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Electrophilic Cyclization of Phenylalkynediols to Naphthyl(aryl)iodonium Triflates with Chelating Hydroxyls: Preparation and X-ray Analyses

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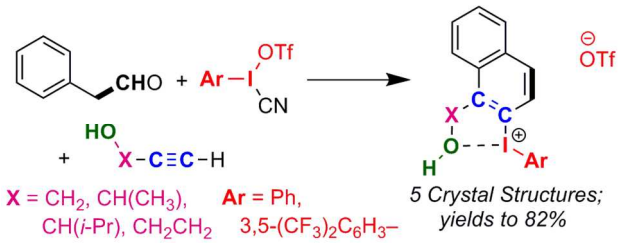


Abstract.

Alkynediols containing one propargylic alcohol as well as a second alcohol, which is propargylic or homopropargylic, react with $PhI^{+}CN^{-}OTf$ (Stang's reagent) or 3,5-$(CF_3)_2C_6H_3I^{+}CN^{-}OTf$ to afford naphthyl(aryl)iodonium triflates. The reaction occurs at room temperature over the course of 6-12 hours and provides 36-82% yields of microcrystalline solids. Slow diffusion of Et_2O into CH_3CN solutions of the salts afforded X-ray quality crystals of five compounds with hydroxyl groups forming five- and six-membered chelation complexes with the iodine atom. Crystallizations from larger scale reactions (≥ ~ 0.25 mmol) were generally facile from CH_2Cl_2.

† Detailed questions about X-ray structure analyses should be directed to Robert D. Pike, PhD, Department of Chemistry, The College of William & Mary; rdpike@wm.edu.

Introduction.

Hypervalent iodine compounds are used extensively in many forms of organic and polymer chemistry.[1] Dess-Martin periodinane[2] is, perhaps, the most widely-recognized I(V) compound whereas phenyliodine(III) diacetate (PIDA)[3] and phenyliodine bis(trifluoroacetate) (PIFA)[4] are among the most recognized I(III) compounds. Many other derivatives, however, are also known.[1,5] Both PIDA and PIFA have been used extensively in a variety of reactions, including C-H activation.[6] Alkenyl, heteroaryl, and diaryl[7] iodonium salts can be used for alkenylations,[8] cross-coupling reactions,[9] α-arylations of carbonyl compounds,[10] functionalization of indoles,[11] and a host of other reactions.[1] Typical syntheses of diaryl iodonium salts include: (a) reactions of bis(acetoxy)iodoarenes, with TfOH in the presence of a second aromatic compound to afford mixed diaryl salts;[12] (b) reactions of arylboronic acids and aryl iodides with *m*CPBA and acids;[13] and (c) reactions of elemental iodine or aryl iodides with aromatic compounds in the presence of strong oxidants.[14] Stang and co-workers developed a particularly mild iodonium–transfer reagent, ($PhI^{+}CN^{-}OTf$),[15] which is sometimes called "Stang's reagent." This I(III) electrophile is generally used to convert aryl, alkynyl,[15,16] or alkenyl stannanes[17] to the corresponding iodonium salts (eq 1), but has also been used to initiate Pummerer-like rearrangements in the synthesis of alkaloids;[18] analogs have also been used for additions across alkynes[19] and the synthesis of thiocyanates.[20]

(1)

In the course of developing a domino[21] reaction involving an alkynyl-Prins/Friedel-Crafts/aromatization cascade, we envisioned that Stang's reagent might react with alkynediols

containing one propargylic and one homopropargylic alcohol.[22] Herein we report that Stang's reagent as well as the 3,5-bis(CF_3)phenyl analog can be used to synthesize naphthyl(aryl)-iodonium triflate salts from alkyne diols in which at least one hydroxyl moiety is propargylic. This represents a new and surprisingly efficient cyclization-aromatization method for the synthesis of novel naphthyl(aryl)iodonium salts.[23]

Results and Discussion.

We initially reacted 1 equiv of Stang's reagent (PhI^+CN^-OTf) with 6-phenylhex-3-yne-1,5-diol **1a** in CD_3CN at room temperature. The reaction immediately began to turn light yellow and then became darker over time. ^1H NMR spectroscopic analyses (**Fig. 1**) over the course of 10 h clearly showed depletion of Stang's reagent by disappearance of the *ortho*-hydrogen resonance at 8.32 ppm and appearance of a much more complex series of resonances in the aromatic region, the most downfield of which appeared at 8.26 ppm. The fact that the new resonance was still below 8 ppm implied that a different iodonium salt had formed. Two new resonances also appeared at 3.7 and 3.9 ppm while the two sets of methylene resonances of starting alkynediol **1a** (6-phenylhex-3-yne-1,5-diol) at 2.4 and 2.9 ppm decreased. With 1 equiv of Stang's, however, some starting alkynediol remained; subsequent analyses showed that between 1.2-1.3 equiv of Stang's reagent was required to completely consume the starting alkynediol in acetonitrile. The resulting microcrystalline solid could be precipitated from solution by addition of Et_2O with rapid stirring at room temperature. Slow diffusion of Et_2O into a CD_3CN NMR sample afforded X-ray quality crystals, one of which was analyzed to reveal a naphthyl(phenyl)iodonium salt (**Fig. 2**). Interestingly, the homopropargylic alcohol was still intact as shown in the

