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An unprecedented deoxygenation protocol of benzylic alcohols using *bis*(1-benzotriazolyl) methanethione

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A facile and regioselective two-step deoxygenation protocol of benzylic alcohols using *bis*(benzotriazole)methanethione has been devised. The benzotriazole derivative benzyloxythioacylbenzotriazoles (ROCSBt) on reaction with silanes or Bu_3SnH under microwave or conventional heating undergo free radical *β*-scission of *C-O* bond instead of *N-N* bond (benzotriazole ring cleavage) to afford deoxy product. The methodology have a wide scope as it deoxygenate selectively the benzylic alcohols with an aid of relatively nontoxic $(TMS)_3SiH$ reagent as an acceptable alternate to Bu_3SnH.

Introduction

The advantages associated with utilizing benzotriazole methodology for common organic transformations lies in enabling it rather efficient, fast, and inexpensive.[1] Deoxygenation plays important role in numerous synthetic transformations. Some common methods include well known Barton–McCombie deoxygenation,[2] Markó–Lam deoxygenation,[3] the Wolff–Kishner reductions,[4] opening of epoxide ring, *via* addition to unsaturated compounds[5] or by hydride reduction of corresponding mesylates or tosylates.[6] The replacement of an allylic or benzylic hydroxyl group through hydride displacement is sometimes complicated by difficulties in activation of hydroxyl function into a suitable leaving group. The most commonly used activated derivatives *viz* chlorides, bromides and arylsulfonates, may be so reactive as to be hard to obtain the product in satisfactory purity and cannot be stored long. Corey *et al* used pyridine-sulfurtrioxide complex with $LiAlH_4$ in THF for the hydroxyl activation;[7] however, the harsh reduction condition limits its scope towards the wide range of substrate. A report by Kim *et al* on selective deoxygenation of alkoxyalkyl ether (EE or MOM) of allylic alcohols by Pd(dppe) Cl_2-catalyzed reduction with $LiBHEt_3$ is well documented.[8] However, the involvement of three-step reaction sequences with moderate yield, use of expensive and carcinogenic Pd-catalyst limits the wide applicability of this method.

In classical Barton–McCombie deoxygenation, thiocarbonyl moiety is commonly present that can be readily desulfurized in fairly mild reaction condition. Deoxygenation via *bis*(benzotriazole)methanethione **2** has several important features: firstly their preparation from the readily available benzotriazole is an easy process, long term stability of benzotriazole derived thiocarbamate intermediate and moreover, these compounds should incorporate a relatively more weaker benzylic *C-O* bond rather than benzotriazolyl *N-N* bond beta (*β*) to the thiocarbonyl moiety, which would likely to be cleaved similar to Barton–McCombie deoxyzation (Figure 1). Additionally, the mentioned radical deoxygenation is rather efficient under microwave conditions.

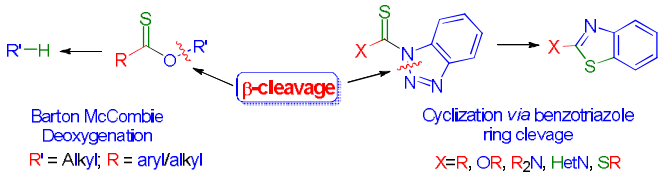

Figure 1. Barton–McCombie deoxygenation and cyclization *via* benzotriazole ring cleavage

In growing continuum to our ongoing work on benzotriazole methodology[9] recently, we have reported the synthesis of 2-*N*/*S*/*C*/*O*-substituted benzothiazoles *via* the cyclative-cleavage of benzotriazole ring using silanes or stannane reagents.[9j-k] However, the phenomenon seems to be unusual in case of benzylic alcohols, which under similar reaction condition undergo deoxygenation unparalleled, instead of cyclization, that we wish to report herein.

Results and discussion

Our investigation begins with the thioacylation of benzylic alcohols using the benzotriazole based reagent **2** to afford corresponding benzyloxythioacylbenzotriazoles (ROCSBt),[9,10] which on further treatment with silanes or stannane under conventional heating or microwave (*MW*) condition gives deoxy product with moderate to good yield (Scheme 1c). The case was different with aliphatic alcohols, which under similar reaction condition undergoes cyclization to afford good

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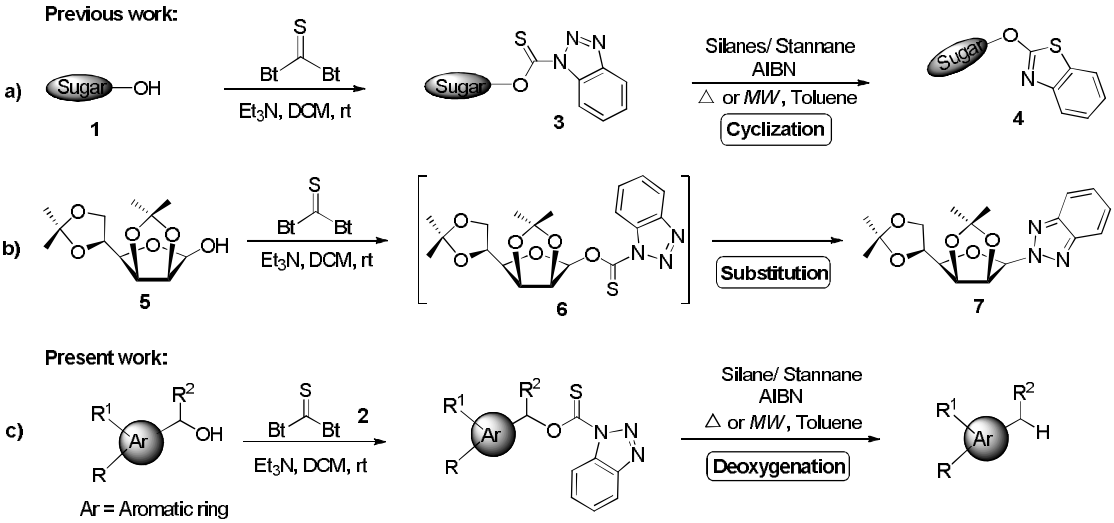
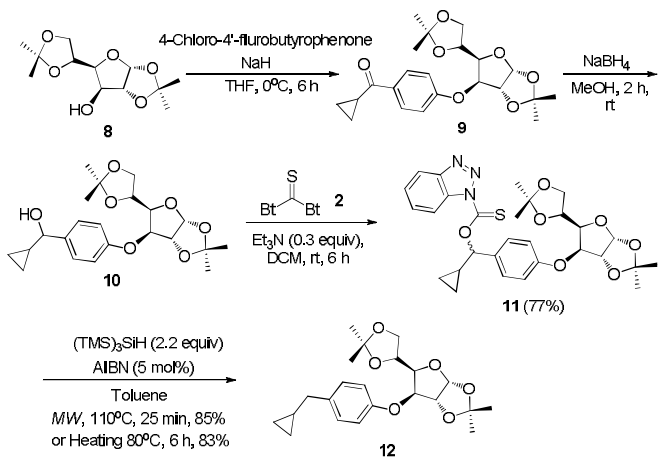


Scheme 1. Comparative illustration of previous and present work

to excellent yield of 2-(alkoxy)benzothiazoles *via* free radical intramolecular cyclative-cleavage of *N-N* bond of benzotriazole ring (Scheme 1a).[9] However, 2,3:5,6-di-*O*-isopropylidene mannose on reaction with **2** in presence of Et_3N and pyridine in anhydrous CH_2Cl_2 afford 2-*N*-benzotriazole-2′,3′:5′,6′-di-*O*-isopropylidene-*β*-D-mannofuranoside (Scheme 1b).[11] That is, the three alcohols *viz* benzylic, aliphatic and anomeric gives different results under similar condition.

