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Haloamidation of alkynes and related reactions using zirconacycles and isocyanates

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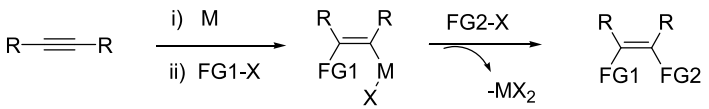
Abstract—Zirconacyclopentenes reacted with isocyanates to give aza- or oxazirconacycles which were conveniently coverted into the corresponding haloamidation products of alkynes after halogenation. 1,4-Bistrimethylsilyl substituted zirconacyclopentadiene afforded a low yield of iodoamidation product, whereas zirconium–alkyne complexes stabilized with phosphine gave the iodoamidation products in moderate yields. On the other hand, zirconacyclopentanes reacted with isocyanates to give trimerization products of isocyanate, isocyanurates.

1. Introduction

Metallacycles are very useful intermediates in organic synthesis since they can be readily prepared from alkynes or alkenes and low-valent metal species.[1] Zirconacycles, including zirconacyclopentanes,[2] zirconacyclopentenes,[3] and zirconacyclopentadienes,[4] have been conveniently prepared from Cp_2ZrEt_2 or Cp_2ZrBu_2. A variety of novel reactions have been developed by the reaction of zirconacycles with alkynes,[5] alkenes[6] and other unsaturated molecules.[7] Addition of two functional groups to alkynes is one of the most important and attractive reactions to obtain stereodefined bifunctionalized olefins from alkynes. Stepwise bifunctionalization of alkynes using Zr can be classified into two ways. One way is shown in Scheme 1 where M traps the leaving group X from FG1–X in the intermediate.

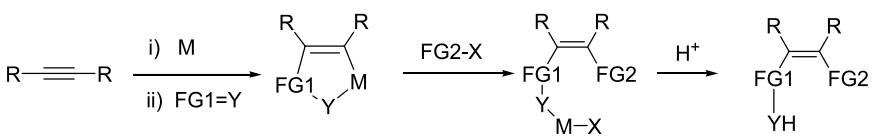
This way consists of allylzirconation of alkynes,[8] vinylzirconation of alkynes,[9] alkynylzirconation of alkynes[10] and metalloesterification of alkynes.[11] The other way is shown in Scheme 2 where coupling reaction of alkynes with unsaturated compounds on Zr affords zirconacycles. Haloamidation reaction we describe here belongs to this way.

Herein we would like to report haloamidation of alkynes by the reaction of zirconacyclopentenes with isocyanates (Scheme 3). Iodoamidation of trimethylsilyl substituted



FG1, FG2: functional groups

Scheme 1. FG1, FG2: functional groups.



Scheme 2.

Keywords: Zirconacyclopentene; Zirconacyclopentadiene; Zirconacyclopentane; Haloamidation; Isocyanate; Isocyanurate; Trimerization of isocyanate.
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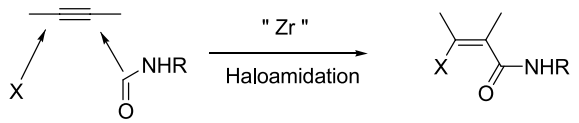


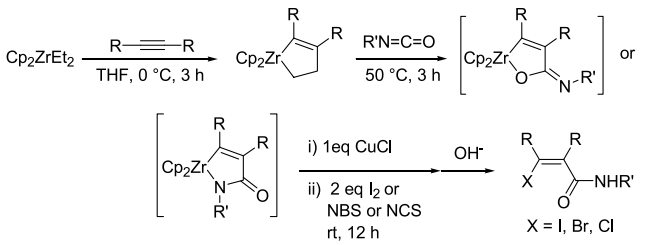
Scheme 3.

alkynes could be also achieved through zirconacylopentadienes. On the other hand, we found that zirconacyclopentane is a reactive catalyst for trimerization of isocyanates.

2. Results and discussion

2.1. Haloamidation of alkynes using zirconacyclopentenes and isocyanates

We have already reported that Cp_2ZrEt_2, prepared in situ from Cp_2ZrCl_2 and 2 equiv. of EtMgBr, reacted with an alkyne to give zirconacyclopentenes. The ethylene moiety of zirconacyclopentenes could be easily replaced by unsaturated compounds via β,β′ carbon–carbon bond cleavage reaction. We have also reported the formation of symmetrical or unsymmetrical zirconacyclopentadienes with the second alkynes,[4c] oxazirconacyclopentenes with aldehydes,[12] and azazirconacyclopentadienes with nitriles[12] using this strategy. In a similar way, as shown in Eq. 1, reaction of zirconacyclopentenes with isocyanates as unsaturated compounds smoothly gave oxa- or aza-zirconacycles[13d] which afforded the iodoamidation products of an alkyne by treatment with I_2 in the presence of CuCl followed by hydrolysis (Eq. 1). In the absence of CuCl, the reaction did not complete even when 4 equiv. of halogenation reagent was added.