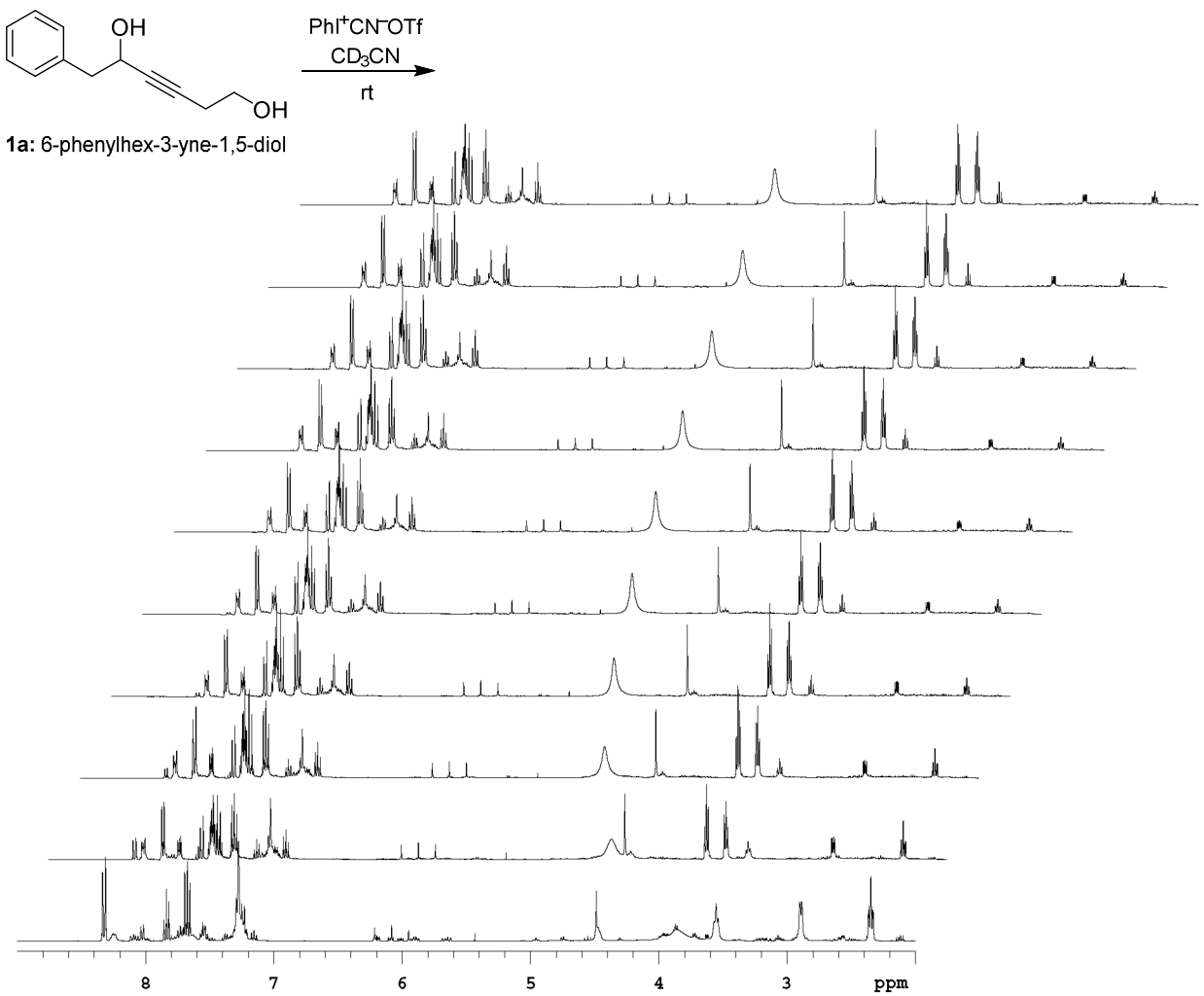


Figure 1. Time-arrayed ^{1}H NMR spectra of reaction between Stang's reagent and 1.0 equiv diol **1a**. The first spectrum was recorded at 10 min in CD_3CN at rt and another spectrum taken every hour. The final spectrum was recorded at 10h.

X-ray structure and ^{1}H NMR spectrum, but it was coordinated to the iodine atom in a six-membered ring chelate. To the best of our knowledge, no other crystal structures of compounds with a simple, pendant hydroxyl moiety coordinated directly to an I(III) center have been reported, although a number of other coordinating groups have been reported.[1,24] The closest-contact triflate counterion in **2a** (shown) appears in the neighboring unit cell and the hydroxyl hydrogen was located during data acquisition (see supporting information).

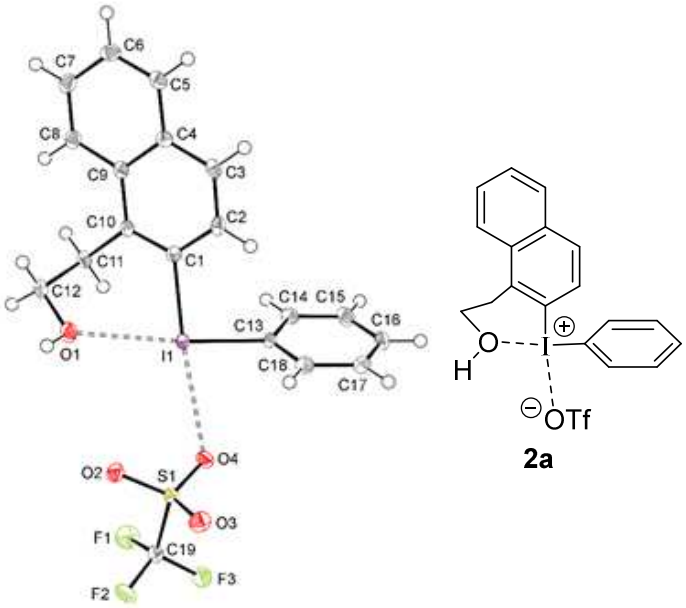
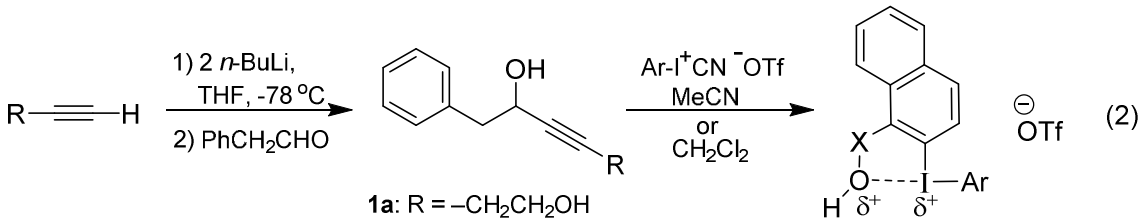


