Syntheses of Substituted Furans and Pyrroles by Platinum-Catalyzed Cyclizations of Propargylic Oxiranes and Aziridines in Aqueous Media

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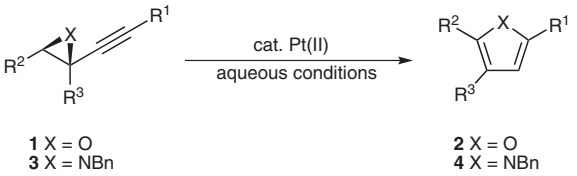
Abstract: The reactions of propargylic oxiranes and aziridines with a platinum catalyst in aqueous media are described. Furans having a variety of substituents were conveniently synthesized by the platinum-catalyzed reaction of propargylic oxiranes. The reaction in the presence of *N*-iodosuccinimide afforded the 3-iodo-substituted furan, which was further functionalized to tetrasubstituted furans with high efficiency. Propargylic aziridines were also reacted with the platinum catalyst to produce the corresponding substituted pyrroles in good yields.

Key words: alkyne, epoxide, furan, platinum, pyrrole

Substituted furans and pyrroles are an important class of heteroaromatic molecules that are components in a variety of biologically active natural products and industrially useful compounds.[1] They are also extensively utilized as synthetic intermediates for acyclic, carbocyclic, and heterocyclic compounds in organic synthesis.[2] For these reasons, considerable effort has been devoted toward finding efficient syntheses of substituted furans and pyrroles.[3] Among them, cycloisomerization of propargylic oxiranes is one of the most useful methodologies for the synthesis of substituted furans.[4] It has been reported that a variety of reagents activate the process that leads to the corresponding substituted furans. For example, Hashmi reported the gold-catalyzed cycloisomerization of propargylic oxiranes to furans.[4h] The reaction allows the synthesis of substituted furans under mild conditions, but the reaction examples were limited to only 2,4-disubstituted furans and the chemical yields were moderate to low. During the course of our studies on the reaction of propargylic oxiranes with a transition metal catalyst,[5] we focused on the reactivity of a platinum(II) catalyst.[6] We report herein full details of a platinum-catalyzed reaction of propargylic oxiranes, in which various substituted furans can be conveniently synthesized in aqueous media with high efficiency.[7] The application of this reaction to propargylic aziridines for the synthesis of substituted pyrroles is also described (Scheme 1).



1 X = O
3 X = NBn

2 X = O
4 X = NBn

Scheme 1

Propargylic oxiranes **1** for platinum-catalyzed cyclization were easily prepared by the epoxidation of the corresponding enynes (Table 1). Thus, enynes **5a–k** having a variety of substituents were converted into the corresponding propargylic oxiranes **1a–k** in moderate to good yields by employing 3-chloroperbenzoic acid under basic conditions.

The initial attempts at the synthesis of substituted furans were carried out using phenyl-substituted propargylic oxirane **1a**. Treatment of **1a** with 10 mol% of platinum(II) chloride in dioxane at 100 °C for 180 minutes gave tetrahydrobenzofuran **2a** in 90% yield (Table 2, entry 1). Further efforts revealed that the presence of water enhanced the reactivity (entries 2 and 3). Thus, the reaction in dioxane–water (2:1) was complete within 10 minutes to afford the product **2a** in 96% yield (entry 3). The yields of **2a** decreased as the temperature was lowered (entries 4–6). The reaction also proceeded in a mixture of various aqueous solvents to give **2a** in good yields (entries 7–11). The reactivity was maintained even in the presence of 5 mol% platinum catalyst (entry 12), but with 2 mol% of catalyst, the production of **2a** decreased (entry 13). The Brønsted acid catalyzed reaction in the presence of hydrochloric acid also proceeded, but the yield was very low (entry 14). Treatment of **1a** with 10 mol% gold(III) chloride in acetonitrile at room temperature in accordance with Hashmi's procedure[4h] gave **2a** in 21% yield (entry 15).

Table 3 shows our attempts using various substituted propargylic oxiranes **1b–k**. The reaction of **1b**, having a butyl group at the alkynyl position, with platinum(II) chloride yielded tetrahydrobenzofuran **2b** in 83% yield (entry 1). The benzyl- and siloxyethyl-substituted propargylic oxiranes **1c** and **1d** were transformed into the corresponding products **2c** and **2d**, each in 92% yield (entries 2 and 3). Furthermore, the propargylic oxirane with a free hydroxy group, **1e**, was uneventfully converted into **2e** in 79% yield (entry 4). The reaction of **1f** containing a 2-vinylphenyl group also afforded furan **2f** without any problems due to the vinyl group (entry 5). When cyclopentyl-substituted substrate **1g** was subjected to the reaction, 5,6-dihydrocyclopentafuran **2g** was obtained in 34% yield (entry 6). The low yield can be attributed to the difficulties encountered in constructing the strained 5,6-dihydro-4*H*-cyclopen-

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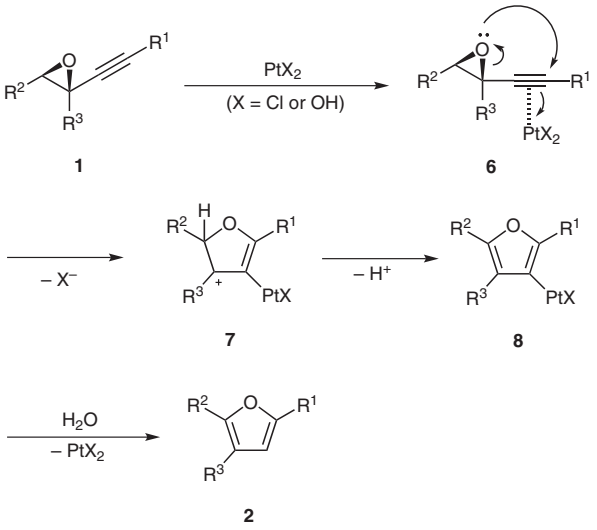
ta[*b*]furan ring system. The reactions of substrates **1h** and **1i**, which contain seven- and eight-membered rings, successfully afforded the corresponding furans **2h** and **2i** in 92% and 89% yields, respectively (entries 7 and 8). Reaction of acyclic propargylic oxirane **1j** gave 2,4-disubstituted furan **2j** in 90% yield (entry 9).[8] Similarly, the 2,5-disubstituted furan **2k** was obtained in yields of 82% and 83% from the reactions of *trans*-**1k** and *cis*-**1k** (entries 10 and 11).

A plausible mechanism for the reaction of propargylic oxiranes **1** is shown in Scheme 2. The platinum catalyst activates the C≡C bond in the substrate **1** by coordination as shown in **6**. The epoxide oxygen attacks the distal position of the alkyne to form the cyclized intermediate **7**. Aromatization by elimination of the proton followed by proto-demetalation from the resulting furyl–platinum species **8** produces the furan **2**. As to the cause of the increased reactivity under aqueous conditions, it is presumed that the platinum hydroxide complex, which would enhance the reactivity of the proto-demetalation from the intermediate **8**, exists as an active species in the aqueous media.[9]



Scheme 2

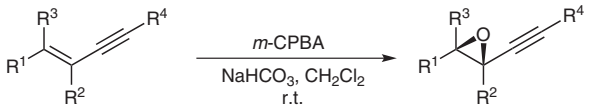
Biographical Sketches

Masahiro Yoshida was born in Aichi prefecture, Japan in 1974. He received his B.S. in 1996 from the Tohoku University under the direction of Emeritus Professor Keiichiro Fukumoto and his Ph.D. in 2001 from Tohoku University under the direction of Emeritus Professor Masataka Ihara. After he joined Professor Mark Lautens' group at the University of Toronto as a postdoctoral fellow during 2001–2002, he was appointed as a Research Associate at Tohoku University in 2002. In 2005, he moved to the Graduate School of Pharmaceutical Sciences, University of Tokushima, as an Associate Professor. His awards include an Encouraging Award from The Pharmaceutical Society of Japan, Tohoku District, in 2003, and a FUJIFILM Award in Synthetic Organic Chemistry, Japan, in 2005. At present, his research is focused on the development of new catalytic reactions using transition metal complexes and their application to the synthesis of natural products.

Mohammad Al-Amin was born in Chandpur, Bangladesh in 1979. He received his B.S. in 2003, and M.S. degree in 2005 from Jahangirnagar University under the supervision of Professor Md. Rabiul Islam. He is currently carrying out his Ph.D. studies in the group of Professor Yoshida and Professor Shishido at the Graduate School of Pharmaceutical Sciences, University of Tokushima, as a MEXT scholarship student. His research interests include the development of synthetic methods for heteroaromatic compounds based on transition-metal-catalyzed reactions.

Kozo Shishido was born in Miyagi prefecture, Japan in 1946, and received his B.S. in 1970 and Ph.D. in 1976 from Tohoku University under the direction of the late Professor Tetsuji Kametani. After he was appointed as an Assistant Professor at Tohoku University in 1972, he joined the late Professor A. I. Scott's group at Texas A&M University and then Professor M. E. Jung's group at the University of California, Los Angeles as a postdoctoral fellow from 1978–1980. He then moved to the University of Tokushima as an Associate Professor in 1989. In 1994, he rose to the rank of Full Professor at University of Tokushima, where he is currently Professor of the Graduate School of Pharmaceutical Sciences. His research interest is in the area of total synthesis of biologically significant molecules.

