Preparation, Molecular Structure, and Diels–Alder Cycloaddition Chemistry of β-Functionalized Alkynyl(phenyl)iodonium Salts

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Abstract: A variety of functionalized alkynyliodonium salts **4a–o** are prepared in good yields via a novel iodonium-transfer process between the appropriate alkynylstannanes **2** and $PhI^+CN,^-OTf$. The electron-deficient acetylenes **4** readily undergo cycloaddition reactions at room temperature with endocyclic, exocyclic, and acyclic 1,3-dienes to afford functionalized vinyliodonium adducts of type **5**, **6**, **7**, and **9**.

Alkynyl(phenyl)iodonium salts **1** have recently emerged as valuable reagents for organic synthesis. These tricoordinate iodine(III) compounds[1,2] have been utilized as precursors to

$$R{-}C{\equiv}C{-}I^+Ph\ {}^-X$$

1

microbiocides,[3] conjugated enynes,[4] unsymmetrical diacetylenes,[5] alkynyl thiocyanates,[6] unique vinyliodinane species,[7] and alkynyl carboxylate, phosphate, and sulfonate esters.[8] They also undergo cyclopentene annulations[9] and serve as alkynylating agents in reactions with both organic[10–12] and organometallic[13] substrates. However, with the exception of the β-trimethylsilyl-substituted compound[10] (**1**: R = Me_3Si), no β-functionalized alkynyliodonium salts were known,[14] thereby limiting the scope and usefulness of alkynyl(phenyl)iodonium salts **1** as synthons. We envisioned that functionalized alkynyliodonium salts, especially those compounds possessing electron-withdrawing β-substituents, would be highly reactive both toward nucleophiles and in cycloaddition reactions. The additional functionality should prove useful for further synthetic manipulation, permitting the synthesis of a large variety of highly functionalized acetylenes and cycloadducts.

In this paper we wish to report the preparation, characterization, and [2 + 4] cycloaddition chemistry of a series of β-functionalized alkynyl(phenyl)iodonium triflates, as well as the X-ray molecular structure of $NC{-}C{\equiv}C{-}I^+Ph,^-OTf$ (**4a**) and the cycloadduct **5h**.

Results and Discussion

Preparation and Characterization of 4a–o. Several methods have been developed for the preparation of alkynyliodonium salts **1**: (a) interaction of Koser's reagent, [hydroxy(tosyloxy)iodo]-benzene, with terminal alkynes,[15] (b) reaction of iodosobenzene/boron trifluoride etherate complex with alkynylsilanes,[16] (c) reaction of μ-oxobis[(hexafluoroantimonato)(phenyl)iodine], μ-oxobis[(tetrafluoroborato)(phenyl)iodine], or μ-oxobis[(hexafluorophosphato)(phenyl)iodine]with a terminal alkyne,[17] and (d) interaction of Zefirov's reagent, iodosobenzene/triflic anhydride complex, with alkynylsilanes[9] or an alkynylstannane.[18] None of these methods, however, proved satisfactory for the synthesis of functionalized alkynyliodonium salts.

A variety of synthetically useful, hitherto unknown functionalized alkynyl(phenyl)iodonium salts **4** can be prepared in good yields in a single step via a new, versatile iodonium-transfer process involving the recently discovered[19] mixed phenyliodonium triflate $PhI^+CN,^-OTf$ (**3**) as the transfer agent.[20] Interaction of the appropriate, readily available alkynylstannanes[21] **2** with reagent **3** in CH_2Cl_2 at low temperature affords the corresponding functionalized alkynyl(phenyl)iodonium triflates **4a–o** as microcrystalline solids in 42–89% isolated yields (Scheme I). Compounds **4a–o** are isolated by low-temperature filtration under a N_2 atmosphere and are recrystallized from CH_2Cl_2/pentane. The majority of pure functionalized alkynyliodonium salts are stable, white, microcrystalline solids that can be stored at room

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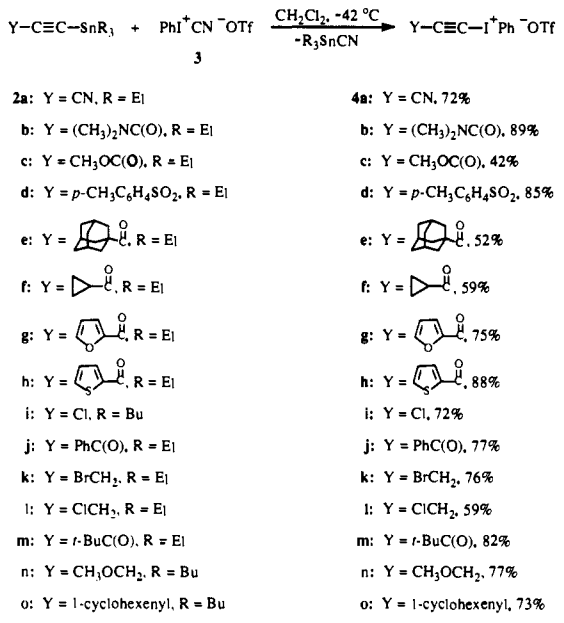
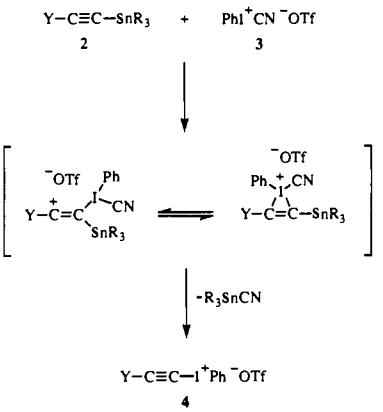
Scheme I



Scheme II



temperature for several days or in a refrigerator for extended periods without change. Salts **4c**, **4g**, and **4o**, however, decompose at room temperature but can be stored at −20 °C for long periods.

Alkynyliodonium salts **4a–o** were fully characterized by multinuclear NMR, IR, and elemental analysis and/or high-resolution mass spectrometry. The infrared spectra display characteristic acetylenic stretches between 2135 and 2270 cm^{-1} and absorptions due to the triflate as well as the various other functional groups. The ^1H NMR spectra display the expected 2:1:2 aromatic resonances between 8.20 and 7.55 ppm typical of phenyliodonium salts[22] as well as the appropriate signals for the remaining protons. The ^{19}F NMR spectra consist solely of a singlet located at ≈ −78 ppm due to the three equivalent fluorine atoms of the triflate moiety. The ^{13}C NMR spectra are particularly diagnostic of the individual functionalized alkynyl(phenyl)iodonium salts **4**. The acetylenic carbons located α to the phenyliodonium group resonate between 45.4 and 13.8 ppm while the acetylenic carbons located β to the phenyliodonium group appear between 109.7 and 83.6 ppm. The quaternary carbon of the triflate group appears as a quartet centered at ≈121 ppm with a $^1J_{C-F}$ = 319 Hz.

The mechanism of formation of functionalized alkynyl(phenyl)iodonium triflates **4** deserves comment. In general, the formation of alkynyliodonium salts **1** proceeds via an initial electrophilic addition of an iodonium species to an alkyne with concomitant formation of a vinyl cation. A likely mechanism for the reaction

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Table I. Crystallographic Data for **4a** and **5h**

	4a	**5h**
formula	$C_{20}H_{10}O_6N_2S_2F_6I_2$	$C_{19}H_{14}O_4S_2F_3I$
formula wt (g/mol)	806.239	554.348
space group	$P\bar{1}$	$P2_1/n$
space group no.	2	14
crystal system	triclinic	monoclinic
cell constants		
a (Å)	11.447(1)	9.873(1)
b (Å)	12.132(1)	9.876(1)
c (Å)	12.654(2)	20.696(2)
α (deg)	95.38(1)	90.00(0)
β (deg)	116.58(1)	96.05(1)
γ (deg)	110.03(1)	90.00(0)
cell volume (Å^3)	1415.10	2006.76
z	2	4
calcd density (g/cm^3)	1.892	1.835
crystal dimens (mm)	0.24 × 0.21 × 0.18	0.41 × 0.40 × 0.25
absorption coeff (cm^{-1})	197.290	18.263
radiation (Å)	Cu 1.54056	Mo 0.71073
reflections measured	5064	4046
unique data	4794	3752
2θ limits (deg)	4.00–130.00	3.00–46.00
scan technique	$\theta/2\theta$ scan	$\theta/2\theta$ scan
scan speed (deg/min)		3.0
scan range	0.8000 + 1.400 (tan θ)°	K −1.3 to K +1.3
data coll. position	bisecting, with ω = 0	
absorption correction	empirical	empirical
min % transmissioin	46.7847	78.40
max % transmission	99.8468	99.99
av % transmission	73.5925	
highest peak in final diff Fourier (e/Å^3)	1.764 about 0.74 Å from I atom	0.650
max ρ value in finall diff Fourier (e/Å^3)	1248.250	652.816
weighting scheme	non-Poisson contribution	non-Poisson contribution
data rejected	$I < 3.00\sigma(I)$	$I < 3.00\sigma(I)$
no. of obsvns	3335	3080
no. of variables	344	305
data-to-parameter ratio	9.695	10.098
shift-to-error ratio	0.004	0.011
error in an obsvn of unit wt.	0.9020	4.9677
R factor	0.0516	0.0321
weighted R factor	0.0559	0.0333

electron-deficient alkynylstannanes **2** with reagent **3** is shown in Scheme II. Vinyl cations located adjacent to an electron-withdrawing group are expected to be high-energy intermediates and therefore not easily obtainable.[23] This probably explains why all attempts at utilizing existing methodologies for the preparation of functionalized alkynyliodonium salts have failed. We were hopeful that use of a highly electrophilic iodonium-transfer reagent such as **3** would facilitate the reaction. However, neither electron-deficient terminal acetylenes nor electron-deficient alkynylsilanes were found to react with reagent **3**. Recently, Lambert and co-workers demonstrated that a β-stannyl substituent[24] stabilizes a cation some 6–7 orders of magnitude better than the already powerful stabilizing effect of a β-silyl group.[25] Utilizing this hyperconjugative β-stabilization effect by employing alkynylstannanes **2** in addition to using the highly electrophilic cyano(phenyl)iodonium triflate (**3**) permits the ready formation of previously unknown functionalized alkynyl(phenyl)-iodonium salts even with powerful electron-withdrawing β-substituents.

