Extended Supporting Information

Synthesis, Structure, and Stability of a Novel 2H-azirine Under Pressure

Alexa Cabrera [a], Fatemah Safari [b], Ravhi Kumar [b], Haoran Zhu [a], Muhtar Ahart [b], Zhenxian Liu,[b] Tom Driver [a], Russell J. Hemley [a,b,c]

[a] Department of Chemistry, University of Illinois Chicago, Chicago, IL 60607
[b] Department of Physics, University of Illinois Chicago, Chicago, IL 60607
[c] Department of Earth and Environmental Sciences, University of Illinois Chicago, Chicago, IL 60607

*Corresponding Author E-mail: rhemley@uic.edu

Table of Contents

1. Experimental Details

a. *Synthesis*

The synthesis procedure is summarized in Figure. S2; 2,3 Diphenyl-2H-azirine was synthesized from a mixture of phenyl benzyl ketone (10 mmol, 1.962 g, 1.0 equiv), $NH_2OH \cdot HCl$ (15 mmol, 1.042 g, 1.5 equiv), and sodium acetate (15 mmol, 1.230 g, 1.5 equiv) in $MeOH/H_2O$ (20:1, 80 mL:4 mL) which was stirred at room temperature until the ketone had been completely consumed. Next, the solution was diluted with H_2O, extracted with CH2Cl2, and sat. $NaHCO_3$ and brine. Then, the collected organic layer was dried over Na_2SO_4. Concentration led to the corresponding oxime being used directly for the next step without further purification. The oxime (1.0 equiv) in dry THF has triethylamine (1.5 equiv) and methanesulfonyl chloride (1.5 equiv) sequentially at room temperature. The solution got cloudy after the addition of methane sulfonyl chloride.[38] The resulting mixture was stirred for 30 minutes, and DBU (1.5 equiv) was added over 10 minutes. After stirring for an additional 30 min, the reaction mixture was passed through a pad of silica gel and washed with ethyl acetate. The solution was concentrated in vacuo, and the resulting residue was purified by column chromatography on silica gel to make the 2,3-diphenyl-2H-azirine a pale-yellow solid.^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.92 (d, J = 5.0 Hz, 2H), 7.62-7.54 (m, 3H), 7.30-7.24 (m, 3H), 7.16 (d, J = 5.0 Hz, 2H), 3.33 (s, 1H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 163.5 (C), 140.9 (C), 133.2 (C), 129.9 (CH), 129.3 (CH), 128.3 (CH), 127.1 (CH), 126.1 (CH), 124.1 (CH), 34.5 (CH).
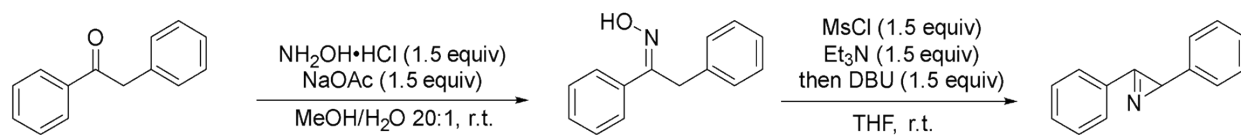

Figure S1. Schematic synthesis of diagram of the 2H-azirine.
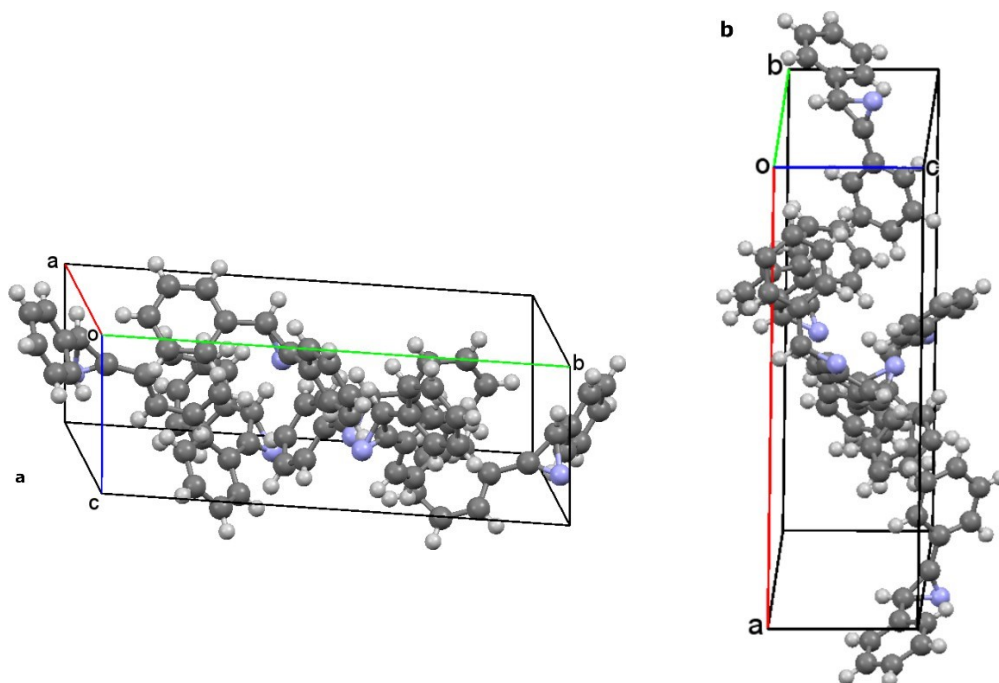
b. *Crystallographic information*

