihydro-2H-pyrrole1-oxide (2o)

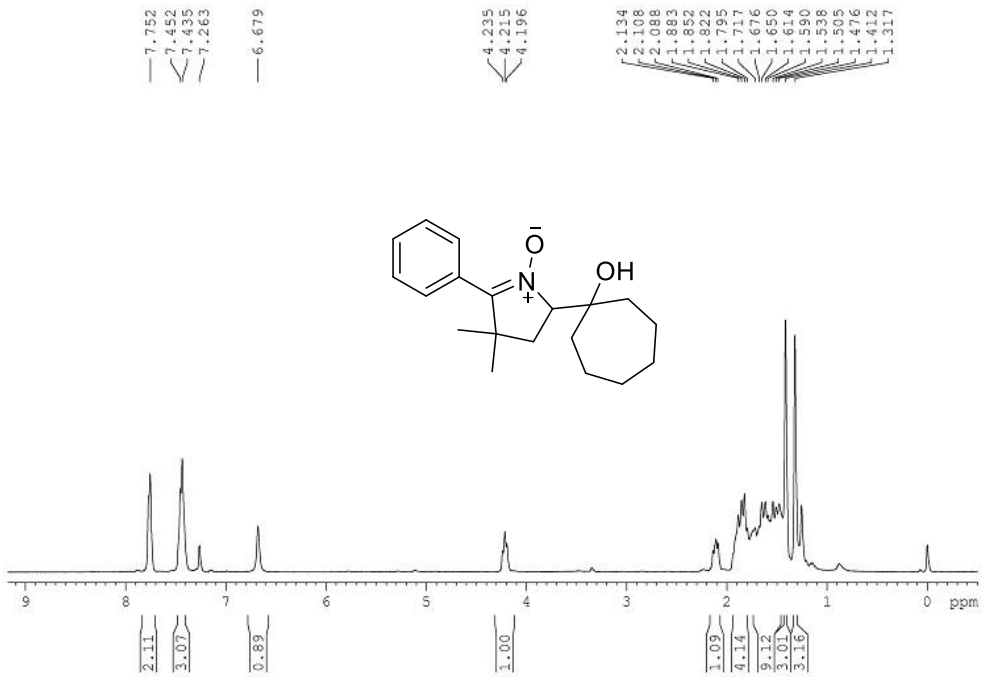


^{1}H NMR (500 MHz, $CDCl_3$)

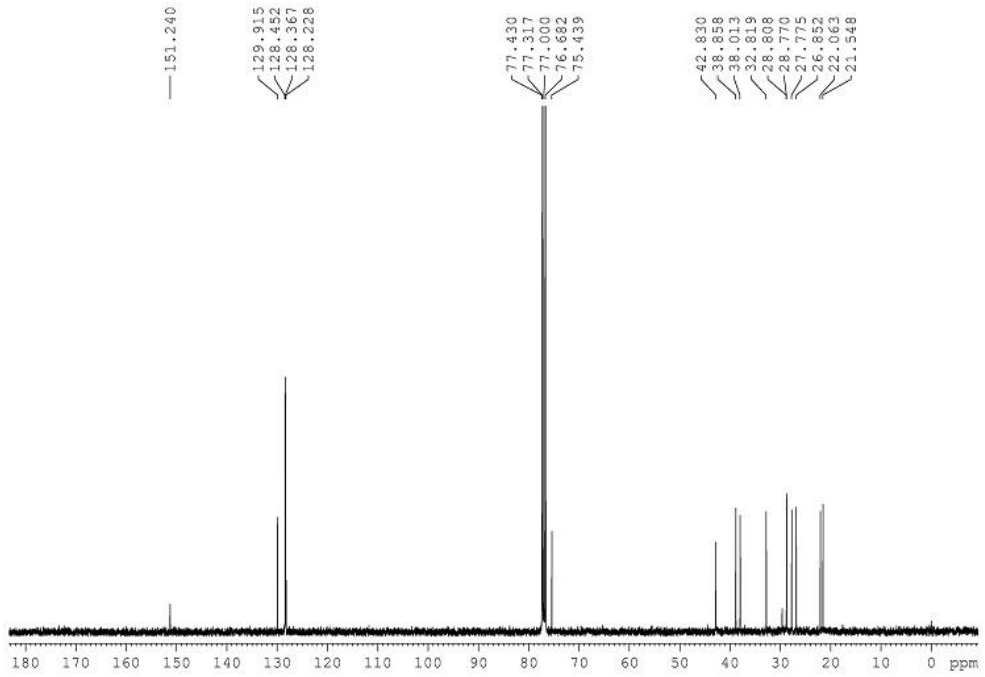


^{13}C NMR (125 MHz, $CDCl_3$)

2-(1-hydroxycycloheptyl)-4,4-dimethyl-5-phenyl-3,4-dihydro-2H-pyrrole 1-oxide (2p)

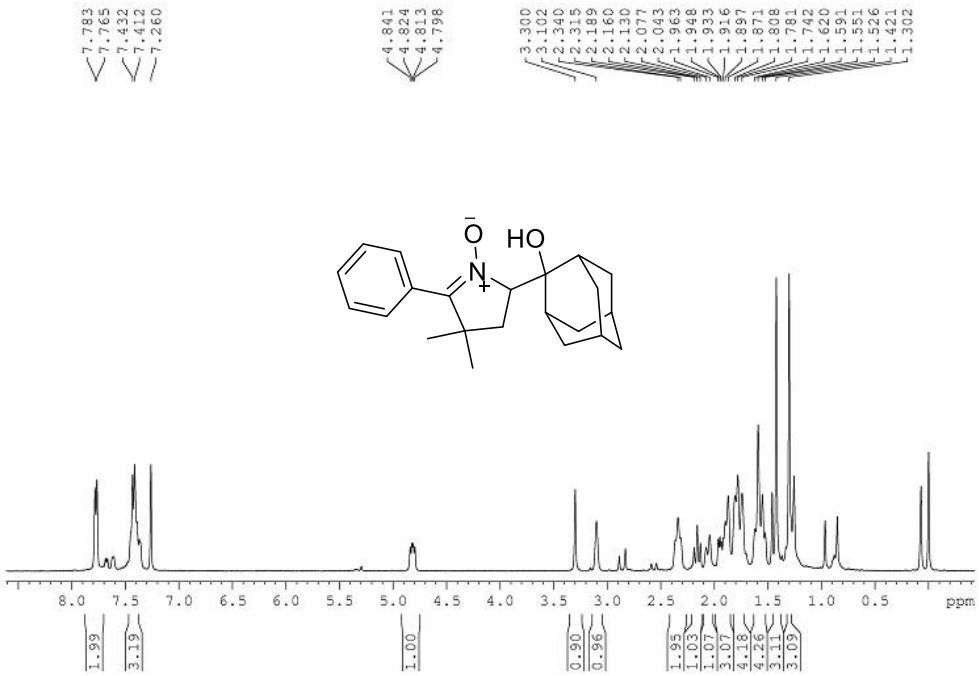


^{1}H NMR (500 MHz, $CDCl_3$)