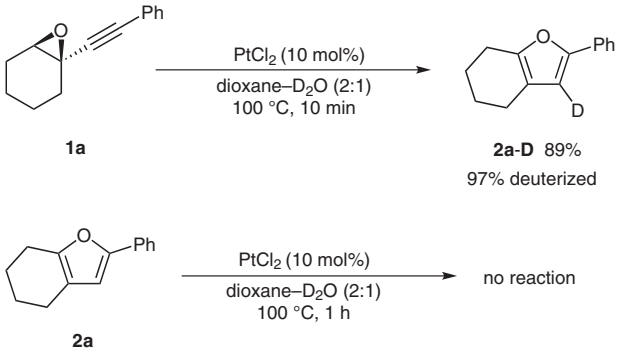
Table 1 Synthesis of Propargylic Oxiranes **1a–k**



5a–k **1a–k**

Entry	Substrate	R^1	R^2	R^3	R^4	Product	Yield (%)
1	**5a**	$(CH_2)_4$		H	Ph	**1a**	69
2	**5b**	$(CH_2)_4$		H	Bu	**1b**	82
3	**5c**	$(CH_2)_4$		H	Bn	**1c**	65
4	**5d**	$(CH_2)_4$		H	$(CH_2)_2$OTBDPS	**1d**	71
5	**5e**	$(CH_2)_4$		H	$(CH_2)_2$OH	**1e**	79
6	**5f**	$(CH_2)_4$		H	2-H_2C=CHC_6H_4	**1f**	43
7	**5g**	$(CH_2)_3$		H	Ph	**1g**	52
8	**5h**	$(CH_2)_5$		H	Ph	**1h**	67
9	**5i**	$(CH_2)_6$		H	Ph	**1i**	86
10	**5j**	H	Me	H	$(CH_2)_3$OH	**1j**	64
11	(*E*)-**5k** (*Z*)-**5k**	Ph/H	H	H/Ph	Ph	*trans*-**1k** *cis*-**1k**	34 39

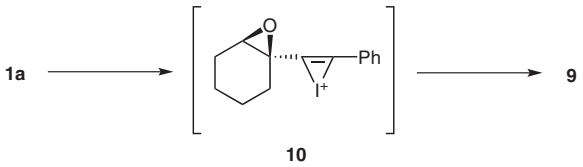
Information on the reaction mechanism was gained when the reaction was conducted in deuterium oxide (Scheme 3). In this case, 97% of deuterium was incorporated at the 3-position on the furan ring to give **2a-D** in 89% yield. No reaction occurred when the isolated furan **2a** was subjected to the same reaction condition. These results support the hypothesis that the reaction proceeds via the formation of the furyl–platinum intermediate **8**.



Scheme 3

To further highlight the potential of this process, we tried to trap the furyl–platinum species with electrophilic iodine prior to protonation (Table 4).[10] When propargylic oxirane **1a** was treated with *N*-iodosuccinimide in the presence of platinum(II) chloride in dioxane–water (2:1), 3-iodotetrahydrobenzofuran **9** was produced in 63% yield (entry 1). Examination of the reaction in various aqueous solvents (entries 2–5) revealed that the yield of **9** increased to 69% when the reaction was carried out in acetonitrile–water (2:1) (entry 5). The product **9** was obtained even in the absence of platinum catalyst, but the yield decreased to 22% (entry 6). This result indicates that the reaction also proceeds via iodonium intermediate **10** (Scheme 4), but the pathway involving the furyl–platinum species **8** is preferred in this reaction.[11]

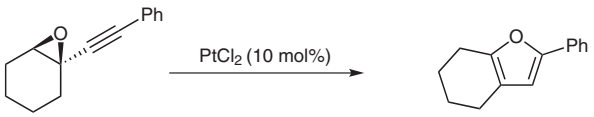
The presence of the iodo functional group on the furan ring provided an opportunity for further functionalization (Scheme 5). The 4-methoxyphenyl group was introduced to give **11a** in 98% yield using the Miyaura–Suzuki coupling reaction of **9** with 4-methoxyphenylboronic acid. Compound **9** also underwent Sonogashira and Stille coupling reactions with phenylacetylene and tributyl(vinyl)tin to produce the corresponding 3-alkynyl- and 3-vinyl-substituted furans **11b** and **11c** in 93% and 52% yields, respectively. Heck reaction of **9** with methyl acrylate also proceeded to afford **11d** in 98% yield.



Scheme 4

We next turned our attention to the synthesis of substituted pyrroles. Although many examples of cyclizations of propargylic oxiranes to furans have been reported, there are few focusing on the conversion of propargylic aziri-

Table 2 Platinum-Catalyzed Cyclizations of **1a**



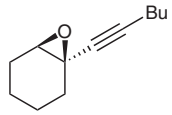
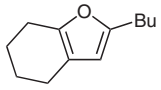
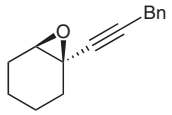
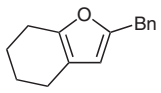
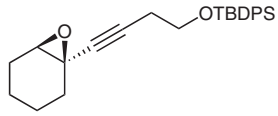
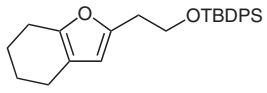
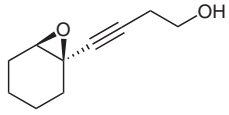
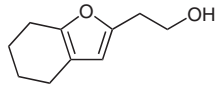
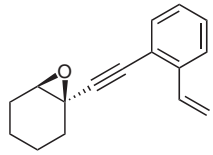
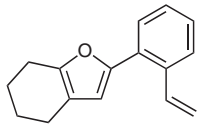
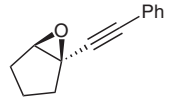
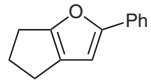
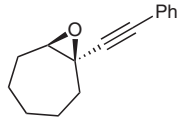
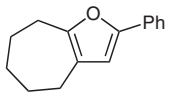
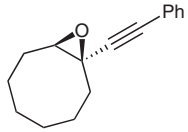
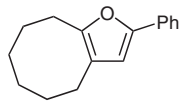
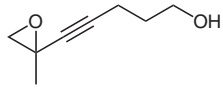
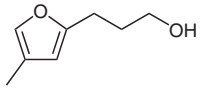
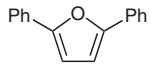
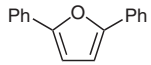
1a **2a**

Entry	Solvent	Temp (°C)	Time (min)	Yield (%)
1	dioxane	100	180	90
2	dioxane–H_2O (1:2)	100	10	87
3	dioxane–H_2O (2:1)	100	10	96
4	dioxane–H_2O (2:1)	80	15	95
5	dioxane–H_2O (2:1)	60	45	61
6	dioxane–H_2O (2:1)	25	600	27
7	MeCN–H_2O (2:1)	100	40	76
8	THF–H_2O (2:1)	100	10	86
9	DMF–H_2O (2:1)	100	10	87
10	toluene–H_2O (2:1)	100	60	91
11	DMSO–H_2O (2:1)	100	20	83
12[a]	dioxane–H_2O (2:1)	100	10	94
13[b]	dioxane–H_2O (2:1)	100	30	34
14[c]	dioxane–H_2O (2:1)	100	10	10
15[d]	MeCN	25	36 h	21 (29)[e]

[a] 5 mol% of $PtCl_2$ was used.
[b] 2 mol% of $PtCl_2$ was used.
[c] 10 mol% HCl was used.
[d] 10 mol% $AuCl_3$ was used.
[e] The yield in parenthesis is based on recovered starting material.

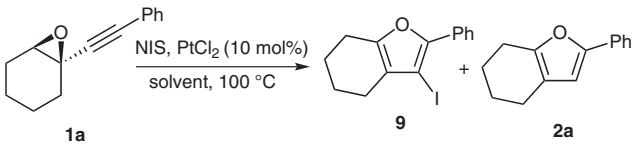
dines into pyrroles.[12,13] We expected that our platinum-catalyzed conditions could be applied to the synthesis of substituted pyrroles and, therefore, attempted the reaction of propargylic aziridines. The substrates **3a–k** for the cyclization reactions were synthesized as follows (Scheme 6). According to Chemla's procedure,[14] the reaction of the imine **12a** with the allenylzinc reagent **13a** gave the corresponding trimethylsilyl-substituted propargylic aziridine, which was subjected to the reaction with potassium carbonate in methanol to afford the desilylated compound **3g**. Various substituents at the terminal position of alkyne **3g** were introduced to give **3a** and **3c–e** by reactions with butyllithium and alkyl bromides **14a** and **14c–e**. The phenyl-substituted propargylic aziridine **3b** was obtained directly by the reaction of imine **12a** with allenylzinc reagent **13b**. Compound **3f** containing a free hydroxy group was obtained in 98% yield from the reaction of **3e** with tetrabutylammonium fluoride. The propargylic aziridines **3h–k**, which have a substituent on the aziridine ring, were also prepared from the corresponding imines **12h–k** in three steps.

Table 3 Reactions with Various Propargylic Oxiranes **1b–k**[a]

Entry	Substrate	Product	Yld. (%)
1	 **1b**	 **2b**	83
2	 **1c**	 **2c**	92
3	 **1d**	 **2d**	92
4	 **1e**	 **2e**	79
5	 **1f**	 **2f**	73
6	 **1g**	 **2g**	34
7	 **1h**	 **2h**	92
8	 **1i**	 **2i**	89
9	 **1j**	 **2j**	90
10	 *trans*-**1k**	 **2k**	82
11	 *cis*-**1k**	 **2k**	83

[a] $PtCl_2$ (10 mol%), dioxane–H_2O (2:1), 100 °C, 10 min.

