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Facile deprotection of dithioacetals by using a novel 1,4-benzoquinone/cat. NaI system

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ABSTRACT

The combination of 1,4-benzoquinone and a catalytic amount of NaI was found to be effective for the deprotection of dithioacetals. The reactions proceeded efficiently under mild, near-neutral reaction conditions, producing a wide range of aryl and alkyl aldehydes and ketones generally in high yields with good functional group compatibility. The method developed therefore represents a general, facile, and highly applicable approach for deprotecting dithioacetals.

1. Introduction

Dithioacetals have extensively been employed as important protecting groups for carbonyl moieties in organic synthesis due to their stability toward both acidic and basic conditions.[1] Furthermore, cyclic dithioacetals, such as 1,3-dithianes can be considered as useful building blocks, serving as acyl anion equivalents, which participate in C–C bond forming reactions.[2] A variety of procedures have so far been developed for the deprotection of dithioacetals, including heavy metal (e.g., Hg) mediated processes[3] as well as some oxidative methods (e.g., using DDQ,[4] hypervalent iodines,[5] *m*CPBA[6]), most of these methods suffer from several drawbacks, such as harsh reaction conditions, use of a stoichiometric amount or an excess of toxic and/or expensive (metal) reagents, and a narrow substrate scope. Use of electrophilic halonium ions also provides another approach for the deprotection. An excess amount of *N*-halosuccinimides (NBS and NCS) has classically been chosen for this purpose.[7] In 2001, the combination of H_2O_2 and NH_4Br in the presence of a catalytic amount of V_2O_5, possibly forming a bromonium cation in situ, has been reported by Khan et al. to effect dethioacetalization.[8] Oxone was also successfully employed as an oxidant in the presence of KBr, mediating the deprotection of dithioacetals, in which the formation of bromonium cation was proposed.[9] Kirihara et al. recently developed a similar deprotection method based on the iodonium ion, derived from a catalytic combination of $TaCl_5$/NaI or $NbCl_5$/NaI along with H_2O_2.[10] Herein, we describe a new entry for the deprotection of dithioacetals. The method features the use of a novel combination, such as 1,4-benzoquinone (BQ)/catalytic NaI under an air atmosphere, which successfully effects the deprotection process under mild, near-neutral conditions to afford a wide range of aryl and alkyl aldehydes and ketones generally in high yields. Indeed, BQ has never been employed as an oxidant for this kind of deprotection. The method developed provides a general, facile, thus highly applicable approach for dethioacetalization.[11]

2. Results and discussion

Using BQ as a stoichiometric oxidant, the deprotection of 1,3-dithiane **1a** in the presence of a variety of metal halides was first examined (Table 1). Pleasingly, most of the metal iodides employed exhibited a remarkable catalytic activity, providing aldehyde **2a** in high yields (entries 1, 3–6). For example, the combination of 1 mol % NaI and 1.2 equiv of BQ in the solvent system, such as H_2O/MeCN (1:10) provided the desired product **2a** in 90% isolated yield (entry 6). Interestingly, the corresponding bromide (NaBr) and chloride (NaCl) turned out much less efficient for the process (entries 7 and 8). Examination of the optimal solvent led to the finding that H_2O/MeCN provided the best result (entries 6 vs 9–13). Essentially, the reaction did not proceed at all in the absence of BQ (entry 14). In addition, only a moderate yield was obtained when

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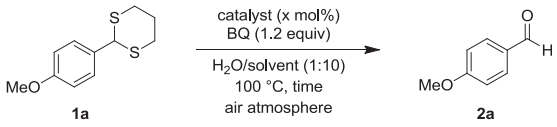
Table 1
Effect of reaction parameters[a]



Entry	Catalyst (*x* mol %)	Solvent	Time (h)	Yield[b] (%)
1	CuI (10)	MeCN	14	98
2	AgI (10)	MeCN	36	8
3	AuI (2)	MeCN	9	(95)[c]
4	LiI (1)	MeCN	38	quant.
5	KI (1)	MeCN	38	quant.
6	NaI (1)	MeCN	40	quant. (90)[c]
7	NaCl (1)	MeCN	48	3
8	NaBr (1)	MeCN	48	3
9	NaI (1)	Acetone	24	94
10	NaI (1)	THF	24	92
11	NaI (1)	AcOEt	24	81
12	NaI (1)	DMSO	24	68
13	NaI (1)	DMF	24	56
14[d]	NaI (1)	MeCN	24	0
15	None	MeCN	24	47
16[e]	NaI (1)	MeCN	40	quant.

[a] Reaction was run on a 0.5 mmol scale in H_2O/solvent (2.2 mL).
[b] Yield based on ^1H NMR spectroscopy using 1,1,2-trichloroethane as an internal standard.
[c] Isolated yield.
[d] In the absence of BQ.
[e] Under an Ar atmosphere.

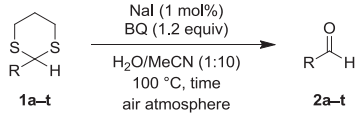
the deprotection was carried out in the absence of NaI (entry 15). These results clearly indicate that both BQ and NaI are crucial for the efficient deprotection. Moreover, it is interesting to note that the use of an Ar atmosphere instead of an air atmosphere resulted in the formation of **2a** in high yield, suggesting that the oxygen is not involved in the process (entry 16).

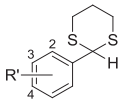
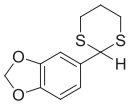
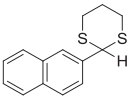
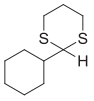
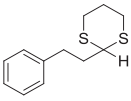
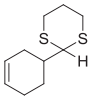
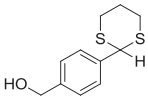
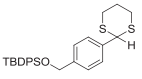
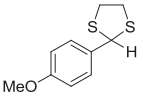
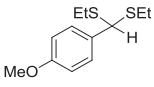
The newly developed deprotection method was further investigated in the reactions of a range of dithioacetals **1b**–**t** (Table 2). Substrates **1a**–**f** possessing an electron-donating (–OMe) or an electron-withdrawing group (–CN, $-NO_2$, $-CO_2Me$) at the *para*-, *meta*-, or *ortho*-position of the benzene ring were all suitable for the process, providing the corresponding aldehydes **2a**–**f** in high yields (entries 1–6). Halogen atoms, such as –Cl, –Br, and –I, as well as phenolic –OH on the benzene ring were well tolerated during the process (entries 7–10). Moreover, reactions of both condensed aromatic compound **1l** and heteroaromatic compound **1m** proceeded smoothly under the optimized conditions to give rise to aldehydes **2l** and **2m** in excellent yields (entries 12 and 13). In addition, the conversions of aliphatic aldehyde-derived dithianes **1n**–**p** were successfully carried out using our method (entries 14–16). It is worth noting that the alkene moiety of compound **1p** remained intact during the process (entry 16). The reactions of dithiane **1q**, possessing an alcoholic –OH, and its TBDPS-protected dithiane **1r** also successfully delivered the deprotected aldehydes (entries 17 and 18). Furthermore, dithiolane **1s** and acyclic dithioacetal **1t** were successfully deprotected under our catalytic conditions (entries 19 and 20).

