Lewis Acid/Metal Amide Hybrid as an Efficient Catalyst for Carbon-Carbon Bond Formation

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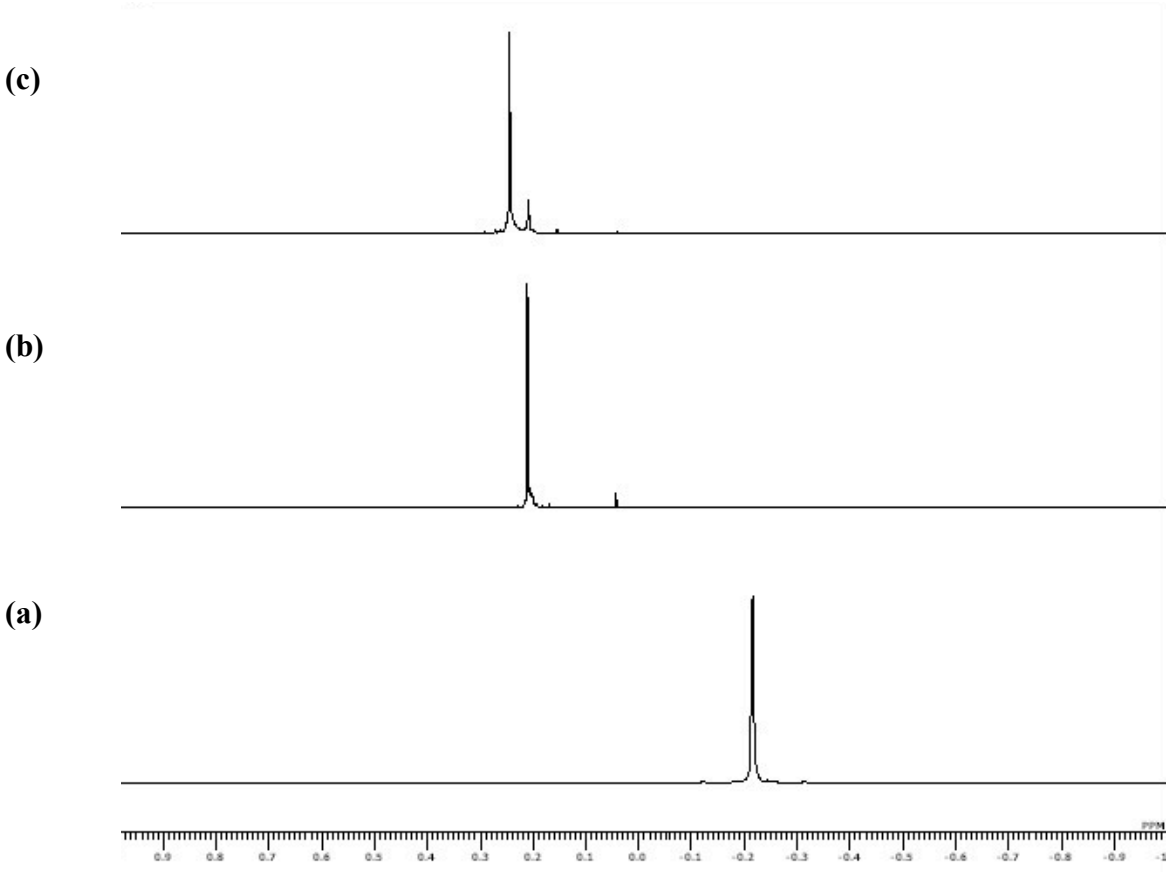
Electronic Supplementary Material (ESI)

Contents

1. NMR Study of Indium Catalyst Structures

Formation of $In(HMDS)_2OTf$ was investigated by NMR experiments. Chemical shift change of the methyl peak of HMDS was monitored by ^1H NMR analysis (Figure S1). AgOTf was added to a solution of isolated $In(HMDS)_2Cl$ in THF-d_8 (In:Ag = 1.1:1), and formation of colorless precipitates was confirmed. The solution was examined by ^1H NMR analysis at rt, and it was found that clear change of the peak chemical shift occurred accompanying a small peak of $In(HMDS)_2Cl$ species remained. This result indicates that $In(HMDS)_2OTf$ clearly formed in THF-d_8.

Figure S1 ^{1}H NMR experiment for formation of In(HMDS)$_2$OTf in THF-d$_8$



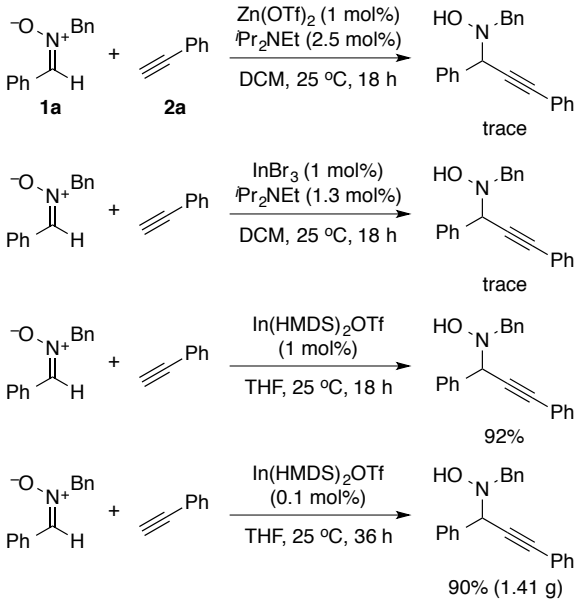
(a) KHMDS; (b) Isolated In(HMDS)$_2$Cl; (c) In(HMDS)$_2$Cl + AgOTf (1.1:1)

2. Comparison of Catalysts

As mentioned in the text, two catalysts, Zn(OTf)$_2$/^{i}Pr$_2$NEt and InBr$_3$/^{i}Pr$_2$NEt, have been reported for the reactions of nitrones with terminal alkynes. These catalysts and our new hybrid catalyst were compared.

First, the reaction of nitrone **1a** with phenylacetylene **2a** was chosen as a model reaction, and the three catalysts were compared (Scheme S1). When the catalyst loading was set as 1 mol%, Zn(OTf)$_2$/^{i}Pr$_2$NEt and InBr$_3$/^{i}Pr$_2$NEt gave only trace amounts of the product. On the contrary, the reaction proceeded smoothly to afford the desired product in 94% yield using 1 mol% of In(HMDS)$_2$OTf. Moreover, even **0.1 mol% of In(HMDS)$_2$OTf** worked well to give the product in 90% yield, A gram-scale synthesis has been also attained by a very simple procedure (see below).

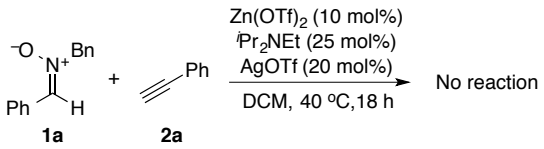
Scheme S1. The reaction of nitrone **1a** with terminal phenylacetylene **2a**

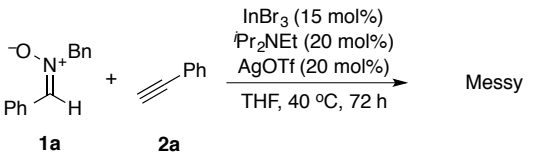


Next, we compared the catalysts in the tandem addition/cyclization reactions (Figure 4 in the text, Scheme S2). In the isoxazoline synthesis, no reaction occurred in the $Zn(OTf)_2$/$^{i}Pr_2NEt$ system and the reaction became messy using the $InBr_3$/$^{i}Pr_2NEt$ system. Interestingly, even the addition product was not obtained in these cases. On the contrary, the desired isoxazoline derivative was obtained in 96% yield using our hybrid catalyst system. Similar results were obtained in the aziridine synthesis. No reaction occurred in the $Zn(OTf)_2$/$^{i}Pr_2NEt$ system and the reaction became messy using the $InBr_3$/$^{i}Pr_2NEt$ system. On the contrary, the desired aziridine derivative was obtained in 83% yield using our hybrid catalyst system.

