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BiI_3 mediated difunctionalization of α-methylstyrenes, including azidohydroxylation and azidoiodination

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ABSTRACT

BiI_3 mediated vicinal azidohydroxylation of α-methylstyrenes **1** with NaN_3 in wet DMF affords β-azidoalcohols **4** in good yields. In dry DMF, β-azidoiodides **6** are also obtained by BiI_3 mediated vicinal azidoiodination of α-methylstyrenes **1** with NaN_3. This present protocol provides the bond formations of carbon-azido/carbon-hydroxy (N_3—**CC**—OH) bond and carbon-azido/carbon-iodo (N_3—**CC**—I) under water-controlled conditions.

1. Introduction

Vicinal difunctionalization of olefin has attracted much attention, resulting in various synthetic strategies for its construction. Among these diversified routes, halogenation, halohydroxylation and dihydroxylation reactions are commonly found di-heterofunctionalization reactions in fundamental textbooks. These organic molecules containing vicinal di-heteroatoms form one of the most important motifs present in natural sources, functionalized materials and bioactive molecules. Recently, a number of transition metal complexes, bases or oxidants mediated one-pot methods for preparing various 1,2-difunctionalized alkenes have been developed,[1] including Ni^{2+} catalyzed alkylarylation (*R*—CC—*Ar*),[1a] Pd^{2+}/Cu^{2+} catalyzed diarylation (*Ar*—CC—*Ar*),[1b] H_2O_2/SeO_2 promoted alkoxyhydroxylation (*HO*—CC—*OR*),[1c-1d] I^{3+} mediated diacetalation (*ROCO*—CC—*OCOR*),[1e] organocatalyst mediated bromohydroxylation (*Br*—CC—*OH*),[1f] Bi^{3+} promoted hydroarylation (*H*—CC—*Ar*),[1g] Select fluoro mediated aminofluorination (*F*—CC—*NHR*),[1h] Er^{3+} promoted aminohydroxylation (*HO*—CC—*NHR*),[1i] $I^-/S_2O_8^{2-}$ mediated acetamidosulfenylation (*RS*—CC—*NHCOR*),[1j] Cu^+ mediated hydroxytrifluoromethylation (F_3C—CC—*OH*),[1k] Fe^{3+} catalyzed acyloxyalkylation (*R*—CC—*OCOR*),[1l] Cu^+/Mn^{2+} cyanophosphinoylation (*NC*—CC—POR_2)[1m] and Cu^{2+}/I^{3+} catalyzed azidocyananation (N_3—CC—*CN*).[1n] However, straightforward vicinal azidohydroxylation (N_3—CC—*OH*) across unsymmetrical olefins in a requisite regioselective fashion is rare.[2]

For this 1,2-azidohydroxylation reaction, different organoreagents promoting the intermolecular one-step are the major pathways, as shown in Scheme 1. Sudalai and coworkers developed a I_2/TBHP-controlled regiodivergent azidohydroxylation of alkenes with NaN_3.[2a] Studer and Zhang demonstrated a TEMPONa-mediated stereoselective radical azidooxygenation of alkenes with a N_3-iodine(III) reagent.[2b] Liang et al. reported a $PhI(OAc)_2$-mediated metal-free three-component oxyazidation of alkenes, $TMSN_3$ and *N*-hydroxyphthalimide (NHPI).[2c] Chavan and Subbarao described a $(NH_4)_2Ce(NO_3)_6$ mediated azidoalkoxylation of olefins with NaN_3 and alcohols.[2d] Jiao group investigated a $MnBr_2$-mediated hydroxyazidation of olefins with $TMSN_3$ under open-vessel condition.[2e] Yang and Lu explored a visible-light (LEDs)-promoted aerobic hydroxyazidation of olefins with $TMSN_3$.[2f] For the present 1,2-azidohydroxylation, diverse oxidants or catalysts and azido sources have been highlighted via a one-pot, direct route under different reaction conditions.

The literature reveals that intermolecular direct installation of hydroxyl and azido synthons into alkenes could provide the most convenient access to vicinal azidohydroxylation of substituted α-

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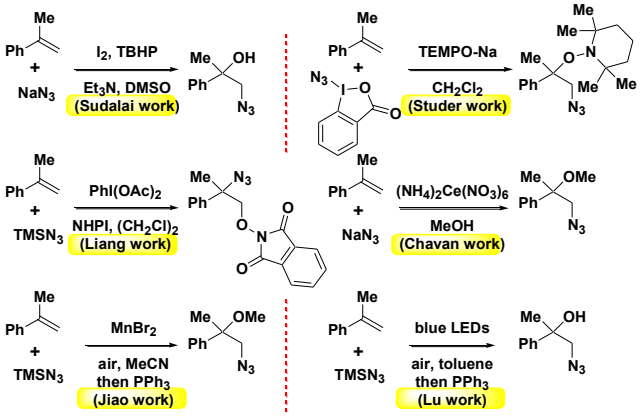
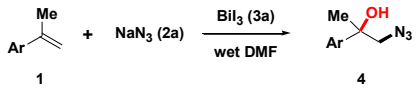


Scheme 1. Synthetic routes for azidohydroxylation.

methylstyrenes. Based on the above-mentioned routes, herein, we developed an economical synthesis of β-azidoalcohol **4** via a bismuth iodide (BiI_3, **3a**) mediated regioselective 1,2-azidohydroxylation of substituted α-methylstyrene **1** (an unsymmetrical olefin) with sodium azide (NaN_3, **2a**) in wet DMF (a cosolvent of DMF and H_2O, v/v = 10:1) at rt in good yields (Scheme 2). BiI_3 is a stable, commercially available solid that has been underutilized in organic synthesis.[3,4] BiI_3 mediated functional group transformations included: (1) guanylation of thioureas,[4a] (2) deprotection of ketals or acetals,[4b] (3) allylation of aldehydes,[4c-e] and (4) sulfenylation of carbonyl synthons.[4f]