Figure 2. ORTEP representation of naphthyl(phenyl)iodonium triflate **2a**. Thermal elipsoids are shown at the 50% probability level. Selected bond distances and angles: I1-C1 2.116(2) Å, I1-C13 2.111(2) Å, I1-O1 2.7645(17) Å, I1-O4 2.9295(16) Å; C1-I1-C13 95.76(9) °, C1-I1-O1 78.83(7) °, C13-I1-O4 173.76(7) °. The closest-contact triflate ion is shown whereas the triflate within the same unit cell as the cationic core was omitted for clarity.

We then performed the reaction with alkynediols **1b** - **1d** (eq 2) and found that the same electrophilic cyclization, dehydration/aromatization process occurred to form five- as well as six-membered hydroxyl-coordinated naphthyl(aryl)iodonium salts **2b-2d**, as shown in eq 2 and **Table 1**. Alkynediol **1e**, which would have led to a seven-membered chelation product only led



1a: R = –CH_2CH_2OH
1b: R = –CH_2OH
1c: R = –$CH(CH_3)OH$
1d: R = –CH(*i*-Pr)OH
1e: R = –$CH_2CH_2CH_2OH$

2a: X = –CH_2CH_2–; Ar = Ph: 82%
2b: X = –CH_2–; Ar = Ph, 76%
2c: X = –$CH(CH_3)$–; Ar = Ph, 80%
2d: X = –CH(*i*-Pr)–; Ar = Ph, 36%
2e: X = –CH_2CH_2–; Ar = 3,5-$(CF_3)_2C_6H_3$–, 62%

to rapid decomposition. A final salt was synthesized by reaction of alkynediol **1a** with the 3,5-bis(trifluoromethyl)phenyl analog of Stang's reagent[15] to afford salt **2e**.

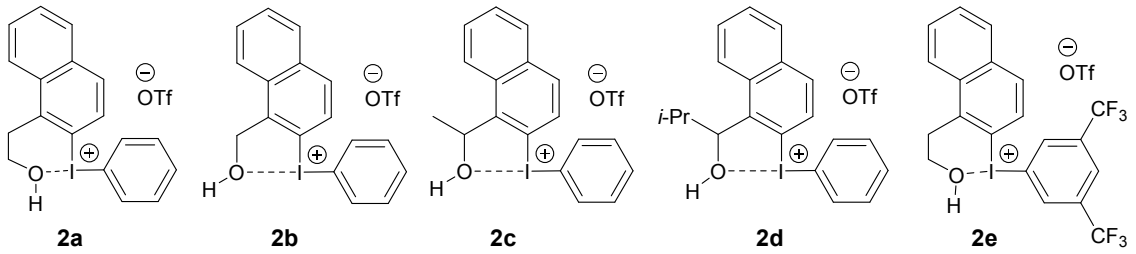
While we were able to isolate **2a-2e** from reactions run in CH_3CN, rapid addition of Et_2O solvent frequently led to oils rather than solids. We later found that isolation was far more efficient if the reactions were run in CH_2Cl_2 for 6-12 hours followed by addition of Et_2O and *n*-hexane. Although Stang's reagent is only sparingly soluble in CH_2Cl_2, the reactions did become homogeneous as the reactions progressed. In a direct comparison of different reactions in the two solvents, salt **2b** was isolated in 46% yield from CH_3CN whereas it was obtained in 72% yield from CH_2Cl_2 on a 0.28 mmol scale. Isolation from DCM was facile in all cases except for the isopropyl-substituted 5-ring chelate, **2d**. In this particular example, the reaction in CH_2Cl_2 was not nearly as clean as the others and the product was also more soluble in Et_2O.

Salts **2a-2e** were fully-characterized by ^1H, ^{13}C and ^{19}F NMR spectroscopy as well as high resolution mass spectrometry. The aromatic regions of ^1H NMR spectra for **2a-2e** were surprisingly complex because of overlapping resonances with varying coupling constants. This phenomenon is likely due to restricted rotation about the iodine-aryl bonds making positions on the phenyl moiety diastereotopic.

All salts were also analyzed by X-ray diffraction[25] of crystals grown by slow diffusion of Et_2O into CD_3CN solutions at rt. The resulting crystallographic data displayed R1 values (**Table 1**, row 2) between 0.0142 and 0.0490, with the largest value resulting from analysis of **2e**, which contained three different CF_3 moieties. The bond lengths for all I–C bonds in **2a**-**2e** are remarkably consistent at 2.10–2.14 Å (**Table 1**, rows 3-4).

As with most iodonium salts, the crystal structure of **2a** reveals a distorted T-shape, but in **2a-2e**, the coordination involves a hydroxyl, naphthyl, and phenyl moieties around the iodine(III)

Table 1. Yields, analytical data and structural features of iodonium salts **2a-2e**.