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Table II. Selected Bond Distances for 4a[a]

bonds	distances (Å)	bonds	distances (Å)
C1–C2	1.19(2)	C1′–C2′	1.17(2)
C1–1	2.00(1)	C1′–1′	2.01(1)
C4–1	2.11(1)	C4′–1′	2.10(1)
C2–C3	1.38(2)	C2′–C3′	1.40(2)
C3–N1	1.15(1)	C3′–N1′	1.12(2)

[a] Numbers in parentheses are estimated standard deviatiions in the least significant digits.

Table III. Selected Bond Angles for 4a[a]

bonds	angles (deg)	bonds	angles (deg)
C1–C2–C3	179(1)	C1′–C2′–C3′	177(2)
C2–C3–N1	175(2)	C2′–C3′–N1′	178(2)
C2–C1–1	179(1)	C2′–C1′–I′	172(1)
C1–1–C4	92.1(4)	C1′–I′–C4′	93.6(5)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

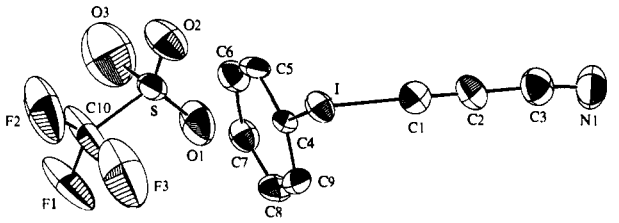


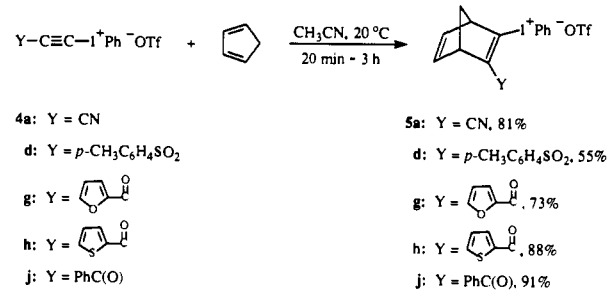
Figure 1. ORTEP of cyanoethynyl(phenyl)iodonium triflate (4a).

X-ray Structure of 4a. A suitable single crystal of compound **4a**, grown from a saturated CD_3CN solution at low temperature, was subjected to standard X-ray analysis. The crystal and structural data for **4a** are summarized in Tables I–III, and an ORTEP representation is shown in Figure 1. Interestingly, the unit cell of **4a** consists of two distinct molecules. In both molecules the geometry about the iodine atom can be described as distorted pseudo-trigonal-bipyramidal or T-shaped. This configuration is in accord with the 10-I-3 nature[26] of **4a**. The phenyl group and two sets of lone-pair electrons occupy equatorial positions while the more electronegative alkyne and anion reside in axial positions.

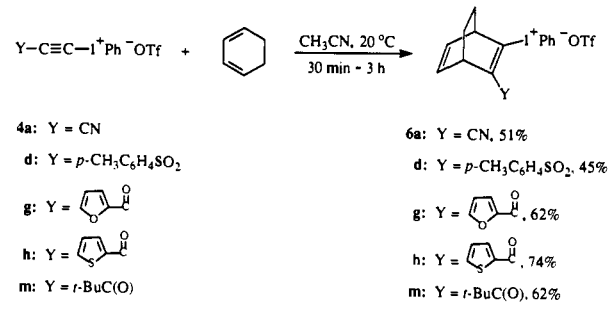
The structural data reveal a normal C≡C bond length for both molecules. More noteworthy are the differing I–O1 and I′–O1′ distances of 2.56 and 2.62 Å, both of which are well outside the computed covalent I–O single-bond length of 1.99 Å. One molecule in the unit cell possesses three nearly identical S′–O′ bond lengths of 1.422 ± 0.029 Å while the other molecule contains two S–O bond lengths of 1.37 ± 0.01 Å and a third S–O bond length of 1.54 ± 0.01 Å. These values clearly indicate that both molecules in the unit cell of **4a** are considerably ionic in character, although to different extents. Moreover, despite the presence of the electronegative cyano substituent, the overall structural features of **4a** do not deviate substantially from those observed for the parent ethynyl(phenyl)iodonium triflate.[18]

Cycloaddition Reactions of Iodonium Salts 4 with 1,3-Dienes. The Diels–Alder reaction has found widespread application in organic synthesis for the construction of unsaturated six-membered carbocycles as a result of its generality, efficiency, and high degree of atom economy.[27] Functionalized alkynyliodonium salts **4**, by virtue of possessing two powerful electron-withdrawing substituents, are expected to display enhanced dienophilic reactivity. Indeed, cycloaddition reactions of representative β-functionalized alkynyliodonium salts with various types of 1,3-dienes (e.g. cyclopentadiene, 1,3-cyclohexadiene, 2,3-dimethyl-1,3-butadiene, and exocyclic diene **8**) in CH_3CN occur under extremely mild conditions (Schemes III–VI). The corresponding cycloadducts of type **5**, **6**, **7**, and **9** are isolated in 45–91% yield as crystalline solids and characterized by spectral and analytical means.

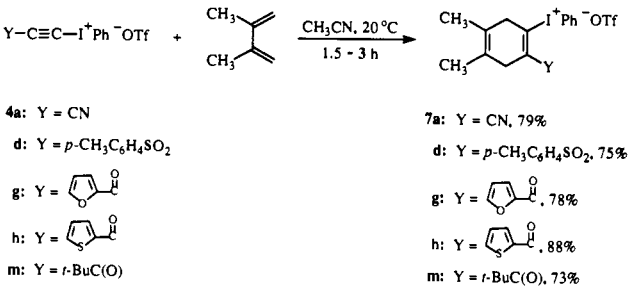
Scheme III



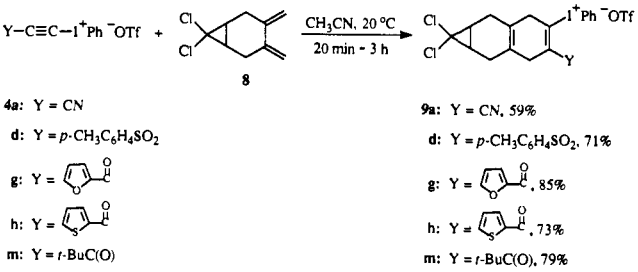
Scheme IV



Scheme V



Scheme VI



X-ray Structure of 5h. The structure of cycloadduct **5h** was unambiguously determined by a single-crystal X-ray analysis. A suitable crystal was grown from a saturated CD_3CN solution at low temperature. The crystal and structural data for **5h** are summarized in Tables I, IV, and V, and an ORTEP representation is shown in Figure 2. The structural data reveal two normal C≡C bond lengths of 1.33 and 1.30 Å in the norbornadienyl portion of the molecule, a C2–I distance of 2.08 Å, and a C13–I–C2 bond angle close to 90°. The I–C2–C3 and C8–C3–C2 bond angles of 123° and 122° in **5h** are closer to the 120° angles expected for an sp^2-hybridized framework than the corresponding angles in the related bis[phenyl[[(trifluoromethyl)sulfonyl]oxy]-iodo]norbornadiene adduct (Figure 3).[23]

Cycloadducts of type **5**, **6**, **7**, and **9** are members of a new class of functionalized alkenyl(phenyl)iodonium salts. These com-

(26) Martin, J. C. *Science* **1983**, *221*, 509. In the J. C. Martin formalism, a 10-I-3 species is a compound in which the central atom, iodine, has ten electrons in its valence shell and possesses three ligands.

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(28) Stang, P. J.; Zhdankin, V. V. *J. Am. Chem. Soc.* **1991**, *113*, 4571.

Table IV. Selected Bond Distances for **5h**[a]

bonds	distances (Å)	bonds	distances (Å)	bonds	distances (Å)
C2–C3	1.327(3)	C1–C7	1.548(3)	C8–C9	1.432(3)
C2–C1	1.520(3)	C7–C4	1.556(3)	C9–S1	1.720(2)
C3–C4	1.543(3)	C2–I	2.078(2)	S1–C12	1.682(3)
C4–C5	1.527(3)	I–C13	2.100(2)	C9–C10	1.384(3)
C1–C6	1.528(3)	C3–C8	1.473(3)	C10–C11	1.405(3)
C5–C6	1.302(3)	C8–O1	1.236(2)	C11–C12	1.336(3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table V. Selected Bond Angles for **5h**[a]

bonds	angles(deg)	bonds	angles (deg)
C2–I–C13	93.71(7)	C2–C1–C6	104.8(2)
C3–C8–C9	123.3(2)	C3–C4–C5	106.1(2)
C3–C8–O1	116.3(2)	C3–C4–C7	97.8(2)
I–C2–C3	122.8(1)	C6–C1–C7	99.5(2)
I–C2–C1	126.8(1)	C1–C7–C4	92.8(2)
C8–C3–C2	121.5(2)	C1–C6–C5	107.4(2)
C8–C3–C4	133.8(2)	C8–C9–S1	117.2(1)
C2–C3–C4	104.7(2)	C8–C9–C10	132.3(2)
C1–C2–C3	110.4(2)	C9–S1–C12	91.2(1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

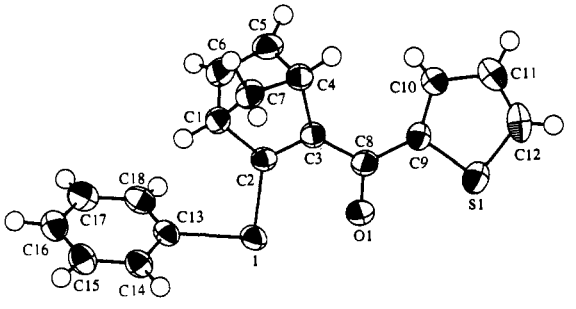

Figure 2. ORTEP of cycloadduct **5h**.