(1)

Representative results were summarized in Table 1. Alkyl substituted alkynes (Table 1, entries 1, 3, and 4), such as 3-hexyne, 4-octyne, could be used in the reaction and gave moderate yields of the products (45, 48, 43% for **1a**, **1c**, **1d**, respectively). Aryl substituted alkynes, for example, dithienyl acetylene (Table 1, entry 12), bis(methoxyphenyl) acetylene (Table 1, entry 13) also gave the corresponding iodoamidation products (**1l**, **1m**) in good yields. In the case of diphenyl acetylene, phenyl isocyanate as well as butyl isocyanate could be employed in the reaction and resulted in the formation of the desired products (**1h**, **1i**) in high yields (Table 1, entries 8 and 9).

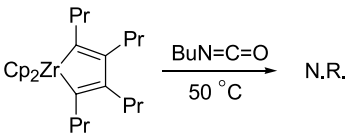
There were several reports on a coupling reaction of an alkyne and an isocyanate on early transition metals. However, only hydrolysis or other type of reaction have been reported.[13] Moreover, there is no information on the metal-containing species. In order to observe the intermediate, we monitored this reaction by NMR spectroscopy. When diphenyl substituted zirconacyclopentene reacted with butyl isocyanate at 50 °C for 3 h, ^{1}H NMR spectrum of the reaction mixture showed the peak of Cp protons at 6.05 ppm as a singlet. Its ^{13}C NMR spectrum showed the Cp at 112.38 ppm. Other signals appeared at 228.13 ppm (C–Zr), 152.18 ppm (β-carbon), 178.52 ppm (carbonyl- or imino-carbon), and four carbons for the butyl group at 14.45, 20.61, 32.09, 41.67 ppm, respectively. It indicated that there was only one kind of zirconacycle produced in the reaction mixture. Although we could not make clear whether it is an azazirconacycle or an oxazirconacycle. Effort was also made for preparing crystals suitable for X-ray analysis, but not successful so far.

When thus formed aza- or oxa-zirconacycles were treated with *N*-bromosuccinimide (NBS) in the presence of stoichiometric amount of CuCl, the corresponding bromoamidation products were obtained. Results of bromoamidation of various alkynes were also shown in Table 1. Not only the alkyl and aryl substituted alkynes (Table 1, entries 2, 5, 7, and 10) resulted in good yields of the bromoamidation products (**1b**, **1e**, **1g**, **1j**), but also the trimethyl silyl substituted alkynes (Table 1, entry 14) gave reasonable yields of the desired product (**1n**).

We applied the similar strategy for the chloroamidation of alkynes. It should be pointed out that EtMgCl was used instead of EtMgBr for the preparing of Cp_2ZrEt_2 in order to avoid the halogen exchange reaction.[11] When *N*-chlorosuccinimide (NCS) was employed instead of NBS in the reaction, the corresponding chloride derivatives (**1f**, **1k**) were produced in good to high yields (Table 1, entries 6 and 11).

2.2. Iodoamidation of alkynes using zirconacyclopentadienes and isocyanates

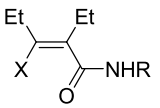
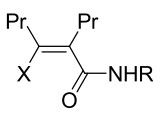
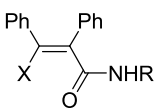
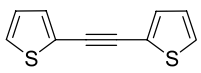
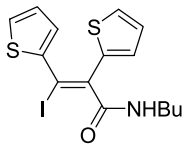
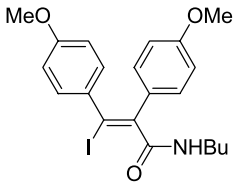
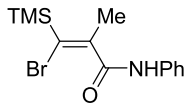
Tetrapropyl substituted zirconacyclopentadiene, prepared in situ from Cp_2ZrBu_2 and 2 equiv. of 4-octyne, did not react with butyl isocyanate. Zirconacyclopentadienes remained unreacted (Eq. 2).



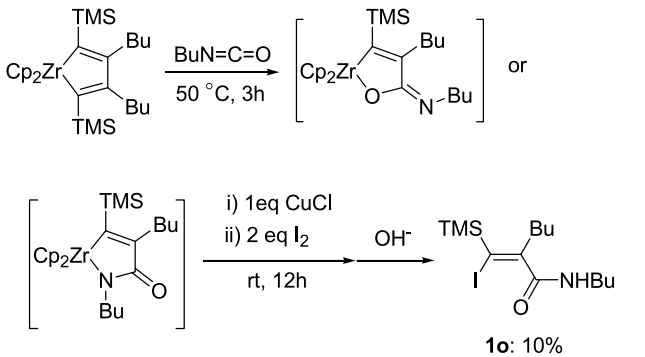
(2)

When 2 equiv. of CuCl or 1 equiv. of $NiCl_2(PPh_3)_2$ was added to the reaction mixture, the zirconacyclopentadiene was consumed, but no identified products were obtained. Yet if the 1,4-bis-trimethylsilyl substituted zirconacyclopentadiens were employed in the reaction, oxa- or aza-zirconacycle was formed, but around 50% of the zirconacyclopentadiene remained.[14] Therefore, iodoamidation product **1o** of alkyne was produced in low yield (10%) after iodination (Eq. 3).

