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Tetrahedron
Tetrahedron 63 (2007) 6614–6624

Lewis acid-controlled reactions of zirconacyclopentadienes with isocyanates and isothiocyanates. One-pot three- or four-component synthesis of multiply substituted iminocyclopentadienes and butadiene-tethered 1,6-bisamides and electrophilic cyclization

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Received 10 December 2006; revised 2 February 2007; accepted 5 February 2007
Available online 9 February 2007

Abstract—Multiply substituted zirconacyclopentadienes including bicyclic zirconacyclopentadienes and zirconaindenes reacted with isocyanates and isothiocyanates in the presence of Lewis acids to afford iminocyclopentadienes and conjugated 1,6-bisamides, depending on the nature of Lewis acids, isocyanates, and isothiocyanates used. Only in the presence of BF_3 could iminocyclopentadienes be obtained in high isolated yields when zirconacyclopentadienes were treated with isocyanates. On the contrary, BF_3 could not mediate the reaction of zirconacyclopentadienes with isothiocyanates. For the reactions of zirconacyclopentadienes with isothiocyanates, $EtAlCl_2$ was found effective to generate iminocyclopentadienes as the products. Interestingly, however, for the reactions of zirconacyclopentadienes with isocyanates, $EtAlCl_2$ was found to work very differently from BF_3. Instead of iminocyclopentadienes, conjugated 1,6-bisamides and conjugated monoamides were obtained as products in high isolated yields from the reactions of zirconacyclopentadienes with isocyanates, depending on the substituents of isocyanates. The reaction path and products could be controlled by Lewis acids. As a demonstration of the usefulness of thus obtained unsaturated bisamides, electrophilic cyclization using acids, NBS, and I_2 was carried out. Electrophilic cyclization of multisubstituted conjugated 1,6-bisamide derivatives afforded cyclic iminoethers in excellent yields with perfect selectivity. Only one of the amide groups took part in the electrophilic cyclization.

1. Introduction

Transition metal mediated C–C bond forming reactions are frequently used in organic synthesis. On the other hand, classical Lewis acids, including $AlCl_3$, BF_3, $TiCl_4$, and $SnCl_4$, are well known to promote or catalyze a variety of organic transformations.[1] Combination of these two powerful protocols would result in synthetically useful and conceptually new methodologies.[2–11] Indeed, Lewis acids play a very important role in many transition metal mediated C–C bond forming reactions, including promotion of reactivity and increase of selectivity.[3–11]

We started our research project on the cooperation of Lewis acids with zirconocene-mediated C–C bond forming reactions in 1998. Our results have demonstrated that the cooperation between Lewis acids and zirconacycles is very effective and leads to a variety of unprecedented reactions.[12–14] For example, Lewis acid-mediated reaction of zirconacyclopentadienes with aldehydes afforded cyclopentadiene derivatives via cleavage of the C=O double bond of aldehydes.[12] Recently, we applied this strategy in the reactions of zirconacyclopentadienes with isocyanates;[15] iminocyclopentadiene derivatives were formed in one-pot reaction via selective cleavage of the C=O double bond of RN=C=O.[15] During our further investigation into this synthetically useful reaction, we found that, in addition to promoting the reactivity, Lewis acids could also control the reaction direction. Thus, different products could be obtained from the same reagents only by applying different Lewis acids. It was also found that isocyanates and isothiocyanates behaved remarkably different from each other when treated with zirconacyclopentadienes in the presence of Lewis acids.

In this full paper, we would like to report: (1) formation of iminocyclopentadiene derivatives and indenimine derivatives

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doi:10.1016/j.tet.2007.02.015

from zirconacyclopentadiene/RNCO/$BF_3 \cdot Et_2O$ and zirconacyclopentadiene/RNCS/$EtAlCl_2$, (2) formation of conjugated 1,6-bisamides from zirconacyclopentadiene/RNCO/$EtAlCl_2$, (3) electrophilic cyclization of multisubstituted conjugated 1,6-bisamides, and (4) mechanistic aspects.

2. Results and discussion

2.1. Formation of iminocyclopentadiene derivatives and indenimine derivatives from zirconacyclopentadiene/RNCO/$BF_3 \cdot Et_2O$ and zirconacyclopentadiene/RNCS/$EtAlCl_2$

Zirconacyclopentadienes can be readily generated from alkynes, diynes, and benzynes with low-valent zirconocene species.[16–19] No reaction proceeded when a zirconacyclopentadiene was treated with an isocyanate or an isothiocyanate, which are important and useful hetero-cumulenes. Since isocyanates and isothiocyanates can form adducts with Lewis acids and hence activated, we tried a variety of Lewis acids as additives to the mixture of zirconacyclopentadienes with isocyanates or isothiocyanates.

Reaction of zirconacyclopentadienes with isocyanates in the presence of $BF_3 \cdot Et_2O$ proceeded smoothly, affording iminocyclopentadiene derivatives as the sole products in high isolated yields (Fig. 1). It should be pointed out that only aromatic isocyanates can be used. Aliphatic isocyanates lead to messy mixture of products even at lower temperatures (−78 °C), probably due to their relatively higher reactivity. Both products **2f** and **2g** were formed in lower yields from their corresponding ArNCO. The electron-donating substituents of the phenyl isocyanates are considered responsible for the lower yields of products, probably because these isocyanates have relatively higher reactivity, which would lead to more byproducts. Other Lewis acids did not lead to good results: $AlCl_3$ and $FeCl_3$ led to inseparable messy mixture of products even at lower temperature (−78 °C); $TiCl_4$, $InCl_3$, $CoCl_2$, VCl_3, and $Sc(CF_3SO_3)_3$ did not promote the reaction and the zirconacyclopentadienes remained even at higher temperature (80 °C). When $EtAlCl_2$ was used, totally different products were obtained. The result will be discussed later. Thus, among those Lewis acids investigated, only BF_3 could mediate formation of iminocyclopentadienes from zirconacyclopentadienes and isocyanates.

However, when we treated isothiocyanates with zirconacyclopentadienes in the presence of BF_3, we found BF_3 could not mediate the reaction of zirconacyclopentadienes with isothiocyanates. Surprisingly, after a survey of various Lewis acids, $EtAlCl_2$ was found to be effective for promoting the reaction of zirconacyclopentadienes with isothiocyanates, leading to iminocyclopentadienes (Fig. 1), the same type of products were obtained from zirconacyclopentadiene/RNCO/$BF_3 \cdot Et_2O$. Although the reason is not clear yet, the electron-donating substituents of the isothiocyanates did not show remarkable influences on the yield of products, for example, product **2f** was obtained from TolylNCS in 85% isolated yield.

Similarly, as shown in Figure 2, indenimines were successfully obtained from zirconaindene/RNCO/$BF_3 \cdot Et_2O$ or from zirconaindene/RNCS/$EtAlCl_2$.[17] In these reactions,

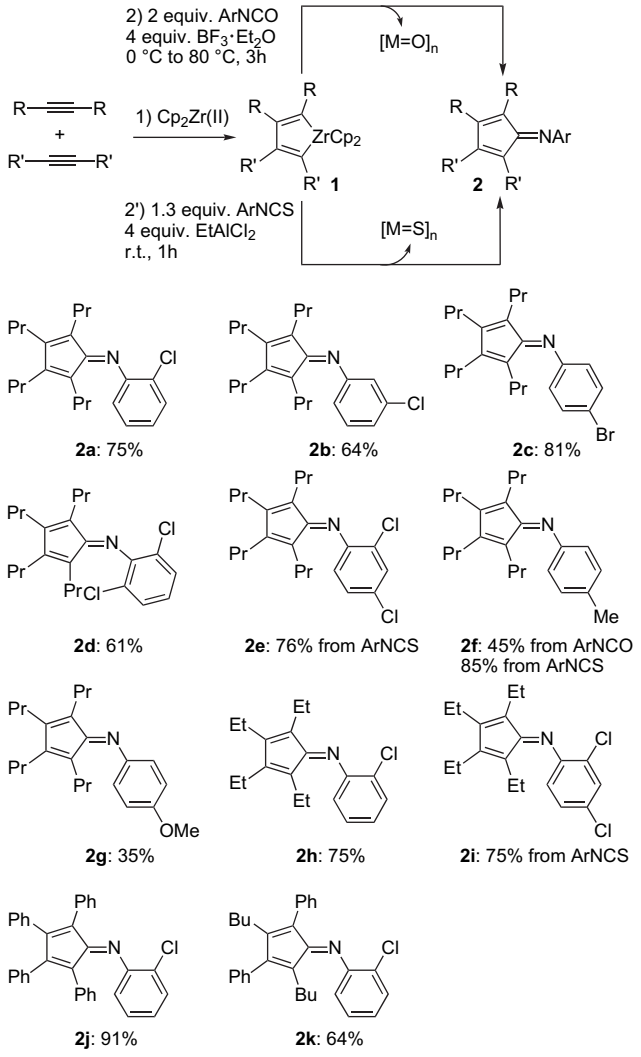


Figure 1. Formation of iminocyclopentadienes from zirconacyclopentadiene/ArNCO/$BF_3 \cdot Et_2O$ or zirconacyclopentadiene/ArNCS/$EtAlCl_2$. If not specified, products were obtained from ArNCO.

