Supporting information

for

A novel method of alkoxyamines homolysis activation via photochemical rearrangement

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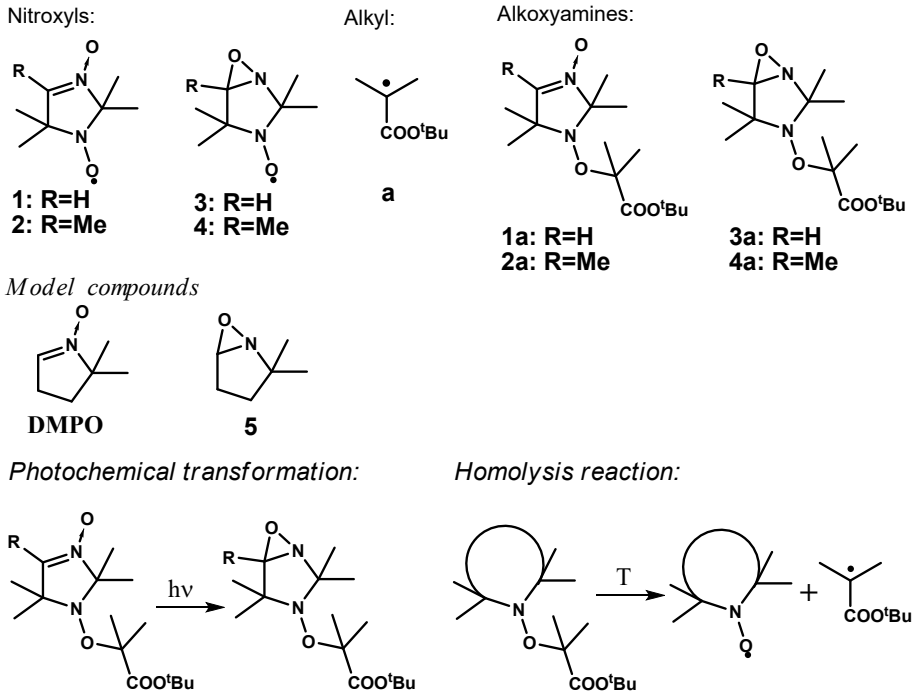


Scheme 1SI – Compounds and reactions under study.

SECTION 1. INTERACTION BETWEEN 5 AND THIOPHENOL.

Oxaziridines are strong oxidants, which are readily to react with wide range of reducing agents, e.g. with thiols used as radical scavengers. In the figure 1SI one can see some changes in the aromatic part of the spectrum, as well as a decrease in the intensity of the signals of model oxaziridine **5** in the presence of thiophenol, which indicates chemical transformations involving thiophenol. It means the impossibility to use thiophenol as radical scavenger for accurate measurement of alkoxyamines **3a**/**4a** homolysis rate konstant k_d.

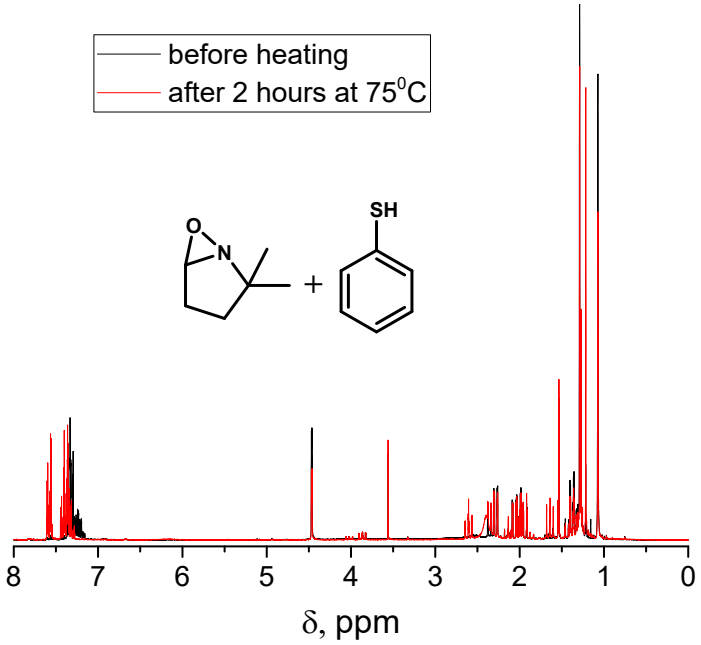


Figure 1SI – ^{1}H NMR spectra of a mixture of thiophenol and model oxaziridine before and after heating.

SECTION 2. QUANTUM YIELD OF STUDIED PHOTOCHEMICAL PROCESSES.

The experiment was set up in such a way that the laser spot almost completely covered the area of the frontal layer of the sample. At the same time, a high concentration of the irradiated compound causes a linear conversion with time at the initial stages of the experiment. Based on the appearance of the UV spectra of compounds **1a** and **2a** (Figure 2SI), it can be seen that at a wavelength of 266 nm, the absorption coefficient ε is less than 1000 l/mol/cm. This means that already at concentrations of the order of 1 mM, with an optical path length of 1 cm, 99% of the light is absorbed. In our experiments, the concentration was much higher (90-180 mM). Thus, the number of molecules transformed under the action of light is N = φN0 = αt, where φ is the quantum yield, and α is the slope of the function N(t), which is linear at short irradiation times. Since the signals in the NMR spectra (Figure 3SI) are proportional to the concentration, knowing the initial concentration and irradiation power, one can estimate the quantum yield. The energy of absorbed photons W is equal to:

$$W = I \times t \tag{1}$$

where I is the radiation power (J/s) and t is the time. The energy of one quantum of light is equal to:

$$E = \frac{hc}{\lambda} \tag{2}$$

Then the number of absorbed photons is:

$$N_0 = \frac{W}{E} = \frac{I\lambda}{hc}t \tag{3}$$

In this way:

$$\varphi = \frac{\alpha hc}{I\lambda} \tag{4}$$

Let's move from the number of molecules to concentration:

$$\mathrm{C} = \frac{N}{N_A V} = \frac{\varphi N_0}{N_A V} = \frac{\varphi I\lambda}{hcN_A V}t \tag{5}$$

Using expression 6, the quantum yield of the photochemical rearrangement of alkoxyamines **1a** and **2a** was estimated, in both cases the obtained value was approximately 0.4.

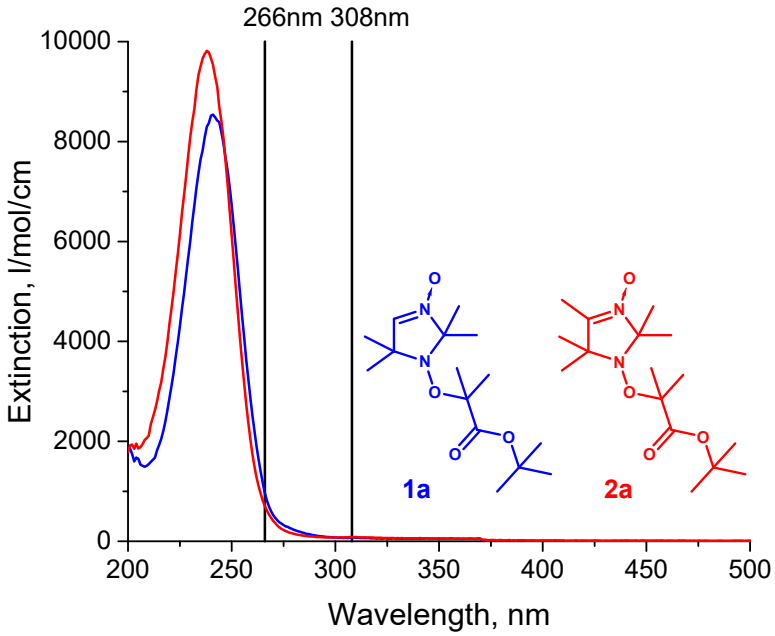


*Figure 2SI – UV-vis spectra of alkoxyamines **1a** and **2a**.*

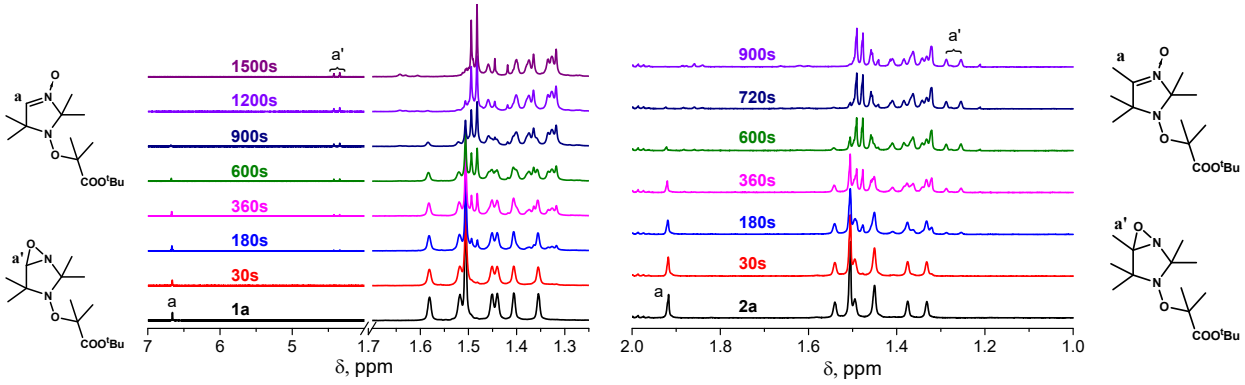
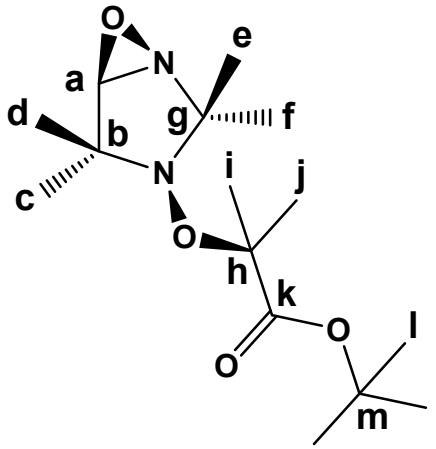
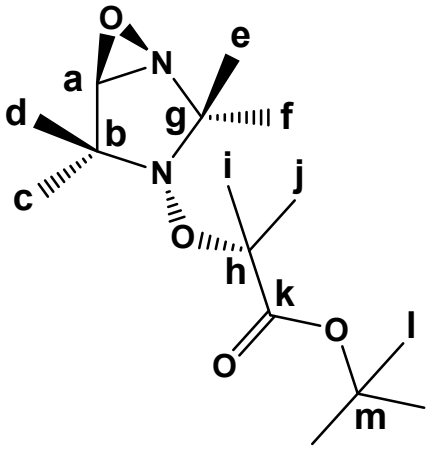


*Figure 3SI – Evolution of ^{1}H NMR spectra of alkoxyamines **1a** (left) and **2a** (right) during irradiation using Nd:YAG laser. C(**1a**) = 0.18 M, C(**2a**) = 0.09 M, λ = 266 nm, l = 1 cm, W = 100 mW, v = 10 Hz.*

SECTION 3. NMR SPECTRA OF STUDIED OXAZIRIDINE-CONTAINING COMPOUNDS.



3a (cis-isomer 1)



3a (trans-isomer 2)