Table 1. Haloamidation of alkynes using zirconacyclopentenes[a]

Entry	Alkyne	Isocyanate	Product	Yield (%)[b]
1	Et—≡—Et	RN=C=O	 (R=Ph, X=I: **1a**)	45
2			(R=Ph, X=Br: **1b**)	58
3			(R=Bu, X=I: **1c**)	48
4	Pr—≡—Pr	RN=C=O	 (R=Ph, X=I: **1d**)	43
5			(R=Ph, X=Br: **1e**)	62
6			(R=Ph, X=Cl: **1f**)	53
7			(R=Bn, X=Br: **1g**)	70
8	Ph—≡—Ph	RN=C=O	 (R=Ph, X=I: **1h**)	70
9			(R=Bu, X=I: **1i**)	57
10			(R=Bu, X=Br: **1j**)	46
11			(R=Bu, X=Cl: **1k**)	90
12		BuN=C=O	 (**1l**)	56
13	MeO—≡—OMe	BuN=C=O	 (**1m**)	82
14	TMS—≡—Me	PhN=C=O	 (**1n**)	38

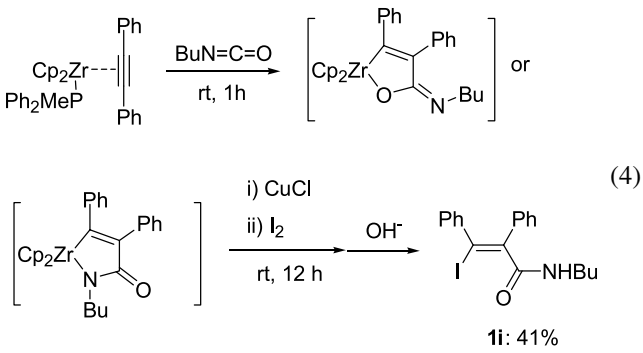
[a] Reaction conditons: 1:1.5:1:2 molar ratio of alkyne, isocyanete, CuCl and halogenation reagent, hydrolyzed with sat. $NaHCO_3$ aq.
[b] Isolated yield.



(3)

2.3. Iodoamidation of alkynes mediated by zirconium alkyne complexes

It is known that a zirconium alkyne complex stabilized by $MePPh_2$ reacted with isocyanate to give the corresponding oxa- or aza-zirconacycle.[15] Iodoamidation products were obtained after iodination (Eq. 4).



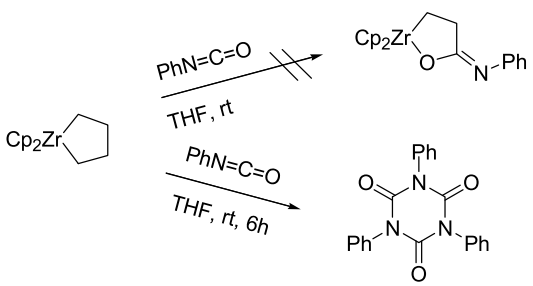
(4)

When diphenylacetylene was used in the reaction, compound **1i** was obtained in 41% isolated yield. Alkyl substituted alkynes usually are not suitable for this reaction because its zirconium alkyne complexes were not stable and gave homocoupling products.

2.4. Reaction of zirconacyclopentanes with isocyanates

In order to investigate the scope of the reaction of zirconacycles, we tried the reaction of zirconacyclopentane with isocyanates. Zirconacyclopentane has shown similar

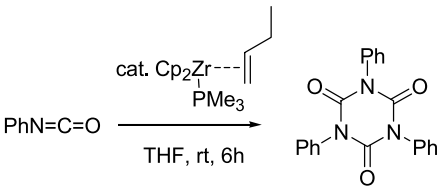
reactivity towards aldehydes or ketones to afford oxazirconacyclopentanes. We expected the similar oxa- or azazirconacycles would be formed in the case of isocyanates. However, cyclotrimerization compound **2a** of phenyl isocyanate was obtained as the sole product when phenyl isocyanate was employed (Eq. 5).



(5)

2a: 79%

Cyclotrimerization of phenyl isocyanate was reported by many groups using base or Lewis acid.[16] Catalytic cyclotrimerization of isocyanates using metallocene, however, has not been reported. This prompted us to investigate the trimerization using various zirconocene compounds. The use of catalytic amount (10 mol%) of the zirconium 1-butene complex stabilized with trimethyl phosphine afforded cyclotrimerization product in 71% yield (Eq. 6).

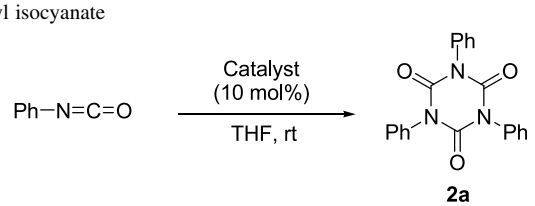


(6)

2a: 71%

Various group 4 metallocenes were used for the trimerization. The results were summarized in Table 2. Dibutylzirconocene and dibutyl hafnocene catalyzed the trimerization and both gave the product in 82% yields in 6 h. Dibutyltitanocene gave only 7% of the isocyanurate. This may be due to the instability of the titanocene complex. While zirconocene complex bearing bulky ligand such as *t*-butylcyclopentadienyl could catalyze the reaction smoothly. Metallocene dihalide of group 4 metals gave low yields of the corresponding trimer even after 48 h. In the case of dimethylzirconocene, product was obtained in 46% yield within 24 h.

