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Note

One-pot synthesis of aryl butyl tellurides from tellurium tetrachloride and activated aromatics through a solventless step

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Abstract

A solventless preparation of aryl tellurium trichlorides from activated aromatic compounds avoiding the use of hazardous solvents as carbon tetrachloride and chloroform is described. The trichlorides were reduced and alkylated leading to aryl butyl tellurides in a one-pot procedure. Transmetallation of these tellurides with *n*-butyllithium followed by reaction with benzaldehyde gave the corresponding benzhydrols in good yields.

Keywords: Tellurium trichlorides; Arylic tellurides; One-pot synthesis; Transmetallation; Aryllithiums

1. Introduction

Organotellurium compounds have been used as precursors of molecule fragments, such as dienes and enediynes [1], present in the structure of important classes of natural products [2]. Some of the transformations involving organic tellurides developed in the last years have already been applied in the total synthesis of natural products [3], what shows that this branch of organic chemistry is not merely a potential synthetic tool, but has been incorporated to the synthetic methodology arsenal. Most of the synthetic methods developed are based on transformations using vinylic tellurides [4]. Several years ago, Sonoda and coworkers [5] reported the transformation of phenyl *n*-propyl telluride into phenyllithium. Recently we found that aromatic tellurides can directly generate aryl cyanocuprates through reaction with easily prepared dilithium diorgano cyanocuprates [6]. However, the aromatic derivatives of tellurium, which were the focus of the pioneering works in this area [7], have been neglected and most of them are still prepared by methodologies developed more than fifty years ago, employing hazardous solvents such as benzene, dioxane, carbon tetrachloride and chloroform [8]. In view of these facts we turned our attention to the practical preparation of butyl aryl tellurides.

2. Results and discussion

In this communication, we report the solventless preparation of aryl tellurium trichlorides by reaction of tellurium tetrachloride with the corresponding activated aromatic compounds. This reaction required in the past prolonged heating of the reagents in carbon tetrachloride or chloroform [8]. Initially we added a

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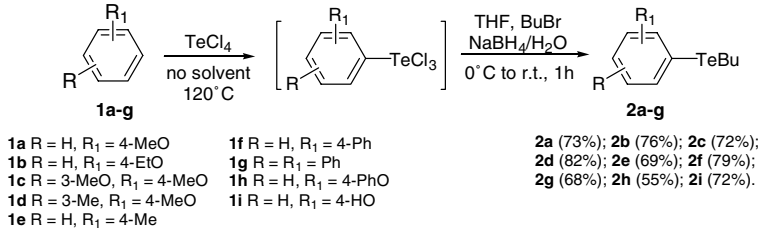
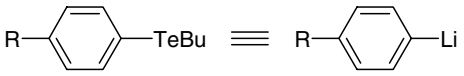


Scheme 1.

stoichiometric amount of anisole to a pre-heated flask in an oil bath at 120 °C containing tellurium tetrachloride. After 3 min, *p*-anisyl tellurium trichloride was obtained in a 98% isolated yield. As our interest was to prepare aryl butyl tellurides to be used as sources of reactive aryl organometallics, we performed the solventless reaction with a number of activated aromatic compounds (**1a**–**i**) and in situ transformed the aryl tellurium trichlorides into the corresponding aryl butyl tellurides (**2a**–**i**), by sequential reaction with aqueous sodium borohydride and *n*-butyl bromide at 0 °C (Scheme 1) [9].

The yields obtained for the tellurides **2a**–**i** refer to the overall process, corresponding to the formation of the aryl tellurium trichlorides, reduction to the aryl tellurolates and alkylation with *n*-bromobutane. In the case of the strongly activated substrates **1a**–**d** and **1h**–**i** the yields were good and the reaction time for the electrophilic aromatic substitution was around 3 min. The reaction with toluene (**1e**) required reflux of a stoichiometric mixture of the reactants for 12 h. For the less activated substrates (**1f** and **1g**) the reaction time for the electrophilic aromatic substitution was around 10 min and the yields were less satisfactory. However, the preparation of these aryl tellurium trichlorides using solvents was also a low yield process [8]. In the case of naphthalene (**1g**) an excess of substrate was required and the reaction was performed by melting first the substrate in a flask in an oil bath at 120 °C, followed by the addition of tellurium tetrachloride. In all the cases, the aryl tellurium trichlorides were not isolated. To perform the reduction followed by alkylation, the crude residue was cooled to room temperature, dissolved in tetrahydrofuran and mixed with *n*-bromobutane. To the mixture was added an aqueous solution of sodium borohydride at 0 °C and the reaction was allowed to stir at room temperature for 1 h. Usual