The deoxy product **12**, a carbohydrate derivative has been synthesized from benzylic alcohol **10**[12] by means of the radical deoxygenation of intermediate **11**. The treatment of compound **10** with *bis*(benzotriazole)methanethione **2** in presence of Et_3N (0.3 equiv) in anhydrous CH_2Cl_2 at room temperature furnished compound **11**, which was further treated with the reagent capable of free radical induction in dry toluene afford compound **12** in good yield (Scheme 2).



Scheme 2. Synthesis of compound **12** using compound **2**

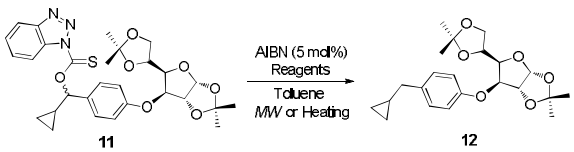
The compound **11** characterized by its characteristic NMR signals. The peak corresponds to benzotriazolyl protons in ^{1}H NMR appears in aromatic region; also, a characteristic peak of thiocarbonyl carbon appears at δ 167.7 ppm in ^{13}C NMR spectrum of **11** (see supporting). The compound **12** characterized by the disappearance of signals corresponds to benzotriazolyl proton in its ^{1}H NMR spectra; also, the disappearance of characteristic peak of thiocarbonyl carbon and appearance of methylene carbon signal at δ 47.2 ppm in ^{13}C NMR suggests its formation (see Supporting file). In addition, the mass spectrum of compound **12** exhibited $[M+H]^+$ peak at *m/z* 391, which was 177 units less than the molecular ion peak $[M+H]^+$ of compound **11** observed at *m/z* 568. Together with NMR, mass and elemental data suggest deoxygenation would be happen here, not the well-known cyclization.

For the aforementioned deoxygenation, we briefly investigated the effect of diverse range of silanes in terms of yield and reaction time, the results obtained has been summarized in Table 1. The obtained results clearly demonstrate that the reagent feasibility depends solely on the Si-H, and Sn-H bond strength among silanes and stannane. The deoxygenation carried out in presence of triethylsilane (Et_3SiH), *tris*(iso-propyl)silane (Pr^i_3SiH) and diphenylsilane (Ph_2SiH_2) resulted in poor yields. Compared to 1,2-dimethyl-1,2-diphenydiailane $(Ph(CH_3)SiH)_2$, disilanes 1,1,2,2-tetraphenyldisilane $((Ph)_4Si_2H_2)$ performed better. The deoxygenation with *tris*(trimethylsilyl)silane $(TMS)_3SiH$, and $(Ph)_4Si_2H_2$ is comparatively better, however higher yield of compound **12** was noticed with *n*-Bu_3SnH. In deoxygenation carried out with alkyl-, phenyl- or trimethylsilyl-substituted silanes and disilanes, the yield of compound **12** increased persistently with phenyl or trimethylsilyl substitution. Chatgilialogu *et al.* described the use of $(TMS)_3SiH$ as a substitute of Bu_3SnH under moderate conditions.[13] In

comparison to *n*-Bu_3Sn·, the trialkylsilyl radicals are more reactive in addition to multiple bonds[14] and abstraction of halogen;[15] however, they are rather poor H-atom donors toward alkyl radicals, and therefore support chain reactions only at elevated temperatures. Also, the greater strength of the Si-H bond (78 kcal·mol^{-1}) in $(TMS)_3SiH$ compared to Sn-H bond (74 kcal·mol^{-1}) in *n*-Bu_3SnH, causes deoxygenation with silanes relatively slow and require considerably high temperature or added initiators.[16]

The factors that moderate Si-H bond dissociation enthalpies are not yet completely understood, however, the available thermo-chemical data on Si-H bond dissociation energies[17] and the rate constant for the reaction of some radicals with a variety of silicon hydrides suggest for the bond-weakening effects operative on trimethylsilyl or phenyl substitution, due to the radical stabilization by π-conjugation of phenyl group(s) and *d*-orbital participation of trimethylsilyl group.[18] The high cost of disilane $(Ph)_4Si_2H_2$ limits its further exploration in our free radical deoxygenation, while the use of Bu_3SnH was ruled out on green perspectives.[18b,19] Moreover, it appeared inappropriate to utilize toxic Bu_3SnH as radical reducing agent for synthesis of compounds having value to medicine and agriculture.

Table 1. Optimization[a] of radical conversion of compound **11** to **12** using 2.2 molar equivalents of reagents.



11 **12**

Entry	Reagent[b]	Initiator[c] (Mol%)	Temp (°C)[d]	Yield % (time)[e]	Yield % (time)[f]
1	Et_3SiH	5	80	trace(12)	trace
2	Et_3SiH	0	150	trace (12)	trace
3	$Pr^i{}_3SiH$	5	80	trace (12)	trace
4	$Pr^i{}_3SiH$	0	150	trace (12)	trace
5	Ph_2SiH_2	5	80	trace (12)	trace
6	Ph_2SiH_2	0	150	trace (12)	trace
7	Bu^tPh_2SiH	5	80	40(6)	44
8	Bu^tPh_2SiH	0	150	42(12)	47
9	$(Ph(CH_3)SiH)_2$	5	80	48(6)	54
10	$(Ph(CH_3)SiH)_2$	0	150	50(12)	47
11	Ph_3SiH	5	80	66(6)	68
12	Ph_3SiH	0	150	63(12)	65
13	$(TMS)_3SiH$	5	80	75(6)	74
14	$(TMS)_3SiH$	0	150	73(12)	69
15	$(Ph)_4Si_2H_2$	5	80	78(6)	76
16	$(Ph)_4Si_2H_2$	0	150	65(12)	71
17	Bu_3SnH	5	80	83(6)	85
18	Bu_3SnH	0	80	73(12)	74

[a]All reactions in microwave carried at 110°C; [b]Reagents arranged on the basis of increasing order of yield; [c]AIBN used as radical initiator; [d]Reaction temperature 80-150 °C; [e]Isolated yield and reaction time in hours under conventional heating; [f]Isolated yield for reactions in microwave of 30 min exposure.

