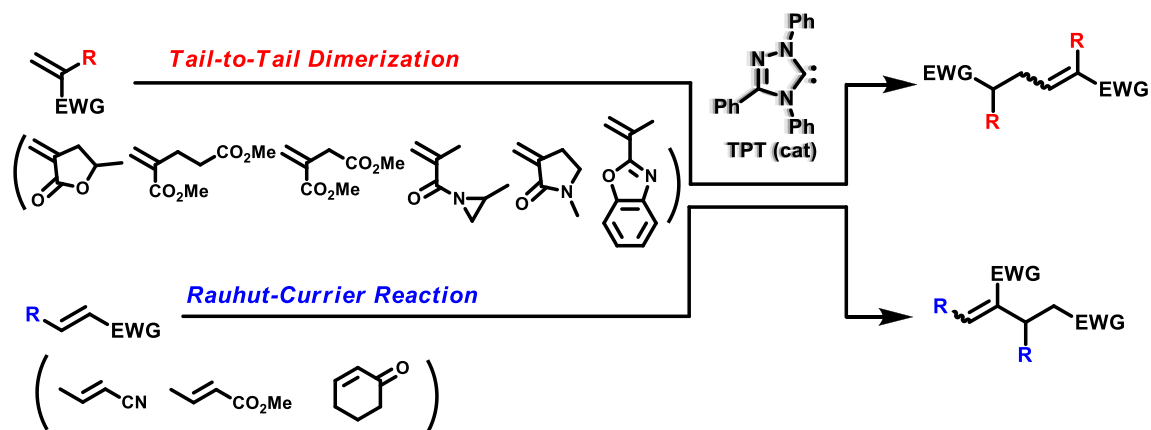


## Graphical Abstract

### Tail-to-Tail Dimerization and Rauhut-Currier Reaction of Disubstituted Michael Acceptors Catalyzed by N-Heterocyclic Carbene

Shin-ichi Matsuoka,\* Naoki Awano, Masanori Nakazawa, Masato Suzuki





## Tail-to-Tail Dimerization and Rauhut-Currier Reaction of Disubstituted Michael Acceptors Catalyzed by N-Heterocyclic Carbene

Shin-ichi Matsuoka,\* Naoki Awano, Masanori Nakazawa, Masato Suzuki

*Department of Life Science and Applied Chemistry, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, Aichi 466-8555, Japan*

### ARTICLE INFO

#### Article history:

Received  
Received in revised form  
Accepted  
Available online

#### Keywords:

N-Heterocyclic Carbene  
Tail-to-Tail Dimerization  
Rauhut-Currier Reaction  
Disubstituted Michael Acceptors  
deoxy-Breslow intermediate

### ABSTRACT

The N-heterocyclic carbene (NHC)-catalyzed dimerizations of a variety of disubstituted Michael acceptors have been investigated. In addition to the tail-to-tail dimerization of methacrylates reported previously, the scope of vinylidene substrates expands to  $\gamma$ -methyl- $\alpha$ -methylene- $\gamma$ -butyrolactone, dimethyl 2-methylenepentanedioate, dimethyl itaconate, methacrylamides, and 2-isopropenylbenzoxazole, none of which have been dimerized by metal-catalyzed counterparts. In contrast, vinylene substrates, such as crotononitrile, methyl crotonate, and 2-cyclohexen-1-one, do not undergo the dimerization probably due to the steric hindrance of the  $\beta$ -substituent. Instead, the Rauhut-Currier (RC) reaction of these was found to proceed. The stoichiometric reaction of crotononitrile with NHC indicates that this RC reaction also involves the deoxy-Breslow intermediate and the reversible proton transfer.

