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Indium(III) bromide catalyzed direct azidation of α-hydroxyketones using $TMSN_3$

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ABSTRACT

The direct catalytic azidation of 2-hydroxy-1,2,2-triarylethanones occurs at room temperature using 2 mol % of $InBr_3$ as Lewis acid and $TMSN_3$ as soluble azide source. 2-Azido-1,2,2-triarylethanones have been isolated in excellent yields. The role of aryl group and stereoelectronic factors indicate that the mechanism may involve the formation of a stable carbenium ion towards azidation.

1. Introduction

Azides represent an important class of compounds used for various organic transformations as they are the potential precursors for the synthesis of amines, nitrenes and heterocyclic compounds.[1] Azides are also used for the synthesis of antituberculosis 1,2,3-triazoles via 1,3-dipolar cycloaddition using click chemistry.[2] The azide functional group exists in anti HIV-1 drugs such as azidothymidine (AZT).[3] In recent years, α-azidoketones, a unique family of azides, have become the subject of interest as they are considered as versatile candidates for the synthesis of biologically active β-amino alcohols[4] and 1,3-oxazoles.[5] α-Azidoketones can thus serve as building blocks for a variety of potentially useful classes of compounds, but the synthetic procedure of α-azidoketones is very limited.

The frequently used method for the preparation of α-azidoketones involves the nucleophilic substitution of the corresponding α-substituted ketones having a good leaving group with sodium azide.[6] In such cases, preactivation of the α-hydroxyketone as their halide, mesylate, triflate, tosylate, nosylate or phosphate is required before α-azidation.[7] Moreover, various sodium salts that result in azidation with NaN_3 pose considerable problems in homogeneity, rate and workup of the reactions. To develop an economically and environmentally benign protocol, direct azidation of alcohols is highly desirable. However, the literature is devoid of such methods, except a single example in which azidation of benzoin has been carried out to obtain its α-azidoketone using NaN_3 as azide source and stoichiometric amounts of $BF_3 \cdot OEt_2$ as Lewis acid.[8] Thus, attention is still awaiting a precise method to synthesize α-azidoketones directly from α-hydroxyketones using catalytic quantity of Lewis acid.

Recently, direct catalytic azidation of vinyl carbinols and allylic alcohols has been reported to give corresponding azides using a combination of $BF_3 \cdot OEt_2/TMSN_3$ and $AgOTf/TMSN_3$, respectively.[9] Similarly, direct protocol for cyanation of various alcohols has been given by Chen and co-workers using $InBr_3$ and TMSCN.[10] It has been shown in these reactions that alcohols are activated by Lewis acids to undergo nucleophilic substitution, and $InBr_3$ proved to be an effective catalyst for such activation. Considering the above-mentioned aspects, we hypothesized that it may be possible to activate the hydroxyl group of α-hydroxyketones for direct azidation with Lewis acid such as $InBr_3$. The prior transformation of alcohols to better leaving groups can thus be completely eliminated. This will provide an effective and general method to replace OH by N_3 directly. Therefore, we report herein a direct catalytic azidation of α-hydroxyketones and other alcohols using $InBr_3$ as Lewis acid and $TMSN_3$ as soluble azide source.

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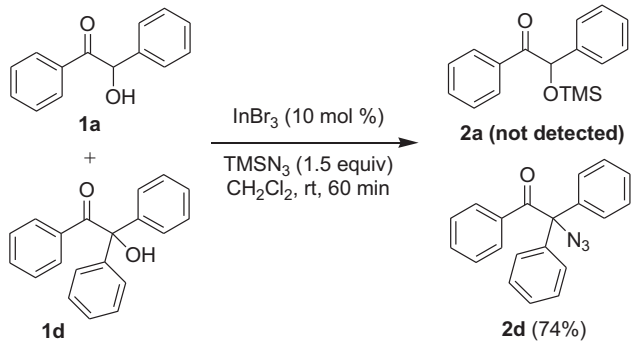
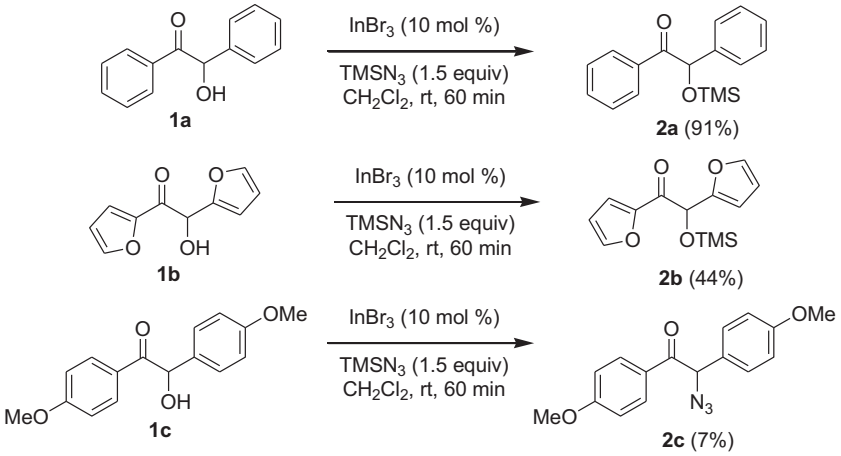
2. Results and discussion

In order to investigate the above hypothesis that nucleophilic substitution of hydroxyl group by azide ion (N_3^-) can be carried out directly from α-hydroxyketones, 2-hydroxy-1,2,-diphenylethanone (**1a**) was selected (Scheme 1). To this α-hydroxyketone, 10 mol % of $InBr_3$ and 1.5 equiv of $TMSN_3$ in CH_2Cl_2 at room temperature were added. After 1 h stirring, the reactant underwent complete conversion to the product, as analyzed by TLC. Subsequently the reaction was quenched with water. After usual workup, the product was identified as trimethylsilyl protected benzoin (**2a**) instead of 2-azido-1,2-diphenylethanone on the basis of various spectroscopic data including IR spectrum. A singlet for nine protons at δ 0.02 in ^1H NMR confirms the presence of trimethylsilyl group. Similar results were obtained during the azidation of furoin (**1b**) under similar reaction conditions (Scheme 1). However, in the case anisoin (**1c**), a small amount of its corresponding azide **2c** was observed[11] (Scheme 1). This outcome suggested that there must be some electronic factors, which results in the azidation of anisoin.

(Scheme 3). After 1 h stirring, the TLC of the reaction mixture indicated the presence of a single product, which was identified as 2-azido-1,2,2-triphenylethanone (**2d**). The exclusive formation of **2d** leaving out any possibility of **2a**, clearly demonstrates the crucial role of the phenyl ring towards the azidation.

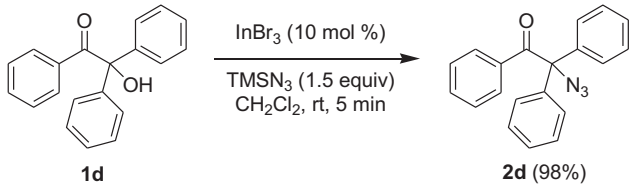


Scheme 3. Reaction of equimolar mixture of benzoin (**1a**) and phenyl benzoin (**1d**) with $TMSN_3$ in the presence of $InBr_3$.



