

Supporting Information for

Pressure Accelerated 1,3-Dipolar Cycloaddition of Azide and Alkyne Groups in Crystals

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Experimental Section

High pressure experiments were performed using symmetric sapphire anvil cell (SAC) at room temperature. Sample was placed in the gasket hole together with a few small ruby chips for *in situ* measurements of the sample pressure using the standard ruby fluorescent technique.¹ A copper gasket was preindented by the sapphires and then drilled to produce a 0.25 mm diameter cavity for the sample.

Synchrotron X-ray Diffraction

In situ ADXRD experiments were performed at 4W2 High-Pressure Station of Beijing Synchrotron Radiation Facility (BSRF). The monochromatic radiation at a wavelength of 0.6199 Å was used for data collection, and the incident beam size was 20×30 μm². CeO₂ was used as the standard to calibrate the sample-detector distance and geometric parameters. The typical Bragg rings were recorded with an image-plate area detector (Mar 345). The average acquisition time of 300 s was adopted for each spectrum. The obtained two-dimensional data were converted to plots of intensity versus 2θ using the Fit2D software.²

In situ Raman Spectra

The Raman scattering measurements were carried out using the Renishaw system (inVia Raman microscope) with a 514 nm argon ion laser as the excitation source. The laser power on the sample was kept at 2 mW, and the Raman spectra were recorded in backscattering geometry. Prior to each measurement, the spectrometer was calibrated using the Si line. The resolution of the system was about 1 cm⁻¹.

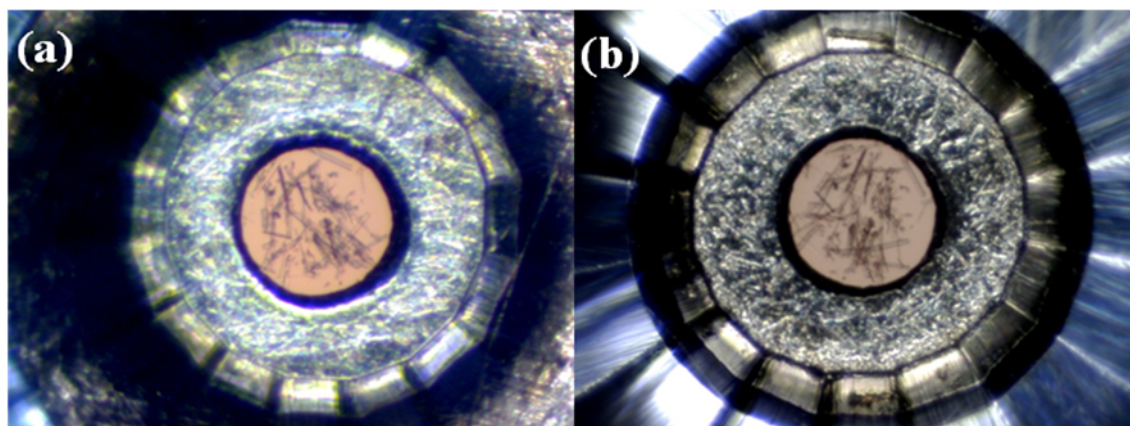
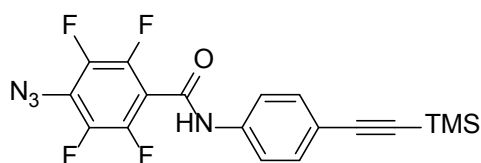


Figure S1. Images of compound **1**(a) at atmosphere pressure and 1,3-dipolar cycloaddition product **2** at 1.0 GPa in SAC, with dimethyl silicon oil as pressure transmitting medium.

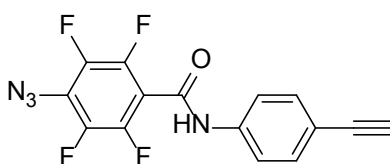
Synthetic Details

Chemicals were used as received unless otherwise indicated. All oxygen or moisture sensitive reactions were performed under nitrogen atmosphere using standard Schlenk method. Reagent grade toluene was distilled from sodium prior to use. ^1H , ^{13}C , and ^{19}F NMR spectra were recorded on Varian Mercury plus 300 (300 MHz) using acetone- d_6 as the solvent unless otherwise noted. Chemical shifts in ^1H and ^{13}C NMR spectra were reported in parts per million (ppm) with TMS (0 ppm) and CDCl_3 (77.23 ppm) as internal standards, respectively. Chemical shifts in ^{19}F NMR spectra were reported in parts per million (ppm) with CF_3COOH (0 ppm) as external standard. EI mass spectra were recorded on a ZAB-HS magnetic mass spectrometer (Micromass). Elemental analyses were performed using a German Vario EL III elemental analyzer



4-Azido-N-(4-(2-trimethylsilylethynyl)phenyl)-2,3,5,6-tetrafluorobenzamide. A solution of 4-azido-2,3,5,6-tetrafluorobenzoic (2.4 g, 10 mmol),³ 4-(2-trimethylsilylethynyl)aniline (1.9 g, 10 mmol),⁴ DCC (2.0 g, 10 mmol), and DMAP (0.061 g, 0.5 mmol) in toluene was heated at 60 °C for 24 hours. The reaction mixture was filtered, and solid was washed by dichloromethane. The combined filtrations were dried over MgSO_4 . After removal of solvents under *vacuo*, column chromatography

over silica gel eluted by petroleum ether/dichloromethane (2/1, v/v) afforded **4-Azido-*N*-(4-(2-trimethylsilylethynyl)phenyl)-2,3,5,6-tetrafluorobenzamide** as a white solid (2.4 g, 58%). ¹H NMR (300 MHz, acetone-*d*₆, ppm): δ 10.17 (s, 1H), 7.76 (m, 2H), 7.49 (m, 2H), 0.24 (s, 9H). ¹³C NMR (75 MHz, acetone-*d*₆, ppm): δ 156.9, 145.1 (*J*_{C-F} = 250 Hz), 141.8 (*J*_{C-F} = 250 Hz), 139.9, 133.9, 123.4, 120.9, 120.6, 113.7, 106.1, 94.8, 0.5. ¹⁹F NMR (282 MHz, acetone-*d*₆, ppm): δ -65.2, -74.2. LR-MS (EI, *m/z*): 406 (*M*⁺). Elem. Anal.: Calcd. For C₁₈H₁₃F₄N₃O₂Si: C, 53.20; H, 3.47; N, 13.79. Found: C, 53.10; H, 3.18; N, 13.92.