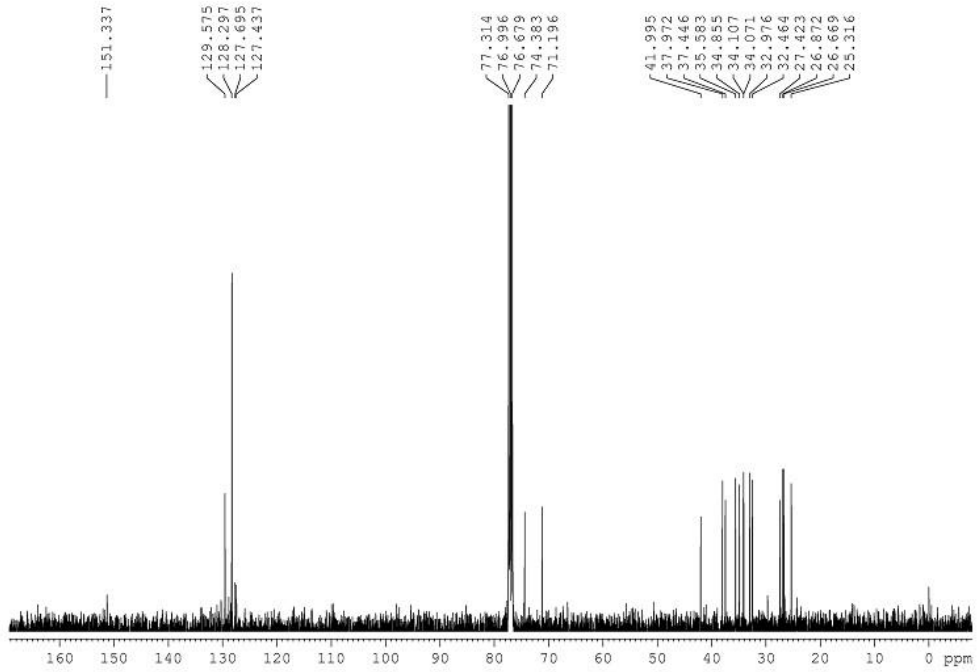


^{13}C NMR (125 MHz, $CDCl_3$)

2-((1r,3r,5r,7r)-2-hydroxyadamantan-2-yl)-4,4-dimethyl-5-phenyl-3,4-dihydro-2H-pyrrole 1-oxide(2q)

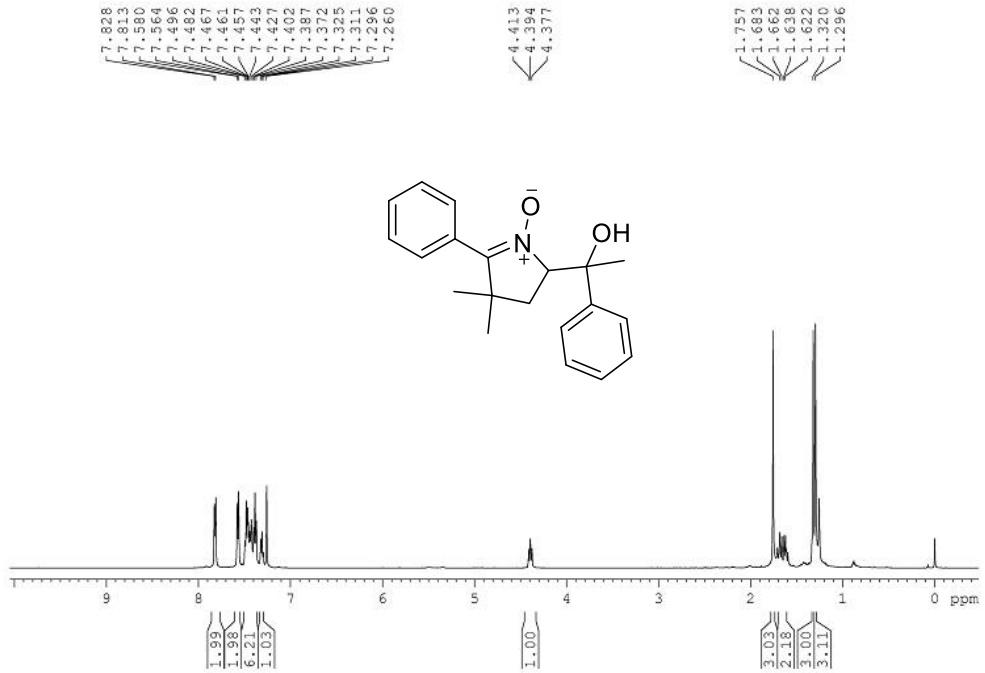


^{1}H NMR (500 MHz, $CDCl_3$)

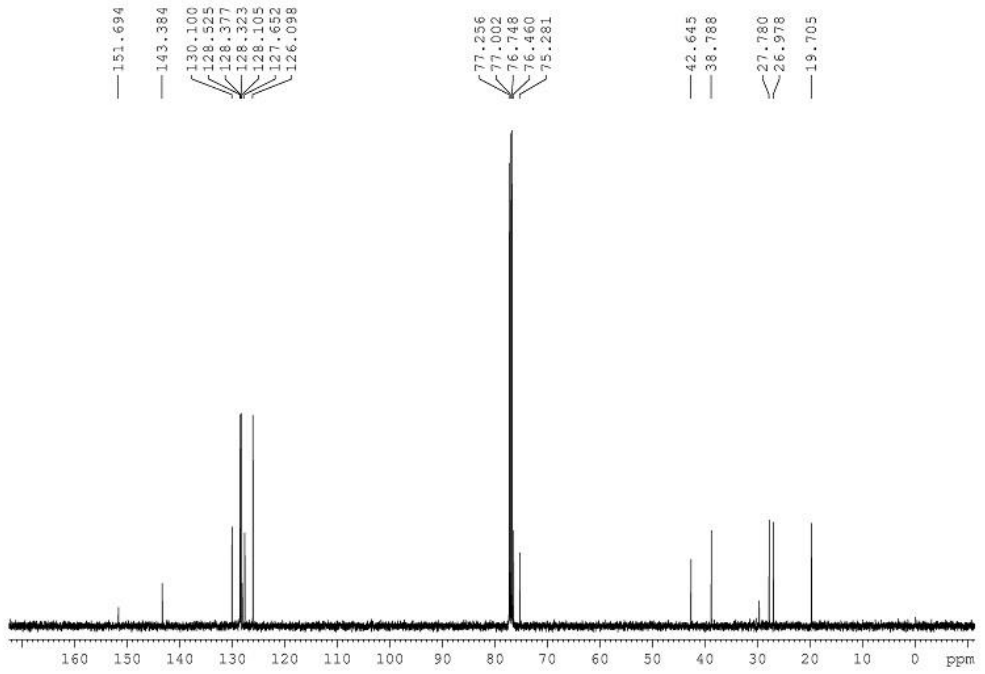


^{13}C NMR (125 MHz, $CDCl_3$)

