Supporting Information

for

Topochemical 1,3-dipolar Cycloaddition Polymerization Assisted by Non-covalent Interactions

Xiao Meng,[a,c]* Shu Xu,[a] Changqing Chen,[b] Lihui Guo[a] and Yuguo Ma[a]*

a. Beijing National Laboratory for Molecular Sciences (BNLMS), Center for Soft Matter Science and Engineering, Key Lab of Polymer Chemistry & Physics of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China

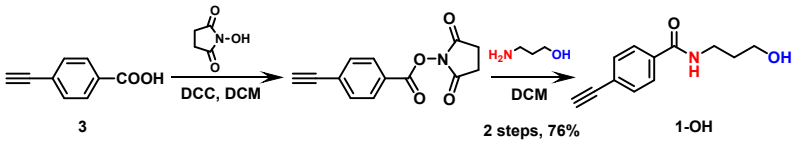
b. Department of Chemistry and Physics, Salem State University, Salem, MA 01970, U.S.A

c. School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China

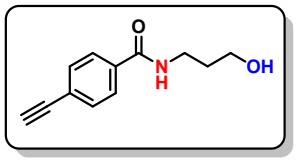
Table of Contents **Pages**

1. Experimental Section

Compound **3**, **4** and **2-OH** were synthesized according to references.[1-3]



4-ethynyl-N-(3-hydroxypropyl)benzamide (1-OH): 1-OH was synthesized according to the reference[3].



^{1}H NMR (400 MHz, CDCl3): δ 7.73 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 6.76 (m, 1H), 3.74 (dd, 2H), 3.64 (dd, 2H), 3.2 (s, 1H), 2.99 (m, 1H), 1.81 (m, 2H); ^{13}C NMR (100 MHz, CDCl3): δ 167.5, 134.2, 132.3, 126.9, 125.4, 82.7, 79.5, 60.1, 37.5, 31.9; HR-MS (ESI, $C_{12}H_{13}NO_2$, solvent: CDCl3, m/z): Anal. Calcd. for [(M+Na)+]: 225.1961, Found 225.1955, Error: -0.61 mDa.

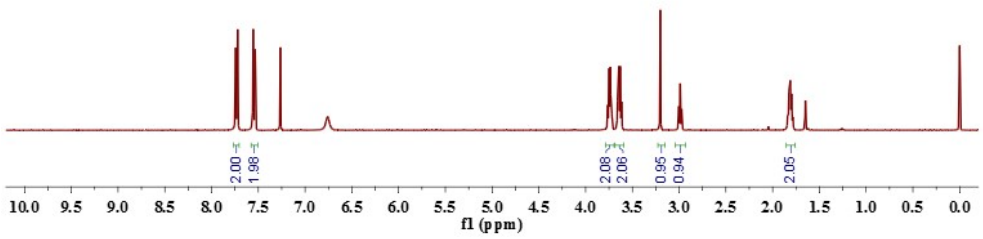


Figure S1-1. ^{1}H NMR spectrum of **1-OH** in $CDCl_3$.

