Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Synthesis of mono-nitroxides and of bis-nitroxides with varying electronic through-bond communication

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Additional CW-EPR spectra

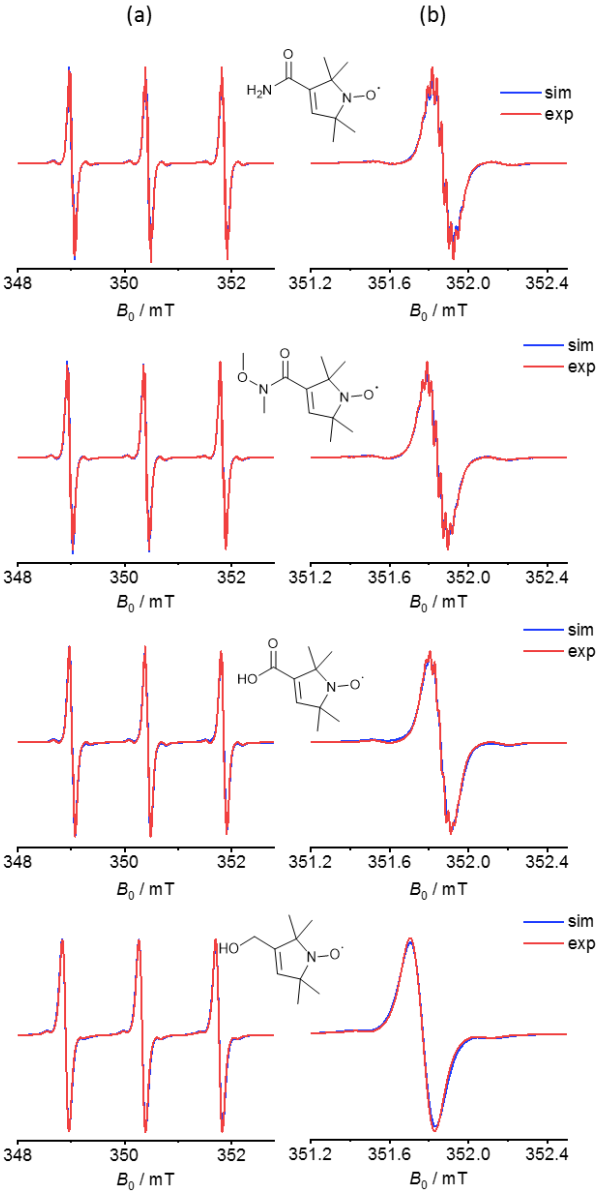


Figure S1 CW-EPR of mono-radicals recorded at room temperature at X-band (a) full spectrum and (b) zoom-in the high field ^{14}N line with the experiment and simulation in red and blue colour, respectively. Simulations were run with Easyspin and simulation parameters are given in **Table S1**.

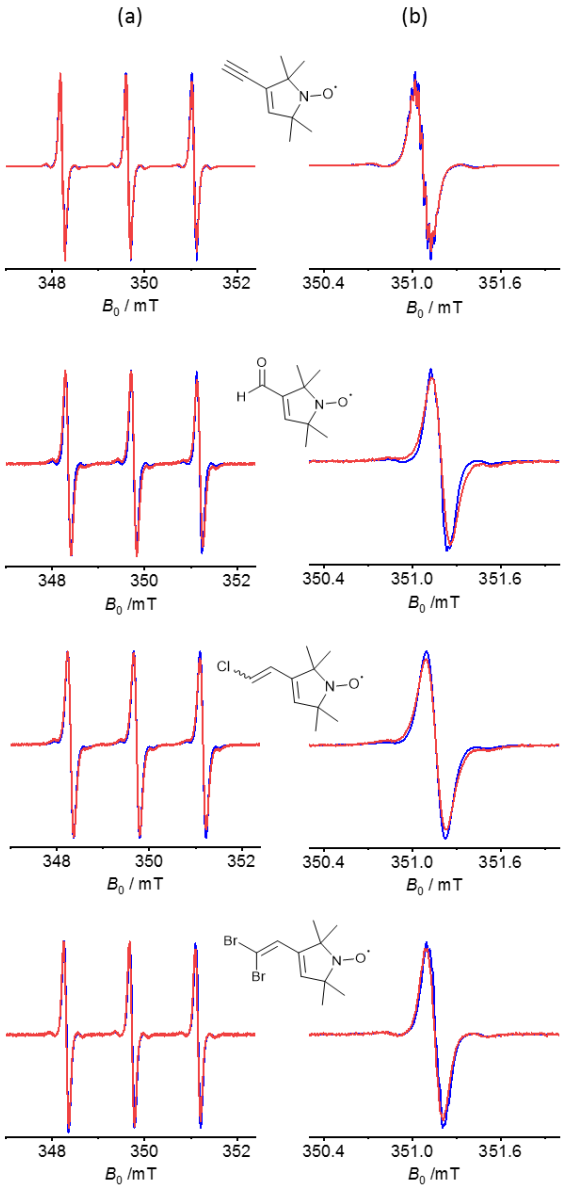


Figure S1 continued CW-EPR of mono-radicals recorded at room temperature at X-band (a) full spectrum and (b) zoom-in the high field ^{14}N line with the experiment and simulation in red and blue colour, respectively. Simulations were run with Easyspin and simulation parameters are given in **Table S1**.

Table S1 Parameters used for the simulations of the mono-radicals.

	g-value	$A_{^{14}N}$ / MHz	$A_{^{1}H(1)}$ / MHz	$A_{^{1}H(2)}$ / MHz	$A_{^{13}C}$ / MHz	linewidth / Voigtian
4	2.01049	40.044	0.655	1.31	17.45	0.010, 0.035
5	2.00776	39.95	0.66	1.32	16.75	0.007 0.037
6	2.00393	39.8	0.625	1.25	16.75	0.00, 0.047
9	2.00594	40.044	0.655	1.3	16.75	0.017, 0.025
10	2.00658	40.3	0.625	1.25	16.75	0.00, 0.09
12	2.00613	40.19	0.645	1.29	16.75	0.00, 0.04
14	2.00901	40.25	0.685	1.37	16.75	0.013, 0.075
15	2.00898	40.090	0.65	1.3	17.13	0.005, 0.034

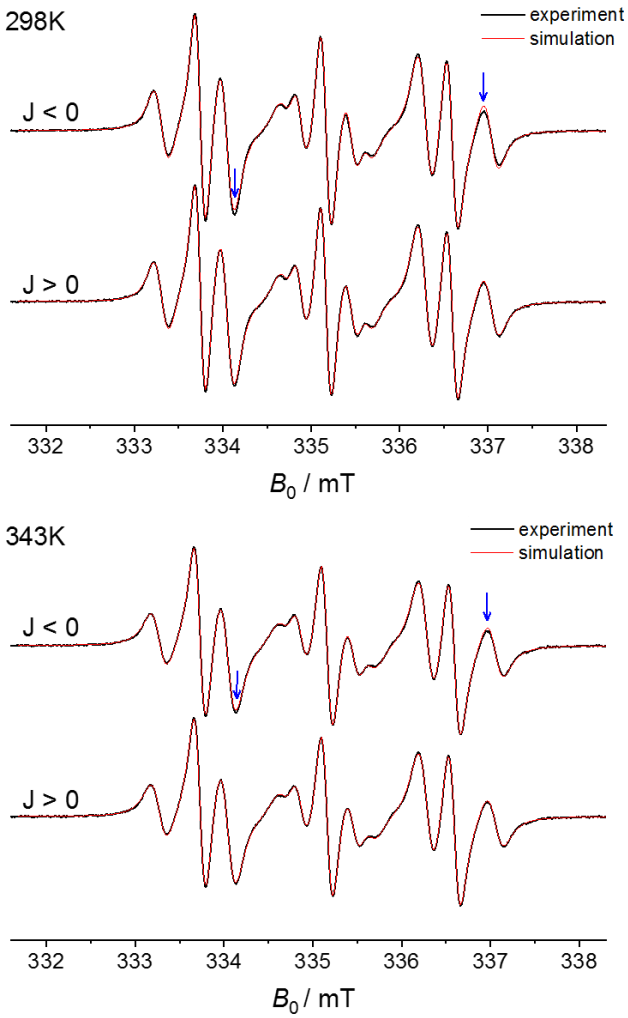


Figure S2 CW-EPR of **3** recorded at room temperature (298 K) and at 343 K at X-band along with simulations in black and red colour, respectively. Simulations were run with positive and negative value of *J* using a self-written Matlab script with the simulation parameters given in main text. The blue arrows denote the deviation of the simulation from the experimental spectrum, suggesting a $J > 0$. Parameters of experiment: 9.48 GHz, 23 dB attenuation, modulation amplitude 0.01 mT, 10 scans.

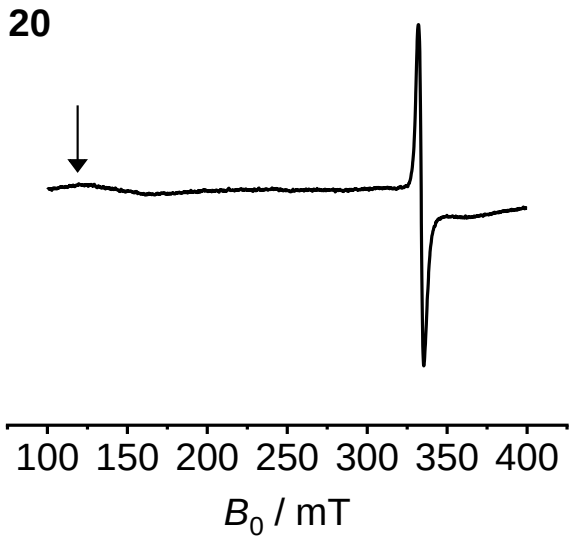


Figure S3 CW-EPR of **20** recorded at 5 K with the arrow indicating the half-field transition. Parameters of experiment: 9.346GHz, 13 dB attenuation, modulation amplitude 0.2 mT, 1 scan.

Characterization spectra

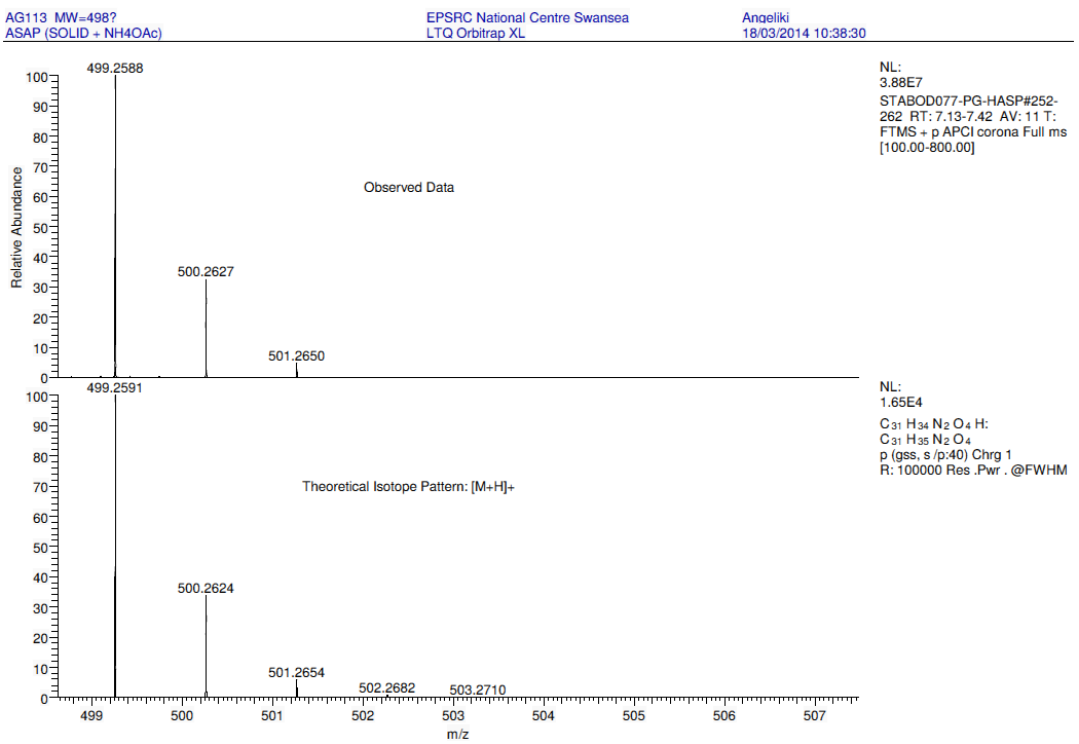


Figure S4 Mass spectrum of **2**.