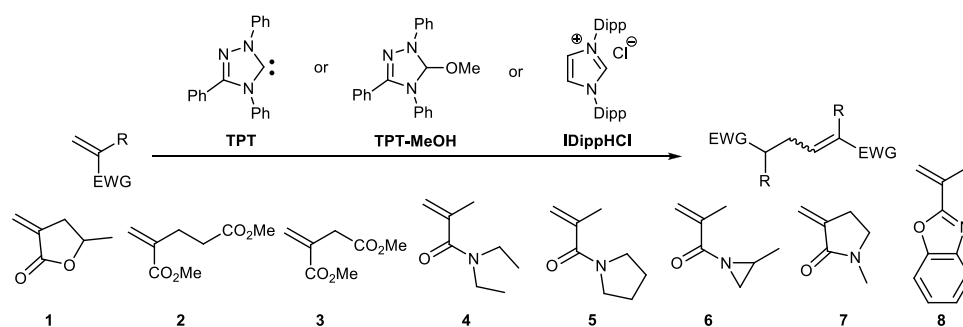
### 1. Introduction

Dimerizations of Michael acceptors, such as the Rauhut-Currier (RC) reaction<sup>1</sup> and the tail-to-tail dimerization,<sup>2-4</sup> are important C–C bond forming reactions for the synthesis of bifunctional compounds. The RC reaction, namely the vinylogous Morita-Baylis-Hillman reaction, is usually catalyzed by nucleophilic phosphines or amines to form the C–C bond at the  $\alpha$ -carbon of Michael acceptors. The reaction has been applied for various transformations including not only intermolecular dimerization but also intramolecular cyclization, enantioselective synthesis, and total synthesis. Alternatively, the tail-to-tail dimerization is a C–C bond forming reaction between the  $\beta$  carbons of Michael acceptors. The transition metal catalysis of these reactions has been investigated for more than two decades. The dimers produced from acrylates and acrylonitrile are expected to be precursors of adipic acid and hexamethylenediamine. However, the metal-catalyzed dimerization of vinylidene substrates is a difficult process. Indeed, there are only a few reports on the metal-catalyzed dimerization of methacrylates,<sup>4</sup> and, to our knowledge, none of other vinylidene substrates.

N-Heterocyclic carbene (NHC)<sup>5</sup> has been extensively used in synthetic chemistry. This unique nucleophile can catalyze *umpolung* reactions of Michael acceptors,<sup>6</sup> as the electrophilic  $\beta$ -carbons of Michael acceptors can be converted to the key nucleophilic intermediate, termed, the deoxy-Breslow

intermediate. This leads to various reactions, including cyclization,<sup>7</sup> tail-to-tail dimerization,<sup>8</sup> rearrangement,<sup>9</sup> polyaddition,<sup>8i, 10</sup> and transfer hydrogenation.<sup>11</sup> The key intermediate is produced by the proton transfer of the zwitterionic intermediate generated from NHC and the substrate. Alternatively, the zwitterionic intermediate, in some cases, directly reacts with electrophiles, leading to RC reaction,<sup>12</sup> Morita-Baylis-Hillman reaction,<sup>13</sup> cycloaddition,<sup>14</sup> cyclopropanation,<sup>15</sup> and oxa-Michael addition.<sup>16</sup> We and the Glorius groups independently reported the first tail-to-tail dimerization catalyzed by NHC in 2011.<sup>8a, b</sup> The only effective NHC catalyst has been 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene (TPT),<sup>17</sup> developed by Enders, while the scope of substrates of the tail-to-tail dimerization has been expanded to methacrylates,<sup>8a, b, c</sup> methacrylonitrile,<sup>8d</sup> activated styrenes,<sup>8e, f</sup> vinylpyridines,<sup>8e, f</sup> acrylates,<sup>8f</sup> acrylamides,<sup>8f, g</sup> and acrylonitrile.<sup>8f</sup> In contrast to the metal-catalyzed system, a much broader substrate scope has been achieved, since the NHC has enough nucleophilicity to add to various Michael acceptors and good tolerance to functional groups. Recently, Waymouth et al. reported that the RC reactions of crotonates were catalyzed by 1,3-diisopropyl-4,5-dimethyl-imidazol-2-ylidene (IiPr<sub>2</sub>Me<sub>2</sub>) or *t*-BuOK, but not by other NHC catalysts, 1,3-dimesitylimidazol-2-ylidene (IMes) and TPT.<sup>12</sup> In this paper, we report the tail-to-tail dimerizations and RC reactions of electron-deficient vinylidene and vinylene substrates, respectively, catalyzed by TPT.

