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of Organic Compounds

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In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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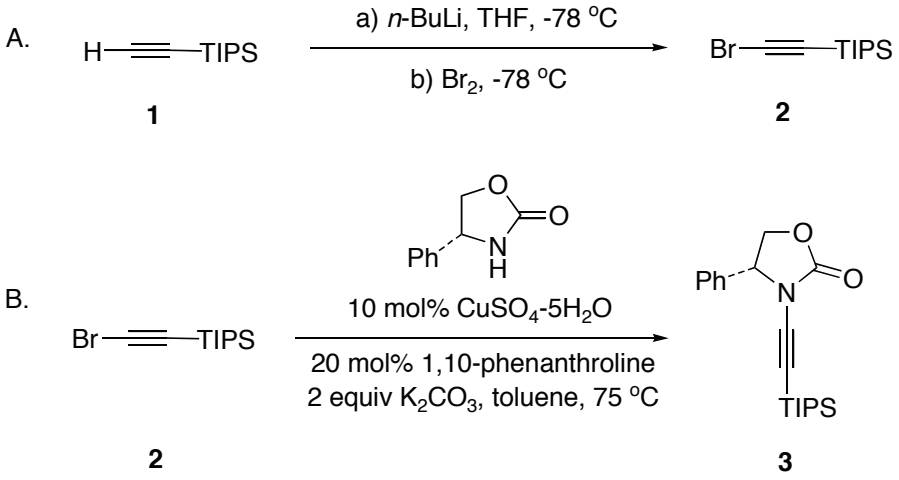
PRACTICAL SYNTHESIS OF A CHIRAL YNAMIDE: (*R*)-4-PHENYL-3-(2-TRIISOPROPYLSILYL-ETHYNYL)OXAZOLIDIN-2-ONE

[2-Oxazolidinone, 4-Phenyl-3-(2-triisopropylsilyl-ethynyl)-, (4*R*)-]



Submitted by I. K. Sagamanova, K. C. M. Kurtz, and R. P. Hsung.[1]
Checked by Karen M. Marcantonio and David J. Mathre.

1. Procedures

*A. 1-Bromo-2-triisopropylsilyl-ethyne (**2**).* To a flame-dried single-necked 1-L round-bottomed flask equipped with a magnetic stir bar is added a solution of triisopropylsilylacetylene (22.0 g, 120.6 mmol) (Note 1) in anhydrous THF (500 mL) (Note 2). The solution is cooled to – 78 °C, and *n*-BuLi (50.7 mL, 126.7 mmol, 1.05 equiv) (Note 3) is added by syringe through the septum. The reaction is stirred for 30 min at – 78 °C, and Br_2 (6.80 mL, 132.7 mmol, 1.10 equiv) (Note 4) is added slowly through the septum using a syringe. The reddish brown color from Br_2 disappears as it is consumed upon addition. The solution remains reddish brown when the addition is complete. The mixture is stirred for 15 min at –78 °C and then quenched by addition of saturated aqueous $Na_2S_2O_3$ (150 mL) after removal of the septum. The reaction mixture is transferred to a separatory funnel and the layers separated. The aqueous layer is further extracted with methyl *tert*-butyl ether (MTBE) (3 × 50 mL), and the combined organic extracts are washed with saturated aqueous NaCl (50 mL), dried over Na_2SO_4, filtered and concentrated on a rotary evaporator (20 – 30 mmHg, 50 °C) to yield the

crude alkynyl bromide **2** (30.22–30.24 g, 96%) as a pale yellow oil (Note 5). Alkynyl bromide **2** is used without further purification (Note 6).

