Supplementary Material For
Alkynyl-Zirconation of Alkynes and Application
to One-pot Bis-alkynylation of Alkynes

Yuanhong Liu, Zhenqi Zhong, Kiyohiko Nakajima,[†] Tamotsu Takahashi^{*}

Contents: Tables of crystallographic data, The X-ray crystal structure of compound **10** (Figure S1), atomic coordinates, thermal parameters and bond lengths and angles for **10**. NMR spectra of compounds **3a-3b**, **3d-3g**, **4-10**, **11b-11f**.

X-ray Crystallography of 10. A colorless prismatic crystal having approximate dimensions of 0.20 × 0.30 × 0.70 mm was mounted on a glass fiber. X-ray data were collected on a Rigaku AFC7S diffractometer with graphite-monochromated Cu $K\alpha$ radiation ($\lambda=1.54178$ Å). Data were processed by the PROCESS-AUTO program package. The linear absorption coefficient, μ , for Cu $K\alpha$ radiation was 6.96 cm⁻¹, and an empirical absorption correction based on azimuthal scans of several reflections was applied. The structure was solved by direct methods (SIR92¹) and expanded using Fourier techniques (DIRDIF94²). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at calculated positions but not refined. All calculations were performed using the teXsan³ crystallographic software package of Molecular Structure Corporation.

- 1) Altomare, A., Burla, M. C., Camalli, M., Cascarano, M., Giacovazzo, C., Guagliardi, A., Polidori, G., (1994). J. Appl. Cryst. 27, 435.
- 2) Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., de Gelder, R., Israel, R. and Smits, J. M. M. (1994). The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.
- 3) Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1999).

Crystallographic Data and Experimental Details of **10**

Compound	10
Formula	C ₃₀ H ₂₁ F ₃
<i>M</i>	438.49
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> , (Å)	11.115(2)
<i>b</i> , (Å)	12.946(3)
<i>c</i> , (Å)	9.819(2)
α , (°)	94.12(1)
β , (°)	110.78(1)
γ , (°)	110.13(1)
<i>V</i> , (Å ³)	1209.6(4)
<i>Z</i>	2
μ (Cu <i>K</i> α), (cm ⁻¹)	6.96
Transm factor	0.7747 – 0.9995
Crystal color	colorless
Crystal habit	prism
Crystal size, (mm ³)	0.20 × 0.30 × 0.70
<i>D</i> _{calcd} , (g cm ⁻³)	1.204
<i>F</i> (000)	456
Diffractometer	Rigaku AFC7S
λ (Cu <i>K</i> α), (Å)	1.54178
<i>T</i> , (K)	298
Scan range, (°)	1.79 + 0.30 tan θ
Scan mode	ω -2 θ
Scan speed, (° min ⁻¹)	6
2 θ _{max} , (°)	140.0
No. of reflections measd	4997 (Unique: 4556, <i>R</i> _{int} = 0.010)
No. of reflections obsd [<i>I</i> > 2 σ (<i>I</i>)]	3107
No. of parameters refined	325
<i>R</i>	0.044
<i>R</i> _w	0.059
<i>S</i> , goodness of fit	1.60
(Δ/δ) _{max}	0.000
Largest diff peak, (e Å ⁻³)	0.08
Largest diff hole, (e Å ⁻³)	-0.13

$$R = \sum ||Fo| - |Fc|| / \sum |Fo|, R_w = [\sum w(|Fo| - |Fc|)^2 / \sum w|Fo|^2]^{1/2}, w = [\sigma_c^2(F_o) + (p^2/4)|F_o|^2]^{-1}, p = 0.0500$$

$$S = [\sum w(|Fo| - |Fc|)^2 / (m - n)]^{1/2} \quad (m = \text{no. of used reflections}, n = \text{no. of refined parameters})$$

