

Generation of allyl- and benzyllithiums from the corresponding halides by the aid of lithium–tellurium exchange reactions

Takahiro Kanda and Shinzi Kato

Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido 1–1, Gifu, 501-11 (Japan)

Takushi Sugino, Nobuaki Kambe and Noboru Sonoda

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565 (Japan)

(Received February 23, 1994; in revised form April 6, 1994)

Abstract

A variety of allyl- and benzyllithiums were prepared by lithium–tellurium exchange reactions of allylic and benzylic tellurides generated in situ from the corresponding halides. The produced organolithiums were trapped successfully with electrophiles such as aldehydes, ketones, and trimethylchlorosilane. Benzyllithiums having an alkyl, alkoxy, fluoro, chloro, or cyano substituent(s) on their aromatic ring were generated efficiently in THF. Benzylic tellurides bearing a bromo or iodo substituent afforded a mixture of products under similar conditions arising from the competing lithium–halogen exchange and/or the displacement of the halogen atom with organolithiums used, but they were converted selectively to benzyllithiums in ether without affecting halogen substituents on the benzene ring. Several allyllithiums including dilithioisobutene were generated from allylic halides in a similar way via allylic tellurides. Wurtz-type coupling was negligible in any reactions examined.

Key words: Tellurium; Lithium; Allyl; Benzyl; Halide

1. Introduction

Organic halides are, in general, very useful precursors of organolithium compounds [1]. But this is not the case of allylic and benzylic halides, since their reaction with lithium metal or organolithium reagents often results in Wurtz-type coupling. In order to avoid this crucial problem, alternative preparative methods such as hydrogen abstraction, cleavage of allylic and benzylic ethers, or lithium–metal (or metalloid) exchange have been developed so far [1,2]. Here we report that allyl- and benzyllithiums **3** could be generated conveniently and efficiently by a one-pot operation from allylic and benzylic halides **1**. This reaction involves lithium–tellurium exchange of in situ generated tellurides **2** as expressed by the following general equation (eqn. (1)) [3]. This procedure provides the first practical method for conversion of allylic and

benzylic halides to the corresponding organolithiums with suppression of Wurtz-type coupling [4].

2. Results and discussion

The reaction of allylic and benzylic halides with lithium *n*-butanetellurolate affords the corresponding allylic and benzylic tellurides **2**, respectively, in almost quantitative yields. Since these tellurides generated by this reaction are sufficiently pure for further manipulation and since they are somewhat labile toward oxygen and/or light, we employed a one-pot procedure for generation of allyl- and benzyllithiums **3** from halides **1** without isolation of tellurides **2** [5].

For example, 1-phenylethyl bromide **1b** was allowed to react at 0°C with lithium *n*-butanetellurolate prepared from *n*-butyllithium and tellurium in THF at room temperature, and then another portion of *n*-butyllithium was added at –70°C into the solution. Quenching of the reaction with benzophenone at the temperature afforded an addition product **5** in 88%

Correspondence to: Dr. N. Kambe or Dr. N. Sonoda.

TABLE 1. Generation of allyl- and benzyllithiums **3** from the corresponding halides **1** and their trapping with electrophiles ^a


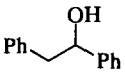
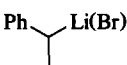
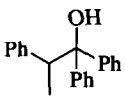
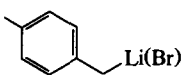
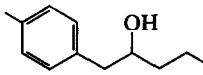
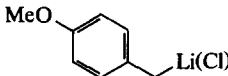
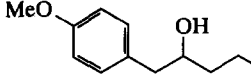
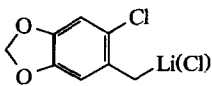
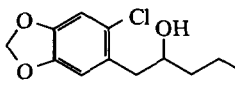
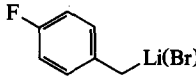
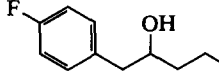
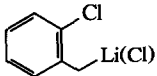
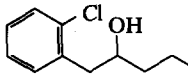
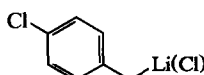
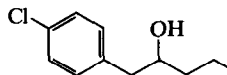
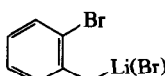
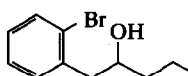
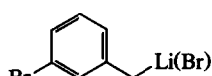
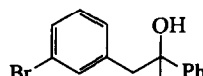
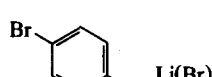
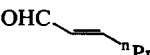
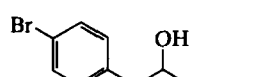
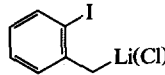

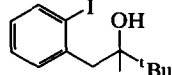
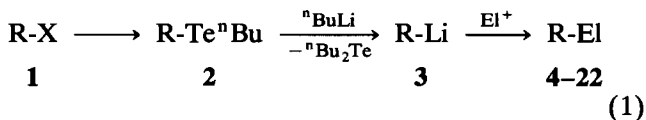
Run	3 (X in 1)	Solvent	Temp. (°C)	Electrophile	Product	Isolated yield (%)
1	 3a	THF	-70	PhCHO	 4	89
2	 3b	THF	-70	Ph ₂ CO	 5	88
3	 3c	THF	-70	ⁿ PrCHO	 6	72
4	 3d	THF	-70	ⁿ PrCHO	 7	88
5	 3e	THF	-70	ⁿ PrCHO	 8	78
6	 3f	THF	-70	ⁿ PrCHO	 9	73
7	 3g	THF	-70	ⁿ PrCHO	 10	74 ^b
8	 3h	THF	-70	ⁿ PrCHO	 11	72 ^b
9	 3i	Et ₂ O	-70	ⁿ PrCHO	 12	68
10	 3j	Et ₂ O	-70	Ph ₂ CO	 13	95
11	 3k	Et ₂ O	-70		 14	91 ^c
12	 3l	Et ₂ O	-105		 15	65 ^d

TABLE 1 (continued)

Run	3 (X in 1)	Solvent	Temp. (°C)	Electrophile	Product	Isolated yield (%)
13		Et ₂ O/THF (1:1)	-105	Me ₃ SiCl		96
14	3m	THF	-70	Me ₃ SiCl	16	74
15		Et ₂ O/THF	-105			96 ^d
16		Et ₂ O/THF (1:1)	-105	ⁿ PrCHO		86 86
17		THF	-70	PhCHO		73 ^e
18		THF	-70	PhCHO		90
19		THF	-70	PhCHO		59 ^f
20		THF	-70	PhCHO		72 ^g
21	3s	Et ₂ O/THF (1:1)	-105	PhCHO		82 ^g

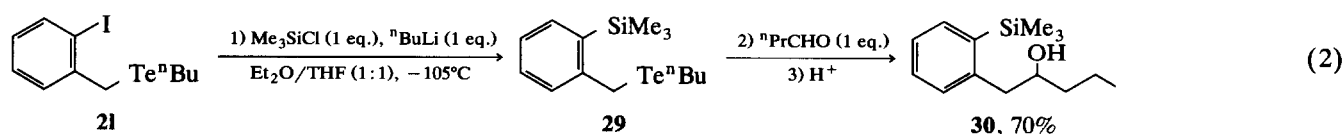
^a Reactions were carried out as follows unless otherwise stated: 1) tellurium (2 mmol), ⁿBuLi (2 mmol, 1.6 M in hexane), solvent (5 ml), 25°C, 15 min; 2) **1** (2 mmol), 0°C, 30 min; 3) ⁿBuLi (2 mmol, 1.6 M in hexane), -70°C (or -105°C), 15 min; 4) electrophile (2 mmol), 5 min, then warmed to 25°C in 1 h. ^b The Li-Te exchange reaction was performed in the presence of 2 mmol of hexamethylphosphoric triamide (HMPA) as an additive. ^c Only 1,2-addition product was obtained. ^d The electrophile was added before Li-Te exchange reaction was conducted. ^e A 1:1 mixture of diastereomers accompanied by 12% of the α -adduct. ^f Accompanied by an α -adduct (17%). ^g The amount of **3s** used was 1 mmol.

yield after column chromatography. In the same manner, benzylic halides having a methyl, alkoxy, fluoro, and chloro substituent(s) were converted efficiently to the corresponding benzyllithiums which were trapped with benzophenone or n-butanal to give addition products (Table 1, entries 1–8). From a synthetic point of view, 3,4-(methylenedioxy)benzyllithium **3e** is an interesting species as a building block of podorhizon, a member of the podophyllotoxin anticancer family [6].



R = allyl or benzyl
X = Cl, Br

On the other hand, reactions of benzylic halides carrying a bromo or iodo substituent on the aromatic ring (**1i–l**) under the same conditions were problematic [7]. Since the substitution of halogen atoms at the benzylic position with lithium n-butanetelluroate proceeds effectively even in these cases, we carried out lithium-tellurium exchange reactions of tellurides **2i–l** under various different conditions and carefully examined product mixtures obtained by quenching with n-butanal [8]. The results are shown in Table 2 along with structures of several identified products. Reactions of bromo substituted tellurides **2i–k** with n-butyllithium in THF afforded only moderate yields of desired products. Formation of **26** as the major by-product might indicate that the lithium-bromine exchange competed with the lithium-tellurium exchange. This is also consistent with a fact that yields of dibutyl tel-



luride, which should be formed by Li-Te exchange, were relatively low (*ca.* 50%) in runs 1, 3, and 5. Replacement of the benzylic bromine atom with butyl group leading to **26** may probably be via S_N2 substitution with benzyl lithiums of bromobutane generated by Li-Br exchange at the aromatic ring [8c,9]. When we used ether as a solvent, the Li-Br exchange was largely retarded resulting in the formation of desired products in good yields (runs 2, 4, and 6). Similar reactions using benzophenone and 2-hexenal afforded excellent yields of products as shown in runs 10 and 11 of Table 1, with only 1,2-addition product in the latter case.

