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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 protocol for the deoxygenation of benzylic alcohols using bis(benzotriazole)methanethione has been devised. Benzotriazole derivatives, namely, benzyloxythioacylbenzotriazoles (ROCSBt), on reaction with silanes or Bu_3SnH under microwave irradiation or conventional heating undergo a free radical β-scission of C–O bond instead of N–N bond (benzotriazole ring cleavage) to afford a deoxy product. The methodology has various applications because it selectively deoxygenates benzylic alcohols with the aid of a relatively nontoxic $(TMS)_3SiH$ reagent as an acceptable alternate to Bu_3SnH.

Introduction

The advantages associated with utilizing benzotriazole as a synthetic auxiliary for common organic transformations lie in enabling them to be rather efficient, fast, and inexpensive.[1] Deoxygenation plays an important role in numerous synthetic transformations. Some common methods include well-known Barton–McCombie deoxygenation,[2] Marko–Lam de-oxygenation,[3] Wolff–Kishner reduction,[4] opening of epoxide ring *via* addition to unsaturated compounds[5] or by the hydride reduction of corresponding mesylates or tosylates.[6] The replacement of an allylic or a benzylic hydroxyl group through hydride displacement is sometimes complicated because the activation of the hydroxyl function into a suitable leaving group is difficult. The most commonly used activated derivatives, *viz.*, chlorides, bromides and arylsulfonates, may be reactive to such an extent that it is difficult to obtain the product with satisfactory purity, and they cannot be stored for a long period of time. Corey *et al.* used a pyridine–sulfurtrioxide complex with $LiAlH_4$ in THF for the activation of hydroxyl groups;[7] however, the harsh reduction condition limited its scope towards a wide range of substrates. A report by Kim *et al.* on the 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 a three-step reaction sequence to obtain only moderate yields and the use of expensive and carcinogenic Pd-catalyst limits the wide applicability of this method.

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

Recently, to widen the approach of our ongoing study on benzotriazole methodology,[9] we reported the synthesis of 2-N/S/C/O-substituted benzothiazoles *via* the cyclic-cleavage of benzotriazole ring using silane or stannane reagents.[9j,k] However, the phenomenon appears to be unusual in the case of

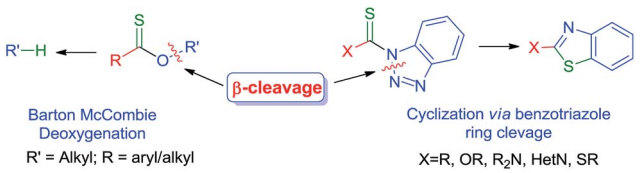

Fig. 1 Barton–McCombie deoxygenation and cyclization *via* benzotriazole ring cleavage.

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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** and **32** has been provided. CCDC 978009–978011. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5ra01545f

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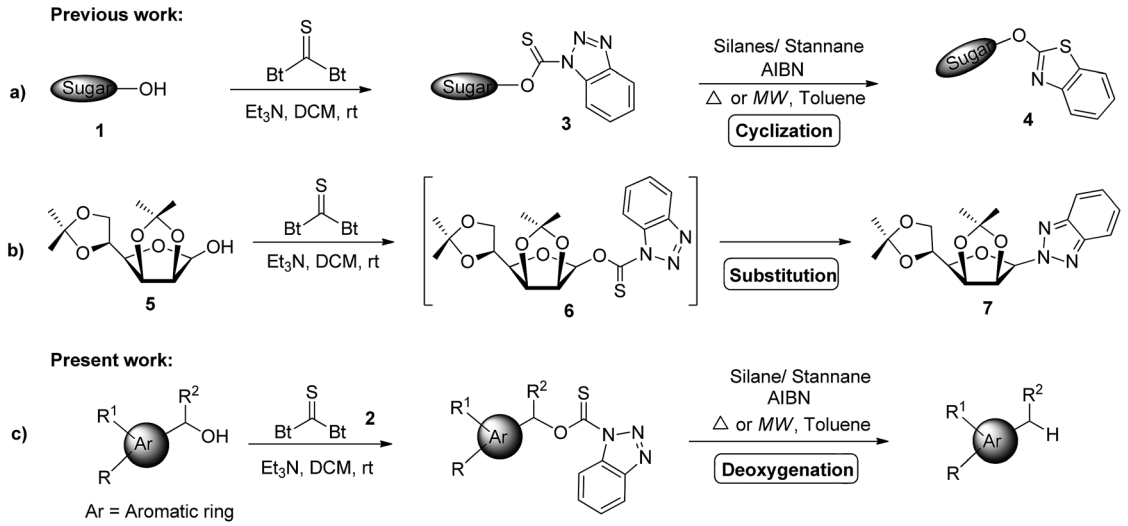
benzylic alcohols, which under similar reaction condition undergo unparalleled deoxygenation instead of cyclization, which has been reported herein.

