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Palladium-Catalyzed Carboxy-Alkynylation of Propargylic Amines Using Carbonate Salts as Carbon Dioxide Source

Phillip D. G. Greenwood and Jerome Waser^{*[a]}

Abstract: A palladium-catalyzed multi-component reaction of propargylic amines, alkynyl bromides and cesium hydrogen carbonate to access oxazolidinones is reported. In contrast to previous reports, only a slight excess of cesium hydrogen carbonate is used as surrogate of carbon dioxide. The reaction gives access to oxazolidinones bearing alkyl- and aryl polysubstituted enynes in good yield and very high *E* stereoselectivity.

Introduction

The utilisation of the greenhouse gas CO₂ has attracted significant interest over recent years.^[1] For the organic chemistry community, focus has been on incorporating CO₂ into organic molecules for the synthesis of valuable compounds and commodity chemicals.^[2] As an important application, insertion of CO₂ into propargylic amines to form oxazolidinones has been achieved using a range of diverse conditions (Scheme 1).^[3,4] Transformations without metal catalysts require harsh or specialized conditions, such as super bases^[3a-d] or super critical CO₂.^[3e,f] A number of transition-metal catalysed processes allowing milder reaction conditions have been developed using ruthenium^[4a] palladium,^[4b,c] silver,^[4d-i] gold^[4j,k] and zinc^[4l] catalysts, as well as a copper substituted ionic liquid.^[4m] In all of these reported methods, the addition of CO₂ has been combined with protonation of the triple bond in the propargylic amines, resulting in the formation of a C-O and a C-H bond (Scheme 1A).^[5] Recently the Nevado group demonstrated through the use of palladium catalysis that a carboxylation-arylation sequence can be performed as part a new multicomponent synthesis of oxazolidinones (Scheme 1B).^[6] Using gaseous CO₂ at atmospheric pressure, they obtained tetra-substituted alkenes via C-O and C-C bond formation, allowing for a broader range of oxazolidinones to be synthesised. Developing efficient methods to access oxazolidinones is important, as they are useful as intermediates^[7] or chiral auxiliaries^[8] in organic synthesis. They are also found in agrochemicals and antibacterial drugs^[9] and their material properties have even been exploited for applications in lithium battery technology.^[10]

As most carboxylation reactions, the developed approaches are usually based on the use of gaseous CO₂, which is convenient as it is widely available. However, the use of a gas leads to inefficient mass transport at the gas/liquid interface,^[11] resulting in a poor atom economy. For example, a 1 mmol reaction with a 2 litre balloon of CO₂ has an excess of 89 equivalents of CO₂. Therefore, it is sometimes advantageous to have a solid CO₂ source to enable easier handling and better reaction efficiency. In this context, a limited number of examples have been reported

with a carbonate salt as source of CO₂ in a reaction or acting directly as a nucleophile/electrophile.^[3a,b,12] In 1996, Costa and co-workers developed an organic super base catalysed carboxylation of propargylic amines. This publication contained a single example of the use of a tetramethylguanidinium carbamate amine complex as a carrier for CO₂.^[3a] In a subsequent work two years later they showed the use of sodium hydrogen carbonate as the CO₂ source.^[3b] The reaction between epoxide and sodium hydrogen carbonate catalysed by tetrabutylammonium bromide was also developed as a viable pathway to access cyclic carbonates.^[12] Trost and co-workers reported the use of carbonates in the palladium-catalyzed enantioselective ring-opening of vinyl epoxides to give either diols or cyclic carbonates.^[13]

A) Hydrocarboxylation of propargylic amines with CO₂

B) Nevado: Aryl-carboxylation of propargylic amines with CO₂

C) This work: Alkynyl-carboxylation of propargylic amines with CsHCO₃

Scheme 1. Synthesis of oxazolidinones from propargylic amines.

Herein, we describe a convenient method for the palladium catalysed three-component synthesis of oxazolidinones from propargylic amines with cesium hydrogen carbonate as the C1 source instead of gaseous CO₂ (Scheme 1C). Alkynyl bromide **1** was used as a third partner, resulting in a new stereoselective synthesis of highly substituted enynes.^[14]

Results and Discussion

While working on the palladium catalysed oxyalkynylation of propargylic amines tethered by trifluoroacetaldehyde

[a] Phillip Greenwood, and Prof. Dr. Jerome Waser
Laboratory of Catalysis and Organic Synthesis
Ecole Polytechnique Fédérale de Lausanne
EPFL SB ISIC LCSO, BCH 4306, 1015 Lausanne (CH)
Fax: (+)41 21 693 97 00
E-mail: jerome.waser@epfl.ch
Homepage: <http://lcsso.epfl.ch/>

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derivatives,^[15] an unexpected side reaction was observed: When the reaction of propargylic amine **2a** with silyl alkynyl bromide **1** and half acetal **3** was examined, oxazolidinone product **5a** was observed in addition to the expected product **4** (Scheme 2). This was confusing, as there was no obvious source of CO₂ in the reaction. When the reaction was performed in the absence of hemiacetal tether with or without a balloon of CO₂, exclusive formation of oxazolidinone **5a** was observed. The formation of **5a** could be finally suppressed to give **4** in high yield by the use of non-carbonate bases, establishing the latter as the source of the CO₂ group. When considering the lack of reports in the use of carbonate salts in the palladium-catalyzed multi-component synthesis of oxazolidinones, combined with the fact that enynes were never reported as products, we decided to optimize the formation of **5a**. CsHCO₃ was finally identified as the best CO₂ source, with a palladium-DPEPhos complex as catalyst in DCE at 60 °C (Table 1, entry 1). Under these conditions, product **5a** was obtained in 77% isolated yield.

Scheme 2. Unexpected formation of oxazolidinone **5a** observed during the tethered oxyalkynylation of propargylic amine **2a**.

Not surprisingly, the structure of the base had a strong impact on the outcome of the reaction. The carbonate salts of both cesium and rubidium gave the desired product albeit with modest yield (entry 2). The use of salts of smaller cations gave poor yields and calcium and barium carbonates gave no product formation at all (entry 3). A higher temperature of 75 °C (entry 4), and a lower temperature of 50 °C (entry 5) both led to a lower yield of 64%, with the latter giving incomplete conversion. The choice of ligand played a central role in the oxyalkynylation reaction using hemiacetal tether **3**.^[15,16] Therefore, we examined again the most successful ligands from the previous protocol (DCEPhos, XantPhos and dppf). However, they led to the the formation of oxazolidinone **5a** in low yields only (entries 6-8). Different solvents (entries 9-11) and palladium sources were also explored (see Supporting Information), but none of the changes provided any improvement. Both the palladium loading (entry 12) and the equivalence of base (entry 13) could be decreased. However, this led to longer reaction time and incomplete conversion. Finally, when the reaction was carried out with a balloon of CO₂, the same yield was obtained (entry 14). The addition of 4 Å molecular sieves had no influence on the reaction outcome (entry 15). The transformation was clean and only starting material and product were observed.

With the optimised conditions in hand, we moved on to study the scope of the reaction (Scheme 3). We start by looking at aliphatic groups on the nitrogen; *para*-methoxy benzyl and ferrocenylmethyl protected propargylic amines were used successfully in the reaction to give **5b** and **5c**. On the alkyne, a primary benzyl (**5d**) and a secondary cyclopropyl (**5e**) groups were both well tolerated in the reaction. The *tert*-butyl substituted enyne **5f** was obtained in lower yields and required longer reaction times and higher temperature for full conversion. We then

moved on to propargylic amines bearing aromatic groups on the alkyne. N-benzyl-3-phenylprop-2-yn-1-amine with an unsubstituted phenyl ring gave enyne **5g** in 81% yield. Substituting the nitrogen with a methyl group gave **5h** with a reduced yield of 66%. 4-Methoxy (**5i**), 4-trifluoromethyl (**5j**) and 3-bromo (**5k**) substituents were tolerated on the aryl ring, giving moderate to good yields. Introducing two methyl substituents at the meta positions (**5l**) had no detrimental effect on the reaction. Finally, a propargylic amine with a heteroaromatic thiophene group on the alkyne gave enyne **5m** in 47% yield. Substrates with aromatic substituents on the alkyne required increased reaction temperatures and longer reaction time to reach full conversion. All reactions gave a single isomer of the product and the *E* configuration of the olefin was established by X-ray analysis on compound **5g**.^[17] The configuration of the other compounds was assumed to be the same based on the similar NMR spectra.

Table 1. Optimisation of the carboxylation-alkynylation of **2a**.^[a]

Entry	Changes to Standard conditions	5a (%) ^[b]	2a (%)
1	none	80 (77) ^[c]	
2	Cs ₂ CO ₃ or Rb ₂ CO ₃ as base ^[d]	40	<9
3	Other carbonates ^[e] as base ^[d]	<14	30-40
4	at 75 °C	64	
5	at 50 °C	64	7
6	DCEPhos instead of DPEPhos	2	15
7	XantPhos instead of DPEPhos	4	50
8	dppf instead of DPEPhos	50	20
9	Chlorobenzene instead of DCE	3	46
10	Trifluorotoluene instead of DCE	41	5
11	Chloroform instead of DCE	40	4
12	half catalyst loading	68	5
13	1 equivalent base	69	5
14	With a CO ₂ balloon	80	-
15	In presence of 4 Å MS	76	-

[a] Reaction conditions: 0.10 mmol **2a**, 0.13 mmol **1**, 0.20 mmol CsHCO₃ in DCE at 60 °C. [b] NMR yields using *p*-difluorobenzene as internal standard. [c] Isolated yield. [d] Reactions run at 75 °C [e] Li₂CO₃, Na₂CO₃, K₂CO₃, NaHCO₃, CaCO₃, and BaCO₃ were examined.

When a terminal acetylene substrate, N-benzyl propynylamine, was subjected to the same reaction conditions, only trace amounts of carboxylation product was observed. The use of substrates with substituents at the propargylic position or an attempt of carboxy-arylation as well as carboxy-alkynylation

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with aryl- or alkyl- substituted bromoalkynes were also not successful, even with the ligands applied to these classes of substrates in the amination-tethered oxyalkynylation reaction (trifuryl phosphine and RuPhos). These reactions were also performed under CO₂ atmosphere, but the carboxylation products were still not observed.

The mechanism that is generally proposed for the carboxylation of propargylic amines involves the nucleophilic attack of the nitrogen onto the carbon of CO₂ to give a carbamate anion which then undergoes a 5-exo-dig cyclisation onto the triple bond activated by palladium (Scheme 4A). In our case, this seems unlikely, as the carbon of the hydrogen carbonate anion is much less electrophilic and the reaction also works with carbonates. It may be possible that the carbonate is undergoing decomposition under the reaction conditions to produce CO₂. However, this seems unlikely as the yields obtained would be very high for the generation of only one or two equivalents of CO₂ gas. Furthermore, many palladium-catalyzed reactions use carbonate bases under similar conditions, but report of CO₂ incorporation remains exceedingly rare, speaking against an efficient generation of gaseous CO₂ from the carbonates.

Scheme 3. Scope of the carboxylation-alkynylation reaction. [a] Product isolated with 1-7.5% dba as impurity. Substrates with aromatic alkynyl groups required 24-48 h at 75 °C.

We propose therefore an alternative pathway for the mechanism of this reaction (Scheme 4B). First, oxidative addition of the palladium(0) complex on alkynyl bromide **1** generates palladium(II) complex **I**. Coordination of the alkyne substrate leads then to activation of the triple bond (**II**).^[18] This step most probably requires first dissociation of the bromide anion to generate a more reactive cationic palladium intermediate with a free coordination site.^[19] The carbonate attacks as a nucleophile,^[13,20] to give *trans* oxy-palladation intermediate **III**. Intramolecular nucleophilic attack by the nitrogen gives with elimination of water gives then vinyl palladium complex **IV**. Reductive elimination finally leads to the observed product. In this scenario, the oxypalladation step would probably not occur with high regioselectivity, but may be reversible. Fast formation of the oxazolidinone product is possible only for the drawn regioisomer. Alternatively, hydrogen bonding between the amine and the carbonate may direct the attack of the nucleophile. Further investigation will be needed to support this mechanism hypothesis.