4-Azido-*N*-(4-ethynylphenyl)-2,3,5,6-tetrafluorobenzamide (1). A Schlenk-adapted tube was charged with 1.2 g (3.0 mmol) of 4-Azido-*N*-(4-(2-trimethylsilylethynyl)phenyl)-2,3,5,6-tetrafluorobenzamide, 0.56 g (3.0 mmol) of potassium fluoride dihydrate and 100 mL of acetonitrile under nitrogen atmosphere. After the mixture was stirred for 8 h at room temperature, the reaction was quenched with water. The mixture was extracted with dichloromethane and combined organic layer was dried over MgSO₄. After filtration, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography over silica gel (petroleum ether/CH₂Cl₂, 1:1) to afford **1** as a white solid (0.97 g, 2.9 mmol, 97%). ¹H NMR (300 MHz, acetone-*d*₆, ppm): δ 10.18 (s, 1H), 7.77 (m, 2H), 7.53 (m, 2H), 3.63 (s, 1H). ¹³C NMR (75 MHz, acetone-*d*₆, ppm): δ 156.7, 144.8 (*J*_{C-F} = 250 Hz), 141.5 (*J*_{C-F} = 250 Hz), 139.7, 133.8, 123.2, 120.7, 119.6, 113.3, 84.0, 79.2. ¹⁹F NMR (282 MHz, acetone-*d*₆, ppm): δ -65.0, -74.1. LR-MS (EI, *m/z*): 334 (*M*⁺). Elem. Anal. Calcd. for C₁₅H₅F₄N₃O₂: C, 53.90; H, 1.81; N, 16.76. Found: C, 53.88; H, 1.43; N, 16.92.

FT-IR and Raman spectroscopy, XRD

Infrared and Raman spectra were recorded in solid phase. Infrared spectra were recorded on a Bio-Rad FTS-65A FT-IR spectrometer. Raman spectra were recorded on a Micro-Raman spectroscopy using a Renishaw System-1000 spectrometer with a 532 nm Yd-YAG laser, CCD detector, and 5x, 20x, 50x, and 80x objective lenses. X-ray diffraction data were collected on a PHILIPS X'Pert Pro diffractometer with an X'celerator detector in the reflection mode, using

monochromatized Cu K α radiation.

Table S1. Cell parameters of **1-4**.⁵

compd	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (°)	β (°)	γ (°)
3	6.2824	7.5328	29.6338	90.00	93.05	90.00
4	6.3574	7.8459	28.0876	90.00	91.95	90.00
1	6.1141	7.6346	29.8502	90.00	90.00	90.00
2	6.0356	7.6615	28.1753	90.00	90.00	90.00

Crystal data and structure refinement for compound **1**.

Identification code	1	
Empirical formula	C ₁₅ H ₆ F ₄ N ₄ O	
Formula weight	334.24	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	<i>a</i> = 6.1396(12) Å	α = 90°
	<i>b</i> = 7.5599(15) Å	β = 90°
	<i>c</i> = 30.535(6) Å	γ = 90°
Volume	1417.3(5) Å ³	
Z	4	
Density (calculated)	1.566 Mg/m ³	
Absorption coefficient	0.139 mm ⁻¹	
F(000)	672	
Crystal size	0.80 x 0.40 x 0.10 mm ³	
Theta range for data collection	2.67 to 27.47°	
Index ranges	-7 ≤ <i>h</i> ≤ 7, -9 ≤ <i>k</i> ≤ 9, -39 ≤ <i>l</i> ≤ 39	
Reflections collected	11630	
Independent reflections	1905 [R(int) = 0.047]	
Completeness to theta = 25.02°	99.8 %	

Absorption correction	Empirical
Max. and min. transmission	0.9862 and 0.8968
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1905 / 0 / 217
Goodness-of-fit on F ²	0.97
Final R indices [I>2sigma(I)]	R1 = 0.0386, wR2 = 0.0616
R indices (all data)	R1 = 0.1025, wR2 = 0.0701
Largest diff. peak and hole	0.199 and -0.201 e. Å ⁻³

References:

- (1) Mao, H. K.; Xu, J.; Bell, P. M. *J. Geophys. Res.* **1986**, *91*(B5), 4673–4676.
- (2) Hammersley, A. P.; Svensson, S. O.; Hanfland, M.; Fitch, A. N.; Hausermann, D. *High Pressure Res.* **1996**, *14*, 235–248.
- (3) Keana, J. F. W.; Cai, S. X. *J. Org. Chem.* **1990**, *55*, 3640-3647.
- (4) Lavastre, O.; Ollivier, L.; Dixneuf, P. H.; Sibandhit, S. *Tetrahedron* **1996**, *52*, 5495-5504.
- (5) Cell parameters were calculated from powder XRD data. The parameters for compound **1** were consisted with single crystal data. The difference in cell dimensions are smaller than 2%.