Tetrahedron 66 (2010) 6026–6031

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Rhodium-catalyzed carbometalation of ynamides with organoboron reagents

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ARTICLE INFO

Article history:
Received 12 April 2010
Accepted 7 June 2010
Available online 12 June 2010

ABSTRACT

In the presence of catalytic [Rh(cod)(MeCN)$_2$]BF$_4$, ynamides undergo carbometalation with boronic acids, arylboronic esters, and triarylboroxines. These reactions enable the regio- and stereocontrolled synthesis of multisubstituted enamides.

1. Introduction

As a result of the increasing interest in the chemistry of enamides,[1] we recently initiated a program to address limitations associated with the synthesis of more highly substituted congeners.[2] These studies resulted in the development of rhodium-catalyzed carbozincations of ynamides[3] using organozinc reagents.[2] Virtues of these processes include the preparation of β,β′-disubstituted and α,β,β′-trisubstituted enamides with high levels of regio- and stereocontrol, and the ability to employ organozinc halides containing moderately base- and nucleophile-sensitive functional groups.[4]

To increase the range of enamides accessible through ynamide carbometalation reactions further, we became interested in the development of new catalytic protocols employing organometallics that exhibit even greater functional group compatibility. Boronic acids, boronic esters, and boroxines are attractive candidates, given their ready availability and high stability to air and moisture.[5] In this regard, metal-catalyzed hydroarylations of alkynes using arylboron compounds have been studied in some depth.[6–11] With unsymmetrical alkynes, control of regioselectivity is one of the principal challenges, and high regioselectivities are typically observed when there are substantial differences in the steric and/or electronic properties between the two substituents attached to the alkyne. The use of a directing group in the substrate[7b,c,8c,12] is another tactic to control regioselectivity, and it was our hope that the directing effect of the carbonyl group of ynamides as proposed in previous ynamide carbometalation procedures[2,4] could also be beneficial in carbometalation reactions involving organoboron reagents. To our knowledge, the simple carbometalation of ynamides using organoboron compounds has not been described previously, despite the potential utility of such a process for preparing multisubstituted enamides.[13] In this article, the successful implementation of this strategy is described.

2. Results and discussion

Reactions between oxazolidin-2-one-substituted ynamides and arylboronic acids were used to evaluate various metal precatalysts and reaction conditions. These experiments led to the finding that heating a mixture of ynamide, arylboronic acid (2.0 equiv), and [Rh(cod)(MeCN)$_2$]BF$_4$ (8 mol %) in 20:1 THF/H$_2$O for 10 min at 90 °C under microwave irradiation was effective in promoting carbometalation.[14] Representative results using these conditions are presented in Table 1.

In addition to phenylboronic acid, which resulted in enamides **2a**, **2e**, and **2h**, the process tolerated arylboronic acids containing electron-donating (products **2b** and **2c**) or electron-withdrawing substituents (products **2f**, **2g**, **2i**, and **2l**). Sterically hindering *ortho*-substitution on the arylboronic acid was also tolerated, though yields were slightly diminished (products **2d** and **2j**). The sense of regioselection observed in these reactions was as expected, with the aryl group introduced distal to the ynamide nitrogen atom in regioisomeric ratios ranging from modest (6:1 rr) to high (>19:1). Regarding the scope of the ynamide, oxazolidin-2-one-containing substrates with aliphatic or aromatic substituents underwent the reaction with comparable efficiency, though with **1a**, small quantities of the imide **3a** (Fig. 1) resulting from hydration of the ynamide were sometimes observed (with products **2a**, **2b**, and **2d**).

Pyrrolidin-2-one-containing ynamides, such as **1d** proved to be inferior to oxazolidin-2-one-substituted ynamides **1a–c**, which was surprising in light of related Rh-catalyzed ynamide carbozincations.[2] For example, carbometalation of **1d** with 4-acetylphenylboronic acid produced a complex mixture of products from which **2l** was isolated in only 25% yield. Acyclic ynamides, such as **1e** were not effective substrates; although carbometalation was successful, regioselectivity was negligible. Similar behavior has

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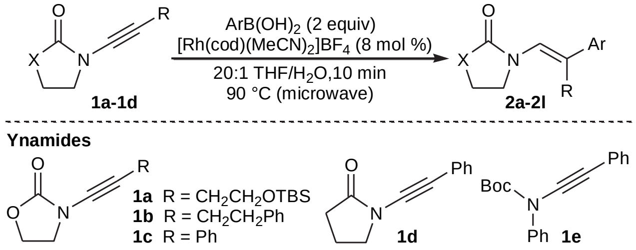
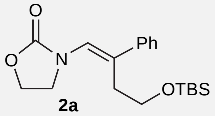
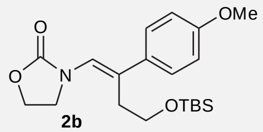
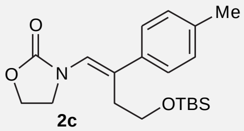
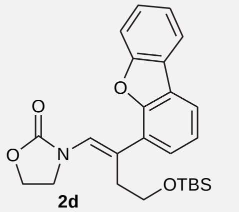
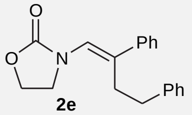
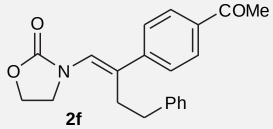
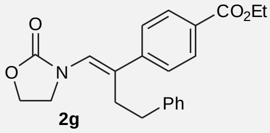
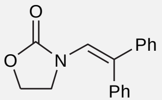
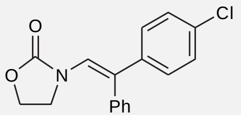
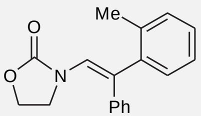
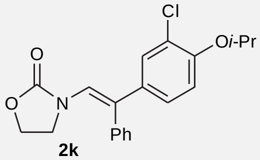
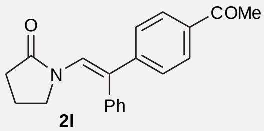
doi:10.1016/j.tet.2010.06.021