A) Established mechanism for carboxylation with CO₂

B) Proposed mechanism for carboxylation with carbonate

Scheme 4. Proposed mechanism for the carboxy-alkynylation reaction.

Conclusions

In summary, we have presented an unprecedented palladium catalyzed carboxylation-alkynylation reaction using a solid inorganic hydrogen carbonate source of CO₂. It gives access to highly substituted enynes substrates with very high stereoselectivity. The exceptional efficiency of the reaction may suggest an interesting mechanism pathway, which should be more strongly supported by further studies.

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Keywords: palladium catalysis • alkynes • heterocycles • carbon dioxide • multi-component reactions

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Catalysis

Phillip D. G. Greenwood and Jerome Waser*

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Palladium-Catalyzed Carboxy-Alkynylation of Propargylic Amines Using Carbonate Salts as Carbon Dioxide Source

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1. General methods.

All reactions were carried out in oven dried glassware under an atmosphere of nitrogen, unless stated otherwise. For quantitative flash chromatography technical grade solvents were used. For flash chromatography for analysis, HPLC grade solvents from Sigma-Aldrich were used. THF, Et₂O, CH₃CN, toluene, hexane and CH₂Cl₂ were dried by passage over activated alumina under nitrogen atmosphere (H₂O content < 10 ppm, *Karl-Fischer* titration). Unless otherwise stated, degassed solvents were prepared using freeze-pump-thaw cycle. All chemicals were purchased from Acros, Aldrich, Fluka, VWR, Fluorochem or Merck and used without further purification. Chromatographic purification was performed as flash chromatography using Silicycle silica 40-63, 60 Å, using the solvents indicated as eluent with 0.1-0.5 bar pressure. TLC was performed on Merck silica gel 60 F254 TLC glass plates and visualized with UV light and potassium permanganate stain. ^1H -NMR spectra were recorded on a Bruker DPX-400 400 MHz spectrometer in chloroform-*d*. All signals are reported in ppm with the internal chloroform signal at 7.26 ppm. The data is being reported as (s = singlet, d = doublet, t = triplet, q = quadruplet, qi = quintet, m = multiplet or unresolved, bs = broad signal, coupling constant(s) in Hz, integration, assignment). ^{13}C -NMR spectra were recorded with $\{^1\text{H}\}$ decoupling on a Bruker DPX-400 100 MHz spectrometer in chloroform-*d* unless otherwise stated. All signals are reported in ppm with the internal chloroform signal at 77.0 ppm as standard unless otherwise stated. Infrared spectra were recorded on a JASCO FT-IR B4100 spectrophotometer with an ATR PRO410-S and a ZnSe prisma and are reported as cm⁻¹ (w = weak, m = medium, s = strong, br = broad). High resolution mass spectrometric measurements were performed by the mass spectrometry service of ISIC at the EPFL on a MICROMASS (ESI) QTOF. Cesium hydrogen carbonate (99.99%) was purchased from AlfaAesar and stored and used under anhydrous glovebox conditions. Tris(Dibenzylideneacetone)dipalladium was purchased from fluorochem and recrystallized in 200 mg portions following reported procedure.¹ DPEPhos was purchased from Acros. Deactivated silica gel was prepared by making a slurry of silica gel (230-400mesh) with 5% Et₃N in pentane solution followed by complete removal of solvent by rotary evaporation until it is a free flowing powder. The solvent system ULTRA comprises 71% DCM, 24% methanol and 5% aq. ammonia (25% solution).

2. Synthesis of amine starting materials

N-Benzyl but-2-ynylamine (2a)

A solution of benzyl amine (4-6 equiv.) in DCM (15 mL) at 0 °C was stirred vigorously while a solution of bromo-2-butyne (2.5 mL, 27 mmol, 1 equiv.) in DCM (15 mL) was slowly added. The reaction mixture was then warmed to room temperature and stirred for 5 hours. It was then filtered through silica gel, eluting with 40% EtOAc in pentane and the resulting solution concentrated. Purification was performed by column chromatography (SiO₂, 10-40% EtOAc in pentane) to afford benzyl butynylamine (**2a**) as a straw yellow oil (3.4g, 21 mmol, 74% yield). Further purification could be achieved by Kugelrohr distillation (86 °C at 5x10⁻¹ mbar).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.21 (m, 5H, ArH), 3.86 (s, 2H, ArCH₂), 3.38 (q, *J* = 2.4 Hz, 2H, CH₂C≡C), 1.85 (t, *J* = 2.4 Hz, 3H, CH₃), 1.57 (bs, 1H NH).

¹³C NMR (101 MHz, Chloroform-*d*) δ 139.7, 128.4, 128.3, 127.0, 79.1, 77.1, 52.5, 37.8, 3.5.

Spectra data was consistent with the values reported in literature.²

N-(4-methoxybenzyl)but-2-yn-1-amine (1b)

A solution of 4-methoxy benzyl amine (6.3 g, 48 mmol, 5 equiv.) in DCM (15 mL) at 0 °C was stirred vigorously while a solution of bromo-2-butyne (1.2 g, 9.1 mmol, 1 equiv.) in DCM (15 mL) was slowly added over a period of 10 minutes. After complete addition, the reaction mixture was allowed to warm to room temperature and stirring continued for 5 hours. It was then filtered through silica gel eluting with 40% EtOAc in pentane and the resulting solution concentrated. Purification was performed by column chromatography (SiO₂, 10-40% EtOAc in pentane) to afford N-(4-methoxybenzyl)but-2-yn-1-amine (**2b**) as a straw yellow oil (1.0 g, 5.3 mmol, 60% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.24 (m, 2H, ArH), 6.90 – 6.84 (m, 2H, ArH), 3.81 (s, 2H, ArCH₂), 3.80 (s, 3H, OCH₃), 3.37 (dq, *J* = 3.4, 2.1 Hz, 2H, CH₂C≡C), 1.85 (dd, *J* = 2.8, 1.9 Hz, 3H, CH₃).

¹³C NMR (101 MHz, Chloroform-*d*) δ 158.6, 131.8, 129.5, 113.7, 79.1, 77.2, 55.2, 51.9, 37.7, 3.5.

HRMS (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₁₂H₁₆NO⁺ 190.1226; Found 190.1225.

Ferrocenylmethyl-but-2-ynylamine (6)

A solution of ferrocenecarboxaldehyde (3.3 g, 15 mmol, 1 equiv) and allylamine (0.97 g, 17 mmol, 1.1 equiv.) in methanol (66 mL) was stirred at room temperature for 30 minutes before the reaction mixture was cooled to 0 °C by an ice bath. NaBH₄ (700 mg, 18.5 mmol, 1.2 equiv.) was carefully added and the reaction mixture was stirred for a further 20 minutes before it was warmed to room temperature for 4 hours. The reaction was diluted with EtOAc (30 mL) and the organic layer washed with saturated NaHCO₃ solution (30 mL). The aqueous layer was washed with additional EtOAc (2 x 30 mL). The combined organic portions were washed with brine (30 mL), dried over MgSO₄, filtered and concentrated. To the crude material was added pentane (100 mL) causing precipitation of solid which was filtered off to afford ferrocenylmethyl allylamine (**6**) as a brown solid (3.7 g, 14, 93% yield) which was sufficiently pure to be used without further purification.

¹H NMR (400 MHz, Chloroform-*d*) δ 5.92 (ddt, *J* = 17.2, 10.3, 6.0 Hz, 1H, CH=CH₂), 5.19 (dq, *J* = 17.2, 1.7 Hz, 1H, CH=CH₂), 5.11 (dq, *J* = 10.2, 1.4 Hz, 1H, CH=CH₂), 4.22 – 4.07 (m, 9H, ferroceneH), 3.51 (s, 2H, ferroceneCH₂), 3.28 (dt, *J* = 6.0, 1.4 Hz, 2H, CH₃).

Spectra data was consistent with the values reported in literature.³

Ferrocenylmethyl-but-2-ynylamine (2c)

To a solution of Ferrocenylmethyl allylamine (**6**) (0.65 g, 2.5 mmol, 1 equiv.) in MeCN (12 mL) was added bromobutyne (0.24 mL, 2.8 mmol, 1.1 equiv.) TBAB (0.16 g, 0.51 mmol, 20 mol%) and K₂CO₃ (0.70 g, 5.1 mmol, 2 equiv.). The reaction mixture was heated to 55 °C and left to stir over night. It was then filtered through a short pad of Celite, which was washed with EtOAc and the filtrate concentrated under reduced pressure. The crude material was dry loaded onto SiO₂ and purified by column chromatography (SiO₂, 5-15% EtOAc in pentane) to afford N-allyl-N-Ferrocenylmethyl-but-2-yn-1-amine as a dark orange oil (0.49 g, 1.6 mmol, 62% yield)

¹H NMR (400 MHz, Chloroform-*d*) δ 5.83 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H, CH=CH₂), 5.23 (dq, *J* = 17.2, 1.6 Hz, 1H, CH=CH₂), 5.15 (ddt, *J* = 10.1, 2.2, 1.2 Hz, 1H, CH=CH₂), 4.24 – 4.07 (m, 9H, ferroceneH), 3.47 (s, 2H, ferroceneCH₂), 3.20 (q, *J* = 2.3 Hz, 2H, NCH₂C≡C), 3.08 (dt, *J* = 6.6, 1.4 Hz, 2H, NCH₂CHCH₂), 1.88 (t, *J* = 2.4 Hz, 3H, CH₃).

¹³C NMR (101 MHz, CDCl₃) δ 135.9, 117.7, 83.0, 80.6, 74.0, 70.1, 68.5, 68.0, 56.4, 52.3, 41.4, 3.6.

IR (cm⁻¹) 3087 (m), 2920 (m), 2811 (m), 1645 (m), 1431 (m), 1330 (m), 1107 (s), 1000 (s), 922 (s), 819 (s)

HRMS (APCI/QTOF) *m/z*: [M]⁺ Calcd for C₁₈H₂₁FeN⁺ 307.1018; Found 307.1025.

The tertiary amine obtained from the previous step (0.45 g, 1.5 mmol, 1 equiv.) was added to a solution of Pd(PPh₃)₄ (34 mg, 29 μmol, 2 mol%) and 1,3-dimethylbarbituric acid (0.34 g, 2.2 mmol, 1.5 equiv.) in DCM (10 mL) under an N₂ atmosphere. The reaction mixture was stirred at room temperature for 6 hours. Reaction completion was checked by TLC (2 % EtOAc in pentane). The reaction mixture was diluted with ether (40 mL) and washed with sat. NaHCO₃ (3 x 15 mL). The organic layer was extracted with aq. HCl (1.0 M; 3 x 15 mL) after which the combined aqueous layers and any precipitated solids were basified with

K₂CO₃ (pH >7) and extracted with DCM (3 x 20 mL). The combined extracts were dried over MgSO₄, filtered and concentrated by rotary evaporation. The collected crude product was sufficiently pure to be used without any further purification. Ferrocenylmethyl-but-2-ynylamine (**2c**) was obtained as a dark brown oil (0.37 g, 1.4 mmol, 94% yield)

¹H NMR (400 MHz, Chloroform-*d*) δ 4.22 – 4.09 (m, 9H, ferroceneH), 3.57 (s, 2H, ferroceneCH₂), 3.39 (q, *J* = 2.4 Hz, 2H, NCH₂C≡C), 1.85 (t, *J* = 2.4 Hz, 3H, CH₃).

¹³C NMR (101 MHz, Chloroform-*d*) δ 86.0, 79.1, 68.4, 68.3, 67.8, 47.4, 37.9, 3.5.

HRMS (ESI/QTOF) *m/z*: [M]⁺ Calcd for C₁₅H₁₇FeN⁺ 267.0705; Found 267.0706.