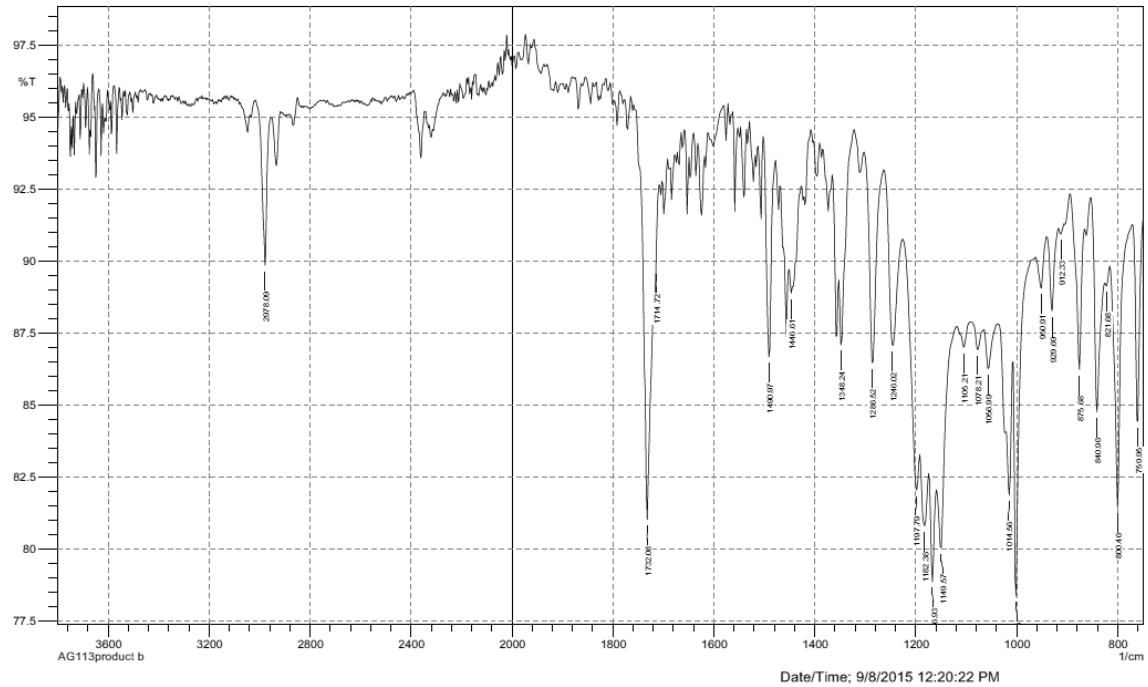


Figure S5 IR spectrum of **2.**

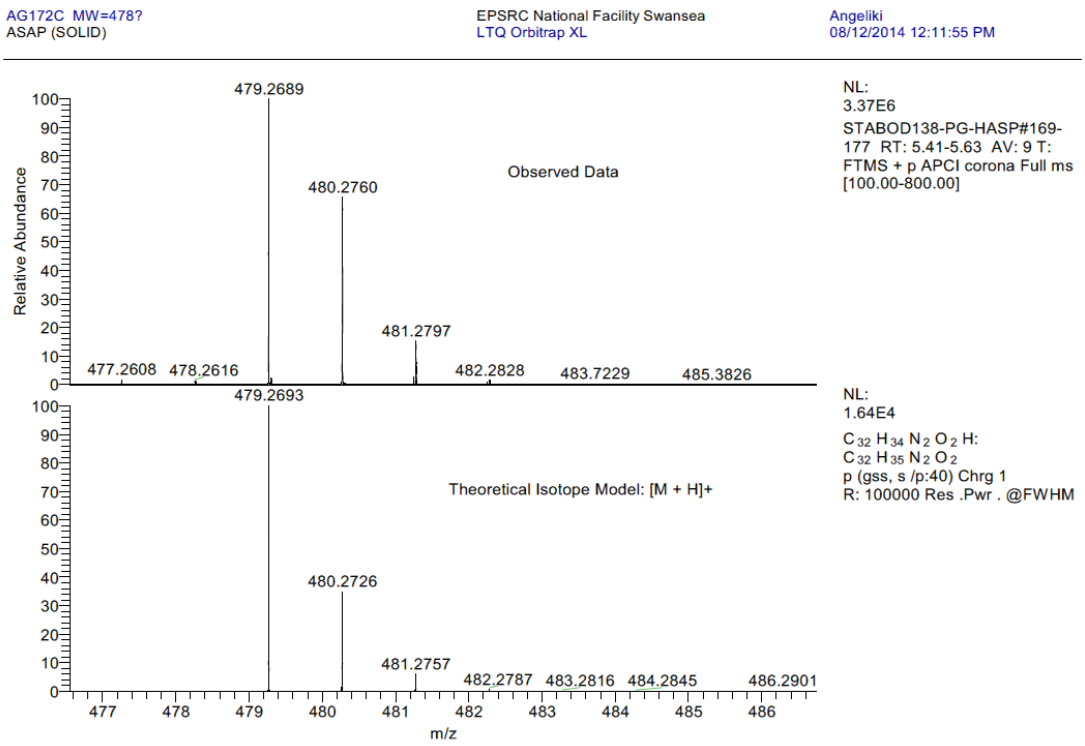


Figure S6 Mass spectrum of **3**.

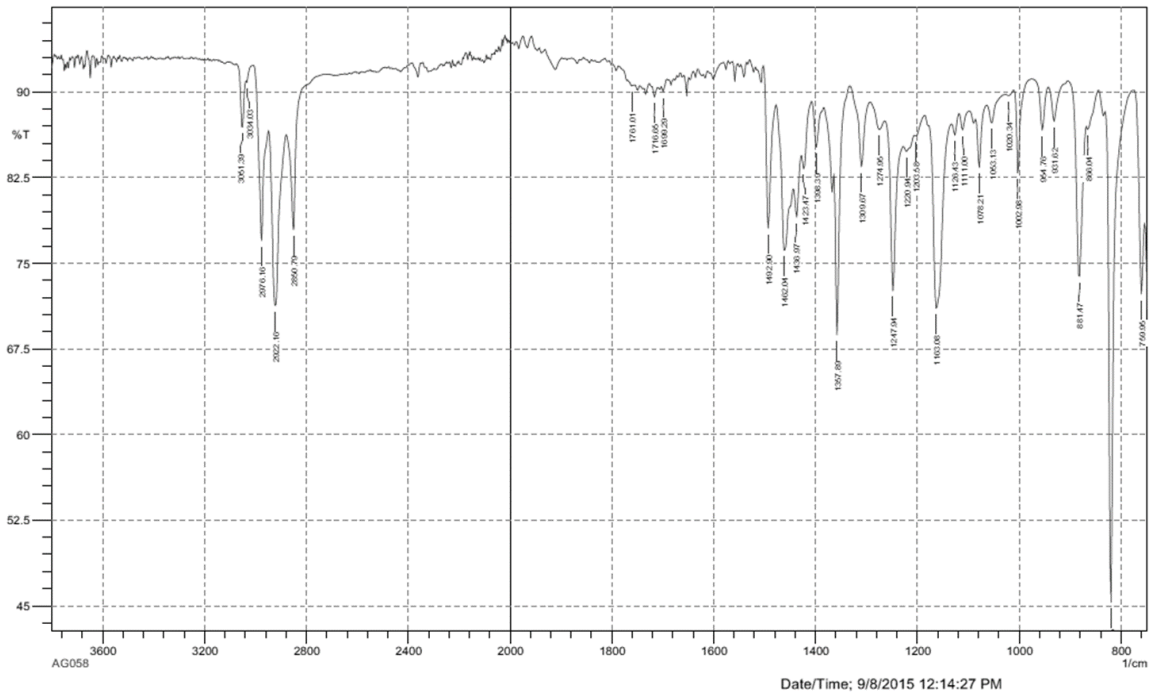


Figure S7 IR spectrum of **3**.

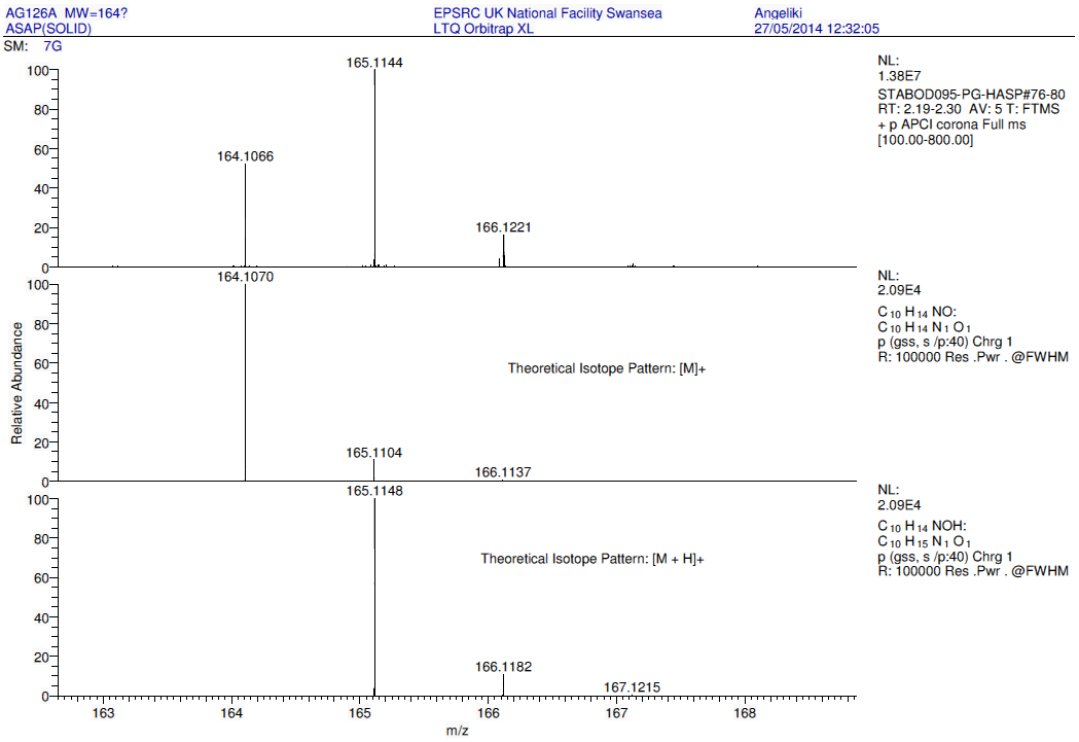


Figure S8 Mass spectrum of **4** from **15**.

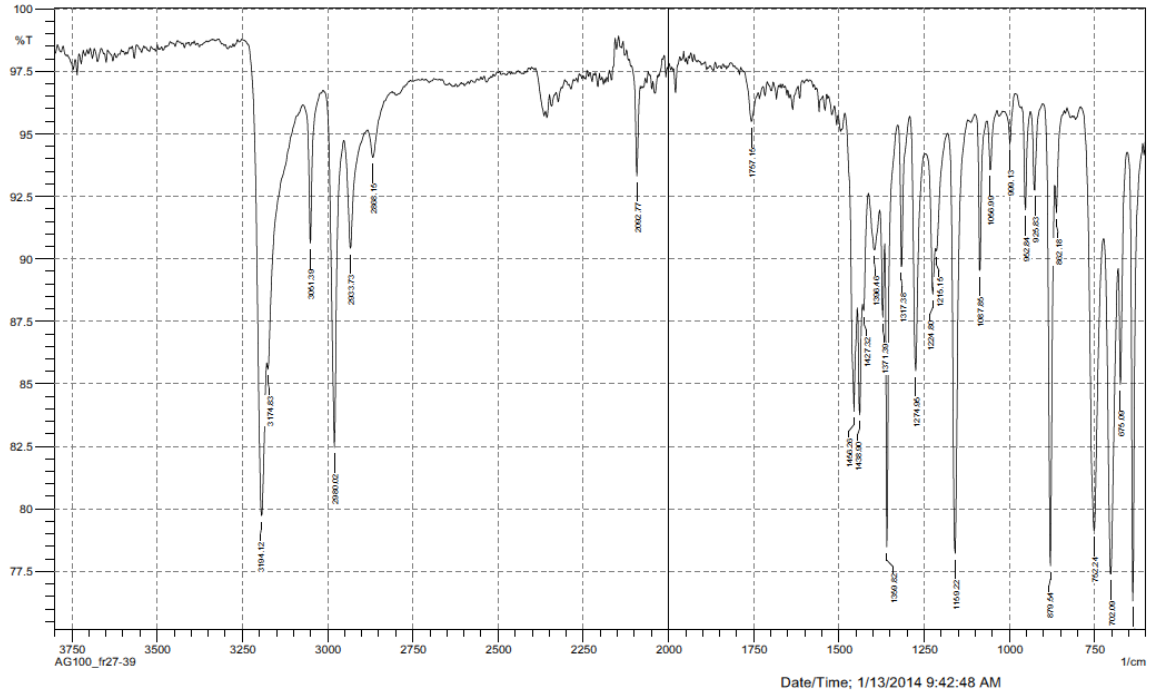


Figure S9 IR spectrum of **4**.