Several kinds of ketone-derived dithioacetals **1u**–**z** were also treated with the above-mentioned BQ/cat. NaI system, all of which resulted in the successful deprotection to produce **2u**–**z** in good-to-high yields (Table 3).

Although the precise reaction mechanism remains to be elucidated, the process probably involves the catalytic cycle similar to that in the previous report by Kirihara et al., in which iodonium cation is formed in situ in the presence of NaI and the oxidant.[10] To determine the involvement of such an iodonium species, γ,δ-

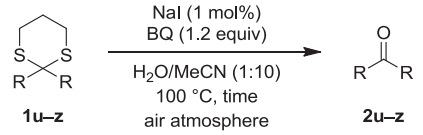
Table 2
Deprotection of dithianes derived from aldehydes[a]

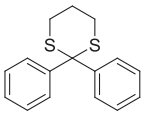
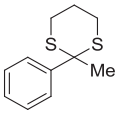
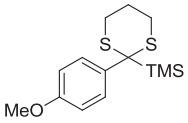
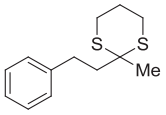
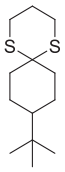


Entry	Substrate	1	Time (h)	Yield[b] (%)
1		**1a** (R′=4-OMe)	40	90
2		**1b** (R′=3-OMe)	24	91
3		**1c** (R′=2-OMe)	24	98
4		**1d** (R′=4-CN)	24	86[c]
5		**1e** (R′=4-NO_2)	36	76[c]
6		**1f** (R′=4-CO_2Me)	31	86[c]
7		**1g** (R′=4-Cl)	24	86
8		**1h** (R′=4-Br)	24	82
9		**1i** (R′=2-I)	48	72[c]
10		**1j** (R′=4-OH)	22	78
11		**1k**	24	91
12		**1l**	48	96[c]
13		**1m**	48	quant.[d]
14		**1n**	72	96[d]
15		**1o**	29	38
16		**1p**	72	74[d]
17		**1q**	48	73
18		**1r**	25	70
19		**1s**	24	79
20		**1t**	48	85

[a] Reaction was run on a 0.5 mmol scale in H_2O/MeCN (2.2 mL).
[b] Isolated yield.
[c] Yield based on ^1H NMR spectroscopy using 1,1,2-trichloroethane as an internal standard.
[d] Yield determined by GC analysis versus a calibrated internal standard.

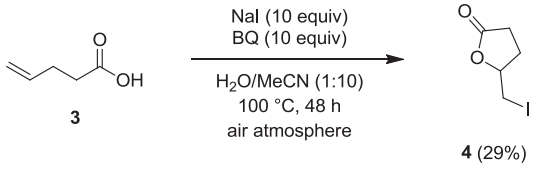
Table 3
Deprotection of dithianes derived from ketones[a]



Entry	Substrate	1	Time (h)	Yield[b] (%)
1		**1u**	35	quant.
2		**1v**	19	70
3		**1w**	19	79[c]
4		**1x**	12	71
5		**1y**	48	81[d]
6		**1z**	19	71

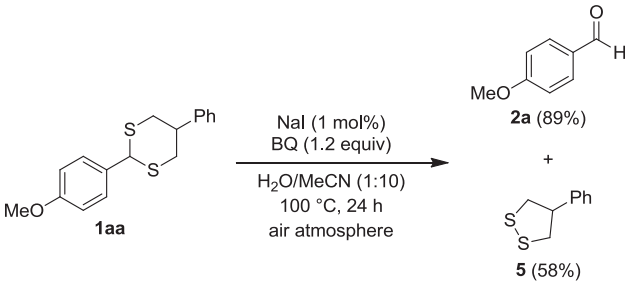
[a] Reaction was run on a 0.5 mmol scale in H_2O/MeCN (2.2 mL).
[b] Isolated yield.
[c] Yield based on ^{1}H NMR spectroscopy using 1,1,2-trichloroethane as an internal standard.
[d] Yield determined by GC analysis versus a calibrated internal standard.

alkenoic acid **3** was subjected to the reaction using 10 equiv NaI and 10 equiv BQ in H_2O/MeCN solvent (Scheme 1).



Scheme 1. Iodolactonization.

Although the yield was not high, the iodolactonization product **4** was indeed obtained, suggesting the possible formation of the iodonium cation during our deprotection process.[12] In addition, radical scavengers, such as BHT (di-*tert*-butylhydroxytoluene) and galvinoxyl were found to have no effect on the process, indicating that the reaction might be proceeding via an ionic pathway, rather than a radical pathway. Furthermore, from the reaction of **1aa** under the optimal conditions (Scheme 2), it was found that the dithiane moiety was transformed into the corresponding disulfide during the reaction (Scheme 2).



Scheme 2. Disulfide formation.

3. Conclusions

In summary, we have developed a novel, efficient method for the deprotection of dithioacetals using the combination consisting of BQ and a catalytic amount of NaI. Using our method, a wide range of aryl and alkyl aldehydes and ketones can be obtained generally in high yields under mild conditions. Good functional group compatibility is also observed in the process. Investigation to unveil the reaction mechanism as well as to broaden the substrate scope is currently underway. We are also applying this novel catalytic system to other oxidation processes.

4. Experimental section

4.1. General

Dithioacetals (**1a**–**z** except **1w**) were prepared according to the previously reported methods from the corresponding aldehydes or ketones.[13,14] Compound **1w** was also prepared according to the previously reported method.[15] All other chemicals employed in this work are commercially available and were used as received. Melting points were measured with a Yazawa micro melting point apparatus and uncorrected. IR spectra were recorded on a SHIMADZU IRAffinity. ^{1}H NMR spectra were recorded on a JEOL JNM-AL400 (400 MHz) spectrometer. Chemical shifts (δ) are given from TMS (0 ppm) and coupling constants are expressed in hertz (Hz). The following abbreviations are used: s=singlet, d=doublet, t=triplet, dd=double doublet, td=triple doublet, m=multiplet, and br s=broad singlet. ^{13}C NMR spectra were recorded on a JEOL JNM-AL400 (100 MHz) spectrometer and chemical shifts (δ) are given from $^{13}CDCl_3$ (77.0 ppm). Mass spectra and high resolution mass spectra were measured on a JEOL JMS-DX 303 and JMS-700/JMS-T 100 GC instruments, respectively. Elemental analyses were performed by Yanaco CHN CORDER MT-6.

4.2. Representative procedure for preparation of 1,3-dithianes

4.2.1. Method A.[13] $CuSO_4$ (3.5 g, 22.0 mmol) was added to a mixture of 4-methoxybenzaldehyde (2.7 g, 19.7 mmol) and 1,3-propandithiol (2.3 g, 21.0 mmol) in CH_2Cl_2 (100 mL) at room temperature and stirred at the same temperature until the starting aldehyde had been completely consumed (checked by TLC analysis). The reaction mixture was filtered through a pad of Celite and the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography (eluent: hexane/AcOEt=5:1) followed by recrystallization (AcOEt/hexane) to give

2-(4-methoxyphenyl)-1,3-dithiane **1a** (3.2 g, 71%) as colorless prisms.