N-Benzyl 4-phenyl-but-2-ynylamine (2d)

Following an adapted version of a reported procedure.² To a solution of CuBr (0.18 g, 1.3 mmol, 12 mol%) in MeCN (60 mL) was added allyl benzylamine (1.9 g, 13 mmol, 1.3 equiv), formaldehyde (2.5 mL, 33 mmol 36% aq. solution, 3.1 equiv) and phenylpropyne (1.2 g, 10 mmol, 1 equiv.). The reaction mixture was stirred at room temperature for 16 hours after which it was concentrated by rotary evaporation. The residue was diluted with Et₂O (20 mL) and washed with aq. NaOH solution (5.0 M, 3 x 10 mL), dried over MgSO₄, filtered and concentrated by rotary evaporation. Purification of the crude product by column chromatography (SiO₂, 0-2% EtOAc in pentane) to afford N-allyl-N-benzyl-4-phenyl-but-2-ynylamine as a colourless oil (2.6 g, 9.3 mmol, 89% yield)

¹H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.28 (m, 10H, ArH), 5.97 (dddd, *J* = 17.3, 12.4, 6.5, 2.3 Hz, 1H, CH=CH₂), 5.34 (dq, *J* = 17.2, 1.7 Hz, 1H, CH=CH₂), 5.24 (dq, *J* = 10.4, 1.6 Hz, 1H, CH=CH₂), 3.79 – 3.73 (m, 4H, ArCH₂N, CH₂CH=CH₂), 3.44 (q, *J* = 2.5 Hz, 2H, C≡CCH₂Ph), 3.27 (dt, *J* = 6.6, 1.6 Hz, 2H, NCH₂C≡C).

¹³C NMR (101 MHz, Chloroform-*d*) δ 138.7, 137.1, 135.7, 129.1, 128.4, 128.2, 127.8, 127.0, 126.5, 117.8, 82.9, 77.0, 57.3, 56.7, 41.8, 25.1.

The tertiary amine obtained from the previous step (1.0 g, 3.6 mmol, 1 equiv.) was added to a solution of Pd(PPh₃)₄ (84 mg, 73 μmol, 2 mol%) and 1,3-dimethylbarbituric acid (0.85 g, 5.5 mmol, 1.5 equiv.) in DCM (22 mL) under an N₂ atmosphere. The reaction mixture was stirred at room temperature for 6 hours. Reaction completion was checked by TLC (2 % EtOAc in pentane). The reaction mixture was diluted with ether (40 mL) and washed with sat. NaHCO₃ (3 x 15 mL). The organic layer was extracted with aq. HCl (1.0 M; 3 x 15 mL) after which the combined aqueous layers and any precipitated solids were basified with K₂CO₃ (pH >7) and extracted with DCM (3 x 25 mL). The combined extracts were dried over MgSO₄, filtered and concentrated by rotary evaporation. Purification by flash column chromatography (SiO₂, 20-30 %

EtOAc in pentane) to afford N-benzyl-4-phenyl-but-2-ynylamine (**2d**) as a straw coloured oil (0.76 g, 3.0 mmol, 83% yield)

^1H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.20 (m, 10H, ArH), 3.90 (s, 2H, ArCH₂N), 3.65 (t, *J* = 2.3 Hz, 2H, C $\equiv$ CCH₂Ph), 3.48 (t, *J* = 2.3 Hz, 2H, NCH₂C $\equiv$ C), 1.65 (bs, 1H, NH).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.5, 137.0, 128.5, 128.4 (2C), 127.9, 127.1, 126.6, 81.4, 80.2, 52.5, 37.9, 25.2.

IR (cm⁻¹) 3025 (s), 3063 (s), 2919 (s), 2838 (s), 1606 (s), 1496 (s), 1454 (s), 728 (s), 695 (s)

HRMS (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₁₇H₁₈N⁺ 236.1434; Found 236.1436.

Spectra data was consistent with the values reported in literature.⁴

N-Benzyl 3-cyclopropyl-prop-2-ynylamine (2e)

Following an adapted version of a reported procedure.² To a solution of CuBr (0.36 g, 2.5 mmol, 12 mol%) in MeCN (130 mL) was added allyl benzylamine (3.9 mL, 25 mmol, 1.3 equiv), formaldehyde (36% aq. solution; 5.0 mL, 65 mmol, 3.3 equiv.) and ethynylcyclopropane (1.7 mL, 20 mmol, 1 equiv.). The reaction was stirred at room temperature for 16 hours before being concentrated by rotary evaporation. The resulting residue was diluted with Et₂O (20 mL) and washed with aq. NaOH (5.0 M; 3 x 10 mL), dried over MgSO₄, filtered and concentrated by rotary evaporation. Purification of the crude material by column chromatography (SiO₂, 0-2% EtOAc in pentane) afforded N-allyl-N-benzyl 3-cyclopropyl-prop-2-ynylamine as a colourless oil (4.0 g, 18 mmol, 89% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.19 (m, 5H, ArH), 5.88 (ddt, *J* = 16.8, 10.1, 6.5 Hz, 1H, CH=CH₂), 5.25 (dq, *J* = 17.2, 1.6 Hz, 1H, CH=CH₂), 5.16 (ddt, *J* = 10.1, 2.2, 1.2 Hz, 1H, CH=CH₂), 3.61 (s, 2H, ArCH₂), 3.24 (d, *J* = 1.9 Hz, 2H, CH₂C $\equiv$ C), 3.14 (dt, *J* = 6.5, 1.3 Hz, 2H, CH₂C=C), 1.28 (dddd, *J* = 10.1, 8.6, 5.0, 2.5 Hz, 1H, CH cyclopropane), 0.81 – 0.75 (m, 2H, CH₂ cyclopropane), 0.70 – 0.66 (m, 2H, CH₂ cyclopropane).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.7, 135.8, 129.2, 128.2, 127.0, 117.8, 88.9, 69.8, 57.2, 56.6, 41.8, 8.3, -0.5.

Under a nitrogen atmosphere, the tertiary amine obtained from the previous step (1.0 g, 4.4 mmol, 1.0 equiv.) was added to a solution of Pd(PPh₃)₄ (0.10 g, 89 μ mol, 2 mol%) and 1,3-dimethylbarbituric acid (1.0 g, 6.7 mmol, 1.5 equiv.) in DCM (22 mL). The reaction mixture was stirred at room temperature for 6 hours. The mixture was then diluted with Et₂O (50 mL), washed with sat. aq. NaHCO₃ (3 x 20 mL) and then extracted with 1M HCl (3 x 20 mL). The combined aqueous layers were basified with K₂CO₃ (until pH >7) and then extracted with DCM (3 x 20 mL) after which the combined organic layers were dried over MgSO₄, filtered and concentrated by rotary evaporation. The crude material was purified by column chromatography (SiO₂, 20-30% EtOAc in pentane) to afford N-benzyl 3-cyclopropyl-prop-2-ynylamine (**2e**) as a lightly straw coloured oil (0.82 g, 4.4 mmol, 99% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.19 (m, 5H, ArH), 3.84 (s, 2H, ArCH₂), 3.2 Hz, 1H, CH cyclopropane), 0.80 – 0.63 (m, 4H, CH₂ cyclopropane).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.7, 128.4 (2C), 127.0, 87.0, 73.3, 52.5, 37.9, 8.1, -0.5.

Spectra data was consistent with the values reported in literature.²

N-Benzyl 4,4-dimethyl-pent-2-ynylamine (2f)

Into an oven dried microwave vial containing a stirring bar was weighed $\text{Y}(\text{N}(\text{TMS})_2)_3$ (0.11 g, 0.20 mmol, 10 mol%). Dry toluene (degassed; 13 mL), N-Benzyl but-2-ynylamine (**2a**) (0.32 g, 2.0 mmol, 1 equiv.) and 3,3-dimethylbut-1-yn-3-ol (0.66 g, 8.0 mmol, 4 equiv.) were added. The reaction mixture was stirred at 130 °C for 24 hours, after which, the reaction mixture was cooled to room temperature, and was loaded directly onto silica for purification by column chromatography (SiO₂, 5:5:90-5:10:85 Ultra and EtOAc in pentane), which afforded N-benzyl 4,4-dimethyl-pent-2-ynylamine (**2f**) as a straw yellow oil (0.27 g, 1.3 mmol, 66% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.21 (m, 5H, ArH), 3.87 (s, 2H, ArCH₂), 3.40 (s, 2H, CH₂C≡C), 1.88 (bs, 1H, NH), 1.24 (s, 9H, C(CH₃)₃).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.4, 128.5, 128.4, 127.1, 92.8, 77.2, 52.2, 37.7, 31.2, 27.4.

Spectra data was consistent with the values reported in literature.²

N-benzyl-3-phenylprop-2-yn-1-amine (2g)

Following an adapted version of a reported procedure.² To a solution of CuBr (0.20 g, 1.4 mmol, 12 mol%) in MeCN (70 mL) was added allyl benzylamine (2.0 g, 14 mmol, 1.3 equiv.), formaldehyde (2.5 mL, 33 mmol 36% aq. solution, 3 equiv.) and phenylpropyne (1.2 g, 11 mmol, 1 equiv.). The reaction mixture was stirred at room temperature for 16 hours, after which it was concentrated by rotary evaporation. The residue was diluted with Et₂O (20 mL) and washed with aq. NaOH solution (5.0 M; 3 x 10 mL), dried over MgSO₄, filtered and concentrated by rotary evaporation. Purification of the crude product by column chromatography (SiO₂, 0-2% EtOAc in pentane) to afford N-allyl-N-methyl-4-phenyl-but-2-ynylamine as a colourless oil (2.7 g, 10.3 mmol, 95% yield)

^1H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.22 (m, 10H, ArH), 5.93 (ddt, J = 16.7, 10.1, 6.5 Hz, 1H, CH=CH₂), 5.31 (dq, J = 17.1, 1.6 Hz, 1H, CH=CH₂), 5.20 (ddt, J = 10.1, 2.2, 1.2 Hz, 1H, CH=CH₂), 3.72 (s, 2H, ArCH₂), 3.53 (s, 2H, CH₂C≡C), 3.26 (dt, J = 6.5, 1.4 Hz, 2H, 2H, CH₂C=C).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.7, 135.7, 131.7, 129.2, 128.3, 128.3, 128.0, 127.1, 123.4, 118.0, 85.7, 84.4, 57.4, 56.8, 42.1.

The tertiary amine obtained from the previous step (1.5 g, 5.7 mmol, 1 equiv.) was added to a solution of $\text{Pd}(\text{PPh}_3)_4$ (0.13 g, 0.12 mol, 2 mol%) and 1,3-dimethylbarbituric acid (1.3 g, 8.6 mmol, 1.5 equiv.) in DCM (35 mL) under an N_2 atmosphere. The reaction mixture was stirred at room temperature for 6 hours. Reaction completion was checked by TLC (20 % EtOAc in pentane). The reaction mixture was concentrated to a quarter of its original volume and diluted with ether (50 mL) and washed with sat. NaHCO_3 (3 x 15 mL). The organic layer was extracted with aq. HCl (1.0 M; 3 x 15 mL) after which the combined aqueous layers and precipitated solids were basified with K_2CO_3 (pH >7) and extracted with DCM (3 x 25 mL). The combined extracts were dried over MgSO_4 , filtered and concentrated by rotary evaporation. Purification by flash column chromatography (SiO_2 , 10-30 % EtOAc in pentane) to afford N-benzyl-3-phenylprop-2-yn-1-amine (**2g**) as a straw yellow oil (1.1 g, 5.0 mmol, 87% yield)

^1H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.20 (m, 10H, ArH), 3.96 (s, 2H, ArCH_2), 3.66 (s, 2H, $\text{CH}_2\text{C}\equiv\text{C}$), 1.73 (bs, 1H, NH).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.5, 131.7, 128.5 (2C), 128.3, 128.1, 127.2, 123.2, 87.5, 83.8, 52.5, 38.3.