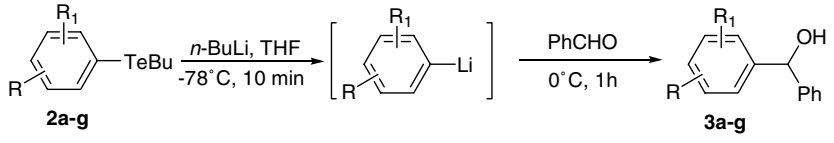


Scheme 2.

work-up and filtration through a silica gel column using hexanes as the eluent gave the aryl butyl tellurides in the yields shown in Scheme 1. The compounds obtained were stable, except telluride **2i**. In this case, telluride **2i** was transformed in situ into the corresponding diorgano tellurium dichloride by reaction with sulfuryl chloride [10] that was stable and could be isolated as colorless crystals in a 84% yield.

The structures of the obtained aryl butyl tellurides were confirmed by spectral data. GC–MS analysis, ^{1}H and ^{13}C NMR spectra indicated the exclusive formation of the isomers shown in (Scheme 1). The butyl tellurium group is positioned in *para* to the more activating group and, in the case of telluride **2g**, the product obtained was the β isomer. As mentioned before [5], phenyl *n*-propyl telluride is an efficient source of phenyllithium. In this way, the compounds presented in (Scheme 1) could be source of *para*-substituted aryl lithiums (Scheme 2), which are prepared mainly by lithium–halogen exchange [11]. However, the halogenation of the aromatic rings leads very often to mixture of regioisomers [12], in contrast to the telluration process using tellurium tetrachloride, which gives the *para*-isomer exclusively.

In order to confirm the generality of this transformation the prepared aryl butyl tellurides **2a**–**g** were transmetallated with *n*-butyllithium followed by capture of the *para*-substituted aryl lithiums with benzaldehyde as described by Sonoda and coworkers [5]. The expected benzhydrols **3a**–**g** were isolated in good yields in all cases (Scheme 3).



3a (73%); **3b** (76%); **3c** (72%); **3d** (82%);
3e (69%); **3f** (79%); **3g** (68%)

Scheme 3.

3. Conclusion

In conclusion, we showed that aryl tellurium trichlorides can be prepared avoiding the use of hazardous solvents and that these compounds can be transformed in a one pot procedure into aryl butyl tellurides, which are sources of *para*-substituted aryl lithiums. As organolithiums can be transformed by transmetallation in any other class of organometallic compounds in which the metal is more electronegative than lithium, the sequence of reactions described in this paper formally represents an access to important *para*-substituted aryl organometallics such as aryl copper, aryl cadmium, aryl magnesium and aryl zinc compounds.

4. Experimental section

All solvents and chemicals used were previously purified according to the usual methods [13]. THF was distilled from sodium/benzophenone under N_2, immediately before use in the transmetallation reactions. *n*-Butyllithium was titrated using 1,10-phenanthroline as indicator prior to use [14]. Tellurium tetrachloride was prepared according to the literature procedure [9]. The transmetallation reactions were carried out in dried glassware, under an inert atmosphere of dried and deoxygenated N_2. A dried and inert atmosphere is not required for the preparation of aryl butyl tellurides. Column chromatography was carried out with Merck silica gel (230–400 Mesh). Thin layer chromatography (TLC) was performed on silica gel F-254 on aluminum. ^1H and ^{13}C NMR spectra were recorded on either a Varian DPX-300, Bruker DRX-500 or a Bruker AC-200 spectrometers using as internal standard tetramethylsilane and the central peak of $CDCl_3$ (77 ppm), respectively. Chemical shifts (δ) are given in ppm, coupling constants (J) in Hz and multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), qn (quintet), sext (sextet), m (multiplet) and br (broad). Infrared spectra were recorded on a Bomem MB-100 spectrophotometer. Peaks area reported in cm^{-1} with indicated relative intensities: s (strong, 67–100%); m (medium, 34–66%), w (weak, 0–33%). Low resolution mass spectrometry was performed in a Shimadzu CGMS-17A/QP5050A instrument. Elemental analysis was performed at the Microanalytical Laboratory of the Chemistry Institute – University of São Paulo. The IUPAC names were obtained using the software ChemDraw Ultra®, version 7.0.1.