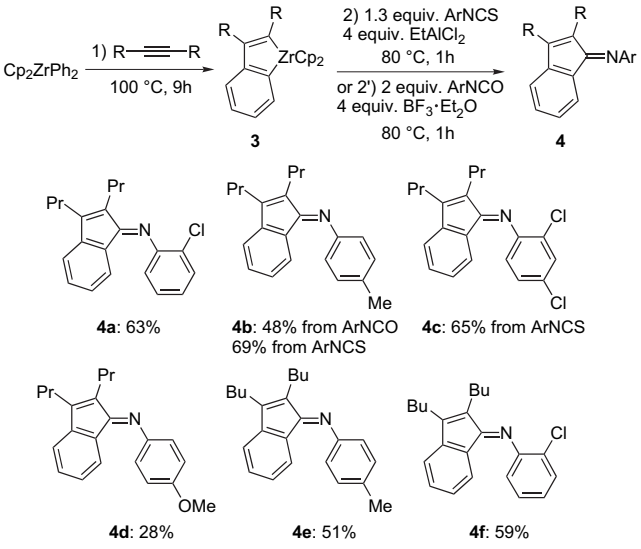
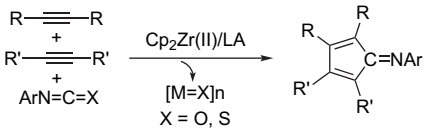


Figure 2. One-pot synthesis of indenimine derivatives from one benzyne, one normal alkyne, and one isocyanate or isothiocyanate.

similarly, low yields of products were obtained when ArNCO having electron-donating substituents were used (for example, **4b** and **4d**).

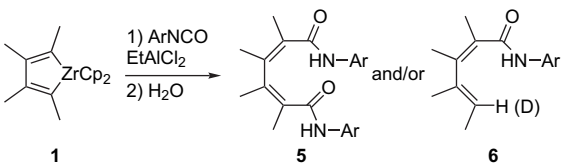
A number of useful preparation methods for iminocyclopentadiene derivatives have been developed.[20,21] Our method represents an alternative route to highly substituted iminocyclopentadiene, via a one-pot three-component process combining zirconacene-mediated C–C bond forming reactions with Lewis acid-mediated organic transformation (Eq. 1). It should be pointed out that these reactions are highly site-selective; only the C=O double bond in ArN=C=O or the C=S double bond in ArN=C=S is cleaved to form the cyclopentadienyl imines.



(1)

2.2. One-pot synthesis of butadiene-tethered 1,6-bisamide derivatives

As mentioned above, Lewis acid $EtAlCl_2$ behaved for the reaction of zirconacyclopentadienes with isothiocyanates similarly as BF_3 did for the reaction of zirconacyclopentadienes with isocyanates. Both of the reaction systems of zirconacyclopentadiene/RNCO/$BF_3\cdot Et_2O$ and zirconacyclopentadiene/RNCS/$EtAlCl_2$ afforded iminocyclopentadiene derivatives. However, when $EtAlCl_2$ was added to the mixture of zirconacyclopentadienes **1** with isocyanates, a reaction did take place, generating conjugated bisamide **5** and mono-amide **6** derivatives, rather than those iminocyclopentadiene derivatives **2**. In fact, totally no formation of iminocyclopentadiene derivatives **2** was observed from the reaction system of zirconacyclopentadiene/RNCO/$EtAlCl_2$. Furthermore, it was found that this $EtAlCl_2$-mediated reaction of zirconacyclopentadienes with isocyanates was substrate-dependent, affording either mono-amide and/or bisamide derivatives depending on the substituents of ArNCO (Eq. 2). Both the mono-amide and the bisamide derivatives are very useful compounds, since the functional groups (amides) and the butadienyl skeletons can be further applied for the synthesis of diversified structures.[22–24]

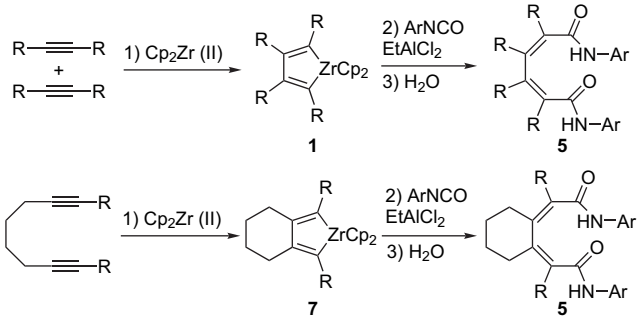


(2)

As shown in Table 1, phenyl isocyanate, 2-chlorophenyl isocyanate, and 2,4-dichlorophenyl isocyanate reacted with zirconacyclopentadienes including bicyclic zirconacyclopentadienes **7** resulting in the formation of conjugated 1,6-bisamide derivatives **5** as the sole products. Mono-amides **6** were not formed in these cases.

When aryl isocyanates such as 4-chlorophenyl, 4-fluorophenyl, and 4-methylphenyl isocyanates were used for the above mentioned reactions, both bisamides **5** and mono-amides **6** were obtained as a mixture (Table 2). Interestingly, when 4-bromophenyl isocyanate was used, the reaction gave only the mono-amide **6a** (entry 4, Table 2) as the product. No bisamide was obtained in this case. Deuterolysis of the reaction mixture afforded a D-incorporated product **6eD** (entry 5, Table 2), which indicated that the intermediate could be further used. As an example of application, we added a different isocyanate to the proposed reaction intermediate **8** (Scheme 1). In this way, mixed bisamide derivatives **9a** and **9b** could be prepared in one-pot from two alkynes and two different isocyanates. When the reaction mixture was treated with I_2, the butadienyl iodide product **6I** was obtained in 68% isolated yield.

Table 1. Four-component one-pot synthesis of conjugated 1,6-bisamides from two alkynes and two isocyanates

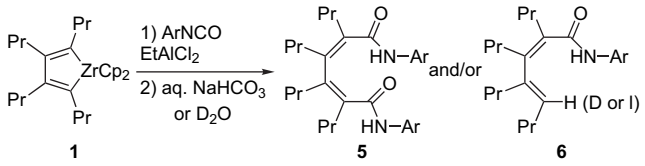


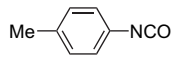
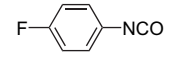
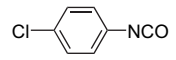
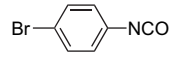
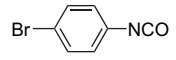
Entry	Alkyne	Isocyanate	Isolated yield of **5** (%)
1	Pr—≡—Pr	NCO	**5a** (65)
2	Pr—≡—Pr	Cl, NCO	**5b** (80)
3	Pr—≡—Pr	Cl, Cl, NCO	**5c** (89)
4	Et—≡—Et	Cl, NCO	**5d** (71)
5	Pr, Pr	Cl, NCO	**5e** (59)
6	Ph, Ph	Cl, NCO	**5f** (62)

2.3. Electrophilic cyclization of multisubstituted butadiene-tethered 1,6-bisamides

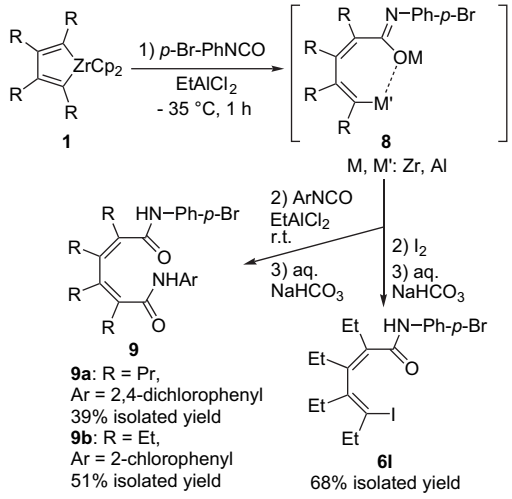
Electrophilic cyclization of unsaturated amides is a very useful direct way to construct various functionalized lactones, lactams, and oxazolines.[22,23] We have recently reported that electrophilic cyclization of dienamides **6** (butadienyl amides), generated from 1-lithio-1,3-diene derivatives with RNCO, affords substituted cyclic iminoethers in excellent yields with perfect selectivity (Scheme 2).[24] As

Table 2. $EtAlCl_2$-mediated substituent-dependent formation of bisamides and/or mono-amides from zirconacyclopentadienes and ArNCO



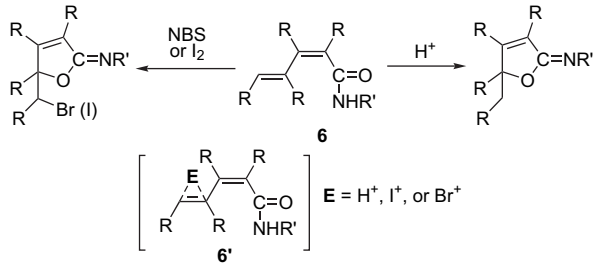
Entry	ArNCO	Isolated yield of **5** (%)	Isolated yield of **6** (%)
1		**5g** (34)	**6a** (21)
2		**5h** (26)	**6b** (40)
3		**5i** (23)	**6c** (30)
4		**5j** (0)	**6d** (54)
5[a]		**5k** (0)	**6eD** (48)

[a] Quenched with D_2O.