Table 1
Rhodium-catalyzed carbometalation of ynamides with arylboronic acids[a]



 **2a** >19:1 rr, 63%[b]	 **2b** >19:1 rr, 75%[c]
 **2c** 14:1 rr, 61%	 **2d** 8:1 rr, 46%[d]
 **2e** 10:1 rr, 89%	 **2f** 6:1 rr, 60%
 **2g** 7:1 rr, 56%	 **2h** 67%[e]
 **2i** 65%[e]	 **2j** 10:1 rr, 53%
 **2k** >19:1 rr, 82%	 **2l** 25%[e]

[a] rr=Regioisomeric ratio as determined by ^{1}H NMR analysis of the unpurified reaction mixtures. Unless otherwise indicated, cited yields are of isolated major regioisomers.

[b] Isolated as an 8:1 inseparable mixture of **2a** and the imide **3a** (Fig. 1). Cited yield of **2a** has been adjusted to reflect this impurity.

[c] Isolated as a 16:1 inseparable mixture of **2b** and the imide **3a** (Fig. 1). Cited yield of **2b** has been adjusted to reflect this impurity.

[d] Isolated as a 13:1 inseparable mixture of **2d** and the imide **3a** (Fig. 1). Cited yield of **2d** has been adjusted to reflect this impurity.

[e] The regioisomeric ratio could not be determined with accuracy.

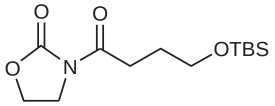
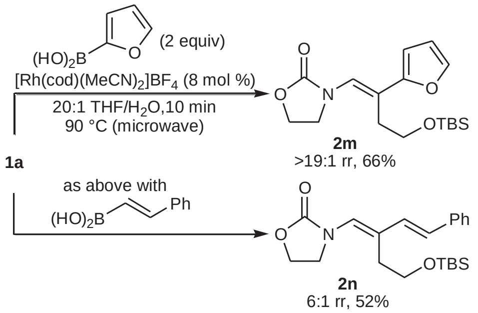

3a

Figure 1. Side-product resulting from hydration of ynamide **1a**.

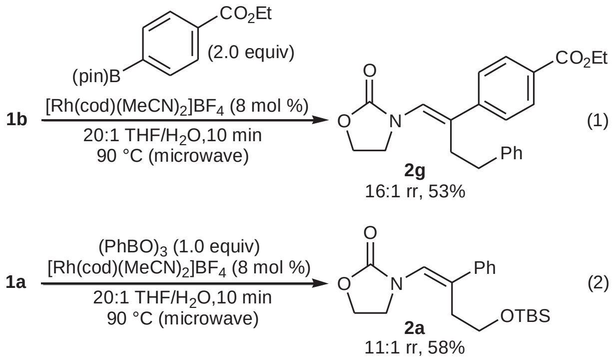
been documented previously in related rhodium-catalyzed carbozincations of ynamides.[2]

Boronic acids containing non-benzene groups are also viable reagents in this process. For example, carbometalation of ynamide **1a** with 2-furanboronic acid proceeded smoothly to give enamide **2m** as the only observable regioisomer in 66% yield (Scheme 1), while the use of (*E*)-2-phenylvinylboronic acid gave dienamide **2n** in 52% yield.



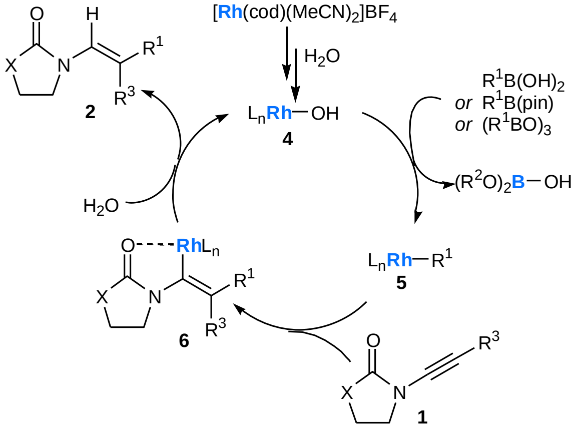
Scheme 1. Rhodium-catalyzed ynamide carbometalation with heteroaryl and alkenylboronic acids. rr=Regioisomeric ratio as determined by ^{1}H NMR analysis of the unpurified reaction mixtures. Cited yields are of isolated major regioisomers.

Next, the use of organoboron reagents other than boronic acids was explored. Pleasingly, arylboronic esters and triarylboroxines were found to be competent arylating reagents under conditions identical to those employed using arylboronic acids, as demonstrated by the formation of enamides **2g** and **2a**. (Scheme 2, Eq. 1 and 2, respectively, compare with results in Table 1). However, attempted carbometalation of ynamide **1a** with potassium phenyltrifluoroborate was unrewarding, providing a complex mixture of products.[15]



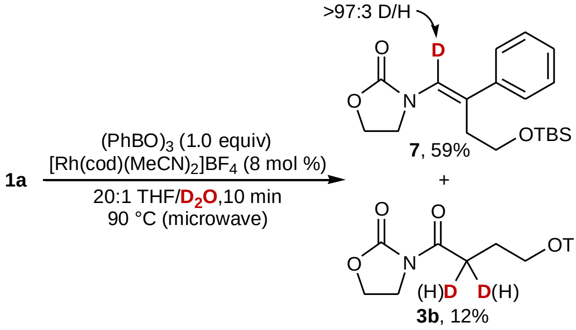
Scheme 2. Rhodium-catalyzed ynamide carbometalation with an arylboronic ester and triphenylboroxine. rr=Regioisomeric ratio as determined by ^{1}H NMR analysis of the unpurified reaction mixtures. Cited yields are of isolated major regioisomers.