Scheme S2. The tandem addition/cyclization reactions

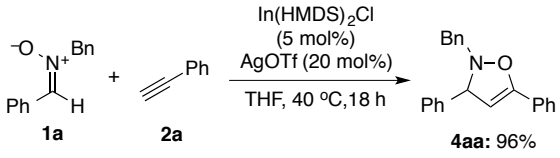
Isoxazoline synthesis



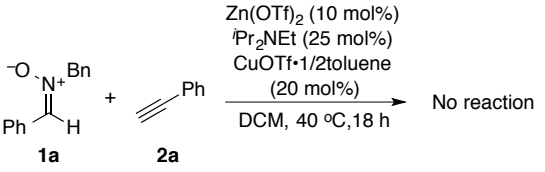


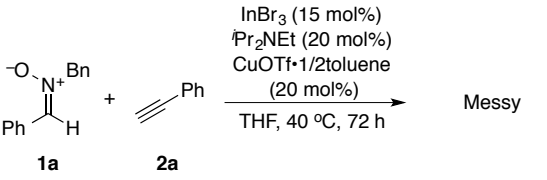
(Figure 4)

(A)



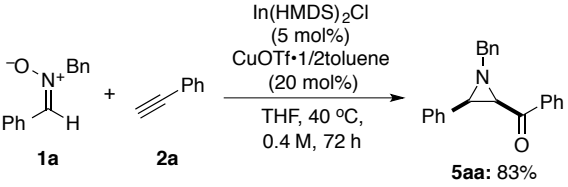
Aziridine Synthesis



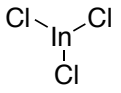
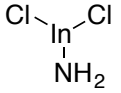
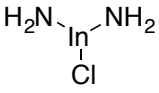
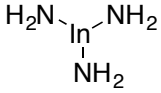
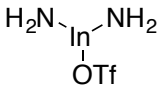


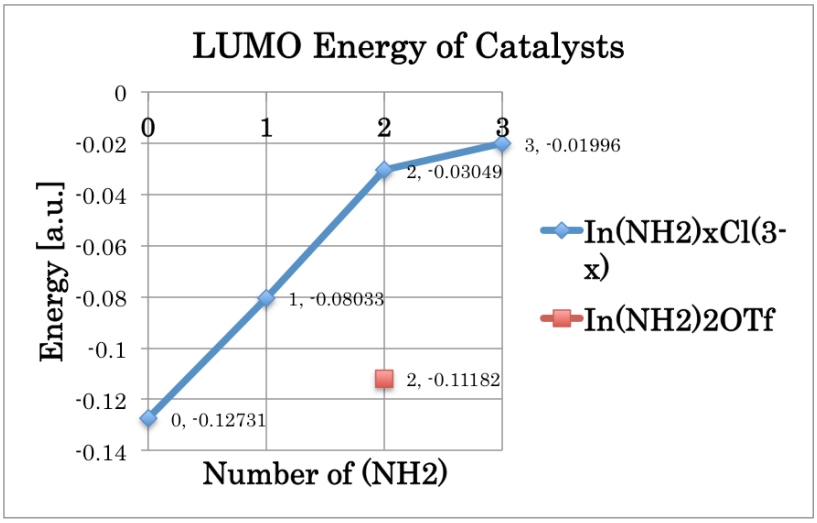
(Figure 4)

(B)



3. DFT calculation of the indium species

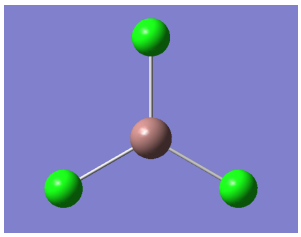
					
LUMO enrgy [a.u.]	-0.12731	-0.08033	-0.03049	-0.01996	-0.11182



DFT calculations were performed to evaluate catalyst activities of the In amide species (the amide part was changed from HMDS to NH_2 for simplification). It was found that LUMO energy levels of the In species depended on the number of the chloride group on the In atom. In comparison of $In(NH_2)_2Cl$ with $In(NH_2)_2OTf$, the LUMO level of $In(NH_2)_2OTf$ is much lower than that of $In(NH_2)_2Cl$, which indicates that $In(NH_2)_2OTf$ is more Lewis acidic than $In(NH_2)_2Cl$.

The calculations were conducted using the Gaussian 09 suite of programs at the B3LYP/LanL2DZ level of theory with the IEFPCM dielectric continuum solvation model and the default parameters for THF ($\varepsilon = 7.6$) referring reported In(III) complex.[1]

3-1 $InCl_3$

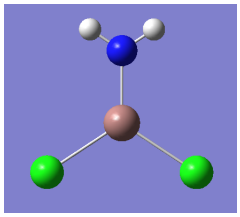


Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	In1	0.000000	0.000000	0.000000
2	Cl1	0.000000	2.350882	0.000000
3	Cl2	2.035923	-1.175441	0.000000
4	Cl3	-2.035923	-1.175441	0.000000

B3LYP/LanL2DZ Energy = -46.88805468 a.u.

Number of Imaginary Frequencies = 0

3-2 $In(NH_2)Cl_2$

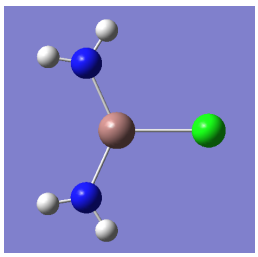


Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	In1	-0.000022	0.282034	-0.000011
2	N1	0.003612	2.200175	0.000009
3	H1	0.851675	2.758566	0.000199
4	H2	-0.841902	2.762392	-0.000060
5	Cl1	-1.985968	-1.020134	0.000014
6	Cl2	1.983971	-1.023505	0.000007

B3LYP/LanL2DZ Energy = -87.87129091 a.u.

Number of Imaginary Frequencies = 0

3-3 $In(NH_2)_2Cl$

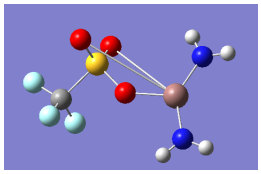


Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	In1	-0.306207	0.000100	-0.000030
2	N1	-1.101802	1.765913	0.000046
3	H1	-0.567614	2.628830	0.000409
4	H2	-2.103772	1.931597	-0.000263
5	N2	-1.106376	-1.763715	0.000077
6	H3	-2.108755	-1.926752	0.000297
7	H4	-0.574390	-2.627971	-0.000148
8	Cl1	2.106818	-0.001529	0.000020

B3LYP/LanL2DZ Energy = -128.84409738 a.u.

Number of Imaginary Frequencies = 0

3-4 $In(NH_2)_2OTf$



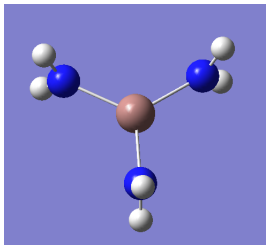
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z

1	In1	1.967406	-0.122011	-0.021927
2	N1	2.660773	-1.900751	0.244798
3	H1	3.639692	-2.151213	0.152156
4	H2	2.075735	-2.693450	0.488142
5	N2	2.613998	1.654446	-0.410136
6	H3	2.003766	2.447859	-0.579148
7	H4	3.596183	1.899678	-0.481521
8	O1	-0.035756	-0.232419	0.169635
9	S1	-1.358622	0.799348	0.264016
10	O2	-1.362596	1.901252	-0.921956
11	O3	-1.658641	1.263135	1.783335
12	C1	-2.727410	-0.593449	-0.209583
13	F1	-3.973646	-0.004115	-0.253362
14	F2	-2.719226	-1.586577	0.745007
15	F3	-2.427494	-1.129840	-1.443054

B3LYP/LanL2DZ Energy = -687.05158335 a.u.

Number of Imaginary Frequencies = 0

3-5 $In(NH_2)_3$



Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	In1	0.003326	-0.006513	-0.035316
2	N1	-0.305063	2.171744	-0.025667
3	H1	-1.176410	2.383142	0.416791

4	H2	0.440935	2.611867	0.473816
5	N2	2.043928	-0.828523	-0.051011
6	H3	2.684988	-0.135696	0.278743
7	H4	2.083984	-1.632682	0.541803
8	N3	-1.728886	-1.362759	-0.029270
9	H5	-1.693876	-1.944655	0.783057
10	H6	-2.572473	-0.826091	-0.022085

B3LYP/LanL2DZ Energy = -169.77395288 a.u.