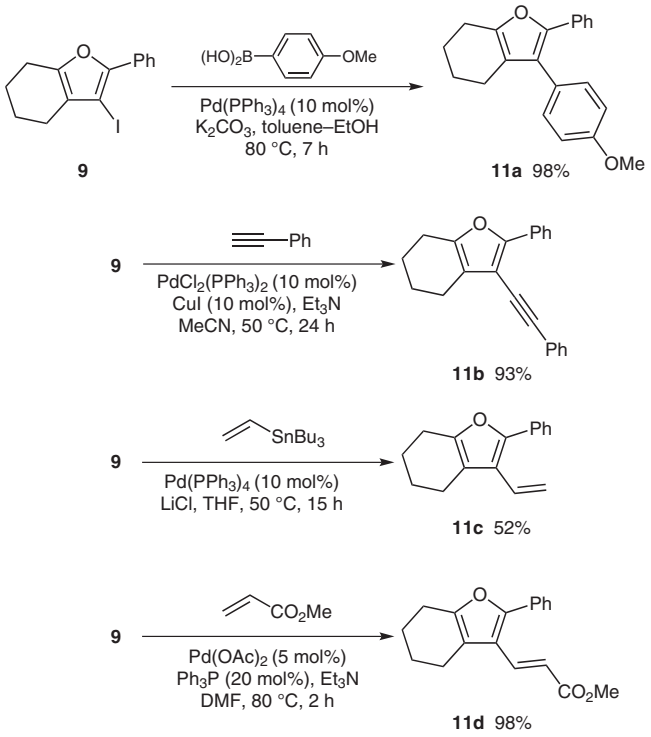
Table 4 Platinum-Catalyzed Cyclizations of **1a** in the Presence of *N*-Iodosuccinimide



1a **9** **2a**

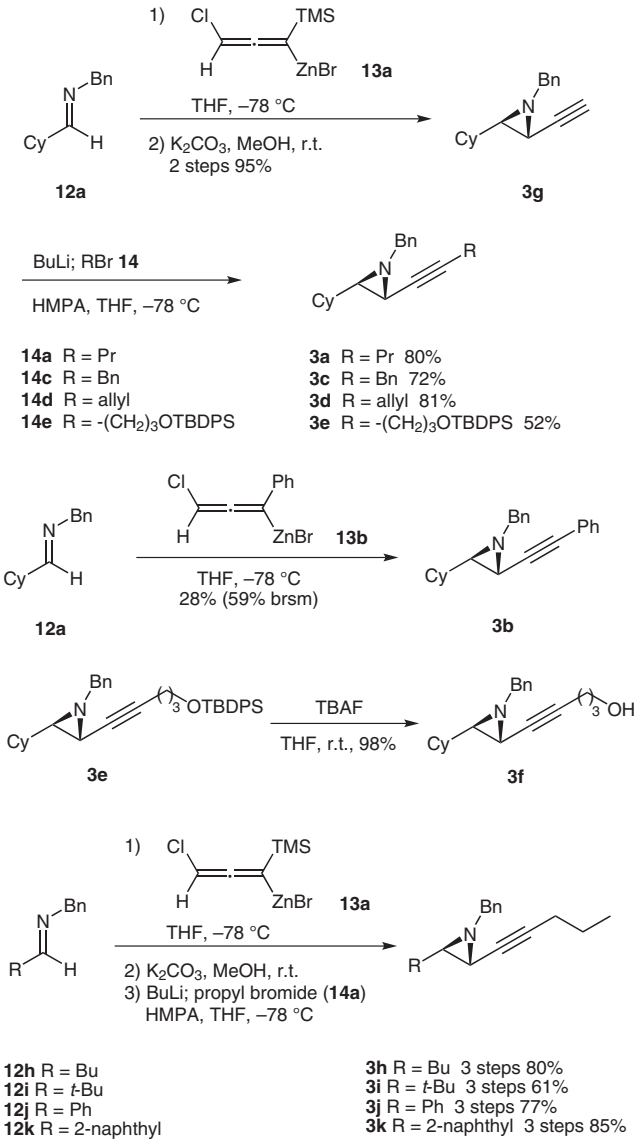
Entry	Solvent	Time (min)	Yield (%)	
			9	**2a**
1	dioxane–H_2O (1:2)	10	63	–
2	CH_2Cl_2–H_2O (2:1)	60	44	–
3	DMF–H_2O (2:1)	10	40	23
4	DMSO–H_2O (2:1)	10	56	31
5	MeCN–H_2O (2:1)	10	69	–
6[a]	MeCN–H_2O (2:1)	10	22	–

[a] Reaction was carried out in the absence of $PtCl_2$.



Scheme 5

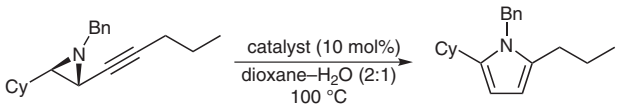
Attempts to synthesize substituted pyrroles were performed using **3a** (Table 5). When **3a** was treated with 10 mol% of platinum(II) chloride in dioxane–water (2:1) at 100 °C for 120 minutes, the desired 2,5-disubstituted pyrrole **4a** was produced in 77% yield (entry 1). To compare the effects of the catalyst in this reaction, catalyst screening using other transition metals was carried out (entries 2–5). Gold(III) chloride catalyzed the reaction of **3a** to produce **4a** in 51% yield (entry 2). The yields of **4a** decreased to 38% when platinum(II) chloride and dichloro(*p*-cymene)ruthenium(II) dimer were used (entries 3 and 4). The Brønsted acid catalyzed reaction in the presence of hydrochloric acid also proceeded, but the yield was only 18% (entry 5). These results suggest that the platinum catalyst is the most suitable in the conversion of the propargylic aziridine into the pyrrole.



Scheme 6

The reactions of various substituted propargylic aziridines **3b–k** are summarized in Table 6. When substrates **3b–e** having respectively a phenyl, benzyl, allyl, and 3-siloxypropyl group at the alkynyl position were subjected to the platinum-catalyzed reaction, the corresponding products **4b–e** were produced in good yields (entries 1–4). The propargylic aziridine containing a free hydroxy group, **3f**, was uneventfully transformed into pyrrole **4f** in 70% yield (entry 5). The monosubstituted pyrrole **4g** was obtained by the reaction of the unsubstituted substrate **3g**, but the yield decreased to 38% (entry 6). The reactions of substrates **3h** and **3i**, which contain butyl and *tert*-butyl

Table 5 Platinum-Catalyzed Cyclizations of **3a**

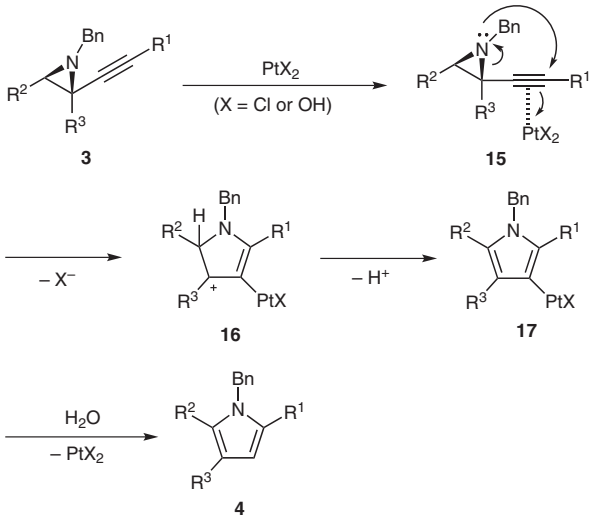


3a **4a**

Entry	Catalyst	Time (min)	Yield (%)
1	$PtCl_2$	120	77
2	$AuCl_3$	45	51
3	$PdCl_2$	20	38
4	[(*p*-cymene)$RuCl_2$]$_2$	240	38
5	HCl	60	18

groups on the aziridine ring, successfully afforded pyrroles **4h** and **4i** in 81% and 71% yields, respectively (entries 7 and 8). The phenyl- and 2-naphthyl-substituted substrates **3j** and **3k** were also converted into the corresponding products **4j** and **4k** in 72% and 48% yields, respectively (entries 9 and 10).

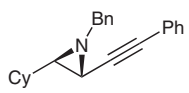
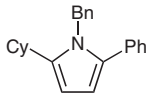
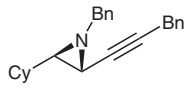
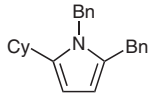
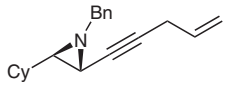
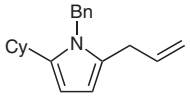
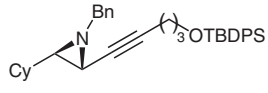
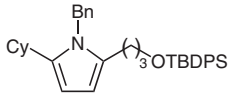
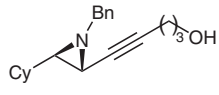
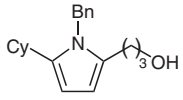
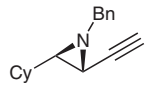
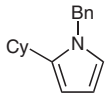
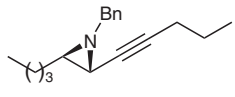
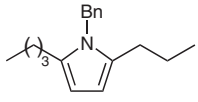
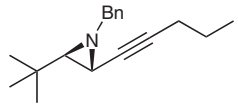
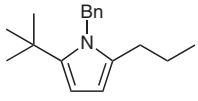
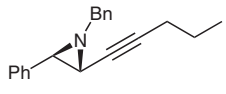
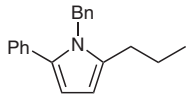
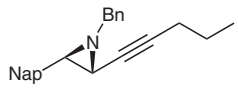
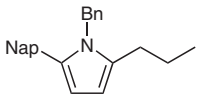
A plausible mechanism for the reaction of propargylic aziridines **3** is shown in Scheme 7. Coordination of platinum to the C≡C bond as in **15** followed by attack of the aziridine nitrogen on the alkyne produces the cyclized intermediate **16**. Aromatization by elimination of the proton forms the pyrrolyl–platinum species **17**, which further undergoes proto-demetalation to afford pyrrole **4**.



Scheme 7

In conclusion, we have developed a methodology for the synthesis of substituted furans and pyrroles using a platinum catalyst. The reactions afforded a variety of substituted furans and pyrroles under aqueous conditions and the process provided an efficient and convenient protocol for the preparation of these derivatives. Efforts to extend the scope of these reactions and their subsequent application to the syntheses of natural products are currently in progress.

Table 6 Reactions with Various Propargylic Aziridines **3b–k**[a]

Entry	Substrate	Product	Yield (%)
1	 **3b**	 **4b**	79
2	 **3c**	 **4c**	68
3	 **3d**	 **4d**	65
4	 **3e**	 **4e**	72
5	 **3f**	 **4f**	70
6	 **3g**	 **4g**	38
7	 **3h**	 **4h**	81
8	 **3i**	 **4i**	71
9	 **3j**	 **4j**	72
10[b]	 **3k**	 **4k**	48

[a] $PtCl_2$ (10 mol%), dioxane–H_2O (2:1), 100 °C, 1–2 h.
[b] Nap = 2-naphthyl.

