Electronic Supplementary Material (ESI) for ChemComm.

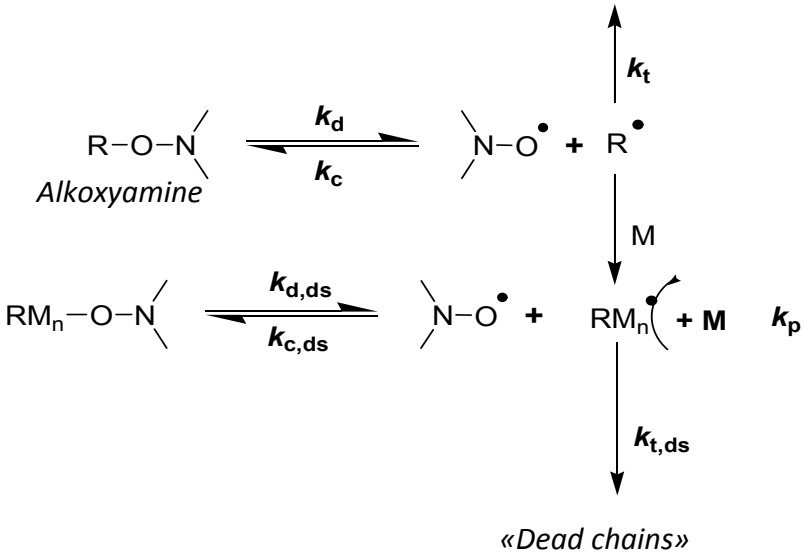
Supporting Information

for

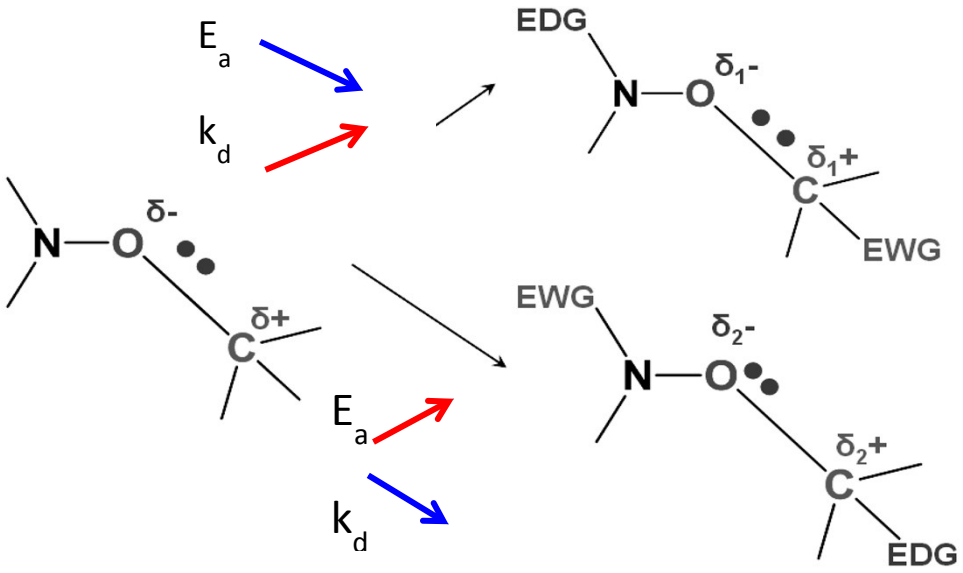
Versatile approach to activation of alkoxyamine homolysis by 1,3-dipolar cycloaddition for efficient and safe nitroxide mediated polymerization

Mariya Edeleva,[1,2] Denis Morozov, [1,2] Dmitriy Parkhomenko,[1] Yulia Polienko,[1,2] Anna Iurchenkova,[2] Igor Kirilyuk,[1,2] Elena Bagryanskaya,[1,2]

[1]*N.N. Vorozhtsov Institute of Organic Chemistry SB RAS, 9 Pr. Lavrentjeva, Novosibirsk 630090, Russia*
[2]*Novosibirsk State University, 2 Pirogova Str., Novosibirsk 630090, Russia*



Scheme 1SI The reaction scheme of Nitroxide Mediated Polymerization.



Scheme 2SI. Influence of electron-withdrawing groups (EWG) and electron-donating groups (EDG) introduction into alkyl and nitroxyl part of alkoxyamine onto polarity of C-ON bond and thus rate of homolysis.

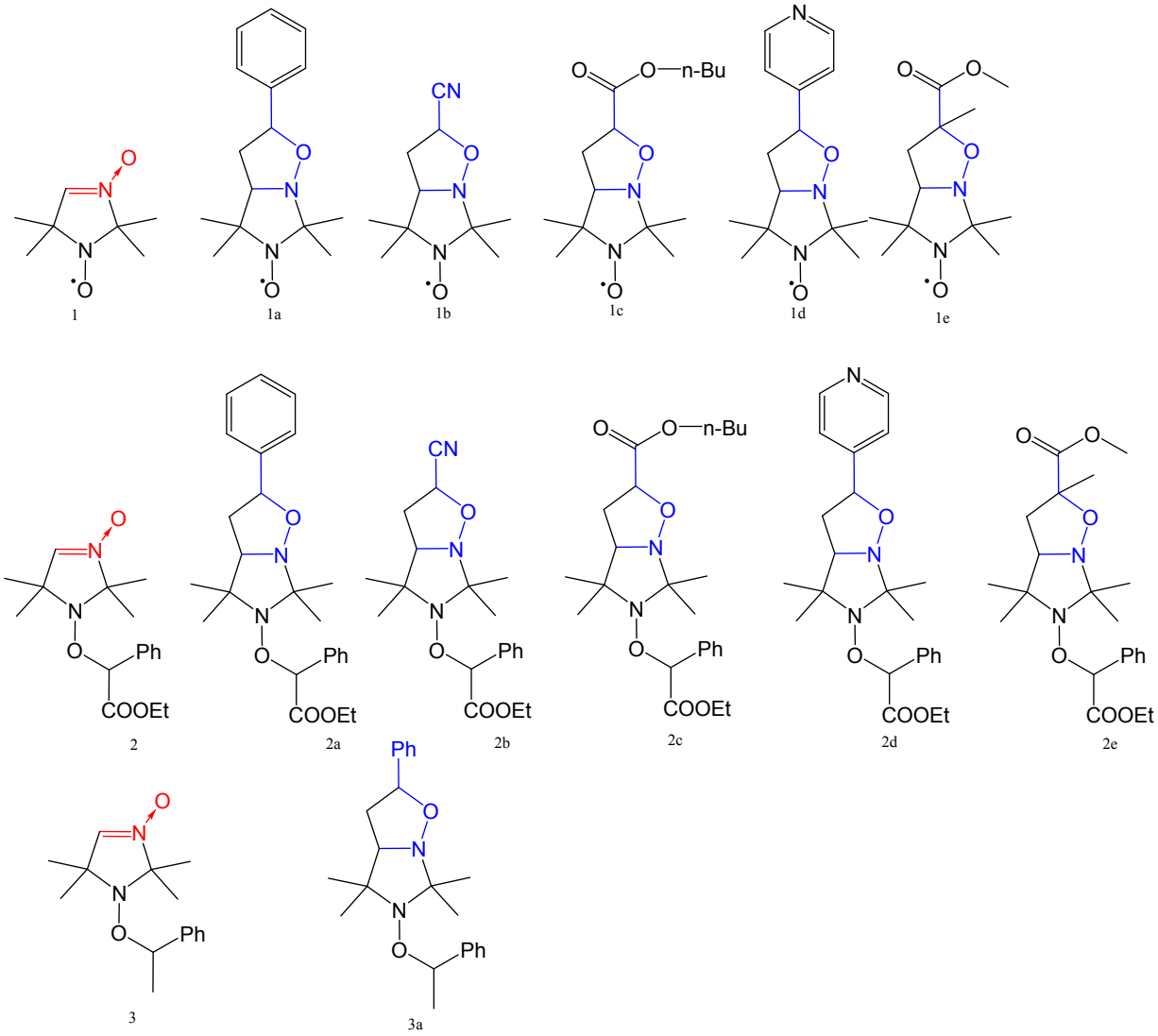


Chart 1SI. Structures of alkoxyamines and nitroxides under discussion.