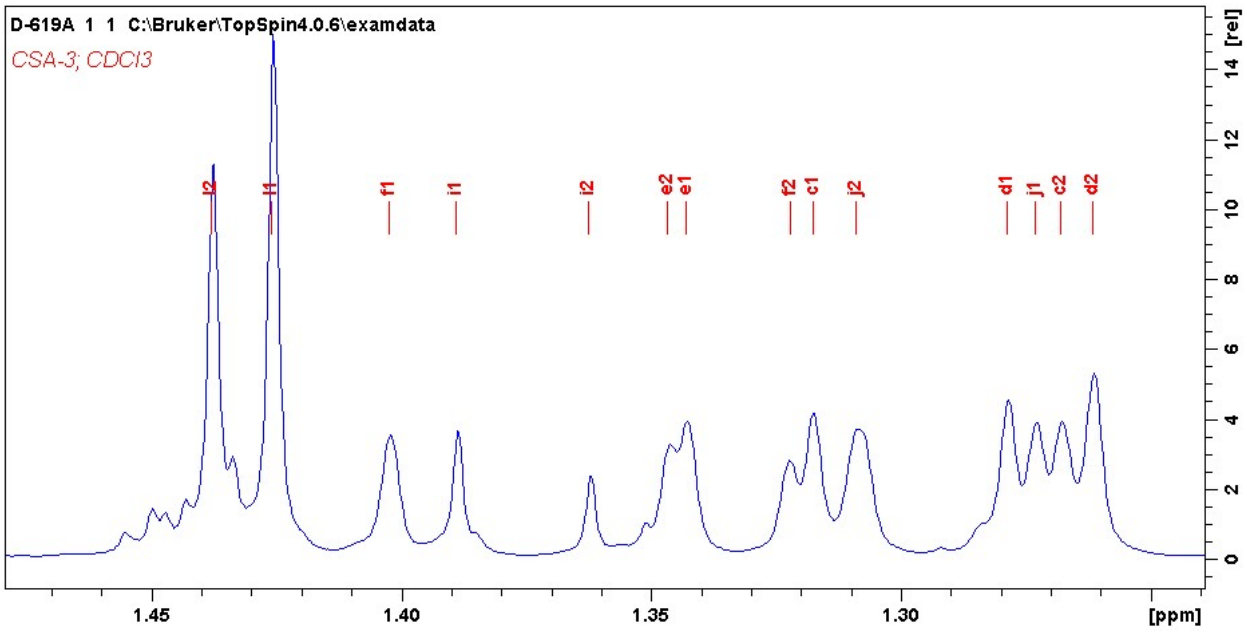


*Figure 4SI – ^{1}H NMR spectrum of alkoxyamine **3a**, aliphatic region.*

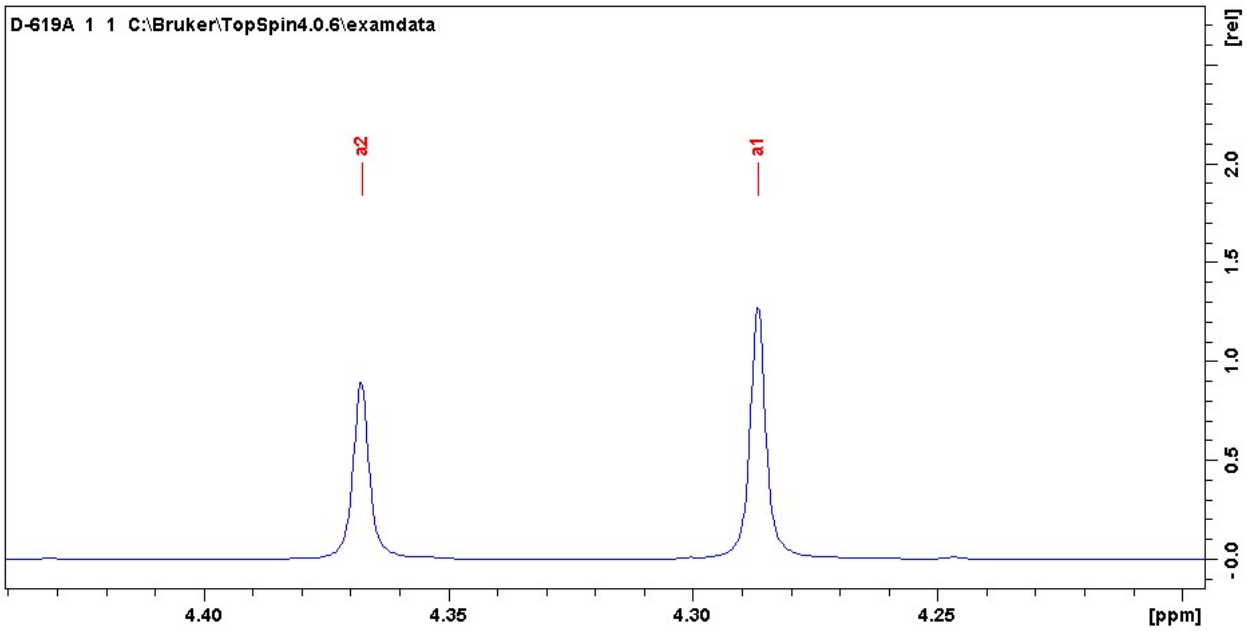


*Figure 5SI – ^{1}H NMR spectrum of alkoxyamine **3a**, mid-field region.*

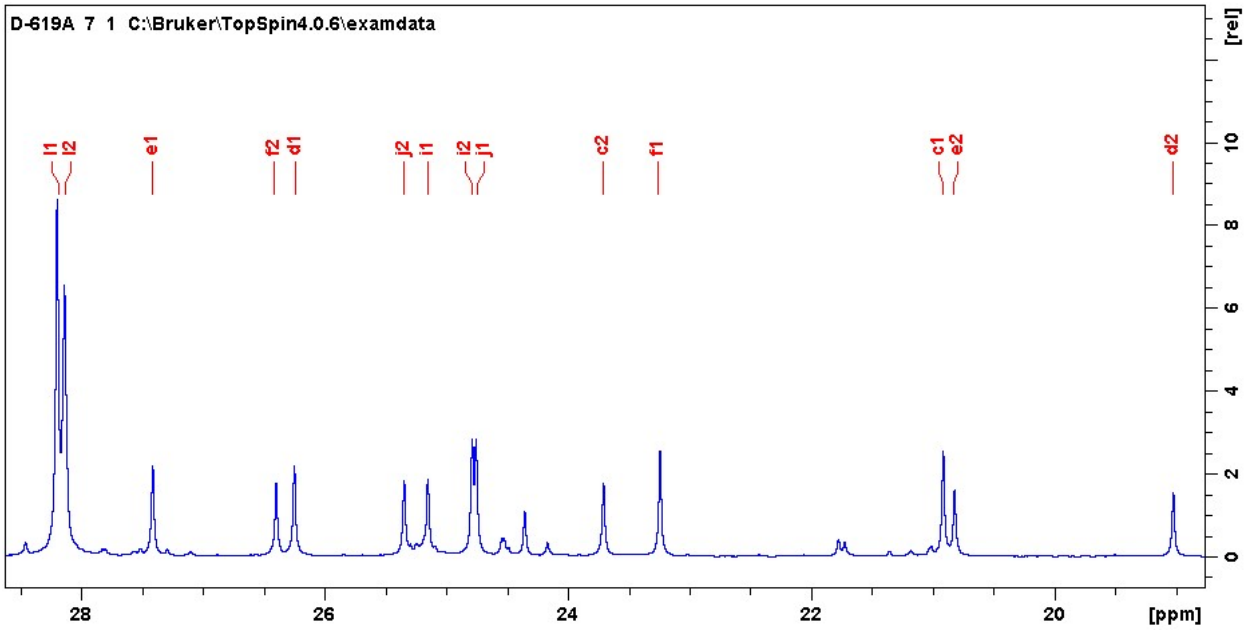


*Figure 6SI – ^{13}C NMR spectrum of alkoxyamine **3a**, aliphatic region.*

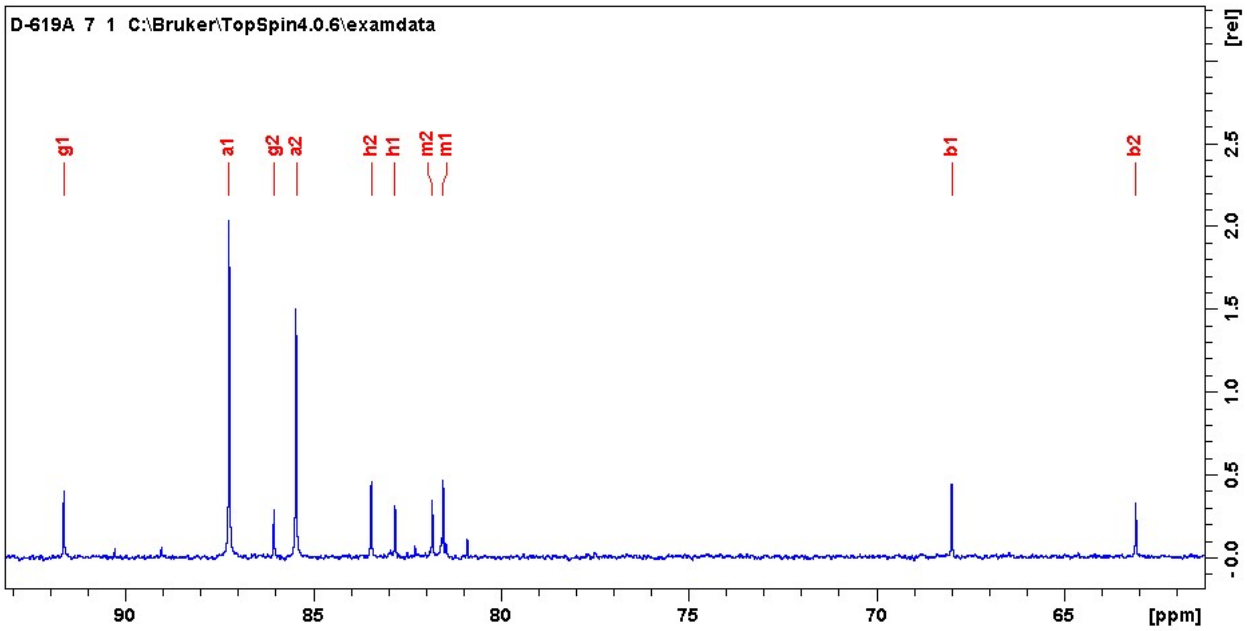


*Figure 7SI – ^{13}C NMR spectrum of alkoxyamine **3a**, mid-field region.*

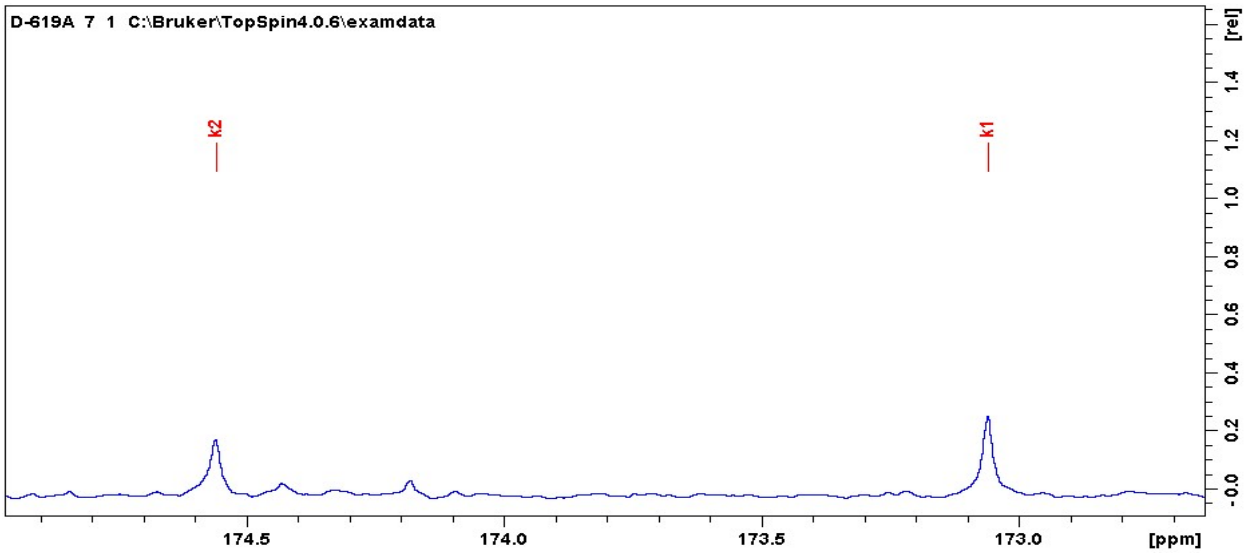


*Figure 8SI – ^{13}C NMR spectrum of alkoxyamine **3a**, region of location of carboxylic carbon signals.*

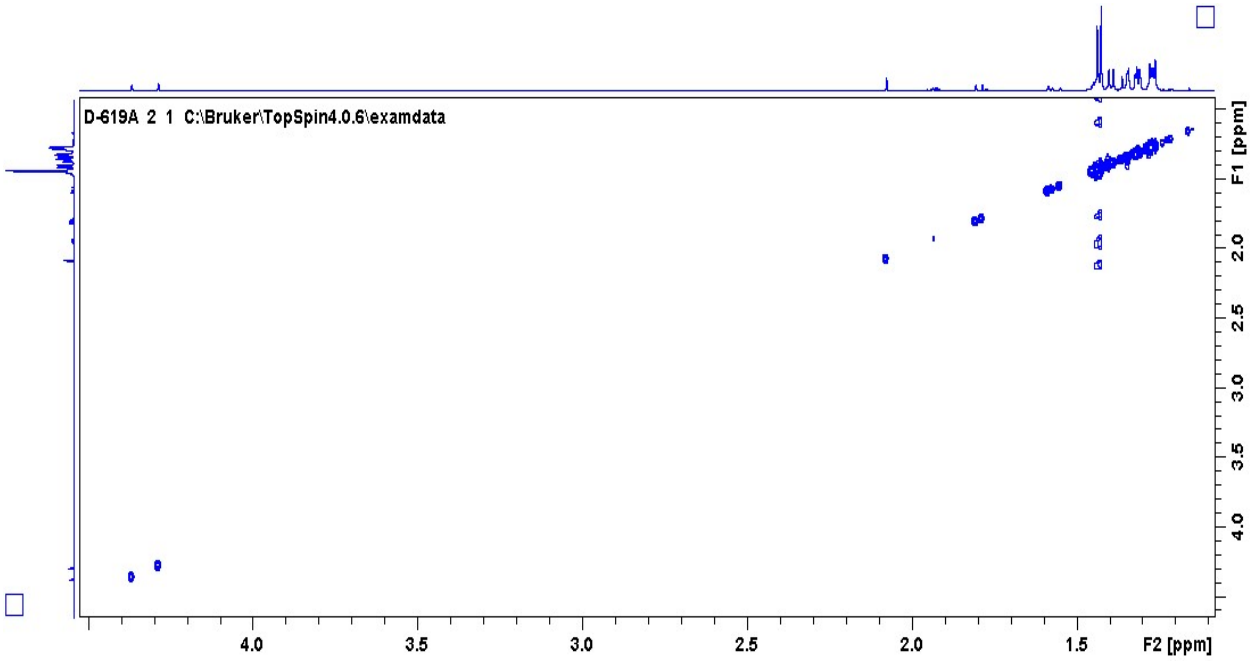


Figure 9SI – ^{1}H-^{1}H 2D NMR spectrum (COSY).

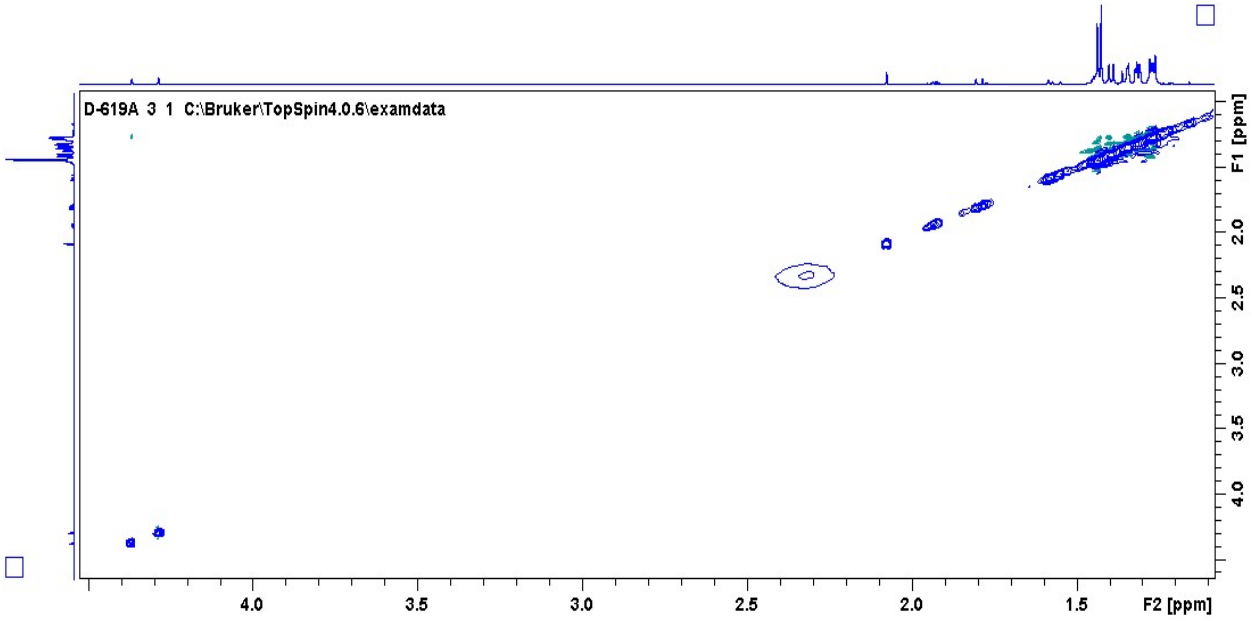


Figure 10SI – ^{1}H-^{1}H 2D NMR spectrum (NOESY).