4.1. General procedure for the preparation of aryl tellurium trichlorides

A one-necked round-bottomed flask containing tellurium tetrachloride (5.38 g, 20 mmol) was heated to 120 °C and the corresponding aromatic compound (20 mmol) was added at once, dissolving the tellurium tetrachloride promptly. An evolution of HCl was observed and a yellow solid was formed. The system was cooled to room temperature and the trichloride was used crude in the reduction/alkylation procedure.

4.2. General procedure for the preparation of aryl butyl tellurides (**2a–d**, **2f**, **2h** and **2i**)

The trichloride prepared previously was dissolved in THF (80 mL) and bromobutane (5.48 g, 40 mmol) was added. The mixture was cooled to 0 °C and a solution of sodium borohydride (3 g, 80 mmol) in water (80 mL) was added dropwise. The mixture turned to dark with the addition of the first drops and then to light yellow after the completion of the addition. The reaction was stirred for further 20 min at room temperature and quenched with saturated solution of NH_4Cl (50 mL). The mixture was extracted with ethyl acetate (2×80 mL) and washed with brine (2×60 mL). The organic phases were combined, dried over $MgSO_4$ and concentrated at reduced pressure. The desired telluride was purified by silica gel column chromatography using hexanes as eluent.

4-Methoxy-1-butyltellanylbenzene (**2a**) [95849-63-1] (4.42 g, 76%). ^1H NMR (200 MHz, $CDCl_3$) δ ppm 7.68 (d, J 8.8 Hz, 2H); 6.72 (d, J 8.8 Hz, 2H); 3.79 (s, 3H); 2.82 (t, J 7.5 Hz, 2H); 1.74 (qn, J 7.3 Hz, 2H); 1.16 (sext, J 7.3 Hz, 2H); 0.88 (t, J 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 159.7 (C_4), 140.9 (C_2), 115.2 (C_3), 100.6 (C_1), 55.2 (OCH_3), 33.9 (CH_2CH_3), 25.0 ($TeCH_2CH_2$), 13.4 (CH_2CH_3), 8.69 ($TeCH_2$). LRMS *m/z* (rel. int., ion) 294 (13, M^+), 292 (12, $M^+ - 2$), 290 (7, $M^+ - 4$), 237 (7), 235 (7), 233 (5), 108 (100), 77 (9), 57 (15). IR (neat, cm^{-1}) 3000 (m), 2957 (m), 2926 (m), 2865 (m), 2840 (m), 1879 (w), 1616 (w), 1586 (s), 1488 (s), 1457 (m), 1244 (s), 1176 (s), 1032 (m), 818 (m), 588 (w), 514 (m).

4-Ethoxy-1-butyltellanylbenzene (**2b**) [95849-64-2] (4.27 g, 70%). ^1H NMR (300 MHz, $CDCl_3$) δ ppm 7.66 (d, J 8.7 Hz, 2H), 7.75 (d, J 8.7 Hz, 2H), 4.02 (q, J 7.0 Hz, 2H), 2.82 (t, J 7.5 Hz, 2H), 1.73 (qn, J 7.5 Hz, 2H), 1.41 (t, J 7.0 Hz, 3H), 1.37 (sext, J 7.2 Hz, 2H), 0.88 (t, J 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 159.3 (C_4), 141.1 (C_2), 115.9 (C_3), 100.6 (C_1), 63.6 (OCH_2CH_3), 34,1 (CH_2CH_3), 25.2 ($TeCH_2CH_2$), 15.0 (OCH_2CH_3), 13.7 (CH_2CH_3), 8.96 ($TeCH_2$). LRMS *m/z* (rel. int., ion) 308 (20, M^+), 306 (18, $M^+ - 2$), 304 (11, $M^+ - 4$), 251 (6), 249 (5), 247 (4), 223 (11), 221 (10), 219 (6), 122 (100), 94 (62), 57 (24). IR (neat, cm^{-1}) 2976 (s), 2957 (s), 2926 (s), 2871 (m), 1970 (w), 1883 (w), 1585 (s), 1488 (s), 1391 (m), 1279 (m), 1242 (s), 1176 (m), 1048 (m), 821 (m), 515 (m). Anal. Calc. for $C_{12}H_{18}OTe$: C, 47.12; H, 5.93. Found: C, 47.40, H, 6.04%.