2a **2b** **2c** **2d** **2e**

Row	Compound	**2a**	**2b**	**2c**	**2d**	**2e**
1	Mp (^{o}C)	118-120	125-131	150-153	193-196	125-129
2	X-ray data, R1	0.0205	0.0142	0.0147	0.0178	0.0490
3[a]	I-C_{naphth}, (Å)	2.116(2)	2.1410(15)	2.1309(16)	2.1341(16)	2.129(6)
4[b]	I-C_{Ar}, (Å)	2.111(2)	2.1041(15)	2.1070(16)	2.1002(16)	2.124(4)
5 [a,b]	C_{naphth}-I-C_{Ar} (^{o})	95.76(9)	95.08(6)	95.48(6)	95.20(6)	95.1(2)
6[a]	HO-I-C_{naphth} (^{o})	78.83(7)	71.78(5)	72.47(5)	72.23(5)	77.92(18)
7[b]	HO-I-C_{Ar} (^{o})	173.76(7)	166.08(5)	166.17(5)	158.66(5)	171.37(17)
8	I-OH, Å	2.7645(17)	2.6164(11)	2.5953(12)	2.6046(12)	2.691(5)
9	I-OTf, Å	2.9295(16)	3.0143(12)	2.9330(12)	2.9660(13)	2.759(5)
10[b]	HO-$plane_{ClC}$ (Å)	0.149(3)	0.203(2)	0.299(2)	-0.751(2)	-0.238(8)

[a] C_{naphth} indicates the carbon on the naphthyl moiety to which the iodine atom is attached.
[b] C_{Ar} indicates the carbon on the phenyl or 3,5-bis(trifluoromethyl)phenyl moiety to which the iodine is attached.
[c] Deviation of hydroxylic oxygen from least-squares plane defined by the iodine-bonded aromatic carbons and iodine.

center.[1] If one also considers the triflate counter-ion, however, the geometry is approximately square planar around the iodine. The C_{napth}–I– C_{Ph} bond angle of **2a** (**Table 1**, row 5) is 95.76(9) ^{o}, which is similar to bond angles typical of other diaryl salts (ca. 90 ^{o})[1] as well as alkenyl(aryl)iodonium triflates we reported.[26] There is little deviation from this angle in any of the other structures.

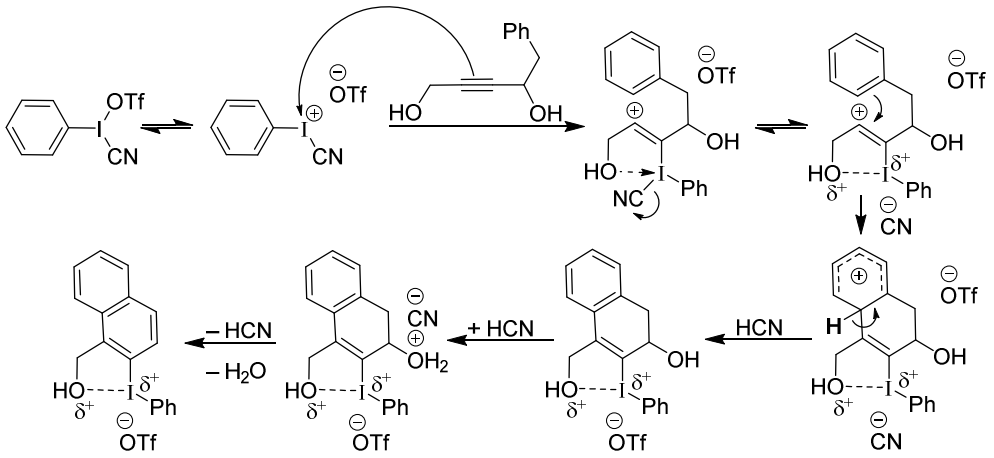
The HO–I–C_{napth} bond angle (**Table 1**, row 6) is, however, reduced from ca. 79 ^{o} in **2a** to near 72 ^{o} in the five-membered hydroxyl-chelated structures **2b-d** because of geometric constraints. As might be expected, the HO–I–C_{Ph} angle (row 7) also decreases from a nearly linear relationship of approximately 174 ^{o} for **2a** and 171 ^{o} for **2e** to a low of 158 ^{o} for **2d**.

For **2a**, the chelated hydroxyl revealed an I–OH interaction of 2.7645(17) Å (**Table 1**, row 8), but the five-membered ring chelated structures **2b**-**2d** had I–OH distances that were significantly shorter, ranging from approximately 2.60 to 2.62 Å.

For most iodonium salts, the I–O distances between the iodine atom and anion range from 2.3-2.7 Å[1] and in alkenyl(aryl)iodonium triflates we reported,[26] the I–OTf distances ranged from 2.77 to 2.91 Å. In **2a**-**2e**, the I–OTf distances of 2.76-3.01 Å (**Table 1**, row 9), were similar to the alkenyl(aryl)iodonium triflates, with the most electron-deficient salt, **2e**, displaying the shortest of the I-OTf interactions. All of these I-O distances are, however, well-within the 3.5 Å sum of the van der Waals radii for iodine and oxygen.[27] Other heterocyclic, five-membered ring systems such as those described by Togni and co-workers contain much shorter (2.1176(14) Å) covalent bonds between oxygen and iodine.[28]

We also used the iodine and *ipso* carbons of *both* the aryl and naphthyl moieties to define a plane and calculated how much the hydroxyl oxygen deviated from that plane (**Table 1**, row 10). The isopropyl-substituted salt, **2d**, showed the greatest deviation from the plane at 0.751(2) Å and this is surely the result of steric congestion.