*B. (R)-4-Phenyl-3-(2-triisopropylsilyl-ethynyl)oxazolidin-2-one (**3**).* To a solution of 1-bromo-2-triisopropylsilylacetylene (**2**) (28.19 g, 107.9 mmol) (Note 7) in freshly distilled anhydrous toluene (100 mL) (Note 2) in a 250-mL, single-necked, round-bottomed flask fitted with a magnet stir bar are added *R*-phenyloxazolidinone (17.60 g, 107.9 mmol, 1.00 equiv) (Note 8), K_2CO_3 (29.81 g, 215.7 mmol, 2.00 equiv) (Note 9), $CuSO_4 \bullet 5H_2O$ (2.69 g, 10.8 mmol, 0.10 equiv) (Note 10), and 1,10-phenanthroline (3.89 g, 21.6 mmol, 0.20 equiv) (Note 11). The flask is fitted with a reflux condenser topped with a septum and N_2 inlet, and heated in an oil bath at 75 °C (bath temperature) for 48 h. The reaction is monitored using TLC analysis (Note 12). Upon completion, the reaction mixture is cooled to room temperature and filtered through a 200-mL coarse-fritted vacuum filtration funnel containing a 5-cm layer of silica gel covered with a 1-cm layer of Celite. The mixture is washed through with 50% EtOAc/hexanes (400 mL), and the filtrate is concentrated on a rotary evaporator (20 – 30 mmHg, 70 °C). The crude residue is purified using silica gel column flash chromatography (Note 13) to give ynamide **3** (29.5–32.7 g, 81–88%) (Notes 14 and 15) as a yellow oil.

2. Notes

1. Triisopropylacetylene (97%) was purchased from GFS Chemicals.

2. Anhydrous solvents were obtained from an MBraun solvent purification system. Unstabilized THF was purchased from JT Baker, and toluene was purchased from Aldrich.

3. *N*-Butyllithium (2.5 *M* solution in hexanes) was purchased from Aldrich Chemical Co.

4. Bromine (99+%) was purchased from Fisher Scientific.

5. Characterization of **2**: R_f = 0.72 [25% EtOAc in hexanes]; yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.06–1.10 (m, 21 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.2, 18.4, 61.6, 83.4.

6. This purification step was not necessary, because, in most cases, high purity was obtained judging from ^{1}H NMR. However, product **2** was stable to silica gel column flash chromatography and could be eluted with

hexanes. Other alkynyl bromides may require silica gel column flash chromatography for purification.

7. The amidation reaction was performed successfully on a variety of scales [see Discussion section].

8. *R*-Phenyloxazolidinone (98%) was purchased from Aldrich and used as received.

9. Potassium carbonate (98%; ~ 325 mesh powder) was purchased from Aldrich.

10. $CuSO_4 \bullet 5H_2O$ (99.3%) was purchased from J. T. Baker. The solid was ground into a powder with a mortar and pestle before use.

11. 1,10-Phenanthroline (99+%) was purchased from Aldrich. The solid was ground into a powder with a mortar and pestle before use.

12. TLC analysis (25% EtOAc/hexanes): R_f(oxazolidinone) = 0.03, R_f(**2**) = 0.72, R_f(**3**) = 0.39.

13. The crude product was dissolved in 200 mL of CH_2Cl_2 in a round-bottomed-flask, and 75 g silica gel was added to the flask. The CH_2Cl_2 was removed on a rotary evaporator (20–30 mmHg, 35 °C) equipped with a bump trap. The dried contents of the flask were loaded onto the column (size $l \times d$ = 30 cm × 5 cm) containing a slurry of silica gel and hexanes layered with sand. Gradient elution [EtOAc in hexanes]: 800 mL 0%, 800 mL 2%, 1000 mL 5%, 1500 mL 7%, 2000 mL 10%.

14. GC analysis of ynamide **3** shows its purity to be ≥98.0%.

15. Characterization of **3**: R_f = 0.39 [25% EtOAc in hexanes]; clear oil; $[\alpha]_D^{23}$ – 133.7 (c 1.21, CH_2Cl_2); Chiralcel OD-H (250 x 4.6 mm), 5% IPA/heptane, 1.0 mL/min, 215 nm, t_R (*R*) 10.77 min, t_R (*S*) 13.66 min: >99.5 % ee R. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.90–0.93 (m, 21 H), 4.28 (dd, 1 H, *J* = 7.6, 8.8 Hz), 4.73 (t, 1 H, *J* = 8.8 Hz), 5.06 (dd, 1 H, *J* = 7.6, 8.8 Hz), 7.34–7.45 (m, 5 H);^{13}C NMR (75 MHz, $CDCl_3$) δ: 11.0, 18.3, 62.2, 70.4, 71.9, 91.8, 127.1, 129.1, 129.4, 135.7, 155.2; IR (thin film) cm^{-1} 2943 (m), 2185 (w), 1782 (s), 1394 (m), 883 (m); mass spectrum (APCI): *m/z* (% relative intensity) 344 (13) $(M + H)^+$, 334 (33), 318 (100); *m/z* calcd for $C_{20}H_{29}NO_2Si$ 344.2040, found 344.2047