## 2. Results and Discussion

Table 1. Tail-to-Tail Dimerization of **1-8** Catalyzed by NHC

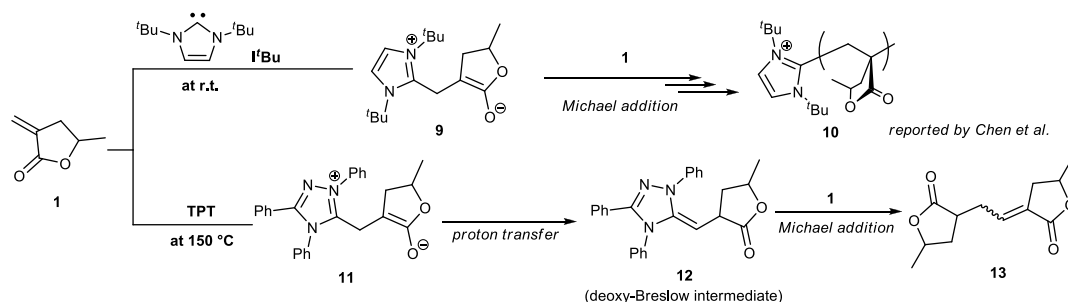
Entry	Substrate	Cat		Additive		Temp <sup>a</sup> °C	Solvent	Time h	Yield (%)		E/Z <sup>b</sup>
		Type	mol%	Type	mol%				Isolated	NMR	
1	<b>1</b>	TPT	10			r.t.	1,4-DOX	24		trace	-
2	<b>1</b>	TPT	10			60	1,4-DOX	2		27	—
3	<b>1</b>	TPT	10			80	1,4-DOX	2		60	98:2
4	<b>1</b>	TPT	10			80	toluene	2		11	—
5	<b>1</b>	TPT-MeOH	10			100	1,4-DOX	2		75	94:6
6	<b>1</b>	TPT	10			150	1,4-DOX	2		57	89:11
7	<b>1</b>	TPT-MeOH	10			150	1,4-DOX	2	74	83	93:7
8	<b>1</b>	IDippHCl	10	DBU	10	150	1,4-DOX	2		trace	
9	<b>1</b>	IDippHCl	10	<i>t</i> -BuOK	10	150	1,4-DOX	2		0	
10	<b>2</b>	TPT	10			150	1,4-DOX	2		36	72:28
11	<b>2</b>	TPT	10	MeOH	200	150	1,4-DOX	2		48	75:25
12	<b>2</b>	TPT-MeOH	10			150		2	68	100	79:21
13	<b>2</b>	TPT-MeOH	2			150		2		13	71:29
14	<b>2</b>	TPT-MeOH	2	MeOH	200	150		2		11	62:38
15	<b>3</b>	TPT-MeOH	10			150		2	40		83:17
16	<b>4</b>	TPT-MeOH	10			150		2		0	
17	<b>5</b>	TPT-MeOH	10			150		2		0	
18	<b>6</b>	TPT-MeOH	10			130		2		0	
19	<b>6</b>	TPT-MeOH	10			100	1,4-DOX	2	50	90	99:1
20	<b>7</b>	TPT-MeOH	10			150		2		trace	
21	<b>7</b>	TPT-MeOH	10			130		2	70	78	99:1
22	<b>8</b>	TPT-MeOH	10			150		2	21		30:70

<sup>a</sup> entries 2-4; oil bath heating, entries 5-22; microwave irradiation.

<sup>b</sup> calculated by <sup>1</sup>H NMR. For entries 7, 12, 19, and 21, the data of isolated product are shown. The E/Z ratio of the crude product of entry 21 is 87:13.

Chen *et al.* reported that the vinyl addition polymerization of  $\gamma$ -methyl- $\alpha$ -methylene- $\gamma$ -butyrolactone (**1**) was initiated by 1,3-di-*tert*-butylimidazolin-2-ylidene (I*t*Bu) in DMF at room temperature.<sup>18</sup> IMes and TPT were less effective for this polymerization, and no tail-to-tail dimer of **1** was obtained. Our previous report showed that the tail-to-tail dimerization of acrylates and acrylonitrile requires high temperature (~150 °C) despite their high electron-deficiency.<sup>8f</sup> Thus, we envisioned that use of TPT at such a high temperature would promote the dimerization of vinylidene substrates. Our results for the dimerization of **1** are summarized in Table 1 (entries 1-9). The reaction at room temperature did not give the dimer (entry 1), but the broad <sup>1</sup>H NMR signals of the crude product suggested the polymerization took place. The increase of the temperature to 80, 100, and 150 °C led to the formation of the tail-to-tail dimer in good yields as expected (entries 3, 5-7). The best yield was obtained at 150 °C, and the product was isolated in 74% yield with a high E/Z ratio of 93:7 (entry 7). 1,4-Dioxane (1,4-DOX) was a better solvent than toluene (entries 3 and 4), and the methanol TPT adduct (TPT-MeOH), which generates TPT *in situ*, was a more efficient catalyst than TPT prepared from TPT-MeOH before use (entries 3, 6 and 7).