Table 2. Group 4 metallocene complexes catalyzed cyclotrimerization of phenyl isocyanate

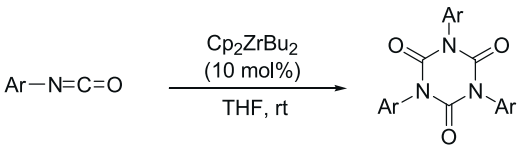


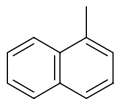
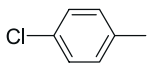
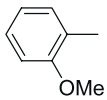
2a

Entry	Catalyst	Time (h)	Yield (%)[a]
1	Cp_2ZrBu_2	6	82
2	Cp_2TiBu_2	6	7
3	Cp_2HfBu_2	6	82
4	$(t\text{-}BuC_5H_4)_2ZrBu_2$	6	79
5	Cp_2ZrCl_2	48	28
6	Cp_2TiCl_2	48	28
7	Cp_2HfCl_2	48	20
8	Cp_2ZrMe_2	24	46

[a] Isolated yield.

Table 3. Zirconocene catalyzed cyclotrimerization of aryl isocyanates

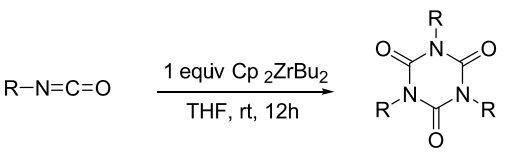


Entry	Ar	Time (h)	Product	Yield (%)[a]
1		6	**2b**	82
2		6	**2c**	78
3		24	**2d**	60

[a] Isolated yield.

Among all these catalysts, dibutyl zirconocene gave the best result. We applied these conditions to the trimerization of other aryl isocyanates. Results were given in Table 3. 1-Naphthyl isocyanate reacted smoothly to give the corresponding isocyanurate **2b** in 82% yield for 6 h. Isocyanate containing electron-withdrawing group such as *p*-chloro phenyl isocyanate also gave 78% (**2c**) yields, while 2-methoxyphenyl isocyanate gave moderate yield of the product (**2d**) even after prolonged reaction time (24 h).

Alkyl isocyanates are less reactive for the trimerization reaction compared with aryl isocyantes.[16g] Dibutylzirconocene could not catalyze its trimerization. Stoichiometric amount of the dibutyl zirconocene was necessary to achieve reasonable yields of the trimer (Eq. 7).



(7)

2e: R = Et, 61%
2f: R = Bn, 68%

3. Conclusion

Alkyl, aryl as well as trimethylsilyl substituted alkynes could be conveniently converted to the corresponding iodoamidation bromoamidation chloroamidation products in good to high yields using zirconacyclopentenes. Zirconacyclopentenes reacted with isocyanates to give oxa- or azazirconacycles. The intermediate was observed by NMR study. Aryl isocyanates were trimerized by a catalytic amount of zirconacyclopentane and dibutylzirconocene.

Trimerization of alkyl isocyanates required a stoichiometric amount of zirconocene complex.

4. Experimental

4.1. General

Unless otherwise noted, all starting materials were commercially available and were used without further purification All reactions were run under a slightly positive pressure of dry N_2. THF was refluxed and distilled from sodium benzophenone ketyl under a nitrogen atmosphere. Zirconocene dichloride was purchased from Nichia Corporation. Ethylmagnesium bromide(THF solution), *n*-butyllithium(hexane solution), were purchased from Kanto Chemicals Co., Ltd. CuCl was purchased from Wako. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker-400 or JEOL JNM-300 NMR spectrometer. GC analysis was performed on a gas chromatograph equipped with a flame ionization detector using a capillary column (CBP1-M25-025).

4.2. Haloamidation reaction

4.2.1. A typical procedure for iodoamidation of alkynes via zirconacyclopentenes. To a solution of Cp_2ZrCl_2 (1.75 g, 6.0 mmol) in 25 mL of THF, EtMgBr (0.89 M hexane solution, 13.5 mL, 12.0 mmol) was added at 78 °C. After stirring for 1 h at −78 °C, 4-octyne (0.734 mL, 5.0 mmol) was added and the reaction mixture was warmed to 0 °C for 3 h. Then phenyl isocyanate (0.815 mL, 7.5 mmol) was added and the reaction mixture was stirred at 50 °C for 3 h. And then CuCl (495 mg, 5.0 mmol) and iodine (2.53 g, 10.0 mmol) were added. The reaction mixture was stirred at room temperature for 12 h. Then it was quenched with saturated $NaHCO_3$ solution, filtrated through celite, extracted with AcOEt. The organic layer was dried over Na_2SO_4. Purification by flash column chromatography gave **1d** (43%).

4.2.2. A typical procedure for bromoamidation of alkynes via zirconacyclopentenes. A similar procedure as described above for iodoamidation. Using NBS instead of I_2 gave the bromination products.