Scheme 1. Formation of mixed bisamide derivatives in one-pot from two alkynes and two different isocyanates or butadienyl iodide.

a demonstration of the usefulness of the butadiene-tethered 1,6-bisamides, we carried out electrophilic cyclization reactions of butadiene-tethered 1,6-bisamides **5**, expecting formation of structurally interesting heterocycles.



Scheme 2. Electrophilic cyclization of butadienyl amides.

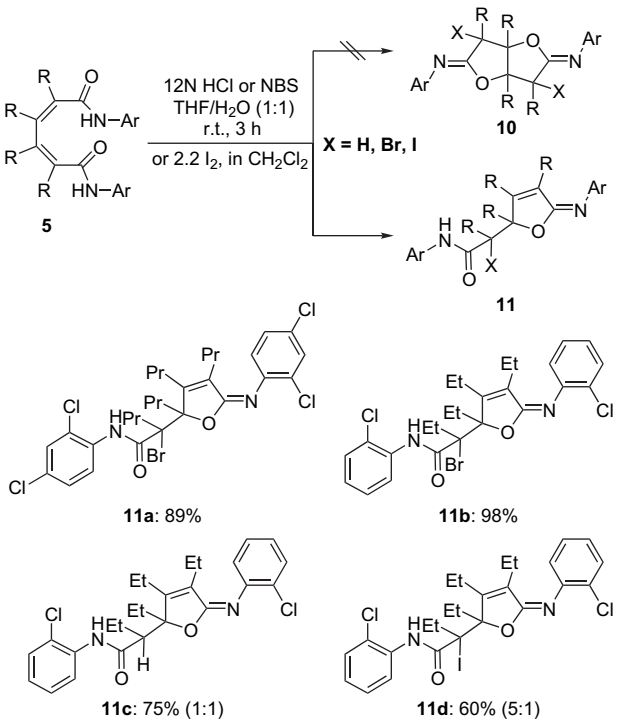


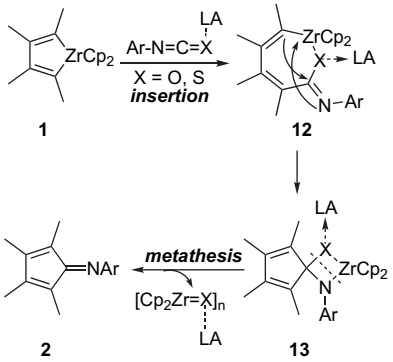
Figure 3. Electrophilic cyclization of butadiene-bridged 1,6-bisamides **5**.

As expected, butadiene-tethered 1,6-bisamides **5** did undergo electrophilic cyclization smoothly when treated with strong acids, NBS, or I_2, affording, however, not the expected fused-ring products **10**, but monocyclic iminoethers **11**, analogous to the electrophilic cyclization products of **6** (Fig. 3). These multisubstituted butadiene-tethered 1,6-bisamides **5** behaved similarly with **6** in the electrophilic cyclization reaction. Only O-attack pathway was involved and *exo* cyclization product was obtained as the sole products.

2.4. Aspects of reaction mechanisms

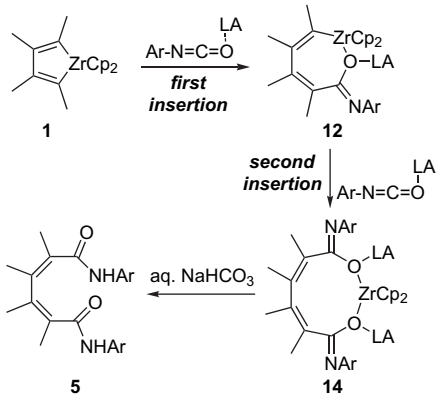
In our previous work,[12,15] we proposed that Lewis acids played a very important role in promoting reactivity of zirconacyclopentadienes with aldehydes and isocyanates, probably via transmetalation or coordination. In this work, analogous functions of Lewis acids are assumed to operate.

Scheme 3 shows a proposed reaction mechanism for the formation of iminocyclopentadienes from reactions of

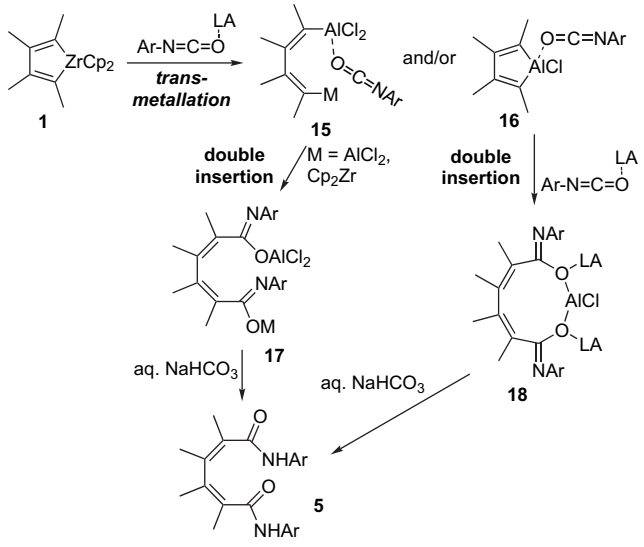


Scheme 3. A proposed reaction mechanism for the formation of iminocyclopentadienes. When X=O, LA=BF_3, while X=S, LA=$EtAlCl_2$.

zirconacyclopentadienes with isocyanates and isothiocyanates promoted by Lewis acids. An adduct between an isocyanate or an isothiocyanate is firstly generated in situ in the reaction mixture. Upon activation through this form of adduct interaction, insertion of the C═X moiety of ArN═C═X (X═O or S) into the Zr–C bond of zirconacyclopentadienes took place to afford seven-membered zirconacycles **12**, which underwent intramolecular nucleophilic attack to form intermediates **13**. Isolation of **13** has been so far failed. However, metathesis of **13** is proposed to play an essential role for the final formation of iminocyclopentadienes **2**.[25] Indeed, hydrolysis of the reaction mixtures gave an unstable compound, which transformed into cyclopentadienone derivatives in $CHCl_3$ after 3 days. In addition, NMR spectra showed that iminocyclopentadienes **2** were already formed in situ before hydrolysis. It should be pointed out that specific combination of substrates with Lewis acids, e.g., zirconacyclopentadiene/RNCO/$BF_3\cdot Et_2O$ and zirconacyclopentadiene/RNCS/$EtAlCl_2$, is very important for the formation of iminocyclopentadiene derivatives and indenimine derivatives.



Scheme 4. A proposed reaction mechanism for the formation of bisamides via double insertion of ArNCO.



Scheme 5. Proposed reaction mechanisms for the formation of bisamides via transmetalation followed by double insertion of ArNCO.

Alternatively, zirconacyclopentadienes **1** might undergo double insertion by the above mentioned adduct. Thus, as shown in Scheme 4, the first insertion gave seven-membered ring intermediate **12**, the remaining Zr–C bond of which was inserted by a second molecule of the adduct to generate intermediate **14**. Hydrolysis of **14** afforded the butadiene-tethered bisamides **5**. In this type of reaction, only the combination of zirconacyclopentadiene/ArNCO/$EtAlCl_2$ worked.

For the combination of zirconacyclopentadiene/ArNCO/$EtAlCl_2$ to afford bisamides, transmetalation of Zr–C bond to Al–C bond might also be involved. As given in Scheme 5, transmetalation of **1** might give intermediates **15** and **16**. Both of the intermediates **15** and **16** then react with two molecules of ArNCO via double insertion to generate acyclic intermediate **17** and cyclic intermediate **18**.