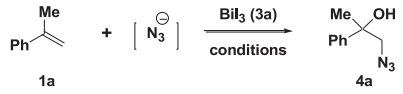
2. Results and discussion

According to reports on the direct azidohydroxylation of α-methylstyrene **1** having an unsymmetrical olefin motif, Sudalai,[2a] Studer,[2b] Liang[2c] and Chavan[2d] showed that oxidants promoted carbon-azido and carbon-hydroxy bond formations with different azido sources (NaN_3, $TMSN_3$ and N_3-iodine(III) reagent). In the study, three azides (**2a**, NaN_3; **2b**, LiN_3; **2c** $TMSN_3$) were examined first for different reaction solvents (DMF, $MeNO_2$, MeCN and DMSO), temperature (rt and reflux) and time (1, 2, 3 and 20 h) during BiI_3 (**3a**) mediated azidohydroxylation of the model substrate **1a** process, as shown in Table 1. When the reaction of **1a** and **3a** was treated with NaN_3 in DMF at rt for 2 and 20 h (entries 1–2), no reactions were observed. After elevating the temperature (25 → 100 → reflux), the isolated yields of the desired **4a** were increased to 30% and 82% for 2 h, respectively (entries 3–4). The optimal yield was obtained in 2 h, and prolonging or shortening reaction time to 3 or 1 h afforded lower yields of the desired **4a** (entries 5–6). Furthermore, the factor of reaction solvent was studied. After changing the solvents from boiling DMF to $MeNO_2$, MeCN or DMSO, the results showed that only MeCN (entry 7) provided a moderate yield producing **4a** (66%) in contrast to $MeNO_2$ and DMSO (entries 8–9). For the azidohydroxylation of α-methylstyrene **1a**, we believe that DMF should be an optimal solvent among these polar solvents. With the results in hand, other azide sources (**2b** and **2c**) were explored next. Under similar conditions, LiN_3 gave only a 58% yield of **4a**; however, there was no reaction for



Scheme 2. Our route for azidohydroxylation.

Table 1
Reaction Conditions.[a]

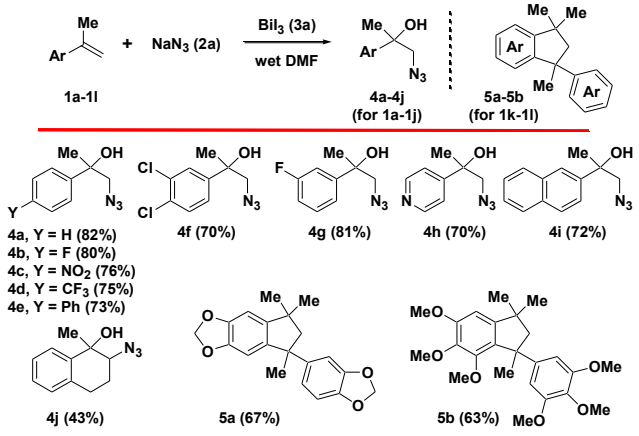


entry	**2**, azides	solvent	temp (°C)	time (h)	**4a** (%)[b]
1	**2a**, NaN_3	DMF	25	2	-[c]
2	**2a**, NaN_3	DMF	25	20	-[c]
3	**2a**, NaN_3	DMF	100	2	30
4	**2a**, NaN_3	DMF	reflux	2	82
5	**2a**, NaN_3	DMF	reflux	3	78
6	**2a**, NaN_3	DMF	reflux	1	69
7	**2a**, NaN_3	MeCN	reflux	2	66
8	**2a**, NaN_3	$MeNO_2$	reflux	2	15
9	**2a**, NaN_3	DMSO	reflux	2	-[d]
10	**2b**, LiN_3	DMF	reflux	2	58
11	**2c**, $TMSN_3$	DMF	reflux	2	-[c]
12	**2a**, NaN_3	DMF	reflux	2	-[c–e]

[a] Reactions were run on a 0.5 mmol scale with **1a**, azides (**2**, 1.2 equiv) in H_2O (0.5 mL), BiI_3 (**3a**, 1.2 equiv), solvent (5 mL), 2 h.
[b] Isolated yields.
[c] No reaction.
[d] Complex mixture.
[e] No addition of BiI_3 (**3a**).

$TMSN_3$ (entries 10–11). Other metal iodides (**3b**, AgI; **3c**, CuI; **3d**, MgI_2; **3e**, InI_3) were also investigated, but no reactions were initiated under the above conditions (boiling DMF, NaN_3, 2 h). By the removal of BiI_3, no reaction was observed, and **4a** was not isolated (entry 12). In terms of optimal yield and reactivity, we believe that the BiI_3/NaN_3 combination system should be an optimal combination for the formation of **4a**.

According to above optimal reaction conditions, we explored the substrate scope, and the results are shown in Scheme 3. To adjust the Ar group of **1a**-**1j** (Ar = **a**, Ph; **b**, 4-FC_6H_4; **c**, 4-$NO_2C_6H_4$; **d**, 4-$CF_3C_6H_4$; **e**, 4-PhC_6H_4; **f**, 3,4-$Cl_2C_6H_3$; **g**, 3-FC_6H_4; **h**, 4-pyridinyl; **i**, 4-naphthyl; **j**, tetralinyl), **4a**-**4j** were provided in a range of 43%–82% yields. For the Ar substituent, the electron-neutral aryl groups and electron-withdrawing aryl groups were well tolerated. The heterocyclic (for **1h**) and bicyclic (for **1i**, **1j**) ring systems also performed well, especially, for the BiI_3 mediated reaction of **1k**-**1l** with the electron-donating aryl group (**k**, 3,4-$CH_2O_2C_6H_3$; **l**, 3,4,5-$(MeO)_3C_6H_2$) and NaN_3, where no desired 1,2-azidoalcohol product was obtained, and only **5a**-**5b** having the indane skeleton were isolated in 67% and 63% yield, respectively.[5]



Scheme 3. Synthesis of **4**–**5**.

