

## Supporting Information

### The simplest alkynyl thiocyanate HCCSCN and its isomers

Bo Lu,<sup>a</sup> Zhuang Wu,<sup>a</sup> Lina Wang,<sup>a</sup> Bifeng Zhu,<sup>a</sup> Guntram Rauhut,<sup>b</sup> and Xiaoqing Zeng\*<sup>a</sup>

<sup>a</sup>Department of Chemistry, Fudan University, Shanghai 200433 (China)

E-mail: xqzeng@fudan.edu.cn

<sup>b</sup>Institute for Theoretical Chemistry, University of Stuttgart Pfaffenwaldring 55, Stuttgart 70569 (Germany)

## Table of Contents

Experimental and computational details.....	S3
Temperature-pressure curve of HC≡CSCN (Figure S1).....	S5
UV-Vis IR spectra of HC≡CSCN (Figure S2).....	S5
IR difference spectra for the photochemistry of HCCC(O)NCS (Figure S3).....	S6
Calculated potential energy profile of HCCSCN (Figure S4).....	S7
Calculated and observed NMR data (Table S1).....	S8
Calculated and observed IR frequencies of HC≡CSCN (Table S2).....	S9
Calculated and observed IR frequencies of HC≡CSNC (Table S3).....	S10
Calculated and observed IR frequencies of NCC(H)CS (Table S4).....	S11
Calculated IR frequencies of HC≡CCNS (Table S5).....	S12
Calculated vertical transitions of HC≡CSCN and different isomers (Table S6).....	S13
References.....	S14
Calculated atomic coordinates and energies for all optimized structures.....	S16

## Experimental and computational details

### Sample preparation

Alkynyl thiocyanate HCCSCN was prepared according to the reference for the synthesis of PhCCSCN<sup>1</sup> with modifications. Briefly, sodium thiocyanate (0.162 g, 2.0 mmol) was added to the alkynyl iodonium triflate (0.567 g, 1.5 mmol) in 2.0 mL dichloromethane. The mixture was stirred at 25°C for 4 h. Then, all the volatiles were separated by low-temperature fractional condensation using three successive cold U-traps at -60°C, -80 °C, and -196 °C under dynamic vacuum conditions (10 Pa). The desired product HCCSCN (60 mg, 0.7 mmol) was retained in the first trap as white solid. The purity of the substance was checked by NMR spectroscopy (Bruker AVANCE NEO 400 MHz spectrometer). UV/Vis spectra of gaseous HCCSCN were recorded in a closed quartz cell at 300 K with a Shimadzu UV 3600 spectrometer.

Propiolyl isocyanate HCCC(O)NCS was synthesized by treatment of the corresponding propiolyl chloride with sodium thiocyanate. Briefly, propiolyl chloride (0.16 mL, 2.0 mmol) was added dropwise to a solution of sodium thiocyanate (0.203 g, 2.5 mmol) in 0.5 mL propylene carbonate. The mixture was stirred at 25 °C for 4 h. Then, all the volatiles were separated by fractional condensation using three successive cold U-traps at -40, -65, and -196 °C under dynamic vacuum conditions (10 Pa). The desired product HCCC(O)NCS (0.167 g, 1.5 mmol) was retained in the middle trap as white solid. The purity of the substance was checked by gas phase IR ( $\nu = 3328/3320, 2128, 2029, 1970/1967, 1735/1725, 1201/1166, 975/937, 724/720, 689, 656, \text{ and } 592 \text{ cm}^{-1}$ ) and NMR spectroscopy.

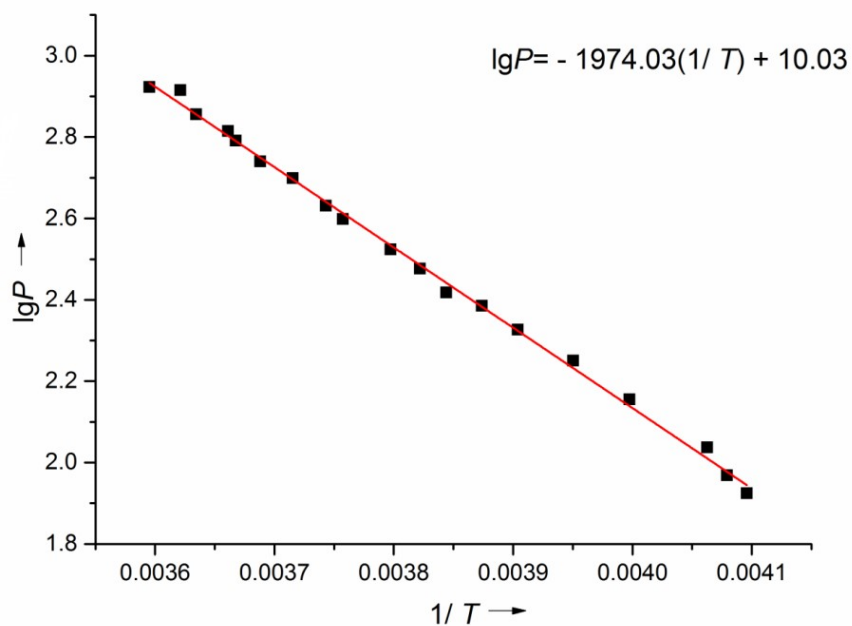
### Matrix-isolation IR Spectroscopy

Matrix IR spectra were recorded on a FT-IR spectrometer (Bruker 70 V) in a reflectance mode using a transfer optic. A KBr beam splitter and liquid nitrogen cooled mercury cadmium telluride (MCT) detector were used in the mid-IR