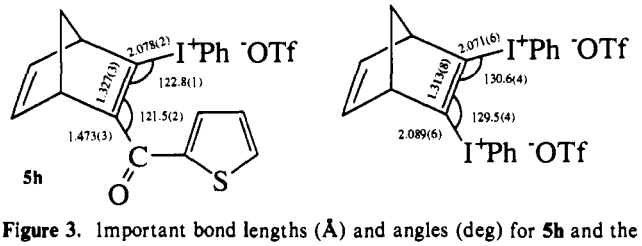

Figure 3. Important bond lengths (Å) and angles (deg) for **5h** and the bis iodonium salt adduct (**5**: Y = PhI^+).

pounds, like their functionalized alkynyliodonium salt precursors, should be highly reactive toward nucleophiles due to the high reactivity and excellent leaving-group ability of the phenyliodonium moiety. In addition, vinyliodonium salts are known to undergo substitution by a variety of nucleophiles.[29] Hence, functionalized vinyliodonium adducts such as **5**, **6**, **7**, and **9** should provide ready access to numerous diversely-functionalized, unsaturated carbocycles.

Conclusions. A variety of functionalized alkynyl(phenyl)-iodonium salts **4a–o** are prepared in good isolated yields in a single step by a newly discovered iodonium-transfer reaction between readily available alkynylstannanes and cyano(phenyl)-iodonium triflate (**3**). These new functionalized alkynyliodonium salts undergo facile [2 + 4] cycloadditions with both cyclic and acyclic 1,3-dienes providing synthetically useful functionalized vinyliodonium adducts. Further chemistry and uses of these functionalized alkynyl(phenyl)iodonium salts are under investigation and will be the subject of future reports.

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Experimental Section

General Methods. Melting points were obtained with a Mel-Temp capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Mattson Polaris FT-IR spectrometer. NMR spectra were recorded on a Varian XL-300 spectrometer. ^1H chemical shifts are reported relative to chloroform at δ 7.24 or acetonitrile at δ 1.93, and ^{13}C chemical shifts are expressed relative to $CDCl_3$ at δ 77.0 or CD_3CN at δ 1.3. The ^{19}F NMR spectra are referenced to $CFCl_3$ (sealed capillary) in the appropriate deuterated solvent. Mass spectra were obtained with a VG Micromass 7050E double-focusing high-resolution mass spectrometer with a VG data system 2000 under positive-ion fast-bombardment (FAB) conditions at 8 keV. 3-Nitrobenzyl alcohol was used as a matrix in CH_2Cl_2 or $CHCl_3$ as solvent, and polypropylene glycol was used as a reference for peak matching. X-ray data for **4a** were collected on a CAD4 diffractometer while data for **5h** were collected using a Syntex P$\bar{1}$ diffractometer. The structures were solved by standard heavy-atom techniques with the SDP/VAX package. Non-hydrogen atoms were refined with anisotropic thermal parameters. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

Materials. Reagent-grade methylene chloride, pentane, and acetonitrile were distilled from calcium hydride prior to use. Acetonitrile was passed through activated, basic alumina immediately before use. The preparation of [cyano[[(trifluoromethyl)sulfonyl]oxy]iodo]benzene (**3**) has been reported previously.[19] Alkynylstannanes **2a–h** and **2j–m** were prepared via reaction of bis(triethyltin) oxide[30] with the appropriate terminal acetylene. Compound **2i** was prepared from tetrachloroethylene, *n*-butyllithium, and tributyltin chloride.[31] Similarly, alkynylstannanes **2n** and **2o** were prepared from the terminal acetylenes by established methods.[32] Ethynyl *p*-tolyl sulfone[33] and the acetylenic ketones were made by the Friedel–Crafts acylation[34] of bis(trimethylsilyl)acetylene followed by fluoride ion promoted removal of the remaining trimethylsilyl group at low temperature.[35] *N,N*-Dimethylpropiolamide was prepared from methyl propiolate and dimethylamine. Propiolonitrile was prepared according to the method of Truce and Gorbaty.[36] Methyl propargyl ether, propargyl bromide, propargyl chloride, 1-ethynylcyclohexene, dicyclopentadiene, 1,3-cyclohexadiene, and 2,3-dimethyl-1,3-butadiene were purchased from Aldrich Chemical Company, and methyl propiolate was purchased from Farchan and used as received. Exocyclic diene **8** was prepared by a published procedure.[37] Reaction flasks were flame-dried and flushed with nitrogen prior to use.

General Procedure for the Preparation of Alkynyl(phenyl)iodonium Triflates 4a–o. A solution of the appropriate functionalized alkynylstannane **2a–o** (1.03–30.9 mmol, a 3% molar excess) in CH_2Cl_2 (10 mL) was added dropwise to a stirred 0.1 M suspension of reagent **3** (1.00–30.0 mmol) in CH_2Cl_2 at –42 °C (CH_3CN/dry ice slush bath) under nitrogen. (The initial suspension gave way to a clear solution upon completion of the addition.) Stirring was maintained at –42 °C for 45 min followed by addition of an equal volume of Et_2O to precipitate the product. The microcrystalline solid was filtered from the cold solution under a nitrogen atmosphere, washed with Et_2O (3 × 30 mL), immediately recrystallized from CH_2Cl_2/pentane, and dried in vacuo.

Cyano[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]acetylene (4a). Reaction of cyano(triethylstannyl)acetylene (**2a**) (0.450 g, 1.76 mmol) with reagent **3** (0.645 g, 1.70 mmol) afforded 0.493 g (72%) of **4a** as a tan microcrystalline solid, mp 100–101 °C dec: IR (CCl_4) 3095, 3072, 2268 (C≡N), 2124 (C≡C), 1582, 1562, 1471, 1447, 1285, 1280, 1263, 1231, 1215, 1185, 1017, 982, 675, 635 cm^{-1}; ^1H NMR (CD_3CN) δ 8.23 (d, 2 H), 7.80 (t, 1 H), 7.63 (t, 2 H); ^{19}F NMR (CD_3CN) δ –78.60 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 136.54, 134.84, 133.93, 121.05 (q, J = 319 Hz, $CF_3SO_3^-$), 118.12, 104.74 (C≡Cl$^+$), 76.23 (CN), 38.20 (C≡*C*l$^+$); FAB HRMS m/z 253.946 514 (M – $CF_3SO_3^-$)$^+$, calcd for C_9H_5NI 253.946 856 2.

(*N,N*-Dimethylcarbamoyl)[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]-acetylene (4b). Reaction of (*N,N*-dimethylcarbamoyl)(triethylstannyl)-

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acetylene (**2b**) (3.84 g, 12.7 mmol) with reagent **3** (4.63 g, 12.2 mmol) afforded 4.90 g (89%) of **4b** as an off-white microcrystalline solid, mp 85–86 °C dec: IR (CCl_4) 3082, 2998, 2940, 2182 (C≡C), 1643 (CO), 1562, 1474, 1444, 1403, 1292, 1236, 1219, 1169, 1029, 987, 674, 637 cm^{-1}; ^1H NMR (CD_3CN) δ 8.21 (d, 2 H), 7.75 (t, 1 H), 7.59 (t, 2 H), 3.05 (s, 3 H), 2.85 (s, 3 H); ^{19}F NMR (CD_3CN) δ −78.51 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 152.05 (CO), 136.02, 134.25, 133.51, 121.23 (q, J = 319 Hz, $CF_3SO_3^-$), 118.11, 96.63 (*C*≡Cl^+), 40.67 (C≡*C*l^+), 38.59 (CH_3), 34.76 (CH_3); FAB HRMS m/z 299.988 416 (M − $CF_3SO_3^-$)$^+$, calcd for $C_{11}H_{11}ONI$ 299.988 484.

Carbomethoxy[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]acetylene (4c). Reaction of carbomethoxy(triethylstannyl)acetylene (**2c**) (0.298 g, 1.03 mmol) with reagent **3** (0.379 g, 1.00 mmol) afforded 0.181 g (42%) of **4c** as an off-white microcrystalline solid,[38] mp 48–50 °C dec: IR (CCl_4) 3056, 2960, 2921, 2179 (C≡C), 1722 (CO), 1562, 1474, 1444, 1334, 1304, 1255, 1231, 1209, 1180, 1023, 989, 676, 638 cm^{-1}; ^1H NMR (CD_3CN, −35 °C) δ 8.20 (d, 2 H), 7.79 (t, 1 H), 7.62 (t, 2 H), 3.73 (s, 3 H); ^{19}F NMR (CD_3CN, −35 °C) δ −79.05 (s, $CF_3SO_3^-$).

***p*-Toluenesulfonyl[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]acetylene (4d).** Reaction of *p*-toluenesulfonyl(triethylstannyl)acetylene (**2d**) (2.50 g, 6.50 mmol) with reagent **3** (2.39 g, 6.31 mmol) afforded 2.85 g (85%) of **4d** as a white microcrystalline solid, mp 117–118 °C dec: IR (CCl_4) 3091, 3073, 3060, 2928, 2135 (C≡C), 1596, 1563, 1471, 1447, 1331 (Ts), 1313, 1265, 1232, 1207, 1161, 1084, 1021, 983, 664, 636 cm^{-1}; ^1H NMR (CD_3CN) δ 8.11 (d, 2 H), 7.81 (d, 2 H), 7.77 (t, 1 H), 7.58 (t, 2 H), 7.47 (d, 2 H), 2.46 (s, 3 H); ^{19}F NMR (CD_3CN) δ −78.73 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 148.72, 137.03, 136.18, 134.60, 133.78, 131.49, 128.75, 117.85, 99.41 (*C*≡Cl^+), 45.40 (C≡*C*l^+), 21.83 (CH_3). Anal. Calcd for $C_{16}H_{12}O_5S_2F_3I$: C, 36.04; H, 2.46; S, 12.02. Found: C, 36.17; H, 2.45; S, 11.93.