Number of Imaginary Frequencies = 0

4. Experimental section

General

^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM-ECA500 and JNM-ECX600 spectrometers in $CDCl_3$ or DMSO-d_6 or THF-d_8 unless otherwise noted. In NMR analysis using $CDCl_3$ as a solvent, tetramethylsilane (TMS) served as internal standard ($\delta = 0$) for ^{1}H NMR, and $CDCl_3$ served as internal standard ($\delta = 77.0$) for ^{13}C NMR. In NMR analysis using DMSO-d_6 as a solvent, DMSO served as internal standard for ^{1}H NMR ($\delta = 2.54$), and DMSO-d_6 served as internal standard for ^{13}C NMR ($\delta = 40.4$). In NMR analysis using THF-d_8 as a solvent, THF served as internal standard for ^{1}H NMR ($\delta = 3.58$), and THF-d_8 served as internal standard for ^{13}C NMR ($\delta = 67.6$). IR spectra were measured with a JASCO FT/IR-4200 spectrometer. High resolution mass spectrometry was recorded with a JEOL JMS-T100TD (DART®). Column chromatography was conduced using Silica gel 60N (Kanto Chemical Co., Inc.). Potassium bis(trimethylsilyl)amide (KHMDS) was purchased from Aldrich Co., Ltd. and used without further purification. Silver triflate (AgOTf) was purchased from Tokyo Chemical Industry Co., Ltd. (TCI) and used without further purification. Indium trichloride ($InCl_3$) and Indium triisopropoxide ($In(O^{i}Pr)_3$) were purchased from Kojundo Chemical laboratory Co., Ltd. and used without further purification. All of the solvents except for dichloromethane were purchased from Wako Pure Chemical Industries, Ltd. or TCI as dry solvents and purified by distillation in the presence of benzophenone and sodium. Dichloromethane was purchased from Wako Pure Chemical Industries, Ltd. as a dry solvent. The deuterated THF (THF-d_8) was

purchased from Aldrich Co., Ltd. and dried over activated MS 5A inside a glovebox fulfilled with Ar. Nitrones and terminal alkynes were prepared following literatures.[2] Compounds **7** were purchased from Wako Pure Chemical Industries, Ltd. and purified by distillation or recrystallization.

Synthesis of $In(HMDS)_2Cl$.

Under Ar atmosphere, KHMDS (6.0 mmol) in THF (10 mL) was added dropwise to a stirred suspension of $InCl_3$ (3.0 mmol) in THF (10 mL) during 15 min at 0 ^oC. The reaction temperature was raised to rt, and the reaction mixture was stirred for 10 h at the same temperature. The mixture was filtered, and the filtrate was evaporated under reduced pressure. Dry petroleum ether was added to the residue obtained, and the precipitate was filtrated off. The filtrate was evaporated again under reduced pressure, and a colorless solid was obtained. The solid was purified by sublimation (120 ^oC, 0.1 mmHg) to afford powdered $In(HMDS)_2Cl$ (46% yield). The sample of $In(HMDS)_2Cl$ for X-ray crystal structure analysis was obtained after recrystallization from dry petroleum ether (20% yield). ^1H NMR (600 MHz, THF-d_8, ppm) δ ppm (s); ^{13}C NMR (150 MHz, THF-d_8, ppm) δ 5.7; Elemental analysis, calcd. for $C_{12}H_{36}ClInN_2Si_4$: C 30.60, H 7.70, N 5.95; found C 30.00, H 7.64, N 5.59.

NMR experiment for identification of $In(HMDS)_2OTf$.

$In(HMDS)_2OTf$: In a well-dried 6 ml glass vial, $In(HMDS)_2Cl$ (5.89 mg, 0.0125 mmol) and AgOTf (3.21 mg, 0.0125 mmol) were placed inside a glove box fulfilled with Ar, and anhydrous THF-d_8 (0.3 mL) was added. In the solution, formation of colorless precipitates was observed. After stirring for 30 minutes, the solution was transferred into a NMR tube using a syringe and rinsed with another anhydrous THF-d_8 (0.4 mL) to prepare the measurement sample.

Experimental procedure of catalytic addition reaction of nitrones 1 with terminal alkynes 2 by using $In(HMDS)_2OTf$ (Figure 3):

A solution of $In(HMDS)_2Cl$ (0.011 mmol), AgOTf (0.010 mmol) in THF (1.0 mL) in a flame dried glass tube (10 mL) with septa was stirred for 30 min at 25 ^oC under Ar atmosphere. Nitrone **1** (1.0 mmol) and terminal acetylene **2** (1.1 mmol) in THF (1.5 mL) were successively added, and the mixture was stirred for 18 h at 25 ^oC. The

reaction mixture was quenched with H_2O (5 mL), and the aqueous layer was extracted with dichloromethane (10 ml x 3). After the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure after filtration, the residue was purified by column chromatography using silica gel with hexane-dichloromethane (4:6) as eluent to give the desired product **3**.

A gram-scale synthesis of 3aa using using 0.1 mol% of In(HMDS)$_2$OTf (Figure 4):

A solution of In(HMDS)$_2$Cl (0.0055 mmol), AgOTf (0.005 mmol) in THF (0.5 mL) in a flame dried glass tube (10 mL) with septa was stirred for 30 min at 25 ^oC under Ar atmosphere. Nitrone **1a** (5.0 mmol) and terminal acetylene **2a** (5.5 mmol) were successively added, and the mixture was stirred for 36 h at 25 ^oC. The reaction mixture was quenched with H_2O (5 mL), and the aqueous layer was extracted with dichloromethane (10 ml x 3). After the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure after filtration, the residue was purified by column chromatography using silica gel with hexane-dichloromethane (4:6) as eluent to give the desired product **3aa** (4.5 mmol, 1.41 g, 90%).

Experimental procedure of the tandem addition/cyclization reaction for the synthesis of isoxazoline (Figure 5(A)):

A solution of In(HMDS)$_2$Cl (0.025 mmol) and AgOTf (0.05 mmol) in THF (1.0 mL) in a flame dried glass tube (10 mL) with septa was stirred for 30 min at 40 ^oC under Ar atmosphere. **2a** (0.55 mmol) and **1a** (0.50 mmol) in THF (1.5 mL) were added, and the mixture was stirred for 24 h at the same temperature. The reaction mixture was quenched with H_2O (5 mL), and the aqueous layer was extracted with dichloromethane (10 ml x 3). After the combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure, the residue was purified by column chromatography with hexane-dichloromethane (4:6) as eluent to give the desired compound **4aa** (96%).

Experimental procedure of the tandem addition/cyclization reaction using the Zn(OTf)$_2$/^{i}Pr$_2$NEt catalyst system (Scheme S2):

A solution of Zn(OTf)$_2$ (0.040 mmol), ^{i}Pr$_2$NEt (0.10 mmol) and AgOTf (0.080 mmol) in DCM (1.0 mL) in a flame dried glass tube (10 mL) with septa was stirred for

30 min at 40 °C under Ar atmosphere. **2a** (0.80 mmol) and **1a** (0.40 mmol) in DCM (1.0 mL) were added, and the mixture was stirred for 24 h at the same temperature. The reaction mixture was quenched with H_2O (5 mL), and the aqueous layer was extracted with dichloromethane (10 ml x 3). After the combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure, the residue was diluted with $CDCl_3$ and was analyzed by ^1H NMR. It was found that no reaction occurred.

Experimental procedure of the tandem addition/cyclization reaction using the $InBr_3$/^{i}Pr$_2$NEt catalyst system (Scheme S2):

A solution of $InBr_3$ (0.10 mmol), ^{i}Pr$_2$NEt (0.10 mmol) and AgOTf (0.080 mmol) in DCM (1.0 mL) in a flame dried glass tube (10 mL) with septa was stirred for 30 min at 40 °C under Ar atmosphere. **2a** (0.80 mmol) and **1a** (1.20 mmol) in DCM (1.0 mL) were added, and the mixture was stirred for 24 h at the same temperature. The reaction mixture was quenched with H_2O (5 mL), and the aqueous layer was extracted with dichloromethane (10 ml x 3). After the combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure, the residue was diluted with $CDCl_3$ and was analyzed by ^1H NMR. It was found that the reaction became messy and that neither addition product nor **4aa** was detected.