A proposed mechanism for this new electrophilic cyclization to naphthyl(aryl)iodonium salts is shown in **Scheme 1**. The I–OTf interaction is largely ionic leaving [Ph–I^+–CN] as the electrophile that the alkyne π-electrons attack to generate an incipient alkenyl cation. Coordination with either of the two hydroxyls could assist in initial delivery of the alkyne to the electrophile. Coordination would also assist in departure of cyanide, which does not appear in any of the X-ray structures. Attack of the pendant phenyl would then afford an arenium ion that



Scheme 1. Proposed mechanism for electrophilic cyclization of alkynediols.

would re-aromatize. Subsequent protonation of the propargylic hydroxyl by HCN and final dehydration would afford the second ring of the naphthyl moiety and generate the observed salts with H_2O and HCN as byproducts. The hypothesis that hydroxyl coordination assists in the reaction is supported by the fact that decomposition occurred almost instantaneously when Stang's reagent was reacted with 1-phenylhept-3-yne-2,7-diol **1e**, which would form a seven-membered chelate rather than the five- or six-membered chelates observed.

Conclusions.

We have discovered that alkynediols containing a tethered phenyl moiety react with Stang's reagent (PhI^+CN^-OTf) or the bis(trifluoromethyl)phenyl analog to form naphthyl(aryl)iodonium triflate compounds. The reaction occurs over the course of 6-12 hours at room temperature by initial attack of the alkyne on the electrophilic, hypervalent iodine center. Subsequent Friedel-Crafts reaction and dehydration then afford the majority of salts in greater than 70% yield. This reaction represents a novel reaction manifold for Stang's reagent(s) and a new method for synthesizing unsymmetric diaryliodonium salts.

Experimental

Materials and Methods. All reactions were carried out under argon gas unless otherwise noted. Dichloromethane and CH_3CN were distilled from CaH_2. Flash column chromatography was performed on silica gel (200-400 mesh). Thin layer chromatography was conducted using general-purpose silica gel TLC plates on glass. Visualization was accomplished with UV light or by heating plates dipped in cerium ammonium molybdate (CAM) or basic potassium permanganate staining solutions. Fourier transform infrared (FT-IR) spectra were recorded as ATR samples on an FTIR spectrophotometer. ^{1}H NMR spectra were recorded at 400 MHz and are reported in ppm using solvent or TMS as internal standards. When a resonance appears as a simplified splitting pattern, "app" is used as an abbreviation for "apparent." ^{19}F NMR spectra were recorded at 376 MHz using $CFCl_3$ as an external standard (0.0 ppm). Proton-decoupled ^{13}C-NMR spectra (attached proton test) were recorded at 100 MHz and are reported in ppm using solvent or TMS as internal standards. Quaternary (C) and methylene (CH_2) carbons, which are positive in the apt spectra, are listed as (e), whereas methine (CH) and methyl carbons (CH_3) are listed as (o). All HRMS analyses were obtained using positive-ion mode electrospray ionization.

X-Ray quality crystals of naphthyl(aryl)iodonium triflates **2a**-**2e** were obtained by slow diffusion of Et_2O into CD_3CN solutions of the corresponding salts at room temperature. Details of the X-ray experiments and crystal data are summarized in the supporting information (CIF files). Selected bond lengths and bond angles are given in Table 1. Crystallographic data for the structures reported herein have been deposited with the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 1559387-1559391. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Procedure; preparation of 6-Phenylhex-3-yne-1,5-diol (1a). 3-Butyne-1-ol (5.40 mL, 71.3 mmol) was dissolved in dry THF (100 mL), the solution cooled to -78 ^{o}C, and *n*-BuLi (2.5 M, 57 mL, 144 mmol) added dropwise to afford a suspension. The resulting suspension was stirred for 45 minutes and phenylacetaldehyde (8.10 mL, 69.4 mmol) was added dropwise via syringe. The cold bath was removed and the solution allowed to warm for 1 h. The reaction was quenched with NH_4Cl_{aq} (50 mL). The reaction mixture was extracted with Et_2O (3 x 50 mL), the organic portion dried ($MgSO_4$) and concentrated in vacuo. The diol was then purified by column chromatography using gradient elution of hexanes/EtOAc (1/1 - 2/3) to afford 5.79g (43%) of the diol as a viscous, light yellow oil that solidified upon standing: mp = 51-53 ^{o}C; R_f = 0.30 (1/1 hexanes/EtOAc); IR (ATR) 3240 (s), 2941 (w), 2918 (w), 1493 (m), 1175 (s), 1136 (s), 1055 (vs), 1020 (vs) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.22-7.32 (m, 5H), 4.55 (td, *J* = 5.8, 1.8 Hz, 1H), 3.64 (t, *J* = 6.4 Hz, 2H), 2.97 (d, *J* = 6.4 Hz, 2H), 2.42 (td, *J* = 6.0, 1.8 Hz, 2H); ^{13}C{^{1}H} (apt) NMR (100 MHz, $CDCl_3$) δ = 137.07 and 137.06 (e, diastereomeric pair), 129.9 (o), 128.6 (o), 127.1 (o), 83.4 (e), 82.6 (e), 63.5 (o), 61.0 (e), 44.4 (e), 23.2 (e); HRMS (ESI) for sodium-bound dimer *m/z* $[2xM+Na]^+$ calcd for $C_{24}H_{28}O_4Na$: 403.1874; found: 403.1878.