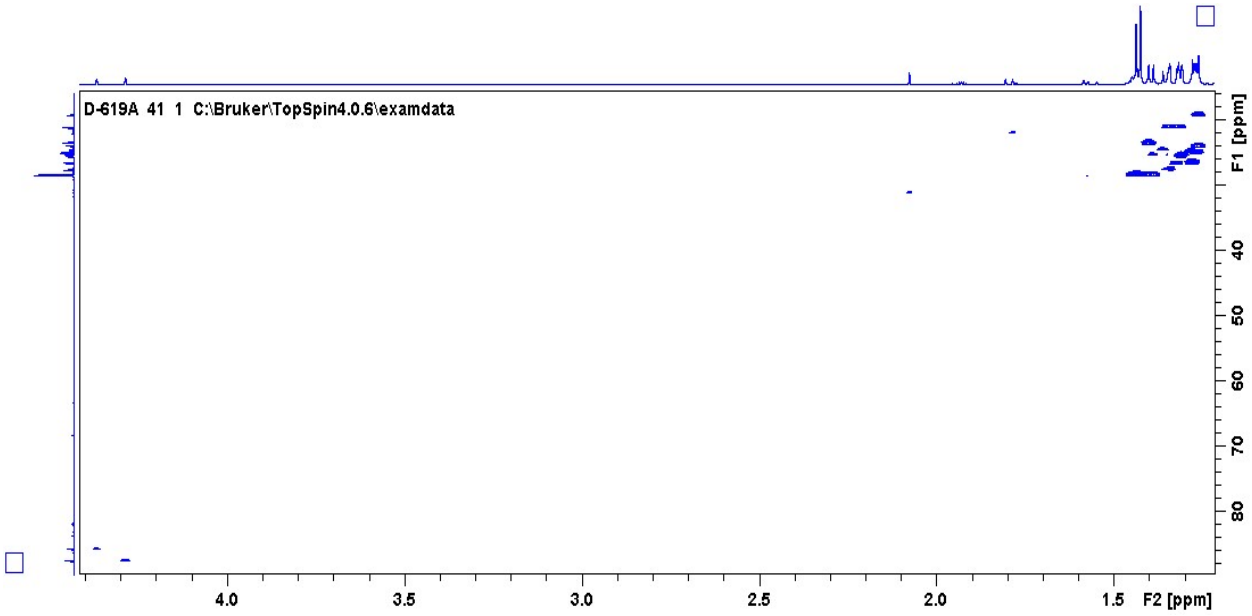


Figure 11SI – ^{1}H-^{13}C 2D NMR spectrum (HSQC).

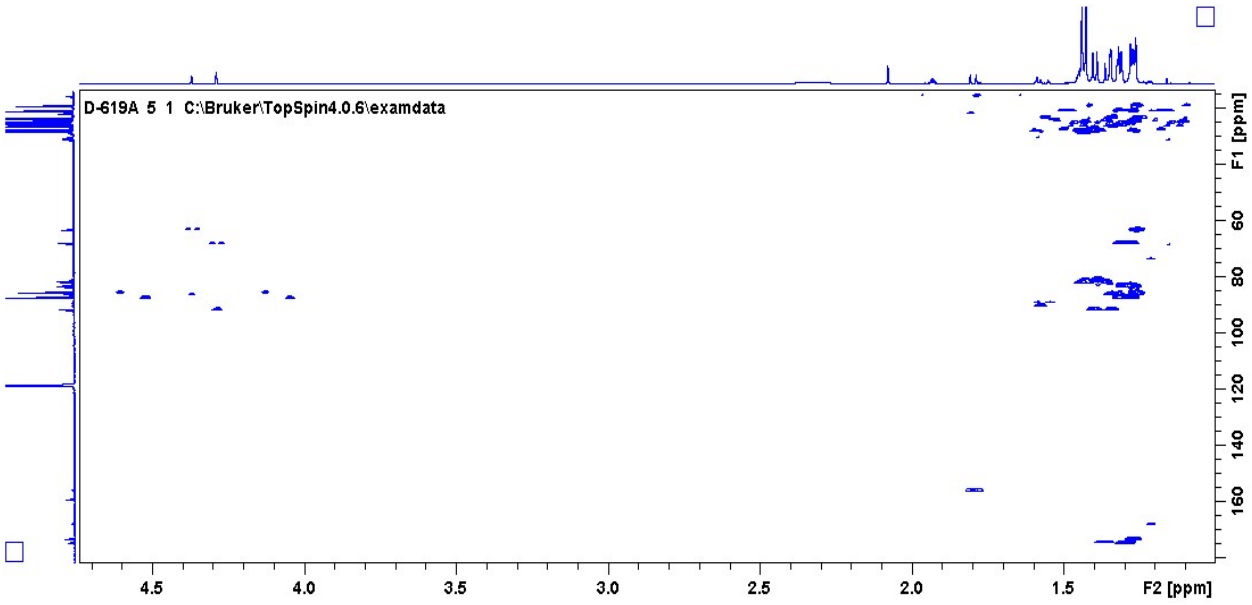


Figure 12SI – ^{1}H-^{13}C 2D NMR spectrum (HMBC).

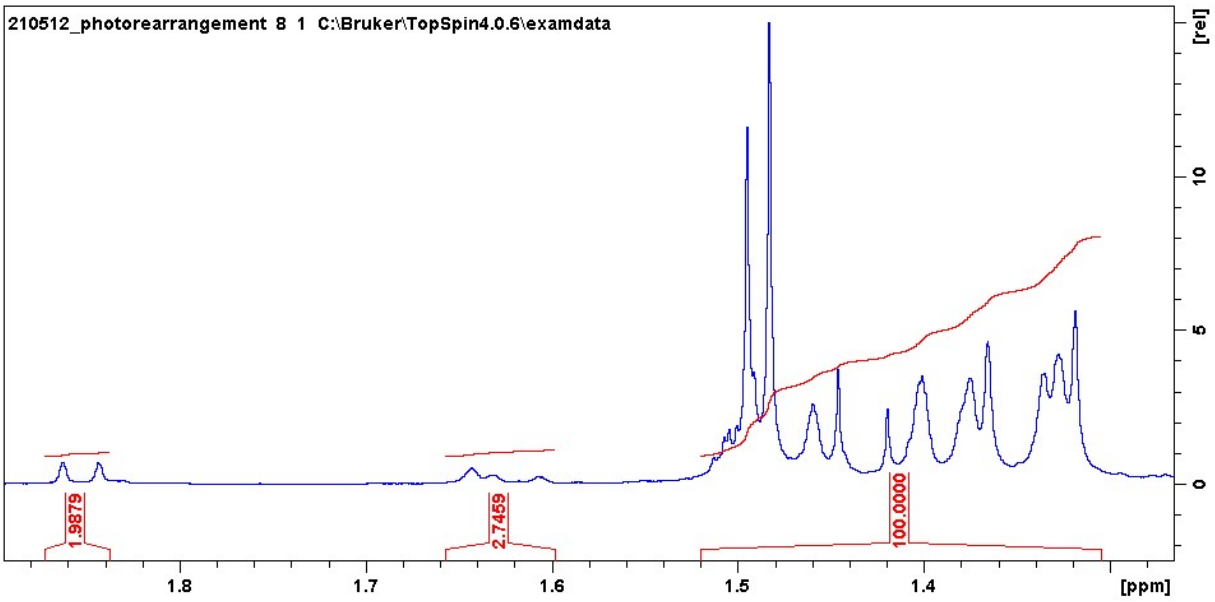
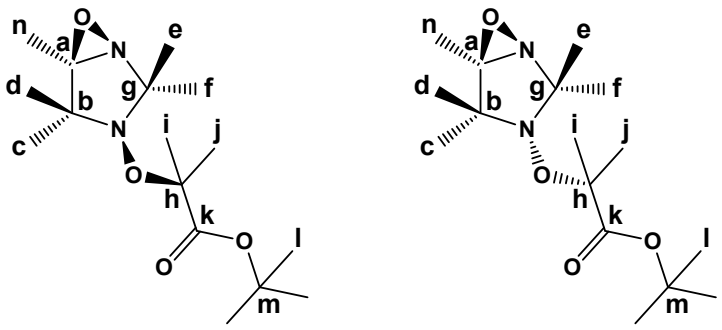


*Figure 13SI – The total integral of the signals of the alkoxyamine **3a** (on the right), as well as the integrals of the signals of the products of secondary photolysis (on the left and in the middle).*



4a (cis-isomer 1) **4a** (trans-isomer 2)

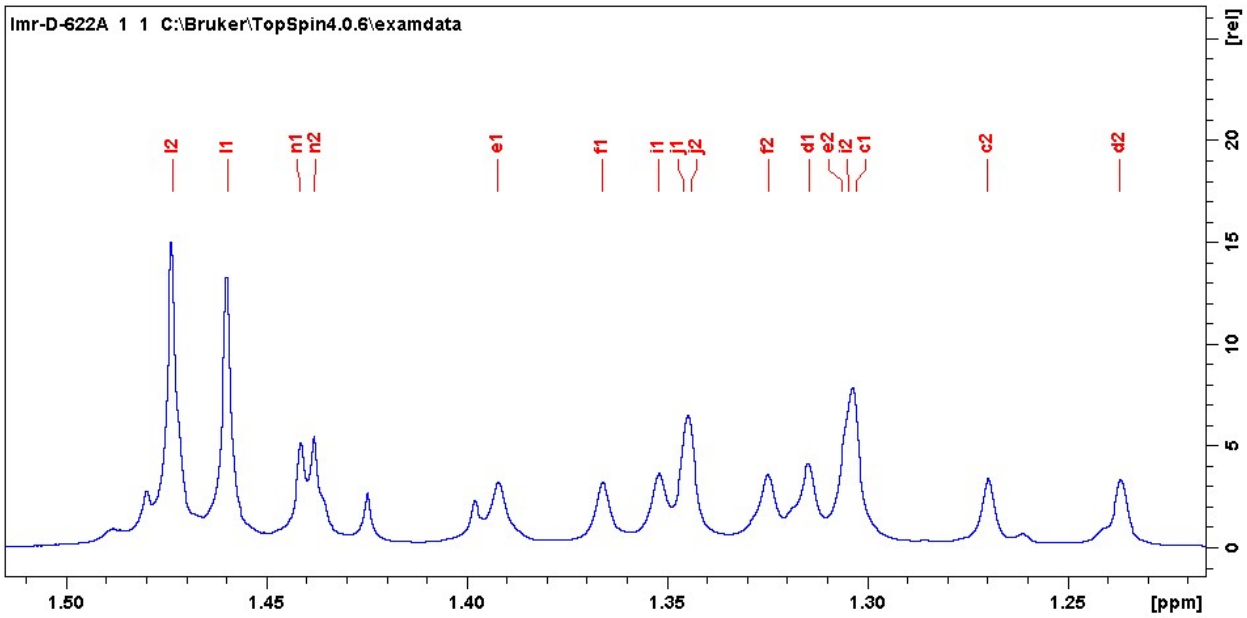


*Figure 14SI – [1]H NMR spectrum of alkoxyamine **4a**.*

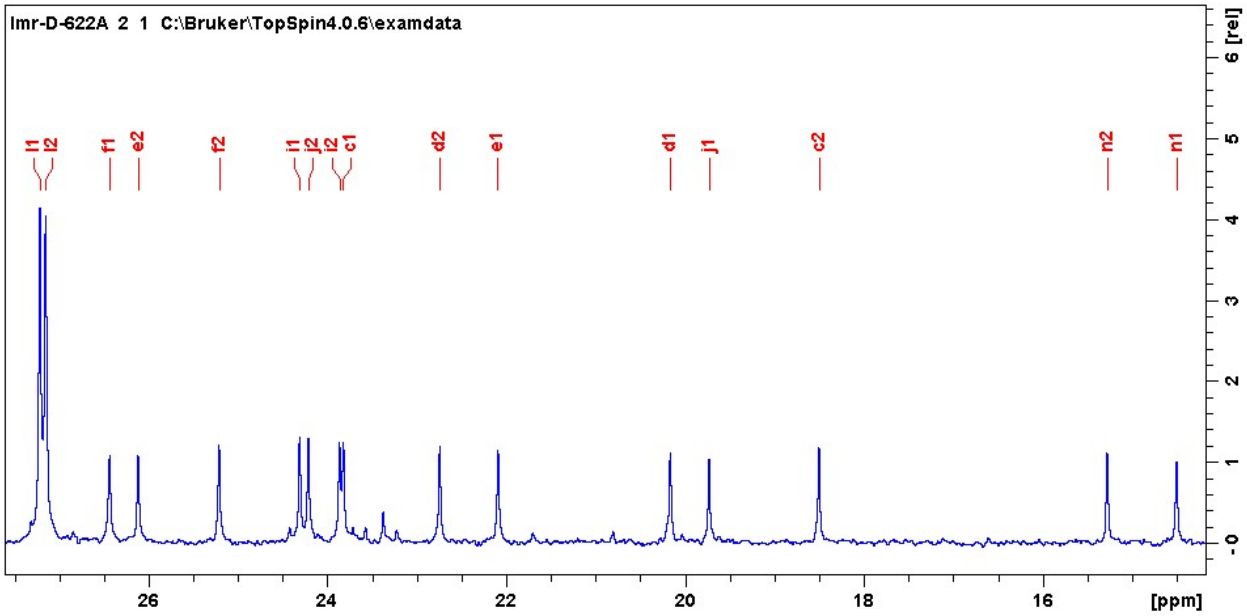


*Figure 15SI – [13]C NMR spectrum of alkoxyamine **4a**, aliphatic region.*

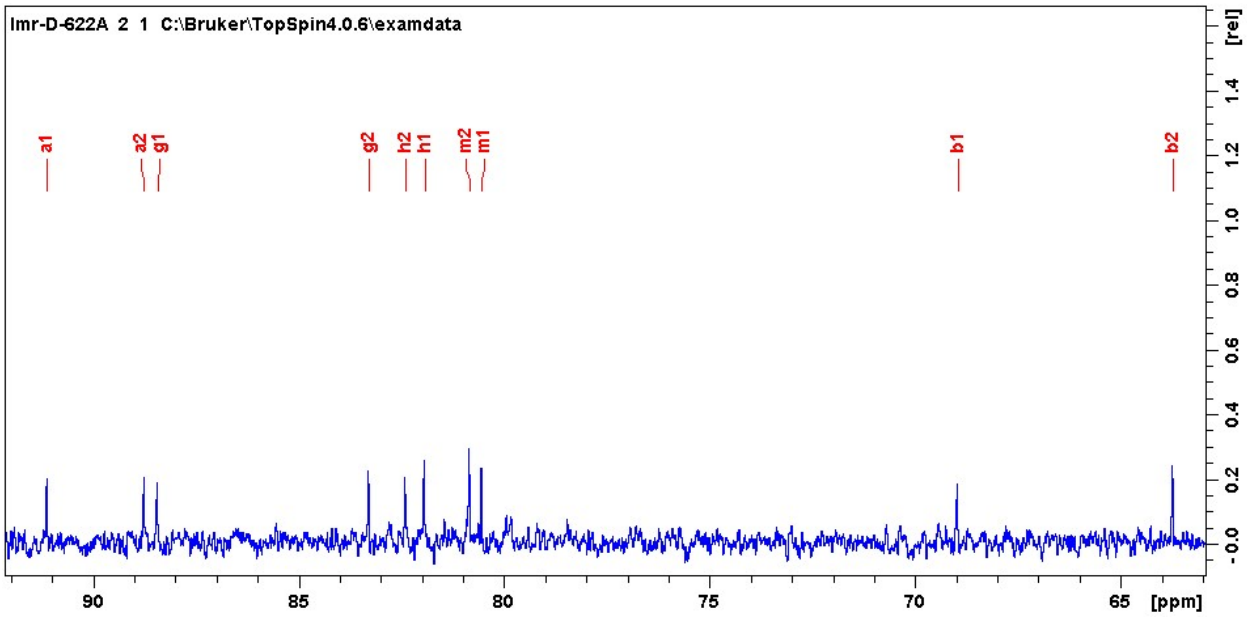


*Figure 16SI – ^{13}C NMR spectrum of alkoxyamine **4a**, mid-field region.*

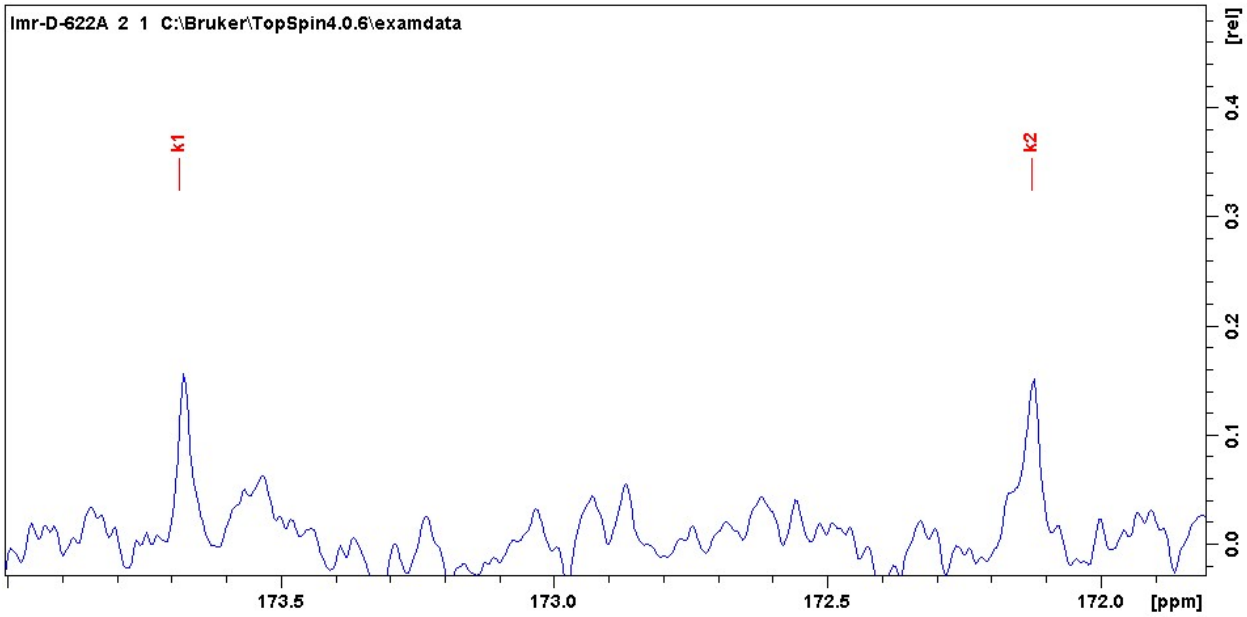


*Figure 17SI – ^{13}C NMR spectrum of alkoxyamine **4a**, region of location of carboxylic carbon signals.*

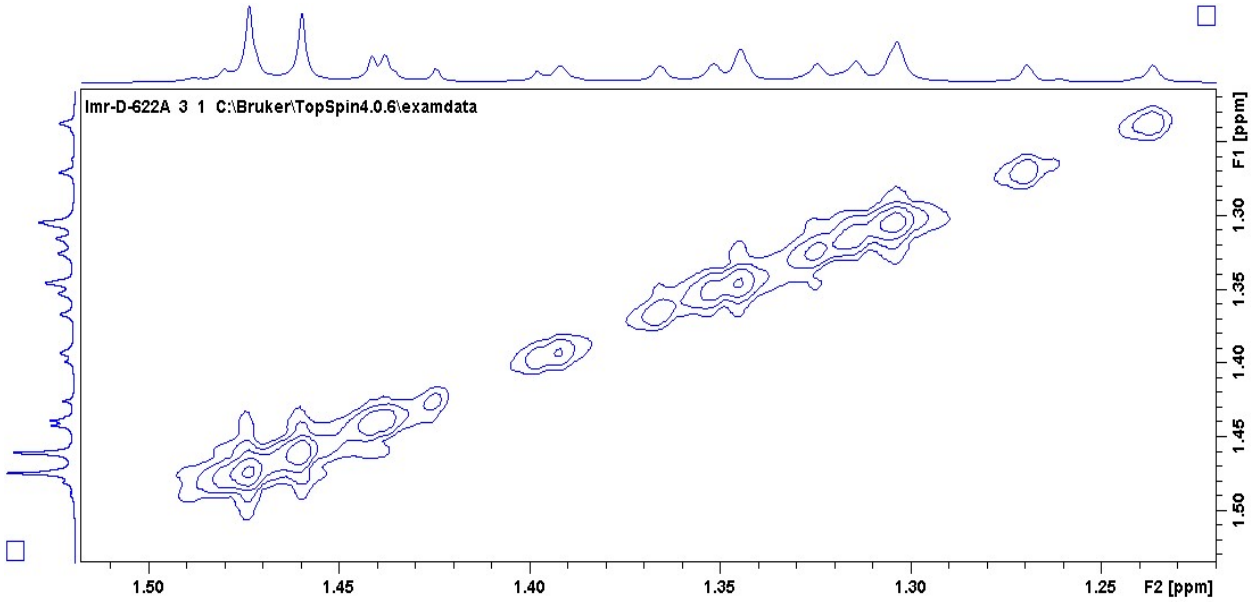


Figure 18SI – ^{1}H-^{1}H 2D NMR spectrum (COSY).

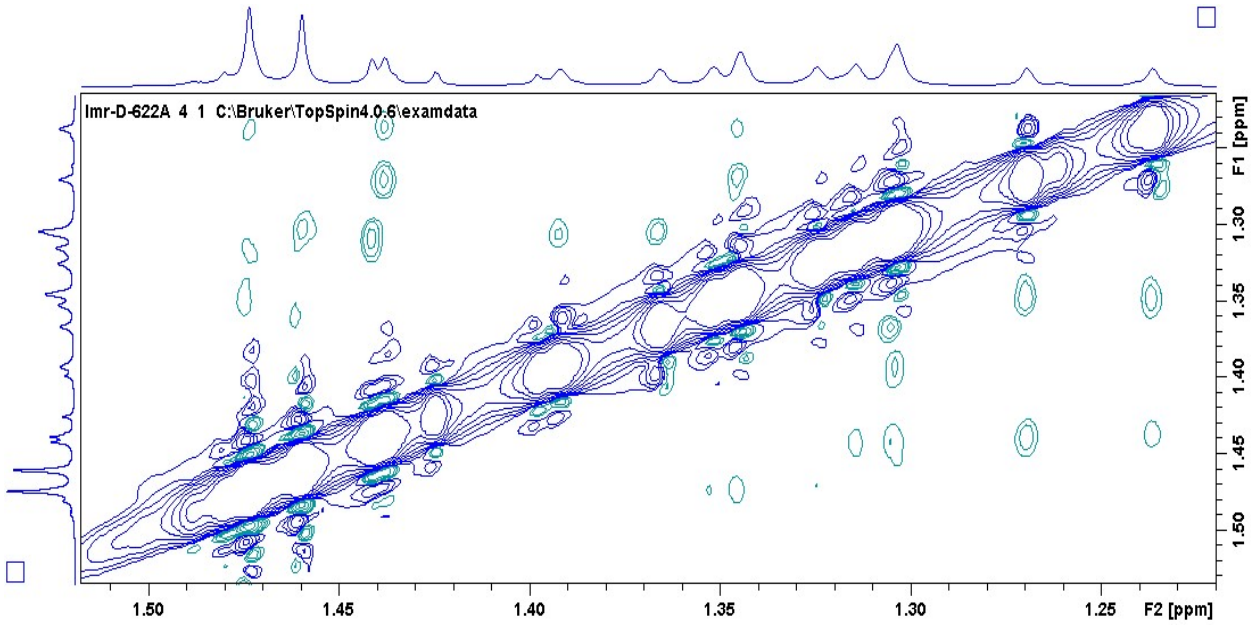


Figure 19SI – ^{1}H-^{1}H 2D NMR spectrum (NOESY).

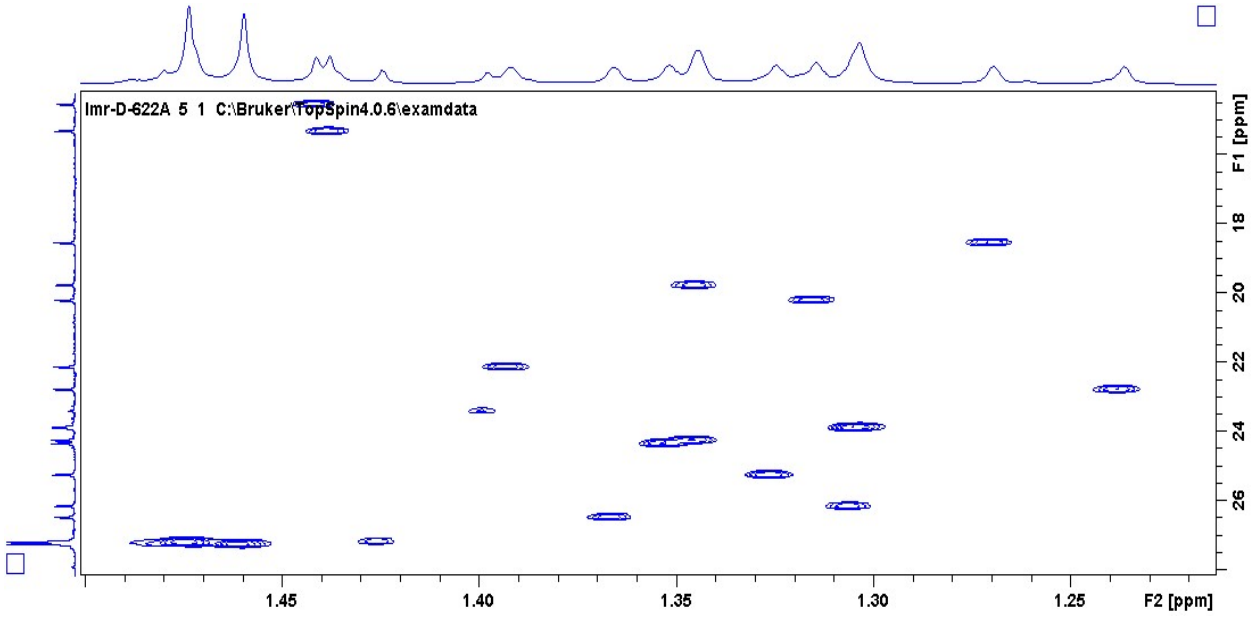


Figure 20SI – ^{1}H-^{13}C 2D NMR spectrum (HSQC).

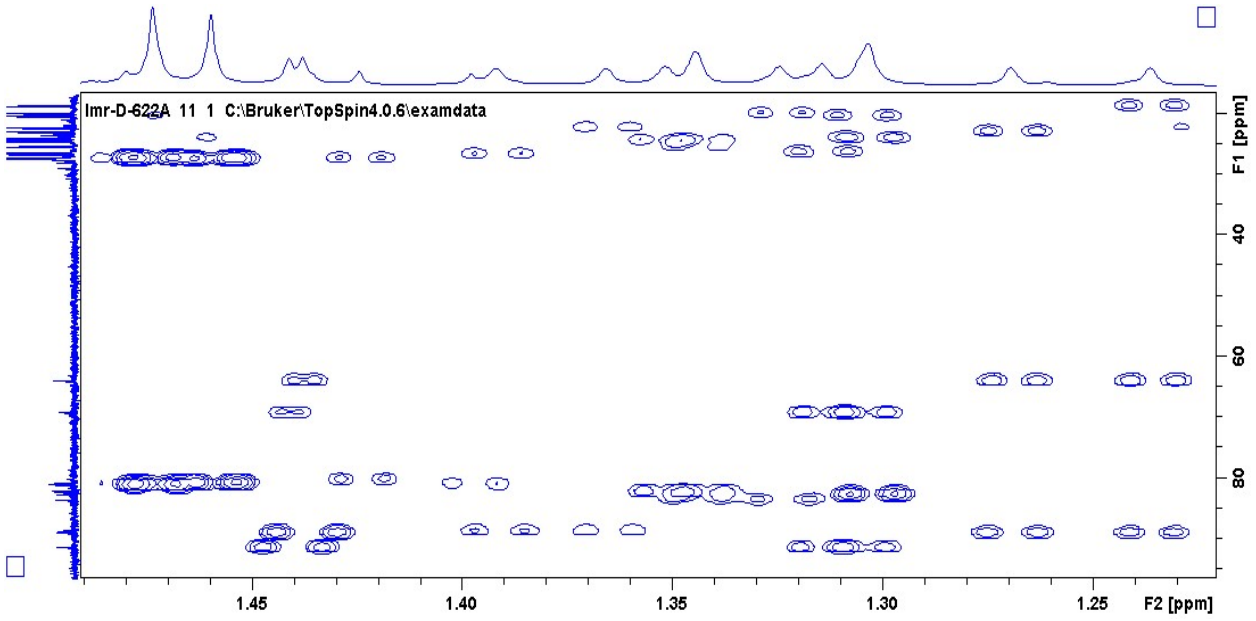
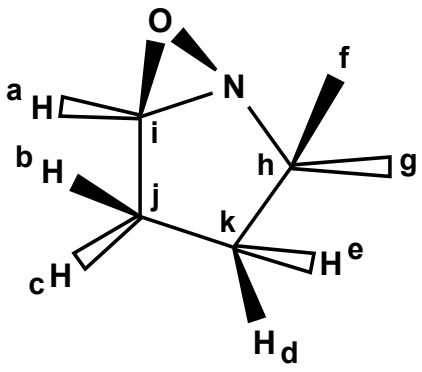


Figure 21SI – ^{1}H-^{13}C 2D NMR spectrum (HMBC).

*Table 1SI – Theoretical and experimental chemical shifts of isomers of alkoxyamines **3a** and **4a**.*

Atom lable	Alkoxyamine **3a**							
	Experiment				Theory			
	Cis-isomer 1		Trans-isomer 2		Cis-isomer 1		Trans-isomer 2	
	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
a	4.287	87.24	4.368	85.46	3.448	72.50	3.521	69.03
b	–[a]	68.00	–[a]	63.10	–[a]	54.57	–[a]	50.32
c	1.318	20.92	1.268	23.72	1.035	15.19	1.220	8.12
d	1.279	26.24	1.262	19.03	0.951	9.70	0.964	13.74
e	1.343	27.43	1.347	20.83	1.323	11.38	1.104	15.29
f	1.403	23.27	1.322	26.42	1.052	19.22	1.011	10.35
g	–[a]	91.66	–[a]	86.06	–[a]	79.95	–[a]	74.41
h	–[a]	82.83	–[a]	83.47	–[a]	70.36	–[a]	70.82
i	1.389	25.16	1.363	24.79	0.972	13.42	1.009	16.42
j	1.273	24.75	1.309	25.35	1.119	13.36	1.099	11.23
k	–[a]	173.06	–[a]	174.56	–[a]	168.38	–[a]	170.32
l	1.426	28.20	1.438	28.14	1.249	16.00	1.251	15.96
m	–[a]	81.55	–[a]	81.85	–[a]	66.62	–[a]	66.41
Atom lable	Alkoxyamine **4a**							
	Experiment				Theory			
	Cis-isomer 1		Trans-isomer 2		Cis-isomer 1		Trans-isomer 2	
	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
a	–[a]	91.12	–[a]	88.76	–[a]	76.35	–[a]	72.72
b	–[a]	68.97	–[a]	63.74	–[a]	56.68	–[a]	51.84
c	1.303	23.83	1.270	18.51	1.024	15.91	0.923	9.34
d	1.315	20.17	1.237	22.75	0.865	10.05	1.213	13.86
e	1.392	22.10	1.306	26.12	1.282	11.34	1.074	15.29
f	1.366	26.44	1.325	25.21	1.033	19.36	0.981	10.27
g	–[a]	88.44	–[a]	83.30	–[a]	78.11	–[a]	72.81
h	–[a]	81.94	–[a]	82.41	–[a]	70.17	–[a]	70.86
i	1.352	24.31	1.305	23.87	1.654	13.57	1.103	11.16
j	1.346	19.73	1.344	24.22	0.968	13.40	1.003	16.49
k	–[a]	173.69	–[a]	172.13	–[a]	168.33	–[a]	170.37
l	1.460	27.22	1.474	27.15	1.245	15.97	1.250	15.93
m	–[a]	80.55	–[a]	80.85	–[a]	66.54	–[a]	66.37
n	1.442	14.51	1.438	15.28	0.959	5.20	0.969	4.51

[a] – quaternary carbon atom



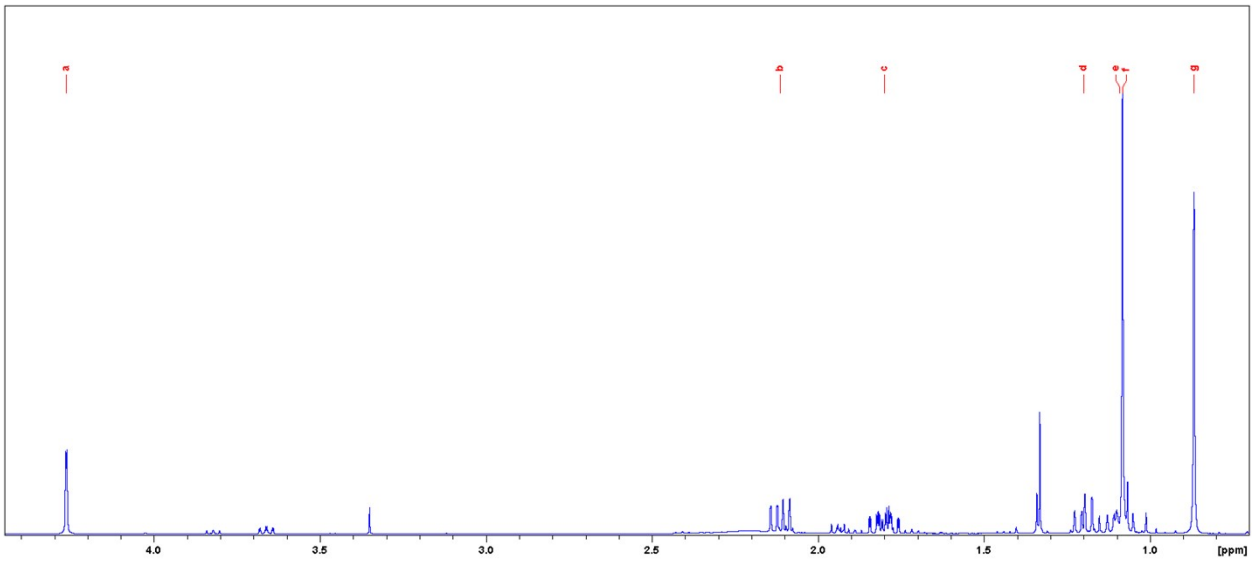


Figure 22SI – ^{1}H NMR spectrum.

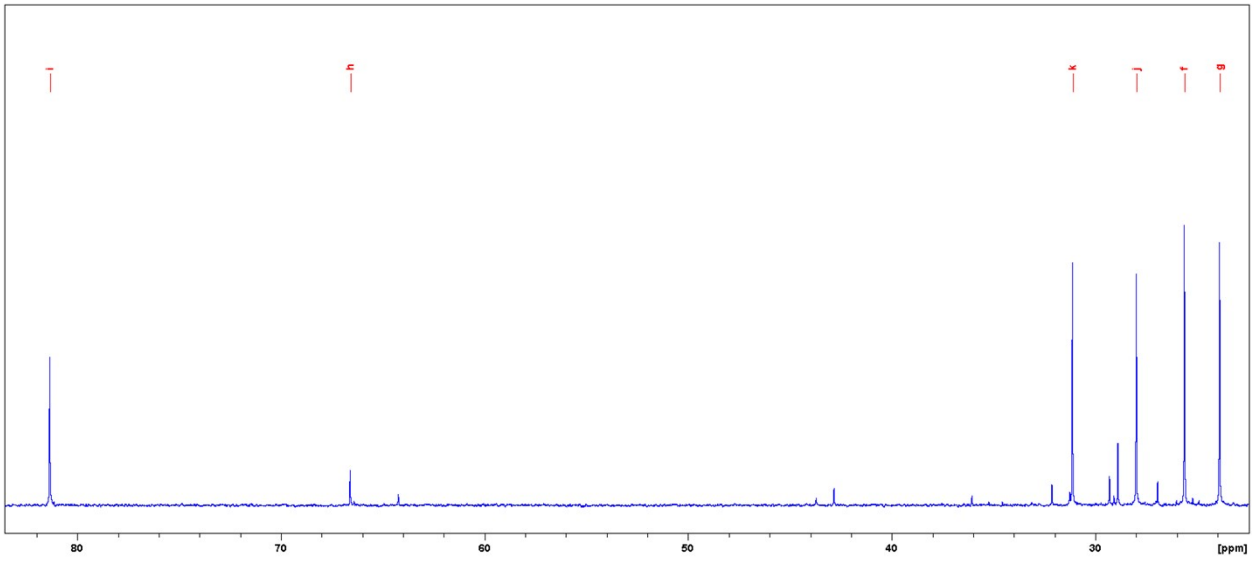


Figure 23SI – ^{13}C NMR spectrum.

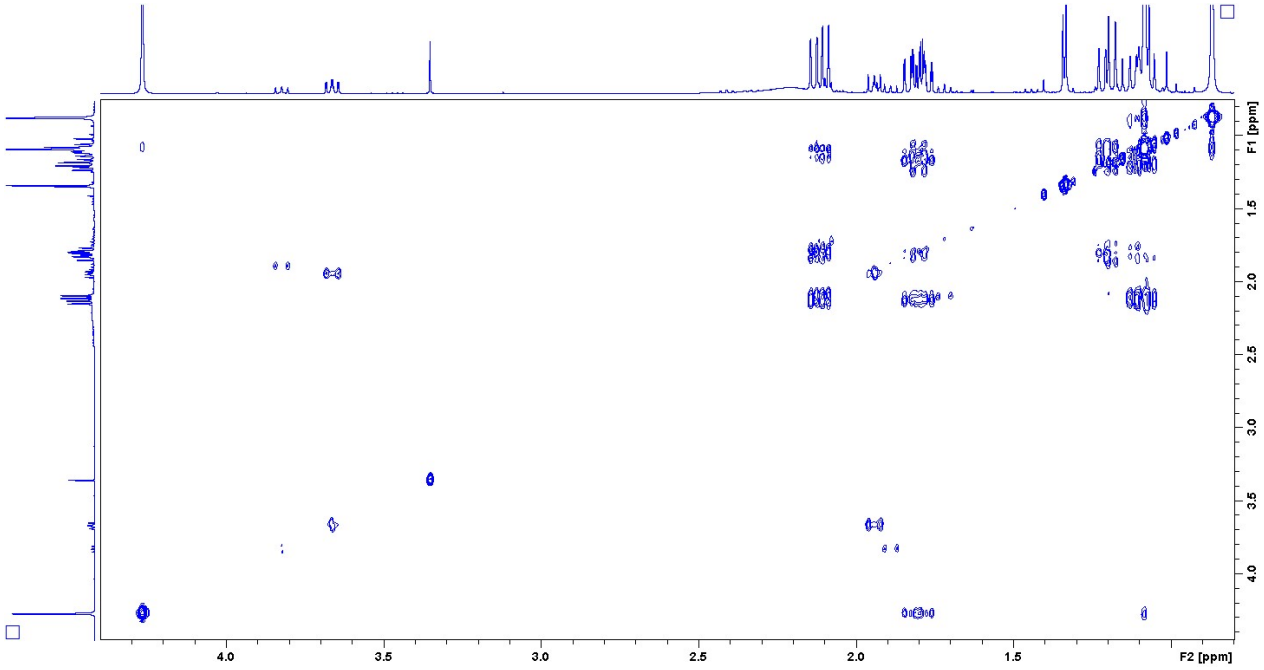


Figure 24SI – ^{1}H-^{1}H 2D NMR spectrum (COSY).

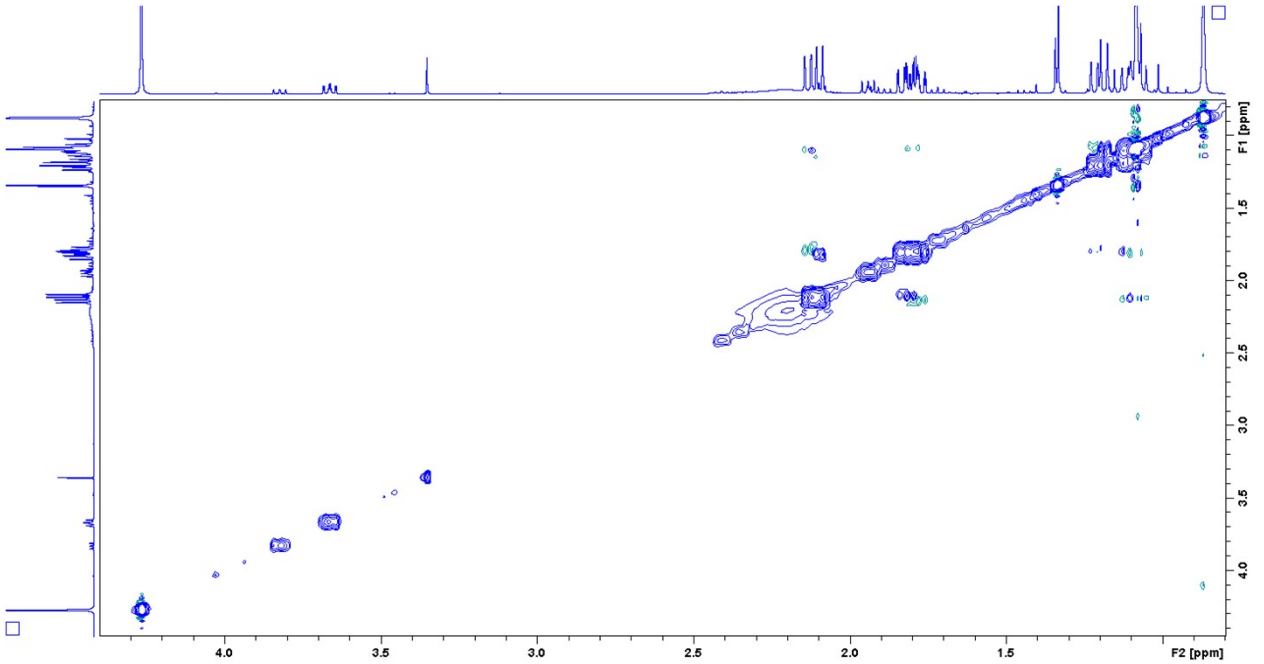


Figure 25SI – ^{1}H-^{1}H 2D NMR spectrum (NOESY).

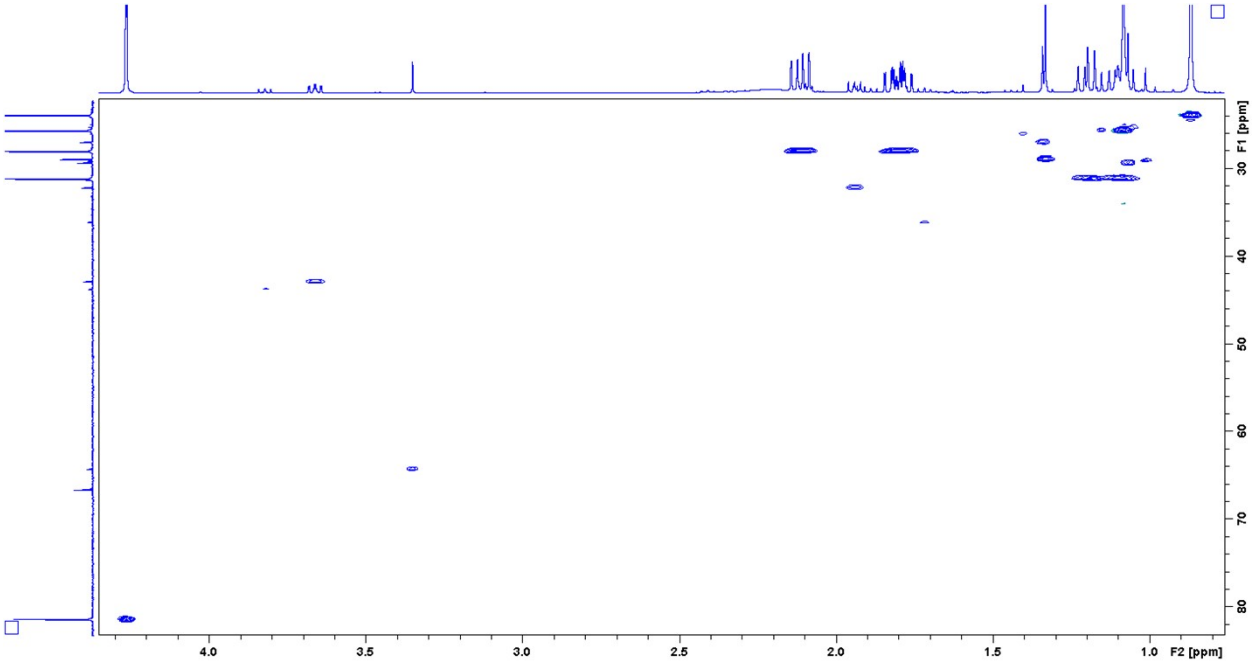


Figure 26SI – ^{1}H-^{13}C 2D NMR spectrum (HSQC).

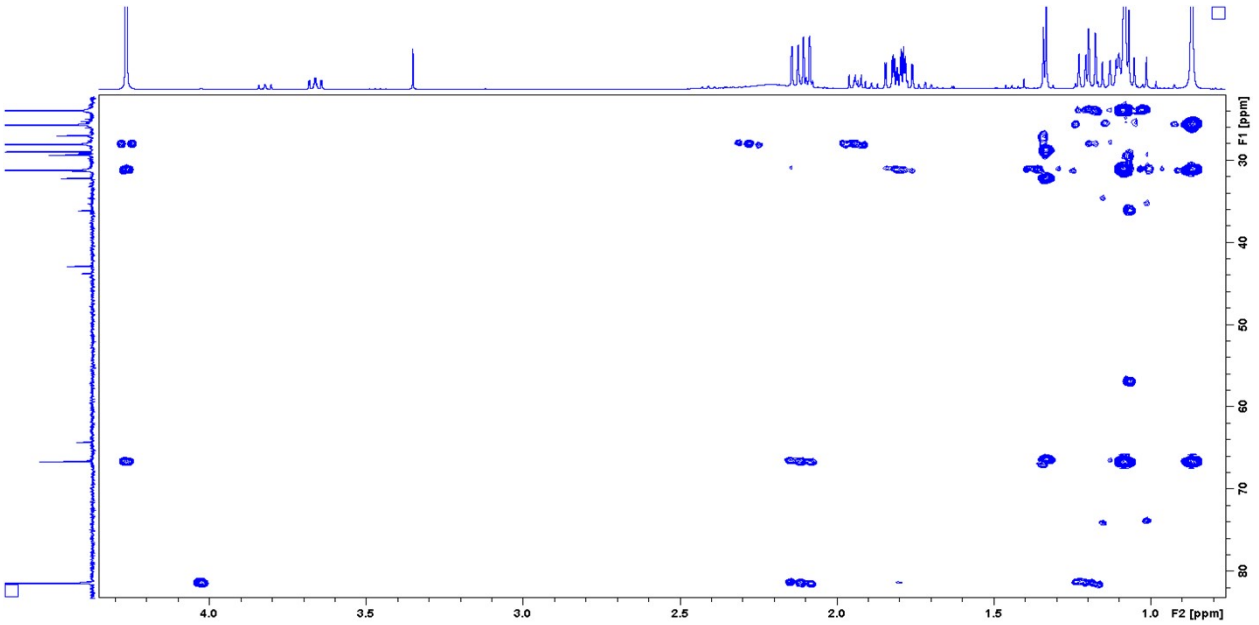


Figure 27SI – ^{1}H-^{13}C 2D NMR spectrum (HMBC).

Table 2SI – ^{1}H-^{1}H coupling constants J (Hz).

	H^a	H^b	H^c	H^d	H^e
H^a	-	-	1.3	-	-
H^b	-	-	14.9	1.3	7.7
H^c	1.3	14.9	-	8.4	10.9
H^d	-	1.3	8.4	-	12.4
H^e	-	7.7	10.9	12.4	-

SECTION 4. PURIFICATION OF ALKOXYAMINE 4A BY VACUUM DRYING.

After purification by vacuum drying of alkoxyamine **4a** formed by the photolysis of **2a** the ^{1}H NMR spectrum (toluene-d8) contained no by-products signal in comparison with those after photolysis of **2a** (acetonitrile-d3, ca. 1.8-1.9 ppm).

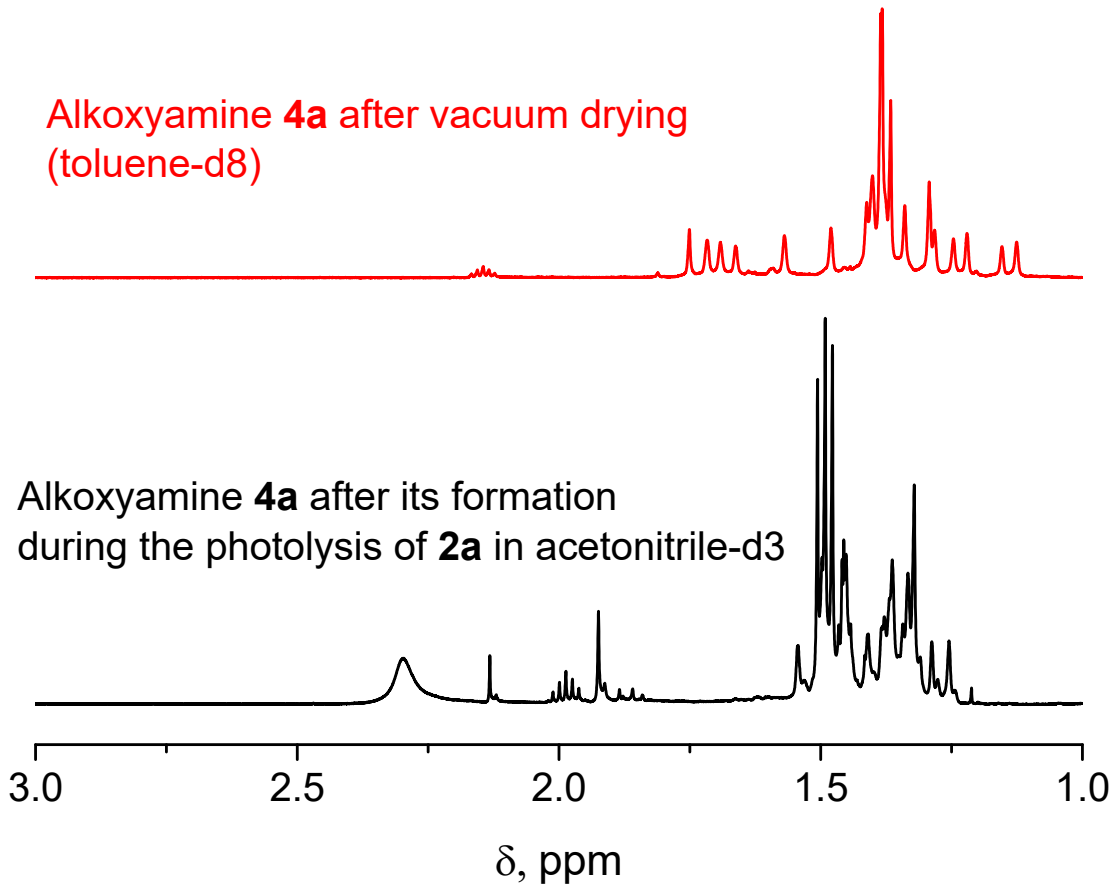


*Figure 28SI – ^{1}H NMR spectra of alkoxyamine **4a** after phtolysis of **2a** (CD_3CN) and after its purification by vacuum drying (toluene-d8).*

SECTION 5. OPTIMIZED GEOMETRIES OF CALCULATED COMPOUNDS.

5.1 OPTIMIZED GEOMETRIES IN TOLUENE

a

C	2.03742100	0.20699600	-0.00007700
C	0.72597500	-0.42312100	-0.00005000
C	3.25108700	-0.65448300	0.00011500
C	2.16716500	1.69413200	-0.00006500
O	0.54476300	-1.63421200	-0.00010700
O	-0.26838300	0.49131500	0.00003300
H	2.98837600	-1.71324900	0.00034600
H	3.87381300	-0.44124400	-0.87948600
H	3.87380900	-0.44085400	0.87962200
H	1.67908600	2.13551600	0.87773800
H	3.21869700	1.99264700	-0.00142500
H	1.67657600	2.13581000	-0.87628800
C	-1.66691500	0.08609600	0.00001800
C	-1.99096800	-0.70167400	1.26752400
C	-1.99099000	-0.70148100	-1.26760100
C	-2.40732200	1.41960200	0.00012600
H	-3.07292900	-0.86073100	1.32485700
H	-1.49254800	-1.67211500	1.27309300
H	-1.68176000	-0.13450400	2.15190800
H	-1.49255800	-1.67191500	-1.27333400
H	-3.07295000	-0.86054400	-1.32492700
H	-1.68181700	-0.13416900	-2.15190600
H	-2.14580900	2.00221400	0.88894300
H	-2.14582300	2.00235000	-0.88860700
H	-3.48793200	1.24756300	0.00011900

1

C	-1.03499900	0.39485700	0.01859000
C	0.37346700	-1.46095900	-0.03143000
C	1.33572900	-0.31022300	0.00491800
C	2.23150400	-0.32204600	1.24651900
H	2.92233600	-1.16935500	1.20228300
H	2.81300600	0.60367600	1.28199600
H	1.63198900	-0.40075600	2.15771600
C	2.16902100	-0.19309500	-1.27532400
H	2.75663000	0.72855700	-1.24215100
H	2.85160100	-1.04428600	-1.35546700
H	1.52538500	-0.17221100	-2.15924600
C	-1.79843900	0.79090500	1.27105600
H	-1.81603900	1.88184700	1.33728100
H	-2.82023600	0.41036100	1.21300900
H	-1.31064600	0.38551600	2.16189600
C	-1.70125300	0.87303500	-1.26169900

H	-2.71731800	0.47621900	-1.31260800
H	-1.73263000	1.96535600	-1.25215800
H	-1.13776100	0.53941900	-2.13766300
N	0.37082800	0.80576200	0.08886800
O	-1.91322700	-1.81151100	-0.05179700
N	-0.86758600	-1.09191900	-0.02465800
O	0.71763800	2.02119700	0.03727100
H	0.62552200	-2.51357400	-0.06392000

2

C	1.26987000	-0.20229300	0.01215900
C	-0.73690000	1.00061800	-0.00400500
C	-1.19015400	-0.43458200	0.01305500
C	-1.60002900	2.20904500	-0.02352300
H	-2.65621400	1.93423000	-0.05515600
H	-1.41350200	2.82173800	0.86553900
H	-1.36006700	2.82887200	-0.89419300
C	-2.01139500	-0.78169200	1.25780400
H	-2.97784200	-0.26915900	1.22986900
H	-2.18948800	-1.86064800	1.28219000
H	-1.48041600	-0.48842400	2.16805500
C	-1.93352900	-0.83175200	-1.26615900
H	-2.12478500	-1.90839100	-1.25363000
H	-2.89140600	-0.30602800	-1.32380100
H	-1.34228800	-0.58675000	-2.15323200
C	2.13175000	-0.30921500	1.25960100
H	2.55896800	-1.31437500	1.30533200
H	2.93511200	0.42900500	1.21337600
H	1.53084400	-0.13359700	2.15638000
C	2.06358300	-0.37668800	-1.27334300
H	2.84904600	0.38069900	-1.31957300
H	2.51247300	-1.37307200	-1.27820600
H	1.41174700	-0.27414000	-2.14559400
N	0.12036100	-1.11071000	0.07053300
O	1.24286800	2.18248700	-0.01957800
N	0.55544700	1.10513200	-0.00437100
O	0.25062900	-2.36768100	0.00532500

3

C	-1.22940600	0.06797100	0.08673100
C	0.65122800	-1.23052000	0.65325000
C	1.24595200	0.03726700	0.07918400
C	1.87766200	0.90217900	1.17171600
H	2.80618200	0.44334600	1.52534200
H	2.10853400	1.88863100	0.76044200
H	1.20552400	1.02844300	2.02599900
C	2.21871600	-0.22633600	-1.06562400
H	2.50326900	0.72609900	-1.52185600
H	3.12075100	-0.71918700	-0.69063500
H	1.75311500	-0.85845700	-1.82595600

C	-1.82690600	0.95826300	1.17247800
H	-2.03224400	1.94377600	0.74637300
H	-2.75865500	0.52101500	1.53993400
H	-1.13766000	1.07467100	2.01357900
C	-2.20952700	-0.20262300	-1.04155600
H	-3.11568200	-0.66417900	-0.64024000
H	-2.47124700	0.74426600	-1.52095400
H	-1.76024100	-0.86775900	-1.78190100
N	0.01693200	0.66455800	-0.44509100
O	-0.07538000	-1.99309600	-0.26036500
N	-0.78505000	-1.17958500	0.73897500
O	0.02537200	1.77813200	-1.04633900
H	1.18893100	-1.77297200	1.42923500

4

C	-1.34281900	-0.30313300	0.13038100
C	0.94723000	-0.87496200	-0.02729100
C	0.93305800	0.64834000	-0.04238200
C	1.45147200	1.25838100	1.26200200
H	2.53574200	1.13141500	1.33805800
H	1.22428500	2.32801400	1.26540300
H	0.98445300	0.80131300	2.13992200
C	1.66334200	1.22612400	-1.25127000
H	1.48959700	2.30520400	-1.29276900
H	2.73995000	1.04917900	-1.16534700
H	1.29602500	0.77182500	-2.17479300
C	-1.92798000	-0.19699000	1.53599300
H	-2.52617000	0.71557900	1.60247300
H	-2.56356600	-1.06238600	1.73995100
H	-1.13763000	-0.15716400	2.29102900
C	-2.41550200	-0.49014400	-0.92844200
H	-3.00753500	-1.38055700	-0.70083400
H	-3.07014100	0.38523600	-0.93168200
H	-1.95820800	-0.59982700	-1.91400800
N	-0.51703300	0.88483200	-0.17993200
O	0.32076400	-1.42362100	-1.15467700
N	-0.37969400	-1.41788600	0.13990200
O	-1.01189500	2.04789500	-0.24768400
C	2.11901200	-1.62136100	0.53535700
H	3.03266300	-1.34866700	-0.00306500
H	2.25528100	-1.38649300	1.59435400
H	1.94452300	-2.69302100	0.42432200

1a

C	-2.74766300	0.39759700	0.03147900
C	-2.53397800	-1.91256800	-0.05060300
C	-1.12175100	-1.42032500	-0.09398000
C	-0.37963500	-1.85802600	1.17423800
H	-0.36875800	-2.95256500	1.21261300

H	0.64861600	-1.49108200	1.16706000
H	-0.87684800	-1.48160700	2.07239200
C	-0.40163700	-1.91672600	-1.35056600
H	0.58751600	-1.45722100	-1.42239600
H	-0.27821700	-3.00541700	-1.32317200
H	-0.96926700	-1.64453900	-2.24502200
C	-3.04556400	1.06827600	1.36445300
H	-2.62709300	2.07702200	1.37849500
H	-4.13054800	1.12430300	1.48042600
H	-2.61902200	0.50202600	2.19636700
C	-3.34172800	1.16406900	-1.14269600
H	-4.42854800	1.20477500	-1.03939900
H	-2.94548500	2.18110100	-1.16119800
H	-3.08407700	0.66729800	-2.08294400
N	-1.31645700	0.06485800	-0.20108400
O	-4.66473900	-1.03539400	0.12219900
N	-3.39699400	-0.96035800	0.03979700
O	-0.50572600	0.74674100	0.72939400
C	0.44464300	1.63532200	0.11821600
C	1.60321000	0.82992300	-0.50691100
C	-0.18109100	2.53716100	-0.93112800
C	0.98336700	2.44372200	1.29645900
O	1.92135500	0.89947000	-1.67265100
O	2.22493800	0.09160200	0.41527100
H	-0.56544100	1.95868100	-1.77218800
H	-0.99424500	3.10792600	-0.47210200
H	0.56829400	3.23890600	-1.30669900
H	1.80743500	3.08617400	0.97015500
H	0.18331300	3.07374000	1.69601600
H	1.34395600	1.77757400	2.08276700
C	3.49144700	-0.59172800	0.13968100
C	4.53409200	0.42167100	-0.32466500
C	3.28639800	-1.71386000	-0.87206800
C	3.86838600	-1.16090200	1.50272400
H	5.51666800	-0.06054800	-0.34177400
H	4.31387900	0.79963700	-1.32423300
H	4.57949200	1.26248800	0.37596700
H	2.98005600	-1.32466300	-1.84531600
H	4.22926100	-2.25696000	-0.99522500
H	2.53264300	-2.42132600	-0.51049100
H	3.99338700	-0.35579600	2.23324300
H	3.09075000	-1.84158800	1.86307600
H	4.80865800	-1.71519600	1.42740800
H	-2.85980800	-2.94563700	-0.06630300

2a

C	-1.05431500	-1.13128400	-0.06784900
C	-3.30198200	-0.52972800	0.01897800
C	-2.56390400	0.78019100	0.06238400
C	-4.77260500	-0.74306000	0.05428400
H	-5.30193500	0.18303900	0.28704100

H	-5.12642000	-1.12055300	-0.91240300
H	-5.01846800	-1.50248500	0.80344300
C	-3.04772500	1.69466000	-1.06843600
H	-4.12446100	1.87544500	-0.97878200
H	-2.54149500	2.66197200	-1.02680100
H	-2.84724600	1.23425400	-2.04047500
C	-2.75933100	1.46286200	1.42116200
H	-2.22681300	2.41710900	1.45272300
H	-3.82587300	1.65829000	1.57346000
H	-2.39608200	0.83616900	2.23979700
C	-0.40911500	-1.72389400	-1.31154000
H	0.60885200	-1.34059000	-1.40910900
H	-0.38380400	-2.81459400	-1.24676600
H	-0.97401100	-1.42657700	-2.19994800
C	-0.42176000	-1.63743000	1.22122600
H	-0.55330700	-2.72183700	1.25816000
H	0.64027900	-1.38954000	1.23985200
H	-0.90092400	-1.18646900	2.09479800
N	-1.14804000	0.34735200	-0.19252800
O	-2.79827700	-2.77345400	-0.11670600
N	-2.49250900	-1.53198100	-0.05888800
O	-0.27179300	0.97166300	0.71986900
C	0.76324100	1.74309900	0.09053700
C	1.83310200	0.81514600	-0.52284000
C	0.23233000	2.69180100	-0.96941500
C	1.39286200	2.50744700	1.25383600
O	2.17978900	0.86038400	-1.68167900
O	2.35246200	0.00562200	0.40257900
H	-0.23444800	2.14627800	-1.79068900
H	-0.49845700	3.36456400	-0.51039600
H	1.05322700	3.29052200	-1.37248100
H	2.27340700	3.06039200	0.91129000
H	0.66439700	3.21928000	1.65303700
H	1.69307800	1.81734100	2.04504100
C	3.55233400	-0.79682900	0.14735800
C	4.69774200	0.11364100	-0.28748700
C	3.26041800	-1.88761300	-0.87685000
C	3.84456700	-1.40758400	1.51307500
H	5.63005700	-0.45991700	-0.28128000
H	4.54000200	0.51165300	-1.29108400
H	4.80484100	0.94571200	0.41704500
H	3.00851400	-1.46451700	-1.85158800
H	4.15080500	-2.51503100	-0.98938600
H	2.43831700	-2.52446100	-0.53394300
H	4.03097200	-0.62270600	2.25254700
H	2.99916700	-2.01409000	1.85234500
H	4.72907900	-2.04851200	1.45140600

3a

C	-2.79676500	0.33771500	0.54851500
C	-2.64467000	-1.83709900	-0.28806300
C	-1.22381500	-1.32180600	-0.26111000

C	-0.46316200	-1.96199300	0.90332500
H	-0.24479400	-3.00856100	0.66426500
H	0.47706500	-1.43098800	1.06480500
H	-1.03443800	-1.94046100	1.83520800
C	-0.52080000	-1.58915500	-1.59184000
H	0.48161100	-1.15067300	-1.59697100
H	-0.41311700	-2.66606500	-1.76381400
H	-1.09373000	-1.15025900	-2.41315700
C	-2.72834900	0.45396700	2.07170200
H	-2.15650000	1.34142300	2.34944700
H	-3.74499100	0.54513700	2.46373800
H	-2.25655500	-0.41715200	2.53070000
C	-3.51028800	1.53947900	-0.05068200
H	-4.52482200	1.61385000	0.35229500
H	-2.96796600	2.45367600	0.21002000
H	-3.55480500	1.44603600	-1.13809000
N	-1.47997900	0.13750800	-0.12442500
O	-3.49803100	-1.17330300	-1.17203900
N	-3.56565400	-0.89577700	0.27485800
O	-0.48095700	0.80056500	0.60893000
C	0.38663000	1.63755500	-0.17807000
C	1.64900000	0.85128700	-0.58530700
C	-0.27406400	2.22491800	-1.41370900
C	0.82493900	2.73153800	0.79717400
O	2.15589900	0.92102700	-1.68346700
O	2.13078700	0.14500000	0.43793900
H	-0.53873300	1.45308400	-2.13742400
H	-1.18040900	2.76101200	-1.12349000
H	0.41888100	2.92551700	-1.88595100
H	1.60386200	3.35688200	0.34967900
H	-0.03790300	3.35956000	1.03981500
H	1.21133100	2.28418400	1.71642000
C	3.38108000	-0.60958300	0.32897100
C	4.53460900	0.33312400	-0.00275700
C	3.22933000	-1.72774300	-0.69798900
C	3.55116800	-1.18767700	1.72933700
H	5.47954500	-0.20919000	0.10474400
H	4.46396900	0.71463300	-1.02221200
H	4.54389700	1.17608100	0.69659200
H	3.09700900	-1.33153000	-1.70673800
H	4.13004100	-2.35020900	-0.68292700
H	2.37298000	-2.36240900	-0.44477000
H	3.61776100	-0.38469000	2.46972800
H	2.70388800	-1.83070400	1.98715200
H	4.46725400	-1.78408800	1.77556600
H	-2.83152300	-2.89969700	-0.13556500

4a

C	-2.58497300	0.79862300	0.55194300
C	-2.69788100	-1.39796800	-0.25989300
C	-1.21735200	-1.04205100	-0.23106600
C	-3.15408600	-2.81507800	-0.07105500

H	-2.72603800	-3.45804600	-0.84749900
H	-2.84843000	-3.19751300	0.90648500
H	-4.24281600	-2.84493300	-0.14454800
C	-0.50420100	-1.73380000	0.93488000
H	-0.37276200	-2.79778900	0.70887400
H	0.47721500	-1.27866500	1.08218600
H	-1.06106000	-1.65330800	1.87261200
C	-0.55372900	-1.39694600	-1.56275500
H	0.48258300	-1.04634500	-1.58688400
H	-0.53888900	-2.48219900	-1.71632100
H	-1.09614000	-0.92514500	-2.38653700
C	-2.50876400	0.90654100	2.07543700
H	-1.82350000	1.70815700	2.35784300
H	-3.50647500	1.13066800	2.46263700
H	-2.16094100	-0.02094500	2.53519100
C	-3.14434700	2.07759300	-0.05178800
H	-4.14578800	2.27176200	0.34387100
H	-2.49889900	2.92166600	0.21142700
H	-3.19345400	1.98572900	-1.13916900
N	-1.30186200	0.43912600	-0.11554800
O	-3.42822600	-0.62203400	-1.17061900
N	-3.49400700	-0.32902700	0.27311600
O	-0.23209300	0.99522500	0.60705200
C	0.71862800	1.72241400	-0.19168100
C	1.88872000	0.80160700	-0.59056500
C	0.12531000	2.35968800	-1.43678900
C	1.27458800	2.77498300	0.76925200
O	2.39765900	0.80231300	-1.68824200
O	2.29697400	0.05941900	0.44294200
H	-0.22930100	1.60916800	-2.14398400
H	-0.71246600	3.00190400	-1.15619800
H	0.89380300	2.96378700	-1.92505300
H	2.11567900	3.30704500	0.31335300
H	0.48516900	3.49538600	1.00520800
H	1.61122600	2.29892800	1.69366600
C	3.45255600	-0.82840200	0.32986200
C	4.70257900	-0.01998400	-0.00878200
C	3.17487800	-1.92459800	-0.69526600
C	3.56348300	-1.42112600	1.73030100
H	5.58277100	-0.66436200	0.08630400
H	4.66402300	0.37373400	-1.02541500
H	4.81248100	0.81245400	0.69467100
H	3.08933200	-1.51732700	-1.70456800
H	3.99749900	-2.64735700	-0.67788300
H	2.25043100	-2.45498100	-0.44129100
H	3.71704500	-0.62942600	2.46988300
H	2.65190100	-1.96793400	1.99082600
H	4.40991900	-2.11317300	1.77606400

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C	1.21805200	-1.32831100	0.24597800
C	3.44793400	-0.78704800	0.23865200

C	2.78446000	0.54121700	0.15776900
C	3.24518600	1.43315300	1.31938400
H	4.33804200	1.49777300	1.33831800
H	2.84720300	2.44275700	1.19632000
H	2.89432400	1.03220600	2.27442400
C	3.17094700	1.15845300	-1.19915000
H	2.67651500	2.12623400	-1.31249700
H	4.25399400	1.30870800	-1.22794100
H	2.87654500	0.50924300	-2.02614800
C	0.61044000	-1.74823200	1.57811400
H	-0.37748200	-1.29495300	1.69436400
H	0.52409000	-2.83794700	1.63329500
H	1.24136000	-1.40012000	2.40245400
C	0.46226100	-1.88473400	-0.94592000
H	0.50621100	-2.97600600	-0.89440700
H	-0.57679000	-1.55503300	-0.91578300
H	0.91795300	-1.56258100	-1.88248700
N	1.34045700	0.18223800	0.26741100
O	3.19600400	-2.31319500	-1.00307500
N	2.62660000	-1.80918900	0.22451400
O	0.60051400	0.76022200	-0.78381100
C	-0.40941000	1.67248800	-0.32083200
C	-1.54064000	0.90036500	0.39343800
C	0.14836500	2.73053600	0.61612700
C	-0.94437700	2.29329300	-1.60798600
O	-1.82795200	1.05560900	1.55906900
O	-2.17207100	0.08145500	-0.44890400
H	0.50915200	2.28352200	1.54326600
H	0.96403400	3.26068100	0.11419900
H	-0.63383500	3.45287700	0.86551500
H	-1.80101000	2.93870800	-1.38959300
H	-0.15822500	2.89772300	-2.07010300
H	-1.25696600	1.51460300	-2.30628900
C	-3.39524300	-0.63092400	-0.06932300
C	-4.46933900	0.37504500	0.33498400
C	-3.10800100	-1.64342300	1.03438200
C	-3.78341200	-1.34148600	-1.36076700
H	-5.42501000	-0.14772700	0.44306500
H	-4.22965600	0.86223800	1.28157000
H	-4.58352600	1.13719000	-0.44342000
H	-2.81177300	-1.15132700	1.96284600
H	-4.01495000	-2.22728100	1.22316700
H	-2.31880700	-2.33593000	0.72314000
H	-3.96213800	-0.61494300	-2.15927200
H	-2.98729800	-2.02154500	-1.67944400
H	-4.69689400	-1.92308700	-1.20491700
H	4.52025300	-0.94241300	0.29754400

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C	1.08184200	-1.09975100	0.44087000
C	3.31170000	-0.51198000	0.21623500

C	2.55587400	0.65325300	-0.34722600
C	3.07459100	2.01349300	0.11285300
H	4.11115500	2.16201800	-0.20517500
H	2.46851300	2.79962600	-0.34826900
H	3.01000900	2.11086500	1.20031800
C	2.64585600	0.55262700	-1.88794700
H	1.94130400	1.26465700	-2.32423600
H	3.65879600	0.81307300	-2.20871400
H	2.41911300	-0.45226400	-2.24561100
C	0.37306900	-1.32889000	1.77008500
H	-0.64744600	-0.93517200	1.73999100
H	0.32560800	-2.39995400	1.99055000
H	0.91600500	-0.82308100	2.57334800
C	0.40172000	-1.85811100	-0.68873200
H	0.40591600	-2.92407700	-0.44798100
H	-0.62530000	-1.50255800	-0.78339700
H	0.91482000	-1.72566900	-1.64012400
N	1.21662000	0.37962900	0.22222100
O	3.07180700	-2.38868600	-0.39571200
N	2.50874000	-1.49759700	0.59747100
O	0.22224100	0.88851100	-0.62934400
C	-0.76158200	1.71587900	0.02289500
C	-1.95450900	0.85902100	0.49654800
C	-0.21672600	2.51914000	1.19160800
C	-1.26606300	2.62653100	-1.09700100
O	-2.47690300	0.98596700	1.58227200
O	-2.36112600	0.02410300	-0.45797800
H	0.11285900	1.87288600	2.00617500
H	0.62438800	3.13017700	0.85675300
H	-1.00409500	3.17762200	1.56599000
H	-2.12176000	3.21690700	-0.75448000
H	-0.46284000	3.30758500	-1.39466500
H	-1.56860400	2.02976900	-1.96084500
C	-3.54548900	-0.82215300	-0.28546900
C	-4.77749100	0.04962900	-0.05871300
C	-3.32102100	-1.81772300	0.84877200
C	-3.64172500	-1.54606800	-1.62341500
H	-5.67317800	-0.57677700	-0.12114600
H	-4.75596400	0.53275500	0.91924400
H	-4.84340800	0.81691500	-0.83764400
H	-3.23960600	-1.31528000	1.81461100
H	-4.16896800	-2.50950400	0.88586200
H	-2.41324500	-2.40370700	0.66910500
H	-3.76678500	-0.82800500	-2.43960300
H	-2.73777600	-2.13368200	-1.81071200
H	-4.50144600	-2.22270400	-1.61678700
C	4.78194000	-0.53316100	0.39943100
H	5.06469900	0.29355900	1.06391200
H	5.09443000	-1.48798500	0.81698300
H	5.28522700	-0.37181800	-0.55995700

5.2 OPTIMIZED GEOMETRIES IN GAS PHASE

3a (cis-isomer 1)

C	1.18388000	-1.40574300	0.15789400
C	3.46046000	-0.93609300	-0.08718600
C	2.81412100	0.40951500	0.18135400
C	3.26557200	0.92253400	1.55161700
H	4.35522000	1.03894000	1.57846000
H	2.81382100	1.89519800	1.76146800
H	2.96951300	0.23007300	2.34603500
C	3.20124700	1.38697800	-0.92643300
H	2.75044400	2.36846400	-0.76406200
H	4.29016200	1.50900600	-0.92127700
H	2.88867400	1.01533500	-1.90351000
C	0.69876700	-1.88884800	1.52337000
H	-0.25090700	-1.40254600	1.76204000
H	0.56954300	-2.97521700	1.52480800
H	1.41885100	-1.62049000	2.30319400
C	0.28933900	-1.88803600	-0.97337500
H	0.25625800	-2.98127000	-0.93426000
H	-0.71958900	-1.49020200	-0.87347900
H	0.69112900	-1.57481500	-1.93798600
N	1.35625200	0.07912800	0.21661300
O	3.07361900	-1.51857800	-1.29080900
N	2.52946300	-2.01342400	-0.01507100
O	0.63482500	0.73795400	-0.79752700
C	-0.34639500	1.64963700	-0.27178000
C	-1.49235500	0.86994900	0.41351200
C	0.23536300	2.62690500	0.73809300
C	-0.86471900	2.36546200	-1.51442400
O	-1.71084700	0.90836000	1.60227900
O	-2.22027900	0.18273900	-0.47235000
H	0.57560600	2.10219700	1.63091500
H	1.06501600	3.17659700	0.28508000
H	-0.53334200	3.34436000	1.03969600
H	-1.69766600	3.02657500	-1.25490600
H	-0.05746800	2.96673800	-1.94331800
H	-1.20590200	1.64129100	-2.25657100
C	-3.42927900	-0.53805200	-0.07405900
C	-4.45949100	0.45574600	0.45593000
C	-3.11180900	-1.62968800	0.94548100
C	-3.89866200	-1.15453900	-1.38702000
H	-5.41300000	-0.06039700	0.60858500
H	-4.14268300	0.89064100	1.40571600
H	-4.61809300	1.25789800	-0.27266600
H	-2.79295800	-1.20829400	1.90004900
H	-4.01378400	-2.22875800	1.11035800
H	-2.32975200	-2.29612400	0.56712800
H	-4.09059900	-0.37383700	-2.12929600
H	-3.13772500	-1.83305900	-1.78544000
H	-4.82131600	-1.72024600	-1.22568600

H	4.48576500	-1.11615000	0.23755400

3a (trans-isomer 2)

C	-2.80065900	0.34083100	0.53732300
C	-2.64073000	-1.84119100	-0.27269400
C	-1.22080200	-1.32248900	-0.25010500
C	-0.45924600	-1.94940800	0.92106500
H	-0.23563000	-2.99745200	0.69199400
H	0.47748300	-1.41225600	1.08295200
H	-1.03438400	-1.92227600	1.85067500
C	-0.51922500	-1.59845300	-1.57991800
H	0.47936700	-1.15179900	-1.59556200
H	-0.40450600	-2.67643400	-1.74240200
H	-1.10025700	-1.17258900	-2.40232700
C	-2.73847600	0.48081900	2.05854000
H	-2.17532400	1.37674600	2.32669700
H	-3.75785300	0.56553000	2.44474500
H	-2.25946800	-0.37926800	2.53093600
C	-3.51731700	1.52893300	-0.08518000
H	-4.53684600	1.59835800	0.30586700
H	-2.98603000	2.45167200	0.16843200
H	-3.54993300	1.41828700	-1.17135900
N	-1.47861300	0.13741200	-0.12543200
O	-3.49428400	-1.19110900	-1.16314300
N	-3.56502700	-0.89803500	0.27964100
O	-0.48451400	0.80429300	0.61184300
C	0.38691300	1.63732700	-0.17359000
C	1.64608100	0.84798600	-0.58364900
C	-0.26949100	2.22872900	-1.40953100
C	0.82975200	2.72647800	0.80493500
O	2.14816200	0.91104100	-1.68259700
O	2.13332700	0.14470100	0.44282500
H	-0.54540300	1.45654000	-2.12836800
H	-1.16874100	2.77701300	-1.11946300
H	0.43185800	2.91651800	-1.88808400
H	1.61208700	3.34941600	0.35966200
H	-0.02995400	3.35808000	1.04950800
H	1.21261100	2.27341700	1.72283200
C	3.38141800	-0.60720700	0.32424700
C	4.53219400	0.33674800	-0.01541600
C	3.22569300	-1.72479000	-0.70337400
C	3.56221400	-1.18705300	1.72277100
H	5.47910300	-0.20489400	0.07935200
H	4.44932500	0.72334300	-1.03208800
H	4.54860900	1.17649200	0.68779900
H	3.08773200	-1.32651300	-1.71052800
H	4.12629300	-2.34785600	-0.69396200
H	2.37041100	-2.35949000	-0.44644200
H	3.63064900	-0.38484800	2.46380500
H	2.71746100	-1.83150900	1.98522000
H	4.47977100	-1.78189000	1.76389300
H	-2.82438300	-2.90294900	-0.10721800

4a (cis-isomer 1)

C	1.02704900	-1.29773600	0.10390800
C	3.28596200	-0.70788000	-0.15800900
C	2.55821100	0.59979800	0.15401200
C	4.72261000	-0.91718600	0.22771700
H	5.35452800	-0.13112500	-0.19917300
H	4.83839700	-0.90530700	1.31486900
H	5.04949300	-1.88520800	-0.15614400
C	2.97153600	1.13510400	1.52860400
H	4.03932700	1.37878100	1.54888600
H	2.41236300	2.04556600	1.75569700
H	2.76448300	0.40351800	2.31664300
C	2.87603600	1.62079800	-0.93763100
H	2.36744200	2.56914200	-0.75121400
H	3.95491300	1.81213700	-0.93796500
H	2.57859300	1.25078600	-1.91981000
C	0.60468200	-1.83775900	1.46927300
H	-0.36709200	-1.41618700	1.74012200
H	0.54263200	-2.92987000	1.44969600
H	1.32573400	-1.54148500	2.23827200
C	0.12962900	-1.80296900	-1.01534600
H	0.15021900	-2.89707000	-0.99556500
H	-0.89503000	-1.45725500	-0.88708500
H	0.49425000	-1.45399600	-1.98242200
N	1.11886600	0.19176000	0.19370900
O	2.87944300	-1.24400500	-1.38557500
N	2.39393300	-1.82390700	-0.12195900
O	0.35542900	0.82849100	-0.80490900
C	-0.67622100	1.67146500	-0.26190500
C	-1.76495100	0.81623000	0.42760700
C	-0.14954400	2.67334900	0.75420800
C	-1.24651600	2.36616400	-1.49357100
O	-1.95117600	0.80743200	1.62245700
O	-2.48461200	0.12100100	-0.45895700
H	0.22315400	2.16152900	1.64134800
H	0.64419800	3.27565000	0.30382300
H	-0.95869800	3.34112600	1.06448500
H	-2.11575600	2.97340800	-1.22187000
H	-0.47995000	3.01876200	-1.92207400
H	-1.54921000	1.62991400	-2.24047400
C	-3.64333600	-0.67194800	-0.04906400
C	-4.70795300	0.25335000	0.53417500
C	-3.24436200	-1.77174200	0.93263400
C	-4.11568100	-1.27798300	-1.36580800
H	-5.62902200	-0.31530100	0.69905600
H	-4.38695900	0.68023700	1.48622300
H	-4.92808700	1.06414100	-0.16838000
H	-2.92373300	-1.35908700	1.89031400
H	-4.11025200	-2.42067800	1.10245000

H	-2.43894400	-2.38710600	0.51859400
H	-4.36765300	-0.48943300	-2.08136400
H	-3.33137400	-1.90492200	-1.80169400
H	-5.00313600	-1.89532300	-1.19645900

4a (trans-isomer 2)

C	-2.58497300	0.79862300	0.55194300
C	-2.69788100	-1.39796800	-0.25989300
C	-1.21735200	-1.04205100	-0.23106600
C	-3.15408600	-2.81507800	-0.07105500
H	-2.72603800	-3.45804600	-0.84749900
H	-2.84843000	-3.19751300	0.90648500
H	-4.24281600	-2.84493300	-0.14454800
C	-0.50420100	-1.73380000	0.93488000
H	-0.37276200	-2.79778900	0.70887400
H	0.47721500	-1.27866500	1.08218600
H	-1.06106000	-1.65330800	1.87261200
C	-0.55372900	-1.39694600	-1.56275500
H	0.48258300	-1.04634500	-1.58688400
H	-0.53888900	-2.48219900	-1.71632100
H	-1.09614000	-0.92514500	-2.38653700
C	-2.50876400	0.90654100	2.07543700
H	-1.82350000	1.70815700	2.35784300
H	-3.50647500	1.13066800	2.46263700
H	-2.16094100	-0.02094500	2.53519100
C	-3.14434700	2.07759300	-0.05178800
H	-4.14578800	2.27176200	0.34387100
H	-2.49889900	2.92166600	0.21142700
H	-3.19345400	1.98572900	-1.13916900
N	-1.30186200	0.43912600	-0.11554800
O	-3.42822600	-0.62203400	-1.17061900
N	-3.49400700	-0.32902700	0.27311600
O	-0.23209300	0.99522500	0.60705200
C	0.71862800	1.72241400	-0.19168100
C	1.88872000	0.80160700	-0.59056500
C	0.12531000	2.35968800	-1.43678900
C	1.27458800	2.77498300	0.76925200
O	2.39765900	0.80231300	-1.68824200
O	2.29697400	0.05941900	0.44294200
H	-0.22930100	1.60916800	-2.14398400
H	-0.71246600	3.00190400	-1.15619800
H	0.89380300	2.96378700	-1.92505300
H	2.11567900	3.30704500	0.31335300
H	0.48516900	3.49538600	1.00520800
H	1.61122600	2.29892800	1.69366600
C	3.45255600	-0.82840200	0.32986200
C	4.70257900	-0.01998400	-0.00878200
C	3.17487800	-1.92459800	-0.69526600
C	3.56348300	-1.42112600	1.73030100
H	5.58277100	-0.66436200	0.08630400
H	4.66402300	0.37373400	-1.02541500

H	4.81248100	0.81245400	0.69467100
H	3.08933200	-1.51732700	-1.70456800
H	3.99749900	-2.64735700	-0.67788300
H	2.25043100	-2.45498100	-0.44129100
H	3.71704500	-0.62942600	2.46988300
H	2.65190100	-1.96793400	1.99082600
H	4.40991900	-2.11317300	1.77606400