

Palladium-catalyzed intermolecular carboazidation of allenes with aryl iodides and trimethylsilyl azide

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Received (in Cambridge, UK) 6th June 2000, Accepted 7th September 2000

First published as an Advance Article on the web 31st October 2000

A new method for the synthesis of highly substituted allyl azides by carboazidation of allenes catalyzed by palladium complexes is described. Treatment of 1,1-dimethylallene (**1a**) with an aromatic iodide **2** (4-CH₃COC₆H₄I, 4-CH₃OC₆H₄I, 3-CH₃OC₆H₄I, 4-CH₃C₆H₄I, 3-CH₃C₆H₄I, 3-C₂H₅OCOC₆H₄I, 4-C₂H₅OCOC₆H₄I, 4-ClC₆H₄I, 3-BrC₆H₄I or 1-iodothiophene), (CH₃)₃SiN₃ and KOAc in the presence of Pd(dba)₂ (dba = dibenzylideneacetone) in DMF at 70 °C gave two regioisomers (CH₃)₂CC(Ar)CH₂N₃ **3** and (CH₃)₂(N₃)CC(Ar)CH₂ **4** in good to excellent yields. The observed regio- and stereoisomer ratios of the allyl azides from these reactions are close to the equilibrium ratio of these isomers at ambient temperature due to a rapid 1,3-shift of the azido group. Reduction of a mixture of **3a** and **4a** (80:20, Ar = 4-C₆H₄COMe) by PPh₃-H₂O afforded only the sterically less hindered (CH₃)₂C=C(Ar)-CH₂NH₂ in 95% yield further supporting a rapid 1,3-azide shift of **3a** and **4a**. Mono-substituted allenes RCHCCH₂ also undergo carboazidation with aryl iodides and (CH₃)₃SiN₃ in good to excellent yields. For *n*-butyl-, cyclopentyl- and cyclohexylallene (**1b–d**), carboazidation gives three isomers **5**, **6** and **7** in *ca.* 1:1:1 ratio. For phenyl- and phenoxyallene (**1e** and **f**), the reaction produces two stereoisomers *Z*- (**5**) and *E*-CHR=C(Ar)CH₂N₃ (**6**), where R = Ph and PhO; the regioisomer RCH(N₃)C(Ar)=CH₂ (**7**) was not observed. In contrast, carboazidation of *tert*-butylallene (**1g**) afforded regioisomer *t*-BuHC(N₃)C(Ar)=CH₂ as the major product (~90% yield). Based on known palladium-allene and -allyl chemistry, a mechanism is proposed to account for this palladium-catalyzed three-component assembling reaction.

Introduction

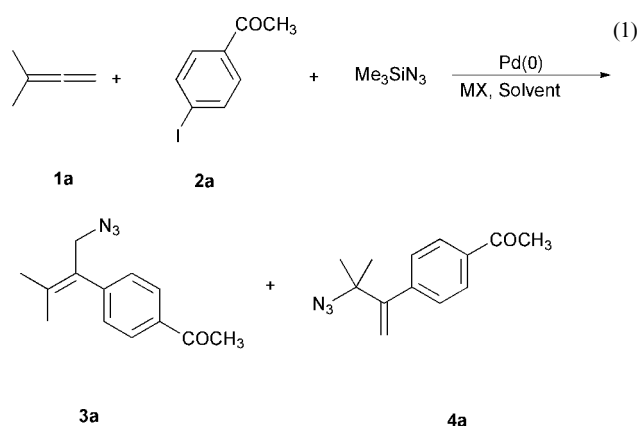
Allyl azides are versatile synthetic intermediates¹ used in 1,3-dipolar cycloaddition,² as precursors of nitrenes³ and particularly for conversion to allylamines.⁴ The latter have found increasing utility in enzyme inhibitors^{5–7} and are important synthetic intermediates of many natural products.⁸ Palladium complexes are employed as catalysts for the synthesis of tertiary allylamines from the corresponding allyl substrates.^{9–11} However, application of the same method to the synthesis of secondary and primary allylamines led to polyallylation and a mixture of primary, secondary and tertiary allylamines. Thus, the reduction of allyl azides to allylamines becomes an important route for the synthesis of primary allylamines. Palladium-catalyzed reactions for synthesis of allyl azides are known.^{12–16} Murahashi and his co-workers reported a palladium-mediated nucleophilic substitution of allyl acetates, phosphates and carbonates by sodium azide to give the corresponding allyl azides.¹² Similar reactions using various allyl substrates and trimethylsilyl azide were observed by Safi *et al.*¹³ Recently, an intramolecular cyclization-addition of an aryl to an allenyl group followed by azide ion attack to give allyl azides was reported by Grigg and his group.¹⁶ We have been interested in new palladium-catalyzed three-component assembling reactions of allenes.¹⁷ In this paper, we report an intermolecular carboazidation of allenes using aryl iodides and Me₃SiN₃ catalyzed by palladium complexes. The scope of the aryl iodides, stereo- and regiochemistry and mechanism of this three-component assembling reaction are described.

Results and discussion

Carboazidation of allenes catalyzed by palladium complexes

The three-component assembling reaction of 1,1-dimethylallene (**1a**), 4-iodoacetophenone (**2a**) and trimethylsilyl azide proceeds

smoothly in the presence of a suitable palladium complex and acetate ion to give two regioisomers of the corresponding allyl azide **3a** and **4a** [eqn. (1)]. No reaction occurs in the absence of



a palladium complex and only traces of **3a** and **4a** were detected without the addition of acetate ion. The use of sodium azide instead of trimethylsilyl azide also afforded the expected three-component assembling product, but the yield was lower than with trimethylsilyl azide and potassium acetate (Table 1, entry 27). The structures of **3a** and **4a** are characterized by their spectral data. The two regioisomers are distinguished by ¹H NMR spectroscopy (*vide infra*).

To optimize this palladium-catalyzed reaction, the effect of reaction conditions on the yield and regioselectivity of the product (**3a** and **4a**) from **1a**, **2a** and trimethylsilyl azide are examined. Table 1 summarizes the results of these studies. The yields of **3a** and **4a** are shown to depend strongly on the palladium catalyst, solvent, base, reaction time, reaction temperature, and amount of phosphine ligand employed. As

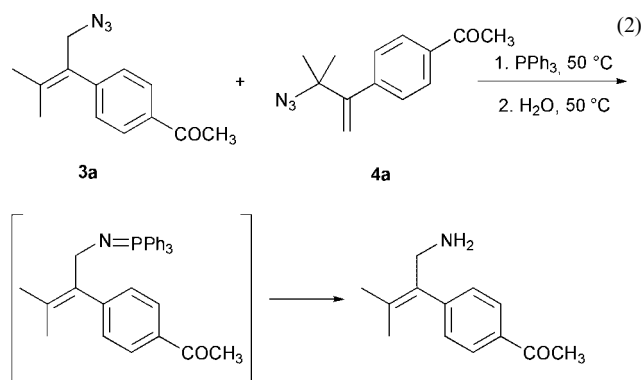
Table 1 Optimization of reaction conditions^a

Entry	Pd/PPh ₃	MX	Temp./°C	Solvent	Yield (%) ^b	3a:4a ^c
1	Pd(dba) ₂	KOAc	rt	DMF	18	84:16
2	Pd(dba) ₂	KOAc	50	DMF	75	82:18
3	Pd(dba) ₂	KOAc	70	DMF	>99	84:16
4	Pd(dba) ₂	KOAc	90	DMF	60	83:17
5	Pd(dba) ₂	—	70	DMF	6	81:19
6	Pd(dba) ₂ /1 PPh ₃	KOAc	70	DMF	94	85:15
7	Pd(dba) ₂ /2 PPh ₃	KOAc	70	DMF	88	85:15
8	Pd(dba) ₂ /3 PPh ₃	KOAc	70	DMF	80	85:15
9	Pd(dba) ₂ /4 PPh ₃	KOAc	70	DMF	67	84:16
10	PdCl ₂ (PPh ₃) ₂	KOAc	70	DMF	88	85:15
11	PdCl ₂ (dppe)	KOAc	70	DMF	26	84:16
12	PdCl ₂ (CH ₃ CN) ₂	KOAc	70	DMF	33	83:17
13	PdCl ₂ (PhCN) ₂	KOAc	70	DMF	13	83:17
14	Pd(OAc) ₂	KOAc	70	DMF	76	85:15
15	PdCl ₂	KOAc	70	DMF	44	84:16
16	Pd(dba) ₂	KOAc	70	DMA	>99	84:16
17	Pd(dba) ₂	KOAc	70	DMSO	84	83:17
18	Pd(dba) ₂	KOAc	70	Toluene	—	—
19	Pd(dba) ₂	KOAc	70	THF	4	69:31
20	Pd(dba) ₂	KOAc	70	CH ₃ CN	27	82:18
21	Pd(dba) ₂	KOAc	70	2-BuOH	10	81:19
22	Pd(dba) ₂	NaOAc	70	DMF	96	84:16
23	Pd(dba) ₂	LiOAc	70	DMF	94	83:17
24	Pd(dba) ₂	Bu ₄ NF	70	DMF	75	83:17
25	Pd(dba) ₂	Bu ₄ NOAc	70	DMF	90	84:16
26	Pd(dba) ₂	Zn(OAc) ₂	70	DMF	16	77:23
27	Pd(dba) ₂	NaN ₃	70	DMF	49	84:16
28	Pd(dba) ₂	LiCl	70	DMF	16	82:18