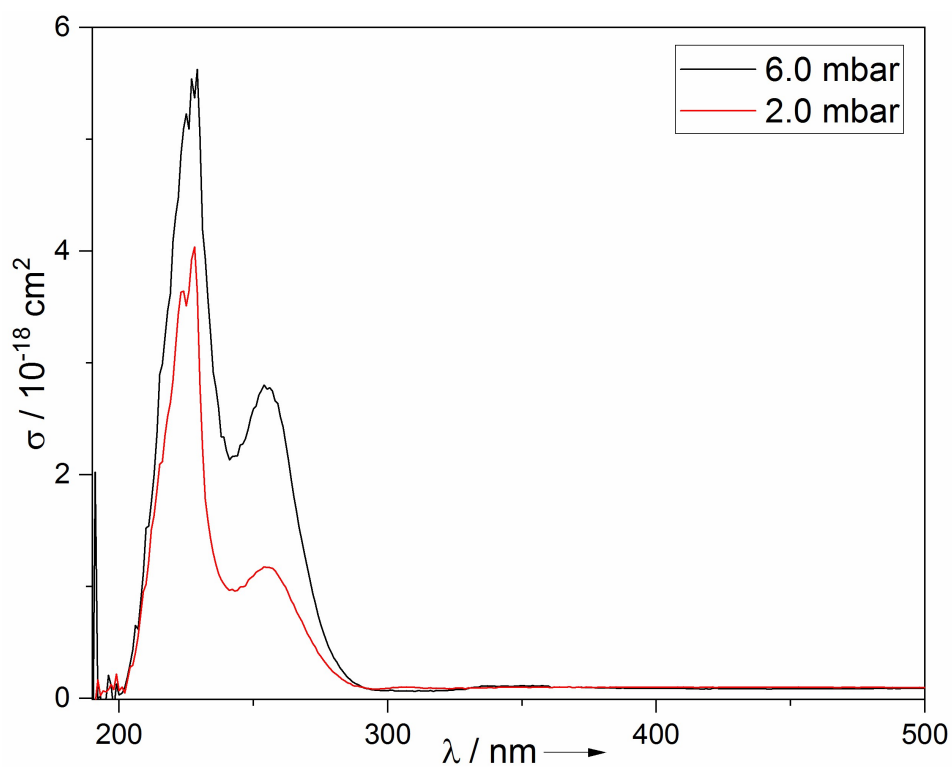
region (4000–450  $\text{cm}^{-1}$ ). For each spectrum, 200 scans at a resolution of 0.5  $\text{cm}^{-1}$  were co-added. The gaseous sample was mixed by passing a flow of Ar gas through a U-trap ( $-54^\circ\text{C}$ ) containing ca. 20 mg of the HCCSCN. Then the mixture (alkynyl thiocyanate/dilution gas  $\approx$  1:1000 estimated) were deposited (2 mmol  $\text{h}^{-1}$ ) onto the Rh-plated copper block matrix support (Ar: 10 K) in a high vacuum ( $\sim 10^{-6}$  Pa). For Propiolyl isocyanate, the sample was evaporated from a U-trap ( $-57^\circ\text{C}$ ) onto the Rh-plated copper block matrix support (Ar: 10 K). Photolysis was performed by using an ArF excimer laser (Gamlaser EX5/250, 3 Hz, 193 nm) and a  $\text{Nd}^{3+}$ :YAG laser (MPL-F-266, 266 nm, 10 mW).

### Quantum chemical calculation methods

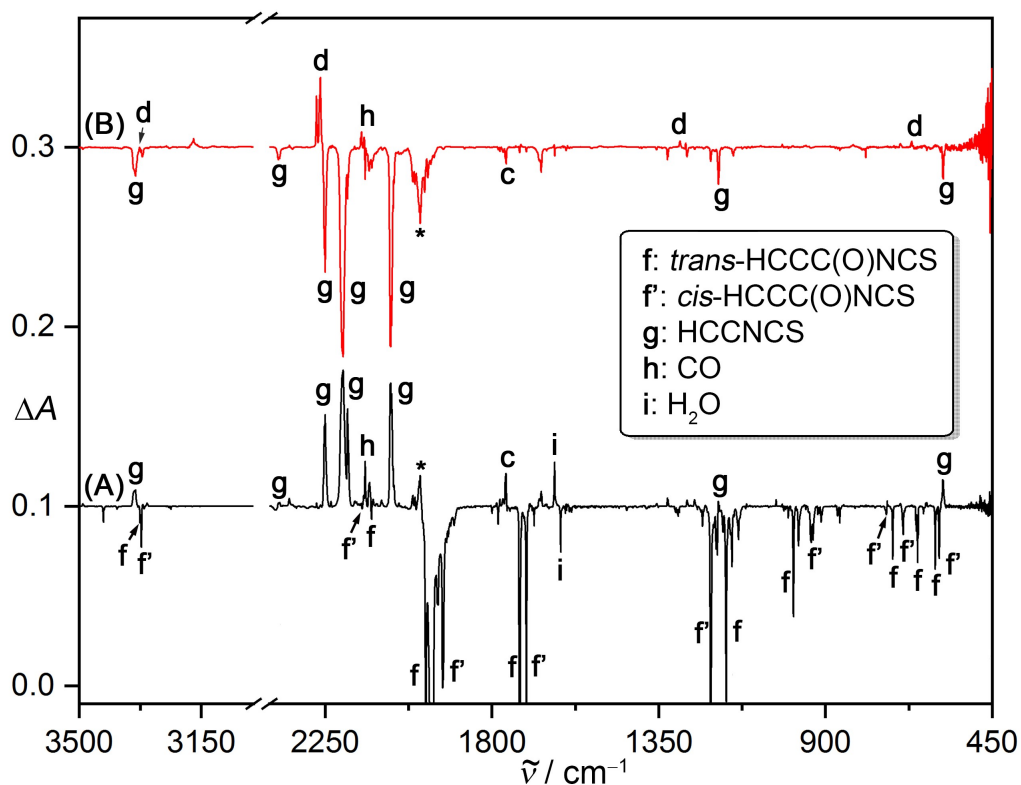
Structures and IR frequencies were calculated using the B3LYP/6-311++G(3df,3pd)<sup>2</sup> and CBS-QB3<sup>3</sup> methods and the ab initio CCSD(T)<sup>4</sup> method at the cc-pVTZ<sup>5</sup> basis set. Anharmonic IR frequencies obtained from configuration-selective vibrational configuration interaction (VCI) theory<sup>6</sup> and second-order vibration perturbation (VPT2) theory<sup>7</sup> were calculated at the CCSD(T)-F12a/cc-pVTZ-F12 and CCSD(T)/cc-pVTZ levels,<sup>8</sup> respectively. Time-dependent (TD) DFT (B3LYP/6-311++G(3df,3pd)) calculations<sup>9</sup> were performed for the prediction of UV-Vis transitions. NMR chemical shift values were calculated using the gauge-independent atomic orbital (GIAO)<sup>10</sup> method and the SMD solvent model at the B3LYP/6-311++G(3df,3pd) level. Local minima were confirmed by vibrational analysis and the transition states were further confirmed by intrinsic reaction coordinate (IRC) calculations.<sup>11</sup> All the DFT calculations were performed using the Gaussian 09 software package.<sup>12</sup> The CCSD(T) and CCSD(T)-F12a calculations were performed with the CFOUR<sup>13</sup> and MOLPRO<sup>14</sup> programs, respectively.