3. Conclusion

Lewis acid-controlled reactions of zirconacyclopentadienes with isocyanates and isothiocyanates have been developed. Thus, a one-pot three-component procedure for the construction of highly substituted iminocyclopentadiene derivatives and indenimine derivatives has been realized from alkynes and isocyanates mediated by zirconocene and BF_3 or from alkynes and isothiocyanates mediated by zirconocene and $EtAlCl_2$. Similarly, butadiene-tethered 1,6-bisamide derivatives were prepared via a one-pot four-component procedure from alkynes and isocyanates mediated by zirconocene and $EtAlCl_2$. This success indicated that novel and synthetically useful methodologies could be developed by combining transition metal mediated C–C bond forming reactions with Lewis acid-mediated organic transformations. Electrophilic cyclization of multisubstituted unsaturated 1,6-bisamides derivatives afforded cyclic iminoethers in excellent yields with perfect selectivity. Only one of the amide groups took part in the electrophilic cyclization.

4. Experimental section

4.1. General

Unless otherwise noted, all starting materials were commercially available and were used without further purification. All reactions involving organometallic compounds were run under a slightly positive pressure of dry N_2 with use of standard Schlenk techniques. Zirconocene dichloride was obtained from Aldrich and Alfa-Aesar. PhMgBr, $EtAlCl_2$, boron trifluoride diethyl etherate ($BF_3\cdot Et_2O$), and *n*-BuLi were purchased from Acros. Toluene was refluxed and distilled from sodium benzophenone ketyl under a nitrogen atmosphere. ^1H and ^{13}C NMR spectra were recorded on a JEOL-300 MHz spectrometer. GC analysis was performed on a gas chromatograph (Shimadzu 14B) equipped with a flame ionization detector and a capillary column (CBP1-M25-25). GC yields were determined using suitable hydrocarbons as internal standards.

4.2. General procedure for the preparation of multiply substituted iminocyclopentadiene derivatives from zirconacyclopentadiene/RNCO/$BF_3 \cdot Et_2O$

An alkyne (4.0 mmol) was added into a toluene solution of [Cp_2ZrBu_2] (Negishi reagent),[16] prepared in situ from Cp_2ZrCl_2 (2.0 mmol, 0.58 g) and *n*-BuLi (4.0 mmol, 2.6 mL, 1.60 M hexane solution) in toluene (20 mL) at −78 °C. The reaction mixture was then stirred at room temperature for 1 h to afford zirconacyclopentadiene. Isocyanate (4.0 mmol) was added to this solution at room temperature, then $BF_3 \cdot Et_2O$ (8.0 mmol, 1.0 mL) was added to this solution at −78 °C. After the reaction mixture was stirred at 0 °C for 1 h, the temperature was allowed rising to 80 °C and maintaining for another 1 h. The above reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with *n*-hexane. The extract was washed with water and brine, and dried over Na_2SO_4. The solvent was then evaporated in vacuo to give red-brown oil, which was purified by column chromatography to the products.

4.3. General procedure for the preparation of multiply substituted iminocyclopentadiene derivatives from zirconacyclopentadiene/RNCS/$EtAlCl_2$

An alkyne (4.0 mmol) was added into a toluene solution of [Cp_2ZrBu_2] (Negishi reagent),[16] prepared in situ from Cp_2ZrCl_2 (2.0 mmol, 0.58 g) and *n*-BuLi (4.0 mmol, 2.6 mL, 1.60 M hexane solution) in toluene (20 mL) at −78 °C. The reaction mixture was then stirred at room temperature for 1 h to afford zirconacyclopentadiene. Isothiocyanate (2.6 mmol) was added to this solution at room temperature and then $EtAlCl_2$ (8.0 mmol, 8.8 mL, 0.9 M hexane solution) was added to this solution at −78 °C. After stirring at room temperature for 1 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with *n*-hexane. The extract was washed with water and brine, and dried over Na_2SO_4. The solvent was then evaporated in vacuo to give red-brown oil, which was purified by column chromatography to the products.

4.3.1. (2-Chloro-phenyl)-(2,3,4,5-tetrapropyl-cyclopenta-2,4-dienylidene)-amine (2a). Red liquid, 75% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.41 (br, 3H), 0.97–1.00 (m, 11H), 1.45–1.64 (m, 8H), 2.17–2.29 (m, 6H), 6.80–7.35 (m, 4H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.1, 14.4, 14.6, 23.0, 23.5, 24.0, 26.1, 27.4, 28.2, 119.6, 122.9, 123.8, 124.3, 126.5, 129.3, 131.3, 147.4, 148.2, 154.0, 172.2. HRMS calcd for $C_{23}H_{32}NCl$: 357.2223, found: 357.2224.

4.3.2. (3-Chloro-phenyl)-(2,3,4,5-tetrapropyl-cyclopenta-2,4-dienylidene)-amine (2b). Red liquid, 64% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): 0.46 (t, J=7.2 Hz, 3H), 0.90–1.00 (m, 11H), 1.45–1.63 (m, 8H), 2.14–2.23 (m, 6H), 6.69–7.25 (m, 4H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.9, 14.4, 14.6, 23.0, 23.8, 24.0, 26.0, 27.4, 28.2, 116.4, 118.2, 122.6, 123.9, 129.2, 131.2, 133.9, 147.4, 152.5, 154.5, 171.2. HRMS calcd for $C_{23}H_{32}NCl$: 357.2223, found: 357.2228.

4.3.3. (4-Bromo-phenyl)-(2,3,4,5-tetrapropyl-cyclopenta-2,4-dienylidene)-amine (2c). Red liquid, 81% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.45 (t, J=7.2 Hz, 3H), 0.89–1.00 (m, 11H), 1.47–1.61 (m, 8H), 2.17–2.26 (m, 6H), 6.68–7.37 (m, 4H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.0, 14.4, 14.6, 23.0, 23.7, 24.1, 26.0, 27.5, 28.2, 115.7, 112.0, 123.8, 131.1, 131.3, 147.3, 150.3, 154.4, 171.2. HRMS calcd for $C_{23}H_{32}NCl$: 401.1718, found: 401.1721.

4.3.4. (2,6-Dichloro-phenyl)-(2,3,4,5-tetrapropyl-cyclopenta-2,4-dienylidene)-amine (2d). Red liquid, 61%. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.45 (br, 3H), 0.98 (t, J=7.2 Hz, 9H), 1.46–1.48 (m, 8H), 2.20 (br, 8H), 6.85–7.30 (m, 3H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.3, 14.5, 23.0, 23.4, 26.1, 27.1, 28.2, 123.4, 123.7, 124.8, 127.8, 131.2, 145.8, 148.0, 153.7, 174.4. HRMS calcd for $C_{23}H_{31}NCl_2$: 391.1834, found: 391.1837.

4.3.5. (2,4-Dichloro-phenyl)-(2,3,4,5-tetrapropyl-cyclopenta-2,4-dienylidene)-amine (2e). Red liquid, 76%. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.47 (br, 3H), 0.98 (br, 11H), 1.47–1.65 (m, 8H), 2.20–2.23 (m, 6H), 6.74–7.36 (m, 3H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.1, 14.3, 14.6, 23.0, 23.4, 23.9, 26.0, 27.3, 28.2, 120.4, 123.7, 124.1, 126.7, 128.2, 129.0, 131.3, 147.0, 147.8, 154.5, 172.9. HRMS calcd for $C_{23}H_{31}NCl_2$: 391.1834, found: 391.1835.

4.3.6. (4-Methyl-phenyl)-(2,3,4,5-tetrapropyl-cyclopenta-2,4-dienylidene)-amine (2f). Red liquid, from ArNCO 45% isolated yield, from ArNCS 85% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.40 (t, J=7.2 Hz, 3H), 0.88–1.00 (m, 11H), 1.36–1.65 (m, 8H), 2.13–2.31 (m, 9H), 6.69–7.26 (m, 4H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.9, 14.4, 14.6, 20.8, 23.1, 23.7, 24.1, 26.1, 27.5, 28.2, 28.3, 118.2, 124.0, 128.7, 131.4, 146.8, 148.9, 153.6, 170.7. HRMS calcd for $C_{24}H_{35}N$: 337.2770, found: 337.2769.

4.3.7. (4-Methoxyl-phenyl)-(2,3,4,5-tetrapropyl-cyclopenta-2,4-dienylidene)-amine (2g). Red liquid, 35% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.44 (t, J=7.2 Hz, 3H), 0.86–1.02 (m, 11H), 1.36–1.53 (m, 6H), 1.63–1.68 (m, 2H), 2.14–2.30 (m, 6H), 3.79 (s, 3H), 6.73–7.26 (m, 4H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.0, 14.4, 14.6, 23.1, 23.6, 24.1, 26.1, 27.6, 28.2, 55.6, 113.7, 119.6, 123.7, 131.5, 144.8, 146.7, 153.7, 156.0, 171.2. HRMS calcd for $C_{24}H_{35}NO$: 353.2719, found: 353.2716.