All nonaqueous reactions were carried out under a positive atmosphere of argon in dried glassware unless otherwise indicated. Materials were obtained from commercial suppliers and used without further purification except when otherwise noted. Solvents were dried and distilled according to standard protocol. The phrase 'resi-

due upon workup' refers to the residue obtained when the organic layer was separated and dried (anhyd $MgSO_4$) and the solvent was evaporated under reduced pressure. Enynes **5a–k** were prepared according to the procedures described in the literature.[5c,15]

1-(Phenylethynyl)-7-oxabicyclo[4.1.0]heptane (1a); Typical Procedure

To a stirred soln of enyne **5a** (1.50 g, 8.2 mmol) in CH_2Cl_2 (60 mL) was added *m*-CPBA (2.83 g, 16.4 mmol) at r.t.; stirring was continued at r.t. for 2 h. The mixture was diluted with sat. aq $NaHCO_3$ (30 mL) and extracted with EtOAc (3 × 40 mL). The combined extracts were washed with brine (2 × 40 mL). After filtration of the mixture using a small amount of basic alumina, the residue upon workup was chromatographed (silica gel, hexane–EtOAc, 95:5) to give **1a** (1.12 g, 69%) as a colorless oil.

The spectral data of **1a–c** and **1g–k** were in complete agreement with that reported in the literature.[4h,5c,11,16,17]

1-[4-(*tert*-Butyldiphenylsiloxy)but-1-ynyl]-7-oxabicyclo[4.1.0]heptane (1d)

Colorless oil; yield: 71%.

IR (neat): 3069, 3028, 2926, 2855, 2197, 1598, 1496, 1475, 1450, 1428, 1389 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.69–7.67 (m, 4 H), 7.45–7.36 (m, 6 H), 3.75 (t, *J* = 6.8 Hz, 2 H), 3.26 (s, 1 H), 2.47 (t, *J* = 7.2 Hz, 2 H), 2.21–2.06 (m, 1 H), 1.98–1.86 (m, 3 H), 1.40–1.34 (m, 1 H), 1.31–1.18 (m, 3 H), 1.05 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.51, 133.50, 129.64, 127.64, 81.76, 79.81, 62.18, 59.93, 50.39, 29.91, 26.72, 24.12, 22.82, 19.42, 19.16, 18.91.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{26}H_{33}O_2Si$: 405.2250; found: 405.2246.

4-(7-Oxabicyclo[4.1.0]hept-1-yl)but-3-yn-1-ol (1e)

Colorless oil; yield: 79%.

IR (neat): 3312, 3064, 3031, 2927, 2852, 2185, 1385 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.71 (t, *J* = 6.4 Hz, 2 H), 3.31 (t, *J* = 2.4 Hz, 1 H), 2.48 (t, *J* = 6.4 Hz, 2 H), 2.17–2.10 (m, 1 H), 2.01–1.88 (m, 3 H), 1.84 (s, 1 H), 1.45–1.33 (m, 2 H), 1.33–1.17 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 82.08, 79.58, 60.61, 60.06, 50.47, 29.73, 23.94, 22.88, 19.25, 18.71.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{10}H_{15}O_2$: 167.1072; found: 167.1077.

1-[(2-Vinylphenyl)ethynyl]-7-oxabicyclo[4.1.0]heptane (1f)

Colorless oil; yield: 43%.

IR (neat): 3098, 3061, 2939, 2860, 2230, 1626, 1477, 1447, 1384, 1347 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.0 Hz, 1 H), 7.43–7.41 (m, 1 H), 7.29–7.26 (m, 2 H), 6.26–6.15 (m, 1 H), 5.80 (d, *J* = 17.6 Hz, 1 H), 5.35 (d, *J* = 11.6 Hz, 1 H), 3.46 (t, *J* = 2.4 Hz, 1 H), 2.29–2.24 (m, 1 H), 2.16–2.09 (m, 1 H), 1.99–1.95 (m, 2 H), 1.50–1.26 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.24, 134.68, 132.72, 128.60, 127.37, 124.50, 121.00, 115.64, 94.27, 80.35, 60.40, 50.75, 29.83, 24.20, 19.46, 18.89.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{17}O$: 225.1279; found: 225.1284.

2-Phenyl-4,5,6,7-tetrahydrobenzofuran (2a); Typical Procedure

To a stirred soln of **1a** (30.0 mg, 0.151 mmol) in dioxane–H_2O (2:1) was added $PtCl_2$ (4.0 mg, 0.015 mmol) at r.t. The mixture was stirred at 100 °C for 10 min and then cooled to r.t. and diluted with the minimum amount of Et_2O. The soln was then dried ($MgSO_4$) and filtered through a small amount of silica gel. Concentration at reduced pressure gave the residue, which was chromatographed (silica gel, pentane–Et_2O, 97:3) to give **2a** (28.8 mg, 96%) as a colorless oil.

IR (neat): 3079, 3058, 2926, 2849, 1634, 1603, 1549, 1486, 1443 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 7.6 Hz, 2 H), 7.39–7.29 (m, 2 H), 7.19 (t, *J* = 7.2 Hz, 1 H), 6.47 (s, 1 H), 2.66 (t, *J* = 6.0 Hz, 2 H), 2.45 (t, *J* = 6.0 Hz, 2 H), 1.89–1.86 (m, 2 H), 1.85–1.83 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.53, 150.75, 131.38, 128.51, 126.49, 123.19, 118.94, 105.97, 23.25, 23.10, 23.04, 22.10.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{14}H_{14}ONa$: 221.0942; found: 221.0936.

2-Butyl-4,5,6,7-tetrahydrobenzofuran (2b)

Colorless oil; yield: 83%.

IR (neat): 3097, 2928, 2852, 1686, 1644, 1573, 1458, 1445 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 5.77 (s, 1 H), 2.55 (q, *J* = 6.8 Hz, 4 H), 2.39–2.35 (m, 2 H), 1.83–1.76 (m, 2 H), 1.73–1.67 (m, 2 H), 1.63–1.54 (m, 2 H), 1.42–1.33 (m, 2 H), 0.94–0.91 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.17, 148.60, 117.09, 105.41, 30.43, 27.85, 23.25, 23.22, 23.12, 22.34, 22.15, 13.83.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{12}H_{18}ONa$: 201.1255; found: 201.1253.

2-Benzyl-4,5,6,7-tetrahydrobenzofuran (2c)

Colorless oil; yield: 92%.

IR (neat): 3087, 3062, 3029, 2926, 2850, 1642, 1604, 1569, 1496, 1454 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.19 (m, 5 H), 5.77 (s, 1 H), 3.90 (s, 2 H), 2.53 (t, *J* = 6.0 Hz, 2 H), 2.36–2.32 (m, 2 H), 1.81–1.76 (m, 2 H), 1.71–1.65 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.17, 149.56, 138.57, 128.75, 128.42, 126.32, 117.34, 107.11, 34.70, 29.69, 23.17, 23.13, 22.10.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{15}H_{17}O$: 213.1279; found: 213.1283.

2-[2-(*tert*-Butyldiphenylsiloxy)ethyl]-4,5,6,7-tetrahydrobenzofuran (2d)

Colorless oil; yield: 92%.

IR (neat): 3084, 3062, 3021, 2936, 2852, 1638, 1604, 1569, 1496, 1454, 1358 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.64–7.62 (m, 4 H), 7.41–7.34 (m, 6 H), 5.83 (s, 1 H), 3.87 (t, *J* = 7.2 Hz, 2 H), 2.85 (t, *J* = 7.2 Hz, 2 H), 2.51 (t, *J* = 6.4 Hz, 2 H), 2.35 (t, *J* = 6.4 Hz, 2 H), 1.83–1.77 (m, 2 H), 1.70–1.66 (m, 2 H), 1.03 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.62, 148.95, 135.55, 133.86, 129.65, 129.52, 127.71, 127.57, 117.26, 107.12, 62.78, 31.79, 26.79, 23.24, 23.10, 22.12, 19.18, 1.02.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{26}H_{33}O_2Si$: 405.2250; found: 405.2254.

2-(4,5,6,7-Tetrahydrobenzofuran-2-yl)ethanol (2e)
Colorless oil; yield: 79%.

IR (neat): 3058, 3022, 2929, 2837, 1632, 1605, 1569, 1497, 1453 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 5.91 (s, 1 H), 3.84 (t, *J* = 6.4 Hz, 2 H), 2.84 (t, *J* = 6.4 Hz, 2 H), 2.54 (t, *J* = 6.0 Hz, 2 H), 2.39–2.36 (m, 2 H), 1.84–1.74 (m, 2 H), 1.71–1.60 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.20, 149.60, 117.34, 107.46, 61.16, 31.67, 23.10, 23.07, 23.02.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{10}H_{14}O_2Na$: 189.0891; found: 189.0895.

2-(2-Vinylphenyl)-4,5,6,7-tetrahydrobenzofuran (2f)
Colorless oil; yield: 73%.

IR (neat): 3073, 3059, 2928, 2850, 1625, 1598, 1541, 1478, 1442 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 7.6 Hz, 1 H), 7.51 (d, *J* = 7.6 Hz, 1 H), 7.31–7.22 (m, 2 H), 7.11 (dd, *J* = 17.2, 10.8 Hz, 1 H), 6.32 (s, 1 H), 5.66 (dd, *J* = 17.2, 1.2 Hz, 1 H), 5.29 (dd, *J* = 10.8, 1.2 Hz, 1 H), 2.67 (t, *J* = 6.0 Hz, 2 H), 2.47 (t, *J* = 6.0 Hz, 2 H), 1.90–1.85 (m, 2 H), 1.79–1.73 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.88, 150.07, 136.76, 135.06, 129.77, 127.62, 127.00, 126.89, 118.86, 115.21, 111.25, 23.27, 23.13, 23.08, 22.15.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{16}ONa$: 247.1099; found: 247.1095.

2-Phenyl-5,6-dihydro-4*H*-cyclopenta[*b*]furan (2g)
Colorless oil; yield: 34%.

IR (neat): 3059, 3034, 2924, 2857, 1627, 1601, 1539, 1483, 1447 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.61 (t, *J* = 7.6 Hz, 2 H), 7.34 (t, *J* = 7.6 Hz, 2 H), 7.20 (t, *J* = 7.6 Hz, 1 H), 6.52 (s, 1 H), 2.78–2.74 (m, 2 H), 2.60–2.57 (m, 2 H), 2.50–2.43 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.42, 128.65, 128.57, 127.58, 126.57, 123.06, 103.58, 29.69, 27.73, 24.79.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{12}ONa$: 207.0786; found: 207.0792.

2-Phenyl-5,6,7,8-tetrahydro-4*H*-cyclohepta[*b*]furan (2h)
Colorless oil; yield: 92%.