From the results, we found that dimerization of vinylarenes having an oxygenated aryl group was easier to initiate than the azidohydroxylation route because the electron-donating group could stabilize the intermediate with tertiary carbocation. Overall, for the electronic effect of a Y substituent on the skeleton of α-methylstyrenes **1**, the electron-donating oxygenated group was inappropriate for the formation of **4**.

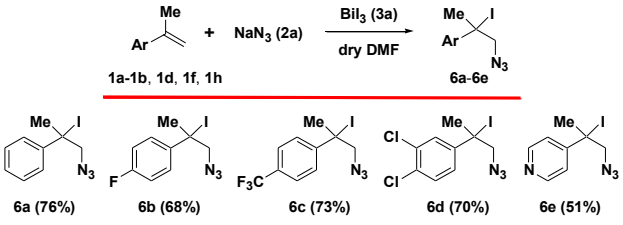
With the results at hand, an anhydrous reaction condition was examined next. Interestingly, when water was removed from the BiI_3 mediated reaction of **1** with NaN_3 under a dry DMF condition, **6**, having the skeleton of 1,2-azidoiodide was generated. As shown in Scheme 4, treatment of **1a**-**b**, **1d**, **1f** and **1h** (Ar = **a**, Ph; **b**, 4-FC_6H_4; **d**, 4-$CF_3C_6H_4$; **f**, 3,4-$Cl_2C_6H_3$; **h**, 4-pyridinyl) with BiI_3 and NaN_3 in the absence of H_2O, provided **6a**-**6e** in a range of 51%–76% yields.

Based on the results, three possible reaction mechanisms were combined and shown in Scheme 5. Initially, the intermediate **A** was generated from the complex of **1a** with BiI_3. Next, **A** was converted to intermediate **B** of a Bi^{3+} complex along with the removal of an iodide ion. For the reactions of **1a**-**1j**, **C-1** was produced by intermolecular substitution of **B** with the water (a wet DMF condition).[3i,6] Among the process, *in-situ* formed HI and azide could generate iodide and HN_3. Then, iodide ion inserted into **C-1** to afford the resulting **D**. Subsequently, the coordination of **D** with HN_3 led to **4** via the five-membered ring transition state. The releasing dioxybismuth iodide ion trapped excess H_2O to produce $Bi(OH)_3$ and iodide ion.[3i,4b]

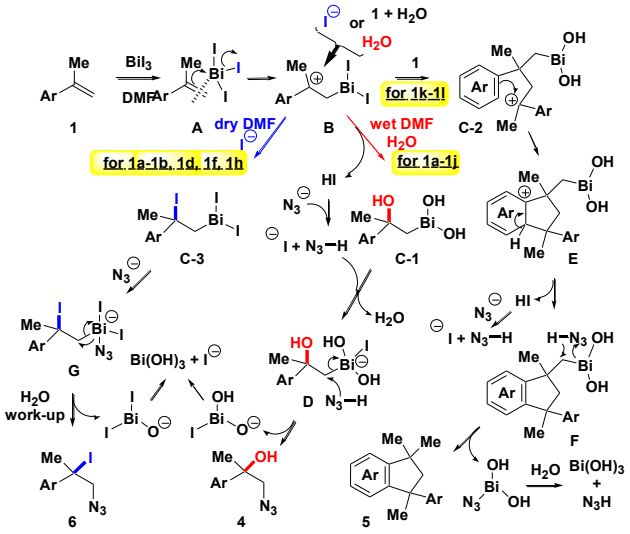
For the reactions of **1k**-**1l**, **C-2** was produced by intermolecular substitution of the other **1** via the ene-reaction route. By intramolecular Friedel-Crafts alkylative ring-closure of **C-2** and sequential dehydrogenative aromatization of **E**, **F** was formed by the cascade dimerization process. Furthermore, the resulting HN_3 continued the debismuthation from **F** to **5**.[7] The resulting azidobismuth dihydroxide ion trapped excess H_2O to produce $Bi(OH)_3$ and HN_3. This results was similar to Hua work (by $BiCl_3$-mediated dimerization reaction of **1**).[5a]

For the reactions of **1a**-**1b**, **1d**, **1f** and **1h**, **C-3** was produced via intermolecular substitution with the releasing iodide ion (a dry DMF condition). After the nucleophilic substitution of **C-3** with azide occurred, **G** was formed. Following a work-up process, **6** was yielded along with the generation of oxybismuth diiodide ion. By the involvement of water, the suspended solids of $Bi(OH)_3$ were produced.