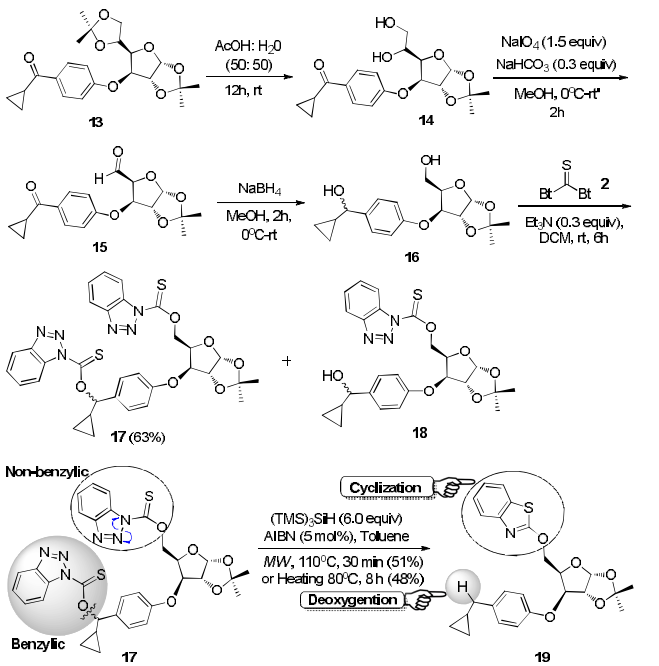
The solvent effect was briefly investigated using various solvents in the presence of AIBN (5 mol %) and $(TMS)_3SiH$ (2.2 molar equiv) at 110 °C (Table 2). The results illustrated the poor performance of cyclohexane, *n*-hexane, benzene, toluene, 1,4-dioxane, dichloromethane and chloroform in terms of yield and reaction time. The higher yield observed with toluene is mainly due to its higher temperature sustaining capacity, that is, higher boiling point, as compared to the dichloromethane, chloroform, cyclohexane, *n*-hexane, and benzene.

Table 2. Solvent optimization for conversion from **11** to **12** using $(TMS)_3SiH$ (2.2 molar equiv) in presence of AIBN (5 mol %)

Entry	Solvent[a]	Time (h)	Yield (%)[b]
1	cyclohexane	6	17
2	*n*-hexane	6	14
3	benzene	6	67
4	toluene	6	85
5	1,4-dioxane	8	80
6	dichloromethane	12	<10[c]
7	chloroform	12	<10[c]

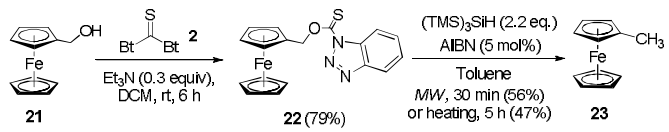
[a]2.0 mL of solvent was used for 1 mmol of **11**. [b]Reaction time 4-12 h. [c]Reaction was carried in sealed tube.

The deoxygenation product **19**, also a carbohydrate derivative has been synthesized from diol **16**, could be obtained from compound **13**[12c] by acid hydrolysis and subsequent $NaBH_4$ reduction of aldehyde **15** generated by periodate cleavage of diol **14** (Scheme 3). Along with compound **17**, a little amount of compound **18** also has been isolated from the reaction mixture. It was found interesting that when both benzylic and aliphatic hydroxyl group present together in the same molecule, the benzylic hydroxyl selectively undergo deoxygenation; while the other deoxygenate under the same reaction condition.



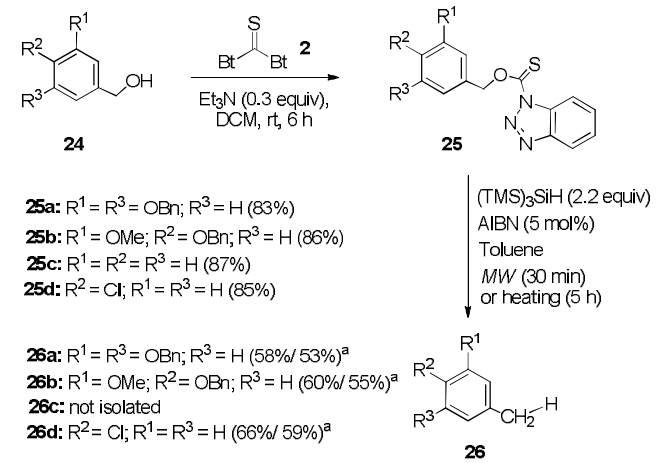
Scheme 3. Synthesis of compound **19** using compound **2**.

The alcohol 1-ferrocenylmethanol **21,** prepared from $NaBH_4$ reduction of ferrocene aldehyde **20,** would further be deoxygenated to methyl-ferrocene **23** *via* intermediate benzotriazole derivative **22** with 79% yield. The reaction takes 5 hours under conventional heating or in microwave only 30 minutes to complete (Scheme 4).



Scheme 4. Synthesis of methyl-ferrocene **23**

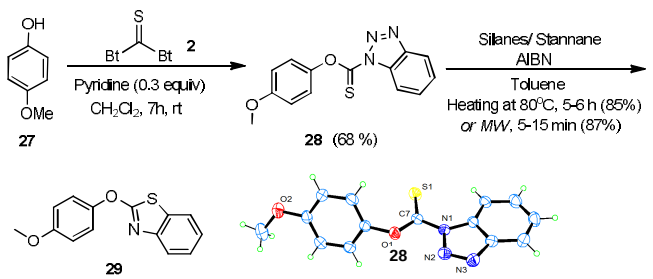
Further, using our standardized reaction condition benzotriazolethiocarbamates **25a-d** deoxygenated to their corresponding deoxy analogs **26a-d** (Scheme 5). Structural assignment of **25a-d** and **26a-d** was supported by ^{1}H and ^{13}C NMR spectra, mass and elemental analyses.



Scheme 5. Deoxygenation of benzylic alcohols **24a-d** to **26a-d.** [a](yield under MW/ yield under conventional heating)

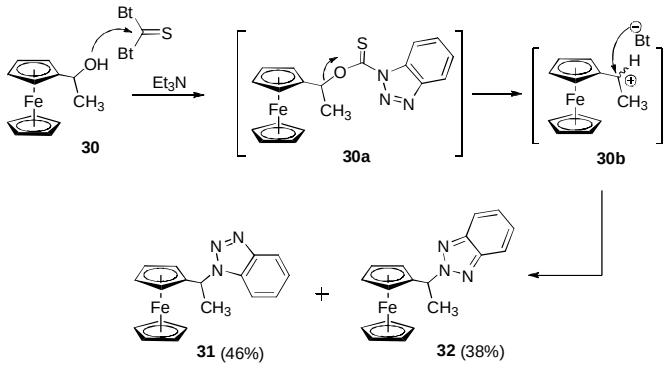
The higher yield of compound **12** is noticeable among the entire synthesized deoxygenation products. This may be due to extra stabilization of corresponding radical by the cyclopropyl substituent.[20a] The optimum overlap between the cyclopropylmethyl radicals *p*–orbital and the cyclopropyl Walsh orbital[20b-c] may provide extra stabilization; also, some report shows the calculated value of stabilization energy of a cyclopropylmethyl radical with an optimum conformation is 12 kJ/mol.[20d-e]

An attempt to deoxygenate aromatic alcohol 4-methoxyphenols **27** under our optimized reaction condition results cyclization to corresponding benzothiazole **29** of intermediate **28**, *via* cyclative ring cleavage of benzotriazole (Scheme 6). The structure of compound **28** has been assigned by single crystal X-ray analysis.