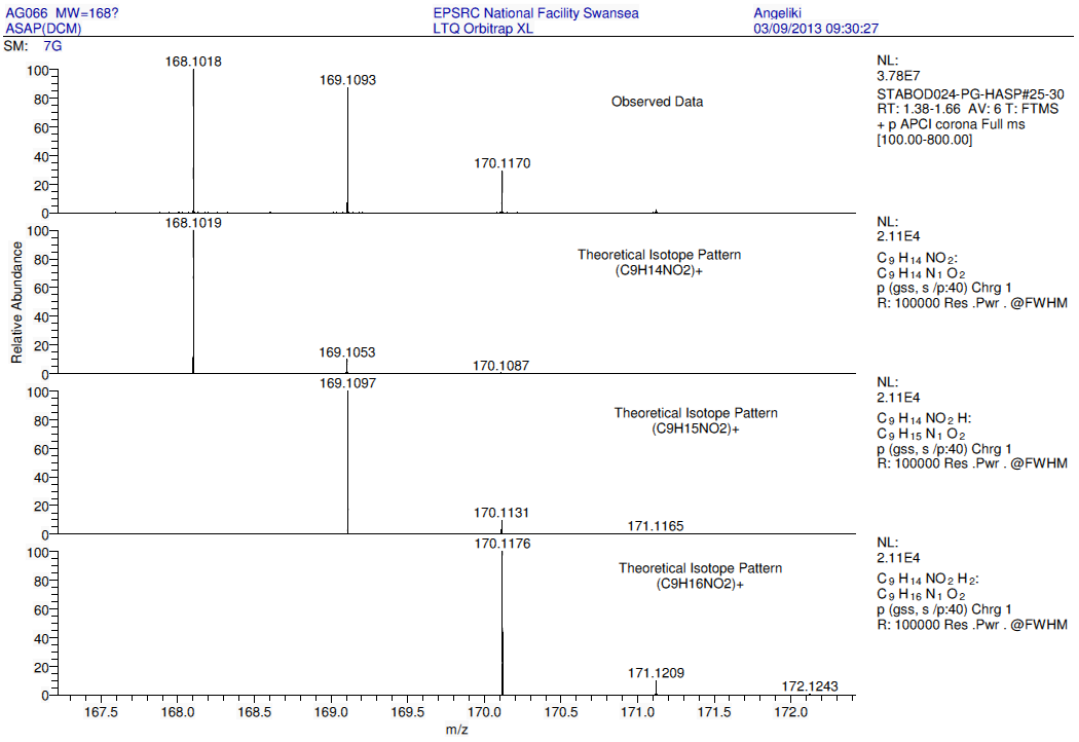


Figure S10 Mass spectrum of **5** from **12**.

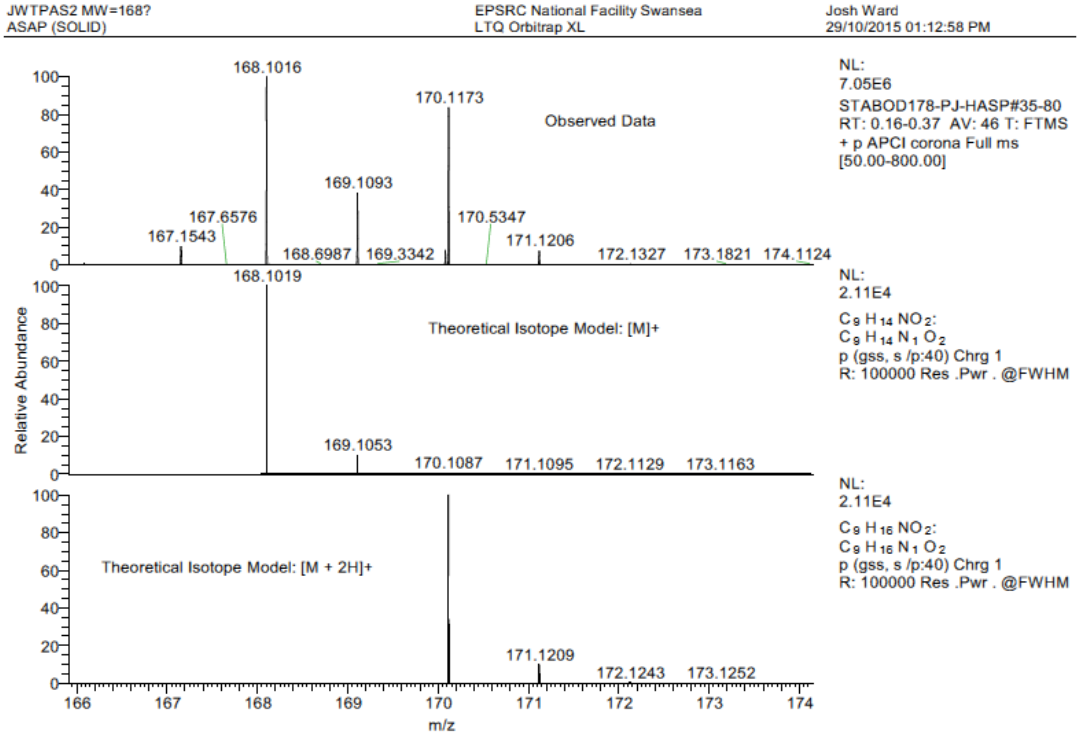


Figure S11 Mass spectrum of **5** from **10**.

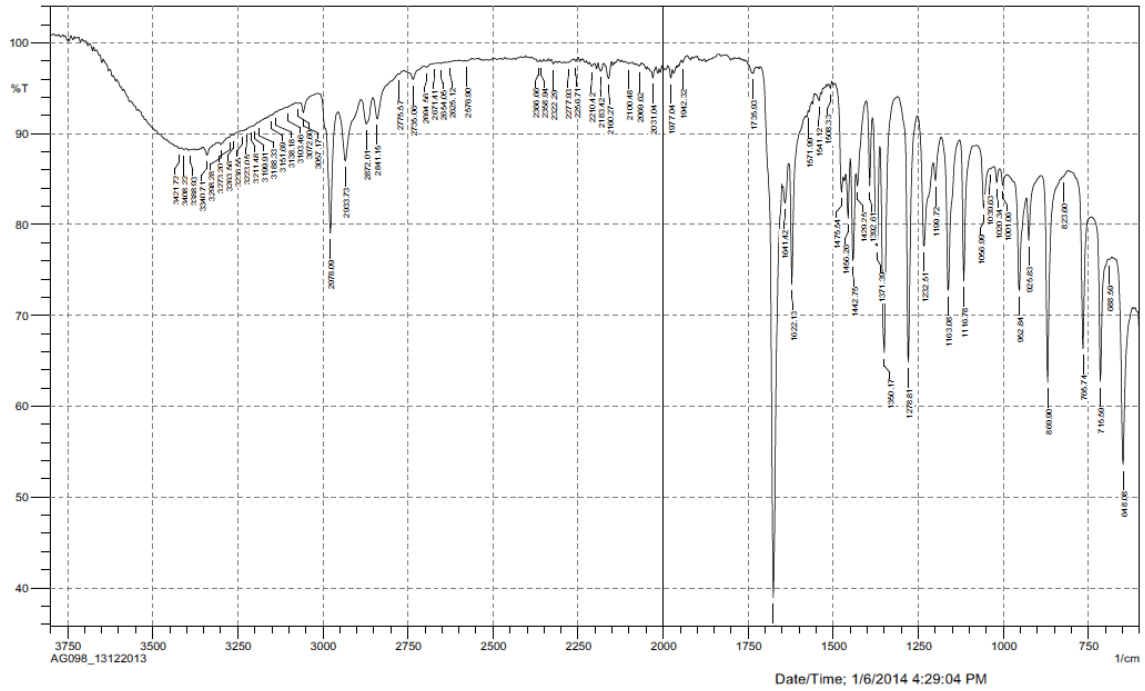


Figure S12 IR spectrum of **5**.

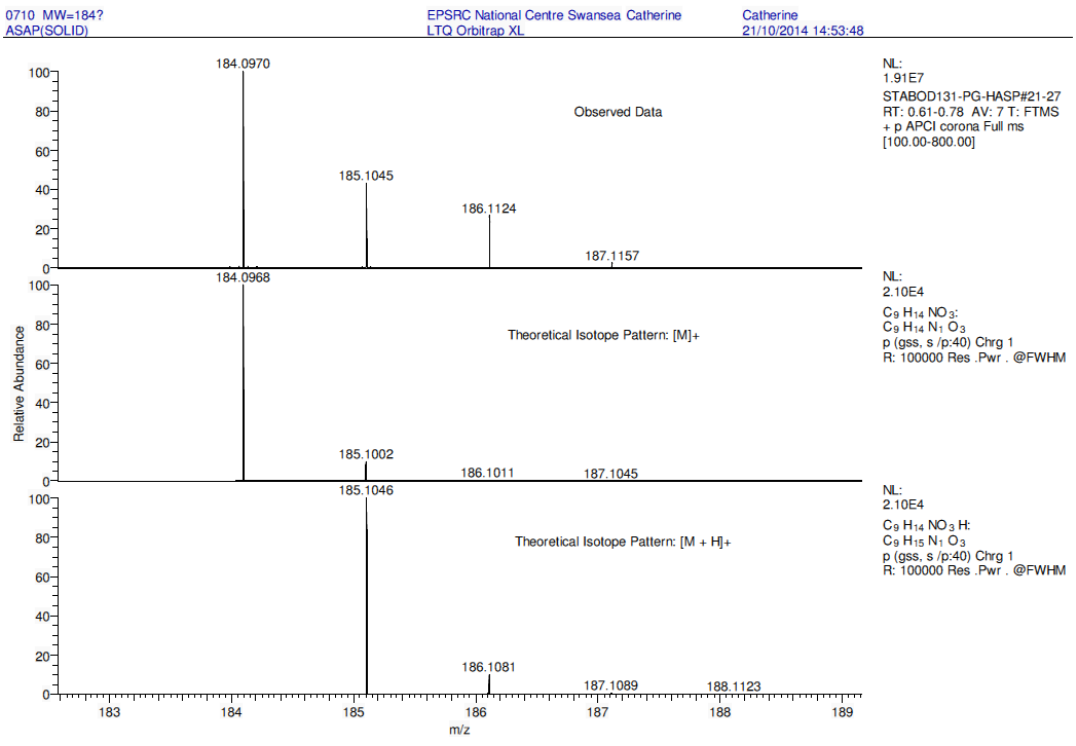


Figure S13 Mass spectrum of **6**.

