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Rare-Earth Silylamide-Catalyzed Monocoupling Reaction of Isocyanides with Terminal Alkynes

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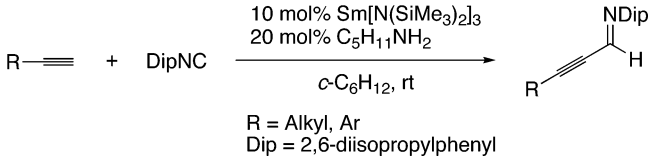

Rare-earth silylamides, $Ln[N(SiMe_3)_2]_3$ (Ln = Y, La, Sm, Yb), serve as good catalysts for monoinsertion of isocyanides into terminal alkynes in the presence of amine additives, leading to 1-aza-1,3-enyens in excellent yields. The reaction is applicable to a diverse set of terminal alkynes with various functionalities such as ethers, acetals, and amino groups. Larger metals (La and Sm) give a better performance than smaller ones (Y and Yb). Using less hindered primary amines and, in contrast, bulky isocyanides is crucial for the coupling reaction; otherwise, competitive oligomerization of the isocyanides occurs predominantly. In the mechanistic study, the rate-determining step of the reaction seems to be the first insertion of the isocyanides into rare-earth alkynides, which is followed by spontaneous protonation with the amine additives.

Introduction

The insertion reaction of carbon−carbon unsaturated compounds into various transition metal−carbon bonds is a powerful method for a carbon chain construction, and thus, it has been widely utilized as the key step in organic synthesis. This process was also utilized in rare-earth catalyzed transformation of alkynes and alkenes: for example, cyclization/hydrosilylation and oligomerization.[1] Moreover, one-carbon extension with carbon monoxide and isocyanides has been recognized as an important tool in the formation of carbonyl and iminoyl functions, which leads to multifunctionalized alcohols and amines.[2] The reaction has been conventionally promoted by various transition metals.[3,4] However, there has been no precedent for the catalytic direct monoinsertion of isocyanides into terminal alkynes. Recently, Eisen et al. reported the insertion of *t*-butyl isocyanide into terminal alkynes catalyzed by actinide complexes.[5] With respect to rare-earth complexes, their unique reactions with carbon monoxide and useful synthetic reactions, although stoichiometric, via isocyanide insertion into the Ln−C bond have been reported.[6,7]

In the previous work, we demonstrated that regio- and stereoselective dimerization of terminal alkynes pro-

(1) For the review: (a) *Lanthanides: Chemistry and Use in Organic Synthesis*; Kobayashi, S., Ed.; Springer: Berlin, 1999. (b) Molander, G. A.; Romero, J. A. C. *Chem. Rev*. **2002**, *102*, 2161. For the dimerization of terminal alkynes: (c) Heeres, H. J.; Teuben, J. H. *Organometallics* **1991**, *10*, 1980. (d) Nishiura, M.; Hou, Z.; Wakatsuki, Y.; Yamaki, T.; Miyamoto, T. *J. Am. Chem. Soc*. **2003**, *125*, 1184. (e) Tazelaar, C. G. J.; Bambirra, S.; Leusen, D.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2004**, *23*, 936.

(2) Recent report on synthetic utilities of iminolyl alkynes: (a) Hachiya, I.; Ogura, K.; Shimizu, M. *Synthesis* **2004**, 1349. (b) Dube, H.; Gommermann, N.; Knochel, P. *Synthesis* **2004**, 2015.

(3) For insertion of isocyanides under stoichiometric conditions; Ti: (a) Klei, E.; Teuben, J. H. *J. Organomet. Chem*. **1980**, *188*, 97. Zr: (b) Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun*. **1982**, 462. Nb: (c) Klazinga, A. H.; Teuben, J. H. *J. Organomet. Chem*. **1980**, *192*, 75. Ta: (d) Klazinga, A. H.; Teuben, J. H. *J. Organomet. Chem*. **1980**, *194*, 309. Ag: (e) Minghetti, G.; Bonati, F.; Massobrio, M. *J. Chem. Soc., Chem. Commun*. **1973**, 260. Cu: (f) Kotenm, G.; Noltes, J. G. *J. Chem. Soc., Chem. Commun*. **1972**, 59. (g) Tsuda, T.; Habu, H.; Horiguchi, S.; Saegusa, T. *J. Am. Chem. Soc*. **1974**, *96*, 5930. (h) Saegusa, T.; Ito, Y. Kinoshita, H.; Tomita, S. *J. Org. Chem*. **1971**, *36*, 3316.

(4) For insertion of isocyanides catalyzed by late transition metal complexes; (a) Breil, H.; Wilke, G. *Angew. Chem., Int. Ed*. **1970**, *9*, 367. (b) Saluste, C. G.; Whitby, R. J.; Furber, M. *Tetrahedron Lett*. **2001**, *42*, 6191. (c) Onitsuka, Y.; Suzuki, S.; Takahashi, S. *Tetraheron Lett*. **2002**, *43*, 6197. (d) Kamijo, S.; Yamamoto, Y. *J. Am. Chem. Soc*. **2002**, *124*, 11940.

(5) Barnea, E.; Andrea, T.; Kapon, M.; Berthet, J.-C.; Ephritikhine, M.; Eisen, M. S. *J. Am. Chem. Soc*. **2004**, *126*, 10860.

(6) (a) Evans, W. J.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Chem. Soc., Chem. Commun*. **1981**, 706. (b) Evans, W. J.; Hughes, L. A.; Drummond, D. K.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc*. **1986**, *108*, 1722.

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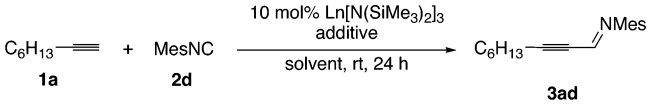
TABLE 1. Optimization of the Reaction Conditions for the Coupling of Oct-1-yne (1a) and MesNC (2d)



					recovery (%)[a]	
entry	Ln	additive (mol %)	solvent	yield (%)[a]	**1a**	**2d**
1	Sm	None	*c*-C_6H_{12}	10	48	11
2	Sm	$C_5H_{11}NH_2$ (10)	*c*-C_6H_{12}	72	10	tr
3	Sm	$C_5H_{11}NH_2$ (20)	*c*-C_6H_{12}	76	16	0
4	Sm	$C_5H_{11}NH_2$ (30)	*c*-C_6H_{12}	71	7	0
5	Sm	$BnNH_2$ (20)	*c*-C_6H_{12}	74	8	0
6	Sm	$PhNH_2$ (20)	*c*-C_6H_{12}	7	66	67
7	Sm	$^tBuNH_2$ (20)	*c*-C_6H_{12}	28	23	0
8	Sm	Et_3N (20)	*c*-C_6H_{12}	9	52	32
9	Sm	$C_5H_{11}NH_2$ (20)	PhMe	62	*b*	0
10	Sm	$C_5H_{11}NH_2$ (20)	THF	12	35	25
11	Yb	$C_5H_{11}NH_2$ (20)	*c*-C_6H_{12}	38	59	28
12	Y	$C_5H_{11}NH_2$ (20)	*c*-C_6H_{12}	35	36	17
13	La	$C_5H_{11}NH_2$ (20)	*c*-C_6H_{12}	62	15	tr

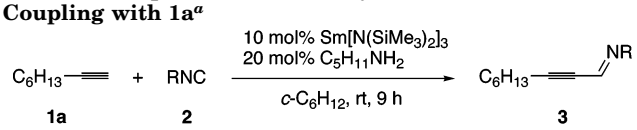
[a] Determined by GC. [b] Not determined.

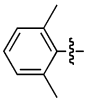
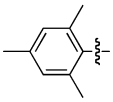
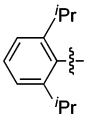
ceeded efficiently with rare-earth silylamide catalysts, Ln(btsa)$_3$ [btsa = N(SiMe$_3$)$_2$], and amine additives through monoinsertion of the alkynes into the lanthanum−alkynide species to give 1,3-enynes.[8] In contrast, our preliminary investigation indicated that a similar reaction in the presence of isocyanides afforded exclusively 1-aza-1,3-enynes, coupling products of the alkynes with the isocyanides.[9] Herein, we would like to report more detailed features of the reaction with isocyanides, particularly the scope and limitation, and the mechanistic aspect.

Results and Discussion

When oct-1-yne (**1a**) was treated with an equimolar amount of mesityl isocyanide, MesNC (**2d**), in the presence of Sm(btsa)$_3$ (10 mol %) for 24 h at room temperature in cyclohexane, the coupling product, 1-(mesitylimino)-non-2-yne (**3ad**), was obtained in only 10% yield as a mixture of syn and anti isomers (45:55). The alkyne **1a** was recovered in 48% yield, whereas the isocyanide **2d** was mostly consumed to provide oligomeric products. With a rise in the reaction temperature, the yield of **3ad** decreased, and the amounts of the oligomers increased, probably because the isocyanide could insert multiply into metal−carbon bonds.[10] In addition, the molar ratio of the isocyanide **2d** to the alkyne **1a** did not change the yield. When the silylamide complex was substituted by LiN(SiMe$_3$)$_2$ and CuI/Et_3N, no reaction took place under similar conditions. Therefore, we focused our attention on inhibiting the oligomerization of the isocyanides by amine additives, which were known to change the catalyst activity and to serve as a proton source in the dimerization of terminal alkynes.[8] These results are shown in Table 1. Fortunately, an addition of amylamine

TABLE 2. Optimization of Isocyanides 2 for the Coupling with 1a[a]



entry	R		product and yield (%)[b]	
1	^{t}Bu (**2a**)		**3aa**	0
2	Ph (**2b**)		**3ab**	0
3		(**2c**)	**3ac**	53
4		(**2d**)	**3ad**	76
5		(**2e**)	**3ae**	88

[a] Similar conditions to entry 3 in Table 1, except for a 9 h reaction. [b] Determined by GC.