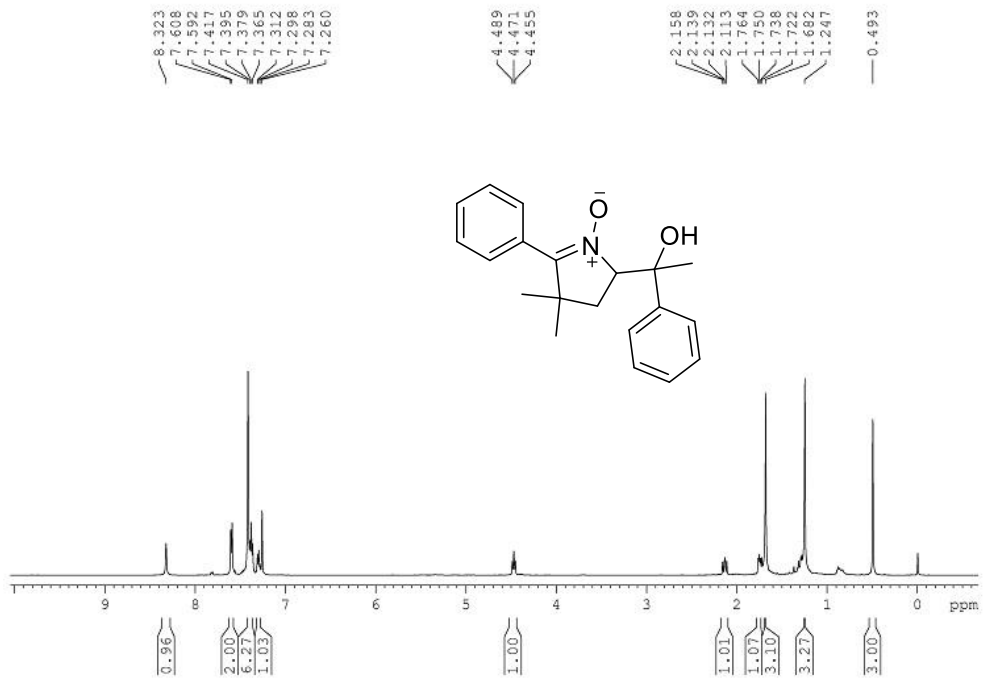
2-(1-hydroxy-1-phenylethyl)-4,4-dimethyl-5-phenyl-3,4-dihydro-2H-pyrrole 1-oxide (2r)



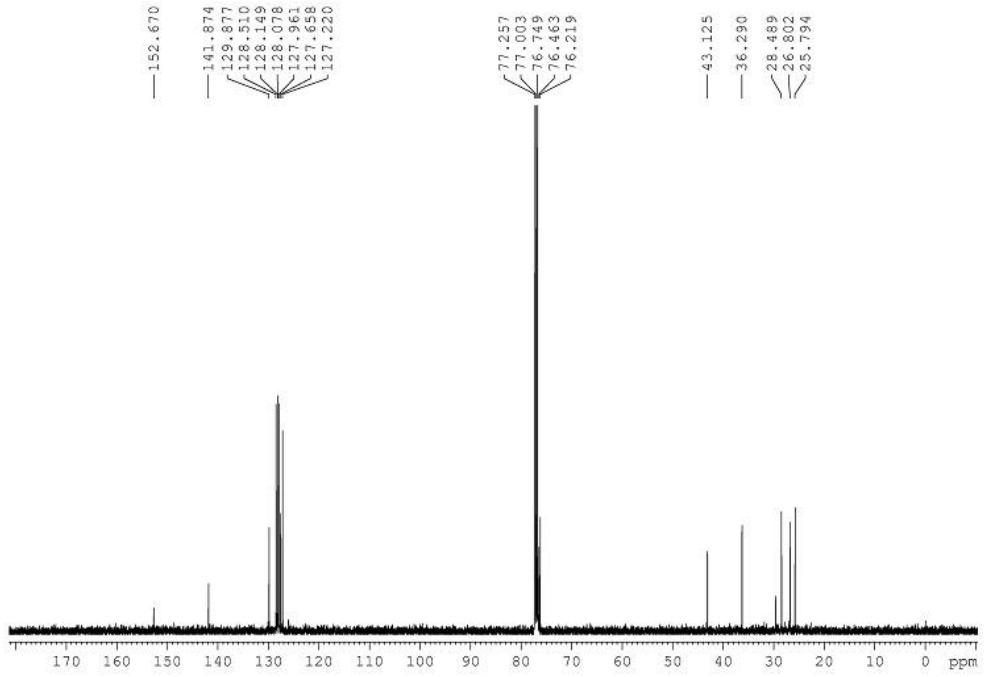
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

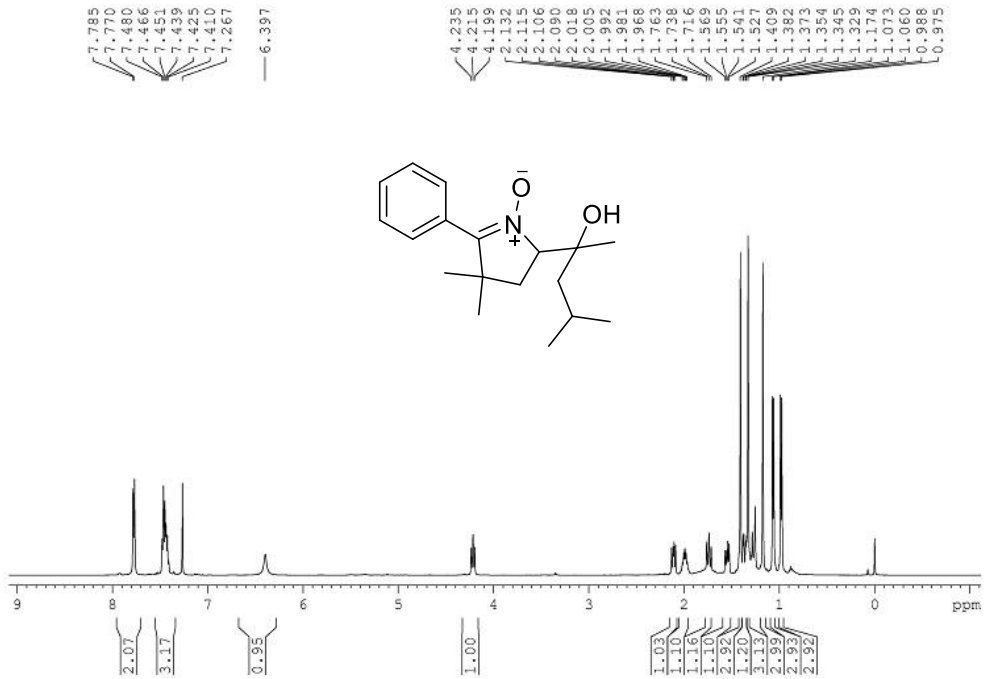


^{1}H NMR (500 MHz, $CDCl_3$)

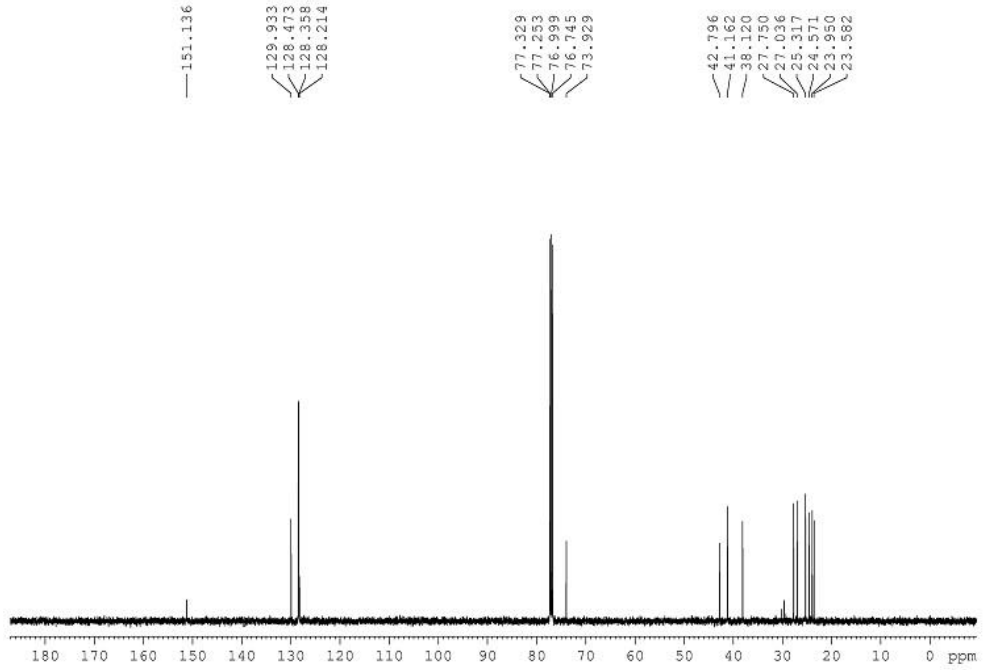


^{13}C NMR (125 MHz, $CDCl_3$)