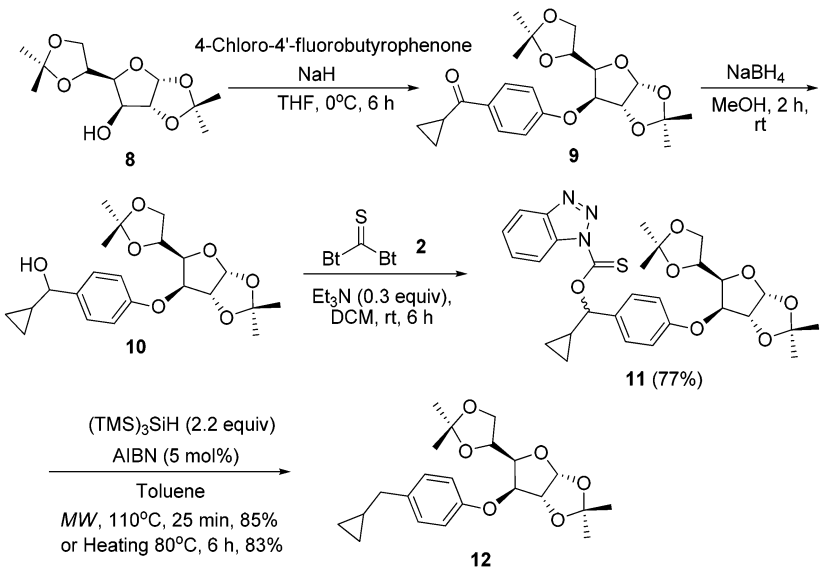
Results and discussion

Our investigation begins with the thioacylation of benzylic alcohols using a benzotriazole based reagent, **2**, to afford the corresponding benzyloxythioacylbenzotriazoles (ROCSBt),[9,10] which on further treatment with silanes or stannanes under conventional heating or microwave (MW) condition give deoxy products with moderate to good yields (Scheme 1c). The case is different with aliphatic alcohols, which under similar reaction condition undergo cyclization to afford good to excellent yields of 2-(alkoxy)benzothiazoles *via* the free radical intramolecular cyclic-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 the presence of Et_3N and pyridine in anhydrous CH_2Cl_2 affords 2-*N*-benzotriazole-2′,3′:5′,6′-di-*O*-isopropylidene-β-D-mannofuranoside (Scheme 1b).[11] Thus, the three alcohols, *viz.*, benzylic, aliphatic and anomeric, give different results under the similar condition.

The deoxy product **12**, a carbohydrate derivative, has been synthesized from benzylic alcohol **10** (ref. 12) by the radical deoxygenation of intermediate **11**. The treatment of compound **10** with bis(benzotriazole)methanethione, **2**, in the 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 that is capable of free radical induction in dry toluene to afford compound **12** in a good yield (Scheme 2).

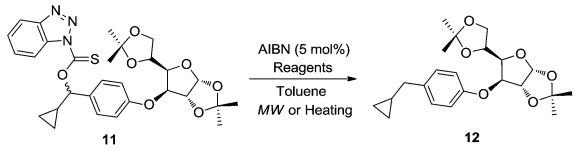


Scheme 1 Comparative illustration of previous and present work.



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

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



Entry	Reagent[b]	Initiator[c] (mol%)	Temp[d] (°C)	Yield[e] % (time)	Yield[f] % (time)
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 the reactions are carried out under microwave conditions at 110 °C. [b] Reagents are arranged on the basis of increasing order of yield. [c] AIBN is used as the radical initiator. [d] Reaction temperature is 80–150 °C. [e] Isolated yield and reaction time are presented in hours under conventional heating. [f] Isolated yield obtained for reactions under microwave exposure for 30 min.

