Tryptal Cation-Catalyzed Hosomi-Sakurai Reaction of Allylsilane with β,γ-Unsaturated α-Ketoester to Form γ,γ-Disubstituted α-Ketoesters

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Abstract: (Ph₃C)₄[BPh(F)₄]-catalyzed Hosomi-Sakurai allylation of allylsilanes with β,γ-unsaturated α-ketoesters has been developed to give γ,γ-disubstituted α-ketoesters in high yields with excellent chemoselectivity. Preliminary mechanistic studies suggest that trityl cation dominates the catalysis, while the silyl cation plays a minor role.

Keywords: allylsilane; α-ketoester; Hosomi-Sakurai allylation; trityl cation

1. Introduction

α-Ketoesters are important synthons [1–3] and can be transformed into a variety of building blocks, which have found wide utility in natural products synthesis. As shown in Scheme 1, a Bi(OTf)₃-catalyzed intermolecular cascade annulation of α-ketoesters with alkyons has been developed to construct γ-spiroketol-γ-lactones [4], a core structure in massarinoline A [5]. α-Ketoesters can also react with α-ketoacids to form isotetronic acids [6], a core structure in aspernolide A [7], by an asymmetric aldol/lactonization/enolization reaction. In this regard, development of new methods enabling an efficient synthesis of structurally diverse α-ketoesters is highly desirable.

Scheme 1. Synthetic utility of α-ketoesters in the synthesis of natural products. “cat*” refers to chiral catalysts.

Trityl tetrakis (pentafluorophenyl) borate [(Ph₃C)₄[BPh(F)₄]] [8] is well-known for providing stable and easily available carbocations. Since the pioneering work of Mukaiyama and co-workers [9], the use of trityl cations as Lewis acid catalysts has been explored...
in Mukaiyama aldol reactions [10–16], Hosomi-Sakurai allylations [17,18], Michael additions [19], Diels–Alder reactions [20–31], halogenations [32], epoxide rearrangements [27], ene reactions [33,34] and other transformations [35–38]. In these transformations, trityl cations display much higher catalytic reactivity than traditional metal-based Lewis acids. As part of our continuing interests in organosilane chemistry [39–42], we recently reported (Ph3C)3[BPh6]4-catalyzed asymmetric Hosomi-Sakurai allylation of chiral crotyl geminal bis(silane) with aldehydes [43]. In this reaction, (Ph3C)3[BPh6]4 proved superior to traditional metal-based Lewis acids. This success led us to extend trityl cation catalysis to allylsilane-mediated reactions for which metal-based Lewis acids do not work well. We focused on β,γ-unsaturated α-ketoesters as electrophiles. Typical enones undergo Michael-type allylation [44–46] or [2+2] or [3+2] cyclization [47–51], but Ishihara and co-workers observed that Cu(NTf2)2-catalyzed reaction of β,γ-unsaturated α-ketoesters with allylsilanes gave only the inverse-electron-demand Diels-Alder (IEDDA) reaction adducts as the major products (Scheme 2a) [52]. Sugimura and co-workers achieved the desired allylation using β,γ-unsaturated α,α-dimethoxy esters as the variant (Scheme 2b) [53]. A stoichiometric amount of BF3•Et2O (1.1 equiv.) was required to give γ-substituted α,β-unsaturated α-methoxy esters as a mixture of Z/E isomers.

![Scheme 2](image)

Scheme 2. Reaction of allylsilane with β,γ-unsaturated α-ketoesters and their variants. “L*” refers to chiral ligands.

Here we report a (Ph3C)3[BPh6]4-catalyzed Hosomi-Sakurai allylation of allylsilanes with β,γ-unsaturated α-ketoesters (Scheme 2c). The trityl cation shows high catalytic efficiency, giving the γ,γ-disubstituted α-ketoesters in high yields with excellent chemoselectivity. Mechanistic studies suggest that silyl cation catalysis is not a major pathway. Instead, the reaction most likely proceeds via trityl cation catalysis, although we cannot completely rule out Brønsted acid catalysis.