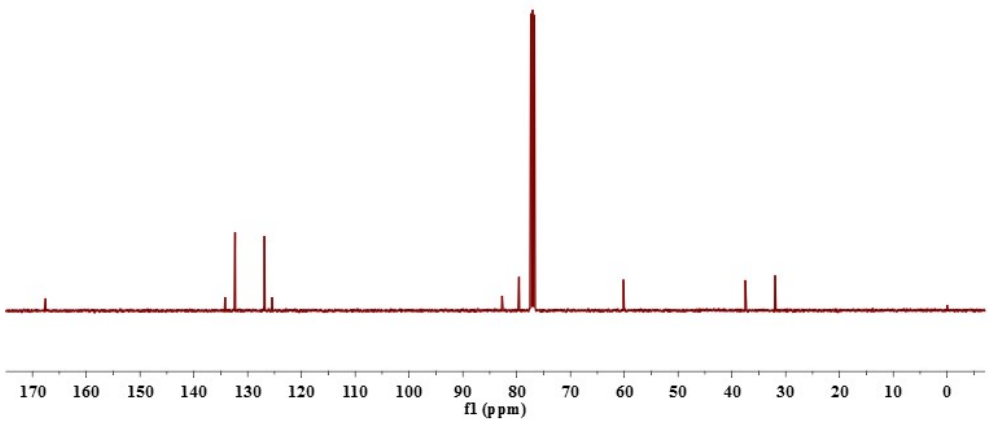


Figure S1-2. ^{13}C NMR spectrum of **1-OH** in $CDCl_3$.

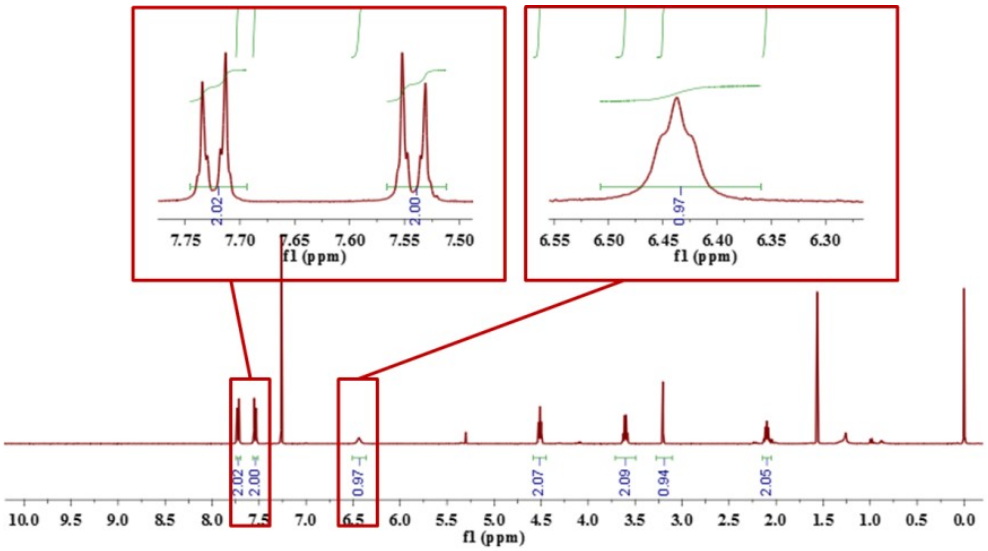


Figure S1-3. ^{1}H NMR spectrum of **1** in $CDCl_3$.

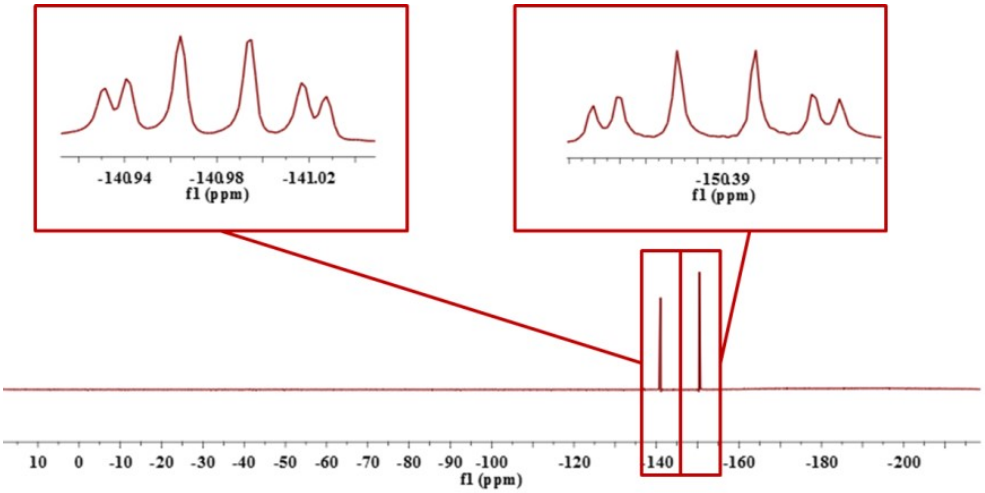


Figure S1-4. ^{19}F NMR spectrum of **1** in $CDCl_3$.

