Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

Lewis Acid stabilization and Activation of Primary N-Nitrosamides

D. Scott Bohle, Zhijie Chua, Inna Perepichka, Kristopher Rosadiuk*

Department of Chemistry, McGill University, 801 Sherbrooke St. W., Montreal, Quebec, H3A 0B8, Canada

Email: scott.bohle@mcgill.ca

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Experimental Details for Ethyl derivative of N-Nitrosocarbamates and their Re complexes

Synthesis of N-nitrosoethylcarbamate, $C_2H_5OC(O)NHNO$ (**2**)[1] as a mixture of isomers

Ammonium N-nitroethylcarbamate[2] (1.00 g, 6.62 mmol) is dissolved in a mixture of acetic acid (0.84 g, 12.6 mmol) and cold deionised H_2O (15 mL) at a temperature less than 25 °C. Commercial zinc dust stored under nitrogen (0.600 g, 10.2 mmol) is added in portions to the reaction mixture such that temperature remains below 25 °C. Some ice can be added if the reaction temperature gets above 30 °C. The reaction mixture turns yellow and is allowed to stir for 1 h during which a yellow-green suspension is observed.

Ice (~ 10 g) is added and cold conc. aqueous ammonia (3.9 mL, 56.6 mmol) is added in excess and stirred for 5 min to give a yellow solution which is filtered through a plug of Celite. If the residue is yellow, it is washed with dilute aqueous ammonia (0.5 mL conc. NH_4OH in 2 mL deionised H_2O) and deionised H_2O until the washings are colourless. Ice (~ 50 g) is added into the yellow filtrate followed by a solution of $AgNO_3$ (0.80 g, 4.71 mmol) with rapid stirring. Acetic acid is added slowly, forming initially a white suspension, which dissolves on further addition of acid. A yellow suspension initially forms and acetic acid is added till the solution is acidic to pH paper (Total volume ~ 150 mL). The reaction mixture is left standing between 10 - 15 min during which substantial yellow precipitate appears. The yellow precipitate, $Ag[C_2H_5OC(O)NNO)]$ (assumed 1.06 g, 4.71 mmol) is filtered and washed consecutively with deionised H_2O, C_2H_5OH and CH_3OH and processed immediately as it rapidly decomposes on prolonged exposure to moisture. The filtrate is observed to be colourless.

NaCl (0.280 g, 4.79 mmol) is dissolved in an ice-water solution and added to $Ag[C_2H_5OC(O)NNO]$ (assumed 1.06 g, 4.71 mmol) and stirred/shaken vigourously for 5 min to give a yellow suspension. The yellow suspension is filtered through Celite and washed successively with cold deionised H_2O till the filtrate is colourless. The filtrate is transferred into a separatory funnel containing CH_2Cl_2 (20 mL), ice (~ 2 g) and conc. H_2SO_4 (0.231 g, 2.35 mmol). The organic layer is separated, kept and the yellow aqueous layer further extracted with CH_2Cl_2 (5 x 20 mL) or till the aqueous layer is colourless. The organic extracts are combined and dried over anhydrous $CaCl_2$, kept cold and under a N_2 atmosphere for 30 min. The yellow CH_2Cl_2 suspension is filtered and CH_2Cl_2 is removed using a rotary evaporator without heating to give bright yellow solids of N-nitrosoethylcarbamate which is further purified by vacuum sublimation (ice-water condenser) at 27- 28 °C to give bright yellow crystals of N-nitrosoethylcarbamate (**2**) (0.190 g, 1.61 mmol, 34 % yield).

(Note: to minimize the loss of **2** due to its low melting point, the sublimator is cooled to around 6-7 °C before the vacuum is applied.) Decomposition point: 57.4 °C (-86.1 kJ mol^{-1}). IR (cm^{-1}): 3430 vs, 2989 w, 2930 vw, 2859 vw, 1748 s, 1615 m, 1520 m, 1474 m, 1447 m, 1431 m, 1393 m, 1376 m, 1329 s, 1257 s, 1233 m, 1205 m, 1093 vs, 1073 vs, 999 m, 862 w, 541 w. ^{1}H NMR (400 MHz, $CDCl_3$) ppm: δ = Isomer α (minor) 1.35 (t, C*H*$_3$, *J* = 6.8 Hz), 4.35 (q, C*H*$_2$, *J* = 6.8 Hz); Isomer β (major) 1.44 (t, C*H*$_3$, *J* = 6.8 Hz), 4.50 (q, C*H*$_2$, *J* = 6.8 Hz), 10.73 (N*H*, broad) relative ratio of 0.16: 1. UV: (CH_3OH λ_{max}, nm (ε, M^{-1} cm^{-1})): 366sh (13.8), 385sh (32.2), 401 (63.5), 417 (91.1), 436 (79.1).

Isomers of alkaline metal salts of N-nitrosoethylcarbamate, M[$C_2H_5OC(O)NNO$] M = K (**4**), Na (**4-Na**)

N-Nitrosoethylcarbamate (**2**) (0.085 g, 0.720 mmol) is dissolved in dry CH_2Cl_2 (10 mL) and $KOCH_3$ (0.050 g, 0.679 mmol) is added. The white suspension is stirred overnight to give a yellow suspension. The solvent is removed and the yellow residue dissolved in CH_3OH and filtered to give a yellow filtrate. The solvent is removed and recrystallized from dry CH_3OH/ether to give yellow crystals of K[$C_2H_5OC(O)NNO$] (**4**) (0.085 g, 0.545 mmol , 80 % yield). Note: The yellow crystals are hygroscopic, sensitive to friction and can detonate! IR (cm^{-1}):2989w, 2905w, 1711m, 1683vs, 1615m, 1484w, 1464w, 1411m, 1361m, 1316m, 1260vs, 1225vs, 1181vs, 1120w, 1085s, 1064s, 810w, 793m, 786m, 468w. ^{1}H NMR (500 MHz, CD_3OD) ppm: δ = Isomer α (minor) 1.26 (t, CH_3, *J* = 7 Hz), 4.10 (q, CH_2, *J* = 7 Hz); Isomer β (major) 1.35 (t, CH_3, *J* = 7.2 Hz), 4.28 (q, CH_2, *J* = 7.2 Hz); Isomer γ (minor) 1.48 (t, CH_3, *J* = 7.2 Hz), 4.43 (q, CH_2, *J* = 7.2 Hz), relative ratio of 0.16: 1: 0.03.

N-nitrosoethylcarbamate (**2**) (0.085 g, 0.720 mmol) is dissolved in dry THF 7 ml) under an N_2 atmosphere. The yellow solution is cooled in an ice-bath and NaH (0.028 g, 0.700 mmol) is added in portions during which some bubbling is observed. The suspension is allowed to warm to room temperature and stirred overnight. The solvent is removed *in vacuo* to give pale yellow solids. Dry pentanes is added and the solids sonicated to remove the mineral oil and decanted. The pale yellow residue is washed with diethylether twice and the solids collected into a sample vial as a suspension in ether and subsequently dried under vacuum to give pale yellow powder of Na[$C_2H_5OC(O)NNO$] (**4-Na)** (0.060 g, 0.429 mmol, 61 % yield). Note: The yellow crystals are hygroscopic, sensitive to friction and can detonate! IR (cm^{-1}): 2994w, 2919w, 1680m, 1666s, 1484m, 1444m, 1385m, 1362m, 1307m, 1261s, 1196vs, 1106m, 1073s, 1015m, 880w, 816m, 800m, 618m, 570m, 470m. ^{1}H NMR (400 MHz, CD_3OD) ppm: δ = Isomer α (minor) 1.26 (t, CH_3, *J* = 7 Hz), 4.10 (q, CH_2, *J* = 7 Hz); Isomer β (major) 1.35 (t, CH_3, *J* = 7 Hz), 4.28 (q, CH_2, *J* = 7 Hz), relative ratio of 0.21: 1. UV: (CH_3OH λ_{max}, nm (ε, M^{-1} cm^{-1})) λ_{max} = 361 (22.5), 393 (25.6), 398 (25.8). HRMS (ESI): *m*/*z* $[M-Na]^-$ calcd for $C_3H_5O_3N_2$: 117.0306 ; Found: 117.0303.

Synthesis of isomers of Re(η^2-$C_2H_5OC(O)NNO$)$(CO)_2(PPh_3)_2$

Room temperature reaction: [Re($CH_3CN)_2(CO)_2(PPh_3)_2$](ClO_4) (0.030 g, 0.032 mmol) is dissolved in CH_2Cl_2 (2 mL) and added to a solution of potassium N-nitrosoethylcarbamate (**4**) (0.006 g, 0.038 mmol) in degassed CH_3OH or C_2H_5OH (6 mL) in a 50 mL flask. The white suspension was stirred overnight during which the suspension turned into a bright yellow. The solvent is removed and the residue extracted with CH_2Cl_2 (10 mL) followed by filtration through a sintered glass filter. The solvent is removed to give yellow solids containing isomers of Re(η^2-$C_2H_5OC(O)NNO$)$(CO)_2(PPh_3)_2$ (**7**) (0.010 g, 0.011 mmol, 35 % yield). IR (cm^{-1}): 3054w, 1939vs (CO), 1864vs (CO), 1738m, 1636m (broad), 1480m, 1434s, 1386m, 1372m, 1312m, 1285m, 1169m, 1091s, 1068m, 1025m, 997w, 744m, 695s, 517s. ^1H NMR (400 MHz, $CDCl_3$) ppm: 0.89 (t, CH_3, J = 7.2 Hz, minor isomer = 0.43), 1.10 (t, CH_3, J = 7.2 Hz, major isomer = 0.57), 3.43 (q, CH_2, J = 7.2 Hz, minor isomer = 0.43), 3.78 (q, CH_2, J = 7.2 Hz, major isomer = 0.57), 7.39 (m, 18H-PPh_3), 7.52 (m, 12H-PPh_3). $^{31}P[^1H]$ NMR (162 MHz, $CDCl_3$) ppm: δ = 23.43 (s, minor isomer = 0.43), 28.96 (s, major isomer = 0.57).