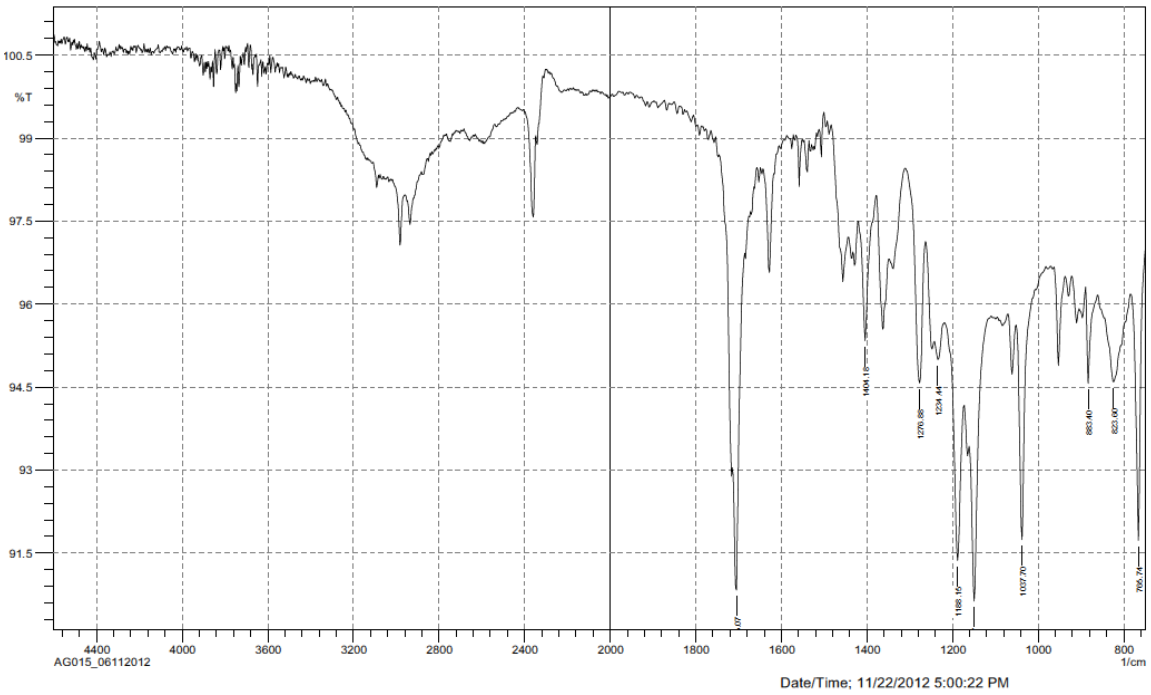


Figure S14 IR spectrum of **6**.

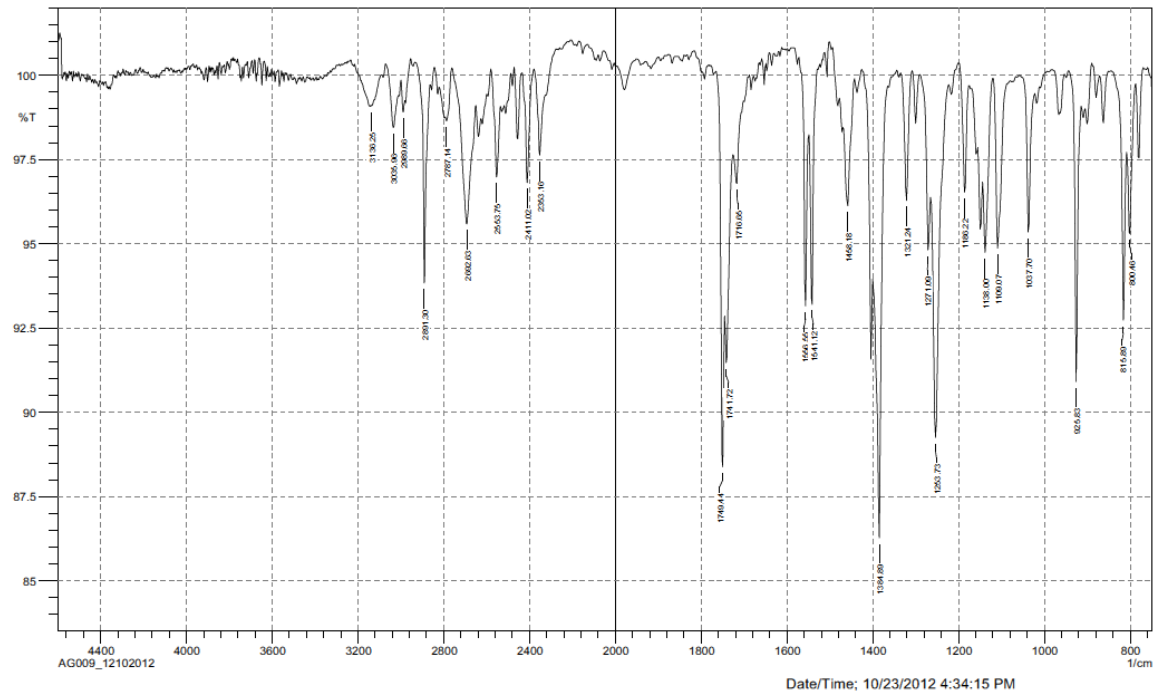


Figure S15 IR spectrum of the first product of reaction from **7** to **8**.

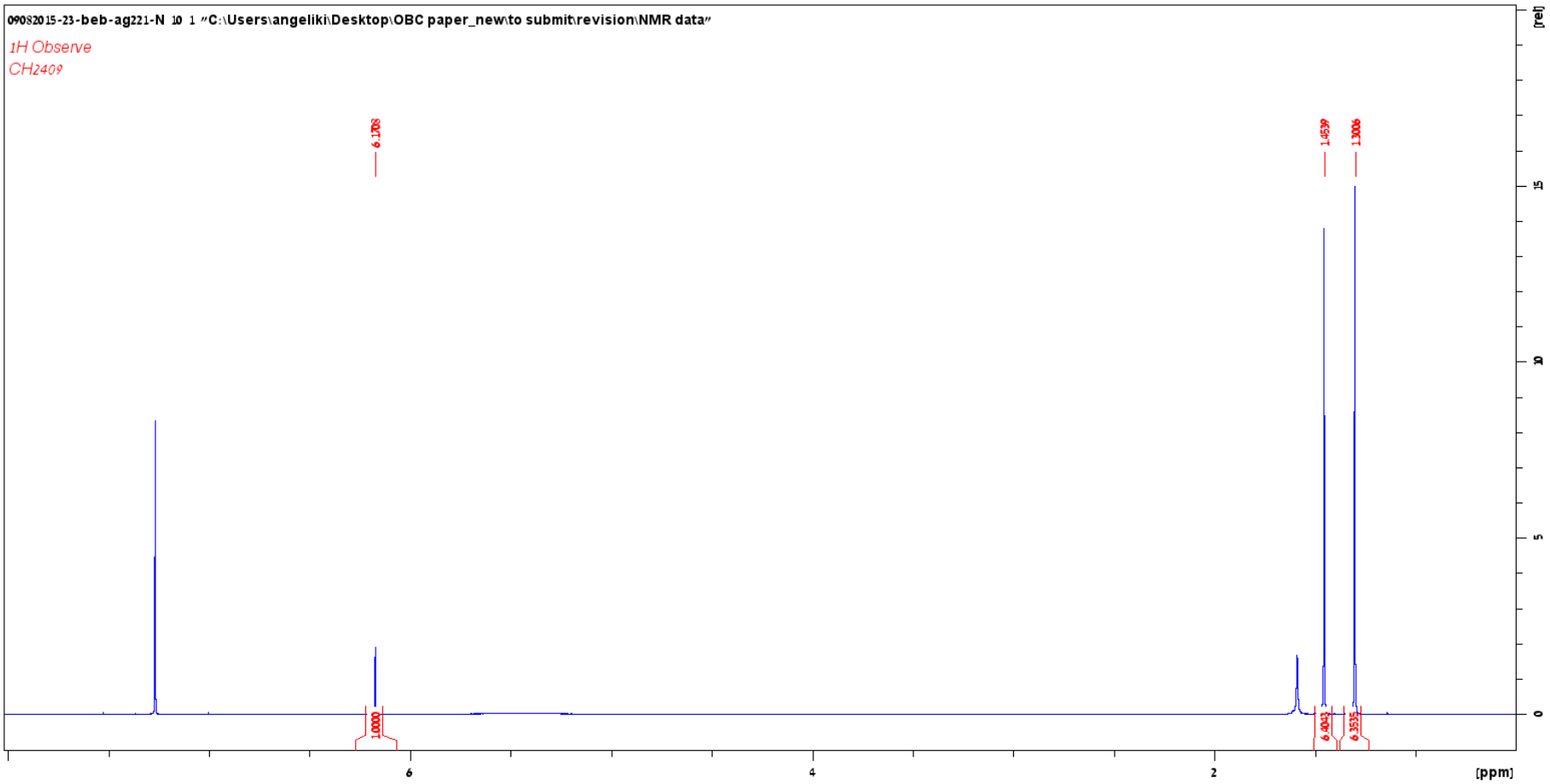


Figure S16 ^{1}H NMR spectrum of **8**.

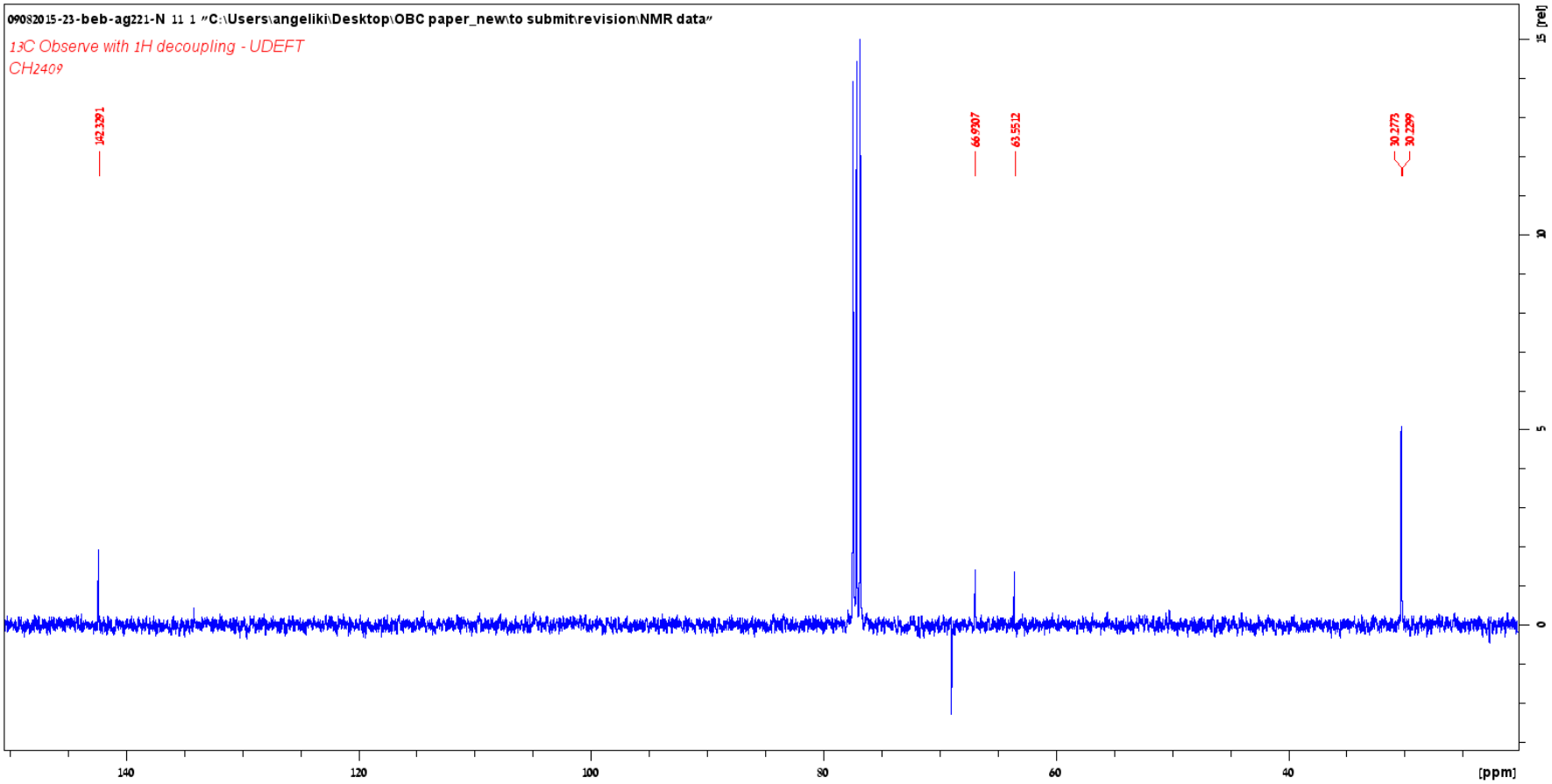


Figure S17 ^{13}C NMR with ^{1}H decoupling spectrum of **8**.