Fig. S2. Visualization of the unit cell along the (a) *a* and (b) *b* crystallographic directions. The hydrogen, carbon, and nitrogen atoms are shown in white, grey, and blue, respectively.

c. *Raman spectroscopy*

In the first experiment, the sample was loaded without pressure-transmitting medium in a symmetric DAC with a rhenium gasket with an approximately 250 μm diameter; pressure was calibrated by the ruby-fluorescence method under quasi-hydrostatic conditions.[39] A Renishaw inVia Raman Microscope was used for high-pressure Raman studies with a 785 nm excitation source laser and a 20x/0.90 microscope equipped with an 1800 l/mm grating with a resolution of ±0.5 cm^{-1} and data collected up to 12.0 GPa.
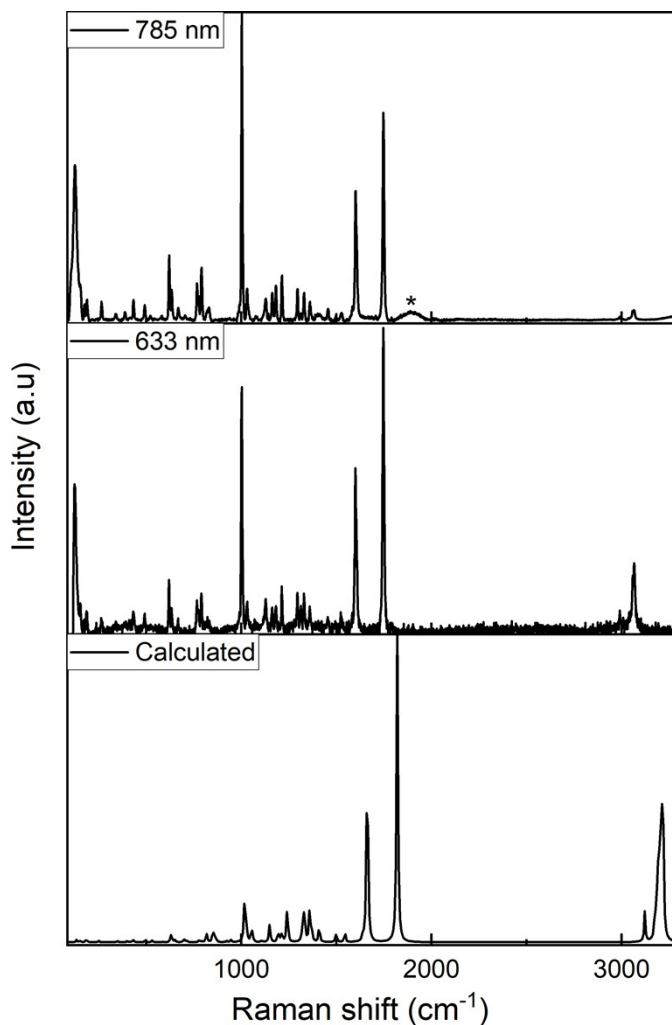