^a All reactions were carried out using 1,1-dimethylallene **1** (2.00 mmol), 4-iodoacetophenone **2a** (1.00 mmol), 5 mol% of Pd catalyst (0.0500 mmol), MX (1.60 mmol), trimethylsilyl azide (1.50 mmol) and solvent (2.0 mL); reaction time: 24 h. ^b Yields were determined by ¹H NMR. ^c The ratios were determined by ¹H NMR.

indicated in Table 1, optimal conditions for the catalytic reaction consist of 4-iodoacetophenone (**2a**) (1.0 mmol), 1,1-dimethylallene (**1a**) (2.0 mmol), Pd(dba)₂ (5.0 mol%), Me₃SiN₃ (1.5 mmol) and KOAc (1.5 mmol) in DMF (2 mL) at 70 °C for 24 h. Under these conditions, the total yield of **3a** and **4a** is essentially quantitative with a **3a**:**4a** ratio about 84:16. A number of palladium complexes are active in the present catalytic reaction. Excess triphenylphosphine inhibits this catalytic reaction. The total yield decreases with increasing PPh₃:Pd ratio (entries 6–9). The retardation of catalytic activity is even more prominent when the bidentate 1,2-bis(diphenylphosphino)ethane (dppe) ligand is employed (entry 11). The catalytic activity of palladium complexes for carboazidation follows the order Pd(dba)₂ > PdCl₂(PPh₃)₂ > Pd(OAc)₂ > PdCl₂ > PdCl₂(CH₃CN)₂ > PdCl₂(dppe) > PdCl₂(PhCN)₂. Pd(dba)₂ without phosphine ligands shows the best reactivity compared to other palladium catalyst systems (entry 3). The solvent used also greatly affects the total yield of the two products (entries 3, 16–20): the highest yield was observed in DMF and DMA. The presence of a metal salt in the catalytic reaction is crucial for the reaction to proceed smoothly. In the absence of an anion, the total yield of **3a** and **4a** is only 6% (entry 5). Of the salts used, metal acetates such as KOAc, NaOAc and LiOAc are most effective. The strong driving force of acetate ion in the present catalytic reaction is likely the formation of a stable silyl product Me₃SiOAc compared to the very reactive Me₃SiI in the absence of a metal salt.¹⁸ The optimal temperature for reaction 1 is around 70 °C. Raising or lowering the reaction temperature caused a reduction of the total yield (entries 1–4). Variation of reaction conditions exhibits a great effect on the total yield of **3a** and **4a**, but shows little influence on the ratio of these two regioisomers (*vide infra*). These observations can be understood in terms of the facile thermal 1,3-rearrangement of allyl azides.¹⁹ Evidence for the interconversion of **3a** and **4a** is the decrease in the **3a**:**4a** ratio as temperature increases. The observed ratios of **3a** and **4a** in Table 1 are likely close to the equilibrium values of these two

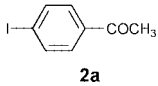
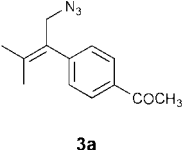
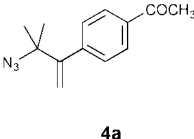
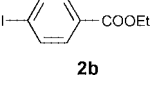
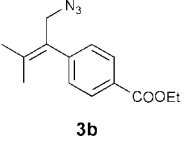
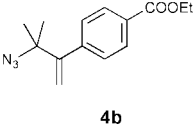
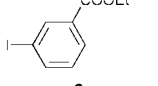
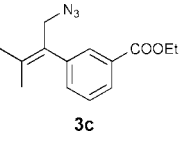
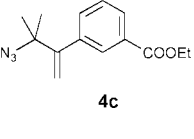
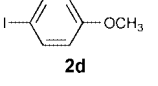
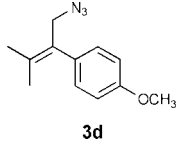
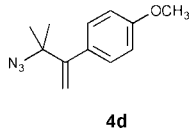
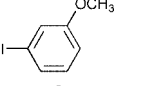
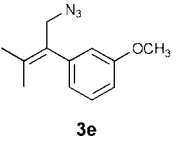
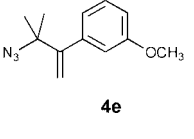
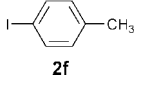
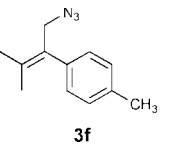
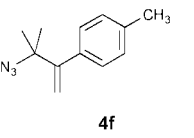
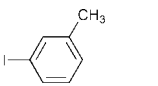
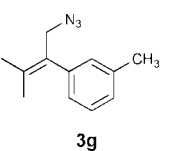
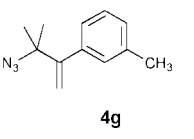
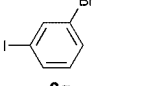
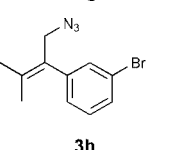
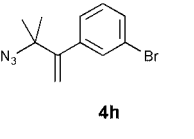
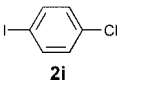
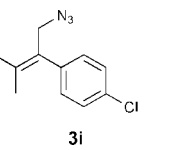
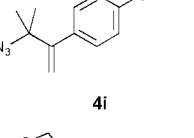
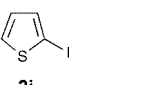
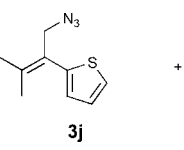
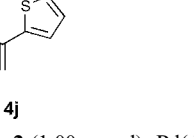
species at ambient temperature. The facile interconversion of **3a** and **4a** is further supported by the results of reduction of **3a** and **4a** (80:20) by PPh₃ and water in deuterated chloroform at 50 °C. The ¹H NMR spectrum of the resulting solution shows that only the amine with the amino group attached to the unsubstituted terminal carbon of the dimethylallene moiety was produced in 95% yield [eqn. (2)].



Carboazidation of 1,1-dimethylallene (**1a**) with other aryl iodides (**2**) and trimethylsilyl azide

Under similar reaction conditions, substituted aryl iodides, ethyl 4-iodobenzoate, ethyl 3-iodobenzoate, 3- and 4-iodoanisole, 3- and 4-iodotoluene, 1-bromo-3-iodobenzene, 1-chloro-4-iodobenzene and 2-iodothiophene react with 1,1-dimethylallene (**1a**) and trimethylsilyl azide in the presence of Pd(dba)₂ and KOAc to give the corresponding allyl azides in good to excellent yields. In all cases, two regioisomers **3** and **4** were observed with **3** as the major product. The observed ratios of **3**:**4** fall in the narrow range 88:12 to 80:20. The results of this carboazidation are summarized in Table 2. Fine tuning of the reaction conditions is required for each aryl iodide employed in order to achieve a high yield. The reaction of aryl

Table 2 Results of palladium-catalyzed carboazidation of 1,1-dimethylallene **1a** with aryl iodide **2** and trimethylsilyl azide^a

Entry	Ar-I	Allyl azide	Yield(%) ^b (ratio 3 : 4) ^c	
1	 2a	 3a	 4a	96 (84:16)
2	 2b	 3b	 4b	85 (82:18)
3	 2c	 3c	 4c	89 (83:17)
4 ^d	 2d	 3d	 4d	75 (86:14)
5 ^d	 2e	 3e	 4e	73 (81:19)
6 ^d	 2f	 3f	 4f	73 (88:12)
7 ^d	 2f	 3g	 4g	67 (80:20)
8	 2g	 3h	 4h	78 (84:16)
9	 2i	 3i	 4i	64 (82:18)
10	 2j	 3j	 4j	95 (73:27)