Scheme 1. Reaction of benzoin (**1a**), furoin (**1b**) and anisoin (**1c**) with $TMSN_3$ in the presence of $InBr_3$.

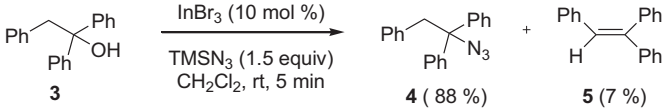
Interestingly, in the case of phenyl benzoin (**1d**), the azidation occurred smoothly within 5 min under the same reaction conditions (Scheme 2). The product was identified as 2-azido-1,2,2-triphenylethanone (**2d**) on the basis of various spectroscopic data. The presence of a sharp peak at wave number 2102 cm^{-1} in the IR spectrum confirms the presence of the azide group (−N_3). The formation of **2d** from **1d** suggests that extra phenyl group plays a decisive role in the azidation process. The introduction of one more phenyl group at the carbon bearing hydroxyl group in **1a** (resulting in **1d**) not only facilitates the direct azidation, but also reduces the time taken to complete the reaction to greater extent.[12] Analysis of the combined outcome from Schemes 1 and 2 indicates that stereoelectronic factors are playing significant role in driving the azidation reaction.



Scheme 2. Reaction of phenyl benzoin (**1d**) with $TMSN_3$ in the presence of $InBr_3$.

To investigate the effect of phenyl group further, a synergistic experiment was carried out. Both benzoin and phenyl benzoin in equimolar quantities were treated with 1 equiv of $TMSN_3$ and 10 mol % of $InBr_3$ in dichloromethane at room temperature

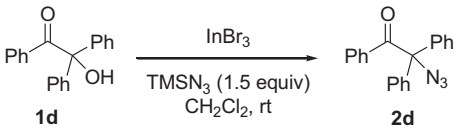
Similarly, in order to study the effect of electron withdrawing carbonyl group, azidation of 1,1,2-triphenylethanol (**3**) has been carried out. Interestingly, the formation of corresponding azide **4** occurred in excellent yield (88%) besides 1,1,2-triphenylethene (**5**) (yield 7%) as dehydration product (Scheme 4). This experiment suggests that the exclusive interaction of the hydroxyl group with $InBr_3$ is responsible for the formation of α-azidoketones. Presence of an electron withdrawing carbonyl group at the carbon bearing OH group has minimal role in driving the azidation process.



Scheme 4. Reaction of 1,1,2-triphenylethanol with $TMSN_3$ in the presence of $InBr_3$.

Based on the above observations, 2-hydroxy-1,2,2-triphenylethanone[13] (**1d**) was selected as a model α-hydroxyketone to optimize the reaction conditions for azidation. The reaction of **1d** with 10 mol % of $InBr_3$ and 1.5 equiv of $TMSN_3$ in various solvents at room temperature was studied (Table 1). Perusal of Table 1 showed that the reaction occurred smoothly in CH_2Cl_2 within 5 min. The absence of product or its poor yield in the case of acetone, acetonitrile, ether and THF may be due to their coordinating behaviour with the catalyst. Further attention was paid to test the efficiency of $InBr_3$ as catalyst in CH_2Cl_2. For this purpose, the catalytic amount of $InBr_3$ was decreased to 0.5 mol % (entry 10),

Table 1
Optimization[a] of reaction conditions using $InBr_3$ and $TMSN_3$



1d **2d**

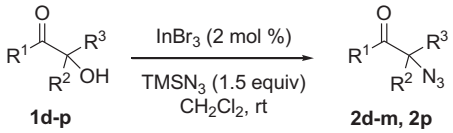
Entry	Solvent	$InBr_3$ (mol %)	Time	Yield[b] (%)
1	CH_2Cl_2	10	5 min	98
2	Acetone	10	24 h	0
3	Acetonitrile	10	24 h	0
4	Ether	10	24 h	3
5	THF	10	24 h	7
6	Chloroform	10	1 h	84
7	CH_2Cl_2	5	5 min	97
8	*CH_2Cl_2*	*2*	*10 min*	*95*
9	CH_2Cl_2	1	5 h	86
10	CH_2Cl_2	0.5	5 h	52

[a] Reactions were performed on 0.35 mmol scale of 2-hydroxy-1,2,2-triphenylethanone in 5 mL of various solvents.
[b] Isolated yields.

though it turned out to give lower yield (52%) in 5 h. Finally using 2 mol % of the catalyst, gave the α-azidoketone equally well as that of 10 mol % of $InBr_3$ (Table 1, entry 8).

The successful azidation of 2-hydroxy-1,2,2-triphenylethanone, which delineated the role of second phenyl group prompted us to investigate the azidation of other α-hydroxyketones. Therefore, a variety of other α-hydroxyketones **1e**–**m** was treated with 2 mol % of $InBr_3$ and 1.5 equiv of $TMSN_3$ in CH_2Cl_2 (Table 2). All α-hydroxyketones were converted to the corresponding azides in excellent yields within a short span under the optimized reaction conditions. In the case of **1k** (entry 8), a trace amount of corresponding benzofuran derivative **6** was also formed during azidation (Table 2, entry 8).[14] In order to study the reactivity of α-hydroxyketones having alkyl groups, azidation of α-hydroxyketones **1n** (entry 11) and **1o** (entry 12) was undertaken.[15] However, they failed to react. To observe the reactivity towards subtle variations in the electronic effects, reaction with an additional methoxy group at *para*-position of **1o** (**1p**, entry 13) was carried out. The azidation did take place in this case, though with poor yield (21%), clearly demonstrating the role of electronic factors towards azidation. All new

Table 2
α-Azidation of various α-hydroxyketones **1d**–**p**[a]