By analogy with related processes,[7] a possible catalytic cycle for these reactions is illustrated in Scheme 3. Presumably, a rhodium(I) hydroxide species **4** is generated under the reaction conditions, which can undergo transmetalation with the organoboron compound to provide organorhodium intermediate **5**. A carbonyl-directed[12] *syn*-carborhodation of **5** with the ynamide **1** would then result in chelated alkenylrhodium species **6**. Finally, protonation of **6** with water would release the product **2** and regenerate **4**.



Scheme 3. Possible catalytic cycle.

In seminal work by Hayashi and co-workers describing related alkyne hydroarylations,[7a] alkenylrhodium intermediates analogous to **6** were found to undergo 1,4-rhodium migration[16] from the alkenyl position to an *ortho*-position of the phenyl group, as suggested by deuterium labeling studies. To establish whether this pathway is significant in the reactions described herein, carbometalation of ynamide **1a** with triphenylboroxine was conducted in 20:1 THF/D_2O (Eq. 3). In addition to providing a small quantity of the imide **3b** (mixture of isotopologues) resulting from hydration of **1a**, this experiment provided enamide **7** with >97% deuterium incorporation at the alkenyl position.[17] This result suggests that 1,4-rhodium migration does not occur to any considerable extent. Presumably, the extra stability conferred onto alkenylrhodium **6** through chelation with the carbonyl group disfavors rhodium migration.[7c]



(3)

3. Conclusion

In summary, rhodium catalysis enables the carbometalation of ynamides using a range of organoboron reagents, including aryl, heteroaryl, and alkenylboronic acids, arylboronic esters, and triarylboroxines. This work further contributes to the growing number of methods for the synthesis of multisubstituted enamides in regio- and stereocontrolled fashion.[2,4]

4. Experimental

4.1. General

THF was dried and purified by passage through activated alumina columns using a solvent purification system. All commercially available reagents were used as received. Thin layer chromatography (TLC) was performed on Merck DF-Alufoilien 60F$_{254}$ 0.2 mm precoated plates. Product spots were visualized by UV light at 254 nm, and subsequently developed using potassium permanganate or ceric ammonium molybdate solution as appropriate. Flash column chromatography was carried out using silica gel (Fisher Scientific 60 Å particle size 35–70 μm). Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. Infra-red spectra were recorded on a Jasco FT/IR-460 Plus instrument as a thin film on sodium chloride plates or as a dilute solution in $CHCl_3$. ^{1}H NMR spectra were recorded on a Bruker AV500 (500 MHz), a Bruker DMX500 (500 MHz) spectrometer, a Bruker DPX360 (360 MHz) spectrometer, or a Bruker ARX250 (250 MHz) spectrometer. Chemical shifts (δ) are quoted in parts per million (ppm) downfield of tetramethylsilane, using residual protonated solvent as internal standard ($CDCl_3$ at 7.27 ppm). Abbreviations used in the description of resonances are: s (singlet), d (doublet), t (triplet), q, (quartet), app (apparent), br (broad). Coupling constants (J) are quoted to the nearest 0.1 Hz. Proton-decoupled ^{13}C NMR spectra were recorded on a Bruker AV500 (125.8 MHz) spectrometer, a Bruker DPX360 (90.6 MHz) spectrometer, or a Bruker ARX250 (62.9 MHz) spectrometer. Chemical shifts (δ) are quoted in parts per million (ppm) downfield of tetramethylsilane, using deuterated solvent as internal standard ($CDCl_3$ at 77.0 ppm). Assignments were made using the DEPT sequence with secondary pulses at 90° and 135°. High resolution mass spectra were recorded on a Finnigan MAT 900 XLT spectrometer or a Finnigan MAT 95XP spectrometer at the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea, or on a Finnigan MAT 900 XLT spectrometer at the School of Chemistry, University of Edinburgh. Microwave reactions were performed using a Biotage microwave synthesizer. Ynamides **1a**–**e** were prepared as described previously.[2a]

4.2. Rhodium-catalyzed carbometalation of ynamides with organoboron reagents: general procedure

A solution of the appropriate ynamide (0.40 mmol), the organoboron reagent (1.0–2.0 equiv), and [Rh(cod)(MeCN)$_2$]BF$_4$ (12 mg, 0.032 mmol) in THF (2 mL) and H_2O (100 μL) was heated at 90 °C for 10 min under microwave irradiation. Saturated aqueous $NaHCO_3$ solution (5 mL) was added and the mixture was extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification of the residue by column chromatography gave the desired enamide.

4.2.1. With boronic acids.

*4.2.1.1. 3-[(E)-4-(tert-Butyldimethylsilyloxy)-2-phenylbut-1-enyl]oxazolidin-2-one (**2a**).* The general procedure was followed using ynamide **1a** (108 mg, 0.40 mmol) and phenylboronic acid (98 mg, 0.80 mmol). Purification by column chromatography (10% EtOAc/hexane→20% EtOAc/hexane) gave an 8:1 inseparable mixture of the *enamide* **2a** and the imide **3a** as a pale orange oil (96 mg, 63%, adjusted yield of **2a**).

Data for **2a**: R_f=0.78 (60% EtOAc/hexane); IR (film) 2928, 2857, 1755 (C=O), 1653, 1471, 1297, 1257, 1042, 733 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.35–7.25 (5H, m, ArH), 6.61 (1H, s, =CH), 4.43 (2H, app dd, J=9.0, 6.9 Hz, CH_2O), 4.13 (2H, app dd, J=9.0, 6.9 Hz, CH_2N), 3.61 (2H, t, J=6.5 Hz, CH_2OSi), 2.83 (2H, t, J=6.5 Hz, =CCH_2), 0.84 (9H, s, SiC(CH_3)$_3$), −0.05 (6H, s, Si(CH_3)$_2$); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 157.3 (C), 140.5 (C), 128.3 (2×CH), 127.2 (CH), 126.8 (2×CH), 126.3 (C), 123.8 (CH), 62.4 (CH_2), 61.1 (CH_2), 46.2 (CH_2), 32.7 (CH_2), 25.8 (3×CH_3), 18.2 (C), −5.5 (2×CH_3); HRMS (ES) exact mass calcd for $C_{19}H_{30}NO_3Si$ [M+H]$^+$: 348.1989, found: 348.1992.

