Supporting Information

Pressure-accelerated copper-free cycloaddition of azide and alkyne pre-organized in crystalline state at room temperature

Hao Chen, Ben-Bo Ni, Fan Gao, Yuguo Ma*

Beijing National Laboratory for Molecular Sciences (BNLMS), Key Lab of Polymer Chemistry & Physics of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China

Email: ygma@pku.edu.cn

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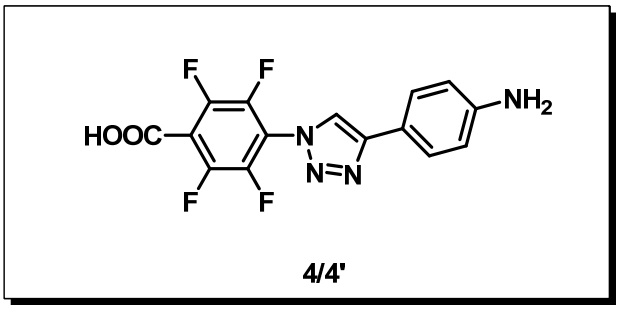
1. Experimental Section

General Methods: Chemicals were purchased commercially and used without further purification. All air and moisture sensitive reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. Tetrahydrofuran (THF) was freshly distilled from sodium under N_2 prior to use. ^{1}H and ^{19}F NMR spectra were recorded on a Varian Mercury-300 (300 MHz) spectrometer using DMSO-d_6 as solvent. ^{13}C spectra were recorded on a Bruker-500 (500 MHz) spectrometer using DMSO-d_6 as solvent. Chemical shifts are reported in parts per million (ppm) and coupling constants are reported in hertz (Hz). ^{1}H NMR chemical shifts were referenced versus TMS (0 ppm), ^{13}C NMR chemical shifts were referenced versus DMSO-d_6 (39.52 ppm) and ^{19}F NMR chemical shifts were referenced versus a CF_3CO_2H external standard (0 ppm). Mass spectra were recorded on a VG ZAB-HS mass spectrometer. Elemental analysis was performed using an Elementar VARIO EL elemental analyzer. 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 system using a Renishaw System-1000 spectrometer with a 633 nm Yd-YAG laser, CCD detector, and 5x, 20x, 50x, and 80x objective lenses. X-ray diffraction data was collected on a PHILIPS X'Pert Pro diffractometer with an X'celerator detector in the reflection mode at 30 ^{o}C, using monochromatized Cu Kα radiation. Single crystal X-ray diffraction data were collected with a NONIUS KappaCCD diffractometer for **1'·2** and **2·3**, with graphite monochromator and Mo Kα radiation [λ (MoKα) = 0.71073 Å]. Structures were solved by direct methods with

SHELXS-97 and refined against F^2 with SHELXS-97. High pressure equipment used here were Atlas manual hydraulic press and 13 mm evacuable pellet die from Specac Company.

Compounds **1** and **2** were synthesized according to references.[1-2]



4/4'

4-(4-(4-Aminophenyl)-1*H*-1,2,3-triazol-1-yl)-2,3,5,6-tetrafluorobenzoic acid (4): 130 mg (0.55 mmol) of **2**, 65 mg (0.55 mmol) of **1** were dissolved in 5 mL anhydrous THF. The solvent was removed under reduced pressure at room temperature to generate the yellow salt **1·2**. Then salt **1·2** was quickly put into a 13 mm evacuable pellet die and kept under 1 GPa pressure using hydraulic press overnight. The yellow salt changed into pale salt after the reaction. After washing with $CHCl_3$ and acetone，165 mg of **4** was collected and the yield was 85%. ^{1}H NMR (300 MHz, DMSO-d_6, ppm): δ 8.82 (s, 1H, -C=C*H*-N-), 7.64 (d, 2H, J = 8.4, Ar-*H*), 6.72 (d, 2H, J = 8.4, Ar-*H*); ^{13}C NMR (125 MHz, DMSO-d_6): δ 159.9, 149.1, 148.3, 147.2, 145.2 ($J_{C\text{-}F}$ = 250 Hz), 142.7, 140.7 ($J_{C\text{-}F}$ = 250 Hz), 127.1, 122.2, 117.7, 117.4, 114.9, 109.1. ^{19}F NMR (282 MHz, DMSO-d_6): δ -64.9, -74.7. MS (ESI, $C_{15}H_5D_3F_4N_4O_2$, solvent: DMSO-d_6, *m/z*): 355 (M^+). HR-MS (ESI, $C_{15}H_8F_4N_4O_2$, solvent: DMSO, *m/z*): Anal. Calcd. for [$(M+H)^+$]: 353.06561, Found 353.06515[$(M+H)^+$], Error: 0.5 mDa. Anal. Calcd. for $C_{15}H_8F_4N_4O_2$: C, 51.15; H, 2.29; N, 15.91. Found: C, 50.65; H, 2.43; N,

15.76.

4-(4-(4-Aminophenyl)-1*H*-1,2,3-triazol-1-yl)-2,3,5,6-tetrafluorobenzoic acid (4'): A Schlenk tube was charged with 98 mg (0.8 mmol) of **1** and 235 mg (0.8 mmol) of **2**, 30 mg (0.16 mmol) of CuI, 15 mL of THF and 7 mL of diisopropylamine or triethylamine under nitrogen atmosphere. After stirred for 14 h at room temperature, the mixture was filtrated and the residue was washed with acetone and CH_2Cl_2 to afford a pale solid as **4'** (105 mg, 32%).

2. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra

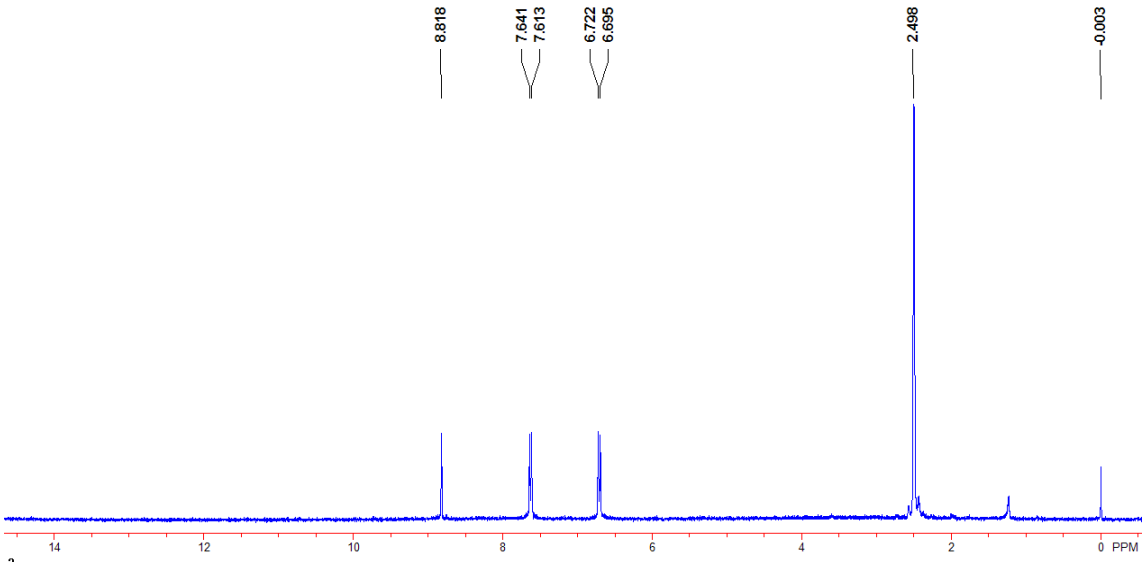


Figure S1. ^{1}H NMR spectrum of **4** in DMSO-d_6

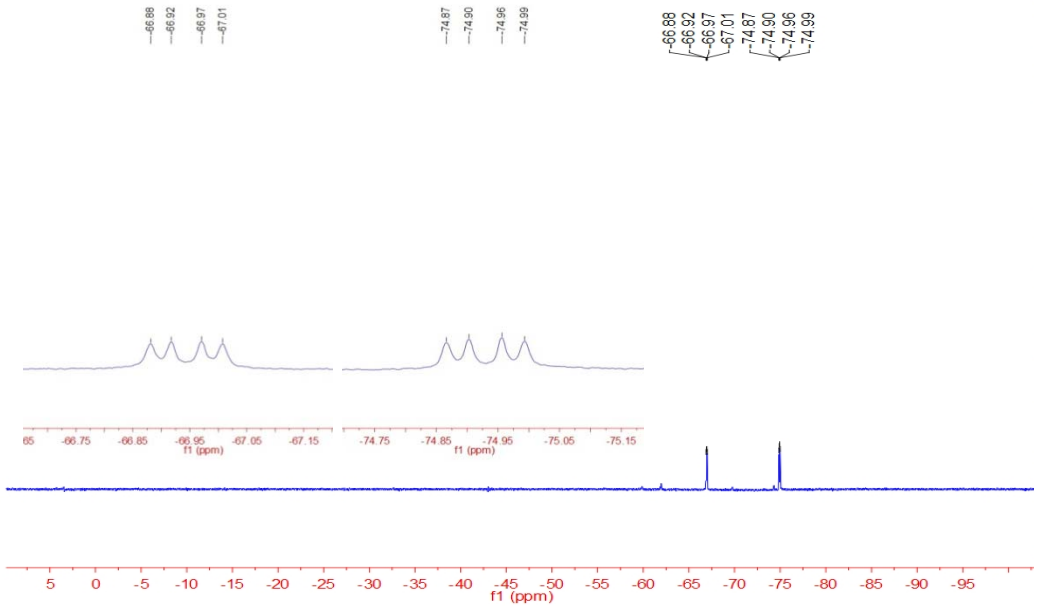


Figure S2. ^{19}F NMR spectrum of **4** in DMSO- d_6

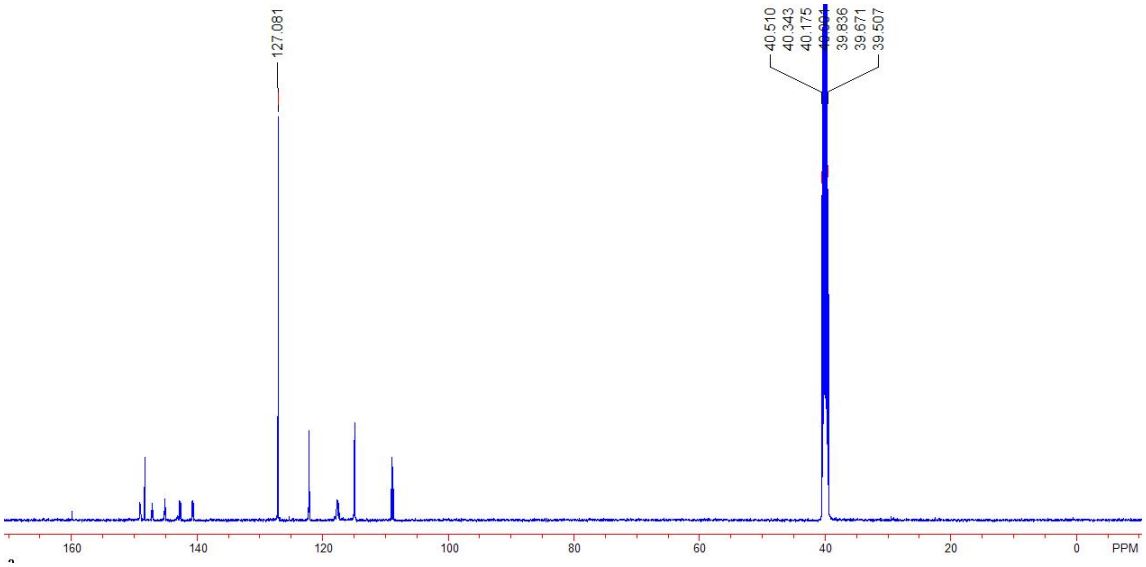


Figure S3. ^{13}C NMR spectrum of **4** in DMSO-d_6

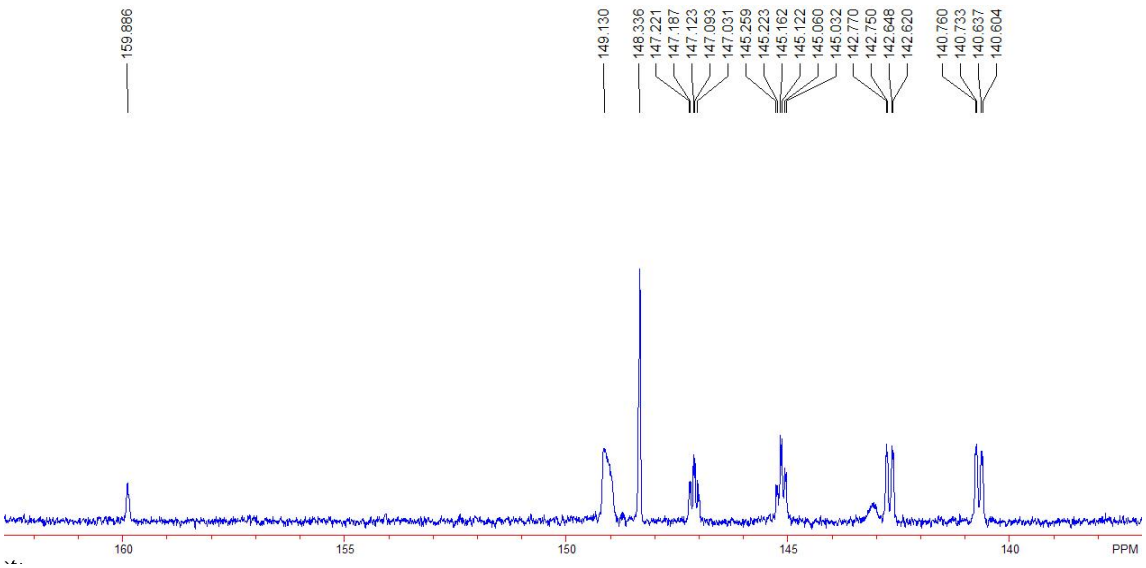


Figure S4. Partial ^{13}C NMR spectrum of **4** in DMSO-d_6 (from 135 to 165 ppm)

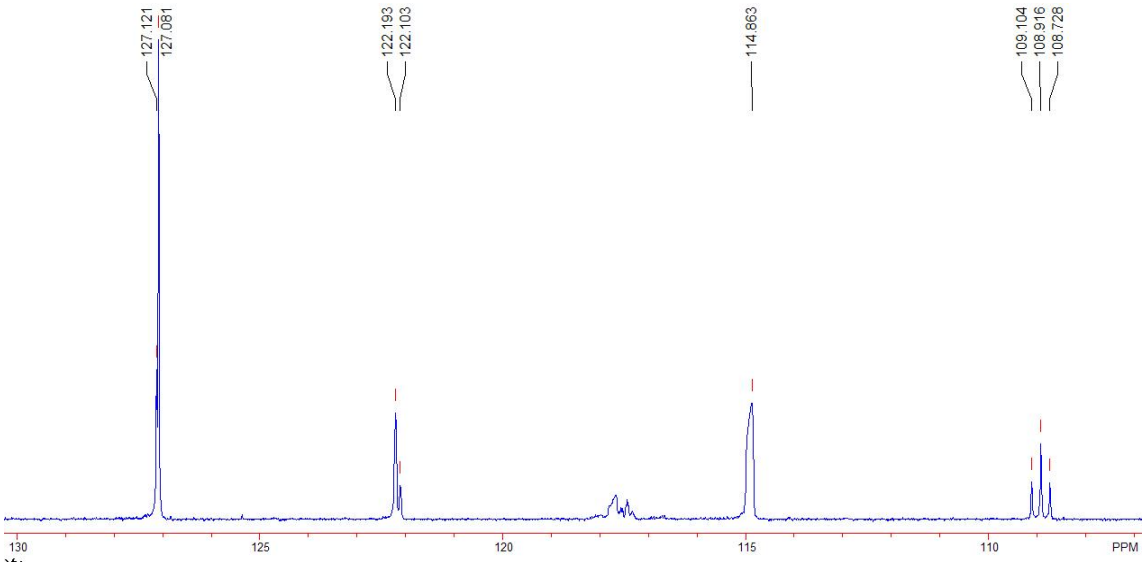


Figure S5. Partial ^{13}C NMR spectrum of **4** in DMSO-d_6 (from 105 to 130 ppm)