1d-p **2d-m, 2p**

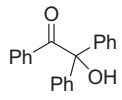
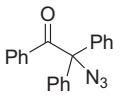
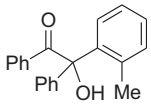
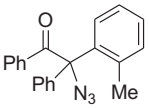
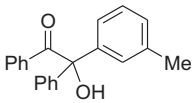
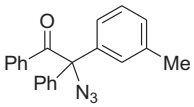
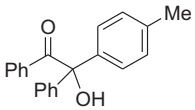
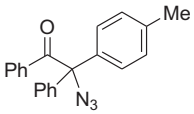
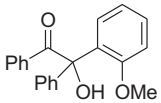
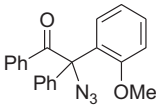
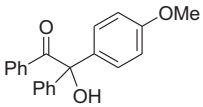
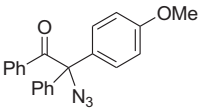
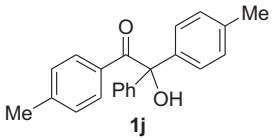
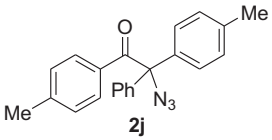
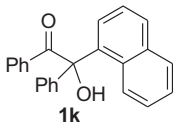
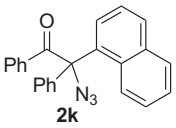
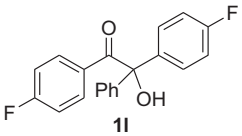
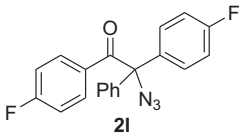
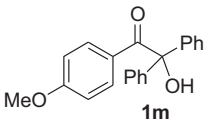
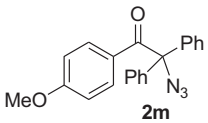
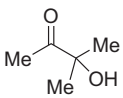
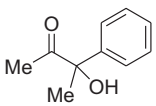
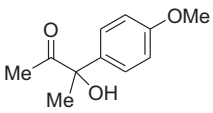
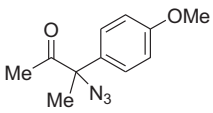
Entry	α-Hydroxyketone	α-Azidoketone	Time (min)	Yield[b] (%)
1	 **1d**	 **2d**	10	95
2	 **1e**	 **2e**	10	98
3	 **1f**	 **2f**	13	94
4	 **1g**	 **2g**	15	96
5	 **1h**	 **2h**	50	96
6	 **1i**	 **2i**	12	91

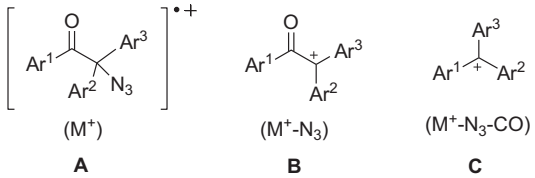
Table 2 (*continued*)

Entry	α-Hydroxyketone	α-Azidoketone	Time (min)	Yield[b] (%)
7	 **1j**	 **2j**	22	93
8	 **1k**	 **2k**	20	91[c]
9	 **1l**	 **2l**	15	97
10	 **1m**	 **2m**	30	86
11	 **1n**	NR[d]	120	—
12	 **1o**	NR[d]	120	—
13	 **1p**	 **2p**	120	21

[a] Reactions were performed on 0.70 mmol scale of α-hydroxyketones in CH_2Cl_2 (5 mL) containing $InBr_3$ (2 mol %) and $TMSN_3$ (1.5 equiv).
[b] Isolated yields.
[c] Trace amount of 3-(1-naphthyl)-2-phenyl benzofuran (**6**) was also formed (see Experimental).[14]
[d] No reaction.

compounds have been characterized using various spectral data (see Experimental).

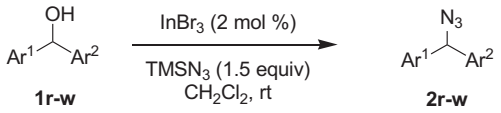
The IR spectra of α-azidoketones showed absorption bands for the azido group in the range of 2102–2104 cm^{-1}. The carbonyl stretching frequencies in all the ketones are characteristics of conjugative aryl ketones in the range of 1678–1694 cm^{-1}. Compound **2d** absorbs at 1694 cm^{-1} and **2m** at 1678 cm^{-1}. The lowest frequency for the carbonyl at 1678 cm^{-1} is the result of a prominent resonance effect of *p*-OMe group present in the phenyl ring in **2m**. ^1H NMR of all ketones displayed signals in the range of δ 6.69–7.86 for aromatic protons and peaks for other substituents at expected chemical shift values. Compounds **2d**–**g** and **2i**–**m** showed *ortho* aromatic protons (2H) downfield in the range of δ 7.64–7.86 due to anisotropic effect of the carbonyl group whereas in case of **2h**, it seems that *ortho* protons are merged into multiplets with other aromatic protons. ^{13}C NMR spectra showed expected chemical shifts in the range of δ 194.8–198.2 for carbonyl carbons. The molecular ion peak (**A**) in ESI mass spectra was absent in all α-azidoketones **2d**–**m** (Scheme 5). The base peak appeared at *m*/*z* M^+-N_3 (**B**) in **2h**, **2k** and **2p** by the loss of azido group (Scheme 5). Other α-azidoketones showed base peak at *m*/*z* M^+-N_3-CO (**C**) by the facile loss of both N_3 as well as CO group (Scheme 5). It may be due to the loss of CO from **B** to give more stable triaryl methyl cation (**C**).

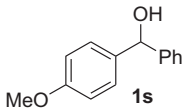
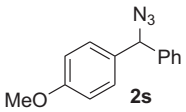
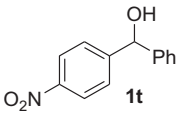
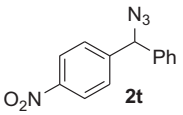
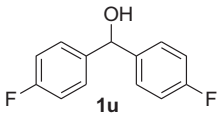
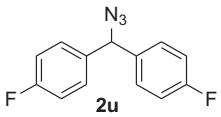
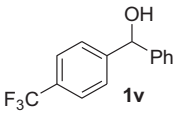
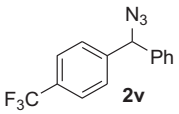
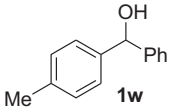
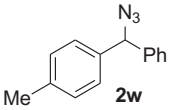


Scheme 5. ESI mass fragmentation of 2-azido-1,2,2-triarylethanones.

Keeping in view that 2-hydroxy-1,2,2-triphenylethanone (**1d**) has benzoyl and benzhydrol moieties, it was of interest to explore our present method for the azidation of alcohols without benzoyl moiety such as benzyl alcohol and benzhydrol. In addition, these two systems will help us to extrapolate the role of the phenyl ring in benzhydrol, and –COAr in α-hydroxyketones for the azidation. Therefore, benzyl alcohol (**1q**) and 1,1-diphenylmethanol (**1r**, Table 3, entry 1) were also treated with $InBr_3$ and $TMSN_3$. Interestingly, 1-azido-1,1-diphenylmethane (**2r**) was formed from

Table 3
Azidation of 1,1-diarylmethanols[a]



Entry	Alcohol	Product	Time (min)	Yield[b] (%)
1	 **1r**	 **2r**	5	97
2	 **1s**	 **2s**	5	98
3	 **1t**	 **2t**	55	89
4	 **1u**	 **2u**	30	90
5	 **1v**	 **2v**	25	88
6	 **1w**	 **2w**	10	93

[a] Reactions were performed on 1 mmol scale of 1,1-diarylmethanol in CH_2Cl_2 (5 mL) using 1.5 equiv of $TMSN_3$.
[b] Isolated yields obtained after flash chromatography.