Experimental procedures

Calculations

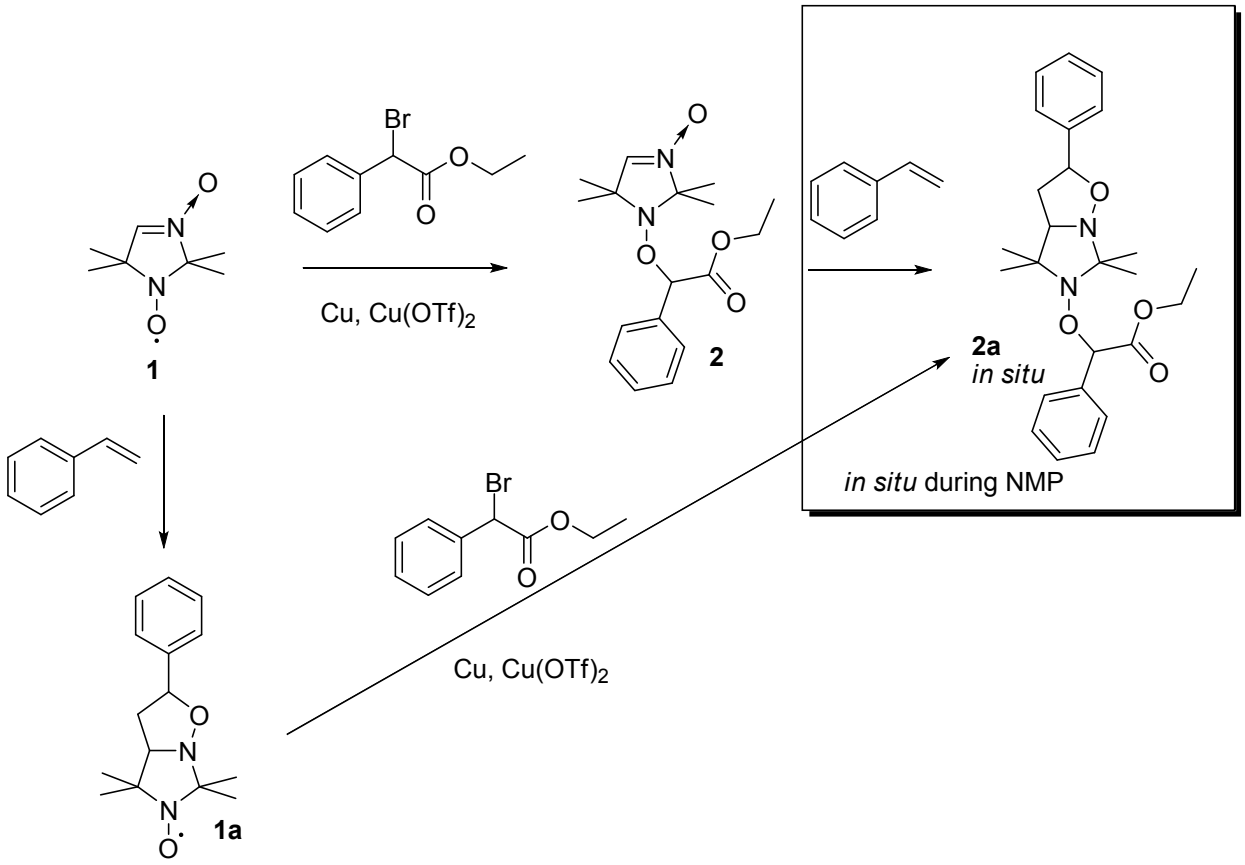
The geometry optimizations and frequency calculations of the alkoxyamines and radical products made use of the Truhlar's group M06-2X density functional[1] and the 6-31+G(d) basis set. All equilibrium structures were ascertained to be the minima points on the potential energy surfaces (PESs). The frequencies were scaled by the recommended scaling factor 0.967.[2] The corresponding thermal corrections calculated using the harmonic oscillator-rigid rotor (RRHO) assumption were included to obtain the enthalpy and Gibbs free energy values at 298 K. The values of energy were then refined at the M06-2X/6-311++(2df,p)//M06-2X/6-31+(d) level of theory. All calculations were performed in Gaussian 09 [3] software package.

Energies

Compound	**ZPE**, Hartree	**E**, Hartree	**H**, Hartree	**G**, Hartree
2	0.386118	-1072.454321	-1072.043561	-1072.122946
2a	0.523359	-1382.098573	-1381.544367	-1381.638179
2b	0.443006	-1243.308498	-1242.837602	-1242.924174
2c	0.569826	-1496.858376	-1496.254721	-1496.35473
2d	0.512088	-1398.140038	-1397.597271	-1397.690632
2e	0.513332	-1418.251024	-1417.70552	-1417.802361
1	0.196749	-534.337820	-534.127842	-534.179126
1a	0.334401	-843.987424	-843.633903	-843.69917
1b	0.253882	-705.196306	-704.926227	-704.984258
1c	0.381266	-958.747279	-958.343067	-958.418512
1d	0.322966	-860.028547	-859.686569	-859.751794
1e	0.324159	-880.139134	-879.794456	-879.862241
3	0.343191	-844.58333	-844.219785	-844.28789
3a	0.480639	-1154.226216	-1153.719197	-1153.802493
alkyl	0.18344	-538.053446	-537.857692	-537.909015
Phenyl ethyl	0.139561	-310.176340	-310.028315	-310.069115

General

Synthesis



Scheme 3 SI. Synthesis of aldonitrone-nitroxide and subsequent "inactive" alkoxyamine **2** and activated with styrene "presynthesized" alkoxyamine **2a**.

The alkoxyamines were prepared using the method developed by Matyjaszewski et al. A mixture of the nitroxide **1** or **1a** (2.54 mmol), ethyl 2-bromo-2-phenylacetate (0.74 g, 3.05 mmol), Cu powder (1615 mg, 25.4 mmol), 4,4`-ditert-butyl-2,2`-bipyridine (34 mg, 0.013 mmol), $Cu(OTf)_2$ (42 mg, 0.013 mmol), and benzene (10 mL) was placed to a Schlenk flask and degassed by three freeze-pump-thaw cycles. The solution was stirred for 24 h at 40 °C. The benzene was removed in vacuum and the residue was separated by column chromatography (silica gel 60, EtOAc (for **2**) or EtOAc/Hexane 4:1 (for **2a**)).

1-(2-Ethoxy-2-oxo-1-phenylethoxy)-2,2,5,5-tetramethyl-2,5-dihydro-1H-imidazole 3-oxide (2).

Yield: 60%; m.p. 63-68 °C;

UV (EtOH) λ_{max} (log ε), nm: _231 (4,02);

IR (KBr) ν: 698.14, 786.85, 863.99, 10018.28, 1062.63, 1083.85, 1162.92, 1178.35, 1207.28, 1226.56, 1278.63, 1342.27, 1369.27, 1461.85, 1496.56, 1598.77, 1739.56, 2871.62, 2933.33, 2979.62, 29696.98, 3035.55;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18-1.24 m, 3H (CH_3, Et); 1.26, 1.28, 1.38, 1.44, 1.48, 1.54, 1.59, 1.74 all s, 12 H (4*CH_3); 4.06-4.12, m, 1H (CH_2, Et); 4.19-4.25, m, 1H (CH_2, Et); 5.13, 5.14, both s, 1H (CH); 6.60, 6.64, both s, 1H (CH);

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.90, 13.96 (CH_3, Et); 21.19, 21.30, 21.81, 22.08, 27.32, 28.06, 28.07, 28.96 (4*CH_3); 61.05, 61.07 (CH_2, Et); 66.26, 66.28 (^{5}C); 86.08, 86.35 (CH); 93.77, 94.32 (^{2}C); 127.32, 128.36, 128.93, 134.67 (Ph); 134.87, 135.59 (CH=N); 170.50, 170.60 (C=O).

Microanalysis: Found for $C_{17}H_{24}N_2O_4$: C 63.43, H 7.30, N 8.77; Calc. C 63.73, H 7.55, N 8.74

Ethyl 2-phenyl-2-((4,4,6,6-tetramethyl-2-phenyltetrahydroimidazo[1,5-b]isoxazol-5(6H)-yl)oxy)acetate (2a).

Yield: 65%;

IR (KBr) ν: 642.21, 700.07, 730.92, 754.07, 850.49, 91799, 1025.99, 1081.92, 1157.13, 1178.35, 1199.56, 1249.70, 1270.92, 1365.42, 1454.13, 1546.70, 1587.20, 1731.84, 2856.19, 2933.33, 2981.55;

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.20-1.26 m, 3H (CH_3, Et); 1.23-1.26 m, 3H (CH_3); 1.30, 1.31, 1.38, 1.45, 1.49, 1.52 all s, 9H (3*CH_3); 2.14-2.26 m, 1H ($^3CH_2$); 2.57-2.68 m, 1H ($^3CH_2$); 3.72-3.75, 3.76-3.87, m, 1H (^{3a}CH); 4.09-4.17 m, 1H (CH_2, Et); 4.18-4.25 m, 1H (CH_2, Et); 5.02-5.07 m, 1H (CH_2-CH); 5.23, 5.25 both s, 1H (CHC=O); 7.22-7.38 m, 8H (Ph); 7.43-7.48 m, 2H (Ph).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.03, 14.06 (CH_3, Et); 24.50, 24.52, 24.76, 24.80, 25.75, 25.85, 25.97, 26.01 (4*CH_3); 40.45, 40.57 ($^3CH_2$); 60.87, 60.94 (CH_2, Et); 62.85, 62.89 (^{4}C); 70.71, 70.99 (^{3a}CH); 80.75, 80.96 (^{2}CH); 85.81, 85.89 (^{6}C); 86.70, 87.04 (CH-COO); 125.80, 127.20, 127.29, 127.41, 128.32, 128.35, 128.38, 128.45, 128.48, 128.69 (10*CH, 2*Ph); 136.66, 136.78 (2*C, Ph); 171.18, 171.28 (C=O).

Microanalysis: Found for $C_{25}H_{32}N_2O_4$: C 70.55, H 7.63, N 6.75 ; Calc. C 70.73, H 7.60, N 6.60

2,2,5,5-tetramethyl-2,5-dihydro-1H-imidazole 3-oxide (1)

EPR parameters: g_{iso} =2.0057 , triplet a_{Niso} =1.42mT

4,4,6,6-tetramethyl-2-phenyltetrahydroimidazo[1,5-b]isoxazol-5(6H)-yl)oxy (1a)

EPR parameters: g_{iso} =2.0056 , triplet a_{Niso} =1.45mT

Measurement of k_d by ^{1}H NMR spectroscopy

The volume of 600 mkl of 0.02 M solution of alkoxyamine in $C_6D_4Cl_2$ with calculated amount of monomer (0, 6, 30-45 eqv respective to alkoxyamine) and thioethanol (6 eqv respective to alkoxyamine) were placed into conventional NMR tube, degassed by Ar bubbling for 5 min and sealed with rubber septum. Than the probhead of conventional NMR spectrometer (Bruker DRX-500 MHz) was heated to 373 K, the sample was placed inside and a series of ^{1}H NMR spectra were recorded with time delay 30 s. ^{1}H NMR spectrum (Bruker DRX-500 MHz NMR spectrometer) was recorded at room temperature before and after the experiment. The integration of NOC(**H**)PhCOOEt and NOC(H)**Ph**COOEt signal was used to estimate the kinetics of homolysis. Experimental data was fitted with monoexponent function to obtain the value of k_d.