Scheme 6. Reaction of 4-methoxyphenol **27** with compound **2**

In another case, the reaction of 1-ferrocenylethanol **30** with **2** in presence of Et_3N in anhydrous dichloromethane afford a mixture of regioisomer, 1-ferrocenyl-1-(1*N*-benzotriazolyl)ethane **31** and 1-ferrocenyl-1-(2*N*-benzotriazolyl)ethane **32**, instead of desired benzotriazolemethanethione adduct **30a** (Scheme 7). The structure of compound **31** and **32** has been assigned by single crystal X-ray analysis (Figure 2).



Scheme 7. Reaction of 1-ferrocenylethanol **30** with compound **2**

The chemistry described here offers a novel route to access benzotriazole derivatives of ferrocene, using compound **2**. The reaction proceeds through Et_3N promoted nucleophilic addition of 1-ferrocenylethanol to compound **2**, by the substitution of one of the benzotriazole moiety. However, the resulting adduct **30a** decomposes to the products **31** and **32**. The mechanism of formation two regioisomers is supposed to be S_N1 and passes through the intermediate carbocation **30b**. The intermediate carbocation **30b** has been stabilized by three hyperconjugated hydrogens and charge dispersal through delocalization over the cyclopentyl ring of the ferrocene moiety and being captured by benzotriazole anion *via* *N*1 and *N*2 nucleophilic center and afford a mixture of two regioisomer **31** and **32** in ratio of 60:40. The two regioisomers has been separated by flash column chromatography. The configuration at carbon *C*7 observed in single crystal X-ray structure of compound **31** and **32** is exclusively C7-(*R*) (figure 2). The crystallographic and instrumental data for the compound **28**, **31**, and **32** has been summarized as table 3 (see Supporting Information CIF file for details).

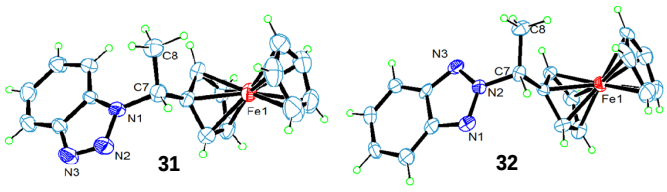


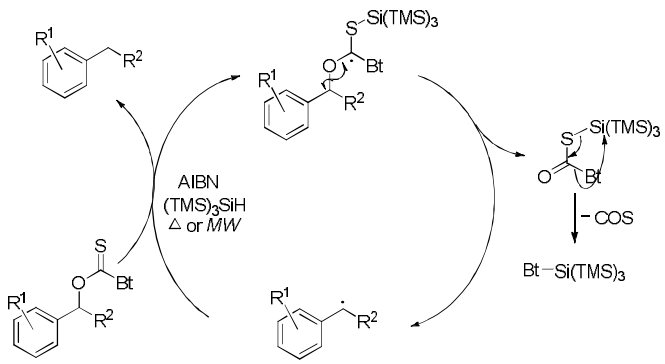
Figure 2. Single-crystal X-ray molecular structure of **31** & **32.** The displacement thermal ellipsoids are drawn at the 40%

Table 3. Crystallographic refinement data[a] for compound **28, 31** & **32**

Property	28	31	32
Mol. Formula	C_{14} H_{11} N_3 O_2 S	C_{18} H_{17} Fe N_3	C_{18} H_{17} Fe N_3
Formula Weight	285.33	331.20	331.20
Crystal System	Triclinic	Monoclinic	Monoclinic
Space group	P -1	P 1 21/n 1	P 1 21 1
a (Å)	4.2311(7)	6.6888(7)	6.1853(6)
b (Å)	8.0019(16)	28.847(2)	30.023(3)
c (Å)	20.415(3)	8.3300(10)	8.4797(9)
β (°)	92.671(13)	104.396(11)	104.478(10)
V (Å^3)	676.2(2)	1556.8(3)	1524.7(3)
Z	2	4	4
Density (calc)	1.401	1.413	1.443
F(000)	280	688.0	688
μ (mm^{-1})	0.234	0.968	0.988
Crystal Size [mm]	0.16 x 0.17 x 0.24	0.13 x 0.15 x 0.23	0.12 x 0.18 x 0.20
Temperature (K)	293	293	293
Radiation (Mo*K*α)	0.71073	Mo*K*α 0.71073	Mo*K*α 0.71073
θ Min-Max [°]	3.31, 28.87	3.22, 29.13	3.40, 29.08
h, k, l	-5:5; -8:10; -26:22	-8:8; -18:39; -5:11	-8:7; -38:39; -9:11
Tot.,UniqData, R(int)	5013, 3051, 0.0264	6934, 3558, 0.0425	6476, 4835, 0.0328
Obs. data [I > 2.0 σ(I)]	1550	2076	3163
Nref, Npar	3580, 181	4193, 259	4835, 433
R1, wR2, S	0.0590, 0.1104, 1.019	0.0694, 0.1545, 1.097	0.0611, 0.1212, 1.046
Min. - Max. resd. dens. [e/ Å^3]	-0.205, 0.167	-0.288, 0.370	-0.349, 0.416
CCDC	**978009**	**978010**	**978011**

[a]For details see supporting information file (CIF) enclosed with manuscript.

The proposed free-radical catalytic cycle shows application of deoxygenation approach to a $(TMS)_3SiH$ catalyzed variant of the Barton–McCombie deoxygenation reaction is outlined in Scheme 8.[2,9k,21] The radical reduction of a thionocarbonate by $(TMS)_3SiH$ afford carbon oxide sulfide (COS), the desired alkane, and $(TMS)_3Si$–Bt.[22]



Scheme 8. Plausible $(TMS)_3SiH$ mediated radical deoxygenation

Conclusions

The developed methodology is new, concise, efficacious and $(TMS)_3SiH$ mediated toxic metal free approach, for deoxygenation under mild conditions. Also, it has compatibility under microwave conditions and gives a new way to avoid the use of highly toxic *n*-Bu_3SnH for radical deoxygenation. The methodology is extremely important in terms of green chemistry perspectives and is selectively for the benzylic alcohols. Thus, this approach should be of further interest to synthetic and medicinal chemists.

Experimental

General remarks

All the reactions were executed in anhydrous solvents under an Ar-atmosphere in oven dried glassware at 110 °C. All reagents and solvents used were of analytical grade. Laboratory grade dichloromethane was first distilled and then was further purified and dried by distillation from calcium hydride. Dry toluene and all the reagents were purchase from Sigma-Aldrich Chemical Company, Inc., with >99% purity, was used without further purification. 2,2'-Azo*bis*(isobutyronitrile) (AIBN) (98%; Spectrochem Chemical Company, Inc.) was used without purification. Thin layer chromatography (TLC) was performed on silica gel 60 F_{254}, pre-coated on aluminum plates and revealed with either a UV lamp (λ_{max} = 254 nm) or by spraying with methanolic-H_2SO_4 solution and subsequent charring by heating at 100 °C. ^{1}H and ^{13}C NMR were recorded at 300 and 75 MHz, respectively. Chemical shifts are given in ppm downfield from internal TMS; *J* values given in Hz. Mass spectra recorded using electrospray ionization mass spectrometry (ESI-MS). Infrared spectra recorded as Nujol mulls in KBr plates. Elemental analysis was performed using a C, H, N analyzer and results were found to be within ± 0.4% of the calculated values. Reactions under microwave were carried out in a single-mode microwave reactor.