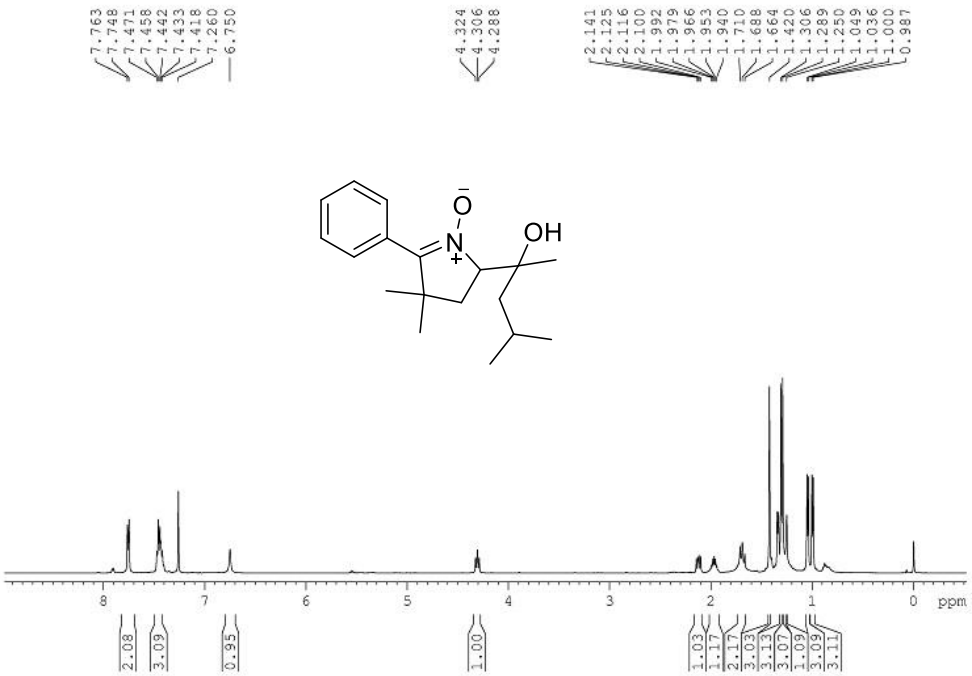
2-(2-hydroxy-4-methylpentan-2-yl)-4,4-dimethyl-5-phenyl-3,4-dihydro-2H-pyrrole1-oxide (2s)



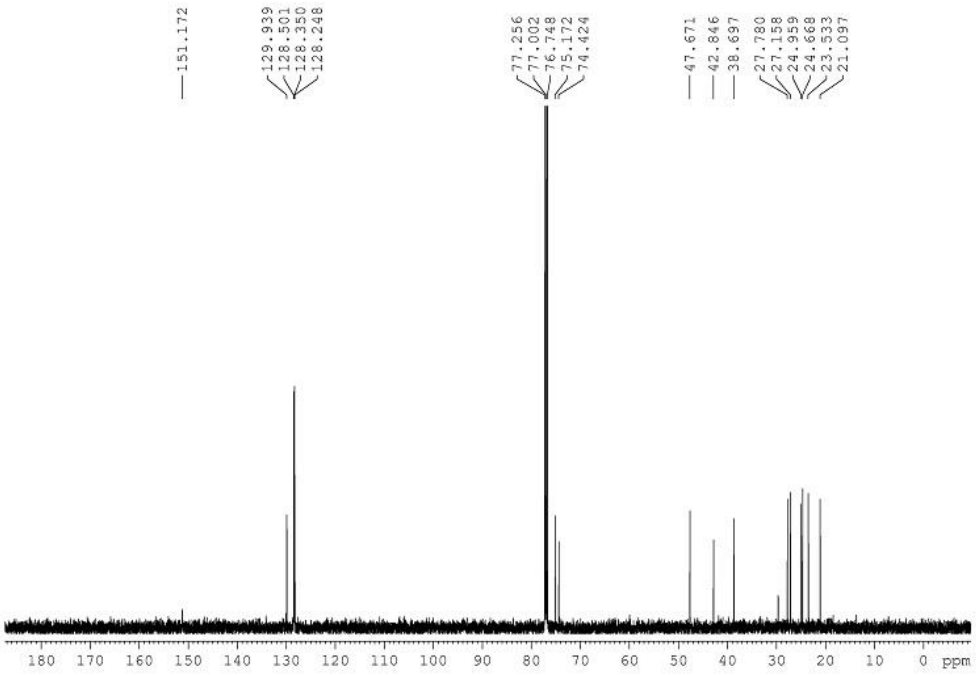
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

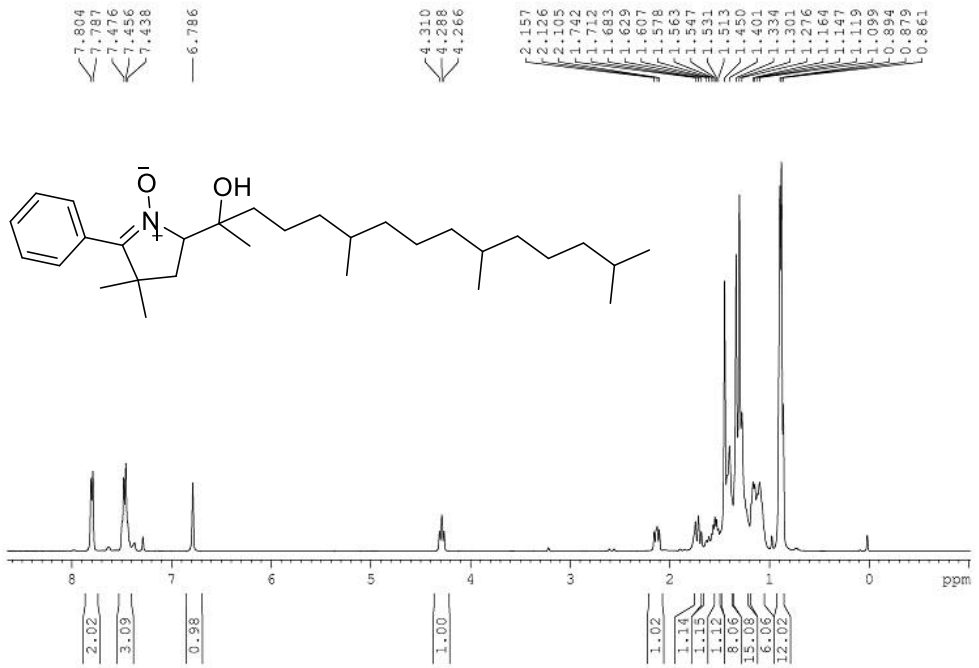


^{1}H NMR (500 MHz, $CDCl_3$)