4.2.2. Method B.[14] Under an Ar atmosphere, 1,3-propanedithiol (1.1 g, 10.5 mmol) was added to a mixture of methyl 4-formylbenzoate (1.6 g, 10.0 mmol) and Na_2SO_4 (1.0 g) in $CHCl_3$ (15 mL) at room temperature. After distilled $BF_3{\cdot}OEt_2$ (1.36 mL, 11.0 mmol) was added dropwise to the mixture at 0 °C, the whole reaction mixture was gradually warmed up to room temperature and then stirred overnight. After the addition of saturated aqueous $NaHCO_3$ (50 mL), the mixture was extracted with $CHCl_3$ (50 mL×2) and the organic layer was washed with $NaHCO_3$ (50 mL×1), H_2O (50 mL×1), and brine (50 mL×1). The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography (eluent: hexane/AcOEt=5:1) followed by recrystallization (AcOEt) to give methyl 4-(1,3-dithian-2-yl)benzoate **1f** (2.3 g, 91%) as colorless needles.

*4.2.3. 2-(4-Methoxyphenyl)-1,3-dithiane (**1a**).*[15] Prepared according to the Method A. Recrystallized from AcOEt/hexane, colorless prisms, mp 116–117 °C (lit.[15] mp 115–118 °C). IR (neat): 2901, 1607, 1559, 1507, 1247, 1179, 1109, 1030, 815, 775, 675 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.90–1.93 (m, 1H), 2.13–2.18 (m, 1H), 2.88–2.92 (m, 2H), 3.01–3.08 (m, 2H), 3.79 (s, 3H), 5.13 (s, 1H), 6.86 (d, J=8.8 Hz, 2H), 7.39 (d, J=8.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 25.0, 32.1, 50.7, 55.2, 114.0, 128.9, 131.2, 159.5. LRMS (EI) m/z: 226 (M^+). HRMS: calcd for $C_{11}H_{14}OS_2$: 226.0486, found: 226.0477.

*4.2.4. 2-(3-Methoxyphenyl)-1,3-dithiane (**1b**).*[15] Prepared according to the Method B. Recrystallized from AcOEt/hexane, colorless prisms, mp 61–63 °C (lit.[15] mp 62.5–62.9 °C). IR (neat): 2934, 2899, 1595, 1490, 1266, 1157, 1085, 1033, 861, 746 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.88–2.00 (m, 1H), 2.14–2.21 (m, 1H), 2.89–2.94 (m, 2H), 3.03–3.10 (m, 2H), 3.81 (s, 3H), 5.14 (s, 1H), 6.83–6.86 (m, 1H), 7.03–7.06 (m, 2H), 7.22–7.27 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 25.1, 32.1, 51.5, 55.2, 113.0, 114.4, 120.0, 129.7, 140.5, 159.8. LRMS (EI) m/z: 226 (M^+). HRMS: calcd for $C_{11}H_{14}OS_2$: 226.0486, found: 226.0485.

*4.2.5. 2-(2-Methoxyphenyl)-1,3-dithiane (**1c**).*[15] Prepared according to the Method B. Recrystallized from AcOEt/hexane, colorless plates, mp 127–129 °C (lit.[15] mp 128–129 °C). IR (neat): 2959, 2897, 2831, 1490, 1289, 1242, 1096, 1051, 1021, 756, 719, 674 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.88–1.98 (m, 1H), 2.12–2.19 (m, 1H), 2.86–2.91 (m, 2H), 3.07–3.14 (m, 2H), 3.86 (s, 3H), 5.71 (s, 1H), 6.86 (d, J=8.3 Hz, 1H), 6.96 (d, J=8.3 Hz, 1H), 7.25 (d, J=8.3 Hz, 1H), 7.58 (d, J=8.3 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 25.3, 32.4, 43.6, 55.7, 110.7, 121.0, 127.3, 129.1, 129.3, 155.4. LRMS (EI) m/z: 226 (M^+). HRMS: calcd for $C_{11}H_{14}OS_2$: 226.0486, found: 226.0491.

*4.2.6. 2-(4-Cyanophenyl)-1,3-dithiane (**1d**).*[11b] Prepared according to the Method B. Recrystallized from AcOEt/hexane, colorless needles, mp 115–116 °C. IR (neat): 2908, 2222, 1607, 1506, 1414, 1278, 1178, 883, 864, 767 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.89–2.04 (m, 1H), 2.16–2.23 (m, 1H), 2.90–2.96 (m, 2H), 3.03–3.10 (m, 2H), 5.18 (s, 1H), 7.59 (d, J=8.8 Hz, 2H), 7.63 (d, J=8.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 24.8, 31.7, 50.7, 112.2, 118.4, 128.7, 132.5, 144.2. LRMS (EI) m/z: 221 (M^+). HRMS: calcd for $C_{11}H_{11}NS_2$: 221.0333, found: 221.0321.

*4.2.7. 2-(4-Nitrophenyl)-1,3-dithiane (**1e**).*[16] Prepared according to the Method A. Recrystallized from AcOEt, yellowish prisms, mp 141–143 °C (lit.[16] mp 144–145 °C). IR (neat): 2908, 1603, 1513, 1409, 1342, 1272, 1111, 871, 729, 691 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.90–2.02 (m, 1H), 2.16–2.24 (m, 1H), 2.91–2.97 (m, 2H), 3.04–3.11 (m, 2H), 5.23 (s, 1H), 7.65 (d, J=8.8 Hz, 2H), 8.20 (d, J=8.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 24.7, 31.7, 50.3, 123.9, 128.9, 146.1, 147.6. LRMS (EI) m/z: 241 (M^+). HRMS: calcd for $C_{10}H_{11}NO_2S_2$: 241.0231, found: 241.0222.

*4.2.8. Methyl 4-(1,3-dithian-2-yl)benzoate (**1f**).*[17] Prepared according to the Method B. Recrystallized from AcOEt, colorless needles, mp 138–140 °C (lit.[17] mp 132–134 °C). IR (neat): 2948, 2901, 1715, 1559, 1271, 1176, 1111, 1018, 872, 736, 699 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.88–2.00 (m, 1H), 2.15–2.22 (m, 1H), 2.90–2.95 (m, 2H), 3.03–3.10 (m, 2H), 3.91 (s, 3H), 5.20 (s, 1H), 7.55 (d, J=8.6 Hz, 2H), 8.01 (d, J=8.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 25.0, 31.9, 51.0, 52.1, 127.9, 130.0, 130.1, 143.9, 166.5. LRMS (EI) m/z: 254 (M^+). HRMS: calcd for $C_{12}H_{14}O_2S_2$: 254.0435, found: 254.0438.

*4.2.9. 2-(4-Chlorophenyl)-1,3-dithiane (**1g**).*[15] Prepared according to the Method A. Recrystallized from AcOEt/hexane, colorless prisms, mp 88–90 °C (lit.[15] mp 82–83 °C). IR (neat): 2891, 1487, 1405, 1275, 1169, 1083, 851, 755, 671 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.86–1.96 (m, 1H), 2.12–2.19 (m, 1H), 2.87–2.92 (m, 2H), 3.00–3.07 (m, 2H), 5.12 (s, 1H), 7.30 (d, J=8.6 Hz, 2H), 7.40 (d, J=8.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 25.0, 32.0, 50.5, 128.8, 129.1, 134.0, 137.5. LRMS (EI) m/z: 230 (M^+). HRMS: calcd for $C_{10}H_{11}{}^{35}ClS_2$: 229.9991, found: 229.9987.