Spectra data was consistent with the values reported in literature.²

N-Methyl 4-phenyl-but-2-ynylamine (2h)

Following an adapted version of a reported procedure.² To a solution of CuBr (0.20 g, 1.4 mmol, 13 mol%) in MeCN (70 mL) was added allyl methylamine (0.98 g, 14 mmol, 1.3 equiv.), formaldehyde (2.5 mL, 33 mmol 36% aq. solution, 3 equiv.) and phenylpropyne (1.2 g, 11 mmol, 1 equiv.). The reaction mixture was stirred at room temperature for 16 hours after which it was concentrated by rotary evaporation. The residue was diluted with Et_2O (20 mL) and washed with aq. NaOH solution (5.0 M; 3 x 10 mL), dried over MgSO_4 , filtered and concentrated by rotary evaporation. Purification of the crude product by column chromatography (SiO_2 , 0-2% EtOAc in pentane) to afford N-allyl-N-benzyl-4-phenyl-but-2-ynylamine as a colourless oil (1.8 g, 9.7 mmol, 88% yield)

^1H NMR (400 MHz, Chloroform-*d*) δ 7.44 (dd, J = 6.7, 3.0 Hz, 2H, ArH), 7.36 – 7.26 (m, 3H, ArH), 5.91 (ddt, J = 16.9, 10.3, 6.7 Hz, 1H, $\text{CH}=\text{CH}_2$), 5.32 – 5.18 (m, 2H, $\text{CH}=\text{CH}_2$), 3.59 (s, 2H, $\text{CH}_2\text{C}\equiv\text{C}$), 3.18 (d, J = 6.6 Hz, 2H, $\text{CH}_2\text{C}=\text{C}$), 2.42 (s, 3H, CH_3).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.7, 131.7, 128.3, 128.1, 123.0, 118.7, 85.8, 83.7, 59.0, 45.8, 41.5.

The tertiary amine obtained from the previous step (1.0 g, 3.6 mmol, 1 equiv.) was added to a solution of $\text{Pd}(\text{PPh}_3)_4$ (0.37 g, 0.32 mol, 6 mol%) and 1,3-dimethylbarbituric acid (1.7 g, 11 mmol, 2 equiv.) in DCM (50 mL) under an N_2 atmosphere. The reaction mixture was stirred at room temperature for 6 hours. Reaction completion was checked by TLC (20 % EtOAc in pentane). The reaction mixture was concentrated to a quarter of its original volume and diluted with ether (40 mL) and washed with sat. NaHCO_3 (3 x 15 mL). The organic layer was extracted with aq. HCl (1.0 M; 3 x 15 mL) after which the combined aqueous layers and any precipitated solids were basified with K_2CO_3 (pH >7) and extracted with DCM (3 x 25 mL). The combined extracts were dried over MgSO_4 , filtered and concentrated by rotary evaporation. Purification by flash column chromatography (SiO_2 , 20-50 % EtOAc in pentane) to afford N-methyl-3-phenylprop-2-yn-1-amine (**2h**) as an orange viscous oil (0.46 g, 3.1 mmol, 58% yield)

^1H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.41 (m, 2H, ArH), 7.33 (m, 3H, ArH), 3.68 (s, 2H, $\text{NCH}_2\text{C}\equiv\text{C}$), 3.16 (s, 1H, NH), 2.59 (s, 3H, CH_3).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 131.7, 128.3, 128.1, 123.0, 86.5, 84.1, 40.5, 34.9.

Spectra data was consistent with the values reported in literature.²

N-Benzyl propargylamine (7)

A solution of benzyl amine (9.8 g, 92 mmol, 4 equiv.) in DCM (15 mL) at 0 °C was stirred vigorously while a solution of bromopropyne (2.5 mL, 23 mmol, 80%wt in toluene, 1 equiv.) in DCM (10 mL) was slowly added over 10 min. After complete addition, the reaction mixture was warmed to room temperature and stirred for 5 hours. It was then filtered through silica gel washing with 40% EtOAc in pentane and the resulting solution concentrated. Purification was performed by column chromatography (SiO_2 , 10-40% EtOAc in pentane) followed by distillation (70 °C at 5×10^{-1} mbar) to obtain pure benzyl propargylamine (**7**) as a clear straw yellow oil (2.2 g, 15 mmol, 68% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.22 (m, 5H, ArH), 3.90 (s, 2H, CH_2Ar), 3.44 (d, J = 2.4 Hz, 2H, $\text{CH}_2\text{C}\equiv\text{C}$), 2.27 (t, J = 2.4 Hz, 1H, $\text{C}\equiv\text{CH}$), 1.85 (bs, 1H, NH).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.1, 128.4, 128.4, 127.2, 81.8, 71.7, 52.2, 37.3.

Spectra data was consistent with the values reported in literature.⁵

N-Benzyl-3-(4-methoxyphenyl)prop-2-yn-1-amine (2i)

Following a modified version of a reported procedure.⁶ To a stirred solution of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (90 mg, 0.13 mmol, 5 mol%), dppf (86 mg, 0.16 mmol, 6 mol%), CuI (25 mg, 0.13 mmol, 5 mol%), DABCO (0.76 g, 6.8

mmol, 2.6 equiv.) and 4-iodo-anisole (0.79 g, 6.4 mmol, 1.3 mmol) in DMSO (10 mL; degassed by bubbling N₂) under a N₂ atmosphere was added N-Benzyl propargylamine (**7**) (0.38 g, 2.6 mmol, 1.0 equiv.). The reaction mixture was heated to 60 °C and stirred for 6 hours. The progress of the reaction was determined by TLC (30 % EtOAc in pentane). The reaction was then quenched by the addition of H₂O (10 mL) and the mixture diluted with EtOAc (12 mL). The layers were separated and the aqueous layer extracted with EtOAc (2 x 12 mL). The combined organic layers were washed with brine (2 x 24 mL), dried over MgSO₄, which was then filtered through a pad of SiO₂ (washed with EtOAc), and the filtrate was concentrated under rotary evaporation. The crude material was dry-loaded onto SiO₂ and purified by column chromatography (SiO₂, 15-30% EtOAc in pentane) afforded N-benzyl-3-(4-methoxyphenyl)prop-2-yn-1-amine (**2i**) as a light orange solid (0.28 g, 1.1 mmol, 43 % yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.23 (m, 7H, ArH), 6.87 – 6.81 (m, 2H, ArH), 3.95 (s, 2H, ArCH₂), 3.81 (s, 3H, CH₃), 3.64 (s, 2H, CH₂C≡C), 1.64 (bs, 1H, NH).

¹³C NMR (101 MHz, Chloroform-*d*) δ 159.4, 139.6, 133.0, 128.4 (2C), 127.1, 115.3, 113.9, 86.0, 83.5, 55.3, 52.5, 38.3.

Spectra data was consistent with the values reported in literature.⁶

N-Benzyl-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-amine (2j**)**

Following a modified version of a reported procedure.⁶ To a stirred solution of Pd(PPh₃)₂Cl₂ (90 mg, 0.13 mmol, 5 mol%), dppf (86 mg, 0.16 mmol, 6 mol%), CuI (25 mg, 0.13 mmol, 5 mol%), DABCO (0.76 g, 6.8 mmol, 2.6 equiv.) and 4-trifluoro-iodobenzene (0.92 g, 3.4 mmol, 1.3 equiv.) in DMSO (10 mL; degassed by bubbling N₂) under a N₂ atmosphere was added N-Benzyl propargylamine (**7**) (0.38 g, 2.6 mmol, 1.0 equiv.). The reaction mixture was heated to 60 °C and stirred for 6 hours. The progress of the reaction was determined by TLC (30 % EtOAc in pentane). The reaction was then quenched by the addition of H₂O (10 mL) and the mixture diluted with EtOAc (12 mL). The layers were separated and the aqueous layer extracted with EtOAc (2 x 12 mL). The combined organic layers were washed with brine (2 x 24 mL), dried over MgSO₄, which was then filtered through a pad of SiO₂ (washed with EtOAc), and the filtrate was concentrated under rotary evaporation. The crude material was dry-loaded onto SiO₂ and purified by column chromatography (SiO₂, 10-20% EtOAc in pentane) afforded N-benzyl-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-amine (**2j**) as a dark orange oil (0.55 g, 1.9 mmol, 72 % yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.24 (m, 9H, ArH), 3.95 (s, 2H, ArCH₂), 3.67 (s, 2H, CH₂C≡C), 1.76 (bs, 1H, NH).

¹³C NMR (101 MHz, Chloroform-*d*) δ 139.3, 131.9, 129.8 (q, *J* = 32.7 Hz), 128.5, 128.4, 127.2, 127.0, 125.2 (q, *J* = 3.9 Hz), 123.91 (q, *J* = 272.2 Hz), 90.2, 82.5, 52.6, 38.2.

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -63.2.

Spectra data was consistent with the values reported in literature.⁶

N-Benzyl Propynyl trifluoroacetamide (8)

Following a modified version of a reported procedure.⁷ In a flame dried round bottom flask, to a solution ethyl trifluoroacetate (8.0 g, 56 mmol, 1.2 equiv.) in THF (12 mL) at $0\text{ }^\circ\text{C}$ was slowly added propargylamine (2.6 g, 47 mmol, 1 equiv.). The reaction mixture was stirred at this temperature for 10 minutes; it was then allowed to warm to room temperature and stirred for a further 7 hours. The solvent was removed by rotary evaporation and the product was isolated by distillation ($90\text{ }^\circ\text{C}$ at 17 mbar) to afford propynyl trifluoroacetamide a colourless oil (5.5 g, 37 mmol, 78% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 6.94 (bs, 1H, NH), 4.14 (dd, $J = 6.0, 2.5$ Hz, 2H, $\text{CH}_2\text{C}\equiv\text{C}$), 2.32 (q, $J = 2.2$ Hz, 1H, $\text{C}\equiv\text{CH}$).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.0 (q, $J = 38.1$ Hz), 115.5 (q, $J = 287.5$ Hz), 77.0, 73.1, 29.6.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -76.3.

Spectra data was consistent with the values reported in literature.⁷

To a mixture of K_2CO_3 (8.2 g, 59 mmol, 2 equiv.) and TBAB (0.95 g, 3.0 mmol, 0.1 equiv.) in MeCN (150 mL) was added propynyl trifluoroacetamide (4.5 g, 30 mmol, 1 equiv.) and benzyl bromide (6.0 g, 33 mmol, 1.1 equiv.) after which the reaction mixture was stirred at $60\text{ }^\circ\text{C}$. After 3 hours (progress determined by TLC (SiO_2 , 20% EtOAc in pentane)), the mixture was filtered through a plug of Celite, which was washed with Et_2O . The resulting filtrate was concentrated by rotary evaporation. Purification of the crude product by column chromatography (SiO_2 , 0-8% EtOAc in Pent) to afforded N-Benzyl propynyl trifluoroacetamide (**8**) as a colourless oil (5.0 g, 21 mmol, 71% yield)

^1H NMR (400 MHz, Chloroform-*d*; 1:1.2 mixture of rotamers) δ 7.46 – 7.23 (m, 5H, ArH), 4.79 (s, 2H, CH_2Ar), 4.77 (s, 2H, CH_2Ar), 4.12 (d, $J = 2.5$ Hz, 2H, $\text{CH}_2\text{C}\equiv\text{C}$), 4.06 (d, $J = 2.4$ Hz, 2H, $\text{CH}_2\text{C}\equiv\text{C}$), 2.37 (t, $J = 2.4$ Hz, 1H, $\text{C}\equiv\text{CH}$), 2.29 (t, $J = 2.5$ Hz, 1H, $\text{C}\equiv\text{CH}$).

^{13}C NMR (101 MHz, Chloroform-*d*; 1:1.2 mixture of rotamers) δ 156.7 (q, $J = 36.5$ Hz), 134.5, 133.8, 129.1, 129.0, 128.6, 128.6, 128.3, 127.7, 116.4 (q, $J = 287.9$ Hz), 116.3 (q, $J = 288.1$ Hz), 76.6 (overlapping with solvent), 76.5, 73.7, 73.3, 49.7 (q, $J = 3.6$ Hz), 48.7, 35.8 (q, $J = 4.2$ Hz), 34.4.

^{19}F NMR (376 MHz, Chloroform-*d*; 1:1.2 mixture of rotamers) δ -68.5, -69.3.

HRMS (LTQ-Orbitrap) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{12}\text{H}_{11}\text{F}_3\text{NO}^+$ 242.0787; Found 242.0783.