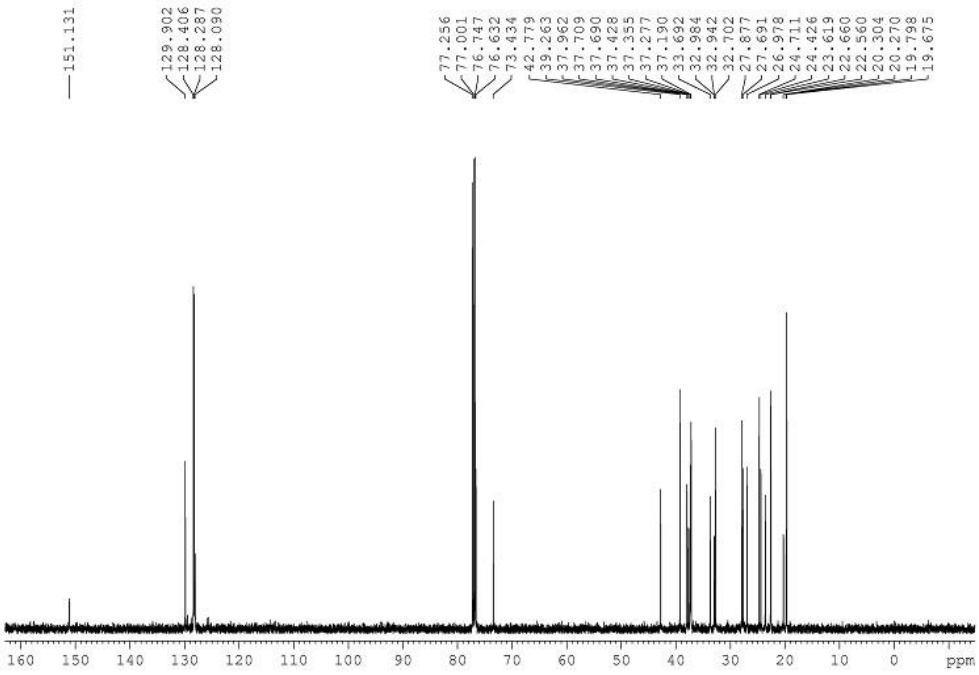


^{13}C NMR (125 MHz, $CDCl_3$)

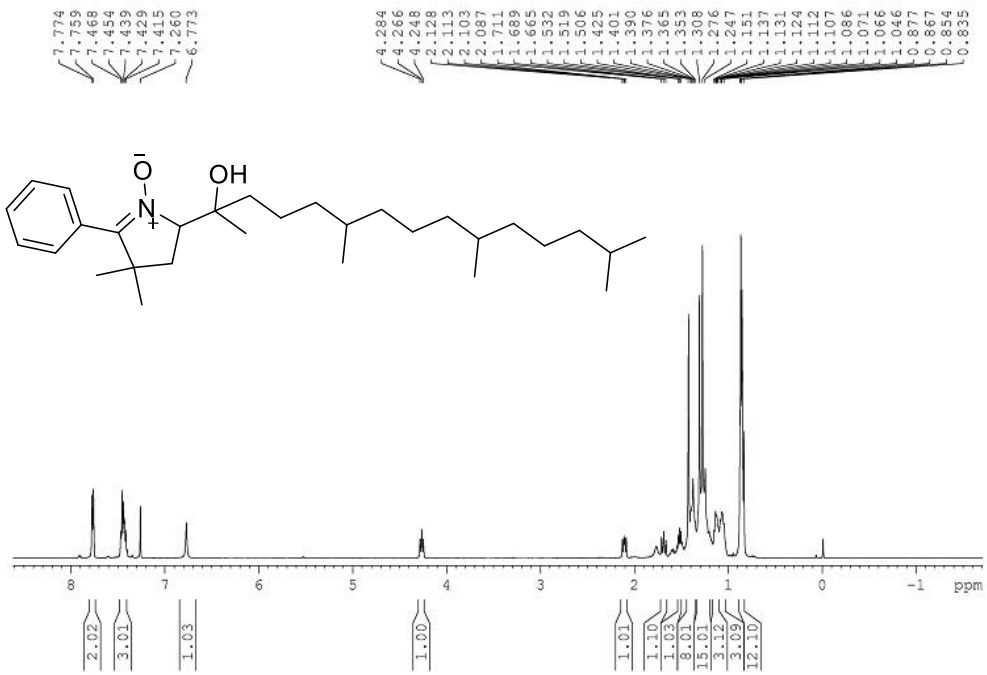
2-(2-hydroxy-6,10,14-trimethylpentadecan-2-yl)-4,4-dimethyl-5-phenyl-3,4-dihydro-2H-pyrrole 1-oxide (2t)



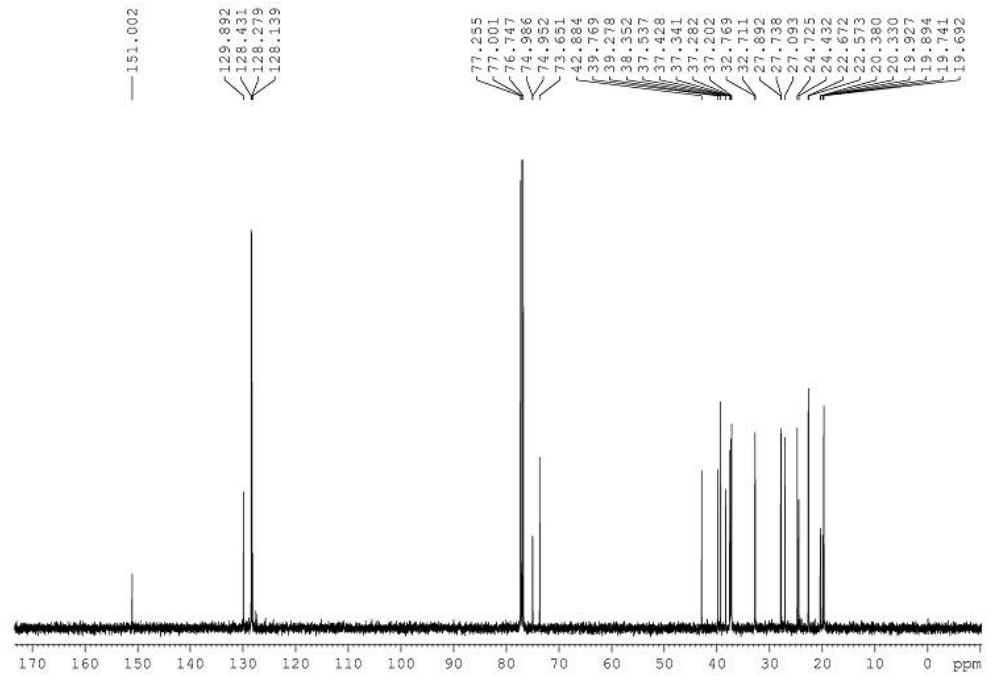
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