1,1-diphenylmethanol in excellent yield within 5 min. This result suggested that there is not much effect of the −COAr group present at the carbon bearing the hydroxyl group in α-hydroxyketones.[16] The reaction did not occur in the case of benzyl alcohol, which also highlights the role of phenyl group (see Experimental). Azidation of various benzhydrols **1s**–**w** having electron withdrawing group (EWG) and electron donating group (EDG) has been carried out to study the electronic effects during azidation (Table 3). It has been found that the reaction of benzhydrol having electron withdrawing nitro group (**1t**, Table 3, entry 3) proceeds slowly. All other benzhydrols gave corresponding azides within a short period of time. Benzhydryl azides have been characterized by various spectral data (see Experimental). The IR spectra of compounds **2r**–**w** showed absorption bands for the azido group in the range of 2097–2102 cm^{-1}. ^1H NMR spectra of azides **2r**–**w** displayed characteristic singlet at δ 5.55–5.72 (s, 1H) for benzhydrylic protons and multiplets at δ 6.79–8.15 for the aromatic protons.

It is worth linking all the information obtained from the above experiments that are useful for predicting the mechanism. The azidation of benzoin (2-hydroxy-1,2-diphenylethanone) under identical conditions does not take place rather it gives the trimethylsilyl protected benzoin (TMS ether). The azidation of phenyl benzoins (2-hydroxy-1,2,2-triarylethanones), however, occurs smoothly. These experiments indicate that substitution of OH at carbon bearing two phenyl groups occurs with $TMSN_3$ where N_3^- acts as nucleophile. This finds support by the azidation of various 1,1-diarylmethanols. The azidation of enantioenriched 1-(4-nitrophenyl)-1-phenylmethanol (**1t**), however, results in a racemic mixture of 1-azido-1-(4-nitrophenyl)-1-phenylmethane (**2t**). The formation of a carbenium ion as an intermediate may thus be considered as one of the possibilities towards azidation. The formation of a trace amount of 1,1,2-triphenylethene (**5**) via elimination of water from **3** also falls in the above line. Similarly, the isolation of 3-(1-naphthyl)-2-phenyl benzofuran (**6**) as a rearrangement product in α-hydroxyketone **1k** indicates the intermediacy of an α-ketocarbenium ion.[16]

3. Conclusions

An economically and environmentally benign protocol for the azidation of various alcohols to give their corresponding azides has been uncovered. Various α-hydroxyketones and 1,1-diarylmethanols are converted to α-azidoketones and 1-azido-1,1-diarylmethanes, respectively, using $TMSN_3$ as a soluble azide source and catalytic amount of $InBr_3$ as Lewis acid. There is no need for the preactivation of α-hydroxyketones prior to azidation. The formation of α-azidoketones from α-hydroxyketones except benzoin (**1a**) and furoin (**1b**) indicates the crucial role of aryl group and stereoelectronic factors towards azidation. The successful azidation of benzhydrols **1r**–**w** and 1,1,2-triphenylethanol (**3**) suggests that the presence of carbonyl group in α-hydroxyketones has a minimal role in driving the azidation process. Thus, through this protocol, an efficient strategy for the synthesis of an important class of organic azides has been put forward. Further work is to discover the catalytic system and/or soluble azide source for enantioselective azidation of α-hydroxyketones.

4. Experimental

4.1. Equipments/chemicals

Melting points were recorded in open capillaries and are uncorrected. IR spectra were recorded with Perkin Elmer IR 1800 spectrophotometer. A thin film or KBr pellets were used to record the FTIR spectra. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions on Bruker Avance II 400 NMR spectrometer operating at 400 MHz and 100.62 MHz, respectively. Chemical shifts (δ) are reported in parts per million downfield from tetramethyl silane as internal standard. Coupling constants (J) are in hertz (Hz). Multiplicity of the signal is defined as 's' (singlet), 'd' (doublet), 't' (triplet), 'q' (quartet), 'm' (multiplet). Mass spectra were obtained with Waters Q-ToF Micro mass spectrometer running under Mass Lynx version 4.0 software and equipped with an ESI source. Relative intensities are given in parentheses. TLC analyses were performed using aluminium backed plates pre-coated with silica gel containing fluorescent material and examining them under UV light (λ=254 and 355 nm). Azidotrimethylsilane ($TMSN_3$), indium(III) bromide, 3-hydroxy-3-methyl-2-butanone, benzil and substituted benzils were purchased from Sigma–Aldrich and used as such without purification. 2-Hydroxy-1,2,2-triarylethanones were prepared by reacting the appropriate Grignard reagent with benzil or substituted benzil. Dichloromethane (DCM) was dried over phosphorus pentoxide and distilled before use. HPLC analysis for compound **1t** was performed on Chiralcel OD column by using hexane/ethylacetate (95:5) as eluent with flow rate of 0.5 mL/min. While for **2t**, HPLC analysis was performed on Chiralpak ASH column by using hexane/ethyl acetate (95:2) as eluent with flow rate of 0.5 mL/min.[17] Flash chromatography was performed by using 40–63 μm silica gel (230–400 mesh) and applying nitrogen pressure from the top of the column.[18]

4.2. 1,2-Diphenyl-2-trimethylsilanyloxyethanone[19] (2a)

A solution of 2-hydroxy-1,2-diphenyl ethanone, **1a** (200 mg, 0.94 mmol) in dry CH_2Cl_2 (5 mL) and $TMSN_3$ (163 mg, 1.41 mmol) were placed in a 25 mL round-bottom flask fitted with guard tube. $InBr_3$ (17 mg, 0.094 mmol) was added to this reaction mixture. The contents were stirred at room temperature for 60 min. The reaction was quenched with water. The product was extracted with CH_2Cl_2 (3×15 mL), washed with 10% Na_2CO_3 (20 mL), water (20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give brownish oil. Purification by flash chromatography afforded the product **2a** as white solid. Mp: 80–81 °C. Yield: 91%; ^{1}H NMR (400 MHz, $CDCl_3$): 7.89 (2H, d, ^3J=7.1 Hz, ArH), 7.35–7.39 (3H, m, ArH), 7.21–7.27 (4H, m, ArH), 7.15–7.17 (1H, m, ArH), 5.73 (1H, s, CH), 0.02 (9H, s, 3×CH_3); ^{13}C NMR (100.53 MHz, $CDCl_3$): 198.6, 138.9, 134.7, 132.9, 129.7, 128.7, 128.3, 128.0, 126.4, 79.5, 0.1.