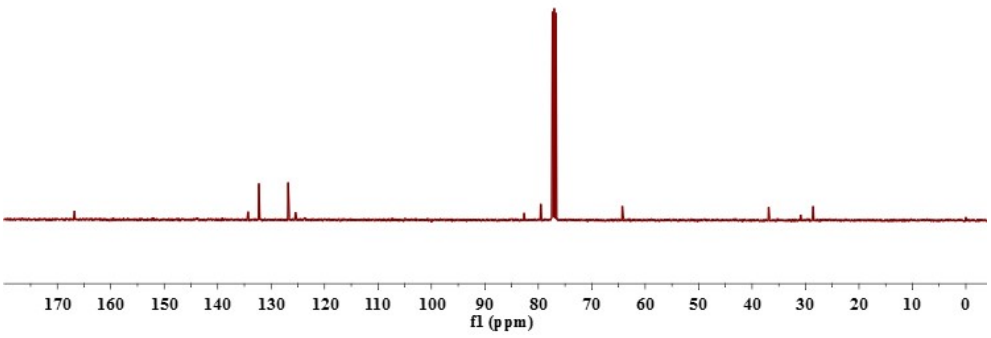


Figure S1-5. ^{13}C NMR spectrum of **1** in $CDCl_3$.

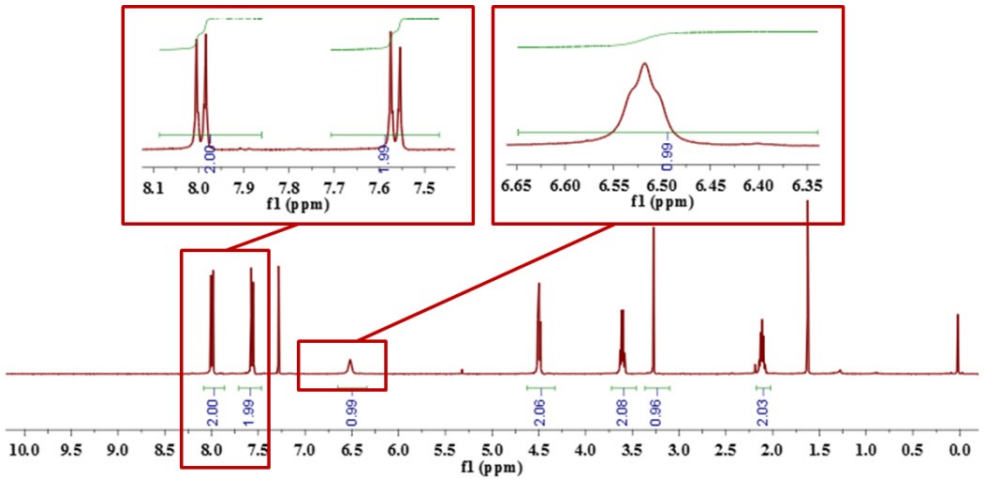


Figure S1-6. ^{1}H NMR spectrum of **2** in $CDCl_3$.