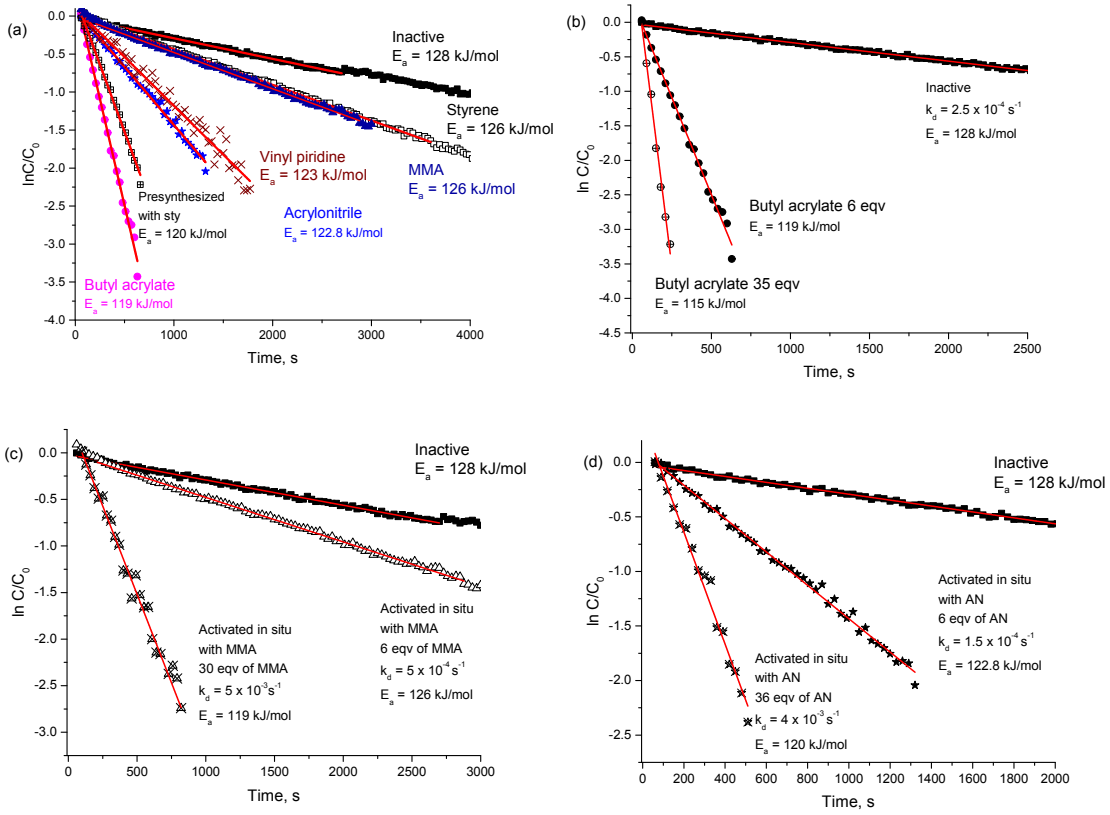


Figure 1 SI Kinetics of inactive alkoxyamine homolysis in different conditions. The temperature of all experiments is 373 K. Solvent used is $C_6D_4Cl_2$. (a) Kinetics of inactive alkoxyamine homolysis in the presence of 6 eqv of activators: (black squares) pure inactive alkoxyamine (k_d = 2.5 x 10^{-4} s^{-1}, E_a = 128 kJ/mol), (white squares) – styrene (k_d = 5 x 10^{-4} s^{-1}, E_a = 126 kJ/mol), (blue triangles) – MMA (k_d = 5 x 10^{-4} s^{-1}, E_a = 126 kJ/mol), (brown crosses) – 4-vinyl pyridine (k_d = 1.3 x 10^{-3} s^{-1}, E_a = 123 kJ/mol), (blue stars) – acrylonitrile (k_d = 1.5 x 10^{-3} s^{-1}, E_a = 122.8 kJ/mol), (purple circles) – n-butyl acrylate (k_d = 5.6 x 10^{-3} s^{-1}, E_a = 119 kJ/mol), (half-colored squares) – presynthesized with styrene alkoxyamine (k_d = 3.6 x 10^{-3} s^{-1}, E_a = 120 kJ/mol). (b)

Table 1 SI. Results of DFT calculation and experimental measurement of homolysis rate constants k_d for inactive alkoxyamine **2** in the presence of 6 and 30-45 eqv of different activators. The temperature of all experiments is 373 K. Solvent used is $C_6D_4Cl_2$.

Activator (target alkoxyamine)	**$\Delta(\Delta G^r)$[a], kJ/mol**	**ΔG^r kJ/mol**	**Amount of activator, eqv**	**k_d, s^{-1} 10^{-3}**	**E_a, kJ/mol**	**$\tau_{,100}$, s**	**$\tau_{,RT}$, days**	**$\varphi([B]_{tot})$**
-	0	91	-	0.25	128	4000	1350	-
Pre-synthesized **2a**	-	-	-	3.6	120	278	53	-
Sty (**2a**)	-12	79	6	0.5	126	417		0.75
			33	2.4	121			
BA (**2c**)	-20	71	6	5.6	119	54		0.96
			35	18.4	115			
MMA (**2e**)	-9	82	6	0.5	126	200		0.77
			30	4	120			
AN (**2b**)	-10	81	6	1.5	123	250		0.9
			30	5	119			
4VP (**2d**)	-13	78	6	1.3	123	250		
			45	5	119			
3	13	104	-	-	-			
3a	-1	90	-	-	-			

[a] relative to the value of **2**

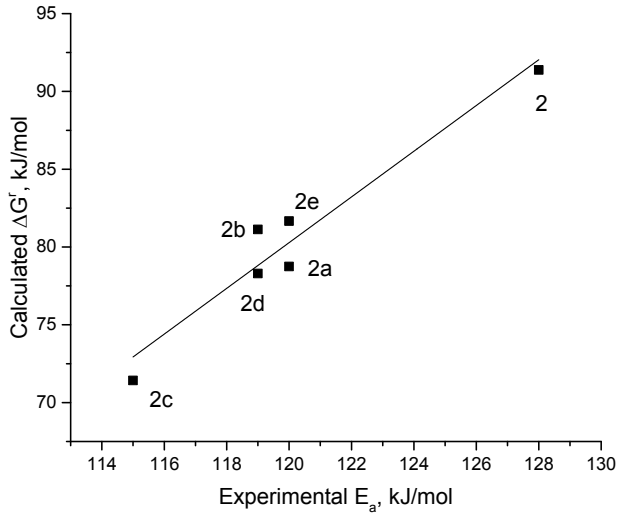
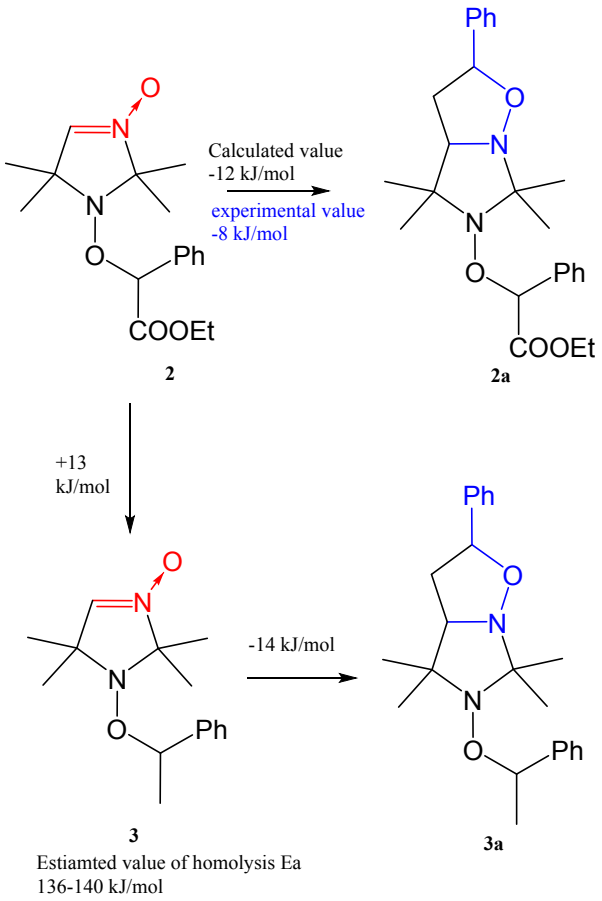
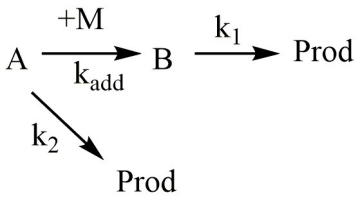


Fig. 2 SI Correlation between measured E_a and calculated ΔG^r of alkoxyamine homolysis



Scheme 4SI. The results of DFT calculations for ΔG^r of C-ON bond homolysis reaction for alkoxyamines under investigations (2 and 2a) and alkoxyamines with phenyl ethyl alkyl substituent mimicking polystyrene polymer chain. Calculated values in black, experimental values in blue.