*4.2.1.2. 3-[(E)-4-(tert-Butyldimethylsilyloxy)-2-(4-methoxyphenyl)but-1-enyl]oxazolidin-2-one (**2b**).* The general procedure was followed using ynamide **1a** (108 mg, 0.40 mmol) and 4-methoxyphenylboronic acid (122 mg, 0.80 mmol). Purification by column chromatography (15% EtOAc/hexane) gave a 16:1

inseparable mixture of the *enamide* **2b** and the imide **3a** as a pale orange oil (119 mg, 75%, adjusted yield of **2b**).

Data for **2b**: R_f=0.72 (60% EtOAc/hexane); IR (film) 2929, 2857, 1747 (C=O), 1654, 1470, 1300, 1248, 1037, 733 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.26 (2H, d, J=8.8 Hz, Ar*H*), 6.85 (2H, d, J=8.8 Hz, Ar*H*), 6.50 (1H, s, =C*H*), 4.42 (2H, app dd, J=8.9, 7.0 Hz, CH_2O), 4.08 (2H, app dd, J=8.9, 7.0 Hz, CH_2N), 3.81 (3H, s, OCH_3), 3.60 (2H, t, J=6.5 Hz, CH_2OSi), 2.79 (2H, t, J=6.5 Hz, $=CCH_2$), 0.84 (9H, s, $SiC(CH_3)_3$), −0.05 (6H, s, $Si(CH_3)_2$); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 158.9 (C), 157.4 (C), 132.7 (C), 127.9 (2×CH), 126.9 (C), 122.6 (CH), 113.7 (2×CH), 62.4 (CH_2), 61.1 (CH_2), 55.2 (CH_3), 46.4 (CH_2), 32.8 (CH_2), 25.8 ($3\times CH_3$), 18.2 (C), −5.5 ($2\times CH_3$); HRMS (ES) exact mass calcd for $C_{20}H_{32}NO_4Si$ [M+H]$^+$: 378.2095, found: 378.2103.

*4.2.1.3. 3-[(E)-4-(tert-Butyldimethylsilyloxy)-2-p-tolylbut-1-enyl] oxazolidin-2-one (**2c**).* The title compound was prepared according to the general procedure using ynamide **1a** (108 mg, 0.40 mmol) and 4-tolylboronic acid (109 mg, 0.80 mmol) and purified by column chromatography (15% EtOAc/hexane → 20% EtOAc/hexane) to give a pale orange oil (89 mg, 61%). R_f=0.81 (60% EtOAc/hexane); IR (film) 2928, 2857, 1754 (C=O), 1654, 1481, 1297, 1257, 1042, 778 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.23 (2H, d, J=8.1 Hz, Ar*H*), 7.13 (2H, d, J=8.1 Hz, Ar*H*), 6.57 (1H, s, =C*H*), 4.43 (2H, app dd, J=8.9, 7.0 Hz, CH_2O), 4.11 (2H, app dd, J=8.9, 7.0 Hz, CH_2N), 3.61 (2H, t, J=6.5 Hz, CH_2OSi), 2.82 (2H, t, J=6.5 Hz, $=CCH_2$), 2.35 (3H, s, $ArCH_3$), 0.85 (9H, s, $SiC(CH_3)_3$), −0.04 (6H, s, $Si(CH_3)_2$); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 157.4 (C), 137.4 (C), 136.9 (C), 129.0 (2×CH), 126.7 (2×CH), 126.5 (C), 123.1 (CH), 62.4 (CH_2), 61.2 (CH_2), 46.3 (CH_2), 32.7 (CH_2), 25.8 ($3\times CH_3$), 21.0 (CH_3), 18.2 (C), −5.5 ($2\times CH_3$); HRMS (ES) exact mass calcd for $C_{20}H_{32}NO_3Si$ [M+H]$^+$: 362.2146, found: 362.2143.

*4.2.1.4. 3-[(E)-4-(tert-Butyldimethylsilyloxy)-2-(4-dibenzofuranyl)but-1-enyl]oxazolidin-2-one (**2d**).* The general procedure was followed using ynamide **1a** (108 mg, 0.40 mmol) and 4-dibenzofuranboronic acid (169 mg, 0.80 mmol). Purification by column chromatography (10% EtOAc/hexane → 20% EtOAc/hexane) gave a 13:1 inseparable mixture of the *enamide* **2d** and the imide **3a** as a cream solid (84 mg, 46%, adjusted yield of **2d**).

Data for **2d**: R_f=0.49 (50% EtOAc/hexane); mp 88–91 °C; IR ($CHCl_3$) 2954, 2928, 2857, 1759 (C=O), 1655, 1404, 1264, 1226, 1187, 1090, 837, 750, 704 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (1H, d, J=7.7, Ar*H*), 7.88 (1H, dd, J=7.5, 1.4 Hz, Ar*H*), 7.57 (1H, d, J=8.2 Hz, Ar*H*), 7.48–7.45 (1H, m, Ar*H*), 7.38–7.34 (2H, m, Ar*H*), 7.31 (1H, t, J=7.6 Hz, Ar*H*), 6.91 (1H, s, =C*H*), 4.51–4.47 (2H, m, OCH_2CH_2N), 4.30–4.26 (2H, m, CH_2N), 3.62 (2H, t, J=6.4 Hz, CH_2OSi), 3.11 (2H, t, J=6.4 Hz, $=CCH_2$), 0.84 (9H, s, $SiC(CH_3)_3$), −0.08 (6H, s, $Si(CH_3)_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 157.2 (C), 155.8 (C), 153.6 (C), 127.3 (CH), 127.1 (CH), 126.1 (CH), 125.7 (C), 124.4 (C), 124.1 (C), 122.9 (CH), 122.7 (CH), 120.9 (C), 120.6 (CH), 119.5 (CH), 111.7 (CH), 62.5 (CH_2), 61.2 (CH_2), 46.1 (CH_2), 32.6 (CH_2), 25.8 ($3\times CH_3$), 18.2 (C), −5.6 ($2\times CH_3$); HRMS (ES) exact mass calcd for $C_{25}H_{32}NO_4Si$ [M+H]$^+$: 438.2095, found: 438.2091.