Figure S3. Comparison of ambient pressure Raman spectra measured with 785 nm and 633 nm laser excitation and that calculated for the isolated molecule. The star above the peak in the 785 nm excitation spectrum is a fluorescence peak (*i.e.*, not visible using the 633 nm laser).
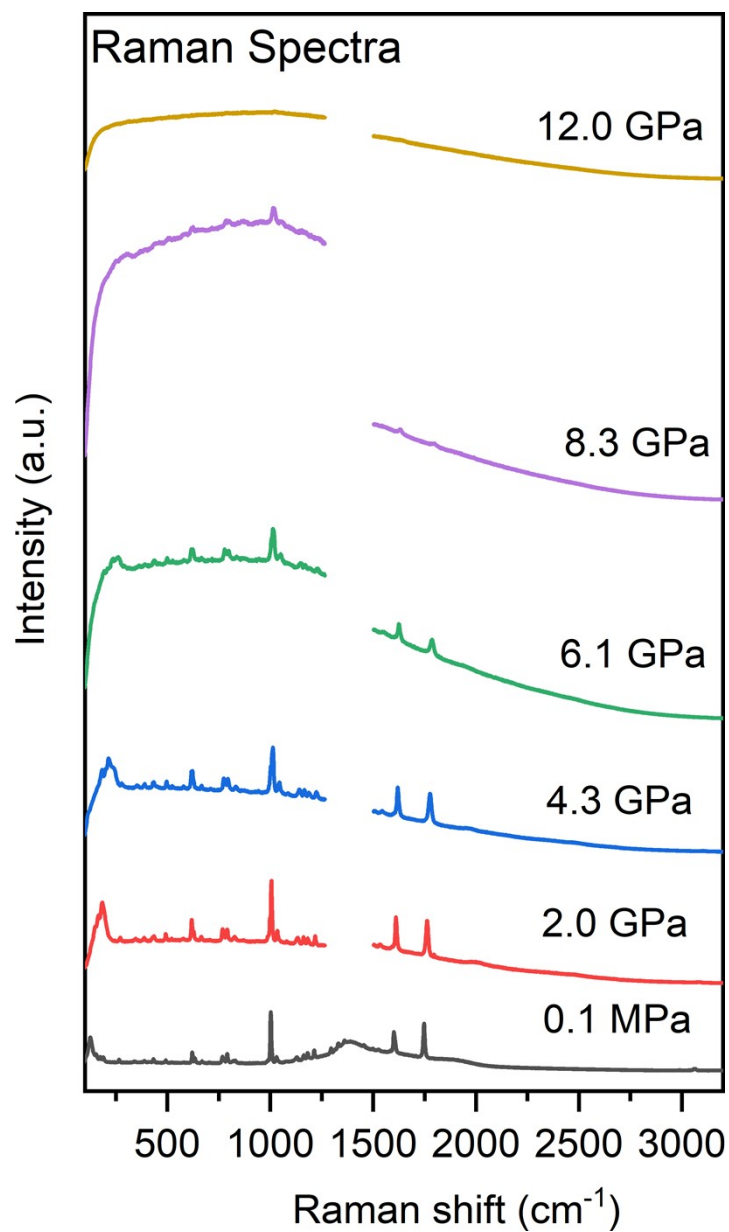
Figure S4. Raman spectra of 2,3-diphenyl-2H-azirine acquired using