2. Results and Discussion

2.1. Synthesis

We initially screened the metal-based Lewis acid catalysts using β,γ-unsaturated α-ketoester 1a and allytrimethylsilane 2a as model substrates in CH2Cl2 at 25 °C (Table 1). In the presence of 10 mol % of TiCl4, inverse-electron-demand Diels-Alder adduct (+)-4a was obtained in 97% yield; no desired Hosomi-Sakurai allylation product 3a was detected (entry 1). SnCl4, AlCl3 and FeCl3 provided a mixture of 3a and (+)-4a, in which 3a was the minor isomer and the 3a: (+)-4a ratio ranged from 23:77 to 45:55 (entries 2–4). BF3•Et2O and TMSCl proved to be ineffective catalysts, leading to less than 30% conversion even after 4 days (entries 5 and 6). We also tested lanthanide-based Lewis acids such as Sc(OTf)3 and Yb(OTf)3 (entries 7 and 8). Sc(OTf)3 afforded undesired (+)-4a as the sole detectable
product; no reaction occurred using Yb(OTf)$_3$. In sharp contrast to metal-based Lewis acids, the trityl salt (Ph$_3$C)[BPh$_4$] displayed excellent catalytic ability, generating 3a as a single chemoisomer in 97% yield (entry 9). In fact, 1 mol % of (Ph$_3$C)[BPh$_4$] was efficient enough to provide 3a in comparably high yield and selectivity (entry 10).

Table 1. Screening of Reaction Conditions.

| Entry | Cat.     | Time   | $3a/(±)-4a$ (%) $^b,c$ | $3a/(±)-4a$ $^d$ |
|-------|----------|--------|------------------------|------------------|
| 1     | TiCl$_4$ (10 mol %) | 10 min | 0 (97)                | ≤5:95           |
| 2     | SnCl$_4$ (10 mol %)  | 10 min | 22 (74)               | 23:77           |
| 3     | AlCl$_3$ (10 mol %)  | 10 min | 32 (63)               | 33:67           |
| 4     | FeCl$_3$ (10 mol %)  | 10 min | 43 (51)               | 45:55           |
| 5     | BF$_3$•Et$_2$O (10 mol %) | 4 days | 10 (0)   | ≤5:95           |
| 6     | TMSOTf (10 mol %)    | 4 days | 20 (<5)              | 17:83           |
| 7     | Sc(OTf)$_3$ (10 mol %) | 8 h    | 95 (0)               | ≤5:95           |
| 8     | Yb(OTf)$_3$ (10 mol %) | 24 h  | N.R.                 | N.D.            |
| 9     | (Ph$_3$C)[BPh$_4$] (10 mol %) | 10 min | 97 (0)  | ≥95:5           |
| 10    | (Ph$_3$C)[BPh$_4$] (1 mol %) | 10 min | 97 (0)  | ≥95:5           |

$^a$ Reaction conditions: 0.11 mmol of 1a, 0.13 mmol of 2a in 2.0 mL of CH$_2$Cl$_2$ at 25 °C. $^b$ The initially formed silyl enol ether was treated with PTS in MeOH to release α-ketoester 3a. $^c$ Isolated yields. $^d$ Ratios were determined by $^1$H NMR spectroscopy of the crude products.

With the optimal reaction conditions in hand, we examined the scope of β,γ-unsaturated α-ketoesters (Scheme 3). Reactions of aryl-substituted ketoesters gave rise to 3b–3j in excellent yields. The reaction tolerated substrates containing functionalized phenyl rings, naphthyl rings or heterocycles. An electron-donating substitution on the phenyl ring slightly decreased chemoselectivity, as shown in 3c (H-S/D-A = 90:10) and 3f (H-S/D-A = 95:5). The reaction generated 3k and 3l from the corresponding alkyl-substituted ketoesters. Allylation of dienyl ketoester with 2a gave 3m in 80% yield, with 1,4-regioselectivity dominating over 1,6-regioselectivity. β,γ-unsaturated α-ketimine ester performed well in the reaction, giving enamido ester 3n in 75% yield. Interestingly, propargyl α-keto ester underwent 1,2-allylation exclusively, leading to α-tertiary hydroxy ester 3o in 93% yield. Switching the ester group from OMe to a bulkier i-Pr group decreased chemoselectivity (3p, H-S/D-A = 91:9).