Elevated temperature reaction: [Re($CH_3CN)_2(CO)_2(PPh_3)_2$](BF_4) (0.030 g, 0.032 mmol) and potassium N-nitrosoethylcarbamate (**4**) (0.006 g, 0.039 mmol) were placed in 50 mL flask. Degassed CH_3OH or C_2H_5OH (8 mL) is added and the reaction heated to reflux for 2 h under an N_2 atmosphere. The white suspension turned into a bright yellow suspension. The solvent is removed and the residue extracted with CH_2Cl_2 (10 mL) and filtered through a glass frit. The CH_2Cl_2 solvent is removed in *vacuo* to give orange solids containing isomers of Re(η^2-$C_2H_5OC(O)NNO$)$(CO)_2(PPh_3)_2$ (**8**) (0.020 g, 0.023 mmol, 71 % yield). IR (cm^{-1}): 3053w, 2964vw, 1947vs (CO), 1870vs (CO), 1640m, 1552m, 1542m, 1480m, 1434s, 1391m, 1372m, 1311s, 1263m, 1176m, 1158m, 1093s, 1065s, 1027m, 1012m, 806m, 743s, 695s, 614m, 519vs. ^1H NMR (500 MHz, $CDCl_3$) ppm: δ = 0.87 (t, CH_3, J = 7 Hz, major isomer = 0.82), 1.09 (t, CH_3, J = 7 Hz, minor isomer = 0.18), 3.40 (q, CH_2, J = 7 Hz, major isomer = 0.82), 3.77 (q, CH_2, J = 7 Hz, minor isomer = 0.18) 7.38 (m, 18H-PPh_3), 7.45 (m, 12H-PPh_3). $^{31}P[^1H]$ NMR (202 MHz, $CDCl_3$) ppm: δ = 23.43 (s, major isomer = 0.82), 28.96 (s, minor isomer = 0.18).

A sample containing a mixture of both isomers was sent for elemental analysis. Anal. calcd. for $C_{40}H_{33}N_2O_5P_2Re\cdot 0.5CH_2Cl_2$ (926.39 g mol^{-1}) % C, 53.81; H, 3.92; N, 3.02. Found % C, 54.00; H, 3.75; N, 2.90.

Table S1. λ_{max}, abs and Δν values of 3.2 mM of **1** in CH_3OH and $CHCl_3$.

1 in CH_3OH			**1** in $CHCl_3$		
λ_{max} (nm)	ε (M^{-1} cm^{-1})	Δν (cm^{-1})	λ_{max} (nm)	ε (M^{-1} cm^{-1})	Δν (cm^{-1})
366	12.6	1348	368	21.3	1064
385	34.1	1036	383	43.0	857
401	61.6	956	396	75.0	981
417	88.5	1045	412	105.0	1016
436	76.7		430	88.7	

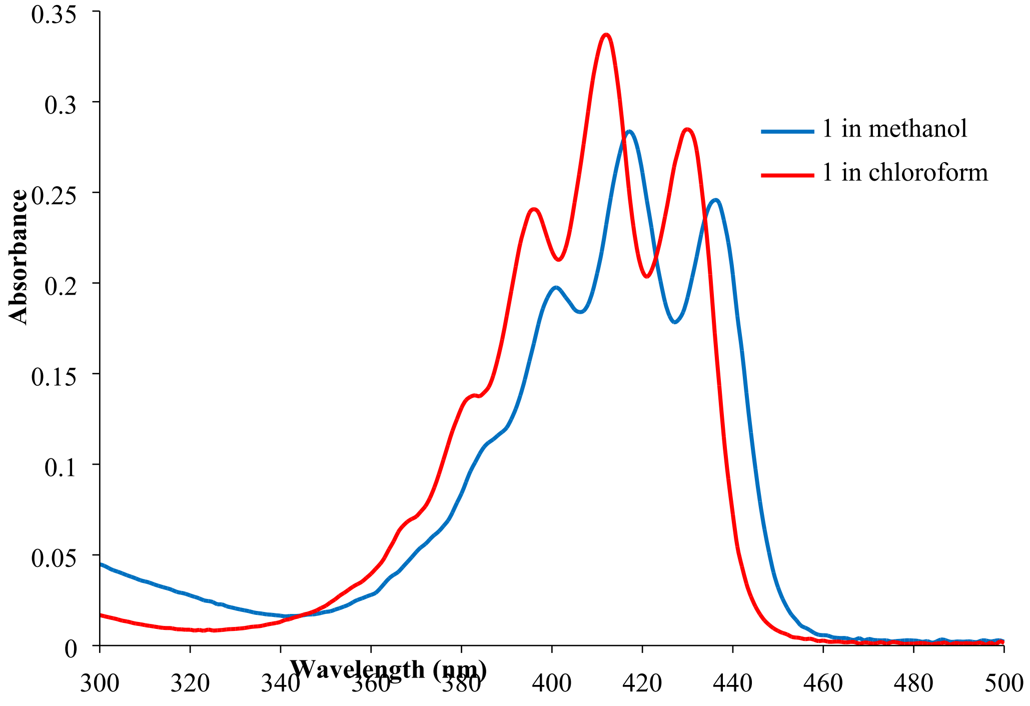


Figure S1. UV-vis absorption spectrum of 3.2 mM of **1** in CH_3OH (blue) and $CHCl_3$ (red).

Table S2. λ_{max}, abs and $\Delta\nu$ values of 3.2 mM **1** in CH_3OH and CD_3OD.

1 in CH_3OH			**1** in CD_3OD		
λ_{max} (nm)	ε (M^{-1} cm^{-1})	$\Delta\nu$ (cm^{-1})	λ_{max} (nm)	ε (M^{-1} cm^{-1})	$\Delta\nu$ (cm^{-1})
366	12.6	1348	366	13.8	1483
385	34.1	1036	387	38.4	902
401	61.6	956	401	67.0	956
417	88.5	1045	417	97.0	992
436	76.7		435	85.1	

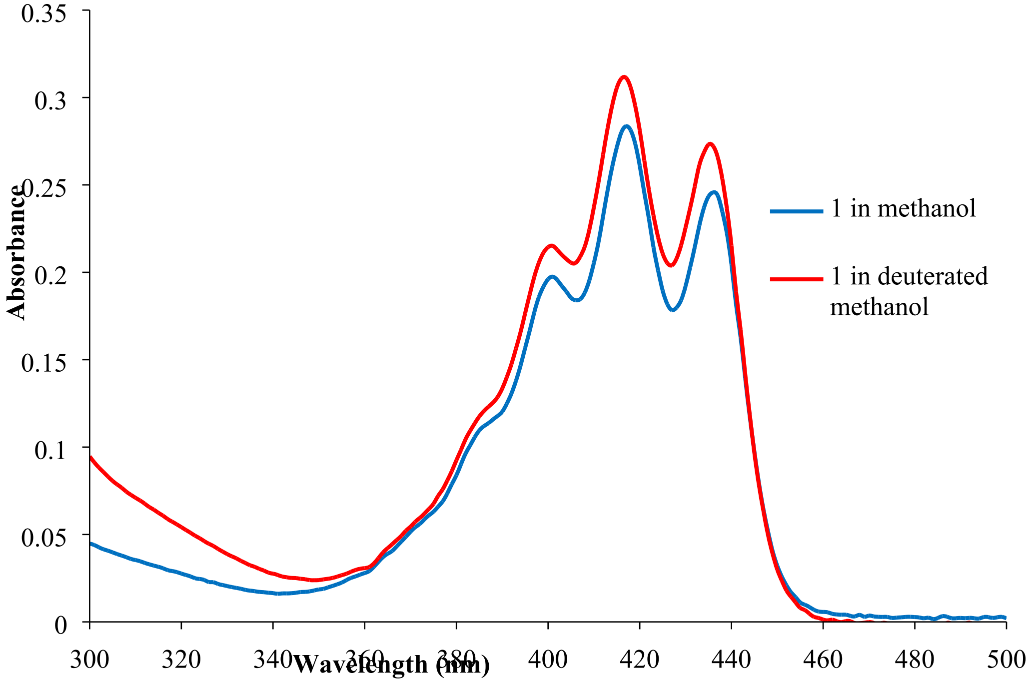


Figure S2. UV-vis absorption spectrum of **1** in CH_3OH (blue) and CD_3OD (red).

Table S3. λ_{max}, abs and $\Delta\nu$ values of 2.8 mM **2** in $CHCl_3$.