A similar treatment of *o*-iodobenzyl telluride **2i** in THF afforded **24** and **27** as the major products, in which the iodine atom on the aromatic ring was replaced by butyl group (run 7 in Table 2). When the reaction was conducted in ether at -105°C , the desired product **23** was obtained in 21% yield (run 8), and the yield was improved by the use of methyl-, or phenyllithiums (runs 9 and 10). The formation of **24**

and **27** in large amounts in run 7 may be due to rapid alkylation of the aryllithium with iodobutane in THF at -70°C , both of which are generated concomitantly by Li-I exchange [10]. Although the same aryllithium is formed from **2i** in run 1 of Table 2, it did not react with bromobutane and was trapped with *n*-butanal to give **26i** probably because bromobutane is less powerful electrophile than iodobutane. The preferred Li-I exchange over Li-Te exchange of **2i** in THF was demonstrated by the reaction of **2i** with *n*-butyllithium in the presence of trimethylchlorosilane where silylation took place only at an aromatic carbon on which iodine was attached to give **30** (eqn. (2)). On the contrary, addition of *n*-butyllithium to a mixture of **2i** and pinacolone in ether gave the desired product **15** in 65% yield as shown in run 12 of Table 1, indicating that Li-Te exchange predominated in ether. These results show that both of Li-Te and Li-I exchange reactions proceed easily under these conditions leading to complex results unless organolithium compounds generated in

TABLE 2. Reactions of benzylic tellurides having bromo and iodo substituents with organolithium reagents

Run	telluride 2	RLi	temp(°)	solvent	glc(isolated) yields of products (%)						
					23	24	25	26	27	28	ⁿ BuTeR
1		ⁿ BuLi	-70	THF	(44) ^a	0	9	(33)	0	6	(55)
2		ⁿ BuLi	-70	Et ₂ O	79(68) ^a	0	2	0	0	< 1	70
3		ⁿ BuLi	-70	THF	(42)	0	0	(17)	0	0	(51)
4		ⁿ BuLi	-70	Et ₂ O	81(75)	0	2	0	0	< 1	82
5		ⁿ BuLi	-70	THF	(32)	0	6	(14)	0	5	(47)
6		ⁿ BuLi	-70	Et ₂ O	63(53)	0	6	2	0	8	76
7		ⁿ BuLi	-70	THF	5	28	0	0	51	0	(30)
8		ⁿ BuLi	-105	Et ₂ O	21	3	3	< 1	32	0	23
9		MeLi	-105	Et ₂ O	49	0	3	0	39	0	- ^b
10		PhLi	-105	Et ₂ O	46	0	0	9	32 ^c	< 1	51

Conditions: benzylic tellurides **2** were prepared in THF (5 ml) from **1** (2 mmol), tellurium (2 mmol) and butyllithium (2 mmol, 1.6 M in hexane) and used without isolation. The exchange reactions were conducted using RLi (2 mmol) at the temperature indicated for 15 min and quenched with butanal (2 mmol). The solution was warmed to room temperature, washed with saturated $\text{NH}_4\text{Cl}_{\text{aq}}$, and the resulting mixture was analyzed by glc and/or NMR. Yields of **24**, **26** and **27** are based on RLi used, and that of **28** on **2**.^a The product **23i** in runs 1 and 2 is the same as **12**.

^b Not determined. ^c NMR yield.

situ are trapped rapidly with an electrophile present in the reaction medium. Reactions of runs 10–12 in Table 1 are the first examples of the generation of **3j**–**l** [8c].

We then tried the preparation of benzyllithiums having a cyano group which is also prone to react with organolithium reagents. As in the cases of bromo and iodo substituted ones, better yields were attained when the reaction was carried out at lower temperatures using ether as a solvent instead of THF. It should be noted that **3n** was generated and trapped in an excellent yield only when the exchange reaction was conducted in the presence of an electrophile. *o*-Cyano-benzyllithium **3n** is particularly unstable due to rapid self-condensation [11].

Generation of allyllithiums **3p**–**s** from the corresponding allylic halides was tested also in a similar manner as employed for generation of benzyllithiums. Lithium–tellurium exchange reactions of allylic tellurides generated *in situ* with *n*-butyllithium proceeded efficiently in THF at -70°C to give allyllithiums, which afforded homoallylic alcohols after trapping with benzaldehyde. As shown in runs 17 and 19 allyllithiums reacted with benzaldehyde predominantly at the more substituted γ position. Interestingly 1,1-bis(*n*-butyltelluromethyl)ethylene **2s** was converted successfully into a dilithio species of trimethylenemethane dianion **3s** [12] to give an allylic diol **22** in 72% yield under the same conditions and in 82% yield at -105°C . An attempt to generate dilithiobutene from (*Z*)-1,4-bis(*n*-butyltelluro)but-2-ene failed and resulted in the formation of butadiene by the elimination of lithium *n*-butanetellurolate from a mono lithiated intermediate. This is supported by the fact that $^n\text{Bu}_2\text{Te}$ (45%) and $^n\text{Bu}_2\text{Te}_2$ (40%) were obtained after usual workup.

3. Conclusion

A convenient and practical preparative method of allyl- and benzyllithiums from the corresponding allylic and benzylic halides, respectively, has been developed by the combination of substitution of the halogen with *n*-butanetellurolate and subsequent lithium–tellurium exchange reaction. Both steps can be performed in the same flask. The exchange reactions are very fast even at low temperatures and enable to generate benzyllithiums having a variety of substituents on the aromatic ring including ones which are prone to react with organolithium reagents.

4. Experimental details

4.1. General procedures

All reactions were carried out under argon atmosphere. Melting points were measured with a Yanagi-

moto micro melting point apparatus (uncorrected). Boiling points represented refer to the oven temperature of Kugerrohr distillation apparatus. Infrared spectra were recorded on a Perkin-Elmer model 1610 FT-IR spectrometer. The ^1H NMR (270 MHz) and ^{13}C NMR (68 MHz) spectra were recorded on a JEOL JNM270-GSX FT-NMR spectrometer using CDCl_3 and Me_4Si as a solvent and an internal standard, respectively. Mass spectra were recorded on a Shimadzu GCMS-QP2000 or -QP1000. High resolution mass spectroscopy (HRMS) and elemental analyses were performed at Analysis Center of Osaka University. Gas chromatography (GLC) was carried out on a Shimadzu GC-8A equipped with a flame ionization detector using a capillary column (Hicap-CBP1-S25-050, $0.25\text{ mm} \times 25\text{ m}$). The products were isolated by flash column chromatography on silica gel (Fuji Silysia Chemical Ltd. BW820-MH) or by preparative thin-layer chromatography (PTLC) on silica gel (Wakogel B-5F) or by bulb to bulb distillation using Kugerrohr distillation apparatus.

Ether and THF were purchased from Nacalai Tesque, Inc. and used after distillation from sodium [13]. *n*-Butyllithium (1.6 M in hexane solution), phenyllithium (1.1 M in cyclohexane/ether solution) and methylithium (1.1 M in ether solution) were purchased from Kanto Chem. Co., Inc. and used after titration [14]. *n*-Butanal, *trans*-2-hexenal, benzaldehyde, benzophenone, and pinacolone were purified according to procedures in a literature [13]. Other reagents and solvents were used as purchased without purification. $^n\text{Bu}_2\text{Te}$ [15] and $^n\text{BuTePh}$ [16] were synthesized by published methods.

4.2. Preparation of allylic and benzylic tellurides (**2**) [5]

Into a THF suspension (5 ml) of metallic tellurium (2 mmol) was added dropwise *n*-butyllithium (*ca.* 2 mmol) by a syringe at 20°C until a pale yellow homogeneous solution was obtained. Then an allylic or benzylic halide was added at 0°C and the solution was stirred for 30 min at the temperature. The solvent was removed under vacuum and a small amount of hexane (*ca.* 10 ml) was added to the residue. Elimination of the precipitated salt by filtration with a cintered glass filter (G4 grade) followed by evaporation afforded an essentially pure allylic or benzylic telluride which shows reasonable NMR spectra as presented below. Structures of some selected tellurides were confirmed also by mass spectroscopy. Any efforts for elemental analysis of these tellurides were unsuccessful due to their high susceptibility toward oxygen and/or light. For generation of allyl- and benzyllithiums, tellurides prepared as above were used immediately without any further purification (*vide infra*).

4.2.1. Benzyl *n*-butyl telluride (2a)

A yellow oil; $^1\text{H NMR}$ (CDCl_3 , 270 MHz) δ 0.97 (t, $J = 7.3$ Hz, 3 H, CH_3), 1.42 (sextet, $J = 7.3$ Hz, 2 H, CH_2), 1.76 (quintet, $J = 7.3$ Hz, 2 H, CH_2), 2.68 (t, $J = 7.3$ Hz, 2 H, CH_2Te), 4.09 (s, $^2J_{\text{Te-H}} = 27.8$ Hz, 2 H, PhCH_2), 7.23–7.42 (m, 5 H, *Ph*); $^{13}\text{C NMR}$ (CDCl_3 , 68 MHz) δ 4.4 ($^1J_{\text{C-Te}} = 156$ Hz), 4.9 ($^1J_{\text{C-Te}} = 144$ Hz), 13.3, 25.1, 34.1, 125.8, 128.3, 129.0, 141.2. HRMS. Found: 278.0319 (calculated for $\text{C}_{11}\text{H}_{16}^{130}\text{Te}$: 278.0314).

4.2.2. *n*-Butyl 1-phenylethyl telluride (2b)

A yellow oil; $^1\text{H NMR}$ (CDCl_3 , 270 MHz) δ 0.82 (t, $J = 7.3$ Hz, 3 H, $\text{CH}_3(\text{CH}_2)_3\text{Te}$), 1.26 (sextet, $J = 7.3$ Hz, 2 H, CH_2), 1.59 (quintet, $J = 7.3$ Hz, 2 H, CH_2), 1.88 (d, $J = 7.3$ Hz, 3 H, CH_3CHTe), 2.47 (t, $J = 7.3$ Hz, 2 H, CH_2Te), 4.58 (q, $J = 7.3$ Hz, 1 H, CHTe), 7.09–7.29 (m, 5 H, *Ph*); $^{13}\text{C NMR}$ (CDCl_3 , 68 MHz) δ 5.9 ($^1J_{\text{C-Te}} = 162$ Hz), 13.3, 18.1 ($^1J_{\text{C-Te}} = 170$ Hz), 24.3, 25.1, 34.1, 126.0, 126.8, 128.1, 145.9; MS (EI, 70 eV) m/e (relative intensity, %) 292 (^{130}Te , M^+ , 5), 290 (^{128}Te , M^+ , 4), 288 (^{126}Te , M^+ , 2), 277 (2), 275 (1), 105 (55), 77 (100), 57 (5).

4.2.3. *n*-Butyl *p*-methylbenzyl telluride (2c)

A yellow oil; $^1\text{H NMR}$ (CDCl_3 , 270 MHz) δ 0.88 (t, $J = 7.3$ Hz, 3 H, CH_3), 1.34 (sextet, $J = 7.3$ Hz, 2 H, CH_2), 1.67 (quintet, $J = 7.3$ Hz, 2 H, CH_2), 2.29 (s, 3H, CH_3Ar), 2.57 (t, $J = 7.3$ Hz, 2 H, CH_2Te), 3.97 (s, $^2J_{\text{Te-H}} = 27.2$ Hz, 2 H, ArCH_2), 7.04 (d, $J = 7.8$ Hz, 2 H, *Ar*), 7.13 (d, $J = 7.8$ Hz, 2 H, *Ar*); $^{13}\text{C NMR}$ (CDCl_3 , 68 MHz) δ 4.4 ($^1J_{\text{C-Te}} = 156$ Hz), 4.7 ($^1J_{\text{C-Te}} = 142$ Hz), 13.4, 21.0, 25.2, 34.1, 129.1, 129.7, 135.4, 138.1.

4.2.4. *n*-Butyl *p*-methoxybenzyl telluride (2d)

A yellow oil; $^1\text{H NMR}$ (CDCl_3 , 270 MHz) δ 0.88 (t, $J = 7.3$ Hz, 3 H, CH_3), 1.33 (sextet, $J = 7.3$ Hz, 2 H, CH_2), 1.67 (quintet, $J = 7.3$ Hz, 2 H, CH_2), 2.56 (t, $J = 7.3$ Hz, 2 H, CH_2Te), 3.76 (s, 3 H, CH_3O), 3.97 (s, $^2J_{\text{Te-H}} = 27.8$ Hz, 2 H, ArCH_2), 6.78 (d, $J = 8.5$ Hz, 2 H, *Ar*), 7.17 (d, $J = 8.5$ Hz, 2 H, *Ar*); $^{13}\text{C NMR}$ (CDCl_3 , 68 MHz) δ 4.3 ($^1J_{\text{C-Te}} = 152$ Hz), 4.3 ($^1J_{\text{C-Te}} = 142$ Hz), 13.4, 25.2, 34.2, 55.2, 113.8, 129.4, 133.1, 157.8.