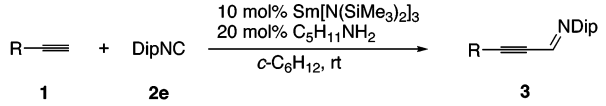
increased the product yield up to 76%, wherein the effect was not strictly dependent on the amount added (entries 2−4). Benzylamine improved the efficiency to a certain extent (entry 5). On the other hand, the addition of aromatic amines such as aniline retarded the reaction (entry 6), and bulky primary amines such as *t*-butylamine preferentially promoted the oligomerization (entry 7). Triethylamine showed no obvious effect (entry 8). Testing of the solvent effect indicated that tetrahydrofuran predominantly induced the oligomerization of **2d** in comparison with cyclohexane and toluene (entries 3 and 9 vs 10). With respect to the size of rare-earth metals, larger catalysts (La and Sm) were superior to smaller ones (Yb and Y) (entries 3 and 11−13).

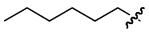
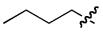
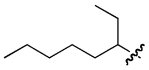
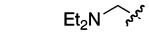
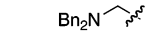
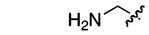
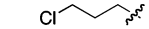
Next, a selection of isocyanides **2** was investigated under the optimized conditions (Table 2). The reaction of oct-1-yne (**1a**) with *t*-butyl isocyanide (**2a**) did not commence at room temperature, whereas most of **2a** was changed to oligomers with a little consumption of **1a** at elevated temperature (65 °C) (entry 1). Phenyl isocyanide (**2b**) gave a similar result (entry 2). These results implied that the second and subsequent insertion of isocyanide **2** into the metal−carbon bond of the iminoyl species, initially formed by the first reaction, took place faster than its competitive protonation (vide infra). In fact, it was clear that with the aromatic isocyanides having a bulkier substituent at the ortho position, the selectivity of **3** became higher due to the inhibition of the oligomerization (entries 3−5). Thus, the yield of product **3ae** increased up to 88% by using 2,6-diisopropylphenyl isocyanide, DipNC (**2e**), (entry 5). The selection of **2** was also valid in the reaction of phenylacetylene (**1m**), which showed the following order of increasing yield of the corresponding products **3**: R = ^{t}Bu and Ph (0%) < 2-Xyl, 2,6-$Me_2C_6H_3$, (48%) < Mes (74%) < Dip (95%).

Using the bulky isocyanide **2e**, compatibility of the present reaction was tested in the screening of various

(7) Murakami, M.; Kawano, T.; Ito, H.; Ito, H. *J. Org. Chem.* **1993**, *58*, 1458.
(8) Komeyama, K.; Takehira, K.; Takaki, K. *Synthesis* **2004**, 1062.
(9) Komeyama, K.; Sasayama, D.; Kawabata, T.; Takehira, K, Takaki, K. *Chem. Commun.* **2005**, 634.
(10) (a) Ito, Y.; Ihara, E.; Murakami, M. *J. Am. Chem. Soc.* **1990**, *112*, 6446. (b) Ito, Y.; Ohara, T.; Shima, R.; Suginome, M. *J. Am. Chem. Soc.* **1996**, *118*, 9188.

TABLE 3. Coupling of Various Terminal Alkynes 1 with DipNC (2e)



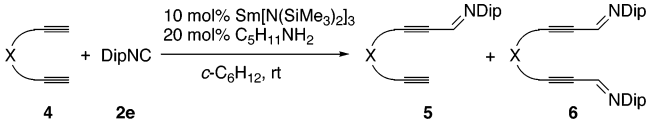
entry	R		time (h)	product and yield (%)[a]	
1		(**1a**)	9	**3ae**	88
2		(**1b**)	9	**3be**	94
3		(**1c**)	9	**3ce**	99
4	^{t}Bu	(**1d**)	9	**3de**	86
5	TMS	(**1e**)	9	**3ee**	87
6		(**1f**)	24	**3fe**	12
7		(**1g**)	24	no rection	
8		(**1h**)	24	**3he**	88
9		(**1i**)	6	**3ie**	97
10		(**1j**)	6	**3je**	94
11		(**1k**)	14	no reaction	
12		(**1l**)	9	**3le**	83
13	Ph	(**1m**)	6	**3me**	95
14	4-MeOC$_6$H$_4$	(**1n**)	6	**3ne**	95
15	4-MeC$_6$H$_4$	(**1o**)	6	**3oe**	92
16	2-MeC$_6$H$_4$	(**1p**)	6	**3pe**	93
17	4-BrC$_6$H$_4$	(**1q**)	9	**3qe**	85
18	4-FC$_6$H$_4$	(**1r**)	24	**3re**	79
19	4-(CH$_2$O)$_2$CHC$_6$H$_4$	(**1s**)	8	**3se**	83

[a] Determined by GC.

terminal alkynes. These results are summarized in Table 3. Substitution of the primary carbon at the propargylic position by secondary and tertiary carbons caused no noticeable change (entries 1−4). Trimethylsilylacetylene (**1e**) was readily converted to the corresponding iminoalkyne **3ee** in 87% yield (entry 5). Although very little or no coupling products were obtained from methoxy- and trimethylsilyloxypropynes **1f** and **1g**, the reaction tolerated TBDMS-protected propargyl alcohol **1h** to provide **3he** in 88% yield after longer reaction time (entries 6−8). Remarkably, tertiary amino groups of **1i** and **1j** did not prevent the high selectivity of the coupling products, **3ie** and **3je**, in contrast to propargylamine (**1k**) that was recovered unchanged together with **2e** (entries 9−11). The silylamide catalyst allowed 5-chloropent-1-yne (**1l**) to convert into the product **3le** in high yield, although halogenated aliphatic compounds were rarely used in the reaction with basic rare-earth catalysts (entry 12).

Aromatic alkynes are more reactive than aliphatic ones in general, in which electron-donating substituents slightly facilitated the reaction as compared to electron-with-

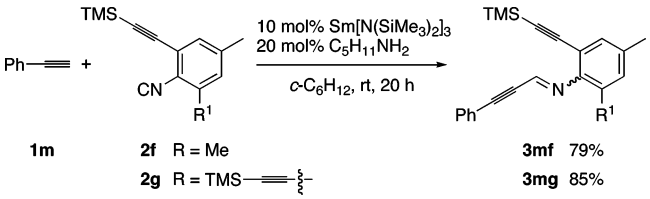
TABLE 4. Coupling of α,ω-Diynes 4 with DipNC (2e)



entry	X		ratio of **2e/4**	time (h)	production and yield (%)[a]			
1	(CH$_2$)$_4$	(**4a**)	1	8	(**5ae**)	71	(**6ae**)	tr
2			2	12		tr		99
3	(CH$_2$)$_5$	(**4b**)	1	16	(**5be**)	72	(**6be**)	tr
4			2	15		tr		88
5	(CH$_2$)$_{10}$	(**4c**)	1	9	(**5ce**)	72	(**6ce**)	tr
6			2	17		4		85
7	BnN	(**4d**)	1	7	(**5de**)	50	(**6de**)	13
8			2	13		0		86

[a] Determined by GC and ^{1}H NMR.

SCHEME 1. Coupling of Phenylacetylene (1m) with Aromatic Isocyanides 2f−g

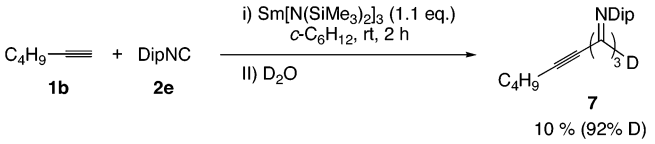


drawing groups in the same position (entries 14 and 15 vs 17 and 18). A methyl substituent on the ortho position did not decrease the product yield (entry 16). Although acetalated formyl groups have been known to usually disturb rare-earth-catalyzed reactions because of their strong acidity,[1b] the present silylamide catalyst can notably perform the coupling reaction of **1s** to give **3se** in 83% yield (entry 19). However, 4-formyl- and 4-methoxycarbonyl groups were not permissible in the reaction, that is, the Tischenko product, 4-ethynylbenzyl 4-ethynylbenzoate, was obtained in the former, and no reaction took place in the latter.

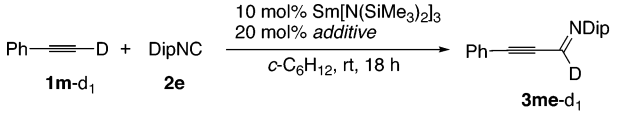
Next, we investigated the insertion reaction of DipNC (**2e**) to α,ω-diynes **4** (Table 4). Treatment of 1,7-octadiyne (**4a**) with equimolar amounts of **2e** gave a monoinsertion product, 1-(2,6-diisopropylphenylimino)-non-2,8-diyne (**5ae**), in 71% yield together with a trace amount of 1,-10-bis(2,6-diisopropylphenylimino)-dec-2,8-diyne (**6ae**) (entry 1). On the other hand, an excellent yield of the bis-insertion product **6ae** was given by using 2 equiv of **2e** (entry 2), albeit a longer reaction time was required, as compared with the monoinsertion. Similarly, good selectivities caused by the ratio of **2e** to **4** were kept for other linear diynes **4b**−**c** irrespective of their carbon-chain length (entries 3−6). In the reaction of aminodiyne 4d, exclusive formation of the bis-insertion product **6de** was accomplished, despite the lower selectivity for monoinsertion (entries 7 and 8).

In the reaction of α,ω-diynes having a long carbon chain like **4c**, cyclization products, which may be formed by the intramolecular reaction of the postulated iminoyl−samarium intermediate with another ethynyl group, have not been detected at all. Thus, we tested further possibilities of similar cyclization by using 2-(trimethylsilylethynyl)phenyl isocyanides **2f**−**g** in expectation of the formation of nitrogen-heterocycles (Scheme 1). However,

SCHEME 2. D_2O Quenching of the Stoichiometric Reaction of Hex-1-yne (1b) and DipNC (2e)



SCHEME 3. Coupling of Deuterated Phenylacetylene (1m-d_1) and DipNC (2e)



none	69% yield (100% D)
$(Me_3Si)_2NH$	67% yield (99% D)
$C_5H_{11}NH_2$	93% yield (68% D)

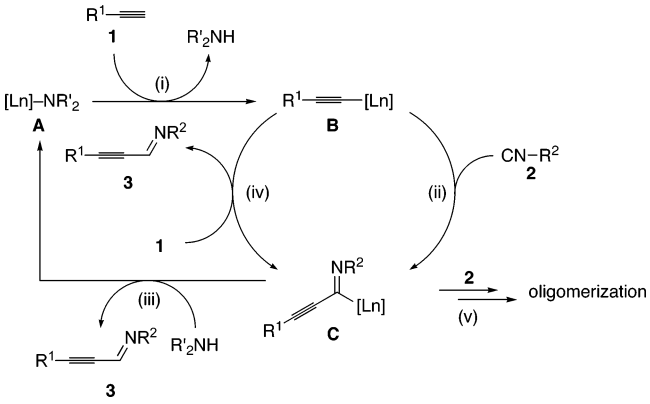
this trial was unsuccessful, leading to the simple coupling products **3mf** and **3 mg** in high yields.