4.3.8. (2-Chloro-phenyl)-(2,3,4,5-tetraethyl-cyclopenta-2,4-dienylidene)-amine (2h). Red liquid, 75% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.58–0.62 (m, 3H), 1.07–1.13 (m, 9H), 1.72–1.74 (m, 2H), 2.22–2.38 (m, 6H), 6.82–7.34 (m, 4H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.2, 14.4, 14.6, 15.6, 17.1, 18.0, 18.8, 119.6, 122.9, 124.0, 125.2, 126.5, 129.3, 132.3, 148.2, 155.4, 171.8. HRMS calcd for $C_{19}H_{24}NCl$: 301.1597, found: 301.1593.

4.3.9. (2,4-Dichloro-phenyl)-(2,3,4,5-tetraethyl-cyclopenta-2,4-dienylidene)-amine (2i). Red liquid, 75% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.62 (br, 3H), 1.11 (br, 9H), 1.73 (br, 2H), 2.29 (br, 6H), 6.76–7.36 (m, 3H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.2, 14.3, 14.6, 15.6, 17.1, 18.0, 18.9, 120.4, 123.7, 125.0, 126.7, 128.4, 129.0, 132.3, 146.9, 148.6, 155.9, 172.5. HRMS calcd for $C_{19}H_{23}NCl_2$: 355.1208, found: 355.1214.

4.3.10. (2-Chloro-phenyl)-(2,3,4,5-tetraphenyl-cyclopenta-2,4-dienylidene)-amine (2j). Dark solid, 91%

isolated yield, mp: 189–190 °C. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 6.47–7.38 (m, 24H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 120.5, 123.0, 124.3, 125.9, 126.2, 127.0, 127.3, 127.5, 128.6, 129.8, 130.1, 131.3, 132.5, 132.8, 133.4, 133.6, 134.0, 147.2, 148.5, 153.9, 169.6. HRMS calcd for $C_{35}H_{24}NCl$: 493.1597, found: 493.1592. Anal. Calcd for $C_{35}H_{24}ClN$: C, 85.09%; H, 4.90%; N, 2.84%. Found: C, 85.21%; H, 4.93%; N, 2.76%.

4.3.11. (2-Chloro-phenyl)-(2,4-dibutyl-3,5-diphenyl-cyclopenta-2,4-dienylidene)-amine (2k). Red liquid, 64% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.52–0.60 (br, 3H), 0.83 (t, J=7.2 Hz, 3H), 0.96–1.06 (m, 4H), 1.27–1.34 (m, 2H), 1.53–1.64 (m, 2H), 1.75 (br, 2H), 2.17–2.45 (m, 2H), 6.37–7.46 (m, 14H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.4, 14.0, 22.3, 22.8, 24.0, 26.0, 30.3, 32.9, 121.0, 124.0, 124.2, 124.7, 125.8, 128.9, 127.2, 127.5, 128.2, 128.4, 128.6, 129.3, 134.5, 134.7, 135.3, 147.06, 147.10, 156.8, 170.4. HRMS calcd for $C_{31}H_{32}NCl$: 453.2223, found: 453.2209.

4.4. General procedure for the preparation of multiply substituted indenyl imine derivatives from zircona-cyclopentadiene/RNCO/$BF_3\cdot Et_2O$

An alkyne (2.0 mmol) was added to a solution of [Cp_2ZrPh_2][17] in toluene, prepared in situ from Cp_2ZrCl_2 (2.0 mmol, 0.58 g) and PhLi (4.0 mmol, 2.0 mL, 2.0 M dibutyl ether) in toluene (20 mL) at 0 °C. The reaction mixture was then stirred at 100 °C for 9 h to afford zirconaindene. The solution was cooled to room temperature and isocyanate (4.0 mmol) was added. Then $BF_3\cdot Et_2O$ (8.0 mmol, 1.0 mL) was added to this solution at −78 °C. After the reaction mixture was stirred at 0 °C for 1 h, the temperature was allowed rising to 80 °C and maintaining for another 1 h. The above reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with *n*-hexane. The extract was washed with water and brine, and dried over Na_2SO_4. The solvent was then evaporated in vacuo to give red-brown oil, which was purified by column chromatography to the products.

4.5. General procedure for the preparation of multiply substituted indenyl imines derivatives from zircona-cyclopentadiene/RNCS/$EtAlCl_2$

An alkyne (2.0 mmol) was added to a solution of [Cp_2ZrPh_2][17] in toluene, prepared in situ from Cp_2ZrCl_2 (2.0 mmol, 0.58 g) and PhLi (4.0 mmol, 2.0 mL, 2.0 M dibutyl ether) in toluene (20 mL) at 0 °C. The reaction mixture was then stirred at 100 °C for 9 h to afford zirconaindene. The solution was cooled to room temperature and isothiocyanate (2.6 mmol) was added. Then $EtAlCl_2$ (8.0 mmol, 8.8 mL, 0.9 M hexane solution) was added to this solution at −78 °C. After stirring at 80 °C for 1 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with *n*-hexane. The extract was washed with water and brine, and dried over Na_2SO_4. The solvent was then evaporated in vacuo to give red-brown oil, which was purified by column chromatography to the products.

4.5.1. (2-Chloro-phenyl)-(2,3-dipropyl-inden-1-ylidene)-amine (4a). Orange liquid, 63% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 1.01 (t, J=7.2 Hz, 3H), 1.03 (t, J=7.2 Hz, 3H), 1.59–1.71 (m, 4H), 2.28–2.58 (m, 4H), 6.28–7.44 (m, 8H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.4, 14.6, 21.7, 23.4, 26.1, 28.0, 118.8, 119.6, 123.1, 124.4, 124.6, 126.3, 127.3, 129.1, 129.9, 131.0, 137.6, 146.1, 149.3, 149.5, 168.4. HRMS calcd for $C_{21}H_{22}NCl$: 323.1441, found: 323.1446.

4.5.2. (4-Methyl-phenyl)-(2,3-dipropyl-inden-1-ylidene)-amine (4b). Orange liquid, from ArNCO 48% isolated yield, from ArNCS 69% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.98 (t, J=7.2 Hz, 3H), 1.04 (t, J=7.2 Hz, 3H), 1.56–1.71 (m, 4H), 2.38 (s, 3H), 2.46–2.56 (m, 4H), 6.35–7.24 (m, 8H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.4, 14.5, 21.0, 21.7, 23.5, 26.1, 28.0, 118.2, 118.6, 125.1, 125.8, 128.7, 129.6, 130.4, 133.0, 137.8, 146.3, 148.3, 149.6, 166.8. HRMS calcd for $C_{22}H_{25}N$: 303.1987, found: 303.1982.

4.5.3. (2,4-Dichloro-phenyl)-(2,3-dipropyl-inden-1-ylidene)-amine (4c). Orange liquid, 65% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.97–1.07 (m, 6H), 1.58–1.72 (m, 4H), 2.46–2.55 (m, 4H), 6.35–7.44 (m, 7H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.3, 14.5, 21.6, 23.3, 26.0, 28.0, 119.0, 120.5, 123.9, 124.3, 126.3, 127.6, 128.97, 128.99, 129.6, 131.2, 137.4, 146.1, 147.5, 149.9, 168.9. HRMS calcd for $C_{21}H_{21}NCl_2$: 357.1051, found: 357.1052.

4.5.4. (4-Methoxyl-phenyl)-(2,3-dipropyl-inden-1-ylidene)-amine (4d). Orange liquid, 28% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.99 (t, J=7.2 Hz, 3H), 1.05 (t, J=7.2 Hz, 3H), 1.58–1.68 (m, 4H), 2.46–2.57 (m, 4H), 3.85 (s, 3H), 6.41–7.26 (m, 8H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.4, 14.5, 21.7, 23.5, 26.1, 28.0, 55.5, 114.3, 118.6, 119.6, 125.0, 125.9, 128.65, 130.4, 137.9, 145.4, 146.3, 148.3, 156.4, 167.3. HRMS calcd for $C_{22}H_{25}NO$: 319.1936, found: 319.1938.

4.5.5. (4-Methyl-phenyl)-(2,3-dibutyl-inden-1-ylidene)-amine (4e). Red liquid, 51% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.94 (t, J=7.2 Hz, 3H), 0.97 (t, J=7.2 Hz, 3H), 1.37–1.62 (m, 8H), 2.38 (s, 3H), 2.47–2.57 (m, 4H), 6.35–7.16 (m, 8H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.0, 14.1, 21.0, 23.0, 23.1, 23.8, 25.7, 30.5, 32.5, 118.2, 118.5, 125.1, 125.8, 128.8, 129.6, 130.4, 133.0, 137.9, 146.3, 148.4, 149.6, 166.8. HRMS calcd for $C_{24}H_{29}N$: 331.2300, found: 331.2302.