λ_{max} (nm)	ε (M^{-1} cm^{-1})	$\Delta\nu$ (cm^{-1})
366	13.8	1348
385	32.2	1036
401	63.5	957
417	91.1	1045
436	79.1	

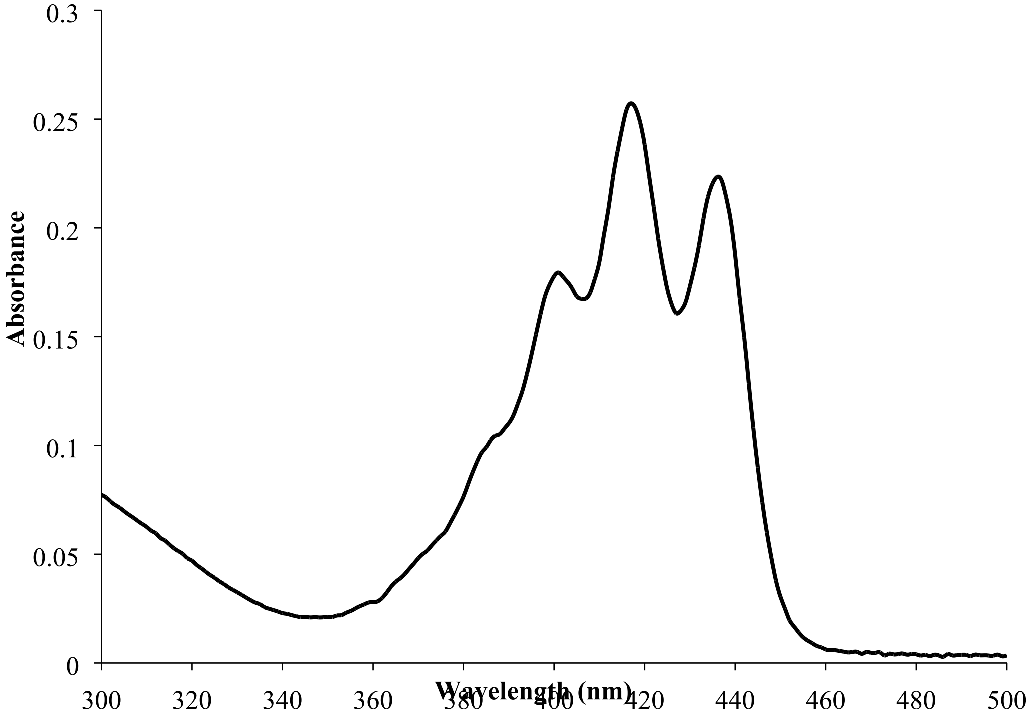


Figure S3. UV-vis absorption spectrum of 2.8 mM **2** in CH_3OH.

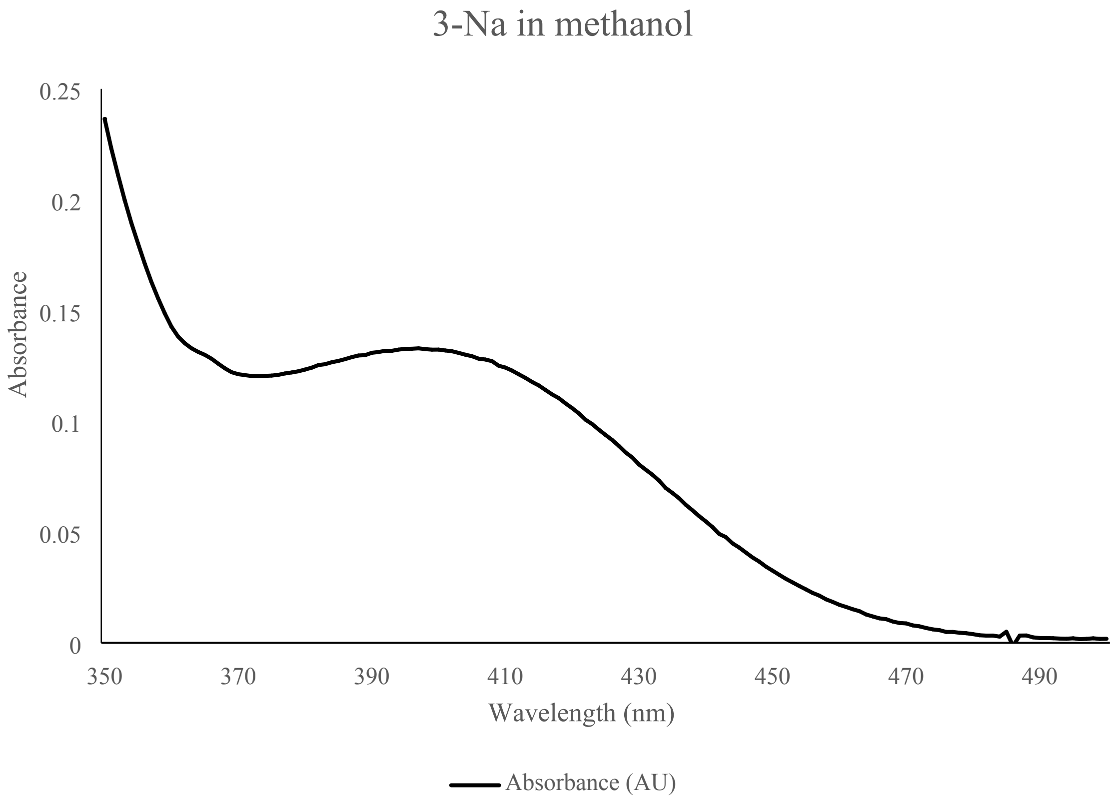


Figure S4. UV-vis absorption spectrum of 3.4 mM **3-Na** in CH_3OH.

Table S4. λ_{max}, abs and $\Delta\nu$ values of 7.1 mM **4-Na** in CH_3OH.

λ_{max} (nm)	ε (M^{-1} cm^{-1})	$\Delta\nu$ (cm^{-1})
361	22.5	2256
393	25.6	320
398	25.8	

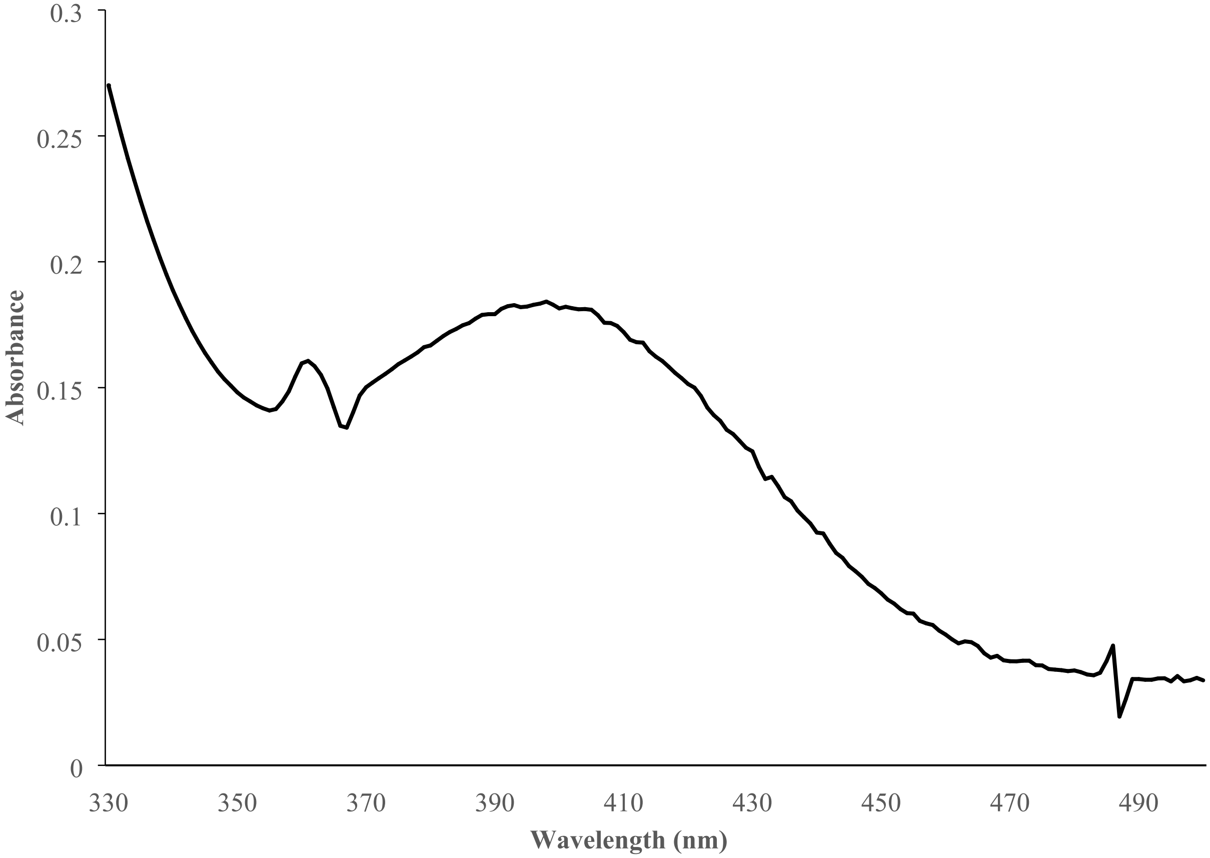


Figure S5. UV-vis absorption spectrum of 7.1 mM **4-Na** in CH_3OH.