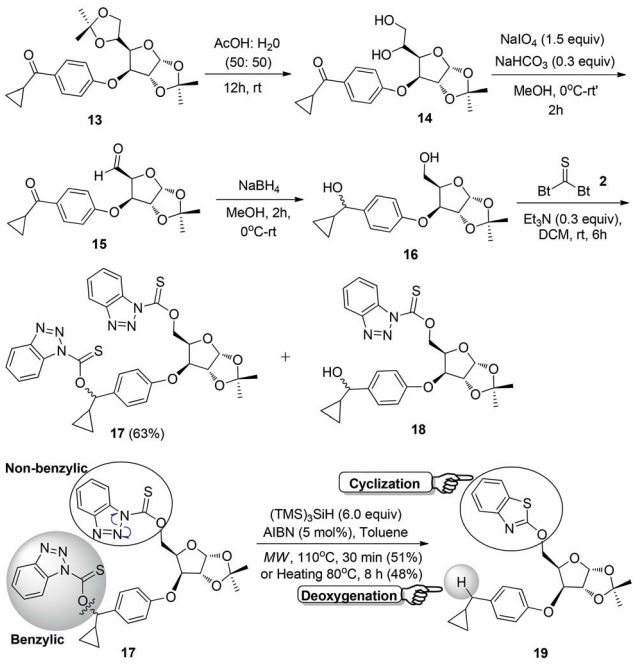
Table 2 Solvent optimization for the conversion of **11** to **12** using $(TMS)_3SiH$ (2.2 molar equiv.) in the presence of AIBN (5 mol%)

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]

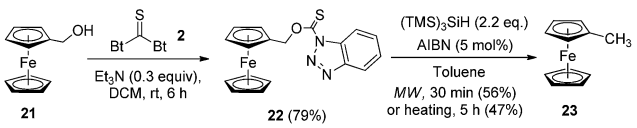
[a] 2.0 mL of solvent was used for 1 mmol of **11**. [b] Reaction time 4–12 h. [c] Reaction was carried out in a sealed tube.

Compound **11** was characterized by its characteristic NMR signals. A peak corresponding to benzotriazolyl protons in ^1H NMR appears in the aromatic region; moreover, a characteristic peak of thiocarbonyl carbon appears at δ 167.7 ppm in ^{13}C NMR spectrum of **11** (see ESI†). The compound **12** was characterized by the disappearance of signals that correspond to benzotriazolyl proton in its ^1H NMR spectra; in addition, the disappearance of the characteristic peak of thiocarbonyl carbon and the appearance of a methylene carbon signal at δ 47.2 ppm in ^{13}C NMR suggest the formation of compound **12** (see ESI file†). In addition, the mass spectrum of compound **12** exhibited an $[M + H]^+$ 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 also suggest that deoxygenation would occur in this condition rather than the well-known cyclization.

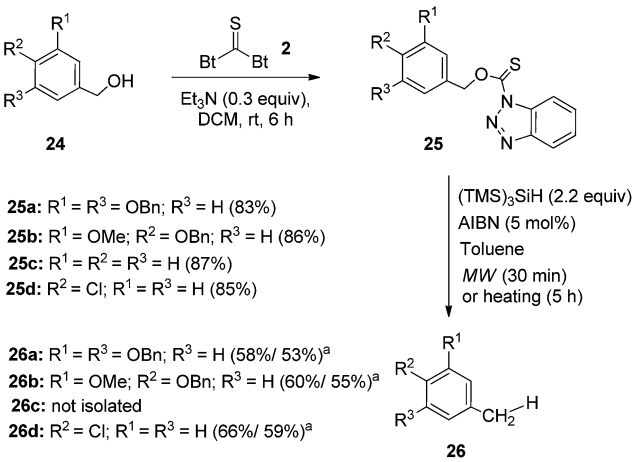
For the aforementioned deoxygenation, we briefly investigated the effect of the diverse range of silanes in terms of yield and reaction time; the results obtained have been summarized in Table 1. The obtained results clearly demonstrate that reagent feasibility depends solely on the Si–H and Sn–H bond strength among silanes and stannanes. The deoxygenation carried out in the presence of triethylsilane (Et_3SiH), tris(isopropyl)silane (Pr^i_3SiH) and diphenylsilane (Ph_2SiH_2) resulted in poor yields. Compared to 1,2-dimethyl-1,2-diphenyldisilane ($Ph(CH_3)SiH)_2$, 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, the higher yield of compound **12** was noticed with *n*-Bu_3SnH. For deoxygenation carried out with alkyl-, phenyl- or trimethylsilyl-substituted silanes and disilanes, the yield of compound **12** increased persistently with phenyl or trimethylsilyl substitution. Chatgilialoglu *et al.* described the use of $(TMS)_3SiH$ as a substitute to Bu_3SnH under moderate conditions.[13] In comparison to *n*-Bu_3SnH, the trialkylsilyls are more reactive towards addition to multiple bonds[14] and abstraction of halogen;[15] however, they are rather poor H-atom donors toward