4.5.6. (2-Chloro-phenyl)-(2,3-dibutyl-inden-1-ylidene)-amine (4f). Orange liquid in 59% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.94 (t, J=7.2 Hz, 3H), 0.98 (t, J=7.2 Hz, 3H), 1.39–1.67 (m, 8H), 2.50–2.58 (m, 4H), 6.28–7.44 (m, 8H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.0, 14.1, 22.9, 23.1, 23.8, 25.7, 30.5, 32.3, 118.8, 119.6, 123.1, 124.4, 124.5, 126.2, 127.3, 129.1, 129.9, 131.0, 137.6, 146.1, 148.9, 149.5, 168.3. HRMS calcd for $C_{23}H_{26}NCl_2$: 351.1754, found: 351.1756.

4.6. General procedure for the preparation of multiply substituted hexa-2,4-dienedioic acid bisamide derivatives (5a–f)

An alkyne (4.0 mmol) was added into a toluene solution of [Cp_2ZrBu_2] (Negishi reagent),[16] prepared in situ from Cp_2ZrCl_2 (2.0 mmol, 0.58 g) and *n*-BuLi (4.0 mmol,

2.6 mL, 1.60 M hexane solution) in toluene (20 mL) at −78 °C. The reaction mixture was then stirred at room temperature for 1 h to afford zirconacyclopentadiene. Isocyanate (4.0 mmol) and $EtAlCl_2$ (8.0 mmol, 8.8 mL, 0.9 M hexane solution) were added to this solution at −78 °C. After stirring the reaction mixture at −30 °C for 1 h, the above reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with Et_2O. The extract was washed with water and brine, and dried over Na_2SO_4. The solvent was then evaporated in vacuo to give yellow oil, which was purified by column chromatography to the products.

4.6.1. (2*Z*,4*Z*)-*N*1,*N*6-Bis(4-phenyl)-2,3,4,5-tetrapropyl hexa-2,4-dienediamide (5a). White solid, 65% isolated yield, mp: 184–185 °C. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.82–1.94 (m, 12H), 1.27–1.46 (m, 8H), 2.09–2.13 (m, 4H), 2.29–2.32 (m, 4H), 7.08–7.62 (m, 10H), 9.24 (s, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.1, 14.7, 21.6, 22.1, 32.6, 37.0, 119.9, 124.1, 128.9, 134.3, 138.3, 142.3, 170.4. HRMS calcd for $C_{30}H_{40}N_2O_2$: 460.3090, found: 460.3083. Anal. Calcd for $C_{30}H_{40}N_2O_2$: C, 78.22%; H, 8.75%; N, 6.08%. Found: C, 78.45%; H, 8.79%; N, 6.01%.

4.6.2. (2*Z*,4*Z*)-*N*1,*N*6-Bis(2-chlorophenyl)-2,3,4,5-tetrapropyl hexa-2,4-dienediamide (5b). White solid, 80% isolated yield, mp: 130–131 °C. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.89 (t, J=7.2 Hz, 6H), 0.92 (t, J=7.2 Hz, 6H), 1.33–1.57 (m, 8H), 2.15–2.22 (m, 4H), 2.35 (t, J=7.8 Hz, 4H), 6.99–8.27 (m, 8H), 8.88 (s, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.1, 14.8, 21.6, 22.0, 32.5, 37.0, 122.7, 123.8, 124.7, 127.5, 129.2, 133.4, 134.9, 144.1, 169.8. HRMS calcd for $C_{30}H_{38}N_2O_2Cl_2$: 528.2310, found: 528.2310. Anal. Calcd for $C_{30}H_{38}N_2O_2Cl_2$: C, 68.24%; H, 7.28%; N, 5.22%. Found: C, 68.04%; H, 7.23%; N, 5.29%.

4.6.3. (2*Z*,4*Z*)-*N*1,*N*6-Bis(2,4-dichlorophenyl)-2,3,4,5-tetrapropyl hexa-2,4-dienediamide (5c). White solid, 89% isolated yield, mp: 133–134 °C. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.89 (t, J=7.5 Hz, 6H), 0.92 (t, J=7.5 Hz, 6H), 1.34–1.51 (m, 8H), 2.14–2.20 (m, 4H), 2.34 (t, J=7.8 Hz, 4H), 7.21–8.24 (m, 6H), 8.88 (s, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.1, 14.8, 21.6, 22.0, 32.5, 37.0, 123.4, 124.4, 127.7, 128.9, 129.2, 133.3, 133.7, 144.4, 169.8. HRMS calcd for $C_{30}H_{36}N_2O_2Cl_4$: 596.1531, found: 596.1518. Anal. Calcd for $C_{30}H_{36}N_2O_2Cl_4$: C, 60.21%; H, 4.68%; N, 6.06%. Found: C, 60.36%; H, 4.59%; N, 6.12%.

4.6.4. (2*Z*,4*Z*)-*N*1,*N*6-Bis(2-chlorophenyl)-2,3,4,5-tetraethyl hexa-2,4-dienediamide (5d). White solid, 71% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 1.03–1.08 (m, 12H), 2.24–2.46 (m, 8H), 7.01–8.30 (m, 8H), 8.86 (s, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 12.8, 13.3, 23.4, 27.3, 122.6, 123.7, 124.8, 127.5, 129.2, 134.2, 134.9, 144.5, 169.7. HRMS calcd for $C_{26}H_{30}N_2O_2Cl_2$: 472.1684, found: 472.1686.

4.6.5. Compound 5e. White solid, 59% isolated yield, mp: 127–128 °C. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.86 (t, J=7.2 Hz, 6H), 1.35–1.39 (m, 4H), 1.52–1.76 (m, 4H), 2.03–2.11 (m, 2H), 2.22–2.31 (m, 4H), 2.86–2.91 (m, 2H), 6.95–7.61 (m, 8H), 8.41–8.44 (m, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.0, 22.3, 28.7, 32.1, 34.1, 121.6, 122.2, 124.2, 127.8, 128.6, 132.4, 134.8, 143.4, 168.2. HRMS calcd for $C_{28}H_{32}N_2O_2Cl_2$: 498.1841, found: 498.1831. Anal. Calcd for $C_{28}H_{32}N_2O_2Cl_2$: C, 67.33%; H, 6.46%; N, 5.61%. Found: C, 67.58%; H, 6.54%; N, 5.42%.

4.6.6. Compound 5f. White solid, 62% isolated yield, mp: 101–102 °C. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 1.55–1.85 (m, 4H), 2.42–2.61 (m, 4H), 6.76–7.49 (m, 18H), 8.39 (m, 1H), 8.41 (m, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 28.7, 36.0, 120.2, 122.2, 123.8, 127.5, 128.2, 129.0, 129.7, 130.0, 134.8, 136.8, 151.9, 166.4. HRMS calcd for $C_{34}H_{28}N_2O_2Cl_2$: 566.1528, found: 566.1528. Anal. Calcd for $C_{34}H_{28}N_2O_2Cl_2$: C, 71.96%; H, 4.97%; N, 4.94%. Found: C, 72.13%; H, 5.06%; N, 4.83%.

4.7. General procedure for the preparation of multiply substituted hexa-2,4-dienedioic acid bisamide derivatives (5) and multiply substituted penta-2,4-dienoic acid amide derivatives (6)

The procedure was basically the same as above. Depending on the substituents of the Ar group of ArNCO, mono-amide and/or bisamide derivatives were obtained as mixtures.

4.7.1. (2*Z*,4*Z*)-*N*1,*N*6-Bis(4-methylphenyl)-2,3,4,5-tetrapropyl hexa-2,4-dienediamide (5g). White solid, 34% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.86 (t, J=7.2 Hz, 6H), 0.87 (t, J=7.2 Hz, 6H), 1.30–1.50 (m, 8H), 2.09–2.15 (m, 4H), 2.25–2.33 (m, 10H), 7.09–7.51 (m, 8H), 9.06 (s, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.1, 14.7, 20.9, 21.6, 22.1, 32.6, 37.0, 119.9, 129.3, 133.6, 134.4, 135.8, 142.1, 170.2. HRMS calcd for $C_{32}H_{44}N_2O_2$: 488.3403, found: 488.3407.