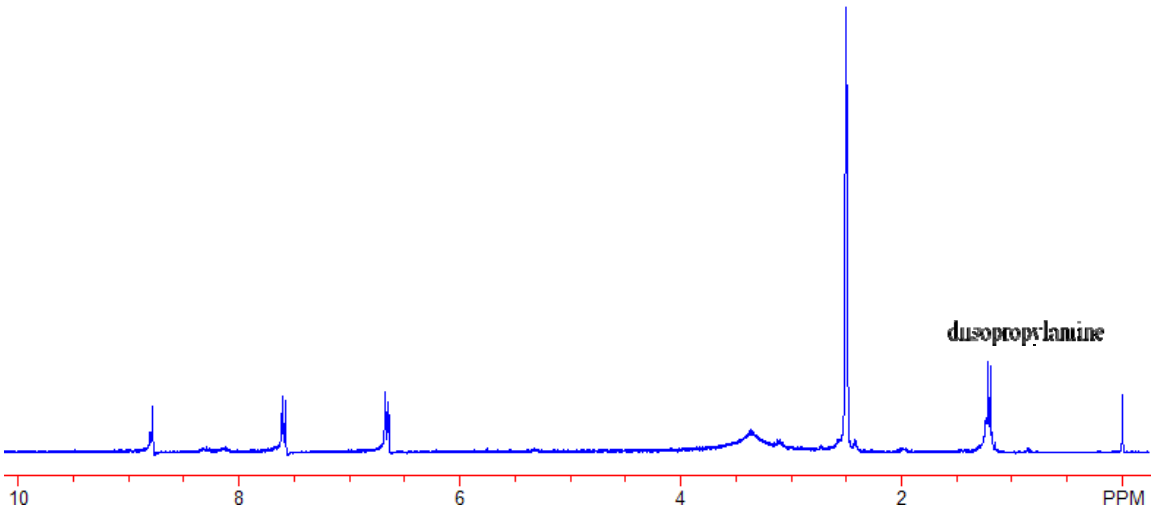


Figure S6. ^{1}H NMR spectrum of **4'** in DMSO-d_6

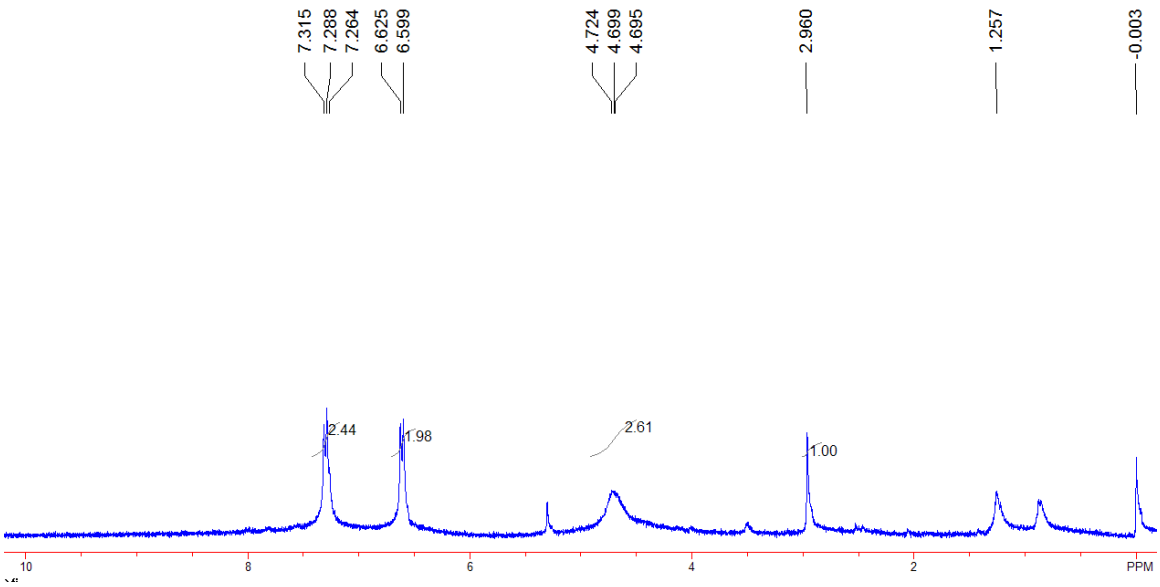


Figure S7. ^{1}H NMR spectrum of **1·2** in C*D*Cl$_3$ before reaction

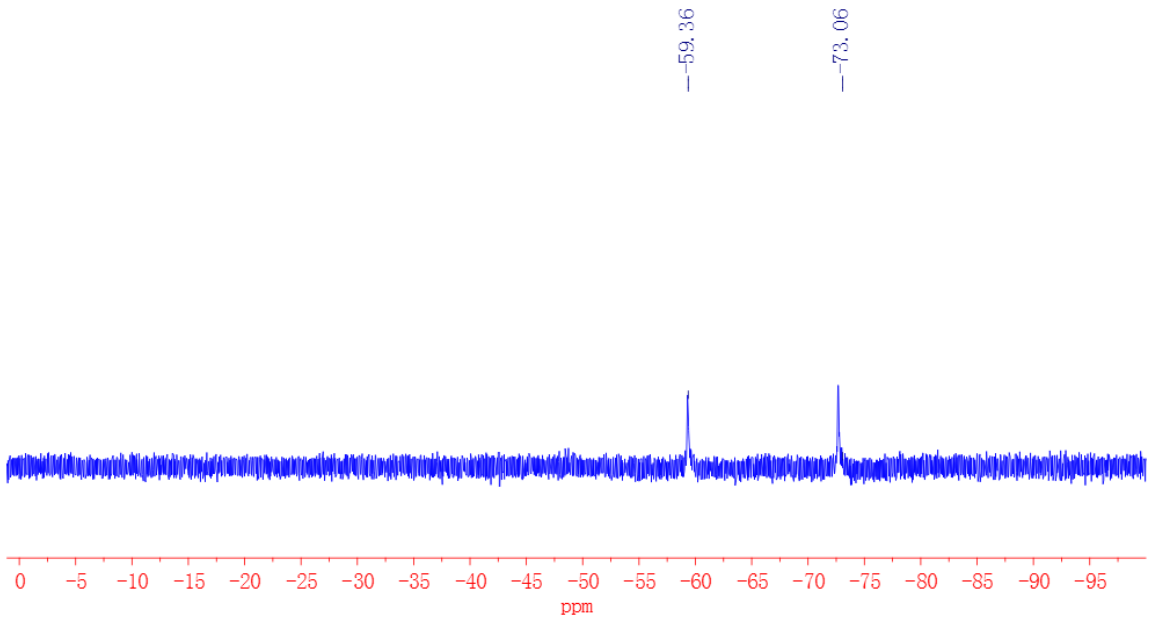
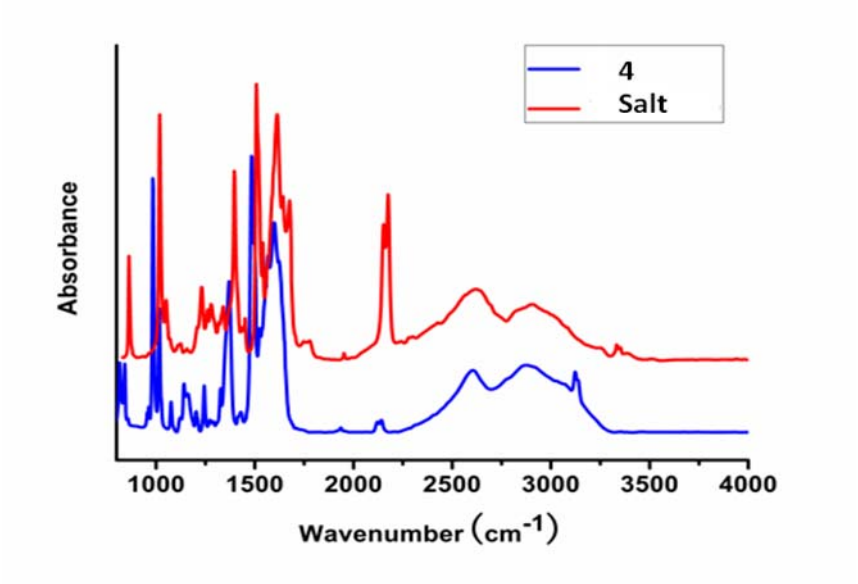