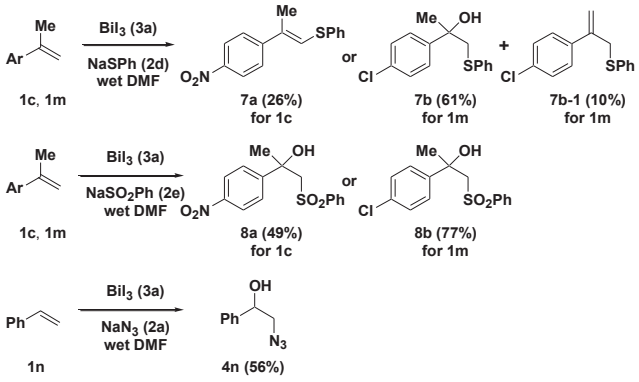
A variety of hydroxysulfenylated and hydroxysulfonylated products were obtained when the sodium salt was changed from NaN_3 (**2a**) to NaSPh (**2d**) or $NaSO_2Ph$ (**2e**), respectively, as shown in Scheme 6. Under the similar conditions, BiI_3 mediated reaction of **1c** (Ar = 4-$NO_2C_6H_4$) with **2d** was studied first. However, no hydroxysulfenylated product was detected and only **7a** was isolated in a low (26%) yield because the nitro substituent is a strong electron-withdrawing group. After changing **1c** to **1m** (Ar = 4-ClC_6H_4), the desired 1,2-hydroxysulfide **7b** was produced in a 61% yield along with 10% dehydrated **7b-1**. For the isolation of different olefinic isomers **7a** and **7b-1**, the results should be controlled by



Scheme 4. Synthetic route to azidoiodination.



Scheme 5. Possible mechanisms.



Scheme 6. Synthesis of **7**–**8**.

electronic inductive effect. For the generation of **7a** with a more stable trisubstituted *endo*-olefin (via Zaitsev rule), a stronger deactivating nitro group could stabilize the *in-situ* formed tertiary carbocation under the thermodynamic condition. In the other way, a weaker deactivating chloro group could not stabilize easily the formed tertiary carbocation such that **7b-1** having a terminal *exo*-olefin was obtained in low yield (by Hoffman rule). By BiI_3 mediated hydroxysulfenylation of **1** with **2d**, obvious variants were detected in the distribution of different products. Furthermore, attempts to produce BiI_3 mediated hydroxysulfonylation of **1c** and **1m** with **2e** also provided **8a** and **8b** in 49% and 77% yields, respectively. The structural frameworks of **8a** and **8b** were determined by single-crystal X-ray crystallography (Figs. 1–2).[8] Besides the α-methylstryrene (**1a**), a simple styrene (**1n**) was treated with the optimal condition, however, the desired **4n** was isolated in only a 56% yield. Based on the experimental results, the present optimal BiI_3/NaN_3 mediated conditions were appropriate for the hydroxysulfenylation and hydroxysulfonylation of α-methylstyrenes and the azidohydroxylation of styrene.

As an extension for vicinal difunctionalization of α-methylstyrene, changing the promoter from BiI_3 to I_2 was explored next, as shown in Scheme 7. By the removal of NaN_3, treatment of **1g** with I_2 provided **9a** in a 64% yield. This implies that I_2 activates **1g** to afford the iodonium ion intermediate. After intermolecular cross-coupling of the resulting tertiary carbocation of **1g** and another

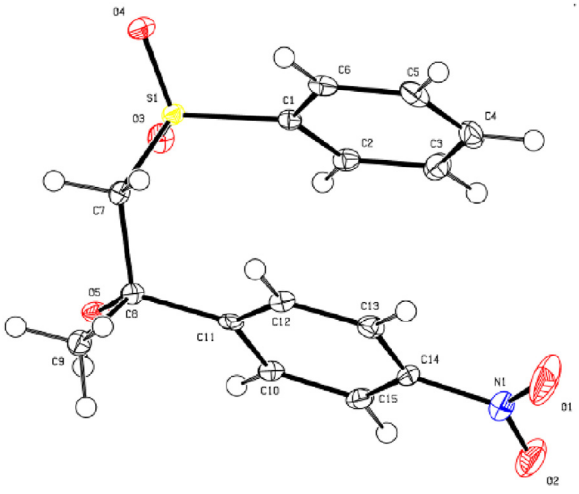


Fig. 1. X-ray structure of **8a**.

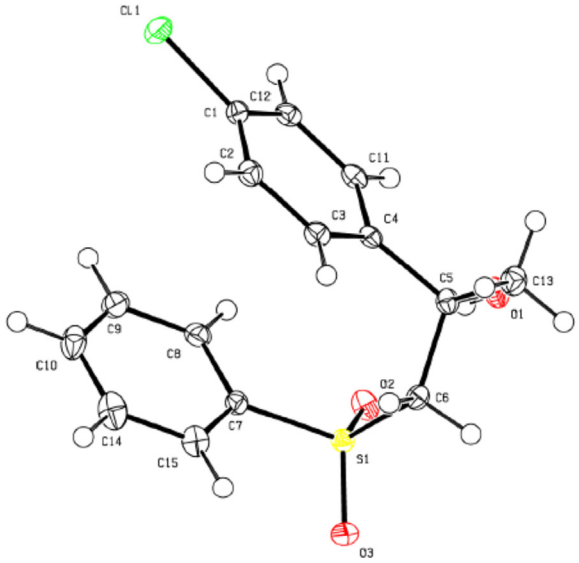
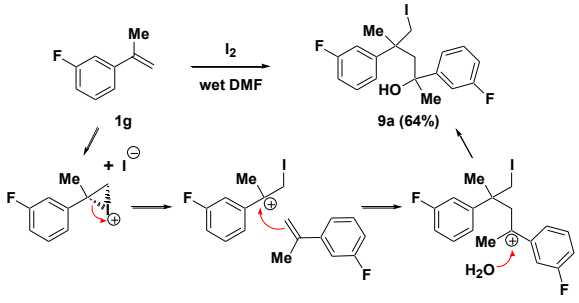


Fig. 2. X-ray structure of **8b**.



Scheme 7. Synthesis of **9a**.

1g, a resulting dimer with a new tertiary carbocation was generated. Subsequently, **9a** was generated in the presence of water.