4.2.5. *n*-Butyl 5-(6-chloro-1,3-dioxaindanyl)methyl telluride (2e)

A yellow oil; $^1\text{H NMR}$ (CDCl_3 , 270 MHz) δ 0.90 (t, $J = 7.3$ Hz, 3 H, CH_3), 1.36 (sextet, $J = 7.3$ Hz, 2 H, CH_2), 1.73 (quintet, $J = 7.3$ Hz, 2 H, CH_2), 2.71 (t, $J = 7.3$ Hz, 2 H, CH_2Te), 3.98 (s, $^2J_{\text{Te-H}} = 27.4$ Hz, 2 H, ArCH_2Te), 5.94 (s, 2 H, OCH_2O), 6.72 (s, 1 H, *Ar*), 6.78 (s, 1 H, *Ar*); $^{13}\text{C NMR}$ (CDCl_3 , 68 MHz) δ 2.6

($^1J_{\text{C-Te}} = 142$ Hz), 4.5 ($^1J_{\text{C-Te}} = 136$ Hz), 13.4, 25.2, 34.4, 101.7, 109.2, 110.0, 124.7, 132.5, 146.6, 146.6. MS (EI, 20 eV) m/e (relative intensity, %) 356 (^{130}Te , M^+ , 7), 354 (^{128}Te , M^+ , 6), 352 (^{126}Te , M^+ , 3), 171 (41), 169 (100), 139 (2), 141 (1), 75 (10), 57 (6).

4.2.6. *n*-Butyl *p*-fluorobenzyl telluride (2f)

A yellow oil; $^1\text{H NMR}$ (CDCl_3 , 270 MHz) δ 0.88 (t, $J = 7.3$ Hz, 3 H, CH_3), 1.33 (sextet, $J = 7.3$ Hz, 2 H, CH_2), 1.67 (quintet, $J = 7.3$ Hz, 2 H, CH_2), 2.57 (t, $J = 7.3$ Hz, 2 H, CH_2Te), 3.98 (s, $^2J_{\text{Te-H}} = 27.4$ Hz, 2 H, ArCH_2Te), 6.93 (d, $J = 8.5$ Hz, 2 H, *Ar*), 7.21 (dd, $J = 8.5$ Hz, $^2J_{\text{H-F}} = 5.4$ Hz, 2 H, *Ar*); $^{13}\text{C NMR}$ (CDCl_3 , 68 MHz) δ 3.9 ($^1J_{\text{C-Te}} = 132$ Hz), 4.6 ($^1J_{\text{C-Te}} = 142$ Hz), 13.4, 25.2, 34.1, 115.3 ($^2J_{\text{C-F}} = 21$ Hz), 129.8 ($^3J_{\text{C-F}} = 8$ Hz), 137.0 ($^4J_{\text{C-F}} = 3$ Hz), 161.1 ($^1J_{\text{C-F}} = 245$ Hz).

4.2.7. *n*-Butyl *o*-chlorobenzyl telluride (2g)

A yellow oil; $^1\text{H NMR}$ (CDCl_3 , 270 MHz) δ 0.88 (t, $J = 7.3$ Hz, 3 H, CH_3), 1.33 (sextet, $J = 7.3$ Hz, 2 H, CH_2), 1.67 (quintet, $J = 7.3$ Hz, 2 H, CH_2), 2.68 (t, $J = 7.3$ Hz, 2 H, CH_2Te), 4.03 (s, $^2J_{\text{Te-H}} = 28.2$ Hz, 2 H, ArCH_2Te), 7.15–7.41 (m, 4 H, *Ar*); $^{13}\text{C NMR}$ (CDCl_3 , 68 MHz) δ 4.7 ($^1J_{\text{C-Te}} = 146$ Hz), 4.9 ($^1J_{\text{C-Te}} = 151$ Hz), 13.4, 25.2, 34.1, 126.9, 127.5, 128.3, 128.7, 139.9, 142.1.

4.2.8. *n*-Butyl *p*-chlorobenzyl telluride (2h)

A yellow oil; $^1\text{H NMR}$ (CDCl_3 , 270 MHz) δ 0.88 (t, $J = 7.3$ Hz, 3 H, CH_3), 1.33 (sextet, $J = 7.3$ Hz, 2 H, CH_2), 1.67 (quintet, $J = 7.3$ Hz, 2 H, CH_2), 2.58 (t, $J = 7.3$ Hz, 2 H, CH_2Te), 3.95 (s, $^2J_{\text{Te-H}} = 28.2$ Hz, 2 H, ArCH_2Te), 7.17 (d, $J = 9.2$ Hz, 2 H, *Ar*), 7.21 (d, $J = 9.2$ Hz, 2 H, *Ar*); $^{13}\text{C NMR}$ (CDCl_3 , 68 MHz) δ 4.0 ($^1J_{\text{C-Te}} = 156$ Hz), 4.7 ($^1J_{\text{C-Te}} = 150$ Hz), 13.4, 24.6, 34.1, 128.5, 129.7, 131.5, 140.0.

4.2.9. *o*-Bromobenzyl *n*-butyl telluride (2i)

A yellow oil; $^1\text{H NMR}$ (CDCl_3 , 270 MHz) δ 0.88 (t, $J = 7.3$ Hz, 3 H, CH_3), 1.34 (sextet, $J = 7.3$ Hz, 2 H, CH_2), 1.70 (quintet, $J = 7.3$ Hz, 2 H, CH_2), 2.69 (t, $J = 7.3$ Hz, 2 H, CH_2Te), 4.06 (s, $^2J_{\text{Te-H}} = 26.6$ Hz, 2 H, ArCH_2Te), 6.99 (d, $J = 8.1$ Hz, 1 H, *Ar*), 7.18 (t, $J = 8.1$ Hz, 1 H, *Ar*), 7.22 (t, $J = 8.1$ Hz, 1 H, *Ar*), 7.49 (d, $J = 8.1$ Hz, 1 H, *Ar*); $^{13}\text{C NMR}$ (CDCl_3 , 68 MHz) δ 4.6 ($^1J_{\text{C-Te}} = 156$ Hz), 5.6 ($^1J_{\text{C-Te}} = 152$ Hz), 13.3, 25.0, 34.1, 123.7, 127.3, 127.4, 129.6, 133.0, 141.1.

4.2.10. *m*-Bromobenzyl *n*-butyl telluride (2j)

A yellow oil; $^1\text{H NMR}$ (CDCl_3 , 270 MHz) δ 0.81 (t, $J = 7.3$ Hz, 3 H, CH_3), 1.27 (sextet, $J = 7.3$ Hz, 2 H, CH_2), 1.60 (quintet, $J = 7.3$ Hz, 2 H, CH_2), 2.52 (t, $J = 7.3$ Hz, 2 H, CH_2Te), 3.86 (s, $^2J_{\text{Te-H}} = 27.8$ Hz, 2

H, ArCH₂Te), 6.98–7.31 (m, 4 H, Ar); ¹³C NMR (CDCl₃, 68 MHz) δ 3.9 (¹J_{C-Te} = 154 Hz), 4.8 (¹J_{C-Te} = 142 Hz), 13.3, 25.1, 34.0, 122.2, 127.0, 128.9, 129.9, 131.2, 143.8.

4.2.11. *p*-Bromobenzyl *n*-butyl telluride (2k)

A yellow oil; ¹H NMR (CDCl₃, 270 MHz) δ 0.88 (t, *J* = 7.3 Hz, 3 H, CH₃), 1.33 (sextet, *J* = 7.3 Hz, 2 H, CH₂), 1.67 (quintet, *J* = 7.3 Hz, 2 H, CH₂), 2.58 (t, *J* = 7.3 Hz, 2 H, CH₂Te), 3.94 (s, ²J_{Te-H} = 27.8 Hz, 2 H, ArCH₂Te), 7.12 (d, *J* = 8.3 Hz, 2 H, Ar), 7.36 (d, *J* = 8.3 Hz, 2 H, Ar); ¹³C NMR (CDCl₃, 68 MHz) δ 4.0 (¹J_{C-Te} = 148 Hz), 4.8 (¹J_{C-Te} = 154 Hz), 13.4, 25.2, 34.1, 119.5, 130.1, 131.5, 140.5.

4.2.12. *n*-Butyl *o*-iodobenzyl telluride (2l)

A yellow oil; ¹H NMR (CDCl₃, 270 MHz) δ 0.88 (t, *J* = 7.3 Hz, 3 H, CH₃), 1.34 (sextet, *J* = 7.3 Hz, 2 H, CH₂), 1.73 (quintet, *J* = 7.3 Hz, 2 H, CH₂), 2.68 (m, *J* = 7.3 Hz, 2 H, CH₂), 4.05 (s, ²J_{Te-H} = 25.8 Hz, 2 H, ArCH₂Te), 6.79–6.81 (m, 1 H, Ar), 7.20 (t, *J* = 7.8 Hz, 1 H, Ar), 2.23 (t, *J* = 7.8 Hz, 1 H, Ar), 7.77–7.79 (m, 1 H, Ar); ¹³C NMR (CDCl₃, 68 MHz) δ 4.9 (¹J_{C-Te} = 156 Hz), 5.6 (¹J_{C-Te} = 150 Hz), 13.4, 25.1, 34.2, 100.4, 127.5, 128.2, 128.6, 139.7, 144.1.

4.2.13. *n*-Butyl *o*-cyanobenzyl telluride (2m)

A yellow oil; ¹H NMR (CDCl₃, 270 MHz) δ 0.89 (t, *J* = 7.3 Hz, 3 H, CH₃), 1.35 (sextet, *J* = 7.3 Hz, 2 H, CH₂), 1.71 (quintet, *J* = 7.3 Hz, 2 H, CH₂), 2.74 (t, *J* = 7.3 Hz, 2 H, CH₂Te), 4.17 (s, ²J_{Te-H} = 28.8 Hz, 2 H, ArCH₂Te), 7.23 (td, *J* = 7.6, 1.2 Hz, 1 H, Ar), 7.34 (d, *J* = 7.6 Hz, 1 H, Ar), 7.46 (t, *J* = 7.6 Hz, 1 H, Ar), 7.56 (dd, *J* = 7.6, 1.2 Hz, 1 H, Ar); ¹³C NMR (CDCl₃, 68 MHz) δ 2.0 (¹J_{C-Te} = 144 Hz), 5.5 (¹J_{C-Te} = 142 Hz), 13.3, 25.1, 34.0, 111.3, 117.7, 126.3, 129.3, 132.7, 132.9, 146.5; MS (EI, 70 eV) *m/e* (relative intensity, %) 303 (¹³⁰Te, M⁺, 10), 301 (¹²⁸Te, M⁺, 9), 299 (¹²⁶Te, M⁺, 5), 247 (6), 245 (5), 243 (3), 187 (1), 185 (1), 183 (0.5), 145 (1), 143 (1), 141 (0.5), 116 (100), 89 (13), 57 (20). HRMS. Found: 303.0290 (calculated for C₁₂H₁₅N¹³⁰Te: 303.0266).

