molbank

MDPI

Communication

Tetra(phenylethynyl)tin Is a New Reagent for Solvent-Free Alkynylation of Imines

Andrey S. Levashov, Elena V. Dvirnaya, Dzhamilay N. Konshina and Valery V. Konshin *

Department of Chemistry and High Technology, Kuban State University, Stavropolskaya st 149, 350040 Krasnodar, Russia

* Correspondence: organotin@mail.ru; Tel.: +7-(953)-104-3352

Abstract: The first $ZnCl_2$-catalyzed alkynylation of aldimines with tetra(phenylethynyl)tin was achieved under solvent-free conditions. The present methodology provides propargylamines in 38–62% yields.

Keywords: tetraalkynyltin; alkynylation; Lewis acid; imines; propargylamines

1. Introduction

Along with the use of classical reagents (Li, Na, Mg, Zn acetylides, and alkynylsilanes) in organic synthesis for the introduction of an alkyne fragment into various substrates [1,2], considerable attention is paid to the development and study of the reactivity of new non-classical alkynylating reagents and new protocols for the use of well-known reagents. Variants of applying calcium carbide in organic synthesis for ethynylation of different substrates [3–5], including boron [6–9] and aluminum [10] alkynylides, 5-(alkynyl)dibenzothiophenium salts [11,12], alkynylbenziodoxolones [13,14], and sulfonyl acetylenes [15] are shown (Figure 1).

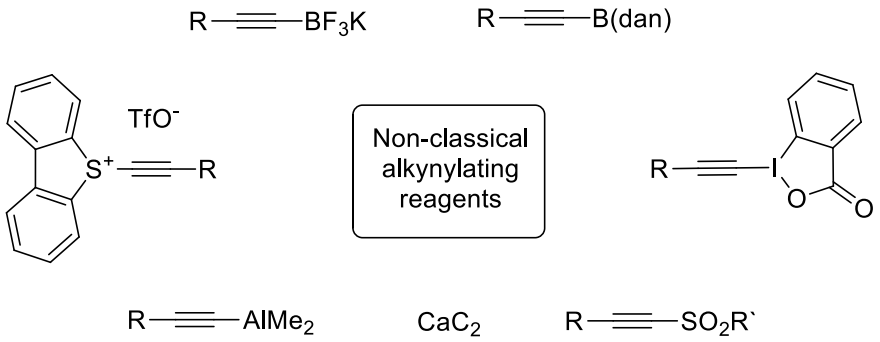


Figure 1. Examples of non-classical alkynylating reagents.

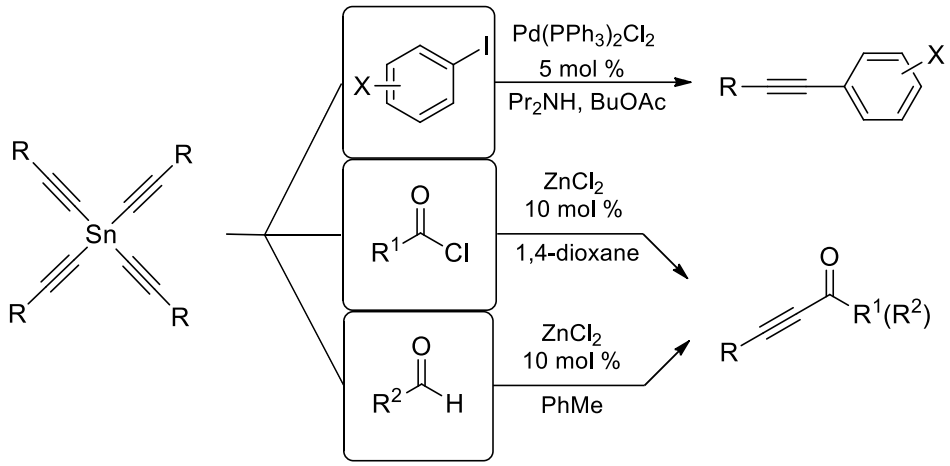
Tin alkynylides, which within more than half a century proved to be reliable reagents [16–19], continue to be used in organic synthesis; however, they have two significant disadvantages: first, they are highly toxic and, second, these compounds do not meet atom-sparing requirements and considerably reduce the reaction mass efficiency [20] due to a large ballast moiety (Bu_3Sn and Me_3Sn). We are developing a methodology for the use of easily available tin tetraalkynylides in organic synthesis [21], which have been found to be convenient reagents for the alkynylation of haloaromatic substrates under conditions of the Stille reaction [22], carbonyl compounds [23], and acyl chlorides under the Lewis catalysis [24] (Scheme 1).