*4.2.1.5. 3-[(E)-2,4-Diphenylbut-1-enyl]oxazolidin-2-one (**2e**).* The title compound was prepared according to the general procedure using ynamide **1b** (86 mg, 0.40 mmol) and phenylboronic acid (98 mg, 0.80 mmol) and purified by column chromatography (15% EtOAc/hexane → 20% EtOAc/hexane) to give a pale brown oil (105 mg, 89%). R_f=0.71 (60% EtOAc/hexane); IR (film) 2985, 2923, 1751 (C=O), 1480, 1405, 1221, 1087, 908, 734 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.32–7.25 (4H, m, Ar*H*), 7.23–7.15 (3H, m, Ar*H*), 7.11–7.03 (3H, m, Ar*H*), 6.28 (1H, s, =C*H*), 4.21–4.17 (2H, m, CH_2O), 3.49–3.45 (2H, m, CH_2N), 2.78 (2H, t, J=7.6 Hz, CH_2CH_2Ph), 2.58 (2H, t, J=7.6 Hz, CH_2CH_2Ph); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 157.0 (C), 141.4 (C), 140.0 (C), 131.3 (C), 128.5 (4×CH), 128.3 (2×CH), 127.4 (CH), 126.8 (2×CH), 126.0 (CH), 122.5 (CH), 62.2 (CH_2), 46.9 (CH_2), 34.2 (CH_2), 31.5 (CH_2); HRMS (ES) exact mass calcd for $C_{19}H_{23}N_2O_2$ [M+NH_4]$^+$: 311.1754, found: 311.1748.

*4.2.1.6. 3-[(E)-2-(4-Acetylphenyl)-4-phenylbut-1-enyl]oxazolidin-2-one (**2f**).* The title compound was prepared according to general procedure using ynamide **1b** (86 mg, 0.40 mmol) and 4-acetylphenylboronic acid (131 mg, 0.80 mmol) and purified by column chromatography (12% EtOAc/hexane → 25% EtOAc/hexane) to give an orange solid (81 mg, 60%). R_f = 0.47 (60% EtOAc/hexane); mp 116–118 °C; IR ($CHCl_3$) 2985, 2920, 1759 (C=O), 1679 (C=O), 1479, 1404, 1212, 1087, 910, 731 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97–7.95 (2H, m, Ar*H*), 7.50–7.48 (2H, m, Ar*H*), 7.30–7.27 (2H, m, Ar*H*), 7.22–7.18 (1H, m, Ar*H*), 7.13–7.11 (2H, m, Ar*H*), 6.56 (1H, s, =C*H*), 4.34–4.31 (2H, m, CH_2O), 3.66–3.63 (2H, m, CH_2N), 2.91 (2H, t, J=7.6 Hz, CH_2CH_2Ph), 2.68 (2H, t, J=7.6 Hz, CH_2CH_2Ph), 2.62 (3H, s, CH_3); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 197.5 (C), 156.9 (C), 145.2 (C), 141.0 (C), 135.9 (C), 128.7 (2×CH), 128.4 (4×CH), 128.3 (C), 126.8 (2×CH), 126.2 (CH), 124.3 (CH), 62.3 (CH_2), 45.7 (CH_2), 34.4 (CH_2), 31.1 (CH_2), 26.6 (CH_3); HRMS (ES) exact mass calcd for $C_{21}H_{22}NO_3$ [M+H]$^+$: 336.1594, found: 336.1592.

*4.2.1.7. 4-{1-[1-(2-Oxooxazolidin-3-yl)meth-(E)-ylidene]-3-phenylpropyl}benzoic acid ethyl ester (**2g**).* The title compound was prepared according to the general procedure using ynamide **1b** (86 mg, 0.40 mmol) and 4-ethoxycarbonylphenylboronic acid (155 mg, 0.80 mmol) and purified by column chromatography (10% EtOAc/hexane → 20% EtOAc/hexane) to give a pale yellow oil (82 mg, 56%). R_f=0.44 (50% EtOAc/hexane); IR (film) 2982, 2926, 1759 (C=O), 1712 (C=O), 1479, 1403, 1212, 1107, 910, 756 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (2H, d, J=8.5 Hz, Ar*H*), 7.47 (2H, d, J=8.5 Hz, Ar*H*), 7.30–7.27 (2H, m, Ar*H*), 7.22–7.19 (1H, m, Ar*H*), 7.13–7.11 (2H, m, Ar*H*), 6.54 (1H, s, =C*H*), 4.41 (2H, q, J=7.1 Hz, OCH_2CH_3), 4.35–4.32 (2H, m, OCH_2CH_2N), 3.66–3.63 (2H, m, CH_2N), 2.92 (2H, t, J=7.6 Hz, CH_2CH_2Ph), 2.69 (2H, t, J=7.6 Hz, CH_2CH_2Ph), 1.43 (3H, t, J=7.1 Hz, OCH_2CH_3); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 166.3 (C), 156.9 (C), 144.9 (C), 141.1 (C), 129.8 (2×CH), 129.2 (C), 128.8 (C), 128.4 (4×CH), 126.6 (2×CH), 126.2 (CH), 124.0 (CH), 62.3 (CH_2), 60.9 (CH_2), 45.7 (CH_2), 34.3 (CH_2), 31.2 (CH_2), 14.3 (CH_3); HRMS (ES) exact mass calcd for $C_{22}H_{24}NO_4$ [M+H]$^+$: 366.1700, found: 366.1697.