Single-crystal X-ray data of compounds were collected on Xcalibur Eos (Oxford) CCD-Diffractometer using graphite monochromated Mo*K*α radiation (λ = 0.71073 Å). The data integration and reduction were processed with CrysAlis Pro software.[23] The structures were solved by the direct method and then refined on F^2 by the full matrix least-squares technique with the SHELX-97 set of software[24] using the WinGX (version 1.80.05) program package.[25] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as riding atoms using SHELX default parameters. Molecular structures have drawn using ORTEP software given in scheme 6 and figure 2. Further information on the crystal structure determination (excluding structure factors) has been given as Table 3 and also deposited in the Cambridge Crystallographic Data Centre as supplementary publications nos. 978009 (**28**), 978010 (**31**) and 978011 (**32**). Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033. e-mail: deposit@ccdc.cam.ac.uk) or via internet.

General procedure for the synthesis of benzyloxythioacyl benzotriazoles (11, 17, 22 & 25a-d).

A stirring solution of alcohol **1** in anhydrous CH_2Cl_2 was treated with *bis*(benzotriazolyl)methanethione **2** in presence of Et_3N under inert atmosphere. After completion of reaction (monitored by TLC), the reaction mixture was *in vacuo* concentrated. Extraction with CH_2Cl_2, washing with 10% Na_2CO_3, water and brine solution followed by drying over anhydrous Na_2SO_4, the organic layer was concentrated under reduced pressure. Further purification using flash column chromatography using ethyl acetate/ *n*-hexane as eluent afforded the respective pure benzotriazole methanethiones **11, 17, 22** and **25a-d**.

General procedure for the MW-assisted deoxygenation

A stirring solution of benzotriazolemethanethione **11, 17, 22** and **25a-d** (1.0 mmol) in anhydrous toluene was added with *tris*(trimethylsilyl)silane (2.2 equiv) and AIBN (5 mol %) under inert atmosphere. The reaction mixture was stirred under heating at 110 °C as well as exposed to single-mode microwave reactor with a new sealed pressure regulation 10-mL pressurized vial with ''snap-on'' cap and teflon-coated magnetic stir bar. The standard temperature control system consisted non-contact calibrated infrared sensor which monitors and controls the temperature conditions of the reaction vessel located in the instrument cavity. For each reaction, the reaction temperature is 110 ^oC. After completion of reaction (monitored by TLC), the reaction mixture was *in vacuo* concentrated, extracted with CH_2Cl_2, washed with 10% LiOH, water and brine solutions. The organic layer was dried over anhydrous Na_2SO_4 followed by *in vacuo* concentration. Purification using flash column chromatography afforded products **12, 19, 23,** and **26a-d**.

Physical data of developed compounds

***Bis(1H-benzo[d][1,2,3]triazol-1-yl)methanethione (2)*:** Yellow crystals; IR (KBr) ν_{max} 1597, 1536, 1067, 1007, 959, 891, 728, 692, 650 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.27 (d, J = 8.4 Hz, 2H), 8.22 (d, J = 8.1 Hz, 2H), 7.74 (t, J = 7.8 Hz, 2H), 7.60 (t, J = 7.5 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.6 (2C), 146.7 (2C), 133.0 (2C), 130.5 (2C), 126.9 (2C), 120.9 (2C), 113.8 (2C) ppm.

3'-O-(4-(hydroxy)(cyclopropyl)methyl)*-phenyl-*1',2':5',6'-di-O-isopropylidene-α-D-glucofuranose (10): Colorless solid; IR (KBr) ν_{max} 3641, 2983, 2942, 1616, 1589, 1105, 1087, 889, 764 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.37 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 8.4 Hz, 2H), 5.92 (d, J = 3.3 Hz, 1H), 4.72 (s, 1H), 4.60 (d, J = 3.6 Hz, 1H), 4.48-4.46 (m, 1H), 4.33 (d, J = 7.8 Hz, 1H), 4.15-4.11 (m, 2H), 3.96 (d, J = 8.4 Hz, one isomer), 3.45 (d, J = 7.8 Hz, other isomer), 3.23 (s, 1H), 1.55, 1.43, 1.32 and 1.30 (each s, each 3H), 0.66-0.60 (m, 1H), 0.58-0.53 (m, 1H), 0.47-0.43 (m, 1H), 0.38-0.30 (m, 1H), 0.24-0.19 (m, 1H) ppm.

O-(Cyclopropyl(4-(1',2':5',6'-di-O-isopropylidine-α-D-glucofuranoxy)phenyl)methyl)-1H-benzo[d][1,2,3]triazole-1-carbothioate (11): The compound **10** (0.406 g, 1.0 mmol) on treatment **2** (0.31 g, 1.1 mmol) and Et_3N (0.3 equiv.) in dry CH_2Cl_2 (15 mL) was stirred for 8 h at room temperature. The crude product was purified by flash column chromatography (10 % ethyl acetate/*n*-hexane) afforded a yellowish viscous liquid **11** (0.436 g, 77 %, R_f = 0.60, 20% ethyl acetate/*n*-hexane). IR (Nujol) ν_{max} 1744, 1616, 1579, 1088, 1067, 1054, 986, 974, 734 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.15 (d, J = 8.1 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.50 (m, 1H), 7.46 (d, J = 8.7 Hz, 2H), 6.97 (d, J = 8.4 Hz, 2H), 5.90 (s, J = 3.6 Hz, 1H), 4.71 (d, J = 2.7 Hz, 1H), 4.59 (d, J = 3.6 Hz, 1H), 4.43 (dd, J = 6.0, 7.2 Hz, 1H), 4.31-4.25 (m, 2H), 4.13-4.08 (m, 2H), 1.54 (s, 3H), 1.42 (s, 3H), 1.29 (s, 6H), 0.78-0.70 (m, 2H), 0.68-0.56 (m, 1H), 0.50-0.43 (m, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.6, 156.1, 146.1, 134.4, 130.7, 130.4, 129.1 (2C), 126.1, 120.2, 115.3 (2C), 113.6, 112.0, 109.1, 105.2, 82.0, 80.3, 79.7, 72.1, 66.9, 54.0, 26.7, 26.6, 26.1, 25.1, 16.9, 6.5, 6.2 ppm; MS: *m/z* 568 $[M+H]^+$; Anal. Calcd. for $C_{29}H_{33}N_3O_7S$: C, 61.36; H, 5.86; N, 7.40; Found: C, 61.51; H, 5.98; N, 7.57.