Experimental procedure of the tandem addition/cyclization reaction for the synthesis of aziridine (Figure 5(B)):

A solution of $In(HMDS)_2Cl$ (0.025 mmol) and CuOTf-1/2Toluene (0.10 mmol) in THF (0.5 mL) in a flame dried glass tube (10 mL) with septa was stirred for 30 min at 40 °C under Ar atmosphere. **2a** (0.55 mmol) and **1a** (0.50 mmol) in THF (0.75 mL) were added, and the mixture was stirred for 72 h at the same temperature. The reaction mixture was quenched with H_2O (5 mL), and the aqueous layer was extracted with dichloromethane (10 ml x 3). After the combined borganic layers were dried over Na_2SO_4 and concentrated under reduced pressure, the residue was purified by column chromatography with hexane-ethylacetate (5:1) as eluent to give the desired compound **5aa** (83%).

Experimental procedure of the tandem addition/cyclization reaction using the $Zn(OTf)_2$/^{i}Pr$_2$NEt catalyst system (Scheme S2):

A solution of $Zn(OTf)_2$ (0.040 mmol), $^{i}Pr_2NEt$ (0.10 mmol) and CuOTf-1/2Toluene (0.080 mmol) in DCM (1.0 mL) in a flame dried glass tube (10 mL) with septa was stirred for 30 min at 40 ^{o}C under Ar atmosphere. **2a** (0.80 mmol) and **1a** (0.40 mmol) in DCM (1.0 mL) was added, and the mixture was stirred for 72 h at the same temperature. The reaction mixture was quenched with H_2O (5 mL), and the aqueous layer was extracted with dichloromethane (10 ml x 3). After the combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure, the residue was diluted with $CDCl_3$ and was analyzed by ^{1}H NMR. It was found that no reaction occurred.

Experimental procedure of the tandem addition/cyclization reaction using the $InBr_3$/$^{i}Pr_2NEt$ catalyst system (Scheme S2):

A solution of $InBr_3$ (0.10 mmol), $^{i}Pr_2NEt$ (0.10 mmol) and CuOTf-1/2Toluene (0.080 mmol) in DCM (1.0 mL) in a flame dried glass tube (10 mL) with septa was stirred for 30 min at 40 ^{o}C under Ar atmosphere. **2a** (1.20 mmol) and **1a** (0.40 mmol) in DCM (1.0 mL) was added, and the mixture was stirred for 72 h at the same temperature. The reaction mixture was quenched with H_2O (5 mL), and the aqueous layer was extracted with dichloromethane (10 ml x 3). After the combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure, the residue was diluted with $CDCl_3$ and was analyzed by ^{1}H NMR. It was found that the reaction became messy and that neither addition product nor **4aa** was detected.

Experimental procedure of the catalytic addition reaction of *p*-nitrobenzaldehyde (7a) with phenylacetylene (2a) by using $In(HMDS)_2Cl$ (Figure 6(A)):

A solution of $In(HMDS)_2Cl$ (0.015 mmol) in DME (0.5 mL) in a flame dried glass tube (10 mL) with septa was stirred for 30 min at 40 ^{o}C under Ar atmosphere. **7b** (0.50 mmol) and **2a** (1.0 mmol) in DME (0.5 mL) were successively added, and the mixture was stirred for 48 h at 40 ^{o}C. The reaction mixture was quenched with H_2O (5 mL), and the aqueous layer was extracted with dichloromethane (10 ml x 3). After the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure after filtration, the residue was purified by column chromatography using silica gel with hexane-ethyl acetate (4:1) as eluent to give the desired product (72%).

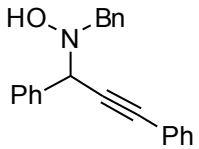
Experimental procedure of the catalytic addition reaction of cyclohexanecarboxaldehyde (7b) with phenylacetylene (2a) by using $In(HMDS)_2F$ (Figure 6(B)):

A solution of InF_3 (0.010 mmol) and KHMDS (0.020 mmol) in DME (1.0 mL) in a flame dried glass tube (10 mL) with septa was stirred for 30 min at 40 ^oC under Ar atmosphere. At this stage, $In(HMDS)_2F$ was formed, which was confirmed by NMR analysis. **7b** (1.0 mmol) and **2a** (2.0 mmol) were thensuccessively added, and the mixture was stirred for 48 h at 40 ^oC. The reaction mixture was quenched with H_2O (5 mL), and the aqueous layer was extracted with dichloromethane (10 ml x 3). After the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure after filtration, the residue was purified by column chromatography using silica gel with hexane-ethyl-acetate (4:1) as eluent to give the desired product (72%).

Experimental procedure of catalytic addition reaction of cyclohexanone (7c) with phenylacetylene (2a) by using $In(HMDS)_2F$ (Figure 6(C)):

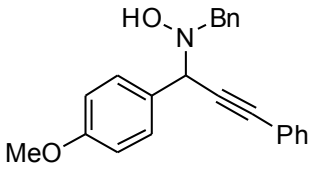
A solution of InF_3 (0.010 mmol) and KHMDS (0.020 mmol) in DME (1.0 mL) in a flame dried glass tube (10 mL) with septa was stirred for 30 min at 40 ^oC under Ar atmosphere. **7c** (1.0 mmol) and **2a** (2.0 mmol) were successively added, and the mixture was stirred for 48 h at 40 ^oC. The reaction mixture was quenched with H_2O (5 mL), and the aqueous layer was extracted with dichloromethane (10 ml x 3). After the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure after filtration, the residue was purified by column chromatography using silica gel with hexane-ethyl acetate (4:1) as eluent to give the desired product.

***N*-Benzyl-*N*-(1,3-diphenyl-prop-2-ynyl)-hydroxylamine (3aa)[3]:**



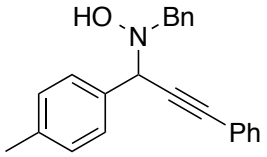
^1H NMR (600 MHz, $CDCl_3$, ppm) δ 7.53 - 7.49 (4H, m), 7.31 – 7.16 (11H, m), 5.68 (1H, s), 4.78 (1H, s), 3.90 (1H, d, J = 12.4 Hz), 3.79 (1H, d, J = 12.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 137.4, 137.1, 131.69, 131.9, 129.7, 128.9, 128.4, 128.4, 128.32, 128.29, 128.28, 128.1, 127.5, 122.8, 88.7, 84.5, 63.1, 60.6.

***N*-Benzyl-*N*-[1-(4-methoxyphenyl)-3-phenylprop-2-ynyl]-hydroxylamine (3ba):**



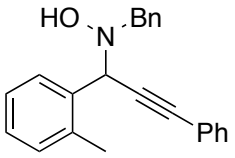
^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.57 (2H, q, *J* = 3.2 Hz), 7.50 (2H, q, *J* = 4.1 Hz), 7.36 – 7.24 (8H, m), 6.89 (2H,l d, *J* = 8.9 Hz), 5.79 (1H, s), 4.81 (1H, s), 3.95 (1H, d, *J* = 13.1 Hz), 3.86 (1H, d, *J* = 13.1 Hz), 3.79 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 159.4, 140.4, 138.3, 137.3, 132.1, 131.9, 130.1, 129.7, 129.1, 128.4, 128.32, 128.27, 127.4, 122.8, 118.9, 114.6, 113.7, 88.4, 84.8, 62.5, 55.3; IR (KBr, cm^{-1}) 3329, 2926, 2363, 2344, 2067, 1963, 1891, 1608, 1512, 1461, 1334, 1251, 1174, 1036, 916, 869, 837, 801, 785, 644; m.p. 128 ^{o}C; HRMS (DART) calculated for $C_{23}H_{22}NO_2$ [M+H]: 344.1651; found 344.1649.