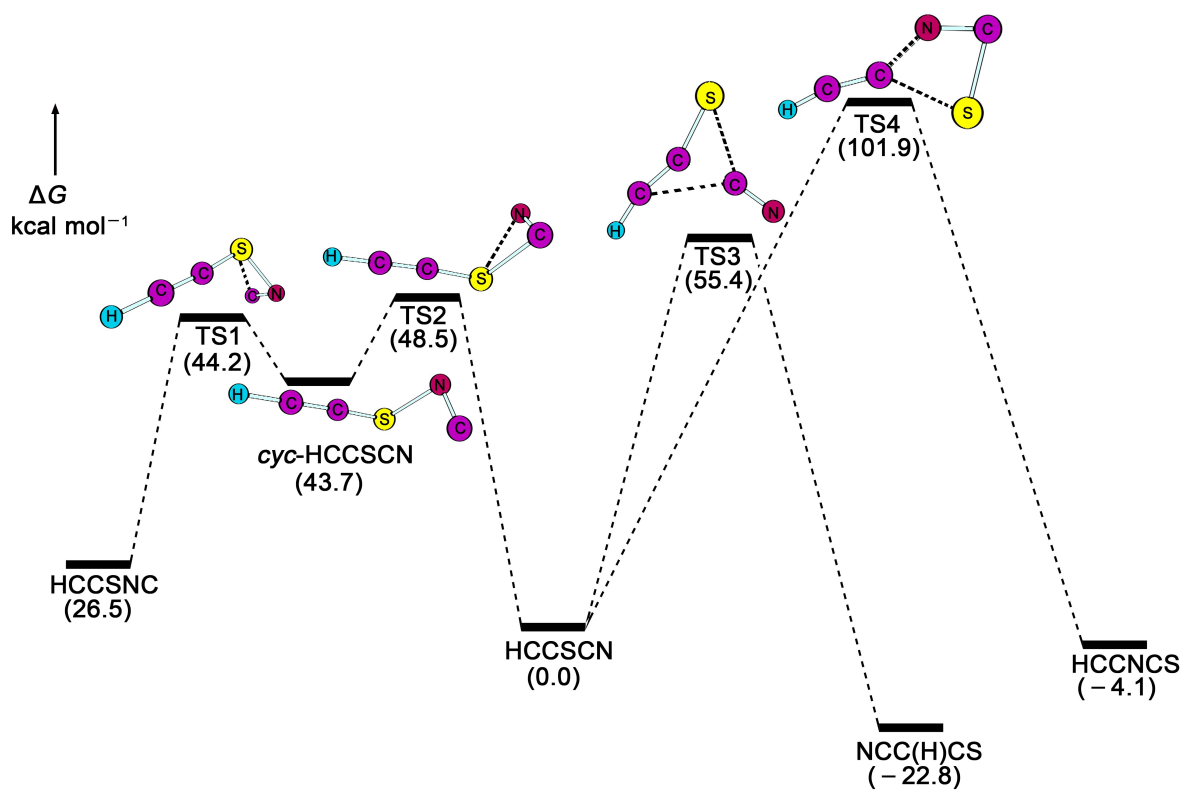
**Fig. S1** Temperature-pressure curve for HC≡CSCN in the temperature range from -29 to 10 °C.



**Fig. S2** UV/Vis IR spectra of gaseous HC≡CSCN at 300 K. The two absorptions ( $\lambda_{\max}$ ) at 255 and 230 nm correspond to the computed vertical transitions at 264/249 and 210 nm at the TD-B3LYP/6-311++G(3df,3pd) level of theory (Table S6).



**Fig. S3** A) IR difference spectrum reflecting the change of Ar-matrix isolated HCCC(O)NCS (*trans*: f; *cis*: f') upon a 266 nm laser photolysis (180 min). B) IR difference spectrum reflecting the change of Ar-matrix upon subsequent 193 nm laser photolysis (7 min). The IR band at 1994.1 cm<sup>-1</sup> for an unknown species is labeled with an asterisk, and it is different from the IR band for HCCCO• radical (2308.6 cm<sup>-1</sup>, Ar-matrix).<sup>15</sup>



**Fig. S4** Calculated potential energy profile (Gibbs free energy,  $\Delta G$ ) for the isomerization of HCCSCN at the CCSD(T)-F12a/aug-cc-pVTZ//B3LYP/6-311++G(3df,3pd) level of theory (with zero-point vibrational energy corrections).