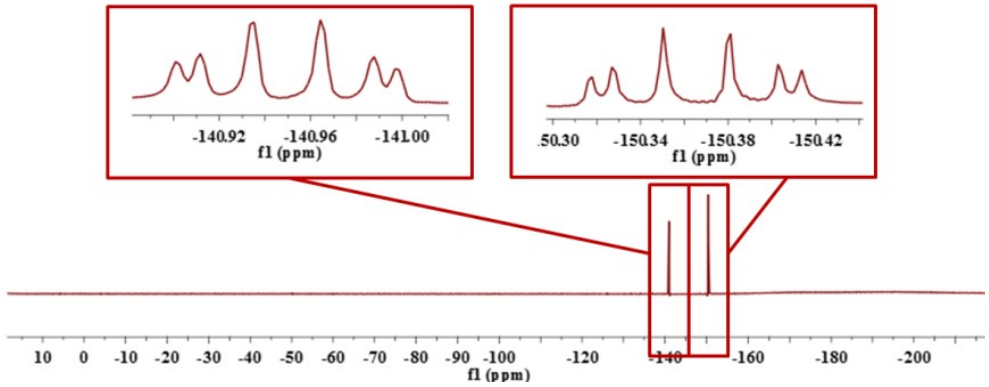


Figure S1-7. ^{19}F NMR spectrum of **2** in $CDCl_3$.

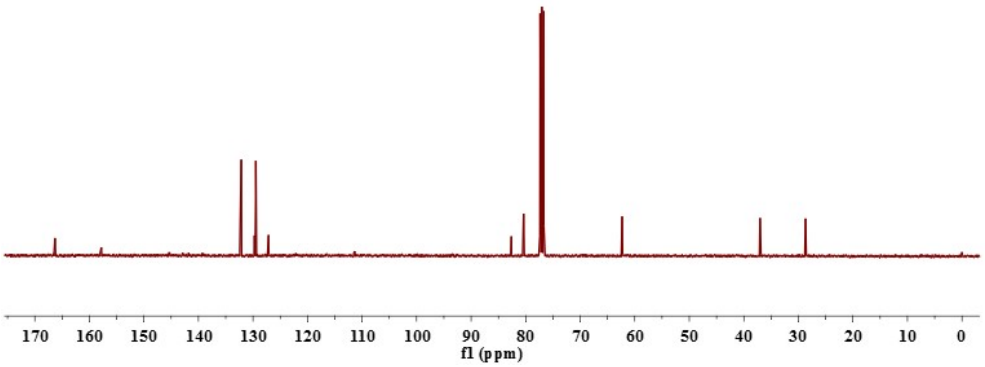


Figure *S1-8.* ^{13}C NMR spectrum of **2** in $CDCl_3$.

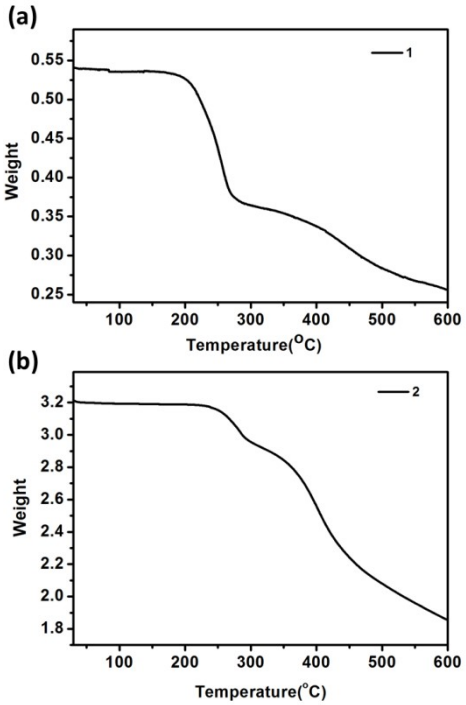


Figure *S1-9.* Thermogravimetric analysis (TGA) spectra of **1**(a) and **2** (b).