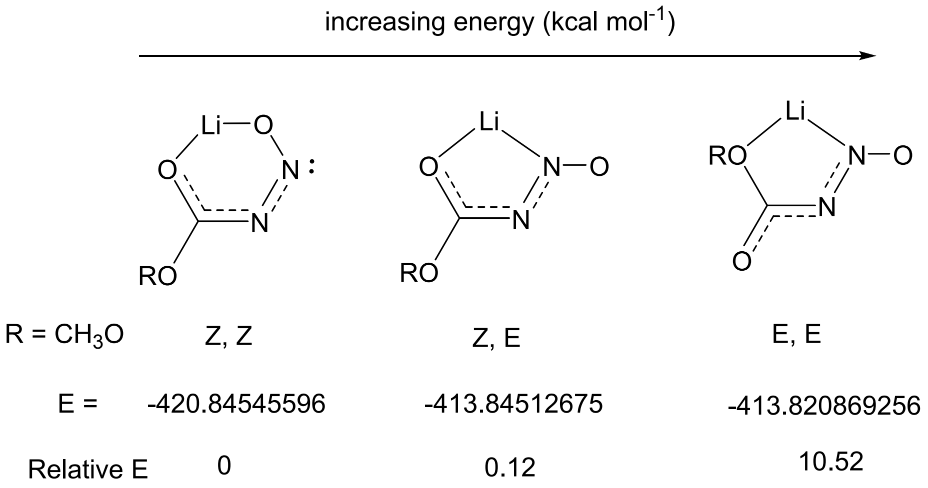
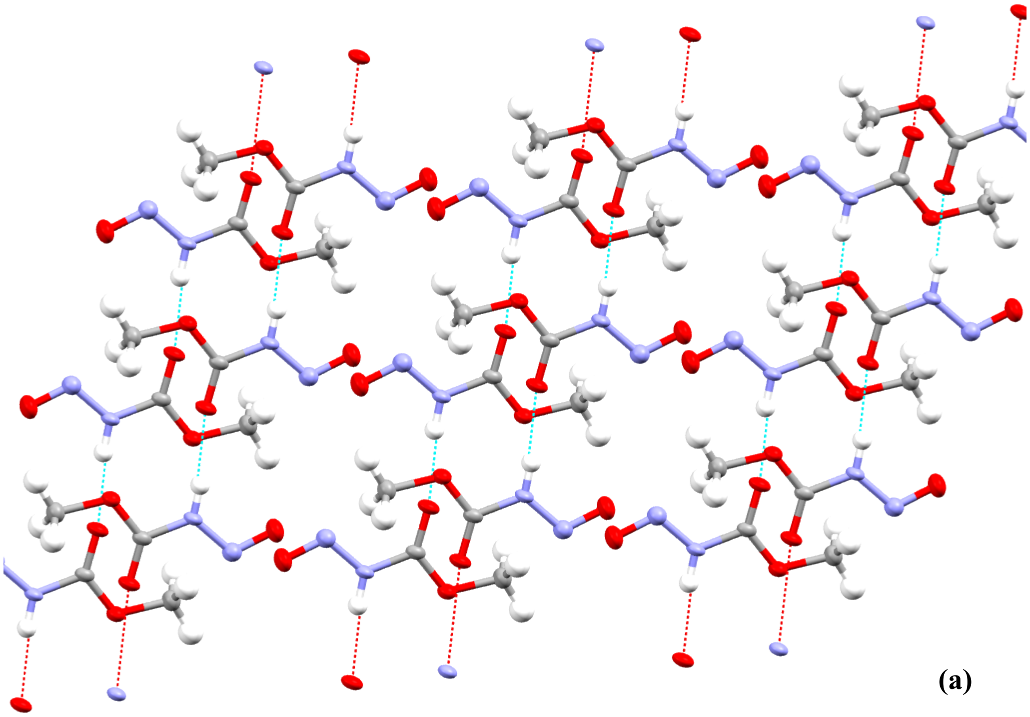


Figure S6. DFT calculated energy level of isomers of **3-Li**.

Table S5. Crystallographic data of N-nitrosocarbamates, their potassium salts and Re complexes.

Compound	**1**	**2**	**3**	**5**	**6**	**8**
empirical formula	$C_2H_4N_2O_3$	$(0.94)C_3H_6N_2O_3$. $(0.06)C_3H_6N_2O_4$	$C_2H_3KN_2O_3$	$C_{40}H_{33}ReP_2N_2O_5$	$2(C_{40}H_{33}ReP_2N_2O_5).CH_2Cl_2$	$C_{41}H_{35}ReP_2N_2O_5$
CCDC number	1416401	1416402	1416403	1435727	1435728	1435738
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
fw (g mol^{-1})	104.07	118.10	142.16	869.82	1824.57	883.85
cryst sys	Monoclinic	monoclinic	orthorhombic	rhombohedral	monoclinic	monoclinic
space group	$P2_1/m$	$P2_1/m$	$P2_12_12_1$	R-3	$P2_1/c$	$P2_1/c$
a (Å)	4.8755(14)	4.7863(15)	5.8792(7)	44.728(3)	11.1714(7)	11.2939(10)
b (Å)	5.9345(18)	6.0338(19)	6.8542(8)	44.728(3)	46.877(3)	22.8887(19)
c (Å)	7.808(2)	9.375(3)	12.8207(14)	12.0440(9)	17.9886(8)	17.8433(11)
α (deg)	90	90	90	90	90	90
β (deg)	99.205(3)	90.945(3)	90	90	128.081(3)	128.455(4)
γ (deg)	90	90	90	120	90	90
V (Å^3)	223.01(11)	266.67(15)	516.64(10)	20867(3)	7415.1(8)	3612.1(5)
Z	2	2	4	18	4	4
density (g cm^{-3})	1.550	1.471	1.828	1.246	1.634	1.625
abs coeff (mm^{-1})	0.145	0.131	0.938	2.726	3.483	3.501
No. of reflns collected	2534	2603	5630	63501	85200	36709
No. of indep reflns	569	571	1201	8142	17490	6726
Data/restraints/parameters	569/0/43	571/0/55	1201/0/74	8142/251/498	17490/841 /1131	6726/0/444
Final R indices [$I > 2s(I)$] R1	0.0471	0.0364	0.0215	0.0465	0.0541	0.0284

*w*R2	0.1220	0.0868	0.0537	0.1030	0.1131	0.0572
R indices (all data) R1	0.0589	0.0526	0.0222	0.0707	0.0811	0.0411
*w*R2	0.1301	0.0919	0.0539	0.1110	0.1234	0.0617
Goodness-of-fit on F^2	1.149	1.100	1.140	1.072	1.066	1.021



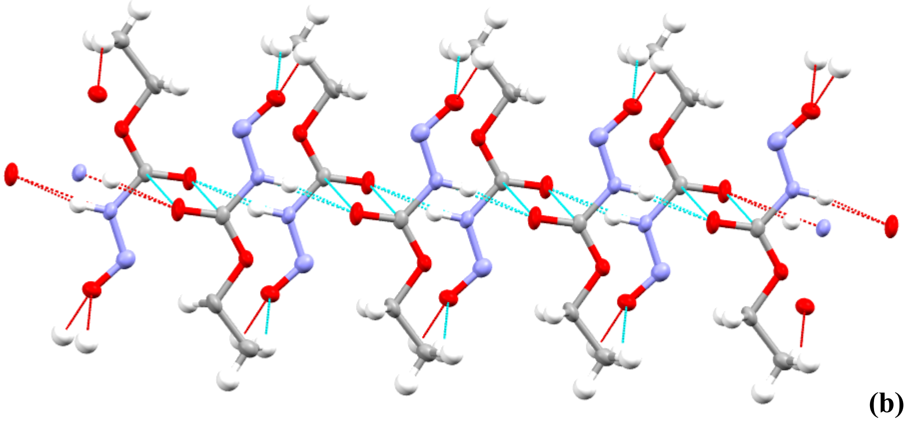


Figure S7. Crystal packing of (a) **1** and (b) **2** with Hydrogen bonds.