**Table S1.** Calculated<sup>a</sup> and observed<sup>b</sup> NMR spectroscopic data of acetylene, azidoacetylene, alkynyl isocyanate, and alkynyl thiocyanate.

Compound	Signal (solvent)	$\delta_{\text{calc}}$	$\delta_{\text{obs}}^c$	$\Delta_{\text{ref}}^d$	$\delta_{\text{calc}} + \Delta_{\text{ref}}$	Coupling constants $J_{\text{CH}}$ (Hz)	
						obs	calc <sup>g</sup>
HC≡CH	<sup>1</sup> H (CD <sub>2</sub> Cl <sub>2</sub> )	-29.8	2.0	31.8	2.0	49.4 <sup>f</sup>	48.5
HC≡CH	<sup>13</sup> C (CD <sub>2</sub> Cl <sub>2</sub> )	-109.8	72.0	181.8	72	249.6 <sup>f</sup>	247.2
HC≡CN <sub>3</sub>	<sup>1</sup> H (CD <sub>2</sub> Cl <sub>2</sub> )	-29.1	2.55	31.8	2.7		
HC≡CN <sub>3</sub>	<sup>13</sup> C (CD <sub>2</sub> Cl <sub>2</sub> )	-109.6	71.9	181.8	72.2	57.5 <sup>f</sup>	56.6
HC≡CN <sub>3</sub>	<sup>13</sup> C (CD <sub>2</sub> Cl <sub>2</sub> )	-128.2	54.5	181.8	53.6	262.8 <sup>f</sup>	261.5
HC≡CNCO	<sup>1</sup> H (CD <sub>2</sub> Cl <sub>2</sub> )	-29.9	3.78	31.8	1.9		
HC≡CNCO	<sup>13</sup> C (CD <sub>2</sub> Cl <sub>2</sub> )	-70.8	124.79 <sup>e</sup>	181.8	111.0		
HC≡CNCO	<sup>13</sup> C (CD <sub>2</sub> Cl <sub>2</sub> )	-116.1	65.48 <sup>e</sup>	181.8	65.7	59 <sup>f</sup>	58.2
HC≡CNCO	<sup>13</sup> C (CD <sub>2</sub> Cl <sub>2</sub> )	-141.3	44.46 <sup>e</sup>	181.8	40.5	267 <sup>f</sup>	282.8
HC≡CSCN	<sup>1</sup> H (CDCl <sub>3</sub> )	-28.1	3.3	31.8	3.7		
HC≡CSCN	<sup>13</sup> C (CDCl <sub>3</sub> )	-65.8	106.2	181.8	116.0		
HC≡CSCN	<sup>13</sup> C (CDCl <sub>3</sub> )	-119.9	59.3	181.8	61.9	53	61.1
HC≡CSCN	<sup>13</sup> C (CDCl <sub>3</sub> )	-84.3	89.5	181.8	97.5	262	265.0

<sup>a</sup>All geometries and NMR chemical shifts were calculated at the B3LYP/6-311++G(3df,3pd) level of theory. <sup>b</sup><sup>1</sup>H (600 MHz) and <sup>13</sup>C (150 MHz) NMR spectra were recorded at 25 °C. <sup>c</sup>The observed NMR chemical shifts of HC≡CH and HC≡CN<sub>3</sub> are from reference.<sup>16</sup> <sup>d</sup>The reference quantity  $\Delta_{\text{ref}}$  was determined by using  $\delta_{\text{calc}}$  and  $\delta_{\text{obs}}$  of acetylene in the case of <sup>1</sup>H NMR and <sup>13</sup>C NMR data. <sup>e</sup>The observed NMR chemical shifts of HC≡CNCO are from reference.<sup>17</sup> <sup>f</sup>The observed data are taken from reference.<sup>16,17</sup> <sup>g</sup>Calculated coupling constants at the B3LYP/6-311++G(3df,3pd) level of theory.



**Table S2.** Observed and calculated vibrational data ( $> 450 \text{ cm}^{-1}$ ) for HCCSCN.

CCSD(T)-F12a <sup>a</sup>	CCSD(T) <sup>b</sup>	Ar-matrix <sup>c</sup>	Gas-phase <sup>d</sup>	Assign <sup>e</sup>
3318 (94)	3326 (72)	3324.4 (100)	3325 (vs)	$\nu_1$ , $\nu(\text{C-H})$
2186 (20)	2179 (1)	2181.2 (5)	2183 (w)	$\nu_2$ , $\nu(\text{C}\equiv\text{N})$
2078 (1)	2076 ( $< 1$ )	2080.8 (1)	2072 (vw)	$\nu_3$ , $\nu(\text{C}\equiv\text{C})$
1401 (9)	1376 (9)	1390.7 (6)	1389 (ms)	$2 \nu_5$
1190 (18)	1179 (14)	1170.8 (7)	1165 (s)	$2 \nu_7$
714 (12)	703 (6)	712.7 (7)	712 (sh)	$\nu_4$ , $\delta_{\text{i.p.}}(\text{CH})$
705 (38)	689 (35)	697.3 (32)	698(vs)	$\nu_5$ , $\nu(\text{CC-S})$
677 (5)	632 (709)	672.8 (2)	n.o. <sup>f</sup>	$\nu_6$ , $\nu(\text{S-CN})$
583 (62)	585 (47)	586.5 (45)	585 (vs)	$\nu_7$ , $\delta_{\text{o.o.p.}}(\text{CH})$
478 (9)	477 (7)	484.7 (9)	481 (ms)	$\nu_8$ , $\delta_{\text{i.p.}}(\text{CSC})$

<sup>a</sup>Calculated anharmonic IR frequencies and intensities in parentheses ( $\text{km mol}^{-1}$ ) at the CCSD(T)-F12a/cc-pVTZ-F12 level using configuration-selective vibrational configuration interaction (VCI) theory. <sup>b</sup>Calculated anharmonic IR frequencies and intensities in parentheses ( $\text{km mol}^{-1}$ ) at the CCSD(T)/cc-pVTZ level using second-order vibration perturbation (VPT2) theory. <sup>c</sup>Observed band positions and relative integrated intensities (in parentheses) in Ar-matrix at 10 K. <sup>d</sup>Observed band positions and relative intensities (vs: very strong, s: strong, ms: medium strong, w: weak, sh: shoulder) in the gas phase at 300 K. <sup>e</sup>Tentative assignment of the modes based on the calculated vibrational displacement vectors. <sup>f</sup>The abbreviation “n.o.” denotes “not observed”.