*4.2.10. 2-(4-Bromophenyl)-1,3-dithiane (**1h**).*[18] Prepared according to the Method B. Recrystallized from AcOEt/hexane, colorless needles, mp 93–94 °C (lit.[18] mp 82–83 °C). IR (neat): 2944, 2899, 1481, 1411, 1275, 1066, 1008, 854, 811, 753 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.87–1.97 (m, 1H), 2.13–2.19 (m, 1H), 2.87–2.93 (m, 2H), 3.00–3.08 (m, 2H), 5.11 (s, 1H), 7.35 (d, J=8.8 Hz, 2H), 7.46 (d, J=8.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 24.9, 31.9, 50.6, 122.3, 129.5, 131.8, 138.1. LRMS (EI) m/z: 274 (M^+). HRMS: calcd for $C_{10}H_{11}{}^{79}BrS_2$: 273.9486, found: 273.9469.

*4.2.11. 2-(2-Iodophenyl)-1,3-dithiane (**1i**).*[19] Prepared according to the Method B. Recrystallized from AcOEt/hexane, colorless prisms, mp 109–111 °C. IR (neat): 2897, 1560, 1462, 1420, 1272, 1175, 1160, 1011, 910, 742 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.88–2.00 (m, 1H), 2.15–2.22 (m, 1H), 2.90–2.96 (m, 2H), 3.09–3.16 (m, 2H), 5.42 (s, 1H), 6.97 (td, J_1=7.8 Hz, J_2=1.4 Hz, 1H), 7.35 (td, J_1=7.8 Hz, J_2=1.4 Hz, 1H), 7.65 (dd, J_1=7.8 Hz, J_2=1.4 Hz, 1H), 7.82 (dd, J_1=7.8 Hz, J_2=1.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 25.1, 32.3, 56.7, 99.4, 128.9, 129.1, 129.9, 139.6, 141.5. LRMS (EI) m/z: 322 (M^+). HRMS: calcd for $C_{10}H_{11}IS_2$: 321.9347, found: 321.9349.

*4.2.12. 2-(4-Hydroxyphenyl)-1,3-dithiane (**1j**).*[20] Prepared according to the Method B. Recrystallized from AcOEt/hexane, colorless prisms, mp 156–158 °C (lit.[20] mp 155–158 °C). IR (neat): 3368, 2887, 1511, 1442, 1241, 1103, 851, 815, 762, 674 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.85–1.97 (m, 1H), 2.13–2.20 (m, 1H), 2.87–2.92 (m, 2H), 3.01–3.09 (m, 2H), 4.81 (br s, 1H), 5.12 (s, 1H), 6.78 (d, J=8.8 Hz, 2H), 7.34 (d, J=8.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 25.1, 32.2, 50.7, 115.5, 129.2, 131.5, 155.5. LRMS (EI) m/z: 212 (M^+). HRMS: calcd for $C_{10}H_{12}OS_2$: 212.0330, found: 212.0328.

*4.2.13. 2-(3,4-Methylenedioxyphenyl)-1,3-dithiane (**1k**).*[21] Prepared according to the Method B. Recrystallized from AcOEt/hexane, colorless prisms, mp 87–89 °C (lit.[21] mp 84.5–85.5 °C). IR (neat): 2886, 1499, 1440, 1362, 1253, 1240, 1171, 1038, 933, 758 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.84–1.95 (m, 1H), 2.11–2.18 (m, 1H), 2.85–2.91 (m, 2H), 2.99–3.07 (m, 2H), 5.08 (s, 1H), 5.94 (s, 2H), 6.75 (d, J=7.8 Hz, 1H), 6.93 (dd, J_1=7.8 Hz, J_2=1.5 Hz, 1H), 6.98 (d, J=1.5 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 25.0, 32.1,

51.1, 101.1, 108.3 (2C), 121.2, 132.9, 147.5, 147.7. LRMS (EI) *m*/*z*: 240 (M^+). HRMS: calcd for $C_{11}H_{12}O_2S_2$: 240.0279, found: 240.0262.

*4.2.14. 2-(2-Naphthyl)-1,3-dithiane (**1l**).*[22] Prepared according to the Method B. Recrystallized from AcOEt/hexane, colorless needles, mp 113–115 °C (lit.[22] mp 112 °C). IR (neat): 2891, 1599, 1505, 1420, 1279, 1185, 896, 868, 816, 758 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.90–2.03 (m, 1H), 2.13–2.20 (m, 1H), 2.90–2.95 (m, 2H), 3.04–3.11 (m, 2H), 5.32 (s, 1H), 7.43–7.48 (m, 2H), 7.57 (dd, J_1=8.8 Hz, J_2=1.9 Hz, 1H), 7.79–7.83 (m, 3H), 7.95 (d, J=1.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 25.1, 32.1, 51.5, 125.6, 126.22, 126.25, 126.8, 127.6, 128.0, 128.4, 133.2, 133.3, 136.4. LRMS (EI) *m*/*z*: 246 (M^+). HRMS: calcd for $C_{14}H_{14}S_2$: 246.0537, found: 246.0529.

*4.2.15. 2-(2-Thienyl)-1,3-dithiane (**1m**).*[23] Prepared according to the Method A. Recrystallized from hexane, colorless prisms, mp 77–78 °C (lit.[23] mp 79–80 °C). IR (neat): 2902, 2362, 2342, 1419, 1257, 1181, 904, 850, 764 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.92–2.03 (1H, m), 2.12–2.20 (1H, m), 2.91–3.03 (4H, m), 5.41 (1H, s), 6.96 (1H, dd, J_1=5.4 Hz, J_2=3.4 Hz), 7.16 (1H, dd, J_1=3.4 Hz, J_2=1.0 Hz), 7.27 (1H, dd, J_1=5.4, J_2=1.0 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 25.0, 31.0, 44.7, 125.7, 126.2, 126.8, 142.6. LRMS (EI) *m*/*z*: 201 (M^+). HRMS: $C_8H_{10}S_3$: 201.9945, found: 201.9927.

*4.2.16. 2-Cyclohexyl-1,3-dithiane (**1n**).*[24] Prepared according to the Method A. Recrystallized from hexane, colorless plates, mp 52–54 °C (lit.[24] mp 49–50 °C). IR (neat): 3753, 2921, 2850, 2360, 1653, 1559, 1276, 1184, 908, 759 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.12–1.31 (m, 5H), 1.63–1.91 (m, 7H), 2.07–2.14 (m, 1H), 2.79–2.92 (m, 4H), 4.04 (d, J=5.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 26.2, 26.2, 26.4, 30.4, 30.9, 43.1, 55.3. LRMS (EI) *m*/*z*: 202 (M^+). HRMS: calcd for $C_{10}H_{18}S_2$: 202.0850, found: 202.0840.

*4.2.17. 2-(2-Phenylethyl)-1,3-dithiane (**1o**).*[22] Prepared according to the Method B. Obtained as colorless oil. IR (neat): 3025, 2898, 1602, 1496, 1422, 1274, 1029, 907, 784, 749 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.82–1.92 (m, 1H), 2.05–2.14 (m, 3H), 2.81–2.85 (m, 6H), 3.99 (t, J=7.1 Hz, 1H), 7.20–7.31 (m, 5H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 26.0, 30.2, 32.5, 36.9, 46.6, 126.1, 128.4, 128.5, 140.9. LRMS (EI) *m*/*z*: 224 (M^+). HRMS: calcd for $C_{12}H_{16}S_2$: 224.0693, found: 224.0684.