Using stoichiometric amounts of $Sm(btsa)_3$, the reaction of hex-1-yne (**1b**) with **2e** was carried out without any amine additives to obtain information on the reaction mechanism (Scheme 2). Quenching of the reaction with D_2O provided a mixture of oligomers instead of a 1:1 adduct, in which compound **7**, derived from **1b** and three molecules of **2e**, was isolated as the lowest molecular fraction in 10% yield with a high deuterium content on the iminoyl carbon (92% by ^1H NMR). This result implies that the insertion of **2e** into the initially generated iminoyl species would take place faster than that into samarium−alkynides in the absence of a proton source. In contrast, it has been reported that the monoiminoylsamariums could be selectively formed by the stoichiometric reaction of alkylsamariums with 2-xylyl isocyanide.[7] The difference is not clear at present. Furthermore, catalytic reactions of deuterated phenylacetylene **1m**-d_1 with **2e** in the absence of amines afforded a quantitatively deuterated product **3me**-d_1 in 69% yield as shown in Scheme 3. A similar result was given in the presence of $(Me_3Si)_2NH$ additive (20 mol %). Importantly, the addition of amylamine decreased the deuterium content of **3me**-d_1 to 68%, whereas the product yield increased to 93%. From these results, the order of the protonation ability is amylamine > terminal alkyne ≫ $HN(TMS)_2$.

The reaction mechanism can be explained as depicted in Scheme 4. At first, rare-earth alkynide **B** is generated from silyl- and alkylamide **A**, and terminal alkyne **1** (step i) is followed by insertion of isocyanide **2** to yield iminoyl species **C** (step ii). Facile protonation of **C** with the amine additive selectively affords 1-aza-1,3-enyne **3** and the amide **A** (step iii). In the absence of the additive, protonation with **1** leading to the product and alkynide **B** (step iv), and multiple insertion of **2** leading to oligomers (step v), take place competitively, wherein the latter process predominates in general.

To the study mechanistic aspects further, a semicatalytic reaction of 3-diethylaminoprop-1-yne (**1i**) with DipNC (**2e**) using $La(btsa)_3$ and benzylamine was monitored by H^1 NMR under the conditions depicted in Figure 1. On the addition of benzylamine to the catalyst in C_6D_6, a white precipitate appeared immediately. The TMS signal of $HN(TMS)_2$ and some [La]-$N(TMS)_2$ species were

SCHEME 4. Possible Reaction Mechanism



observed at 0.1 and 0.3 ppm, respectively, in a ratio of 2:1. In contrast, signals assignable to benzylamine at 1.4 and 3.6 ppm and the aromatic region were very small: less than 0.4 equiv estimated based on the TMS signals, throughout the reaction. The reaction mixture became homogeneous by the subsequent addition of the alkyne **1i**, wherein the signal of the silylamide completely disappeared and a new set of signals (asterisk) other than those of **1i** was clearly found, although small (Figure 1A). These new signals would be assignable to the lanthanum−alkynide species **B**. If this holds true, the amounts of **B** and **1i** are 2.0 and 1.5 equiv, respectively, being in rough agreement with the initial amounts of **1i**. Combining these results, **B** seems to exist formally as a bis-alkynide complex like $(RNH)(RNH_2)La(C{\equiv}CR)_2$. On the addition of isocyanide **2e**, the product **3ie** was formed in 33% yield 10 min later, whereas the signals of **B** still remained (Figure 1B). When the reaction was completed, the alkynide species **B** disappeared in the NMR spectra, which would be changed to the amide **A** (Figure 1C).

Additional evidence for the alkynide species **B** was obtained by a ^{13}C NMR trace reaction with the Y catalyst, which induced a slower reaction than La. During the course of the reaction, six signals were observed in the sp-carbon region as shown in Figure 2. Two alkynyl carbons of **1i** appeared at 72.7 and 78.9 ppm, and four of syn- and anti-product **3ie** appeared at 80.7−93.7. The other two signals at 67.8 and 97.5 ppm could be assignable to yttrium alkynide **B**, which disappeared on completion of the reaction as well as those of **1i**. Because = alkynide **B** is the only intermediate detected during the reaction as described previously, insertion of isocyanide **2** into **B** would be the rate-determining step (Scheme 4, step ii).

Stereochemistry of products **3** is worthy of comment. The coupling product **3ie** was isolated by Kugelrohr distillation as a 60:40 mixture of the syn- and anti-isomer, determined by NOE measurement. However, the NMR tube reaction indicated that the ratio of the syn isomer decreased as the reaction proceeded. For example, the 80:20 (2 h) ratio was changed to 70:30 (15.5 h) with the Y catalyst. Thus, it is likely that *syn*-iminoyl lanthanide **C** would be formed due to the coordination of the nitrogen atom, and then, isomerization to the anti-isomer takes place during the reaction and workup.

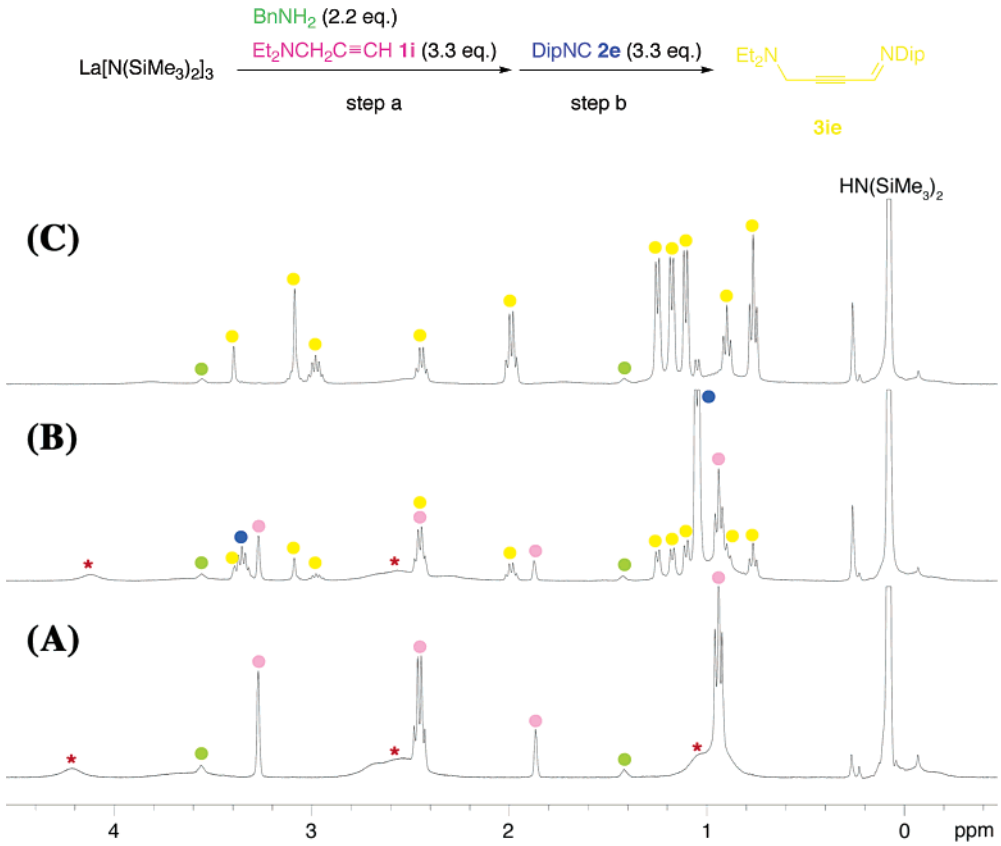


FIGURE 1. ^{1}H NMR trace reaction of **1i** with **2e** using La[N(SiMe$_3$)$_2$]$_3$ and benzylamine in C_6D_6 at room temperature: (A) step a, 10 min; (B) step b, 10 min; and (C) step b, 2.5 h. Asterisks (*) are tentatively assigned to resonances of the La-alkynide intermediate.

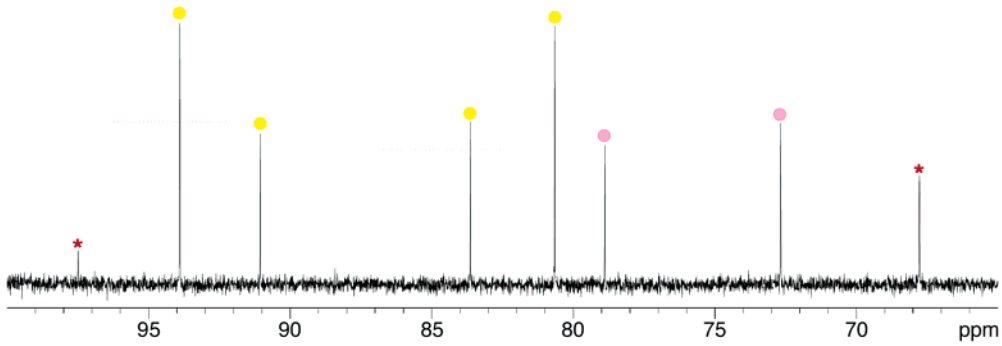


FIGURE 2. ^{13}C NMR spectra (sp-C region) of the reaction mixture of **1i** with **2e** using Y[N(SiMe$_3$)$_2$]$_3$ and benzylamine in C_6D_6 at room temperature. Conditions: **1i** and **2e** (3.3 equiv each) and the amine (2.2 equiv), measured after 10 h.