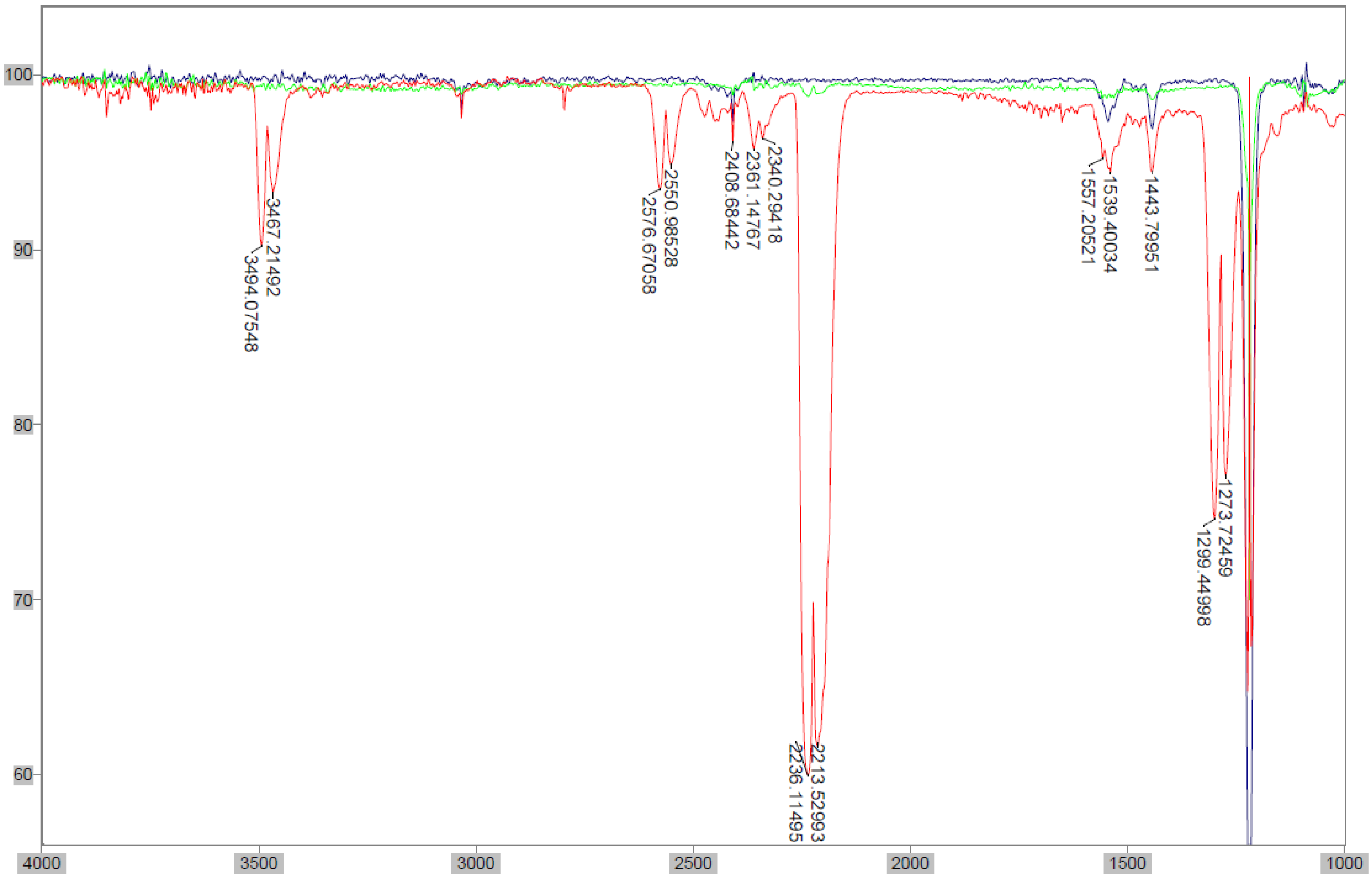


Figure S8. Gas-phase IR monitoring of decomposition of nitramide (H_2NNO_2) using K_2CO_3 in $CHCl_3$. Bands (ν: cm^{-1}): 2236, 2214 (asymm) and 1299, 1274 (sym) are from N_2O (g). Green: $CHCl_3$; Blue: H_2NNO_2; Red: H_2NNO_2 with K_2CO_3.

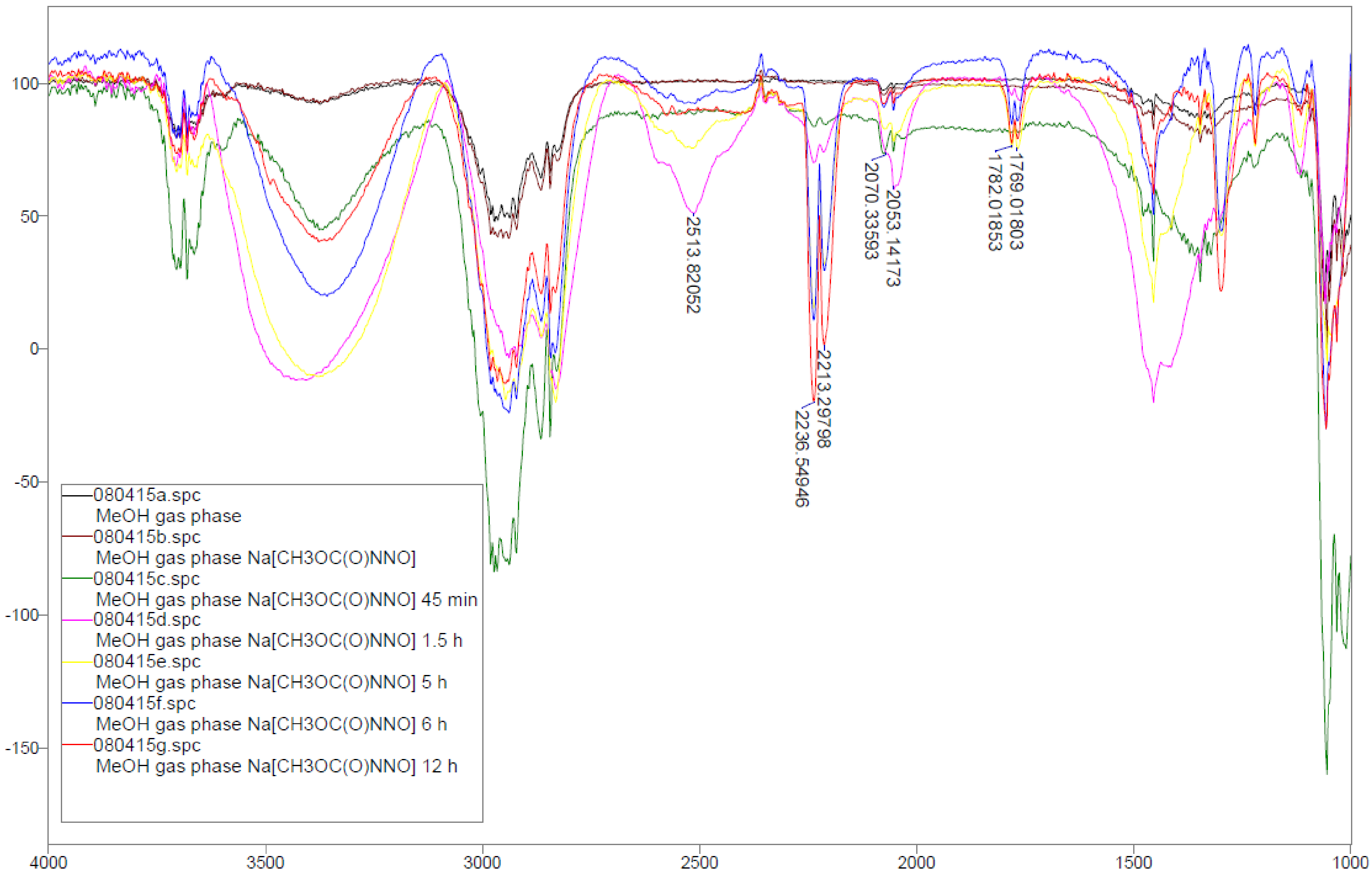


Figure S9. Gas-phase IR monitoring of **3-Na** in CH_3OH. Weak bands (ν: cm^{-1}) 2240, 2214 are from N_2O (g). Strong overlap with solvent bands around 1300 cm^{-1} prevent identification of N_2O symmetric band. Black: CH_3OH; Brown: CH_3OH with **3-Na** initial; Green: after 45 min; Pink: after 1.5 h; Yellow: after 5 h; Blue: after 6 h; Red: after 12 h.

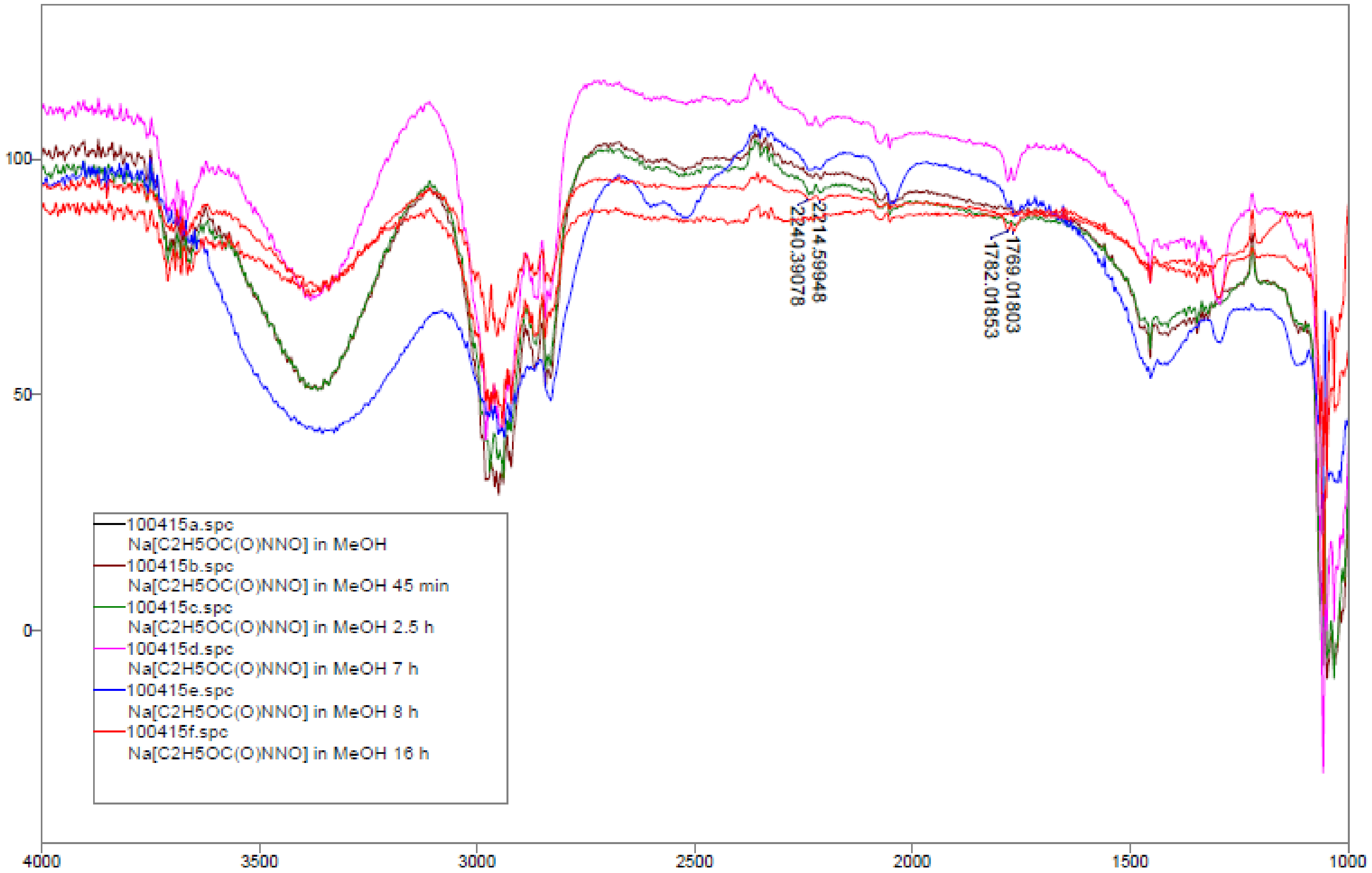


Figure S10. Gas-phase IR monitoring of **4-Na** in CH_3OH. Weak bands (ν: cm^{-1}) 2240, 2214 are from N_2O (g). Black: Initial; Brown: after 45 min; Green: after 2.5 h; Pink: after 7 h; Blue: after 8 h; Red: after 16 h.