3,4-Dimethoxy-1-butyltellanylbenzene (**2c**) (4.56 g, 71%). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.33 (dd, *J* 8.1, 1.8 Hz, 1H), 7.26 (d, *J* 1.5 Hz, 1H), 6.72 (d, *J* 8.4 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 2.86 (t, *J* 7.7 Hz, 2H), 1.76 (qn, *J* 7.7 Hz, 2H), 1.39 (sext, *J* 7.4 Hz, 2H), 0.90 (t, *J* 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 149.3 (C_3), 149.0 (C_4), 132.4 (C_5), 122.5 (C_2), 112.2 (C_6), 100.4 (C_1), 56.0 (3-OCH_3^*), 55.8 (4-OCH_3^*), 33.9 (CH_2CH_3), 25.0 ($TeCH_2CH_2$), 13.4 (CH_2CH_3), 8.95 ($TeCH_2$). LRMS *m*/*z* (rel. int., ion) 324 (18, M^+), 322 (16, $M^+ - 2$), 320 (10, $M^+ - 4$), 267 (12), 265 (11), 263 (7), 138 (100), 123 (15), 94 (34), 79 (22), 57 (15). IR (neat, cm^{-1}) 2997 (m), 2965 (s), 2927 (s), 2836 (m), 2052 (w), 1898 (w), 1843 (w), 1731 (w), 1576 (s), 1500 (s), 1250 (s), 1228 (s), 1139 (s), 1026 (s), 847 (m), 802 (m), 760 (m), 588 (m), 503 (w), 460 (w), 389 (w). Anal. Calc. for $C_{12}H_{18}O_2Te$: C, 44.78; H, 5.45. Found: C, 44.64; H, 5.45%.

4-Methoxy-3-methyl-1-butyltellanylbenzene (**2d**) (3.05 g, 50%). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.57–7.54 (m, 2H), 6.67 (d, *J* 7.8 Hz, 1H), 3.81 (s, 3H), 2.82 (t, *J* 7.6 Hz, 2H), 2.18 (s, 3H), 1.74 (qn, *J* 7.5 Hz, 2H), 1.38 (sext, *J* 7.4 Hz, 2H), 0.89 (t, *J* 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 158.1 (C_4), 142.0 (C_2), 138.6 (C_6), 128.1 (C_3), 111.2 (C_5), 100.5 (C_1), 55.5 (OCH_3), 34.2 (CH_2CH_3), 25.3 ($TeCH_2CH_2$), 16.2 (CH_3), 13.7 (CH_2CH_3), 8.90 ($TeCH_2$). LRMS *m*/*z* (rel. int., ion) 308 (16, M^+), 306 (15, $M^+ - 2$), 304 (10, $M^+ - 4$), 251 (9), 249 (9), 247 (6), 122 (100), 91 (11), 78 (21), 57 (11). IR (neat, cm^{-1}) 2956 (s), 2926 (s), 2866 (m), 2836 (m), 1993 (w), 1861 (w), 1774 (w), 1584 (m), 1488 (s), 1460 (m), 1293 (m), 1245 (s), 1176 (m), 1138 (s), 1032 (s), 883 (m), 805 (m), 699 (m), 592 (m), 500 (m), 438 (m). Anal. Calc. for $C_{12}H_{18}OTe$: C, 47.12; H, 5.93. Found: C, 47.12; H, 5.78%.