Trimethylallylsilanes 2b–2e bearing alkyl or aryl substituents at the 2-position reacted well with 1a, giving 3q–3t in 85–96% yields (Table 2, entries 1–4). The high catalytic ability of (Ph$_3$C)[BPh$_4$] also allowed facile anti-SE’ allylation of the bulky 3,3-dimethyl-1-trimethylallylsilanes 2f with 1a (entry 5). However, this catalyst did not efficiently control the diastereoselectivity of allylation: the reaction of Z-crotyltrimethylsilane 2g-Z afforded 3v in 96% yield but as a 3:2 mixture of anti- and syn-diastereomers (entry 6). A similar ratio of 3:1 was obtained using E-crotyltrimethylsilane 2g-E (entry 7).
Scheme 3. Scope of β,γ-Unsaturated α-Ketoesters. a. Reaction conditions: 0.11 mmol of 1a, 0.13 mmol of 2a, 1.0 mol % of (Ph₃C)[BPh₄] in 2.0 mL of CH₂Cl₂ at 25 °C. b. Isolated yields. c Ratios were determined by ¹H NMR spectroscopy of the crude products.

The trimethylsilyl enol ethers that initially formed in the reactions shown in Scheme 3 and Table 2 were difficult to isolate because of their instability. Switching the silyl moiety from Me₃Si to a bulkier Et₃Si group in allylsilane 2h–2j led to formation of the stable silyl enol ethers 5a–5e in good to high yields (Scheme 4). The Z-silyl enol ether was favored either as a single isomer (5a and 5c) or the major isomer (5b).

Scheme 4. Formation of Silyl Enol Ethers using Triethylsilylallylsilanes. a. Reaction conditions: 0.11 mmol of 1a, 0.13 mmol of 2, 1.0 mol % of (Ph₃C)[BPh₄] in 2.0 mL of CH₂Cl₂ at 25 °C. b. Isolated yields. c Ratios were determined by ¹H NMR spectroscopy of the crude products.
Table 2. Scope of Allylsilanes.

| Entry | Allysilanes | Products | Yield  |
|-------|-------------|----------|--------|
| 1     | Me₃Si–Me    | 2b       | Me₃Si–Me, Ph(CO_2)Me | 95%\(^b\) |
| 2     | Me₃Si–n-C₇H₁₅ | 2c       | Me₃Si–n-C₇H₁₅, Ph(CO_2)Me | 95% |
| 3     | Me₃Si–Ph     | 2d       | Me₃Si–Ph, 1-naphthyl | 85% |
| 4     | Me₃Si–1-naphthyl | 2e | Me₃Si–1-naphthyl, Ph(CO_2)Me | 96% |
| 5     | Me₃Si–Me     | 2f       | Me₃Si–Me, Ph(CO_2)Me | 93% |
| 6     | Me₃Si–Me     | 2g-Z     | Me₃Si–Me, Ph(CO_2)Me | 96%\(^c\) |
| 7     | Me₃Si–Me     | 2g-E     | Me₃Si–Me, Ph(CO_2)Me | 91%\(^c\) |

\(^a\) Reaction conditions: 0.21 mmol of 1a, 0.26 mmol of 2, 1.0 mol % of (Ph_2C)[BPh(4)]_3 in 4.0 mL of CH_2Cl_2 at 25 °C.
\(^b\) Isolated yields.
\(^c\) anti/.syn = 3:2 from 2g-Z; anti/.syn = 3:1 from 2g-E.