Since we have shown that the additive alcohol promotes the intermolecular proton transfer in the tail-to-tail dimerizations of methacrylonitrile<sup>8d</sup> and acrylates<sup>8f</sup>, the methanol generated *in situ* from TPT-MeOH may have such an effect on the catalysis. 1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (IDipp), generated *in situ* from IDippHCl and base (*t*BuOK or DBU), was not effective (entries 8 and 9). This catalyst specificity has been similarly observed for other substrates reported previously.<sup>8</sup> As shown in Scheme 1, the reaction of **1** with a catalytic amount of NHC results in two distinct pathways, the polymerization and the tail-to-tail dimerization. The zwitterionic ester enolate (**9**) generated from I*t*Bu and **1** undergoes consecutive Michael addition at room temperature to produce the polymer (**10**). In contrast, the analogous intermediate (**11**) derived from TPT is selectively transformed to the deoxy-Breslow intermediate (**12**) by the proton transfer at high temperature, and the subsequent Michael addition to **1** produces the tail-to-tail dimer (**13**). The structure of NHC and the reaction temperature are key factors to determine the reaction pathway, the Michael addition or the proton transfer, of the zwitterionic intermediates (**9** and **11**).



**Scheme 1.** Polymerization<sup>18</sup> and Tail-to-Tail Dimerization of **1** Initiated and Catalyzed by NHCs.

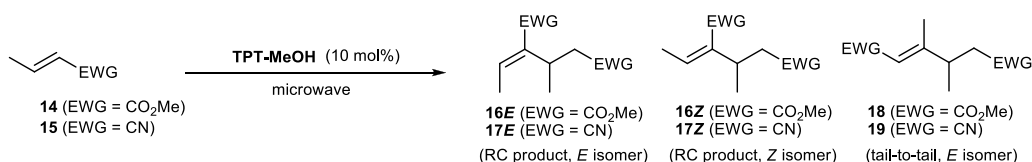
We next examined the dimerization of **2**, which is the RC dimer produced from methyl acrylate by tri-*n*-butyl phosphine catalyst. The reaction of **2** using 10 mol% of TPT-MeOH at 150 °C without solvent gave the tail-to-tail dimer in 100% <sup>1</sup>H NMR yield (68% isolated yield) (entry 12), though the yields were less than moderate when using 1,4-dioxane as the solvent (entries 10 and 11). The yield was decreased at 2 mol% of catalyst loading, and the additive alcohol was not effective (entries 13 and 14). It is interesting to note that the tetraester (the dimer of **2**) can be synthesized from methyl acrylate by the two-step organocatalytic reactions, i.e., the RC reaction and the subsequent tail to-tail dimerization. A similar diester substrate, dimethyl itaconate (**3**), also afforded the corresponding dimer in 40% isolated yield (entry 15).

The dimerizations of four kinds of methacrylamides (**4-7**) were attempted under similar conditions (entries 16-21). No reactions of **4** and **5** took place at 150 °C without solvent, while the dimers of **6** and **7** were obtained. The reaction of **6** at 130 °C without solvent gave a complex mixture, but the milder conditions of 100 °C in 1,4-dioxane produced the dimer in 90% <sup>1</sup>H NMR yield. The reaction of the cyclic substrate, **7**, proceeded at 130 °C without solvent to give the dimer in 70% isolated yield. It is known that the  $\pi$ -conjugation between the vinylidene and carbonyl groups of *N,N*-dialkyl methacrylamide is poor due to

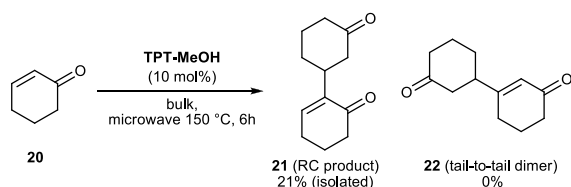
the steric hindrance between *N*-alkyl and vinylidene groups.<sup>19</sup> Thus, no nucleophilic attack of NHC to **4** and **5** occurs at all. In contrast, **6** and **7** are conjugated substrates, because the sterically less hindered aziridinyll group of **6** and the restricted conformation of **7** did not cause such a twisted conformation.<sup>19, 20</sup> The reaction of 2-isopropenylbenzoxazole (**8**) at 150 °C also proceeded to give the dimer in 21% yield (entry 22). The *Z* isomer is somewhat favored in this case. Since **8** has an anionic polymerizability comparable to methacrylates,<sup>21</sup> the benzoxazole group shows an electron-withdrawing property enough to undergo this dimerization.