3'-O-(4-(Cyclopropylmethyl)phenyl)-1',2';5',6'-di-O-isoprppylideneglucofuranose (12): Colorless viscous liquid; yield 85 %; R_f = 0.68 (20% ethyl acetate/*n*-hexane); MS: *m/z* 391 $[M+H]^+$; IR (Nujol) ν_{max} 2938, 1597, 1072, 1032, 981, 972, 875, 766, 732 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.26 (d, J = 8.4 Hz, 2H), 6.96 (d, J = 8.4 Hz, 2H), 5.93 (d, J = 3.3 Hz, 1H), 4.73 (d, J = 3.0 Hz, 1H), 4.62 (d, J = 3.9 Hz, 1H), 4.48 (dd, J = 12.3, 5.7 Hz, 1H), 4.33 (dd, J = 13.5, 3.0 Hz, 1H), 4.15-4.12 (m, 2H), 3.48 (d, J = 7.8 Hz, 2H), 2.72-2.55 (m, 1H), 1.55 (s, 3H), 1.44 (s, 3H), 1.32 (s, 3H), 1.31 (s, 3H), 1.17-1.09 (m, 1H), 0.68-0.60 (m, 1H), 0.48-0.43 (m, 2H), 0.26-0.18 (m, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.1, 134.9, 128.0 (2C), 115.1 (2C), 111.9, 109.0, 105.1, 82.0, 80.3, 79.6, 72.1, 66.9, 47.2, 26.7, 26.6, 26.1, 25.1, 17.4, 4.2, 1.7 ppm.

3'-(4-((Cyclopropyl)hydroxymethyl)phenyl)-1',2'-O-isopropylidene-α-D-xylofuranose (16): Viscous liquid; IR (Nujol) ν_{max} 3589, 2943, 1578, 1544, 1263, 1187, 979, 874, 763, 665 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.37 (d, J = 8.1 Hz, 2H), 6.93 (d, J = 7.8 Hz, 2H), 5.96 (s, 1H), 4.70 (s, 1H), 4.61 (m, 2H), 4.42-4.39 (m, 2H), 3.97 (d, J = 9.9 Hz, 1H), 2.18 (bs, 1H), 1.55 (s, 3H), 1.31 (s, 3H), 1.23 (m, 1H), 0.61-0.59 (m, 1H), 0.54 (m, 1H), 0.45 (m, 1H), 0.34 (m, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.9, 137.4, 127.4 (2C), 114.9 (2C), 112.0, 105.1, 82.0, 80.2, 77.7, 77.6, 62.0, 26.6, 26.1, 19.0, 3.4, 2.6 ppm.

3'-O-(4-((Cyclopropyl)(1H-benzotriazolylmethanethionyl) methyl)phenyl)-1',2'-O-isopropylidine-α-D-xylofuranose-5'-1H-benzotriazolecarbothioate (17): The compound **16** (0.672 g, 2.0 mmol) on treatment with **2** (1.193 g, 4.2 mmol) and Et_3N (0.4 equiv) in anhydrous CH_2Cl_2 (20 mL) was stirred for 12 h at room temperature. The crude product was purified by flash column chromatography (10% ethyl acetate/n-hexane) and afforded a light yellowish viscous liquid **17** (0.825 g, 63 %, R_f = 0.70, 30% ethyl acetate/*n*-hexane). MS: *m/z* 659 $[M+H]^+$; IR (Nujol) ν_{max} 1726, 1613, 1545, 1107, 1055, 1044, 876, 784, 637 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.33 (d, J = 7.8 Hz, 1H),

8.31-8.07 (m, 3H), 7.63-7.55 (m, 2H), 7.46-7.44 (m, 4H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.06 (d, *J* = 3.3 Hz, 1H), 5.16-5.14 (m, 2H), 4.96-4.91 (m, 2H), 4.71 (m, 1H), 4.25 (d, *J* = 9.3 Hz, 1H), 1.57 (s, 3H), 1.45-1.42 (m, 1H), 1.33 (s, 3H), 0.79-0.70 (m, 2H), 0.58 (m, 1H), 0.47 (m, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 182.4, 167.5, 155.8, 146.2, 146.1, 134.8, 131.1, 130.7, 130.4, 129.2 (2C), 126.1, 125.9, 125.7, 120.5, 120.2, 115.2 (2C), 114.8, 113.5, 112.4, 105.2, 82.1, 80.1, 76.7, 69.8, 53.9, 26.7, 26.2, 16.7, 6.5, 6.1 ppm.

3'-O-(4-(Cyclopropyl(hydroxy)methyl)phenoxy)-1',2'-O-isopropylidine-α-D-glucofuranoxy-5'-1H-benzo[d][1,2,3]triazole-1-carbothioate (18): Viscous liquid; R_f = 0.50, 60% ethyl acetate/*n*-hexane); MS: *m/z* 498 $[M+H]^+$; IR (Nujol) ν_{max} 3568, 2921, 1663, 1557, 1211, 1189, 794, 768, 654 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.35 (d, *J* = 8.1 Hz, 1H), 8.09 (d, *J* = 8.1 Hz, 1H), 7.60 (dd, *J* = 7.5, 7.2 Hz, 1H), 7.46 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 7.8 Hz, 2H), 6.06 (s, 1H), 5.17-5.16 (m, 2H), 4.94 (d, *J* = 11.4 Hz, 1H), 4.92 (m, 1H), 4.71 (d, *J* = 3.0 Hz, 1H), 3.94 (d, *J* = 8.1 Hz, 1H), 2.18 (bs, 1H), 1.57 (s, 3H), 1.34 (s, 3H), 1.14 (m, 1H), 0.59 (m, 1H), 0.51 (m, 1H), 0.43 (m, 1H), 0.31 (m, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 182.4, 155.7, 146.2, 137.6, 131.1, 130.4, 127.4 (2C), 125.9, 120.4, 115.0 (2C), 114.8, 112.3, 105.2, 82.2, 80.1, 77.7, 77.6, 69.9, 26.7, 26.2, 19.0, 3.4, 2.6 ppm.

5'-O-(Benzothiazol-2-yl)-3'-O-(4-(cyclopropylmethyl)phenyl)-1',2'-O-isopropylidine-α-D-xylofuranose (19): Viscous liquid; yield 51%; R_f = 0.75 (20% ethyl acetate/*n*-hexane); 6 equivalents of $(TMS)_3SiH$ has been used. IR (Nujol) ν_{max} 3013, 1598, 1535, 1075, 1021, 845, 756, 644 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64-7.60 (m, 2H), 7.34-7.32 (m, 3H), 7.20 (dd, *J* = 7.8, 7.5 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 2H), 6.01 (s, 1H), 4.97-4.81 (m, 4H), 4.65 (m, 1H), 3.37-3.34 (m, 1H), 2.04 (d, *J* = 3.3 Hz, 1H), 1.56 (s, 3H), 1.42-1.40 (m, 1H), 1.32 (s, 3H), 0.73-0.71 (m, 1H), 0.57 (m , 1H), 0.37-0.29 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.3, 155.6, 149.0, 137.4, 132.0, 128.4 (2C), 125.9, 123.5, 121.2, 120.8, 115.1 (2C), 112.2, 105.3, 82.0, 80.2, 77.5, 68.8, 48.7, 26.7, 26.2, 20.2, 6.3, 6.0 ppm; MS: *m/z* 454 $[M+H]^+$; Anal. Calcd. for $C_{25}H_{27}NO_5S$: C, 66.20; H, 6.00; N, 3.09; Found: C, 66.37; H, 6.03; N, 3.13.