2.2. Mechanistic Investigations

Some mechanistic investigations have been performed for trityl cation catalysis by different groups, but the results appear to be contradictory, particularly in the case of reactions involving allylsilanes or silyl enol ethers. For example, three catalytic species have been suggested for Mukaiyama aldol reactions. Denmark [14] and Mukaiyama [9–13,17,19] proposed the catalytic species to be a trityl cation. In this path, intramolecular transfer of the silyl group releases the product and regenerates the trityl cation catalyst. Bosnich [18] and Chen [16] proposed the catalytic species to be a silyl cation, which is a stronger Lewis acid than trityl cation. In another case, Kagan [20–22] proposed the catalytic species to be a Brønsted acid, potentially generated by decomposition of the trityl cation.
The accessibility of silyl enol ethers allowed us to perform detailed mechanistic investigations for our reaction (Scheme 5). Allylsilanes \(2a, 2i, 2h\) and \(2b\) were reacted separately with \(\beta,\gamma\)-unsaturated \(\alpha\)-ketoester \(1a\). In the merged \(1^H\) NMR spectra of the resulting crude silyl enol ethers \(5d, 5b, 5a\) and \(5e\), we were able to clearly distinguish the H\(^a\) signals of the different products (Scheme 5(b1)). Therefore, we reacted a mixture of \(2a\) (1.2 equiv.) and \(2i\) (1.2 equiv.) with \(1a\) (2.0 equiv.) in one pot (Scheme 5a). A mixture of \(5d, 5b, 5a\) and \(5e\) was generated in a ratio of \(93(5d + 5b):7(5a + 5e)\) (Scheme 5(b2)). We attribute the formation of \(5a\) and \(5e\) to crossed silyl cation catalysis. This result implies that 7% of \(5d\) and \(5b\) may form via silyl cation catalysis, meaning that the ratio of trityl to silyl cation catalysis should be approximately \((93 - 7):(7 + 7)\) or 86:14. Next we reacted a mixture of \(2b\) (1.2 equiv.) with \(1a\) (2.0 equiv.) in one pot. A mixture of \(5d, 5b, 5a\) and \(5e\) was generated in a ratio of \(6(5d + 5b):94(5a + 5e)\) (Scheme 5(b3)). The ratio of trityl to silyl cation catalysis in this reaction should be \((94 - 6):(6 + 6)\) or 88:12. The results from these two control reactions suggest that silyl cation catalysis occurs but makes a minor contribution to our results.

Scheme 5. Mechanistic studies (a); \(1^H\) NMR spectra of enol ethers \(5d, 5b, 5a\) and \(5e\) (b); possible competing catalytic pathway (c); proposed catalytic cycle (d).

Brønsted acid catalysis is another competing catalytic pathway, which we cannot rule out currently. This pathway seems unlikely to make a major contribution based on our
observations (Scheme 5c) that in the presence of 1.0 equiv. of Ph₃C⁺•BF₄⁻, the desired allylation product 3a was obtained in 45% yield, while the by-product (±)-4a also formed in 45% yield. However, neither 3a nor (±)-4a was detected when 1.0 equiv. of HBF₄ was used.

Based on these results, we propose a trityl cation-based catalytic mechanism (Scheme 5d). Activation of the ketone in β,γ-unsaturated α-ketoester 1 by trityl cation generates 6 [55]. Subsequent allylation with allylsilane may occur via an unusual closed transition state 7, which allows internal C-to-O silyl transfer to give the non-crossed silyl enol ether 5 as the major product (Scheme 5(b2,b3)). This also regenerates the trityl cation and catalyzes the next cycle.

3. Materials and Methods

3.1. General Procedures for the Synthesis of γ,γ-Disubstituted α-Ketoesters 3a–3v

To a solution of β,γ-unsaturated α-ketoester 1 (0.11 mmol) and allylsilane 2 (0.13 mmol) and in anhyd. CH₂Cl₂ (2 mL) under argon atmosphere was added (Ph₃C)BPHEF₄ (1.0 mol %) at 25 °C. After stirring for 10 min, the reaction was quenched with p-TsOH (0.5 M in MeOH, 0.1 mL). The mixture was directly concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0–2.0% of EtOAc/petroleum ether) afforded γ,γ-disubstituted α-ketoester 3. The characterization data for all synthetic compounds are provided in the Supplementary Materials.

Methyl 2-oxo-4-phenylhept-6-enoate (3a): ¹H NMR (400 MHz, CDCl₃) δ 2.37 (dd, 1H, J₁ = 7.2 Hz, J₂ = 14.0 Hz), 2.45 (dd, 1H, J₁ = 7.2 Hz, J₂ = 14.0 Hz), 3.19 (d, 2H, J = 7.2 Hz), 3.34 (dddd, 1H, J₁ = 7.2 Hz), 3.80 (s, 3H), 5.00 (d, 1H, J = 8.0 Hz), 5.03 (d, 1H, J = 15.2 Hz), 5.66 (m, 1H), 7.20 (m, 3H), 7.28 (d, 1H, J = 3.6 Hz), 7.31 (d, 1H, J = 7.6 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 40.2, 40.8, 44.9, 52.9, 117.3, 126.7, 127.5, 128.5, 135.8, 143.2, 161.3, 192.9; IR (neat) cm⁻¹ 3029, 2954, 2923, 1731, 1442, 1277, 1253, 1089, 919; HRMS (MALDI, m/z) calcd for C₁₅H₁₈O₃Na (M+Na)⁺: 255.0992, found 255.0989.