With suitable reaction conditions for the dimerizations of the vinylidenes in hand, we then examined vinylene substrates (Table 2). The reaction of methyl crotonate (**14**) at 150 °C and 200 °C without solvent gave a mixture of dimers in ~10% yields (entries 1 and 2). The mixture contains the tail-to-tail dimer (**18**) and the *E* and *Z* isomers of the RC products. For the dimerization of crotononitrile (**15**), the total yield of the dimer mixture was more than 30%, when the reaction was carried out at 150 °C without solvent (entry 4). The yield of the tail-to-tail dimer (**19**) was only minimal, while the *E* isomer of the RC product (**17E**) was obtained in 26% yield. 2-Cyclohexen-1-one (**20**) also undergoes the RC reaction selectively to give **21**, without formation of the tail-to-tail dimer (**22**) (Scheme 2).

**Table 2.** Rauhut-Currier (RC) Reaction of Methyl Crotonate and Crotononitrile.



Entry	Substrate	Temp °C	Solvent	<sup>1</sup> H NMR Yield (%)		
				<b>16E, 17E</b>	<b>16Z, 17Z</b>	<b>18, 19</b>
1	<b>14</b>	150	-	4	2	3
2	<b>14</b>	200	-	6	4	3
3	<b>15</b>	100	-	16	3	trace
4	<b>15</b>	150	-	26	6	trace
5	<b>15</b>	150	1,4-DOX	9	2	trace
6	<b>15</b>	200	-	12	3	trace

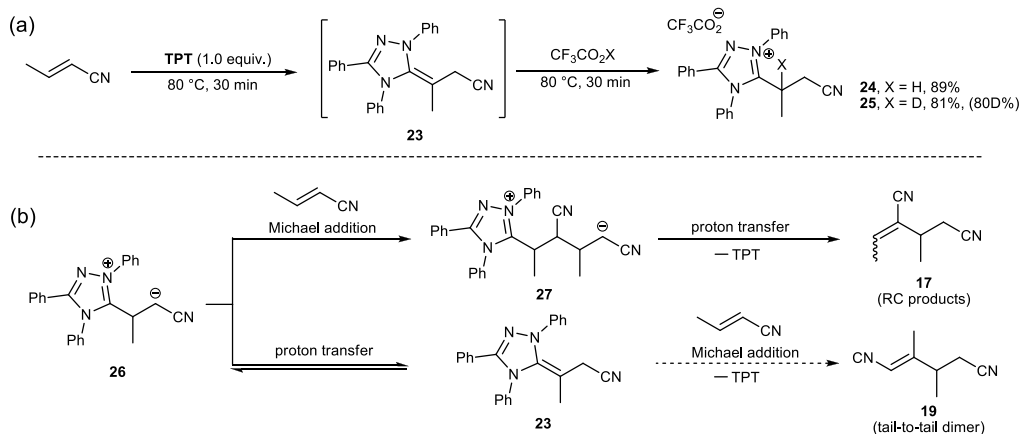


**Scheme 2.** Rauhut-Currier Reaction of 2-Cyclohexen-1-one.

This interesting difference between the tail-to-tail dimerization and the RC reaction prompted us to consider the reaction mechanism. Previously, Waymouth *et al.* mentioned two possible mechanisms in the RC reaction of crotonates catalyzed by  $\text{I}Pr_2\text{Me}$ : the nucleophilic attack of NHC to the  $\beta$ -carbon (nucleophilic mechanism) and the abstraction of  $\gamma$ -proton (base mechanism), and suggested that the base mechanism is more conceivable.<sup>12</sup> They also reported that the deoxy-Breslow intermediate was generated from TPT or IMes and methyl crotonate at 25 °C. To prove the reaction intermediate, we performed the stoichiometric reaction of crotononitrile with TPT