4.7.2. (2*Z*,4*Z*)-*N*1,*N*6-Bis(4-fluorophenyl)-2,3,4,5-tetrapropyl hexa-2,4-dienediamide (5h). White solid, 26% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.85 (t, J=7.2 Hz, 6H), 0.87 (t, J=7.2 Hz, 6H), 1.22–1.50 (m, 8H), 2.10–2.20 (m, 4H), 2.26–2.34 (m, 4H), 6.96–7.59 (m, 8H), 9.30 (s, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.1, 14.7, 21.6, 22.1, 32.6, 37.0, 115.5 (d, J=22.3 Hz, 2C), 121.6 (d, J=8.1 Hz, 2C), 134.2, 134.3 (d, J=3.1 Hz, 1C), 142.3, 159.3 (d, J=241.1 Hz, 1C), 170.4. HRMS calcd for $C_{30}H_{38}N_2O_2F_2$: 496.2901, found: 496.2902.

4.7.3. (2*Z*,4*Z*)-*N*1,*N*6-Bis(4-chlorophenyl)-2,3,4,5-tetrapropyl hexa-2,4-dienediamide (5i). White solid, 23% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.86 (t, J=7.2 Hz, 12H), 1.24–1.49 (m, 8H), 2.08–2.13 (m, 4H), 2.30 (t, J=7.8 Hz, 4H), 7.25–7.57 (m, 8H), 9.17 (s, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.1, 14.7, 21.6, 22.1, 32.6, 37.0, 121.1, 128.9, 129.1, 134.2, 136.8, 142.6, 170.5. HRMS calcd for $C_{30}H_{38}N_2O_2Cl_2$: 528.2310, found: 528.2303.

4.7.4. 2,3,4-Tripropyl-octa-2,4-dienoic acid (4-methylphenyl)-amide (6a). White solid, 21% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.81 (t, J=7.5 Hz, 3H), 0.89–0.97 (m, 9H), 1.23–1.51 (m, 8H), 1.93–1.98 (m, 2H), 2.00–2.18 (m, 4H), 2.29 (s, 3H), 2.34–2.39 (m, 2H), 5.47 (t, J=7.2 Hz, 1H), 7.07–7.34 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.9, 14.1, 14.8, 20.8, 21.4, 22.2, 22.6, 22.9, 30.2, 32.3, 33.2, 119.4, 129.4, 130.8, 133.4, 134.9, 135.8, 139.9, 144.4, 170.0. HRMS calcd for $C_{24}H_{37}NO$: 355.2875, found: 355.2871.

4.7.5. 2,3,4-Tripropyl-octa-2,4-dienoic acid (4-fluorophenyl)-amide (6b). White solid, 40% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.80 (t, J=7.5 Hz, 3H), 0.90–0.98 (m, 9H), 1.24–1.49 (m, 8H), 1.95–1.99 (m, 2H), 2.11–2.19 (m, 4H), 2.34–2.39 (m, 2H), 5.46 (t, J=7.2 Hz, 1H), 7.20–7.43 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.9, 14.1, 14.8, 21.4, 22.3, 22.7, 22.9, 30.2, 32.33, 32.38, 33.1, 115.5 (d, J=22.2 Hz, 2C), 121.0 (d, J=7.4 Hz, 2C), 130.9, 134.4 (d, J=2.5 Hz, 1C), 134.7, 139.9, 144.9, 159.2 (d, J=241.1 Hz, 1C), 170.1. HRMS calcd for $C_{23}H_{34}NOF$: 359.2624, found: 359.2637.

4.7.6. 2,3,4-Tripropyl-octa-2,4-dienoic acid (4-chlorophenyl)-amide (6c). White solid, 30% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.80 (t, J=7.5 Hz, 3H), 0.90–0.98 (m, 9H), 1.20–1.25 (m, 2H), 1.36–1.48 (m, 6H), 1.94–1.97 (m, 2H), 2.10–2.19 (m, 4H), 2.33–2.39 (m, 2H), 5.46 (t, J=7.2 Hz, 1H), 7.22–7.42 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.9, 14.1, 14.8, 21.4, 22.3, 22.7, 22.9, 30.2, 32.3, 32.26, 33.31, 120.5, 128.7, 128.9, 131.1, 134.6, 137.0, 140.0, 145.1, 170.2. HRMS calcd for $C_{23}H_{34}NOCl$: 375.2329, found: 375.2331.

4.7.7. 2,3,4-Tripropyl-octa-2,4-dienoic acid (4-bromophenyl)-amide (6d). White solid, 54% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.80 (t, J=7.2 Hz, 3H), 0.89–0.98 (m, 9H), 1.18–1.50 (m, 8H), 1.91–1.99 (m, 2H), 2.09–2.18 (m, 4H), 2.33–2.38 (m, 2H), 5.45 (t, J=7.2 Hz, 1H), 7.21–7.41 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.9, 14.1, 14.8, 21.4, 22.3, 22.7, 22.9, 30.2, 32.2, 32.3, 33.1, 116.2, 120.7, 131.1, 131.9, 134.6, 137.4, 139.8, 145.2, 170.2. HRMS calcd for $C_{23}H_{34}NOBr$: 419.1824, found: 419.1837.

4.8. Procedure for the preparation of (2*Z*,4*E*)-4-deutero-(4-bromophenyl)-2,3,4-tripropylhepta-2,4-dienamide (6eD)

4-Octyne (4.0 mmol) was added into a toluene solution of [Cp_2ZrBu_2] (Negishi reagent), prepared in situ from Cp_2ZrCl_2 (2.0 mmol, 0.58 g) and *n*-BuLi (4.0 mmol, 2.6 mL, 1.60 M hexane solution) in toluene (20 mL) at −78 °C. The reaction mixture was then stirred at room temperature for 1 h to afford zirconacyclopentadiene. 4-Bromophenyl isocyanate (4.0 mmol) and $EtAlCl_2$ (8.0 mmol, 8.8 mL, 0.9 M hexane solution) were added to this solution at −78 °C. After stirring the reaction mixture at −30 °C for 1 h, the above reaction mixture was quenched with DCl (0.3 mL, 20%) and extracted with Et_2O. The extract was washed with water and brine, and dried over $MgSO_4$. The solvent was then evaporated in vacuo to give yellow oil, which was purified by column chromatography to the products as yellow oil in 47% isolated yield, D>90%. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.80 (t, J=7.2 Hz, 3H), 0.89–0.98 (m, 9H), 1.20–1.47 (m, 8H), 1.92–1.97 (m, 2H), 2.09–2.18 (m, 4H), 2.33–2.38 (m, 2H), 7.19–7.41 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.9, 14.1, 14.8, 21.4, 22.3, 22.7, 22.8, 30.1, 32.2, 32.3, 33.1, 116.2, 120.7, 131.9, 134.6, 137.4, 139.7, 145.1, 170.2. HRMS calcd for $C_{23}H_{33}DNOBr$: 420.1887, found: 420.1874.

4.9. Procedure for the preparation of butadienyl iodide 6I

3-Hexyne (4.0 mmol) was added into a toluene solution of [Cp_2ZrBu_2] (Negishi reagent), prepared in situ from Cp_2ZrCl_2 (2.0 mmol, 0.58 g) and *n*-BuLi (4.0 mmol, 2.6 mL, 1.60 M hexane solution) in toluene (20 mL) at −78 °C. The reaction mixture was then stirred at room temperature for 1 h to afford zirconacyclopentadiene. 4-Bromophenyl isocyanate (4.0 mmol) and $EtAlCl_2$ (8.0 mmol, 8.8 mL, 0.9 M hexane solution) were added to this solution at −78 °C. After being stirred at −30 °C for 1 h, the above reaction mixture was treated with I_2 (2 mmol) and stirred for another 1 h before quenching with saturated aqueous $NaHCO_3$ and extracting with Et_2O. The extract was washed with water and brine, and dried over $MgSO_4$. The solvent was then evaporated in vacuo to give yellow oil, which was purified by column chromatography to give the product **6I** as yellow oil in 68% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.92–1.13 (m, 12H), 2.13–2.59 (m, 8H), 7.39–7.50 (m, 4H), 7.91 (s, 1NH). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 12.6, 12.8, 13.0, 14.8, 22.9, 26.1, 27.4, 34.4, 110.1, 116.3, 120.7, 131.9, 135.1, 137.3, 145.7, 148.6, 168.6. HRMS calcd for $C_{19}H_{25}NOBrI$: 489.0164, found: 489.0168.