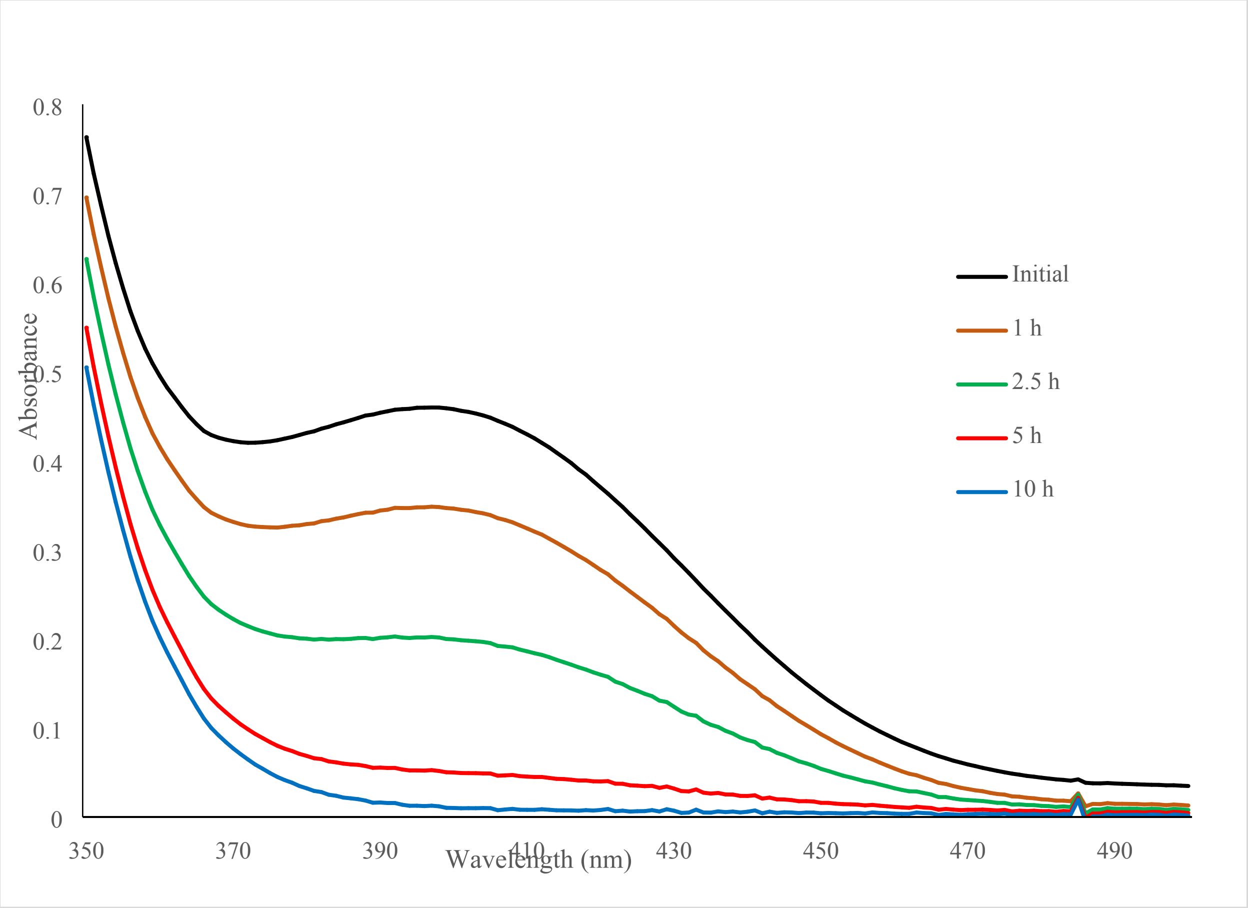


Figure S11. UV-vis monitoring spectra of the decomposition of **3-Na** in methanol. Black (initial); Brown (after 1 h); Green (after 2.5 h); Red (after 5 h); Blue (after 10 h).

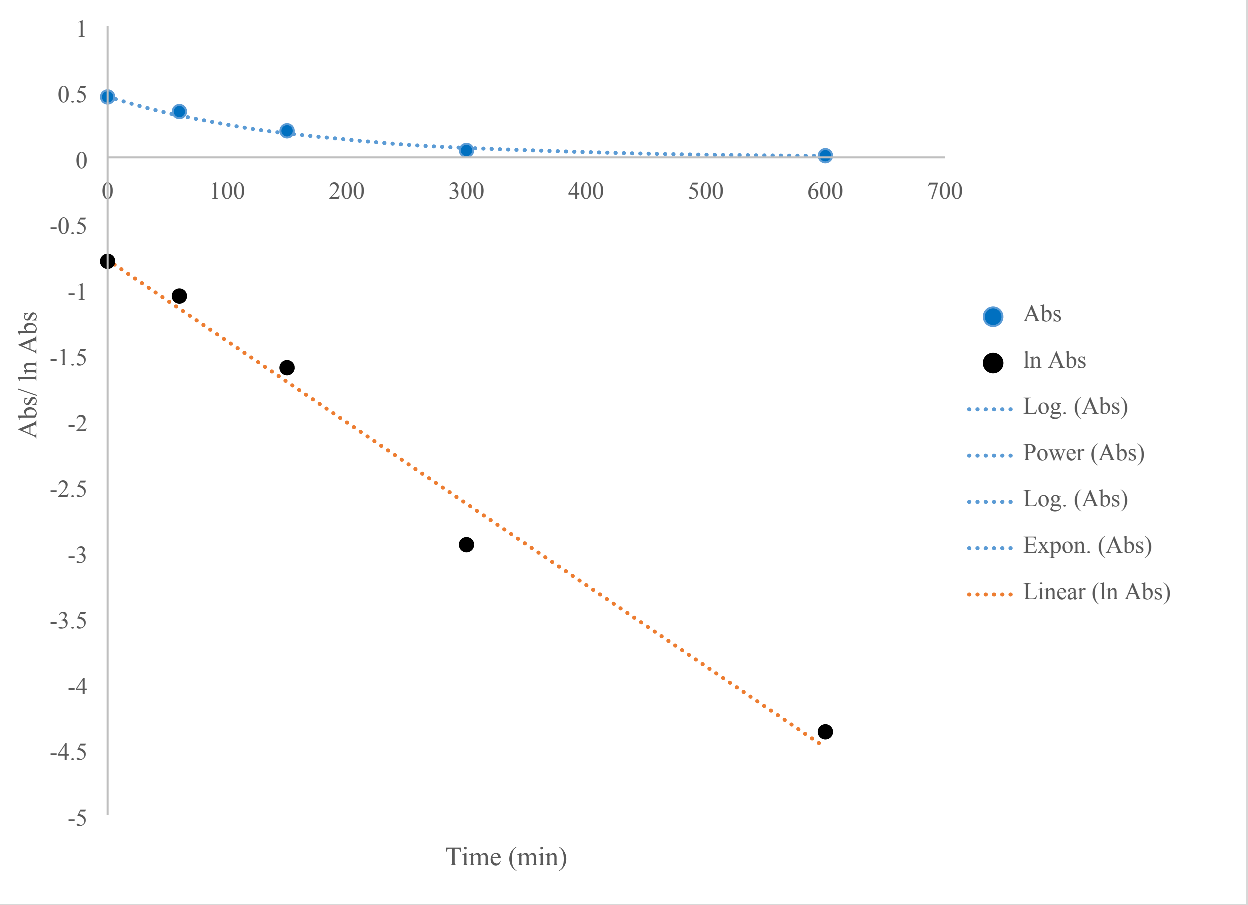
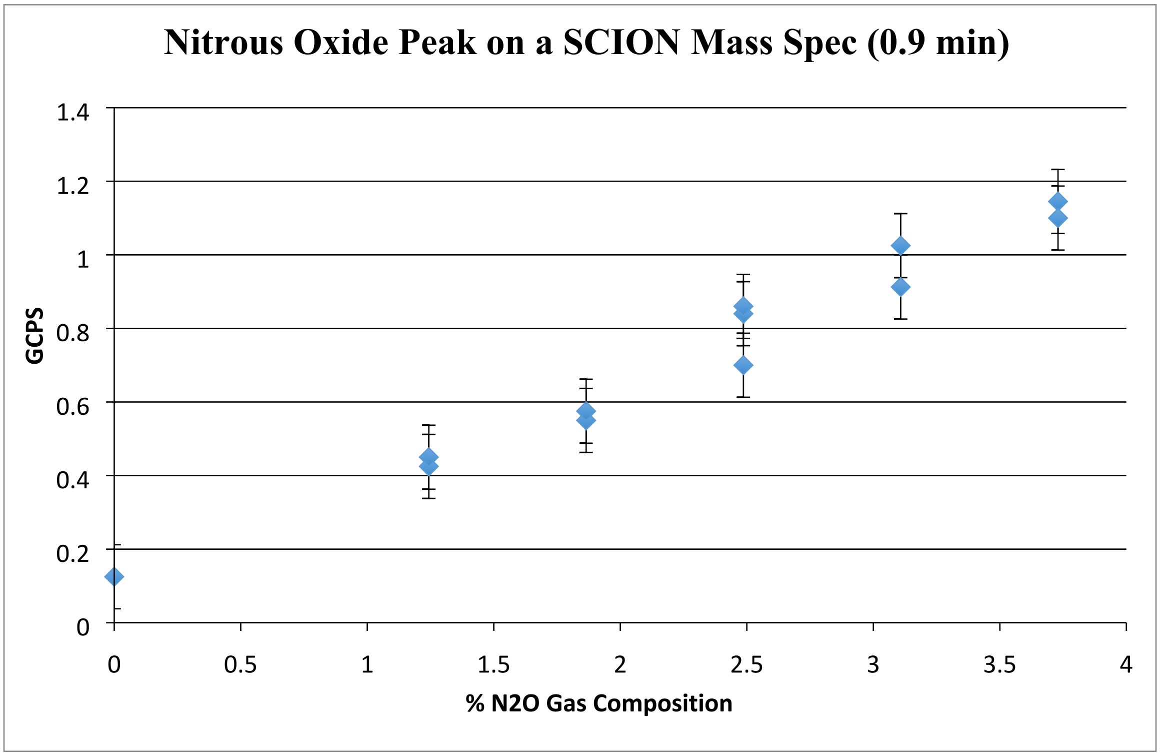