4.2.14. *n*-Butyl *m*-cyanobenzyl telluride (2n)

A yellow oil; ¹H NMR (CDCl₃, 270 MHz) δ 0.89 (t, *J* = 7.3 Hz, 3 H, CH₃), 1.34 (sextet, *J* = 7.3 Hz, 2 H, CH₂), 1.68 (quintet, *J* = 7.3 Hz, 2 H, CH₂), 2.64 (t, *J* = 7.3 Hz, 2 H, CH₂Te), 3.99 (s, ²J_{Te-H} = 26.8 Hz, 2 H, ArCH₂), 7.35 (t, *J* = 7.6 Hz, 1 H, Ar), 7.43 (d, *J* = 7.6 Hz, 1 H, Ar), 7.49 (d, *J* = 7.6 Hz, 1 H, Ar), 7.53 (s, 1 H, Ar); ¹³C NMR (CDCl₃, 68 MHz) δ 3.5 (¹J_{C-Te} = 156 Hz), 5.0 (¹J_{C-Te} = 142 Hz), 13.3, 25.1, 33.9, 112.3, 118.6, 129.2, 129.5, 131.6, 132.7, 143.3; MS (EI, 20 eV) *m/e* (relative intensity, %) 303 (¹³⁰Te, M⁺, 2), 301

(¹²⁸Te, M⁺, 2), 299 (¹²⁶Te, M⁺, 1), 247 (5), 116 (100), 89 (8).

4.2.15. *n*-Butyl *p*-cyanobenzyl telluride (2o)

A yellow oil; ¹H NMR (CDCl₃, 270 MHz) δ 0.88 (t, *J* = 7.3 Hz, 3 H, CH₃), 1.35 (sextet, *J* = 7.3 Hz, 2 H, CH₂), 1.72 (quintet, *J* = 7.3 Hz, 2 H, CH₂), 2.75 (t, *J* = 7.3 Hz, 2 H, CH₂Te), 4.16 (s, ²J_{Te-H} = 28.8 Hz, 2 H, ArCH₂Te), 7.34 (d, *J* = 7.8 Hz, 2 H, Ar), 7.60 (d, *J* = 7.8 Hz, 2 H, Ar); ¹³C NMR (CDCl₃, 68 MHz) δ 2.0 (¹J_{C-Te} = 144 Hz), 5.5 (¹J_{C-Te} = 142 Hz), 13.3, 25.1, 34.0, 111.0, 119.1, 130.3, 132.3, 144.7; MS (EI, 70 eV) *m/e* (relative intensity, %) 303 (¹³⁰Te, M⁺, 15), 301 (¹²⁸Te, M⁺, 14), 116 (100).

4.2.16. (*E*)-But-2-enyl *n*-butyl telluride (2p)

A yellow oil; ¹H NMR (CDCl₃, 270 MHz) δ 0.93 (t, *J* = 7.3 Hz, 3 H, CH₃), 1.37 (sextet, *J* = 7.3 Hz, 2 H, CH₂), 1.71 (quintet, *J* = 7.3 Hz, 2 H, CH₂), 1.87 (dd, *J* = 7.9, 1.2 Hz, 3 H, CH₃C=), 2.58 (t, *J* = 7.3 Hz, 2 H, CH₂Te), 3.30 (d, *J* = 7.9 Hz, ²J_{Te-H} = 29.0 Hz, 2 H, =CHCH₂Te), 5.35 (dtq, *J* = 19.6, 7.9, 1.2 Hz, 1 H, =CHCH₂Te), 5.62 (dq, *J* = 19.6, 7.9 Hz, 1 H, CH₃CH=); ¹³C NMR (CDCl₃, 68 MHz) δ 3.8 (¹J_{C-Te} = 156 Hz), 3.9 (¹J_{C-Te} = 154 Hz), 13.4, 22.3, 25.1, 34.2, 125.5, 129.6.

4.2.17. *n*-Butyl 2-methylprop-2-enyl telluride (2q)

A yellow oil; IR (neat) 3075, 2957, 2924, 2871, 1635, 1282, 1135, 880 cm⁻¹; ¹H NMR (CDCl₃, 270 MHz) δ 0.92 (t, *J* = 7.2 Hz, 3 H, CH₃), 1.38 (sextet, *J* = 7.2 Hz, 2 H, CH₂), 1.73 (quintet, *J* = 7.2 Hz, 2 H, CH₂), 1.90 (s, 3 H, =CCH₃), 2.61 (t, *J* = 7.3 Hz, 2 H, CH₂Te), 3.38 (s, ²J_{Te-H} = 29.2 Hz, 2 H, =CCH₂Te), 4.71 (d, *J* = 1.8 Hz, 1 H, =CH₂), 4.80 (d, *J* = 1.8 Hz, 1 H, =CH₂); ¹³C NMR (CDCl₃, 68 MHz) δ 4.5 (¹J_{C-Te} = 158 Hz), 10.4 (¹J_{C-Te} = 142 Hz), 13.4, 21.6, 25.2, 34.0, 110.9, 143.8; MS (EI, 70 eV) *m/e* (relative intensity, %) 242 (¹³⁰Te, M⁺, 20), 240 (¹²⁸Te, M⁺, 18), 238 (¹²⁶Te, M⁺, 11), 185 (19), 183 (17), 180 (7), 55 (100), 41 (16), 29 (27). HRMS. Found: 242.0335 (calculated for C₈H₁₆¹³⁰Te: 242.0314).

4.2.18. *n*-Butyl 3-methylbut-2-enyl telluride (2r)

A yellow oil; ¹H NMR (CDCl₃, 270 MHz) δ 0.91 (t, *J* = 7.1 Hz, 3 H, CH₃), 1.35 (sextet, *J* = 7.1 Hz, 2 H, CH₂), 1.62 (s, 3 H, CH₃), 1.70 (s, 3 H, CH₃), 1.74 (quintet, *J* = 7.1 Hz, 2 H, CH₂), 2.61 (t, *J* = 7.1 Hz, 2 H, CH₂Te), 3.39 (d, *J* = 8.6 Hz, ²J_{Te-H} = 23.6 Hz, 2 H, CH₂Te), 5.40 (t, *J* = 8.6 Hz, 1 H, =CH); ¹³C NMR (CDCl₃, 68 MHz) δ 3.6 (¹J_{C-Te} = 128 Hz), 3.9 (¹J_{C-Te} = 132 Hz), 13.3, 25.1, 25.4, 34.6, 122.8, 132.6.

4.2.19. 1,1-Bis(*n*-butyltelluromethyl)ethene (2s)

A yellow oil; ¹H NMR (CDCl₃, 270 MHz) δ 0.91 (t, *J* = 7.1 Hz, 6 H, CH₃), 1.35 (sextet, *J* = 7.1 Hz, 4 H,

CH_2), 1.74 (quintet, $J = 7.1$ Hz, 4 H, CH_2), 2.59 (t, $J = 7.1$ Hz, 4 H, CH_2Te), 3.41 (s, 4 H, CH_2TeBu), 5.01 (s, 2 H, $\text{H}_2\text{C}=\text{C}$); ^{13}C NMR (CDCl_3 , 68 MHz) δ 3.5 ($^1J_{\text{C}-\text{Te}} = 152$ Hz), 3.8 ($^1J_{\text{C}-\text{Te}} = 146$ Hz), 13.1, 25.0, 34.2, 116.2, 143.2; MS (CIDI) m/e (relative intensity, %) 428 ($\text{M}^+ + 1$, ^{130}Te , 8), 241 (18), 184 (22), 57 (100).

4.3. Generation of allyl- and benzyl lithiums from the corresponding halides

4.3.1. General procedures

A hexane solution of $^n\text{BuLi}$ (2 mmol) was injected at desired temperature into a THF solution (5 ml) of **2** (2 mmol) freshly prepared as mentioned above in a two necked round-bottomed flask under argon atmosphere. The resulting solution was stirred for 15 min at the same temperature and then an electrophile (2 mmol) was added. After allowing to warm to 20°C in about 1 h, a saturated aqueous solution (1 ml) of NH_4Cl was added to the mixture and the organic layer was extracted with ether (20 ml \times 3). Combined organic extracts were dried over MgSO_4 and concentrated under reduced pressure. Chromatography on silica gel or bulb to bulb distillation of the residue afforded a desired product.

When the exchange reaction was attempted in ether, a THF solution of **2** prepared from lithium *n*-butanetellurolate and a corresponding halide (*vide supra*) was subjected to evaporation under vacuum to remove THF, and ether (5 ml) was added to the resulting mixture. The subsequent exchange reaction was performed as above without removal of salts.

Analytical data of addition products **4** [17], **5** [17], **19** [18], **20** [18], **21** [18], **22** [19], **25k** [20], **27l** ($\text{R} = \textit{ortho}$ -Ph [21]) and **28k** ($\text{Z} = \textit{para}$ -Br) [22] were in good accordance with reported values available.

4.3.2. Generation of *o*-iodobenzyl lithium (**3l**) in the presence of pinacolone (run 12)

A hexane solution of $^n\text{BuLi}$ (1.6 M, 1.29 ml, 2.12 mmol) was injected at -105°C under argon atmosphere into an ethereal solution (10 ml) of pinacolone (0.211 g, 2.12 mmol) and **2l** which was freshly prepared from the corresponding chloride **1l** (2.12 mmol) and $^n\text{BuTeLi}$ (2.12 mmol). The mixture was stirred for 15 min and warmed up to 20°C in about 1 h. Ether (50 ml) and a saturated aqueous solution of NH_4Cl (1 ml) were added to the mixture and products were extracted into ether. The extract was dried on magnesium sulfate, concentrated under vacuum, and subjected to chromatography on silica gel [20 mm ϕ \times 80 mm] to give 0.404 g (65%) of **15** in an ethereal eluent (*ca.* 80 ml) along with 0.368 g (71%) of dibutyl telluride in a hexane eluent (*ca.* 100 ml).

1-(2-Iodophenyl)-2,3,3-trimethylbutan-2-ol (**15**); a pale yellow oil; bp $165\text{--}170^\circ\text{C}/0.7$ mmHg; IR (neat) 3490, 2967, 2874, 1467, 1374, 1080, 1011, 758, 734 cm^{-1} ; ^1H NMR (CDCl_3 , 270 MHz) δ 1.01 (s, 3 H, $\text{CH}_3\text{C}(\text{OH})$), 1.08 (s, 9 H, ^tBu), 1.31 (s, 1 H, OH), 3.02 (d, $J = 13.7$ Hz, 1 H, ArCH_2), 3.08 (d, $J = 13.7$ Hz, 1 H, ArCH_2), 6.90 (td, $J = 7.6, 1.7$ Hz, 1 H, *Ar*), 7.27 (td, $J = 7.6, 1.7$ Hz, 1 H, *Ar*), 7.39 (dd, $J = 7.6, 1.7$ Hz, 1 H, *Ar*), 7.83 (dd, $J = 7.6, 1.7$ Hz, 1 H, *Ar*); ^{13}C NMR (CDCl_3 , 68 MHz) δ 21.0, 25.5, 38.4, 45.4, 77.6, 103.6, 127.8, 128.0, 131.7, 139.7, 142.0; MS (EI, 20 eV) m/e (relative intensity, %) 303 ($\text{M}^+ - \text{CH}_3$, 1), 300 (1), 285 (1), 261 (32), 218 (43), 158 (2), 134 (8), 101 (100), 91 (19), 83 (30), 57 (12), 43 (36). Anal. Found: C, 49.19; H, 6.15. $\text{C}_{13}\text{H}_{19}\text{IO}$ calcd.: C, 49.07; H, 6.02%.