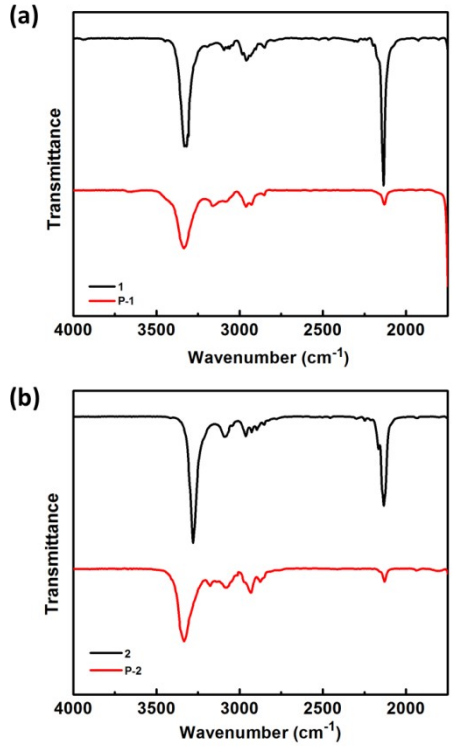


Figure *S1-10.* FT-IR spectra of **1** (a) and the product after heating at 90 °C for 24 hours, as well as **2** (b) and the product after heating at 90 °C for 24 hours.

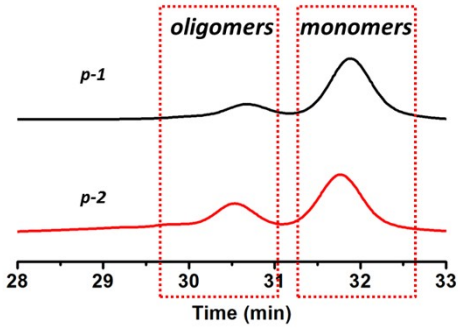


Figure *S1-11.* GPC chromatogram of the obtained products of compound **1** and **2** from metal-free 1,3-dipolar cycloaddition polymerization at 90 °C for 30 minutes.

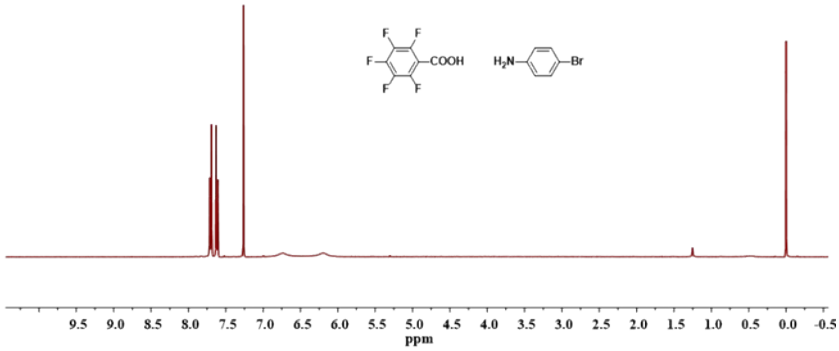


Figure *S1-12.* ^{1}H NMR of mixture (inset: chemical structure) after 90 °C for 30 min in solid state.

2. X-ray Diffraction Pattern

Cambridge Crystallographic Data Centre (CCDC) Deposition Number:

1: 1448790.

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

Identification code	**1**	
Empirical formula	C19 H12 F4 N4 O3	
Formula weight	420.33	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*P*21/*c*	
Unit cell dimensions	a = 6.925(3) Å	α = 90 °
	b = 27.776(11) Å	β = 106.46(3) °
	c = 9.963(5) Å	γ = 90 °
Volume	1837.8(14) Å^3	
Z	4	

Density (calculated)	1.519 Mg/m^3
Absorption coefficient	0.132 mm^{-1}
F(000)	856
Crystal size	0.43 x 0.26 x 0.07 mm^3
Theta range for data collection	1.466 to 25.197 °
Index ranges	-8<=h<=8, -32<=k<=33, -11<=l<=11
Reflections collected	14246
Independent reflections	3293 [R(int) = 0.0375]
Completeness to theta = 25.242°	98.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.8349
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3293 / 0 / 275
Goodness-of-fit on F^2	1.192
Final R indices [I>2sigma(I)]	R1 = 0.0869, wR2 = 0.2070
R indices (all data)	R1 = 0.1017, wR2 = 0.2163
Extinction coefficient	n/a
Largest diff. peak and hole	0.436 and -0.192 e.$Å^{-3}$