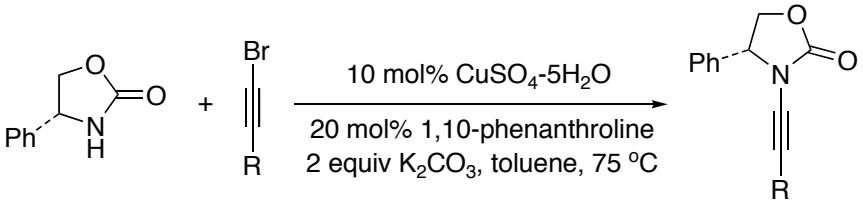
Safety and Waste Disposal Information

All hazardous materials should be handled and disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

3. Discussion

It is noteworthy that this cooper-catalyzed amidation of alkynyl bromide can be carried out with scales ranging from 48 to 107 mmol. The respective ynamide products were isolated with yields ranging from 86–89%.

Table 1

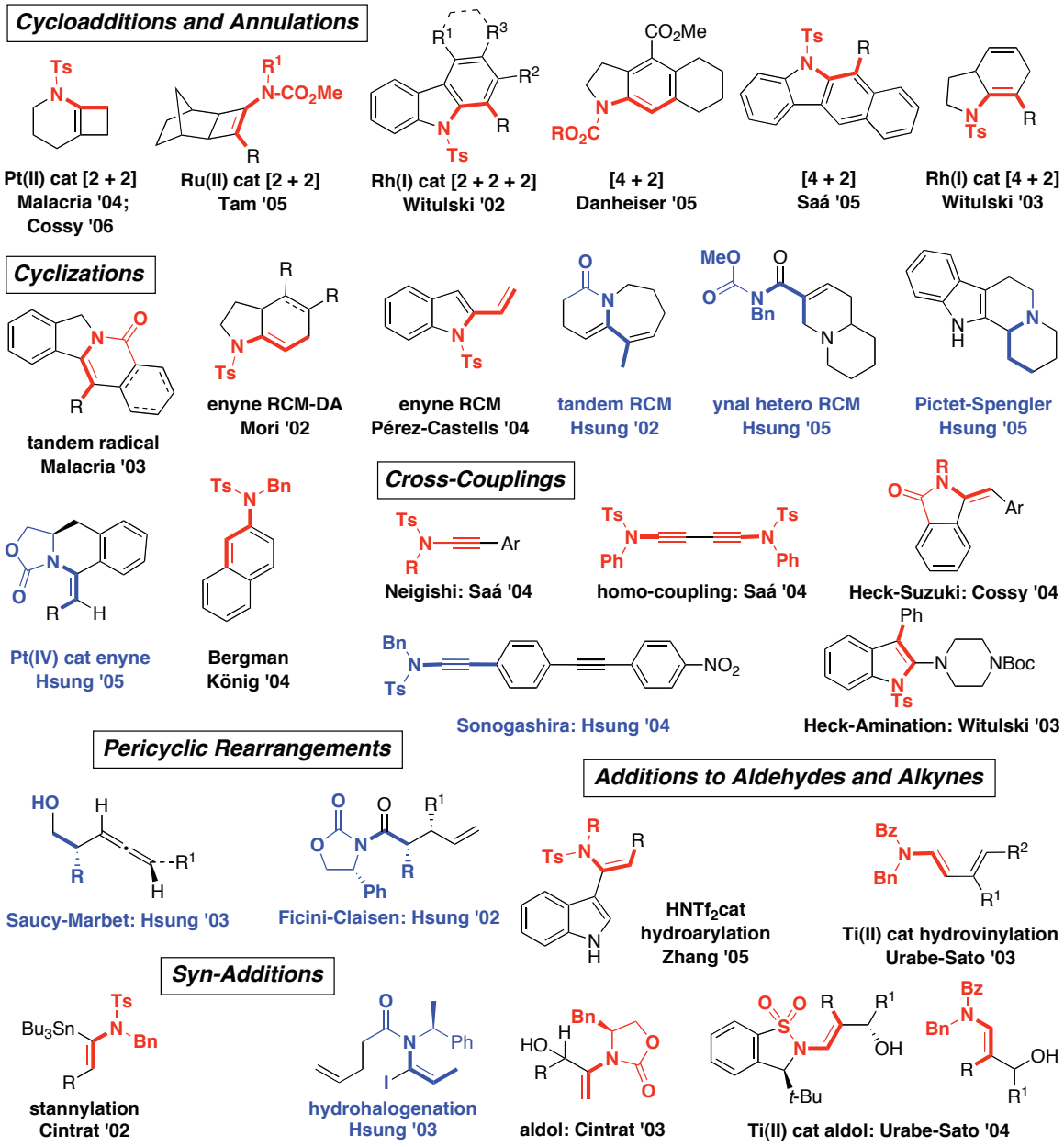


halide	R =	scale [mmols]	product	isolated yield [%, g]
2a	TIPS	48	**3a**	89 [14.63 g]
	TIPS	107		86 [32.07 g]
2b	Ph	18	**3b**	60 [4.66 g]
	Ph	35		71 [6.72 g]

The level of purity of the ynamides prepared using this procedure can be unambiguously established using GC/HPLC analysis for ynamide **3**. The level of optical purity of the product is dependent upon the optical purity of the chiral auxiliaries acquired from commercial sources. The $[\alpha]_D^{20}$ value for the commercial (*R*)-2-phenyloxazolidinone used in this preparation was –52.3 [c 2.0, $CHCl_3$]. The $[\alpha]_D^{20}$ values reported by Aldrich for (*R*)-2-phenyloxazolidinone and (*S*)-2-phenyloxazolidinone are –48.0 [c 2.0, $CHCl_3$], which indicates that the *ee* or optical integrity of the Evans' auxiliary used for this work was very high. Severe erosion of the auxiliary's *ee* is unlikely under the amidation conditions described herein. The anticipated high *ee* of chiral ynamide (*R*)-**3** was confirmed by chiral HPLC.