*4.2.18. 2-(3-Cyclohexenyl)-1,3-dithiane (**1p**).*[2a] Prepared according to the Method A. Obtained as colorless oil. IR (neat): 3020, 2894, 2834, 1653, 1421, 1275, 1180, 1043, 908, 763 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.49–1.58 (m, 1H), 1.84–1.92 (m, 1H), 1.96–2.25 (m, 7H), 2.84–2.93 (m, 4H), 4.10 (d, J=2.9 Hz, 1H), 5.66–5.69 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 25.3, 26.3, 26.4, 29.0, 30.6, 30.7, 38.9, 54.2, 125.8, 126.8. LRMS (EI) *m*/*z*: 200 (M^+). HRMS: calcd for $C_{10}H_{16}S_2$: 200.0693, found: 200.0690.

*4.2.19. 2-(4-Hydroxymethylphenyl)-1,3-dithiane (**1q**).* Prepared according to the Method A. Recrystallized from AcOEt/hexane, colorless prisms, mp 101–103 °C. IR (neat): 3392, 2893, 2360, 1209, 1112, 1003, 856, 751 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.74 (s, 1H), 1.87–1.99 (m, 1H), 2.14–2.21 (m, 1H), 2.88–2.93 (m, 2H), 3.02–3.10 (m, 2H), 4.67 (s, 2H), 5.16 (s, 1H), 7.33 (d, J=8.3 Hz, 2H), 7.46 (d, J=8.3 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 25.1, 32.1, 51.1, 64.9, 127.3, 127.7, 138.5, 141.1. LRMS (EI) *m*/*z*: 226 (M^+). HRMS: calcd for $C_{11}H_{14}OS_2$: 226.0486, found: 226.0492.

*4.2.20. 2-[4-(tert-Butyldiphenylsiloxy)methylphenyl]-1,3-dithiane (**1r**).* Prepared according to the Method A. Obtained as colorless powder, mp 122–123 °C. IR (neat): 2955, 2855, 2364, 1425, 1106, 1050, 872, 822, 758 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.09 (s, 9H), 1.87–1.99 (m, 1H), 2.13–2.20 (m, 1H), 2.88–2.93 (m, 2H), 3.03–3.10 (m, 2H), 4.75 (s, 2H), 5.17 (s, 1H), 7.30–7.44 (m, 10H), 7.66–7.69 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 19.3, 25.1, 26.8, 32.1, 51.3, 65.2, 126.3, 127.6, 127.7, 129.7, 133.4, 135.5, 137.7, 141.4. LRMS (EI) *m*/*z*: 464 (M^+). HRMS: calcd for $C_{27}H_{32}OS_2Si$: 464.1664, found: 464.1649.

*4.2.21. 2-(4-Methoxyphenyl)-1,3-dithiolane (**1s**).*[25] Prepared according to the method A. Recrystallized from AcOEt/hexane, colorless needles, mp 60–61 °C (lit.[25] mp 60.2–61 °C). IR (neat): 2919, 1606, 1585, 1509, 1251, 1228, 1175, 1030, 838, 754 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 3.30–3.38 (m, 2H), 3.46–3.54 (m, 2H), 3.79 (s, 3H), 5.64 (s, 1H), 6.84 (d, J=8.8 Hz, 2H), 7.45 (d, J=8.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 40.2, 55.3, 56.1, 113.9, 129.1, 131.8, 159.4. LRMS (EI) *m*/*z*: 212 (M^+). HRMS: calcd for $C_{10}H_{12}OS_2$: 212.0330, found: 212.0315.

*4.2.22. 1-[Bis(ethylthio)methyl]-4-methoxybenzene (**1t**).*[26] Prepared according to the method A. Recrystallized from AcOEt/hexane, colorless plates, mp 39–40 °C (lit.[26] mp 40–41 °C). IR (neat): 2967, 1610, 1509, 1302, 1257, 1174, 1107, 1025, 841, 770 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.22 (t, J=7.3 Hz, 6H), 2.47–2.64 (m, 4H), 3.80 (s, 3H), 4.91 (s, 1H), 6.86 (d, J=8.3 Hz, 2H), 7.37 (d, J=8.3 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 14.3, 26.2, 51.8, 55.2, 113.8, 128.8, 132.5, 159.1. LRMS (FAB) *m*/*z*: 241 (M^+–1). HRMS: calcd for $C_{12}H_{17}OS_2$: 241.0721. Found: 241.0707.

*4.2.23. 2,2-Diphenyl-1,3-dithiane (**1u**).*[22] Prepared according to the Method B. Recrystallized from AcOEt, colorless prisms, mp 111–112 °C (lit.[22] mp 108 °C). IR (neat): 3062, 2892, 1480, 1444, 1282, 1035, 930, 890, 864, 737 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.97–2.03 (m, 2H), 2.77–2.80 (m, 4H), 7.24–7.28 (m, 2H), 7.31–7.36 (m, 4H), 7.69–7.71 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 24.5, 29.4, 62.7, 127.5, 128.4, 129.3, 142.5. LRMS (EI) *m*/*z*: 272 (M^+). HRMS: calcd for $C_{16}H_{16}S_2$: 272.0693, found: 272.0683.

*4.2.24. 2-Methyl-2-phenyl-1,3-dithiane (**1v**).*[27] Prepared according to the Method B. Obtained as colorless oil. IR (neat): 2903, 1594, 1487, 1441, 1275, 1177, 1071, 1026, 906, 762, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.80 (s, 3H), 1.93–1.98 (m, 2H), 2.71–2.75 (m, 4H), 7.24–7.28 (m, 1H), 7.36–7.40 (m, 2H), 7.93–7.96 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 24.6, 28.1, 32.8, 53.9, 127.0, 127.7, 128.5, 143.8. LRMS (EI) *m*/*z*: 210 (M^+). HRMS: calcd for $C_{11}H_{14}S_2$: 210.0537, found: 210.0535.

*4.2.25. 2-(4-Methoxyphenyl)-2-trimethylsilyl-1,3-dithane (**1w**).*[15] Under an Ar atmosphere, BuLi (3.3 mL, 3.3 mmol, 1.0 M in hexane) was added to a solution of 2-(4-methoxyphenyl)-1,3-dithiane (**1a**) (0.68 g, 3.0 mmol) in THF (7.5 mL) at −20 °C and the mixture was stirred for 1 h. Trimethylsilyl chloride (0.32 mL, 3.7 mmol) was slowly added and the whole mixture was gradually warmed up to 0 °C, then stirred for 1 h. H_2O (10 mL) was added and the mixture was extracted with $CHCl_3$ (30 mL×3). The organic layer was washed with brine (30 mL×1), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (eluent: hexane) followed by recrystallization (hexane) to give 2-(4-methoxyphenyl)-2-trimethylsilyl-1,3-dithiane (**1w**) (0.34 g, 38%) as a colorless solid. Recrystallized from hexane, colorless prisms, mp 85–89 °C (lit.[15] mp 79.8–81 °C). IR (neat): 2902, 1605, 1499, 1289, 1241, 1177, 1037, 916, 889, 843 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.06 (s, 9H), 1.86–1.92 (m, 1H), 1.97–2.04 (m, 1H), 2.39–2.44 (m, 2H), 2.75–2.82 (m, 2H), 3.83 (s, 3H), 6.90 (d, J=9.2 Hz, 2H), 7.79 (d, J=9.2 Hz, 2H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): −3.9, 24.9, 25.2, 46.9, 55.2, 113.6, 130.8, 132.1, 157.3. LRMS (EI) *m*/*z*: 298 (M^+). HRMS: calcd for $C_{14}H_{22}OS_2Si$ 298.0881, found: 298.0867.