Figure S8. ^{19}F NMR spectrum of **1·2** in C*D*Cl$_3$ before reaction

3. FT-IR and Raman Spectra



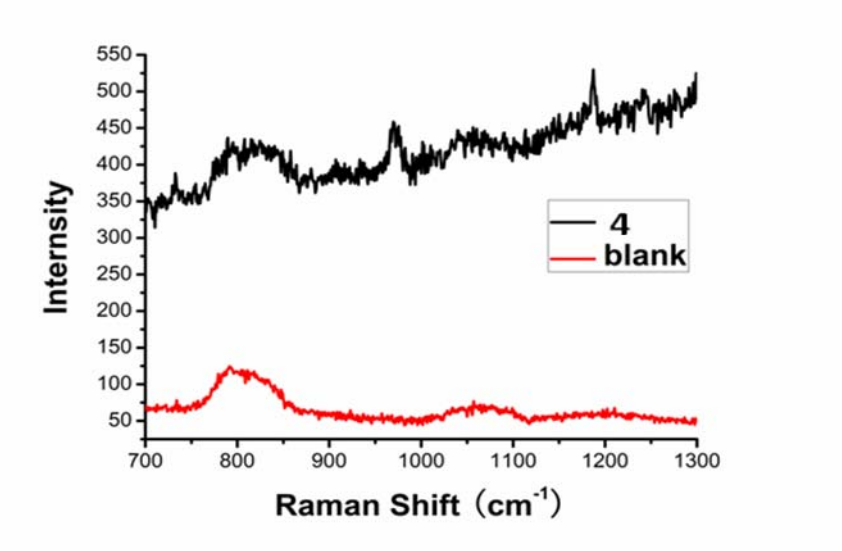


Figure S9. FT-IR spectra (top) and Raman spectra (bottom)

In the FT-IR spectra of both **4** and complex **1·2**, the peak at 1580 cm^{-1} indicates that the carboxylic acid group is dissociated into the carboxylate anionic group. In the FT-IR spectrum of **4**, the band emerged at 840 cm^{-1} can be assigned to triazole, and the signal at 2133 cm^{-1} of azide stretching mode decreased in intensity significantly. Raman spectrum of **4** showed a characteristic band at 967 cm^{-1}, which can be assigned as in-plane ring bending band of triazole ring. [3]

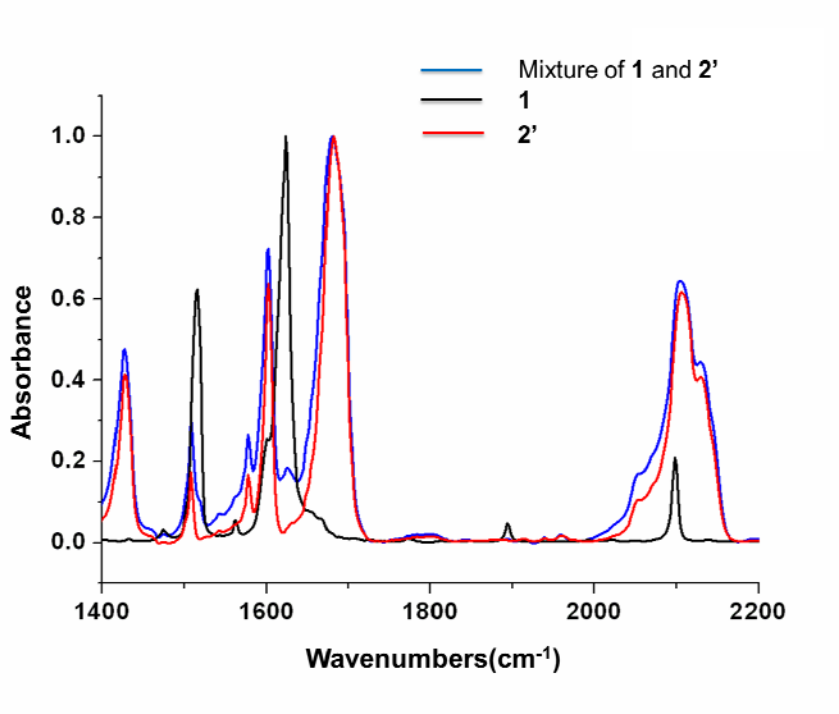


Figure S10. FT-IR in solid state: blue, black, red lines are corresponding to the mixture of **1** and **2'**, **1** and **2'**, respectively.

In the FT-IR spectra of both **2'** and the mixture of **1** and **2'**, the peak at 1700 cm^{-1} indicates that the carboxylic acid group is not dissociated into the carboxylate anionic group because **2'** is less acidic than **2** due to the lack of fluorine substituents.

4. X-ray Diffraction Patterns

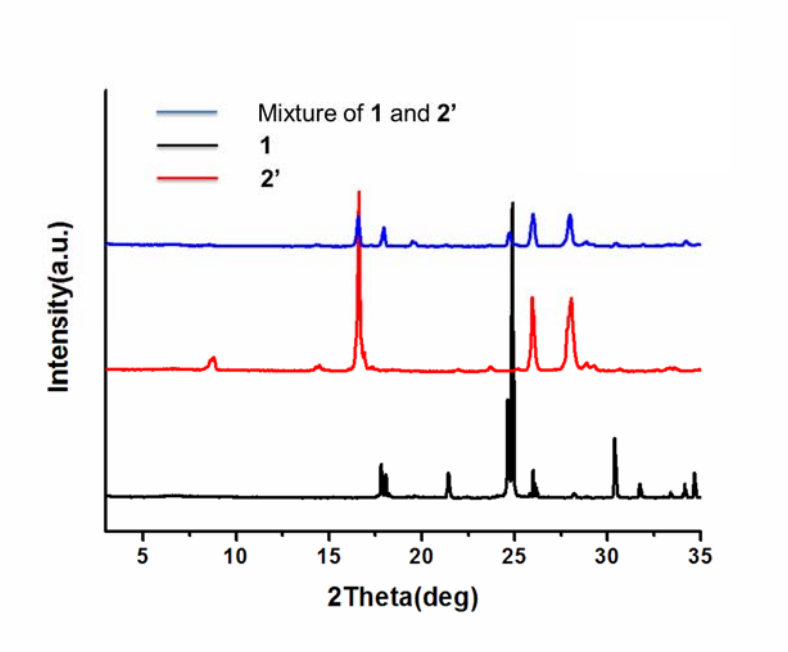


Figure S11. Powder X-ray diffraction: blue, black, red lines are corresponding to the mixture of **1** and **2'**, **1** and **2'**, respectively.

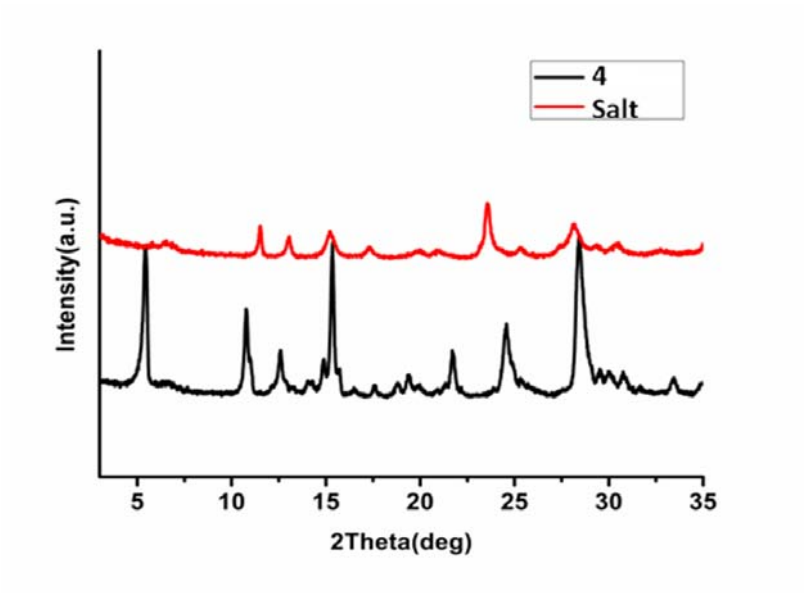


Figure S12. X-ray diffraction patterns of the salt **1·2** (top) and **4** (bottom)

XRD pattern of the salt shows multiple diffraction peaks in the 2θ range of 2 to 35

degree. The similarity of XRD patterns of **4** and salt **1·2** indicates that the crystal parameter did not change significantly after 1,3-dipolar cycloaddition in solid. The broad peak at ca. 6° is from aluminum foil.