^a All reactions were carried out using 1,1-dimethylallene **1** (2.00 mmol), aryl iodide **2** (1.00 mmol), Pd(dba)₂ (0.0500 mmol), KOAc (1.50 mmol), Me₃SiN₃ (1.50 mmol) and DMF (2.0 mL) at 75 °C for 24 h. ^b Isolated yields. ^c The ratios were determined by ¹H NMR. ^d 48 h.

iodides bearing an electron-donating group such as 4- and 3-iodoanisole and 4- and 3-iodotoluene required 80 °C and 48 h in DMF to afford the best yields, whereas for aryl iodides with an electron-withdrawing substituent optimal yields were obtained at 70 °C for 24 h. In general, aryl iodides with an electron-withdrawing substituent give higher product yields than those bearing an electron-donating group. However, 1-iodo-4-nitrobenzene afforded only the direct coupling

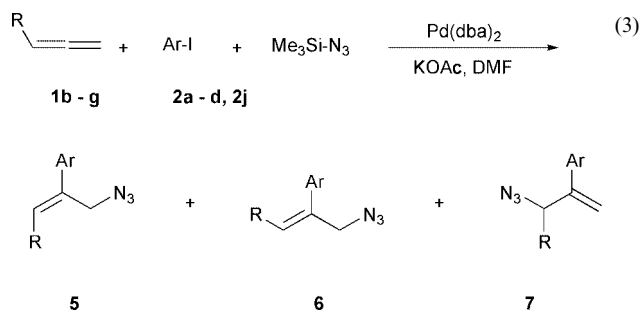
product 1-azido-4-nitrobenzene suggesting insertion of 1,1-dimethylallene (**1a**) into the Pd–aryl bond is slow relative to direct coupling of Pd–aryl species with trimethylsilyl azide. The position of substituents on aryl iodides shows a significant influence on the product yield. Under similar reaction conditions, 4- and 3-iodoanisole and 4- and 3-iodotoluene react smoothly to yield the expected products, but 2-iodoanisole and 2-iodotoluene give no three-component assembling products.

All products **3** show a characteristic singlet in the region δ 4.0–4.2 ppm for the two allylic protons and two singlets at 2.0–1.6 ppm for the two methyl groups in the ^1H NMR spectra. On the other hand, products **4** exhibit characteristic singlets at 5.4–5.1 ppm for the two terminal olefin protons and a singlet at 1.40 ppm for the two methyl groups. In the IR spectra, both products **3** and **4** exhibit absorption at about 2100 cm^{-1} for the azido group. The exact molecular masses of these products determined by a high-resolution mass spectrometer are also in agreement with the proposed structures.

Aryl bromides and aryl chlorides undergo three-component assembling reactions with 1,1-dimethylallene (**1a**) and trimethylsilyl azide very slowly. The reaction of 1-bromo-3-iodobenzene (**2h**) with 1,1-dimethylallene (**1a**) gave only 2-(3-bromophenyl)-3-methylbut-2-enyl azide (**3h**) and 2-(3-bromophenyl)-1,1-dimethylallyl azide (**4h**). This result suggests that only the C–I bond in 1-bromo-3-iodobenzene undergoes oxidative addition to the palladium center. Under similar reaction conditions, vinylic iodides including ethyl *cis*-3-iodoacrylate and 3-iodo-5,5-dimethylcyclohex-2-en-1-one also failed to react with 1,1-dimethylallene (**1a**) and potassium acetate to afford three-component assembling products.

Carboazidation of monosubstituted allenes

Phenylallene (**1e**) and phenoxyallene (**1f**) undergo three-component assembling with aryl iodides and trimethylsilyl azide in the presence of KOAc and Pd(dba)₂ [eqn. (3)]. The



reaction is completely regioselective with the azide anion adding only to the terminal carbon of the allene moiety and giving stereoisomers **5** and **6** (Table 3, entries 10–13). Regioisomer **7** obtained from attack of the azide ion at the carbon at which the phenyl group is attached was not observed. The three-component assembling reactions of *n*-butylallene (**1b**), cyclopentylallene (**1c**) and cyclohexylallene (**1d**), give both regio and stereoisomers **5**, **6** and **7** in nearly a 1:1:1 ratio. Interconversion of isomers **5**, **6** and **7** also occurs and the observed 1:1:1 ratio appears to reveal a thermodynamic ratio of these regio- and stereoisomers. The original regio and stereoselectivity of this palladium-catalyzed three-component assembling is no longer discernible due to the 1,3-azido group shift.

Unlike other allenes, *tert*-butylallene (**1g**) is less reactive and requires a higher reaction temperature, 85 °C, and 60 h for the three-component reaction to proceed smoothly. Although the reaction also affords three isomers, the major product is regioisomer **7** with the azide ion attacking at the carbon at which the *tert*-butyl group is attached (Table 3, entries 14–17). For the reactions with 4-iodoacetophenone, ethyl 3-iodobenzoate, ethyl 4-iodobenzoate, and 2-iodothiophene, *ca.* 90% of isolated products corresponds to regioisomer **7**. The reason for the unusual regioselectivity of *tert*-butylallene (**1g**) is unclear.

The stereochemistry of **5** and **6** was determined using typical ^1H NMR NOE techniques. For example, there are three isomers **5a**, **6a** and **7a** isolated from the carboazidation of *n*-butylallene (**1b**) with ethyl 4-iodobenzoate (**2b**) and trimethylsilyl azide. Regioisomer **7a**, obtained from attack of azide ion at the carbon at which the *n*-butyl group is attached, exhibits ^1H NMR signals at 5.50 and 5.39 ppm for the two olefin protons

Table 3 Reactions of allenes **1b–g** with aryl iodide **2** and Me₃SiN₃ in the presence of Pd(dba)₂ and KOAc^a

Entry	Allene 1	Ar-I 2	Yield (%) ^b	5 : 6 : 7 ^c
1		1b 2b	96	5a : 6a : 7a 38:31:31
2		1b 2c	95	5b : 6b : 7b 35:33:32
3		1c 2a	95	5c : 6c : 7c 37:29:34
4		1c 2b	94	5d : 6d : 7d 33:32:35
5		1c 2c	96	5e : 6e : 7e 33:33:34
6 ^d		1c 2d	90	5f : 6f : 7f 31:26:43
7		1d 2a	92	5g : 6g : 7g 43:31:26
8		1d 2b	83	5h : 6h : 7h 43:30:27
9		1d 2c	62	5i : 6i : 7i 40:34:26
10		1e 2a	86	5j : 6j : 7j 56:44:—
11		1e 2b	93	5k : 6k : 7k 55:45:—
12		1e 2c	89	5l : 6l : 7l 60:40:—
13		1f 2a	62	5m : 6m : 7m 65:35:—
14 ^e		1g 2a	57	5n : 6n : 7n 5:3:92
15 ^e		1g 2b	64	5o : 6o : 7o 7:4:89
16 ^e		1g 2c	55	5p : 6p : 7p 8:5:87
17 ^e		1g 2j	54	5q : 6q : 7q 3:2:95

^a All reactions were carried out using an allene (2.00 mmol), aryl iodide **2** (1.00 mmol), Pd(dba)₂ (0.0500 mmol), KOAc (1.50 mmol), Me₃SiN₃ (1.50 mmol) and DMF (2.0 mL) at 75 °C for 24 h. ^b Isolated yields. ^c The ratios were determined by ^1H NMR. ^d 48 h. ^e At 85 °C for 60 h.

