Supporting Information

Preparation and Photochemistry of Hydroxy Isocyanate

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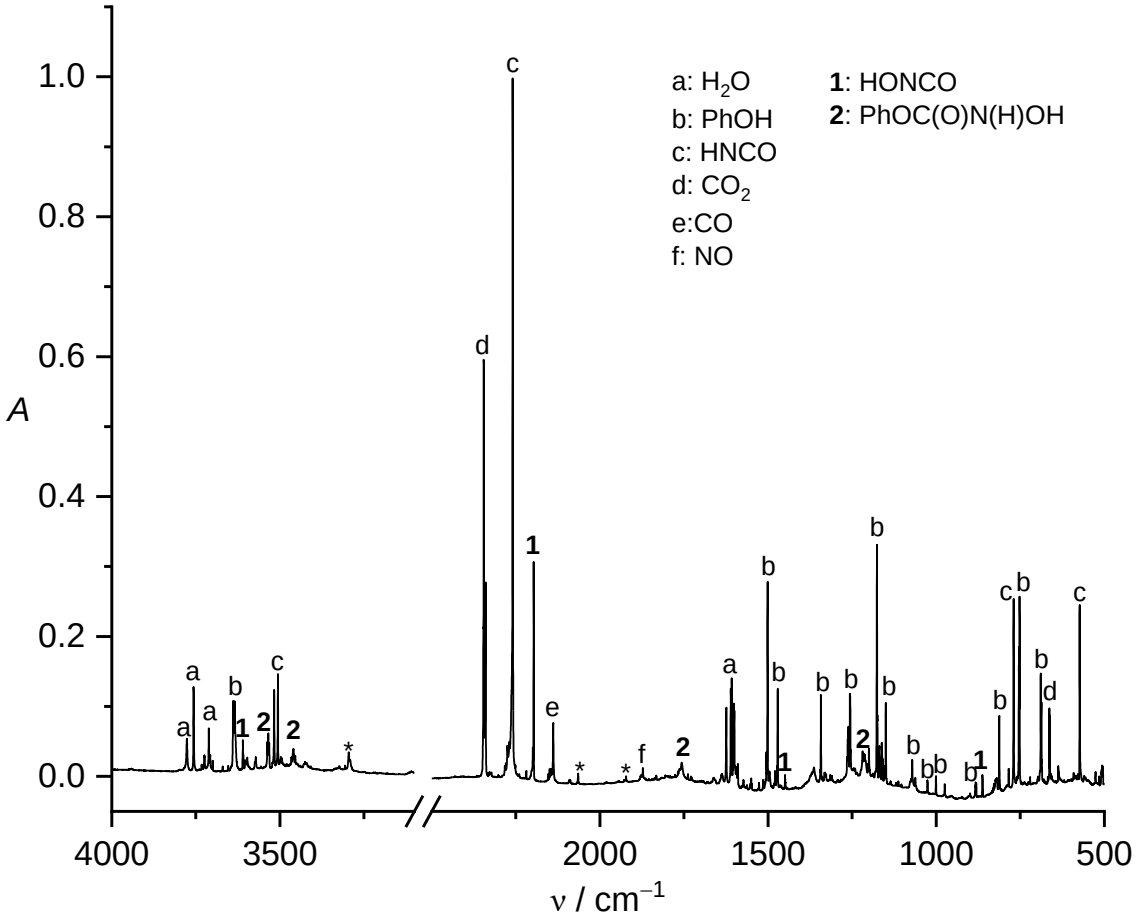

Figure S1. IR spectrum showing the product of pyrolysis of **2** with subsequent trapping in an argon matrix at 12 K. Unknown species are marked with *.