N-benzyl-3-(3-bromophenyl)prop-2-yn-1-amine (2k)

Following a modified version of a reported procedure.⁸ To a solution of **8** (0.80 g, 3.3 mmol, 1 equiv.), 1-bromo-3-iodobenzene (0.95 g, 3.4 mmol, 1.01 equiv.) and Et_3N (2.3 mL, 17 mmol, 5 equiv.) in acetonitrile (30 mL) was added $\text{PdCl}_2(\text{PPh}_3)_2$ (47 mg, 66 μmol , 2 mol%) and CuI (13 mg, 66 μmol , 2 mol%) in a single portion. The resulting mixture was allowed to stir for 7 hours at 60 °C. Water (20 mL) was added and the reaction mixture extracted with EtOAc (3 x 30 mL); the combined organic extracts were dried over MgSO_4 , filtered and concentrated by rotary evaporation. The crude material was purified by flash column chromatography (SiO_2 , 0-5% EtOAc in pentane) afforded N-benzyl-N-(3-(3-bromophenyl)prop-2-yn-1-yl)-2,2,2-trifluoroacetamide as a yellow oil (1.2 g, 3.04 mmol, 92% yield)

^1H NMR (400 MHz, CHCl_3 - d ; 1:1.2 mixture of rotamers) δ 7.54 (t, J = 1.8 Hz, 1H, ArH), 7.48 (dddd, J = 7.9, 6.7, 2.0, 1.1 Hz, 1H, ArH), 7.44 – 7.29 (m, 6H, ArH), 7.20 (td, J = 7.9, 5.4 Hz, 1H, ArH), 4.83 (s, 1H, ArCH_2), 4.81 (s, 1H, ArCH_2), 4.33 (s, 1H, $\text{CH}_2\text{C}\equiv\text{C}$), 4.30 (s, 1H, $\text{CH}_2\text{C}\equiv\text{C}$).

^{13}C NMR (101 MHz, CHCl_3 - d ; 1:1.2 mixture of rotamers, some unresolved peaks) δ 134.7, 134.6, 134.6, 133.9, 132.1, 131.9, 130.4, 130.3, 129.8, 129.8, 129.1, 129.0, 128.6, 128.4, 127.7, 124.1, 123.8, 122.2, 122.1, 83.8, 83.5, 83.3, 83.1, 50.1, 49.3, 36.8, 35.4.

Following an adapted version of a reported procedure.⁹ To the trifluoroacetamide obtained from the previous step (0.84 g, 2.4 mmol, 1 equiv.) was added a solution of KOH (0.50 g, 9.0 mmol, 3.0 equiv.) in water (15 mL) and methanol (15 mL) and the resulting mixture was heated to 60 °C for 3 hours. The reaction was then cooled to room temperature and acidified with aq. HCl (1.0 M; 5 mL) followed by basification with sat. aq. NaHCO_3 (pH >7). The resulting mixture was extracted with DCM (3 x 10 mL), dried over MgSO_4 , filtered and concentrated by rotary evaporation. Purification by column chromatography (SiO_2 , 10-30% EtOAc in pentane) afforded N-benzyl-3-(3-bromophenyl)prop-2-yn-1-amine (**2k**) as a light yellow oil (0.80 g, 2.7 mmol, 88% yield)

^1H NMR (400 MHz, CHCl_3 - d) δ 7.59 (t, J = 1.7 Hz, 1H, ArH), 7.45 (ddd, J = 8.0, 2.1, 1.1 Hz, 1H, ArH), 7.43 – 7.24 (m, 6H, ArH), 7.18 (t, J = 7.9 Hz, 1H, ArH), 3.96 (s, 2H, ArCH_2), 3.66 (s, 2H, $\text{CH}_2\text{C}\equiv\text{C}$), 2.37 (s, 1H, NH).

^{13}C NMR (101 MHz, CHCl_3 - d) δ 138.7, 134.4, 131.3, 130.2, 129.7, 128.5, 128.5, 127.4, 125.1, 122.1, 88.4, 82.6, 52.3, 37.9.

HRMS (ESI/QTOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{15}^{79}\text{BrN}^+$ 300.0382; Found 300.0384.

N-Benzyl-3-(3,5-dimethylphenyl)prop-2-ynylamine (2I)

Following a modified version of a reported procedure.⁸ To a solution of $\text{PdCl}_2(\text{PPh}_3)_2$ (0.14 g, 0.20 mmol, 5 mol%), PPh_3 (0.21 g, 0.80 mmol, 20 mol%) and CuI (76 mg, 0.40 mmol, 10 mol%) in DMF (3.3 mL) and Et_3N (10 mL) was added **7** (0.97 g, 4.0 mmol, 1 equiv.) and 1-iodo-3,5-dimethylbenzene (1.1 g, 4.8 mmol, 1.2 equiv.). The resulting mixture was heated to 60 °C for 6 hours. After cooling to room temperature, water (25 mL) was added and the reaction mixture extracted with EtOAc (3 x 40 mL); the combined organic extracts were dried over MgSO_4 , filtered and concentrated by rotary evaporation. The crude material was purified by flash column chromatography (SiO_2 , 0-5% EtOAc in pentane) afforded N-benzyl-N-(3-(3,5-dimethylphenyl)prop-2-ynyl)-trifluoroacetamide as an orange oil (1.2 g, 3.6 mmol, 90% yield)

^1H NMR (400 MHz, Chloroform-*d*; mixture of rotamers) δ 7.44 – 7.29 (m, 5, CH_2ArH , both rotamers), 7.06 (m, 2H, PhH , both rotamers), 7.00 (s, 1H, PhH), 6.99 (s, 1H, PhH), 4.85 (s, 2H, ArCH_2), 4.83 (s, 2H, PhCH_2), 4.36 (s, 2H, $\text{CH}_2\text{C}\equiv\text{C}$), 4.29 (s, 1H, $\text{CH}_2\text{C}\equiv\text{C}$), 2.31 (s, 6H, CH_3), 2.30 (s, 6H, CH_3).

^{13}C NMR (101 MHz, Chloroform-*d*; mixture of rotamers, some unresolved aromatic peaks) δ 156.75 (qd, J = 36.1, 10.0 Hz), 138.0, 138.0, 134.8, 134.1, 133.8, 133.7, 130.8, 130.7, 129.5, 129.5, 129.1, 129.0, 128.7, 128.6, 128.5, 128.5, 128.3, 127.8, 121.7, 121.4, 116.5 (qd, J = 288.1, 7.9 Hz), 85.8, 85.5, 81.1, 80.9, 49.74 (q, J = 3.6 Hz), 49.0, 36.9 (q, J = 4.3 Hz), 35.4, 21.1.

HRMS (ESI/QTOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{18}\text{F}_3\text{NNaO}^+$ 368.1233; Found 368.1235.

Following an adapted version of a reported procedure.⁹ To the trifluoroacetamide obtained from the previous step (0.84 g, 2.4 mmol, 1 equiv.) was added a solution of KOH (0.15 g, 2.7 mmol, 1.3 equiv.) in water (5 mL) and methanol (5 mL) and the resulting mixture was heated to 60 °C for 2 hours. The reaction was then cooled to room temperature and acidified with aq. HCl (1.0 M; 5 mL) followed by basification with sat. aq. NaHCO_3 (pH >7). The resulting mixture was extracted with DCM (3 x 10 mL), dried over MgSO_4 , filtered and concentrated by rotary evaporation. Purification by column chromatography (SiO_2 , 10-40% EtOAc in pentane) afforded N-benzyl-3-(3,5-dimethylphenyl)prop-2-ynylamine (**2I**) as an orange oil (0.49 g, 2.0 mmol, 76% yield)

^1H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.24 (m, 5H, ArH), 7.08 (m, 2H, ArH), 6.95 (m, 1H, ArH), 3.96 (s, 2H, ArCH_2), 3.65 (s, 2H, $\text{CH}_2\text{C}\equiv\text{C}$), 2.29 (s, 6H, CH_3), 2.09 (bs, 1H, NH).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.3, 137.8, 130.0, 129.3, 128.5, 128.4, 127.2, 122.8, 86.5, 84.2, 52.3, 38.1, 21.1.

HRMS (ESI/QTOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{20}\text{N}^+$ 250.1590; Found 250.1593.

Spectra data was consistent with the values reported in literature.⁴

N-benzyl-3-(3-bromophenyl)prop-2-yn-1-amine (2m)

Following a modified version of a reported procedure.⁸ To a solution of **6** (0.50 g, 2.0 mmol, 1 equiv.) and 2-iodothiophene (0.43 g, 2.0 mmol, 1.01 equiv.) and Et_3N (1.4 mL, 10 mmol, 5 equiv.) in acetonitrile (30 mL) was added $\text{PdCl}_2(\text{PPh}_3)_2$ (36 mg, 51 μmol , 2 mol%) and CuI (12 mg, 66 μmol , 3 mol%) in a single portion. The resulting mixture was stirred at room temperature for 7 hours. Water (20 mL) was added and the reaction mixture extracted with EtOAc (3 x 30 mL); the combined organics portions were dried over MgSO_4 , filtered and concentrated by rotary evaporation. The crude material was purified by flash column chromatography (SiO_2 , 0-5% EtOAc in pentane) afforded N-benzyl-2,2,2-trifluoro-N-(3-(thiophen-2-yl)prop-2-yn-1-yl)acetamide as a yellow oil (0.58 g, 1.8 mmol, 88% yield).

^1H NMR (400 MHz, Chloroform-*d* mixture of rotamers) δ 7.44 – 7.27 (m, 6H, ArH), 7.22 (ddd, J = 4.9, 3.6, 1.2 Hz, 1H, ArH), 6.99 (td, J = 5.2, 3.6 Hz, 1H, ArH), 4.82 (d, J = 8.8 Hz, 2H, ArCH_2), 4.35 (d, J = 23.4 Hz, 2H, $\text{CH}_2\text{C}\equiv\text{C}$).

^{13}C NMR (101 MHz, Chloroform-*d* mixture of rotamers, some unresolved peaks) δ 134.7, 134.0, 133.0, 132.8, 129.1, 129.0, 128.6, 128.5, 128.3, 127.9, 127.8, 127.7, 127.1, 127.0, 122.0, 121.6, 85.9, 85.6, 78.7, 78.5, 50.0, 49.2, 37.0, 35.6.

Following an adapted version of a reported procedure.⁹ To the trifluoroacetamide obtained from the previous step (0.58 g, 1.8 mmol, 1 equiv.) was added a solution of KOH (0.30 g, 5.4 mmol, 3.0 equiv.) in water (9 mL) and methanol (9 mL) and the resulting mixture was heated to 60°C for 4 hours. The reaction was then cooled to room temperature and acidified with aq. HCl (1.0 M; 5 mL) followed by basification with sat. aq. NaHCO_3 (pH >7). The resulting mixture was extracted with DCM (3 x 10 mL), dried over MgSO_4 , filtered and concentrated by rotary evaporation. Purification by column chromatography (SiO_2 , 10-30% EtOAc in pentane) afforded N-benzyl-3-(3-bromophenyl)prop-2-yn-1-amine (**2m**) as an orange amorphous solid (0.38 g, 1.7 mmol, 93% yield)

^1H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.27 (m, 5H, ArH), 7.24 (dd, J = 5.2, 1.2 Hz, 1H, ArH), 7.20 (dd, J = 3.6, 1.1 Hz, 1H, ArH), 6.97 (dd, J = 5.2, 3.6 Hz, 1H, ArH), 3.95 (s, 2H, ArCH_2), 3.68 (s, 2H, $\text{CH}_2\text{C}\equiv\text{C}$), 3.00 (s, 1H NH).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.8, 131.8, 128.5, 128.5, 127.3, 126.9, 126.8, 123.1, 91.0, 77.3, 52.3, 38.2.

HRMS (ESI/QTOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{14}\text{NS}^+$ 228.0841; Found 228.0844.

3. Synthesis of Bromoalkyne

triisopropylsilyl bromoacetylene (**1**)

Following a reported procedure.¹⁰ triisopropylsilylacetylene (0.81 g, 4.5 mmol, 1.00 equiv.) was dissolved in acetone (30 mL). *N*-bromosuccinimide (0.93 g, 5.2 mmol, 1.16 equiv.) was added, followed by AgNO₃ (76 mg, 0.44 mmol, 0.1 equiv.). The resulting mixture was stirred at room temperature for 3 h and it was then poured onto ice. After ice being allowed to melt, the aqueous layer was extracted with pentane (3 x 30 mL). The combined organic layers were dried over MgSO₄, filtered through a plug of silica and concentrated by rotary evaporation to afford pure triisopropylsilyl bromoacetylene (**1**) as a colourless oil. (1.16 g, 4.43 mmol, 99% yield)

¹H NMR (400 MHz, Chloroform-*d*) δ 1.20-0.97 (m, 21H, TIPS).