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

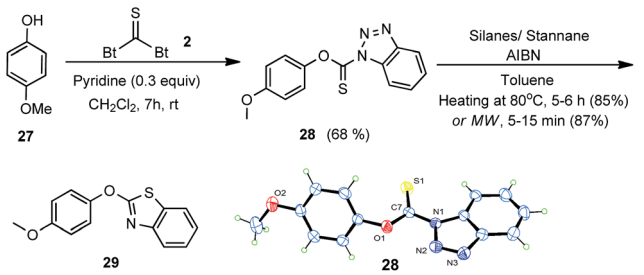


Scheme 4 Synthesis of methyl-ferrocene **23**.

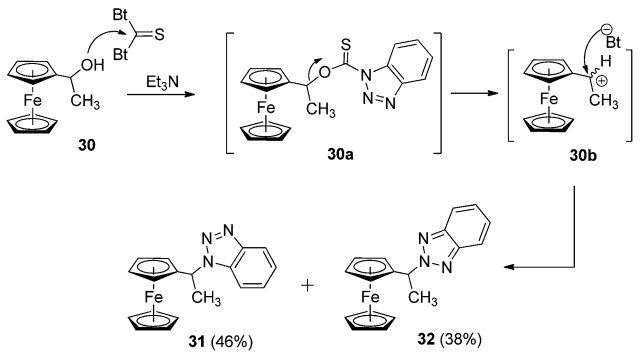


Scheme 5 Deoxygenation of benzylic alcohols **24a–d** to **26a–d**. [a]Yield under MW/yield under conventional heating.

alkyl radicals, and therefore support chain reactions only at elevated temperatures. Moreover, 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 results in relatively slow deoxygenation with silanes and requires considerably high temperatures or addition of initiators.[16]



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



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

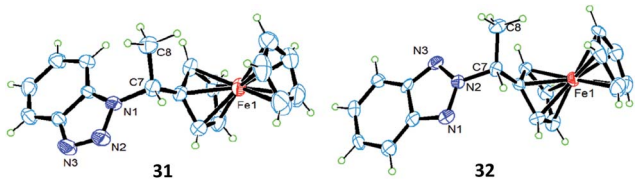


Fig. 2 Single-crystal X-ray molecular structure of **31** and **32**. The displacement thermal ellipsoids are drawn at 40%.

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 that the bond-weakening effects are operative on trimethylsilyl or phenyl substitution due to radical stabilization by the π-conjugation of phenyl group(s) and the 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, whereas the use of Bu_3SnH was ruled out for green perspectives.[18b,19] Moreover, it appeared inappropriate to utilize toxic Bu_3SnH as radical reducing agent for the synthesis of compounds that have value in medicine and agriculture.