3.2. General Procedures for the Synthesis of Silyl Enol Ethers 5a–5e

To a solution of β,γ-unsaturated α-ketoester 1 (0.22 mmol) and allylsilane 2 (0.26 mmol) and in anhyd. CH₂Cl₂ (4 mL) under argon atmosphere was added (Ph₃C)BPHEF₄ (1.0 mol %) at 25 °C. After stirring for 10 min, the reaction was quenched with NEt₃ (1.32 mmol). The mixture was directly concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0–2.0% of EtOAc/petroleum ether) afforded silyl enol ether 5. The characterization data for all synthetic compounds are provided in the Supplementary Materials.

Methyl (Z)-4-phenyl-2-((triethylsilyl)oxy)hepta-2,6-dienoate (5a): ¹H NMR (600 MHz, CDCl₃) δ 0.79 (q, 6H, J = 7.8 Hz), 1.05 (t, 9H, J = 7.8 Hz), 2.56 (m, 2H), 3.82 (s, 3H), 3.99 (m, 1H), 5.05 (d, 1H, J = 10.2 Hz), 5.11 (d, 1H, J = 16.8 Hz), 5.78 (m, 1H), 7.30 (m, 3H), 7.38 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 5.5, 6.8, 40.6, 41.8, 51.9, 116.4, 124.6, 126.4, 127.5, 128.5, 135.0, 140.1, 143.3, 165.3; IR (neat) cm⁻¹ 2955, 2878, 1727, 1642, 1439, 1372, 1266, 1232, 1143, 1010, 913; HRMS (MALDI, m/z) calcd for C₂₀H₃₀O₃SiNa (M+Na)⁺: 369.1856, found 369.1856.

4. Conclusions

In summary, we have developed a (Ph₃C)BPHEF₄-catalyzed Hosomi-Sakurai allylation of allylsilanes with β,γ-unsaturated α-ketoesters. Various γ,γ-disubstituted α-ketoesters α-ketoesters were synthesized in high yields with excellent chemoselectivity. Mechanistic studies suggest that the trityl cation dominates catalysis, while the silyl cation plays only a minor role. Verification of this mechanism also makes the trityl cation-catalyzed asymmetric reaction possible, which is a challenging task and little progress has been achieved. The related work is ongoing in our group.
Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/molecules27154730/s1, Scheme S1: Reaction of 2a and 2i with 1a; Scheme S2: Reaction of 2h and 2b with 1a; Scheme S3: The 1H NMR titration experiment of [(Ph3C)[BPh(4)]] with β,γ-unsaturated α-ketoester 1a and allylsilane 2a.