¹³C NMR (100 MHz, Chloroform-*d*) δ 83.5, 61.7, 18.5, 11.3.

Spectra data was consistent with the values reported in literature.¹⁰

Procedure copied from previous publication from the group.¹¹

4. Optimisation of the Carbo-Oxygenation reaction.

Entry	Pd source	Ligand	Base	Solvent	T (°C)	Yield ^a	SM
1	Pd ₂ (dba) ₃ .CHCl ₃ (2.5 mol%)	DPEPhos	Cs ₂ CO ₃	DCE	60	44	14
2 ^[c]	Pd ₂ (dba) ₃ .CHCl ₃ (2.5 mol%)	DPEPhos	Cs ₂ CO ₃	DCE	60	80	0
3	Pd ₂ (dba) ₃ .CHCl ₃ (2.5 mol%)	DPEPhos	Cs ₂ CO ₃	DCE	75	40	6
4	Pd ₂ (dba) ₃ .CHCl ₃ (2.5 mol%)	DPEPhos	Li ₂ CO ₃	DCE	75	0	36
5	Pd ₂ (dba) ₃ .CHCl ₃ (2.5 mol%)	DPEPhos	Na ₂ CO ₃	DCE	75	13	31
6	Pd ₂ (dba) ₃ .CHCl ₃ (2.5 mol%)	DPEPhos	K ₂ CO ₃	DCE	75	12	
7	Pd ₂ (dba) ₃ .CHCl ₃ (2.5 mol%)	DPEPhos	Rb ₂ CO ₃	DCE	75	40	-
8	Pd ₂ (dba) ₃ .CHCl ₃ (2.5 mol%)	DPEPhos	BaCO ₃	DCE	75	0	-
9	Pd ₂ (dba) ₃ .CHCl ₃ (2.5 mol%)	DPEPhos	CaCO ₃	DCE	75	0	-
10	Pd ₂ (dba) ₃ .CHCl ₃ (2.5 mol%)	DPEPhos	NaHCO ₃	DCE	75	14	-
11	Pd ₂ (dba) ₃ .CHCl ₃ (2.5 mol%)	DPEPhos	CsHCO ₃	DCE	75	64	-
12	Pd ₂ (dba) ₃ .CHCl ₃ (2.5 mol%)	DPEPhos	CsHCO ₃	DCE	60	73	-

13	Pd ₂ (dba) ₃ .CHCl ₃ (2.5 mol%)	DCEPhos	CsHCO ₃	DCE	60	2	15
14	Pd ₂ (dba) ₃ .CHCl ₃ (2.5 mol%)	XantPhos	CsHCO ₃	DCE	60	4	50
15	Pd ₂ (dba) ₃ .CHCl ₃ (2.5 mol%)	dppf	CsHCO ₃	DCE	60	50	20
16	Pd ₂ (dba) ₃ .CHCl ₃ (2.5 mol%)	dppe	CsHCO ₃	DCE	60	8	19
17	Pd ₂ (dba) ₃ .CHCl ₃ (2.5 mol%)	RuPhos	CsHCO ₃	DCE	60	3	46
18	Pd ₂ (dba) ₃ .CHCl ₃ (2.5 mol%)	DPEPhos	CsHCO ₃	Cl-Benzene	60	21	22
19	Pd ₂ (dba) ₃ .CHCl ₃ (2.5 mol%)	DPEPhos	CsHCO ₃	CPME	60	7	31
20	Pd ₂ (dba) ₃ .CHCl ₃ (2.5 mol%)	DPEPhos	CsHCO ₃	EtOAc	60	15	27
21	Pd ₂ (dba) ₃ .CHCl ₃ (2.5 mol%)	DPEPhos	CsHCO ₃	F ₃ Toluene	60	41	5
22	Pd ₂ (dba) ₃ .CHCl ₃ (2.5 mol%)	DPEPhos	CsHCO ₃	DCM	60	50	0
23	Pd ₂ (dba) ₃ .CHCl ₃ (2.5 mol%)	DPEPhos	CsHCO ₃	CHCl ₃	60	4	4
24	Pd(OAc) ₂ . (5 mol%)	DPEPhos	CsHCO ₃	DCE	60	15	5
25	Pd(acac) ₂ . (5 mol%)	DPEPhos	CsHCO ₃	DCE	60	37	2
26	Pd(PPh ₃) ₂ Cl ₂ . (5 mol%)	DPEPhos	CsHCO ₃	DCE	60	3	3
27	Pd(dba) ₃ . (5 mol%)	DPEPhos	CsHCO ₃	DCE	60	48	50
28	Pd(DPEPhos)Cl ₂ . (5 mol%)	DPEPhos	CsHCO ₃	DCE	60	14	35
29	Pd ₂ (dba) ₃ .CHCl ₃ (2.5 mol%)	DPEPhos	CsHCO ₃	DCE	50	64	7
30	Pd ₂ (dba) ₃ .CHCl ₃ (1.25 mol%)	DPEPhos	CsHCO ₃	DCE	60	68	5
31	Pd ₂ (dba) ₃ .CHCl ₃ (2.5 mol%)	DPEPhos	CsHCO ₃ ^[b]	DCE	60	69	5
32^[c]	Pd ₂ (dba) ₃ .CHCl ₃ (2.5 mol%)	DPEPhos	CsHCO ₃	DCE	60	80	0
33^[d]	Pd ₂ (dba) ₃ .CHCl ₃ (2.5 mol%)	DPEPhos	CsHCO ₃	DCE	60	50	30
34^[e]	Pd ₂ (dba) ₃ .CHCl ₃ (2.5 mol%)	DPEPhos	CsHCO ₃	DCE	60	80 (77)	0
35	Pd(Cp)cinnamyl (5 mol%)	DPEPhos	CsHCO ₃	DCE	60	73	0
34^[f]	Pd ₂ (dba) ₃ .CHCl ₃ (2.5 mol%)	DPEPhos	CsHCO ₃	DCE	60	76	0

[a] Yields were calculated from ¹H NMR spectra by using 1,2-difluorobenzene as internal standard. [b] 1 equiv Base. [c] CO₂ balloon. [d] 0.4 mmol scale, inefficient stirring. [e] 0.4 mmol scale, effective stirring. [f] addition of 4 ÅMs.

5. Scope of the Carbo-Oxygenation Reaction.

General procedure for the carboxylation-alkynylation reaction of propargylic amines

A vial was charged with Pd₂(dba)₃.CHCl₃ (10.4 mg, 10.0 μmol, 2.5 mol%), DPEPhos (16.0 mg, 30.0 μmol, 7.5 mol%) and CsHCO₃ (155 mg, 0.520 mmol, 2.0 equiv.). The vial was sealed and purged with argon. To this was added DCE (2.0 mL) and the mixture was heated at 60 °C for 2-3 minutes, after which it took on an orange colour. Internal propargylic amine **2a-m** (0.400 mmol), and triisopropylsilyl bromoacetylene **1** (136 mg, 0.520 mmol, 1.3 equiv.) were then added directly to the reaction mixture and left to stir at 60 °C for 18-24 hours. After this time, the reaction mixture was removed from heating, cooled to room temperature, unsealed and diluted with pentane (4 mL) and passed through a small plug of silica gel (deactivated by Et₃N) rinsing with 10% EtOAc in pentane (8 mL) and concentrated by rotary evaporation. The crude material was dry-loaded onto deactivated silica gel prior to column chromatography.

(E)-3-benzyl-5-(4-(triisopropylsilyl)but-3-yn-2-ylidene)oxazolidin-2-one (**5a**)

Using **2a** (58.1 mg, 0.400 mmol). The crude product was purified by column chromatography (SiO₂; 0-3% EtOAc in pentane) afforded (E)-3-benzyl-5-(4-(triisopropylsilyl)but-3-yn-2-ylidene)oxazolidin-2-one (**5a**) as a straw yellow oil (119 mg, 0.309 mmol, 77% yield)

¹H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.24 (m, 5H, *ArH*), 4.51 (s, 2H, *ArCH*₂), 4.12 (q, *J* = 2.2 Hz, 2H, *NCH*₂*C=C*), 1.84 (t, *J* = 2.2 Hz, 3H, *CH*₃), 1.06 – 1.00 (m, 21H, *TIPS*).

¹³C NMR (101 MHz, Chloroform-*d*) δ 155.1, 148.7, 134.7, 129.0, 128.3 (2C), 104.0, 94.6, 94.4, 48.0, 48.0, 18.6, 14.7, 11.1.

IR (ν_{max}, cm⁻¹) 2942 (m), 2865 (m), 2141 (w), 1794 (s), 1686 (s), 1469 (m), 1418 (m), 1244 (m), 1081 (m), 1047 (s)

HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₂₃H₃₃NNaO₂Si⁺ 406.2173; Found 406.2168.

(E)-3-(4-methoxybenzyl)-5-(4-(triisopropylsilyl)but-3-yn-2-ylidene)oxazolidin-2-one (5b)

Using **2b** (76.0 mg, 0.400 mmol). The crude product was purified by column chromatography (SiO₂; 0-3% EtOAc in pentane) afforded (E)-3-(4-methoxybenzyl)-5-(4-(triisopropylsilyl)but-3-yn-2-ylidene)oxazolidin-2-one (**5b**) as a straw yellow oil (127 mg, 0.293 mmol, 77% yield)

¹H NMR (400 MHz, Chloroform-*d*) δ 7.20 (m, 2H, *ArH*), 6.89 (m, 2H, *ArH*), 4.42 (s, 2H, *ArCH*₂), 4.07 (q, *J* = 2.2 Hz, 2H, *NCH*₂*C=C*), 3.81 (s, 3H, *OCH*₃), 1.81 (t, *J* = 2.2 Hz, 3H, *CH*₃), 1.05 – 1.00 (m, 21H, *TIPS*).

¹³C NMR (101 MHz, Chloroform-*d*) δ 159.6, 155.0, 148.9, 129.7, 126.8, 114.3, 104.1, 94.5, 94.3, 55.3, 47.9, 47.3, 18.6, 14.6, 11.1.

IR (ν_{max}, cm⁻¹) 2946 (m), 2868 (m), 2140 (w), 1789 (s), 1686 (s), 1515 (s), 1468 (m), 1416 (m), 1248 (s), 1042 (s), 679 (s), 661 (s)

HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₂₄H₃₅NNaO₃Si⁺ 436.2278; Found 436.2291.

(E)-3-ferrocenylmethyl-5-(4-(triisopropylsilyl)but-3-yn-2-ylidene)oxazolidin-2-one (5c)

Using **2c** (107 mg, 0.400 mmol). The crude product was purified by column chromatography (SiO₂; 0-3% EtOAc in pentane) afforded (E)-3-ferrocenylmethyl-5-(4-(triisopropylsilyl)but-3-yn-2-ylidene)oxazolidin-2-one (**5c**) as an amorphous orange solid (127 mg, 0.260 mmol, 65% yield) the product was isolated with 6.5% dibenzylideneacetone which was removed upon preparative TLC (10% Et₂O in pentane).

¹H NMR (400 MHz, Chloroform-*d*) δ 4.28 (s, 2H, ferroceneCH₂), 4.17 (d, *J* = 3.7 Hz, 9H ferroceneH), 4.11 (q, *J* = 2.2 Hz, 2H, NCH₂C=C), 1.78 (t, *J* = 2.1 Hz, 3H, CH₃), 1.04 (m, *J* = 1.6 Hz, 21H, TIPS).

¹³C NMR (101 MHz, Chloroform-*d*) δ 154.6, 149.0, 104.2, 94.3, 94.1, 80.6, 69.0, 68.8, 68.7, 48.0, 43.5, 18.6, 14.5, 11.1.

IR (ν_{max}, cm⁻¹) 2943 (m), 2864 (m), 2146 (w), 1788 (s), 1772 (s), 1688 (s), 1468 (m), 1313 (m), 1245 (s), 1198 (m), 1058 (s), 665 (s)

HRMS (ESI/QTOF) *m/z*: [M]⁺ Calcd for C₂₇H₃₇FeNO₂Si⁺ 491.1937; Found 491.1939.