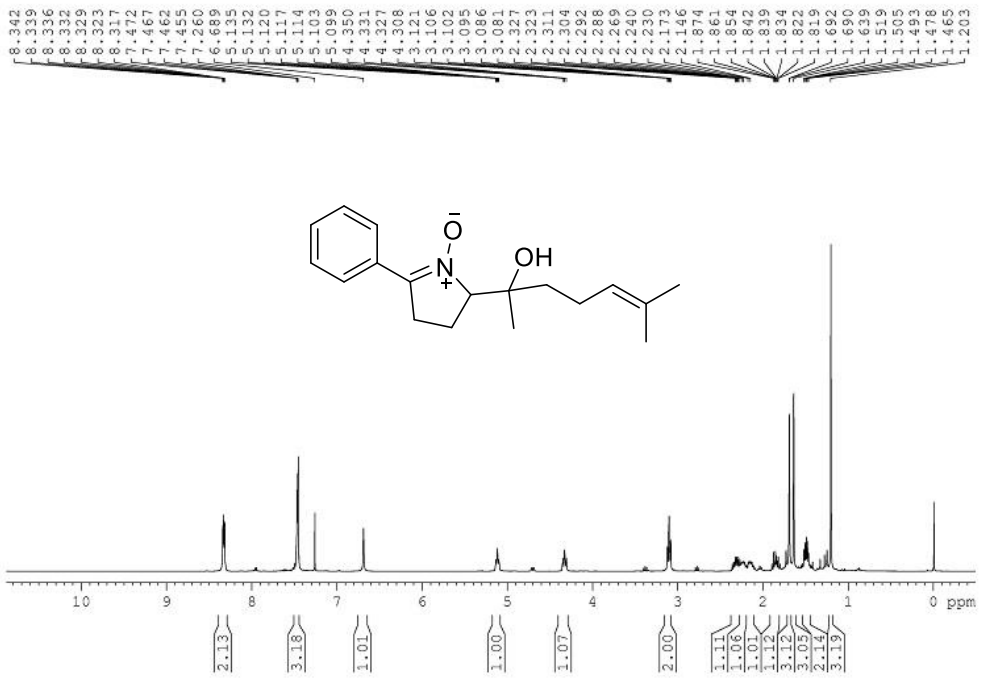


^{1}H NMR (500 MHz, $CDCl_3$)

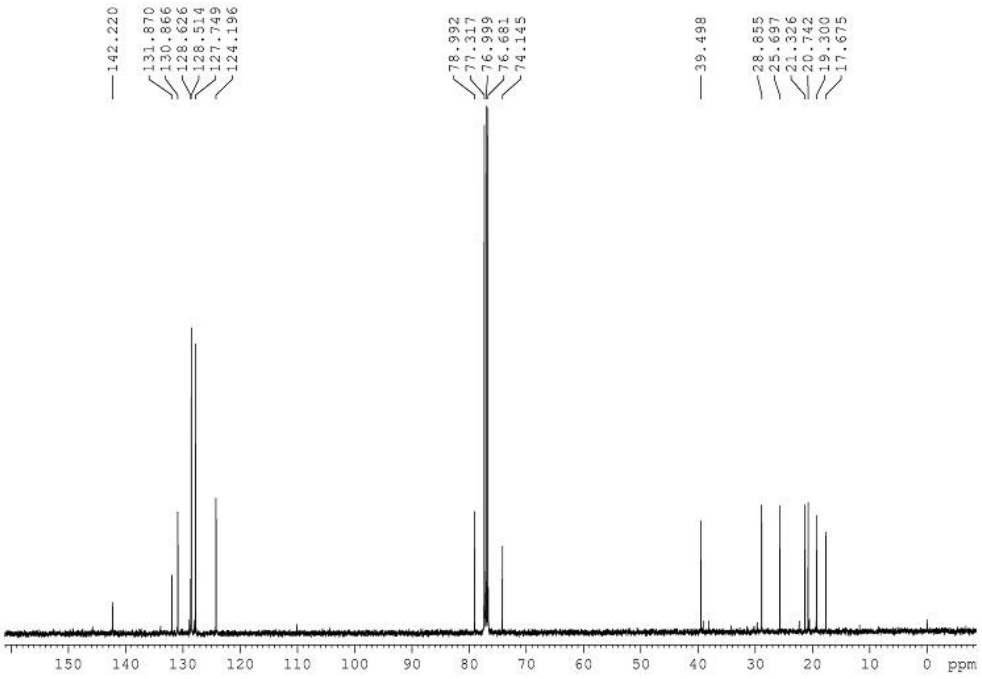


^{13}C NMR (125 MHz, $CDCl_3$)

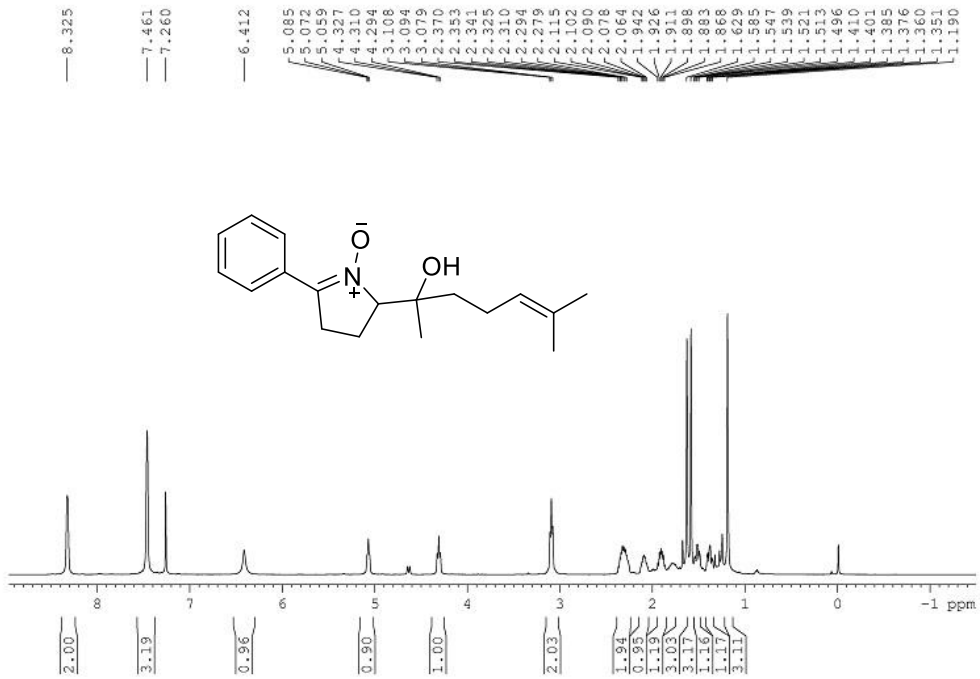
2-(2-hydroxy-6-methylhept-5-en-2-yl)-5-phenyl-3,4-dihydro-2H-pyrrole 1-oxide (2u)