4.10. General procedure for the preparation of mixed bisamide derivative

A monoyne (2.0 mmol) was added into a toluene solution of [Cp_2ZrBu_2] (Negishi reagent),[16] prepared in situ from Cp_2ZrCl_2 (1.0 mmol, 0.29 g) and *n*-BuLi (2.0 mmol, 1.3 mL, 1.60 M hexane solution) in toluene (10 mL) at −78 °C. The reaction mixture was then stirred at room temperature for 1 h to afford zirconacyclopentadiene. The first isocyanate (1.4 mmol) and $EtAlCl_2$ (5.6 mmol, 6.2 mL, 0.9 M hexane solution) were added to this solution at −78 °C and the reaction mixture was stirred at −35 °C for 1 h. Then, the second isocyanate (1.5 mmol) was added to the above reaction mixture at −35 °C. After stirring at room temperature for 12 h, the above reaction mixture was quenched with 3 N HCl and extracted with EtOAc. The extract was washed with water and brine, and dried over MgSO4. The solvent was then evaporated in vacuo to give yellow oil, which was purified by column chromatography to the products.

4.10.1. (2*Z*,4*Z*)-*N*1-(4-Bromophenyl)-*N*6-(2,4-dichlorophenyl)-2,3,4,5-tetrapropyl hexa-2,4-dienediamide (9a). White solid, 39% isolated yield, mp: 116–117 °C. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.79–0.92 (m, 12H), 1.22–1.52 (m, 8H), 2.01–2.22 (m, 6H), 2.42–2.48 (m, 2H), 7.26–7.54 (m, 6H), 7.85 (s, 1H), 8.28 (d, J=8.7 Hz, 1H), 10.36 (s, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.0, 14.2, 14.67, 14.69, 21.3, 21.75, 21.84, 22.6, 32.2, 32.8, 36.9, 37.2, 115.8, 120.8, 122.9, 124.0, 128.1, 129.0, 130.0, 131.65, 131.74, 132.7, 136.1, 138.2, 139.4, 147.2, 169.5, 171.1. HRMS calcd for $C_{30}H_{37}BrCl_2N_2O_2$: 606.1416, found: 606.1421. Anal. Calcd for $C_{30}H_{37}BrCl_2N_2O_2$: C, 59.22%; H, 6.13%; N, 4.60%. Found: C, 59.34%; H, 6.09%; N, 4.45%.

4.10.2. (2*Z*,4*Z*)-*N*1-(4-Bromophenyl)-*N*6-(2-chlorophenyl)-2,3,4,5-tetraethyl hexa-2,4-dienediamide (9b). White solid, 51% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.95–1.09 (m, 12H), 2.10–2.36 (m, 6H), 2.45–2.57 (m, 2H), 7.12–7.87 (m, 8H), 8.30–8.33 (m, 1H), 10.56 (s, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 12.5, 13.0, 13.2, 13.8, 23.3, 23.4, 27.4, 115.7, 120.8, 122.3, 123.6, 125.5, 127.9, 129.3, 131.6, 132.7, 133.9, 136.9, 138.2, 139.9, 147.2, 169.6,

171.0. HRMS calcd for $C_{26}H_{30}N_2O_2BrCl$: 516.1179, found: 516.1184.

4.11. General procedure for the preparation of compounds 11

To a THF and H_2O (1:1, 5 mL) solution of compound **2** (1.0 mmol) at room temperature was added NBS (1.0 mmol). The above reaction mixture was then stirred at room temperature for 3 h to generate compound **11**, which was monitored by GC analysis or by TLC. The above reaction mixture was then extracted with diethyl ether. The extract was washed with brine and dried over $MgSO_4$. The solvent was evaporated in vacuo to give a red-orange oil, which was purified by column chromatography to afford **11**.

4.11.1. Compound 11a. White solid, 89% isolated yield, mp: 89–90 °C. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.85–1.09 (m, 12H), 1.62–1.72 (m, 8H), 2.34–2.38 (m, 8H), 6.76–7.82 (m, 6H), 8.96 (s, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.9, 14.0, 14.5, 15.1, 17.0, 20.5, 21.5, 21.6, 26.6, 29.7, 34.1, 39.0, 81.9, 97.0, 122.2, 123.4, 125.1, 126.7, 127.2, 127.7, 128.3, 128.78, 128.81, 130.2, 132.7, 134.7, 144.0, 154.7, 162.5, 165.4. HRMS calcd for $C_{30}H_{35}N_2O_2Cl_4Br$: 674.0636, found: 674.0636. Anal. Calcd for $C_{30}H_{35}N_2O_2Cl_4Br$: C, 53.20%; H, 5.21%; N, 4.14%. Found: C, 53.42%; H, 5.19%; N, 4.05%.

4.11.2. Compound 11b. White solid, 98% isolated yield, mp: 92–93 °C. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.74 (t, J=7.2 Hz, 3H), 1.07 (t, J=6.8 Hz, 3H), 1.23–1.90 (m, 6H), 1.95–2.03 (m, 2H), 2.42–2.59 (m, 6H), 6.67–7.91 (m, 8H), 9.06 (s, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 8.0, 11.4, 12.6, 13.0, 17.8, 20.1, 25.1, 30.4, 83.2, 97.1, 121.8, 122.8, 123.7, 124.7, 125.4, 126.5, 126.6, 128.4, 129.0, 129.1, 134.1, 136.3, 145.1, 154.1, 161.7, 162.3. HRMS calcd for $C_{26}H_{29}N_2O_2Cl_2Br$: 550.0789, found: 550.0785. Anal. Calcd for $C_{26}H_{29}N_2O_2Cl_2Br$: C, 56.54%; H, 5.29%; N, 5.07%. Found: C, 56.62%; H, 5.26%; N, 4.89%.

4.11.3. Compound 11c (1:1 mixture). Colorless oil, 75% isolated yield. *Isomer 1*: ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.77 (t, J=7.2 Hz, 3H), 0.97 (t, J=7.3 Hz, 3H), 1.17 (t, J=7.5 Hz, 3H), 1.24 (t, J=7.8 Hz, 3H), 1.60–2.63 (m, 9H), 6.92–8.06 (m, 9H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 7.2, 12.1, 12.6, 13.3, 17.6, 19.5, 20.8, 27.4, 58.0, 94.2, 122.9, 123.0, 123.9, 124.2, 125.3, 126.8, 126.9, 127.5, 129.1, 129.4, 133.9, 134.5, 145.1, 155.8, 162.2, 169.7. HRMS calcd for $C_{26}H_{30}N_2O_2Cl_2$: 472.1684, found: 472.1682. *Isomer 2*: ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.73 (t, J=7.2 Hz, 3H), 0.98 (t, J=7.5 Hz, 3H), 1.20 (t, J=7.8 Hz, 3H), 1.28 (t, J=7.5 Hz, 3H), 1.41–2.63 (m, 9H), 6.93–8.19 (m, 9H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 7.1, 11.6, 12.6, 13.4, 17.7, 18.7, 20.4, 27.6, 57.5, 94.2, 122.4, 122.5, 123.9, 124.2, 124.7, 125.7, 127.1, 127.3, 128.9, 129.7, 134.4, 145.3, 154.3, 161.8, 170.8. HRMS calcd for $C_{26}H_{30}N_2O_2Cl_2$: 472.1684, found: 472.1688.

4.11.4. Compound 11d (1:5 mixture). White solid, 60% isolated yield. *Isomer 1*: ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.81 (t, J=7.2 Hz, 3H), 1.09 (t, J=6.9 Hz, 3H), 1.23 (t, J=7.8 Hz, 6H), 1.94–2.52 (m, 8H), 6.92–8.10 (m, 8H), 9.02 (s, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 8.2, 12.5, 13.0, 14.7, 18.0, 20.3, 26.4, 33.6, 74.3, 97.0, 121.5, 123.1, 124.1, 124.7, 125.7, 126.9, 127.1, 127.4, 129.3, 129.4, 134.4, 136.3, 144.7, 154.2, 161.0, 166.1. *Isomer 2*: ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.79 (t, J=7.2 Hz, 3H), 1.12 (t, J=6.8 Hz, 3H), 1.31 (t, J=7.7 Hz, 6H), 1.91–2.55 (m, 8H), 6.68–7.81 (m, 8H), 8.70 (s, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 8.7, 12.6, 12.9, 15.1, 17.9, 20.3, 24.9, 32.0, 71.9, 97.1, 122.3, 122.7, 123.8, 125.4, 125.6, 126.5, 126.7, 127.2, 129.1, 129.3, 134.4, 136.7, 145.0, 155.3, 161.2, 166.0. HRMS calcd for $C_{26}H_{29}N_2O_2Cl_2I$: 598.0651, found: 598.0660. Anal. Calcd for $C_{26}H_{29}N_2O_2Cl_2I$: C, 52.10%; H, 4.88%; N, 4.67%. Found: C, 52.26%; H, 4.99%; N, 4.61%. Mp: 118–119 °C.

Acknowledgements

This work was supported by the Natural Science Foundation of China and the Major State Basic Research Development Program (2006CB806105). Cheung Kong Scholars Programme, Qiu Shi Science and Technologies Foundation, and Dow Corning Corporation are gratefully acknowledged.

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.02.015.

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