(E)-3-benzyl-5-(1-phenyl-4-(triisopropylsilyl)but-3-yn-2-ylidene)oxazolidin-2-one (5d)

Using **2d** (94.0 mg, 0.400 mmol). The crude product was purified by column chromatography (Et₃N-deactivated SiO₂; 0-2% EtOAc in pentane) afforded (E)-3-benzyl-5-(1-phenyl-4-(triisopropylsilyl)but-3-yn-2-ylidene)oxazolidin-2-one (**5d**) as an orange oil (110 mg, 0.239 mmol, 60% yield) [10% SM in crude NMR]

¹H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.14 (m, 10H, ArH), 4.49 (s, 2H, ArCH₂N), 4.12 (t, *J* = 1.5 Hz, 2H, NCH₂C=C), 3.51 (d, *J* = 1.5 Hz, 2H, ArCH₂C), 0.99 – 0.92 (m, 21H, TIPS).

¹³C NMR (101 MHz, Chloroform-*d*) δ 154.9, 148.7, 138.5, 134.6, 129.0, 128.9, 128.4 (2C), 128.3, 126.4, 102.8, 99.1, 96.6, 48.1, 48.0, 34.8, 18.5, 11.1.

IR (ν_{max}, cm⁻¹) 882 (s), 1045 (s), 1248 (s), 1417 (s), 1469 (s), 1672 (s), 1794 (s), 2141 (s), 2864 (s), 2941 (s)

HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₂₉H₃₇NNaO₂Si⁺ 482.2486; Found 482.2495.

(E)-3-benzyl-5-(1-cyclopropyl-3-(triisopropylsilyl)prop-2-yn-1-ylidene)oxazolidin-2-one (5e)

Using **2e** (74.0 mg, 0.400 mmol). The crude product was purified by column chromatography (SiO₂; 0-2% EtOAc in pentane) afforded (E)-3-benzyl-5-(1-cyclopropyl-3-(triisopropylsilyl)prop-2-yn-1-ylidene)oxazolidin-2-one (**5e**) as a dark orange oil (135 mg, 0.329 mmol, 82% yield)

¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.23 (m, 5H, *ArH*), 4.49 (s, 2H, *ArCH*₂), 4.12 (s, 2H, *NCH*₂C=C), 1.81 (tt, *J* = 8.0, 5.2 Hz, 1H, *CH*(-CH₂CH₂-)), 1.08 – 0.95 (m, 21H, *TIPS*), 0.76 – 0.60 (m, 4H, *CH*(-CH₂CH₂-)).

¹³C NMR (101 MHz, Chloroform-*d*) δ 155.1, 148.0, 134.7, 128.9, 128.2 (2C), 102.0, 99.3, 96.5, 48.3, 47.9, 18.5, 11.0, 8.3, 4.8.

IR (ν_{max}, cm⁻¹) 2945 (m), 2865 (m), 2150 (w), 1791 (s), 1671 (s), 1467 (m), 1419 (m), 1248 (m), 1060 (s), 1040 (s), 1000 (s)

HRMS (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₂₅H₃₆NO₂Si⁺ 410.2510; Found 410.2508.

(E)-3-benzyl-5-(1-cyclopropyl-3-(triisopropylsilyl)prop-2-yn-1-ylidene)oxazolidin-2-one (5f)

Using **2f** (81.0 mg, 0.400 mmol). The crude product was purified by column chromatography (SiO₂; 0-2% EtOAc in pentane) which afforded (E)-3-benzyl-5-(1-cyclopropyl-3-(triisopropylsilyl)prop-2-yn-1-ylidene)oxazolidin-2-one (**5f**) as a yellow oil (74.2 mg, 0.174 mmol, 44% yield)

¹H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.21 (m, 5H, *ArH*), 4.48 (s, 2H, *ArCH*₂), 4.08 (s, 2H, *NCH*₂C=C), 1.22 (s, 9H, C(CH₃)₃), 1.08 – 0.95 (m, 21H, *TIPS*).

¹³C NMR (101 MHz, Chloroform-*d*) δ 155.1, 147.6, 134.7, 129.0, 128.6, 128.4, 108.1, 103.3, 96.6, 49.6, 48.0, 33.8, 29.6, 18.6, 11.2.

IR (ν_{max}, cm⁻¹) 664 (s), 700 (s), 1041 (s), 1145 (s), 1415 (s), 1463 (s), 1650 (s), 1795 (s), 2131 (s), 2868 (s), 2958 (s)

HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₂₈H₃₅NNaO₂Si⁺ 468.2329; Found 468.2335.

(E)-3-benzyl-5-(1-phenyl-3-(triisopropylsilyl)prop-2-yn-1-ylidene)oxazolidin-2-one (5g)

Using **2g** (89.0 mg, 0.400 mmol). The crude product was purified by column chromatography (Et_3N -deactivated SiO_2 ; 0-2% EtOAc in pentane) which afforded (E)-3-benzyl-5-(1-phenyl-3-(triisopropylsilyl)prop-2-yn-1-ylidene)oxazolidin-2-one (**5g**) as a straw yellow solid (145 mg, 0.325 mmol, 81% yield). The product was isolated with 7.5% dibenzylideneacetone which was removed upon preparative TLC (10% Et_2O in pentane) to give an off-white crystalline solid, m.p. 81-82 °C.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.80 (m, 2H, ArH), 7.44 – 7.21 (m, 8H, ArH), 4.55 (s, 2H, ArCH₂), 4.31 (s, 2H, NCH₂C=C), 1.08 – 1.03 (m, 21H, TIPS)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.8, 149.2, 134.4, 132.7, 129.1, 128.5, 128.5, 128.3, 127.7, 127.5, 102.1, 99.9, 96.9, 49.7, 48.1, 18.6, 11.2.

IR (ν_{max} , cm^{-1}) 2941 (m), 2863 (m), 2140 (w), 1802 (s), 1647 (m), 1463 (m), 1417 (m), 1261 (m), 1129 (m), 1034 (s)

HRMS (ESI/QTOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{28}\text{H}_{35}\text{NNaO}_2\text{Si}^+$ 468.2329; Found 468.2335.

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(E)-3-methyl-5-(1-phenyl-3-(triisopropylsilyl)prop-2-yn-1-ylidene)oxazolidin-2-one (5h)

Using **2h** (58.0 mg, 0.400 mmol). The crude product was purified by column chromatography (Et_3N -deactivated SiO_2 ; 0-4% EtOAc in pentane) affording the named compound (E)-3-methyl-5-(1-phenyl-3-(triisopropylsilyl)prop-2-yn-1-ylidene)oxazolidin-2-one (**5h**) as an amorphous orange solid (97.9 mg, 0.265 mmol, 66% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, J = 8.0 Hz, 2H, ArH), 7.36 (t, J = 7.5 Hz, 2H, ArH), 7.26 (m, 1H, ArH), 4.49 (s, 2H, NCH₂C=C), 3.05 (s, 3H, CH₃), 1.20 – 1.07 (m, 21H, TIPS).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.0, 148.9, 132.8, 128.3, 127.7, 127.5, 102.0, 99.8, 97.0, 52.2, 30.6, 18.7, 11.2.

IR (ν_{max} , cm^{-1}) 2945 (m), 2862 (m), 2147 (w), 1808 (s), 1649 (m), 1463 (m), 1403 (m), 1269 (m), 1132 (s), 1080 (s), 1006 (s), 883 (m), 765 (m), 660 (s)

HRMS (APPI/LTQ-Orbitrap) m/z : $[M]^+$ Calcd for $C_{22}H_{31}NO_2Si^+$ 369.2119; Found 369.2116.

(E)-3-benzyl-5-(1-(4-methoxyphenyl)-3-(triisopropylsilyl)prop-2-yn-1-ylidene)oxazolidin-2-one (5i)

Using **2i** (101 mg, 0.400 mmol). The crude product was purified by column chromatography (Et_3N -deactivated SiO_2 ; 0-2% EtOAc in pentane) (E)-3-benzyl-5-(1-(4-methoxyphenyl)-3-(triisopropylsilyl)prop-2-yn-1-ylidene)oxazolidin-2-one (**5i**) as a pale amorphous orange solid (129 mg, 0.271 mmol, 68% yield).

1H NMR (400 MHz, Chloroform- d) δ 7.80 – 7.71 (m, 2H, ArH), 7.44 – 7.27 (m, 5H, ArH), 6.94 – 6.85 (m, 2H, ArH), 4.55 (s, 2H, ArCH $_2$), 4.30 (s, 2H, NCH $_2$ C=C), 3.82 (s, 3H, CH $_3$), 1.10 – 1.00 (s, 21H, TIPS).

^{13}C NMR (101 MHz, Chloroform- d) δ 158.8, 154.9, 147.7, 134.4, 129.0, 128.9, 128.5, 128.4, 125.3, 113.6, 102.3, 99.4, 96.6, 55.2, 49.6, 48.0, 18.6, 11.2.

IR (ν_{max} , cm^{-1}) 2946 (m), 2867 (m), 2143 (m), 1790 (s), 1647 (m), 1512 (s), 1249 (s), 1182 (s), 1031 (s), 836 (s)

HRMS (ESI/QTOF) m/z : $[M + Na]^+$ Calcd for $C_{29}H_{37}NNaO_3Si^+$ 498.2435; Found 498.2443.

(E)-3-benzyl-5-(1-(4-(trifluoromethyl)phenyl)-3-(triisopropylsilyl)prop-2-yn-1-ylidene)oxazolidin-2-one (5j)

Using **2j** (116 mg, 0.400 mmol). The crude product was purified by column chromatography (Et_3N -deactivated SiO_2 ; 0-2% EtOAc in pentane) (E)-3-benzyl-5-(1-(4-(trifluoromethyl)phenyl)-3-(triisopropylsilyl)prop-2-yn-1-ylidene)oxazolidin-2-one (**5j**) as a red oil (105 mg, 0.204 mmol, 51% yield).

1H NMR (400 MHz, Chloroform- d) δ 7.92 (d, J = 8.2 Hz, 2H, ArH), 7.61 (d, J = 8.3 Hz, 2H, ArH), 7.45 – 7.27 (m, 5H, ArH), 4.57 (s, 2H, ArCH $_2$), 4.33 (s, 2H, NCH $_2$ C=C), 1.07 (m, 21H, TIPS).

^{13}C NMR (101 MHz, Chloroform- d) δ 154.3, 151.0, 136.3, 134.2, 129.1, 128.6, 128.5, 127.8, 125.2 (q, J = 3.9 Hz), 124.1 (q, J = 272.0 Hz), 101.2, 98.8, 97.8, 49.8, 48.1, 18.6, 11.1. One carbon not resolved.

^{19}F NMR (376 MHz, Chloroform- d) δ -62.5.

IR ($\nu_{\max}$, cm^{-1}) 662 (s), 882 (s), 1052 (s), 1201 (s), 1247 (s), 1324 (s), 1416 (s), 1468 (s), 1686 (s), 1792 (s), 2148 (s), 2867 (s), 2940 (s)

HRMS (ESI/QTOF) m/z : $[M + \text{Na}]^+$ Calcd for $\text{C}_{29}\text{H}_{34}\text{F}_3\text{NNaO}_2\text{Si}^+$ 536.2203; Found 536.2195.

(E)-5-(1-(3-bromophenyl)-3-(triisopropylsilyl)prop-2-yn-1-ylidene)-3-phenyloxazolidin-2-one
(5k)

Following general procedure B using **2k** (120 mg, 0.400 mmol). The crude product was dry loaded onto deactivated SiO_2 and purified by column chromatography (SiO_2 ; 0-3% EtOAc in pentane) which afforded (E)-5-(1-(3-bromophenyl)-3-(triisopropylsilyl)prop-2-yn-1-ylidene)-3-phenyloxazolidin-2-one (**5k**) as a brown amorphous solid (124 mg, 0.243 mmol, 61% yield)

^1H NMR (400 MHz, Chloroform- d) δ 7.94 (t, $J = 1.9$ Hz, 1H, ArH), 7.76 (dt, $J = 7.9, 1.3$ Hz, 1H, ArH), 7.44 – 7.27 (m, 6H, ArH), 7.22 (t, $J = 7.9$ Hz, 1H, ArH), 4.56 (s, 2H, ArCH₂), 4.30 (s, 2H, NCH₂C=C), 1.10 – 1.04 (m, 21H, TIPS).