Figure S12. UV-vis monitoring at 397 nm of the decomposition of **3-Na** in methanol. Plot of Abs/ln Abs over time (min).

Calibration of GCMS for nitrous oxide quantification.

Calibration was by means of nitrous oxide produced from nitramide (H_2NNO_2) decay. Each N_2O sample was prepared by adding a small amount (10 - 30 mg) of nitramide to a large (>250 mL) flask along with a like amount of sodium carbonate. The flask was flushed with argon, sealed with a septum, and 500 µL of water was introduced with a syringe, leading to the immediate decay of the nitramide into water and nitrous oxide. The flask is mixed for 1 min and the water present is assumed to reach the saturation point with regards to nitrous oxide, using the Henry's Law constants of Weiss and Price.[3] The majority of the gas produced is trapped in the liquid, with never more 4% of the total volume produced, so the pressure change is assumed to be insignificant. The mixture of argon and nitrous oxide is assumed to behave ideally. The gas is collected with a sealable 1 mL SGE gas tight syringe and injected manually into the GCMS system. The peak due to N_2O is detected between 0.9-1 min after injection. The following calibration curve was prepared:



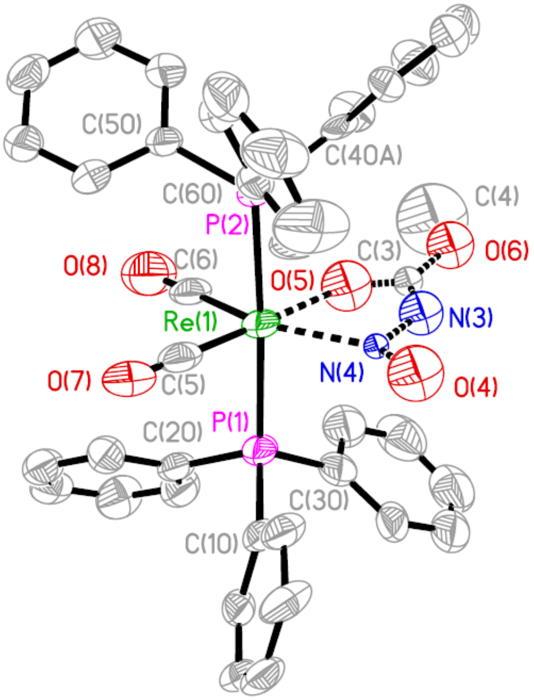


Figure S13. Other disordered five-membered ring of **5**.

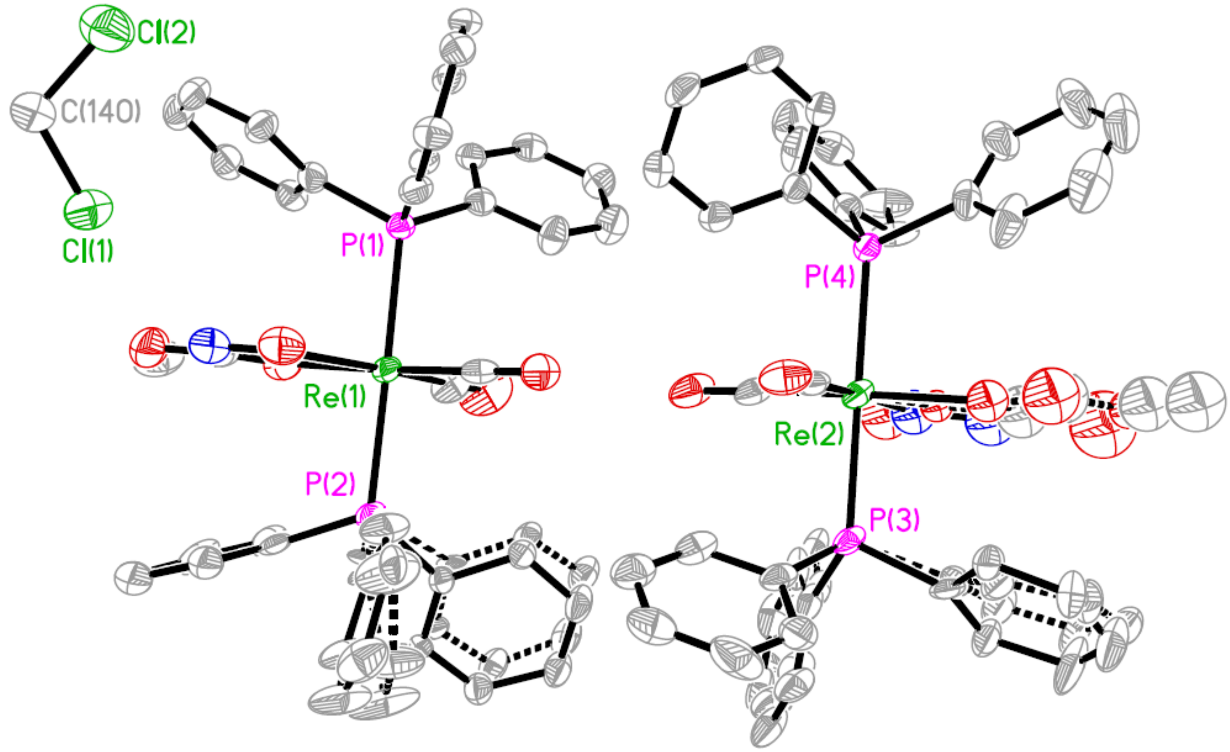


Figure S14. Solid state diagram of **6** with two independent Re complexes (Thermal ellipsoids at 50 % probability, **6A** (left) and **6B** (right). A CH_2Cl_2 solvate is also shown.