*4.2.26. 2-Methyl-2-(2-phenylethyl)-1,3-dithiane (**1x**).*[28] Prepared according to the Method B. Obtained as yellowish oil. IR (neat): 3025, 2905, 1602, 1497, 1422, 1370, 1275, 1057, 907, 748 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.68 (s, 3H), 1.93–2.03 (m, 2H), 2.21–2.25 (m, 2H), 2.78–2.94 (m, 6H), 7.18–7.23 (m, 3H), 7.28–7.32 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 25.2, 26.5, 27.8, 31.2, 43.4, 48.9, 125.9, 128.5 (2C), 141.8. LRMS (EI) *m*/*z*: 238 (M^+). HRMS: calcd for $C_{13}H_{18}S_2$: 238.0850, found: 238.0833.

*4.2.27. 1,5-Dithiaspiro[5.5]undecane (**1y**).* Prepared according to the Method A. Recrystallized from hexane, colorless plates, mp 39–41 °C. IR (neat): 3753, 2972, 2850, 2360, 1653, 1559, 1419, 1269, 1130, 1010, 758 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.43–1.49 (m, 2H), 1.60–1.66 (m, 4H), 1.96–2.01 (m, 6H), 2.78–2.82 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 22.0, 25.8, 25.9, 26.1, 37.9, 50.3. LRMS (EI) *m*/*z*: 188 (M^+). HRMS: calcd for $C_9H_{16}S_2$: 188.0693, found: 188.0685.

*4.2.28. 9-tert-Butyl-1,5-dithiaspiro[5.5]undecane (**1z**).* Prepared according to the Method B. Recrystallized from hexane, colorless prisms, mp 71–72 °C. IR (neat): 2940, 2843, 1444, 1361, 1280, 1242, 1023, 1005, 910, 787 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.86 (s, 9H), 0.99–1.06 (m, 1H), 1.43–1.68 (m, 6H), 1.95–2.01 (m, 2H), 2.36–2.41 (m, 2H), 2.72–2.75 (m, 2H), 2.87–2.89 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 22.9, 25.7, 26.2, 26.3, 27.5, 32.4, 38.4, 48.0, 50.2. LRMS (EI) *m*/*z*: 244 (M^+). HRMS: calcd for $C_{13}H_{24}S_2$: 244.1319, found: 244.1304.

*4.2.29. 2-(4-Methoxyphenyl)-5-phenyl-1,3-dithiane (**1aa**).* Under an Ar atmosphere, diethyl phenylmalonate (4.5 g, 19.0 mmol) was added dropwise to a solution of $LiAlH_4$ (1.9 g, 50.0 mmol) in THF (90 mL) at 0 °C. The reaction mixture was warmed up to room temperature and stirred overnight. After the addition of Na_2SO_4, the mixture was extracted with AcOEt (30 mL×3) and the combined organic layer was washed with H_2O (50 mL×2) and brine (50 mL×1). The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography (eluent: hexane/AcOEt=1:3) to give 2-phenyl-1,3-propanediol (0.85 g, 28%) as colorless oil. Under an Ar atmosphere, a solution of *p*-toluenesulfonyl chloride (6.0 g, 31.5 mmol) in MeCN (16 mL) was added dropwise to a solution of 2-phenyl-1,3-propanediol (1.6 g, 10.5 mmol), $Me_3N{\cdot}HCl$ (0.20 g, 2.1 mmol), and Et_3N (3.2 g, 31.5 mmol) in MeCN (7 mL) at 0 °C and stirred for 5 h at the same temperature. After the addition of *N*,*N*′-dimethylethylenediamine (2 mL), the mixture was extracted with AcOEt (30 mL×3) and the combined organic layer was washed with H_2O (50 mL×2) and brine (50 mL×1). The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography (eluent: hexane/AcOEt=3:1) to give 2-phenyl-1,3-propaneditosylate (0.88 g, 18%) as a colorless solid. Under an Ar atmosphere, thiourea (1.4 g, 19.0 mmol) was added to a solution of 2-phenyl-1,3-propaneditosylate (0.88 g, 1.9 mmol) in EtOH (10 mL) at room temperature, and the mixture was heated under reflux overnight. After the reaction mixture was cooled down to room temperature, 20% NaOH (10 mL) was added and the whole mixture was heated under reflux overnight. After the addition of 1 M HCl (30 mL), the mixture was extracted with CH_2Cl_2 (50 mL×3) and the combined organic layer was washed with H_2O (50 mL×1) and brine (50 mL×1). The organic layer was dried over $MgSO_4$ and concentrated in vacuo to give 2-phenyl-1,3-propanedithiol (0.48 g) as yellowish oil, which was used to the next reaction without further purification. According to the Method A, **1aa** was prepared from the above-obtained 2-phenyl-1,3-propanedithiol and *p*-anisaldehyde (0.27 g, 75% over two steps). Recrystallized from AcOEt, colorless needles, mp 165–167 °C. IR (neat): 2892, 1605, 1509, 1248, 1170, 1022, 851, 818, 767, 725 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 2.92–2.96 (m, 2H), 3.16–3.30 (m, 3H), 3.80 (s, 3H), 5.22 (s, 1H), 6.88 (d, *J*=8.8 Hz, 2H), 7.22–7.27 (m, 3H), 7.32–7.36 (m, 2H), 7.44 (d, *J*=8.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 38.3, 42.8, 50.4, 44.3, 114.2, 126.7, 127.1, 128.87, 128.92, 130.3, 144.9, 159.7. LRMS (EI) *m*/*z*: 302 (M^+). HRMS: calcd for $C_{17}H_{18}OS_2$: 302.0799, found: 302.0780.

4.3. Deprotection of 1,3-dithianes

4.3.1. Representative procedure for deprotection of 1,3-dithianes (Table 2, entry 3). A mixture of 2-(2-methoxyphenyl)-1,3-dithiane (**1c**) (0.11 g, 0.50 mmol), 1,4-benzoquinone (64.8 mg, 0.60 mmol), and NaI (0.70 mg, 0.005 mmol) in MeCN (2 mL) and H_2O (0.2 mL) was stirred at 100 °C for 24 h. The reaction mixture was filtered through a pad of Celite and the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography (eluent: hexane/AcOEt=15/1) to give 2-methoxybenzaldehyde (**2c**, 66.5 mg, 98%) as colorless oil.