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References and Notes
1. Deng, R.; Han, T.-J.; Gao, X.; Yang, Y.-F.; Mei, G.-J. Further Developments of β,γ- Unsaturated α-Ketoesters as Versatile Synthons in Asymmetric Catalysis. *iScience* **2022**, *25*, 103913. [CrossRef] [PubMed]
2. Morisaki, K.; Morimoto, H.; Mashima, K.; Ohshima, T. Direct Enantioselective Alkynylation of α-Ketoesters and α-Ketiminoesters Catalyzed by [bis(Oxazoline)phenyl]rhodium(III) Complexes. *Heterocycles* **2017**, *85*, 637–661.
3. Blaser, H.-U.; Jalett, H.-P.; Muller, M.; Studer, M. Enantioselective Hydrogenation of α-ketoesters Using Cinchona Modified Platinum Catalysts and Related Systems: A Review. *Catal. Today* **1997**, *37*, 441–463. [CrossRef]
4. Kambale, D.A.; Thorat, S.S.; Pratapure, M.S.; Gonnade, R.G. Lewis Acid Catalyzed Cascade Annulation of Alkynols with α-Ketoesters: A Facile Access to γ-Spiroketal-γ-lactones. *Chem. Commun*. **2017**, *53*, 6641–6644. [CrossRef] [PubMed]
5. Oh, H.; Gloer, J.B.; Shearer, C.A. Massarinolins A–C: New Bioactive Sesquiterpenoids from the Aquatic Fungus Massarina tunicata. *J. Nat. Prod.* **1999**, *62*, 497–501. [CrossRef] [PubMed]
6. Chen, P.; Wang, K.; Zhang, B.; Guo, W.; Liu, Y.; Li, H. Water Enables an Asymmetric Cross Reaction of α-Keto Acids with α-Keto Esters for the Synthesis of Quaternary Isotetronic Acids. *Chem. Commun.* **2019**, *55*, 12813–12816. [CrossRef] [PubMed]
7. Haritakun, R.; Rachtawee, P.; Chanthaket, R.; Boonyuen, N.; Isaka, M. Butyrolactones from the Fungus Aspergillus terreus BCC 4651. *Chem. Pharm. Bull.* **2010**, *58*, 1545–1548. [CrossRef]
8. Chien, J.C.W.; Tsi, W.M.; Raush, M.D. Isospecific Polymerization of Propylene Catalyzed by rac-Ethylenebis(indenyl)methylzirconium Cation. *J. Am. Chem. Soc.* **1991**, *113*, 8570–8571. [CrossRef] [PubMed]
9. Mukaiyama, T.; Kobayashi, S.; Murakami, M. Trityl Perchlorate as an Efficient Catalyst in the Aldol-Type Reaction. *Chem. Lett.* **1984**, *13*, 1759–1762. [CrossRef]
10. Mukaiyama, T.; Kobayashi, S.; Murakami, M. An Efficient Method for the Preparation of Three Cross-Aldols from Silyl Enol Ethers and Aldehydes Using Trityl Perchlorate as a Catalyst. *Chem. Lett.* **1985**, *14*, 447–450. [CrossRef]
11. Kobayashi, S.; Murakami, M.; Mukaiyama, T. Trityl Salts as Efficient Catalysts in the Aldol Reaction. *Chem. Lett.* **1985**, *14*, 1535–1538. [CrossRef]
12. Kobayashi, S.; Matsui, S.; Mukaiyama, T. Trityl Salt Catalyzed Aldol Reaction between α,β-Acetylenic Ketones and Silyl Enol Ethers. *Chem. Lett.* **1988**, *17*, 1491–1494. [CrossRef]
13. Mukaiyama, T.; Akamatsu, H.; Han, J.S. A Convenient Method for Stereoselective Synthesis of β-Aminoesters. Iron(II) Iodide or Trityl Hexachloroantimonate as an Effective Catalyst in the Reaction of Ketene Silyl Acetals with Imines. *Chem. Lett.* **1990**, *19*, 889–892. [CrossRef]
14. Wehrmann, H.; Schulze, B. Cationic Nickel(II) Complexes: A New Class of Catalytic Systems for Asymmetric Allylation. *Chem. Rev.* **1999**, *99*, 2397–2429. [PubMed]
15. Chien, J.C.W.; Tsi, W.M.; Raush, M.D. Isospecific Polymerization of Propylene Catalyzed by rac-Ethylenebis(indenyl)methylzirconium Cation. *J. Am. Chem. Soc.* **1991**, *113*, 8570–8571. [CrossRef] [PubMed]
16. Chen, P.; Wang, K.; Zhang, B.; Guo, W.; Liu, Y.; Li, H. Water Enables an Asymmetric Cross Reaction of α-Keto Acids with α-Keto Esters for the Synthesis of Quaternary Isotetronic Acids. *Chem. Commun.* **2019**, *55*, 12813–12816. [CrossRef] [PubMed]
17. Haritakun, R.; Rachtawee, P.; Chanthaket, R.; Boonyuen, N.; Isaka, M. Butyrolactones from the Fungus Aspergillus terreus BCC 4651. *Chem. Pharm. Bull.* **2010**, *58*, 1545–1548. [CrossRef]
18. Chien, J.C.W.; Tsi, W.M.; Raush, M.D. Isospecific Polymerization of Propylene Catalyzed by rac-Ethylenebis(indenyl)methylzirconium Cation. *J. Am. Chem. Soc.* **1991**, *113*, 8570–8571. [CrossRef] [PubMed]
19. Mukaiyama, T.; Kobayashi, S.; Murakami, M. Trityl Perchlorate as an Efficient Catalyst in the Aldol-Type Reaction. *Chem. Lett.* **1984**, *13*, 1759–1762. [CrossRef]
20. Mukaiyama, T.; Kobayashi, S.; Murakami, M. An Efficient Method for the Preparation of Three Cross-Aldols from Silyl Enol Ethers and Aldehydes Using Trityl Perchlorate as a Catalyst. *Chem. Lett.* **1985**, *14*, 447–450. [CrossRef]
21. Kobayashi, S.; Murakami, M.; Mukaiyama, T. Trityl Salts as Efficient Catalysts in the Aldol Reaction. *Chem. Lett.* **1985**, *14*, 1535–1538. [CrossRef]
22. Kobayashi, S.; Matsui, S.; Mukaiyama, T. Trityl Salt Catalyzed Aldol Reaction between α,β-Acetylenic Ketones and Silyl Enol Ethers. *Chem. Lett.* **1988**, *17*, 1491–1494. [CrossRef]
23. Mukaiyama, T.; Akamatsu, H.; Han, J.S. A Convenient Method for Stereoselective Synthesis of β-Aminoesters. Iron(II) Iodide or Trityl Hexachloroantimonate as an Effective Catalyst in the Reaction of Ketene Silyl Acetals with Imines. *Chem. Lett.* **1990**, *19*, 889–892. [CrossRef]
24. Wehrmann, H.; Schulze, B. Cationic Nickel(II) Complexes: A New Class of Catalytic Systems for Asymmetric Allylation. *Chem. Rev.* **1999**, *99*, 2397–2429. [PubMed]
19. Kobayashi, S.; Murakami, M.; Mukaiyama, T. The Trityl Perchlorate Catalyzed Michael Reaction. *Chem. Lett.* 1985, 14, 953–956. [CrossRef]