a 785 nm excitation laser without background subtraction. At 12.0 GPa, the Raman peaks are overwhelmed by the fluorescence. Signal in the vicinity of the strong T_{2g} Raman mode from the diamond anvils was removed in the high-pressure spectra.
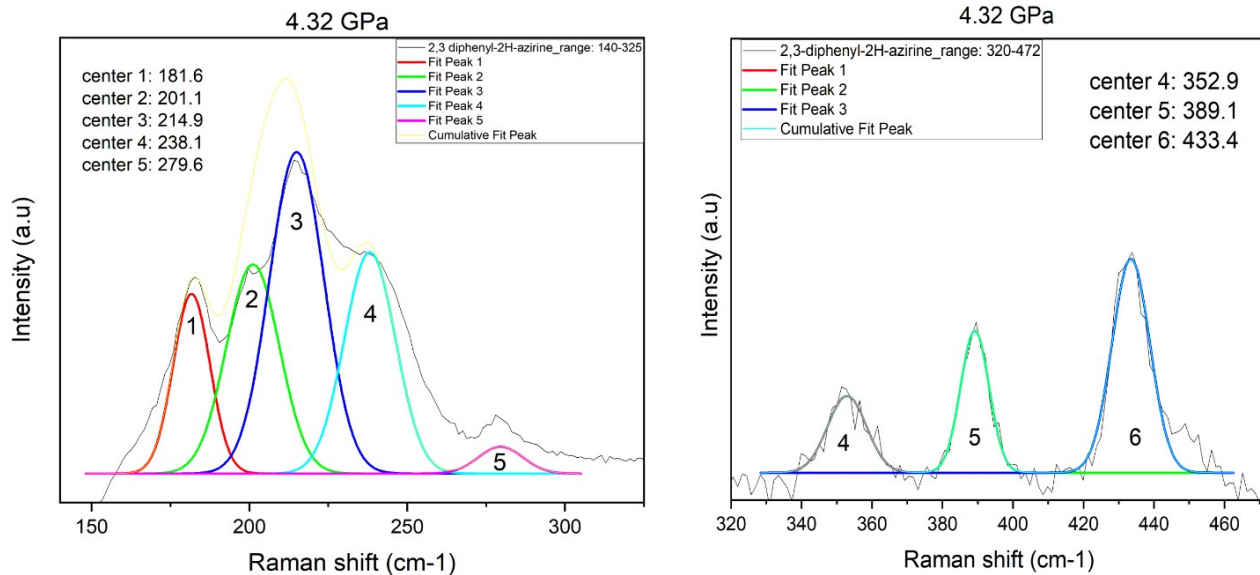
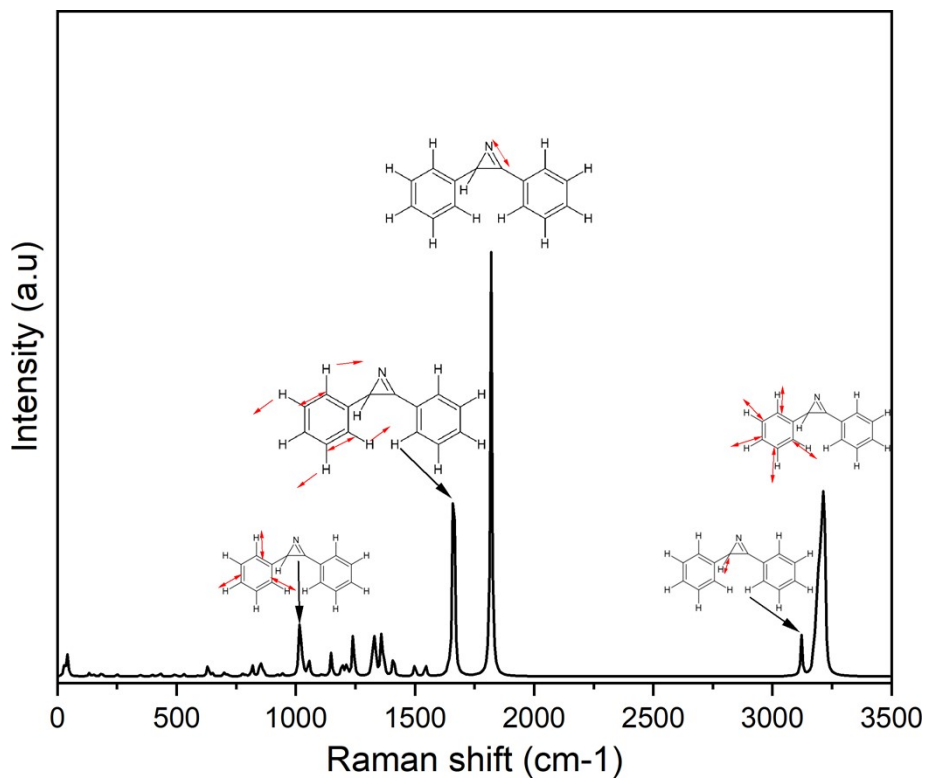**Figure S5.** Examples of deconvolution of Raman spectra.