1-Adamantoyl[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]acetylene (4e). Reaction of 1-adamantoyl(triethylstannyl)acetylene (**2e**) (4.01 g, 10.2 mmol) with reagent **3** (3.79 g, 10.0 mmol) afforded 2.80 g (52%) of **4e** as a white microcrystalline solid, mp 116–117 °C dec: IR (CCl_4) 3092, 3061, 2934, 2905, 2894, 2852, 2157 (C≡C), 1661 (CO), 1562, 1474, 1454, 1445, 1288, 1233, 1216, 1175, 1167, 1024, 735, 637 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.09 (d, 2 H), 7.64 (t, 1 H), 7.49 (t, 2 H), 1.98 (br s, 3 H), 1.74 (d, 6 H), 1.70–1.57 (m, 6 H); ^{19}F NMR ($CDCl_3$) δ −78.30 (s, $CF_3SO_3^-$); ^{13}C NMR ($CDCl_3$) δ 190.37 (CO), 134.70, 132.88, 132.35, 119.47 (q, J = 319 Hz, $CF_3SO_3^-$), 116.81, 101.04 (*C*≡Cl^+), 47.34, 39.94 (C≡*C*l^+), 37.16, 35.99, 27.43; FAB HRMS m/z 391.055 767 (M − $CF_3SO_3^-$)$^+$, calcd for $C_{19}H_{20}OI$ 391.056 565. Anal. Calcd for $C_{20}H_{20}O_4SF_3I$: C, 44.46; H, 3.73; S, 5.93. Found: C, 44.53; H, 3.80; S, 5.82.

Cyclopropoyl[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]acetylene (4f). Reaction of cyclopropoyl(triethylstannyl)acetylene (**2f**) (2.46 g, 8.24 mmol) with reagent **3** (3.03 g, 8.00 mmol) afforded 2.10 g (59%) of **4f** as a white microcrystalline solid, mp 93–94 °C dec: IR (CCl_4) 3108, 3091, 3019, 2166 (C≡C), 1660 (CO), 1563, 1471, 1447, 1287, 1234, 1221, 1179, 1165, 1026, 992, 908, 733, 671, 634 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.08 (d, 2 H), 7.67 (t, 1 H), 7.52 (t, 2 H), 2.11 (m, 1 H), 1.27 (m, 2 H), 1.13 (m, 2 H); ^{19}F NMR ($CDCl_3$) δ −78.35 (s, $CF_3SO_3^-$); ^{13}C NMR ($CDCl_3$) δ 185.19 (CO), 134.72, 133.04, 132.59, 119.54 (q, J = 319 Hz, $CF_3SO_3^-$), 116.49, 100.75 (*C*≡Cl^+), 38.35 (C≡*C*l^+), 24.57 (CH), 12.33 (CH_2); FAB HRMS m/z 296.976 814 (M − $CF_3SO_3^-$)$^+$, calcd for $C_{12}H_{10}OI$ 296.977 517.

2-Furanoyl[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]acetylene (4g). Reaction of 2-furanoyl(triethylstannyl)acetylene (**2g**) (1.67 g, 5.15 mmol) with reagent **3** (1.90 g, 5.00 mmol) afforded 1.77 g (75%) of **4g** as an off-white microcrystalline solid, mp 74–75 °C dec: IR (CCl_4) 3133, 3118, 3090, 2163 (C≡C), 1638 (CO), 1556, 1472, 1459, 1447, 1401, 1290, 1260, 1236, 1221, 1171, 1049, 1024, 1014, 987, 635 cm^{-1}; ^1H NMR (CD_3CN) δ 8.26 (d, 2 H), 7.84 (s, 1 H), 7.71 (t, 1 H), 7.62 (t, 2 H), 7.46 (d, 1 H), 6.67 (t, 1 H); ^{19}F NMR (CD_3CN) δ −78.43 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 161.39 (CO), 152.55, 151.65, 136.14, 134.42, 133.63, 125.60, 121.09 (q, J = 319 Hz, $CF_3SO_3^-$), 118.08, 114.49, 100.21 (*C*≡Cl^+), 40.63 (C≡*C*l^+); FAB HRMS m/z 322.957 152 (M − $CF_3SO_3^-$)$^+$, calcd for $C_{13}H_8O_2I$ 322.956 781.

(2-Thiofuranoyl)[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]acetylene (4h). Reaction of (2-thiofuranoyl)(triethylstannyl)acetylene (**2h**) (2.11 g, 6.18 mmol) with reagent **3** (2.27 g, 6.00 mmol) afforded 2.58 g (88%) of **4h** as a white powder, mp 103–105 °C dec: IR (CCl_4) 3118, 3094, 3082, 3070, 2168 (C≡C), 1618 (CO), 1517, 1470, 1444, 1411, 1354, 1291, 1283, 1229, 1212, 1181, 1085, 1063, 1014, 985, 973, 675, 647, 628 cm^{-1}; ^1H NMR (CD_3CN) δ 8.26 (d, 2 H), 7.98 (d, 1 H), 7.88 (d, 1 H), 7.80 (t, 1 H), 7.65 (t, 2 H), 7.22 (t, 1 H); ^{19}F NMR (CD_3CN) δ −78.64 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 167.19 (CO), 143.54, 139.33, 138.69, 136.22, 134.54, 133.73, 130.19, 121.28 (q, J = 319 Hz, $CF_3SO_3^-$), 117.86, 100.50 (*C*≡Cl^+), 40.79 (C≡*C*l^+); FAB HRMS m/z 339.933 939 (M − $CF_3SO_3^-$)$^+$, calcd for $C_{13}H_8OSI$ 339.932 202.

Chloro[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]acetylene (4i). Reaction of chloro(tributylstannyl)acetylene (**2i**) (9.00 g, 25.8 mmol) with reagent **3** (9.48 g, 25.0 mmol) afforded 7.45 g (72%) of **4i** as a white microcrystalline solid, mp 105–106 °C dec: IR (CCl_4) 3085, 3065, 2173 (C≡C), 1583, 1564, 1472, 1446, 1299, 1219, 1171, 1023, 987, 673, 636 cm^{-1}; ^1H NMR (CD_3CN) δ 8.17 (d, 2 H), 7.76 (t, 1 H), 7.60 (t, 2 H); ^{19}F NMR (CD_3CN) δ −78.64 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 135.98, 134.21, 133.43, 121.24 (q, J = 319 Hz, $CF_3SO_3^-$), 117.43, 83.64 (*C*≡Cl^+), 13.84 (C≡*C*l^+); FAB HRMS m/z 262.912 482 (M − $CF_3SO_3^-$)$^+$, calcd for C_8H_5ICl 262.912 330. Anal. Calcd for $C_9H_5O_3SClF_3I$: C, 26.20; H, 1.22; S, 7.77. Found: C, 26.30; H, 1.29; S, 7.84.

Benzoyl[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]acetylene (4j). Reaction of benzoyl(triethylstannyl)acetylene (**2j**) (1.04 g, 3.09 mmol) with reagent **3** (1.14 g, 3.00 mmol) afforded 1.11 g (77%) of **4j** as a white microcrystalline solid, mp 113–114 °C dec: IR (CCl_4) 3085, 3071, 2158 (C≡C), 1642 (CO), 1599, 1579, 1471, 1451, 1442, 1294, 1261, 1243, 1221, 1162, 1036, 1019, 736, 698, 626 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.15 (d, 2 H), 8.10 (d, 2 H), 7.70 (t, 1 H), 7.63 (t, 1 H), 7.56 (t, 2 H), 7.47 (t, 2 H); ^{19}F NMR ($CDCl_3$) δ −78.33 (s, $CF_3SO_3^-$); ^{13}C NMR ($CDCl_3$) δ 174.88 (CO), 135.52, 134.99, 134.81, 133.15, 132.70, 130.15, 129.06, 119.62 (q, J = 319 Hz, $CF_3SO_3^-$), 116.66, 101.55 (*C*≡Cl^+), 40.64 (C≡*C*l^+). Anal. Calcd for $C_{16}H_{10}O_4SF_3I$: C, 39.85; H, 2.09; S, 6.65. Found: C, 39.91; H, 2.12; S, 6.59.

3-Bromo-1-[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]propyne (4k). Reaction of 3-bromo-1-(triethylstannyl)propyne (**2k**) (2.50 g, 7.72 mmol) with reagent **3** (2.84 g, 7.49 mmol) afforded 2.66 g (76%) of **4k** as a white microcrystalline solid, mp 108–109 °C dec: IR (CCl_4) 3058, 3016, 2993, 2968, 2938, 2185 (C≡C), 1561, 1471, 1447, 1440, 1296, 1288, 1277, 1233, 1219, 1172, 1055, 1025, 986, 663, 636 cm^{-1}; ^1H NMR (CD_3CN) δ 8.16 (d, 2 H), 7.75 (t, 1 H), 7.60 (t, 2 H), 4.26 (s, 2 H); ^{19}F NMR (CD_3CN) δ −78.36 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 135.89, 134.21, 133.51, 121.29 (q, J = 319 Hz, $CF_3SO_3^-$), 117.57, 103.18 (*C*≡Cl^+), 30.05 (C≡*C*l^+), 14.11 (CH_2). Anal. Calcd for $C_{10}H_7O_3SF_3BrI$: C, 25.50; H, 1.50; S, 6.81. Found: C, 25.43; H, 1.51; S, 6.86.

3-Chloro-1-[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]propyne (4l). Reaction of 3-chloro-1-(triethylstannyl)propyne (**2l**) (2.88 g, 10.3 mmol) with reacgent **3** (3.79 g, 10.0 mmol) afforded 2.52 g (59%) of **4l** as a white microcrystalline solid, mp 107–108 °C dec: IR (CCl_4) 3092, 3086, 3070, 3005, 2963, 2191 (C≡C), 1583, 1562, 1471, 1447, 1293, 1269, 1213, 1171, 1022, 986, 672, 636 cm^{-1}; ^1H NMR (CD_3CN) δ 8.17 (d, 2 H), 7.74 (t, 1 H), 7.58 (t, 2 H), 4.50 (s, 2 H); ^{19}F NMR (CD_3CN) δ −78.33 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 135.75, 134.04, 133.34, 121.05 (q, J = 319 Hz, $CF_3SO_3^-$), 117.40, 102.76 (*C*≡Cl^+), 31.06 (CH_2), 30.45 (C≡*C*l^+); FAB HRMS m/z 276.927 980 (M − $CF_3SO_3^-$)$^+$, calcd for C_9H_7ClI 276.927 969. Anal. Calcd for $C_{10}H_7O_3SClF_3I$: C, 28.16; H, 1.65; S, 7.52. Found: C, 28.07; H, 1.63; S, 7.42.