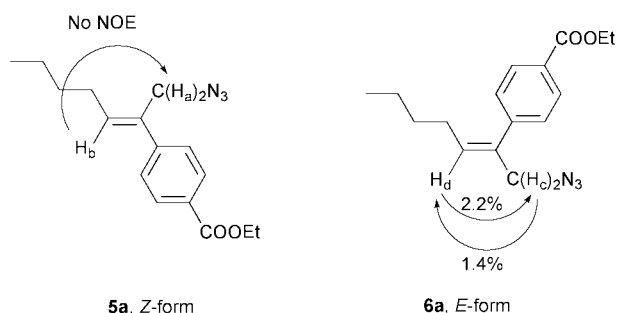
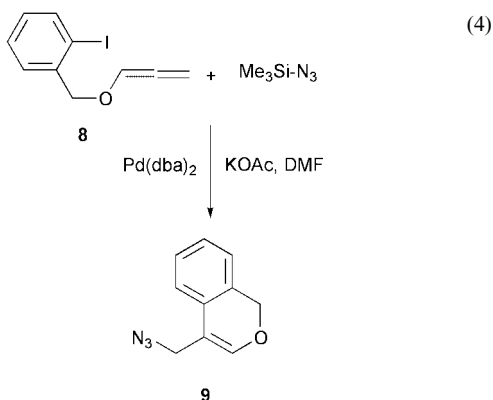


Fig. 1

and at 4.23 ppm for the methine proton. The other two isomers **5a** and **6a** are stereoisomers; **5a** exhibits ^1H NMR signals at 4.21 and 6.20 ppm for the methylene (H_a) and olefin proton (H_b), respectively. Irradiation at H_a and H_b signals showed essentially no change of the intensity of H_b and H_a signals, respectively (Fig. 1). The other stereoisomer **6a** exhibits ^1H NMR signals at 3.98 and 5.79 ppm for the methylene (H_c) and olefin proton (H_d), respectively. In contrast to the results of isomer **5a**, irradiation at the H_c signal led to an increase of the intensity of H_d by 1.4% and irradiation at the H_d signal resulted in an increase of the intensity of H_c by 2.2%. These NOE results clearly show the product **5a** is a *Z*-form isomer, while **6a** is an *E*-form product.

Palladium-catalyzed carboannulation and azidation of allenes

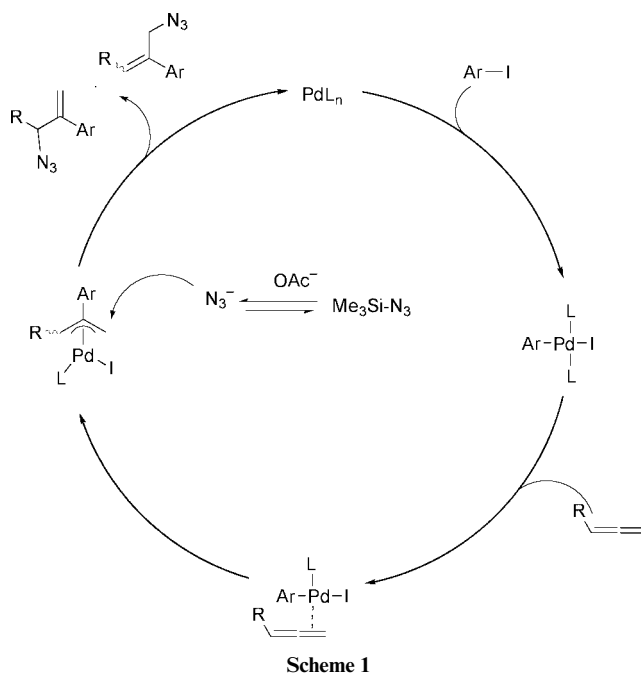
Under similar reaction conditions for the intermolecular carboazidation of allenes, compound **8** undergoes carboannulation and then azidation with trimethylsilyl azide to give product **9** in 88% yield [eqn. (4)]. No other regioisomer was observed in this



reaction. The product was prepared by Grigg *et al.* using the same substrate and sodium azide.¹⁶ A much higher yield was obtained by our method.

Proposed mechanism for carboazidation

Based on known palladium chemistry, we propose the catalytic cycle as illustrated in Scheme 1 to account for the present



palladium-catalyzed carboazidation. Formation of a Pd(II)-aryl intermediate from oxidative addition of aryl iodide to Pd(0), and coordination of allene to the palladium center followed by migration of the aryl group to the central carbon of allene gives a π -allylpalladium intermediate. Nucleophilic attack of azide ion released from gradual reaction of trimethylsilyl azide with acetate ion at the π -allylpalladium intermediate provides the final products and regenerates the Pd(0) species. Oxidative addition of aryl iodides to palladium(0) species,²⁰ and insertion of allene in the palladium(II)-aryl bond to give a π -allylpalladium species are demonstrated in many palladium-mediated reactions.²¹ In addition, direct attack (*trans* attack) of azide ion at π -allylpalladium intermediates was established by Murahashi and his co-workers.¹²

Conclusion

The present palladium-catalyzed carboazidation provides an efficient method for the assembling of allenes, aryl iodides and Me_3SiN_3 to give the corresponding allyl azides. Regio- and stereoisomers of the allyl azide were observed in each reaction. For most allyl azides prepared by the present method, the ratio of the isomers is likely close to equilibrium values of these isomers due to a rapid 1,3-shift of the azido group. In agreement with this rapid 1,3-shift, reduction of a mixture of regioisomers **3a** and **4a** by $\text{PPh}_3:\text{H}_2\text{O}$ gave solely allyl amines with the amino group attached to the unsubstituted terminal carbon of the allene moiety. For *tert*-butyllallene, the allyl azide products show high regioselectivity at the substituted allene carbon, completely different from the trend of other allenes used in the present work. Detailed investigation of the mechanism in order to understand these interesting observations is in progress.

Experimental

All reactions were carried out under a nitrogen atmosphere in oven-dried glassware unless otherwise mentioned. All solvents were dried according to known methods and distilled prior to use. $\text{PdCl}_2(\text{PPh}_3)_2$,²² $\text{PdCl}_2(\text{dppe})$,²³ $\text{PdCl}_2(\text{CH}_3\text{CN})_2$,²³ $\text{PdCl}_2(\text{PhCN})_2$,²³ $\text{Pd}(\text{dba})_2$,²⁴ 1,1-dimethylallene,²⁵ *n*-butyllallene,²⁶ cyclopentyllallene,²⁶ cyclohexyllallene,²⁶ *tert*-butyllallene,²⁶ phenyllallene,²⁶ phenoxyallene,²⁶ and 1-iodo-2-[(propa-1,2-dienyloxy)methyl]benzene²⁷ were prepared according to procedures previously reported. Other reagents were commercially available and used as purchased. The purity of each product was checked by NMR analysis.

Effect of reaction conditions on carboazidation of 1,1-dimethylallene and 4-iodoacetophenone

A mixture of palladium catalyst (0.00500 mmol), a ligand, Me_3SiN_3 (0.182 g, 1.50 mmol), 4-iodoacetophenone (0.250 g, 1.00 mmol), 1,1-dimethylallene (2.00 mmol), a base (1.60 mmol) and solvent (2.0 mL) was stirred at a temperature between 25 and 90 °C for 24 h under nitrogen. At the end of the reaction, the solution was diluted with ether (50 mL) and extracted with ether and water. The organic layer was collected and dried over MgSO_4 and the solvent was removed by a rotary evaporator. The yield and ratio of allylic azides were determined by ^1H NMR analysis using mesitylene as internal standard. The results for the carboazidation are listed in Table 1.

General procedure for carboazidation of allenes with aryl iodides and trimethylsilyl azide

A 25 mL round-bottomed flask containing $\text{Pd}(\text{dba})_2$ (0.0287 g, 0.0500 mmol), an aryl iodide (1.00 mmol) and potassium acetate (1.50 mmol) was purged with nitrogen gas several times. To the flask were then added DMF (2.0 mL), an allene (1.50 mmol) and Me_3SiN_3 (0.182 g, 1.50 mmol). The reaction mixture was heated with stirring at 70 or 80 °C for 24–48 h. As the reaction approached completion, a black precipitate of palladium metal surrounding the wall of the flask appeared gradually. At the end of the reaction, the solution was diluted with ether (50 mL) and extracted with ether and water. The organic layer was collected and dried over MgSO_4 . After removal of the solvent on a rotary evaporator, the residue was separated on a silica gel column to give the desired allylic azide as a yellow liquid.

Compounds **3a–j**, **4a–j**, **5a–m**, **6a–m**, and **7a–i** were prepared according to this method. Product yields of these reactions are listed in Table 2 and 3, while spectral data are shown below.

Carboazidation of 1,1-dimethylallene (1a) with 4-iodoacetophenone (2a) and Me_3SiN_3 . The product mixture was separated on a silica gel column using a mixture of ethyl acetate–hexane

(1:30) as eluent to give isomers **3a** and **4a** in a 84:16 ratio as determined by ^1H NMR analysis. ^1H NMR (400 MHz, CDCl_3) **3a**: δ 7.93 (d, $J = 8$ Hz, 2 H), 7.25 (d, $J = 8$ Hz, 2 H), 4.08 (s, 2 H, CH_2N_3), 2.59 (s, 3 H), 1.94 (s, 3 H), 1.67 (s, 3 H); **4a**: (d, $J = 8$ Hz, 2 H), 7.38 (d, $J = 8$ Hz, 2 H), 5.46 (s, 1 H, CH=), 5.19 (s, 1 H, CH=), 2.59 (s, 3 H), 1.40 (s, 6 H); IR (neat) 2100 cm^{-1} ; HRMS calcd for $\text{C}_{13}\text{H}_{15}\text{N}_3\text{O}$ 229.1215, found 229.1215.