*4.3.2. 4-Methoxybenzaldehyde (**2a**).* Obtained as colorless oil. IR (neat): 2840, 2739, 1679, 1595, 1425, 1314, 1255, 1156, 1021, 829, 758 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 3.90 (s, 3H), 7.01 (d, *J*=8.8 Hz, 2H), 7.85 (d, *J*=8.8 Hz, 2H), 9.89 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 55.5, 114.3, 130.0, 131.9, 164.6, 190.8. LRMS (EI) *m*/*z*: 136 (M^+). HRMS: calcd for C_8H_8O: 136.0524, found: 136.0545.

*4.3.3. 3-Methoxybenzaldehyde (**2b**).* Obtained as colorless oil. IR (neat): 2839, 2729, 1699, 1586, 1485, 1261, 1148, 1037, 785, 737 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 3.87 (s, 3H), 7.17–7.21 (m, 1H), 7.39–7.40 (m, 1H), 7.45–7.47 (m, 2H), 9.98 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 55.4, 112.0, 121.5, 123.5, 130.0, 137.8, 160.1, 192.1. LRMS (EI) *m*/*z*: 136 (M^+). HRMS: calcd for $C_8H_8O_2$: 136.0524, found: 136.0505.

*4.3.4. 2-Methoxybenzaldehyde (**2c**).* Obtained as colorless oil. IR (neat): 2843, 1683, 1597, 1484, 1394, 1285, 1242, 1160, 1021, 834, 733 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 3.93 (s, 3H), 6.98–7.05 (m, 2H), 7.55 (t, *J*=7.8 Hz, 1H), 7.83 (d, *J*=7.8 Hz, 1H), 10.48 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 55.6, 111.6, 120.6, 124.8, 128.5, 135.9, 161.8, 189.8. LRMS (EI) *m*/*z*: 136 (M^+). HRMS: calcd for $C_8H_8O_2$: 136.0524, found: 136.0511.

*4.3.5. 4-Cyanobenzaldehyde (**2d**).* Recrystallized from AcOEt/hexane, colorless needles, mp 97–99 °C. IR (neat): 2846, 2229, 1701, 1607, 1387, 1296, 1202, 1172, 826, 737 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 7.86 (d, *J*=8.3 Hz, 2H), 8.01 (d, *J*=8.3 Hz, 2H), 10.11 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 117.5, 117.6, 129.8, 132.8, 138.7, 190.6. LRMS (EI) *m*/*z*: 131 (M^+). HRMS: calcd for C_8H_5NO: 131.0371, found: 131.0555.

*4.3.6. 4-Nitrobenzaldehyde (**2e**).* Recrystallized from AcOEt/hexane, yellowish prisms, mp 107–109 °C. IR (neat): 2851, 1701, 1540, 1340, 1195, 1103, 1007, 849, 813, 738, 677 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 8.11 (d, *J*=8.8 Hz, 2H), 8.41 (d, *J*=8.8 Hz, 2H), 10.19 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 124.1, 130.3, 139.9, 150.9, 190.2. LRMS (EI) *m*/*z*: 151 (M^+). HRMS: calcd for $C_7H_5NO_3$: 151.0269, found: 151.0279.

*4.3.7. 4-(Methoxycarbonyl)benzaldehyde (**2f**).* Recrystallized from AcOEt, colorless prisms, mp 60–62 °C. IR (neat): 1720, 1683, 1576, 1432, 1278, 1194, 1105, 851, 807, 755, 681 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 3.96 (s, 3H), 7.95 (d, *J*=8.3 Hz, 2H), 8.17 (d,

J=8.3 Hz, 2H), 10.10 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 52.3, 129.2, 129.9, 134.8, 138.9, 165.7, 191.4. LRMS (EI) m/z: 164 (M^+). HRMS: calcd for $C_9H_8O_3$: 164.0473, found: 164.0496.

*4.3.8. 4-Chlorobenzaldehyde (**2g**).* Recrystallized from AcOEt, colorless needles, mp 47–48 °C. IR (neat): 1684, 1590, 1424, 1282, 1253, 1169, 1090, 1015, 818, 739, 681 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 7.50 (d, J=7.8 Hz, 2H), 7.82 (d, J=7.8 Hz, 2H), 9.98 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 129.2, 130.7, 134.6, 140.7, 190.6. LRMS (EI) m/z: 140 (M^+). HRMS: calcd for $C_7H_5{}^{35}ClO$: 140.0029, found: 140.0019.

*4.3.9. 4-Bromobenzaldehyde (**2h**).* Recrystallized from AcOEt/hexane, colorless prisms, mp 58–59 °C. IR (neat): 2860, 1686, 1587, 1573, 1480, 1384, 1205, 1066, 1009, 809 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 7.68 (d, J=8.8 Hz, 2H), 7.75 (d, J=8.8 Hz, 2H), 9.97 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 129.7, 130.9, 132.4, 135.1, 191.0. LRMS (EI) m/z: 184 (M^+). HRMS: calcd for $C_7H_5{}^{79}BrO$: 183.9524, found: 183.9529.

*4.3.10. 2-Iodobenzaldehyde (**2i**).* Recrystallized from AcOEt/hexane, colorless needles, mp 37–38 °C. IR (neat): 2938, 2924, 1490, 1453, 1221, 1207, 1027, 970, 770, 712 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 7.29 (td, J_1=7.8 Hz, J_2=1.5 Hz, 1H), 7.47 (t, J=7.8 Hz, 1H), 7.88 (dd, J_1=7.8 Hz, J_2=1.5 Hz, 1H), 7.96 (d, J=7.8 Hz, 1H), 10.07 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 100.6, 128.7, 130.2, 135.1, 135.4, 140.6, 195.7. LRMS (EI) m/z: 232 (M^+). HRMS: calcd for C_7H_5IO: 231.9385, found: 231.9369.

*4.3.11. 4-Hydroxybenzaldehyde (**2j**).* Recrystallized from AcOEt, brownish plates, mp 113–119 °C. IR (neat): 3159, 1669, 1559, 1457, 1288, 1217, 1161, 1113, 832, 699 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 6.02 (s, 1H), 6.97 (d, J=8.6 Hz, 2H), 7.82 (d, J=8.6 Hz, 2H), 9.86 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 116.0, 130.0, 132.5, 161.4, 191.1. LRMS (EI) m/z: 122 (M^+). HRMS: calcd for $C_7H_6O_2$: 122.0368, found: 122.0362.

*4.3.12. Piperonal (**2k**).* Obtained as colorless oil. IR (neat): 2919, 1794, 1671, 1600, 1446, 1253, 1034, 929, 811, 784 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 6.08 (s, 2H), 6.94 (d, J=7.8 Hz, 1H), 7.34 (d, J=1.5 Hz, 1H), 7.42 (dd, J_1=7.8 Hz, J_2=1.5 Hz, 1H), 9.81 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 102.1, 106.9, 108.3, 128.7, 131.8, 148.7, 153.1, 190.3. LRMS (EI) m/z: 150 (M^+). HRMS: calcd for $C_8H_6O_3$: 150.0317, found: 150.0301.

*4.3.13. 2-Naphthaldehyde (**2l**).* Recrystallized from hexane, colorless prisms, mp 63–64 °C. IR (neat): 3062, 2831, 1689, 1460, 1344, 1257, 1165, 1118, 835, 749 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 7.56–7.66 (m, 2H), 7.88–8.00 (m, 4H), 8.32 (s, 1H), 10.15 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 122.7, 127.0, 128.0, 129.0, 129.1, 129.5, 132.6, 134.1, 134.5, 136.4, 192.2. LRMS (EI) m/z: 156 (M^+). HRMS: calcd for $C_{11}H_8O$: 156.0575, found: 156.0552.