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 performances 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 was

Table 3 Crystallographic refinement data[a] for compounds **28**, **31** and **32**

Property	**28**	**31**	**32**
Mol. formula	$C_{14}H_{11}N_3O_2S$	$C_{18}H_{17}FeN_3$	$C_{18}H_{17}FeN_3$
Formula weight	285.33	331.20	331.20
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	P121/*n*1	P1211
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
M (mm^{-1})	0.234	0.968	0.988
Crystal size [mm]	0.16 × 0.17 × 0.24	0.13 × 0.15 × 0.23	0.12 × 0.18 × 0.20
Temperature (K)	293	293	293
Radiation (MoKα)	0.71073	MoKα 0.71073	MoKα 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., uniq data, *R*(int)	5013, 3051, 0.0264	6934, 3558, 0.0425	6476, 4835, 0.0328
Obs. data [$I > 2.0\sigma(I)$]	1550	2076	3163
N_{ref}, N_{par}	3580, 181	4193, 259	4835, 433
R_1, wR_2, *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 ESI file (CIF) enclosed with manuscript.

mainly due to its capacity to sustain higher temperatures, *i.e.*, it has a higher boiling point compared to dichloromethane, chloroform, cyclohexane, *n*-hexane, and benzene.

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

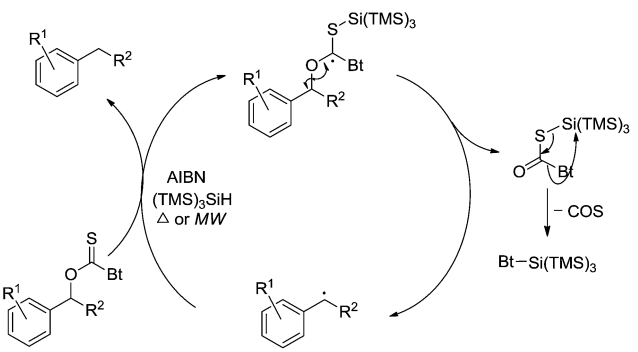
The alcohol 1-ferrocenylmethanol, **21**, prepared from $NaBH_4$ reduction of ferrocene aldehyde, **20**, would be further deoxygenated to methyl-ferrocene, **23**, *via* intermediate benzotriazole derivative, **22**, with 79% yield. The completion of reaction takes 5 hours under conventional heating,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

Furthermore, using our standardized reaction conditions, benzotriazolethiocarbamates, **25a–d**, were deoxygenated to their corresponding deoxy analogs, **26a–d**, (Scheme 5). The structural assignments of **25a–d** and **26a–d** were supported by ^{1}H and ^{13}C NMR spectra, mass and elemental analyses.

The higher yield of compound **12** is noticeable among all the synthesized deoxygenation products. This may be due to the extra stabilization of the corresponding radical by the cyclopropyl substituent.[20a] The optimum overlap between the p-orbital of cyclopropylmethyl radicals and the Walsh orbital[20b,c] of the cyclopropyl group may provide extra stabilization; moreover, some reports show that the calculated value of the stabilization energy of a cyclopropylmethyl radical with an optimum conformation is 12 kJ mol^{-1}.[20d,e]

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

In another case, the reaction of 1-ferrocenylethanol, **30**, with **2** in the presence of Et_3N in anhydrous dichloromethane afforded a mixture of regioisomer, namely, 1-ferrocenyl-1-(1*N*-benzotriazolyl)ethane, **31**, and 1-ferrocenyl-1-(2*N*-benzotriazolyl)-ethane, **32**, instead of the desired benzotriazolemethanethione



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

adduct, **30a**, (Scheme 7). The structures of compounds **31** and **32** were assigned by single crystal X-ray analysis (Fig. 2).

The chemistry described herein offers a novel route to access the benzotriazole derivatives of ferrocene using compound **2**. The reaction proceeds through the 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 form products **31** and **32**. The mechanism of formation of the two regioisomers is supposed to be S_N1, involving the formation of an intermediate carbocation **30b**. The carbocation intermediate, **30b**, was stabilized by three hyperconjugated hydrogens and charge dispersal through delocalization over the cyclopentyl ring of the ferrocene moiety, and the charge after being captured by a benzotriazole anion *via* N1 and N2 nucleophilic center afforded a mixture of two regioisomer, namely, **31** and **32**, in the ratio of 60 : 40. The two regioisomers were separated by flash column chromatography. The configuration at the carbon C7 observed in the single crystal X-ray structures of compounds **31** and **32** is exclusively C7-(*R*) (Fig. 2). The crystallographic and instrumental data for the compounds **28**, **31**, and **32** has been summarized in Table 3 (see ESI† CIF file for details).