Figure S1, The X-ray crystal structure of compound **10**

Positional parameters and B(eq) of **10**

atom	x	y	z	B(eq)
F(1)	1.375(1)	0.9341(7)	1.032(1)	10.0(3)
F(2)	1.1864(10)	0.8904(9)	1.042(1)	11.7(3)
F(3)	1.354(1)	0.8834(9)	1.2191(10)	12.9(2)
F(4)	1.213(1)	0.9079(8)	1.005(1)	13.7(3)
F(5)	1.305(1)	0.8787(8)	1.211(1)	11.5(3)
F(6)	1.419(1)	0.9225(8)	1.082(2)	13.8(3)
C(1)	1.1018(2)	0.3959(1)	0.7895(2)	4.50(4)
C(2)	0.9806(2)	0.3544(1)	0.6646(2)	4.54(4)
C(3)	0.8996(2)	0.4211(2)	0.6241(2)	4.81(4)
C(4)	0.8304(2)	0.4764(2)	0.5944(2)	5.07(4)
C(5)	1.1586(2)	0.5167(1)	0.8669(2)	4.46(4)
C(6)	1.1844(2)	0.5469(2)	1.0158(2)	5.44(5)
C(7)	1.2277(2)	0.6580(2)	1.0836(2)	5.84(5)
C(8)	1.2504(2)	0.7414(2)	1.0047(2)	4.97(4)
C(9)	1.2288(2)	0.7131(2)	0.8575(2)	5.14(4)
C(10)	1.1836(2)	0.6017(2)	0.7895(2)	5.01(4)
C(11)	1.2949(3)	0.8618(2)	1.0756(3)	6.70(6)
C(12)	1.1797(2)	0.3272(1)	0.8589(2)	4.81(4)
C(13)	1.1110(2)	0.2200(2)	0.8756(2)	5.95(5)
C(14)	1.1864(3)	0.1580(2)	0.9420(3)	7.18(6)
C(15)	1.3284(3)	0.2004(2)	0.9913(3)	7.60(7)
C(16)	1.3980(2)	0.3059(2)	0.9761(3)	7.41(7)
C(17)	1.3249(2)	0.3696(2)	0.9119(2)	6.11(5)
C(18)	0.9203(2)	0.2419(1)	0.5623(2)	4.80(4)
C(19)	0.7773(2)	0.1770(2)	0.5069(2)	6.16(5)
C(20)	0.7190(3)	0.0740(2)	0.4097(3)	7.75(6)
C(21)	0.8018(4)	0.0351(2)	0.3641(3)	8.05(7)
C(22)	0.9421(3)	0.0988(2)	0.4158(3)	7.19(7)
C(23)	1.0020(2)	0.2016(2)	0.5149(2)	5.67(5)
C(24)	0.7605(2)	0.5521(2)	0.5697(2)	5.31(5)
C(25)	0.8053(3)	0.6454(2)	0.6803(3)	6.57(6)
C(26)	0.7400(3)	0.7202(2)	0.6580(4)	8.22(9)
C(27)	0.6288(3)	0.7026(3)	0.5250(4)	8.55(10)
C(28)	0.5860(3)	0.6105(3)	0.4158(4)	8.54(9)
C(29)	0.6482(2)	0.5346(2)	0.4351(3)	6.62(6)
C(30)	0.5590(4)	0.7861(4)	0.5047(6)	14.4(2)
H(1)	1.1720	0.4903	1.0720	6.5264
H(2)	1.2421	0.6771	1.1850	7.0110
H(3)	1.2451	0.7703	0.8028	6.1724
H(4)	1.1694	0.5829	0.6881	6.0088
H(5)	1.0119	0.1890	0.8414	7.1442
H(6)	1.1382	0.0849	0.9532	8.6200
H(7)	1.3790	0.1569	1.0360	9.1218
H(8)	1.4971	0.3356	1.0099	8.8915
H(9)	1.3746	0.4434	0.9040	7.3349
H(10)	0.7190	0.2041	0.5366	7.3909
H(11)	0.6213	0.0298	0.3740	9.3000

H(12)	0.7617	-0.0360	0.2968	9.6637
H(13)	0.9991	0.0721	0.3833	8.6231
H(14)	1.1000	0.2449	0.5506	6.8062
H(15)	0.8816	0.6585	0.7725	7.8787
H(16)	0.7720	0.7842	0.7351	9.8684
H(17)	0.5106	0.5986	0.3232	10.2437
H(18)	0.6151	0.4706	0.3575	7.9403
H(19)	0.6264	0.8591	0.5165	17.2345
H(20)	0.4859	0.7637	0.4075	17.2345
H(21)	0.5212	0.7878	0.5773	17.2345