Solution of alkoxyamine activation by 1,3-cycloaddition reaction scheme with subsequent homolysis.



The reaction scheme consists of the following reactions: (i) inactive alkoxyamine **A** reacts with monomer **M** via 1,3-dipolar cycloaddition to form activated alkoxyamine **B** with the rate constant k_{add}, (ii) activated alkoxyamine **B** undergoes C-ON bond homolysis with rate constant k_1, (iii) inactive alkoxyamine **A** undergoes C-ON bond homolysis with rate constant k_2. In the k_d measurement experiment we monitor the resulting decomposition of activated and non-activated forms. So we are interested in the kinetic equation for (**A**+**B**)(t). The following differential equations describe this kinetic scheme:

$$\frac{dA}{dt} = -\left(k_{add} * M + k_2\right) * A$$

$$\frac{dB}{dt} = k_{add} * M * A - k_1 * B$$

Assuming an excess of **M** over **A** , so the change in concentration of **M** in reaction with **A** could be omitted and time dependence of **A** could be described as first order decay with effective rate constant k_{add} *M+ k_2 :

$$A(t) = A_0 * e^{-(k_{add} * M + k_2) * t}$$

$$B(t) = \frac{k_{add} * M * A_0}{k_1 - k_2 - k_{add} * M} * (e^{-(k_{add} * M + k_2) * t} - e^{-k_1 * t})$$

$$(A + B)(t) = \frac{A_0}{k_1 - k_2 - k_{add} * M} * ((k_1 - k_2) * e^{-(k_{add} * M + k_2) * t} - k_1 * e^{-k_1 * t}) \quad (1)$$

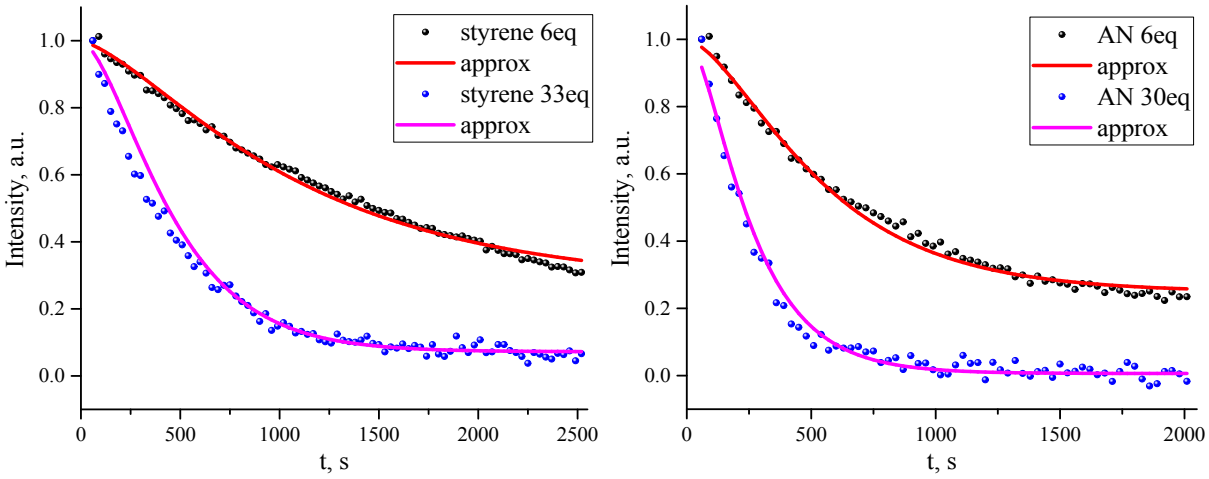
The quota of initial alkoxyamine transformed into active form can be calculated as following:

$$[B]_{tot} = [A]_0 \frac{k_{add} * [M]}{k_{add} * [M] + k_2} \quad (2)$$

$$\varphi([B]_{tot}) = \frac{k_{add} * [M]}{k_{add} * [M] + k_2} \quad (3)$$

Expression (1) was used to approximate the experimental kinetics of alkoxyamine **2** homolysis in the presence of various amounts of monomers. As k_2 we used the value of k_d for **2**. For styrene we used the value of k_d for pre- synthesized **2a** as k_1. The values of k_1 for other monomers were assumed to be k_d's when 30–45 eqv of monomers were used as activators. The figures below (Fig. 3 SI a-d) present the experimental data fitted with eqv. (1).

According to eq. (3), the quota of activated alkoxyamine in cases of small amount of monomer is calculated in table 1SI.



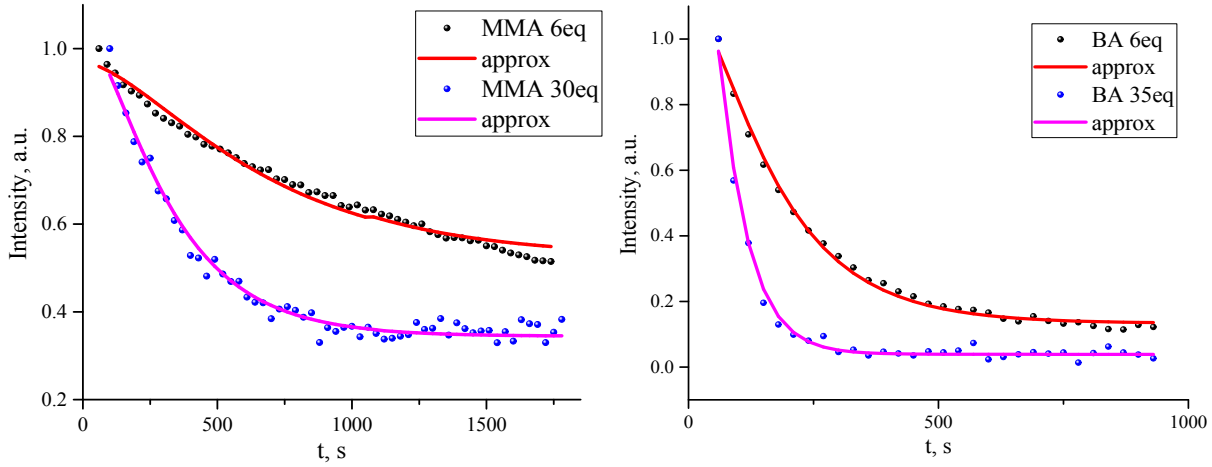


Figure 3SI. Experimental data (points) and fitting curves used for estimation of alken to aldonitrone addition rate constant (See table 1) for different monomers.

Polymerization

Calculated amount of initiator was placed into a 2 ml flask with 1 ml of styrene (distilled prior to use). The reaction vessel was closed with a septum, degassed with bubbling argon for 15 min and placed into the preheated oil bath. Sampling was performed at various time intervals and analyzed for monomer conversion and polymer molecular masses. Conversion was determined by ^{1}H NMR for samples of 20 mkl of reaction mixture diluted to 0.5 ml in $CDCl_3$. Molecular masses are determined by gel permeation chromatography on Agilent LC 1200 chromatograph equipped with two PL-gel-Mixed B columns calibrated with polystyrene samples, and eluted with THF, and refractometric detector to determine molecular masses of the samples.

Living character was determined by both, chain extension experiment and chain end analysis. For chain extension experiment 5 mg of precipitated polymer (M_n =12.7 kDa, D = 1.3) was dissolved in 0.5 ml of styrene, purged with argon and heated at 110 ^{o}C. After 2 h of heating we observed formation of polymer with 19.3 kDa of molecular mass and D = 1.27 highlighting “living” character of chains in polymerization experiment. The fraction of “living” chains was estimated to be 85%.

For end group analysis 1 mg of precipitated polymer (M_n =12.7 kDa, D = 1.3) was dissolved in 100 mkl of toluene ($7x10^{-4}$ M), saturated with oxygen and heated at 110 ^{o}C for 1 h. We observed formation of nitroxide **1a** by EPR as compared to the solution of pure **1a**. (Figure 5 SI)

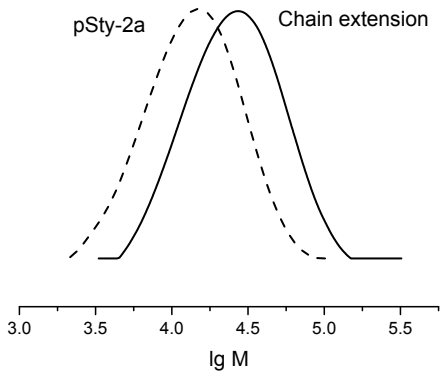


Figure 4 SI. GPC traces obtained for pSty-2a polymer obtained in the NMP experiment after precipitation that was used as macroinitiator (dashed line) and p-Sty obtained after chain extension experiment (solid line)

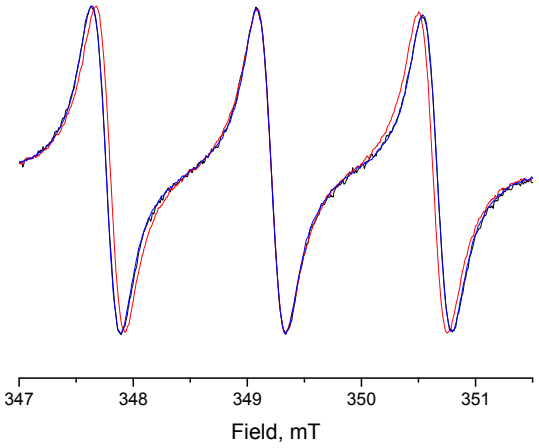


Figure 5 SI. EPR spectra of **1** (red), **1a** (black) and nitroxide obtained after heating of final polymer in oxygen saturated solution (blue).