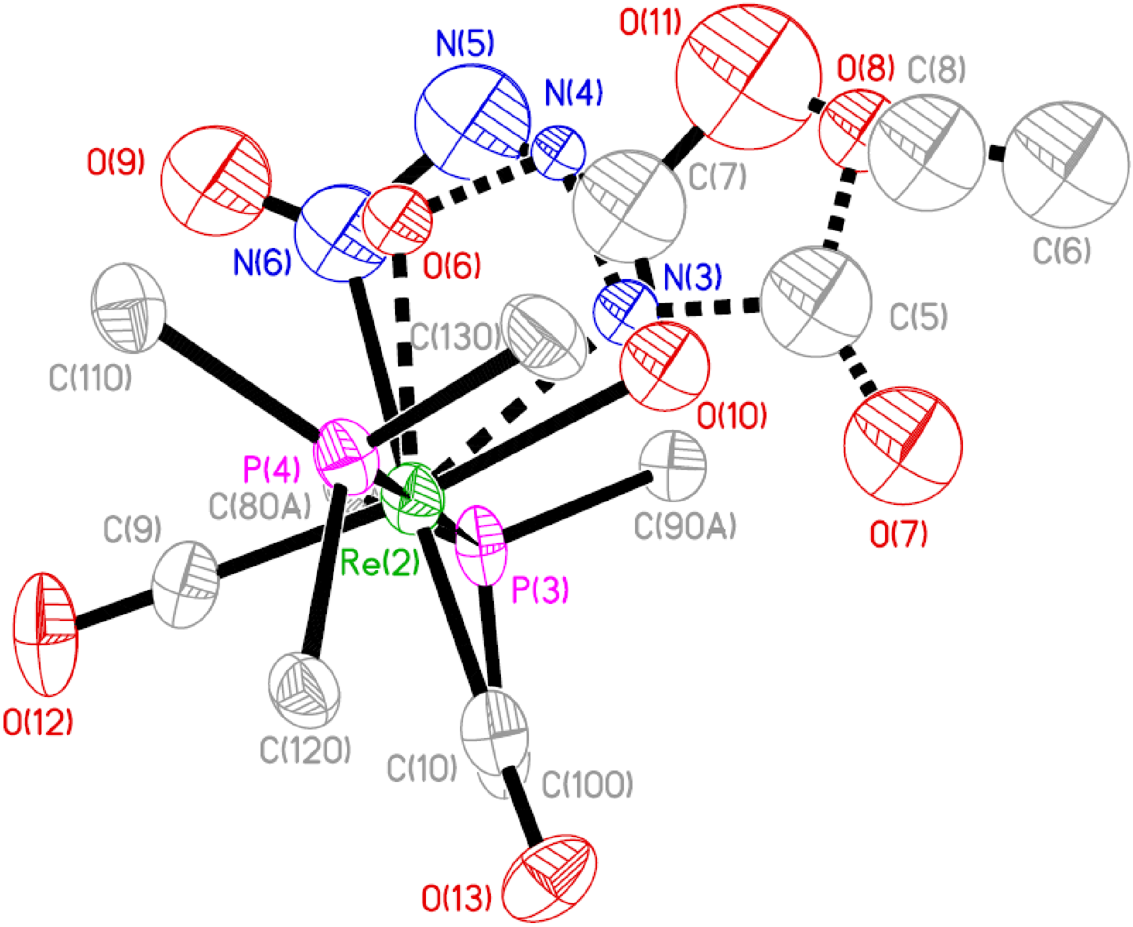


Figure S15. Molecular structure of **6B** with highlight on the disorder of the ligand. Dotted lines refer to four-membered ring coordination. Full black lines refer to five-membered coordination. Phenyl rings of PPh_3 not shown and hydrogen atoms and solvent molecules have been omitted for clarity.

SQUEEZE results and discussion

The estimated volume and electron density within the solvent channels for **5** (5362 Å^3**,** 1470 e$^-$) when taken into account of a non-H atom which has an approximate radius of 18 Å^3, gives rise to approximately 298 non-H atoms respectively. On average these non-H atoms when taking the charge divided by number of atoms, has an approximate charge of 5 e$^-$. This charge is close to the number of electrons of the lighter elements carbon and oxygen and indicates the likely presence of methanol and ethanol (solvents used in reaction). However, dividing the number of non-H atoms by 3 (assumed ethanol) results in 99 ethanol molecules per unit cell in **5**. Taking into account the number of channels per unit cell (3) and site symmetry within the solvent channels (6), the asymmetric unit will contain an estimated 5.5 ethanol molecules in **5**. These numbers are significantly higher than the estimated number of solvent molecules in the rough disorder model (2.3 – 2.5). Therefore, it is likely that there are some amounts of CH_2Cl_2 (greater number of electrons) within these solvent channels too which contribute to the heterogeneous nature of the solvent molecules in the channels. ^{1}H NMR spectra of the crystals of **5** also indicates the presence of CH_2Cl_2.

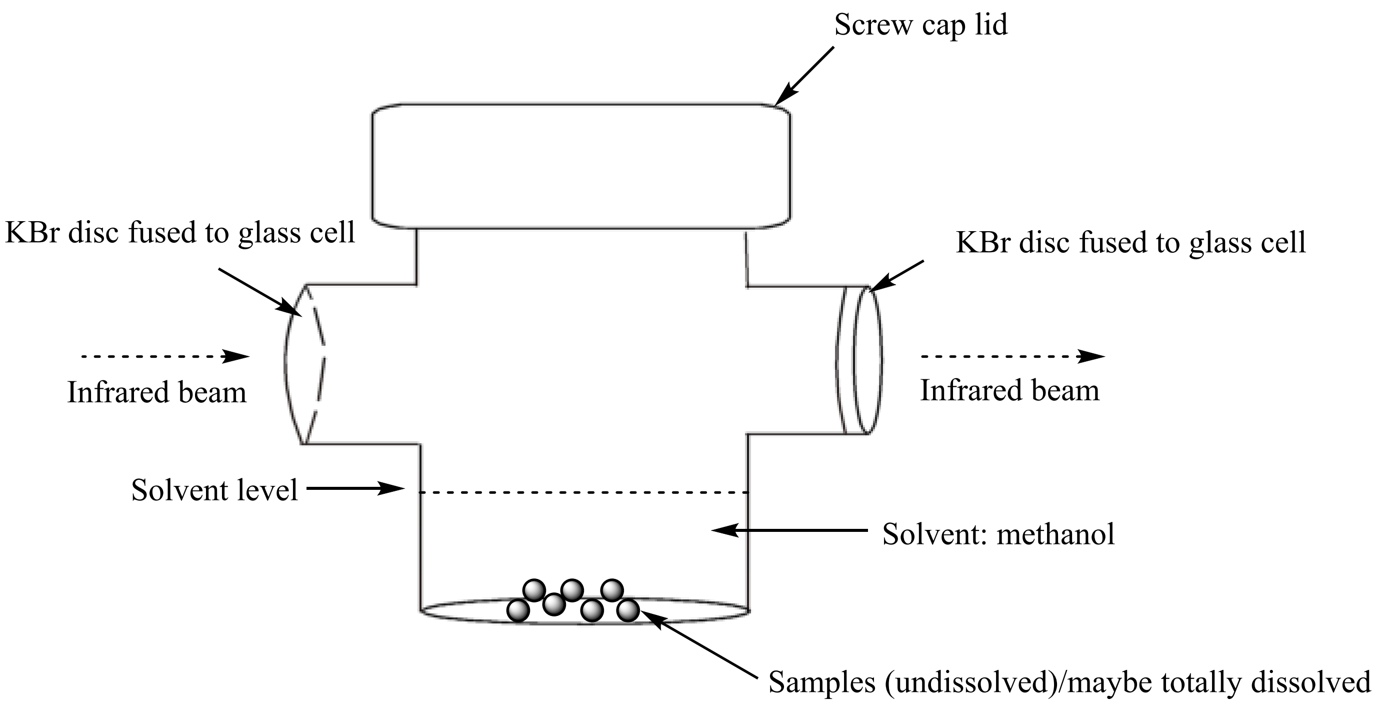


Figure S16. Diagram of custom-made IR gas cell.

Table S6. Crystallographic data of **4**.

Compound	**4**
empirical formula	$(0.45)C_3H_5KN_2O_3$. $(0.55)C_3H_5KN_2O_4$
CCDC number	1416404
T (K)	298(2)
fw (g mol^{-1})	156.19
cryst sys	tetragonal
space group	$P4_32_12$
a (Å)	7.1748(5)
b (Å)	7.1748(5)
c (Å)	25.2226(17)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	1298.4(2)
Z	8
density (g cm^{-3})	1.598
abs coeff (mm^{-1})	0.754
No. of reflns collected	12746
No. of indep reflns	1148
Data/restraints/parameters	1148/19/100
Final R indices [$I > 2s(I)$] R1 *w*R2	0.0259 0.0549
R indices (all data) R1 *w*R2	0.0289 0.0560
Goodness-of-fit on F^2	1.141

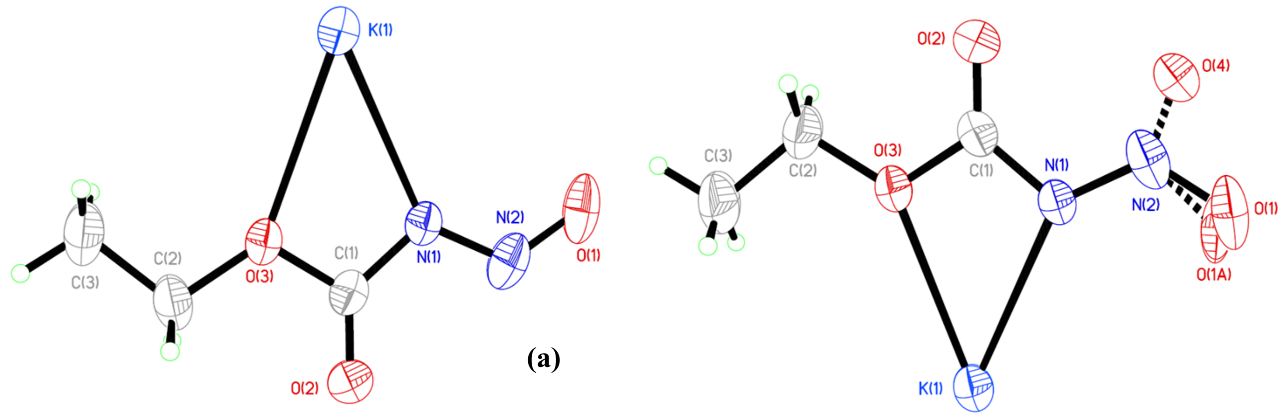


Figure S17. Molecular structure of a) **4** b) **4** with nitroethylcarbamate component at 50 % ellipsoid.

References

1. J. Thiele and A. Lachman, *Liebigs Ann.*, 1895, **288**, 267-311.
2. O. A. Luk'yanov, O. V. Anikin, V. P. Gorelik and V. A. Tartakovsky, *Russ Chem Bull*, 1994, **43**, 1457-1461.
3. R. F. Weiss and B. A. Price, *Marine Chemistry*, 1980, **8**, 347-359.