for 30 min followed by the addition of  $\text{CF}_3\text{CO}_2\text{H}$  (Scheme 3 (a)). The addition product (**24**) was obtained in 89% yield. Use of  $\text{CF}_3\text{CO}_2\text{D}$  instead resulted in the selective deuterium incorporation at the  $\beta$ -carbon (**25**), indicating that the deoxy-Breslow intermediate (**23**) was involved. Our experimental results propose the mechanism in Scheme 3(b). NHC attacks to the  $\beta$ -carbon of crotonitrile to generate the zwitterionic intermediate (**26**), followed by the proton transfer to give **23**. The selective formation of the proton or deuterium adduct of **23**

indicates that the intermediate **23** is a stable species and the resting state in the catalysis. Reaction of this intermediate with the substrate to give the tail-to-tail dimer (**19**) is difficult probably due to the steric hindrance at the  $\beta$ -carbons. The proton transfer between **23** and **26** is in equilibrium at such high temperatures, and the regenerated **26** undergoes the Michael addition to give **27**. The transfer of the  $\alpha$ -proton of **27** and elimination of NHC affords RC product **17**.



**Scheme 3.** (a) Stoichiometric Reaction of Crotonitrile with TPT, and (b) Reaction Mechanism of Its RC Reaction.

### 3. Conclusion

We have shown the tail-to-tail dimerization of six vinylidene substrates bearing electron-withdrawing groups, such as ester, amide, and 2-oxazole, catalyzed by TPT at 100–150 °C. The NHC (tBu) was previously reported to initiate the addition polymerization of **1** at an ambient temperature, but switching to TPT and increasing the reaction temperature to 150 °C led to dimerization. The experiments using a series of dialkyl methacrylamides indicate that the  $\pi$ -conjugations between the C=C bond and carbonyl groups in the substrates are required. Given that there is no previous report on the dimerization of the vinylidenes (**1–8**), the NHC catalysis is the most general synthetic procedure to synthesize various bifunctional compounds from Michael acceptors. In contrast to the tail-to-tail mode of reactivity, TPT was found to catalyze the RC reaction of three vinylene substrates. This NHC catalysis also involves the deoxy-Breslow intermediate, but which do not react further with the substrate due to steric hindrance. The intermediate instead undergoes the reversible proton transfer, leading to the RC reaction. These two types of reactivities, depending on the substrate structure, are expected to lead to new NHC catalysis of Michael acceptors.

### Acknowledgments

This work was supported by JSPS KAKENHI Grant Number JP 15K17868.