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

Conclusions

The developed methodology is new, concise, efficacious and $(TMS)_3SiH$-mediated toxic metal-free approach for deoxygenation under mild conditions. Moreover, it is compatible under microwave conditions and gives a new method to avoid the use of highly toxic *n*-Bu_3SnH for radical deoxygenation. The methodology is extremely important in terms for green chemistry perspectives, and it is selective for 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 the reagents and solvents used were of analytical grade. Laboratory grade dichloromethane was first distilled and then further purified and dried by distillation from calcium hydride. Dry toluene and all the reagents were purchased from Sigma-Aldrich Chemical Company, Inc., with >99% purity and were used without further purification. 2,2′-Azobis(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, which were analysed under either a UV lamp ($\lambda_{max} = 254$ nm) or by spraying with methanolic-H_2SO_4 solution and subsequent charring by heating at 100 °C. ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. Chemical shifts are given in ppm downfield from internal TMS; *J* values are given in Hz. Mass spectra were recorded using electrospray ionization mass spectrometry (ESI-MS). Infrared spectra were recorded as Nujol mulls in KBr plates. Elemental analysis was performed using a C, H, and N analyzer, and results were found to be within ±0.4% of the calculated values. The reactions under microwave conditions were carried out in a single-mode microwave reactor.

The single-crystal X-ray data of compounds were collected on an Xcalibur Eos (Oxford) CCD-Diffractometer using graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å). The data integration and reduction were processed with the 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 been drawn using the ORTEP software, as illustrated in Scheme 6 and Fig. 2. Further information on the crystal structure determination (excluding structure factors) has been given in Table 3.†

General procedure for the synthesis of benzyloxythioacyl benzotriazoles (11, 17, 22 and 25a–d)

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

General procedure for the MW-assisted deoxygenation

A solution of benzotriazolemethanethione **11**, **17**, **22** and **25a–d** (1.0 mmol) in anhydrous toluene, which was continuously stirred, was treated 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 of a non-contact calibrated infrared sensor, which monitored and controlled the temperature conditions of the reaction vessel located in the cavity of the instrument. For each reaction, the reaction temperature was 110 °C. After the completion of the reaction (monitored by TLC), the reaction mixture was concentrated *in vacuo*, 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 concentration

in vacuo. Purification using flash column chromatography afforded the products, namely, **12**, **19**, **23**, and **26a–d**.

Physical data of the developed compounds

Bis(1*H*-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)-1*H*-benzo[*d*][1,2,3]triazole-1-carbothioate (11).** The compound **10** (0.406 g, 1.0 mmol) after treatment with **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) to afford 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*-isopropylideneglucofuranose (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)(1*H*-benzotriazolylmethanethionyl)methyl)phenyl)-1′,2′-*O*-isopropylidine-α-D-xylofuranose-5′-1*H*-benzotriazolecarbothioate (17). The compound **16** (0.672 g, 2.0 mmol) after 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) to afford 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′-1*H*-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}; ^1H 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}; ^1H 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}; ^1H NMR (300 MHz, $CDCl_3$): δ 4.32–4.11 (m, 11H), 1.58 (bs, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 83.7, 69.3, 68.4 (3C), 68.2 (4C), 67.8, 60.7 ppm.

***O*-(Ferrocenylmethyl)-1*H*-benzo[*d*][1,2,3]triazole-1-carbothioate (22).** The compound **21** (0.434 g, 2.0 mmol) after 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) to afford 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}; ^1H 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}; ^1H 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}; ^1H 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}; ^1H 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-1*H*-benzo[*d*][1,2,3]triazole-1-carbothioate (25a).** The compound **24a** (0.641 g, 2.0 mmol) after 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) to afford 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}; ^1H 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-1*H*-benzo[*d*][1,2,3]triazole-1-carbothioate (25b).** The compound **24b** (0.49 g, 2.0 mmol) after 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) to afford 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}; ^1H 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 1*H*-benzo[*d*][1,2,3]triazole-1-carbothioate (25c).**[30] The compound **24c** (0.217 g, 2.0 mmol) after 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) to afford 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 1*H*-benzo[*d*][1,2,3]triazole-1-carbothioate (25d).** The compound **24d** (0.285 g, 2.0 mmol) after 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) to afford 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, 1043, 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)-1*H*-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), 7.61 (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-(1*N*-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-(2*N*-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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