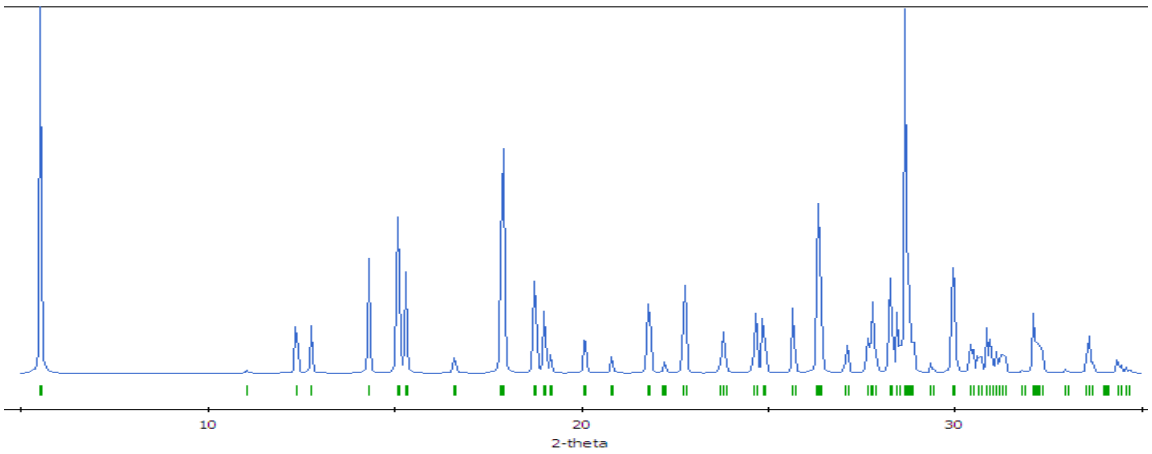


Figure S13. Simulated diffraction patterns of the salt **1'·2** by Materials Studio program Package (version 5.0).

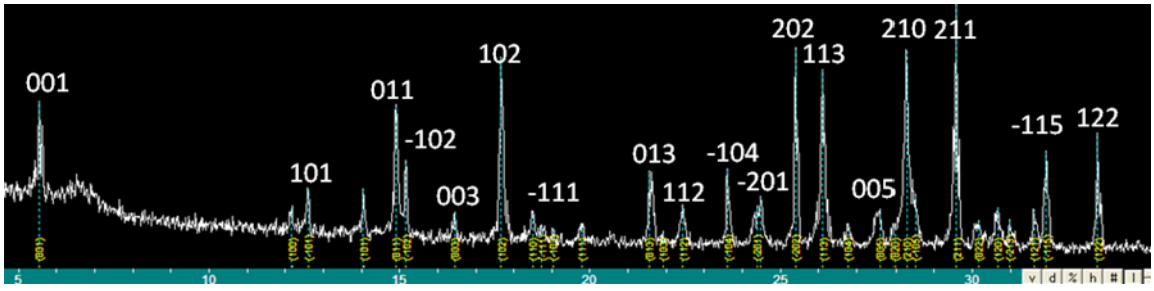


Figure S14. X-ray diffraction patterns of the salt **1'·2**

The simulated diffraction patterns of crystal of **1'·2** fits the experimental result well.

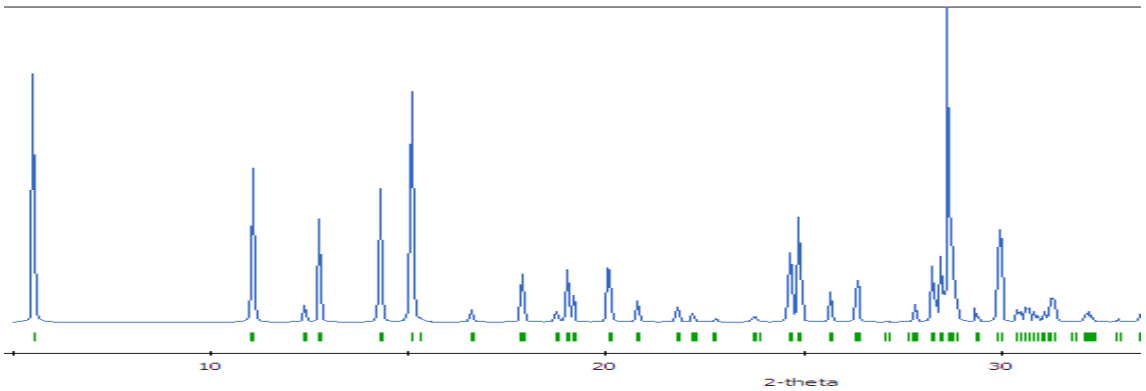


Figure S15. Simulated diffraction patterns of the salt **1·2** by Materials Studio program Package (version 5.0)

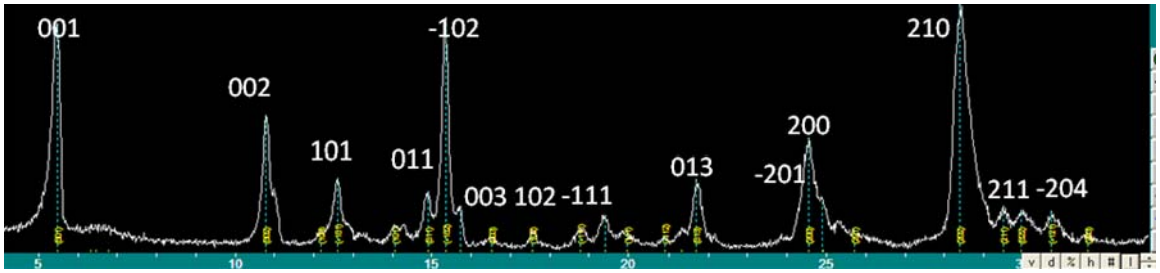


Figure S16. X-ray diffraction patterns of the salt **1·2**

The simulated diffraction patterns of crystal of **1·2** fits the experimental result well.

Table *S1.* The experimental Miller Indices and 2Theta of **1·2** and **1'·2**

h	k	l	2-Theta (1·2)	2-Theta (1'·2)
0	0	1	5.49780	5.47580
1	0	1	14.0913	14.1019
0	1	1	14.8696	14.9623
-1	0	2	15.2548	15.1813
0	0	3	16.5445	16.4779
1	0	2	17.5939	17.5987
-1	1	1	18.7745	18.8309
0	1	3	21.6101	21.6293
-2	0	1	24.3908	24.3556
2	1	1	29.5041	29.5695

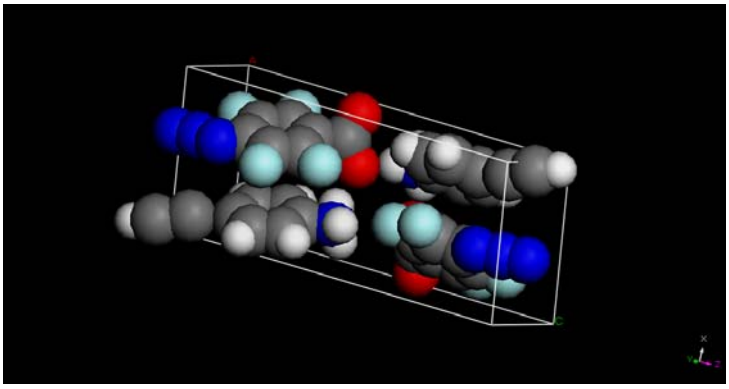


Figure S17. Crystal structure of the salt **1·2** using Materials Studio program Package (version 5.0) (CPK model)

5. Crystal Data and Structure Refinement

Table *S2-1*. Crystal data and structure refinement for **2·3**.