Figure S6. Raman spectrum of the 2,3-diphenyl-2H-azirine molecule calculated after geometry optimization using density functional theory (DFT) in the Gaussian 09 package. The calculation was conducted using B3LYP and the corresponding set of basis functions for carbon, nitrogen, and hydrogen atoms and 6-31g(d). The atomic vibrational displacements for the modes corresponding to selected strong peaks are indicated: 1015 cm^{-1} (C-H asymmetric stretch); 1659 cm^{-1} (C=C scissoring of the phenyl ring); 1820 cm^{-1} (N=C stretch); 3122 cm^{-1} (C-H symmetric stretch); 3213 (C-H symmetric stretch).

d. Infrared spectroscopy

Far-IR absorption spectra were measured at the Frontier Infrared Spectroscopy (FIS) beamline at the National Synchrotron Light Source II, Brookhaven National Laboratory. A pure sample was mounted on a DAC with a rhenium gasket without a pressure medium for ambient pressure measurement. Petroleum jelly was used as a pressure-transmitting medium for the high pressure experiments. Mid-IR absorption spectra were measured at UIC using a Bruker Hyperion-II with the LN-MCT-D316-025 microscope. Samples were prepared as pellets and suspended in the air for the ambient pressure measurements. High-pressure mid-IR spectra were measured with KBr as the pressure-transmitting medium using a symmetric DAC with rhenium gaskets and ~150 μm diameter sample chamber. The pressure was determined from the ruby-fluorescence method using a quasi-hydrostatic scale.[39]
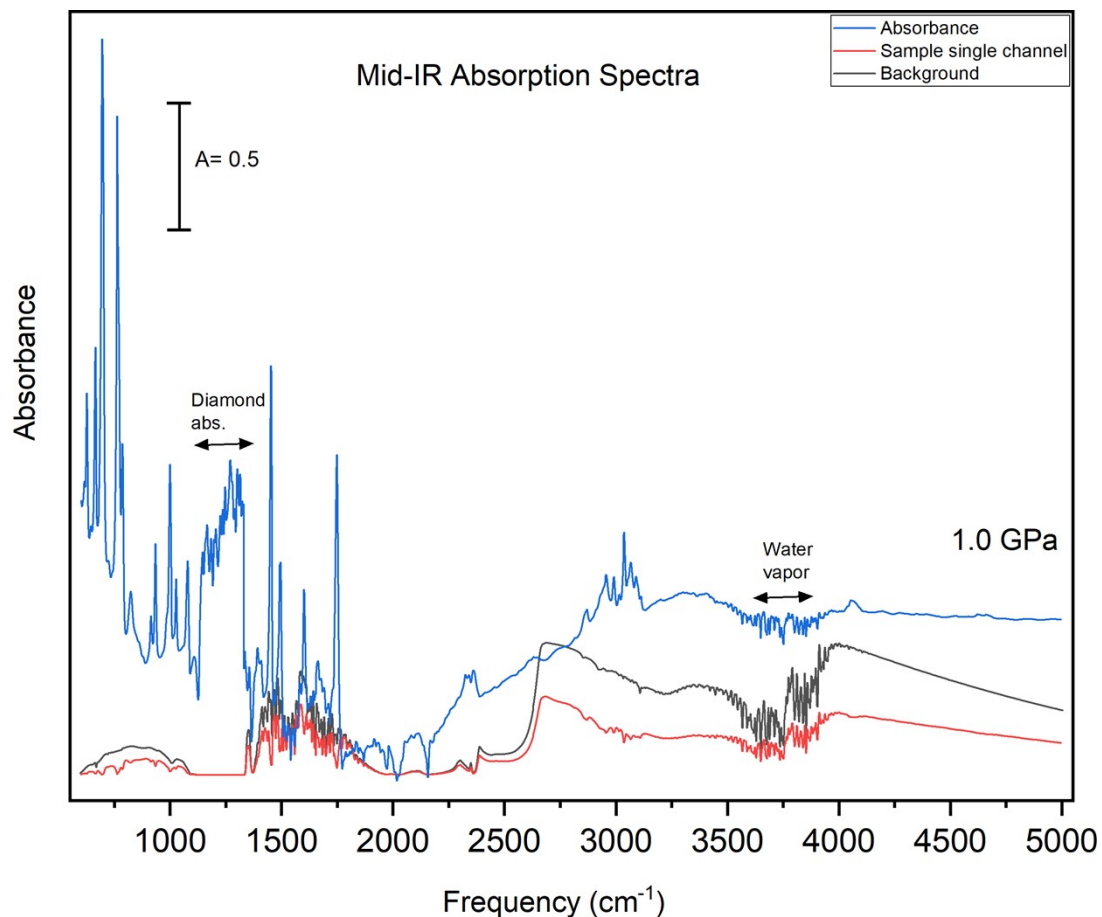
Figure S7. A comparison of high-pressure mid-IR absorption with the single channel (I) and background (I_0) was used to calculate the absorption spectrum. Absorption due to background water vapor and the diamond anvil is evident.

e. *High-pressure X-ray diffraction*

The high-pressure powder diffraction measurements were performed at HPCAT beamline 16-IDD, Sector 16, Advanced Photon Source, Argonne National Laboratory. The 2,3 diphenyl-2H-azirine was mounted in a symmetric DAC equipped with diamond anvils with 300 μm diameter culets. A rhenium gasket was prepared by pre-indenting it to 22 GPa and laser drilling the hole to 150 μm diameter, and pressure was calibrated by the ruby-fluorescence method.[39] Neon gas was used as the pressure-transmitting medium, and data were collected with X-ray wavelength λ=0.4246 at 0.74 GPa, 1.6 GPa, 3.7 GPa, 6.7 GPa, 8.2 GPa, and 10.5 GPa.
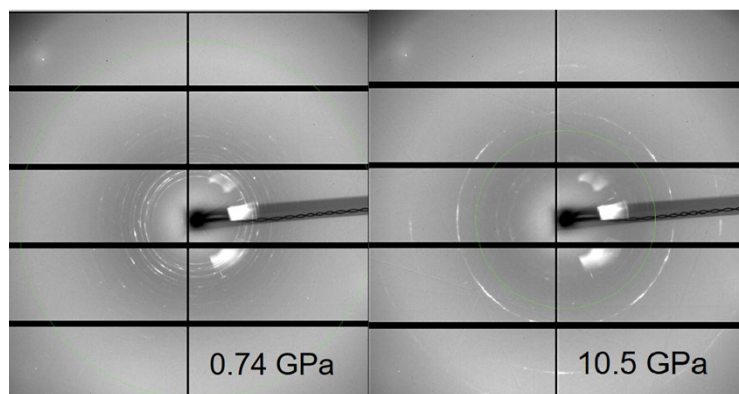
Figure S8. Images of the powder diffraction patterns of the sample at different pressures. The diffuse spots are due to the scattering from the edge of the pinhole.