**Table S3.** Observed and calculated vibrational data ( $> 450 \text{ cm}^{-1}$ ) for HCCSNC.

CCSD(T)-F12a <sup>a</sup>	CCSD(T) <sup>b</sup>	Ar-matrix <sup>c</sup>	Assign <sup>d</sup>
3321 (80)	3325 (103)	3308.6 (76)	$\nu_1$ , $\nu(\text{C-H})$
2066 (39)	2064 (2)	2062.8 (36)	$\nu_2$ , $\nu(\text{C}\equiv\text{C})$
2049 (312)	2044 (168)	2044.9 (100)	$\nu_3$ , $\nu(\text{N}\equiv\text{C})$
721 (13)	711 (1955)	755.0 (5)	$\nu_4$ , $\delta_{\text{i.p.}}(\text{CH})$
709 (49)	707 (2069)	712.0 (57)	$\nu_5$ , $\nu(\text{C-S})$
685 (27)	651 (38)	623.0 (54)	$\nu_6$ , $\nu(\text{S-N})$
561 (70)	562 (50)	557.3 (65)	$\nu_7$ , $\delta_{\text{o.o.p.}}(\text{CH})$
446 (15)	441 (10)	n.o. <sup>e</sup>	$\nu_8$ , $\delta_{\text{i.p.}}(\text{CSN})$

<sup>a</sup>Calculated anharmonic IR frequencies and intensities in parentheses ( $\text{km mol}^{-1}$ ) at the CCSD(T)-F12a/cc-pVTZ-F12 level using configuration-selective vibrational configuration interaction (VCI) theory. <sup>b</sup>Calculated anharmonic IR frequencies and intensities in parentheses ( $\text{km mol}^{-1}$ ) at the CCSD(T)/cc-pVTZ level using second-order vibration perturbation (VPT2) theory. <sup>c</sup>Observed band positions and relative integrated intensities (in parentheses) in Ar-matrix at 10 K. <sup>d</sup>Tentative assignment of the modes based on the calculated vibrational displacement vectors. <sup>e</sup>The abbreviation “n.o.” denotes “not observed”.

**Table S4.** Observed and calculated vibrational data ( $> 450 \text{ cm}^{-1}$ ) for NCC(H)CS.

VPT2 <sup>a</sup>	CCSD(T) <sup>b</sup>	Ar-matrix <sup>c</sup>	Assign <sup>d</sup>
3084 (8)	3063 (26)	3062.3 (3)	$\nu_1$ , $\nu(\text{C-H})$
2230 (103)	2230 (20)	2230.0 (8)	$\nu_2$ , $\nu(\text{C}\equiv\text{N})$
1761 (791)	1762 (319)	1760.7 (100)	$\nu_3$ , $\nu(\text{C=C})$
1259 (133)	1238 (147)	1256.2 (2)	$\nu_4$ , $\delta_{\text{i.p.}}(\text{CH})$
1043 (35)	1026 (1)	1052.2 ( $< 1$ )	$\nu_5$ , $\nu(\text{C-C})$
851 (27)	844 (10)	854.6 (5)	$\nu_6$ , $\nu(\text{C=S})$
618 (42)	628 (31)	629.7 (1)	$\nu_7$ , $\delta_{\text{o.o.p.}}(\text{CH})$
550 (494)	547 (3)	n.o. <sup>e</sup>	$\nu_8$ , $\delta_{\text{i.p.}}(\text{CCC})$

<sup>a</sup>Calculated anharmonic IR frequencies and intensities in parentheses ( $\text{km mol}^{-1}$ ) at the CCSD(T)-F12a/cc-pVTZ-F12 level using second-order vibration perturbation (VPT2) theory.

<sup>b</sup>Calculated anharmonic IR frequencies and intensities in parentheses ( $\text{km mol}^{-1}$ ) at the CCSD(T)/cc-pVTZ level using second-order vibration perturbation (VPT2) theory. <sup>c</sup>Observed band positions and relative integrated intensities (in parentheses) in Ar-matrix at 10 K.

<sup>d</sup>Tentative assignment of the modes based on the calculated vibrational displacement vectors. <sup>e</sup>The abbreviation "n.o." denotes "not observed".

**Table S5.** Calculated IR frequencies ( $> 450 \text{ cm}^{-1}$ ) of  $\text{HC}\equiv\text{CCNS}$ .

CCSD(T)-F12a <sup>a</sup>	CCSD(T) <sup>b</sup>	B3LYP <sup>c</sup>	Assign <sup>d</sup>
3315	3451	3463	$\nu_1$ , $\nu(\text{C-H})$
2205	2259	2291	$\nu_2$ , $\nu_{\text{asymm}}(\text{CCN})$
2042	2077	2124	$\nu_3$ , $\nu_{\text{symm}}(\text{CCN})$
1071	1102	1115	$\nu_4$ , $\nu_{\text{asymm}}(\text{CNS})$
594	607	642	$\nu_5$ , $\delta_{\text{i.p.}}(\text{C-H})$
553	566	579	$\nu_6$ , $\nu(\text{NS})$

<sup>a</sup>Calculated VPT2 anharmonic IR frequencies at the CCSD(T)/cc-pVTZ level. <sup>b</sup>Calculated harmonic IR frequencies at the CCSD(T)/cc-pVTZ level. <sup>c</sup>Calculated anharmonic IR frequencies at the B3LYP/6-311++G(3df,3pd) level. <sup>d</sup>Tentative assignment based on the calculated vibrational displacement vectors.