3. Conclusion

In summary, we have shown that BiI_3 mediated vicinal azidohydroxylation and azidoiodination of substituted α-methylstyrenes with NaN_3 in wet and dry DMF afford β-azidoalcohols and β-azidoiodides in moderate to good yields. The plausible mechanisms have been discussed and proposed. On the other hand, we also described BiI_3 mediated hydroxysulfenylation and hydroxysulfonylation of α-methylstyrenes with NaSPh and $NaSO_2Ph$ in wet DMF. Further investigation regarding synthetic applications of α-methylstyrenes will be conducted and published in due course.

4. Experimental section

4.1. General

All reagents and solvents were obtained from commercial sources and used without further purification. Reactions were routinely carried out under an atmosphere of dry air with magnetic stirring. Products in organic solvents were dried with anhydrous magnesium sulfate before concentration in vacuo. Melting points were determined with a SMP3 melting apparatus. ^1H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 spectrometer operating at 400 and 100 MHz, respectively. Chemical shifts (δ) are reported in parts per million (ppm) and the coupling constants (J) are given in Hertz. High resolution mass spectra (HRMS) were measured with a mass spectrometer Finnigan/Thermo Quest MAT 95XL. X-ray crystal structures were obtained with an Enraf-Nonius FR-590 diffractometer (CAD4, Kappa CCD).

4.2. A representative synthetic procedure of compounds *4a-4j*, *4n* and *5a-5b* is as follows

BiI_3 (**3a**, 354 mg, 0.6 mmol) was added to a stirred solution of **1a-1l**, **1n** (0.5 mmol) in DMF (5 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 15 min NaN_3 (**2a**, 39 mg, 0.6 mmol) in H_2O (0.5 mL) was added to the reaction mixture at 25 °C. Then, the reaction mixture was stirred at reflux for 2 h. The reaction mixture was cooled to 25 °C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 8/1–4/1) afforded **4a-4j**, **4n** and **5a-5b**.

4.2.1. 1-Azido-2-phenylpropan-2-ol (*4a*)

Yield = 82% (73 mg); Colorless oil; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_9H_{12}N_3O$ 178.0980, found 178.0985; ^1H NMR (400 MHz, $CDCl_3$): δ 7.48–7.45 (m, 2H), 7.41–7.36 (m, 2H), 7.33–7.28 (m, 1H), 3.61 (d, J = 12.4 Hz, 1H), 3.45 (d, J = 12.0 Hz, 1H), 2.21 (br s, 1H), 1.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.62, 128.45 (2×), 127.48, 124.80 (2×), 74.54, 62.09, 27.08.

4.2.2. 1-Azido-2-(4-fluorophenyl)propan-2-ol (*4b*)

Yield = 80% (78 mg); Colorless oil; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_9H_{11}FN_3O$ 196.0886, found 196.0892; ^1H NMR (400 MHz, $CDCl_3$): δ 7.45–7.40 (m, 2H), 7.08–7.02 (m, 2H), 3.57 (d, J = 12.0 Hz, 1H), 3.43 (d, J = 12.0 Hz, 1H), 2.38 (br s, 1H), 1.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.09 (d, J = 244.8 Hz), 140.41 (d, J = 3.0 Hz), 126.69 (d, J = 7.6 Hz, 2×), 115.22 (d, J = 21.3 Hz, 2×), 74.24, 62.12, 27.19.

4.2.3. 1-Azido-2-(4-nitrophenyl)propan-2-ol (*4c*)

Yield = 76% (84 mg); Colorless oil; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_9H_{11}N_4O_3$ 223.0831, found 223.0839; ^1H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 9.2 Hz, 2H), 3.61 (d, J = 12.4 Hz, 1H), 3.52 (d, J = 12.4 Hz, 1H), 2.60 (br s, 1H), 1.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.97, 147.10, 126.06 (2×), 123.54 (2×), 74.47, 61.53, 27.06.

*4.2.4. 1-Azido-2-(4-trifluoromethylphenyl)propan-2-ol (**4d**)*

Yield = 75% (92 mg); Colorless oil; HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{10}H_{11}F_3N_3O$ 246.0854, found 246.0859; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 3.61 (d, J = 12.4 Hz, 1H), 3.49 (d, J = 12.4 Hz, 1H), 2.43 (br s, 1H), 1.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.62, 129.71 (q, J = 32.6 Hz), 125.36 (4×), 121.34 (d, J = 270.6 Hz), 74.42, 61.77, 27.08.

*4.2.5. 1-Azido-2-biphenyl-4-ylpropan-2-ol (**4e**)*

Yield = 73% (92 mg); Colorless oil; HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{15}H_{16}N_3O$ 254.1293, found 254.1299; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–7.58 (m, 4H), 7.53 (d, J = 8.4 Hz, 2H), 7.47–7.43 (m, 2H), 7.38–7.34 (m, 1H), 3.66 (d, J = 12.4 Hz, 1H), 3.50 (d, J = 12.4 Hz, 1H), 2.20 (br s, 1H), 1.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.66, 140.56, 140.43, 128.78 (2×), 127.38, 127.19 (2×), 127.08 (2×), 125.33 (2×), 74.51, 62.10, 27.18.

*4.2.6. 1-Azido-2-(3,4-dichlorophenyl)propan-2-ol (**4f**)*

Yield = 70% (86 mg); Colorless oil; HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_9H_{10}Cl_3N_3O$ 246.0201, found 246.0208; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 2.4 Hz, 1H), 7.43 (d, J = 8.4 Hz, 1H), 7.25 (dd, J = 2.4, 8.4 Hz, 1H), 3.55 (d, J = 12.4 Hz, 1H), 3.44 (d, J = 12.4 Hz, 1H), 2.41 (br s, 1H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.94, 132.60, 131.52, 130.33, 127.31, 124.40, 73.97, 61.65, 27.00.