Carboazidation of 1,1-dimethylallene (1a) with ethyl 4-iodobenzoate (2b) and Me_3SiN_3 . Products **3b** and **4b** in a 82:18 ratio were obtained after separation of the reaction mixture on a silica gel column using a mixture of ethyl acetate–hexane (1:50) as eluent. ^1H NMR (400 MHz, CDCl_3) **3b**: δ 8.01 (d, $J = 8.4$ Hz, 2 H), 7.22 (d, $J = 8.4$ Hz, 2 H), 4.36 (q, $J = 7.2$ Hz, 2 H), 4.08 (s, 2 H, CH_2N_3), 1.93 (s, 3 H), 1.66 (s, 3 H), 1.38 (t, $J = 7.2$ Hz, 3 H); **4b**: δ 8.00 (d, $J = 8.4$ Hz, 2 H), 7.38 (d, $J = 8.4$ Hz, 2 H), 5.45 (s, 1 H, CH=), 5.18 (s, 1 H, CH=), 4.35 (q, $J = 7.2$ Hz, 2 H), 1.39 (s, 6 H), 1.37 (t, $J = 7.2$ Hz, 3 H); IR (neat) 2100 cm^{-1} ; HRMS calcd for $\text{C}_{14}\text{H}_{17}\text{N}_3\text{O}_2$ 259.1321, found 259.1321.

Carboazidation of 1,1-dimethylallene (1a) with ethyl 3-iodobenzoate (2c) and Me_3SiN_3 . Products **3c** and **4c** in a 83:17 ratio were obtained after separation of the reaction mixture on a silica gel column using a mixture of ethyl acetate–hexane (1:50) as eluent. ^1H NMR (400 MHz, CDCl_3) **3c**: δ 8.00–7.30 (m, 4 H), 4.42–4.35 (m, 2 H), 4.09 (s, 2 H, CH_2N_3), 1.93 (s, 3 H), 1.65 (s, 3 H), 1.45–1.36 (m, 3 H); **4c**: δ 8.00–7.30 (m, 4 H), 5.45 (s, 1 H, CH=), 5.17 (s, 1 H, CH=), 4.42–4.35 (m, 2 H), 1.45–1.36 (m, 3 H), 1.40 (s, 6 H); IR (neat) 2099 cm^{-1} ; HRMS calcd for $\text{C}_{14}\text{H}_{17}\text{N}_3\text{O}_2$ 259.1321, found 259.1328.

Carboazidation of 1,1-dimethylallene (1a) with 4-iodoanisole (2d) and Me_3SiN_3 . A mixture of **3d** and **4d** was obtained after separation of the reaction mixture on a silica gel column using a mixture of ethyl acetate–hexane (1:50) as eluent. ^1H NMR (400 MHz, CDCl_3) **3d**: δ 7.07 (d, $J = 8.8$ Hz, 2 H), 6.87 (d, $J = 8.8$ Hz, 2 H), 4.05 (s, 2 H, CH_2N_3), 3.80 (s, 3 H), 1.90 (s, 3 H), 1.67 (s, 3 H); **4d**: δ 7.21 (d, $J = 8.8$ Hz, 2 H), 6.84 (d, $J = 8.8$ Hz, 2 H), 5.35 (s, 1 H, CH=), 5.12 (s, 1 H, CH=), 3.80 (s, 3 H), 1.39 (s, 6 H); IR (neat) 2098 cm^{-1} ; HRMS calcd for $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}$ 217.1215, found 217.1216.

Carboazidation of 1,1-dimethylallene (1a) with 3-iodoanisole (2e) and Me_3SiN_3 . A mixture of **3e** and **4e** was obtained from the reaction after separation on a silica gel column using a mixture of ethyl acetate–hexane (1:50) as eluent. ^1H NMR (400 MHz, CDCl_3) **3e**: δ 7.24 (s, 1 H), 6.95–6.66 (m, 3 H), 4.05 (s, 2 H, CH_2N_3), 3.79 (s, 3 H), 1.91 (s, 3 H), 1.67 (s, 3 H); **4e**: δ 7.24 (s, 1 H), 6.95–6.66 (m, 3 H), 5.40 (s, 1 H, CH=), 5.08 (s, 1 H, CH=), 3.80 (s, 3 H), 1.40 (s, 6 H); IR (neat) 2098 cm^{-1} ; HRMS calcd for $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}$ 217.1215, found 217.1216.

Carboazidation of 1,1-dimethylallene (1a) with 4-iodotoluene (2f) and Me_3SiN_3 . A mixture of **3f** and **4f** was obtained from the reaction after separation on a silica gel column using a mixture of ethyl acetate–hexane (1:50) as eluent. ^1H NMR (400 MHz, CDCl_3) **3f**: δ 7.18–7.01 (m, 4 H), 4.06 (s, 2 H, CH_2N_3), 2.33 (s, 3 H), 1.91 (s, 3 H), 1.67 (s, 3 H); **4f**: δ 7.18–7.01 (m, 4 H), 5.37 (s, 1 H, CH=), 5.12 (s, 1 H, CH=), 2.33 (s, 3 H), 1.39 (s, 6 H); IR (neat) 2099 cm^{-1} ; HRMS calcd for $\text{C}_{12}\text{H}_{15}\text{N}_3$ 201.1266, found 201.1266.

Carboazidation of 1,1-dimethylallene (1a) with 3-iodotoluene (2g) and Me_3SiN_3 . A mixture of **3g** and **4g** was obtained from the reaction after separation on a silica gel column using a mixture of ethyl acetate–hexane (1:50) as eluent. ^1H NMR (400 MHz, CDCl_3) **3g**: δ 7.24–6.92 (m, 4 H), 4.06 (s, 2 H, CH_2N_3), 2.34 (s, 3 H), 1.91 (s, 3 H), 1.66 (s, 3 H); **4g**: δ 7.24–6.92 (m, 4 H), 5.38 (s, 1 H, CH=), 5.12 (s, 1 H, CH=), 2.34 (s, 3 H), 1.39 (s, 6 H); IR (neat) 2099 cm^{-1} ; HRMS calcd for $\text{C}_{12}\text{H}_{15}\text{N}_3$ 201.1266, found 201.1269.

Carboazidation of 1,1-dimethylallene (1a) with 1-bromo-3-iodotoluene (2h) and Me_3SiN_3 . A mixture of **3h** and **4h** was obtained from the reaction after separation on a silica gel column using a mixture of ethyl acetate–hexane (1:50) as eluent. ^1H NMR (400 MHz, CDCl_3) **3h**: δ 7.44–7.05 (m, 4 H), 4.04 (s, 2 H, CH_2N_3), 1.91 (s, 3 H), 1.66 (s, 3 H); **4h**: δ 7.44–7.05 (m, 4 H), 5.42 (s, 1 H, CH=), 5.15 (s, 1 H, CH=), 1.39 (s, 6 H); IR (neat) 2097 cm^{-1} ; HRMS calcd for $\text{C}_{11}\text{H}_{12}\text{BrN}_3$ 265.0215, found 265.0219.

Carboazidation of 1,1-dimethylallene (1a) with 1-chloro-4-iodobenzene (2i) and Me_3SiN_3 . A mixture of **3i** and **4i** was obtained from the reaction after separation on a silica gel column using a mixture of ethyl acetate–hexane (1:50) as eluent. ^1H NMR (400 MHz, CDCl_3) **3i**: δ 7.33–7.05 (m, 4 H), 4.04 (s, 2 H, CH_2N_3), 1.91 (s, 3 H), 1.65 (s, 3 H); **4i**: δ 7.33–7.05 (m, 4 H), 5.40 (s, 1 H, CH=), 5.14 (s, 1 H, CH=), 1.38 (s, 6 H); IR (neat) 2099 cm^{-1} ; HRMS calcd for $\text{C}_{11}\text{H}_{12}\text{ClN}_3$ 221.0720, found 221.0739.