Table *S2-2*. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
F1	2742(5)	4976(1)	9483(3)	80(1)
F2	3986(5)	5679(1)	11317(3)	80(1)
F3	3618(4)	6763(1)	7591(3)	74(1)
F4	2458(4)	6052(1)	5785(3)	77(1)
O1	5466(5)	7009(1)	10310(4)	82(1)
O2	3741(4)	6635(1)	11594(3)	62(1)
O3	133(5)	7577(1)	14939(3)	65(1)
N1	1307(10)	4332(2)	6875(7)	127(2)
N2	1642(7)	4732(2)	6804(5)	84(1)
N3	1909(6)	5159(2)	6489(4)	73(1)
N4	47(5)	7330(1)	12789(3)	47(1)
C1	2580(6)	5492(2)	7572(4)	56(1)
C2	2966(6)	5420(1)	9004(5)	57(1)
C3	3602(6)	5792(2)	9943(4)	57(1)

C4	3849(6)	6256(1)	9534(4)	53(1)
C5	3453(6)	6320(2)	8113(4)	53(1)
C6	2843(6)	5957(2)	7160(4)	53(1)
C7	4476(6)	6675(2)	10522(5)	61(1)
C8	4190(7)	7028(2)	12601(5)	62(1)
C9	3260(6)	6901(2)	13744(4)	60(1)
C10	979(6)	6868(2)	13273(4)	53(1)
C11	-268(5)	7660(1)	13663(4)	46(1)
C12	-1061(5)	8141(1)	13103(3)	43(1)
C13	-1088(5)	8503(2)	14064(4)	51(1)
C14	-1641(6)	8964(2)	13645(4)	53(1)
C15	-2198(5)	9084(2)	12230(4)	52(1)
C16	-2227(6)	8720(2)	11253(4)	55(1)
C17	-1672(5)	8255(1)	11671(4)	49(1)
C18	-2737(6)	9570(2)	11777(4)	61(1)
C19	-3115(8)	9976(2)	11441(5)	71(1)

Table *S2-3*. Bond lengths [Å] and angles [deg] for **1**.

F1-C2	1.348(5)	F2-C3-C4	120.7(4)
F2-C3	1.355(5)	C4-C3-C2	122.9(4)
F3-C5	1.354(5)	C3-C4-C7	124.4(4)
F4-C6	1.345(5)	C5-C4-C3	114.8(4)
O1-C7	1.208(5)	C5-C4-C7	120.7(4)
O2-C7	1.311(5)	F3-C5-C4	119.9(4)
O2-C8	1.455(5)	F3-C5-C6	116.5(4)
O3-C11	1.244(4)	C6-C5-C4	123.6(4)
N1-N2	1.141(6)	F4-C6-C1	118.7(4)
N2-N3	1.253(6)	F4-C6-C5	119.8(4)
N3-C1	1.397(6)	C5-C6-C1	121.6(4)
N4-C10	1.455(5)	O1-C7-O2	125.4(4)
N4-C11	1.324(5)	O1-C7-C4	123.5(4)
C1-C2	1.390(6)	O2-C7-C4	111.1(4)
C1-C6	1.384(6)	O2-C8-C9	107.1(3)
C2-C3	1.381(6)	C8-C9-C10	114.3(3)
C3-C4	1.377(6)	N4-C10-C9	112.0(3)
C4-C5	1.375(6)	O3-C11-N4	120.9(4)
C4-C7	1.506(6)	O3-C11-C12	120.0(3)
C5-C6	1.366(6)	N4-C11-C12	119.1(3)
C8-C9	1.500(6)	C13-C12-C11	117.7(3)
C9-C10	1.518(6)	C13-C12-C17	118.5(4)
C11-C12	1.493(5)	C17-C12-C11	123.6(3)
C12-C13	1.391(5)	C14-C13-C12	121.6(4)
C12-C17	1.404(5)	C13-C14-C15	120.4(4)
C13-C14	1.368(6)	C14-C15-C16	118.5(4)
C14-C15	1.392(5)	C14-C15-C18	120.9(4)
C15-C16	1.400(6)	C16-C15-C18	120.6(4)
C15-C18	1.439(6)	C17-C16-C15	121.3(4)
C16-C17	1.377(6)	C16-C17-C12	119.7(4)
C18-C19	1.185(6)	C19-C18-C15	177.4(5)
C7-O2-C8	116.2(3)		
N1-N2-N3	169.5(6)		
N2-N3-C1	118.2(4)		
C11-N4-C10	122.2(3)		
C2-C1-N3	128.5(4)		
C6-C1-N3	115.6(4)		
C6-C1-C2	115.9(4)		
F1-C2-C1	119.2(4)		
F1-C2-C3	119.5(4)		
C3-C2-C1	121.3(4)		
F2-C3-C2	116.3(4)		