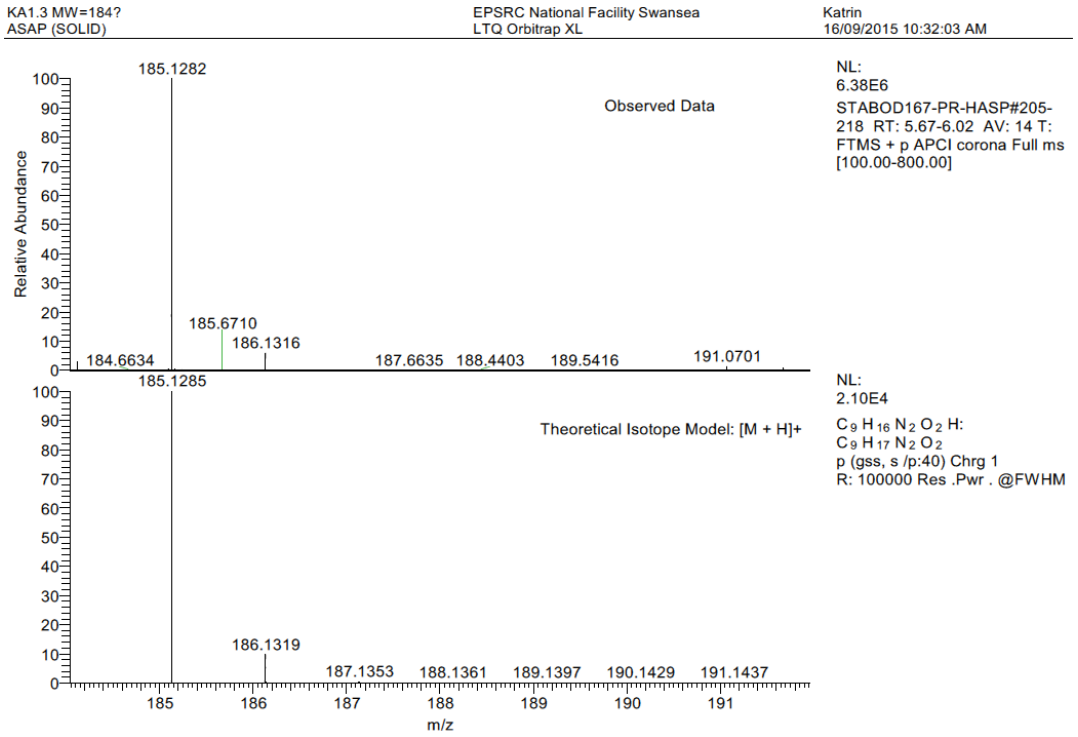


Figure S18 Mass spectrum of **9**.

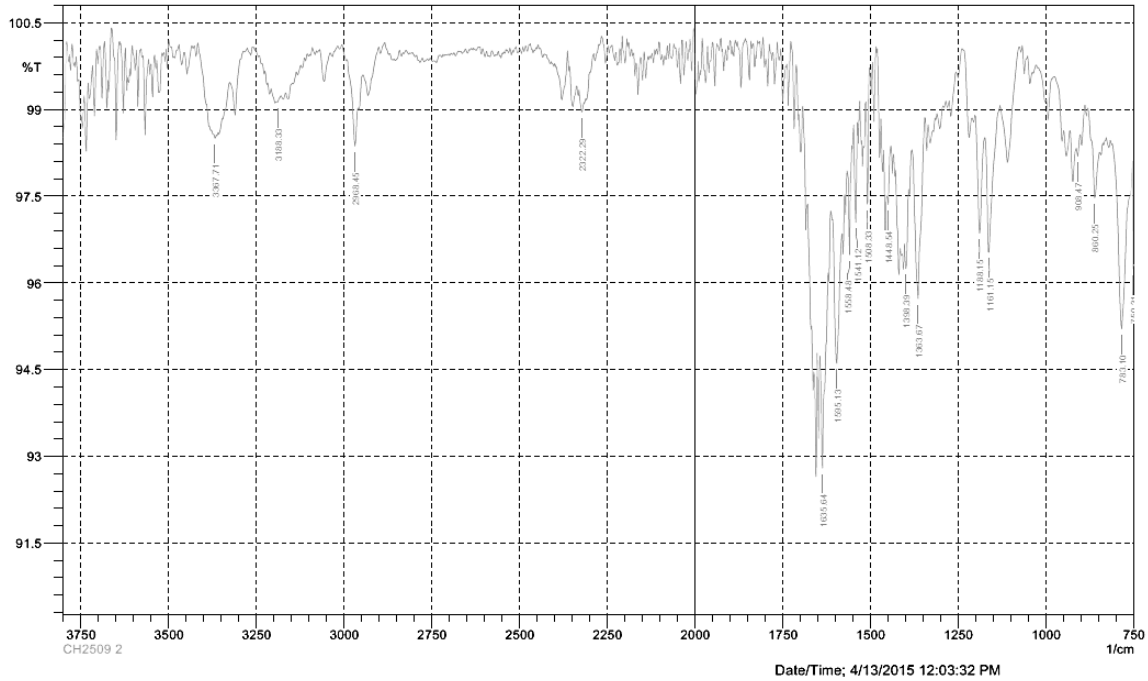


Figure S19 IR spectrum of **9**.

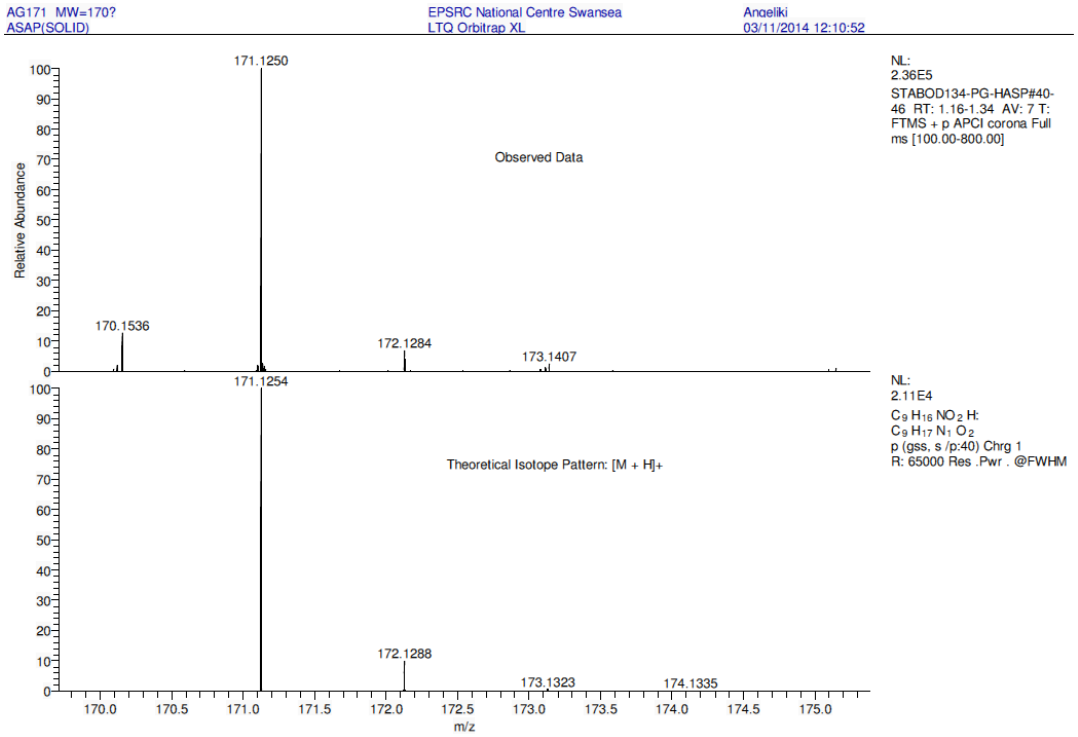


Figure S20 Mass spectrum of **10**.

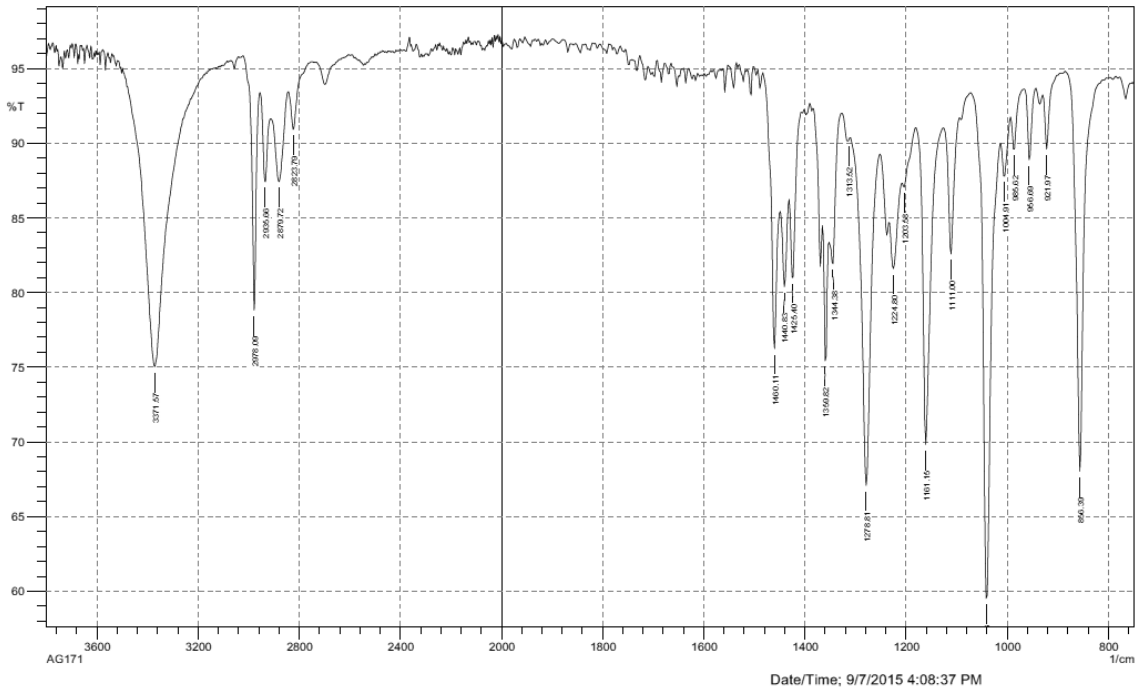


Figure S21 IR spectrum of **10**.