Identification code	**2·3**
Empirical formula	$C_{15}H_{10}F_4N_4O_3$
Formula weight	370.27
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 5.7206(11) Å alpha = 86.60(3) deg.
	b = 10.897(2) Å beta = 84.86(3) deg.
	c = 12.306(3) Å gamma = 80.87(3) deg.
Volume	753.5(3) $Å^3$
Z, Calculated density	2, 1.632 Mg/m^3
Absorption coefficient	0.149 mm^{-1}
F(000)	376
Crystal size	0.36 x 0.23 x 0.13 mm
Theta range for data collection	1.66 to 27.52 deg.
Limiting indices	-7<=h<=7, -14<=k<=14, -15<=l<=15
Reflections collected / unique	6742 / 3423 [R(int) = 0.0400]
Completeness to theta = 27.52	99.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.6893
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3423 / 0 / 236
Goodness-of-fit on F^2	1.098
Final R indices [I>2sigma(I)]	R1 = 0.0532, wR2 = 0.1303
R indices (all data)	R1 = 0.0604, wR2 = 0.1360
Largest diff. peak and hole	0.314 and -0.254 e. $Å^{-3}$

Table *S2-2*. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2·3**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
F(1)	9130(2)	8351(1)	3456(1)	37(1)
F(2)	10813(2)	6403(1)	2297(1)	35(1)
F(3)	4039(2)	4562(1)	3545(1)	37(1)
F(4)	2370(2)	6528(1)	4688(1)	37(1)
O(1)	8141(2)	3231(1)	2585(1)	42(1)
O(2)	9552(2)	4510(1)	1301(1)	38(1)
O(3)	8917(2)	7399(1)	-192(1)	34(1)
N(1)	4988(3)	8615(1)	4651(1)	37(1)
N(2)	3042(3)	8743(1)	5217(1)	34(1)
N(3)	1391(3)	9022(2)	5755(2)	46(1)
N(4)	3873(3)	11825(1)	2696(1)	35(1)
C(1)	5684(3)	7517(1)	4093(1)	27(1)
C(2)	4465(3)	6510(1)	4096(1)	27(1)
C(3)	5354(3)	5484(1)	3503(1)	27(1)
C(4)	7497(3)	5394(1)	2861(1)	25(1)
C(5)	8699(3)	6408(1)	2864(1)	26(1)
C(6)	7843(3)	7426(1)	3468(1)	27(1)
C(7)	8438(3)	4258(1)	2233(1)	28(1)
C(8)	5218(3)	6664(2)	105(2)	34(1)
C(9)	6875(3)	7564(1)	262(1)	25(1)
C(10)	6085(3)	8630(1)	933(1)	23(1)
C(11)	3824(3)	8841(1)	1493(1)	26(1)
C(12)	3106(3)	9882(2)	2086(1)	28(1)
C(13)	4606(3)	10775(1)	2131(1)	26(1)
C(14)	6883(3)	10563(1)	1588(1)	26(1)
C(15)	7589(3)	9513(1)	1006(1)	25(1)

Table *S2-3*. Bond lengths [Å] and angles [deg] for **2·3**.

Bond lengths [Å]	Angles [deg]
F(1)-C(6)	1.3376(17)
F(2)-C(5)	1.3402(18)
F(3)-C(3)	1.3429(17)
F(4)-C(2)	1.3436(18)
O(1)-C(7)	1.209(2)
O(2)-C(7)	1.297(2)
O(2)-H(2)	0.8399
O(3)-C(9)	1.2395(19)
N(1)-N(2)	1.252(2)
N(1)-C(1)	1.400(2)
N(2)-N(3)	1.115(2)
N(4)-C(13)	1.363(2)
N(4)-H(4B)	0.8600
N(4)-H(4A)	0.8600
C(1)-C(6)	1.388(2)
C(1)-C(2)	1.390(2)
C(2)-C(3)	1.375(2)
C(3)-C(4)	1.390(2)
C(4)-C(5)	1.391(2)
C(4)-C(7)	1.499(2)
C(5)-C(6)	1.373(2)
C(8)-C(9)	1.499(2)
C(8)-H(8C)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8A)	0.9800
C(9)-C(10)	1.454(2)
C(10)-C(15)	1.400(2)
C(10)-C(11)	1.402(2)
C(11)-C(12)	1.372(2)
C(11)-H(11)	0.9500
C(12)-C(13)	1.402(2)
C(12)-H(12)	0.9500
C(13)-C(14)	1.402(2)

Bond lengths [Å]	Angles [deg]
C(14)-C(15)	1.372(2)
C(14)-H(14)	0.9500
C(15)-H(15)	0.9500
C(7)-O(2)-H(2)	107.9
N(2)-N(1)-C(1)	118.30(14)
N(3)-N(2)-N(1)	169.73(18)
C(13)-N(4)-H(4B)	117.9
C(13)-N(4)-H(4A)	120.9
H(4B)-N(4)-H(4A)	120.3
C(6)-C(1)-C(2)	116.49(14)
C(6)-C(1)-N(1)	116.03(14)
C(2)-C(1)-N(1)	127.48(15)
F(4)-C(2)-C(3)	118.72(14)
F(4)-C(2)-C(1)	119.81(13)
C(3)-C(2)-C(1)	121.47(14)
F(3)-C(3)-C(2)	117.27(14)
F(3)-C(3)-C(4)	120.32(14)
C(2)-C(3)-C(4)	122.39(14)
C(3)-C(4)-C(5)	115.63(14)
C(3)-C(4)-C(7)	121.27(14)
C(5)-C(4)-C(7)	123.08(14)
F(2)-C(5)-C(6)	117.10(14)
F(2)-C(5)-C(4)	120.51(14)
C(6)-C(5)-C(4)	122.35(14)
F(1)-C(6)-C(5)	119.06(14)
F(1)-C(6)-C(1)	119.29(14)
C(5)-C(6)-C(1)	121.65(14)
O(1)-C(7)-O(2)	125.40(15)
O(1)-C(7)-C(4)	121.59(15)
O(2)-C(7)-C(4)	113.01(13)
C(9)-C(8)-H(8C)	109.5
C(9)-C(8)-H(8B)	109.5
H(8C)-C(8)-H(8B)	109.5
C(9)-C(8)-H	109.5

Bond lengths [Å]	Angles [deg]
H(8C)-C(8)-H(8A)	109.5
H(8B)-C(8)-H(8A)	109.5
O(3)-C(9)-C(10)	120.22(14)
O(3)-C(9)-C(8)	119.55(14)
C(10)-C(9)-C(8)	120.23(13)
C(15)-C(10)-C(11)	117.66(14)
C(15)-C(10)-C(9)	119.62(13)
C(11)-C(10)-C(9)	122.70(14)
C(12)-C(11)-C(10)	121.11(14)
C(12)-C(11)-H(11)	119.4
C(10)-C(11)-H(11)	119.4
C(11)-C(12)-C(13)	120.72(14)
C(11)-C(12)-H(12)	119.6
C(13)-C(12)-H(12)	119.6
N(4)-C(13)-C(14)	120.57(14)
N(4)-C(13)-C(12)	120.82(14)
C(14)-C(13)-C(12)	118.62(14)
C(15)-C(14)-C(13)	120.09(14)
C(15)-C(14)-H(14)	120.0
C(13)-C(14)-H(14)	120.0
C(14)-C(15)-C(10)	121.78(14)
C(14)-C(15)-H(15)	119.1
C(10)-C(15)-H(15)	119.1

Table *S2-4*. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **2·3**. The anisotropic displacement factor exponent takes the form: $-2\ pi^2\ [h^2\ a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
F(1)	47(1)	27(1)	40(1)	-8(1)	2(1)	-16(1)
F(2)	31(1)	33(1)	41(1)	-9(1)	8(1)	-10(1)
F(3)	33(1)	31(1)	49(1)	-11(1)	6(1)	-13(1)
F(4)	31(1)	39(1)	41(1)	-11(1)	9(1)	-5(1)
O(1)	52(1)	23(1)	50(1)	-9(1)	11(1)	-7(1)
O(2)	49(1)	27(1)	37(1)	-11(1)	12(1)	-4(1)
O(3)	31(1)	31(1)	39(1)	-14(1)	6(1)	-5(1)
N(1)	46(1)	30(1)	35(1)	-13(1)	6(1)	-5(1)
N(2)	46(1)	25(1)	30(1)	-6(1)	-3(1)	2(1)
N(3)	51(1)	36(1)	48(1)	-14(1)	9(1)	5(1)
N(4)	34(1)	31(1)	41(1)	-14(1)	2(1)	-3(1)
C(1)	35(1)	21(1)	23(1)	-5(1)	-4(1)	0(1)
C(2)	26(1)	29(1)	25(1)	-4(1)	2(1)	-1(1)
C(3)	28(1)	24(1)	31(1)	-4(1)	-3(1)	-7(1)
C(4)	29(1)	21(1)	26(1)	-5(1)	-2(1)	-2(1)
C(5)	28(1)	26(1)	25(1)	-2(1)	-1(1)	-4(1)
C(6)	34(1)	22(1)	27(1)	-3(1)	-4(1)	-8(1)
C(7)	26(1)	24(1)	33(1)	-7(1)	-1(1)	-2(1)
C(8)	35(1)	28(1)	42(1)	-10(1)	-1(1)	-9(1)
C(9)	28(1)	24(1)	24(1)	-2(1)	-3(1)	-2(1)
C(10)	25(1)	23(1)	22(1)	-2(1)	-2(1)	-3(1)
C(11)	23(1)	27(1)	30(1)	-3(1)	0(1)	-8(1)
C(12)	24(1)	30(1)	30(1)	-4(1)	3(1)	-4(1)
C(13)	28(1)	26(1)	22(1)	-4(1)	-3(1)	0(1)
C(14)	25(1)	25(1)	30(1)	-4(1)	-3(1)	-6(1)
C(15)	22(1)	27(1)	27(1)	-3(1)	0(1)	-4(1)

Table *S2-5*. Hydrogen coordinates (x10^4) and isotropic displacement parameters (Å^2 x 10^3) for **2·3**.

	x	y	z	U(eq)
H(2)	10013	3838	992	46
H(4B)	4808	12373	2667	42
H(4A)	2432	11996	2974	42
H(8C)	3762	7115	-180	51
H(8B)	4823	6242	807	51
H(8A)	5987	6047	-414	51
H(11)	2772	8254	1463	32
H(12)	1576	9998	2469	33
H(14)	7940	11147	1623	31
H(15)	9139	9382	644	30

Table *S2-6*. Torsion angles [deg] for **2·3**.