***N*-Benzyl-*N*-[1-(4-methylphenyl)-3-phenylprop-2-ynyl]-hydroxylamine (3ca):**



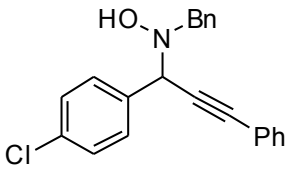
^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.57 – 7.55 (2H, m), 7.47 (2H, d, *J* = 7.6 Hz), 7.37 – 7.24 (8H, m), 7.17 (2H, d, *J* = 8.2 Hz), 5.64 (1H, s), 4.84 (1H, s), 3.97 (1H, d, *J* = 13.1 Hz), 3.90 (1H, d, *J* = 13.1 Hz), 2.34 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 137.8, 137.3, 134.5, 131.9, 129.6, 129.0, 128.8, 128.3, 128.3, 128.3, 127.4, 122.9, 88.4, 84.9, 62.9, 60.3, 21.1; IR (KBr, cm^{-1}) 3241, 2921, 2366, 2344, 1957, 1899, 1597, 1488, 1298, 1178, 1030, 864, 701; m.p. 129 ^{o}C; HRMS (DART) calculated for $C_{23}H_{22}NO$ [M+H]: 328.1701; found 344.1709.

***N*-Benzyl-*N*-[1-(2-methylphenyl)-3-phenylprop-2-ynyl]-hydroxylamine (3da):**



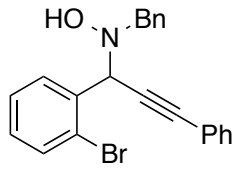
^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.83 (1H, d, *J* = 6.2 Hz), 7.52 (2H, s), 7.35 – 7.16 (11H, m), 5.25 (1H, s), 5.10 (1H, s), 3.98 (1H, d, *J* = 12.4 Hz), 3.90 (1H, d, *J* = 11.7 Hz), 2.26 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 137.1, 137.0, 135.7, 131.9, 130.5, 129.9, 129.6, 128.32, 128.30, 128.27, 128.1, 127.5, 125.8, 122.9, 88.4, 85.0, 61.2, 60.1, 19.1; IR (KBr, cm^{-1}) 3229, 2926, 2361, 2343, 1599, 1490, 1326, 1030, 755, 701; m.p. 132 – 133 ^{o}C; HRMS (DART) calculated for $C_{23}H_{22}NO$ [M+H]: 326.1701; found 328.1703.

***N*-Benzyl-*N*-[1-(4-chlorophenyl)-3-phenylprop-2-ynyl]-hydroxylamine (3ea):**



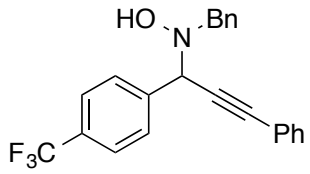
^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.58 - 7.55 (2H, m), 7.51 (2H, d, *J* = 8.2 Hz), 7.39 – 7.31 (9H, m), 7.30 – 7.26 (1H, m), 5.69 (1H, s), 4.81 (1H, s), 3.97 (1H, d, *J* = 12.4 Hz), 3.89 (1H, d, *J* = 13.1 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 136.9, 136.0, 133.9, 131.9, 130.2, 129.6, 128.6, 128.44, 128.41, 128.33, 128.32, 127.6, 122.29, 89.0, 83.9, 62.3;IR (KBr, cm^{-1}) 3230, 2869, 2360, 2344, 1889, 1597, 1487, 1407, 1293, 1092, 1015, 917, 861, 700; m.p. 148 – 151 ^{o}C; HRMS (DART) calculated for $C_{22}H_{19}ClNO$ [M+H]: 348.1155; found 344.1142.

***N*-Benzyl-*N*-[1-(2-bromophenyl)-3-phenylprop-2-ynyl]-hydroxylamine (3fa):**



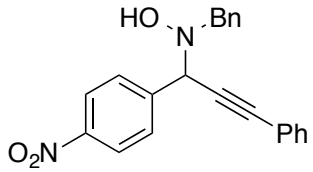
^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.92 (1H, t, *J* = 3.8 Hz), 7.59 – 7.56 (3H, m), 7.44 (2H, d, *J* = 7.6 Hz), 7.36 – 7.26 (7H, m), 7.19 – 7.17 (1H, m), 5.41 (1H, s), 4.73 (1H, s), 4.15 (1H, d, *J* = 13.1 Hz), 4.06 (1H, d, *J* = 13.1 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 137.2, 133.0, 133.0, 132.0, 131.6, 129.7, 129.6, 128.5, 128.33, 128.28, 127.5, 127.2, 124.8, 122.7, 88.6, 84.3, 62.6, 61.8; IR (KBr, cm^{-1}) 3231, 2863, 2362, 1596, 1489, 1439, 1361, 1159, 1028, 914, 811, 794; m.p. 158 – 160 ^{o}C; HRMS (DART) calculated for $C_{22}H_{19}BrNO$ [M+H]: 392.0650; found 392.0649.

***N*-Benzyl-*N*-[3-phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-ynyl]-hydroxylamine (3ga):**



^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.79 (2H, d, *J* = 8.3 Hz), 7.64 (2H, d, *J* = 8.3 Hz), 7.58 (2H, d, *J* = 3.2 Hz), 7.43 (2H, d, *J* = 7.7 Hz), 7.37 – 7.26 (6H, m), 5.07 (1H, s), 6.43 (1H, s), 4.20 (1H, d, *J* = 13.1 Hz), 4.05 (1H, d, *J* = 13.1 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 141.6, 136.8, 132.0, 130.3, 129.6, 129.2, 128.7, 128.5, 128.4, 127.7, 125.28, 124.1, 122.4, 89.4, 83.5, 62.6, 61.1; IR (KBr, cm^{-1}) 3239, 2870, 2362, 2343, 1953, 1809, 1619, 1598, 1490, 1333, 1161, 915, 730; m.p. 120 – 122 ^{o}C; HRMS (DART) calculated for $C_{23}H_{19}H_3F_3NO$ [M+H]: 382.1419; found 344.1422.

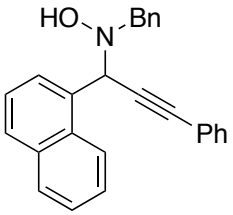
***N*-Benzyl-*N*-[1-(4-nitrophenyl)-3-phenylprop-2-ynyl]-hydroxylamine (3ha):**



^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 8.22(2H, d, *J* = 8.3 Hz),

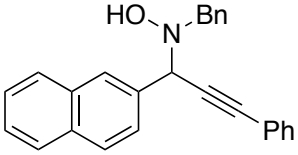
7.82 (2H, d, J = 9.18 Hz), 7.59 – 7.56 (2H, m), 7.43 – 7.25 (8H, m), 5.40 (1H, s), 4.85 (1H, s), 4.17 (1H, d, 13.1 Hz), 4.06 (1H, d, J = 12.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 147.7, 145.1, 136.7, 132.0, 129.5, 128.9, 128.6, 128.6, 128.5, 128.45, 128.41, 127.8, 123.5, 122.1, 89.9, 82.8, 62.4, 61.4; IR (KBr, cm^{-1}) 3217, 2872, 2362, 2338, 1951, 1810, 1598, 1489, 1309, 1106, 1013, 918, 690; m.p. 142 – 144 ^{o}C; HRMS (DART) calculated for $C_{22}H_{19}N_2O_3$ [M+H]: 359.1396; found 344.1409.

***N*-Benzyl-*N*-[1-(1-naphthyl)-3-phenylprop-2-ynyl]-hydroxylamine (3ia):**



^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 8.02 (2H, d, 6.9 Hz), 7.83 – 7.79 (2H, m), 7.59 – 7.58(2H, m), 7.47 – 7.44 (3H, m), 7.34 – 7.17 (8H, m), 5.66 (1H, s), 4.99 (1H, s), 4.06 (1H, d, J = 13.1 Hz), 4.01 (1H, d, J = 12.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 137.1, 133.9, 133.9, 133.0, 131.9, 131.3, 129.6, 129.1, 128.6, 128.4, 128.30, 128.28, 128.2, 127.8, 127.5, 126.0, 125.6, 125.1, 124.1, 122.9, 88.9, 84.8, 61.1, 60.6; IR (KBr, cm^{-1}) 3243, 2860, 2360, 2336, 1813, 1598, 1489, 1442, 1311, 1261, 1072, 1008, 916, 730, 690; m.p. 145 – 146 ^{o}C; HRMS (DART) calculated for $C_{26}H_{22}NO$ [M+H]: 364.1704; found 364.1691.