20. Riant, O.; Samuel, O.; Kagan, H.B. A General Asymmetric Synthesis of Ferrocenes with Planar Chirality. *J. Am. Chem. Soc.* 1993, 115, 5835–5836. [CrossRef]

21. Brunner, A.; Taudien, S.; Riant, O.; Kagan, H.B. Stereoselective Synthesis of Some Chiral α-Ferrocenyl Carbenium Ions. *Chirality* 1997, 9, 478–486. [CrossRef]

22. Taudien, S.; Riant, O.; Kagan, H.B. Synthesis of Chiral Carbocations Linked to a Ferrocene Unit. *Tetrahedron Lett.* 1995, 36, 3513–3516. [CrossRef]

23. Sammakia, T.; Latham, H.A. On the Use of Ferrocenyl Cations as Chiral Lewis Acids: Evidence for Proton Acid Catalysis. *Tetrahedron Lett.* 1995, 36, 6687–6690. [CrossRef]

24. Klare, H.F.T.; Bergander, K.; Oestreich, M. Taming the Silylium Ion for Low-Temperature Diels–Alder Reactions. *Angew. Chem. Int. Ed.* 2009, 48, 9077–9079. [CrossRef] [PubMed]

25. Schmidt, R.K.; Müther, K.; Mück-Lichtenfeld, C.; Grimme, S.; Oestreich, M. Silylium Ion-Catalyzed Challenging Diels–Alder Reactions: The Danger of Hidden Proton Catalysis with Strong Lewis Acids. *J. Am. Chem. Soc.* 2012, 134, 4421–4428. [CrossRef] [PubMed]

26. Bah, J.; Franzén, J. Carbocations as Lewis Acid Catalysts in Diels–Alder and Michael Addition Reactions. *Chem. A Eur. J.* 2014, 20, 1066–1072. [CrossRef]

27. Bah, J.; Naidu, V.R.; Teske, J.; Franzén, J. Carbocations as Lewis Acid Catalysts: Reactivity and Scope. *Adv. Synth. Catal.* 2015, 357, 148–158. [CrossRef]

28. El Remaily, M.A.E.A.; Naidu, V.R.; Ni, S.; Franzén, J. Carboxylation Catalysis: Oxa-Diels–Alder Reactions of Unactivated Aldehydes and Simple Dienes. *Eur. J. Org. Chem.* 2015, 2015, 6610–6614. [CrossRef]

29. Ni, S.; Naidu, V.R.; Franzén, J. Chiral Anion Directed Asymmetric Carbocation-Catalyzed Diels–Alder Reactions. *Eur. J. Org. Chem.* 2016, 2016, 1708–1713. [CrossRef]

30. Ni, S.; El Remaily, M.A.E.A.; Franzén, J. Carboxylation Catalyzed Bromination of Alkyl Arenes, a Chemoselective sp3 vs. sp2 C–H functionalization. *Adv. Synth. Catal.* 2018, 360, 4197–4204. [CrossRef]