*4.2.7. 1-Azido-2-(3-fluorophenyl)propan-2-ol (**4g**)*

Yield = 81% (79 mg); Colorless oil; HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_9H_{11}FN_3O$ 196.0886, found 196.0892; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.27 (m, 1H), 7.18–7.14 (m, 2H), 6.98–6.93 (m, 1H), 3.55 (d, J = 12.4 Hz, 1H), 3.41 (d, J = 12.4 Hz, 1H), 2.41 (br s, 1H), 1.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.91 (d, J = 244.0 Hz), 147.42 (d, J = 6.8 Hz), 129.98 (d, J = 8.3 Hz), 120.44 (d, J = 3.0 Hz), 114.33 (d, J = 21.2 Hz), 112.32 (d, J = 22.8 Hz), 74.28 (d, J = 1.5 Hz), 61.85, 27.05.

*4.2.8. 1-Azido-2-pyridin-4-ylpropan-2-ol (**4h**)*

Yield = 70% (62 mg); Colorless solid; mp = 103–105 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_8H_{11}N_4O$ 179.0933, found 179.0938; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (d, J = 6.4 Hz, 2H), 7.39 (d, J = 6.4 Hz, 2H), 5.15 (br s, 1H), 3.47 (d, J = 12.4 Hz, 1H), 3.40 (d, J = 12.4 Hz, 1H), 1.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.16, 148.83 (2×), 120.51 (2×), 73.60, 61.18, 26.48.

*4.2.9. 1-Azido-2-naphthalen-2-yl-propan-2-ol (**4i**)*

Yield = 72% (82 mg); Colorless oil; HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{13}H_{14}N_3O$ 228.1137, found 228.1135; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 2.0 Hz, 1H), 7.86 (d, J = 8.8 Hz, 2H), 7.86–7.83 (m, 1H), 7.54–7.47 (m, 3H), 3.72 (d, J = 12.4 Hz, 1H), 3.56 (d, J = 12.4 Hz, 1H), 2.41 (br s, 1H), 1.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.99, 133.14, 132.60, 128.26, 128.19, 127.54, 126.32, 126.14, 123.76, 122.99, 74.74, 62.01, 27.18.

*4.2.10. 2-Azido-1-methyl-1,2,3,4-tetrahydronaphthalen-1-ol (**4j**)*

Yield = 43% (44 mg); Colorless oil; HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{11}H_{14}N_3O$ 204.1137, found 204.1133; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, J = 8.8 Hz, 1H), 7.27–7.19 (m, 2H), 7.08 (d, J = 8.0 Hz, 1H), 3.74 (dd, J = 3.6, 12.0 Hz, 1H), 2.96–2.92 (m, 2H), 2.40 (br s, 1H), 2.20–2.13 (m, 1H), 1.96–1.85 (m, 1H), 1.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.68, 133.79, 128.24, 27.43, 126.64, 126.10, 74.26, 67.67, 27.51, 25.83, 25.26.

*4.2.11. 5-Benzo[1,3]dioxol-5-yl-5,7,7-trimethyl-6,7-dihydro-5H-indeno[5,6-d][1,3]dioxole (**5a**)*

Yield = 67% (54 mg); Colorless oil; HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{20}H_{21}O_4$ 325.1440, found 325.1438; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.71–6.62 (m, 4H), 6.53 (s, 1H), 5.96 (d, J = 1.6 Hz, 1H), 5.95 (d, J = 1.2 Hz, 1H), 5.91 (d, J = 2.0 Hz, 1H), 5.91 (d, J = 1.6 Hz, 1H), 2.34 (d, J = 13.2 Hz, 1H), 2.16 (d, J = 12.8 Hz, 1H), 1.61 (s, 3H), 1.29 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.35, 147.19, 146.73, 145.33, 145.19 (2×), 141.49, 119.42, 107.63, 107.41, 104.90, 102.79, 101.01, 100.77, 59.68, 50.33, 42.56, 30.93, 30.87, 30.37.

*4.2.12. 4,5,6-Trimethoxy-1,1,3-trimethyl-3-(3,4,5-trimethoxyphenyl)indan (**5b**)*

Yield = 63% (66 mg); Colorless oil; HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{24}H_{33}O_6$ 417.2277, found 417.2273; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.43 (s, 1H), 6.37 (s, 2H), 3.85 (s, 3H), 3.78 (s, 3H), 3.76 (s, 3H), 3.72 (s, 6H), 3.57 (s, 3H), 2.29 (d, J = 12.8 Hz, 1H), 2.09 (d, J = 13.2 Hz, 1H), 1.73 (s, 3H), 1.27 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.68, 152.21 (2×), 149.99, 147.48, 146.73, 140.81, 135.52, 132.56, 130.75 (2×), 100.66, 60.52, 60.25, 59.97, 59.82, 55.84, 55.76, 55.74, 50.79, 43.19, 30.81, 30.34, 28.91.

*4.2.13. 1-Azido-2-phenylethan-2-ol (**4n**)*

Yield = 56% (46 mg); Colorless oil; HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_8H_{10}N_3O$ 164.0824, found 164.0823; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.32 (m, 5H), 4.88 (dd, J = 3.6, 8.0 Hz, 1H), 3.48 (dd, J = 8.0, 12.4 Hz, 1H), 3.42 (dd, J = 3.6, 12.4 Hz, 1H), 2.60 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.66, 128.75 (2×), 128.34, 125.92 (2×), 73.25, 58.11.