### References

- For reviews of RC Reaction, see: a) Methot, J. L.; Roush, W. R. *Adv. Synth. Catal.* **2004**, *346*, 1035. b) Xie, P.; Huang, Y. *Eur. J. Org. Chem.* **2013**, 6213. c) Aroyan, C. E.; Dermenci, A.; Miller, S. J. *Tetrahedron* **2009**, *65*, 4069.
- For selected examples of tail-to-tail dimerization of acrylates catalyzed by transition metal complexes, see: a) Brookhart, M.; Sabo-Etienne, S. J. *Am. Chem. Soc.* **1991**, *113*, 2777. b) Pertici, P.; Ballantini, V.; Salvadori, P.; Bennett, M. A. *Organometallics* **1995**, *14*, 2565. c) DiRenzo, G. M.; White, P. S.; Brookhart, M. J. *Am. Chem. Soc.* **1996**, *118*, 6225. d) Kaneko, Y.; Kanke, T.; Kiyooka, S.; Isobe, K. *Chem. Lett.* **1997**, 23. e) Zimmermann, J.; Tkatchenko, I.; Wasserscheid, P. *Adv. Synth. Catal.* **2003**, *345*, 402. f) Hirano, M.; Sakate, Y.; Komine, N.; Komiya, S.; Bennett, M. A. *Organometallics* **2009**, *28*, 4902.
- For selected examples of tail-to-tail dimerization of acrylonitrile catalyzed by transition metal complexes, see: a) Kashiwagi, K.; Sugise, R.; Shimakawa, T.; Matuura, T.; Shirai, M.; Kakiuchi, F.; Murai, S. *Organometallics* **1997**, *16*, 2233. b) Fukuoka, A.; Nagano, T.; Furuta, S.; Yoshizawa, M.; Hirano, M.; Komiya, S. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1409. c) Kashiwagi, K.; Sugise, R.; Shimakawa, T.; Matuura, T.; Shirai, M. *Chem. Lett.* **2006**, *35*, 186.
- For tail-to-tail dimerization of methacrylates catalyzed by transition metal complexes, see: a) Oehme, G. *J. Prakt. Chem.* **1984**, *326*, 779. b) Oehme, G.; Grassert, I.; Mennenga, H.; Baudisch, H. *J. Mol. Catal.* **1986**, *37*, 53. c) Hirano, M.; Hiroi, Y.; Komine, N.; Komiya, S. *Organometallics* **2010**, *29*, 3690.
- For a recent review on NHC, see: Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. *Nature*, *510*, 485.
- For reviews dealing with NHC-catalyzed *umpolung* of Michael acceptors, see: a) Bugaut, X.; Glorius, F. *Chem. Soc. Rev.* **2012**, *41*, 3511. b) Ryan, S. J.; Candish, L.; Lupton, D. W. *Chem. Soc. Rev.* **2013**, *42*, 4906. c) Chen, X.-Y.; Ye, S. *Org. Biomol. Chem.* **2013**, *11*, 7991. d) Flanigan, D. M.; Romanov-Michailidis, F.; White, N. A.; Rovis, T. *Chem. Rev.* **2015**, *115*, 9307. e) Matsuoka, S. *Polym. J.*, **2015**, *47*, 713.
- a) Fischer, C.; Smith, S. W.; Powell, D. A.; Fu, G. C. *J. Am. Chem. Soc.* **2006**, *128*, 1472. b) Matsuoka, S.; Tochigi, Y.; Takagi, K.; Suzuki, M. *Tetrahedron* **2012**, *68*, 9836. c) Matsuoka, S.; Namera, S.; Washio, A.; Takagi, K.; Suzuki, M. *Org. Lett.* **2013**, *15*, 5916. d) Ottou, W. N.; Bourichon, D.; Vignolle, J.; Wirotius, A.-L.; Robert, F.; Landais, Y.; Sotiropoulos, J.-M.; Miqueu, K.; Taton, D. *Chem.-Eur. J.* **2014**, *20*, 3989. e) Nakano, Y.; Lupton, D. W. *Angew. Chem. Int. Ed.* **2016**, *55*, 3135.
- a) Matsuoka, S.; Ota, Y.; Washio, A.; Katada, A.; Ichioke, K.; Takagi, K.; Suzuki, M. *Org. Lett.* **2011**, *13*, 3722. b) Biju, A. T.; Padmanaban, M.; Wurzl, N. E.; F. Glorius, *Angew. Chem., Int. Ed.* **2011**, *50*, 8412. c) Kato, T.; Ota, Y.; Matsuoka, S.; Takagi, K.; M. Suzuki, *J. Org. Chem.* **2013**, *78*, 8739. d) Kato, T.; Matsuoka, S.; Suzuki, M. *J. Org. Chem.* **2014**, *79*, 4484. e) Schedler, M.; Wurzl, N. E.; Daniliuc, C. G.; Glorius, F. *Org. Lett.* **2014**, *16*, 3134. f) Matsuoka, S.; Nakazawa, M.; Suzuki, M. *Bull. Chem. Soc. Jpn.* **2015**, *88*, 1093. g) Rajachan, O.; Paul, M.; Yatham, V. R.; Neudörfel, J.-M.; Kanokmedhakul, K.; Kanokmedhakul, S.; Berkessel, A. *Tetrahedron Lett.* **2015**, *56*, 6537. Computation Study see: h) Li, Y.; Zhu, Y.; Zhang, W.; Wei, D.; Ran, Y.; Zhao, Q.; Tang, M. *Phys. Chem. Chem. Phys.*, **2014**, *16*, 20001. i) Hong, M.; Tang, X.; Falivene,