4.3. 1,2-Bis(2-furyl)-2-trimethylsilanyloxyethanone[20] (2b)

A solution of 2-hydroxy-1,2-bis(2-furyl) ethanone, **1b** (200 mg, 1.04 mmol) in dry CH_2Cl_2 (5 mL) and $TMSN_3$ (180 mg, 1.56 mmol) were placed in a 25 mL round-bottom flask fitted with guard tube. $InBr_3$ (37 mg, 0.104 mmol) was added to this reaction mixture. The contents were stirred at room temperature for 60 min. The reaction was quenched with water. The product was extracted with CH_2Cl_2 (3×15 mL), washed with 10% Na_2CO_3 (20 mL), water (20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give brownish oil. Purification by flash chromatography afforded the product **2b** as white solid. Yield: 44%; ^{1}H NMR (400 MHz, $CDCl_3$): 7.53 (1H, d, J=1.3 Hz, ArH), 7.36 (1H, d, J=3.6 Hz, ArH), 7.31 (1H, d, J=1.2 Hz, ArH), 6.45–6.46 (1H, m, ArH), 6.25–6.29 (2H, m, ArH), 5.68 (1H, s, CH), 0.06 (9H, s, 3×CH_3); ^{13}C NMR (100.53 MHz, $CDCl_3$): 184.5, 151.3, 150.2, 147.0, 142.9, 120.2, 112.2, 110.7, 109.1, 72.1, −0.1.

4.4. 2-Azido-1,2-bis(4-methoxyphenyl) ethanone[21] (2c)

A solution of 2-hydroxy-1,2-bis(4-methoxyphenyl) ethanone, **1c** (500 mg, 1.84 mmol) in dry CH_2Cl_2 (5 mL) and $TMSN_3$ (317 mg, 2.76 mmol) were placed in a 25 mL round-bottom flask fitted with guard tube. $InBr_3$ (66 mg, 0.18 mmol) was added to this reaction mixture. The contents were stirred at room temperature for 60 min. The reaction was quenched with water. The product was extracted with CH_2Cl_2 (3×15 mL), washed with 10% Na_2CO_3 (20 mL), water (20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give brownish oil. Purification by flash chromatography afforded the product **2c** as light yellowish oil. Yield: 7%; IR (neat): 2933, 2839, 2095, 1677, 1595, 1573, 1508, 1459, 1441, 1305, 1251, 1166, 1027 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.77 (2H, d, J=8.9 Hz, ArH), 7.22 (2H, d, J=8.7 Hz, ArH), 6.82 (2H, d, J=8.7 Hz, ArH), 6.77 (2H, d, J=8.9 Hz, ArH), 5.55 (1H, s, CH), 3.73 (3H, s, OCH_3), 3.69 (3H, s, OCH_3); ^{13}C NMR (100.53 MHz, $CDCl_3$): 192.9, 163.8, 160.2, 132.3, 131.2, 129.6, 127.2, 126.2, 114.8, 113.9, 67.1, 55.4, 55.2.

4.5. 1-Azido-1,1,2-triphenylethane (4)

A solution of 1,1,2-triphenylethanol (**3**) (200 mg, 0.73 mmol) in dry CH_2Cl_2 (5 mL) and $TMSN_3$ (127 mg, 1.09 mmol) were placed in a 25 mL round-bottom flask fitted with guard tube. $InBr_3$ (5.0 mg, 0.014 mmol) was added to this reaction mixture. The contents were stirred at room temperature for 10 min. The reaction was quenched with water. The product was extracted with CH_2Cl_2 (3×15 mL), washed with 10% Na_2CO_3 (20 mL), water (20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give brownish oil. Purification by flash chromatography afforded the product **4**. White solid. Mp: 86–87 °C. Yield: 88%; R_f (5% hexane/ethylacetate) 0.70; IR (KBr): 3060, 3029, 2925, 2105, 1599, 1584, 1495, 1445, 1376, 1318, 1257, 1078 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.15–7.24 (10H, m, ArH), 6.99–7.08 (3H, m, ArH), 6.64–6.67 (2H, m, ArH), 3.58 (2H, s, CH_2); ^{13}C NMR (100.53 MHz, $CDCl_3$): 142.6, 135.6, 130.5, 128.1, 127.6, 127.5, 126.5, 73.2, 45.0; HRMS (ESI): calcd for $C_{20}H_{17}$ (M^+-N_3) m/z 257.1325. Found 257.1362.

4.6. General procedure for the preparation of α-azidoketones

A solution of 2-hydroxy-1,2,2-triarylethanones, **1d**–**p** (200 mg, 0.58–0.66 mmol) in dry CH_2Cl_2 (5 mL) and $TMSN_3$ (1.5 equiv) were placed in a 25 mL round-bottom flask (RBF) fitted with guard tube. $InBr_3$ (2 mol %) was added to this reaction mixture. The contents were stirred at room temperature and the progress of reaction was monitored by TLC analyses. After stirring the contents for appropriate time period, the reaction was quenched with water. The product was extracted with CH_2Cl_2 (3×15 mL), washed with 10% Na_2CO_3 (20 mL), water (20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give brownish oil. Purification by flash chromatography afforded the products **2d**–**m**, **2p** and **6**.

*4.6.1. 2-Azido-1,2,2-triphenylethanone (**2d**).* White solid. Mp: 55–56 °C. Yield: 95%; R_f (10% hexane/ethylacetate) 0.53; IR (KBr): 3054, 3032, 2102, 1694, 1594, 1492, 1445, 1254, 1203, 1171, 1032 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.84–7.86 (2H, m, ArH), δ 7.33–7.50 (13H, m, ArH); ^{13}C NMR (100.53 MHz, $CDCl_3$): 197.1, 138.7, 135.7, 132.7, 130.3, 128.7, 128.6, 128.3, 128.1, 80.3; ESI-MS: 272 (10.7), 271 (58.8, M^+-N_3), 244 (16.8), 243 (100, M^+-N_3-CO), 228

(5.2), 165 (23.1%); HRMS (ESI): calcd for $C_{20}H_{15}O$ (M^+-N_3) *m*/*z* 271.1117. Found 271.1117.

*4.6.2. 2-Azido-2-(2-methylphenyl)-1,2-diphenylethanone (**2e**).* Colourless oil. Yield: 98%; R_f (10% hexane/ethylacetate) 0.54; IR (thin film): 3061, 3022, 2973, 2869, 2103, 1681, 1596, 1578, 1485, 1445, 1241, 1182 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 7.65–7.67 (2H, m, ArH), 7.43–7.46 (2H, m, ArH), 7.31–7.40 (4H, m, ArH), 7.17–7.25 (4H, m, ArH), 7.01–7.05 (1H, m, ArH), 6.77 (1H, d, ^3J=8 Hz, ArH), 2.20 (3H, s, CH_3); ^{13}C NMR (100.53 MHz, $CDCl_3$): 197.0, 137.8, 137.6, 137.5, 135.9, 132.5, 132.1, 130.2, 129.8, 129.0, 128.9, 128.6, 128.2, 127.9, 125.6, 80.7, 21.8; ESI-MS: 350 (5.4, M+Na), 286 (10.3), 285 (45, M^+-N_3), 258 (20.4), 257 (100, M^+-N_3-CO), 196 (12), 179 (20.2), 165 (5.8), 105 (4.7%); HRMS (ESI): calcd for $C_{21}H_{17}O$ (M^+-N_3) *m*/*z* 285.1274. Found 285.1276.