Geometry parameters of calculated compounds

Geometries

Alkoxyamines

2

C	-2.29462000	0.62803200	-0.47538800
C	-3.60299500	-1.17303400	0.19200000
C	-2.22212500	-1.54445700	0.63515900
H	-4.50636200	-1.75903900	0.30962000
N	-1.48145100	-0.26076000	0.39192100
N	-3.64423500	-0.03594700	-0.42126200
C	-2.44553200	2.00828700	0.14576000
H	-1.47354800	2.50558900	0.14771500
H	-3.16083100	2.59800000	-0.43242700
H	-2.80093800	1.91728700	1.17615300
C	-2.17894400	-1.88123600	2.12868700
H	-2.82558400	-2.73837800	2.34758300
H	-1.15963100	-2.14287600	2.43134600
H	-2.51125400	-1.02448500	2.72072800
C	-1.85447600	0.69354500	-1.93060400

H	-2.62012300	1.23695500	-2.49007300
H	-0.89756900	1.21492600	-2.00017600
H	-1.74180100	-0.30764100	-2.35622300
C	-1.69016800	-2.72288000	-0.19115100
H	-0.67841200	-2.99723300	0.12130000
H	-2.34738700	-3.58565000	-0.03916800
H	-1.67025900	-2.48431700	-1.25779000
O	-4.62996800	0.55379000	-0.94762800
O	-0.23983600	-0.53082600	-0.22334800
C	0.81453300	-0.28737900	0.68019400
H	0.58866300	-0.72192700	1.66048200
C	2.08625200	-0.89221600	0.11438600
C	3.22716300	-0.93636500	0.92117600
C	2.14260500	-1.37410200	-1.19339100
C	4.41518100	-1.46425100	0.42417400
H	3.18095200	-0.55020300	1.93724600
C	3.33454300	-1.90631200	-1.68595100
H	1.25606100	-1.33361600	-1.81787600
C	4.47079000	-1.95227100	-0.88152200
H	5.29726700	-1.49578700	1.05694200
H	3.37333000	-2.28336700	-2.70389400
H	5.39711500	-2.36575100	-1.26951700
C	1.05761800	1.20184300	0.91864000
O	1.44410900	1.64398300	1.97400500
O	0.86519200	1.92408800	-0.18809000
C	1.20213700	3.32214000	-0.10258000
H	0.64872200	3.78385300	-0.92318100
H	0.83657300	3.71398600	0.85039100
C	2.69863600	3.52076000	-0.25216600
H	2.93356400	4.58962900	-0.24431500
H	3.23334300	3.04365300	0.57315900
H	3.04835500	3.09445400	-1.19666400

2a

C	0.29862800	-1.75255100	-0.22157900
C	1.79860600	-1.23300000	1.53777900
C	0.79159700	-0.06574200	1.47046300
N	-0.29981700	-0.77324200	0.75592000
N	1.69745700	-1.93351300	0.23578600
C	-0.39104000	-3.09989500	-0.01464000
H	-1.46386500	-3.00354400	-0.20105500
H	0.02953100	-3.84394200	-0.69766900
H	-0.24725600	-3.44322800	1.01410200
C	0.32247700	0.33272500	2.86849100
H	1.16345200	0.72190800	3.45537600
H	-0.43135000	1.12629000	2.81016700
H	-0.11011900	-0.52473900	3.39350100

C	0.20458200	-1.31363800	-1.67709300
H	0.76706800	-2.01790200	-2.29620800
H	-0.84476000	-1.31353500	-1.97906500
H	0.61238800	-0.31301800	-1.82768800
C	1.28313100	1.18610500	0.73014000
H	0.47482700	1.92204500	0.69094400
H	2.12428300	1.64226300	1.26275400
H	1.60597900	0.96704700	-0.28821200
O	2.59116000	-1.16005100	-0.59280300
O	-1.14791700	0.15816000	0.11694200
C	-2.42013100	0.15163100	0.72545000
H	-2.32016100	0.06545400	1.81236500
C	-3.14997800	1.43044400	0.36175300
C	-4.30536000	1.77026700	1.07085700
C	-2.70965000	2.24886600	-0.67884900
C	-5.01203800	2.92497800	0.74727600
H	-4.65050900	1.12336100	1.87460500
C	-3.41868300	3.40734400	-0.99768400
H	-1.81486300	1.97812400	-1.23045600
C	-4.56845500	3.74755100	-0.28825800
H	-5.90644300	3.18450000	1.30606800
H	-3.07025800	4.04449400	-1.80559800
H	-5.11734300	4.65031100	-0.54001000
C	-3.28626300	-1.02969200	0.28957900
O	-4.08296100	-1.56761000	1.02156000
O	-3.10236700	-1.34278500	-0.99594300
C	-3.94592900	-2.38055900	-1.52772200
H	-3.39890300	-2.75524600	-2.39576800
H	-4.03823400	-3.17572300	-0.78280500
C	-5.30207000	-1.82110100	-1.91420500
H	-5.91103700	-2.60670100	-2.37256300
H	-5.82751100	-1.44726500	-1.03152100
H	-5.18771500	-1.00504600	-2.63322600
H	1.47056600	-1.93208600	2.31480500
C	3.28395300	-0.89373300	1.64610100
H	3.80241600	-1.57983700	2.32002200
H	3.45128200	0.12521700	2.00439200
C	3.77209000	-1.08105500	0.18325500
H	4.30001600	-2.04382600	0.10910000
C	4.65432000	0.02504500	-0.33947900
C	4.34495900	0.72985600	-1.50320100
C	5.82392800	0.34196100	0.35868700
C	5.18985200	1.74450000	-1.95460800
H	3.44216400	0.48080700	-2.05237700
C	6.66736500	1.35279300	-0.09226800
H	6.07603500	-0.20786700	1.26392700
C	6.35044400	2.05991700	-1.25245000

H	4.93778800	2.28939600	-2.85994700
H	7.57142500	1.58966900	0.46134600
H	7.00629000	2.85009700	-1.60605900

2b

C	-1.32650900	1.39596900	-0.36229300
C	-2.92648800	0.50355900	1.12291500
C	-1.72012400	-0.45848500	1.18183000
N	-0.68311500	0.44964400	0.62231100
N	-2.78609300	1.26668300	-0.13462200
C	-0.96995400	2.82143700	0.05677200
H	0.11453100	2.95210800	0.03155800
H	-1.43927300	3.53975900	-0.62167800
H	-1.31659000	3.01780200	1.07594100
C	-1.38888200	-0.80297600	2.63393700
H	-2.23044400	-1.32749000	3.10309600
H	-0.52101200	-1.46857000	2.68749500
H	-1.17016700	0.10289500	3.20746200
C	-0.93925500	1.13983600	-1.81203400
H	-1.52878900	1.79817400	-2.45616200
H	0.12300400	1.35760500	-1.93687500
H	-1.12370800	0.10560100	-2.10550500
C	-1.87504200	-1.75633000	0.37595800
H	-0.97129800	-2.36176900	0.48420300
H	-2.71536700	-2.34755100	0.75589500
H	-2.03559600	-1.57146000	-0.68705000
O	-3.34569700	0.34552200	-1.10621300
O	0.34471700	-0.30363900	0.01445900
C	1.53490100	-0.21007400	0.76723400
H	1.33617500	-0.38545300	1.82981300
C	2.51743300	-1.23326300	0.23272200
C	3.61506700	-1.59834500	1.01606300
C	2.36262500	-1.77915500	-1.04247000
C	4.54930900	-2.50985700	0.53029900
H	3.73793400	-1.16266900	2.00546000
C	3.29593500	-2.69685700	-1.52249700
H	1.51029600	-1.48805800	-1.64810700
C	4.38929300	-3.06339200	-0.73992400
H	5.39914400	-2.79125000	1.14518200
H	3.16726600	-3.12599800	-2.51200700
H	5.11407600	-3.77867100	-1.11767200
C	2.18777600	1.16878600	0.68347500
O	2.74420400	1.69512500	1.61734400
O	2.13067700	1.67495900	-0.55208900
C	2.83944900	2.90879000	-0.77126700
H	2.38270800	3.32610800	-1.67137700
H	2.65494500	3.57654000	0.07501400
C	4.32153000	2.64576200	-0.96150400
H	4.83827000	3.58168100	-1.19575600
H	4.75661000	2.22968700	-0.04924500
H	4.48155300	1.94339100	-1.78447700
H	-2.85394900	1.21717700	1.95071600
C	-4.32307300	-0.10101700	1.01399700
H	-5.06352500	0.50504600	1.53881400

H	-4.37306100	-1.11977700	1.40305300
C	-4.57299300	-0.03486200	-0.51933700
H	-5.34561900	0.70984100	-0.74861000
C	-4.97342900	-1.32711700	-1.10017600
N	-5.31718400	-2.34559800	-1.52331500