Table *S2-4*. Anisotropic displacement parameters ($Å^2x10^3$) for **1**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U^{11} + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F1	101(2)	62(2)	81(2)	8(1)	29(2)	5(1)
F2	108(2)	80(2)	55(2)	7(1)	28(1)	10(2)
F3	76(2)	66(2)	88(2)	10(1)	38(1)	2(1)
F4	80(2)	102(2)	52(2)	10(1)	22(1)	3(1)
O1	83(2)	77(2)	104(3)	-21(2)	56(2)	-20(2)
O2	64(2)	65(2)	66(2)	-17(1)	35(2)	-7(1)
O3	92(2)	77(2)	32(1)	5(1)	26(1)	14(2)
N1	162(6)	69(3)	131(5)	-26(3)	13(4)	-15(3)
N2	79(3)	84(3)	83(3)	-23(3)	12(2)	2(2)
N3	75(3)	73(3)	72(3)	-15(2)	22(2)	-8(2)
N4	57(2)	63(2)	23(2)	2(2)	16(1)	-1(2)
C1	48(2)	62(3)	60(3)	-5(2)	17(2)	8(2)
C2	55(2)	50(2)	71(3)	14(2)	24(2)	11(2)
C3	60(2)	71(3)	44(2)	1(2)	20(2)	13(2)
C4	46(2)	55(2)	63(3)	-5(2)	26(2)	6(2)
C5	43(2)	57(2)	66(3)	6(2)	27(2)	10(2)
C6	44(2)	71(3)	48(2)	1(2)	20(2)	6(2)
C7	56(2)	63(3)	71(3)	-7(2)	28(2)	0(2)
C8	57(2)	65(3)	71(3)	-18(2)	28(2)	-5(2)
C9	60(2)	73(3)	46(2)	-3(2)	11(2)	10(2)
C10	65(2)	61(2)	36(2)	2(2)	19(2)	-2(2)
C11	42(2)	68(2)	32(2)	4(2)	16(2)	-3(2)
C12	36(2)	65(2)	32(2)	-1(2)	14(1)	-4(2)
C13	46(2)	73(3)	39(2)	-1(2)	18(2)	1(2)
C14	48(2)	67(3)	46(2)	-3(2)	17(2)	3(2)
C15	40(2)	62(2)	58(2)	7(2)	18(2)	1(2)
C16	49(2)	73(3)	39(2)	10(2)	8(2)	2(2)
C17	47(2)	61(2)	39(2)	-2(2)	11(2)	0(2)
C18	50(2)	79(3)	57(2)	6(2)	21(2)	-1(2)
C19	78(3)	70(3)	64(3)	13(2)	21(2)	7(2)

Table *S2-5*. Hydrogen coordinates ($x10^4$) and isotropic displacement parameters ($Å^2$ $x10^3$) for **1**.

	x	y	z	U(eq)
H8A	3631	7327	12155	75
H8B	5635	7066	12981	75
H9A	3653	7142	14477	72
H9B	3799	6594	14145	72
H10A	571	6635	12522	64

H10B	507	6756	14046	64
H13	-720	8430	15013	62
H14	-1645	9199	14309	63
H16	-2630	8793	10303	65
H17	-1701	8017	11008	59
H19	-3411	10295	11177	85
H4	-140(60)	7392(14)	12040(40)	44(11)

Table *S2-6*. Torsion angles [deg] for **1**.