4.3.3. Reaction of *n*-butyl *o*-iodobenzyl telluride (**2l**) with *n*-BuLi in the presence of trimethylchlorosilane (eqn. (2))

A hexane solution of $^n\text{BuLi}$ (1.6 M, 1.30 ml, 2.14 mmol) was injected into a solution (ether/THF = 1/1) of **2l**, prepared from **1l** (0.540 g, 2.14 mmol), tellurium (0.273 g, 2.14 mmol) and $^n\text{BuLi}$ (1.64 M, 1.30 ml, 2.14 mmol), in the presence of Me_3SiCl (0.228 g, 2.10 mmol) under argon at -105°C . The mixture was stirred for 15 min and warmed up to 20°C in 1 h. A mass spectroscopy of the resulting solution showed signals of $m/e = 350, 348$ and 346 , which were assigned to molecular ion peaks of **29** containing tellurium isotopes ^{130}Te , ^{128}Te , ^{126}Te , respectively, with reasonable relative intensities. From a ^1H NMR spectrum of the crude product obtained after usual workup mentioned above, the yield of **29** was estimated to be *ca.* 86% (1.80 mmol) by the use of trioxane as an internal standard.

n-Butyl *o*-(trimethylsilyl)benzyl telluride (**29**); a yellow oil; ^1H NMR (CDCl_3 , 270 MHz) δ 0.00 (s, 9 H, SiCH_3), 0.91 (t, $J = 7.1$ Hz, 3 H, CH_3), 1.32 (sextet, $J = 7.1$ Hz, 2 H, CH_2), 1.66 (quintet, $J = 7.1$ Hz, 2 H, CH_2), 2.65 (t, $J = 7.1$ Hz, 2 H, CH_2Te), 3.97 (s, $^2J_{\text{Te}-\text{H}} = 26.8$ Hz, 2 H, ArCH_2Te), 6.91–7.44 (m, 4 H, *Ar*); ^{13}C NMR (CDCl_3 , 68 MHz) δ -1.40 ($^1J_{\text{Si}-\text{C}} = 50$ Hz), 4.0 ($^1J_{\text{C}-\text{Te}} = 154$ Hz), 5.1 ($^1J_{\text{C}-\text{Te}} = 152$ Hz), 13.3, 24.5, 34.2, 124.5, 125.1, 126.9, 129.3, 137.0, 141.5; MS (EI, 70 eV) m/e (relative intensity, %) 350 (^{130}Te , M^+ , 5), 163 (80), 57 (100).

Into a solution of **29** prepared as above was added $^n\text{BuLi}$ (1.1 ml, 1.80 mmol) at -70°C with an assumption that **29** was formed in the same amount. After stirring for 15 min, *n*-butanal (0.130 g, 1.80 mmol) was added to the mixture. Usual workup afforded **30** in 70% yield (0.332 g) based on **1l**.

1-(2-Trimethylsilylphenyl)pentan-2-ol (**30**); a colorless oil; bp $105\text{--}110^\circ\text{C}/2.5$ mmHg; IR (neat) 3374, 3060, 3020, 2956, 2872, 1486, 1451, 1418, 1248, 1208,

1184, 1156, 1058, 1023, 847, 771, 755, 694 cm^{-1} ; ^1H NMR (CDCl_3 , 270 MHz) δ 0.03 (s, 9 H, SiCH_3), 0.97 (t, $J = 7.2$ Hz, 3 H, CH_3), 1.30–1.90 (m, 5 H, $\text{CH}_2\text{CH}_2\text{CH}_3$ and OH), 2.15 (d, $J = 7.8$ Hz, 2 H, ArCH_2), 4.84–4.86 (m, 1 H, CHOH), 6.95–7.46 (m, 4 H, Ar); ^{13}C NMR (CDCl_3 , 68 MHz) δ -1.43 ($^1J_{\text{Si-C}} = 52$ Hz), 14.0, 19.4, 23.0, 40.5, 70.3, 124.6, 125.3, 126.9, 129.3, 137.1, 141.4; MS (EI, 70 eV) m/e (relative intensity, %) 218 ($\text{M}^+ - 18$, 9), 193 (2), 146 (30), 131 (46), 117 (13), 104 (17), 91 (7), 73 (100), 59 (8), 45 (12). Anal. Found: C, 70.88; H, 9.97. $\text{C}_{14}\text{H}_{24}\text{OSi}$ calcd.: C, 71.12; H, 10.23%.

4.3.4. Generation of *o*-cyanobenzyl lithium (3m) (run 13)

A hexane solution of $^n\text{BuLi}$ (1.6 M, 1.33 mL, 2.12 mmol) was injected into a solution (THF/ $\text{Et}_2\text{O} = 1:1$, 10 ml) of *n*-butyl *o*-cyanobenzyl telluride (2m) prepared from 1m (2.12 mmol) and $^n\text{BuTeLi}$ (2.12 mmol) under argon at -105°C and the reaction mixture was stirred for 15 min. Into it was added Me_3SiCl (0.229 g, 2.12 mmol). The mixture was stirred for another 1 h and warmed up to 20°C . Water (10 ml) was poured into the resulting mixture and products were extracted with ether (20 ml \times 3), dried over MgSO_4 , concentrated *in vacuo*, and chromatographed on silica gel [40 mm ϕ \times 80 mm] to give 0.381 g (96%) of 16 in an ethereal eluent (80 ml) along with 0.487 g (95%) of dibutyl telluride in a hexane eluent (150 ml).

o-Cyanobenzyltrimethylsilane (16); a colorless oil; 130–135 $^\circ\text{C}/5$ mmHg; IR (neat) 2956, 2223, 1483, 1250, 1151, 852, 775, 758 cm^{-1} ; ^1H NMR (CDCl_3 , 270 MHz) δ 0.06 (s, 9 H, SiCH_3), 2.39 (s, 2 H, ArCH_2), 7.12 (td, $J = 7.8$, 1.2 Hz, 1 H, Ar), 7.15 (dd, $J = 7.8$, 1.2 Hz, 1 H, Ar), 7.42 (td, $J = 7.8$, 1.2 Hz, 1 H, Ar), 7.54 (dd, $J = 7.8$, 1.2 Hz, 1 H, Ar); ^{13}C NMR (CDCl_3 , 68 MHz) δ -1.8 ($^1J_{\text{C-Si}} = 50$ Hz), 26.3 ($^1J_{\text{C-Si}} = 42$ Hz), 110.9, 118.8, 124.4, 128.8, 132.3, 132.6, 145.5; MS (EI, 70 eV) m/e (relative intensity, %) 189 (M^+ , 35), 174 (29), 146 (3), 117 (2), 73 (100), 45 (12). Anal. Found: C, 70.03; H, 8.26; N, 7.56. $\text{C}_{11}\text{H}_{15}\text{NSi}$ calcd.: C, 69.78; H, 7.99; N, 7.40%.

4.3.5. 1-(4-Methoxyphenyl)pentan-2-ol (7)

A colorless oil; IR (neat) 3402, 2957, 2932, 2871, 2836, 1612, 1513, 1464, 1300, 1247, 1178, 1113, 1037 cm^{-1} ; ^1H NMR (CDCl_3 , 270 MHz) δ 0.93 (t, $J = 6.1$ Hz, 3 H, CH_3), 1.41–1.53 (m, 4 H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.61 (s, 1 H, OH), 2.58 (dd, $J = 13.7$, 8.3 Hz, 1 H, ArCH_2), 2.77 (dd, $J = 13.7$, 4.3 Hz, 1 H, ArCH_2), 3.76–3.79 (m, 1 H, CH), 3.79 (s, 3 H, CH_3O), 6.86 (d, $J = 8.8$ Hz, 2 H, Ar), 7.13 (d, $J = 8.8$ Hz, 2 H, Ar); ^{13}C NMR (CDCl_3 , 68 MHz) δ 14.1, 19.0, 38.9, 43.1, 55.3, 72.5, 114.0, 130.4, 130.6, 158.3; MS (EI, 70 eV) m/e (relative

intensity, %) 194 (M^+ , 26), 176 (1), 151 (61), 123 (100), 108 (32), 91 (34), 77 (26), 55 (17), 43 (21). Anal. Found: C, 74.42; H, 9.31. $\text{C}_{12}\text{H}_{18}\text{O}_2$ calcd.: C, 74.19; H, 9.34%.

4.3.6. 1-[5-(6-Chloro-1,3-dioxaindanyl)]pentan-2-ol (8)

Colorless needles; mp 60.0–60.5 $^\circ\text{C}$; IR (KBr) 3206, 2962, 2924, 1503, 1484, 1250, 1231, 1119, 1043, 1020, 938 cm^{-1} ; ^1H NMR (CDCl_3 , 270 MHz) δ 0.94 (t, $J = 6.5$ Hz, 3 H, CH_3), 1.47–1.58 (m, 5 H, $\text{CH}(\text{OH})\text{-CH}_2\text{CH}_2\text{CH}_3$), 2.64 (dd, $J = 13.7$, 8.6 Hz, 1 H, ArCH_2), 2.90 (dd, $J = 13.7$, 4.2 Hz, 1 H, ArCH_2), 3.85–3.89 (m, 1 H, CH), 5.95 (s, 2 H, OCH_2O), 6.75 (s, 1 H, Ar), 6.84 (s, 1 H, Ar); ^{13}C NMR (CDCl_3 , 68 MHz) δ 14.1, 18.9, 39.3, 41.5, 71.3, 101.7, 110.0, 111.1, 125.5, 129.5, 146.6, 146.9; MS (EI, 70 eV) m/e (relative intensity, %) 244 (^{37}Cl , M^+ , 6), 242 (^{35}Cl , M^+ , 17), 201 (1), 199 (3), 172 (37), 170 (100), 169 (40), 43 (17). Anal. Found: C, 59.50; H, 6.19. $\text{C}_{12}\text{H}_{15}\text{O}_3\text{Cl}$ calcd.: C, 59.38; H, 6.23%.