2c

C	-0.03438853	-1.67850633	0.07730992
C	1.49528281	-0.67632833	1.60421510
C	0.47823518	0.41515176	1.21738531
N	-0.61358824	-0.48811571	0.78855172
N	1.36585601	-1.73726840	0.57188799
C	-0.72947808	-2.93033895	0.60771534
H	-1.80018525	-2.89257742	0.38698315
H	-0.30067961	-3.82176711	0.14022541
H	-0.60106877	-3.00195809	1.69159916
C	0.01360549	1.21539548	2.43175817
H	0.84291010	1.79789429	2.85014891
H	-0.77235478	1.92183543	2.13850543
H	-0.38205203	0.55212023	3.20749719
C	-0.13185397	-1.60601913	-1.44137617
H	0.40545955	-2.45358014	-1.87537938
H	-1.18529109	-1.65555337	-1.72482486
H	0.29732205	-0.68462514	-1.83611826
C	0.95127497	1.38154357	0.12282470
H	0.10055720	1.98102253	-0.21438579
H	1.69937720	2.07249405	0.52693595
H	1.39361720	0.87127753	-0.73401153
O	2.26580200	-1.27617799	-0.46158385
O	-1.55217977	0.20861697	-0.00002842
C	-2.80538981	0.23557403	0.65010735
H	-2.66052555	0.27767345	1.73443980
C	-3.60288282	1.43595417	0.17636618
C	-4.75776613	1.78754662	0.88096057
C	-3.23108784	2.16509253	-0.95328682
C	-5.53259781	2.86554862	0.46422427
H	-5.04845761	1.20849639	1.75483656
C	-4.00895088	3.24786497	-1.36599130
H	-2.33744020	1.88377352	-1.50153396
C	-5.15824935	3.59978404	-0.66148148
H	-6.42634694	3.13430399	1.01980194
H	-3.71480344	3.81586652	-2.24403373
H	-5.76025188	4.44349457	-0.98640362
C	-3.64063596	-1.01630799	0.37973536
O	-4.39617185	-1.49358296	1.19373910
O	-3.48022244	-1.46940913	-0.86605720
C	-4.30236874	-2.58640263	-1.25077075

H	-3.77279289	-3.03371760	-2.09445972
H	-4.33716866	-3.29944343	-0.42238473
C	-5.69163831	-2.11798541	-1.64109146
H	-6.28627299	-2.96804565	-1.99012303
H	-6.19938309	-1.66964084	-0.78320606
H	-5.63294779	-1.37934136	-2.44552495
H	1.19602719	-1.11421100	2.56256666
C	2.98255748	-0.31872482	1.57197119
H	3.52561806	-0.73051898	2.42420157
H	3.13975315	0.76340151	1.55658392
C	3.44110264	-0.99532455	0.25070868
H	3.98625821	-1.92111913	0.47491049
C	4.31344891	-0.08567214	-0.58904758
O	3.95053252	0.57391807	-1.52882118
O	5.56335298	-0.08510465	-0.10124030
C	6.50121407	0.77010046	-0.77477713
C	7.84885966	0.59488990	-0.10469871
H	6.14368152	1.80397675	-0.71259238
H	6.53259162	0.48915325	-1.83296308
C	8.93001860	1.44191126	-0.77547179
H	7.76295207	0.86694617	0.95513819
H	8.12975825	-0.46537199	-0.14028213
H	9.00424642	1.16534303	-1.83534868
H	8.63589593	2.49941119	-0.75026484
C	10.29150300	1.27155261	-0.10454186
H	10.61493248	0.22533252	-0.13825667
H	11.05869541	1.87611855	-0.59734208
H	10.24930844	1.57352712	0.94772279

2d

C	0.30492500	-1.74913100	-0.21086400
C	1.80423200	-1.21199500	1.54430800
C	0.79454000	-0.04785300	1.46802000
N	-0.29483900	-0.76420100	0.75965600
N	1.70461600	-1.92356500	0.24807100
C	-0.38061600	-3.09689900	0.00628000
H	-1.45350800	-3.00472800	-0.18136300
H	0.04214200	-3.84497400	-0.67092600
H	-0.23658200	-3.43186000	1.03773600
C	0.32491700	0.36107500	2.86279500
H	1.16407700	0.75997900	3.44573400
H	-0.43274200	1.15028100	2.79737800
H	-0.10335500	-0.49350900	3.39587600
C	0.20961500	-1.32130400	-1.66950600
H	0.77206900	-2.02948800	-2.28415000
H	-0.84001300	-1.32482800	-1.97022800
H	0.61514500	-0.32096400	-1.82801200
C	1.28209800	1.19930700	0.71697500

H	0.47277200	1.93380000	0.67518300
H	2.12397300	1.66143000	1.24348200
H	1.59973500	0.97372900	-0.30163600
O	2.59838500	-1.15521000	-0.58710900
O	-1.14630500	0.15964800	0.11532700
C	-2.41917000	0.15144000	0.72393500
H	-2.31846100	0.07142300	1.81119900
C	-3.15379400	1.42540400	0.35370000
C	-4.30435400	1.76945700	1.06853100
C	-2.72332400	2.23469500	-0.69816400
C	-5.01611800	2.91945300	0.73933400
H	-4.64174700	1.12990300	1.88137300
C	-3.43726200	3.38861100	-1.02246400
H	-1.83231600	1.96084000	-1.25438500
C	-4.58229900	3.73302000	-0.30736000
H	-5.90675300	3.18239100	1.30248300
H	-3.09665300	4.01867200	-1.83918000
H	-5.13504800	4.63216300	-0.56344000
C	-3.28023500	-1.03587900	0.29444600
O	-4.07410000	-1.57307800	1.02983800
O	-3.09525000	-1.35527900	-0.98942400
C	-3.93728300	-2.39728400	-1.51618000
H	-3.39039800	-2.77404800	-2.38340300
H	-4.02681900	-3.18971200	-0.76801600
C	-5.29509000	-1.84241500	-1.90321900
H	-5.90262300	-2.63121200	-2.35791300
H	-5.82055300	-1.46657200	-1.02141100
H	-5.18348400	-1.02887700	-2.62549600
H	1.47833600	-1.90604900	2.32658100
C	3.28912200	-0.86956700	1.65134400
H	3.80921700	-1.54893900	2.33046600
H	3.45450800	0.15272400	2.00096400
C	3.77579300	-1.07075200	0.18998000
H	4.31069200	-2.03015800	0.12302800
C	4.65562100	0.03050300	-0.33918800
C	4.35063700	0.74413100	-1.49543800
C	5.83376800	0.35832400	0.33455900
C	5.22571300	1.74753000	-1.91221100
H	3.45080600	0.52223900	-2.05965100
C	6.63729300	1.37657100	-0.16784200
H	6.12581500	-0.16945500	1.23963000
H	5.00710900	2.32091000	-2.81048500
H	7.55842800	1.64987900	0.34228000
N	6.35050900	2.07172500	-1.27249900

2e

C	-0.08387516	-1.85077399	0.10016517

C	1.49731851	-1.00776084	1.64097481
C	0.52430980	0.15547282	1.35228083
N	-0.61332764	-0.64639160	0.83810462
N	1.33120828	-1.96847190	0.53025774
C	-0.79592069	-3.08386267	0.65420907
H	-1.87261106	-3.00370359	0.48158115
H	-0.41814806	-3.98626023	0.16441892
H	-0.62580355	-3.16808454	1.73185072
C	0.11718620	0.86102388	2.64451805
H	0.98694893	1.34053887	3.11009905
H	-0.61723655	1.64746550	2.43698851
H	-0.31976231	0.15240082	3.35497445
C	-0.23340132	-1.76862189	-1.41297830
H	0.25885750	-2.63543026	-1.86276969
H	-1.29582956	-1.77747204	-1.66341491
H	0.22043795	-0.86397219	-1.81890215
C	1.03340603	1.19706687	0.34630019
H	0.26903934	1.96565168	0.20102031
H	1.92841058	1.69448730	0.73960111
H	1.27946573	0.76026419	-0.62233421
O	2.18585072	-1.40181490	-0.49221874
O	-1.44285852	0.15410525	0.02254420
C	-2.69630530	0.33979861	0.64057874
H	-2.56916004	0.50078396	1.71641630
C	-3.38807925	1.53193798	0.00601563
C	-4.54725155	2.03418110	0.60432813
C	-2.90553217	2.11419974	-1.16658880
C	-5.21558379	3.11582179	0.03849866
H	-4.92506987	1.57168270	1.51366261
C	-3.57714245	3.20018436	-1.72894173
H	-2.00732090	1.71886864	-1.63019896
C	-4.73037973	3.70269865	-1.13059711
H	-6.11314430	3.50294655	0.51195151
H	-3.19578595	3.65279381	-2.63980683
H	-5.24937140	4.54896825	-1.57133788
C	-3.61640635	-0.87311135	0.50465800
O	-4.40779987	-1.19854677	1.35811345
O	-3.48583752	-1.47498929	-0.68015288
C	-4.38894152	-2.56330850	-0.94765888
H	-3.88745364	-3.14695212	-1.72274463
H	-4.48912679	-3.16820632	-0.04228374
C	-5.73203013	-2.03709473	-1.41784380
H	-6.39056658	-2.87302929	-1.67362649
H	-6.20968225	-1.44912872	-0.62972326
H	-5.60624082	-1.40824176	-2.30371823
H	1.18301352	-1.50794021	2.56363626
C	2.99174806	-0.71224429	1.62621974

H	3.52540675	-1.34537254	2.33948662
H	3.22019848	0.32779877	1.86981830
C	3.39691035	-1.09705982	0.17481708
C	4.03075776	0.05742061	-0.59351477
O	3.68546659	0.46107149	-1.67351963
O	5.08074374	0.55159627	0.08708790
C	5.79367541	1.60076938	-0.57260838
H	5.12979979	2.44753486	-0.76129508
H	6.19671866	1.24277508	-1.52281703
H	6.59723960	1.88269265	0.10591352
C	4.33969874	-2.30346441	0.14366198
H	4.58036171	-2.56593391	-0.89070277
H	5.26332312	-2.08886838	0.68851479
H	3.82957609	-3.15028644	0.61160254