IR (neat): 3079, 3056, 2927, 2850, 1638, 1609, 1594, 1532, 1486, 1448 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.60–7.57 (m, 2 H), 7.35–7.28 (m, 2 H), 7.20–7.16 (m, 1 H), 6.42 (s, 1 H), 2.83 (t, *J* = 6.0 Hz, 2 H), 2.50 (t, *J* = 5.6 Hz, 2 H), 1.80–1.70 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.31, 149.75, 131.28, 128.51, 126.41, 123.14, 122.91, 108.69, 30.77, 29.01, 28.68, 26.60, 26.21.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{16}ONa$: 235.1099; found: 235.1099.

2-Phenyl-4,5,6,7,8,9-hexahydrocycloocta[*b*]furan (2i)
Colorless oil; yield: 89%.

IR (neat): 3080, 3056, 2927, 2845, 1624, 1607, 1542, 1485, 1454, 1352 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.62–7.59 (m, 2 H), 7.35–7.31 (m, 2 H), 7.20–7.16 (m, 1 H), 6.42 (s, 1 H), 2.83 (t, *J* = 6.0 Hz, 2 H), 2.57 (t, *J* = 6.0 Hz, 2 H), 1.79–1.75 (m, 2 H), 1.71–1.67 (m, 2 H), 1.53–1.50 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.71, 150.46, 131.35, 128.50, 126.36, 123.09, 120.53, 108.10, 28.87, 27.39, 26.10, 26.07, 25.29, 23.83.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{18}ONa$: 249.1255; found: 249.1260.

3-(4-Methylfuran-2-yl)propan-1-ol (2j)
Colorless oil; yield: 90%.

IR (neat): 3373, 2927, 2850, 1617, 1551, 1446, 1384 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.06 (s, 1 H), 5.88 (s, 1 H), 3.68 (t, *J* = 6.0 Hz, 2 H), 2.68 (t, *J* = 7.2 Hz, 2 H), 1.98 (s, 3 H), 1.93–1.85 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.53, 137.45, 120.46, 107.87, 62.02, 30.94, 24.34, 9.72.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_8H_{12}O_2Na$: 163.0735; found: 163.0747.

2,5-Diphenylfuran (2k)
White solid; yield: 82% (*trans*-**1k**) and 83% (*cis*-**1k**).

IR (neat): 3056, 3036, 1670, 1609, 1598, 1539, 1488, 1479, 1468, 1448 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.70 (m, 4 H), 7.43–7.36 (m, 4 H), 7.34–7.20 (m, 2 H), 6.74 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.35, 130.77, 128.70, 127.32, 123.71, 107.21.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{12}ONa$: 243.0786; found: 243.0784.

3-Deuterio-2-phenyl-4,5,6,7-tetrahydrobenzofuran (2a-D)
To a stirred soln of **1a** (30.0 mg, 0.151 mmol) in dioxane–D_2O (2:1) was added $PtCl_2$ (4.0 mg, 0.015 mmol) at r.t. The mixture was stirred at 100 °C for 10 min and then cooled to r.t. and diluted with the minimum amount of Et_2O. The soln was dried ($MgSO_4$) and filtered through a small amount of silica gel. Concentration at reduced pressure gave the residue, which was chromatographed (silica gel, pentane–Et_2O, 95:5) to give the deuterated furan **2a-D** (26.74 mg, 89%, 97% deuterized) as a colorless oil.

IR (neat): 3078, 3058, 2929, 2850, 1669, 1604, 1542, 1484, 1444, 1408 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 7.6 Hz, 2 H), 7.33 (t, *J* = 7.6 Hz, 2 H), 7.19 (t, *J* = 7.2 Hz, 1 H), 2.66 (t, *J* = 6.0 Hz, 2 H), 2.45 (t, *J* = 6.0 Hz, 2 H), 1.89–1.83 (m, 2 H), 1.77–1.71 (m, 2 H).

^{13}C–NMR (100 MHz, $CDCl_3$): δ = 151.51, 150.79, 131.41, 128.53, 126.52, 123.22, 118.89, 105.99, 23.28, 23.12, 23.07, 22.11.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{14}{}^1H_{13}{}^2HONa$: 222.1005; found: 222.1006.

3-Iodo-2-phenyl-4,5,6,7-tetrahydrobenzofuran (9)
To a stirred soln of **1a** (30.0 mg, 0.151 mmol) in MeCN–H_2O (2:1) was added $PtCl_2$ (4.0 mg, 0.015 mmol) and NIS (40.8 mg, 0.181 mmol) at r.t. The mixture was stirred at 100 °C for 10 min and then it was cooled to r.t. and diluted with the minimum amount of Et_2O. The soln was then dried ($MgSO_4$) and filtered through a small amount of silica gel. Concentration at reduced pressure gave the residue, which was chromatographed (silica gel, hexane–EtOAc, 97:3) to give the iodofuran **9** (33.9 mg, 69%) as a colorless oil.

IR (neat): 3078, 3057, 2929, 2847, 1628, 1603, 1542, 1484, 1443, 1400 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 7.2 Hz, 2 H), 7.39 (t, *J* = 7.2 Hz, 2 H), 7.28 (t, *J* = 7.2 Hz, 1 H), 2.64 (t, *J* = 6.0 Hz, 2 H), 2.31 (t, *J* = 6.0 Hz, 2 H), 1.89–1.83 (m, 2 H), 1.77–1.71 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.23, 148.98, 130.82, 128.27, 127.46, 125.80, 123.23, 66.55, 23.28, 23.26, 23.17, 22.88.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{14}H_{13}IONa$: 346.9909; found: 346.9905.

3-(4-Methoxyphenyl)-2-phenyl-4,5,6,7-tetrahydrobenzofuran (11a)

To a stirred soln of iodofuran **9** (30.0 mg, 0.093 mmol) in toluene–EtOH (3:1) was added 4-methoxyphenylboronic acid (42.2 mg, 0.278 mmol), $Pd(PPh_3)_4$ (10.7 mg, 0.009 mmol), and K_2CO_3 (38.4 mg, 0.278 mmol) at r.t. The mixture was stirred at 80 °C for 7 h and then it was cooled to r.t. and then filtered through a pad of Celite. Concentration at reduced pressure gave the residue, which was chromatographed (silica gel, hexane–EtOAc, 97:3) to give **11a** (27.5 mg, 98%) as a yellow oil.

IR (neat): 3064, 3019, 2932, 2846, 1600, 1561, 1511, 1485, 1442, 1384 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.39 (m, 2 H), 7.32–7.20 (m, 4 H), 7.14 (t, *J* = 7.6 Hz, 1 H), 6.93–6.88 (m, 2 H), 3.84 (s, 3 H), 2.69 (t, *J* = 6.4 Hz, 2 H), 2.34 (t, *J* = 6.4 Hz, 2 H), 1.91–1.82 (m, 2 H), 1.77–1.71 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.60, 150.09, 146.34, 131.73, 130.52, 128.19, 126.63, 126.45, 125.41, 122.00, 119.61, 114.17, 114.03, 55.31, 55.18, 23.30, 23.07, 22.96, 21.38.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{21}H_{20}O_2Na$: 327.1361; found: 327.1366.

2-Phenyl-3-(phenylethynyl)-4,5,6,7-tetrahydrobenzofuran (11b)

To a stirred soln of iodofuran **9** (30.0 mg, 0.093 mmol) in Et_3N–MeCN (4:1) was added $PdCl_2(PPh_3)_2$ (3.3 mg, 0.005 mmol) and CuI (2.0 mg, 0.009 mmol) at r.t. Phenylacetylene (48.1 μL, 0.372 mmol) was then added to the stirred soln over 10 min at the same temperature. The mixture was stirred at r.t. for 25 h and it was quenched with aq sat. NH_4Cl and extracted with EtOAc (3 × 10 mL). The combined extracts were washed with brine (20 mL) and dried ($MgSO_4$). Concentration at reduced pressure gave the residue, which was chromatographed (silica gel, hexane–EtOAc, 99:1) to give **11b** (25.6 mg, 93%) as a white solid.

IR (neat): 3060, 3020, 2934, 2852, 2210, 1638, 1600, 1552, 1498, 1484, 1444, 1351 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 7.6 Hz, 2 H), 7.53 (dd, *J* = 7.6, 1.2 Hz, 2 H), 7.42–7.32 (m, 5 H), 7.26 (t, *J* = 7.6 Hz, 1 H), 2.64 (t, *J* = 6.0 Hz, 2 H), 2.53 (t, *J* = 6.0 Hz, 2 H), 1.91–1.85 (m, 2 H), 1.81–1.76 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.55, 150.22, 131.36, 130.98, 128.46, 128.36, 128.03, 127.30, 124.36, 123.76, 120.96, 103.53, 95.26, 82.53, 23.08, 22.93, 22.70, 20.91.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{22}H_{18}ONa$: 321.1255; found: 321.1252.

2-Phenyl-3-vinyl-4,5,6,7-tetrahydrobenzofuran (11c)

To a stirred soln of iodofuran **9** (35.5 mg, 0.110 mmol) in THF (2.0 mL) was added $Pd(PPh_3)_4$ (12.7 mg, 0.011 mmol), LiCl (14.0 mg, 0.330 mmol), and tributyl(vinyl)tin (64 μL, 0.220 mmol) at r.t. The mixture was stirred at 50 °C for 15 h and it was cooled to r.t. and then filtered through a pad of Celite. Concentration at reduced pressure gave the residue, which was chromatographed (silica gel, hexane–EtOAc–Et_3N, 98.5:1:0.5) to give the coupled product **11c** (12.8 mg, 52%) as a pale yellow oil.

IR (neat): 3096, 3066, 3029, 2940, 2848, 1636, 1604, 1597, 1480, 1461, 1431, 1354 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (t, *J* = 7.2 Hz, 2 H), 7.41–7.37 (m, 2 H), 7.32–7.25 (m, 1 H), 6.82 (dd, *J* = 17.6, 11.2 Hz, 1 H), 5.50 (dd, *J* = 17.6, 1.6 Hz, 1 H), 5.23 (dd, *J* = 11.2, 1.6 Hz, 1 H), 2.67–2.60 (m, 4 H), 1.89–1.84 (m, 2 H), 1.82–1.76 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.72, 148.79, 131.60, 128.72, 128.48, 128.43, 128.23, 127.06, 126.60, 119.34, 117.70, 114.97, 22.29, 23.20, 22.78, 22.60.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{16}H_{16}ONa$: 247.1099; found: 247.1094.