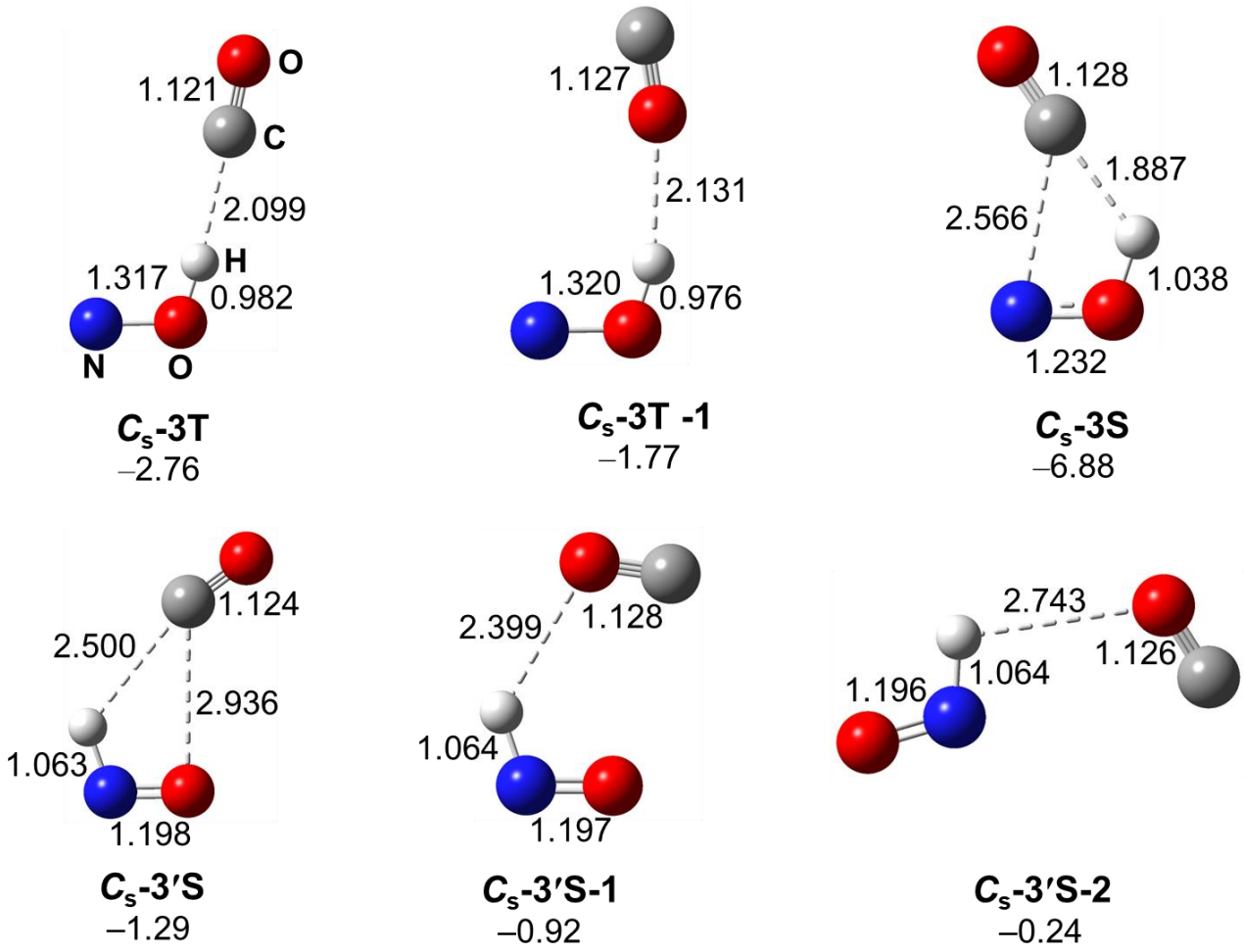

Figure S2. Computed structures (bond lengths in Å) and binding energies (ΔH_0 in kcal mol^{-1}) for the complexes at the B3LYP-D3(BJ)/def2-TZVP level of theory.

Table S1. Experimentally observed and computed IR frequencies of **1** and *d*-**1**, band origins in cm^{-1}, computed intensities (km mol^{-1}) in parentheses.