3

C	2.07342300	-0.93830500	0.06101400
C	3.13046000	1.04497000	-0.51190100
C	1.71054600	1.44568800	-0.25170100
H	3.94657600	1.68673600	-0.82052400
N	1.18405200	0.19862400	0.39075400
N	3.32917900	-0.22277600	-0.35141500
C	2.38456400	-1.77491400	1.29019600
H	1.47716400	-2.29550300	1.60879300
H	3.15826600	-2.50847500	1.05167100
H	2.73270200	-1.13301600	2.10446100
C	1.63623300	2.60629600	0.74581500
H	2.14963500	3.48853800	0.34682000
H	0.59373300	2.88156800	0.93530800
H	2.10258500	2.32154900	1.69280600
C	1.62640300	-1.80674000	-1.11010000
H	2.46042300	-2.45808900	-1.38478800
H	0.77079500	-2.41765000	-0.81395000
H	1.34096200	-1.20168400	-1.97399900
C	0.99108600	1.82246800	-1.55340600
H	-0.05177000	2.08684500	-1.35630200
H	1.49246900	2.68679000	-2.00181600
H	1.00552300	1.00066600	-2.27309900
O	4.38903200	-0.89332600	-0.50926500
O	-0.11830300	-0.08963400	-0.05664600
C	-1.09070300	0.19744700	0.95556100
H	-0.96648500	1.24134900	1.27488200
C	-2.44124000	0.03983100	0.29582000
C	-3.49245700	0.88994800	0.64217200
C	-2.66949900	-0.98502100	-0.62683900
C	-4.75785700	0.71787800	0.08287400
H	-3.32054700	1.69386400	1.35543400

C	-3.93145800	-1.15372500	-1.19221500
H	-1.85011000	-1.64023800	-0.90969300
C	-4.97937400	-0.30484300	-0.83731500
H	-5.56750700	1.38665200	0.36061500
H	-4.09660300	-1.94843400	-1.91414000
H	-5.96267100	-0.43755400	-1.27907100
C	-0.93460600	-0.72450800	2.15820300
H	-1.04528000	-1.76807200	1.84171000
H	0.04760600	-0.58505700	2.61729700
H	-1.70903400	-0.50686900	2.90043800

3a

C	-0.02519100	-1.61029100	-1.04351500
C	1.22112300	-1.60354900	0.99247600
C	0.05209800	-0.61845600	1.17111700
N	-0.84858000	-1.20460800	0.14677100
N	1.32746000	-1.84405100	-0.47074600
C	-0.52258300	-2.95982100	-1.55346900
H	-1.54064400	-2.86946600	-1.94210700
H	0.13271300	-3.31183900	-2.35554500
H	-0.51511200	-3.69461500	-0.74263200
C	-0.57616300	-0.75184500	2.55701100
H	0.17151700	-0.53753800	3.33039700
H	-1.39299100	-0.03218400	2.68310400
H	-0.96638900	-1.76282200	2.71208700
C	-0.02989900	-0.59240700	-2.18133700
H	0.68336900	-0.90705900	-2.94772500
H	-1.03143500	-0.55973800	-2.61735300
H	0.23623800	0.41008200	-1.84484300
C	0.40684700	0.85483700	0.92282100
H	-0.51608600	1.42210400	0.76959900
H	0.91655400	1.27288500	1.79753900
H	1.05666800	0.99206000	0.05699800
O	2.22988100	-0.80283500	-0.89901900
O	-1.85902700	-0.29816000	-0.22569500
C	-3.12970700	-0.69911300	0.29561800
H	-3.01079200	-0.93393500	1.36077000
C	-4.05650400	0.48665900	0.15379500
C	-5.10730100	0.64459300	1.06017800
C	-3.92002400	1.39969800	-0.89486000
C	-6.01528200	1.69164400	0.92154400
H	-5.21422500	-0.05907900	1.88391100
C	-4.82538800	2.45131100	-1.03190200
H	-3.09626400	1.28856800	-1.59450700
C	-5.87577900	2.59912300	-0.12746800
H	-6.82582700	1.80310600	1.63609600
H	-4.70824800	3.15930200	-1.84759000

H	-6.57984400	3.41886100	-0.23705700
C	-3.67519300	-1.92691100	-0.42371500
H	0.95023400	-2.55638300	1.46016000
C	2.62067000	-1.13163700	1.39221900
H	3.15256900	-1.88186700	1.98205200
H	2.58851800	-0.20314800	1.96871300
C	3.30133400	-0.91417400	0.01660200
H	3.88249900	-1.81368400	-0.23769800
C	4.18063200	0.30659900	-0.07353700
C	3.98064300	1.29049900	-1.04282500
C	5.23622200	0.44628700	0.83300700
C	4.82500700	2.40025700	-1.09949700
H	3.16546800	1.18254700	-1.75182700
C	6.07803200	1.55287100	0.77608500
H	5.40035700	-0.31875600	1.58987400
C	5.87355900	2.53555600	-0.19318700
H	4.66115900	3.16082200	-1.85764800
H	6.89282200	1.64948200	1.48794800
H	6.52853900	3.40063500	-0.23962700
H	-3.01692100	-2.78343700	-0.25761700
H	-4.67295100	-2.17033400	-0.04458900
H	-3.75341500	-1.72638100	-1.49833400

Nitroxides

1

C	-1.03228600	-0.39638400	-0.02147600
C	0.36884900	1.46479400	0.03403100
C	1.33351800	0.31588400	-0.00583000
H	0.61280300	2.51914900	0.06915600
N	0.37301100	-0.80222100	-0.10619500
N	-0.87388800	1.09182200	0.02811900
C	-1.80596300	-0.78702600	-1.26902100
H	-1.81616100	-1.87771100	-1.34432100
H	-2.82797200	-0.40850800	-1.19902900
H	-1.32798800	-0.37115500	-2.16062600
C	2.23882800	0.33211400	-1.24056200
H	2.93479500	1.17535500	-1.18849500
H	2.81418700	-0.59765300	-1.27859600
H	1.64535000	0.41897000	-2.15521000
C	-1.68772100	-0.88304900	1.26095400
H	-2.70017000	-0.47862000	1.32712400
H	-1.72197100	-1.97532100	1.24265800
H	-1.11289000	-0.55998300	2.13373800

C	2.16047100	0.18582400	1.27741400
H	2.73696600	-0.74303600	1.24477900
H	2.85193400	1.02969000	1.36524200
H	1.51239800	0.16918600	2.15830200
O	-1.91865700	1.80045900	0.05926900
O	0.72499300	-2.01552300	-0.04442600

1a

C	2.26769000	-1.04677200	-0.21129800
C	1.10328200	0.82918100	-1.06373600
C	1.57225700	1.26354400	0.35396200
N	2.25149600	0.02830400	0.80857600
N	1.18861500	-0.65886900	-1.11868300
C	3.58822100	-1.00239100	-0.98298300
H	4.41352900	-1.10297400	-0.27262700
H	3.62294700	-1.82247300	-1.70488300
H	3.70710800	-0.05782700	-1.52219700
C	2.58108600	2.40996700	0.28557100
H	2.09731100	3.30955400	-0.11127200
H	2.96701100	2.62788700	1.28523700
H	3.42764300	2.15349000	-0.36002100
C	2.05893800	-2.40353500	0.43949600
H	1.95968500	-3.16932400	-0.33472100
H	2.92710900	-2.62832400	1.06410500
H	1.16354800	-2.40380300	1.06190900
C	0.46917400	1.59470800	1.35981900
H	0.91955500	1.64472300	2.35651700
H	0.01382000	2.56638800	1.14085400
H	-0.31180000	0.82958000	1.36623300
O	-0.05788500	-1.03785000	-0.50015500
O	3.02480900	0.01343600	1.81006800
H	1.79427700	1.22808400	-1.81189200
C	-0.35557900	1.09526000	-1.44493200
H	-0.44026300	1.40204100	-2.49004200
H	-0.81303800	1.86865600	-0.82428400
C	-1.02064800	-0.29202400	-1.22242800
H	-1.17338400	-0.77476300	-2.19859300
C	-2.32229400	-0.25817600	-0.46187600
C	-2.46361900	-0.84527200	0.79611300
C	-3.41822500	0.38977800	-1.04042300
C	-3.68438700	-0.77483400	1.46876800
H	-1.61664800	-1.35582400	1.24445800
C	-4.63478200	0.46066100	-0.36909800
H	-3.31641100	0.84149300	-2.02588500
C	-4.77063700	-0.12214600	0.89171900
H	-3.78421200	-1.23380300	2.44829900
H	-5.47765300	0.96779300	-0.82984300

H	-5.71917100	-0.06900000	1.41805800

1b

C	-1.31108400	-1.07403400	0.04317700
C	0.08847400	0.48472500	1.14448800
C	-0.56627300	1.29393600	-0.00842700
N	-1.41069400	0.24491300	-0.62510200
N	-0.07190700	-0.95962900	0.81606200
C	-2.47399500	-1.24464200	1.02222700
H	-3.41226400	-1.14544000	0.46966600
H	-2.42457300	-2.23233300	1.48767200
H	-2.45385200	-0.48494600	1.80959800
C	-1.44911200	2.42015700	0.52696700
H	-0.83265900	3.16487500	1.04280700
H	-1.97307900	2.90765900	-0.29932200
H	-2.19700400	2.03611300	1.22851900
C	-1.28782300	-2.19313700	-0.98409200
H	-1.11225600	-3.14908800	-0.48312300
H	-2.25792700	-2.22060600	-1.48666600
H	-0.50790200	-2.02621800	-1.72747200
C	0.38329700	1.83258700	-1.08091600
H	-0.21941300	2.17509700	-1.92807700
H	0.95991000	2.68557000	-0.70796900
H	1.07060700	1.06174200	-1.44017700
O	1.02869800	-1.16438100	-0.10297700
O	-2.35289600	0.51871100	-1.42296000
H	-0.45090400	0.67270300	2.07705200
C	1.59970500	0.61729000	1.34589600
H	1.86592900	0.57802600	2.40348000
H	2.00043600	1.53931400	0.92223900
C	2.13060800	-0.64637100	0.61415600
H	2.48750600	-1.38934900	1.33790800
C	3.20754600	-0.36099000	-0.34635600
N	4.07159700	-0.11169600	-1.07115500