Conclusion

Catalytic monoinsertion of isocyanides into terminal alkynes has been achieved with rare-earth silylamides in the presence of aliphatic primary amine additives under mild conditions. Variously functionalized terminal alkynes could be converted to the corresponding 1-aza-1,3-enynes in excellent yields owing to fairly good compatibility of the silylamide catalyst. Although an attempt to carry out insertion/cyclization was unsuccessful, the isocyanides were selectively inserted to one or both terminal C−H of α,ω-diynes. Mechanistic investigation reveals that the amine additives play an important role as proton sources to prevent the oligomerization of isocyanides and as suitable ligands to activate the rare-earth catalysts. Moreover, the resting state of catalysts seems to be rare-earth alkynides; therefore, subsequent insertion of isocyanides would be the rate-determining step.

Experimental Procedures

General. ^{1}H and ^{13}C NMR spectra were recorded at 397.95 and 99.5 MHz, respectively. Mass spectra (EI) were obtained at 70 eV on a GC−MS apparatus. Microanalyses were performed at our analytical laboratory. All reactions were carried out under argon. Solvents were distilled from sodium/benzophenone ketyl and stored under argon. The silylamide complex was prepared by modified Bradley's method.[11] Thus, after refluxing a THF solution of sodium hexamethyldisilazane and anhydrous rare-earth trichloride for 24 h and removal of

the solvent under vacuum, the residue was dried over under vacuum at 40−50 °C for 10 h. Subsequently, the solid was extracted with hexane, and the solution was recrystallized to provide the aciculate silylamide in high yield (80−90%). The terminal alkynes were obtained as previously described,[9] except for **4a**−**d**.[12] Isocyanides **2a**−**e**[4d] and **2f**−**g**[13] were prepared based on the reported procedure. All other materials were commercially available and used after drying and purification.

General Procedure for Coupling of Isocyanides and Terminal Alkynes (Entry 1, Table 3). A 20 mL Schlenk flask was charged with $Sm[(N(SiMe_3)_2)_3$ (28 mg, 0.046 mmol). A solution of **1a** (65 μL, 0.44 mmol), **2e** (82 mg, 0.44 mmol), and amylamine (10 μL, 0.088 mmol) in cyclohexane (0.45 mL) was added to the Sm complex. After stirring at room temperature for 9 h, the reaction mixture was quenched with distilled water (1 mL) and diluted with ether (2 mL). GC yield (88%) was determined by using tridecane as an internal standard. The aqueous layer was extracted with ether (20 mL), and then the combined organic layer was washed with brine (20 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by Kugelrohr distillation (250 °C/10^{-2} Torr) to provide 77 mg (59%) of **3ae**, whose stereochemistry and the ratio of syn- and anti-isomers was decided by NOE and NMR studies.

1-(2-Xylylimino)non-2-yne (3ac). Isolated as a yellow oil (78 mg, 30%, syn/anti = 54:46) by Kugelrohr distillation (150−160 °C/10^{-2} Torr); IR (neat) 2208, 1653 cm^{-1}; ^1H NMR ($CDCl_3$) syn isomer (assignable peaks only): δ 0.91 (3H, t, J = 7.0 Hz), 1.60−1.67 (2H, m), 2.12 (6H, s), 2.44 (2H, dt, J = 1.6 and 7.2 Hz), 7.02 (2H, d, J = 7.2 Hz), 7.76 (1H, t, J = 1.6 Hz), anti isomer: 0.86 (3H, t, J = 7.2 Hz), 1.10−1.33 (6H, m), 1.41−1.48 (2H, m), 2.06 (6H, s), 2.14 (2H, dt, J = 1.6 and 6.8 Hz), 6.88−6.95 (1H, m), 7.00 (2H, d, J = 7.0 Hz), 7.43 (1H, t, J = 1.6 Hz); ^{13}C NMR ($CDCl_3$) syn isomer: δ 14.0, 18.2, 19.0, 22.4, 27.9, 28.6, 31.3, 76.0, 99.5, 123.4, 125.8, 127.6, 144.8, 150.8, anti isomer: 14.0, 17.8, 19.5, 22.5, 27.7, 27.9, 31.2, 78.9, 97.2, 124.2, 126.9, 128.0, 144.9, 147.7; MS *m/z* 242 (M^+ + 1, 11), 241 (M^+, 65), 184 (82), 170 (100). Anal. Calcd for $C_{17}H_{23}N$: C, 84.59; H, 9.60; N; 5.80. Found: C, 84.45; H, 9.94; N, 5.60.

1-(Mesitylimino)non-2-yne (3ad). Isolated as a yellow oil (94 mg, 57%, syn/anti = 45:55) by Kugelrohr distillation (170−180 °C/10^{-2} Torr); IR (neat) 2216, 1603 cm^{-1}; ^1H NMR ($CDCl_3$) anti isomer: δ 0.87 (3H, t, J = 7.2 Hz), 1.11−1.33 (6H, m), 1.41−1.48 (2H, m), 2.09 (6H, s), 2.16 (2H, dt, J = 1.6 and 6.8 Hz), 2.26 (3H, s), 6.85 (2H, s), 7.42 (1H, t, J = 1.6 Hz); syn isomer: 0.91 (3H, t, J = 7.1 Hz), 1.11−1.33 (6H, m), 1.59−1.67 (2H, m), 2.03 (6H, s), 2.26 (3H, s), 2.44 (2H, dt, J = 1.5 and 7.2 Hz), 6.83 (2H, s), 7.76 (1H, t, J = 1.5 Hz); ^{13}C NMR ($CDCl_3$) anti isomer: δ 14.01, 18.2, 19.1, 20.7, 22.5, 27.8, 28.0, 31.3, 76.2, 99.3, 126.9, 128.7, 132.6, 144.9, 147.1, syn isomer: 14.04, 17.8, 19.5, 20.69, 22.4, 27.97, 28.6, 31.2, 79.0, 96.9, 125.7, 128.3, 133.5, 147.7, 148.4; MS *m/z* 255 (M^+, 31), 198 (28), 184 (43), 146 (20), 29 (100). Anal. Calcd for $C_{18}H_{25}N$: C, 84.65; H, 9.87; N; 5.48. Found: C, 84.46; H, 9.92; N, 5.62.

1-(2,6-Diisopropylphenylimino)non-2-yne (3ae). Isolated as a yellow oil (77 mg, 59%, syn/anti = 35:65) by Kugelrohr distillation (250 °C/10^{-2} Torr); IR (neat) 2208, 1608 cm^{-1}; ^1H NMR ($CDCl_3$) anti isomer: δ 0.91 (3H, t, J = 7.0 Hz), 1.01−1.49 (18 H, m), 1.61−1.69 (2H, m), 2.46 (2H, dt, J = 1.5 and 7.2 Hz), 2.92 (2H, sept, J = 6.9 Hz), 7.03−7.14 (3H, m), 7.40 (1H, t, J = 1.5 Hz); syn isomer (assignable peaks only): 0.84 (3H, t, J = 7.2 Hz), 1.01−1.49 (18 H, m), 2.14 (2H, dt, J = 1.4 and 6.9 Hz), 2.82 (2H, sept, J = 6.9 Hz), 7.03−7.14 (3H, m), 7.84 (1H, t, J = 1.4 Hz); ^{13}C NMR ($CDCl_3$) anti isomer: δ 14.0, 19.5, 22.5, 23.5, 27.71, 27.86, 28.0, 31.3, 78.9, 97.0, 123.0, 124.6, 137.5, 147.1, 148.6; syn isomer: 14.1, 19.0, 22.4, 23.3, 27.67, 27.84, 28.7, 31.2, 76.5, 100.3, 122.7, 124.1, 136.3, 145.2, 147.3; MS *m/ z* 297 (M^+, 36), 282 (100), 212 (35). Anal. Calcd for $C_{21}H_{31}N$: C, 84.79; H, 10.50; N; 4.71. Found: C, 84.89; H, 10.62; N, 4.49.

1-(2,6-Diisopropylphenylimino)hept-2-yne (3be). Isolated as a yellow oil (197 mg, 59%, syn/anti = 46:54) by Kugelrohr distillation (190 °C/10^{-2} Torr); IR (neat) 2208, 1609 cm^{-1}; ^1H NMR ($CDCl_3$) anti isomer: δ 0.96 (3H, t, J = 7.2 Hz), 1.16 (12H, d, J = 7.0 Hz), 1.18−1.26 (2H, m), 1.60−1.67 (2H, m), 2.46 (2H, dt, J = 1.5 and 7.2 Hz), 2.91 (2H, sept, J = 7.0 Hz), 7.04−7.14 (3H, m), 7.40 (1H, t, J = 1.5 Hz), syn isomer: 0.72 (3H, t, J = 7.4 Hz), 0.97−1.04 (2H, m), 1.17 (12H, d, J = 6.9 Hz), 1.43−1.53 (2H, m), 2.13 (2H, dt, J = 1.5 and 6.9 Hz), 2.82 (2H, sept, J = 6.9 Hz), 7.04−7.14 (3H, m), 7.83 (1H, t, J = 1.5 Hz); ^{13}C NMR ($CDCl_3$) anti isomer: δ 13.5, 19.1, 21.0, 23.4, 27.6, 30.0, 76.5, 96.7, 122.9, 124.6, 136.2, 147.0, 148.6; syn isomer: 13.3, 18.6, 22.0, 23.2, 27.8, 29.6, 78.9, 100.0, 122.6, 124.0, 137.4, 145.1, 147.3; MS *m/z* 269 (M^+, 59), 254 (100), 212 (83). Anal. Calcd for $C_{19}H_{27}N$: C, 84.70; H, 10.10; N, 5.20. Found: C, 84.75; H, 10.24; N, 5.01.

1-(2,6-Diisopropylphenylimino)-4-ethylnon-2-yne (3ce). Isolated as a yellow oil (241 mg, 77%, syn/anti = 64:36) by Kugelrohr distillation (230 °C/10^{-2} Torr); IR (neat) 2208, 1607, 1589 cm^{-1}; ^1H NMR ($CDCl_3$) syn isomer: δ 0.67 (3H, t, J = 7.5 Hz), 0.85 (3H, t, J = 7.3 Hz), 0.96−1.68 (22H, m), 2.13−2.21 (1H, m), 2.82 (2H, sept, J = 6.9 Hz), 7.02−7.13 (3H, m), 7.85 (1H, d, J = 1.2 Hz), anti isomer: 0.91 (3H, t, J = 6.9 Hz), 0.96−1.68 (22H, m), 1.07 (3H, t, J = 7.5 Hz), 2.50−2.55 (1H, m), 2.93 (2H, sept, J = 6.9 Hz), 7.02−7.13 (3H, m), 7.43 (1H, d, J = 1.5 Hz); ^{13}C NMR ($CDCl_3$) syn isomer: δ 11.2, 14.03, 22.4, 23.2, 27.0, 27.5, 27.8, 31.57, 33.9, 33.99, 77.4, 103.2, 122.9, 124.1, 137.5, 145.3, 147.5, anti isomer: 11.8, 13.96, 22.5, 23.5, 26.5, 27.4, 27.7, 31.6, 33.97, 34.1, 80.1, 100.2, 122.7, 124.6, 136.1, 147.1, 148.7; MS *m/z* 325 (M^+, 49), 310 (100). Anal. Calcd for $C_{23}H_{35}N$: C, 84.86; H, 10.84; N, 4.30. Found: C, 84.44; H, 11.14; N, 4.40.