*4.2.1.8. 3-[2,2-Diphenylvinyl]oxazolidin-2-one (**2h**).* The title compound was prepared according to the general procedure using ynamide **1c** (75 mg, 0.40 mmol) and phenylboronic acid (98 mg, 0.80 mmol) and purified by column chromatography (15% EtOAc/hexane → 20% EtOAc/hexane) to give a colorless solid (71 mg, 67%). R_f=0.72 (60% EtOAc/hexane); mp 90–92 °C; IR (film) 2925, 2855, 1755 (C=O), 1685, 1444, 1265, 1213, 1042, 736 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.39–7.35 (3H, m, Ar*H*), 7.29–7.22 (5H, m, Ar*H*), 7.20–7.17 (2H, m, Ar*H*), 7.15 (1H, s, =C*H*), 4.22–4.18 (2H, m, CH_2O), 3.16–3.12 (2H, m, CH_2N); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 157.2 (C), 140.8 (C), 138.0 (C), 130.8 (2×CH), 128.2 (4×CH), 127.8 (CH), 127.0 (3×CH), 126.1 (C), 122.4 (CH), 62.6 (CH_2), 44.9 (CH_2); HRMS (ES) exact mass calcd for $C_{17}H_{16}NO_2$ [M+H]$^+$: 266.1176, found: 266.1183.

*4.2.1.9. 3-[(E)-2-(4-Chlorophenyl)-2-phenylvinyl]oxazolidin-2-one (**2i**).* The title compound was prepared according to the general procedure using ynamide **1c** (75 mg, 0.40 mmol) and 4-chlorophenylboronic acid (125 mg, 0.80 mmol) and purified by column chromatography (15% EtOAc/hexane → 20% EtOAc/hexane) to give a pale yellow solid (79 mg, 65%). R_f=0.57 (50% EtOAc/hexane); mp 136–138 °C; IR (film) 2918, 2865, 1759 (C=O), 1637, 1405, 1262, 1211, 1039, 744 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.39–7.37 (3H, m, Ar*H*), 7.24–7.22 (4H, m, Ar*H*), 7.14–7.10 (3H, m, Ar*H* and =C*H*), 4.21 (2H, app t, J=7.9 Hz, CH_2O), 3.14 (2H, app t, J=7.9 Hz, CH_2N); ^{13}C

NMR (62.9 MHz, $CDCl_3$) δ 157.2 (C), 139.4 (C), 137.5 (C), 132.8 (C), 130.8 (2×CH), 128.4 (2×CH), 128.3 (2×CH), 128.2 (2×CH), 128.0 (CH), 124.8(C), 122.7 (CH), 62.6 (CH_2), 44.8 (CH_2); HRMS (ES) exact mass calcd for $C_{17}H_{15}{}^{35}ClNO_2$ $[M+H]^+$: 300.0786, found: 300.0784.

*4.2.1.10. 3-[(E)-2-Phenyl-2-o-tolylvinyl]oxazolidin-2-one (**2j**).* The title compound was prepared according to the general procedure using ynamide **1c** (75 mg, 0.40 mmol) and *o*-tolylboronic acid (109 mg, 0.80 mmol) and purified by column chromatography (10% EtOAc/hexane→12% EtOAc/hexane) to give a pale yellow solid (59 mg, 53%). *Rf*=0.76 (60% EtOAc/hexane); mp 99–101 °C; IR (film) 3059, 2983, 2921, 1759 (C=O), 1636, 1443, 1308, 1219, 1038, 732 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34–7.31 (2H, m, Ar*H*), 7.29–7.13 (7H, m, Ar*H*), 6.74 (1H, s, =C*H*), 4.30–4.27 (2H, m, CH_2O), 3.37–3.33 (2H, m, CH_2N), 2.08 (3H, s, CH_3); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 157.5 (C), 140.7 (C), 138.4 (C), 136.8 (C), 130.9 (CH), 130.5 (CH), 129.9 (2×CH), 128.0 (2×CH), 127.7 (C), 127.6 (CH), 127.4 (CH), 125.5 (CH), 124.1 (CH), 62.7 (CH_2), 45.1 (CH_2), 20.6 (CH_3); HRMS (ES) exact mass calcd for $C_{18}H_{18}NO_2$ $[M+H]^+$: 280.1332, found: 280.1330.

*4.2.1.11. 3-[(E)-2-(3-Chloro-4-isopropoxyphenyl)-2-phenylvinyl]oxazolidin-2-one (**2k**).* The title compound was prepared according to the general procedure using ynamide **1c** (75 mg, 0.40 mmol) and 3-chloro-4-isopropoxyphenyl boronic acid (172 mg, 0.80 mmol) and purified by column chromatography (15% EtOAc/hexane→20% EtOAc/hexane) to give a colorless solid (117 mg, 82%). R_f=0.68 (60% EtOAc/hexane); mp 122–124 °C; IR (film) 2978, 2920, 1761 (C=O), 1639, 1496, 1276, 1214, 1108, 732 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.39–7.37 (3H, m, Ar*H*), 7.24–7.23 (2H, m, Ar*H*), 7.18 (1H, app d, *J*=1.4 Hz, Ar*H*), 7.06 (1H, s, =C*H*), 7.01 (1H, dd, *J*=8.5, 1.4 Hz, Ar*H*), 6.84 (1H, d, *J*=8.5 Hz, Ar*H*), 4.52 (1H, quint, *J*=6.0 Hz, $CH(CH_3)_2$), 4.19 (2H, app t, *J*=8.0 Hz, CH_2O), 3.11 (2H, app t, *J*=8.0 Hz, CH_2N), 1.36 (6H, d, *J*=6.0 Hz, $CH(CH_3)_2$); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 157.2 (C), 152.7 (C), 137.5 (C), 134.5 (C), 130.7 (2×CH), 128.8 (CH), 128.3 (2×CH), 127.9 (CH), 126.0 (CH), 124.7 (C), 124.0 (C), 121.8 (CH), 115.5 (CH), 72.1 (CH), 62.6 (CH_2), 44.8 (CH_2), 22.0 (2×CH_3); HRMS (ES) exact mass calcd for $C_{20}H_{21}{}^{35}ClNO_3$ $[M+H]^+$: 358.1203, found: 358.1203.