Carboazidation of 1,1-dimethylallene (1a) with 2-iodothiophene (2j) and Me_3SiN_3 . A mixture of **3j** and **4j** was obtained from the reaction after separation on a silica gel column using a mixture of ethyl acetate–hexane (1:50) as eluent. ^1H NMR (400 MHz, CDCl_3) **3j**: δ 7.27–6.85 (m, 4 H), 4.08 (s, 2 H, CH_2N_3), 1.94 (s, 3 H), 1.85 (s, 3 H); **4j**: δ 7.27–6.85 (m, 4 H), 5.46 (s, 1 H, CH=), 5.32 (s, 1 H, CH=), 1.48 (s, 6 H); IR (neat) 2098 cm^{-1} ; HRMS calcd for $\text{C}_9\text{H}_{11}\text{N}_3\text{S}$ 193.0674, found 193.0676.

Carboazidation of *n*-butylallene (1b) with ethyl 4-iodobenzoate (2b) and Me_3SiN_3 . A mixture of **5a**, **6a** and **7a** was obtained from the reaction after separation on a silica gel column using a mixture of ethyl acetate–hexane (1:50) as eluent. ^1H NMR (400 MHz, CDCl_3) **5a**: δ 8.08–7.24 (m, 4 H), 6.20 (t, $J = 7.6$ Hz, 1 H, CH=), 4.40–4.35 (m, 2 H), 4.21 (s, 2 H, CH_2N_3), 2.35 (q, $J = 7.6$ Hz, 2 H), 1.60–0.78 (m, 10 H); **6a**: δ 8.08–7.24 (m, 4 H), 5.79 (t, $J = 7.4$ Hz, 1 H, CH=), 4.40–4.35 (m, 2 H), 3.98 (s, 2 H, CH_2N_3), 2.01 (q, $J = 7.4$ Hz, 2 H), 1.60–0.78 (m, 10 H); **7a**: δ 8.08–7.24 (m, 4 H), 5.50 (s, 1 H, CH=), 5.39 (s, 1 H, CH=), 4.40–4.35 (m, 2 H, OCH_2), 4.26 (t, $J = 7$ Hz, 1 H, CHN_3), 1.60–0.78 (m, 12 H); IR (neat) 2098 cm^{-1} ; HRMS calcd for $\text{C}_{16}\text{H}_{21}\text{N}_3\text{O}_2$ 287.1634, found 287.1633.

Carboazidation of *n*-butylallene (1b) with ethyl 3-iodobenzoate (2c) and Me_3SiN_3 . A mixture of **5b**, **6b** and **7b** was obtained from the reaction after separation on a silica gel column using a mixture of ethyl acetate–hexane (1:50) as eluent. ^1H NMR (400 MHz, CDCl_3) **5b**: δ 8.08–7.13 (m, 4 H), 6.14 (t, $J = 7.6$ Hz, 1 H, CH=), 4.42–4.32 (m, 2 H), 4.23 (s, 2 H, CH_2N_3), 2.29 (q, $J = 7.6$, 2 H), 1.62–0.79 (m, 10 H); **6b**: δ 8.08–7.13 (m, 4 H), 5.79 (t, $J = 7.2$ Hz, 1 H, CH=), 4.42–4.32 (m, 2 H), 3.99 (s, 2 H, CH_2N_3), 2.01 (q, $J = 7.2$, 2 H), 1.62–0.79 (m, 10 H); **7b**: δ 8.08–7.13 (m, 4 H), 5.48 (s, 1 H, CH=), 5.37 (s, 1 H, CH=), 4.42–4.32 (m, 2 H), 4.27 (t, $J = 7$ Hz, 1 H, CHN_3), 1.62–0.79 (m, 12 H); IR (neat) 2099 cm^{-1} ; HRMS calcd for $\text{C}_{16}\text{H}_{21}\text{N}_3\text{O}_2$ 287.1634, found 287.1635.

Carboazidation of cyclopentylallene (1c) with 4-iodoacetophenone (2a) and Me_3SiN_3 . A mixture of **5c**, **6c** and **7c** was obtained from the reaction after separation on a silica gel column using a mixture of ethyl acetate–hexane (1:30) as eluent. ^1H NMR (400 MHz, CDCl_3) **5c**: δ 7.97–7.30 (m, 4 H), 6.13 (d, $J = 9.6$ Hz, 1 H, CH=), 4.22 (s, 2 H, CH_2N_3), 2.58 (s, 3 H), 2.45–1.05 (m, 9 H, C_5H_9); **6c**: δ 7.97–7.30 (m, 4 H), 5.70 (d, $J = 10$ Hz, 1 H, CH=), 3.97 (s, 2 H, CH_2N_3), 2.59 (s, 3 H), 2.45–1.05 (m, 9 H, C_5H_9); **7c**: δ 7.97–7.30 (m, 4 H), 5.51 (s, 1 H, CH=), 5.38 (s, 1 H, CH=), 4.00 (d, $J = 9.6$ Hz, 1 H, CHN_3), 2.60 (s, 3 H), 2.45–1.05 (m, 9 H, C_5H_9); IR (neat) 2097 cm^{-1} ; HRMS calcd for $\text{C}_{16}\text{H}_{19}\text{N}_3\text{O}$ 269.1529, found 269.1531.

Carboazidation of cyclopentylallene (1c) with ethyl 4-iodobenzoate (2b) and Me₃SiN₃. A mixture of **5d**, **6d** and **7d** was obtained from the reaction after separation on a silica gel column using a mixture of ethyl acetate–hexane (1:50) as eluent. ¹H NMR (400 MHz, CDCl₃) **5d**: δ 8.05–7.26 (m, 4 H), 6.11 (d, *J* = 10 Hz, 1 H, CH=), 4.43–4.30 (m, 2 H), 4.21 (s, 2 H, CH₂N₃), 2.88–1.05 (m, 12 H); **6d**: δ 8.05–7.26 (m, 4 H), 5.69 (d, *J* = 10 Hz, 1 H, CH=), 4.43–4.30 (m, 2 H), 3.97 (s, 2 H, CH₂N₃), 2.88–1.05 (m, 12 H); **7d**: δ 8.05–7.26 (m, 4 H), 5.49 (s, 1 H, CH=), 5.36 (s, 1 H, CH=), 4.43–4.30 (m, 2 H), 4.01 (d, *J* = 10.4 Hz, 1 H, CHN₃), 2.88–1.05 (m, 14 H); IR (neat) 2098 cm⁻¹; HRMS calcd for C₁₇H₂₁N₃O₂ 299.1634, found 299.1638.

Carboazidation of cyclopentylallene (1c) with ethyl 3-iodobenzoate (2c) and Me₃SiN₃. A mixture of **5e**, **6e** and **7e** was obtained from the reaction after separation on a silica gel column using a mixture of ethyl acetate–hexane (1:50) as eluent. ¹H NMR (400 MHz, CDCl₃) **5e**: δ 8.05–7.37 (m, 4 H), 6.06 (d, *J* = 9.6 Hz, 1 H, CH=), 4.41–4.25 (m, 2 H), 4.23 (s, 2 H, CH₂N₃), 2.95–1.04 (m, 12 H); **6e**: δ 8.05–7.37 (m, 4 H), 5.69 (d, *J* = 10.4 Hz, 1 H, CH=), 4.41–4.25 (m, 2 H), 3.98 (s, 2 H, CH₂N₃), 2.95–1.04 (m, 12 H); **7e**: δ 8.05–7.37 (m, 4 H), 5.47 (s, 1 H, CH=), 5.34 (s, 1 H, CH=), 4.41–4.25 (m, 2 H), 4.02 (d, *J* = 9.6 Hz, 1 H, CHN₃), 2.95–1.04 (m, 14 H); IR (neat) 2099 cm⁻¹; HRMS calcd for C₁₇H₂₁N₃O₂ 299.1634, found 299.1635.

Carboazidation of cyclopentylallene (1c) with 4-iodoanisole (2d) and Me₃SiN₃. A mixture of **5f**, **6f** and **7f** was obtained from the reaction after separation on a silica gel column using a mixture of ethyl acetate–hexane (1:75) as eluent. ¹H NMR (400 MHz, CDCl₃) **5f**: δ 7.39–6.80 (m, 4 H), 5.91 (d, *J* = 10 Hz, 1 H, CH=), 4.17 (s, 2 H, CH₂N₃), 3.80 (s, 3 H), 2.92–1.03 (m, 9 H, C₅H₉); **6f**: δ 7.39–6.80 (m, 4 H), 5.59 (d, *J* = 9.6 Hz, 1 H, CH=), 3.93 (s, 2 H, CH₂N₃), 3.80 (s, 3 H), 2.92–1.03 (m, 9 H, C₅H₉); **7f**: δ 7.39–6.80 (m, 4 H), 5.36 (s, 1 H, CH=), 5.20 (s, 1 H, CH=), 3.97 (d, *J* = 9.6 Hz, 1 H, CHN₃), 3.79 (s, 3 H), 2.92–1.03 (m, 9 H, C₅H₉); IR (neat) 2097 cm⁻¹; HRMS calcd for C₁₅H₁₉N₃O 257.1528, found 257.1528.