4.2.3. A typical procedure for the chloroamidation of alkynes via zirconacyclopentenes. This reaction was also carried out in a similar manner as that for iodination. EtMgCl should be used instead of EtMgBr to avoid halogen exchange reaction.[11] The use of NCS instead of I_2 gave the desired products.

4.2.4. A typical procedure for the iodoamidation of alkynes via zirconacyclopentadiene. To a solution of Cp_2ZrCl_2 (351 mg, 1.2 mmol) in 5 mL of THF, *n*-BuLi (1.58 M hexane solution, 1.52 mL, 2.4 mmol) was added at −78 °C. After stirring for 1 h at −78 °C, 1-trimethylsilyl-1-hexyne (0.404 mL, 2.0 mmol) was added and the reaction mixture was warmed to room temperature for 1 h. Then butyl isocyanate (0.163 mL, 1.5 mmol) was added and the reaction mixture was heated to 50 °C for 3 h. Then CuCl (99 mg, 1.0 mmol) and I_2 (1012 mg, 4.0 mmol) were added. The resulting mixture was stirred for 12 h. After quenching with saturated $NaHCO_3$ solution the mixture was extracted with AcOEt. The organic layer was dried over Na_2SO_4. Purification by flash column chromatography gave the product in 40 mg (isolated yield 10%).

4.2.5. A typical procedure for the iodoamidation of alkynes via zirconium alkyne complexes. To a solution of Cp_2ZrCl_2 (351 mg, 1.2 mmol) in 5 mL of THF, *n*-BuLi (1.58 M hexane solution, 1.52 mL, 2.4 mmol) was added at −78 °C. After stirring for 1 h at −78 °C, $MePPh_2$ (0.223 mL, 1.2 mmol) was added and the reaction mixture was warmed to room temperature for 1 h. Then diphenyl acetylene (178 mg, 1.0 mmol) was added and the mixture was stirred for 1 h. Then butyl isocyanate (0.163 mL, 1.5 mmol) was added and the reaction mixture was stirred for 1 h. To the mixture CuCl (99 mg, 1.0 mmol) and I_2 (1012 mg, 4.0 mmol) were added and the mixture was stirred for 12 h. After quenching with saturated $NaHCO_3$ solution the mixture was extracted with AcOEt. The organic layer was dried over Na_2SO_4. Purification by flash column chromatography gave the product in 167 mg (isolated yield 41%).

4.3. Preparation of aza- or oxa-zirconacycle

To a THF solution of 2.0 mmol of Cp_2ZrEt_2, which was prepared from Cp_2ZrCl_2 (2.2 mmol, 643 mg) and EtMgBr (0.86 M THF solution, 5.2 mL, 4.4 mmol) in 5.0 mL THF at −78 °C, was added diphenylacetylene (356 mg, 2.0 mmol). After stirring the mixture at 0 °C for 3 h, buthyl isocyanate (0.335 mL, 3.0 mmol) was added to the reaction mixture at 0 °C. The mixture was kept at 50 °C for 3 h and evaporated to dry in vacuo. The residue was dissolved in 5.0 mL of benzene. After filtration, the resulting solid was dissolved in C_6D_6 and characterized by NMR.

4.3.1. 2-Ethyl-3-iodopent-2-enoic acid phenylamide (1a). Isolated yield 45%. Colorless solid: mp 109–112 °C. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.13 (t, J=7.6 Hz, 3H), 1.14 (t, J=7.4 Hz, 3H), 2.48 (q, J=7.6 Hz, 2H), 2.61 (q, J=7.4 Hz, 2H), 7.12–7.16 (m, 1H), 7.26 (bs, 1H), 7.32–7.37 (m, 2H), 7.56–7.58 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.44, 14.12, 25.07, 34.24, 105.11, 120.12, 124.67, 129.00, 137.35, 145.54, 169.09; IR (nujol) 3193, 1647, 1592, 758 cm^{-1}; HRMS calcd for $C_{13}H_{16}INO$ 329.0277, found 329.0285.

4.3.2. 3-Bromo-2-ethylpent-2-enoic acid phenylamide (1b). Isolated yield 58%. Colorless solid: mp 104–106 °C. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.14 (t, J=7.6 Hz, 3H), 1.20 (t, J=7.3 Hz, 3H), 2.53 (q, J=7.6 Hz, 2H), 2.64 (q, J=7.3 Hz, 2H), 7.14–7.18 (m, 2H), 7.34–7.38 (m, 2H), 7.53–7.55 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.05, 13.88, 28.50, 32.74, 119.84, 124.86, 129.18, 132.84, 137.23, 138.33, 166.44; IR (nujol) 3252, 2988, 1636, 1539, 760 cm^{-1}; HRMS calcd for $C_{13}H_{16}BrNO$ 281.0415, found 281.0409.