5-phenylpent-2-yne-1,4-diol (1b). This known[29] alkynediol was made according to the general procedure with propargyl alcohol (3.0 mL, 55.3 mmol) and phenylacetaldehyde (6.5 mL, 55.3 mol). The diol was then purified by column chromatography using hexanes/EtOAc (1/1) as eluent to afford 3.73 g (38%) of the diol as a light yellow oil that solidified upon standing: mp = 53-55 ^{o}C; R_f = 0.28 (1/1 hexanes/EtOAc; IR (ATR) 3238 (s), 2941 (w), 2918 (w), 1493 (m), 1175 (s), 1136 (s), 1055 (vs), 1020 (v)s cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.22-7.34 (m, 5H), 4.58 (br s, 1H), 4.21 (br s, 2H), 2.98 (d, *J* = 6.4Hz, 2H); ^{13}C{^{1}H} (apt) NMR (100 MHz,

$CDCl_3$) δ = 136.8 (e), 129.9 (o), 128.6 (o), 127.1 (o), 86.2 (e), 84.1 (e), 63.3 (o), 50.9 (e), 44.1 (e).

1-Phenylhex-3-yne-2,5-diol (1c). This known compound[30] was prepared by the general method from 3-butyne-2-ol (3.2g, 45.5 mmol), *n*-Bu-Li (36.4 mL, 91.1mmol) and phenylacetaldehyde (4.8 mL, 41.0 mmol). Chromatographic purification using hexanes/EtOAc (1/1) afforded 4.58 g (52.9%) of **1c** as a light yellow oil which contained a mixture of diastereomers: R_f = 0.37 (1/1 hexanes/EtOAc); IR (ATR) 3316 (m), 3030 (w), 2984 (w), 2932 (w), 1667 (w), 1371 (m), 1454 (m), 1144 (s), 1079 (w), 1030 (vs), cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.18-7.31 (m, 5H), 4.52 (ddd, *J* = 6.4Hz, 6.2Hz, 1.2Hz, 1H), 4.45 (dq, *J* = 6.4Hz, 6.8Hz, 1H), 3.55 (br s, 1H), 2.94 (d, *J* = 6.4Hz, 2H), 1.36 (d, *J* = 6.4Hz, 1.5H), 1.35 (d, *J* = 6.8Hz, 1.5H); $^{13}C\{^1H\}$ (apt) NMR (100 MHz, $CDCl_3$) δ = 136.8 (e), 130.0 (o), 128.6 (o), 127.1 (o), 87.9 (e), 84.6 (e), 63.3 (o), 58.4 (o), 44.18 (e), 44.15 (e), 24.29 (o), 24.27 (o); HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{12}H_{14}O_2Na$: 213.0886; found: 213.0884

6-Methyl-1-phenylhept-3-yne-2,5-diol (1d). The title compound was isolated as a byproduct of the synthesis of 6-methyl-1-phenylhept-3-yne-2,6-diol according to the published method[22] with 1-phenyl-3-butyne-2-ol (3.11 g, 21.3 mmol), *n*-BuLi (17.9 mL, 44.7 mmol) and isobutylene oxide (4.00 mL, 32.8 mmol). The diol was then isolated by column chromatography using hexanes/EtOAc (1/1) as eluent to afford 0.49 g (11%) of the diol as a light yellow oil: R_f = 0.47 (1/1 hexanes/EtOAc); IR (ATR) 3335 (m), 2961 (m), 2926 (m), 1705 (m), 1497 (m), 1250 (w), 1142 (w), 1028 (vs) cm^{-1}. ^1H NMR (400 MHz, CD_3CN) δ = 7.25-7.35 (m, 4H), 7.19-7.24 (m, 1H), 4.51 (br s, 1H), 4.02-4.08 (m, 1H), 3.32-3.41 (m, 1H), 3.14 (br s, 1H), 2.93 (dd, *J* = 13.2, 6.8 Hz, 1H), 2.88 (dd, *J* = 12.8, 7.2 Hz, 1H), 1.66-1.77 (m, 1H), 0.89 (dd, *J* = 6.6, 1.2 Hz, 3H),

0.89 (d, J = 6.4Hz, 3H). $^{13}C\{^{1}H\}$ (apt) NMR (100 MHz, CD_3CN) δ = 139.1 (e), 131.1 (o) 129.4 (o), 127.8(o), 87.1 (e), 87.0 (e), 86.3 (e), 86.3 (e), 68.2 (o), 64.0 (o), 45.47 (e), 45.45 (e), 35.8 (o), 18.8 (o), 18.2 (o). HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{14}H_{18}O_2Na$: 241.1199; found: 241.1198.

7-Phenylhept-4-yne-1,6-diol (1e). The title compound was prepared according to the general procedure with 4-pentyne-1-ol (5.93 g, 70.5 mmol) and phenylacetaldehyde (8.60 mL, 73.5 mol) added dropwise via syringe. The diol was then purified by column chromatography using hexanes/EtOAc (1/1) as eluent to afford 4.81 g (33%) of the diol as a light yellow oil, which is a mixture of diastereomers: R_f = 0.33 (1/1 hexanes/EtOAc); IR (ATR) 3333 (m), 2943 (w), 2879 (w), 1496 (m), 1453 (m), 1077 (m), 1030 (vs) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.20-7.32 (m, 5H), 4.52 (tt, J = 6.6, 2.0, Hz, 1H), 3.62 (t, J = 6.2 Hz, 2H), 2.94 (d, J = 6.6 Hz, 2H), 2.80-3.02 (br s, 2H), 2.28 (dt, J = 6.2, 2.0 Hz, 2H), 1.67 (quintet, J = 6.2 Hz, 2H); $^{13}C\{^{1}H\}$ (apt) NMR (100 MHz, $CDCl_3$) δ = 137.2 (e), 130.0 (o), 128.6 (o), 127.0 (o), 85.8 (e), 81.6 (e), 63.6 (o), 61.8 (e), 44.7 (e), 31.4 (e), 15.5 (e); HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{13}H_{16}O_2Na$: : 227.1043; found: 227.1041.