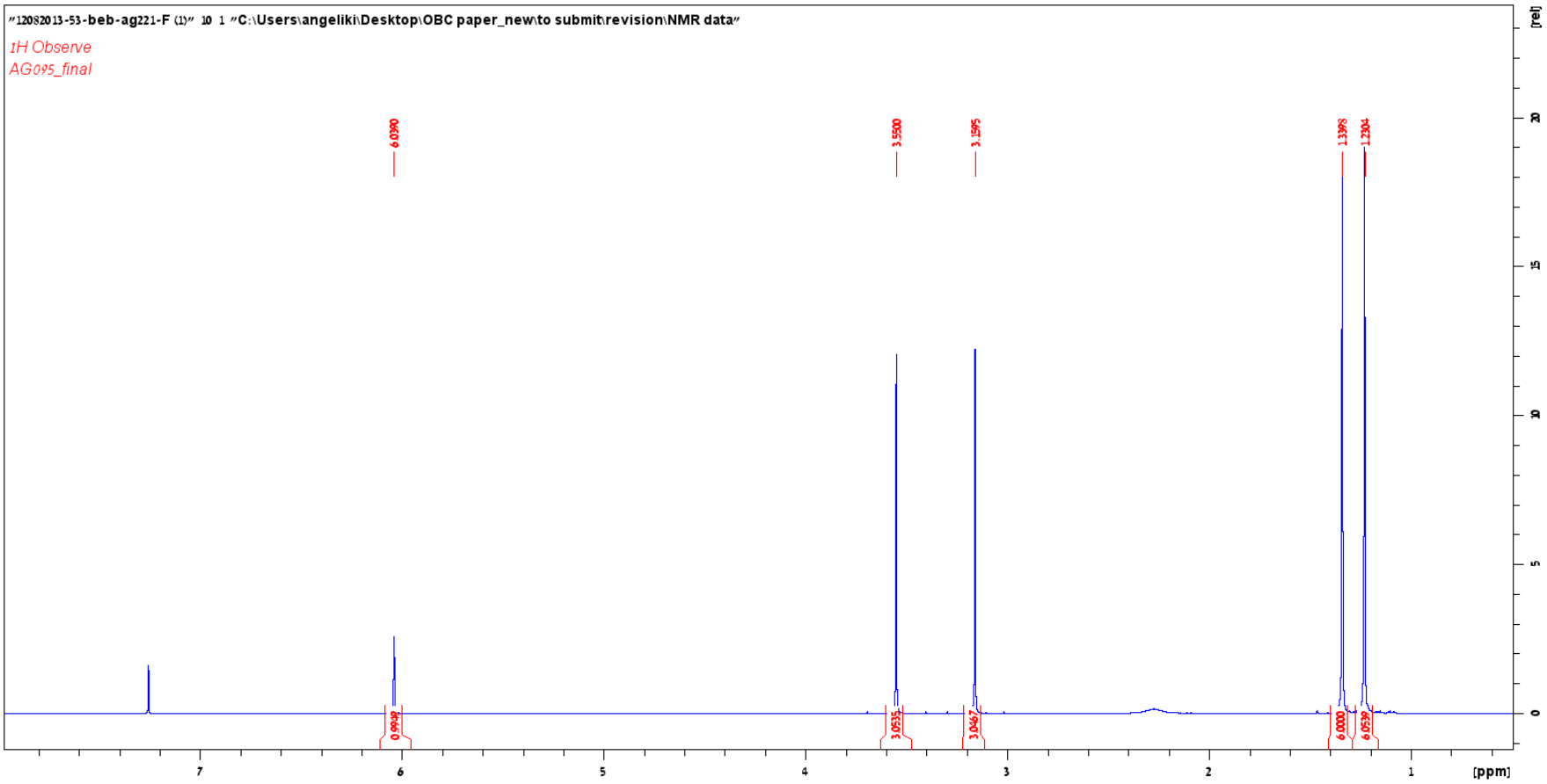


Figure S22 ^{1}H NMR spectrum of **11**.

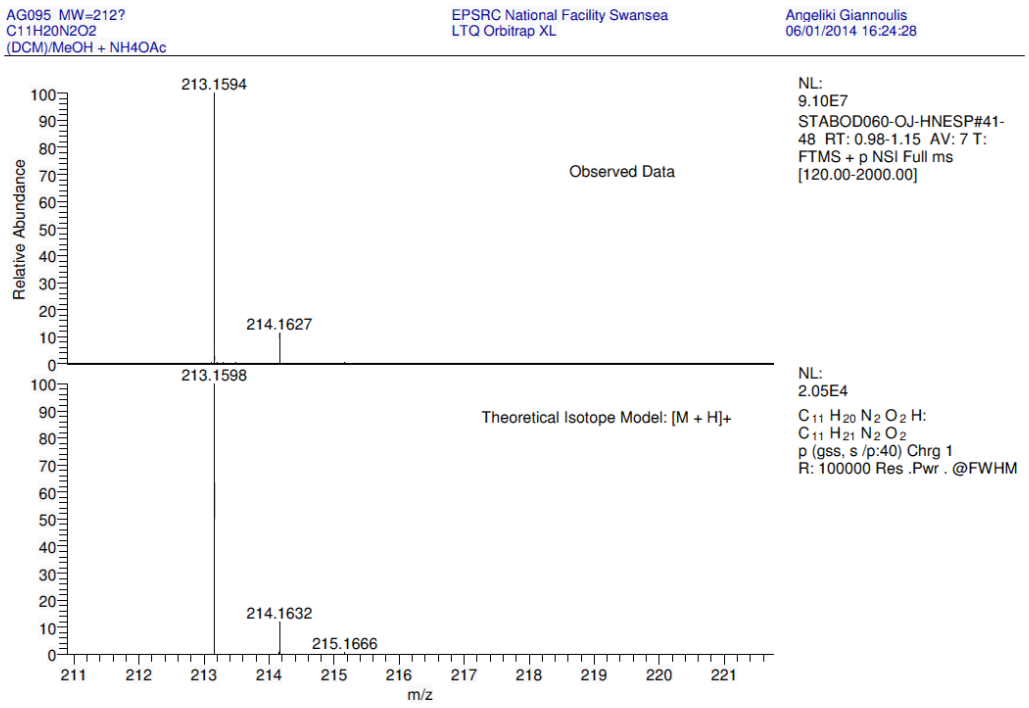


Figure S23 Mass spectrum of **11**.

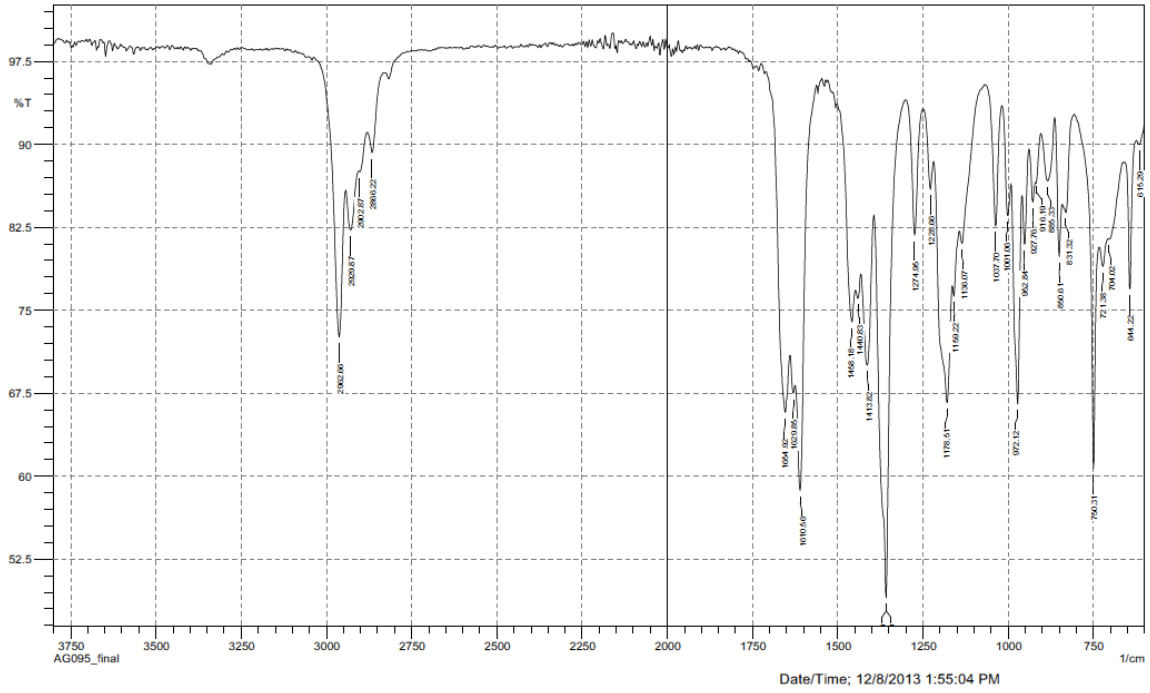


Figure S24 IR spectrum of **11**.

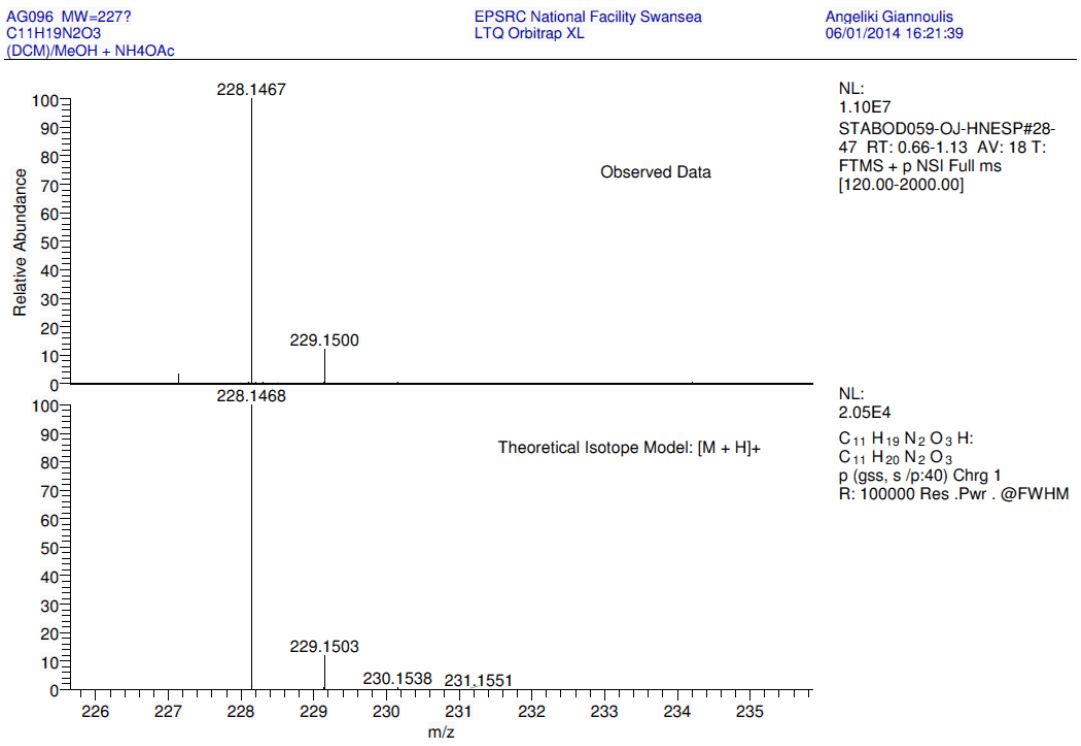


Figure S25 Mass spectrum of **12.**

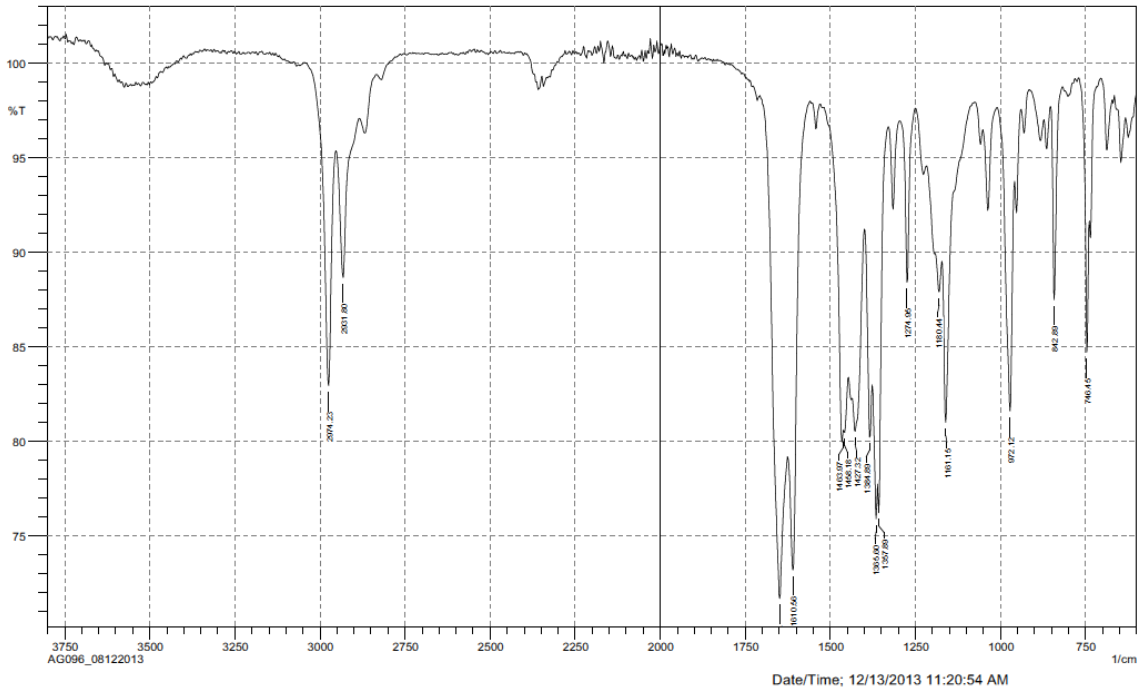


Figure S26 IR spectrum of **12**.