1-(2,6-Diisopropylphenylimino)-4,4-dimethylpent-2-yne (3de). Isolated as a yellow oil (152 mg, 53%, syn/anti = 57:43) by Kugelrohr distillation (140 °C/10^{-2} Torr); IR (neat) 2216, 1607 cm^{-1}; ^1H NMR ($CDCl_3$) syn isomer: δ 0.95 (9H, s), 1.16 (12H, d, J = 6.9 Hz), 2.92 (2H, sept, J = 6.9 Hz), 7.01−7.13 (3H, m), 7.79 (1H, s); anti isomer: 1.14 (12H, d, J = 7.0 Hz), 1.35 (9H, s), 2.81 (2H, sept, J = 7.0 Hz), 7.01−7.13 (3H, m), 7.40 (1H, s); ^{13}C NMR ($CDCl_3$) syn isomer: δ 23.3, 23.6, 27.6, 29.9, 75.2, 104.3, 122.6, 124.0, 137.5, 145.4, 147.6; anti isomer: 23.5, 23.6, 27.8, 30.4, 77.4, 107.8, 122.9, 124.6, 136.1, 147.1, 148.6; MS *m/z* 269 (M^+, 69), 254 (100), 212 (74). Anal. Calcd for $C_{19}H_{27}N$: C, 84.70; H, 10.10; N, 5.20. Found: C, 84.67; H, 10.26; N, 5.01.

1-(2,6-Diisopropylphenylimino)-3-trimethylsilylprop-2-yne (3ee). Isolated as a yellow oil (160 mg, 69%, syn/anti = 38:62) by Kugelrohr distillation (155−160 °C/10^{-2} Torr); IR (neat) 2363, 2341, 1605, 1589, 1252 cm^{-1}; ^1H NMR ($CDCl_3$) anti isomer: δ 0.31 (9H, s), 1.13−1.20 (12H, m), 2.93 (2H, sept, J = 6.9 Hz), 7.03−7.18 (3H, m), 7.42 (1H, s); syn isomer: −0.03 (9H, s), 1.13−1.20 (12H, m), 2.80 (2H, sept, J = 6.9 Hz), 7.03−7.18 (3H, m), 7.85 (1H, s); ^{13}C NMR ($CDCl_3$) anti isomer: −0.51, 23.6, 27.7, 98.4, 101.2, 123.0, 124.9, 137.4, 146.6, 148.4; syn isomer: δ −0.96, 23.5, 27.9, 100.8, 104.5, 122.7, 124.3, 136.0, 144.9, 147.4; MS *m/z* 285 (M^+, 62), 284 (38), 73 (100). Anal. Calcd for $C_{18}H_{27}NSi$: C, 75.72; H, 9.53; N, 4.91. Found: C, 75.47; H, 9.68; N, 5.02.

1-(2,6-Diisopropylphenylimino)-4-methoxybut-2-yne (3fe). Isolated as a yellow oil (14 mg, 7%, syn/anti = 37:63) by Kugelrohr distillation (220 °C/10^{-2} Torr); IR (neat) 2193, 1609 cm^{-1}; ^1H NMR ($CDCl_3$) anti isomer: δ 1.16 (12H, d, J = 6.9 Hz), 2.90 (2H, sept, J = 6.9 Hz), 3.48 (3H, s), 4.36 (2H, s), 7.05−7.13 (3H, m), 7.47 (1H, s); syn isomer (assignable peaks only): 2.81 (2H, sept, J = 6.8 Hz), 2.97 (3H, s), 4.04 (2H, s), 7.05−7.13 (3H, m), 7.94 (1H, s); ^{13}C NMR ($CDCl_3$) anti isomer: δ 23.5, 27.8, 58.2, 60.1, 83.8, 90.1, 123.1, 125.0, 137.3, 146.1, 148.3; syn isomer: 23.2, 27.7, 57.1, 59.5, 81.2, 93.6, 122.9,

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(13) Ezquerra, J.; Prdregal, C.; Lamas, C. *J. Org. Chem.* **1996**, *61*, 5804.

124.5, 136.2, 144.1, 147.0; MS *m/ z* 257 (M^+, 100), 242 (81). Anal. Calcd for $C_{17}H_{23}NO$: C, 79.33; H, 9.01; N, 5.44. Found: C, 79.26; H, 9.13; N, 5.49.

1-(2,6-Diisopropylphenylimino)-4-(*t*-butyldimethylsilyloxy)but-2-yne (3he). Isolated as an orange oil (106 mg, 76%, syn/anti = 35:65) by Kugelrohr distillation (>250 °C/10^{-2} Torr); IR (neat) 2114, 1609 cm^{-1}; ^1H NMR ($CDCl_3$) anti isomer: δ 0.19 (6H, s), 0.96 (9H, s), 1.17 (12H, d, J = 6.9 Hz), 2.91 (2H, sept, J = 6.9 Hz), 4.58 (2H, s), 7.08−7.18 (3H, m), 7.47 (1H, s); syn isomer (assignable peaks only): −0.06 (6H, s), 0.82 (9H, s), 2.83 (2H, sept, J = 6.8 Hz), 4.26 (2H, s), 7.08−7.18 (3H, m), 7.95 (1H, s); ^{13}C NMR ($CDCl_3$) anti isomer: δ −5.22, 18.3, 23.5, 25.8, 27.7, 52.0, 82.4, 92.9, 123.0, 124.8, 137.3, 146.3, 148.5; syn isomer: −5.49, 18.1, 23.4, 25.6, 27.9, 51.5, 79.2, 96.4, 122.8, 136.1, 136.1, 144.1, 146.9; MS *m/z* 357 (M^+, 94), 342 (100). Anal. Calcd for $C_{22}H_{35}NOSi$: C, 73.89; H, 9.87; N, 3.92. Found: C, 74.00; H, 9.90; N, 4.12.

1-(2,6-Diisopropylphenylimino)-4-(*N*,*N*-diethylamino)-but-2-yne (3ie). Isolated as an orange oil (234 mg, 76%, syn/anti = 60:40) by Kugelrohr distillation (>250 °C/10^{-2} Torr); IR (neat) 2171, 1589 cm^{-1}; ^1H NMR ($CDCl_3$) syn isomer: δ 0.84 (6H, t, J = 7.1 Hz), 1.10−1,20 (12H, m), 2.04 (4H, q, J = 7.1 Hz), 2.81 (2H, sept, J = 6.9 Hz), 3.39 (2H, s), 7.03−7.13 (3H, m), 7.86 (1H, s); anti isomer: 1.12 (6H, t, J = 7.2 Hz), 1.10−1,20 (12H, m), 2.64 (4H, q, J = 7.2 Hz), 2.91 (2H, sept, J = 6.9 Hz), 3.67 (2H, s), 7.03−7.13 (3H, m), 7.43 (1H, s); ^{13}C NMR ($CDCl_3$) syn isomer: δ 12.52, 23.5, 27.9, 40.6, 46.8, 82.7, 93.6, 122.7, 124.1, 136.1, 144.6, 147.6; anti isomer: 12.54, 23.2, 27.7, 41.6, 47.4, 80.3, 90.9, 123.0, 124.7, 137.4, 146.5, 148.5; MS *m/z* 298 (M^+, 0.3), 283 (12), 188 (45). Anal. Calcd for $C_{20}H_{30}N_2$: C, 80.48; H, 10.13; N; 9.39. Found: C, 80.21; H, 9.98; N, 9.33.

1-(2,6-Diisopropylphenylimino)-4-(*N*,*N*-dibenzylamino)-but-2-yne (3je). Isolated as an orange oil (158 mg, 40%, syn/anti = 70:30) by MPLC on alumina (hexane/EtOAc = 50, R_f = 0.43); IR (neat) 2174, 1605 cm^{-1}; ^1H NMR ($CDCl_3$) syn isomer: δ 1.18−1.28 (12H, m), 2.91 (2H, sept, J = 6.9 Hz), 3.21 (2H, d, J = 1.2 Hz), 3.23 (4H, s), 7.12−7.44 (13H, m), 7.95 (1H, t, J = 1.2 Hz); anti isomer: 1.18−1.28 (12H, m), 2.94 (2H, sept, J = 6.9 Hz), 3.53 (2H, d, J = 1.2 Hz), 3.78 (4H, s), 7.12−7.44 (13H, m), 7.49 (1H, t, J = 1.2 Hz); ^{13}C NMR ($CDCl_3$) syn isomer: δ 23.50, 28.1, 41.5, 57.0, 80.7, 93.8, 123.0, 124.5, 127.1, 128.2, 128.9, 136.2, 138.4, 144.6. 147.8; anti isomer (assignable peaks only): 23.2, 27.8, 42.2, 57.8, 83.6, 90.8, 123.1, 124.8, 127.3, 128.4, 129.0, 137.4, 138.5, 146.4, 148.6. Anal. Calcd for $C_{30}H_{34}N_2$: C, 85.26; H, 8.11; N, 6.63. Found: C, 85.01; H, 8.18; N, 6.81.