*4.6.3. 2-Azido-2-(3-methylphenyl)-1,2-diphenylethanone (**2f**).* Colourless oil. Yield: 94%; R_f (10% hexane/ethylacetate) 0.57; IR (thin film): 3060, 2922, 2860, 2103, 1681, 1596, 1578, 1488, 1446, 1230, 1182 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.72–7.74 (2H, m, ArH), 7.15–7.38 (9H, m, ArH), 7.07–7.10 (3H, m, ArH), 2.25 (3H, s, CH_3); ^{13}C NMR (100.53 MHz, $CDCl_3$): 197.1, 138.8, 138.5, 138.4, 135.8, 132.6, 130.2, 129.4, 128.8, 128.6, 128.5, 128.4, 128.2, 128.0, 125.3, 80.3, 21.6; ESI-MS: 350 (14, M+Na), 286 (12.8), 285 (56.6, M^+-N_3), 258 (20.5), 257 (100, M^+-N_3-CO), 196 (18.8), 179 (17.2), 165 (4.1%); HRMS (ESI): calcd for $C_{21}H_{17}O$ (M^+-N_3) *m*/*z* 285.1274. Found 285.1279.

*4.6.4. 2-Azido-2-(4-methylphenyl)-1,2-diphenylethanone (**2g**).* Colourless oil. Yield: 96%; R_f (10% hexane/ethylacetate) 0.60; IR (thin film): 3058, 3027, 2921, 2102, 1682, 1596, 1573, 1510, 1492, 1446, 1237, 1183 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.72–7.75 (2H, m, ArH), 7.36–7.38 (1H, m, ArH), 7.21–7.33 (7H, m, ArH), 7.10–7.16 (4H, m, ArH), 2.28 (3H, s, CH_3); ^{13}C NMR (100.53 MHz, $CDCl_3$): 197.1, 138.8, 138.5, 135.7, 135.6, 132.6, 130.2, 129.3, 128.6, 128.5, 128.3, 128.2, 128.0, 80.2, 21.1; ESI-MS: 350 (15.1, M+Na), 286 (12.3), 285 (55.9, M^+-N_3), 258 (21.5), 257 (100, M^+-N_3-CO), 196 (11.3), 179 (14.7), 165 (3.4%); HRMS (ESI): calcd for $C_{20}H_{17}$ (M^+-N_3-CO) *m*/*z* 257.1325. Found 257.1340.

*4.6.5. 2-Azido-2-(2-methoxyphenyl)-1,2-diphenylethanone (**2h**).* White solid. Mp: 83–84 °C. Yield: 96%; R_f (10% hexane/ethylacetate) 0.48; IR (KBr): 3061, 2936, 2837, 2103, 1681, 1597, 1486, 1446, 1247, 1180 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.57–7.63 (4H, m, ArH), 7.31–7.38 (4H, m, ArH), 7.22–7.28 (3H, m, ArH), 6.86 (1H, d, ^3J=8 Hz, ArH), 6.79–6.83 (1H, m, ArH), 6.69–6.72 (1H, m, ArH), 3.64 (3H, s, OCH_3); ^{13}C NMR (100.53 MHz, $CDCl_3$): 197.4, 156.3, 137.0, 136.9, 131.8, 130.4, 129.8, 129.3, 129.2, 128.7, 128.4, 128.2, 127.8, 120.7, 111.5, 78.1, 55.4; ESI-MS: 366 (23.6, M+Na), 302 (22.8), 301 (100, M^+-N_3), 274 (14.7), 273 (66.7, M^+-N_3-CO), 210 (12.3), 195 (10.5), 167 (26.8%); HRMS (ESI): calcd for $C_{21}H_{17}O_2$ (M^+-N_3) *m*/*z* 301.1223. Found 301.1228.

*4.6.6. 2-Azido-2-(4-methoxyphenyl)-1,2-diphenylethanone (**2i**).* Colourless oil. Yield: 91%. R_f (10% hexane/ethylacetate) 0.41; IR (thin film): 3060, 3035, 2956, 2837, 2484, 2103, 1681, 1606, 1579, 1493, 1445, 1372, 1300, 1253, 1181, 1078 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.64 (2H, d, *J*=7.5 Hz, ArH), 7.13–7.30 (8H, m, ArH), 7.08 (2H, d, *J*=6.8 Hz, ArH), 6.75 (2H, d, *J*=6.8 Hz, ArH), 3.65 (3H, s, OCH_3); ^{13}C NMR (100.53 MHz, $CDCl_3$): 198.2, 159.5, 138.9, 135.7, 132.6, 130.6, 130.2, 129.7, 128.6, 128.5, 128.2, 128.0, 113.9, 80.1, 55.3; ESI-MS: 366 (11.9, M+Na), 302 (18), 301 (82.5, M^+-N_3), 274 (21.2), 273 (100, M^+-N_3-CO), 212 (8.6), 195 (6.8%); HRMS (ESI): calcd for $C_{20}H_{17}O$ (M^+-N_3-CO) *m*/*z* 273.1274. Found 273.1255.

*4.6.7. 2-Azido-1,2-bis(4-methylphenyl)-2-phenylethanone (**2j**).* Colourless oil. Yield: 93%. R_f (10% hexane/ethylacetate) 0.70; IR (thin film): 3057, 3028, 2953, 2922, 2867, 2103, 1681, 1605, 1570, 1510, 1492, 1446, 1408, 1249, 1182 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.65–7.67 (2H, m, ArH), 7.24–7.32 (5H, m, ArH), 7.09–7.16 (4H, m, ArH), 7.02 (2H, d, *J*=8 Hz, ArH), 2.27 (3H, s, CH_3), 2.24 (3H, s, CH_3); ^{13}C NMR (100.53 MHz, $CDCl_3$): 196.4, 143.5, 139.0, 138.4, 135.8, 132.9, 130.5, 129.3, 128.7, 128.5, 128.4, 128.3, 128.2, 80.2, 21.6, 21.1; ESI-MS: 364 (19.9, M+Na), 301 (20.3), 299 (57.2, M^+-N_3), 272 (24.9), 271 (100, M^+-N_3-CO), 196 (10), 79 (7.6%); HRMS (ESI): calcd for $C_{22}H_{19}O$ (M^+-N_3) *m*/*z* 299.1430. Found 299.1463.

*4.6.8. 2-Azido-2-(1-naphthyl)-1,2-diphenylethanone (**2k**).* White solid. Mp: 104–105 °C. Yield: 91%; R_f (10% hexane/ethylacetate) 0.51; IR (KBr): 3059, 2954, 2926, 2104, 1682, 1596, 1578, 1493, 1366, 1240, 1181 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.84 (1H, d, *J*=8.4 Hz, ArH), 7.76–7.80 (2H, m, ArH), 7.70–7.72 (2H, m, ArH), 7.46–7.49 (2H, m, ArH), 7.31–7.41 (6H, m, ArH), 7.14–7.27 (3H, m, ArH), 7.02 (1H, d, *J*=7.2 Hz, ArH); ^{13}C NMR (100.53 MHz, $CDCl_3$): 197.4, 137.7, 136.0, 135.6, 134.5, 132.6, 130.9, 130.5, 130.3, 129.2, 129.1, 128.9, 128.8, 128.4, 128.0, 126.5, 126.1, 125.8, 124.4, 80.8; ESI-MS: 386 (12.8, M+Na), 322 (28.7), 321 (100, M^+-N_3), 294 (6), 293 (15, M^+-N_3-CO), 215 (17.6), 179 (5), 105 (4.4%); HRMS (ESI): calcd for $C_{23}H_{17}$ (M^+-N_3-CO) *m*/*z* 293.1325. Found 293.1381.