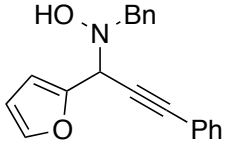
***N*-Benzyl-*N*-[1-(2-naphthyl)-3-phenylprop-2-ynyl]-hydroxylamine (3ja):**



^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 8.00 (1H, s), 7.79 – 7.73 (3H, m), 7.62 – 7.60 (1H, m), 7.54 – 7.51 (2H, m), 7.41 – 7.35 (2H, m), 7.32 – 7.15 (8H, m), 7.53(1H, s), 5.00 (1H, s), 3.95 (2H, s); ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 137.2, 134.9, 133.1, 131.99, 131.97, 129.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.6, 127.5, 126.5, 126.2, 126.1, 122.8, 88.9, 84.6, 63.4, 60.6. ; IR (KBr, cm^{-1}) 3231, 2909, 2362, 2344, 1952, 1599, 1490, 1363, 1162, 1061, 897, 777; m.p. 145 – 147 ^{o}C; HRMS (DART) calculated for $C_{26}H_{22}NO$ [M+H]: 364.1701; found 364.1684.

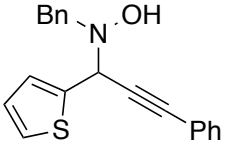
***N*-Benzyl-*N*-[1-(2-furyl)-3-phenylprop-2-ynyl]-hydroxylamine (3ka)[4]:**

^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ7.49 - 7.46 (2H, m), 7.36 – 7.17 (9H, m), 6.48 (1H, d, J = 2.8 Hz), 6.30 (1H, d, J = 2.7 Hz), 5.55 (1H, s), 4.94 (1H, s), 3.94 (1H, d, J = 13.1 Hz), 3.90 (1H, d, J = 13.0 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 150.6, 142.7, 136.9,



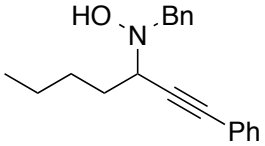
132.0, 129.7, 128.6, 128.4, 128.3, 127.5, 122.5, 110.4, 109.8, 87.1, 82.7, 60.4, 57.4.

***N*-Benzyl-*N*-[1-(2-thiophenyl)-3-phenylprop-2-ynyl]-hydroxylamine (3la):**



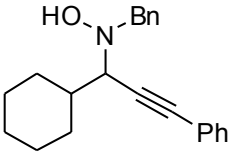
^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.58 – 7.55 (2H, m), 7.42 (2H, d, *J* = 7.6 Hz), 7.37 – 7.25 (8H, m), 7.00 – 6.99 (1H, m), 5.29 (1H,s), 5.22 (1H, s), 4.04 (1H, d, *J* = 13.1 Hz), 4.00 (1H, d, *J* = 13.1 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 141.2, 137.2, 132.0, 129.5, 128.6, 128.4, 128.3, 127.5, 126.8, 126.5, 126.1, 122.5, 87.8, 84.1, 60.2, 59.3; IR (KBr, cm^{-1}) 3230, 2867, 2361, 3244, 1597, 1489, 1346, 1289, 1180, 1070, 1030, 920, 809, 694; m.p. 131 – 132 ^{o}C; HRMS (DART) calculated for $C_{20}H_{18}NOS$ [M+H]: 320.1109; found 320.1094.

***N*-Benzyl-*N*-(1-phenyl-1-heptyn-3-yl)-hydroxylamine (3ma)[5]:**



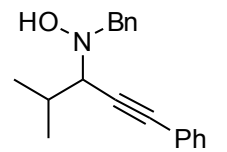
^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.42 (2H, d, *J* = 7.57 Hz), 7.26 – 7.15 (8H, m), 5.83 (1H, s), 4.49 (1H, s), 3.77 (1H, d, *J* = 11.7 Hz), 3.63 (1H, d, *J* = 12.4 Hz), 2.32 – 2.29 (2H, m), 1.56 – 1.39 (4H, m), 0.89 (3H, t, *J* = 7.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 137.9, 137.2, 129.7, 128.9, 128.2, 128.1, 127.8, 127.4, 89.4, 74.7, 62.4, 60.1, 31.0, 22.0, 18.6, 13.6.

***N*-Benzyl-*N*-(1-cyclohexyl-3-phenyl-prop-2-ynyl)-hydroxylamine (3na)[3]:**



^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.48 – 7.46 (2H, m), 7.37 (2H, d, *J* = 6.9 Hz), 7.31 – 7.28 (5H, m), 7.23 (1H, q, *J* = 8.2 Hz), 4.52 (1H, s), 4.15 (1H, d, *J* = 13.1 Hz), 3.86 (1H, d, *J* = 13.1 Hz), 3.41 (1H, d, *J* = 8.9 Hz), 2.09 – 2.05 (2H, m), 1.80 – 1.62 (4H, m), 1.28 – 0.94 (5H, m); ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 137.5, 131.9, 129.3, 128.34, 128.25, 128.2, 127.3, 123.0, 88.0, 85.0, 65.1, 40.1, 30.5, 26.6, 26.1, 25.9.

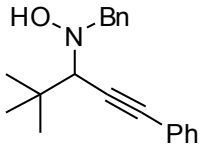
***N*-Benzyl-*N*-(4-methyl-1-phenyl-1-pentyn-3-yl)-hydroxylamine (3oa):**



^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.51 - 7.50 (2H, m), 7.42 – 7.41 (2H, m), 7.35 – 7.28 (6H, m), 4.61 (1H, s), 4.20 (1H, d, *J* = 13.1 Hz), 3.89 (1H, d, *J* = 13.1 Hz), 3.36 (1H, d, *J* = 8.2 Hz), 2.12 (1H, dsep, *J* = 6.2, 8.2 Hz), 1.09 (6H, dd, *J* = 6.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 137.6,

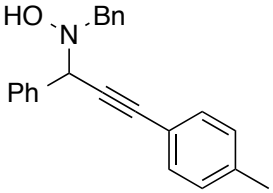
131.8, 129.3, 128.33, 128.25, 128.2, 127.3, 123.0, 87.8, 85.2, 66.3, 62.3, 30.9, 20.0; IR (KBr, cm^{-1}) 3231, 2913, 2366, 3243, 1956, 1886, 1816, 1762, 1599, 1470, 1387, 1299, 1073, 917, 755, 651; m.p. 119 – 120 ^{o}C; HRMS (DART) calculated for $C_{19}H_{22}NO$ [M+H]: 280.1701; found 280.1699.

***N*-Benzyl-*N*-(4,4-dimethyl-1-phenyl-1-pentyn-3-yl)-hydroxylamine (3pa)[1a]:**



^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.52 (2H, q, *J* = 3.2 Hz), 7.40 (2H, d, *J* = 6.9 Hz), 7.34 – 7.32 (5H, m), 7.28 (1H, d, *J* = 7.6 Hz), 4.32 (1H, s), 4.16 (1H, d, *J* = 12.4 Hz), 3.88 (1H, d, *J* = 13.1 Hz), 3.44 (1H, s), 1.08 (9H, s); ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 137.4, 131.88, 131.87, 129.3, 128.33, 128.28, 127.4, 122.8, 89.2, 83.4, 68.5, 64.5, 35.7, 27.7.

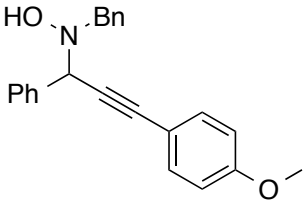
***N*-Benzyl-*N*-[3-(4-methylphenyl)-1-phenyl-2-propynyl]-hydroxylamine (3ab):**



^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.57 – 7.55 (2H, m), 7.48 (2H, d, *J* = 7.6 Hz), 7.37 – 7.30 (8H, m), 7.27 – 7.22 (1H, m), 7.17 (2H, d, *J* = 8.2 Hz), 5.43 (1H, s), 4.90 (1H, s), 3.98 (1H, d, *J* = 13.1 Hz), 3.94 (1H, d, *J* = 13.1 Hz), 2.36 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$, ppm)

δ 137.8, 137.3, 134.5, 131.9, 129.6, 129.0, 128.8, 128.34, 128.31, 128.26, 127.4, 122.9, 88.4, 84.9, 62.9, 60.3, 21.1; IR (KBr, cm^{-1}) 3230, 2918, 2361, 2344, 1902, 1602, 1508, 1453, 1355, 1290, 1020, 861, 816, 696; m.p. 138 – 140 ^{o}C; HRMS (DART) calculated for $C_{23}H_{22}NO$ [M+H]: 328.1701; found 328.1717.