Carboazidation of cyclohexylallene (1d) with 4-iodoacetophenone (2a) and Me₃SiN₃. A mixture of **5g**, **6g** and **7g** was obtained from the reaction after separation on a silica gel column using a mixture of ethyl acetate–hexane (1:30) as eluent. ¹H NMR (400 MHz, CDCl₃) **5g**: δ 7.95–7.25 (m, 4 H), 6.04 (d, *J* = 10 Hz, 1 H, CH=), 4.22 (s, 2 H, CH₂N₃), 2.59 (s, 3 H), 2.45–0.82 (m, 11 H, C₆H₁₁); **6g**: δ 7.95–7.25 (m, 4 H), 5.61 (d, *J* = 10.4 Hz, 1 H, CH=), 3.94 (s, 2 H, CH₂N₃), 2.60 (s, 3 H), 2.45–0.82 (m, 11 H, C₆H₁₁); **7g**: δ 7.95–7.25 (m, 4 H), 5.53 (s, 1 H, CH=), 5.36 (s, 1 H, CH=), 4.02 (d, *J* = 8.4 Hz, 1 H, CHN₃), 2.61 (s, 3 H), 2.45–0.82 (m, 11 H, C₆H₁₁); IR (neat) 2098 cm⁻¹; HRMS calcd for C₁₇H₂₁N₃O 283.1685, found 283.1683.

Carboazidation of cyclohexylallene (1d) with ethyl 4-iodobenzoate (2b) and Me₃SiN₃. A mixture of **5h**, **6h** and **7h** was obtained from the reaction after separation on a silica gel column using a mixture of ethyl acetate–hexane (1:50) as eluent. ¹H NMR (400 MHz, CDCl₃) **5h**: δ 8.05–7.24 (m, 4 H), 6.02 (d, *J* = 10 Hz, 1 H, CH=), 4.40–4.31 (m, 2 H), 4.21 (s, 2 H, CH₂N₃), 2.43–0.84 (m, 14 H); **6h**: δ 8.05–7.24 (m, 4 H), 5.60 (d, *J* = 9.6 Hz, 1 H, CH=), 4.40–4.31 (m, 2 H), 3.93 (s, 2 H, CH₂N₃), 2.43–0.84 (m, 14 H); **7h**: δ 8.05–7.24 (m, 4 H), 5.50 (s, 1 H, CH=), 5.34 (s, 1 H, CH=), 4.40–4.31 (m, 2 H), 4.02 (d, *J* = 8.4 Hz, 1 H, CHN₃), 2.43–0.84 (m, 14 H); IR (neat) 2099 cm⁻¹; HRMS calcd for C₁₈H₂₃N₃O₂ 313.1790, found 313.1798.

Carboazidation of cyclohexylallene (1d) with ethyl 3-iodobenzoate (2c) and Me₃SiN₃. A mixture of products isomers **5i**, **6i** and **7i** was obtained from the reaction after separation on a silica gel column using a mixture of ethyl acetate–hexane (1:50) as eluent. ¹H NMR (400 MHz, CDCl₃) **5i**: δ 8.38–7.13 (m, 4 H),

5.96 (d, *J* = 10 Hz, 1 H, CH=), 4.41–4.32 (m, 2 H), 4.23 (s, 2 H, CH₂N₃), 2.43–0.95 (m, 14 H); **6i**: δ 8.38–7.13 (m, 4 H), 5.60 (d, *J* = 9.6 Hz, 1 H, CH=), 4.41–4.32 (m, 2 H), 3.95 (s, 2 H, CH₂N₃), 2.43–0.95 (m, 14 H); **7i**: δ 8.38–7.13 (m, 4 H), 5.50 (s, 1 H, CH=), 5.32 (s, 1 H, CH=), 4.41–4.32 (m, 2 H), 4.03 (d, *J* = 8.4 Hz, 1 H, CHN₃), 2.43–0.95 (m, 14 H); IR (neat) 2098 cm⁻¹; HRMS calcd for C₁₈H₂₃N₃O₂ 313.1790, found 313.1793.

Carboazidation of phenylallene (1e) with 4-iodoacetophenone (2a) and Me₃SiN₃. A mixture of **5j** and **6j** was obtained from the reaction after separation on a silica gel column using a mixture of ethyl acetate–hexane (1:50) as eluent. ¹H NMR (400 MHz, CDCl₃) **5j**: δ 8.05–6.95 (m, 9 H), 7.21 (s, 1 H, CH=), 4.41 (s, 2 H, CH₂N₃), 2.62 (s, 3 H); **6j**: δ 8.05–6.95 (m, 9 H), 6.75 (s, 1 H, CH=), 4.16 (s, 2 H, CH₂N₃), 2.59 (s, 3 H). IR (neat) 2096 cm⁻¹; HRMS calcd for C₁₇H₁₅N₃O 277.1217, found 277.1216.

Carboazidation of phenylallene (1e) with ethyl 4-iodobenzoate (2b) and Me₃SiN₃. A mixture of **5k** and **6k** was obtained from the reaction after separation on a silica gel column using a mixture of ethyl acetate–hexane (1:50) as eluent. ¹H NMR (400 MHz, CDCl₃) **5k**: δ 8.11–6.95 (m, 9 H), 7.20 (s, 1 H, CH=), 4.45–4.33 (m, 2 H), 4.40 (s, 2 H, CH₂N₃), 1.42–1.35 (m, 3 H); **6k**: δ 8.11–6.95 (m, 9 H), 6.74 (s, 1 H, CH=), 4.45–4.33 (m, 2 H), 4.15 (s, 2 H, CH₂N₃), 1.42–1.35 (m, 3 H); IR (neat) 2097 cm⁻¹; HRMS calcd for C₁₈H₁₇N₃O₂ 307.1321, found 307.1321.

Carboazidation of phenylallene (1e) with ethyl 3-iodobenzoate (2c) and Me₃SiN₃. A mixture of **5l** and **6l** was obtained from the reaction after separation on a silica gel column using a mixture of ethyl acetate–hexane (1:50) as eluent. ¹H NMR (400 MHz, CDCl₃) **5l**: δ 8.22–6.94 (m, 9 H), 7.16 (s, 1 H, CH=), 4.43–4.28 (m, 2 H), 4.42 (s, 2 H, CH₂N₃), 1.45–1.35 (m, 3 H); **6l**: δ 8.22–6.94 (m, 9 H), 6.73 (s, 1 H, CH=), 4.43–4.28 (m, 2 H), 4.17 (s, 2 H, CH₂N₃), 1.45–1.35 (m, 3 H); IR (neat) 2097 cm⁻¹; HRMS calcd for C₁₈H₁₇N₃O₂ 307.1321, found 307.1322.

Carboazidation of phenoxyallene (1f) with 4-iodoacetophenone (2a) and Me₃SiN₃. A mixture of **5m** and **6m** was obtained from the reaction after separation on a silica gel column using a mixture of ethyl acetate–hexane (1:50) as eluent. ¹H NMR (400 MHz, CDCl₃) **5m**: δ 7.98–6.85 (m, 9 H), 5.90 (s, 1 H, CH=), 4.13 (s, 2 H, CH₂N₃), 2.60 (s, 3 H); **6m**: δ 7.98–6.85 (m, 9 H), 5.90 (s, 1 H, CH=), 4.40 (s, 2 H, CH₂N₃), 2.59 (s, 3 H); IR (neat) 2105 cm⁻¹; HRMS calcd for C₁₇H₁₅N₃O₂ 293.1164, found 293.1170.

General procedure for the palladium-catalyzed carboazidation of *tert*-butylallene (1g) with aryl iodides and trimethylsilyl azide. A 25 mL round-bottomed flask containing Pd(dba)₂ (0.0287 g, 0.0500 mmol), an aryl iodide (1.00 mmol) and potassium acetate (1.50 mmol) was purged with nitrogen gas several times. To the flask were then added DMF (2.0 ml), an allene (1.50 mmol) and Me₃SiN₃ (0.182 g, 1.50 mmol). The reaction mixture was heated with stirring at 85 °C for 60 h. As the reaction approached completion, a black precipitate of palladium metal surrounding the wall of the flask appeared gradually. At the end of the reaction, the solution was diluted with ether (50 mL) and extracted with ether and water. The organic layer was collected and dried over MgSO₄. After removal of the solvent on a rotary evaporator, the residue was separated on a silica gel column to give the desired allylic azide as a yellow liquid.