*4.2.1.12. 1-[(E)-2-(4-Acetylphenyl)-2-phenylvinyl]pyrrolidin-2-one (**2l**).* The title compound was prepared according to general procedure using ynamide **1d** (74 mg, 0.40 mmol) and 4-acetylphenylboronic acid (131 mg, 0.80 mmol) and purified by column chromatography (20% EtOAc/hexane) to give an orange oil (31 mg, 25%). R_f=0.38 (60% EtOAc/hexane); IR (film) 2958, 2926, 1681 (C=O), 1460, 1392, 1269, 1222, 907, 733, 650 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.86–7.83 (2H, m, Ar*H*), 7.46 (1H, s, =C*H*), 7.42–7.37 (3H, m, Ar*H*), 7.28–7.26 (2H, m, Ar*H*), 7.23–7.21 (2H, m, Ar*H*), 3.00–2.88 (2H, m, CH_2N), 2.58 (3H, s, CH_3), 2.45–2.42 (2H, t, *J*=7.7 Hz, CH_2C=O), 1.89 (2H, quint, *J*=7.7 Hz, CH_2CH_2N); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 197.6 (C), 175.7 (C), 146.3 (C), 138.0 (C), 135.3 (C), 130.9 (2×CH), 128.3 (2×CH), 128.2 (2×CH), 127.9 (CH), 127.1 (2×CH), 125.1 (C), 124.1 (CH), 48.2 (CH_2), 30.4 (CH_2), 26.6 (CH_3), 18.8 (CH_2); HRMS (ES) exact mass calcd for $C_{20}H_{20}NO_2$ $[M+H]^+$: 306.1489, found: 306.1494.

*4.2.1.13. 3-[(E)-4-(tert-Butyldimethylsilyloxy)-2-(2-furanyl)but-1-enyl]oxazolidin-2-one (**2m**).* The title compound was prepared according to the general procedure using ynamide **1a** (108 mg, 0.40 mmol) and 2-furanboronic acid (90 mg, 0.80 mmol) and purified by column chromatography (10% EtOAc/hexane→20% EtOAc/hexane) to give a cream solid (89 mg, 66%). R_f=0.67 (50% EtOAc/hexane); mp 54–56 °C; IR ($CHCl_3$) 3055, 2986, 1759 (C=O), 1654, 1421, 1403, 1265, 1226, 1082, 739, 705 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33 (1H, d, *J*=1.8 Hz, Ar*H*), 7.17 (1H, s, =C*H*), 6.37 (1H, dd, *J*=3.3, 1.8 Hz, Ar*H*), 6.21 (1H, d, *J*=3.3 Hz, Ar*H*), 4.44–4.41 (2H, m, OCH_2CH_2N), 4.19–4.17 (2H, m, CH_2N), 3.75 (2H, t, *J*=6.5 Hz, CH_2OSi), 2.71 (2H, t, *J*=6.5 Hz, $=CCH_2$), 0.86 (9H, s, $SiC(CH_3)_3$), −0.02 (6H, s, $Si(CH_3)_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 156.9 (C), 154.2 (C), 141.3 (CH), 121.9 (CH), 112.6 (C), 111.1 (CH), 104.7 (CH), 62.4 (CH_2), 61.9 (CH_2), 45.6 (CH_2), 30.5 (CH_2), 25.8 (3×CH_3), 18.3 (C), −5.5 (2×CH_3); HRMS (ES) exact mass calcd for $C_{17}H_{28}NO_4Si$ $[M+H]^+$: 338.1782, found: 338.1778.

*4.2.1.14. 3-{(1E,3E)-2-[2-(tert-Butyldimethylsilyloxy)ethyl]-4-phenylbuta-1,3-dienyl}-oxazolidin-2-one (**2n**).* The title compound was prepared according to the general procedure using ynamide **1a** (108 mg, 0.40 mmol) and *trans*-2-phenylvinylboronic acid (118 mg, 0.8 mmol) and purified by column chromatography (10% EtOAc/hexane) to give a pale brown solid (78 mg, 52%). R_f=0.80 (60% EtOAc/hexane); mp 130–132 °C; IR (film) 2925, 1731 (C=O), 1635, 1461, 1406, 1337, 1250, 1224, 1044, 756 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39–7.37 (2H, m, Ar*H*), 7.33–7.30 (2H, m, Ar*H*), 7.22–7.19 (1H, m, Ar*H*), 6.77 (1H, s, =C*H*), 6.75 (1H, d, *J*=16.1 Hz, CH=C*H*), 6.45 (1H, d, *J*=16.1 Hz, C*H*=CH), 4.41 (2H, app dd, *J*=9.2, 6.9 Hz, CH_2O), 4.21 (2H, app dd, *J*=9.2, 6.9 Hz, CH_2N), 3.77 (2H, t, *J*=6.4 Hz, CH_2OSi), 2.70 (2H, t, *J*=6.4 Hz, $=CCH_2$), 0.87 (9H, s, $SiC(CH_3)_3$), 0.02 (6H, s, $Si(CH_3)_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 156.7 (C), 137.6 (C), 130.9 (CH), 128.6 (2×CH), 127.4 (CH), 127.0 (CH), 126.0 (2×CH), 125.1 (CH), 120.1 (C), 62.3 (CH_2), 61.6 (CH_2), 45.5 (CH_2), 29.0 (CH_2), 25.8 (3×CH_3), 18.3 (C), −5.4 (2×CH_3); HRMS (ES) exact mass calcd for $C_{21}H_{32}NO_3Si$ $[M+H]^+$: 374.2146, found: 374.2136.