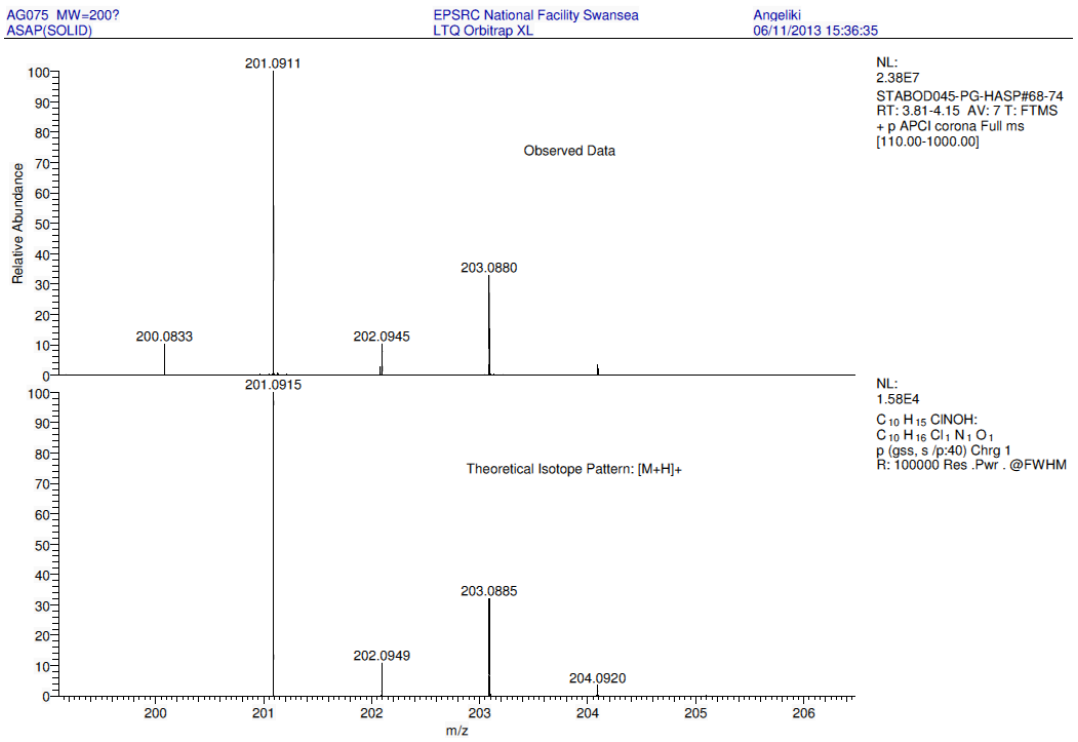


Figure S27 Mass spectrum of **14**.

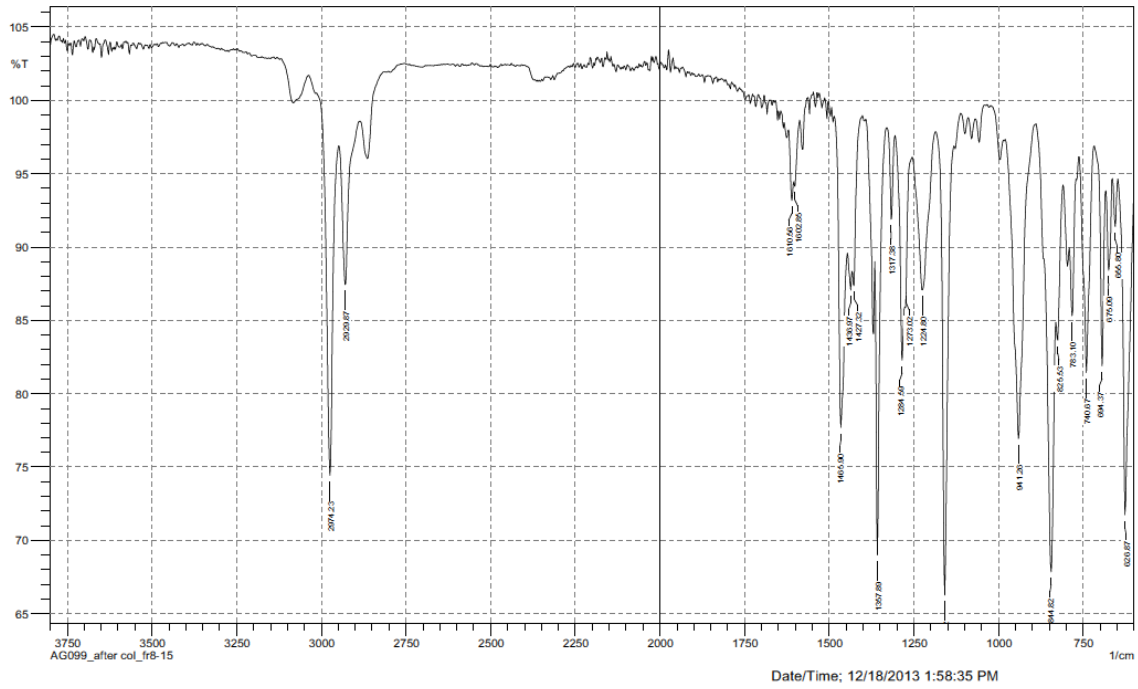


Figure S28 IR spectrum of **14**.

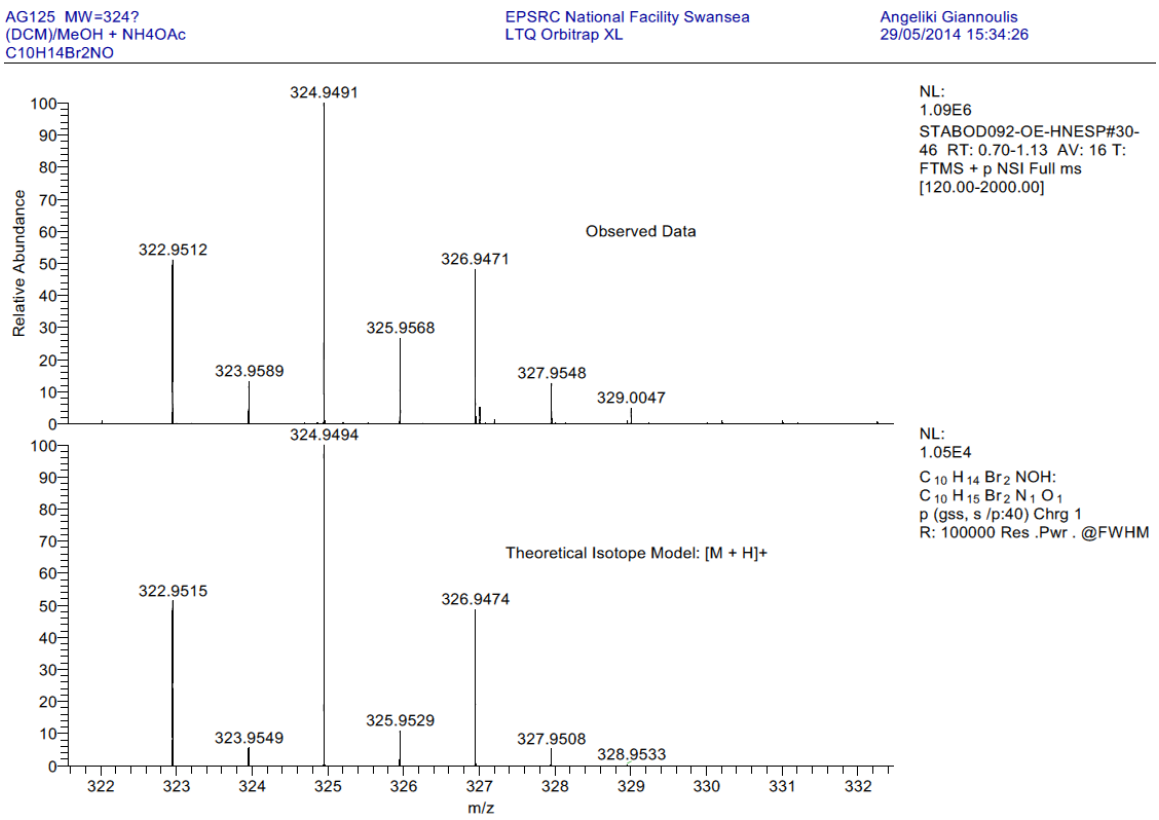


Figure S29 Mass spectrum of **15**.

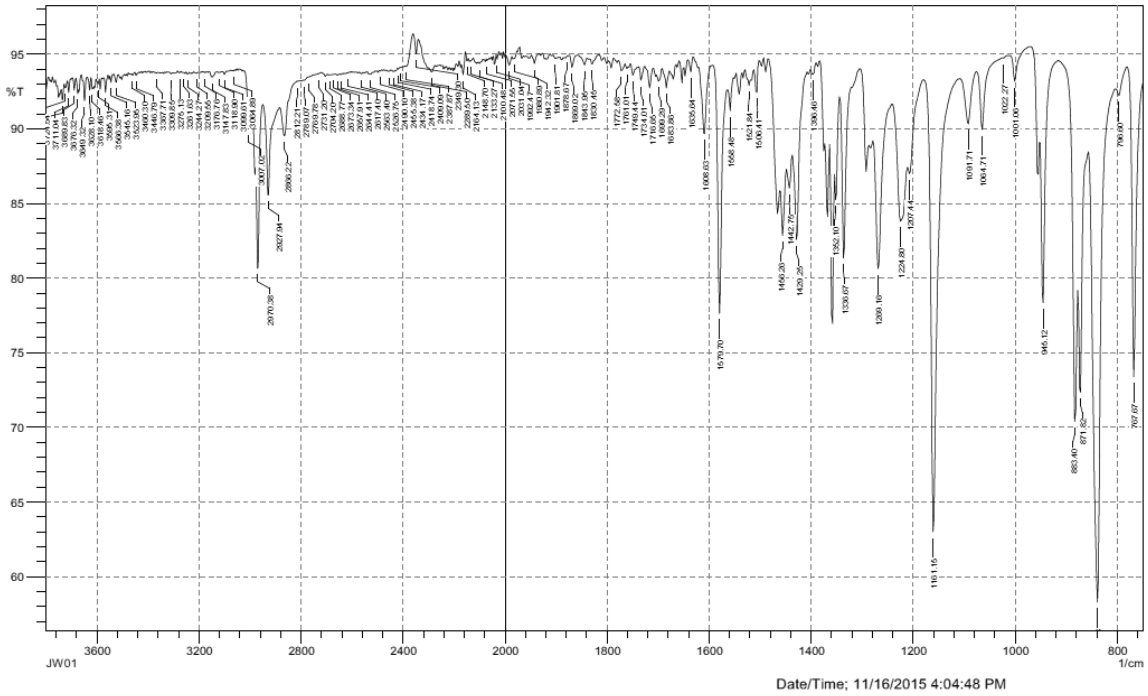


Figure S30 IR spectrum of **15**.