Ynamides[2-9] have become a highly attractive building block for developing synthetic methodologies.[10-11] As illustrated in Figure 1, there have been at least 30 reports in the last few years describing dozens of different strategies employing ynamides. Particularly attractive are those in

which the nitrogen atom of ynamides becomes an integral part of various products that possess potential in alkaloid synthesis. These efforts demonstrate that there can be a distinct advantage in utilizing ynamides over simple alkynes. Therefore, the key issue, in part being addressed in this *Organic Syntheses* procedure, is their preparation. We, as well as others, have exerted much effort toward this goal.[3-9]



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5. For some examples of alkynyl iodonium triflate salts, see: (a) Feldman, K. S.; Bruendl, M. M.; Schildknegt, K.; Bohnstedt, A. C. *J. Org. Chem.* **1996**, *61*, 5440. (b) Witulski, B.; Stengel, T. *Angew. Chem. Int. Ed.* **1998**, *37*, 489. (c) Witulski, B.; Stengel, T.; Fernàndez-Hernàndez, J. M. *Chem. Commun*. **2000**, 1965. (d) Witulski, B.; Buschmann, N.; Bergsträßer, U. *Tetrahedron* **2000**, *56*, 8473. (e) Rainier, J. D.; Imbriglio, J. E. *J. Org. Chem.* **2000**, *65*, 7272. (f) Brückner, D. *Synlett* **2000**,1402. (g) Fromont, C.; Masson, S. *Tetrahedron* **1999**, *55*, 5405.

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9. Also see: Couty, S.; Barbazanges, M.; Meyer, C.; Cossy, J. *Synlett* **2005**, 906.