**Table S6.** Calculated vertical transitions (> 170 nm) of HC≡CSCN and different isomers at the TD-B3LYP/6-311++G(3df,3pd) level.

HCCSCN		HCCSNC		HCCNCS		NCC(H)CS		HCCCNCS		HCCNSC	
energy (nm)	oscillator strength ( <i>f</i> )	energy (nm)	oscillator strength ( <i>f</i> )	energy (nm)	oscillator strength ( <i>f</i> )	energy (nm)	oscillator strength ( <i>f</i> )	energy (nm)	oscillator strength ( <i>f</i> )	energy (nm)	oscillator strength ( <i>f</i> )
264	0.0003	279	0.0005	205	0.0453	511	0.0001	227	1.4124	576	0.0323
249	0.0008	241	0.0012	187	0.0003	246	0.1591	223	0.0165	423	0.0064
210	0.0251	220	0.0027			237	0.0001	212	0.0074	372	0.0010
204	0.0006	208	0.0007			233	0.0128			318	0.0002
189	0.0163	196	0.0450			216	0.0022			302	0.3433
182	0.0381	194	0.0004			201	0.0711			253	0.0003
179	0.0121	193	0.1910			198	0.0061			248	0.0357
178	0.0001	185	0.0098			191	0.0007			241	0.0076
177	0.0006	181	0.0980			190	0.5786			226	0.0010
		175	0.0054			187	0.0005				

## References

1. (a) P. J. Stang, *J. Org. Chem.*, 2003, **68**, 2997–3008; (b) D. R. Fischer, B. L. Williamson and P. J. Stang, *Synlett*, 1992, **1992**, 535–536.
2. (a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652; (b) M. J. Frisch, J. A. Pople and J. S. Binkley, *J. Chem. Phys.*, 1984, **80**, 3265–3269.
3. J. A. Montgomery Jr., M. J. Frisch, J. W. Ochterski and G. A. Petersson, *J. Chem. Phys.*, 2000, **112**, 6532–6542.
4. K. Raghavachari, G. W. Trucks, J. A. Pople and M. Head-Gordon, *Chem. Phys. Lett.*, 1989, **157**, 479–483.
5. T. H. Dunning Jr., *J. Chem. Phys.*, 1989, **90**, 1007–1023.
6. M. Neff and G. Rauhut, *J. Chem. Phys.*, 2009, **131**, 124129.
7. V. Barone, *J. Chem. Phys.*, 2005, **122**, 014108.
8. (a) T. B. Adler, G. Knizia and H. Werner, *J. Chem. Phys.*, 2007, **127**, 221106; (b) K. A. Peterson, T. B. Adler and H. Werner, *J. Chem. Phys.*, 2008, **128**, 084102.
9. (a) R. E. Stratmann, G. E. Scuseria and M. J. Frisch, *J. Chem. Phys.*, 1998, **109**, 8218–8224; (b) J. B. Foresman, M. Head-Gordon, J. A. Pople and M. J. Frisch, *J. Phys. Chem.*, 1992, **96**, 135–149.
10. K. Wolinski, J. F. Hinton and P. Pulay, *J. Am. Chem. Soc.*, 1990, **112**, 8251–8260.
11. (a) K. Fukui, *Acc. Chem. Res.*, 1981, **14**, 363–368; (b) H. P. Hratchian and H. B. Schlegel, *J. Chem. Theory Comput.*, 2005, **1**, 61–69.
12. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, Gaussian 09, Revision A.02.
13. CFOUR, Coupled-Cluster techniques for Computational Chemistry, a quantum-chemical program package by J. F. Stanton, J. Gauss, M. E. Harding, P. G. Szalay with contributions from A. A. Auer, R. J. Bartlett, U. Benedikt, C. Berger, D. E. Bernholdt, Y. J. Bomble, L. Cheng, O. Christiansen, M. Heckert, O. Heun, C. Huber, T. -C. Jagau, D. Jonsson, J. Jusélius, K. Klein, W. J. Lauderdale, D. A. Matthews, T. Metzroth, L. A. Mück, D. P. O'Neill, D. R.

- Price, E. Prochnow, C. Puzzarini, K. Ruud, F. Schiffmann, W. Schwalbach, S. Stopkowicz, A. Tajti, J. Vázquez, F. Wang, J. D. Watts and the integral packages MOLECULE (J. Almlöf, P. R. Taylor), PROPS (P. R. Taylor), ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, J. Olsen), and ECP routines by A. V. Mitin and C. van Wüllen. For the current version, see <http://www.cfour.de>.
14. (a) H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby and M. Schütz, *WIREs Comput. Mol. Sci.*, 2012, **2**, 242–253; (b) A package of ab initio programs written by H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, P. Celani, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklaß, D. P. O’Neill, P. Palmieri, D. Peng, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson and M. Wang, MOLPRO, version, 2012.1, <http://www.molpro.net>.
  15. Q. Jiang and W. R. M. Graham, *J. Chem. Phys.*, 1993, **98**, 9251–9255.
  16. K. Banert, R. Arnold, M. Hagedorn, P. Thoss and A. A. Auer, *Angew. Chem. Int. Ed.*, 2012, **51**, 7515–7518.
  17. Y. Y. Qin, B. Lu, G. Rauhut, M. Hagedorn, K. Banert, C. Song, X. X. Chu, L. N. Wang and X. Q. Zeng, *Angew. Chem. Int. Ed.*, 2019, **58**, 17277–17281.