4-Phenyl-1-butyltellanylbenzene (**2f**) (2.36 g, 35%). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.70 (d, *J* 8.1, 2H), 7.48 (dd, *J* 7.2 Hz, 1.5 Hz, 2H), 7.32 (dd, *J* 8.1 Hz, 6.3 Hz, 2H), 7.35–7.28 (m, 2H), 7.26–7.22 (m, 1H), 2.84 (t, *J* 7.6 Hz, 2H), 1.74 (qn, *J* 7.5 Hz, 2H), 1.34 (sext, *J* 7.4 Hz, 2H), 0.85 (t, *J* 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 140.2 ($C_{1'}$), 139.9 (C_4), 138.3 ($C_{3'}$), 128.5 ($C_{2'}$), 127.4 (C_3), 127.1 ($C_{4'}$), 126.6 (C_2), 110.7 (C_1), 33.7 (CH_2CH_3), 24.9 ($TeCH_2CH_2$), 13.2 (CH_2CH_3), 8.33 ($TeCH_2$). LRMS *m*/*z* (rel. int., ion) 340 (15, M^+), 338 (14, $M^+ - 2$), 336 (8, $M^+ - 4$), 283 (6), 281 (5), 279 (4), 154 (100), 153 (19), 152 (41), 77 (6), 57 (31). IR (neat, cm^{-1}) 3060 (m), 3026 (m), 2957 (s), 2925 (s), 2866 (m), 1947 (w), 1902 (w), 1801 (w), 1751 (w), 1663 (w), 1622 (w), 1596 (m), 1477 (s), 1003 (m), 825 (m), 756 (s), 697 (s), 491 (m). Anal. Calc. for $C_{16}H_{18}Te$: C, 56.87; H, 5.37. Found: C, 57.15; H, 5.56%.

4-Phenoxy-1-butyltellanylbenzene (**2h**) (3.88 g, 55%). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.68 (d, *J* 8.7, 2H), 7.34 (dd, *J* 8.4 Hz, 7.4 Hz, 2H), 7.12 (tt, *J* 7.4 Hz, 1.1 Hz, 1H), 7.02 (dd, *J* 8.5 Hz, 1.0 Hz, 2H), 6.84 (d, *J* 9.0 Hz, 2H), 2.89 (t, *J* 7.5 Hz, 2H), 1.76 (qn, *J* 7.5 Hz, 2H), 1.39 (sext, *J* 7.4 Hz, 2H), 0.90 (t, *J* 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 157.5 ($C_{1'}$), 156.8 (C_4), 140.5 (C_2), 129.8 ($C_{3'}$), 123.6 ($C_{4'}$), 119.5 ($C_{2'}$), 119.2 (C_3), 104.0 (C_1), 33.8 (CH_2CH_3), 24.9 ($TeCH_2CH_2$), 13.4 (CH_2CH_3), 8.77 ($TeCH_2$). LRMS *m*/*z* (rel. int., ion) 356 (19, M^+), 354 (15, $M^+ - 2$), 352 (9, $M^+ - 4$), 299 (5), 297 (4), 295 (2), 170 (100), 141 (19), 115 (11), 77 (35), 57 (33). IR (neat, cm^{-1}) 3065 (w), 3068 (w), 2957 (m), 2926 (m), 2869 (w), 2029 (w), 1957 (w), 1888 (w), 1777 (w), 1721 (w), 1651 (w), 1576 (m), 1483 (s), 1239 (s), 1166 (m), 1009 (m), 866 (m), 751 (m), 691 (m), 486 (m). Anal. Calc. for $C_{16}H_{18}OTe$: C, 54.30; H, 5.13. Found: C, 54.44; H, 5.33%.