f. Single crystal X-ray diffraction

The single crystal was grown by the evaporation method from a methanol/ethanol mixture (1:1). S Rigaku Oxford diffractometer at 298 K was used with Cu Kα radiation and Hybrid Photon Counting (HPC) detector to collect single crystal data at ambient conditions. The UB-matrix determination and data reduction were performed with the program CrysAlisPro [49,] and the structures were refined by using full-matrix least-squares on F^2 using the program Shelx-S incorporated in Olex2.[50]

Table S1. Vibrational overtone and combination band frequencies were measured in the IR compared with corresponding component IR and Raman fundamental frequencies (all at 0.1 MPa).

IR (cm⁻¹) observed	Raman (cm⁻¹) observed	Observed Combination Peaks (cm⁻¹)	Calculated Combination Peaks (cm⁻¹)	Observed - Calculated (cm⁻¹)	Mode Assignment
2865	1177	4042	4042	0	v_2+v_4
3083	1268	4351	4343	8	v_3+v_5
1390	3062	4452	4443	9	v_1+v_8
3006	1523	4529	4527	2	v_2+v_6
2865	1747	4612	4613	1	v_2+v_7
3060	1602	4662	4657	5	v_2+v_6

Table S2. *P-V* data obtained from X-ray diffraction.

P (GPa)	Volume (Å³)
0.1 MPa	1708.0(1)
0.74	1614.1(2)
1.6	1554.7(7)
2.6	1484.3(1)
3.8	1441.6(5)
6.8	1376.0(4)
8.2	1344.1(4)
10.4	1334.4(4)

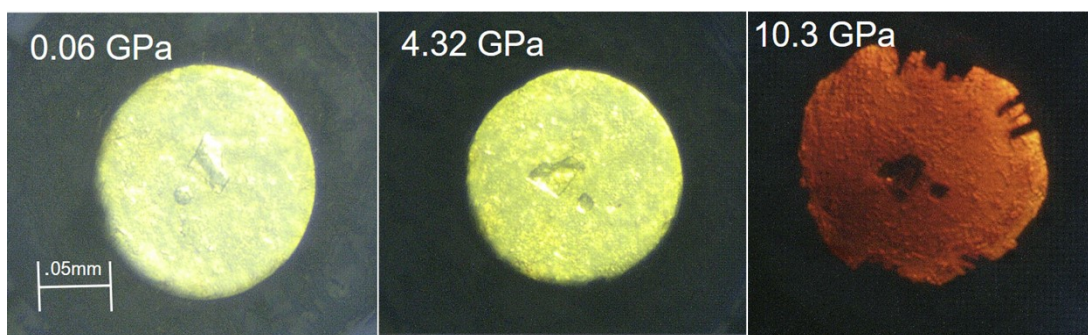## 2. Optical images of the sample

Figure S9. Optical images of a 2H-azirine sample inside the DAC showing pressure-induced changes in optical absorption consistent with the increase in fluorescence observed over this pressure range with 785 nm laser irradiation. There are two spherical ruby grains in the center, which appear dark in the 10.3 GPa sample, but no laser-induced damage in the sample was evident from either the micrographs or the Raman spectra measured.