4.2.2. With arylboronic esters.

*4.2.2.1. 4-{1-[1-(2-Oxooxazolidin-3-yl)meth-(E)-ylidene]-3-phenylpropyl}benzoic acid ethyl ester (**2g**).* The title compound was prepared according to the general procedure using ynamide **1b** (86 mg, 0.40 mmol) and ethyl-(4-(4,4,5,5)-tetramethyl-1,3,2,dioxaborolan-2-yl)benzoate (220 mg, 0.80 mmol) and purified by column chromatography (10% EtOAc/hexane→20% EtOAc/hexane) to give a pale yellow oil (77 mg, 53%).

4.2.3. With triphenylboroxine.

*4.2.3.1. 3-[((E)-4-(tert-Butyldimethylsilyloxy)-2-phenyl)but-1-enyl]oxazolidin-2-one (**2a**).* The title compound was prepared according to the general procedure using ynamide **1a** (108 mg, 0.40 mmol) and triphenylboroxine (124 mg, 0.40 mmol) and purified by column chromatography (10% EtOAc/hexane→15% EtOAc/hexane) to give a pale orange oil (81 mg, 58%).

4.3. Deuterium incorporation experiment

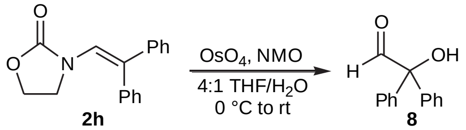
*4.3.1. 3-[((E)-4-(tert-Butyldimethylsilyloxy)-1-deuterio-2-phenyl)but-1-enyl]oxazolidin-2-one (**7**).* A solution of ynamide **1a** (108 mg, 0.40 mmol), triphenylboroxine (124 mg, 0.40 mmol), and $[Rh(cod)(MeCN)_2]BF_4$ (12 mg, 0.032 mmol) in THF (2 mL) and D_2O (100 μL) was heated at 90 °C for 10 min under microwave irradiation. Saturated aqueous $NaHCO_3$ solution (5 mL) was added and the mixture was extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification of the residue by column chromatography (10% EtOAc/hexane→15% EtOAc/hexane) gave a ca. 5:1 inseparable mixture of the *enamide* **7** and the imide **3b** (mixture of isotopologues) as a pale orange oil (96 mg, 59%, adjusted yield of **7**).

Data for **7**: R_f=0.80 (60% EtOAc/hexane); IR (film) 2929, 2857, 1753 (C=O), 1639, 1598, 1471, 1297, 1255, 1051, 733 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34–7.30 (4H, m, Ar*H*), 7.27–7.24 (1H, m, Ar*H*), 4.43 (2H, app dd, *J*=8.8, 7.1 Hz, CH_2O), 4.14 (2H, app dd, *J*=9.0, 6.9 Hz, CH_2N), 3.60 (2H, t, *J*=6.5 Hz, CH_2OSi), 2.83 (2H, t, *J*=6.5 Hz, $=CCH_2$), 0.84 (9H, s, $SiC(CH_3)_3$), −0.06 (6H, s, $Si(CH_3)_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 157.3 (C), 140.6 (C), 128.3 (2×CH), 127.1 (CH), 126.8 (2×CH), 125.6 (C), 123.5 (CD, t, J_D=26 Hz), 62.4 (CH_2), 61.1 (CH_2), 46.1 (CH_2), 32.6 (CH_2), 25.8 (3×CH_3), 18.2 (C), −5.5 (2×CH_3); HRMS (ES) exact mass calcd for $C_{19}H_{26}DNO_3Si$ $[M+H]^+$: 349.2052, found: 349.2050.

4.4. Regio-/stereochemical determinations

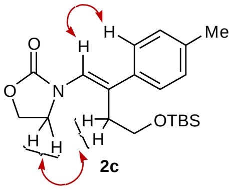
The regioselectivities of the rhodium-catalyzed carbometalation reactions of alkyl-substituted ynamides **1a** and **1b** were obvious from the ^1H NMR spectra of the corresponding enamide products (by consideration of the signals of the alkene proton, which did not exhibit vicinal proton–proton coupling).

The regiochemical outcome of the rhodium-catalyzed carbometalation reaction producing enamide **2h** was determined by dihydroxylation of **2h**, which provided known α-hydroxyaldehyde **8**[18] in low conversion.



2h **8**

The stereoselectivities of the rhodium-catalyzed carbometalation reactions producing enamides **2c**, **2g**, **2l**, and **2n** were determined on the basis of NOESY experiments, which displayed the following diagnostic enhancements:



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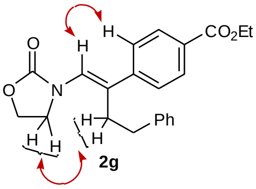
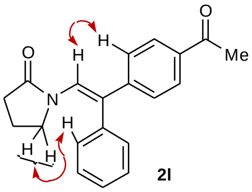
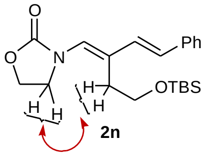


2g



2l



2n

Acknowledgements

This work was supported by the European Commission (Project No. MEST-CT-2005-020744), the EPSRC, AstraZeneca, and the University of Edinburgh. We thank the EPSRC National Mass Spectrometry Service Centre at the University of Wales, Swansea, for providing high-resolution mass spectra.

Supplementary data

Copies of ^1H and ^{13}C NMR spectra for new compounds. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.06.021.

References and notes

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