General Procedure for Preparation of Naphthyl(aryl)iodonium Triflates. (1-(2-Hydroxyethyl)naphthalen-2-yl)(phenyl)iodonium trifluoromethanesulfonate (2a). 6-Phenylhex-3-yne-1,5-diol **1a** (50 mg, 0.26 mmol) was dissolved in CH_2Cl_2 and Stang's reagent (132 mg, 0.35 mmol) was added. After stirring at rt overnight, the product was precipitated by slowly adding 5 mL Et_2O followed by 2 mL *n*-hexane to the CH_2Cl_2 solution, then cooling in freezer for 48 h. Isolation by vacuum filtration afforded 81 mg (82%) of **2a** as an off-white microcrystalline solid: mp = 118-120 ^{o}C; IR (ATR) 3374 (m), 3094 (w), 2916 (w), 2880 (w),

1231 (vs), 1221 (vs), 1161 (vs), 1022 (vs) cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ = 8.22-8.30 (m, 1H), 8.10-8.15 (m, 2H), 7.94-8.01 (m, 1H), 7.80 (d, *J* = 9.2 Hz, 1H), 7.70-7.77 (m, 3H), 7.68 (d, *J* = 9.2 Hz, 1H), 7.56 (app tt, *J* = 8.1, 2.0 Hz, 2H), 4.15 (t, *J* = 4.1 Hz, 1H), 3.88 (dt, *J* = 5.5, 4.1 Hz, 2H), 3.73 (t, *J* = 5.5 Hz, 2H); ^{19}F NMR (376 MHz, CD_3CN) δ = –78.05; $^{13}C\{^1H\}$ (apt) NMR (100 MHz, CD_3CN) δ = 141.2 (e), 137.4 (o), 136.1 (e), 134.3 (o), 133.6 (e), 133.4 (o), 132.7 (o), 130.5 (o), 130.4 (o), 130.2 (o), 129.9 (o), 126.6 (o), 120.4 (e), 115.7 (e), 62.7 (e), 38.5 (e); HRMS (ESI) *m/z* $[M\text{-}OTf]^+$ calcd for $C_{18}H_{16}IO$: 375.0240; found: 375.0234.

(1-(Hydroxymethyl)naphthalen-2-yl)(phenyl)iodonium trifluoromethanesulfonate (2b). 5-Phenyl-2-pentyne-1,4-diol **1b** (51 mg, 0.29 mmol) was dissolved in CH_2Cl_2 and Stang's reagent (146 mg, 0.38 mmol) was added. After stirring at rt for 8 h, the product was precipitated by slowly adding 8 mL Et_2O to the CH_2Cl_2 solution. Isolation by vacuum filtration afforded 112 mg (76%) of **2b** as an off-white microcrystalline solid: mp = 125-131 ^oC; IR (ATR) 3242 (m), 1277 (vs), 1234 (vs), 1221 (vs), 1163 (vs), 1022 (vs) cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ = 8.15 (m, 2H), 8.01-8.08 (m, 1H), 7.95-8.01 (m, 1H), 7.88 (app tt, *J* = 7.8 Hz, 1.3 Hz, 1H), 7.81 (d, *J* = 9.2 Hz, 1H), 7.70-7.75 (m, 2H), 7.67 (app tt, *J* = 7.8 Hz, 1.7 Hz, 2H), 7.06 (d, *J* = 9.2 Hz, 1H), 5.60 (br quintet, *J* = 5.1 Hz, 1H), 5.49 (d, *J* = 5.1 Hz, 2H); ^{19}F NMR (376 MHz, CD_3CN) δ = –78.10; $^{13}C\{^1H\}$ (apt) NMR (100 MHz, CD_3CN) δ = 139.3 (o), 137.8 (e), 135.1 (o), 135.0 (e), 133.9 (o), 132.9 (o), 132.8 (e), 130.3 (o), 130.1 (o), 129.7 (o), 126.4 (o), 124.4 (o), 111.8 (e), 109.4 (e), 62.5 (e); HRMS (ESI) *m/z* $[M\text{-}OTf]^+$ calcd for $C_{17}H_{14}IO$: 361.0084; found: 361.0079.

(1-(1-Hydroxyethyl)naphthalen-2-yl)(phenyl)iodonium trifluoromethanesulfonate (2c). 1-Phenylhex-3-yne-2,5-diol **1c** (51 mg, 0.27 mmol) was dissolved in CH_2Cl_2 and Stang's reagent (132 mg, 0.35 mmol) added. After stirring at rt overnight, the product was precipitated by slowly

adding 10 mL Et_2O followed by 8 mL *n*-hexane to the CH_2Cl_2 solution, then cooling in the freezer for 48 h. Isolation by vacuum filtration afforded 81 mg (80%) of **2c** as an off-white microcrystalline solid: mp = 150-153 ^oC; IR (ATR) 3254 (m), 3084 (w), 2980 (w), 2928 (w), 1229 (vs), 1219 (vs), 1163 (vs), 1022 (vs) cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ = 8.16 (dd, *J* = 8.1, 1.2 Hz, 2H), 8.07 (d, *J* = 8.1 Hz, 1H), 7.96 (dd, *J* = 6.2, 2.4 Hz, 1H), 7.88 (t, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 9.0, 1H), 7.63-7.74 (m, 4H), 6.96 (d, *J* = 9.0, 1H), 5.98-6.11 (overlapping br s, 1H; q, *J* = 6.7 Hz, 1H), 1.69 (d, *J* = 6.7 Hz, 3H); ^{19}F NMR (376 MHz, CD_3CN) δ = –78.09; $^{13}C\{^1H\}$ (apt) NMR (100 MHz, CD_3CN) δ = 141.6 (e), 139.5 (o), 135.1 (e), 135.1 (o), 133.8 (o), 132.9 (o), 132.5 (e), 130.4 (o), 129.8 (o), 129.7 (o), 125.9 (o), 124.5 (o), 112.0 (e), 107.4 (e), 68.6 (o), 22.9 (o); HRMS (ESI) *m/z* $[M\text{-}OTf]^+$ calcd for $C_{18}H_{16}IO$: 375.0240; found: 375.0236.