***N*-Benzyl-*N*-[3-(4-methoxyphenyl)-1-phenyl-2-propynyl]-hydroxylamine (3ac):**

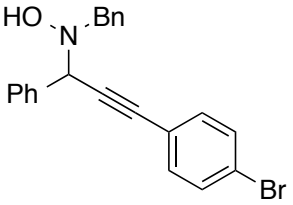


^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.55 (2H, d, *J* = 7.6 Hz), 7.44 – 7.42 (2H, m), 7.32 – 7.17 (8 H, m), 6.81 – 6.79 (2H, m), 5.18 (1H, s), 4.87 (1H, s), 3.92 (2H, s), 3.75 (3H, s) ; ^{13}C NMR (150 MHz, $CDCl_3$, ppm)

δ 159.7, 137.7, 137.3, 133.4, 129.5, 128.8, 128.4, 128.3, 128.0, 127.4, 114.9, 113.9, 88. 7, 82.9, 63.3, 60.7, 55.3; IR (KBr, cm^{-1}) 3230, 2870, 2543, 2366, 2344, 1893, 1818, 1605, 1508, 1453, 1247, 1174, 1028, 833, 700, 622; m.p. 121 – 122 ^{o}C; HRMS (DART) calculated for $C_{23}H_{22}NO_2$ [M+H]: 344.1651; found 344.1652.

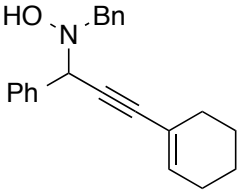
***N*-Benzyl-*N*-[3-(4-bromophenyl)-1-phenyl-2-propynyl]-hydroxylamine (3ad)[4]:**

^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.63 (2H, d, *J* = 7.6 Hz), 7.49 (2H, d, *J* = 8.3 Hz), 7.43 – 7.26 (10H, m), 5.03 (1H, s), 4.72 (1H, s), 4.11 (1H, d, *J* = 13.1 Hz), 4.00 (1H, d, *J* = 13.1 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, ppm)



δ 137.4, 137.3, 133.4, 131.6, 129.5, 128.8, 128.4, 128.2, 128.1, 127.5, 122.7, 121.8, 87.6, 86.0, 63.3, 60.8.

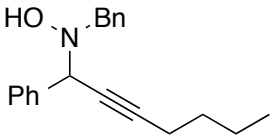
***N*-Benzyl-*N*-[3-(1-cyclohexenyl)-1-phenyl-2-propynyl]-hydroxylamine (3ae)[4]:**



^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.42 (2H, d, *J* = 7.6 Hz), 7.26 – 7.15 (8H, m), 6.17 (1H, quintet, *J* = 1.4 Hz), 5.80 (1H, s),4.61 (1H, s), 3.79 (1H, d, *J* = 12.4 Hz), 3.65 (1H, d, *J* = 12.4 Hz), 2.17 (2H, dd, *J* = 5.5, 2.8 Hz), 2.05 (2H, dt, *J* = 2.8, 3.4 Hz), 1.62 – 1.18 (4H, m); ^{13}C NMR (150 MHz, $CDCl_3$, ppm)

δ 137.7, 137.2, 135.3, 129.7, 128.9, 128.2, 128.0, 127.9, 127.4, 120.2, 90.7, 81.3, 62.9, 60.2, 29.4, 25.6, 22.3, 21.5.

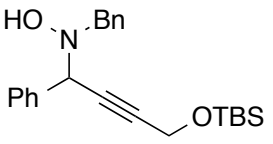
***N*-Benzyl-*N*-(1-phenyl-2-heptynyl)hydroxylamine (3af)[3]:**



^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.42 (2H, d, *J* = 7.6 Hz), 7.26 – 7.15 (8H, m), 5.83 (1H, s), 4.49 (1H, s), 3.78 (1H, d, *J* = 11.7 Hz), 3.63 (1H, d, *J* = 12.4 Hz), 2.31 (2H, dt, *J* = 7.2, 2.1 Hz), 1.56 – 1.51 (2H, m), 1.42 (2H, dt, *J* = 14.6, 7.1 Hz), 0.88 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, ppm)

δ 137.9, 137.2, 129.7, 128.9, 128.3, 128.1, 127.8, 127.4, 89.4, 74.7, 62.4, 60.4, 31.0, 22. 0, 18.6, 13.6.

***N*-Benzyl-*N*-[4-(*tert*-butyldimethylsilyloxy)-1-phenyl-2-butynyl]hydroxylamine (3ag):**

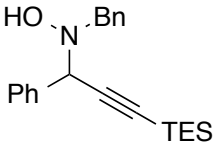


^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.34 (2H, d, *J* = 7.6 Hz), 7.18 – 7.08 (8H, m), 5.72 (1H, s), 4.35 (1H, s), 4.35 (2H, s), 3.71 (1H, d, *J* = 13.1 Hz), 3.59 (1H, d, *J* = 12.4 Hz), 0.77 (9H, s), 0.00 (6H, s); ^{13}C NMR (150 MHz, $CDCl_3$, ppm)

δ 137.2, 137.1, 129.7, 128.9, 128.3, 128.2, 128.1, 127.5, 87.3, 79.8, 62.5, 60.1, 51.9, 25. 8, 18.3; IR (KBr, cm^{-1}) 3230 2845, 2362, 1955, 1900, 1814, 1602, 1495, 1366, 1259,

1064, 918, 629; m.p. 85 °C; HRMS (DART) calculated for $C_{23}H_{32}NO_2Si$ [M+H]: 382.2202; found 382.2210.

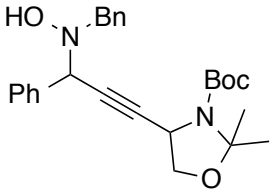
***N*-Benzyl-*N*-(1-phenyl-3-triethylsilyl-2-heptynyl)hydroxylamine (3ah):**



^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.56 (2H, d, *J* = 8.2 Hz), 7.36 – 7.24 (8H, m), 5.04 (1H, s), 4.76 (1H, s), 3.95 (1H,d, *J* = 12.4 Hz), 3.91 (1H, d, *J* = 13.0 Hz), 1.08 (9H, t, *J* = 7.9 Hz), 0.71 (6H, q, *J* = 7.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, ppm)

δ 137.3, 137.2, 129.5, 128.8, 128.3, 128.2, 127.9, 127.4, 101.5, 91.3, 63.3, 60.7, 7.6, 4.5 ; IR (KBr, cm^{-1}) 3244, 2959, 2361, 2343, 1951, 1879, 1805, 1603, 1496, 1455, 1335, 1237, 1026, 865, 746; m.p. 67 °C; HRMS (DART) calculated for $C_{22}H_{30}NOSi$ [M+H]: 352.2097; found 352.2087.

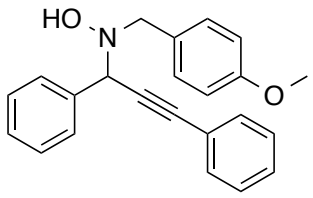
***tert*-butyl**
4-(3-(Benzyl(hydroxy)amino)-3-phenylprop-1-yn-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (3ai):



^{1}H NMR (600 MHz, DMSO-d_6, 90 °C, ppm) δ 7.54 – 7.46 (2H, m), 7.31 – 7.19 (8H, m), 4.80 (1H, s), 4.71 (1H, s), 4.09 (1H, t, *J* = 6.9 Hz), 3.99 (1H, d, *J* = 8.2 Hz), 3.88 (s, 2H), 1.59 (3H, d, *J* = 11.0 Hz), 1.46 – 1.44 (12H, m) ; ^{13}C NMR (150 MHz, DMSO-d6, 90 °C, ppm)

δ150.4, 138.1, 138.02, 138.00, 128.5, 128.1, 127.4, 126.9, 126.2, 93.0, 86.7, 79.1, 78.1, 68.3, 62.2, 59.7, 48.0, 27.6, 25.8, 24.2; IR (KBr, cm^{-1}) 3436, 2982, 2363, 2344, 1951, 1883, 1813, 1709, 1365, 1090, 847, 738, 702; m.p. 44 °C; HRMS (DART) calculated for $C_{26}H_{33}N_2O_4$ [M+H]: 437.2440; found 437.2427.