4.3.3. 2-Ethyl-3-iodopent-2-enoic acid butylamide (1c). Isolated yield 48%. Pale yellow oil. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.95 (t, J=7.3 Hz, 3H), 1.07 (t, J=7.6 Hz, 3H), 1.09 (t, J=7.3 Hz, 3H), 1.37–1.46 (m, 2H), 1.53–1.62 (m, 2H), 2.39 (q, J=7.6 Hz, 2H), 2.55 (q, J=7.3 Hz, 2H), 3.31–3.36 (m, 2H), 5.46 (bs, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ

13.43, 13.71, 14.12, 20.23, 24.82, 31.23, 34.14, 39.30, 104.13, 145.75, 171.12; IR (neat) 3283, 2938, 1631, 1547 cm^{-1}; HRMS calcd for $C_{11}H_{20}INO$ 309.0590, found 309.0570.

4.3.4. 3-Iodo-2-propylhex-2-enoic acid phenylamide (1d). Isolated yield 43%. Colorless solid: mp 95–96 °C. ^1H NMR ($CDCl_3$, Me_4Si) δ 0.96 (t, J=7.3 Hz, 3H), 0.98 (t, J=7.4 Hz, 3H), 1.53–1.65 (m, 4H), 2.42–2.46 (m, 2H), 2.54–2.58 (m, 2H), 7.07 (bs, 1H), 7.13–7.17 (m, 1H), 7.34–7.38 (m, 2H), 7.55–7.57 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.10, 13.19, 21.99, 22.61, 34.05, 42.39, 103.95, 120.12, 124.74, 129.06, 137.33, 145.18, 169.19; IR (nujol) 3249, 2973, 1599, 1539, 758 cm^{-1}. Anal. calcd for $C_{15}H_{20}INO$: C,50.43; H, 5.64; N, 3.92. Found: C, 50.71; H, 5.63; N, 3.60.

4.3.5. 3-Bromo-2-propylhex-2-enoic acid phenylamide (1e). Isolated yield 62%. Colorless solid: mp 72–74 °C. ^1H NMR ($CDCl_3$, Me_4Si) δ 0.95 (t, J=7.3 Hz, 3H), 0.96 (t, J=7.3 Hz, 3H), 1.52–1.67 (m, 4H), 2.37–2.41 (m, 2H), 2.49–2.52 (m, 2H), 7.10–7.14 (m, 1H), 7.30–7.34 (m, 2H), 7.58–7.59 (m, 2H), 7.65 (bs, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.19, 13.79, 21.34, 21.65, 33.76, 38.71, 120.04, 124.40, 124.81, 128.80, 137.47, 138.46, 167.67; IR (nujol) 3276, 2967, 1651, 1537, 754 cm^{-1}. Anal. Calcd for $C_{15}H_{20}BrNO$: C, 58.07; H, 6.50; Br, 25.76; N, 4.51. Found: C, 57.76; H, 6.46; Br, 25.69; N, 4.44.

4.3.6. 3-Chloro-2-propylhex-2-enoic acid phenylamide (1f). Isolated yield 53%. Colorless solid: mp 85–86.5 °C. ^1H NMR ($CDCl_3$, Me_4Si) δ 0.96 (t, J=7.4 Hz, 3H), 0.98 (t, J=7.4 Hz, 3H), 1.50–1.57 (m, 2H), 1.64–1.70 (m, 2H), 2.38–2.45 (m, 4H), 7.12–7.15 (m, 1H), 7.30 (bs, 1H), 7.32–7.36 (m, 2H), 7.55–7.57 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.41, 13.87, 20.71, 21.88, 33.25, 37.03, 119.98, 124.53, 128.98, 132.98, 135.27, 137.52, 166.71; IR (nujol) 3268, 2977, 1659, 1618, 1537, 756 cm^{-1}; HRMS calcd for $C_{15}H_{20}ClNO$ 265.1233, found 265.1246.

4.3.7. 3-Bromo-2-propylhex-2-enoic acid benzylamide (1g). Isolated yield 70%. Colorless solid: mp 54–56 °C. ^1H NMR ($CDCl_3$, Me_4Si) δ 0.93 (t, J=7.3 Hz, 3H), 0.94 (t, J=7.3 Hz, 3H), 1.45–1.66 (m, 4H), 2.31–2.36 (m, 2H), 2.44–2.49 (m, 2H), 4.52 (d, J=5.7 Hz, 2H), 5.08 (bs, 1H), 7.27–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.24, 13.84, 21.41, 21.77, 33.80, 38.77, 43.79, 124.40, 127.60, 128.15, 128.65, 137.67, 138.32, 169.51; IR (nujol) 3243, 3108, 1628, 1559, 1316, 731 cm^{-1}; HRMS calcd for $C_{16}H_{22}BrNO$ 323.0884, found 323.0877.

4.3.8. 3-Iodo-2,3,*N*-triphenylacrylamide (1h). Isolated yield 70%. Colorless solid: mp 222–223 °C. ^1H NMR ($CDCl_3$, Me_4Si) δ 7.13–7.25 (m, 11H), 7.33–7.37 (m, 3H), 7.58–7.60 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 100.82, 120.18, 124.89, 128.15, 128.18, 128.38, 128.45, 128.97, 129.08, 129.47, 135.28, 137.36, 142.35, 145.91, 167.71; IR (nujol) 2975, 2867, 1653, 1545, 754, 696 cm^{-1}; HRMS calcd for $C_{21}H_{16}INO$ 405.0590, found 405.0591.