*4.3. A representative synthetic procedure of compounds **6a**-**6e** is as follows*

BiI_3 (**3a**, 354 mg, 0.6 mmol) was added to a stirred solution of **1a**-**1b**, **1d**, **1f** and **1h** (0.5 mmol) in dry DMF (5 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 15 min NaN_3 (**2a**, 39 mg, 0.6 mmol) was added to the reaction mixture at 25 °C. Then, the reaction mixture was stirred at reflux for 2 h. The reaction mixture was cooled to 25 °C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 8/1–4/1) afforded **6a**-**6e**.

*4.3.1. (2-Azido-1-iodo-1-methylethyl)benzene (**6a**)*

Yield = 76% (109 mg); Colorless oil; HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_9H_{11}IN_3$ 287.9998, found 287.9990; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46–7.39 (m, 4H), 7.36–7.32 (m, 1H), 3.51 (d, J = 14.4 Hz, 1H), 3.48 (d, J = 14.4 Hz, 1H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.73, 128.79 (2×), 128.27, 125.60 (2×), 65.07, 25.16, 17.68.

*4.3.2. 1-(2-Azido-1-iodo-1-methylethyl)-4-fluorobenzene (**6b**)*

Yield = 68% (104 mg); Colorless oil; HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_9H_{10}FIN_3$ 305.9904, found 305.9910; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44–7.39 (m, 2H), 7.11–7.05 (m, 2H), 3.49 (d, J = 10.4 Hz, 1H), 3.45 (d, J = 10.4 Hz, 1H), 1.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.26 (d, J = 247.2 Hz), 136.56 (d, J = 3.8 Hz), 127.47 (d, J = 8.3 Hz, 2×), 115.55 (d, J = 21.2 Hz, 2×), 64.55, 25.07, 17.43.

4.3.3. 1-(2-Azido-1-iodo-1-methylethyl)-4-trifluoromethylbenzene (**6c**)

Yield = 73% (130 mg); Colorless oil; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{10}H_{10}F_3IN_3$ 355.9872, found 355.9879; ^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 3.51 (s, 2H), 1.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.88, 130.36 (q, J = 31.9 Hz), 126.10 (2×), 125.69 (q, J = 3.8 Hz, 2×), 123.80 (d, J = 270.6 Hz), 64.71, 25.05, 16.47.

4.3.4. 4-(2-Azido-1-iodo-1-methylethyl)-1,2-dichlorobenzene (**6d**)

Yield = 70% (124 mg); Colorless oil; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_9H_9Cl_2IN_3$ 355.9218, found 355.9219; ^1H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 2.4 Hz, 1H), 7.46 (d, J = 8.4 Hz, 1H), 7.25 (dd, J = 2.4, 8.4 Hz, 1H), 3.45 (br s, 2H), 1.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.20, 132.92, 132.44, 130.62, 127.91, 125.05, 64.23, 24.93, 16.44.

4.3.5. 4-(2-Azido-1-iodo-1-methylethyl)pyridine (**6e**)

Yield = 51% (73 mg); Colorless oil; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_8H_{10}IN_4$ 288.9950, found 288.9953; ^1H NMR (400 MHz, $CDCl_3$): δ 8.64 (d, J = 6.4 Hz, 2H), 7.32 (d, J = 6.4 Hz, 2H), 3.47 (s, 2H), 1.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.33 (2×), 149.83, 120.50 (2×), 64.24, 24.79, 15.38.

4.4. A representative synthetic procedure of compounds **7a**, **7b** and **7b-1** is as follows

BiI_3 (**3a**, 354 mg, 0.6 mmol) was added to a stirred solution of **1c** and **1m** (0.5 mmol) in DMF (5 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 15 min. A solution of NaSPh (**2d**, 79 mg, 0.6 mmol) in H_2O (0.5 mL) was added to the reaction mixture at 25 °C. Then, the reaction mixture was stirred at reflux for 2 h. The reaction mixture was cooled to 25 °C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 8/1–4/1) afforded **7a**, **7b** and **7b-1**.

4.4.1. 2-(4-Nitrophenyl)-1-phenylsulfanylpropene (**7a**)

Yield = 26% (35 mg); Colorless oil; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{15}H_{14}NO_2S$ 272.0745, found 272.0740; ^1H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 8.8 Hz, 2H), 7.97 (d, J = 8.4 Hz, 2H), 7.67–7.63 (m, 1H), 7.59 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 8.8 Hz, 2H), 6.65 (d, J = 1.2 Hz, 1H), 2.57 (d, J = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.65, 148.28, 146.40, 141.28, 133.65, 130.31, 129.39 (2×), 127.34 (4×), 123.89 (2×), 17.20.

4.4.2. 2-(4-Chlorophenyl)-1-phenylsulfanylpropan-2-ol (**7b**)

Yield = 61% (85 mg); Colorless oil; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{15}H_{16}ClOS$ 279.0610, found 279.0613; ^1H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 8.4 Hz, 2H), 7.33–7.30 (m, 2H), 7.27 (d, J = 8.4 Hz, 2H), 7.23–7.18 (m, 3H), 3.50 (d, J = 13.6 Hz, 1H), 3.32 (d, J = 13.6 Hz, 1H), 2.91 (br s, 1H), 1.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.67, 136.03, 132.90, 130.22 (2×), 128.97 (2×), 128.30 (2×), 126.59, 126.38 (2×), 73.70, 49.54, 29.38.