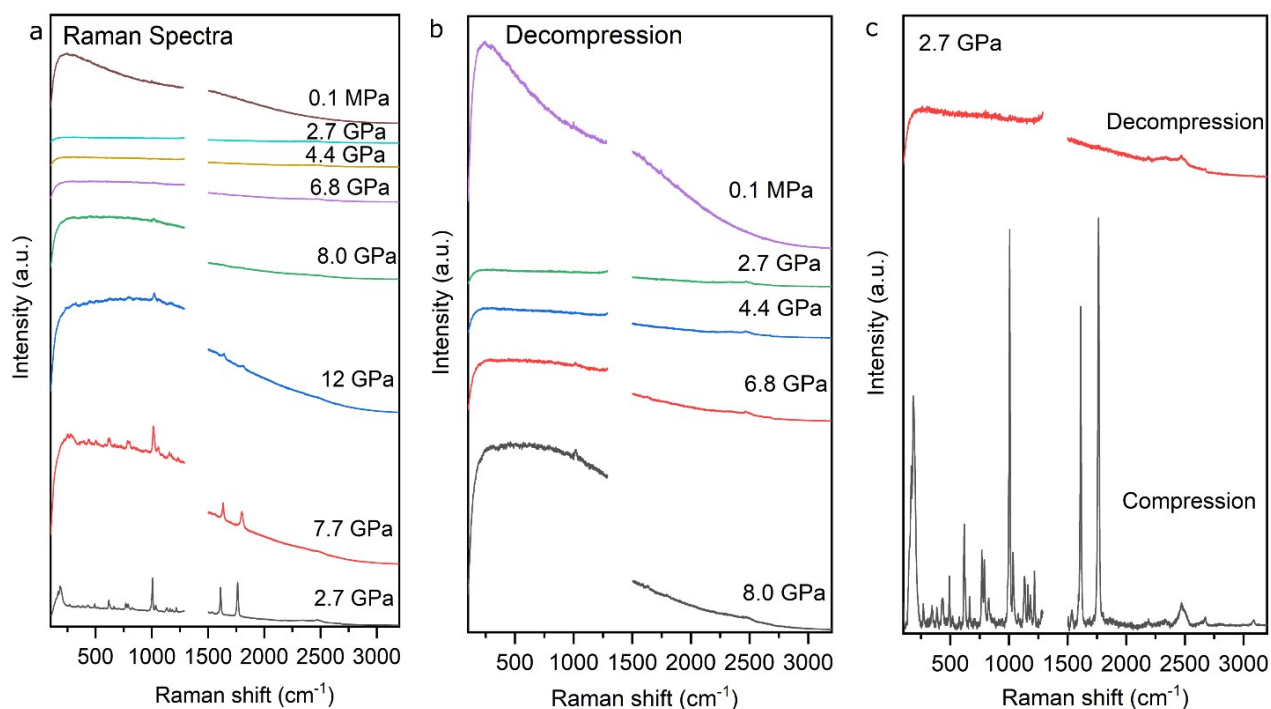## 5. Spectroscopic studies on decompression of samples