4-Hydroxy-1-butyltellanylbenzene (**2i**) (3.98 g, 72%). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.58 (d, *J* 8.5 Hz, 2H), 6.70 (d, *J* 8.5 Hz, 2H), 5.44 (br s, 1H), 2.80 (t, *J* 7.6 Hz, 2H), 1.72 (qn, *J* 7.5 Hz, 2H), 1.36 (sext, *J* 7.5 Hz, 2H), 0.87 (t, *J* 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 156.3 (C_4), 141.3 (C_3), 117.1 (C_2), 100.5 (C_1), 34.1 (CH_2CH_3), 25.2 ($TeCH_2CH_2$), 13.7 (CH_2CH_3), 9.15 ($TeCH_2$). LRMS *m*/*z* (rel. int., ion) 280 (10, M^+), 278 (9, $M^+ - 2$), 276 (6, $M^+ - 4$), 223 (6), 221 (5), 219 (4), 94 (100), 57 (23). IR (neat, cm^{-1}) 3355 (br), 2957 (s), 2926 (s), 2869 (m), 1998 (w), 1883 (w), 1640 (w), 1576 (m), 1486 (s), 1375 (m), 1243 (s), 1171 (s), 823 (s), 695 (w), 512 (m).

4-Methyl-1-butyltellanylbenzene (**2e**) [56950-02-8]. To a one-necked round-bottomed flask equipped with a reflux condenser containing tellurium tetrachloride (5.38 g, 20 mmol), toluene (2.13 mL, 20 mmol) was added at once, dissolving the tellurium tetrachloride promptly. The reaction was refluxed for 12 h and a yellow solid was formed. The system was cooled to room temperature and the trichloride was used crude in the reduction/alkylation procedure. (4.23 g, 77%) ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.61 (d, *J* 8.1 Hz, 2H), 7.01 (d, *J* 7.8 Hz, 2H), 2.86 (t, *J* 7.5 Hz, 2H), 2.32 (s, 3H), 1.76 (qn, *J* 7.3 Hz, 2H), 1.38 (sext, *J* 7.4 Hz, 2H), 0.89 (t, *J* 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 139.0 (C_2), 137.7 (C_4), 130.3 (C_3), 107.8 (C_1), 34.2 (CH_2CH_3), 25.3 ($TeCH_2CH_2$), 21.5 (CH_3), 13.7 (CH_2CH_3), 8.74 ($TeCH_2$). LRMS *m*/*z* (rel. int., ion) 278 (12, M^+), 276 (11, $M^+ - 2$), 274 (7, $M^+ - 4$), 221 (4), 219 (4), 217 (3), 92 (67), 91 (100), 57 (22). IR (neat, cm^{-1}) 3062 (m), 3015 (m), 2957 (s), 2924 (s), 2865 (m), 1631 (w), 1588 (w), 1563 (w), 1486 (m), 1457 (m), 1181 (w), 1162 (w), 1013 (w), 797 (s), 480 (s). Anal. Calc. for $C_{11}H_{16}Te$: C, 47.90; H, 5.85. Found: C, 48.02; H, 5.74%.

β-Butyltellanylnaphthalene (**2g**) [95849-65-3]. A one-necked round-bottomed flask containing naphthalene (10.25 g, 80 mmol) was melted at 120 °C and tellurium tetrachloride (5.38 g, 20 mmol) was added at once. An evolution of HCl was observed and a yellow solid was formed. The system was cooled to room temperature

and the trichloride was used crude in the reduction/alkylation procedure. (2.18 g, 35%) ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 8.21 (s, 1H), 7.80–7.71 (m, 3H), 7.63 (d, *J* 8.4 Hz, 1H), 7.47–7.43 (m, 2H), 2.96 (t, *J* 7.6 Hz, 2H), 1.80 (qn, *J* 7.5 Hz, 2H), 1.40 (sext, *J* 7.2 Hz, 2H), 0.89 (t, *J* 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 137.9, 135.3, 134.5 (C_9), 132.8 (C_{10}), 128.4, 128.0, 127.5, 126.5, 126.4, 109.6 (C_2), 34.3 (CH_2CH_3), 25.4 ($TeCH_2CH_2$), 13.7, 8.92 ($TeCH_2$). LRMS *m/z* (rel. int., ion) 314 (12, M^+), 312 (11, $M^+ - 2$), 310 (7, $M^+ - 4$), 257 (6), 255 (5), 253 (4), 128 (100), 127 (35), 57 (14). IR (neat, cm^{-1}) 3049 (m), 2957 (s), 2925 (s), 2865 (m), 1946 (w), 1912 (w), 1829 (w), 1757 (w), 1701 (w), 1620 (m), 1581 (m), 1497 (m), 1458 (m), 1162 (m), 811 (s), 740 (s), 625 (m), 473 (s). Anal. Calc. for $C_{14}H_{16}Te$: C, 53.92; H, 5.17. Found: C, 54.01; H, 5.19%.