Methyl 3-(2-Phenyl-4,5,6,7-tetrahydrobenzofuran-3-yl)acrylate (11d)

To a stirred soln of iodofuran **9** (30.0 mg, 0.093 mmol) in DMF (1.5 mL) was added methyl acrylate (16.7 μL, 0.186 mmol), $Pd(OAc)_2$ (2.0 mg, 0.009 mmol), Ph_3P (2.4 mg, 0.009 mmol) ,and Et_3N (38.8 μL, 0.279 mmol) at r.t. The mixture was stirred at 80 °C for 2.5 h, the mixture was diluted with brine (10 mL) and extracted with EtOAc (3 × 15 mL). The combined extracts were washed with brine (20 mL) and dried ($MgSO_4$). Concentration at reduced pressure gave the residue, which was chromatographed (silica gel, hexane–EtOAc, 97:3) to give **11d** (25.6 mg, 98%) as a gray solid.

IR (neat): 3094, 3066, 2945, 2849, 1720, 1636, 1624, 1547, 1480, 1461, 1433, 1348 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 16.0 Hz, 1 H), 7.58 (t, *J* = 7.6 Hz, 2 H), 7.44 (t, *J* = 7.6 Hz, 2 H), 7.35 (t, *J* = 7.2 Hz, 1 H), 6.23 (d, *J* = 16.0 Hz, 1 H), 3.76 (s, 3 H), 2.67–2.62 (m, 4 H), 1.89–1.79 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.90, 153.54, 151.64, 137.08, 130.52, 128.71, 128.21, 127.36, 117.43, 117.28, 117.23, 51.48, 23.14, 22.95, 22.81, 22.36.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{18}H_{19}O_3$: 283.1334; found: 283.1331.

(2*R,3*R**)-1-Benzyl-2-cyclohexyl-3-ethynylaziridine (3g)**

To a stirred soln of (3-chloroprop-1-ynyl)trimethylsilane (500 mg, 3.41 mmol) in THF (10.0 mL) was added $ZnBr_2$ (1.54 g, 6.82 mmol) at –78 °C. A freshly prepared soln of 1.0 M LDA in THF (6.82 mL, 6.82 mmol) was slowly added dropwise to the resulting white suspension and stirring was continued at the same temperature for 1 h to produce allenylzinc compound **13a**. *N*-Benzylimine **12a** (686 mg, 3.41 mmol) in THF (4.0 mL) was then added dropwise to the resulting soln of **13a** at –78 °C. The temperature was slowly allowed to rise to r.t. and the mixture was stirred for a further 8 h at this temperature. The mixture was quenched with aq sat. NH_4Cl and extracted with Et_2O (3 × 20 mL). The combined organic extracts were washed with H_2O (2 × 20 mL) and brine (20 mL) and dried ($MgSO_4$). Concentration at reduced pressure gave the residue, which was purified by flash chromatography, (hexane–EtOAc, 97:3) to give 1-benzyl-2-cyclohexyl-3-[(trimethylsilyl)ethynyl]aziridine as a yellow oil. To a stirred soln of 1-benzyl-2-cyclohexyl-3-[(trimethylsilyl)ethynyl]aziridine (600 mg, 1.93 mmol) in MeOH (18 mL) was added K_2CO_3 (532 mg, 3.85 mmol) at r.t., and stirring was continued for 0.5 h at this temperature. The mixture was then poured into H_2O–Et_2O (1:1) and extracted with Et_2O (3 × 25 mL). The combined organic extracts were washed with brine (2 × 20 mL) and dried ($MgSO_4$). The solvent was evaporated at reduced pressure and the residue was chromatographed (silica gel, hexane–EtOAc, 92:8) to give **3g** (458 mg, 95% 2 steps) as a colorless oil.

IR (neat): 3295, 3086, 3062, 3029, 2922, 2850, 2114, 1603, 1495, 1450, 1416, 1383, 1354 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.37 (m, 2 H), 7.35–7.33 (m, 2 H), 7.28–7.24 (m, 1 H), 3.90 (d, *J* = 13.2 Hz, 1 H), 3.48 (d, *J* = 13.2 Hz, 1 H), 2.41 (dd, *J* = 3.2, 2.0 Hz, 1 H), 2.22 (d, *J* = 2.0

Hz, 1 H), 1.71–1.68 (m, 2 H), 1.60–1.51 (m, 4 H), 1.15–0.86 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.02, 128.56, 128.09, 126.86, 80.48, 71.59, 58.53, 53.17, 40.60, 30.56, 30.30, 29.75, 26.10, 25.58, 25.44.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{21}NNa$: 262.1572; found: 262.1576.

(2*R,3*R**)-1-Benzyl-2-cyclohexyl-3-(pent-1-ynyl)aziridine (3a); Typical Procedure**

To a stirred soln of **3g** (250 mg, 1.04 mmol) in THF (2.0 mL) was added dropwise 2.6 M BuLi in hexane (1.2 mL, 3.13 mmol) at –78 °C. The mixture was stirred for 1 h and then a soln of PrBr (**14a**, 0.30 mL, 3.12 mmol) and HMPA (0.40 mL, 3.12 mmol) in THF (1.0 mL) was added dropwise to the stirred soln at the same temperature of the mixture was allowed gradually rise to r.t. The mixture was stirred at r.t. for 3 h and then it was quenched with aq sat. NH_4Cl and extracted with Et_2O (3 × 10 mL). The combined organic extracts were washed with brine (2 × 15 mL) and dried ($MgSO_4$). The solvent was evaporated at reduced pressure and the residue was chromatographed (silica gel, hexane–EtOAc, 94:6) to give **3a** (235 mg, 80%) as a colorless oil.

IR (neat): 3086, 3062, 3028, 2924, 2850, 2230, 1603, 1495, 1450, 1380 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 6.8 Hz, 2 H), 7.34–7.30 (m, 2 H), 7.26–7.23 (m, 1 H), 3.86 (d, *J* = 13.2 Hz, 1 H), 3.47 (d, *J* = 13.2 Hz, 1 H), 2.41–2.39 (m, 1 H), 2.22–2.18 (m, 2 H), 1.70–1.67 (m, 2 H), 1.60–1.43 (m, 8 H), 1.14–1.07 (m, 4 H), 0.96 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.61, 128.74, 128.18, 126.85, 83.98, 76.57, 58.54, 53.29, 40.90, 31.71, 30.54, 29.30, 26.28, 25.77, 25.61, 22.20, 20.84, 13.44.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{27}NNa$: 304.2041; found: 304.2042.

(2*R,3*R**)-1-Benzyl-2-cyclohexyl-3-(phenylethynyl)aziridine (3b)**

To a stirred soln of (3-chloroprop-1-ynyl)benzene (300 mg, 1.99 mmol) in THF (8.0 mL) was added $ZnBr_2$ (896 mg, 3.98 mmol) at –78 °C. A freshly prepared soln of 1.0 M LDA in THF (3.98 mL, 3.98 mmol) was slowly added dropwise to the resulting white suspension and the stirring was continued for 1 h at this temperature to produce allenylzinc compound **13b**. *N*-Benzylimine **12a** (400 mg, 1.99 mmol) in THF (3.0 mL) was then added dropwise to the resulting soln of **13b** at –78 °C. The temperature was slowly allowed to rise to r.t. and stirring was continued at this temperature for 8 h. The mixture was quenched with aq sat. NH_4Cl and extracted with Et_2O (3 × 20 mL). The combined organic extracts were washed with H_2O (2 × 20 mL) and brine (20 mL) and dried ($MgSO_4$). Concentration at reduced pressure gave the residue, which was purified by flash chromatography (hexane–EtOAc, 95:5), to give **3b** (176 mg, 28%) as a yellow oil.

IR (neat): 3064, 3028, 2924, 2849, 2219, 1597, 1490, 1449, 1353 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.39 (m, 4 H), 7.35–7.24 (m, 6 H), 3.95 (d, *J* = 13.2 Hz, 1 H), 3.58 (d, *J* = 13.2 Hz, 1 H), 2.61 (d, *J* = 3.2 Hz, 1 H), 1.76–1.58 (m, 6 H), 1.26–0.89 (m, 6 H).

^{13}C–NMR (100 MHz, $CDCl_3$): δ = 139.32, 131.60, 128.75, 128.23, 128.04, 126.96, 122.96, 86.43, 83.48, 58.88, 53.93, 40.89, 31.67, 30.53, 29.97, 26.24, 25.73, 25.59.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{23}H_{25}NNa$: 338.1885; found: 338.1884.

(2*R,3*R**)-1-Benzyl-2-cyclohexyl-3-(3-phenylprop-1-ynyl)aziridine (3c)**

Following the typical procedure for **3a** using **3g** with BnBr (**14c**) gave **3c** as a colorless oil; yield: 72%.

IR (neat): 3062, 3029, 2925, 2850, 2195, 1644, 1603, 1495, 1451, 1419, 1354 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.35 (m, 2 H), 7.33–7.28 (m, 5 H), 7.27–7.22 (m, 3 H), 3.87 (d, *J* = 13.2 Hz, 1 H), 3.64 (d, *J* = 2.0 Hz, 2 H), 3.53 (d, *J* = 13.6 Hz, 1 H), 2.47 (dt, *J* = 3.2, 2.0 Hz, 1 H), 1.72–1.70 (m, 2 H), 1.59–1.54 (m, 3 H), 1.51 (dd, *J* = 7.2, 3.2 Hz, 1 H), 1.30–1.26 (m, 2 H), 1.24–1.02 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.31, 136.68, 128.70, 128.53, 128.23, 127.82, 126.92, 126.56, 81.50, 78.67, 58.51, 53.37, 40.75, 31.67, 30.54, 30.01, 26.27, 25.74, 25.59, 25.26.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{24}H_{27}NNa$: 352.2041; found: 352.2041.

(2*R,3*R**)-1-Benzyl-2-cyclohexyl-3-(pent-4-en-1-ynyl)aziridine (3d)**

Following the typical procedure for **3a** using **3g** with allyl bromide (**14d**) gave **3d** as a colorless oil; yield: 81%.