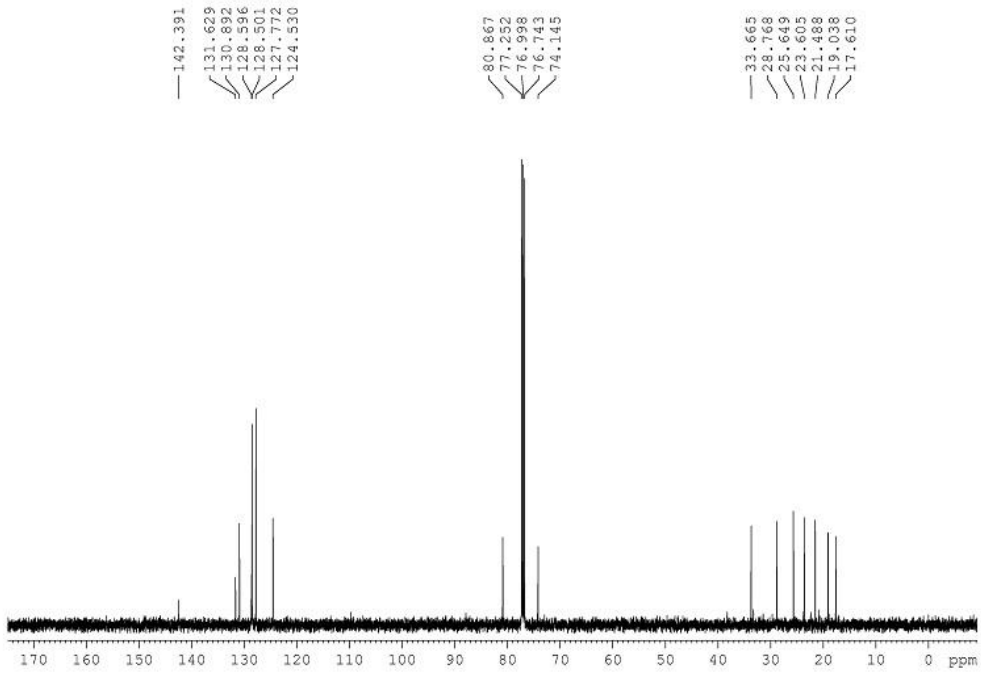
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



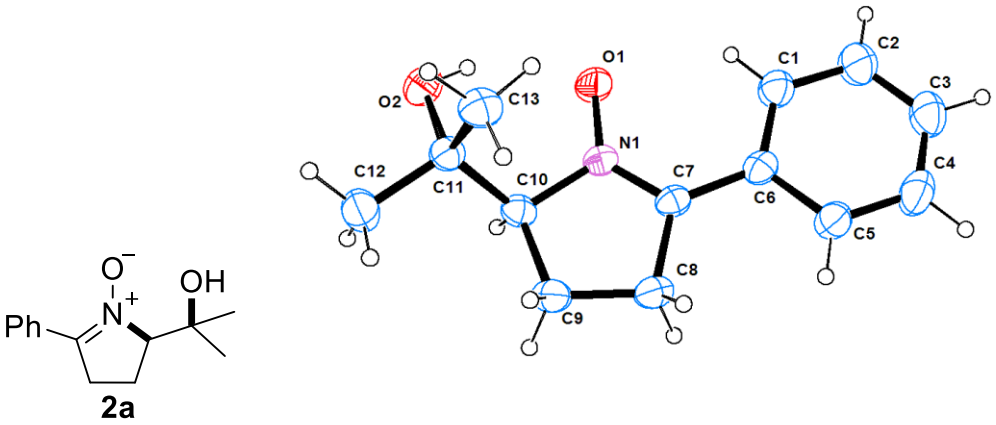
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

(D) The X-ray Single-Crystal Diffraction Analysis of 2a (CCDC: 2106796)

Method for crystal growth: In a vial (25 mL) the product **2a** was dissolved in dichloromethane (1 mL), followed by addtion of petroleum ether (2 mL). Then, the big was covered with rubber cap (Don't seal it completely) and was set aside till the crystal formed. The crystal data for **2a** were integrated using the program SAINT and corrected for absorption effects using the program SADABS.[5] The structures were solved by direct methods and refined on F2 by full-matrix least squares using SHELXTL-2014 software.



The thermal ellipsoid plot of 2a with 30% displacement ellipsoids

Table S1. Crystal data and structure refinement for A.

Identification code	A	
Empirical formula	C13 H17 N O2	
Formula weight	219.27	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$Pna2_1$	
Unit cell dimensions	a = 10.1132(13) Å	α= 90°.
	b = 5.7769(7) Å	β= 90°.
	c = 20.392(3) Å	γ = 90°.
Volume	1191.3(3) $Å^3$	
Z	4	
Density (calculated)	1.223 Mg/m^3	
Absorption coefficient	0.082 mm^{-1}	

F(000)	472
Crystal size	0.220 x 0.160 x 0.150 mm^3
Theta range for data collection	3.666 to 25.495°.
Index ranges	-12<=h<=12, -6<=k<=6, -24<=l<=23
Reflections collected	8463
Independent reflections	2194 [R(int) = 0.0203]
Completeness to theta = 25.242°	99.7 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2194 / 1 / 148
Goodness-of-fit on F^2	1.040
Final R indices [I>2sigma(I)]	R1 = 0.0284, wR2 = 0.0738
R indices (all data)	R1 = 0.0321, wR2 = 0.0772
Absolute structure parameter	1.1(4)
Extinction coefficient	n/a
Largest diff. peak and hole	0.090 and -0.104 $e.Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for A. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	1744(2)	-3144(2)	1439(1)	60(1)
O(2)	769(2)	-3144(3)	210(1)	62(1)
C(7)	1178(2)	174(3)	2037(1)	43(1)
C(8)	175(2)	2058(4)	1987(1)	55(1)
C(9)	-514(2)	1654(4)	1330(1)	55(1)
C(10)	-28(2)	-688(4)	1079(1)	46(1)
C(6)	2127(2)	-40(4)	2575(1)	47(1)
C(5)	2127(3)	1673(5)	3059(1)	61(1)
C(1)	3030(2)	-1846(4)	2640(1)	60(1)
C(2)	3885(3)	-1930(6)	3168(1)	75(1)
C(4)	2984(3)	1544(5)	3585(1)	74(1)
C(3)	3864(3)	-238(6)	3642(1)	72(1)
N(1)	1052(2)	-1274(3)	1548(1)	44(1)
C(13)	1702(2)	691(4)	266(1)	58(1)
C(12)	-627(2)	-54(5)	-95(1)	68(1)
C(11)	470(2)	-785(4)	370(1)	47(1)

Table S3. Bond lengths [Å] and angles [°] for A.

O(1)-N(1)	1.306(2)
O(2)-C(11)	1.433(3)
O(2)-H(2)	0.8200
C(7)-N(1)	1.307(3)
C(7)-C(6)	1.463(3)
C(7)-C(8)	1.491(3)
C(8)-C(9)	1.527(3)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-C(10)	1.528(3)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-N(1)	1.492(3)
C(10)-C(11)	1.531(3)
C(10)-H(10)	0.9800
C(6)-C(1)	1.393(3)
C(6)-C(5)	1.398(3)
C(5)-C(4)	1.381(4)
C(5)-H(5)	0.9300
C(1)-C(2)	1.380(4)
C(1)-H(1A)	0.9300
C(2)-C(3)	1.376(4)
C(2)-H(2A)	0.9300
C(4)-C(3)	1.366(4)
C(4)-H(4)	0.9300
C(3)-H(3)	0.9300
C(13)-C(11)	1.524(3)
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(12)-C(11)	1.521(3)
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(11)-O(2)-H(2)	109.5
N(1)-C(7)-C(6)	125.57(18)