***1-Ferrocenylmethanol (21)*[26]:** Red crystals; IR (KBr) ν_{max} 3507, 2949, 2883, 1563, 1478, 1247, 1149, 884, 745 cm^{-1}; ^{1}H NMR (300 MHz, CDC_{l3}): δ 4.32-4.11 (m, 11H), 1.58 (bs, 1H) ppm; ^{13}C NMR (75 MHz, CDC_{l3}): δ 83.7, 69.3, 68.4 (3C), 68.2 (4C), 67.8, 60.7 ppm.

O-(Ferrocenylmethyl)-1H-benzo[d][1,2,3]triazole-1-carbothioate (22): The compound **21** (0.434 g, 2.0 mmol) on treatment with **2** (0.59 g, 2.1 mmol) and Et_3N (0.3 equiv.) in dry CH_2Cl_2 (15 mL) was stirred for 6 h at room temperature. The crude product was purified by flash column chromatography (20% ethyl acetate/*n*-hexane) afforded a red solid **22** (0.598 g, 79 %, R_f = 0.70, 20% ethyl acetate/*n*-hexane). MS: *m/z* 378 $[M+H]^+$; IR (KBr) ν_{max} 2945, 1744, 1625, 1609, 1532, 177, 1025, 1008, 936, 714, 598 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.1 Hz, 1H), 8.09 (d, *J* = 8.1 Hz, 1H), 7.63 (dd, *J* = 7.2, 7.8 Hz, 1H), 7.47 (dd, *J* = 7.2, 7.5 Hz, 1H), 4.31 (s, 2H), 4.21 (m, 7H), 4.16 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.2, 146.1, 130.7, 130.4, 126.0, 120.2, 113.5, 82.4, 68.8, 68.3, 30.5 ppm.

***Methylferrocene (23)*[27]:** Orange solid; yield 56%; R_f = 0.75 (20% ethyl acetate/n-hexane); IR (KBr) ν_{max} 2943, 1555, 1514, 1244, 1186, 1138, 813, 741, 613 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.43 (s, 2H), 4.18-4.15 (m, 7H), 1.70 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 83.8, 69.3, 68.99, 68.90, 68.6, 68.2, 67.8, 14.4 ppm.

***3,5-Bis(benzyloxy)phenyl)methanol (24a)*[28]:** White solid; IR (KBr) ν_{max} 3567, 2921, 2841, 1578, 1531, 1267, 1178, 1112, 798, 655 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-7.29 (m, 10H), 6.59 (s, 2H), 6.52 (s, 1H), 4.99 (s, 4H), 4.57 (s, 2H), 1.90 (bs, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.0 (2C), 143.3, 136.7 (2C), 128.5 (4C), 127.9 (2C), 127.4 (4C), 105.7, 105.6, 101.1, 70.0 (2C), 65.1 ppm.

***(4-(Benzyloxy)-3-methoxyphenyl)methanol (24b)*[29]:** White solid; IR (KBr) ν_{max} 3609, 2944, 1611, 1509, 1498, 1248, 1143, 898, 765 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43-7.27 (m, 5H), 6.92 (s, 1H), 6.83 (dd, *J* = 8.1, 15.3 Hz, 2H), 5.13 (s, 2H), 4.56 (s, 2H), 3.87 (s, 3H), 1.89 (bs, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.7, 147.5, 137.0, 134.1, 128.4 (2C), 127.7, 127.1 (2C), 119.2, 113.9, 110.9, 71.0, 65.1, 55.9 ppm.

O-3,5-bis(benzyloxy)benzyl-1H-benzo[d][1,2,3]triazole-1-carbothioate (25a): The compound **24a** (0.641 g, 2.0 mmol) on treatment with **2** (0.59 g, 2.1 mmol) and Et_3N (0.3 equiv.) in dry CH_2Cl_2 (15 mL) was stirred for 6 h at room temperature. The crude product was purified by flash column chromatography (20% ethyl acetate/*n*-hexane) afforded a white solid **25a** (0.78 g, 83 %, R_f = 0.60, 20% ethyl acetate/*n*-hexane); IR (KBr) ν_{max} 1737, 1641, 1613, 1511, 1164, 1037, 1013, 909, 794, 697 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.31 (d, *J* = 4.2 Hz, 1H), 8.21 (d, *J* = 5.1 Hz, 1H), 7.60 (dd, *J* = 7.2, 7.5 Hz, 1H), 7.47 (dd, *J* = 7.5, 8.1 Hz, 1H), 7.39-7.24 (m, 10H), 6.76 (d, *J* = 1.5 Hz, 2H), 6.64 (d, 1H), 5.79 (d, *J* = 3.9 Hz, 2H), 5.05 (d, *J* = 3.9 Hz, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 180.5, 160.2 (2C), 146.4, 136.5, 135.8, 131.3, 130.4, 128.5 (4C), 128.0 (2C), 127.4 (4C), 125.9, 129.6, 120.5, 114.9, 114.8, 107.5 (2C), 102.6, 74.4, 70.1 ppm.

O-4-(Benzyloxy)-3-methoxybenzyl-1H-benzo[d][1,2,3]triazole-1-carbothioate (25b): The compound **24b** (0.49 g, 2.0 mmol) on treatment with **2** (0.59 g, 2.1 mmol) and Et_3N (3.0 equiv.) in dry CH_2Cl_2 (15 mL) was stirred for 6 h at room temperature. The crude product was purified by flash column chromatography (20% ethyl acetate/*n*-hexane) afforded a white solid **25b** (0.674 g, 86 %), R_f = 0.65 (20% ethyl acetate/*n*-hexane). MS: *m/z* 406 $[M+H]^+$; IR (KBr) ν_{max} 1746, 1638, 1510, 1144, 1007, 909, 794, 697 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.1 Hz, 1H), 7.63 (dd, *J* = 7.2, 7.8 Hz, 1H), 7.47 (dd, *J* = 7.5, 7.8 Hz, 1H), 7.42-7.27 (m, 5H), 6.97 (s, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 5.13 (s, 2H), 4.35 (s, 2H), 3.89 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.0, 149.7, 147.8, 146.1,

136.9, 130.7, 130.4, 128.7, 128.4, 127.8 (2C), 127.1 (2C), 126.1, 121.3, 120.3, 113.9, 113.5, 112.6, 70.9, 55.9, 34.3 ppm.

***O-benzyl 1H-benzo[d][1,2,3]triazole-1-carbothioate (25c)*[30]:** The compound **24c** (0.217 g, 2.0 mmol) on treatment with **2** (0.59 g, 2.1 mmol) and Et_3N (0.3 equiv.) in dry CH_2Cl_2 (15 mL) was stirred for 6 h at room temperature. The crude product was purified by flash column chromatography (20% ethyl acetate/*n*-hexane) afforded a white solid **25c** (0.488 g, 87 %, R_f = 0.7, 20% ethyl acetate/*n*-hexane). IR (KBr) ν_{max} 1766, 1641, 1565, 1224, 1107, 949, 889, 767, 645 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.05 (d, J = 7.8 Hz, 1H), 7.35-7.27 (m, 8H), 5.83 (s, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.0, 146.2, 134.7, 132.7, 128.8 (2C), 128.4, 127.5 (2C), 127.3, 123.8, 120.0, 109.6, 52.2 ppm.