10. For an impressive array of reports on the chemistry of ynamides just in the last three years, see: (a) For a special issue dedicated to the chemistry of ynamides, see: *Tetrahedron-Symposium-In-Print:* "Chemistry of Electron-Deficient Ynamines and Ynamides." *Tetrahedron* **2006**, *62*, Issue No.16. (b) Tanaka, K.; Takeishi, K.;

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Appendix
Chemical Abstracts Nomenclature; (Registry Number)

n-Butyllithium: Butyllithium; (109-72-8)
Triisopropylsilylacetylene: Silane, ethynyltris(1-methylethyl)-; (89343-06-6)
Copper sulfate pentahydrate; (7758-99-8)
1-Bromo-2-triisopropylsilyl-ethyne: Silane, (bromoethynyl)tris(1-methylethyl)-; (111409-79-1)
R-Phenyloxazolidinone: (4*R*)-4-Phenyl-2-Oxazolidinone; (90319-52-1)
1,10-Phenanthroline; (66-71-7)

Richard P. Hsung was born in China in 1966. After growing up in New York City and Boston, he obtained his B.S. in Chemistry and Mathematics in 1988 from Calvin College. He attended The University of Chicago and received his Ph.D. degree in Organic Chemistry in 1994, under the supervision of Professors Jeff Winkler and Bill Wulff. He completed his training as an NIH post-doctoral fellow in Professor Gilbert Stork's laboratory at Columbia University. In 1997, he began his academic career at the University of Minnesota, moving to University of Wisconsin at Madison in 2006. He is a recipient of numerous awards including the Camille Dreyfus Teacher-Scholar Award and National Science Foundation Career Award. His current research focuses on the development of cycloaddition and annulation strategies to natural product syntheses.

Irina K. Sagamanova was born in Noyabrsk, Russia, in 1985, and received a B.S. in Chemistry from The Higher Chemical College Russia Academy of Science in Moscow in 2006. She went to University of Minnesota and worked in Professor Richard P. Hsung's research group during the summer of 2005. Her research involves improving synthesis of chiral ynamides and exploring their reactivities.

Kimberly C. M. Kurtz was born in Findlay, OH, in 1979, and received a B.S. in Chemistry from Ohio Northern University, Ada, OH in 2001. Her father, David Kurtz, was a long time Organic Chemistry faculty at ONU. She enrolled at University of Minnesota-Twin Cities and worked in Professor Richard P. Hsung's laboratory. Her research involved improving synthesis of chiral ynamides and exploring their reactivity in various pericyclic and ring-closing reactions. In 2006, she obtained her Ph.D. in Organic Chemistry, and is currently a senior scientist in the Corporate Research Laboratory at 3M in Saint Paul, MN.

Karen Marcantonio was born and raised in Cranston, RI. She earned her BS in chemistry in 1997 at Connecticut College, doing research under Dr. Timo Ovaska and Dr. Bruce Branchini. After a summer internship at Pfizer, she began graduate school at UPenn, earning her masters from Marisa Kozlowski in 1999. She has been working in Merck Process Research since November 1999.

TIPS-alkyne-Br

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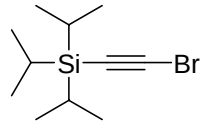

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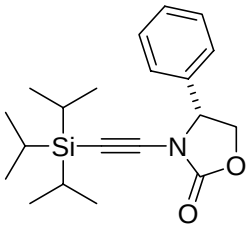

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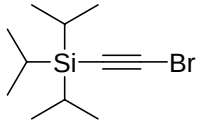
GB                    0
PC                 1.00
```

TIPS-alkyne-Br



```
Current Data Parameters
NAME        67605-285-3
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20060307
Time              11.07
INSTRUM           spect
PROBHD   5 mm QNP  1H/1
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   28
DS                    2
SWH            6561.680 Hz
FIDRES         0.200247 Hz
AQ            2.4969716 sec
RG                101.6
DW               76.200 usec
DE                 6.00 usec
TE                300.2 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                10.00 usec
PL1               -5.00 dB
SFO1        400.1322007 MHz

F2 - Processing parameters
SI                16384
SF          400.1300050 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00
```

step 2 1H NMR