Mode	**1**			*d*-**1**			Assignment
	Harmonic[a]	**Anharmonic**[a]	Ar, 3.5 K[b]	**Harmonic**[a]	**Anharmonic**[a]	Ar, 3.5 K[b]	
9 (A)	3841.6 (94)	3651.3 (71)	3610.3	2798.9 (43)	2697.7 (36)	2669.0	OH str.
8 (A)	2253.4 (623)	2209.0 (516)	2196.9	2253.3 (623)	2204.5 (769)	2190.0	NCO asym. str.
7 (A)	1493.2 (56)	1441.5 (3)	1449.4	1365.0 (<1)	1331.4 (<1)	_	HON bend.
6 (A)	1269.5 (48)	1233.0 (38)	1241.6	1027.5 (78)	1006.3 (185)	1000.7	NO str. + HON bend.
5 (A)	883.1 (51)	858.2 (46)	862.5	874.3 (36)	851.9 (35)	855.6	NO str.
4 (A)	694.6 (17)	690.0 (14)	686.3	692.6 (16)	688.2 (15)	684.6	NCO bend.
3 (A)	514.3 (9)	514.1 (9)	515.6	513.1 (12)	512.2 (12)	514.7	NOC bend.
2 (A)	226.2 (8)	217.7 (9)	_	221.6 (8)	214.5 (9)	_	
1 (A)	204.9 (127)	171.1 (113)	_	150.9 (65)	134.7 (64)	_	

[a] CCSD(T)/cc-pVTZ. [b] not observed.

Table S2. Computed IR frequencies of **1** and *d*-**1**, band origins in cm^{-1}, computed intensities (km mol^{-1}) in parentheses.

Mode	**1** Computed[a]	d-**1** Computed[a]	Assignment
9	3786 (97)	2767 (45)	OH str.
8	2287 (697)	2287 (698)	NCO asym. str.
7	1500 (36)	1404 (<1)	HON bend.
6	1292 (77)	1024 (89)	NO str. + HON bend.
5	886 (58)	878 (41)	NO str.
4	702 (22)	700 (22)	NCO bend.
3	533 (13)	532 (16)	NOC bend.
2	238 (138)	233 (8)	
1	237 (8)	176 (70)	

[a] B3LYP/def2-TZVP, harmonic approximation, unscaled frequencies, intensities (in parentheses) in km mol^{-1}. [b] not observed.

Table S3. Experimentally observed and computed IR frequencies of **3** and d-**3**, band origins in cm^{-1}, computed intensities (km mol^{-1}) in parentheses.

Mode	**3** computed [a]	**3** Ar, 3.5 K[b]	d-**3** computed [a]	d-**3** Ar, 3.5 K[b]	Assignment
9	3487 (540)	3364.4	2545 (274)	2490.3	OH str.
8	2248 (69)	2165.4	2248 (73)	2166.0	CO str.
7	1280 (<1)	–	1205 (93)	1163.1	ON str.
6	1169 (157)	1127.2	922 (41)	904.1	OH bend.
5	418 (87)	–	310(41)	–	
4	168 (8)	–	164 (7)	–	
3	133 (2)	–	131 (2)	–	
2	87 (9)	–	85 (9)	–	
1	49 (6)	–	48 (6)	–	

[a] B3LYP(D3)/def2-TZVP, harmonic approximation, unscaled frequencies, intensities (in parentheses) in km mol^{-1}. [b] not observed.

Table S4. Experimentally observed and computed IR frequencies of **3′** and d-**3′**, band origins in cm^{-1}, computed intensities (km mol^{-1}) in parentheses.

Mode	**3′** computed [a]	**3′** Ar, 3.5 K[b]	d-**3′** computed [a]	d-**3′** Ar, 3.5 K[b]	Assignment
9	2872 (68)	2744.1	2106 (36)	2012.0	NH str.
8	2221 (92)	2145.6	2221 (93)	2145.9	CO str.
7	1676 (64)	–	1667 (56)	–	NO str.
6	1570 (28)	1568.9	1195 (13)	–	NH bend.
5	292 (77)	–	220 (38)	–	
4	203 (20)	–	193 (17)	–	
3	121 (<1)	–	118 (<1)	–	
2	66 (<1)	–	66 (<1)	–	
1	57 (3)	–	57 (3)	–	

[a] B3LYP(D3)/def2-TZVP, harmonic approximation, unscaled frequencies, intensities (in parentheses) in km mol^{-1}. [b] not observed.