(Trimethylacetyl)[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]acetylene (4m). Reaction of (trimethylacetyl)(triethylstannyl)acetylene (**2m**) (8.11 g, 25.8 mmol) with reagent **3** (9.48 g, 25.0 mmol) afforded 9.48 g (82%) of **4m** as a white microcrystalline solid, mp 119 °C dec: IR (CCl_4) 3084, 2973, 2154 (C≡C), 1681 (CO), 1562, 1481, 1470, 1446, 1373, 1293, 1234, 1217, 1165, 1087, 1023, 987, 634 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.09 (d, 2 H), 7.67 (t, 1 H), 7.53 (t, 2 H), 1.15 (s, 9 H); ^{19}F NMR ($CDCl_3$) δ −77.59 (s, $CF_3SO_3^-$); ^{13}C NMR ($CDCl_3$) δ 190.65 (CO), 134.54, 132.91, 132.45, 119.43 (q, J = 318 Hz, $CF_3SO_3^-$), 116.70, 100.99 (*C*≡Cl^+), 45.20, 40.11 (C≡*C*l^+), 25.42 (CH_3). Anal. Calcd for $C_{14}H_{14}O_4SF_3I$: C, 36.38; H, 3.05; S, 6.94. Found: C, 36.32; H, 3.00; S, 6.88.

3-Methoxy-1-[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]propyne (4n). Reaction of 3-methoxy-1-(tributylstannyl)propyne (**2n**) (11.1 g, 30.9 mmol) with reagent **3** (11.4 g, 30.0 mmol) afforded 9.69 g (77%) of **4n** as an off-white microcrystalline solid, mp 72–73 °C dec: IR (CCl_4) 3091, 3063, 2965, 2923, 2835, 2189 (C≡C), 1581, 1562, 1471, 1456, 1448, 1435, 1359, 1281, 1272, 1243, 1225, 1177, 1162, 1099, 1024, 987, 676, 635 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.05 (d, 2 H), 7.62 (t, 1 H), 7.51 (t, 2 H), 4.35 (s, 2 H), 3.35 (s, 3 H); ^{19}F NMR ($CDCl_3$) δ −77.71 (s, $CF_3SO_3^-$); ^{13}C NMR ($CDCl_3$) δ 134.10, 132.51, 132.34, 119.60 (q, J = 318 Hz, $CF_3SO_3^-$), 116.40, 104.80 (*C*≡Cl^+), 60.60 (CH_2), 58.40 (CH_3),

(38) Due to the limited solubility and low stability of **4c**, the ^{13}C NMR spectrum and elemental analyses were unobtainable.

30.20 (C≡*C*I⁺). Anal. Calcd for $C_{11}H_{10}O_4SF_3I$: C, 31.30; H, 2.39; S, 7.59. Found: C, 31.22; H, 2.47; S, 7.65.

1-Cyclohexenyl[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]acetylene (4o). Reaction of 1-cyclohexenyl(tributylstannyl)acetylene (**2o**) (1.02 g, 2.58 mmol) with reagent **3** (0.948 g, 2.50 mmol) afforded 0.839 g (73%) of **4o** as an off-white microcrystalline solid,[39] mp 45–46 °C explodes: IR (CCl_4) 3089, 3064, 2945, 2908, 2863, 2150 (C≡C), 1582, 1562, 1469, 1445, 1285, 1231, 1170, 1022, 988, 677, 636 cm⁻¹; ^{1}H NMR ($CDCl_3$, −35 °C) δ 8.00 (d, 2 H), 7.61 (t, 1 H), 7.49 (t, 2 H), 6.41 (br s, 1 H), 2.10 (br d, 4 H), 1.55 (br s, 4 H); ^{19}F NMR ($CDCl_3$, −35 °C) δ −78.54 (s, $CF_3SO_3^-$); ^{13}C NMR ($CDCl_3$, −35 °C) δ 144.57, 133.59, 132.30, 132.14, 119.37 (q, *J* = 319 Hz, $CF_3SO_3^-$), 118.56, 116.35, 109.73 (*C*≡CI⁺), 28.06 (C≡*C*I⁺), 27.68 (CH_2), 25.76 (CH_2), 21.43 (CH_2), 20.61 (CH_2).

General Procedure for [2 + 4] Cycloaddition Reactions of Alkynyl(phenyl)iodonium Salts 4 with 1,3-Dienes. The appropriate diene (1.2–4.5 molar equiv) was added dropwise to a degassed, stirred solution of the iodonium salt **4** (0.40–1.2 mmol) in CH_3CN (10 mL) at 20 °C under nitrogen. Stirring was maintained at room temperature for 20 min–3 h, after which time the solvent and excess diene were removed using a rotary evaporator. The crude product was taken up in CH_2Cl_2 (5 mL) and crystallized by the addition of Et_2O (10 mL) and pentane (5 mL). The microcrystalline solid was further purified by recrystallization from CH_2Cl_2/Et_2O/pentane, isolated by filtration, washed with Et_2O (2 × 10 mL), and dried in vacuo.

2-Cyano-3-[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]-2,5-norbornadiene (5a). Reaction of iodonium salt **4a** (0.164 g, 0.407 mmol) with freshly-distilled cyclopentadiene (0.160 mL, 1.94 mmol) in CH_3CN for 3 h according to the general procedure afforded 0.154 g (81%) of **5a** as a tan microcrystalline solid, mp 156–157 °C dec: IR (CCl_4) 3089, 3061, 3014, 2970, 2942, 2217 (C≡N), 1581, 1558, 1471, 1447, 1269, 1242, 1226, 1182, 1163, 1024, 990, 680, 636 cm⁻¹; ^{1}H NMR (CD_3CN) δ 8.04 (d, 2 H), 7.75 (t, 1 H), 7.57 (t, 2 H), 6.84 (t, 1 H), 6.64 (t, 1 H), 4.15 (br s, 1 H), 4.06 (br s, 1 H), 2.41 (d, 1 H), 2.21 (d, 1 H); ^{19}F NMR (CD_3CN) δ −78.58 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 142.30, 142.11, 142.04, 139.68, 137.02, 134.20, 133.34, 121.63 (q, *J* = 320 Hz, $CF_3SO_3^-$), 114.75 (CN), 113.10, 76.27 (CH_2), 60.59 (bridgehead CH), 58.17 (bridgehead CH); FAB HRMS *m/z* 319.993 501 (M − $CF_3SO_3^-$)⁺, calcd for $C_{14}H_{11}NI$ 319.994 521. Anal. Calcd for $C_{15}H_{11}O_3SNF_3I$: C, 38.40; H, 2.36; S, 6.83; N, 2.99. Found: C, 38.46; H, 2.31; S, 6.75; N, 3.06.

2-(*p*-Toluenesulfonyl)-3-[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]-2,5-norbornadiene (5d). Reaction of iodonium salt **4d** (0.399 g, 0.750 mmol) with freshly-distilled cyclopentadiene (0.280 mL, 3.39 mmol) in CH_3CN for 20 min according to the general procedure afforded 0.245 g (55%) of **5d** as an off-white microcrystalline solid, mp 171–172 °C dec: IR (CCl_4) 3080, 3066, 3003, 2959, 2927, 1595, 1582, 1557, 1473, 1449, 1299, 1235, 1220, 1163, 1153, 1132, 1086, 1026, 990, 717, 675, 637 cm⁻¹; ^{1}H NMR (CD_3CN) δ 8.14 (d, 2 H), 7.87 (t, 1 H), 7.79 (d, 2 H), 7.66 (t, 2 H), 7.51 (d, 2 H), 6.60–6.53 (m, 2 H), 3.89 (br s, 1 H), 3.43 (br s, 1 H), 2.47 (s, 3 H), 2.39 (d, 1 H), 2.10 (d, 1 H); ^{19}F NMR (CD_3CN) δ −78.75 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 159.91, 148.20, 142.94, 141.01, 138.22, 134.94, 133.89, 133.65, 131.67, 129.26 ($CF_3SO_3^-$ not observed), 117.63, 111.54, 74.92 (CH_2), 58.78 (bridgehead CH), 55.18 (bridgehead CH), 21.81 (CH_3); FAB HRMS (*m/z* 449.007 104 (M − $CF_3SO_3^-$)⁺, calcd for $C_{20}H_{18}O_2SI$ 449.004 641. Anal. Calcd for $C_{21}H_{18}O_5S_2F_3I$: C, 42.15; H, 3.03; S, 10.72. Found: C, 42.23; H, 3.00; S, 10.63.

2-(2-Furanoyl)-3-[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]-2,5-norbornadiene (5g). Reaction of iodonium salt **4g** (0.472 g, 1.00 mmol) with freshly-distilled cyclopentadiene (0.380 mL, 4.60 mmol) in CH_3CN for 30 min according to the general procedure afforded 0.391 g (73%) of **5g** as an off-white microcrystalline solid, mp 120–122 °C dec: IR (CCl_4) 3132, 3083, 3012, 2998, 2950, 2879, 1596 (CO), 1561, 1521, 1472, 1457, 1446, 1391, 1331, 1312, 1285, 1244, 1180, 1156, 1045, 1029, 992, 681, 636 cm⁻¹; ^{1}H NMR (CD_3CN) δ 8.08 (d, 2 H), 7.99 (s, 1 H), 7.84 (t, 1 H), 7.70–7.63 (m, 3 H), 7.15 (m, 1 H), 6.80 (t, 1 H), 6.73 (t, 1 H), 4.73 (br s, 1 H), 3.26 (br s, 1 H), 2.62 (d, 1 H), 2.37 (m, 1 H); ^{19}F NMR (CD_3CN) δ −78.70 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 176.20 (CO), 156.49, 152.22, 151.35, 145.14, 144.30, 142.06, 137.84, 134.30, 132.99, 124.16, 121.85 (q, *J* = 321 Hz, $CF_3SO_3^-$), 114.85, 111.90, 75.47 (CH_2), 56.24 (bridgehead CH), 55.21 (bridgehead CH); FAB HRMS *m/z* 389.003 732 (M − $CF_3SO_3^-$)⁺, calcd for $C_{18}H_{14}O_2I$ 389.001 970 2.