***N*-(1,3-Diphenyl-prop-2-ynyl)-*N*-(4-methoxyphenylmethyl)hydroxylamine (3qa):**

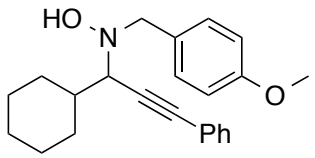


^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.65 (2H, d, *J* = 7.6 Hz), 7.58 – 7.56 (2H, m), 7.43 – 7.26 (8H, m), 6.88 (2H, d, *J* = 8.3 Hz), 5.04 (1H, s), 4.80 (1H, s), 4.10 (1H, d, *J* = 13.1 Hz), 4.00 (1H, d, *J* = 13.8 Hz), 3.80 (3H, s) ; ^{13}C NMR (150 MHz, $CDCl_3$, ppm)

δ159.1, 137.5, 131.9, 130.9, 130.9, 129.0, 129.0, 128.4, 128.3, 128.0, 122.9, 113.8, 88.

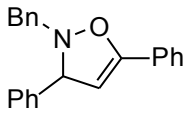
6, 84.6, 62.5, 59.9, 55.2; IR (KBr, cm^{-1}) 3233, 2907, 2362, 2344, 1610, 1513, 1299, 1251, 1174, 1030, 865, 759, 695; m.p. 150 ^{o}C; HRMS (DART) calculated for $C_{23}H_{22}NO_2$ [M+H]: 344.1651; found 344.1638.

***N*-(1-Cyclohexyl-3-phenyl-prop-2-ynyl)-*N*-(4-methoxyphenylmethyl)hydroxylamin e (3ra):**



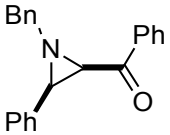
^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.51-7.50 (2H, m), 7.33 – 7.31 (5H, m), 6.87 (2H, d, *J* = 8.3 Hz), 4.42 (1H, s), 4.14 (1H, d, *J* = 13.1 Hz), 3.84 (1H, d, *J* = 12.4 Hz), 3.81 (3H, s), 3.43 (1H, d, *J* = 8.3 Hz), 2.10 – 2.08 (2H, m), 1.84 – 1.57 (4H, m), 1.32 – 0.96 (5H, m); ^{13}C NMR (150 MHz, $CDCl_3$, ppm)
δ 159.0, 131.9, 130.5, 129.5, 128.3, 128.2, 123.0, 113.8, 88.1, 85.0, 64.8, 61.8, 55.3, 40. 1, 30.5, 26.6, 26.1; IR (KBr, cm^{-1}) 3231, 2937, 2362, 1882, 1611, 1445, 1352, 1254, 1173, 1034, 924, 806, 694; m.p. 127 ^{o}C; HRMS (DART) calculated for $C_{23}H_{28}NO_2$ [M+H]: 350.2120; found 350.2108.

2-Benzyl-3,5-diphenyl-2,3-dihydro-isoxazole (4aa)[1a]:



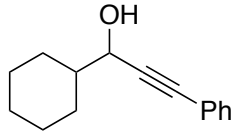
^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.59 – 7.22 (15H, m), 5.43 (1H, d, *J* = 2.8 Hz), 5.06 (1H, d, *J* = 2.8 Hz), 4.44 (1H, d, *J* = 12.5 Hz), 4.12 (1H, d, *J* = 13.0 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 152.8, 142.0, 136.4, 129.6, 129.0, 128.7, 128.5, 128.4, 128.3, 127.5, 127.1, 125.7, 95.7, 73.6, 63.4.

***cis*-3-Benzoyl-1-benzyl-2-phenylethyleneimine (5aa)[6]:**



^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.85 (dd, 2H, *J* = 8.2, 1.4 Hz), 7.48 – 7.11 (m, 13H), 4.02 (d, 1H, *J* = 13.7 Hz), 3.81 (d, 1H, *J* = 13.7 Hz), 3.39 (d, 1H, *J* = 6.9 Hz), 3.31 (d, 1H, *J* = 7.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, ppm)
δ 193.1, 137.8, 136.9, 134.9, 132.9, 128.41, 128.40, 128.36, 128.1, 127.94, 127.85, 127. 53, 127.52, 127.4, 127.2, 63.8, 51.1, 49.1.

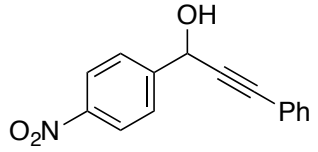
1-cyclohexyl-3-phenyl-prop-2-yn-1-ol (8aa)[6]:



^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.36 – 7.34 (2H, m), 7.23 -

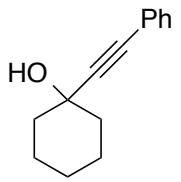
7.20 (3H, m), 4.30 (1H, d, J = 6.2 Hz), 2.00 (1H, s), 1.86 – 1.83 (2H, m), 1.73 – 1.72 (1H, m), 1.71 – 1.56 (2H, m), 1.22 – 1.04 (5H, m); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 131.6, 128.22, 128.20, 122.7, 89.2, 85.6, 67.6, 44.2, 28.6, 28.1, 26.3, 25.9, 25.8

4-nitro-α-(phenylethynyl)-benzenemethanol (8ba)[7];



^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 8.19 – 8.16 (2H, m) 7.73 – 7.70 (2H, m), 7.40 – 7.38 (2H, m), 7.31 – 7.24 (m, 3H), 5.72 (1H, s), 2.54 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 147.8, 147.3, 131.7, 129.1, 128.4, 127.4, 123.8, 121.7, 87.6, 87.3, 64.0

1-hydroxy-1-(2-phenylethynyl)cyclohexane (8ca)[8];



^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.37 – 7.34 (2H, m), 7.24 – 7.22 (3H, m), 1.96 – 1.90 (3H, m), 1.71 (7H, m), 1.24 – 1.18 (1H, m); ^{13}C NMR (125 MHz, $CDCl_3$, ppm)
δ 131.7, 128.22, 128.18, 92.8, 84.3, 69.1, 40.0, 25.2, 23.4

5. References

[1] Mirabdolbaghi R.; Dudding T.; *Org. Lett*. **2012**, *14*, 3748.

[2] (a) Aschwanden, P.; Frantz, D. E.; Carreira, E. M. *Org. Lett.* **2000**, 2, 2331; (b) Rosiak, A.; Frey, W.; Christoffers, J. *European J. Org. Chem.* **2006** , 17, 4044; (c) Eastmond, R. *et al. Tetrahedron*, **1972** , 28, 4601; (d) Falck, J. R.; He, A.; Fukui, H.; Tsutsui, H.; Radha, A. *Angew. Chem. Int. Ed.* **2007**, 46, 4527; (e) Inman, Wayne D.; Sanchez, Kenneth A. J.; Chaidez, Manuel A.; Paulson, Donald R. *J. Org. Chem.* **1989**, 54, 4872.

[3] Aschwanden,P.; Kvaernoe, L.; Geisser, R. W.; Kleinbeck, F.; Carreira, E. M. *Org. Lett.* **2005**, *7*, 5741.

[4] Bunlaksananusorn, T.; Lecourt, T.; Micouin, L. *Tetrahedron Lett.* **2007**, *48*, 1457.

[5] Ji, D.-M.; Xu, M.-H. *Tetrahedron Lett.* **2009**, *50*, 2952.

[6] Ishikawa, T.; Kudoh, T.; Manabe, S.; Saito, S.; Yasuhara, A.; Yoshida, J. *Org. Lett.* **2002**, *4*, 1907.

[6] C. Wade Downey; Braian D. Mahoney; Vincent R. Lipari *J. Org. Chem.* **2009**, 74, 2904.

[7] Sakai, N.; Kanada, R.; Hirasawa, M.; Konakahara, *Tetrahedron*, **2005**, 61, 9298.

[8] Yasukawa T.; Miyamura. H.; Kobayashi S.; *Org. Biomol. Chem*. **2011**, 9, 6208.