4.3.9. *N*-Butyl-3-iodo-2,3-diphenylacrylamide (1i). Isolated yield 57%. Colorless solid: mp 131–132 °C. ^1H NMR ($CDCl_3$, Me_4Si) δ 0.92 (t, J=7.3 Hz, 3H), 1.36–1.41 (m, 2H), 1.54–1.62 (m, 2H), 3.34–3.39 (m, 2H), 5.78 (m, 1H), 7.09–7.20 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.68, 20.12, 31.18, 39.56, 99.63, 127.81, 127.99, 128.09, 128.17, 128.79, 129.43, 135.60, 142.48, 146.29, 169.86; IR (nujol) 2969, 1640, 1543, 694 cm^{-1}; HRMS calcd for $C_{19}H_{20}INO$ 405.0590, found 405.0591.

4.3.10. 3-Bromo-*N*-butyl-2,3-diphenylacrylamide (1j). Isolated yield 46%. Colorless solid: mp 138–139.5 °C. ^1H NMR ($CDCl_3$, Me_4Si) δ 0.93 (t, J=7.3 Hz, 3H), 1.34–1.45 (m, 2H), 1.53–1.62 (m, 2H), 3.35–3.41 (m, 2H), 5.77 (bs, 1H), 7.14–7.26 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.69, 20.09, 31.31, 39.52, 122.47, 127.94, 128.08, 128.31, 128.63, 128.78, 129.78, 135.60, 138.77, 140.00, 168.48; IR (nujol) 3279, 1628, 1543, 694 cm^{-1}; HRMS calcd for $C_{19}H_{20}BrNO$ 357.0728, found 357.0723.

4.3.11. *N*-Butyl-3-chloro-2,3-diphenylacrylamide (1k). Isolated yield 90%. Colorless solid: mp 152–155 °C. ^1H NMR ($CDCl_3$, Me_4Si) δ 0.74 (t, J=7.3 Hz, 3H), 0.92–1.01 (m, 2H), 1.08–1.15 (m, 2H), 3.01–3.06 (m, 2H), 5.39 (bs, 1H), 7.33–7.44 (m, 6H), 7.53–7.54 (m, 2H), 7.57–7.61 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.61, 19.71, 30.81, 39.47, 128.34, 128.37, 128.38, 128.41, 128.80, 129.42, 134.79, 136.08, 137.18, 138.13, 167.21; IR (nujol) 3241, 1626, 1543, 696 cm^{-1}; HRMS calcd for $C_{19}H_{20}ClNO$ 313.1254, found 313.1233.

4.3.12. 3-Iodo-*N*-phenyl-2,3-dithiophen-2-ylacrylamide (1l). Isolated yield 56%. Colorless solid: mp 104–107 °C. ^1H NMR ($CDCl_3$, Me_4Si) δ 0.96 (t, J=7.3 Hz, 3H), 1.41–1.47 (m, 2H), 1.60–1.67 (m, 2H), 3.42–3.47 (m, 2H), 5.79 (m, 1H), 6.86 (dd, J=5.1, 3.7 Hz, 1H), 6.98 (dd, J=5.1, 3.7 Hz, 1H), 7.03 (dd, J=3.7, 0.8 Hz, 1H), 7.12 (dd, J=3.7, 0.8 Hz, 1H), 7.20 (dd, J=5.1, 0.8 Hz, 1H), 7.42 (dd, J=5.1, 0.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.69, 20.17, 31.08, 39.71, 86.18, 126.33, 127.23, 128.23, 128.28, 129.35, 129.58, 136.70, 142.32, 144.09, 169.03; IR (nujol) 2936, 1638, 1547, 702 cm^{-1}; HRMS calcd for $C_{15}H_{16}INOS_2$ 416.9736, found 416.9718.

4.3.13. 3-Iodo-2,3-bis (4-methoxyphenyl)-*N*-phenylacrylamide (1m). Isolated yield 82%. Colorless solid: mp 138–140 °C. ^1H NMR ($CDCl_3$, Me_4Si) δ 0.93 (t, J=7.3 Hz, 3H), 1.35–1.44 (m, 2H), 1.54–1.62 (m, 2H), 3.34–3.40 (m, 2H), 3.73 (s, 3H), 3.76 (s, 3H), 5.62 (bt, J=5.3 Hz, 1H), 6.64–6.70 (m, 4H), 7.03–7.05 (m, 2H), 7.14–7.17 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.65, 20.09, 31.18, 39.48, 55.02, 55.11, 113.35, 113.53, 128.07, 130.12, 130.99, 134.96, 145.02, 158.82, 158.97, 170.42; IR (nujol) 2942, 1634, 1505, 1254 cm^{-1}; HRMS calcd for $C_{21}H_{24}INO_3$ 465.0795, found 465.0801.