4-Hydroxy-1-butyldichloro-λ^4-tellanylbenzene (**2j**). To a solution of crude 4-hydroxy-1-butyltellanylbenzene in dry benzene (40 mL) at 10 °C, sulfuryl chloride (2.70 g, 20 mmol) was added. The reaction was stirred for 20 min at room temperature, the solvent was removed at reduced pressure and a colorless oil was obtained. The oil was solubilized in dry dichloromethane and hexanes was added until the precipitation of a white solid. Then the solution was cooled in an ice bath and the white solid was filtered off, washed with hexanes and recrystallized from a dichloromethane/hexanes mixture (85:15). (2.92 g, 84%); m.p.: 164–166 °C, uncorrected. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.98 (d, *J* 9.0 Hz, 2H), 6.95 (d, *J* 9.0 Hz, 2H), 3.71 (t, *J* 7.8 Hz, 2H), 2.23 (qn, *J* 7.6 Hz, 2H), 1.56 (sext, *J* 7.4 Hz, 2H), 1.02 (t, *J* 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 158.7 (C_4), 135.1 (C_2), 119.9 (C_1), 117.2 (C_3), 51.9 ($TeCH_2$), 27.2 (CH_2CH_3), 24.3 ($TeCH_2CH_2$), 13.5 (CH_2CH_3). IR (KBr, cm^{-1}) 3343 (br), 2954 (m), 2925 (m), 2863 (m), 1888 (w), 1638 (w), 1586 (s), 1492 (s), 1277 (s), 1206 (s), 1173 (m), 822 (s), 580 (m), 510 (m). Anal. Calc. for $C_{10}H_{14}Cl_2OTe$: C, 34.44; H, 4.05. Found: C, 34.68; H, 3.83%.

4.3. General procedure for the preparation of benzhydrols (*3a–g*)

In a two-necked round-bottomed flask a solution of the corresponding telluride (2 mmol) in 30 mL of THF was treated with *n*-butyllithium (1.54 mL, 1.43 M, 2.2 mmol) at −78 °C. The mixture was stirred for 15 min at the same temperature and benzaldehyde (0.23 mL, 2 mmol) was added in one portion. The solution was allowed to reach room temperature and was stirred for 1 h. The reaction was quenched with diluted aqueous HCl (10%, 50 mL) and extracted with ether (3×30 mL). The organic phases were combined, dried over $MgSO_4$ and concentrated at reduced pressure. The residual crude was purified by silica gel flash column chromatography using a mixture of hexanes:ethyl acetate (9:1) as eluent. Benzhydrols **3a** [15], **3b** [16], **3c** [17], **3e** [18], **3f** [19], **3g** [20] are known and the analytical data obtained were in accordance with previously reported data.

(4-Methoxy-3-methyl-phenyl)-phenyl-methanol (**3d**) (0.37 g, 82%). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.37–7.20 (m, 5H), 7.13–7.10 (m, 2H), 6.74 (d, *J* 8.7 Hz, 1H), 5.71 (s, 1H), 3.78 (s, 3H), 2.40 (br s, 1H), 2.18 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 157.5 (C_4), 144.4 ($C_{1'}$), 136.0 (C_3), 129.4 ($C_{3'}$), 128.6 ($C_{2'}$), 127.6 (C_2), 127.0 (C_1), 126.7 ($C_{4'}$), 125.4 (C_6), 110.0 (C_5), 76.1 (*C*HOH), 55.6 (OCH_3), 16.6 (CH_3). LRMS *m/z* (int. rel., ion) 228 (33, M^+), 211 (6), 197 (4), 149 (38), 123 (100), 105 (60), 91 (25), 77 (54), 51 (19). IR (neat, cm^{-1}) 3387 (br), 2950 (m), 2836 (w), 1609 (w), 1502 (m), 1457 (m), 1252 (m), 1130 (m), 1033 (m), 811 (m), 701 (w), 595 (w). Anal. Calc. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.60; H, 7.07%.

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