1-(2,6-Diisopropylphenylimino)-6-chlorohex-2-yne (3le). Isolated as an orange oil (117 mg, 62%, syn/anti = 57:43) by Kugelrohr distillation (220 °C/10^{-2} Torr); IR (neat) 2210, 1589 cm^{-1}; ^1H NMR ($CDCl_3$) syn isomer: δ 1.18−1.28 (12H, m), 1.65 (2H, quant, J = 6.4 Hz), 2.34 (2H, dt, J = 1.3 and 6.5 Hz), 2.80 (2H, sept, J = 6.8 Hz), 3.70 (2H, t, J = 6.3 Hz), 7.02−7.19 (3H, m), 7.82 (1H, t, J = 1.3 Hz); anti isomer: 1.18−1.28 (12H, m), 2.10 (2H, quant, J = 6.6 Hz), 2.67 (2H, dt, J = 1.6 and 6.9 Hz), 2.90 (2H, sept, J = 6.9 Hz), 3.02 (2H, t, J = 6.3 Hz), 7.02−7.19 (3H, m), 7.40 (1H, t, J = 1.6 Hz); ^{13}C NMR ($CDCl_3$) syn isomer: δ 16.3, 23.5, 27.7, 30.3, 43.5, 77.2, 94.3, 122.8, 124.3, 137.4, 144.9, 147.4; anti isomer: 16.9, 23.2, 27.9, 30.7, 42.4, 79.6, 97.6, 123.0, 124.8, 136.3, 146.7, 148.5; MS *m/z* 289 (M^+, 93), 274 (100), 278 (91). Anal. Calcd for $C_{18}H_{24}ClN$: C, 74.59; H, 8.35; N, 4.83. Found: C, 74.95; H, 8.28; N, 5.00.

1-(2-Xylylphenylimino)-3-phenylprop-2-yne (3mc). Isolated as a yellow solid (60 mg, 35%, syn/anti = 41:59) by Kugelrohr distillation (200 °C/10^{-2} Torr); IR (neat) 2203, 1649 cm^{-1}; ^1H NMR ($CDCl_3$) anti isomer: δ 2.16 (6H, s), 6.94−7.62 (8H, m), 7.71 (1H, s); syn isomer: 2.11 (6H, s), 6.94−7.62 (8H, m), 8.00 (1H, s); ^{13}C NMR ($CDCl_3$) anti isomer: δ 17.9, 86.8, 94.2, 120.8, 124.4, 126.8, 128.1, 128.5, 129.87, 132.41, 147.3, 150.8; syn isomer: 18.3, 83.4, 96.6, 121.2, 123.8, 125.9, 127.6, 128.3, 129.85, 132.39, 144.4, 149.8; MS *m/z* 233 (M^+, 82), 233 (100). Anal. Calcd for $C_{17}H_{15}N$: C, 87.52; H, 6.48; N; 6.00. Found: C, 87.55; H, 6.64; N, 5.81.

1-(Mesitylphenylimino)-3-phenylprop-2-yne (3md). Isolated as a yellow solid (51 mg, 29%, syn/anti = 35:65) by Kugelrohr distillation (250 °C/10^{-2} Torr); IR (neat) 2205, 1601 cm^{-1}; ^1H NMR ($CDCl_3$) anti isomer: δ 2.14 (6H, s), 2.27 (3H, s), 6.87 (2H, s), 7.16−7.62 (5H, m), 7.66 (1H, s); syn isomer: 2.08 (6H, s), 2.29 (3H, s), 6.87 (2H, s), 7.16−7.62 (5H, m), 8.00 (1H, s); ^{13}C NMR ($CDCl_3$) anti isomer: δ 18.2, 20.7, 86.8, 94.0, 121.2, 126.8, 128.3, 128.5, 129.8, 132.4, 133.8, 147.3, 148.4; syn isomer: 17.8, 20.7, 83.6, 96.3, 120.9, 125.8, 128.8 (two peaks were overlapped.), 129.8, 132.3, 132.6, 144.4, 147.2; MS *m/z* 247 (M^+, 88), 246 (100). Anal. Calcd for $C_{18}H_{17}N$: C, 87.41; H, 6.93; N; 5.66. Found: C, 87.25; H, 6.98; N, 5.67.

1-(2,6-Diisopropylphenylimino)-3-phenylprop-2-yne (3me). Isolated as a yellow oil (126 mg, 60%, syn/anti = 42:58) by Kugelrohr distillation (>250 °C/10^{-2} Torr); IR (neat) 2196, 1604 cm^{-1}; ^1H NMR ($CDCl_3$) anti isomer: δ 1.19 (12H, d, J = 6.9 Hz), 2.98 (2H, sept, J = 6.9 Hz), 7.12−7.64 (8H, m), 7.65 (1H, s); syn isomer (assignable peaks only): 2.89 (2H, sept, J = 6.9 Hz), 8.04 (1H, s); ^{13}C NMR ($CDCl_3$) anti isomer: δ 23.6, 27.8, 86.8, 94.0, 120.8, 123.1, 124.9, 128.5, 129.9, 132.5, 137.5, 146.8, 148.6; syn isomer: 23.5, 27.9, 83.8, 97.3, 121.1, 122.7, 124.3, 128.4, 129.8, 132.3, 136.5, 144.8, 147.4; MS *m/z* 289 (M^+, 82), 274 (95), 115 (100). Anal. Calcd for $C_{21}H_{23}N$: C, 87.15; H, 8.01; N; 4.84. Found: C, 86.91; H, 8.06; N, 5.10.

1-(2,6-Diisopropylphenylimino)-3-(4-anisyl)prop-2-yne (3ne). Isolated as a yellow oil (48 mg, 18%, syn/anti = 42:58) by Kugelrohr distillation (>250 °C/10^{-2} Torr); IR (neat) 2192, 1587 cm^{-1}; ^1H NMR ($CDCl_3$) anti isomer: δ 1.19 (12H, d, J = 6.8 Hz), 3.00 (2H, sept, J = 6.8 Hz), 3.78 (3H, s), 6.71−7.58 (7H, m), 7.64 (1H, s); syn isomer: 1.18 (12H, d, J = 6.8 Hz), 2.91 (2H, sept, J = 6.8 Hz), 3.71 (3H, s), 6.71−7.58 (7H, m), 8.04 (1H, s); ^{13}C NMR ($CDCl_3$) anti isomer: δ 23.5, 27.7, 55.14, 86.2, 94.6, 113.0, 114.10, 122.9, 124.7, 134.1, 137.4, 146.7, 148.7, 160.81; syn isomer: 23.4, 27.8, 55.08, 83.5, 98.1, 112.6, 113.98, 122.6, 124.1, 134.0, 136.5, 144.8, 147.5, 160.76; MS *m/z* 319 (M^+, 82), 304 (100), 276 (45). Anal. Calcd for $C_{22}H_{25}NO$: C, 82.72; H, 7.89; N; 4.38. Found: C, 82.78; H, 8.12; N, 4.67.

1-(2,6-Diisopropylphenylimino)-3-(4-tolyl)prop-2-yne (3oe). Isolated as a yellow solid (82 mg, 33%, syn/anti = 42:58) by Kugelrohr distillation (>250 °C/ 10^{-2} Torr); IR (neat) 2195, 1689 cm^{-1}; ^1H NMR ($CDCl_3$) anti isomer: δ 1.19 (12H, d, J = 7.0 Hz), 2.38 (3H, s), 2.99 (2H, sept, J = 7.0 Hz), 6.98−7.53 (7H, m), 7.64 (1H, s); syn isomer (assignable peaks only): 2.29 (3H, s), 2.89 (2H, sept, J = 6.9 Hz), 8.06 (1H, s); ^{13}C NMR ($CDCl_3$) anti isomer: δ 21.5, 23.6, 27.8, 86.5, 97.8, 118.1, 122.7, 124.8, 129.3, 132.4, 136.5, 140.38, 146.8, 148.7; syn isomer: 21.6, 23.5, 27.9, 83.7, 94.5, 117.7, 123.0, 124.3, 129.1, 132.2, 137.5, 140.36, 144.9, 147.5; MS *m/z* 303 (M^+, 70), 288 (100), 115 (56). Anal. Calcd for $C_{22}H_{25}N$: C, 87.08; H, 8.30; N; 4.62. Found: C, 86.98; H, 8.64; N, 4.38.

1-(2,6-Diisopropylphenylimino)-3-(2-tolyl)prop-2-yne (3pe). Isolated as a yellow oil (165 mg, 69%, syn/anti = 68:32) by Kugelrohr distillation (220 °C/10^{-2} Torr); IR (neat) 2359, 2191, 1645 cm^{-1}; ^1H NMR ($CDCl_3$) syn isomer: δ 1.17 (12H, d, J = 6.9 Hz), 1.81 (3H, s), 2.88 (2H, sept, J = 6.9 Hz), 7.03−7.61 (7H, m), 8.13 (1H, s); anti isomer: 1.19 (12H, d, J = 6.9 Hz), 2.55 (3H, s), 2.99 (2H, sept, J = 6.9 Hz), 7.03−7.61 (7H, m), 7.68 (1H, s); ^{13}C NMR ($CDCl_3$) syn isomer: δ 19.6, 23.6, 28.0, 87.7, 96.0, 120.6, 123.0, 124.3, 125.5, 129.5, 130.0, 132.7, 136.1, 141.9, 145.0, 147.8; anti isomer: 20.7, 23.3, 27.8, 90.6, 93.1, 121.0, 123.1, 124.8, 125.7, 129.7, 129.9, 133.0, 137.5, 141.4, 146.7, 148.8; MS *m/z* 303 (M^+, 76), 288 (100), 115 (59). Anal. Calcd for $C_{22}H_{25}N$: C, 87.08; H, 8.30; N; 4.62. Found: C, 87.04; H, 8.20; N, 4.69.

1-(2,6-Diisopropylphenylimino)-3-(4-bromophenyl)prop-2-yne (3qe). Isolated as a yellow solid (144 mg, 60%, syn/anti = 38:62) by Kugelrohr distillation (250 °C/10^{-2} Torr); IR (neat) 2193, 1585 cm^{-1}; ^1H NMR ($CDCl_3$) anti isomer: δ 1.19 (12H, d, J = 6.8 Hz), 2.96 (2H, sept, J = 6.8 Hz), 6.93−6.96 (1H, m),

7.10−7.17 (3H, m), 7.36−7.39 (1H, m), 7.47−7.54 (2H, m), 7.63 (1H, s); syn isomer: 1.16 (12H, d, J = 7.0 Hz), 2.86 (2H, sept, J = 7.0 Hz), 6.93−6.96 (1H, m), 7.10−7.17 (3H, m), 7.36−7.39 (1H, m), 7.47−7.54 (2H, m), 8.07 (1H, s); ^{13}C NMR ($CDCl_3$) anti isomer: δ 23.5, 27.9, 87.7, 92.7, 120.2, 123.1, 124.5, 131.9, 133.8, 137.4, 146.4, 146.6, 148.6; syn isomer: 23.5, 27.9, 84.7, 96.0, 119.7, 122.8, 125.0, 131.9, 133.8, 136.5, 144.5, 144.6, 147.4; MS *m/z* 369 (M^+ + 2, 46), 368 (M^+ + 1 38), 367 (M^+, 39), 173 (100). Anal. Calcd for $C_{21}H_{22}BrN$: C, 68.48; H, 6.02; N; 3.80. Found: C, 68.42; H, 5.85; N, 3.72.