4.3.14. 3-Bromo-2-methyl-*N*-phenyl-3-trimethylsilylacrylamide (1n). Isolated yield 38%. Colorless solid: mp 115–117 °C. ^1H NMR ($CDCl_3$, Me_4Si) δ 0.34 (s, 9H), 2.13 (s, 3H), 7.13–7.16 (m, 1H), 7.21 (bs, 1H), 7.33–7.37 (m, 2H), 7.56–7.58 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 0.33, 20.12, 120.09, 124.69, 124.93, 129.05, 137.26, 146.58, 168.20; IR (nujol) 2934, 1657, 1615, 1250 cm^{-1}; HRMS calcd for $C_{13}H_{18}BrNOSi$ 311.0341, found 311.0361.

4.3.15. 2-(Iodotrimethylsilanylmethylene)hexanoic acid butylamide (1o). Isolated yield 10%. Pale yellow oil: ^1H

NMR ($CDCl_3$, Me_4Si) δ 0.16 (s, 9H), 0.74 (t, J=7.3 Hz, 3H), 0.79 (t, J=7.3 Hz, 3H), 1.12–1.21 (m, 2H), 1.23–1.33 (m, 4H), 1.39–1.47 (m, 2H), 2.25–2.29 (m, 2H), 3.16–3.21 (m, 2H), 5.49 (bt, J=5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 1.39, 13.56, 13.67, 20.09, 22.38, 30.93, 31.07, 35.13, 39.01, 104.62, 158.51, 171.32; IR (neat) 2965, 1631, 1615, 1250 cm^{-1}; HRMS calcd for $C_{14}H_{28}INOSi$ 381.0985, found 381.0980.

4.4. A typical procedure for the preparation of triphenyl isocyanurate

To a solution of Cp_2ZrCl_2 (29 mg, 0.1 mmol) in THF (5 mL) was added *n*-BuLi (1.58 M hexane solution, 0.13 mL, 0.2 mmol) at −78 °C and stirred for 1 h. The mixture was warmed to room temperature and stirred for 1 h. Phenyl isocyanate (357 mg, 3.0 mmol) was added and stirred for 6 h at room temperature. Then the reaction mixture was quenched with saturated $NaHCO_3$ and extracted with EtOAc. The extract was washed with brine and dried over $MgSO_4$. The solvent was evaporated in vacuo and the residue was purified by chromatography on silica gel.

4.4.1. Triphenyl isocyanurate (2a).[16] Isolated yield 82%. Colorless solid: mp 279–280 °C. ^1H NMR ($CDCl_3$, Me_4Si) δ 7.33–7.51 (m, 15H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 128.21, 128.75, 129.16, 133.40, 148.45; HRMS calcd for $C_{21}H_{15}N_3O_3$ 357.1113, found 351.1154.

4.4.2. Tris(1-naphthyl) isocyanurate (2b). Isolated yield 82%. Colorless solid: mp >300 °C. ^1H NMR ($CDCl_3$, Me_4Si) δ 7.52 (d, J=7.3 Hz, 3H), 7.58 (d, J=8.1 Hz, 3H), 7.67 (d, J=7.5 Hz, 3H), 7.70 (d, J=6.9 Hz, 3H), 7.90–7.97 (m, 9H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 120.59, 125.45, 126.55, 127.28, 127.74, 129.03, 129.90, 129.99, 130.32, 134.58, 148.74; HRMS calcd for $C_{33}H_{21}N_3O_3$ 507.1583, found 507.1609.

4.4.3. Tris(*p*-chlorophenyl) isocyanurate (2c).[16a] Isolated yield 78%. Colorless solid: mp >300 °C. ^1H NMR ($CDCl_3$, Me_4Si) δ 7.31 (d, J=8.8 Hz, 6H), 7.47 (d, J=8.6 Hz, 6H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 129.70, 129.73, 131.71, 135.59, 148.13; HRMS calcd for $C_{21}H_{12}Cl_3N_3O_3$ 458.9941, found 458.9930.

4.4.4. Tris(*o*-methoxyphenyl) isocyanurate (2d).[16a] Isolated yield 60%. Colorless solid: mp 259–261 °C. ^1H NMR ($CDCl_3$, Me_4Si) δ 3.86 (s, 9H), 6.86 (dd, J=7.6,1.3 Hz, 3H), 6.94–6.99 (m, 6H), 8.10 (dd, J=7.6, 1.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 55.66, 110.06, 119.56, 121.19, 122.82, 128.08, 148.08; HRMS calcd for $C_{24}H_{21}N_3O_6$ 447.1430, found 447.1462.

4.4.5. Triethyl isocyanurate (2e).[16g] Isolated yield 61%. Pale yellow solid: mp 92–94 °C. ^1H NMR ($CDCl_3$, Me_4Si) δ 1.20 (d, J=6.9 Hz, 9H), 3.91 (t, J=6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.05, 38.08, 148.58; HRMS calcd for $C_9H_{15}N_3O_3$ 213.1103, found 213.1089.

4.4.6. Tribenzyl isocyanurate (2f). Isolated yield 68%. Colorless solid: mp 157–158 °C. ^1H NMR ($CDCl_3$, Me_4Si) δ 5.02 (s, 6H), 7.28–7.34 (m, 9H), 7.43 (dd, J=7.2, 1.6 Hz, 6H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 46.24, 128.14, 128.61, 129.05, 135.76, 149.09; HRMS calcd for $C_{24}H_{21}N_3O_3$ 399.1583, found 399.1557.

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