Anisotropic Displacement Parameters of **10**

atom	U11	U22	U33	U12	U13	U23
F(1)	0.171(10)	0.056(3)	0.176(7)	0.020(5)	0.118(7)	0.030(4)
F(2)	0.130(5)	0.085(4)	0.26(1)	0.059(3)	0.102(7)	0.018(5)
F(3)	0.231(8)	0.079(4)	0.084(5)	0.024(4)	0.001(5)	-0.017(3)
F(4)	0.24(1)	0.082(4)	0.144(4)	0.092(7)	-0.006(6)	0.009(3)
F(5)	0.28(1)	0.083(4)	0.125(7)	0.081(5)	0.138(8)	0.024(4)
F(6)	0.135(6)	0.088(6)	0.24(1)	-0.034(4)	0.093(7)	-0.053(6)
C(1)	0.060(1)	0.0532(9)	0.0590(10)	0.0254(8)	0.0226(8)	0.0136(8)
C(2)	0.060(1)	0.0585(10)	0.0581(10)	0.0277(8)	0.0241(9)	0.0152(8)
C(3)	0.062(1)	0.065(1)	0.055(1)	0.0277(9)	0.0198(8)	0.0131(8)
C(4)	0.067(1)	0.071(1)	0.061(1)	0.0335(10)	0.0258(9)	0.0214(9)
C(5)	0.058(1)	0.0559(10)	0.0554(10)	0.0264(8)	0.0179(8)	0.0153(8)
C(6)	0.086(1)	0.058(1)	0.057(1)	0.0238(10)	0.0267(10)	0.0198(9)
C(7)	0.094(2)	0.064(1)	0.055(1)	0.022(1)	0.030(1)	0.0096(9)
C(8)	0.063(1)	0.056(1)	0.066(1)	0.0214(9)	0.0237(9)	0.0114(9)
C(9)	0.074(1)	0.056(1)	0.064(1)	0.0257(9)	0.0262(9)	0.0214(9)
C(10)	0.074(1)	0.063(1)	0.0541(10)	0.0295(9)	0.0243(9)	0.0168(8)
C(11)	0.099(2)	0.061(1)	0.085(2)	0.024(1)	0.035(1)	0.012(1)
C(12)	0.067(1)	0.057(1)	0.0576(10)	0.0295(9)	0.0194(9)	0.0128(8)
C(13)	0.083(1)	0.065(1)	0.076(1)	0.031(1)	0.027(1)	0.022(1)
C(14)	0.118(2)	0.066(1)	0.091(2)	0.046(1)	0.035(1)	0.029(1)
C(15)	0.116(2)	0.086(2)	0.091(2)	0.067(2)	0.021(1)	0.021(1)
C(16)	0.079(2)	0.089(2)	0.109(2)	0.050(1)	0.018(1)	0.019(1)
C(17)	0.068(1)	0.069(1)	0.088(1)	0.031(1)	0.020(1)	0.017(1)
C(18)	0.063(1)	0.059(1)	0.059(1)	0.0251(9)	0.0221(9)	0.0139(8)
C(19)	0.069(1)	0.076(1)	0.076(1)	0.023(1)	0.023(1)	0.005(1)
C(20)	0.085(2)	0.076(2)	0.097(2)	0.009(1)	0.022(1)	0.000(1)
C(21)	0.127(2)	0.066(1)	0.089(2)	0.026(2)	0.033(2)	-0.004(1)
C(22)	0.116(2)	0.074(1)	0.091(2)	0.044(1)	0.047(2)	0.008(1)
C(23)	0.078(1)	0.068(1)	0.073(1)	0.032(1)	0.032(1)	0.0122(10)
C(24)	0.069(1)	0.081(1)	0.073(1)	0.041(1)	0.038(1)	0.036(1)
C(25)	0.101(2)	0.086(1)	0.086(1)	0.053(1)	0.046(1)	0.031(1)
C(26)	0.130(2)	0.098(2)	0.137(2)	0.070(2)	0.084(2)	0.048(2)
C(27)	0.108(2)	0.122(2)	0.165(3)	0.082(2)	0.088(2)	0.084(2)

C(28)	0.080(2)	0.150(3)	0.131(2)	0.071(2)	0.050(2)	0.080(2)
C(29)	0.071(1)	0.108(2)	0.086(1)	0.047(1)	0.032(1)	0.042(1)
C(30)	0.169(3)	0.186(4)	0.310(6)	0.144(3)	0.143(4)	0.140(4)