^{13}C NMR (101 MHz, Chloroform- d) δ 154.4, 150.2, 134.8, 134.3, 130.6, 130.4, 129.8, 129.1, 128.6, 128.5, 126.2, 122.4, 101.3, 98.6, 97.7, 49.7, 48.1, 18.6, 11.2.

IR ($\nu_{\max}$, cm^{-1}) 702 (s), 1033 (s), 1253 (s), 1416 (s), 1464 (s), 1649 (s), 1803 (s), 2147 (s), 2866 (s), 2947 (s).

HRMS (ESI/QTOF) m/z : $[M + \text{H}]^+$ Calcd for $\text{C}_{28}\text{H}_{35}^{79}\text{BrNO}_2\text{Si}^+$ 524.1615; Found 524.1601.

(E)-3-benzyl-5-(1-(3,5-dimethylphenyl)-3-(triisopropylsilyl)prop-2-yn-1-ylidene)oxazolidin-2-one
(5l)

Using **2l** (100 mg, 0.400 mmol). The crude product was dry loaded onto deactivated SiO_2 and purified by column chromatography (SiO_2 ; 0-3% EtOAc in pentane) which afforded (E)-3-benzyl-5-(1-(3,5-dimethylphenyl)-3-(triisopropylsilyl)prop-2-yn-1-ylidene)oxazolidin-2-one (**5l**) as an orange amorphous solid (151 mg, 0.331 mmol, 80% yield)

^1H NMR (400 MHz, Chloroform-*d*) δ 7.43 (s, 2H, ArH), 7.42 – 7.29 (m, 5H, ArH), 6.94 – 6.86 (m, 1H, ArH), 4.55 (s, 2H, ArCH₂), 4.30 (s, 2H, NCH₂C=C), 2.32 (s, 6H, ArCH₃), 1.11 – 1.02 (m, 21H, TIPS).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.9, 148.8, 137.7, 134.5, 132.5, 129.2, 129.0, 128.5, 128.4, 125.5, 102.5, 100.0, 96.6, 49.7, 48.0, 21.4, 18.6, 11.2.

IR (ν_{max} , cm⁻¹) 674 (m), 702 (s), 851 (m), 884 (m), 1037 (s), 1133 (m), 1236 (m), 1415 (m), 1463 (m), 1645 (m), 1800 (s), 2142 (w), 2866 (m), 2942 (m).

HRMS (ESI/QTOF) m/z : [M + H]⁺ Calcd for C₃₀H₄₀NO₂Si⁺ 474.2823; Found 474.2822.

(Z)-3-benzyl-5-(1-(thiophen-2-yl)-3-(triisopropylsilyl)prop-2-yn-1-ylidene)oxazolidin-2-one (5m)

Using **2m** (91.0 mg, 0.400 mmol). The crude product was dry loaded onto deactivated SiO₂ and purified by column chromatography (SiO₂; 0-3% EtOAc in pentane) which afforded (Z)-3-benzyl-5-(1-(thiophen-2-yl)-3-(triisopropylsilyl)prop-2-yn-1-ylidene)oxazolidin-2-one (**5m**) as an orange oil (91.4 mg, 0.189 mmol, 47% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.25 (m, 5H, ArH, 2H, thiopheneH), 7.03 (dd, J = 5.1, 3.7 Hz, 1H, thiopheneH), 4.56 (s, 2H, ArCH₂), 4.28 (s, 2H, NCH₂C=C), 1.12-1.02 (m, 21H, TIPS).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.4, 147.0, 136.1, 134.4, 129.1, 128.5, 128.4, 127.1, 126.1, 125.6, 100.5, 96.9, 95.4, 48.9, 48.1, 18.6, 11.2.

IR (ν_{max} , cm⁻¹) 2942 (m), 2864 (m), 2148 (w), 1796 (s), 1651 (m), 1462 (m), 1414 (m), 1253 (s), 1097 (m), 1039 (s), 882 (m), 744 (m), 697 (s), 665(s).

HRMS (ESI/QTOF) m/z : [M + H]⁺ Calcd for C₂₆H₃₄NO₂SSi⁺ 452.2074; Found 452.2071.

(E)-3-benzyl-5-(1-(p-tolyl)ethylidene)oxazolidin-2-one (9) and (Z)-3-benzyl-5-ethylideneoxazolidin-2-one (10)

A vial was charged with $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (2.6 mg, 2.5 μmol , 2.5 mol%), DPEPhos (4.4 mg, 7.5 μmol , 7.5 mol%), AgBF_4 (25 mg, 0.13 mmol, 1.3 equiv.) and CsHCO_3 (38 mg, 2.0 mmol, 2.0 equiv.). The vial was sealed and purged with argon. To this was added DCE (0.3 mL) and the mixture was heated at 60 °C for 2-3 minutes, after which it took on a black colour. N-benzylbut-2-yn-1-amine (**2a**) (16 mg, 0.1 mmol, 1.0 equiv.) and a solution of 4-iodotoluene (28 mg, 0.13 mmol, 1.3 equiv.) in DCE (200 μL) were added directly to the reaction mixture and left to stir at 60 °C for 20 hours. After this time, the reaction mixture was removed from heating, cooled to room temperature, unsealed, diluted with pentane (2 mL) and passed through a small plug of silica gel (deactivated by Et_3N) rinsing with 10% EtOAc in pentane (4 mL) and concentrated by rotary evaporation. The crude material was purified by preparative TLC (15% EtOAc in pentane) to afford a mixture of the named compounds **9** and **10** in a 1.5:1 ratio as a straw yellow oil (13.5 mg, 53.0 μmol 53% yield) containing some impurities.

^1H NMR (400 MHz, Chloroform-*d*; as a 1.5:1 mixture of **9** and **10**) δ 7.41 – 7.21 (m, 5H, ArH; 5H, ArH), 7.12 (d, J = 7.9 Hz, 2H, ArH), 7.05 – 7.00 (m, 2H, ArH), 4.55 (qt, J = 6.9, 2.2 Hz, 1H, $\text{C}=\text{CH}$), 4.46 (s, 2H, ArCH_2), 4.45 (s, 2H, ArCH_2), 4.03 (q, J = 2.2 Hz, 2H, $\text{NCH}_2\text{C}=\text{C}$), 3.96 (p, J = 2.2 Hz, 2H, $\text{NCH}_2\text{C}=\text{C}$), 2.31 (s, 3H, ArCH_3), 2.07 (t, J = 2.2 Hz, 3H, CH_3), 1.67 (dt, J = 7.0, 2.3 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, Chloroform-*d*; as a 1.5:1 mixture of **9** and **10**, some signals could not be attributed) δ 156.0, 155.9, 141.6, 138.1, 136.9, 135.9, 135.2, 129.3, 128.9, 128.1, 128.1, 128.1, 127.1, 112.1, 97.6, 47.9, 47.9, 47.4, 47.1, 21.1, 16.5, 9.9.

IR (ν_{max} , cm^{-1}) 3031 (w), 2921 (w), 2863 (w), 1777 (s), 1716 (m), 1422 (m), 1258 (m), 1083 (s), 1062 (s), 821 (m), 754 (m), 703 (s).

HRMS (nanochip-ESI/LTQ-Orbitrap) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{20}\text{NO}_2^+$ 294.1489; Found 294.1490.

HRMS (nanochip-ESI/LTQ-Orbitrap) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_2^+$ 204.1019; Found 204.1020.

The spectra of **9** closely resembles similar structure in literature.⁶

6. References.

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7. Structures determined by X-ray measurement.

Cambridge Crystallographic Data Centre entry – 1905359

8. ¹H & ¹³C NMR spectra of new compounds.

N-benzyl-3-(3-bromophenyl)prop-2-yn-1-amine (2k)

¹H-NMR (400 MHz, chloroform-*d*)

¹³C-NMR (101 MHz, chloroform-*d*)

N-benzyl-3-(3-bromophenyl)prop-2-yn-1-amine (2m)

¹H-NMR (400 MHz, chloroform-d)

¹³C-NMR (101 MHz, chloroform-d)

(E)-3-benzyl-5-(4-(triisopropylsilyl)but-3-yn-2-ylidene)oxazolidin-2-one (5a)

¹H-NMR (400 MHz, chloroform-*d*)

¹³C-NMR (101 MHz, chloroform-*d*)

(E)-3-(4-methoxybenzyl)-5-(4-(triisopropylsilyl)but-3-yn-2-ylidene)oxazolidin-2-one (5b)

¹H-NMR (400 MHz, chloroform-*d*)

¹³C-NMR (101 MHz, chloroform-*d*)

(E)-3-ferrocenylmethyl-5-(4-(triisopropylsilyl)but-3-yn-2-ylidene)oxazolidin-2-one (5c)

¹H-NMR (400 MHz, chloroform-*d*)

¹³C-NMR (101 MHz, chloroform-*d*)

(E)-3-benzyl-5-(1-phenyl-4-(triisopropylsilyl)but-3-yn-2-ylidene)oxazolidin-2-one (5d)

^1H -NMR (400 MHz, chloroform- d)

^{13}C -NMR (101 MHz, chloroform- d)

(E)-3-benzyl-5-(1-cyclopropyl-3-(triisopropylsilyl)prop-2-yn-1-ylidene)oxazolidin-2-one (5e)

$^1\text{H-NMR}$ (400 MHz, chloroform- d)

$^{13}\text{C-NMR}$ (101 MHz, chloroform- d)

(E)-3-benzyl-5-(1-cyclopropyl-3-(triisopropylsilyl)prop-2-yn-1-ylidene)oxazolidin-2-one (5f)

^1H -NMR (400 MHz, chloroform- d)

^{13}C -NMR (101 MHz, chloroform- d)

(E)-3-benzyl-5-(1-phenyl-3-(triisopropylsilyl)prop-2-yn-1-ylidene)oxazolidin-2-one (5g)

¹H-NMR (400 MHz, chloroform-*d*)

¹³C-NMR (101 MHz, chloroform-*d*)

(E)-3-methyl-5-(1-phenyl-3-(triisopropylsilyl)prop-2-yn-1-ylidene)oxazolidin-2-one (5h)

¹H-NMR (400 MHz, chloroform-*d*)

¹³C-NMR (101 MHz, chloroform-*d*)

(E)-3-benzyl-5-(1-(4-methoxyphenyl)-3-(triisopropylsilyl)prop-2-yn-1-ylidene)oxazolidin-2-one (5i)

^1H -NMR (400 MHz, chloroform-*d*)

^{13}C -NMR (101 MHz, chloroform-*d*)

(E)-3-benzyl-5-(1-(4-(trifluoromethyl)phenyl)-3-(triisopropylsilyl)prop-2-yn-1-ylidene)oxazolidin-2-one
(5j)

$^1\text{H-NMR}$ (400 MHz, chloroform-*d*)

$^{13}\text{C-NMR}$ (101 MHz, chloroform-*d*)

(E)-5-(1-(3-bromophenyl)-3-(triisopropylsilyl)prop-2-yn-1-ylidene)-3-phenyloxazolidin-2-one (5k)

$^1\text{H-NMR}$ (400 MHz, chloroform- d)

$^{13}\text{C-NMR}$ (101 MHz, chloroform- d)

(E)-3-benzyl-5-(1-(3,5-dimethylphenyl)-3-(triisopropylsilyl)prop-2-yn-1-ylidene)oxazolidin-2-one (5I)

¹H-NMR (400 MHz, chloroform-*d*)

¹³C-NMR (101 MHz, chloroform-*d*)

(Z)-3-benzyl-5-(1-(thiophen-2-yl)-3-(triisopropylsilyl)prop-2-yn-1-ylidene)oxazolidin-2-one (5m)

¹H-NMR (400 MHz, chloroform-*d*)

¹³C-NMR (101 MHz, chloroform-*d*)

(E)-3-benzyl-5-(1-(p-tolyl)ethylidene)oxazolidin-2-one (9) and (Z)-3-benzyl-5-ethylideneoxazolidin-2-one (10)

^1H -NMR (400 MHz, chloroform- d)

^{13}C -NMR (101 MHz, chloroform- d)