check for updates

Citation: Levashov, A.S.; Dvirnaya, E.V.; Konshina, D.N.; Konshin, V.V. Tetra(phenylethynyl)tin Is a New Reagent for Solvent-Free Alkynylation of Imines. *Molbank* **2023**, *2023*, M1534. https://doi.org/10.3390/M1534

Academic Editors: Maria Luisa Di Gioia, Luísa Margarida Martins and Isidro M. Pastor

Received: 26 November 2022
Revised: 21 December 2022
Accepted: 23 December 2022
Published: 27 December 2022

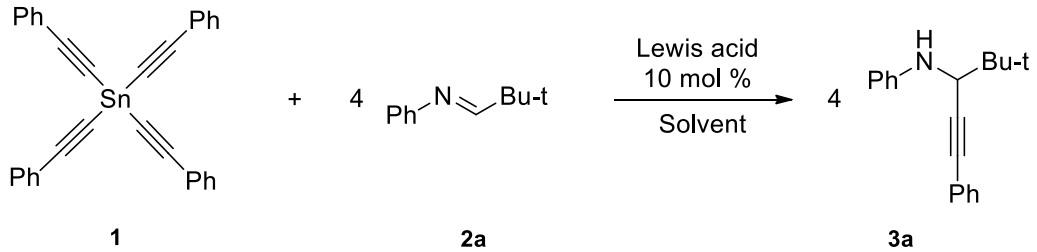


Scheme 1. Examples of various alkynylation substrates with tin tetraalkynylides.

Continuing this research trend, it seemed interesting to study whether tetra (phenylethynyl)tin could be used for the alkynylation of imines. Alkynylation of imines is an important reaction affording propargylamines, which are valuable building blocks for the synthesis of different bioactive compounds [25]. Current synthesis protocols for propargylamines mostly reduce to a ternary reaction, A^3-coupling [26,27], and numerous versions of a catalytic alkynylation reaction of imines [28–30].

2. Results and Discussion

Screening for reaction conditions was carried out on a model reaction of tetra (phenylethynyl)tin **1** with (2,2-dimethylpropylidene)aniline **2a** using an equimolar amount of alkynylating reagent, varying Lewis acid, solvent and its amount, reaction time, and temperature. The course of the reaction was controlled by chromatography–mass spectrometry (Scheme 2, Table 1). $ZnCl_2$ (Entry 2) showed the best catalytic activity in the reaction using a solvent with the highest yield of 92% being observed at the minimum solvent amount (100 μL per 0.19 mmol **1**), which favored more efficient stirring of the reaction mixture. An increase in the solvent amount led to a dramatic decrease in the yield of **3a** to 7% (400 μL per 0.19 mmol **1**) (Entry 2**). The catalytic activity of aluminum and indium(III) chlorides (Entry 3, 4) and boron trifluoride etherates (Entry 5) was far less efficient. Among solvents, toluene was found to be the optimum medium. The yield of **3a** dramatically decreased in 1,2-dichloroethane (Entry 6), and only traces of the product formed using dichloromethane. 1,4-Dioxane strongly coordinating with a Lewis acid is not suitable (Entry 8). The reaction features the possibility of being carried out in a solvent-free manner: the best conversion (98%) to the product was achieved by using $ZnCl_2$ (Entry 9); in this case, the reaction proceeded in a melt of reagents. Other Lewis acids were also less efficient when used without a solvent (Entries 10–12).



1 **2a** **3a**

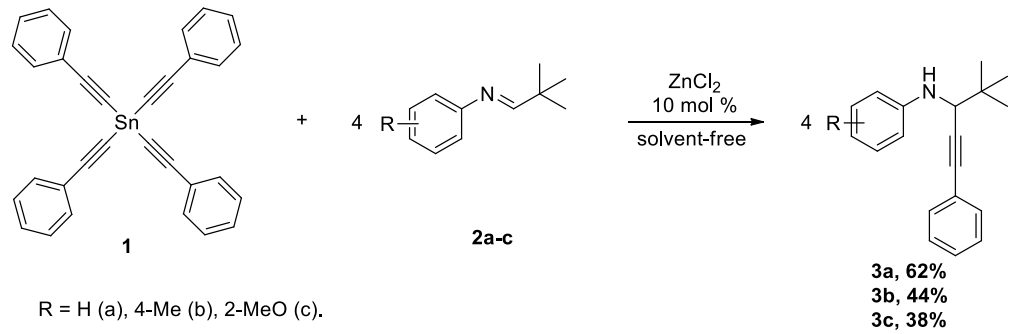
Scheme 2. The model reaction of tetra(phenylethynyl)tin **1** with imine **2a**.

Table 1. The effect of Lewis acid, solvent, and time on the yields **3a** *.

Entry	Lewis Acid (10 mol %)	Solvent	Temp, °C	Time, h	Yield 3a,% (GS/MS)
1	$ZnCl_2$	PhMe	100	3	36
2	$ZnCl_2$	PhMe	100	9	92 (7 **)
3	$InCl_3$	PhMe	100	9	58
4	$AlCl_3$	PhMe	100	9	17
5	$BF_3{\cdot}OEt_2$	PhMe	100	9	52
6	$ZnCl_2$	DCE	80	9	30
7	$ZnCl_2$	DCM	30	9	3
8	$ZnCl_2$	1,4-dioxane	100	9	-
9	$ZnCl_2$	-	100	12	98
10	$InBr_3$	-	100	9	25
11	$Sc(OTf)_3$	-	100	9	9
12	$Cu(OTf)_2$	-	100	9	18

* 0.19 mmol **1**, 0.77 mmol **2a**, 0.0077 mmol Lewis acid and 0.1 mL solvent; ** 0.4 mL solvent.

The preparative-scale reaction was carried out with imines **2a–c** (Scheme 3). The effect of donor substituents in the benzene ring of the imine leads to a decrease in the yield of propargylamines, and **3b** and **3c** were synthesized in preparative yields of 44% and 38%, respectively. The target product, **3a–c**, was purified by flash chromatography. The structure of product **3a–c** was confirmed by ^1H, ^{13}C NMR, IR spectroscopy, and mass spectrometry.



Scheme 3. Reaction of tetra(phenylethynyl)tin **1** with imines.

When tetra(phenylethynyl)tin was replaced tetrakis(phenylethynyl)silane, the yield of **3a** decreased to 7%. Tetrakis(phenylethynyl)germanium (IV) did not react with imine under the above-mentioned conditions.

In conclusion, a new approach is proposed to obtain propargylamines by the solvent-free $ZnCl_2$-catalyzed alkynylation of imines with tetra(phenylethynyl)tin.

3. Materials and Methods

The reactions were monitored by GC/MS recorded on a GCMS−QP2010Plus (Shimadzu, Kyoto, Japan) and in EI ionization mode (70 eV and ionization chamber temperature 25 °C). The ^1H-NMR, ^{13}C-NMR spectra were acquired on ECA400 (JEOL, Tokyo, Japan) (400 and 100 MHz, respectively), spectrometers in $CDCl_3$ were at room temperature. The chemical shifts δ were measured in ppm with reference to the residual solvent resonances (^1H: $CDCl_3$, δ = 7.25 ppm and ^{13}C: $CDCl_3$, δ = 77.2 ppm). The splitting patterns are referred to as s, singlet; d, doublet; t, triplet; and m, multiplet. Coupling constants (J) are given in hertz. IR spectra were recorded on an IR Prestige (Shimadzu, Kyoto, Japan), using tablets of samples with KBr. High-resolution and accurate mass measurements were carried out using a MaXis Impact (Bruker, Bremen,·Germany) (electrospray ionization/time of flight). The melting points were determined on a Stuart SMP30 apparatus and left uncorrected. Column chromatography was performed using silica 60 (40–63 μm, Mecherey-Nagel, Düren, Germany).

The commercial reagents employed in the synthesis were pivalaldehyde (96%, Aldrich, St. Louis, MO, USA), aniline, p-toluidine, o-anisidine (99%, ABCR GmbH & Co. KG). Imines **2a**–**c** were synthesized from the anilines and pivalaldehyde in benzene medium. Their constants and parameters of the NMR spectra accorded to published data [31–33]. Tetra(phenylethynyl)tin, tetrakis(phenylethynyl)silane, and tetrakis(phenylethynyl) germanium (IV) were synthesized by previously described methods [21,34,35].

General Procedure for the Synthesis of Propargylamine

Lewis acid (0.077 mmol), solvent (0.1–0.4 mL), imine **2a** 0.126 g (0.77 mmol) (0.135 g **2b** and 0.147 g **3c**), and 0.1 g (0.19 mmol) tetraphenylethynyltin were placed in a reaction vial. The reaction mixture was vigorously stirred at 30–100 °C for 3–12 h. Reactions were monitored by GC/MS. After the complete reaction, 1 mL of chloroform and 3 mL of water were added, the organic layer was separated, and the aqueous layer was extracted with chloroform (3 × 1 mL). The propargylamines **3a**–**c** were purified by flash chromatography on silica gel using hexane—ethyl acetate (1:1) as the eluent.

N-(4,4-dimethyl-1-phenylpent-1-yn-3-yl)aniline **3a**. Yield 0,126 g (62%); light yellowish crystals; and mp 82 °C. IR (KBr): ν = 3396 (NH), 3084, 3055, 3018 (Csp^2-H), 2976, 2960, 2931, 2897, 2866 (Csp^3-H), 1604, 1504 (Csp^2-Csp^2), 1489, 1431, 1363, 1313, 1253, 1105, 1070, 1028, 974, 920, and 871 cm^{-1} (SI, Figure S1). ^{1}H NMR ($CDCl_3$, 399.78 MHz): δ = 1.14 (s, 9H, CH_3), 3.74 (br. s, 1H, NH), 4.02 (s, 1H, CH), 6.73–6.76 (m, 3H, CH), 7.17–7.22 (m, 2H, CH), 7.23–7.26 (m, 3H, CH), and 7.32–7.36 (m, 2H, CH) (SI, Figure S2). ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 26.5 (CH_3), 35.6 (C), 56.3 (CH), 83.6 (Csp), 89.2 (Csp), 114.1 (CH), 118.2 (CH), 123.2 (C), 127.9 (CH), 128.1 (CH), 129.1 (CH), 131.6 (CH), and 147.5 (C) (SI, Figure S3). MS (EI, 70 eV), *m*/*z* (Irel, %): 263 [M^+] (3), 248 (1), 206 (100), 178 (2), 128 (4), 115 (3), and 104 (8) (SI, Figure S4). HRMS ESI TOF: *m*/*z* = 264,1746 [M + H]$^+$ (264,1747 calcd for $C_{19}H_{21}N$) (SI, Figure S3). The compound is described earlier [36].

N-(4,4-dimethyl-1-phenylpent-1-yn-3-yl)-4-methylaniline **3b**. Yield 0.094 g (44%); light yellowish oil; and IR (KBr): ν = 3379, 3363 (NH), 3099, 3076, 3059, 3016 (Csp^2-H), 2958, 2924, 2864 (Csp^3-H), 2164 (Csp-Csp), 1612, 1516 (Csp^2-Csp^2), 1489, 1475, 1440, 1367, 1319, 1292, 1244, 1126, 1085, 1031, 808, and 756 (SI, Figure S6). ^{1}H NMR ($CDCl_3$, 399.78 MHz): δ = 1.15 (s, 9H, CH_3), 2.26 (s, 3H, CH_3), 3.61 (br. s, 1H, NH), 3.98 (s, 1H, CH), 6.68–6.72 (m, 2H, CH), 7.01–7.05 (m, 2H, CH), 7.24–7.28 (m, 3H, CH), and 7.33–7.37 (m, 2H, CH) (SI, Figure S7). ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 20.4 (CH_3) 26.5 (CH_3), 35.6 (C), 57.1 (CH), 83.6 (Csp), 89.4 (Csp), 114.4 (CH), 123.4 (C), 127.4 (C), 127.8 (CH), 128.1 (CH), 129.6 (CH), 131.6 (CH), and 145.3 (C) (SI, Figure S8). MS (EI, 70 eV), *m*/*z* (Irel, %): 277 [M^+] (3), 220 (100), 204 (3), 118 (18), 102 (3), and 91 (33) (SI, Figure S9). HRMS ESI TOF: *m*/*z* = 278,1907 [M + H]$^+$ (278,1903 calcd for $C_{20}H_{23}N$) (SI, Figure S10).

N-(4,4-dimethyl-1-phenylpent-1-yn-3-yl)-2-methoxyaniline **3c**. Yield 0.086 g (38%); light yellowish oil; and IR (KBr): ν = 3431 (NH), 3059 (Csp^2-H), 2997, 2958, 2904, 2866, 2833 (Csp^3-H), 1600, 1510 (Csp^2-Csp^2), 1489, 1458, 1427, 1392, 1363, 1313, 1246, 1220, 1176, 1126, 1051, and 1028. (SI, Figure S11). ^{1}H NMR ($CDCl_3$, 399.78 MHz): δ = 1.18 (s, 9H, CH_3), 3.86 (s, 3H, CH_3O), 4.03 (s, 1H, CH), 4.47 (br. s, 1H, NH), 6.68–6.72 (m, 1H, CH), 6.78–6.85 (m, 2H, CH), 6.88–6.92 (m, 1H, CH), 7.23–7.27 (m, 3H, CH), and 7.34–7.37 (m, 2H, CH) (SI, Figure S12). ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 26.5 (CH_3), 35.7 (C), 55.6 (CH_3O), 56.0 (CH), 83.3 (Csp), 89.4 (Csp), 109.7 (CH), 111.2 (CH), 116.9 (CH), 121.2 (CH), 123.4 (C), 127.8 (CH), 128.1 (CH), 131.7 (CH), 137.5 (C), and 147.2 (C) (SI, Figure S13). MS (EI, 70 eV), *m*/*z* (Irel, %): 293 [M^+] (4), 236 (100), 220 (4), 193 (3), 134 (21), and 115 (6) (SI, Figure S14). HRMS ESI TOF: *m*/*z* = 294,1853 [M + H]$^+$ (294,1852 calcd for $C_{20}H_{23}NO$) (SI, Figure S15). The compound is described earlier [37].

Supplementary Materials: Figure S1: IR-spectrum of **3a**; Figure S2: ^{1}H NMR of **3a**; Figure S3: ^{13}C NMR of **3a**; Figure S4: MS of **3a**; Figure S5: HRMS of **3a**; Figure S6: IR-spectrum of **3b**; Figure S7: ^{1}H NMR of **3b**; Figure S8: ^{13}C NMR of **3b**; Figure S9: MS of **3b**; Figure S10: HRMS of **3b**; Figure S11: IR-spectrum of **3c**; Figure S12: ^{1}H NMR of **3c**; Figure S13: ^{13}C NMR of **3c**; Figure S14: MS of **3c**; and Figure S15: HRMS of **3c**.

Author Contributions: Conceptualization, V.V.K. and A.S.L.; methodology, V.V.K. and A.S.L.; software, D.N.K.; validation, V.V.K. and D.N.K.; formal analysis, D.N.K.; investigation, E.V.D.; resources, E.V.D.; data curation, V.V.K.; writing—original draft preparation, V.V.K. and D.N.K.; writing—review and editing, V.V.K. and D.N.K.; supervision, V.V.K.; project administration, V.V.K.; funding acquisition, V.V.K. and D.N.K. All authors have read and agreed to the published version of the manuscript.

Funding: This publication was financially supported by the Russian Ministry of Education and Science (project no. FZEN-2020-0022). The reported study was funded by the RFBR and Krasnodar region according to the research project no. 19-43-230009.

Data Availability Statement: Data available from the corresponding authors upon reasonable request.

Acknowledgments: The GC/MS, HRMS study was accomplished with the use of scientific equipment of the Collective Employment Centre "Ecoanalytical Centre", Kuban State University (A. Z. Temerdashev).

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

References

1. Diederich, F.; Stang, P.J.; Tykwinski, R.R. *Acetylene Chemistry: Chemistry, Biology, and Material Science*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2005; pp. 1–508. [CrossRef]
2. Trost, B.M.; Li, C.-J. *Modern Alkyne Chemistry: Catalytic and Atom-Economic Transformations*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2005; pp. 1–402. [CrossRef]
3. Rodygin, K.S.; Werner, G.; Kucherov, F.A.; Ananikov, V.P. Calcium carbide: A unique reagent for organic synthesis and nanotechnology. *Chem. Asian J.* **2016**, *11*, 965–976. [CrossRef] [PubMed]
4. Rodygin, K.S.; Ledovskaya, M.S.; Voronin, V.V.; Lotsman, K.A.; Ananikov, V.P. Calcium carbide: Versatile synthetic applications, green methodology and sustainability. *Eur. J. Org. Chem.* **2021**, *2021*, 43–52. [CrossRef]
5. Van Bonn, P.; Bolm, C. Mechanochemical synthesis of diarylethynes from aryl iodides and CaC_2. *Synlett* **2022**, *33*, 893–897. [CrossRef]
6. Nandy, S.; Paul, S.; Das, K.K.; Kumar, P.; Ghorai, D.; Panda, S. Synthesis and reactivity of alkynyl boron compounds. *Org. Biomol. Chem.* **2021**, *19*, 7276–7297. [CrossRef] [PubMed]
7. Tani, T.; Sawatsugawa, Y.; Sano, Y.; Hirataka, Y.; Takahashi, N.; Hashimoto, S.; Sugiura, T.; Tsuchimoto, T. Alkynyl−B(dan)s in Various Palladium-Catalyzed Carbon−Carbon Bond-Forming Reactions Leading to Internal Alkynes, 1,4-Enynes, Ynones, and Multiply Substituted Alkenes. *Adv. Synth. Catal.* **2019**, *361*, 1815–1834. [CrossRef]
8. Stefani, H.A.; Cella, R.; Vieira, A.S. Recent advances in organotrifluoroborates chemistry. *Tetrahedron* **2007**, *63*, 3623–3658. [CrossRef]
9. Buendia, M.B.; Balin, J.-G.J.; Andersen, M.E.; Lian, Z.; Kramer, S. Copper-catalyzed alkynylation of benzylic C-H bonds with alkynylboronic esters. *Synlett* **2022**, *33*, 150–154. [CrossRef]
10. Micouin, L.; Piccardi, R.; Turcaud, S.; Benedetti, E. Synthesis and Reactivity of Mixed Dimethylalkynylaluminum Reagents. *Synthesis* **2019**, *50*, 97–106. [CrossRef]
11. Kafuta, K.; Rugen, C.J.; Heilmann, T.; Liu, T.; Golz, C.; Alcarazo, M. Reactivity of 5-(Alkynyl)dibenzothiophenium Salts: Synthesis of Diynes, Vinyl Sulfones, and Phenanthrenes. *Eur. J. Org. Chem.* **2021**, *51*, 4038–4048. [CrossRef]
12. Waldecker, B.; Kraft, F.; Golz, C.; Alcarazo, M. 5-(alkynyl)dibenzothiophenium triflates: Sulfur-based reagents for electrophilic alkynylation. *Angew. Chem. Int. Ed.* **2018**, *57*, 12538–12542. [CrossRef]
13. Amos, S.G.E.; Cavalli, D.; Le Vaillant, F.; Waser, J. Direct photoexcitation of ethynylbenziodoxolones: An alternative to photocatalysis for alkynylation reactions. *Angew. Chem. Int. Ed.* **2021**, *60*, 23827–23834. [CrossRef]
14. Amos, S.G.E.; Waser, J. Radical alkynylations with EthynylBenziodoXolones: From photocatalysis to direct excitation. *Chimia* **2022**, *76*, 312–315. [CrossRef]
15. García Ruano, J.L.; Alemán, J.; Parra, A.; Marzo, L. Sulfonyl Acetylenes as Alkynylating Reagents Under Radical or Anionic Conditions. *Eur. J. Org. Chem.* **2014**, *2014*, 1577–1588. [CrossRef]
16. Andrei, M.; Undheim, K. Clarithromycin macrolides modified by unsaturation at the C10-position. *Phytochem. Lett.* **2022**, *50*, 128–133. [CrossRef]
17. Makhloutah, A.; Hatych, D.; Chartier, T.; Rocard, L.; Goujon, A.; Felpin, F.-X.; Hudhomme, P. An investigation of palladium-catalyzed Stille-type cross-coupling of nitroarenes in perylenediimide series. *Org. Biomol. Chem.* **2022**, *20*, 362–365. [CrossRef]
18. Yokose, D.; Nagashima, Y.; Kinoshita, S.; Nogami, J.; Tanaka, K. Enantioselective synthesis of axially chiral styrene-carboxylic esters by rhodium-catalyzed chelation-controlled [2+2+2] cycloaddition. *Angew. Chem. Int. Ed.* **2022**, *61*, e202202542. [CrossRef]
19. Ouadoudi, O.; Kaehler, T.; Çevik, E.G.; Bolte, M.; Stöger, B.; Virovets, A.; Lerner, H.-W.; Wagner, M. Late-stage derivatization of a $(B,O)_2$-doped perylene. *Dalton Trans.* **2022**, *51*, 13195–13198. [CrossRef]

20. Lapkin, A.; Constable, D.J.C. *Green Chemistry Metrics: Measuring and Monitoring Sustainable Processes. Green Chemistry Metrics: Measuring and Monitoring Sustainable Processes*; Blackwell Publishing Ltd.: Hoboken, NJ, USA, 2009; pp. 1–324. [CrossRef]
21. Levashov, A.S.; Andreev, A.A.; Konshin, V.V. Lewis acid promoted direct synthesis of tetraalkynylstannanes. *Tetrahedron Lett.* **2015**, *56*, 1870–1872. [CrossRef]
22. Levashov, A.S.; Buryi, D.S.; Goncharova, O.V.; Konshin, V.V.; Dotsenko, V.V.; Andreev, A.A. Tetraalkynylstannanes in the stille cross coupling reaction: A new effective approach to arylalkynes. *New J. Chem.* **2017**, *41*, 2910–2918. [CrossRef]
23. Levashov, A.S.; Aksenov, N.A.; Aksenova, I.V.; Konshin, V.V. Oxidative coupling of tetraalkynyltin with aldehydes leading to alkynyl ketones. *New J. Chem.* **2017**, *41*, 8297–8304. [CrossRef]
24. Levashov, A.S.; Buryi, D.S. Lewis acid promoted reaction of tetraalkynylstannanes with acyl chlorides: An effective approach towards alkynyl ketones. *Tetrahedron Lett.* **2017**, *58*, 4476–4478. [CrossRef]
25. Lauder, K.; Toscani, A.; Scalacci, N.; Castagnolo, D. Synthesis and reactivity of propargylamines in organic chemistry. *Chem. Rev.* **2017**, *117*, 14091–14200. [CrossRef] [PubMed]
26. Jesin, I.; Nandi, G.C. Recent advances in the A^3 coupling reactions and their applications. *Eur. J. Org. Chem.* **2019**, *2019*, 2704–2720. [CrossRef]
27. Volkova, Y.; Baranin, S.; Zavarzin, I. A^3 coupling reaction in the synthesis of heterocyclic compounds. *Adv. Synth. Catal.* **2021**, *363*, 40–61. [CrossRef]
28. Monleón, A.; Blay, G.; Pedro, J.R. Catalytic enantioselective cyclopropylalkynylation of aldimines generated in situ from α-amido sulfones. *Molecules* **2022**, *27*, 3763. [CrossRef]
29. Blay, G.; Monleon, A.; Pedro, J. Recent Developments in Asymmetric Alkynylation of Imines. *Curr. Org. Chem.* **2009**, *13*, 1498–1539. [CrossRef]
30. Jiang, B.; Si, Y.-G. Lewis acid promoted alkynylation of imines with terminal alkynes: Simple, mild and efficient preparation of propargylic amines. *Tetrahedron Lett.* **2003**, *44*, 6767–6768. [CrossRef]
31. Mokuolu, Q.F.; Duckmanton, P.A.; Hitchcock, P.B.; Wilson, C.; Blake, A.J.; Shukla, L.; Love, J.B. Early-late, mixed-metal compounds supported by amidophosphine ligands. *Dalton Transactions* **2004**, *13*, 1960–1970. [CrossRef]
32. Nanni, D.; Pareschi, P.; Walton, J.C. An electron paramagnetic resonance study of intermediates generated from aromatic aldimines. *J. Chem. Soc. Perkin Trans.* **2002**, *6*, 1098–1104. [CrossRef]
33. Yamashita, Y.; Noguchi, A.; Fushimi, S.; Hatanaka, M.; Kobayashi, S. Chiral metal salts as ligands for catalytic asymmetric mannich reactions with simple amides. *J. Am. Chem. Soc.* **2021**, *143*, 5598–5604. [CrossRef]
34. Spesivaya, E.S.; Lupanova, I.A.; Konshina, D.N.; Konshin, V.V. $Zn(OTf)_2$/i-Pr_2NEt promoted synthesis of tetraalkynylsilanes. *Tetrahedron Lett.* **2021**, *63*, 152713. [CrossRef]
35. Andreev, A.A.; Konshin, V.V.; Vinokurov, N.A.; Komarov, N.V. Synthesis of tri-and tetraalkynylgermanes. *Russ. Chem. Bull.* **2006**, *55*, 1430–1432. [CrossRef]
36. Li, C.-J.; Wei, C. Highly efficient Grignard-type imine additions via C-H activation in water and under solvent-free conditions. *Chem. Commun.* **2002**, *3*, 268–269. [CrossRef]
37. Zani, L.; Alesi, S.; Cozzi, P.G.; Bolm, C. Dimethylzinc-Mediated Alkynylation of Imines. *J. Org. Chem.* **2006**, *71*, 1558–1562. [CrossRef]