1c

C	2.75043191	-0.98558416	-0.08040973
C	1.26631265	0.50844493	-1.16158317
C	1.86465843	1.33170443	0.01260871
N	2.77736782	0.32800568	0.60552601
N	1.51388708	-0.92964037	-0.86152685
C	3.92986159	-1.07849325	-1.05024419
H	4.85727588	-0.93190965	-0.48982668
H	3.94062973	-2.06183797	-1.52762662
H	3.87074664	-0.31235409	-1.82942220
C	2.67180809	2.52572817	-0.49422515
H	2.00821648	3.23939935	-0.99549227
H	3.16164074	3.02808499	0.34412260

H	3.44436636	2.20730595	-1.20236095
C	2.77935710	-2.11624194	0.93407207
H	2.67092451	-3.07512466	0.41961965
H	3.74095543	-2.08906730	1.45302306
H	1.97566662	-2.00418678	1.66242198
C	0.88199011	1.77575646	1.09850270
H	1.46263791	2.13873727	1.95289921
H	0.25034089	2.59849637	0.74516203
H	0.25021898	0.94943451	1.43579413
O	0.41732153	-1.22509199	0.03375175
O	3.70410690	0.64519153	1.40605014
H	1.80068513	0.75030332	-2.08504828
C	-0.24967780	0.55148720	-1.36847125
H	-0.51151591	0.53474362	-2.42766015
H	-0.70397704	1.43802861	-0.91982240
C	-0.70414305	-0.76436415	-0.67623976
H	-1.00920999	-1.49994430	-1.43125300
C	-1.84579898	-0.54410270	0.29507451
O	-1.75672800	-0.49448839	1.49455804
O	-2.98630280	-0.36712212	-0.38798457
C	-4.15184326	-0.07454734	0.40154717
C	-5.33325861	0.03589545	-0.54022703
H	-3.97757005	0.85879753	0.94895420
H	-4.28782391	-0.87434894	1.13704652
C	-6.61971222	0.39004129	0.20584749
H	-5.11942105	0.79981314	-1.29858863
H	-5.45805707	-0.91606227	-1.07175474
H	-6.81134367	-0.36135185	0.98289384
H	-6.48762918	1.34801014	0.72562515
C	-7.82224838	0.47678452	-0.73173368
H	-7.99693067	-0.48174344	-1.23245763
H	-8.73361215	0.74346708	-0.18855786
H	-7.65906593	1.23340939	-1.50705730

1d

C	2.26095300	-1.04974400	-0.20164900
C	1.09880500	0.81935500	-1.07292300
C	1.56505600	1.26632000	0.34159000
N	2.24188100	0.03431900	0.80850200
N	1.18370900	-0.66913600	-1.11512300
C	3.58276300	-1.01259000	-0.97133900
H	4.40630300	-1.10723800	-0.25819000
H	3.61886900	-1.83913100	-1.68570300
H	3.70365000	-0.07289700	-1.51852000
C	2.57462900	2.41150600	0.26467500
H	2.09235100	3.30815200	-0.14049700
H	2.95908300	2.63765800	1.26300500
H	3.42204600	2.14884100	-0.37715200

C	2.05025100	-2.40070300	0.46040000
H	1.95210800	-3.17340700	-0.30701800
H	2.91734200	-2.62027000	1.08827000
H	1.15450100	-2.39543600	1.08230200
C	0.46048200	1.60744200	1.34246500
H	0.90996800	1.67091200	2.33866400
H	0.00260900	2.57523300	1.11191600
H	-0.31776100	0.83959100	1.35966800
O	-0.06477100	-1.04217100	-0.49501700
O	3.01180900	0.02761800	1.81244800
H	1.79065000	1.21120300	-1.82384700
C	-0.35893900	1.08388200	-1.46046300
H	-0.44148800	1.37814600	-2.50910200
H	-0.81576600	1.86535000	-0.84943400
C	-1.02351200	-0.30103500	-1.22413100
H	-1.18544300	-0.79261600	-2.19435700
C	-2.32031400	-0.25735400	-0.46047500
C	-2.47750700	-0.85384500	0.78842400
C	-3.42063900	0.40551800	-1.00767200
C	-3.71417200	-0.75143900	1.42663400
H	-1.65534900	-1.38608300	1.25550600
C	-4.60928000	0.44760700	-0.28601200
H	-3.35738500	0.88322200	-1.98285800
H	-3.86059400	-1.20667000	2.40362000
H	-5.47929700	0.95897200	-0.69201900
N	-4.76904100	-0.11612900	0.91507300

1e

C	2.75949600	-0.97555242	-0.07559430
C	1.26864794	0.47323243	-1.20366988
C	1.79056919	1.30861094	-0.00203408
N	2.71757590	0.33538000	0.61641255
N	1.55083715	-0.95585748	-0.90137412
C	3.97732932	-1.02168483	-1.00021128
H	4.87673536	-0.84631930	-0.40355210
H	4.04100710	-2.00094499	-1.48161535
H	3.92109630	-0.25229023	-1.77631283
C	2.56737275	2.53875578	-0.46835944
H	1.89418574	3.23330093	-0.98359545
H	3.00913695	3.04849608	0.39221180
H	3.37541646	2.25966047	-1.15296569
C	2.78989074	-2.11095313	0.93382063
H	2.72780156	-3.06902003	0.41001293
H	3.73299630	-2.05852287	1.48363254
H	1.95921478	-2.02994625	1.63546491
C	0.75101394	1.70608799	1.04810273
H	1.28006762	2.12274945	1.91142817

H	0.07363539	2.47595249	0.66206203
H	0.17313650	0.84243761	1.38702851
O	0.43625180	-1.28925164	-0.04157052
O	3.59741291	0.67896365	1.45805191
H	1.83230983	0.74101472	-2.10236722
C	-0.23546436	0.46203661	-1.47264634
H	-0.44228627	0.39638662	-2.54367346
H	-0.73813437	1.35189008	-1.08907781
C	-0.69876433	-0.84280088	-0.76221816
C	-1.79462187	-0.59112101	0.26553117
O	-1.74121735	-0.85617692	1.43812935
O	-2.86848093	-0.04286272	-0.32919384
C	-3.98102684	0.20723376	0.53396241
H	-3.69183553	0.89469462	1.33211164
H	-4.33324094	-0.72757071	0.97557210
H	-4.74937138	0.65009950	-0.09775936
C	-1.15895045	-1.91183176	-1.75555892
H	-1.44898126	-2.82142978	-1.22138789
H	-2.00770176	-1.55237077	-2.34344120
H	-0.32550627	-2.14672772	-2.42344343

Alkyl radical

C	0.05858900	1.26619600	-0.02050000
H	-0.04309800	2.33977500	0.10212400
C	-1.13575900	0.48697200	-0.00134200
C	-2.35688100	1.18445800	0.19302200
C	-1.20032200	-0.92085200	-0.16300700
C	-3.57119000	0.52028200	0.22569600
H	-2.32680100	2.26403300	0.31801400
C	-2.42284000	-1.57577500	-0.12960500
H	-0.28721600	-1.48105400	-0.31457100
C	-3.61163300	-0.86762900	0.06403400
H	-4.49011800	1.07887700	0.37693300
H	-2.45218300	-2.65418300	-0.25620400
H	-4.56180200	-1.39285300	0.08881000
C	1.45260100	0.86874000	-0.18330100
O	2.36111400	1.68049400	-0.18972900
O	1.65763700	-0.45785300	-0.32890900
C	3.02586000	-0.87408800	-0.47257500
H	2.95811100	-1.86371300	-0.92913800
H	3.53246600	-0.19073000	-1.15879900
C	3.72768500	-0.92885100	0.87212600
H	4.73988400	-1.32612700	0.74569400
H	3.80041300	0.07026700	1.30817100
H	3.18369100	-1.58214000	1.56078900

Phenylethyl radical

C	1.83277800	-0.65860200	0.00001600
H	2.08240200	-1.71576000	0.00002200
C	0.45758900	-0.30522900	0.00003800
C	-0.54505800	-1.30964100	0.00000700
C	0.02834400	1.04644600	0.00003600
C	-1.89051700	-0.98154600	-0.00002500
H	-0.23920500	-2.35347600	0.00002400
C	-1.32217400	1.36586100	0.00000900
H	0.76730000	1.84292300	0.00000300
C	-2.29140800	0.35946000	-0.00002000
H	-2.63719500	-1.77096200	-0.00002500
H	-1.62629800	2.40904100	-0.00000400
H	-3.34660100	0.61513800	-0.00004800
C	2.94362800	0.33944900	-0.00003700
H	3.91795000	-0.15407100	-0.00014700
H	2.90120200	0.99504700	-0.88133600
H	2.90136100	0.99492700	0.88136200

---

[1] Zhao, Y., Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Non-covalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Functionals. *Theor. Chem. Acc*. 2008, 120, 215−241.

[2] Alecu, I. M., Zheng, J., Zhao, Y., Truhlar, D. G. Computational thermochemistry: scale factor databases and scale factors for vibrational frequencies obtained from electronic model chemistries. *Journal of chemical theory and computation*, 2010, *6*(9), 2872-2887.

[3] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.