Intramolecular Distances Involving the Nonhydrogen Atoms of **10**

F(1) -C(11)	1.269(9)	C(12)-C(13)	1.389(3)
F(2) -C(11)	1.321(9)	C(12)-C(17)	1.389(3)
F(3) -C(11)	1.287(9)	C(13)-C(14)	1.387(3)
F(4) -C(11)	1.286(9)	C(14)-C(15)	1.360(4)
F(5) -C(11)	1.292(8)	C(15)-C(16)	1.367(3)
F(6) -C(11)	1.31(1)	C(16)-C(17)	1.383(3)
C(1) -C(2)	1.357(2)	C(18)-C(19)	1.389(3)
C(1) -C(5)	1.494(2)	C(18)-C(23)	1.380(3)
C(1) -C(12)	1.483(2)	C(19)-C(20)	1.376(3)
C(2) -C(3)	1.430(2)	C(20)-C(21)	1.372(4)
C(2) -C(18)	1.490(3)	C(21)-C(22)	1.364(4)
C(3) -C(4)	1.200(2)	C(22)-C(23)	1.381(3)
C(4) -C(24)	1.430(3)	C(24)-C(25)	1.379(3)
C(5) -C(6)	1.384(2)	C(24)-C(29)	1.396(3)
C(5) -C(10)	1.388(2)	C(25)-C(26)	1.382(3)
C(6) -C(7)	1.379(3)	C(26)-C(27)	1.380(4)
C(7) -C(8)	1.379(3)	C(27)-C(28)	1.364(4)
C(8) -C(9)	1.378(3)	C(27)-C(30)	1.519(4)
C(8) -C(11)	1.492(3)	C(28)-C(29)	1.371(4)
C(9) -C(10)	1.379(3)		

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms of **10**

C(2) -C(1) -C(5)	118.8(2)	F(5) -C(11)-C(8)	114.7(5)
C(2) -C(1) -C(12)	124.0(2)	F(6) -C(11)-C(8)	110.3(6)
C(5) -C(1) -C(12)	117.2(1)	C(1) -C(12)-C(13)	121.6(2)
C(1) -C(2) -C(3)	119.3(2)	C(1) -C(12)-C(17)	120.6(2)
C(1) -C(2) -C(18)	125.7(2)	C(13)-C(12)-C(17)	117.8(2)
C(3) -C(2) -C(18)	115.0(2)	C(12)-C(13)-C(14)	120.4(2)
C(2) -C(3) -C(4)	177.6(2)	C(13)-C(14)-C(15)	120.9(2)
C(3) -C(4) -C(24)	174.1(2)	C(14)-C(15)-C(16)	119.6(2)
C(1) -C(5) -C(6)	121.3(2)	C(15)-C(16)-C(17)	120.4(2)
C(1) -C(5) -C(10)	120.4(2)	C(12)-C(17)-C(16)	120.9(2)
C(6) -C(5) -C(10)	118.2(2)	C(2) -C(18)-C(19)	119.9(2)
C(5) -C(6) -C(7)	120.9(2)	C(2) -C(18)-C(23)	121.6(2)
C(6) -C(7) -C(8)	120.2(2)	C(19)-C(18)-C(23)	118.4(2)
C(7) -C(8) -C(9)	119.6(2)	C(18)-C(19)-C(20)	120.8(2)

C(7) -C(8) -C(11)	120.9(2)	C(19)-C(20)-C(21)	120.0(2)
C(9) -C(8) -C(11)	119.5(2)	C(20)-C(21)-C(22)	119.7(2)
C(8) -C(9) -C(10)	120.0(2)	C(21)-C(22)-C(23)	120.8(2)
C(5) -C(10)-C(9)	121.0(2)	C(18)-C(23)-C(22)	120.3(2)
F(1) -C(11)-F(2)	102.3(7)	C(4) -C(24)-C(25)	119.7(2)
F(1) -C(11)-F(3)	107.3(8)	C(4) -C(24)-C(29)	121.6(2)
F(1) -C(11)-C(8)	115.7(5)	C(25)-C(24)-C(29)	118.7(2)
F(2) -C(11)-F(3)	106.2(7)	C(24)-C(25)-C(26)	120.6(2)
F(2) -C(11)-C(8)	111.1(5)	C(25)-C(26)-C(27)	120.6(3)
F(3) -C(11)-C(8)	113.3(5)	C(26)-C(27)-C(28)	118.4(2)
F(4) -C(11)-F(5)	105.4(7)	C(26)-C(27)-C(30)	119.2(4)
F(4) -C(11)-F(6)	106.1(7)	C(28)-C(27)-C(30)	122.4(4)
F(4) -C(11)-C(8)	113.8(5)	C(27)-C(28)-C(29)	122.2(3)
F(5) -C(11)-F(6)	105.8(8)		

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parenthese