4.3.7. 1-(4-Fluorophenyl)pentan-2-ol (9)

Colorless needles; mp 44.5–45.0 $^\circ$; IR (KBr) 3336, 2957, 2932, 2908, 2873, 1601, 1509, 1221, 1158, 505 cm^{-1} ; ^1H NMR (CDCl_3 , 270 MHz) δ 0.93 (t, $J = 6.8$ Hz, 3 H, CH_3), 1.41–1.50 (m, 4 H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.65 (brs, 1 H, OH), 2.61 (dd, $J = 13.7$, 8.1 Hz, 1 H, ArCH_2), 2.78 (dd, $J = 13.7$, 2.2 Hz, 1 H, ArCH_2), 3.81–3.87 (m, 1 H, CH), 6.98 (dd, $J = 8.7$ Hz, $^4J_{\text{H-F}} = 8.7$ Hz, 2 H, Ar), 7.17 (dd, $J = 8.7$ Hz, $^3J_{\text{H-F}} = 14.3$ Hz, 2 H, Ar); ^{13}C NMR (CDCl_3 , 68 MHz) δ 14.0, 18.9, 38.9, 43.1, 72.3, 115.2 ($^2J_{\text{C-F}} = 20.8$ Hz), 130.8 ($^3J_{\text{C-F}} = 8.3$ Hz), 134.4, 161.6 ($^1J_{\text{C-F}} = 245.0$ Hz); MS (EI, 70 eV) m/e (relative intensity, %) 182 (M^+ , 1.2), 164 (0.6), 139 (5), 121 (4.5), 110 (100), 73 (17), 55 (54), 43 (22). Anal. Found: C, 72.24; H, 8.25. $\text{C}_{11}\text{H}_{15}\text{FO}$ calcd.: C, 72.50; H, 8.30%.

4.3.8. 1-(2-Chlorophenyl)pentan-2-ol (10)

A colorless oil; bp 200 $^\circ\text{C}/8$ mmHg; IR (neat) 3359, 3067, 2959, 2931, 2872, 1572, 1475, 1444, 1122, 1052, 1040, 1013, 750, 682 cm^{-1} ; ^1H NMR (CDCl_3 , 270 MHz) δ 0.94 (t, $J = 6.1$ Hz, 3 H, CH_3), 1.38–1.53 (m, 4 H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.66 (brs, 1 H, OH), 2.73 (dd, $J = 13.4$, 8.5 Hz, 1 H, ArCH_2), 3.00 (dd, $J = 13.4$, 4.1 Hz, 1 H, ArCH_2), 3.89–3.93 (m, 1 H, CH), 7.13–7.37 (m, 4 H, Ar); ^{13}C NMR (CDCl_3 , 68 MHz) δ 14.0, 18.9, 39.3, 41.7, 70.9, 126.7, 127.8, 129.6, 131.8, 134.3, 136.7; MS (EI, 70 eV) m/e (relative intensity, %) 200 (^{37}Cl , M^+ , 0.1), 198 (^{35}Cl , M^+ , 0.4), 182 (0.1), 180 (0.4), 157 (2), 155 (7), 139 (1), 137 (3), 128 (37), 126 (100), 91 (47), 73 (16), 55 (50), 43 (20). Anal. Found: C, 66.80; H, 7.92. $\text{C}_{11}\text{H}_{15}\text{ClO}$ calcd.: C, 66.50; H, 7.61%.

4.3.9. 1-(4-Chlorophenyl)pentan-2-ol (11)

Colorless needles; mp 72.5–73.0°C; IR (KBr) 3333, 2960, 2932, 1490, 1097, 1016, 805 cm⁻¹; ¹H NMR (CDCl₃, 270 MHz) δ 0.94 (t, *J* = 6.8 Hz, 3 H, CH₃), 1.46–1.65 (m, 4 H, CH₂CH₂CH₃), 1.60 (br, 1 H, OH), 2.62 (dd, *J* = 13.7, 8.3 Hz, 1 H, ArCH₂), 2.79 (dd, *J* = 13.6, 4.3 Hz, 1 H, ArCH₂), 3.78–3.91 (m, 1 H, CH), 7.15 (d, *J* = 8.3 Hz, 2 H, Ar), 7.28 (d, *J* = 8.5 Hz, 2 H, Ar); ¹³C NMR (CDCl₃, 68 MHz) δ 14.1, 18.9, 39.0, 43.3, 72.3, 128.6, 130.8, 132.3, 137.2; MS (EI, 70 eV) *m/e* (relative intensity, %) 200 (³⁷Cl, M⁺, 0.6), 198 (³⁵Cl, M⁺, 2), 182 (0.4), 180 (1), 128 (37), 126 (100), 91 (49), 73 (22), 55 (85), 43 (30). Anal. Found: C, 66.31; H, 7.58. C₁₁H₁₅ClO calcd.: C, 66.50; H, 7.61%.

4.3.10. 1-(2-Bromophenyl)pentan-2-ol (12)

Colorless needles; mp 38.0–39.0°C; IR (KBr) 3376, 2958, 2930, 1470, 1025, 749 cm⁻¹; ¹H NMR (CDCl₃, 270 MHz) δ 0.95 (t, *J* = 6.7 Hz, 3 H, CH₃), 1.41 (brs, 1 H, OH), 1.47–1.55 (m, 4 H, CH₂CH₂CH₃), 2.74 (dd, *J* = 13.6, 8.7 Hz, 1 H, ArCH₂), 3.01 (dd, *J* = 13.4, 4.0 Hz, 1 H, ArCH₂), 3.89–3.92 (m, 1 H, CH), 7.08 (t, *J* = 7.9 Hz, 1 H, Ar), 7.23–7.27 (m, 2 H, Ar), 7.55 (d, *J* = 7.9 Hz, 1 H, Ar); ¹³C NMR (CDCl₃, 68 MHz) δ 14.0, 18.9, 39.3, 44.1, 70.9, 124.9, 127.3, 128.1, 131.8, 133.0, 138.4; MS (EI, 70 eV) *m/e* (relative intensity, %) 244 (⁸¹Br, M⁺, 0.4), 242 (⁷⁹Br, M⁺, 0.4), 226 (0.3), 224 (0.3), 201 (4), 199 (4), 172 (98), 170 (100), 91 (53), 73 (21), 55 (63), 43 (25); HRMS. Found: 242.0279 (calculated for C₁₁H₁₅⁷⁹BrO: 242.0306). Anal. Found C, 54.44; H, 6.12. C₁₁H₁₅BrO calcd.: C, 54.34; H, 6.22%.

4.3.11. 2-(3-Bromophenyl)-1,1-diphenylethanol (13)

Colorless plates; mp 106–107°C; IR (KBr) 3546, 3057, 3022, 2964, 2934, 1595, 1567, 1494, 1474, 1445, 1429, 1342, 1268, 1235, 1164, 1073, 1052, 1036, 1008, 995, 949, 834, 789, 775, 753, 718, 696, 669, 647, 608, 568 cm⁻¹; ¹H NMR (CDCl₃, 270 MHz) δ 2.22 (s, 1 H, OH), 3.57 (s, 2 H, ArCH₂), 6.78 (d, *J* = 7.8 Hz, 1 H, Ar), 6.98 (t, *J* = 7.8 Hz, 1 H, Ar), 7.04 (t, *J* = 7.8 Hz, 1 H, Ar), 7.21–7.40 (m, 11 H, Ar); ¹³C NMR (CDCl₃, 68 MHz) δ 47.6, 78.0, 121.9, 126.2, 127.1, 128.2, 129.3, 129.4, 129.7, 133.9, 138.5, 146.2; MS (EI, 20 eV) *m/e* (relative intensity, %) 336 (⁸¹Br, M⁺ – 18, 5), 334 (⁷⁹Br, M⁺ – 18, 5), 255 (2), 254 (2), 253 (2), 252 (2), 183 (100), 171 (1.5), 169 (2), 165 (3), 105 (50), 90 (3), 77 (22), 51 (3). Anal. Found: C, 67.95; H, 4.78. C₂₀H₁₇BrO calcd.: C, 68.00; H, 4.85%.

4.3.12. (E)-1-(4-Bromophenyl)hept-3-en-2-ol (14)

E-Configuration was confirmed by the coupling constant (*J* = 15.5 Hz) between vinylic protons on ¹H NMR; pale white crystals; mp 33.5–34.0°C; IR (KBr)

3242, 2949, 2925, 2866, 1487, 1464, 1071, 1046, 1012, 970, 807, 784, 640, 609, 525, 402 cm⁻¹; ¹H NMR (CDCl₃, 270 MHz) δ 0.80 (t, *J* = 7.3 Hz, 3 H, CH₃), 1.30 (sextet, *J* = 7.3 Hz, 2 H, CH₂), 1.55 (brs, 1 H, OH), 1.93 (td, *J* = 7.3, 6.5 Hz, 2 H, CH=CHCH₂), 2.69 (d, *J* = 5.6 Hz, 2 H, ArCH₂), 4.19 (dd, *J* = 6.5, 5.6 Hz, 1 H, CHOH), 5.41 (dd, *J* = 15.5, 6.5 Hz, 1 H, CH(OH)CH=CH), 5.54 (dt, *J* = 15.5, 6.5 Hz, 1H, CH(OH)CH=CH), 7.01 (d, *J* = 8.3 Hz, 2 H, Ar), 7.34 (d, *J* = 8.3 Hz, 2 H, Ar); ¹³C NMR (CDCl₃, 68 MHz) δ 13.6, 22.2, 34.2, 43.4, 73.5, 120.3, 131.3, 131.4, 131.9, 132.6, 137.1; MS (EI, 20 eV) *m/e* (relative intensity, %) 270 (⁸¹Br, M⁺, 0.4), 268 (⁷⁹Br, M⁺, 0.5), 252 (3), 250 (2), 223 (2), 221 (2), 184 (1), 182 (1), 172 (46), 170 (47), 142 (4), 128 (4), 115 (2), 99 (14), 57 (100). Anal. Found: C, 58.03; H, 6.36. C₁₃H₁₇BrO calcd.: C, 58.01; H, 6.37%.

4.3.13. 1-(3-Cyanophenyl)-2,3,3-trimethylbutan-2-ol (17)

Dark white crystals; mp 72.5–73.0°C; IR (KBr) 3522, 2984, 2971, 2954, 2874, 2235, 1482, 1374, 1365, 1141, 1104, 1094, 942, 802, 738, 686 cm⁻¹; ¹H NMR (CDCl₃, 270 MHz) δ 0.94 (s, 3 H, CH₃COH), 1.05 (s, 9 H, ^{*t*}Bu), 1.16 (s, 1 H, OH), 2.65 (d, *J* = 13.2 Hz, 1 H, ArCH₂), 2.97 (d, *J* = 13.2 Hz, 1 H, ArCH₂), 7.37 (dd, *J* = 7.6, 1.2 Hz, 1 H, Ar), 7.39 (dd, *J* = 7.6, 1.2 Hz, 1 H, Ar), 7.50 (t, *J* = 7.6 Hz, 1 H, Ar), 7.55 (s, 1 H, Ar); ¹³C NMR (CDCl₃, 68 MHz) δ 21.5, 25.4, 38.1, 41.6, 76.1, 111.9, 119.1, 128.5, 129.8, 134.4, 135.5, 140.1; MS (EI, 70 eV) *m/e* (relative intensity, %) 218 (M⁺ + 1, 1), 202 (2), 199 (1), 184 (4), 160 (60), 142 (5), 118 (20), 101 (100), 89 (6), 83 (37), 71 (5), 55 (15), 43 (49). Anal. Found: C, 77.09; H, 8.73; N, 6.34. C₁₄H₁₉NO calcd.: C, 77.38; H, 8.81; N, 6.45%.