IR (neat): 3086, 3062, 3029, 2924, 2850, 2195, 1642, 1605, 1496, 1450, 1418, 1354 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.37 (m, 2 H), 7.35–7.30 (m, 2 H), 7.28–7.23 (m, 1 H), 5.86–5.76 (m, 1 H), 5.31–5.27 (m, 1 H), 5.12–5.09 (m, 1 H), 3.89 (d, *J* = 13.2 Hz, 1 H), 3.48 (d, *J* = 13.2 Hz, 1 H), 3.03–3.00 (m, 2 H), 2.44–2.43 (m, 1 H), 1.71–1.68 (m, 2 H), 1.60–1.55 (m, 3 H), 1.50–1.47 (m, 1 H), 1.15–1.04 (m, 4 H), 0.90–0.86 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.48, 132.48, 128.71, 128.26, 126.90, 116.07, 80.40, 78.97, 58.66, 53.33, 40.90, 31.56, 30.53, 29.98, 26.26, 25.75, 25.59, 23.19.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{25}NNa$: 302.1885; found: 302.1880.

(2*R,3*R**)-1-Benzyl-3-[3-(*tert*-butyldiphenylsiloxy)propyl]-2-cyclohexylaziridine (3e)**

Following the typical procedure for **3a** using **3g** with (3-bromopropoxy)-*tert*-butyldiphenylsilane (**14e**) gave **3e** as a colorless oil; yield: 52%.

IR (neat): 3069, 3029, 2927, 2854, 2196, 1589, 1496, 1471, 1450, 1428, 1389, 1359 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67–7.64 (m, 4 H), 7.43–7.20 (m, 11 H), 3.79 (d, *J* = 13.2 Hz, 1 H), 3.72 (t, *J* = 6.4 Hz, 2 H), 3.40 (d, *J* = 13.2 Hz, 1 H), 2.39–2.36 (m, 3 H), 1.76–1.67 (m, 4 H), 1.60–1.54 (m, 3 H), 1.30–1.24 (m, 3 H), 1.14–1.07 (m, 2 H), 1.04 (s, 9 H), 0.89 (t, *J* = 6.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.57, 135.54, 133.84, 129.57, 128.74, 128.18, 127.62, 126.85, 83.59, 77.31, 62.42, 58.59, 53.28, 40.93, 31.70, 31.67, 30.58, 30.03, 26.83, 25.79, 25.64, 22.64, 19.23, 14.10.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{36}H_{45}NOSiNa$: 558.3168; found: 558.3162.

(2*R,3*R**)-5-(1-Benzyl-3-cyclohexylaziridin-2-yl)pent-4-yn-1-ol (3f)**

To a stirred soln of **3e** (70.0 mg, 0.131 mmol) in THF (3.0 mL) was added 1.0 M TBAF in THF (0.5 mL, 0.524 mmol) at 0 °C, and stirring was continued at r.t. for 1.5 h. The mixture was poured into aq sat. NH_4Cl, and extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed with brine (2 × 15 mL) and dried ($MgSO_4$). The solvent was evaporated under reduced pressure and

the residue was chromatographed (silica gel, hexane–EtOAc, 65:35) to give **3f** (38.1 mg, 98%) as a colorless oil.

IR (neat): 3310, 3064, 3031, 2926, 2851, 2242, 1604, 1497, 1450, 1352 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.23 (m, 5 H), 3.84 (d, *J* = 13.2 Hz, 1 H), 3.66 (t, *J* = 6.4 Hz, 2 H), 3.49 (d, *J* = 13.2 Hz, 1 H), 2.40 (d, *J* = 2.4 Hz, 1 H), 2.35–2.31 (m, 2 H), 1.93 (br s, 1 H), 1.75–1.67 (m, 4 H), 1.60–1.53 (m, 3 H), 1.47–1.43 (m, 1 H), 1.18–1.04 (m, 4 H), 0.94–0.83 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.43, 128.62, 128.20, 126.90, 83.26, 76.69, 61.42, 58.51, 53.31, 40.84, 31.62, 31.37, 30.53, 29.97, 26.25, 25.72, 25.58, 15.39.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{20}H_{27}NONa$: 320.1990; found: 320.1992.

(2*R,3*R**)-1-Benzyl-2-butyl-3-(pent-1-ynyl)aziridine (3h)**
Following the typical procedure for **3a** using imine **12h** gave **3h** in 3 steps as a colorless oil; yield: 80% (3 steps).

IR (neat): 3062, 3028, 2959, 2931, 2870, 2162, 1604, 1495, 1454, 1379, 1353 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 7.2 Hz, 2 H), 7.33 (t, *J* = 7.2 Hz, 2 H), 7.24 (t, *J* = 7.2 Hz, 1 H), 3.87 (d, *J* = 13.6 Hz, 1 H), 3.54 (d, *J* = 13.6 Hz, 1 H), 2.35 (s, 1 H), 2.22–2.18 (m, 2 H), 1.65–1.61 (m, 1 H), 1.57–1.48 (m, 2 H), 1.44–1.41 (m, 2 H), 1.37–1.26 (m, 4 H), 0.97 (t, *J* = 7.6 Hz, 3 H), 0.90–0.83 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.63, 128.38, 128.13, 126.72, 84.05, 76.40, 58.15, 48.05, 32.63, 32.30, 29.06, 22.26, 22.14, 20.78, 13.86, 13.37.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{18}H_{26}N$: 256.2065; found: 256.2065.

(2*R,3*R**)-1-Benzyl-2-*tert*-butyl-3-(pent-1-ynyl)aziridine (3i)**
Following the typical procedure for **3a** using imine **12i** gave **3i** in 3 steps as a colorless oil; yield: 61% (3 steps).

IR (neat): 3063, 3030, 2958, 2904, 2870, 2227, 1605, 1496, 1477, 1455, 1413, 1382, 1362 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 7.2 Hz, 2 H), 7.31 (t, *J* = 7.2 Hz, 2 H), 7.23 (t, *J* = 7.2 Hz, 1 H), 3.91 (d, *J* = 13.2 Hz, 1 H), 3.68 (d, *J* = 13.2 Hz, 1 H), 2.45 (s, 1 H), 2.18 (t, *J* = 6.8 Hz, 2 H), 1.56–1.47 (m, 3 H), 0.96 (t, *J* = 7.6 Hz, 3 H), 0.75 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.95, 128.78, 128.57, 126.77, 83.53, 76.81, 58.66, 57.47, 30.47, 28.30, 27.60, 22.24, 20.85, 13.56.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{18}H_{25}NNa$: 278.1885; found: 278.1884.

(2*R,3*R**)-1-Benzyl-2-(pent-1-ynyl)-3-phenylaziridine (3j)**
Following the typical procedure for **3a** using imine **12j** gave **3j** in 3 steps as a colorless oil; yield: 77% (3 steps).

IR (neat): 3061, 3029, 2962, 2931, 2870, 2241, 1602, 1495, 1453, 1383, 1353 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 6.8 Hz, 2 H), 7.32–7.22 (m, 8 H), 4.06 (d, *J* = 14.0 Hz, 1 H), 3.83 (d, *J* = 14.0 Hz, 1 H), 2.67 (d, *J* = 2.8 Hz, 1 H), 2.65–2.63 (m, 1 H), 2.26–2.23 (m, 2 H), 1.60–1.51 (m, 2 H), 0.99 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.42, 138.75, 128.23, 128.20, 128.03, 127.13, 126.73, 126.11, 84.83, 75.65, 57.88, 49.42, 36.91, 22.12, 20.84, 13.46.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{20}H_{22}N$: 276.1752; found: 276.1750.

(2*R,3*R**)-1-Benzyl-2-(2-naphthyl)-3-(pent-1-ynyl)aziridine (3k)**
Following the typical procedure for **3a** using imine **12k** gave **3k** in 3 steps as a colorless oil; yield: 85% (3 steps).

IR (neat): 3061, 3028, 2963, 2932, 2872, 2239, 1603, 1509, 1497, 1454, 1380, 1357 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.76–7.72 (m, 4 H), 7.45–7.33 (m, 5 H), 7.28–7.15 (m, 3 H), 4.12 (d, *J* = 14.4 Hz, 1 H), 3.87 (d, *J* = 14.4 Hz, 1 H), 2.82 (d, *J* = 2.4 Hz, 1 H), 2.74 (d, *J* = 2.4 Hz, 1 H), 2.23 (t, *J* = 6.8 Hz, 2 H), 1.60–1.51 (m, 2 H), 1.00 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.37, 136.26, 133.24, 132.80, 128.24, 127.99, 127.97, 127.61, 126.75, 126.00, 125.49, 124.93, 124.14, 84.98, 75.65, 56.91, 49.64, 37.11, 22.13, 20.85, 13.48.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{24}H_{23}NNa$: 348.1728; found: 348.1722.

1-Benzyl-2-cyclohexyl-5-propyl-1*H*-pyrrole (4a); Typical Procedure
To a stirred soln of **3a** (40.0 mg, 0.142 mmol) in dioxane–H_2O (2:1) was added $PtCl_2$ (3.78 mg, 0.014 mmol) at r.t. The mixture was stirred at 100 °C for 2 h and then cooled to r.t. and diluted with the minimum amount of Et_2O. The soln was dried ($MgSO_4$) and filtered through a small amount of silica gel. Concentration at reduced pressure gave the residue, which was chromatographed (silica gel, hexane–EtOAc, 98:2) to give **4a** (30.8 mg, 77%) as a yellow oil.

IR (neat): 3061, 3026, 2928, 2851, 1605, 1495, 1450, 1426, 1376, 1352 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.20 (m, 3 H), 6.84 (d, *J* = 7.2 Hz, 2 H), 5.91 (s, 2 H), 5.04 (s, 2 H), 2.37–2.31 (m, 2 H), 1.82–1.79 (m, 2 H), 1.71–1.60 (m, 3 H), 1.58–1.54 (m, 3 H), 1.36–1.30 (m, 2 H), 1.23–1.19 (m, 3 H), 0.90 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.22, 138.82, 132.37, 128.59, 126.87, 125.52, 104.40, 102.35, 46.30, 35.85, 34.22, 28.70, 26.73, 26.13, 21.74, 14.11.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{20}H_{27}NNa$: 304.2041; found: 304.2040.