Computed atomic coordinates and energies of species for optimized structures.

1

B3LYP/def2-TZVP

0 1

H	2.32452100	0.25404500	0.00001100
C	-0.65903100	0.07118900	-0.00000200
O	-1.79691000	-0.17599700	-0.00000900
N	0.47955300	0.51725200	0.00000500
O	1.58100900	-0.36174600	0.00000400

Zero-point correction= 0.026109

Thermal correction to Energy= 0.030336

Thermal correction to Enthalpy= 0.031280

Thermal correction to Gibbs Free Energy= 0.000103

Sum of electronic and zero-point Energies= -243.905128

Sum of electronic and thermal Energies= -243.900901

Sum of electronic and thermal Enthalpies= -243.899957

Sum of electronic and thermal Free Energies= -243.931134

1

CCSD(T)/cc-pVTZ

0 1

O	0.00000000	0.00000000	0.00000000
H	0.00000000	0.00000000	0.96229311
C	1.75181938	0.00000000	-1.44421561
N	1.39601000	-0.00001234	-0.26005818
O	2.27458712	0.00000832	-2.49131839

Zero-point correction= 0.02559936

Sum of electronic Energies= -243.47819309

3-singlet

B3LYP-D3(BJ)/def2-TZVP

0 1

H	-0.71612700	-0.99686100	0.00005600
C	1.02670400	-0.27454200	0.00007400
O	2.07997000	0.12812900	0.00008800
N	-1.32609700	0.74861200	-0.00013200
O	-1.60014700	-0.45265000	-0.00003600

Zero-point correction= 0.021274

Thermal correction to Energy= 0.026438

Thermal correction to Enthalpy= 0.027382

Thermal correction to Gibbs Free Energy= -0.006730

Sum of electronic and zero-point Energies= -243.819750

Sum of electronic and thermal Energies= -243.814586

Sum of electronic and thermal Enthalpies= -243.813642

Sum of electronic and thermal Free Energies= -243.847754

3-triplet

B3LYP-D3(BJ)/def2-TZVP

0 3

H	0.00000000	0.79614600	0.00000000
C	-0.92044500	-1.09070300	0.00000000
O	-1.38856300	-2.10971000	0.00000000
N	1.79561100	1.36131600	0.00000000
O	0.50773700	1.63706800	0.00000000

Zero-point correction= 0.020588

Thermal correction to Energy= 0.026628

Thermal correction to Enthalpy= 0.027572

Thermal correction to Gibbs Free Energy= -0.010515

Sum of electronic and zero-point Energies= -243.846791

Sum of electronic and thermal Energies= -243.840751

Sum of electronic and thermal Enthalpies= -243.839806

Sum of electronic and thermal Free Energies= -243.877893

3′-singlet

B3LYP-D3(BJ)/def2-TZVP

0 1

O	-1.43798800	-0.65386600	0.00000000
H	-1.08695600	1.14576400	0.00000000
C	1.30052700	0.40403100	-0.00000100
N	-1.89351600	0.45367000	0.00000100
O	2.25528900	-0.18933900	0.00000100

Zero-point correction= 0.020679

Thermal correction to Energy= 0.026823

Thermal correction to Enthalpy= 0.027768

Thermal correction to Gibbs Free Energy= -0.009439

Sum of electronic and zero-point Energies= -243.877509

Sum of electronic and thermal Energies= -243.871365

Sum of electronic and thermal Enthalpies= -243.870421

Sum of electronic and thermal Free Energies= -243.907627

3′-triplet

B3LYP-D3(BJ)/def2-TZVP

0 3

O	-2.42567500	-0.43077600	-0.00002000
H	-0.64235600	0.36812000	-0.00366700
C	1.62973200	0.05688300	-0.00271600
N	-1.66283300	0.52496000	0.00101600
O	2.73864900	-0.11724200	0.00162700