1-(2,6-Diisopropylphenylimino)-3-(4-fuluorophenyl)-prop-2-yne (3re). Isolated as a brown oil (118 mg, 41%, syn/anti = 40:60) by Kugelrohr distillation (> 250 °C/10^{-2} Torr); IR (neat) 2206, 1587 cm^{-1}; ^{1}H NMR ($CDCl_3$) anti isomer: δ 1.16−1.23 (12H, m), 2.97 (2H, sept, J = 6.8 Hz), 6.91−7.64 (7H, m), 7.63 (1H, s); syn isomer: 1.16−1.23 (12H, m), 2.88 (2H, sept, J = 6.8 Hz), 6.91−7.64 (7H, m), 8.06 (1H, s); ^{13}C NMR ($CDCl_3$) anti isomer: δ 23.57, 23.59, 27.75, 27.84, 86.7, 92.9, 115.9, 117.3 (d, J = 3.3 Hz), 123.1, 124.9, 134.5, 137.5, 146.6, 148.6, 163.5 (d, J = 252 Hz); syn isomer: 23.4, 23.5, 27.9, 28.0, 83.8, 96.3, 115.9, 116.9 (d, J = 3.3 Hz), 122.8, 124.4, 134.5, 136.5, 144.7, 147.4, 163.5 (d, J = 252 Hz); MS *m/z* 307 (M^+, 88), 306 (67), 292 (100). Anal. Calcd for $C_{21}H_{22}FN$: C, 82.05; H, 7.21; N; 4.56. Found: C, 81.75; H, 7.31; N, 4.62.

1-(2,6-Diisopropylphenylimino)-3-[4-(1,3-dioxoranyl)-phenyl]prop-2-yne (3se). Isolated as a yellow oil (305 mg, 68%, syn/anti = 38:62) by Kugelrohr distillation (>250 °C/10^{-2} Torr); IR (neat) 2199, 1587 cm^{-1}; ^{1}H NMR ($CDCl_3$) anti isomer: δ 1.19 (12H, d, J = 6.9 Hz), 2.98 (2H, sept, J = 6.9 Hz), 3.95−4.14 (4H, m), 7.10−7.17 (3H, m), 7.34−7.66 (4H, m), 7.65 (1H, s); syn isomer: 1.16 (12H, d, J = 7.0 Hz), 2.88 (2H, sept, J = 7.0 Hz), 3.95−4.14 (4H, m), 7.10−7.17 (3H, m), 7.34−7.66 (4H, m), 8.08 (1H, s); ^{13}C NMR ($CDCl_3$) anti isomer: δ 23.52, 23.54, 27.7, 27.8, 65.3, 87.1, 93.5, 103.0, 121.4, 123.0, 124.9, 126.6, 132.4, 137.4, 139.6, 144.7, 148.6; syn isomer: 23.3, 23.4, 27.8, 27.9, 65.2, 84.2, 96.9, 102.8, 121.8, 122.7, 124.3, 126.4, 132.3, 136.4, 139.7, 146.6, 147.4; MS *m/z* 361 (M^+, 75), 360 (26), 73 (100). Anal. Calcd for $C_{24}H_{27}NO_2$: C, 79.74; H, 7.53; N; 3.87. Found: C, 79.61; H, 7.72; N, 3.75.

1-[2-(Trimethylsilylethynyl)-4,6-dimethylphenylimino]-3-phenylprop-2-yne (3mf). Isolated as a yellow oil (86 mg, 79%, syn/anti = 81:19) by Kugelrohr distillation (>250 °C/10^{-2} Torr); IR (neat) 2359, 2341, 2204, 2151, 1607 cm^{-1}; ^{1}H NMR ($CDCl_3$) syn isomer: δ 0.23 (9H, s), 2.17 (3H, s), 2.22 (3H, s), 6.98 (1H, s), 7.17 (1H, s), 7.26−7.44 (3H, m), 7.59−7.61 (2H, m), 8.00 (1H, s); anti isomer (assignable peaks only): 0.17 (9H, s), 2.11 (3H, s), 2.27 (3H, s); ^{13}C NMR ($CDCl_3$) syn isomer: δ −0.14, 18.2, 20.6, 87.0, 94.8, 96.9, 103.1, 112.0, 121.5, 128.5, 129.7, 130.4, 131.0, 131.6, 132.4, 134.4, 144.5, 148.0; anti isomer (assignable peaks only): −0.06, 17.9, 128.3, 129.8, 132.3. Anal. Calcd for $C_{22}H_{23}NSi$: C, 80.19; H, 7.04; N; 4.25. Found: C, 80.21; H, 7.05; N, 4.19.

1-[2,6-Bis(trimethylsilylethynyl)-4-methylphenylimino]-3-phenylprop-2-yne (3mg). Isolated as a yellow oil (152 mg, 85%, syn/anti = 73:27) by vacuum distillation (>250 °C/10^{-2} Torr); IR (neat) 2361, 2341, 2197, 1605, 1587 cm^{-1}; ^{1}H NMR ($CDCl_3$) syn isomer: δ 0.24 (18H, s), 2.24 (3H, s), 7.25−7.60 (7H, m), 7.99 (1H, s); anti isomer (assignable peaks only): δ 0.19 (18H, s), 2.26 (3H, s). ^{13}C NMR ($CDCl_3$) TMS-carbons of syn and anti isomer: δ −0.23, −0.20, −0.19; syn isomer: 20.4, 86.9, 95.2, 99.0, 101.3, 1224.4, 121.4, 128.4, 132.2, 133.5, 134.3, 144.6, 148.5, 153.2; anti isomer: 20.2, 83.9, 97.6, 98.7, 101.8, 1123.6, 121.1, 128.2, 129.7, 132.4, 133.3, 144.7, 148.7, 152.8. Anal. Calcd for $C_{26}H_{29}NSi_2$: C, 75.85; H, 7.10; N; 3.40. Found: C, 75.65; H, 7.11; N, 3.30.

1-(2,6-Diisopropylphenylimino)non-2,8-diyne (5ae). Isolated as an orange oil (70 mg, 38%, syn/anti = 54:46) by Kugelrohr distillation (220 °C/10^{-2} Torr); IR (neat) 2210, 1607 cm^{-1}; ^{1}H NMR ($CDCl_3$) syn isomer: δ 1.13−1.40 (14H, m), 1.67−1.82 (2H, m), 1.97 (1H, t, J = 2.8 Hz), 2.27 (2H, dt, J = 2.8 and 6.8 Hz), 2.50 (2H, dt, J = 1.5 and 6.9 Hz), 2.81 (2H, sept, J = 6.9 Hz), 7.03−7.14 (3H, m), 7.83 (1H, t, J = 1.5 Hz); anti isomer: 1.13−1.40 (14H, m), 1.67−1.82 (2H, m), 1.90 (1H, t, J = 2.8 Hz), 1.98 (2H, dt, J = 2.8 and 6.8 Hz), 2.18 (2H, dt, J = 1.6 and 6.6 Hz), 2.91 (2H, sept, J = 7.0 Hz), 7.03−7.14 (3H, m), 7.40 (1H, t, J = 1.6 Hz); ^{13}C NMR ($CDCl_3$) syn isomer: δ 17.9, 19.1, 23.5, 26.3, 26.9, 27.7, 68.5, 76.9, 83.77, 96.0, 123.0, 124.2, 136.3, 146.9, 148.6; anti isomer: 17.7, 18.5, 23.3, 26.4, 27.6, 27.9, 68.7, 79.2, 83.80, 99.3, 122.7, 124.7, 137.5, 145.1, 147.4; MS *m/z* 293 (M^+, 21), 292 (26), 278 (100). Anal. Calcd for $C_{21}H_{27}N$: C, 85.95; H, 9.27; N; 4.77. Found: C, 85.64; H, 9.30; N, 4.94.

1-(2,6-Diisopropylphenylimino)dec-2,9-diyne (5be). Isolated as a pale yellow oil (80 mg, 35%, syn/anti = 41:59) by Kugelrohr distillation (230 °C/10^{-2} Torr); IR (neat) 2210, 1607 cm^{-1}; ^{1}H NMR ($CDCl_3$) anti isomer: δ 1.10−1.58 (15H, m), 1.57−1.69 (3H, m), 1.95 (1H, t, J = 2.7 Hz), 2.23 (2H, dt, J = 2.7 and 6.7 Hz), 2.48 (2H, dt, J = 1.6 and 7.1 Hz), 2.92 (2H, sept, J = 6.9 Hz), 7.08−7.14 (3H, m), 7.40 (1H, t, J = 1.6 Hz); syn isomer: 1.10−1.58 (15H, m), 1.57−1.69 (3H, m), 1.92 (1H, t, J = 2.7 Hz), 2.07 (2H, dt, J = 2.7 and 7.2 Hz), 2.16 (2H, dt, J = 1.5 and 6.8 Hz), 2.82 (2H, sept, J = 6.9 Hz), 7.08−7.14 (3H, m), 7.83 (1H, t, J = 1.5 Hz); ^{13}C NMR ($CDCl_3$) anti isomer: δ 18.2, 19.4, 23.5, 27.19, 27.7, 27.87, 28.0, 68.4, 76.7, 84.2, 96.5, 123.0, 124.7, 136.3, 147.0, 148.6; syn isomer: 18.1, 18.9, 23.3, 27.17, 27.5, 27.84, 27.87, 68.2, 79.1, 84.3, 99.7, 122.7, 124.1, 137.5, 145.1, 147.3; MS *m/z* 307 (M^+, 6), 306 (17), 292 (100). Anal. Calcd for $C_{22}H_{29}N$: C, 85.94; H, 9.51; N; 4.56. Found: C, 85.73; H, 9.55; N, 4.72.