**Calculated atomic coordinates and energies (Hartrees) for all optimized structures.**

**HC≡CSCN**

B3LYP/6-311++G(3df,3pd)

C	2.25077900	-0.90339900	0.00000000
H	3.10783000	-1.53053300	0.00000000
C	1.27215600	-0.20730800	0.00000000
C	-1.34445600	-0.13967300	0.00000000
S	0.00000000	0.90157600	0.00000000
N	-2.31124300	-0.77034300	0.00000000

Zero-point correction=	0.028062
Thermal correction to Energy=	0.033388
Thermal correction to Enthalpy=	0.034333
Thermal correction to Gibbs Free Energy=	-0.000743
Sum of electronic and zero-point Energies=	-567.813248
Sum of electronic and thermal Energies=	-567.807921
Sum of electronic and thermal Enthalpies=	-567.806977
Sum of electronic and thermal Free Energies=	-567.842052

**HC≡CSNC**

B3LYP/6-311++G(3df,3pd)

C	2.20602700	-0.98208100	0.00000000
H	3.05114700	-1.62517700	0.00000000
C	1.24253400	-0.26141800	0.00000000
S	0.00000000	0.86542300	0.00000000
C	-2.38316300	-0.66642200	0.00000000
N	-1.34907600	-0.10886800	0.00000000

Zero-point correction=	0.027079
Thermal correction to Energy=	0.032692
Thermal correction to Enthalpy=	0.033636
Thermal correction to Gibbs Free Energy=	-0.001977
Sum of electronic and zero-point Energies=	-567.772980
Sum of electronic and thermal Energies=	-567.767368
Sum of electronic and thermal Enthalpies=	-567.766424
Sum of electronic and thermal Free Energies=	-567.802036

**HC≡CNCS**

B3LYP/6-311++G(3df,3pd)

C	0.00000000	0.00000000	3.08841800
---	------------	------------	------------



H	0.00000000	0.00000000	4.14878300
C	0.00000000	0.00000000	1.88438600
N	0.00000000	0.00000000	0.59564400
C	0.00000000	0.00000000	-0.59264700
S	0.00000000	0.00000000	-2.16245200

Zero-point correction=	0.029099
Thermal correction to Energy=	0.034326
Thermal correction to Enthalpy=	0.035270
Thermal correction to Gibbs Free Energy=	0.007225
Sum of electronic and zero-point Energies=	-567.838396
Sum of electronic and thermal Energies=	-567.833169
Sum of electronic and thermal Enthalpies=	-567.832225
Sum of electronic and thermal Free Energies=	-567.860270

### HC≡CCNS

B3LYP/6-311++G(3df,3pd)

C	0.00000000	0.00000000	-3.15332200
H	0.00000000	0.00000000	-4.21516500
C	0.00000000	0.00000000	-1.94430400
S	0.00000000	0.00000000	2.15190300
C	0.00000000	0.00000000	-0.60187500
N	0.00000000	0.00000000	0.56881700

Zero-point correction=	0.029248
Thermal correction to Energy=	0.034576
Thermal correction to Enthalpy=	0.035520
Thermal correction to Gibbs Free Energy=	0.003008
Sum of electronic and zero-point Energies=	-567.806007
Sum of electronic and thermal Energies=	-567.800680
Sum of electronic and thermal Enthalpies=	-567.799735
Sum of electronic and thermal Free Energies=	-567.832248

### syn-HC≡CCSN

B3LYP/6-311++G(3df,3pd)

C	-2.48168500	1.15016800	0.00000000
H	-3.50512100	1.43257800	0.00000000
C	-1.30138000	0.82743400	0.00000000
C	0.00000000	0.59007300	0.00000000
S	1.34661700	-0.31788300	0.00000000
N	0.66537600	-1.67892800	0.00000000

Zero-point correction=	0.025261
Thermal correction to Energy=	0.031183
Thermal correction to Enthalpy=	0.032127
Thermal correction to Gibbs Free Energy=	-0.004700
Sum of electronic and zero-point Energies=	-567.657801
Sum of electronic and thermal Energies=	-567.651879
Sum of electronic and thermal Enthalpies=	-567.650935
Sum of electronic and thermal Free Energies=	-567.687762

***anti*-HC≡CCSN**

B3LYP/6-311++G(3df,3pd)

C	2.23495800	1.85296100	0.00000000
H	3.13334100	2.41882500	0.00000000
C	1.20790300	1.20265800	0.00000000
C	0.00000000	0.60694400	0.00000000
S	-0.64752700	-0.83134200	0.00000000
N	-1.91858200	-1.58467500	0.00000000

Zero-point correction=	0.026101
Thermal correction to Energy=	0.031751
Thermal correction to Enthalpy=	0.032695
Thermal correction to Gibbs Free Energy=	-0.002307
Sum of electronic and zero-point Energies=	-567.664725
Sum of electronic and thermal Energies=	-567.659075
Sum of electronic and thermal Enthalpies=	-567.658131
Sum of electronic and thermal Free Energies=	-567.693133

**HC≡CNSC**

B3LYP/6-311++G(3df,3pd)

C	2.68335900	-0.25476900	-0.00038100
H	3.69232000	-0.58116500	0.00121700
C	1.53371500	0.13784900	0.00014300
N	0.36308600	0.71325700	0.00002000
S	-1.01455900	-0.25620600	0.00001900
C	-2.55057100	0.06486400	-0.00003800

Zero-point correction=	0.024419
Thermal correction to Energy=	0.030420
Thermal correction to Enthalpy=	0.031364
Thermal correction to Gibbs Free Energy=	-0.004733
Sum of electronic and zero-point Energies=	-567.641327
Sum of electronic and thermal Energies=	-567.635325

Sum of electronic and thermal Enthalpies= -567.634381  
Sum of electronic and thermal Free Energies= -567.670479