Zero-point correction= 0.020077

Thermal correction to Energy= 0.026434

Thermal correction to Enthalpy= 0.027378

Thermal correction to Gibbs Free Energy= -0.011921

Sum of electronic and zero-point Energies= -243.861930

Sum of electronic and thermal Energies= -243.855573

Sum of electronic and thermal Enthalpies= -243.854629

Sum of electronic and thermal Free Energies= -243.893928

HON-CO

B3LYP-D3(BJ)/def2-TZVP

0 1

O	1.99798500	-0.22985700	-0.15734900
H	2.42042500	-0.57392300	0.68207500
C	-1.30892700	-0.46339000	0.05809900
N	1.05776600	0.56583200	0.07927400
O	-2.24438800	0.15403700	-0.04084900

Zero-point correction= 0.019942

Thermal correction to Energy= 0.026197

Thermal correction to Enthalpy= 0.027141

Thermal correction to Gibbs Free Energy= -0.010704

Sum of electronic and zero-point Energies= -243.811484

Sum of electronic and thermal Energies= -243.805230

Sum of electronic and thermal Enthalpies= -243.804286

Sum of electronic and thermal Free Energies= -243.842131

TS1

B3LYP-D3(BJ)/def2-TZVP

0 1

O	1.89953100	-0.21651000	-0.14794200
H	2.31680800	-0.51184300	0.70149500

C	-1.13993500	-0.41247600	0.04713200
N	0.91576900	0.54926700	0.06418000
O	-2.13547900	0.10923900	-0.03125100

Zero-point correction= 0.020812
Thermal correction to Energy= 0.025791
Thermal correction to Enthalpy= 0.026735
Thermal correction to Gibbs Free Energy= -0.007157
Sum of electronic and zero-point Energies= -243.808304
Sum of electronic and thermal Energies= -243.803325
Sum of electronic and thermal Enthalpies= -243.802381
Sum of electronic and thermal Free Energies= -243.836273

TS2

B3LYP-D3(BJ)/def2-TZVP

0 1

O	2.13674300	-0.24752300	-0.07415800
H	2.20685500	-0.79221800	0.76011300
C	-1.49599400	-0.50038700	-0.12178200
N	1.22036200	0.60304700	-0.00691200
O	-2.35842100	0.19417400	0.07652800

Zero-point correction= 0.019271
Thermal correction to Energy= 0.025145
Thermal correction to Enthalpy= 0.026089
Thermal correction to Gibbs Free Energy= -0.011456
Sum of electronic and zero-point Energies= -243.810212
Sum of electronic and thermal Energies= -243.804339
Sum of electronic and thermal Enthalpies= -243.803394
Sum of electronic and thermal Free Energies= -243.840939

TS3

B3LYP-D3(BJ)/def2-TZVP

0 1

O	2.20039800	-0.36069100	-0.19281900
H	2.12469000	0.01161500	0.85012200
C	-1.55425800	-0.35246100	0.30272500
N	1.31034400	0.57962300	0.06315500
O	-2.44684200	0.11641500	-0.19575100

Zero-point correction= 0.015222

Thermal correction to Energy= 0.021949

Thermal correction to Enthalpy= 0.022894

Thermal correction to Gibbs Free Energy= -0.017270

Sum of electronic and zero-point Energies= -243.757159

Sum of electronic and thermal Energies= -243.750431

Sum of electronic and thermal Enthalpies= -243.749487

Sum of electronic and thermal Free Energies= -243.789651

TS4

B3LYP-D3(BJ)/def2-TZVP

0 3

H	-0.72116100	-0.03308300	0.00000700
C	1.29961900	0.02852300	0.00001700
O	2.42009900	-0.01940600	-0.00000900
N	-1.77984700	-0.70005800	-0.00000200
O	-1.74730200	0.61470000	-0.00000200

Zero-point correction= 0.015529

Thermal correction to Energy= 0.021320

Thermal correction to Enthalpy= 0.022264

Thermal correction to Gibbs Free Energy= -0.014980

Sum of electronic and zero-point Energies= -243.794143

Sum of electronic and thermal Energies= -243.788353

Sum of electronic and thermal Enthalpies= -243.787409

Sum of electronic and thermal Free Energies= -243.824653