2-(2-Thiofuranoyl)-3-[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]-2,5-norbornadiene (5h). Reaction of iodonium salt **4h** (0.415 g, 0.850 mmol) with freshly-distilled cyclopentadiene (0.330 mL, 3.99 mmol) in CH_3CN for 20 min according to the general procedure afforded 0.414 g (88%) of **5h** as an off-white microcrystalline solid, mp 136–138 °C dec: IR (CCl_4) 3096, 3077, 3060, 3014, 3000, 2982, 2946, 2876, 1583 (CO), 1559, 1518, 1505, 1475, 1447, 1407, 1360, 1315, 1287, 1247, 1223, 1172, 1159, 1068, 1027, 992, 675, 636 cm⁻¹; ^{1}H NMR (CD_3CN) δ 8.15 (d, 1 H), 8.07 (m, 3 H), 7.84 (t, 1 H), 7.65 (t, 2 H), 7.34 (t, 1 H), 7.21 (t, 1 H), 6.74 (t, 1 H), 4.60 (br s, 1 H), 3.30 (br s, 1 H), 2.64 (d, 1 H), 2.36 (m, 1 H); ^{19}F NMR (CD_3CN) δ −78.57 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 181.49 (CO), 157.00, 145.10, 143.68, 142.37, 141.94, 139.32, 137.75, 137.13, 134.22, 132.94, 130.57, 121.81 (q, *J* = 321 Hz, $CF_3SO_3^-$), 112.12, 75.77 (CH_2), 56.43 (bridgehead CH), 55.69 (bridgehead CH); FAB HRMS *m/z* 404.980 890 (M − $CF_3SO_3^-$)⁺, calcd for $C_{18}H_{14}OSI$ 404.980 431. Anal. Calcd for $C_{19}H_{14}O_4S_2F_3I$: C, 41.17; H, 2.55; S, 11.57. Found: C, 41.08; H, 2.48; S, 11.50.

2-Benzoyl-3-[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]-2,5-norbornadiene (5j). Reaction of iodonium salt **4j** (0.194 g, 0.402 mmol) with freshly-distilled cyclopentadiene (0.150 mL, 1.82 mmol) in CH_3CN for 1 h according to the general procedure afforded 0.201 g (91%) of **5j** as an off-white microcrystalline solid, mp 102–103 °C dec: IR (CCl_4) 3082, 3073, 3063, 3011, 3001, 2962, 2883, 1593 (CO), 1573, 1560, 1509, 1475, 1445, 1322, 1312, 1289, 1249, 1224, 1170, 1156, 1029, 992, 673, 637 cm⁻¹; ^{1}H NMR (CD_3CN) δ 8.09 (d, 2 H), 7.90–7.84 (m, 3 H), 7.76 (t, 2 H), 7.72–7.61 (m, 3 H), 7.29 (t, 1 H), 6.78 (t, 1 H), 4.38 (br s, 1 H), 3.35 (br s, 1 H), 2.65 (d, 1 H), 2.37 (d, 1 H); ^{19}F NMR (CD_3CN) δ −78.29 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 191.22 (CO), 158.42, 144.98, 144.30, 142.35, 137.93, 136.66, 135.51, 134.51, 133.22, 130.28, 130.13, 121.87 (q, *J* = 321 Hz, $CF_3SO_3^-$), 111.83, 76.42 (CH_2), 56.88 (bridgehead CH), 56.46 (bridgehead CH); FAB HRMS *m/z* 399.024 467 (M − $CF_3SO_3^-$)⁺, calcd for $C_{20}H_{16}OI$ 399.022 224. Anal. Calcd for $C_{21}H_{16}O_4SF_3I$: C, 46.00; H, 2.94; S, 5.85. Found: C, 45.21; H, 3.01; S, 5.81.

2-Cyano-3-[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]bicyclo[2.2.2]-octa-2,5-diene (6a). Reaction of iodonium salt **4a** (0.164 g, 0.407 mmol) with 1,3-cyclohexadiene (0.180 mL, 1.85 mmol) in CH_3CN for 2.5 h according to the general procedure afforded 0.100 g (51%) of **6a** as a tan microcrystalline solid, mp 149–150 °C dec: IR (CCl_4) 3083, 3070, 3060, 3019, 2985, 2961, 2935, 2882, 2215 (C≡N), 1591, 1563, 1471, 1446, 1278, 1260, 1241, 1225, 1215, 1163, 1024, 990, 701, 636 cm⁻¹; ^{1}H NMR (CD_3CN) δ 8.07 (d, 2 H), 7.76 (t, 1 H), 7.58 (t, 2 H), 6.38 (t, 1 H), 6.22 (t, 1 H), 4.39 (m, 1 H), 4.18 (m, 1 H), 1.55–1.39 (br m, 4 H); ^{19}F NMR (CD_3CN) δ −78.63 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 136.88, 134.22, 134.01, 133.77, 133.43, 128.69, 121.67 (q, *J* = 321 Hz, $CF_3SO_3^-$), 116.02 (CN), 113.48, 48.50 (bridgehead CH), 45.52 (bridgehead CH), 26.25 (CH_2), 24.69 (CH_2); FAB HRMS *m/z* 334.009 151 (M − $CF_3SO_3^-$)⁺, calcd for $C_{15}H_{13}NI$ 334.007 774. Anal. Calcd for $C_{16}H_{13}O_3SNF_3I$: C, 39.77; H, 2.71; S, 6.63; N, 2.90. Found: C, 39.81; H, 2.69; S, 6.70; N, 3.00.

2-(*p*-Toluenesulfonyl)-3-[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]-bicyclo[2,2,2]octa-2,5-diene (6d). Reaction of iodonium salt **4d** (0.399 g, 0.750 mmol) with 1,3-cyclohexadiene (0.320 mL, 3.29 mmol) in CH_3CN for 30 min according to the general procedure afforded 0.207 g (45%) of **6d** as an off-white microcrystalline solid, mp 136–138 °C dec: IR (CCl_4) 3089, 3066, 3044, 2970, 2957, 2942, 2923, 2887, 1594, 1584, 1473, 1447, 1332, 1312, 1292, 1231, 1154, 1133, 1087, 1024, 993, 707, 658, 636 cm⁻¹; ^{1}H NMR (CD_3CN) δ 8.19 (d, 2 H), 7.90 (t, 1 H), 7.85 (d, 2 H), 7.69 (t, 2 H), 7.53 (d, 2 H), 6.25 (t, 1 H), 6.16 (t, 1 H), 4.16 (d, 1 H), 3.49 (d, 1 H), 2.47 (s, 3 H), 1.57–1.46 (m, 1 H), 1.40–1.22 (br m, 2 H), 1.18–1.06 (m, 1 H); ^{19}F NMR (CD_3CN) δ −78.66 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 148.81, 148.23, 142.67, 138.81, 135.08, 134.56, 133.75, 133.61, 131.62, 129.20 ($CF_3SO_3^-$ not observed), 121.19, 110.24, 45.00 (bridgehead CH), 43.52 (bridgehead CH), 26.26 (CH_2), 25.86 (CH_2), 21.80 (CH_3); FAB HRMS *m/z* 463.022 754 (M − $CF_3SO_3^-$)⁺, calcd for $C_{21}H_{20}O_2SI$ 463.022 038. Anal. Calcd for $C_{22}H_{20}O_5S_2F_3I$: C, 43.15; H, 3.29; S, 10.47. Found: C, 43.24; H, 3.42; S, 10.36.

2-(2-Furanoyl)-3-[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]bicyclo-[2,2,2]octa-2,5-diene (6g). Reaction of iodonium salt **4g** (0.472 g, 1.00 mmol) with 1,3-cyclohexadiene (0.440 mL, 4.53 mmol) in CH_3CN for 3 h according to the general procedure afforded 0.341 g (62%) of **6g** as an off-white microcrystalline solid, mp 129–130 °C dec: IR (CCl_4) 3143, 3129, 3118, 3100, 3080, 3071, 2942, 2875, 1618 (CO), 1588, 1556. 1515, 1475, 1460, 1454, 1446, 1391, 1335, 1302, 1256, 1235, 1222, 1160, 1149, 1107, 1028, 996, 705, 686, 635 cm⁻¹; ^{1}H NMR (CD_3CN) δ 8.11 (d, 2 H), 8.01 (s, 1 H), 7.86 (t, 1 H), 7.72 (d, 1 H), 7.67 (t, 2 H), 6.82 (t, 1 H), 6.57 (t, 1 H), 6.28 (t, 1 H), 5.13 (m, 1 H), 3.51 (m, 1 H), 1.66–1.37 (br m, 4 H); ^{19}F NMR (CD_3CN) δ −78.73 (s, $CF_3SO_3^-$); ^{13}C NMR

(39) Elemental analyses for **4o** were not obtained due to the low stability of the isolated salt.

(CD_3CN) δ 177.08 (CO), 152.06, 146.49, 138.49, 135.77, 134.54, 133.71, 133.11, 130.82, 124.99, 121.93 (q, J = 320 Hz, $CF_3SO_3^-$), 114.85, 110.99, 43.78 (bridgehead CH), 43.68 (bridgehead CH), 26.22 (CH_2), 25.21 (CH_2); FAB HRMS m/z 403.019 382 ($M - CF_3SO_3^-$)$^+$, calcd for $C_{19}H_{16}O_2I$ 403.016 816.

2-(2-Thiofuranoyl)-3-[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]bicyclo[2.2.2]octa-2,5-diene (6h). Reaction of iodonium salt **4h** (0.488 g, 1.00 mmol) with 1,3-cyclohexadiene (0.440 mL, 4.53 mmol) in CH_3CN for 3 h according to the general procedure afforded 0.421 g (74%) of **6h** as an off-white microcrystalline solid, mp 126–128 °C dec: IR (CCl_4) 3099, 3063, 3044, 2988, 2942, 2877, 1618 (CO), 1583, 1517, 1493, 1475, 1443, 1408, 1355, 1282, 1252, 1225, 1153, 1056, 1031, 980, 714, 703, 637 cm^{-1}; ^{1}H NMR (CD_3CN) δ 8.13–8.07 (m, 4 H), 7.85 (t, 1 H), 7.65 (t, 2 H), 7.35 (t, 1 H), 6.60 (t, 1 H), 6.30 (t, 1 H), 4.92 (d, 1 H), 3.55 (d, 1 H), 1.74–1.66 (br m, 3 H); ^{19}F NMR (CD_3CN) δ −78.50 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 183.01 (CO), 147.24, 140.96, 139.03, 138.30, 137.41, 135.51, 134.41, 133.73, 133.02, 130.45, 130.25, 121.81 (q, J = 320 Hz, $CF_3SO_3^-$), 110.97, 44.82 (bridgehead CH), 43.83 (bridgehead CH), 26.20 (CH_2), 25.37 (CH_2); FAB HRMS m/z 418.996 540 ($M - CF_3SO_3^-$)$^+$, calcd for $C_{19}H_{16}OSI$ 418.995 749. Anal. Calcd for $C_{20}H_{16}O_4S_2F_3I$: C, 42.27; H, 2.84; S, 11.28. Found: C, 42.36; H, 2.84; S, 11.21.