C(1)-N(1)-N(2)-N(3)	-180(1)
N(2)-N(1)-C(1)-C(6)	179.38(16)
N(2)-N(1)-C(1)-C(2)	-0.8(3)
C(6)-C(1)-C(2)-F(4)	179.58(14)
N(1)-C(1)-C(2)-F(4)	-0.2(3)
C(6)-C(1)-C(2)-C(3)	-0.4(2)
N(1)-C(1)-C(2)-C(3)	179.75(16)
F(4)-C(2)-C(3)-F(3)	0.8(2)
C(1)-C(2)-C(3)-F(3)	-179.18(14)
F(4)-C(2)-C(3)-C(4)	179.38(15)
C(1)-C(2)-C(3)-C(4)	-0.6(3)
F(3)-C(3)-C(4)-C(5)	179.04(14)
C(2)-C(3)-C(4)-C(5)	0.5(2)
F(3)-C(3)-C(4)-C(7)	-2.2(2)
C(2)-C(3)-C(4)-C(7)	179.32(15)
C(3)-C(4)-C(5)-F(2)	178.15(14)
C(7)-C(4)-C(5)-F(2)	-0.6(2)
C(3)-C(4)-C(5)-C(6)	0.6(2)
C(7)-C(4)-C(5)-C(6)	-178.15(15)
F(2)-C(5)-C(6)-F(1)	0.4(2)
C(4)-C(5)-C(6)-F(1)	178.03(14)
F(2)-C(5)-C(6)-C(1)	-179.32(14)
C(4)-C(5)-C(6)-C(1)	-1.7(3)
C(2)-C(1)-C(6)-F(1)	-178.19(14)
N(1)-C(1)-C(6)-F(1)	1.7(2)
C(2)-C(1)-C(6)-C(5)	1.6(2)
N(1)-C(1)-C(6)-C(5)	-178.60(15)
C(3)-C(4)-C(7)-O(1)	-34.8(2)
C(5)-C(4)-C(7)-O(1)	143.86(18)
C(3)-C(4)-C(7)-O(2)	144.81(16)
C(5)-C(4)-C(7)-O(2)	-36.5(2)
O(3)-C(9)-C(10)-C(15)	4.2(2)
C(8)-C(9)-C(10)-C(15)	-175.28(15)
O(3)-C(9)-C(10)-C(11)	-177.85(15)
C(8)-C(9)-C(10)-C(11)	2.7(2)
C(15)-C(10)-C(11)-C(12)	0.5(2)

C(9)-C(10)-C(11)-C(12)	-177.51(15)
C(10)-C(11)-C(12)-C(13)	1.1(3)
C(11)-C(12)-C(13)-N(4)	178.32(15)
C(11)-C(12)-C(13)-C(14)	-2.1(2)
N(4)-C(13)-C(14)-C(15)	-178.92(15)
C(12)-C(13)-C(14)-C(15)	1.5(2)
C(13)-C(14)-C(15)-C(10)	0.1(2)
C(11)-C(10)-C(15)-C(14)	-1.1(2)
C(9)-C(10)-C(15)-C(14)	176.97(15)

Table *S2-7*. Hydrogen bonds for **2·3** [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2)...O(3)#1	0.84	1.72	2.5509(17)	171.3
N(4)-H(4B)...O(1)#2	0.86	2.24	3.071(2)	161.0

Table *S3-1*. Crystal data and structure refinement for **1'·2**.

Identification code	**1'·2**
Empirical formula	$C_{13}H_7F_4IN_4O_2$
Formula weight	454.13
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 7.2406(14) Å alpha = 90 deg.
	b = 6.3111(11) Å beta = 98.719(7) deg.
	c = 16.211(3) Å gamma = 90 deg.
Volume	732.2(2) $Å^3$
Z, Calculated density	2, 2.060 Mg/m^3
Absorption coefficient	2.249 mm^{-1}
F(000)	436
Crystal size	0.49 x 0.30 x 0.08 mm^3
Theta range for data collection	2.85 to 27.48 deg.
Limiting indices	-9<=h<=9, -8<=k<=8, -19<=l<=21
Reflections collected / unique	5741 / 3087 [R(int) = 0.0264]
Completeness to theta = 27.48	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8406 and 0.4054
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3087 / 1 / 217
Goodness-of-fit on F^2	1.051
Final R indices [I>2sigma(I)]	R1 = 0.0261, wR2 = 0.0618
R indices (all data)	R1 = 0.0265, wR2 = 0.0621
Absolute structure parameter	-0.018(18)
Largest diff. peak and hole	0.868 and -0.520 e. $Å^{-3}$

Table *S3-2*. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å ^{2}x 10^3) for **1'·2**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
I(1)	1225(1)	10877(1)	701(1)	40(1)
F(1)	5666(3)	12323(3)	2960(1)	27(1)
F(2)	6413(3)	9716(3)	4251(1)	26(1)
F(3)	8616(3)	4605(3)	2506(1)	26(1)
F(4)	7757(3)	7171(4)	1208(1)	30(1)
O(1)	6505(3)	5151(4)	4523(2)	25(1)
O(2)	9498(3)	4777(4)	4361(2)	31(1)
N(1)	6225(4)	11343(5)	1410(2)	29(1)
N(2)	6166(3)	10808(13)	667(2)	29(1)
N(3)	6016(5)	10602(9)	-26(2)	41(1)
N(4)	2832(4)	6951(5)	4312(2)	22(1)
C(1)	6696(4)	9844(5)	2041(2)	20(1)
C(2)	6402(4)	10424(5)	2843(2)	20(1)
C(3)	6812(4)	9054(5)	3507(2)	20(1)
C(4)	7555(4)	7052(5)	3435(2)	20(1)
C(5)	7887(4)	6509(5)	2638(2)	21(1)
C(6)	7440(4)	7834(5)	1962(2)	21(1)
C(7)	7911(4)	5529(5)	4171(2)	20(1)
C(8)	1765(4)	9534(6)	1897(2)	24(1)
C(9)	1417(4)	10738(8)	2569(2)	25(1)
C(10)	1774(4)	9894(6)	3372(2)	23(1)
C(11)	2462(4)	7855(5)	3476(2)	20(1)
C(12)	2789(4)	6638(5)	2803(2)	21(1)
C(13)	2438(4)	7479(6)	2003(2)	24(1)

Table *S3-3*. Bond lengths [Å] and angles [deg] for **1'·2.**

Bond lengths [Å]	Angles [deg]
I(1)-C(8)	2.098(3)
F(1)-C(2)	1.337(4)
F(2)-C(3)	1.349(4)
F(3)-C(5)	1.343(4)
F(4)-C(6)	1.344(4)
O(1)-C(7)	1.263(4)
O(2)-C(7)	1.239(4)
N(1)-N(2)	1.246(4)
N(1)-C(1)	1.396(4)
N(2)-N(3)	1.120(4)
N(4)-C(11)	1.458(4)
N(4)-H(4A)	0.9100
N(4)-H(4C)	0.9100
N(4)-H(4B)	0.9100
C(1)-C(6)	1.392(5)
C(1)-C(2)	1.398(4)
C(2)-C(3)	1.377(5)
C(3)-C(4)	1.385(5)
C(4)-C(5)	1.392(5)
C(4)-C(7)	1.524(5)
C(5)-C(6)	1.377(5)
C(8)-C(9)	1.383(5)
C(8)-C(13)	1.387(5)
C(9)-C(10)	1.393(5)
C(9)-H(9)	0.9500
C(10)-C(11)	1.381(5)
C(10)-H(10)	0.9500
C(11)-C(12)	1.382(5)
C(12)-C(13)	1.389(5)
C(12)-H(12)	0.9500
C(13)-H(13)	0.9500
N(2)-N(1)-C(1)	119.5(5)
N(3)-N(2)-N(1)	170.3(8)