4.3.14. 1-(4-Cyanophenyl)pentan-2-ol (18)

Colorless crystals; mp 40.0–40.5°C; IR (KBr) 3427, 2958, 2872, 2228, 1675, 1608, 1506, 1413, 1178, 1122, 1016, 817 cm⁻¹; ¹H NMR (CDCl₃, 270 MHz) δ 0.94 (t, *J* = 6.8 Hz, 3 H, CH₃), 1.40–1.52 (m, 4 H, CH₂CH₂CH₃), 1.64 (brs, 1 H, OH), 2.73 (dd, *J* = 13.7, 7.8 Hz, 1 H, ArCH₂), 2.87 (dd, *J* = 13.7, 4.4 Hz, 1 H, ArCH₂), 3.84–3.87 (m, 1 H, CH), 7.34 (d, *J* = 7.8 Hz, 2 H, Ar), 7.60 (d, *J* = 7.8 Hz, 2 H, Ar); ¹³C NMR (CDCl₃, 68 MHz) δ 14.0, 18.9, 39.3, 44.0, 72.1, 110.3, 119.0, 130.3, 132.2, 144.7; MS (CIDI) *m/e* (relative intensity, %) 190 (M⁺ + 1, 0.6), 189 (M⁺, 0.9), 117 (100). Anal. Found: C, 76.05; H, 8.15; N, 7.35. C₁₂H₁₅NO calcd.: C, 76.16; H, 7.99; N, 7.40%.

4.3.15. 1-(3-Bromophenyl)pentan-2-ol (23j)

A colorless oil; IR (neat) 3368, 3019, 2958, 2931, 2872, 1515, 1456, 1020, 809 cm⁻¹; ¹H NMR (CDCl₃,

270 MHz) δ 0.92 (t, $J = 7.1$ Hz, 3 H, CH_3), 1.43–1.51 (m, 4 H, CH_2), 1.77 (brs, 1 H, OH), 2.59 (dd, $J = 13.7$, 8.4 Hz, 1 H, ArCH_2), 2.75 (dd, $J = 13.7$, 4.1 Hz, 1 H, ArCH_2), 3.75–3.78 (m, 1 H, CH), 7.12–6.36 (m, 4 H, Ar); ^{13}C NMR (CDCl_3 , 68 MHz) δ 14.0, 18.9, 39.0, 43.6, 72.1, 122.5, 128.1, 129.4, 129.9, 132.4, 141.2; MS (EI, 70 eV) m/e (relative intensity, %) 244 (^{81}Br , M^+ , 0.8), 242 (^{79}Br , M^+ , 0.9), 226 (0.3), 224 (0.3), 201 (3), 199 (4), 172 (82), 170 (83), 91 (38), 73 (44), 55 (100),

43 (38). HRMS Found: 242.0301 (calculated for $\text{C}_{11}\text{H}_{15}^{79}\text{BrO}$: 242.0306). Anal. Found: C, 54.46; H, 6.27. $\text{C}_{11}\text{H}_{15}\text{BrO}$ calcd.: C, 54.34; H, 6.22%.

4.3.16. 1-(4-Bromophenyl)pentan-2-ol (23k)

Colorless needles; mp 88.5–89.0°C; IR (KBr) 3245, 2956, 2931, 2909, 2870, 1487, 1011, 800 cm^{-1} ; ^1H NMR (CDCl_3 , 270 MHz) δ 0.93 (t, $J = 6.4$ Hz, 3 H, CH_3), 1.39–1.48 (m, 4 H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.50 (brs, 1 H, OH), 2.60 (dd, $J = 13.7$, 8.2 Hz, 1 H, ArCH_2), 2.75 (dd, $J = 13.7$, 4.1 Hz, 1 H, ArCH_2), 3.77–3.81 (m, 1 H, CH), 7.09 (d, $J = 8.2$ Hz, 2 H, Ar), 7.42 (d, $J = 8.2$ Hz, 2 H, Ar); ^{13}C NMR (CDCl_3 , 68 MHz) δ 14.1, 18.9, 39.0, 43.4, 72.3, 120.3, 131.2, 131.6, 137.7; MS (EI, 70 eV) m/e (relative intensity, %) 244 (^{81}Br , M^+ , 2.8), 242 (^{79}Br , M^+ , 2.9), 226 (0.2), 224 (0.2), 201 (3), 199 (3), 172 (83), 170 (85), 91 (48), 73 (41), 55 (100), 43 (37). Anal. Found: C, 54.28; H, 6.27; Br, 32.74. $\text{C}_{11}\text{H}_{15}\text{BrO}$ calcd.: C, 54.34; H, 6.22; Br, 32.86%.

4.3.17. 1-(2-Iodophenyl)pentan-2-ol (23l)

Colorless needles; mp 59.5–60.0°C; IR (KBr) 3354, 3286, 2956, 2926, 2872, 2861, 2836, 1496, 1463, 1432, 1124, 1063, 1034, 1018, 1008, 962, 845, 748, 716, 647, 644 cm^{-1} ; ^1H NMR (CDCl_3 , 270 MHz) δ 0.96 (t, $J = 7.1$ Hz, 3 H, CH_3), 1.49 (br 1 H, OH), 1.50–1.56 (m, 4 H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.77 (dd, $J = 13.7$, 8.8 Hz, 1 H, ArCH_2), 2.97 (dd, $J = 13.7$, 6.5 Hz, 1 H, ArCH_2), 3.91–3.93 (m, 1 H, CH), 6.91 (d, $J = 8.1$ Hz, 1 H, Ar); 7.26 (t, $J = 8.1$ Hz, 1 H, Ar), 7.29 (t, $J = 8.1$ Hz, 1 H, Ar), 7.84 (d, $J = 8.1$ Hz, 1 H, Ar); ^{13}C NMR (CDCl_3 , 68 MHz, only 10 peaks were found) δ 14.3, 18.9, 39.3, 48.4, 71.1, 101.1, 128.3, 131.0, 139.7, 141.7; MS (EI, 70 eV) m/e (relative intensity, %) 290 (M^+ , 0.8), 272 (1), 247 (1.7), 218 (100), 120 (3), 91 (37), 73 (10), 55 (32), 43 (13). Anal. Found: C, 45.70; H, 5.18. $\text{C}_{11}\text{H}_{15}\text{IO}$ calcd.: C, 45.54; H, 5.21%.

4.3.18. 1-(2-Butylphenyl)pentan-2-ol (ortho-24, R = Bu)

A colorless oil; IR (neat) 3400, 2957, 2929, 2871, 1463, 909, 734 cm^{-1} ; ^1H NMR (CDCl_3 , 270 MHz) δ 0.90 (t, $J = 7.1$ Hz, 3 H, CH_3), 0.94 (t, $J = 7.1$ Hz, 3 H, CH_3), 1.38–1.62 (m, 7 H, CH_2 and OH), 1.74–1.80 (m,

2 H, CH_2), 2.81 (dd, $J = 13.8$, 8.3 Hz, 1 H, $\text{ArCH}_2\text{-CHOH}$), 2.88 (t, $J = 7.6$ Hz, 2 H, $^n\text{PrCH}_2\text{Ar}$), 2.99 (dd, $J = 13.8$, 4.2 Hz, 1 H, ArCH_2), 3.79–3.81 (m, 1 H, CH), 7.05 (d, $J = 7.6$ Hz, 1 H, Ar), 7.21 (t, $J = 7.6$ Hz, 1 H, Ar), 7.22 (t, $J = 7.6$ Hz, 1 H, Ar), 7.69 (d, $J = 7.6$ Hz, 1 H, Ar); ^{13}C NMR (CDCl_3 , 68 MHz) δ 8.9, 13.4, 14.1, 19.0, 25.2, 33.6, 39.3, 48.1, 72.2, 117.3, 127.3, 127.7, 130.0, 137.9, 142.3. HRMS. Found 220.1829 (calculated for $\text{C}_{15}\text{H}_{24}\text{O}$: 220.1827).

4.3.19. 2-Iodophenylpentane (ortho-25, Z = I)

A colorless oil; ^1H NMR (CDCl_3 , 270 MHz) δ 0.91 (t, $J = 7.1$ Hz, 3 H, CH_3), 1.36–1.39 (m, 4 H, $\text{CH}_2\text{-CH}_2\text{CH}_3$), 1.52–1.73 (m, 2 H, $^n\text{PrCH}_2$), 2.70 (t, $J = 7.1$ Hz, 2 H, ArCH_2), 6.86 (td, $J = 8.1$, 1.2 Hz, 1 H, Ar), 7.20 (dd, $J = 8.1$, 1.2 Hz, 1 H, Ar), 7.25 (t, 8.1 Hz, 1 H, Ar), 7.80 (d, $J = 8.1$ Hz, 1 H, Ar); ^{13}C NMR (CDCl_3 , 68 MHz, only 10 peaks were found) δ 14.1, 22.6, 30.0, 31.6, 40.9, 101.2, 127.5, 128.2, 129.4, 139.5; MS (EI, 70 eV) m/e (relative intensity, %) 274 (M^+ , 56), 217 (60), 91 (100).

4.3.20. 1-(2-Pentylphenyl)butan-1-ol (ortho-26, R = Bu)

A colorless oil; ^1H NMR (CDCl_3 , 270 MHz) δ 0.90 (t, $J = 7.1$ Hz, 3 H, CH_3), 0.94 (t, $J = 7.1$ Hz, 3 H, CH_3), 1.26–1.85 (m, 11 H, CH_2 and OH), 2.59–2.66 (m, 2 H, ArCH_2), 4.96 (dd, $J = 8.1$, 4.6 Hz, 1 H, CH), 7.12–7.25 (m, 3 H, Ar), 7.45–7.49 (m, 1 H, Ar); ^{13}C NMR (CDCl_3 , 68 MHz, only 14 peaks were found) δ 14.0, 19.4, 22.6, 31.5, 31.9, 32.4, 41.0, 69.8, 125.5, 126.3, 127.2, 129.4, 139.5, 142.6; MS (EI, 70 eV) m/e (relative intensity, %) 220 (M^+ , 0.05), 202 ($\text{M}^+ - 18$, 32), 177 (32), 145 (55), 131 (33), 117 (100), 91 (37). HRMS. Found 220.1821 (calculated for $\text{C}_{15}\text{H}_{24}\text{O}$: 220.1827).

4.3.21. 1-(3-Pentylphenyl)butan-1-ol (meta-26, R = Bu)

A colorless oil; IR (neat) 3360, 2957, 2929, 2858, 1487, 1466, 1028, 795, 705 cm^{-1} ; ^1H NMR (CDCl_3 , 270 MHz) δ 0.85 (t, $J = 6.8$ Hz, 3 H, CH_3), 0.89 (t, $J = 7.3$ Hz, 3 H, CH_3), 1.26–1.32 (m, 6 H, $\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 1.54–1.63 (m, 4 H, $\text{CH}_3(\text{CH}_2)_2\text{CH}(\text{OH})$), 1.75 (d, $J = 2.4$ Hz, 1 H, OH), 2.56 (t, $J = 7.8$ Hz, 2 H, ArCH_2), 4.61 (td, $J = 8.6$, 2.4 Hz, 1 H, CH), 7.06 (t, $J = 8.1$ Hz, 1 H, Ar), 7.11 (s, 1 H, Ar), 7.20 (d, $J = 8.1$ Hz, 1 H, Ar), 7.22 (d, $J = 8.1$ Hz, 1 H, Ar); ^{13}C NMR (CDCl_3 , 68 MHz, only 13 peaks were found) δ 14.0, 14.1, 19.1, 22.6, 31.2, 31.6, 36.0, 41.3, 74.6, 123.2, 126.0, 127.6, 128.3, 143.2, 144.9; MS (EI, 70 eV) m/e (relative intensity, %) 220 (M^+ , 3), 202 ($\text{M}^+ - 18$, 9), 177 (76), 131 (25), 91 (29), 71 (33), 43 (100). HRMS. Found 220.1829 (calculated for $\text{C}_{15}\text{H}_{24}\text{O}$: 220.1827).