F1-C2-C3-F2	0.7(6)	C3-C4-C7-O2	-34.4(5)
F1-C2-C3-C4	-179.4(4)	C4-C5-C6-F4	179.0(3)
F2-C3-C4-C5	178.6(3)	C4-C5-C6-C1	-0.1(6)
F2-C3-C4-C7	-2.2(6)	C5-C4-C7-O1	-32.8(6)
F3-C5-C6-F4	0.5(5)	C5-C4-C7-O2	144.8(4)
F3-C5-C6-C1	-178.5(3)	C6-C1-C2-F1	-180.0(3)
O2-C8-C9-C10	-64.1(5)	C6-C1-C2-C3	-0.9(6)
O3-C11-C12-C13	7.9(5)	C7-O2-C8-C9	-178.5(4)
O3-C11-C12-C17	-175.8(3)	C7-C4-C5-F3	-0.3(5)
N1-N2-N3-C1	179(3)	C7-C4-C5-C6	-178.7(3)
N2-N3-C1-C2	-1.7(7)	C8-O2-C7-O1	-0.5(7)
N2-N3-C1-C6	-179.9(4)	C8-O2-C7-C4	-178.0(3)
N3-C1-C2-F1	1.8(6)	C8-C9-C10-N4	-64.3(5)
N3-C1-C2-C3	-179.1(4)	C10-N4-C11-O3	-3.8(5)
N3-C1-C6-F4	-0.4(5)	C10-N4-C11-C12	174.5(3)
N3-C1-C6-C5	178.6(4)	C11-N4-C10-C9	-83.1(4)
N4-C11-C12-C13	-170.4(3)	C11-C12-C13-C14	174.8(3)
N4-C11-C12-C17	5.9(5)	C11-C12-C17-C16	-174.6(3)
C1-C2-C3-F2	-178.3(3)	C12-C13-C14-C15	0.0(6)
C1-C2-C3-C4	1.5(6)	C13-C12-C17-C16	1.7(5)
C2-C1-C6-F4	-178.9(3)	C13-C14-C15-C16	1.6(5)
C2-C1-C6-C5	0.2(6)	C13-C14-C15-C18	-178.5(4)
C2-C3-C4-C5	-1.3(6)	C14-C15-C16-C17	-1.6(6)
C2-C3-C4-C7	178.0(4)	C15-C16-C17-C12	0.0(6)
C3-C4-C5-F3	179.0(3)	C17-C12-C13-C14	-1.7(5)
C3-C4-C5-C6	0.5(6)	C18-C15-C16-C17	178.5(4)
C3-C4-C7-O1	148.1(5)		

Table *S2-7*. Hydrogen bonds for **1** [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N4-H4...O3#1	0.74(4)	2.16(4)	2.869(4)	162(4)

Symmetry transformations used to generate equivalent atoms:
#1 x,-y+3/2,z-1/2

Reference:

[1] J. F. W. Keana and S. X. Cai, *J. Org. Chem.* 1990, **55**, 3640-3647.
[2] N.-H. Nguyen, J. W. Apriletti, J. D. Baxter and T. S. Scanlan, *J. Am. Chem. Soc.* 2005, **127**, 4599-4608.
[3] S. J. Pastine, D. Okawa, B. Kessler, M. Rolandi, M. Llorente and A. Zettl, J. M. Fréchet, *J. Am. Chem. Soc.* 2008, **130**, 4238-4239.