*4.6.9. 3-(1-Naphthyl)-2-phenyl benzofuran (**6**).* White solid. Mp: 92–93 °C (lit.[14b] mp 94–95 °C). Yield: 63%; R_f (10% hexane/ethylacetate) 0.57; ^1H NMR (400 MHz, $CDCl_3$): 7.83 (1H, d, *J*=8.1 Hz, ArH), 7.63–7.68 (2H, m, ArH), 7.44–7.48 (8H, m, ArH), 7.28–7.32 (1H, m, ArH), 7.14–7.21 (4H, m, ArH); ^{13}C NMR (100.53 MHz, $CDCl_3$): 151.4, 150.1, 134.7, 131.0, 130.9, 130.6, 129.4, 128.9, 128.4, 128.3, 128.2, 127.8, 126.2, 126.0, 124.2, 123.6, 123.1, 119.5, 112.2.

*4.6.10. 2-Azido-1,2-bis(2-fluorophenyl)-2-phenylethanone (**2l**).* Colourless oil. Yield: 97%; R_f (10% hexane/ethylacetate) 0.56; IR (thin film): 3067, 2926, 2104, 1688, 1597, 1504, 1447, 1408, 1233, 1159 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.80–7.84 (2H, m, ArH), 7.31–7.37 (3H, m, ArH), 7.25–7.30 (2H, m, ArH), 7.18–7.22 (2H, m, ArH), 6.99–7.03 (2H, m, ArH), 6.91–6.99 (2H, m, ArH); ^{13}C NMR (100.53 MHz, $CDCl_3$): 194.9, 165.2 (d), 162.5 (d), 138.3, 134.5 (d), 133.2 (d), 131.4 (d), 130.3 (d), 128.9, 128.8, 127.9, 115.5 (d), 115.3 (d), 79.5; ESI-MS: 372 (6.4, M+Na), 308 (11.9), 307 (47.3, M^+-N_3), 280 (24.5), 279 (100, M^+-N_3-CO), 200 (69.7), 123 (44.3%); HRMS (ESI): calcd for $C_{20}H_{13}F_2O$ (M^+-N_3) *m*/*z* 307.0929. Found 307.0927.

*4.6.11. 2-Azido-1-(4-methoxyphenyl)-2,2-diphenylethanone (**2m**).* Colourless oil. Yield: 86%; R_f (10% hexane/ethylacetate) 0.50; IR (thin film): 3060, 3033, 2932, 2839, 2103, 1678, 1599, 1573, 1509, 1493, 1446, 1420, 1310, 1246, 1172 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.80 (2H, d, *J*=7.8 Hz, ArH), 7.24–7.32 (10H, m, ArH), 6.70 (2H, d, *J*=7.8 Hz, ArH), 3.70 (3H, s, OCH_3); ^{13}C NMR (100.53 MHz, $CDCl_3$): 194.8, 163.1, 139.0, 133.0, 128.6, 128.4, 128.3, 127.9, 113.3, 80.1, 55.4; ESI-MS: 366 (6.0, M+Na), 302 (6.5), 301 (29, M^+-N_3), 274 (20.4), 273 (100, M^+-N_3-CO), 195 (11.2), 135 (4.2%); HRMS (ESI): calcd for $C_{20}H_{17}O$ (M^+-N_3-CO) *m*/*z* 273.1274. Found 273.1279.

*4.6.12. 3-Azido-3-(4-methoxyphenyl)-2-butanone (**2p**).* Light yellowish oil. Yield: 21%; R_f (5% hexane/ethylacetate) 0.45; IR (thin film): 2936, 2838, 2091, 1718, 1607, 1581, 1509, 1462, 1375, 1354, 1301, 1246, 1179, 1092, 1029 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.21 (2H, d, *J*=6.7 Hz, ArH), 6.82 (2H, d, *J*=6.7 Hz, ArH), 3.71 (3H, s, OCH_3), 1.98 (3H, s, CH_3), 1.69 (3H, s, CH_3); ^{13}C NMR (100.53 MHz, $CDCl_3$): 204.6, 159.6, 130.2, 127.0, 114.3, 73.2, 55.2, 24.9, 21.6; ESI-MS: 242 (6.3, M+Na), 178 (13.0), 177 (100, M^+-N_3), 163 (22.5),

149 (79.3, M^+-N_3-CO), 126 (11.9), 121 (7.3%); HRMS (ESI): calcd for $C_{11}H_{13}O_2$ (M^+-N_3) *m/z* 177.0910. Found 177.0913.

4.7. General procedure for the preparation of 1-azido-1,1-diaryl methane

A solution of 1,1-diarylmethanol, **1r–w** (200 mg, 0.80–1.08 mmol) in dry CH_2Cl_2 (5 mL) and $TMSN_3$ (1.5 equiv) were placed in a 25 mL round-bottom flask fitted with guard tube. $InBr_3$ (2 mol %) was added to this reaction mixture. The contents were stirred at room temperature and the progress of reaction was monitored by TLC analyses. After stirring the contents for appropriate time period, the reaction was quenched with water. The product was extracted with CH_2Cl_2 (3×15 mL), washed with 10% Na_2CO_3 (20 mL), water (20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give brownish oil. Purification by flash chromatography afforded the products **2r–w**.

4.7.1. 1-Azido-1,1-diphenylmethane[22] (***2r***). Colourless oil. Yield: 97%; R_f (5% hexane/ethylacetate) 0.75; IR (thin film): 3062, 3029, 2098, 1601, 1493, 1453, 1238, 1182, 1079 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.06–7.22 (10H, m, ArH), 5.55 (1H, s, CH); ^{13}C NMR (100.53 MHz, $CDCl_3$): 139.5, 128.7, 128.4, 128.1, 127.4, 127.3, 68.5.

4.7.2. 1-Azido-1-(4-methoxyphenyl)-1-phenylmethane (***2s***). Colourless oil. Yield: 98%; R_f (5% hexane/ethylacetate) 0.57; IR (thin film): 3061, 3030, 3003, 2956, 2836, 2098, 1610, 1512, 1493, 1453, 1249, 1174, 1033 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.20–7.28 (5H, m, ArH), 7.12–7.14 (2H, d, *J*=6.6 Hz, ArH), 6.79 (2H, d, *J*=6.6 Hz, ArH), 5.58 (1H, s, CH), 3.70 (3H, s, OCH_3); ^{13}C NMR (100.53 MHz, $CDCl_3$): 159.3, 139.9, 131.7, 128.8, 128.6, 127.9, 127.2, 114.0, 68.1, 55.3; HRMS (ESI): calcd for $C_{14}H_{13}O$ (M^+-N_3) *m/z* 197.0961. Found 197.0936.

4.7.3. 1-Azido-1-(4-nitrophenyl)-1-phenylmethane (***2t***). Colourless oil. Yield: 89%; R_f (10% hexane/ethylacetate) 0.47; IR (thin film): 3079, 3031, 2856, 2100, 1605, 1519, 1492, 1454, 1411, 1346, 1242, 1180 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 8.11–8.15 (2H, m, ArH), 7.41–7.44 (2H, m, ArH), 7.26–7.34 (3H, m, ArH), 7.18–7.21 (2H, m, ArH), 5.72 (1H, s, CH); ^{13}C NMR (100.53 MHz, $CDCl_3$): 147.4, 146.7, 138.2, 129.1, 128.8, 128.0, 127.5, 123.9, 67.6; HRMS (ESI): calcd for $C_{13}H_{10}NO_2$ (M^+-N_3) *m/z* 212.0706. Found 212.0759.

4.7.4. 1-Azido-1,1-bis(4-fluorophenyl)methane[23] (***2u***). Colourless oil. Yield: 90%; R_f (5% hexane/ethylacetate) 0.64; IR (thin film): 3045, 2926, 2476, 2100, 1898, 1604, 1505, 1417, 1228, 1157 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.17–7.20 (4H, m, ArH), 6.95–7.00 (4H, m, ArH), 5.61 (1H, s, CH); ^{13}C NMR (100.53 MHz, $CDCl_3$): 162.4 (d), 135.2 (d), 129.0 (d), 115.7 (d), 67.1.

4.7.5. 1-Azido-1-(4-trifluoromethylphenyl)-1-phenylmethane (***2v***). Colourless oil. Yield: 88%; R_f (5% hexane/ethylacetate) 0.66; IR (thin film): 3064, 3030, 2958, 2856, 2102, 1618, 1602, 1492, 1453, 1413, 1324, 1253, 1164, 1124, 1089, 1067 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.53 (2H, d, *J*=8.2 Hz, ArH), 7.36 (2H, d, *J*=8.2 Hz, ArH), 7.23–7.32 (3H, m, ArH), 7.20–7.22 (2H, m, ArH), 5.68 (1H, s, CH); ^{13}C NMR (100.53 MHz, $CDCl_3$): 143.5, 138.7, 129.0, 128.5, 127.6, 127.5, 125.7, 125.7, 125.6, 67.9; HRMS (ESI): calcd for $C_{14}H_{10}F_3$ (M^+-N_3) *m/z* 235.0729. Found 235.0727.

4.7.6. 1-Azido-1-(4-methylphenyl)-1-phenylmethane (***2w***). Colourless oil. Yield: 93%; R_f (5% hexane/ethylacetate) 0.78; IR (thin film): 3059, 3028, 2922, 2486, 2097, 1602, 1542, 1493, 1453, 1413, 1379, 1243, 1076 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.21–7.26 (5H, m, ArH), 7.06–7.20 (4H, m, ArH), 5.59 (1H, s, CH), 2.25 (3H, s, CH_3); ^{13}C NMR (100.53 MHz, $CDCl_3$): 139.8, 137.9, 136.6, 129.4, 128.7, 128.0, 127.4, 127.3, 68.4, 21.1; HRMS (ESI): calcd for $C_{14}H_{13}$ (M^+-N_3) *m/z* 181.1012. Found 181.1003.

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Supplementary data

^1H NMR and ^{13}C NMR spectra of all new compounds. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.10.055.

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11. During the azidation of anisoin, there was also a second spot on the TLC plate, but it could not be isolated, as it decomposed back to anisoin.
12. (a) The lack of nucleophilic attack of azide ion (from $TMSN_3$) in the case of benzoin may be due to the non-compatibility of nucleophilicity of azide ion with the electrophilicity of the less stable and short-lived α-ketocarbenium ion. As a result, the leaving group (TMSOH) does not have the time to diffuse away. Alternatively, the facile reaction of hydroxyl group in benzoin occurs with $TMSN_3$ to give trimethylsilyl-protected benzoin. (b) Appel, R.; Mayr, H. *J. Am. Chem. Soc.* **2011**, *133*, 8240–8251 and references cited therein.

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14. (a) In this case, the naphthyl ring, present at the carbon bearing hydroxyl group, tends to stabilize the α-ketocarbenium ion more effectively due to its extended conjugation despite the presence of −COAr, which is an electron-withdrawing group. As a result, the α-ketocarbenium ion has enough time to undergo intramolecular rearrangement to give benzofuran derivative. (b) Kumar, A.; Pal, A. K.; Anand, R. D.; Singh, T. V.; Venugopalan, P. *Tetrahedron* **2011**, *67*, 8308–8313.
15. (a) The azidation of α-hydroxyketone having *tert*-butyl group, such as pivaloin (4-hydroxy-2,2,5,5-tetramethylhexane-3-one) was carried out. To a solution of pivaloin (200 mg, 1.16 mmol) and $TMSN_3$ (200 mg, 1.74 mmol) in CH_2Cl_2 (5 mL) was added $InBr_3$ (40 mg, 0.11 mmol) at room temperature. After stirring the contents for 5 h, the reaction was quenched with water (1 mL). The reaction mixture was extracted with CH_2Cl_2 (2×15 mL), washed with water and dried over anhydrous Na_2SO_4. The solvent was allowed to evaporate at room temperature to obtain a white solid. Its IR and ^1H NMR were recorded. These data showed that the starting material remained unchanged. (b) For the preparation of pivaloin: Newman, M. S.; Arkell, A. *J. Org. Chem.* **1959**, *24*, 385–387.
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17. (a) Synthesis of enantioenriched 1-(4-nitrophenyl)-1-phenylmethanol (**1t**) was carried out according to the reported procedure: A suspension of the $[RuCl_2(\text{-mesitylene})]_2$ (0.01 mmol) and ligand (1*R*,2*R*)-*N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine [(*R*,*R*)-TsDPEN] (0.027 mmol) in DCM was stirred at 20 °C for 30 min. After removal of DCM by a stream of N2, 4-nitrobenzophenone (1 mmol) in a mixture of HCOOH/Et_3N (5:2 mol ratio, 0.25 mL) was added. The reaction mixture was stirred at 50 °C for 2 h. After cooling to room temperature, the reaction mixture was extracted with ethylacetate. The sample was then dissolved in HPLC eluant (4:1) hexane/ethylacetate and analysed by HPLC for the determination of enantiomeric excess. (b) Slungard, S. V.; Krakeli, T.-A.; Thevdt, T. H. K.; Fuglseth, E.; Sundby, E.; Hoff, B. H. *Tetrahedron.* **2011**, *67*, 5642–5650.
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