4.3.22. 1-(4-Pentylphenyl)butan-1-ol (*para*-26, R = Bu)

Colorless oil; IR (neat) 3360, 2957, 2929, 2872, 2858, 1514, 1456, 1418, 1378, 1108, 1027, 961, 839 cm^{-1} ; ^1H NMR (CDCl_3 , 270 MHz), δ 0.89 (t, $J = 8.3$ Hz, 3 H, CH_3), 0.92 (t, $J = 8.3$ Hz, 3 H, CH_3), 1.17–1.85 (m, 11 H, 5 CH_2 and OH), 2.58 (t, $J = 8.3$ Hz, 2 H, ArCH_2), 4.61–4.63 (m, 1 H, CH), 7.15 (d, $J = 7.8$ Hz, 2 H, Ar), 7.24 (d, $J = 7.8$ Hz, 2 H, Ar); ^{13}C NMR (CDCl_3 , 68 MHz) δ 14.0, 14.1, 19.1, 22.6, 31.2, 31.6, 35.6, 41.2, 74.3, 125.9, 128.5, 142.2, 142.3; MS (EI, 70 eV) m/e (relative intensity, %) 220 (M^+ , 2), 202 ($\text{M}^+ - 18$, 39), 177 (89), 145 (100), 131 (68), 117 (30), 91 (39). HRMS. Found 220.1819 (calculated for $\text{C}_{15}\text{H}_{24}\text{O}$: 220.1827).

4.3.23. 2-Ethyl-1-methylbenzene (*ortho*-27, R = Me)

A colorless oil; IR (neat) 3000, 1501 cm^{-1} ; ^1H NMR (CDCl_3 , 270 MHz) δ 1.18 (t, $J = 7.3$ Hz, 3 H, CH_2CH_3), 2.25 (s, 3 H, ArCH_3), 2.57 (q, $J = 7.3$ Hz, 2 H, CH_2), 7.01–7.05 (m, 4 H, Ar); MS (CIDI) m/e (relative intensity, %) 121 ($\text{M}^+ + 1$, 55), 106 (100).

4.3.24. 1-(2-Butylphenyl)pentane (*ortho*-27, R = Bu)

A colorless oil; ^1H NMR (CDCl_3 , 270 MHz) δ 0.91 (t, $J = 7.3$ Hz, 6 H, CH_3), 1.31–1.63 (m, 8 H, CH_2), 1.78 (quintet, $J = 7.3$ Hz, 2 H, CH_2), 2.72 (t, $J = 7.3$ Hz, 2 H, ArCH_2), 2.88 (t, $J = 7.3$ Hz, 2 H, ArCH_2), 6.97–7.03 (m, 1 H, Ar), 7.10–7.18 (m, 2 H, Ar), 7.64 (d, $J = 7.8$ Hz, 1 H, Ar); ^{13}C NMR (CDCl_3 , 68 MHz, only 14 peaks were found) δ 8.0, 13.4, 14.1, 22.6, 25.2, 31.1, 33.7, 40.3, 116.1, 126.6, 127.6, 128.4, 137.4, 147.1; MS (EI, 70 eV) m/e (relative intensity, %) 204 (M^+ , 1), 203 (9), 183 (94), 69 (100).

4.3.25. 2-Benzylbiphenyl (*ortho*-27, R = Ph) [21]

A colorless oil; ^1H NMR (CDCl_3 , 270 MHz) δ 3.94 (s, 2 H, CH_2), 7.20–7.32 (m, 14 H, Ar); ^{13}C NMR (CDCl_3 , 68 MHz) δ 39.3, 126.0, 126.4, 127.1, 127.7, 128.3, 128.5, 129.1, 129.6, 130.4, 130.6, 138.5, 141.7, 141.9, 142.5; MS (EI, 70 eV) m/e (relative intensity, %) 244 (M^+ , 81), 167 (51), 77 (100).

Acknowledgements

This work was supported in part by a Grant in Aid for Scientific Research on Priority Areas (No. 05236101) from the Ministry of Education, Science, and Culture, Japan. We are thankful to Mitsubishi Material Co. and Nippon Aluminum Alkyls Ltd. for donation of tellurium and n-butyllithium, respectively, and also to Instrumental Analysis Center of Faculty of Engineering in Osaka University.

References and notes

- Reviews of organolithium compounds, see for example, (a) B.J. Wakefield, *Organolithium Methods*, Academic Press, New York, 1988; (b) E. Bunzel and T. Durst (eds.), *Comprehensive Carbonion Chemistry*, Elsevier, New York, 1984.
- (a) M. Pereyre, J.-P. Quintard and A. Rahm, *Tin in Organic Synthesis*, Butterworths, London, 1987, Chapter 9; (b) C. Paulmier, *Selenium Reagents and Intermediates in Organic Synthesis*, Pergamon Press, New York, 1986, Chapters 4 and 9; (c) H.J. Reich, in D. Liota (ed.) *Organoselenium Chemistry*, Wiley Interscience, New York, 1987, Chapter 5.
- Our previous studies on lithium–tellurium exchange, (a) T. Hiroy, Y. Atarashi, N. Kambe, S.-I. Fujiwara, A. Ogawa, I. Ryu and N. Sonoda, *Organometallics*, 9 (1990) 1355; (b) T. Hiroy, Y. Morita, T. Inoue, N. Kambe, A. Ogawa, I. Ryu and N. Sonoda, *J. Am. Chem. Soc.*, 112 (1990) 455; (c) T. Hiroy, T. Mogami, N. Kambe, S.-I. Fujiwara and N. Sonoda, *Synth. Commun.*, 20 (1990) 703; (d) T. Hiroy, N. Kambe, A. Ogawa, N. Miyoshi, S. Murai and N. Sonoda, *Angew. Chem., Int. Ed. Engl.*, 26 (1987) 1187.
- A preliminary example of the formation of parent benzyl lithium (**3a**) by the aid of lithium–tellurium exchange has been demonstrated in ref. 3d.
- (a) J.T.B. Ferreira, A.R.M. Oliveira and J.V. Comassetto, *Tetrahedron Lett.*, 33 (1992) 915; (b) S. Uemura, S. Fukuzawa and K. Ohe, *Tetrahedron Lett.*, 26 (1985) 921; (c) J.V. Comassetto, J.T.B. Ferreira and J.A. Fontanillas Val, *J. Organomet. Chem.*, 277 (1984) 261; (d) H.K. Spencer and M.P. Cava, *J. Org. Chem.*, 42 (1977) 2937; (e) H.K. Spencer, M.V. Lakshminantham and M.P. Cava, *J. Am. Chem. Soc.*, 99 (1977) 1470.
- G.H. Posner, T.P. Kogan, S.R. Hains and L.L. Frye, *Tetrahedron Lett.*, 25 (1984) 2627 and references quoted therein.
- As can be expected, direct reaction of *p*-bromobenzyl bromide (**1k**) with $^n\text{BuLi}$ under the same conditions was also unsuccessful resulting in the formation of 1-(*p*-bromophenyl)pentane (**25k**) and bis(4-bromophenyl)ethane (**28k**) in 36% and 42% isolated yields, respectively.
- Several precedential studies on exchange reactions of related compounds have been reported. (Bromophenyl)alkyl bromides and chlorides except bromobenzyl bromide undergo selective lithiation at the aromatic ring; (a) W.E. Parham, C.K. Bradsher and D.C. Reames, *J. Org. Chem.*, 46 (1981) 4804 and references cited therein. On the other hand, lithiation at the side chain predominated in the reaction of *o*-bromophenethyl iodide with $^n\text{BuLi}$ at -98°C in THF, although a complex mixture of products was obtained when quenched with methanol arising from the subsequent Li–Br exchange of the initially formed intermediate; (b) P. Beak, D.J. Allen and W.K. Lee, *J. Am. Chem. Soc.*, 112 (1990) 1629. *o*-Bromobenzyltrimethylstannane undergoes Li–Sn exchange in THF at -70°C by the reaction with n-butyllithium resulting in the selective lithiation at the benzylic position to give **3i**, but in ether the Li–Sn exchange was slow and competed with Li–Br exchange; (c) H.J.R. de Boer, O.S. Akkerman and F. Bickelhaupt, *Organometallics*, 9 (1990) 2898.
- Direct substitution of butyltelluro group at the benzylic position with n-butyllithium can be ruled out because **1a** and other benzylic tellurides without bromo or iodo substituent did not undergo such displacement and because dibutyl ditelluride, which is expected to be formed by air oxidation of lithium n-butanetelluroate generated by the substitution if it proceeds, could not be detected in the reaction mixture in any runs of Table 2.
- Direct displacement of the iodine atom of **2i** with organolithium reagents via $\text{S}_{\text{N}}2$, $\text{S}_{\text{N}}\text{R}$ or $\text{S}_{\text{RN}}1$ mechanisms might not be ruled

- out since phenyllithium also afforded **27** in an appreciable amount as shown in run 10 of Table 2.
- 11 Deprotonation of *m*-tolunitrile with lithium diisopropylamide in THF/HMPA in the presence of benzophenone afforded an addition product in only 41% yield; E.M. Kaiser and J.D. Petty, *J. Organomet. Chem.*, **107** (1976) 219.
 - 12 D.J. Ramón and M. Yus, *Tetrahedron Lett.*, **33** (1992) 2217.
 - 13 D.D. Perrin, W.L.F. Armarego and D.R. Perrin, *Purification of Laboratory Chemicals*, 2nd Ed., Pergamon Press, New York, 1980.
 - 14 L.F. Fieser and M. Fieser, *Reagents for Organic Synthesis*, Vol. 1, John Wiley, New York, 1967, p. 417.
 - 15 M.J. Dabdoub and J.V. Comasseto, *Organometallics*, **7** (1988) 84.
 - 16 K.J. Irgolic, P.J. Busse, R.A. Grigsby and M.R. Smith, *J. Organomet. Chem.*, **88** (1975) 175.
 - 17 C. Bernardon, *J. Organomet. Chem.*, **367** (1989) 11.
 - 18 A. Hosomi, S. Kohara, K. Ogata, T. Yanagi and Y. Tominaga, *J. Org. Chem.*, **55** (1990) 2415.
 - 19 R.B. Bates, W.A. Beavers, B. Gordon III and M.S. Mills, *J. Org. Chem.*, **44** (1979) 3800.
 - 20 G.W. Gray, M. Hird, D. Lacey and K.J. Toyne, *J. Chem. Soc., Perkin Trans. II*, (1989) 2041.
 - 21 R.D. Rieke, L.D. Shulte, B.T. Dawson and S.S. Yang, *J. Am. Chem. Soc.*, **112** (1990) 8388.
 - 22 S.-I. Inaba, H. Matsumoto and R.D. Rieke, *J. Org. Chem.*, **49** (1984) 2093.