*4.3.14. 2-Thiophenecarboxaldehyde (**2m**).* Obtained as yellow oil. IR (neat): 3090, 2821, 2361, 1654, 1513, 1417, 1212, 1045, 863, 723 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 7.22 (dd, J_1=4.8 Hz, J_2=3.2 Hz 1H), 7.77–7.80 (m, 2H), 9.96 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 128.3, 135.1, 136.2, 144.0, 182.9. LRMS (EI) m/z: 111 (M^+). HRMS: calcd for C_5H_4OS: 111.9983, found: 111.9934.

*4.3.15. Cyclohexanecarboxaldehyde (**2n**).* Because of the volatility of the product, the yield was determined by GC analysis versus a calibrated internal standard.

*4.3.16. 3-Phenylpropanal (**2o**).* Obtained as colorless oil. IR (neat): 3028, 2726, 1723, 1603, 1497, 1453, 1389, 1030, 854, 744 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 2.77 (td, J_1=7.8 Hz, J_2=1.0 Hz, 2H), 2.95 (t, J=7.8 Hz, 2H), 7.18–7.22 (m, 3H), 7.27–7.31 (m, 2H), 9.81 (t, J=1.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 28.1, 45.2, 126.3, 128.2, 128.6, 140.3, 201.5. LRMS (EI) m/z: 134 (M^+). HRMS: calcd for $C_9H_{10}O$: 134.0732, found: 134.0725.

*4.3.17. 3-Cyclohexene-1-carboxaldehyde (**2p**).* Because of the volatility of the product, the yield was determined by GC analysis versus a calibrated internal standard.

*4.3.18. 4-Hydroxymethybenzaldehyde (**2q**).* Recrystallized from AcOEt/hexane, colorless prisms, mp 39–40 °C. IR (neat): 3356, 2841, 2375, 1689, 1608, 1205, 1012, 825, 769 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 2.47 (s, 1H), 4.79 (s, 2H), 7.52 (d, J=8.1 Hz, 2H), 7.85 (d, J=8.1 Hz, 2H), 9.97 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 64.4, 126.9, 130.0, 135.6, 147.9, 192.1. LRMS (EI) m/z: 136 (M^+). HRMS: calcd for $C_8H_8O_2$: 136.0524, found: 136.0508.

*4.3.19. 4-(tert-Butyldiphenylsiloxy)methylbenzaldehyde (**2r**).* Obtained as colorless oil. IR (neat): 2963, 2857, 2362, 1696, 1610, 1426, 1214, 1105, 1078, 812, 739 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.03 (s, 9H), 4.74 (s, 2H), 7.26–7.36 (m, 6H), 7.41 (d, J=8.3 Hz, 2H), 7.58–7.61 (m, 4H), 7.75 (d, J=8.3 Hz, 2H), 9.90 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 19.3, 26.8, 65.1, 126.2, 127.8, 129.79, 127.84, 133.1, 135.3, 135.46, 135.45, 191.9. LRMS (EI) m/z: 374 (M^+). HRMS: calcd for $C_{24}H_{26}O_2Si$: 374.1702, found: 374.1675.

*4.3.20. Benzophenone (**2u**).* Recrystallized from hexane, colorless prisms, mp 47–49 °C. IR (neat): 3059, 1656, 1598, 1447, 1275, 1176, 941, 918, 810, 763 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 7.45 (t, J=7.6 Hz, 4H), 7.56 (t, J=7.6 Hz, 2H), 7.79 (d, J=7.6 Hz, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 128.2, 129.9, 132.3, 137.5, 196.5. LRMS (EI) m/z: 182 (M^+). HRMS: calcd for $C_{13}H_{10}O$: 182.0732, found: 182.0718.

*4.3.21. Acetophenone (**2v**).* Obtained as colorless oil. IR (neat): 3062, 1680, 1598, 1449, 1357, 1263, 1180, 1024, 954, 757, 687 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 2.61 (s, 3H), 7.44–7.48 (m, 2H), 7.54–7.58 (m, 1H), 7.94–7.97 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 26.6, 128.3, 128.5, 133.1, 137.1, 198.1. LRMS (EI) m/z: 120 (M^+). HRMS: calcd for C_8H_8O: 120.0575, found: 120.0559.

*4.3.22. (4-Methoxybenzoyl)trimethylsilane (**2w**).* Obtained as yellowish oil. IR (neat): 2960, 1584, 1564, 1506, 1305, 1250, 1218, 1161, 1029, 834 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.36 (s, 9H), 3.87 (s, 3H), 6.96 (d, J=8.3 Hz, 2H), 7.84 (d, J=8.3 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): −1.27, 55.4, 113.7, 129.8, 135.2, 163.1, 232.9. LRMS (EI) m/z: 208 (M^+). HRMS: calcd for $C_{11}H_{16}O_2Si$: 208.0920, found: 208.0877.

*4.3.23. Benzylacetone (**2x**).* Obtained as colorless oil. IR (neat): 3027, 1715, 1602, 1497, 1453, 1356, 1161, 1080, 1031, 748 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 2.13 (s, 3H), 2.75 (t, J=7.8 Hz, 2H), 2.89 (t, J=7.8 Hz, 2H), 7.16–7.20 (m, 3H), 7.25–7.29 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 29.7, 30.0, 45.1, 126.0, 128.2, 128.4, 140.9, 207.8. LRMS (EI) m/z: 148 (M^+). HRMS: calcd for $C_{10}H_{12}O$: 148.0888, found: 148.0885.

*4.3.24. Cyclohexanone (**2y**).* Because of the volatility of the product, the yield was determined by GC analysis versus a calibrated internal standard.

*4.3.25. 4-tert-Butylcyclohexanone (**2z**).* Recrystallized from hexane, colorless prisms, mp 46–48 °C. IR (neat): 2946, 2866, 1723, 1366, 1333, 1223, 1161, 984, 942, 777 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.88 (s, 9H), 1.35–1.46 (m, 3H), 2.03–2.06 (m, 2H),

2.23–2.38 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 27.5, 32.4, 41.2, 46.7, 212.4. LRMS (EI) m/z: 154 (M^+). HRMS: calcd for $C_{10}H_{18}O$: 154.1358, found: 154.1358.

*4.3.26. 4-Phenyl-1,2-dithiolane (**5**).*[29] Recrystallized from hexane, yellowish plates, mp 84–85 °C (lit.[28] mp 82–84 °C). IR (neat): 2850, 1747, 1684, 1579, 1390, 1263, 1202, 1017, 822, 750 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 3.20–3.25 (m, 2H), 3.50–3.54 (m, 2H), 3.63–3.71 (m, 1H), 7.24–7.36 (m, 5H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 45.9, 53.1, 127.28, 127.29, 128.8, 141.5. LRMS (EI) m/z: 182 (M^+). HRMS: calcd for $C_9H_{10}S_2$: 182.0224, found: 182.0240.

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Supplementary data

^1H NMR and ^{13}C NMR spectra for compounds **1** and **2** are available. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.08.061.

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