1-(2,6-Diisopropylphenylimino)pentadec-2,14-diyne (5ce). Isolated as a yellow oil (54 mg, 43%, syn/anti = 43:57) by Kugelrohr distillation (>250 °C/10^{-2} Torr); IR (neat) 2210, 1607 cm^{-1}; ^{1}H NMR ($CDCl_3$) anti isomer: δ 0,98−1.68 (16H, m), 1.14−1.18 (12H, m) 1.94 (1H, t, J = 2.7 Hz), 2.16−2.21 (2H, m), 2.45 (2H, dt, J = 1.5 and 7.2 Hz), 2.92 (2H, sept, J = 6.8 Hz), 7.07−7.14 (3H, m), 7.40 (1H, t, J = 1.5 Hz); syn isomer: 0,98−1.68 (16H, m), 1.14−1.18 (12H, m), 1.93 (1H, t, J = 2.7 Hz), 2.13 (2H, dt, J = 1.5 and 6.8 Hz), 2.16−2.21 (2H, m), 2.82 (2H, sept, J = 6.8 Hz), 7.07−7.14 (3H, m), 7.84 (1H, t, J = 1.5 Hz); ^{13}C NMR ($CDCl_3$) anti isomer: δ 18.4, 19.5, 23.3, 27.9, 28.1, 28.5, 28.7, 29.0, 29.1, 29.3, 29.4 (two peaks were overlapped), 68.4, 76.7, 84.2, 96.5, 123.0, 124.7, 136.3, 147.0, 148.6; syn isomer: 18.4, 19.0, 23.6, 27.71, 27.73, 27.9, 28.0, 28.7, 28.96, 29.1, 29.42, 29.44, 68.2, 79.1, 84.3, 99.7, 122.7, 124.1, 137.5, 145.1, 147.3; MS *m/z* 377 (M^+, 12), 376 (9), 362 (100). Anal. Calcd for $C_{27}H_{39}N$: C, 85.88; H, 10.41; N; 3.71. Found: C, 85.77; H, 10.18; N, 3.99.

1-(2,6-Diisopropylphenylimino)-5-benzyl-5-azaoct-2,7-diyne (5de). Isolated as a yellow oil (98 mg, 45%, syn/anti = 61:39) by Kugelrohr distillation (>250 °C/ 10^{-2} Torr); IR (neat) 2361, 2341, 2208, 1605, 1589 cm^{-1}; ^{1}H NMR ($CDCl_3$) syn isomer: δ 1.15−1.28 (12H, m), 2.17 (1H, t, J = 2.4 Hz), 2.81−2.95 (2H, m), 2.82 (2H, d, J = 2.4 Hz), 3.22 (2H, s), 3.41 (2H, s), 7.06−7.41 (8H, m) 7.91 (1H, t, J = 1.2 Hz); anti isomer: 1.15−1.28 (12H, m), 2.32 (1H, t, J = 2.4 Hz), 2.81−2.95 (2H, m), 3.51 (2H, d, J = 2.4 Hz), 3.68 (2H, s), 3.78 (2H, s), 7.06−7.41 (8H, m), 7.45 (1H, t, J = 1.2 Hz); ^{13}C NMR ($CDCl_3$) syn isomer: δ 23.5, 27.8, 41.5, 41.8, 56.9, 72.9, 79.0, 82.9, 93.4, 122.9, 124.4, 127.3, 128.3, 129.0, 137.4, 144.5, 147.6; anti isomer: 23.2, 27.7, 42.1, 42.7, 57.4, 73.7, 78.4, 80.5, 90.6, 123.0, 124.8, 127.5, 128.4, 129.2, 136.2, 146.4, 148.4. Anal. Calcd for $C_{26}H_{30}N_2$: C, 84.28; H, 8.16; N; 7.56. Found: C, 84.24; H, 8.17; N, 7.59.

1,10-Bis(2,6-diisopropylphenylimino)dec-2,9-diyne (6ae). Isolated as an orange oil (195 mg, 65%, syn−syn/syn−anti/anti−anti = 1:2:1) by column chromatography (alumina, Hex/EtOAc = 20); IR (neat) 2210, 1589 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.19−1.28 (26H, m), 1.38−1.46 (1H, m), 1.83−1.86 (1H, m), 1.90 (1H, m), 2.21−2.25 (2H, m), 2.54 (1H, m), 2.75−2.98 (4H, m), 7.02−7.15 (6H, m), 7.39 (t, J = 1.6 Hz, imine *H* of anti−anti), 7.41 and 7.80 (t, J = 1.5 Hz, syn−anti), 7.84 (t, J = 1.5 Hz, syn−syn); ^{13}C NMR ($CDCl_3$) carbons of three mixtures δ 18.1, 18.5, 18.9, 19.0, 22.4, 23.19, 23.22, 23.47, 23.49, 23.52, 25.3, 25.9, 26.6, 27.1, 27.68, 27.68, 27.79, 27.83, 76.8, 77.0, 79.2,

79.3, 95.7, 95.9, 99.0, 99.1, 122.63, 122.65, 122.8, 123.0, 124.0, 124.2, 124.7, 136.2, 137.41, 137.43, 144.9, 145.0, 146.8, 146.9, 147.3, 147.4, 148.5, 148.6. Anal. Calcd for $C_{34}H_{44}N_2$: C, 84.95; H, 9.23; N; 5.83. Found: C, 84.91; H, 9.11; N, 5.98.

1,11-Bis(2,6-diisopropylphenylimino)undec-2,10-diyne (6be). Isolated as an orange oil (212 mg, 45%, syn−syn/syn−anti/anti−anti = 1:2:1) by column chromatography (Alumina, Hex/EtOAc = 50); IR (neat) 2210, 1589 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00−1.08 (1H, m), 1.13−1.37 (26H, m), 1.42−1.49 (1H, m), 1.64−1.74 (2H, m), 2.02 (1H, dt, J = 1.4 and 6.9 Hz), 2.19 (1H, dt, J = 1.6 and 6.6 Hz), 2.33 (1H, dt, J = 1.5 and 7.4 Hz), 2.50 (1H, dt, J = 1.3 and7.0 Hz), 2.77−2.96 (4H, m), 6.99−7.15 (6H, m), 7.39 (t, J = 1.4 Hz, imine *H* of anti−anti), 7.40 and 7.82 (t, J = 1.6 Hz, syn−anti), 7.84 (t, J = 1.3 Hz, syn−syn); ^{13}C NMR ($CDCl_3$) carbons of three mixtures δ 18.6, 18.8, 19.2, 19.3 22.3, 23.2, 23.47, 23.51 26.3. 26.95, 27.1, 27.3, 27.4, 27.5 27.7, 27.78, 27.80, 76.5, 76.7, 78.9, 79.1, 96.2, 96.4, 99.4, 99.6, 122.58, 122.62, 122.64, 122.9, 124.0, 124.1, 124.6, 136.20. 136.24, 137.4, 145.0, 146.9, 147.27, 147.31, 148.5. Anal. Calcd for $C_{35}H_{46}N_2$: C, 84.97; H, 9.37; N; 5.66. Found: C, 84.90; H, 9.29; N, 5.72.

1,16-Bis(2,6-diisopropylphenylimino)hexadec-2,14-diyne (6ce). Isolated as an orange oil (111 mg, 45%) by column chromatography (Frolisil, Hex/EtOAc = 50); IR (neat) 2210, 1607, 1589 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.99−1.33 (36H, m), 1.41−1.46 (2H, m), 1.61−1.69 (2H, m), 2.11−2.15 (2H, m), 2.43−2.47 (2H, m), 2.77−3.01 (4H, m), 7.01−7.18 (6H, m), 7.40−7.41 (1H, m), 7.83−7.84 (1H, m); ^{13}C NMR ($CDCl_3$) δ 18.9, 19.5, 22.5, 23.2, 23.5, 26.8, 27.6, 27.7, 27.8, 27.97, 28.02, 28.06, 28.3, 28.91, 28.94, 29.0, 29.21, 29.23, 29.34, 29.36, 29.7, 76.4, 78.9, 96.85, 96.88, 100.13, 100.14, 122.6, 122.9, 124.2, 124.1, 124.6, 136.2, 137.4, 145.1, 147.0, 147.3, 148.6. Anal. Calcd for $C_{40}H_{56}N_2$: C, 85.05; H, 9.99; N; 4.96. Found: C, 84.89; H, 10.26; N, 4.72.

1,9-Bis(2,6-diisopropylphenylimino)-5-benzyl-5-azanon-2,7-diyne (6de). Isolated as an orange oil (141 mg, 55%, syn−syn/syn−anti/anti−anti = 35:51:14) by column chromatography (Frolisil, Hex/EtOAc = 40); IR (neat) 2210, 1607, 1589 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.13−1.28 (12H, m), 2.75−2.96 (5H, m), 3.04 (1H, d, J = 1.0 Hz), 3.29 (1H, s), 3.49 (1H, s), 3.78 (1H, d, J = 1.0 Hz), 3.85 (1H, s), 6.92−7.47 (11H, m), 7.39 and 7.84 (t, J = 1.1 Hz, imine *H* of syn−anti), 7.48 (t, J = 1.2 Hz, anti−anti), 7.93 (1H, t, J = 1.0 Hz, syn−syn); ^{13}C NMR ($CDCl_3$) δ 23.17, 23.20, 23.36, 23.40, 23.5, 27.67, 27.69, 27.84, 27.93, 41.5, 42.0, 42.9, 56.5, 57.4, 57.9; syn−anti: 80.8, 82.6, 90.9, 92.9, 122.92, 122.98, 124.5, 124.8, 127.5, 128.3, 129.0, 137.07, 136.2, 137.3, 144.4, 146.15, 147.6, 148.4; syn−syn: 80.1, 93.6, 122.8, 124.3, 127.2, 128.1, 128.7, 136.1, 137.25, 144.3, 147.4; anti−anti: 83.2, 90.0, 123.0, 124.8, 127.6, 128.5, 129.1, 137.13, 137.29, 146.2, 148.3. Anal. Calcd for $C_{39}H_{47}N_3$: C, 83.97; H, 8.49; N; 7.53. Found: C, 82.15; H, 8.39; N, 9.46.

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