2-(Trimethylacetyl)-3-[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]bicyclo[2.2.2]octa-2,5-diene (6m). Reaction of iodonium salt **4m** (0.462 g, 1.00 mmol) with 1,3-cyclohexadiene (0.440 mL, 4.53 mmol) in CH_3CN for 3 h according to the general procedure afforded 0.337 g (62%) of **6m** as a white microcrystalline solid, mp 129–130 °C dec: IR (CCl_4) 3077, 3055, 2998, 2977, 2951, 2935, 2883, 1634 (CO), 1569, 1533, 1476, 1447, 1285, 1273, 1247, 1222, 1159, 1153, 1119, 1029, 983, 637 cm^{-1}; ^{1}H NMR (CD_3CN) δ 8.08 (d, 2 H), 7.86 (t, 1 H), 7.66 (t, 2 H), 6.55 (t, 1 H), 6.25 (t, 1 H), 4.86 (d, 1 H), 3.44 (d, 1 H), 1.56–1.41 (m, 4 H), 1.36 (s, 9 H); ^{19}F NMR (CD_3CN) δ −78.64 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 204.19 (CO), 146.13, 142.65, 138.42, 134.88, 134.45, 134.32, 133.00, 131.38, 121.76 (q, J = 319 Hz, $CF_3SO_3^-$), 110.92, 44.39 (bridgehead CH), 44.31, 43.32 (bridgehead CH), 26.20 (CH_3), 26.00 (CH_2), 24.83 (CH_2); FAB HRMS m/z 393.071 417 ($M - CF_3SO_3^-$)$^+$, calcd for $C_{19}H_{22}OI$ 393.070 990. Anal. Calcd for $C_{20}H_{22}O_4SF_3I$: C, 44.29; H, 4.09; S, 5.91. Found: C, 44.35; H, 4.14; S, 5.99.

1-Cyano-2-[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]-4,5-dimethyl-1,4-cyclohexadiene (7a). Reaction of iodonium salt **4a** (0.164 g, 0.407 mmol) with 2,3-dimethyl-1,3-butadiene (0.220 mL, 1.90 mmol) in CH_3CN for 3 h according to the general procedure afforded 0.156 g (79%) of **7a** as a tan microcrystalline solid, mp 145–146 °C dec: IR (CCl_4) 3091, 3081, 2919, 2878, 2807, 2220 (C≡N), 1566, 1559, 1541, 1472, 1447, 1417, 1366, 1284, 1248, 1234, 1169, 1161, 1026, 989, 637 cm^{-1}; ^{1}H NMR (CD_3CN) δ 8.13 (d, 2 H), 7.78 (t, 1 H), 7.60 (t, 2 H), 3.39 (t, 2 H), 3.21 (t, 2 H), 1.59 (br s, 6 H); ^{19}F NMR (CD_3CN) δ −78.61 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 137.13, 134.39, 133.47, 130.49, 126.24, 123.54, 121.81, 121.68 (q, J = 319 Hz, $CF_3SO_3^-$), 118.11 (CN), 112.85, 42.09 (CH_2), 37.89 (CH_2), 17.97 (CH_3), 17.71 (CH_3); FAB HRMS m/z 336.024 801 ($M - CF_3SO_3^-$)$^+$, calcd for $C_{15}H_{15}NI$ 336.024 164. Anal. Calcd for $C_{16}H_{15}O_3SNF_3I$: C, 39.60; H, 3.12; S, 6.61; N, 2.89. Found: C, 39.63; H, 3.14; S, 6.70; N, 2.95.

1-(*p*-Toluenesulfonyl)-2-[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]-4,5-dimethyl-1,4-cyclohexadiene (7d). Reaction of iodonium salt **4d** (0.339 g, 0.750 mmol) with 2,3-dimethyl-1,3-butadiene (0.390 mL, 3.38 mmol) in CH_3CN for 1.5 h according to the general procedure afforded 0.347 g (75%) of **7d** as a white microcrystalline solid, mp 153–155 °C dec: IR (CCl_4) 3096, 3066, 2996, 2982, 2919, 2874, 1594, 1540, 1471, 1445, 1381, 1357, 1302, 1283, 1241, 1224, 1161, 1145, 1029, 991, 705, 675, 639 cm^{-1}; ^{1}H NMR (CD_3CN) δ 8.17 (d, 2 H), 7.89 (d, 2 H), 7.86 (t, 1 H), 7.63 (t, 2 H), 7.54 (d, 2 H), 3.01 (t, 2 H), 2.66 (t, 2 H), 2.48 (s, 3 H), 1.53 (s, 3 H), 1.33 (s, 3 H); ^{19}F NMR (CD_3CN) δ −78.56 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 148.57, 139.58, 138.65, 135.02, 133.10, 132.96, 131.60, 129.56, 123.12, 122.10, 121.73 (q, J = 321 Hz, $CF_3SO_3^-$), 121.10, 109.29, 41.68 (CH_2), 36.35 (CH_2), 21.85 (CH_3 of Ts), 17.75 (CH_3), 17.51 (CH_3); FAB HRMS m/z 465.038 404 ($M - CF_3SO_3^-$)$^+$, calcd for $C_{21}H_{22}O_2SI$ 465.038 835. Anal. Calcd for $C_{22}H_{22}O_5S_2F_3I$: C, 43.01; H, 3.61; S, 10.44. Found: C, 42.75; H, 3.88; S, 10.33.

1-(2-Furanoyl)-2-[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]-4,5-dimethyl-1,4-cyclohexadiene (7g). Reaction of iodonium salt **4g** (0.472 g, 1.00 mmol) with 2,3-dimethyl-1,3-butadiene (0.520 mL, 4.50 mmol) in CH_3CN for 3 h according to the general procedure afforded 0.429 g (78%) of **7g** as an off-white microcrystalline solid, mp 125–126 °C dec: IR (CCl_4) 3148, 3070, 3001, 2940, 2904, 2885, 2870, 2830, 1638 (CO), 1557, 1543, 1455, 1441, 1390, 1311, 1258, 1223, 1158, 1150, 1132, 1096, 1030, 994, 686, 636 cm^{-1}; ^{1}H NMR (CD_3CN) δ 8.07 (d, 2 H), 8.01 (s, 1 H), 7.83–7.79 (m, 2 H), 7.60 (t, 2 H), 6.81 (d, 1 H), 3.70 (t, 2 H), 2.76 (t, 2 H), 1.73 (s, 3 H), 1.45 (s, 3 H); ^{19}F NMR (CD_3CN) δ −78.70 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 179.08 (CO), 152.04, 151.44, 138.88, 134.29, 134.11, 132.53, 129.35, 126.66, 123.37, 122.67, 121.83 (q, J = 320 Hz, $CF_3SO_3^-$), 114.96, 110.50, 41.09 (CH_2), 38.75 (CH_2), 17.99 (CH_3), 17.91 (CH_3); FAB HRMS m/z 405.035 032 ($M - CF_3SO_3^-$)$^+$, calcd for $C_{19}H_{18}O_2I$ 405.034 408.

1-(2-Thiofuranoyl)-2-[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]-4,5-dimethyl-1,4-cyclohexadiene (7h). Reaction of iodonium salt **4h** (0.488 g, 1.00 mmol) with 2,3-dimethyl-1,3-butadiene (0.520 mL, 4.50 mmol) in CH_3CN for 3 h according to the general procedure afforded 0.501 g (88%) of **7h** as an off-white microcrystalline solid, mp 115–117 °C dec: IR (CCl_4) 3139, 3099, 3085, 2984, 2945, 2929, 2923, 2882, 2870, 1624 (CO), 1535, 1512, 1495, 1443, 1410, 1355, 1279, 1272, 1255, 1241, 1224, 1165, 1152, 1090, 1029, 995, 684, 636 cm^{-1}; ^{1}H NMR (CD_3CN) δ 8.23 (d, 2 H), 8.12 (d, 1 H), 8.07 (d, 2 H), 7.81 (t, 1 H), 7.60 (t, 2 H), 7.33 (t, 1 H), 3.70 (t, 2 H), 2.80 (t, 2 H), 1.73 (s, 3 H), 1.46 (s, 3 H); ^{19}F NMR (CD_3CN) δ −78.57 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 185.11 (CO), 141.09, 140.28, 138.77, 138.49, 135.35, 134.28, 132.55, 130.68, 129.40, 123.30, 122.93, 121.88 (q, J = 320 Hz, $CF_3SO_3^-$), 110.74, 41.32 (CH_2), 39.62 (CH_2), 17.99 (CH_3), 17.93 (CH_3); FAB HRMS m/z 421.012 190 ($M - CF_3SO_3^-$)$^+$, calcd for $C_{19}H_{18}OSI$ 421.013 226.