***O-4-Chlorobenzyl 1H-benzo[d][1,2,3]triazole-1-carbothioate (25d)*:** The compound **24d** (0.285 g, 2.0 mmol) on treatment with **2** (0.59 g, 2.1 mmol) and Et_3N (0.3 equiv.) in dry CH_2Cl_2 (15 mL) was stirred for 6 h at room temperature. The crude product was purified by flash column chromatography (20% ethyl acetate/*n*-hexane) afforded a white solid **25d** (0.515 g, 85 %, R_f = 0.7, 20% ethyl acetate/*n*-hexane). ; MS: *m/z* 305 $[M+H]^+$; IR (KBr) ν_{max} 1783, 1647, 1557, 1278, 1211, 1048, 879, 765, 655 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.06 (d, J = 8.4 Hz, 1H), 7.41-7.31 (m, 3H), 7.28 (d, J = 5.4 Hz, 2H), 7.18 (d, J = 5.4 Hz, 2H), 5.79 (s, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.9, 146.2, 134.3, 133.1, 132.5, 129.1 (2C), 128.8 (2C), 127.5, 123.9, 120.0, 109.4, 51.3 ppm.

***(((5-Methyl-1,3-phenylene)bis(oxy))bis(methylene))dibenzene (26a)*[31]:** *White* solid; yield 58%; R_f = 0.8 (20% ethyl acetate/*n*-hexane); IR (KBr) ν_{max} 2925, 1539, 1508, 1244, 1231, 11043, 1012, 576 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.38-7.33 (m, 10H), 6.63 (s, 1H), 6.58 (d, J = 2.4 Hz, 1H), 5.40 (s, 1H), 5.02 (s, 2H), 5.00 (s, 2H), 2.34 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.0 (2C), 136.7 (2C), 136.6 (2C), 128.5 (4C), 128.0 (2C), 127.5 (4C), 107.3, 70.2, 70.1, 21.3 ppm.

***1-(Benzyloxy)-2-methoxy-4-methylbenzene (26b)*[32]:** White solid; yield 60%; R_f = 0.7 (20% ethyl acetate/*n*-hexane); IR (KBr) ν_{max} 1573, 1510, 1277, 1232, 1167, 1109, 798, 7761, 629, 534 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.41-7.28 (m, 5H), 6.77 (s, 2H), 6.67 (d, J = 6.9 Hz, 1H), 5.13 (s, 2H), 3.87 (s, 3H), 2.37 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.4, 149.5, 147.5, 136.9, 130.34, 130.31, 128.5, 127.8, 127.1, 121.5, 113.7, 112.9, 71.0, 56.0, 21.3 ppm.

***Toluene (26c)*[33]:** Not isolated

***p-Chloro toluene (26d)*[34]:** Liquid; yield 66%; R_f = 0.8 (10% ethyl acetate/n-hexane); ^1H NMR (300 MHz, $CDCl_3$): δ 7.19 (d, J = 8.1 Hz, 2H), 7.06 (d, J = 7.8 Hz, 2H), 2.29 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.1, 131.0, 130.3 (2C), 128.2 (2C), 20.8 ppm.

***O-(4-Methoxyphenyl)-1H-benzo[d][1,2,3]triazole-1-carbothioate (28)*[30]:** Orange crystals, 0.667 g, yield 68%; R_f = 0.7 (20% ethyl acetate/*n*-hexane); IR (KBr) ν_{max} 3234, 2973, 1564, 1525, 1452, 1367, 1023, 1011, 842, 758 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.50 (d, J = 8.1 Hz, 1H), 8.19 (d, J = 7.8 Hz, 1H), 7.70 (dd, J = 7.5, 7.8 Hz, 1H), 7.32 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.1 Hz, 2H), 2.43 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 182.4, 150.5, 146.6, 137.1, 131.7, 130.7, 130.4 (2C), 126.2, 121.6 (2C), 120.8, 115.1, 21.0 ppm.

***2-(4-Methoxyphenoxy)benzo[d]thiazole (29)*[35]:** White solid, 0.196 g, yield 87%; R_f = 0.8 (20% ethyl acetate/*n*-hexane); IR (KBr) ν_{max} 3259, 2942, 1569, 1555, 1465, 1235, 1047, 745, 665 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.86 (d, J = 7.8 Hz, 1H), 7.6 1 (d, J = 7.8 Hz, 3H), 7.37 (t, J = 7.5 Hz, 1H), 7.28-7.20 (m, 4H), 2.39 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.8, 153.8, 139.8, 136.4 (2C), 131.1 (3C), 127.8, 126.4, 124,3, 121.3, 120.2, 22.7 ppm.

***1-Ferrocenylethanol (30)*[36]:** Orange solid; ^1H NMR (300 MHz, $CDCl_3$): δ 4.53 (m, 1H), 4.18-4.15 (m, 9H), 1.88 (bs, 1H), 1.43 (d, J = 6.0 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 94.7, 68.2 (4C), 67.8 (2C), 66.0 (2C), 65.5, 23.6 ppm.

1-Ferrocenyl-1-(1N-benzotriazolyl)ethane (31): Red crystals; ^1H NMR (300 MHz, $CDCl_3$): δ 8.02 (d, J = 7.8 Hz, 1H), 7.35-7.28 (m, 3H), 6.13-6.07 (m, 1H), 4.38 (s, 1H), 4.19-4.10 (m, 8H), 2.03 (d, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.2, 131.6 (2C), 126.7, 123.5, 119.9, 110.4, 87.2, 69.0, 68.9, 68.8, 68.7, 68.2, 68.0, 67.9, 67.8, 66.6, 66.4, 55.7, 55.6, 20.1 ppm.

1-Ferrocenyl-1-(2N-benzotriazolyl)ethane (32): Red crystals, MS: *m/z* 332 $[M+H]^+$; ^1H NMR (300 MHz, $CDCl_3$): δ 7.84 (d, J = 3.3 Hz, 2H), 7.34 (d, J = 3.3 Hz, 2H), 5.98-5.96 (m,1H), 4.38 (s, 1H), 4.32 (s, 1H), 4.13-4.03 (m, 7H), 2.06 (d, J = 6.6 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.8, 126.0 (2C), 118.1 (2C), 88.0, 68.9, 68.7, 68.5, 68.4, 68.0, 67.9, 67.8, 67.6, 66.6, 66.5, 62.6, 62.5 ppm.

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Notes and references

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†**Electronic Supplementary Information (ESI) available:** Copies of ^1H and ^{13}C NMR spectra for all the synthesized compounds and Single Crystal X-ray crystallographic data for compounds **28, 31** & **32** has been provided, can be found in the online version. See DOI: 10.1039/b000000x/

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