1-Benzyl-2-cyclohexyl-5-phenyl-1*H*-pyrrole (4b)
Yellow oil; yield: 79%.

IR (neat): 3066, 3028, 2927, 2850, 1602, 1508, 1496, 1450, 1388, 1359 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.21 (m, 8 H), 6.88 (d, *J* = 7.2 Hz, 2 H), 6.26 (d, *J* = 3.6 Hz, 1 H), 6.08 (d, *J* = 3.6 Hz, 1 H), 5.18 (s, 2 H), 2.38–2.31 (m, 1 H), 1.84–1.65 (m, 5 H), 1.45–1.36 (m, 2 H), 1.28–1.17 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.06, 139.57, 133.90, 133.80, 128.88, 128.58, 128.21, 126.89, 126.55, 125.56, 108.30, 104.20, 47.39, 36.04, 34.29, 26.73, 26.07.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{23}H_{25}NNa$: 338.1885; found: 338.1882.

1,2-Dibenzyl-5-cyclohexyl-1*H*-pyrrole (4c)
Yellow oil; yield: 68%.

IR (neat): 3062, 3027, 2926, 2852, 1604, 1495, 1452, 1427, 1355 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.12 (m, 6 H), 7.08 (d, *J* = 7.2 Hz, 2 H), 6.82 (d, *J* = 6.8 Hz, 2 H), 5.91 (d, *J* = 3.2 Hz, 1 H), 5.83 (d, *J* = 3.2 Hz, 1 H), 4.95 (s, 2 H), 3.73 (s, 2 H), 2.38–2.32 (m, 1 H), 1.82–1.64 (m, 5 H), 1.40–1.34 (m, 2 H), 1.31–1.19 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.68, 139.62, 139.61, 130.50, 128.62, 128.27, 126.93, 126.03, 125.57, 107.17, 102.47, 46.56, 35.89, 34.15, 33.20, 26.71, 26.12.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{24}H_{27}NNa$: 352.2041; found: 352.2044.

2-Allyl-1-benzyl-5-cyclohexyl-1*H*-pyrrole (4d)
Yellow oil; yield: 65%.

IR (neat): 3063, 3028, 2926, 2851, 1638, 1605, 1496, 1450, 1429, 1355 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.20 (m, 3 H), 6.84 (d, *J* = 7.2 Hz, 2 H), 5.92–5.82 (m, 3 H), 5.05–4.96 (m, 4 H), 3.15 (d, *J* = 6.8 Hz, 2 H), 2.40–2.27 (m, 1 H), 1.81–1.65 (m, 5 H), 1.43–1.28 (m, 2 H), 1.25–1.14 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.53, 139.03, 135.88, 129.65, 128.64, 126.93, 125.53, 115.79, 105.74, 102.51, 46.35, 35.84, 34.14, 31.48, 26.70, 26.11.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{25}NNa$: 302.1885; found: 302.1882.

1-Benzyl-2-[3-(*tert*-butyldiphenylsiloxy)propyl]-5-cyclohexyl-1*H*-pyrrole (4e)
Yellow oil; yield: 72%.

IR (neat): 3070, 3050, 2928, 2855, 1589, 1496, 1450, 1427, 1389, 1355 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61–7.58 (m, 4 H), 7.40–7.31 (m, 6 H), 7.26–7.24 (m, 3 H), 6.82 (d, *J* = 7.6 Hz, 2 H), 5.91–5.87 (m, 2 H), 5.03 (s, 2 H), 3.65 (t, *J* = 7.6 Hz, 2 H), 2.47 (t, *J* = 7.6 Hz, 2 H), 2.38–2.33 (m, 1 H), 1.83–1.79 (m, 4 H), 1.72–1.64 (m, 2 H), 1.39–1.19 (m, 6 H), 0.95 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.05, 138.96, 135.54, 133.97, 132.01, 129.48, 128.62, 127.56, 126.89, 125.52, 104.32, 102.35, 63.44, 46.32, 35.84, 34.20, 31.49, 29.69, 26.82, 26.73, 26.12, 22.94, 19.16.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{36}H_{45}NOSiNa$: 558.3168; found: 558.3163.

3-(1-Benzyl-5-cyclohexyl-1*H*-pyrrol-2-yl)propan-1-ol (4f)
Colorless oil; yield: 70%.

IR (neat): 3365, 3094, 3063, 2927, 2852, 1605, 1496, 1450, 1427, 1354 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.20 (m, 3 H), 6.84 (d, *J* = 7.6 Hz, 2 H), 5.93 (d, *J* = 3.6 Hz, 1 H), 5.91 (d, *J* = 3.6 Hz, 1 H), 5.06 (s, 2 H), 3.62 (t, *J* = 6.4 Hz, 2 H), 2.48 (t, *J* = 7.6 Hz, 2 H), 2.39–2.32 (m, 1 H), 1.84–1.79 (m, 4 H), 1.77–1.65 (m, 3 H), 1.39–1.17 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.25, 138.98, 131.39, 128.66, 126.99, 125.48, 104.61, 102.47, 62.50, 46.31, 35.81, 34.17, 31.38, 26.69, 26.09, 22.79.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{27}NONa$: 320.1990; found: 320.1996.

1-Benzyl-2-cyclohexyl-1*H*-pyrrole (4g)
Yellow oil; yield: 38%.

IR (neat): 3063, 3034, 2926, 2852, 1699, 1496, 1451, 1354 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.23 (m, 3 H), 7.00 (d, *J* = 7.2 Hz, 2 H), 6.56–6.54 (m, 1 H), 6.14 (t, *J* = 3.2 Hz, 1 H), 5.97–5.95 (m, 1 H), 5.07 (s, 2 H), 2.45–2.39 (m, 1 H), 1.82–1.69 (m, 4 H), 1.44–1.21 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.72, 138.89, 128.63, 127.27, 126.36, 120.39, 107.15, 103.74, 50.00, 35.58, 34.00, 26.71, 26.10.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{21}NNa$: 262.1572; found: 262.1570.

1-Benzyl-2-butyl-5-propyl-1*H*-pyrrole (4h)
Colorless oil; yield: 81%.

IR (neat): 3063, 3026, 2956, 2929, 2870, 1605, 1509, 1495, 1454, 1423, 1377, 1353 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.19 (m, 3 H), 6.85 (d, *J* = 7.6 Hz, 2 H), 5.90 (s, 2 H), 5.02 (s, 2 H), 2.40 (q, *J* = 7.2 Hz, 4 H), 1.63–1.50 (m, 4 H), 1.37–1.27 (m, 2 H), 0.92 (t, *J* = 7.6 Hz, 3 H), 0.85 (t, *J* = 7.2 Hz, 3 H).

^{13}C–NMR (100 MHz, $CDCl_3$): δ = 138.94, 132.86, 132.73, 128.61, 126.89, 125.53, 104.34, 104.29, 46.39, 30.88, 28.75, 26.26, 22.50, 21.98, 14.06, 13.86.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{25}NNa$: 278.1885; found: 278.1889.

1-Benzyl-2-*tert*-butyl-5-propyl-1*H*-pyrrole (4i)
Colorless oil; yield: 71%.

IR (neat): 3063, 3028, 2960, 2929, 2871, 1605, 1567, 1497, 1467, 1454, 1414, 1394, 1377 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.18 (m, 3 H), 6.79 (d, *J* = 7.2 Hz, 2 H), 5.97 (d, *J* = 3.6 Hz, 1 H), 5.90 (d, *J* = 3.6 Hz, 1 H), 5.28 (s, 2 H), 2.25 (t, *J* = 7.6 Hz, 2 H), 1.64–1.56 (m, 2 H), 1.27 (s, 9 H), 0.89 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.95, 139.65, 134.75, 128.46, 126.68, 125.41, 103.79, 103.67, 48.25, 31.07, 28.58, 21.40, 14.13.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{25}NNa$: 278.1885; found: 278.1889.

1-Benzyl-2-phenyl-5-propyl-1*H*-pyrrole (4j)
Yellow oil; yield: 72%.

IR (neat): 3062, 3028, 2958, 2928, 2870, 1602, 1509, 1495, 1452, 1411, 1384, 1355 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.21 (m, 8 H), 6.92 (d, *J* = 7.6 Hz, 2 H), 6.27 (d, *J* = 3.6 Hz, 1 H), 6.09 (d, *J* = 3.6 Hz, 1 H), 5.16 (s, 2 H), 2.42 (t, *J* = 7.6 Hz, 2 H), 1.66 (sext, *J* = 7.6 Hz, 2 H), 0.96 (t, *J* = 7.6 Hz, 3 H).

^{13}C–NMR (100 MHz, $CDCl_3$): δ = 139.20, 135.12, 134.40, 133.82, 128.74, 128.65, 128.28, 126.91, 126.61, 125.59, 108.04, 105.91, 47.46, 28.78, 21.70, 14.09.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{22}N$: 276.1752; found: 276.1747.

1-Benzyl-2-(2-naphthyl)-5-propyl-1*H*-pyrrole (4k)
Yellow oil; yield: 48%.

IR (neat): 3057, 3017, 2960, 2928, 2872, 1630, 1603, 1497, 1454, 1414, 1379, 1357 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79–7.64 (m, 5 H), 7.46–7.40 (m, 2 H), 7.32–7.23 (m, 3 H), 6.94 (d, *J* = 6.8 Hz, 2 H), 6.37 (d, *J* = 3.6 Hz, 1 H), 6.12 (d, *J* = 3.6 Hz, 1 H), 5.21 (s, 2 H), 2.45 (t, *J* = 7.2 Hz, 2 H), 1.66 (sext, *J* = 7.2 Hz, 2 H), 0.89 (t, *J* = 7.2 Hz, 3 H).

^{13}C–NMR (100 MHz, $CDCl_3$): δ = 139.16, 135.53, 134.34, 133.31, 132.09, 131.14, 128.70, 127.90, 127.81, 127.52, 127.30, 126.97, 126.90, 126.06, 125.61, 125.58, 108.56, 106.10, 47.61, 31.58, 22.64, 14.12.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{24}H_{23}NNa$: 348.1728; found: 348.1724.

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