1-(Trimethylacetyl)-2-[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]-4,5-dimethyl-1,4-cyclohexadiene (7m). Reaction of iodonium salt **4m** (0.462 g, 1.00 mmol) with 2,3-dimethyl-1,3-butadiene (0.520 mL, 4.50 mmol) in CH_3CN for 2 h according to the general procedure afforded 0.400 g (73%) of **7m** as a white microcrystalline solid, mp 101–102 °C dec: IR (CCl_4) 3077, 2988, 2926, 2899, 2878, 1660 (CO), 1571, 1479, 1466, 1443, 1371, 1262, 1224, 1158, 1102, 1029, 993, 691, 636 cm^{-1}; ^{1}H NMR (CD_3CN) δ 8.06 (d, 2 H), 7.80 (t, 1 H), 7.59 (t, 2 H), 3.55 (t, 2 H), 2.74 (t, 2 H), 1.70 (s, 3 H), 1.43 (s, 3 H), 1.36 (s, 9 H); ^{19}F NMR (CD_3CN) δ −78.61 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 208.48 (CO), 138.77, 136.77, 134.25, 132.54, 128.04, 123.21, 122.70, 121.85 (q, J = 319 Hz, $CF_3SO_3^-$), 110.32, 46.05, 41.22 (CH_2), 38.97 (CH_2), 27.02 (CH_3), 17.89 (CH_3); FAB HRMS m/z 395.087 067 ($M - CF_3SO_3^-$)$^+$, calcd for $C_{19}H_{24}OI$ 395.085 460.

1-Cyano-2-[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]-4,5-(7,7-dichloronorcarane-3,4-diyl)-1,4-cyclohexadiene (9a). Reaction of iodonium salt **4a** (0.169 g, 0.420 mmol) with exocyclic diene **8** (0.103 g, 0.546 mmol) in CH_3CN for 3 h according to the general procedure afforded 0.147 g (59%) of **9a** as a tan microcrystalline solid, mp 146–148 °C dec: IR (CCl_4) 3085, 3069, 2912, 2903, 2885, 2837, 223 (C≡N), 1583, 1568, 1472, 1446, 1432, 1424, 1390, 1285, 1229, 1169, 1068, 1023, 989, 636 cm^{-1}; ^{1}H NMR (CD_3CN) δ 8.12 (d, 2 H), 7.78 (t, 1 H), 7.60 (t, 2 H), 3.40–3.24 (m, 2 H), 3.23–3.03 (m, 2 H), 2.36–2.30 (m, 2 H), 2.02–1.94 (m, 4 H); ^{19}F NMR (CD_3CN) δ −78.63 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 137.93, 134.44, 133.48, 129.62, 125.96, 122.10, 121.67 (q, J = 321 Hz, $CF_3SO_3^-$), 120.38, 117.97 (CN), 112.79, 66.12, 40.45 (CH_2), 36.28 (CH_2), 25.29 (CH), 25.25 (CH), 23.98 (CH_2), 23.86 (CH_2); FAB HRMS m/z 441.962 507 ($M - CF_3SO_3^-$)$^+$, calcd for $C_{18}H_{15}NCl_2I$ 441.959 608. Anal. Calcd for $C_{19}H_{15}O_3SNF_3Cl_2I$: C, 38.54; H, 2.55; S, 5.41; N, 2.37. Found: C, 38.62; H, 2.58; S, 5.50; N, 2.42.

1-(*p*-Toluenesulfonyl)-2-[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]-4,5-(7,7-dichloronorcarane-3,4-diyl)-1,4-cyclohexadiene (9d). Reaction of iodonium salt **4d** (0.399 g, 0.750 mmol) with exocyclic diene **8** (0.172 g, 0.908 mmol) in CH_3CN for 20 min according to the general procedure afforded 0.384 g (71%) of **9d** as a white microcrystalline solid, mp 188–189 °C dec: IR (CCl_4) 3098, 3065, 3029, 2971, 2881, 2835, 2823, 1593, 1572, 1472, 1445, 1430, 1385, 1347, 1300, 1283, 1235, 1224, 1158, 1131, 1027, 983, 704, 671, 639 cm^{-1}; ^{1}H NMR (CD_3CN) δ 8.15 (d, 2 H), 7.90–7.85 (m, 3 H), 7.65 (t, 2 H), 7.54 (d, 2 H), 3.04–2.82 (m, 2 H), 2.71–2.49 (m, 2 H), 2.48 (s, 3 H), 2.39–2.26 (m, 1 H), 2.05–1.67 (m, 5 H); ^{19}F NMR (CD_3CN) δ −78.60 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 148.68, 139.60, 138.40, 135.11, 133.06, 132.98, 131.62, 129.62, 121.80 ($CF_3SO_3^-$ not observed), 120.76, 120.48, 109.21, 66.07, 40.10 (CH_2), 34.74 (CH_2), 25.42 (CH), 25.29 (CH), 23.88 (CH_2), 23.76 (CH_2), 21.84 (CH_3); FAB HRMS m/z 570.976 110 ($M - CF_3SO_3^-$)$^+$, calcd for $C_{24}H_{22}O_2SCl_2I$ 570.975 634.

1-(2-Furanoyl)-2-[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]-4,5-(7,7-dichloronorcarane-3,4-diyl)-1,4-cyclohexadiene (9g). Reaction of iodonium salt **4g** (0.472 g, 1.00 mmol) with exocyclic diene **8** (0.229 g, 1.21 mmol) in CH_3CN for 1.25 h according to the general procedure afforded 0.562 g (85%) of **9g** as an off-white microcrystalline solid, mp 140–142 °C dec: IR (CCl_4) 3151, 3133, 3125, 3076, 3070, 2901, 2866, 2851, 2834, 1627 (CO), 1555, 1538, 1505, 1473, 1447, 1424, 1393, 1308, 1281, 1272, 1258, 1241, 1226, 1160, 1030, 1024, 993, 683, 636 cm^{-1}; ^{1}H NMR

(CD_3CN) δ 8.07–8.01 (m, 3 H), 7.85–7.80 (m, 2 H), 7.61 (t, 2 H), 6.82 (t, 1 H), 3.68–3.59 (m, 2 H), 2.73–2.63 (m, 2 H), 2.55–2.46 (m, 1 H), 2.21–2.10 (m, 3 H), 2.02–1.95 (m, 1 H), 1.90–1.77 (m, 1 H); ^{19}F NMR (CD_3CN) δ −78.76 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 178.98 (CO), 152.11, 151.44, 138.91, 134.41, 134.03, 132.64, 128.59, 126.73, 121.98, 121.94 (q, J = 321 Hz, $CF_3SO_3^-$), 121.41, 115.00, 110.42, 66.31, 39.47 (CH_2), 37.09 (CH_2), 25.68 (CH), 25.46 (CH), 24.20 (CH_2), 24.13 (CH_2); FAB HRMS m/z 510.972 738 ($M - CF_3SO_3^-$)$^+$, calcd for $C_{22}H_{18}O_2Cl_2I$ 510.972 809.

1-(2-Thiofuranoyl)-2-[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]-4,5-(7,7-dichloronorcarane-3,4-diyl)-1,4-cyclohexadiene (9h). Reaction of iodonium salt **4h** (0.488 g, 1.00 mmol) with exocyclic diene **8** (0.226 g, 1.19 mmol) in CH_3CN for 2 h according to the general procedure afforded 0.496 g (73%) of **9h** as an off-white microcrystalline solid, mp 155–156 °C dec: IR (CCl_4) 3084, 3070, 2938, 2891, 2872, 2823, 1622 (CO), 1534, 1509, 1474, 1444, 1405, 1362, 1355, 1282, 1251, 1223, 1161, 1151, 1028, 995, 684, 636 cm^{-1}; ^1H NMR (CD_3CN) δ 8.22 (d, 1 H), 8.13 (d, 1 H), 8.05 (d, 2 H), 7.83 (t, 1 H), 7.61 (t, 2 H), 7.34 (t, 1 H), 3.72–3.58 (m, 2 H), 2.81–2.62 (m, 2 H), 2.61–2.42 (m, 1 H), 2.22–2.12 (m, 3 H), 2.02–1.79 (m, 2 H); ^{19}F NMR (CD_3CN) δ −78.70 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 185.07 (CO), 141.03, 140.42, 138.79, 138.48, 135.12, 134.42, 132.67, 130.67, 128.61, 121.98, 121.65 ($CF_3SO_3^-$ not observed), 110.60, 66.26, 39.67 (CH_2), 37.94 (CH_2), 25.64 (CH), 25.44 (CH), 24.16 (CH_2), 24.10 (CH_2); FAB HRMS m/z 526.949 896 ($M - CF_3SO_3^-$)$^+$, calcd for $C_{22}H_{18}OSCl_2I$ 526.947 682.

1-(Trimethylacetyl)-2-[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]-4,5-(7,7-dichloronorcarane-3,4-diyl)-1,4-cyclohexadiene (9m). Reaction of iodonium salt **4m** (0.462 g, 1.00 mmol) with exocyclic diene **8** (0.226 g, 1.19 mmol) in CH_3CN for 3 h according to the general procedure afforded 0.514 g (79%) of **9m** as a white microcrystalline solid, mp 129–130 °C dec: IR (CCl_4) 3056, 2983, 2965, 2875, 1653 (CO), 1568, 1477, 1443, 1429, 1369, 1347, 1280, 1255, 1225, 1156, 1122, 1030, 995, 688, 636 cm^{-1}; ^1H NMR (CD_3CN) δ 8.04 (d, 2 H), 7.82 (t, 1 H), 7.60 (t, 2 H), 3.58–3.31 (m, 2 H), 2.74–2.55 (m, 2 H), 2.54–2.41 (m, 1 H), 2.19–2.05 (m, 2 H), 2.00–1.85 (m, 2 H), 1.83–1.72 (m, 1 H), 1.34 (s, 9 H); ^{19}F NMR (CD_3CN) δ −78.65 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 208.42 (CO), 138.79, 136.44, 134.38, 132.64, 127.44, 121.81, 121.43 ($CF_3SO_3^-$ not observed), 110.28, 66.28, 46.07, 39.60 (CH_2), 37.27 (CH_2), 27.01 (CH_3), 25.66 (CH), 25.40 (CH), 24.08 (CH_2), 24.02 (CH_2); FAB HRMS m/z 501.024 773 ($M - CF_3SO_3^-$)$^+$, calcd for $C_{22}H_{24}OCl_2I$ 501.024 488. Anal. Calcd for $C_{23}H_{24}O_4SF_3Cl_2I$: C, 42.42; H, 3.71; S, 4.92. Found: C, 42.37; H, 3.67; S, 4.98.

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Supplementary Material Available: Ortep drawings and tables of X-ray crystal and structural data for compounds **4a** and **5h** (25 pages); tables of observed and calculated structure factors for **4a** and **5h** (23 pages). Ordering information is given on any current masthead page.