Figure S10. (a) Raman spectra of 2,3-diphenyl-2H-azirine compressed to 12 GPa and then decompressed starting at 9.9 GPa (785 nm laser). (b) Raman spectra of the selected decompression pressures showing peaks at lower frequencies that are appear when decompressed below 8 GPa. (c) Raman spectra of the sample when compressed and decompressed at 2.7 GPa showing the difference in peaks. With the decompression spectrum, fluorescence is producing an intense signal that overwhelms the Raman peaks.
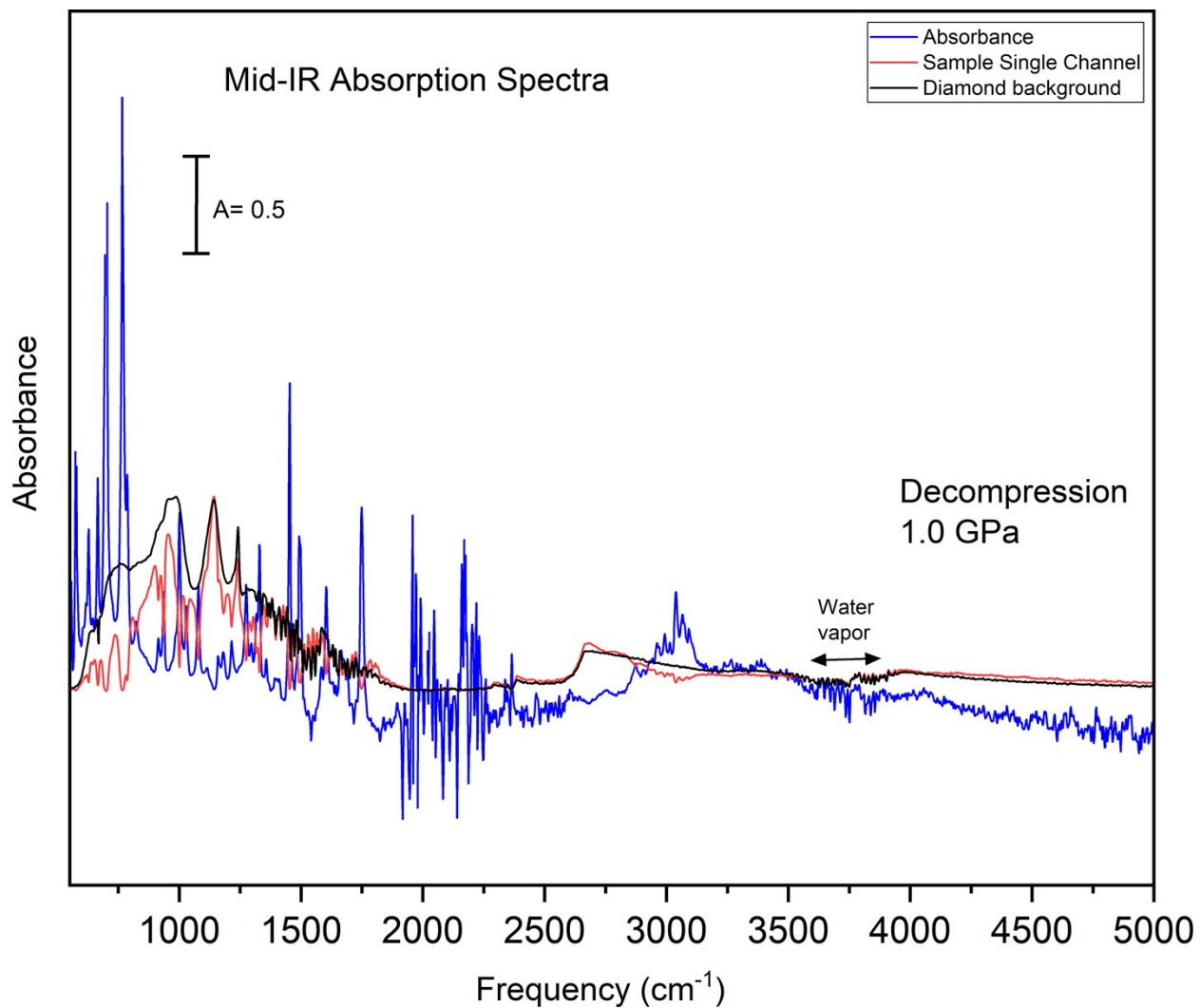
Figure S11. Mid-IR absorption spectrum of the decompression of 2,3-diphenyl-2H-azirine measured at 1.0 GPa. Peaks include those at 2964 cm^{-1}, 2993 cm^{-1}, 3012 cm^{-1}, 3039 cm^{-1}, 3064 cm^{-1}, and 3093 cm^{-1}.
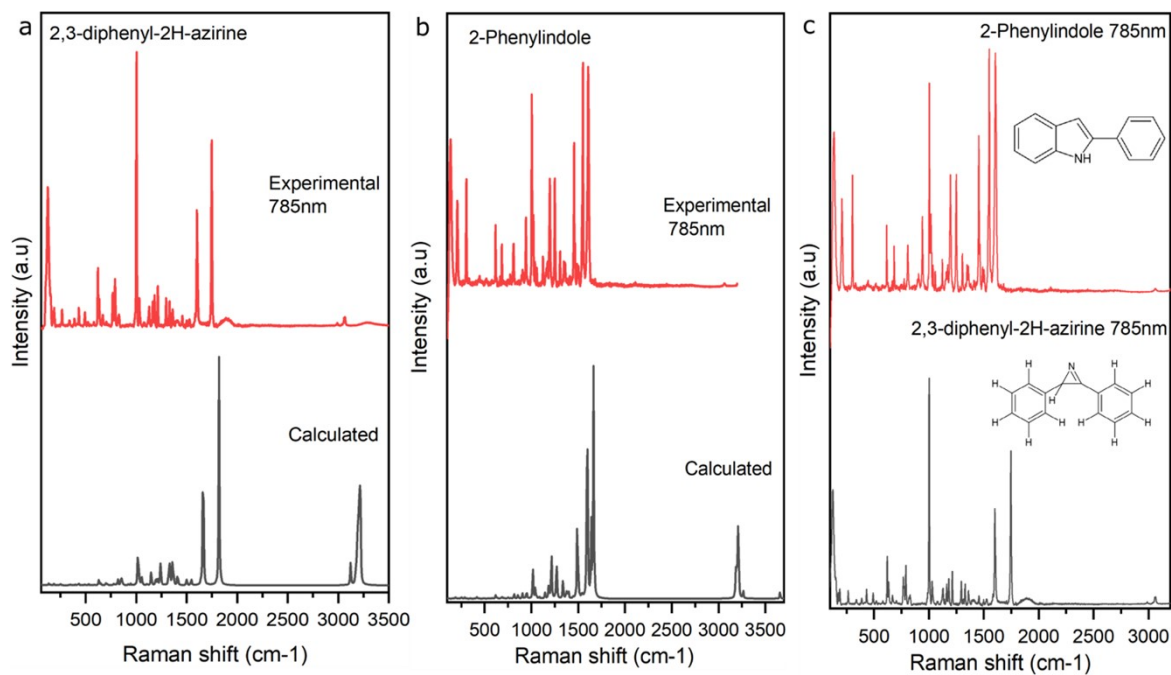
4. Comparison to 2-phenylindole

Figure S12. (a) Raman spectrum of 2,3 diphenyl-2H-azirine compared with the calculated spectrum for the isolated molecule (see text and Fig. S3). (b) Raman spectrum of 2-phenylindole compared with the calculated spectrum for the isolated molecule. (c) Direct comparison of the Raman spectrum of 2-phenylindole and 2,3-diphenyl-2H-azirine.