- L.; Caporaso, L.; Cavallo, L.; E. Chen, Y.-X. *J. Am. Chem. Soc.* **2016**, *138*, 2021. The dimerization of vinylphosphonates by  $\text{PMe}_3$ -catalyzed *umpolung*, see; j) Wang, X.-B.; Saga, Y.; Shen, R.; Fujino, H.; Goto, M.; Han, L.-B. *RSC Adv.* **2012**, *2*, 5935.
9. Atienza, R. L.; Roth, H. S.; Scheidt, K. A. *Chem. Sci.* **2011**, *2*, 1772.
  10. Hong, M.; Chen, E. Y.-X. *Angew. Chem. Int. Ed.* **2014**, *53*, 11900.
  11. Kato, T.; Matsuoka, S.; Suzuki, M. *Chem. Commun.* **2015**, *51*, 13906.
  12. Flanagan, J. C. A.; Kang, E. J.; Strong, N. I.; Waymouth, R. M. *ACS Catal.*, **2015**, *5*, 5328
  13. a) Chen, X.-Y.; Xia, F.; Ye, S. *Org. Biomol. Chem.*, **2013**, *11*, 5722. b) He, L.; Zhang, Y.-R.; Huang, X.-L.; Ye, S. *Synthesis*, **2008**, 2825. c) He, L.; Jian, T.-Y.; Ye, S. *J. Org. Chem.* **2007**, *72*, 7466.
  14. Chen, X.-Y.; Sun, L.-H.; Ye, S. *Chem. Eur. J.* **2013**, *19*, 4441.
  15. Raveendran, A. E.; Paul, R. R.; Suresh, E.; Nair, V. *Org. Biomol. Chem.*, **2010**, *8*, 901.
  16. Oxa-Michael addition through the Lewis base mechanism, see; a) Matsuoka, S.; Shimakawa, S.; Takagi, K.; Suzuki, M. *Tetrahedron Lett.* **2011**, *52*, 6835. b) Matsuoka, S.; Namera, S.; Suzuki, M. *Polym. Chem.* **2015**, *6*, 294.
  17. a) Enders, D.; Breuer, K.; Raabe, G.; Runsink, J.; Teles, J. H.; Melder, J.-P.; Ebel, K.; Brode, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1021. b) Enders, D.; Breuer, K.; Runsink, J.; Teles, J. H. *Liebigs Ann.* **1996**, 2019. c) Enders, D.; Breuer, K.; Teles, J. H.; Ebel, K. *J. Prakt. Chem./Chem.-Ztg.* **1997**, *339*, 397. d) Enders, D.; Breuer, K.; Kallfass, U.; Balensiefer, T. *Synthesis* **2003**, 1292. e) Teles, J. H.; Melder, J.-P.; Ebel, K.; Schneider, R.; Gehrler, E.; Harder, W.; Brode, S.; Enders, D.; Breuer, K.; Raabe, G. *Helv. Chim. Acta* **1996**, *79*, 61.
  18. a) Zhang, Y.; Chen, E. Y.-X. *Angew. Chem. Int. Ed.* **2012**, *51*, 2465. b) Zhang, Y.; Schmitt, M.; Falivene, L.; Caporaso, L.; Cavallo, L.; Chen, E. Y.-X. *J. Am. Chem. Soc.* **2013**, *135*, 17925. c) Gowda, R. R.; Chen, E. Y.-X. *Org. Chem. Front.*, **2014**, *1*, 230. d) Gowda, R. R.; Chen, E. Y.-X. *ACS Macro Lett.* **2016**, *5*, 772.
  19. a) Xie, X.; Hogen-Esch, T. E. *Macromolecules* **1996**, *29*, 1746. b) Kodaira, T.; Tanahashi, H.; Hara, K. *Polym. J.* **1990**, *22*, 649. c) Miyake, G.; Caporaso, L.; Cavallo, L.; Chen E. Y.-X. *Macromolecules* **2009**, *42*, 1462. d) Suzuki, T.; Kusakabe, J.; Kitazawa, K.; Nakagawa, T.; Kawauchi, S.; Ishizone, T. *Macromolecules* **2010**, *43*, 107.
  20. a) Suzuki, T.; Kusakabe, J.; Ishizone, T. *Macromolecules* **2008**, *41*, 1929. b) Ishizone, T.; Kitazawa, K.; Suzuki, T.; Kawauchi, S. *Macromol. Symp.* **2013**, *323*, 86.
  21. Ishizone, T.; Oka, N.; Hirao, A.; Nakahama, S. *Macromolecules* **1996**, *29*, 528.

## Supplementary Material

Experimental section, characterization data of the dimers, and copies of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra.