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Fast and scalable solvent-free access to Lappert's heavier tetrylenes $E\{N(SiMe_3)_2\}_2$ ($E = Ge, Sn, Pb$) and $ECl\{N(SiMe_3)_2\}$ ($E = Ge, Sn$)†

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Iconic Lappert's heavier tetrylenes $E\{N(SiMe_3)_2\}_2$ ($E = Ge$ (1), Sn (2), Pb (3)) have been efficiently prepared from $GeCl_2 \cdot (1,4\text{-dioxane})$, $SnCl_2$ or $PbCl_2$ and $Li\{N(SiMe_3)_2\}$ via a completely solvent-free one-pot mechanochemical route followed by sublimation. This fast, high-yielding and scalable approach (2 has been prepared in a 100 mmol scale), which involves a small environmental footprint, represents a remarkable improvement over any synthetic route reported over the last five decades, being a so far rare example of the use of mechanochemistry in the realm of main group chemistry. This solventless route has been successfully extended to the preparation of other heavier tetrylenes, such as $ECl\{N(SiMe_3)_2\}$ ($E = Ge$ (4), Sn (5)).

Introduction

Over the last two decades the main group arena has experienced a renaissance, from fundamental structural studies, through bonding and reactivity, to applications in catalysis and materials,^{1,2} and the development of new synthetic approaches has proven fundamental to the advancement of chemistry and its neighbouring fields.³

In this context, mechanochemistry represents an effective alternative to classical solution-based methods since it allows for chemical transformations to proceed with minimal (or no) solvent involvement, which has a profound impact, not only reducing solvent waste, but also eliminating time- and energy-consuming solvent purification and removal steps. Hence, mechanosynthesis has been growing as powerful alternative to solution-based thermochemistry for the last two decades⁴ in a wide range of fields.^{5–12} However, it remains underrepresented across the main group element arena.^{8,13}

On the other hand, heavier carbene analogues, also known as heavier tetrylenes (HTs), are currently receiving increasing attention, not only for their rich and unique fundamental chemistry (small molecule activation, insertion into σ -bonds, catalysis, etc.)^{14,15} but also for their rising use as ligands in

coordination chemistry and homogeneous catalysis.^{16,17} In fact, HT species can be very strong electron-donating ligands,¹⁸ stronger than NHCs, being also able to cooperate with the metal in substrate activation processes.¹⁹

With these two precedents in mind, we decided to revisit the currently used synthetic routes to $E\{N(SiMe_3)_2\}_2$ ($E = Ge$ (1), Sn (2), Pb (3)), reported by both Lappert and Zuckerman (only 2) in 1974.²⁰ These are some of the first HTs ever reported different from the long-known heavier group 14 (Ge, Sn and Pb) dihalides. Notably, compounds 1–3 have an extensive chemistry (e.g., materials chemistry,^{21a–c} metal-free catalysis,^{21d,e} CH activation,^{21f,g} coordination chemistry^{16m–p,22}) as well as being popular precursors to other HTs.^{15b,m,n,16p,23} As proof of their synthetical value, compounds 1–3 are commercially available from various chemical suppliers (CAS numbers 55290-25-0, 59863-13-7 and 55147-59-6).

In addition to the original reports (in the 70's), several routes have been described for the synthesis of 1–3 (see Table S1 in the ESI†).^{20,24} In all cases, the solution-based transmetalation process comprises the reaction of $Li\{N(SiMe_3)_2\}$ (prepared *in situ* from $nBuLi$ and $HN(SiMe_3)_2$ or commercially obtained) with the corresponding tetrel dichloride (i.e., ECl_2 , $E = Ge, Sn$ and Pb), followed by one or more purification steps (i.e., solvent evaporation, addition of a different solvent, filtration, solvent evaporation^{20b,24d} and distillation/sublimation;^{20b} filtration, solvent evaporation and distillation/sublimation;^{24a,c,e} or solvent evaporation and distillation/sublimation^{24b,f}) to remove the $LiCl$ produced and other impurities. In addition, these syntheses require environmentally hazardous solvents (e.g., diethyl ether, tetrahydrofuran, hexane, toluene or benzene) that need to be previously dried and deoxygenated (see Fig. 1).

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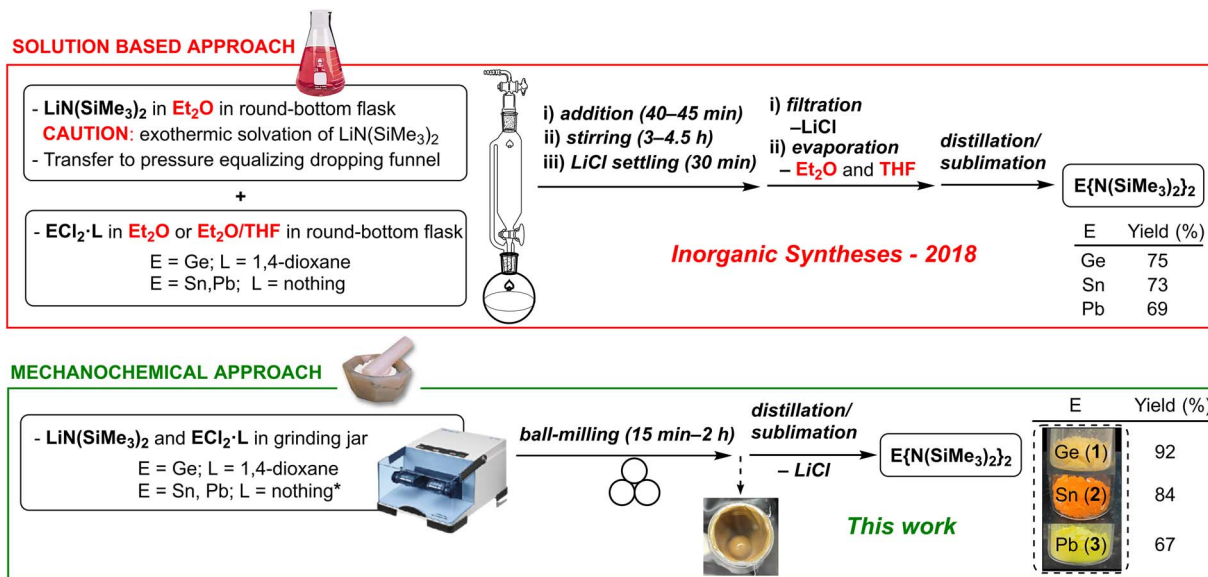


Fig. 1 Conventional solution-based (ref. 24c) vs. mechanochemical syntheses (this work) for compounds 1–3.

Herein, five decades after their first report, we demonstrate that Lappert's homoleptic heavier tetrylenes $\text{E}\{\text{N}(\text{SiMe}_3)_2\}_2$ (E = Ge (1), Sn (2), Pb (3)) as well as the heteroleptic derivatives $\text{ECl}\{\text{N}(\text{SiMe}_3)_2\}$ (E = Ge (4), Sn (5)) can be efficiently prepared in the absence of any solvent using a novel mechanochemical approach (see Fig. 1).

Results and discussion

Synthesis of $\text{E}\{\text{N}(\text{SiMe}_3)_2\}_2$ (E = Ge (1), Sn (2) and Pb (3))

Firstly, a 2 : 1 mixture of solid $\text{Li}\{\text{N}(\text{SiMe}_3)_2\}$ and $\text{GeCl}_2 \cdot (1,4\text{-dioxane})$ was ball-milled at 30 Hz at room temperature. After 15 min, an aliquot of the crude reaction mixture was analysed by *ex situ* ^1H NMR in C_6D_6 , showing almost quantitative formation of compound 1 (Fig. S1†; sharp singlet at 0.33 ppm (ref. 25)). In contrast, under analogous conditions, the reaction of $\text{Li}\{\text{N}(\text{SiMe}_3)_2\}$ with SnCl_2 afforded a 22 : 78 mixture of 2 and $\text{Li}\{\text{N}(\text{SiMe}_3)_2\}$ (determined by the integral ratio of the singlets at 0.30 (ref. 25) and 0.13 (ref. 26) ppm in the ^1H NMR spectrum of the crude mixture, Fig. S4†) after 15 min. Given the incomplete conversion, longer reaction times were attempted. However, only a slight increase in the amount of 2 was observed after 16 h (reaching a 24 : 76 ratio between 2 and $\text{Li}\{\text{N}(\text{SiMe}_3)_2\}$; Fig. S6†).

The absence of a 1,4-dioxane solvate molecule in SnCl_2 was claimed as responsible for the slow progress observed for the formation of stannylene 2 compared to that of germylene 1, in which one equivalent of 1,4-dioxane is present in the reaction medium. In order to assess if the presence of 1,4-dioxane improved the reaction outcome, the synthesis of 2 was attempted using a minute amount of 1,4-dioxane ($\eta = 4 \times 10^{-4}$).²⁷ Still, this approach did not produce any improvement after 15 min of ball-milling (Fig. S7†). However, it significantly accelerated the reaction conversion after 5 h, leading to an 86 : 14 mole ratio between 2 and $\text{Li}\{\text{N}(\text{SiMe}_3)_2\}$ (Fig. S8†), *cf.* 24 : 76 mole ratio for neat grinding after 16 h.

Considering the importance of solvent molecules and solvated species in the main-group arena,^{28,29} together with the concept of “solvate-assisted grinding”, recently proposed by Hanusa *et al.*,³⁰ we mimicked the solvation conditions existing throughout the formation of 1 by using η -solvate (η^{solv}), which we outlined as the formal number of solvate molecules per metal centre. Hence, the synthesis of 2 was carried out by adding one equivalent of 1,4-dioxane to the mixture of reagents ($\eta^{\text{solv}} = 1$).

To our delight, this approach allowed the formation of 2 almost quantitatively after 15 min of ball milling at 30 Hz (an aliquot of the crude was analysed by ^1H NMR, showing a sharp singlet at 0.30 ppm; Fig. S9†). The external addition of an amount of liquid additive for 2 equals the formal intrinsic solvation value, determined by using the $\text{GeCl}_2 \cdot (1,4\text{-dioxane})$ starting material, which allowed to mimic the faster reaction kinetics observed for the synthesis of 1. Notably, while η^{solv} value remains constant on descending the group, η decreases due to the increased atomic weight of the tetrel element (0.21 and 0.19, for 1 and 2, respectively). In this manner, η^{solv} allows to readily quantify the amount of solvent additives involved when solvated and unsolvated species are directly compared. However, whether 1,4-dioxane increases reaction kinetics *via* changes in the rheology of the reaction mixture and/or the formation of more reactive solvate species requires further investigation.

To complete the triad, plumbylene 3 was obtained under the same experimental conditions used for 2. Thus, a 2 : 1 : 1 mixture of solid $\text{Li}\{\text{N}(\text{SiMe}_3)_2\}$, PbCl_2 and 1,4-dioxane (*i.e.*, 500 μL , $\eta^{\text{solv}} = 1$, which corresponds to $\eta = 0.16$) was ball-milled at 30 Hz at room temperature. After 15 min, an aliquot of the crude reaction outcome was analysed by ^1H NMR in C_6D_6 , showing the formation of 3 (singlet at 0.25 ppm (ref. 25)) and an unknown species (singlet at 0.28 ppm), exhibiting signals of similar intensity (Fig. S13†). Longer reaction times (45 min) greatly



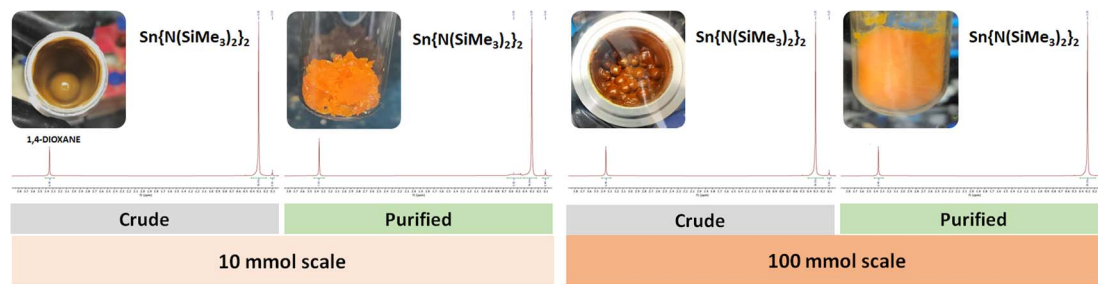


Fig. 2 Side-by-side comparison of the 10 and 100 mmol scale reactions (left and right, respectively) for the synthesis of $\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}_2$ (**2**). The inserts display the crude product obtained in 10 mL and the 250 mL stainless steel jars, and the resulting isolated product stored in a 20 mL vial and a 100 mL Schlenk tube for the small and large scales, respectively. See ESI† for expanded NMRs.

increased the amount of **3** (Fig. S14†), with no further evolution after 2 h of ball-milling (Fig. S15†).

Having developed a new optimised mechanochemical method for the formation of **1**, **2** and **3** as major products, these species were isolated by distillation/sublimation of the crude reaction outcomes in yields of 92%, 84% and 67%, respectively, and characterised employing multinuclear NMR (Fig. 2, S2, S3, S10–S12, S16–S18†).²⁵

Comparative assessment of the environmental footprint

Sustainability and environmental footprint has become increasingly important in synthetic chemistry.^{31–33} However, detailed comparisons between mechanochemical and conventional solution-based methodologies remain rare, especially for the chemistry of main group elements.^{34,35} Therefore, we compared our approach to compounds **1–3** with a contrasted solution-based synthetic route published recently (2018) in *Inorganic Syntheses*.^{24c} Qualitatively, a step-by-step comparison of the different steps required to prepare **1–3** indicates the advantages of the mechanochemical solventless route (fewer steps, less complexity, fewer hazards, shorter times, less waste management and less energy consumption to achieve comparable or better product yields).

In a quantitative manner, a green chemistry metrics (GCM)³⁶ approach was used for comparison. The environmental factor (*E*-factor),³⁷ atom economy (AE), process mass intensity (PMI), and reaction mass efficiency (RME) for both synthetic routes

were calculated (see Table 1; and ESI†). Under mechanochemical conditions, lower *E*-factors were observed (0.57, 0.70 and 1.06 vs. 2.53, 1.48 and 1.56) even though the energy consumption of the solvent purification and deoxygenation steps of the solution route was not taken into account. In the case of **2** and **3**, if the liquid additive used is considered as a solvent, the *E*-factor is further reduced (from 0.70 and 1.06 to 0.45 and 0.79, respectively). The PMI for the mechanochemical synthesis showed much lower values (1.57, 1.70 and 2.06) than their solution-based counterparts (18.07, 12.42 and 12.62). However, since both approaches use the same reagents, RME and AE values are comparable (depending on the yield of isolated products) and equal, respectively, for both processes.

Upscaled synthesis of $\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}_2$ (**2**)

Currently, one of the major challenges for the broader adoption of mechanochemical methodologies is its ability to be implemented at large preparative scales.³⁸ This is especially needed in the main group field, where examples of compounds, complexes and materials at large scales are scarce.³⁵

Based on this, we set off to upscale the route to compound **2**, which is the most used precursor of the series to prepare other HTs (stannylenes in this case),^{15b,m,n,16p,23} using a scale-up batch approach employing a planetary ball mill. A 250 mL jar was used to produce **2** in a 100 mmol scale by milling SnCl_2 (18.96 g, 100 mmol) with $\text{Li}\{\text{N}(\text{SiMe}_3)_2\}$ (33.46 g, 200 mmol) in the presence of 1,4-dioxane (10 mL, $\eta = 0.19$ and $\eta^{\text{sol}} = 1$, respectively) for 30 min. To our delight, the reaction was successfully scaled 10-fold, maintaining an almost quantitative conversion as illustrated by the ^1H NMR of the crude products (see Fig. 2). The larger scale preparation allowed the isolation of **2** by distillation (see Fig. S20–S22†) in a remarkable 88% yield (38.6 g), *cf.* 73% yield for the 100 mmol scale solution-based synthetic route published in *Inorganic Syntheses*,^{24c} demonstrating the suitability of the solventless designed methodology for multigram preparations.

Mechanochemical derivatisation of Lappert's heavier tetrylenes: synthesis of $\text{ECl}\{\text{N}(\text{SiMe}_3)_2\}$ (E = Ge (**4**) and Sn (**5**))

The successful solventless synthesis of **1–3** prompted us to extent our mechanochemical approach to the preparation of other heavier tetrylenes, in particular, the heteroleptic derivatives $\text{ECl}\{\text{N}(\text{SiMe}_3)_2\}$ (E = Ge (**4**), Sn (**5**) and Pb (**6**)).

Table 1 Comparison of green metrics between mechanochemical and a model conventional solution-based route for **1–3**

Compound	<i>E</i> -factor	PMI	RME (%)	AE (%)	Yield (%)
Mechanochemical route (this work)					
1	0.57	1.57	63.9	69.4	92
2	0.70/0.45 ^a	1.70	70.4	83.8	84
3	1.06/0.79 ^a	2.06	57.7	86.2	67
Solution-based route^{24c}					
1	2.53	18.07	52.1	69.4	75
2	1.48	12.42	61.2	83.8	73
3	1.56	12.62	59.4	86.2	69

^a Treating 1,4-dioxane as a “solvent”.



Chloroamido-stannylyene **5** was first isolated by both Lappert and Zuckerman in 1974 (ref. 20*a* and *c*) as a white solid in *ca.* 50% yield (latter improved to 87% in 1991).³⁹ Compound **5** is conventionally obtained following a solution-based⁴⁰ redistribution reaction between SnCl_2 and **2** (ref. 20*a* and 39) or a 1 : 1 transmetalation reaction of SnCl_2 and $\text{Li}\{\text{N}(\text{SiMe}_3)_2\}$.^{20*a,c*}

Chlorogermylene **4** has never been isolated, although it has been proposed as a reaction intermediate during the thermal decomposition of germacyclopentenes as a route to germaisonitriles.⁴¹

Lastly, in contrast to the lighter Ge and Sn counterparts, which identities have been fully confirmed³⁹ and proposed using photoelectron spectroscopy,⁴¹ respectively, chloroplumbylene **6** is unknown, to the best of our knowledge.

We chose the synthesis of **4–6** (Scheme 1) by the redistribution approach because no reaction subproducts were expected as well as it will demonstrate the viability of the mechano-derivatisation of compounds **1–3**, which will prove the broad applicability of mechanochemistry towards the synthesis and derivatisation of tetrylene species.

Therefore, a 1 : 1 mixture of solid **1**, **2** or **3** and the corresponding tetrel dihalide $\text{ECl}_2 \cdot \text{L}$ (E = Ge, Sn, Pb; L = 1,4-dioxane for E = Ge; nothing for E = Sn, Pb), in the presence of one equivalent of 1,4-dioxane for E = Sn, Pb ($\eta^{\text{soliv}} = 1$), was ball-milled at 30 Hz at room temperature. After 2.5 h, aliquots of the crude reaction mixtures were analysed by *ex situ* ^1H NMR in C_6D_6 . For E = Ge and Sn, these spectra displayed sharp singlets at different chemical shifts from those of **1** and **2**, which had entirely disappeared, indicating the formation of **4** (Fig. S23[†]) and **5** (Fig. S26[†]), respectively, as the major reaction products. Both compounds were isolated in 94% yield after evacuating the small amount of 1,4-dioxane present in the reaction medium (see Fig. S24 and S25 for **4** and S27–S29[†] for **5**). The NMR data of **5** is consistent with that reported in the literature,^{39,42} being the ^{119}Sn chemical shift at 124 ppm (Fig. S29[†]) particularly informative (note that the ^{119}Sn NMR spectrum of **2** shows a singlet at 769 ppm; Fig. S12[†]).

In contrast, for the heavier tetrel counterpart (E = Pb), no reaction took place after 2.5 h, with homoleptic **3** being the only

species observed by NMR analysis (Fig. S30-top[†]). An alternative direct mechanochemical synthesis of heteroleptic **6** was attempted by the 1 : 1 reaction of PbCl_2 and $\text{Li}\{\text{N}(\text{SiMe}_3)_2\}$. Unfortunately, the 1 : 1 reaction only led to the formation of **3** (Fig. S30-bottom[†]) and unreacted PbCl_2 . The presence of unreacted PbCl_2 was evidenced by the existence of a large amount of insoluble white solid in C_6D_6 .

The efficient transformation of the homoleptic diamido-HTs **1** and **2** to the heteroleptic chloroamido-HTs **4** and **5**, respectively, encouraged us to seek for further mechano-derivatisations that could show the full potential of mechanochemical approaches in main group chemistry. In this context, since chloroamidostannylyene **5** has been utilised in several reports as a precursor to prepare other HTs^{42,43} employing conventional solution-based protocols; as a proof of concept, we set out to mechanochemically synthesise chloroguanidinatostannylyene $\text{SnCl}\{\text{N}(\text{SiMe}_3)_2\}\{\text{N}^i\text{Pr}\}$ (**7**), previously carried out in diethylether by Ružička *et al.*,⁴³ by reacting **5** with the carbodiimide $^i\text{PrNCN}^i\text{Pr}$. To our delight, 20 min of ball-milling at 30 Hz of a 1 : 1 : 1 mixture of **5**, $^i\text{PrNCN}^i\text{Pr}$ and 1,4-dioxane led to the nearly quantitative formation of **7** (Fig. S31[†]), which was isolated in 72% yield (see Fig. S32–S34[†]).⁴⁴

Conclusions

In summary, a novel mechanochemical approach has been used to prepare heavier tetrylenes, allowing the efficient isolation of Lappert's diamidogermylene **1**, -stannylyene **2** and -plumbylene **3** and their subsequent transformation to the chloroamidogermylene (**4**) and -stannylyene (**5**) derivatives. Additionally, further mechano-derivatisations are possible (synthesis of **7**). These reactions can be readily upscaled, as demonstrated by the preparation of a 100 mmol batch of $\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}_2$ (**2**) in 88% yield.

The solvent-free routes reported in this study surpass all of the solution-based methods reported for their synthesis in the past five decades, as they deliver a rapid, high-yielding, and environmentally benign processes that represent a milestone in the development of mechanochemical methods in the main group arena. The efficient syntheses of **1–5** and **7** anticipate that mechanochemistry holds great potential for a more sustainable synthesis of other homoleptic (*i.e.*, amino-/alkyl-/aryl-/phosphino-) and heteroleptic HTs, a field that currently remains unexplored.

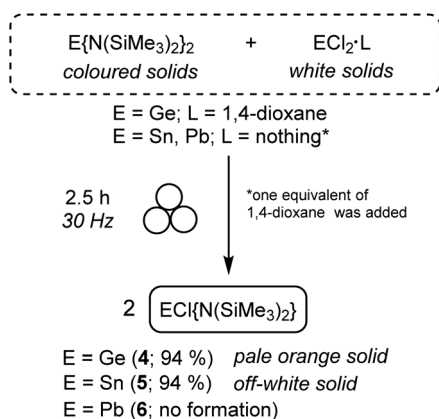
We hope our manuscript encourages more main group and synthetic chemists to incorporate mechanochemical methodologies in their synthetic toolbox throughout their studies.

Data availability

The associated ESI file[†] contains the data supporting this article (synthetic procedures, characterization data, NMR spectra, green metrics calculations).

Author contributions

R. G.-S. and J. F. R. performed the experimental and characterization activities and wrote the draft of the ESL.[†] The work was



Scheme 1 Mechanochemical reactions of homoleptic $\text{E}\{\text{N}(\text{SiMe}_3)_2\}_2$ (E = Ge (**1**), Sn (**2**) and Pb (**3**)) with the corresponding tetrel dihalide to produce heteroleptic $\text{ECl}\{\text{N}(\text{SiMe}_3)_2\}$ (E = Ge (**4**) and Sn (**5**)).



conceived by F. G. and P. G.-Á. and supervised by F. G., P. G.-Á. and J. A. C. The manuscript text and the final version of the ESI file† were written and revised by F. G., P. G.-Á. and J. A. C.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- 1 S. Aldrich and C. Jones, *Chem. Soc. Rev.*, 2016, **45**, 763–764 and articles cited therein.
- 2 P. P. Power, *Nature*, 2010, **463**, 171–177.
- 3 T. Chivers and J. Konu, *Comments Inorg. Chem.*, 2009, **30**, 131–176.
- 4 (a) J.-L. Do and T. Friščić, *ACS Cent. Sci.*, 2017, **3**, 13–19; (b) S. L. James, C. J. Adams, C. Bolm, D. Braga, P. Collier, T. Friščić, F. Grepioni, K. D. Harris, G. Hyett and W. Jones, *Chem. Soc. Rev.*, 2012, **41**, 413–447; (c) T. Friščić, C. Mottillo and H. M. Titi, *Angew. Chem., Int. Ed.*, 2020, **59**, 1030–1041.
- 5 (a) F. Cuccu, L. De Luca, F. Delogu, E. Colacino, N. Solin, R. Mocchi and A. Porcheddu, *ChemSusChem*, 2022, **15**, e202200362; (b) D. Virieux, F. Delogu, A. Porcheddu, F. García and E. Colacino, *J. Org. Chem.*, 2021, **86**, 13885–13894; (c) J. G. Hernández and C. Bolm, *J. Org. Chem.*, 2017, **82**, 4007–4019; (d) V. Declerck, P. Nun, J. Martinez and F. Lamaty, *Angew. Chem., Int. Ed.*, 2009, **48**, 9318–9321.
- 6 (a) D. Tan, L. Loots and T. Friščić, *Chem. Commun.*, 2016, **52**, 7760–7781; (b) P. Ying, J. Yu and W. Su, *Adv. Synth. Catal.*, 2021, **363**, 1246–1271; (c) L. Konnert, B. Reneaud, R. Marcia de Figueiredo, J.-M. Campagne, F. Lamaty, J. Martinez and E. Colacino, *J. Org. Chem.*, 2014, **79**, 10132–10142; (d) O. Galant, G. Cerfeda, A. S. McCalmont, S. L. James, A. Porcheddu, F. Delogu, D. E. Crawford, E. Colacino and S. Spataro, *ACS Sustainable Chem. Eng.*, 2022, **10**, 1430–1439.
- 7 (a) N. R. Rightmire and T. P. Hanusa, *Dalton Trans.*, 2016, **45**, 2352–2362; (b) F. Leon and F. Garcia, *Comprehensive Coordination Chemistry III*, 2021, vol. 9, pp. 620–679.
- 8 (a) A. A. Gečiauskaitė and F. García, *Beilstein J. Org. Chem.*, 2017, **13**, 2068–2077; (b) D. Tan and F. García, *Chem. Soc. Rev.*, 2019, **48**, 2274–2292.
- 9 (a) D. Chen, J. Zhao, P. Zhang and S. Dai, *Polyhedron*, 2019, **162**, 59–64; (b) T. Stolar and K. Užarević, *CrystEngComm*, 2020, **22**, 4511–4525; (c) T. Friščić, *J. Mater. Chem.*, 2010, **20**, 7599–7605; (d) P. A. Julien, C. Mottillo and T. Friščić, *Green Chem.*, 2017, **19**, 2729–2747.
- 10 V. K. Portnoi, V. A. Leonov, S. E. Filippova, A. I. Logacheva, A. G. Beresnev and I. M. Razumovskii, *Inorg. Mater.*, 2016, **52**, 895–901.
- 11 (a) B. Szczesniak, S. Borysiuk, J. Choma and M. Jaroniec, *Mater. Horiz.*, 2020, **7**, 1457–1473; (b) T. F. Grigorieva, A. P. Barinova and N. Z. Lyakhov, *J. Nanopart. Res.*, 2003, **5**, 439–453.
- 12 (a) D. Braga, L. Maini and F. Grepioni, *Chem. Soc. Rev.*, 2013, **42**, 7638–7648; (b) Z. X. Ng, D. Tan, T. Wei Liang, F. Leon, X.-Y. Shi, Y. Sim, Y. Li, R. Ganguly, Z. Yanli, M. Sharmarke and F. García, *Angew. Chem., Int. Ed.*, 2021, **60**, 17481–17490; (c) M. M. Haskins and M. J. Zaworotko, *Cryst. Growth Des.*, 2021, **21**, 4141–4150.
- 13 (a) D. Jędrzkiewicz, J. Mai, J. Langer, Z. Mathe, N. Patel, S. DeBeer and S. Harder, *Angew. Chem., Int. Ed.*, 2022, **61**, e202200511; (b) J. Wang, R. Ganguly, L. Yongxin, J. Diaz, H. S. Soo and F. García, *Dalton Trans.*, 2016, **45**, 7941–7946; (c) N. R. Rightmire, T. P. Hanusa and A. L. Rheingold, *Organometallics*, 2014, **33**, 5952–5955; (d) R. F. Koby, T. P. Hanusa and N. D. Schley, *J. Am. Chem. Soc.*, 2018, **140**, 15934–15942; (e) R. F. Koby, A. M. Doerr, N. R. Rightmire, N. D. Schley, B. K. Long and T. P. Hanusa, *Angew. Chem., Int. Ed.*, 2020, **59**, 9542–9548; (f) I. R. Speight, S. C. Chmely, T. P. Hanusa and A. L. Rheingold, *Chem. Commun.*, 2019, **55**, 2202–2205; (g) I. R. Speight and T. P. Hanusa, *Molecules*, 2020, **25**, 570; (h) Y. Sim, D. Tan, R. Ganguly, Y. Li and F. García, *Chem. Commun.*, 2018, **54**, 6800–6803; (i) Y. Sim, Y.-X. Shi, R. Ganguly, Y. Li and F. García, *Chem.–Eur. J.*, 2017, **47**, 11279–11285; (j) P. Gao, J. Jiang, S. Maeda, K. Kubota and H. Ito, *Angew. Chem., Int. Ed.*, 2022, **61**, e202207118; (k) R. Takahashi, A. Hu, P. Gao, Y. Gao, Y. Pang, T. Seo, J. Jiang, S. Maeda, H. Takaya, K. Kubota and H. Ito, *Nat. Commun.*, 2021, **12**, 6691; (l) Y.-X. Shi, K. Xu, J. Clegg, R. Ganguly, H. Hirao, T. Friscic and F. García, *Angew. Chem., Int. Ed.*, 2016, **55**, 12736–12740; (m) R. F. Koby, A. M. Doerr, N. R. Rightmire, N. D. Schley, W. W. Brennessel, B. K. Long and T. P. Hanusa, *Chem.–Eur. J.*, 2021, **27**, 8195–8202; (n) R. F. Koby, N. D. Schley and T. P. Hanusa, *Angew. Chem., Int. Ed.*, 2021, **60**, 21174–21178.
- 14 Selected recent reviews on general chemistry of HTs (they might include coordination chemistry): (a) S. Yao, A. Saddington, Y. Xiong and M. Driess, *Acc. Chem. Res.*, 2023, **56**, 475–488; (b) Y. Zhang, L. Wu and H. Wang, *Coord. Chem. Rev.*, 2023, **477**, 214942–214961; (c) L. Wang, Y. Li, Z. Li and M. Kira, *Coord. Chem. Rev.*, 2022, **457**, 214413–214431; (d) S. Yao, Y. Xiong, A. Saddington and M. Driess, *Chem. Commun.*, 2021, **57**, 10139–10153; (e) S. Fujimori and S. Inoue, *Eur. J. Inorg. Chem.*, 2020, **33**, 3131–3142; (f) S. Khan and H. W. Roesky, *Chem.–Eur. J.*, 2019, **25**, 1636–1648; (g) S. S. Sen and H. W. Roesky, *Chem. Commun.*, 2018, **54**, 5046–5057; (h) N. Muthukumar, K. Velappan, K. Gour and G. Prabusankar, *Coord. Chem. Rev.*, 2018, **377**, 1–43; (i) T. J. Hadlington, M. Driess and



- C. Jones, *Chem. Soc. Rev.*, 2018, **47**, 4176–4197; (j) R. Tacke and T. Ribbeck, *Dalton Trans.*, 2017, **46**, 13628–13659.
- 15 Selected reviews on general chemistry of HTs (they might include coordination chemistry): (a) E. Rivard, *Chem. Soc. Rev.*, 2016, **45**, 989–1003; (b) C. Marschner, *Eur. J. Inorg. Chem.*, 2015, **23**, 3805–3820; (c) G. Prabusankar, A. Sathyanarayana, P. Suresh, C. N. Babu, K. Srinivas and B. P. R. Metla, *Coord. Chem. Rev.*, 2014, **269**, 96–133; (d) K. Izod, *Coord. Chem. Rev.*, 2013, **257**, 924–945; (e) Y. Xiong, S. Yao and M. Driess, *Angew. Chem., Int. Ed.*, 2013, **52**, 4302–4311; (f) R. S. Ghadwal, R. Azhakar and H. W. Roesky, *Acc. Chem. Res.*, 2013, **46**, 444–456; (g) S. K. Mandal and H. W. Roesky, *Acc. Chem. Res.*, 2012, **45**, 298–307; (h) M. Asay, C. Jones and M. Driess, *Chem. Rev.*, 2011, **111**, 354–396; (i) S. Yao, Y. Xiong and M. Driess, *Organometallics*, 2011, **30**, 1748–1767; (j) S. K. Mandal and H. W. Roesky, *Chem. Commun.*, 2010, **46**, 6016–6041; (k) M. Kira, *Chem. Commun.*, 2010, **46**, 2893–2903; (l) V. Y. Lee and A. Sekiguchi, in *Organometallic Compounds of Low Coordinate Si, Ge, Sn and Pb: From Phantom Species to Stable Compounds*, Wiley-VCH, Chichester, UK, 2010; (m) Y. Mizuhata, T. Sasamori and N. Tokitoh, *Chem. Rev.*, 2009, **109**, 3479–3511; (n) A. V. Zabula and F. E. Hahn, *Eur. J. Inorg. Chem.*, 2008, **33**, 5165–5179.
- 16 For reviews more focused on the coordination chemistry of HTs, see: (a) J. A. Cabeza and P. García-Álvarez, *Chem.–Eur. J.*, 2023, **29**, e202203096; (b) V. L. Lee, *Eur. J. Inorg. Chem.*, 2022, e202200175; (c) R. J. Somerville and J. Campos, *Eur. J. Inorg. Chem.*, 2021, 3488–3498; (d) M. Gosh and S. Khan, *Dalton Trans.*, 2021, **50**, 10674–10688; (e) J. A. Cabeza, P. García-Álvarez and C. J. Laglera-Gándara, *Eur. J. Inorg. Chem.*, 2020, 784–795; (f) M. Saito, *Acc. Chem. Res.*, 2018, **51**, 160–169; (g) M. C. Lipke, A. L. Liberman-Martin and T. D. Tilley, *Angew. Chem., Int. Ed.*, 2017, **56**, 2260–2294; (h) J. Y. Corey, *Chem. Rev.*, 2016, **116**, 11291–11435; (i) L. Alvarez-Rodríguez, J. A. Cabeza, P. Garcia-Alvarez and D. Polo, *Coord. Chem. Rev.*, 2015, **300**, 1–28; (j) J. Baumgartner and C. Marschner, *Rev. Inorg. Chem.*, 2014, **34**, 119–152; (k) B. Blom, M. Stoelzel and M. Driess, *Chem.–Eur. J.*, 2013, **19**, 40–62; (l) R. Waterman, P. G. Hayes and T. D. Tilley, *Acc. Chem. Res.*, 2007, **40**, 712–719; (m) M. Okazaki, H. Tobita and H. Ogino, *Dalton Trans.*, 2003, 493–506; (n) M. F. Lappert and R. S. Rowe, *Coord. Chem. Rev.*, 1990, **100**, 267–292; (o) W. Petz, *Chem. Rev.*, 1986, **86**, 1019–1047; (p) M. F. Lappert and P. P. Power, *J. Chem. Soc., Dalton Trans.*, 1985, 51–57.
- 17 For a review more focused on catalysis with HT-metal complexes, see: Y.-P. Zhou and M. Driess, *Angew. Chem., Int. Ed.*, 2019, **58**, 3715–3728.
- 18 See, for example: (a) Z. Benedek and T. Szilvási, *Organometallics*, 2017, **36**, 1591–1600; (b) Z. Benedek and T. Szilvási, *RSC Adv.*, 2015, **5**, 5077–5086.
- 19 See, for example: (a) Ref. 16c; (b) Y.-P. Zhou, S. Raoufmoghaddam, T. Szilvási and M. Driess, *Angew. Chem., Int. Ed.*, 2016, **55**, 12868–12872; (c) D. Gallego, A. Bruck, E. Irran, F. Meier, M. Kaupp, M. Driess and J. F. Hartwig, *J. Am. Chem. Soc.*, 2013, **135**, 1561–15626; (d) B. Blom, S. Enthaler, S. Inoue, E. Irran and M. Driess, *J. Am. Chem. Soc.*, 2013, **135**, 6703–6713; (e) M. E. Fasulo, M. C. Lipke and T. D. Tilley, *Chem. Sci.*, 2013, **4**, 3882–3887; (f) E. Calimano and T. D. Tilley, *Organometallics*, 2010, **29**, 1680–1692; (g) E. Calimano and T. D. Tilley, *J. Am. Chem. Soc.*, 2009, **131**, 11161–11173; (h) K. E. Litz, J. E. Bender IV, J. W. Kampf and M. M. B. Holl, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 496–498.
- 20 (a) D. H. Harris and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1974, 895–896; (b) M. J. S. Gynane, D. H. Harris, M. F. Lappert, P. P. Power, P. Rivière and M. Rivière-Baudet, *J. Chem. Soc., Dalton Trans.*, 1977, 2004–2009; (c) C. D. Schaeffer and J. J. Zuckerman, *J. Am. Chem. Soc.*, 1974, **96**, 7160–7162.
- 21 See, for example: (a) M. S. Seifner, F. Biegger, A. Lugstein, J. Bernardi and S. Barth, *Chem. Mater.*, 2015, **27**, 6125–6130; (b) M. R. Buck, A. J. Biacchi, E. J. Popczun and R. E. Schaak, *Chem. Mater.*, 2013, **25**, 2163–2171; (c) B. Hernandez-Sanchez, T. J. Boyle, H. D. Pratt, M. A. Rodriguez, L. N. Brewer and D. R. Dunphy, *Chem. Mater.*, 2008, **20**, 6643–6656; (d) S. Kobayashi, S. Iwate and S. Shoda, *Acta Polym.*, 1995, **46**, 471–475; (e) T. Xing, T. J. Prior and C. Redshaw, *Dalton Trans.*, 2021, **50**, 15140–15152; (f) K. A. Miller, J. M. Bartolin, R. M. O'Neill, R. D. Sweeder, T. M. Owens, J. W. Kampf, M. M. Banaszak Holl and N. J. Wells, *J. Am. Chem. Soc.*, 2003, **125**, 8986–8987; (g) J. M. Bartolin, A. Kavara, J. W. Kampf and M. M. Banaszak Holl, *Organometallics*, 2006, **25**, 4738–4740.
- 22 See, for example: (a) N. Hidalgo, S. Bajo, J. J. Moreno, C. Navarro-Gilabert, B. Q. Mercado and J. Campos, *Dalton Trans.*, 2019, **48**, 9127–9138; (b) J. A. Cabeza, J. M. Fernández-Colinas, P. García-Álvarez and D. Polo, *Inorg. Chem.*, 2012, **51**, 3896–3903; (c) J. A. Cabeza, P. García-Álvarez and D. Polo, *Inorg. Chem.*, 2012, **51**, 2569–2576; (d) Z. T. Cygan, J. W. Kampf and M. M. Banaszak Holl, *Inorg. Chem.*, 2003, **42**, 7219–7226; (e) K. E. Litz, J. W. Kampf and M. M. Banaszak Holl, *J. Am. Chem. Soc.*, 1998, **120**, 7484–7492; (f) K. E. Litz, J. E. Bender IV, J. W. Kampf and M. M. Banaszak Holl, *Angew. Chem., Int. Ed.*, 1997, **36**, 496–498; (g) S. M. Hawkins, P. B. Hitchcock, M. F. Lappert and A. K. Rai, *J. Chem. Soc. Chem. Commun.*, 1986, 1689–1690.
- 23 See, for example: (a) P. Sikora, R. Naumann, C. Förster and K. Heinze, *Chem. Sci.*, 2023, **14**, 2489–2500; (b) Y. K. Loh, L. Ying, M. Á. Fuentes, D. C. H. Do and S. Aldridge, *Angew. Chem., Int. Ed.*, 2019, **58**, 4847–4851; (c) J. M. Stauber, P. Müller, Y. Dai, G. Wu, D. G. Nocera and C. C. Cummins, *Chem. Sci.*, 2016, **7**, 6928–6933; (d) I. Orbjartel, N. A. Pott, M. John and D. Stalke, *Organometallics*, 2010, **29**, 5670–5675; (e) A. Murso, M. Straka, M. Kaupp, R. Bertermann and D. Stalke, *Organometallics*, 2005, **24**, 3576–3578; (f) A. V. Zabula, T. Pape, A. Hepp, F. M. Schappacher, U. C. Rodewald, R. Pöttgen and F. E. Hahn, *J. Am. Chem. Soc.*, 2008, **130**, 5648–5649; (g) T. Gans-Eichler, D. Gudat and M. Nieger, *Angew. Chem., Int. Ed.*, 2002, **41**, 1888–1891.
- 24 See, for example: (a) C. D. Schaeffer Jr, L. K. Myers, S. M. Coley, J. C. Otter and C. H. Yoder, *J. Chem. Educ.*,



- 1990, **67**, 347–349; (b) T. Heidemann and S. Mathur, *Eur. J. Inorg. Chem.*, 2014, 506–510; (c) A. J. Veinot, D. L. Stack, J. A. C. Clyburne and J. D. Masuda, *Inorg. Synth.*, 2018, **37**, 26–31; (d) M. Fischer, M. M. D. Roy, L. L. Wales, M. A. Ellwanger, A. Heilmann and S. Aldridge, *J. Am. Chem. Soc.*, 2022, **144**, 8908–8913; (e) G. Bačić, D. Zanders, B. Mallick, A. Devi and S. T. Barry, *Inorg. Chem.*, 2018, **57**, 8218–8226; (f) A. Herve, A. L. Rodriguez and E. Fouquet, *J. Org. Chem.*, 2005, **70**, 1953–1956.
- 25 The NMR data reported for compounds 1–3 in the *Inorganic Syntheses* method (ref. 24c) has been used as reference.
- 26 A $^1\text{H-NMR}$ spectrum of a pure sample of $\text{Li}\{\text{N}(\text{SiMe}_3)\}$ in C_6D_6 is shown in Fig. S5,† showing a singlet at 0.13 ppm.
- 27 It is well known that the use of liquid additives accelerates the solid-state grinding process, mechanochemical technique known as liquid-assisted grinding (LAG). The LAG parameter (η), defined as the ratio of liquid (in μL) to the combined weights of solid reactants (in mg), permits a systematic comparison of the various grinding techniques (e.g., $\eta = 0$, neat grinding; <1 , LAG; ~ 2 – 12 , paste/slurry; >12 , solution)(a) G. A. Bowmaker, *Chem. Commun.*, 2013, **49**, 334–348; (b) T. Frišćić and W. Jones, *Cryst. Growth Des.*, 2009, **9**, 1621–1637; (c) T. Frišćić, S. L. Childs, S. A. A. Rizvi and W. Jones, *CrystEngComm*, 2009, **11**, 418–426.
- 28 For reviews on main group chemistry see: (a) R. Melen, *Science*, 2019, **363**, 479–484; (b) D. Bourissou, *Chem. Rev.*, 2019, **119**, 8229–8230; (c) L. Zhao, S. Pan, N. Holzmann, P. Schwerdtfeger and G. Frenking, *Chem. Rev.*, 2019, **119**, 8781–8845.
- 29 A. G. Massey, *Main Group Chemistry*, Wiley, 2nd edn, 2000.
- 30 H. P. DeGroot and T. P. Hanusa, *Organometallics*, 2021, **40**, 3516–3525.
- 31 P. T. Anastas and J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, New York, 1998, p. 30.
- 32 “United Nations Sustainable Development Goals,” can be found under <https://sdgs.un.org/goals>.
- 33 “Chemistry & Sustainable Development Goals,” can be found under <https://www.acs.org/content/acs/en/sustainability/chemistry-sustainable-development-goals.html>.
- 34 N. Fantozzi, J.-N. Volle, A. Porcheddu, D. Virieux, F. García and E. Colacino, *Chem. Soc. Rev.*, 2023, DOI: **10.1039/D2CS00997H**, advance article.
- 35 (a) V. K. Singh, A. Chamberlain-Clay, H. C. Ong, F. León, G. Hum, M. Y. Par, P. Daley-Dee and F. García, *ACS Sustainable Chem. Eng.*, 2021, **9**, 1152–1160; (b) F. Leon, C. Li, J. F. Reynes, V. K. Singh, X. Lian, H. C. Ong, G. Hum, H. Sun and F. García, *Faraday Discuss.*, 2023, **241**, 63–78.
- 36 A. Lapkin and D. J. C. Constable, *Green Chemistry Metrics: Measuring and Monitoring Sustainable Processes*, 2008, Print ISBN: 9781405159685, Online ISBN: 9781444305432.
- 37 E. Sheldon, *Green Chem.*, 2007, **9**, 1273–1283.
- 38 (a) E. Colacino, V. Isoni, D. Crawford and F. García, *Trends Chem.*, 2021, **3**, 335–339; (b) J. F. Reynes, V. Isoni and F. García, *Angew. Chem., Int. Ed.*, 2023, e202300819, DOI: **10.1002/anie.202300819**.
- 39 R. W. Chorley, P. B. Hitchcock, B. S. Jolly, M. F. Lappert and G. A. Lawless, *J. Chem. Soc., Chem. Commun.*, 1991, 1302–1303.
- 40 No detailed experimental procedure is given for the synthesis of $\text{SnCl}\{\text{N}(\text{SiMe}_3)_2\}$ (5) in ref. 20a and c. A solution-based approach is assumed considering further information provided shortly after (see: P. J. Davidson, D. H. Harris and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1976, 2268–2274) regarding reactivity studies of 5 prepared *in situ*.
- 41 S. Foucat, T. Pigot, G. Pfister-Guillouzo, H. Lavayssière and S. Mazières, *Organometallics*, 1999, **18**, 5322–5329.
- 42 See, for example: (a) H. Braunschweig, R. W. Chorley, P. B. Hitchcock, M. F. Lappert and L. J.-M. Pierssens, *Angew. Chem., Int. Ed.*, 1994, **33**, 1156–1158; (b) P. B. Hitchcock, M. F. Lappert, G. A. Lawless, G. M. de Lima and L. J.-M. Pierssens, *J. Organomet. Chem.*, 2000, **601**, 142–146.
- 43 See, for example: (a) H. Braunschweig, R. W. Chorley, P. B. Hitchcock and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1992, 1311–1312; (b) H. Braunschweig, B. Gehrhus, P. B. Hitchcock and M. F. Lappert, *Z. Anorg. Allg. Chem.*, 1995, **621**, 1922–1928; (c) H. Braunschweig, C. Drost, P. B. Hitchcock, M. F. Lappert and L. J.-M. Pierssens, *Angew. Chem., Int. Ed.*, 1997, **36**, 261–263; (d) C. Drost, P. B. Hitchcock, M. F. Lappert and L. J.-M. Pierssens, *Chem. Commun.*, 1997, 1141–1142; (e) Z.-X. Wang and Y.-X. Li, *Organometallics*, 2002, **21**, 4641–4647; (f) Z.-X. Wang, D.-Q. Wang and J.-M. Dou, *J. Organomet. Chem.*, 2003, **665**, 205–213; (g) H. Cox, P. B. Hitchcock, M. F. Lappert and L. J.-M. Pierssens, *Angew. Chem., Int. Ed.*, 2004, **43**, 4500–4504; (h) C. F. Caro, M. P. Coles, P. B. Hitchcock, M. F. Lappert and L. J.-M. Pierssens, *Dalton Trans.*, 2011, **40**, 9821–9983; (i) H. Vaňkátová, L. Broeckert, F. De Proft, R. Olejník, J. Turek, Z. Padělková and A. Růžička, *Inorg. Chem.*, 2011, **50**, 9454–9464; (j) T. Chlupatý, Z. Padělková, F. De Proft, R. Willem and A. Růžička, *Organometallics*, 2012, **31**, 2203–2211; (k) W.-C. Chang, A. Raj, H. Hiramatsu, H.-J. Li, M. S. Ziegler, Y. Lin, S. Huang and H.-J. Liu, *Chem. Commun.*, 2020, **56**, 6786–6789.
- 44 The NMR data reported for compound 7 in ref. 43j has been used as reference.