N(1)-C(7)-C(8)	110.38(18)
C(6)-C(7)-C(8)	124.01(18)
C(7)-C(8)-C(9)	105.02(17)
C(7)-C(8)-H(8A)	110.7
C(9)-C(8)-H(8A)	110.7
C(7)-C(8)-H(8B)	110.7
C(9)-C(8)-H(8B)	110.7
H(8A)-C(8)-H(8B)	108.8
C(8)-C(9)-C(10)	106.43(18)
C(8)-C(9)-H(9A)	110.4
C(10)-C(9)-H(9A)	110.4
C(8)-C(9)-H(9B)	110.4
C(10)-C(9)-H(9B)	110.4
H(9A)-C(9)-H(9B)	108.6
N(1)-C(10)-C(9)	102.75(16)
N(1)-C(10)-C(11)	110.85(16)
C(9)-C(10)-C(11)	117.06(18)
N(1)-C(10)-H(10)	108.6
C(9)-C(10)-H(10)	108.6
C(11)-C(10)-H(10)	108.6
C(1)-C(6)-C(5)	117.5(2)
C(1)-C(6)-C(7)	124.44(19)
C(5)-C(6)-C(7)	118.0(2)
C(4)-C(5)-C(6)	120.7(3)
C(4)-C(5)-H(5)	119.6
C(6)-C(5)-H(5)	119.6
C(2)-C(1)-C(6)	120.8(2)
C(2)-C(1)-H(1A)	119.6
C(6)-C(1)-H(1A)	119.6
C(3)-C(2)-C(1)	120.9(3)
C(3)-C(2)-H(2A)	119.6
C(1)-C(2)-H(2A)	119.6
C(3)-C(4)-C(5)	121.1(3)
C(3)-C(4)-H(4)	119.5
C(5)-C(4)-H(4)	119.5
C(4)-C(3)-C(2)	119.0(3)
C(4)-C(3)-H(3)	120.5
C(2)-C(3)-H(3)	120.5

O(1)-N(1)-C(7)	127.35(18)
O(1)-N(1)-C(10)	118.07(16)
C(7)-N(1)-C(10)	114.57(16)
C(11)-C(13)-H(13A)	109.5
C(11)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(11)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
O(2)-C(11)-C(12)	105.99(18)
O(2)-C(11)-C(13)	109.17(17)
C(12)-C(11)-C(13)	110.8(2)
O(2)-C(11)-C(10)	108.58(18)
C(12)-C(11)-C(10)	109.78(17)
C(13)-C(11)-C(10)	112.32(18)

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for A. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	73(1)	45(1)	62(1)	-9(1)	-7(1)	20(1)
O(2)	73(1)	50(1)	62(1)	-13(1)	0(1)	-2(1)
C(7)	44(1)	41(1)	46(1)	-1(1)	9(1)	-2(1)
C(8)	54(1)	50(1)	60(1)	-8(1)	8(1)	7(1)
C(9)	50(1)	54(1)	61(1)	-1(1)	4(1)	11(1)
C(10)	38(1)	45(1)	54(1)	0(1)	2(1)	-2(1)
C(6)	48(1)	50(1)	42(1)	0(1)	11(1)	-7(1)
C(5)	59(2)	66(2)	57(2)	-13(1)	5(1)	-1(1)
C(1)	68(2)	62(2)	51(1)	0(1)	-2(1)	7(1)
C(2)	82(2)	82(2)	60(2)	6(1)	-11(1)	11(2)
C(4)	82(2)	90(2)	50(1)	-18(1)	5(1)	-16(2)
C(3)	74(2)	93(2)	50(1)	5(1)	-7(1)	-10(2)
N(1)	46(1)	39(1)	48(1)	-2(1)	4(1)	3(1)
C(13)	51(1)	57(1)	65(2)	1(1)	10(1)	-8(1)
C(12)	56(1)	91(2)	57(2)	2(1)	-7(1)	2(1)
C(11)	43(1)	47(1)	50(1)	-4(1)	2(1)	-3(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for A.

	x	y	z	U(eq)
H(2)	1152	-3755	520	92
H(8A)	598	3565	1995	66
H(8B)	-452	1968	2346	66
H(9A)	-289	2872	1022	66
H(9B)	-1466	1635	1388	66
H(10)	-742	-1822	1130	55
H(5)	1544	2912	3027	73
H(1A)	3057	-3009	2325	72
H(2A)	4484	-3146	3202	90
H(4)	2962	2689	3905	89
H(3)	4440	-307	3997	87
H(13A)	2415	83	525	86
H(13B)	1523	2255	398	86
H(13C)	1944	663	-189	86
H(12A)	-359	-345	-539	102
H(12B)	-803	1567	-40	102
H(12C)	-1413	-923	0	102

Table S6. Torsion angles [°] for A.

N(1)-C(7)-C(8)-C(9)	-5.8(2)
C(6)-C(7)-C(8)-C(9)	176.31(18)
C(7)-C(8)-C(9)-C(10)	9.0(2)
C(8)-C(9)-C(10)-N(1)	-8.7(2)
C(8)-C(9)-C(10)-C(11)	-130.4(2)
N(1)-C(7)-C(6)-C(1)	-0.4(3)
C(8)-C(7)-C(6)-C(1)	177.2(2)
N(1)-C(7)-C(6)-C(5)	-180.0(2)
C(8)-C(7)-C(6)-C(5)	-2.4(3)
C(1)-C(6)-C(5)-C(4)	-0.8(3)
C(7)-C(6)-C(5)-C(4)	178.8(2)
C(5)-C(6)-C(1)-C(2)	0.2(4)
C(7)-C(6)-C(1)-C(2)	-179.3(2)
C(6)-C(1)-C(2)-C(3)	0.3(4)
C(6)-C(5)-C(4)-C(3)	0.8(4)
C(5)-C(4)-C(3)-C(2)	-0.3(4)
C(1)-C(2)-C(3)-C(4)	-0.2(5)
C(6)-C(7)-N(1)-O(1)	-1.0(3)
C(8)-C(7)-N(1)-O(1)	-178.82(19)
C(6)-C(7)-N(1)-C(10)	177.93(18)
C(8)-C(7)-N(1)-C(10)	0.1(2)
C(9)-C(10)-N(1)-O(1)	-175.38(17)
C(11)-C(10)-N(1)-O(1)	-49.6(2)
C(9)-C(10)-N(1)-C(7)	5.6(2)
C(11)-C(10)-N(1)-C(7)	131.45(19)
N(1)-C(10)-C(11)-O(2)	67.6(2)
C(9)-C(10)-C(11)-O(2)	-175.00(17)
N(1)-C(10)-C(11)-C(12)	-176.91(18)
C(9)-C(10)-C(11)-C(12)	-59.5(2)
N(1)-C(10)-C(11)-C(13)	-53.2(2)
C(9)-C(10)-C(11)-C(13)	64.2(2)

Symmetry transformations used to generate equivalent atoms:

Table S7. Hydrogen bonds for A [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(10)-H(10)...O(1)#1	0.98	2.62	3.413(3)	138.2
C(8)-H(8A)...O(1)#2	0.97	2.50	3.383(3)	151.5
O(2)-H(2)...N(1)	0.82	2.54	2.948(2)	111.9
O(2)-H(2)...O(1)	0.82	2.00	2.693(2)	141.9
C(10)-H(10)...O(1)#1	0.98	2.62	3.413(3)	138.2
C(8)-H(8A)...O(1)#2	0.97	2.50	3.383(3)	151.5
O(2)-H(2)...N(1)	0.82	2.54	2.948(2)	111.9
O(2)-H(2)...O(1)	0.82	2.00	2.693(2)	141.9

Symmetry transformations used to generate equivalent atoms:

#1 x-1/2,-y-1/2,z #2 x,y+1,z

(E) References

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