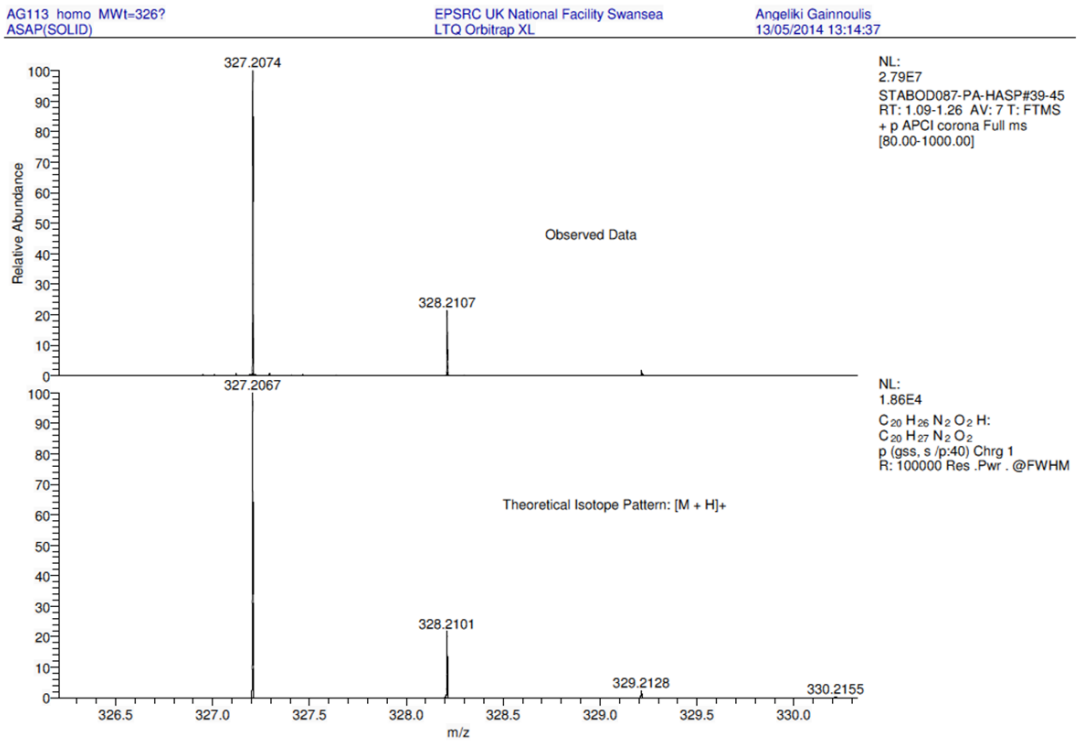


Figure S31 Mass spectrum of **20**.

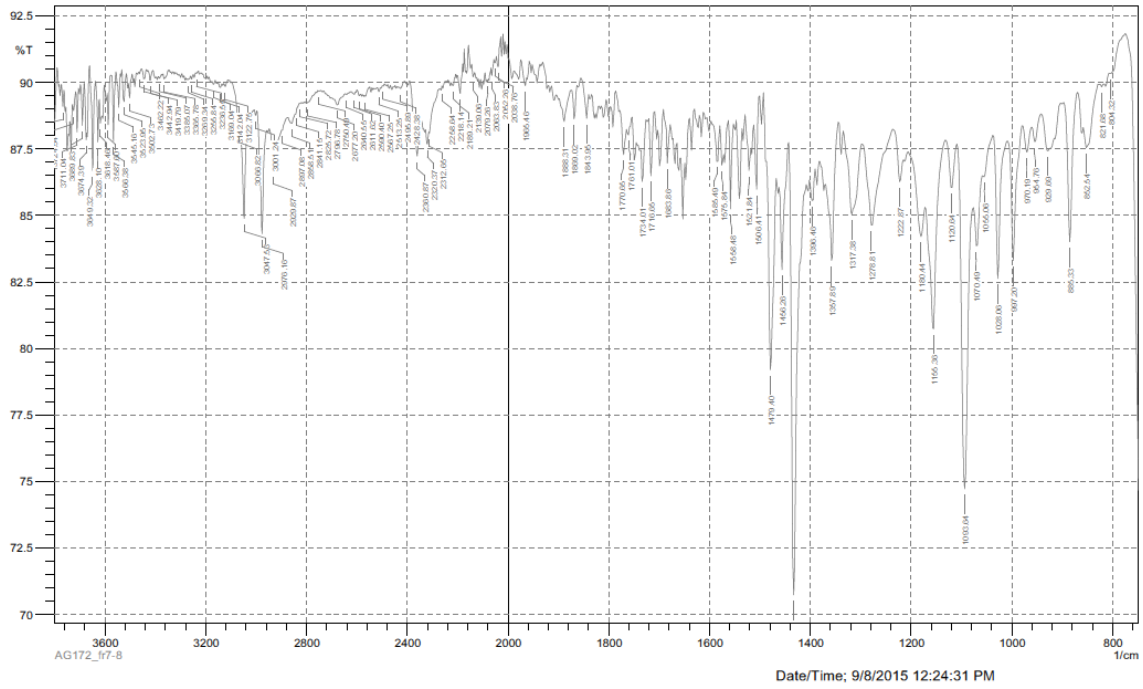
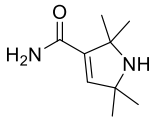


Figure S32 IR spectrum of **20**.

Experiment repeats

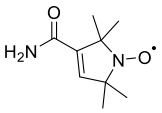
Compound **8:**



Run	ID	SM* (g/mmol)	NH_3 (mL/mmol)	Yield** (g/%)	Reaction time	Temperature
1	AG008	22.8/58.0	71/1286	7.5/**58**	2 h	rt
2	KA1.2	23.0/58.0	79/1431	5.1/38	2 h	rt

*SM refers to the intermediate compound from **7** to **8**
**The yield is with respect to the starting material (over two steps)

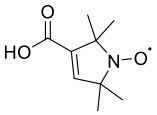
Compound **9**:



Run	ID	SM (g/mmol)	EDTA* (g/mmol)	$Na_2WO_4{\cdot}2H_2O$ (g/mmol)	H_2O_2 (mL/mmol)	Yield (g/%)	Reaction time	Temperature
1	AG011	7.5/45	0.42/1.4	0.4/1.27	8.3/268	1.8/22	5 min then 6 d	rt then 4 °C
2	KA1.3	5.0/30	0.3/0.9	0.3/0.85	5.5/178	4.0/**73**	5 min then 5 d	rt then 4 °C

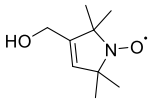
*For AG011 was used EDTA, while for KA1.3 $Na_2{\cdot}EDTA{\cdot}2H_2O$ was used

Compound **6 (TPC)**:

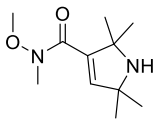


Run	ID	SM (g/mmol)	10% NaOH (mL/mmol)	Yield (g/%)	Reaction time	Temperature
1	AG015	1.78/9.7	45/112	0.7/39	2 h	reflux
2	KA1.4	4.0/22	100/249	2.1/**52**	2 h	reflux
3	JWSTEP3TPC	1.5/8.2	75	0.4/28	2 h	reflux

Compound **10**:



Run	ID	SM (g/mmol)	Red-Al® (mL/mmol)	Yield (g/%)	Reaction time	Temperature
1	AG171	1.0/5.4	6/19.8	0.35/40	1.5 h	55 °C
2	KA2_1	2.0/10.8	12/39	1.6/**87**	1.5 h	55 °C

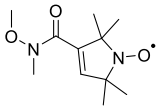


Compound **11**:

Run	ID	SM* (g/mmol)	Me(MeO)NH.HCl (g/mmol)	Yield** (g/%)	Reaction time	Temperature
1	AG061	10/25.0	3.0/30	3.8/71	overnight +6 h	rt+50 °C
2	AG064	13.2/33.5	3.9/40	3.1/44	48 h+6 h	rt+50 °C
3	AG095	24.7/62.8	7.3/75.4	6.7/50	48 h+6 h	rt+50 °C
4	AG119	37.1/94.0	11.0/113.0	5.6/28	overnight +6 h	rt+50 °C
5	AG122	29.8/75.8	8.8/90.1	4.7/29	5 d	rt
6	AG163	33.5/85.2	9.9/101.6	13.0/**65**	7 d	rt

*SM refers to the intermediate compound from **7** to **8**

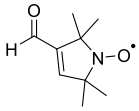
**The yield is with respect to the starting material (over two steps)



Compound **12**:

Run	ID	SM (g/mmol)	EDTA* (g/mmol)	$Na_2WO_4 \cdot 2H_2O$ (g/mmol)	H_2O_2 (mL/mmol)	Yield (g/%)	Reaction time	Temperature
1	AG065	3.1/14.8	0.14/0.5	0.14/0.4	2.75/91	2.5/**75**	8 min then 48 h	rt then rt
2	AG096	6.7/31.6	0.33/1.0	0.30/0.9	6.3/211	3.9/55	8 min then 5 d	rt then rt
3	AG120	5.6/26.3	0.28/0.8	0.25/0.75	5.2/210	3.6/60	8 min then 8 d	rt then rt
4	AG123	4.7/22.3	0.24/0.7	0.21/0.64	4.4/147	3.3/65	8 min then 10 d	rt then rt
5	AG164	13.1/62	0.66/2.0	0.59/1.79	12/400	4.8/34	9 min then 8 d	rt then rt

*For AG065 EDTA was used, while for AG096, AG120, AG123 and AG164 $Na_2 \cdot EDTA \cdot 2H_2O$ was used.

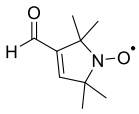


Compound **5** from **12**:

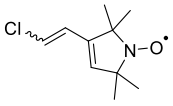
Run	ID	SM (g/mmol)	DIBAL* (mL/mmol)	Yield (g/%)	Reaction time**	Temperature
1	AG066	2.5/11.0	11.3/13.6	1.4/75	50 min	−78 °C
2	AG098	3.9/17.4	18.0/21.6	2.8/**95**	45 min	−78 °C
3	AG124	3.6/15.9	19.6/19.6	1.2/47	35 min	−78 °C
4	AG147	3.3/14.6	18.0/18.0	0.3/12	35 min	−78 °C
5	AG165	4.8/20.9	21.0/25.2	2.4/69	35 min	−78 °C

* For AG066, AG098 and AG165 the concentration of DIBAL was 1.2 M, while for AG124, AG147 1.0 M

** Refers to DIBAL addition time and further stirring

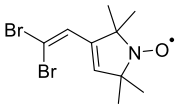
Compound **5** from **10**: 

Run	ID	SM (g/mmol)	$C_2O_2Cl_2$ (mL/mmol)	DMSO (mL/mmol)	Yield (g/%)	Reaction time	Temperature
1	JWTPAS2	0.4/2.4	0.25/2.6	0.4/5.6	0.2/**56**	15 min	−65 °C
2	KA2.2	1.6/9.4	0.93/10.3	1.6/22.4	0.7/44	15 min	-60 (to -53) °C

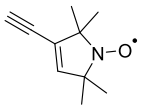
Compound **14**: 

Run	ID	SM (g/mmol)	$ClCH_2P(Cl)(C_6H_5)_3$ (g/mmol)	*n*-BuLi* (mL/mmol)	Yield (g/%)	Reaction time	Temperature
1	AG075	1.4/8.3	11.5/33.0	11.1/29.6	1.6/**98**	30 min	0 °C
2	AG099	1.9/11.4	15.7/45.2	18.2/41.7	0.3/15	45 min	0 °C
3	AG102	1.0/5.7	8.0/23.2	12.4/21	0.1/11	40 min	0 °C
4	AG166	2.4/14.5	5.5/15.9	9.5/16.1	3.0/96	2 h then 1 h	rt then 50 °C
5	KA5.1	0.25/1.5	0.6/1.6	1.0/1.6	0.15/49	2 h then 1 h	rt then 50 °C

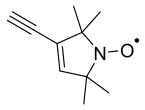
* *n*-BuLi in hexanes in 2.5 M concentation for AG075, 2.3 M for AG099, 1.7 M for AG102 and AG166 determined after titration with diphenylacetic acid

Compound **15**: 

Run	ID	SM (g/mmol)	CBr_4 (g/mmol)	PPh_3 (g/mmol)	Yield (g/%)	Reaction time	Temperature
1	AG125	1.2/7.0	4.6/14.0	7.3/28.0	1.5/**66**	20 min then rt	0 °C then 1 h
2	JW01	0.07/0.4	0.3/0.8	0.4/1.7	0.03/6	15 min	0 °C
3	KA7.1b	0.25/1.5	1.0/3.0	1.6/6.0	0.06/12	15 min	0 °C

Compound **4 (TPA)** from **14**: 

Run	ID	SM (g/mmol)	KO^{t}Bu (g/mmol)	Yield (g/%)	Reaction time	Temperature
1	AG100	0.3/1.6	0.5/4.1	0.06/22	55 °C	2 h
2	AG167	1.0/5.0	1.2/10.9	0.04/5	55 °C	2 h
3	AG169	0.3/1.6	0.5/4.1	0.03/11	55 °C	2 h
4	KA6.1	0.15/0.7	0.5/4.1	0.03/**26**	55 °C	2 h

Compound **4 (TPA)** from **15**: 

Run	ID	SM (g/mmol)	CBr_4 (g/mmol)	Yield (g/%)	Reaction time	Temperature
1	AG126	0.47/1.5	1.5/2.9	0.02/**10**	45 min then 3 h	-78 °C then rt