31. Lv, J.; Zhang, Q.; Zhong, X.; Luo, S. Asymmetric Latent Carbocation Catalysis with Chiral Trityl Phosphate. *J. Am. Chem. Soc.* 2015, 137, 15576–15583. [CrossRef] [PubMed]

32. Ni, S.; Franzén, J. Carbocation Catalysed Ring Closing Aldehyde–Olefin Metathesis. *Chem. Commun.* 2018, 54, 12982–12985. [CrossRef]

33. Ruley, Y.A.; Gugkaeva, Z.T.; Lokutova, A.V.; Maleev, V.I.; Peregudov, A.S.; Wu, X.; North, M.; Belokon, Y.N. Carboxylation/Polyol Systems as Efficient Organic Catalysts for the Preparation of Cyclic Carbonates. *ChemSusChem* 2015, 8, 3996–4003. [CrossRef]

34. Masse, C.E.; Panek, J.S. Diastereoselective Reactions of Chiral Allyl and Allenyl Silanes with Activated C:C pi-Bonds. *Chem. Rev.* 1995, 95, 1293–1316. [CrossRef]

35. Monti, H.; Audran, G.; Leandrini, G.; Monti, J. ZnI2 Catalyzed [2+2] versus [3+2] Cycloaddition of an Allyltrimethylsilane with 3-butyn-2-one: Confirmation of a Cyclobutene By-product Formation. *Tetrahedron Lett.* 1994, 35, 3073–3076. [CrossRef]
48. Brengel, G.P.; Rithner, C.; Meyers, A.I. [2+2] and [3+2] Cycloadditions of Triisopropylallylsilane to alpha., beta.-Unsaturated Bicyclic Lactams. J. Org. Chem. 1994, 59, 5144–5146. [CrossRef]
49. Akiyama, T.; Yamanaka, M. Stereoselective Synthesis of Cyclopentanols by Lewis Acid-mediated [3+2] Annulation of Allyldiisopropylphénylsilane with α,β-Unsaturated Diesters. Tetrahedron Lett. 1996, 38, 7885–7888. [CrossRef]
50. Organ, M.G.; Dragan, V.; Miller, M.; Froese, R.D.J.; Goddard, J.D. Sakurai Addition and Ring Annulation of Allylsilanes with α,β-Unsaturated Esters. Experimental Results and ab Initio Theoretical Predictions Examining Allylsilane Reactivity. J. Org. Chem. 2000, 65, 3666–3678. [CrossRef]
51. Takasu, K.; Hosokawa, N.; Inanaga, K.; Ihara, M. Cyclobutane Ring Formation by Triflic Imide Catalyzed [2+2]-Cycloaddition of Allylsilanes. Tetrahedron Lett. 2006, 47, 6053–6056. [CrossRef]
52. Matsumura, Y.; Suzuki, T.; Sakakura, A.; Ishihara, K. Catalytic Enantioselective Inverse Electron Demand Hetero-Diels–Alder Reaction with Allylsilanes. Angew. Chem. Int. Ed. 2014, 53, 6131–6134. [CrossRef] [PubMed]
53. Sugimura, H.; Miyazaki, H.; Makita, Y. Lewis Acid-promoted Reaction of β,γ-Unsaturated α,α-Dimethoxy Esters with Silyl Nucleophiles. Tetrahedron Lett. 2012, 53, 4584–4587. [CrossRef]
54. The stereochemistry of determined according to the similar structures reported in the reference: Yamamoto, Y.; Nishii, S. The Anti-selective Michael Addition of Allylic Organometals to Ethylidenemalonates and Related Compounds. J. Org. Chem. 1988, 53, 3597–3603. [CrossRef]
55. The 1H NMR titration experiment of [(Ph3C)][BPh(4)] with β,γ-ununsaturated α-ketoester 1a and allylsilane 2a have been performed, respectively. However, both of them did not show strong interaction between [(Ph3C)][BPh(4)] and 1a or 2a. These results suggest that if the mechanism shown Scheme 3d works, weak activation of 1a by [(Ph3C)][BPh(4)] effectively promotes the Hosomi-Sakurai reaction with allylsilane, despite such activation appears being too weak to be probed by 1H NMR.