(1-(1-Hydroxy-2-methylpropyl)naphthalen-2-yl)(phenyl)iodonium trifluoromethane-sulfonate (2d). 6-Methyl-1-phenylhept-3-yne-2,5-diol **1d** (50 mg, 0.23 mmol) was dissolved in CH_2Cl_2 and Stang's reagent (109 mg, 0.29 mmol) was added. After stirring at rt overnight, the product was precipitated by slowly adding 5 mL Et_2O followed by 2 mL *n*-hexane to the CH_2Cl_2 solution. Isolation by vacuum filtration afforded 41 mg (36%) of **2d** as an off-white microcrystalline solid: mp = 193-196 ^oC; IR (ATR) 3227 (w), 2965 (w), 2932 (w), 2876 (w), 1229 (vs), 1219 (vs), 1161 (vs), 1022 (vs) cm^{-1}. ^1H NMR (400 MHz, CD_3CN) δ = 8.16-8.19 (m, 2H), 8.08-8.13 (m, 1H), 7.93-8.00 (m, 1H), 7.90 (app tt, *J* = 7.5 Hz, 1.2 Hz, 1H), 7.81 (d, *J* = 9.2 Hz, 1H), 7.66-7.74 (m, 4H), 6.98 (d, *J* = 9.2 Hz, 1H), 5.97 (d, *J* = 5.1 Hz, 1H), 5.74 (dd, *J* = 5.1, 4.7 Hz, 1H), 2.40 (app dsept, *J* = 6.6, 4.7 Hz, 1H), 1.094 (d, *J* = 6.6 Hz, 3H), 1.092 (d, *J* = 6.6 Hz, 3H). ^{19}F NMR (376 MHz, CD_3CN) δ = –78.10; $^{13}C\{^1H\}$ (apt) NMR (100 MHz, CD_3CN) δ = 140.0 (e), 139.6 (o), 135.2 (e), 135.2 (o), 133.9 (o), 133.5 (e), 133.0 (o), 130.4 (o), 129.8 (o),

129.5 (o), 125.9 (o), 125.2 (o), 111.6 (e), 108.8 (e), 76.0 (o), 35.7 (o), 20.7 (o), 17.6 (o); HRMS (ESI) m/z [M-OTf]$^+$ calcd for $C_{20}H_{20}IO$: 403.0553; found: 403. 0547.

(3,5-bis(trifluoromethyl)phenyl)(1-(2-hydroxyethyl)naphthalen-2-yl)iodonium trifluoromethanesulfonate (2e). 6-Phenylhex-3-yne-1,5-diol **1a** (27 mg, 0.14 mmol) was dissolved in CD_3CN and (3,5-bis(trifluoromethyl)phenyl)(cyano)-λ3-iodanyl trifluoromethanesulfonate (87 mg, 0.17 mmol) added. After stirring at rt overnight, Et_2O was added to the sample to induce crystallization. The solid was then dissolved in CH_2Cl_2 and Et_2O added to produce a solid. Isolation by vacuum filtration afforded 57 mg (62%) of **2e** as an off-white microcrystalline solid: mp = 125-129 ^oC; IR (ATR) 3362 (w), 3075 (w), 2965 (w), 2897 (w), 1275 (vs), 1248 (vs), 1165 (vs), 1130 (vs), 1028 (vs) cm^{-1}; ^{1}H NMR (400 MHz, CD_3CN) δ = 8.71 (s, 2H), 8.35 (s, 1H), 8.27-8.33 (m, 1H), 7.99-8.06 (m, 1H), 7.85 (d, J = 9.0 Hz, 1H), 7.72-7.79 (m, 2H), 7.68 (d, J = 9.0 Hz, 1H), 4.35 (t, J = 4.1 Hz, 1H), 3.90 (dt, J = 5.5, 4.1 Hz, 2H), 3.77 (t, J = 5.5 Hz, 2H); ^{19}F NMR (376 MHz, CD_3CN) δ = –78.13; ^{13}C{^{1}H} (apt) NMR (100 MHz, CD_3CN) δ = 141.7 (e), 138.1 (o; mult), 136.3 (e), 135.0 (e; q, J_{CF} = 35 Hz), 133.5 (e), 133.0 (o), 130.7 (o), 130.6 (o), 130.5 (o), 130.1 (o), 128.4 (o; m), 126.7 (o), 123.7 (e; q, J_{CF} = 273 Hz), 122.4 (e; q, J_{CF} = 320 Hz), 121.1 (e), 116.3 (e), 62.8 (e), 38.3 (e); HRMS (ESI) *m/z* [M-OTf]$^+$ calcd for $C_{20}H_{14}F_6OI$: 510.9988; found: 510.9984.

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Notes

The authors declare no competing financial interest.

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Supporting Information

The Supporting information is available free of charge on the ACS Publications website at DOI: XXXXacs.joc.XXX.

Characterization data, including ^{1}H and ^{13}C APT spectra, for alkynediols **1a**–**1d** as well as all naphthyl(aryl)iodonium products **2a**–**2e**.

ORTEPS for naphthyl(aryl)iodonium products **2a**–**2e** X-ray as well as crystallographic details (CIF).

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