Compounds **5n–q**, **6n–q**, and **7n–q** were prepared according to this method. Product yields of these reactions are listed in Table 3, while compounds **7n–q** spectral data are shown below.

Carboazidation of *tert*-butylallene (1g) with 4-iodoacetophenone (2a) and Me₃SiN₃. 4-[1-(1-azido-2,2-dimethylpropyl)-vinyl]phenylethanone (**7n**) was obtained from the reaction after separation on a silica gel column using a mixture of ethyl

acetate–hexane (1:20) as eluent. ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, $J = 8$ Hz, 2 H), 7.45 (d, $J = 8$ Hz, 2 H), 5.52 (s, 1 H, CH=), 5.41 (s, 1 H, CH=), 4.30 (s, 2 H, CH_2N_3), 2.59 (s, 3 H), 0.79 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.37 (s), 146.92 (s), 145.22 (s), 136.06 (s), 128.46 (d), 127.05 (d), 119.84 (t), 75.18 (d), 35.94 (s), 26.66 (q), 26.48 (q); IR (neat) 2101 cm^{-1} ; GC/MS (rel. intens.) m/z 229 (100, $[\text{M} - \text{N}_2]^+$), HRMS calcd for $\text{C}_{15}\text{H}_{19}\text{N}_3\text{O}$ 257.1530, found 257.1527.

Carboazidation of *tert*-butyllallene (1g) with ethyl 4-iodobenzoate (2b) and Me_3SiN_3 . Ethyl 4-[1-(1-azido-2,2-dimethylpropyl)vinyl]benzoate (7o) was obtained from the reaction after separation on a silica gel column using a mixture of ethyl acetate–hexane (1:20) as eluent. ^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, $J = 8$ Hz, 2 H), 7.41 (d, $J = 8$ Hz, 2 H), 5.53 (s, 1 H, CH=), 5.38 (s, 1 H, CH=), 4.34 (q, $J = 7.2$ Hz, 2 H), 4.29 (s, 2 H, CH_2N_3), 1.36 (t, $J = 7.2$ Hz, 3 H), 0.77 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.12 (s), 146.72 (s), 145.39 (s), 129.65 (d), 126.85 (d), 119.86 (t), 75.31 (d), 60.88 (t), 35.96 (s), 26.69 (q), 14.23 (q); IR (neat) 2103 cm^{-1} ; GC/MS (rel. intens.) m/z 259 (100, $[\text{M} - \text{N}_2]^+$), HRMS calcd for $\text{C}_{16}\text{H}_{21}\text{N}_3\text{O}_2$ 287.1635, found 287.1638.

Carboazidation of *tert*-butyllallene (1g) with ethyl 3-iodobenzoate (2c) and Me_3SiN_3 . Ethyl 3-[1-(1-azido-2,2-dimethylpropyl)vinyl]benzoate (7p) was obtained from the reaction after separation on a silica gel column using a mixture of ethyl acetate–hexane (1:20) as eluent. ^1H NMR (400 MHz, CDCl_3) δ 8.02 (s, 1 H), 7.93 (d, $J = 7.6$ Hz, 1 H), 7.53 (d, $J = 7.6$ Hz, 1 H), 7.38 (t, $J = 7.6$ Hz, 1 H), 5.52 (s, 1 H, CH=), 5.36 (s, 1 H, CH=), 4.36 (q, $J = 6.8$ Hz, 2 H), 4.32 (s, 2 H, CH_2N_3), 1.36 (t, $J = 6.8$ Hz, 3 H), 0.79 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.29 (s), 145.21, 142.61, 131.24 (d), 130.72 (d), 128.59 (d), 128.43 (d), 127.91 (d), 119.20 (t), 75.24 (d), 61.04 (t), 35.99 (s), 26.77 (q), 14.26 (q); IR (neat) 2103 cm^{-1} ; GC/MS (rel. intens.) m/z 259 (100, $[\text{M} - \text{N}_2]^+$), HRMS calcd for $\text{C}_{16}\text{H}_{21}\text{N}_3\text{O}_2$ 287.1635, found 287.1641.

Carboazidation of *tert*-butyllallene (1g) with 2-iodothiophene (2j) and Me_3SiN_3 . 2-[1-(1-azido-2,2-dimethylpropyl)vinyl]thiophene (7q) was obtained from the reaction after separation on a silica gel column using a mixture of ethyl acetate–hexane (1:50) as eluent. ^1H NMR (400 MHz, CDCl_3) δ 7.18 (dd, $J = 5$, 0.8 Hz, 1 H), 7.09 (dd, $J = 4$, 0.8 Hz, 1 H), 6.96 (dd, $J = 5$, 4 Hz, 1 H), 5.67 (s, 1 H, CH=), 5.21 (s, 1 H, CH=), 4.27 (s, 1 H, CHN_3), 0.88 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.52 (s), 138.76 (s), 127.27 (d), 124.76 (d), 124.20 (d), 116.62 (t), 75.32 (d), 35.82 (s), 26.81 (q); IR (neat) 2101 cm^{-1} ; HRMS calcd for $\text{C}_{11}\text{H}_{15}\text{N}_3\text{S}$ 221.0989, found 221.0988.

Carboazidation of 1-iodo-2-[(propa-1,2-dienyloxy)methyl]benzene 8 with Me_3SiN_3

A 25 ml round-bottomed flask containing $\text{Pd}(\text{dba})_2$ (0.0287 g, 0.0500 mmol) and potassium acetate (1.20 mmol) was purged with nitrogen gas several times. To the flask were then added DMF (2.0 ml), 1-iodo-2-[(propa-1,2-dienyloxy)methyl]benzene 8 (1.50 mmol) and Me_3SiN_3 (0.121 g, 1.00 mmol). The reaction mixture was heated with stirring at 70 °C for 6 h. As the reaction approached completion, a black precipitate of palladium metal surrounding the wall of the flask appeared gradually. At the end of the reaction, the solution was diluted with ether (50 mL) and extracted with ether and water. The organic layer was collected and dried over MgSO_4 . After removal of the solvent on a rotary evaporator, the residue was separated on a silica gel column using a mixture of ethyl acetate–hexane (1:30) as eluent to give the desired allylic azide 4-(azidomethyl)-1*H*-isochromene as a yellow liquid in 88% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.32–7.01 (m, 4 H), 6.68 (s, 1 H, CH=), 5.08 (s, 2 H), 4.05 (s, 2 H, CH_2N_3); ^{13}C NMR (100 MHz, CDCl_3) δ 146.60

(d), 129.33 (s), 128.38 (d), 127.98 (s), 127.46 (d), 124.10 (d), 120.46 (d), 110.45 (s), 68.53 (t), 49.39 (t); IR (neat) 2102 cm^{-1} ; HRMS calcd for $\text{C}_{10}\text{H}_9\text{N}_3\text{O}$ 187.0746, found 187.0746.

Reduction of 3a and 4a with PPh_3 and H_2O

To a mixture of 3a and 4a (84:16, 0.230 g, 1.00 mmol) in a 25 ml round-bottomed flask was added PPh_3 (0.393 g, 1.50 mmol) and THF (3.0 ml). The system was purged with nitrogen gas three times and then heated at 50 °C for 2 h. To the flask was added water (0.30 ml) and the system was further heated at 50 °C for 2 h. The solution was concentrated and then separated on a silica gel column using dichloromethane and methanol (5:1 v/v) as eluent to give the desired amine product 4-[1-(aminomethyl)-2-methylprop-1-enyl]phenylethanone (0.192 g) in 95% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 8$ Hz, 2 H), 7.26 (d, $J = 8$ Hz, 2 H), 3.59 (s, 2 H), 2.61 (s, 2 H), 1.89 (s, 3 H), 1.57 (s, 3 H), 1.10 (s, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.63 (s), 147.62 (d), 135.77 (s), 135.09 (s), 130.20 (s), 129.27 (d), 128.16 (d), 44.19 (t), 26.41 (q), 22.16 (q), 19.89 (q); IR (neat) 3358, 2906, 1681, 1611, 1267, 1181, 958, 837 cm^{-1} . HRMS calcd for $\text{C}_{13}\text{H}_{17}\text{NO}$ 203.1310, found 203.1307.

Acknowledgements

We thank the National Science Council of the Republic of China for financial support of this research (NSC 89-2113-M-007-031).

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