4.4.3. 2-(4-Chlorophenyl)-1-phenylsulfanylpropan-2-ol (**7b-1**)

Yield = 10% (13 mg); Colorless oil; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{15}H_{14}ClS$ 261.0505, found 261.0509; ^1H NMR (400 MHz, $CDCl_3$): δ 7.80–7.77 (m, 2H), 7.61–7.56 (m, 1H), 7.48–7.43 (m, 2H), 7.21 (br s, 4H), 5.58 (s, 1H), 5.21 (s, 1H), 4.23 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.29, 137.19, 135.46, 134.01, 133.71, 128.96 (2×), 128.56 (2×), 128.52 (2×), 127.53 (2×), 122.34, 61.98.

4.5. A representative synthetic procedure of compounds **8a** and **8b** is as follows

BiI_3 (354 mg, 0.6 mmol) was added to a stirred solution of **1c** and **1m** (0.5 mmol) in DMF (5 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 15 min. A solution of $NaSO_2Ph$ (**2e**, 98 mg, 0.6 mmol) in H_2O (0.5 mL) was added to the reaction mixture at 25 °C. Then, the reaction mixture was stirred at reflux for 2 h. The reaction mixture was cooled to 25 °C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 8/1–4/1) afforded **8a** and **8b**.

4.5.1. 1-Benzenesulfonyl-2-(4-nitrophenyl)propan-2-ol (**8a**)

Yield = 49% (79 mg); Colorless solid; mp = 131–133 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{15}H_{16}NO_5S$ 322.0749, found 322.0749; ^1H NMR (400 MHz, $CDCl_3$ + DMSO-d_6): δ 7.93 (d, J = 8.8 Hz, 2H), 7.60–7.58 (m, 2H), 7.51–7.46 (m, 3H), 7.36–7.32 (m, 2H), 3.80 (d, J = 14.8 Hz, 1H), 3.66 (d, J = 14.4 Hz, 1H), 3.59 (br s, 1H), 1.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6): δ 152.43, 146.32, 140.13, 133.13, 128.64 (2×), 127.40 (2×), 126.05 (2×), 122.70 (2×), 72.12, 65.94, 30.19. Single-crystal X-Ray diagram: crystal of compound **8a** was grown by slow diffusion of EtOAc into a solution of compound **8a** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group C 2/c, a = 35.682(6) Å, b = 5.6994(9) Å, c = 14.278(2) Å, V = 2783.9(8) Å^3, Z = 8, d_{calcd} = 1.533 g/cm^3, $F(000)$ = 1344, 2θ range 1.190–26.026°, R indices (all data) R1 = 0.0382, w$R2$ = 0.0834.

4.5.2. 1-Benzenesulfonyl-2-(4-chlorophenyl)propan-2-ol (**8b**)

Yield = 77% (119 mg); Colorless solid; mp = 77–79 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{15}H_{16}ClO_3S$ 311.0509, found 311.0518; ^1H NMR (400 MHz, $CDCl_3$): δ 7.40–7.34 (m, 3H), 7.22–7.19 (m, 2H), 7.05–7.02 (m, 2H), 6.92–6.88 (m, 2H), 4.76 (s, 1H), 3.60 (d, J = 14.8 Hz, 1H), 3.45 (d, J = 14.4 Hz, 1H), 1.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.75, 139.60, 132.80, 132.24, 128.48 (2×), 127.52 (2×), 126.96 (2×), 125.95 (2×), 71.94, 65.96, 29.98. Single-crystal X-Ray diagram: crystal of compound **8a** was grown by slow diffusion of EtOAc into a solution of compound **8a** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the orthorhombic crystal system, space group P b c a, a = 15.1722(16) Å, b = 11.7576(14) Å, c = 15.6862(19) Å, V = 1798.2(6) Å^3, Z = 8, d_{calcd} = 1.475 g/cm^3, $F(000)$ = 1296, 2θ range 2.547–26.359°, R indices (all data) R1 = 0.0315, w$R2$ = 0.0699.

4.5.3. 2,4-Bis-(3-fluorophenyl)-5-iodo-4-methylpentan-2-ol (**9a**)

A solution of I_2 (152 mg, 0.6 mmol) in H_2O (0.5 mL) was added to a solution of **1g** (68 mg, 0.5 mmol) in wet DMF (5 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 10 min. Then, the reaction mixture was stirred at reflux for 2 h. The reaction mixture was cooled to 25 °C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 8/1–4/1) afforded **9a**. Yield = 64% (133 mg); Colorless oil; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{18}H_{20}F_2IO$ 417.0527, found 417.0523; ^1H NMR (400 MHz, $CDCl_3$): δ 7.25–7.20 (m, 2H), 7.06–7.03 (m, 1H), 7.01–6.98 (m, 2H), 6.94–6.83 (m, 3H), 3.29 (d, J = 12.4 Hz, 1H), 3.26 (d, J = 12.0 Hz, 1H), 2.49 (d, J = 14.8 Hz, 1H), 2.22 (d, J = 14.8 Hz, 1H), 2.03 (br s, 1H), 1.25 (s, 3H), 1.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.85 (d, J = 244.1 Hz), 162.77 (d, J = 244.1 Hz), 151.42 (d,

$J = 6.0$ Hz), 146.57 (d, $J = 6.8$ Hz), 129.74 (d, $J = 8.3$ Hz), 129.58 (d, $J = 8.3$ Hz), 121.35 (d, $J = 3.0$ Hz), 120.84 (d, $J = 3.1$ Hz), 113.92 (d, $J = 21.2$ Hz), 113.09 (d, $J = 22.0$ Hz), 112.68 (d, $J = 22.8$ Hz), 77.11 (d, $J = 1.5$ Hz), 62.79, 51.16, 37.70 (d, $J = 1.5$ Hz), 31.85, 29.66 (d, $J = 3.7$ Hz), 29.27.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.tet.2018.01.023.

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8. CCDC 1574337 (8a) and 1574338 (8b) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).