### **NCC(H)CS**

B3LYP/6-311++G(3df,3pd)

C	-1.03061300	-0.18964100	0.00000000
H	-2.03198000	0.22671400	0.00000000
C	0.00000000	0.63684500	0.00000000
S	1.18808100	1.61801100	0.00000000
C	-0.88133300	-1.59604500	0.00000000
N	-0.78651900	-2.74597700	0.00000000

Zero-point correction= 0.029654  
Thermal correction to Energy= 0.034536  
Thermal correction to Enthalpy= 0.035480  
Thermal correction to Gibbs Free Energy= 0.001163  
Sum of electronic and zero-point Energies= -567.857041  
Sum of electronic and thermal Energies= -567.852159  
Sum of electronic and thermal Enthalpies= -567.851215  
Sum of electronic and thermal Free Energies= -567.885531

### **CNC(H)CS**

B3LYP/6-311++G(3df,3pd)

C	1.01587800	-0.24980700	0.00000000
H	2.02897700	0.13195700	0.00000000
C	0.00000000	0.59412600	0.00000000
S	-1.16439600	1.60848900	0.00000000
N	0.85052400	-1.60996000	0.00000000
C	0.75873700	-2.77733000	0.00000000

Zero-point correction= 0.029121  
Thermal correction to Energy= 0.034213  
Thermal correction to Enthalpy= 0.035157  
Thermal correction to Gibbs Free Energy= 0.000506  
Sum of electronic and zero-point Energies= -567.815810  
Sum of electronic and thermal Energies= -567.810718  
Sum of electronic and thermal Enthalpies= -567.809774  
Sum of electronic and thermal Free Energies= -567.844425

### **cyc-HC≡CSCN**

B3LYP/6-311++G(3df,3pd)

C	-2.31030600	-0.46707800	0.00075100
H	-3.29019800	-0.87676100	0.00750500
C	-1.19721600	-0.00788400	-0.00976500
C	1.62145400	-0.75697000	-0.59380300
S	0.28835900	0.76013500	-0.03233100
N	1.42755100	-0.55625900	0.58952800

Zero-point correction=	0.025901
Thermal correction to Energy=	0.031686
Thermal correction to Enthalpy=	0.032630
Thermal correction to Gibbs Free Energy=	-0.003111
Sum of electronic and zero-point Energies=	-567.744771
Sum of electronic and thermal Energies=	-567.738986
Sum of electronic and thermal Enthalpies=	-567.738042
Sum of electronic and thermal Free Energies=	-567.773783

### TS1

B3LYP/6-311++G(3df,3pd)

C	-2.30848800	-0.50433900	-0.00339700
H	-3.27881300	-0.93600800	0.00397800
C	-1.20609100	-0.01796600	-0.01417500
C	1.73698300	-0.80687300	-0.54214600
S	0.25867200	0.78023300	-0.04458900
N	1.40080600	-0.51038000	0.58110900

Zero-point correction=	0.025516
Thermal correction to Energy=	0.030768
Thermal correction to Enthalpy=	0.031712
Thermal correction to Gibbs Free Energy=	-0.003147
Sum of electronic and zero-point Energies=	-567.744993
Sum of electronic and thermal Energies=	-567.739741
Sum of electronic and thermal Enthalpies=	-567.738797
Sum of electronic and thermal Free Energies=	-567.773656

### TS2

B3LYP/6-311++G(3df,3pd)

C	2.30967200	-0.52458700	-0.01005300
H	3.27507100	-0.96727400	-0.01107400
C	1.21356000	-0.02216100	-0.00587400
C	-1.44185800	-0.55153700	0.65944700
S	-0.23589300	0.79437900	-0.02838500
N	-1.71271700	-0.73615500	-0.48512600

Zero-point correction=	0.025491 (Hartre)
Thermal correction to Energy=	0.030833
Thermal correction to Enthalpy=	0.031777
Thermal correction to Gibbs Free Energy=	-0.003334
Sum of electronic and zero-point Energies=	-567.738919
Sum of electronic and thermal Energies=	-567.733578
Sum of electronic and thermal Enthalpies=	-567.732634
Sum of electronic and thermal Free Energies=	-567.767745

### TS3

B3LYP/6-311++G(3df,3pd)

C	0.56408600	1.82703500	-0.00018200
H	1.31145100	2.58769100	0.00068600
C	-0.03107900	0.71477800	0.00005400
C	0.85236600	-0.49756800	-0.00001000
S	-1.35887800	-0.38054100	0.00000900
N	1.73119500	-1.25207200	-0.00000200

Zero-point correction=	0.025693 (Hartre)
Thermal correction to Energy=	0.030647
Thermal correction to Enthalpy=	0.031592
Thermal correction to Gibbs Free Energy=	-0.002536
Sum of electronic and zero-point Energies=	-567.718132
Sum of electronic and thermal Energies=	-567.713178
Sum of electronic and thermal Enthalpies=	-567.712234
Sum of electronic and thermal Free Energies=	-567.746361

### TS4

B3LYP/6-311++G(3df,3pd)

C	2.20479200	-0.14929900	0.00002900
H	3.16357500	-0.60533600	0.00014400
C	1.01898500	0.11386600	-0.00007200
N	-0.05504600	1.08510500	-0.00017300
C	-1.30148500	1.00361400	-0.00001200
S	-0.89450100	-0.79996800	0.00008700

Zero-point correction=	0.024467 (Hartre)
Thermal correction to Energy=	0.029552
Thermal correction to Enthalpy=	0.030496
Thermal correction to Gibbs Free Energy=	-0.003658
Sum of electronic and zero-point Energies=	-567.652770

Sum of electronic and thermal Energies=	-567.647684
Sum of electronic and thermal Enthalpies=	-567.646740
Sum of electronic and thermal Free Energies=	-567.680895