Bond lengths [Å]	Angles [deg]
C(11)-N(4)-H(4A)	94.5
C(11)-N(4)-H(4C)	112.7
H(4A)-N(4)-H(4C)	118.8
C(11)-N(4)-H(4B)	108.7
H(4A)-N(4)-H(4B)	113.5
H(4C)-N(4)-H(4B)	107.8
C(6)-C(1)-N(1)	127.3(3)
C(6)-C(1)-C(2)	116.0(3)
N(1)-C(1)-C(2)	116.7(3)
F(1)-C(2)-C(3)	119.7(3)
F(1)-C(2)-C(1)	119.1(3)
C(3)-C(2)-C(1)	121.2(3)
F(2)-C(3)-C(2)	117.0(3)
F(2)-C(3)-C(4)	119.8(3)
C(2)-C(3)-C(4)	123.2(3)
C(3)-C(4)-C(5)	115.2(3)
C(3)-C(4)-C(7)	122.1(3)
C(5)-C(4)-C(7)	122.6(3)
F(3)-C(5)-C(6)	117.9(3)
F(3)-C(5)-C(4)	119.7(3)
C(6)-C(5)-C(4)	122.4(3)
F(4)-C(6)-C(5)	118.9(3)
F(4)-C(6)-C(1)	119.2(3)
C(5)-C(6)-C(1)	121.9(3)
O(2)-C(7)-O(1)	126.6(3)
O(2)-C(7)-C(4)	118.5(3)
O(1)-C(7)-C(4)	114.9(3)
C(9)-C(8)-C(13)	121.2(3)
C(9)-C(8)-I(1)	118.4(3)
C(13)-C(8)-I(1)	120.3(3)
C(8)-C(9)-C(10)	119.7(4)
C(8)-C(9)-H(9)	120.1
C(10)-C(9)-H(9)	120.1
C(11)-C(10)-C(9)	118.9(3)

Bond lengths [Å]	Angles [deg]
C(11)-C(10)-H(10)	120.6
C(9)-C(10)-H(10)	120.6
C(10)-C(11)-C(12)	121.6(3)
C(10)-C(11)-N(4)	119.3(3)
C(12)-C(11)-N(4)	119.1(3)
C(11)-C(12)-C(13)	119.7(3)
C(11)-C(12)-H(12)	120.2
C(13)-C(12)-H(12)	120.2
C(8)-C(13)-C(12)	118.9(3)
C(8)-C(13)-H(13)	120.5
C(12)-C(13)-H(13)	120.5

Table *S3-4*. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1'·2**. The anisotropic displacement factor exponent takes the form: $-2\ pi^2\ [h^2\ a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
I(1)	30(1)	59(1)	30(1)	20(1)	-3(1)	-8(1)
F(1)	28(1)	16(1)	40(1)	-1(1)	10(1)	4(1)
F(2)	31(1)	27(1)	22(1)	-6(1)	7(1)	-1(1)
F(3)	29(1)	17(1)	36(1)	-4(1)	13(1)	5(1)
F(4)	37(1)	32(1)	22(1)	-7(1)	10(1)	0(1)
O(1)	21(1)	30(1)	24(1)	6(1)	6(1)	2(1)
O(2)	19(1)	35(1)	40(2)	13(1)	5(1)	0(1)
N(1)	36(2)	25(2)	24(1)	3(1)	2(1)	0(1)
N(2)	24(1)	36(2)	28(1)	9(2)	3(1)	0(2)
N(3)	40(2)	57(3)	26(2)	5(2)	6(1)	9(2)
N(4)	21(1)	23(1)	21(1)	1(1)	4(1)	-2(1)
C(1)	19(1)	22(2)	20(2)	1(1)	4(1)	-3(1)
C(2)	19(1)	18(2)	24(2)	-5(1)	4(1)	-2(1)
C(3)	18(1)	23(2)	20(2)	-5(1)	6(1)	-2(1)
C(4)	15(1)	22(2)	22(2)	0(1)	4(1)	-3(1)
C(5)	19(1)	15(2)	29(2)	-3(1)	6(1)	-1(1)
C(6)	21(1)	22(2)	20(2)	-6(1)	7(1)	-3(1)
C(7)	21(1)	17(2)	22(1)	-2(1)	2(1)	-3(1)
C(8)	20(1)	29(2)	22(2)	10(1)	-1(1)	-4(1)
C(9)	20(1)	22(2)	33(2)	8(2)	0(1)	1(2)
C(10)	21(2)	19(2)	27(2)	-4(1)	4(1)	1(1)
C(11)	16(1)	22(2)	21(2)	2(1)	1(1)	-3(1)
C(12)	20(1)	17(1)	27(2)	-1(1)	3(1)	1(1)
C(13)	22(2)	26(2)	22(2)	-3(1)	5(1)	-3(1)

Table *S3-5*. Hydrogen coordinates ($x10^4$) and isotropic displacement parameters ($Å^2 x10^3$) for **1'·2**.

	x	y	z	U(eq)
H(4A)	3830	6173	4209	26
H(4C)	3008	7958	4719	26
H(4B)	1834	6150	4398	26
H(9)	937	12135	2485	30
H(10)	1548	10707	3839	27
H(12)	3252	5234	2889	26
H(13)	2656	6660	1536	28

Table *S3-6.* Torsion angles [deg] for **1'·2**.

C(1)-N(1)-N(2)-N(3)	173(3)
N(2)-N(1)-C(1)-C(6)	12.0(5)
N(2)-N(1)-C(1)-C(2)	-168.4(3)
C(6)-C(1)-C(2)-F(1)	-179.1(3)
N(1)-C(1)-C(2)-F(1)	1.3(4)
C(6)-C(1)-C(2)-C(3)	-0.8(4)
N(1)-C(1)-C(2)-C(3)	179.6(3)
F(1)-C(2)-C(3)-F(2)	0.9(4)
C(1)-C(2)-C(3)-F(2)	-177.4(3)
F(1)-C(2)-C(3)-C(4)	179.2(3)
C(1)-C(2)-C(3)-C(4)	0.9(5)
F(2)-C(3)-C(4)-C(5)	179.0(3)
C(2)-C(3)-C(4)-C(5)	0.7(5)
F(2)-C(3)-C(4)-C(7)	1.2(4)
C(2)-C(3)-C(4)-C(7)	-177.1(3)
C(3)-C(4)-C(5)-F(3)	179.6(3)
C(7)-C(4)-C(5)-F(3)	-2.6(4)
C(3)-C(4)-C(5)-C(6)	-2.4(5)
C(7)-C(4)-C(5)-C(6)	175.3(3)
F(3)-C(5)-C(6)-F(4)	-0.2(4)
C(4)-C(5)-C(6)-F(4)	-178.2(3)
F(3)-C(5)-C(6)-C(1)	-179.3(3)
C(4)-C(5)-C(6)-C(1)	2.7(5)
N(1)-C(1)-C(6)-F(4)	-0.6(5)
C(2)-C(1)-C(6)-F(4)	179.9(3)
N(1)-C(1)-C(6)-C(5)	178.6(3)
C(2)-C(1)-C(6)-C(5)	-1.0(5)
C(3)-C(4)-C(7)-O(2)	-125.5(4)
C(5)-C(4)-C(7)-O(2)	56.9(5)
C(3)-C(4)-C(7)-O(1)	55.1(4)
C(5)-C(4)-C(7)-O(1)	-122.5(3)
C(13)-C(8)-C(9)-C(10)	1.0(5)
I(1)-C(8)-C(9)-C(10)	-179.6(2)
C(8)-C(9)-C(10)-C(11)	-0.4(5)
C(9)-C(10)-C(11)-C(12)	-0.5(5)
C(9)-C(10)-C(11)-N(4)	-179.7(3)

C(10)-C(11)-C(12)-C(13)	0.6(5)
N(4)-C(11)-C(12)-C(13)	179.8(3)
C(9)-C(8)-C(13)-C(12)	-0.9(5)
I(1)-C(8)-C(13)-C(12)	179.7(2)
C(11)-C(12)-C(13)-C(8)	0.1(5)

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